Highly Chemoselective 2,4,5-Triaryl-1,3-dioxolane Formation from Intermolecular 1,3-Dipolar Addition of Carbonyl Ylide with Aryl Aldehydes

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General methods. Melting points were determined on a digital melting point apparatus and were uncorrected. HRMS (ESI) Mass spectra were recorded on a BRUCKER FT-MS. NMR spectra were recorded on a Bruker-300MHz spectrometer. Dichloromethane was distilled over calcium hydride before use.

General procedure for the “cross” dioxolanation of phenyldiazoacetate: To a 8 mL CH₂Cl₂ solution of Rh₂(OAc)₄ (4.4 mg, 0.01 mmol), *p*-anisaldehyde **2a** (272 mg, 2.0 mmol) and *p*-nitrobenzaldehyde **3a** (302 mg, 2.0 mmol) was added methyl phenyl diazoacetate **1** (176 mg, 1.0 mmol) in 4 mL of CH₂Cl₂ via a syringe pump over 1 h under refluxing. After completed addition, the reaction mixture was cooled to room temperature. Solvent was removed, and a portion of the crude product was subjected to ¹H NMR analysis for determination of the isomer ratio. The crude product was purified by flash chromatography on silica gel by using petroleum ether:EtOAc=10:1 as eluent to give products **4a** and **5a**, total yield 50%.

Notes: Isomers with larger R_f: **5a**, **4b**, **4c**, **4d**, **4e**, **4f**, **5g**, **5h**, **5j**, **5k**, **5l**.

Isomers with smaller R_f correspondingly: **4a**, **5b**, **5c**, **5d**, **5e**, **5f**, **4g**, **4h**, **4j**, **4k**, **4l**.

Diastereoisomers **4i/5i** and **4m/4m** were inseparable by silica gel chromatography purification, and were characterized as mixtures.

Control reaction (Scheme 4): To a 5 mL CH₂Cl₂ solution of Rh₂(OAc)₄ (2.2 mg, 0.005 mmol), *p*-anisaldehyde **2a** (68 mg, 0.5 mmol) and epoxide **7** (75 mg, 0.25 mmol) was added methyl phenyl diazoacetate **1** (88 mg, 0.5 mmol) in 2 mL of CH₂Cl₂ via a syringe pump over 1 h under refluxing. After completed addition, the reaction mixture was refluxed for additional 1 h and then cooled to room temperature. Solvent was

removed, and a portion of the crude product was subjected to ^1H NMR analysis, there have no any formation of dioxolanes. (Same procedure was used to the control reaction of **1** with **3a** and **6**, there have no any formation of dioxolanes.)

Table of the diagnostic ^1H NMR assignments ($-\text{COOCH}_3$) of compounds **4** and **5**

	4 (δ) ppm	5 (δ) ppm
a	3.89 (s, 3H)	3.52 (s, 3H)
b	3.95 (s, 3H)	3.61 (s, 3H)
c	3.95 (s, 3H)	3.61 (s, 3H)
d	3.94 (s, 3H)	3.60 (s, 3H)
e	3.92 (s, 3H)	3.60 (s, 3H)
f	3.95 (s, 3H)	3.62 (s, 3H)
g	3.86 (s, 3H)	3.52 (s, 3H)
h	3.85 (s, 3H)	3.54 (s, 3H)
i	3.78 (s, 3H)	3.55 (s, 3H)
j	3.84 (s, 3H)	3.56 (s, 3H)
k	3.83 (s, 3H)	3.46 (s, 3H)
l	3.85 (s, 3H)	3.51 (s, 3H)
m	3.86 (s, 3H)	3.67 (s, 3H)

Methyl (2*S,4*R**,5*S**)-2-(4-methoxyphenyl)-4-phenyl-5-(4-nitrophenyl)-1,3-Dioxolane-4-carboxylate, (4a):** mp 105.4-107.0 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.94-7.91 (m, 2H), 7.69-7.66 (m, 2H), 7.37-7.34 (m, 2H), 7.14-7.02 (m, 7H), 6.14 (s, 1H), 6.00 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 172.6, 161.1, 147.5, 143.8, 135.3, 128.7, 128.6, 128.4, 128.1, 127.4, 125.9, 122.9, 114.2, 103.9, 88.6, 84.3, 55.5, 53.5; HRMS: calcd for C₂₄H₂₁NO₇: 435.1318; found: 435.1324 [M+H]⁺.

