Supplementary Materials

A Chirality Chain in Phenylglycine, Phenylpropionic Acid, and Ibuprofen

Henri Brunner,*[1] Takashi Tsuno*[2], and Gábor Balázs[1]

[1]Institut für Anorganische Chemie, Universität Regensburg, 93040 Regensburg, Germany

[2]Department of Applied Molecular Chemistry, College of Industrial Technology, Nihon University, Narashino, Chiba 275-8575, Japan

Contents

Table S1. α-Phenylglycine (*S*)-$NH_3CH(Ph)COO$ and its derivatives (*S*)-$NH_3CH(Ph)COO$(H/R/M) protonated, esterified, and coordinated at the carboxylic group (structures with *R* factors >10% excluded).

En-try	CSD symbol[a]	Chirality chain			Comments	
		Config. at C_α[b]	O_{cis}-C'-C_α-N rotation angle ψ / °	O_{trans}-C'-C_α-O_{cis} pyramidal angle θ / °	Space group	Acid, ester or metal fragment, co-crystallization partners
1	FAPMOZ(1)	(*S*)	-34.17	-177.16	$P2_1$	18-crown-6-ether$(CO_2H)_4$, H_2O
2	BANZEX	(*S*)	-32.13	-176.53	$P2_1$	Me ester, 1-[2-carboxy-6-CF_3-phenyl]-1*H*-pyrrole-2-CO_2H
3	RENKUQ(1)	(*S*)	-30.72	-179.55	$P2_1$	H_2SO_4
4	CCDC1981273[c]	(*S*)	-30.77	-177.79	$P2_1$	Me ester, HCl
5	CCDC1981269(1)[d]	(*S*)	-27.05	-178.70	$P2_1$	-
6	IROVEQ(1)	(*S*)	-25.58	-177.58	$P2_1$	HNO_3
7	RENKUQ(2)	(*S*)	-24.88	-179.55	$P2_1$	H_2SO_4
8	IROVEQ(2)	(*S*)	-24.01	-180.35	$P2_1$	HNO_3
9	HAZGIZ	(*S*)	-23.25	-177.05	*P*bca	HCl
10	FAPMIT	(*S*)	-22.19	-178.61	$P3_1$	18-crown-6-ether$(CO_2H)_4$, H_2O
11	QEPXEP(1)	(*S*)	-21.72	-178.74	$P2_1$	Bn ester, TsOH
12	FAPMOZ(2)	(*S*)	-21.71	-176.60	$P2_1$	18-crown-6-ether$(CO_2H)_4$, H_2O
13	FIVGEW	(*S*)	-21.56	-178.14	$P2_1/c$	-
14	PIDYEH	(*S*)	-19.48	-180.11	$P2_1/n$	^{i}Pr ester, HCl
15	GACVIP(1)	(*S*)	-18.77	-173.15	$P2_1$	$HClO_4$, AcOH, crown ether
16	XALDAP[e]	(*S*)	-18.67	-178.85	$P2_12_12_1$	HCl
17	CCDC1981269(2)[d]	(*S*)	-17.04	-178.12	$P2_1$	-
18	CABVUX	(*S*)	-16.08	-178.98	$P2_12_12_1$	$HClO_4$
19	CCDC2049622(1)	(*S*)	-16.07	-179.19	$P2_1$	Et ester, HCl
20	DOXWAO	(*S*)	-16.02	-181.59	$P2_1$	Me ester, HPF_6, benzo-18-crown-6-ether
21	WIHJII	(*S*)	-15.58	-178.94	$P2_12_12_1$	HBr
22	BALNEK[f]	(*S*)	-13.44	-177.66	$P2_1/c$	MsOH
23	XALCOC	(*S*)	-12.32	-178.81	$P2_12_12_1$	D-campher-SO_3H
24	TEHYUA	(*S*)	-12.14	-178.17	$P2_12_12_1$	$C_4H_2O_4$, H_2O
25	CCDC1981272[g]	(*S*)	-11.65	-179.42	$P2_1/c$	Me ester, HCl
26	FITPUT(1)	(*S*)	-11.46	-178.82	$P2_12_12_1$	Me ester, $HClO_4$, H_2O, binaphthyl-18-crown-6-ether
27	CCDC2049622(2)	(*S*)	-9.45	-179.44	$P2_1$	Et ester, HCl
28	GACVIP(2)	(*S*)	-8.93	-179.89	$P2_1$	$HClO_4$, AcOH, crown ether
29	QEPXEP(2)	(*S*)	-8.92	-180.79	$P2_1$	Bn ester,TsOH
30	FITPUT(2)	(*S*)	-8.10	-181.79	$P2_12_12_1$	Me ester, $HClO_4$, H_2O, binaphthyl-18-crown-6-ether
31	TXHBNP	(*S*)	-6.26	-180.02	$P2_12_12_1$	HPF_6, $CHCl_3$, binaphthyl-18-crown-6-ether
32	XALCOC01	(*S*)	-6.04	-179.72	$P2_12_12_1$	D-campher-SO_3H
33	XALCUI	(*S*)	-3.95	-177.26	*C*2	D-campher-SO_3H
	Average		-17.88	-178.70		

[a]Parenthesis () indicate independent molecules in the unit cell. [b]Rotation and pyramidalization angles of (*R*)-compounds inverted. [c]Average of (R_C)- and (S_C)-methyl α-phenylglycinate hydrochloride: CCDC1981273 and 1981274. [d]Average of conglomerate (S_C)/(R_C)-, (S_C)-, and (R_C)-α-phenylglycine: CCDC1981269, 1981270, and 1981271. [e]Average of XALDAP, NILXUB. [f]Average of BALNEK, UMUXAD. [g]Racemate of (S_C)/(R_C)-methyl α-phenylglycinate hydrochloride: CCDC1981274.

DFT Calculation details: The DFT calculations were performed with the Gaussian 09 program, using the B3LYP functional together with the def2-TZVP basis set. Solvents effects were taken into account by the polarizable continuum model (CPM), using the dielectric constant of water. London dispersion energy effects were considered according to the model proposed by Grimme et al. together with the Becke and Johnson damping. For the relative energies the SCF energies, without corrections for the zero point vibration energies, were used. In the geometry optimizations only the N-C_α-C'-O_{cis} torsion angle was constrained to certain values. All other parameters were freely optimized. The references are cited in the paper.

Table S2. (*S*)-α-Phenylglycine: Relative energy as a function of the rotation angle ψ = O_{cis}-C'-C_α-N and the pyramidalization angle θ = O_{trans}-C'-C_α-O_{cis}, calculated at the B3LYP/def2-TZVP level, including dispersion (GD3BJ) and solvent effects (PCM; water).

