Supporting Information

for

“Ruthenium Catalyzed Stereoselective Intramolecular Carbenoid C–H Insertion for β - and γ -Lactam Formations by Decomposition of α -Diazoacetamides”

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Content	Page
General Experimental Section	S4
General Procedure for the Synthesis of the α -Diazo compounds	S4-S7
General Procedure for the $[\text{RuCl}_2(p\text{-cymene})]_2$ Catalyzed Intramolecular Carbenoid C–H Insertion Reaction & Table S1	S8-S12
General Procedure for the $[\text{RuCl}_2(\text{L}^*)(\text{C}_2\text{H}_4)]$ Catalyzed Asymmetric Intramolecular Carbenoid C–H Insertion Reaction & Table S2	S13
Figure S1. ^1H NMR Spectrum of <i>N-p</i> -Chlorobenzyl- <i>N-tert</i> -butyl- α -ethoxycarbonyl- α -diazoacetamide (1a)	S14
Figure S2. ^1H NMR Spectrum of <i>N</i> -Benzyl- <i>N-tert</i> -butyl- α -ethoxycarbonyl- α -diazoacetamide (1b)	S15
Figure S3. ^1H NMR Spectrum of <i>N-p</i> -Methoxybenzyl- <i>N-tert</i> -butyl- α -ethoxycarbonyl- α -diazoacetamide (1c)	S16
Figure S4. ^1H NMR Spectrum of <i>N-p</i> -Chlorobenzyl- <i>N-tert</i> -butyl- α -carbonyl- α -diazoacetamide (1d)	S17
Figure S5. ^1H NMR Spectrum of <i>N,N</i> -Diisopropyl- α -ethoxycarbonyl- α -diazoacetamide (1e)	S18
Figure S6. ^1H NMR Spectrum of <i>N</i> -Phenylethyl- <i>N-tert</i> -butyl- α -ethoxycarbonyl- α -diazoacetamide (1f)	S19
Figure S7. ^1H NMR Spectrum of <i>N</i> -Phenylethyl- <i>N</i> -benzyl- α -ethoxycarbonyl- α -diazoacetamide (1g)	S20
Figure S8. ^1H NMR Spectrum of <i>N</i> -Benzyl- <i>N-p</i> -methoxybenzyl- α -ethoxycarbonyl- α -diazoacetamide (1h)	S21
Figure S9. ^1H NMR Spectrum of <i>N</i> -Phenylethyl- <i>N-p</i> -methoxybenzyl- α -ethoxycarbonyl- α -diazoacetamide (1i)	S22
Figure S10. ^1H NMR Spectrum of <i>N-tert</i> -Butyl- <i>cis</i> -1-ethoxycarbonyl-2- <i>p</i> -chlorophenyl- β -lactam (2a)	S23
Figure S11. ^1H NMR Spectrum of <i>N-tert</i> -Butyl- <i>cis</i> -1-ethoxycarbonylphenyl- β -lactam (2b)	S24
Figure S12. ^1H NMR Spectrum of <i>N-tert</i> -Butyl- <i>cis</i> -1-ethoxycarbonyl-2- <i>p</i> -methoxyphenyl- β -lactam (2c)	S25
Figure S13. ^1H NMR Spectrum of <i>N-tert</i> -Butyl- <i>trans</i> -1-carbonyl-2- <i>p</i> -chlorophenyl- β -lactam (2d)	S26
Figure S14. ^1H NMR Spectrum of <i>N</i> -Isopropyl-1-ethoxycarbonyl-2,2-dimethyl- β -lactam (2e)	S27
Figure S15. ^1H NMR Spectrum of <i>N-tert</i> -Butyl- <i>cis</i> -1-ethoxycarbonyl-2-benzyl- β -lactam (2f)	S28
Figure S16. ^1H NMR Spectrum of <i>N-tert</i> -Butyl- <i>trans</i> -1-ethoxycarbonyl-2-phenyl- γ -lactam (3)	S29
Figure S17. ^1H NMR Spectrum of <i>N</i> -Phenylethyl- <i>cis</i> -1-ethoxycarbonyl-2-phenyl- β -lactam (2g)	S30
Figure S18. ^1H NMR Spectrum of <i>N</i> -Benzyl- <i>trans</i> -1-ethoxycarbonyl-2-phenyl- γ -lactam (4)	S31
Figure S19. ^1H NMR Spectrum of <i>N</i> -Benzyl-5-methoxy-1,3-dihydro-indol-2-one (5)	S32

