Electronic Supporting Information for:

Boron Schiff bases derived from α-amino acids as nucleoli/cytoplasm cell-staining fluorescent probes *in vitro*.

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1. Experimental section

1.1 General remarks

All precursor materials were procured from Aldrich Chemical Company. Solvents were used without further purification. Melting points were confirmed by Electrothermal Mel-Temp apparatus. UV spectra were obtained with a Shimadzu 2401 PC UV/VIS spectrophotometer and emission measurements were performed on a Fluorolog-3 fluorescence spectrometer. ^{1}H NMR (400.00 MHz), ^{13}C (100.00 MHz) and ^{11}B (96.29 MHz) spectra were recorded using equipment Bruker advance DPX 400. NMR spectra were performed in dimethyl sulfoxide deuterated-d_6 or acetone-d_6 as solvent. The ^{11}B NMR shifts are corresponding to external $BF_3{\cdot}OEt_2$, while ^{1}H and ^{13}C NMR shifts are referenced with respect to $(CH_3)_4Si$. Chemical shifts are given parts per million (ppm) downfield from the reference, and all coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectra were acquired by LC/MSD TOF on an Agilent Technologies instrument with APCI as chemical ionization in positive mode. Mass spectra were recorded on an AB Sciex API 2000^{TM} LC/MS/MS System.

1.2 Crystal structure analysis

The X-ray crystallography data for **3a** (CCDC: 2002773) were measured at 100(2) K on a Bruker D8 Quest with a Photon 100 CMOS detector equipped with an Oxford Cryosystems 700 series cooler, a Triumph monochromator, and a Mo Kα fine-focus sealed tube (λ = 0.71073 Å). Intensity data were processed by using the Bruker Apex II program suite. All the calculations for the structure determination were carried out using the SHELXTL package (version 6.14). Initial atomic positions were located by direct methods using XS, and the structures of the compounds were refined by the least-squares method using SHELXL. Absorption corrections were applied by using SADABS. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized positions and refined as riding atoms with relative isotropic displacement parameters.

*1.3 (E)-2-(((2-((diphenylboryl)oxy)naphathyl)methyleneamino)acetic acid **1a**)*. **Lig1** (0.229 g, 1 mmol) was collocate in a glass beaker with 20 mL of MeOH. After dispersion, diphenylboronic acid (0.218 g, 1.2 mmol) was added to the solution and stirring continued for 1 hour. A clear solution was obtained, and the excess solvent was evaporated under

vacuum, followed by hexane washes. The product was obtained as light yellow solid with a yield of 91.6 % (0.360 g); M.P: 210-212°C. ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K): δ = 4.40 (s, 1 H, H13), 6.96-7.06 (m, 7 H, H3, H16, H16', H16'', H16''', H17, H17'), 7.25 (t, 1 H, *J*= 7.2 Hz, H6), 7.28 (m, 4 H, H15, H15', H15'', H15'''), 7.44 (t, 1 H, *J*= 7.2 Hz, H7), 7.70 (d, 1H, *J* = 8.0 Hz, H5), 7.95 (d, 1 H, *J*= 9.2 Hz, H2), 8.01 (d, 1H, *J* = 8.4 Hz, H8), 9.29 (s, 1 H, H11). ^{13}C NMR (100.61 MHz, $CDCl_3$, 298 K): δ = 54.61 (C13), 110.29 (C9), 119.64 (C8), 121.13 (C3), 123.96 (C6), 126.17 (C17), 126.80 (C16), 127.59 (C4), 128.80 (C7), 129.24 (C5), 132.48 (C10), 133.10 (C15), 139.28 (C2), 163.03 (C11), 163.98 (C1), 168.34 (C12) ppm. . ^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ = 4.80 ppm. MS *m/z*: calcd. for $[C_{25}H_{20}BNO_3 + H]^+$ 394.2490; found 394.2.

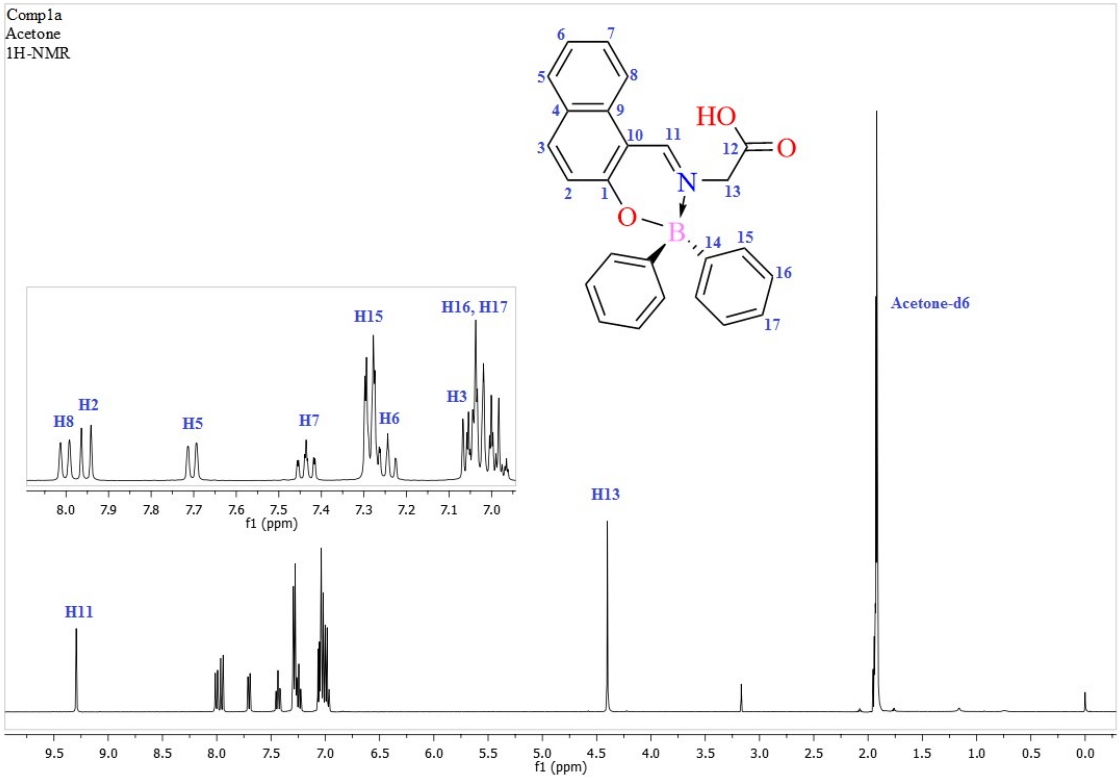

Figure S1. ^{1}H NMR (400 MHz) spectrum of BOSCHIBA **1a** in acetone-d_6.

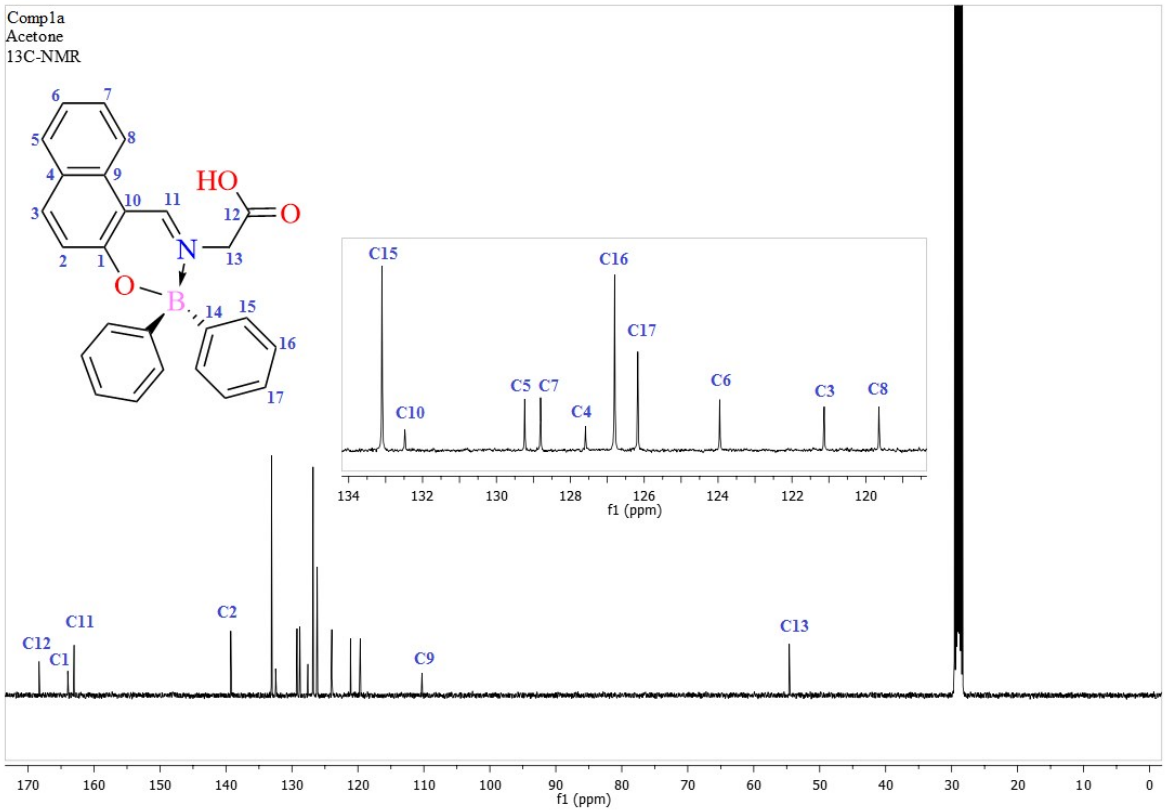

Figure S2. ^{13}C NMR spectrum of BOSCHIBA **1a** in acetone-d_6 at 100 MHz.

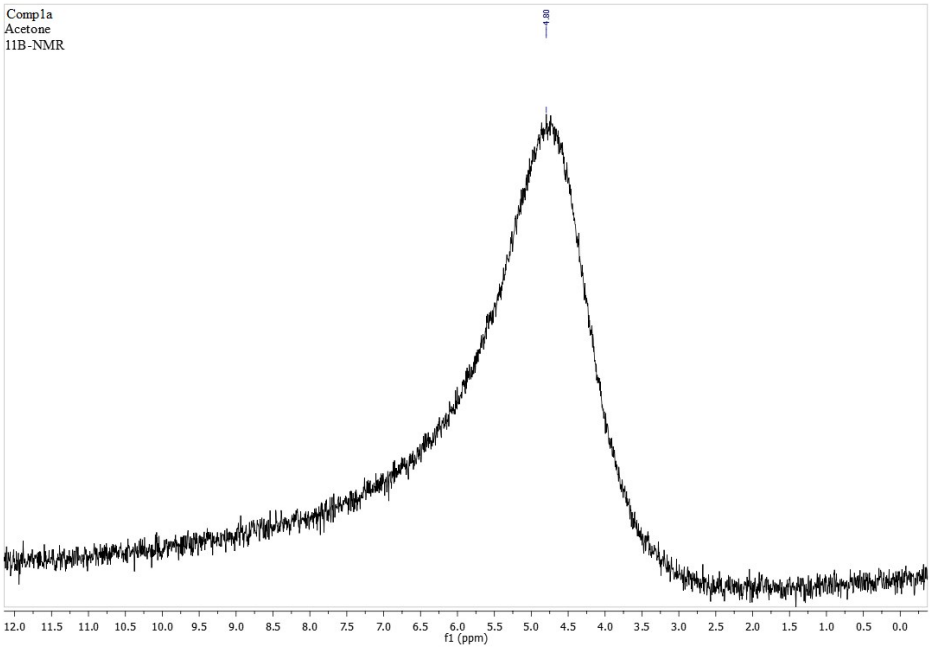

Figure S3. ^{11}B NMR spectrum of BOSCHIBA **1a** in acetone-d_6 at 128 MHz.

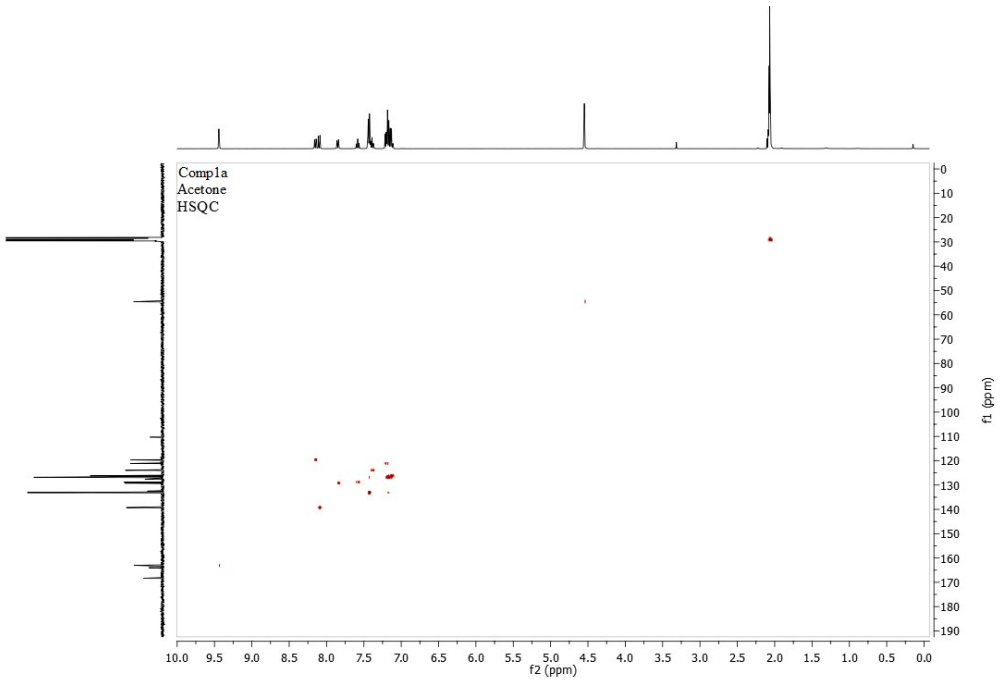

Figure S4. HSQC spectrum of BOSCHIBA **1a** in acetone-d_6.

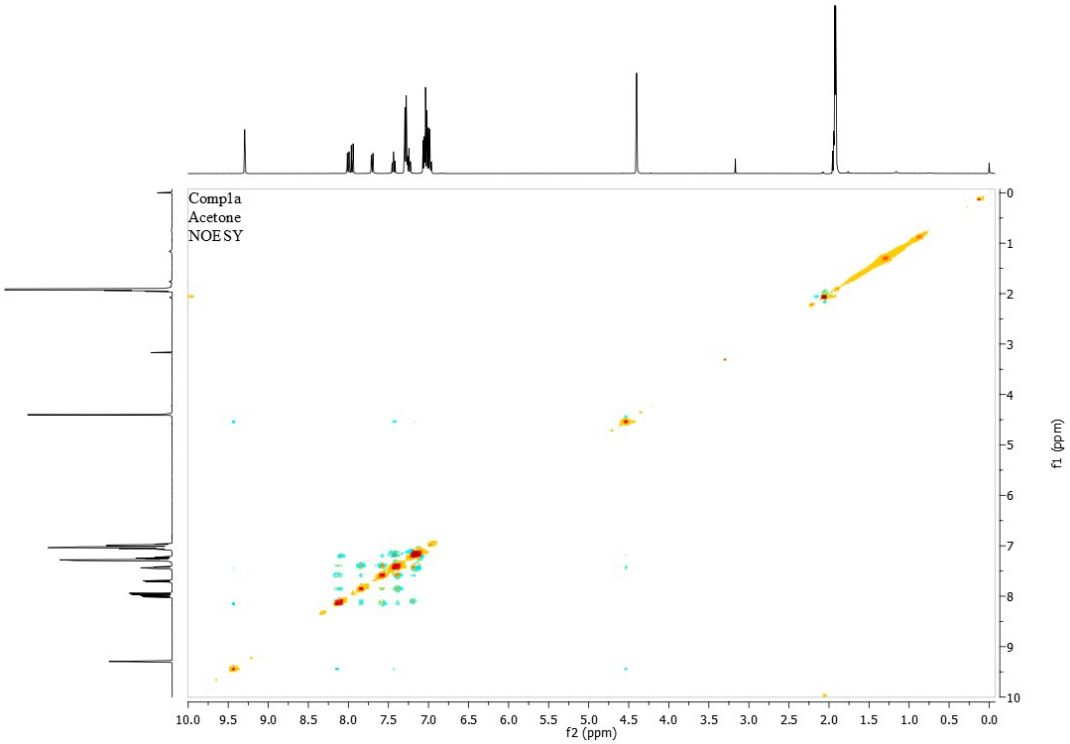

Figure S5. NOESY spectrum of BOSCHIBA **1a** in acetone-d_6.