File	ψ/°	relative energy (kJ/mol)	θ/°
PhG-S-02_00.xyz	0.0	0.13	-180.81
PhG-S-02_01.xyz	-2.5	0.04	-180.48
PhG-S-02_02.xyz	-5.0	0.00	-180.10
PhG-S-02_03.xyz	-7.5	0.00	-179.66
PhG-S-02_04.xyz	-10.0	0.04	-179.24
PhG-S-02_05.xyz	-12.5	0.13	-178.86
PhG-S-02_06.xyz	-15.0	0.33	-178.53
PhG-S-02_07.xyz	-17.5	0.67	-178.24
PhG-S-02_08.xyz	-20.0	1.09	-177.96
PhG-S-02_09.xyz	-22.5	1.59	-177.68
PhG-S-02_10.xyz	-25.0	2.26	-177.41
PhG-S-02_11.xyz	-27.5	3.05	-177.21
PhG-S-02_12.xyz	-30.0	3.97	-177.04
PhG-S-02_13.xyz	-32.5	5.02	-176.92
PhG-S-02_14.xyz	-35.0	6.14	-176.83
PhG-S-02_15.xyz	-37.5	7.40	-176.79
PhG-S-02_16.xyz	-40.0	8.78	-176.83
PhG-S-02_17.xyz	-42.5	10.20	-176.91
PhG-S-02_18.xyz	-45.0	11.75	-177.01
PhG-S-02_19.xyz	-47.5	13.38	-177.17
PhG-S-02_20.xyz	-50.0	15.05	-177.37
PhG-S-02_21.xyz	-52.5	16.72	-177.60
PhG-S-02_22.xyz	-55.0	18.39	-177.83
PhG-S-02_23.xyz	-57.5	20.06	-178.11
PhG-S-02_24.xyz	-60.0	21.65	-178.45
PhG-S-02_25.xyz	-62.5	23.20	-178.81
PhG-S-02_26.xyz	-65.0	24.66	-179.21
PhG-S-02_27.xyz	-67.5	26.04	-179.64
PhG-S-02_28.xyz	-70.0	27.30	-179.96
PhG-S-02_29.xyz	-72.5	28.42	-180.45
PhG-S-02_30.xyz	-75.0	29.43	-180.83
PhG-S-02_31.xyz	-77.5	30.26	-181.24
PhG-S-02_32.xyz	-80.0	30.93	-181.71
PhG-S-02_33.xyz	-82.5	31.43	-182.17
PhG-S-02_34.xyz	-85.0	31.81	-182.58
PhG-S-02_35.xyz	-87.5	31.98	-182.95
PhG-S-02_36.xyz	-90.0	31.98	-183.36
PhG free 01	-6.2	0	-179.85

Table S3. α-Phenylpropionic acid (*S*)-$H_3CH(Ph)COOH$ and its derivatives (*S*)-$CH_3CH(Ph)COO(R/M)$ esterified and coordinated at the carboxylic group (structures with *R* factors >10% excluded).

Entry	CSD symbol[a]	Chirality chain			Comments	
		Config. at C_α[b]	O_{cis}-C'-C_α- C_{Me} rotation angle ψ / º	O_{trans}-C'-C_α-O_{cis} pyramidal angle θ / º	Space group	Acid, ester or metal fragment, co-crystallization partners
1	VATZOI(1)[c]	(*S*)	-84.20	-180.41	$P2_1$	Tb complex
2	REZVAW(1)	(*S*)	-82.14	-180.63	*P*1	Ester, H_2O
3	VATZUO(1)[d]	(*S*)	-81.35	-181.46	$P2_1$	Eu complex
4	VATZUO(2)[d]	(*S*)	-77.88	-179.85	$P2_1$	Eu complex
5	VATZOI(2)[c]	(*S*)	-77.76	-179.72	$P2_1$	Tb complex
6	GOGPIC[e]	(*S*)	-57.93	-179.41	$P2_1$	GOGPEY(inv)
7	REZVAW(2)	(*S*)	-57.20	-179.37	*P*1	Ester, H_2O
8	VATZOI(3)[c]	(*S*)	-52.85	-175.44	$P2_1$	Tb complex
9	VATZUO(3)[d]	(*S*)	-52.69	-174.09	$P2_1$	Eu complex
10	ENOBIT	(*S*)	-52.27	-180.06	*C*2	$BnNH_2$
11	HEPJOB	(*S*)	-50.47	-186.43	$P2_1$	Ester
12	NMACEP02[f]	(*S*)	-50.12	-178.43	$P2_12_12_1$	(*R*)-Ph(Me)$CHNH_2$
13	VATZOI(4)[c]	(*S*)	-45.75	-175.75	$P2_1$	Tb complex
14	VATZUO(4)[d]	(*S*)	-45.55	-176.00	$P2_1$	Eu complex
15	IWIMAC	(*S*)	-44.55	-179.42	$P2_1/c$	(*R*)-Ph(Me)$CHNH_2$
16	YEHGUO(1)	(*S*)	-43.32	-181.16	$P2_12_12$	(*R*)-3-$MeC_6H_3CH(Me)NH_2Co(NH_2CH_2)_2$
17	RONDAA(1)	(*S*)	-43.05	-179.02	*C*2	isonicotinamide
18	BELJAG(1)	(*S*)	-42.25	-175.51	$P2_1$	Ester
19	VATZUO(5)[d]	(*S*)	-40.08	-176.21	$P2_1$	Eu complex
20	TUDYOJ	(*S*)	-39.43	-181.38	$P3_2$	Co complex
21	NUDKIG	(*S*)	-39.32	-178.91	*C*2	Ester
22	VATZUO(6)[d]	(*S*)	-39.18	-180.71	$P2_1$	Eu complex
23	ROLFOO	(*S*)	-39.06	-179.70	*C*2/c	isonicotinamide
24	VATZOI(5)[c]	(*S*)	-38.59	-181.97	$P2_1$	Tb complex
25	NMACEP01	(*S*)	-37.21	-177.05	$P2_12_12_1$	(*R*)-Ph(Me)$CHNH_2$
26	YEHGUO(2)	(*S*)	-36.44	-183.77	$P2_12_12_1$	(*R*)-3-$MeC_6H_3CH(Me)NH_2Co(NH_2CH_2)_2$
27	VATZUO(7)[d]	(*S*)	-35.86	-177.99	$P2_1$	Eu complex
28	VATZOI(6)[c]	(*S*)	-35.42	-178.35	$P2_1$	Tb complex
29	VATZUO(8)[d]	(*S*)	-34.76	-178.32	$P2_1$	Eu complex
30	YOWTEJ(1)	(*S*)	-34.76	-174.87	*P*1	Ester
31	VATZOI(7)[c]	(*S*)	-34.58	-179.25	$P2_1$	Tb complex
32	YAGPUS	(*S*)	-33.37	-177.93	$P2_12_12_1$	Ester
33	YOMRUO	(*S*)	-32.81	-185.15	$P2_1$	(2*S*,3*R*)-$[CH(OH)CH_2NHOH]_2$
34	PMACEP01	(*S*)	-32.43	-178.18	$P2_1$	(*S*)-Ph(Me)$CHNH_2$
35	VATZOI(8)[c]	(*S*)	-31.63	-177.77	$P2_1$	Tb complex
36	BELJEK(1)	(*S*)	-31.06	-177.18	$P2_1$	Ester, $CHCl_3$
37	AFINEJ	(*S*)	-30.83	-177.73	$P2_1$	(*R*)-PhGly
38	BELJEK(2)	(*S*)	-30.20	-176.03	$P2_1$	Ester, $CHCl_3$
39	KAPVAY	(*S*)	-29.13	-178.18	$P2_1$	(1*S*,2*R*)-1-Ammonioindan-2-ol
40	VATZUO(9)[d]	(*S*)	-28.34	-178.79	$P2_1$	Eu complex
41	VATZOI(9)[c]	(*S*)	-27.71	-179.19	$P2_1$	Tb complex
42	TUMLIZ(1)	(*S*)	-27.00	-178.59	$P2_1$	Ester
43	RONDAA(2)	(*S*)	-26.90	-179.03	*C*2	isonicotinamide
44	VATZOI(10)[c]	(*S*)	-26.53	-179.81	$P2_1$	Tb complex
45	VATZUO(10)[d]	(*S*)	-26.09	-180.91	$P2_1$	Eu complex
46	BELJAG(2)	(*S*)	-24.70	-178.54	$P2_1$	Ester
47	BELJAG(3)	(*S*)	-24.29	-179.38	$P2_1$	Ester
48	TUMLIZ(2)	(*S*)	-22.44	-180.25	$P2_1$	Ester
49	VATZOI(11)[c]	(*S*)	-22.11	-178.19	$P2_1$	Tb complex
50	VATZUO(11)[d]	(*S*)	-21.59	-178.33	$P2_1$	Eu complex
51	NOTKIQ(1)	(*S*)	-21.51	-179.59	$P2_1$	Acridine
52	OKIQEE	(*S*)	-21.22	-178.99	*C*2	(1*S*,2*S*)-2-Aminoindanol, H_2O
53	ROJYEU	(*S*)	-19.28	-179.98	*C*2/c	Ester

