Electronic Supplementary Information (SI) for

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Synthesis of *L*-cysteine-based boron compounds and their evaluation as proteasome inhibitors

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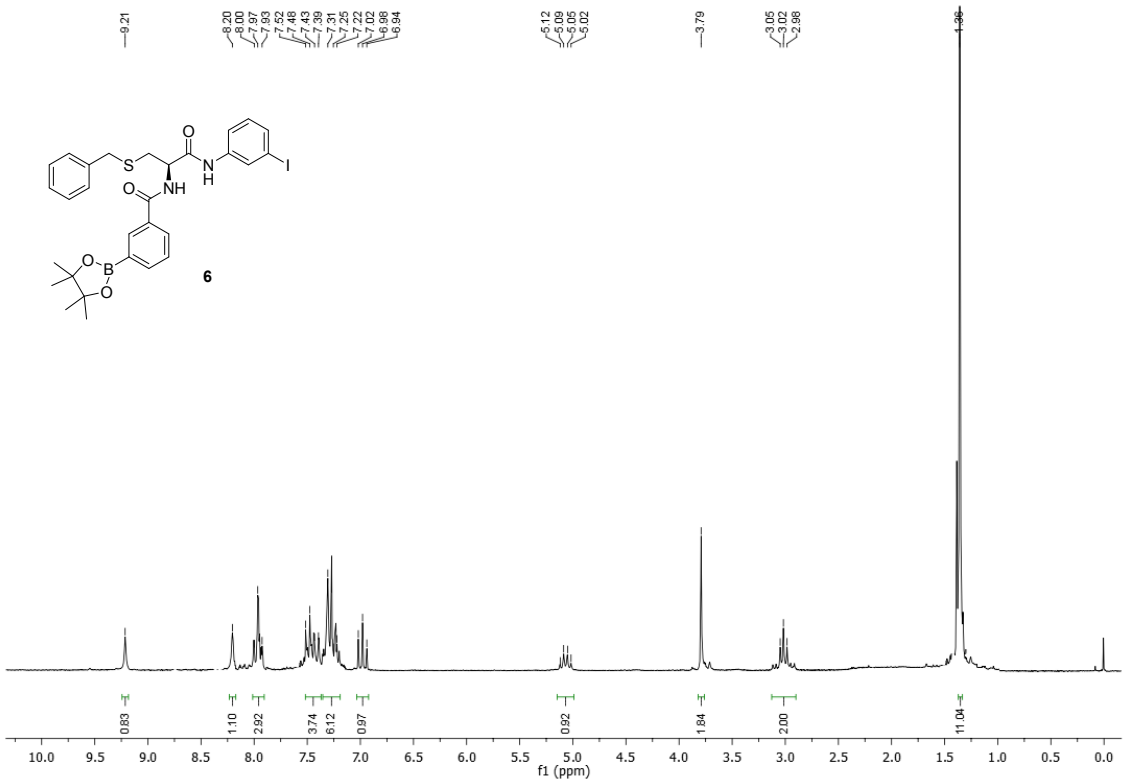


Figure S1: ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **6**.

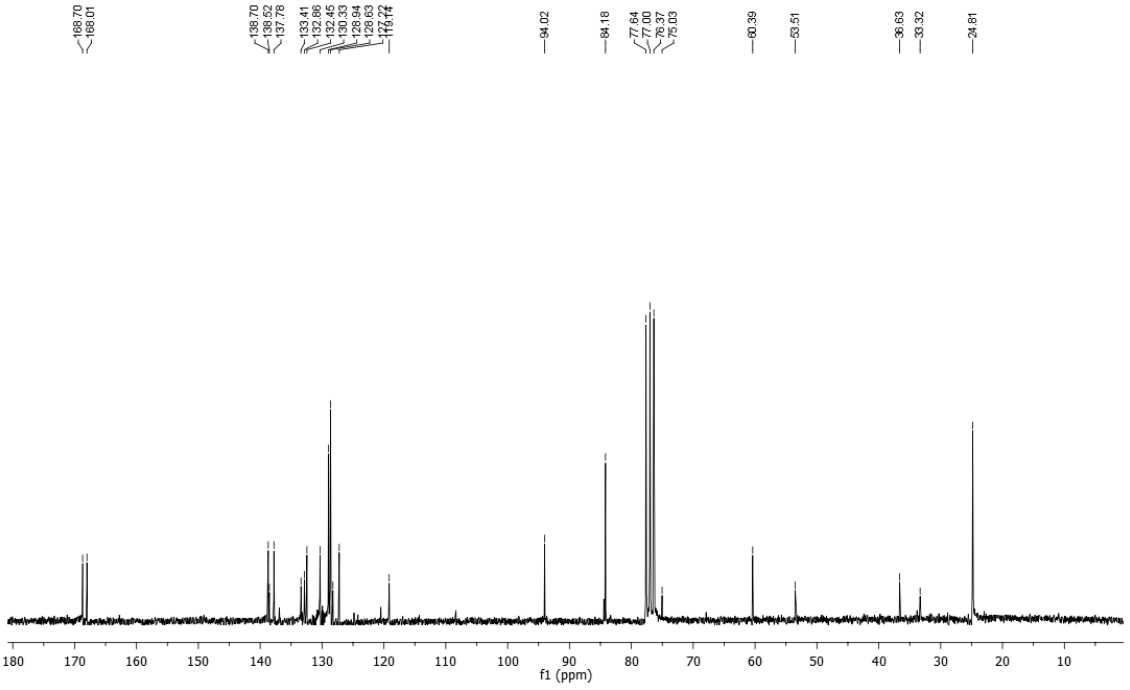
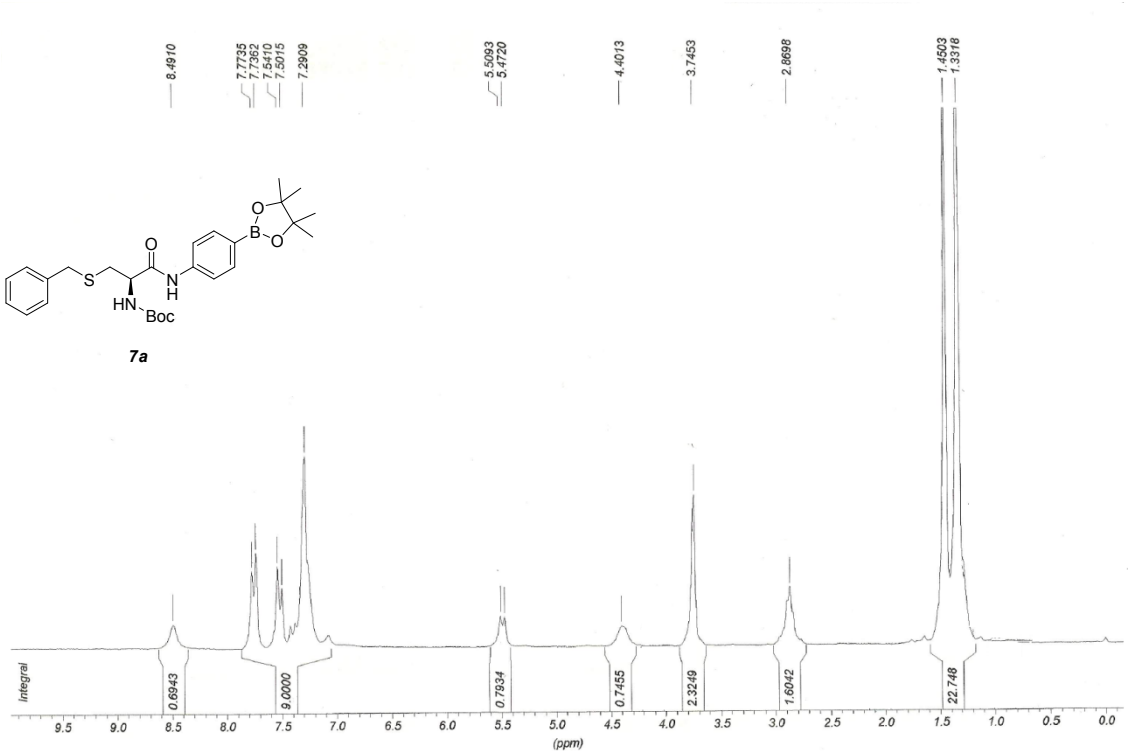


Figure S2:^{13}C NMR spectrum (50 MHz, $CDCl_3$) of compound **6**.