*1.4 (E)-2-(((2-((diphenylboryl)oxy)naphthalen-1-yl)methylene)amino)-3-(1H-indol-3-yl) propanoic acid (**2a**)*. Preparation of **2a** was accomplished like that of **1a** from **Lig2** (0.358 g, 1 mmol) and diphenylboronic acid (0.218 g, 1.2 mmol). The product was obtained as light yellow solid with a yield of 95.2% (0.496 g), M.P.: 108-112°C. ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K): δ = 3.25 (dd, 1 H, J = 7.6 Hz, J = 14.4 Hz, H13), 3.53 (dd, 1 H, J = 4.4 Hz, J = 14.8 Hz, H13), 4.86 (dd, 1 H, J = 4.8 Hz, J = 7.6 Hz, H13), 6.89 (t, 1 H, J = 7.2 Hz, H20) 7.05-7.18 (m, 6 H, H3, H6, H19, H29, H29', H30), 7.21-7.41 (m, 8 H, H7, H8, H16, H18, H21, H25, H25', H26), 7.43 (m, 2 H, H28, H28'), 7.54 (m, 2 H, H24, H24'), 7.79 (d, 1 H, J= 8.0 Hz, H5), 8.04 (d, 1H, J = 8.8 Hz, H2), 8.94 (s, 1 H, H11). ^{13}C NMR (100.61 MHz, $CDCl_3$, 298 K): δ = 29.71 (C14), 63.01 (C13), 108.45 (C17), 109.67 (C9), 111.36 (C18), 118.50 (C21), 119.19 (C20), 119.24 (C8), 120.95 (C3), 121.71 (C19), 123.77 (C16), 124.65 (C6), 126.12 (C30), 126.47 (C26), 126.89 (C29), 127.08 (C25), 127.51 (C4), 128.55 (C7), 129.08 (C5), 132.38 (C10), 132.92 (C28), 133.67 (C24), 136.04 (C15), 139.04 (C2), 160.29 (C11), 163.40 (C1), 171.12 (C12) ppm. . ^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ = 5.04 ppm. MS *m/z*: calcd. for $[C_{34}H_{27}BN_2O_3 + H]^+$ 523.4110; found 523.2.

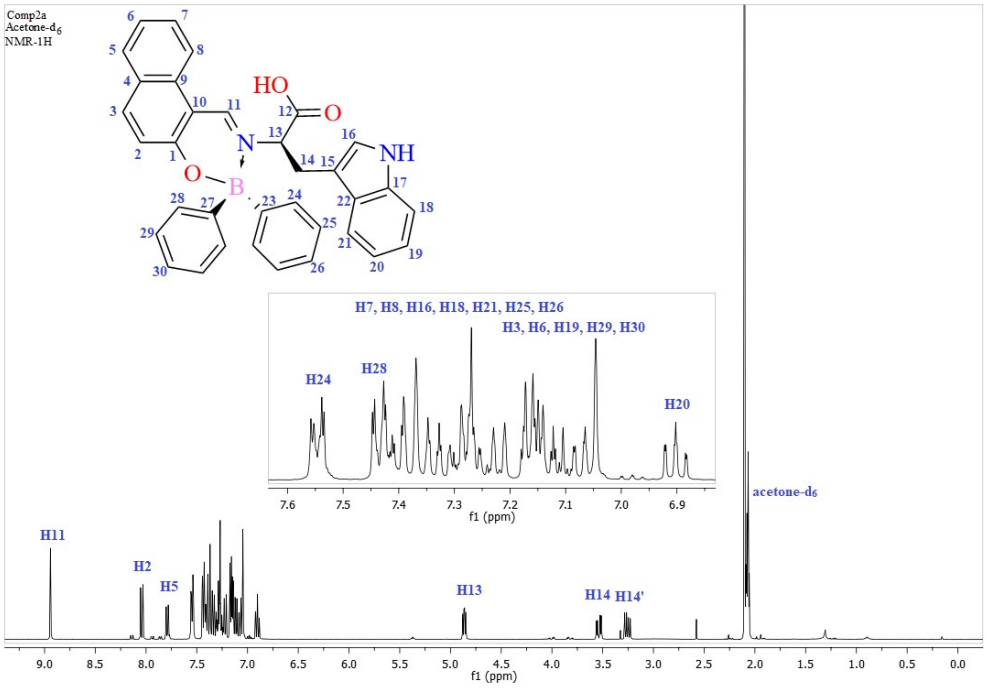

Figure S6. ^{1}H NMR spectrum of BOSCHIBA **2a** in acetone-d_6 at 400MHz.

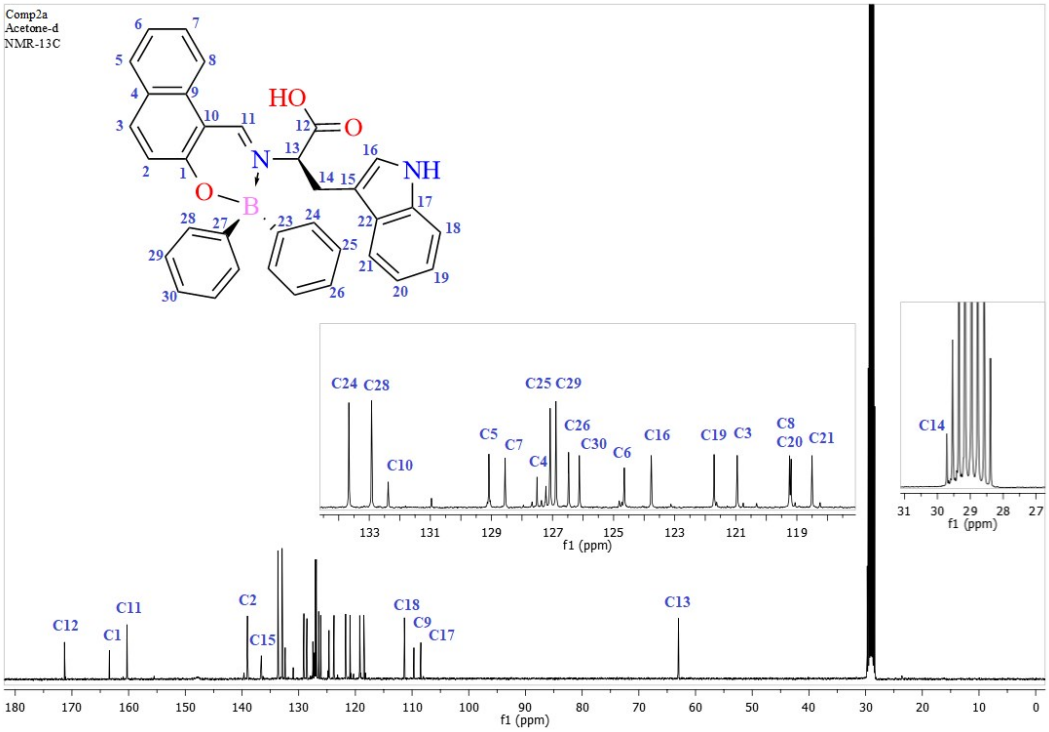

Figure S7. ^{13}C NMR spectrum of BOSCHIBA **2a** in acetone-d_6 at 100MHz.

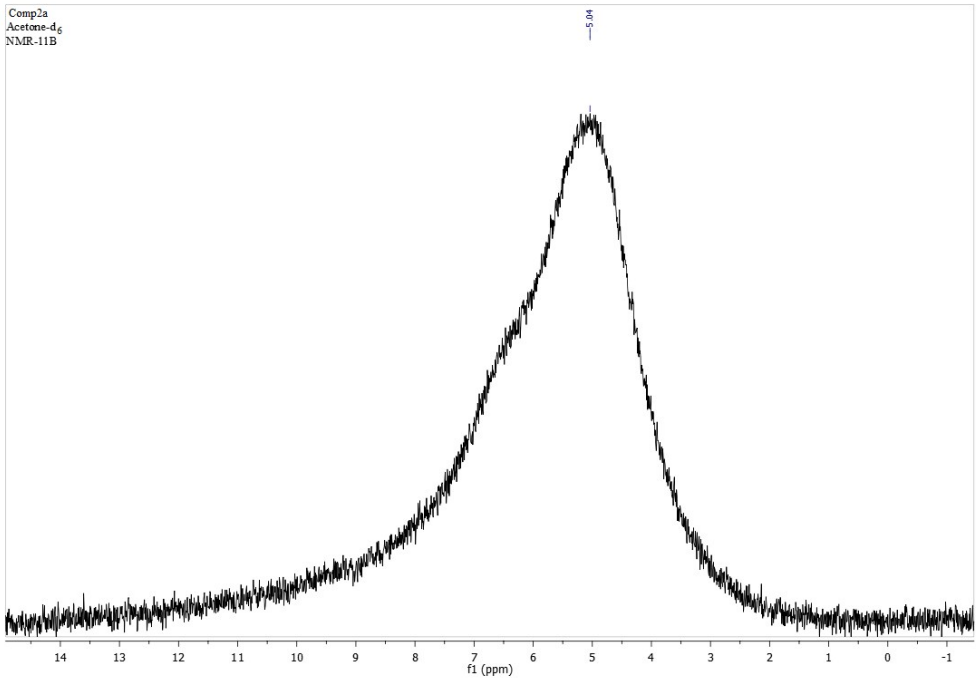

Figure S8. ^{11}B NMR spectrum of BOSCHIBA **2a in** acetone-d_6 at 128MHz.

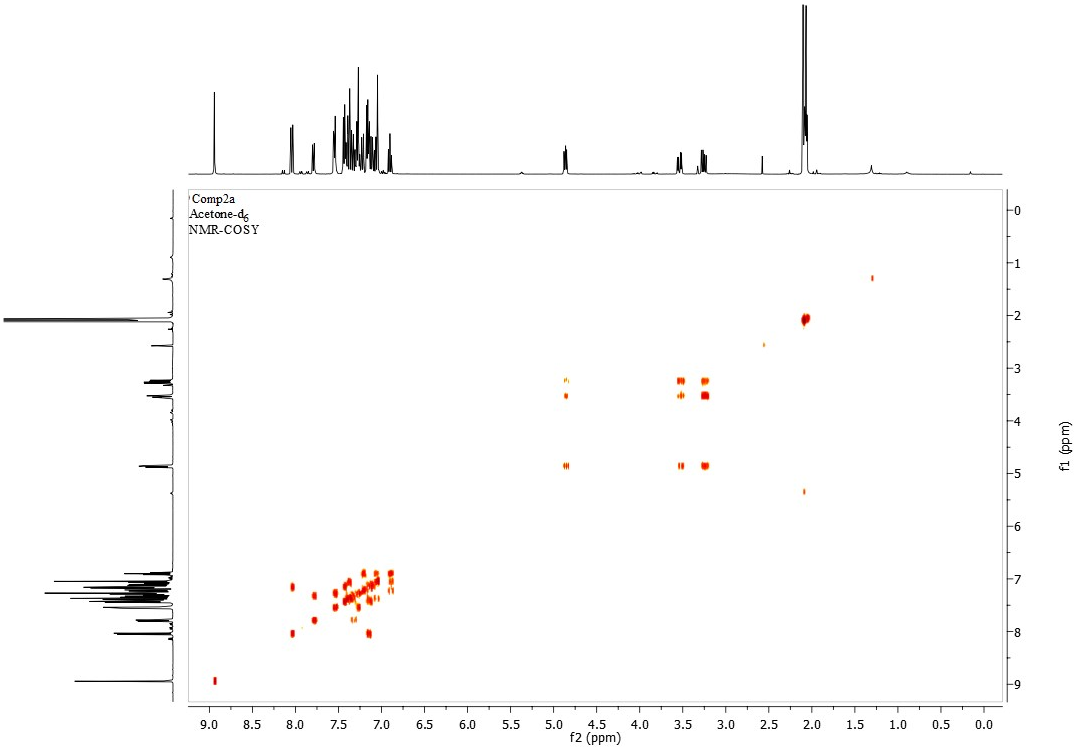

Figure S9. COSY spectrum of BOSCHIBA **2a** in acetone-d_6.

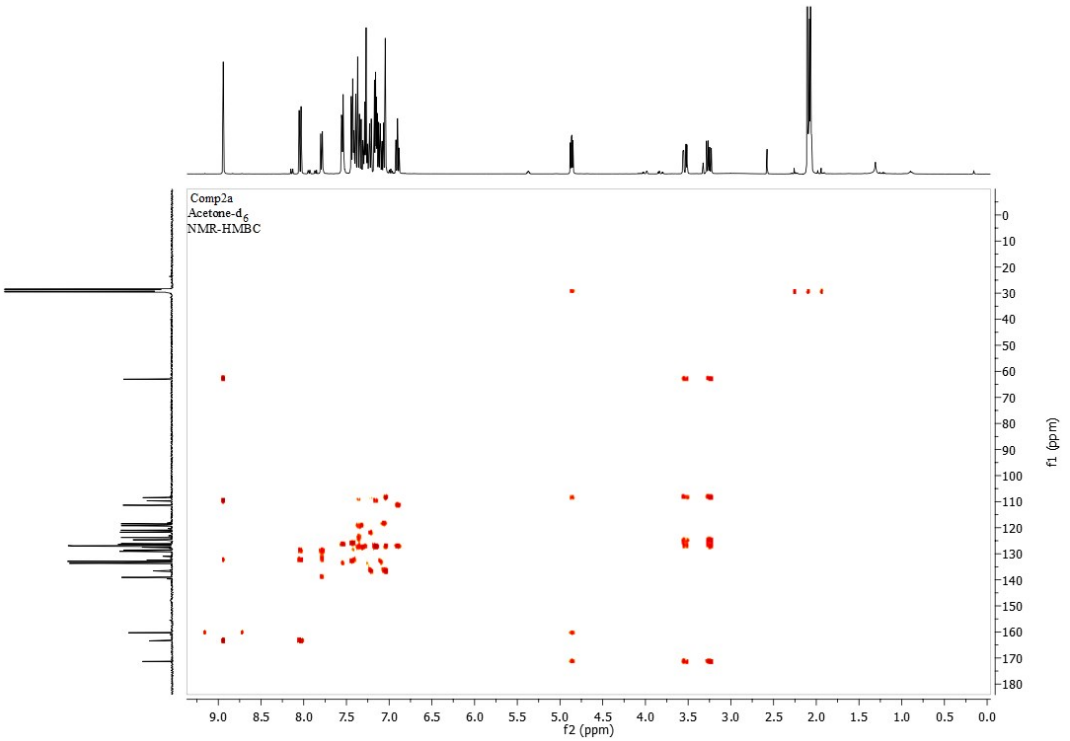

Figure S10. HMBC spectrum of BOSCHIBA **2a** in acetone-d_6.