54	YOWTEJ(2)	(*S*)	-19.17	-173.78	*P*1	Ester
55	VATZUO(12)[d]	(*S*)	-17.28	-177.13	$P2_1$	Eu complex
56	BELJEK(3)	(*S*)	-15.95	-179.78	$P2_1$	Ester, $CHCl_3$
57	VATZOI(12)[c]	(*S*)	-15.19	-178.23	$P2_1$	Tb complex
58	VATZUO(13)[d]	(*S*)	-14.94	-180.88	$P2_1$	Eu complex
59	BELJAG(4)	(*S*)	-14.70	-177.45	$P2_1$	Ester
60	VATZOI(13)[c]	(*S*)	-14.54	-181.46	$P2_1$	Tb complex
61	CURHEC	(*S*)	-14.39	-179.16	$P2_1/c$	Ester, HCl, H_2O
62	NAKLUG	(*S*)	-13.54	-180.33	$P2_1$	Ester
63	GEXNEF(1)	(*S*)	-13.41	-179.16	$P2_12_12_1$	Si-Phthalocyanine
64	BELJEK(4)	(*S*)	-13.09	-180.37	$P2_1$	Ester, $CHCl_3$
65	NOTKIQ(2)	(*S*)	-12.94	-180.04	$P2_1$	Acridine
66	REZVAW(3)	(*S*)	-12.03	-179.84	*P*1	Ester, H_2O
67	VATZUO(14)[d]	(*S*)	-8.38	-182.10	$P2_1$	Eu complex
68	VATZOI(14)[c]	(*S*)	-7.37	-180.23	$P2_1$	Tb complex
69	BALRAH	(*S*)	-7.11	-177.05	$P2_12_12_1$	(1*R*,2*S*)-PhCH(OH)CH(NH_2)Ph
70	REZVAW(4)	(*S*)	-6.08	-181.17	*P*1	Ester, H_2O
71	BELJIO(1)	(*S*)	-5.95	-183.14	$P2_1$	Ir comples, $CHCl_3$, BF_4
72	VATZUO(15)[d]	(*S*)	-2.23	-180.41	$P2_1$	Eu complex
73	VATZUO(16)[d]	(*S*)	-1.34	-181.77	$P2_1$	Eu complex
74	VATZOI(15)[c]	(*S*)	0.57	-182.10	$P2_1$	Tb complex
75	BELJIO(2)	(*S*)	1.13	-179.86	$P2_1$	Ir comples, $CHCl_3$, BF_4
76	VATZOI(16)[c]	(*S*)	1.51	-183.34	$P2_1$	Tb complex
77	JOKRIM(1)	(*S*)	3.86	-183.42	*P*1	Cu complex
78	NEDVUO(1)	(*S*)	4.34	-181.64	*C*2	Ni complex, Ph_4B
79	YEHGOI(1)	(*S*)	4.79	-184.50	*C*2	(*R*)-$C_6H_4CH(Me)NH_2Co(NH_2CH_2)_2$
80	YEHGOI(2)	(*S*)	7.35	-182.42	*C*2	(*R*)-$C_6H_4CH(Me)NH_2Co(NH_2CH_2)_2$
81	ALIBON(1)	(*S*)	21.95	-190.75	$P2_1$	Zn complex
82	NEDVUO(2)	(*S*)	29.80	-182.85	*C*2	Ni complex BPh_4
83	ALIBON(2)	(*S*)	41.41	-186.52	$P2_1$	Zn complex
84	VATZOI(17)[c]	(*S*)	74.94	-175.97	$P2_1$	Tb complex
85	VATZUO(17)[d]	(*S*)	76.03	-177.02	$P2_1$	Eu complex
86	GEXNEF(2)	(*S*)	77.17	-178.37	$P2_12_12_1$	Si-Phthelocyanin
87	JOKRIM(2)	(*S*)	81.60	-181.80	*P*1	Cu complex
	Average		-22.07	-179.72		

[a]Parenthesis () indicate independent molecules in the unit cell. [b]Rotation and pyramidalization angles of (*R*)-compounds inverted. [c]Average of VATZOI, VAVBAY. [d]Average of VATZUO, VAVBEC. [e]Average of GOGPEIC, GOGPEY. [f]Average of NMACEP02, NMACEP03.

