Supporting Information

Metal-Free Alkyne Annulation Enabling π-Extension of Boron-Doped Polycyclic Aromatic Hydrocarbons

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1. Materials and Methods

General considerations. Where indicated, glovebox synthetic manipulations were carried out in an atmosphere of dry, O_2-free N_2 in an MBraun glovebox using oven-dried glassware.1-hydroxy-2-phenyl-1-boraphenalene[1], 1,6-dihydroxy-2,7-diphenyl-1,6-diborapyrene[1] and 1-ethynylnaphthalene[2] were prepared according to literatures reports. Chlorobenzene and 1,2-dichlorobenzene were obtained from Sigma-Aldrich and dried over 4 Å molecular sieves before use. Deuterated solvents were obtained from commercial sources and used without further purification. HPLC hexane was obtained from Sigma Aldrich and used without further purification. All other solvents for spectroscopic measurements were spectroscopic grade and used without further purification. All other reagents and solvents were obtained from commercial sources and used without further purification.

UV-Vis absorption spectra were recorded on a JASCO V-670 spectrophotometer.

Fluorescence spectra were recorded on a HITACHI F-4500 fluorometer. Absolute fluorescence quantum yields were determined on a Hamamatsu PL Quantum Yield Measurement System C9920-02.

NMR spectra were recorded on a Bruker AVIIIHD 400 MHz FT-NMR or a Bruker AVIIIHD 500 MHz FT-NMR spectrometer. Chemical shifts are listed in parts per million and are given relative to $SiMe_4$ and referenced to a residual solvent signal (^1H, ^{13}C) or relative to an external standard (^{11}B: 15% $(Et_2O)BF_3$; ^{19}F: 15% $(Et_2O)BF_3$). Coupling constants (*J*) are quoted in Hertz (Hz). In some cases ^{11}B signals for boron-containing compounds could not be observed due to broadening and/or poor solubility.

Solid-state NMR experiments were carried out at ^{13}C and ^1H frequencies of 100.63 MHz and 400.13 MHz, respectively, on a Bruker Avance III spectrometer with a 2.5 mm probe and a magic angle spinning frequency of 20 kHz. ^{13}C chemical shifts were externally referenced to neat tetramethylsilane (TMS) with adamantane as the secondary standard, assigning the more deshielded peak to 38.48 ppm. For the $^{13}C\{^1H\}$ cross-polarization magic angle spinning (CPMAS) experiment, a contact time of 2 ms was used. The ^{13}C nutation frequency was set to 50 kHz, and the ^1H frequency was linearly ramped through the Hartmann-Hahn matching condition.

High resolution mass spectrometry experiments were performed on a Bruker Daltonic Autoflex Speed or Bruker ultrafleXtreme instrument.

High resolution mass spectrometry experiments were performed on a Bruker Daltonic Autoflex

Speed or Bruker ultrafleXtreme instrument.

Cyclic voltammetry experiments were performed using a commercial electrochemical analyzer (CHI621E, CH Instrument, USA) with a three-electrode single-compartment cell. The supporting electrolyte tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) was purchased from Combiblock and used without further purification. The measurements were recorded using ferrocene (Fc) as an internal standard for the calibration of the potential. An Ag/AgCl reference electrode was used. A Pt disc and a Pt wire were used as working auxiliary electrodes, respectively.

Single crystal X-ray diffraction data were recorded at 100 K on a Bruker D8 Venture SC-XRD with a Photon Ⅲ C28 detector and multi-layered mirror monochromated CuKα radiation. The structures were solved using Shelxt methods, expanded with Fourier techniques and refined with the Shelxt software package.[3] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation on geometrically idealized positions. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre under entries no. 2341631 - 2341636. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data.request/cif.

Chemical vapor deposition. Single crystals of **5a**, **5c**, **5d**, **5f**, and **5g** suitable for X-ray crystallographic analysis were vacuum-deposited in a TENDER (TF-12-95-900) vacuum deposition system at a pressure below 10^{-6} torr at 390 to 420 °C.

Computational details. All DFT calculations were performed using the B3LYP[4] functional enhanced by D3 dispersion with Becke-Johnson damping.[5] A double-z quality basis set, def2-SVP[6] is used for gas-phase geometry optimization and calculations of vibrational frequencies. Verification of local minima required all vibrational frequencies to be positive, while transition states were confirmed by the presence of only one imaginary frequency. A triple-z quality basis set, def2-TZVP[6] is used for more accurate electronic structural analysis, including HOMO-LUMO and NICS(0),[7] by performing a single-point calculation. Time-dependent DFT (TD-DFT) was performed using def2-TZVP in combination of conductor-like polarizable continuum model (CPCM)[8] model in o-$C_6H_4Cl_2$ solvent.

The enthalpy profile required further geometry optimization within the (CPCM) for CH_2Cl_2, using the def2-SVP basis set. More accurate electronic energy and Natural Population Analysis (NPA)[9] were obtained through a single-point calculation using the def2-TZVP basis set, alongside the CPCM solvation model in CH_2Cl_2.

Enthalpies were calculated using the equation:

$$H = E_{elec} + ZPE + H_{vib} + 4RT$$

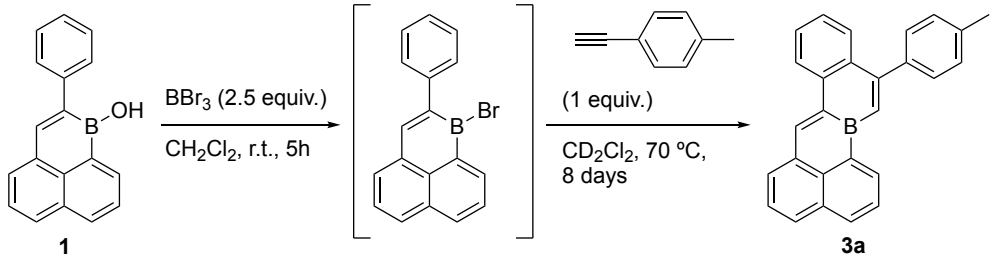
Here, E_{elec}, ZPE, and H_{vib} represent the electronic energy, zero-point vibrational energy, and enthalpic contribution of vibration, respectively. The term 4RT accounts for the translational and rotational thermal corrections, as well as the additional PV term, at T = 298.15 K.

2. Synthetic Procedures

[*CAUTION! Pressure increase will occur when heating solvents above their boiling points in sealed vessels, posing an explosion risk. Use appropriate glassware and safety precautions.*]

2.1 Representative NMR spectroscopic monitoring of the formation of 3a

In an inert atmosphere glovebox, 1-hydroxy-2-phenyl-1-boraphenalene (**1**, 0.020 g, 0.078 mmol, 1 equiv.) was dissolved in 3 mL dry dichloromethane in a 10 mL Schlenk tube equipped with a magnetic stir bar. BBr_3 (18 µL, 0.195 mmol, 2.5 equiv.) was added and the solution was stirred at room temperature for 5 h. The reaction mixture was concentrated in *vacuo*, dissolved in 0.5 mL CD_2Cl_2, and 4-ethynyltoluene (**2a**, 10 µL, 0.078 mmol, 1.0 equiv.) was added. The reaction mixture was transferred into a J-Young NMR tube and heated at 70 ℃ for 8 days (Scheme S1). The reaction was monitored by ^{1}H NMR spectroscopy before heating, and after heating (70 ℃) at 1 hour, 90 hours, and 8 days (Figure S1, S2). 1-(1-bromoethenyl)-4-methylbenzene was identified by comparison of ^{1}H NMR peaks to literature data.[10]



Scheme S1. Formation of **3a** by bromination of **1** followed by alkyne annulation.

