Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Enantio- and Diastereoselective Conjugate Addition of Pyridyl Alkyl Ketones to Enones by Cu(II)-Lewis Acid/Brønsted Base Catalysis

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Supporting Information

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I. General Information

Unless otherwise specified, all reactions were conducted with stirring under nitrogen atmosphere. All reagents including anhydrous solvents were purchased from Alfa Aesar, Sigma Aldrich, and TCI were used as received. Enones were synthesized by aldol reactions of corresponding aldehydes or Meyer-Schuster rearrangement of the corresponding propargyl alcohol.[1] Pyridyl alkyl ketones were produced by the Grignard reaction with the corresponding alkyl magnesium bromide and 2-cyanopyridines.[2] Flash column chromatography was performed on silica gel 60 (40–63 μm) as a stationary phase. Diastereomeric ratios were determined by ^{1}H NMR spectroscopy from the crude mixtures.

NMR spectra were recorded with a Bruker AVANCE III HD 300 (300 MHz) or a Bruker AVANCE III HD 400 (400 MHz) at Yonsei University with $CDCl_3$ as the solvent. Chemical shifts were expressed in parts per million (ppm, δ), referenced to the residual signal of $CDCl_3$ (7.26 ppm for ^{1}H, 77.16 ppm for ^{13}C). All coupling constants (*J*) were expressed in Hertz (Hz). The following abbreviations were used for the descriptions of splitting patterns: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, qd = quartet of doublets, ddd = doublet of doublet of doublets, dtd = doublet of triplet of doublets, dddd = doublet of doublet of doublet of doublets.

High resolution mass spectra were obtained using an Agilent 6530 Accurate-Mass Q-TOF.

GC analyses were carried out on a Shimadzu Nexis GC-2030 system with HP-5 (19091j-433) column.

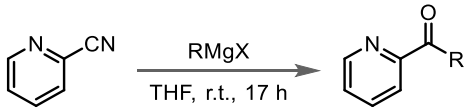
HPLC analyses were carried out on a Shimadzu LC-20A chromatograph with Daicel CHIRALCEL® columns (internal diameter 4.6mm, column length 250 mm, particle size 5μ).

FT-IR analyses were recorded on Bruker VERTEX 70 and employing PIKE MIRacle™ Single Reflection ATR accessory.

Optical rotations were measured on A. Krüss Optronic GmbH P8000-TF Polarimeter.

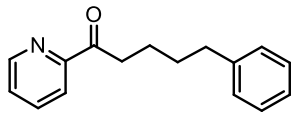
II. Preparation of 2-Pyridyl Alkyl ketones

General Procedure A



Under nitrogen atmosphere, the corresponding alkyl halides (24 mmol, 1.2 equiv) in THF (50 mL) were treated with magnesium [7439-95-4] (30 mmol, 1.5 equiv) and a piece of I_2 in a 250 mL round-bottom flask equipped with a stir bar. The resulting solution was stirred vigorously at room temperature for 1 h. This reaction mixture was then cooled to 0 ºC. A solution of 2-cyano-substituted pyridine (20 mmol, 1.0 equiv) in THF (10 mL) was added dropwise into the reaction mixture at 0 ºC. Subsequently, the resulting mixture was stirred vigorously at room temperature for 16 h. The reaction was quenched by addition of sat. NH_4Cl solution and subsequently basified by adding sat. $NaHCO_3$ solution, and extracted with EtOAc/water. The organic layers were collected, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography with hexanes and EtOAc.

*Note: Pyridyl alkyl ketones **1a**–**1k** were synthesized according to **General Procedure A**.



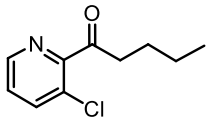
1g

5-phenyl-1-(pyridin-2-yl)pentan-1-one (Table 4, 1g). The title compound was prepared according to **General Procedure A**, using 1-bromo-4-phenylbutane [13633-25-5] (5.1 g, 24 mmol, 1.2 equiv) and 2-cyanopyridine [100-70-9] (2.1 g, 20 mmol, 1.0 equiv). The title compound was afforded as a yellowish sticky liquid (3.25 g, 68%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.6 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.83 (td, *J* = 7.8, 1.6 Hz, 1H), 7.53 – 7.39 (m, 1H), 7.33 – 7.25 (m, 2H), 7.18 (dd, *J* = 7.5, 3.7 Hz, 3H), 3.25 (t, *J* = 7.0 Hz, 2H), 2.67 (t, *J* = 7.3 Hz, 2H), 1.84 – 1.64 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.80, 153.42, 148.85, 142.36, 136.86, 128.41, 128.25, 127.00, 125.66, 121.72, 37.44, 35.77, 31.09, 23.66.

HRMS (ESI) m/z calcd for **$C_{16}H_{18}NO$** $[M + H]^+$: 240.1388, found: 240.1383.



1j

1-(3-chloropyridin-2-yl)pentan-1-one (Table 4, 1j). The title compound was prepared according to **General Procedure A**, using 1-bromobutane [109-65-9] (3.29 g, 24.0 mmol, 1.20 equiv) and 3-chloro-2-pyridinecarbonitrile [38180-46-0] (2.77 g, 20.0 mmol, 1.00 equiv). The title compound was afforded as a yellowish sticky liquid (1.62 g, 41%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.5 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.35 (dd, *J* = 8.1, 4.6 Hz, 1H), 3.08 (t, *J* = 7.4 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.49 – 1.37 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.79, 152.56, 146.79, 139.03, 129.61, 126.26, 40.18, 25.84, 22.40, 13.98.

HRMS (ESI) m/z calcd for **$C_{10}H_{13}ClNO$** $[M + H]^+$: 198.0686, found: 198.0687.

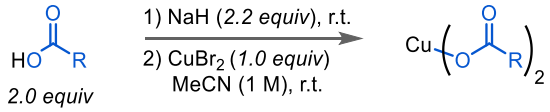
III. Preparation of Cu(II) Complexes

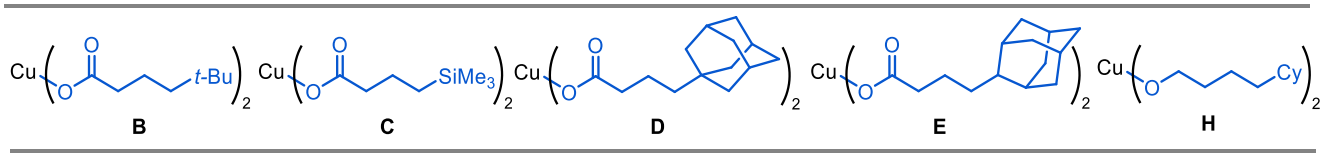
Procedure for preparation of Cu(II) complexes

In a nitrogen-filled glovebox, sodium hydride (60% dispersion in mineral oil) [7646-69-7] (0.80 mg, 0.022 mmol, 2.2 equiv) and the corresponding carboxylic acid (0.02 mmol, 2 equiv) were combined in a dram vial. $CuBr_2$ [7789-45-9] (2.2 mg, 0.010 mmol, 1.0 equiv) in MeCN (50 µL) was added to a dram vial. After 3 minutes, the mixture was filtered through a cotton filter with MeCN (50 µL) and concentrated under reduced pressure. *The copper complex was characterized by FT-IR spectroscopy and used without further purification.*

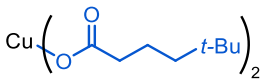
*Note: Cu(II) carboxylates **F**, **G**, and **I** have been reported in the literature.[3]

***Table S1*. Synthesis of Cu(II) Complexes**[a]





[a]Reaction conditions: sodium hydride (60% dispersion in mineral oil) [7646-69-7] (0.80 mg, 0.022 mmol, 2.2 equiv), the corresponding carboxylic acids (0.02 mmol, 2 equiv), and $CuBr_2$ [7789-45-9] (2.2 mg, 0.010 mmol, 1.0 equiv) in MeCN (50 µL) at r.t. for 3 minutes.

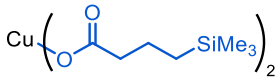


B

Cu(II) 5,5-dimethylhexanoate (Table 2, B). The title compound was prepared using 5,5-dimethylhexanoic acid [24499-80-7] (2.88 mg, 0.0200 mmol, 2.00 equiv) and $CuBr_2$ [7789-45-9] (2.2 mg, 0.010 mmol, 1.0 equiv). The title compound was afforded as a blue powder.

IR (ATR, $\tilde{\upsilon}$ (cm^{-1})) 2953.73, 2925.16, 2854.45, 1562.30, 1408.64, 1365.01, 1309.39, 1081.45, 763.54, 728.73.

HRMS (ESI) m/z calcd for **$C_{16}H_{31}CuO_4$** $[M + H]^+$: 350.1518, found: 350.1510.



C

Cu(II) 4-(trimethylsilyl)butanoate (Table 2, C). The title compound was prepared using 4-(trimethylsilyl)butanoic acid [2345-40-6] (3.2 mg, 0.020 mmol, 2.0 equiv) and $CuBr_2$ [7789-45-9] (2.2 mg, 0.010 mmol, 1.0 equiv). The title compound was afforded as a blue powder.

IR (ATR, $\tilde{\upsilon}$ (cm^{-1})) 3513.51, 1754.72, 1627.04, 1381.70, 1280.36, 1238.40, 1185.50, 1035.51, 990.08, 931.10, 874.81, 802.36, 681.70.

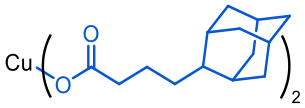
HRMS (ESI) m/z calcd for **$C_{14}H_{30}CuO_4Si_2$** [M]: 381.0976, found: 381.0964.

D

Cu(II) 4-(adamantan-1-yl)butanoate (Table 2, D). The title compound was prepared using 1-adamantanebutyric acid [6240-17-1] (4.4 mg, 0.020 mmol, 2.0 equiv) and $CuBr_2$ [7789-45-9] (2.2 mg, 0.010 mmol, 1.0 equiv). The title compound was afforded as a blue powder.

IR (ATR, ῡ (cm^{-1})) 2910.82, 2851.22, 1763.52, 1621.28, 1543.95, 1445.84, 1416.96, 1375.88, 1183.56, 1035.97, 990.81, 736.60.

HRMS (ESI) m/z calcd for **$C_{28}H_{43}CuO_2$** $[M + H]^+$: 506.2457, found: 506.2452.

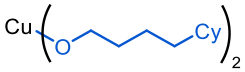


E

Cu(II) 4-(adamantan-2-yl)butanoate (Table 2, E). The title compound was prepared using 2-adamantanebutyric acid [1693982-88-5] (4.4 mg, 0.020 mmol, 2.0 equiv) and $CuBr_2$ [7789-45-9] (2.2 mg, 0.010 mmol, 1.0 equiv). The title compound was afforded as a blue powder.

IR (ATR, ῡ (cm^{-1})) 2912.58, 2852.70, 1667.16, 1571.79, 1416.25, 1188.71, 736.49.

HRMS (ESI) m/z calcd for **$C_{28}H_{43}CuO_2$** $[M + H]^+$: 506.2457, found: 506.2452.



H

Cu(II) 4-cyclohexylbutan-1-olate (Table 2, H). The title compound was prepared using cyclohexanebutanol [4441-57-0] (3.2 mg, 0.020 mmol, 2.0 equiv) and $CuBr_2$ [7789-45-9] (2.2 mg, 0.010 mmol, 1.0 equiv). The title compound was afforded as a blue powder.

IR (ATR, ῡ (cm^{-1})) 3376.24, 2921.26, 2850.91, 1665.38, 1604.14, 1446.98, 1309.18, 1072.31, 731.97.

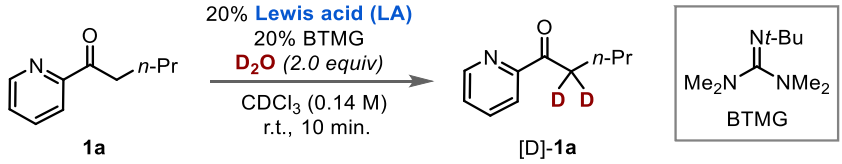
HRMS (ESI) m/z calcd for **$C_{20}H_{39}CuO_2$** $[M + H]^+$: 374.2246, found: 374.2241.

IV. H/D Exchange Experiments by Lewis Acid/Brønsted Base Catalysis

General Procedure B

In a nitrogen-filled glovebox, 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (8.2 mg, 0.050 mmol, 1.0 equiv), the corresponding Lewis acid (0.01 mmol, 0.2 equiv), the corresponding base (0.010 mmol, 0.20 equiv), and D_2O [7789-20-0] (2 mg, 0.1 mmol, 2 equiv) in $CDCl_3$ (0.14 M) were combined in a dram vial. Deuterium incorporation was determined by ^{1}H-NMR analysis.

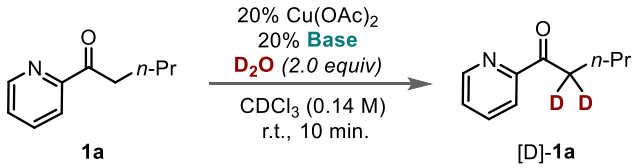
***Table S2*. Effect of Lewis Acids on the H/D Exchange**[a,b]

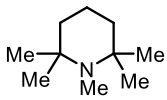
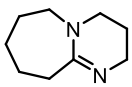
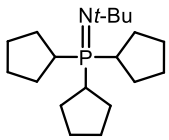


LA	$Cu(OAc)_2$	$Zn(OAc)_2$	$Ni(OAc)_2 \bullet 4H_2O$	AgOAc
D incorporation	50%	<5% (<5%)[c]	<5% (<5%)[c]	<5% (<5%)[c]

[a]Reaction conditions: 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (8.2 mg, 0.050 mmol, 1.0 equiv), the corresponding Lewis acid (0.01 mmol, 0.2 equiv), BTMG [29166-72-1] (1.8 mg, 0.010 mmol, 0.20 equiv), and D_2O [7789-20-0] (2 mg, 0.1 mmol, 2 equiv) in $CDCl_3$ (0.14 M) at r.t. for 10 minutes. [b]Deuterium incorporation was determined by ^{1}H NMR analysis, with full deuteration at both α-protons of **1a** considered as 100%. [c]After 16 h.

***Table S3*. Effect of Brønsted Bases on the H/D Exchange**[a,b]



Base			KO*t*-Bu	Na_2CO_3	
D incorporation	<5% (<5%)[c]	<5% (<5%)[c]	<5% (<5%)[c]	<5% (<5%)[c]	90%

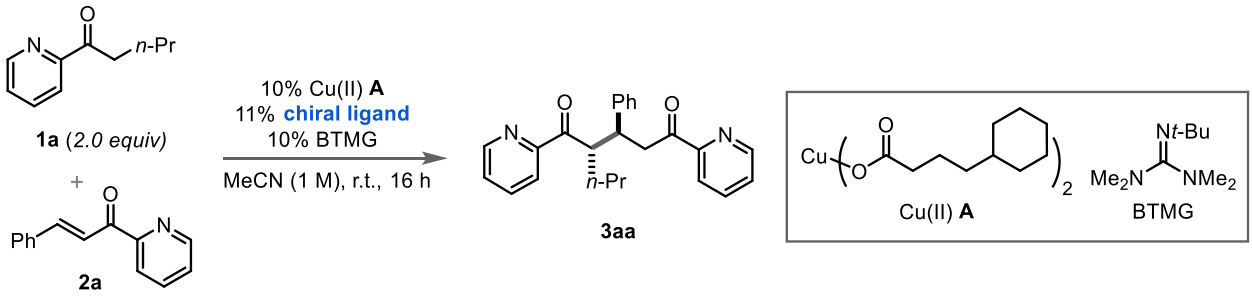
[a]Reaction conditions: 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (8.2 mg, 0.050 mmol, 1.0 equiv), $Cu(OAc)_2$ [142-71-2] (1.8 mg, 0.010 mmol, 0.20 equiv), the corresponding base (0.01 mmol, 0.2 equiv), and D_2O [7789-20-0] (2 mg, 0.1 mmol, 2 equiv) in $CDCl_3$ (0.14 M) at r.t. for 10 minutes. [b]Deuterium incorporation was determined by ^{1}H NMR analysis, with full deuteration at both α-protons of **1a** considered as 100%. [c]After 16 h.

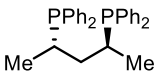
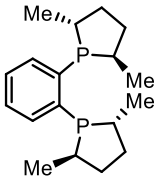
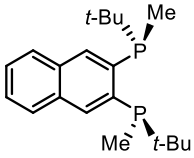
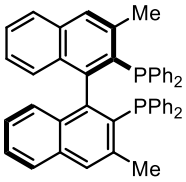
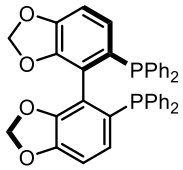
V. Development of the Conjugate Addition of 2-Pyridyl Alkyl Ketones to Enones

General Procedure C

In a nitrogen-filled glovebox, Cu(II) cyclohexanebutyrate **A** [2218-80-6] (2 mg, 0.005 mmol, 0.1 equiv) and the corresponding chiral ligand (0.0055 mmol, 0.11 equiv) in MeCN (50 µL) were combined in a dram vial equipped with a stir bar. After stirring for 3 minutes, 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (16.3 mg, 0.100 mmol, 2.00 equiv), (2*E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (10.5 mg, 0.0500 mmol, 1.00 equiv), and the corresponding base (0.005 mmol, 0.1 equiv) were added. The resulting mixture was stirred vigorously at room temperature for 16 h. The mixture was then exposed to air. Yields and drs of the products were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard. The ee of the products was determined by chiral HPLC analysis (Table 2 in the main paper; 99% yield, 5.4:1 dr, and 98% ee with (*R*,*R*)-Ph-BPE).

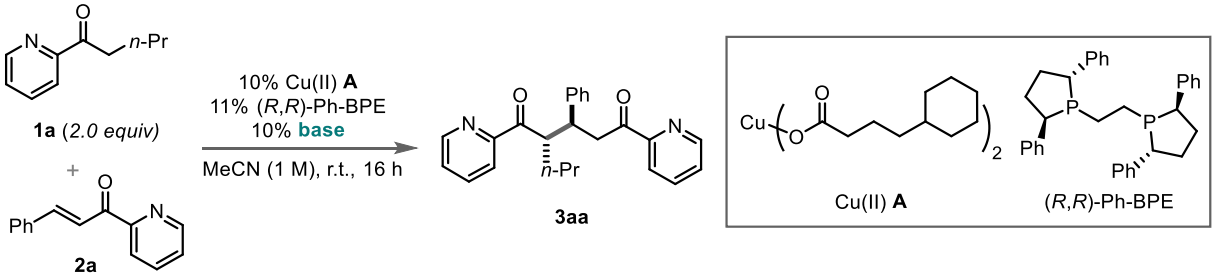
***Table S4*. Effect of Chiral Ligands on the Conjugate Addition of 1a to 2a**[a,b,c]

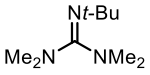
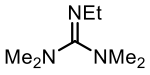
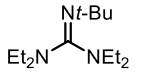
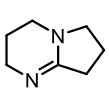
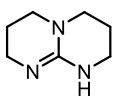
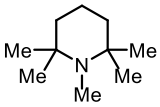
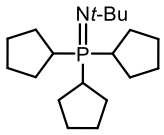


				
(*S*,*S*)-BDPP	(*R*,*R*)-Me-Duphos	(*R*,*R*)-QuinoxP*	(*R*)-3,3'-dimethyl-BINAP	(*R*)-SEGPHOS
93%, 3:1 dr <5% ee	<5%	<5%	<5%	48%, 1:1 dr 20% ee

[a]Reaction conditions: 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (16.3 mg, 0.100 mmol, 2.00 equiv), (*2E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (10.5 mg, 0.0500 mmol, 1.00 equiv), Cu(II) **A** [2218-80-6] (2 mg, 0.005 mmol, 0.1 equiv), the corresponding chiral ligand (0.0055 mmol, 0.11 equiv), and BTMG [29166-72-1] (0.9 mg, 0.005 mmol, 0.1 equiv) in MeCN (1 M) at r.t. for 16 h. [b]Yields and drs of the products were determined by ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as an internal standard. [c]The ee of the products was determined by chiral HPLC analysis.

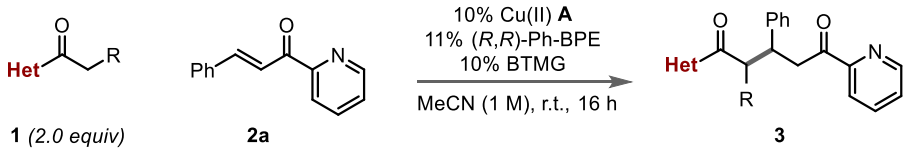
***Table S5.* Effect of Bases on the Conjugate Addition of 1a to 2a**[a,b,c]

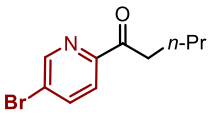
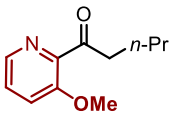
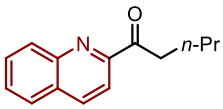
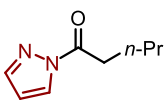
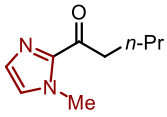
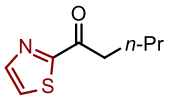
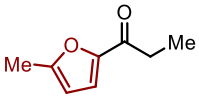
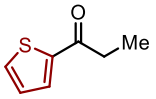


						
99%, 5.4:1 dr 98% ee	15%, 1.0:1 dr -	69%, 3.0:1 dr 98% ee	<5%	<5%	<5%	58%, 1.0:1 dr 61% ee

[a]Reaction conditions: 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (16.3 mg, 0.100 mmol, 2.00 equiv), (*2E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (10.5 mg, 0.0500 mmol, 1.00 equiv), Cu(II) **A** [2218-80-6] (2 mg, 0.005 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (2.8 mg, 0.0055 mmol, 0.11 equiv), and corresponding bases (0.005 mmol, 0.1 equiv) in MeCN (1 M) at r.t. for 16 h. [b]Yields and drs of the products were determined by ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as an internal standard. [c]The ee of the products was determined by chiral HPLC analysis.

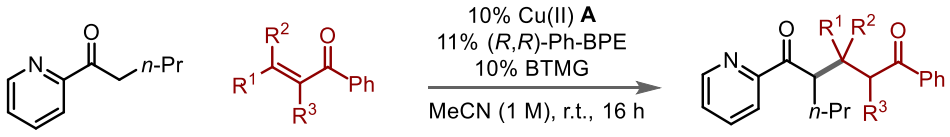
***Table S6.* Unsuccessful Ketones for the Conjugate Addition**[a,b,c]



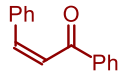
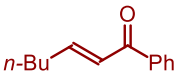
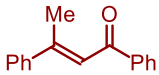
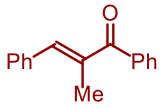
			
22%, 1.0:1 dr	<5%	<5%	52%, 1.0:1 dr <5% ee
			
<5%	<5%	<5%	99%, 1.5:1 dr <5% ee

[a]Reaction conditions: the corresponding heteroaryl-substituted ketone (0.1 mmol, 2 equiv), (*2E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (10.5 mg, 0.0500 mmol, 1.00 equiv), Cu(II) **A** [2218-80-6] (2 mg, 0.005 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (2.8 mg, 0.0055 mmol, 0.11 equiv), and BTMG [29166-72-1] (0.9 mg, 0.005 mmol, 0.1 equiv) in MeCN (1 M) at r.t. for 16 h. [b]Yields and drs of the products were determined by ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as an internal standard. [c]The ee of the products was determined by chiral HPLC analysis.

Table S7. **Unsuccessful Multi-Substituted Enones for the Conjugate Addition**[a,b,c]



1a *(2.0 equiv)* **2** **3**

 (Z/E = 4.0:1)			
<5%	17%, 1.0:1 dr <5% ee	<5%	<5%

[a]Reaction conditions: 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (16.3 mg, 0.100 mmol, 2.00 equiv), the corresponding enone (0.05 mmol, 1 equiv), Cu(II) **A** [2218-80-6] (2 mg, 0.005 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (2.8 mg, 0.0055 mmol, 0.11 equiv), and BTMG [29166-72-1] (0.9 mg, 0.005 mmol, 0.1 equiv) in MeCN (1 M) at r.t. for 16 h. [b]Yields and drs of the products were determined by ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as an internal standard. [c]The ee of the products was determined by chiral HPLC analysis.

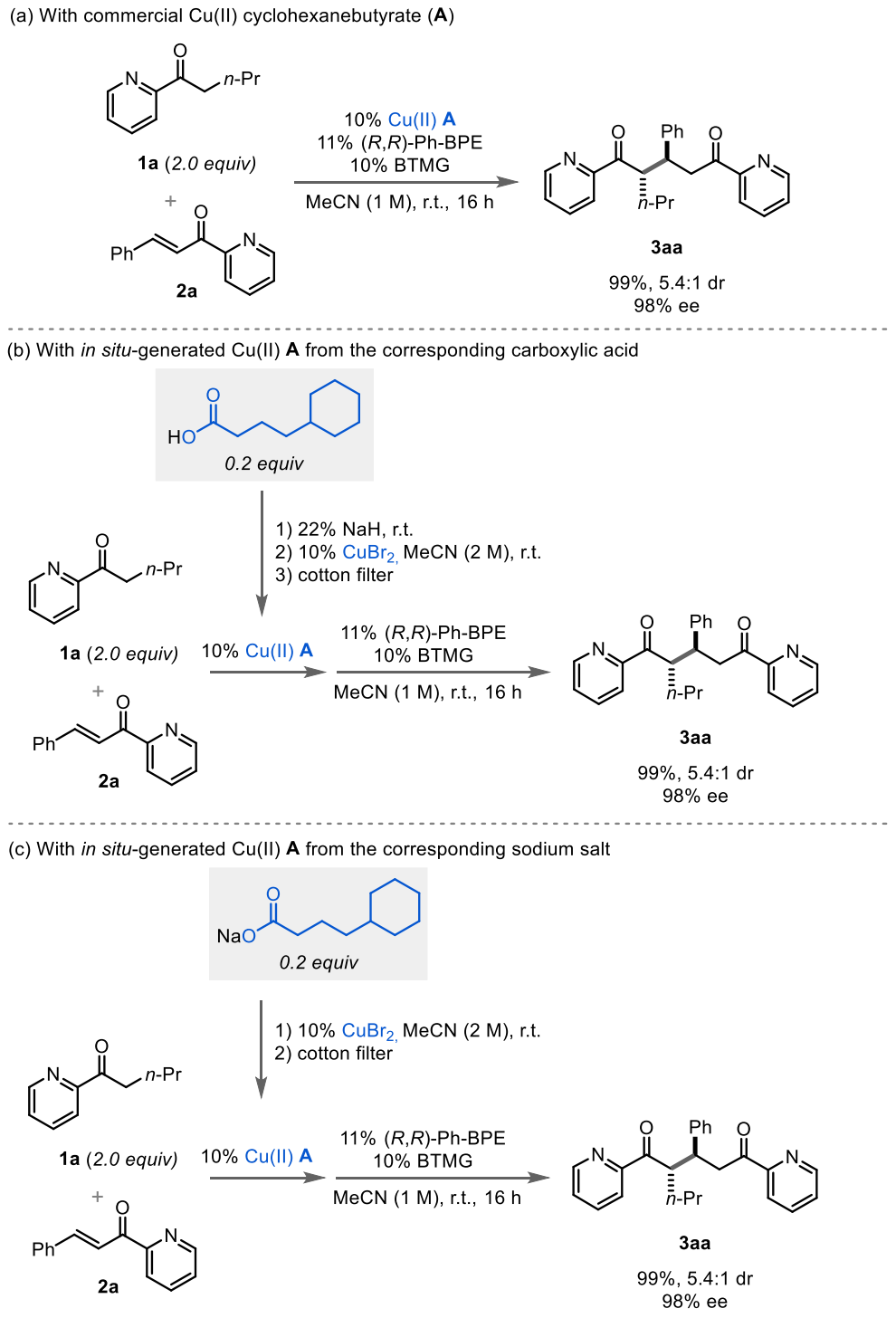
Procedure for Scheme S1b on page S10.

In a nitrogen-filled glovebox, sodium hydride (60% dispersion in mineral oil) [7646-69-7] (0.40 mg, 0.011, 0.22 equiv) and 4-cyclohexylbutanoic acid [4441-63-8] (1.7 mg, 0.010 mmol, 0.20 equiv) were combined in a dram vial. $CuBr_2$ [7789-45-9] (1.1 mg, 0.0050 mmol, 0.10 equiv) in MeCN (50 µL) was then added to this dram vial. After 3 minutes, the mixture was filtered through a cotton filter with MeCN (50 µL) and concentrated under reduced pressure. (*R*,*R*)-Ph-BPE [528565-79-9] (2.8 mg, 0.0055 mmol, 0.11 equiv) in MeCN (50 µL) was then added to this vial with a stir bar. Following an additional 3 minutes of stirring, 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (16.3 mg, 0.100 mmol, 2.00 equiv), (2*E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (10.5 mg, 0.0500 mmol, 1.00 equiv), and BTMG [29166-72-1] (0.9 mg, 0.005 mmol, 0.1 equiv) were combined into the mixture. The resulting mixture was stirred vigorously at room temperature for 16 h. The mixture was then exposed to air. Yields and drs of the products were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard. The ee of the products was determined by chiral HPLC analysis.

Procedure for Scheme S1c on page S10.

In a nitrogen-filled glovebox, sodium cyclohexanebutyrate [61886-29-1] (1.92 mg, 0.0100 mmol, 0.200 equiv) and $CuBr_2$ [7789-45-9] (1.1 mg, 0.0050 mmol, 0.10 equiv) in MeCN (50 µL) were combined in a dram vial. After 3 minutes, the mixture was filtered through a cotton filter with MeCN (50 µL) and concentrated under reduced pressure. (*R*,*R*)-Ph-BPE [528565-79-9] (2.8 mg, 0.0055 mmol, 0.11 equiv) in MeCN (50 µL) was then added to this vial with a stir bar. Following an additional 3 minutes of stirring, 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (16.3 mg, 0.100 mmol, 2.00 equiv), (2*E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (10.5 mg, 0.0500 mmol, 1.00 equiv), and BTMG [29166-72-1] (0.9 mg, 0.005 mmol, 0.1 equiv) were added. The resulting mixture was stirred vigorously at room temperature for 16 h. The mixture was then exposed to air. Yields and drs of the products were determined by ^{1}H NMR spectroscopy with 1,1,2,2-tetrachloroethane as an internal standard. The ee of the products was determined by chiral HPLC analysis.

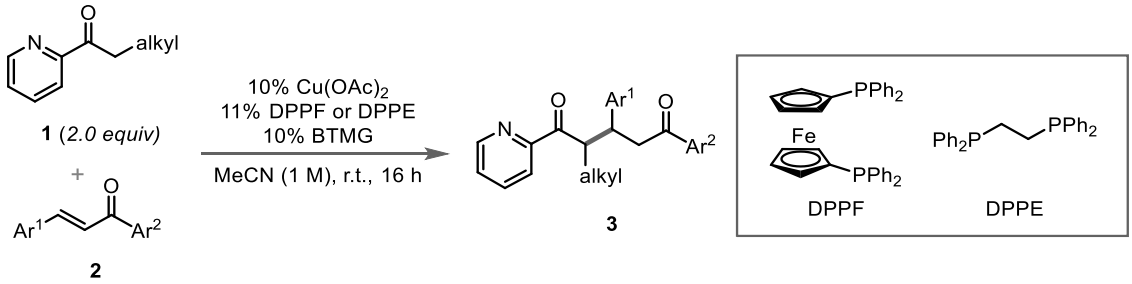
***Scheme S1*. Comparison of the Effect of Cu(II) Carboxylate Catalysts: *Commercial* vs. *In-Situ Prepared*[a,b]**



[a]Yields and drs of the products were determined by ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as an internal standard. [b]The ee of the products was determined by chiral HPLC analysis.

VI. Catalytic Conjugate Addition of 2-Pyridyl Alkyl Ketones to Enones

General Procedure D for the Preparation of Racemic Products 3



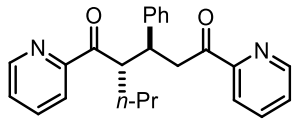
In a nitrogen-filled glovebox, $Cu(OAc)_2$ [142-71-2] (3.6 mg, 0.020 mmol, 0.10 equiv) and DPPF [12150-46-8] (12 mg, 0.022 mmol, 0.11 equiv) or DPPE [1663-45-2] (8.8 mg, 0.022 mmol, 0.11 equiv) in MeCN (0.2 mL) were combined in a dram vial equipped with a stir bar. The corresponding pyridyl alkyl ketone (0.4 mmol, 2 equiv), the corresponding enone (0.2 mmol, 1 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) were added to this vial. The resulting mixture was stirred vigorously at room temperature for 16 h. The mixture was then exposed to air. The residue was purified by flash column chromatography (Hex:EtOAc).

General Procedure E

In a nitrogen-filled glovebox, Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv) and the corresponding chiral ligand (0.022 mmol, 0.11 equiv) in MeCN (0.2 mL) were combined in a dram vial equipped with a stir bar. After stirring 3 minutes, the corresponding pyridyl alkyl ketone (0.4 mmol, 2 equiv), the corresponding enone (0.2 mmol, 1 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) were added to this vial. The mixture was stirred vigorously at room temperature for 16 h. The mixture was then exposed to air. The residue was purified by flash column chromatography (Hex:EtOAc). Diastereomeric ratios (drs) of the crude mixtures and drs of the isolated compounds were determined by ^{1}H NMR analysis.

General Procedure F

In a nitrogen-filled glovebox, sodium hydride (60% dispersion in mineral oil) [7646-69-7] (1.6 mg, 0.044, 0.22 equiv), the corresponding salt (0.04 mmol, 0.2 equiv), and $CuBr_2$ [7789-45-9] (4.4 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.1 mL) were added to a dram vial. After 3 minutes, the mixture was filtered through a cotton filter with MeCN (0.1 mL). The corresponding chiral ligand was then combined with a stir bar. Following an additional 3 minutes of stirring, the corresponding pyridyl alkyl ketone (0.4 mmol, 2 equiv), enones (0.2 mmol, 1 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) were added. The mixture was stirred vigorously at room temperature for 16 h. The mixture was then exposed to air. The residue was purified by flash column chromatography (Hex:EtOAc). The diastereomeric ratios (drs) of the crude sample and drs of the isolated compounds were determined by ^{1}H NMR analysis.



3aa

(2*S*,3*S*)-3-phenyl-2-propyl-1,5-di(pyridin-2-yl)pentane-1,5-dione (Table 4, 3aa). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (2*E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (42 mg, 0.20 mmol, 1.0 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 5.4:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3aa** was afforded as a yellowish sticky liquid (62.6 mg, 84% yield, >20:1 dr (after isolation)).

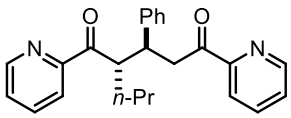
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (d, *J* = 3.9 Hz, 2H), 7.84 (dd, *J* = 12.6, 7.9 Hz, 2H), 7.80 – 7.66 (m, 2H), 7.48 – 7.34 (m, 2H), 7.34 – 7.22 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 4.67 (ddd, *J* = 10.2, 7.0, 3.0 Hz, 1H), 4.02 – 3.90 (m, 1H), 3.84 (dd, *J* = 17.1, 9.9 Hz, 1H), 3.58 (dd, *J* = 17.1, 4.2 Hz, 1H), 1.98 (ddd, *J* = 20.7, 10.4, 5.0 Hz, 1H), 1.70 – 1.54 (m, 1H), 1.34 – 1.08 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 204.69, 200.41, 153.93, 153.56, 148.89, 148.78, 143.00, 136.89, 136.81, 128.55, 128.02, 127.09, 126.80, 126.25, 122.23, 121.91, 49.73, 42.43, 39.52, 30.89, 21.04, 14.47.

HRMS (ESI) m/z calcd for **$C_{24}H_{25}N_2O_2$** $[M + H]^+$: 373.1916, found: 373.1899.

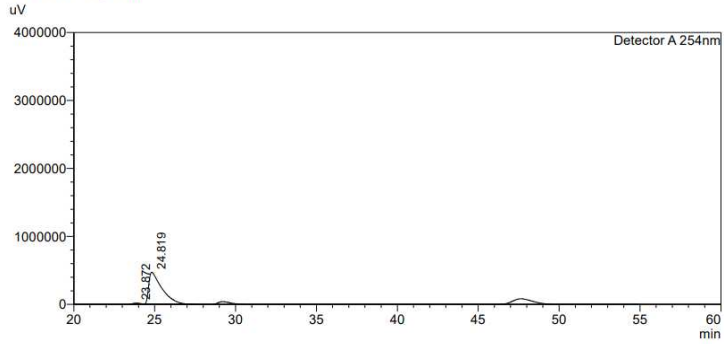
HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 97% [OD-H, 5% i-PrOH in hexanes, 0.3 mL/min], t_R = 23.87 min (*anti* minor), t_R = 24.82 min (*anti* major), t_R = 29.22 (*syn* major), and t_R = 47.65 (*syn* minor).

$[\alpha]_D^{20}$ = +24° (c = 1.4, $CHCl_3$).



(*S*,*S*)-**3aa**
>20:1 dr, 97% ee

<Chromatogram>



<Peak Table>

Detector A 254nm

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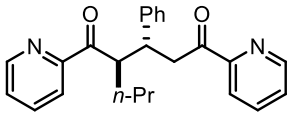
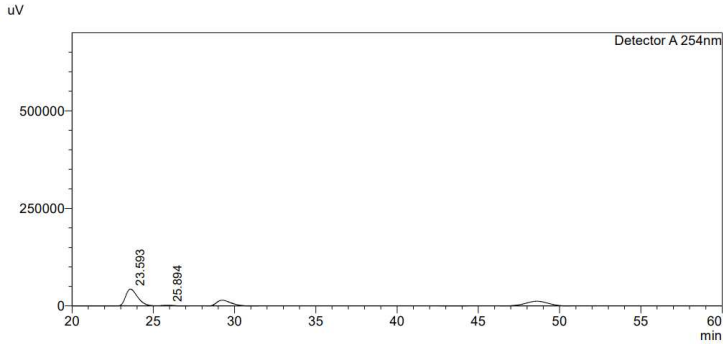
2	24.819	26344882	466394	98.270		M	
Total		26808686	482342				



(*R*,*R*)-**3aa**
10:1 dr, 97% ee

<Chromatogram>



<Peak Table>

Detector A 254nm

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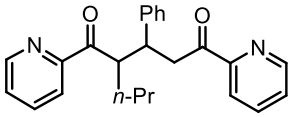
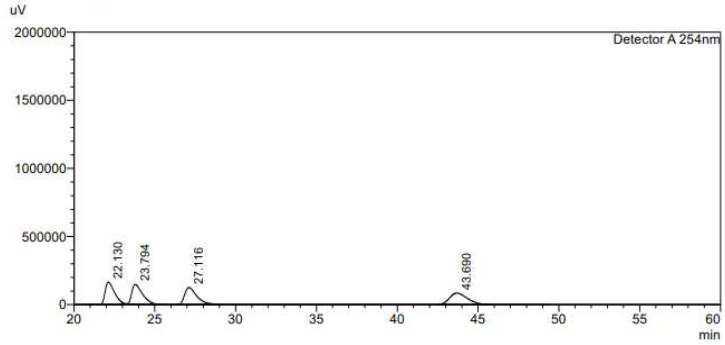
2	25.894	37761	1093	1.586		M	
Total		2381158	44891				



(*rac*)-**3aa**
4:1 dr

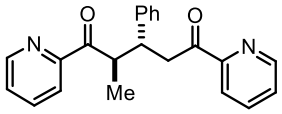
<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.130	6489099	162506	25.079		M	
2	23.794	6492675	143280	25.092		M	
3	27.116	6430808	124598	24.853		M	
4	43.690	6462391	84229	24.975		M	
Total		25874973	514614				



3ba

(2*R*,3*R*)-2-methyl-3-phenyl-1,5-di(pyridin-2-yl)pentane-1,5-dione (Table 4, 3ba). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*S*,*S*)-Ph-BPE [824395-67-7] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(pyridin-2-yl)propan-1-one (**1b**) [3238-55-9] (54 mg, 0.40 mmol, 2.0 equiv), (2*E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (42 mg, 0.20 mmol, 1.0 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 3.3:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ba** was afforded as a yellowish sticky liquid (59 mg, 82% yield, 3.3:1 dr (after isolation)).

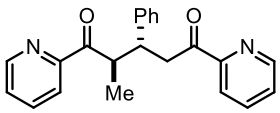
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.2 Hz, 1H of major, 77%), 8.68 (d, *J* = 3.9 Hz, 1H of minor, 23%), 8.12 (d, *J* = 7.8 Hz, 1H of major, 77%), 7.94 – 7.77 (m, 2H), 7.75 – 7.69 (m, 1H of minor, 23%), 7.57 – 7.45 (m, 2H), 7.40 (dd, *J* = 15.1, 7.4 Hz, 2H), 7.28 (d, *J* = 3.9 Hz, 3H), 7.19 (dt, *J* = 10.0, 6.0 Hz, 2H of major, 77%), 7.08 (d, *J* = 7.3 Hz, 1H of minor, 23%), 6.93 (d, *J* = 6.2 Hz, 1H of minor, 23%), 4.73 – 4.66 (m, 1H of minor, 23%), 4.66 – 4.51 (m, 1H of major, 77%), 4.07 – 3.99 (m, 1H of minor, 23%), 3.86 (td, *J* = 9.9, 4.4 Hz, 1H of major, 77%), 3.48 – 3.42 (m, 2H of minor, 23%), 3.41 – 3.19 (m, 2H of major, 77%), 1.29 (d, *J* = 6.9 Hz, 3H of minor, 23%), 0.99 (d, *J* = 6.9 Hz, 3H of minor, 77%).

^{13}C NMR (75 MHz, $CDCl_3$) δ 204.95, 204.09, 198.64, 153.03, 149.03, 148.72, 142.01, 137.31, 137.06, 132.97, 132.82, 128.54, 128.47, 128.44, 128.20, 128.06, 127.37, 127.08, 126.73, 126.40, 44.39, 44.31, 44.25, 42.61, 40.32, 16.59, 13.75.

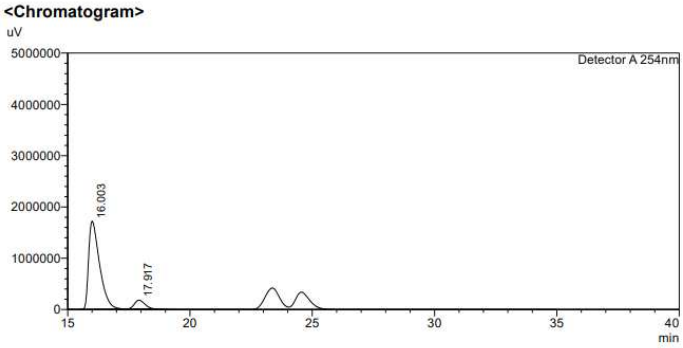
HRMS (ESI) m/z calcd for **$C_{22}H_{21}N_2O_2$** $[M + H]^+$: 345.1603, found: 345.1587.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 83% [OD-H, 20% i-PrOH in hexanes, 0.3 mL/min], t_R = 16.00 min (*anti* major), t_R = 17.92 min (*anti* minor), t_R = 23.37 (*syn* major), and t_R = 24.56 (*syn* minor).

$[\alpha]_D^{20}$ = –141° (c = 0.39, $CHCl_3$).

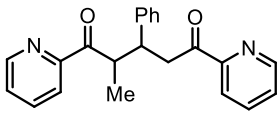


(*R*,*R*)-**3ba**
3.3:1 dr, 83% ee

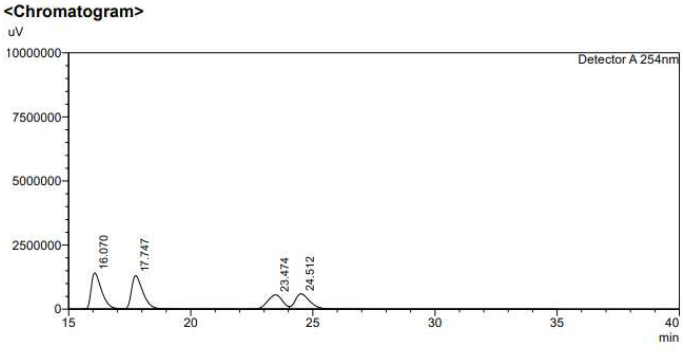


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.003	53336595	1719487	91.464		M	
2	17.917	4977458	170049	8.536		M	
Total		58314053	1889536				

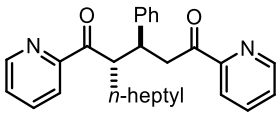


(*rac*)-**3ba**
1.0:1 dr



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.070	42289506	1416835	31.538			
2	17.747	43161739	1306267	32.189		V	
3	23.474	23658179	558429	17.644			
4	24.512	24979758	600742	18.629		V	
Total		134089183	3882273				



3ca

(2*S*,3*S*)-2-heptyl-3-phenyl-1,5-di(pyridin-2-yl)pentane-1,5-dione (Table 4, 3ca). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(pyridin-2-yl)nonan-1-one (**1c**) [143773-13-1] (87.7 mg, 0.400 mmol, 2.00 equiv), (2*E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (42 mg, 0.20 mmol, 1.0 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 3.2:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ca** was afforded as a yellowish sticky liquid (74.6 mg, 87% yield, 6.1:1 dr (after isolation)).

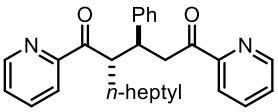
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.90 – 7.78 (m, 2H), 7.73 (dd, *J* = 15.9, 8.0 Hz, 2H), 7.47 – 7.33 (m, 2H), 7.32 – 7.23 (m, 3H of major, 86%), 7.22 – 7.16 (m, 3H of minor, 14%), 7.09 (t, *J* = 7.3 Hz, 2H), 7.00 (d, *J* = 7.2 Hz, 1H), 4.66 (dd, *J* = 12.3, 5.1 Hz, 1H), 3.90 (d, *J* = 15.5 Hz, 1H), 3.80 (d, *J* = 9.7 Hz, 1H), 3.59 (dd, *J* = 17.0, 3.9 Hz, 1H), 2.08 – 1.89 (m, 1H), 1.72 – 1.55 (m, 1H), 1.32 – 1.09 (m, 10H), 0.81 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 204.49, 200.28, 153.77, 153.41, 148.73, 148.63, 144.83, 142.87, 136.73, 136.65, 130.56, 128.85, 128.39, 127.87, 126.95, 126.64, 126.09, 122.09, 121.76, 49.75, 42.28, 39.34, 31.72, 29.78, 29.03, 28.49, 27.58, 22.56, 14.04.

HRMS (ESI) m/z calcd for **$C_{28}H_{33}N_2O_2$** $[M + H]^+$: 429.2542, found: 429.2525.

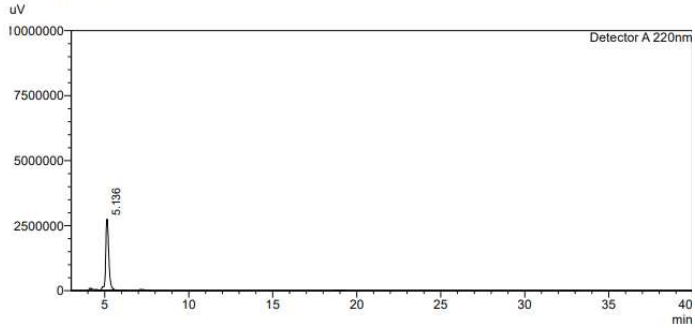
HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be >99% [IC, 20% i-PrOH in hexanes, 1 mL/min], t_R = 5.14 min (*anti* major), t_R = 7.20 min (*syn* isomer A), t_R = 16.69 (*anti* minor), and t_R = 32.70 (*syn* isomer B).

$[\alpha]_D^{20}$ = +66° (c = 1.0, $CHCl_3$).



(*S*,*S*)-**3ca**
6.1:1 dr, >99% ee

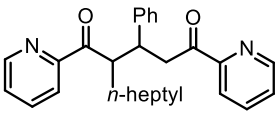
<Chromatogram>



<Peak Table>

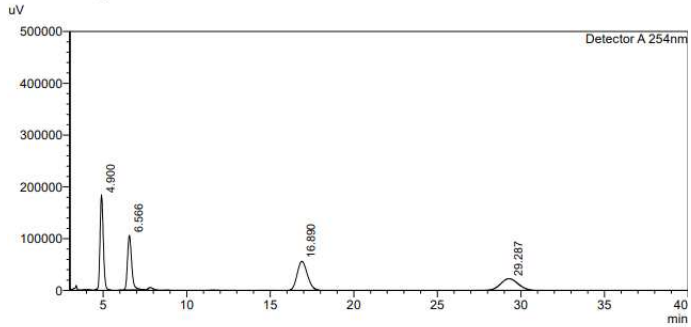
Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.136	35663832	2740762	100.000		M	
Total		35663832	2740762				



(*rac*)-**3ca**
1.0:1 dr

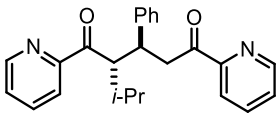
<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.900	2598319	183631	29.902			
2	6.566	1822158	105136	20.970		M	
3	16.890	2464566	56733	28.362			
4	29.287	1804487	23272	20.766			
Total		8689530	368772				



3da

(2*S*,3*S*)-2-isopropyl-3-phenyl-1,5-di(pyridin-2-yl)pentane-1,5-dione (Table 4, 3da). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 3-methyl-1-(pyridin-2-yl)butan-1-one (**1d**) [6952-53-0] (65 mg, 0.40 mmol, 2.0 equiv), (2*E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (42 mg, 0.20 mmol, 1.0 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN:DCE (1:1, 0.8 mL). The diastereomeric ratio was determined to be 5.0:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3da** was afforded as a white crystal (53.6 mg, 72% yield, 12:1 dr (after isolation), mp: 90–95 °C).

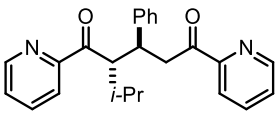
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.50 (d, *J* = 4.0 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H of minor, 8%), 7.87 (d, *J* = 7.3 Hz, 1H of major, 92%), 7.80 – 7.69 (m, 2H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.55 – 7.49 (m, 1H of minor, 8%), 7.41 (s, 1H), 7.36 – 7.28 (m, 1H of major, 92%), 7.20 (d, *J* = 7.4 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 2H), 6.90 (t, *J* = 7.2 Hz, 1H), 4.98 – 4.90 (m, 1H of major, 92%), 4.90 – 4.81 (m, 1H of minor, 8%), 4.34 – 4.22 (m, 1H of minor, 8%), 4.02 (td, *J* = 9.8, 5.1 Hz, 1H of major, 92%), 3.77 – 3.54 (m, 1H and 1H of major, 92%), 3.16 (d, *J* = 16.6 Hz, 1H of minor, 8%), 2.41 – 2.22 (m, 1H), 1.08 (d, *J* = 6.7 Hz, 3H of major, 92%), 0.97 (d, *J* = 6.9 Hz, 3H of major, 92%), 0.86 (d, *J* = 6.7 Hz, 1H of minor, 8%), 0.80 (d, *J* = 7.1 Hz, 1H of minor, 8%).

^{13}C NMR (75 MHz, $CDCl_3$) δ 204.49, 200.36, 154.54, 153.50, 148.71, 148.36, 142.56, 136.77, 136.62, 128.79, 128.57, 128.11, 127.68, 126.93, 126.43, 126.04, 121.79, 121.53, 52.29, 41.80, 41.25, 28.87, 21.85, 17.92.

HRMS (ESI) m/z calcd for **$C_{24}H_{25}N_2O_2$** $[M + H]^+$: 373.1916, found: 373.1899.

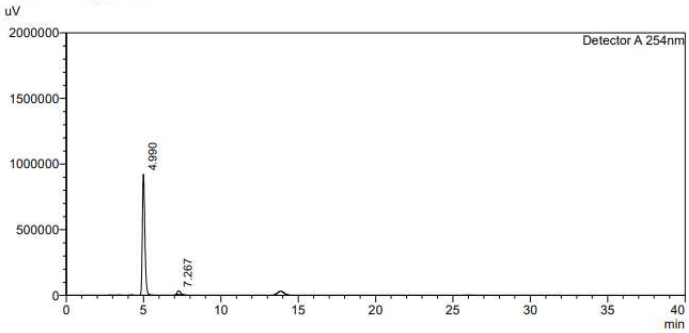
HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 92% [IC, 20% i-PrOH in hexanes, 1 mL/min], t_R = 4.99 min (*anti* major), t_R = 7.27 min (*anti* minor), t_R = 13.86 (*syn* major), and t_R = 27.58 (*syn* minor).

$[\alpha]_D^{20}$ = +84° (c = 0.59, $CHCl_3$).



