Supplementary Information

Discrimination of Enantiomers of Dipeptide Derivatives with Two Chiral Centers by Tetraaza Macrocyclic Chiral Solvating Agents Using ^{1}H NMR Spectroscopy

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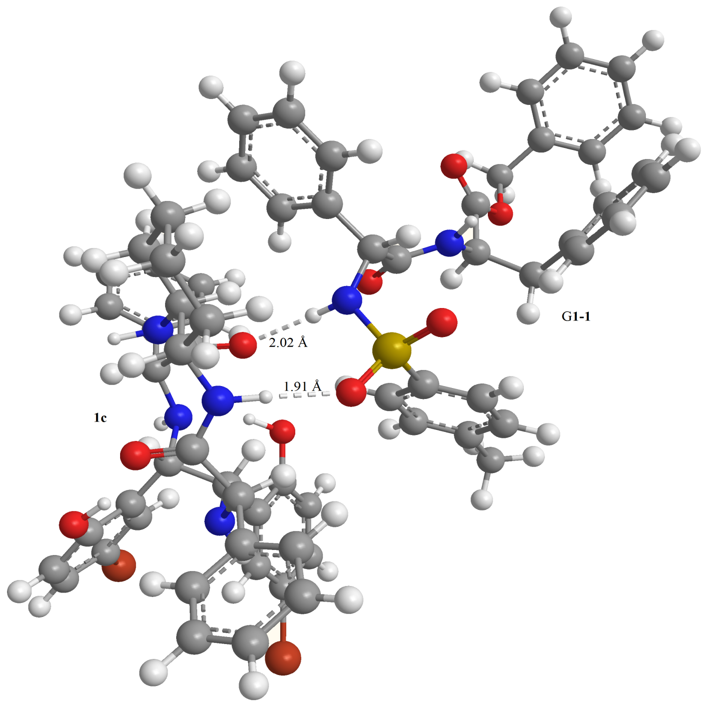
Crystallographic data for TAMCSAs 1a·2CH$_3$COCH$_3$, 1b and 1c·CDCl$_3$

Table S1. Crystallographic data for TAMCSAs **1a**·2CH$_3$COCH$_3$, **1b** and **1c**·CDCl$_3$.

	1a·2CH$_3$COCH$_3$	**1b**	**1c**·CDCl$_3$
Formula	$C_{42}H_{50}N_4O_6$	$C_{36}H_{36}Cl_2N_4O_4$	$C_{37}H_{36}DBr_2Cl_3N_4O_4$
M	706.86	659.59	868.88
Temperature (K)	110(2)	110(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Tetragonal
Space group	*P*2(1)	*C*2	*P*43
a/Å	9.0188(8)	37.839(4)	13.811(3)
b/Å	21.1444(19)	25.190(2)	13.811(3)
c/Å	10.7833(9)	13.6300(14)	20.076(4)
α/deg	90	90	90
β/deg	111.097(2)	101.307(2)	90
γ/deg	90	90	90
V/Å^3	1918.5(3)	12739(2)	3829.5(16)
Z	2	12	4
D_C/Mg m^{-3}	1.224	1.032	1.507
F_{000}	756	4152	1760
μ/mm^{-1}	0.082	0.188	2.370
θ (range)/deg	2.02 to 25.25	1.90 to 25.25	1.790 to 27.514
Reflections collected/unique	9662/3569 [R_{int} = 0.0362]	17687/17687 [R_{int} = 0.0000]	25246/7907 [R_{int} = 0.0384]
Parameters	480	1280	465
R_1 [$I > 2\sigma(I)$]	0.0357	0.0668	0.0317
wR_2 [$I > 2\sigma(I)$]	0.0756	0.1739	0.0679
Goodness of fit on F^{-2}	1.025	1.011	1.027
CCDC deposition numbers	1007044	1007045	1007047



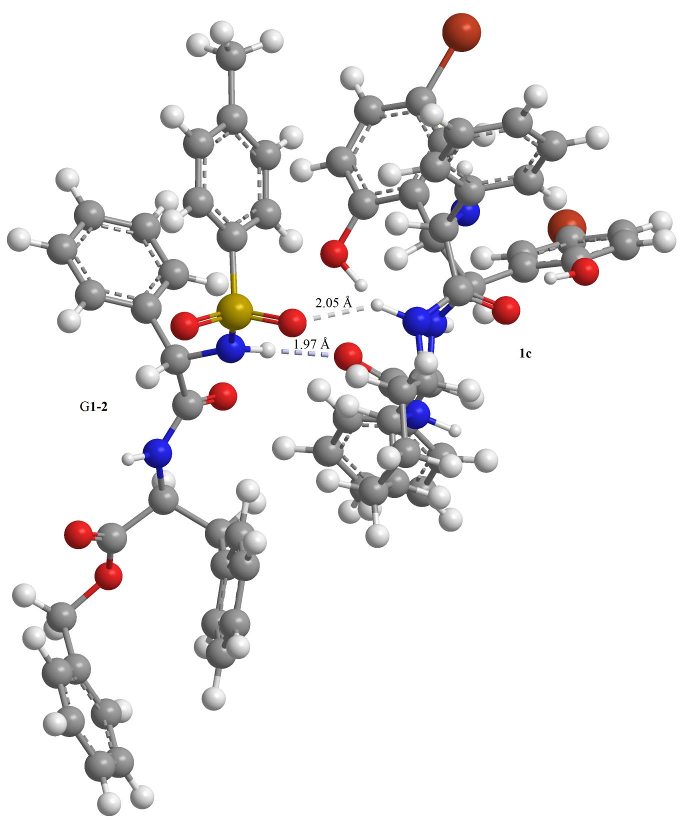
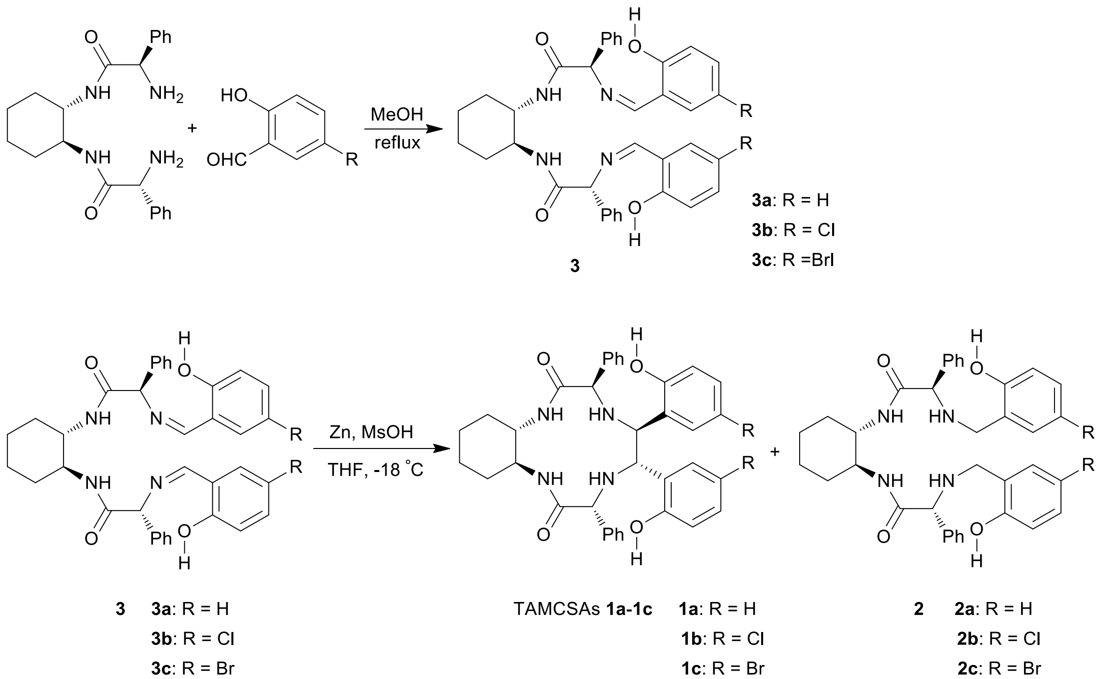


Figure S1. Theoretically proposed model of **G1-1** and **G1-2** with TAMCSA **1c**.

Synthesis of TAMCSAs 1a-1c and chiral diimines 3a-3c.[1]



Procedure of synthesis of chiral diimines 3a-3c. Salicylaldehyde or its derivatives (2 mmol) was added to a solution of diamine (0.76 g, 2 mmol) in dried MeOH (10 mL) and the mixture was refluxed under nitrogen atmosphere. After yellow precipitate was formed, the reaction mixture continued to be stirred for two hours. The chiral diimines **3a**-**3c** was obtained as yellow solid and used in the next step without further purification.

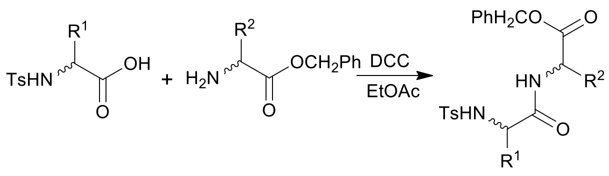
Procedure of synthesis of TAMCSAs 1a-1c. To a solution of chiral diimines **3** (1.2 mmol) in dried THF (60 mL) was added zinc powder (0.78 g, 12 mmol) and MsOH (1.15g, 12 mmol) in dried THF (20 mL) under nitrogen atmosphere at -18°C. The mixture was stirred for 24h. The reaction mixture was basified to pH = 9-10 with saturated $NaHCO_3$ solution. The precipitate formed was filtered off and washed with $CHCl_3$. The organic layer was separated from filtrate. The water layer was extracted with $CHCl_3$ (15 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduce pressure and the residue was purified by column chromatography on silica gel to afford TAMCSAs **1a**-**1c**. Meanwhile, the chiral compounds **2a**-**2c** were also obtained as known chiral compounds.[2]

TAMCSA **1a**: R_f = 0.4 (petroleum ether / ethyl acetate = 2/1); 31% yield; mp. 191-193 °C; $[\alpha]_D^{20}$ -9.3 (*c* 0.03, THF); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.11-1.18 (m, 2H), 1.25-1.31 (m, 2H), 1.62-1.64 (m, 2H), 1.76 (d, *J* = 11.8 Hz, 2H), 4.05 (br, 2H), 4.42 (s, 2H), 4.71 (s, 2H), 6.13 (d, *J* = 7.6 Hz, 2H), 6.50-6.54 (m, 2H), 6.87(d, *J* = 7.2 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 7.03-7.07 (m, 2H), 7.27-7.33 (m, 6H), 7.53-7.54 (m, 4H), 10.14 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.5, 31.7, 53.2, 62.1, 69.4, 117.2, 119.2, 125.9, 127.4, 127.5, 128.3, 128.4, 128.6, 138.2, 155.0, 173.2; IR (KBr): 3300, 2932, 1663, 1527, 1493, 1454, 753, 698 cm^{-1}; ESI-HRMS: calcd for $C_{36}H_{39}N_4O_4$ 591.2971, found 591.2970 ($[M+H]^+$).

TAMCSA **1b**: R_f = 0.3 (petroleum ether / ethyl acetate = 2/1); 29% yield; mp. 188-190 °C; $[\alpha]_D^{20}$ -27.4 (*c* 0.03, THF); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.08-1.16 (m, 2H), 1.21-1.29 (m, 2H), 1.62 (d, *J* = 7.6 Hz, 2H), 1.73 (d, *J* = 12.8 Hz, 2H), 4.04-4.13 (m, 2H), 4.49 (s, 2H), 4.66(s, 2H), 6.06 (d, *J* = 1.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.96-7.02 (m, 4H), 7.33-7.37 (m, 6H), 7.54-7.56 (m, 4H), 10.09 (br, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 24.5, 31.7, 52.7, 62.1, 66.0, 116.5, 121.6, 126.5, 127.3, 127.4, 128.1, 129.0, 139.2, 142.3, 155.0, 172.2; IR (KBr): 3314, 2931, 1662, 1547, 1486, 700 cm^{-1}; ESI-HRMS: calcd for $C_{36}H_{37}Cl_2N_4O_4$ 659.2192, found 659.2198 ($[M+H]^+$).

TAMCSA **1c**: R_f = 0.3 (petroleum ether / ethyl acetate = 2/1); 33% yield; mp. 198-200 °C; $[\alpha]_D^{20}$ -34.4 (*c* 0.03, THF); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.09-1.14 (m, 2H), 1.24-1.27 (m, 2H), 1.63 (d, *J* = 8.2 Hz, 2H), 1.75 (d, *J* = 13.3 Hz, 2H), 1.86 (br, 2H), 4.04 (br, 2H), 4.45 (s, 2H), 4.64(s, 2H), 6.17 (s, 2H), 6.79-6.81 (m, 4H), 7.17 (dd, *J* = 8.6Hz, *J* = 2.2Hz, 2H), 7.34-7.35 (m, 6H), 7.52-7.54 (m, 4H), 10.01 (br, 2H); ^{13}CNMR (100 MHz, DMSO-d_6) δ: 25.0, 32.2, 53.2, 62.5, 66.5, 109.8, 117.5, 127.0, 127.8, 128.6, 130.8, 132.4, 139.7, 156.0, 156.1, 172.6; IR (KBr): 3387, 2933, 1655, 1528, 1483, 698 cm^{-1}; ESI-HRMS: calcd for $C_{36}H_{37}Br_2N_4O_4$ 747.1182, found 747.1184 ($[M+H]^+$).

Synthesis of dipeptide derivatives with two chiral centers G1-1-G8-2.[3]



4 **5** **G1-1-G8-2**

G1-1: *N*-Ts-*D*-Phg-*D*-PheOBn
G1-2: *N*-Ts-*L*-Phg-*L*-PheOBn
G2-1: *N*-Ts-*D*-Phg-*L*-PheOBn
G2-2: *N*-Ts-*L*-Phg-*D*-PheOBn
G3-1: *N*-Ts-*D*-Phe-*D*-PhgOBn
G3-2: *N*-Ts-*L*-Phe-*L*-PhgOBn
G4-1: *N*-Ts-*D*-Phe-*L*-PhgOBn
G4-2: *N*-Ts-*L*-Phe-*D*-PhgOBn
G5-1: *N*-Ts-*D*-Ala-*D*-PheOBn
G5-2: *N*-Ts-*L*-Ala-*L*-PheOBn
G6-1: *N*-Ts-*D*-Val-*D*-PheOBn
G6-2: *N*-Ts-*L*-Val-*L*-PheOBn
G7-1: *N*-Ts-*D*-Glu-*D*-PheOBn
G7-2: *N*-Ts-*L*-Glu-*L*-PheOBn
G8-1: *N*-Ts-*D*-Phg-*D*-AlaOBn
G8-2: *N*-Ts-*L*-Phg-*L*-AlaOBn

For example, synthetic procedure of G**1-1**: *D*-PheOCH$_2$Ph (0.26 g, 1 mmol) was added to a solution of *N*-Ts-*D*-phenylglycine (0.30 g, 1 mmol) in dry ethyl acetate (8 mL) at room temperature. A solution of DCC (0.25 g, 1.2 mmol) in dry ethyl acetate (5 mL) was added dropwise into the above solution while stirring under nitrogen atmosphere at ice-bath. And then the reaction mixture was allowed to room temperature and stirred for over night. The precipitate formed was filtered off and filtrate was concentrated under reduce pressure. The crude product was purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 3/1) to afford dipeptide derivative with two chiral centers **G1-1**.

G1-1. 85% yield; mp. 158-160 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 3/1); $[\alpha]_D^{20}$ -49.1 (*c* 0.02, THF). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.36 (s, 3H), 2.96 (dd, *J* = 13.9 Hz, *J* = 5.8 Hz, 1H), 3.03 (dd, *J* = 13.8 Hz, *J* = 5.8 Hz, 1H), 4.71 (d, *J* = 5.0 Hz, 1H), 4.70-4.75 (m, 1H), 5.01 (d, *J* = 12.0 Hz, 1H), 5.08 (d, *J* = 12.1 Hz, 1H), 5.83 (d, *J* = 4.8 Hz, 1H), 6.11 (d, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 7.0 Hz, 2H), 7.02 (d, *J* = 7.3 Hz, 1H), 7.15 7.34 (m, 10H), 7.35 (d, *J* = 2.9 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 37.5, 53.6, 60.5, 67.4, 127.2, 127.3, 127.5, 128.6, 128.7, 129.0, 129.2, 129.5, 134.8, 135.2, 135.9, 136.6, 143.5, 168.5, 170.3; IR

(KBr): 3273, 1739, 1658, 1548, 1344, 1164, 1084, 707 cm^{-1}; MALDI-HRMS: calcd for $C_{31}H_{30}N_2NaO_5S$ 565.1773, found 565.1768 ($[M+Na]^+$).

G1-2. 80% yield; mp. 155-157 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 3/1); $[\alpha]_D^{20}$ +50.0 (*c* 0.02, THF). ^1H NMR (400 MHz, $CDCl_3$) δ: 2.36 (s, 3H), 2.98 (dd, *J* = 13.9 Hz, *J* = 5.8 Hz, 1H), 3.04 (d, *J* = 13.9 Hz, *J* = 5.8 Hz, 1H), 4.71 (d, *J* = 4.8 Hz, 1H), 4.71-4.75 (m, 1H), 5.01 (d, *J* = 12.1 Hz, 1H), 5.08 (d, *J* = 12.1 Hz, 1H), 5.84 (d, *J* = 4.9 Hz, 1H), 6.12 (d, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 6.8 Hz, 2H), 7.02 (d, *J* = 7.0 Hz, 2H), 7.15-7.23 (m, 10H), 7.34-7.35 (m, 3H),, 9.59 (d, *J* = 8.28 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 37.5, 53.6, 60.5, 67.4, 127.2, 127.3, 127.5, 128.5, 128.6, 128.7, 129.0, 129.2, 129.5, 134.8, 135.2, 136.0, 136.7, 143.5, 168.5, 170.4; IR (KBr): 3269, 2361, 1734, 1655, 1495, 1150, 696 cm^{-1}; ESI-HRMS: calcd for $C_{31}H_{30}N_2NaO_5S$ 565.1768, found 565.1738 ($[M+Na]^+$).

G2-1. 52% yield; mp. 160-162 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 3/1); $[\alpha]_D^{20}$ -39.0 (*c* 0.02, THF). ^1H NMR (400 MHz, $CDCl_3$) δ: 2.36 (s, 3H), 2.89 (dd, *J* = 13.8 Hz, *J* = 5.4 Hz, 1H), 2.97 (dd, *J* = 13.8 Hz, *J* = 5.3 Hz, 1H), 4.73 (d, *J* = 4.8 Hz, 1H), 4.79-4.84 (m, 1H), 5.08 (d, *J* = 12.0 Hz, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 5.87 (d, *J* = 4.8 Hz, 1H), 6.09 (d, *J* = 8.2 Hz, 1H), 6.54 (d, *J* = 7.1 Hz, 2H), 6.98-7.02 (m, 2H), 7.06-7.16 (m, 5H), 7.21-7.30 (m, 5H), 7.37-7.38 (m, 3H), 7.56 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 37.5, 53.2, 60.5, 67.4, 127.0, 127.2, 127.6, 128.5, 128.6, 128.7, 129.0, 129.2, 129.5, 134.8, 134.9, 136.4, 136.7, 143.4, 168.3, 170.6; IR (KBr): 3258, 1734, 1658, 1345, 1161, 1085, 685 cm^{-1}; ESI-HRMS: calcd for $C_{31}H_{30}N_2NaO_5S$ 565.1768, found 565.1734 ($[M+Na]^+$).

G2-2. 70% yield; mp. 159-161 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 3/1); $[\alpha]_D^{20}$ +40.0 (*c* 0.02, THF). ^1H NMR (400 MHz, $CDCl_3$) δ: 2.36 (s, 3H), 2.90 (dd, *J* = 13.9 Hz, *J* = 5.4 Hz, 1H), 2.97 (dd, *J* = 13.9 Hz, *J* = 5.3 Hz, 1H), 4.73 (d, *J* = 4.9 Hz, 1H), 4.79-4.84 (m, 1H), 5.08 (d, *J* = 12.0 Hz, 1H), 5.14 (d, *J* = 12.0 Hz, 1H), 5.87 (d, *J* = 4.8 Hz, 1H), 6.09 (d, *J* = 8.1 Hz, 1H), 6.54 (d, *J* = 7.0 Hz, 1H), 6.98-7.02 (m, 2H), 7.06-7.16 (m, 5H), 7.22-7.30 (m, 5H), 7.37-7.38 (m, 3H), 7.56 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 37.5, 53.1, 60.5, 67.5, 127.0, 127.2, 127.6, 128.5, 128.7, 129.0, 129.1, 129.5, 134.7, 134.8, 136.4, 136.6, 143.4, 168.2, 170.1; IR (KBr): 3269, 1745, 1648, 1344, 1150, 696 cm^{-1}; ESI-HRMS: calcd for $C_{31}H_{30}N_2NaO_5S$ 565.1768, found 565.1743 ($[M+Na]^+$).

G3-1. 50% yield; mp. 156-158 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 3/1); $[\alpha]_D^{20}$ -48.0 (*c* 0.02, THF). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.40 (s, 3H), 2.79 (dd, *J* = 13.9 Hz, *J* = 6.5 Hz, 1H), 3.07 (dd, *J* = 13.9 Hz, *J* = 6.0 Hz, 1H), 3.95-4.00 (m, 1H), 4.91 (d, *J* = 7.5 Hz, 1H), 5.10 (d, *J* = 12.4 Hz, 1H), 5.16 (d, *J* = 12.4 Hz, 1H), 5.44 (d, *J* = 6.8 Hz, 1H), 6.86-6.88 (m, 2H), 7.10-7.13 (m, 2H), 7.16-7.21 (m, 8H),7.28-7.30 (m, 5H), 7.58 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6, 38.3, 56.8, 57.4, 67.4, 127.1, 127.2, 127.9, 128.3, 128.5, 128.8, 128.9, 129.3, 129.8, 135.0, 135.1, 135.9, 136.0, 143.8, 169.6, 169.8; IR (KBr): 3247, 1734, 1648, 1161, 1096, 696 cm^{-1}; ESI-HRMS: calcd for $C_{31}H_{30}N_2NaO_5S$ 565.1768, found 565.1746 ($[M+Na]^+$).

G3-2. 62% yield; mp. 158-160 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 3/1); $[\alpha]_D^{20}$ +46.0 (*c* 0.02, THF). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.40 (s, 3H), 2.79 (dd, *J* = 14.0 Hz, *J* = 6.5 Hz, 1H), 3.07 (dd, *J* = 14.0 Hz, *J* = 6.0 Hz, 1H), 3.95-4.00 (m, 1H), 4.92 (d, *J* = 7.5 Hz, 1H), 5.10 (d, *J* = 12.4 Hz, 1H), 5.16 (d, *J* = 12.4 Hz, 1H), 5.44 (d, *J* = 6.8 Hz, 1H), 6.86-6.88 (m, 2H), 7.10-7.13 (m, 2H),7.16-7.21 (m, 8H), 7.28-7.32 (m, 5H), 7.58 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6, 38.4, 56.8, 57.5, 67.4, 127.1, 127.2, 127.3, 127.9, 128.3, 128.5, 128.8, 128.9, 129.3, 129.8, 135.0, 135.1, 135.9, 136.1, 143.7, 169.6, 169.8; IR (KBr): 3247, 1745, 1658, 1150, 1096, 696 cm^{-1}; ESI-HRMS: calcd for $C_{31}H_{30}N_2NaO_5S$ 565.1768, found 565.1736 ($[M+Na]^+$).

G4-1. 49% yield; mp. 148-150 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 3/1); $[\alpha]_D^{20}$ -7.5 (*c* 0.02, THF). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.38 (s, 3H), 2.92 (dd, *J* = 13.0 Hz, *J* = 5.6 Hz, 1H), 2.97 (dd, *J* = 13.0 Hz, *J* = 5.9 Hz, 1H), 3.89-3.94 (m, 1H), 4.93 (d, *J* = 7.0 Hz, 1H), 5.11 (d, *J* = 12.4 Hz, 1H), 5.17 (d, *J* = 12.3 Hz, 1H), 5.40 (d, *J* = 7.0 Hz, 1H), 6.88 (d, *J* = 7.0 Hz, 2H), 7.10-7.20 (m, 10H), 7.28-7.31 (m, 5H), 7.52 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 38.5, 56.7, 57.7, 67.4, 127.1, 127.2, 127.9, 128.4, 128.5, 128.8, 128.9, 129.2, 129.7, 135.0, 135.6, 135.8, 143.7, 169.5, 170.0; IR (KBr): 3291, 1734, 1648, 1507, 1161, 1452, 1085, 739 cm^{-1}; ESI-HRMS: calcd for $C_{31}H_{30}N_2NaO_5S$ 565.1768, found 565.1744 ($[M+Na]^+$).

G4-2. 50% yield; mp. 149-151 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 3/1); $[\alpha]_D^{20}$ +7.0 (*c* 0.02, THF). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.38 (s, 3H), 2.92 (dd, *J* = 14.0 Hz, *J* = 6.6 Hz, 1H), 2.97 (dd, *J* = 13.9 Hz, *J* = 6.8 Hz, 1H), 3.89-3.94 (m, 1H), 4.93 (d, *J* = 7.0 Hz, 1H), 5.11 (d, *J* = 12.4 Hz, 1H), 5.17 (d, *J* = 12.4 Hz, 1H), 5.40 (d, *J* = 7.0 Hz, 1H), 6.87- 6.89 (m, 2H), 7.10-7.20 (m, 10H), 7.28-7.31 (m, 5H), 7.52 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 38.5, 56.7, 57.7, 67.4, 127.1, 127.2, 127.9, 128.4, 128.5, 128.9, 129.2, 129.7, 135.0, 135.6, 135.8, 143.7, 169.5, 170.0; IR (KBr): 3291, 1745, 1637, 1507, 1161, 1085, 696 cm^{-1}; ESI-HRMS calcd for $C_{31}H_{30}N_2NaO_5S$ 565.1768, found 565.1744 ($[M+Na]^+$).

G5-1: 62% yield; mp. 109-110 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 5/2); $[\alpha]_D^{20}$ = -2.2 (*c* 0.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.22 (d, *J* = 7.1 Hz, 3H), 2.39 (s, 3H), 3.00 (d, *J* = 5.8 Hz, 2H), 3.71-3.78 (m, 1H), 4.75 (dt, *J* = 7.6 Hz, *J* = 5.8 Hz, 1H), 5.09 (d, *J* = 12.1 Hz, 1H), 5.10 (d, *J* = 5.2 Hz, 1H), 5.16 (d, *J* = 12.1 Hz, 1H), 6.38 (d, *J* = 7.6 Hz, 1H), 6.87-6.89 (m, 2H), 7.19-7.22 (m, 3H), 7.27-7.29 (m, 4H), 7.35-7.37 (m, 3H), 7.73 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.5, 21.5, 37.7, 52.3, 53.4, 67.4, 127.1, 127.3, 128.5, 128.6, 128.6, 129.3, 129.8, 134.9, 135.4, 136.7, 143.8, 170.7, 170.8; IR (KBr): 3285, 2917, 1747, 1669, 1156, 1089, 699 cm^{-1}; TOF-HRMS: calcd for $C_{26}H_{29}N_2O_5S$ 481.1791, found 481.1794 ($[M+H]^+$).

G5-2: 72% yield; mp. 110-111 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 5/2); $[\alpha]_D^{20}$ = +2.2 (*c* 0.04, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ: 1.22 (d, *J* = 7.1 Hz, 3H), 2.40 (s, 3H), 3.01 (d, *J* = 5.8 Hz, 2H), 3.74 (dq, *J* = 7.2 Hz, *J* = 7.1 Hz, 1H), 4.75 (dt, *J* = 7.8 Hz, *J* = 5.8 Hz, 1H), 5.07 (d, *J* = 5.9 Hz, 1H), 5.09 (d, *J* = 11.9 Hz, 1H), 5.16 (d, *J* = 12.1 Hz, 1H), 6.36 (d, *J* = 7.6 Hz, 1H), 6.87-6.89 (m, 2H), 7.16-7.22 (m, 3H), 7.28-7.30 (m, 4H), 7.36-7.38 (m, 3H), 7.73 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.6, 21.5, 37.7, 52.2, 53.4, 67.4, 127.1, 127.3, 128.5, 128.6, 129.3, 129.8, 134.9, 145.4, 136.7, 143.8, 170.7, 170.8; IR (KBr): 3289, 2976, 1746, 1641, 1155, 1097, 695 cm^{-1}; TOF-HRMS: calcd for $C_{26}H_{29}N_2O_5S$ 481.1791, found 481.1794 ($[M+H]^+$).

G6-1: 72% yield; mp. 173-174 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 7/2); $[\alpha]_D^{20}$ = -37.5 (*c* 0.02, THF); ^1H NMR (400 MHz, $CDCl_3$) δ: 0.75 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H), 1.92-2.00 (m, 1H), 2.34 (s, 3H), 2.80 (dd, *J* = 13.8 Hz, *J* = 6.1 Hz, 1H), 2.95 (dd, *J* = 13.8 Hz, *J* = 5.3 Hz, 1H), 3.48 (dd, *J* = 8.4 Hz, *J* = 4.8 Hz, 1H), 4.71-4.75 (m, 1H), 5.05 (d, *J* = 12.1 Hz, 1H), 5.12 (d, *J* = 12.1 Hz, 1H), 5.27 (d, *J* = 8.4 Hz, 1H), 6.05 (d, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 7.0 Hz, 2H), 7.17-7.22 (m, 7H), 7.27-7.36 (m, 3H), 7.73 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.1, 19.0, 21.5, 31.7, 37.9, 53.2, 61.7, 67.4, 127.2, 127.4, 128.5, 128.6, 129.2, 134.8, 135.3, 136.8, 143.7, 169.8, 170.7; IR (KBr): 3260, 2916, 2362, 1735, 1653, 1179, 706 cm^{-1}; TOF-HRMS: calcd for $C_{28}H_{33}N_2O_5S$ 509.2104, found 509.2104 ($[M+H]^+$).

G6-2: 80% yield; mp. 168-169 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 7/2); $[\alpha]_D^{20}$ = +37.1 (*c* 0.02, THF); ^1H NMR (400 MHz, $CDCl_3$) δ: 0.75 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.8

Hz, 3H), 1.92-2.00 (m, 1H), 2.34 (s, 3H), 2.80 (dd, *J* = 13.8 Hz, *J* = 6.1 Hz, 1H), 2.95 (dd, *J* = 13.9 Hz, *J* = 5.3 Hz, 1H), 3.48 (dd, *J* = 8.4 Hz, *J* = 4.8 Hz, 1H), 4.71-4.75 (m, 1H), 5.06 (d, *J* = 12.0 Hz, 1H), 5.12 (d, *J* = 12.0 Hz, 1H), 5.26 (d, *J* = 8.4 Hz, 1H), 6.05 (d, *J* = 7.8 Hz, 1H), 6.80-6.82 (m, 2H), 7.17-7.25 (m, 7H), 7.28-7.36 (m, 3H), 7.73 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 17.1, 19.0, 21.5, 31.7, 37.8, 53.2, 61.7, 67.4, 127.2, 127.4, 128.5, 128.6, 129.2, 129.6, 134.8, 135.3, 136.8, 143.7, 169.8, 170.7; IR (KBr): 3272, 2953, 2362, 1746, 1641, 1191, 683 cm^{-1}; TOF-HRMS: calcd for $C_{28}H_{33}N_2O_5S$ 509.2104, found 509.2104 ($[M+H]^+$).

G7-1: 37% yield; mp. 109-110 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 1/3); $[\alpha]_D^{20}$ = -24.4 (*c* 0.02, THF); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.82-1.88 (m, 2H), 2.18-2.24 (m, 2H), 2.35 (s, 3H), 2.91 (dd, *J* = 14.0 Hz, *J* = 7.1 Hz, 1H), 2.97 (dd, *J* = 13.9 Hz, *J* = 6.0 Hz, 1H), 3.74-3.79 (m, 1H), 4.64-4.69 (m, 1H), 5.06 (d, *J* = 12.1 Hz, 1H), 5.13 (d, *J* = 12.1 Hz, 1H), 5.47 (s, 1H), 5.60 (s, 1H), 6.45 (d, *J* = 6.6 Hz, 1H), 6.96-6.98 (m, 2H), 7.20-7.22 (m, 4H), 7.25-7.27 (m, 3H), 7.33-7.35 (m, 3H), 7.69 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 28.7, 31.0, 37.7, 53.7, 55.9, 67.2, 127.0, 127.3, 128.4, 128.5, 128.6, 129.2, 129.7, 135.0, 135.9, 136.6, 143.6, 170.6, 171.1, 175.6; IR (KBr): 3341, 2356, 1724, 1662, 1152, 799 666 cm^{-1}; TOF-HRMS: calcd for $C_{28}H_{32}N_3O_6S$ 538.2006, found 538.2005 ($[M+H]^+$).

G7-2: 41% yield; mp. 176-177 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 1/3); $[\alpha]_D^{20}$ = +24.1 (*c* 0.02, THF); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.84-1.88 (m, 2H), 2.18-2.26 (m, 2H), 2.35 (s, 3H), 2.91 (dd, *J* = 13.9 Hz, *J* = 7.1 Hz, 1H), 2.97 (dd, *J* = 13.9 Hz, *J* = 5.9 Hz, 1H), 3.74-3.79 (m, 1H), 4.64-4.69 (m, 1H), 5.06 (d, *J* = 12.2 Hz, 1H), 5.13 (d, *J* = 12.2 Hz, 1H), 5.47 (s, 1H), 5.60 (s, 1H), 6.46 (d, *J* = 7.2 Hz, 1H), 6.96-6.98 (m, 2H), 7.20-7.22 (m, 4H), 7.25-7.27 (m, 3H), 7.33-7.35 (m, 3H), 7.69 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 28.7, 31.0, 37.7, 53.7, 55.9, 67.2, 127.0, 127.3, 128.4, 128.5, 128.6, 129.2, 129.7, 135.0, 135.9, 136.6, 143.6, 170.6, 171.1, 175.6; IR (KBr): 3329, 2344, 1736, 1662, 1152, 812, 702 cm^{-1}; TOF-HRMS: calcd for $C_{28}H_{32}N_3O_6S$ 538.2006, found 538.2009 ($[M+H]^+$).

G8-1: 33% yield; mp. 152-153 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 5/2); $[\alpha]_D^{20}$ = -37.0 (*c* 0.02, THF); ^1H NMR (400 MHz, $CDCl_3$) δ: 1.29 (d, *J* = 7.2 Hz, 3H), 2.37 (s, 3H), 4.42-4.49 (m, 1H), 4.80 (d, *J* = 5.4 Hz, 1H), 5.05 (d, *J* = 12.2 Hz, 1H), 5.12 (d, *J* = 12.2 Hz, 1H), 5.89 (d, *J* = 5.4 Hz, 1H), 6.20 (d, *J* = 7.0 Hz, 1H), 7.15-7.18 (m, 4H), 7.20-7.24 (m, 5H), 7.33-7.35 (m, 3H), 7.59 (d, *J* = 8.3 Hz, 2H) ; IR (KBr): 3260, 2349, 1723, 1641, 1344, 1155, 683 cm^{-1}; TOF-HRMS: calcd for $C_{25}H_{27}N_2O_5S$ 467.1635, found 467.1632 ($[M+H]^+$).

G8-2 : 36% yield; mp. 153-154 °C; R_f = 0.3 (petroleum ether / ethyl acetate = 5/2); $[\alpha]_D^{20}$ = +37.6 (*c* 0.02, THF); ^1H NMR (400 MHz, $CDCl_3$) δ: 1.29 (d, *J* = 7.1 Hz, 3H), 2.37 (s, 3H), 4.42-4.49 (m, 1H), 4.80 (d, *J* = 5.4 Hz, 1H), 5.05 (d, *J* = 12.2 Hz, 1H), 5.12 (d, *J* = 12.2 Hz, 1H), 5.88 (d, *J* = 5.4 Hz, 1H), 6.19 (d, *J* = 7.0 Hz, 1H), 7.15-7.18 (m, 4H), 7.20-7.25 (m, 5H), 7.32-7.35 (m, 3H), 7.59 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.0, 21.4, 48.6, 60.3, 67.3, 127.3, 127.5, 128.1, 128.5, 128.6, 128.9, 129.4, 135.0, 136.1, 136.8, 143.4, 168.5, 171.8; IR (KBr): 3244, 1736, 1650, 1346, 1164, 678 cm^{-1}; TOF-HRMS: calcd for $C_{25}H_{27}N_2O_5S$ 467.1635, found 467.1633 ($[M+H]^+$).

Determination of enantiomeric excesses of G1 in the presence of TAMCSA 1c.

To evaluate the accuracy of determination of enantiomeric excess (ee) by ^{1}H NMR spectroscopy, the following nine samples were prepared containing **G1-1** with 85, 65, 45, 25, 0, -25, -45, -65 and -85% *ee*, respectively. And then all the samples were obtained by adding 1 equiv of TAMCSA **1c** to the above solutions with a concentration of 5 mM in $CDCl_3$, respectively. Their ^{1}H NMR spectra were recorded on a 400 MHz spectrometer and their enantiomeric purities were calculated based on the integration of ^{1}H NMR signals of *NH* protons of Ts*NH* group of **G1-1** and **G1-2**.

Determination of the stoichiometry of (±)-**G1 with TAMCSA 1c (Job plots)**.[3]

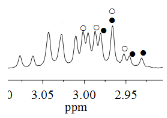
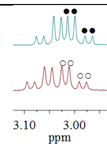
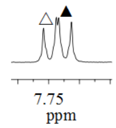
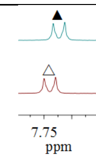
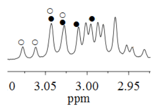
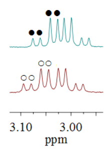
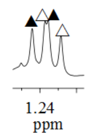
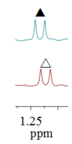
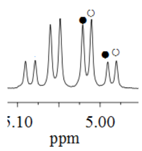
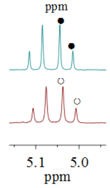
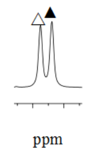
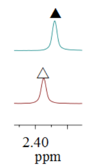
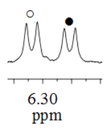
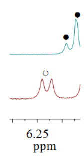
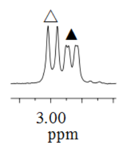
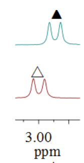
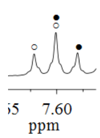
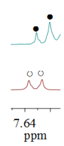
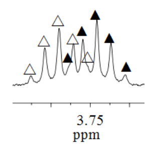
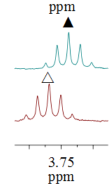
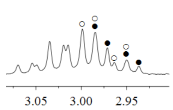
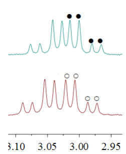
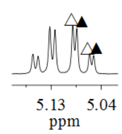
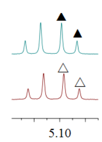
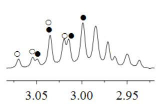
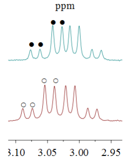
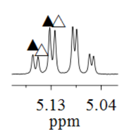
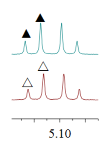
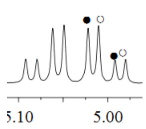
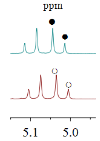
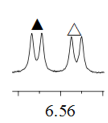
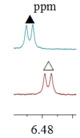
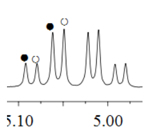
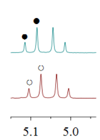
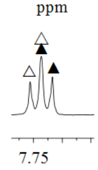
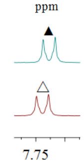
The samples of dipeptide derivative (±)-**G1** with TAMCSA **1c** were dissolved in $CDCl_3$ (0.5 mL) with a concentration of 10 mM, respectively. The solutions were distributed among the nine NMR tubes with the molar fractions X of (±)-**G1** from 0.1 to 0.9. The ^{1}H NMR spectra of all the samples were recorded on a 400 MHz spectrometer. The Job plots of **G1-1** and **G1-2** with TAMCSA **1c** exhibited a maximum value ($X*\Delta\delta$ = 0.042 ppm) at molar fraction of X = 0.5. The results indicate that TAMCSA **1c** can form a 1:1 complex with (±)-**G1**.

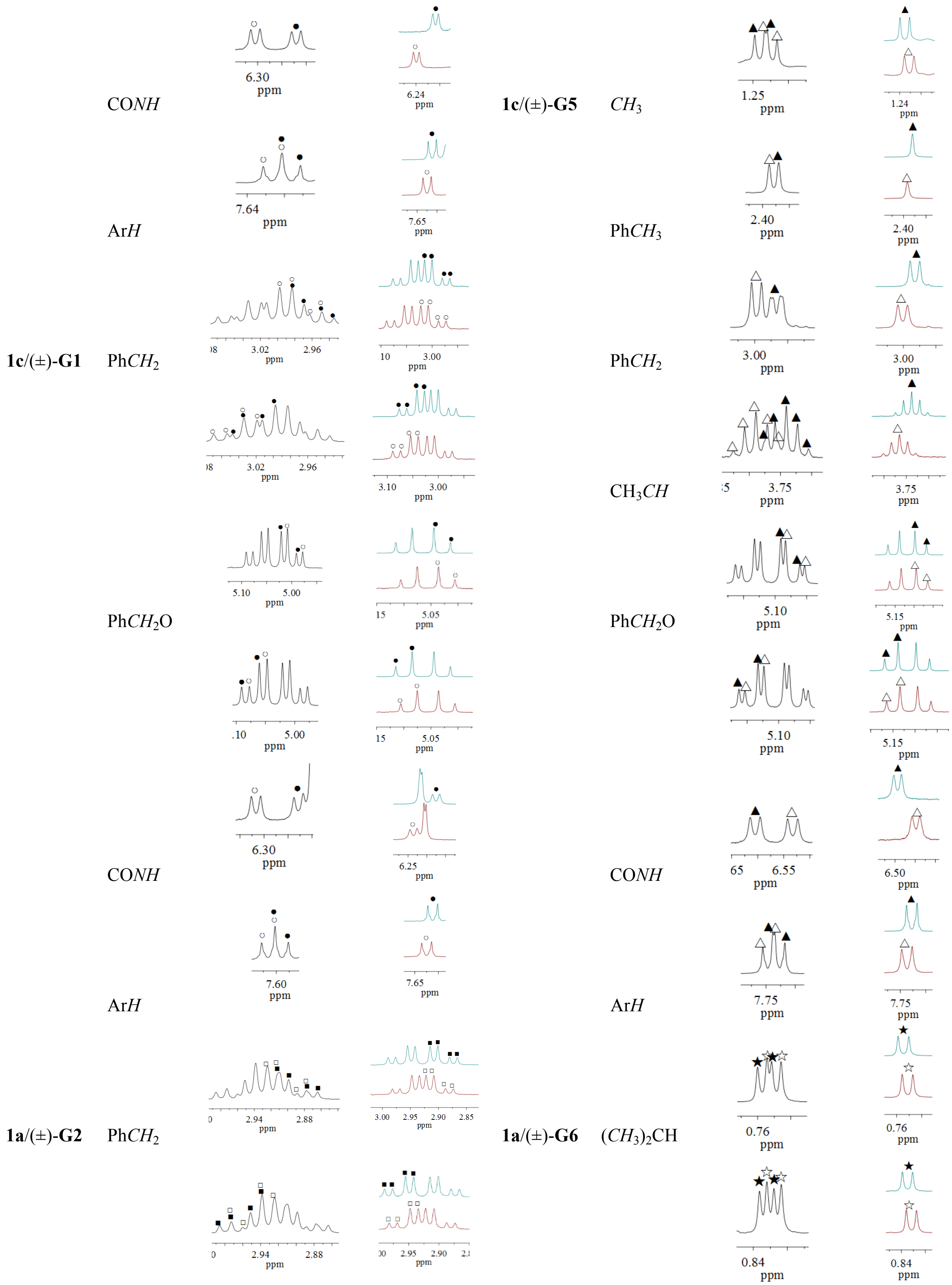
Determination of the association constants of G5-1 and **G5-2 with TAMCSA 1a.**

To determine the association constants, the samples of **G5-1** and **G5-2** with TAMCSA **1a** were prepared with a constant concentration (2 mM) of TAMCSA **1a** and varying concentrations of **G5-1** or **G5-2** with 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 mM in $CDCl_3$, respectively and their ^{1}H NMR spectra were measured. Based on the nonlinear curve-fitting method, the association constants were obtained for their complexes.

Partial ^{1}H NMR spectra of discriminations of enantiomers of (±)-G1-G8.

Table S2. Partial ^{1}H NMR spectra of (±)-**G1-G8** (10×10^{-3} M) in the presence of TAMCSAs **1a-1c** (10×10^{-3} M) by ^{1}H NMR spectroscopy in $CDCl_3$ at room temperature, respectively.