Table S4. Ibuprofen (*S*)-$CH_3CH(C_6H_4Bu^i$-4)COOH and its derivatives (*S*)-$CH_3CH(C_6H_4Bu^i$-4)COO(R/M) esterified and coordinated at the carboxylic group (structures with *R* factors >10% excluded).

En-try	CSD symbol[a]	Chirality chain			Comments	
		Config. at C_α[b]	O_{cis}-C'-C_α- C_{Me} rotation angle ψ / º	O_{trans}-C'-C_α-O_{cis} pyramidal angle θ / º	Space group	Acid, ester or metal fragment, co-crystallization partners
1	LIBHIP(1)	(*S*)	-92.67	-167.42	$P2_1$	Pb, H_2O
2	SOGLAC(1)	(*S*)	-87.15	-182.62	$P2_1$	Nicotinamide
3	SOGLAC(2)	(*S*)	-86.46	-181.20	$P2_1$	Nicotinamide
4	IJIJAN01(1)	(*S*)	-86.04	-181.33	$P2_1$	4,4-bpy
5	IJIHOZ02(1)	(*S*)	-75.87	-169.50	*P*1	4,4-bpy
6	IJIHOZ02(2)	(*S*)	-70.18	-169.92	*P*1	4,4-bpy
7	IJIJAN01(2)	(*S*)	-65.32	-179.12	$P2_1$	4,4-bpy
8	TEJLIF	(*S*)	-64.05	-178.20	*P*ccn	$(4\text{-}PyCH_2)_2Ag$, H_2O
9	YIPKOA(1)	(*S*)	-63.88	-178.53	*C*2	4-H_2N-3-MePy, H_2O
10	CELFAC	(*S*)	-57.95	-179.13	$P4_3$	PhSn
11	KEHZON(1)	(*S*)	-57.93	-178.16	$P\bar{1}$	$(Ph_3PRuCO)_2$
12	YOJHIR	(*S*)	-52.33	-179.16	*P*ca2_1	2-Meimidaxzol
13	UQIDEF	(*S*)	-51.91	-180.08	*P*na2_1	$(bppm)_2Ru$, PF_6
14	SUWTAH	(*S*)	-50.67	-178.23	*C*2	$Zn(OH_2)_2$
15	VAKVEK[c]	(*S*)	-45.20	-177.34	$P2_12_12_1$	(*S*)-PhCH(Me)NH_2
16	JEKNOC(1)[d]	(*S*)	-43.00	-178.49	$P2_1$	-
17	FUDHUK	(*S*)	-42.56	-176.58	*C*2/c	4,4'-Azopy-Zn
18	XAMFOJ	(*S*)	-42.15	-175.67	*C*2/c	$(4,4'\text{-bpy})_2Zn$
19	YIPKEQ	(*S*)	-41.33	-181.31	$P2_1$	4-H_2NPy
20	CEHZEX	(*S*)	-41.06	-176.99	$P\bar{1}$	4,4'-bpyZn$(OH_2)_2$
21	ZAXHEO	(*S*)	-40.90	-176.70	*C*2/c	$(4\text{-}PyCNh_2)_2Zn$
22	YIPKIU(1)	(*S*)	-40.79	-179.14	$P2_1$	2-H_2N-4-MePy
23	CELDUU	(*S*)	-39.40	-177.59	$P2_1$	Me_3Sn
24	XAWJIR	(*S*)	-37.54	-179.20	$P2_1$/c	$(pyrrolidine)_2Cu$, H_2O
25	ENAYAV	(*S*)	-37.21	-179.37	$P2_1$/n	$BnCH_2NH_2$
26	FUYCOS01	(*S*)	-37.16	-178.32	$P\bar{1}$	$Mg(OH_2)_6$, H_2O
27	FUYCOS(1)	(*S*)	-37.06	-180.11	$P\bar{1}$	$Mg(OH_2)_6$, H_2O
28	IBPRAC[e]	(*S*)	-36.99	-177.06	$P2_1$/c	-
29	YIPKIU(2)	(*S*)	-36.54	-179.11	$P2_1$	2-H_2N-4-MePy
30	XAWJEN(1)	(*S*)	-35.22	-179.51	$P\bar{1}$	$(4\text{-MePy})_2Cu(OH)_2$
31	XEXSAX	(*S*)	-33.15	-178.55	$P\bar{1}$	triamterene, DMSO
32	FUYCOS(2)	(*S*)	-31.68	-178.26	$P\bar{1}$	$Mg(OH_2)_6$, H_2O
33	JEKNOC(2)[d]	(*S*)	-29.72	-177.00	$P2_1$	-
34	KATNOJ(1)	(*S*)	-29.52	-178.53	*P*1	Na, H_2O
35	KEHZON(2)	(*S*)	-28.93	-181.43	$P\bar{1}$	$(Ph_3PRuCO)_2$
36	ROQMAN	(*S*)	-28.27	-180.61	$P2_12_12_1$	(*S*)-2-(2-oxopyrrolidin-1-yl)-butanamide
37	ZONSIH	(*S*)	-27.58	-179.52	$P\bar{1}$	4,7-Ph_2-1,10-phenRe$(CO)_3$, CH_2Cl_2
38	QAHYEE	(*S*)	-26.57	-178.63	$P2_1$	(1*R*,2*S*)-1-H_2N-benz(*f*)indan-2-OH
39	HUPPAJ(1)	(*S*)	-26.57	-176.40	$P\bar{1}$	4,4-bpy
40	KATNOJ(2)	(*S*)	-25.12	-178.90	*P*1	Na, H_2O
41	BIPHOA	(*S*)	-24.74	-179.16	$P2_12_12$	1,10-phenRe$(CO)_3$
42	YIPKOA(2)	(*S*)	-24.70	-178.19	*C*2	4-H_2N-3-MePy, H_2O
43	HUPPAJ(2)	(*S*)	-24.68	-178.15	$P\bar{1}$	4,4-bpy
44	TAWSOB	(*S*)	-24.51	-179.55	$P\bar{1}$	2-NH_2pyrimidine
45	KASVEG[f]	(*S*)	-24.15	-179.23	$P\bar{1}$	Na, H_2O
46	PUFZUO[g]	(*S*)	-23.02	-177.02	$P2_1$/n	Ph_3Sn
47	IJIJAN01(3)	(*S*)	-22.43	-177.44	$P2_1$	4,4-bpy
48	MUJFUV(1)	(*S*)	-20.95	-178.02	$P\bar{1}$	$(Nicotinamide)_2Zn$
49	WIKSEP(1)	(*S*)	-20.73	-178.65	$P\bar{1}$	$(DMF_2Fe)_2$
50	IJIJAN01(4)	(*S*)	-20.42	-179.28	$P2_1$	4,4-bpy
51	DORHUP(1)	(*S*)	-20.26	-180.64	$P\bar{1}$	$(2\text{-}NH_2Py)_2Zn$

