Supporting Information for:

Borinic acid Catalysed Peptide Synthesis

Tharwat Mohy El Dine,[a] Jacques Rouden,[a] and Jérôme Blanchet[a]*

[a] Laboratoire de Chimie Moléculaire et Thio-organique, ENSICAEN, Université de Caen Normandie, CNRS, 6 boulevard du Maréchal Juin, 14050 Caen, France.

Table of Contents

General Information.

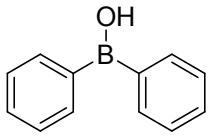
Unless otherwise stated, all reactions were performed under argon atmosphere using flame-dried glassware. Commercially available compounds were used without further purification. Solvents (THF and CH_2Cl_2) were dried and purified from a solvent purification system. Fluorobenzene was distilled from CaH_2. NMR experiments were performed in deuterated solvents. ^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{9}F spectra were recorded on 400 and 500 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) relative to the residual protium in the solvents (^{1}H) or the solvent carbon (^{13}C) as internal standards. ^{1}H NMR spectral data features are tabulated in the following order: chemical shift in ppm (δ) (multiplicity, coupling constant, integration, type of H). The following abbreviations were used in reporting NMR data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplet; td, triplet of doublet; ddd, doublet of doublet of doublet; m, multiplet; sept, septet; quin, quintet. Because of their low intensity (resulting from quadruple coupling), ^{13}C signals arising from the quaternary carbon bearing the borinic acid group were not always observed and therefore were not always listed. Sometimes, the OH group of some borinic acids was not observed due to the exchange with DMSO-d^6. Chromatographic separations were achieved on silica gel columns (Kieselgel 60, 40-63 μm). Detection was accomplished by irradiation with a UV lamp or staining with $KMnO_4$. IR Spectra were recorded on a FTIR spectrometer with frequencies expressed in cm^{-1}. HSQCETGP (2D H-1/X correlation via double inept transfer phase sensitive using Echo/Antiecho-TPPI gradient selection with decoupling during acquisition using trim pulses in inept transfer). HMBCGPLPNDQF (2D H-1/X correlation via heteronuclear zero and double quantum coherence optimized on long range couplings with low-pass J-filter to suppress one-bond correlations no decoupling during acquisition using gradient pulses for selection). DEPT135 (dept polarization transfer with 135 degree read pulse to give XH, XH_3 positive and XH_2 negative with decoupling during acquisition) were used to assign the NMR peaks. Mass Spectra and high resolution mass spectra (HRMS) were obtained on a Q-Tof instrument were recorded using either electron impact (EI) or electrospray ionization (ESI) techniques. Powdered molecular sieves were dried for 3 hours under high vacuum (<1 mbar) at 250 °C using a Kugelrohr instrument.

General Procedure A for the Preparation of Aryl Borinic Acids (9a-o).

Under argon atmosphere, a mixture of magnesium tunings (11 mmol, 267.3 mg, 1.1 equiv.) with a small crystal of iodine in THF (5 mL) was stirred at 40 °C for a period of 30 minutes until complete decolorization. Then, a solution of the aryl bromide (10 mmol, 1 equiv.) and $B(OMe)_3$ (5 mmol, 0.56 mL, 0.5 equiv.) in THF (5 mL) was added dropwise. The reaction was maintained at 40 °C for an additional two hours and then cooled to room temperature. Hydrolysis was achieved by the addition of aqueous 5% HCl (5.75 mL) and the resulting solution was stirred for 30 minutes. The mixture was then extracted with EtOAc (3 x 10 mL) and the organic layer was washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. This crude was then dissolved in EtOAc (1.2 mL) and 2-ethanolamine (10 mmol, 0.60 mL, 1 equiv.) was added. The mixture was then stirred overnight at room temperature, washed with water and brine, extracted with EtOAc (2 x 3 mL) and concentrated under vacuum to obtain a crude 2-aminoethoxydiaryl borinate, which was recrystallized from ethanol, acetone or chloroform to give, unless otherwise stated, a colorless powder.

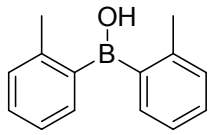
To obtain the desired borinic acid, the 2-aminoethoxydiaryl borinate was dissolved in a 1:1 mixture of MeOH/Acetone and an equivalent volume of aqueous HCl (1 M) was added. The mixture was left to stir at room temperature for two hours. Then, it was extracted with Et_2O or EtOAc, dried over anhydrous $MgSO_4$ and concentrated under high vacuum to yield the corresponding pure borinic acid in the form of oil or a powder.

Phenylborinic acid (**9a**). Known and fully described.[1a] Following the general procedure **A**, the 2-aminoethoxydiaryl borinate of the title compound was prepared using bromobenzene (1.05 mL, 10 mmol) and isolated in the form of a colorless solid (788 mg, 3.50 mmol, 35%). Acid hydrolysis furnished the desired borinic acid **9a** as colorless oil that solidifies upon storage (573 mg, 3.15 mmol, 90%). The overall yield of **9a** is 32%.



M.p: 118 - 120 °C (*lit*: 115 - 130 °C).[1b] The ^{1}H, ^{13}C and ^{11}B data were consistent with those reported in the literature. ^{1}H NMR (400.0 MHz; DMSO-d^6) δ_H = 9.98 (s, OH), 7.68 (dd, J = 6.6 Hz, $4H_{Ar}$), 7.48-7.38 (m, $6H_{Ar}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 134.5 (CH_{Ar}), 130.0 (Cq_{Ar}), 127.5 (CH_{Ar}). ^{11}B NMR (160.4 MHz; DMSO-d^6) δ_B = 46.2 (br s).

2-Methylphenylborinic acid (**9b**). Known and fully described.[2] Following the general procedure **A**, the 2-aminoethoxydiaryl borinate of the title compound was prepared using 2-bromotoluene (1.20 mL, 10 mmol) and isolated in the form of a colorless solid (532 mg, 2.10 mmol, 21%). Acid hydrolysis furnished the desired borinic acid **9b** as brown oil (437 mg, 2.08 mmol, 99%). The overall yield of **9b** is 21%.

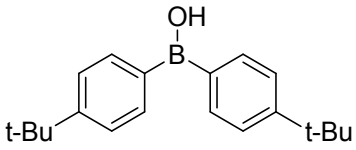


The ^{1}H, ^{13}C and ^{11}B data were consistent with those reported in the literature. ^{1}H NMR (400.0 MHz; DMSO-d^6) δ_H = 10.27 (s, OH), 7.28-1.25 (m, $4H_{Ar}$), 7.16-7.11 (m, $4H_{Ar}$), 2.31 (s, 6H, 2 x CH_3). ^{13}C NMR (101.6 MHz; DMSO-d^6) δ_C = 141.1 (Cq_{Ar}), 133.6 (CH_{Ar}), 129.4 (CH_{Ar}), 129.1 (CH_{Ar}), 124.6 (CH_{Ar}), 22.2 (CH_3). ^{11}B NMR (160.4 MHz; DMSO-d^6) δ_B = 45.0 (br s).

---

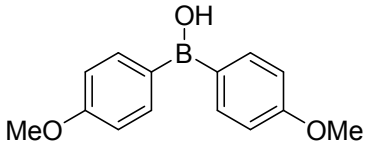
[1] (a) A. Hofer, G. Kovacs, A. Zappatini, M. Leuenberger, M. A.Hediger and M. Lochner, *Bioorg. Med. Chem*., 2013, **21**, 3202. (b) N. Wang, *J. Organomet. Chem*., 1972, **35**, 231.
[2] X. Chen, H. Ke, Y. Chen, C. Guan and G. Zou, *J. Org. Chem*., 2012, **77**, 7572.

4-*t*-Butylphenylborinic acid (**9c**). Following the general procedure **A**, the 2-aminoethoxydiaryl borinate of the title compound was prepared using 1-bromo-4-(*tert*-butyl)benzene (1.73 mL, 10 mmol) and isolated in the form of a colorless solid (2.02 g, 5.99 mmol, 60%). Acid hydrolysis furnished the desired borinic acid **9c** as a colorless solid (1.67 g, 5.68 mmol, 95%). The overall yield of **9c** is 57%.



M.p: 76-78 °C. ^{1}H NMR (400.0 MHz; DMSO-d^{6}) δ_H = 9.80 (s, OH), 7.65 (d, J = 7.7 Hz, 4H$_{Ar}$), 7.44 (d, J = 7.7 Hz, 4H$_{Ar}$), 1.31 (s, 18H, 6 x CH$_3$). ^{13}C NMR (101.6 MHz; DMSO-d^{6}) δ_C = 152.8 (Cq$_{Ar}$), 134.7 (CH$_{Ar}$), 124.3 (CH$_{Ar}$), 34.5 (Cq), 31.1 (CH$_3$). ^{11}B NMR (160.4 MHz; DMSO-d^{6}) δ_B = 45.1 (br s). υ_{max} (neat)/cm^{-1} 3413, 2958, 1607, 1462, 1399, 1299, 1267, 1197, 1138, 1105, 1018, 885, 830, 760, 695. HRMS (ESI-TOF) m/z: [M - H]$^{-}$ Calcd for $C_{20}H_{26}BO$: 293.2077; Found: 293.2087.

4-Methoxyphenylborinic acid (**9d**). Known and fully described.[2,3] Following the general procedure **A**, the 2-aminoethoxydiaryl borinate of the title compound was prepared using 4-bromoanisole (1.25 mL, 10 mmol) and isolated in the form of a colorless solid (1.74 g, 6.12 mmol, 61%). Acid hydrolysis furnished the desired borinic acid **9d** as an off-white solid (1.41 g, 5.82 mmol, 95%). The overall yield of **9d** is 58%.

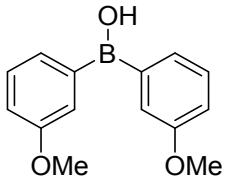


M.p: 93 - 95 °C (*lit*: 115 - 130 °C).[3] The ^{1}H, ^{13}C and ^{11}B data were consistent with those reported in the literature. ^{1}H NMR (400.0 MHz; DMSO-d^{6}) δ_H = 9.58 (s, OH), 7.66 (d, J = 8.6 Hz, 4H$_{Ar}$), 6.97 (d, J = 8.6 Hz, 4H$_{Ar}$), 3.81 (s, 6H, 2 x CH$_3$). ^{13}C NMR (101.6 MHz; DMSO-d^{6}) δ_C = 161.1 (Cq$_{Ar}$), 136.6 (CH$_{Ar}$), 113.1 (CH$_{Ar}$), 54.9 (CH$_3$). ^{11}B NMR (160.4 MHz; DMSO-d^{6}) δ_B = 44.9 (br s).

---

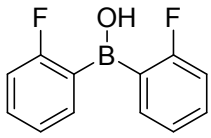
[3] S. Murakami and T. Suzuki, *Patent*: US2015/**105562 A1**, 2015.

3-Methoxyphenylborinic acid (**9e**). Following the general procedure **A**, the 2-aminoethoxydiaryl borinate of the title compound was prepared using 3-bromoanisole (1.27 mL, 10 mmol) and isolated in the form of a colorless solid (2.22 g, 7.78 mmol, 78%). Acid hydrolysis furnished the desired borinic acid **9e** as colorless oil (1.23 g, 5.08 mmol, 65%). The overall yield of **9e** is 51%.



^{1}H NMR (400.0 MHz; DMSO-d^{6}) δ_H = 9.93 (s, OH), 7.33 (t, J = 7.8 Hz, 2H$_{Ar}$), 7.24 (d, J = 4.1 Hz, 4H$_{Ar}$), 6.03 (dd, J = 8.1, 1.9 Hz, 2H$_{Ar}$), 3.78 (s, 6H, 2 x CH$_3$). ^{13}C NMR (101.6 MHz; DMSO-d^{6}) δ_C = 158.5 (Cq$_{Ar}$), 128.7 (CH$_{Ar}$), 127.0 (CH$_{Ar}$), 119.3 (CH$_{Ar}$), 115.8 (CH$_{Ar}$), 54.9 (CH$_3$). ^{11}B NMR (160.4 MHz; DMSO-d^{6}) δ_B = 47.3 (br s). υ_{max} (neat)/cm^{-1} 3437, 3001, 2939, 2836, 1594, 1571, 1484, 1463, 1447, 1416, 1374, 1287, 1235, 1217, 1180, 1149, 1114, 1038, 993, 932, 876, 854, 790, 755, 700. HRMS (ESI-TOF) m/z: [M - H]$^{-}$ Calcd for $C_{14}H_{14}BO_3$: 241.1036; Found: 241.1029.

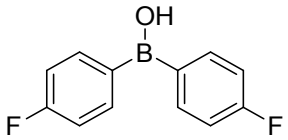
2-Fluorophenylborinic acid (**9f**). Following the general procedure **A**, the 2-aminoethoxydiaryl borinate of the title compound was prepared using 1-bromo-2-fluorobenzene (1.09 mL, 10 mmol) and isolated in the form of a colorless solid (1.44 g, 5.51 mmol, 55%). Acid hydrolysis furnished the desired borinic acid **9f** as yellowish oil (2.11 g, 9.67 mmol, 97%). The overall yield of **9f** is 53%.



^{1}H NMR (400.0 MHz; DMSO-d^{6}) δ_H = 7.53 (t, 6.2 Hz, 2H$_{Ar}$), 7.37-7.32 (m, 2H$_{Ar}$), 7.13 (t, J = 7.3 Hz, 2H$_{Ar}$), 6.99 (t, J = 8.9 Hz, 2H$_{Ar}$). ^{13}C NMR (101.6 MHz; DMSO-d^{6}) δ_C = 165.3 (d, J = 245.9, Cq$_{Ar}$), 134.8 (d, J = 11.2 Hz, CH$_{Ar}$), 130.6 (d, J = 9.1 Hz, CH$_{Ar}$), 123.3 (CH$_{Ar}$), 114.4 (d, J = 25.4 Hz, CH$_{Ar}$). ^{11}B NMR (160.4 MHz; DMSO-d^{6}) δ_B = 31.0 (br s). ^{19}F NMR (375 MHz; DMSO-d^{6}) δ_F = -104.5. υ_{max} (neat)/cm^{-1} 3608, 3077, 1610, 1568, 1477, 1440, 1301, 1280, 1205,

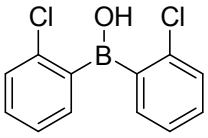
1155, 1104, 1084, 1066, 1030, 650, 876, 821, 782, 770, 698. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{12}H_8BOF_2$: 217.0636; Found: 217.0646.

4-Fluorophenylborinic acid (**9g**). Known and fully described.[1a,2] Following the general procedure **A**, the 2-aminoethoxydiaryl borinate of the title compound was prepared using 1-bromo-4-fluorobenzene (1.10 mL, 10 mmol) and isolated in the form of a colorless solid (2.01 g, 7.70 mmol, 77%). Acid hydrolysis furnished the desired borinic acid **9g** as a colorless solid (1.65 g, 7.56 mmol, 98%). The overall yield of **9g** is 76%.



M.p: 79 - 82 °C (*lit*: 78 - 80 °C).[2] The ^1H and ^{13}C data were consistent with those reported in the literature. ^1H NMR (400.0 MHz; DMSO-d^6) δ_H = 9.86 (s, OH), 7.72 (t, J = 7.4 Hz, $4H_{Ar}$), 7.22 (t, J = 9.0 Hz, $4H_{Ar}$). ^{13}C NMR (101.6 MHz; DMSO-d^6) δ_C = 163.7 (d, J = 249.9, Cq_{Ar}), 136.9 (d, J = 8.1 Hz, CH_{Ar}), 114.4 (d, J = 19.3 Hz, CH_{Ar}). ^{11}B NMR (160.4 MHz; DMSO-d^6) δ_B = 44.4 (br s). ^{19}F NMR (375 MHz; DMSO-d^6) δ_F = -110.4 (s).

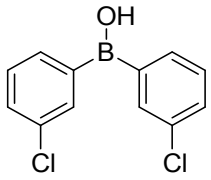
2-Chlorophenylborinic acid (**9h**). Following the general procedure **A**, the 2-aminoethoxydiaryl borinate of the title compound was prepared using 1-bromo-2-chlorobenzene (1.17 mL, 10 mmol) and isolated in the form of a colorless solid (2.11 g, 7.17 mmol, 72%). Acid hydrolysis furnished the desired borinic acid **9h** as yellowish oil (1.69 g, 6.73 mmol, 94%). The overall yield of **9h** is 68%.



^1H NMR (400.0 MHz; DMSO-d^6) δ_H = 9.46 (s, OH), 7.54 (dd, J = 6.9, 1.3 Hz, $2H_{Ar}$), 7.33-7.27 (m, $6H_{Ar}$). ^{13}C NMR (101.6 MHz; DMSO-d^6) δ_C = 136.9 (Cq_{Ar}), 134.6 (CH_{Ar}), 130.4 (CH_{Ar}), 128.7 (CH_{Ar}), 126.0 (CH_{Ar}). ^{11}B NMR (160.4 MHz; DMSO-d^6) δ_B = 39.3 (br s). υ_{max} (neat)/cm^{-1} 3543, 3052, 1588, 1559, 1464, 1425, 1335, 1287, 1260, 1239, 1160, 1123, 1079, 1032, 947, 856,

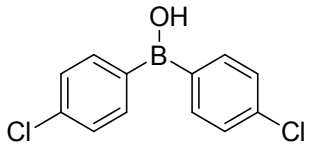
751, 720, 688. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{12}H_8BOCl_2$: 249.0045; Found: 249.0038.

3-Chlorophenylborinic acid (**9i**). Following the general procedure **A**, the 2-aminoethoxydiaryl borinate of the title compound was prepared using 1-bromo-3-chlorobenzene (1.175 mL, 10 mmol) and isolated in the form of a colorless solid (1.76 g, 5.98 mmol, 60%). Acid hydrolysis furnished the desired borinic acid **9i** as yellowish oil (1.43 g, 5.70 mmol, 95%). The overall yield of **9i** is 57%.



^{1}H NMR (400.0 MHz; DMSO-d^6) δ_H = 7.46 (s, 2H$_{Ar}$), 7.38 (d, J = 6.1 Hz, 2H$_{Ar}$), 7.27-7.21 (m, 4H$_{Ar}$). ^{13}C NMR (101.6 MHz; DMSO-d^6) δ_C = 132.3 (Cq$_{Ar}$), 131.9 (CH$_{Ar}$), 131.0 (CH$_{Ar}$), 128.9 (CH$_{Ar}$), 126.6 (CH$_{Ar}$). ^{11}B NMR (160.4 MHz; CDCl$_3$-d^1) δ_B = 45.6 (br s). υ_{max} (neat)/cm^{-1} 3580, 3433, 3060, 2979, 1591, 1558, 1473, 1473, 1399, 1306, 1275, 1248, 1171, 1137, 1081, 997, 888, 787, 702. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{12}H_8BOCl_2$: 249.0045; Found: 249.0039.

4-Chlorophenylborinic acid (**9j**). Following the general procedure **A**, the 2-aminoethoxydiaryl borinate of the title compound was prepared using 1-bromo-4-chlorobenzene (1.91 g, 10 mmol) and isolated in the form of a colorless solid (2.03 g, 6.90 mmol, 69%). Acid hydrolysis furnished the desired borinic acid **9j** as a colorless solid (1.66 g, 6.61 mmol, 96%). The overall yield of **9j** is 66%.

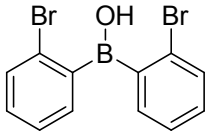


M.p: 62-64 °C. ^{1}H NMR (400.0 MHz; DMSO-d^6) δ_H = 8.73 (s, OH), 7.60 (d, J = 8.2 Hz, 4H$_{Ar}$), 7.40 (d, J = 8.2 Hz, 4H$_{Ar}$). ^{13}C NMR (101.6 MHz; DMSO-d^6) δ_C = 135.7 (CH$_{Ar}$), 134.2 (Cq$_{Ar}$), 127.4 (CH$_{Ar}$). ^{11}B NMR (160.4 MHz; DMSO-d^6) δ_B = 45.7 (br s). υ_{max} (neat)/cm^{-1} 3561, 3443, 3040, 1585, 1557, 1488, 1411, 1393, 1349, 1385, 1251, 1180, 1119, 1082, 1053, 1012, 968, 870,

857, 833, 826, 818, 751, 731, 710, 686. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{12}H_8BOCl_2$: 249.0045; Found: 249.0036.

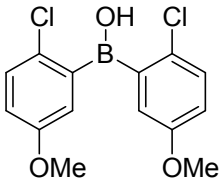
2-Bromophenylborinic acid (**9k**). General procedure **A** failed to deliver the desired product **9k**, propably due to the lack of regioselectivity where both bromine atoms can be involved in the formation of the Grignard. As a result, a mixture of byproducts (mainly non-polar) was obtained and a different method was used for the synthesis of **9k**.

To a solution of 1,2-dibromobenzene (471.8 mg, 2 mmol, 1 equiv.) in 35 mL THF was added *n*-BuLi in hexanes (0.88 mL, 2.2 mmol, 2.5 M, 1.1 equiv.) dropwise at -78 °C. After stirring at this temperature for 1 h, $B(OMe)_3$ (0.11 mL, 1 mmol, 0.5 equiv.) was added and the mixture was warmed up to room temperature and stirred overnight. The reaction was quenched by addition of aqueous HCl (1 M, 20 mL) and then extracted with EtOAc (3 x 15 mL). The solvents were removed on a rotary evaporator and the crude product was purified by column chromatography using pentane/EtOAc (99/1) as the eluent to yield the desired product **9k** as a colorless oil (109 mg, 0.32 mmol, 16%).



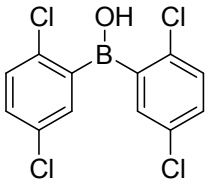
^{1}H NMR (400.0 MHz; DMSO-d^6) δ_H = 9.50 (s, OH), 7.69 (d, J = 7.1 Hz, 1H$_{Ar}$), 7.52 (d, J = 7.1 Hz, 1H$_{Ar}$), 7.43-7.14 (m, 6H$_{Ar}$). ^{13}C NMR (101.6 MHz; $CDCl_3$-d^1) δ_C = 144.6 (Cq$_{Ar}$), 134.8 (CH$_{Ar}$), 129.2 (CH$_{Ar}$), 124.5 (CH$_{Ar}$), 120.4 (CH$_{Ar}$).^{11}B NMR (160.4 MHz; DMSO-d^6) δ_B = 45.1 (br s). υ_{max} (neat)/cm^{-1} 3561, 3302, 2957,1593, 1563, 1464, 1436, 1372, 1338, 1182, 1120, 1026, 1002, 947, 823, 783, 700, 659. HRMS (ESI-TOF) of $C_{12}H_9Br_2BO$ was not possible due to the extreme instability of this product. However, a peak with m/z: 339 was detected.

2-Chloro-5-methoxyphenylborinic acid (**9l**). Following the general procedure **A**, the 2-aminoethoxydiaryl borinate of the title compound was prepared using 3-bromo-4-chloroanisole (1.42 mL, 10 mmol) and isolated in the form of a pink solid (2.02 g, 5.70 mmol, 57%). Acid hydrolysis furnished the desired borinic acid **9l** as brown oil (1.76 g, 5.65 mmol, 99%). The overall yield of **9l** is 56%.



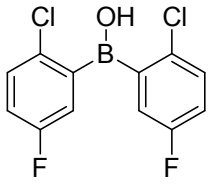
^{1}H NMR (400.0 MHz; DMSO-d^{6}) δ_H = 10.27 (s, OH), 7.30-7.26 (m, 3H$_{Ar}$), 7.18-7.12 (m, 3H$_{Ar}$), 2.32 (s, 6H, 2 x CH$_3$). ^{13}C NMR (101.6 MHz; DMSO-d^{6}) δ_C = 141.1 (Cq$_{Ar}$), 133.6 (CH$_{Ar}$), 129.4 (CH$_{Ar}$), 129.1 (CH$_{Ar}$), 124.6 (CH$_{Ar}$), 22.21 (CH$_3$). ^{11}B NMR (160.4 MHz; DMSO-d^{6}) δ_B = 45.8 (br s). υ_{max} (neat)/cm^{-1} 3590, 3404, 2936, 2838, 1591, 1567, 1462, 1441, 1396, 1334, 1304, 1283, 1176, 1151, 1118, 1048, 1022, 959, 868, 808, 783, 736, 704, 689. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{14}H_{12}BO_3Cl_2$: 309.0257; Found: 309.0262.

2,5-Dichlorophenylborinic acid (**9m**). Following the general procedure **A**, the 2-aminoethoxydiaryl borinate of the title compound was prepared using 2-bromo-1,4-dichlorobenzene (2.26 g, 10 mmol) and isolated in the form of a colorless solid (1.52 g, 4.18 mmol, 42%). Acid hydrolysis furnished the desired borinic acid **9m** as yellowish oil (1.32 g, 4.13 mmol, 99%). The overall yield of **9m** is 42%.



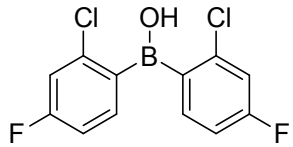
^{1}H NMR (400.0 MHz; DMSO-d^{6}) δ_H = 7.78 (d, J = 2.6 Hz, 2H$_{Ar}$), 7.14-7.08 (m, 4H$_{Ar}$). ^{13}C NMR (101.6 MHz; DMSO-d^{6}) δ_C = 135.8 (Cq$_{Ar}$), 134.7 (CH$_{Ar}$), 130.3 (Cq$_{Ar}$), 130.1 (CH$_{Ar}$), 127.1 (CH$_{Ar}$). ^{11}B NMR (160.4 MHz; CDCl$_3$-d^{1}) δ_B = 44.5 (br s). υ_{max} (neat)/cm^{-1} 3549, 2925, 1582, 1552, 1455, 1378, 1331, 1290, 1252, 1231, 1097, 1037, 902, 817, 766, 745, 736, 698. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{12}H_6BOCl_4$: 316.9266; Found: 316.9265.

2-Chloro-5-fluorophenylborinic acid (**9n**). Following the general procedure **A**, the 2-aminoethoxydiaryl borinate of the title compound was prepared using 2-bromo-1-chloro-4-fluorobenzene (1.20 mL, 10 mmol) and isolated in the form of a colorless solid (1.49 g, 4.51 mmol, 45%). Acid hydrolysis furnished the desired borinic acid **9n** as yellowish oil (1.28 g, 4.46 mmol, 99%). The overall yield of **9n** is 45%.