Figure S20. ^1H NMR Spectrum of <i>N</i> -Phenethyl-5-methoxy-1,3-dihydro-indol-2-one (6)	S33
Figure S21. NOESY of <i>trans</i> -(3)	S34
Figure S22. NOESY of <i>trans</i> -(4)	S35
References	S36

General Experimental Section: All reactions were performed using the standard Schlenk technique under a nitrogen atmosphere. Pyridine bis(oxazoline) ligand (L^*) was obtained commercially and used without further purification unless indicated otherwise. $[\text{RuCl}_2(p\text{-cymene})]_2$ and $[\text{RuCl}_2(L^*)(\text{C}_2\text{H}_4)]$ were synthesized by the literature method.¹ Toluene was freshly distilled from sodium/benzophenone under a nitrogen atmosphere. Dichloromethane was freshly distilled from calcium hydride under a nitrogen atmosphere. Flash chromatography was performed on a silica gel (Merck Kiesegel 60 F₂₅₄ 230-400 mesh) column. ^1H and ^{13}C -NMR spectra were recorded on Bruker DPX-300, 400 or 500 spectrometer. Chemical shifts (δ , ppm) were determined with TMS as internal reference, carbon multiplicities were determined by DEPT-135 experiments. Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer. IR spectra (ν , cm^{-1}) were recorded on a Bio-RAD PTS-165 spectrometer.

General Procedure for the Synthesis of the α -Diazo compounds

To a mixture of malonic acid ethyl esters (10 mmol) and *p*-ABSA (15 mmol) in anhydrous acetonitrile (20 mL), DBU (15 mmol) was added dropwise. The resulting mixture was stirred at room temperature, and the reaction was monitored by TLC (20% EtOAc-hexanes mixture). Upon complete consumption of the starting materials, the reaction mixture was diluted with 20 mL distilled water, followed by extraction with diethyl ether. After washing with 10% NaHCO_3 solution and brine, the combined organic extracts were dried over MgSO_4 and concentrated to ca. 2 mL by rotary evaporation. The residue was purified by flash chromatography (10 – 15% EtOAc-hexanes) to afford the α -diazoacetamides.

N-p-Chlorobenzyl-N-tert-butyl- α -ethoxycarbonyl- α -diazoacetamide (1a).

Yellow solid, 89% yield. ^1H NMR (400 MHz, CDCl_3): δ_{H} 7.30 (d, $J = 6.7$ Hz, 2H), 7.14 (d, $J = 6.7$ Hz, 2H), 4.58 (s, 2H), 4.23 (q, $J = 7.1$ Hz, 2H), 1.38 (s, 9H) 1.29 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 163.6, 138.4, 133.3, 129.0, 128.4, 61.5, 59.2, 51.1, 29.0, 14.6. IR (neat): 2978, 2126, 1764, 1708, 1629, 1492, 1384, 1288, 1196, 1092, 1014, 722, 696, 542. MS (EI): 280(3), 236(4), 165(5), 210(8), 125(18). HRMS (EI): Found 309.1130, $\text{C}_{16}\text{H}_{20}\text{NClO}_3$ requires 309.1132.

N-Benzyl-N-tert-butyl- α -ethoxycarbonyl- α -diazoacetamide (1b). Yellow solid, 90% yield. ^1H NMR (300 MHz, CDCl_3): δ_{H} 7.36-7.19 (m, 5H), 4.62 (s, 2H), 4.23 (q, $J = 7.1$ Hz, 2H), 1.39 (s, 9H), 1.32 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 163.4, 162.7, 139.7, 128.7, 127.4, 126.9, 61.3, 59.0, 51.7, 28.9, 14.5. IR (neat): 2983, 2119, 1692, 1622, 1393, 1292, 1199, 1093, 1018, 966, 715, 464. MS (EI): 288($\text{M}^+ - \text{N}_2$, 3), 246(62), 202(65), 191(11), 190(100), 176(91), 147(49), 131(69). HRMS (EI): Found 288.1347, $\text{C}_{17}\text{H}_{20}\text{NO}_4$ requires 288.1362.