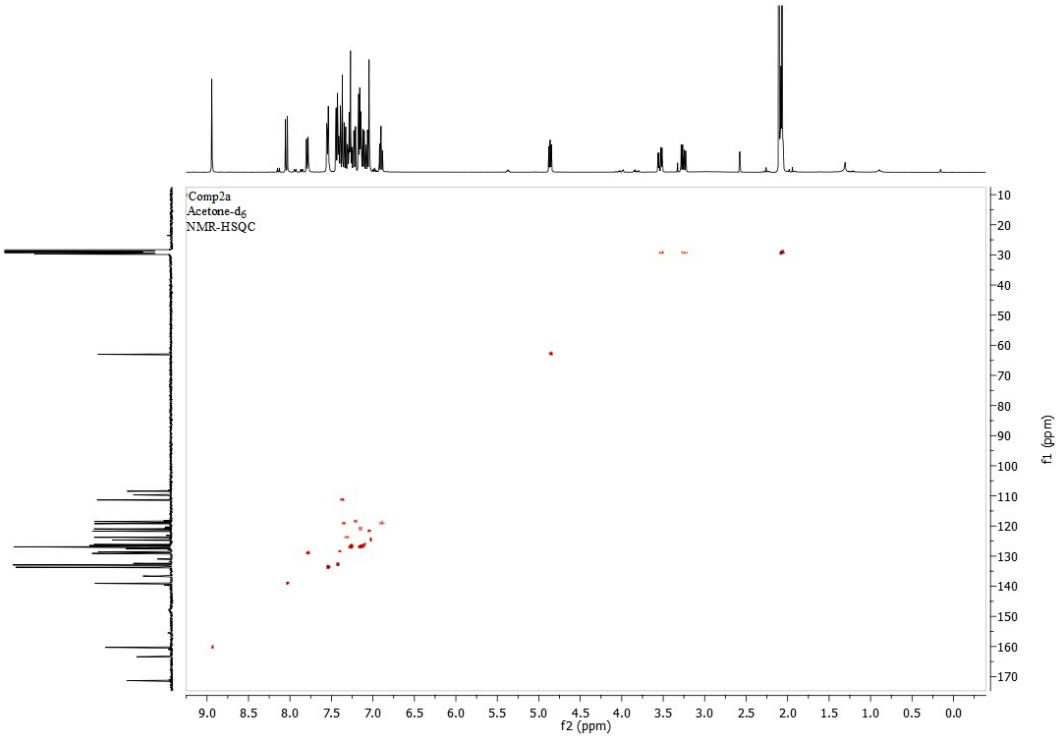

Figure S11. HSQC spectrum of BOSCHIBA **2a** in acetone-d_6.

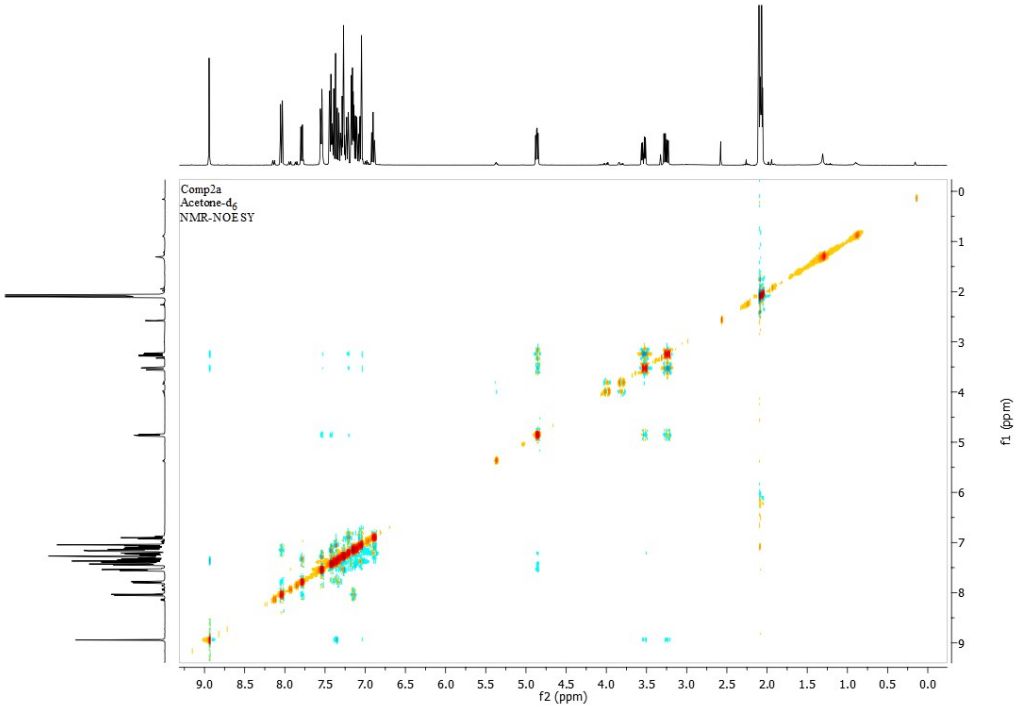

Figure S12. NOESY spectrum of BOSCHIBA **2a** in acetone-d_6.

*1.5 (E)-2-(((2-((diphenylboryl)oxy)naphthalen-1-yl)methylene)amino)-3-phenylpropanoic acid (**3a**).* Preparation of **3a** was accomplished like that of **1a** from **Lig3** (0.319 g, 1 mmol) and diphenylboronic acid (0.218 g, 1.2 mmol). The product was obtained as yellow solid with a yield of 93.2% (0.450 g); M.P.: 112-115°C. ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K): δ = 2.95 (dd, 1 H, J = 8.40 Hz, J = 13.6 Hz, H14'), 3.13 (dd, 1 H, J = 4.80 Hz, J = 13.6 Hz, H14), 4.55 (dd, 1 H, J = 5.20 Hz, J = 8.4 Hz, H13), 6.83 (m, 2 H, H16, H16'), 6.94-7.04 (m, 5 H, H3, H22, H25, H25', H26), 7.08-7.16 (m, 5 H, H17, H17', H18, H21, H21'), 7.23 (t, 1 H, J= 7.20 Hz, H6), 7.27 (m, 2 H, H24, H24'), 7.35 (m, 2 H, H20, H20'), 7.41 (t, 1 H, J= 7.2 Hz, H7), 7.67 (m, 2 H, H5, H8), 7.93 (d, 1 H, J= 9.20 Hz, H2), 9.06 (s, 1 H, H11). ^{13}C NMR (100.61 MHz, $CDCl_3$, 298 K): δ = 48.79 (C14), 63.86 (C13), 109.91 (C9), 119.49 (C8), 121.03 (C3), 124.00 (C6), 126.15 (C26), 126.54 (C22), 126.91 (C25), 127.11 (C21), 127.30 (C18), 127.61 (C4), 128.65 (C17), 128.80 (C7), 129.24 (C5), 129.55 (C16), 132.36 (C10), 132.79 (C24), 133.80 (C20), 1372 (C15), 139.36 (C2), 160.25 (C11), 163.65 (C1), 170.87 (C12) ppm. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ = 5.08 ppm. MS *m/z*: calcd. for $[C_{32}H_{26}BNO_3 + H]^+$ 484.3740; found 484.3.

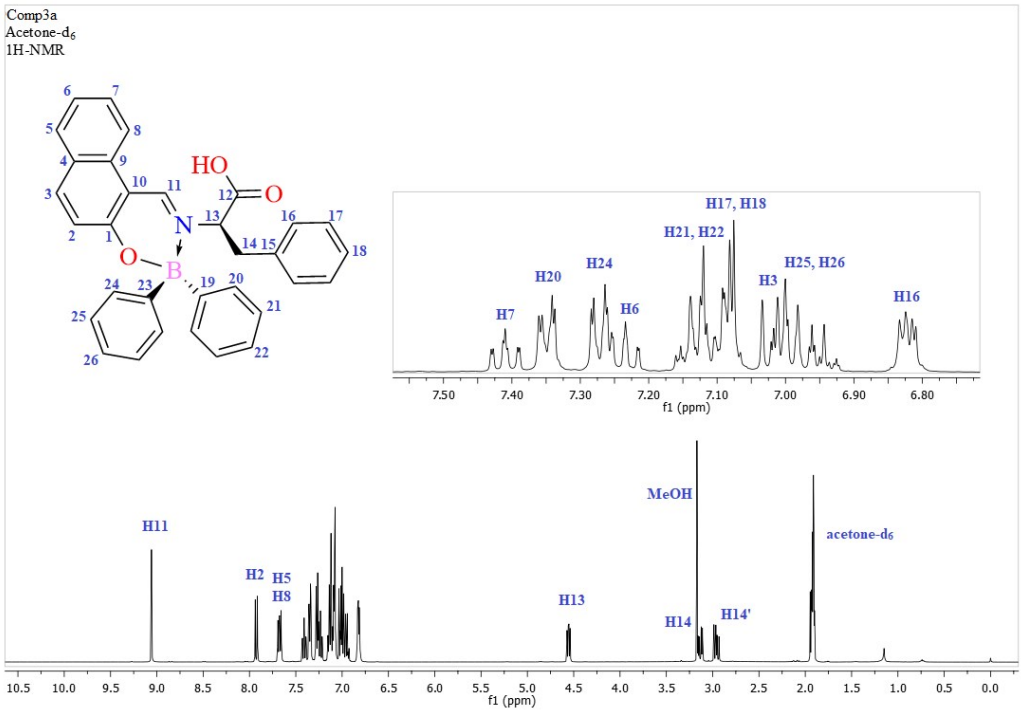

Figure S13. ^{1}H NMR spectrum of BOSCHIBA **3a** in acetone-d_6 at 400 MHz.

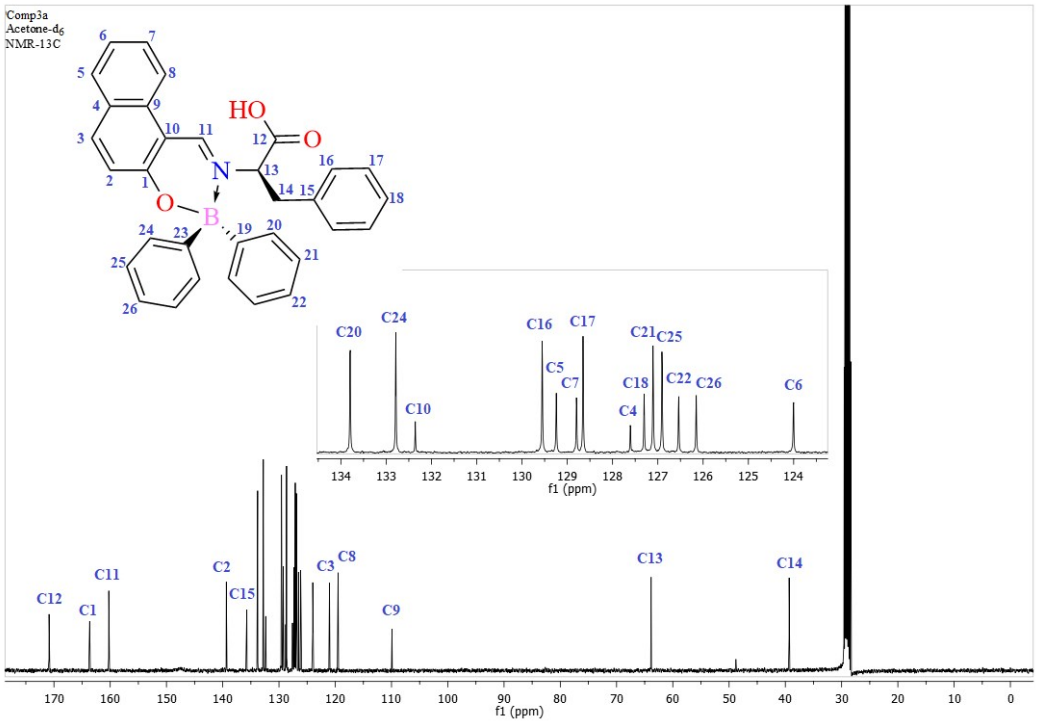

Figure S14. ^{13}C NMR spectrum of BOSCHIBA **3a** in acetone-d_6 at 100 MHz.

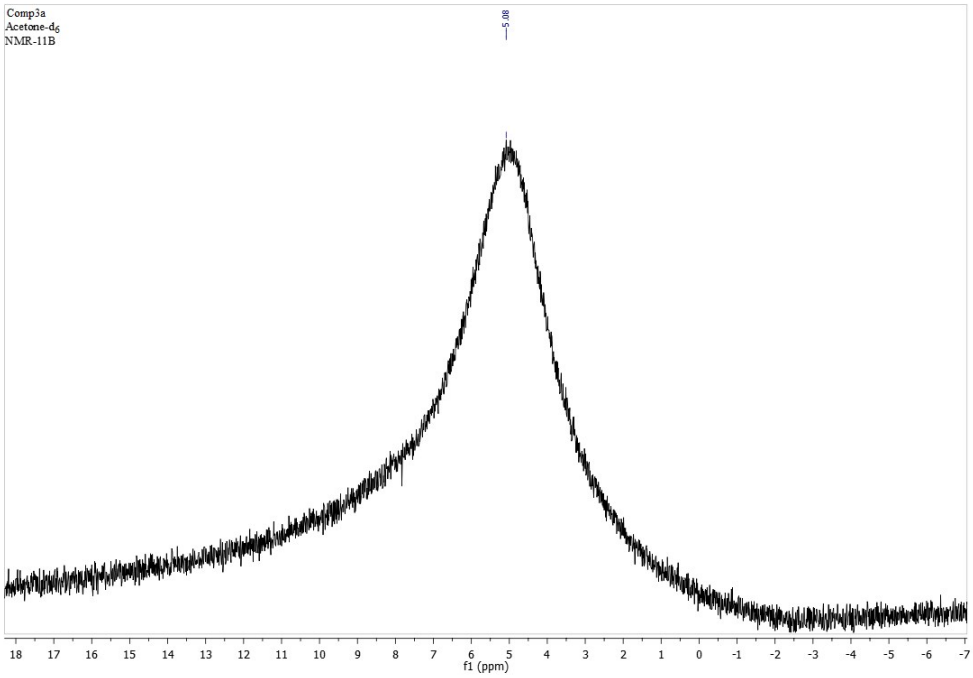

Figure S15. ^{11}B NMR spectrum of BOSCHIBA **3a** in acetone-d_6 at 128 MHz.

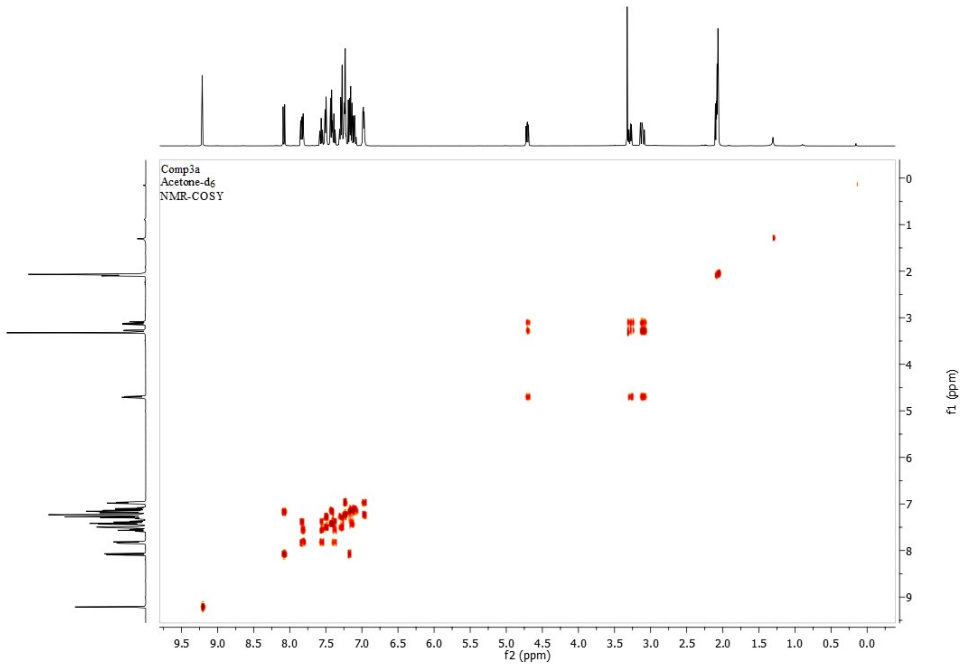

Figure S16. COSY NMR spectrum of BOSCHIBA **3a** in acetone-d_6.