(R)-tert-butyl 3-(benzylthio)-1-oxo-1-(4-(4.4.5.5-tetramethyl-1.3.2-dioxaborolan-2-yl)phenylamino)propan-2-ylcarbamate ***7a****:*



7a

Figure S3: ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **7a**.

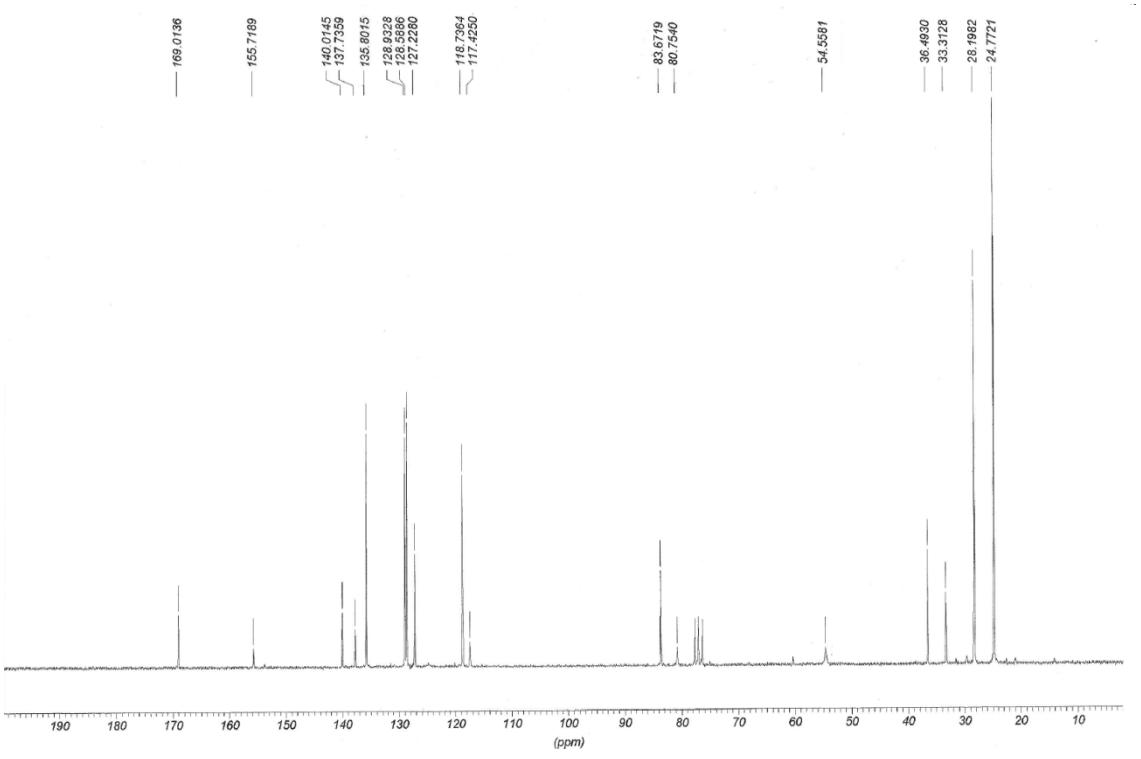


Figure S4: ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of compound **7a**.

(R)-tert-butyl 3-(benzylthio)-1-oxo-1-(3-(4.4.5.5-tetramethyl-1.3.2-dioxaborolan-2-yl)phenylamino)propan-2-ylcarbamate ***7b****:*

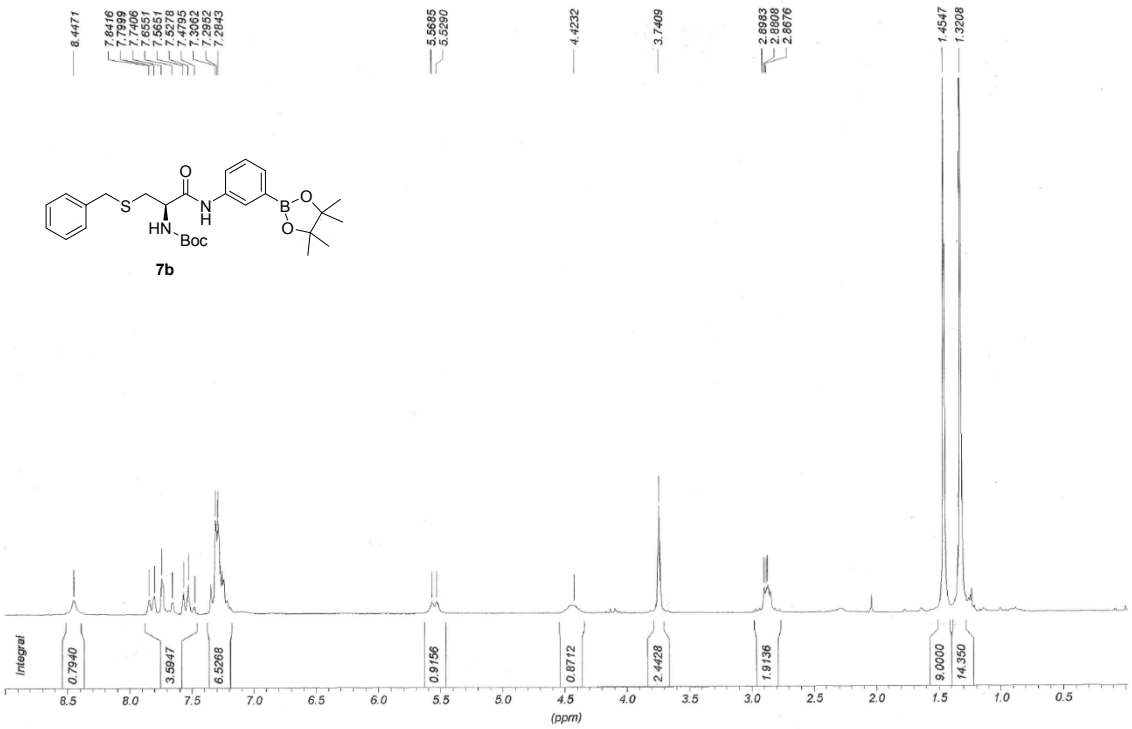


Figure S5: ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **7b**.