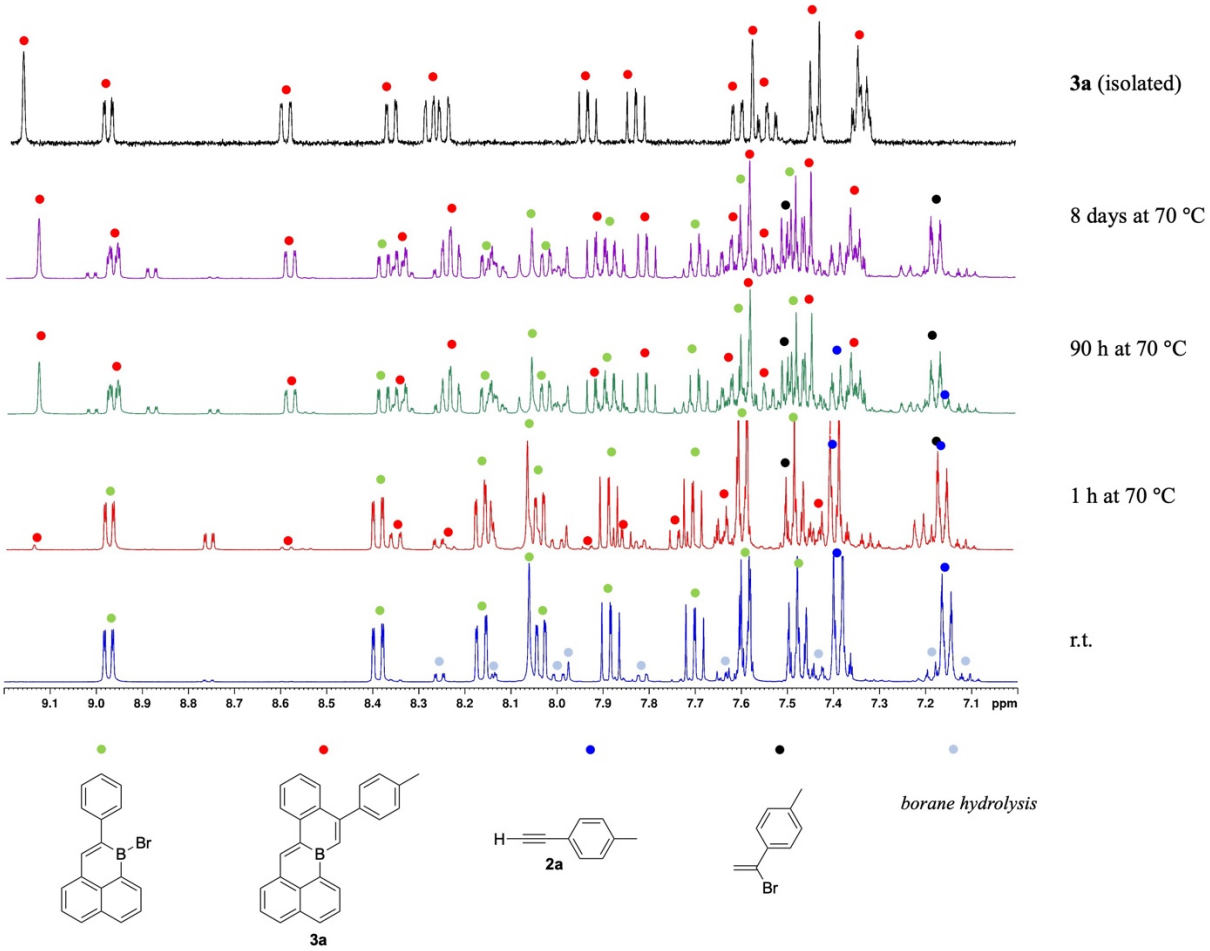


Figure S1: ^{1}H NMR spectra in CD_2Cl_2 (magnified aromatic region) of the reaction progress of the formation of **3a** with a comparison to an authentic sample of **3a**.

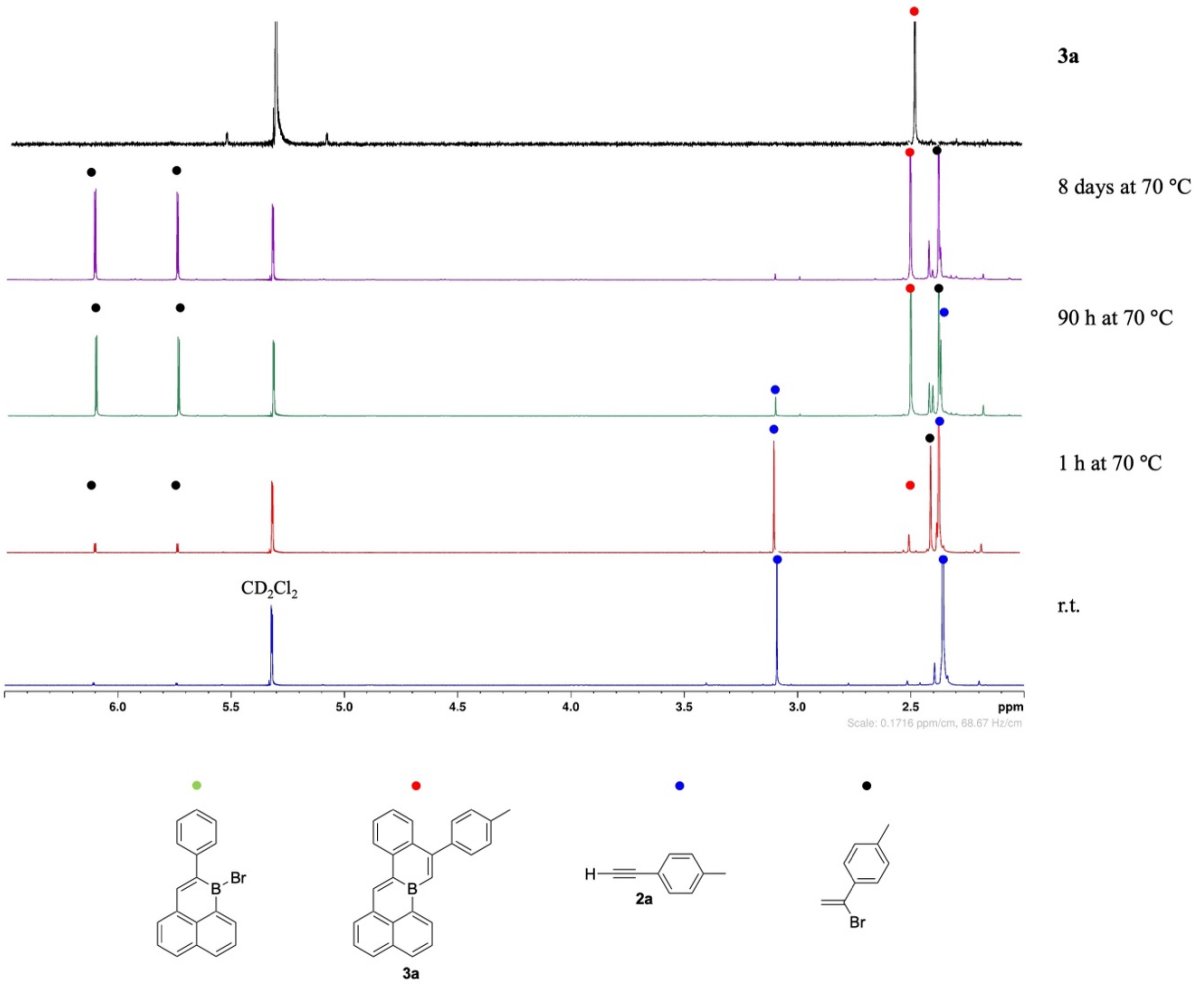
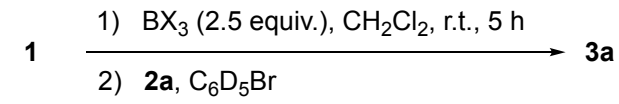


Figure S2: ^{1}H NMR spectra in CD_2Cl_2 (magnified aliphatic region) of the reaction progress of the formation of **3a** with a comparison to an authentic sample of **3a**.

Table S1. Reaction optimization studies of intermolecular alkyne C–H annulations of **1**.[a]



Entry	X	Equivalents **2a**	**3a** [h]
1 [b]	Br	1	45
2 [b]	Br	2	92
3	Cl	2	2
4 [c]	-	2	0
5 [d]	Br	1	20
6 [e]	Br	1	15
7 [f]	Br	1	5
8 [g]	Br	1	0

[a] All volatiles removed *in vacuo* following Step 1. Step 2 carried out at 120 ºC for 180 h unless otherwise noted. [b] Step 2 carried out for 60 h. [c] Step 1 omitted. [d] 1 equiv. of 2,6-di-tert-butyl-4-methylpyridine was added with **2a** in Step 2. [e] 1 equiv. of 2,6-dichloropyridine was added with **2a** in Step 2. [f] 1 equiv. of 2,6-dimethylpyridine was added with **2a** in Step 2. [g] 1 equiv. of 2,2,6,6-tetramethylpiperidine was added with **2a** in Step 2. [h] % conversion estimated by ^{1}H NMR spectroscopy.

2.2 Synthesis of 3a

In an inert atmosphere glovebox, 1-hydroxy-2-phenyl-1-boraphenalene (0.020 g, 0.078 mmol, 1 equiv.) was dissolved in 3 mL dry dichloromethane in a 10 mL Schlenk tube equipped with a magnetic stir bar. BBr_3 (18 µL, 0.195 mmol, 2.5 equiv.) was added and the solution was stirred at room temperature for 5 h. The solvent was removed in v*acuo*, then the reaction mixture was dissolved in 0.5 mL C_6D_5Br and 4-ethynyltoluene (20 µL, 0.156 mmol, 2.0 equiv.) was added. The reaction mixture was transferred into a J-Young NMR tube and heated at 120 ℃ for 60 h. The solvent was concentrated *in vacuo.* The residue was washed with n-hexane (1 mL) and then dissolved in DCM/hexane (1:1, 1 mL). The solution was filtered through celite and slow evaporation gave orange crystals which were collected, washed with *iso*-propanol, and dried *in vacuo* to give **3a** in 33% yield (9 mg, 0.025 mmol).