^{1}H NMR (400.0 MHz; DMSO-d^{6}) δ_H = 7.52 (dd, J = 10.3, 2.6 Hz, 2H$_{Ar}$), 7.10-7.07 (dd, J = 8.6, 5.0 Hz, 2H$_{Ar}$), 6.90 (td, J = 8.4, 3.4 Hz, 2H$_{Ar}$). ^{13}C NMR (101.6 MHz; DMSO-d^{6}) δ_C = 160.4 (d, J = 244.9, Cq$_{Ar}$), 132.2 (d, J = 2.1 Hz, Cq$_{Ar}$), 129.9 (d, J = 8.1 Hz, CH$_{Ar}$), 121.1 (d, J = 20.3 Hz, CH$_{Ar}$), 114.2 (d, J = 23.4 Hz, CH$_{Ar}$). ^{11}B NMR (160.4 MHz; CDCl$_3$-d^{1}) δ_B = 44.6 (br s). ^{19}F NMR (375 MHz; DMSO-d^{6}) δ_F = -119.0 (s). υ_{max} (neat)/cm^{-1} 3545, 3069, 2972, 1574, 1457, 1392, 1334, 1330, 1251, 1215, 1185, 1105, 1078, 1038, 951, 881, 815, 771, 731, 702. HRMS (ESI-TOF) m/z: [M - H]$^-$ Calcd for $C_{12}H_6BOCl_2F_2$: 284.9857; Found: 284.9868.

2-Chloro-4-fluorophenylborinic acid (**9o**). Following the general procedure **A**, the 2-aminoethoxydiaryl borinate of the title compound was prepared using 1-bromo-2-chloro-4-fluorobenzene (1.20 mL, 10 mmol) and isolated in the form of a colorless solid (1.65 g, 5.01 mmol, 50%). Acid hydrolysis furnished the desired borinic acid **9o** as yellowish oil (1.42 g, 4.94 mmol, 99%). The overall yield of **9o** is 50%.

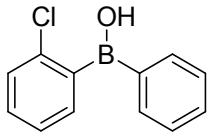


^{1}H NMR (400.0 MHz; DMSO-d^{6}) δ_H = 7.68 (t, J = 7.9 Hz, 2H$_{Ar}$), 7.12-7.04 (m, 4H$_{Ar}$). ^{13}C NMR (101.6 MHz; DMSO-d^{6}) δ_C = 161.8 (d, J = 247.9, Cq$_{Ar}$), 137.9 (d, J = 10.2 Hz, Cq$_{Ar}$), 136.5 (d, J = 8.1 Hz, CH$_{Ar}$), 115.7 (d, J = 23.4 Hz, CH$_{Ar}$), 112.7 (d, J = 19.3 Hz, CH$_{Ar}$).^{11}B NMR (160.4 MHz; CDCl$_3$-d^{1}) δ_B = 45.2 (br s). ^{19}F NMR (375 MHz; DMSO-d^{6}) δ_F = -113.6 (s) and ^{19}F NMR (375 MHz; CDCl$_3$-d^{1}) δ_F = -114.5 (s). υ_{max} (neat)/cm^{-1} 3559, 3350, 3071, 2928, 1586, 1570,

1483, 1380, 1330, 1287, 1260, 1243, 1201, 1119, 1073, 1034, 915, 895, 857, 819, 734, 701, 688. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{12}H_6BOCl_2F_2$: 284.9857; Found: 284.9861.

2-Chlorophenyl(phenyl)borinic acid (**9p**). This unsymmetrical borinic acid was synthesized in two steps. The first step involved the preparation of dimethyl (2-chlorophenyl)boronate according to a reported procedure.[4] TFA (70 μL) was added to a mixture of 2-chlorobenzene boronic acid (1.095 g, 7.0 mmol, 1 equiv.) and trimethyl orthoformate (1.91 mL, 17.5 mmol, 2.5 equiv.). The resulting mixture was stirred vigorously at room temperature for 15 min. Then; the volatile materials were evaporated under vacuum to give pure methyl boronic ester as brown oil (997 mg, 3.99 mmol, 99%).

In the next step,[5] to a solution of bromobenzene (0.32 mL, 3 mmol, 1 equiv.) in 25 mL of dry THF under argon atmosphere at -78 °C was added *n*-BuLi in hexanes (2.5 M, 1.32 mL, 3.3 mmol, 1.1 equiv.) dropwise. After stirring at this temperature for 1 h, a solution of the prepared methyl boronic ester (553 mg, 3 mmol, 1 equiv.) in 6 mL of THF was added dropwise. The mixture was warmed up to room temperature and stirred overnight. The reaction was quenched by addition of 25 mL of water, and then extracted with CH_2Cl_2. The solvents were removed on a rotary evaporator. The crude product was purified by column chromatography using pentane/EtOAc (95/5) as the eluent to yield the desired borinic acid **9p** as colorless oil (341 mg, 1.58 mmol, 53%).



^{1}H NMR (400.0 MHz; DMSO-d^6) δ_H = 10.4 (s, OH), 7.61 (d, J = 6.7 Hz, 2H$_{Ar}$), 7.60-7.34 (m, 7H$_{Ar}$). ^{13}C NMR (101.6 MHz; DMSO-d^6) δ_C = 135.3 (Cq$_{Ar}$), 135.0 (CH$_{Ar}$), 132.6 (CH$_{Ar}$), 131.3 (CH$_{Ar}$), 130.0 (CH$_{Ar}$) 128.3 (CH$_{Ar}$), 127.6 (CH$_{Ar}$), 126.1 (CH$_{Ar}$). ^{11}B NMR (160.4 MHz; DMSO-d^6) δ_B = 43.9 (br s). υ_{max} (neat)/cm^{-1} 3629, 3457, 3065, 2989, 1603, 1574, 1493, 1444, 12780,

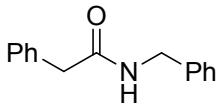
[4] P.K. Elkin, V. V. Levin, A. D. Dilman, M. I. Struchkova, P. A. Belyakov, D. E. Arkhipov, A. A. Korlyukov and V. A. Tartakovsky, *Tetrahedron Lett*., 2011, **52**, 5259.
[5] W.-M. Wan, F. Cheng and F. Jaekle, *Ang. Chem. Int. Ed*., 2014, **53**, 8934.

1266, 1247, 1159, 1104, 1073, 1049, 1030, 959, 886, 856, 771, 750, 703, 667, 656. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{12}H_9BOCl$: 215.0435; Found: 215.0443.

General procedure B for Studying the Reactivity of the Different Borinic Acids 9a-p.

Under argon atmosphere phenylacetic acid **6** (0.55 mmol, 75.0 mg, 1.1 equiv.), the borinic acid **9a-p** (0.05 mmol, 10 mol%) and 1 g of powdered of activated 5Å molecular sieves were introduced. Dry CH_2Cl_2 (7 mL) was added, and the suspension was vigorously stirred for 15 min. Then, benzylamine **7** (0.50 mmol, 54.6 µL, 1 equiv.) was added and the resulting mixture was further stirred for 48 h at room temperature. The suspension was filtered through a pad of celite and washed with CH_2Cl_2 (3 x 5 mL). The filtrate was extracted twice with an aqueous solution of HCl (1M, 10 mL), twice with an aqueous solution of NaOH (1M, 10 mL) and brine (10 mL). The organic layer was collected, dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure to yield the title amide **8** as pure products. ^{1}H NMR conversions were calculated using 1,3,5-trimethoxybenzene (0.05 mmol, 8.40 mg, 10 mol%) as an internal standard.

***N*-Benzyl-2-phenylacetamide** (**8**). Known and fully described.[6] The title compound was prepared according to the general procedure **B** and isolated as a light yellow solid (112 mg, 99% yield).



^{1}H NMR (400.0 MHz; $CDCl_3$) δ_H = 7.35-7.23 (m, 8H_{Ar}), 7.16 (d, *J* = 8 Hz, 2H_{Ar}), 5.70 (br s, NH), 4.39 (d, *J* = 8 Hz, 2H), 3.61 (s, 2H). ^{13}C NMR (100.6 MHz; $CDCl_3$) δ_C = 171.0 (C=O), 138.2 (Cq_{Ar}), 134.9 (Cq_{Ar}), 129.5 (CH_{Ar}), 129.1 (CH_{Ar}), 128.7 (CH_{Ar}), 127.5 (CH_{Ar}), 127.5 (CH_{Ar}), 127.4 (CH_{Ar}), 43.8 (CH_2), 43.6 (CH_2).

[6] T. Mohy El Dine, W. Erb, Y. Berhault, J. Rouden and J. Blanchet, *J. Org. Chem*., 2015, **80**, 4532.

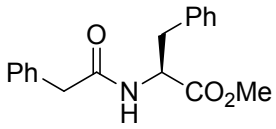
General Procedure C for the Preparation of Amino Acid Ester Free Amines (10a-h).

The amino acid ester hydrochloride salt (10 mmol) was introduced into a separatory funnel and mixed with CH_2Cl_2 (20 mL). An aqueous solution saturated with Na_2CO_3 was added and the solution was vigorously shaked for few minutes and extracted with CH_2Cl_2 (3 x 20 mL).The organic layers were collected, dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure to provide the pure amino acid ester amines **10a-h** in quantitative yields.

General Procedure D for the Synthesis of (11) and the Dipeptides (13a-m).

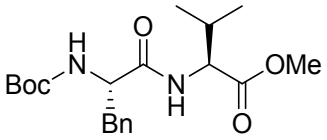
Into a 25 mL round-bottom flask kept under argon atmosphere was added the *N*-protected amino acid **12a-d** (0.46 mmol, 1 equiv.), 2-Chlorophenylborinic acid **9h** (29 mg, 0.115 mmol, 25 mol %) and 1 g of activated powdered 5 Å molecular sieves. Dry fluorobenzene (6.7 mL) was added, and the mixture was vigorously stirred for 15 min at a temperature of 65 °C. Then, the *C*-protected amino acid **10a-h** (0.46 mmol, 1 equiv.) was slowly added using a gastight 100 µL syringe and the resulting mixture was further stirred for 48 h at 65 °C. Then, the solution was filtered through a pad of Celite 545 and the residue washed with CH_2Cl_2 (2 x 5 mL) and EtOAc (3 x 5 mL). Unless otherwise mentioned, the filtrate was evaporated under reduced pressure and the residue was dissolved in CH_2Cl_2, washed with an aqueous solution of HCl (1M, pH = 3) (2 x 10 mL), aqueous basic solution of NaOH (pH = 11) (2 x 10 mL) and brine (10 mL). The organic layer was collected, dried over anhydrous $MgSO_4$, filtered and evaporated again under reduced pressure to provide the crude mixture. For certain products, purification by column chromatography was required.

(*S*)-*N*-Phenylacetyl-Phe OMe (**11**). Known and fully described.[6] The title compound was prepared according to the general procedure **D** using phenylalanine methyl ester **10d**. It was purified using the acid-base aqueous workup and isolated as a colorless solid after flushing with pentane (129 mg, 96%, *ee* > 99.9%).



$[\alpha]_D^{25}$ + 37.6° (*c* = 1.05, $CHCl_3$), $[\alpha]_D^{25}$ (lit) + 37.5° (*c* = 1.06, $CHCl_3$). ^{1}H NMR (400.0 MHz; $CDCl_3$) δ_H = 7.35-7.25 (m, $3H_{Ar}$), 7.22-7.18 (m, $5H_{Ar}$), 6.89-6.86 (m, $2H_{Ar}$), 5.81-5.80 (br s, NH), 4.87-4.82 (dt, *J* = 8.0, 5.8 Hz, 1H), 3.69 (s, 3H), 3.54 (s, 2H), 3.06 (dd, *J* = 14.0, 5.6 Hz, 1H), 2.99 (dd, *J* = 13.6, 5.6 Hz, 1H). ^{13}C NMR (101.6 MHz; $CDCl_3$) δ_C = 171.8 (C=O), 170.5 (C=O), 135.6 (Cq_{Ar}), 134.5 (Cq_{Ar}), 129.4 (CH_{Ar}), 129.2 (CH_{Ar}), 129.0 (CH_{Ar}), 128.6 (CH_{Ar}), 127.4 (CH_{Ar}), 127.1 (CH_{Ar}), 53.0 (CH), 52.3 (CH), 43.6 (CH_2), 37.6 (CH_2). Enantiomeric excess (*ee*) was determined by chiral HPLC on Daicel Chiralpak ASH 4.6 mm, 250 mm, 5 µm, using 60% n-heptane, 40% 2-propanol with a flow rate of 1 mL/min at 20 °C. The retention times (RT) were -10.142 min for the major enantiomer and -20.214 min for the minor enantiomer, respectively. The product **11** was obtained as one enantiomer with RT of -9.914 min.

(*S*,*S*)-Boc-Phe-Val-OMe (**13a**). Known and fully described.[7] The title compound was prepared according to the general procedure **D** using N-Boc-phenylalanine **12a** and valine methyl ester **10a**. It was purified using the acid-base aqueous workup and isolated as a colorless solid (89 mg, 51%).

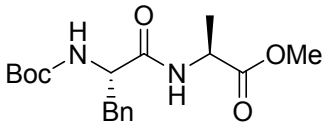


$[\alpha]_D^{25}$ – 7.0° (*c* = 1.0, $CHCl_3$), $[\alpha]_D^{25}$ (lit) – 7.0° (*c* = 1.02, $CHCl_3$).[7] ^{1}H NMR (400.0 MHz; $CDCl_3$) δ_H = 7.34-7.24 (m, $5H_{Ar}$), 6.48 (d, *J* = 8.3 Hz, NH), 5.12 (br s, NH), 4.50 (dd, *J* = 8.6, 5.1 Hz, 1H), 4.41 (d, *J* = 6.4 Hz, 1H), 3.73 (s, 3H), 3.12 (d, *J* = 6.7 Hz, 2H), 2.18-2.10 (m, 1H), 1.45

[7] F. Fécourt, B. Delpech, O. Melnyk and D. Crich, *Org. Lett.*, 2013, **15**, 3758.

(s, 9H), 0.91 (d, J = 6.9 Hz, 3H), 0.89 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101.6 MHz; $CDCl_3$) δ_C = 171.9 (C=O), 171.3 (C=O), 155.6 (C=O), 136.8 (Cq_{Ar}), 129.4 (CH_{Ar}), 128.7 (CH_{Ar}), 127.0 (CH_{Ar}), 80.3 (Cq), 57.4 (CH), 56.0 (CH), 52.2 (CH_3), 38.1 (CH_2), 31.4 (CH), 28.4 (CH_3), 19.0 (CH_3), 17.9 (CH_3).

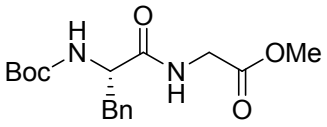
(*S*,*S*)-Boc-Phe-Ala-OMe (**13b**). Known and fully described.[8] The title compound was prepared according to the general procedure **D** using N-Boc-phenylalanine **12a** and alanine methyl ester **10b**. It was purified by column chromatography using EtOAc/pentane (30/70) as the eluent and isolated as colorless oil that solidifies upon storage (76 mg, 47%).



$[\alpha]_D^{25}$ – 19° (c = 1.0, MeOH), $[\alpha]_D^{25}$ (lit) – 22° (c = 0.1, MeOH).[9] ^{1}H NMR (400.0 MHz; $CDCl_3$) δ_H = 7.33-7.22 (m, $5H_{Ar}$), 6.85 (br s, NH), 5.28 (d, J = 8.1 Hz NH), 4.56 (t, J = 7.1 Hz, 1H), 4.47 (br s, 1H), 3.74 (s, 3H), 3.15-3.07 (m, 2H), 1.43 (s, 9H), 1.38 (d, J = 7.2 Hz, 3H). ^{13}C NMR (101.6 MHz; $CDCl_3$) δ_C = 173.0 (C=O), 171.2 (C=O), 155.6 (C=O), 136.7 (Cq_{Ar}), 129.5 (CH_{Ar}), 128.6 (CH_{Ar}), 127.0 (CH_{Ar}), 80.2 (Cq), 55.7 (CH), 52.5 (CH_3), 48.2 (CH), 38.5 (CH_2), 28.3 (CH_3), 18.3 (CH_3).

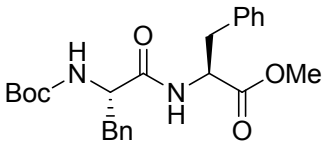
[8] T. V. Nguyen and D. J. M. Lyons, *Chem. Commun*., 2015, **51**, 3131.
[9] S. M. Mali and H. N. Gopi, *J. Org. Chem*., 2014, **79**, 2377.

(*S*)-Boc-Phe-Gly-OMe (**13c**). Known and fully described.[10] The title compound was prepared according to the general procedure **D** using N-Boc-phenylalanine **12a** and glycine methyl ester **10c**. It was purified using the acid-base aqueous workup and isolated as a colorless solid (85 mg, 55%).



$[\alpha]_D^{25}$ – 6.8° (*c* = 0.2, $CHCl_3$), $[\alpha]_D^{25}$ (lit) – 6.4° (*c* = 1.46, MeOH).[11] ^{1}H NMR (400.0 MHz; $CDCl_3$) δ_H = 7.32-7.20 (m, $5H_{Ar}$), 6.43 (br s, NH), 5.00 (br s, NH), 4.40 (br s, 1H), 4.07-3.96 (m, 2H), 3.73 (s, 3H), 3.11-3.06 (m, 2H), 1.40 (s, 9H). ^{13}C NMR (101.6 MHz; $CDCl_3$) δ_C = 170.5 (C=O), 168.9 (C=O), 154.4 (C=O), 135.5 (Cq_{Ar}), 128.3 (CH_{Ar}), 127.7 (CH_{Ar}), 126.0 (CH_{Ar}), 79.4 (Cq), 54.6 (CH), 51.4 (CH_3), 40.2 (CH_2), 37.3 (CH_2), 27.2 (CH_3).

(*S*,*S*)-Boc-Phe-Phe-OMe (**13d**). Known and fully described.[12] The title compound was prepared according to the general procedure **D** using N-Boc-phenylalanine **12a** and phenylalanine methyl ester **10d**. It was purified using the acid-base aqueous workup and isolated as a colorless solid (120 mg, 61%).

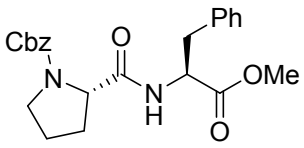


$[\alpha]_D^{25}$ – 13.4° (*c* = 1.0, MeOH), $[\alpha]_D^{25}$ (lit) – 13.5° (*c* = 1.0, MeOH).[13] ^{1}H NMR (400.0 MHz; $CDCl_3$) δ_H = 7.34-7.21 (m, $8H_{Ar}$), 7.03-7.01 (m, $2H_{Ar}$), 6.37 (d, *J* = 6.6 Hz, NH), 5.01 (br s, NH), 4.82 (d, *J* = 6.2 Hz, 1H), 4.38 (d, *J* = 4.9 Hz, 1H), 3.70 (s, 3H), 3.10-3.06 (m, 4H). ^{13}C NMR (101.6 MHz; $CDCl_3$) δ_C = 171.4 (C=O), 170.9 (C=O), 155.4 (C=O), 136.6 (Cq_{Ar}), 135.7 (Cq_{Ar}), 129.4 (CH_{Ar}), 129.3 (CH_{Ar}), 128.7 (CH_{Ar}), 128.6 (CH_{Ar}), 127.2 (CH_{Ar}), 127.0 (CH_{Ar}), 80.3 (Cq), 55.8 (CH), 53.4 (CH), 52.4 (CH_3), 38.3 (CH_2), 38.0 (CH_2), 28.3 (CH_3).

---

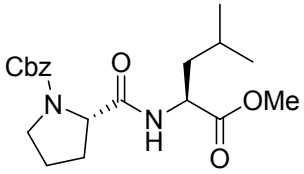
[10] W. W. Gerhardt and M. Weck, *J. Org. Chem.*, 2006, **71**, 6333.
[11] M. Michelot, P. V. C. Magneney and P. Schmitt, *Eur. J. Med. Chem.*, 1988, **23**, 243.
[12] J. Bonnamour, T.-X. Métro, J. Martineza and F. Lamaty, *Green Chem.*, 2013, **15**, 1116.
[13] D. K. Mohapatra and A. Datta, *J. Org. Chem.*, 1999, **64**, 6879.

(*S*,*S*)-Z-Pro-Phe-OMe (**13e**). The title compound was prepared according to the general procedure **D** using N-Cbz-proline **12b** and phenylalanine methyl ester **10d**. It was purified by column chromatography using EtOAc/pentane (40/60) as the eluent and isolated as a colorless solid (113 mg, 60%).



$[\alpha]_D^{25}$ – 33.1° (*c* = 1.0, MeOH), $[\alpha]_D^{25}$ (lit) – 32.8° (*c* = 1.0, MeOH)[14].^{1}H NMR (500.0 MHz; DMSO-d_6, 80 °C) δ_H = 8.0 (d, *J* = 6.3 Hz, NH), 7.36-7.20 (m, 10H_{Ar}), 5.10-5.07 (m, 2H), 4.59-4.56 (m, 1H), 4.29 (dd, *J* = 7.2 , 2.6 Hz, 1H), 3.61 (s, 3H), 3.47-3.40 (m, 2H), 3.13-2.99 (m, 2H), 2.18-2.12 (m, 1H), 1.80-1.76 (m, 3H). ^{13}C NMR (125.7 MHz; DMSO-d_6, 80 °C) δ_C = 171.2 (C=O), 171.0 (C=O), 153.5 (C=O), 136.5 (Cq_{Ar}), 136.4 (Cq_{Ar}), 128.3 (CH_{Ar}), 127.5 (CH_{Ar}), 127.4 (CH_{Ar}), 126.9 (CH_{Ar}), 126.5 (CH_{Ar}), 125.7 (CH_{Ar}), 65.3 (CH_2), 59.0 (CH), 52.7 (CH), 50.9 (CH_3), 46.2 (CH_2), 36.2 (CH_2), 29.6 (CH_2), 22.5 (CH_2). υ_{max} (neat)/cm^{-1} 3446, 3002, 2901, 1743, 1700, 1416, 1261, 1117, 990, 802. HRMS (ESI+ TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{26}N_2O_5Na$: 433.1739; Found: 433.1728.

(*S*,*S*)-Z-Pro-Leu-OMe (**13f**). Known and fully described.[15] The title compound was prepared according to the general procedure **D** using N-Cbz-proline **12b** and leucine methyl ester **10e**. It was purified by column chromatography using EtOAc/pentane (40/60) as the eluent and isolated as a yellow solid (103 mg, 60%).

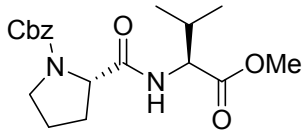


$[\alpha]_D^{25}$ – 56.9° (*c* = 0.5, $CHCl_3$), $[\alpha]_D^{25}$ (lit) – 56.7° (*c* = 0.5, $CHCl_3$).[15] ^{1}H NMR (500.0 MHz; DMSO-d_6, 80 °C) δ_H = 7.97 (d, *J* = 5.8 Hz, NH), 7.35-7.31 (m, 5H_{Ar}), 5.11-5.08 (m, 2H), 4.36-4.31 (m, 2H), 3.67 (s, 3H), 3.64-3.42 (m, 2H), 2.20-2.15 (m, 1H), 1.91-1.83 (m, 3H), 1.58-1.53

[14] P. Revelou, C. G. Kokotos and P. Moutevelis-Minakakis, *Tetrahedron*, 2012, **68**, 8732.
[15] J. Duan, Y. Sun, H. Chen, G. Qiu, H. Zhou, T. Tang, Z. Deng and X. Hong, *J. Org. Chem*., 2013, **78**, 7013.

(m, 3H), 0.90-0.83 (m, 6H). ^{13}C NMR (125.7 MHz; DMSO-d_6, 80 °C) δ_C = 173.2 (C=O), 172.5 (C=O), 154.5 (C=O), 137.6 (Cq_{Ar}), 128.7 (CH_{Ar}), 128.0 (CH_{Ar}), 127.6 (CH_{Ar}), 66.4 (CH_2), 59.9 (CH), 52.0 (CH_3), 50.9 (CH), 50.8 (CH_2), 47.4 (CH_2), 31.1 (CH_2), 24.8 (CH_3), 23.7 (CH_2), 23.0 (CH_3), 21.9 (CH).

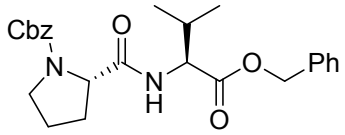
(*S*,*S*)-Z-Pro-Val-OMe (**13g**). The title compound was prepared according to the general procedure **D** using N-Cbz-proline **12b** and valine methyl ester **10a**. It was purified by column chromatography using EtOAc/pentane (30/70) as the eluent and isolated as colorless oil (97 mg, 58%).



$[\alpha]_D^{25}$ – 59.3° (*c* = 1.1, EtOH), $[\alpha]_D^{25}$ (lit) – 60.0° (*c* = 1.01, EtOH).[16] ^{1}H NMR (500.0 MHz; DMSO-d_6, 80 °C) δ_H = 7.85 (d, *J* = 6.5 Hz, NH), 7.35-7.30 (m, 5H_{Ar}), 5.06 (s, 2H), 4.40 (dd, *J* = 7.0 , 4.5 Hz, 1H), 4.19 (dd, *J* = 6.5 , 5.0 Hz, 1H), 3.64 (s, 3H), 3.49-3.40 (m, 2H), 2.20-2.01 (m, 2H), 1.90-1.84 (m, 3H), 0.88-0.85 (m, 6H). ^{13}C NMR (125.7 MHz; DMSO-d_6, 80 °C) δ_C = 171.8 (C=O), 171.2 (C=O), 153.6 (C=O), 136.5 (Cq_{Ar}), 127.7 (CH_{Ar}), 127.0 (CH_{Ar}), 126.7 (CH_{Ar}), 65.4 (CH_2), 58.8 (CH), 57.0 (CH), 50.9 (CH_3), 46.4 (CH_2), 29.4 (CH_2), 28.4 (CH_2), 22.9 (CH_2), 18.3 (CH_3), 17.6 (CH_3). υ_{max} (neat)/cm^{-1} 3444, 3002, 2250, 1739, 1743, 1667, 1216, 1053, 1024, 1006, 998, 821, 758. HRMS (ESI+ TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{26}N_2O_5Na$: 385.1739; Found: 385.1751.

