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Asymmetric [3 + 2] Cycloaddition of Methyleneindolinones with *N,N′*-Cyclic Azomethine Imines Catalyzed by a *N,N′*-Dioxide–$Mg(OTf)_2$ Complex

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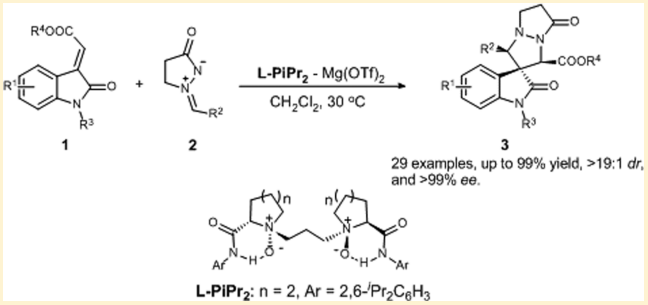
Supporting Information

ABSTRACT: A highly efficient chiral *N,N′*-dioxide–$Mg(OTf)_2$ catalyst system has been developed for the asymmetric 1,3-dipolar cycloaddition between methyleneindolinones and *N,N′*-cyclic azomethine imines. The desired pyrazolidine products with contiguous quaternary–tertiary stereocenters were obtained in up to 99% yields with up to 99% *ee* and >19:1 *dr* under mild reaction conditions.



INTRODUCTION

1,3-Dipolar cycloadditions (1,3-DCs) are among the most powerful tools for the construction of five-membered heterocycles.[1] Up to now, many 1,3-dipoles, such as nitrones,[2] azomethine ylides,[3] nitrile imines[4] and nitrile oxides,[5] have been developed for the cycloadditions. Among them, *N,N′*-cyclic azomethine imines, which were first reported in 1968, can afford useful pyrazolidine motifs by reacting with alkynes or olefins.[6,7] On the other hand, methyleneindolinones are useful structures in synthesizing spirooxindoles, which are valuable for accessing natural products and have attracted considerable attention.[8] The 1,3-DCs of *N,N′*-cyclic azomethine imines with methyleneindolinones can afford products with pyrazolide and spirooxindole structures, both of which are useful structural units in organic synthesis and may have practical use in pharmaceutical field.[9] In 2013, Wang developed a new chiral bis-phosphoric acid bearing triple axial chirality for the enantioselective 1,3-dipolar cycloaddition of *N,N′*-cyclic azomethine imines and methyleneindolinones, creating chiral spiro[pyrazolidin-3,3-oxindoles] in excellent yields and selectivities.[7q] Since the attractive structure might be beneficial for drug discovery, developing new efficient catalysts for this 1,3-dipolar cycloaddition is still helpful.

Chiral metal complex catalysts have shown promising catalytic abilities and potential applications in lab and industry synthesis. Alkaline earth metals are abundant, less toxic and less harmful to human beings, making them competitive to form chiral catalysts.[10,11] On the other hand, *N,N′*-dioxides are proved to have good ability in complexing with alkaline earth metals and have shown a promising ability in the field of catalytic asymmetric synthesis. Herein, we described our effort in developing a highly efficient chiral *N,N′*-dioxide–alkaline earth metal complex, the **L-PiPr$_2$** - $Mg(OTf)_2$,[12] for the asymmetric 1,3-DC reaction between methyleneindolinones and *N,N′*-cyclic azomethine imines, affording products with both spirooxindole and pyrazolidine structures and contiguous quaternary–tertiary stereocenters in up to 99% yield, >19:1 *dr*, and >99% *ee*.

RESULTS AND DISSCUSION

Initially, the 1,3-DC of (*E*)-*tert*-butyl 3-(2-methoxy-2-oxoethylidene)-2-oxoindoline-1-carboxylate (**1a**) with *N,N′*-cyclic azomethine imine (**2a**) was selected as model reaction to optimize the reaction conditions and the representative results are summarized in Table 1. At first, several alkaline metal salts complexing with **L-PiPr$_2$** derived from (*S*)-pipecolic acid were examined in CH_2Cl_2. The complexes of $Ca(OTf)_2$ and $Ba(ClO_4)_2$ both gave high dr values, but moderate yields and *ee* values (Table 1, entries 1–2). Excitingly, the complex of $Mg(OTf)_2$ could offer only one isomer in nearly quantitative yield (Table 1, entry 3). The anions of Mg(II) had no obvious effect on the reaction since the complex of $Mg(NTf_2)_2$ gave similar results with that of $Mg(OTf)_2$ (Table 1, entry 4). Then, the structure of ligand was tested. The chiral backbone of ligand had little effect on *dr* and *ee* and relatively obvious effect on yield. Both L-proline derived **L-PrPr$_2$** and L-ramipril derived **L-RaPr$_2$** gave lower yields (Table 1, entry 3 vs entries 5 and 6). On the contrary, the steric hindrance of the amide moiety affected the reaction greatly. Decreasing the steric hindrance

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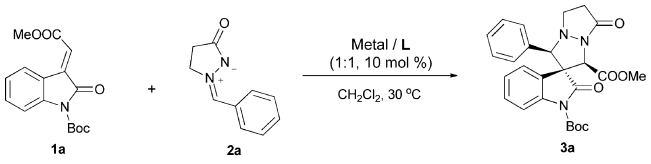
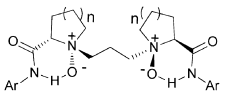
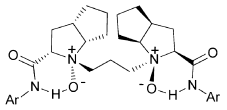
Table 1. Optimization of the Reaction Conditions





L-PiPr$_2$: n = 2, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$
L-PrPr$_2$: n = 1, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$
L-PiPh: n = 2, Ar = C$_6$H$_5$



L-RaPr$_2$: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$

entry[a]	metal	ligand	yield (%)[b]	*dr*	*ee* (%)[c]
1	$Ca(OTf)_2$	**L-PiPr$_2$**	45	15:1	66
2	$Ba(ClO_4)_2$	**L-PiPr$_2$**	38	19:1	63
3	$Mg(OTf)_2$	**L-PiPr$_2$**	99	>19:1	>99
4	$Mg(NTf_2)_2$	**L-PiPr$_2$**	99	19:1	99
5	$Mg(OTf)_2$	**L-PrPr$_2$**	90	>19:1	99
6	$Mg(OTf)_2$	**L-RaPr$_2$**	91	>19:1	98
7	$Mg(OTf)_2$	**L-PiPh**	76	19:1	75
8[d]	$Mg(OTf)_2$	**L-PiPr$_2$**	99	>19:1	99
9[e]	$Mg(OTf)_2$	**L-PiPr$_2$**	74	19:1	98

[a]Unless otherwise noted, the reactions were carried out with **1a** (0.1 mmol) and **2a** (0.1 mmol) in 1.0 mL of CH_2Cl_2, 10 mol % catalyst loading in N_2, at 30 °C for 48 h. [b]Isolated yield. [c]Determined by HPLC. [d]With 5 mol % catalyst loading. [e]With 1 mol % catalyst loading.

from isopropyl to hydrogen led to a dramatic decrease of yield and enantioselectivity (Table 1, entry 7). Delightedly, the catalyst loading could be decreased to 5 mol %, and the results were maintained (Table 1, entry 8). Further the yield decreased to 74%, when the catalyst loading were lowed to 1 mol % (Table 1, entry 9). Thus, the optimized experimental conditions were as follows: 5 mol % **L-PiPr$_2$**- $Mg(OTf)_2$ (1:1) in CH_2Cl_2 at 30 °C.

Under the optimal conditions, the scope of the reaction was examined and the results were summarized in Table 2. First, the scope of **2** was examined. Aryl R^2 with electron-donating or electron-withdrawing groups at *meta*- or *para*- positons on the *N*,*N*′-cyclic azomethine imines gave the corresponding products in excellent yields with high enantioselectivities (Table 2, entries 2−9). But R^2 with a substituent at the *ortho*- position gave lower yield and decreased enantioselectivity (Table 2, entry 10), which might be caused by the steric hindrance of the *ortho*- substituent with the catalyst. When R^2 were ring-fused naphthyl group, heteroaromatic thiophene group as well as furan group, the desired products could also be obtained in 71% to 99% yields with 10:1 to >19:1 *dr* and 90% to 99% *ee* (Table 2, entries 11−13).

