Supporting Information:

Bifunctional AgOAc Catalyzed Asymmetric [3+2] Cycloaddition of Azomethine Ylides

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1. General Procedure for the synthesis of α -iminoesters.

The α -iminoesters are prepared according to the procedure reported by Zhang's group¹. To a suspension of glycine methyl ester hydrochloride (1.1 equiv) and magnesium sulfate (2.0 equiv) in CH_2Cl_2 was added triethylamine (1.1 equiv). This solution was stirred at room temperature for 1 h. The aldehyde (1.0 equiv) was added and the reaction stirred at room temperature overnight. The magnesium sulfate was removed by filtration and the filtrate was washed once with H_2O . The aqueous phase was extracted once with CH_2Cl_2 and the combined organic layers were washed with brine. The organic phase was dried over Na_2SO_4 , filtered and concentrated. Most products could be used directly for the cycloaddition reactions. Further purification can be obtained *via* recrystallization from ethanol.

2. Synthesis of chiral ferrocenyloxazoline derived ligands.

Ligands **1a-1e**, **2**, **3a-3c** are synthesized following the known literature procedure². **3d** is synthesized by slightly modified literature procedure^{2a}.

(*S,S*)-**3a**: Ar = 4-MeOC₆H₄
(*S,S*)-**3b**: Ar = 3,5-Me₂C₆H₃
(*S,S*)-**3c**: Ar = 3,5-(CF₃)₂C₆H₃
(*S,S*)-**3d**: Ar = 4-CF₃C₆H₄

A stirred solution of **11** (345 mg, 1 mmol) and TMEDA (0.2 mL, 1.3 mmol) in Et_2O (10 mL) under nitrogen was cooled to -78°C resulting in the formation of a yellow precipitate. To this mixture was added dropwise $n\text{-BuLi}$ (0.52 mL, 1.3 mmol), the reaction mixture darkening to red/brown. After stirring at -78°C for 2 h, the Schlenk tube was transferred to an ice bath and stirring maintained for a further 15 min. The reaction mixture was then cooled to -78°C again. To the reaction mixture was added (4-CF₃C₆H₄)₂PCl (506 mg, 1.4 mmol) and the reaction mixture was maintained at -78°C for 1.5 h. Then the reaction mixture was quenched with sat. NaHCO_3 (10 mL) and diluted with ether (10 mL). The two layers were separated and the aqueous phase was extracted with Et_2O (10 mL). The organics were combined, dried (MgSO_4), filtered and evaporated. The crude product was purified by column chromatography to afford **3d** 212 mg (32%) of an orange solid. $[\alpha]_D^{22} = -143.8$ (*c* 0.96, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3): δ 7.49-7.66 (m, 6H),

7.19-7.27 (m, 7H), 5.03 (s, 1H), 4.43 (s, 1H), 4.28-4.40 (m, 1H), 4.17-4.23 (m, 1H), 4.18 (s, 5H), 3.75 (t, $J = 7.8$ Hz, 1H), 3.61 (s, 1H), 3.07 (dd, $J = 13.8, 5.0$ Hz, 1H), 2.55 (dd, $J = 13.6, 8.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 42.2, 68.3, 71.6, 72.1, 73.7, 74.4, 76.1 (d, $J_{\text{P-C}} = 17.7$), 76.4 (d, $J_{\text{P-C}} = 14.3$), 125.5, 125.7, 127.1, 129.1, 130.1, 130.6, 130.9, 131.8, 132.1, 133.0, 133.1, 135.9, 136.1, 138.5, 143.3, 143.5, 145.0, 145.2, 165.9; ^{31}P NMR (162 MHz, CDCl_3): δ -17.1; HRMS Calculated for $\text{C}_{34}\text{H}_{27}\text{NOF}_6\text{PFe}$ (M+1) 666.1078, found 666.1129.