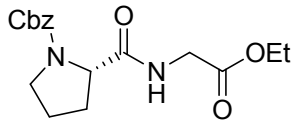
[16] O. E. Edwards and W. Rank, *Can. J. Chem.*, 1990, **68**, 1425.

(*S*,*S*)-Z-Pro-Val-OBn (**13h**). The title compound was prepared according to the general procedure **D** using N-Cbz-proline **12b** and valine benzyl ester **10f**. It was purified by column chromatography using EtOAc/pentane (40/60) as the eluent and isolated as yellowish oil (119 mg, 59%).



$[\alpha]_D^{25}$ – 38.2° (*c* = 1.0, DMF), $[\alpha]_D^{25}$ (lit) – 38.0° (*c* = 1.0, DMF).[17] ^{1}H NMR (500.0 MHz; DMSO-d_6, 80 °C) δ_H = 7.88 (d, *J* = 6.7 Hz, NH), 7.36-7.30 (m, 10H_{Ar}), 5.17-5.12 (m, 2H), 5.05 (br s, 2H), 4.39 (d, *J* = 6.6, 1H), 4.24 (t, *J* = 5.8, 1H), 3.48-3.41 (m, 2H), 2.10-2.05 (m, 2H), 1.84-1.78 (m, 3H), 0.86 (d, *J* = 2.3 Hz, 6H). ^{13}C NMR (125.7 MHz; DMSO-d_6, 80 °C) δ_C = 171.8 (C=O), 170.6 (C=O), 153.6 (C=O), 136.6 (Cq_{Ar}), 135.5 (Cq_{Ar}), 127.8 (CH_{Ar}), 127.7 (CH_{Ar}), 127.6 (CH_{Ar}), 127.5 (CH_{Ar}), 127.1 (CH_{Ar}), 126.7 (CH_{Ar}), 65.5 (CH_2), 65.4 (CH_2), 58.8 (CH), 57.2 (CH), 46.4 (CH_2), 29.7 (CH_2), 29.4 (CH), 22.8 (CH_2), 18.3 (CH_3), 17.6 (CH_3). υ_{max} (neat)/cm^{-1} 3472, 2963, 1739, 1703, 1701, 1544, 1417, 1356, 1262, 1204, 1053, 1025, 1006, 926, 820, 769, 757. HRMS (ESI+ TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{30}N_2O_5Na$: 461.2052; Found: 461.2042.

(*S*)-Z-Pro-Gly-OEt (**13i**). Known and fully described.[18] The title compound was prepared according to the general procedure **D** using N-Cbz-proline **12b** and glycine ethyl ester **10g**. It was purified by column chromatography using EtOAc/pentane (50/50) as the eluent and isolated as colorless oil that solidifies upon storage (112 mg, 73%).

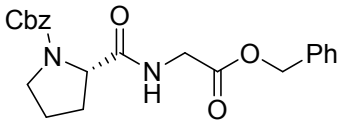


$[\alpha]_D^{25}$ – 24.9° (*c* = 1.35, EtOAc), $[\alpha]_D^{25}$ (lit) – 60.4° (*c* = 2.43, EtOAc).[18] ^{1}H NMR (500.0 MHz; DMSO-d_6, 80 °C) δ_H = 8.06 (br s, NH), 7.37-7.32 (m, 5H_{Ar}), 5.13-5.07 (m, 2H), 4.31 (d, *J* = 5.9

[17] I. Shinoda, A. Fushimi, H. Kato, H. Okai and S. Fukui, *Agric. Biol. Chem*., 1985, **49**, 2587.
[18] H. Chen, M. He, Y. Wang, L. Zhai, Y. Cui, Y. Li, Y. Lee, H. Zhou, X. Hong and Z. Deng, *Green Chem*., 2011, **13**, 2723.

Hz, 1H), 4.16-4.11 (m, 2H), 3.89-3.79 (m, 2H), 3.52-3.46 (m, 2H), 2.17-2.12 (m, 1H), 1.96-1.85 (m, 3H), 1.23 (t, J = 5.6 Hz, 3H). ^{13}C NMR (125.7 MHz; DMSO-d_6, 80 °C) δ_C = 172.0 (C=O), 169.1 (C=O), 153.8 (C=O), 136.7 (Cq_{Ar}), 127.8 (CH_{Ar}), 127.2 (CH_{Ar}), 126.8 (CH_{Ar}), 65.6 (CH_2), 59.9 (CH_2), 59.5 (CH), 46.4 (CH_2), 40.5 (CH_2), 30.1 (CH_2), 22.9 (CH_2), 13.6 (CH_3).

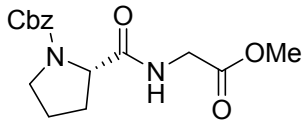
(*S*)-Z-Pro-Gly-OBn (**13j**). The title compound was prepared according to the general procedure **D** using N-Cbz-proline **12b** and glycine benzyl ester **10h**. It was purified by column chromatography using EtOAc/pentane (40/60) as the eluent and isolated as a colorless solid (86 mg, 47%).



$[\alpha]_D^{25}$ – 58.4° (*c* = 1.0, EtOH), $[\alpha]_D^{25}$ (lit) – 58.3° (*c* = 1.0, EtOH).[19] ^{1}H NMR (500.0 MHz; DMSO-d_6, 80 °C) δ_H = 8.07 (br s, NH), 7.35-7.28 (m, 10H_{Ar}), 5.12 (s, 2H), 5.05 (s, 2H), 4.26 (d, J = 6.2 Hz, 1H), 3.88 (t, J = 6.0 Hz, 2H), 3.49-3.38 (m, 2H), 2.10-2.09 (m, 1H), 1.88-1.77 (m, 3H). ^{13}C NMR (125.7 MHz; DMSO-d_6, 80 °C) δ_C = 172.0 (C=O), 169.0 (C=O), 153.7 (C=O), 136.6 (Cq_{Ar}), 135.5 (Cq_{Ar}), 127.9 (CH_{Ar}), 127.7 (CH_{Ar}), 127.5 (CH_{Ar}), 127.3 (CH_{Ar}), 127.1 (CH_{Ar}), 126.8 (CH_{Ar}), 65.5 (CH_2), 65.4 (CH_2), 59.4 (CH), 46.3 (CH_2), 40.4 (CH_2), 29.9 (CH_2), 22.8 (CH_2). υ_{max} (neat)/cm^{-1} 3444, 3003, 2905, 1750, 1699, 1668, 1413, 1178, 1183, 1053, 1006, 996, 821, 758, 766, 700. HRMS (ESI+ TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{24}N_2O_5Na$: 419.1583; Found: 419.1580

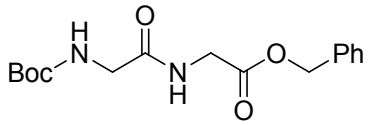
[19] R. Appel, U. Glaesel and V. I. Glaesel, *Chem. Ber*., 1981, **114**, 1542.

(*S*)-Z-Pro-Gly-OMe (**13k**). The title compound was prepared according to the general procedure **D** using N-Cbz-proline **12b** and glycine methyl ester **10c**. It was purified by column chromatography using EtOAc/pentane (30/70) as the eluent and isolated as yellowish oil (75 mg, 51%).



$[\alpha]_D^{25}$ – 62.2° (*c* = 1.0, MeOH), $[\alpha]_D^{25}$ (lit) – 62.0° (*c* = 1.0, MeOH).[20] ^{1}H NMR (500.0 MHz; DMSO-d_6, 80 °C) δ_H = 8.00 (br s, NH), 7.31-7.27 (m, 5H_{Ar}), 5.07-5.01 (m, 2H), 4.25 (d, *J* = 6.4 Hz, 1H), 3.80 (t, *J* = 6.4 Hz, 2H), 3.60 (s, 3H), 3.46-3.39 (m, 2H), 2.11-2.10 (m, 1H), 1.89-1.78 (m, 3H). ^{13}C NMR (125.7 MHz; DMSO-d_6, 80 °C) δ_C = 172.0 (C=O), 169.5 (C=O), 153.7 (C=O), 136.6 (Cq_{Ar}), 127.8 (CH_{Ar}), 127.1 (CH_{Ar}), 126.8 (CH_{Ar}), 65.6 (CH_2), 59.4 (CH), 51.0 (CH_3), 40.2 (CH_2), 46.4 (CH_2), 30.0 (CH_2), 22.9 (CH_2). υ_{max} (neat)/cm^{-1} 3444, 2801, 1739, 1664, 1376, 1205, 1053, 1025, 1006, 996, 828, 765. HRMS (ESI+ TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{20}N_2O_5Na$: 343.1270; Found: 343.1263.

Boc-Gly-Gly-OBn (**13l**). Known and fully described.[21] The title compound was prepared according to the general procedure **D** using N-Boc-glycine **12c** and glycine benzyl ester **10h**. It was purified using the acid-base aqueous workup and isolated as a colorless solid (118 mg, 80%).

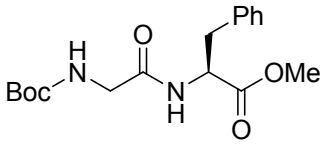


^{1}H NMR (400.0 MHz; $CDCl_3$) δ_H = 7.28-7.24 (m, 5H_{Ar}), 6.89 (br s, NH), 5.34 (br s, NH), 5.08 (s, 2H), 4.0 (d, *J* = 5.4 Hz, 2H), 3.77 (d, *J* = 5.0 Hz, 2H), 1.36 (s, 9H). ^{13}C NMR (101.6 MHz; $CDCl_3$) δ_C = 170.1 (C=O), 169.8 (C=O), 156.2 (C=O), 135.2 (Cq_{Ar}), 128.7 (CH_{Ar}), 128.6 (CH_{Ar}), 128.4 (CH_{Ar}), 80.4 (Cq), 67.3 (CH_2), 44.2 (CH_2), 41.3 (CH_2), 28.4 (CH_3).

---

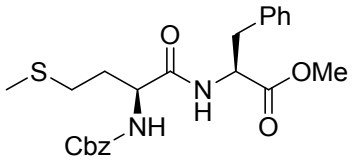
[20] M. Jaouadi, C. Selve, J. R. Dormoy and B. Castro, *Bull. Soc. Chim. Fr.*, 1984, **2**, 409.
[21] (a) S. R. Bull, L. C. Palmer, N. J. Fry, M. A. Greenfield, B. W. Messmore, T. J. Meade and S. I. Stupp, *J. Am. Chem. Soc*., 2008, **130**, 2742. (b) D. W. Brown, M. M. Campbell and C. V. Walker, *Tetrahedron*, 1983, **39**, 1075.

(*S*)-Boc-Gly-Phe-OMe (**13m**). The title compound was prepared according to the general procedure **D** using N-Boc-glycine **12c** and phenylalanine methyl ester **10d**. It was purified using the acid-base aqueous workup and isolated as a yellow solid (111 mg, 72%).



$[\alpha]_D^{25}$ + 4.8° (*c* = 2.0, $CHCl_3$). ^{1}H NMR (400.0 MHz; $CHCl_3$) δ_H = 7.28-7.21 (m, $3H_{Ar}$), 7.09 (d, *J* = 6.6 Hz, $2H_{Ar}$), 6.79 (d, *J* = 6.6 Hz, NH), 5.34 (br s, NH), 4.85 (q, *J* = 6.1 Hz, 1H), 3.78-3.72 (m, 2H), 3.68 (s, 3H), 3.09 (dd, *J* = 3.1, 5.8 Hz, 2H), 1.42 (s, 9H). ^{13}C NMR (101.6 MHz; $CDCl_3$) δ_C = 171.8 (C=O), 169.3 (C=O), 156.1 (C=O), 135.8 (Cq_{Ar}), 128.3 (CH_{Ar}), 128.7 (CH_{Ar}), 128.2 (CH_{Ar}), 80.2 (Cq), 53.2 (CH), 52.4 (CH_3), 44.2 (CH_2), 37.9 (CH_2), 28.3 (CH_3). υ_{max} (neat)/cm^{-1} 3422, 3049, 2979, 1743, 1710, 1683, 1532, 1456, 1367, 1278, 1250, 1214, 1169, 1051, 1024, 1006, 822, 759, 730, 700. HRMS (ESI+ TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{24}N_2O_5Na$: 359.1583; Found: 359.1570.

(*S*,*S*)-Z-Met-Phe-OMe (**13n**). The title compound was prepared according to the general procedure **D** using N-Cbz-methionine **12d** and phenylalanine methyl ester **10d**. It was purified by column chromatography using EtOAc/pentane (30/70) as the eluent and isolated as a yellowish solid (81 mg, 40%).

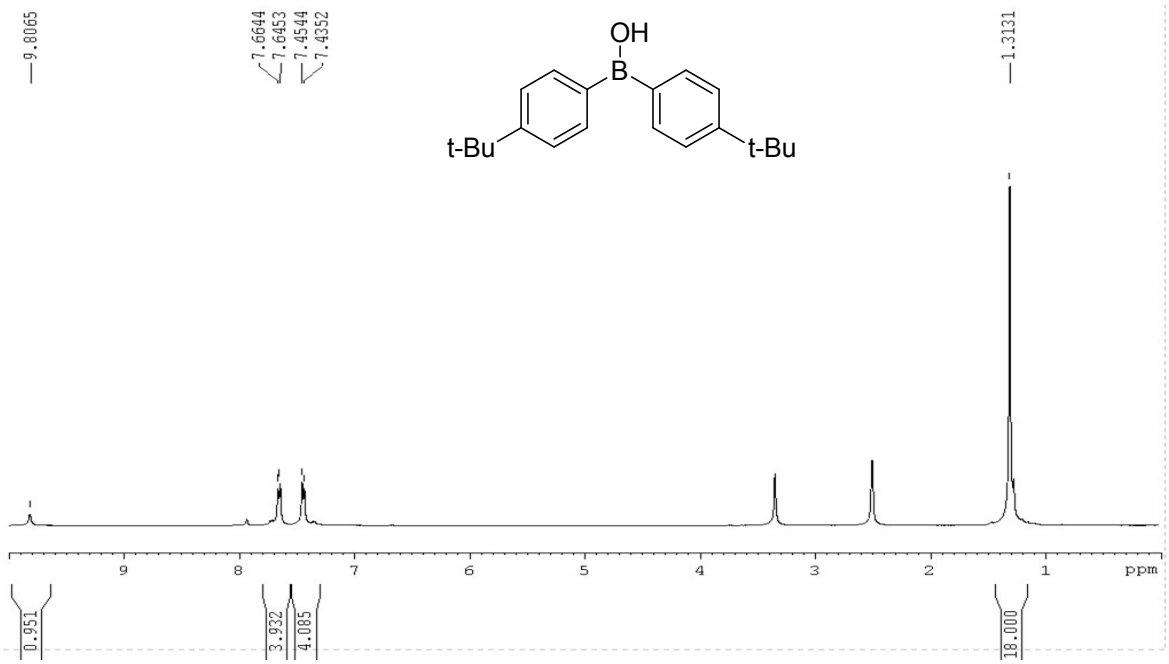


$[\alpha]_D^{25}$ +3.8° (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400.0 MHz; $CHCl_3$) δ_H = 7.35-7.25 (m, $4H_{Ar}$), 7.27-7.09 (m, $4H_{Ar}$), 7.09 (d, *J* = 6.7 Hz, $2H_{Ar}$), 6.58 (d, *J* = 7.1 Hz, NH), 5.45 (d, *J* = 7.4 Hz, NH), 5.1 (s, 2H), 4.85 (q, *J* = 7.7 Hz, 1H), 4.35 (d, *J* = 6.7 Hz, 1H), 3.73 (s, 3H), 3.13-3.09 (m, 2H), 2.50 (s, 2H), 2.03-2.00 (m, 3H), 1.98-1.85 (m, 3H). ^{13}C NMR (101.6 MHz; $CDCl_3$) δ_C = 171.7 (C=O), 170.8 (C=O), 156.0 (C=O), 136.3 (Cq_{Ar}), 135.6 (Cq_{Ar}), 129.3 (CH_{Ar}), 128.8 (CH_{Ar}), 128.7 (CH_{Ar}), 128.4 (CH_{Ar}), 128.2 (CH_{Ar}), 127.4 (CH_{Ar}), 67.2 (CH_2), 53.6 (CH), 53.3 (CH3), 52.5

(CH_3), 37.9 (CH_2), 31.6 (CH_2), 29.8 (CH_2), 15.1 (CH_3). υ_{max} (neat)/cm^{-1} 3302, 3032, 1953, 2925, 2855, 1716, 1661, 1605, 1521, 1497, 1455, 1441, 1281, 1214, 1179, 1114, 1081, 1043, 1028, 913, 742. HRMS (ESI+ TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{28}N_2O_5NaS$: 467.1617; Found: 467.1613.

^{1}H NMR and ^{13}C NMR of Newly Synthesized Aryl Borinic Acids.

^{1}H NMR (400.0 MHz; DMSO-d^{6}) of **9c**



^{13}C NMR (101.6 MHz; DMSO-d^{6}) of **9c**

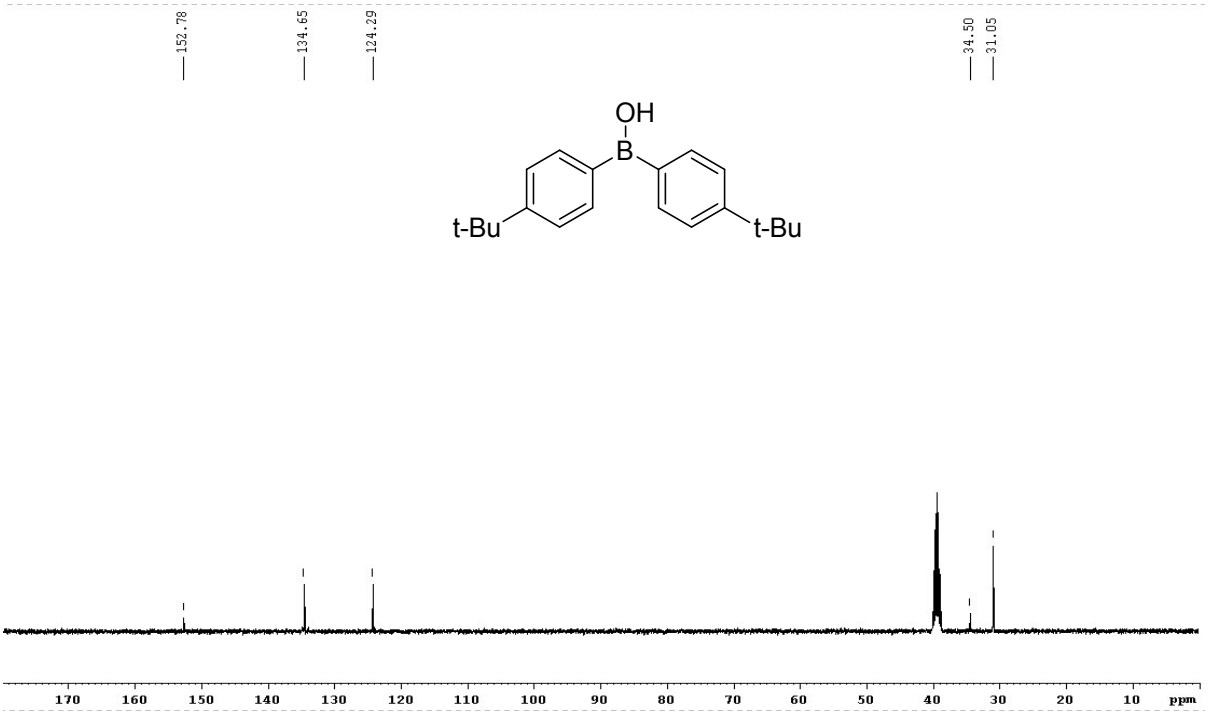
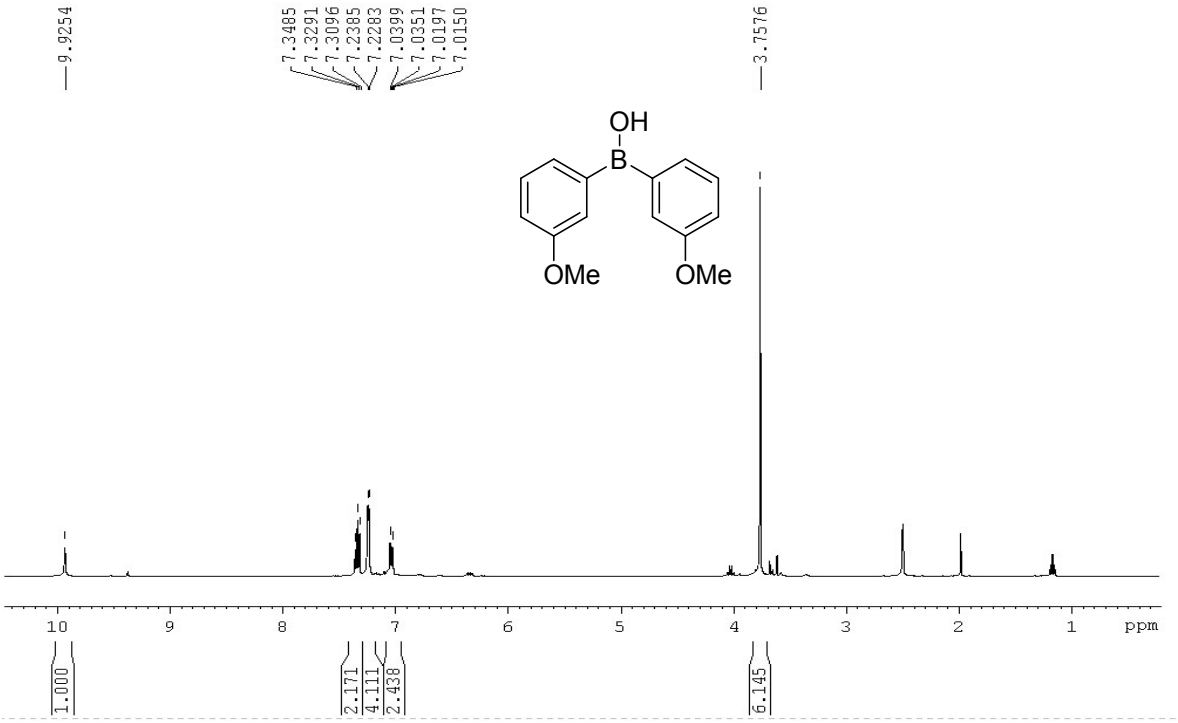


Figure S1. ^{1}H NMR and ^{13}C NMR spectra of **9c.**

^{1}H NMR (400.0 MHz; DMSO-d^{6}) of **9e.**



^{13}C NMR (101.6 MHz; DMSO-d^{6}) of **9e.**

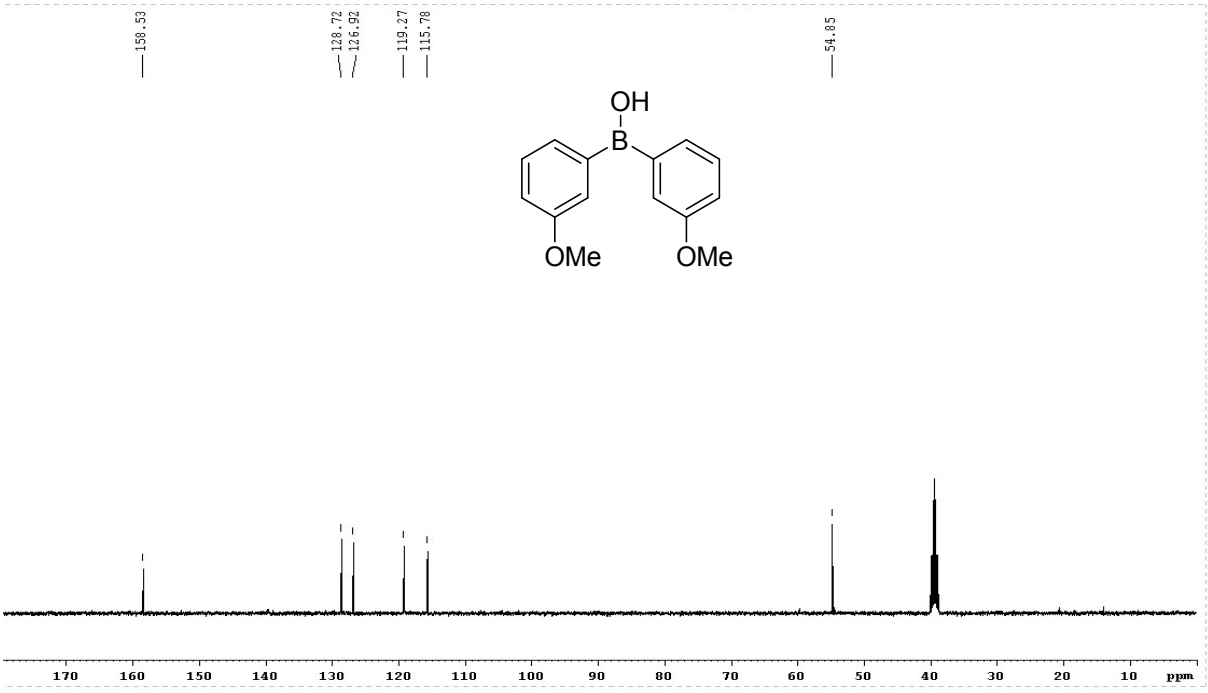
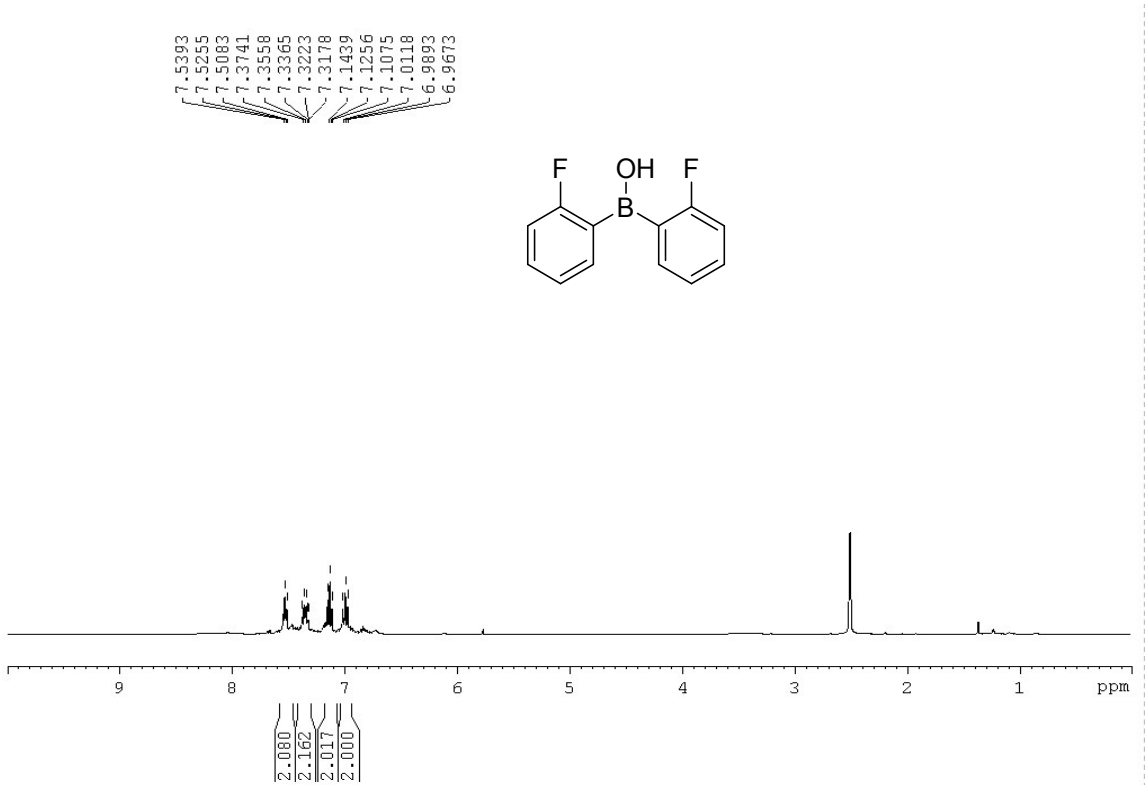