Methyl (2*S,4*R**,5*R**)-2-(4-methoxyphenyl)-4-phenyl-5-(4-nitrophenyl)-1,3-Dioxolane-4-carbolate (5a):** mp 148.7-149.5 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.27-8.24 (m, 2H), 7.66-7.63 (m, 2H), 7.58-7.51 (m, 4H), 7.43-7.40 (m, 3H), 6.96-6.93 (m, 2H), 6.75 (s, 1H), 5.33 (s, 1H), 3.83 (s, 3H), 3.52 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 169.6, 160.7, 148.1, 143.2, 136.1, 130.2, 128.9, 128.6, 128.2, 128.0, 126.4, 123.4, 114.0, 105.5, 89.3, 86.1, 55.4, 52.6; HRMS: calcd for C₂₄H₂₁NO₇: 435.1318; found: 435.1311 [M+H]⁺.

Methyl (2*S,4*R**,5*S**)-2-(4-methoxyphenyl)-4-phenyl-5-(2,4-dinitrophenyl)-1,3-Dioxolane-4-carboxylate (4b):** mp 182.1-183.2 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.58 (d, *J* = 2.4 Hz, 1H), 8.06 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.68-7.64 (m, 2H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.24-7.21 (m, 2H), 7.10-7.02 (m, 5H), 6.82 (s, 1H), 6.26 (s, 1H), 3.95 (s, 3H), 3.89 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 171.0, 161.1, 148.2, 147.1, 140.0, 134.6, 132.0, 128.8, 128.4, 128.2, 127.1, 126.5, 126.1, 119.5, 114.3, 104.1, 89.2, 79.8, 55.5, 53.7; HRMS: calcd for C₂₄H₂₀N₂O₉: 480.1169; found: 480.1174 [M+H]⁺. Single crystal was grown in hexane/ethyl acetate and corresponding X-ray structure was obtained.

Methyl (2*S,4*R**,5*R**)-2-(4-methoxyphenyl)-4-phenyl-5-(2,4-dinitrophenyl)-1,3-Dioxolane-4-carboxylate (5b):** ¹H NMR (300 MHz, CDCl₃) δ 8.72 (d, *J* = 2.4 Hz, 1H), 8.44 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.58-7.54 (m, 2H), 7.52-7.49 (m, 2H), 7.41-7.35 (m, 3H), 6.97-6.93 (m, 2H), 6.54 (s, 1H), 6.20 (s, 1H), 3.84 (s, 3H), 3.61 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 169.2, 160.9, 148.7, 147.7, 138.3, 135.7, 130.7, 129.4, 129.1, 128.9, 128.3, 126.6, 126.0, 120.4, 114.1, 106.0, 90.1, 83.0, 55.5, 53.0; HRMS: calcd for C₂₄H₂₀N₂O₉: 480.1169; found: 480.1165 [M+H]⁺.

Methyl (2*S,4*R**,5*S**)-2-(2-methoxyphenyl)-4-phenyl-5-(2,4-dinitrophenyl)-1,3-Dioxolane-4-carboxylate (4c):** mp 144.8-146.2 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.54 (d, *J* = 2.4 Hz, 1H), 8.06 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.92-7.89 (m, 1H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.52-7.46 (m, 1H), 7.29-7.26 (m, 2H), 7.18-7.01 (m, 5H), 6.90 (s, 1H), 6.56 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 171.0, 158.2, 148.1, 147.0, 140.3, 134.5, 132.2, 131.6, 128.7, 128.2, 127.1, 126.4, 126.0, 122.8, 120.8, 119.4, 111.3, 100.0, 89.2, 79.5, 55.9, 53.7; HRMS: calcd for C₂₄H₂₀N₂O₉: 480.1169; found: 480.1164 [M+NH₄]⁺.