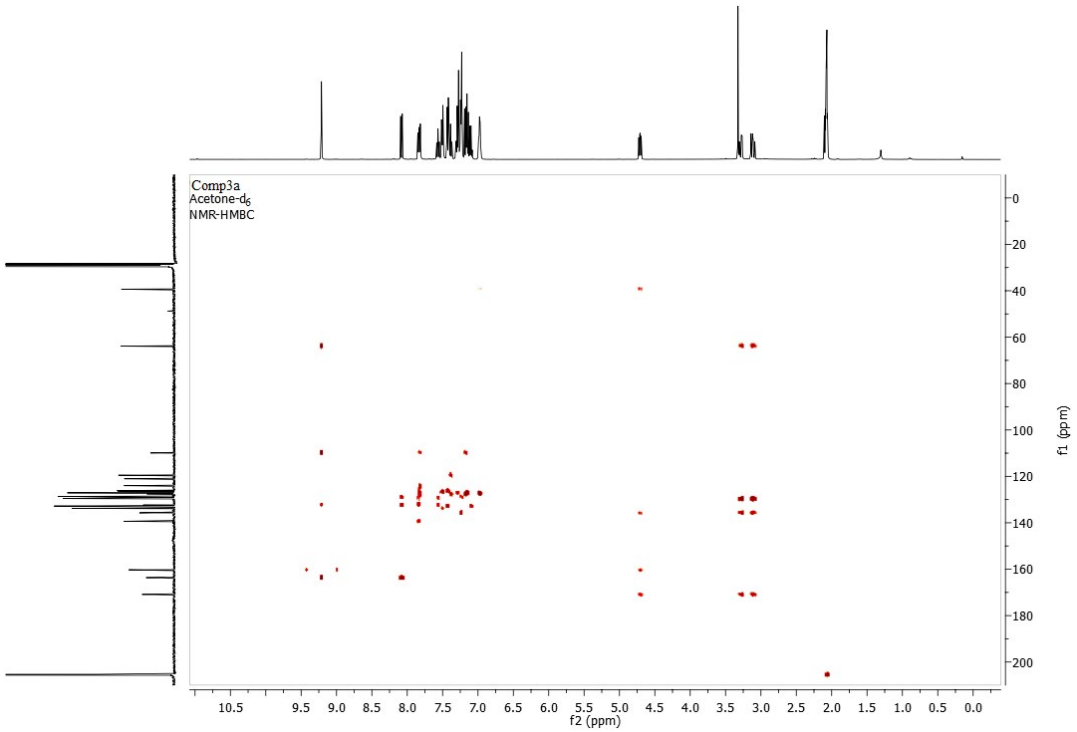

Figure S17. HMBC NMR spectrum of BOSCHIBA **3a** in acetone-d_6.

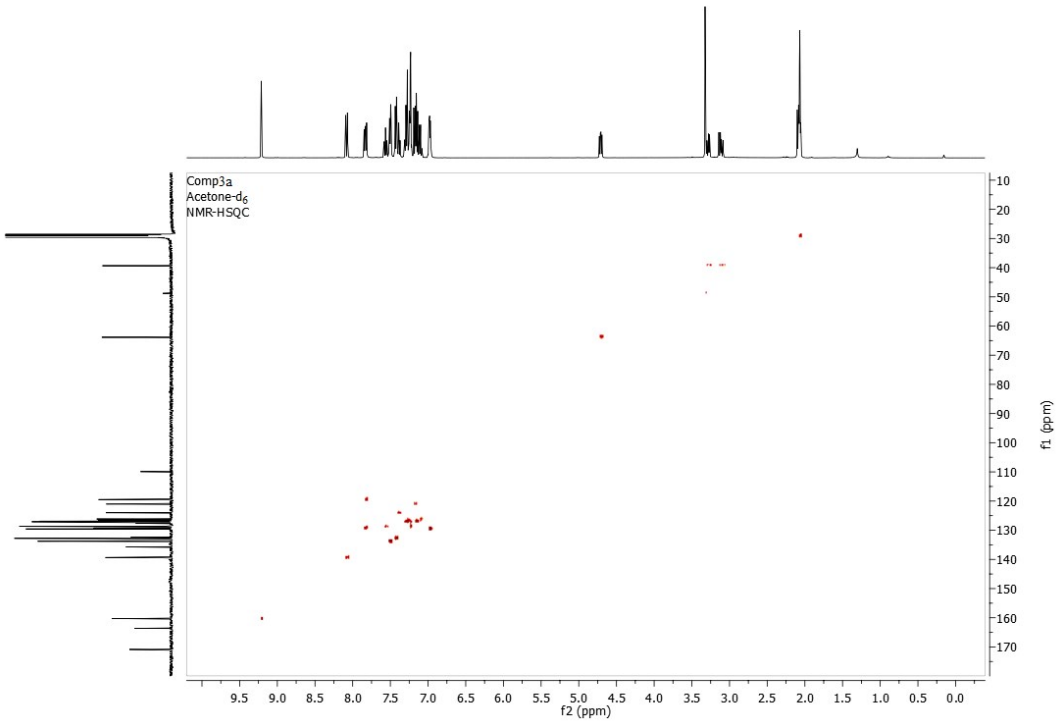

Figure S18. HSQC NMR spectrum of BOSCHIBA **3a** in acetone-d_6.

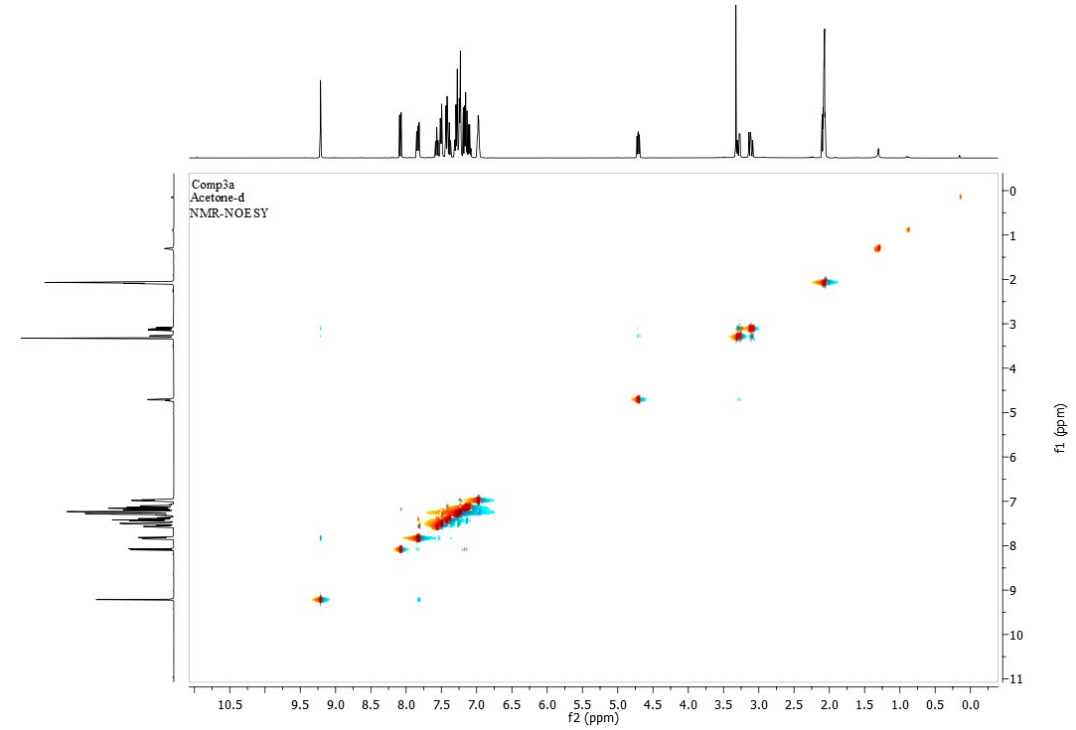

Figure S19. NOESY NMR spectrum of BOSCHIBA **3a** in acetone-d_6.

*1.6 (E)-4-(((2-((diphenylboryl)oxy)naphthalen-1-yl)methylene)amino)phenol(**4a**).*

A homogeneous mixture of 2-hydroxynaphtaldehyde (0.5g, 2.9mmol) with 4-aminophenol (0.317g, 2.9 mmol) and diphenylboronic acid (1.307g, 5.80 mmol) in acetonitrile were heated under reflux for 48 h. The reaction mixture was slowly cooled to room temperature, and the precipitated was filtrated and washed with hexane. The resulting product was obtained as a yellow solid with yield of 85% (2.47 mmol, 1.05 g); FTIR υ_{max} cm^{-1}: 1627 (C=N), 830 (C-H_{Ar}), 1345 (C=C_{Ar}), 703 (O-B); ^{1}H NMR (300.13 MHz, $(CD_3)_2CO$)) δ: 6.68 (d, 2H, ^{3}J = 9 Hz, H-14, H-13), 7.13 (m, 7H, H-3, 4H-*m*, 2H-*p*), 7.33 (d, 2H, ^{3}J = 15 Hz, H-13, H-17), 7.39 (t, 1H, ^{3}J = 15 Hz, H-7), 7.46 (d, 4H, ^{3}J = 6 Hz, 4H-*o*), 7.58 (t, 1H, ^{3}J = 15 Hz, H-8), 7.83 (d, 1H, ^{3}J = 6.0 Hz, H-6), 8.05 (d, 1H, ^{3}J = 9 Hz, H-4), 8.33 (d, 1H, ^{3}J = 9.0 Hz, H-9), 8.66 (s, 1H, C15-OH), 9.37 (s, 1H, H-11) ppm; ^{13}C NMR (75.47 MHz, $(CD_3)_2CO$)) δ: 111.81 (C-1), 114.92 (C-14, C-16), 120.34 (C-9), 121.00 (C-13, C-17), 124.04 (C-3), 125.46 (C-7), 125.89 (C-5), 126.04 (C-*m*), 126.60 (C-*p*), 128.75 (C-8), 129.15 (C-6), 132.59 (C-10), 133.32 (C-4), 133.77 (C-*o*), 138.67 (C-12), 139.27 (C-*i*), 156.95 (C-11), 158.03 (C-15), 164.01 (C-2) ppm; $^{11}B\{^{1}H\}$ NMR (96.29 MHz, $(CD_3)_2CO$)) δ: 8.89 ppm; HRMS (APCI/TOF-Q) *m/z*: calcd. for $[(C_{34}H_{27}N_2O_3B+H)^+]$: 428.1700 ; Exp.: 428.1819 amu.

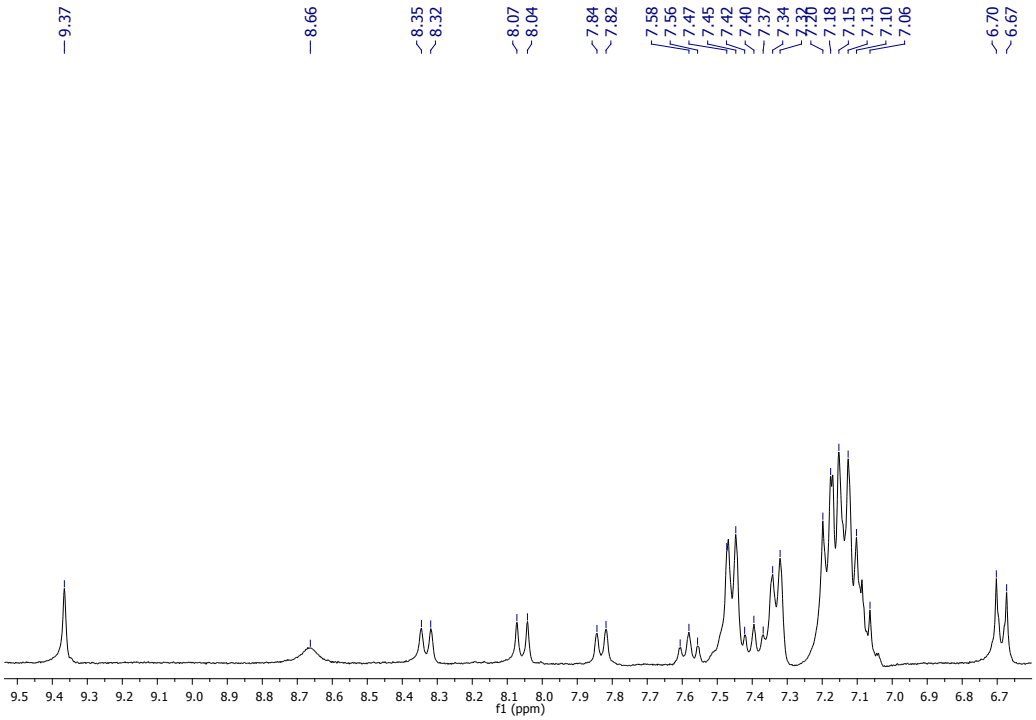

Figure S20. ^{1}H NMR spectrum of BOSCHIBA **4a** in $(CD_3)_2CO$ at 300 MHz.

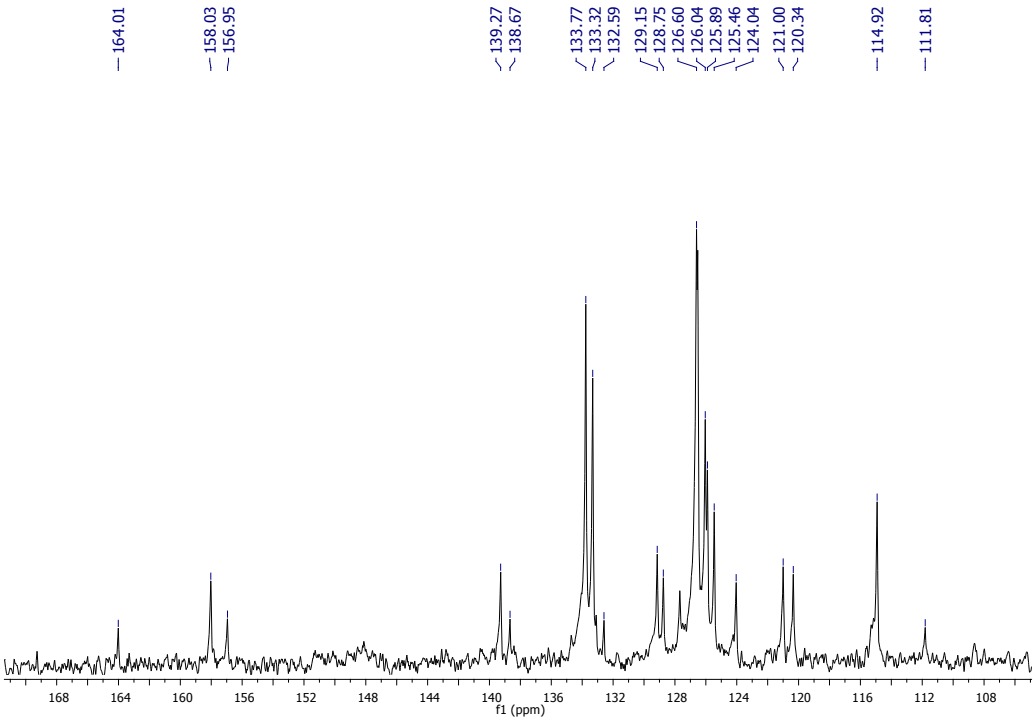

Figure S21. ^{13}C NMR spectrum of BOSCHIBA **4a** in $(CD_3)_2CO$ at 75 MHz.