Then, the scope of methyleneindolinones was determined. Substituent R^1 at different positions of the phenyl groups had little influence on the selectivity. All products were obtained in 90% to 99% *ee* (7:1 to >19:1 *dr*, Table 2, entries 14 to 23). To our delight, when R^2 equaled aliphatic cyclopentyl was also tolerant in the reaction system, giving desired **3ab** in 46% yield with 6:1 *dr* and 99% *ee* (Table 2, entry 24). At last, the ester group and the *N*-protecting group of methyleneindolinones were tested (Scheme 1). The results showed that the bulkier ester groups did not affect the *dr* and *ee*, but caused a decrease of yield. When the protecting group on the nitrogen atom of the amide was changed to ethyl ester group, the enantioselectivity was decreased to 80% *ee* (Scheme 1, **3aa**). The (*E*)-benzyl 3-(2-(*tert*-butoxy)-2-oxoethylidene)-2-oxoindoline-1-carboxylate, which is protected by -Cbz group, was also tested in the reaction system, and the desired product can be obtained with excellent yield (99%) and moderate enantioselectivity (49%) (Scheme 2, **3ac**). We think if the protecting group on the amide of the methyleneindolinones replaced from Boc to ethyl ester group or Cbz group, the steric hindrance of the proposed transition state would decrease when the methyleneindolinones coordinated with the catalyst to react with the *N*,*N*′-cyclic azomethine imine. The absolute configuration of **3t** was determined to be (1′*R*,2′*R*,3′*R*) by X-ray crystallographic analysis, and the others were assigned to be the same by comparing the Cotton effect of the CD spectra with that of **3t** (see Supporting Information).

To show the prospect of the methodology in synthesis, a gram-scale synthesis of **3a** was carried out (Scheme 2). 2.5 mmol of **1a** and **2a** were treated in the optimized reaction conditions, and the product **3a** was obtained in >99% yield (1.19g) with >19:1 *dr* and 98% *ee*.

To gain insight into the reaction mechanism, operando IR experiment of methyleneindolinone (**1a**) and *N*,*N*′-cyclic azomethine imine (**2a**) catalyzed by the **L-PiPr$_2$**-$Mg(OTf)_2$ was carried out (Scheme 3A, see Supporting Information for detail). The results clearly demonstrated that the amount of product increased with the consuming of starting materials. Since no intermediates were observed, the reaction may proceed in a concerted way. Besides, the operando IR experiment also gave some information about the interaction between the catalyst and the substrate **1a**. As shown in Scheme 3B, when $Mg(OTf)_2$ was added to the solution of ligand **L-PiPr$_2$**, the peak at 1674 cm^{-1}, which was caused by the ligand, decreased. Meanwhile, a peak at 1660 cm^{-1} appeared. This change indicated the complexation between the ligand and $Mg(OTf)_2$. After the addition of substrate **1a** (caused peak at 1640 cm^{-1}), a new peak at about 1635 cm^{-1} was formed gradually with disappearance of the catalyst (peak at 1660 cm^{-1}) and substrate **1a** (peak at 1640 cm^{-1}). This change indicated that there was an interaction between the catalyst and the substrate.

A nonlinear effect (NLE) experiment was investigated for the reaction system, by varying the *ee* value of the chiral ligand **L-PiPr$_2$** (Scheme 4). The relationship between the enantiomeric excess of the product **3a** and **L-PiPr$_2$** showed a weak negative nonlinear effect, which suggested that both monomeric and oligomeric species of the catalyst may exist in the reaction system, but the monomeric complex might function as the more active and effective catalyst.

The catalytic composition between substrate and the catalyst were also investigated by ESI-MS (Scheme 5). A mixture of ligand **L-PiPr$_2$**, $Mg(OTf)_2$ and **1a** (1:1:1) in CH_2Cl_2, displayed an ion at *m*/*z* 821.4166 ([**L-PiPr$_2$** + Mg^{2+} + OTf^-]$^+$ *m*/*z* calcd 821.3985), this result suggested that the **L-PiPr$_2$** coordinated with the $Mg(OTf)_2$ in a 1:1 ratio (see Supporting Information for detail). Another characteristic signal of [**L-PiPr$_2$** + Mg^{2+} + OTf^- + **1a**]$^+$ at *m*/*z* 1124.5394 (*m*/*z* calcd 1124.5092) was also observed, which suggested that the catalyst coordinated with **1a** in a 1:1 ratio.

On the basis of the operando IR, NLE and ESI-MS analysis, as well as our previous work[12d,e] and the absolute configuration of the products,[13] a possible transition-state model was proposed. As shown in Scheme 6, the ligand and the oxygen

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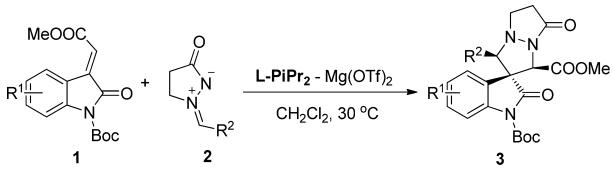
Table 2. Substrate Scope in the Asymmetric [3 + 2] Cycloaddition



Entry[a]	R^1	R^2	Yield (%)[b]	*dr*[c]	*ee* (%)[d]
1	H(**1a**)	C_6H_5(**2a**)	99 (**3a**)	>19 : 1	>99
2	H(**1a**)	4-MeC_6H_4(**2b**)	99(**3b**)	>19 : 1	97
3	H(**1a**)	3-$F_3C$$C_6H_4$(**2c**)	99(**3c**)	7 : 1	97
4	H(**1a**)	3-BrC_6H_4(**2d**)	82(**3d**)	>19 : 1	99
5	H(**1a**)	3,4-$Me_2C_6H_3$(**2e**)	54(**3e**)	10 : 1	99
6	H(**1a**)	4-BrC_6H_4(**2f**)	88(**3f**)	>19 : 1	99
7	H(**1a**)	4-FC_6H_4(**2g**)	91(**3g**)	>19 : 1	99
8	H(**1a**)	4-MeOC_6H_4(**2h**)	91 (**3h**)	>19 : 1	94
9	H(**1a**)	4-ClC_6H_4(**2i**)	75(**3i**)	>19 : 1	99
10	H(**1a**)	2-FC_6H_4(**2j**)	64 (**3j**)	10 : 1	50
11	H(**1a**)	1-Napthyl(**2k**)	71 (**3k**)	>19 : 1	99
12	H(**1a**)	 (**2l**)	90 (**3l**)	10 : 1	94
13	H(**1a**)	 (**2m**)	83 (**3m**)	15 : 1	90
14[e]	5-Cl(**1n**)	C_6H_5(**2a**)	82(**3n**)	>19 : 1	95
15[e]	5-F(**1o**)	C_6H_5(**2a**)	88(**3o**)	>19 : 1	96
16	5-Br(**1p**)	C_6H_5(**2a**)	91(**3p**)	>19 : 1	97
17	6-Br(**1q**)	C_6H_5(**2a**)	71(**3q**)	7 : 1	98
18	5,7-Me_2(**1r**)	C_6H_5(**2a**)	87 (**3r**)	>19 : 1	98
19	5-Me(**1s**)	C_6H_5(**2a**)	91(**3s**)	>19 : 1	99
20[f]	5-MeO(**1t**)	C_6H_5(**2a**)	88(**3t**)	>19 : 1	>99 (1'*R*,2'*R*,3'*R*)
21	6-Cl(**1u**)	C_6H_5(**2a**)	86(**3u**)	>19 : 1	99
22	5-F_3CO(**1v**)	C_6H_5(**2a**)	99(**3v**)	>19 : 1	95
23[e]	7-Br(**1w**)	C_6H_5(**2a**)	81(**3w**)	15 : 1	90
24	H(**1a**)	 (**2ab**)	46(**3ab**)	6 : 1	99

[a]Unless otherwise noted, the reactions were carried out with **1** (0.1 mmol) and **2** (0.1 mmol) in 1.0 mL of CH_2Cl_2, 5 mol % catalyst loading in N_2, at 30 °C for 48 h. [b]Isolated yield. [c]The diastereoselectivities of the products were detected by ^{1}H NMR. [d]Determined by HPLC. [e]Reaction time is 36 h. [f]The absolute configuration was determined by X-ray crystallographic analysis.

atoms of both amide and the *N*-Boc of the methyleneindolinone coordinated with the Mg(II) to form an octahedral complex (in Scheme 3B, the new peak at 1635 cm^{-1} may represent a feature peak of this complex). The *Si* face of the