Synthesis of ligand 3a: It is synthesized following the literature procedure^{2a}. $[\alpha]_{\text{D}}^{22} = -89.2$ (c 0.82, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3): δ 7.40-7.44 (m, 2H), 7.12-7.26 (m, 7H), 6.91 (d, $J = 8.4$ Hz, 2H), 6.81 (d, $J = 8.3$ Hz, 2H), 4.97 (s, 1H), 4.38 (t, $J = 2.5$ Hz, 1H), 4.28-4.32 (m, 1H), 4.18-4.23 (m, 1H), 4.19 (s, 5H), 3.82 (s, 3H), 3.77 (s, 3H), 3.68 (d, $J = 1.1$ Hz, 1H), 3.64 (t, $J = 7.9$ Hz, 1H), 3.09 (dd, $J = 13.7, 4.8$ Hz, 1H), 2.34 (dd, $J = 13.7, 9.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 42.3, 55.7, 55.8, 68.1, 71.4, 72.4, 72.8, 74.7, 75.3, 80.5 (d, $J_{\text{P-C}} = 14.3$), 114.3, 114.4, 114.5, 127.0, 129.1, 129.8, 131.6, 134.3, 134.5, 136.7, 136.9, 138.7, 160.2, 161.0, 167.0; ^{31}P NMR (162 MHz, CDCl_3): δ -20.2; HRMS Calculated for $\text{C}_{34}\text{H}_{33}\text{NO}_3\text{PFe}$ (M+1) 590.1542, found 590.1502.

Synthesis of ligand 3b: It is synthesized following the literature procedure^{2a}. $[\alpha]_{\text{D}}^{22} = -72.1$ (c 0.86, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3): δ 7.08-7.33 (m, 7H), 7.01 (s, 1H), 6.90 (s, 1H), 6.83 (d, $J = 8.0$ Hz, 2H), 4.96 (s, 1H), 4.38 (t, $J = 2.5$ Hz, 1H), 4.27-4.30 (m, 1H), 4.16-4.20 (m, 1H), 4.19 (s, 5H), 3.69 (s, 1H), 3.60 (t, $J = 7.8$ Hz, 1H), 3.10 (dd, $J = 13.6, 4.7$ Hz, 1H), 2.33 (s, 6H), 2.19-2.29 (m, 1H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 22.0, 42.4, 68.2, 71.4 (d, $J_{\text{P-C}} = 7.9$), 72.4, 72.5, 74.8, 75.7, 79.8 (d, $J_{\text{P-C}} = 14.3$), 127.0, 129.1, 129.8, 130.4, 130.7, 130.9, 131.4, 133.1, 133.3, 137.9, 138.1, 138.2, 138.4, 138.6, 138.9, 139.7, 139.8, 167.1; ^{31}P NMR (162 MHz, CDCl_3): δ -16.5; HRMS Calculated for $\text{C}_{36}\text{H}_{37}\text{NOPFe}$ (M+1) 586.1957, found 586.1939.

Synthesis of ligand 3c: It is synthesized following the literature procedure^{2a}. $[\alpha]_{\text{D}}^{22} = -143.0$ (c 1.39, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3): δ 7.90-7.95 (m, 3H), 7.80 (s, 1H), 7.61 (d, $J = 6.1$ Hz, 2H), 7.21-7.34 (m, 5H), 5.03 (m, 1H), 4.47 (t, $J = 2.5$ Hz, 1H), 4.21-4.27 (m, 1H), 4.18 (s, 5H), 3.93-3.95 (m, 1H), 3.50 (d, $J = 1.1$ Hz, 1H), 2.99 (m, 1H), 2.71 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 42.3, 68.5, 71.4, 71.7, 72.1, 72.4, 73.4, 74.1 (d, $J_{\text{P-C}} = 16.6$), 74.5 (d, $J_{\text{P-C}} = 14.1$), 76.4 (d, $J_{\text{P-C}} = 18.5$), 122.5, 123.1, 123.9, 125.2, 127.2, 129.0, 130.3, 131.8, 132.2, 132.3, 132.7, 132.9, 133.1, 134.9, 135.1, 138.5, 142.0, 142.2, 142.8, 143.0, 165.0; ^{31}P NMR (162 MHz, CDCl_3): δ -15.3; HRMS Calculated for $\text{C}_{36}\text{H}_{25}\text{NOF}_{12}\text{PFe}$ (M+1) 802.0826, found 802.0863.

