Supporting Information

SYNTHESIS OF OPTICALLY ACTIVE *γ*-LACTAMS BY PALLADIUM CATALYZED ASYMMETRIC DICARBONYLATION REACTION OF *N*-ARYLSUFONYL HOMOALLYLIC AMINES

Ryosuke Takahashi, Nga Hang Thi Phan, Takuya Suga, Takahiro Soeta, Yutaka Ukaji*

Division of Material Sciences, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma, Kanazawa, Ishikawa 920-1192, Japan; E-mail: ukaji@staff.kanazawa-u.ac.jp

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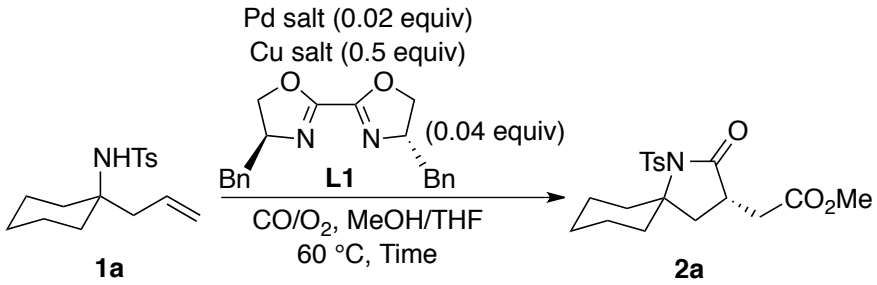
Table S1. Asymmetric dicarbonylation reaction of **1a** in the presence of various palladium and copper salts.



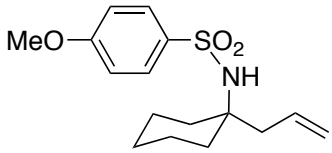
Entry	Pd salt	Cu salt	Time/d	Yield/%	ee/%[a]
1	$PdCl_2$	CuCl	3	52	8
2	$PdCl_2$	CuBr	3	6	n.d[b]
3	$PdCl_2$	CuI	3	trace	--
4	$PdCl_2$	$Cu(MeCN)_4BF_4$	3	61	54
5	$PdCl_2$	$CuOTf(C_6H_5)_{0.5}$	3	53	67
6	$PdCl_2$	$Cu(OTf)_2$	3	24	16
7	$PdCl_2(PhCN)_2$	$CuOTf(C_6H_6)_{0.5}$	3	25	56
8[c]	$[PdCl(allyl)]_2$	$CuOTf(C_6H_6)_{0.5}$	3	42	42
9	$Pd(OAc)_2$	$CuOTf(C_6H_6)_{0.5}$	4	30	42
10	$Pd(TFA)_2$	$CuOTf(C_6H_6)_{0.5}$	3	16	56
11	$[Pd(CH_3CN)_4](OTf)_2$	$CuOTf(C_6H_6)_{0.5}$	4	35	43
12[d]	$Pd(dba)_2$	$CuOTf(C_6H_6)_{0.5}$	3	25	53

[a]Enantioselectivities were determined by HPLC analysis (Daicel CHIRALCEL OJ-H).
[b]n.d. = not determined. [c]0.08 Equiv. of ligand was used. [d]0.04 Equiv. of LiCl was added.

Preparation of ligands and *N*-arylsulfonyl homoallylic amines 1

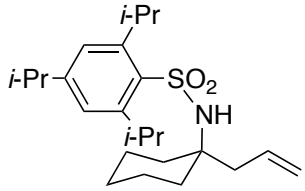
Bioxazoline ligands **L1**–**L3**,[1a] **L4**,[1b] **L5**,[1c] **L6**–**L7**,[1d] **L8**,[1e] and a bis(oxazoline) ligand **L9**[1f] were prepared according to the methods reported in the literature. *N*-Tosyl homoallylic amine **1a** and *N*-tosyl 3-butenylamine were prepared according to the methods previously reported.[2] In a similar manner, *N*-arylsulfonyl homoallylic amines **1b**–**1g** were prepared by the sulfonylation of 1-allyl-1-aminocyclohexane with the corresponding sulfonyl chlorides. Other *N*-tosyl homoallylic amines **1h**–**1k** were prepared by allylation reaction of the corresponding *N*-tosyl imines with allylmagnesium bromide.[3]