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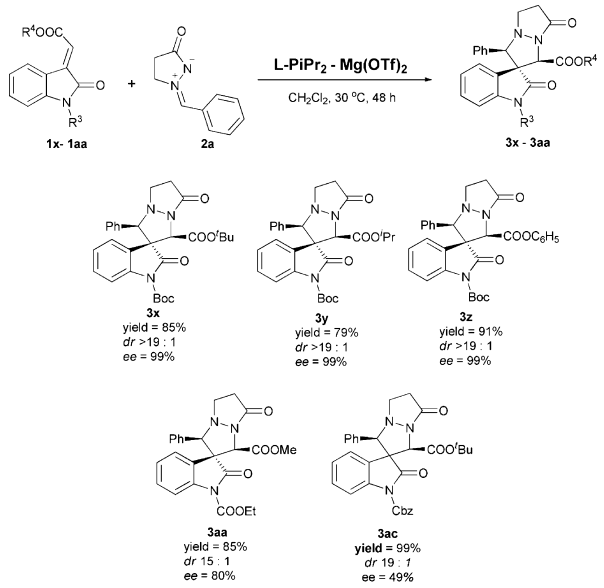
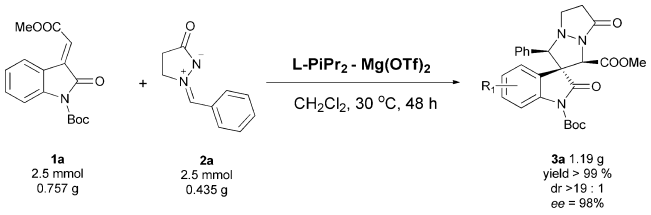
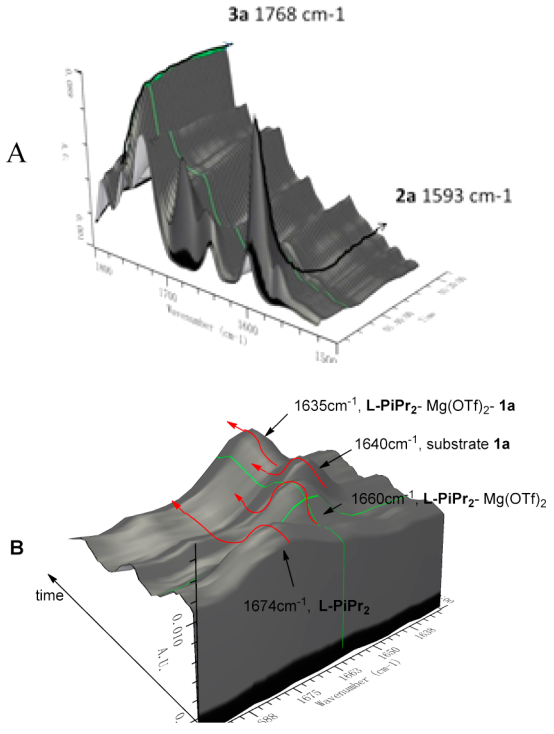
Scheme 1. Substrate Scope of Other Methyleneindolinones



Scheme 2. Gram Scale Synthesis of 3a

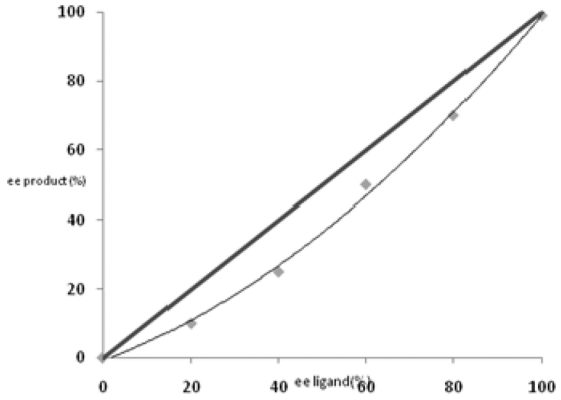


Scheme 3. Operando IR Experiments of Standard Reaction



methyleneindolinone was shielded by the 2,6-diisopropylphenyl group of the ligand, therefore, the *N,N′*-cyclic azomethine imine attacked from the *Re* face to afford the product with

Scheme 4. Nonlinear Effect Experiment of 1a and 2a



(1′*R*,2′*R*,3′*R*) configuration, which was same with the result of the X-ray crystallographic analysis (Scheme 6).

CONCLUSIONS

We have developed a highly efficient chiral *N,N′*-dioxide–$Mg(OTf)_2$ complex for the catalytic asymmetric 1,3-dipolar cycloaddition of methyleneindolinones with *N,N′*-cyclic azomethine imines. With less than 5 mol % catalyst loading, pyrazolidinyl spirooxindole products with contiguous quaternary–tertiary stereocenter were obtained in up to 99% yield, >19:1 *dr* and >99% *ee*.

EXPERIMENTAL SECTION

General Remarks. ^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26; DMSO, δ = 2.49). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0; DMSO, δ = 39.6). Enantiomeric excesses (*ee*) were determined by HPLC analysis using the corresponding commercial chiralpak column as stated in the experimental procedures at 25 °C. Optical rotations were reported as follows: $[a]^T_D$ (*c* g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI Source). All reagents and solvents were obtained from commercial suppliers and used without further purification except as indicated below. All catalytic reactions were run in dried glassware. CH_2Cl_2 was distilled over CaH_2.

General Procedure for Chiral *N,N′*-Dioxide Preparation. The *N,N′*-dioxides were prepared according to the methods reported in the literature.[12a]

General Procedure to Prepare the Substrates. Methacrylate (3.6 mL) was added to the solution of hydrazine hydrate (2 mL) in 10 mL ethanol which was cooled in an ice bath. After addition, the mixture was heated to reflux for 8 h. Then the solvent and the volatile components were removed under reduced pressure. The thick colorless oil, crude pyrazolidin-3-one, was obtained in 80% yield. By subjecting pyrazolidin-3-one (1.1 equiv) to various aromatic aldehydes (1.0 equiv) in methanol (20 mmol in 15 mL of methanol) at room temperature, the crude products of the desired 3-oxo-1,2-pyrazolidinium ylides were formed. After removing the solvent methanol, the crude product was recrystallized in ethanol. Washed by ethyl acetate and dried under a vacuum, the pure product was obtained.

General Procedure to Prepare the Substrates 1ab. Pyrazolidin-3-one (1.1 equiv) was added into the cyclopentanecarbaldehyde (1.0 equiv) in methanol (20 mmol in 15 mL of methanol) at room temperature, the crude products of the desired 3-oxo-1,2-

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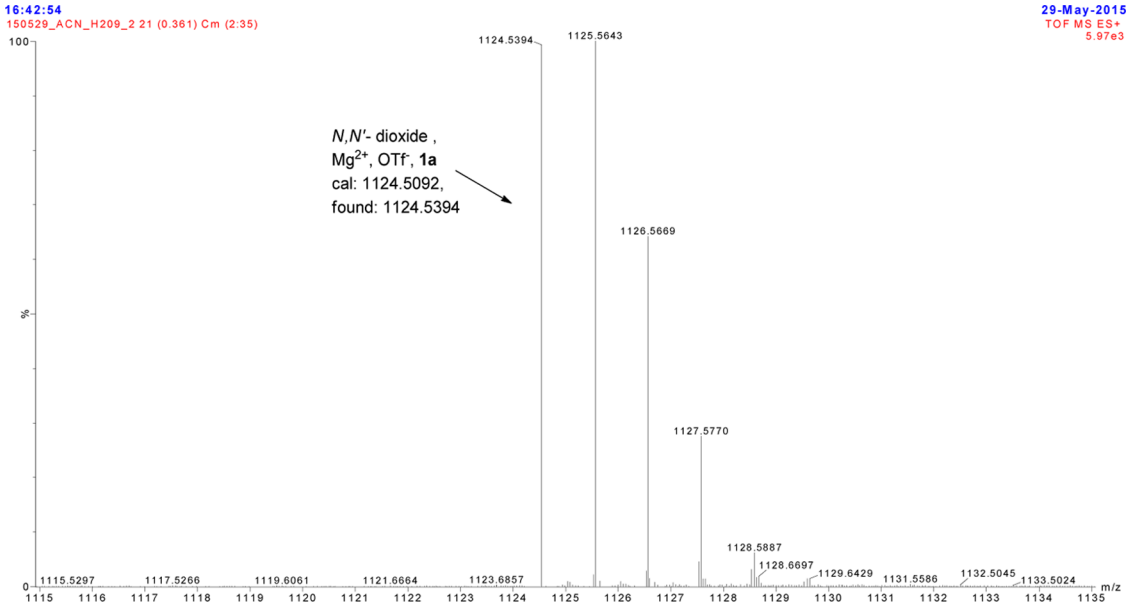
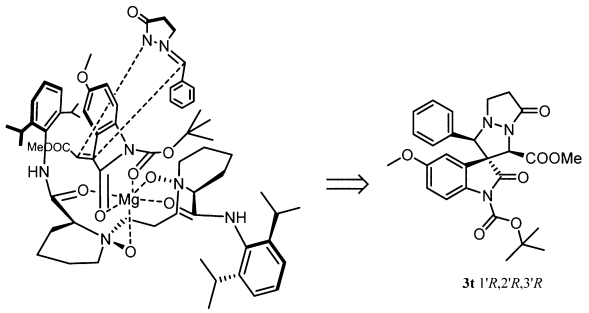
Scheme 5. HRMS of the *N,N′*-Dioxide, Mg^{2+}, OTf^-, and 1a