3. General Procedure for the AgOAc-Catalyzed [3+2] Cycloaddition Reaction.

Ligand (0.0075 mmol) and AgOAc (1.2 mg, 0.007 mmol) were placed in a dried Schlenk tube under a nitrogen atmosphere and Et_2O (1.0 mL) was added. The mixture was stirred at room temperature for about 1 h. After it was cooled to the indicated temperature, imine substrate (0.23 mmol) was added as a solution in Et_2O (0.5 mL) followed by the dipolarophile (0.45 mmol). Upon consumption of the limiting reagent, the reaction was either quenched with saturated ammonium chloride solution or isolated by silica gel chromatography directly.

Progress of the Ag-catalyzed [3+2] cycloaddition reaction was typically monitored by TLC analysis. Absolute configurations were determined by correlation to literature optical rotation values where indicated.

Table 1S. The effect of S/C on enantioselectivity and conversion of cycloaddition of **4** with dimethyl maleate^a

Entry	S/C	Temp. (°C)	Time (h)	Yield (%) ^b	Ee (%) ^c
1	33	0	0.5	98	94
2	33	-25	2	88	98
3	100	0	0.5	93	94
4	100	-25	2	87	98
5	300	0	8.5	84	94

^a Conditions: iminoester (1.0 equiv), dimethyl maleate (1.5 equiv), Et₂O (1.5 mL). ^b Isolated yields by silica gel chromatography. ^c Determined by HPLC.

Table 2S. AgOAc catalyzed cycloaddition of **6a** with other dipolarophile substrates^a

Entry	Dipolarophile	Time (h)	Product	Ee (%) ^c	Yield (%) ^b
1		3	8	93	98
2 ^d		20	9	88	97
3		3	10	89	96

^a Conditions: **6a** (1.0 equiv), dipolarophile (1.5 equiv), AgOAc (3 mol %), ligand **3d** (3.3 mol %), Et₂O (1.5 mL) at -25 °C, unless indicated otherwise. ^b Isolated yield by silica gel chromatography. ^c Enantiomeric excess determined by HPLC. ^d reacted at 0 °C.

(2S,3R,4R,5R)-2-carboethoxy-3,4-dicarbomethoxy-5-(4-chlorophenyl)pyrrolidine (5): 98% *ee*, $[\alpha]_D^{20} = 62.7$ (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.30 (s, 4H), 4.46 (d, *J* = 6.8 Hz, 1H), 4.23-4.29 (m, 2H), 4.13 (d, *J* = 8.6 Hz, 1H), 3.70 (s, 3H), 3.67-3.72 (m, 1H), 3.52-3.58 (m, 1H), 3.27 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 14.8, 51.4, 52.1, 52.7, 53.0, 62.1, 63.0, 65.3, 129.0, 129.1, 134.2, 136.6, 171.1, 171.3, 171.4; HRMS Calculated for C₁₇H₂₁NO₆Cl (M+1) 370.1052, found 370.1030; HPLC (Chiralpak AS-H column, *i*-PrOH/hexane 50/50, detector: 205 nm, 0.8 mL/min, *t*_r = 8.3 and 23.5 min).

(2S,3R,4R,5R)-2, 3, 4-tricarbomethoxy-5-phenylpyrrolidine (7a)³: colorless solid, 97% *ee*, $[\alpha]_D^{21} = 71.7$ (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.28-7.34 (m, 5H), 4.48 (d, *J* = 7.2 Hz, 1H), 4.16 (d, *J* = 8.8 Hz, 1H), 3.81 (s, 3H), 3.70-3.75 (m, 1H), 3.69 (s, 3H), 3.56-3.60 (m, 1H), 3.23 (s, 3H). HPLC (Chiralpak AS-H column, *i*-PrOH/hexane 50/50, detector: 205 nm, 0.8 mL/min, *t*_r =

7.7 and 17.1 min). Literature¹ $[\alpha]_D = 64.7$ (c 1.07, CH₂Cl₂).