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 9.17 (s, 1H), 8.98 (dd, 1H, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.4 Hz), 8.59 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz), 8.36 (dd, 1H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.0 Hz), 8.29-8.24 (m, 2H),

7.94 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.8 Hz), 7.83 (dd, 1H, $^3J_{HH}$ = 8.00 Hz, $^3J_{HH}$ = 7.2 Hz); 7.61 (dd, 1H, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz), 7.57 (s, 1H), 7.56-7.52 (m, 1H), 7.45-7.42 (m, 2H), 7.36-7.32 (m, 3H), 2.47 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, TCE-d_2, 298 K): δ 161.7 (C), 144.4 (C), 141.4 (C), 139.7 (C), 139.4 (C, br, B-*C*), 137.0 (C), 135.9 (C), 135.8 (C), 135.2 (C, br, B-*C*), 135.0 (C), 134.5 (C), 133.6 (C), 133.1(C), 132.0 (C, br, B-*C*), 131.4 (C), 129.9 (C), 129.3 (C), 128.8 (C), 128.7 (C), 127.5 (C), 126.8 (C), 126.5 (C), 126.3 (C), 122.3 (C), 21.3 (C).

^{11}B NMR (128 MHz, C_6D_5Br, 298 K): not observed

HR-MS (MALDI-TOF, Negative mode) *m/z*: $[M]^+$ Calc'd for $C_{27}H_{19}B$ 354.1580; Found 354.1581.

CV (1.0 x 10^{-3} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298K): $E_{1/2\ red\ 1}$ = -1.62 V.

UV-Vis (8.5 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} (ε_{max}) = 365 nm (4500), 445 nm (8300).

Fluorescence (8.5 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} = 587 nm (Φ = 0.14).

2.3 Synthesis of 5a

In an inert atmosphere glovebox, 1,6-dihydroxy-2,7-diphenyl-1,6-diborapyrene (0.100 g, 0.2602 mmol, 1 equiv.) was dissolved in 3 mL dry dichloromethane in a 10 mL Schlenk bomb equipped with a magnetic stir bar. BBr_3 (124 µL, 1.3010 mol, 5 equiv.) was added and the solution was stirred at room temperature for 22 h. The solvent was then removed *in vacuo*, and a solution of 4-ethynyltoluene (132 µL, 1.0408 mmol, 4 equiv.) in 1 mL dry chlorobenzene was added. The Schlenk bomb was sealed and stirred at 120 °C for 60 h. Volatiles were removed *in vacuo* and the residue was suspended in acetone (10 mL), filtered through a glass frit, washed with acetone (3 x 10 mL), H_2O (3 x 10 mL), methanol (4 x 20 mL), DCM (2 x 10 mL) and n-hexane (2 x 10 mL). The compound was dissolved in $CHCl_3$ (100 mL), then passed through celite plug, solvent was removed under reduced pressure and **5a** was collected as black solid in 18 % yield (27 mg, 0.046 mmol).

^{1}H NMR (400 MHz, TCE-d2, 343 K): δ 8.61 (d, 2H, $^3J_{HH}$ = 7.2 Hz), 8.54 (s, 2H), 8.33 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 7.97 (d, 2H, $^3J_{HH}$ = 7.2 Hz), 7.54-7.44 (m, 8H), 7.36-7.28 (m, 8H), 2.51 (s, 6H).

Solid-state ^{13}C{^{1}H} CPMAS NMR (100.63 MHz, 298 K): δ 163.1, 144.2, 138.2, 131.6, 127.9, 122.0, 18.6.

^{11}B NMR (128 MHz, TCE-d_2, 298 K): not observed.

HR-MS (MALDI-TOF, positive mode) *m/z*: $[M]^+$ Calc'd for $C_{44}H_{30}B_2$ 580.2533; Found 580.2526.

CV (1.0 x 10^{-3} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K): $E_{1/2\ red\ 1}$ = -1.01 V. $E_{1/2\ red\ 2}$ = -1.33 V.

UV-Vis (8.5 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} (ε_{max}) = 429 nm (5700), 525 nm (17500), 561 nm (21800).

Fluorescence (8.5 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} = 608 nm (Φ = 0.03).

2.4 Synthesis of 5b

In an inert atmosphere glovebox, 1,6-dihydroxy-2,7-diphenyl-1,6-diborapyrene (0.100 g, 0.2602 mmol, 1 equiv.) was dissolved in 3 mL dry dichloromethane in a 10 mL Schlenk bomb equipped with a magnetic stir bar. BBr_3 (124 µL, 1.3010 mol, 5 equiv.) was added and the solution was stirred at room temperature for 22 h. The solvent was then removed *in vacuo*, and a solution of phenylacetylene (99 µL, 1.0408 mmol, 4 equiv.) in 1 mL dry chlorobenzene was added. The Schlenk bomb was sealed and stirred at 120 ℃ for 60 h. Volatiles were removed *in vacuo* and the residue was suspended in acetone (10 mL), filtered through a glass frit, and washed with acetone (3 x 10 mL), H_2O (3 x 10 mL), methanol (4 x 20 mL), DCM (2 x 10 mL) and n-hexane (2 x 10 mL). The compound was dissolved in $CHCl_3$ (100 mL), then passed through celite plug, solvent was removed under reduced pressure and **5b** was collected as black solid in 8 % yield (11 mg, 0.020 mmol).

^{1}H NMR (400 MHz, TCE-d_2, 343 K): δ 8.61 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 8.54 (s, 2H), 8.33 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 7.97 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 7.55-7.48 (m, 14H), 7.33-7.28 (m, 4H).

Solid-state ^{13}C{^{1}H} CPMAS NMR (100.63 MHz, 298 K): δ 161.1, 144.3, 139.7, 134.6, 128.7, 122.2.

^{11}B NMR (128 MHz, TCE-d_2, 298 K): not observed.

HR-MS (MALDI-TOF, positive mode) *m/z*: $[M]^+$ Calc'd for $C_{42}H_{26}B_2$ 552.2220; Found 552.2215.

CV (8.3 x 10^{-4} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K): $E_{1/2\ red\ 1}$ = -0.98 V. $E_{1/2\ red\ 2}$ = -1.29 V.

UV-Vis: (6.0 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} (ε_{max}) = 431 nm (2600), 521 nm (14400), 559 nm (19400).

Fluorescence: (6.0 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} = 603 nm (Φ = 0.01).

2.5 Synthesis of 5c

In an inert atmosphere glovebox, 1,6-dihydroxy-2,7-diphenyl-1,6-diborapyrene (100 mg, 0.2602mmol, 1 equiv.) was dissolved in 3 mL dry dichloromethane in a 10 mL Schlenk bomb equipped with a magnetic stir bar. BBr_3 (124 µL, 1.3010 mol, 5 equiv.) was added and the solution was stirred at room temperature for 22 hours. The solvent was then removed *in vacuo*, and a solution of 1-ethylnylnaphthalene (159 mg, 1.0408 mmol, 4 equiv.) in 1 mL dry chlorobenzene was

added. The Schlenk bomb was sealed and stirred at 120 °C for 60 hours. Volatiles were removed *in vacuo* and the residue was suspended in acetone (10 mL), filtered through a glass frit, and washed with acetone (3 x 10 mL), H_2O (3 x 10 mL), methanol (4 x 20 mL), DCM (2 x 10 mL) and n-hexane (2 x 10 mL).. The compound was dissolved in $CHCl_3$ (100 mL), then passed through celite plug, solvent was removed under reduced pressure and **5c** was collected as black solid in 24 % yield (40.2 mg, 0.036 mmol).

^{1}H NMR (400 MHz, TCE-d_2, 373 K): δ 8.60-8.58 (m, 4H), 8.35 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 8.00-7.98 (m, 6H), 7.84 (d, 2H, $^3J_{HH}$ = 8.4 Hz), 7.66 (t, 2H, $^3J_{HH}$ = 7.6 Hz), 7.59-7.52 (m, 4H), 7.47-7.38 (m, 6H), 7.17-7.09 (m, 4H).

Solid-state ^{13}C{^{1}H} CPMAS NMR (100.63 MHz, 298 K): δ 163.7, 140.6, 134.5, 131.0, 126.4.

^{11}B NMR (128 MHz, TCE-d_2, 298 K): not observed.

HR-MS (MALDI-TOF, negative mode) *m/z*: $[M]^-$ Calc'd for $C_{50}H_{30}B_2$ 652.2533; Found 652.2534.

CV (8.7 x 10^{-4} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K): $E_{1/2\ red\ 1}$ = -0.97 V. $E_{1/2\ red\ 2}$ = -1.29 V.

UV-Vis: (9.4 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} (ε_{max}) = 432 nm (3600), 519 nm (16300), 556 nm (21900).

Fluorescence: (9.4 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} = 607 nm (Φ = 0.01)

2.6 Synthesis of 5d

In an inert atmosphere glovebox, 1,6-dihydroxy-2,7-diphenyl-1,6-diborapyrene (0.100 g, 0.2602 mmol, 1 equiv.) was dissolved in 3 mL dry dichloromethane in a 10 mL Schlenk bomb equipped with a magnetic stir bar. BBr_3 (124 µL, 1.3010 mol, 5 equiv.) was added and the solution was stirred at room temperature for 22 h. The solvent was then removed *in vacuo*, and a solution of 1-ethynyl-2,4,6-trimethylbenzene (164 µL, 1.0408 mmol, 4 equiv.) in 1 mL dry chlorobenzene was added. The Schlenk bomb was sealed and stirred at 120 °C for 60 h. Volatiles were removed *in vacuo* and the residue was suspended in acetone (10 mL), filtered through a glass frit, and washed with acetone (3 x 10 mL), H_2O (3 x 10 mL), methanol (4 x 20 mL), DCM (2 x 10 mL) and n-hexane (2 x 10 mL). The compound was dissolved in $CHCl_3$ (100 mL), then passed through celite plug, solvent was removed under reduced pressure and **5d** was collected as black solid in 8 % yield (14 mg, 0.022 mmol).