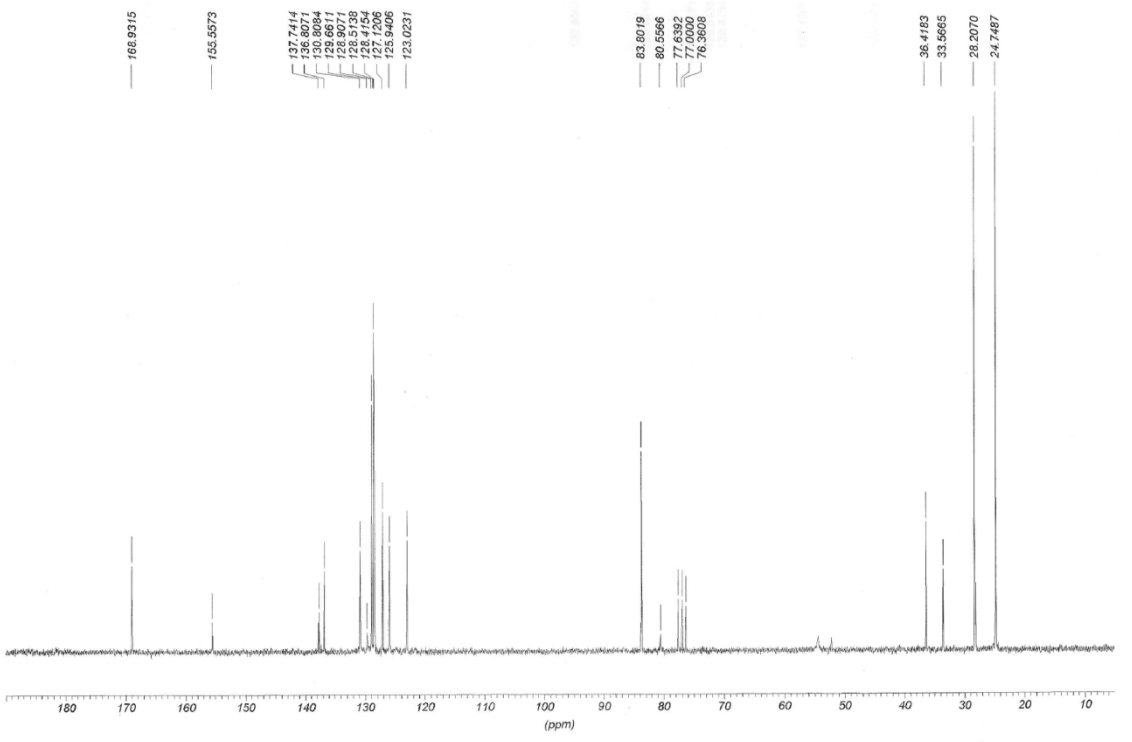


Figure S6: ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of compound **7b**.

(R)-methyl 3-(benzylthio)-1-oxo-1-(3-(4.4.5.5-tetramethyl-1.3.2-dioxaborolan-2-yl)phenylamino)propan-2-ylcarbamate ***7c****:*

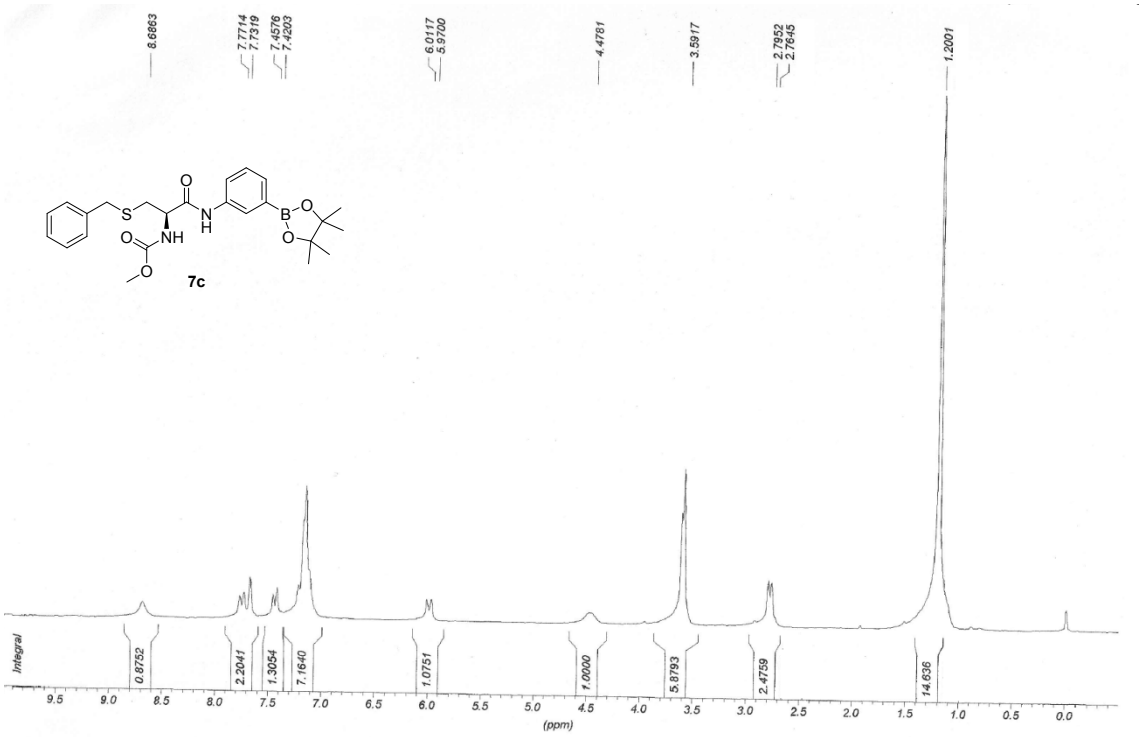


Figure S7: ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **7c**.

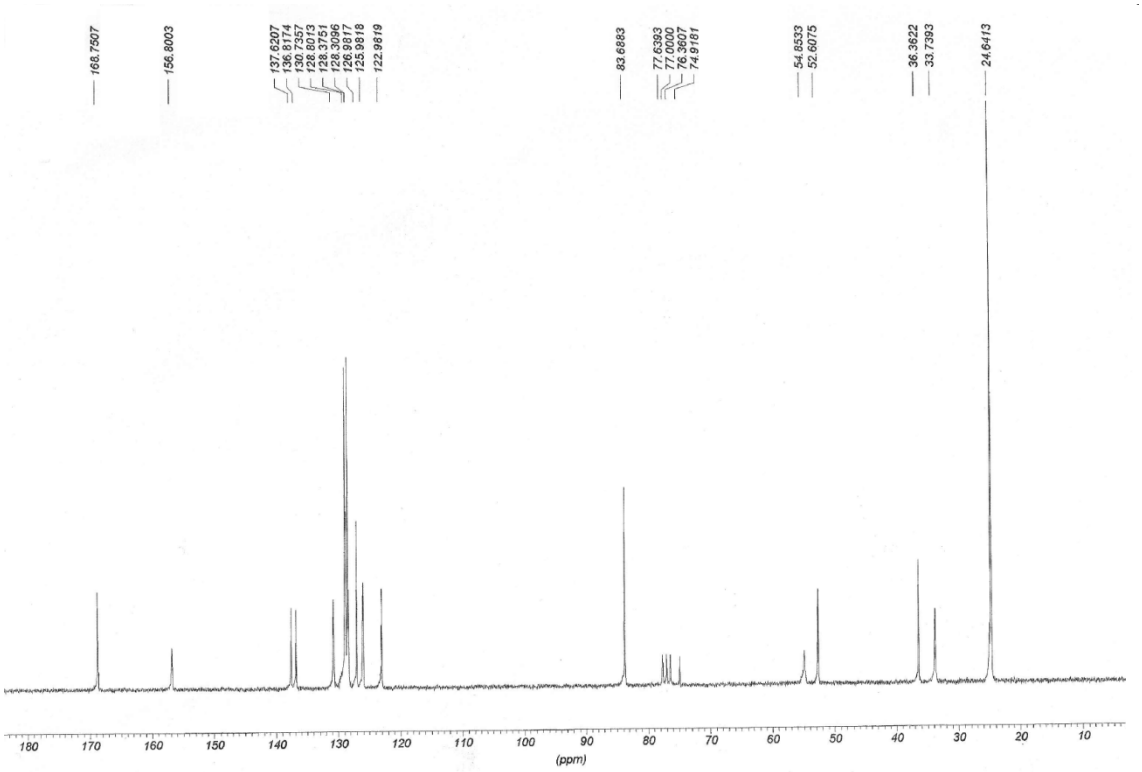


Figure S8: ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of compound **7c**.