(*S*,*S*)-**3da**
12:1 dr, 92% ee

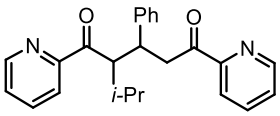
<Chromatogram>



<Peak Table>

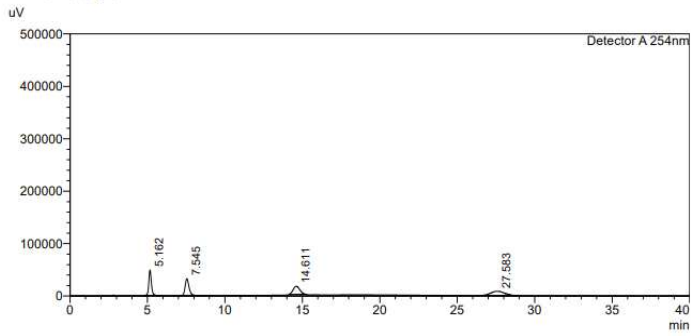
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.990	10372714	923797	96.190		M	
2	7.267	410848	28853	3.810		M	
Total		10783562	952650				



(*rac*)-**3da**
3.0:1 dr

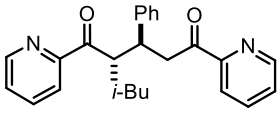
<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.162	569188	48365	27.729		M	
2	7.545	562826	32320	27.420		M	
3	14.611	455433	15242	22.188		M	
4	27.583	465202	7764	22.663		M	
Total		2052649	103691				



3ea

(2*S*,3*S*)-2-isobutyl-3-phenyl-1,5-di(pyridin-2-yl)pentane-1,5-dione (Table 4, 3ea). The title compound was prepared according to **General Procedure F**, using 5,5-dimethylhexanoic acid [24499-80-7] (5.8 mg, 0.040 mmol, 0.20 equiv), $CuBr_2$ [7789-45-9] (4.4 mg, 0.020 mmol, 0.10 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 4-methyl-1-(pyridin-2-yl)pentan-1-one (**1e**) [95188-18-4] (71 mg, 0.40 mmol, 2.0 equiv), (2*E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (42 mg, 0.20 mmol, 1.0 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 2.0:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ea** was afforded as a yellowish sticky liquid (46.4 mg, 60% yield, 13:1 dr (after isolation)).

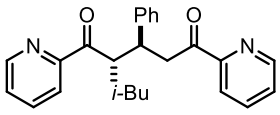
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.65 (m, 1H of major, 93%), 8.63 (d, *J* = 4.4 Hz, 2H of minor, 7%), 8.56 (d, *J* = 4.2 Hz, 1H of major, 93%), 8.04 (d, *J* = 7.8 Hz, 1H), 7.83 – 7.71 (m, 2H), 7.67 (td, *J* = 7.7, 1.6 Hz, 1H), 7.43 (ddd, *J* = 7.4, 4.8, 1.2 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.29 – 7.23 (m, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.09 (dd, *J* = 10.2, 4.3 Hz, 1H), 4.82 – 4.72 (m, 1H), 3.94 – 3.87 (m, 1H), 3.87 – 3.76 (m, 1H), 3.23 (dd, *J* = 16.0, 3.4 Hz, 1H), 1.73 (td, *J* = 13.1, 4.0 Hz, 1H), 1.34 – 1.19 (m, 1H), 1.19 – 1.10 (m, 1H), 0.80 (dd, *J* = 5.8, 3.0 Hz, 6H of minor, 7%), 0.71 (dd, *J* = 10.8, 6.5 Hz, 6H of major, 93%).

^{13}C NMR (101 MHz, $CDCl_3$) δ 206.08, 200.22, 154.37, 153.57, 149.12, 148.79, 142.79, 136.93, 136.70, 128.70, 128.22, 127.04, 126.85, 126.49, 122.25, 121.86, 47.14, 44.64, 42.26, 40.63, 26.36, 23.90, 21.85.

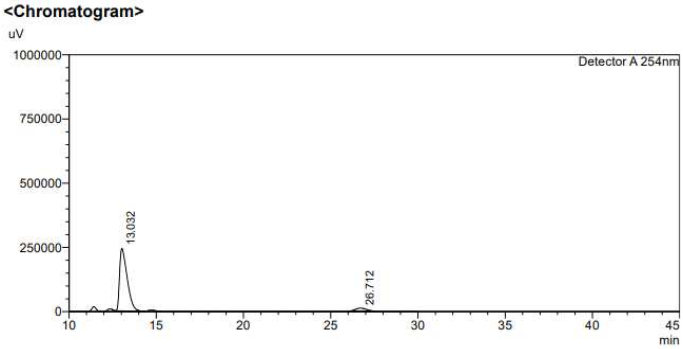
HRMS (ESI) m/z calcd for **$C_{25}H_{27}N_2O_2$** $[M + H]^+$: 387.2072, found: 387.2055.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 88% [OD-H, 5% i-PrOH in hexanes, 0.5 mL/min], t_R = 11.42 min (*syn* isomer A), t_R = 12.36 min (*syn* isomer B), t_R = 13.03 (*anti* major), and t_R = 26.71 (*anti* minor).

$[\alpha]_D^{20}$ = +114° (c = 0.22, $CHCl_3$).

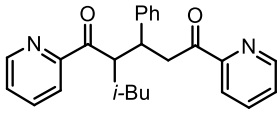


(*S*,*S*)-**3ea**
13:1 dr, 88% ee

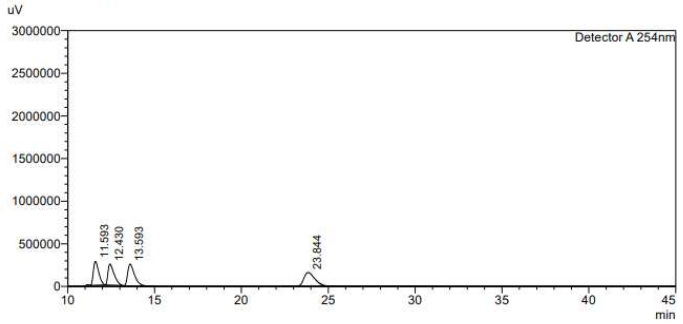


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.032	7318905	243382	93.861		M	
2	26.712	478682	11455	6.139		M	
Total		7797587	254837				

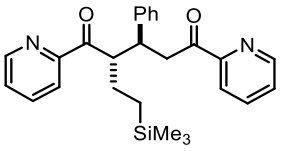


(*rac*)-**3ea**
3.0:1 dr



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.593	5990875	278791	22.285		M	
2	12.430	6078217	246661	22.610		M	
3	13.593	7328898	257553	27.263		M	
4	23.844	7484420	163664	27.841		M	
Total		26882410	946669				



3fa

(2*S*,3*S*)-3-phenyl-1,5-di(pyridin-2-yl)-2-(2-(trimethylsilyl)ethyl)pentane-1,5-dione (Table 4, 3fa). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(pyridin-2-yl)-4-(trimethylsilyl)butan-1-one (**1f**) (89 mg, 0.40 mmol, 2.0 equiv), (2*E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (42 mg, 0.20 mmol, 1.0 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN:DCE (1:1, 0.8 mL). The diastereomeric ratio was determined to be 11:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3fa** was afforded as a yellowish sticky liquid (70 mg, 81% yield, >20:1 dr (after isolation)).

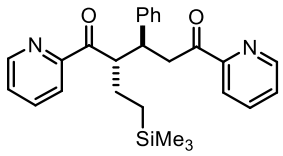
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 – 8.59 (m, 2H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.83 – 7.67 (m, 3H), 7.48 – 7.31 (m, 2H), 7.28 (dd, *J* = 4.8, 3.7 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 2H), 7.00 (d, *J* = 7.3 Hz, 1H), 4.76 – 4.64 (m, 1H), 3.96 (dd, *J* = 7.9, 4.9 Hz, 1H), 3.78 (dd, *J* = 17.1, 9.6 Hz, 1H), 3.63 (dd, *J* = 17.1, 4.9 Hz, 1H), 2.08 – 1.92 (m, 1H), 1.83 – 1.61 (m, 1H), 0.51 – 0.33 (m, 2H), -0.08 (s, 9H of major, 98%), -0.25 (s, 9H of minor 2%).

^{13}C NMR (75 MHz, $CDCl_3$) δ 204.46, 200.46, 153.97, 153.54, 148.85, 148.70, 142.98, 136.91, 136.83, 128.59, 127.98, 127.08, 126.73, 126.22, 122.17, 121.93, 52.46, 42.39, 40.01, 23.16, 13.97, -1.77.

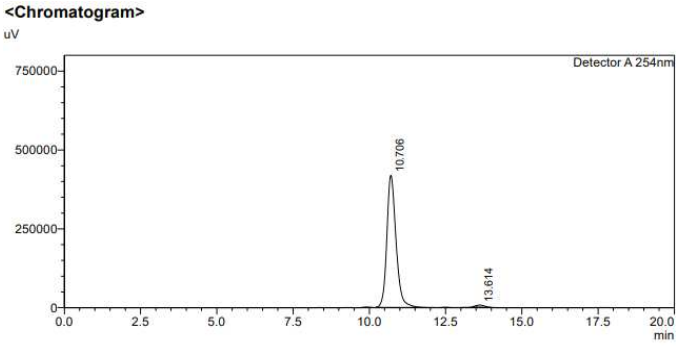
HRMS (ESI) m/z calcd for **$C_{26}H_{31}N_2O_2Si$** $[M + H]^+$: 431.2155, found: 431.2135.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 97% [OD-H, 20% i-PrOH in hexanes, 0.3 mL/min], t_R = 10.71 min (*anti* major), t_R = 13.62 min (*anti* minor).

$[\alpha]_D^{20}$ = +49° (c = 0.90, $CHCl_3$).

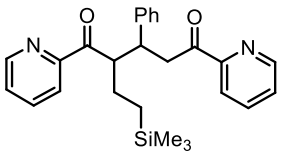


(*S*,*S*)-**3fa**
>20:1 dr, 97% ee

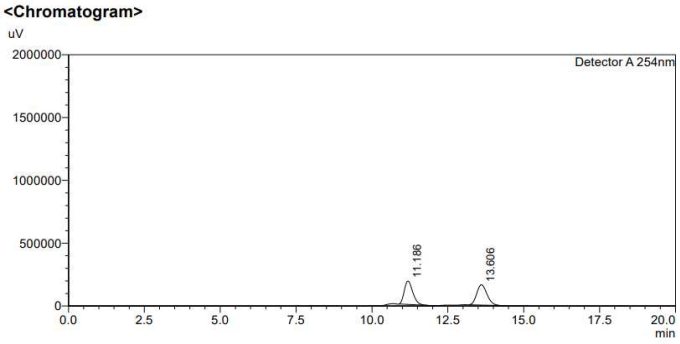


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.706	8778453	418809	98.674		M	
2	13.614	117926	6142	1.326		M	
Total		8896379	424951				

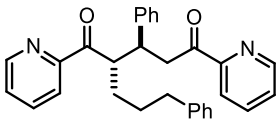


(*rac*)-**3fa**
>20:1 dr



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.186	3632075	186394	49.202		M	
2	13.606	3749961	161147	50.798		M	
Total		7382036	347542				



3ga

(2*S*,3*S*)-3-phenyl-2-(3-phenylpropyl)-1,5-di(pyridin-2-yl)pentane-1,5-dione (Table 4, 3ga). The title compound was prepared according to **General Procedure F**, using 2-adamantanebutyric acid [1693982-88-5] (8.8 mg, 0.040 mmol, 0.20 equiv), $CuBr_2$ [7789-45-9] (4.4 mg, 0.020 mmol, 0.10 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 5-phenyl-1-(pyridin-2-yl)pentan-1-one (**1g**) (96 mg, 0.40 mmol, 2.0 equiv), (2*E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (42 mg, 0.20 mmol, 1.0 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 6.7:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ga** was afforded as a yellowish sticky liquid (77.2 mg, 86% yield, 13:1 dr (after isolation)).

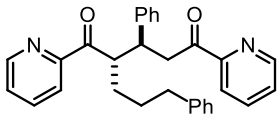
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.5 Hz, 1H of minor, 7%), 8.62 (t, *J* = 4.2 Hz, 2H of major, 93%), 8.56 (d, *J* = 4.7 Hz, 1H of minor, 7%), 8.05 (d, *J* = 7.9 Hz, 1H of minor, 7%), 7.84 (dd, *J* = 18.6, 7.8 Hz, 1H and 1H of major, 93%), 7.73 (dtd, *J* = 9.3, 7.7, 1.6 Hz, 2H), 7.45 – 7.33 (m, 2H), 7.23 – 7.14 (m, 2H), 7.14 – 7.07 (m, 3H), 7.04 (dd, *J* = 7.8, 4.4 Hz, 3H of major, 92%), 6.96 – 6.91 (m, 3H of minor, 8%), 4.73 (ddd, *J* = 10.3, 7.0, 3.0 Hz, 1H), 4.02 – 3.90 (m, 1H), 3.81 (dd, *J* = 17.4, 9.8 Hz, 1H), 3.58 (dd, *J* = 17.4, 4.6 Hz, 1H of major, 93%), 3.24 (d, *J* = 13.3 Hz, 1H of minor, 7%), 2.66 – 2.50 (m, 2H of major, 93%), 2.42 – 2.34 (m, 2H of minor, 7%), 2.18 (d, *J* = 11.2 Hz, 1H of minor, 7%), 2.17 – 1.99 (m, 1H of major, 93%), 1.81 – 1.66 (m, 1H), 1.62 – 1.41 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.33, 200.14, 153.66, 153.32, 148.69, 148.61, 142.66, 142.25, 136.65, 136.58, 128.34, 128.25, 128.07, 127.85, 126.89, 126.64, 126.09, 125.46, 122.02, 121.69, 49.36, 42.22, 39.21, 35.89, 29.40, 28.09.

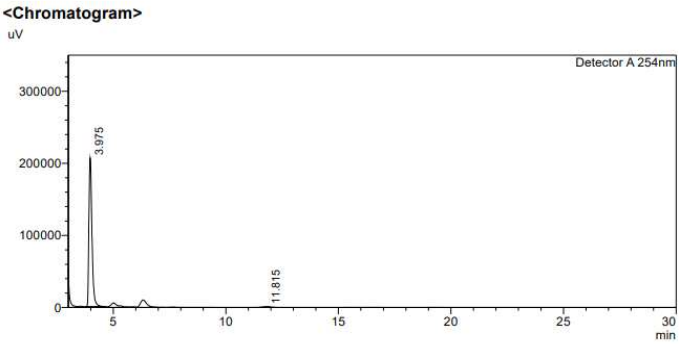
HRMS (ESI) m/z calcd for **$C_{30}H_{29}N_2O_2$** $[M + H]^+$: 449.2229, found: 449.2212.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 94% [IC, 30% i-PrOH in hexanes, 1.1 mL/min], t_R = 3.98 min (*anti* major), t_R = 11.82 min (*anti* minor), t_R = 22.76 (*syn* isomer A), and t_R = 26.41 (*syn* isomer B).

$[\alpha]_D^{20}$ = +42° (c = 1.4, $CHCl_3$).

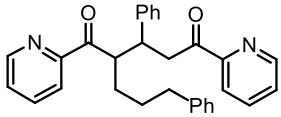


(*S*,*S*)-**3ga**
13:1 dr, 94% ee

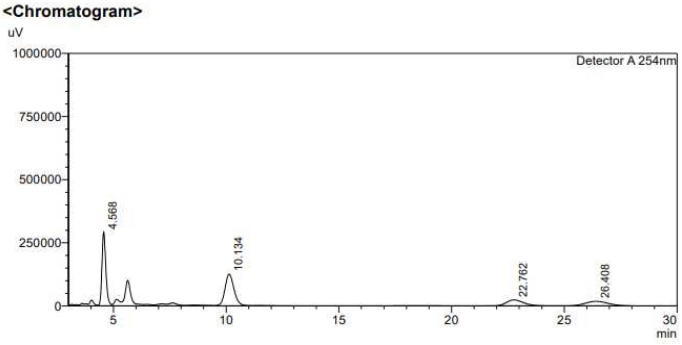


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.975	1948618	206377	97.090		M	
2	11.815	58401	1701	2.910			
Total		2007019	208078				

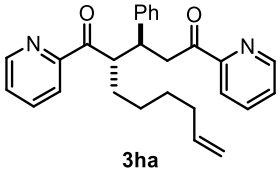


(*rac*)-**3ga**
2.0:1 dr



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.568	3553671	292348	36.463			
2	10.134	3613339	125788	37.076			
3	22.762	1290026	23664	13.237			
4	26.408	1288836	17984	13.224			
Total		9745872	459785				



3ha

(2*S*,3*S*)-2-(hex-5-en-1-yl)-3-phenyl-1,5-di(pyridin-2-yl)pentane-1,5-dione (Table 4, 3ha). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(pyridin-2-yl)oct-7-en-1-one (**1h**) [1697904-52-1] (81 mg, 0.40 mmol, 2.0 equiv), (2*E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (42 mg, 0.20 mmol, 1.0 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 2.3:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ha** was afforded as a yellowish sticky liquid (55.3 mg, 67% yield, 9.0:1 dr (after isolation)).

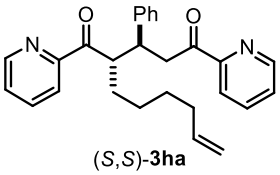
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.4 Hz, 2H), 7.85 (dd, *J* = 9.6, 8.6 Hz, 2H), 7.74 (qd, *J* = 7.7, 1.6 Hz, 2H), 7.47 – 7.32 (m, 2H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 2H), 7.02 (d, *J* = 7.2 Hz, 1H), 5.70 (ddd, *J* = 17.0, 6.7, 3.5 Hz, 1H), 4.87 (t, *J* = 12.4 Hz, 2H), 4.71 – 4.57 (m, 1H), 4.00 – 3.90 (m, 1H), 3.83 (dd, *J* = 17.2, 9.8 Hz, 1H), 3.57 (dd, *J* = 17.2, 4.3 Hz, 1H), 2.33 (t, *J* = 7.5 Hz, 2H of minor, 10%), 2.08 – 1.85 (m, 2H), 1.75 – 1.59 (m, 2H of major, 90%), 1.38 – 1.27 (m, 2H), 1.26 – 1.15 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 204.00, 199.86, 153.34, 153.02, 148.40, 148.29, 142.51, 138.62, 136.57, 136.51, 128.10, 127.63, 126.71, 126.43, 125.86, 121.89, 121.54, 113.88, 49.51, 41.95, 38.98, 33.20, 28.77, 27.87, 26.79.

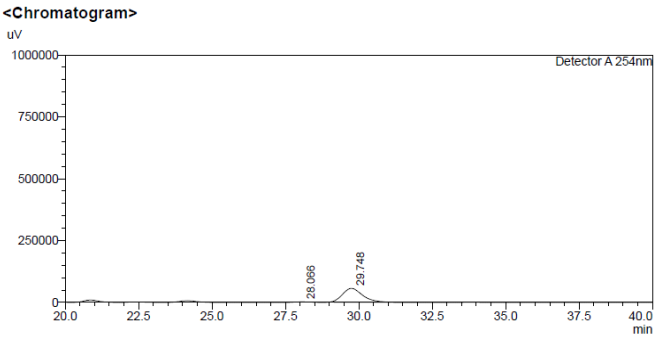
HRMS (ESI) m/z calcd for $\mathbf{C_{27}H_{29}N_2O_2}$ $[M + H]^+$: 413.2229, found: 413.2212.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 92% [AD-H, 5.0% i-PrOH in hexanes, 0.5 mL/min], t_R = 23.65 min (*syn* major), t_R = 26.04 min (*syn* minor), t_R = 27.70 (*anti* minor), and t_R = 29.38 (*anti* major).

$[\alpha]_D^{20}$ = +88° (c = 0.30, $CHCl_3$).

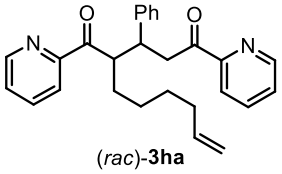


(*S*,*S*)-**3ha**
9.0:1 dr, 92% ee

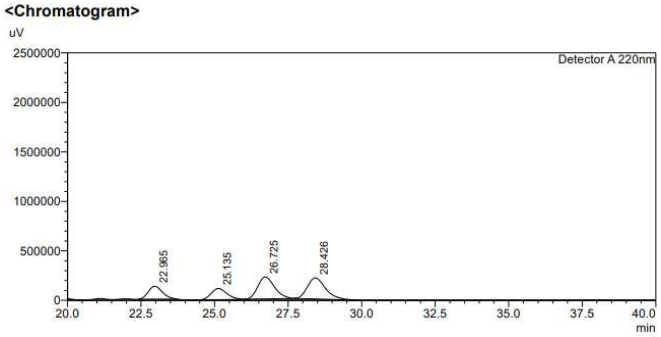


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	28.066	104551	2650	3.824		M	
2	29.748	2629285	55740	96.176		M	
Total		2733836	58391				

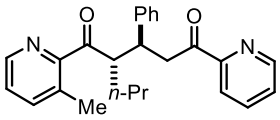


(*rac*)-**3ha**
1.5:1 dr



<Peak Table>
Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.965	4327500	129738	16.336		M	
2	25.135	4234135	113239	15.984		M	
3	26.725	8806080	222237	33.243		M	
4	28.426	9122363	212640	34.437		M	
Total		26490078	677854				



3ia

(2*S*,3*S*)-1-(3-methylpyridin-2-yl)-3-phenyl-2-propyl-5-(pyridin-2-yl)pentane-1,5-dione (Table 4, 3ia). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(3-methylpyridin-2-yl)pentan-1-one (**1i**) [1249752-31-5] (71 mg, 0.40 mmol, 2.0 equiv), (2*E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (42 mg, 0.20 mmol, 1.0 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 7.2:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ia** was afforded as a yellowish sticky liquid (64.9 mg, 84% yield, >20:1 dr (after isolation)).

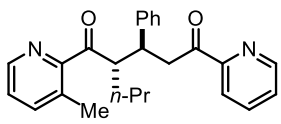
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 4.7, 0.7 Hz, 1H), 8.46 (dd, *J* = 4.6, 1.0 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 1.7 Hz, 1H), 7.47 – 7.34 (m, 2H), 7.25 – 7.15 (m, 3H), 7.02 (dt, *J* = 14.5, 7.0 Hz, 3H), 4.65 – 4.54 (m, 1H), 3.79 (dd, *J* = 17.9, 6.8 Hz, 2H), 3.60 (t, *J* = 7.3 Hz, 1H), 2.25 (s, 3H), 2.06 – 1.90 (m, 1H), 1.69 – 1.57 (m, 1H), 1.35 – 1.20 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 206.74, 200.42, 153.52, 152.72, 148.87, 145.85, 142.92, 139.92, 136.88, 134.83, 128.54, 127.96, 127.09, 126.22, 125.66, 121.90, 51.48, 43.03, 40.31, 31.42, 21.05, 20.04, 14.55.

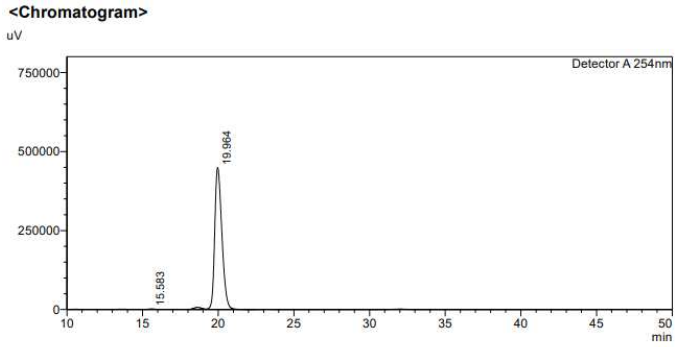
HRMS (ESI) m/z calcd for **$C_{25}H_{27}N_2O_2$** $[M + H]^+$: 387.2073, found: 387.2057.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be >99% [OX-H, 20% i-PrOH in hexanes, 0.3 mL/min], t_R = 15.58 min (*anti* minor), t_R = 19.96 min (*anti* major), t_R = 30.66 (*syn* isomer A), and t_R = 42.14 (*syn* isomer B).

$[\alpha]_D^{20}$ = +34° (c = 0.63, $CHCl_3$).

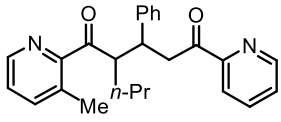


(*S*,*S*)-**3ia**
>20:1 dr, >99% ee

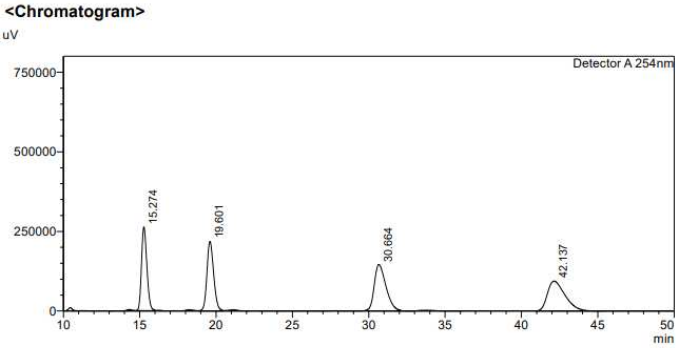


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.583	36111	1434	0.244			
2	19.964	14749573	448827	99.756			
Total		14785684	450261				

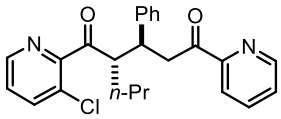


(*rac*)-**3ia**
1.0:1 dr



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.274	6440224	262827	22.709		M	
2	19.601	6697375	218318	23.616			
3	30.664	7703655	145221	27.164		M	
4	42.137	7518650	93918	26.512		M	
Total		28359904	720284				



3ja

(2*S*,3*S*)-1-(3-chloropyridin-2-yl)-3-phenyl-2-propyl-5-(pyridin-2-yl)pentane-1,5-dione (Table 4, 3ja). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(3-chloropyridin-2-yl)pentan-1-one (**1j**) [1249752-31-5] (79 mg, 0.40 mmol, 2.0 equiv), (2*E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (42 mg, 0.20 mmol, 1.0 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 3.5:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ja** was afforded as a yellowish sticky liquid (60.2 mg, 74% yield, 5.2:1 dr (after isolation)).

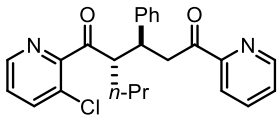
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 – 8.63 (m, 1H of major, 84%), 8.60 (d, *J* = 4.7 Hz, 1H of minor, 16%), 8.53 (dd, *J* = 4.6, 1.3 Hz, 1H of minor, 16%), 8.49 (dd, *J* = 4.5, 1.3 Hz, 1H of major, 84%), 7.86 (d, *J* = 7.8 Hz, 1H), 7.74 (td, *J* = 7.7, 1.7 Hz, 1H), 7.65 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.42 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 7.30 – 7.19 (m, 3H), 7.11 (t, *J* = 7.5 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 4.43 – 4.31 (m, 1H), 4.03 – 3.74 (m, 2H), 3.61 – 3.51 (m, 1H of major, 84%), 3.46 – 3.35 (m, 1H of minor, 16%), 2.08 – 1.94 (m, 1H), 1.67 – 1.52 (m, 1H), 1.43 – 1.17 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H of major, 84%), 0.71 (t, *J* = 7.2 Hz, 3H of minor, 16%).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.11, 200.06, 153.35, 151.90, 151.82, 148.80, 146.36, 142.35, 139.05, 136.76, 130.58, 128.32, 128.00, 127.03, 126.24, 126.17, 121.78, 52.27, 42.26, 39.53, 30.46, 20.84, 14.32.

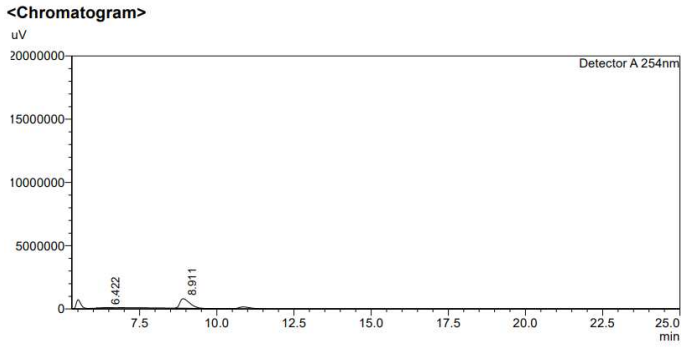
HRMS (ESI) m/z calcd for **$C_{24}H_{24}ClN_2O_2$** $[M + H]^+$: 407.1526, found: 407.1520.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 95% [OX-H, 20% i-PrOH in hexanes, 1 mL/min], t_R = 6.79 min (*anti* minor), t_R = 8.91 min (*anti* major), t_R = 10.54 (*syn* isomer A), and t_R = 19.02 (*syn* isomer B).

$[\alpha]_D^{20}$ = +25° (c = 0.84, $CHCl_3$).

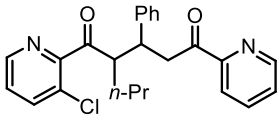


(*S*,*S*)-**3ja**
5.2:1 dr, 95% ee

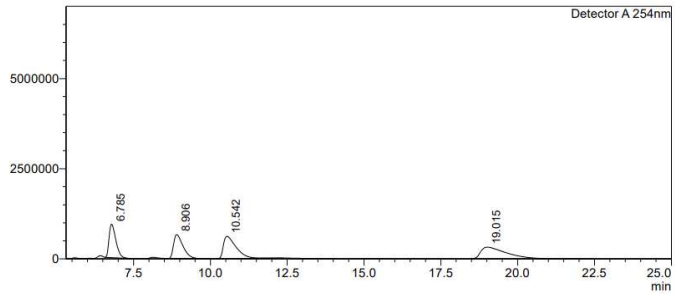


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.422	446709	31530	2.640		M	
2	8.911	16475111	746072	97.360		M	
Total		16921820	777602				

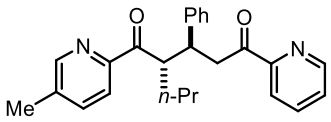


(*rac*)-**3ja**
1.5:1 dr



<Peak Table>
Detector A 254nm

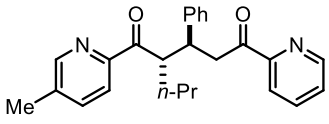
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.785	14127916	927126	21.892		M	
2	8.906	14113008	658824	21.869		M	
3	10.542	17595144	614773	27.265		M	
4	19.015	18697185	321236	28.973		M	
Total		64533253	2521958				



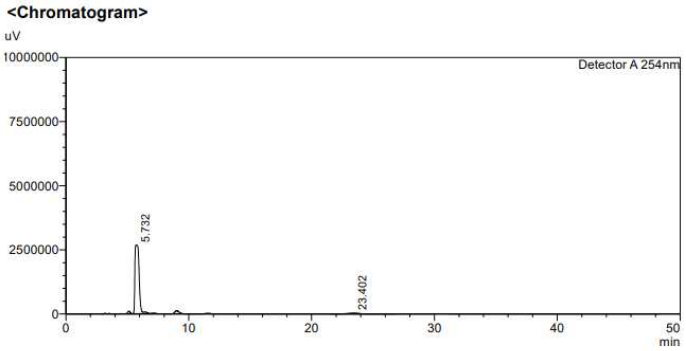
3ka

(2*S*,3*S*)-1-(5-methylpyridin-2-yl)-3-phenyl-2-propyl-5-(pyridin-2-yl)pentane-1,5-dione (Table 4, 3ka). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(5-methylpyridin-2-yl)pentan-1-one (**1k**) [2008303-13-5] (71 mg, 0.40 mmol, 2.0 equiv), (2*E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] (42 mg, 0.20 mmol, 1.0 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 2.2:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ka** was afforded as a yellowish sticky liquid (51.8 mg, 67% yield, 13:1 dr (after isolation)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.7 Hz, 1H of major, 93%), 8.54 (dd, *J* = 11.7, 3.1 Hz, 2H of minor, 7%), 8.45 (s, 1H of major, 93%), 7.89 – 7.83 (m, 1H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H of major, 93%), 7.44 – 7.38 (m, 1H of major, 93%), 7.38 – 7.35 (m, 2H of minor, 7%), 7.29 (d, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 2H), 7.04 – 6.96 (m, 1H), 4.74 – 4.60 (m, 1H), 3.99 – 3.88 (m, 1H), 3.83 (dd, *J* = 17.3, 9.9 Hz, 1H), 3.57 (dd, *J* = 17.4, 4.3 Hz, 1H), 2.37 (s, 3H), 2.07 (d, *J* = 6.4 Hz, 1H of minor, 7%), 2.02 – 1.93 (m, 1H of major, 93%), 1.70 – 1.52 (m, 1H), 1.26 – 1.09 (m, 2H), 0.82 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.39, 200.47, 153.62, 151.70, 149.29, 148.90, 143.15, 137.19, 136.85, 128.53, 128.01, 127.05, 126.19, 121.96, 121.89, 49.59, 42.34, 39.44, 30.87, 21.02, 18.79, 14.47.
HRMS (ESI) m/z calcd for **$C_{25}H_{27}N_2O_2$** $[M + H]^+$: 387.2073, found: 387.2055.
HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 91% [IC, 30% i-PrOH in hexanes, 1 mL/min], t_R = 5.73 min (*anti* major) t_R = 9.03 min (*syn* major), t_R = 23.40 (*anti* minor), and t_R = 45.53 (*syn* minor).
$[\alpha]_D^{20}$ = +40° (c = 0.78, $CHCl_3$).

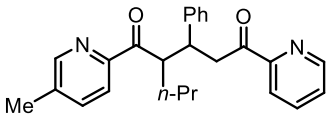


(*S*,*S*)-**3ka**
13:1, 91% ee

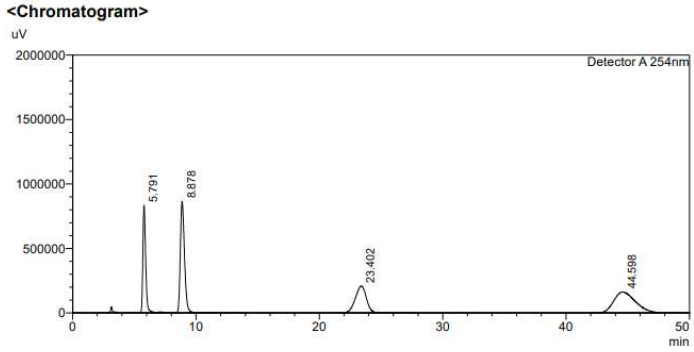


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.732	63797823	2675963	95.653		M	
2	23.402	2899034	40564	4.347			
Total		66696857	2716527				

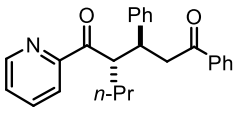


(*rac*)-**3ka**
1.0:1 dr



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.791	13561916	833151	19.954			
2	8.878	20755239	863092	30.538		V	
3	23.402	13185952	209479	19.401			
4	44.598	20461647	163363	30.106			
Total		67964756	2069086				



3ab

(2*S*,3*S*)-3,5-diphenyl-2-propyl-1-(pyridin-2-yl)pentane-1,5-dione (Table 4, 3ab). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*)-Tol-BINAP [99646-28-3] (15 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-chalcone (**2b**) [614-47-1] (42 mg, 0.20 mmol, 1.0 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 4.0:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ab** was afforded as a yellowish sticky liquid (59.4 mg, 80% yield, 8.1:1 dr (after isolation)).

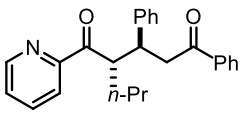
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.3 Hz, 1H of major, 89%), 8.66 (d, *J* = 4.6 Hz, 1H of minor, 11%), 8.09 (d, *J* = 7.8 Hz, 1H of major, 89%), 7.95 (d, *J* = 7.7 Hz, 1H of minor, 11%), 7.85 (td, *J* = 7.7, 1.5 Hz, 1H), 7.81 – 7.67 (m, 2H), 7.51 – 7.44 (m, 2H), 7.42 (d, *J* = 7.9 Hz, 2H of minor, 11%), 7.37 (t, *J* = 7.7 Hz, 2H of major, 89%), 7.30 – 7.21 (m, 4H), 7.18 – 7.11 (m, 1H of major, 89%), 7.04 (t, *J* = 7.2 Hz, 1H of minor 11%), 4.68 (td, *J* = 9.8, 3.7 Hz, 1H), 4.02 – 3.90 (m, 1H of minor, 11%), 3.84 (td, *J* = 10.2, 3.9 Hz, 1H of major, 89%), 3.52 – 3.44 (m, 1H of minor, 11%), 3.43 – 3.32 (m, 1H of major, 89%), 3.15 (dd, *J* = 15.8, 3.9 Hz, 1H), 1.66 – 1.54 (m, 1H), 1.39 – 1.24 (m, 1H), 1.21 – 0.97 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H of minor, 11%), 0.67 (t, *J* = 7.3 Hz, 3H of major, 89%).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.87, 198.68, 154.20, 149.13, 142.29, 137.19, 137.16, 132.83, 128.52, 128.51, 128.45, 128.23, 127.28, 126.71, 122.34, 49.07, 44.06, 44.03, 33.47, 20.14, 14.30.

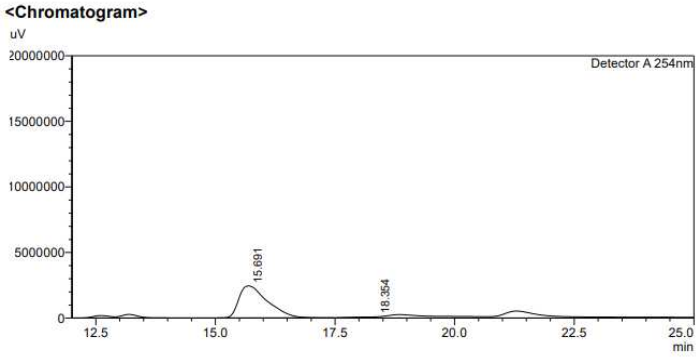
HRMS (ESI) m/z calcd for **$C_{25}H_{26}NO_2$** $[M + H]^+$: 372.1964, found: 372.1947.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be >99% [AD-H, 20% i-PrOH in hexanes, 0.3 mL/min], t_R = 15.69 min (*anti* major), t_R = 18.35 min (*anti* minor), t_R = 18.85 (*syn* minor), and t_R = 21.30 (*syn* major).

$[\alpha]_D^{20}$ = +121° (c = 0.28, $CHCl_3$).

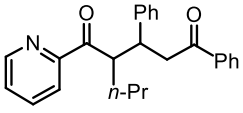


(*S*,*S*)-**3ab**
8.1:1 dr, >99% ee

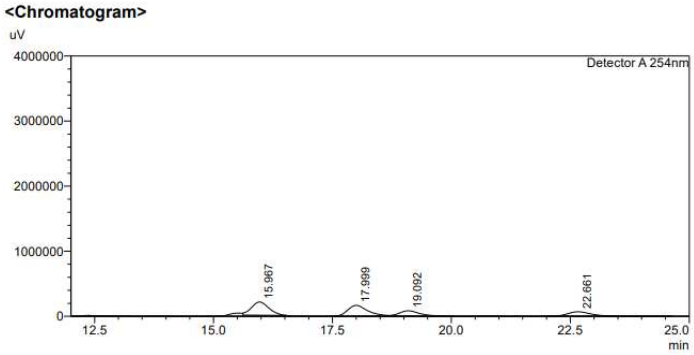


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.691	101648553	2439221	99.868		M	
2	18.354	133870	9540	0.132		M	
Total		101782423	2448760				

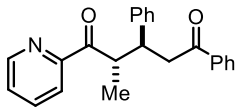


(*rac*)-**3ab**
2.0:1 dr



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.967	5222396	203513	34.072		M	
2	17.999	5006565	167960	32.664		M	
3	19.092	2539637	82664	16.569		M	
4	22.661	2559034	70678	16.696			
Total		15327632	524815				



3bb

(2*S*,3*S*)-2-methyl-3,5-diphenyl-1-(pyridin-2-yl)pentane-1,5-dione (Table 4, 3bb). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(pyridin-2-yl)propan-1-one (**1b**) [3238-55-9] (54 mg, 0.40 mmol, 2.0 equiv), (*E*)-chalcone (**2b**) [614-47-1] (42 mg, 0.20 mmol, 1.0 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 2.0:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3bb** was afforded as a yellowish sticky liquid (55.6 mg, 81% yield, 3.2:1 dr (after isolation)).

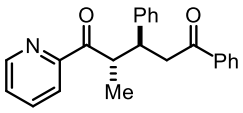
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.0 Hz, 1H of major, 76%), 8.67 (d, *J* = 4.1 Hz, 1H of minor, 24%), 8.10 (d, *J* = 7.8 Hz, 1H of major, 76%), 7.91 – 7.81 (m, 3H), 7.79 – 7.72 (m, 1H of minor, 24%), 7.55 – 7.33 (m, 4H), 7.32 – 7.21 (m, 3H), 7.21 – 7.11 (m, 2H of major, 76%), 7.10 – 7.01 (m, 2H of minor), 4.73 – 4.48 (m, 1H), 4.07 – 3.95 (m, 1H of minor, 24%), 3.84 (td, *J* = 9.9, 4.4 Hz, 1H of major, 76%), 3.49 – 3.20 (m, 2H), 1.27 (d, *J* = 7.0 Hz, 3H of minor, 24%), 0.97 (d, *J* = 7.0 Hz, 3H of major, 76%).

^{13}C NMR (75 MHz, $CDCl_3$) δ 204.98, 204.08, 199.40, 198.69, 153.11, 152.85, 149.03, 148.65, 143.13, 142.05, 137.38, 137.29, 137.12, 133.01, 132.85, 128.61, 128.59, 128.52, 128.49, 128.27, 128.23, 128.12, 127.40, 127.11, 126.78, 126.44, 122.77, 122.65, 44.49, 44.47, 44.36, 44.31, 42.69, 40.37, 16.65, 13.79.

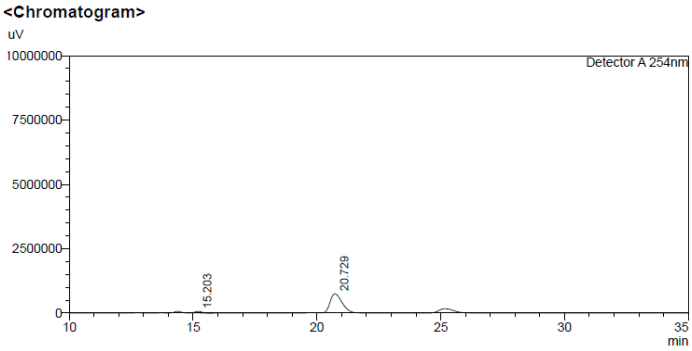
HRMS (ESI) m/z calcd for **$C_{23}H_{22}NO_2$** $[M + H]^+$: 344.1651, found: 344.1633.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 90% [OX-H, 30% i-PrOH in hexanes, 0.3 mL/min], t_R = 15.20 min (*anti* minor), t_R = 19.82 min (*syn* minor), t_R = 20.73 (*anti* major), and t_R = 25.18 (*syn* major).

$[\alpha]_D^{20}$ = +66° (c = 0.89, $CHCl_3$).

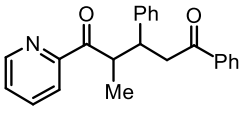


(*S*,*S*)-**3bb**
3.2:1 dr, 90% ee

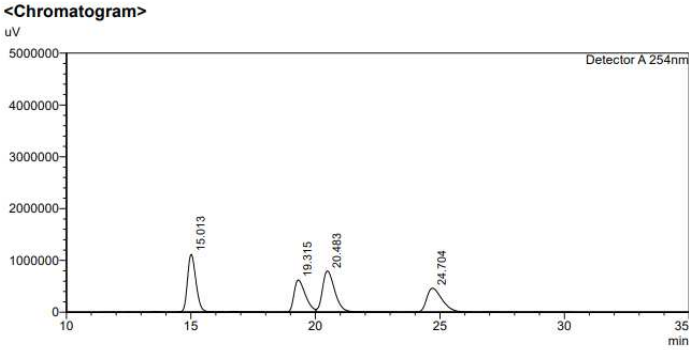


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.203	1344328	62689	4.927		M	
2	20.729	25942023	752205	95.073			
Total		27286351	814893				

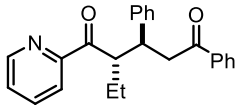


(*rac*)-**3bb**
1.0:1 dr



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.013	26587805	1113105	28.202			
2	19.315	19749186	619922	20.948			
3	20.483	27652334	795293	29.331		V	
4	24.704	20287208	462931	21.519		V	
Total		94276533	2991252				



3lb

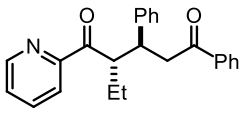
(2*S*,3*S*)-2-ethyl-3,5-diphenyl-1-(pyridin-2-yl)pentane-1,5-dione (Table 4, 3lb). The title compound was prepared according to **General Procedure F**, using 5,5-dimethylhexanoic acid [24499-80-7] (5.8 mg, 0.040 mmol, 0.20 equiv), $CuBr_2$ [7789-45-9] (4.4 mg, 0.020 mmol, 0.10 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(pyridin-2-yl)butan-1-one (**1l**) [22971-32-0] (60 mg, 0.40 mmol, 2.0 equiv), (*E*)-chalcone (**2b**) [614-47-1] (42 mg, 0.20 mmol, 1.0 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 3.0:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3lb** was afforded as a yellowish sticky liquid (60.8 mg, 85% yield, 3.3:1 dr (after isolation)).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.7 Hz, 1H of major, 77%), 8.64 (d, *J* = 4.1 Hz, 1H of minor, 23%), 8.09 (d, *J* = 7.8 Hz, 1H of major, 77%), 7.89 – 7.74 (m, 3H), 7.72 (dd, *J* = 7.8, 1.6 Hz, 1H of minor, 23%), 7.54 – 7.32 (m, 4H), 7.31 – 7.20 (m, 3H), 7.14 – 7.03 (m, 2H), 4.62 (td, *J* = 10.1, 3.9 Hz, 1H), 4.00 – 3.92 (m, 1H of minor, 23%), 3.86 (td, *J* = 10.3, 3.9 Hz, 1H of major, 77%), 3.52 – 3.28 (m, 1H and 1H of minor, 23%), 3.16 (dd, *J* = 15.8, 3.9 Hz, 1H of major, 77%), 2.09 – 1.88 (m, 1H of minor, 23%), 1.75 – 1.66 (m, 1H of minor, 23%), 1.66 – 1.38 (m, 2H of major, 77%), 0.83 (t, *J* = 7.4 Hz, 3H of minor, 23%), 0.66 (t, *J* = 7.5 Hz, 3H of major 77%).

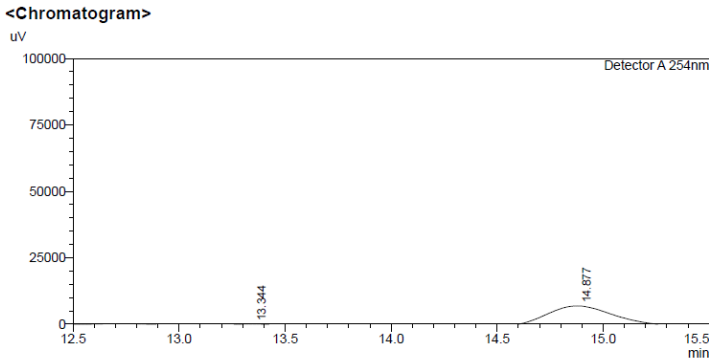
^{13}C NMR (75 MHz, $CDCl_3$) δ 205.35, 198.69, 154.09, 149.07, 148.73, 142.88, 142.28, 137.37, 137.19, 133.04, 132.87, 128.65, 128.61, 128.55, 128.51, 128.42, 128.28, 128.23, 128.14, 127.35, 127.06, 126.76, 126.46, 122.44, 122.41, 51.19, 50.51, 44.26, 43.30, 42.21, 40.58, 24.03, 21.75, 12.13, 10.96.

HRMS (ESI) m/z calcd for **$C_{24}H_{24}NO_2$** $[M + H]^+$: 358.1807, found: 358.1787.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 87% [AD-H, 30% i-PrOH in hexanes, 0.3 mL/min], t_R = 13.34 min (*anti* minor), t_R = 14.88 min (*anti* major), t_R = 15.83 (*syn* major), and t_R = 18.25 (*syn* minor).
$[\alpha]_D^{20}$ = +89° (c = 0.43, $CHCl_3$).

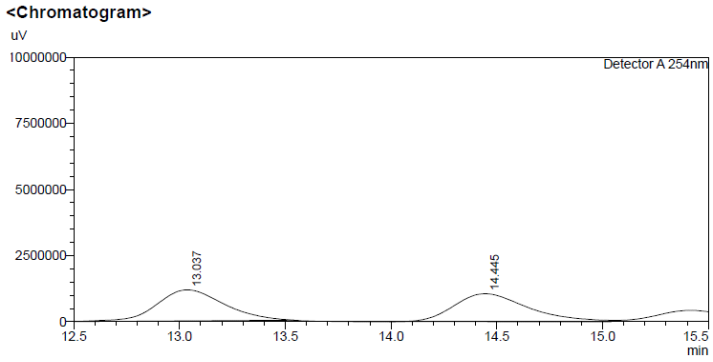


(*S*,*S*)-**3lb**
3.3:1 dr, 87% ee



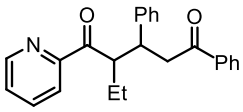
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.344	13368	743	6.444			
2	14.877	194092	8017	93.556			
Total		207461	8760				

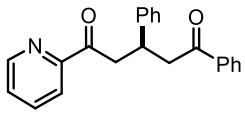


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.037	25994015	1173952	50.166		M	
2	14.445	25821650	1057559	49.834		M	
Total		51815665	2231511				



(*rac*)-**3lb**
>20:1



3mb

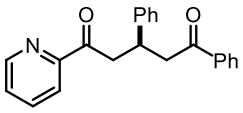
(*S*)-1,3-diphenyl-5-(pyridin-2-yl)pentane-1,5-dione (Table 4, 3mb). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(pyridin-2-yl)ethan-1-one (**1m**) [1122-62-9] (48.5 mg, 0.400 mmol, 2.00 equiv), (*E*)-chalcone (**2b**) [614-47-1] (42 mg, 0.20 mmol, 1.0 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). After purification by flash column chromatography (Hex:EtOAc), **3mb** was afforded as a white crystal (65.2 mg, 99%, mp: 60–65 °C).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (d, *J* = 4.2 Hz, 1H), 8.05 – 7.89 (m, 3H), 7.81 (td, *J* = 7.7, 1.7 Hz, 1H), 7.62 – 7.51 (m, 1H), 7.50 – 7.41 (m, 3H), 7.41 – 7.35 (m, 2H), 7.29 (dd, *J* = 10.0, 4.9 Hz, 2H), 7.23 – 7.10 (m, 1H), 4.27 – 4.10 (m, 1H), 3.74 (qd, *J* = 17.6, 7.1 Hz, 2H), 3.44 (qd, *J* = 16.7, 7.1 Hz, 2H).

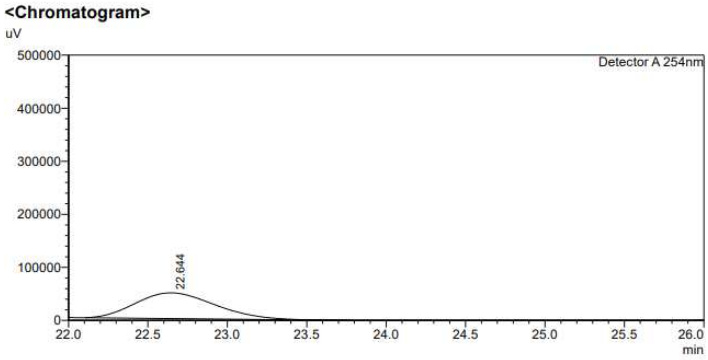
^{13}C NMR (75 MHz, $CDCl_3$) δ 199.98, 198.54, 153.34, 148.86, 144.27, 137.05, 136.89, 132.98, 128.55, 128.51, 128.12, 127.61, 127.14, 126.51, 121.84, 45.23, 43.91, 36.59.

HRMS (ESI) m/z calcd for **$C_{22}H_{20}NO_2$** $[M + H]^+$: 330.1494, found: 330.1476.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be >99% of major. [OD-H, 20% i-PrOH in hexanes, 0.3 mL/min], t_R = 22.64 min (major) and t_R = 24.21 min (minor).
$[\alpha]_D^{20}$ = +52° (c = 0.7, $CHCl_3$).