52	IJIHOZ02(3)	(*S*)	-19.45	-179.65	$P1$	4,4-bpy
53	WIKSAL(1)	(*S*)	-18.45	-179.44	$P\bar{1}$	$(DMF_2Fe)_2$
54	FEHGIL	(*S*)	-18.32	-180.08	$P2/c$	$(Me_2NCH_2CH_2NH_2)_2Cu(OH_2)$
55	IJIHOZ02(4)	(*S*)	-17.67	-181.45	$P1$	4,4-bpy
56	MUJFUV(2)	(*S*)	-15.81	-177.95	$P\bar{1}$	$(Nicotinamide)_2Zn$
57	WIKSAL(2)	(*S*)	-15.71	-180.64	$P\bar{1}$	$(DMF_2Fe)_2$
58	KIPPAD(1)	(*S*)	-15.50	-183.81	$P\bar{1}$	$4\text{-}H_2NCOPy$
59	XAWJEN(2)	(*S*)	-15.12	-179.04	$P\bar{1}$	$(4\text{-}MePy)_2Cu(OH)_2$
60	ZIXZUD	(*S*)	-15.11	-179.15	$P2_1$	Ester
61	XAWJOX(1)	(*S*)	-14.02	-179.33	$P\bar{1}$	$(3\text{-}MePy)_2Cu(OH)_2$
62	KIPPAD(2)	(*S*)	-13.40	-186.40	$P\bar{1}$	$4\text{-}H_2NCOPy$
63	WIKSEP(2)	(*S*)	-13.33	-180.19	$P\bar{1}$	$(DMF_2Fe)_2$
64	VUCHOR[h]	(*S*)	-11.10	-179.07	$P2_12_12_1$	(*R*)-$PhCH(Me)NH_2$
65	XAWJOX(2)	(*S*)	-8.09	-179.62	$P\bar{1}$	$(3\text{-}MePy)_2Cu(OH)_2$
66	UCOBUK(1)	(*S*)	-7.14	-180.84	$P\bar{1}$	$Sr(OH_2)_2$
67	ENAYID	(*S*)	-3.74	-183.88	$P2_1/c$	$2\text{-}(H_2NCH_2CH_2)indol$
68	SODDIZ(1)[i]	(*S*)	-1.41	-181.26	$Pca2_1$	Nicotinamide
69	SOGLAC(3)	(*S*)	-1.37	-180.24	$P2_1$	Nicotinamide
70	YIPKUG	(*S*)	-1.29	-181.68	$P2_1/n$	$2,6\text{-}(H_2N)_2Py$
71	SOGLAC(4)	(*S*)	-0.18	-181.60	$P2_1$	Nicotinamide
72	UCOBUK(2)	(*S*)	0.33	-181.10	$P\bar{1}$	$Sr(OH_2)_2$
73	ENAYEZ	(*S*)	0.45	-182.86	$P2_1/c$	$4\text{-}HOC_6H_4CH_2CH_2NH_2$
74	DORHUP(2)	(*S*)	1.60	-186.90	$P\bar{1}$	$(2\text{-}NH_2Py)_2Zn$
75	OWIGEH	(*S*)	2.41	-180.03	$P\bar{1}$	$(4\text{-}PyCH_2)_2$
76	SODDIZ(2)[i]	(*S*)	3.74	-178.19	$Pca2_1$	Nicotinamide
77	IBPRAC04	(*S*)	7.96	-228.42[j]	$P2_1/c$	-
78	CUGPIF	(*S*)	14.86	-189.20	$P2_1/c$	$(HOCH_2)_3CNH_2$
79	ENAYOJ	(*S*)	20.12	-176.52	$P\bar{1}$	$1\text{-}H_2NCH_2Nap$
80	LIBHIP(2)	(*S*)	71.63	-179.27	$P2_1$	Pb, H_2O
	Average		-27.97	-179.83		

[a]Parenthesis () indicate independent molecules in the unit cell. [b]Rotation and pyramidalization angles of (*R*)-compounds inverted. [c]Average of VAKVEK, VUCHIL. [d]Average of JEKNOC, JEKNOC10~12. [e]Average of IBPRAC, IBPRAC01, 05~7, 09,10, 16~19. [f]Average of KAVSVEG, KAVSVEG01~04. [g]Average of PUFZUO, PUFZUO01. [h]Average of VUVHOR, VUVHOR01. [i]Average of SODDIZ, SODDIZ01. [j]Excluded from averaging.

X-ray structure analysis

(*R*/*S*)-, (*R*)-, and (*S*)-α-Phenylglycine, and (*R*)-methyl α-phenylglycinate hydrochloride were purchased from TCI Ltd. (*S*)-methyl α-phenylglycinate hydrochloride was purchased from Wako pure chemical Ltd. (*R*)-Ethyl α-phenylglycinate hydrochloride was obtained according to a published procedure [1]. Single crystals of (*R*/*S*)-, (*R*)-, and (*S*)-α-phenylglycine and (*R*)- and (*S*)-methyl α-phenylglycinate hydrochloride suitable for X-ray diffraction analyses were obtained by crystallization from 5% NaCl aqueous solutions. (*R*/*S*)-, (*R*)-, and (*S*)-α-phenylglycine crystallized as colorless thin rods, while (*R*)- and (*S*)-methyl α-phenylglycinate hydrochloride crystallized as colourless plates. Single crystals of (*R*/*S*)-methyl α-phenylglycinate hydrochloride were obtained as colorless blocks from a 1:1 mixture of (*R*)- and (*S*)-methyl α-phenylglycinate hydrochloride in 5% NaCl aqueous solution. Single crystals of (*R*)-ethyl α-phenylglycinate hydrochloride were suitable for X-ray diffraction analyses were obtained by crystallization from ethanol/diethyl ether. The purities were analyzed with a 500 MHz ^{1}H NMR spectrometer (Bruker Avance III). All diffraction data were collected with a 173 K Rigaku XtaLAB mini2 benchtop X-ray crystallography system, equipped with a Mo rotating-anode X-ray generator with monochromated Mo-K_α radiation (λ = 0.71073 Å) and were processed using the CrysAlisPro program [2]. The structures were solved by SHELXT [3], and refined with the full-matrix least-squares technique F^2 with SHELXL [4]. Non-hydrogen atoms were refined with anisotropic displacement and almost all of the hydrogen atoms were located at the calculated positions and refined as riding models. The crystal data and the details of the data collection and refinement of (*R*/*S*)-, (*R*)-, and (*S*)-α-phenylglycine, (*R*/*S*)-, (*R*)-, and (*S*)-methyl α-phenylglycinate hydrochloride, and (*R*C)-ethyl α-phenylglycinate hydrochloride are summarized in Table S5 and can be obtained as CIFs from the Cambridge Crystallographic Data Centre (CCDC). Deposition numbers of (*R*/*S*)-, (*R*)-, and (*S*)-α-phenylglycine, (*R*/*S*)-, (*R*)-, and (*S*)-methyl α-phenylglycinate hydrochloride, and (*R*)-ethyl α-phenylglycinate hydrochloride are CCDC1981269-1981274, and 2049622 (Table S5), respectively. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