Figure S2. ^{1}H NMR and ^{13}C NMR spectra of **9e.**

^{1}H NMR (400.0 MHz; DMSO-d^{6}) of **9f.**



^{13}C NMR (101.6 MHz; DMSO-d^{6}) of **9f.**

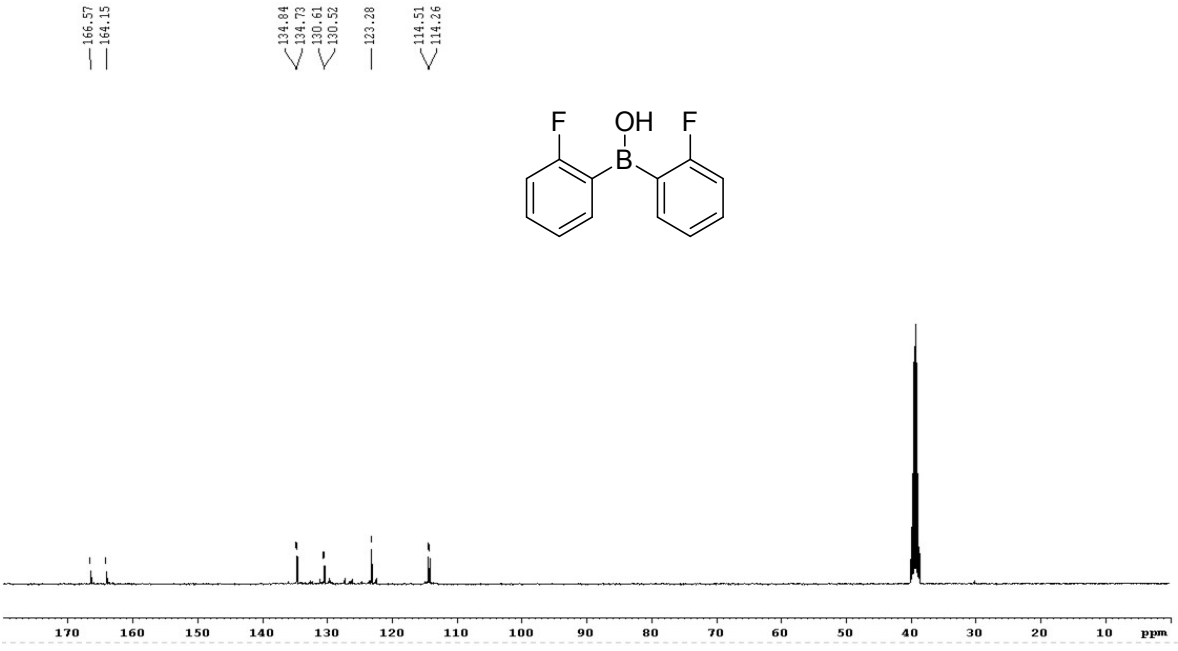
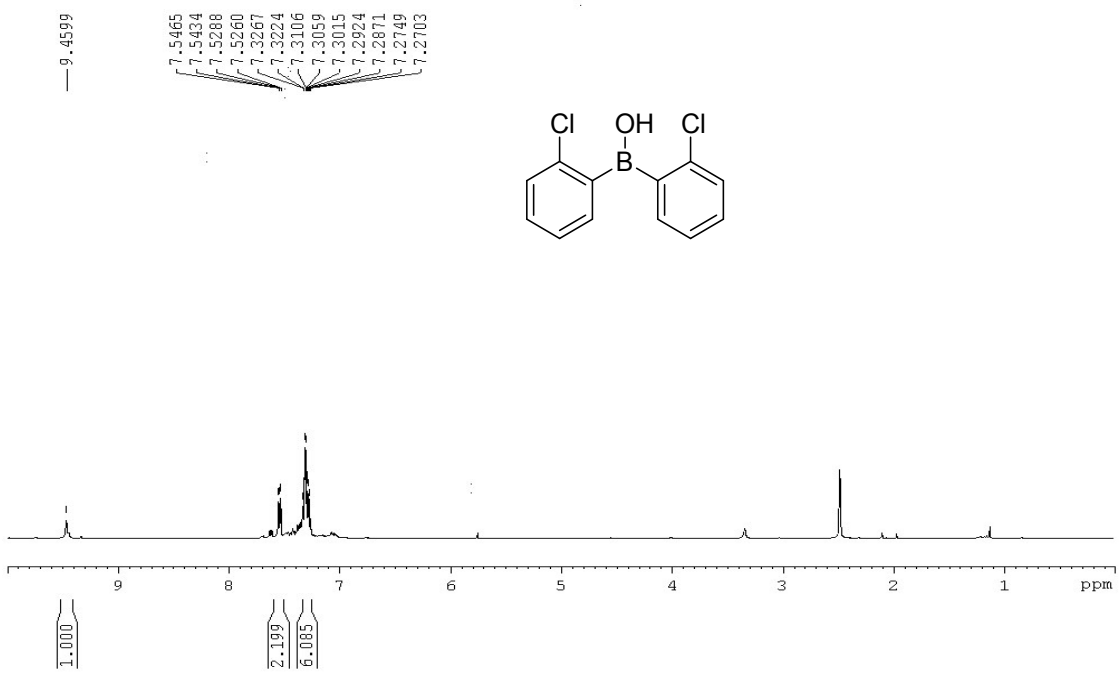


Figure S3. ^{1}H NMR and ^{13}C NMR spectra of **9f.**

^{1}H NMR (400.0 MHz; DMSO-d^{6}) of **9h.**



^{13}C NMR (101.6 MHz; DMSO-d^{6}) of **9h.**

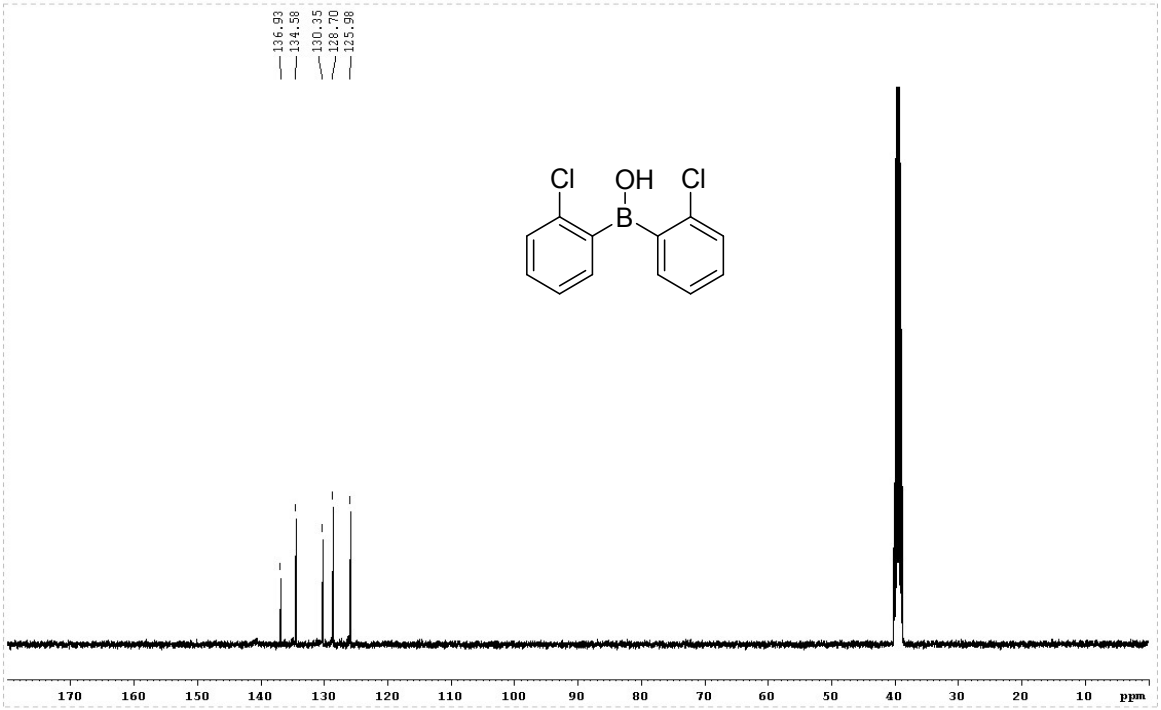
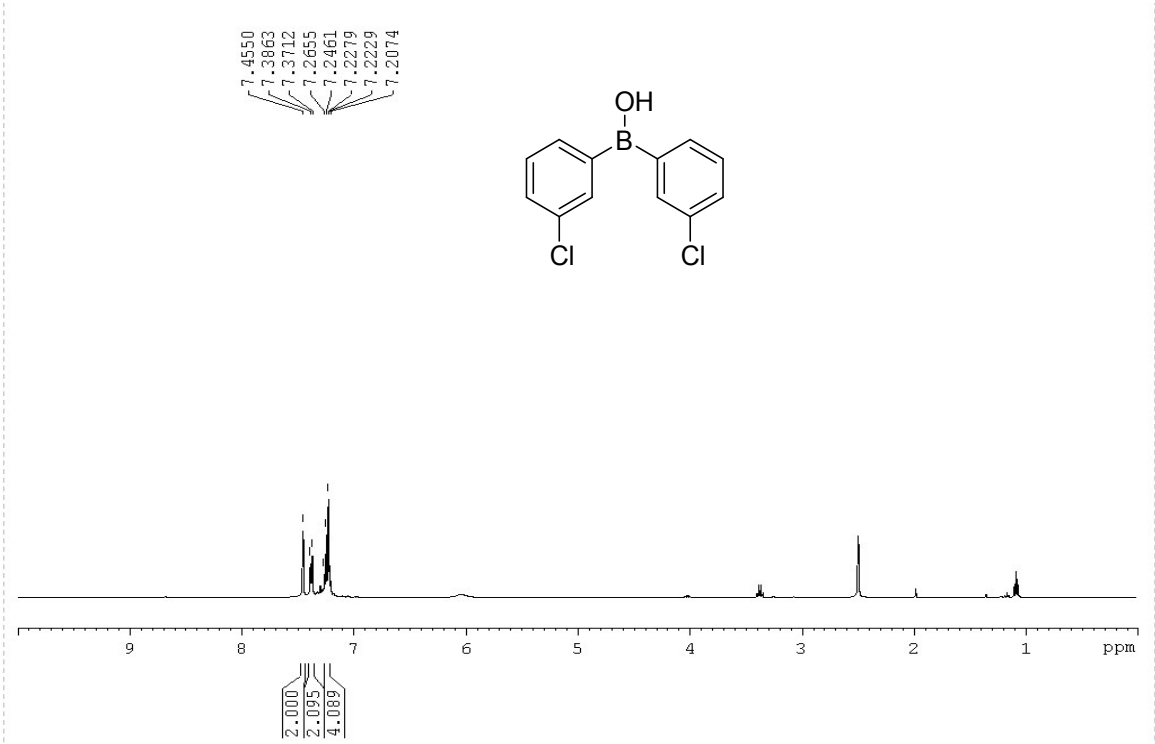


Figure S4. ^{1}H NMR and ^{13}C NMR spectra of **9h.**

^{1}H NMR (400.0 MHz; DMSO-d^{6}) of **9i.**



^{13}C NMR (101.6 MHz; DMSO-d^{6}) of **9i.**

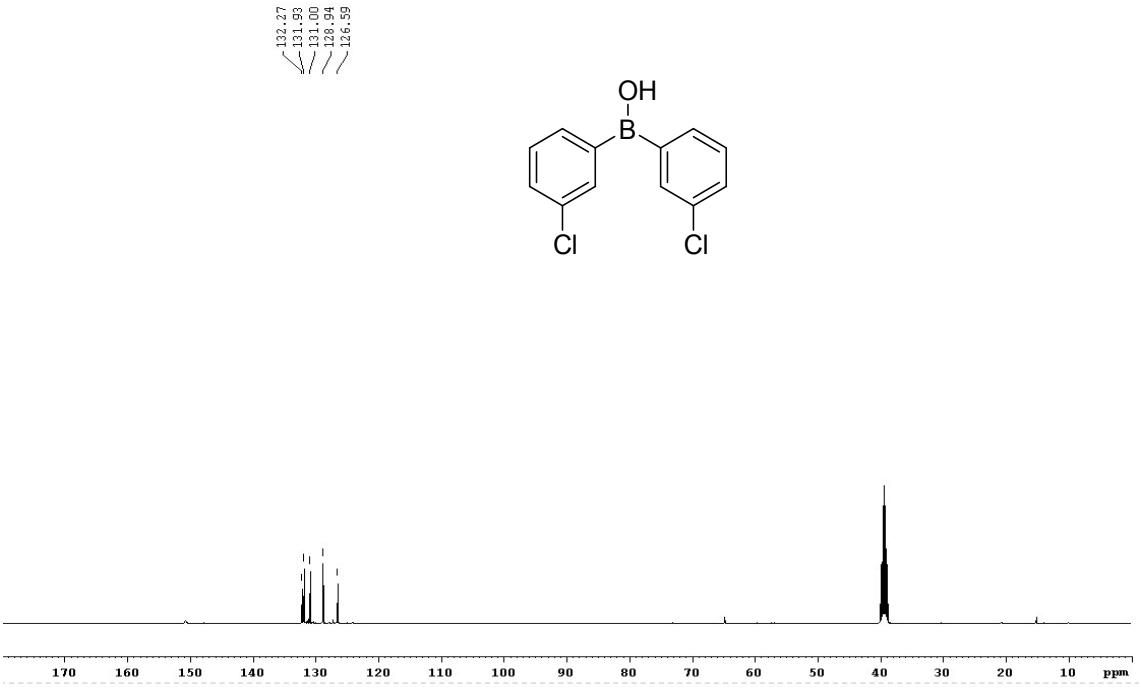
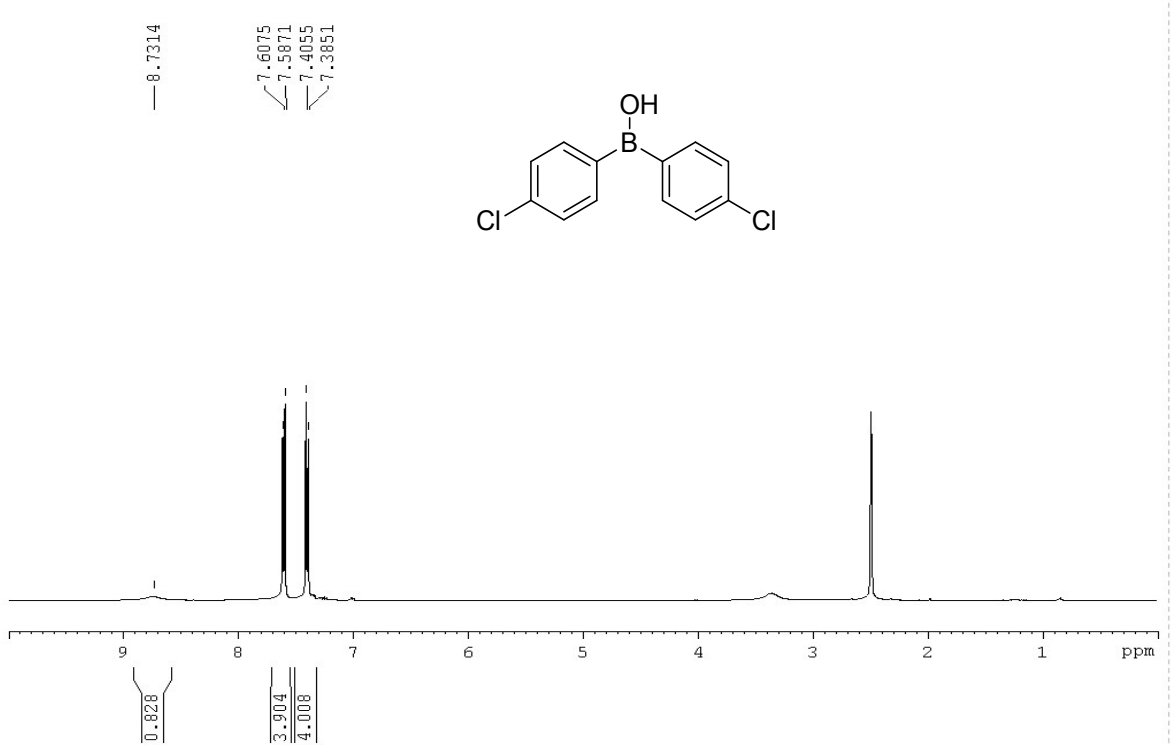


Figure S5. ^{1}H NMR and ^{13}C NMR spectra of **9i.**

^{1}H NMR (400.0 MHz; DMSO-d^{6}) of **9j.**



^{13}C NMR (101.6 MHz; DMSO-d^{6}) of **9j.**

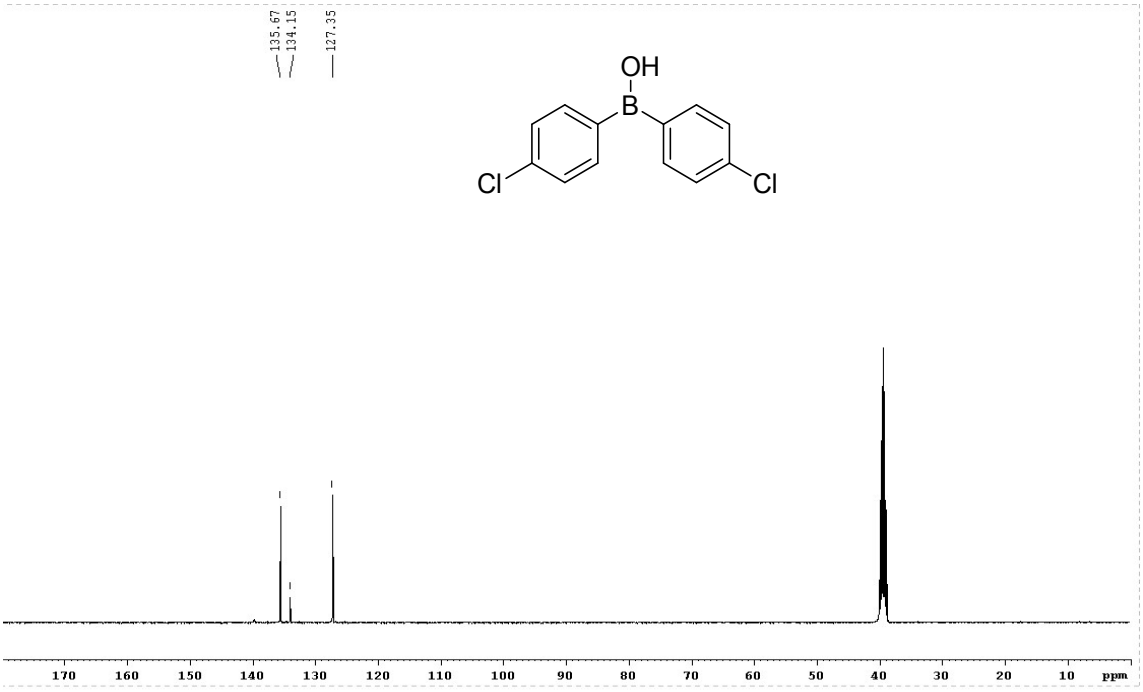
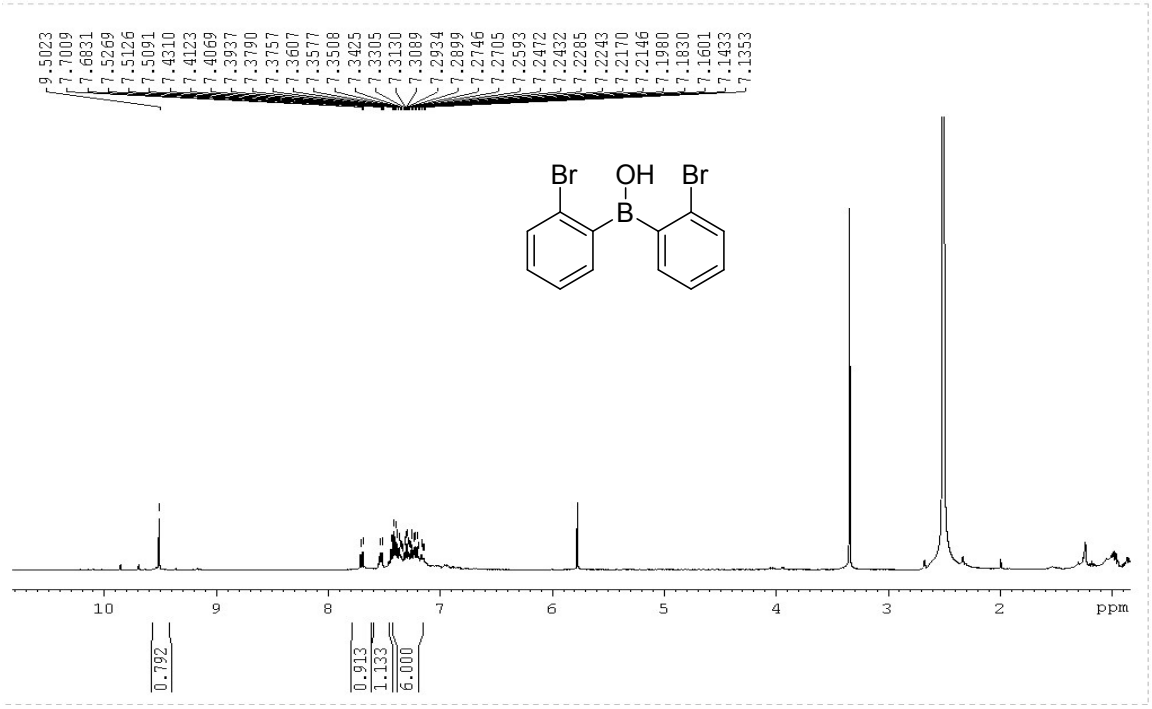


Figure S6. ^{1}H NMR and ^{13}C NMR spectra of **9j.**

^{1}H NMR (400.0 MHz; DMSO-d^{6}) of **9k.**



^{13}C NMR (101.6 MHz; $CDCl_3$-d^{1}) of **9k.**

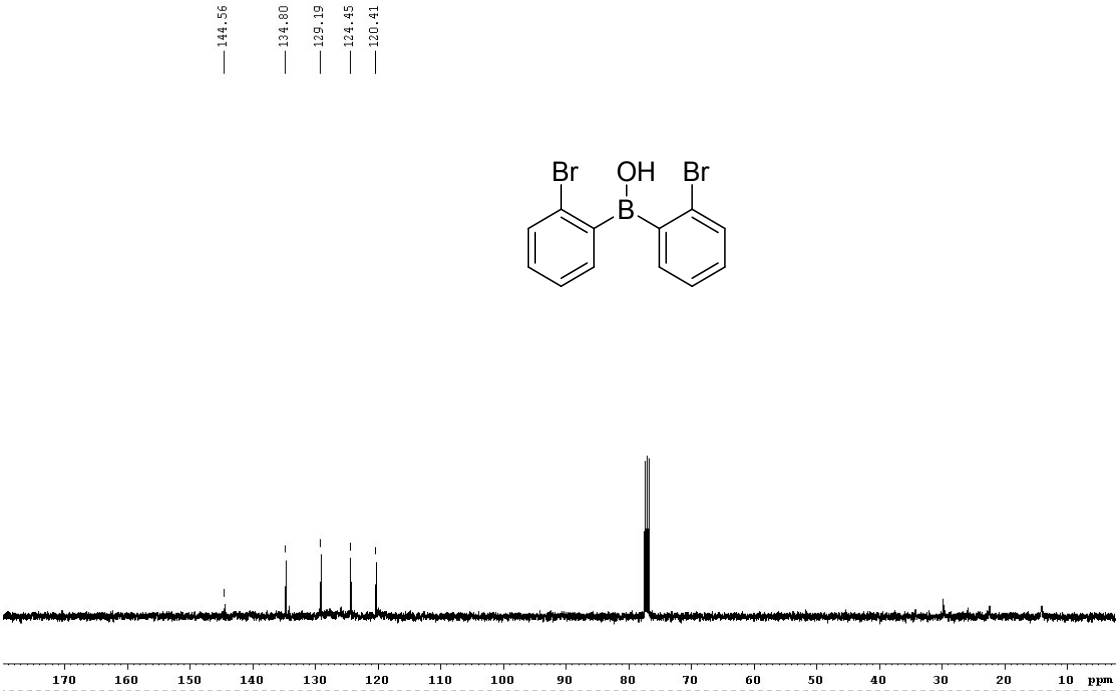
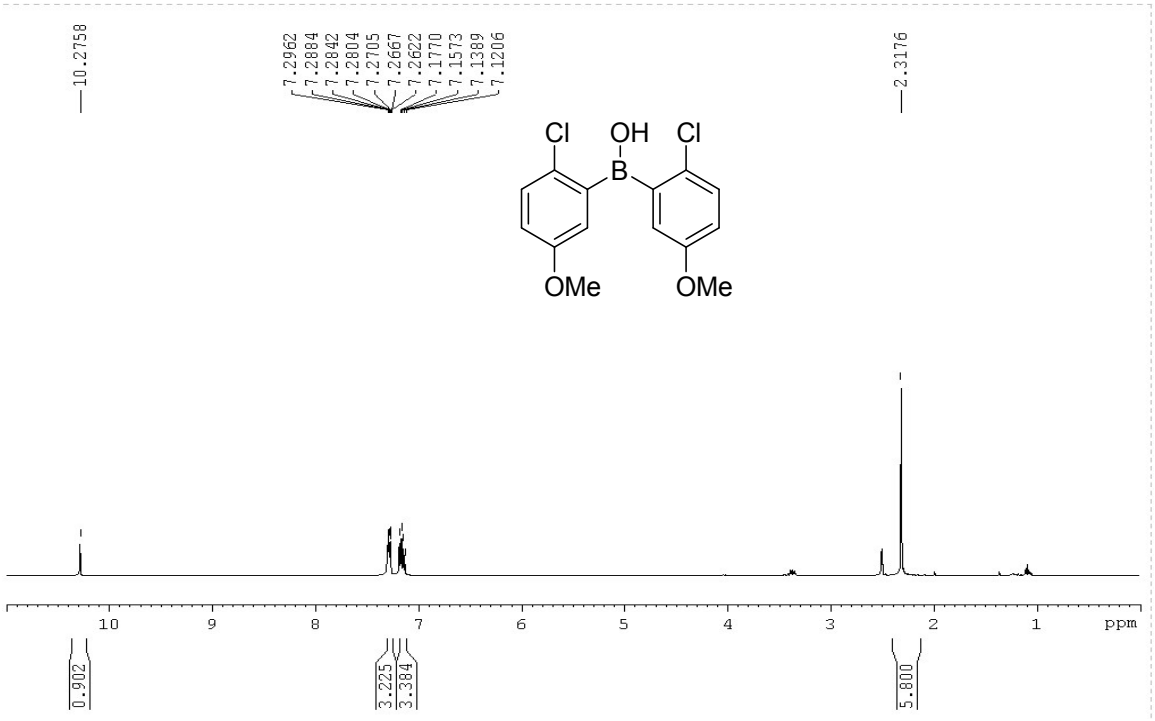