^{1}H NMR (400 MHz, TCE-d2, 373 K): δ 8.58-8.55 (m, 4H), 8.32 (d, 2H, $^3J_{HH}$ =8.0 Hz), 7.97 (d, 2H, $^3J_{HH}$ =6.8 Hz), 7.48-7.44 (m, 2H), 7.25-7.22 (m, 4H), 7.12 (d, 2H, $^3J_{HH}$ =7.2 Hz), 7.05 (s, 4H), 2.45 (s, 6H), 2.17 (s, 12H).

Solid-state ^{13}C{^{1}H} CPMAS NMR (100.63 MHz, 298 K): δ 164.4, 145.1, 142.6, 139.6, 137.4, 135.6,

129.1, 122.7, 21.9, 20.9, 19.1.

^{11}B NMR (128 MHz, TCE-d_2, 298 K): not observed.

HR-MS (MALDI-TOF, negative mode) *m/z*: $[M]^-$ Calc'd for $C_{48}H_{38}B_2$ 636.3159; Found 636.3176.

CV (1.1 x 10^{-3} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K): $E_{1/2\ red\ 1}$ = -1.00 V. $E_{1/2\ red\ 2}$ = -1.49 V.

UV-Vis: (4.5 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} (ε_{max}) = 430 nm (3900), 515 nm (21100), 553 nm (29000).

Fluorescence: (4.5 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} = 610 nm (Φ = 0.01).

2.7 Synthesis of 5e

In an inert atmosphere glovebox, 1,6-dihydroxy-2,7-diphenyl-1,6-diborapyrene (0.100 g, 0.2602 mmol, 1 equiv.) was dissolved in 3 mL dry dichloromethane in a 10 mL Schlenk bomb equipped with a magnetic stir bar. BBr_3 (124 µL, 1.3010 mol, 5 equiv.) was added and the solution was stirred at room temperature for 22 h. The solvent was then removed *in vacuo*, and a solution of methyl 4-ethynylbenzoate (169 mg, 1.0408 mmol, 4 equiv.) in 1 mL dry chlorobenzene was added. The Schlenk bomb was sealed and stirred at 120 ℃ for 60 h. Volatiles were removed *in vacuo* and the residue was suspended in acetone (10 mL), filtered through a glass frit, and washed with acetone (3 x 10 mL), H_2O (3 x 10 mL), methanol (4 x 20 mL), DCM (2 x 10 mL) and n-hexane (2 x 10 mL). The compound was dissolved in $CHCl_3$ (100 mL), then passed through celite plug, solvent was removed under reduced pressure and **5e** was collected as black solid in 7 % yield (14 mg, 0.020 mmol).

^{1}H NMR (400 MHz, TCE-d_2, 343 K): δ 8.61-8.55 (m, 4H), 8.34 (d, 2H, $^3J_{HH}$ = 7.2 Hz), 8.20 (d, 4H, $^3J_{HH}$ = 6.4 Hz), 7.98 (d, 2H, $^3J_{HH}$ = 5.2 Hz), 7.62 (d, 4H, $^3J_{HH}$ = 6.8 Hz), 7.49 (br, 2H), 7.36-7.32 (m, 6H), 4.01 (s, 6H).

Solid-state ^{13}C{^{1}H} CPMAS NMR (100.63 MHz, 298 K): δ 167.5, 161.8, 148.0, 145.2, 139.8, 136.1, 133.5, 128.2, 122.7, 52.4.

^{11}B NMR (128 MHz, TCE-d_2, 298 K): not observed.

HR-MS (MALDI-TOF, negative mode) *m/z*: $[M]^-$ Calc'd for $C_{46}H_{30}B_2O_4$ 668.2330; Found 668.2339.

CV (9.0 x 10^{-4} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K): $E_{1/2\ red\ 1}$ = -0.95 V. $E_{1/2\ red\ 2}$ = -1.24 V.

UV-Vis: (6.0 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} (ε_{max}) = 433 nm (8500), 521 nm (23600), 558 nm (28800).

Fluorescence: (6.0 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} = 607 nm (Φ < 0.01).

2.7 Synthesis of 5f

In an inert atmosphere glovebox, 1,6-dihydroxy-2,7-diphenyl-1,6-diborapyrene (100 mg, 0.2602mmol, 1 equiv.) was dissolved in 3 mL dry dichloromethane in a 10mL Schlenk bomb equipped with a magnetic stir bar. BBr_3 (124 µL, 1.3010 mol, 5 equiv.) was added and the solution was stirred at room temperature for 22 hours. The solvent was then removed *in vacuo*, and a solution of 4-ethynylflourobenzene (125 mg, 1.0408 mmol, 4 equiv.) in 1 mL dry chlorobenzene was added. The Schlenk bomb was sealed and stirred at 120 ℃ for 60 hours. Volatiles were removed *in vacuo* and the residue was suspended in acetone (10 mL), filtered through a glass frit, and washed with acetone (3 x 10 mL), H_2O (3 x 10 mL), methanol (4 x 20 mL), DCM (2 x 10 mL) and n-hexane (2 x 10 mL). The compound was dissolved in $CHCl_3$ (100 mL), then passed through celite plug, solvent was removed under reduced pressure and **5f** was collected as black solid in 17 % yield (26.0 mg, 0.044 mmol).

^{1}H NMR (400 MHz, TCE-d_2, 343 K): δ 8.62 (d, 2H, $^3J_{HH}$ = 6.8 Hz), 8.55 (s, 2H), 8.34 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 7.98 (d, 2H, $^3J_{HH}$ = 6.8 Hz), 7.54-7.43 (m, 8H), 7.34-7.31 (m, 4H), 7.23 (t, 4H, $^3J_{HH}$ = 8.4 Hz).

Solid-state ^{13}C{^{1}H} CPMAS NMR (100.63 MHz, 298 K): δ 163.1, 140.8, 134.4, 130.2, 123.5, 116.1.

^{19}F NMR (376 MHz, TCE-d_2, 343 K): δ -113.8.

^{11}B NMR (128 MHz, TCE-d_2, 298 K): not observed.

HR-MS (MALDI-TOF, negative mode) m/z: Calc'd for $C_{42}H_{24}B_2F_2$ 588.2032; Found 588.2025.

CV (5.3 x 10^{-4} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K): $E_{1/2\ red\ 1}$ = -0.97 V. $E_{1/2\ red\ 2}$ = -1.26 V.

UV-Vis: (2.5 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} (ε_{max}) = 431 nm (5500), 520 nm (19400), 559 nm (25000).

Fluorescence: (2.5 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} = 616 nm (Φ < 0.01).

2.8 Synthesis of 5g

In an inert atmosphere glovebox, 1,6-dihydroxy-2,7-diphenyl-1,6-diborapyrene (0.100 g, 0.2602 mmol, 1 equiv.) was dissolved in 3 mL dry dichloromethane in a 10 mL Schlenk bomb equipped with a magnetic stir bar. BBr_3 (124 µL, 1.3010 mol, 5 equiv.) was added and the solution was stirred at room temperature for 22 h. The solvent was then removed *in vacuo*, and a solution of 3-ethynylthiophene (120 µL, 1.0408 mmol, 4 equiv.) in 1 mL dry chlorobenzene was added. The reaction mixture was degassed and stirred at 120 ℃ for 60 h. Volatiles were removed *in vacuo* and the residue was suspended in acetone (10 mL), filtered through a glass frit, and washed with acetone

acetone (3 x 10 mL), H_2O (3 x 10 mL), methanol (4 x 20 mL), DCM (2 x 10 mL) and n-hexane (2 x 10 mL). The compound was dissolved in $CHCl_3$ (100 mL), then passed through celite plug, solvent was removed under reduced pressure and **5g** was collected as black solid in 18 % yield (27 mg, 0.046 mmol).

^{1}H NMR (400 MHz, TCE-d2, 343 K): δ 8.63 (d, 2H, $^3J_{HH}$ = 6.8 Hz), 8.54 (s, 2H), 8.34 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 7.98 (d, 2H, $^3J_{HH}$ = 6.8 Hz), 7.69 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 7.55-7.51 (m, 6H), 7.43 (s, 2H), 7.37-7.33 (m, 4H).

Solid-state ^{13}C{^{1}H} CPMAS NMR (100.63 MHz, 298 K): δ 155.5, 146.8, 140.1, 135.1, 132.1, 126.2, 122.4.

^{11}B NMR (128 MHz, TCE-d_2, 298 K): not observed.

HR-MS (MALDI-TOF, negative mode) *m/z*: $[M]^+$ Calc'd for $C_{38}H_{22}B_2S_2$ 564.1349; Found 564.1332.

CV (1.2 x 10^{-3} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K): $E_{1/2\ red\ 1}$ = -0.99 V. $E_{1/2\ red\ 2}$ = -1.30 V.