(R)-3-(benzylthio)-2-pivalamido-N-(3-(4.4.5.5-tetramethyl-1.3.2-dioxaborolan-2-yl)phenylpropanamide ***7d****:*

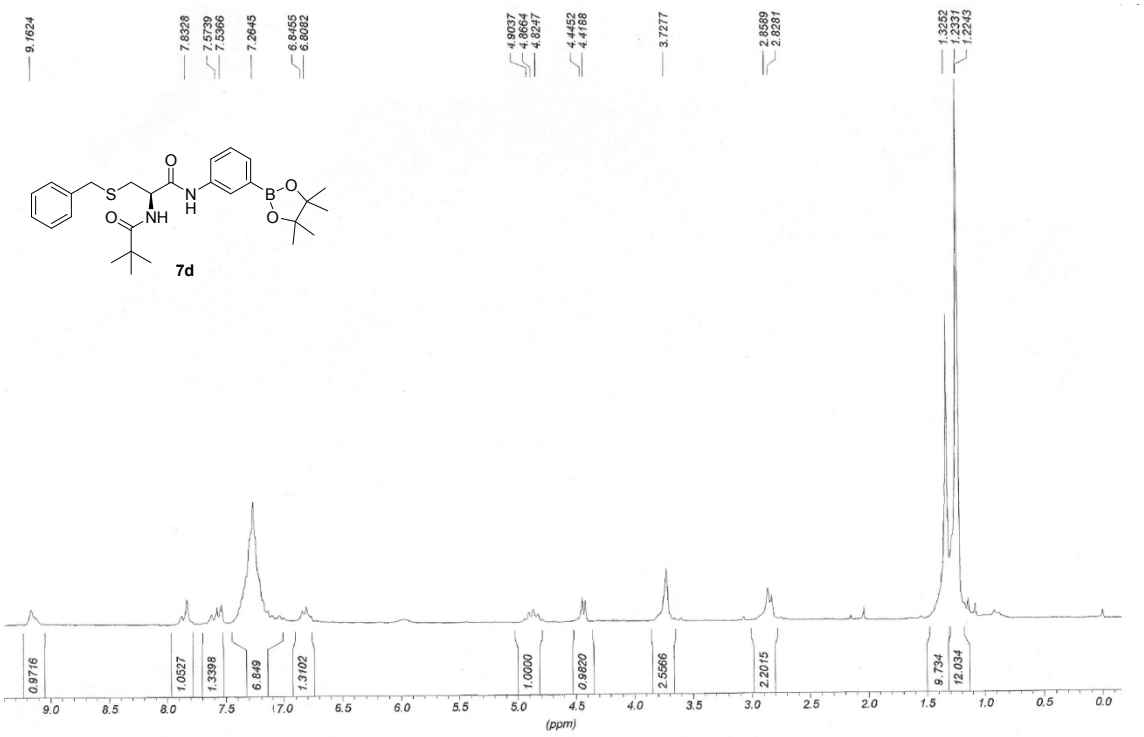


Figure S9: ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **7d**.

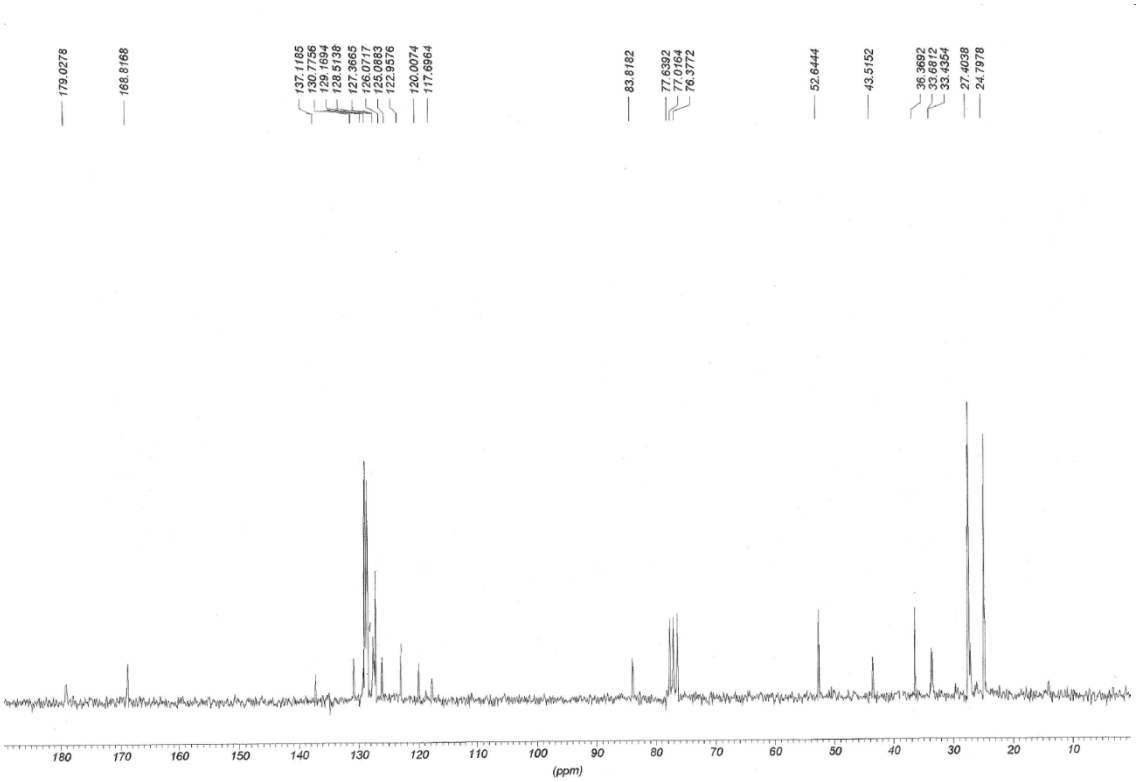


Figure S10: ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of compound **7d**.

(R)-tert-butyl-3-(methylthio)-1-oxo-1-(3-(4.4.5.5-tetramethyl-1.3.2-dioxaborolan-2-yl)phenylamino)propan-2-ylcarbamate ***7e:***

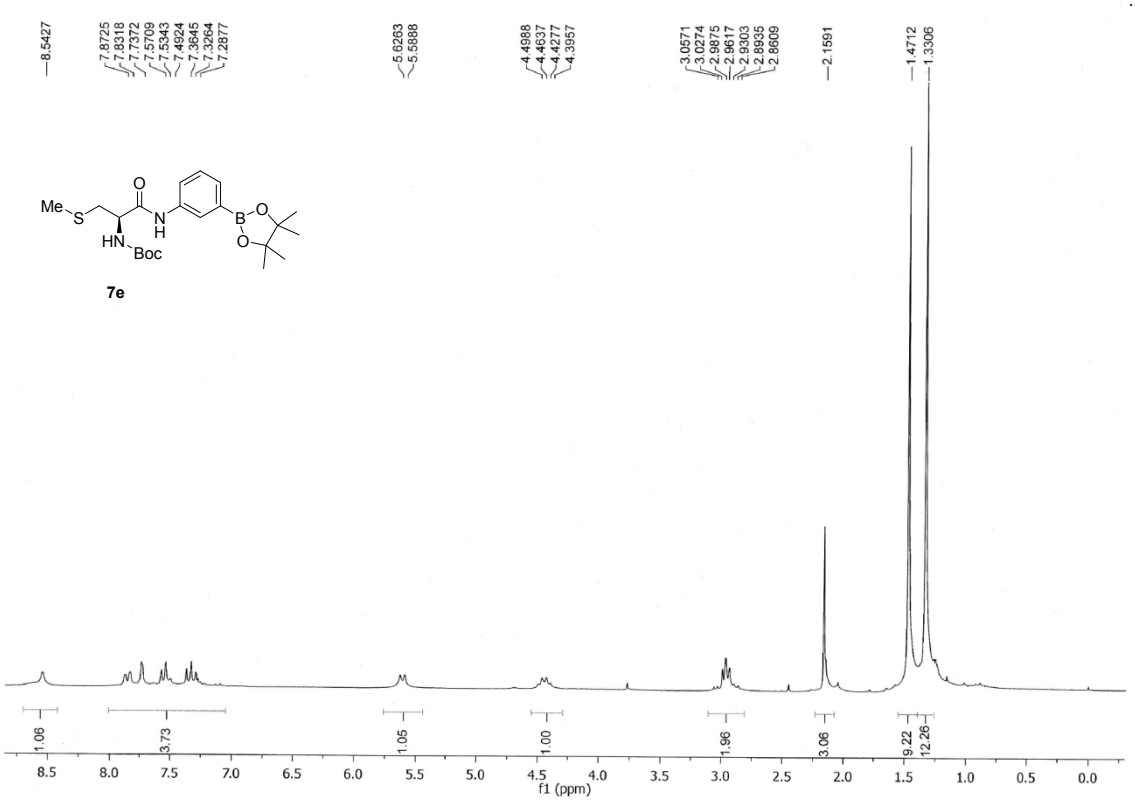


Figure S11: ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **7e**.