Figure S7. ^{1}H NMR and ^{13}C NMR spectra of **9k.**

^{1}H NMR (400.0 MHz; DMSO-d^{6}) of **9l.**



^{13}C NMR (101.6 MHz; DMSO-d^{6}) of **9l.**

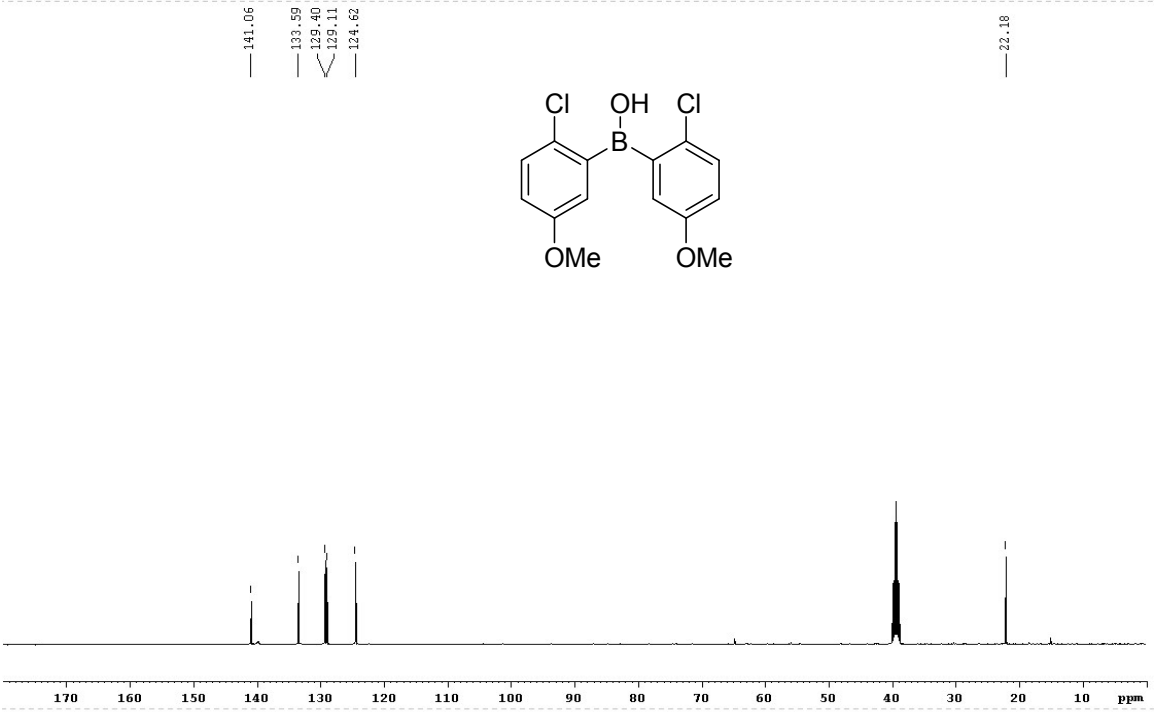
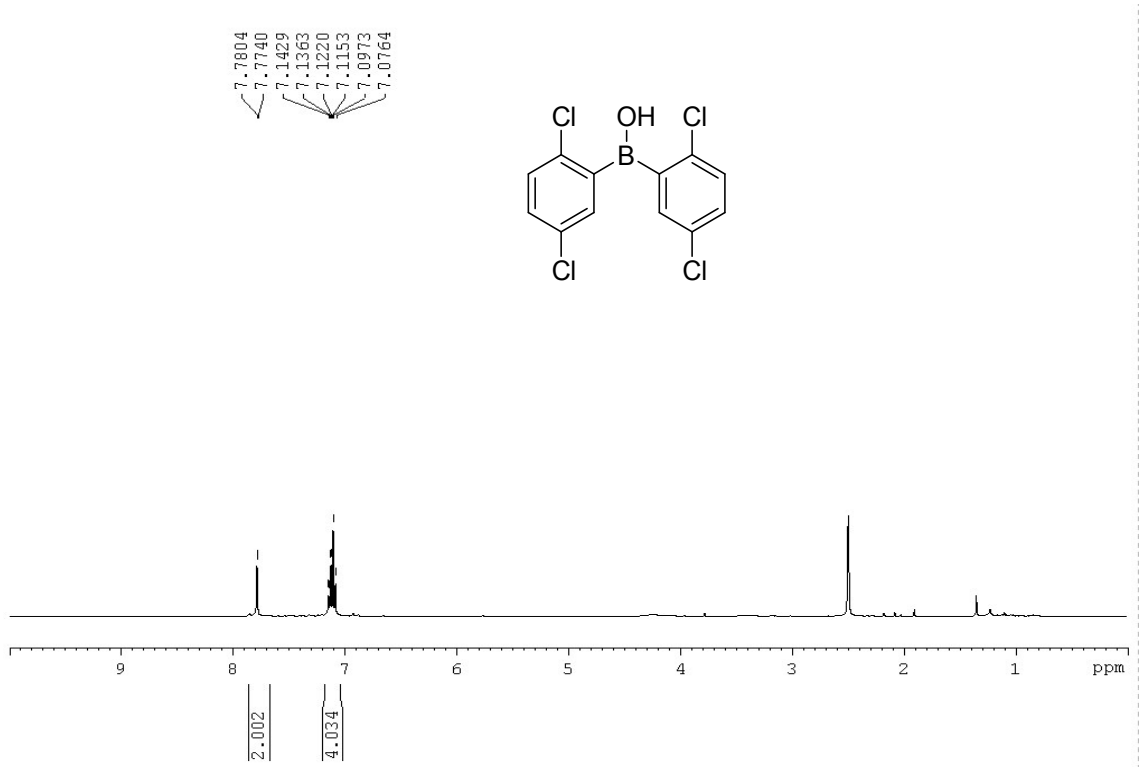


Figure S8. ^{1}H NMR and ^{13}C NMR spectra of **9l.**

^{1}H NMR (400.0 MHz; DMSO-d^{6}) of **9m.**



^{13}C NMR (101.6 MHz; DMSO-d^{6}) of **9m.**

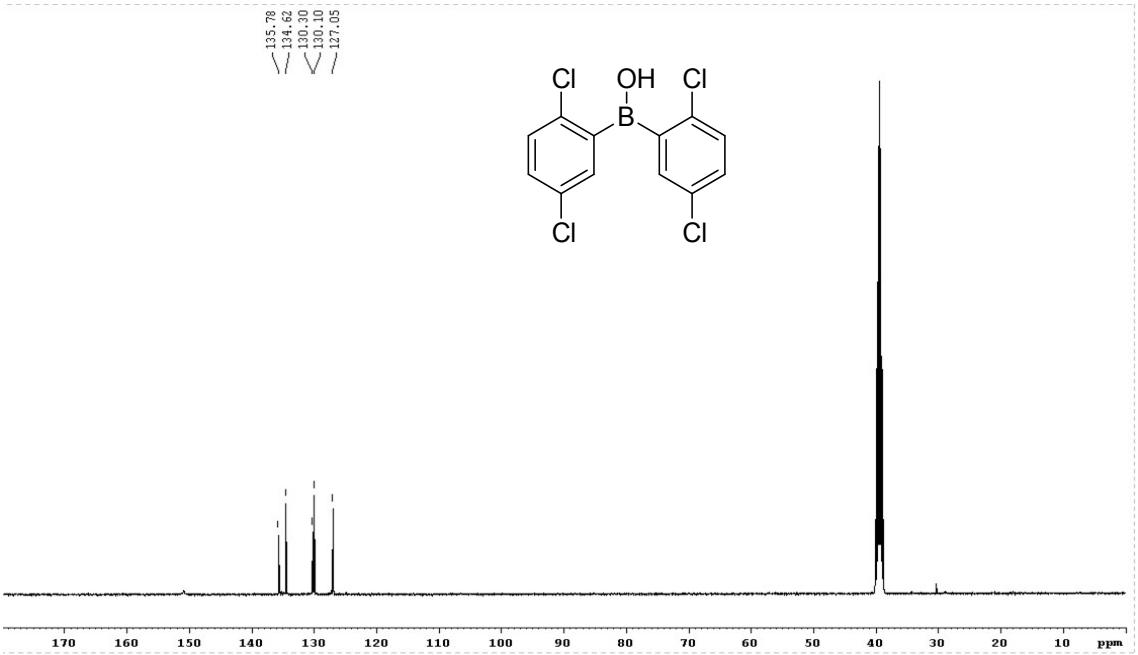
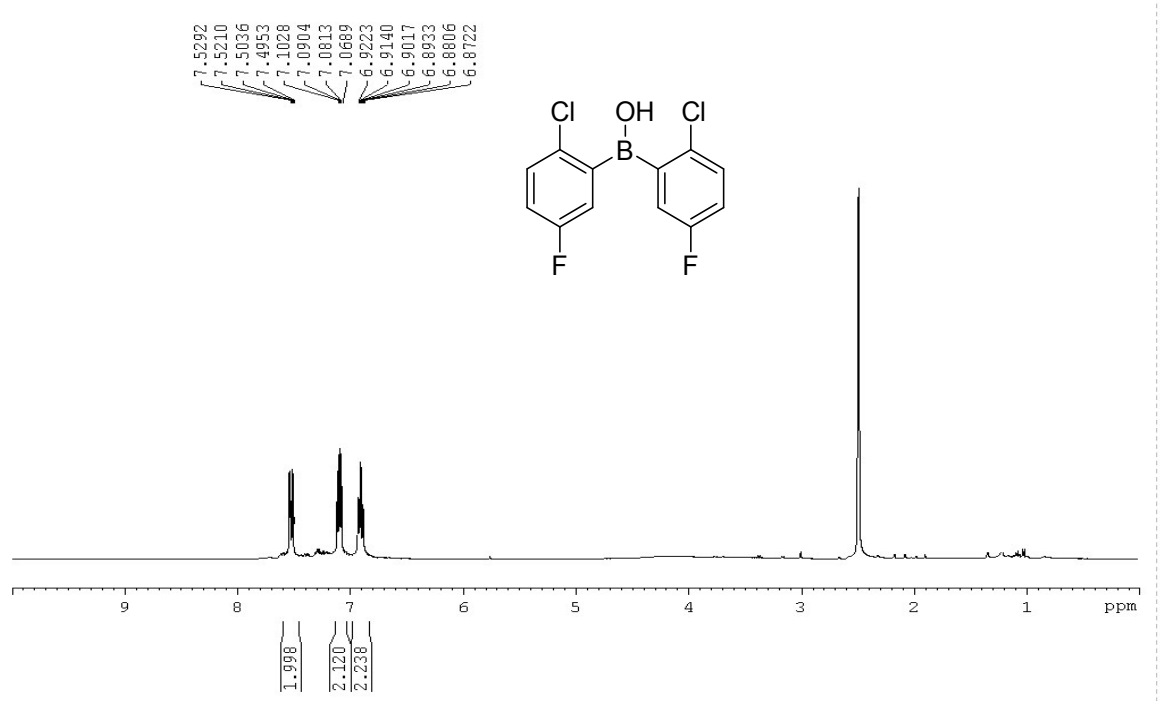


Figure S9. ^{1}H NMR and ^{13}C NMR spectra of **9m.**

^{1}H NMR (400.0 MHz; DMSO-d^{6}) of **9n.**



^{13}C NMR (101.6 MHz; DMSO-d^{6}) of **9n.**

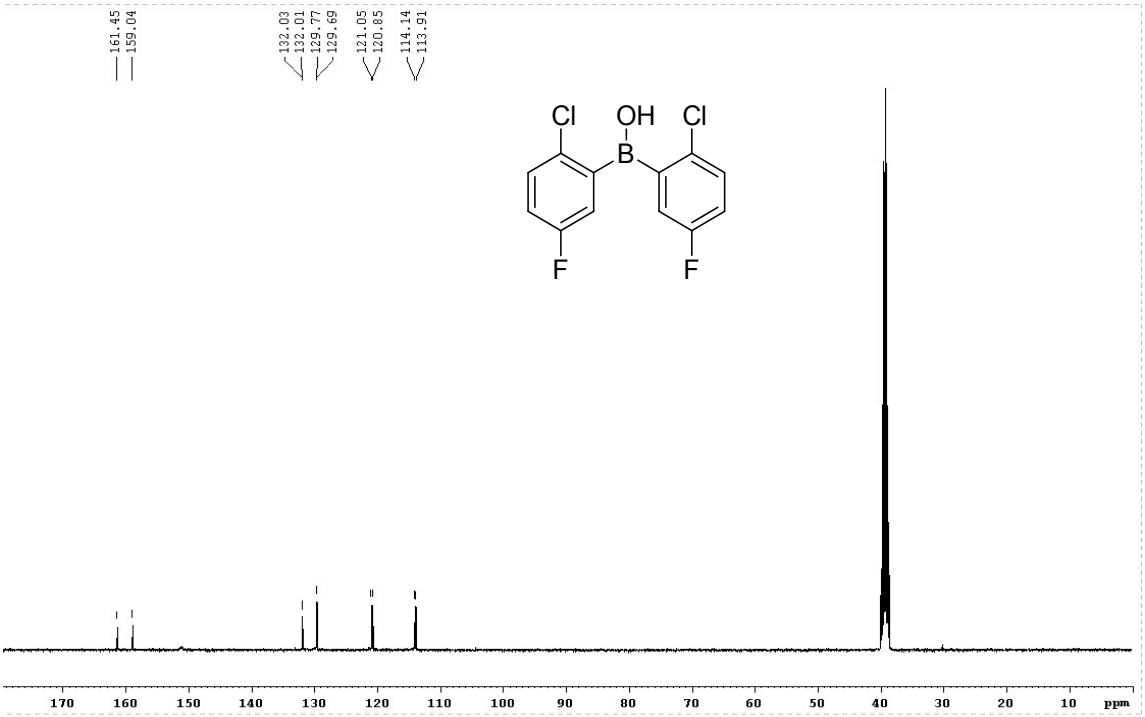
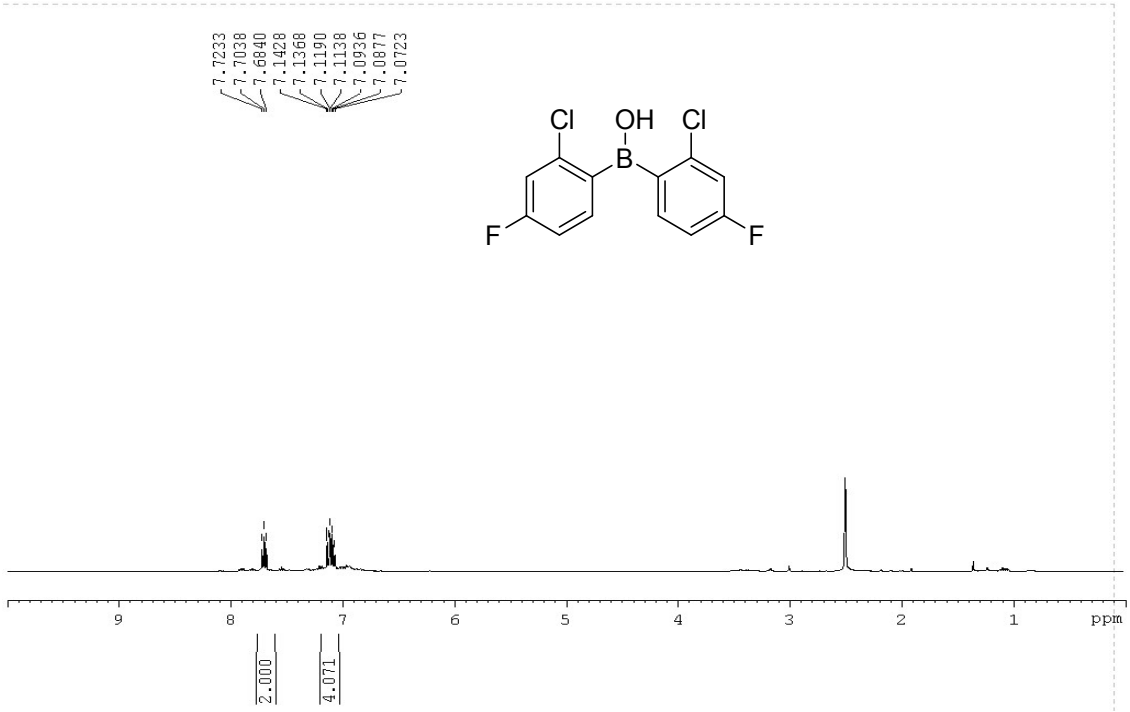


Figure S10. ^{1}H NMR and ^{13}C NMR spectra of **9n.**

^{1}H NMR (400.0 MHz; DMSO-d^{6}) of **9o.**



^{13}C NMR (101.6 MHz; DMSO-d^{6}) of **9o.**

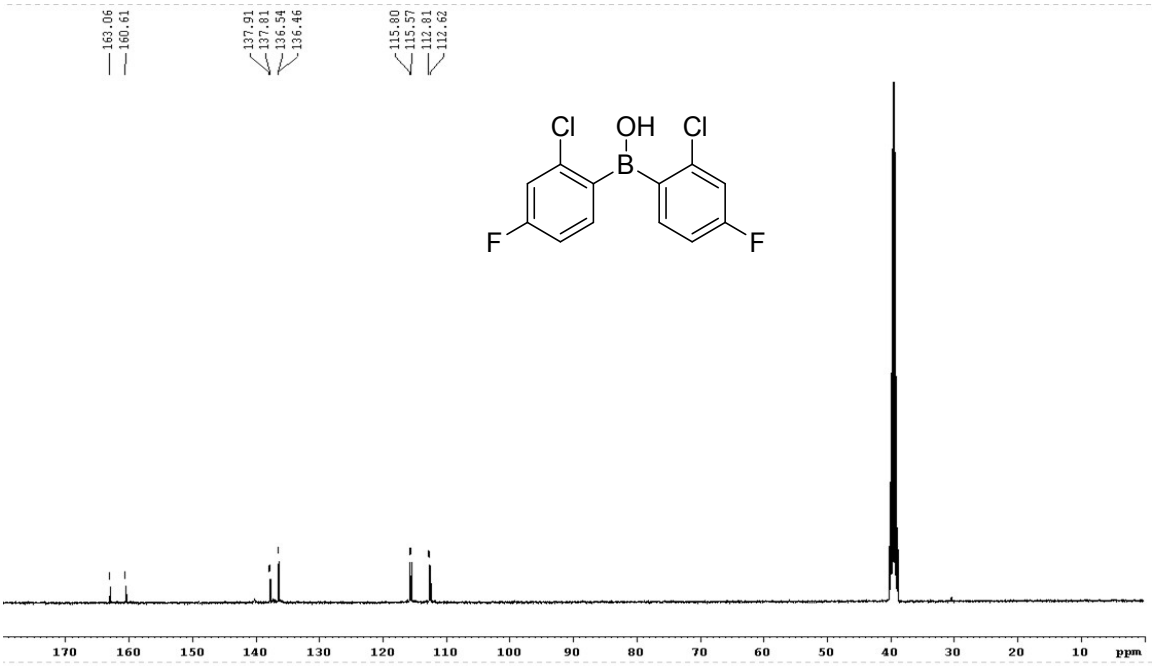
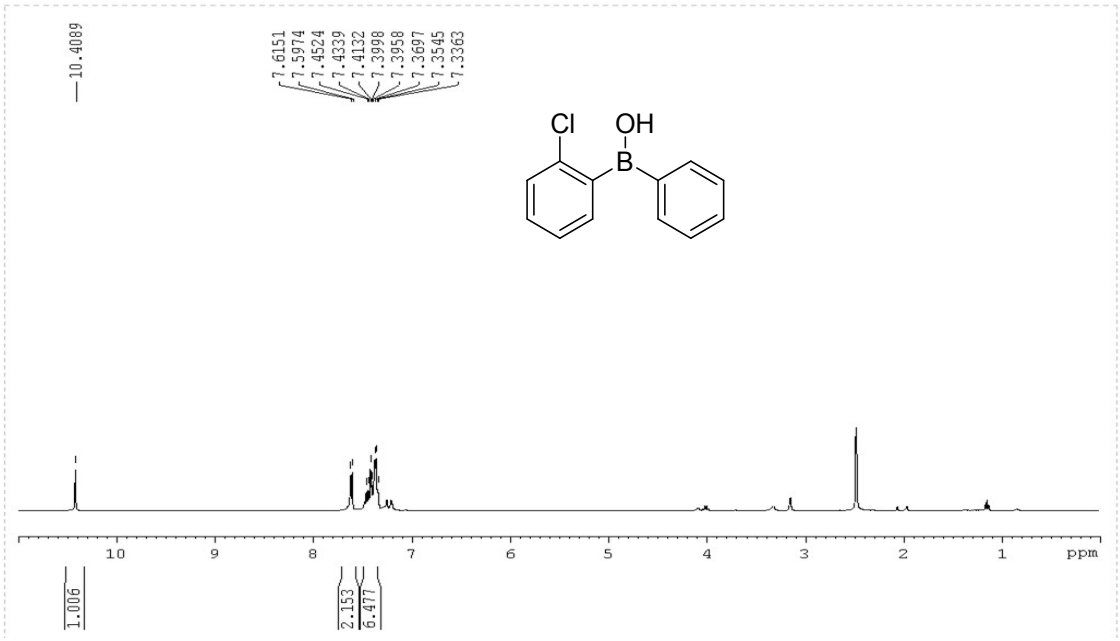


Figure S11. ^{1}H NMR and ^{13}C NMR spectra of **9o.**

^{1}H NMR (400.0 MHz; DMSO-d^{6}) of **9p.**



^{13}C NMR (101.6 MHz; DMSO-d^{6}) of **9p.**

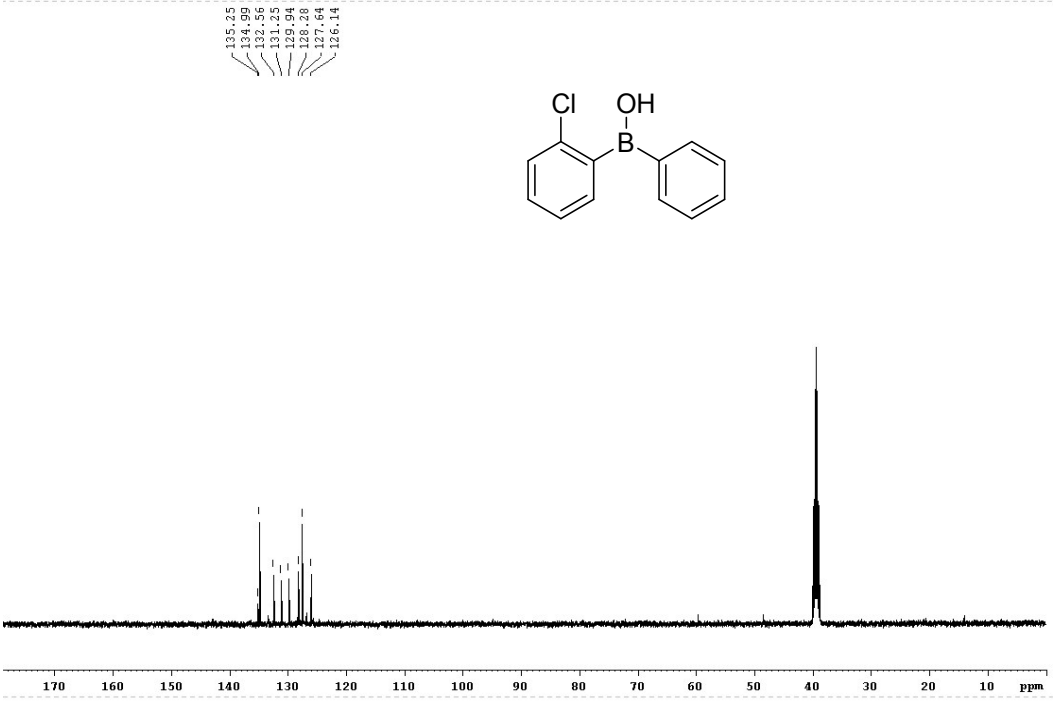
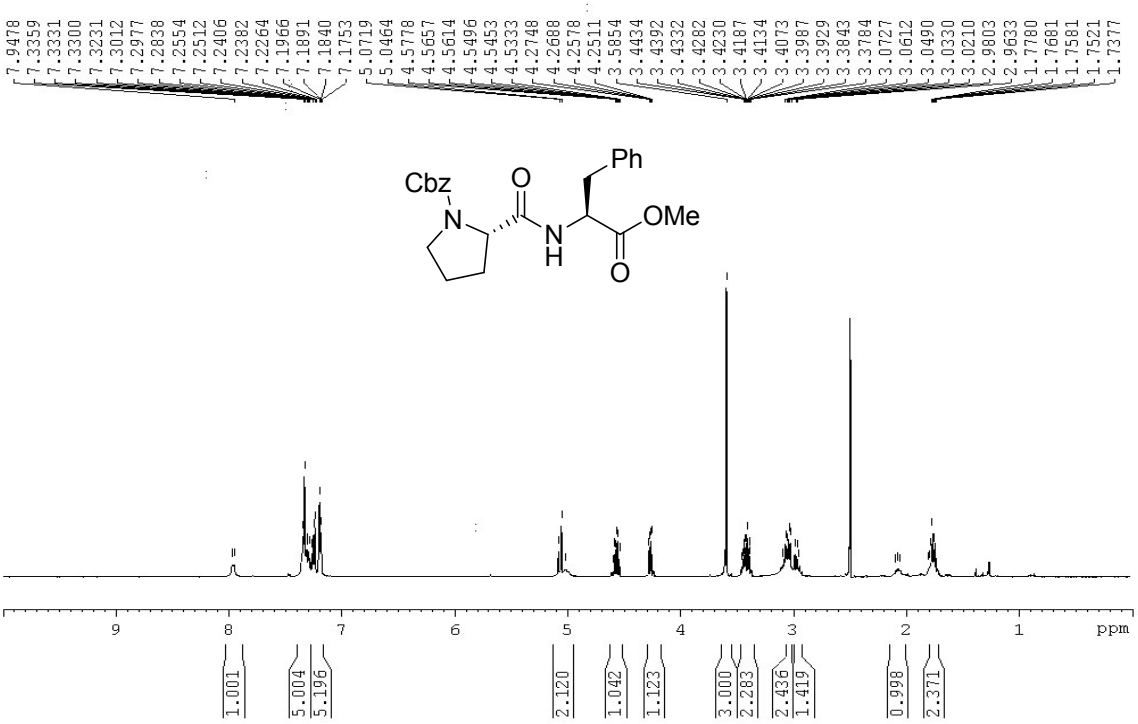


Figure S12. ^{1}H NMR and ^{13}C NMR spectra of **9p.**

^{1}H NMR and ^{13}C NMR of Newly Synthesized Dipeptides.