UV-Vis: (6.0 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} (ε_{max}) = 430 nm (8700), 527 nm (28700), 563 nm (36200).

Fluorescence: (6.0 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} = 616 nm (Φ < 0.01).

2.9 Synthesis of 5h

In an inert atmosphere glovebox, 1,6-dihydroxy-2,7-diphenyl-1,6-diborapyrene (0.100 g, 0.2602 mmol, 1 equiv.) was dissolved in 3 mL dry dichloromethane in a 10 mL Schlenk bomb equipped with a magnetic stir bar. BBr_3 (124 µL, 1.3010 mol, 5 equiv.) was added and the solution was stirred at room temperature for 22 h. The solvent was then removed *in vacuo*, and a solution of 1-hexyne (120 µL, 1.0408 mmol, 4 equiv.) in 1 mL dry chlorobenzene was added. The Schlenk bomb was sealed and stirred at 120 ℃ for 60 h. Volatiles were removed *in vacuo* and the residue was suspended in DMSO (10 mL), filtered through a glass frit, and washed with DMSO (3 x 10 mL), H_2O (3 x 10 mL), methanol (4 x 20 mL), and n-hexane (2 x 10 mL). The compound was dissolved in $CHCl_3$ (100 mL), then passed through celite plug, solvent was removed under reduced pressure and **5h** was collected as black solid in 3 % yield (4.2 mg, 0.008 mmol).

^{1}H NMR (500 MHz, TCE-d2, 323 K): δ 8.61 (d, 2H, $^3J_{HH}$ =7.0 Hz), 8.46 (s, 2H), 8.30 (d, 2H, $^3J_{HH}$ =7.5 Hz,), 7.94 (d, 2H, $^3J_{HH}$ =7.0 Hz), 7.85 (d, 2H, $^3J_{HH}$ =8.0 Hz), 7.49-7.41 (m, 4H), 7.30 (s, 2H), 3.01 (t, 4H, $^3J_{HH}$ =7.75 Hz), 1.86-1.79 (m, 4H), 1.61-1.55 (m, 4H), 1.06 (t, 6H, $^3J_{HH}$ =7.2 Hz).

Solid-state ^{13}C{^{1}H} CPMAS NMR (100.63 MHz, 298 K): δ 162.3, 145.2, 141.4, 138.7, 136.4, 134.2,

129.9, 126.5, 38.7, 34.7, 25.6, 16.0.

^{11}B NMR (128 MHz, TCE-d_2, 298 K): not observed.

HR-MS (MALDI-TOF, negative mode) *m/z*: $[M]^-$ Calc'd for $C_{38}H_{34}B_2$ 512.2846; Found 512.2857.

CV (8.2 x 10^{-4} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K): $E_{1/2\ red\ 1}$ = -1.05 V. $E_{1/2\ red\ 2}$ = -1.36 V.

UV-Vis: (4.4 x 10^{-5} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} (ε_{max}) = 425 nm (4700), 510 nm (19400), 559 nm (25400).

Fluorescence: (4.4 x 10^{-5} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} = 604 nm (Φ < 0.01).

2.10 Synthesis of 5i

In an inert atmosphere glovebox, 1,6-dihydroxy-2,7-diphenyl-1,6-diborapyrene (0.100 g, 0.2602 mmol, 1 equiv.) was dissolved in 3 mL dry dichloromethane in a 10 mL Schlenk bomb equipped with a magnetic stir bar. BBr_3 (124 µL, 1.3010 mol, 5 equiv.) was added and the solution was stirred at room temperature for 22 h. The solvent was then removed *in vacuo*, and a solution of 1-octyne (169 µL, 1.0408 mmol, 4 equiv.) in 1 mL dry chlorobenzene was added. The Schlenk bomb was sealed and stirred at 120 °C for 60 h. Volatiles were removed *in vacuo* and the residue was suspended in DMSO (10 mL), filtered through a glass frit, and washed with DMSO (3 x 10 mL), H_2O (3 x 10 mL), methanol (4 x 20 mL), and n-hexane (2 x 10 mL). The compound was dissolved in $CHCl_3$ (100 mL), then passed through celite plug, solvent was removed under reduced pressure and **5i** was collected as black solid in 3 % yield (4.6 mg, 0.008 mmol).

^{1}H NMR (500 MHz, TCE-d2, 298 K): δ 8.61 (d, 2H, $^3J_{HH}$ =7.0 Hz), 8.46 (s, 2H), 8.29 (dd, 2H, $^3J_{HH}$ =8.0 Hz, $^4J_{HH}$ =1.5 Hz), 7.94 (d, 2H, $^3J_{HH}$ =7.5 Hz), 7.83 (d, 2H, $^3J_{HH}$ =8.0 Hz), 7.49-7.41 (m, 4H), 7.28 (s, 2H), 2.98 (t, 4H, $^3J_{HH}$ =7.75 Hz), 1.83-1.77 (m, 4H), 1.54-1.50 (m, 4H), 1.43-1.35 (m, 8H), 0.94 (t, 6H, $^3J_{HH}$ =7.0 Hz).

Solid-state ^{13}C{^{1}H} CPMAS NMR (100.63 MHz, 298 K): δ 159.7, 144.5, 139.8, 136.3, 131.5, 126.4, 122.8, 44.2, 35.3, 26.3, 22.1, 17.2.

^{11}B NMR (128 MHz, TCE-d_2, 298 K): not observed.

HR-MS (MALDI-TOF, negative mode) *m/z*: $[M]^-$ Calc'd for $C_{42}H_{42}B_2$ 568.3472; Found 568.3468.

CV (7.0 x 10^{-4} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K): $E_{1/2\ red\ 1}$ = -1.08 V. $E_{1/2\ red\ 2}$ = -1.39 V.

UV-Vis: (7.8 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} (ε_{max}) = 426 nm (6500), 509 nm (23700), 546 nm (29400).

Fluorescence: (7.8 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} = 601 nm (Φ < 0.01).

2.11 Synthesis of 5j

In an inert atmosphere glovebox, 1,6-dihydroxy-2,7-diphenyl-1,6-diborapyrene (100 mg, 0.2602mmol, 1 equiv.) was dissolved in 3 mL dry dichloromethane in a 10 mL Schlenk bomb equipped with a magnetic stir bar. BBr_3 (124 µL, 1.3010 mol, 5 equiv.) was added and the solution was stirred at room temperature for 22 hours. The solvent was then removed *in vacuo*, and a solution of 1-ethynyl-1-cyclohexene (135 µL, 1.0546 mmol, 4 equiv.) in 1 mL dry chlorobenzene was added. The Schlenk bomb was sealed and stirred at 120 ℃ for 60 hours. Volatiles were removed *in vacuo* and the residue was suspended in DMSO (10 mL), filtered through a glass frit, and washed with DMSO (3 x 10 mL), H_2O (3 x 10 mL), methanol (4 x 20 mL), and n-hexane (2 x 10 mL). The compound was dissolved in $CHCl_3$ (100 mL), then passed through celite plug, solvent was removed under reduced pressure and **5j** was collected as black solid in 3 % yield (4.2 mg, 0.007 mmol).

^{1}H NMR (400 MHz, TCE-d_2, 343 K): δ 8.62 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 8.47 (s, 2H), 8.27 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 7.93 (d, 2H, $^3J_{HH}$ = 4.0 Hz), 7.75 (d, 2H, $^3J_{HH}$ = 8.0 Hz), 7.45 (t, 2H, $^3J_{HH}$ = 8.0 Hz), 7.38 (t, 2H, $^3J_{HH}$ = 8.0 Hz), 7.18 (s, 2H), 5.86 (s, 2H), 2.42 (brs, 4H), 2.32 (brs, 4H), 1.90-1.85 (m, 8H).

Solid-state ^{13}C{^{1}H} CPMAS NMR (100.63 MHz, 298 K): δ 173.5, 151.6, 139.3, 134.3, 130.4, 121.2, 43.9, 26.5.

^{11}B NMR (128 MHz, TCE-d_2, 343 K): not observed.

HR-MS (MALDI-TOF, negative mode) *m/z*: $[M]^-$ Calc'd for $C_{42}H_{34}B_2$ 560.2846; Found 560.2831.

CV (5.0 x 10^{-4} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K): $E_{1/2\ red\ 1}$ = -1.02 V. $E_{1/2\ red\ 2}$ = -1.33 V.

UV-Vis: (4.2 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} (ε_{max}) = 427 nm (6400), 516 nm (16600), 551 nm (20300).

Fluorescence: (4.2 x 10^{-6} M in *o*-$C_6H_4Cl_2$, 298 K): λ_{max} = 607 nm (Φ < 0.01).