TAMCSA /Guest	Proton	Spectra[b,d]	Spectra[c,d]	TAMCSA /Guest	Proton	Spectra[b,d]	Spectra[c,d]
1a/(±)-**G1**	Ph*CH*$_2$				Ar*H*		
				**1b**/(±)-**G5**	*CH*$_3$		
	Ph*CH*$_2$O				Ph*CH*$_3$		
	CO*NH*				Ph*CH*$_2$		
	Ar*H*				CH$_3$*CH*		
1b/(±)-**G1**	Ph*CH*$_2$				Ph*CH*$_2$O		
							
	Ph*CH*$_2$O				CO*NH*		
					Ar*H*		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CONH
ArH
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PhCH2
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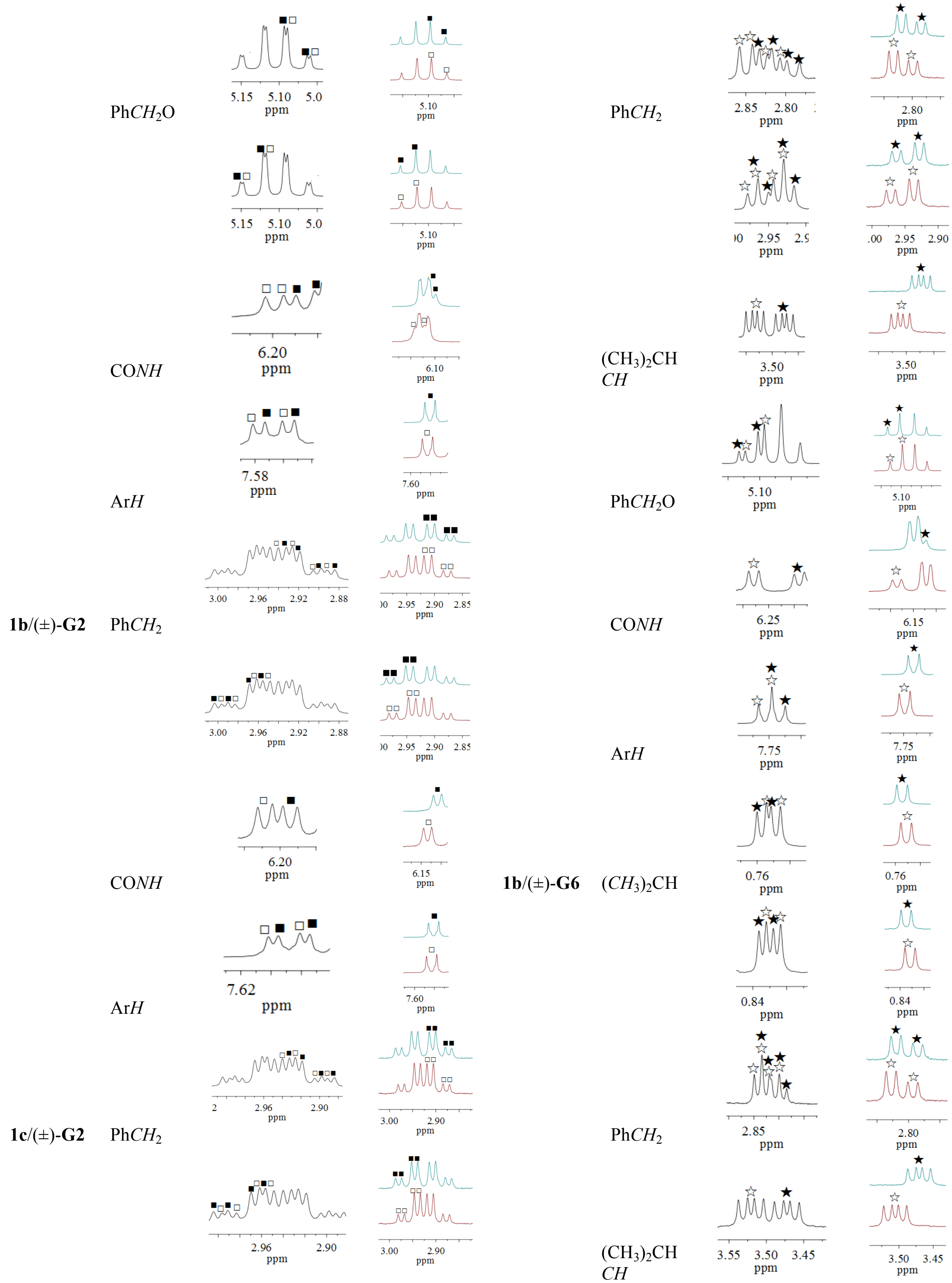
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ppm
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ppm
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ppm
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7.60
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2 2.96 2.90
ppm
3.00 2.90
ppm
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ppm
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ppm
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.00 2.95 2.90
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CONH
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ppm
ArH
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ppm
(CH3)2CH
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ppm
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ppm
3.55 3.50 3.45
ppm
3.50 3.45
ppm


1a/(±)-G3
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ArH
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PhCH2
PhCH2O
PhCH
ArH
1b/(±)-G3
PhCH3
PhCH2
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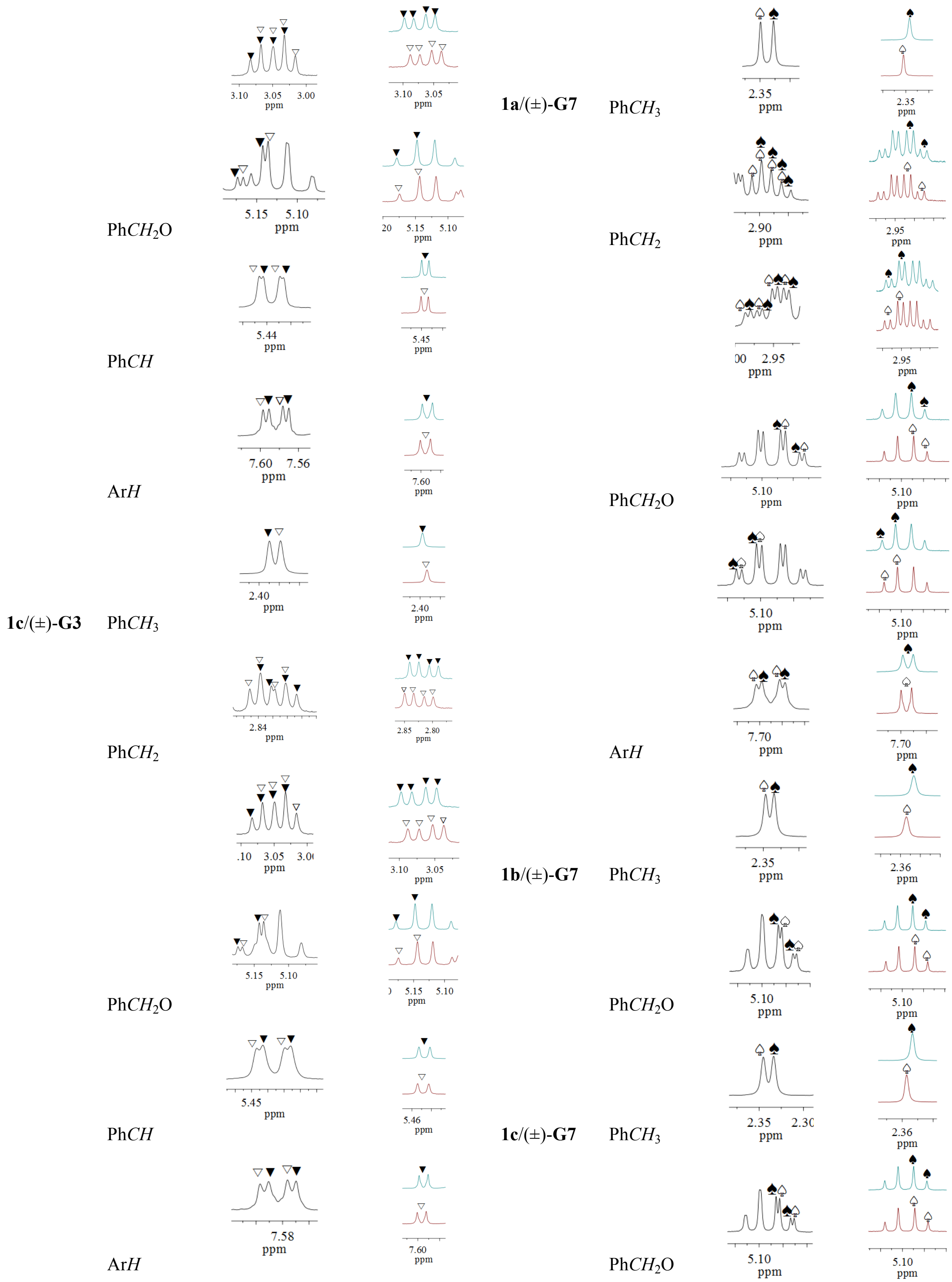
CONH
ArH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PhCH2O
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PhCH2O
1c/(±)-G7
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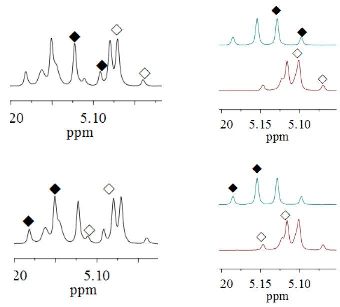
PhCH2O
ppm

1a/(±)-**G4** PhCH_2O



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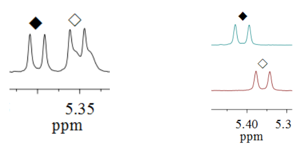

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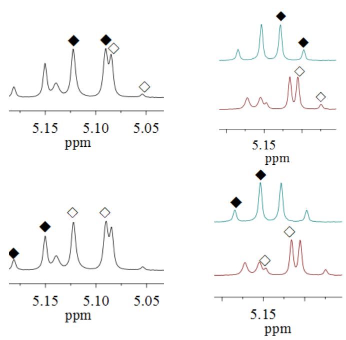

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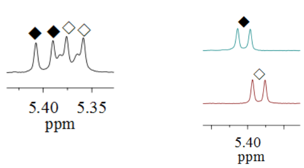

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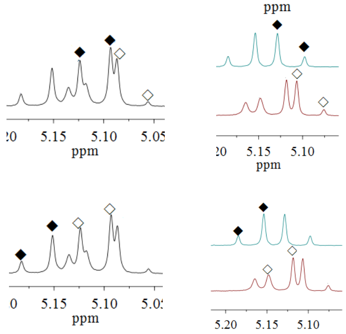

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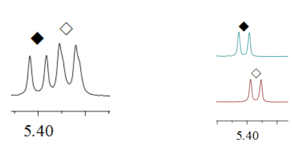

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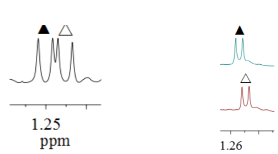

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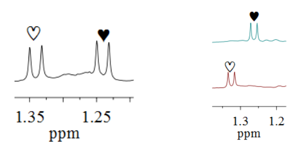

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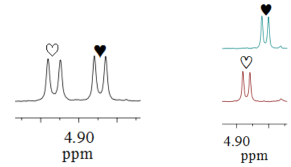

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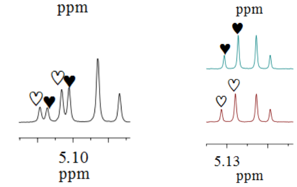

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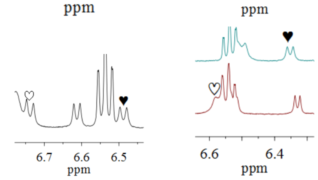

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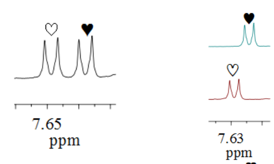

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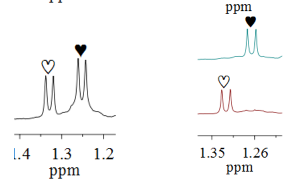

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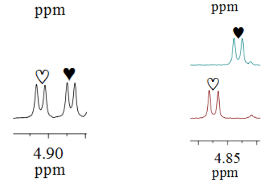

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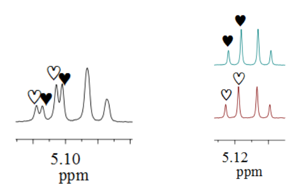

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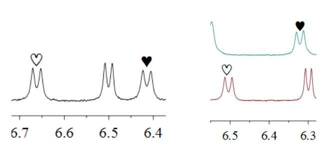

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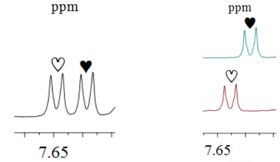
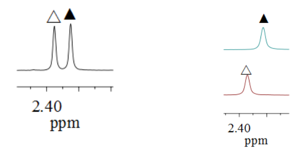
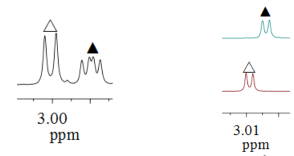
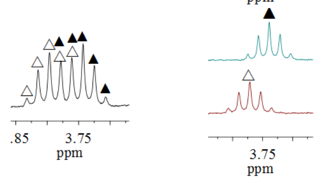
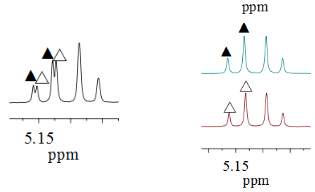
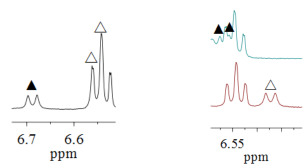
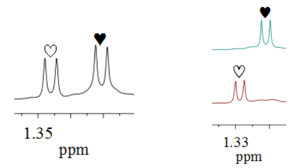
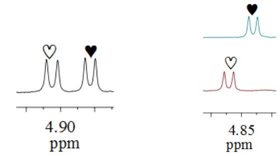
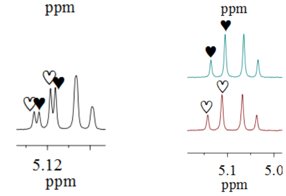
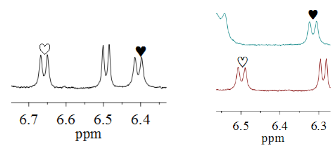
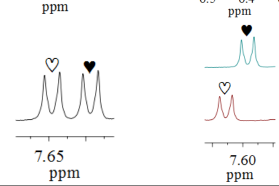


	PhCH_3		
	PhCH_2		
	CH_3CH		
	PhCH_2O		
	CONH		
1c/(±)-**G8**	CH_3		
	PhCH		
	PhCH_2O		
	CONH		
	ArH		

[a] $\Delta\Delta\delta = \Delta\delta_1 - \Delta\delta_2$; $\Delta\delta_1 = \delta_1 - \delta_{free}$; $\Delta\delta_2 = \delta_2 - \delta_{free}$, the numbers "1 and 2" present a pair of enantiomers of dipeptide derivatives, respectively.

[b] Partial ^{1}H NMR spectra of the corresponding protons of (±)-**G1-G8** (10×10^{-3} M), H:G = 1:1.

[c] Overlaid ^{1}H NMR spectra of the corresponding protons of one of the two enantiomers of (±)-**G1-G8** (10×10^{-3} M).

[d] The following different signs stand for the corresponding stereoisomers: **G1-1** (○), **G1-2** (●); **G2-1** (□), **G2-2** (■); **G3-1** (▽), **G3-2** (▼); **G4-1** (◇), **G4-2** (◆); **G5-1** (△), **G5-2** (▲); **G6-1** (☆), **G6-2** (★); **G7-1** (♤), **G7-2** (♠); **G8-1** (♡), **G8-2** (♥).

^{1}H NMR, ^{13}C NMR, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC and HRMS Spectra

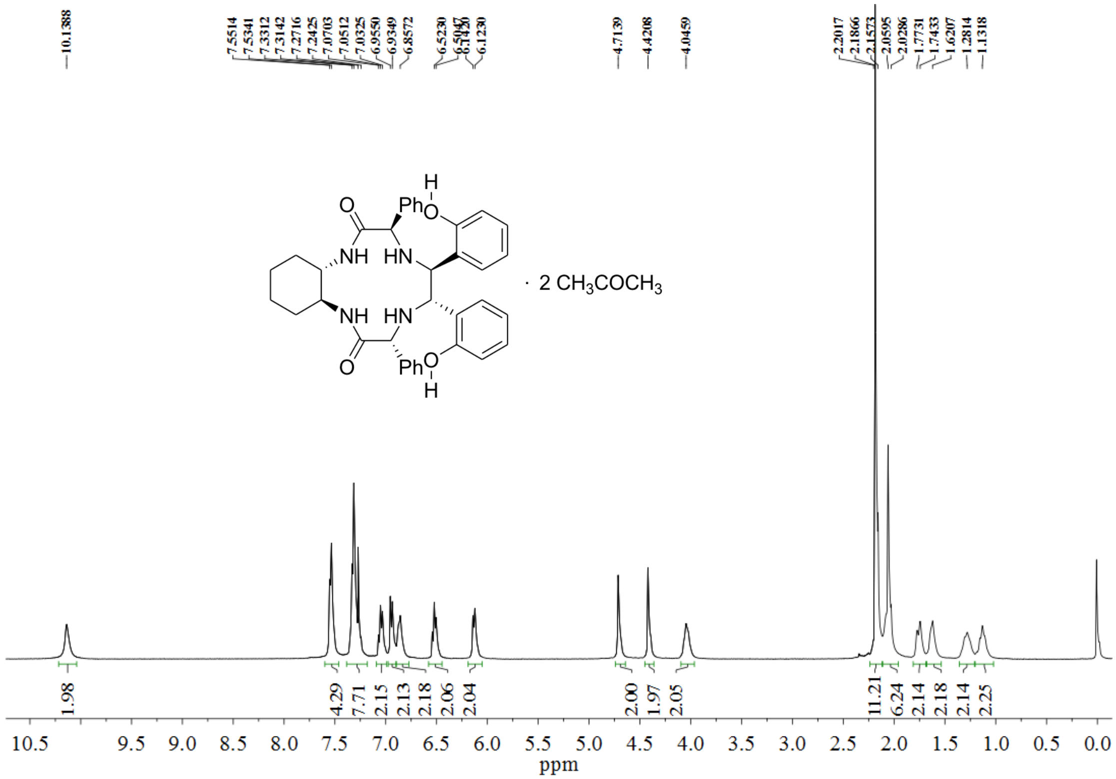


Figure S2. ^{1}H NMR spectrum of TAMCSA **1a**·2·CH_3COCH_3 in $CDCl_3$ (400 MHz).

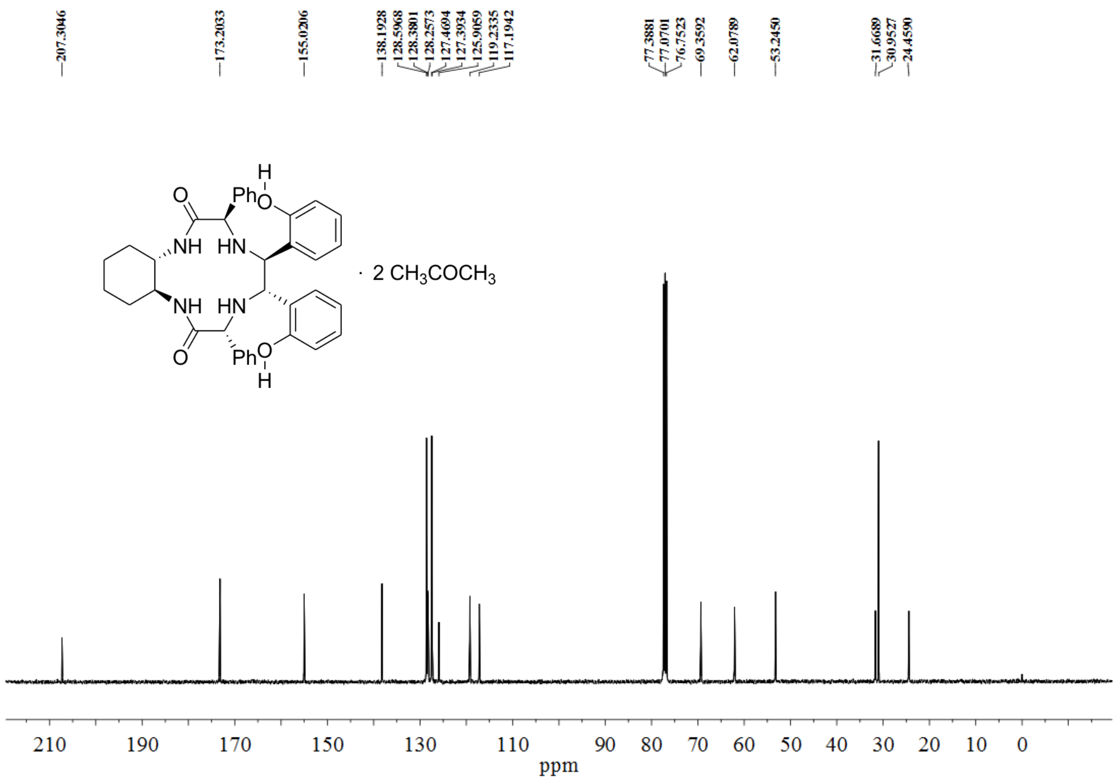


Figure S3. ^{13}C NMR spectrum of TAMCSA **1a**·2·CH_3COCH_3 in $CDCl_3$ (100 MHz).

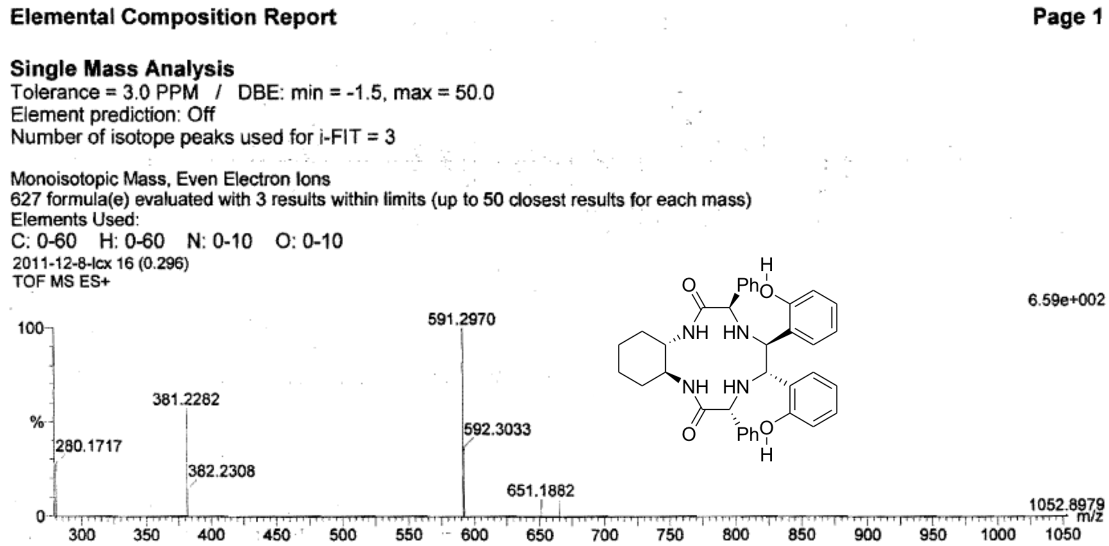


Figure S4. HRMS spectrum of TAMCSA **1a**.

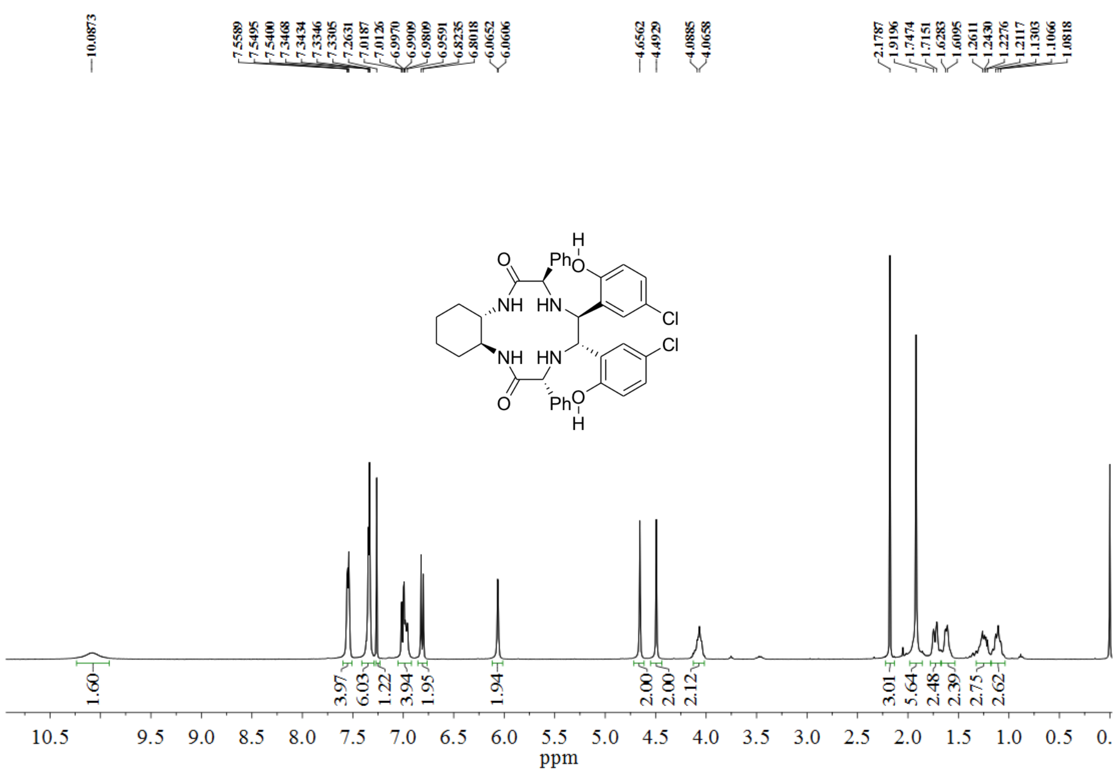


Figure S5. ^{1}H NMR spectrum of TAMCSA **1b** in $CDCl_3$ (400 MHz).

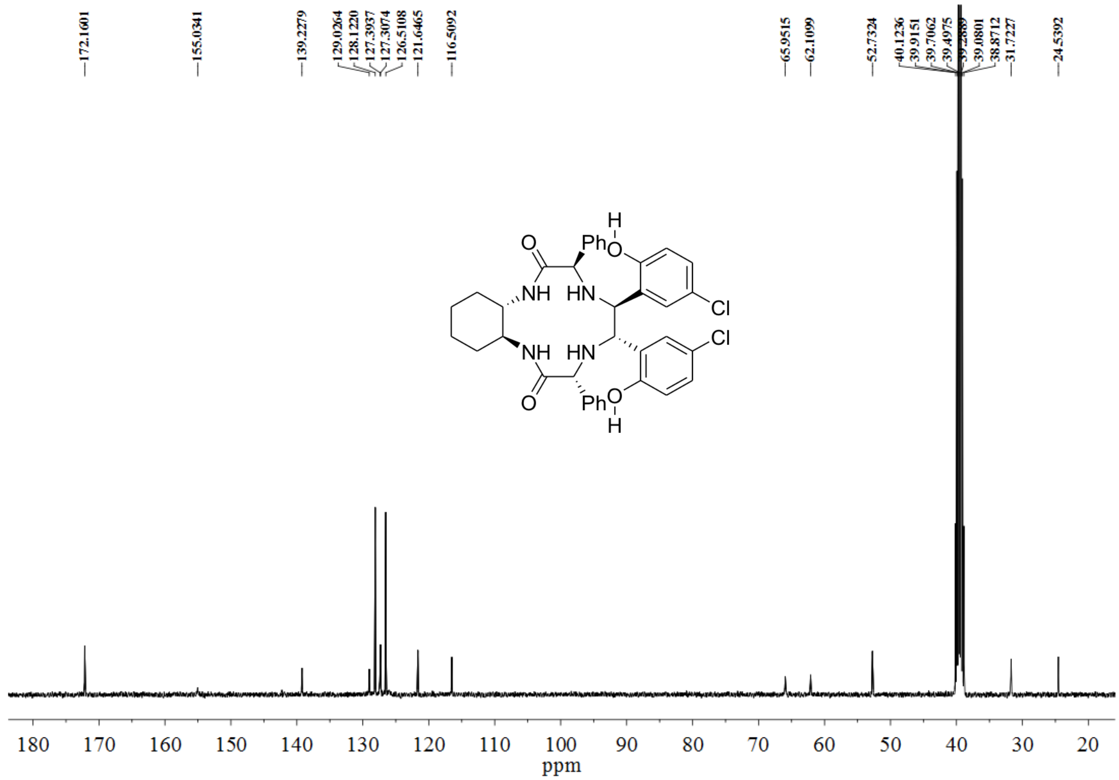


Figure S6. ^{13}C NMR spectrum of TAMCSA **1b** in DMSO-d_6 (100 MHz).

Elemental Composition Report **Page 1**

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Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
260 formula(e) evaluated with 2 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
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LCX-20121022 9 (0.154)
TOF MS ES+

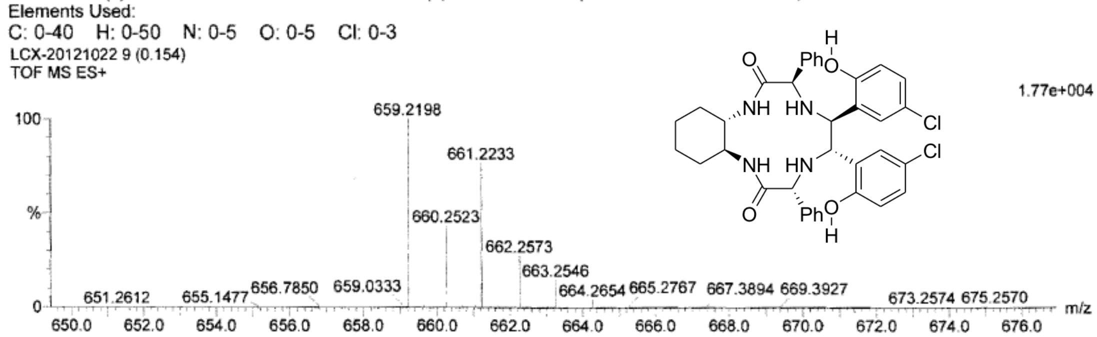


Figure S7. HRMS spectrum of TAMCSA **1b**.

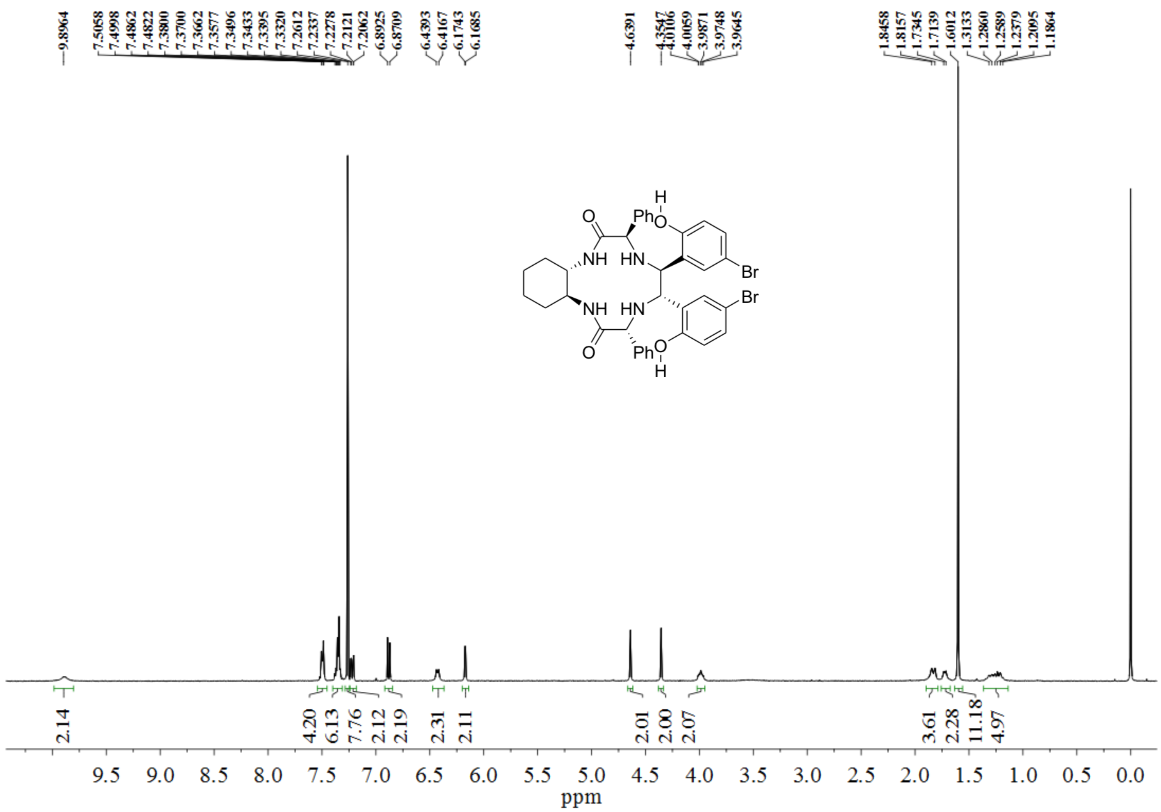


Figure S8. ^{1}H NMR spectrum of TAMCSA **1c** in $CDCl_3$ (400 MHz).

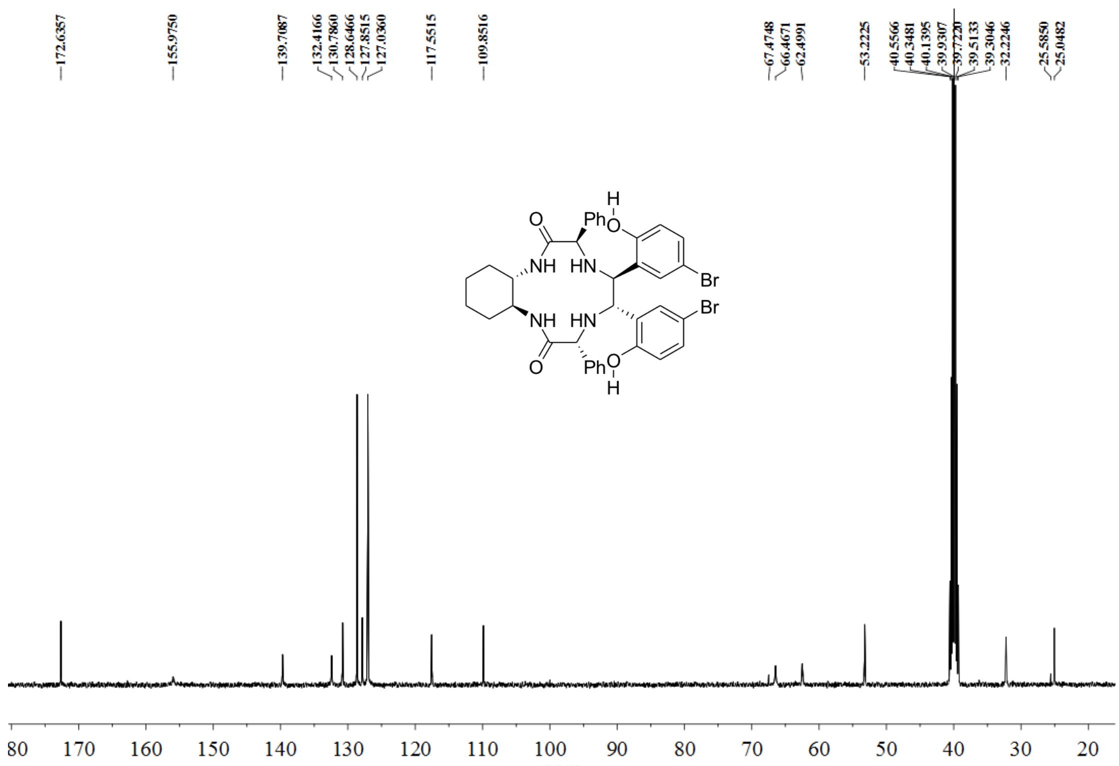


Figure S9. ^{13}C NMR spectrum of TAMCSA **1c** in DMSO-d_6 (100 MHz).

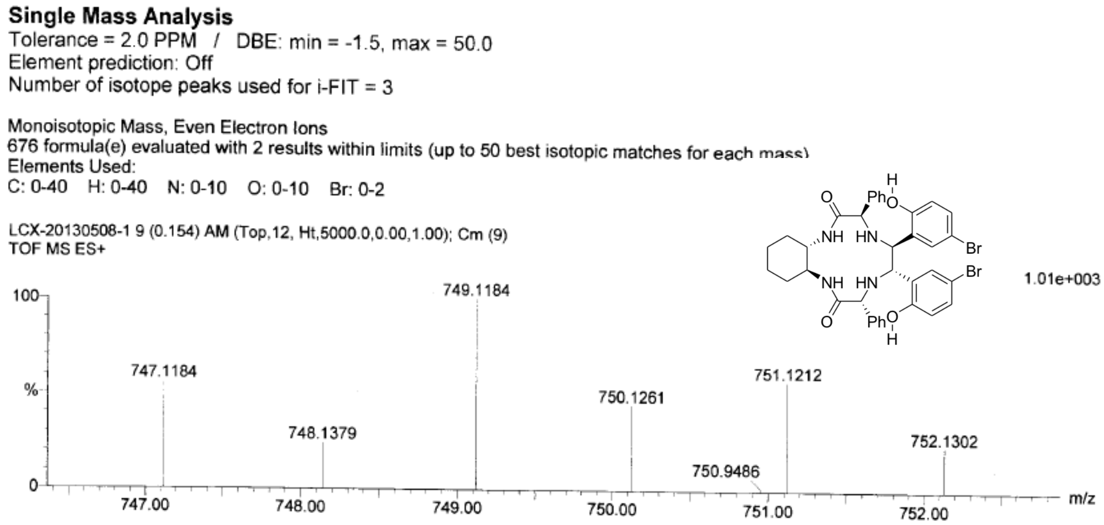


Figure S10. HRMS specutrum of TAMCSA **1c**.

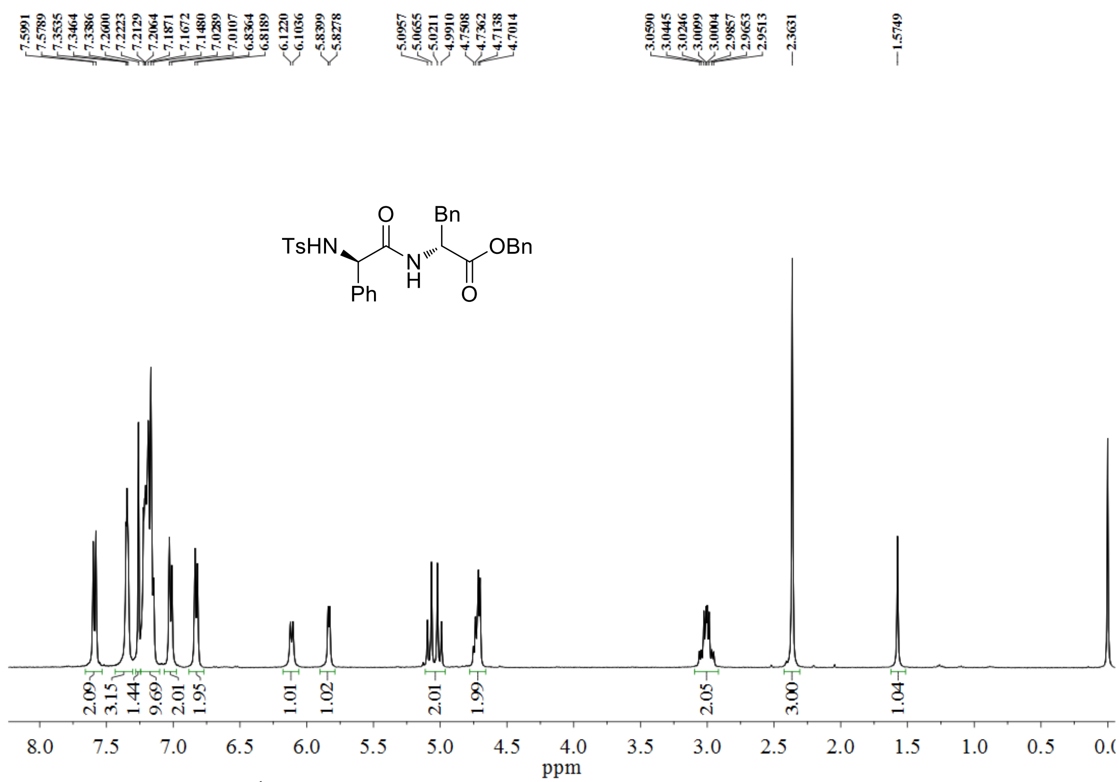


Figure S11. ^{1}H NMR spectrum of dipeptide derivative **G1-1** in $CDCl_3$ (400 MHz).

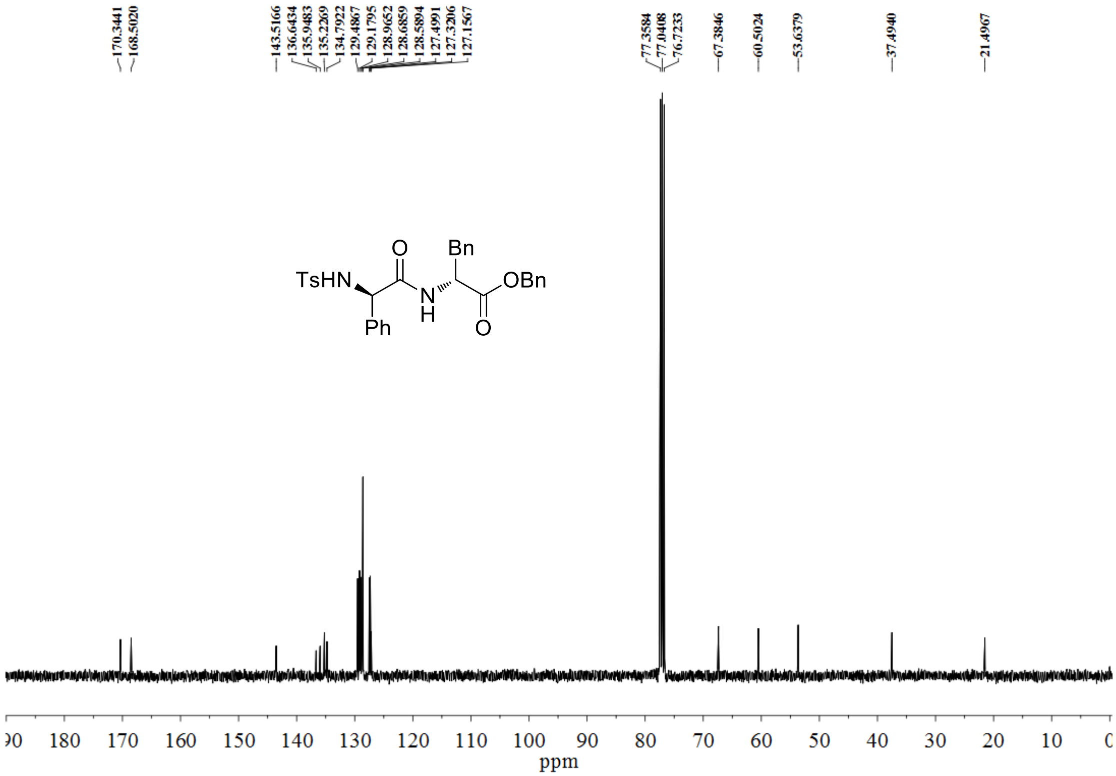
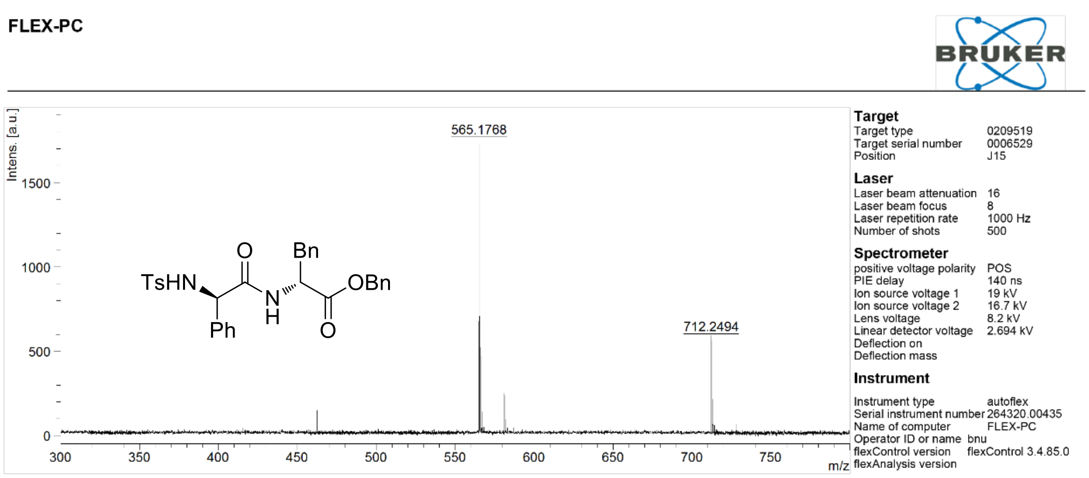


Figure S12. ^{13}C NMR spectrum of dipeptide derivative **G1-1** in $CDCl_3$ (100 MHz).



SmartFormula

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Performed by | Date / Sign | Viewed by | Date / Sign

printed: 4/29/2015 9:51:58 AM

Figure S13. HRMS spectrum of dipeptide derivative **G1-1**.

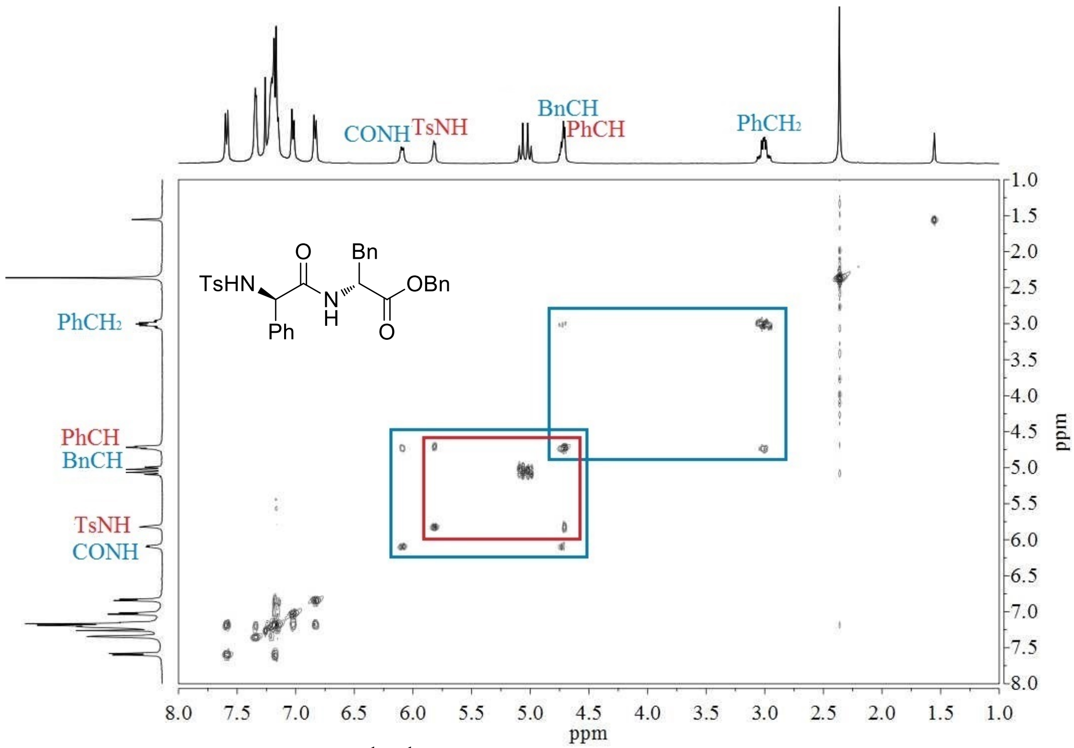


Figure S14. ^{1}H-^{1}H COSY of dipeptide derivative **G1-1**.