1. Juárez, J.; Gnecco, D.; Galindo, A.; Enríquez, R.G.; Marazano, C.; Reynolds, W.F. Synthesis of α-phenyl-1-(*R*)-(-)-piperidineacetic esters. *Tetrahedron: Asymmetry*, **1997**, *8*, 203-206.
2. Rigaku OD. CrysAlisPRO. Rigaku Corporation, Tokyo, Japan, 2018.
3. Sheldrick, G.M. SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. A*, **2015**, *A71*, 3-8.
4. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. Sect. C* **2015**, *C71*, 3-8.

Table S5. Crystallographic data for (*R*)/(*S*)-, (*R*)-, and (*S*)-α-phenylglycine, (*R*)/(*S*)-, (*R*)-, and (*S*)-methyl α-phenylglycinate hydrochloride, and (*R*)-ethyl α-phenylglycinate hydrochloride

Compound	(*R*)/(*S*)-α-Phenylglycine	(*R*)-α-Phenylglycine	(*S*)-α-Phenylglycine	(*R*)/(*S*)-Methyl α-phenylglycinate hydrochloride	(*R*)-Methyl α-phenylglycinate hydrochloride	(*S*)-Methyl α-phenylglycinate hydrochloride
Radiation source (Å)	Mo*K*α (0.71073)	Mo*K*α (0.71073)	Mo*K*α (0.71073)	Mo*K*α (0.71073)	Mo*K*α (0.71073)	Mo*K*α (0.71073)
Empirical formula	$2(C_8H_{10}NO_2)$	$2(C_8H_{10}NO_2)$	$2(C_8H_{10}NO_2)$	$C_9H_{12}NO_2$, Cl	$C_9H_{12}NO_2$, Cl	$C_9H_{12}NO_2$, Cl
Formula weight	303.33	303.33	303.33	201.65	201.65	201.65
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1/c$	$P2_1$	$P2_1$
a (Å)	9.7130(4)	9.7104(7)	9.7225(15)	11.4654(3)	9.1423(12)	9.1508(6)
b (Å)	5.1510(4)	5.1544(6)	5.1571(8)	5.3359(2)	5.1954(6)	5.2102(3)
c (Å)	15.0780(9)	15.0826(19)	15.086(3)	16.5779(5)	11.4409(13)	11.4474(9)
α (°)	90	90	90	90	90	90
β (°)	89.956(4)	90.101(10)	90.078(16)	101.170(3)	97.696(11)	97.707(7)
γ (°)	90	90	90	90	90	90
V (Å)^3	754.38(8)	754.90(14)	756.4(2)	994.99(6)	538.52(11)	540.85(6)
Z	2	2	2	4	2	2
ρ_{calcd} (Mg/m^3)	1.335	1.334	1.327	1.346	1.244	1.238
Abs coeff (mm^{-1})	0.097	0.097	0.096	0.351	0.324	0.323
Abs correct	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Transmiss max/min	1.0000/0.66075	1.0000/0.61224	1.0000 /0.71945	1.0000 /0.97309	1.00000/0.48311	1.00000/0.68995
F (000)	322	322	320	424	212	212
Crystal size (mm)	0.431 x 0.096 x 0.083	0.75 x 0.087 x 0.025	0.75 x 0.025 x 0.015	0.194 x 0.206 x 0.465	0.105 x 0.275 x 0.800	0.103 x 0.204 x 0.51
θ range (°)	2.0990 -29.1610	2.097 - 30.373	2.095 - 30.615	1.810 - 30.445	1.796 - 30.369	1.795 - 30.352
Rflns/unique	7994/3745	4395/2994	6033 / 3746	10294/2914	7927/3086	5389/2810
R_{int}	0.0235	0.0184	0.0477	0.0194	0.0734	0.0397
Data/params	3745/273	2994/273	3746/273	2914/120	3086/120	2810/120
Goodness of fit F^2	1.016	0.963	0.974	1.076	0.993	1.156
R_1/wR_2 ($I>2\sigma(I)$)	0.0547/0.1183	0.0715/0.16427	0.0558 / 0.1265	0.0319/0.0886	0.0594/0.1404	0.0553/0.1631
R_1/wR_2 (all data)	0.0547/0.1258	0.1084/0.1850	0.0883 / 0.1394	0.0390/0.0918	0.0698/ 0.1462	0.0672/0.1693
Abs. struct. param	-1.7(10)	-0.9(10)	-0.2(10)	-	-0.03(8)	-0.11(6)
Largest diff. peak and hole (e Å^{-3})	0.277/-0.233	0.352/-0.440	0.224/-0.249	0.302/-0.207	0.508/-0.680	0.593/-0.253
CCDC No.	1981269	1981270	1981271	1981272	1981273	1981274

Compound	(*R*)-Ethyl α-phenylglycinate hydrochloride
Radiation source (Å)	Mo*K*α (0.71073)
Empirical formula	$2(C_9H_{12}NO_2)$, 2Cl
Formula weight	431.34
Crystal system	monoclinic
Space group	$P2_1$
a (Å)	11.7886(7)
b (Å)	5.6808(3)
c (Å)	17.6370(12)
α (°)	90
β (°)	101.645(6)
γ (°)	90
V (Å)^3	538.52(11)
Z	2
ρ_{calcd} (Mg/m^3)	1.238
Abs coeff (mm^{-1})	0.306
Abs correct	multi-scan
Transmiss max/min	1.00000/0.92306
F (000)	456
Crystal size (mm)	0.121 x 0.279 x 0.704
θ range (°)	1.913 - 30.398
Rflns/unique	10877/5649
R_{int}	0.0393
Data/params	5649/257
Goodness of fit F^2	1.040
R_1/wR_2 ($I>2\sigma(I)$)	0.0583/0.1418
R_1/wR_2 (all data)	0.0870/0.1588
Abs. struct. param	-0.05(4)
Largest diff. peak and hole (e Å^{-3})	0.474/-0.451
CCDC No.	2049622