^{1}H NMR (500.0 MHz; DMSO-d^{6}, 80 °C) of **13e.**



^{13}C NMR (125.7 MHz; DMSO-d^{6}, 80 °C) of **13e.**

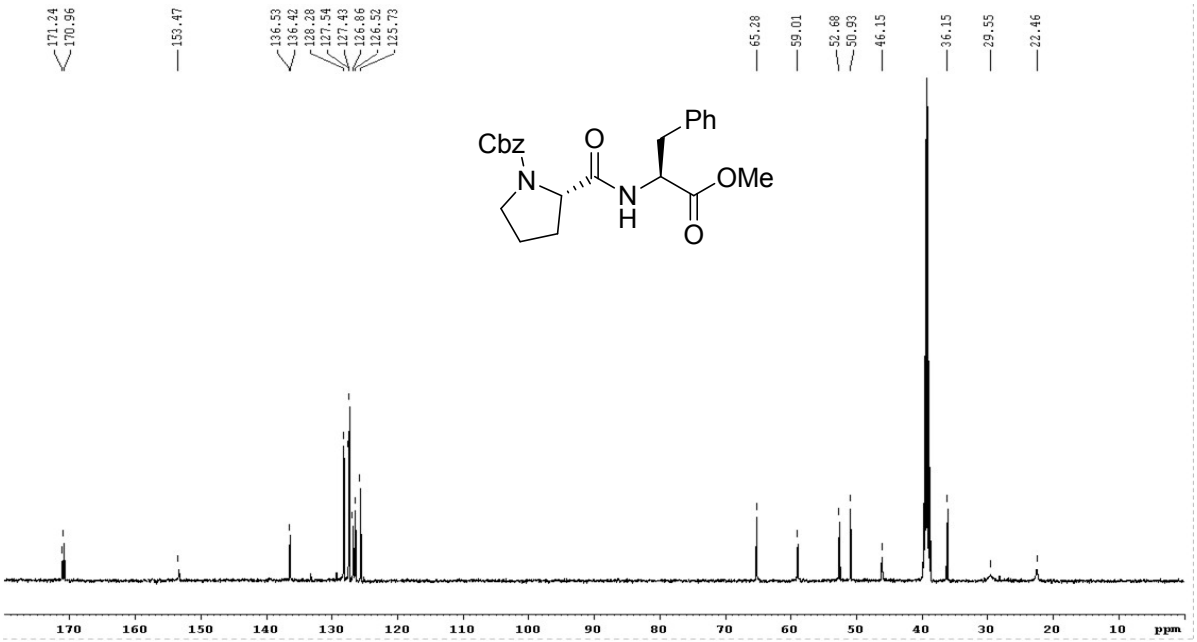
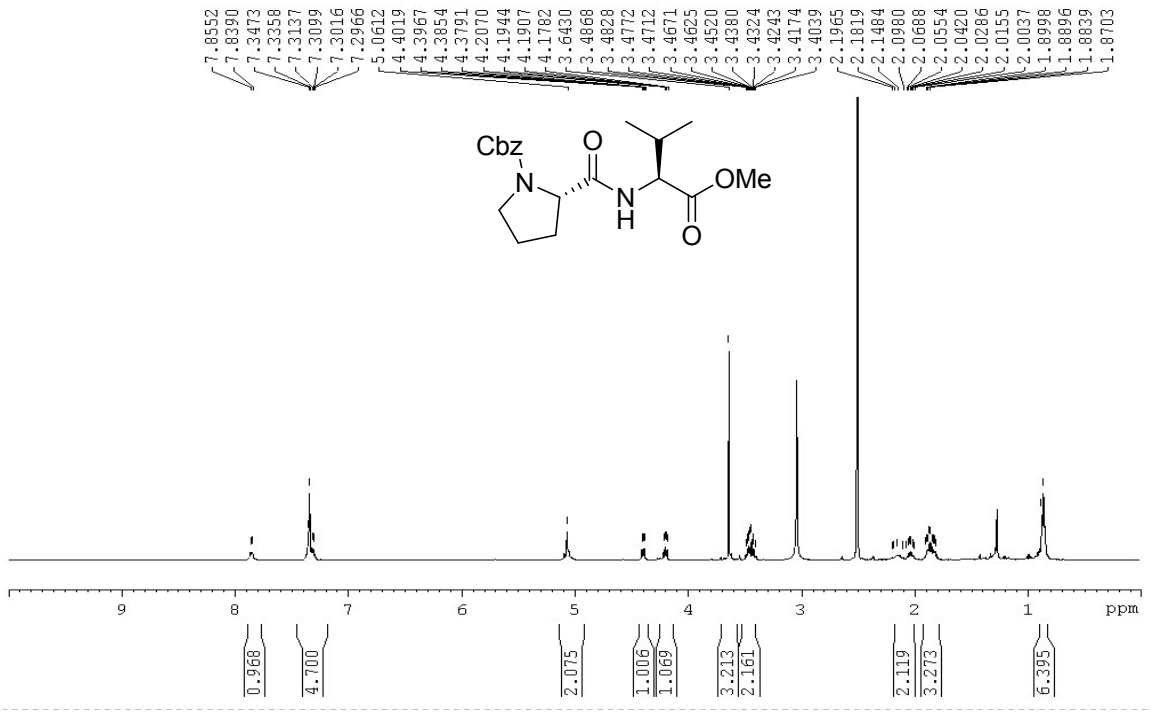


Figure S13. ^{1}H NMR and ^{13}C NMR spectra of **13e.**

^{1}H NMR (500.0 MHz; DMSO-d^{6}, 80 °C) of **13g.**



^{13}C NMR (125.7 MHz; DMSO-d^{6}, 80 °C) of **13g.**

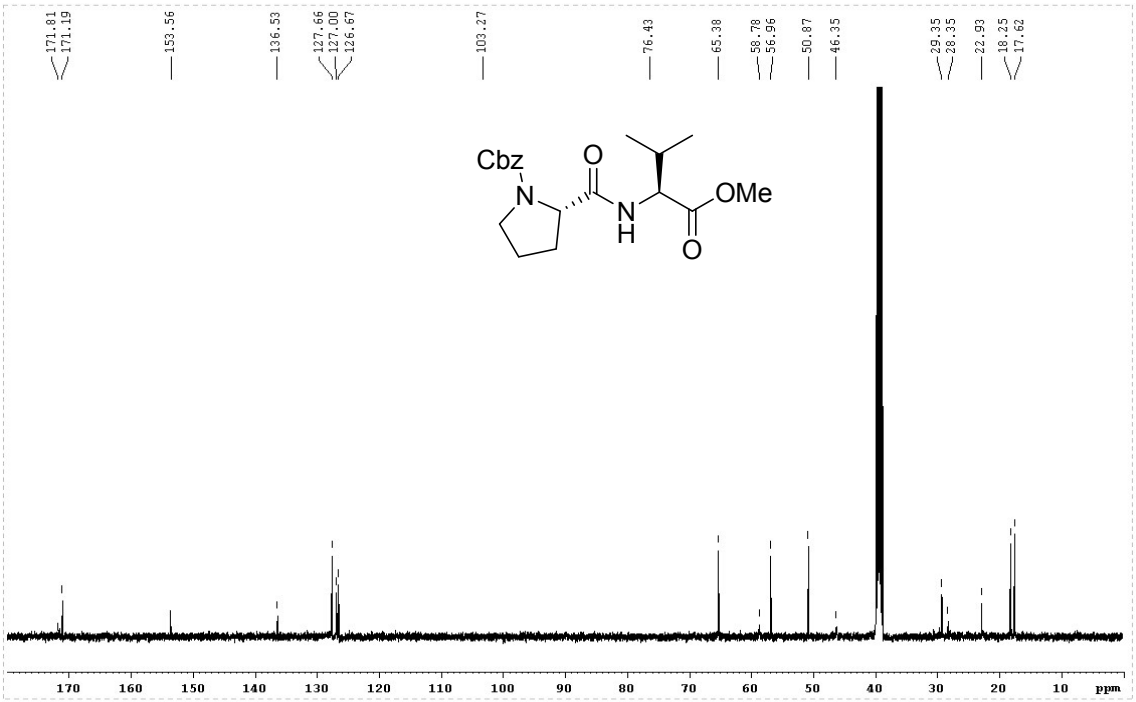
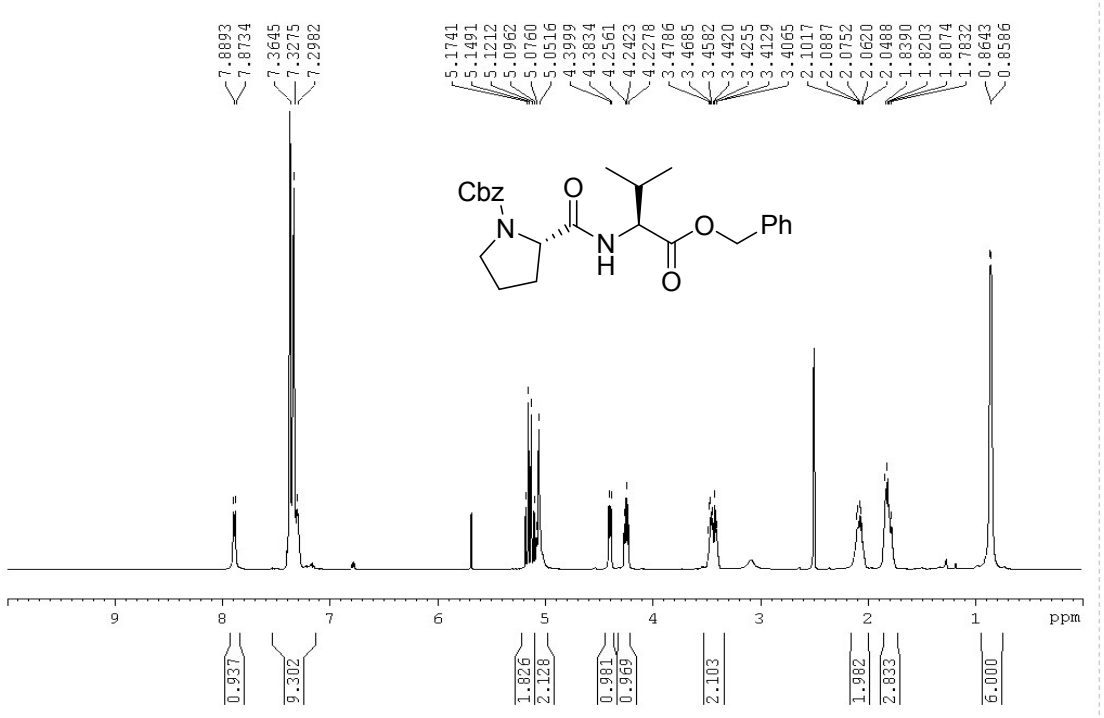


Figure S14. ^{1}H NMR and ^{13}C NMR spectra of **13g.**

^{1}H NMR (500.0 MHz; DMSO-d^{6}, 80 °C) of **13h.**



^{13}C NMR (125.7 MHz; DMSO-d^{6}, 80 °C) of **13h.**

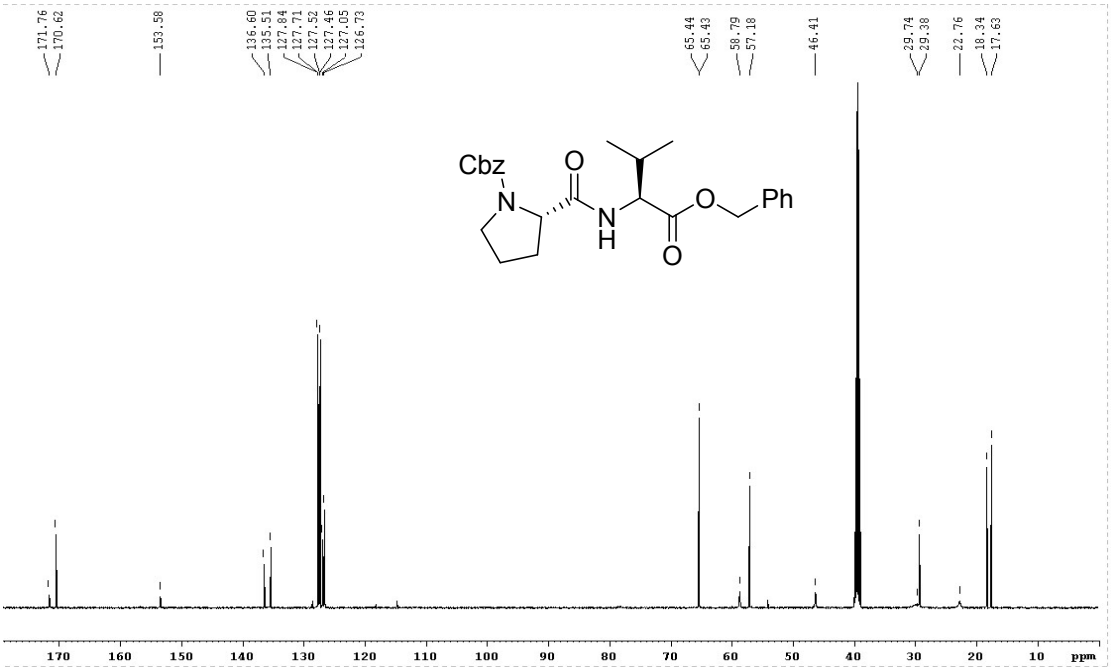
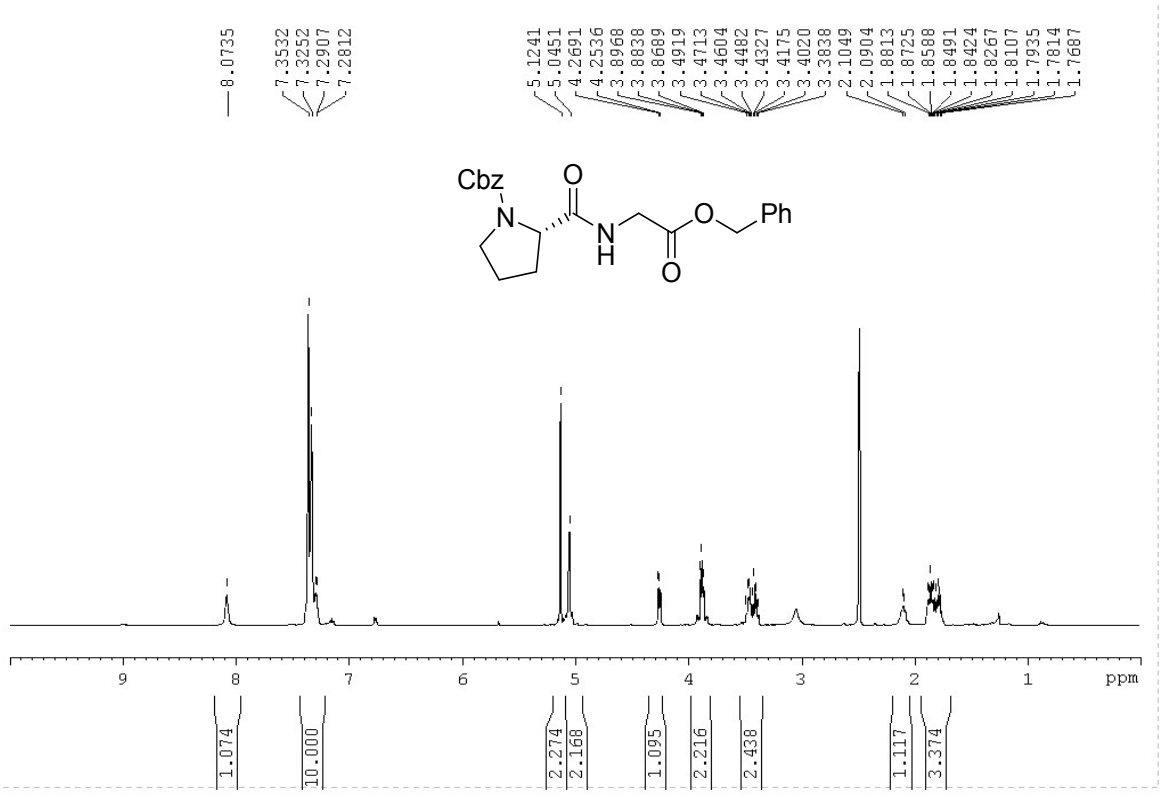


Figure S15. ^{1}H NMR and ^{13}C NMR spectra of **13h.**

^{1}H NMR (500.0 MHz; DMSO-d^{6}, 80 °C) of **13j.**



^{13}C NMR (125.7 MHz; DMSO-d^{6}, 80 °C) of **13j.**

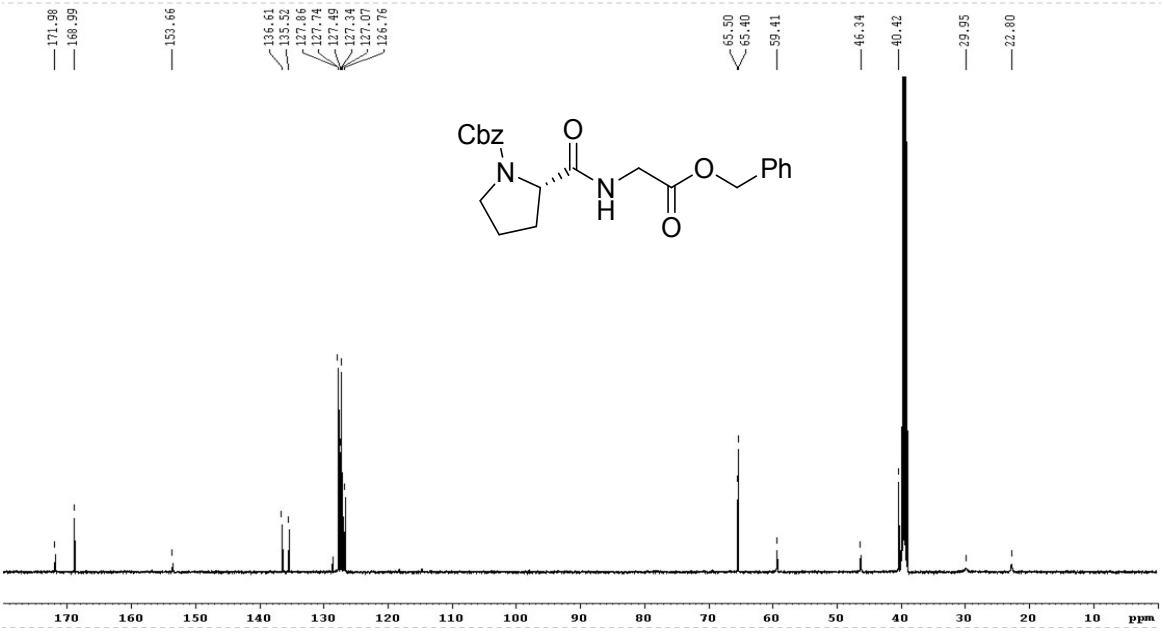
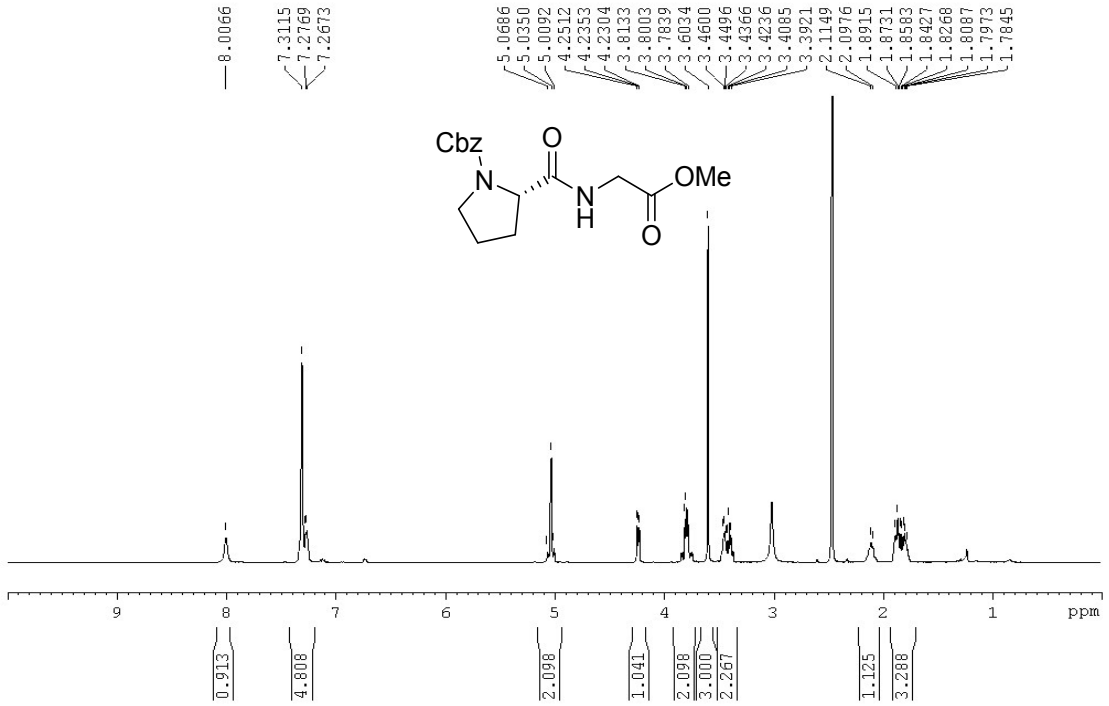