Scheme 6. Possible Transition-State Model



pyrazolidinium ylide was formed. After removing the solvent methanol, the crude product was recrystallized in ethanol. Washed by ethyl acetate and dried under a vacuum, the pure product was obtained in 50% yield, white powder.

General Procedure of the Catalytic Reactions. A mixture of *N,N′*-dioxide **L-PiPr$_2$** (3.3 mg, 0.005 mmol), $Mg(OTf)_2$ (1.6 mg, 0.005 mmol), **1a** (30.3 mg, 0.1 mmol), was stirred in dry CH_2Cl_2 (1 mL) at 30 °C in the N_2 for 30 min. Then, *N,N′*-cyclic azomethine imine (**2a**) (17.4 mg, 0.1 mmol) was added. The reaction mixture was stirred at 30 °C for 48 h. After complete consumption of the starting materials, the mixture was directly purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 2:1) to afford **3a** (47.2 mg, 99% yield) as a light yellow powder.

1-tert-Butyl 3′-methyl 2,5′-dioxo-1′-phenyl-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3a)***. Yield 47.2 mg, 99%; yellow powder, mp 90−92 °C; 99% *ee*, >19:1 *dr*; $[\alpha]^{21}_D$ = −25.7 (*c* = 0.68 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH; 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 9.52 min, $t_{R(minor)}$ = 14.16 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.50 (m, 2H), 7.16−7.00 (m, 7H), 5.21 (s, 1H), 4.24 (s, 1H), 3.79−3.75 (m, 1H), 3.23 (s, 3H), 3.12−3.02 (m, 1H), 2.95−2.93 (m, 1H), 2.88−2.75 (m, 1H), 1.63 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 172.9, 166.9, 148.5, 139.3, 131.3, 129.4, 128.7, 128.2, 127.2, 125.9, 123.9, 123.8, 114.4, 84.9, 78.5, 77.4, 77.0, 76.7, 65.2, 63.5, 52.3, 47.0, 31.6, 28.0, 0.0. HRMS (ESI-TOF) calcd for $C_{26}H_{27}N_3NaO_6$ $[M + Na]^+$ 500.1798, found 500.1793.

1-tert-Butyl 3′-methyl 2,5′-dioxo-1′-(p-tolyl)-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3b)***. Yield 48.7 mg, 99%; yellow oil; 97% *ee*, >19:1 *dr*; $[\alpha]^{21}_D$ = −22.5 (*c* = 0.75 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH; 90/10, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 8.95 min, $t_{R(minor)}$ = 11.77 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.50 (m, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.90−6.88(m, 4H), 5.19 (s, 1H), 4.21 (s, 1H), 3.76−3.73 (m, 1H), 3.22 (s, 3H), 3.10−3.01 (m, 1H), 3.00−2.89 (m, 1H), 2.87−2.76 (m, 1H), 2.17 (s, 3H), 1.63 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 173.0, 166.9, 148.5, 139.4, 138.5, 129.3, 128.9, 128.1, 127.1, 126.0, 123.9, 114.4, 84.9, 78.4, 77.4, 77.3, 77.1, 76.7, 65.1, 63.6, 52.2, 47.0, 31.6, 28.0, 21.1. HRMS (ESI-TOF) calcd for $C_{27}H_{29}N_3NaO_6$ $[M + Na]^+$ 514.1954, found 514.1953.

1-tert-Butyl 3′-methyl 2,5′-dioxo-1′-(3-(trifluoromethyl)phenyl)-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]-pyrazole]-1,3′-dicarboxylate ***(3c)***. Yield 54.2 mg; 99%, yellow oil; 99% *ee*, 7:1 *dr*; $[\alpha]^{21}_D$ = −13.9 (*c* = 0.74 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) t_{R1} = 12.18 min, t_{R2} = 20.27 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 12.8, 4.8 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.31 (s, 1H), 7.23−7.19(m, 2H), 7.14 (td, *J* = 8.0, 1.4 Hz, 1H), 7.05 (td, *J* = 7.6, 0.8 Hz, 1H), 5.24 (s, 1H), 4.28 (s, 1H), 3.82−3.78 (m, 1H), 3.25 (s, 3H), 3.15−3.02 (m, 1H), 2.96−2.93 (m, 1H), 2.92−2.75 (m, 1H), 1.63 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 172.5, 171.2, 166.7, 148.3, 139.1, 132.6, 130.8, 130.4, 129.7, 128.7, 125.7, 125.6, 125.5, 124.1, 124.0, 123.9, 123.2, 114.5, 85.3, 77.9, 77.4, 77.1, 76.7, 65.3, 63.2, 60.4, 52.4, 47.1, 31.5, 27.9, 21.1, 14.2, 0.0. HRMS (ESI-TOF) calcd for $C_{27}H_{26}F_3N_3NaO_6$ $[M + Na]^+$ 568.1671, found 568.1674.

1-tert-Butyl 3′-methyl 1′-(3-bromophenyl)-2,5′-dioxo-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3d)***. Yield 45.2 mg, 82%; yellow oil; 99% *ee*, >19:1 *dr*; $[\alpha]^{25}_D$ = −20.2 (*c* = 0.61 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 22.93 min, $t_{R(minor)}$ = 38.30 min; ^{1}H NMR (400 MHz, CDCl3) δ 7.54 (t, *J* = 8.6 Hz, 2H), 7.26−7.13 (m, 3H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.96−6.92 (m, 2H), 5.20 (s, 1H), 4.18 (s, 1H), 3.80−3.76 (m, 1H), 3.24 (s, 3H), 3.11−2.92 (m, 2H), 2.90−2.76 (m, 1H), 1.64 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 172.6, 166.8, 148.3, 139.2, 133.7, 131.9, 130.2, 129.7, 129.7, 125.8, 125.7, 124.0, 123.3, 122.3, 114.5, 85.2, 77.7, 77.4, 77.3, 77.1, 76.7, 65.2, 63.3, 52.3, 47.1, 31.5, 28.0. HRMS (ESI-TOF) calcd for $C_{26}H_{26}{}^{78.9183}BrN_3NaO_6$ $[M + Na]^+$ 578.0903, found 578.0912. $C_{26}H_{26}{}^{80.9163}BrN_3NaO_6$ $[M + Na]^+$ 580.0882, found 580.0900.

1-tert-Butyl 3′-methyl 1′-(3,4-dimethylphenyl)-2,5′-dioxo-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]-pyrazole]-1,3′-dicarboxylate ***(3e)***. Yield 27.2 mg, 54%; yellow oil; 99% *ee*, 10:1 *dr*; $[\alpha]^{21}_D$ = −16.8 (*c* = 0.12 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 9.20 min, $t_{R(minor)}$ = 13.46 min; ^{1}H NMR (400 MHz, $CDCl_3$)

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δ 7.48−7.45 (m, 2H), 7.07 (t, J = 7.6 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 6.72 (q, J = 7.6 Hz, 3H), 5.12 (s, 1H), 4.09 (s, 1H), 3.69−3.65 (m, 1H), 3.15 (s, 3H), 3.02−2.81 (m, 2H), 2.78−2.64 (m, 1H), 2.00 (s, 3H), 1.98 (s, 3H), 1.56 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 173.0, 167.0, 148.6, 139.4, 137.1, 136.5, 129.4, 129.3, 128.5, 128.4, 126.0, 124.7, 124.0, 123.8, 114.4, 84.8, 78.5, 77.4, 77.0, 76.7, 65.2, 63.5, 52.2, 47.1, 31.7, 28.1, 19.5, 19.4. HRMS (ESI-TOF) calcd for $C_{28}H_{31}N_3NaO_6$ $[M + Na]^+$ 528.2111, found 528.2117.