(2S,3R,4R,5R)-2,3,4-tricarbomethoxy-5-(4-methoxyphenyl)pyrrolidine (7b)⁴: colorless solid, 98% *ee*, $[\alpha]_D^{20} = 76.7$ (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.25 (d, *J* = 8.4 Hz, 2H), 6.84 (m, 2H), 4.43 (d, *J* = 7.2 Hz, 1H), 4.13 (d, *J* = 8.8 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.66-3.70 (m, 1H), 3.68 (s, 3H), 3.50-3.54 (m, 1H), 3.27 (s, 3H). HPLC (Chiralpak AS-H column, *i*-PrOH/hexane 50/50, detector: 205 nm, 0.8 mL/min, *t*_r = 17.3 and 35.8 min). Literature¹ $[\alpha]_D = 60.6$ (c 1.03, CH₂Cl₂).

(2S,3R,4R,5R)-2,3,4-tricarbomethoxy-5-(4-chlorophenyl)pyrrolidine (7c)¹: colorless solid, 97% *ee*, $[\alpha]_D^{20} = 76.8$ (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.30 (s, 4H), 4.45 (d, *J* = 7.2 Hz, 1H), 4.16 (d, *J* = 8.8 Hz, 1H), 3.80 (s, 3H), 3.67-3.70 (m, 1H), 3.68 (s, 3H), 3.55-3.58 (m, 1H), 3.28 (s, 3H). HPLC (Chiralpak AS-H column, *i*-PrOH/hexane 50/50, detector: 205 nm, 0.8 mL/min, *t*_r = 16.3 and 26.6 min). Literature¹ $[\alpha]_D = 55.6$ (c 1.09, CH₂Cl₂).

(2S,3R,4R,5R)-2,3,4-tricarbomethoxy-5-(4-florophenyl)pyrrolidine (7d)¹: colorless solid, 97% *ee*, $[\alpha]_D^{21} = 73.6$ (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.31-7.36 (m, 2H), 6.99-7.03 (m, 2H), 4.47 (d, *J* = 7.2 Hz, 1H), 4.15 (d, *J* = 8.8 Hz, 1H), 3.80 (d, *J* = 6.0 Hz, 3H), 3.69-3.73 (m, 1H), 3.69 (s, 3H), 3.54-3.58 (m, 1H), 3.25 (d, *J* = 6.0 Hz, 3H). HPLC (Chiralpak AS-H column, *i*-PrOH/hexane 50/50, detector: 205 nm, 0.8 mL/min, *t*_r = 8.7 and 14.6 min). Literature¹ $[\alpha]_D = 62.4$ (c 1.22, CH₂Cl₂).

(2S,3R,4R,5R)-2,3,4-tricarbomethoxy-5-(4-cynaophenyl)pyrrolidine (7e)¹: colorless solid, 97% *ee*, $[\alpha]_D^{21} = 74.4$ (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 4.53 (d, *J* = 7.2 Hz, 1H), 4.18 (d, *J* = 8.8 Hz, 1H), 3.81 (s, 3H), 3.72-3.77 (m, 1H), 3.70 (s, 3H), 3.61-3.65 (m, 1H), 3.27 (s, 3H). HPLC (Chiralpak AD-H column, *i*-PrOH/hexane 50/50, detector: 205 nm, 0.8 mL/min, *t*_r = 14.3 and 25.7 min). Literature¹ $[\alpha]_D = 59.1$ (c 1.13, CH₂Cl₂).

(2S,3R,4R,5R)-2,3,4-tricarbomethoxy-5-(2-chlorophenyl)pyrrolidine (7f)¹: colorless oil, 97% *ee*, $[\alpha]_D^{23} = 141.8$ (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.20-7.28 (m, 2H), 4.75 (d, *J* = 6.8 Hz, 1H), 4.14 (d, *J* = 9.2 Hz, 1H), 3.86-3.90 (m, 1H), 3.83 (s, 3H), 3.75-3.80 (m, 1H), 3.66 (s, 3H), 3.18 (s, 3H). HPLC (Chiralpak AS-H column, *i*-PrOH/hexane 50/50, detector: 205 nm, 0.8 mL/min, *t*_r = 9.1 and 19.2 min). Literature¹ $[\alpha]_D = 116.2$ (c 1.04, CH₂Cl₂).