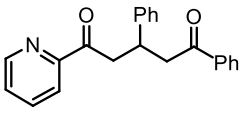


(*S*)-**3mb**
>99% ee

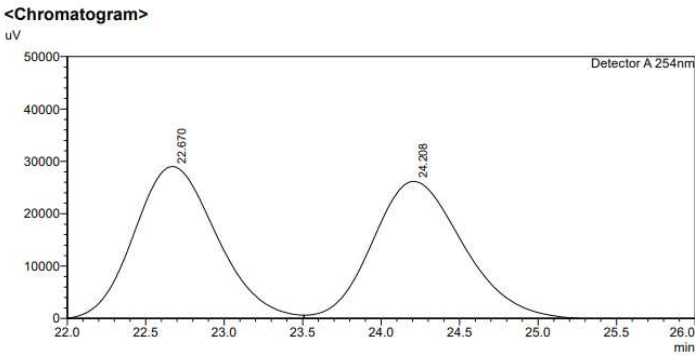


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.644	1686861	48451	100.000		M	
Total		1686861	48451				

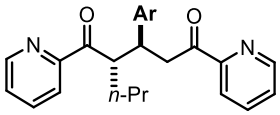


(*rac*)-**3mb**



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.670	1089400	29302	49.762			
2	24.208	1099808	26569	50.238		V	
Total		2189208	55872				



3ac (Ar = 2-MeC_6H_4)

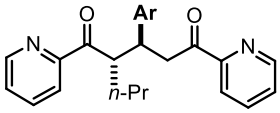
(2*S*,3*S*)-2-propyl-1,5-di(pyridin-2-yl)-3-(o-tolyl)pentane-1,5-dione (Table 5, 3ac). The title compound was prepared according to **General Procedure F**, using 4-(trimethylsilyl)butanoic acid [2345-40-6] (6.4 mg, 0.040 mmol, 0.20 equiv), $CuBr_2$ [7789-45-9] (4.4 mg, 0.020 mmol, 0.10 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-1-(pyridin-2-yl)-3-(o-tolyl)prop-2-en-1-one (**2c**) [16212-59-2] (44.7 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 2.5:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ac** was afforded as a yellowish sticky liquid (54.7 mg, 71% yield, 9.0:1 dr (after isolation)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 4.0, 0.7 Hz, 1H of major), 8.61 (dd, *J* = 4.7, 1.1 Hz, 1H of major), 8.04 (d, *J* = 7.8 Hz, 2H of minor, 10%), 7.83 (d, *J* = 7.9 Hz, 1H), 7.69 (dddd, *J* = 11.2, 8.6, 7.3, 1.7 Hz, 3H), 7.41 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 7.34 (ddd, *J* = 6.8, 4.8, 1.8 Hz, 1H), 7.20 (dd, *J* = 7.3, 1.7 Hz, 1H), 7.00 – 6.90 (m, 1H), 6.81 (td, *J* = 6.5, 1.6 Hz, 2H), 4.69 (ddd, *J* = 11.0, 8.3, 3.1 Hz, 1H), 4.13 – 4.03 (m, 1H), 3.88 (dd, *J* = 17.5, 9.7 Hz, 1H), 3.66 (dd, *J* = 17.5, 4.4 Hz, 1H of major, 90%), 3.21 (dd, *J* = 17.1, 9.7 Hz, 1H of minor, 10%), 2.47 (s, 3H of minor, 10%), 2.43 (s, 3H of major, 90%), 2.07 – 1.96 (m, 1H of major, 90%), 1.76 – 1.67 (m, 1H of major, 90%), 1.56 – 1.47 (m, 1H of minor, 10%), 1.47 – 1.39 (m, 1H of minor, 10%), 1.29 – 1.14 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H of minor, 10%), 0.84 (t, *J* = 7.3 Hz, 3H of major, 90%).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.33, 200.55, 154.21, 153.63, 148.92, 148.61, 141.23, 136.92, 136.86, 136.66, 130.20, 127.52, 127.05, 126.66, 125.98, 125.34, 121.87, 121.83, 48.64, 41.04, 37.74, 31.95, 20.96, 20.10, 14.53.

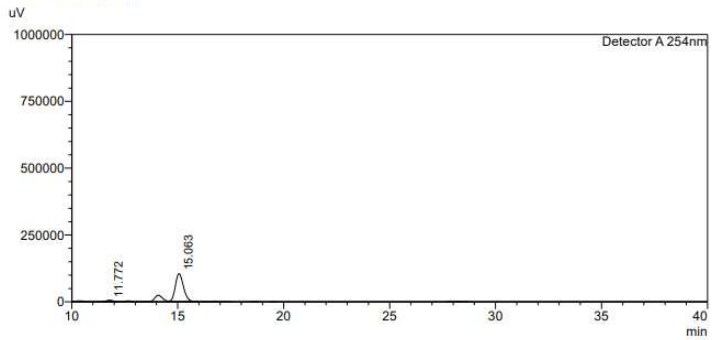
HRMS (ESI) m/z calcd for **$C_{25}H_{27}N_2O_2$** $[M + H]^+$: 387.2073, found:387.2058.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 94% [OX-H, 30% i-PrOH in hexanes, 0.3 mL/min], t_R = 11.77 min (*anti* minor), t_R = 14.08 min (*syn* major), t_R = 15.06 (*anti* major), and t_R = 29.80 (*syn* minor). $[\alpha]_D^{20}$ = +46° (c = 0.82, $CHCl_3$).



(*S*,*S*)-**3ac** (Ar = 2-MeC_6H_4)
9.0:1 dr, 94% ee

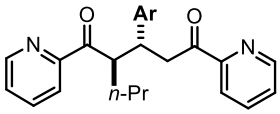
<Chromatogram>



<Peak Table>

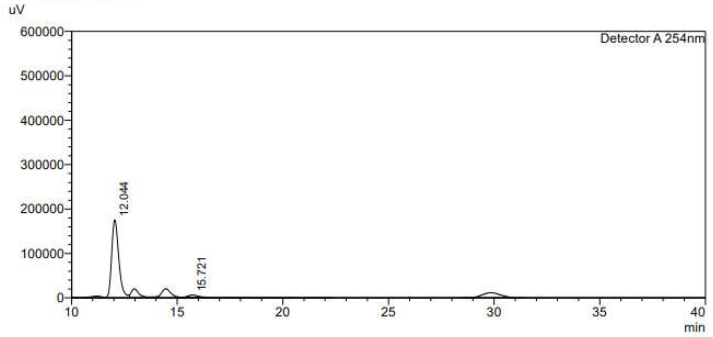
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.772	82228	4342	2.774		M	
2	15.063	2881582	105533	97.226		M	
Total		2963810	109875				



(*R*,*R*)-**3ac** (Ar = 2-MeC_6H_4)
9.0:1 dr, 94% ee

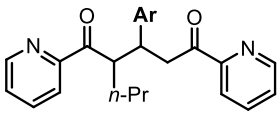
<Chromatogram>



<Peak Table>

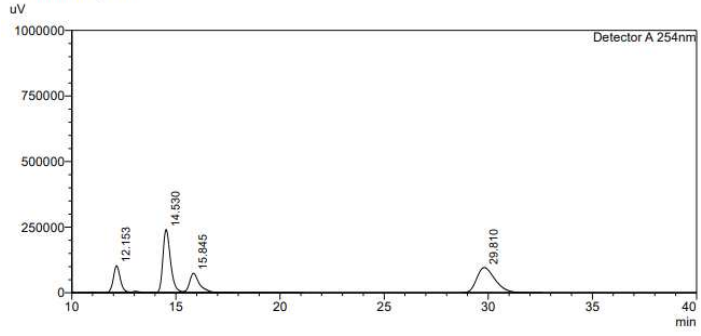
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.044	4169008	175842	96.730		M	
2	15.721	140929	4958	3.270		M	
Total		4309938	180800				



(*rac*)-**3ac** (Ar = 2-MeC_6H_4)
0.5:1 dr

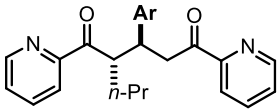
<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.153	2425688	102825	13.947			
2	14.530	6207534	240684	35.691			
3	15.845	2526297	74304	14.525		V	
4	29.810	6233148	97528	35.838			
Total		17392667	515341				



3ad (Ar = 2-OMeC$_6$H$_4$)

(2*S*,3*S*)-3-(2-methoxyphenyl)-2-propyl-1,5-di(pyridin-2-yl)pentane-1,5-dione (Table 5, 3ad). The title compound was prepared according to **General Procedure F**, using 1-adamantanebutyric acid [6240-17-1] (8.8 mg, 0.040 mmol, 0.20 equiv), $CuBr_2$ [7789-45-9] (4.4 mg, 0.020 mmol, 0.10 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-3-(2-methoxyphenyl)-1-(pyridin-2-yl)prop-2-en-1-one (**2d**) [16212-40-1] (47.9 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 2.2:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ad** was afforded as a brown crystal (79.7 mg, 83% yield, 2.2:1 dr (after isolation), mp: 90–93 °C).

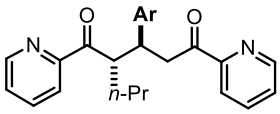
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (dt, *J* = 10.1, 4.7 Hz, 2H), 8.02 (d, *J* = 7.8 Hz, 1H of major, 69%), 7.86 (d, *J* = 7.8 Hz, 1H of minor, 31%), 7.89 – 7.60 (m, 3H), 7.43 – 7.30 (m, 2H), 7.22 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.17 – 7.04 (m, 1H), 6.95 (d, *J* = 1.0 Hz, 1H of minor, 31%), 6.77 (dd, *J* = 13.5, 7.4 Hz, 1H), 6.68 – 6.55 (m, 1H of major, 69%), 4.85 – 4.77 (m, 1H of minor, 31%), 4.78 – 4.67 (m, 1H of major, 69%), 4.39 – 4.28 (m, 1H of major, 69%), 4.12 (dd, *J* = 14.5, 7.7 Hz, 1H of minor, 31%), 3.96 (dd, *J* = 16.8, 10.1 Hz, 1H of major, 69%), 3.75 (d, *J* = 7.0 Hz, 2H of minor, 31%), 3.67 (s, 3H of major, 69%), 3.63 (s, 3H of minor, 31%), 3.37 (dd, *J* = 16.8, 4.5 Hz, 1H of major, 69%), 2.03 – 1.90 (m, 1H of minor, 31%), 1.75 – 1.65 (m, 1H of minor, 31%), 1.61 – 1.49 (m, 1H of major, 69%), 1.49 – 1.35 (m, 1H of major, 69%), 1.29 – 0.99 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H of minor, 31%), 0.71 (t, *J* = 7.3 Hz, 3H of major, 69%).

^{13}C NMR (75 MHz, $CDCl_3$) δ 205.29, 204.72, 200.51, 200.32, 157.51, 157.10, 154.31, 154.09, 153.59, 153.51, 148.68, 148.61, 148.54, 148.31, 136.51, 136.46, 136.44, 136.32, 130.46, 130.18, 129.63, 128.97, 126.19, 121.81, 121.57, 120.07, 119.78, 110.41, 110.31, 55.03, 54.96, 47.57, 47.25, 40.81, 39.55, 37.93, 36.66, 32.12, 31.95, 20.73, 20.16, 14.33, 14.16.

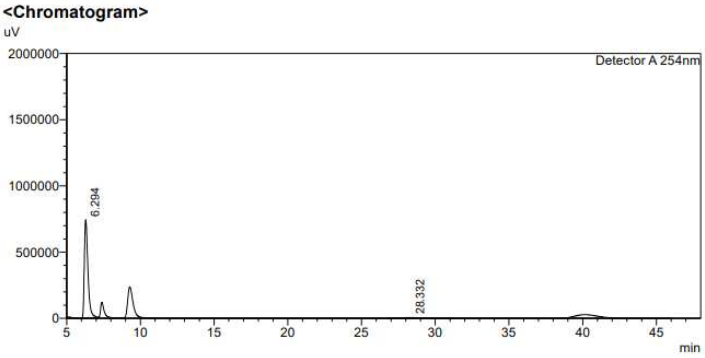
HRMS (ESI) m/z calcd for **$C_{25}H_{27}N_2O_3$** $[M + H]^+$: 403.2022, found: 403.2005.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 93% [IC, 30% i-PrOH in hexanes, 1 mL/min], t_R = 6.29 min (*anti* major), t_R = 9.29 min (*syn* major), t_R = 28.33 (*anti* minor), and t_R = 40.16 (*syn* minor).

$[\alpha]_D^{20}$ = +52° (c = 0.68, $CHCl_3$).

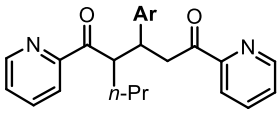


(*S*,*S*)-**3ad** (Ar = 2-OMeC$_6$H$_4$)
2.2:1 dr, 93% ee

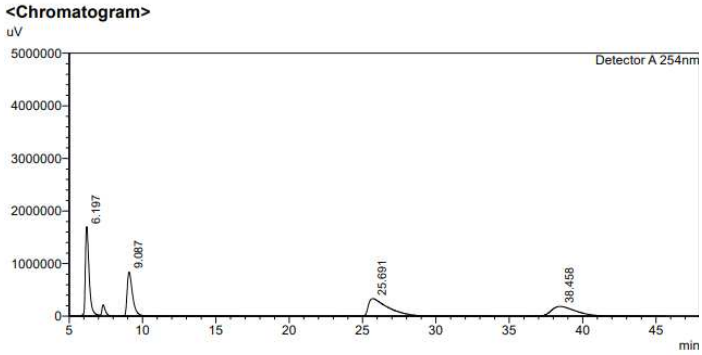


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.294	12805235	742922	96.383			
2	28.332	480594	5785	3.617			
Total		13285829	748706				

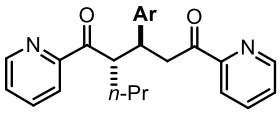


(*rac*)-**3ad** (Ar = 2-OMeC$_6$H$_4$)
2.0:1 dr



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.197	30736235	1703729	28.880			
2	9.087	22346545	840431	20.997		S	
3	25.691	31716910	334502	29.801			
4	38.458	21628844	185052	20.322			
Total		106428534	3063714				



3ae (Ar = 2-ClC$_6$H$_4$)

(2*S*,3*S*)-3-(2-chlorophenyl)-2-propyl-1,5-di(pyridin-2-yl)pentane-1,5-dione (Table 5, 3ae). The title compound was prepared according to **General Procedure F**, using 5,5-dimethylhexanoic acid [24499-80-7] (5.8 mg, 0.040 mmol, 0.20 equiv), $CuBr_2$ [7789-45-9] (4.4 mg, 0.020 mmol, 0.10 equiv), (*R*)-Tol-BINAP [99646-28-3] (15 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-3-(2-chlorophenyl)-1-(pyridin-2-yl)prop-2-en-1-one (**2e**) [16212-55-8] (48.7 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 3.0:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ae** was afforded as a black crystal (54.5 mg, 67% yield, 4.9:1 dr (after isolation), mp: 85–88 °C).

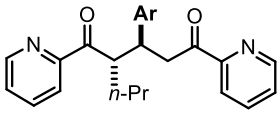
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.1 Hz, 1H), 8.57 (d, *J* = 4.8 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H of major, 83%), 7.96 (d, *J* = 7.8 Hz, 1H of minor, 17%), 7.88 (d, *J* = 7.8 Hz, 2H of minor 17%), 7.83 – 7.73 (m, 2H of major, 83%), 7.73 – 7.64 (m, 1H), 7.45 – 7.27 (m, 4H), 7.12 – 6.98 (m, 2H of major, 83%), 6.91 (t, *J* = 3.7 Hz, 2H of minor, 17%), 4.87 – 4.69 (m, 1H), 4.54 – 4.42 (m, 1H of major, 83%), 4.41 – 4.33 (m, 1H of minor, 17%), 3.98 – 3.80 (m, 1H), 3.75 – 3.66 (m, 1H of minor, 17%), 3.39 (dd, *J* = 17.2, 4.1 Hz, 1H of major, 83%), 2.06 – 1.92 (m, 1H of minor, 17%), 1.79 – 1.62 (m, 1H of major, 83%), 1.47 – 1.33 (m, 1H), 1.26 – 1.00 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H of minor, 17%), 0.71 (t, *J* = 7.3 Hz, 3H of major, 83%).

^{13}C NMR (75 MHz, $CDCl_3$) δ 205.13, 200.00, 154.15, 153.43, 149.05, 148.86, 140.46, 137.02, 136.90, 135.28, 129.76, 127.56, 127.10, 127.06, 126.82, 122.31, 121.94, 41.48, 39.26, 33.03, 32.20, 20.54, 14.42.

HRMS (ESI) m/z calcd for **$C_{24}H_{24}ClN_2O_2$** $[M + H]^+$: 407.1526, found: 407.1509.

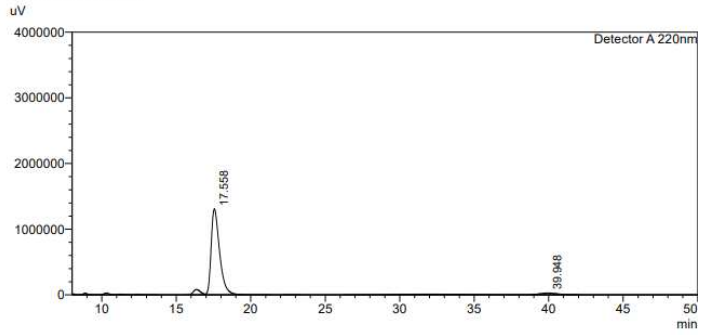
HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 91% [IC, 30% i-PrOH in hexanes, 0.5 mL/min], t_R = 10.42 min (*syn* minor), t_R = 16.75 min (*syn* major), t_R = 17.56 (*anti* major), and t_R = 39.95 (*anti* minor).

$[\alpha]_D^{20}$ = +66° (c = 0.78, $CHCl_3$).



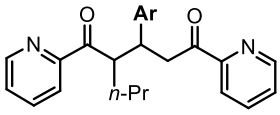
(*S*,*S*)-**3ae** (Ar = 2-ClC_6H_4)
4.9:1 dr, 91% ee

<Chromatogram>



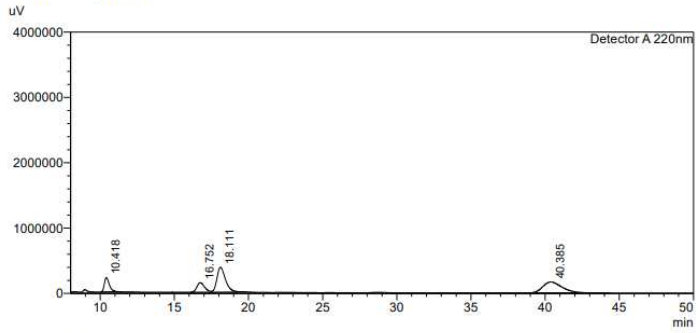
<Peak Table>
Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.558	52781288	1313081	95.604			
2	39.948	2426934	28524	4.396		M	
Total		55208222	1341605				



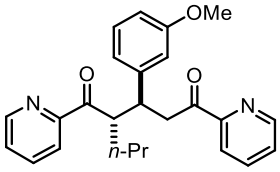
(*rac*)-**3ae** (Ar = 2-ClC_6H_4)
1.0:1 dr

<Chromatogram>



<Peak Table>
Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.418	5064966	216803	12.386		M	
2	16.752	5338775	147154	13.055		M	
3	18.111	15185518	380522	37.134		M	
4	40.385	15304513	166953	37.425		M	
Total		40893773	911432				



3af

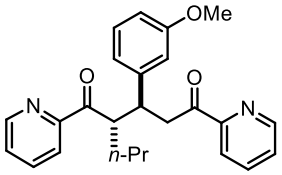
(2*S*,3*S*)-3-(3-methoxyphenyl)-2-propyl-1,5-di(pyridin-2-yl)pentane-1,5-dione (Table 5, 3af). The title compound was prepared according to **General Procedure F**, using 2-adamantanebutyric acid [1693982-88-5] (8.8 mg, 0.040 mmol, 0.20 equiv), $CuBr_2$ [7789-45-9] (4.4 mg, 0.020 mmol, 0.10 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-3-(3-methoxyphenyl)-1-(pyridin-2-yl)prop-2-en-1-one (**2f**) [16212-43-4] (47.9 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 3.6:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3af** was afforded as a yellowish sticky liquid (41.9 mg, 56% yield, >20:1 dr (after isolation)).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 – 8.57 (m, 2H), 7.85 (dd, *J* = 9.1, 8.2 Hz, 2H), 7.79 – 7.64 (m, 2H), 7.44 – 7.31 (m, 2H), 7.01 (t, *J* = 8.1 Hz, 1H), 6.94 – 6.79 (m, 2H), 6.60 – 6.52 (m, 1H), 4.67 (ddd, *J* = 10.2, 6.7, 3.1 Hz, 1H), 3.99 – 3.74 (m, 2H), 3.67 (s, 3H), 3.53 (dd, *J* = 16.5, 3.5 Hz, 1H), 2.08 – 1.86 (m, 1H), 1.69 – 1.53 (m, 1H), 1.32 – 1.10 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H).

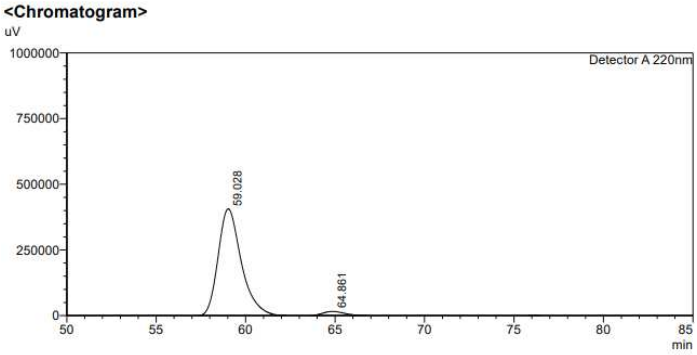
^{13}C NMR (75 MHz, $CDCl_3$) δ 204.61, 200.40, 159.26, 153.95, 153.57, 148.90, 148.80, 144.72, 136.87, 136.80, 128.95, 127.09, 126.80, 122.24, 121.92, 121.02, 113.96, 112.00, 55.13, 49.63, 42.46, 39.42, 30.86, 21.07, 14.48.

HRMS (ESI) m/z calcd for **$C_{25}H_{27}N_2O_3$** $[M + H]^+$: 403.2022, found: 403.2010.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 90% [AD-H, 5% i-PrOH in hexanes, 0.3 mL/min], t_R = 59.03 min (*anti* major), t_R = 64.86 min (*anti* minor), t_R = 71.07 (*syn* isomer A), and t_R = 76.05 (*syn* isomer B). $[\alpha]_D^{20}$ = +47° (c = 0.52, $CHCl_3$).

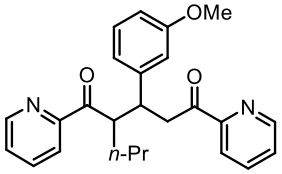


(*S*,*S*)-**3af**
>20:1 dr, 90% ee

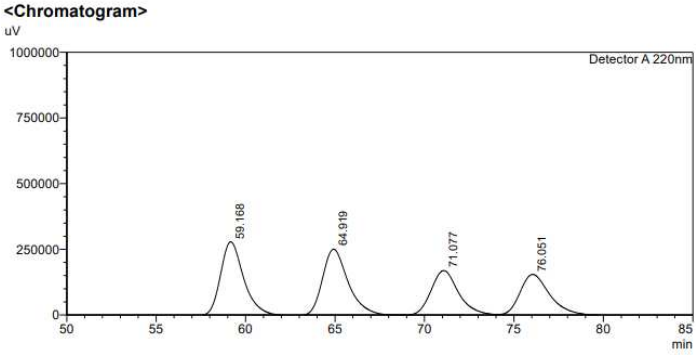


<Peak Table>
Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	59.028	37417679	409049	95.210			
2	64.861	1882498	18410	4.790		V	
Total		39300177	427459				

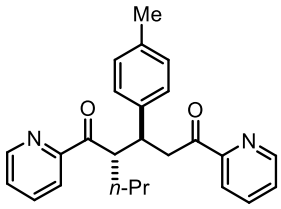


(*rac*)-**3af**
1.5:1 dr



<Peak Table>
Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	59.168	25660763	281411	28.872			
2	64.919	25715573	253335	28.934		V	
3	71.077	18865927	171824	21.227		V	
4	76.051	18634823	157031	20.967		V	
Total		88877086	863601				



3ag

(2*S*,3*S*)-2-propyl-1,5-di(pyridin-2-yl)-3-(p-tolyl)pentane-1,5-dione (Table 5, 3ag). The title compound was prepared according to **General Procedure F**, using 5,5-dimethylhexanoic acid [24499-80-7] (5.8 mg, 0.040 mmol, 0.20 equiv), $CuBr_2$ [7789-45-9] (4.4 mg, 0.020 mmol, 0.10 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-1-(pyridin-2-yl)-3-(p-tolyl)prop-2-en-1-one (**2g**) [158014-83-6] (44.7 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 5.2:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ag** was afforded as a yellowish sticky liquid (64.2 mg, 83% yield, 6.7:1 dr (after isolation)).

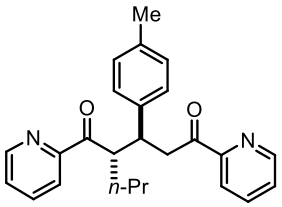
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 2H), 7.90 – 7.79 (m, 2H), 7.78 – 7.67 (m, 2H), 7.39 (dd, *J* = 11.5, 4.9 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.91 (d, *J* = 7.5 Hz, 2H), 4.63 (dd, *J* = 6.7, 3.2 Hz, 1H), 3.89 (d, *J* = 4.6 Hz, 1H), 3.85 – 3.72 (m, 1H), 3.57 (dd, *J* = 17.3, 4.3 Hz, 1H), 2.26 (s, 3H of minor, 13%), 2.17 (s, 3H of major, 87%), 2.06 – 1.84 (m, 1H), 1.61 (dd, *J* = 12.6, 6.8 Hz, 1H), 1.30 – 1.06 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.54, 200.09, 154.13, 153.53, 149.05, 148.71, 139.63, 136.97, 136.70, 135.81, 128.95, 128.51, 127.05, 126.84, 122.25, 121.86, 49.13, 42.78, 42.63, 33.05, 21.13, 20.08, 14.32.

HRMS (ESI) m/z calcd for **$C_{25}H_{27}N_2O_2$** $[M + H]^+$: 387.2073, found: 387.2055.

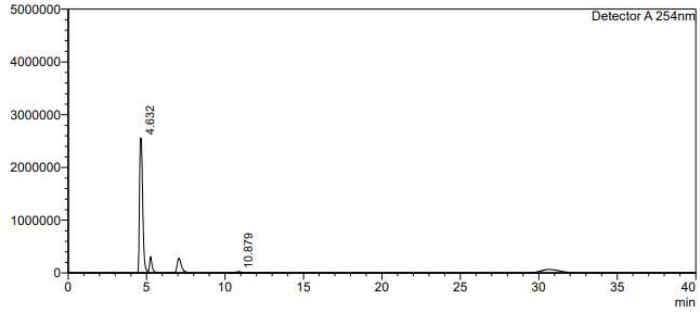
HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 96% [IC, 30% i-PrOH in hexanes, 1 mL/min], t_R = 4.63 min (*anti* major), t_R = 7.06 min (*syn* isomer A), t_R = 10.88 (*anti* minor), and t_R = 30.68 (*syn* isomer B).

$[\alpha]_D^{20}$ = +24° (c = 0.69, $CHCl_3$).



(*S*,*S*)-**3ag**
6.7:1 dr, 96% ee

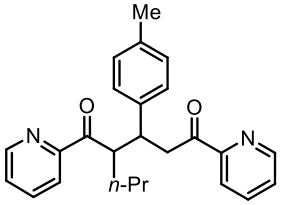
<Chromatogram>



<Peak Table>

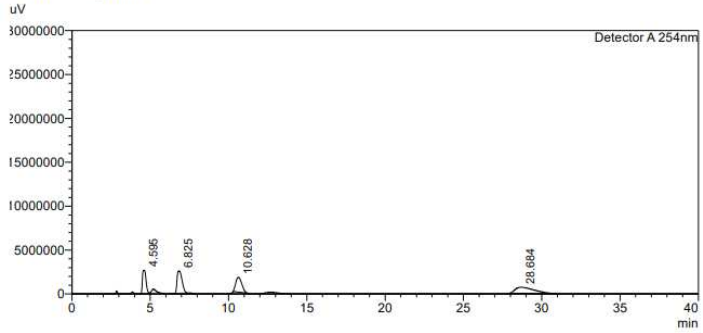
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.632	36010661	2562398	97.938			
2	10.879	758332	22626	2.062			
Total		36768993	2585024				



(*rac*)-**3ag**
1.0:1 dr

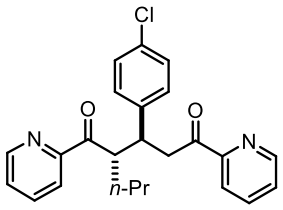
<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.595	43879534	2705234	21.066			
2	6.825	60449751	2594995	29.021		M	
3	10.628	44574781	1666224	21.400		M	
4	28.684	59392211	702325	28.513		M	
Total		208296277	7668779				



3ah

(2*S*,3*S*)-3-(4-chlorophenyl)-2-propyl-1,5-di(pyridin-2-yl)pentane-1,5-dione (Table 5, 3ah). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-3-(4-chlorophenyl)-1-(pyridin-2-yl)prop-2-en-1-one (**2h**) [16231-98-4] (48.7 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 4.9:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ah** was afforded as a yellowish sticky liquid (74.9 mg, 92% yield, 4.9:1 dr (after isolation)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 2H), 7.90 – 7.80 (m, 2H), 7.80 – 7.70 (m, 2H), 7.46 – 7.37 (m, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 4.65 (t, *J* = 7.5 Hz, 1H), 3.94 – 3.87 (m, 1H), 3.87 – 3.75 (m, 1H), 3.56 (dd, *J* = 17.2, 3.9 Hz, 1H),

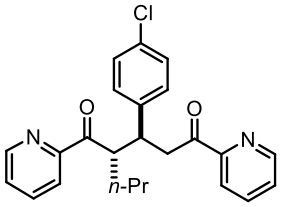
2.02 – 1.87 (m, 1H), 1.68 – 1.55 (m, 1H), 1.27 – 1.10 (m, 2H), 0.96 – 0.92 (m, 3H of minor 17%), 0.83 (t, J = 7.3 Hz, 3H of major, 83%).

^{13}C NMR (101 MHz, $CDCl_3$) δ 204.38, 200.14, 153.63, 148.86, 148.77, 141.57, 137.03, 136.99, 131.91, 129.94, 128.14, 127.24, 126.99, 122.27, 121.94, 49.46, 41.98, 39.68, 31.16, 20.89, 14.44.

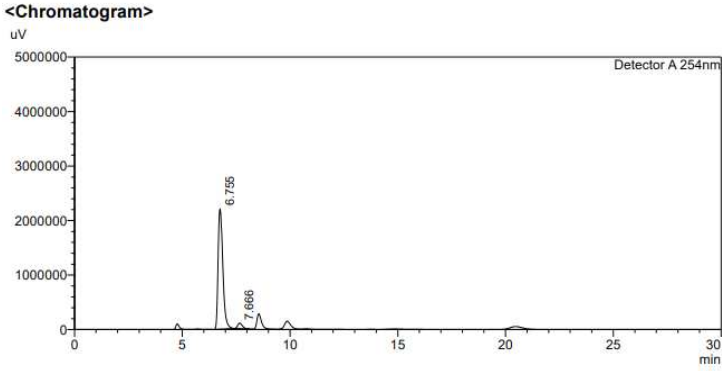
HRMS (ESI) m/z calcd for **$C_{24}H_{24}ClN_2O_2$** $[M + H]^+$: 407.1526, found: 407.1508.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 91% [IC, 30% i-PrOH in hexanes, 0.5 mL/min], t_R = 6.76 min (*anti* major), t_R = 7.67 min (*anti* minor), t_R = 9.87 (*syn* major), and t_R = 20.47 (*syn* minor).

$[\alpha]_D^{20}$ = +39° (c = 1.2, $CHCl_3$).



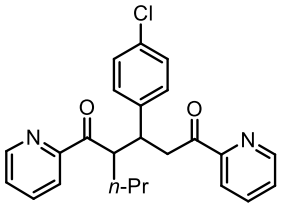
(*S*,*S*)-**3ah**
4.9:1 dr, 91% ee



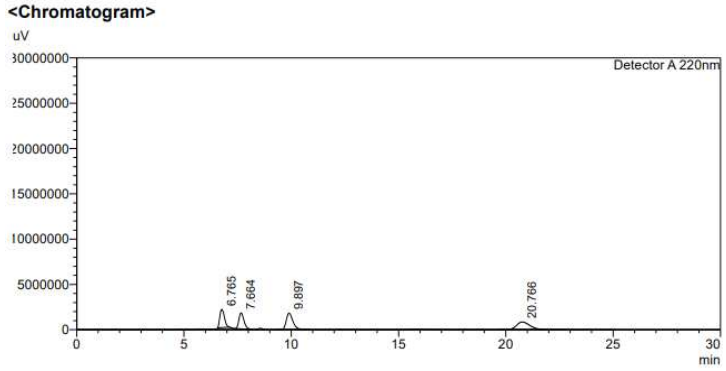
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.755	32938841	2200827	95.590		M	
2	7.666	1519461	100436	4.410		M	
Total		34458303	2301263				



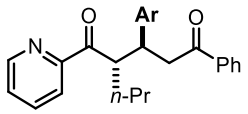
(*rac*)-**3ah**
1.0:1 dr



<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.765	28812925	2003504	21.338		M	
2	7.664	28631605	1751744	21.204		M	
3	9.897	39011567	1810086	28.891		M	
4	20.766	38573335	862569	28.567		M	
Total		135029431	6427903				



3ai (Ar = 2-BrC_6H_4)

(2*S*,3*S*)-3-(2-bromophenyl)-5-phenyl-2-propyl-1-(pyridin-2-yl)pentane-1,5-dione (Table 5, 3ai). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-3-(2-bromophenyl)-1-phenylprop-2-en-1-one (**2i**) [22966-10-5] (48.7 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 5.0:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ai** was afforded as a yellowish sticky liquid (72 mg, 80% yield, 7.3:1 dr (after isolation)).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 – 8.64 (m, 1H of major, 88%), 8.64 – 8.59 (m, 1H of minor, 12%), 8.05 (d, J = 7.8 Hz, 1H of major, 88%), 7.86 (d, J = 7.1 Hz, 1H of minor, 12%), 7.80 (td, J = 7.7, 1.6 Hz, 3H of major, 88%), 7.69 (td, J = 7.7, 1.7 Hz,

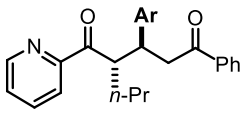
3H of minor, 12%), 7.55 – 7.34 (m, 6H), 7.15 (td, *J* = 7.6, 1.1 Hz, 1H), 6.96 (td, *J* = 7.9, 1.7 Hz, 1H), 4.87 – 4.72 (m, 1H), 4.44 (dt, *J* = 9.5, 4.7 Hz, 1H of major, 88%), 4.40 – 4.28 (m, 1H of minor, 12%), 4.10 – 3.98 (m, 1H of minor, 12%), 3.61 (dd, *J* = 16.9, 4.9 Hz, 1H of minor, 12%), 3.50 – 3.20 (m, 2H of major, 88%), 2.31 – 2.16 (m, 1H of minor, 12%), 1.72 (ddd, *J* = 18.8, 9.8, 4.8 Hz, 1H of major, 88%), 1.44 – 1.29 (m, 1H), 1.25 – 1.03 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H of minor, 12%), 0.71 (t, *J* = 7.3 Hz, 3H of major, 88%).

^{13}C NMR (75 MHz, $CDCl_3$) δ 205.40, 204.62, 198.23, 154.00, 148.97, 141.46, 136.89, 136.83, 133.04, 132.80, 128.40, 128.18, 127.84, 127.37, 127.04, 122.07, 48.29, 42.48, 42.27, 33.07, 20.36, 14.17.

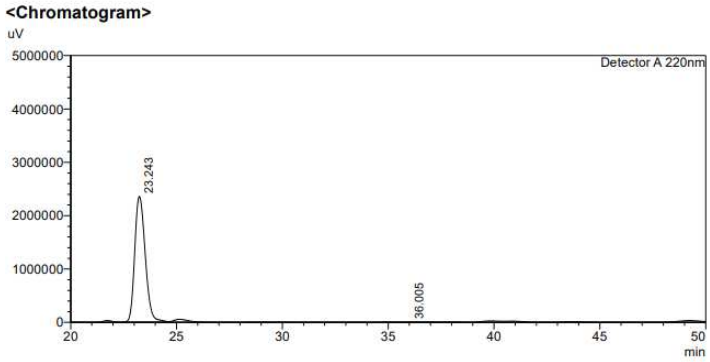
HRMS (ESI) m/z calcd for **$C_{25}H_{25}BrNO_2$** $[M + H]^+$: 450.1069, found: 450.1053.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be >99% [IC, 10% i-PrOH in hexanes, 0.3 mL/min], t_R = 23.24 min (*anti* major), t_R = 36.01 min (*anti* minor), t_R = 40.84 (*syn* major), and t_R = 46.10 (*syn* minor).

$[\alpha]_D^{20}$ = +20° (c = 1.4, $CHCl_3$).

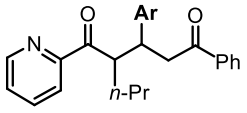


(*S*,*S*)-**3ai** (Ar = 2-BrC_6H_4)
7.3:1 dr, >99% ee

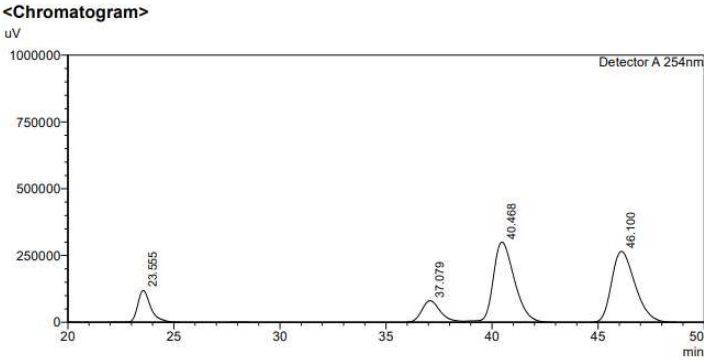


<Peak Table>
Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.243	82279480	2358676	99.791			
2	36.005	172702	1808	0.209			
Total		82452182	2360485				

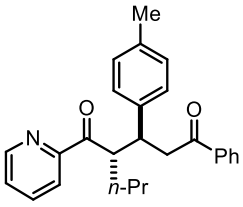


(*rac*)-**3ai** (Ar = 2-BrC_6H_4)
0.5:1 dr



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.555	5236396	120480	10.004			
2	37.079	5274891	82651	10.077			
3	40.468	21204857	301524	40.511		V	
4	46.100	20627547	266787	39.408			
Total		52343691	771442				



3aj

(2*S*,3*S*)-5-phenyl-2-propyl-1-(pyridin-2-yl)-3-(p-tolyl)pentane-1,5-dione (Table 5, 3aj). The title compound was prepared according to **General Procedure F**, using 2-adamantanebutyric acid [1693982-88-5] (8.8 mg, 0.040 mmol, 0.20 equiv), $CuBr_2$ [7789-45-9] (4.4 mg, 0.020 mmol, 0.10 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-

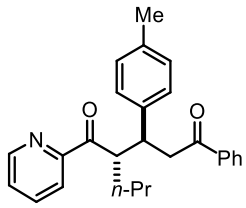
pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-1-phenyl-3-(p-tolyl)prop-2-en-1-one (**2j**) [22252-14-8] (44.5 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 3.3:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3aj** was afforded as a yellowish sticky liquid (62.4 mg, 81% yield, 6.7:1 dr (after isolation)).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (d, *J* = 4.1 Hz, 1H of major, 87%), 8.64 (d, *J* = 5.0 Hz, 1H of minor, 13%), 8.08 (d, *J* = 7.8 Hz, 1H), 7.84 (td, *J* = 7.8, 1.6 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.52 – 7.33 (m, 5H), 7.24 – 7.17 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.95 – 6.89 (m, 1H), 4.63 (td, *J* = 9.7, 3.7 Hz, 1H of major, 87%), 4.09 – 4.04 (m, 1H of minor, 13%), 3.94 – 3.87 (m, 1H of minor, 13%), 3.79 (td, *J* = 10.1, 4.0 Hz, 1H of major, 87%), 3.33 (dd, *J* = 15.7, 10.3 Hz, 1H), 3.13 (dd, *J* = 15.7, 4.0 Hz, 1H), 2.27 (s, 3H of major, 87%), 2.20 (s, 3H of minor, 13%), 1.67 – 1.47 (m, 1H), 1.42 – 1.28 (m, 1H), 1.16 – 0.94 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H of minor, 13%), 0.67 (t, *J* = 7.3 Hz, 3H of major, 87%).

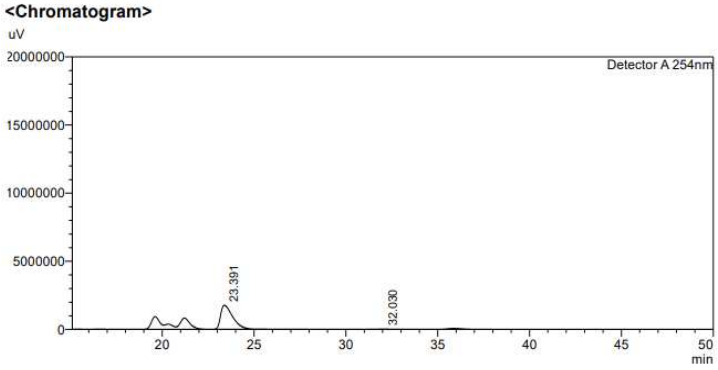
^{13}C NMR (75 MHz, $CDCl_3$) δ 205.78, 198.59, 154.04, 148.97, 138.93, 137.03, 132.63, 129.00, 128.73, 128.57, 128.33, 128.18, 128.10, 127.09, 122.18, 49.00, 44.06, 43.56, 33.21, 21.04, 20.00, 14.15.

HRMS (ESI) m/z calcd for **$C_{26}H_{28}NO_2$** $[M + H]^+$: 386.2120, found: 386.2103.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 98% [AD-H, 20% i-PrOH in hexanes, 0.3 mL/min], t_R = 17.29 min (*syn* isomer A), t_R = 18.53 min (*syn* isomer B), t_R = 23.39 (*anti* major), and t_R = 32.03 (*anti* minor). $[\alpha]_D^{20}$ = +82° (c = 0.18, $CHCl_3$).

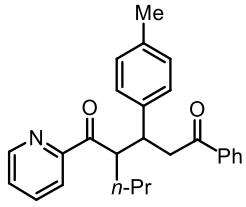


(*S*,*S*)-**3aj**
6.7:1 dr, 98% ee

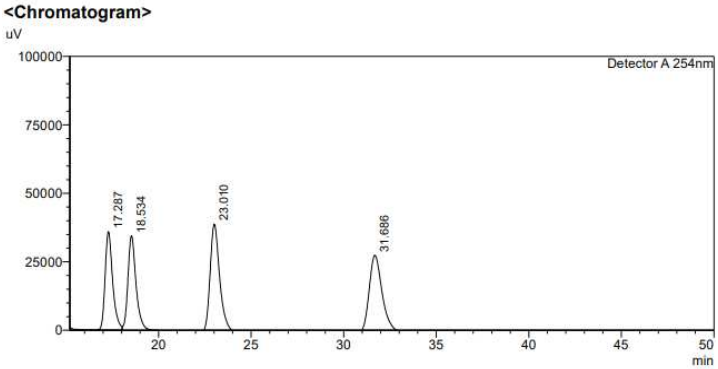


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.391	81382270	1763250	99.059		M	
2	32.030	772679	15229	0.941		M	
Total		82154949	1778479				

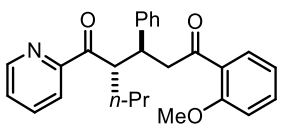


(*rac*)-**3aj**
1.0:1 dr



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.287	1024495	36023	20.668			
2	18.534	1065410	34644	21.494		V	
3	23.010	1428754	39416	28.824			
4	31.686	1438165	28587	29.014			
Total		4956825	138670				



3ak

(2*S*,3*S*)-5-(2-methoxyphenyl)-3-phenyl-2-propyl-1-(pyridin-2-yl)pentane-1,5-dione (Table 5, 3ak). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-1-(2-methoxyphenyl)-3-phenylprop-2-en-1-one (**2k**) [40524-62-7] (47.7 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 2.5:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ak** was afforded as a yellowish sticky liquid (67.5 mg, 84% yield, 3.3:1 dr (after isolation)).

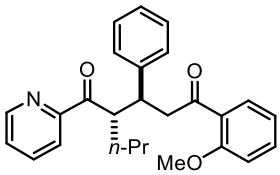
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 4.7, 0.7 Hz, 1H of major, 77%), 8.63 (d, *J* = 4.1 Hz, 1H of minor 23%), 8.09 (d, *J* = 7.8 Hz, 1H of major, 77%), 7.82 (ddd, *J* = 12.9, 9.4, 4.8 Hz, 1H), 7.68 (td, *J* = 7.7, 1.7 Hz, 1H of minor, 23%), 7.46 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 1H), 7.40 – 7.30 (m, 1H), 7.26 – 7.03 (m, 6H), 6.90 – 6.86 (m, 2H of minor, 23%), 6.86 – 6.79 (m, 2H of major, 77%), 4.70 – 4.56 (m, 1H), 3.83 (s, 3H of minor, 23%), 3.71 (s, 3H of major, 77%), 3.63 (td, *J* = 10.4, 4.1 Hz, 1H of major, 77%), 3.46 (dd, *J* = 16.6, 7.6 Hz, 2H of minor, 23%), 3.42 – 3.32 (m, 1H), 3.17 (dd, *J* = 16.2, 4.0 Hz, 1H of major, 77%), 1.93 (dd, *J* = 13.2, 5.3 Hz, 1H of minor, 23%), 1.65 (d, *J* = 5.2 Hz, 1H of major, 77%), 1.32 – 1.16 (m, 1H), 1.16 – 0.96 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H of minor, 23%), 0.66 (t, *J* = 7.3 Hz, 3H of major, 77%).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.82, 204.52, 201.49, 201.12, 157.95, 154.28, 149.00, 148.62, 142.84, 142.56, 137.02, 136.75, 133.05, 132.96, 130.22, 128.57, 128.44, 128.10, 127.82, 127.06, 126.72, 126.36, 126.08, 122.07, 122.01, 120.60, 120.43, 111.26, 111.13, 55.43, 55.28, 49.58, 48.91, 48.68, 46.05, 44.58, 42.86, 33.38, 31.05, 20.89, 20.37, 14.40, 14.19.

HRMS (ESI) m/z calcd for **$C_{26}H_{28}NO_3$** $[M + H]^+$: 402.2069, found: 402.2053.

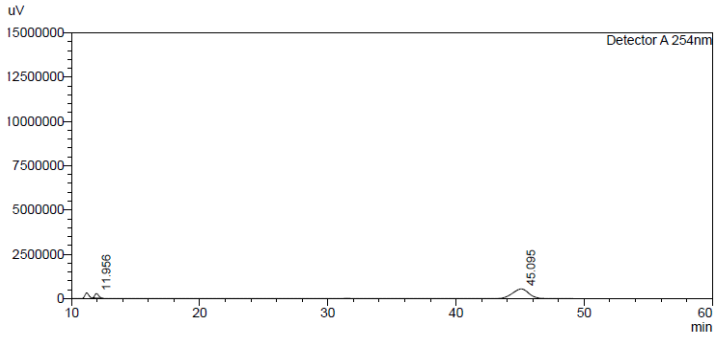
HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 80% [IC, 30% i-PrOH in hexanes, 0.5 mL/min], t_R = 11.20 min (*syn* major), t_R = 11.96 min (*anti* minor), t_R = 31.50 (*syn* minor), and t_R = 45.10 (*anti* major).

$[\alpha]_D^{20}$ = +47° (c = 1.0, $CHCl_3$).



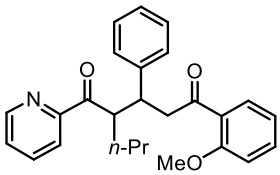
(*S*,*S*)-**3ak**
3.3:1 dr, 80% ee

<Chromatogram>



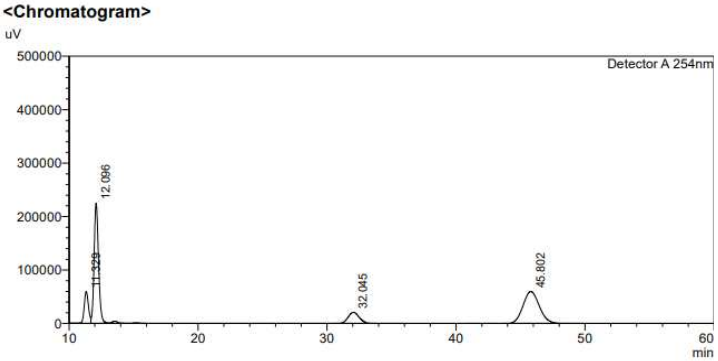
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.956	5199821	250419	9.782		M	
2	45.095	47955660	537898	90.218		M	
Total		53155480	788317				



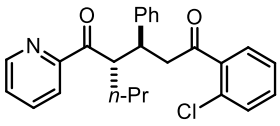
(*rac*)-**3ak**
1.0:1 dr

<Chromatogram>



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.329	1354201	59757	10.103			
2	12.096	5428379	225159	40.499		V	
3	32.045	1293731	21118	9.652			
4	45.802	5327448	60106	39.746			
Total		13403760	366140				



3al

(2*S*,3*S*)-5-(2-chlorophenyl)-3-phenyl-2-propyl-1-(pyridin-2-yl)pentane-1,5-dione (Table 5, 3al). The title compound was prepared according to **General Procedure F**, using 5,5-dimethylhexanoic acid [24499-80-7] (5.8 mg, 0.040 mmol, 0.20 equiv), $CuBr_2$ [7789-45-9] (4.4 mg, 0.020 mmol, 0.10 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-1-(2-chlorophenyl)-3-phenylprop-2-en-1-one (**2l**) [144017-77-6] (48.5 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 3.0:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3al** was afforded as a yellowish sticky liquid (57.6 mg, 71% yield, 8.1:1 dr (after isolation)).

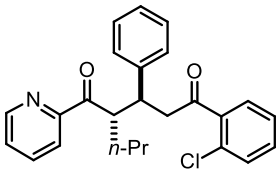
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.7 Hz, 1H of major, 89%), 8.64 (d, *J* = 4.8 Hz, 1H of minor, 11%), 8.08 (d, *J* = 7.8 Hz, 1H of major, 89%), 7.99 – 7.92 (m, 1H of minor, 11%), 7.85 (t, *J* = 7.8 Hz, 1H of major, 89%), 7.71 (t, *J* = 7.7 Hz, 1H of minor, 11%), 7.50 – 7.45 (m, 1H of major, 89%), 7.41 – 7.37 (m, 1H of minor, 11%), 7.27 – 7.12 (m, 7H), 7.03 (d, *J* = 7.4 Hz, 1H of minor, 11%), 6.93 (d, *J* = 7.7 Hz, 1H of major, 89%), 4.72 – 4.65 (m, 1H of minor, 11%), 4.61 (td, *J* = 9.8, 3.6 Hz, 1H of major, 89%), 3.84 – 3.77 (m, 1H of minor, 11%), 3.68 (td, *J* = 10.5, 3.9 Hz, 1H of major, 89%), 3.47 (dd, *J* = 17.1, 5.0 Hz, 1H of minor, 11%), 3.37 (dd, *J* = 16.2, 11.0 Hz, 1H), 3.11 (dd, *J* = 16.2, 3.9 Hz, 1H of major, 89%), 1.92 (d, *J* = 9.1 Hz, 1H of minor, 11%), 1.84 – 1.75 (m, 1H of minor, 11%), 1.63 – 1.52 (m, 1H of major, 89%), 1.33 – 1.24 (m, 1H of major 89%), 1.20 – 1.16 (m, 2H of minor, 11%), 1.12 – 0.95 (m, 2H of major, 89%), 0.82 (t, *J* = 7.3 Hz, 3H of minor, 11%), 0.65 (t, *J* = 7.3 Hz, 3H of major, 89%).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.73, 201.84, 154.08, 149.11, 141.83, 139.54, 137.21, 131.44, 130.77, 130.25, 129.06, 128.68, 128.43, 127.31, 126.80, 126.70, 122.29, 120.11, 48.87, 47.90, 45.29, 44.31, 42.98, 33.40, 20.22, 14.27.

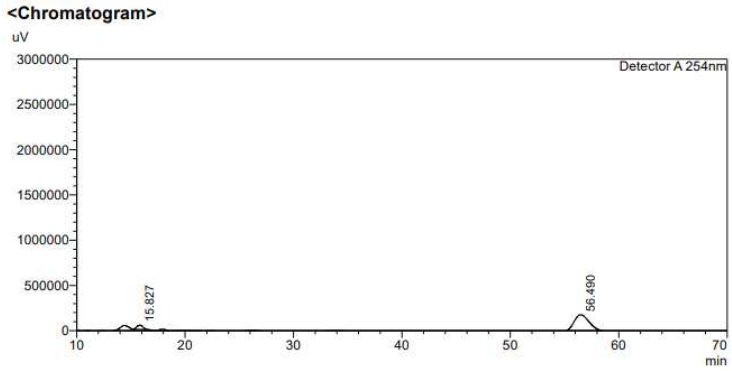
HRMS (ESI) m/z calcd for **$C_{25}H_{25}ClNO_2$** $[M + H]^+$: 406.1574, found: 406.1558.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 83% [IC, 30% i-PrOH in hexanes, 0.3 mL/min], t_R = 13.03 min (*syn* minor), t_R = 14.29 min (*syn* major), t_R = 15.83 (*anti* minor), and t_R = 56.49 (*anti* major).