N-p-Methoxybenzyl-N-tert-butyl- α -ethoxycarbonyl- α -diazoacetamide (1c).

Yellow solid, 92% yield. ^1H NMR (300 MHz, CDCl_3): δ_{H} 7.11 (d, $J = 8.6$ Hz, 2H), 6.86(d, $J = 8.6$ Hz, 2H), 4.55 (s, 2H), 4.24 (q, $J = 7.1$ Hz, 2H), 3.81 (s, 3H), 1.37 (s, 9H), 1.29 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 163.4, 162.8, 159.0, 131.6, 128.2, 114.2, 61.4, 59.0, 55.5, 51.2, 28.9, 14.6. IR (neat): 2965, 2121, 1703, 1607, 1511, 1396, 1289, 1241, 1107, 817, 756, 554, 421. MS (EI): 305($\text{M}^+ - \text{N}_2$, 1), 232(11), 206(8), 176(8), 161(6), 121(15). HRMS (EI): Found 305.1627, $\text{C}_{17}\text{H}_{20}\text{NO}_4$ requires 305.1627.

N-p-Chlorobenzyl-N-tert-butyl- α -carbonyl- α -diazoacetamide (1d). Yellow solid, 90% yield. ^1H NMR (300 MHz, CDCl_3): δ_{H} 7.32 (d, $J = 6.6$ Hz, 2H), 7.13(d, $J = 6.6$ Hz, 2H), 4.56 (s, 2H), 2.26 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 163.3, 162.5, 137.8, 133.5, 129.1, 127.7, 59.3, 50.7, 28.8, 27.3. IR (neat): 2978, 2126, 1764, 1708, 1629, 1492, 1384, 1288, 1196, 1092, 1014, 722, 696, 542. MS (EI): 281(M^+ , 15), 131(100), 111(97). HRMS (EI): Found 280.9824, $\text{C}_{15}\text{H}_{20}\text{ClNO}_2$ requires 281.1183.

***N,N*-Diisopropyl- α -ethoxycarbonyl- α -diazoacetamide (1e).** Yellow oil, 95% yield. ^1H NMR (400 MHz, CDCl_3): δ_{H} 4.24 (q, $J = 7.1$ Hz, 2H), 3.71 (m, 2H), 1.34 (d, $J = 6.7$ Hz, 12H), 1.29 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 163.2, 159.5, 61.2, 20.9, 14.4. IR (neat): 2972, 2121, 1712, 1625, 1438, 1334, 1282, 1135, 1089, 1036, 918, 836, 756, 619, 531. MS (EI): 226($\text{M}^+ - \text{CH}_3$, 12), 128(100), 124(32), 110(97). HRMS (EI): Found 226.1189, $\text{C}_{10}\text{H}_{16}\text{N}_3\text{O}_3$ requires 226.1192.

***N*-Phenylethyl-*N*-*tert*-butyl- α -ethoxycarbonyl- α -diazoacetamide (1f).** Yellow oil, 86% yield. ^1H NMR (300 MHz, CDCl_3): δ_{H} 7.33-7.15 (m, 5H), 4.20 (q, $J = 7.1$ Hz, 2H), 3.66 (t, $J = 7.4$ Hz, 2H), 2.85 (t, $J = 7.4$ Hz, 2H), 1.54 (s, 9H), 1.26 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 162.6, 162.4, 138.4, 128.8, 128.7, 126.7, 61.2, 58.0, 53.9, 38.3, 29.2, 14.4. IR (neat): 2980, 2126, 1706, 1632, 1390, 1290, 1196, 1095, 1020, 761, 701. MS (EI): Found 317(M^+), 226(54), 170(100), 105(13). HRMS (EI): Found 317.1757, $\text{C}_{17}\text{H}_{23}\text{N}_3\text{O}_3$ requires 317.1739.