1-tert-Butyl 3′-methyl 1′-(4-bromophenyl)-2,5′-dioxo-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3f)***. Yield 49.0 mg, 88%; yellow oil; 99% *ee*, >19:1 *dr*; $[\alpha]^{21}_D$ = −15.5 (c = 0.91 in $CHCl_3$); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 27.28 min, $t_{R(minor)}$ = 39.19 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (t, J = 7.4 Hz, 2H), 7.27 (s, 1H), 7.20−7.16(m, 2H), 7.06 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 8.4 Hz, 2H), 5.19 (s, 1H), 4.20 (s, 1H), 3.85−3.68 (m, 1H), 3.22 (s, 3H), 3.10−2.89 (m, 2H), 2.89−2.72 (m, 1H), 1.64 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 172.8, 166.7, 148.3, 139.3, 131.5, 130.4, 129.7, 128.9, 125.9, 124.0, 123.4, 122.9, 114.7, 85.2, 77.8, 77.4, 77.3, 77.1, 76.7, 65.0, 63.6, 52.3, 47.1, 31.6, 28.0, 0.0. HRMS (ESI-TOF) calcd for $C_{26}H_{26}{}^{78.9183}BrN_3NaO_6$ $[M + Na]^+$ 578.0903, found 578.0907. $C_{26}H_{26}{}^{80.9163}BrN_3NaO_6$ $[M + Na]^+$ 580.0882, found 580.0886.

1-tert-Butyl 3′-methyl 1′-(4-fluorophenyl)-2,5′-dioxo-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3g)***. Yield 45.5 mg, 91%; yellow solid, mp 62−64 °C; >99% *ee*, >19:1 *dr*; $[\alpha]^{21}_D$ = −22.9 (c = 0.73 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 10.28 min, $t_{R(minor)}$ = 15.35 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.50 (m, 2H), 7.17 (t, J = 8.0 Hz, 1H), 7.09−7.00 (m, 3H), 6.78 (t, J = 8.4 Hz, 2H), 5.20 (s, 1H), 4.22 (s, 1H), 3.84−3.70 (m, 1H), 3.23 (s, 3H), 3.09−2.91 (m, 2H), 2.88−2.74 (m, 1H), 1.63 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 172.8, 166.8, 163.9, 161.5, 148.4, 139.3, 129.6, 129.0, 128.9, 127.1, 127.0, 125.8, 124.0, 123.6, 115.4, 115.2, 114.6, 85.1, 77.8, 77.4, 77.3, 77.1, 76.7, 65.1, 63.4, 52.3, 47.0, 31.6, 28.0, 0.0. HRMS (ESI-TOF) calcd for $C_{26}H_{26}FN_3NaO_6$ $[M + Na]^+$ 518.1703, found 518.1707.

1-tert-Butyl 3′-methyl 1′-(4-methoxyphenyl)-2,5′-dioxo-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3h)***. Yield 46.4 mg, 91%; yellow oil; 94% *ee*, >19:1 *dr*; $[\alpha]^{21}_D$ = −18.7 (c = 0.93 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 11.50 min, $t_{R(minor)}$ = 16.80 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.42 (m, 2H), 7.09−7.07(m, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.53 (d, J = 8.7 Hz, 2H), 5.23 (s, 1H), 5.12 (s, 1H), 4.12 (s, 1H), 3.75−3.63 (m, 1H), 3.60 (s, 3H), 3.13 (d, J = 13.2 Hz, 3H), 3.02−2.93 (m, 1H), 2.92−2.82 (m, 1H), 2.82−2.67 (m, 1H), 1.56 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 173.0, 167.0, 159.7, 148.5, 139.3, 129.4, 128.5, 125.9, 123.9, 123.8, 123.0, 114.5, 113.6, 84.9, 78.3, 77.4, 77.1, 76.8, 65.1, 63.5, 55.1, 53.5, 52.3, 47.0, 31.6, 28.0, 1.0. HRMS (ESI-TOF) calcd for $C_{27}H_{29}N_3NaO_7$ $[M + Na]^+$ 530.1903, found 530.1904.

1-tert-Butyl 3′-methyl 1′-(4-chlorophenyl)-2,5′-dioxo-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3i)***. Yield 38.6 mg, 75%; yellow oil; >99% *ee*, >19:1 *dr*; $[\alpha]^{21}_D$ = −19.6 (c = 0.57 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 10.56 min, $t_{R(minor)}$ = 16.02 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.53(m, 2H), 7.18 (t, J = 7.8 Hz, 1H), 7.06 (t, J = 7.6 Hz, 3H), 7.00 (d, J = 8.4 Hz, 2H), 5.19 (s, 1H), 4.21 (s, 1H), 3.83−3.69 (m, 1H), 3.22 (s, 3H), 3.10−2.91 (m, 2H), 2.88−2.77 (m, 1H), 1.64 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 172.8, 166.8, 148.3, 139.3, 134.6, 129.9, 129.7, 128.6, 128.5, 125.9, 124.0, 123.4, 114.6, 85.2, 77.7, 77.4, 77.3, 77.0, 76.7, 65.0, 63.6, 52.3, 47.1, 31.6, 28.1, 0.0. HRMS (ESI-TOF) calcd for $C_{26}H_{26}{}^{34.9689}ClN_3NaO_6$ $[M + Na]^+$ 534.1408, found 534.1416. $C_{26}H_{26}{}^{36.9659}ClN_3NaO_6$ $[M + Na]^+$ 536.1378, found 536.1376.

1-tert-Butyl 3′-methyl 1′-(2-fluorophenyl)-2,5′-dioxo-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3j)***. Yield 31.9 mg, 64%; yellow oil; 50% *ee*, 10:1 *dr*; $[\alpha]^{20}_D$ = −6.2 (c = 0.13 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 8.10 min, $t_{R(minor)}$ = 13.22 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.2 Hz, 1H), 7.27−7.20(m, 2H), 7.04−7.00(m, 2H), 6.92−6.65 (m, 3H), 5.21 (s, 1H), 4.43 (s, 1H), 3.77−3.72(m, 1H), 3.14 (s, 3H), 3.10−2.99 (m, 1H), 2.80−2.75(m, 2H), 1.58 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 171.8, 166.0, 160.8, 158.3, 147.7, 138.6, 129.0, 128.9, 128.3, 128.2, 128.1, 124.4, 123.0, 122.9, 122.8, 122.7, 118.8, 118.6, 114.1, 113.9, 113.6, 83.7, 76.3, 76.0, 75.7, 70.8, 63.1, 62.8, 51.2, 45.6, 29.8, 27.0, −0.0. HRMS (ESI-TOF) calcd for $C_{26}H_{26}FN_3NaO_6$ $[M + Na]^+$ 518.1703, found 518.1712.

1-tert-Butyl 3′-methyl 1′-(naphthalen-1-yl)-2,5′-dioxo-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3k)***. Yield 45.3 mg, 86%; yellow solid, mp 86−88 °C; >99% *ee*, >19:1 *dr*; $[\alpha]^{20}_D$ = −187.1 (c = 0.87 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 7.71 min, $t_{R(minor)}$ = 13.77 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.62−7.51 (m, 3H), 7.45−7.41 (m, 3H), 7.38−7.28 (m, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.07−6.97 (m, 2H), 5.41 (s, 1H), 5.01 (s, 1H), 3.88−3.71 (m, 1H), 3.22 (s, 3H), 3.09−3.01 (m, 1H), 2.96−2.77 (m, 2H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1, 174.3, 173.8, 167.2, 148.1, 139.2, 133.3, 132.0, 131.2, 129.2, 129.0, 128.9, 128.7, 128.3, 127.1, 127.0, 126.6, 125.9, 125.6, 124.6, 124.1, 123.8, 122.4, 114.5, 84.6, 77.4, 77.3, 77.1, 76.8, 74.2, 64.9, 64.0, 52.2, 46.6, 31.0, 31.0, 27.9. HRMS (ESI-TOF) calcd for $C_{30}H_{29}N_3NaO_6$ $[M + Na]^+$ 550.1954, found 550.1953.