$[\alpha]_D^{20}$ = +140° (c = 0.37, $CHCl_3$).

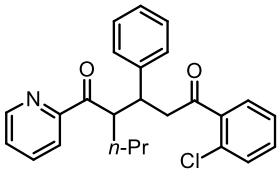


(*S*,*S*)-**3al**
8.1:1 dr, 83% ee

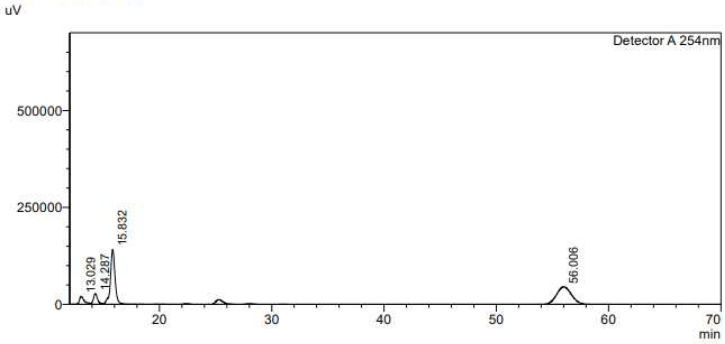


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.827	1836500	47549	8.734		M	
2	56.490	19190905	188031	91.266			
Total		21027405	235580				

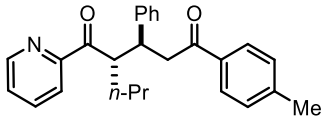


(*rac*)-**3al**
1.5:1 dr



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.029	623506	20415	6.354			
2	14.287	733392	28245	7.473		V	
3	15.832	4151393	141466	42.303		V	
4	56.006	4305242	45723	43.870			
Total		9813533	235850				



3am

(2*S*,3*S*)-3-phenyl-2-propyl-1-(pyridin-2-yl)-5-(p-tolyl)pentane-1,5-dione (Table 5, 3am). The title compound was prepared according to **General Procedure F**, using 4-(trimethylsilyl)butanoic acid [2345-40-6] (6.4 mg, 0.040 mmol, 0.20 equiv), $CuBr_2$ [7789-45-9] (4.4 mg, 0.020 mmol, 0.10 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-3-phenyl-1-(p-tolyl)prop-2-en-1-one (**2m**) [14802-30-3] (44.5 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 3.0:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3am** was afforded as a yellowish sticky liquid (51.7 mg, 67% yield, 9.0:1 dr (after isolation)).

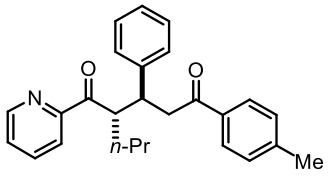
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.5 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.61 (dd, *J* = 6.7, 5.3 Hz, 1H), 7.25 (d, *J* = 12.7 Hz, 5H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.70 (td, *J* = 9.5, 3.7 Hz, 1H), 4.06 – 3.96 (m, 1H of minor, 10%), 3.83 (td, *J* = 9.8, 4.3 Hz, 1H of major, 90%), 3.41 (dd, *J* = 15.9, 9.9 Hz, 1H), 3.16 (dd, *J* = 15.9, 4.2 Hz, 1H), 2.35 (s, 3H), 1.66 – 1.51 (m, 1H), 1.43 – 1.31 (m, 1H), 1.15 – 1.01 (m, 2H), 0.89 – 0.81 (t, *J* = 7.2 Hz, 3H of minor, 10%), 0.67 (t, *J* = 7.2 Hz, 3H of 90% major).

^{13}C NMR (75 MHz, $CDCl_3$) δ 203.86, 198.36, 152.27, 147.78, 143.65, 142.11, 139.25, 134.62, 129.21, 128.51, 128.38, 127.76, 126.76, 123.20, 49.72, 43.98, 43.53, 33.45, 21.71, 20.14, 14.30.

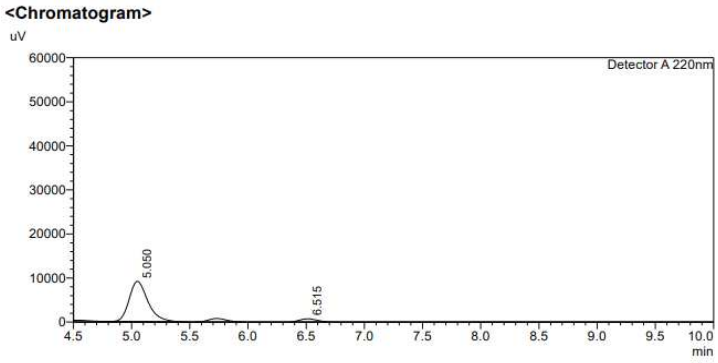
HRMS (ESI) m/z calcd for **$C_{26}H_{28}NO_2$** $[M + H]^+$: 386.2120, found: 386.2103.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 82% [AD-H, 30% i-PrOH in hexanes, 1 mL/min], t_R = 5.05 min (*anti* major), t_R = 5.73 min (*syn* minor), t_R = 6.52 (*anti* minor), and t_R = 9.30 (*syn* minor).

$[\alpha]_D^{20}$ = +145° (c = 0.37, $CHCl_3$).

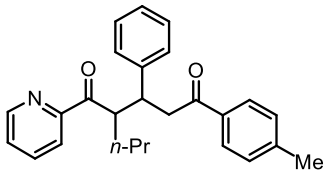


(*S*,*S*)-**3am**
9.0:1 dr, 82% ee

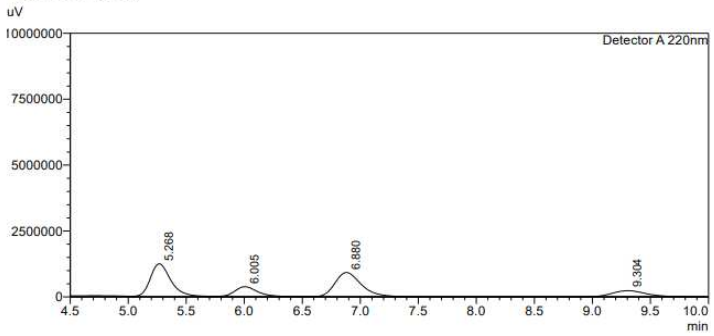


<Peak Table>
Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.050	103475	9167	91.075		M	
2	6.515	10140	851	8.925		M	
Total		113615	10018				

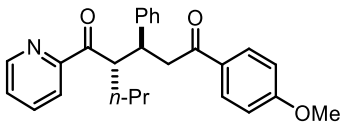


(*rac*)-**3am**
3.0:1 dr



<Peak Table>
Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.268	15961569	1258657	38.292			
2	6.005	5754065	387678	13.804		V	
3	6.880	15025921	925406	36.048		V	
4	9.304	4942028	234801	11.856			
Total		41683584	2806543				



3an

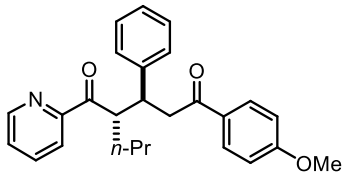
(2*S*,3*S*)-5-(4-methoxyphenyl)-3-phenyl-2-propyl-1-(pyridin-2-yl)pentane-1,5-dione (Table 5, 3an). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (**2n**) [22966-19-4] (47.7 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 2.6:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3an** was afforded as a yellowish sticky liquid (52 mg, 65% yield, 12:1 dr (after isolation)).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.3 Hz, 1H of major, 92%), 8.68 (d, *J* = 4.3 Hz, 1H of minor 8%), 8.10 (d, *J* = 7.8 Hz, 1H), 7.95 – 7.84 (m, 1H), 7.77 (d, *J* = 8.9 Hz, 2H), 7.52 (dd, *J* = 6.5, 4.9 Hz, 1H), 7.30 – 7.21 (m, 5H of major, 92%), 7.17 – 7.08 (m, 5H of minor, 8%), 6.84 (d, *J* = 8.9 Hz, 2H), 4.73 – 4.60 (m, 1H), 3.90 – 3.74 (m, 4H), 3.32 (dd, *J* = 15.6, 10.2 Hz, 1H), 3.10 (dd, *J* = 15.6, 4.1 Hz, 1H), 1.66 – 1.49 (m, 1H), 1.40 – 1.24 (m, 1H), 1.16 – 0.98 (m, 2H), 0.84 (t, *J* = 7.3 Hz, 3H of minor, 8%), 0.66 (t, *J* = 7.3 Hz, 3H of major, 92%).

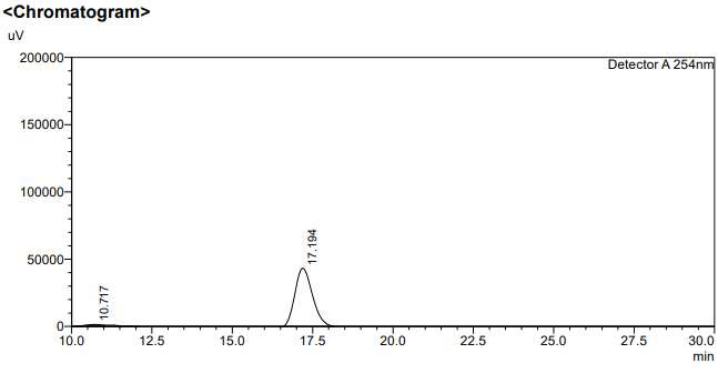
^{13}C NMR (75 MHz, $CDCl_3$) δ 205.16, 197.06, 163.16, 153.47, 148.62, 142.13, 137.65, 130.39, 130.11, 128.37, 128.31, 127.28, 126.56, 122.46, 113.51, 55.39, 49.13, 44.13, 43.47, 33.33, 20.01, 14.17.

HRMS (ESI) m/z calcd for **$C_{26}H_{28}NO_3$** $[M + H]^+$: 402.2069, found: 402.2056.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 99% [OX-H, 30% i-PrOH in hexanes, 0.5 mL/min], t_R = 10.72 min (*anti* minor), t_R = 11.92 min (*syn* isomer A), t_R = 14.08 (*syn* isomer B), and t_R = 17.19 (*anti* major). $[\alpha]_D^{20}$ = +62° (c = 0.51, $CHCl_3$).

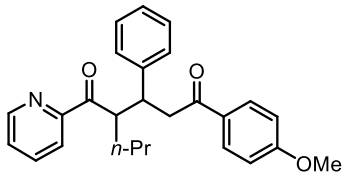


(*S*,*S*)-**3an**
12:1 dr, 99% ee

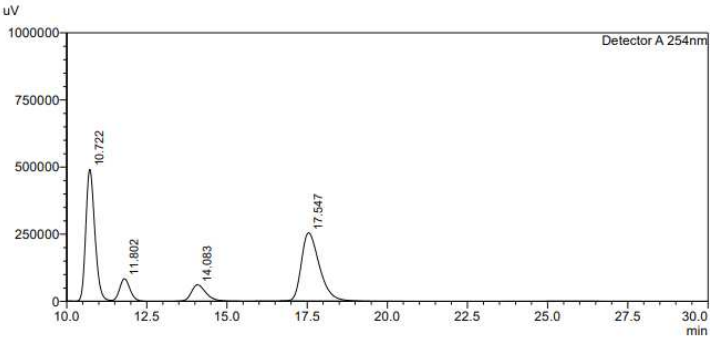


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.717	10212	576	0.569		M	
2	17.194	1783706	44536	99.431			
Total		1793918	45111				

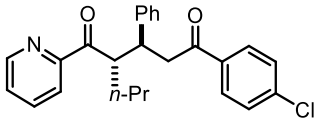


(*rac*)-**3an**
2.0:1 dr



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.722	9771411	491635	41.097			
2	11.802	1981082	84816	8.332		V	
3	14.083	2014530	61756	8.473			
4	17.547	10009540	254262	42.098			
Total		23776563	892469				



3ao

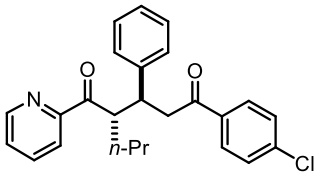
(2*S*,3*S*)-5-(4-chlorophenyl)-3-phenyl-2-propyl-1-(pyridin-2-yl)pentane-1,5-dione (Table 5, 3ao). The title compound was prepared according to **General Procedure E**, using Cu(II) **A** [2218-80-6] (8 mg, 0.02 mmol, 0.1 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-1-(4-chlorophenyl)-3-phenylprop-2-en-1-one (**2o**) [22966-22-9] (48.5 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 3.0:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ao** was afforded as a dark crystal (59.3 mg, 73% yield, 8.1:1 dr (after isolation), mp: 92–96 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.7 Hz, 1H of major, 89%), 8.65 (d, *J* = 4.7 Hz, 1H of minor, 11%), 8.10 (d, *J* = 7.8 Hz, 1H of major, 89%), 8.02 (d, *J* = 7.8 Hz, 1H of minor, 11%), 7.88 (td, *J* = 7.7, 1.6 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.51 (dd, *J* = 6.9, 4.8 Hz, 1H of major, 89%), 7.47 (dd, *J* = 7.0, 5.2 Hz, 1H of minor, 11%), 7.36 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 6.1 Hz, 3H), 7.19 (dd, *J* = 8.8, 4.5 Hz, 1H), 4.69 (td, *J* = 9.7, 3.7 Hz, 1H), 3.82 (td, *J* = 10.2, 4.0 Hz, 1H), 3.32 (dd, *J* = 15.6, 10.3 Hz, 1H), 3.14 (dd, *J* = 15.6, 4.0 Hz, 1H), 1.63 – 1.53 (m, 1H), 1.43 – 1.29 (m, 1H), 1.25 – 0.99 (m, 2H), 0.78 (t, *J* = 7.3 Hz, 3H of minor, 11%), 0.68 (t, *J* = 7.3 Hz, 3H of major, 89%).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.51, 197.25, 153.80, 148.82, 148.55, 141.71, 138.93, 136.92, 135.12, 129.38, 128.52, 128.21, 128.14, 127.03, 126.53, 122.04, 48.74, 43.80, 33.17, 20.62, 19.72, 13.96.

HRMS (ESI) m/z calcd for **$C_{25}H_{25}ClNO_2$** $[M + H]^+$: 406.1574, found: 406.1555.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 98% [IC, 30% i-PrOH in hexanes, 1 mL/min], t_R = 3.88min (*syn* isomer A), t_R = 4.37 min (*syn* isomer B), t_R = 15.63 (*anti* minor), and t_R = 33.07 (*anti* major). $[\alpha]_D^{20}$ = +60° (c = 0.43, $CHCl_3$).



(*S*,*S*)-**3ao**
8.1:1 dr, 98% ee

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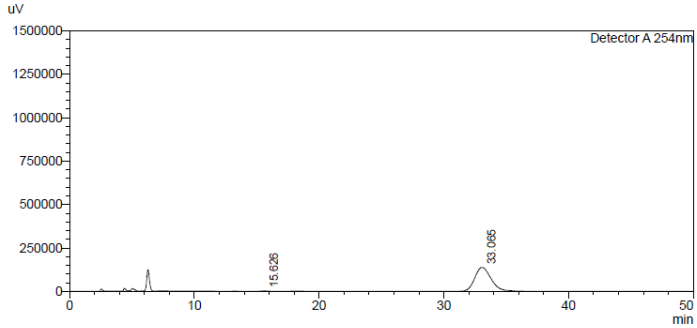
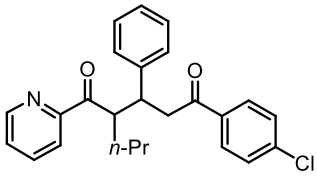


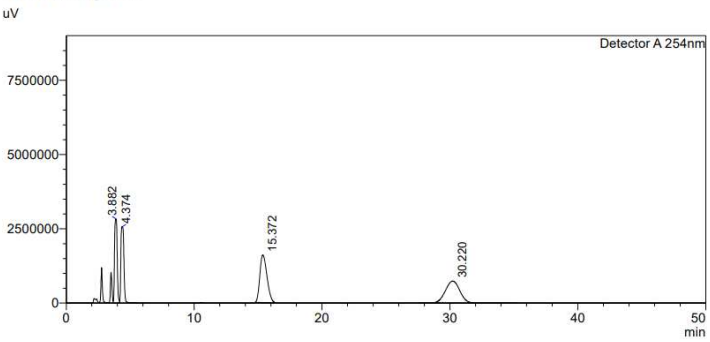
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.626	102619	3121	0.801			
2	33.065	12704654	138234	99.199			
Total		12807273	141355				



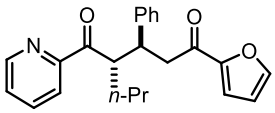
(*rac*)-**3ao**
1.0:1 dr

<Chromatogram>



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	3.882	40833242	2835856	20.009			
2	4.374	41762537	2568161	20.464		M	
3	15.372	61869400	1601213	30.317		M	
4	30.220	59611553	748037	29.210		M	
Total		204076734	7753268				



3ap

(2*S*,3*S*)-5-(furan-2-yl)-3-phenyl-2-propyl-1-(pyridin-2-yl)pentane-1,5-dione (Table 5, 3ap). The title compound was prepared according to **General Procedure F**, using 5,5-dimethylhexanoic acid [24499-80-7] (5.8 mg, 0.040 mmol, 0.20 equiv), $CuBr_2$ [7789-45-9] (4.4 mg, 0.020 mmol, 0.10 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-1-(furan-2-yl)-3-phenylprop-2-en-1-one (**2p**) [42811-81-4] (39.6 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 2.0:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ap** was afforded as a yellowish sticky liquid (49.2 mg, 68% yield, 3.3:1 dr (after isolation)).

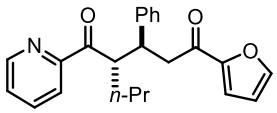
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 (d, *J* = 4.7 Hz, 1H of major, 77%), 8.65 (d, *J* = 4.7 Hz, 1H of minor, 23%), 8.08 (d, *J* = 7.8 Hz, 1H of major, 77%), 7.83 (dd, *J* = 7.6, 6.2 Hz, 1H), 7.71 (dd, *J* = 15.3, 5.9 Hz, 1H of minor, 23%), 7.63 – 7.52 (m, 1H), 7.52 – 7.43 (m, 2H of major, 77%), 7.42 – 7.34 (m, 2H of minor, 23%), 7.24 – 6.99 (m, 6H), 4.68 (td, *J* = 9.7, 3.6 Hz, 1H), 3.97 – 3.88 (m, 1H of minor, 23%), 3.83 (td, *J* = 10.3, 4.0 Hz, 1H of major, 77%), 3.43 (dd, *J* = 16.4, 9.5 Hz, 1H of minor, 23%), 3.30 (ddd, *J* = 19.6, 11.7, 6.7 Hz, 1H), 3.06 (dd, *J* = 15.2, 4.0 Hz, 1H of major, 77%), 2.04 – 1.87 (m, 1H of minor, 23%), 1.74 – 1.49 (m, 1H of major, 77%), 1.44 – 0.98 (m, 3H), 0.83 (t, *J* = 7.3 Hz, 3H of minor, 23%), 0.65 (t, *J* = 7.2 Hz, 3H of major, 77%).

^{13}C NMR (75 MHz, $CDCl_3$) δ 205.50, 191.13, 153.88, 148.89, 141.61, 144.32, 141.77, 136.92, 136.64, 133.19, 131.73, 128.23, 128.10, 127.90, 127.76, 127.07, 126.73, 126.54, 122.06, 48.96, 48.60, 44.57, 44.22, 42.45, 41.19, 33.19, 20.69, 19.83, 14.21, 14.03.

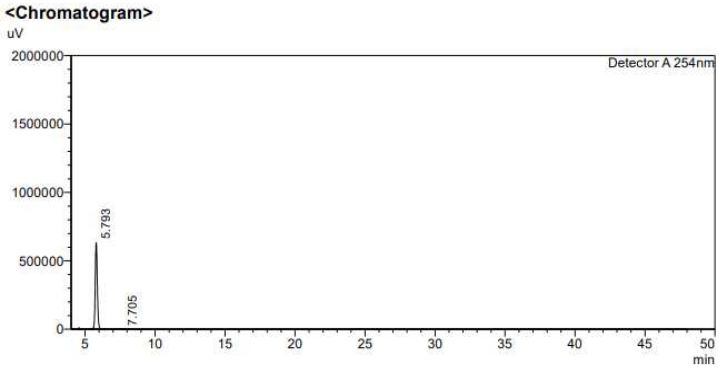
HRMS (ESI) m/z calcd for **$C_{23}H_{24}NO_3$** $[M + H]^+$: 362.1756, found: 362.1740.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 97% [IC, 30% i-PrOH in hexanes, 1 mL/min], t_R = 5.79 min (*anti* major), t_R = 7.71 min (*anti* minor), t_R = 30.34 (*syn* isomer A), and t_R = 37.69 (*syn* isomer B).

$[\alpha]_D^{20}$ = +59° (c = 1.2, $CHCl_3$).

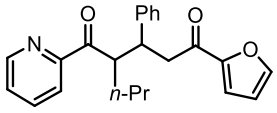


(*S*,*S*)-**3ap**
3.3:1 dr, 97% ee

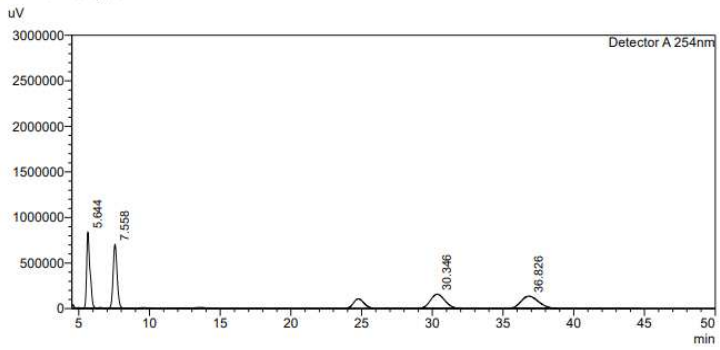


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.793	6614149	636105	98.675			
2	7.705	88796	2923	1.325			
Total		6702944	639028				

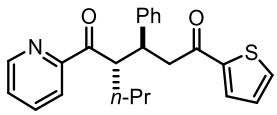


(*rac*)-**3ap**
1.1:1 dr



<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.644	13563581	831055	27.540		M	
2	7.558	13522167	699093	27.456		M	
3	30.346	11106577	156038	22.551		M	
4	36.826	11058287	132155	22.453		M	
Total		49250612	1818341				



3aq

(2*S*,3*S*)-3-phenyl-2-propyl-1-(pyridin-2-yl)-5-(thiophen-2-yl)pentane-1,5-dione (Table 5, 3aq). The title compound was prepared according to **General Procedure F**, using 4-(trimethylsilyl)butanoic acid [2345-40-6] (6.4 mg, 0.040 mmol, 0.20 equiv), $CuBr_2$ [7789-45-9] (4.4 mg, 0.020 mmol, 0.10 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-3-phenyl-1-(thiophen-2-yl)prop-2-en-1-one (**2q**) [39078-33-6] (42.9 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN (0.2 mL). The diastereomeric ratio was determined to be 3.3:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3aq** was afforded as a yellowish sticky liquid (69.5 mg, 92% yield, 3.3:1 dr (after isolation)).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.3 Hz, 1H of major, 77%), 8.63 (d, *J* = 4.5 Hz, 1H of minor, 23%), 8.06 (d, *J* = 7.8 Hz, 1H of major, 77%), 7.88 – 7.76 (m, 1H), 7.69 (td, *J* = 7.7, 1.4 Hz, 1H of minor, 23%), 7.50 – 7.40 (m, 2H of major, 77%),

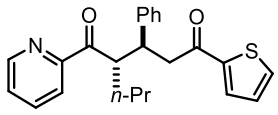
7.37 (dd, J = 6.4, 5.1 Hz, 2H of minor, 23%), 7.31 – 7.21 (m, 4H), 7.17 – 7.08 (m, 1H), 7.08 – 6.98 (m, 1H), 6.43 (dd, J = 3.4, 1.5 Hz, 1H of minor, 23%), 6.38 (dd, J = 3.3, 1.4 Hz, 1H of major, 77%), 4.66 (td, J = 9.6, 3.5 Hz, 1H), 4.0 – 3.88 (m, 1H of minor, 23%), 3.81 (td, J = 10.4, 4.2 Hz, 1H of major, 77%), 3.34 – 3.17 (m, 1H and 1H of minor, 23%), 2.92 (dd, J = 15.4, 4.1 Hz, 1H of major, 77%), 2.02 – 1.85 (m, 1H of minor, 23%), 1.68 – 1.50 (m, 1H of major, 77%), 1.39 – 0.99 (m, 3H), 0.81 (t, J = 7.3 Hz, 3H of minor, 23%), 0.65 (t, J = 7.2 Hz, 3H of major, 77%).

^{13}C NMR (75 MHz, $CDCl_3$) δ 205.56, 204.36, 187.74, 187.41, 154.02, 153.66, 152.93, 152.69, 149.02, 148.73, 146.06, 142.34, 141.94, 137.03, 136.76, 128.38, 128.32, 128.26, 128.00, 127.17, 126.83, 126.63, 126.31, 122.16, 117.02, 116.75, 112.16, 112.00, 49.17, 48.70, 43.88, 43.65, 42.24, 40.41, 33.30, 30.92, 20.80, 20.00, 14.34, 14.17.

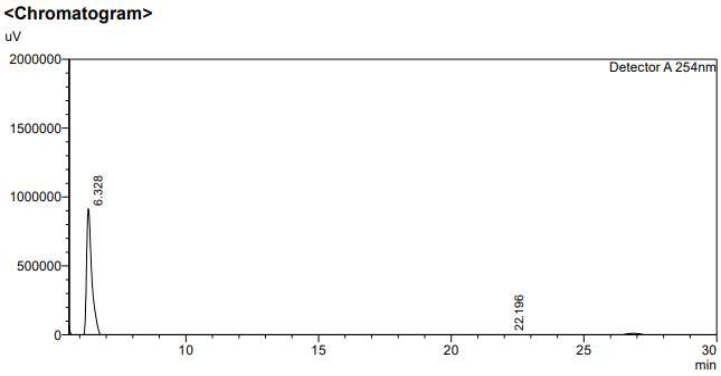
HRMS (ESI) m/z calcd for **$C_{23}H_{24}NO_2S$** $[M + H]^+$: 378.1528, found: 378.1511.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 92% [IC, 30% i-PrOH in hexanes, 1 mL/min], t_R = 6.33 min (*anti* major), t_R = 10.98 min (*syn* isomer A), t_R = 22.20 (*anti* minor), and t_R = 26.86 (*syn* isomer B).

$[\alpha]_D^{20}$ = +43° (c = 0.50, $CHCl_3$).



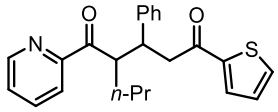
(*S*,*S*)-**3aq**
3.3:1 dr, 92% ee



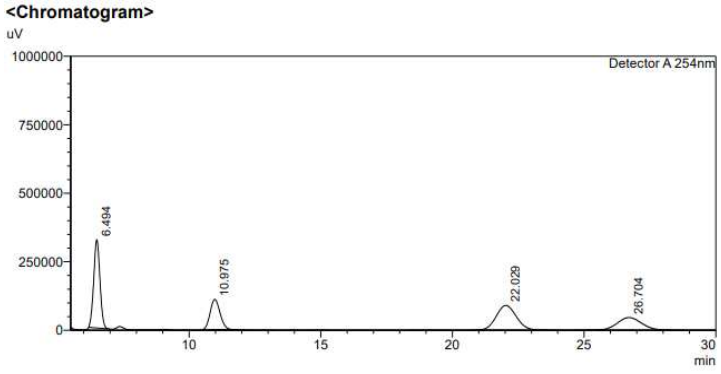
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.328	13251088	932918	95.735		M	
2	22.196	590378	11398	4.265		M	
Total		13841466	944316				



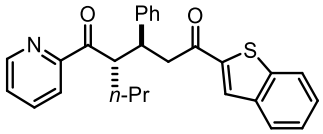
(*rac*)-**3aq**
1.1:1 dr



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.494	5285212	321980	32.983		M	
2	10.975	2896516	110541	18.076		M	
3	22.029	4819200	90371	30.075			
4	26.704	3023057	46242	18.866			
Total		16023986	569134				



3ar

(2*S*,3*S*)-5-(benzo[b]thiophen-2-yl)-3-phenyl-2-propyl-1-(pyridin-2-yl)pentane-1,5-dione (Table 5, 3ar). The title compound was prepared according to **General Procedure F**, using 4-(trimethylsilyl)butanoic acid [2345-40-6] (6.4 mg, 0.040 mmol, 0.20 equiv), $CuBr_2$ [7789-45-9] (4.4 mg, 0.020 mmol, 0.10 equiv), (*R*,*R*)-Ph-BPE [528565-79-9] (11.2 mg, 0.0220 mmol, 0.110 equiv), 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] (65.2 mg, 0.400 mmol, 2.00 equiv), (*E*)-1-(benzo[b]thiophen-2-yl)-3-phenylprop-2-en-

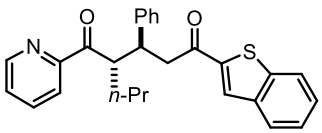
1-one (**2r**) [93486-61-4] (52.9 mg, 0.200 mmol, 1.00 equiv), and BTMG [29166-72-1] (3.6 mg, 0.020 mmol, 0.10 equiv) in MeCN:DCE (1:1, 0.8 mL). The diastereomeric ratio was determined to be 3.0:1 from the crude sample. After purification by flash column chromatography (Hex:EtOAc), **3ar** was afforded as a yellowish sticky liquid (63.3 mg, 74% yield, 4.0:1 dr (after isolation)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.2 Hz, 1H of major, 80%), 8.68 (d, *J* = 4.6 Hz, 1H of minor, 20%), 8.11 (d, *J* = 7.9 Hz, 1H of major, 80%), 8.06 (d, *J* = 8.0 Hz, 1H of minor, 20%), 7.86 (ddd, *J* = 7.8, 7.3, 4.0 Hz, 3H), 7.81 – 7.72 (m, 1H), 7.51 – 7.36 (m, 3H), 7.34 – 7.24 (m, 3H), 7.20 – 7.09 (m, 2H of major, 80%), 7.04 (t, *J* = 7.3 Hz, 2H of minor, 20%), 4.73 (tt, *J* = 6.1, 3.9 Hz, 1H), 3.98 (dd, *J* = 4.7, 2.4 Hz, 1H of minor, 20%), 3.95 – 3.85 (m, 1H of major, 80%), 3.57 – 3.51 (m, 1H of minor, 20%), 3.50 – 3.34 (m, 1H), 3.30 – 3.10 (m, 1H of major, 80%), 2.00 (dtd, *J* = 13.3, 10.2, 5.4 Hz, 1H of minor, 20%), 1.70 – 1.56 (m, 1H), 1.45 – 1.30 (m, 1H of major, 80%), 1.31 – 1.02 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H of minor, 21%), 0.69 (t, *J* = 7.3 Hz, 3H of major, 79%).

^{13}C NMR (101 MHz, $CDCl_3$) δ 205.55, 192.96, 153.93, 149.02, 148.71, 143.99, 142.54, 142.35, 141.86, 139.21, 137.33, 129.14, 128.87, 128.54, 128.45, 128.34, 128.22, 127.40, 127.40, 127.36, 127.30, 127.05, 126.88, 126.54, 126.02, 125.03, 124.91, 123.03, 122.98, 122.42, 122.38, 49.36, 49.00, 44.68, 44.54, 42.78, 41.24, 33.47, 31.04, 20.98, 20.06, 14.46, 14.27.

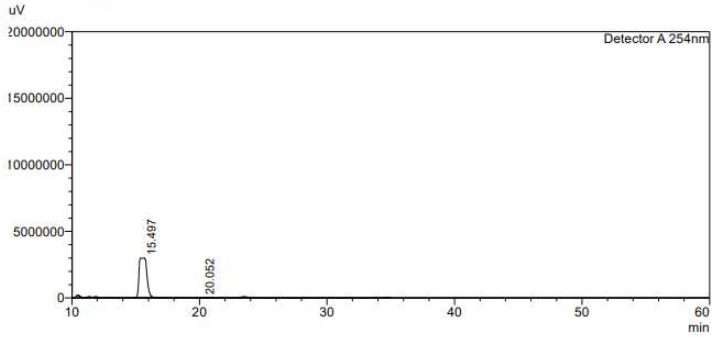
HRMS (ESI) m/z calcd for **$C_{27}H_{26}NO_2S$** $[M + H]^+$: 428.1684, found: 428.1670.

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be >99% [AD-H, 30% i-PrOH in hexanes, 0.3 mL/min], t_R = 15.50 min (*anti* major), t_R = 18.72 min (*syn* isomer A), t_R = 20.05 (*anti* minor), and t_R = 26.94 (*syn* isomer B). $[\alpha]_D^{20}$ = +70° (c = 0.93, $CHCl_3$).



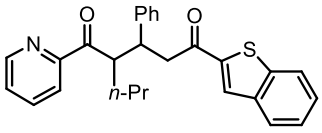
(*S*,*S*)-**3ar**
4.0:1 dr, >99% ee

<Chromatogram>



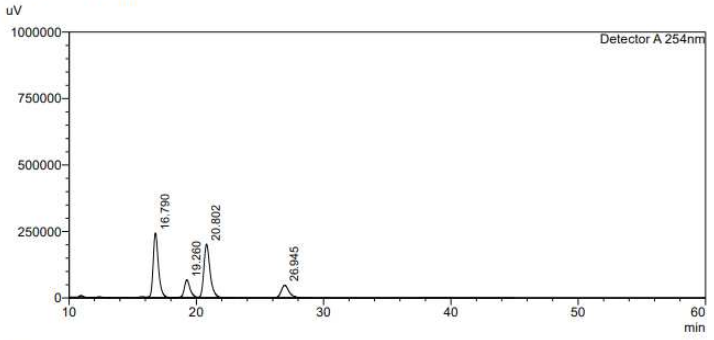
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.497	127975074	2989225	99.546			
2	20.052	583572	8662	0.454			
Total		128558646	2997887				



(*rac*)-**3ar**
1.0:1 dr

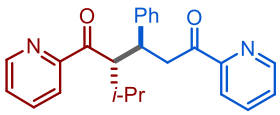
<Chromatogram>



<Peak Table>
Detector A 254nm

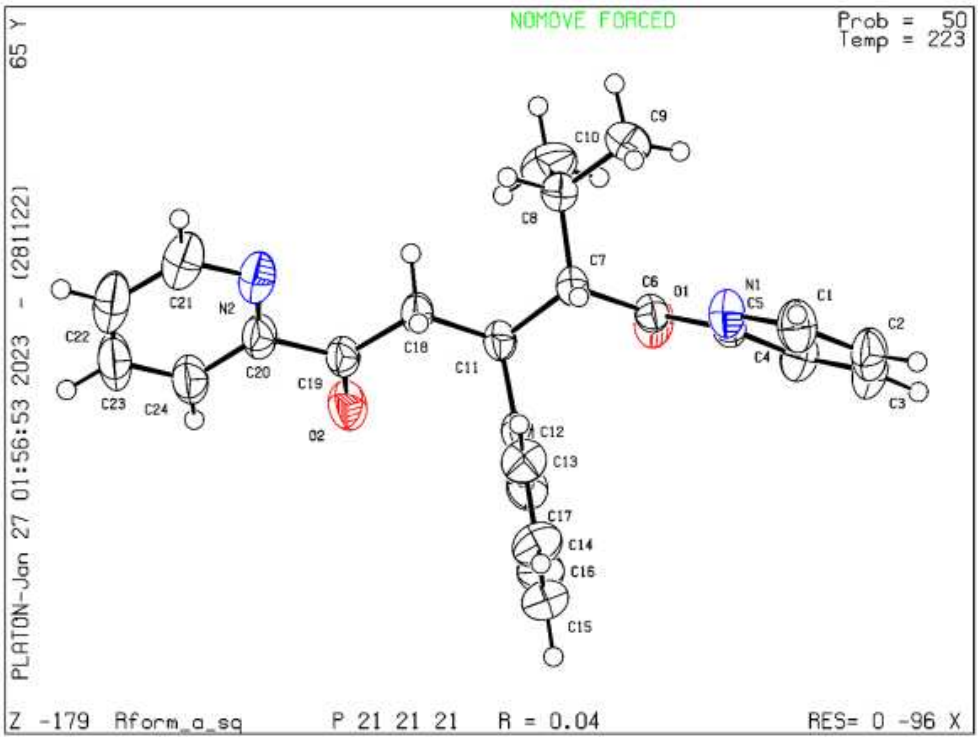
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.790	7038711	244263	38.626			
2	19.260	2230877	67533	12.242		V	
3	20.802	6881373	201686	37.762		V	
4	26.945	2071947	47702	11.370			
Total		18222909	561184				

VII. Determination of Absolute Configurations



3da

The Crystal (CCDC 2286253) of (2*S*,3*S*)-2-isopropyl-3-phenyl-1,5-di(pyridin-2-yl)pentane-1,5-dione (Table 4, **3da**) suitable for X-ray crystallography were grown from the saturated solution of hexanes/MeCN at room temperature. The absolute stereochemistry was determined to be (2*S*,3*S*) by X-ray crystallography. The configurations of other *anti*-products were assigned by analogy.



The crystal structures of the crystals were determined by standard crystallographic methods. A colorless needle-shaped crystal (0.320 x 0.138 x 0.128 mm^3) was used for single-crystal Xray diffraction. The data were collected at 173(2) K using a Bruker D8 Venture equipped with IμS micro-focus sealed tube Cu K_α (λ= 1.54178 Å) and a PHOTON III M14 detector in Western Seoul Center of Korea Basic Science Institute. Data collection and integration were performed with SMART APEX3 software package (SAINT+).[4] Absorption correction was performed by multiscan method implemented in SADABS.[5] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL program package (version 6.14).[6] All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions.

Table S8. Crystal Data and Structure Refinement for 3da

Identification code	Rform_a_sq	
Empirical formula	C24 H24 N2 O2	
Formula weight	372.45	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.8511(3) Å	a= 90°.
	b = 18.1921(10) Å	b= 90°.
	c = 21.3063(11) Å	g = 90°.
Volume	2267.9(2) $Å^3$	
Z	4	
Density (calculated)	1.091 Mg/m^3	
Absorption coefficient	0.070 mm^{-1}	
F(000)	792	
Crystal size	0.320 x 0.138 x 0.128 mm^3	
Theta range for data collection	2.239 to 28.336°.	
Index ranges	-5<=h<=7, -24<=k<=24, -28<=l<=28	
Reflections collected	50659	
Independent reflections	5640 [R(int) = 0.0439]	
Completeness to theta = 25.242°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6930	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5640 / 0 / 255	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0380, wR2 = 0.0870	
R indices (all data)	R1 = 0.0551, wR2 = 0.0964	
Absolute structure parameter	0.1(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.142 and -0.113 $e.Å^{-3}$	

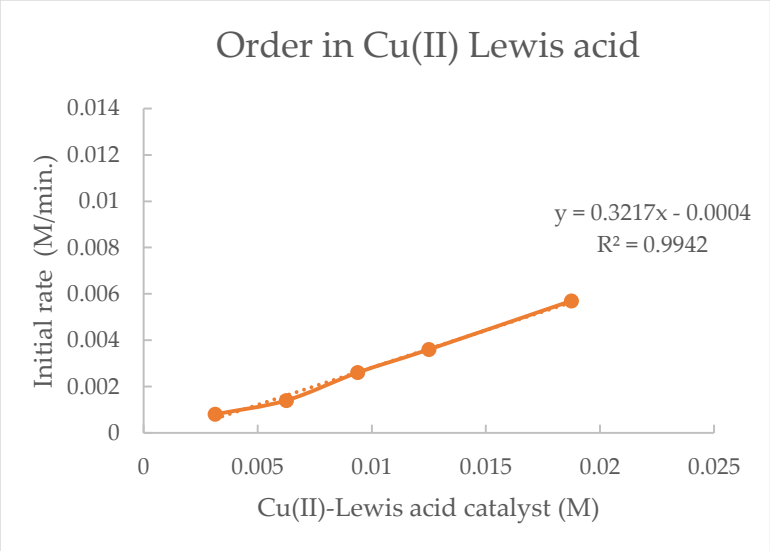
VIII. Kinetic Studies

Determination of the Rate Law: Conjugate Addition of Pyridyl Alkyl Ketone 1a to Enone 2a

In a nitrogen-filled glovebox, Cu(II) **A** [2218-80-6], (*R*,*R*)-Ph-BPE [528565-79-9] in MeCN (50 µL) were combined in a dram vial equipped with a stir bar. After stirring 3 minutes, 1-(2-pyridinyl)-1-pentanone (**1a**) [7137-97-5] and (*2E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**) [53940-12-8] were added to this vial. One minute later, BTMG [29166-72-1] and *n*-dodecane (11.3 µL, 0.0500 mmol, 1.00 equiv) as an internal standard were introduced into the mixture. The reaction mixture was stirred vigorously at room temperature. An aliquot (5.0 µL) of the mixture was removed on time and diluted with EtOAc (95.0 µL) under air. The amount of the product was determined by GC analysis.

Table S8. **Observed Initial Rates**

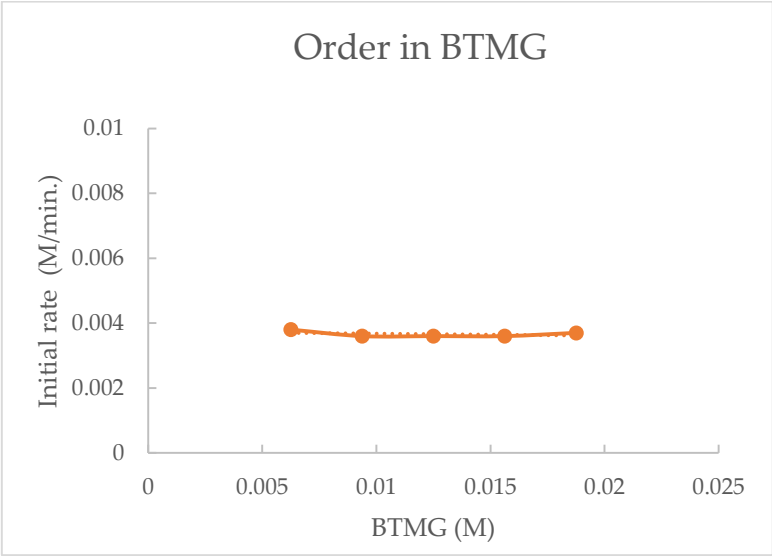
$[Cu(II)\text{-Lewis acid}]_{initial}$ (M)[a]	k_{obs} (M/min)
0.0031	0.00080
0.0062	0.0014
0.0094	0.0026
0.012	0.0036
0.019	0.0057



[a] Reaction conditions: $[BTMG]_{initial}$ = 0.012 M, [1-(2-pyridinyl)-1-pentanone **1a**]$_{initial}$ = 0.25 M, [(*2E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one **2a**]$_{initial}$ = 0.12 M.

Table S9. **Observed Initial Rates**

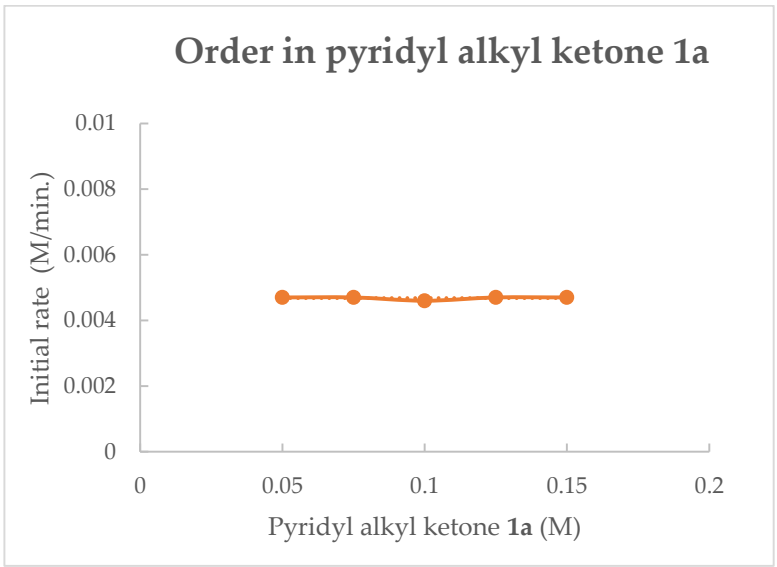
$[BTMG]_{initial}$ (M)[a]	k_{obs} (M/min)
0.0062	0.0038
0.0094	0.0036
0.012	0.0036
0.016	0.0036
0.019	0.0037



[a] Reaction conditions: [Cu(II)-Lewis acid]$_{initial}$ = 0.012 M, [1-(2-pyridinyl)-1-pentanone (**1a**)]$_{initial}$ = 0.25 M, [(*2E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**)]$_{initial}$ = 0.12 M.

***Table S10*. Observed Initial Rates**

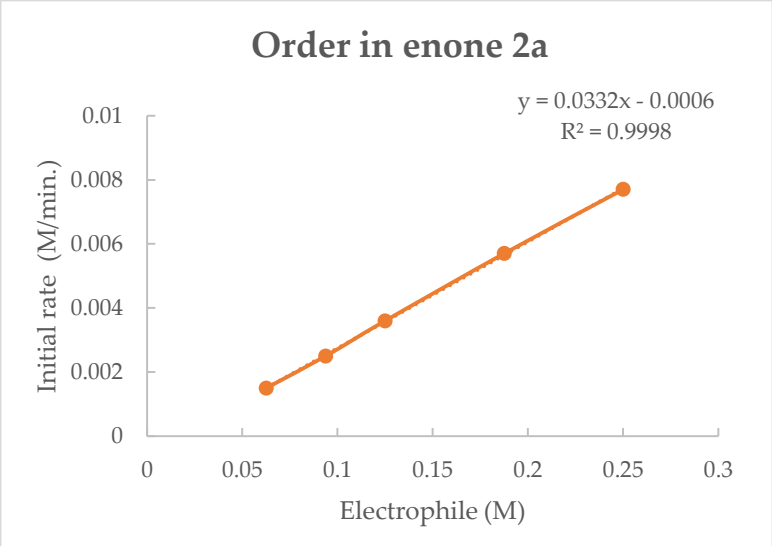
[pyridyl alkyl ketone **1a**]$_{initial}$ (M)[a]	k_{obs} (M/min)
0.050	0.0047
0.075	0.0047
0.10	0.0046
0.12	0.0047
0.15	0.0047



[a] Reaction conditions: [Cu(II)-Lewis acid]$_{initial}$ = 0.01 M, [BTMG]$_{initial}$ = 0.01 M, [(*2E*)-3-phenyl-1-(2-pyridinyl)-2-propen-1-one (**2a**)]$_{initial}$ = 0.1 M.

***Table S11*. Observed Initial Rates**

[enone **2a**]$_{initial}$ (M)[a]	k_{obs} (M/min)
0.062	0.0015
0.094	0.0025
0.12	0.0036
0.19	0.0056
0.25	0.0077

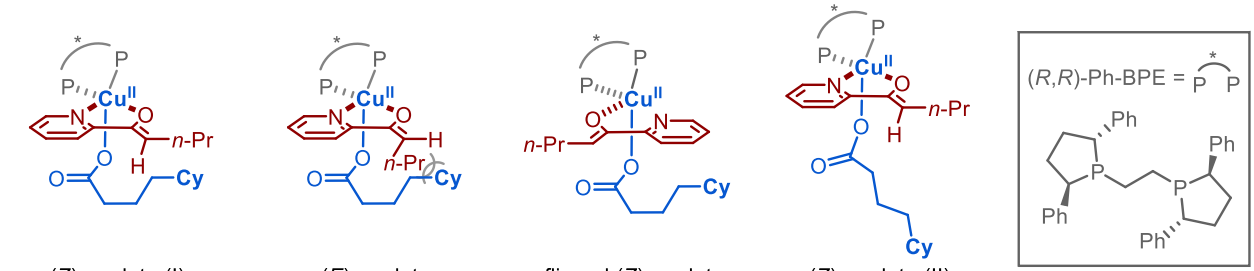


[a] Reaction conditions: [Cu(II)-Lewis acid]$_{initial}$ = 0.012 M, [BTMG]$_{initial}$ = 0.012 M, [1-(2-pyridinyl)-1-pentanone (**1a**)]$_{initial}$ = 0.25 M.