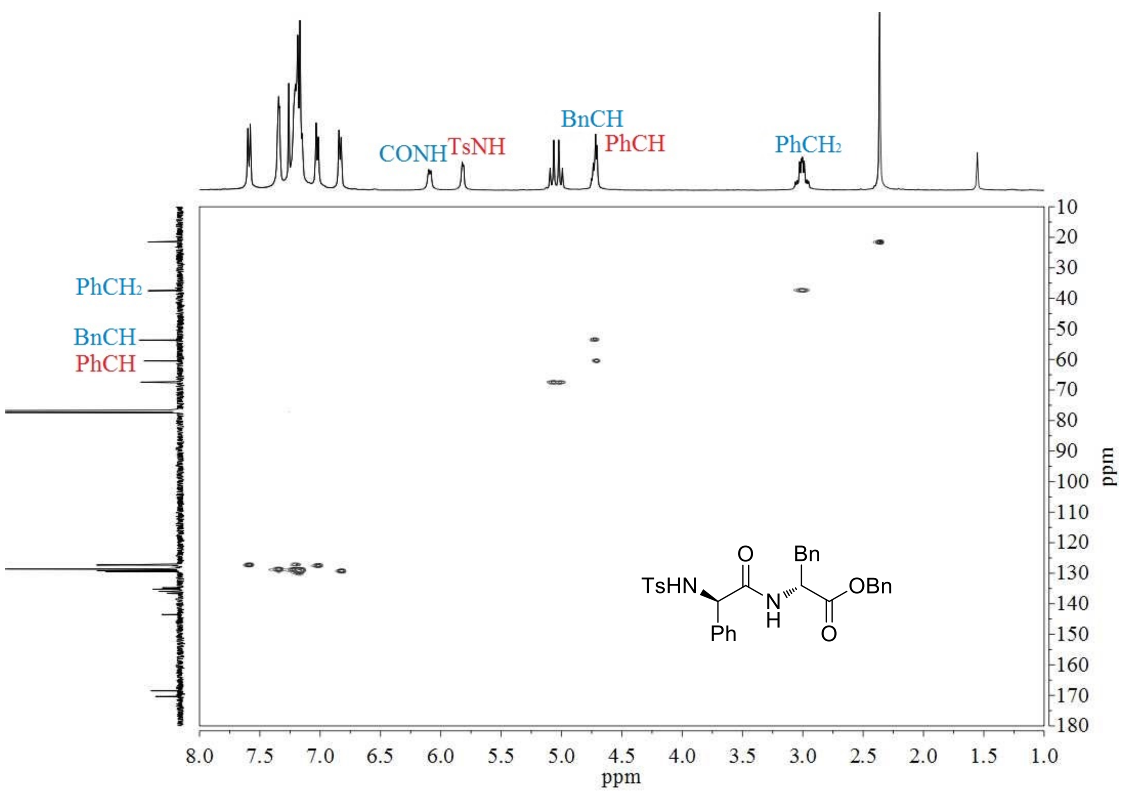


Figure S15. ^{1}H-^{13}C HSQC of dipeptide derivative **G1-1**.

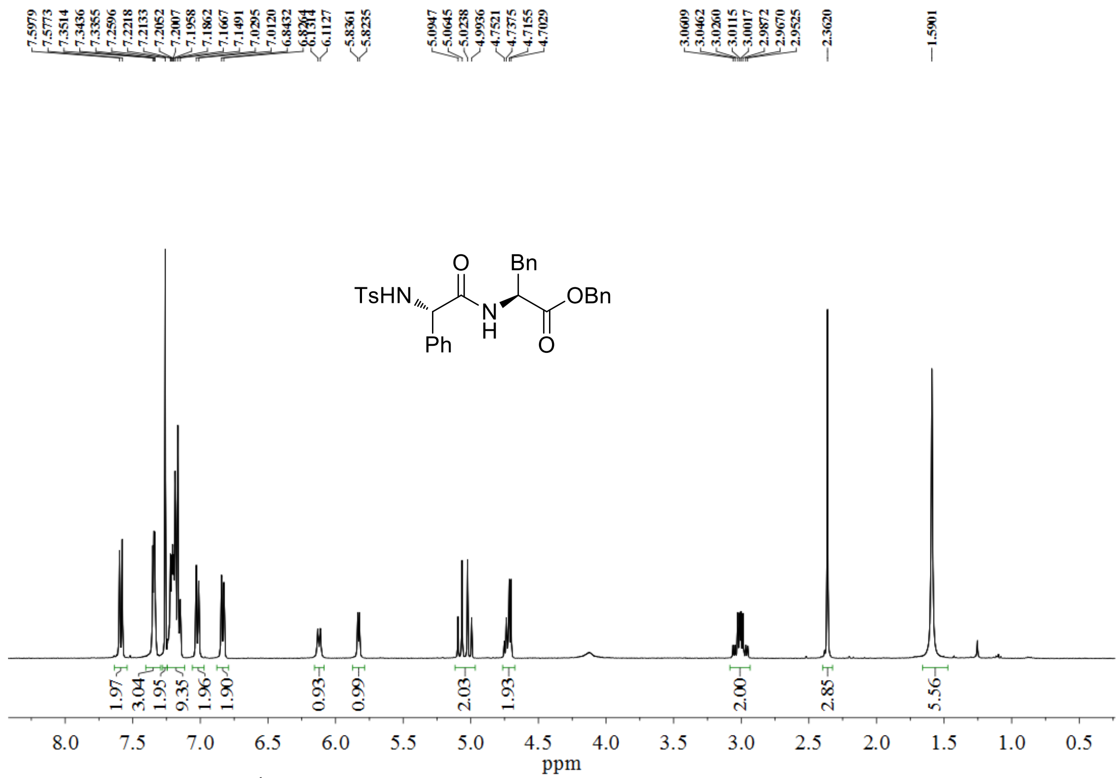


Figure S16. ^{1}H NMR spectrum of dipeptide derivative **G1-2** in $CDCl_3$ (400 MHz).

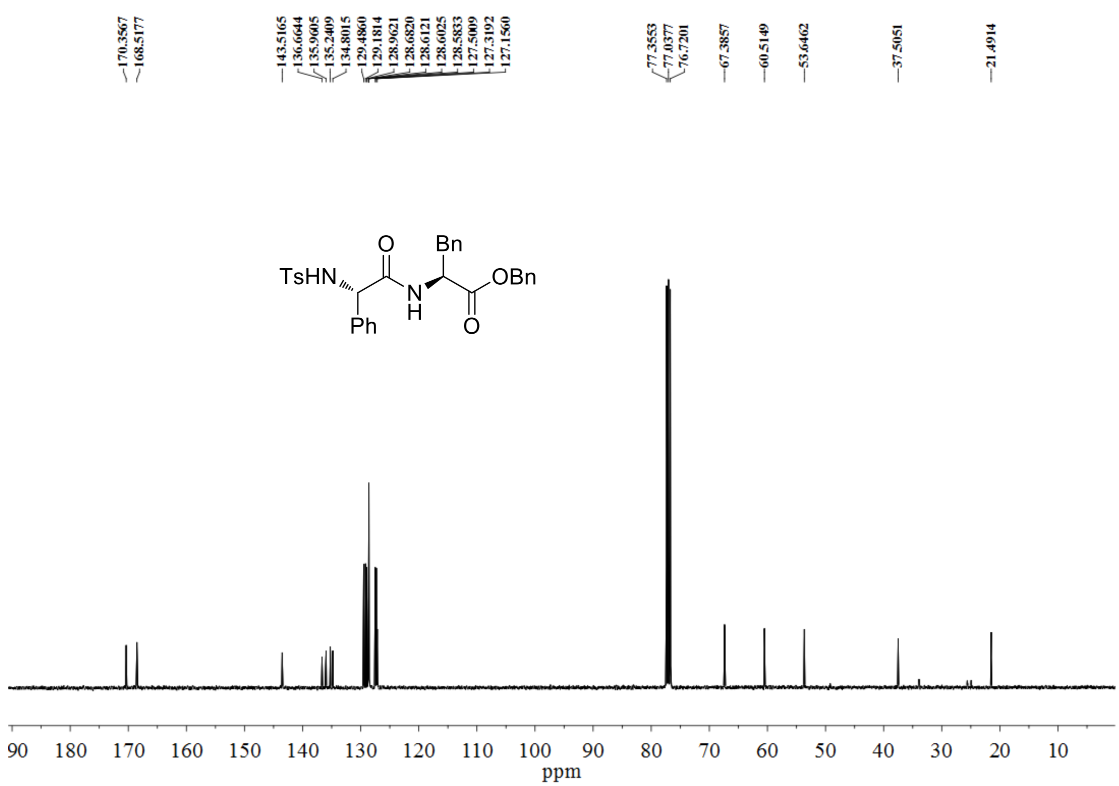


Figure S17. ^{13}C NMR spectrum of dipeptide derivative **G1-2** in $CDCl_3$ (100 MHz).

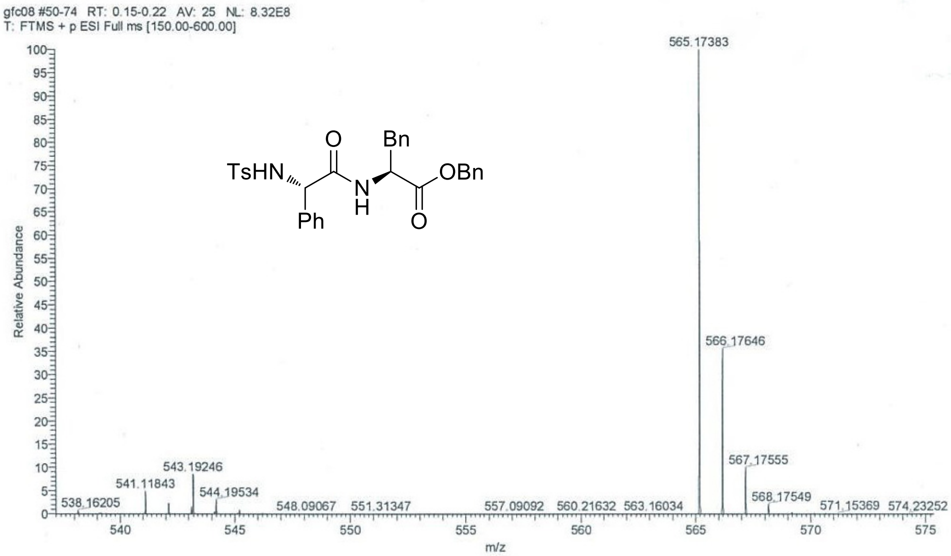


Figure S18. HRMS spectrum of dipeptide derivative **G1-2**.

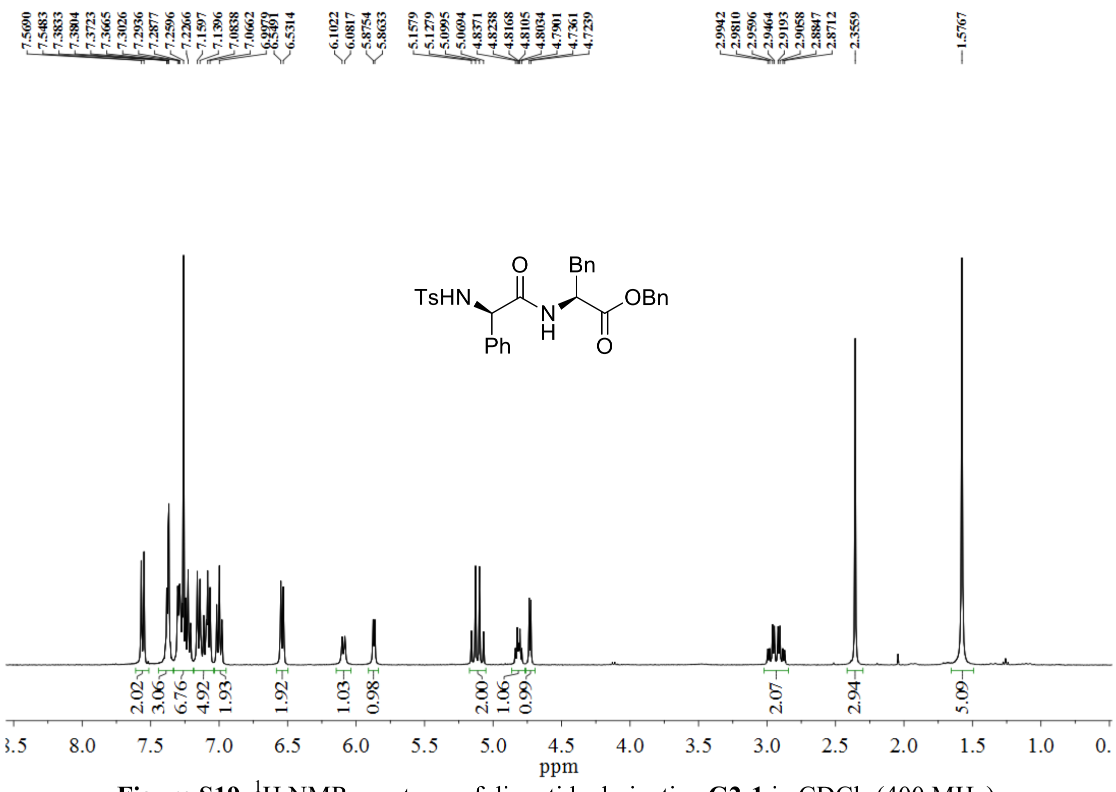


Figure S19. ^{1}H NMR spectrum of dipeptide derivative **G2-1** in $CDCl_3$ (400 MHz).

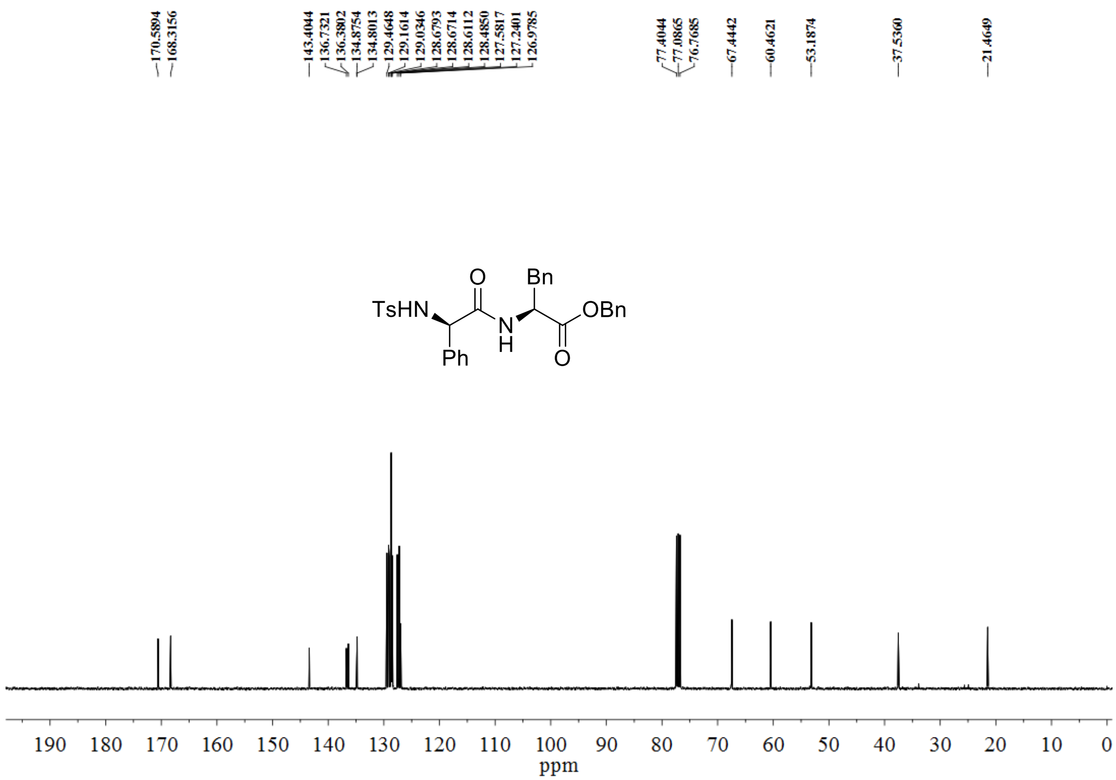


Figure S20. ^{13}C NMR spectrum of dipeptide derivative **G2-1** in $CDCl_3$ (100 MHz).

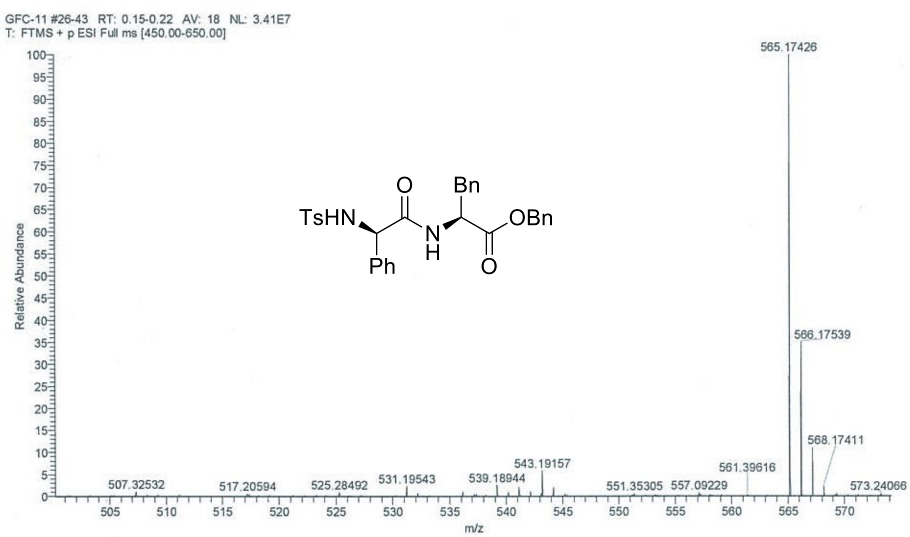


Figure S21. HRMS spectrum of dipeptide derivative **G2-1**.

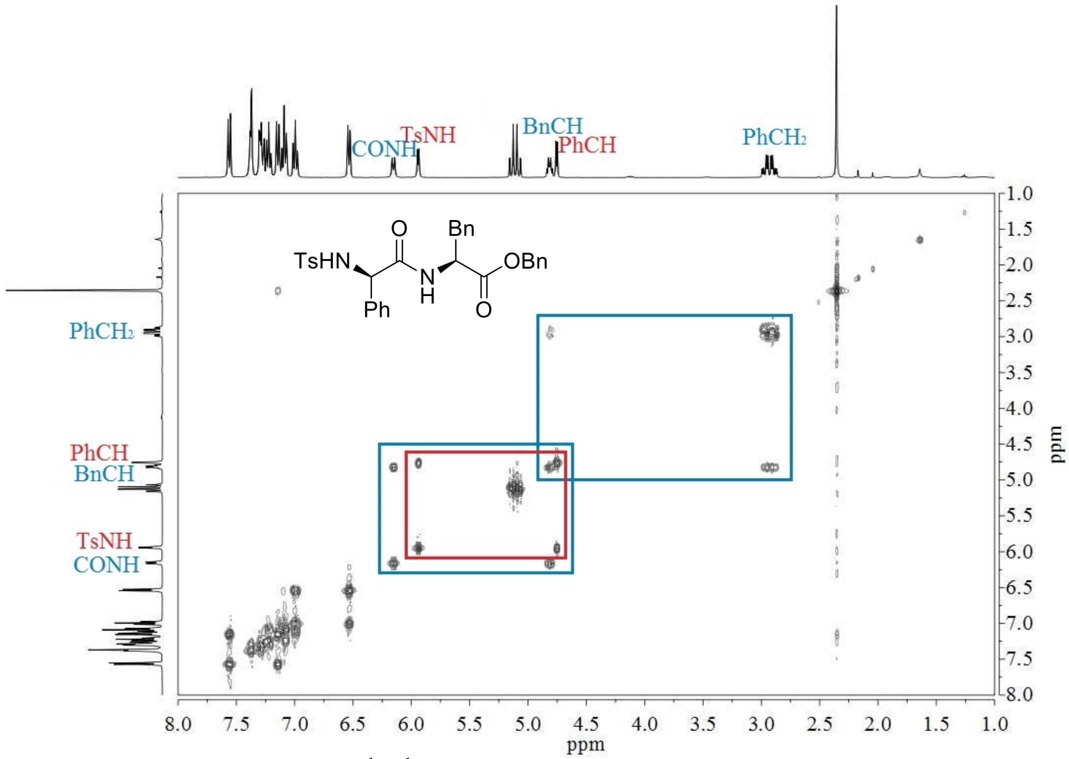


Figure S22. ^{1}H-^{1}H COSY of dipeptide derivative **G2-1**.

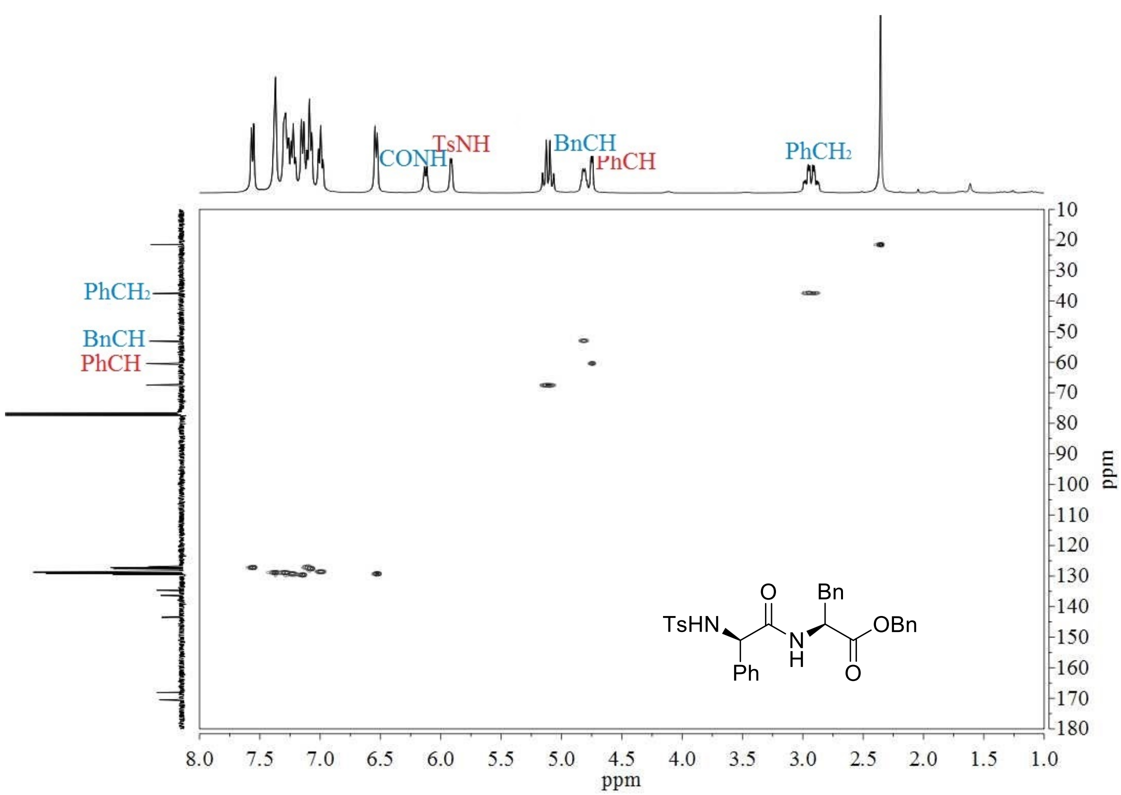


Figure S23. ^{1}H-^{13}C HSQC of dipeptide derivative **G2-1**.

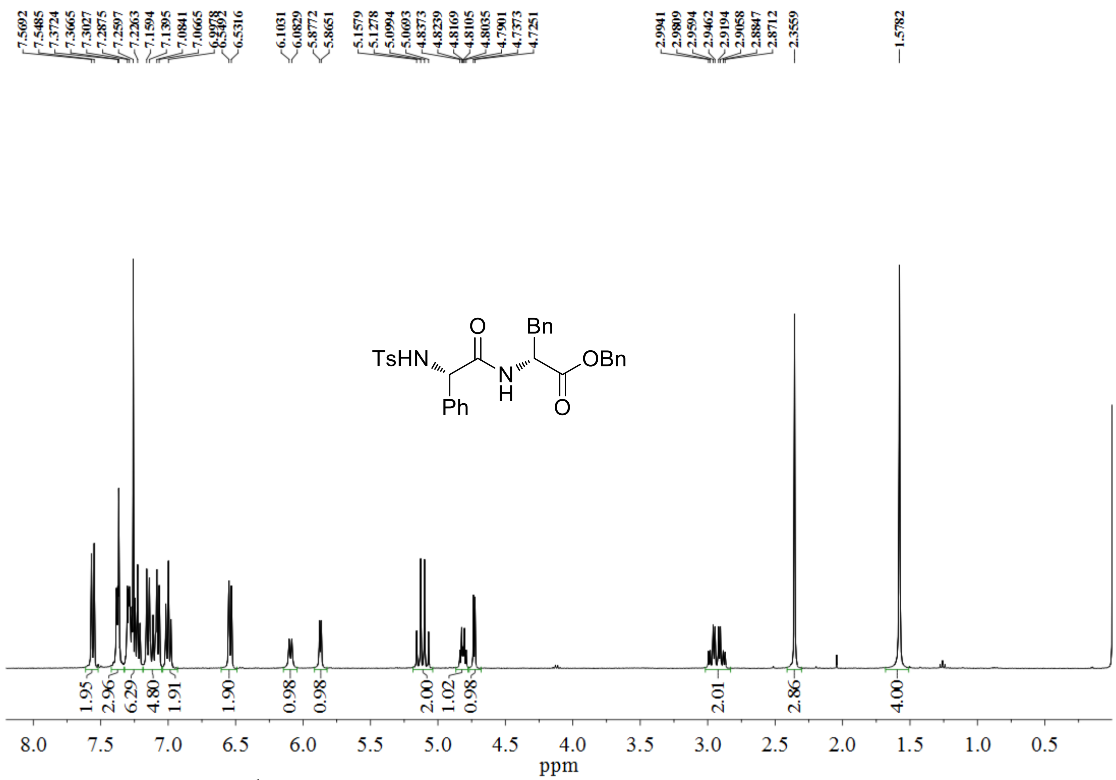


Figure S24. ^{1}H NMR spectrum of dipeptide derivative **G2-2** in $CDCl_3$ (400 MHz).

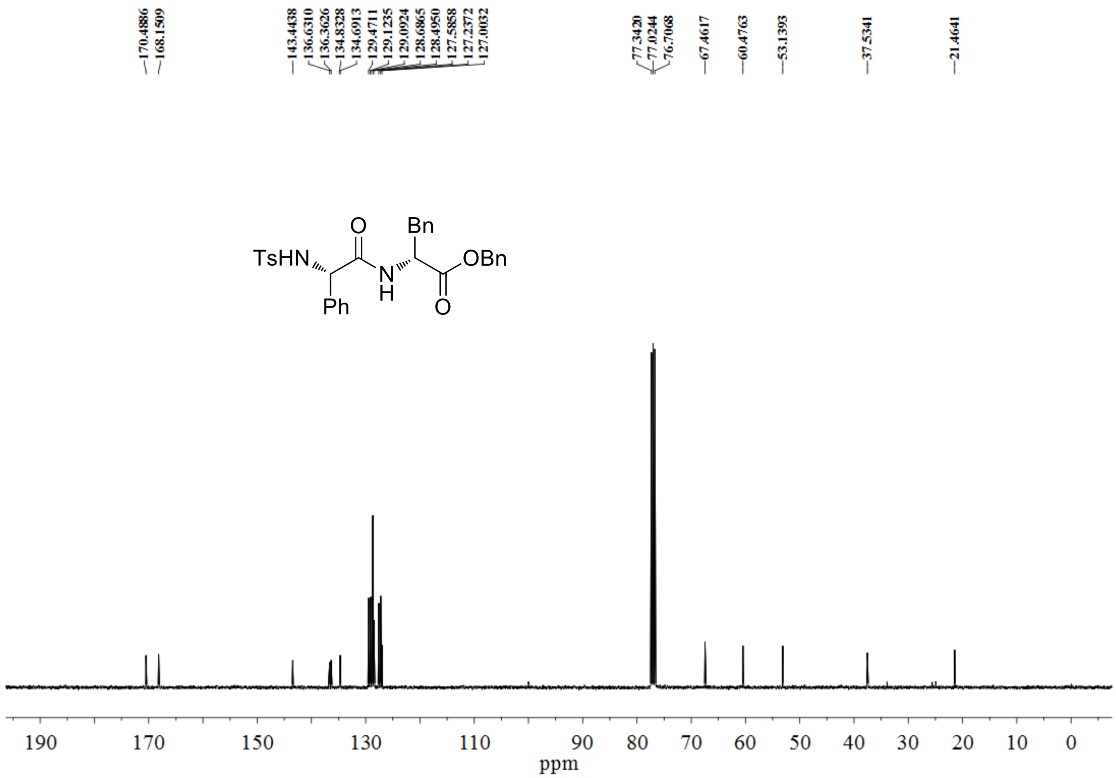


Figure S25. ^{13}C NMR spectrum of dipeptide derivative **G2-2** in $CDCl_3$ (100 MHz).

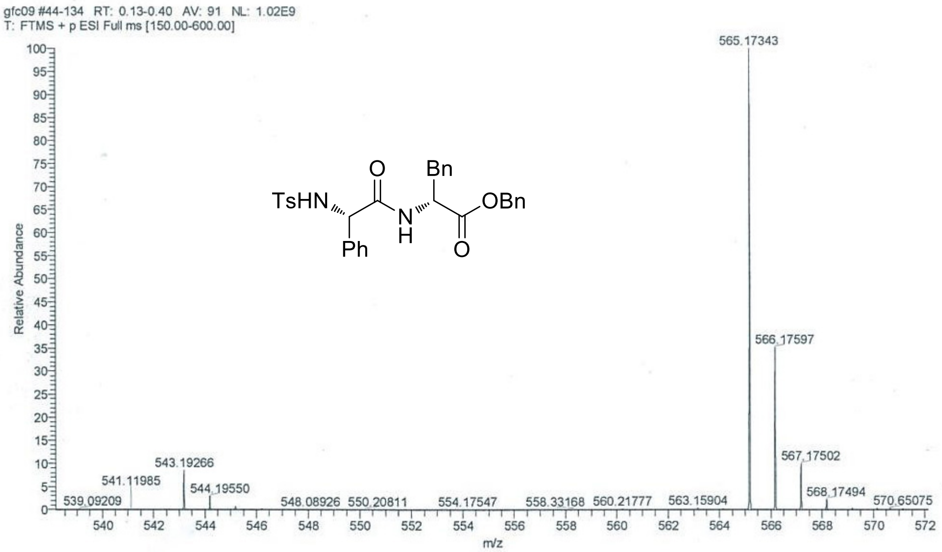


Figure S26. HRMS spectrum of dipeptide derivative **G2-2**.

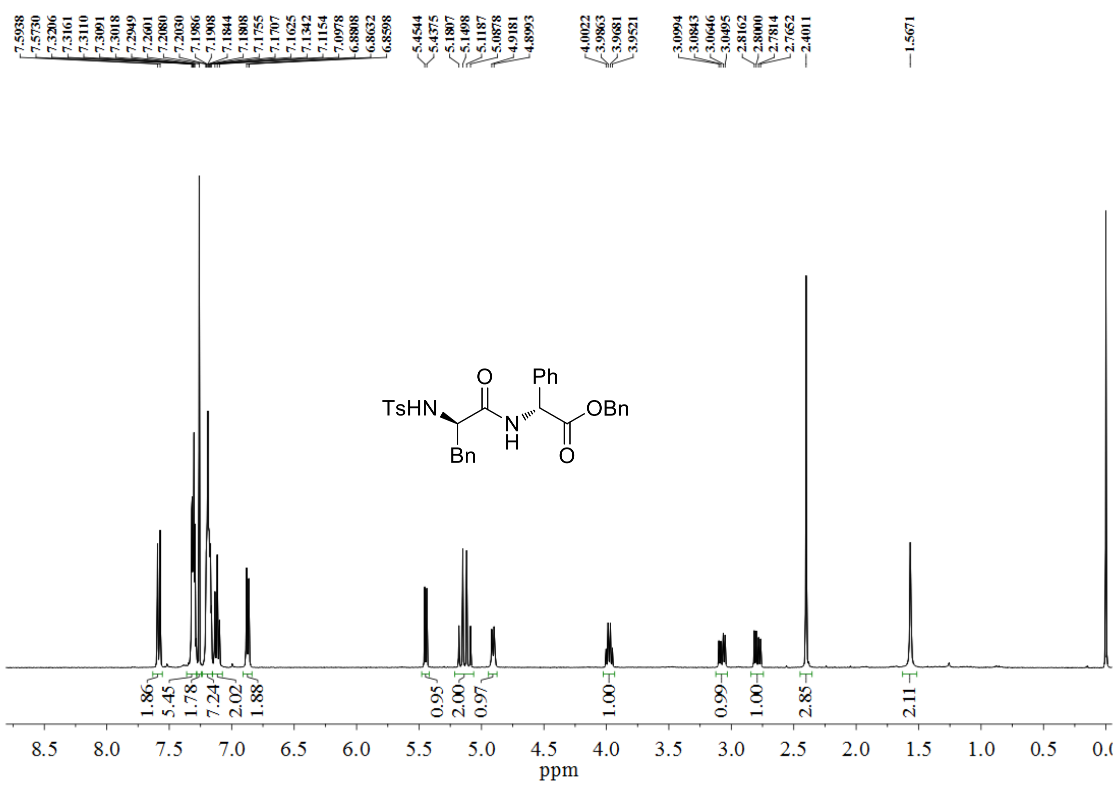


Figure S27. ^{1}H NMR spectrum of dipeptide derivative **G3-1** in $CDCl_3$ (400 MHz).

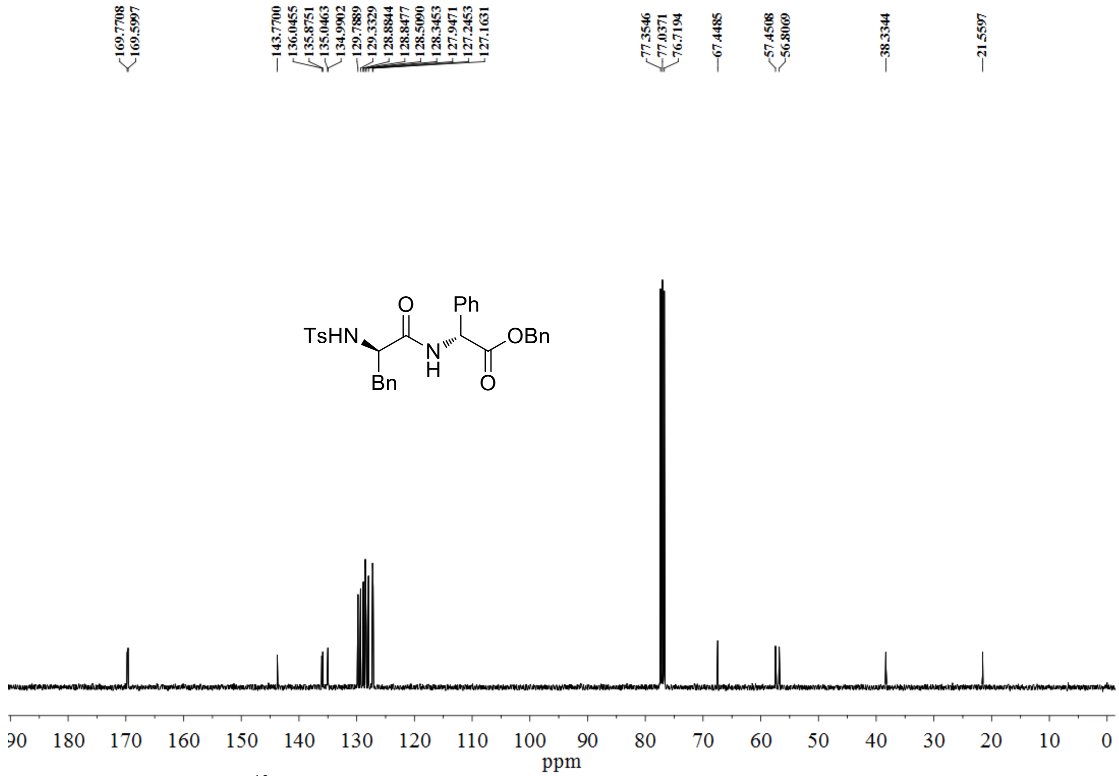


Figure S28. ^{13}C NMR spectrum of dipeptide derivative **G3-1** in $CDCl_3$ (100 MHz).

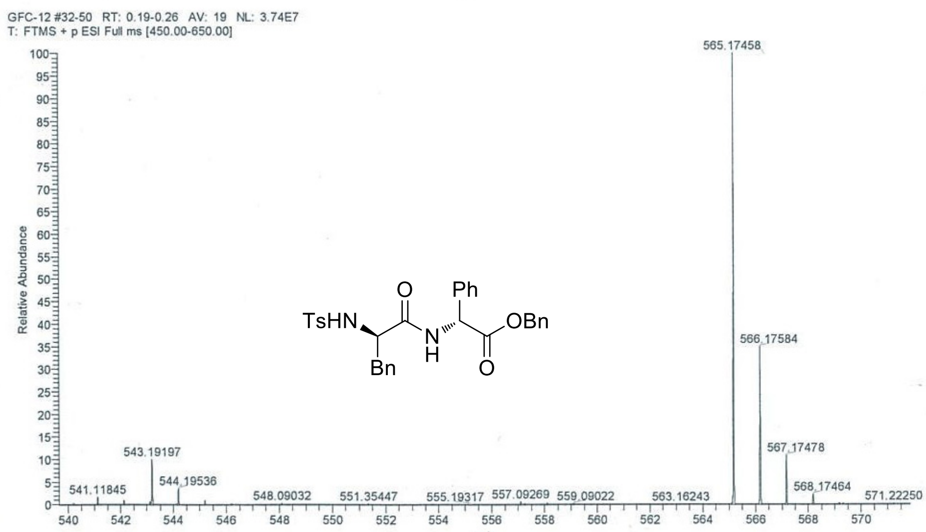


Figure S29. HRMS spectrum of dipeptide derivative **G3-1**.

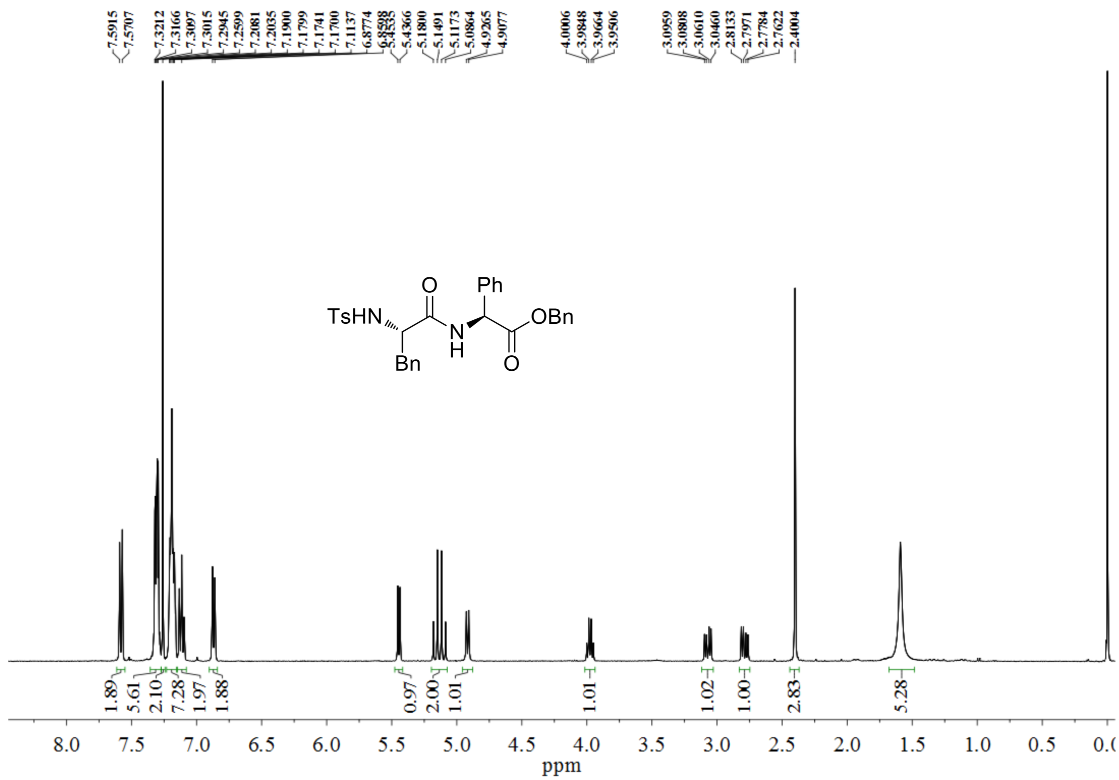


Figure S30. ^{1}H NMR spectrum of dipeptide derivative **G3-2** in $CDCl_3$ (400 MHz).

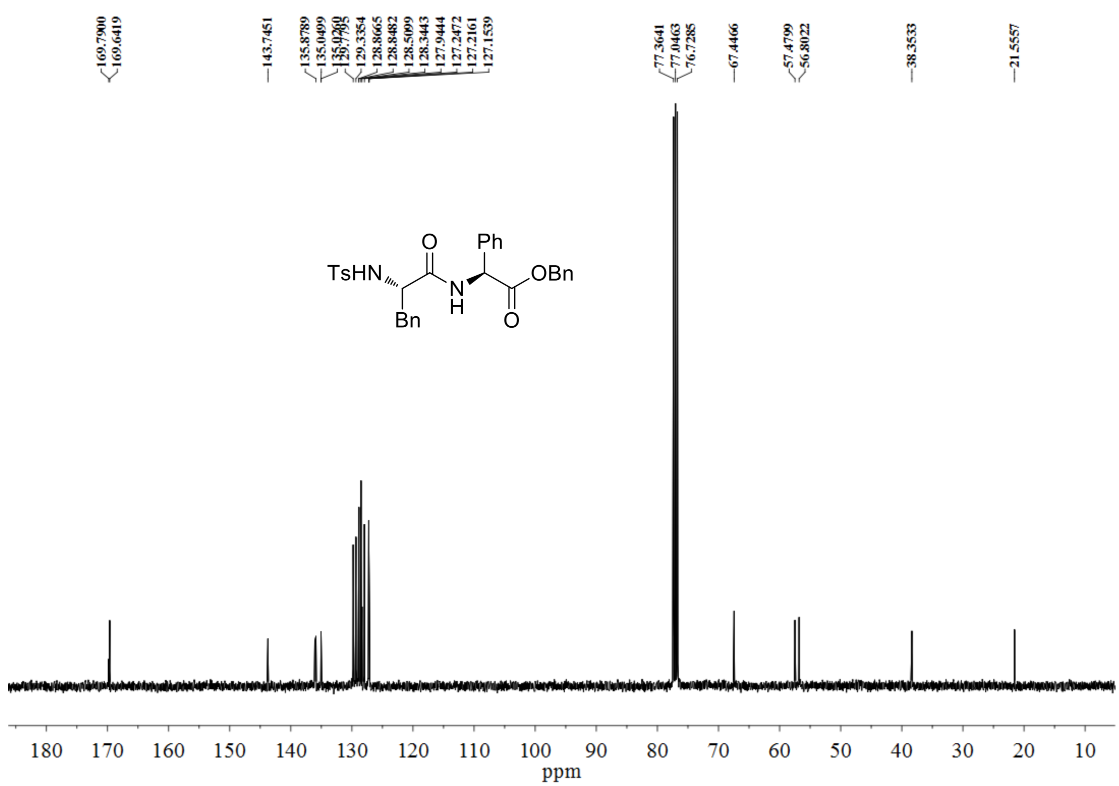


Figure S31. ^{13}C NMR spectrum of dipeptide derivative **G3-2** in $CDCl_3$ (100 MHz).

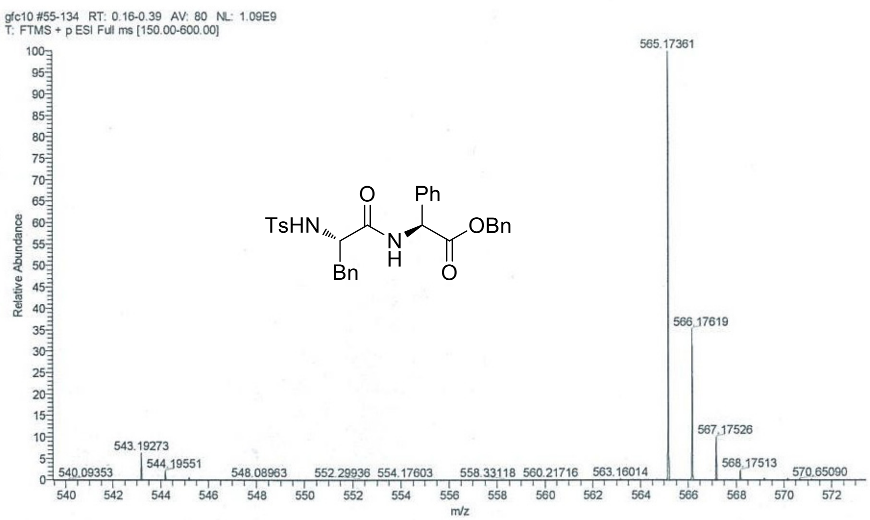


Figure S32. HRMS spectrum of dipeptide derivative **G3-2**.

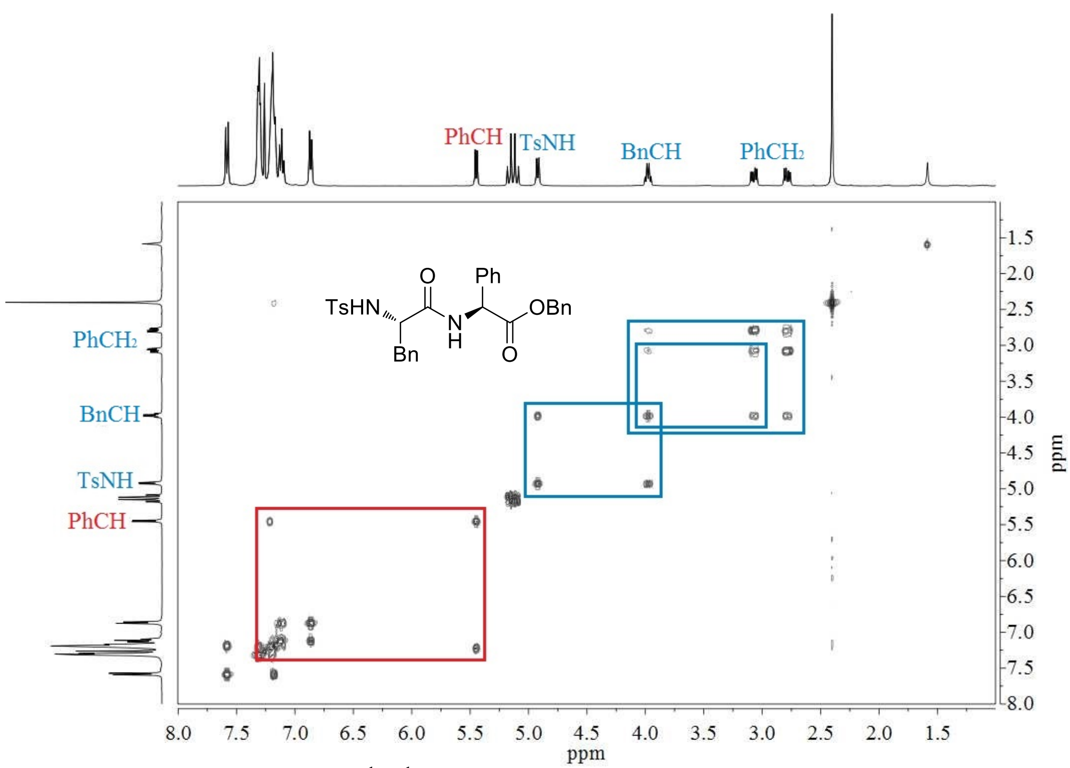


Figure S33. ^{1}H-^{1}H COSY of dipeptide derivative **G3-2**.