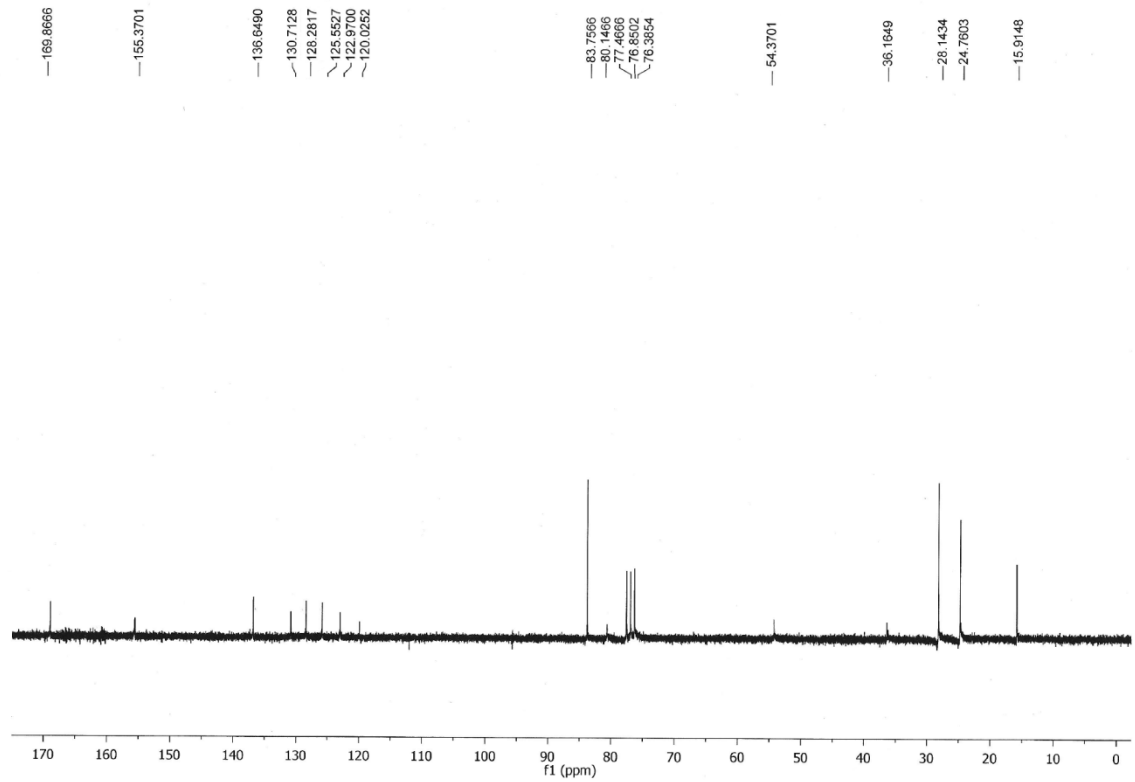


Figure S12: ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of compound **7e**.

*(R)-N-(3-(benzylthio)-1-oxo-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenylamino)propan-2-yl)pyrazine-2-carboxamide **7f**:*

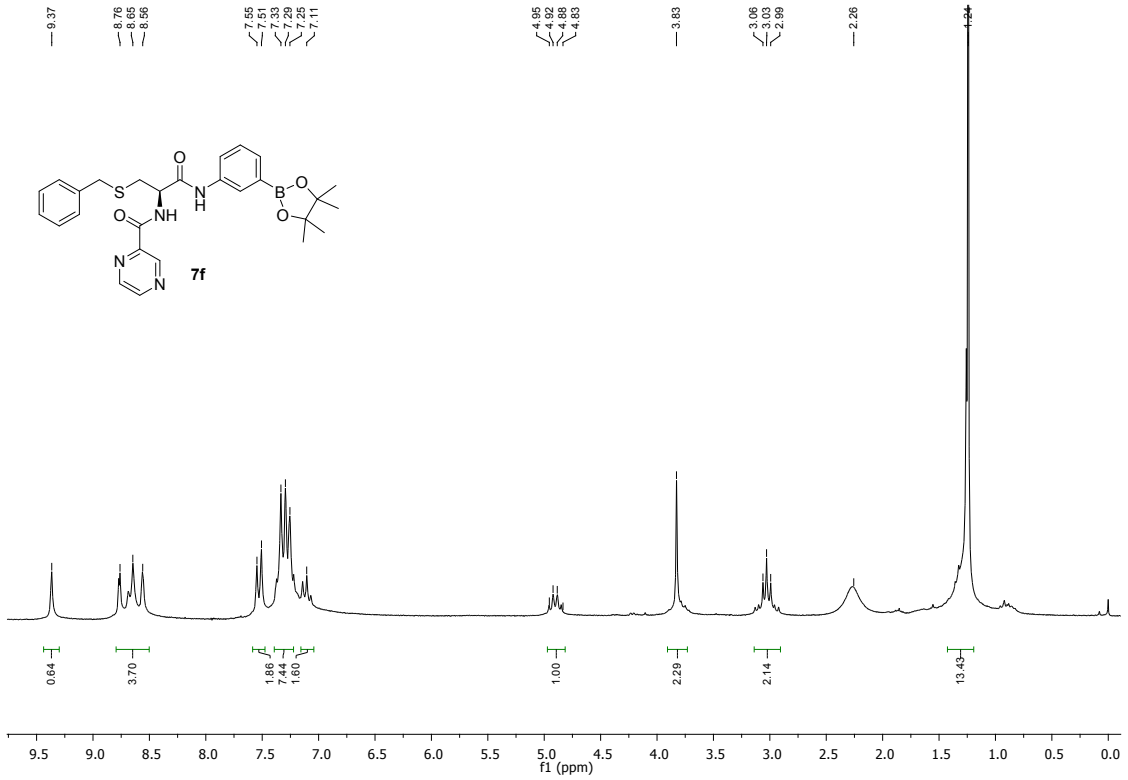


Figure S13: ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **7f**.