***N*-Phenylethyl-*N*-benzyl- α -ethoxycarbonyl- α -diazoacetamide (1g).** Pale yellow oil, 81%. ^1H NMR (300 MHz, CDCl_3): δ_{H} 7.35-7.10 (m, 10H), 4.60 (s, 2H), 4.23 (q, $J = 7.1$ Hz, 2H), 3.51 (t, $J = 7.4$ Hz, 2H), 2.84 (t, $J = 7.4$ Hz, 2H), 1.26 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 162.4, 161.8, 138.5, 136.5, 128.8, 128.6, 128.5, 127.7, 127.6, 126.5, 61.3, 51.0, 49.1, 34.0, 14.4. IR (neat): 2127, 1711, 1627, 1496, 1454, 1421, 1292, 1104, 753, 700. MS (EI): 323($[\text{M} - \text{N}_2]^+ 24$), 260(57), 250(81), 232(19), 131(29), 118(100). HRMS (EI): Found 323.1518, $\text{C}_{20}\text{H}_{21}\text{NO}_3$ requires 323.1521.

***N*-Benzyl-*N*-*p*-methoxybenzyl- α -ethoxycarbonyl- α -diazoacetamide (1h).** Yellow solids, 72% yield. ^1H NMR (300 MHz, CDCl_3): δ_{H} 7.26-7.21 (m, 5H), 6.98 (d, J = 6.7 Hz, 2H), 6.80 (d, J = 6.7 Hz, 2H), 4.94 (s, 2H), 4.07 (q, J = 7.1 Hz, 2H), 3.76 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 162.4, 162.1, 160.9, 158.5, 137.0, 134.9, 128.6, 128.4, 128.1, 127.5, 118.2, 114.4, 61.4, 55.4, 54.4, 14.3. IR (neat): 2981, 2119, 1722, 1634, 1512, 1388, 1297, 1249, 1107, 1027, 837, 730, 700, 626, 565. MS (EI): 325(10), 279(19), 91(17). HRMS (EI): Found 353.1372, $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}_4$ requires 353.1376.

***N*-Phenylethyl-*N*-*p*-methoxybenzyl- α -ethoxycarbonyl- α -diazoacetamide (1i).** Yellow oil, 84% yield. ^1H NMR (400 MHz, CDCl_3): δ_{H} 7.27-7.17 (m, 5H), 7.00 (d, J = 6.7 Hz, 2H), 6.87 (d, J = 6.7 Hz, 2H), 4.09 (q, J = 7.1 Hz, 2H), 3.93 (t, J = 7.9 Hz, 2H), 3.80 (s, 3H), 2.90 (t, J = 7.9 Hz, 2H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (400 MHz, CDCl_3): δ_{C} 162.3, 160.7, 158.7, 138.9, 135.2, 129.0, 128.6, 128.1, 126.5, 114.7, 61.4, 55.6, 53.2, 33.9, 14.4. IR (neat): 2932, 2117, 1724, 1635, 1511, 1298, 1249, 1107, 1028, 750, 701. MS (EI): 367(M^+ , 14), 339(19), 293(21), 267(100), 248(31), 222(30), 202(60), 176(96), 163(16), 148(69), 136(18), 134(16), 133(19), 105(20). HRMS (EI): Found 367.1522, $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_4$ requires 367.1532.

General Procedure for the [RuCl₂(*p*-cymene)]₂Catalyzed Intramolecular Carbenoid C–H Insertion Reaction

A mixture of **1a** (0.1 mmol) and [RuCl₂(*p*-cymene)]₂ (0.5 mol%) were stirred in a solvent (10 mL) at 70°C. After 0.5 – 1.5h, the mixture was concentrated to ca. 2 mL by vacuum evaporation and the yield of **2a** was determined by ¹H NMR using the internal standard method. Results are summarized in Table S1.

Table S1. Ru-Catalyzed Cyclization of α -Diazoacetamide **1a** to *cis*- β -Lactam **2a**

entry	solvent	temp / °C	time / h	%conv	%yield
1	toluene	70	0.5	100	>99 ^b
2	EtOAc	70	1	100	>99
3	acetone	70	1	100	>99
4	CHCl ₃	70	1.5	78	>99 ^c
5	CH ₂ Cl ₂	40	1.5	62	61 ^c
6	THF	70	1.5	60	>99 ^c
7	DMF	70	1.5	5	trace
8	CH ₃ OH	70	1.5	0	0
9	CH ₃ CN	70	1.5	0	0

^a: Reaction conditions: A mixture of **1a** (0.1 mmol) and [RuCl₂(*p*-cymene)]₂ (0.5 mol%) were stirred in a solvent at 70 °C (oil bath temperature) in an open atmosphere. Yield of **2a** was determined by ¹H NMR using the internal standard method. ^b: Identical yield was obtained when the reaction was carried out under N₂ atmosphere. ^c: Yield was determined based on % substrate conversion

A mixture of diazo compound (0.1 mmol) and $[\text{RuCl}_2(p\text{-cymene})]_2$ (0.5 – 2.5 mol%) were stirred in toluene (10 mL) at 70°C. By means of TLC analysis (20% EtOAc – hexanes), the reaction was monitored for complete consumption of the diazo starting materials. To work-up, the mixture was concentrated to ca. 2 mL by vacuum evaporation, and the residue was purified by flash chromatography (5 – 20% EtOAc-hexanes) to afford the lactams.