(2S,3R,4R,5R)-2,3,4-tricarbomethoxy-5-(2-methylphenyl)pyrrolidine (7g)¹: colorless oil, 98% *ee*, $[\alpha]_D^{22} = 121.8$ (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.37 (d, *J* = 6.9 Hz, 1H), 7.12-7.20 (m, 3H), 4.61 (dd, *J* = 7.0, 1.7 Hz, 1H), 4.11 (dd, *J* = 8.6, 1.9 Hz, 1H), 3.83 (d, *J* = 2.3 Hz, 3H), 3.64-3.76 (m, 2H), 3.68 (d, *J* = 1.6 Hz, 3H), 3.12 (d, *J* = 2.2 Hz, 3H), 2.35 (d, *J* = 1.8 Hz, 3H). HPLC (Chiralpak AS-H column, *i*-PrOH/hexane 50/50, detector: 205 nm, 0.8 mL/min, *t*_r = 7.7 and 19.7 min). Literature¹ $[\alpha]_D = 100.1$ (c 1.12, CH₂Cl₂).

(2S,3R,4R,5R)-2,3,4-tricarbomethoxy-5-(1-naphthyl)pyrrolidine (7h)¹: colorless solid, 98% *ee*, $[\alpha]_D^{20} = 242.7$ (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 6.8 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.44-7.53 (m, 3H), 5.19 (s, 1H), 4.22-4.27 (m, 1H), 3.84-3.87 (m, 5H), 3.65 (s, 3H), 2.95 (s, 3H). HPLC (Chiralpak AS-H column, *i*-PrOH/hexane 50/50, detector: 205 nm, 0.8 mL/min, *t*_r = 8.7 and 31.1 min). Literature¹ $[\alpha]_D = 199.8$ (c 1.12, CH₂Cl₂).

(2S,3R,4R,5R)-2,3,4-tricarbomethoxy-5-(2-naphthyl)pyrrolidine (7i)⁵: colorless solid, 98% *ee*, $[\alpha]_D^{22} = 60.7$ (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.79-7.84 (m, 4H), 7.42-7.49

(m, 3H), 4.62 (d, $J = 6.6\text{Hz}$, 1H), 4.22 (d, $J = 9.0\text{Hz}$, 1H), 3.88 (s, 3H), 3.76-3.84 (m, 1H), 3.69 (s, 3H), 3.65-3.69 (m, 1H), 3.16 (s, 3H). HPLC (Chiralpak AS-H column, *i*-PrOH/hexane 50/50, detector: 205 nm, 0.8 mL/min, $t_r = 15.9$ and 38.4 min). Literature¹ $[\alpha]_D = 46.4$ (c 1.12, CH₂Cl₂).

(2S,3R,4R,5R)-2,3,4-tricarbomethoxy-5-(3-pyridinyl)pyrrolidine (7j)¹: colorless solid, 93% *ee*, $[\alpha]_D^{20} = 64.9$ (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 8.58 (s, 1H), 8.52 (d, $J = 4.0\text{Hz}$, 1H), 7.76 (d, $J = 8.0\text{Hz}$, 1H), 7.24-7.27 (m, 1H), 4.52 (s, 1H), 4.14 (m, 1H), 3.80 (s, 3H), 3.72-3.74 (m, 1H), 3.69 (s, 3H), 3.60-3.64 (m, 1H), 3.27 (s, 3H). HPLC (Chiralpak AS-H column, *i*-PrOH/hexane 50/50, detector: 205 nm, 0.8 mL/min, $t_r = 10.8$ and 12.8 min). Literature¹ $[\alpha]_D = 61.0$ (c 1.05, CH₂Cl₂).

(2S,3R,4R,5S)-2,3,4-tricarbomethoxy-5-isopropylpyrrolidine (7k)¹: colorless oil, 88% *ee*, $[\alpha]_D^{22} = 16.6$ (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 4.09 (d, $J = 10.1\text{Hz}$, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 3.67 (s, 3H), 3.55-3.60 (m, 1H), 3.19-3.21 (m, 1H), 2.72-2.75 (m, 1H), 1.65 (m, 1H), 1.09 (d, $J = 6.6\text{Hz}$, 1H), 0.97 (d, $J = 6.6\text{Hz}$, 1H). GC (Chiral Select 1000, 160 °C, 1.0 ml / min, $t_r = 20.9$ and 22.3 min). Literature¹ $[\alpha]_D = 14.8$ (c 1.17, CH₂Cl₂).