(Methyl (2*S,4*R**,5*R**)-2-(2-methoxyphenyl)-4-phenyl-5-(2,4-dinitrophenyl)-1,3-Dioxolane-4-carboxylate (5c):** mp 126.6-128.7 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.74 (d, *J* = 2.4 Hz, 1H), 8.45 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.60-7.53 (m, 3H), 7.43-7.35 (m, 4H), 7.01-6.96 (m, 2H), 6.83 (s, 1H), 6.32 (s, 1H), 3.93 (s, 3H), 3.61 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 169.3, 157.9, 148.7, 147.6, 138.8, 135.9, 131.3, 130.8, 129.3, 128.8, 127.8, 126.6, 126.1, 124.6, 120.6, 120.4, 111.1, 102.8, 90.1, 82.9, 55.8, 52.9; HRMS: calcd for C₂₄H₂₀N₂O₉: 480.1169; found: 480.1173 [M+ NH₄]⁺.

Methyl (2*S,4*R**,5*S**)-2-piperonyl-4-phenyl-5-(2,4-dinitrophenyl)-1,3-Dioxolane-4-carboxylate (4d):** mp 145.7-147.2 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.58 (d, *J* = 2.4 Hz, 1H), 8.06 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.22-7.17 (m, 4H), 7.10-7.04 (m, 3H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.79 (s, 1H), 6.20 (s, 1H), 6.06 (s, 2H), 3.94 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 170.9, 149.2, 148.1, 148.0, 147.0, 139.7, 134.4, 131.9, 128.7, 128.6, 128.1, 126.5, 126.0, 121.3, 119.5, 108.5, 107.0, 103.8, 101.6, 89.0, 79.8, 53.7; HRMS: calcd for C₂₄H₁₈N₂O₁₀: 494.0962; found: 494.0959 [M+H]⁺.

Methyl (2*S,4*R**,5*R**)-2-piperonyl-4-phenyl-5-(2,4-dinitrophenyl)-1,3-Dioxolane-4-carboxylate (5d):** mp 172.1-172.9 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.71 (d, *J* = 2.4 Hz, 1H), 8.44 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.57-7.54 (m, 2H), 7.41-7.36 (m, 3H), 7.08-7.04 (m, 2H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.48 (s, 1H), 6.18 (s, 1H), 6.00 (s, 2H), 3.60 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 169.1, 149.0, 148.6, 148.1, 147.7, 138.1, 135.5, 130.8, 130.7, 129.5, 128.9, 126.6, 125.9, 121.1, 120.4, 108.3, 106.9, 105.8, 101.5, 90.1, 83.0, 53.0; HRMS: calcd for C₂₄H₁₈N₂O₁₀: 494.0962; found: 494.0962 [M+H]⁺.

Methyl (2*S,4*R**,5*S**)-2-(3-methylphenyl)-4-phenyl-5-(2,4-dinitrophenyl)-1,3-Dioxolane-4-carboxylate (4e):** mp 137.5-138.7 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.53 (d, *J* = 2.4 Hz, 1H), 8.02 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.57-7.50 (m, 3H), 7.42-7.39 (m, 1H), 7.31-7.29 (m, 1H), 7.23-7.19 (m, 2H), 7.07-7.02 (m, 3H), 6.82 (s, 1H), 6.24 (s, 1H), 3.92 (s, 3H), 2.44 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 170.8, 148.0, 146.9, 139.8, 138.6, 134.8, 134.4, 131.9, 130.8, 128.7, 128.6, 128.0, 127.5, 126.4, 126.0, 123.6, 119.4, 103.9, 89.1, 79.7, 53.5, 21.5; HRMS: calcd for C₂₄H₂₀N₂O₈: 464.1220; found: 464.1228 [M+H]⁺.