N-tert-Butyl-cis-1-ethoxycarbonyl-2-p-chlorophenyl-β-lactam (2a).² White oil, >99% yield. ^1H NMR (300 MHz, CDCl_3): δ_{H} 7.33–7.27 (m, 4H), 4.89 (d, $J = 6.3$ Hz, 1H), 4.21 (d, $J = 6.3$ Hz, 1H), 3.81 (q, $J = 7.1$ Hz, 2H), 1.26 (s, 9H), 0.91 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 166.9, 163.9, 136.4, 135.7, 129.7, 62.2, 60.1, 57.0, 56.2, 30.8, 29.2, 14.8. IR (neat): 2978, 1764, 1723, 1492, 1371, 1093, 1014, 842, 588, 511. MS (EI): 210(100), 182(38), 165(82). HRMS (EI): Found M^+ 309.1124, $\text{C}_{16}\text{H}_{20}\text{NClO}_3$ requires 309.1132.

N-tert-Butyl-cis-1-ethoxycarbonylphenyl-β-lactam (2b). Yellow solid, >99% yield. ^1H NMR (300 MHz, CDCl_3): δ_{H} 7.34–7.27 (m, 5H), 4.91 (d, $J = 6.3$ Hz, 1H), 4.21 (d, $J = 6.3$ Hz, 1H), 3.76 (q, $J = 7.1$ Hz, 2H), 1.31 (s, 9H), 0.84 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ_{C} 166.0, 163.1, 136.8, 128.8, 128.4, 127.3, 118.3, 61.0, 59.1, 56.7, 28.2, 13.7. IR (neat): 2978, 1762, 1730, 1634, 1457, 1369, 1325, 1229, 1186, 1186, 1022, 753, 701. MS (EI): 275(M^+ , 3), 177(42), 176(100), 148(26), 131(183). HRMS (EI): Found M^+ 275.1521, $\text{C}_{16}\text{H}_{21}\text{ClNO}_3$ requires 275.1522.

N-tert-Butyl-cis-1-ethoxycarbonyl-2-p-methoxyphenyl-β-lactam (2c). White solid, >99% yield. ^1H NMR (300MHz, CDCl_3): δ_{H} 7.31 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.5$ Hz, 2H), 4.87 (d, $J = 6.2$ Hz, 1H), 4.18 (d, $J = 6.2$ Hz, 1H), 3.83 (q, $J = 7.1$ Hz, 2H), 3.82 (s, 3H), 1.30 (s, 9H), 0.91 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ_{C} 166.2, 163.0, 159.9, 128.51, 128.46, 113.7, 61.0, 59.1, 56.2, 55.3, 29.7,

28.1, 13.8. IR (neat): 2976, 1761, 1723, 1614, 1514, 1369, 1249, 1176, 1031, 841, 771, 526. MS (EI): 305(M^+ , 25), 248(11), 232(22), 206(100), 176(86), 161(78). HRMS (EI): Found M^+ 305.1625, $C_{17}H_{23}NO_4$ requires 305.1627.

***N*-tert-Butyl-*trans*-1-carbonyl-2-*p*-chlorophenyl- β -lactam (2d).** Yellow oil, >99% yield. 1H NMR (400 MHz, $CDCl_3$): δ_H 7.35 (s, 4H), 5.00 (d, $J = 2.2$ Hz, 1H), 3.87 (d, $J = 2.2$ Hz, 1H), 2.29 (s, 3H), 1.25 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 199.6, 163.0, 138.1, 129.3, 128.1, 71.0, 55.3, 53.8, 30.1, 28.2. IR (neat): 2975, 1749, 1713, 1493, 1369, 1224, 1171, 1091, 1012, 841, 567, 527, 421. MS (EI): 279(M^+ , 3), 222(3), 180(52), 165(100), 145(52), 136(20). HRMS (EI): Found M^+ 279.1028, $C_{15}H_{18}NClO_2$ requires 279.1026.