(2S,3R,4R,5R)-methyl-4,7-diphenyl-6,8-dioxo-3,7-diazabicyclo [3.3.0] octane-2-carboxylate (8)⁶: colorless solid, 93% *ee*, $[\alpha]_D^{23} = 92.9$ (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.30-7.45 (m, 8H), 7.12-7.14 (m, 2H), 4.56 (d, $J = 8.8\text{Hz}$, 1H), 4.10 (m, 1H), 3.85 (s, 3H), 3.66-3.70 (m, 1H), 3.52-3.54 (m, 1H). HPLC (Chiralpak AS-H column, *i*-PrOH/hexane 70/30, detector: 205 nm, 0.6 mL/min, $t_r = 17.5$ and 39.6 min). Literature¹ $[\alpha]_D = 91.1$ (c 1.22, CH₂Cl₂).

(2S,4S,5R)-5-phenyl-pyrrolidine-2,4-dicarboxylic-4-tert-butyl ester-2-methyl ester (9)⁷: colorless solid, 88% *ee*, $[\alpha]_D^{23} = 26.1$ (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.24-7.36 (m, 5H), 4.47 (d, $J = 7.6\text{Hz}$, 1H), 3.95 (t, $J = 8.4\text{Hz}$, 1H), 3.81 (s, 3H), 3.26 (m, 1H), 2.41-2.47 (m, 1H), 2.29-2.34 (m, 1H), 1.02 (s, 9H). HPLC (Chiralpak AS-H column, *i*-PrOH/hexane 20/80, detector: 205 nm, 0.8 mL/min, $t_r = 6.6$ and 8.9 min). Literature¹ $[\alpha]_D = 33.1$ (c 1.11, CH₂Cl₂).

(2S,3S,4R,5R)-2,3,4-tricarbomethoxy-5-phenylpyrrolidine (10)³: colorless oil, 89% *ee*, $[\alpha]_D^{22} = 19.2$ (c 1.0, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ 7.24-7.36 (m, 5H), 4.66 (d, $J = 8.0\text{Hz}$, 1H), 4.21 (d, $J = 7.6\text{Hz}$, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.64-3.66 (m, 1H), 3.56-3.60 (m, 1H), 3.21 (s, 3H). HPLC (Chiralcel OJ-H column, *i*-PrOH/hexane 50/50, detector: 205 nm, 0.8 mL/min, $t_r = 13.7$ and 19.9 min). Literature¹ $[\alpha]_D = 9.04$ (c 1.54, CH₂Cl₂).

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¹³C NMR (WZ-1-63A in CDCl₃)

Applied Biosystems Mariner System 5303

Mariner Spec /18.69 (T 0.29:1.19) -2.26 (T -0.29:1.19) -66.86 (T -0.00:0.00) ASC => MCTBP = 370.1, 253]

```
--> Mariner System State <--
Instrument State      ON
Ion Polarity         POS
Auxillary Gas        ON
Curtain Gas          ON
Nebulizer Gas        ON
Calibration Constant A 5.0255052E-007
Calibration Constant B 68.020555
TDC Deadtime         10
--> Source Settings <--
Spray Tip Potential   4988.67
SCIEX Heater         300.05
--> API Interface Settings <--
Nozzle Potential      90.09
Skimmer 1 Potential   10.01
Quadrupole DC Potential 6.01
Deflection Voltage     0.29
Einzel Lens Potential -25.00
Quadrupole RF Voltage  999.76
Quadrupole Temperature 140.01
Nozzle Temperature    140.01
--> Analyzer Settings <--
Push Pulse Potential   499.97
Pull Pulse Potential   198.94
Pull Bias Potential     10.00
Acceleration Potential 3999.94
Reflector Potential    1549.99
Detector Voltage       1750.06
--> Spectrum Acquisition Settings <--
Seconds Per Spectrum   1.00
Ion Count Threshold     0.00
First Mass             100.00
Last Mass              1000.00
Accumulate Spectra     OFF
Standby at End of Acquisition OFF
--> Centroid Spectra Settings <--
Centroid Spectra       OFF
--> System Settings <--
Gas Control Mode        Manual
Syringe Pump Mode       Disabled
Min Analyzer Mass       40.00
Max Analyzer Mass       4000.00
```