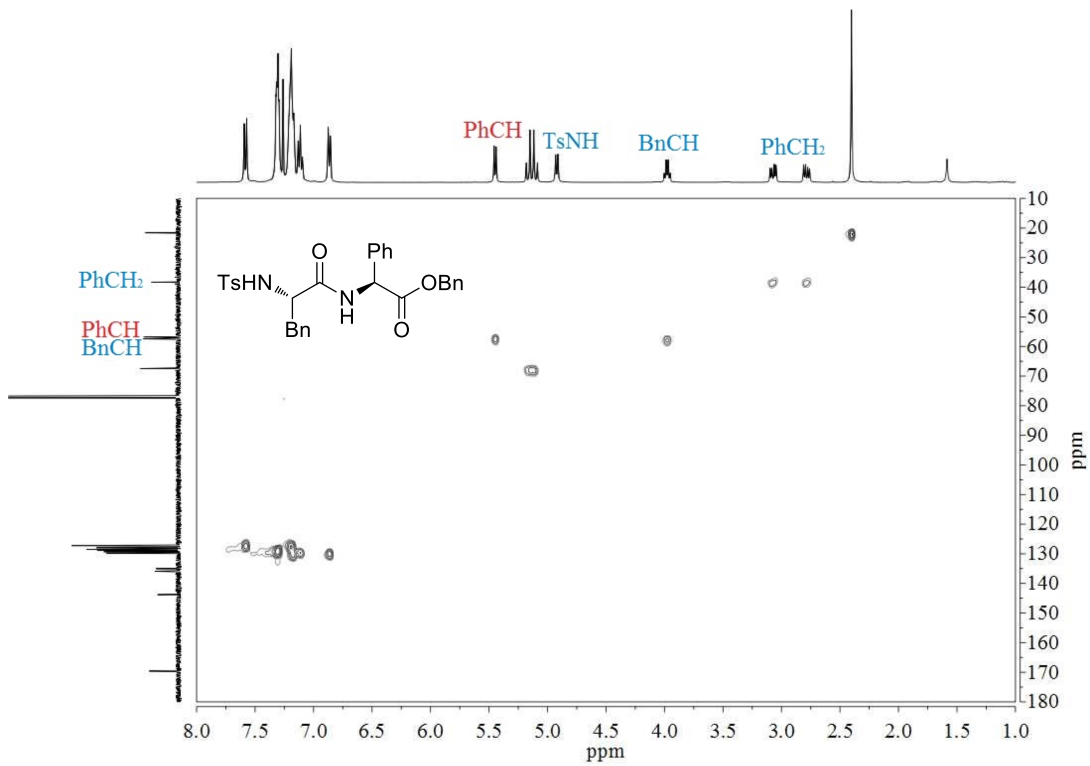


Figure S34. ^{1}H-^{13}C HSQC of dipeptide derivative **G3-2**.

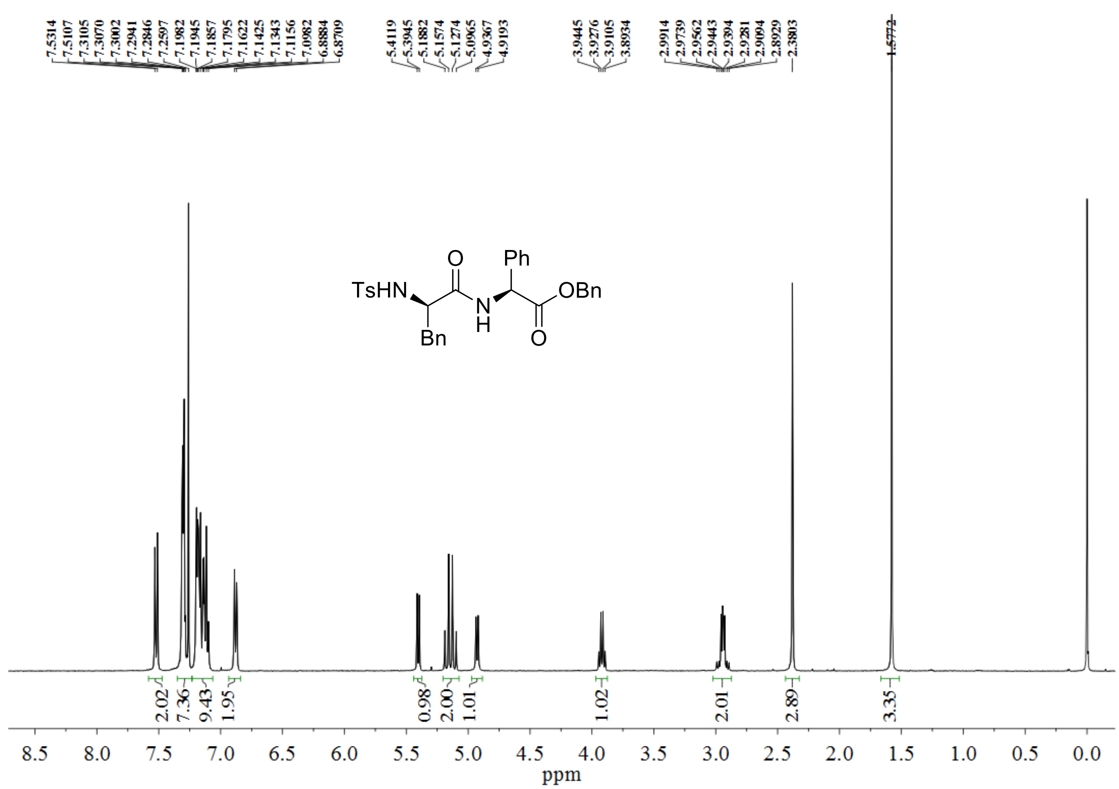


Figure S35. ^{1}H NMR spectrum of dipeptide derivative **G4-1** in $CDCl_3$ (400 MHz).

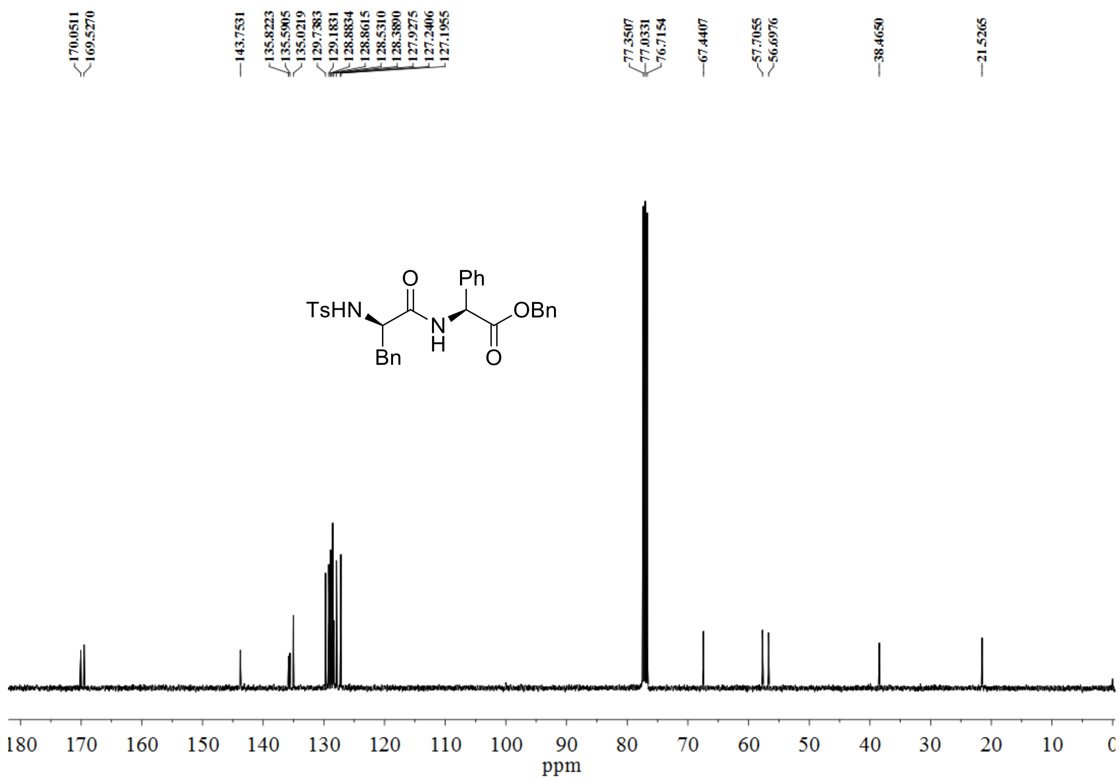


Figure S36. ${}^{13}C$ NMR spectrum of dipeptide derivative **G4-1** in $CDCl_3$ (100 MHz).

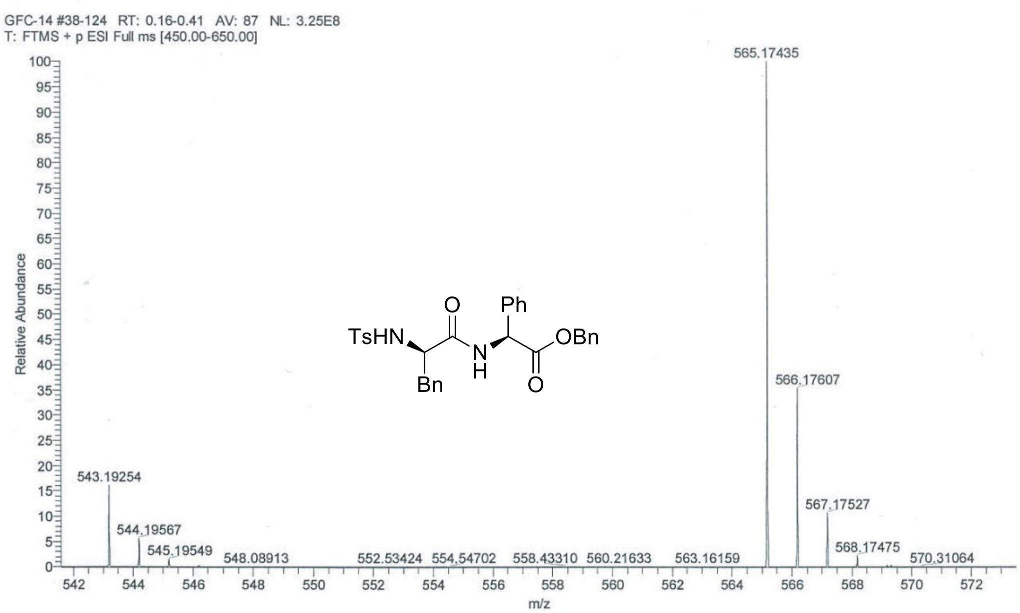


Figure S37. HRMS spectrum of dipeptide derivative **G4-1**.

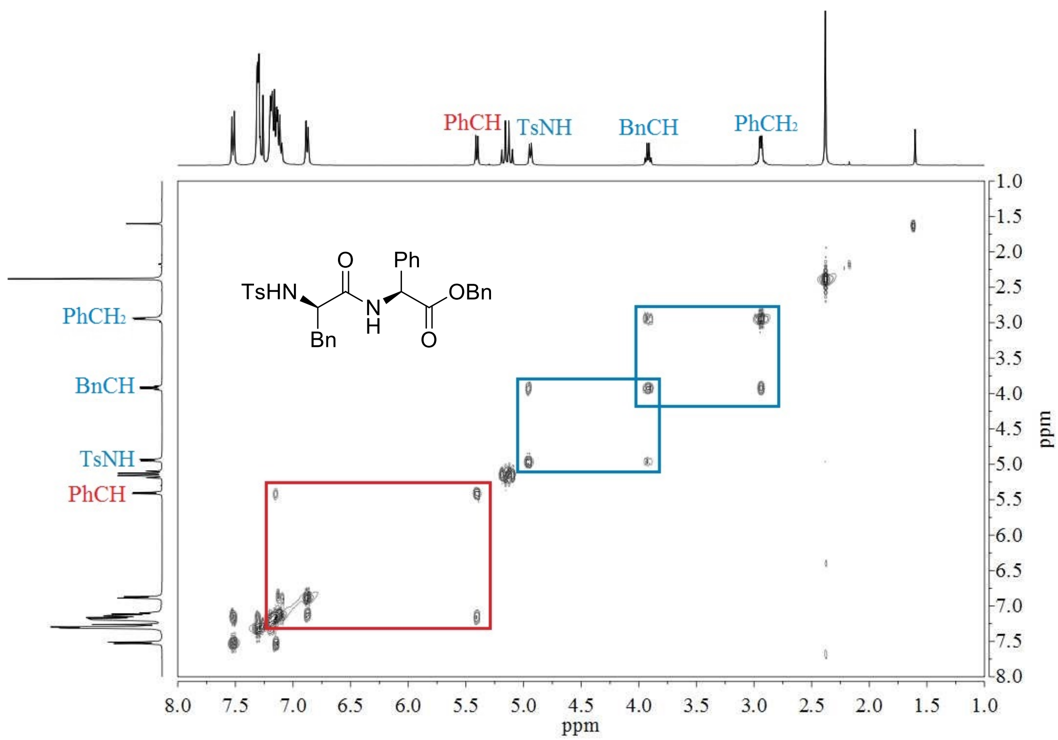


Figure S38. ^{1}H-^{1}H COSY of dipeptide derivative **G4-1**.

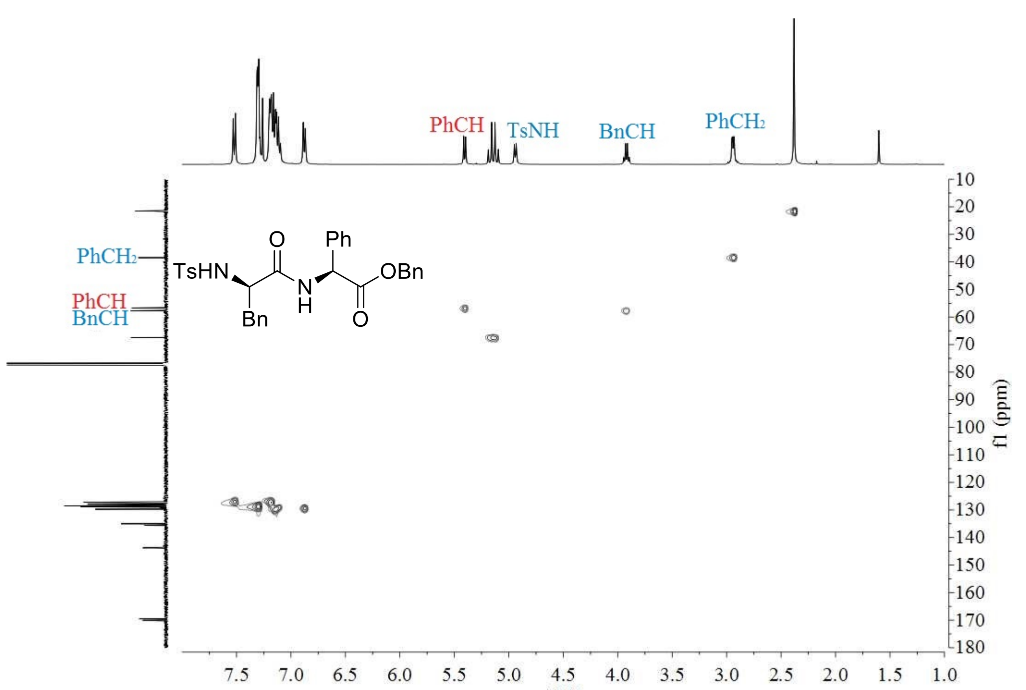


Figure S39. HSQC of dipeptide derivative **G4-1**.

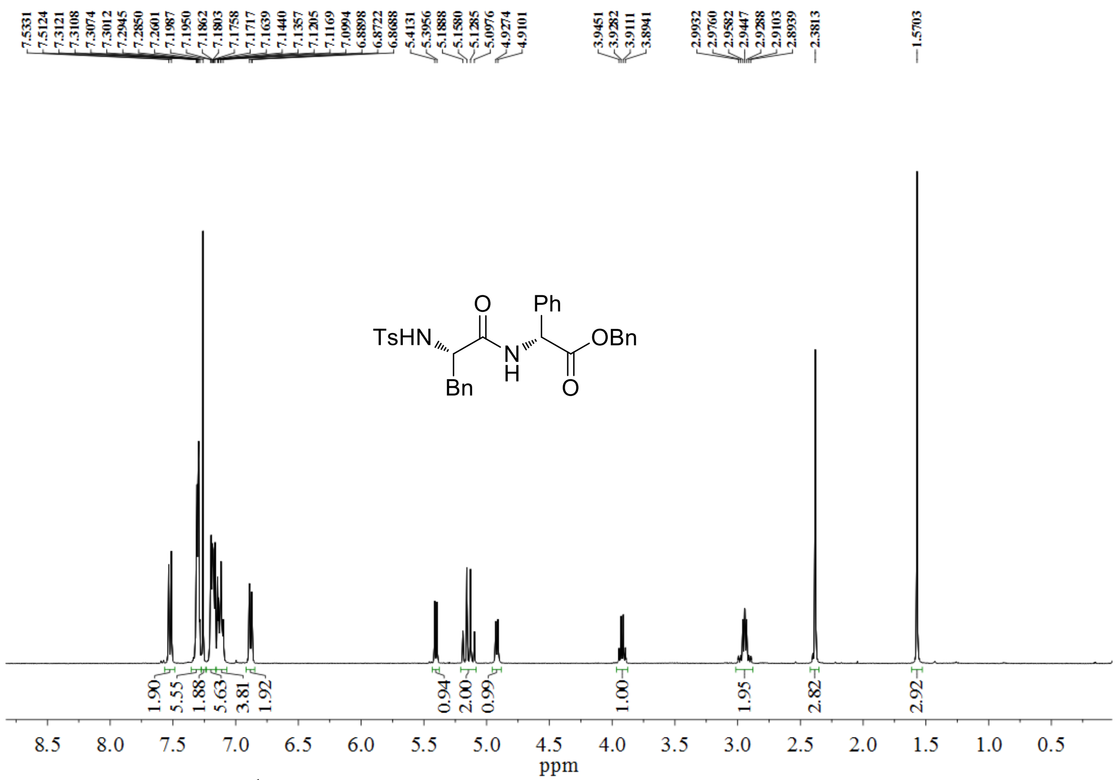


Figure S40. ^{1}H NMR spectrum of dipeptide derivative **G4-2** in $CDCl_3$ (400 MHz).

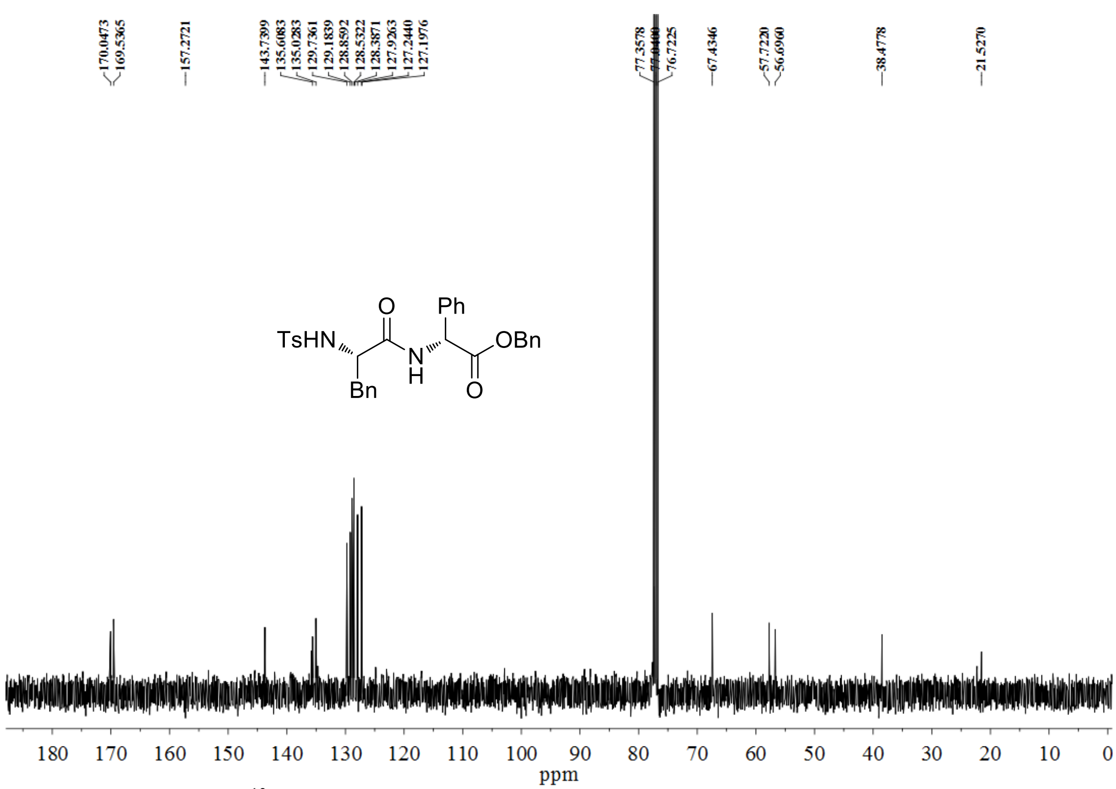


Figure S41. ^{13}C NMR spectrum of dipeptide derivative **G4-2** in $CDCl_3$ (100 MHz).

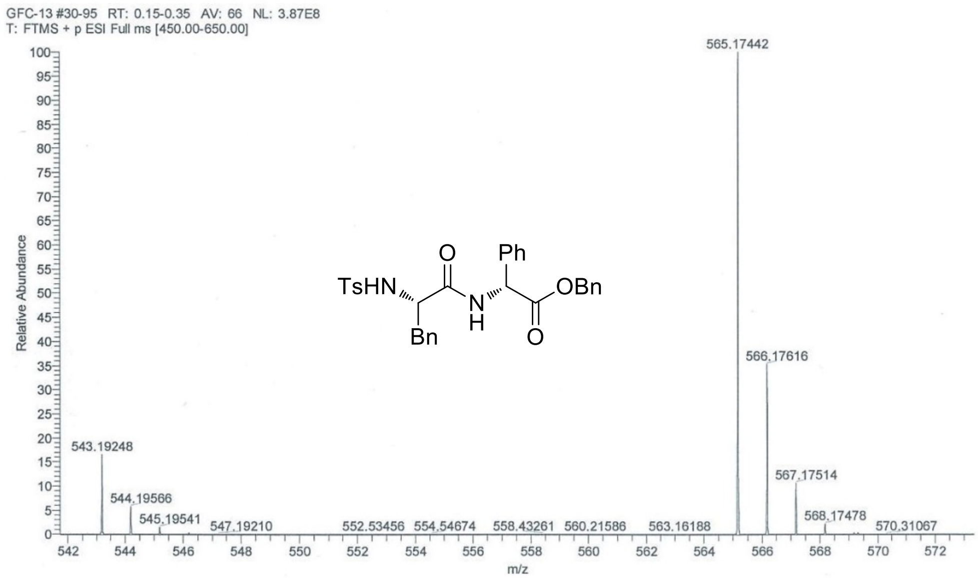


Figure S42. HRMS spectrum of dipeptide derivative **G4-2**.

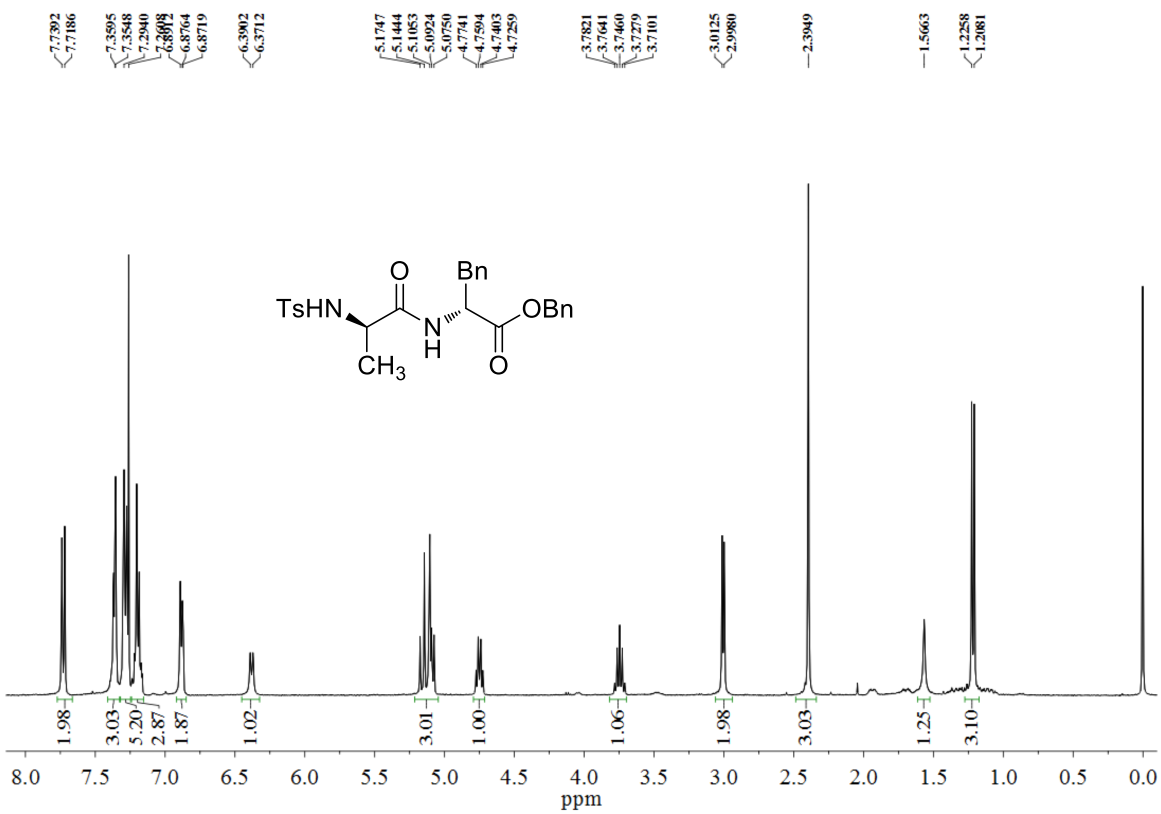


Figure S43. ^{1}H NMR spectrum of dipeptide derivative **G5-1** in $CDCl_3$ (400 MHz).

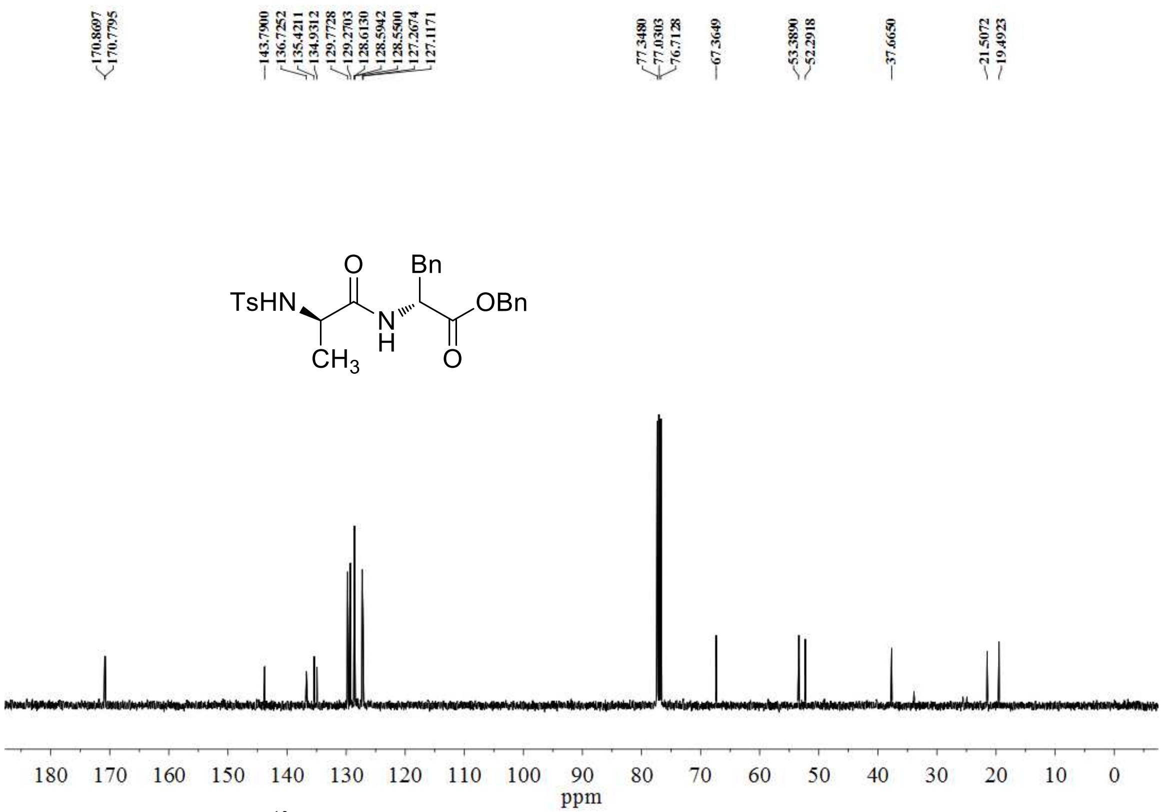


Figure S44. ^{13}C NMR spectrum of dipeptide derivative **G5-1** in $CDCl_3$ (100 MHz).

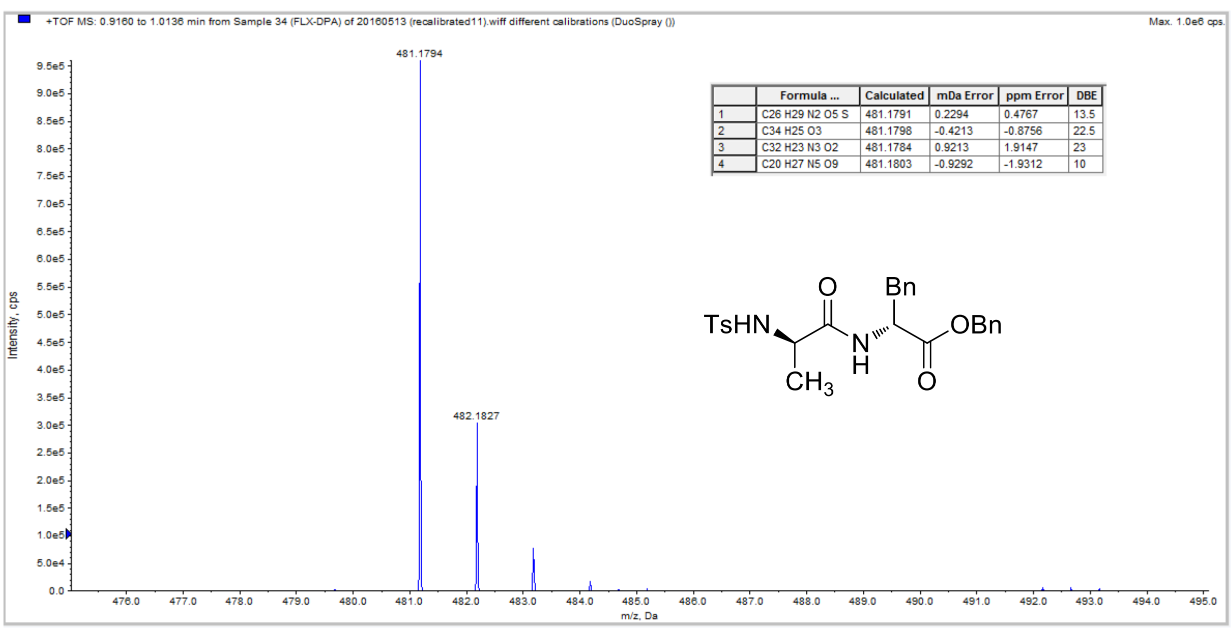


Figure S45. HRMS spectrum of dipeptide derivative **G5-1**.

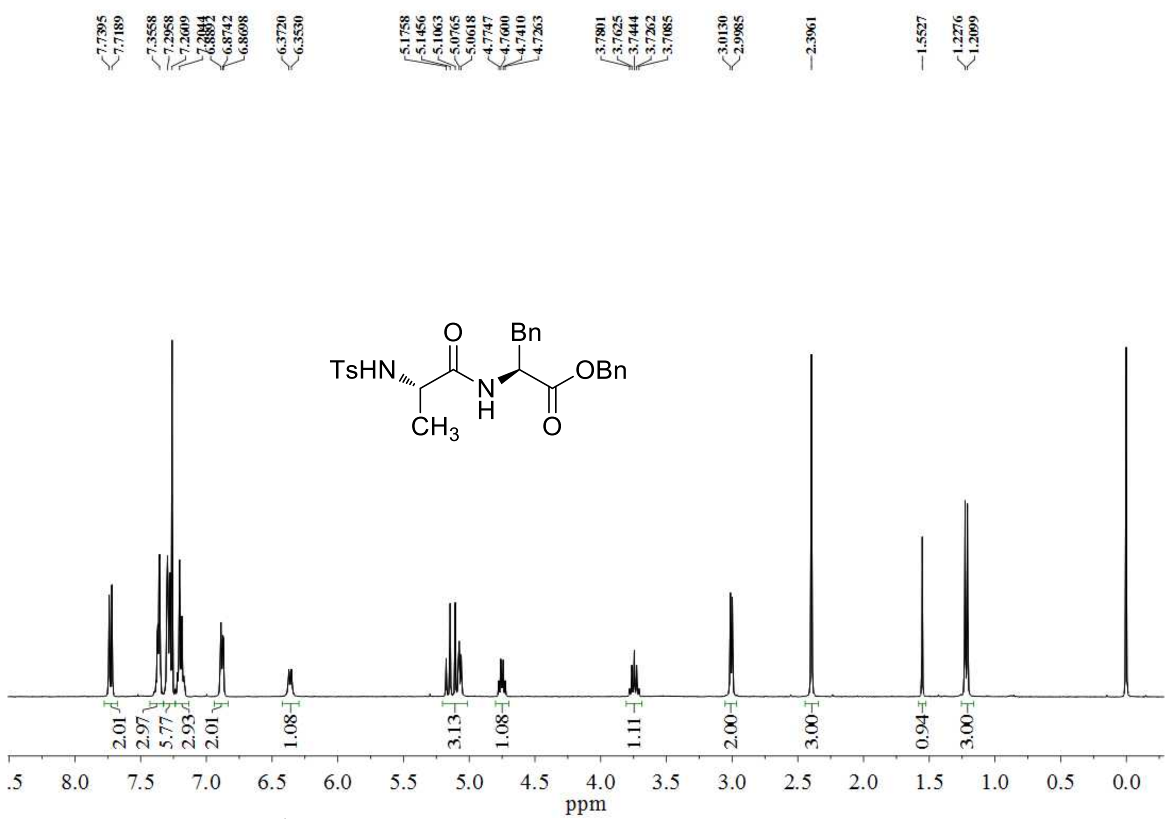


Figure S46. ^{1}H NMR spectrum of dipeptide derivative **G5-2** in $CDCl_3$ (400 MHz).

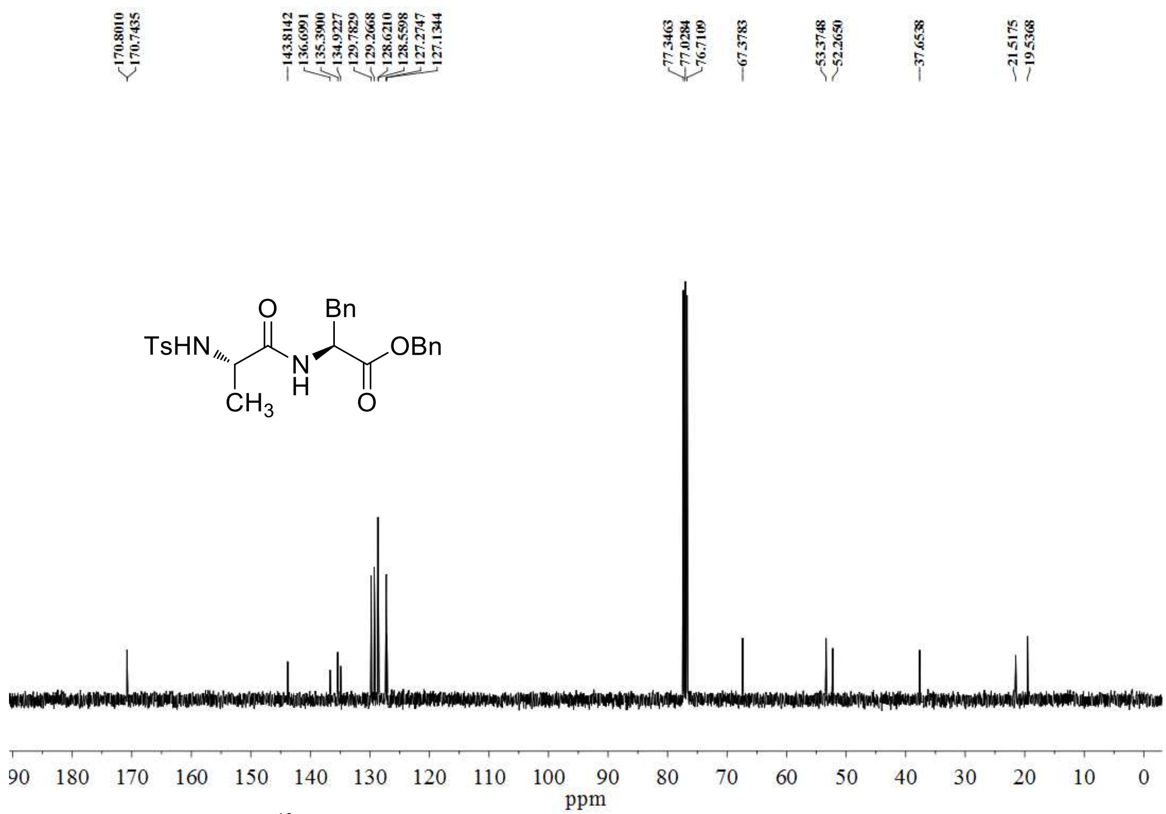
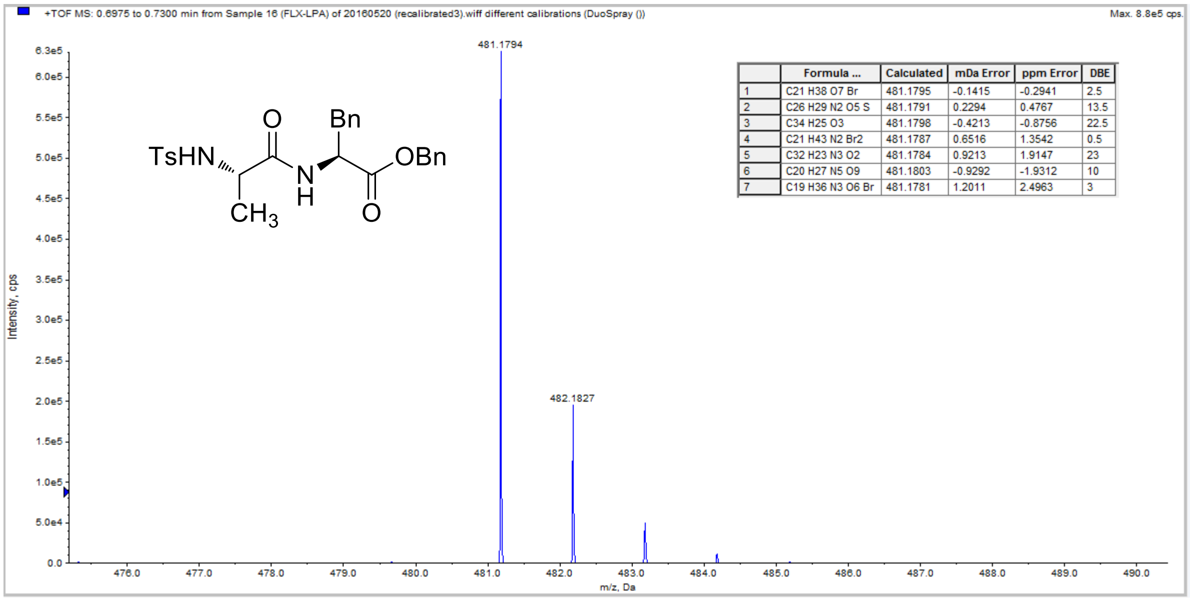


Figure S47. ^{13}C NMR spectrum of dipeptide derivative **G5-2** in $CDCl_3$ (100 MHz).



	Formula ...	Calculated	mDa Error	ppm Error	DBE
1	C21 H38 O7 Br	481.1795	-0.1415	-0.2941	2.5
2	C26 H29 N2 O5 S	481.1791	0.2294	0.4767	13.5
3	C34 H25 O3	481.1798	-0.4213	-0.8756	22.5
4	C21 H43 N2 Br2	481.1787	0.6516	1.3542	0.5
5	C32 H23 N3 O2	481.1784	0.9213	1.9147	23
6	C20 H27 N5 O9	481.1803	-0.9292	-1.9312	10
7	C19 H36 N3 O6 Br	481.1781	1.2011	2.4963	3

Figure S48. HRMS spectrum of dipeptide derivative **G5-2**.

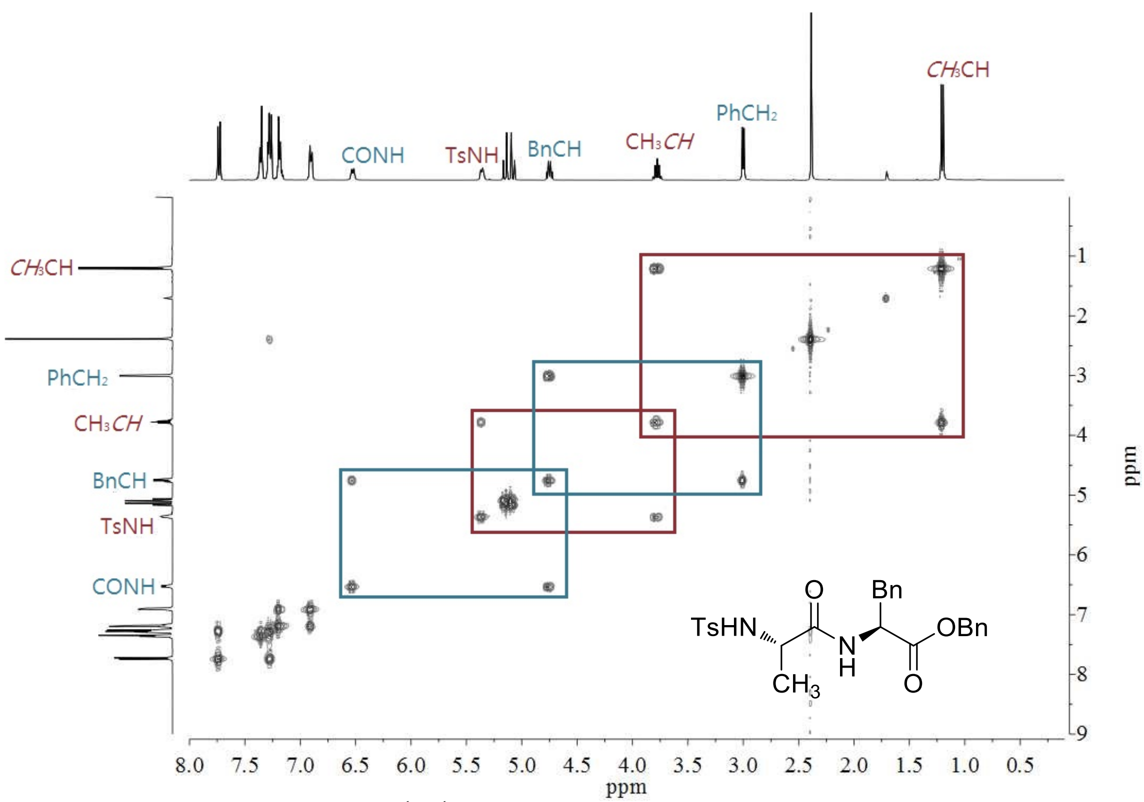


Figure S49. ^{1}H-^{1}H COSY of dipeptide derivative **G5-2**.

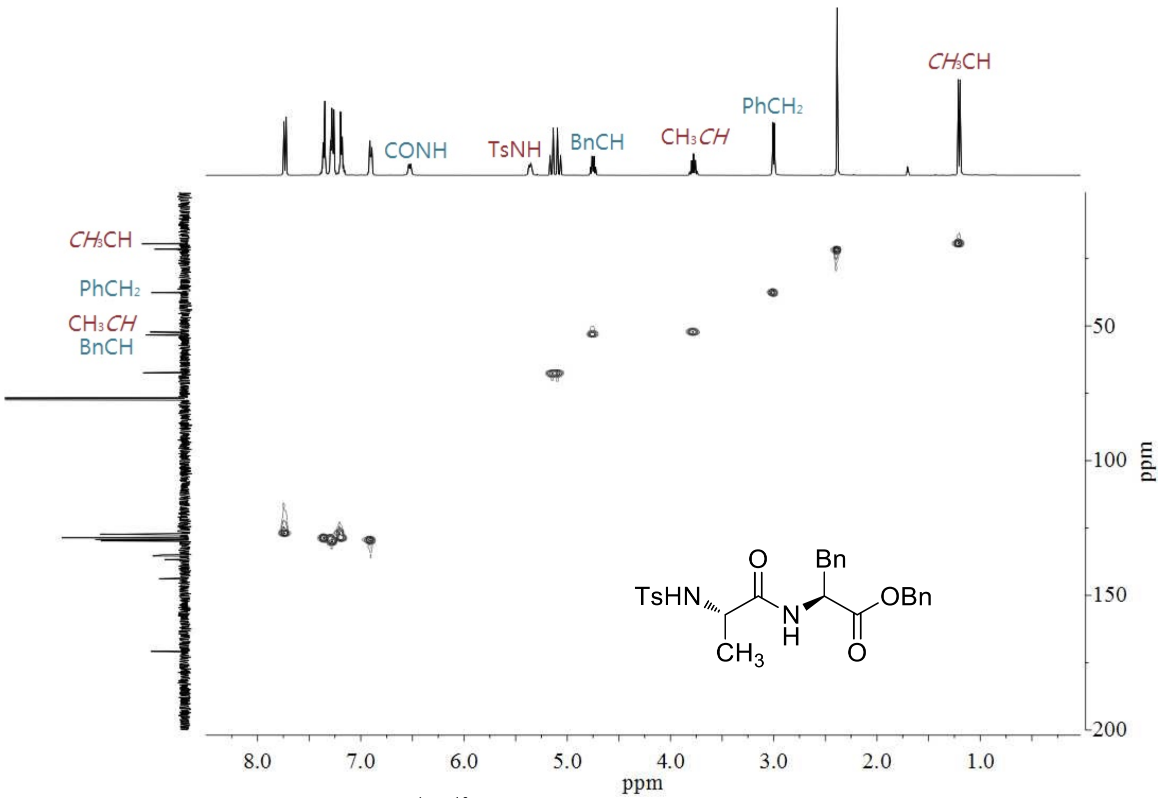


Figure S50. ^{1}H-^{13}C HSQC of dipeptide derivative **G5-2**.