***N*-Isopropyl-1-ethoxycarbonyl-2,2-dimethyl- β -lactam (2e).** Yellow oil, 89% yield. 1H NMR (300 MHz, $CDCl_3$): δ_H 4.27-4.16 (m, 2H), 3.64 (s, 1H), 3.62-3.55 (m, 1H), 1.63-1.29 (m, 12H), 1.26 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 167.4, 161.0, 63.8, 61.2, 59.2, 44.6, 27.4, 22.2, 21.8, 21.7, 14.3. IR (neat): 2977, 1759, 1729, 1373, 1253, 1182, 1030, 798, 669, 596. MS (EI): 213(M^+ , 5), 198(5), 128(95), 113(9), 100(71), 84(16), 83(100). HRMS (EI): Found M^+ 213.1362, $C_{11}H_{19}NO_3$ requires 213.1365.

***N*-tert-Butyl-*cis*-1-ethoxycarbonyl-2-benzyl- β -lactam (2f).**³ Yellow oil, 12% yield. 1H NMR (300 MHz, $CDCl_3$): δ_H 7.31-7.11 (m, 5H), 4.28-4.21 (m, 1H), 4.12-4.01 (m, 1H), 3.95-3.87 (m, 1H), 3.85 (d, $J = 5.7$ Hz, 1H), 3.32 (dd, $J = 14.5$ Hz, 4.2 Hz, 1H), 3.20 (dd, $J = 14.5$ Hz, 10.6 Hz, 1H), 1.44 (s, 9H), 1.08 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 168.2, 161.8, 137.3, 128.6, 128.5, 126.8, 70.0, 55.3, 54.6, 52.7, 36.0, 29.1, 28.2, 13.9. IR (neat): 2976, 1730, 1691, 1456, 1367, 1158, 1030, 760, 700, 504. MS (EI): 289(M^+ , 68), 243(17), 216(36), 198(100), 188(18), 160(47), 153(40), 142(40), 136(26). HRMS (EI): Found M^+ 289.1676, $C_{17}H_{23}NO_3$ requires 289.1678.

***N*-tert-Butyl-*trans*-1-ethoxycarbonyl-2-phenyl- γ -lactam (3).**³ White solid. 51% yield. ¹H NMR (400 MHz, CDCl₃:C₆D₆ = 2:1): δ_{H} 7.24-7.13 (m, 5H), 4.22-4.05(m, 2H), 3.82 (q, J = 8.6 Hz, 1H), 3.69 (t, J = 8.8 Hz, 1H), 3.53 (d, J = 9.5 Hz, 1H), 3.22 (t, J = 8.8 Hz, 1H), 1.35 (s, 9H), 1.17 (t, J = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ_{C} 170.0, 169.1, 128.9, 128.1, 127.4, 127.0, 61.4, 57.3, 54.7, 50.8, 41.1, 27.5, 13.9. IR (neat): 2976, 1737, 1690, 1456, 1366, 1156, 1030, 761, 700, 669, 421. MS (EI): 289(M⁺, 93), 274(100), 246(29), 234(24), 228(28), 216(23), 200(16), 188(32), 160(34), 145(11), 131(17), 117(12). HRMS (EI): Found M⁺ 289.1688, C₁₇H₂₃NO₃ requires 289.1678.

***N*-Phenylethyl-*cis*-1-ethoxycarbonyl-2-phenyl- β -lactam (2g).** Colorless oil, 28% yield. ¹H NMR (300 MHz, CDCl₃): δ_{H} 7.33-7.14 (m, 10H), 4.58 (d, J = 6.0 Hz, 1H), 4.25 (d, J = 6.0 Hz, 1H), 3.83-3.90 (m, 1H), 3.73(q, J = 7.1 Hz, 2H), 3.20-3.13 (m, 1H), 3.29-2.87 (m, 2H), 0.83 (t, J = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ_{C} 165.8, 163.0, 138.3, 134.0, 129.0, 128.8, 128.7, 128.6, 127.3, 126.8, 61.1, 60.5, 58.1, 42.4, 34.0, 29.8, 13.7. IR (neat): 1771, 1507, 1457, 750, 669. MS (EI): 323(M⁺, 14), 250(10), 232(15), 131(57), 118(100), 104(56), 103(11). HRMS (EI): Found M⁺ 323.1509, C₂₀H₂₁NO₃ requires 323.1521.