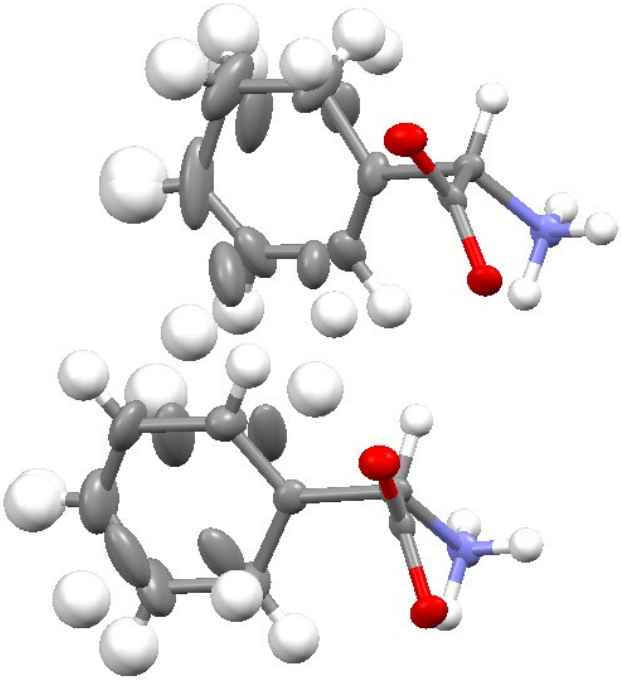

Figure S1. ORTEP drawing of conglomerate (*R*)/(*S*)-α-phenylglycine: CCDC1981269.

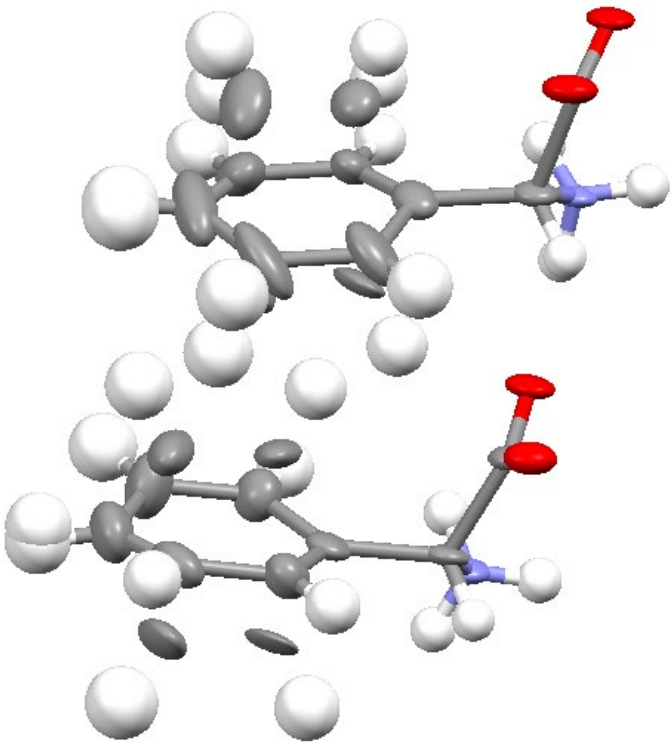

Figure S2. ORTEP drawing of (*R*)-α-phenylglycine: CCDC1981270.

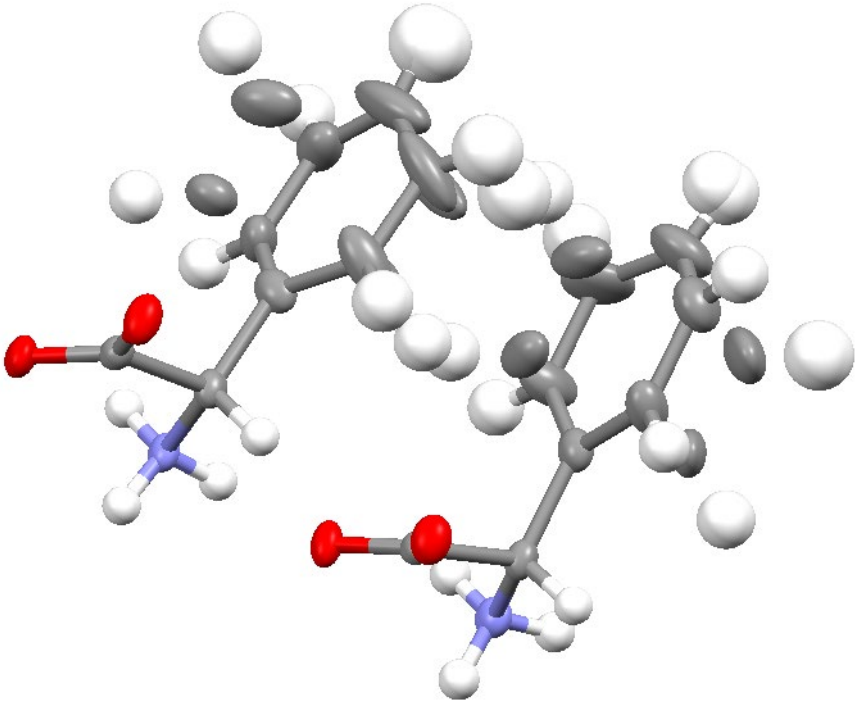

Figure S3. ORTEP drawing of (*S*)-α-phenylglycine. CCDC1981271.

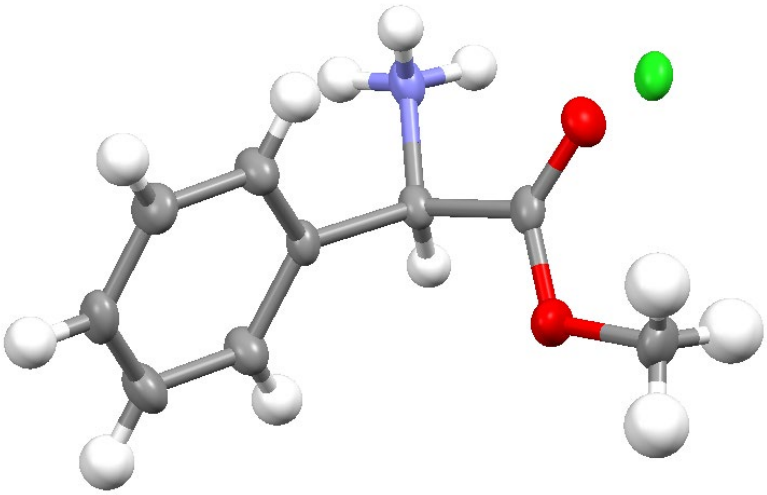

Figure S4. ORTEP drawing of racemate (*R*)/(*S*)-methyl α-phenylglycinate hydrochloride: CCDC1981272.