Methyl (2*S,4*R**,5*R**)-2-(3-methylphenyl)-4-phenyl-5-(2,4-dinitrophenyl)-1,3-Dioxolane-4-carboxylate (5e):** ¹H NMR (300 MHz, CDCl₃) δ 8.70 (d, *J* = 2.4 Hz, 1H), 8.42 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.56-7.53 (m, 2H), 7.38-7.30 (m, 6H), 7.23-7.20 (m, 1H), 6.53 (s, 1H), 6.19 (s, 1H), 3.60 (s, 3H), 2.37 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 169.0, 147.5, 138.4, 138.1, 136.8, 135.4, 130.6, 130.5, 129.3, 128.7, 128.5, 128.0, 127.2, 126.4, 125.9, 123.6, 120.3, 105.9, 90.0, 82.9, 52.8, 21.4; HRMS: calcd for C₂₄H₂₀N₂O₈: 464.1220; found: 464.1225 [M+H]⁺.

Methyl (2*S,4*R**,5*S**)-2,4-diphenyl-5-(2,4-dinitrophenyl)-1,3-Dioxolane-4-carboxylate (4f):** mp 171.5-172.5 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.57 (d, *J* = 2.4 Hz, 1H), 8.05 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.75-7.72 (m, 2H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.55-7.51 (m, 3H), 7.24-7.20 (m, 2H), 7.10-7.04 (m, 3H), 6.85 (s, 1H), 6.30 (s, 1H), 3.95 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 170.9, 148.1, 147.1, 139.9, 135.0, 134.4, 132.0, 130.2, 128.9, 128.8, 128.2, 126.8, 126.5, 126.1, 119.5, 104.0, 89.3, 79.8 53.7; HRMS: calcd for C₂₃H₁₈N₂O₈: 450.1063; found: 450.1064 [M+H]⁺.

Methyl (2*S,4*R**,5*R**)-2,4-diphenyl-5-(2,4-dinitrophenyl)-1,3-Dioxolane-4-carboxylate (5f):** mp 134.0-135.7 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.73 (d, *J* = 2.4 Hz, 1H), 8.44 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 1H), 7.59-7.54 (m, 4H), 7.45-7.26 (m, 6H), 6.59 (s, 1H), 6.21 (s, 1H), 3.62 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 169.1, 148.6, 147.7, 138.1, 137.0, 135.4, 130.8, 130.0, 129.5, 128.9, 128.7, 126.7, 126.6, 126.0, 120.4, 105.9, 90.2, 83.0, 53.0; HRMS: calcd for C₂₃H₁₈N₂O₈: 450.1063; found: 450.1066 [M+ NH₄]⁺.

Methyl (2*S,4*R**,5*S**)-2-(2,4-dimethoxyphenyl)-4-phenyl-5-(4-nitrophenyl)-1,3-Dioxolane-4-carboxylate (4g):** mp 169.8-170.5 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.92-7.89 (m, 2H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.36-7.33 (m, 2H), 7.18-7.15 (m, 2H), 7.08-7.03 (m, 3H), 6.65 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 6.43 (s, 1H), 6.00 (s, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 172.7, 162.4, 159.4, 147.3, 144.2, 135.4, 128.7, 128.4, 128.3, 128.0, 125.9, 122.8, 115.8, 104.7, 99.5, 98.7, 88.4, 84.1, 55.8, 55.5, 53.4; HRMS: calcd for C₂₅H₂₃NO₈: 465.1424; found: 465.1418 [M+H]⁺.

Methyl (2*S,4*R**,5*R**)-2-(2,4-dimethoxyphenyl)-4-phenyl-5-(4-nitrophenyl)-1,3-Dioxolane-4-carboxylate (5g):** mp 121.7-122.4 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.26-8.22 (m, 2H), 7.68-7.64 (m, 2H), 7.59-7.56 (m, 2H), 7.48-7.38 (m, 4H), 7.00 (s, 1H), 6.51-6.48 (m, 2H), 5.35 (s, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.52 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 169.8, 162.2, 159.2, 148.1, 143.6, 136.4, 128.8, 128.6, 128.5, 128.4, 126.5, 123.4, 118.3, 104.3, 102.2, 98.8, 89.1, 85.9, 55.7, 55.5, 52.5; HRMS: calcd for C₂₅H₂₃NO₈: 465.1424; found: 465.1424 [M+H]⁺.