***N*-Benzyl-*trans*-1-ethoxycarbonyl-2-phenyl- γ -lactam (4).** Colorless oil, 53% yield. ¹H NMR (500 MHz, CDCl₃): δ_{H} 7.40-7.28 (m, 10H), 4.56 (dd, J = 50.7 Hz, 14.8 Hz, 2H), 4.27-4.15 (m, 2H), 4.03-3.98 (m, 1H), 3.76 (d, J = 9.8 Hz, 1H), 3.65 (dd, J = 8.4 Hz, 9.6 Hz, 1H), 3.31 (dd, J = 8.7 Hz, 9.4 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ_{C} 169.6, 168.7, 140.3, 136.8, 128.9, 128.7, 128.1, 127.6, 127.3, 127.2, 61.1, 56.0, 51.6, 46.4, 42.3, 13.8. IR (neat): 1700, 1698, 1507, 1456, 1255, 1028, 759, 700, 419. MS (EI): 323(M⁺, 100), 250(70), 209(21), 131(40), 119(50). HRMS (EI): Found M⁺ 323.1520, C₂₀H₂₁NO₃ requires 323.1521.

***N*-Benzyl-5-methoxy-1,3-dihydro-indol-2-one (5).** Yellow oil, 97% yield. ^1H NMR (300 MHz, CDCl_3): δ_{H} 7.32-7.23 (m, 5H), 6.87 (s, 1H), 6.68 (d, $J = 8.5$ Hz, 1H), 6.59 (d, $J = 8.5$ Hz, 1H), 4.88 (s, 2H), 3.74 (s, 3H), 3.59 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ_{C} 174.8, 155.9, 137.9, 136.0, 128.8, 127.6, 127.4, 125.9, 112.2, 112.0, 109.4, 55.8, 43.9, 36.2. IR (neat): 2915, 1716, 1558, 1490, 1385, 1179, 1035, 772, 670, 420. MS (EI): 253(M^+ , 100), 162(17). HRMS (EI): Found M^+ 253.1099, $\text{C}_{16}\text{H}_{15}\text{NO}_2$ requires 253.1103.

***N*-Phenethyl-5-methoxy-1,3-dihydro-indol-2-one (6).** Yellow oil, 92% yield. ^1H NMR (300 MHz, CDCl_3): δ_{H} 7.31-7.22 (m, 5H), 6.88 (s, 1H), 6.77 (d, $J = 8.5$ Hz, 1H), 6.67 (d, $J = 8.5$ Hz, 1H), 3.90 (t, $J = 7.8$ Hz, 2H), 3.79 (s, 3H), 3.48 (s, 2H), 2.95 (t, $J = 7.8$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 174.5, 155.7, 138.4, 138.0, 128.8, 128.7, 126.7, 126.0, 112.2, 112.0, 108.5, 55.9, 41.7, 36.2, 33.8. IR (neat): 2927, 1705, 1600, 1494, 1351, 1287, 1172, 1024, 802, 702, 547, 426. MS (EI): 268(M^+ , 18), 267(93), 176(100), 148(69), 133(13). HRMS (EI): Found M^+ 267.1261, $\text{C}_{17}\text{H}_{17}\text{NO}_2$ requires 267.1259.

General Procedure for the $[\text{RuCl}_2(\text{L}^*)(\text{C}_2\text{H}_4)]$ Catalyzed Asymmetric Intramolecular Carbenoid C–H Insertion Reaction

A mixture of diazo compound (0.1 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (5 mol%) and L^* (10 mol%) were stirred in toluene (10 mL) at 70 °C under N_2 atmosphere. By means of TLC analysis (20% EtOAc – hexanes), the reaction was monitored for complete consumption of the diazo starting materials. To work-up, the mixture was concentrated to ca. 2 mL by vacuum evaporation, and the residue was purified by flash chromatography (5 – 20% EtOAc-hexanes) to afford the product β -lactams. Results are summarized in Table S2.