1-tert-Butyl 3′-methyl 2,5′-dioxo-1′-(thiophen-2-yl)-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3l)***. Yield 43.6 mg, 90%; yellow oil; 94% *ee*, 10:1 *dr*; $[\alpha]^{20}_D$ = −1.63(c = 0.046 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(minor)}$ = 7.85 min, $t_{R(major)}$ = 10.31 min; ^{1}H NMR (400 MHz, CDCl3) δ 7.63 (t, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 1H), 7.12−7.08(m, 2H), 6.88−6.71 (m, 2H), 5.17 (s, 1H), 4.50 (s, 1H), 3.78−3.76(m, 1H), 3.24 (s, 3H), 3.14−3.08 (m, 1H), 2.94−2.90(m, 1H), 2.86−2.78 (m, 1H), 1.63 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 129.8, 127.1, 126.4, 124.1, 114.6, 85.1, 77.3, 77.0, 76.7, 75.0, 64.8, 63.6, 52.3, 47.0, 31.4, 28.0. HRMS (ESI-TOF) calcd for $C_{24}H_{25}N_3NaO_6S$ $[M + Na]^+$ 506.1362, found 506.1366.

1-tert-Butyl 3′-methyl 1′-(furan-3-yl)-2,5′-dioxo-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3m)***. Yield 38.6 mg, 83%; yellow solid, mp 116−118 °C; 95% *ee*, 15:1 *dr*; $[\alpha]^{20}_D$ = −13.38 (c = 0.16 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 10.77 min, $t_{R(minor)}$ = 15.08 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 6.8 Hz, 1H), 7.25−7.05 (m, 5H), 5.13 (s, 1H), 4.12 (s, 1H), 3.26−3.20 (m, 3H), 3.17 (dd, J = 4.2, 1.6 Hz, 1H), 3.13−3.05 (m, 1H), 2.94−2.87 (m, 1H), 2.86−2.78 (m, 1H), 1.63 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 172.7, 166.8, 148.5, 143.4, 141.4, 139.7, 129.7, 129.0, 128.2, 125.8, 125.3, 124.3, 124.1, 116.3, 114.7, 109.0, 100.0, 85.2, 77.4, 77.0, 76.7, 71.6, 64.2, 63.6, 53.5, 52.3, 46.8, 31.5, 28.0, 21.5. HRMS (ESI-TOF) calcd for $C_{24}H_{25}N_3NaO_7$ $[M + Na]^+$ 490.1590, found 490.1586.

1-tert-Butyl 3′-methyl 5-chloro-2,5′-dioxo-1′-phenyl-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3n)***. Yield 41.9 mg, 82%; yellow solid, 76−78 °C; 95% *ee*, >19:1 *dr*; $[\alpha]^{25}_D$ = −62.5 (c = 0.64 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 10.06 min, $t_{R(minor)}$ = 14.64 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 2.0 Hz, 1H), 7.47 (d, J = 8.8 Hz, 1H), 7.20−6.98 (m, 6H), 5.20 (s, 1H), 4.24 (s, 1H), 3.90−3.76 (m, 1H), 3.33 (s, 3H), 3.10−3.07(m, 1H), 2.97−2.94(m, 1H), 2.89−2.75 (m, 1H), 1.62 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 172.2, 166.7, 148.2, 137.8, 130.9, 129.5, 129.4, 128.9, 128.4, 127.0, 125.9, 125.6, 115.7, 85.3, 78.3, 77.4, 77.1, 76.8, 65.1, 63.3, 60.4, 52.5, 46.8, 31.4, 28.0, 21.1, 14.2, −0.2. HRMS (ESI-TOF) calcd for $C_{26}H_{26}{}^{34.9689}ClN_3NaO_6$ $[M + Na]^+$ 534.1408, found 534.1417. $C_{26}H_{26}{}^{36.9659}ClN_3NaO_6$ $[M + Na]^+$ 536.1378, found 536.1390.

1-tert-Butyl 3′-methyl 5-fluoro-2,5′-dioxo-1′-phenyl-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3o)***. Yield 43.7 mg, 88%; yellow oil; 96% *ee*, >19:1 *dr*; $[\alpha]^{20}_D$ = −23.8 (c = 0.61 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-

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hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 8.99 min, $t_{R(minor)}$ = 17.49 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, J = 9.0, 4.5 Hz, 1H), 7.33 (dd, J = 8.0, 2.8 Hz, 1H), 7.19−7.07 (m, 3H), 7.05 (dd, J = 7.6, 1.8 Hz, 2H), 6.86−6.81(m, 1H), 5.21 (s, 1H), 4.25 (s, 1H), 3.89−3.73 (m, 1H), 3.32 (s, 3H), 3.10−3.07(m, 1H), 2.98−2.94(m, 1H), 2.89−2.75 (m, 1H), 1.63 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 172.4, 166.8, 160.3, 157.9, 148.4, 135.4, 135.3, 131.0, 128.9, 128.4, 127.0, 125.7, 125.6, 116.1, 115.8, 115.7, 113.5, 113.3, 85.2, 78.3, 77.4, 77.1, 76.8, 65.3, 65.2, 63.3, 60.4, 52.5, 46.8, 31.4, 28.0, 21.1, 14.2, −0.2. HRMS (ESI-TOF) calcd for $C_{26}H_{26}FN_3NaO_6$ [M + Na]$^+$ 518.1703, found 518.1705.

1-tert-Butyl 3′-methyl 5-bromo-2,5′-dioxo-1′-phenyl-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3p)***. Yield 50.5 mg, 91%; white solid, mp 132−134 °C; 97% *ee*, >19:1 *dr*; $[\alpha]^{22}_D$ = −72.0 (c = 0.76 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) t_{R1} = 3.51 min, t_{R2} = 4.02 min t_{R3} = 10.18 t_{R4} = 14.04; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 2.0 Hz, 1H), 7.42 (d, J = 8.8 Hz, 1H), 7.26 (dd, J = 8.8, 2.4 Hz, 1H), 7.18−6.97 (m, 5H), 5.20 (s, 1H), 4.24 (s, 1H), 3.89−3.75 (m, 1H), 3.34 (s, 3H), 3.10−3.07(m, 1H), 2.99−2.94(m, 1H), 2.90−2.73 (m, 1H), 1.63 (d, J = 3.2 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 172.0, 166.8, 148.2, 138.4, 132.3, 131.0, 129.0, 128.7, 128.4, 128.2, 127.2, 127.0, 126.0, 116.9, 116.1, 85.4, 78.3, 77.4, 77.1, 76.8, 65.1, 63.3, 60.4, 52.5, 46.7, 31.4, 28.0, 21.1, 14.2, 0.0. HRMS (ESI-TOF) calcd for $C_{26}H_{26}{}^{78.9183}BrN_3NaO_6$ [M + Na]$^+$ 578.0903, found 578.0908. $C_{26}H_{26}{}^{80.9163}BrN_3NaO_6$ [M + Na]$^+$ 580.0882, found 580.0886.

1-tert-Butyl 3′-methyl 6-bromo-2,5′-dioxo-1′-phenyl-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3q)***. Yield 39.7 mg, 71%; white solid, mp 133−135 °C; 98% *ee*, 7:1 *dr*; $[\alpha]^{21}_D$ = −31.2 (c = 0.49 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 8.31 min, $t_{R(minor)}$ = 12.34 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 1.6 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.20 (dd, J = 8.0, 1.6 Hz, 1H), 7.18−7.06 (m, 3H), 7.07−6.97 (m, 2H), 5.19 (s, 1H), 4.23 (s, 1H), 3.89−3.70 (m, 1H), 3.29 (s, 3H), 3.08−3.06(m, 1H), 2.95−2.92(m, 1H), 2.86−2.75 (m, 1H), 1.63 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 172.4, 166.8, 148.2, 140.3, 131.0, 129.0, 128.5, 127.0, 127.0, 123.2, 122.8, 118.0, 85.6, 78.2, 77.4, 77.1, 76.74, 65.0, 63.4, 52.5, 46.8, 31.4, 28.0, 0.0. HRMS (ESI-TOF) calcd for $C_{26}H_{26}{}^{78.9183}BrN_3NaO_6$ [M + Na]$^+$ 578.0903, found 578.0910. $C_{26}H_{26}{}^{80.9163}BrN_3NaO_6$ [M + Na]$^+$580.0882, found 580.0886.