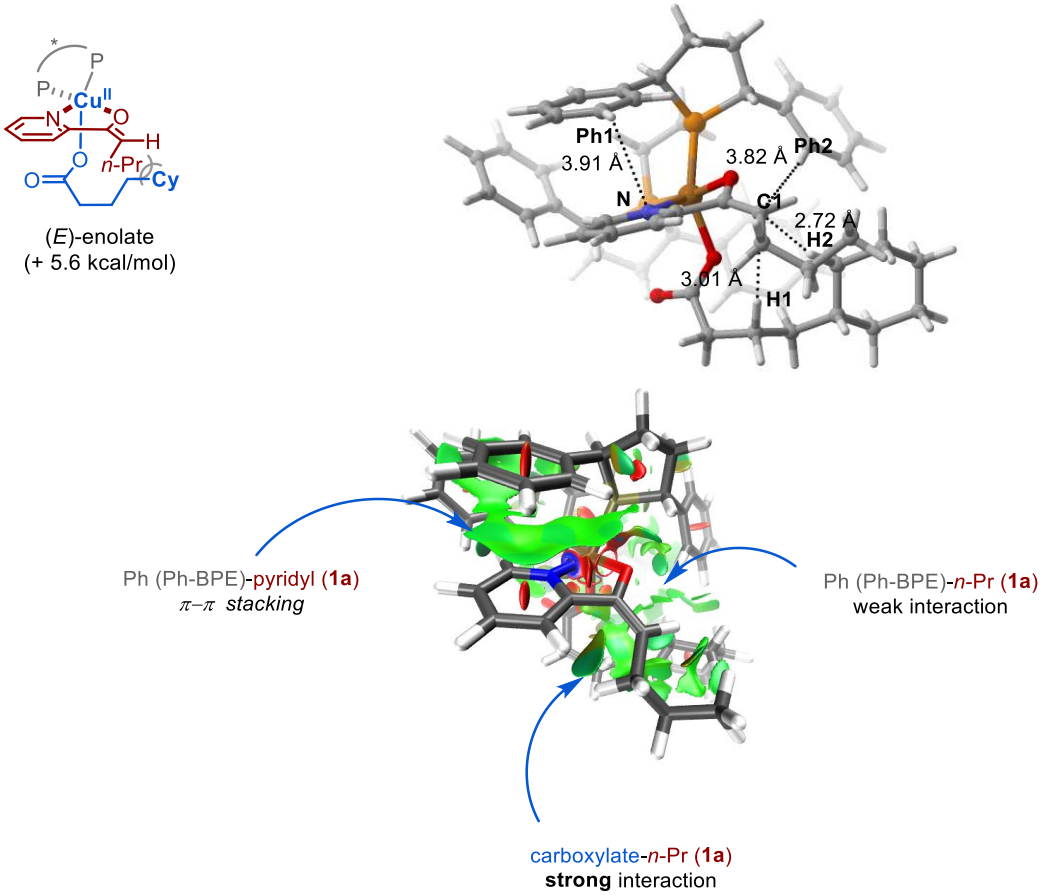
IX. Computational Studies

All DFT calculations were conducted using the ORCA 5.0.4 software package.[7] The ωB97X functional[8] coupled with D4 dispersion[9] was employed for geometry optimization, using def2-TZVP as the basis set for copper complexes and def2-SVP for all other atoms.[10] The CPCM (Continuum Polarizable Charge Model)[11] was integrated in an MeCN setting for these computations. To confirm optimal structure of the main catalyst, a numerical hessian was calculated to verify the absence of imaginary frequency. The def2-TZVP basis set within the CPCM (MeCN) solvation model was applied to compute ωB97X-D4 single-point energies. The Resolution of Identity for Coulomb and Chain-of-Sphere for Hartree-Fock exchange integrals (RIJCOSX)[12] approximation was used for all these computations with the def2/J auxiliary basis set.[13] Non-covalent interactions were examined through RDG (Reduced Density Gradient) analysis utilizing the Multiwfn.[14,15] For graphical representations, VMD and CYLview were utilized.[16,17]

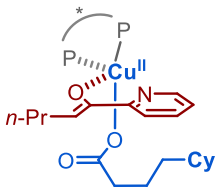
***Scheme S2*. Analysis of the Optimized Structure of Chiral Enolates Derived from Cu(II) A, (*R*,*R*)-Ph-BPE, and 1a**



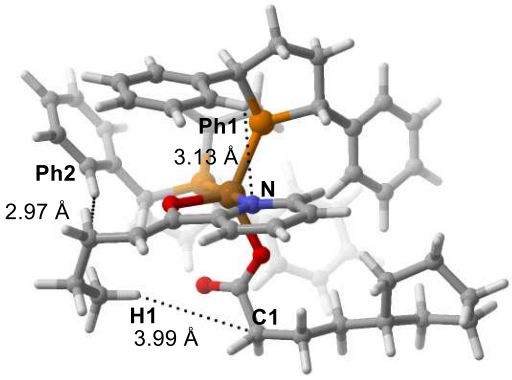
***Scheme S3*. NCIPLOT Analysis of the (*E*)-Enolate**



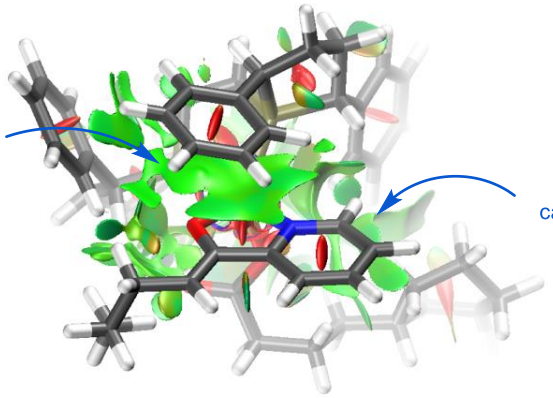
***Scheme S4*. NCIPLOT Analysis of the Flipped (*Z*)-Enolate**



flipped (*Z*)-enolate
(+ 7.2 kcal/mol)

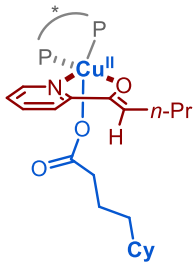


Ph (Ph-BPE)-**1a**
strong interaction

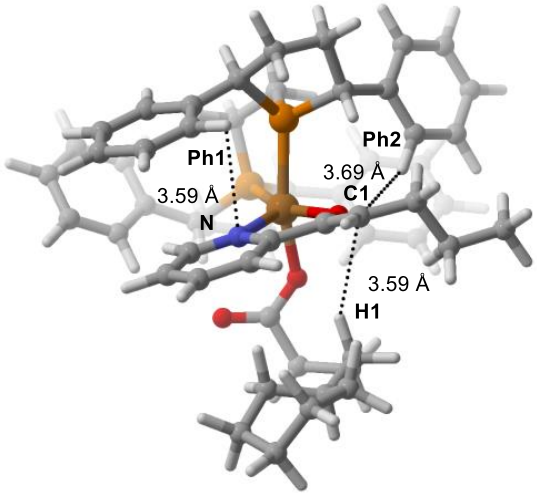


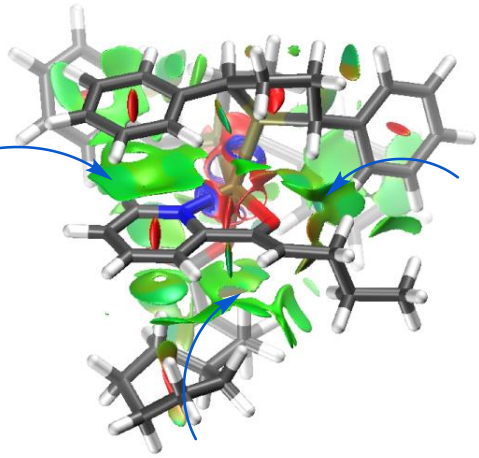
carboxylate-pyridyl (**1a**)
moderate interaction

***Scheme S5*. NCIPLOT Analysis of the Chiral (*Z*)-enolate (II)**



(*Z*)-enolate (II)
(+ 9.1 kcal/mol)



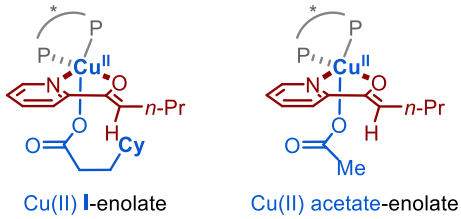


Ph (Ph-BPE)-pyridyl (**1a**)
π–π stacking

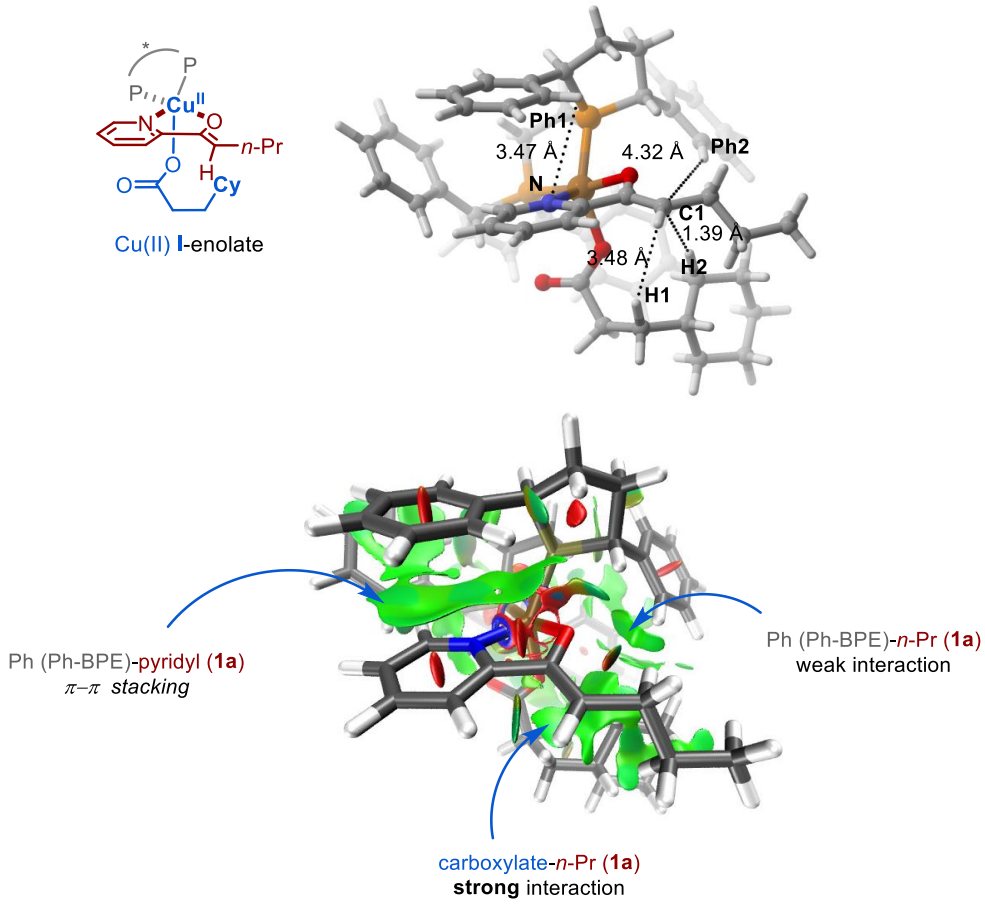
Ph (Ph-BPE)-*n*-Pr (**1a**)
strong interaction

carboxylate-*n*-Pr (**1a**)
weak interaction

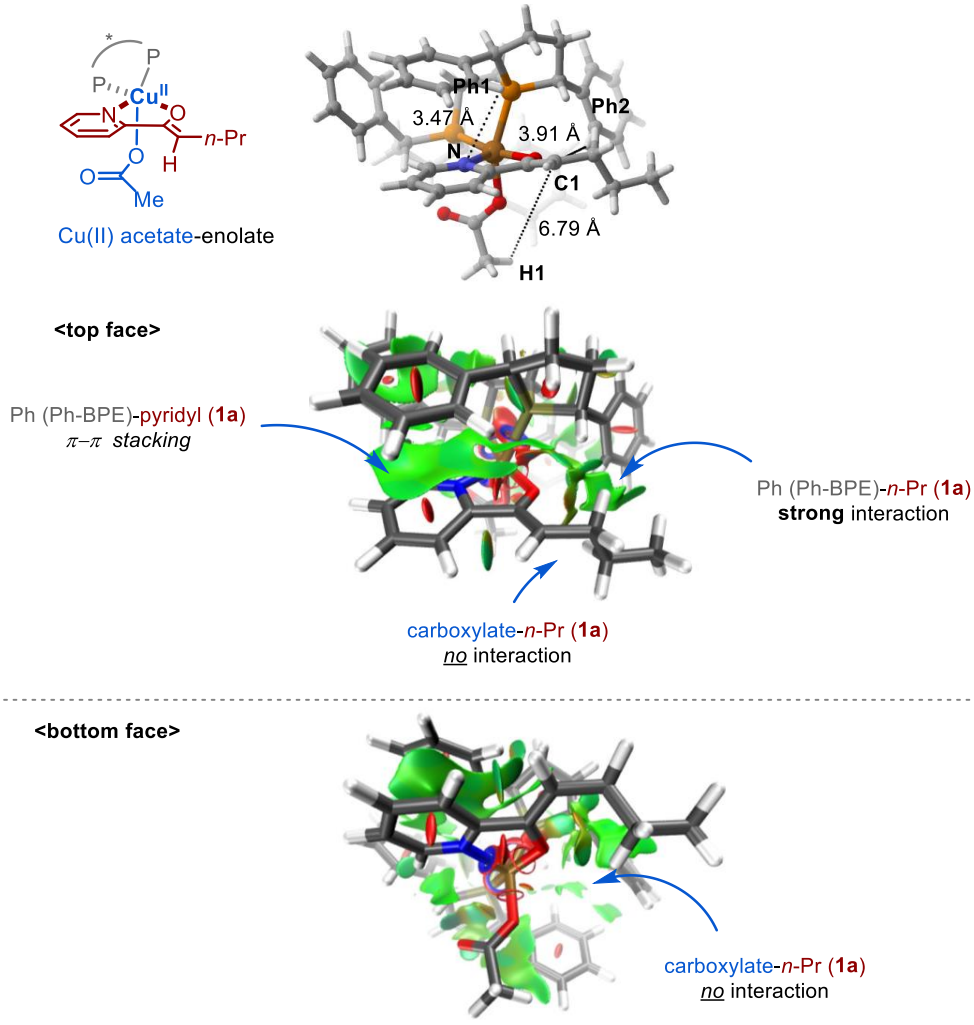
***Scheme S6*. Analysis on the Optimized Structure of the Other Chiral (Z)-Enolates**



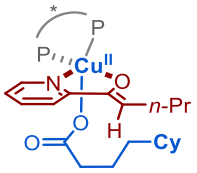
***Scheme S7*. NCIPLOT Analysis of the Chiral (*Z*)-Enolate Derived from Cu(II) cyclohexanepropanoate I, (*R*,*R*)-Ph-BPE, and 1a**



***Scheme S8*. NCIPLOT Analysis of the Chiral (*Z*)-Enolate Derived from $Cu(OAc)_2$**



Cartesian Coordinates (Å) and Energies of the Optimized Structures



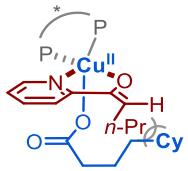
(*Z*)-enolate (I)

E = –4698.33303875767 a.u.

Cu	17.259344	1.919388	6.738629
P	15.709074	3.650981	6.500594
P	15.392841	0.479287	6.249937
O	18.612119	3.385045	6.892434
N	18.043103	1.591916	8.765877
C	19.472953	3.315829	7.881488
C	19.183778	2.273449	8.934465
C	17.673130	0.670639	9.655188
C	18.428030	0.359923	10.777080
C	19.628060	1.047241	10.961787
C	20.010673	2.009688	10.036374
H	18.085044	-0.400125	11.482615

H	20.265070	0.833308	11.824680
C	20.547343	4.138562	8.006930
C	20.897214	5.219628	7.026422
H	21.192317	4.047253	8.885194
C	22.382813	5.252707	6.662043
H	20.619838	6.213038	7.434658
H	20.294282	5.094153	6.109938
C	22.755015	6.428896	5.767793
H	22.650966	4.301287	6.167495
H	22.982369	5.289528	7.589553
H	23.820949	6.410222	5.491339
H	22.167062	6.419446	4.835099
H	22.557427	7.388213	6.274227
O	18.711086	0.701478	6.066017
C	18.932510	-0.498975	6.425937
O	18.067925	-1.329587	6.744077
C	20.407076	-0.911776	6.507296
C	21.397364	0.076761	5.902525
H	20.504637	-1.910914	6.049287
H	20.609336	-1.058308	7.583291
C	21.319977	0.125956	4.376879
H	22.423035	-0.192074	6.209885
H	21.195906	1.074874	6.324564
C	21.941241	1.364237	3.726808
H	20.261245	0.078261	4.073271
H	21.799917	-0.781610	3.966246
C	21.084833	2.619318	3.945546
C	21.675089	3.854399	3.266550
H	20.939234	2.811135	5.022552
H	20.076156	2.424462	3.529727
C	22.163459	1.148944	2.224995
H	22.933165	1.544163	4.189956
C	22.765883	2.375293	1.541326
H	21.187104	0.913797	1.757980
H	22.805906	0.265964	2.065584
C	21.909259	3.618828	1.774809
H	22.888480	2.189716	0.461259
H	23.779220	2.552458	1.946678
H	22.636862	4.109897	3.748663
H	21.011588	4.723708	3.421112
H	22.377694	4.503791	1.312966
H	20.933971	3.481854	1.270326
C	13.929827	1.614313	6.196411
C	14.306065	2.951342	5.546057
H	13.446591	3.639647	5.523512
H	14.647214	2.808782	4.506837
C	16.289460	5.207117	5.691502
C	15.347919	6.288127	6.234736
C	15.217785	6.020484	7.733977
H	14.357151	6.223708	5.754043
H	15.748723	7.294229	6.032685
C	14.885581	4.526517	7.939089
H	14.445155	6.647808	8.204404
H	16.174568	6.261446	8.224029
C	15.274354	-0.428237	4.608092
C	15.292674	-1.914824	4.993411
C	14.421411	-2.056789	6.235379
H	16.319047	-2.226591	5.238059
H	14.932065	-2.531056	4.154537
C	14.926384	-1.027017	7.264136
H	14.470469	-3.070179	6.664079

H	13.365308	-1.857430	5.983894
C	14.026170	-0.841137	8.463815
H	15.913655	-1.370148	7.610186
C	14.504555	-1.144261	9.745708
C	13.691481	-1.014577	10.871706
C	12.372388	-0.585384	10.734506
C	11.871434	-0.306935	9.461766
C	12.687189	-0.441634	8.339121
H	12.265607	-0.241919	7.350035
H	15.529508	-1.509788	9.862448
H	14.092478	-1.256346	11.860323
H	11.731426	-0.480235	11.614514
H	10.831792	0.010361	9.339026
C	16.209530	-0.012624	3.494293
H	14.250568	-0.191879	4.273125
C	15.789359	0.947955	2.562859
C	16.598348	1.314178	1.488158
C	17.846318	0.714751	1.317935
C	18.273670	-0.245531	2.234518
C	17.467944	-0.600168	3.317128
H	14.798031	1.402606	2.669306
H	16.246686	2.065095	0.775179
H	18.481043	0.987719	0.469374
H	19.246639	-0.728575	2.105117
H	17.824955	-1.346176	4.031683
C	16.498552	5.094864	4.201448
C	17.728668	4.618647	3.721672
C	17.964061	4.506537	2.353261
C	16.971972	4.865853	1.438904
C	15.742137	5.327066	1.905359
C	15.505987	5.439450	3.277327
H	14.957062	5.607761	1.197072
H	14.536638	5.807983	3.625561
H	18.930287	4.135987	1.997343
H	17.156587	4.781658	0.364038
H	18.503718	4.336927	4.444147
C	15.202142	3.954716	9.304295
H	13.807655	4.385234	7.757137
C	14.264688	3.137582	9.949573
C	14.532311	2.587684	11.203572
C	15.746457	2.850953	11.836822
C	16.688967	3.662237	11.203853
C	16.421518	4.204253	9.947849
H	13.303548	2.933121	9.464092
H	13.784236	1.951569	11.685538
H	15.959358	2.421432	12.820147
H	17.185235	4.817839	9.458533
H	17.649761	3.864799	11.686817
H	16.723593	0.165892	9.459643
H	20.948891	2.550147	10.167446
H	13.089742	1.137147	5.668129
H	13.605060	1.782929	7.236746
H	17.278291	5.341214	6.161175



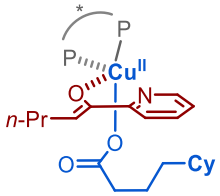
(*E*)-enolate

E = –4698.32476566826 a.u.

Cu	17.203549	2.101207	6.650864
P	15.490453	3.671585	6.374594
P	15.458840	0.472303	6.236756
O	18.402237	3.700821	6.770133
N	18.079650	1.885722	8.681482
C	19.445130	3.520855	7.564102
C	19.159265	2.679383	8.780397
C	17.736462	1.094369	9.693321
C	18.446918	1.043993	10.888320
C	19.542876	1.890299	11.026563
C	19.898465	2.723575	9.968636
H	18.128543	0.376253	11.692029
H	20.114703	1.913125	11.958622
C	20.662063	4.054604	7.283559
C	21.998407	3.877585	7.957930
H	20.667420	4.659826	6.368415
C	23.170523	3.982393	6.972782
H	22.158359	4.627310	8.759946
H	22.051217	2.894481	8.455045
C	23.355005	5.367147	6.360203
H	23.032090	3.235815	6.168778
H	24.096915	3.697207	7.499835
H	24.234372	5.395969	5.697414
H	22.483264	5.671708	5.758976
H	23.501483	6.129215	7.143913
O	18.763752	1.002293	5.988349
C	18.987981	-0.219144	6.268216
O	18.129673	-1.051661	6.599877
C	20.452888	-0.669492	6.238760
C	21.435527	0.303666	5.599820
H	20.487937	-1.657375	5.748564
H	20.718991	-0.854612	7.294464
C	21.284838	0.384301	4.081327
H	22.468321	0.004607	5.850728
H	21.279818	1.297948	6.047719
C	21.915644	1.616978	3.431457
H	20.211428	0.379170	3.830647
H	21.711064	-0.531135	3.630359
C	21.090787	2.881169	3.701222
C	21.702773	4.123724	3.057222
H	20.963127	3.036053	4.784205
H	20.073960	2.720646	3.290241
C	22.094392	1.435602	1.920132
H	22.923182	1.768389	3.871572
C	22.710081	2.668861	1.258957
H	21.101471	1.235601	1.471699
H	22.713176	0.544203	1.718889
C	21.897729	3.929903	1.553703
H	22.799717	2.515331	0.170609
H	23.738224	2.805057	1.642501
H	22.681159	4.331801	3.529916
H	21.068111	5.005716	3.253325

H	22.382918	4.813981	1.107534
H	20.905913	3.839963	1.070964
C	13.902017	1.477881	6.165958
C	14.146929	2.816171	5.461594
H	13.229928	3.425538	5.433153
H	14.482821	2.669855	4.421846
C	15.885819	5.248111	5.498481
C	14.778107	6.205865	5.953584
C	14.656115	6.019578	7.466559
H	13.821248	5.960115	5.462723
H	15.022959	7.247334	5.690715
C	14.579326	4.507705	7.783465
H	13.777337	6.537026	7.880675
H	15.544998	6.455427	7.949246
C	15.380782	-0.504831	4.629777
C	15.442026	-1.974913	5.069777
C	14.594595	-2.096741	6.330254
H	16.479315	-2.249763	5.309679
H	15.085325	-2.631347	4.260104
C	15.086692	-1.018249	7.313297
H	14.678514	-3.093443	6.791759
H	13.529363	-1.936001	6.089720
C	14.212668	-0.820804	8.530291
H	16.094349	-1.308323	7.645980
C	14.755453	-0.992737	9.810713
C	13.975674	-0.832662	10.956370
C	12.624843	-0.508218	10.841585
C	12.060172	-0.366474	9.572796
C	12.843959	-0.529006	8.431148
H	12.374477	-0.433469	7.448198
H	15.807485	-1.276969	9.911190
H	14.428172	-0.968710	11.943049
H	12.009633	-0.380175	11.736776
H	10.996448	-0.133557	9.468507
C	16.301710	-0.103438	3.497112
H	14.352033	-0.312625	4.282375
C	15.887441	0.879795	2.586255
C	16.676200	1.232100	1.492395
C	17.897249	0.592459	1.277045
C	18.317576	-0.392128	2.170000
C	17.533921	-0.729599	3.274498
H	14.913670	1.363482	2.720944
H	16.327463	2.001752	0.798156
H	18.514628	0.852400	0.411808
H	19.270440	-0.904664	2.009071
H	17.889823	-1.491269	3.972204
C	16.168546	5.094869	4.023325
C	17.458986	4.720851	3.615096
C	17.768849	4.592372	2.263134
C	16.791564	4.827785	1.293655
C	15.502921	5.181310	1.689324
C	15.192307	5.312888	3.045098
H	14.729281	5.364893	0.937884
H	14.177241	5.599661	3.334950
H	18.783211	4.310100	1.963231
H	17.034800	4.733613	0.231362
H	18.218479	4.532934	4.382960
C	15.031950	4.103600	9.170209
H	13.534455	4.179549	7.662486
C	14.257994	3.217407	9.930262
C	14.652559	2.840699	11.215192

C	15.829906	3.348710	11.762178
C	16.615169	4.223321	11.010155
C	16.221953	4.592500	9.725758
H	13.325387	2.819755	9.512919
H	14.029832	2.149855	11.791406
H	16.140207	3.058395	12.770127
H	16.860145	5.264305	9.143022
H	17.548218	4.617157	11.424138
H	16.842857	0.482047	9.545390
H	20.730663	3.418473	10.076876
H	13.095090	0.910926	5.675931
H	13.584456	1.660507	7.206364
H	16.826170	5.550579	5.990073



flipped (*Z*)-enolate

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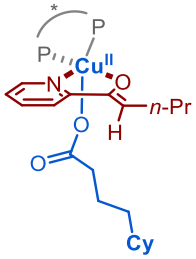
Cu	17.156616	2.008067	7.381660
P	15.518301	3.635249	6.723261
P	15.515229	0.409002	6.700034
O	17.314910	1.394064	9.339154
N	18.547620	3.353078	8.091866
C	18.319265	1.911902	9.999740
C	18.998919	3.074892	9.323304
C	19.092120	4.341087	7.372795
C	20.114543	5.139556	7.855955
C	20.585096	4.884821	9.147082
C	20.028366	3.848995	9.881537
H	20.528617	5.937437	7.235986
H	21.386611	5.492262	9.576374
C	18.773560	1.487092	11.209632
C	18.157332	0.374246	12.009369
H	19.643218	1.981744	11.650225
C	18.855063	-0.987935	11.868840
H	17.096223	0.265727	11.729032
H	18.165383	0.656944	13.076967
C	18.687705	-1.630218	10.496811
H	18.466054	-1.673683	12.642381
H	19.930370	-0.861719	12.089593
H	19.244144	-2.578225	10.425712
H	17.626728	-1.852987	10.290833
H	19.041766	-0.967118	9.691251
O	18.750477	1.278730	6.291218
C	19.162368	0.084877	6.449182
O	18.477519	-0.859370	6.877729
C	20.629632	-0.196286	6.110737
C	21.426086	0.968828	5.537740
H	20.650797	-1.066498	5.431244
H	21.082323	-0.552146	7.051950
C	21.105512	1.262942	4.075058
H	22.505455	0.755011	5.630975
H	21.230657	1.862508	6.152972
C	21.762201	2.530471	3.528370
H	20.010307	1.350809	3.955225

H	21.413998	0.395446	3.462118
C	21.222874	3.800788	4.227872
C	21.236693	5.042225	3.323844
H	21.814990	4.001229	5.137398
H	20.191222	3.611486	4.574330
C	21.597692	2.652259	2.010995
H	22.849347	2.458974	3.729506
C	22.402186	3.828838	1.436518
H	20.523961	2.781350	1.783164
H	21.901211	1.711879	1.521328
C	22.454052	5.028566	2.402052
H	21.957944	4.137347	0.475416
H	23.429070	3.498949	1.205949
H	21.219459	5.957374	3.938179
H	20.318933	5.069010	2.709110
H	23.363639	4.970739	3.025724
H	22.529176	5.971575	1.836961
C	13.955413	1.390296	6.572043
C	14.233358	2.687724	5.805466
H	13.316665	3.286879	5.689995
H	14.622332	2.478531	4.794365
C	15.888361	5.124293	5.681689
C	14.716814	6.069278	5.970585
C	14.522744	6.055791	7.486762
H	13.804558	5.713029	5.461679
H	14.923420	7.085831	5.600221
C	14.505304	4.590598	7.979153
H	13.598183	6.569757	7.790491
H	15.360395	6.594085	7.957842
C	15.455357	-0.681648	5.171915
C	15.761318	-2.086604	5.712323
C	14.950398	-2.240219	6.994345
H	16.834622	-2.174215	5.936283
H	15.494767	-2.846917	4.960926
C	15.230541	-1.011878	7.880326
H	15.202218	-3.163294	7.539722
H	13.877959	-2.292211	6.744158
C	14.228370	-0.753846	8.982125
H	16.224461	-1.137689	8.336688
C	14.682855	-0.474992	10.275439
C	13.789358	-0.239896	11.319825
C	12.415341	-0.271068	11.083714
C	11.947199	-0.542497	9.796617
C	12.844771	-0.785994	8.757273
H	12.455790	-0.999172	7.756877
H	15.760066	-0.421034	10.447464
H	14.172246	-0.029221	12.323285
H	11.709428	-0.086426	11.898691
H	10.871494	-0.568132	9.599333
C	16.190600	-0.278496	3.913826
H	14.380192	-0.661636	4.926348
C	15.493060	0.381918	2.891457
C	16.108943	0.684926	1.678144
C	17.439829	0.328415	1.462309
C	18.145860	-0.325627	2.471851
C	17.528099	-0.625731	3.686278
H	14.439744	0.642666	3.043956
H	15.543124	1.197173	0.894412
H	17.925575	0.558430	0.509421
H	19.190050	-0.611317	2.312593
H	18.086475	-1.148350	4.466276

C	16.226344	4.808434	4.241906
C	17.258255	3.901714	3.946355
C	17.619232	3.635951	2.629085
C	16.950090	4.262626	1.575581
C	15.915737	5.151513	1.856355
C	15.557257	5.423458	3.179496
H	15.380643	5.645988	1.040408
H	14.749678	6.132741	3.377643
H	18.421715	2.921311	2.424974
H	17.229296	4.048590	0.539869
H	17.782219	3.377729	4.754836
C	14.918654	4.372527	9.417946
H	13.484412	4.193660	7.862641
C	14.142256	3.553847	10.246304
C	14.509167	3.321565	11.572897
C	15.660923	3.909791	12.093262
C	16.446873	4.722897	11.274552
C	16.080986	4.948466	9.948982
H	13.233432	3.090726	9.844925
H	13.886357	2.679005	12.202150
H	15.949451	3.731169	13.133171
H	16.719695	5.575461	9.317723
H	17.359891	5.179269	11.668919
H	18.696939	4.490037	6.363886
H	20.388112	3.639790	10.889398
H	13.159524	0.800834	6.090867
H	13.616820	1.616963	7.597870
H	16.784346	5.568031	6.152742



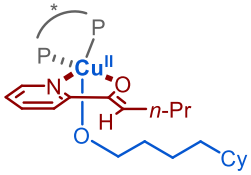
(*Z*)-enolate (II)

E = –4698.320446965585 a.u.

Cu	16.757448	2.082694	7.549292
P	15.530993	3.976508	6.720218
P	15.115699	0.829508	6.407545
O	18.361040	3.279948	7.691489
N	16.817362	2.543078	9.732812
C	18.561617	3.926877	8.811716
C	17.791669	3.421052	10.006859
C	16.113854	1.996873	10.727176
C	16.347835	2.290749	12.063394
C	17.351259	3.211149	12.365811
C	18.077797	3.784175	11.330939
H	15.752278	1.813268	12.844524
H	17.573026	3.473108	13.404517
C	19.414622	4.980966	8.925381
C	20.237317	5.455619	7.759133
H	19.543892	5.470650	9.893570
C	21.397423	4.517103	7.402967
H	20.637937	6.464843	7.958968
H	19.594417	5.549384	6.863326
C	22.148114	4.940465	6.146187
H	20.985657	3.501238	7.271701

H	22.093072	4.458464	8.259569
H	21.473604	4.957915	5.272931
H	22.572682	5.952455	6.254698
H	22.976539	4.252979	5.913328
O	17.892819	0.414411	7.675903
C	17.916316	-0.512657	8.554492
O	17.000951	-0.788434	9.341562
C	19.198404	-1.347424	8.563570
C	20.477790	-0.572104	8.239328
H	19.058419	-2.136833	7.802996
H	19.262998	-1.871831	9.528082
C	20.741347	0.714093	9.029692
H	20.453018	-0.301102	7.170177
H	21.337894	-1.255121	8.359434
C	21.001869	0.598945	10.535099
H	19.912233	1.424255	8.861447
H	21.631068	1.189635	8.577726
C	21.691230	1.887852	11.034809
C	21.543164	2.117696	12.548993
H	21.256087	2.747494	10.492087
H	22.758470	1.856178	10.754079
C	19.754287	0.354732	11.391993
H	21.692955	-0.251991	10.695497
C	20.122393	0.061975	12.857229
H	19.127498	1.261885	11.336206
H	19.129430	-0.456691	10.995536
C	21.404133	0.791752	13.292434
H	19.281831	0.361908	13.506899
H	20.249417	-1.024316	13.002669
H	22.398548	2.696487	12.933146
H	20.644530	2.728379	12.748711
H	22.287333	0.167167	13.070955
H	21.405531	0.949871	14.383086
C	13.791039	2.006472	5.905124
C	14.457452	3.287303	5.388604
H	13.710666	4.026960	5.059676
H	15.106388	3.067464	4.522709
C	16.508636	5.363539	5.964866
C	15.589500	6.584234	6.084130
C	14.990127	6.520911	7.484920
H	14.783847	6.543086	5.332078
H	16.150865	7.517121	5.916584
C	14.379974	5.119476	7.676593
H	14.225325	7.295094	7.652780
H	15.795053	6.690567	8.217534
C	15.478113	-0.115698	4.830752
C	15.382946	-1.593727	5.253523
C	14.196546	-1.713572	6.204585
H	16.311914	-1.894925	5.768618
H	15.276743	-2.234208	4.364116
C	14.391934	-0.642385	7.289809
H	14.129268	-2.712710	6.662955
H	13.257604	-1.539637	5.652119
C	13.213679	-0.356129	8.188693
H	15.230323	-0.955628	7.934231
C	13.386407	-0.391215	9.578683
C	12.319574	-0.134031	10.439854
C	11.058141	0.159040	9.921642
C	10.872017	0.190421	8.538485
C	11.940317	-0.067053	7.679652
H	11.776493	-0.043316	6.597591

H	14.377104	-0.635012	9.977175
H	12.474865	-0.166335	11.522364
H	10.219163	0.360077	10.594195
H	9.884991	0.413763	8.123222
C	16.709061	0.224110	4.021432
H	14.597893	0.099495	4.202393
C	16.569854	0.580604	2.673898
C	17.689880	0.788054	1.867332
C	18.969730	0.645204	2.400148
C	19.119798	0.311834	3.747217
C	18.000818	0.103341	4.552577
H	15.567028	0.681425	2.245433
H	17.557798	1.059607	0.815748
H	19.849697	0.805724	1.770392
H	20.120737	0.212555	4.179086
H	18.128449	-0.136657	5.612747
C	17.110876	5.048894	4.614851
C	18.261321	4.245727	4.554010
C	18.863568	3.960189	3.331490
C	18.319938	4.457027	2.144778
C	17.169260	5.240434	2.194042
C	16.569547	5.536992	3.420960
H	16.733878	5.634729	1.271081
H	15.673262	6.163076	3.436595
H	19.763240	3.338987	3.304027
H	18.792248	4.230660	1.184322
H	18.672742	3.851207	5.490249
C	14.033897	4.731726	9.100159
H	13.444218	5.079101	7.094770
C	12.949586	3.874980	9.338462
C	12.564626	3.540676	10.636270
C	13.256418	4.066037	11.727197
C	14.341775	4.911866	11.504565
C	14.729578	5.237735	10.205491
H	12.379015	3.478264	8.490551
H	11.711630	2.873970	10.792010
H	12.953079	3.815005	12.747684
H	15.587634	5.899763	10.062391
H	14.898162	5.324069	12.351411
H	15.332063	1.289972	10.436576
H	18.883994	4.487010	11.547523
H	13.131764	1.558616	5.145457
H	13.171237	2.221241	6.791085
H	17.338791	5.487918	6.681657



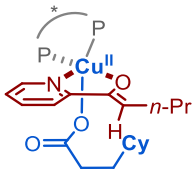
Cu(II) **H**-enolate

E = –4624.320071296098 a.u.

Cu	17.281262	1.638797	6.994884
P	15.734597	3.498728	6.921931
P	15.352632	0.374920	6.079202
O	18.763373	3.099825	6.842626
N	17.938090	1.908548	9.118799
C	19.191021	3.615569	7.963051

C	18.943046	2.787895	9.203054
C	17.654609	1.119836	10.155459
C	18.374532	1.148213	11.342652
C	19.435169	2.047913	11.442104
C	19.722808	2.876718	10.364548
H	18.109523	0.478098	12.163570
H	20.040959	2.095796	12.351616
C	19.808227	4.825765	8.079128
C	20.127487	5.700152	6.895166
H	20.119766	5.164652	9.070956
C	21.209725	5.139997	5.965272
H	19.220381	5.869592	6.284594
H	20.442560	6.699369	7.243441
C	21.457297	6.016963	4.743399
H	20.905644	4.127168	5.647476
H	22.147576	5.014171	6.535361
H	22.273282	5.623883	4.116580
H	20.553327	6.080235	4.113296
H	21.727957	7.045077	5.037271
O	18.410815	0.095667	6.978620
C	18.614792	-0.628145	5.819637
C	19.123052	0.183828	4.630033
C	20.512120	0.795232	4.773282
H	18.390502	0.988969	4.431255
H	19.103631	-0.459340	3.731447
C	22.269914	2.254307	3.525849
C	22.400987	3.236991	2.355186
C	23.796345	3.850246	2.248698
H	21.638225	4.029741	2.452867
H	22.170304	2.696287	1.417130
C	23.368233	1.187352	3.441848
C	24.766358	1.798753	3.342103
H	23.178611	0.561726	2.548061
H	23.316199	0.512965	4.312531
C	24.873453	2.769430	2.166586
H	25.523791	1.002242	3.252420
H	24.991174	2.340915	4.279298
H	23.986227	4.480657	3.137381
H	23.852544	4.518788	1.373339
H	25.876492	3.226527	2.133878
H	24.751762	2.208818	1.221362
C	13.922533	1.517901	6.336081
C	14.297103	2.940302	5.909296
H	13.444079	3.627206	6.022267
H	14.596077	2.970450	4.848242
C	16.333636	5.080991	6.156840
C	15.401199	6.158160	6.721871
C	15.279877	5.859292	8.210894
H	14.407261	6.110364	6.246364
H	15.807469	7.165234	6.535180
C	14.897918	4.375746	8.371272
H	14.537853	6.499503	8.713161
H	16.254715	6.053957	8.685051
C	14.992986	-0.366365	4.366961
C	14.719055	-1.855745	4.631561
C	14.033248	-1.984397	5.981495
H	15.669890	-2.411260	4.673734
H	14.125340	-2.288668	3.811338
C	14.907651	-1.207325	6.974424
H	13.931936	-3.035562	6.294395
H	13.019374	-1.552019	5.940007

C	14.353877	-1.100374	8.375167
H	15.879609	-1.725927	7.042084
C	15.163447	-1.431115	9.469426
C	14.661438	-1.408797	10.770875
C	13.331688	-1.058184	11.000109
C	12.512774	-0.726387	9.920057
C	13.018435	-0.749253	8.620736
H	12.353849	-0.503787	7.787257
H	16.202898	-1.726165	9.290894
H	15.312729	-1.675819	11.608455
H	12.931707	-1.046958	12.018154
H	11.466698	-0.454446	10.088625
C	15.945233	-0.082670	3.218266
H	14.033062	0.105849	4.097688
C	16.126251	1.228324	2.753425
C	16.929452	1.497931	1.648149
C	17.578679	0.459681	0.978006
C	17.407059	-0.847262	1.425064
C	16.596663	-1.113957	2.530424
H	15.624710	2.060681	3.259480
H	17.042414	2.529285	1.306339
H	18.206836	0.671689	0.108103
H	17.902527	-1.675375	0.909757
H	16.475069	-2.151853	2.846324
C	16.553182	5.062384	4.661564
C	17.777653	4.601235	4.150696
C	18.043901	4.658198	2.784289
C	17.082890	5.150705	1.898519
C	15.849311	5.572285	2.391320
C	15.588213	5.532880	3.763031
H	15.084771	5.949201	1.705681
H	14.622359	5.890697	4.130691
H	19.012233	4.312189	2.407149
H	17.293320	5.199373	0.826021
H	18.516380	4.200129	4.853926
C	15.092729	3.796734	9.757678
H	13.825932	4.279458	8.135578
C	14.193284	2.832626	10.232426
C	14.298780	2.322397	11.526127
C	15.309450	2.770593	12.375129
C	16.218435	3.721350	11.911764
C	16.113105	4.225919	10.616329
H	13.379546	2.488450	9.583401
H	13.577810	1.576934	11.872386
H	15.389284	2.376624	13.392544
H	16.844940	4.963871	10.276786
H	17.023127	4.074079	12.563769
H	16.812844	0.432213	10.028166
H	20.564130	3.570633	10.406846
H	13.028983	1.156165	5.803517
H	13.685532	1.502198	7.413035
H	17.318835	5.203688	6.635540
H	19.345071	-1.446143	6.017785
H	17.685060	-1.150248	5.479381
C	20.863397	1.655528	3.561366
H	21.254313	-0.013305	4.903435
H	20.549535	1.415634	5.685289
H	20.129080	2.481849	3.501216
H	20.714737	1.062202	2.637413
H	22.425812	2.825882	4.462934



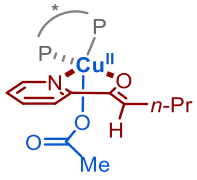
Cu(II) **I**-enolate

E = –4585.04453758105 a.u.

Cu	17.365882	1.695581	7.017647
P	15.807084	3.554740	6.833847
P	15.544445	0.427218	5.989991
O	18.829604	3.159277	6.983869
N	17.838214	1.986005	9.205645
C	19.173092	3.684089	8.130007
C	18.834099	2.866913	9.354502
C	17.483490	1.205858	10.226294
C	18.120030	1.241964	11.460245
C	19.170636	2.143087	11.627300
C	19.530657	2.965805	10.566911
H	17.799872	0.576399	12.265110
H	19.712444	2.197683	12.575957
C	19.785987	4.892733	8.277826
C	20.219161	5.725147	7.102128
H	20.028491	5.244627	9.284363
C	21.517391	5.241728	6.441855
H	19.429601	5.722996	6.329731
H	20.345046	6.779728	7.405029
C	21.842232	5.980592	5.148847
H	21.422719	4.160462	6.238958
H	22.351470	5.345162	7.158177
H	22.783299	5.624793	4.699488
H	21.041566	5.835397	4.402373
H	21.941319	7.065457	5.320663
O	18.495636	0.149467	7.118328
C	18.816309	-0.643359	6.035168
C	19.608915	0.058284	4.931710
C	20.938730	0.640804	5.401457
H	18.973346	0.856850	4.508363
H	19.771298	-0.665084	4.112428
C	21.802109	1.292206	4.312757
C	21.100572	2.461094	3.610231
C	22.008109	3.137073	2.582485
H	20.754338	3.194553	4.359886
H	20.195168	2.087631	3.097871
C	22.321858	0.290238	3.274154
C	23.230353	0.957070	2.240693
H	21.463262	-0.171992	2.751932
H	22.856924	-0.531022	3.782613
C	22.529249	2.130812	1.556357
H	23.564266	0.219293	1.491969
H	24.142531	1.327030	2.744174
H	22.864686	3.604407	3.103359
H	21.471584	3.957644	2.075094
H	23.211358	2.623649	0.843616
H	21.676565	1.748735	0.963982
C	14.077715	1.545460	6.113484
C	14.460691	2.972841	5.714764
H	13.589188	3.644561	5.758019
H	14.841537	3.005580	4.680067
C	16.423426	5.150285	6.107740

C	15.437040	6.209355	6.611181
C	15.215880	5.906233	8.086515
H	14.478789	6.144080	6.069546
H	15.837509	7.223599	6.452556
C	14.852375	4.415341	8.219649
H	14.427493	6.531421	8.534152
H	16.149613	6.119137	8.630182
C	15.366526	-0.308100	4.249366
C	15.008637	-1.787157	4.480119
C	14.209145	-1.902541	5.767983
H	15.930352	-2.378233	4.601042
H	14.472391	-2.194541	3.608941
C	15.024782	-1.157855	6.832775
H	14.054342	-2.952898	6.061298
H	13.212927	-1.443978	5.650033
C	14.384838	-1.056533	8.196753
H	15.982465	-1.692687	6.956199
C	15.132056	-1.376653	9.337504
C	14.555572	-1.353183	10.607621
C	13.212310	-1.011303	10.758192
C	12.454391	-0.691827	9.631004
C	13.034254	-0.716788	8.362788
H	12.416983	-0.480567	7.491167
H	16.183085	-1.661682	9.221097
H	15.159572	-1.611134	11.482706
H	12.754524	-0.997412	11.751553
H	11.398444	-0.426650	9.737467
C	16.466869	-0.066522	3.228369
H	14.467311	0.200130	3.861800
C	16.775014	1.236241	2.807793
C	17.712128	1.466736	1.803272
C	18.375207	0.399735	1.195637
C	18.085438	-0.898114	1.605813
C	17.138948	-1.126614	2.606774
H	16.269732	2.093406	3.266875
H	17.922731	2.491785	1.491044
H	19.109340	0.583249	0.405358
H	18.590549	-1.749301	1.139854
H	16.926666	-2.159186	2.890069
C	16.722433	5.134911	4.626704
C	17.965319	4.659686	4.180230
C	18.306997	4.722878	2.831228
C	17.399951	5.226706	1.896639
C	16.146898	5.661109	2.324418
C	15.813117	5.621861	3.679867
H	15.423718	6.048215	1.600676
H	14.833548	5.990391	3.996346
H	19.290860	4.371296	2.505732
H	17.669143	5.275892	0.837455
H	18.659993	4.244076	4.918878
C	14.962638	3.848524	9.620140
H	13.801677	4.296791	7.909545
C	14.043201	2.882201	10.049183
C	14.068223	2.392830	11.355232
C	15.017292	2.863554	12.261285
C	15.947996	3.814271	11.842931
C	15.922859	4.297859	10.536110
H	13.277778	2.520277	9.352653
H	13.332470	1.645961	11.665791
H	15.033367	2.487122	13.288312
H	16.669092	5.036767	10.232266

H	16.706155	4.183619	12.540019
H	16.652233	0.517712	10.046170
H	20.366061	3.661381	10.663368
H	13.241475	1.165233	5.505919
H	13.748181	1.528452	7.165918
H	17.378240	5.293921	6.640764
H	19.419363	-1.513399	6.385162
H	17.913116	-1.096652	5.554944
H	21.529290	-0.159698	5.886748
H	20.727960	1.390401	6.182554
H	22.692031	1.714278	4.821020



Cu(II) acetate-enolate

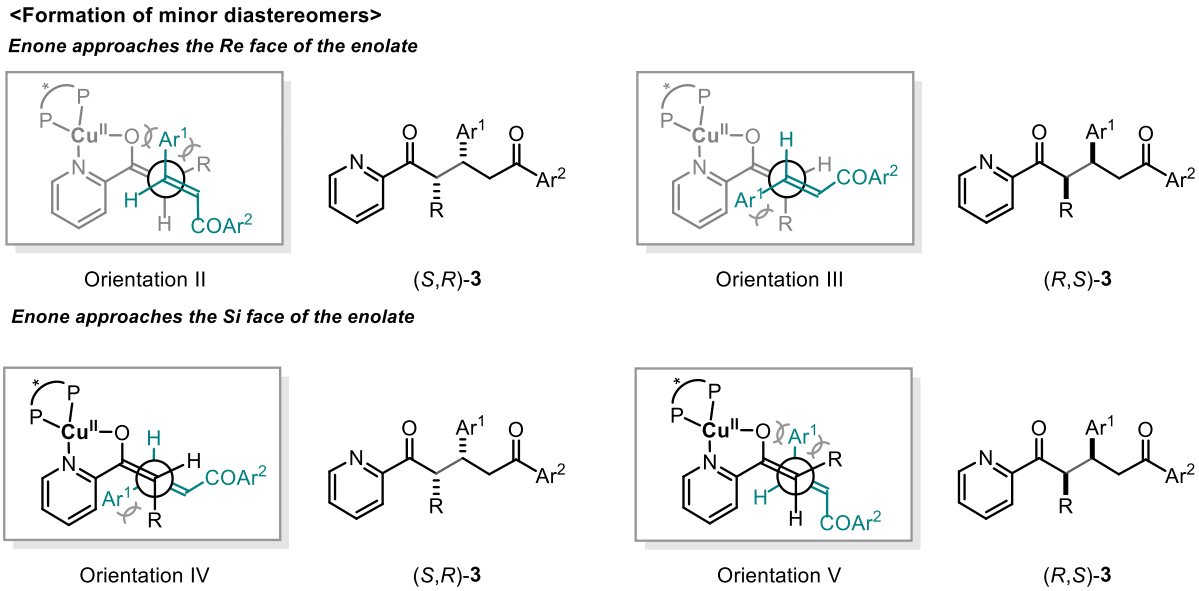
E = –4385.30191399977 a.u.

Cu	17.461961	1.810394	6.779055
P	15.940859	3.622731	6.609212
P	15.514456	0.454475	6.255948
O	18.874321	3.227387	6.914887
N	18.109022	1.600791	8.884960
C	19.397028	3.471313	8.092471
C	19.098225	2.459069	9.168065
C	17.748986	0.678744	9.779499
C	18.366204	0.546705	11.015330
C	19.413323	1.418102	11.316968
C	19.784759	2.380628	10.387585
H	18.038711	-0.223463	11.717199
H	19.940873	1.345036	12.272214
C	20.147810	4.573273	8.359019
C	20.457312	5.590798	7.294911
H	20.559496	4.717158	9.360939
C	21.463812	5.110968	6.241800
H	20.835626	6.519777	7.755656
H	19.526089	5.869683	6.765313
C	21.660534	6.113260	5.110732
H	21.105280	4.150232	5.834175
H	22.429686	4.898773	6.733355
H	22.402959	5.762740	4.376561
H	20.713232	6.285163	4.571325
H	22.004103	7.088199	5.495230
O	18.838514	0.575055	6.011782
C	18.866559	-0.695996	6.130804
O	17.969734	-1.391123	6.626229
C	20.134711	-1.350684	5.605292
H	20.998376	-0.995039	6.187651
C	14.106531	1.656436	6.207472
C	14.555266	2.984047	5.587749
H	13.723786	3.704615	5.538803
H	14.933562	2.842450	4.562002
C	16.564007	5.184727	5.840060
C	15.603823	6.266286	6.346355
C	15.413430	5.991530	7.836682
H	14.633060	6.206162	5.826013
H	16.014468	7.272247	6.164419
C	15.053072	4.501704	8.013068

H	14.631300	6.624975	8.282902
H	16.354911	6.217426	8.362732
C	15.343127	-0.426446	4.598576
C	15.232409	-1.914504	4.960246
C	14.358321	-2.001265	6.205313
H	16.227234	-2.321927	5.191987
H	14.811797	-2.481784	4.114684
C	14.945991	-1.031562	7.247942
H	14.324692	-3.021670	6.618847
H	13.321191	-1.712767	5.961241
C	14.068364	-0.811285	8.458375
H	15.906565	-1.449163	7.583090
C	14.545594	-1.152755	9.731277
C	13.746309	-1.013818	10.865723
C	12.443006	-0.533486	10.746499
C	11.945329	-0.207612	9.484046
C	12.746900	-0.352687	8.352324
H	12.326671	-0.116387	7.370636
H	15.557018	-1.559294	9.832169
H	14.144365	-1.289588	11.846619
H	11.812229	-0.422270	11.633185
H	10.918657	0.154324	9.376416
C	16.322851	-0.064308	3.503726
H	14.347403	-0.100571	4.254960
C	16.030757	1.003195	2.642529
C	16.894009	1.352753	1.605683
C	18.071308	0.632599	1.403598
C	18.367096	-0.441265	2.242491
C	17.501017	-0.786455	3.280441
H	15.095036	1.558209	2.771250
H	16.640198	2.189140	0.948418
H	18.749812	0.899644	0.588297
H	19.280673	-1.023516	2.086876
H	17.747873	-1.634182	3.923430
C	16.844424	5.091221	4.359899
C	18.091856	4.608560	3.933321
C	18.396140	4.524592	2.576018
C	17.455810	4.916283	1.620866
C	16.208467	5.381571	2.034274
C	15.903853	5.467964	3.394641
H	15.464025	5.687312	1.293249
H	14.922908	5.842984	3.700972
H	19.375979	4.153440	2.260506
H	17.694498	4.855264	0.555001
H	18.820715	4.300350	4.691621
C	15.259605	3.927983	9.398141
H	13.987050	4.379993	7.761183
C	14.280878	3.095402	9.956455
C	14.434305	2.561753	11.236231
C	15.573172	2.857059	11.984112
C	16.555815	3.683535	11.438605
C	16.402992	4.209274	10.156629
H	13.374816	2.868260	9.383049
H	13.655491	1.913411	11.647313
H	15.695777	2.441372	12.988580
H	17.197816	4.837384	9.742226
H	17.457299	3.915850	12.013247
H	16.929699	0.016222	9.486940
H	20.609431	3.062724	10.599902
H	13.249919	1.227826	5.664145
H	13.778562	1.822807	7.247177

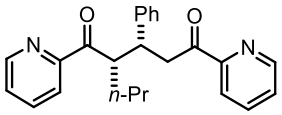
H	17.530490	5.315702	6.354261
H	20.072036	-2.444362	5.676219
H	20.301182	-1.051827	4.559286

***Scheme S9*. Plausible approaches for the formation of minor diastereomers (*S*,*R*)-3 and (*R*,*S*)-3**

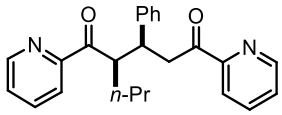


*Note: *The minor diastereomer was obtained as racemates rather than in enantiomerically pure forms, as determined by chiral HPLC analysis.*

<HPLC traces of the minor diastereomer of **3aa**, **3ba**, and **3ea**>

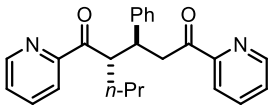


(*S*,*R*)-**3aa**



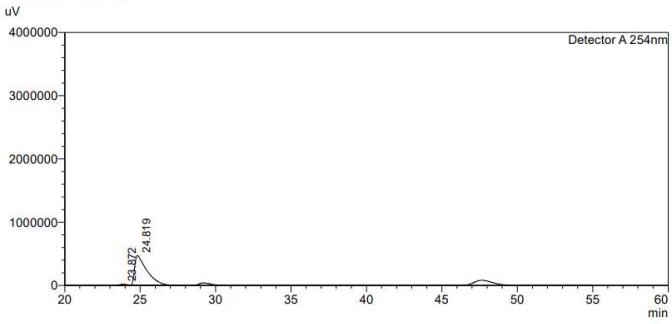
(*R*,*S*)-**3aa**

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be <5% [OD-H, 5% i-PrOH in hexanes, 0.3 mL/min], t_R = 23.87 min (*anti* minor), t_R = 24.82 min (*anti* major), t_R = 29.22 (*syn* major), and t_R = 47.65 (*syn* minor).