Acquired: Jun 27 11:32:00 2005
Mariner Mass Spectrum
E:\WF2\ZW\05-06-27\WZ-4-63A-001.dat

Printed: 12:16, June 27, 2005

3a

¹³C NMR (WZ-2-17A in CDCl₃)

Applied Biosystems Mariner System 5303

Mariner Spec /133:147 (T /2.29:2.54) -1.61 (T /2.29:2.54) -149:178 (T /-0.00:0.00) ASC => MC(BP = 590.2, 274)

```
--> Mariner System State <--
Instrument State      ON
Ion Polarity         POS
Auxiliary Gas        ON
Curtain Gas          ON
Nebulizer Gas        ON
Calibration Constant A 5.0255052E-007
Calibration Constant B 68.020555
TDC Deadtime         10
--> Source Settings <--
Spray Tip Potential   4988.67
SCIEX Heater         300.05
--> API Interface Settings <--
Nozzle Potential      90.09
Skimmer 1 Potential   10.01
Quadrupole DC Potential 6.01
Deflection Voltage     0.29
Einzel Lens Potential -25.00
Quadrupole RF Voltage 999.76
Quadrupole Temperature 140.01
Nozzle Temperature    140.01
--> Analyzer Settings <--
Push Pulse Potential   499.97
Pull Pulse Potential   198.94
Pull Bias Potential    10.00
Acceleration Potential 3999.94
Reflector Potential    1549.99
Detector Voltage       1750.06
--> Spectrum Acquisition Settings <--
Seconds Per Spectrum   1.00
Ion Count Threshold     0.00
First Mass             100.00
Last Mass              1000.00
Accumulate Spectra     OFF
Standby at End of Acquisition OFF
--> Centroid Spectra Settings <--
Centroid Spectra       OFF
--> System Settings <--
Gas Control Mode       Manual
Syringe Pump Mode      Disabled
Min Analyzer Mass       40.00
Max Analyzer Mass      4000.00
```

Acquired: Jun 27 11:23:00 2005
Mariner Mass Spectrum
E:\WF2\ZW\05-06-27\WZ-2-17A-001.dat

Printed: 11:57, June 27, 2005

Applied Biosystems Mariner System 5303

Mariner Spec /46.56 (T -0.78;1.13) -5.33 (T -0.78;1.13) -54.104 (T -0.00;0.00) ASC=>MC(RP = 586.2, 103)

```
--> Mariner System State <--
Instrument State      ON
Ion Polarity         POS
Auxiliary Gas        ON
Curtain Gas          ON
Nebulizer Gas        ON
Calibration Constant A 5.0255052E-007
Calibration Constant B 68.020555
TDC Deadtime         10
--> Source Settings <--
Spray Tip Potential   4988.67
SCIEX Heater         300.05
--> API Interface Settings <--
Nozzle Potential      90.09
Skimmer 1 Potential  10.01
Quadrupole DC Potential 6.01
Deflection Voltage    0.29
Einzel Lens Potential -25.00
Quadrupole RF Voltage 999.76
Quadrupole Temperature 140.01
Nozzle Temperature    140.01
--> Analyzer Settings <--
Push Pulse Potential  499.97
Pull Pulse Potential  198.94
Pull Bias Potential   10.00
Acceleration Potential 3999.94
Reflector Potential   1549.99
Detector Voltage      1750.06
--> Spectrum Acquisition Settings <--
Seconds Per Spectrum  1.00
Ion Count Threshold    0.00
First Mass             100.00
Last Mass              1000.00
Accumulate Spectra     OFF
Standby at End of Acquisition OFF
--> Centroid Spectra Settings <--
Centroid Spectra      OFF
--> System Settings <--
Gas Control Mode       Manual
Syringe Pump Mode      Disabled
Min Analyzer Mass      40.00
Max Analyzer Mass      4000.00
```