3. NMR Spectra

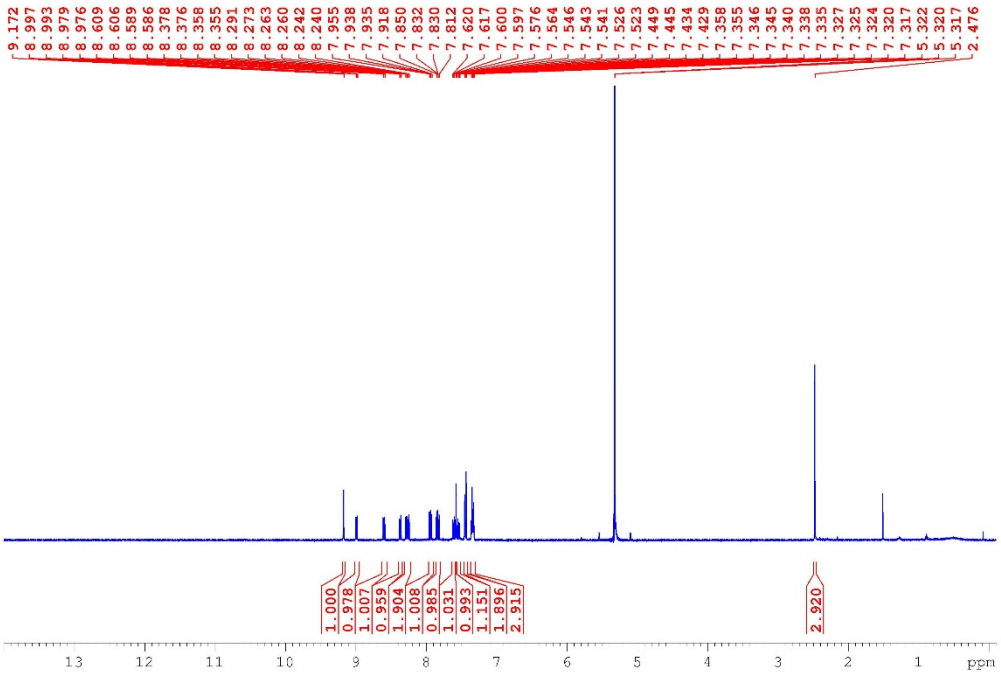


Figure S3: ^{1}H NMR Spectrum of compound **3a** (400 MHz, CD_2Cl_2, 298 K).

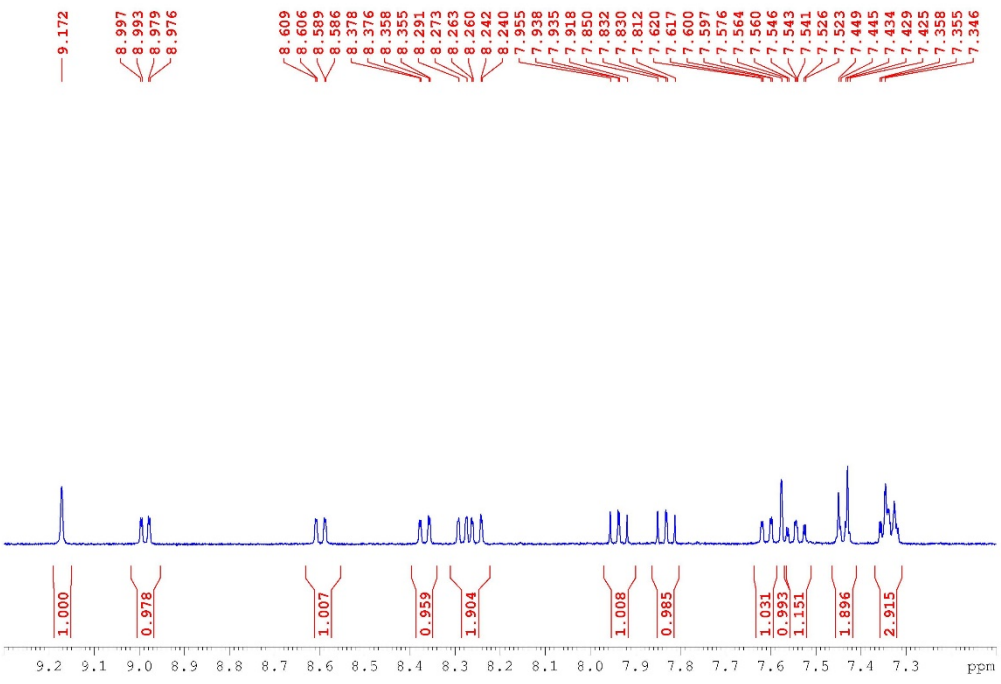


Figure S4: Magnified aromatic region of the ^{1}H NMR spectrum of compound **3a** (400 MHz, CD_2Cl_2, 298 K)

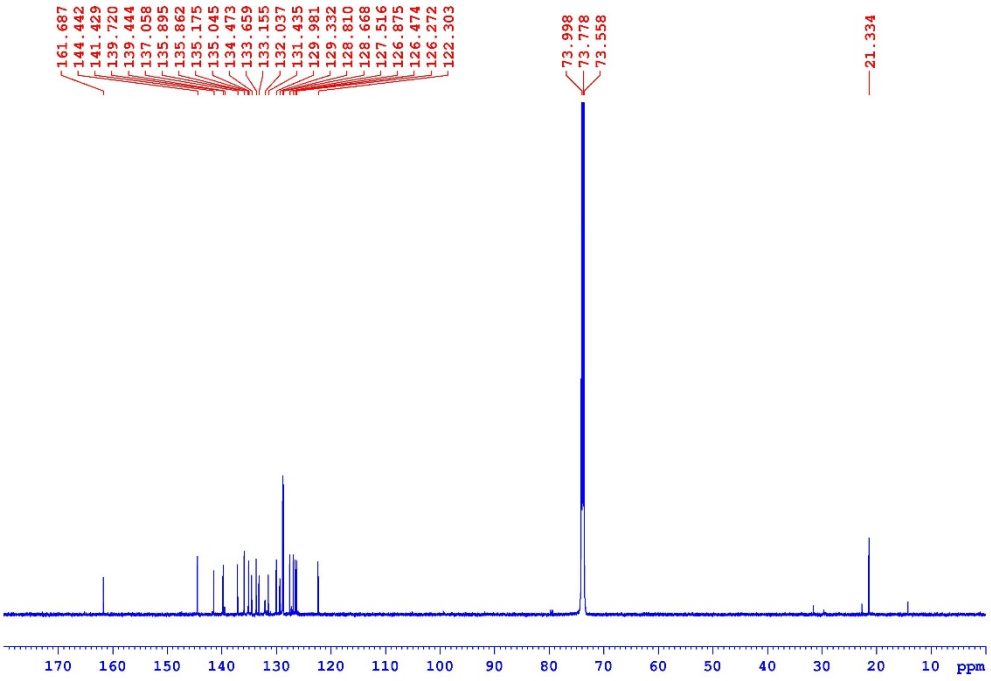


Figure S5: ^{13}C NMR spectrum of compound **3a** (125 MHz, TCE-d2, 298 K).

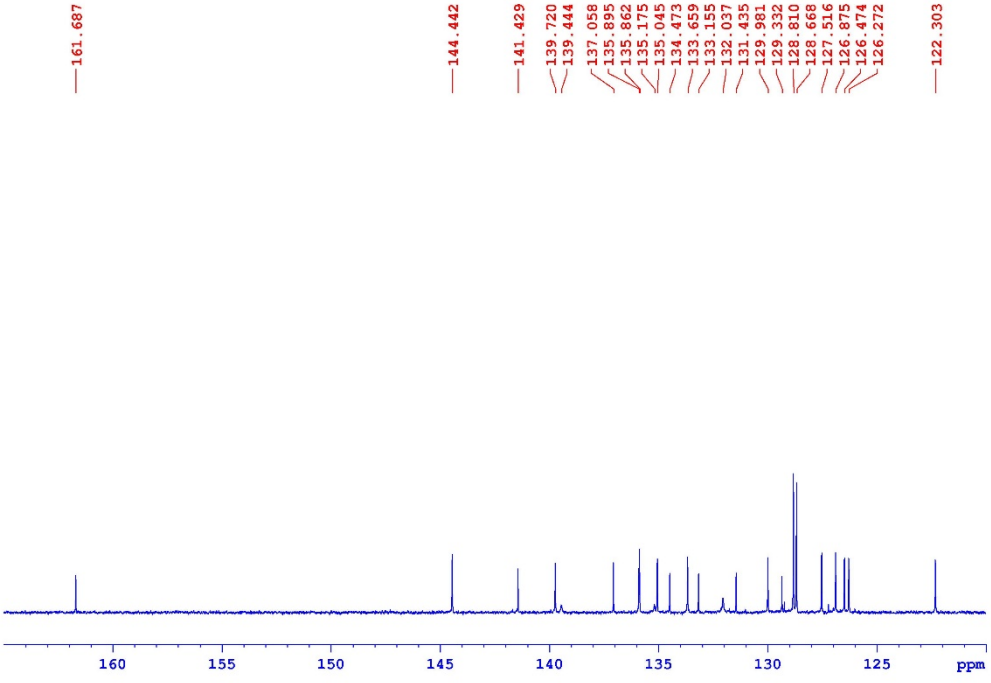


Figure S6: Magnified aromatic region of the ^{13}C NMR spectrum of compound **3a** (125 MHz, TCE-d2, 298 K).