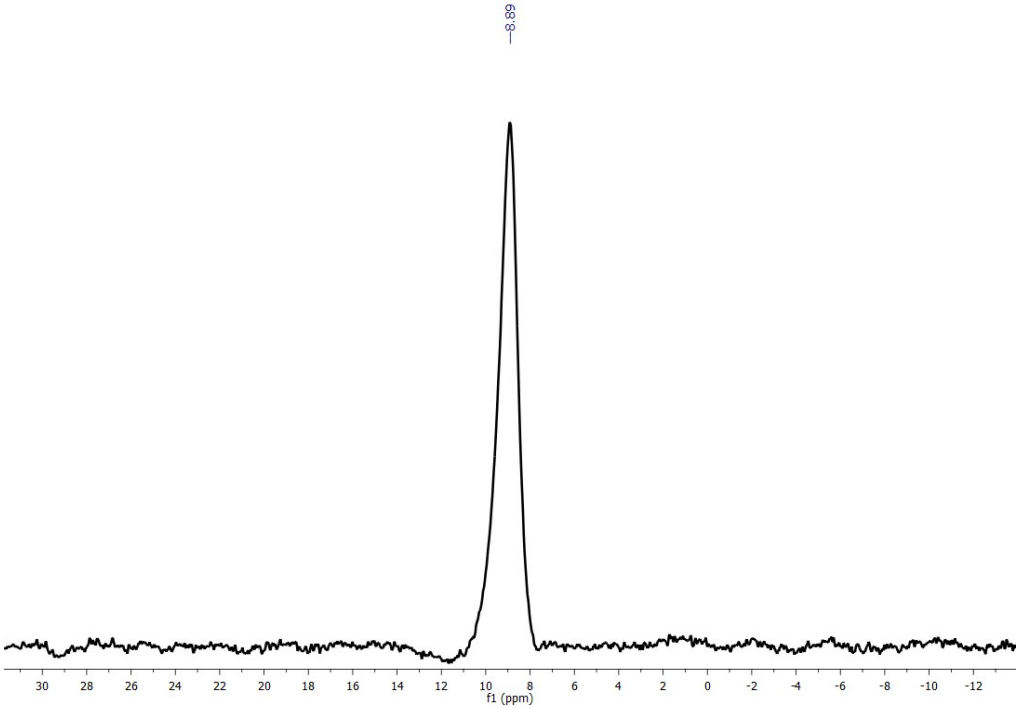

Figure S22. ^{11}B NMR spectrum of BOSCHIBA **4a** in acetone-d6 at 128 MHz.

*1.7 (E)-2-(((2-hydroxynaphthalen-1-yl)methylene)amino)-3-(1H-indol-3-yl)propanoic acid (**Lig2**)*. Preparation of **Lig2** was accomplished like that of **Lig1** from 2-hydroxynaphtaldehyde (0.344 g, 2 mmol) and *L*-tryptophan (0.408 g, 2 mmol). The product was obtained as light yellow solid with a yield of 89.5% (0.321 g); M.P: 162-164°C. ^{1}H NMR (400.13 MHz, $(CD_3)_2SO$, 298 K): δ = 3.32 (dd, 1 H, ^{3}J = 14.8 Hz, ^{3}J = 7.6 Hz, H14'), 3.45 (dd, 1 H, ^{3}J = 15.2 Hz, ^{3}J = 4.8 Hz, H14), 4.77 [dd, 1 H, ^{3}J = 7.6 Hz, ^{3}J = 4.8 Hz, H13], 6.71 (d, 1 H, ^{3}J = 9.2 Hz, H3), 6.98 (t, 1 H, ^{3}J = 7.2 Hz, H20), 7.07 (t, 1 H, ^{3}J = 6.8 Hz, H19), 7.16 (s, 1 H, H16), 7.18 (t, 1 H, ^{3}J = 7.6 Hz, H6), 7.33 (d, 1 H, ^{3}J = 8.0 Hz, H18), 7.35 (t, 1 H, ^{3}J = 7.2 Hz, H7), 7.61 (m, 2 H, H21-H5), 7.71 (d, 1 H, ^{3}J = 9.6 Hz, H2), 7.72 (d, 1 H, ^{3}J = 8.4 Hz, H8), 8.83 [s, 1 H, H11], 10.93 (s, 1 H, –NH), 14.17 (s, 1 H, –OH) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 298 K): δ = 29.84 (C14), 64.36 (C13), 106.42 (C9), 109.04 (C15), 111.89 (C18), 118.83 (C21), 118.86 (C8), 119.03 (C20), 121.56 (C19), 122.83 (C6), 124.72 (C16), 125.47 (C3), 125.82 (C4), 127.52 (C22), 128.34 (C7), 129.34 (C5), 134.54 (C10), 136.59 (C17), 137.65 (C2), 159.09 (C11), 172.57 (C1), 176.86 (C12) ppm. COSY correlations (δ_H/δ_H): δ =3.32/3.45 (H14'/H14), 3.32/4.77 (H14'/H13), 3.45/4.77 (H14/H13), 6.71/7.71 (H3/H2), 6.98/7.61 (H20/H21), 7.07/7.33 (H19/H18), 7.16/10.93 (H16/NH), 7.18/7.61 (H6/H5), 7.35/7.72 (H7/H8). HSQC correlations (δ_H/δ_C): δ = 3.32/29.84 (H14'/C14), 3.45/29.84 (H14/C14), 4.77/64.36 (H13/C13), 6.71/125.47 (H3/C3), 7.16/124.72 (H16/C16), 7.18/122.83 (H6/C6), 7.61/129.34 (H5/C5), 7.71/137.65 (H2/C2), 7.72/118.86 (H8/C8), 8.83/159.09 (H11/C11). HRMS (APCI/TOF-Q) *m/z*: calcd. for $[C_{22}H_{18}N_2O_3 + H]^+$ 359.1396; found 359.139019, error: 0.094347 ppm.

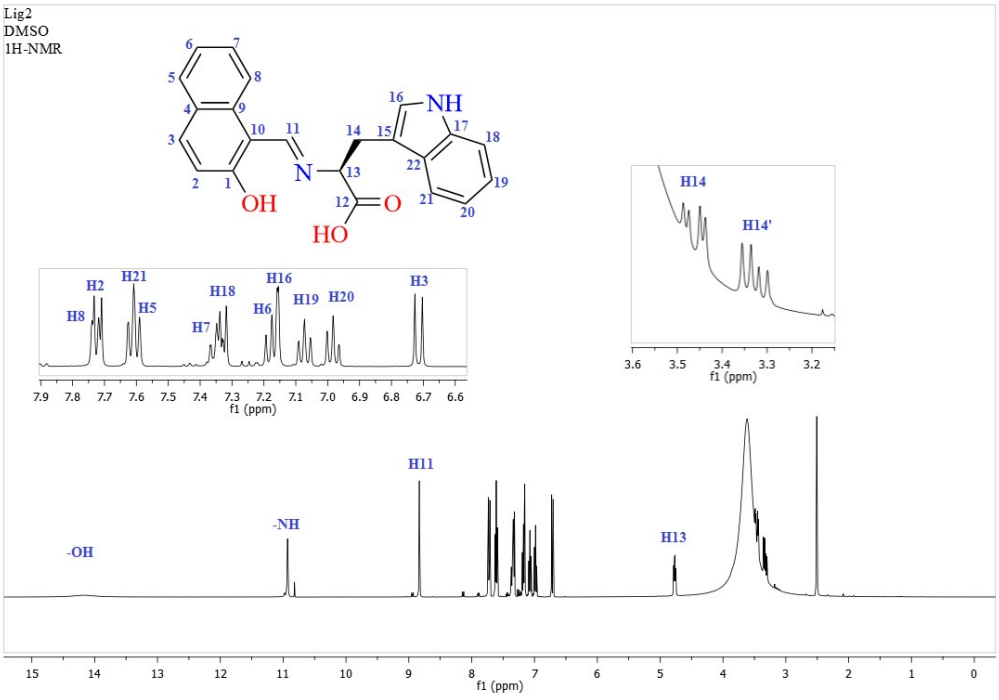

Figure S23. ^{1}H NMR spectrum of **Lig2** in DMSO-d_6 at 400 MHz.

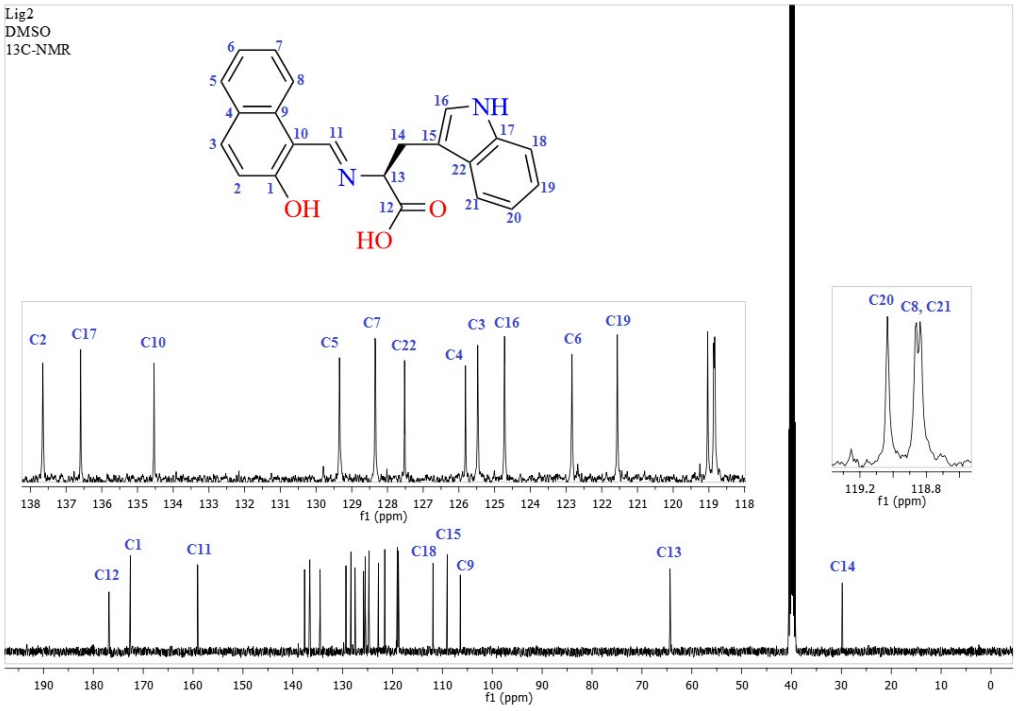

Figure S24. ^{13}C NMR spectrum of **Lig2** in DMSO-d_6 at 100 MHz.

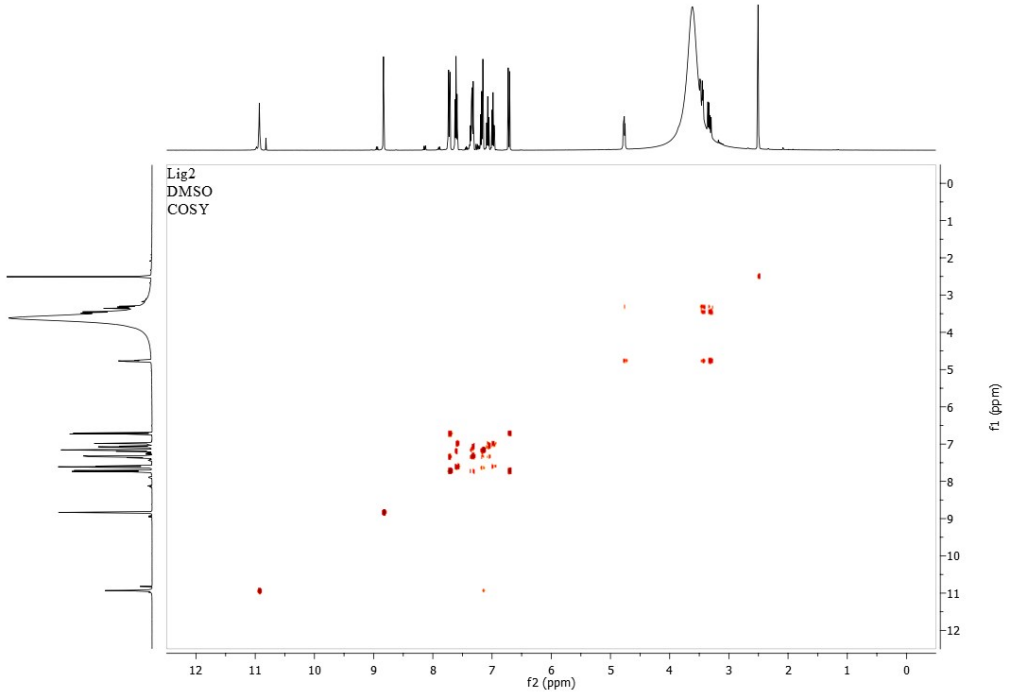

Figure S25. COSY NMR spectrum of **Lig2** in DMSO-d_6.

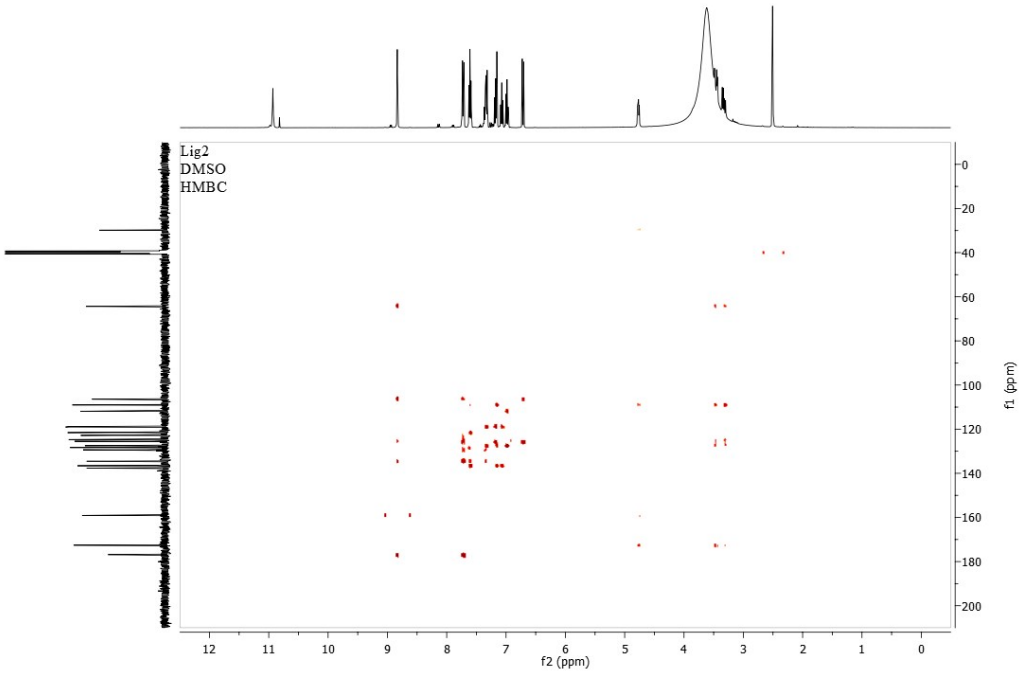

Figure S26. HMBC NMR spectrum of **Lig2** in DMSO-d_6.

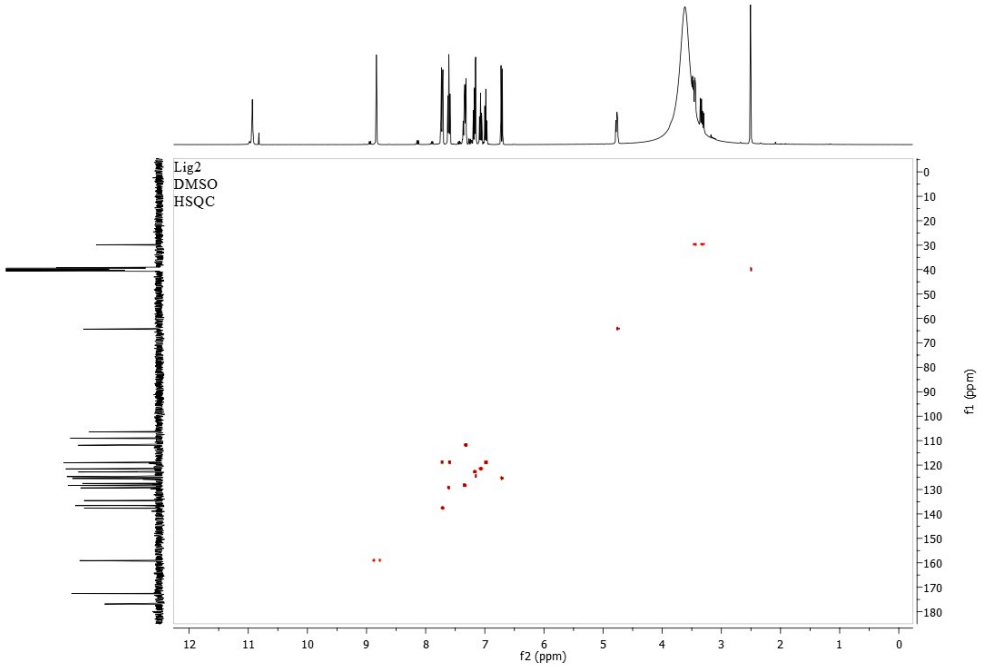

Figure S27. HSQC NMR spectrum of **Lig2** in DMSO-d_6.