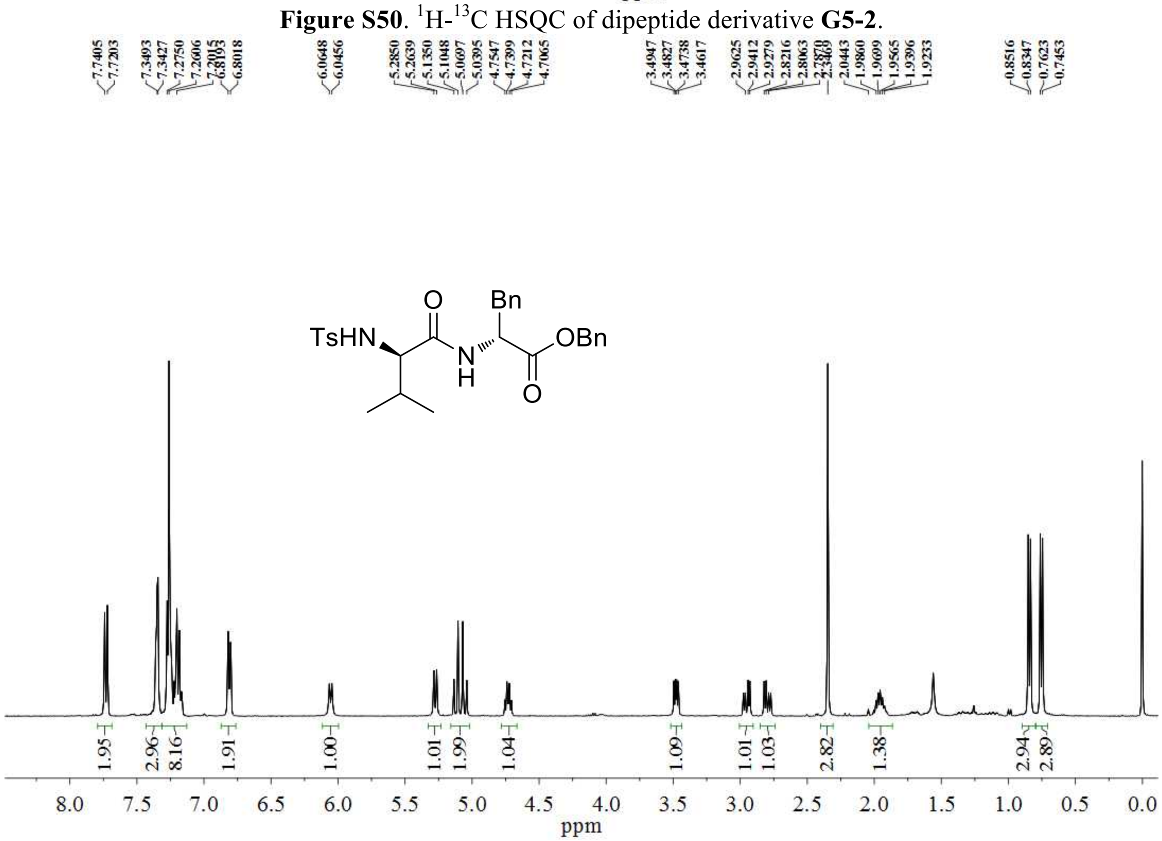


Figure S51. ^{1}H NMR spectrum of dipeptide derivative **G6-1** in $CDCl_3$ (400 MHz).

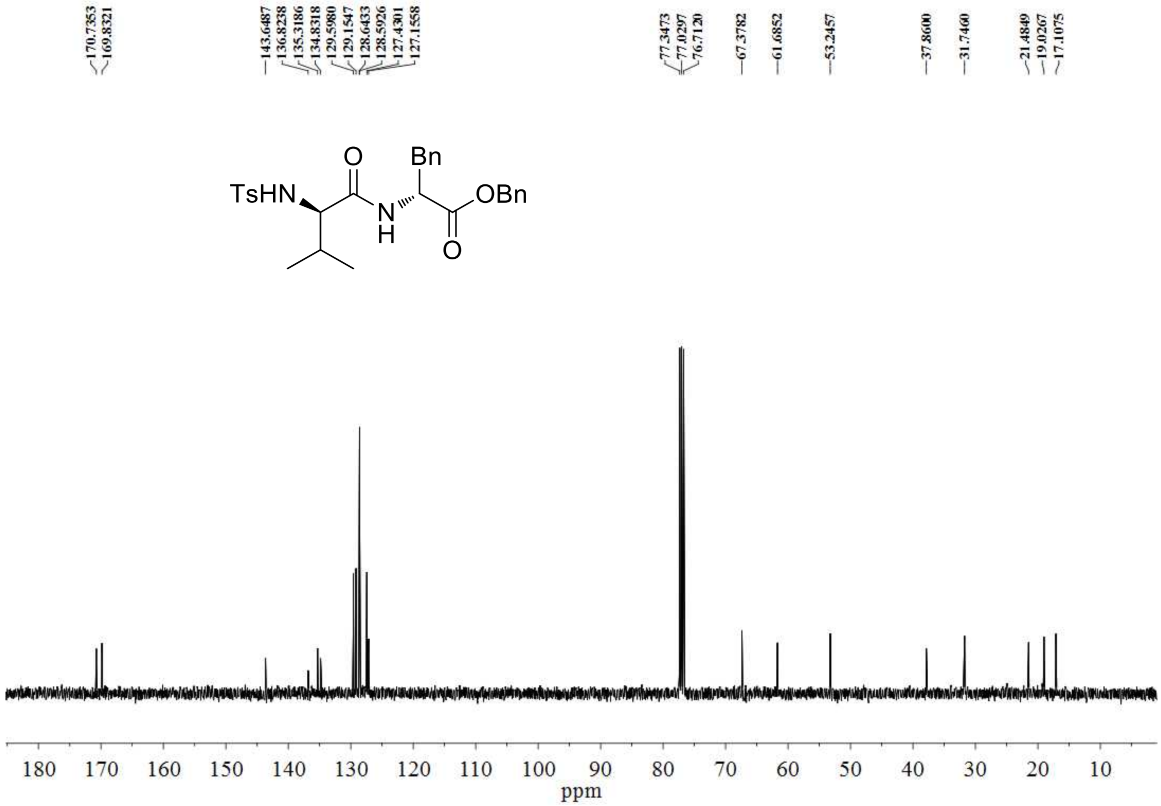
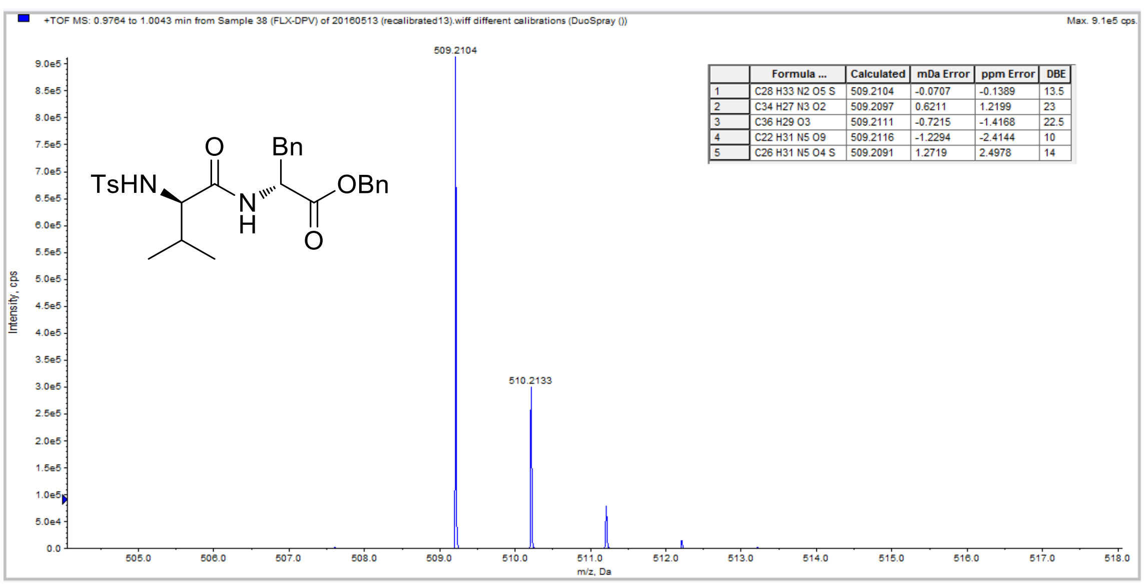


Figure S52. ^{13}C NMR spectrum of dipeptide derivative **G6-1** in $CDCl_3$ (100 MHz).



	Formula ...	Calculated	mDa Error	ppm Error	DBE
1	C28 H33 N2 O5 S	509.2104	-0.0707	-0.1389	13.5
2	C34 H27 N3 O2	509.2097	0.6211	1.2199	23
3	C36 H29 O3	509.2111	-0.7215	-1.4168	22.5
4	C22 H31 N5 O9	509.2116	-1.2294	-2.4144	10
5	C26 H31 N5 O4 S	509.2091	1.2719	2.4978	14

Figure S53. HRMS spectrum of dipeptide derivative **G6-1**.

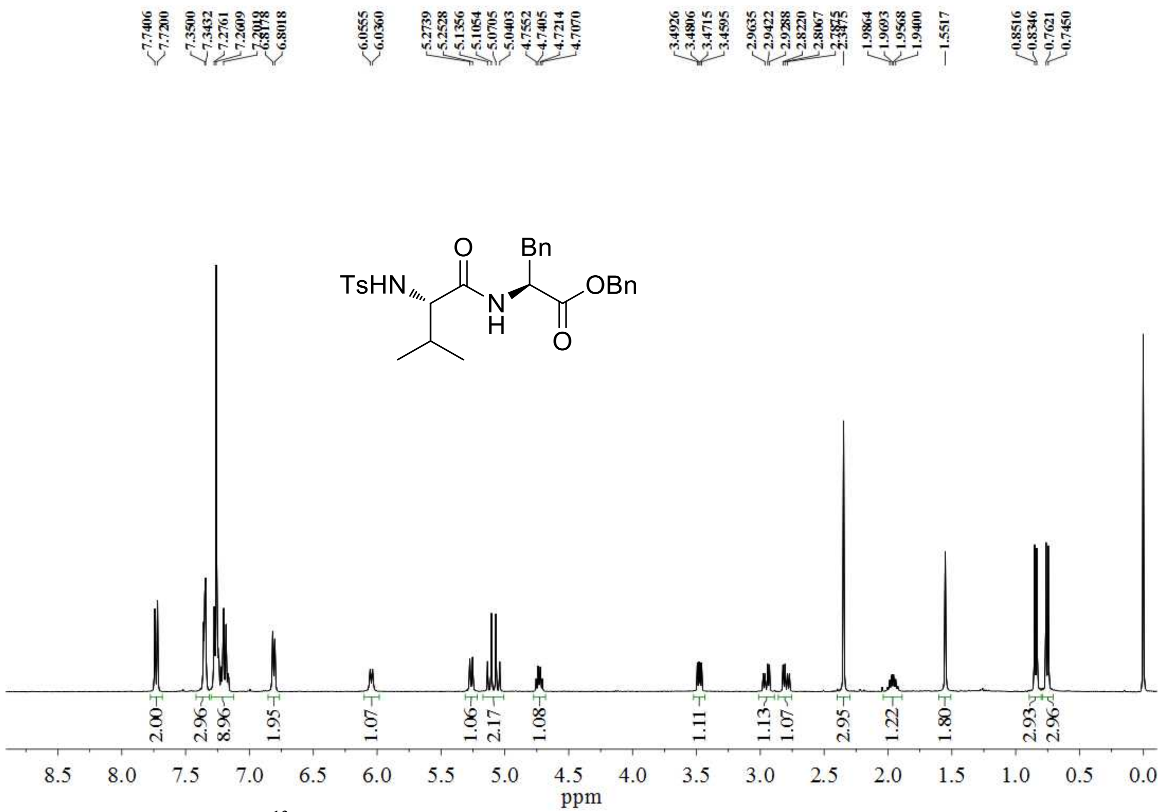


Figure S54. ^{13}C NMR spectrum of dipeptide derivative **G6-2** in $CDCl_3$ (100 MHz).

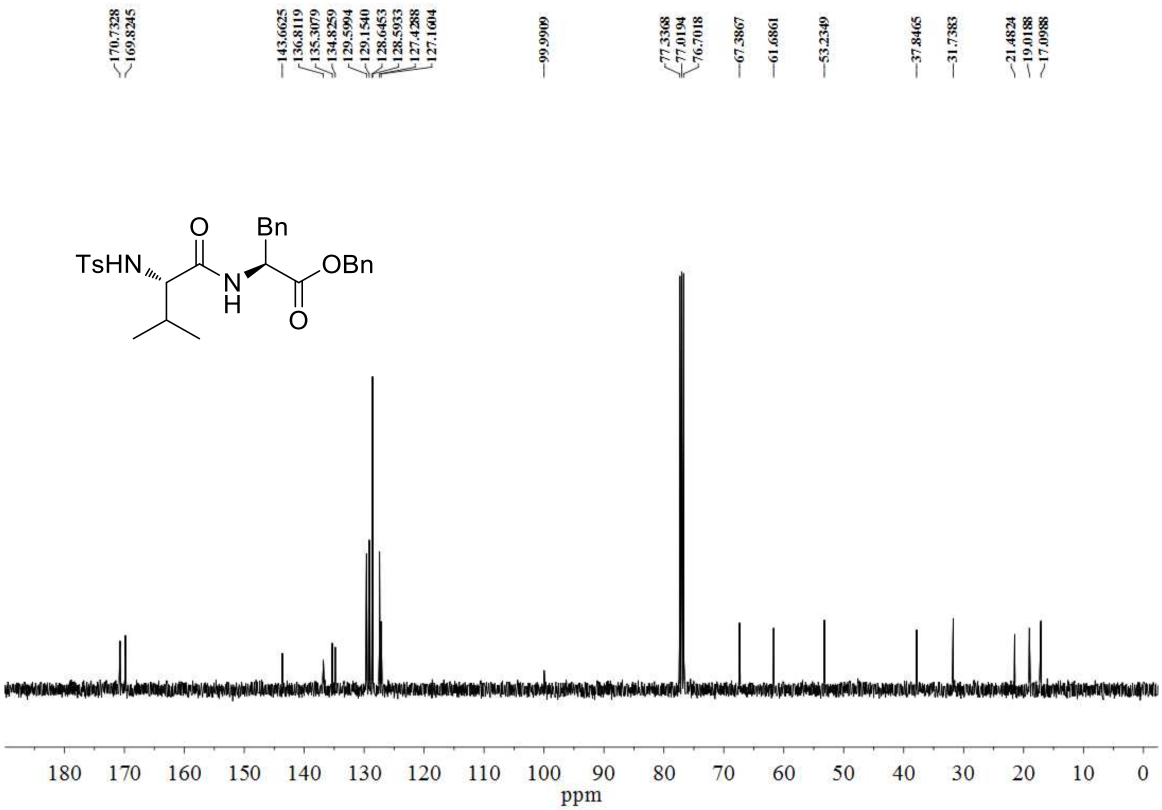


Figure S55. ^{13}C NMR spectrum of dipeptide derivative **G6-2** in $CDCl_3$ (100 MHz).

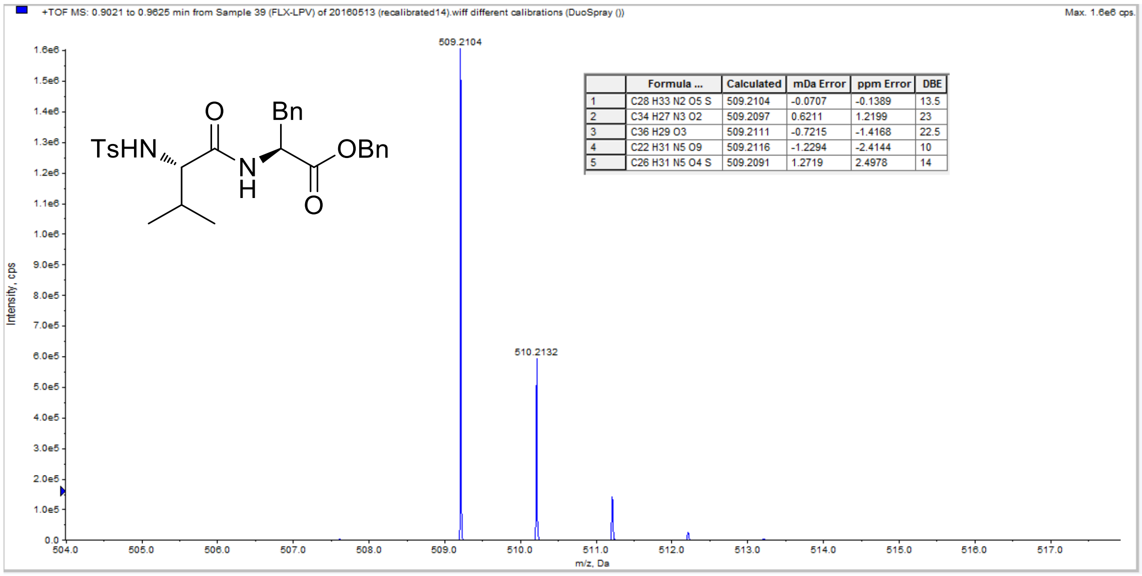


Figure S56. HRMS spectrum of dipeptide derivative **G6-2**.

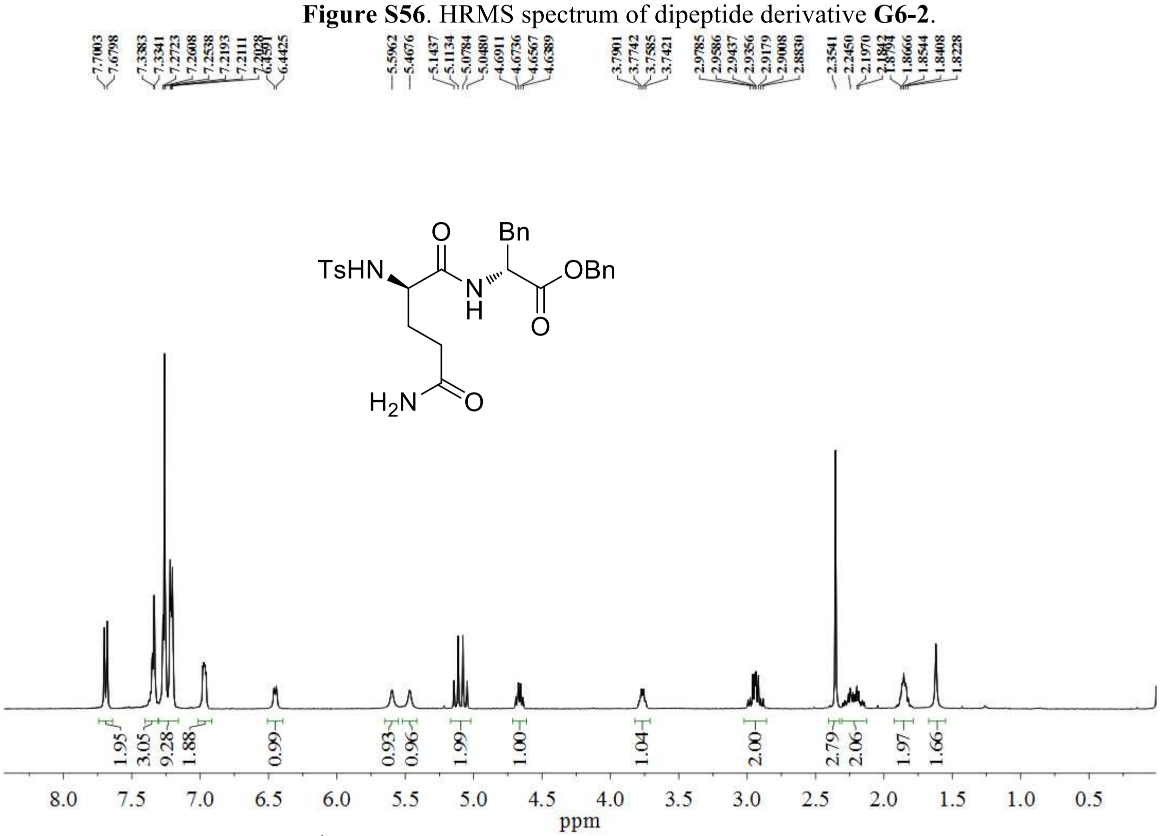


Figure S57. ^{1}H NMR spectrum of dipeptide derivative **G7-1** in $CDCl_3$ (400 MHz).

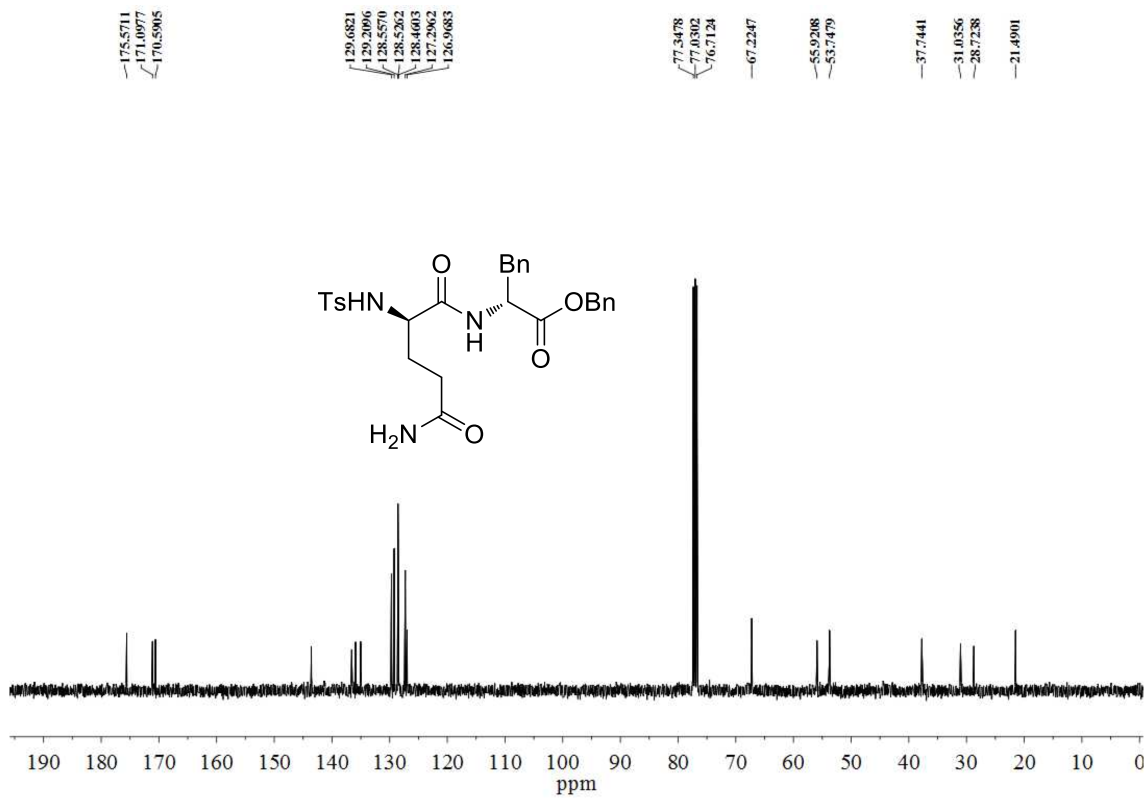


Figure S58. [13]C NMR spectrum of dipeptide derivative **G7-1** in $CDCl_3$ (100 MHz).

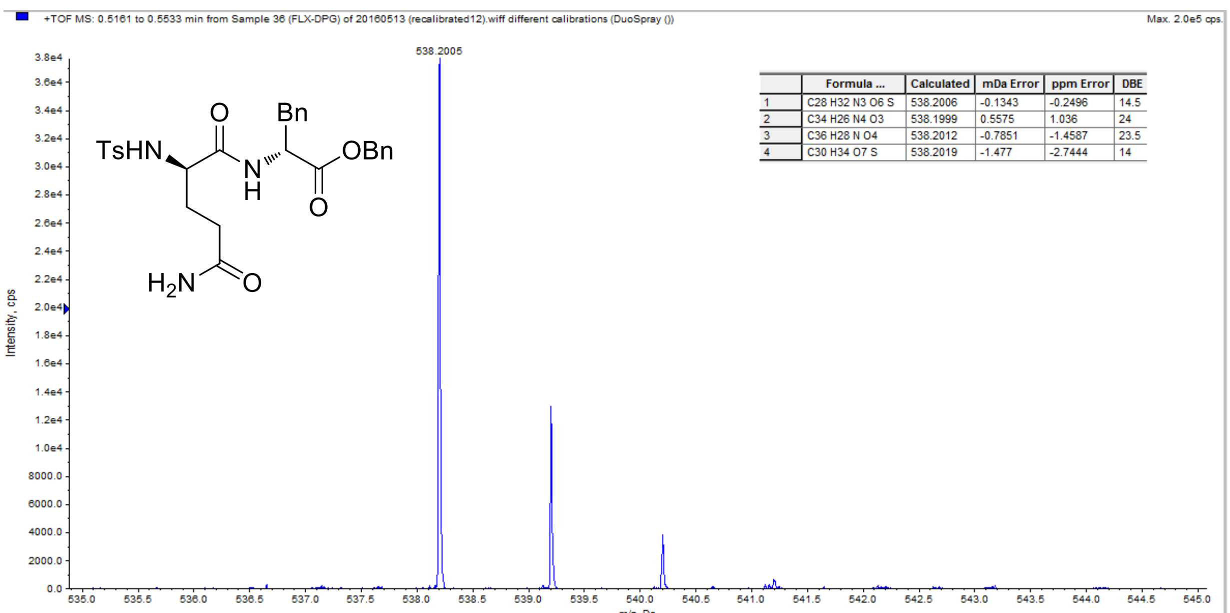


Figure S59. HRMS spectrum of dipeptide derivative **G7-1**.

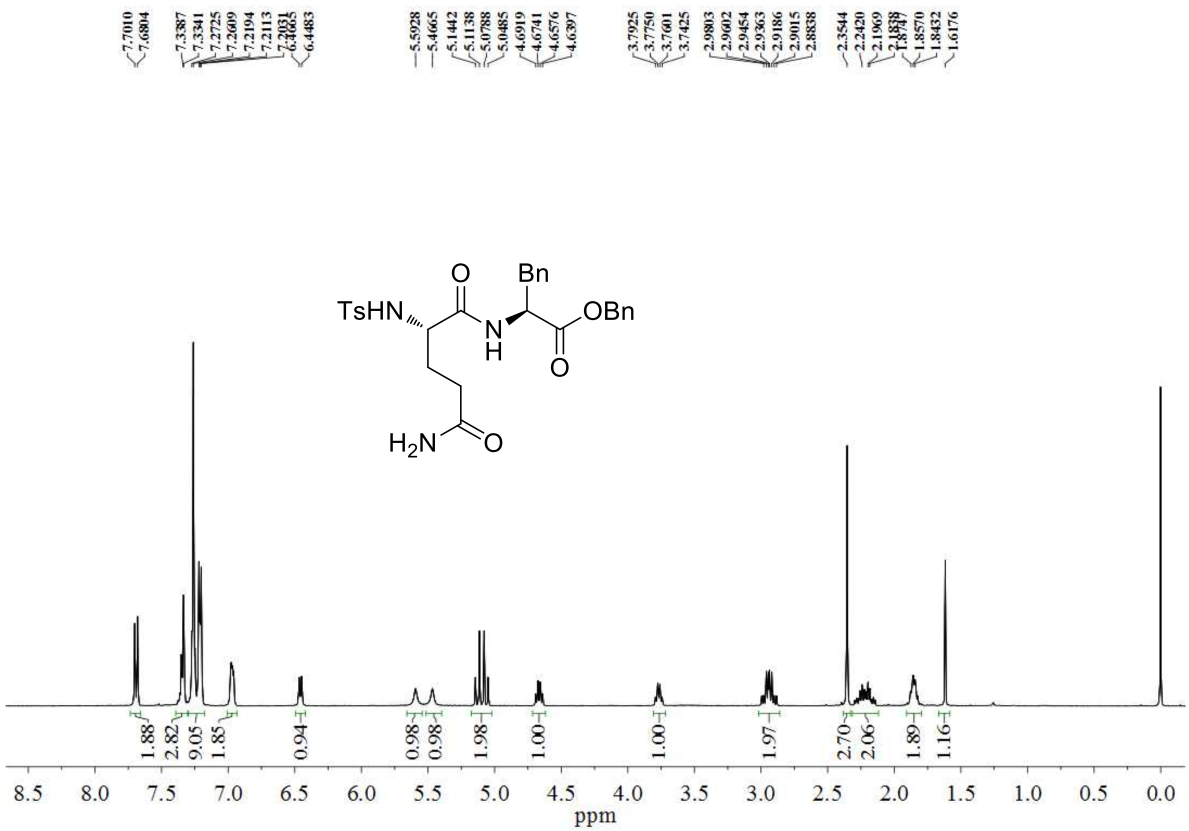


Figure S60. ^{1}H NMR spectrum of dipeptide derivative **G7-2** in $CDCl_3$ (400 MHz).

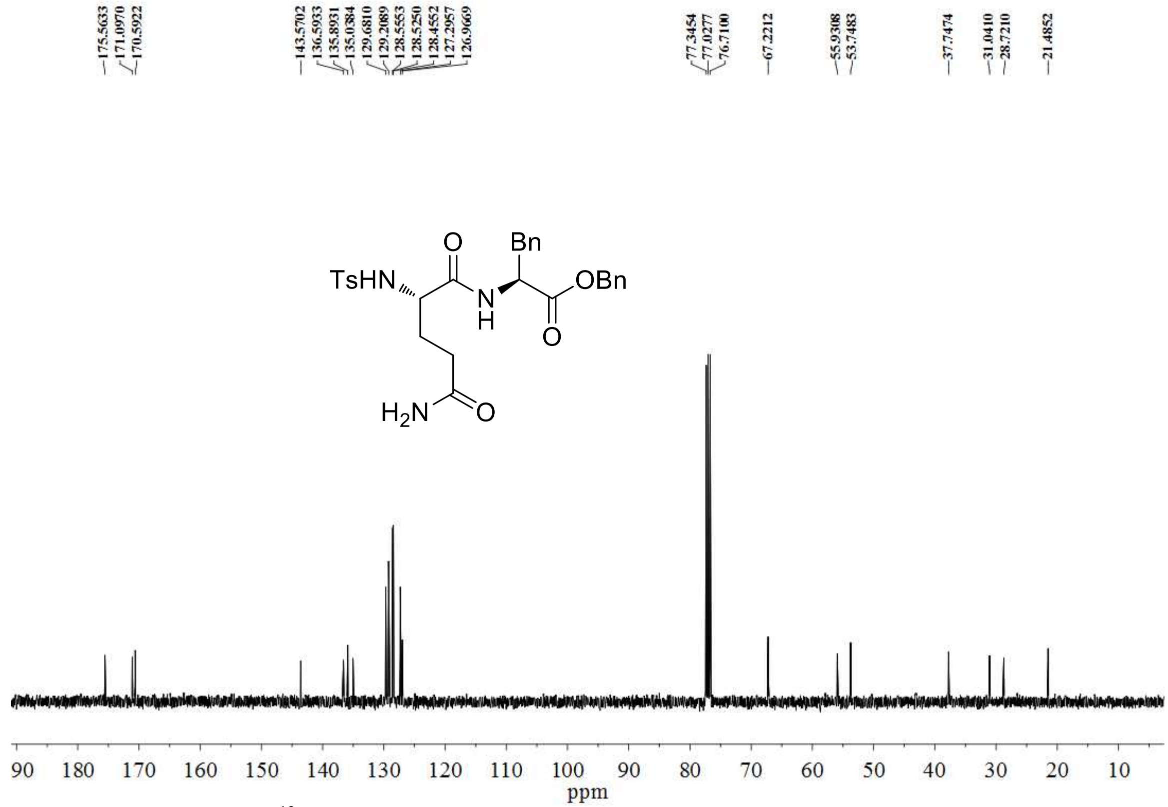
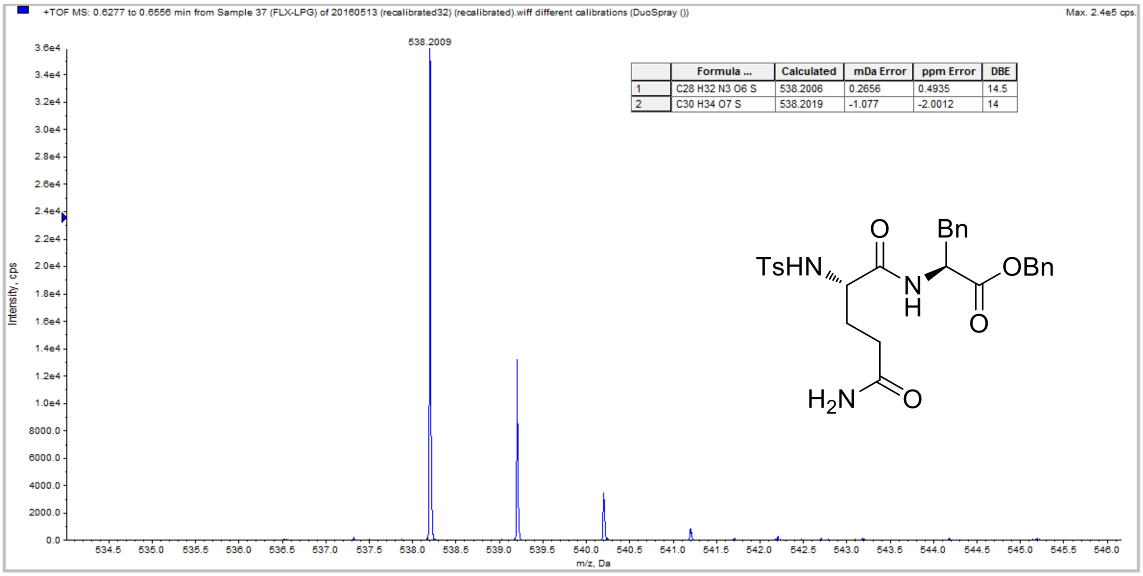


Figure S61. ^{13}C NMR spectrum of dipeptide derivative **G7-2** in $CDCl_3$ (100 MHz).



	Formula ...	Calculated	mDa Error	ppm Error	DBE
1	C28 H32 N3 O6 S	538.2006	0.2656	0.4935	14.5
2	C30 H34 O7 S	538.2019	-1.077	-2.0012	14

Figure S62. HRMS spectrum of dipeptide derivative **G7-2**.

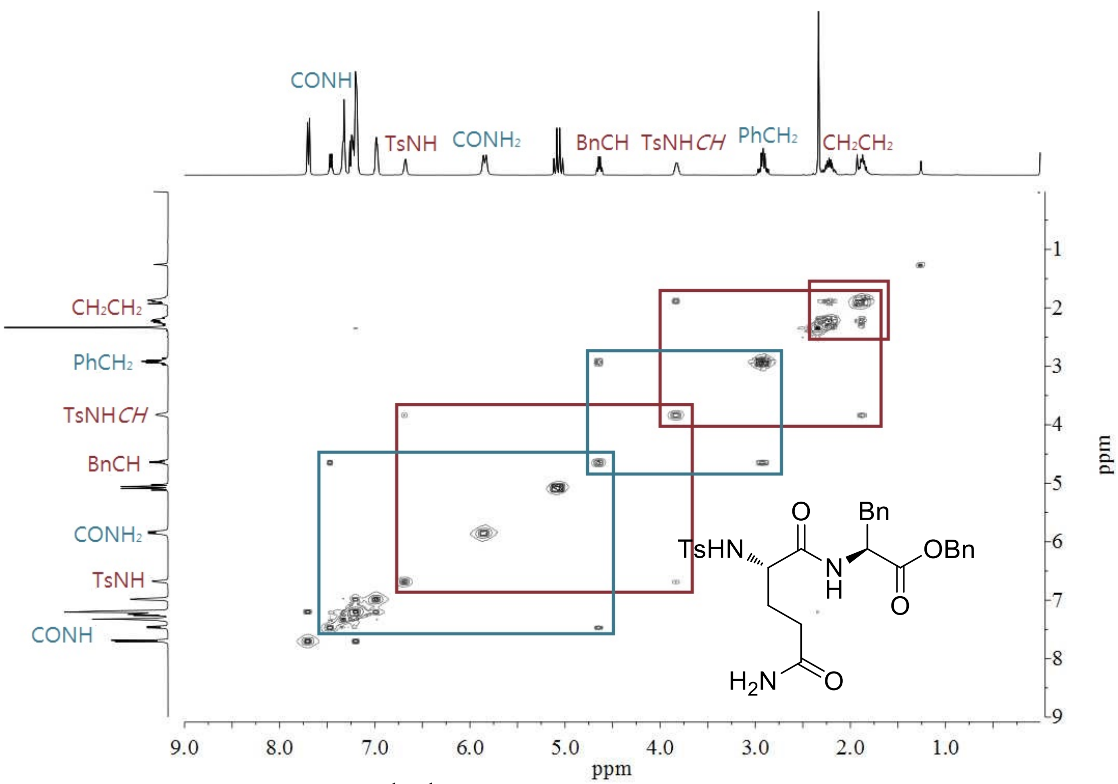


Figure S63. ^{1}H-^{1}H COSY of dipeptide derivative **G7-2**.

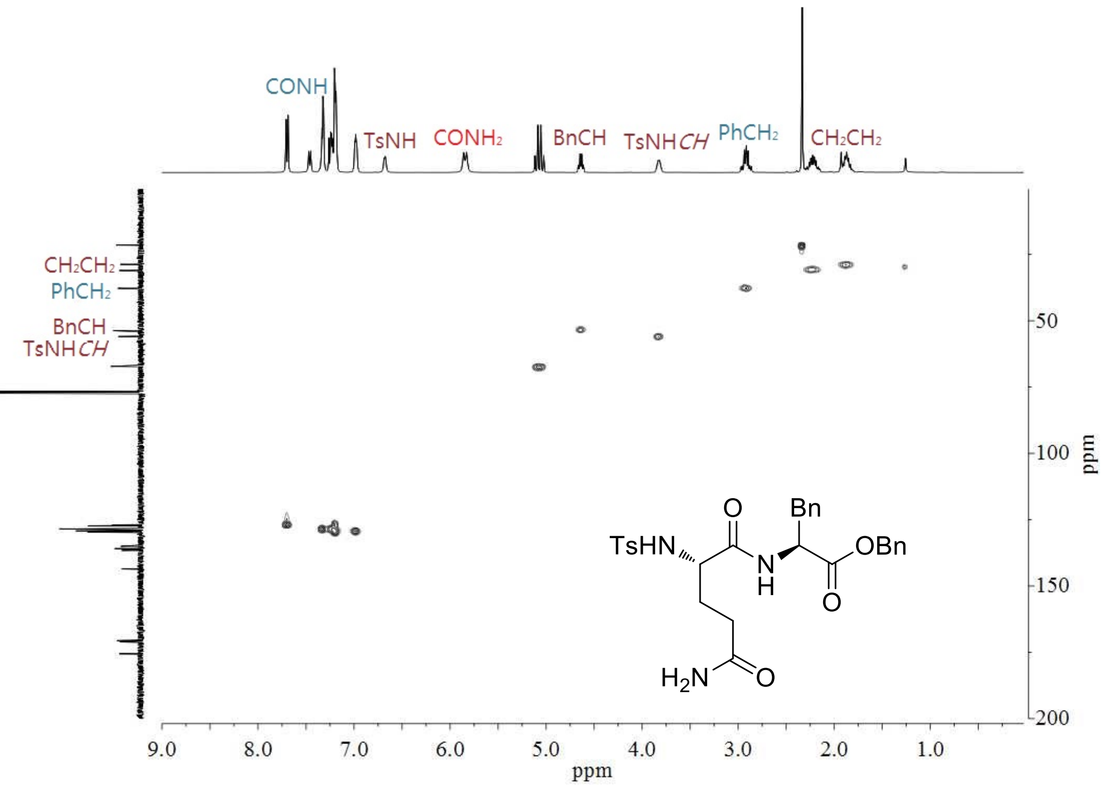


Figure S64. HSQC of dipeptide derivative **G7-2**.

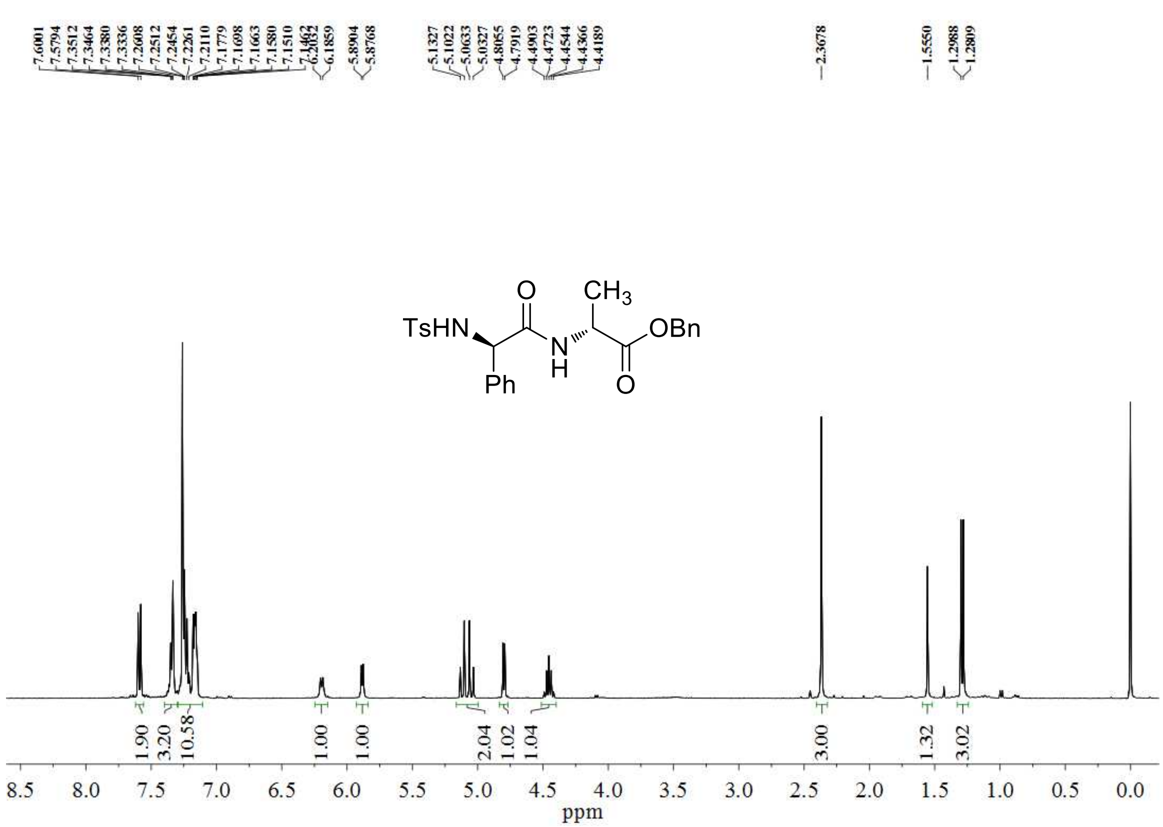


Figure S65. ^{1}H NMR spectrum of dipeptide derivative **G8-1** in $CDCl_3$ (400 MHz).

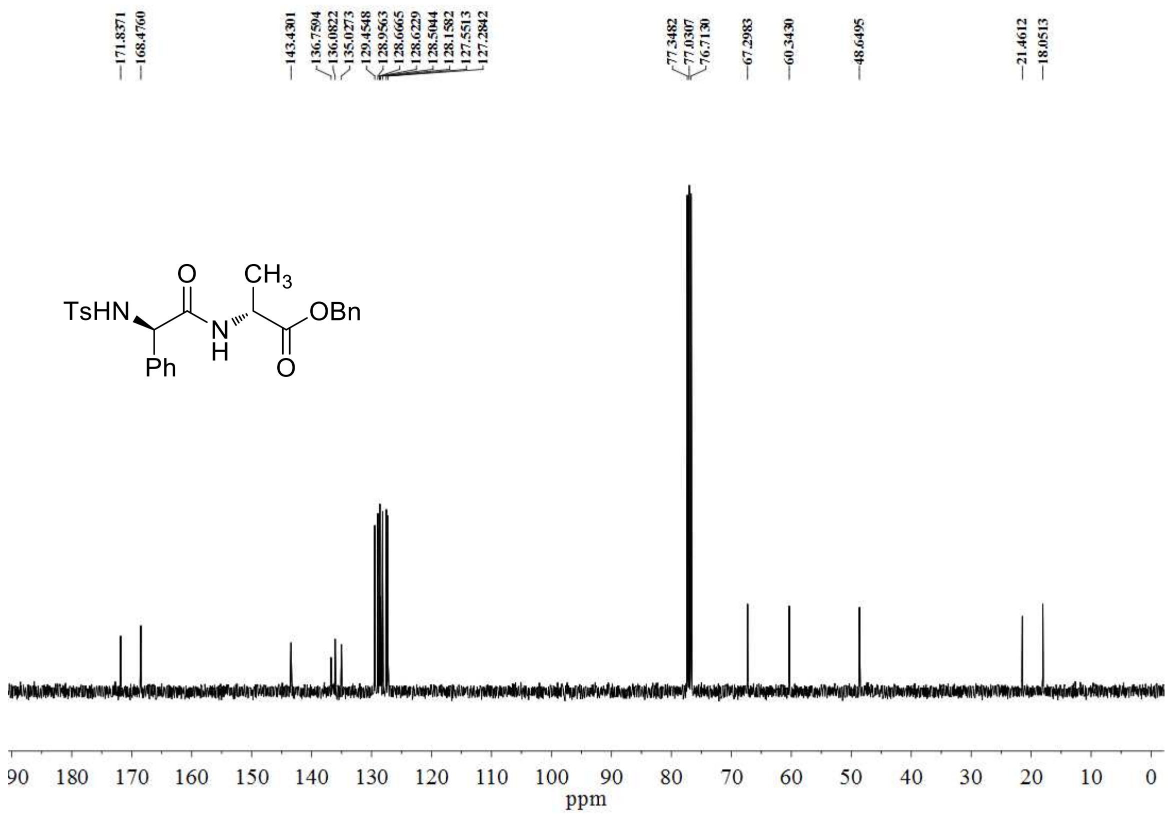


Figure S66. ^{13}C NMR spectrum of dipeptide derivative **G8-1** in $CDCl_3$ (100 MHz).