Methyl (2*S,4*R**,5*S**)-2-(2,4,6-trimethoxyphenyl)-4-phenyl-5-(4-nitrophenyl)-1,3-Dioxolane-4-carboxylate (4h):** mp 195.6-196.5 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.95-7.90 (m, 2H), 7.49-7.45 (m, 2H), 7.31-7.28 (m, 2H), 7.05-7.01 (m, 3H), 6.62 (s, 1H), 6.20 (s, 2H), 5.93 (s, 1H), 3.89 (s, 6H), 3.87 (s, 3H), 3.85 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 173.6, 163.1, 161.3, 147.3, 145.0, 135.9, 128.8, 128.0, 127.6, 126.2, 122.7, 102.3, 98.7, 90.9, 87.9, 84.0, 55.6, 55.5, 53.3; HRMS: calcd for C₂₆H₂₅NO₉: 495.1529; found: 495.1522 [M+H]⁺.

Methyl (2*S,4*R**,5*R**)-2-(2,4,6-trimethoxyphenyl)-4-phenyl-5-(4-nitrophenyl)-1,3-Dioxolane-4-carboxylate (5h):** mp 190.0-190.9 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.24-8.19 (m, 2H), 7.69-7.66 (m, 2H), 7.57-7.54 (m, 2H), 7.42-7.36 (m, 3H), 7.31 (s, 1H), 6.15 (s, 2H), 5.48 (s, 1H), 3.82 (s, 3H), 3.76 (s, 6H), 3.54 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 170.0, 162.8, 160.7, 147.9, 144.5, 136.4, 128.6, 128.3, 128.2, 126.6, 123.2, 105.7, 100.5, 90.9, 89.5, 86.9, 55.8, 55.4, 52.4; HRMS: calcd for C₂₆H₂₅NO₉: 495.1529; found: 495.1525 [M+H]⁺.

Methyl (2*S,4*R**,5*S**)-2-(2,4,6-trimethoxyphenyl)-4-phenyl-5-(2-nitrophenyl)-1,3-Dioxolane-4-carboxylate and Methyl (2*S**,4*R**,5*R**)-2-(2,4,6-trimethoxyphenyl)-4-phenyl-5-(2-nitrophenyl)-1,3-Dioxolane-4-carboxylate (4i+5i)** (mixture of diastereomers) ¹H NMR (300 MHz, CDCl₃) δ (7.74-7.70 (m, 1 H); minor diastereomer, **5i**), (7.70-7.69 (m, 1H)), 7.76-7.72 (m, 1H; major diastereomer, **4i**), (7.66-7.62 (m, 2H)), 7.66-7.65 (m, 1H), (7.59-7.56 (m, 1H)), (7.48-7.42 (m, 1H)), 7.38-7.30 (m, 4H), (7.22 (s, 1H)), (7.20-7.15 (m, 3H)), 7.02-6.99 (m, 3H), 6.81 (s, 1H), 6.55 (s, 1H), (6.28 (s, 1H)), 6.19 (s, 2H), (6.13 (s, 2H)), (3.89 (s, 6H)), 3.88 (s, 6H), 3.83 (s, 3H), (3.81 (s, 3H)), 3.78 (s, 3H), (3.55 (s, 3H)); ¹³C NMR (75 MHz, CDCl₃) δ 172.2(170.0), 163.0(162.6), 161.3(160.7), 148.6(149.2), 136.4(136.2), 133.4(131.5), 132.3(132.2), 130.8(129.6), 128.3(129.0), 128.1(128.5), 127.1(127.5), 126.7(126.2), 123.4(124.7), 100.4(105.8), 98.6(102.4), 90.9(90.8), 87.7(89.6), 80.0(82.7), 55.7(55.4), 55.5(53.1), 55.4(52.3); HRMS: calcd for C₂₆H₂₅NO₉: 495.1529; found: 495.1529 [M+H]⁺.