(*S*,*S*)-**3aa**
>20:1 dr, 97% ee

<Chromatogram>

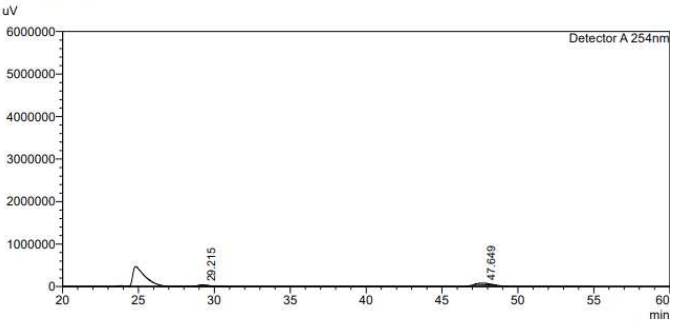


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.872	463804	15949	1.730		M	
2	24.819	26344882	466394	98.270		M	
Total		26808686	482342				

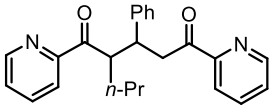
minor diastereomers
(*S*,*R*)- and (*R*,*S*)-**3aa**
racemic

<Chromatogram>



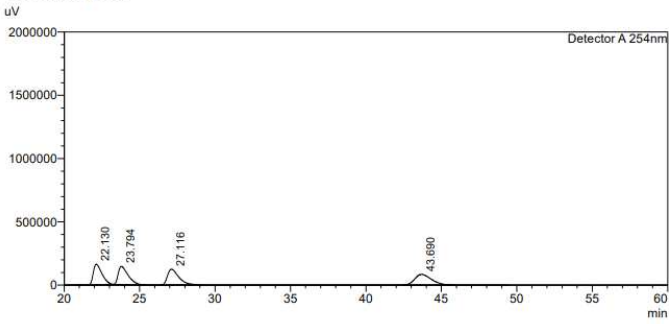
<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	29.215	1939974	38654	51.342		M	
2	47.649	1838572	36563	48.658		M	
Total		3778547	75217				



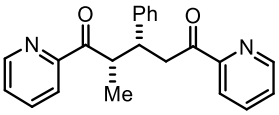
(*rac*)-**3aa**
4:1 dr

<Chromatogram>

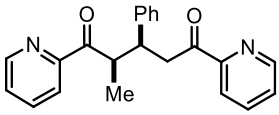


<Peak Table>
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.130	6489099	162506	25.079		M	
2	23.794	6492675	143280	25.092		M	
3	27.116	6430808	124598	24.853		M	
4	43.690	6462391	84229	24.975		M	
Total		25874973	514614				

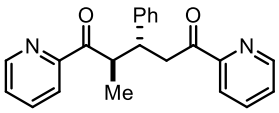


(*S*,*R*)-**3ba**



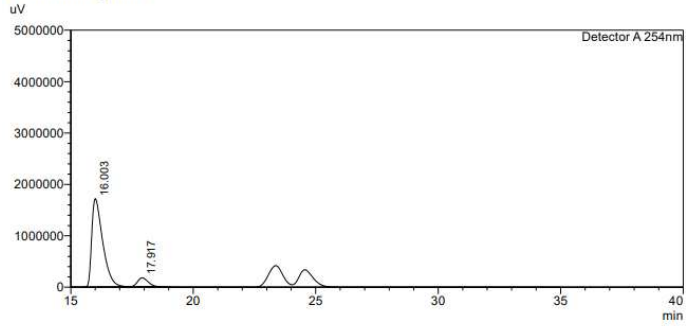
(*R*,*S*)-**3ba**

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be 5% [OD-H, 20% i-PrOH in hexanes, 0.3 mL/min], t_R = 16.00 min (*anti* major), t_R = 17.92 min (*anti* minor), t_R = 23.37 (*syn* major), and t_R = 24.56 (*syn* minor).



(*R*,*R*)-**3ba**
3.3:1 dr, 83% ee

<Chromatogram>



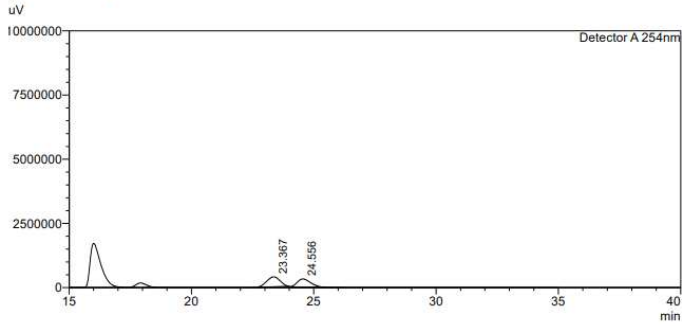
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.003	53336595	1719487	91.464		M	
2	17.917	4977458	170049	8.536		M	
Total		58314053	1889536				

minor diastereomers
(*R*,*S*)- and (*S*,*R*)-**3ba**
racemic

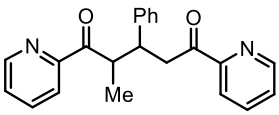
<Chromatogram>



<Peak Table>

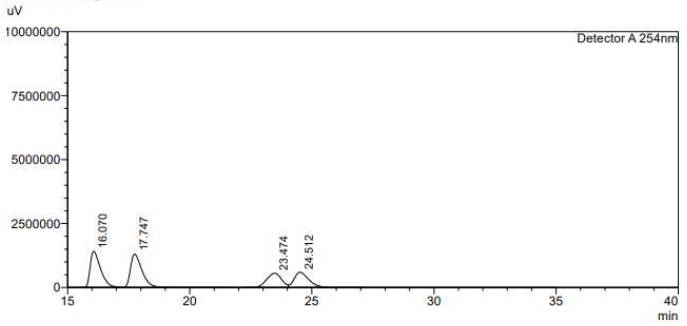
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.367	14584945	385144	52.590		M	
2	24.556	13148413	324780	47.410		M	
Total		27733358	709923				



(*rac*)-**3ba**
1.0:1 dr

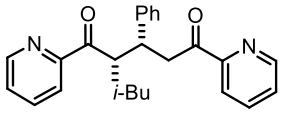
<Chromatogram>



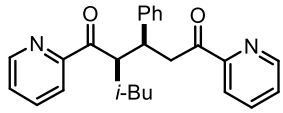
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.070	42289506	1416835	31.538			
2	17.747	43161739	1306267	32.189		V	
3	23.474	23658179	558429	17.644			
4	24.512	24979758	600742	18.629		V	
Total		134089183	3882273				

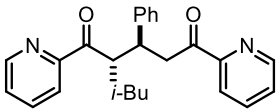


(*S*,*R*)-**3ea**



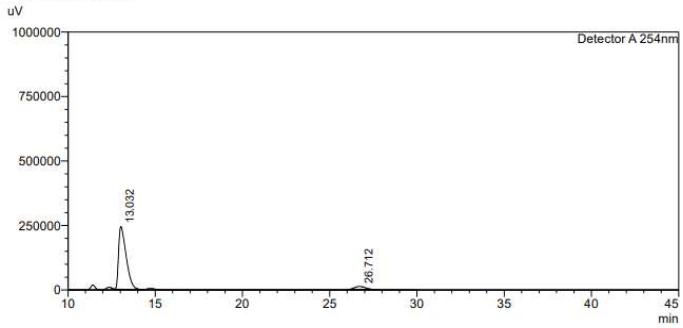
(*R*,*S*)-**3ea**

HPLC analysis: The ee of the product was determined by chiral HPLC analysis to be <5% [OD-H, 5% i-PrOH in hexanes, 0.5 mL/min], t_R = 11.42 min (*syn* isomer A), t_R = 12.36 min (*syn* isomer B), t_R = 13.03 (*anti* major), and t_R = 26.71 (*anti* minor).



(*S*,*S*)-**3ea**
13:1 dr, 88% ee

<Chromatogram>



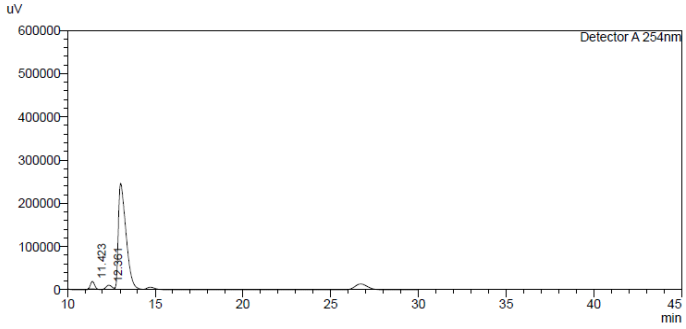
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.032	7318905	243382	93.861		M	
2	26.712	478682	11455	6.139		M	
Total		7797587	254837				

minor diastereomers
(*S*,*R*)- and (*R*,*S*)-**3ea**
racemic

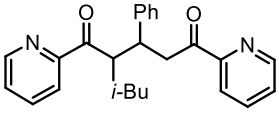
<Chromatogram>



<Peak Table>

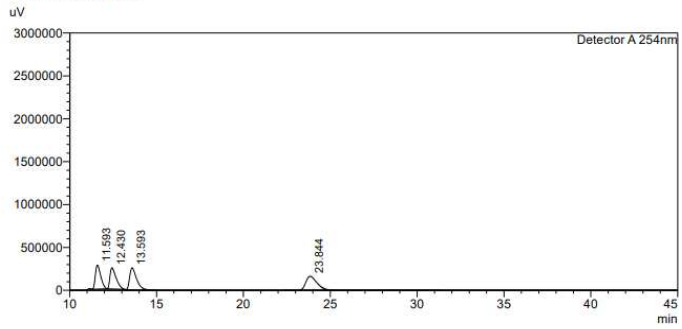
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.423	266828	17201	50.497		M	
2	12.361	261580	10401	49.503		M	
Total		528408	27602				



(*rac*)-**3ea**
3.0:1 dr

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.593	5990875	278791	22.285		M	
2	12.430	6078217	246661	22.610		M	
3	13.593	7328898	257553	27.263		M	
4	23.844	7484420	163664	27.841		M	
Total		26882410	946669				

X. NMR Spectra of Isolated Compounds

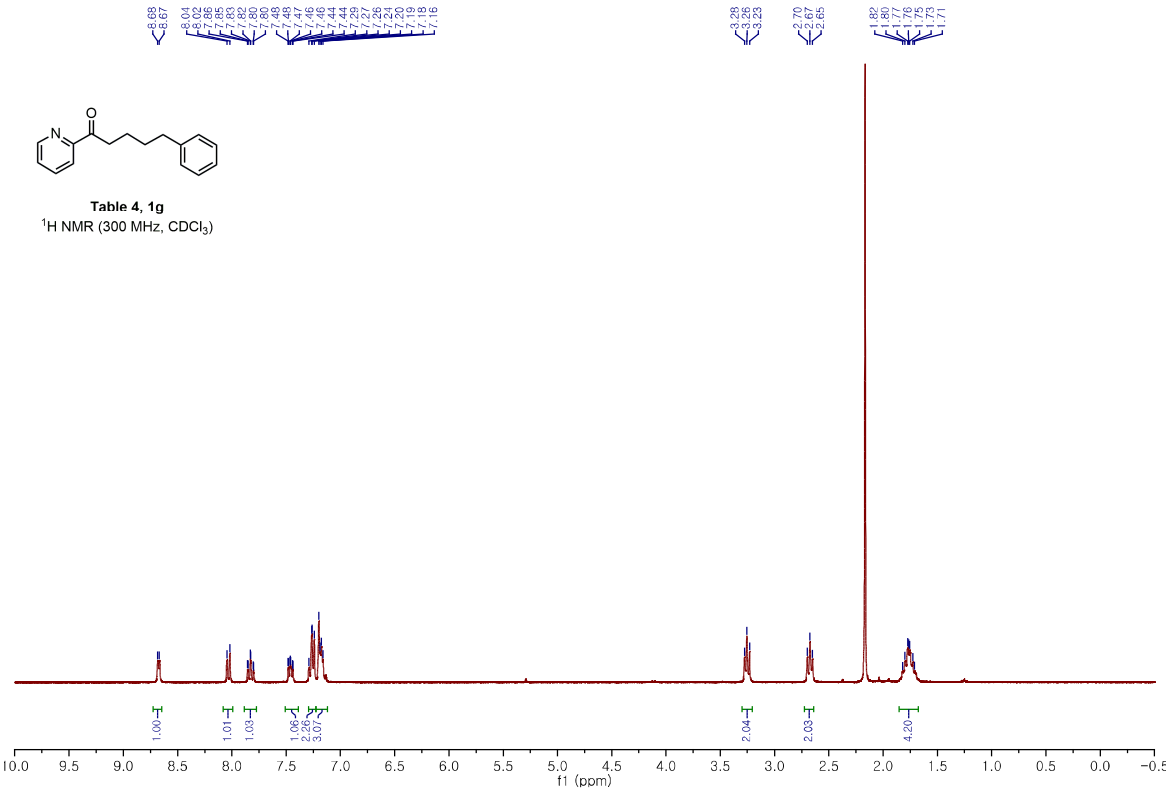


Table 4, 1g
^{1}H NMR (300 MHz, $CDCl_3$)

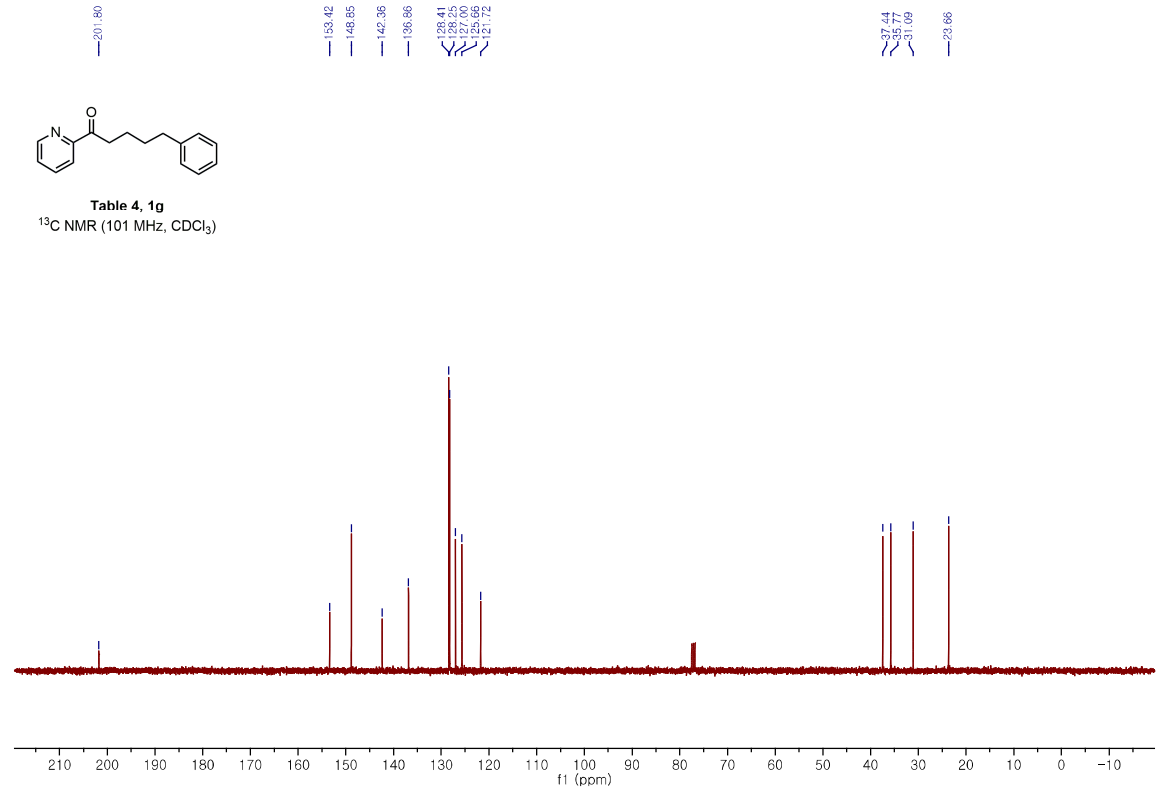


Table 4, 1g
^{13}C NMR (101 MHz, $CDCl_3$)

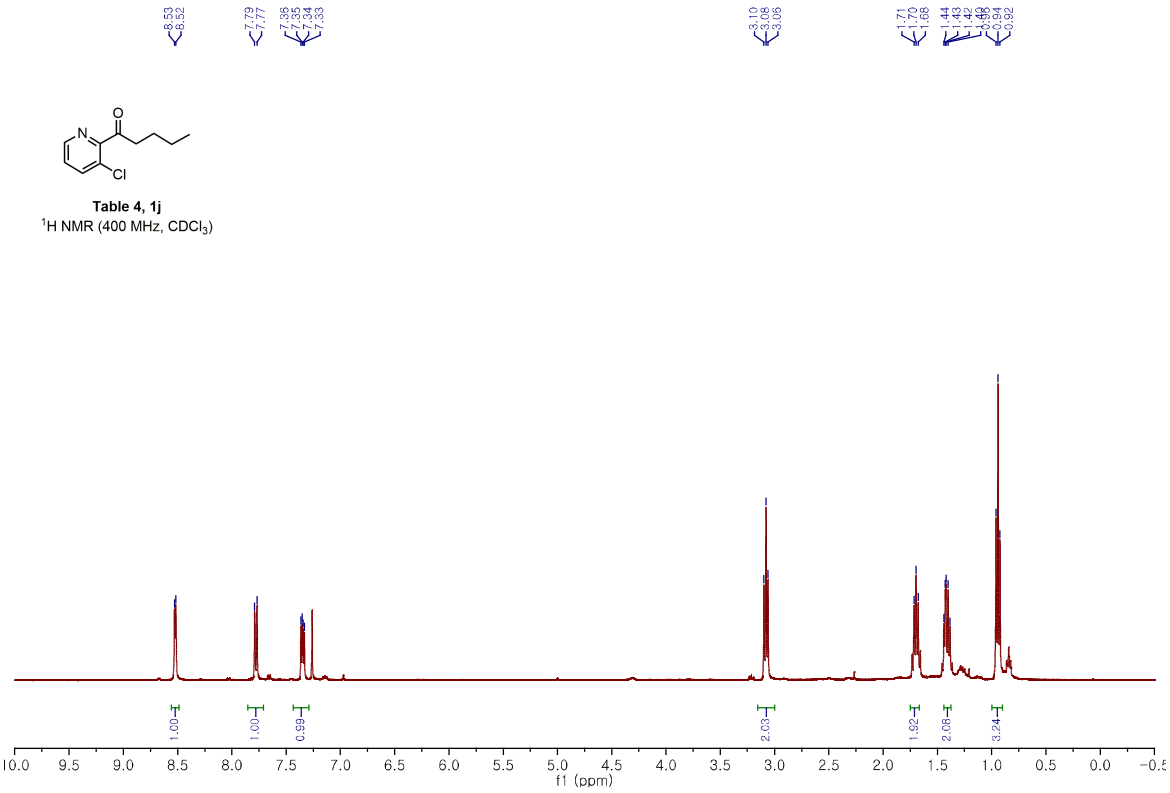


Table 4, 1j
^{1}H NMR (400 MHz, $CDCl_3$)

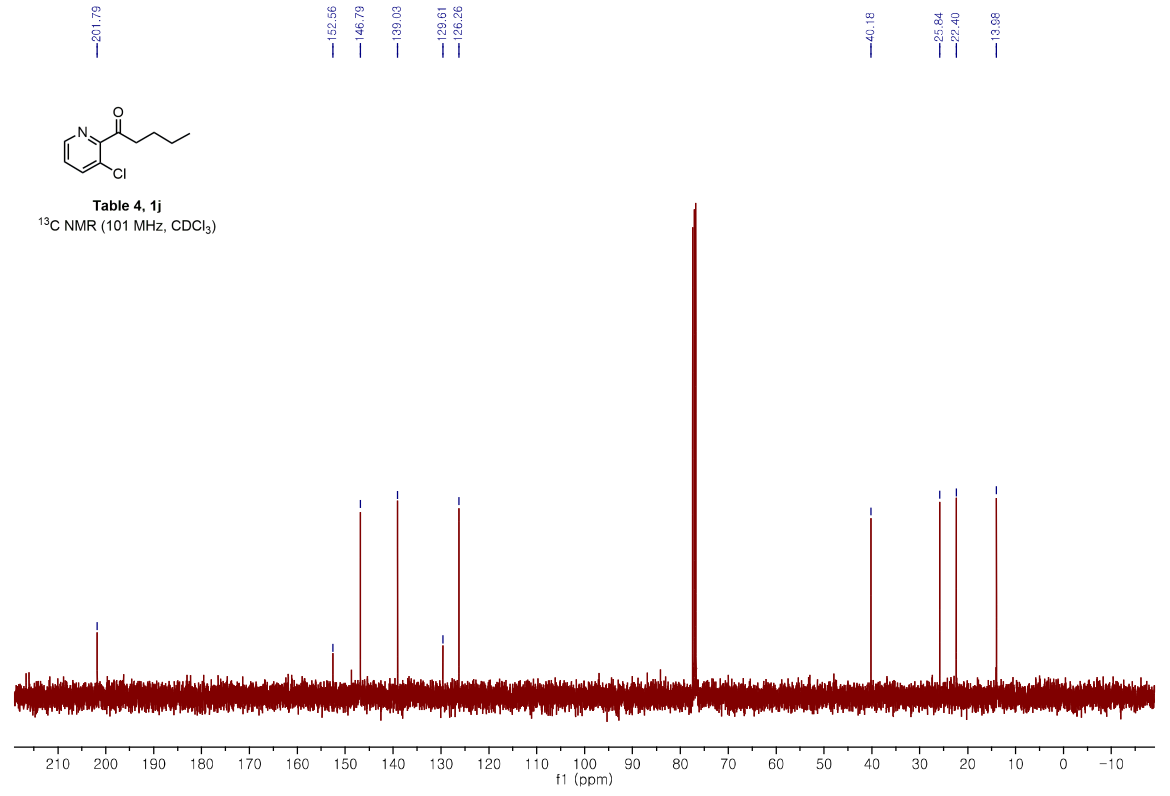


Table 4, 1j
^{13}C NMR (101 MHz, $CDCl_3$)

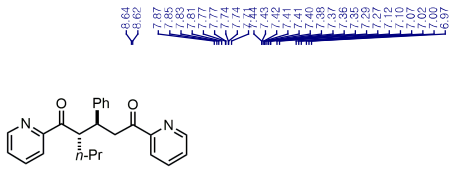


Table 4, (*S*,*S*)-**3aa**
^{1}H NMR (300 MHz, $CDCl_3$)
>20:1 dr

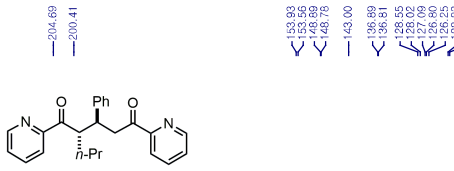
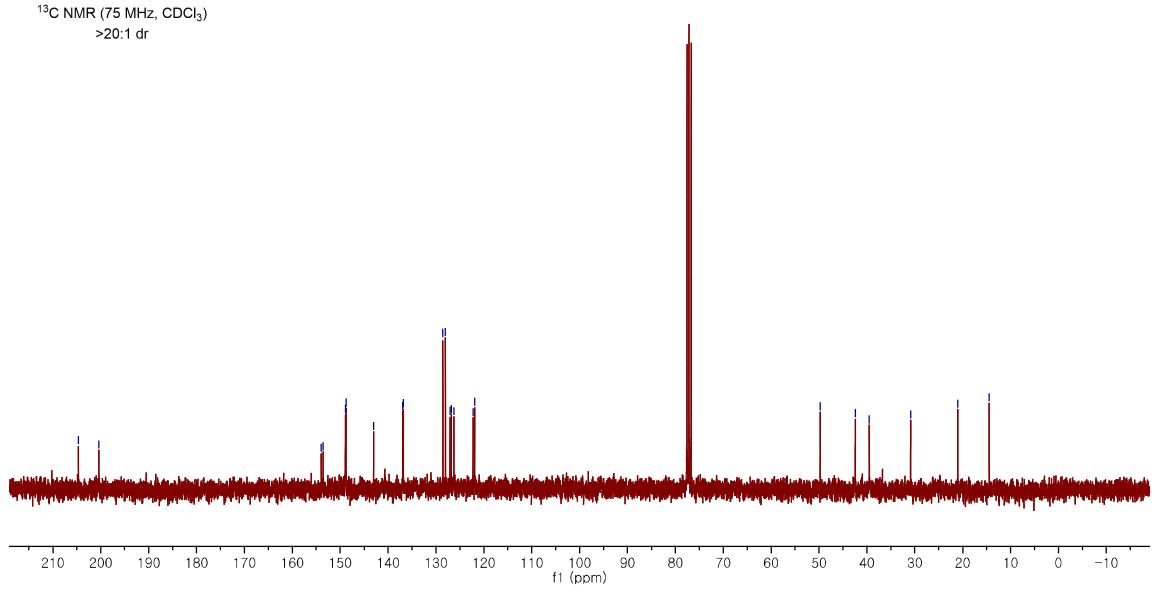


Table 4, (*S*,*S*)-**3aa**
^{13}C NMR (75 MHz, $CDCl_3$)
>20:1 dr



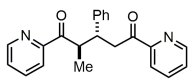
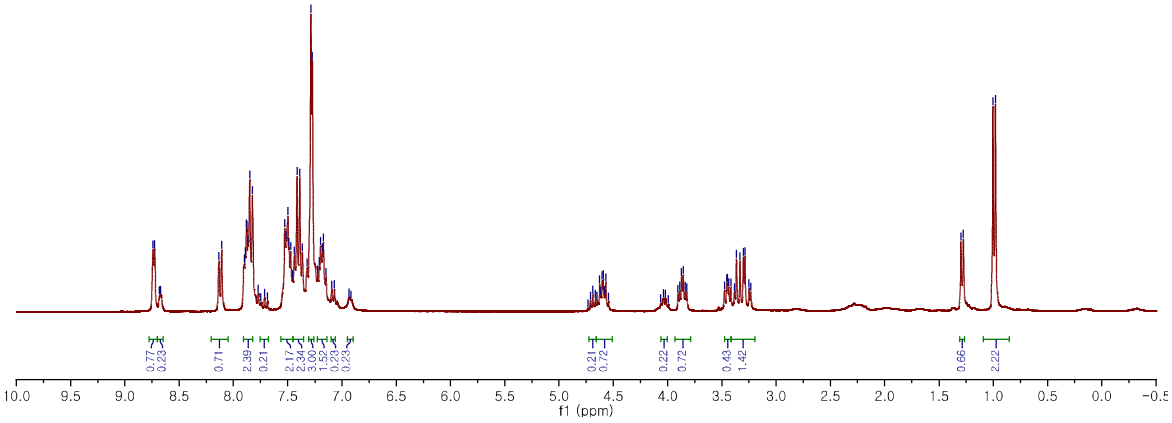


Table 4, (*R*,*R*)-**3ba**
^{1}H NMR (300 MHz, $CDCl_3$)
3.3:1 dr



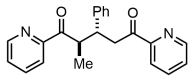
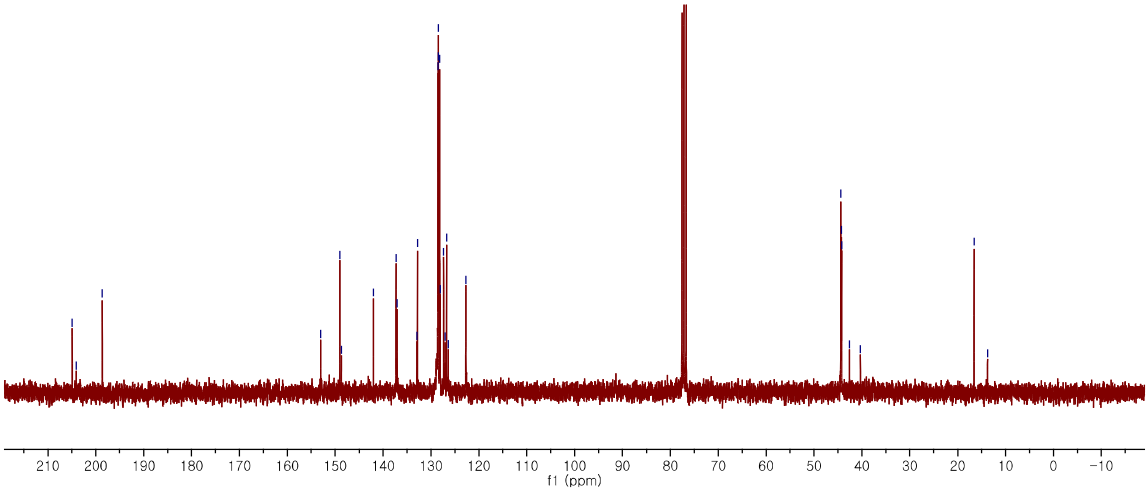


Table 4, (*R*,*R*)-**3ba**
^{13}C NMR (75 MHz, $CDCl_3$)
3.3:1 dr



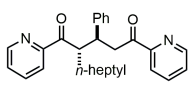
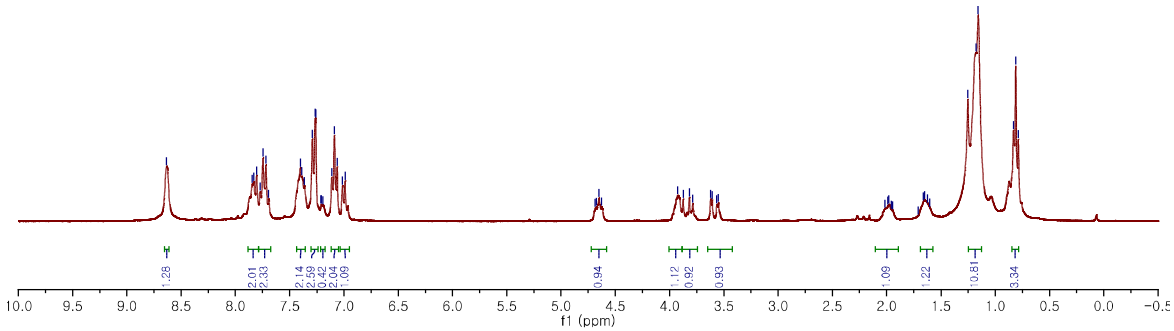


Table 4, (*S*,*S*)-**3ca**
^{1}H NMR (300 MHz, $CDCl_3$)
6.1:1 dr



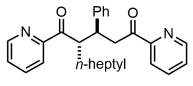


Table 4, (*S*,*S*)-**3ca**
^{13}C NMR (75 MHz, $CDCl_3$)
6.1:1 dr

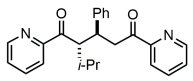
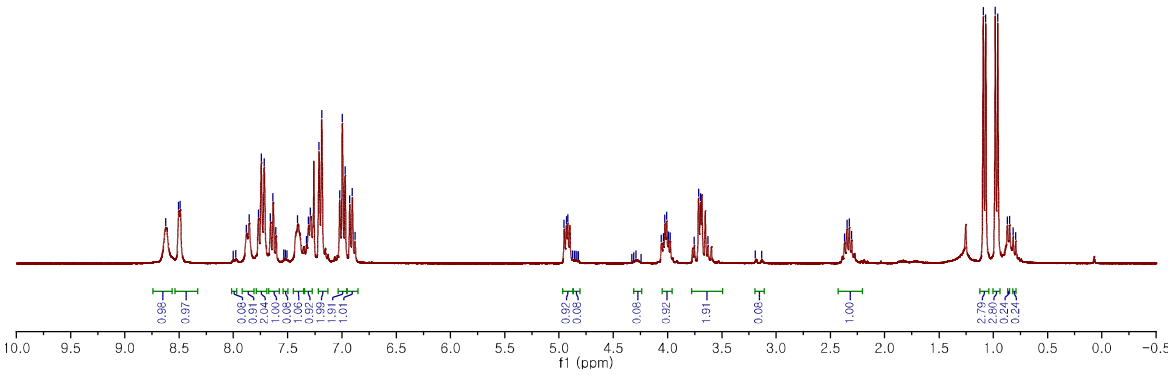


Table 4, (*S*,*S*)-**3da**
^{1}H NMR (300 MHz, $CDCl_3$)
12:1 dr



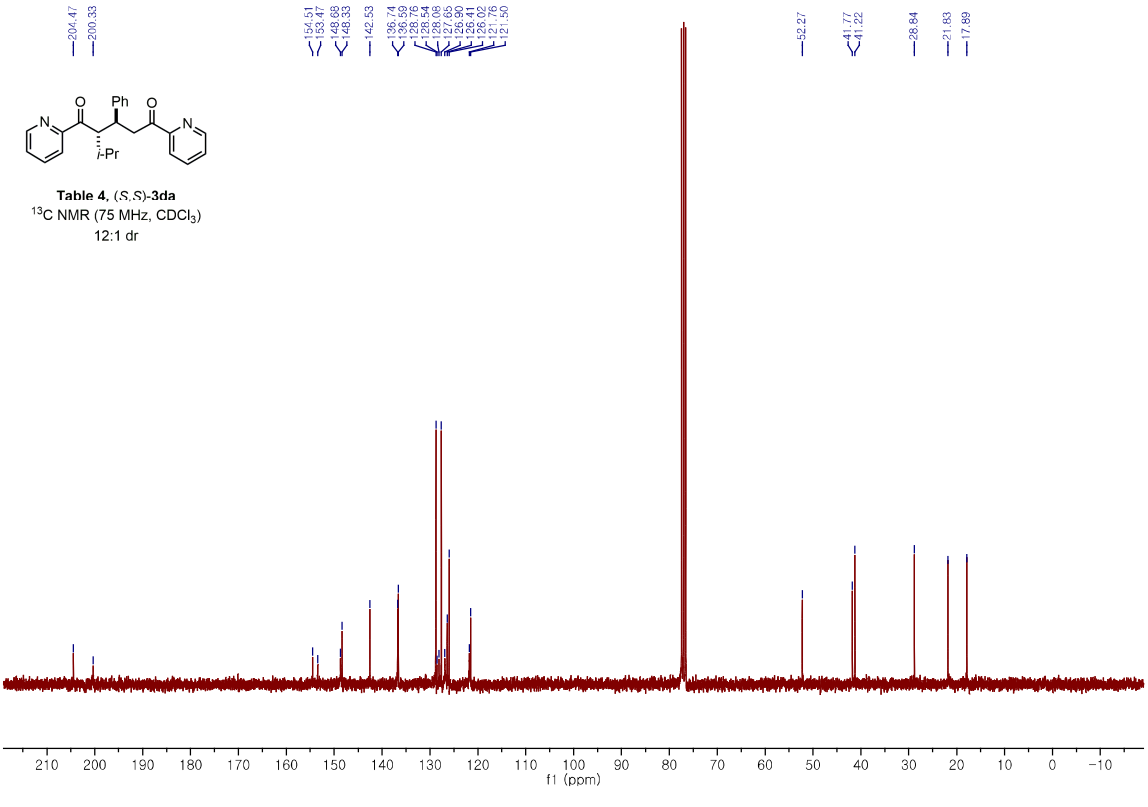


Table 4, (*S*,*S*)-**3da**
^{13}C NMR (75 MHz, $CDCl_3$)
12:1 dr

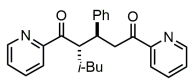
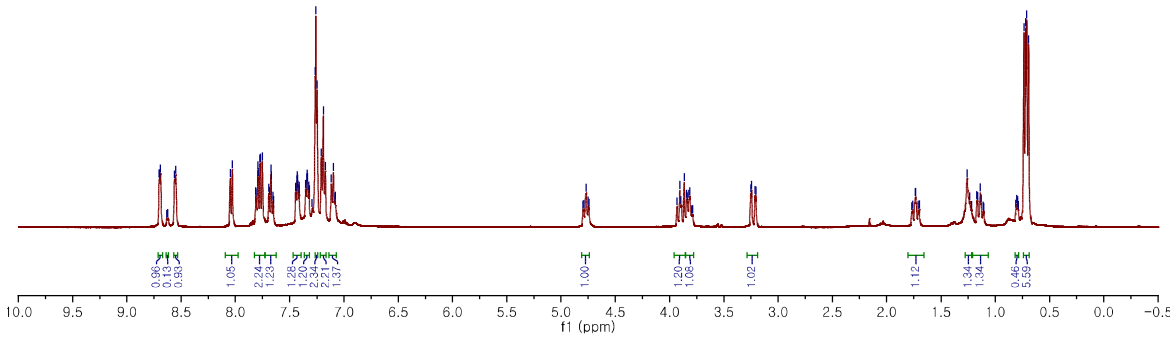


Table 4, (*S*,*S*)-**3ea**
^{1}H NMR (400 MHz, $CDCl_3$)
13:1 dr



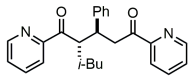
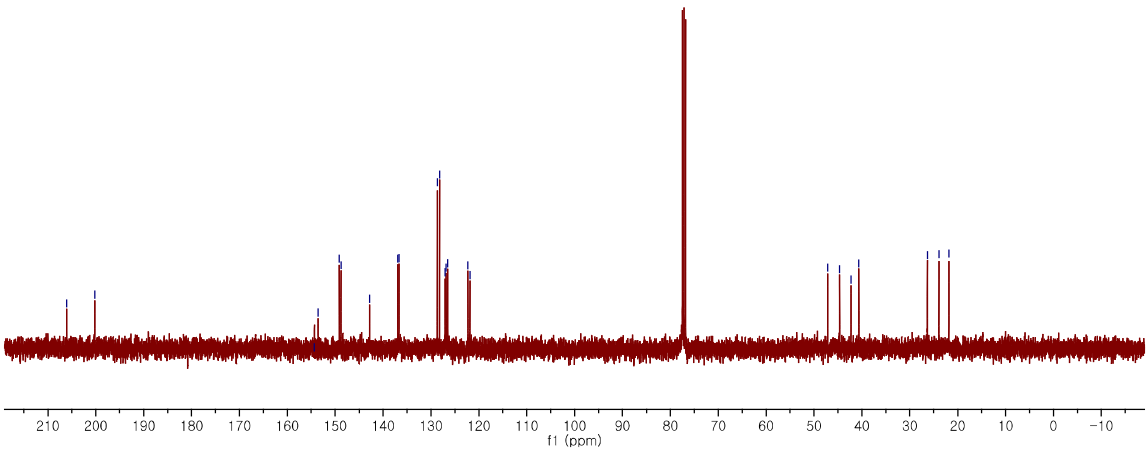


Table 4, (*S*,*S*)-**3ea**
^{13}C NMR (101 MHz, $CDCl_3$)
13:1 dr



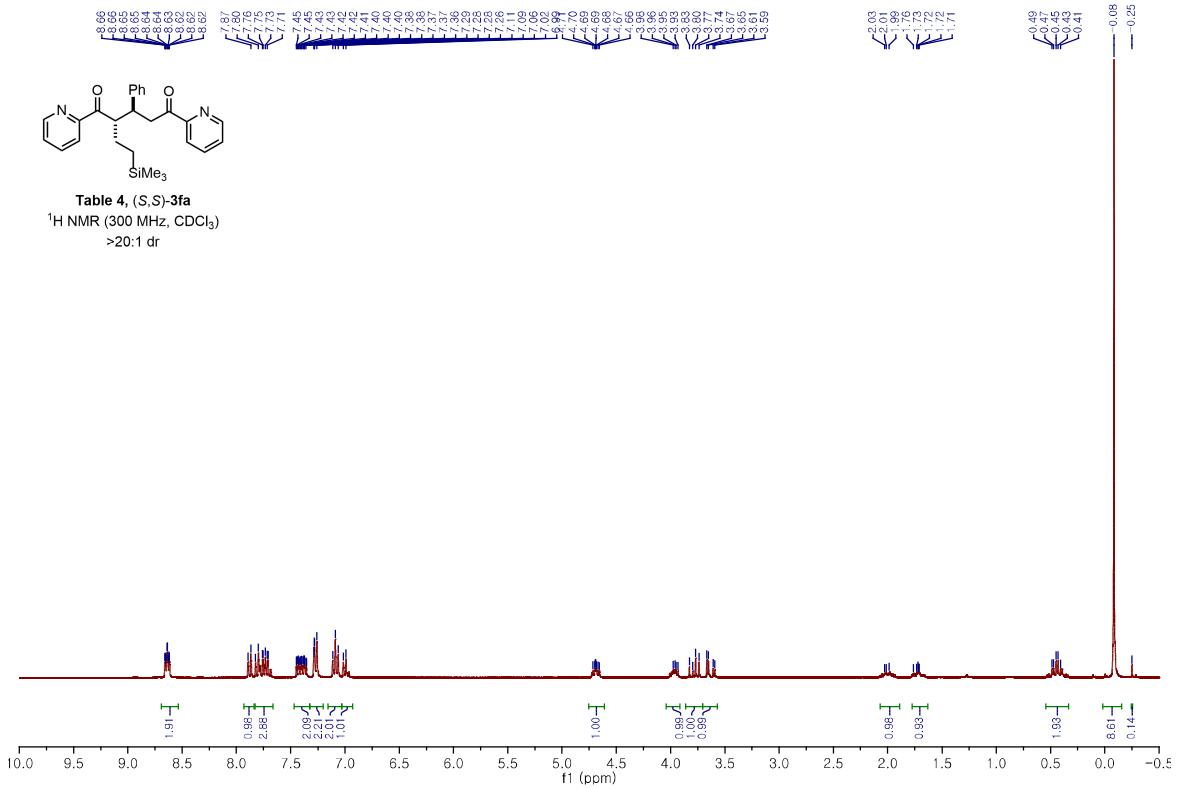


Table 4, (*S*,*S*)-**3fa**
^{1}H NMR (300 MHz, $CDCl_3$)
>20:1 dr

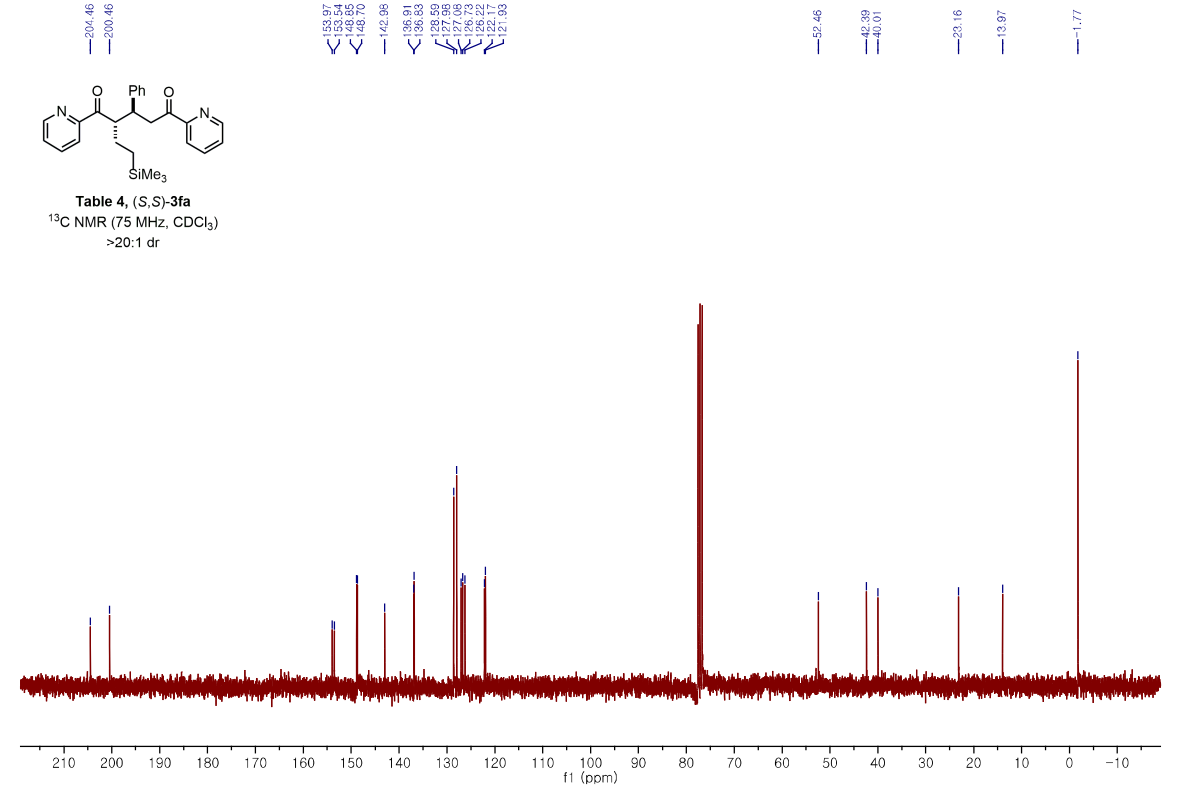


Table 4, (*S*,*S*)-**3fa**
^{13}C NMR (75 MHz, $CDCl_3$)
>20:1 dr

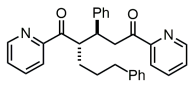
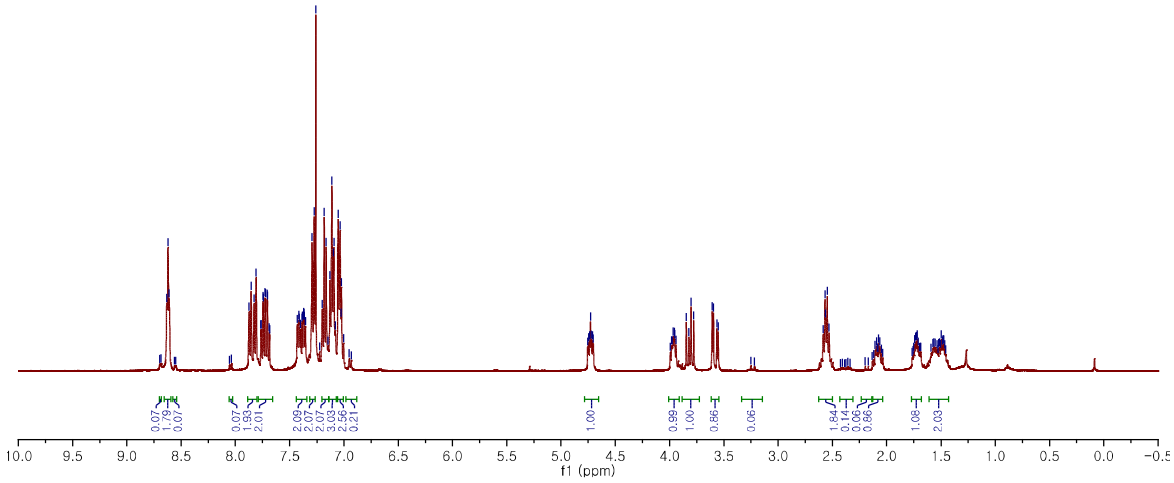


Table 4, (*S*,*S*)-**3ga**
^{1}H NMR (400 MHz, $CDCl_3$)
13:1 dr



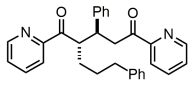
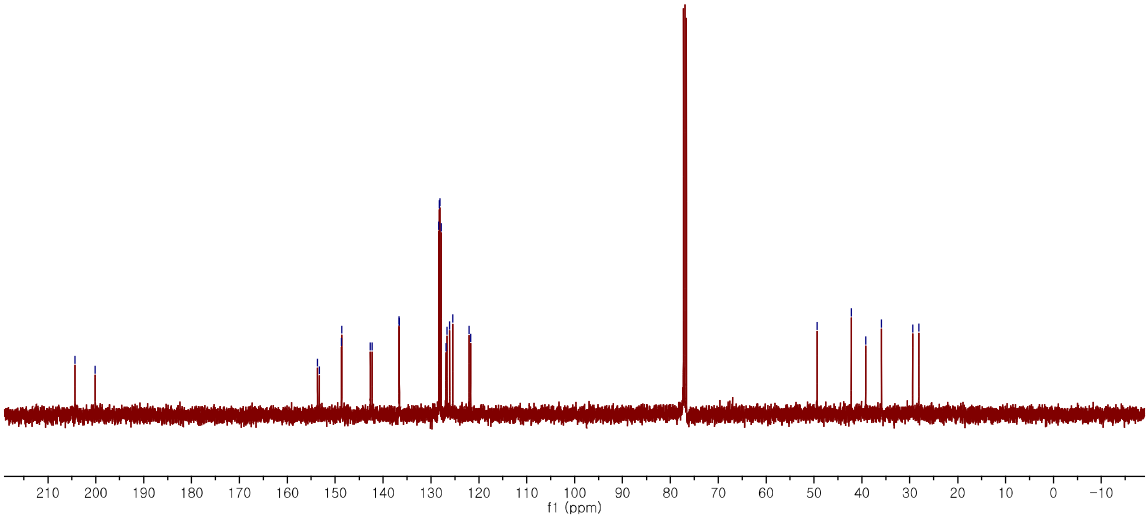


Table 4, (*S*,*S*)-**3ga**
^{13}C NMR (101 MHz, $CDCl_3$)
13:1 dr



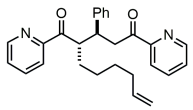
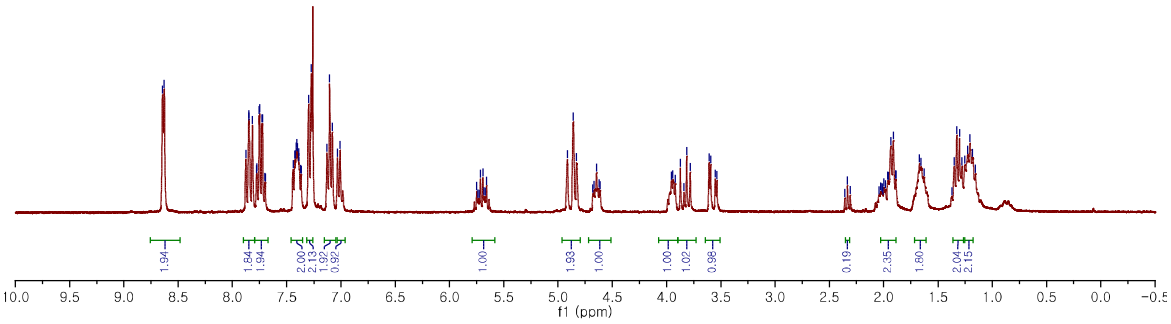


Table 4, (*S*,*S*)-**3ha**
^{1}H NMR (300 MHz, $CDCl_3$)
9.0:1 dr



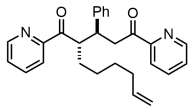
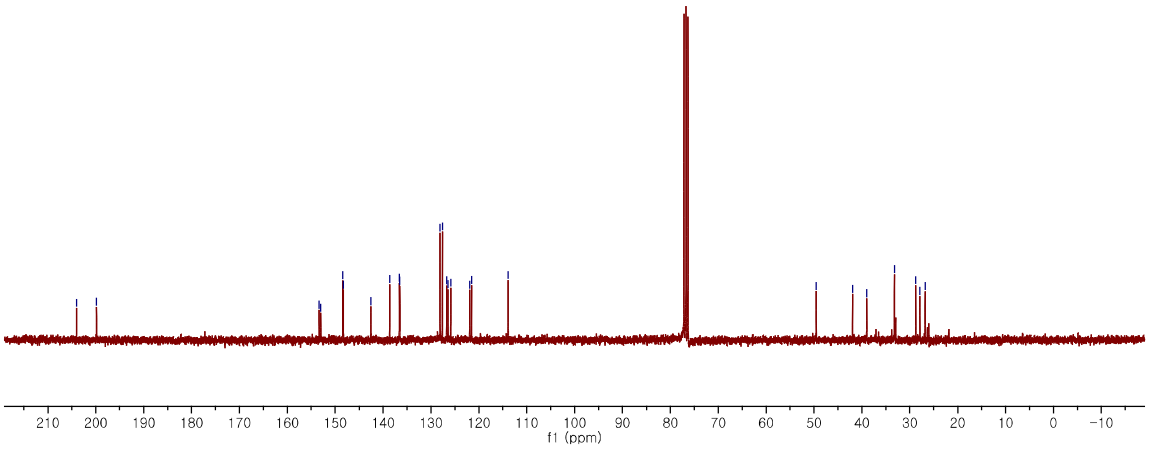