1-tert-Butyl 3′-methyl 5,7-dimethyl-2,5′-dioxo-1′-phenyl-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3r)***. Yield 43.8 mg, 87%; yellow solid, mp 150−152 °C; 99% *ee*, >19:1 *dr*; $[\alpha]^{21}_D$ = −51.0 (c = 0.67 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 8.50 min, $t_{R(minor)}$ = 10.43 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.15−6.99 (m, 5H), 6.73 (s, 1H), 5.17 (s, 1H), 4.23 (s, 1H), 3.87−3.73 (m, 1H), 3.21 (s, 3H), 3.14−3.03 (m, 1H), 3.02−2.91 (m, 1H), 2.88−2.73 (m, 1H), 2.25 (s, 3H), 1.98 (s, 3H), 1.60 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 173.8, 166.8, 148.3, 135.7, 133.5, 132.6, 131.5, 128.6, 128.1, 127.2, 124.8, 124.1, 123.0, 84.8, 78.2, 77.4, 77.1, 76.8, 65.5, 63.5, 52.2, 47.3, 31.8, 27.8, 20.9, 19.2, 0.0. HRMS (ESI-TOF) calcd for $C_{28}H_{31}N_3NaO_6$ [M + Na]$^+$ 528.2111, found 528.2119.

1-tert-Butyl 3′-methyl 5-methyl-2,5′-dioxo-1′-phenyl-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3s)***. Yield 44.9 mg, 91%; yellow oil; 99% *ee*, >19:1 *dr*; $[\alpha]^{21}_D$ = −42.6 (c = 0.80 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 9.39 min, $t_{R(minor)}$ = 12.78 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.32 (m, 2H), 7.16−7.00 (m, 5H), 6.92 (d, J = 8.4 Hz, 1H), 5.20 (s, 1H), 4.24 (s, 1H), 3.84−3.70 (m, 1H), 3.24 (s, 3H), 3.13−2.94 (m, 2H), 2.89−2.78 (m, 1H), 2.29 (s, 3H), 1.62 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 173.1, 166.9, 148.50, 136.9, 133.5, 131.4, 129.7, 128.7, 128.2, 127.2, 126.4, 123.6, 114.2, 84.8, 78.4, 77.4, 77.3, 77.1, 76.7, 65.2, 63.5, 52.2, 47.2, 31.7, 28.0, 21.0. HRMS (ESI-TOF) calcd for $C_{27}H_{29}N_3NaO_6$ [M + Na]$^+$ 514.1954, found 514.1959.

1-tert-Butyl 3′-methyl 5-methoxy-2,5′-dioxo-1′-phenyl-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3t)***. Yield 44.9 mg, 88%; white solid, mp 166−168 °C; 99% *ee*, >19:1 *dr*; $[\alpha]^{25}_D$ = −67.0 (c = 0.10 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) t_{R1} = 9.34 min, t_{R2} = 10.38 min, t_{R3} = 11.31 min, t_{R4} = 31.56 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.8 Hz, 1H), 7.09−6.99(m, 6H), 6.66−6.64(m, 1H), 5.21 (s, 1H), 4.24 (s, 1H), 3.87−3.67 (m, 4H), 3.27 (s, 3H), 3.09−2.97(m, 1H), 2.95−2.93(m, 1H), 2.87−2.75 (m, 1H), 1.62 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 173.0, 167.0, 156.2, 148.5, 132.7, 131.3, 128.7, 128.3, 127.1, 124.9, 115.4, 115.0, 111.5, 84.7, 78.4, 77.4, 77.0, 76.7, 65.5, 63.5, 55.9, 52.4, 46.9, 31.5, 28.0. HRMS (ESI-TOF) calcd for $C_{27}H_{29}N_3NaO_7$ [M + Na]$^+$ 530.1903, found 530.1910.

1-tert-Butyl 3′-methyl 6-chloro-2,5′-dioxo-1′-phenyl-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3u)***. Yield 43.9 mg, 86%; yellow oil; 99% *ee*, >19:1 *dr*; $[\alpha]^{20}_D$ = −31.5 (c = 0.71 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) t_{R1} = 15.531 min, t_{R2} = 17.75 min, t_{R3} = 19.47 min, t_{R4} = 29.67 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 1.6 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.16−7.09 (m, 3H), 7.04−7.01(m, 3H), 5.19 (s, 1H), 4.23 (s, 1H), 3.79−3.75(m, 1H), 3.29 (s, 3H), 3.13−3.04 (m, 1H), 3.00−2.90 (m, 1H), 2.87−2.77 (m, 1H), 1.63 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 172.5, 166.8, 148.2, 140.2, 135.2, 131.0, 129.0, 128.4, 127.0, 126.8, 124.0, 122.2, 115.3, 85.5, 78.3, 77.4, 77.3, 77.1, 76.7, 64.9, 63.4, 52.5, 46.8, 31.4, 28.0. HRMS (ESI-TOF) calcd for $C_{26}H_{26}{}^{34.9689}ClN_3NaO_6$ [M + Na]$^+$ 534.1408, found 534.1416. $C_{26}H_{26}{}^{36.9659}ClN_3NaO_6$ [M + Na]$^+$ 536.1378, found 536.1403.

1-tert-Butyl 3′-methyl 2,5′-dioxo-1′-phenyl-5-(trifluoromethoxy)-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3v)***. Yield 57.2 mg, 99%; yellow oil; 95% *ee*, >19:1 *dr*; $[\alpha]^{25}_D$ = −31.3 (c = 0.91 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH, 1.0 mL/min, λ = 254 nm) t_{R1} = 14.23 min, t_{R2} = 16.84 min, t_{R3} = 19.34 min, t_{R4} = 23.79 min, t_{R5} = 25.12 min, t_{R6} = 44.28 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.8 Hz, 1H), 7.49 (d, J = 1.6 Hz, 1H), 7.15−7.06 (m, 3H), 7.01−6.99(m, 3H), 5.22 (s, 1H), 4.25 (s, 1H), 3.90−3.74 (m, 1H), 3.31 (s, 3H), 3.19−3.03 (m, 1H), 3.01−2.76 (m, 2H), 1.63 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 172.3, 166.8, 148.2, 145.0, 138.0, 130.9, 129.0, 128.4, 127.0, 125.6, 122.6, 119.5, 119.2, 115.6, 85.5, 78.3, 77.4, 77.3, 77.0, 76.7, 65.2, 63.3, 52.4, 46.5, 31.2, 28.0. HRMS (ESI-TOF) calcd for $C_{27}H_{26}F_3N_3NaO_7$ [M + Na]$^+$ 584.1621, found 584.1625.

1-tert-Butyl 3′-methyl 7-bromo-2,5′-dioxo-1′-phenyl-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3w)***. Yield 45.3 mg, 81%; white solid, mp 88−90 °C; 90% *ee*, 15:1 *dr*; $[\alpha]^{21}_D$ = −16.5 (c = 0.70 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 10.58 min, $t_{R(minor)}$ = 13.52 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.6 Hz, 1H), 7.37−7.26 (m, 2H), 7.21−6.99 (m, 5H), 6.91 (t, J = 8.0 Hz, 1H), 5.18 (s, 1H), 4.27 (s, 1H), 3.81−3.77(m, 1H), 3.23 (s, 3H), 3.18−3.03 (m, 1H), 2.89 (m, 2H), 1.62 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 173.1, 166.6, 146.9, 138.5, 134.0, 131.0, 128.9, 128.4, 127.5, 127.1, 125.1, 124.9, 106.2, 85.9, 77.9, 77.4, 77.3, 77.0, 76.7, 65.7, 63.5, 52.3, 46.9, 31.4, 27.7. HRMS (ESI-TOF) calcd for $C_{26}H_{26}{}^{78.9183}BrN_3NaO_6$ [M + Na]$^+$ 578.0903, found 578.0901. $C_{26}H_{26}{}^{80.9163}BrN_3NaO_6$ [M + Na]$^+$ 580.0882, found 580.0883.