Methyl (2*S,4*R**,5*S**)-2-(2,4,6-trimethoxyphenyl)-4-phenyl-5-(2-formylphenyl)-1,3-Dioxolane-4-carboxylate (4j):** ¹H NMR (300 MHz, CDCl₃) δ 10.46 (s, 1H), 7.68-

7.61 (m, 2H), 7.34-7.20 (m, 4H), 7.03-6.99 (m, 3H), 6.69 (s, 1H), 6.46 (s, 1H), 6.19 (s, 2H), 3.89 (s, 6H), 3.85 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 192.9, 173.5, 163.1, 161.3, 138.7, 136.1, 135.0, 133.0, 130.4, 128.6, 128.3, 127.8, 127.4, 126.6, 102.2, 98.6, 90.9, 87.3, 83.3, 55.7, 55.5, 53.2; HRMS: calcd for $\text{C}_{27}\text{H}_{26}\text{O}_8$: 478.1628; found: 478.1627 $[\text{M}+\text{H}]^+$.

Methyl (2*S,4*R**,5*R**)-2-(2,4,6-trimethoxyphenyl)-4-phenyl-5-(2-formylphenyl)-1,3-Dioxolane-4-carboxylate (5j):** mp 126.5-127.8 °C; ^1H NMR (300 MHz, CDCl_3) δ 9.87 (s, 1H), 7.95-7.92 (m, 1H), 7.73-7.58 (m, 4H), 7.51-7.46 (m, 1H), 7.35-7.31 (m, 3H), 6.26 (s, 1H), 6.16 (s, 2H), 3.82 (s, 3H), 3.79 (s, 6H), 3.56 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 190.6, 170.1, 162.6, 160.7, 138.4, 135.6, 134.6, 133.3, 129.5, 128.62, 128.64 (overlap, 2C), 128.2, 126.6, 106.1, 100.0, 90.8, 89.7, 83.3, 55.7, 55.4, 52.3; HRMS: calcd for $\text{C}_{27}\text{H}_{26}\text{O}_8$: 478.1628; found: 478.1625 $[\text{M}+\text{H}]^+$.

Methyl (2*S,4*R**,5*S**)-2-(2,4,6-trimethoxyphenyl)-4-phenyl-5-(4-trifluoromethylphenyl)-1,3-Dioxolane-4-carboxylate (4k):** mp 132.0-133.5 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.25 (m, 6H), 7.03-7.01 (m, 3H), 6.62 (s, 1H), 6.18 (s, 2H), 5.88 (s, 1H), 3.87 (s, 6H), 3.84 (s, 3H), 3.83 (s, 3H); ^{19}F (282 MHz, CDCl_3) δ -62.52; ^{13}C NMR (75 MHz, CDCl_3) δ 173.7, 163.0, 161.3, 141.3, 136.1, 129.6 (q, $^2J(\text{C},\text{F}) = 32$ Hz), 128.4, 127.6, 127.3, 126.3, 124.3 (q, $^3J(\text{C},\text{F}) = 4$ Hz), 124.1 (q, $^1J(\text{C},\text{F}) = 270$ Hz), 102.6, 98.5, 90.9, 87.6, 84.5, 55.5, 55.4, 53.1; HRMS: calcd for $\text{C}_{27}\text{H}_{25}\text{F}_3\text{O}_7$: 518.1552; found: 518.1553 $[\text{M}+\text{H}]^+$.

Methyl (2*S,4*R**,5*R**)-2-(2,4,6-trimethoxyphenyl)-4-phenyl-5-(4-trifluoromethylphenyl)-1,3-Dioxolane-4-carboxylate (5k):** mp 173.5-174.3 °C; ^1H

NMR (300 MHz, CDCl₃) δ 7.70-7.67 (m, 2H), 7.64-7.61 (m, 2H), 7.56-7.53 (m, 2H), 7.39-7.33 (m, 4H), 6.13 (s, 2H), 5.48 (s, 1H), 3.78 (s, 3H), 3.71 (s, 6H), 3.46 (s, 3H); ¹⁹F (282 MHz, CDCl₃) δ -62.35; ¹³C NMR (75 MHz, CDCl₃) δ 170.2, 162.6, 160.7, 141.3 (q, ⁴J(C,F) = 1 Hz), 137.0, 130.4 (q, ²J(C,F) = 32 Hz), 128.2, 128.0, 127.8, 126.7, 124.9 (q, ³J(C,F) = 4 Hz), 124.2 (q, ¹J(C,F) = 270 Hz), 106.1, 100.6, 90.8, 89.5, 87.2, 55.6, 55.3, 52.1; HRMS: calcd for C₂₇H₂₅F₃O₇: 518.1552; found: 518.1554 [M+H]⁺.