*1.8 (E)-2-(((2-hydroxynaphthalen-1-yl)methylene)amino)-3-phenylpropanoic acid (**Lig3**).* Preparation of **Lig3** was accomplished like that of **Lig1** from 2-hydroxynaphtaldehyde (0.334 g, 2 mmol) and *L*-phenylalanine (0.330 g, 2 mmol). The product was obtained as light yellow solid with a yield of 92% (0.293 g); M.P.: 150-153°C; ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K): δ = 3.17 (dd, 1 H, J = 14.0 Hz, J = 8.4 Hz, H14'), 3.35 (dd, 1 H, J = 14.0 Hz, J = 5.2 Hz, H14), 4.72 [dd, 1 H, J = 8.4 Hz, J = 4.8 Hz, H13], 6.75 (d, 1 H, J = 9.6 Hz, H3), 7.02 (d, 2 H, J = 8.4 Hz, H17), 7.16-7.23 (m, 2 H, H18-H6), 7.23-7.30 (m, 4 H, H16-H17), 7.40 (t, 1 H, J = 7.2 Hz, H7), 7.64 (d, 1 H, J = 7.6 Hz, H5), 7.75 (d, 1 H, J = 9.6 Hz, H2), 7.86 (d, 1 H, J = 8.4 Hz, H8), 8.89 [s, 1 H, H11], 14.22 (s, 1 H, –OH) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 298 K): δ = 39.41 (C14), 65.76 (C13), 106.64 (C9), 119.01 (C8), 122.95 (C6), 124.99 (C3), 126.00 (C4), 127.19 (C18), 128.37 (C7), 128.83 (C17), 129.37 (C5), 129.93 (C16), 134.38 (C10), 137.03 (C15), 137.42 (C2), 159.76 (C11), 172.17 (C1), 175.63 (C12) ppm. COSY correlations (δ_H/δ_H): δ =3.17/3.35 (H14'/H14), 3.17/4.72 (H14'/H13), 3.35/4.72 (H14/H13), 6.75/7.74 (H3/H2), 7.19/7.64 (H6/H5), 7.19/7.40 (H6/H7), 7.40/7.86 (H7/H8). HSQC correlations (δ_H/δ_C): δ = 3.17/39.41 (H14'/C14), 3.35/39.41 (H14/C14), 4.72/65.76 (H13/C13), 6.75/124.99 (H3/C3), 7.18/127.19 (H18/C18), 7.19/122.95 (H6/C6), 7.25/128.83 (H17/C17), 7.26/129.93 (H16/C16), 7.40/128.37 (H7/C7) 7.64/129.37 (H5/C5), 7.74/137.42 (H2/C2), 7.86/119.01 (H8/C8), 8.89/159.76 (H11/C11). HRMS (APCI/TOF-Q) *m/z*: calcd. for $[C_{20}H_{17}NO_3 + H]^+$ 320.1288; found 320.128120, error: 1.018127 ppm.

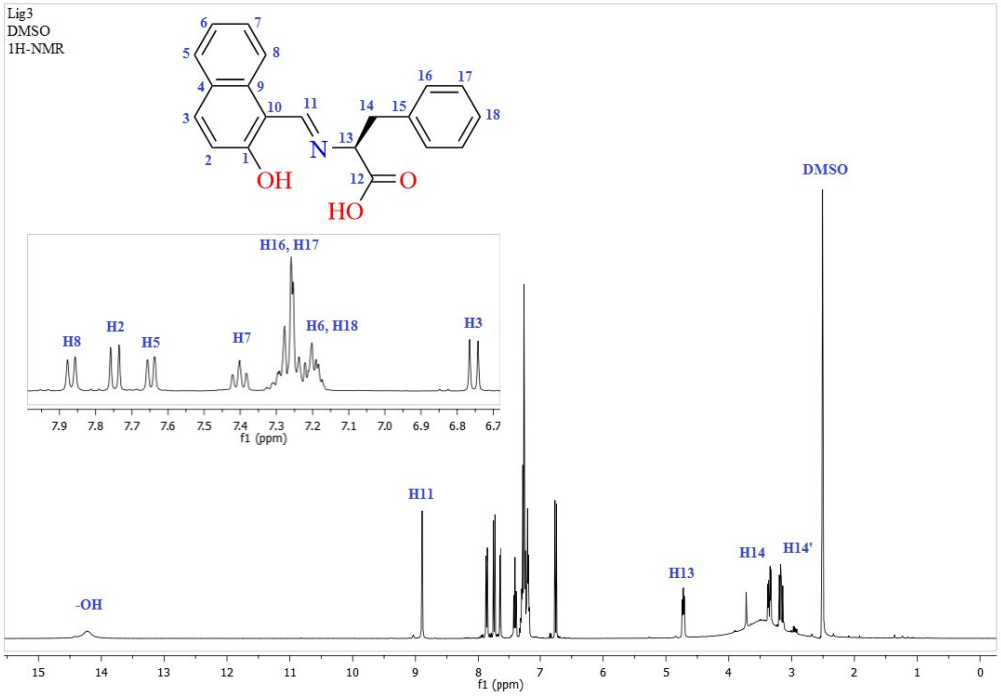

Figure S28. ^{1}H NMR spectrum of **Lig3** in DMSO-d_6 at 400 MHz.

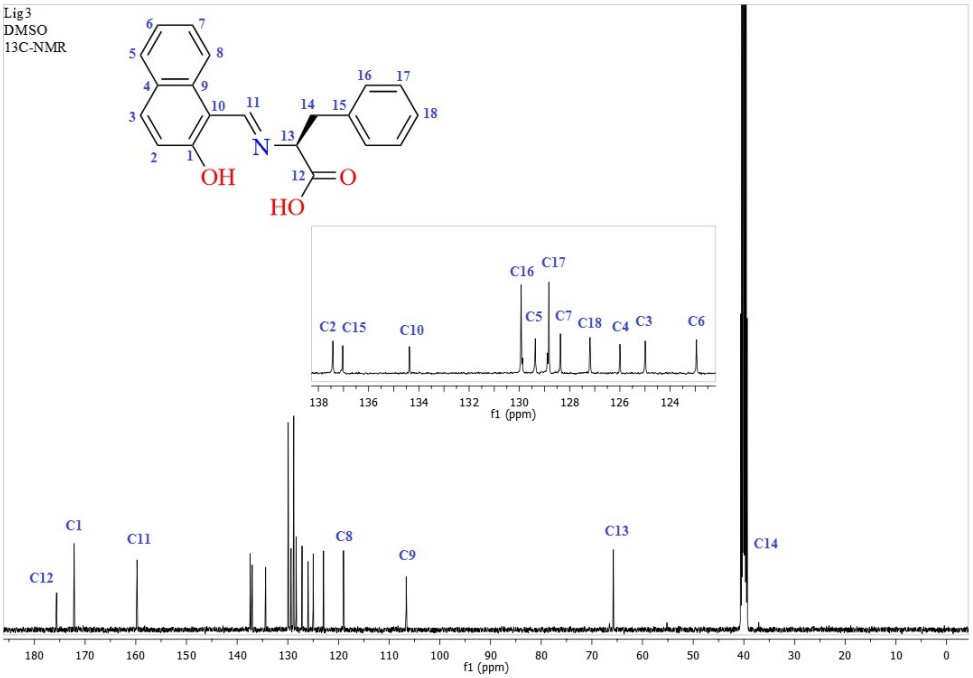

Figure S29. ^{13}C NMR spectrum of **Lig3** in DMSO-d_6 at 100 MHz.

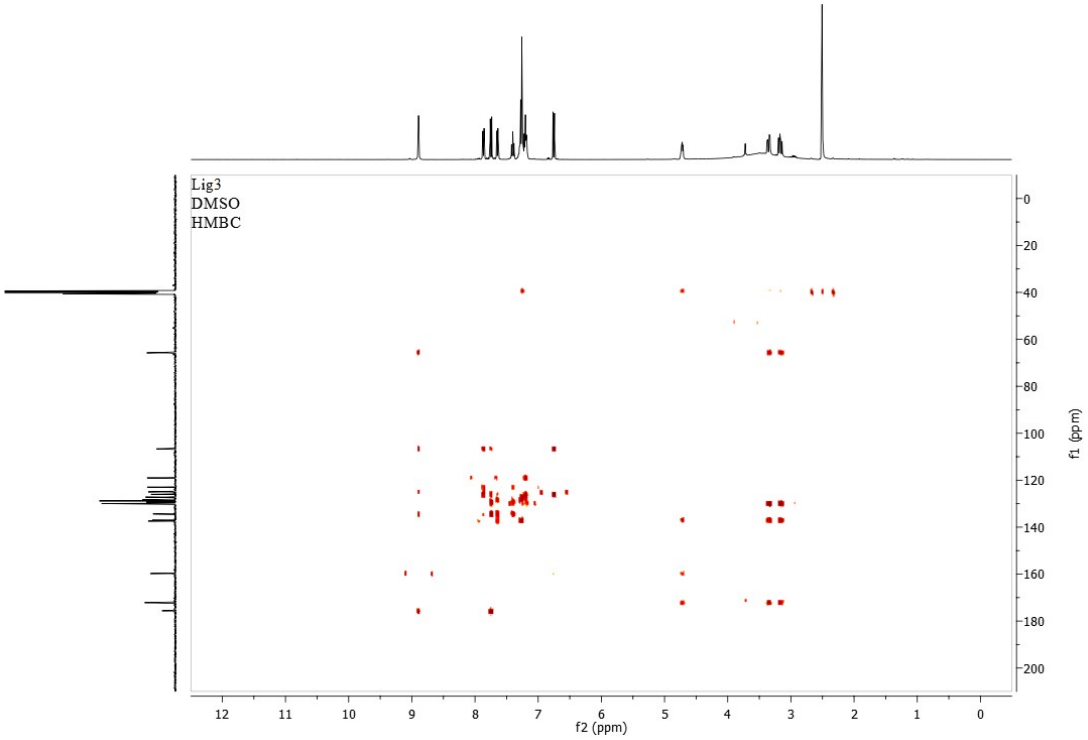

Figure S30. HMBC NMR spectrum of **Lig3** in DMSO-d_6.

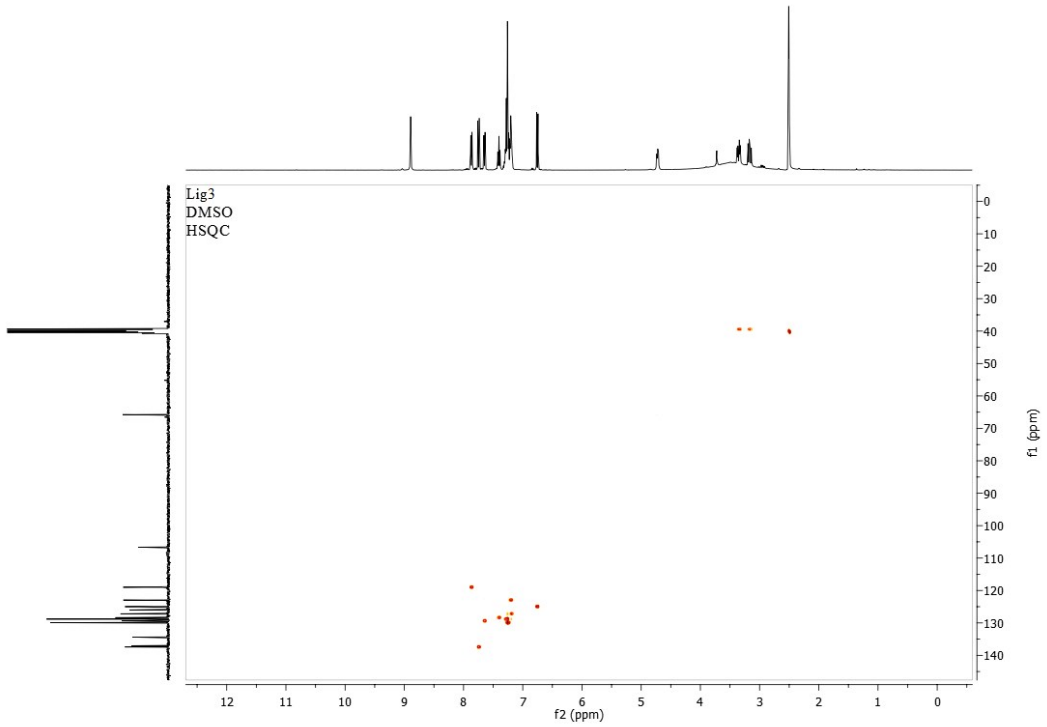

Figure S31. HSQC NMR spectrum of **Lig3** in DMSO-d_6.