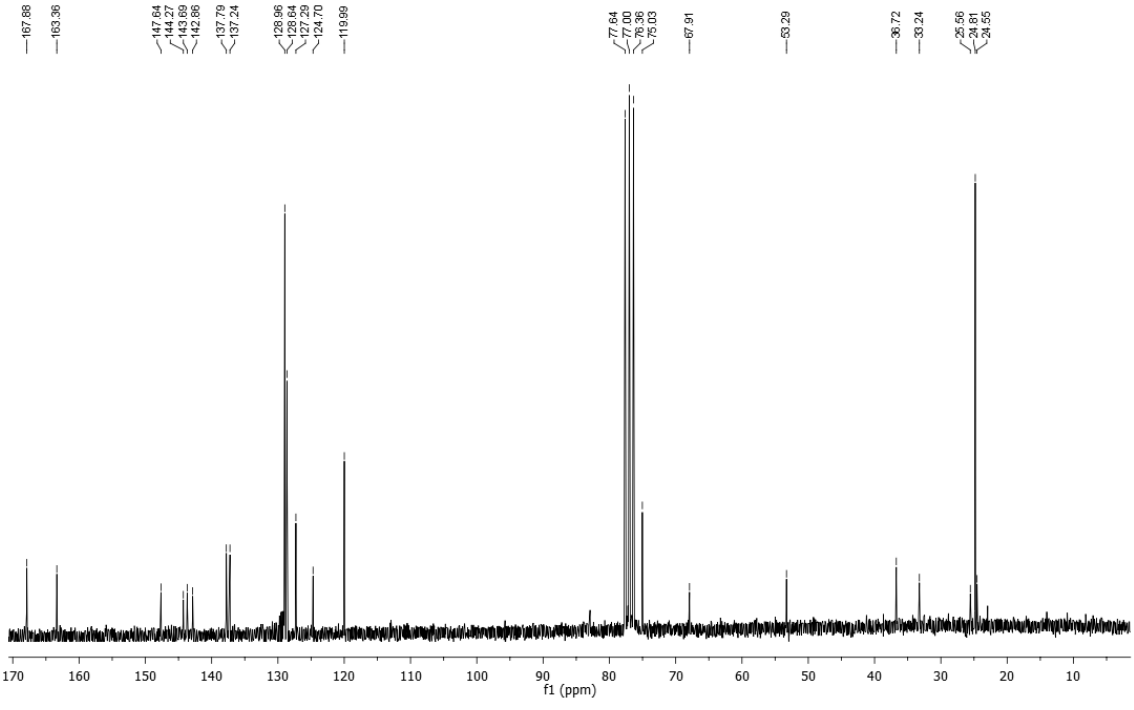


Figure S14: ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of compound **7f**.

(R)-3-(3-(benzylthio)-2-(methoxycarbonylamino)propanamido)phenylboronic acid ***7g****:*

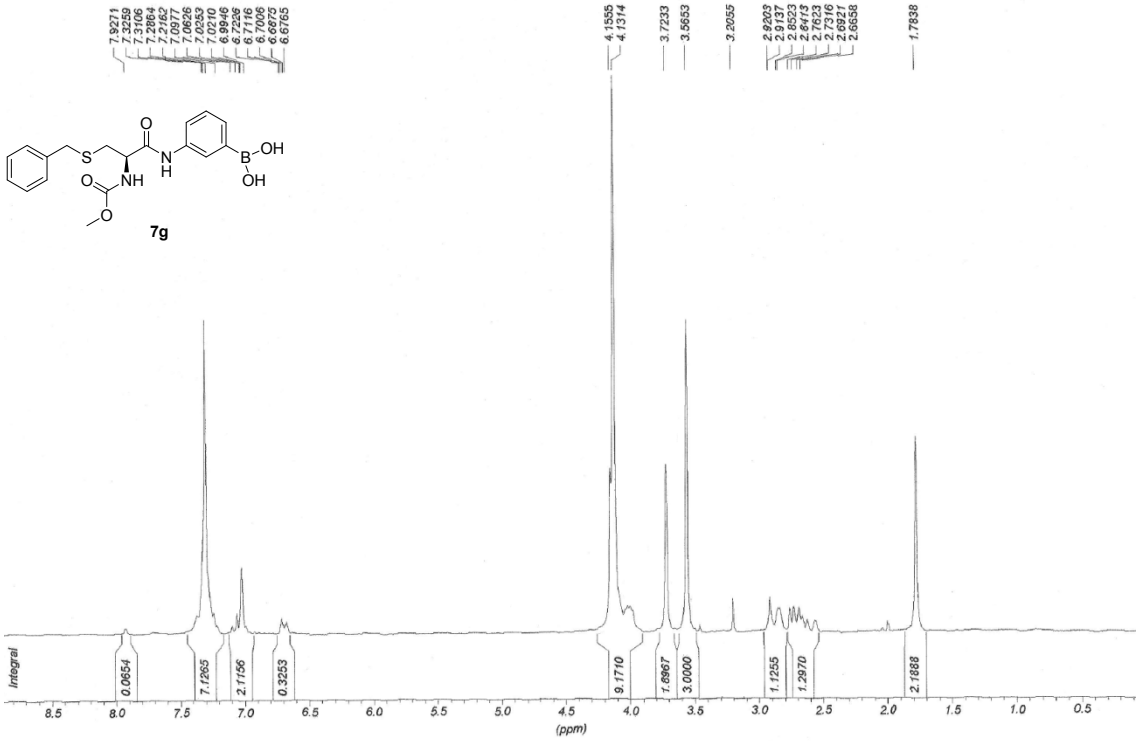


Figure S15: ^{1}H NMR spectrum (200 MHz, DMSO + D_2O) of compound **7g**.

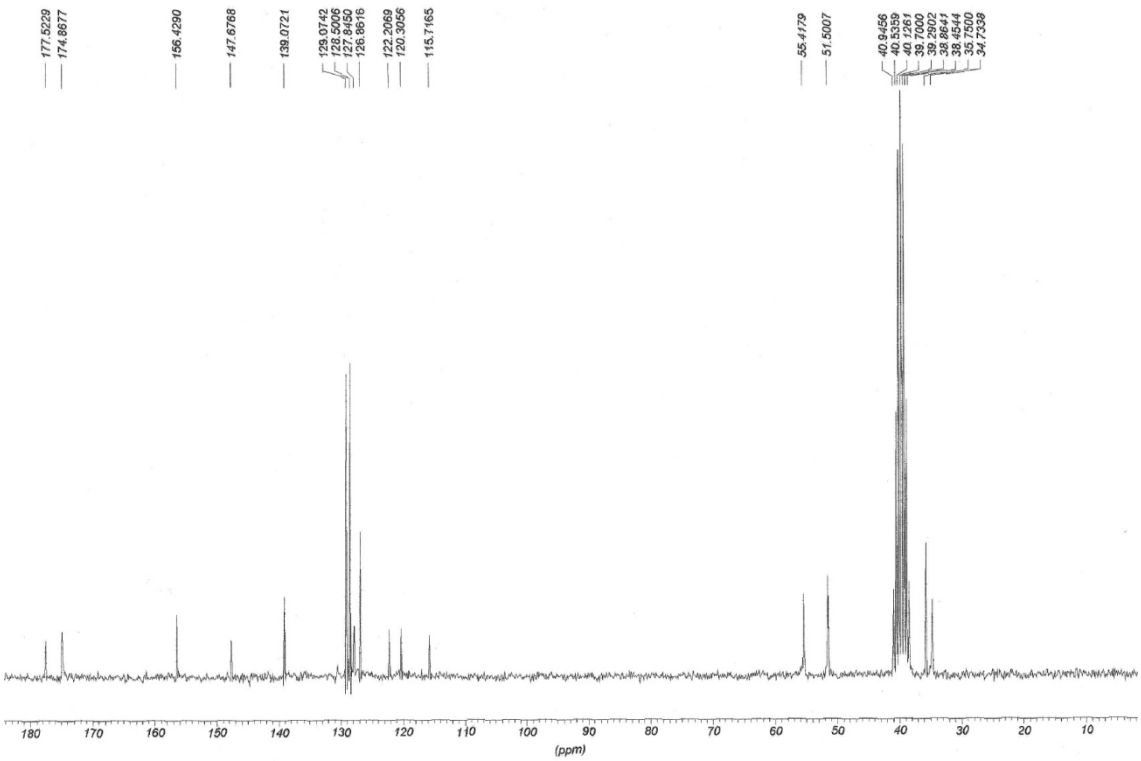


Figure S16: ^{13}C NMR spectrum (50 MHz, DMSO + D_2O) of compound **7g**.