***N*-(1-Allylcyclohexyl)-4-methoxybenzenesulfonamide (1b):**



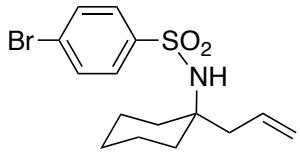
A solid. Mp 156–157 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22–1.52 (m, 8H), 1.68–1.78 (m, 2H), 2.39 (d, J = 7.3 Hz, 2H), 3.87 (s, 3H), 4.34 (brs, 1H), 5.08 (d, J = 18.8 Hz, 1H), 5.11 (d, J = 12.4 Hz, 1H), 5.67–5.81 (m, 1H), 6.95 (d, J = 8.7 Hz, 2H), 7.83 (d, J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.5, 25.2, 35.5, 43.0, 55.6, 59.3, 113.9, 119.2, 129.0, 133.0, 135.3, 162.4. IR (KBr) 3295, 3077, 3010, 2944, 2853, 1639, 1597, 1499, 1453, 1418, 1313, 1258, 1188, 1141, 1096, 1000, 914, 851, 832, 766, 675 cm^{-1}. HRMS (DART) *m/z*: Calcd for $C_{16}H_{24}NO_3S$ $[M+H]^+$: 310.1477, Found: 310.1478.

***N*-(1-Allylcyclohexyl)-2,4,6-triisopropylbenzenesulfonamide (1c):**



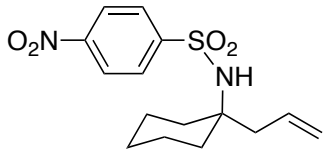
A solid. Mp 71–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (d, J = 6.9 Hz, 6H), 1.27 (d, J = 6.9 Hz, 12H), 1.35–1.53 (m, 8H), 1.77–1.84 (m, 2H), 2.50 (d, J = 7.3 Hz, 2H), 2.89 (sep, J = 6.9 Hz, 1H), 4.21 (brs, 1H), 4.25 (sep, J = 6.9 Hz, 2H), 5.11 (d, J = 17.4 Hz, 1H), 5.12 (d, J = 10.0 Hz, 1H), 5.70–5.81 (m, 1H), 7.14 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 23.6, 24.8, 25.3, 29.5, 34.1, 35.8, 43.2, 60.1, 119.3, 123.7, 133.1, 136.0, 149.2, 152.1. IR (KBr) 3286, 2964, 2876, 1640, 1599, 1447, 1421, 1315, 1155, 1094, 993, 915, 815, 667 cm^{-1}. HRMS (ESI) *m/z*: Calcd for $C_{24}H_{40}NO_2S$ $[M+H]^+$: 406.2780, Found: 406.2770.

***N*-(1-Allylcyclohexyl)-4-bromobenzenesulfonamide (1d):**



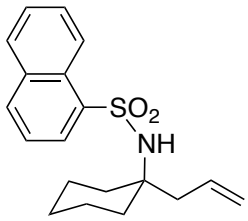
A solid. Mp 126–127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22–1.50 (m, 8H), 1.65–1.74 (m, 2H), 2.40 (d, J = 7.3 Hz, 2H), 4.53 (brs, 1H), 5.09 (d, J = 17.4 Hz, 1H), 5.13 (d, J = 10.1 Hz, 1H), 5.73 (ddt, J = 17.4, 10.1, 7.3 Hz, 1H), 7.63 (d, J = 8.7 Hz, 2H), 7.77 (d, J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.5, 25.1, 35.4, 43.0, 59.8, 119.4, 126.9, 128.4, 132.1, 132.7, 142.7. IR (KBr) 3292, 3070, 2941, 2857, 1637, 1577, 1469, 1450, 1423, 1335, 1291, 1152, 1094, 1001, 920, 823, 739, 704, 670 cm^{-1}. HRMS (DART) *m/z*: Calcd for $C_{15}H_{21}Br_1NO_2S$ $[M+H]^+$: 358.0476, Found: 358.0476.

***N*-(1-Allylcyclohexyl)-4-nitrobenzenesulfonamide (1e):**



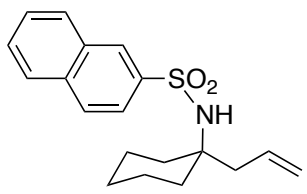
A solid. Mp 112–113 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.23–1.51 (m, 8H), 1.68–1.76 (m, 2H), 2.43 (d, J = 7.3 Hz, 2H), 4.54 (brs, 1H), 5.11 (d, J = 16.9 Hz, 1H), 5.15 (d, J = 10.5 Hz, 1H), 5.66–5.77 (m, 1H), 8.08 (d, J = 8.7 Hz, 2H), 8.35 (d, J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.6, 25.0, 35.4, 43.0, 60.4, 119.8, 124.2, 128.1, 132.3, 149.2, 149.6. IR (KBr) 3282, 3102, 2936, 2862, 1643, 1607, 1530, 1451, 1422, 1347, 1173, 1155, 1097, 1004, 925, 857, 735, 673 cm^{-1}. HRMS (DART) *m/z*: Calcd for $C_{15}H_{21}N_2O_4S$ $[M+H]^+$: 325.1222, Found: 325.1223.