*1.9 IR spectra of **Lig2**, **Lig3**, **1a-4a**.*

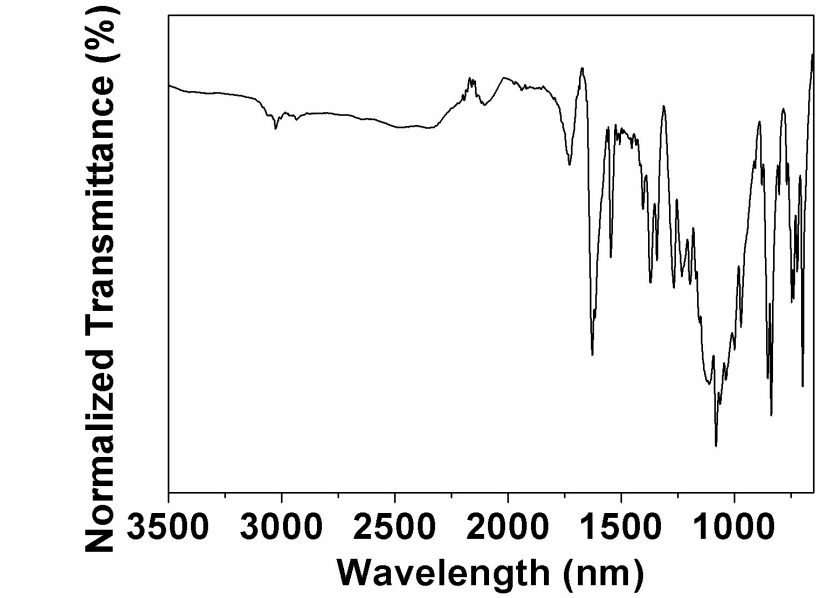

Figure S32. ATR FT-IR spectrum of **Lig2.**

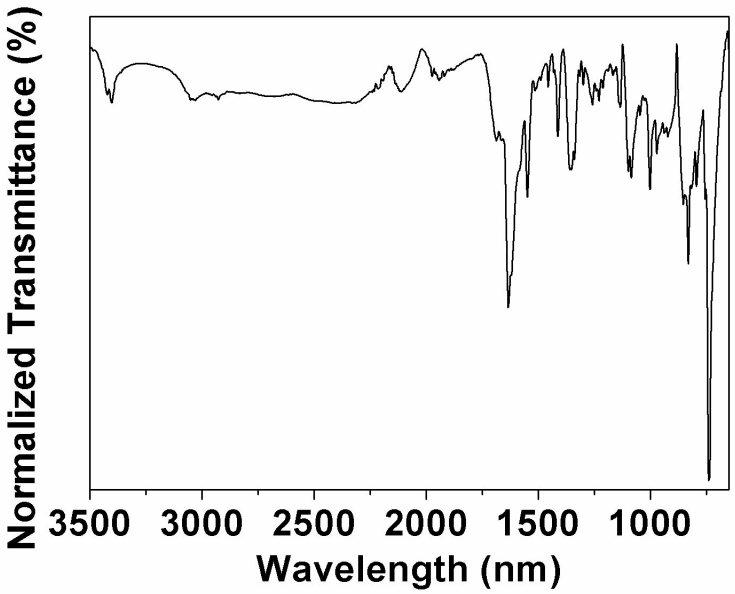

Figure S33. ATR FT-IR spectrum of **Lig3.**

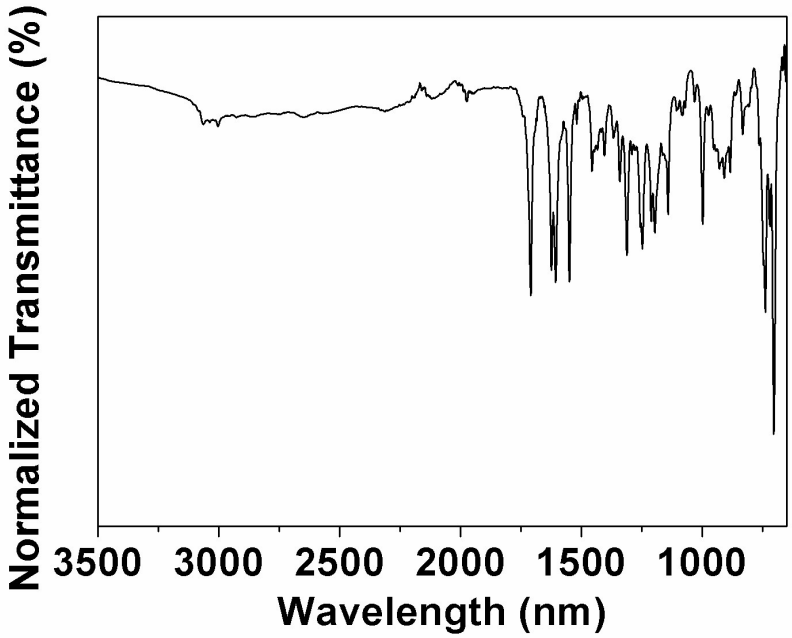

Figure S34. ATR FT-IR spectrum of BOSCHIBA **1a**.

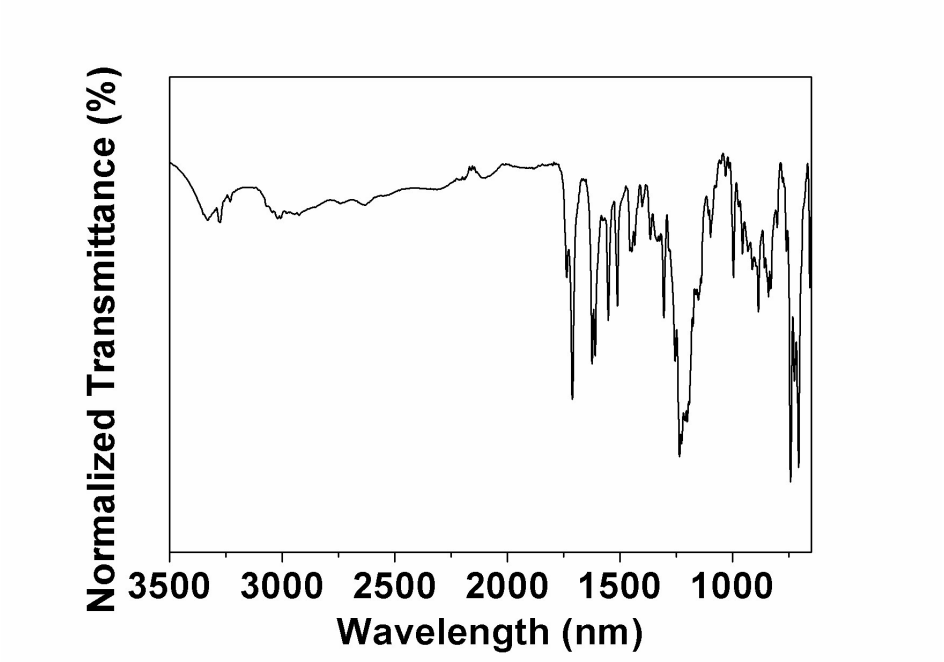

Figure S35. ATR FT-IR spectrum of BOSCHIBA **2a.**

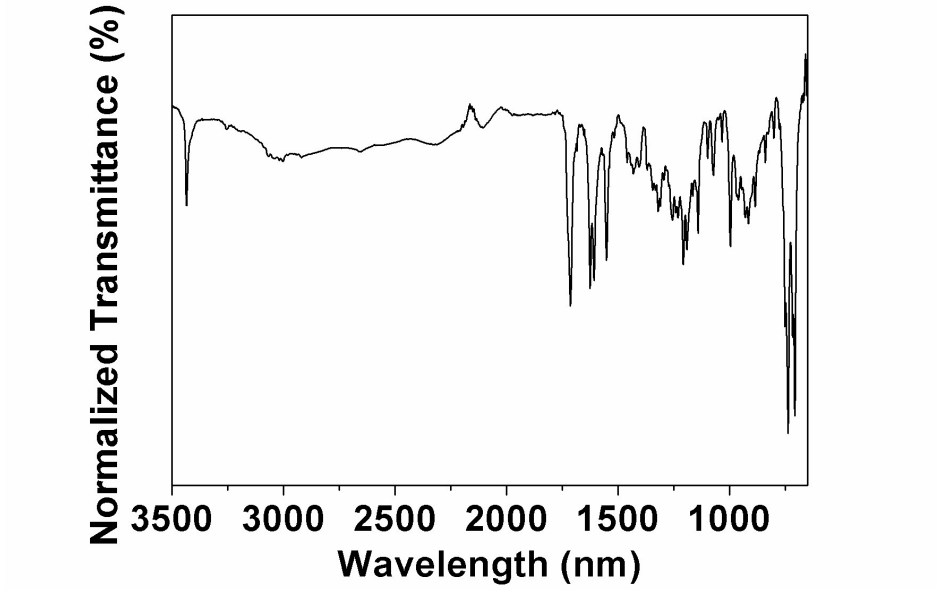

Figure S36. ATR FT-IR spectrum of BOSCHIBA **3a.**

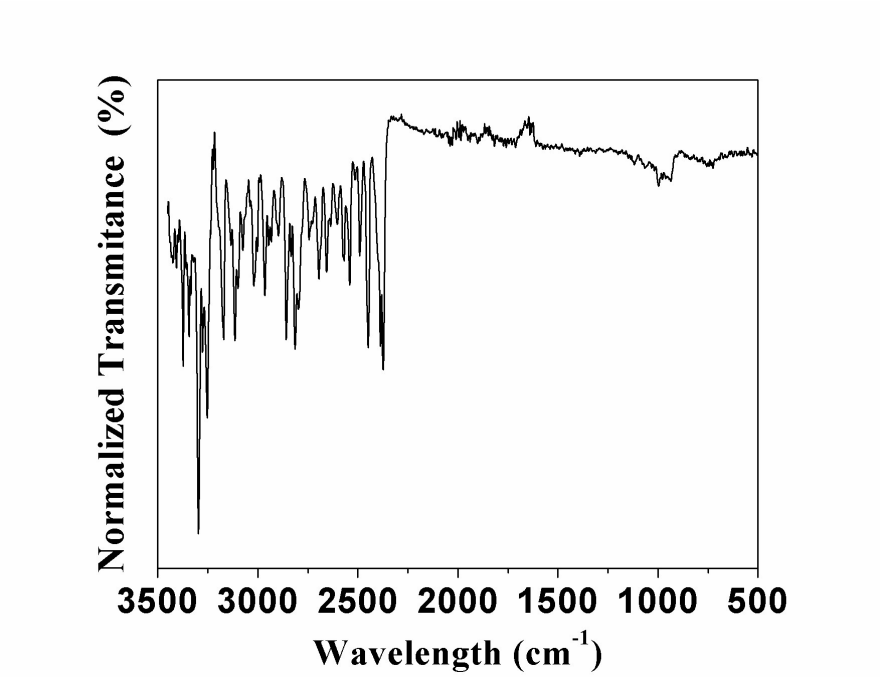

Figure S37. ATR FT-IR spectrum of BOSCHIBA **4a**.