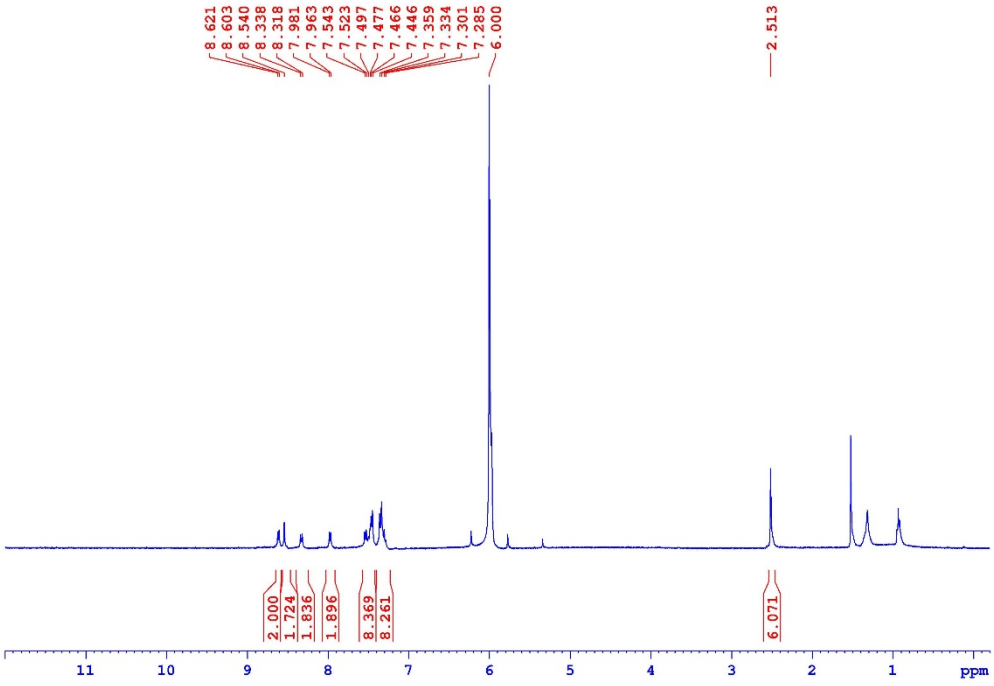


Figure S7: ^{1}H NMR Spectrum of compound **5a** (400 MHz, TCE-d2, 343 K).

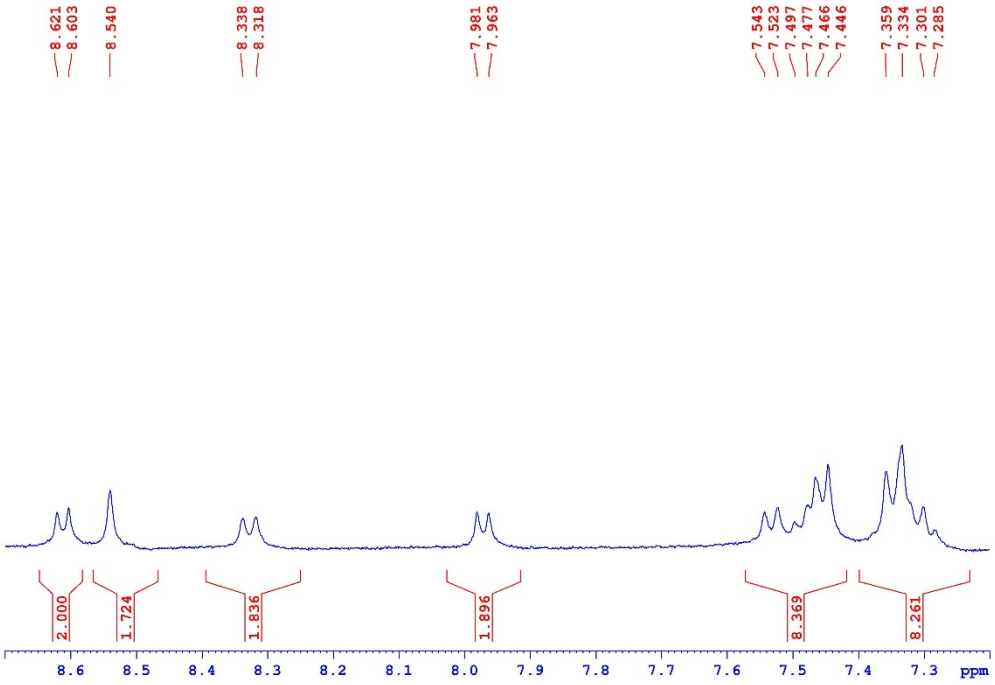


Figure S8: Magnified aromatic region of the ^{1}H NMR spectrum of compound **5a** (400 MHz, TCE-d2, 343 K).

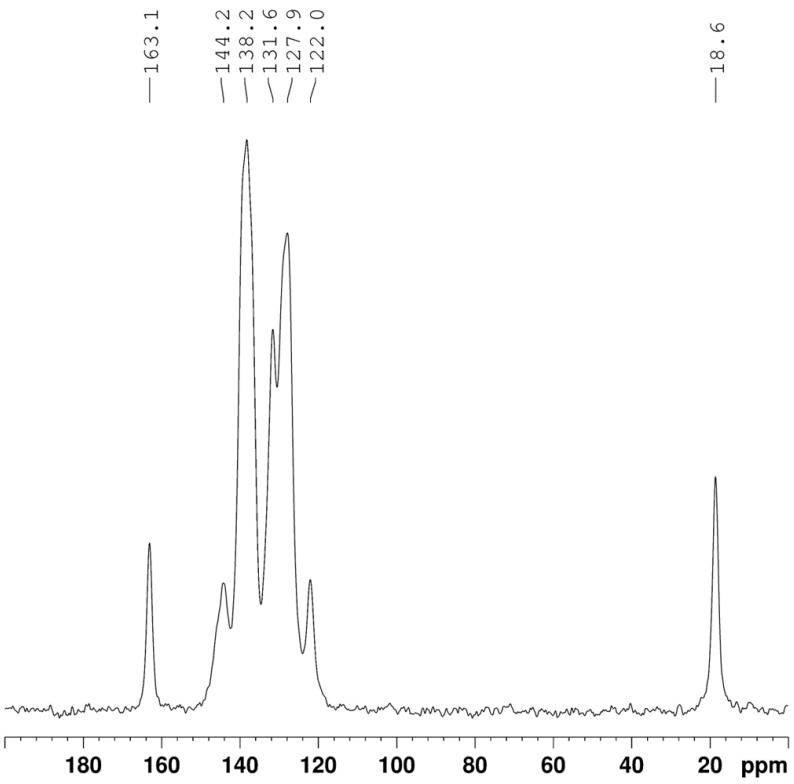


Figure S9: Solid-state $^{13}C\{^{1}H\}$ CPMAS NMR spectrum of compound **5a** (100.63 MHz, 298 K).

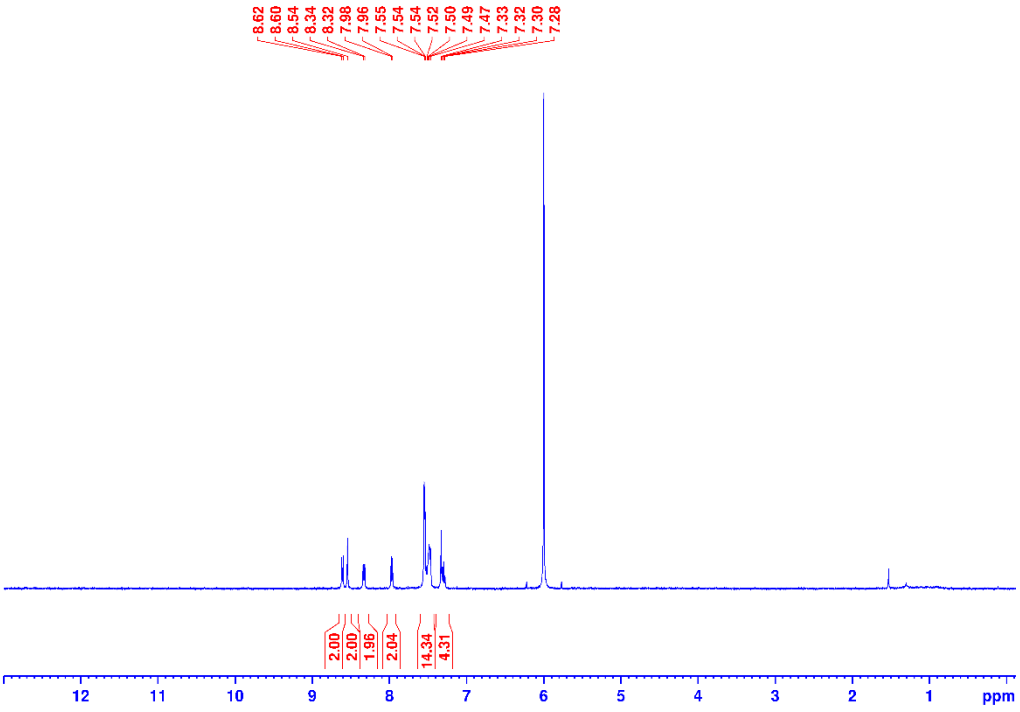


Figure S10: ^{1}H NMR Spectrum of compound **5b** (400 MHz, TCE-d2, 343 K).