Figure S16. ^{1}H NMR and ^{13}C NMR spectra of **13j.**

^{1}H NMR (500.0 MHz; DMSO-d^{6}, 80 °C) of **13k.**



^{13}C NMR (125.7 MHz; DMSO-d^{6}, 80 °C) of **13k.**

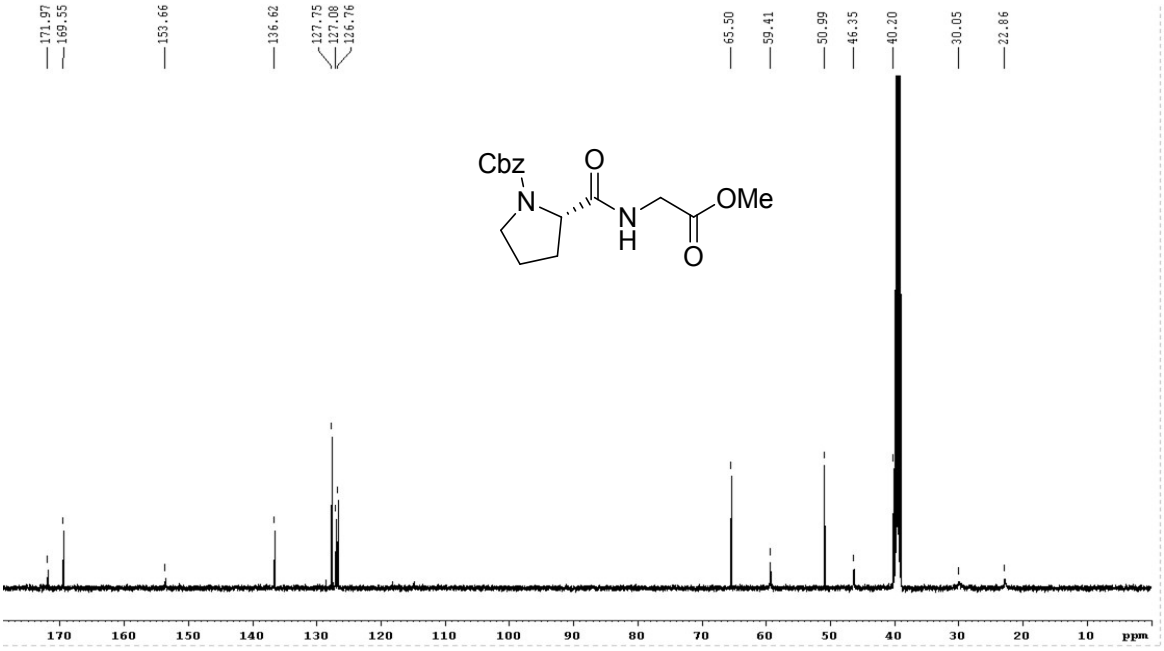
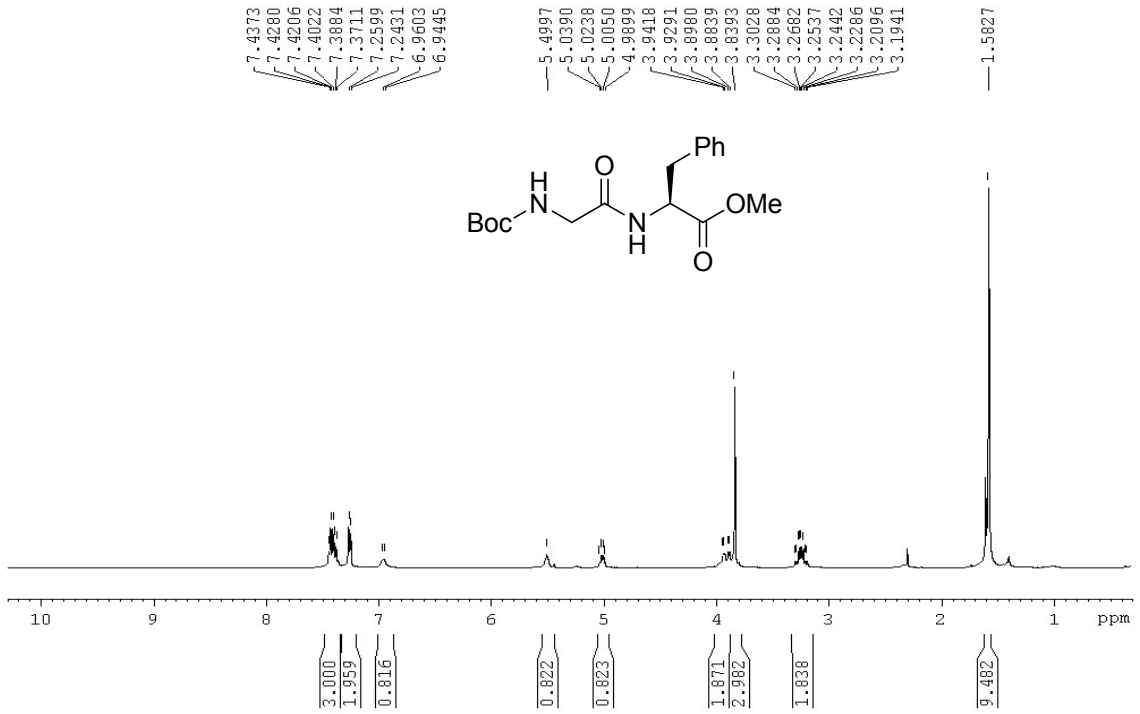


Figure S17. ^{1}H NMR and ^{13}C NMR spectra of **13k.**

^{1}H NMR (400.0 MHz; $CDCl_3$) of **13m.**



^{13}C NMR (101.6 MHz; $CDCl_3$) of **13m.**

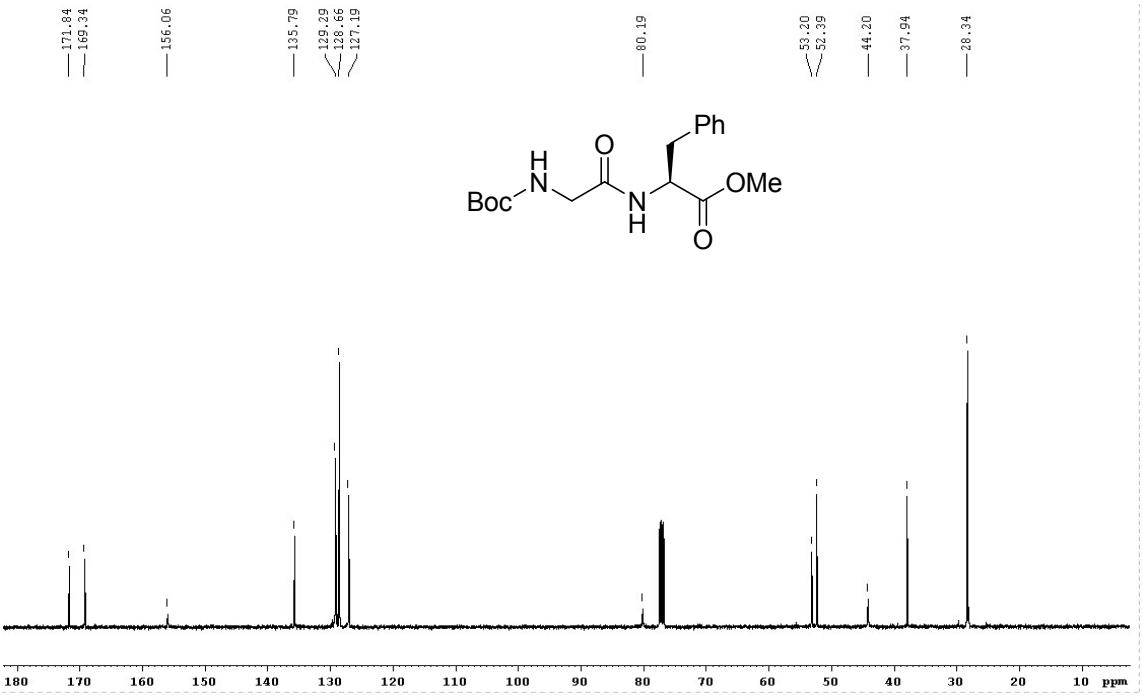
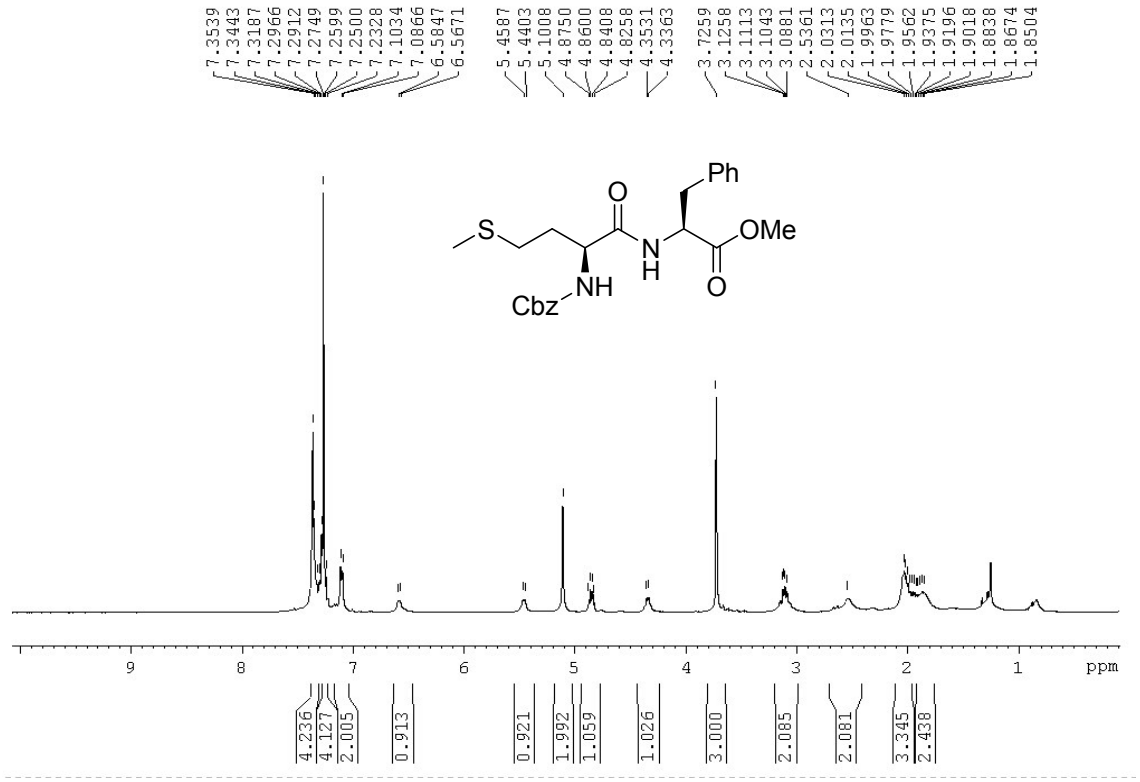


Figure S18. ^{1}H NMR and ^{13}C NMR spectra of **13m.**

^{1}H NMR (400.0 MHz; $CDCl_3$) of **13n.**



^{13}C NMR (101.6 MHz; $CDCl_3$) of **13n.**

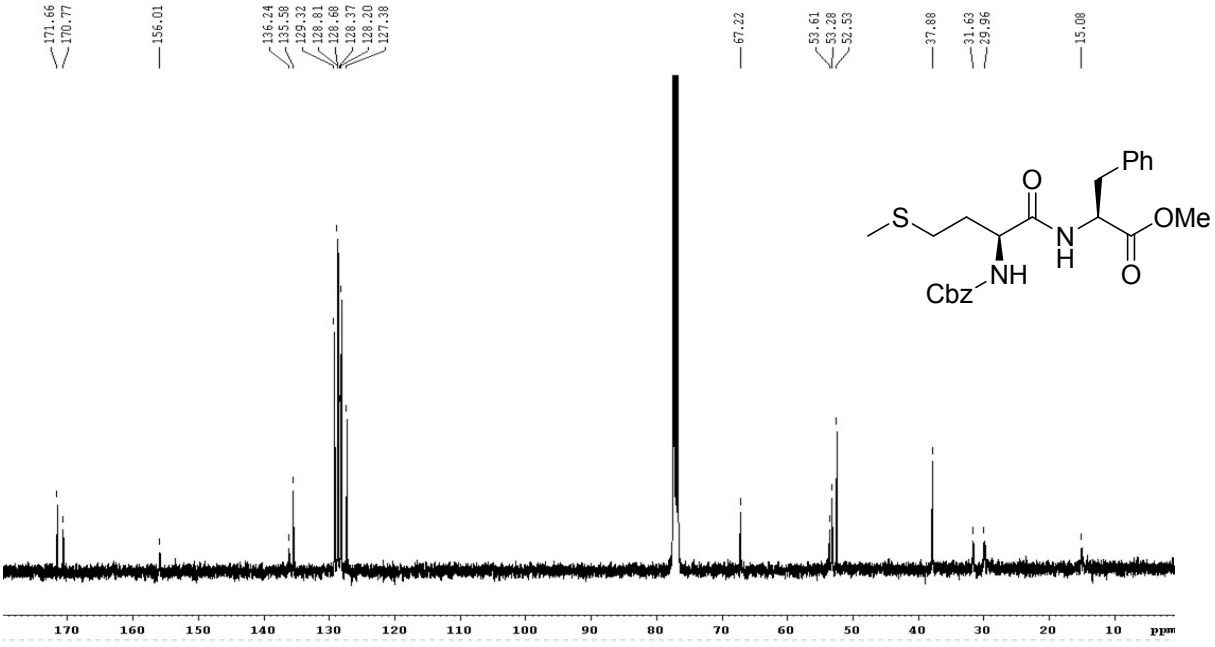


Figure S19. ^{1}H NMR and ^{13}C NMR spectra of **13n.**

HPLC Spectra of (*S*)-*N*-Phenylacetyl-Phe-OMe (11).

Empower software

RAPPORT HPLC

Reported by User: System

Project Name: IC_OBH_ASH_2013

TM-642

Instrument Method: IC 1mL60%nhep40%prop_20dC

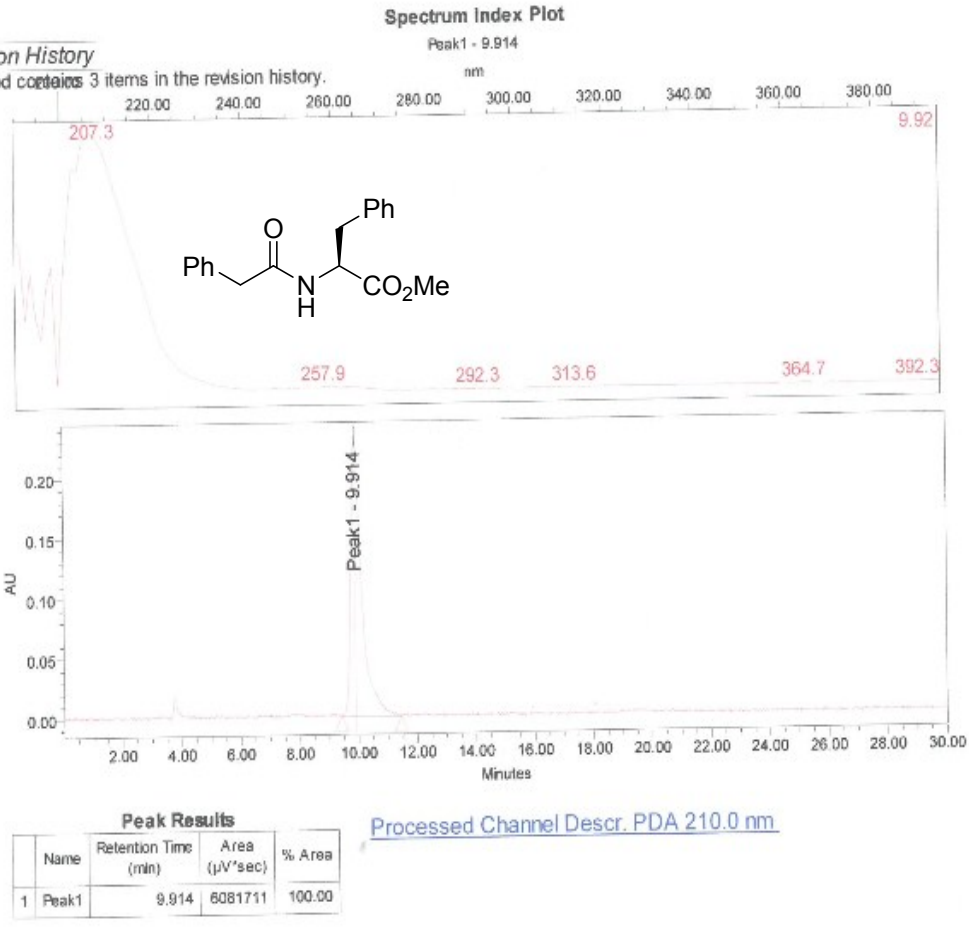
Stored: 11/20/2014 10:57:08 AM

Method Information

Comments	Col. Daicel Chiralpak IC 4,6mmx250mm 5µm 1mL/mn 60%n-heptane40%propanol-2 éch.+col.à 20°C
Modified User	System
Locked	No
Method Id	5980
Method Version	2
Edit User	

Revision History

This method contains 3 items in the revision history.

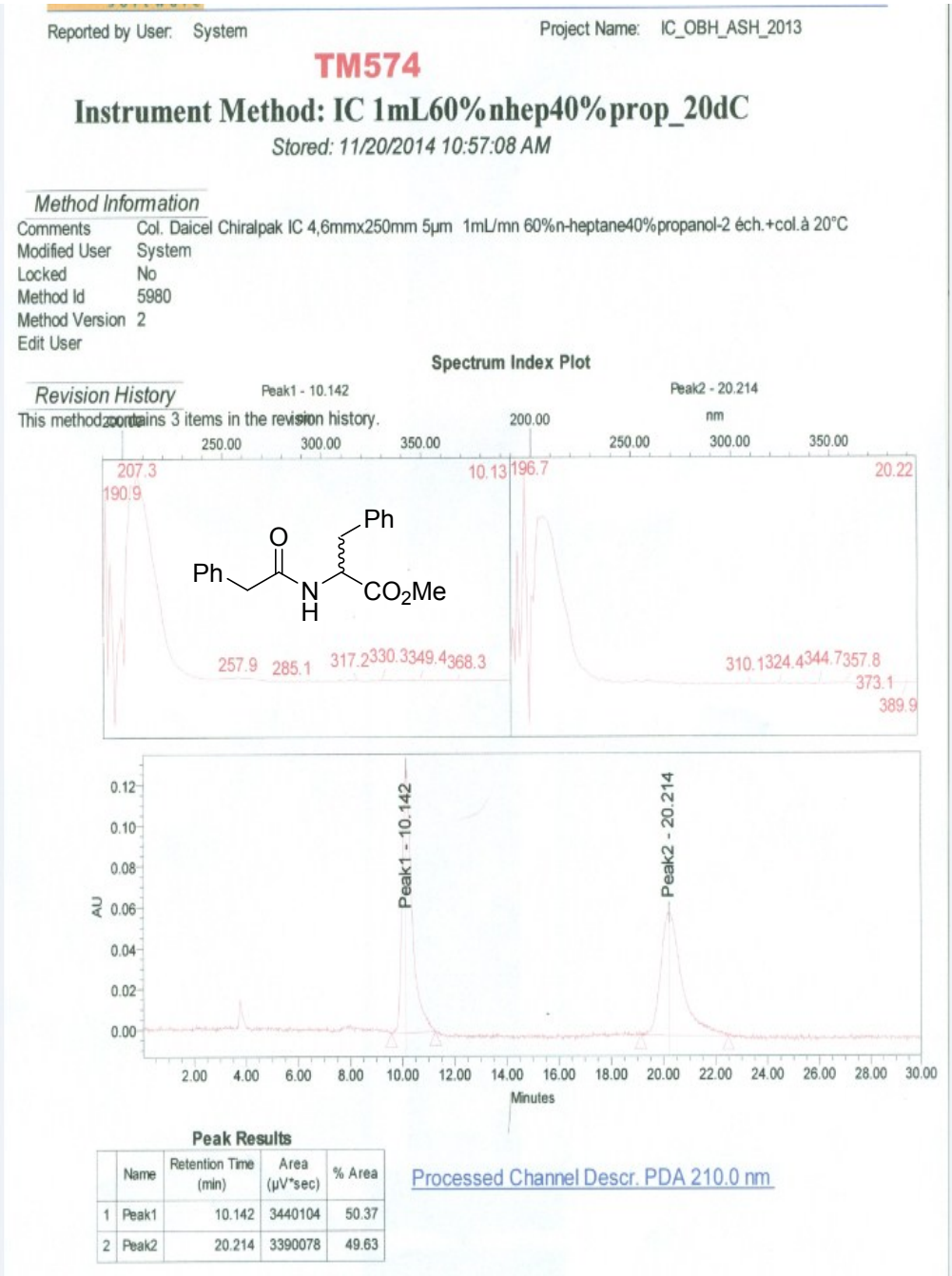


Peak Results

Processed Channel Descr. PDA 210.0 nm

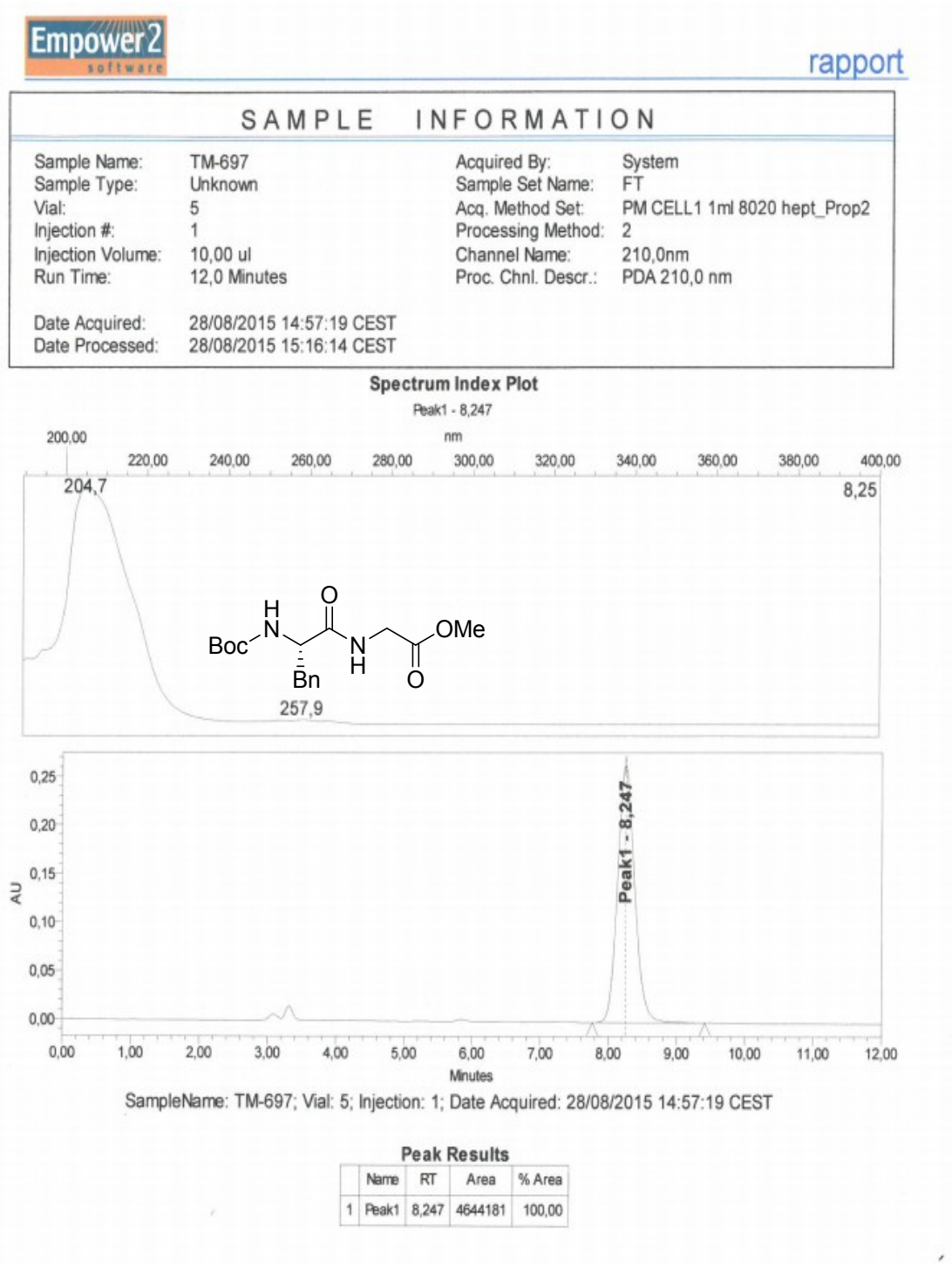
	Name	Retention Time (min)	Area (µV*sec)	% Area
1	Peak1	9.914	6081711	100.00

HPLC Spectra of *Rac*-*N*-Phenylacetyl-Phe-OMe



HPLC Spectra of Dipeptides

HPLC Spectra of (*S*)-Boc-Phe-Gly-OMe (13c)



HPLC Spectra of *Rac*-Boc-Phe-Gly-OMe

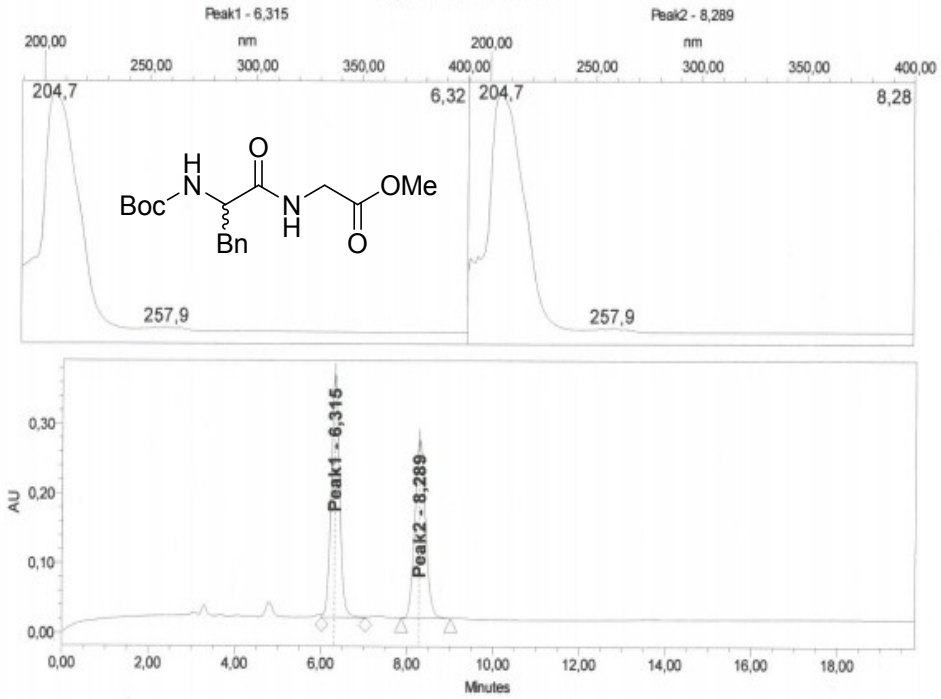
Empower 2 software

rapport

SAMPLE INFORMATION

Sample Name:	TM-855	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	FR
Vial:	1	Acq. Method Set:	PM CELL1 1ml 8020 hept_Prop2
Injection #:	1	Processing Method:	2
Injection Volume:	10,00 ul	Channel Name:	210,0nm@1
Run Time:	210,0 Minutes	Proc. Chnl. Descr.:	PDA 210,0 nm
Date Acquired:	26/08/2015 15:15:38 CEST		
Date Processed:	26/08/2015 15:35:24 CEST		

Spectrum Index Plot



SampleName: TM-855; Vial: 1; Injection: 1; Date Acquired: 26/08/2015 15:15:38 CEST