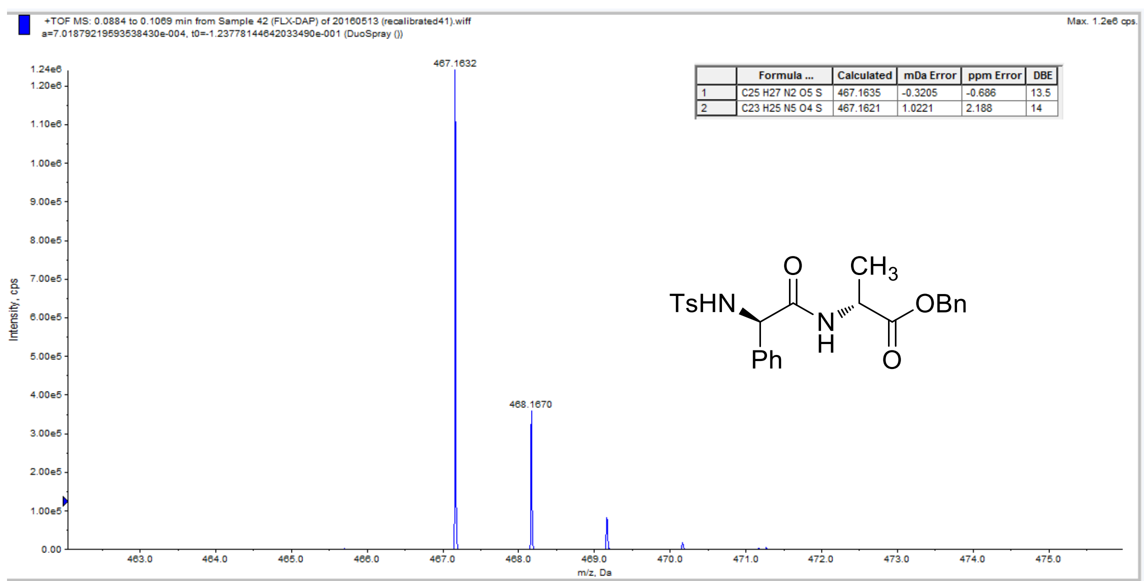


Figure S67. HRMS spectrum of dipeptide derivative **G8-1**.

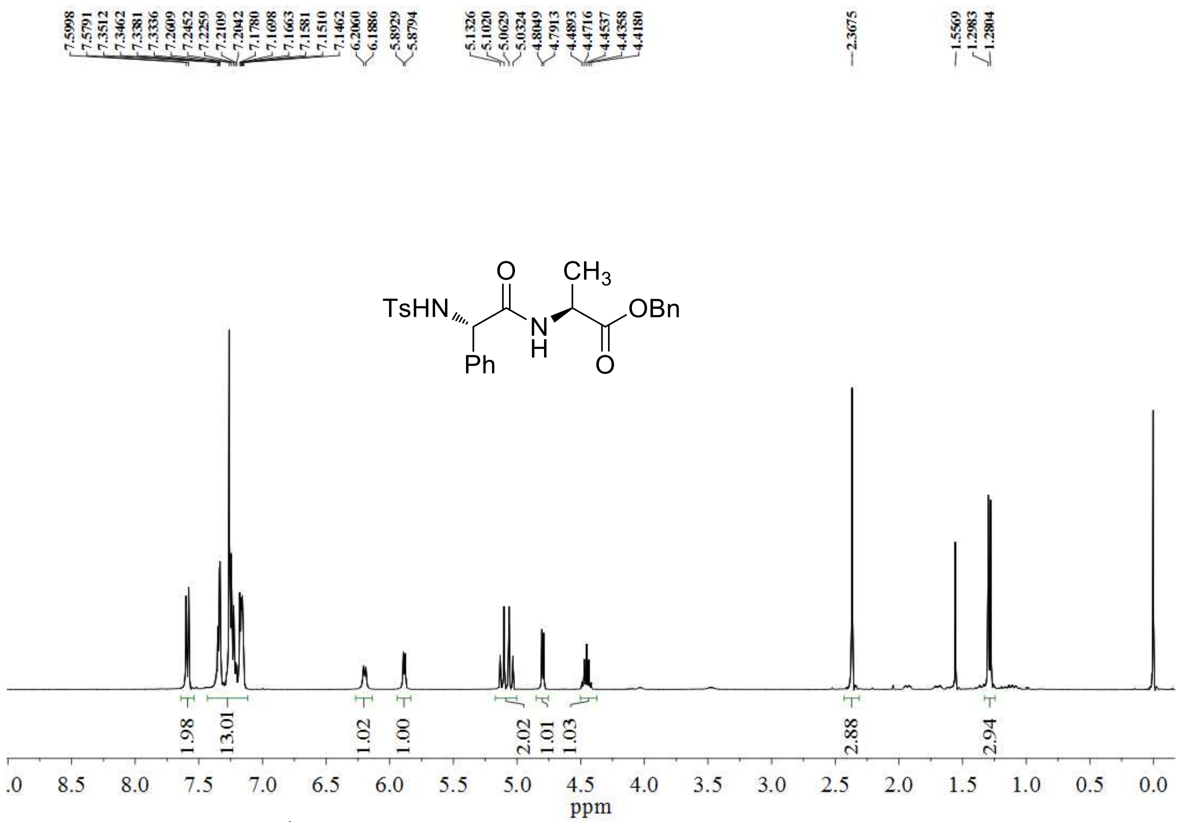


Figure S68. ^{1}H NMR spectrum of dipeptide derivative **G8-2** in $CDCl_3$ (400 MHz).

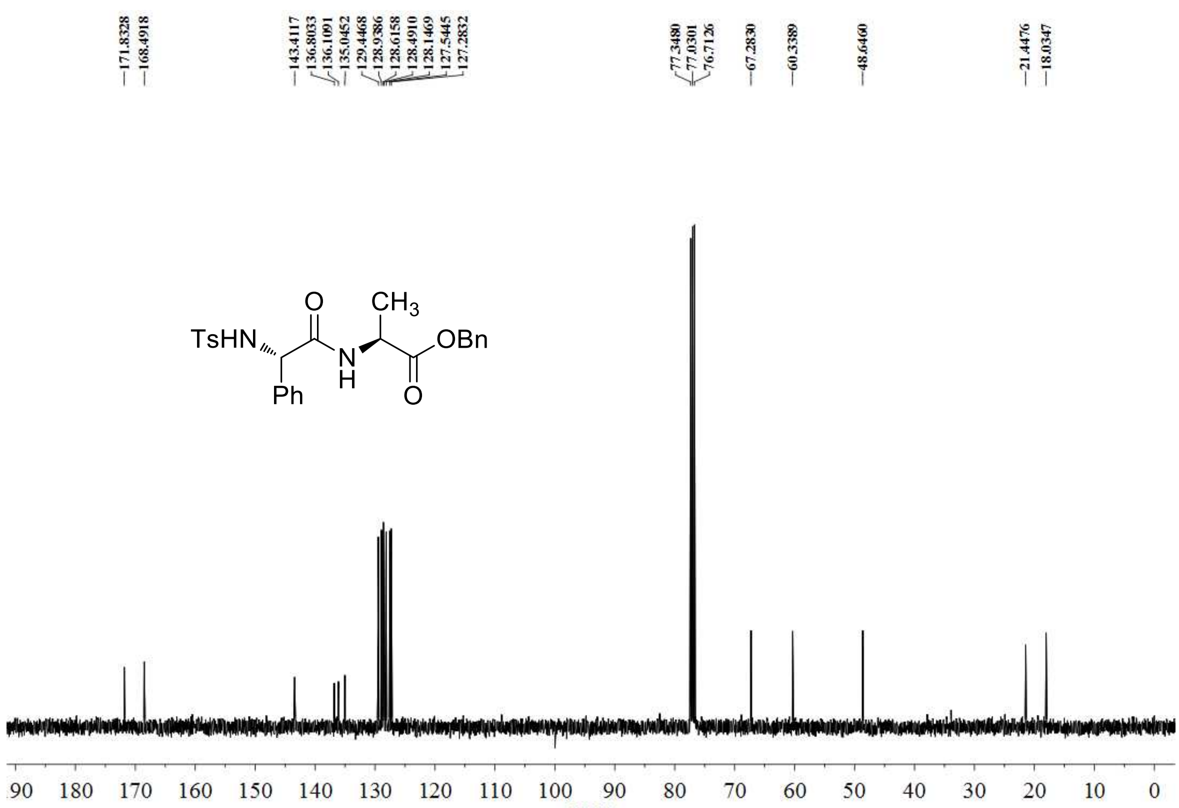


Figure S69. ^{13}C NMR spectrum of dipeptide derivative **G8-2** in $CDCl_3$ (100 MHz).

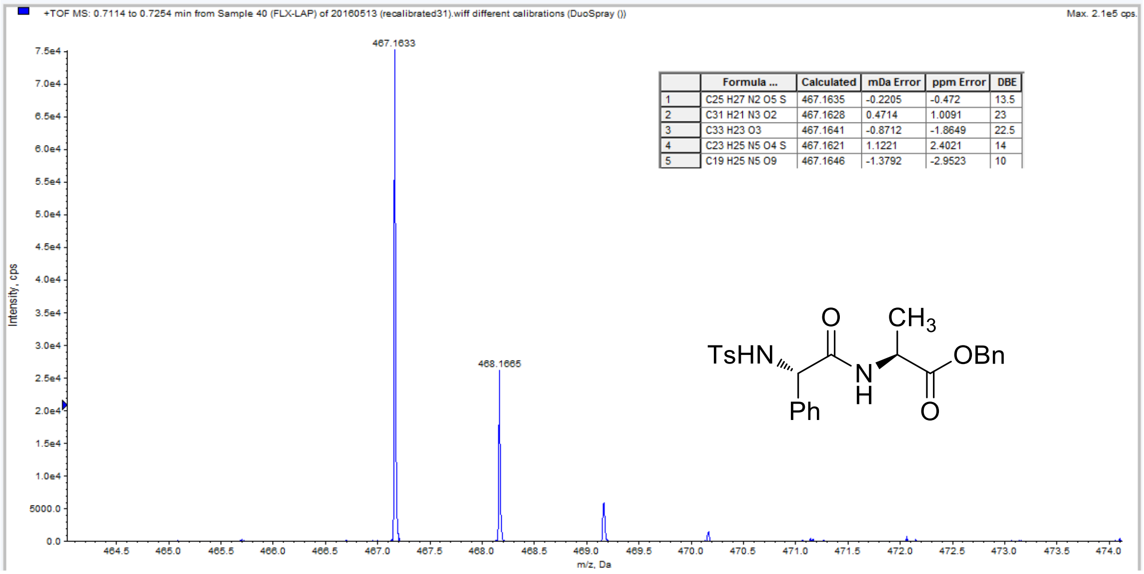


Figure S70. HRMS spectrum of dipeptide derivative **G8-2**.

[1]H NMR spectra of discrimination of enantiomers of (±)-G1-G8.

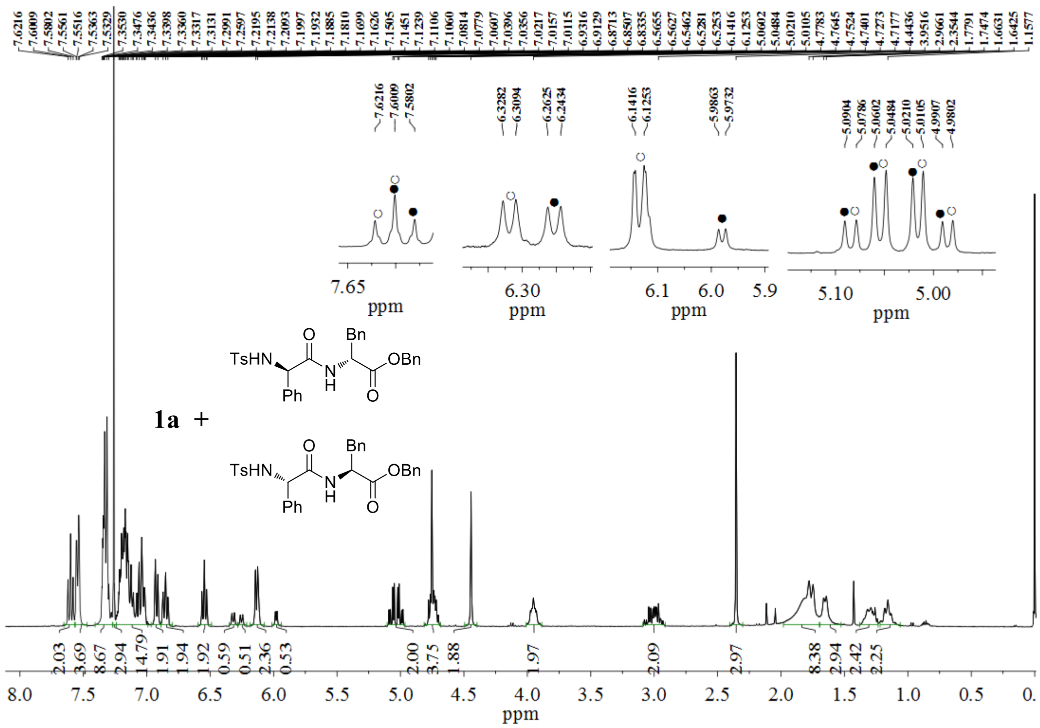


Figure S71. ^{1}H NMR spectrum of **(±)-G1** with TAMCSA **1a** (1:1) in $CDCl_3$ (400 MHz), [**1a**] = 10 mM.

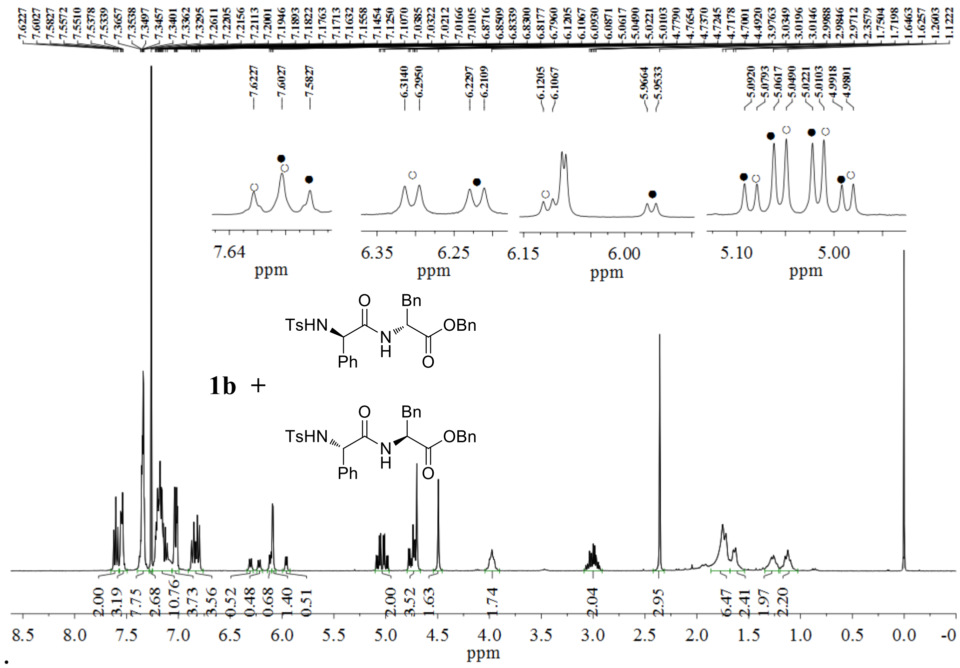


Figure S72. ^{1}H NMR spectrum of **(±)-G1** with TAMCSA **1b** (1:1) in $CDCl_3$ (400 MHz), [**1b**] = 10 mM.

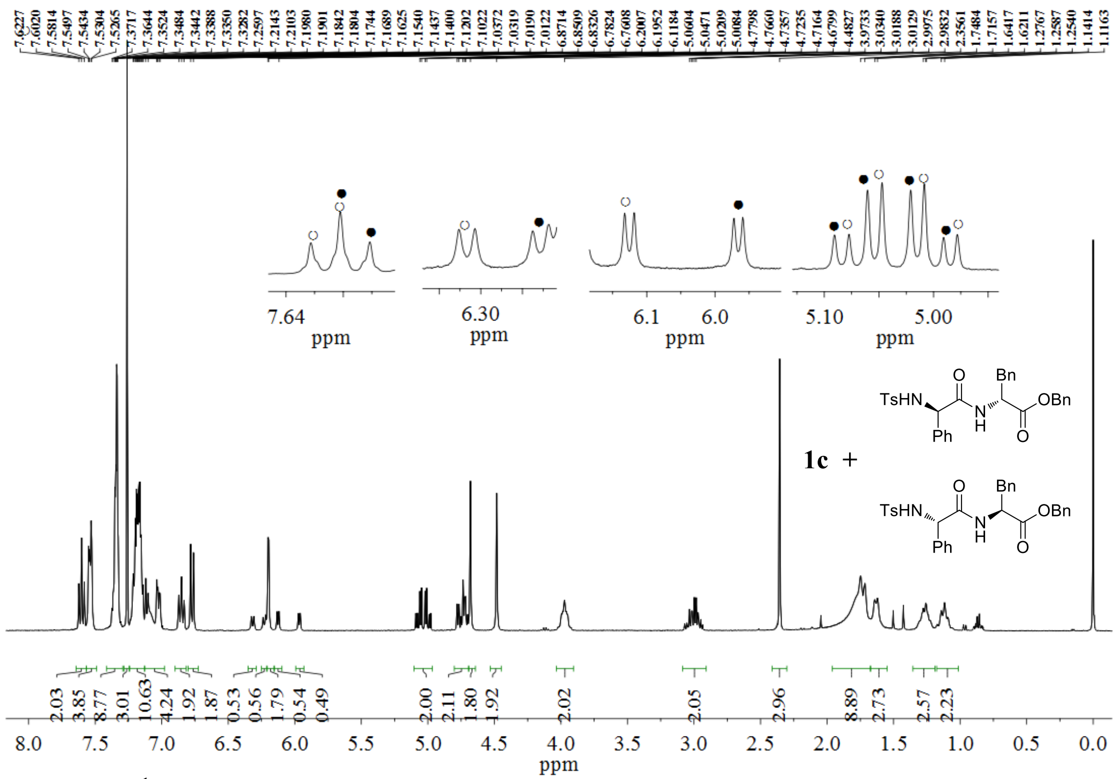


Figure S73. ^{1}H NMR spectrum of **(±)-G1** with TAMCSA **1c** (1:1) in $CDCl_3$ (400 MHz), [**1c**] = 10 mM.

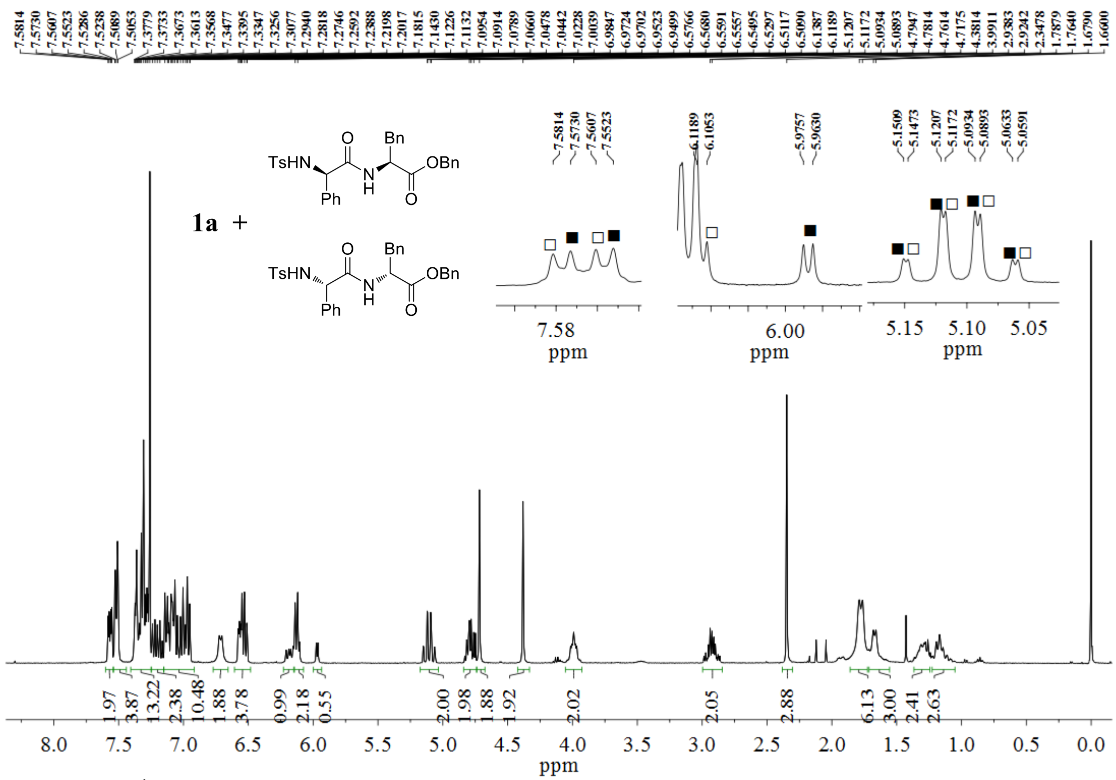


Figure S74. [1]H NMR spectrum of **(±)-G2** with TAMCSA **1a** (1:1) in $CDCl_3$ (400 MHz), [**1a**] = 10 mM.

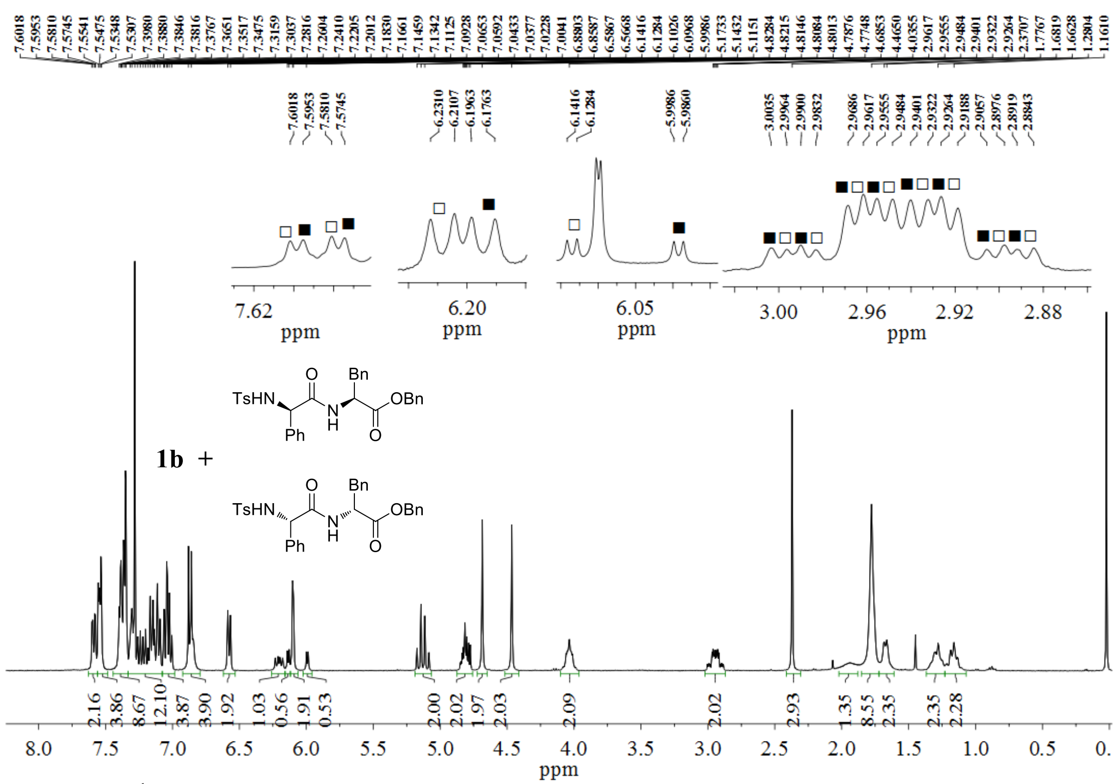


Figure S75. [1]H NMR spectrum of **(±)-G2** with TAMCSA **1b** (1:1) in $CDCl_3$ (400 MHz), [**1b**] = 10 mM.

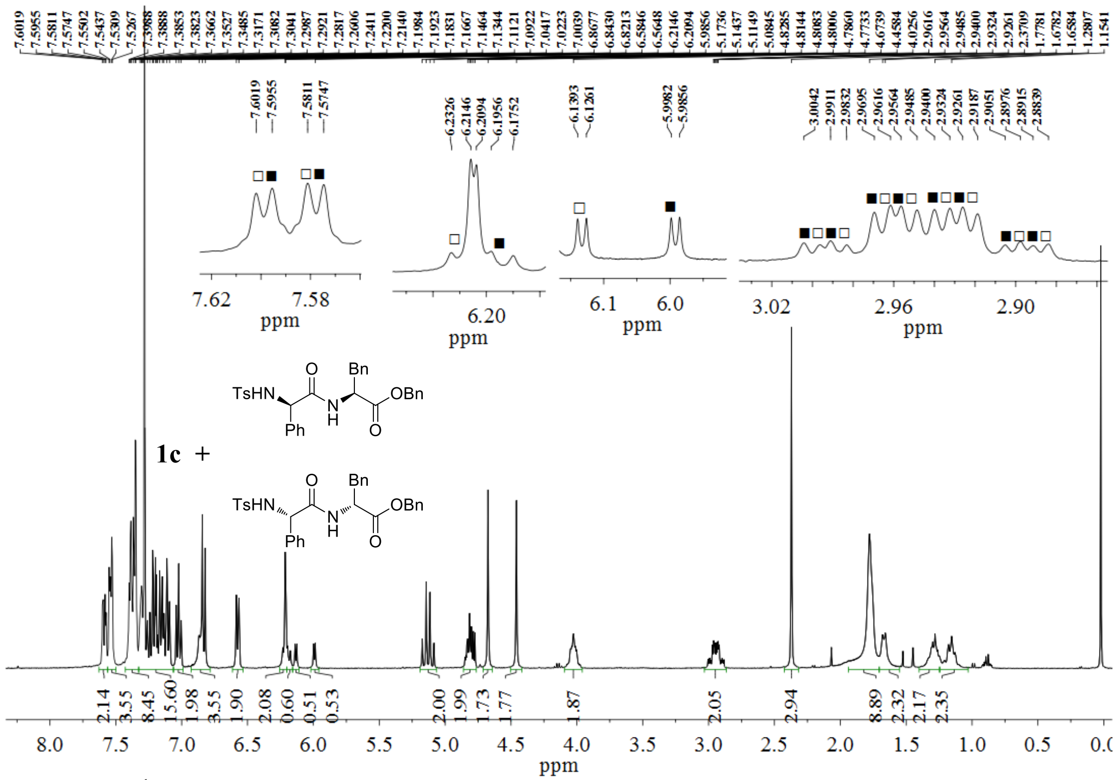


Figure S76. ^{1}H NMR spectrum of **(±)-G2** with TAMCSA **1c** (1:1) in $CDCl_3$ (400 MHz), [**1c**] = 10 mM.

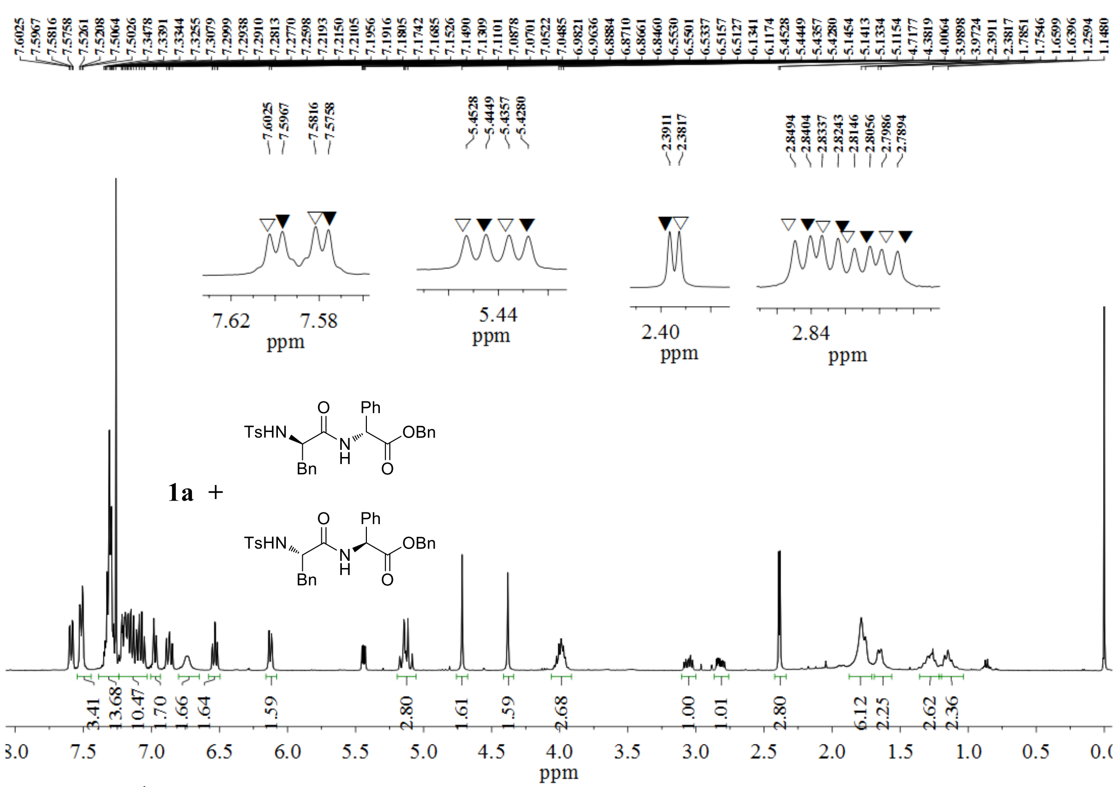


Figure S77. ^{1}H NMR spectrum of **(±)-G3** with TAMCSA **1a** (1:1) in $CDCl_3$ (400 MHz), [**1a**] = 10 mM.

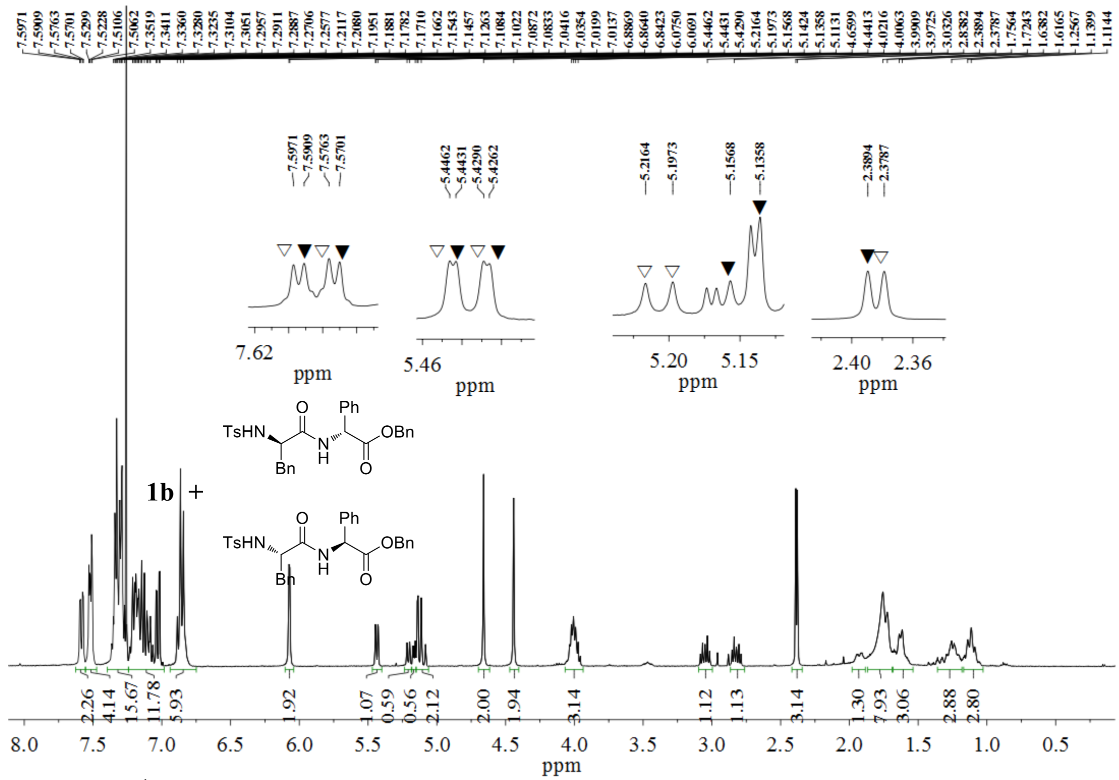


Figure S78. ^{1}H NMR spectrum of **(±)-G3** with TAMCSA **1b** (1:1) in $CDCl_3$ (400 MHz), [**1b**] = 10 mM.

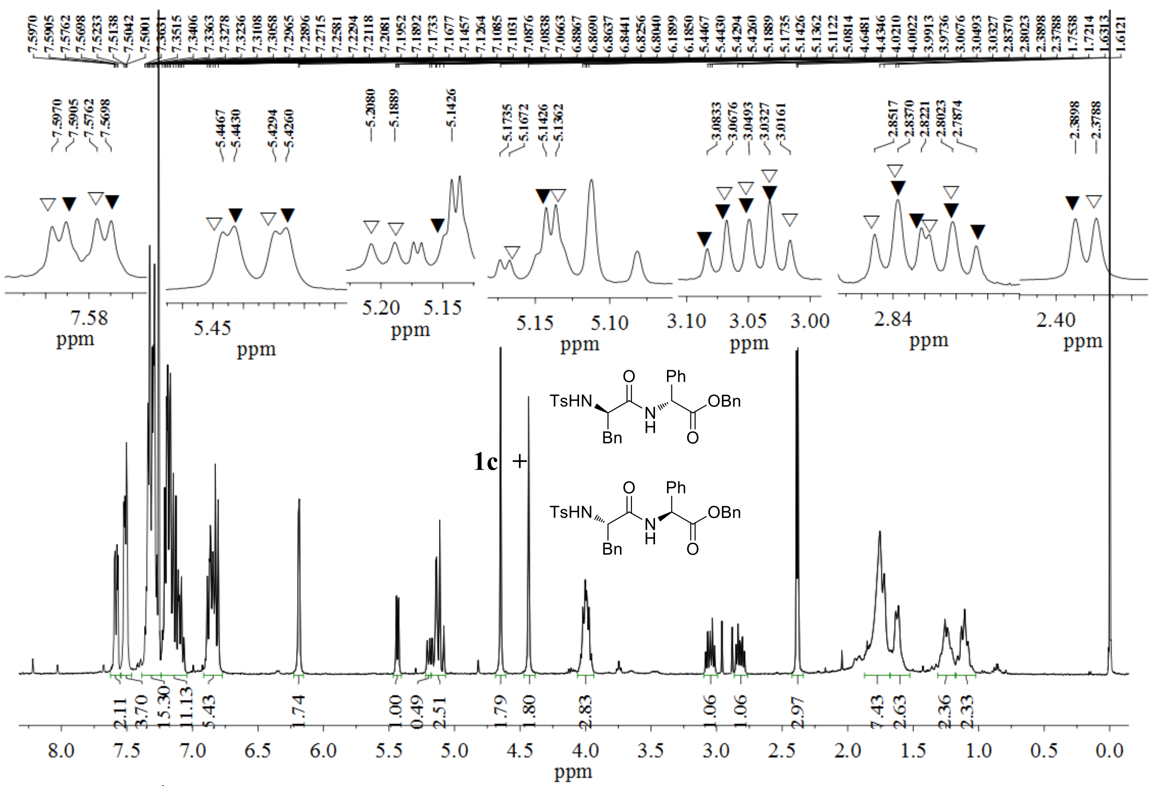


Figure S79. ^{1}H NMR spectrum of **(±)-G3** with TAMCSA **1c** (1:1) in $CDCl_3$ (400 MHz), [**1c**] = 10 mM.

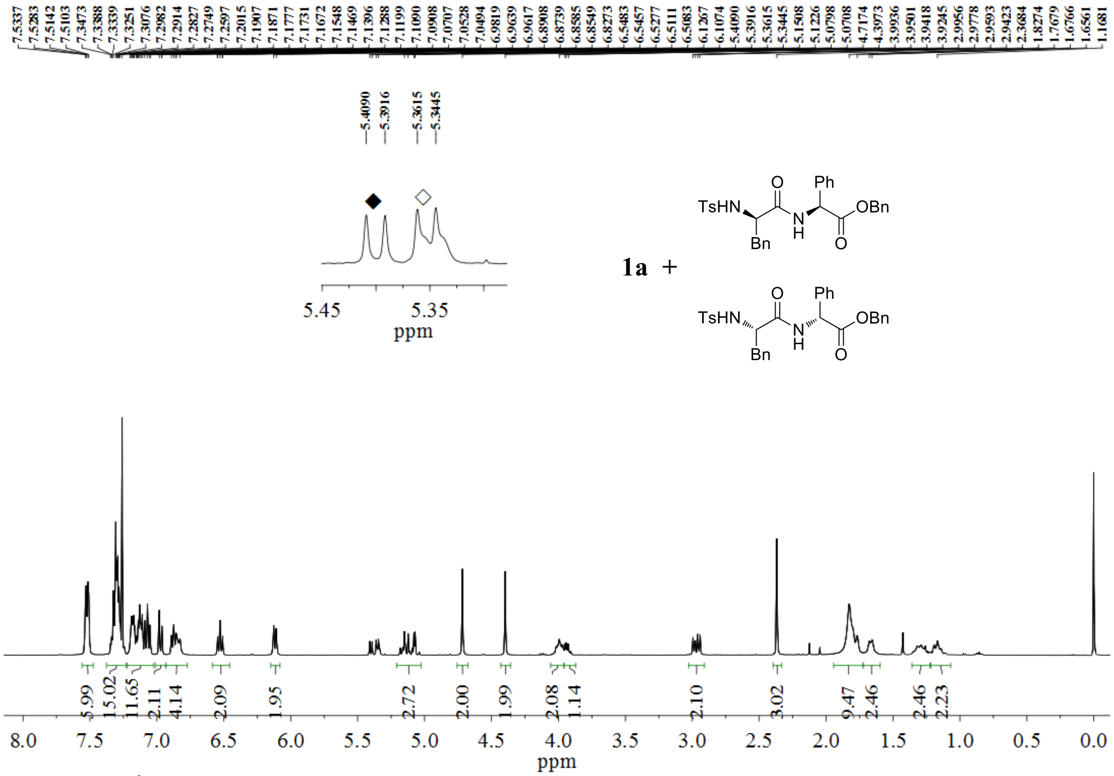


Figure S80.[1]H NMR spectrum of **(±)-G4** with TAMCSA **1a** (1:1) in $CDCl_3$ (400 MHz), [**1a**] = 10 mM.

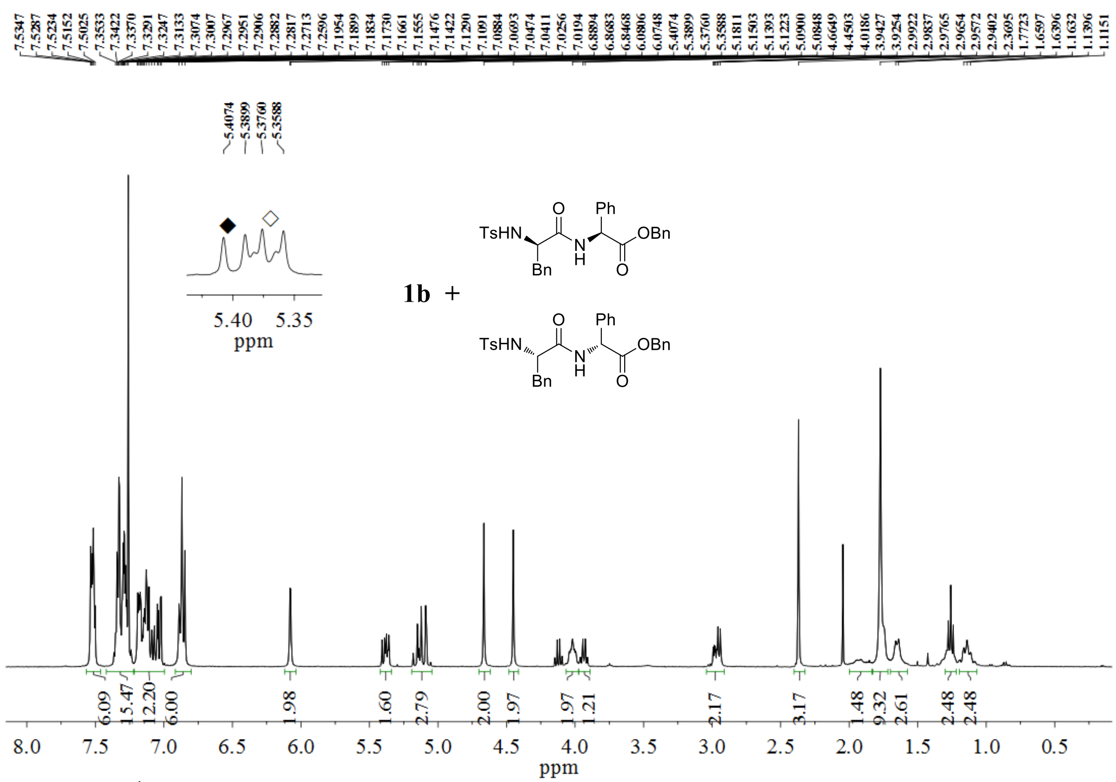


Figure S81.[1]H NMR spectrum of **(±)-G4** with TAMCSA **1b** (1:1) in $CDCl_3$ (400 MHz), [**1b**] = 10 mM.

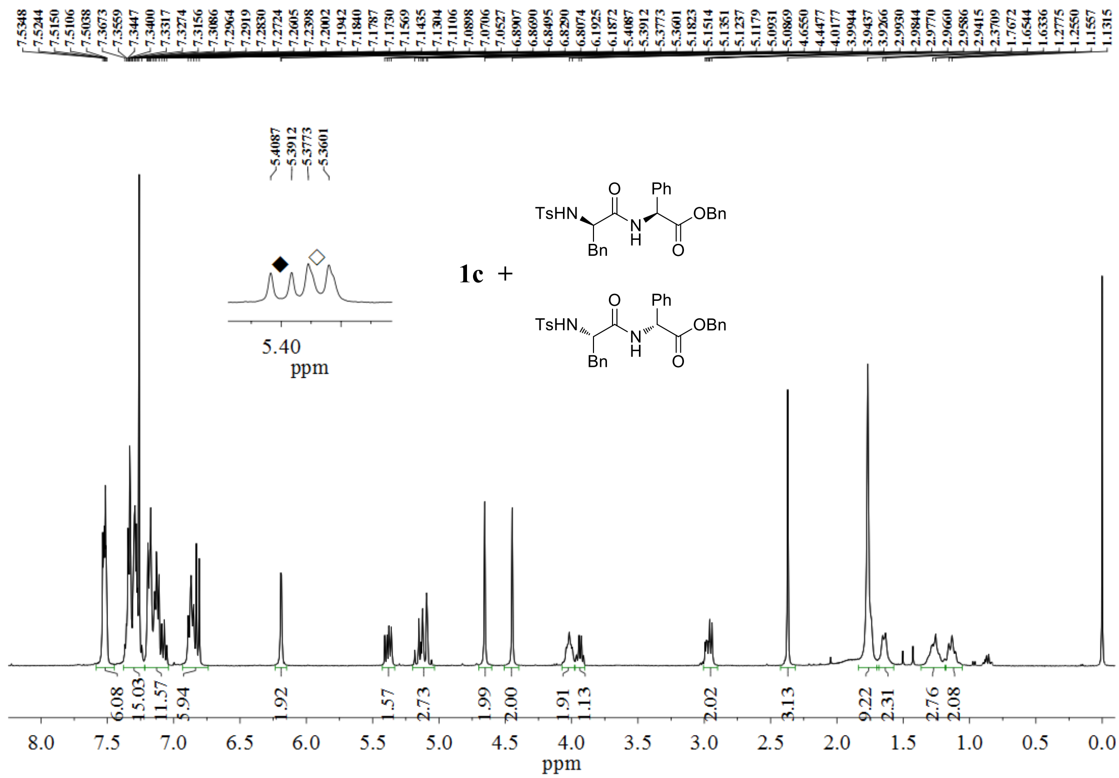


Figure S82. ^{1}H NMR spectrum of 1:1 mixture of **1c** with **(±)-G4** (1:1) in $CDCl_3$ (400 MHz), [**1c**] = 10 mM.

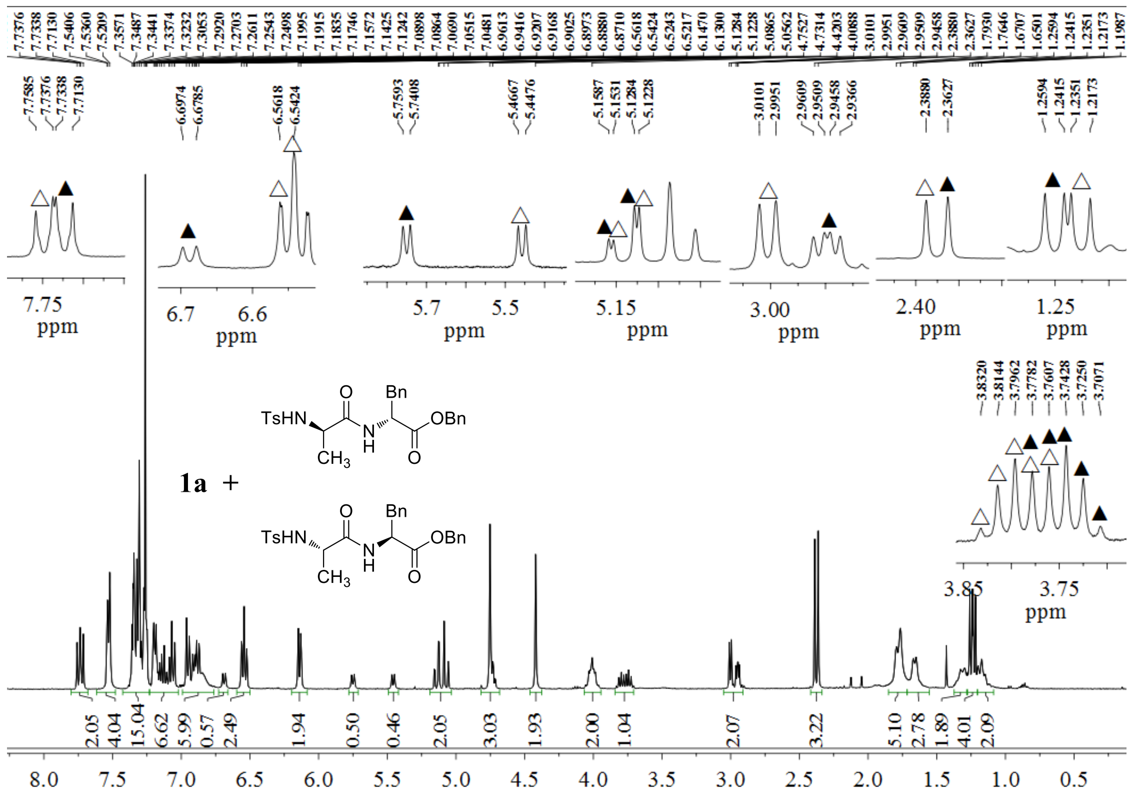


Figure S83.^{1}H NMR spectrum of **(±)-G5** with TAMCSA **1a** (1:1) in $CDCl_3$ (400 MHz), [**1a**] = 10 mM.