(R)-tert-butyl 3-(benzylthio)-1-oxo-1-((3-(4.4.5.5-tetramethyl-1.3.2-dioxaborolan-2-yl)propylamino)propan-2-ylcarbamate ***8a****:*

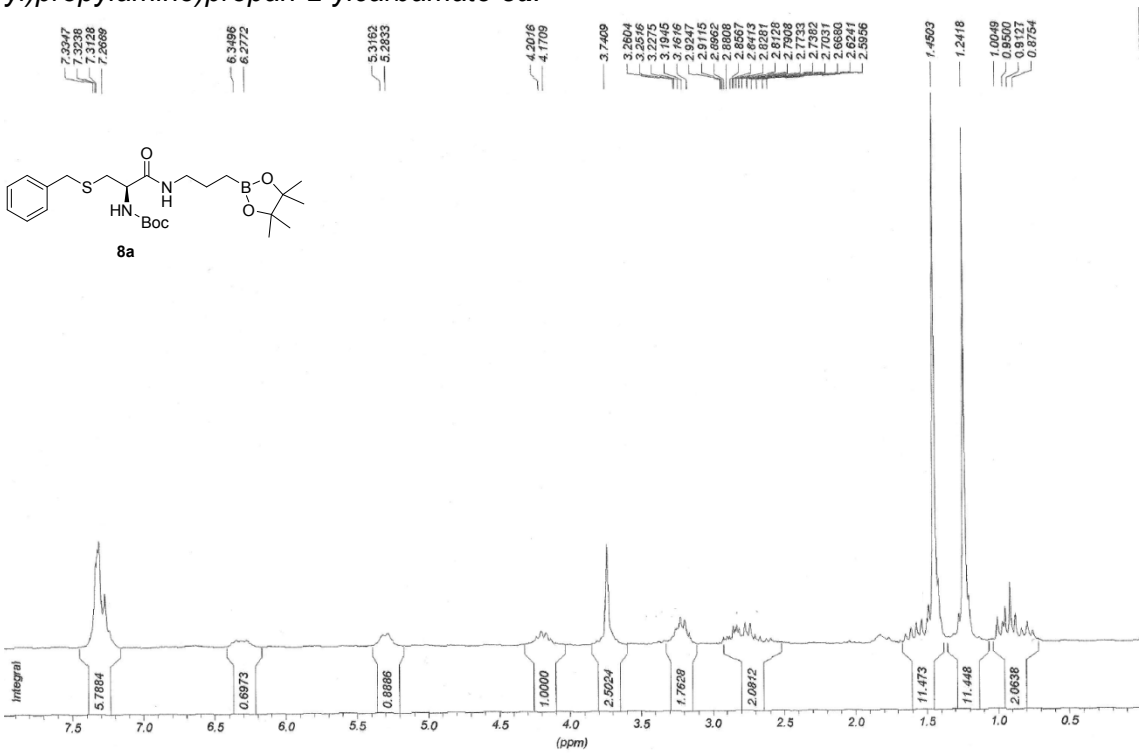


Figure S17: ^{1}H NMR spectrum (200 MHz, $CDCl_3$) of compound **8a**.

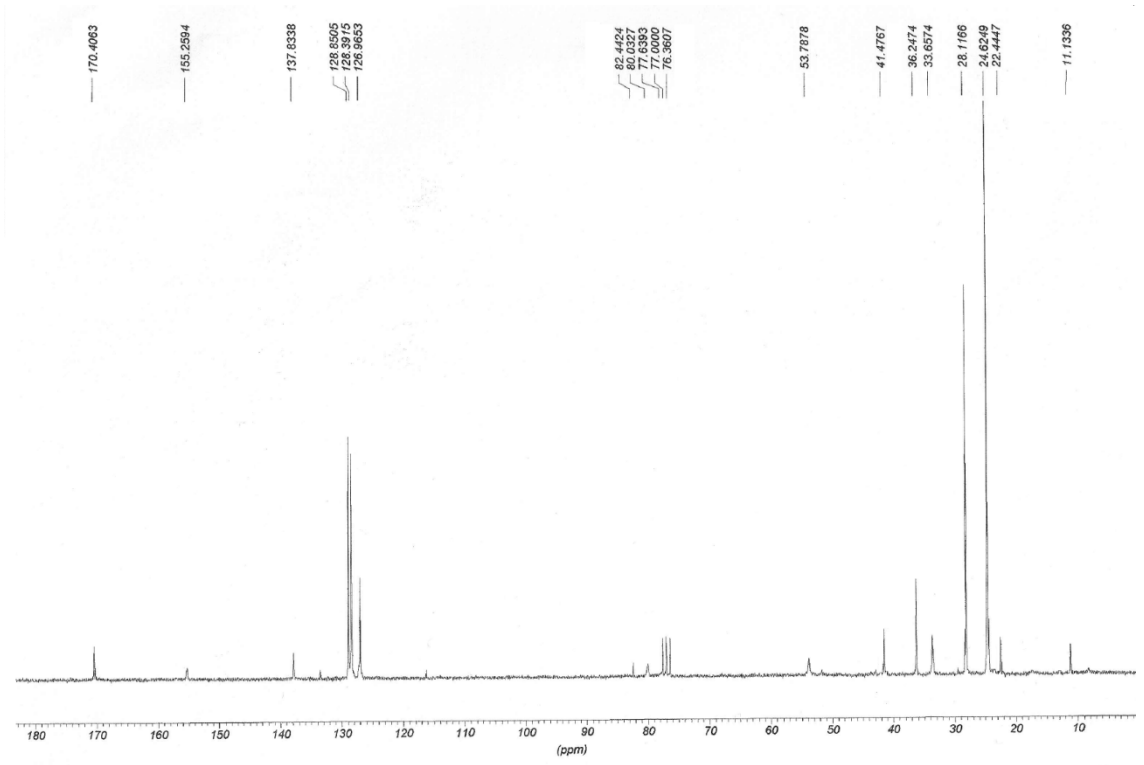


Figure S18: ^{13}C NMR spectrum (50 MHz, $CDCl_3$) of compound **8a**.

*(R)-(3-(3-(benzylthio)-2-((tert-butoxycarbonylamino)propanamido)propylboronic acid **8b***

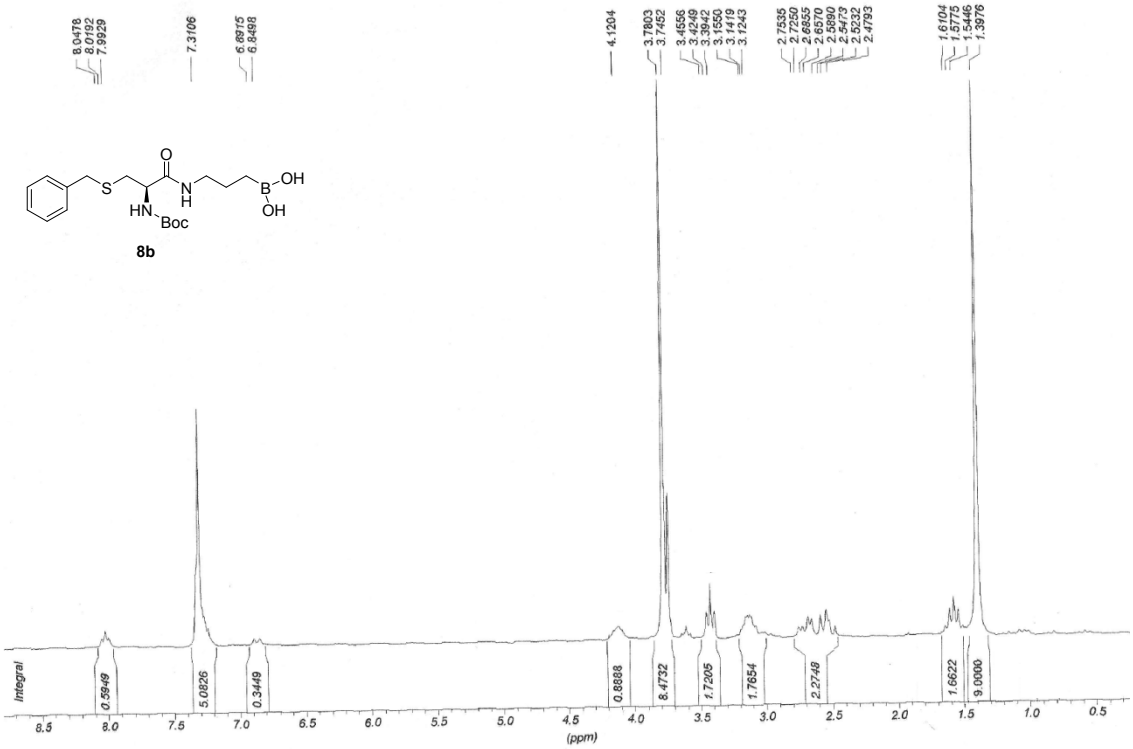


Figure S19: ^{1}H NMR spectrum (200 MHz, DMSO + D_2O) of compound **8b**.