***N*-(1-Allylcyclohexyl)naphthalene-1-sulfonamide (1f):**



A solid. Mp 138–139 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.04–1.34 (m, 8H), 1.66–1.76 (m, 2H), 2.40 (d, J = 7.3 Hz, 2H), 4.56 (s, 1H), 5.02–5.09 (m, 2H), 5.63–5.77 (m, 1H), 7.50–7.72 (m, 3H), 7.94 (d, J = 8.2 Hz, 1H), 8.04 (d, J = 8.2 Hz, 1H), 8.31 (d, J = 7.3 Hz, 1H), 8.61 (d, J = 8.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.4, 25.1, 35.3, 43.5, 59.9, 119.4, 124.2, 124.6, 126.7, 128.0, 128.1, 128.9, 129.0, 132.9, 133.9, 134.1, 138.2. IR (KBr) 3308, 2926, 2862, 1640, 1593, 1508, 1448, 1416, 1310, 1199, 1127, 1005, 921, 854, 830, 805, 774, 678 cm^{-1}. HRMS (DART) *m/z*: Calcd for $C_{19}H_{24}NO_2S$ $[M+H]^+$: 330.1528, Found: 330.1519.

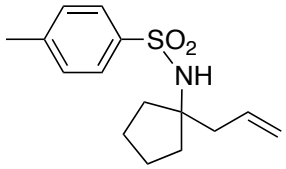
***N*-(1-Allylcyclohexyl)naphthalene-2-sulfonamide (1g):**



A solid. Mp 160–161 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.26–1.33 (m, 6H), 1.38–1.47 (m, 2H), 1.72–

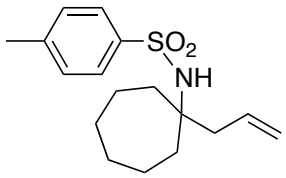
1.79 (m, 2H), 2.43 (d, J = 7.3 Hz, 2H), 4.48 (s, 1H), 5.07 (d, J = 17.4 Hz, 1H), 5.11 (d, J = 10.5 Hz, 1H), 5.75 (ddt, J = 17.4, 10.5, 7.3 Hz, 1H), 7.58–7.66 (m, 2H), 7.86–7.96 (m, 4H), 8.45 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 25.1, 35.5, 43.1, 59.6, 119.3, 122.6, 127.4, 127.77, 127.85, 128.6, 129.19, 129.24, 132.1, 132.9, 134.5, 140.3. IR (KBr) 3282, 2939, 2858, 1641, 1591, 1504, 1452, 1419, 1314, 1128, 1073, 1036, 1002, 915, 861, 820, 749, 660 cm^{-1}. HRMS (DART) *m/z*: Calcd for $C_{19}H_{24}N_1O_2S$ $[M+H]^+$: 330.1528, Found: 330.1528.

_N_-(1-Allylcyclopentyl)-4-methylbenzenesulfonamide (1h):



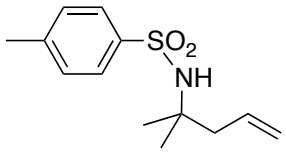
A solid. Mp 107–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.44–1.54 (m, 6H), 1.77–1.84 (m, 2H), 2.40 (d, J = 7.3 Hz, 2H), 2.42 (s, 3H), 4.55–4.58 (br, 1H), 5.09 (dd, J = 16.9, 1.8 Hz, 1H), 5.11 (dd, J = 10.1, 1.8 Hz, 1H), 5.76 (ddt, J = 16.9, 10.1, 7.3 Hz, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 22.7, 37.3, 43.6, 67.4, 119.2, 126.9, 129.4, 133.7, 140.2, 142.8. IR (KBr) 3286, 2964, 2876, 1640, 1599, 1447, 1421, 1315, 1155, 1094, 993, 915, 815, 667 cm^{-1}. HRMS (ESI) *m/z*: Calcd for $C_{15}H_{21}NO_2SNa$ $[M+Na]^+$: 302.1191, Found: 302.1189.