Table S2. Asymmetric Intramolecular Carbenoid C-H Insertion of α -Diazoacetamides

entry	diazo compound	product	% yield ^b		% ee ^c	
			trans	cis	trans	cis
1			80	-	50	-
2 ^d			72	-	53	-
3			70	-	30	-
4			70	-	41	-
5			56	8	53	55

^a : Reaction conditions: A mixture of diazo **1** (0.1 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (5 mol%) and L^* (10 mol%) was stirred in toluene at 70 °C under N_2 atmosphere. ^b : Isolated yield. ^c : Determined by ^1H NMR analysis using $\text{Eu}(\text{hfc})_3$ as chiral shift reagent. ^d : Using $[\text{RuCl}_2(\text{L}^*)(\text{C}_2\text{H}_4)]$ (10 mol%) as catalyst

Figure S1. ^1H NMR Spectrum of *N-p*-Chlorobenzyl-*N-tert*-butyl- α -ethoxycarbonyl- α -diazoacetamide (**1a**)

Figure S2. ^1H NMR Spectrum of
N-Benzyl-*N*-*tert*-butyl- α -ethoxycarbonyl- α -diazoacetamide (**1b**)

Figure S3. ^1H NMR Spectrum of *N*-*p*-Methoxybenzyl-*N*-*tert*-butyl- α -ethoxycarbonyl- α -diazoacetamide (**1c**)

Figure S4. ^1H NMR Spectrum of *N-p*-Chlorobenzyl-*N-tert*-butyl- α -carbonyl- α -diazoacetamide (**1d**)

Figure S5. ^1H NMR Spectrum of *N,N*-Diisopropyl- α -ethoxycarbonyl- α -diazoacetamide (**1e**)

Figure S6. ^1H NMR Spectrum of *N*-Phenylethyl-*N*-*tert*-butyl- α -ethoxycarbonyl- α -diazoacetamide (**1f**)

Figure S7. ^1H NMR Spectrum of *N*-Phenylethyl-*N*-benzyl- α -ethoxycarbonyl- α -diazoacetamide (**1g**)

Figure S8. ^1H NMR Spectrum of *N*-Benzyl-*N*-*p*-methoxybenzyl- α -ethoxycarbonyl- α -diazoacetamide (**1h**)

Figure S9. ^1H NMR Spectrum of *N*-Phenylethyl-*N*-*p*-methoxybenzyl- α -ethoxycarbonyl- α -diazoacetamide (**1i**)

Figure S10. ^1H NMR Spectrum of *N-tert-Butyl-*cis*-1-ethoxycarbonyl-2-*p*-chlorophenyl- β -lactam (2a)*

Figure S11. ^1H NMR Spectrum of *N-tert*-Butyl-*cis*-1-ethoxycarbonylphenyl- β -lactam (**2b**)

Figure S12. ^1H NMR Spectrum of *N-tert-Butyl-1-ethoxycarbonyl-2-p-methoxyphenyl- β -lactam (2c)*

Figure S13. ^1H NMR Spectrum of *N-tert-Butyl-trans-1-carbonyl-2-p-chlorophenyl- β -lactam (2d)*

Figure S14. ^1H NMR Spectrum of *N*-Isopropyl-1-ethoxycarbonyl-2,2-dimethyl- β -lactam (**2e**)

Figure S15. ^1H NMR Spectrum of *N-tert-Butyl-1-cis-1-ethoxycarbonyl-2-benzyl- β -lactam (2f)*

Figure S16. ^1H NMR Spectrum of *N*-*tert*-Butyl-*trans*-1-ethoxycarbonyl-2-phenyl- γ -lactam (**3**)

Figure S17. ^1H NMR Spectrum of *N*-Phenylethyl-*cis*-1-ethoxycarbonyl-2-phenyl- β -lactam (**2g**)

Figure S18. ^1H NMR Spectrum of *N*-Benzyl-*trans*-1-ethoxycarbonyl-2-phenyl- γ -lactam (**4**)

Figure S19. ^1H NMR Spectrum of *N*-Benzyl-5-methoxy-1,3-dihydro-indol-2-one (**5**)

Figure S20. ^1H NMR Spectrum of *N*-Phenethyl-5-methoxy-1,3-dihydro-indol-2-one (**6**)

Figure S21. NOESY of *trans*-(**3**)

Figure S22. NOESY of *trans*-(4)

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