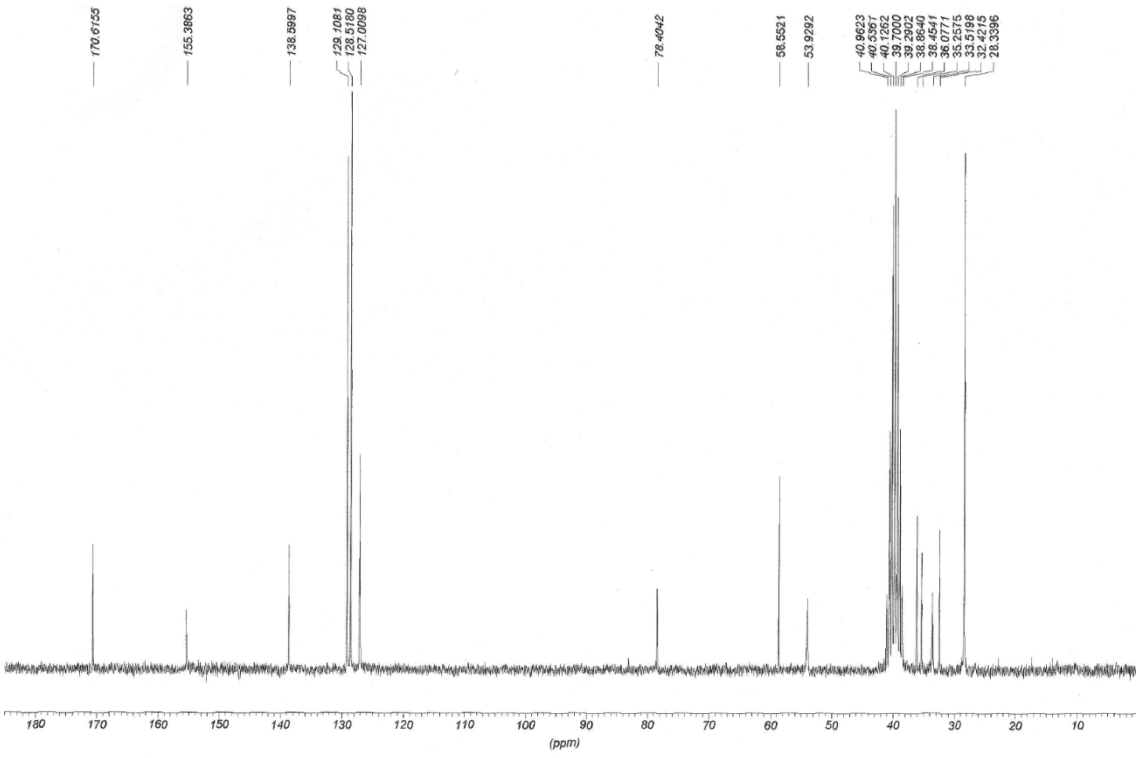
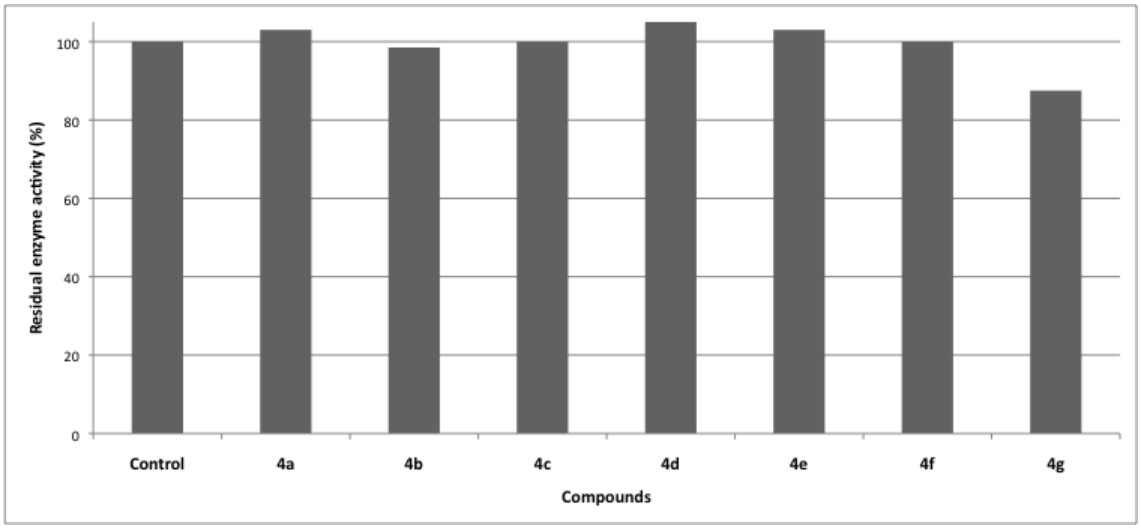


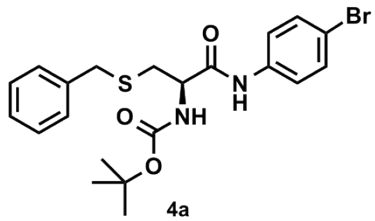
Figure S20: ^{13}C NMR spectrum (200 MHz, DMSO + D_2O) of compound **8b**.

Determination of V_{max} e K_m of proteasome 20S and complex proteasome 20S/inhibitor in different concentrations.

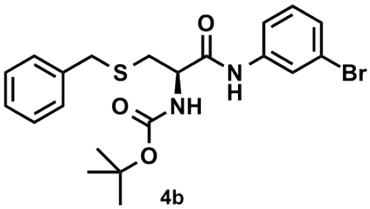
	V_{max}	K_m
Control	3.764	0.078
Inhibitor 50 μM	2.198	0.109
Inhibitor 100 μM	2.108	0.140
Inhibitor 150 μM	2.038	0.171

- Evaluation of 4a-g as inhibitors of the β5-site (chymotrypsin-like) of the mammalian 20S proteasome

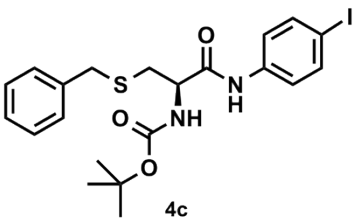




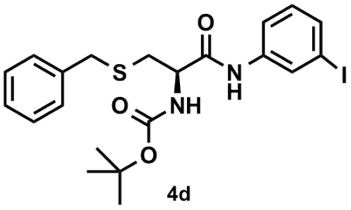
4a



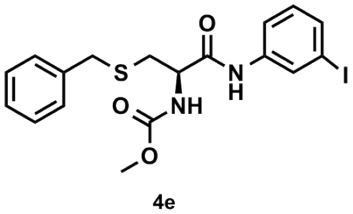
4b



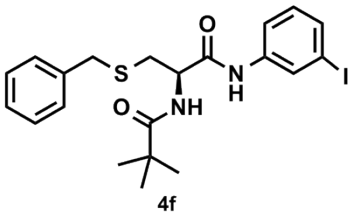
4c



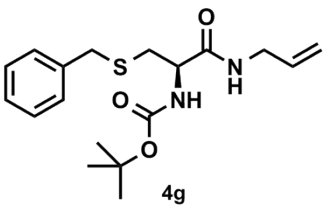
4d



4e



4f



4g