Table 4, (*S*,*S*)-**3ha**
^{13}C NMR (75 MHz, $CDCl_3$)
9.0:1 dr



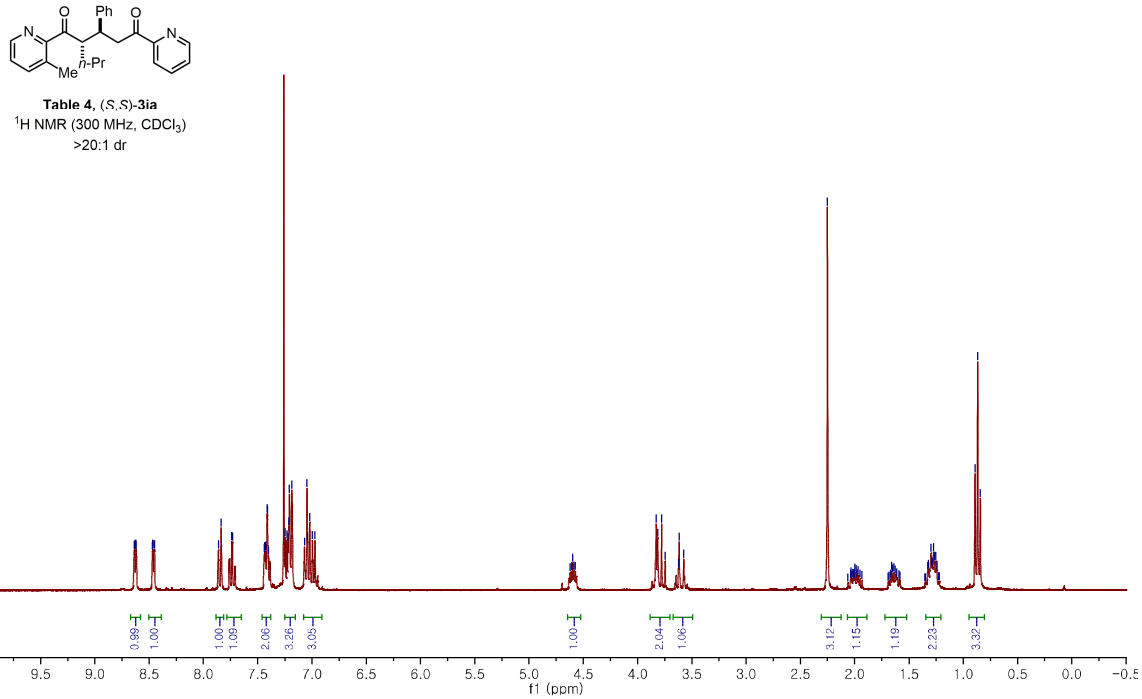


Table 4, (*S*,*S*)-**3ia**
^{1}H NMR (300 MHz, $CDCl_3$)
>20:1 dr

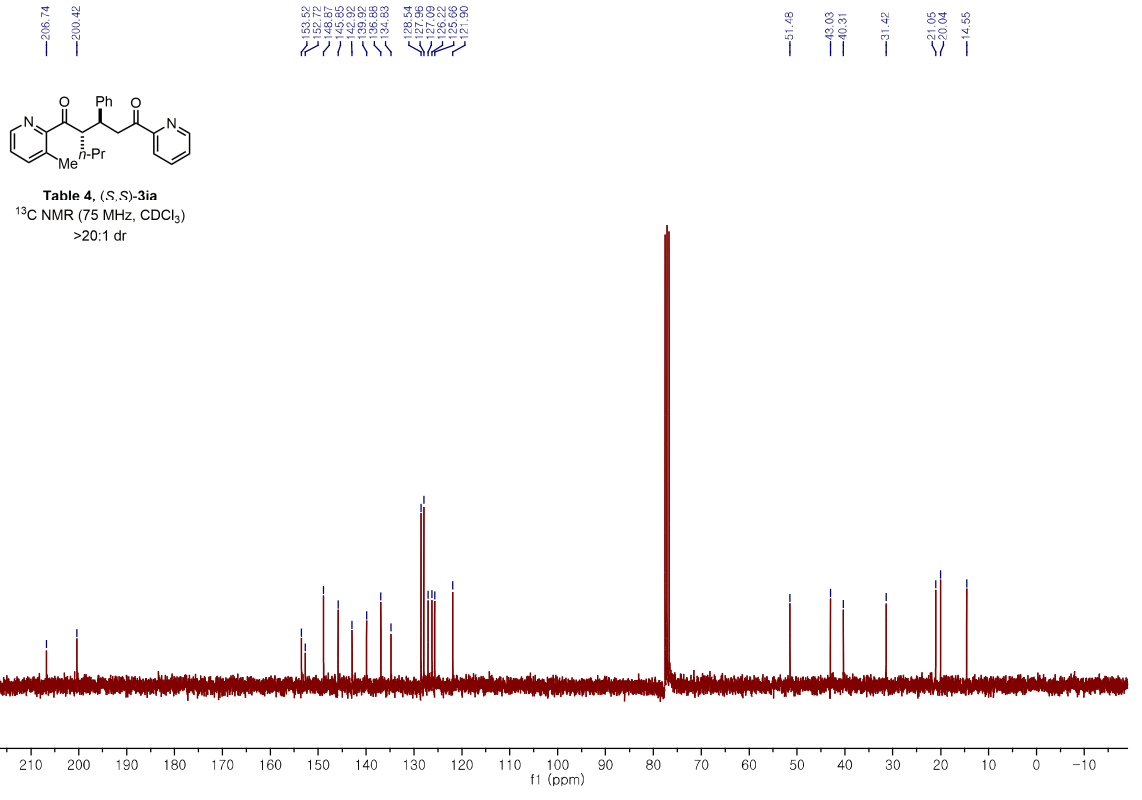


Table 4, (*S*,*S*)-**3ia**
^{13}C NMR (75 MHz, $CDCl_3$)
>20:1 dr

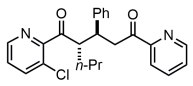
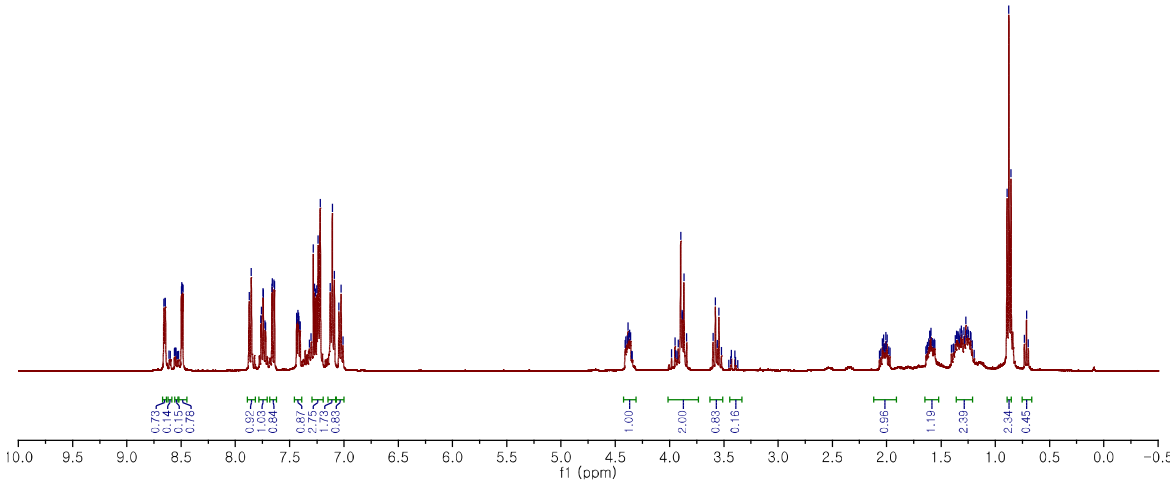


Table 4, (*S*,*S*)-**3ja**
^{1}H NMR (400 MHz, $CDCl_3$)
5.2:1 dr



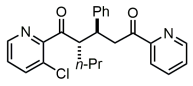
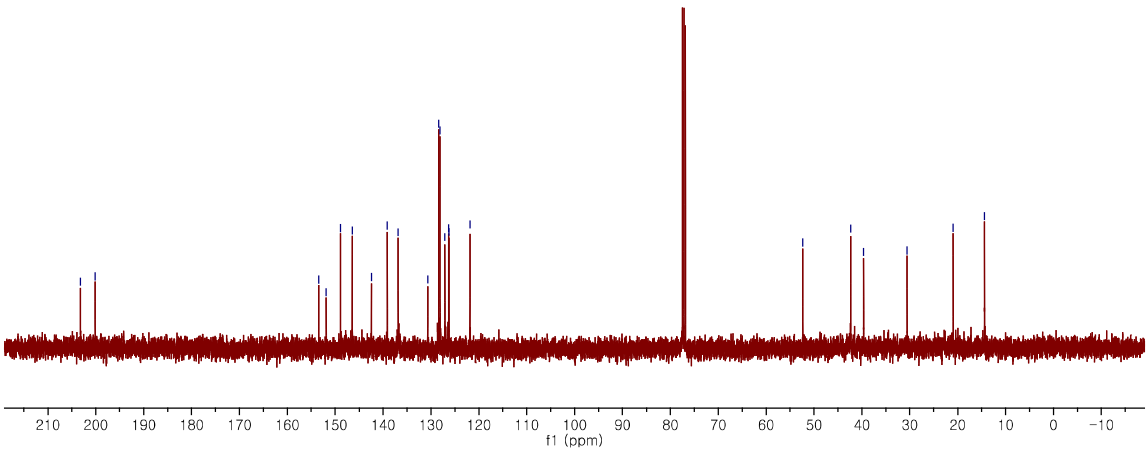


Table 4, (*S*,*S*)-**3ja**
^{13}C NMR (101 MHz, $CDCl_3$)
5.2:1 dr



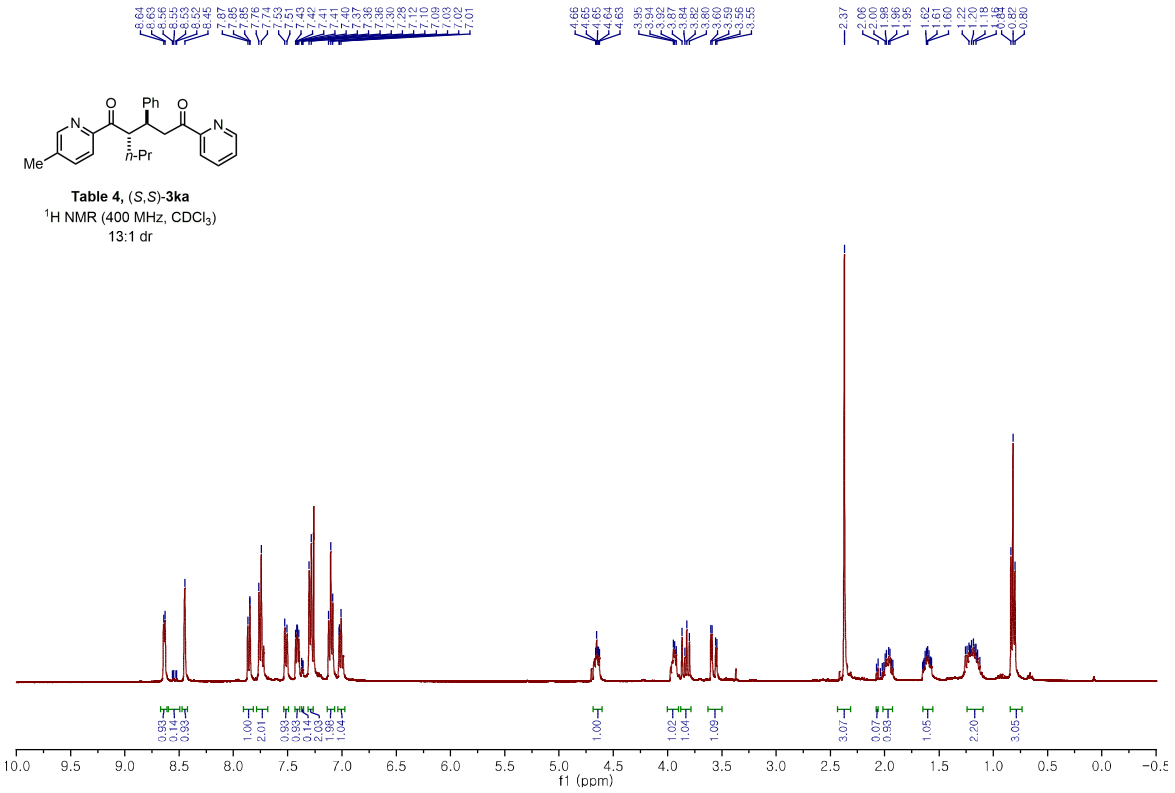


Table 4, (*S*,*S*)-**3ka**
^{1}H NMR (400 MHz, $CDCl_3$)
13:1 dr

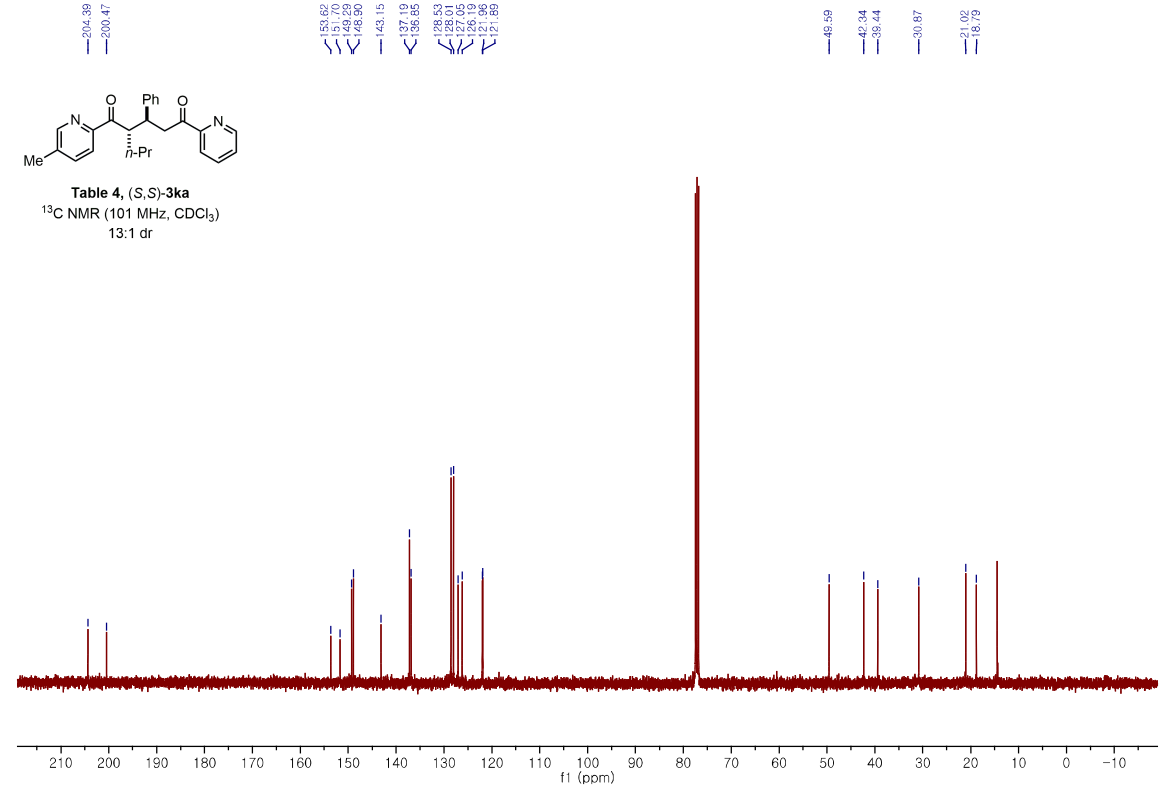


Table 4, (*S*,*S*)-**3ka**
^{13}C NMR (101 MHz, $CDCl_3$)
13:1 dr

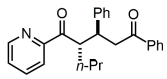
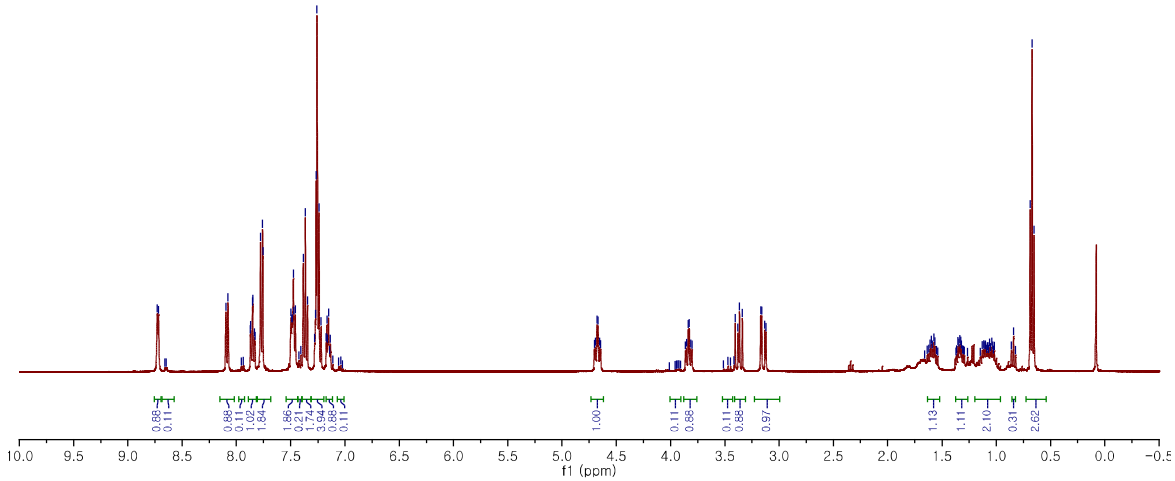


Table 4, (*S,S*)-**3ab**
^{1}H NMR (400 MHz, $CDCl_3$)
8.1:1 dr



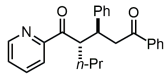
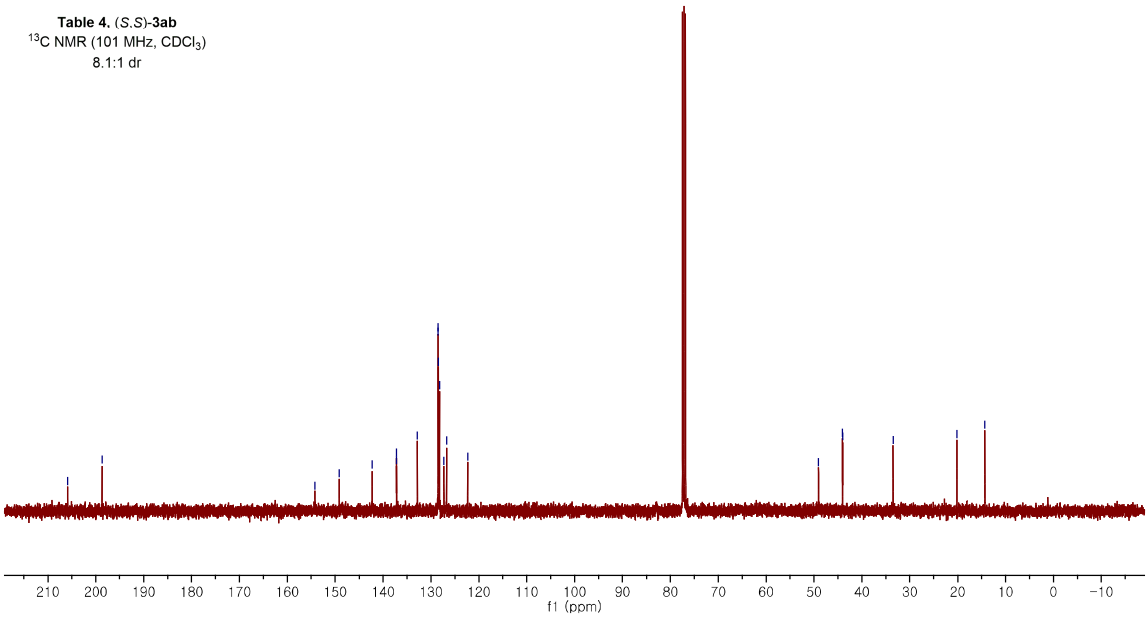


Table 4. (*S.S*)-**3ab**
^{13}C NMR (101 MHz, $CDCl_3$)
8.1:1 dr



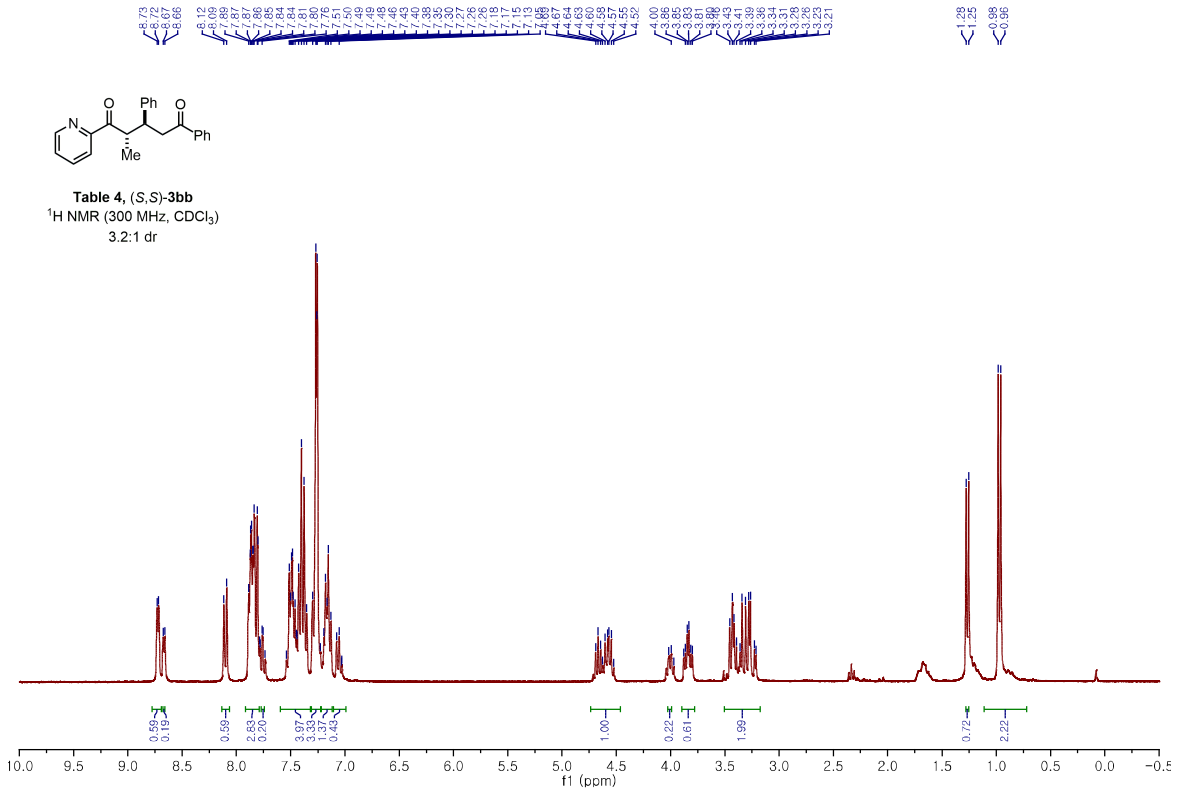


Table 4, (*S*,*S*)-**3bb**
^{1}H NMR (300 MHz, $CDCl_3$)
3.2:1 dr

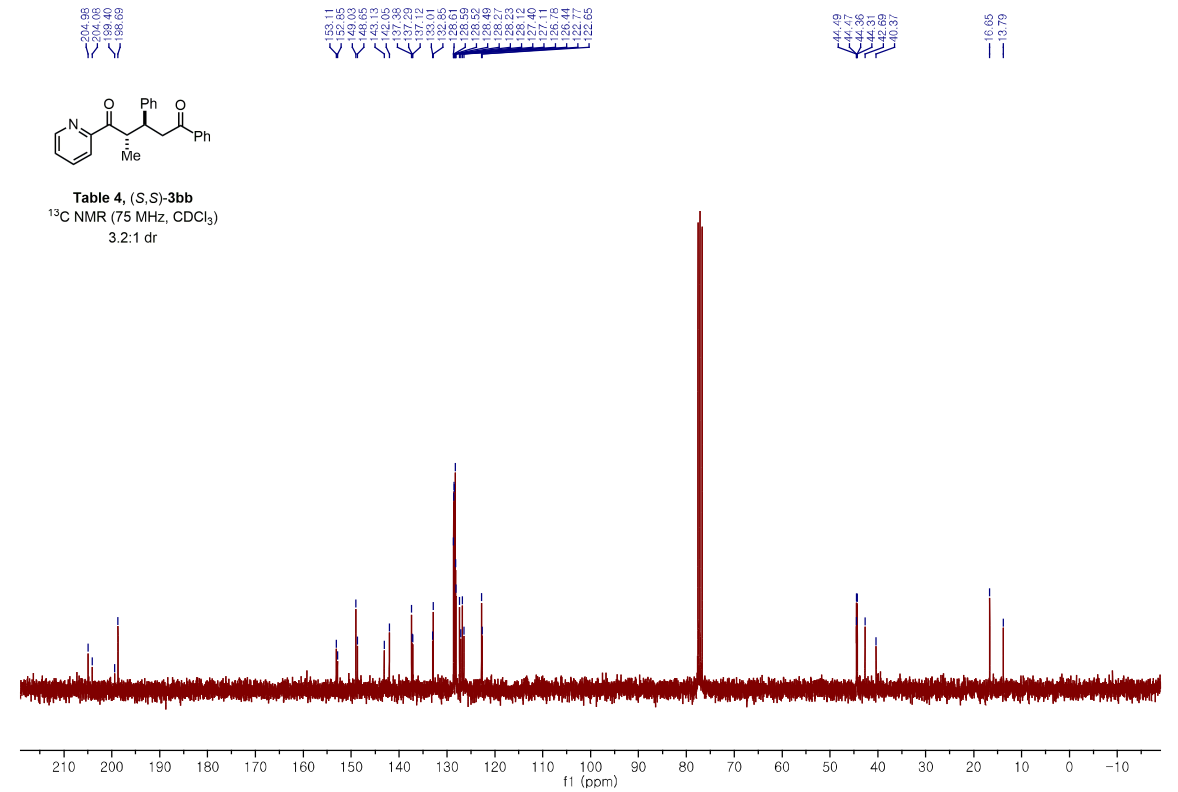


Table 4, (*S*,*S*)-**3bb**
^{13}C NMR (75 MHz, $CDCl_3$)
3.2:1 dr

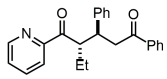
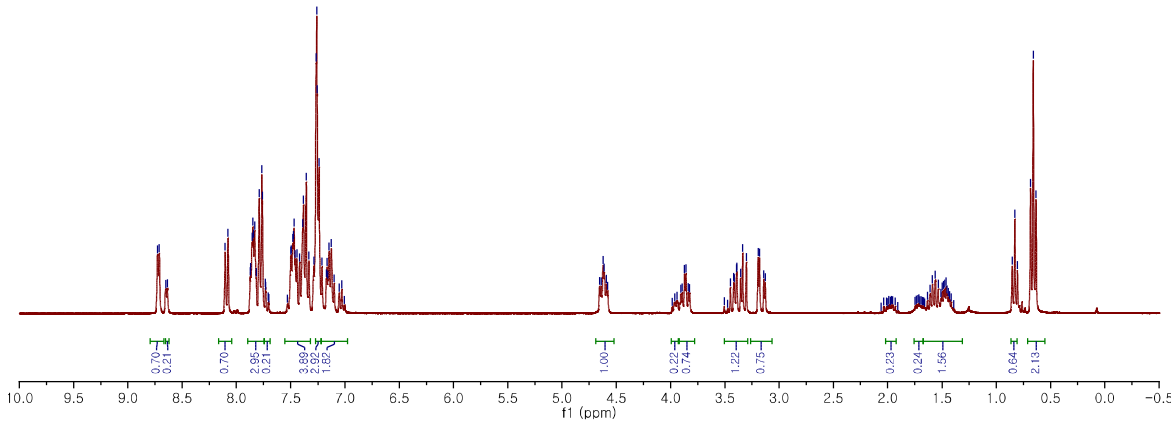


Table 4, (*S,S*)-**3lb**
^{1}H NMR (300 MHz, $CDCl_3$)
3.3:1 dr



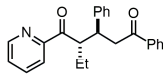
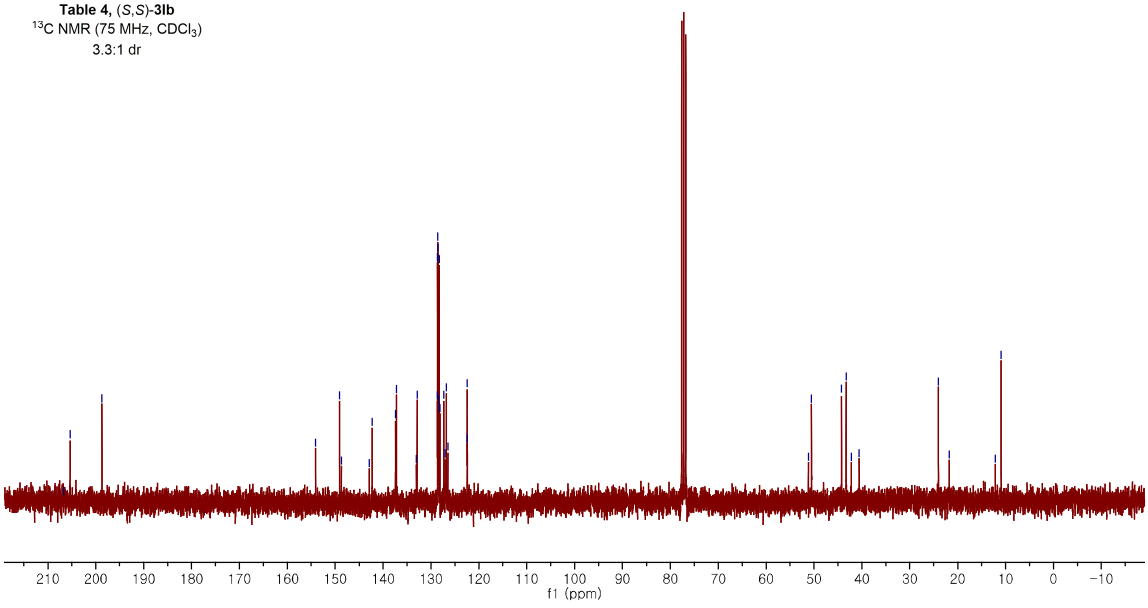


Table 4, (*S,S*)-**3lb**
^{13}C NMR (75 MHz, $CDCl_3$)
3.3:1 dr



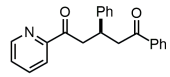
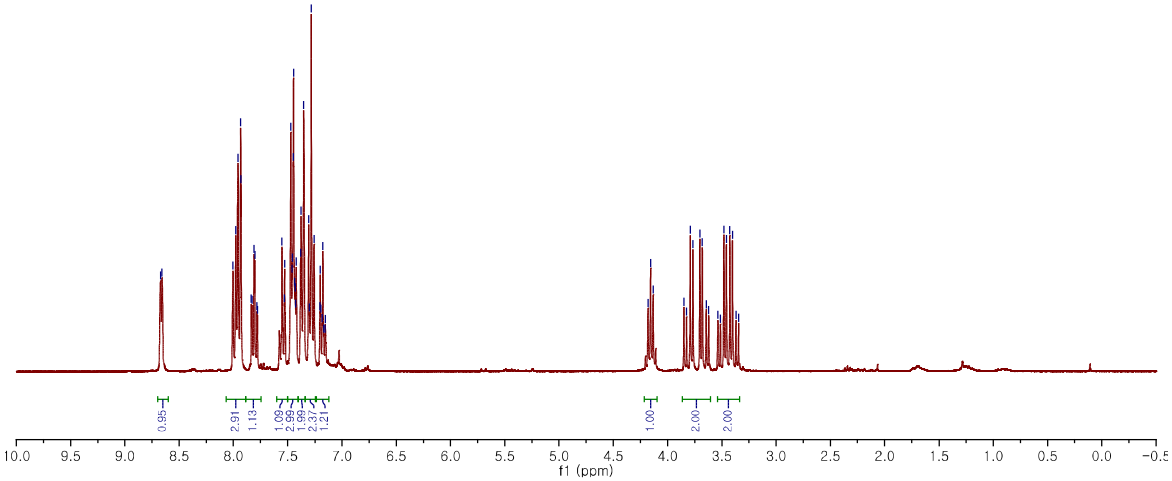


Table 4, (*S*,*S*)-**3mb**
^{1}H NMR (300 MHz, $CDCl_3$)



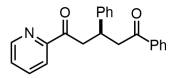
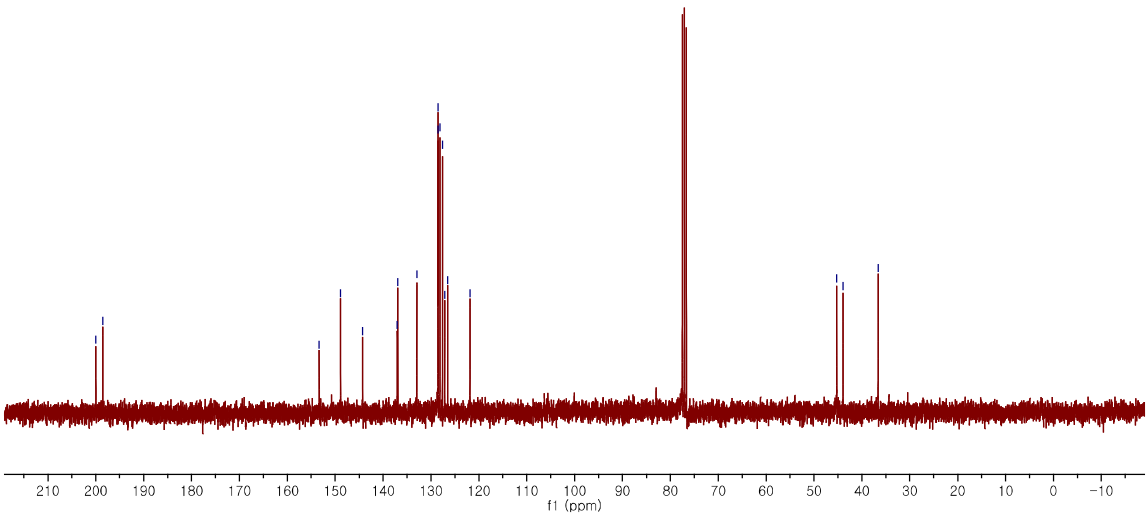


Table 4, (*S*,*S*)-**3mb**
^{13}C NMR (75 MHz, $CDCl_3$)



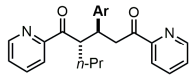
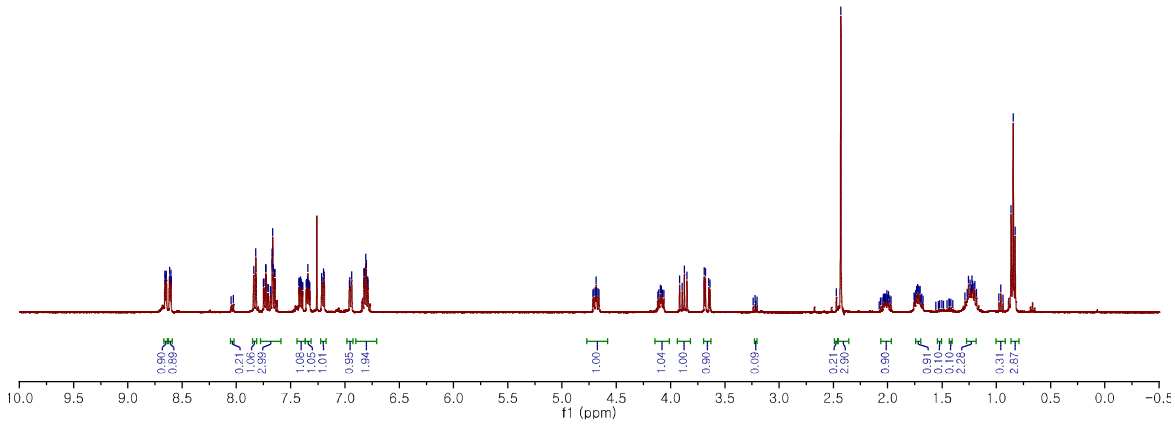


Table 5, (*S*,*S*)-**3ac** (Ar = 2-MeC_6H_4)
^{1}H NMR (400 MHz, $CDCl_3$)
9.0:1 dr



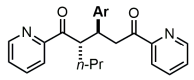
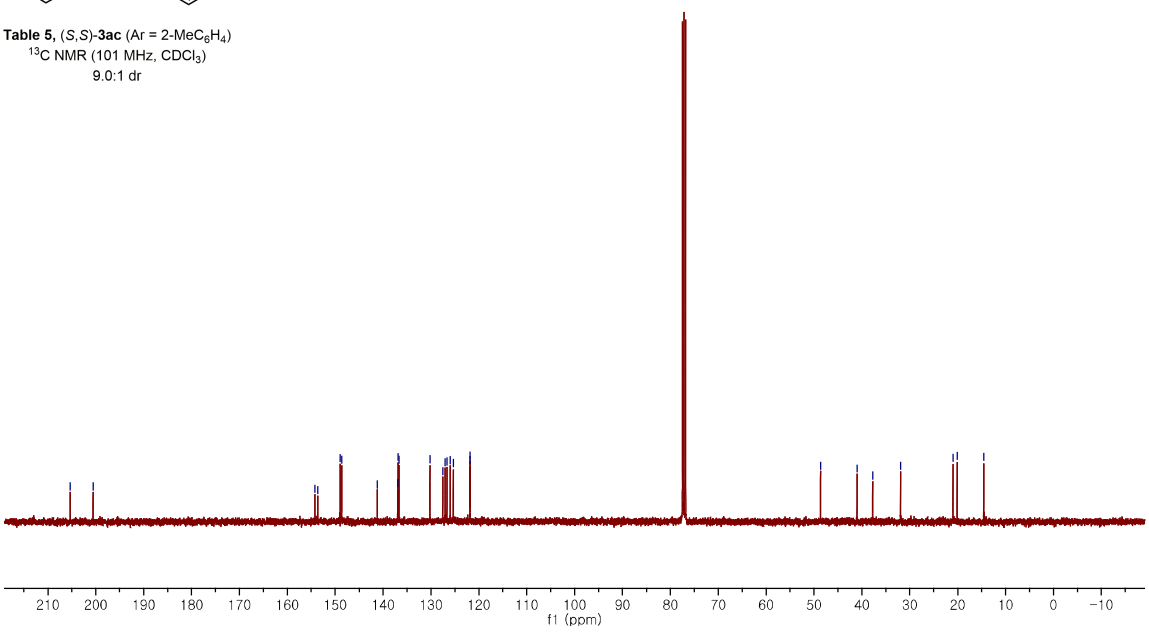


Table 5, (*S*,*S*)-**3ac** (Ar = 2-MeC_6H_4)
^{13}C NMR (101 MHz, $CDCl_3$)
9.0:1 dr



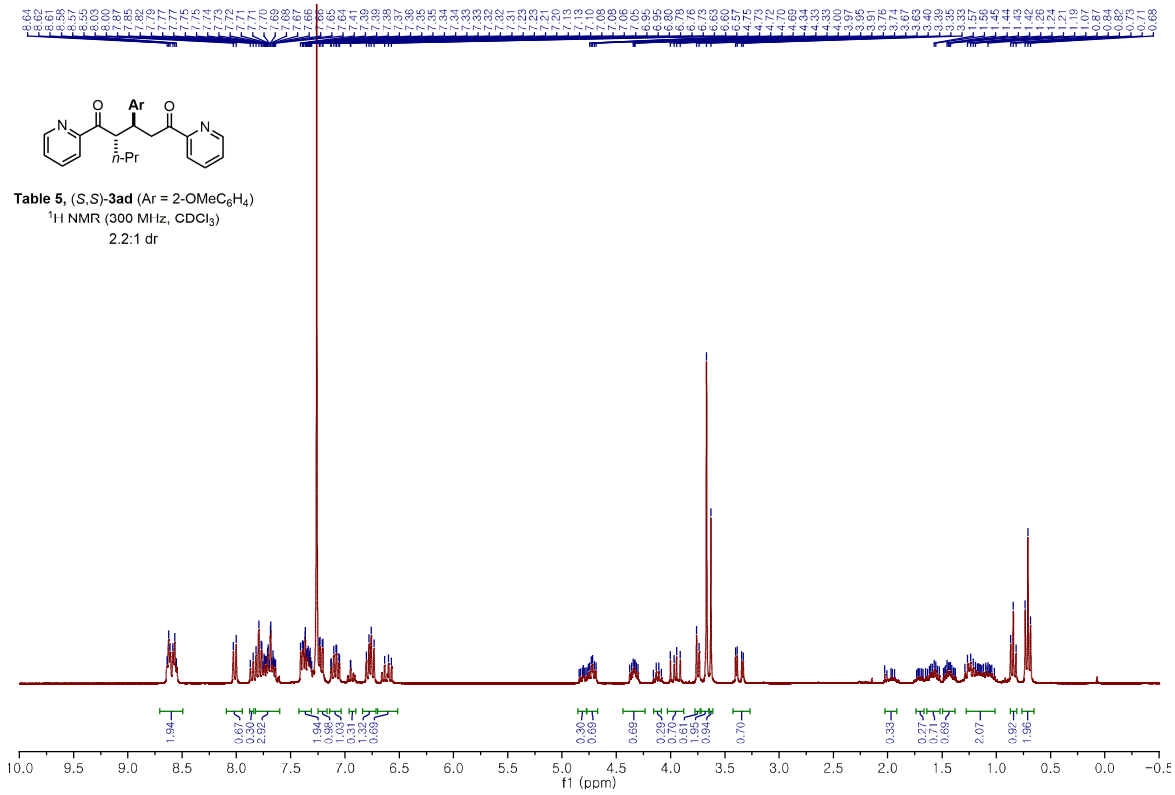


Table 5, (*S*,*S*)-**3ad** (Ar = 2-OMeC$_6$H$_4$)
^{1}H NMR (300 MHz, CDCl$_3$)
2.2:1 dr

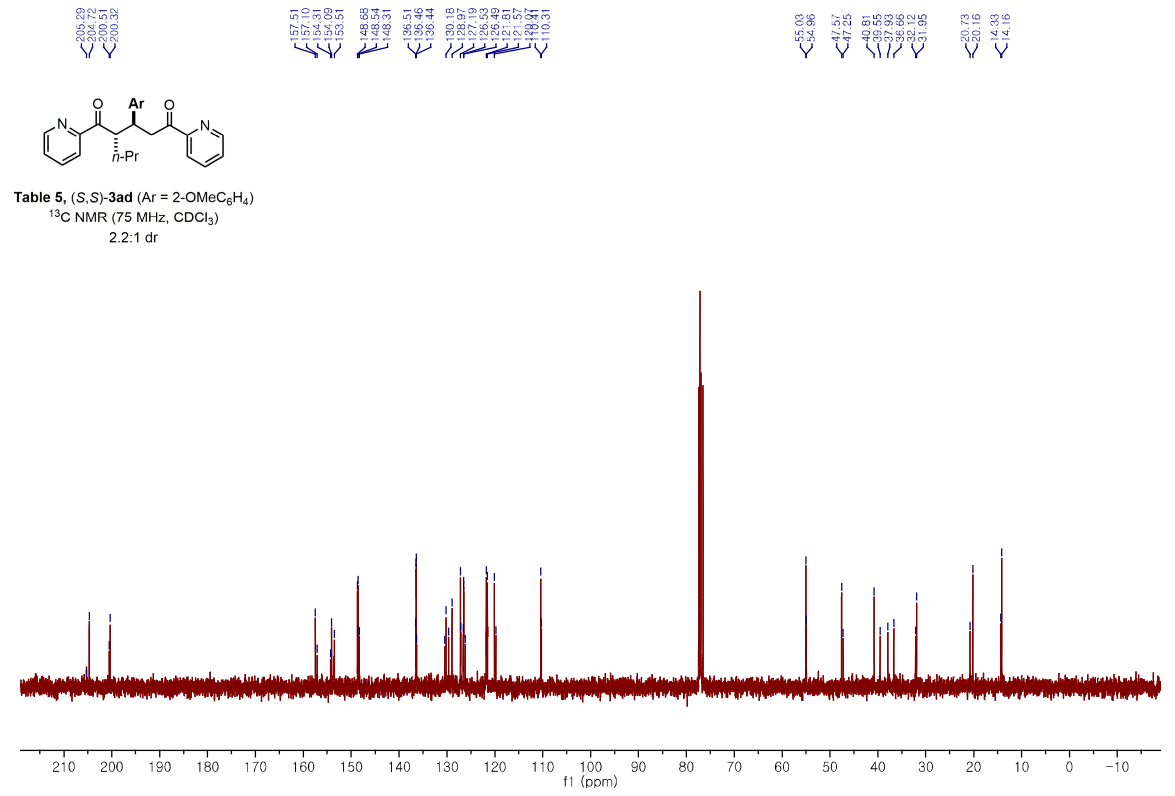


Table 5, (*S*,*S*)-**3ad** (Ar = 2-OMeC$_6$H$_4$)
^{13}C NMR (75 MHz, CDCl$_3$)
2.2:1 dr

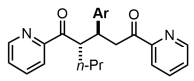
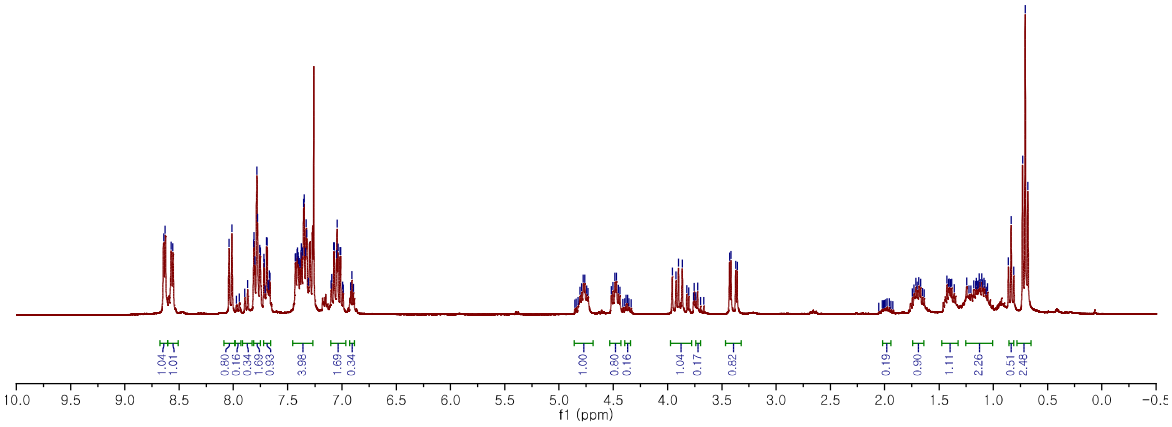


Table 5, (*S*,*S*)-**3ae** (Ar = 2-ClC$_6$H$_4$)
^{1}H NMR (300 MHz, CDCl$_3$)
4.9:1 dr



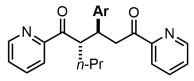
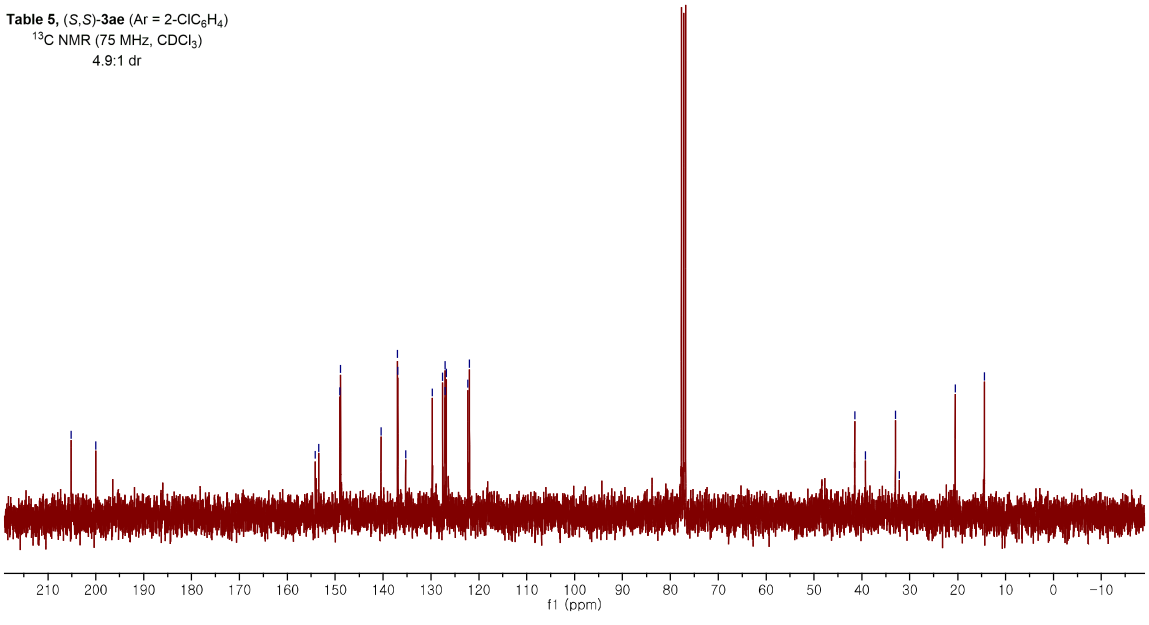


Table 5, (*S*,*S*)-**3ae** (Ar = 2-ClC$_6$H$_4$)
^{13}C NMR (75 MHz, CDCl$_3$)
4.9:1 dr



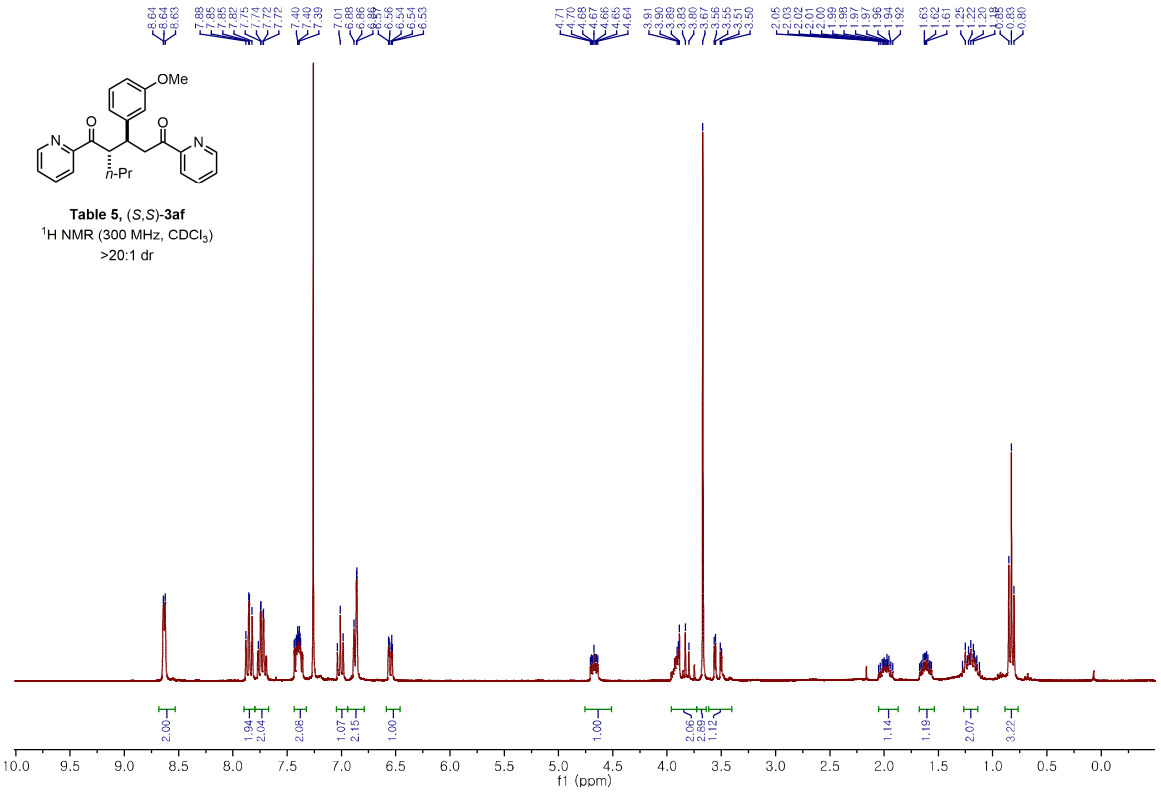


Table 5, (*S*,*S*)-**3af**
^{1}H NMR (300 MHz, $CDCl_3$)
>20:1 dr

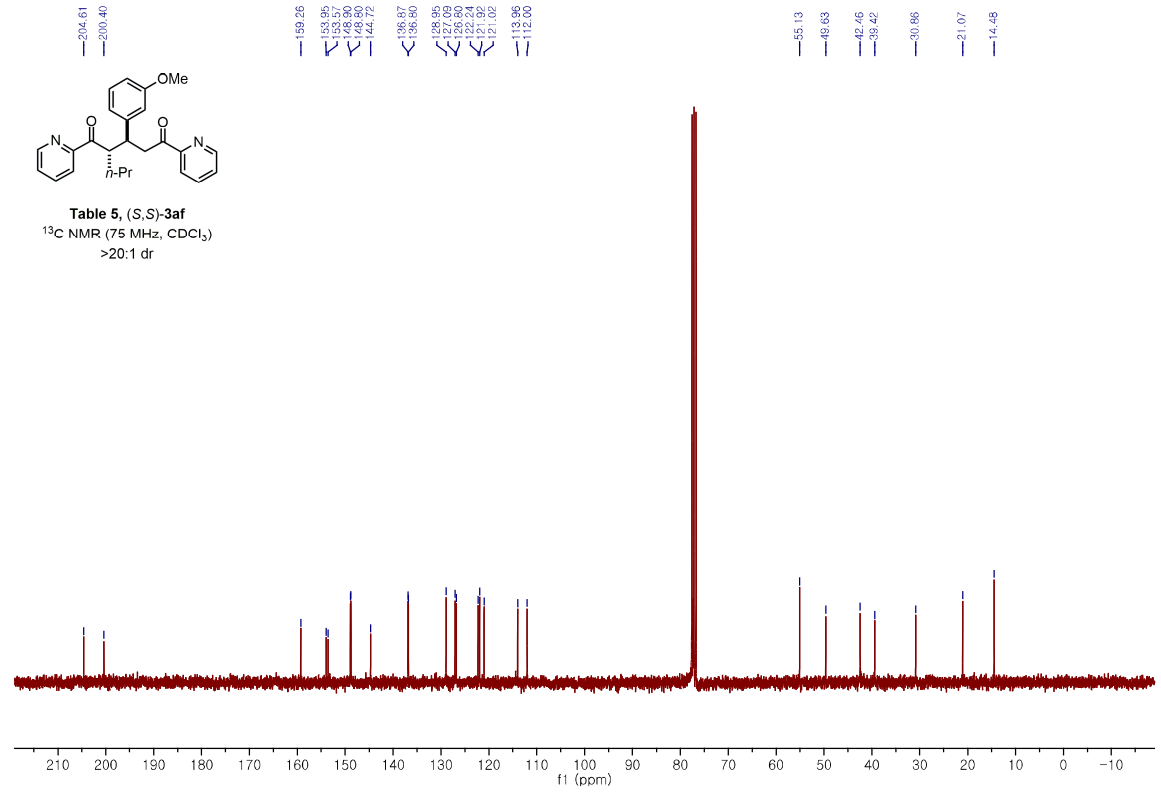


Table 5, (*S*,*S*)-**3af**
^{13}C NMR (75 MHz, $CDCl_3$)
>20:1 dr

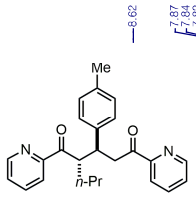


Table 5, (*S*,*S*)-**3ag**
^{1}H NMR (400 MHz, $CDCl_3$)
6.7:1 dr

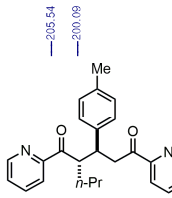


Table 5, (*S*,*S*)-**3ag**
^{13}C NMR (101 MHz, $CDCl_3$)
6.7:1 dr

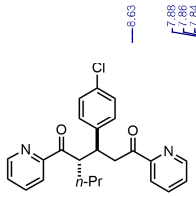
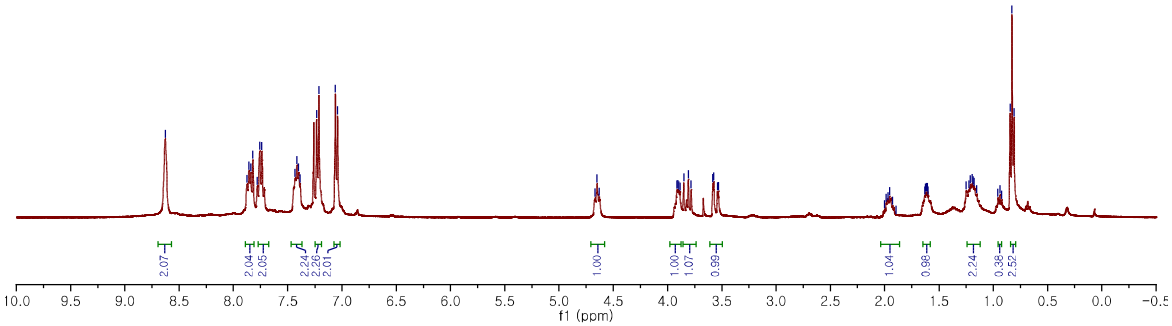