1.10 High resolution and mass spectra of ***Lig1, Lig2, Lig3, 1a-4a****.*

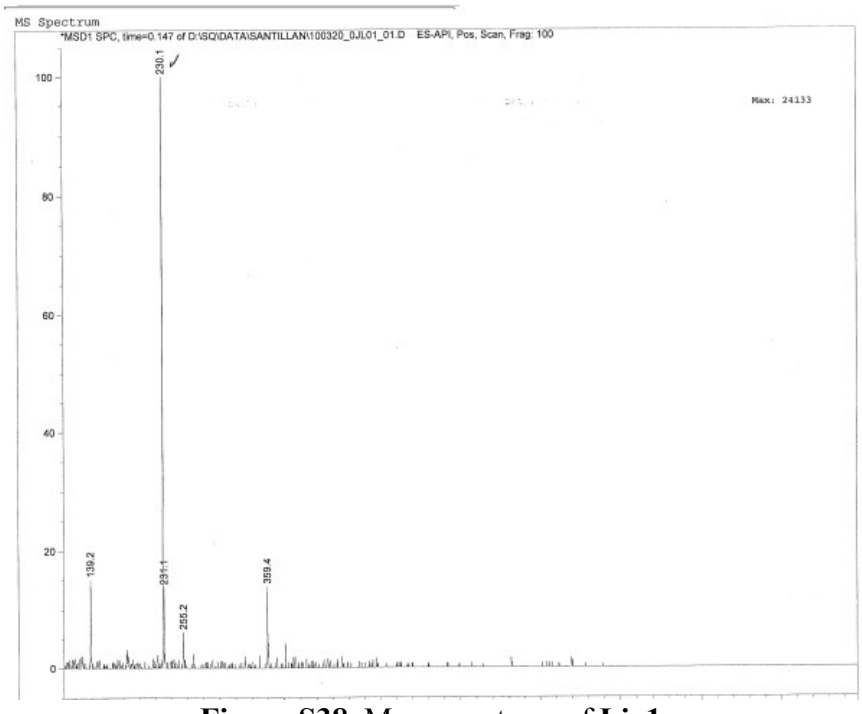

Figure S38. Mass spectrum of **Lig1.**

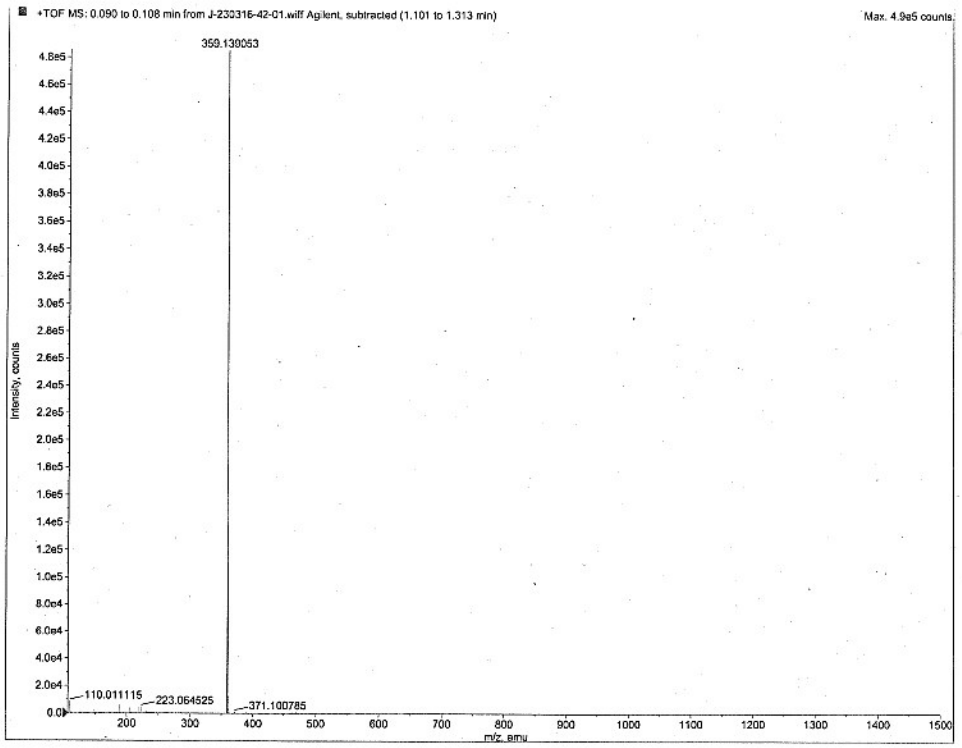

Figure S39. High resolution mass spectrum of **Lig2.**

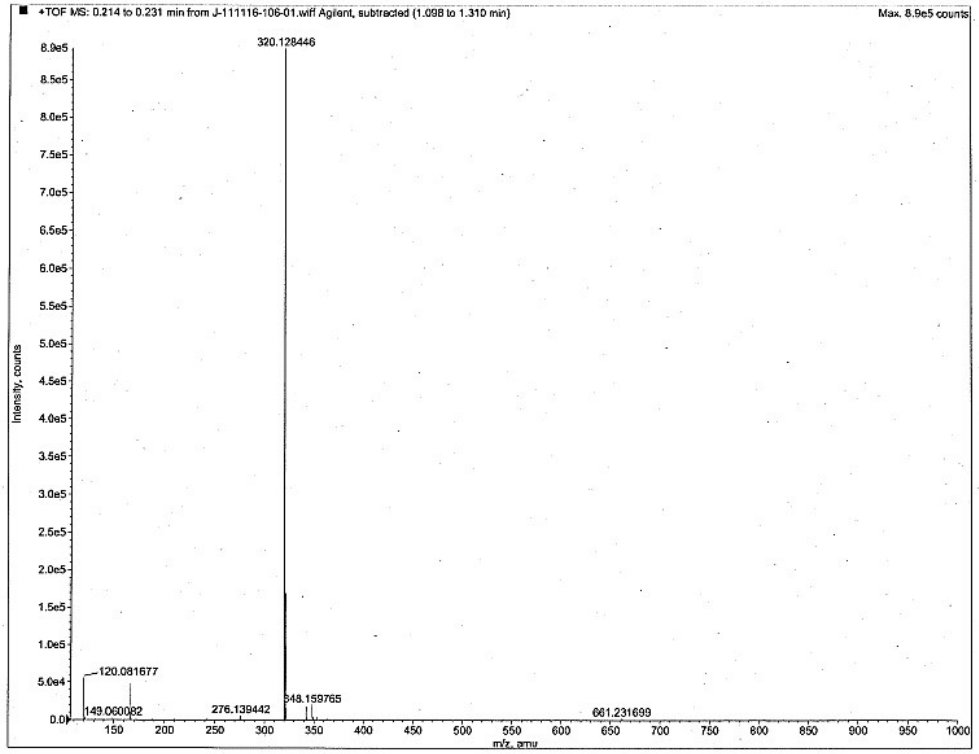

Figure S40. High resolution mass spectrum of **Lig3.**

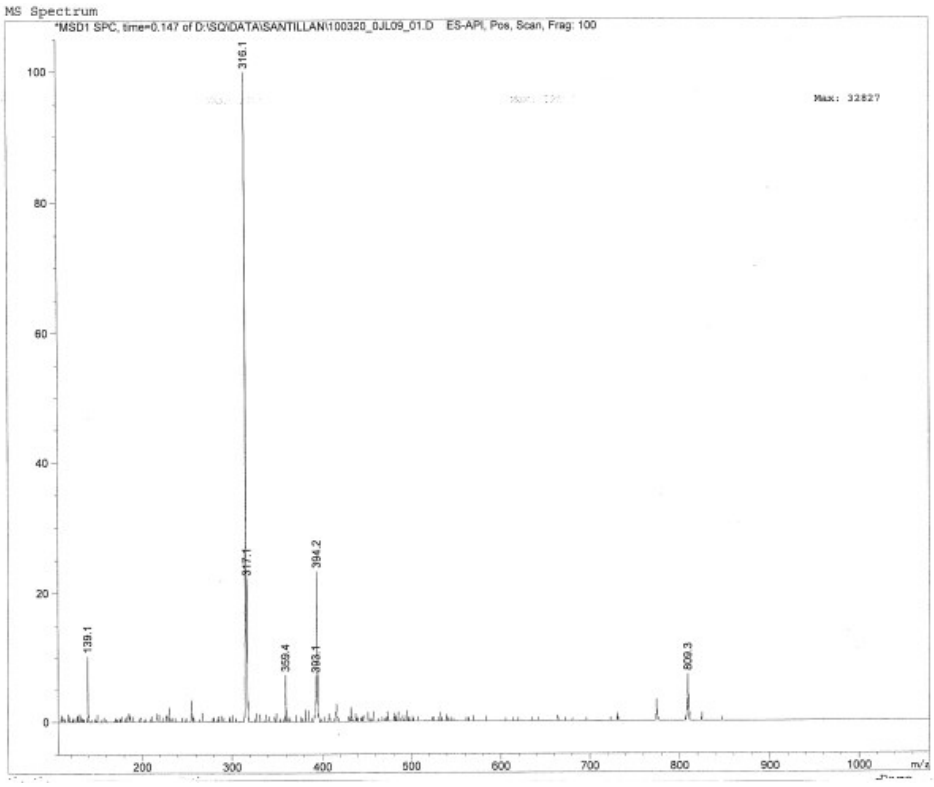

Figure S41. Mass spectrum of **1a.**

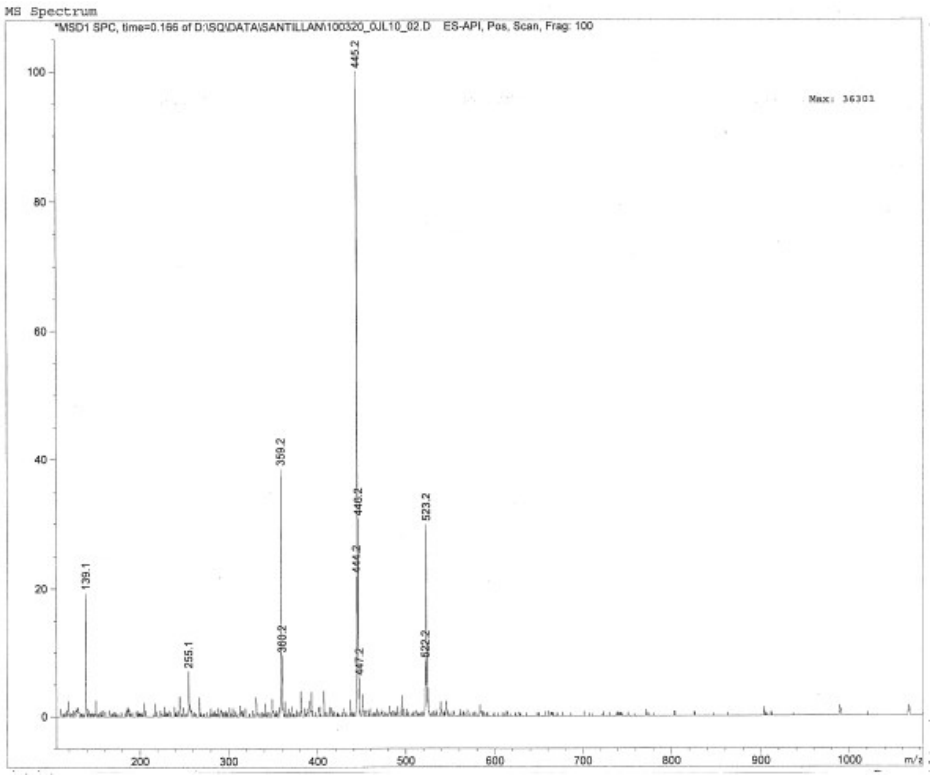

Figure S42. Mass spectrum of **2a**.

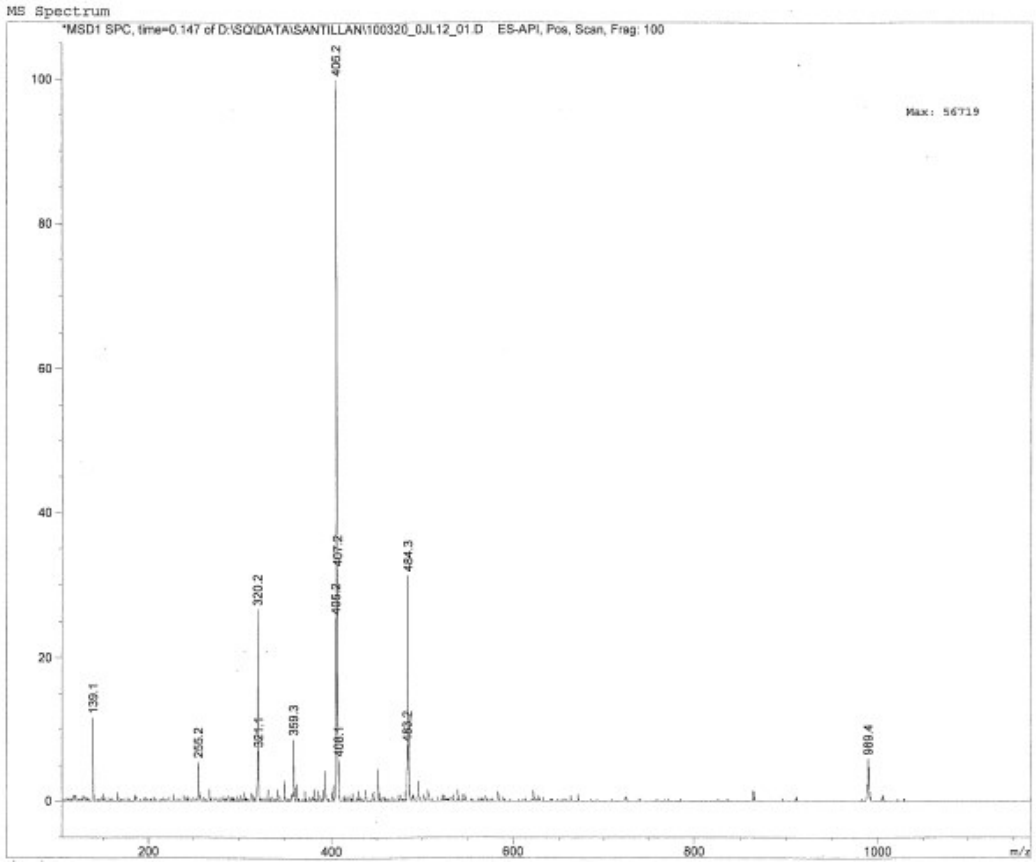

Figure S43. Mass spectrum of **3a.**

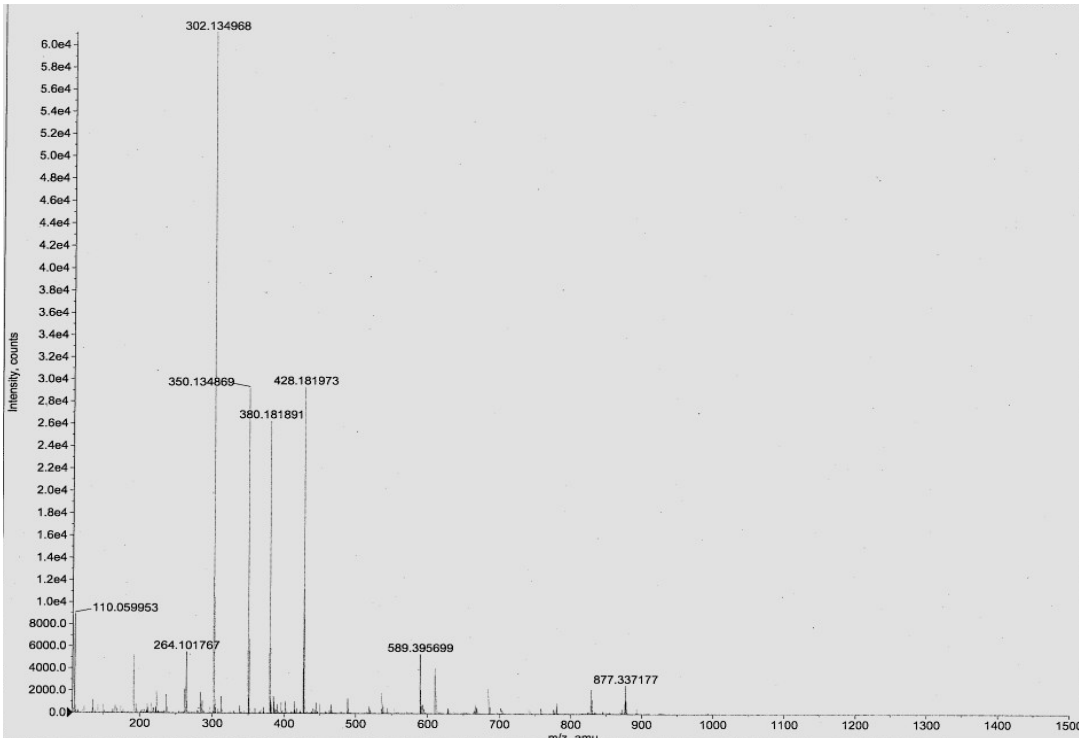

Figure S44. High resolution mass spectrum of BOSCHIBA **4a.**

*1.11 UV absorption spectra of **1a-4a**.*

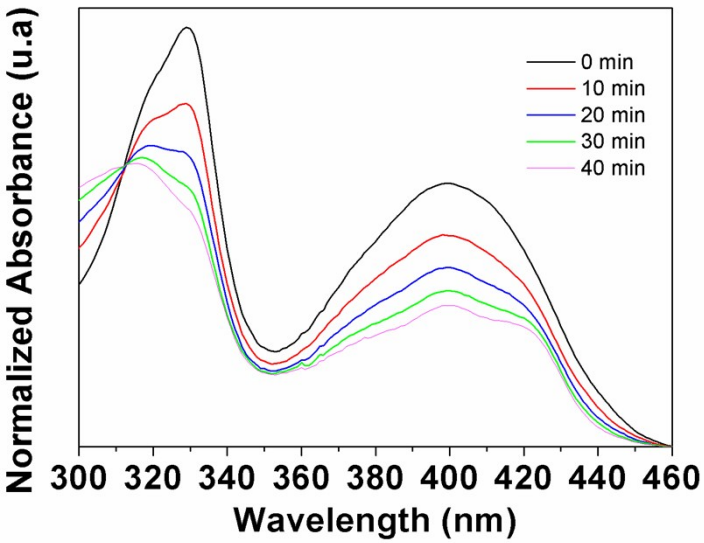

Figure S45. Photostability of **1a** (8.0 M) in chloroform under UV light irradiation (365 nm).

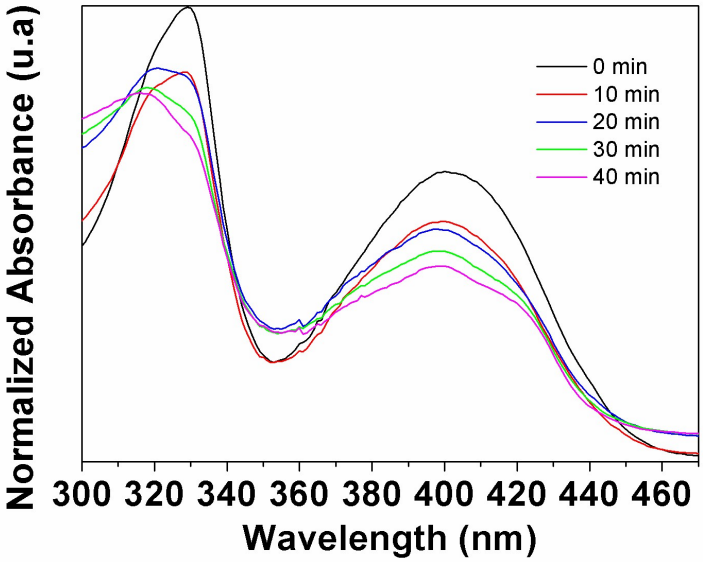

Figure S46. Photostability of **2a** (8.0 M) in chloroform under UV light irradiation (365 nm).

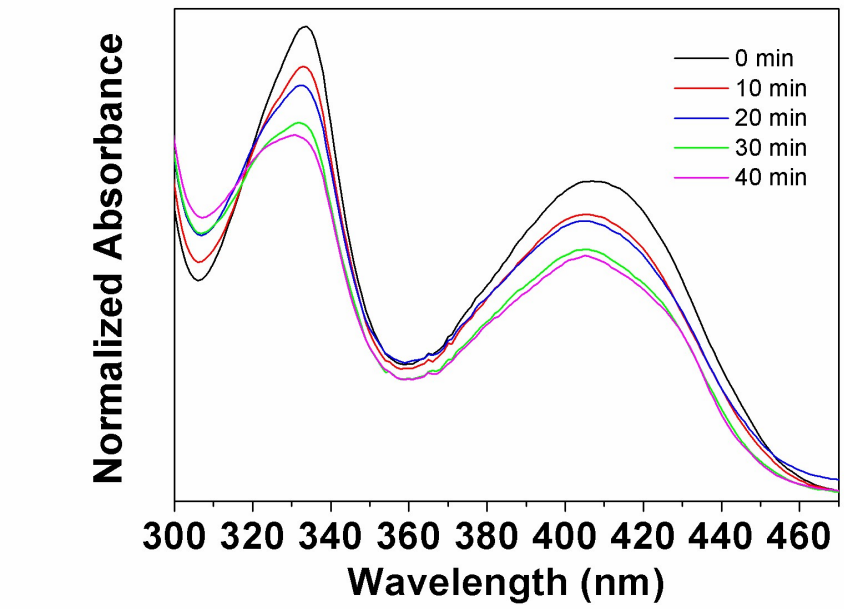

Figure S47. Photostability of **3a** (8.0 M) in chloroform under UV light irradiation (365 nm).

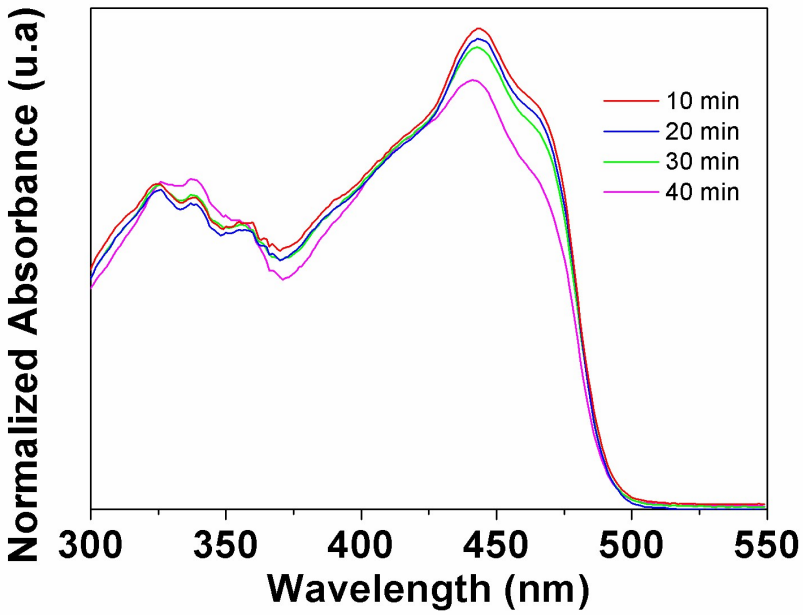

Figure S48. Photostability of **4a** (8.0 M) in chloroform under UV light irradiation (365 nm).