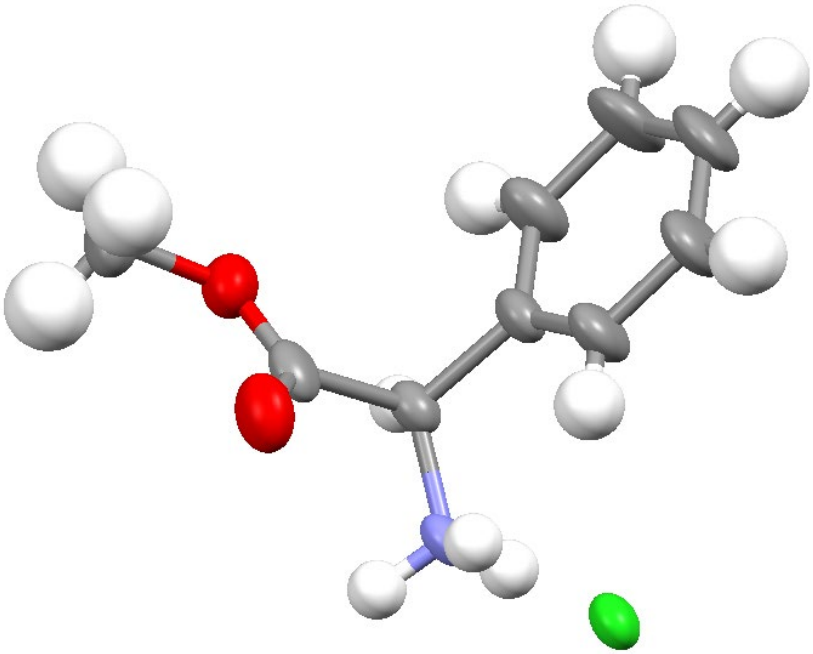

Figure S5. ORTEP drawing of (*R*)-methyl α-phenylglycinate hydrochloride: CCDC1981273.

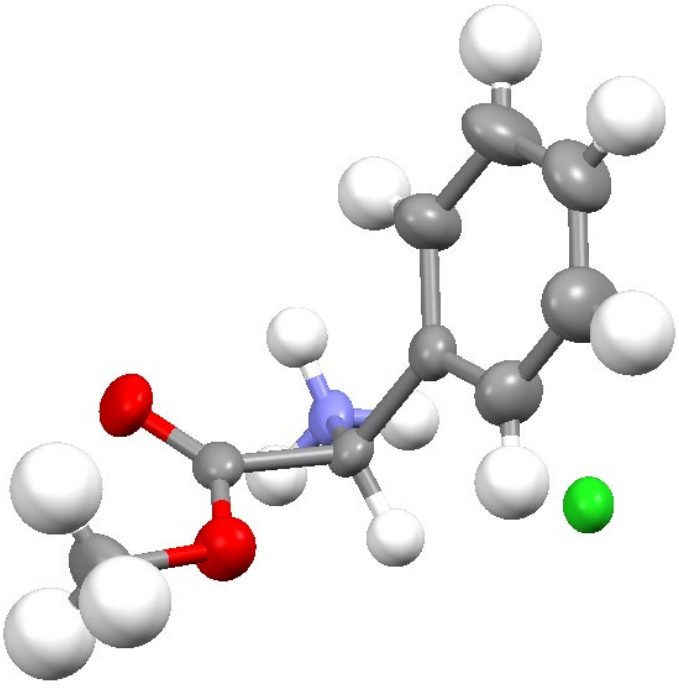

Figure S6. ORTEP drawing of (*S*)-methyl α-phenylglycinate hydrochloride: CCDC1981274.

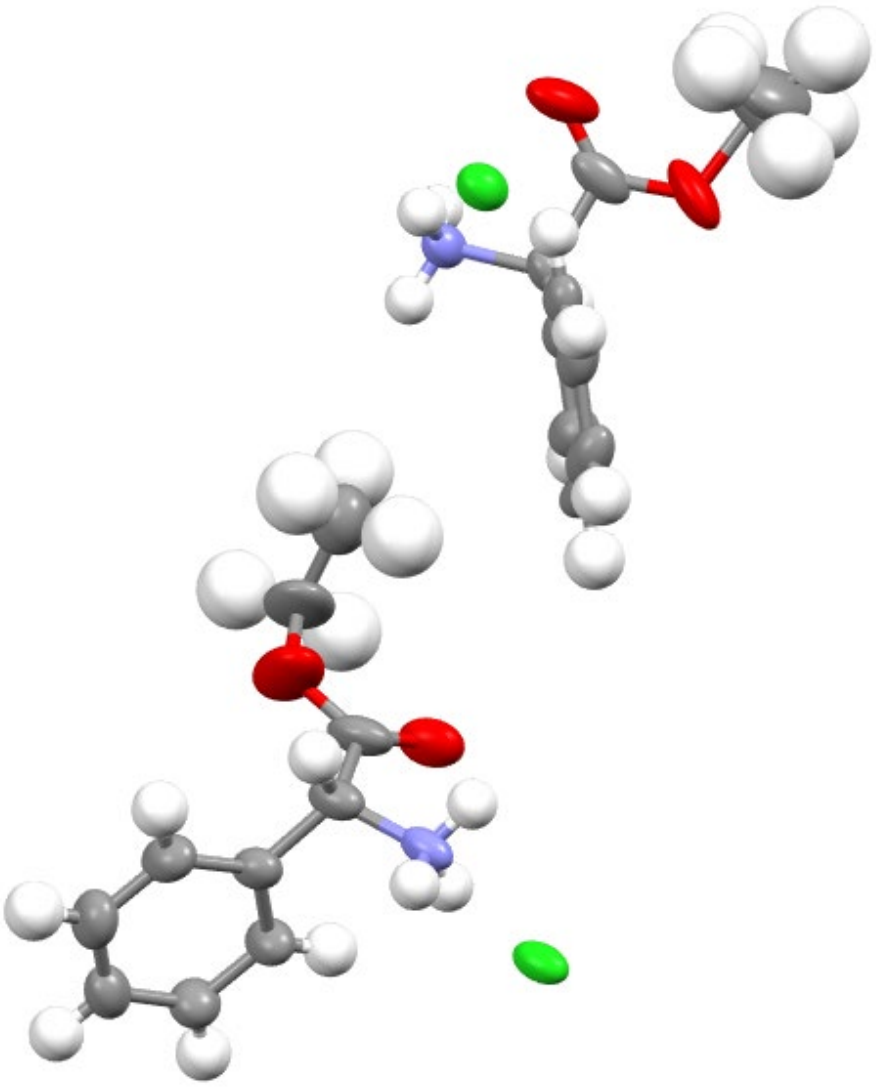

Figure S7. ORTEP drawing of (*R*)-ethyl α-phenylglycinate hydrochloride: CCDC2049622.