Peak Results

	Name	RT	Area	% Area
1	Peak1	6,315	4806926	51,87
2	Peak2	8,289	4460694	48,13

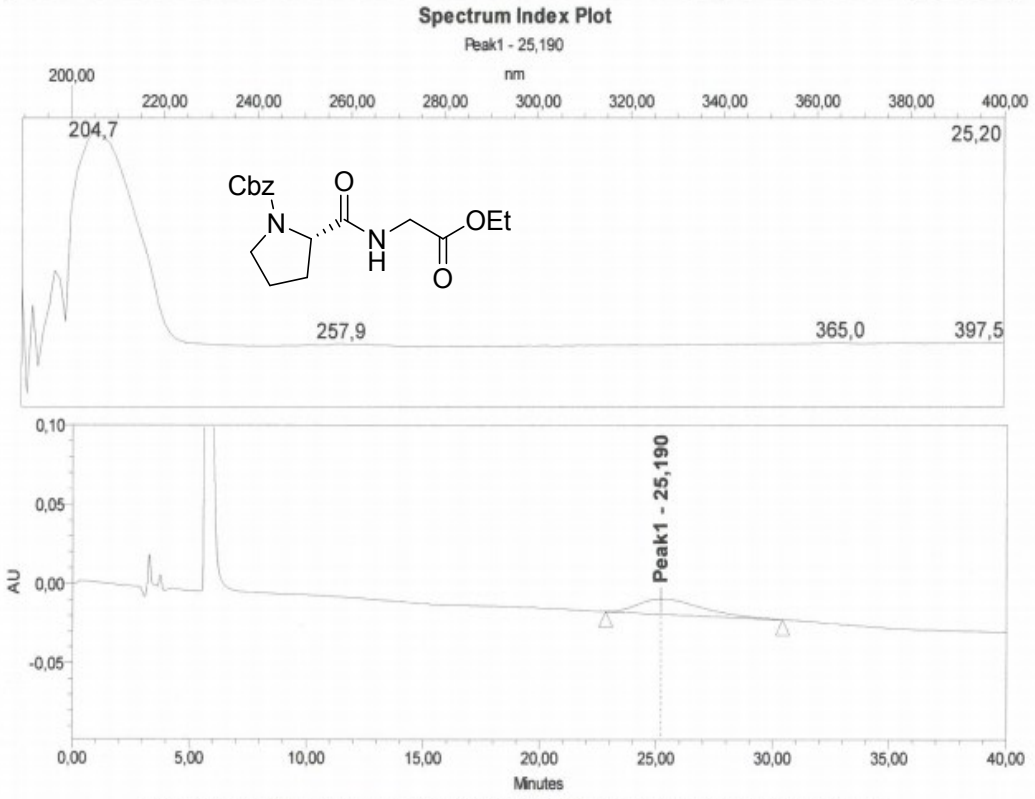
HPLC Spectra of (*S*)-Z-Pro-Gly-OEt (13i)

Empower 2 software

rapport

SAMPLE INFORMATION

Sample Name:	TM-803	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	R
Vial:	8	Acq. Method Set:	PM AMYL2 1ml 5050 hept_Prop2
Injection #:	1	Processing Method:	2
Injection Volume:	10,00 ul	Channel Name:	210,0nm
Run Time:	40,0 Minutes	Proc. Chnl. Descr.:	PDA 210,0 nm
Date Acquired:	31/08/2015 17:30:09 CEST		
Date Processed:	01/09/2015 09:25:35 CEST		



SampleName: TM-803; Vial: 8; Injection: 1; Date Acquired: 31/08/2015 17:30:09 CEST

Peak Results

	Name	RT	Area	% Area
1	Peak1	25,190	1876084	100,00

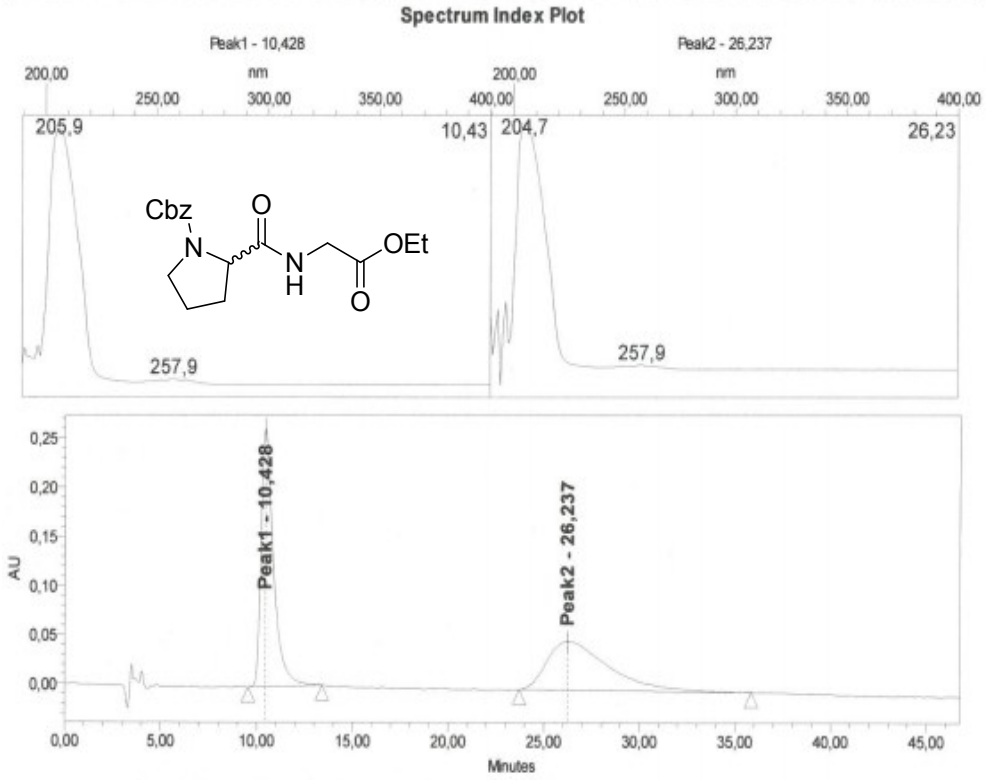
HPLC Spectra of *Rac*-Z-Pro-Gly-OEt

Empower2 software

rapport

SAMPLE INFORMATION

Sample Name:	TM-856	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	G
Vial:	2	Acq. Method Set:	PM AMYL2 1ml 5050 hept_Prop2
Injection #:	1	Processing Method:	2
Injection Volume:	10,00 ul	Channel Name:	210,0nm
Run Time:	210,0 Minutes	Proc. Chnl. Descr.:	PDA 210,0 nm
Date Acquired:	27/08/2015 14:39:38 CEST		
Date Processed:	31/08/2015 11:22:59 CEST		

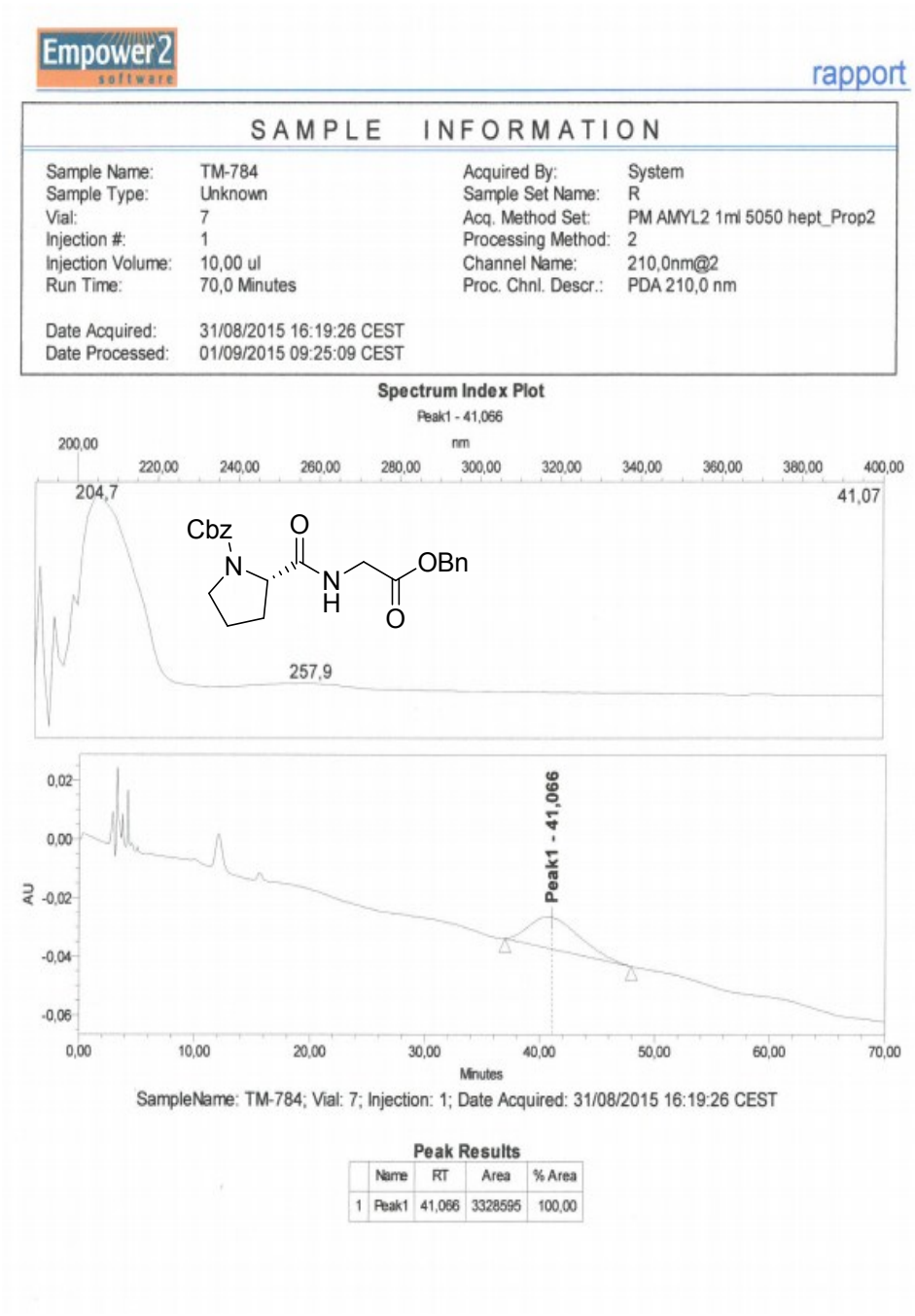


SampleName: TM-856; Vial: 2; Injection: 1; Date Acquired: 27/08/2015 14:39:38 CEST

Peak Results

	Name	RT	Area	% Area
1	Peak1	10,428	11731073	51,62
2	Peak2	26,237	10995925	48,38

HPLC Spectra of (*S*)-Z-Pro-Gly-OBn (13j)



HPLC Spectra of *Rac*-Z-Pro-Gly-OBn

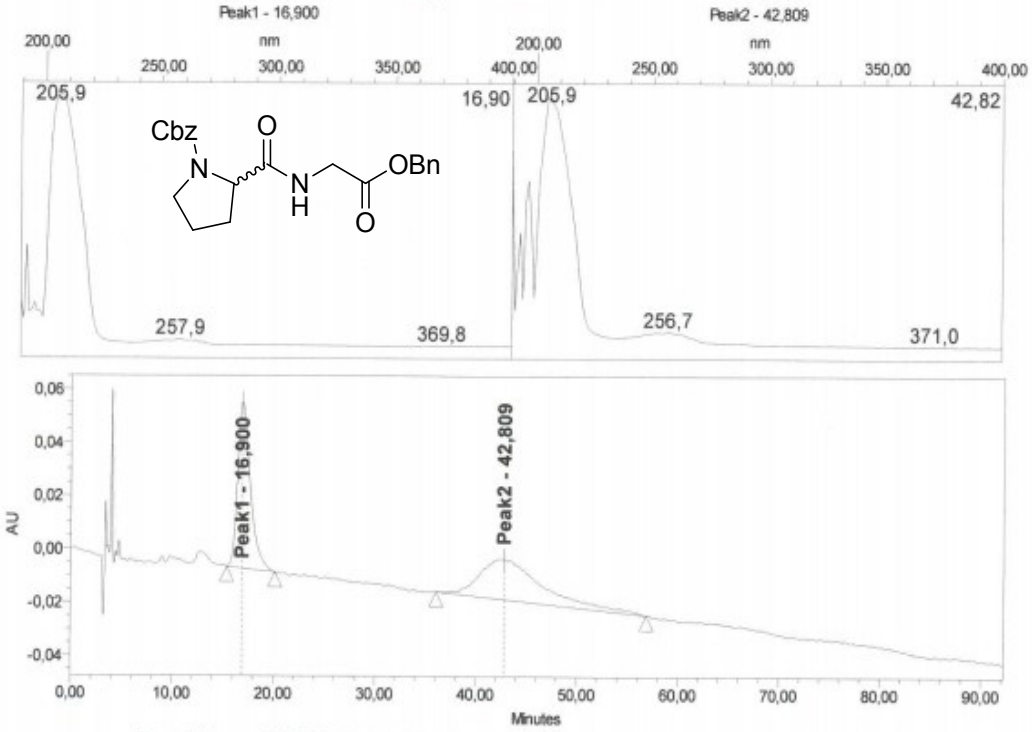
Empower2 software

rapport

SAMPLE INFORMATION

Sample Name:	TM-858	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	1
Vial:	4	Acq. Method Set:	PM AMYL2 1ml 5050 hept_Prop2
Injection #:	1	Processing Method:	2
Injection Volume:	10,00 ul	Channel Name:	210,0nm
Run Time:	210,0 Minutes	Proc. Chnl. Descr.:	PDA 210,0 nm
Date Acquired:	27/08/2015 15:27:21 CEST		
Date Processed:	31/08/2015 11:23:48 CEST		

Spectrum Index Plot

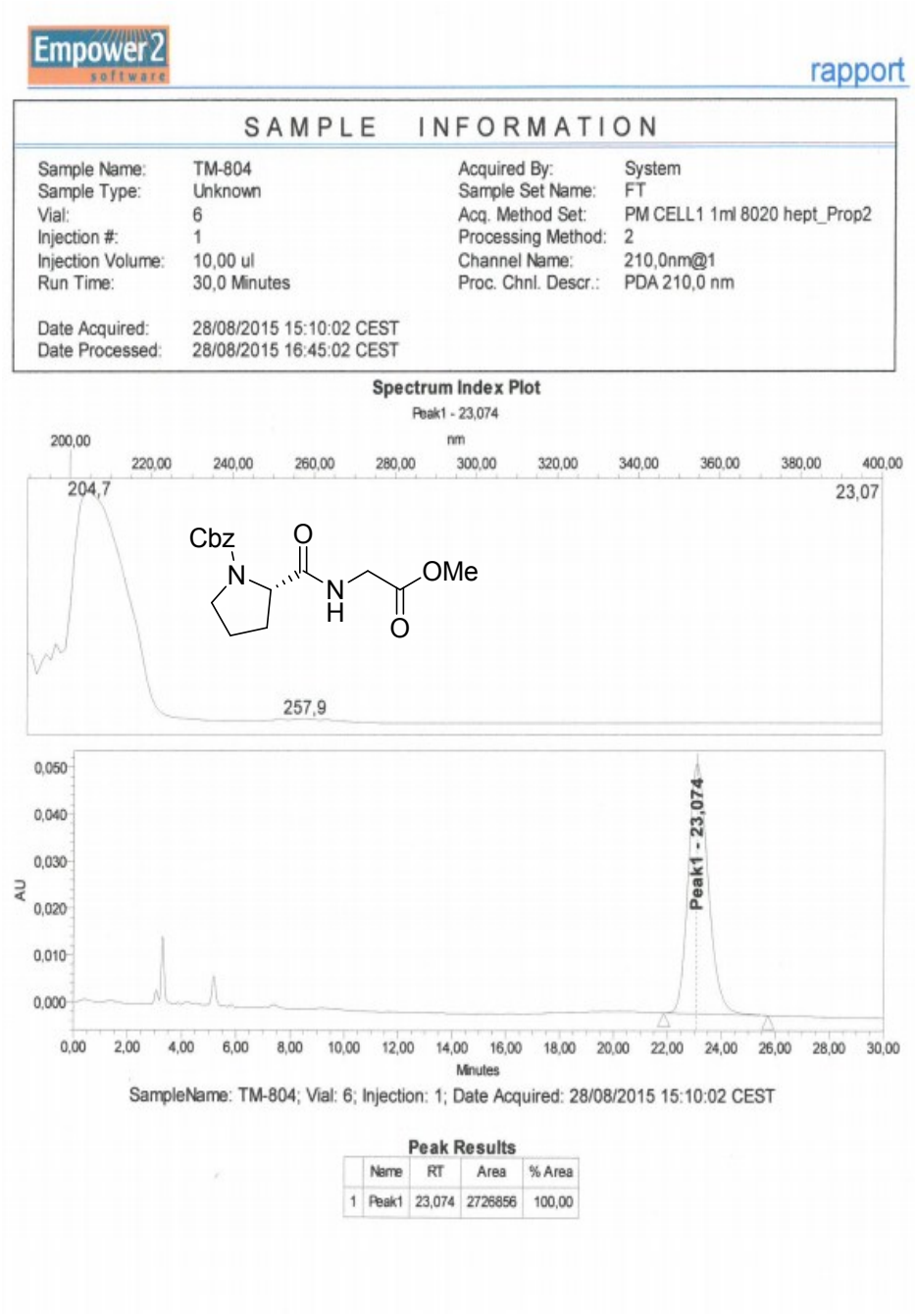


SampleName: TM-858; Vial: 4; Injection: 1; Date Acquired: 27/08/2015 15:27:21 CEST

Peak Results

	Name	RT	Area	% Area
1	Peak1	16,900	5484165	45,49
2	Peak2	42,809	6571993	54,51

HPLC Spectra of (*S*)-Z-Pro-Gly-OMe (13k).



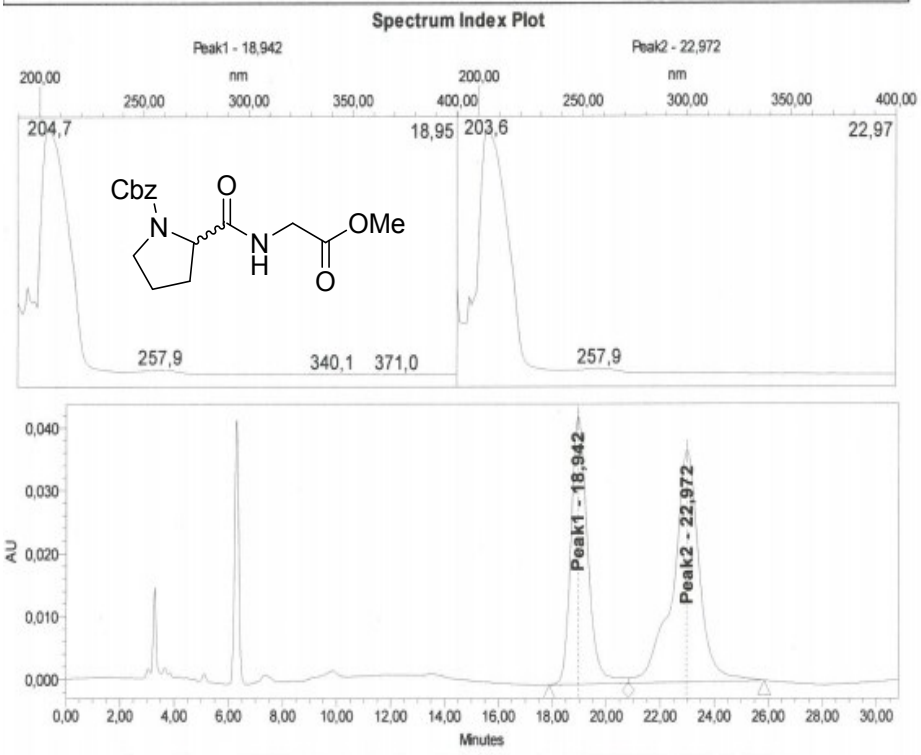
HPLC Spectra of *Rac*- Z-Pro-Gly-OMe

Empower 2 software

rapport

SAMPLE INFORMATION

Sample Name:	TM-857	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	1
Vial:	3	Acq. Method Set:	PM CELL1 1ml 8020 hept_Prop2
Injection #:	1	Processing Method:	2
Injection Volume:	10,00 ul	Channel Name:	210,0nm
Run Time:	210,0 Minutes	Proc. Chnl. Descr.:	PDA 210,0 nm
Date Acquired:	26/08/2015 16:23:40 CEST		
Date Processed:	28/08/2015 14:39:04 CEST		



SampleName: TM-857; Vial: 3; Injection: 1; Date Acquired: 26/08/2015 16:23:40 CEST

Peak Results

	Name	RT	Area	% Area
1	Peak1	18,942	1830017	42,30
2	Peak2	22,972	2495846	57,70

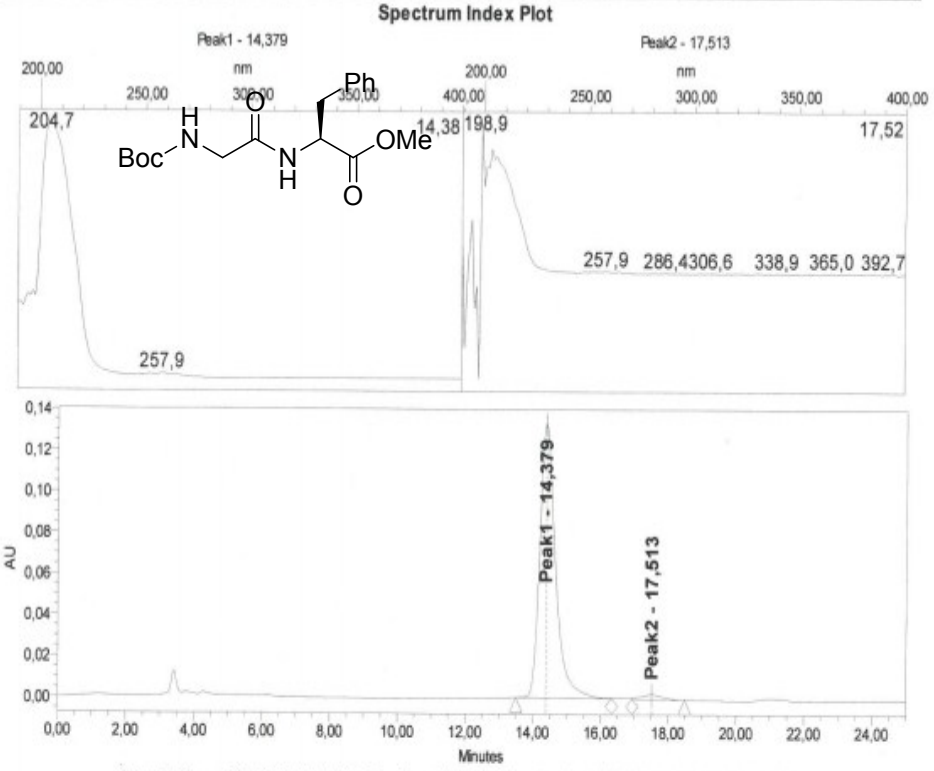
HPLC Spectra of (*S*)-Boc-Gly-Phe-OMe (13m)

Empower2 software

rapport

SAMPLE INFORMATION

Sample Name:	TM785	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	1
Vial:	41	Acq. Method Set:	PM IA 1ml 9010 hept_Prop2 20dc
Injection #:	1	Processing Method:	2
Injection Volume:	10,00 ul	Channel Name:	210,0nm
Run Time:	25,0 Minutes	Proc. Chnl. Descr.:	PDA 210,0 nm
Date Acquired:	11/06/2015 11:33:57 CEST		
Date Processed:	11/06/2015 11:59:54 CEST		



SampleName: TM785; Vial: 41; Injection: 1; Date Acquired: 11/06/2015 11:33:57 CEST

Peak Results

	Name	RT	Area	% Area
1	Peak1	14,379	4292344	97,69
2	Peak2	17,513	101430	2,31

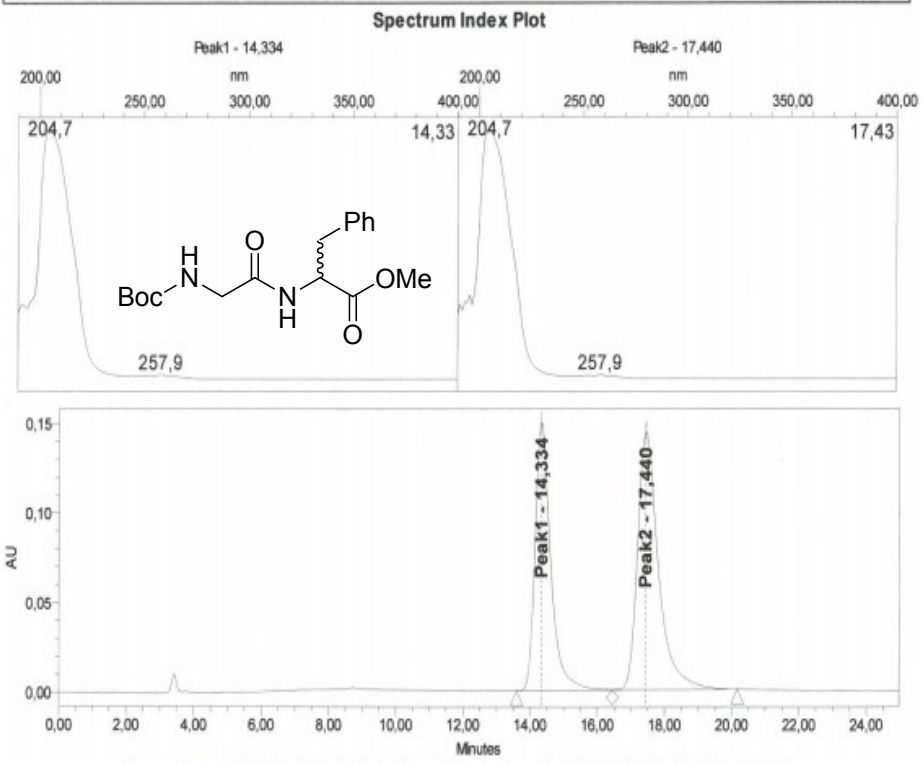
HPLC Spectra of *Rac*-Boc-Gly-Phe-OMe

Empower2 software

rapport

SAMPLE INFORMATION

Sample Name:	TM817	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	1
Vial:	40	Acq. Method Set:	PM IA 1ml 9010 hept_Prop2 20dc
Injection #:	1	Processing Method:	2
Injection Volume:	10,00 ul	Channel Name:	210,0nm
Run Time:	235,0 Minutes	Proc. Chnl. Descr.:	PDA 210,0 nm
Date Acquired:	11/06/2015 11:07:55 CEST		
Date Processed:	11/06/2015 11:33:35 CEST		



SampleName: TM817; Vial: 40; Injection: 1; Date Acquired: 11/06/2015 11:07:55 CEST

Peak Results

	Name	RT	Area	% Area
1	Peak1	14,334	4863770	43,91
2	Peak2	17,440	6213538	56,09