_N_-(1-Allylcycloheptyl)-4-methylbenzenesulfonamide (1i):



A solid. Mp 100–101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (dd, J = 15.1, 9.2 Hz, 2H), 1.34–1.45 (m, 6H), 1.58 (dd, J = 14.7, 8.7 Hz, 2H), 1.59 (dd, J = 14.7, 9.2 Hz, 2H), 2,36 (d, J = 7.3 Hz, 2H), 2.42 (s, 3H), 4.39 (brs, 1H), 5.09 (d, J = 14.7 Hz, 1H), 5.11 (d, J = 10.1 Hz, 1H), 5.79 (ddt, J = 14.7, 10.1, 7.3 Hz, 1H), 7.28 (d, J = 8.2 Hz, 3H), 7.77 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 22.0, 29.9, 38.6, 45.0, 63.2, 119.4, 126.9, 129.4, 133.4, 140.6, 142.7. IR (KBr) 3283, 2929, 2857, 1598, 1466, 1447, 1327, 1152, 1093, 1001, 915, 816 cm^{-1}. HRMS (ESI) *m/z*: Calcd for $C_{17}H_{25}NO_2SNa$ $[M+Na]^+$: 330.1504, Found: 330.1512.

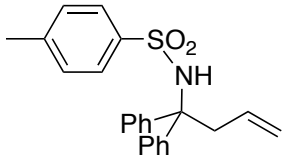
4-Methyl-_N_-(2-methylpent-4-en-2-yl)benzenesulfonamide (1j):



A solid. Mp 81–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (s, 6H), 2.24 (d, J = 7.3 Hz, 2H), 2.42 (s, 3H),

4.55–4.58 (br, 1H), 5.11 (d, J = 16.9 Hz, 1H), 5.16 (d, J = 10.1 Hz, 1H), 5.76 (ddt, J = 16.9, 10.1, 7.3 Hz, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 27.4, 47.5, 56.3, 119.8, 126.9, 129.5, 132.9, 140.5, 142.8. IR (KBr) 3230, 2981, 2934, 1640, 1596, 1430, 1327, 1155, 1092, 995, 925, 818, 683 cm^{-1}. HRMS (ESI) *m/z*: Calcd for $C_{13}H_{19}NO_2SNa$ $[M+Na]^+$: 276.1034, Found: 276.1047.

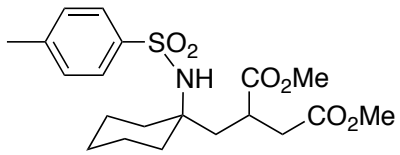
_N_-(1,1-Diphenylbut-3-en-1-yl)-4-methylbenzenesulfonamide (1k)[4]:



A solid. Mp 112–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H), 3.31 (d, J = 6.9 Hz, 2H), 5.16 (dd, J = 9.6, 2.3 Hz, 1H), 5.27 (dd, J = 16.9, 2.3 Hz, 1H), 5.31 (brs, 1H), 5.38 (ddt, J = 16.9, 9.6, 6.9 Hz, 1H), 6.96 (d, J = 8.2 Hz, 2H), 7.10–7.15 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.4, 45.0, 66.2, 121.1, 126.9, 127.1, 127.7, 128.0, 128.8, 132.7, 138.9, 142.2, 142.4.

Byproduct of asymmetric dicarbonylation reaction of 1a

Dimethyl 2-((1-((4-methylphenyl)sulfonamido)cyclohexyl)methyl)succinate:



Dimethyl 2-((1-((4-methylphenyl)sulfonamido)cyclohexyl)methyl)succinate was isolated as a byproduct of asymmetric dicarbonylation reaction of **1a** by further purification of the byproducts using recycle HPLC. An oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18–1.68 (m, 9H), 1.75–1.85 (m, 1H), 1.85 (dd, J = 14.7, 2.3 Hz, 1H), 2.12 (dd, J = 14.7, 9.2 Hz, 1H), 2.42 (s, 3H), 2.45 (dd, J = 16.9, 6.0 Hz, 1H), 2.68 (dd, J = 16.9, 8.7 Hz, 1H), 2.94–3.02 (m, 1H), 3.69 (s, 3H), 3.72 (s, 3H), 4.71 (s, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 21.6, 25.0, 35.5, 36.7, 37.8, 40.6, 51.8, 52.2, 59.4, 126.8, 129.5, 140.4, 142.8, 172.0, 176.1. IR (KBr): 3288, 2938, 2864, 1738, 1599, 1438, 1321, 1287, 1153, 1093, 1043, 995, 817, 666 cm^{-1}. HRMS (ESI) *m/z*: Calcd for $C_{20}H_{29}NO_6SNa$ $[M+Na]^+$: 434.1613, Found: 434.1608.

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