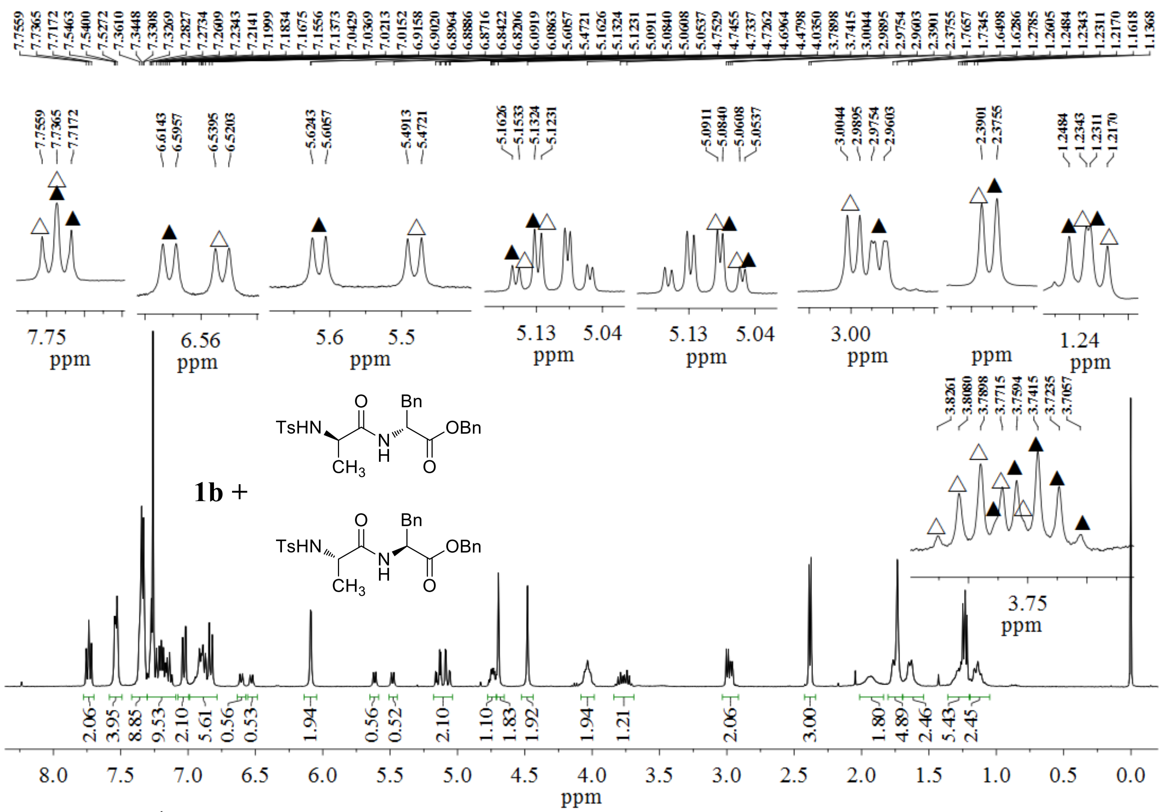


Figure S84.[1]H NMR spectrum of **(±)-G5** with TAMCSA **1b** (1:1) in $CDCl_3$ (400 MHz), [**1b**] = 10 mM.

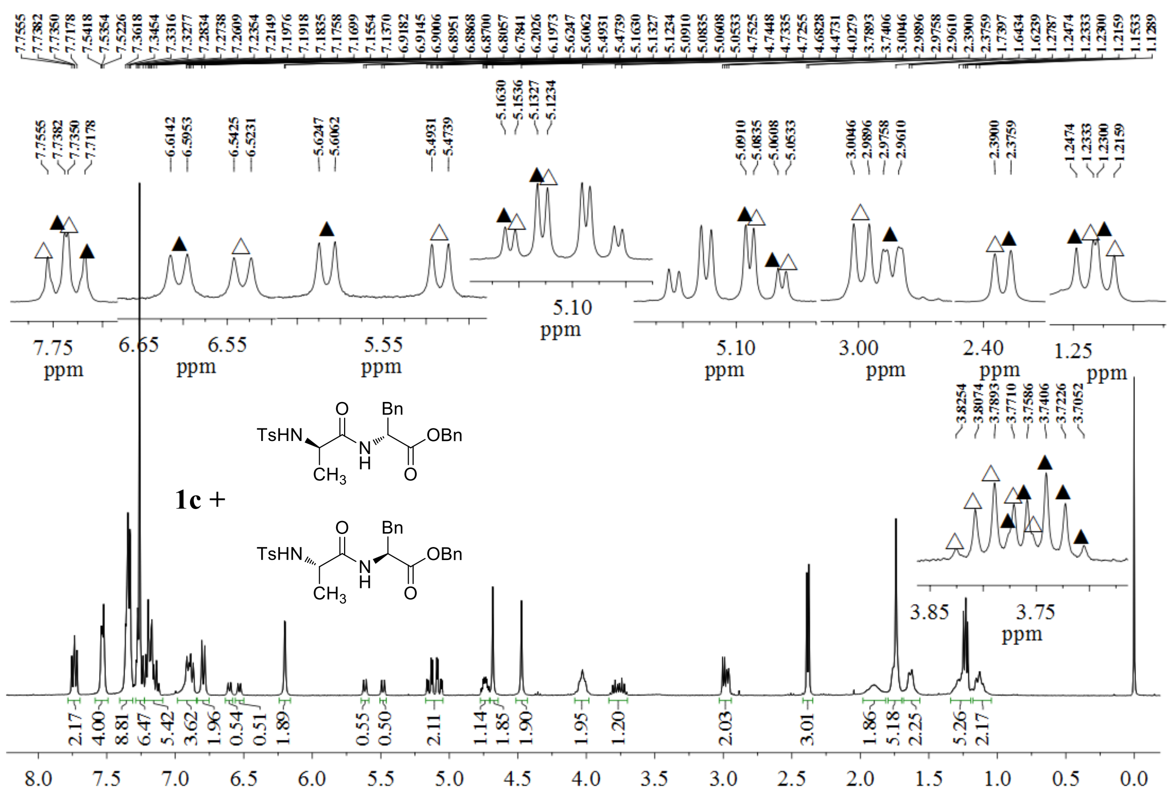


Figure S85.[1]H NMR spectrum of **(±)-G5** with TAMCSA **1c** (1:1) in $CDCl_3$ (400 MHz), [**1c**] = 10 mM.

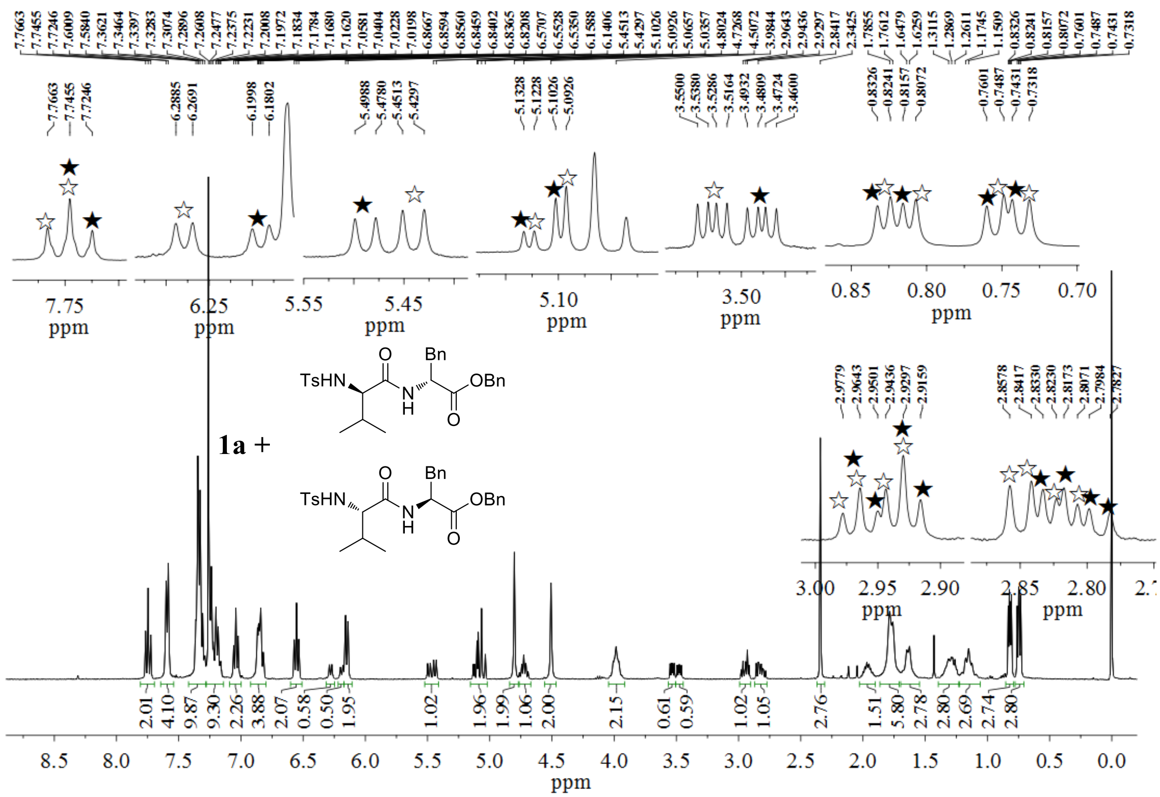


Figure S86.[1]H NMR spectrum of **(±)-G6** with TAMCSA **1a** (1:1) in $CDCl_3$ (400 MHz), [**1a**] = 10 mM.

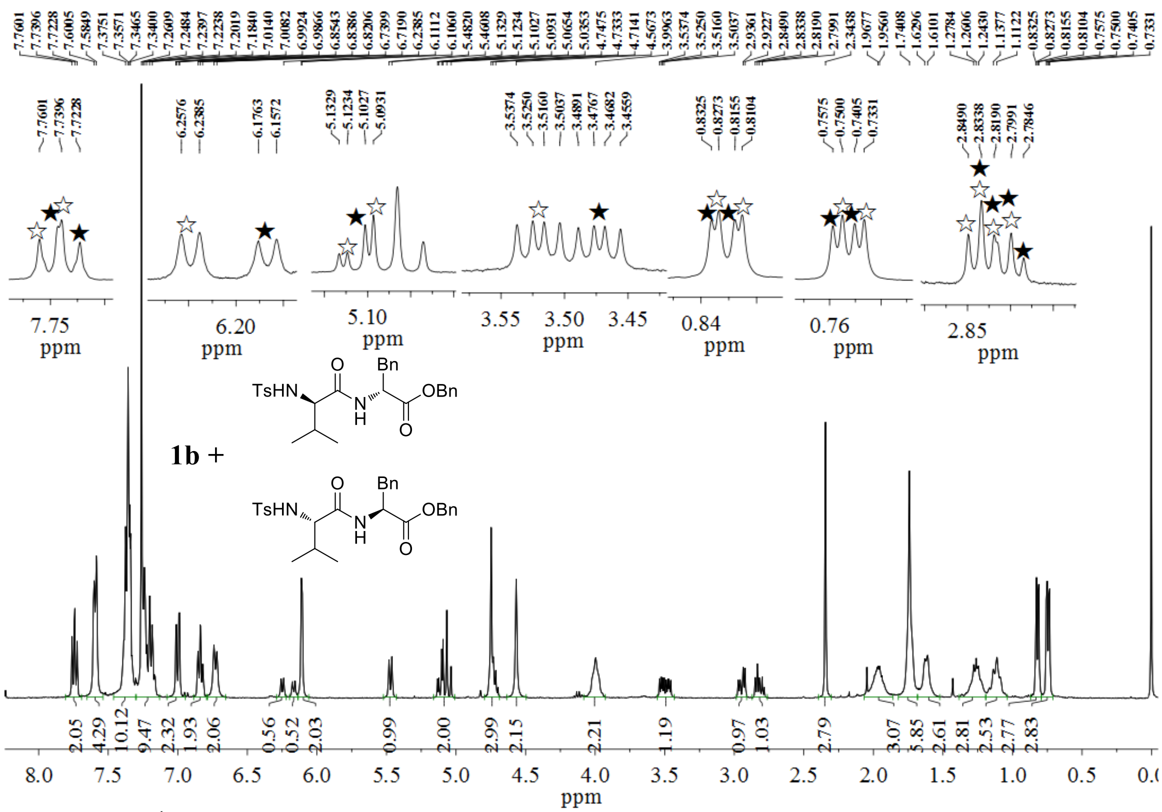


Figure S87.[1]H NMR spectrum of **(±)-G6** with TAMCSA **1b** (1:1) in $CDCl_3$ (400 MHz), [**1b**] = 10 mM.

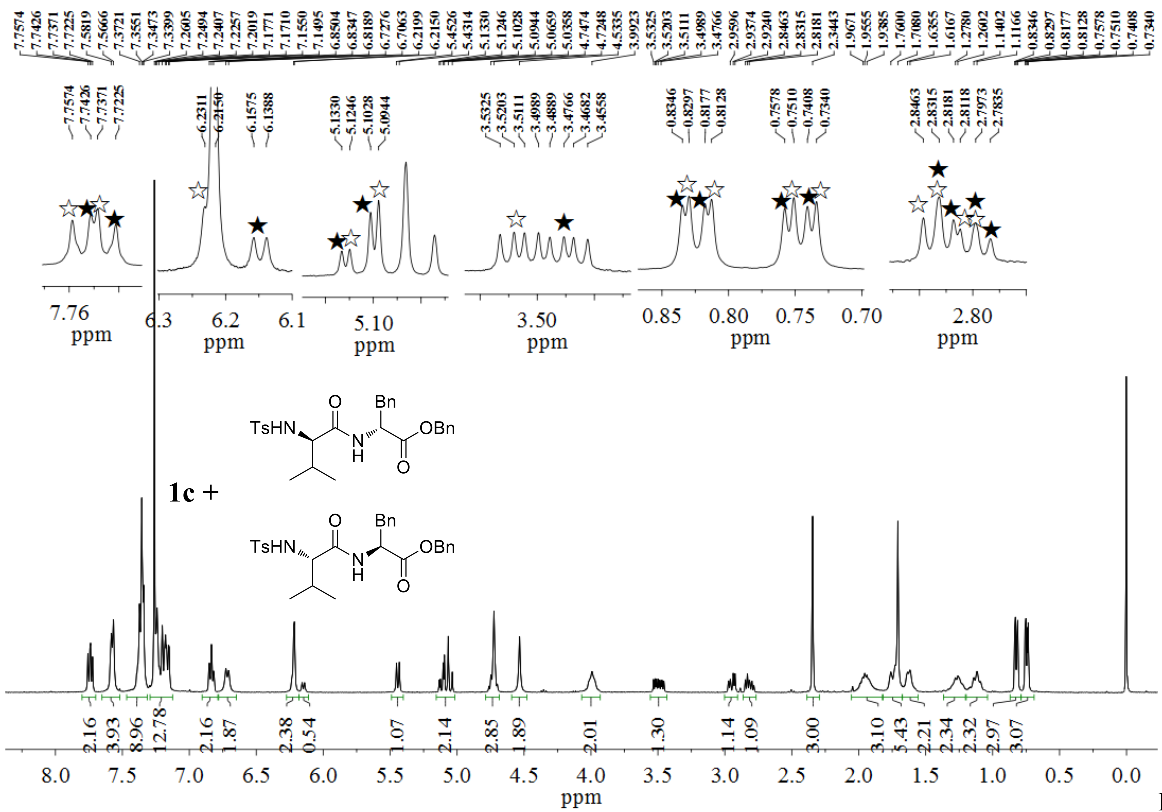


Figure S88. [1]H NMR spectrum of **(±)-G6** with TAMCSA **1c** (1:1) in $CDCl_3$ (400 MHz), [**1c**] = 10 mM.

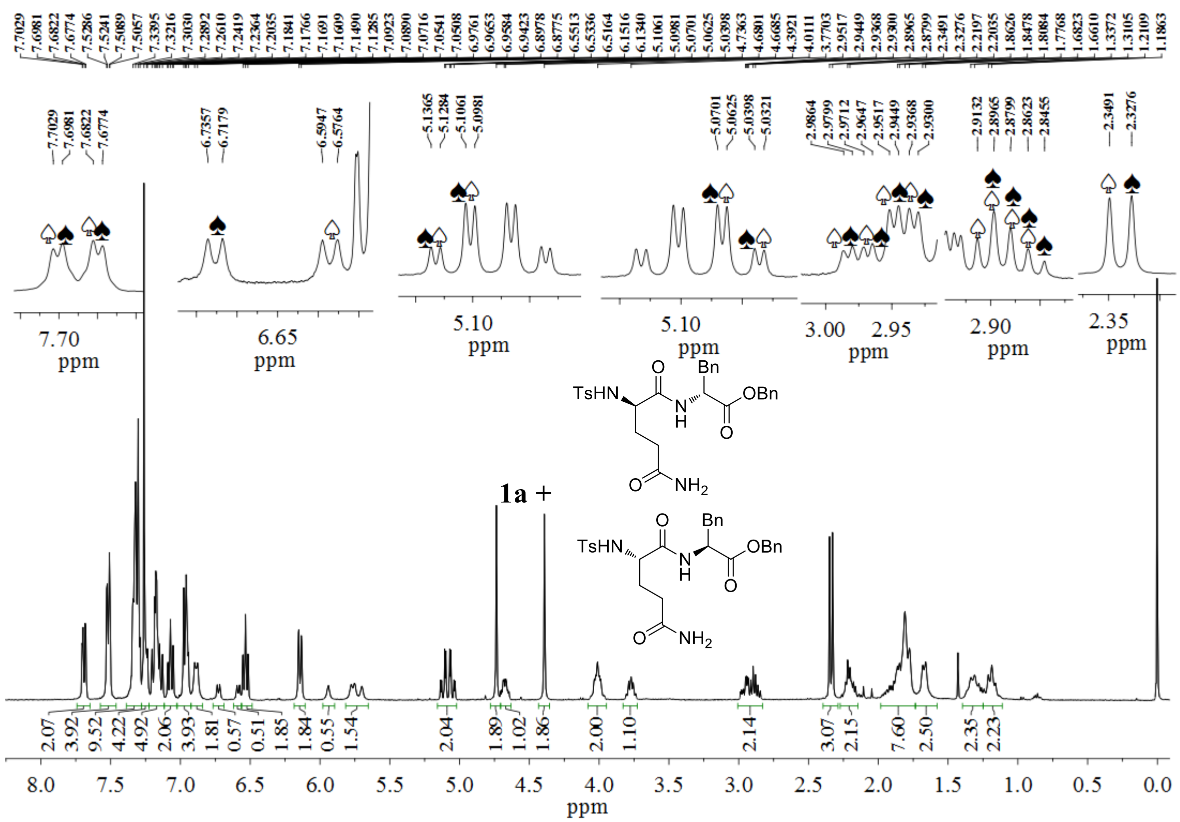


Figure S89. [1]H NMR spectrum of **(±)-G7** with TAMCSA **1a** (1:1) in $CDCl_3$ (400 MHz), [**1a**] = 10 mM.

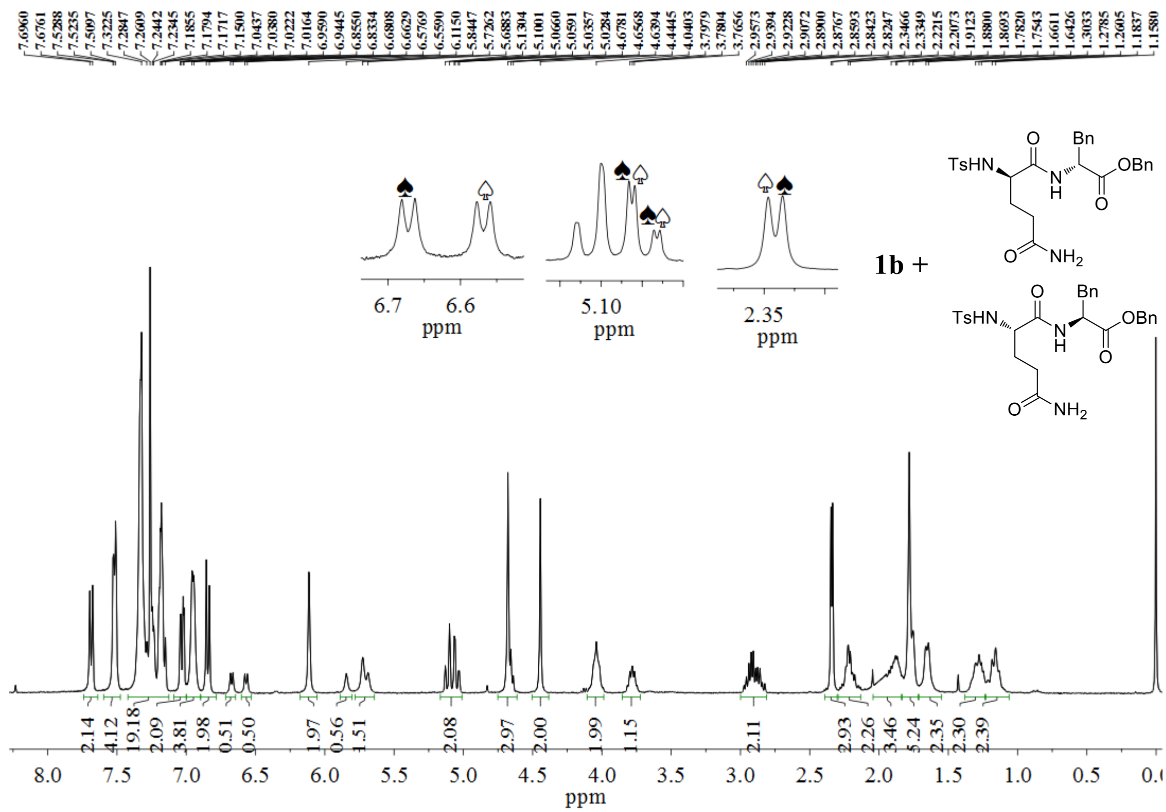


Figure S90.[1]H NMR spectrum of **(±)-G7** with TAMCSA **1b** (1:1) in $CDCl_3$ (400 MHz), [**1b**] = 10 mM.

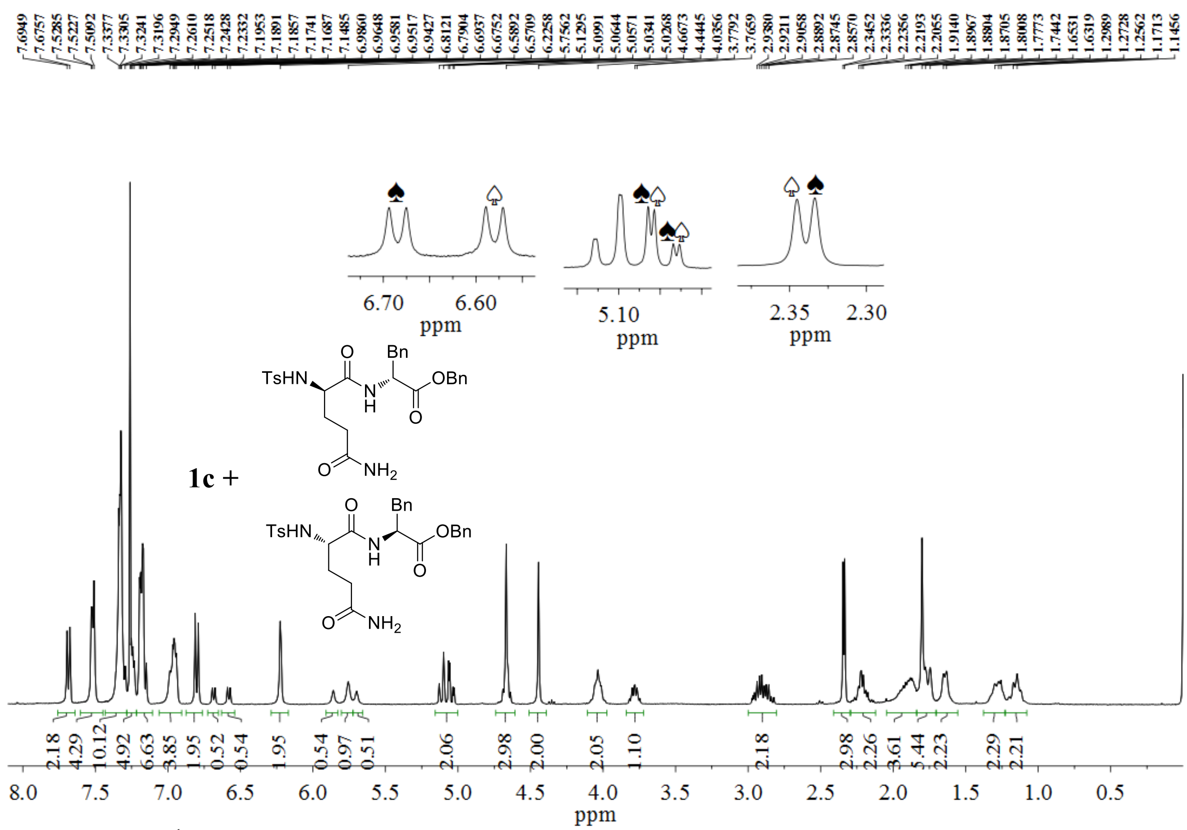


Figure S91.[1]H NMR spectrum of **(±)-G7** with TAMCSA **1c** (1:1) in $CDCl_3$ (400 MHz), [**1c**] = 10 mM.

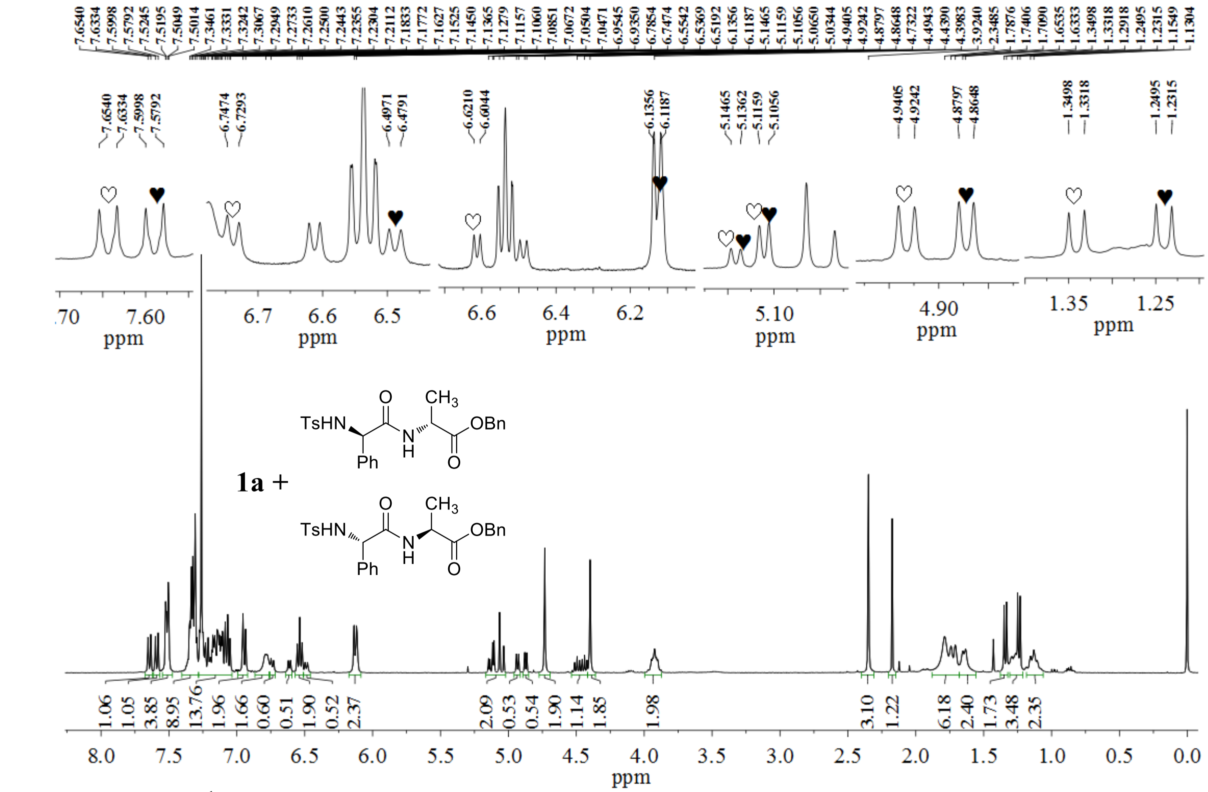


Figure S92.[1]H NMR spectrum of **(±)-G8** with TAMCSA **1a** (1:1) in $CDCl_3$ (400 MHz), [**1a**] = 10 mM.

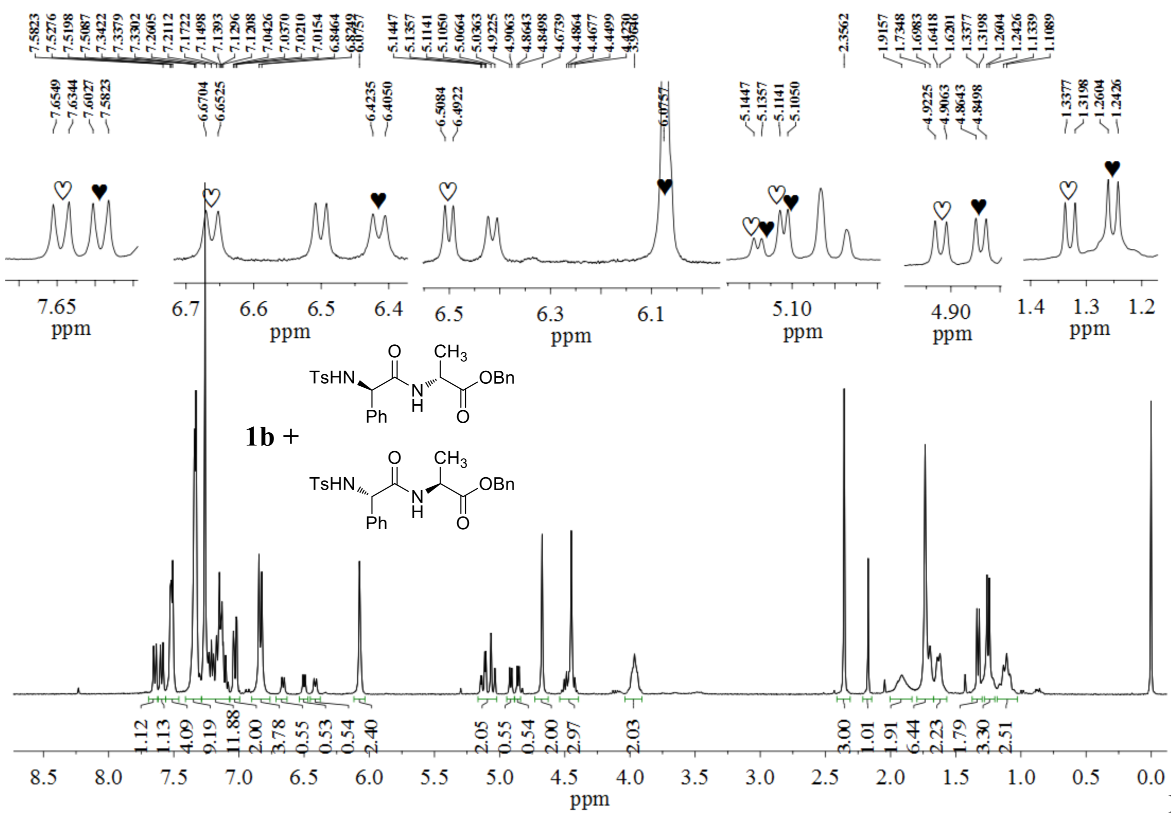


Figure S93.[1]H NMR spectrum of 1:1 mixture of **1b** with **(±)-G8** (1:1) in $CDCl_3$ (400 MHz), [**1b**] = 10 mM.

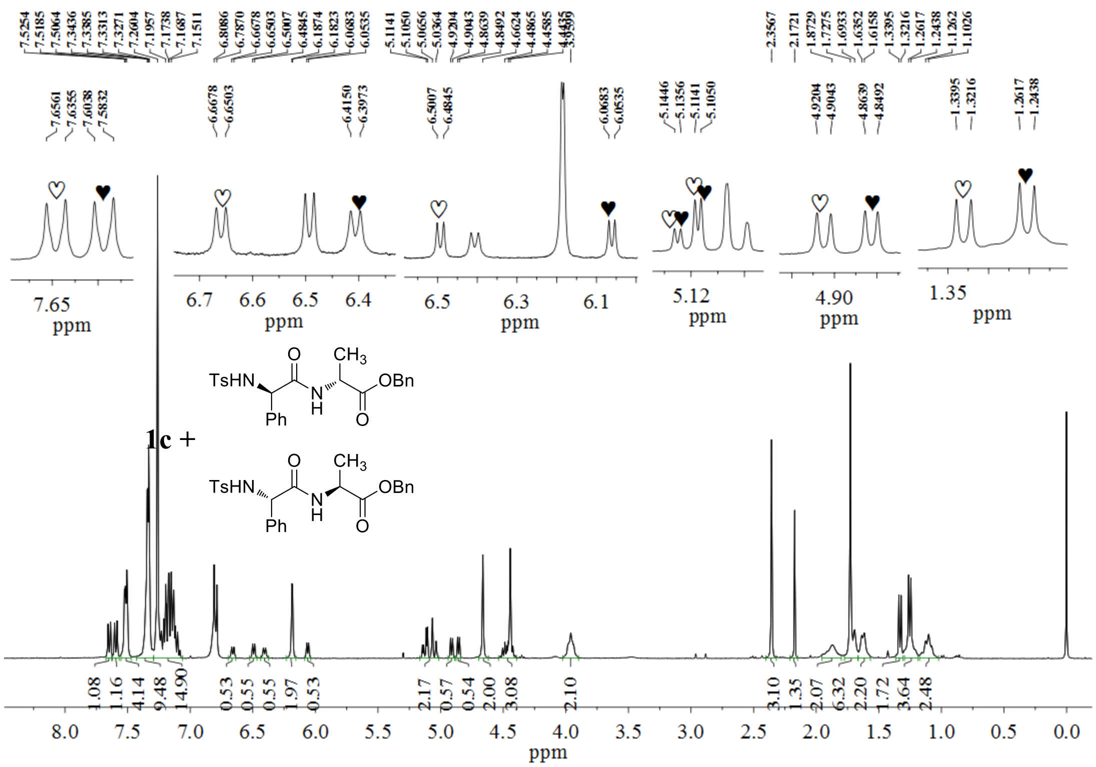


Figure S94.[1]H NMR spectrum of **(±)-G8** with TAMCSA **1c** (1:1) in $CDCl_3$ (400 MHz), [**1c**] = 10 mM.

[1]H NMR spectra of determination of enantiomeric excesses of G1 in the presence of TAMCSA 1c.

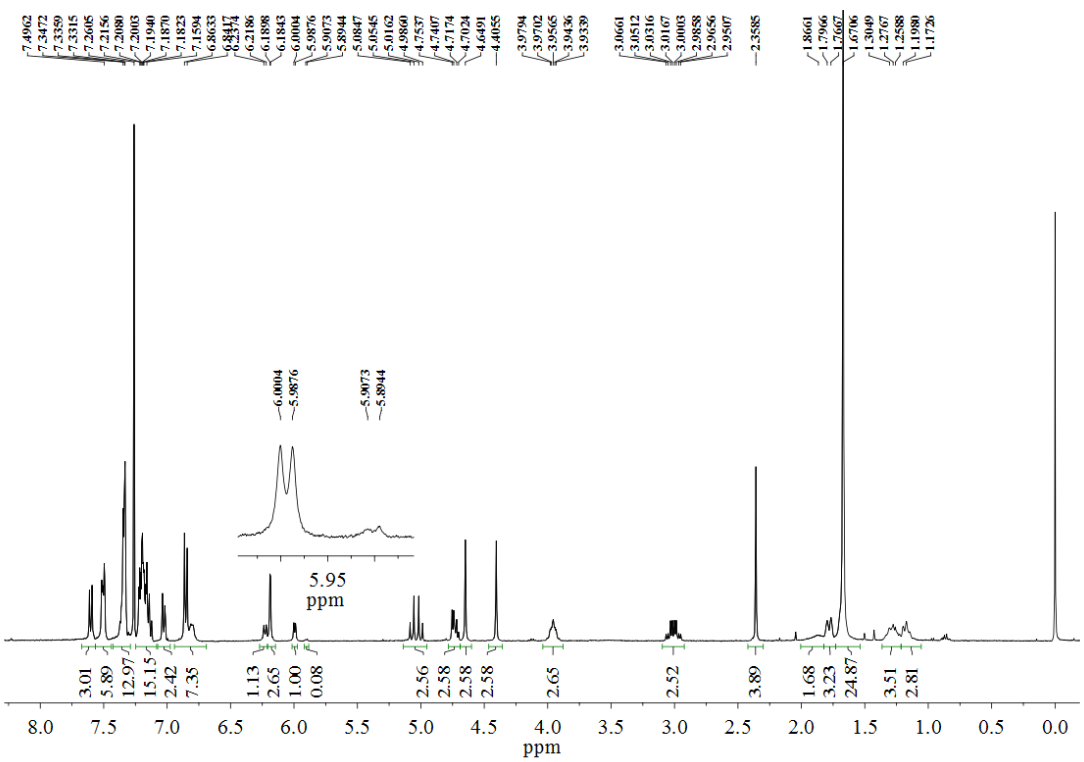


Figure S95.[1]H NMR spectrum of **G1-1** and **G1-2** (*ee* $_{G1-1}$% = 85 %**)** with TAMCSA **1c** in $CDCl_3$ (400 MHz), [**1c**] = 5 mM.

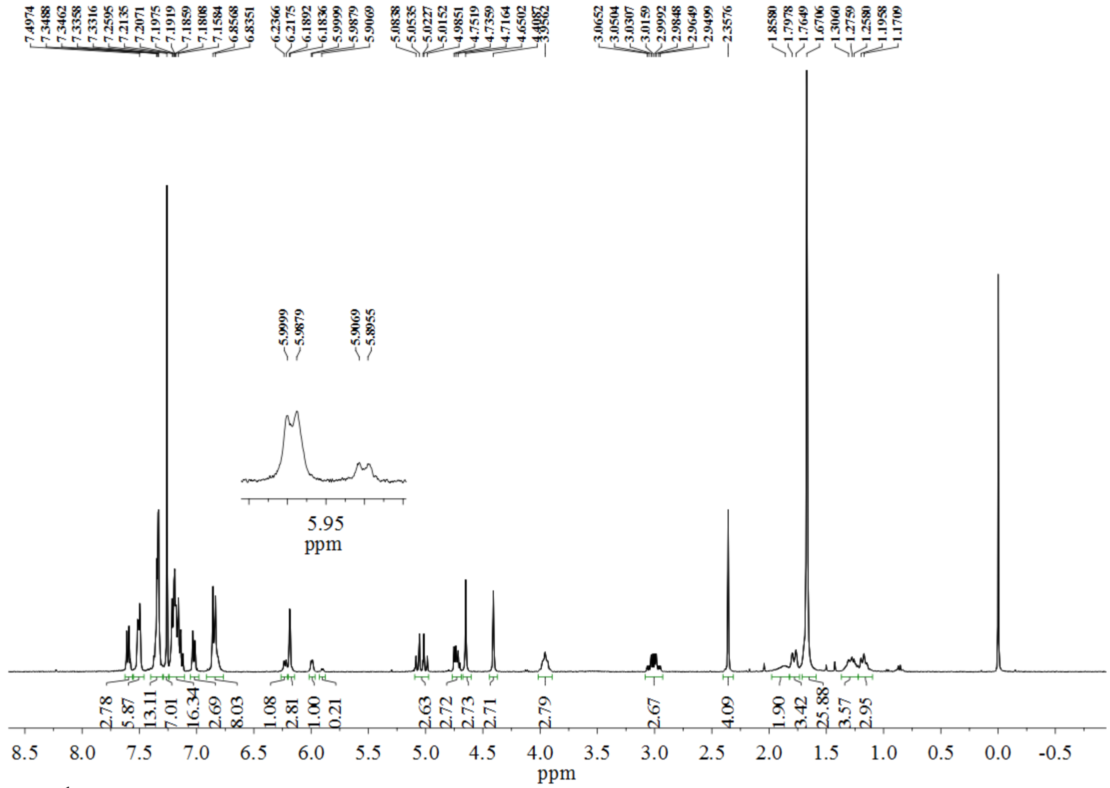


Figure S96.[1]H NMR spectrum of **G1-1** and **G1-2** (*ee* $_{\mathbf{G1\text{-}1}}$% = 65 %**)** with TAMCSA **1c** in $CDCl_3$ (400 MHz), [**1c**] = 5 mM.

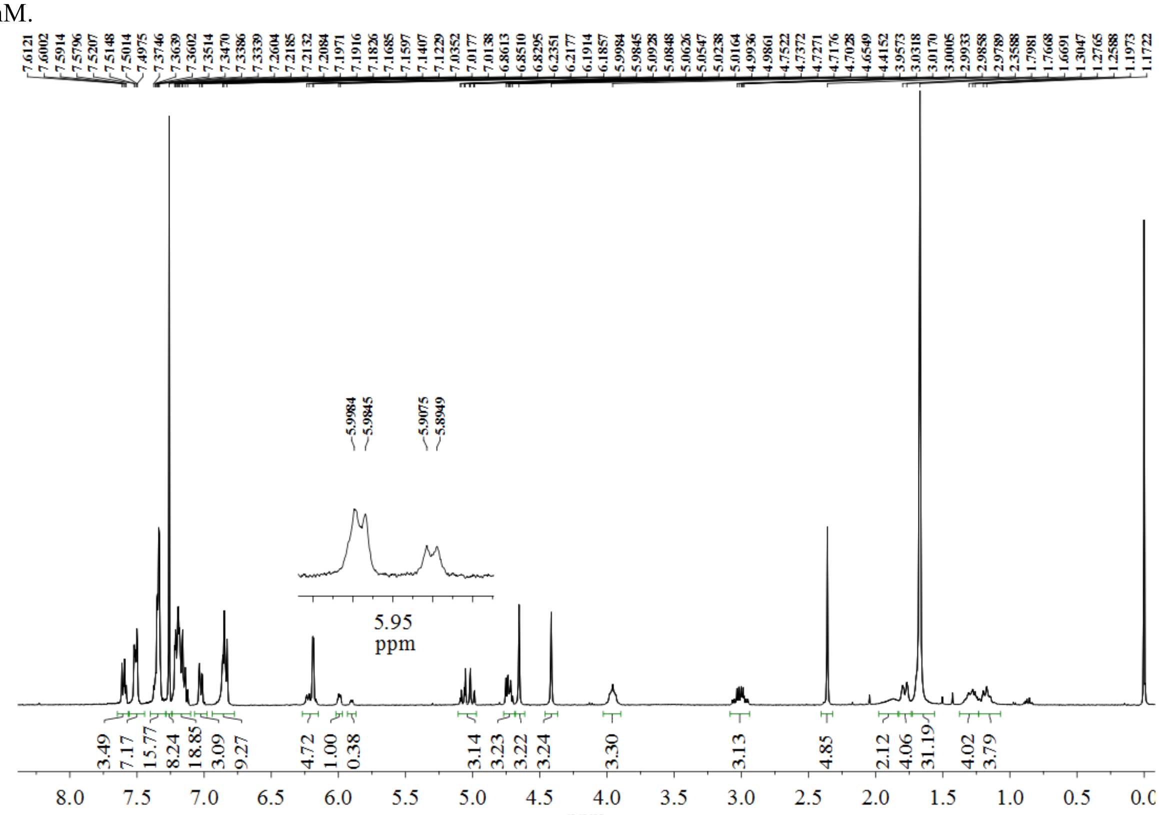


Figure S97.[1]H NMR spectrum of **G1-1** and **G1-2** (*ee* $_{\mathbf{G1\text{-}1}}$% = 45 %**)** with TAMCSA **1c** in $CDCl_3$ (400 MHz), [**1c**] = 5 mM.

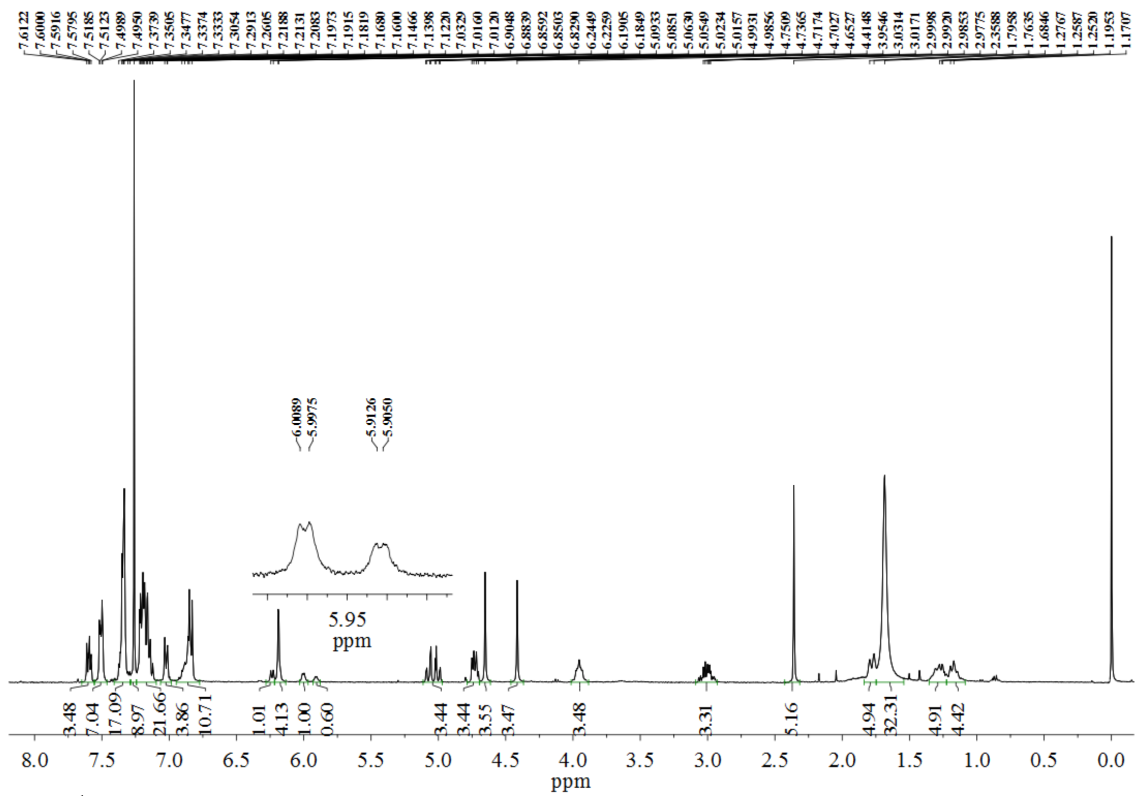


Figure S98.[1]H NMR spectrum of **G1-1** and **G1-2** (*ee* $_{\mathbf{G1\text{-}1}}$% **=** 25 %**)** with TAMCSA **1c** in $CDCl_3$ (400 MHz), [**1c**] = 5 mM.