Acquired: Jun 27 11:26:00 2005
Mariner Mass Spectrum
E:\WF2\ZW\05-06-27\WZ-2-17B-001.dat

Printed: 12:06, June 27, 2005

¹³C NMR (WZ-2-18 in CDCl₃)

Applied Biosystems Mariner System 5303

Mariner Spec (19.36 (T -0.31:0.61) -5.26 (T -0.31:0.61) -73.98 (T -0.00:0.00) ASC= >MC[B0] = 802.0, 172]

```
--> Mariner System State <--
Instrument State      ON
Ion Polarity          POS
Auxiliary Gas         ON
Curtain Gas           ON
Nebulizer Gas         ON
Calibration Constant A 5.0255052E-007
Calibration Constant B 68.020555
TDC Deadtime          10
--> Source Settings <--
Spray Tip Potential    4988.67
SCIEX Heater           300.05
--> API Interface Settings <--
Nozzle Potential       90.09
Skimmer 1 Potential    10.01
Quadrupole DC Potential 6.01
Deflection Voltage      0.29
Einzel Lens Potential  -25.00
Quadrupole RF Voltage   999.76
Quadrupole Temperature 140.01
Nozzle Temperature     140.01
--> Analyzer Settings <--
Push Pulse Potential    499.97
Pull Pulse Potential    198.94
Pull Bias Potential     10.00
Acceleration Potential  3999.94
Reflector Potential     1549.99
Detector Voltage        1750.06
--> Spectrum Acquisition Settings <--
Seconds Per Spectrum    1.00
Ion Count Threshold      0.00
First Mass               100.00
Last Mass               1000.00
Accumulate Spectra      OFF
Standby at End of Acquisition OFF
--> Centroid Spectra Settings <--
Centroid Spectra        OFF
--> System Settings <--
Gas Control Mode        Manual
Syringe Pump Mode       Disabled
Min Analyzer Mass       40.00
Max Analyzer Mass       4000.00
```

Acquired: Jun 27 11:28:00 2005
Mariner Mass Spectrum
E:\WF2\ZW\05-06-27\WZ-2-18-001.dat

Printed: 12:13, June 27, 2005

3d

¹³C NMR (WZ-2-36 in CDCl₃)

Applied Biosystems Mariner System 5303

Mariner Spec /15.31 (T /0.34/0.52) -3.20 (T /0.34/0.52) -49.100 (T /0.00/0.00) ASC => MCI(BP = 666.1, 154)

```
--> Mariner System State <--
Instrument State      ON
Ion Polarity         POS
Auxiliary Gas        ON
Curtain Gas          ON
Nebulizer Gas        ON
Calibration Constant A 5.0255052E-007
Calibration Constant B 68.020555
TDC Deadtime         10
--> Source Settings <--
Spray Tip Potential   4988.67
SCIEX Heater         300.05
--> API Interface Settings <--
Nozzle Potential      90.09
Skimmer 1 Potential   10.01
Quadrupole DC Potential 6.01
Deflection Voltage     0.29
Einzel Lens Potential -25.00
Quadrupole RF Voltage  999.76
Quadrupole Temperature 140.01
Nozzle Temperature    140.01
--> Analyzer Settings <--
Push Pulse Potential   499.97
Pull Pulse Potential   198.94
Pull Bias Potential    10.00
Acceleration Potential 3999.94
Reflector Potential    1549.99
Detector Voltage       1750.06
--> Spectrum Acquisition Settings <--
Seconds Per Spectrum   1.00
Ion Count Threshold     0.00
First Mass             100.00
Last Mass              1000.00
Accumulate Spectra     OFF
Standby at End of Acquisition OFF
--> Centroid Spectra Settings <--
Centroid Spectra      OFF
--> System Settings <--
Gas Control Mode       Manual
Syringe Pump Mode      Disabled
Min Analyzer Mass      40.00
Max Analyzer Mass      4000.00
```

Acquired: Jun 27 11:30:00 2005
Mariner Mass Spectrum
E:\WF2\ZW\05-06-27\WZ-2-36-001.dat

Printed: 12:15, June 27, 2005