Di-tert-butyl 2,5′-dioxo-1′-phenyl-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate ***(3x)***. Yield 43.0 mg, 85%; yellow oil; >99% *ee*, >19:1 *dr*; $[\alpha]^{22}_D$ = −28.7 (c = 0.99 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 12.29 min, $t_{R(minor)}$ = 20.37 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.21−6.98 (m, 7H), 5.08 (s, 1H), 4.27 (s, 1H), 3.86−3.69 (m, 1H), 3.13−2.91 (m, 2H), 2.88−2.68 (m, 1H), 1.62 (s, 9H), 0.92 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 173.0, 164.7, 148.5, 139.7, 131.5, 129.3, 128.6, 128.2, 127.3, 126.8, 124.1, 124.0, 114.3, 84.9, 82.7, 77.9, 77.4, 77.3, 77.1, 76.8, 64.9, 64.1, 47.3, 32.0, 28.0, 27.1. HRMS (ESI-TOF) calcd for $C_{29}H_{33}N_3NaO_6$ [M + Na]$^+$ 542.2267, found 542.2267.

1-tert-Butyl 3′-isopropyl 2,5′-dioxo-1′-phenyl-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarbox-

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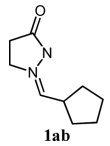
*ylate (**3y**).* Yield 39.3 mg, 78%; yellow oil; >99% *ee*, >19:1 *dr*; $[\alpha]^{22}_{D}$ = −31.9 (*c* = 0.73 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 10.05 min, $t_{R(minor)}$ = 15.14 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.57 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.32−7.30 (m, 1H), 7.22−6.95 (m, 8H), 5.15 (s, 1H), 4.58−4.54 (m, 1H), 4.26 (s, 1H), 3.83−3.71 (m, 1H), 3.10−2.93 (m, 2H), 2.87−2.73 (m, 2H), 1.63 (s, 9H), 1.02 (d, *J* = 6.4 Hz, 3H), 0.35 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 173.0, 165.6, 148.4, 139.6, 131.3, 129.3, 129.0, 128.7, 128.2, 127.2, 126.5, 124.0, 123.8, 119.5, 114.4, 84.9, 78.3, 77.4, 77.3, 77.1, 76.7, 69.6, 65.1, 63.5, 60.5, 47.3, 45.6, 31.9, 29.7, 28.0, 26.0, 23.8, 21.6, 20.2. HRMS (ESI-TOF) calcd for $C_{28}H_{31}N_3NaO_6$ $[M + Na]^+$528.2111, found 528.2114.

*1-tert-Butyl 3′-phenyl 2,5′-dioxo-1′-phenyl-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate (**3z**).* Yield 49.1 mg, 91%; yellow solid, mp 96−98 °C; 99% *ee*, >19:1 *dr*; $[\alpha]^{22}_{D}$ = −48.5 (*c* = 1.01 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{R(major)}$ = 9.32 min, $t_{R(minor)}$ = 16.79 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.4 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.17−7.05 (m, 9H), 6.22 (d, *J* = 7.8 Hz, 2H), 5.46 (s, 1H), 4.32 (s, 1H), 3.90−3.73 (m, 1H), 3.20−3.06 (m, 1H), 3.05−2.74 (m, 2H), 1.60 (s, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 172.8, 165.0, 149.5, 148.4, 139.7, 131.2, 129.6, 129.2, 128.8, 128.2, 127.2, 126.5, 126.1, 124.2, 123.7, 120.9, 114.7, 85.0, 78.6, 77.4, 77.3, 77.1, 76.8, 65.2, 63.4, 46.6, 31.3, 28.0. HRMS (ESI-TOF) calcd for $C_{31}H_{29}N_3NaO_6$ $[M + Na]^+$ 562.1954, found 562.1956.

*1-Ethyl 3′-methyl 2,5′-dioxo-1′-phenyl-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate (**3aa**).* Yield 41.2 mg, 92%; yellow oil; 80% *ee*, 15:1 *dr*; $[\alpha]^{20}_{D}$ = −21.74 (*c* = 0.20 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) t_{R1} = 10.25 min, t_{R2} = 13.81 min, t_{R3} = 15.97 min, t_{R4} = 25.38 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.09−7.07(m, 1H), 7.05−6.95 (m, 6H), 5.13 (s, 1H), 4.40 (q, *J* = 7.2 Hz, 2H), 4.19 (s, 1H), 3.78−3.66 (m, 1H), 3.14 (s, 3H), 3.06−2.97 (m, 1H), 2.96−2.84 (m, 1H), 2.83−2.71 (m, 1H), 1.39 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 171.8, 165.8, 149.1, 138.0, 130.2, 128.5, 127.7, 127.3, 126.2, 125.1, 123.2, 122.8, 113.4, 77.4, 76.3, 76.2, 76.0, 75.7, 64.1, 62.8, 62.7, 51.3, 46.1, 30.6, 13.2, −0.0. HRMS (ESI-TOF) calcd for $C_{24}H_{23}N_3NaO_6$ $[M + Na]^+$ 472.1485, found 472.1493.

*1-tert-Butyl 3′-methyl 1′-cyclopentyl-2,5′-dioxo-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate (**3ab**).* Yield 21.6 mg, 46%; 99% *ee*, 6:1 *dr*, yellow solid, mp: 64−66 °C; this product is not stable; $[\alpha]^{20}_{D}$ = +7.8 (*c* = 0.41 in $CHCl_3$); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min) $t_{R(1)}$ = 6.92 min, $t_{R(2)}$ = 7.85 min, $t_{R(3)}$ = 8.38 min, $t_{R(4)}$ = 10.77 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 4.93 (s, 1H), 3.81 (dd, *J* = 8.0, 6.2 Hz, 1H), 3.16 (s, 3H), 3.10 (dd, *J* = 9.1, 4.9 Hz, 2H), 3.02 (d, *J* = 9.8 Hz, 1H), 2.79−2.66 (m, 1H), 1.87−1.76 (m, 1H), 1.66 (s, 9H), 1.59−1.48 (m, 2H), 1.47−1.35 (m, 2H), 1.19−1.10(m, 2H), 0.98−0.84(m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 166.5, 166.0, 148.8, 140.0, 129.7, 126.3, 124. 3, 124.2, 114.8, 85.1, 79.9, 77.4, 77.3, 77.1, 76.7, 63.7, 62.6, 53.8, 52.2, 40.1, 35.1, 32.1, 29.7, 28.1, 27.6, 25.2, 23.9. HRMS (ESI-TOF) calcd for: $C_{25}H_{31}N_3NaO_6$ $[M + Na]^+$: 492.2111, found 492.2121.

*1-Benzyl 3′-tert-butyl 2,5′-dioxo-1′-phenyl-3′,5′,6′,7′-tetrahydro-1′H-spiro[indoline-3,2′-pyrazolo[1,2-a]pyrazole]-1,3′-dicarboxylate (**3ac**).* Yield 55.0 mg, 99%; 49% *ee*, yellow oil; $[\alpha]^{20}_{D}$ = −11.4 (*c* = 1.06, in $CHCl_3$); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min) $t_{R(1)}$ = 20.03 min, $t_{R(2)}$ = 23.87 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 1H), 7.65−7.55 (m, 1H), 7.52−7.44 (m, 2H), 7.44−7.26 (m, 5H), 7.16 (td, *J* = 8.0, 1.2 Hz, 1H), 7.10−7.04 (m, 2H), 7.03−6.91 (m, 2H), 5.43 (s, 2H), 5.09 (s, 1H), 4.28 (s, 1H), 3.78−3.76(m, 1H), 3.11−2.92 (m, 2H), 2.86−2.76 (m, 1H), 0.86 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 172.7, 164.6, 150.1, 139.2, 134.8, 131.3, 129.4, 128.7, 128.7, 128.6, 128.3, 128.3, 128.0, 127.8, 127.3, 127.2, 126.8, 124.4, 124.2, 114.4, 82.8, 78.1, 77.4, 77.1, 76.8, 68.8, 65.0, 64.1, 53.5, 47.3, 31.9, 28.0, 27.1, 27.0. ESI-HRMS calcd for $[C_{32}H_{31}N_3NaO_6+]$: 576.2111, found 576.2119.



1ab

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (d, *J* = 7.8 Hz, 1H), 2.16−2.05 (m, 2H), 1.89−1.78 (m, 2H), 1.71−1.67 (m, 3H), 1.66−1.57 (m, 3H), 1.53−1.41 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.5, 144.2, 77.4, 77.1, 76.7, 56.0, 41.8, 39.6, 33.4, 31.3, 30.8, 30.7, 30.3, 26.5, 25.8, 25.5, −0.0.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01760.

Optimization detail, ^{1}H and ^{13}C NMR spectra, HPLC data. (PDF)

Crystal data. (CIF)

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Notes

The authors declare no competing financial interest.

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