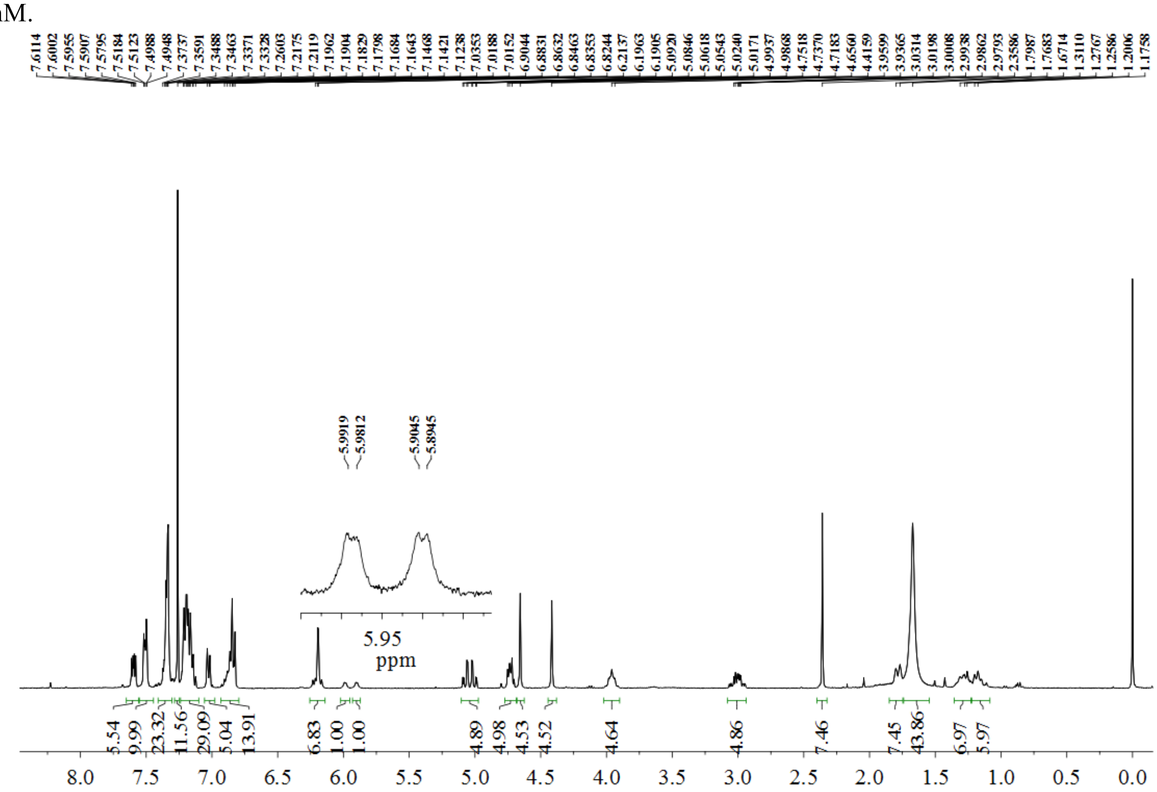


Figure S99.[1]H NMR spectrum of **G1-1** and **G1-2** (*ee* $_{\mathbf{G1\text{-}1}}$% **=** 0 %**)** with TAMCSA **1c** in $CDCl_3$ (400 MHz), [**1c**] = 5 mM.

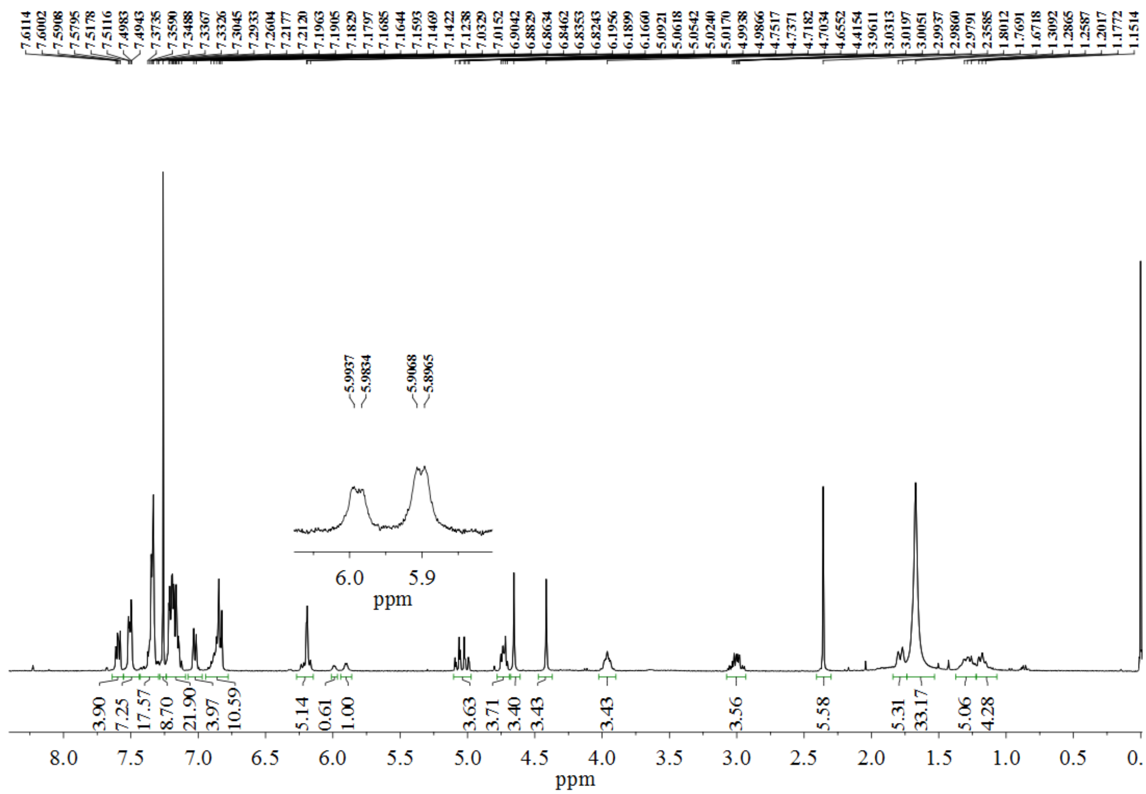


Figure S100.[1]H NMR spectrum of **G1-1** and **G1-2** (*ee* $_{G1-1}$% **= -25 %)** with TAMCSA **1c** in $CDCl_3$ (400 MHz), [**1c**] = 5 mM.

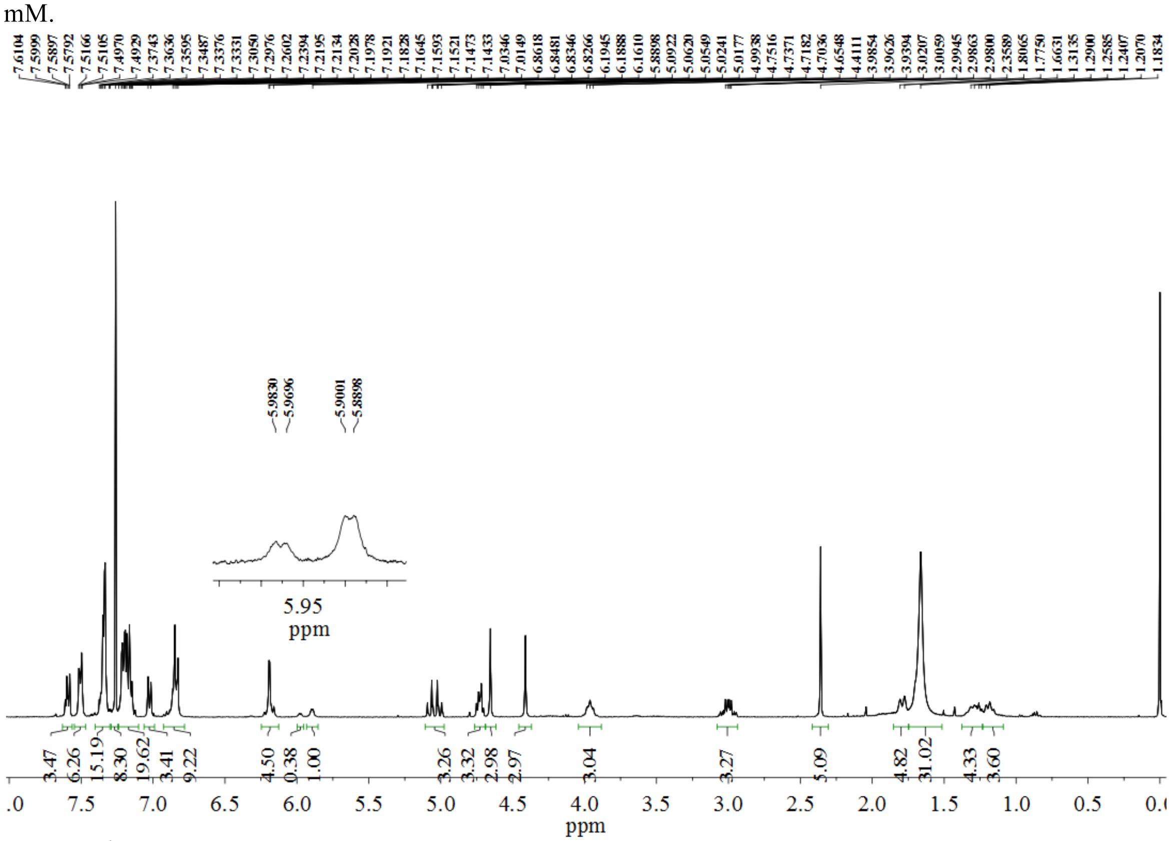


Figure S101.[1]H NMR spectrum of **G1-1** and **G1-2** (*ee* $_{G1-1}$% **= -45 %)** with TAMCSA **1c** in $CDCl_3$ (400 MHz), [**1c**] = 5 mM.

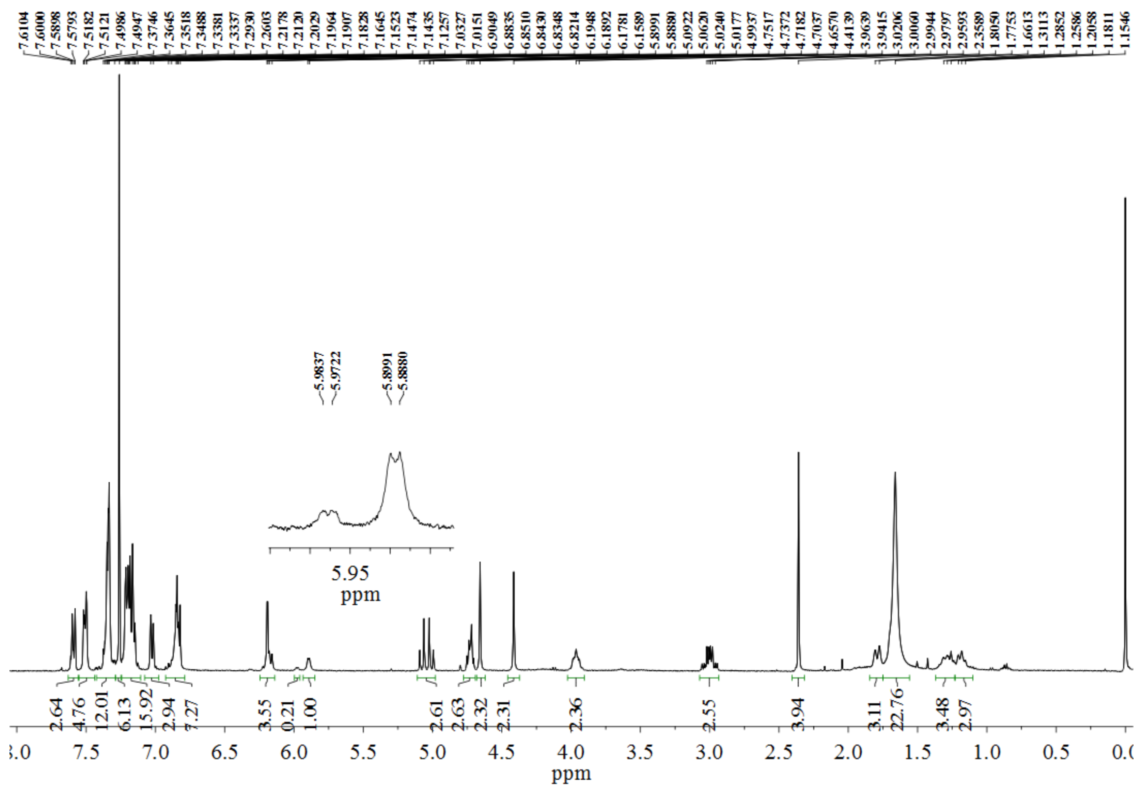


Figure S102. ^{1}H NMR spectrum of **G1-1** and **G1-2** (*ee* $_{\mathbf{G1-1}}$% = -65 %**)** TAMCSA **1c** with in $CDCl_3$ (400 MHz), [**1c**] = 5 mM.

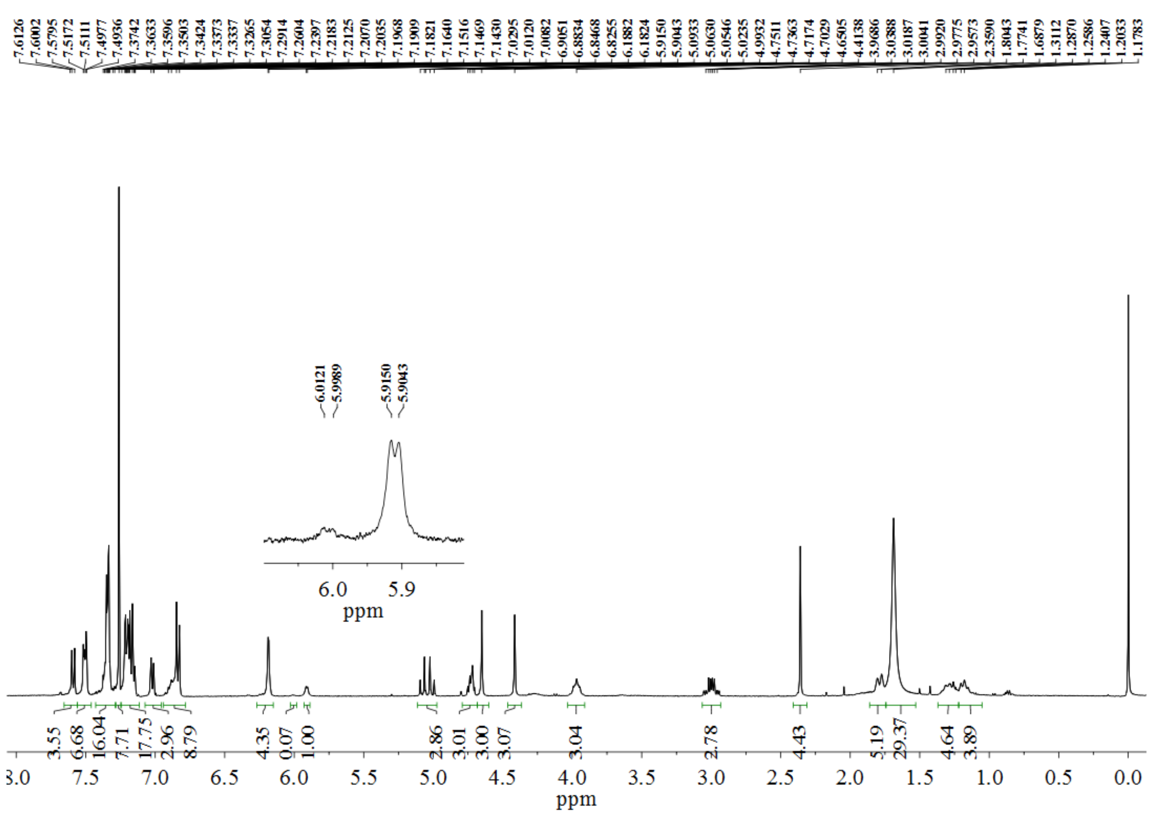


Figure S103. ^{1}H NMR spectrum of **G1-1** and **G1-2** (*ee* $_{\mathbf{G1-1}}$% = -85 %**)** TAMCSA **1c** with in $CDCl_3$ (400 MHz), [**1c**] = 5 mM.

^{1}H NMR spectra of (±)-G1 with TAMCSA 1c (Job plots).

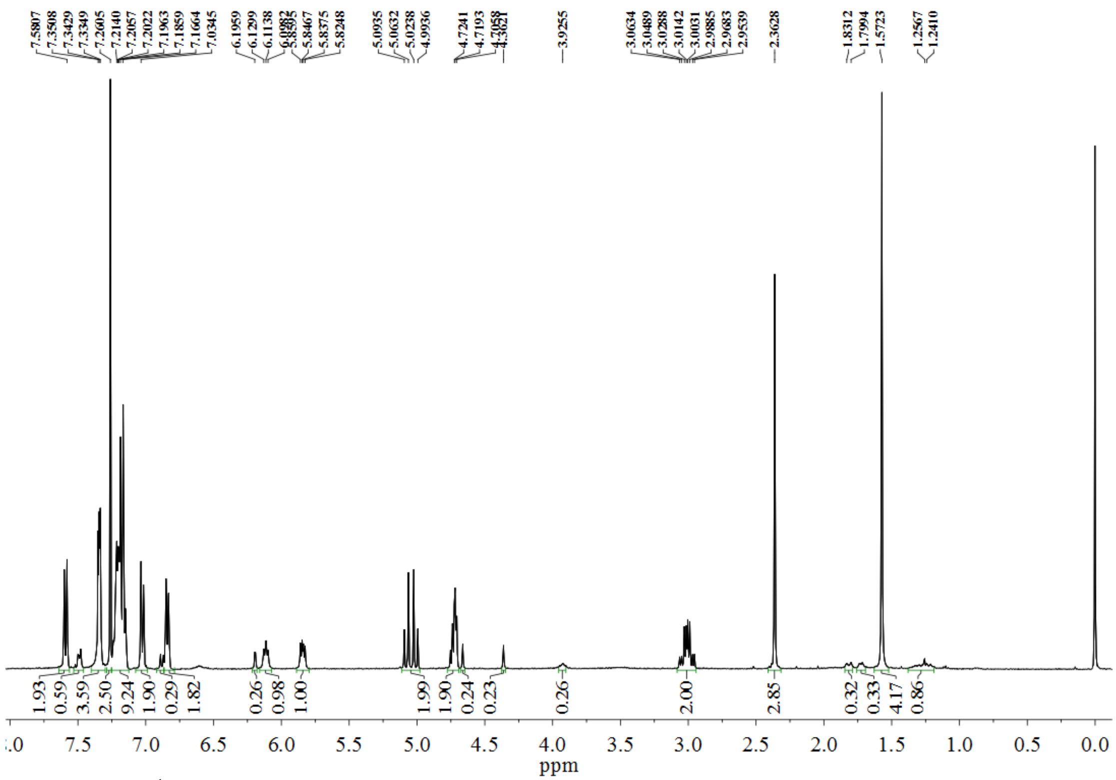


Figure S104. ^{1}H NMR spectrum of **(±)-G1** with TAMCSA **1c** (0.9:0.1) in $CDCl_3$ (400 MHz), [**1c**] + [(±)-**G1**] = 10 mM.

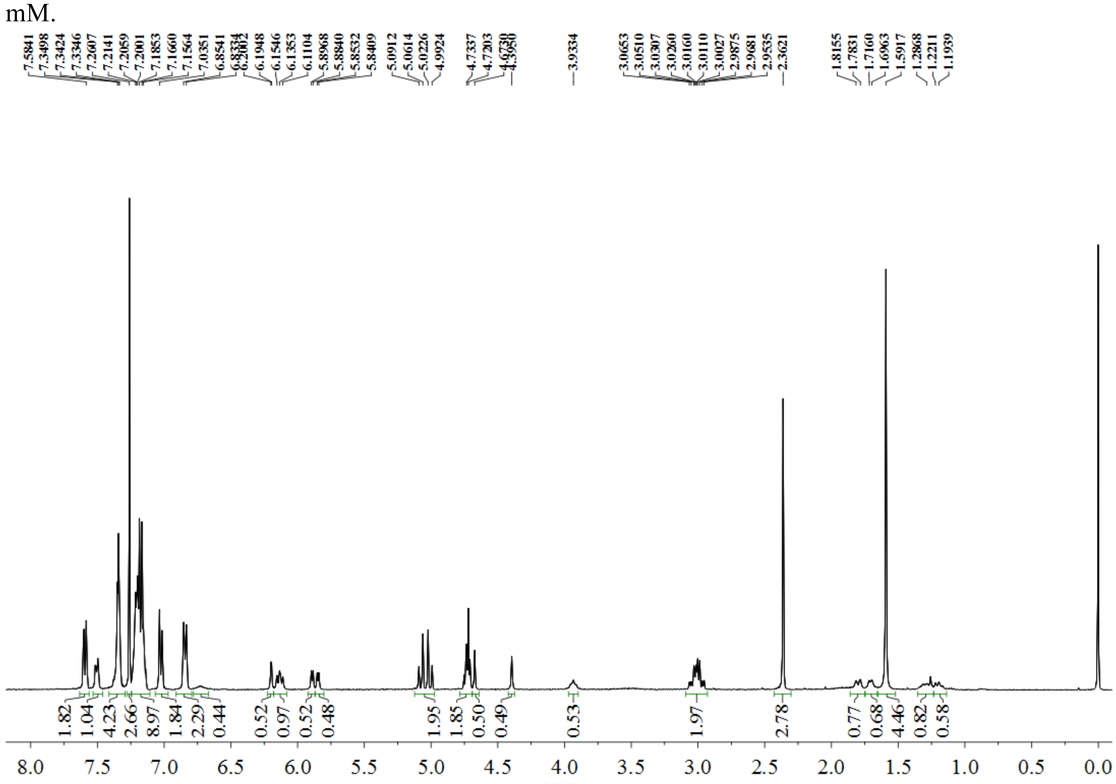


Figure S105. ^{1}H NMR spectrum of **(±)-G1** with TAMCSA **1c** (0.8:0.2) in $CDCl_3$ (400 MHz), [**1c**] + [(±)-**G1**] = 10 mM.

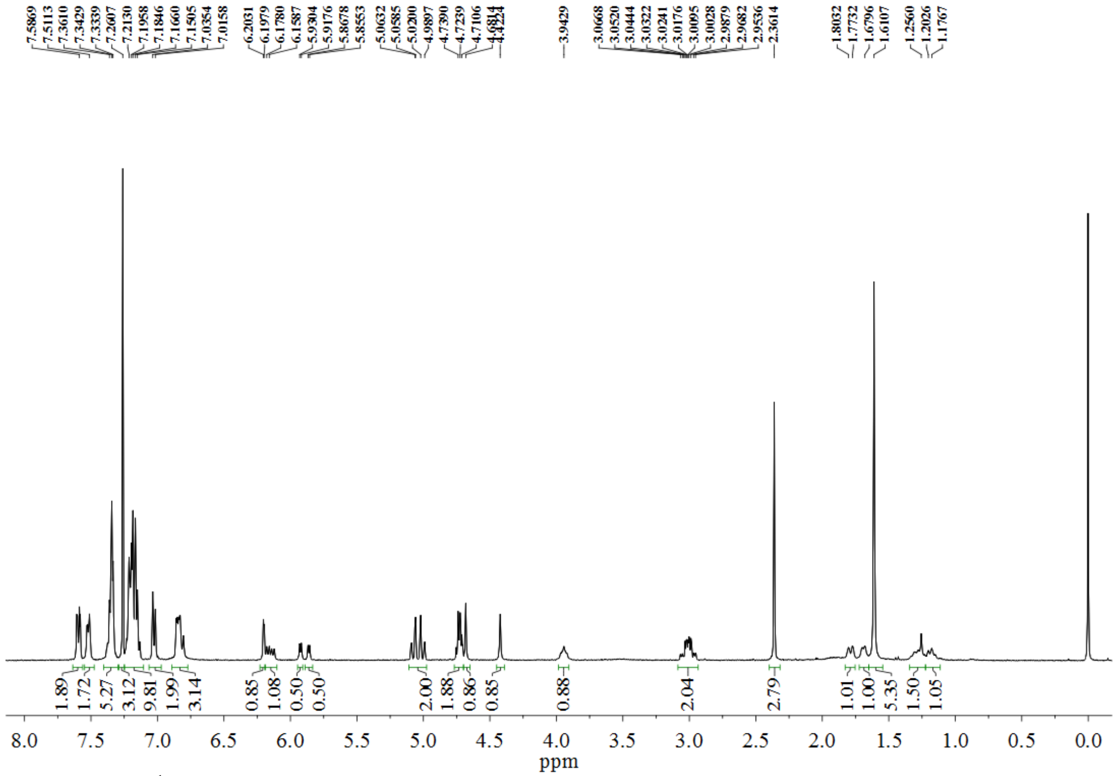


Figure S106. [1]H NMR spectrum of **(±)-G1** with TAMCSA **1c** (0.7:0.3) in $CDCl_3$ (400 MHz), [**1c**] + [(±)-**G1**] = 10 mM.

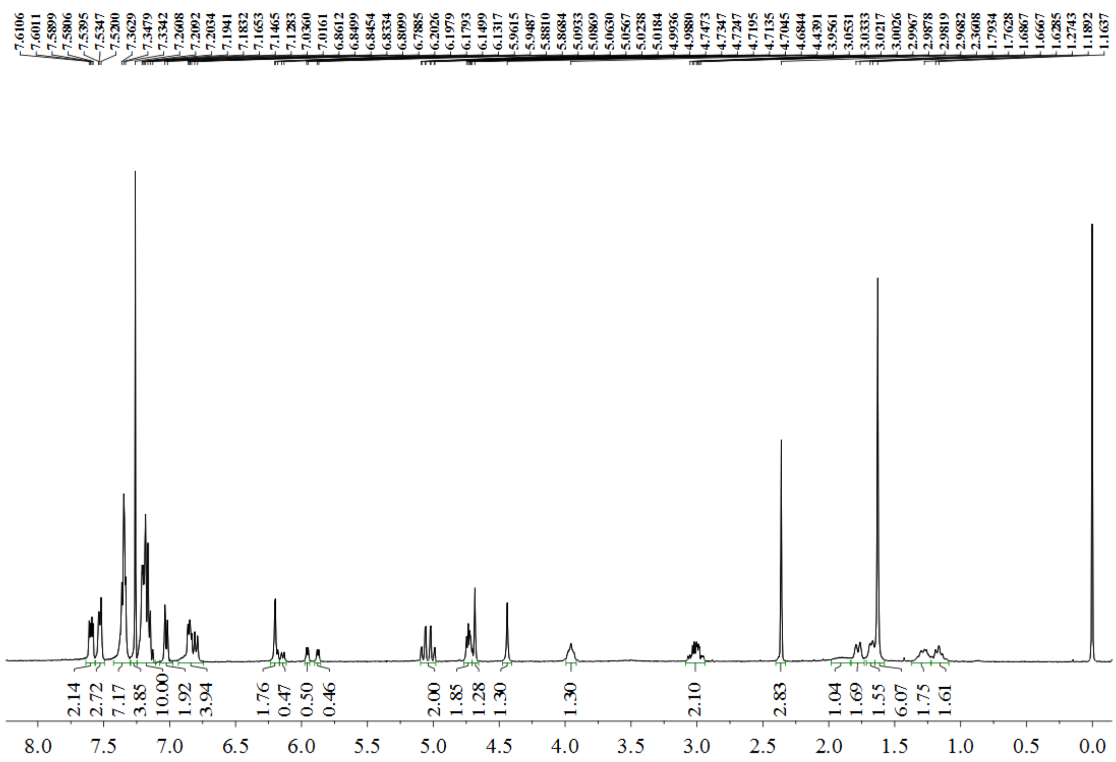


Figure S107. [1]H NMR spectrum of **(±)-G1** with TAMCSA **1c** (0.6:0.4) in $CDCl_3$ (400 MHz), [**1c**] + [(±)-**G1**] = 10 mM.

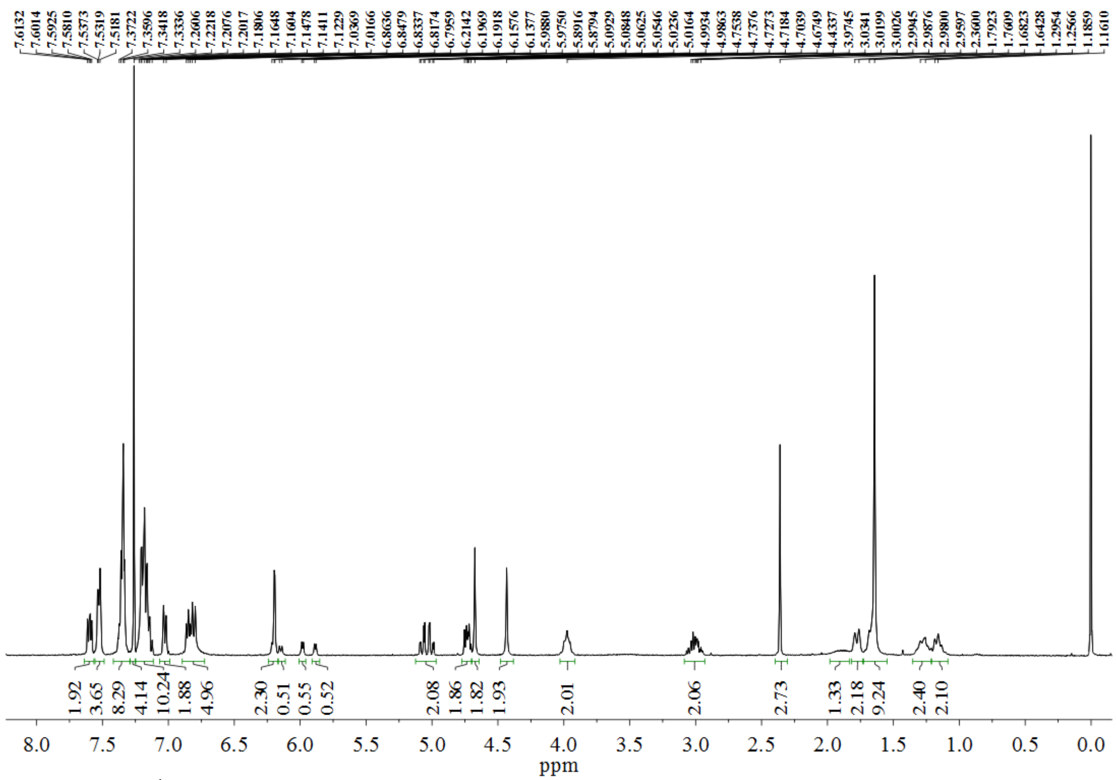


Figure S108. ^{1}H NMR spectrum of **(±)-G1** with TAMCSA **1c** (0.5:0.5) in $CDCl_3$ (400 MHz), [**1c**] + [(±)-**G1**] = 10 mM.

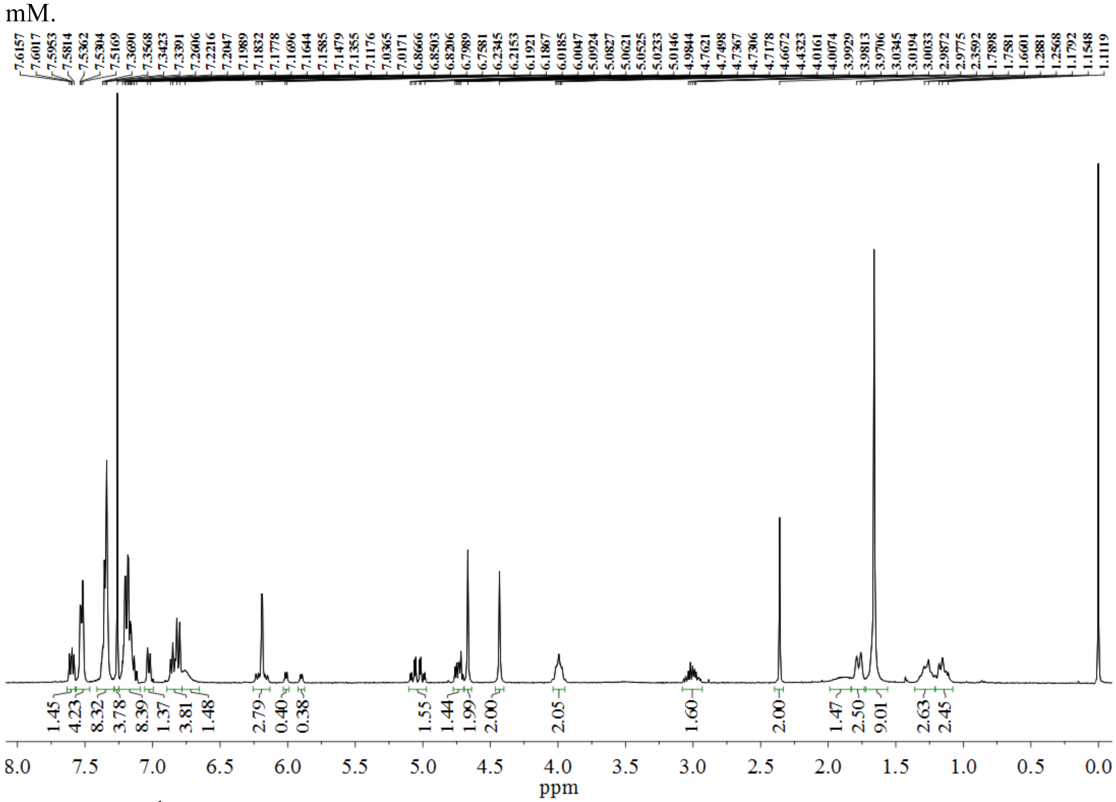


Figure S109. ^{1}H NMR spectrum of **(±)-G1** with TAMCSA **1c** (0.4:0.6) in $CDCl_3$ (400 MHz), [**1c**] + [(±)-**G1**] = 10 mM.

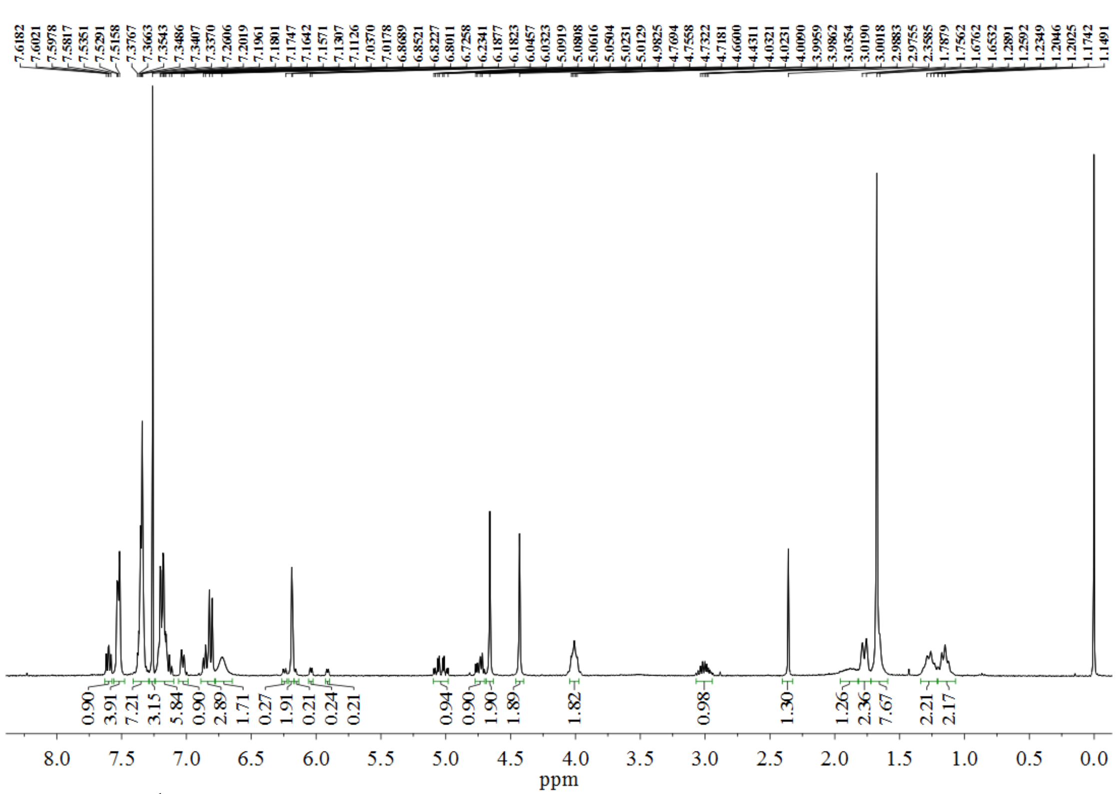


Figure S110. ^{1}H NMR spectrum of **(±)-G1** with TAMCSA **1c** (0.3:0.7) in $CDCl_3$ (400 MHz), [**1c**] + [(±)-**G1**] = 10 mM.

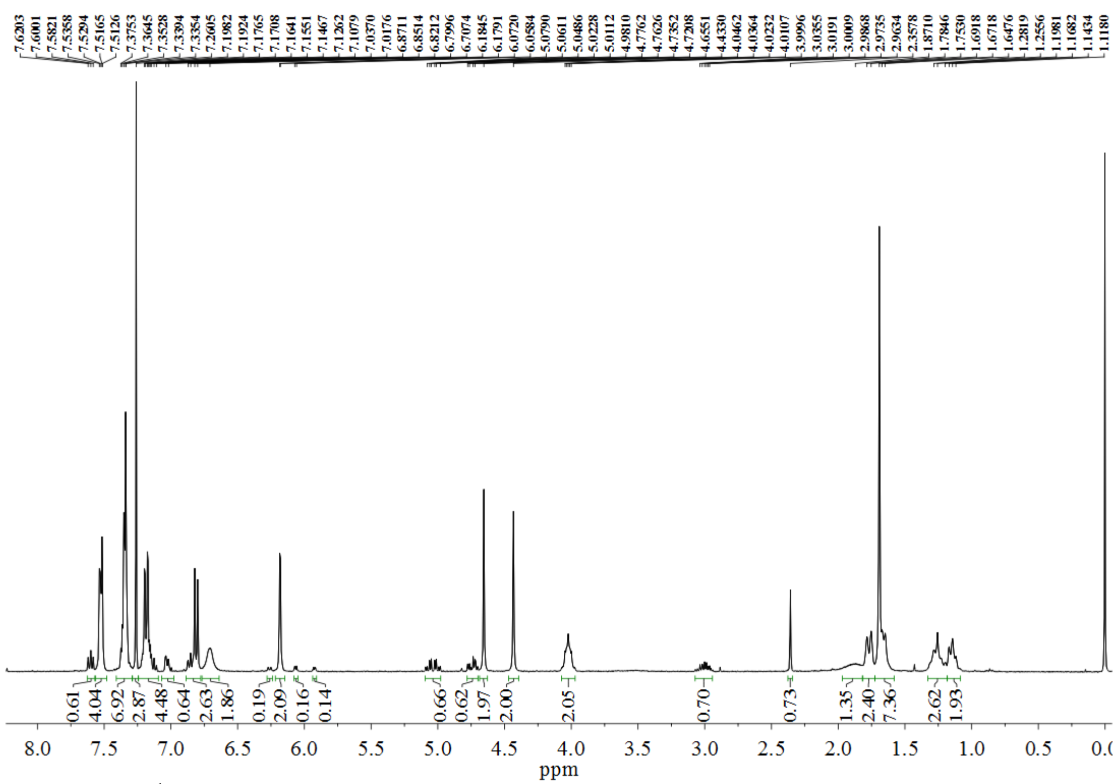


Figure S111. ^{1}H NMR spectrum of **(±)-G1** with TAMCSA **1c** (0.8:0.2) in $CDCl_3$ (400 MHz), [**1c**] + [(±)-**G1**] = 10 mM.

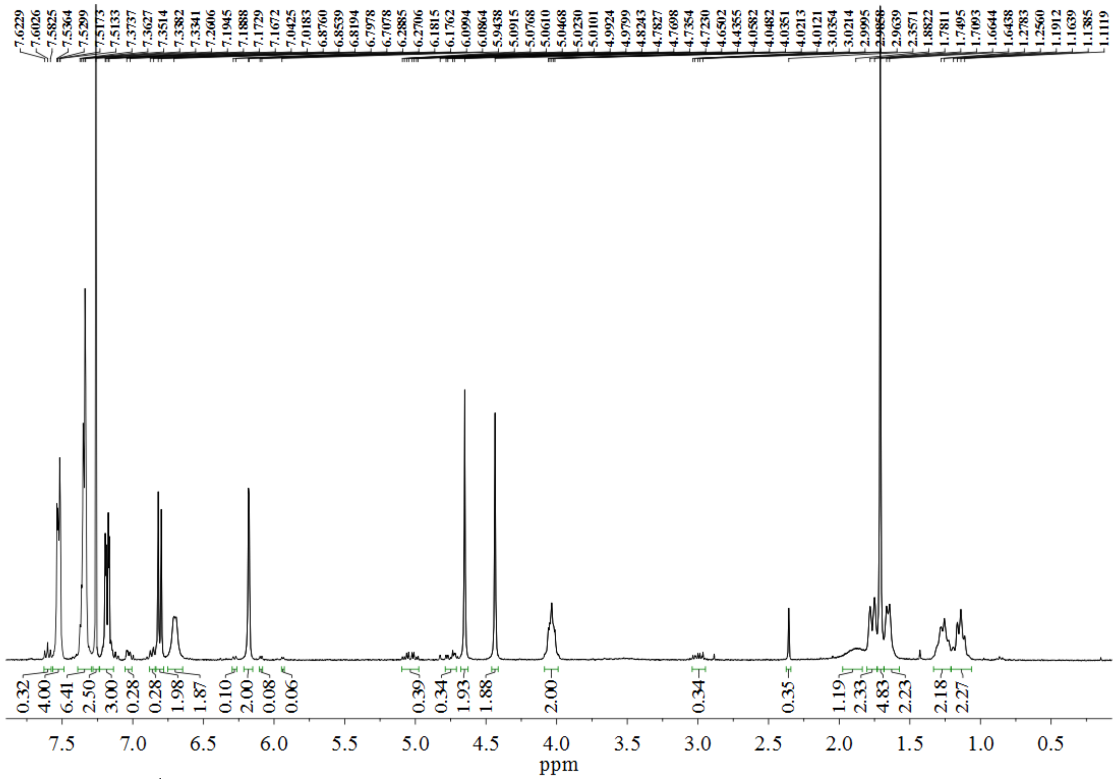


Figure S112. [1]H NMR spectrum of **(±)-G1** with TAMCSA **1c** (0.1:0.9) in $CDCl_3$ (400 MHz), [**1c**] + [(±)-**G1**] = 10 mM.

ESI mass spectrum of complex of (±)-G1 with TAMCSA 1c.

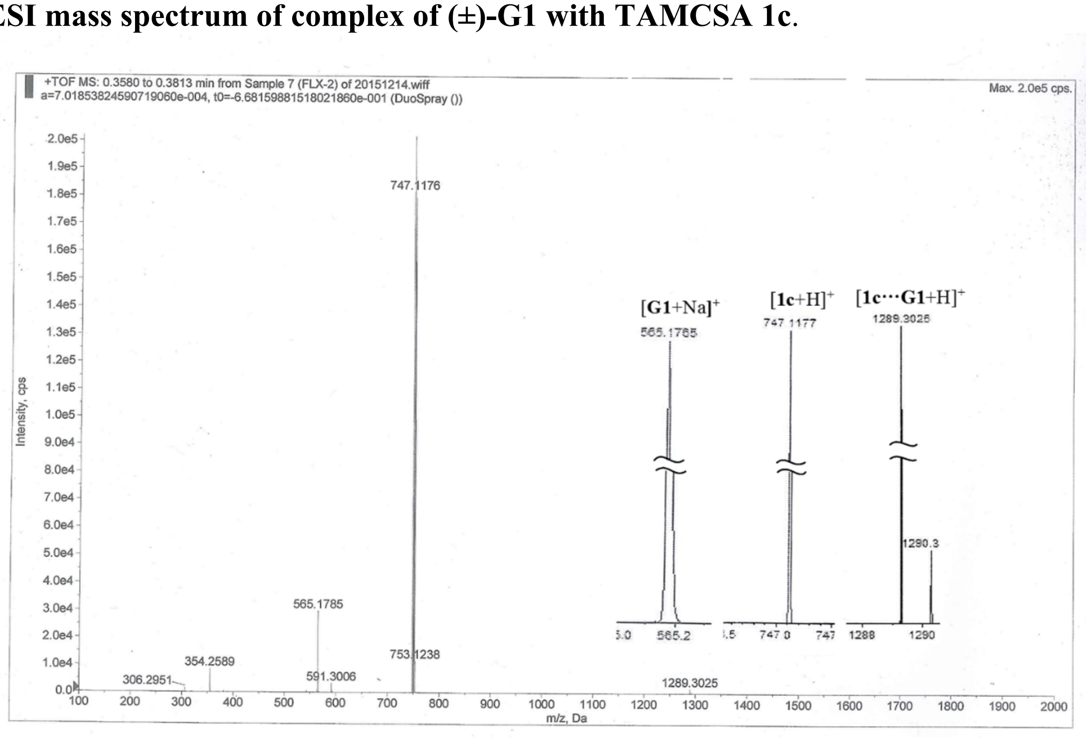


Figure S113. ESI mass spectrum of complex of dipeptide derivative **(±)-G1** with TAMCSA **1c**.

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1 (a) T. Shono, N. Kise, H. Oike, M. Yoshimoto, E. Okazaki, *Tetrahedron Lett*., 1992, **38**, 5559-5562; (b) N. Kise, H. Oike, E. Okazaki, M. Yoshimoto and T. Shono, *J. Org. Chem*., 1995, **60**, 3980-3992; (c) T. J. Wenzel and J. E. Thurston, *J. Org. Chem*., 2000, **65**, 1243-1248; (d) N. Kise, T. Iwasaki, Y. Yasuda and T. Sakurai, *Tetrahedron Lett*., 2008, **49**, 7074-7077.

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