Table 5, (*S*,*S*)-**3ah**
^{1}H NMR (400 MHz, $CDCl_3$)
4.9:1 dr



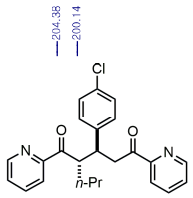


Table 5, (*S*,*S*)-**3ah**
^{13}C NMR (101 MHz, $CDCl_3$)
4.9:1 dr

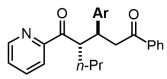
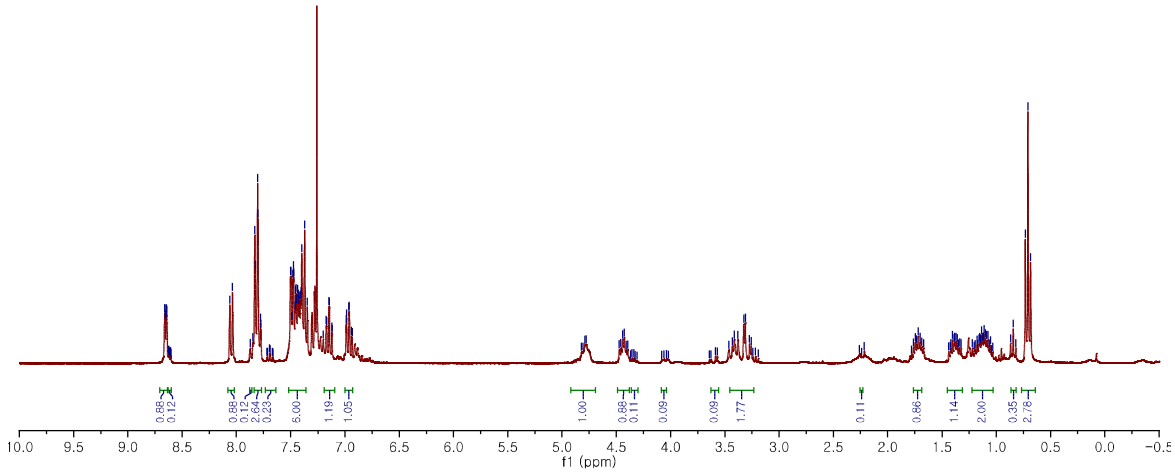


Table 5, (*S*,*S*)-**3ai** (Ar = 2-BrC_6H_4)
^{1}H NMR (300 MHz, $CDCl_3$)
7.3:1 dr



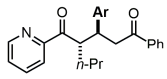
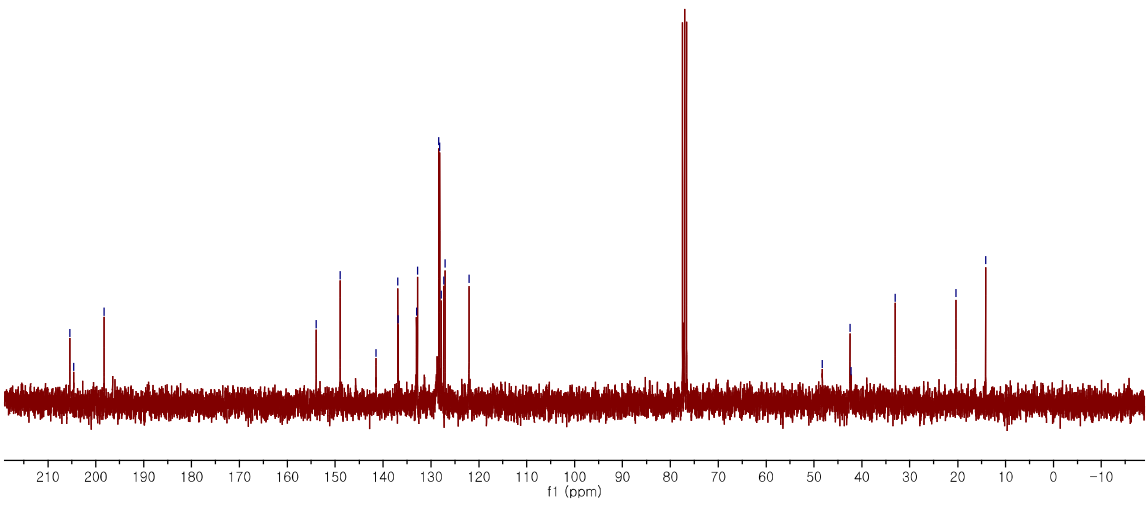


Table 5, (*S*,*S*)-**3ai** (Ar = 2-BrC_6H_4)
^{13}C NMR (75 MHz, $CDCl_3$)
7.3:1 dr



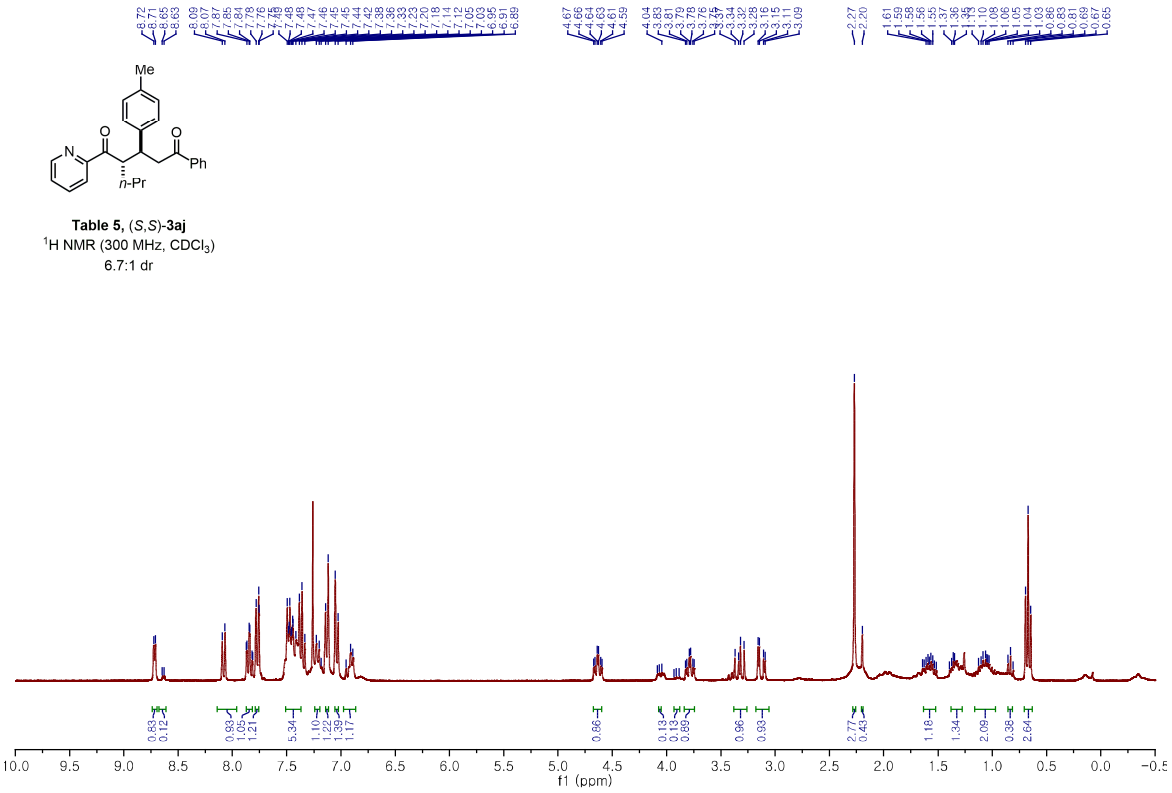


Table 5, (*S*,*S*)-**3aj**
^{1}H NMR (300 MHz, $CDCl_3$)
6.7:1 dr

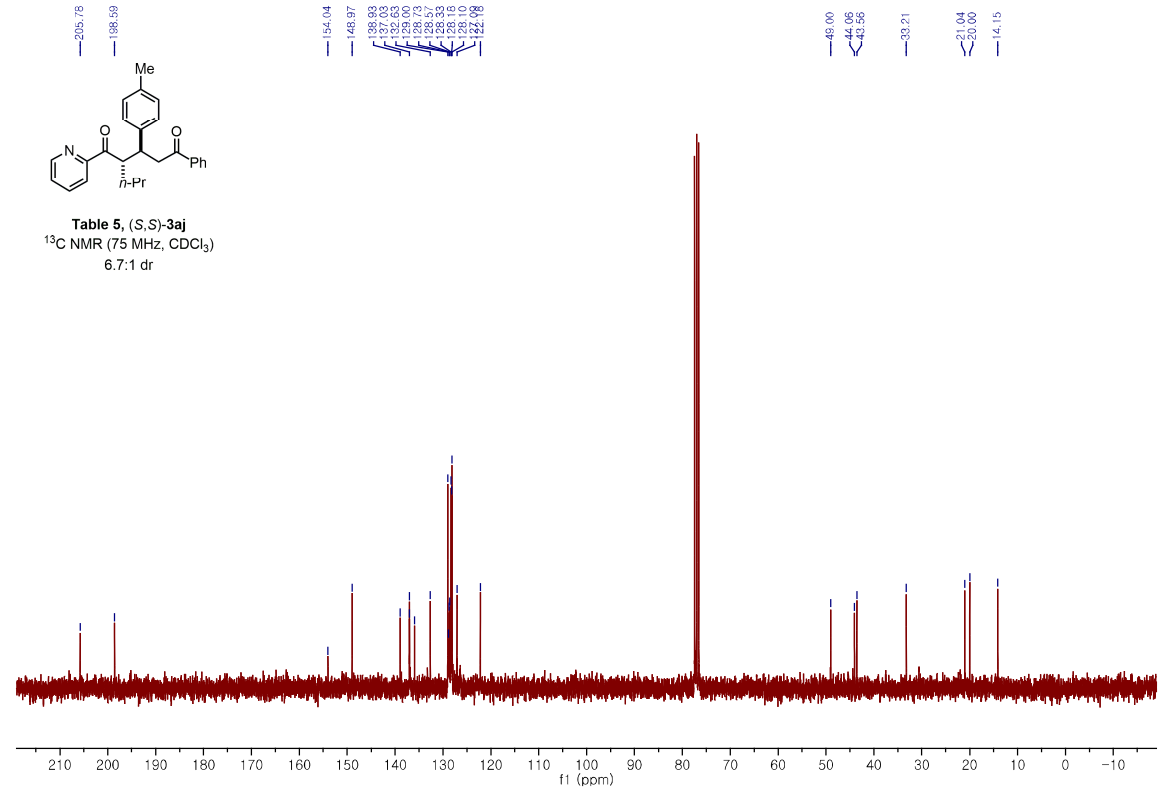
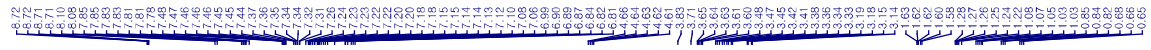


Table 5, (*S*,*S*)-**3aj**
^{13}C NMR (75 MHz, $CDCl_3$)
6.7:1 dr



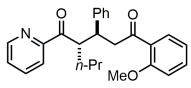
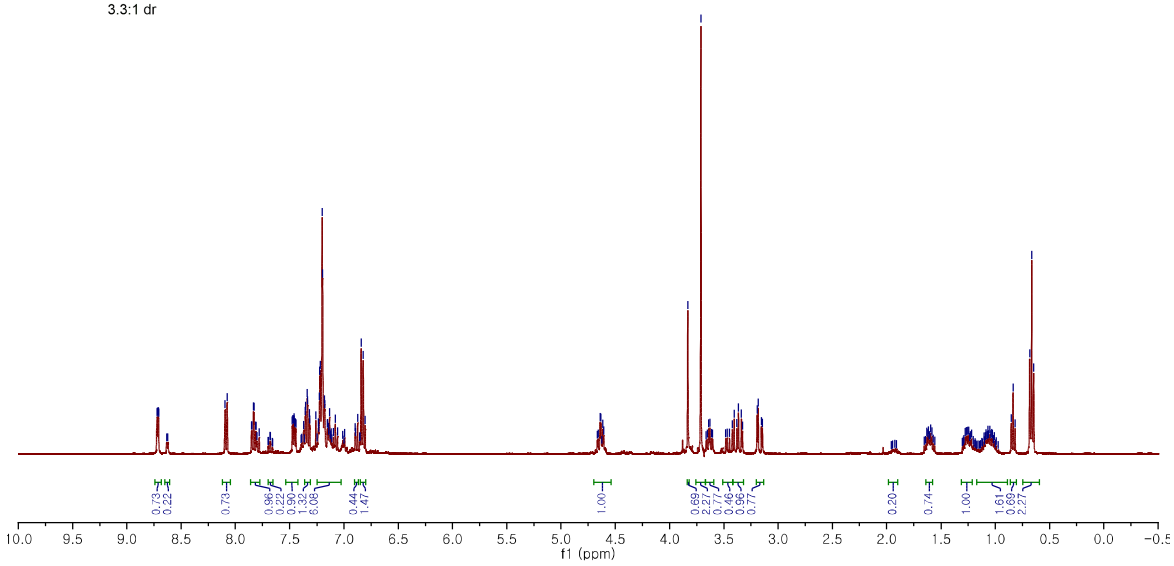


Table 5, (*S*,*S*)-**3ak**
^{1}H NMR (400 MHz, $CDCl_3$)
3.3:1 dr



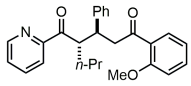
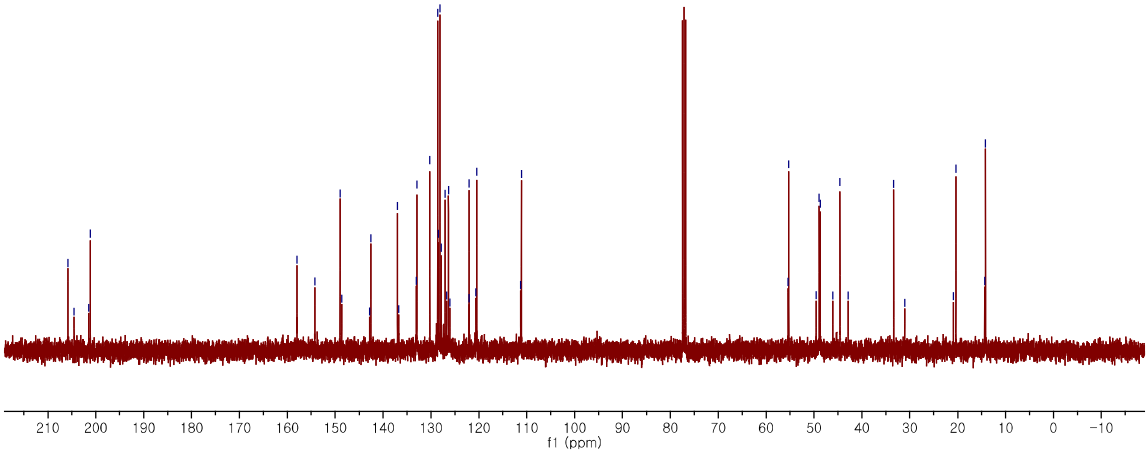


Table 5, (*S*,*S*)-**3ak**
^{13}C NMR (101 MHz, $CDCl_3$)
3.3:1 dr



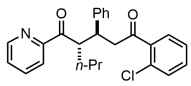
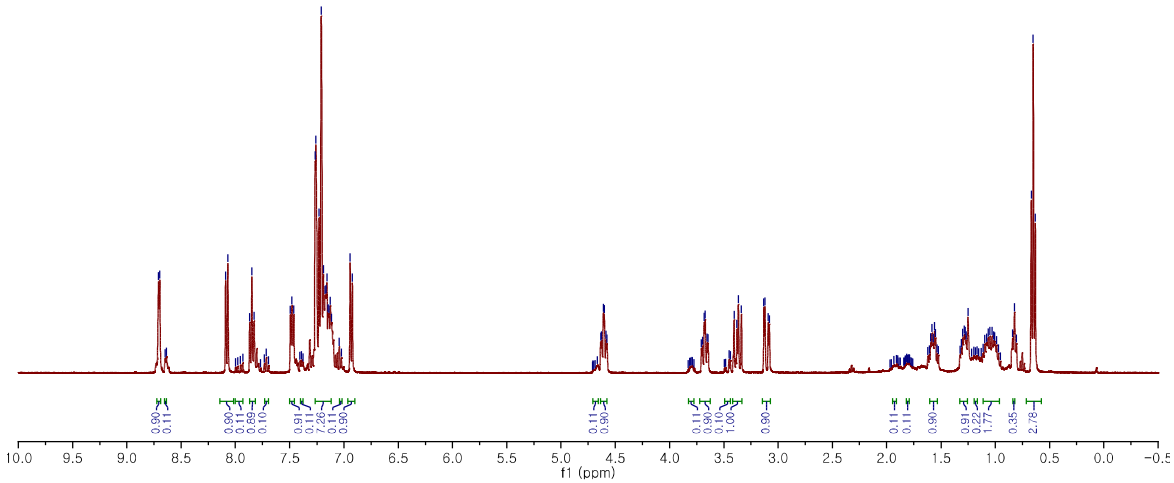


Table 5, (*S*,*S*)-**3al**
^{1}H NMR (400 MHz, $CDCl_3$)
8.1:1 dr



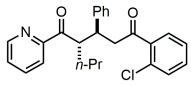
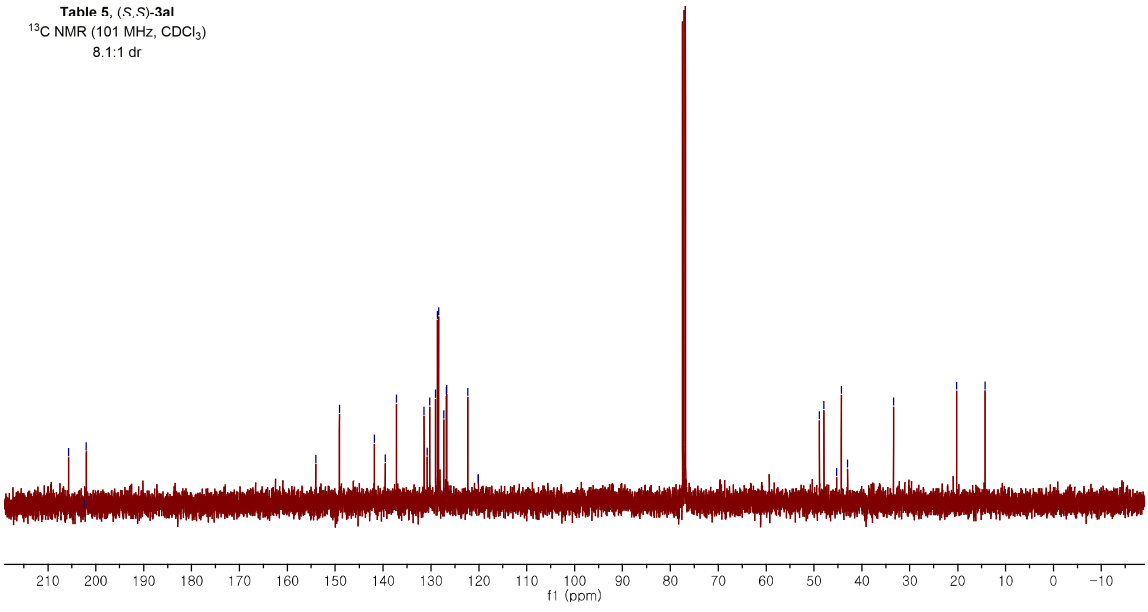


Table 5, (*S*,*S*)-**3al**
^{13}C NMR (101 MHz, $CDCl_3$)
8.1:1 dr



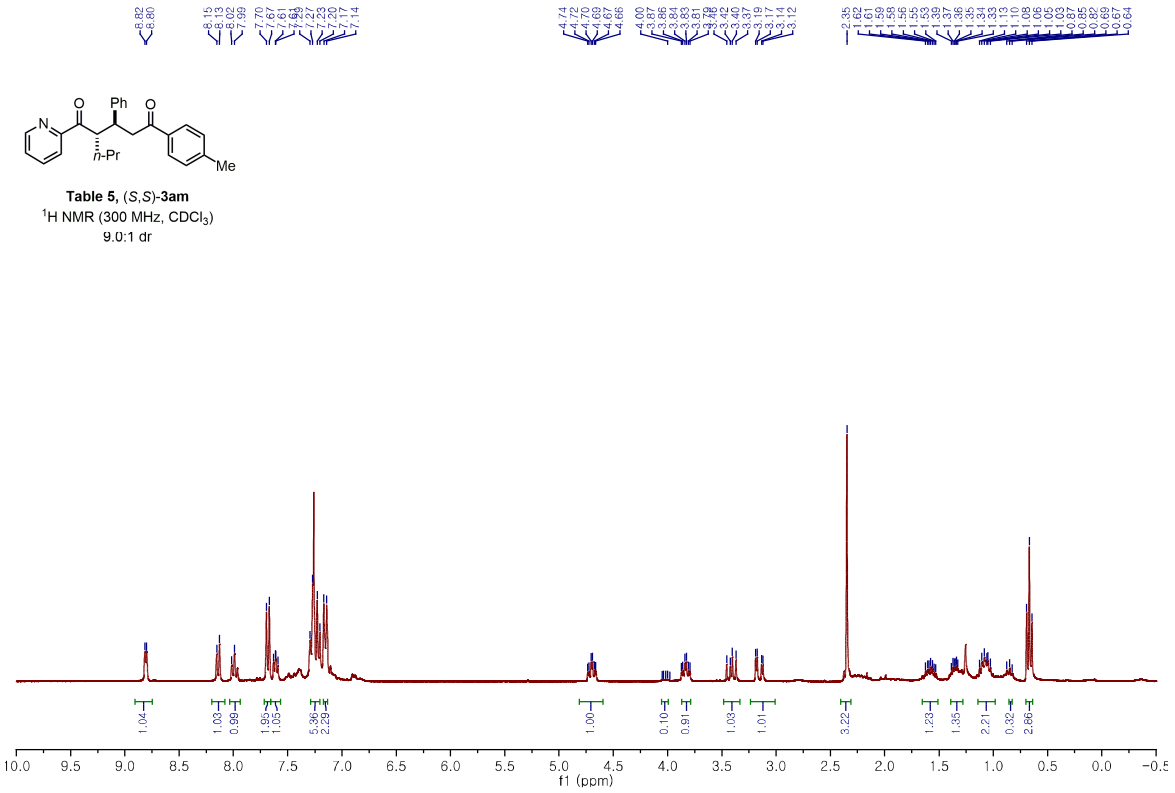


Table 5, (*S*,*S*)-**3am**
^{1}H NMR (300 MHz, $CDCl_3$)
9.0:1 dr

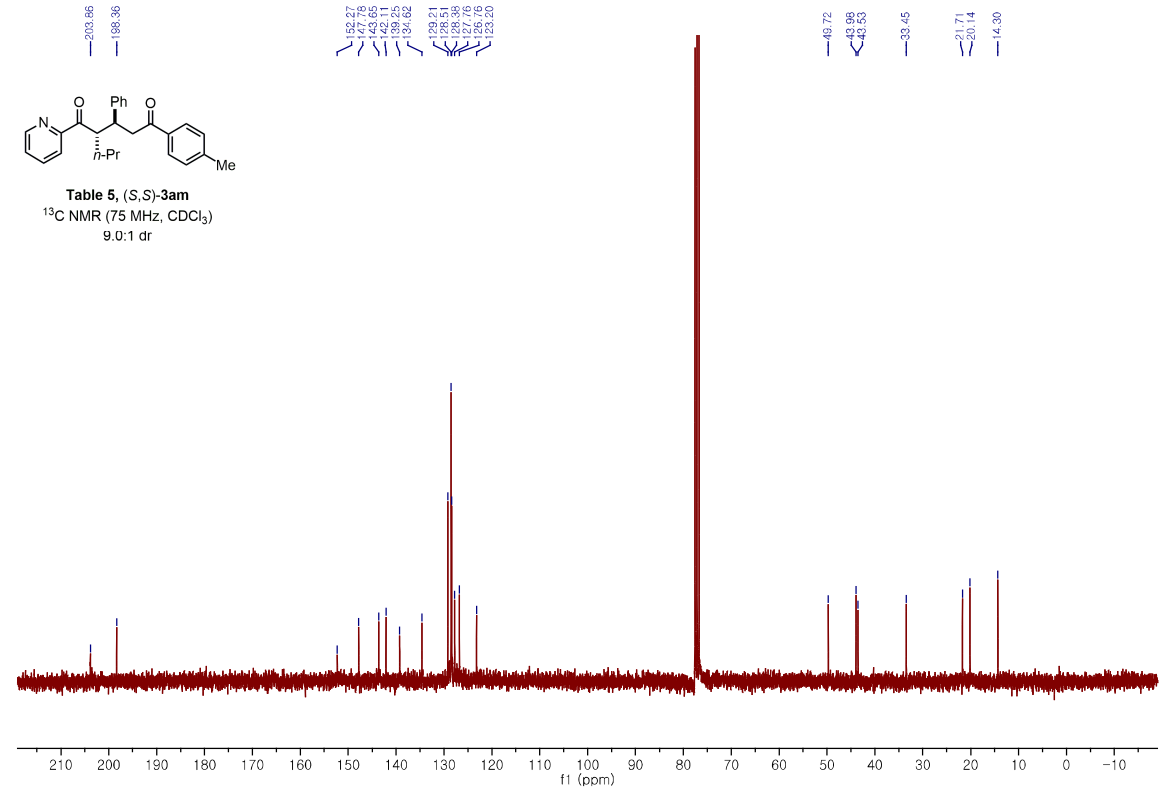


Table 5, (*S*,*S*)-**3am**
^{13}C NMR (75 MHz, $CDCl_3$)
9.0:1 dr

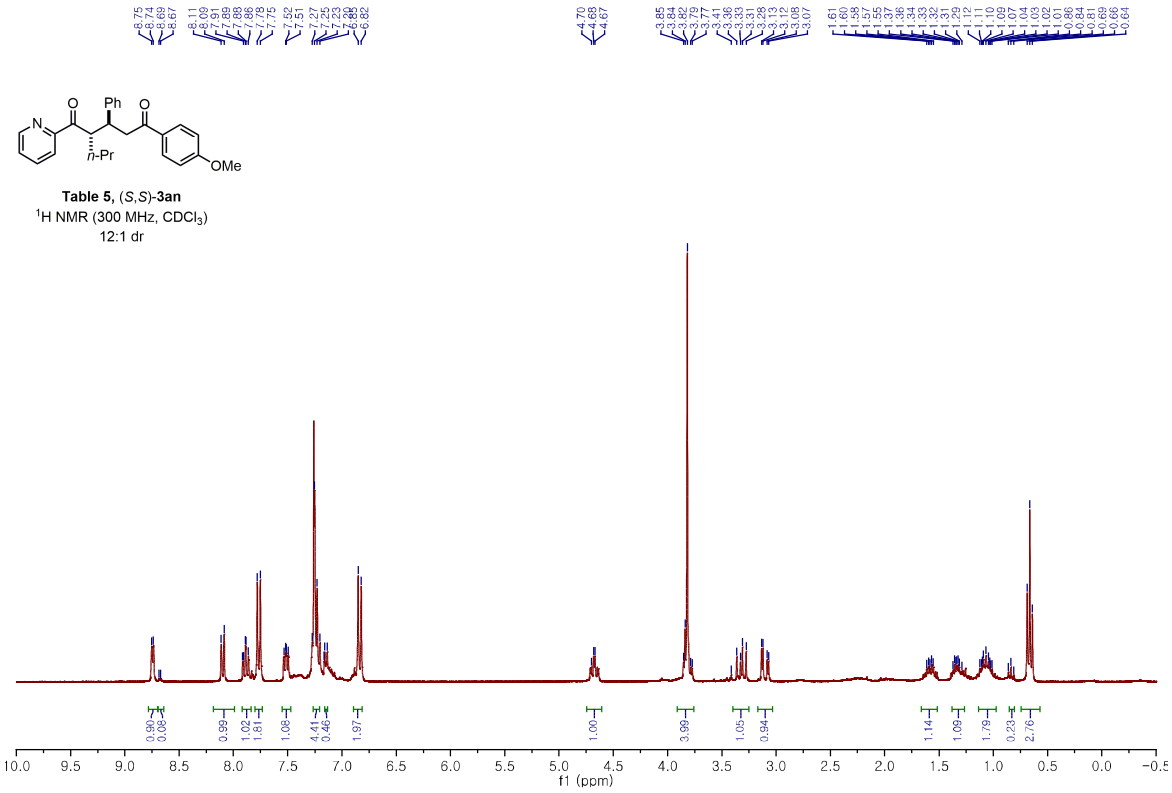


Table 5, (*S*,*S*)-**3an**
^{1}H NMR (300 MHz, $CDCl_3$)
12:1 dr

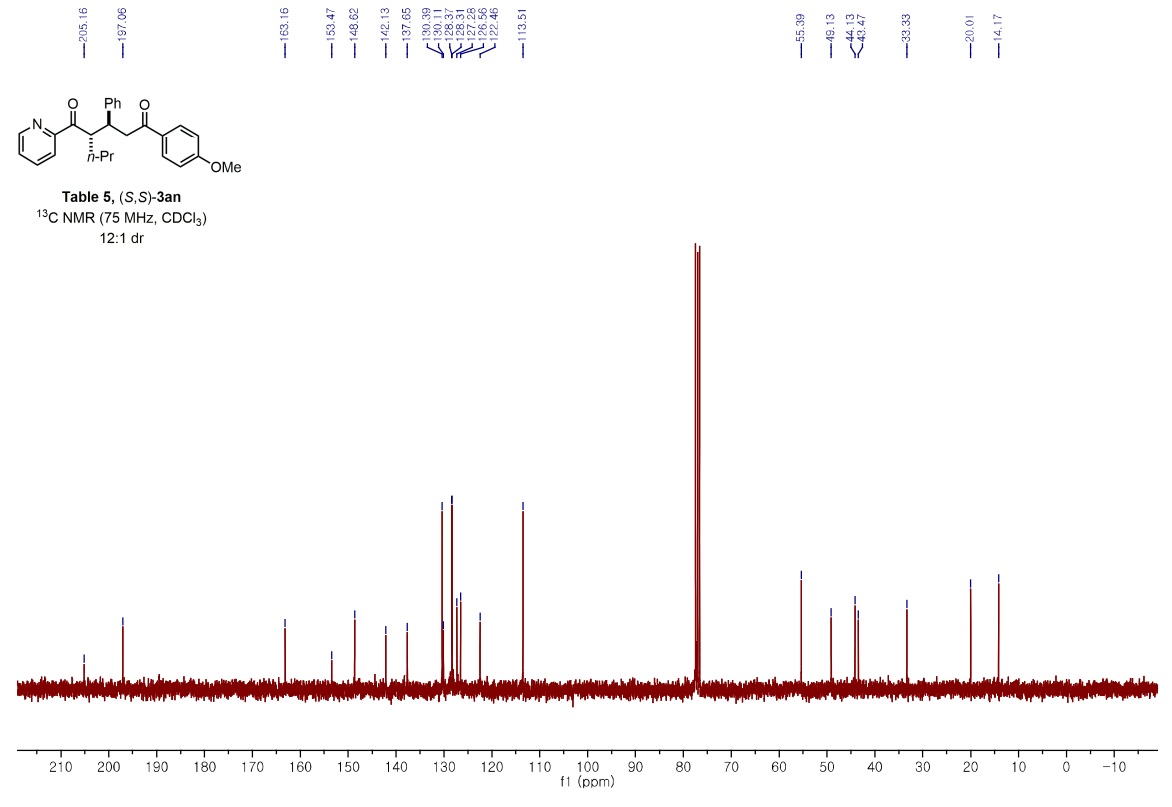


Table 5, (*S*,*S*)-**3an**
^{13}C NMR (75 MHz, $CDCl_3$)
12:1 dr

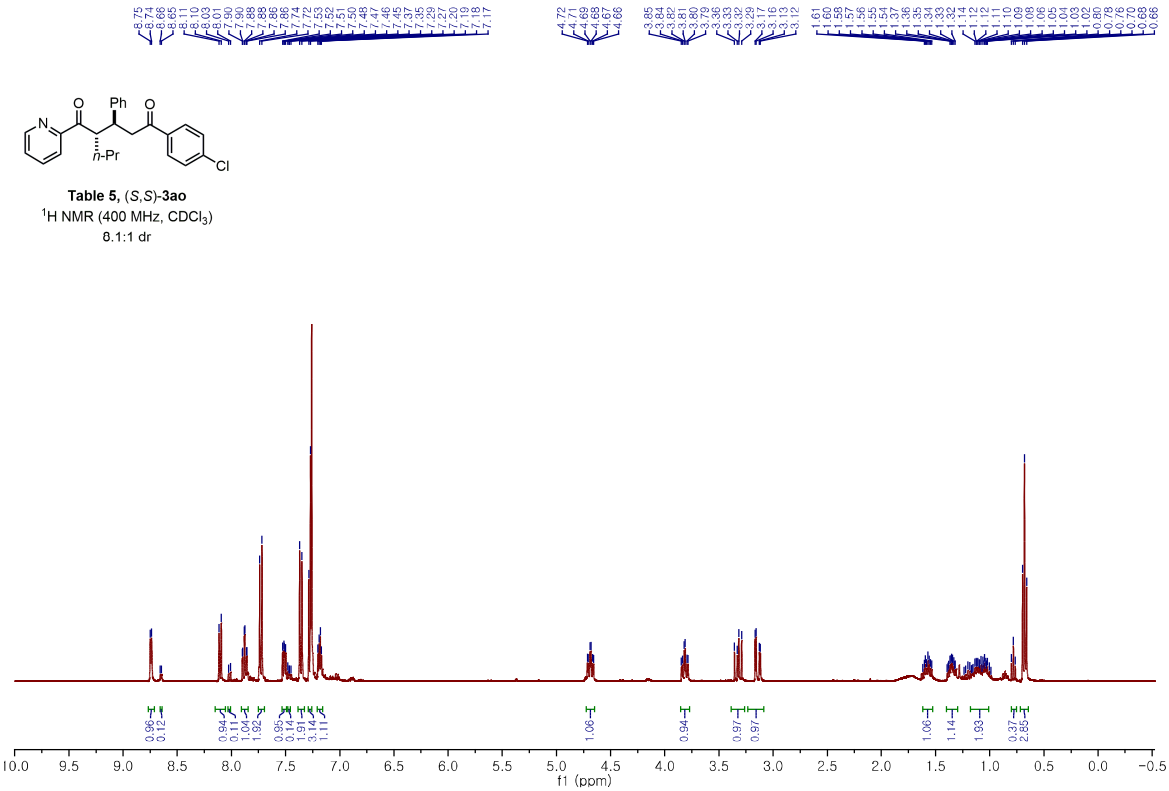


Table 5, (*S*,*S*)-**3ao**
^{1}H NMR (400 MHz, $CDCl_3$)
8.1:1 dr

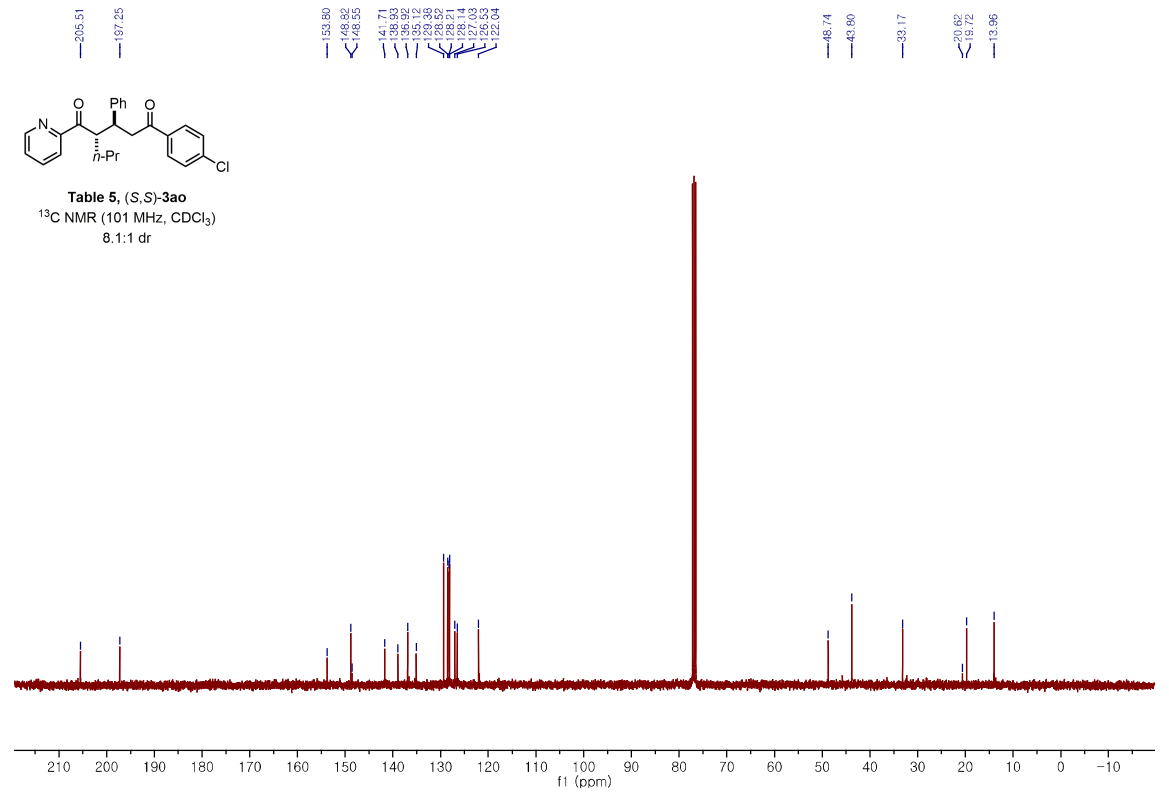


Table 5, (*S*,*S*)-**3ao**
^{13}C NMR (101 MHz, $CDCl_3$)
8.1:1 dr

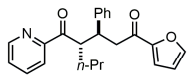
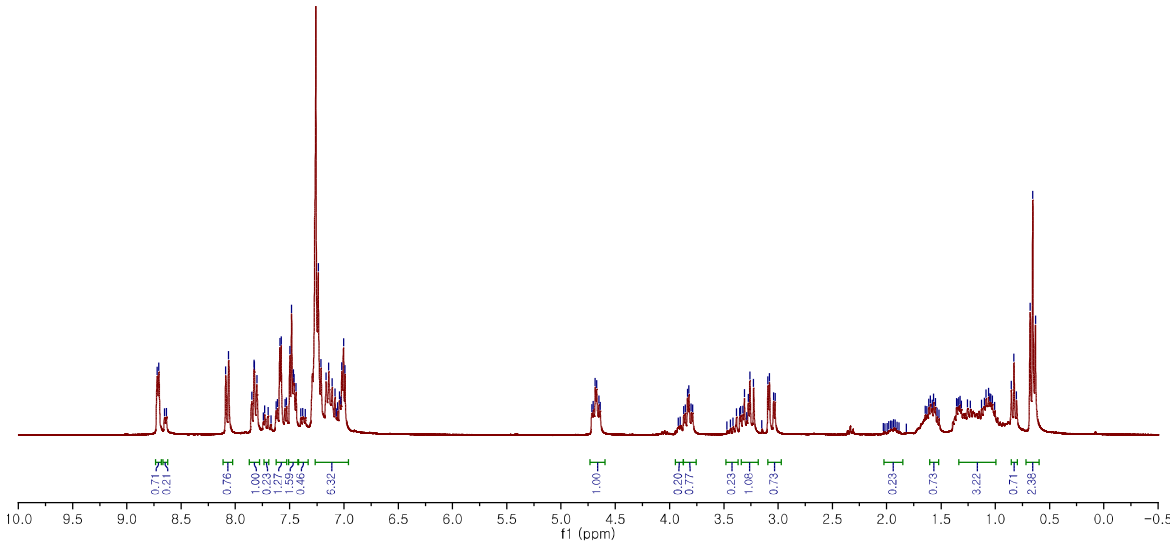


Table 5, (*S*,*S*)-**3ap**
^{1}H NMR (300 MHz, $CDCl_3$)
3.3:1 dr



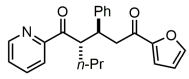
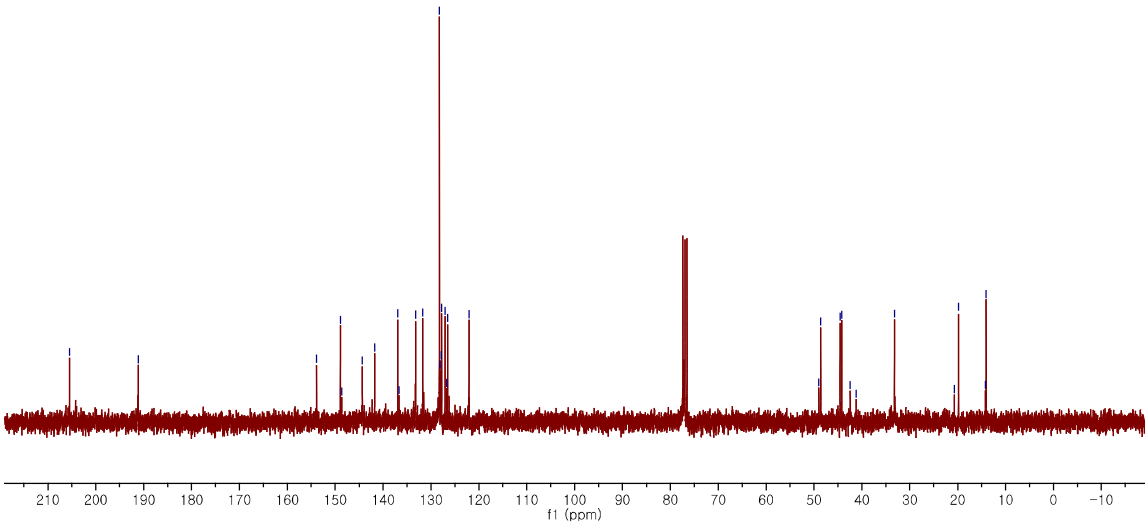


Table 5, (*S*,*S*)-**3ap**
^{13}C NMR (75 MHz, $CDCl_3$)
3.3:1 dr



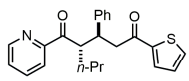
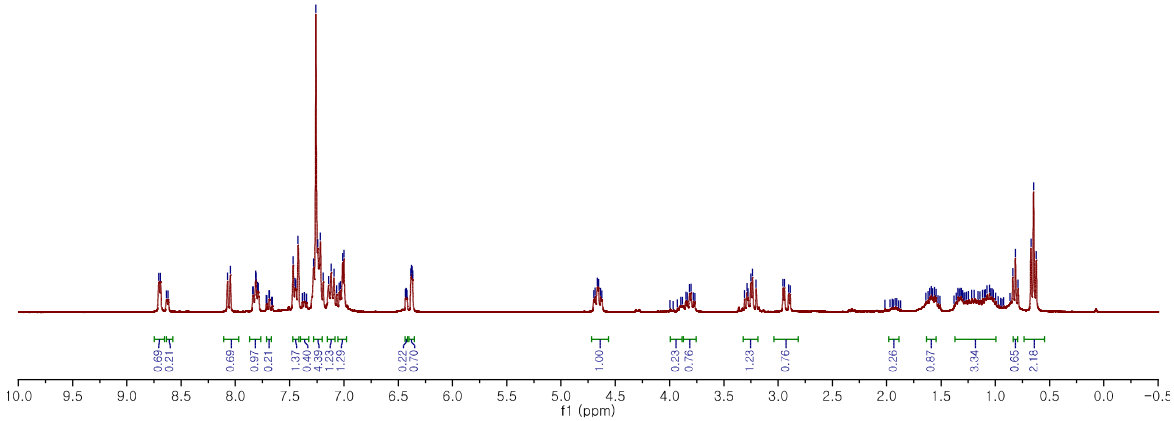


Table 5, (*S*,*S*)-**3aq**
^{1}H NMR (300 MHz, $CDCl_3$)
3.3:1 dr



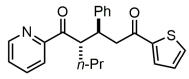
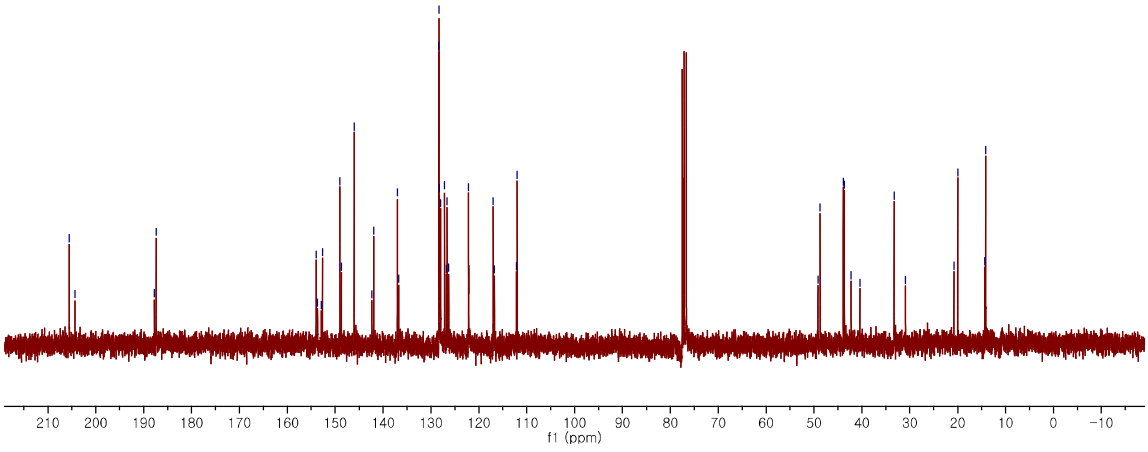


Table 5, (*S*,*S*)-**3aq**
^{13}C NMR (75 MHz, $CDCl_3$)
3.3:1 dr



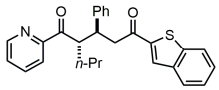
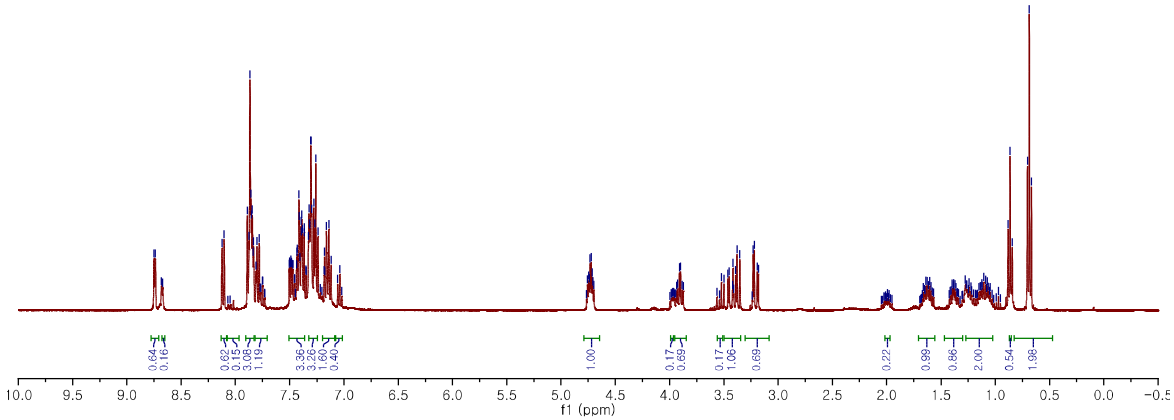


Table 5, (*S*,*S*)-**3ar**
^{1}H NMR (400 MHz, $CDCl_3$)
4.0:1 dr



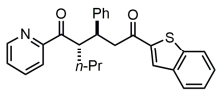


Table 5, (*S*,*S*)-**3ar**
^{13}C NMR (101 MHz, $CDCl_3$)
4.0:1 dr

XI. References

1. (a) G. Zhang, C. Zhu, D. Liu, J. Pan, J. Zhang, D. Hu and B. Song, Solvent-Free Enantioselective Conjugate Addition and Bioactivities of Nitromethane to Chalcone Containing Pyridine, *Tetrahedron*, 2017, **73**, 129; (b) M. Egi, M. Umemura, T. Kawai and S. Akai, Heteropoly Compound Catalyzed Synthesis of Both *Z*- and *E*-*α*,*β*-Unsaturated Carbonyl Compounds, *Angew. Chem., Int. Ed.*, 2011, **50**, 12197.
2. H. Yang, N. Huo, P. Yang, H. Pei, H. Lv and X. Zhang, Rhodium Catalyzed Asymmetric Hydrogenation of 2-Pyridine Ketones, *Org. Lett.,* 2015, **17**, 4144.
3. D. A. Sable, A. Gholap, S. P. Kommyreddy, D. J. Fartade, S. J. Gharpure, C. Schulzke and A. R. Kapdi, Heteroatom-Assisted Regio- and Stereoselective Palladium-Catalyzed Carboxylation of 9-Allyl Adenine, *J. Org. Chem.,* 2022, **87**, 12574.
4. SMART, SAINT and SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2016.
5. G. M. Sheldrick, SADABS v 2.03, University of Göttingen, Germany, 2002.
6. SHELXTL v 6.14; Bruker AXS, Inc: Madison, Wisconsin, USA, 2000.
7. F. Neese, F. Wennmohs, U. Becker and C. Riplinger, The ORCA Quantum Chemistry Program Package, *J. Chem. Phys.*, 2020, **152**, 224108.
8. J.-D. Chai and M. Head-Gordon, Systematic Optimization of Long-Range Corrected Hybrid Density Functionals, *J. Chem. Phys.*, 2008, **128**, 084106.
9. (a) E. Caldeweyher, C. Bannwarth and S. Grimme, Extension of the D3 Dispersion Coefficient Model, *J. Chem. Phys.*, 2017, **147**, 034112; (b) E. Caldeweyher, S. Ehlert, A. Hansen, H. Neugebauer, S. Spicher, and C. Bannwarth and S. Grimme, A Generally Applicable Atomic-Charge Dependent London Dispersion Correction, *J. Chem. Phys.*, 2019, **150**, 154122; (c) E. Caldeweyher, J.-M. Mewes, S. Ehlert and S. Grimme, Extension and Evaluation of the D4 London-Dispersion Model for Periodic Systems, *Phys. Chem. Chem. Phys.*, 2020, **22**, 8499.
10. F. Weigend and R. Ahlrichs, Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.
11. V. Barone and M. Cossi, Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model, *J. Phys. Chem. A*, 1998, **102**, 1995.
12. R. Izsák and F. Neese, An Overlap Fitted Chain of Spheres Exchange Method, *J. Chem. Phys.*, 2011, **135**, 144105.
13. F. Weigend, Accurate Coulomb-Fitting Basis Sets for H to Rn, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057.
14. E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-Gracía, A. J. Cohen and W. Yang, Revealing Noncovalent Interactions, *J. Am. Chem. Soc.,* 2010, **132**, 6498.
15. T. Lu and F. Chen, Multiwfn: A Multifunctional Wavefunction Analyzer, *J. Comput. Chem.*, 2012, **33**, 580.
16. W. Humphrey, A. Dalke, and K. Schulten, VMD: Visual Molecular Dynamics, *J. Molec. Graphics*, 1996, **14**, 33.
17. C. Y. Legault, Université de Sherbrooke, 2020, (http://www.cylview.org).