Methyl (2*S,4*R**,5*S**)-2-(2,4,6-trimethoxyphenyl)-4-phenyl-5-(4-cyanomethylphenyl)-1,3-Dioxolane-4-carboxylate (4l):** mp 152.0-152.6 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.41-7.33 (m, 4H), 7.29-7.26 (m, 2H), 7.06-7.01 (m, 3H), 6.61 (s, 1H), 6.19 (s, 2H), 5.87 (s, 1H), 3.88 (s, 6H), 3.86 (s, 3H), 3.85 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 173.6, 163.1, 161.3, 142.9, 136.0, 131.3, 128.7, 127.9, 127.5, 126.2, 119.0, 111.3, 102.4, 98.6, 90.9, 87.8, 84.3, 55.6, 55.5, 53.3; HRMS: calcd for C₂₇H₂₅NO₇: 475.1631; found: 475.1634 [M+H]⁺. Single crystal was grown in hexane/ethyl acetate and corresponding X-ray structure was obtained.

Methyl (2*S,4*R**,5*R**)-2-(2,4,6-trimethoxyphenyl)-4-phenyl-5-(4-cyanomethylphenyl)-1,3-Dioxolane-4-carboxylate (5l):** mp 171.1-171.9 °C; ¹H NMR (300 MHz, CDCl₃) δ 7.68-7.63 (m, 4H), 7.52-7.50 (m, 2H), 7.40-7.36 (m, 3H), 7.30 (s, 1H), 6.14 (s, 2H), 5.44 (s, 1H), 3.82 (s, 3H), 3.74 (s, 6H), 3.51 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 170.0, 162.7, 160.7, 142.6, 136.6, 131.8, 128.5, 128.2, 128.0, 126.6, 118.9, 112.1, 105.8, 100.5, 90.9, 89.5, 87.0, 55.7, 55.4, 52.3; HRMS: calcd for C₂₇H₂₅NO₇: 475.1631; found: 475.1620 [M+H]⁺. Single crystal was grown in hexane/ethyl acetate and corresponding X-ray structure was obtained.

Methyl (2*S,4*R**,5*S**)-2-(2,4,6-trimethoxyphenyl)-4-phenyl-5-(2,4-dinitrophenyl)-1,3-Dioxolane-4-carboxylate and Methyl (2*S**,4*R**,5*R**)-2-(2,4,6-trimethoxyphenyl)-4-phenyl-5-(2,4-dinitrophenyl)-1,3-Dioxolane-4-carboxylate (4*m*+5*m*)** (mixture of diastereomers): ¹H NMR (300 MHz, CDCl₃) δ (8.64 (d, *J* = 2.4 Hz, 1H); minor diastereomer, **5*m***), 8.54 (m, 1H; major diastereomer, **4*m***), (8.39 (dd, *J* = 8.7, 2.4 Hz, 1H)), 8.04 (m, 2H), (7.94 (d, *J* = 8.7 Hz, 1H)), (7.63-7.59 (m, 2H)), 7.39-7.30 (m, 2H), (7.39-7.32 (m, 3H)), (7.11 (s, 1H)), 7.05-7.02 (m, 3H), 6.75 (s, 1H), 6.66 (s, 1H), (6.25 (s, 1H)), 6.21 (s, 2H), (6.16 (s, 2H)), 3.92 (s, 6H), 3.91 (s, 3H), 3.86 (s, 3H), (3.84 (s, 9H)), (3.67 (s, 3H)); ¹³C NMR (75 MHz, CDCl₃) δ 171.6(169.7), 163.3(163.0), 161.2(160.7), 148.2(148.8), 146.8(147.4), 140.8(138.3), 135.7(135.1), 132.8(131.4), 128.6(129.1), 127.7(128.3), 126.3(125.97), 125.89(126.03), 119.0(120.2), 100.3(105.1), 99.1(101.9), 91.0(90.9), 88.3(89.8), 79.3(82.8), 55.6(55.8), 55.5(55.4), 53.4(52.8) ; HRMS: calcd for C₂₆H₂₄N₂O₁₁: 540.1380; found: 540.1385 [M+H]⁺.

Procedure for Reaction of Phenyldiazoacetate with 2,4-dinitrobenzaldehyde: To a 8 mL CH₂Cl₂ solution of Rh₂(OAc)₄ (4.4 mg, 0.01 mmol), 2,4-dinitrobenzaldehyde(196 mg, 1.0 mmol) was added methyl phenyl diazoacetate (176 mg, 1.0 mmol) in 4 mL of CH₂Cl₂ via a syringe pump over 1 h under refluxing. After completed addition, the reaction mixture was cooled to room temperature. Solvent was removed and a portion of crude product was subjected to ¹H NMR analysis for determination of the isomer ratio. Only one stereoisomer was observed. The crude product was purified by flash chromatography on silica gel by using petroleum ether:EtOAc=10:1 as eluent to give stereospecific epoxide 196 mg (57% yield, white powder).

Methyl (2*R, 3*R**)-2-phenyl-3-(2,4-dinitrophenyl)-oxirane-2-carboxylate:** mp 152.4-153.7 °C; ¹H NMR (300 MHz, CDCl₃) δ 9.05 (d, *J* = 2.4 Hz, 1H), 8.55 (dd, *J* = 8.7, 2.4 Hz, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.74-7.69 (m, 2H), 7.50-7.43 (m, 3H), 4.76 (s, 1H), 3.48 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 166.6, 148.0, 147.5, 137.2, 133.5, 131.2, 129.5, 128.8, 128.2, 127.0, 120.3, 66.8, 63.0, 53.0; HRMS: calcd for C₁₆H₁₂N₂O₇: 344.0645; found: 344.0644 [M+H]⁺.

X-ray structure of **4b**

L04031882

L040318B1

L04040501R

L040406D2

L04040BA1

L040409A2

L04040881

L040408B2

L04042181

L04042182

L040409B1P

L040413A2

L040414a2

L040414A1

L040415B2

L04041531

L040419A

4i+5i

Current Data Parameters
 NAME 1399-1cd-611
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20040419
 Time 15.53
 INSTRUM av300
 PROBHD 5 mm QNP 1H/13
 PULPROG zgpg30
 TO 69536
 SOLVENT D2O
 NS 143
 DS 4
 SWH 22675.736 Hz
 FIDRES 0.345004 Hz
 AQ 1.445188 sec
 RG 8132
 DM 22.050 usec
 DE 6.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 d12 0.00002000 sec

***** CHANNEL f1 *****
 NUC1 13C
 P1 5.50 usec
 PL1 -6.00 dB
 SF01 75.477598 MHz

***** CHANNEL f2 *****
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -2.00 dB
 PL12 17.70 dB
 PL13 17.71 dB
 SF02 500.1312005 MHz

F2 - Processing parameters
 SI 65536
 SF 75.4677473 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 10.00 cm
 ZP 180.484 gpm
 F1 13620.75 Hz
 F2 3049.17 Hz
 GPCPM 7.00404 gpm/cm
 437M 437M2 437M

L04041962

L04041981

L040420C2

L04C420C1

Current Data Parameters
NAME 1399-1cd-622
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20040421
Time 11.12
INSTRUM av300
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 2688
SOLVENT DMSO
NS 441
DS 4
SWH 22575.735 Hz
FIDRES 0.346004 Hz
AQ 1.4451109 sec
RG 8192
CW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.60000000 sec
d11 0.03000000 sec
d12 0.00000000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SF01 75.4775598 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 12.71 dB
SF02 300.1312005 MHz

F2 - Processing parameters
SI 65536
SF 75.4677480 MHz
WDW EN
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
Ck 20.00 cm
Cv 10.00 cm
ZfP 200.000 ppm
F1 15093.55 Hz
F2P 0.000 ppm
F2 0.00 Hz
-FNUC 10.00000 ppm/cm
-FZCM 754.67749 Hz/cm

L040421A2

L040421A1

1.0404204