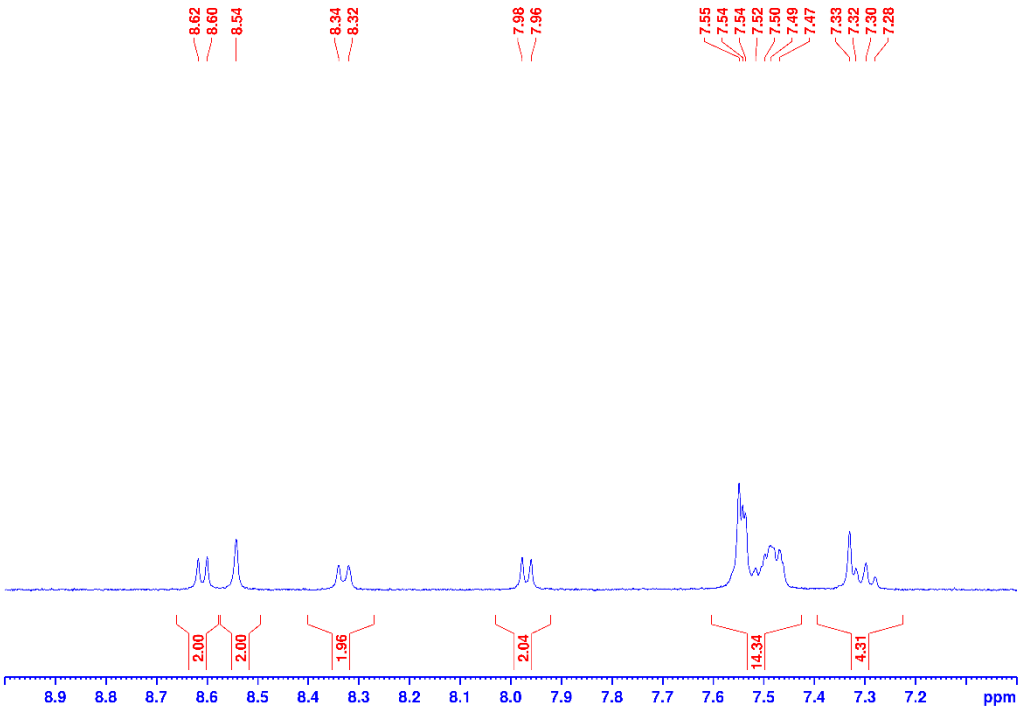


Figure S11: Magnified aromatic region of the ^{1}H NMR spectrum of compound **5b** (400 MHz, TCE-d2, 343 K).

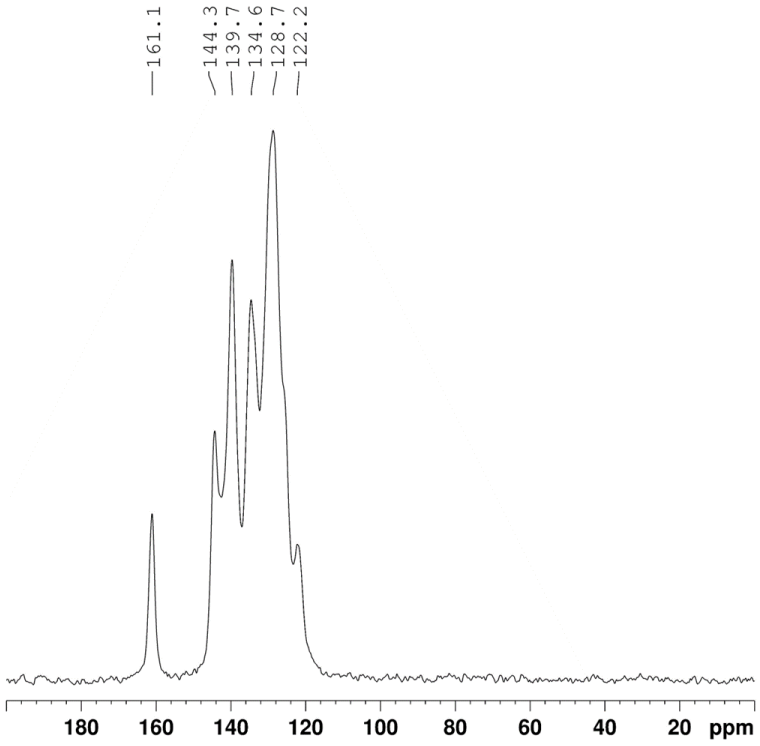


Figure S12: Solid-state ^{13}C{^{1}H} CPMAS NMR spectrum of compound **5b** (100.63 MHz, 298 K).

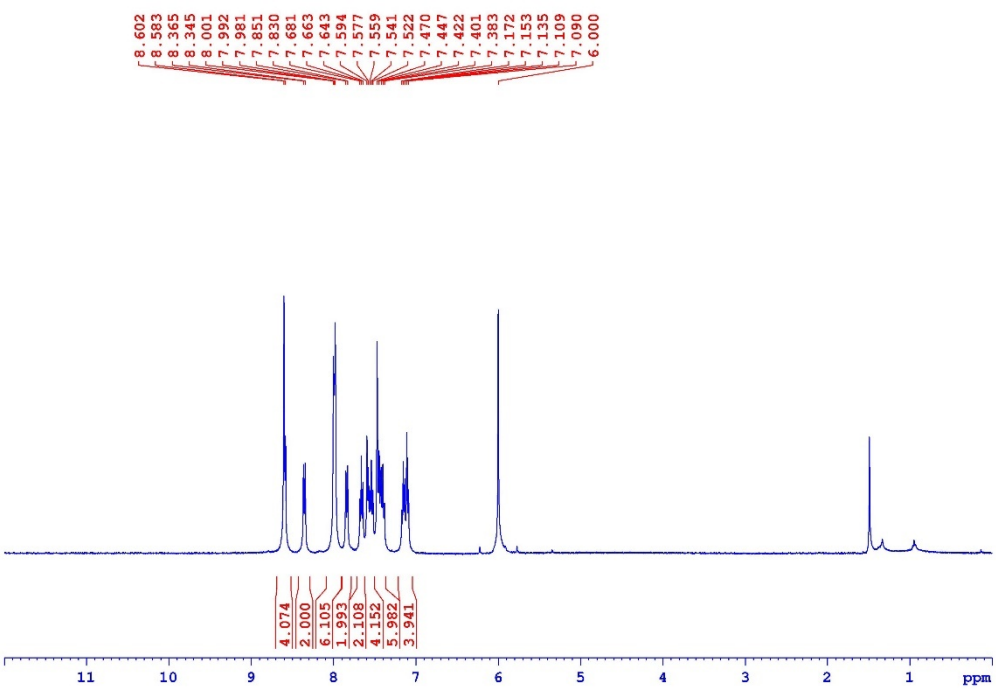


Figure S13: ^{1}H NMR Spectrum of compound **5c** (400 MHz, TCE-d2, 373 K).

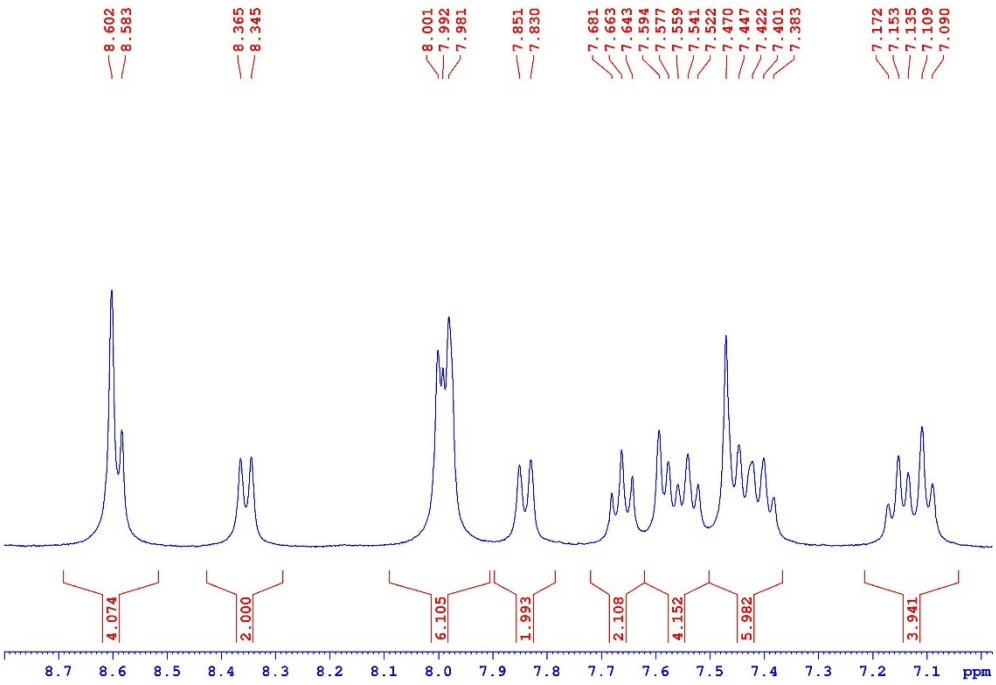


Figure S14: Magnified aromatic region of the ^{1}H NMR spectrum of compound **5c** (400 MHz, TCE-d2, 373 K).

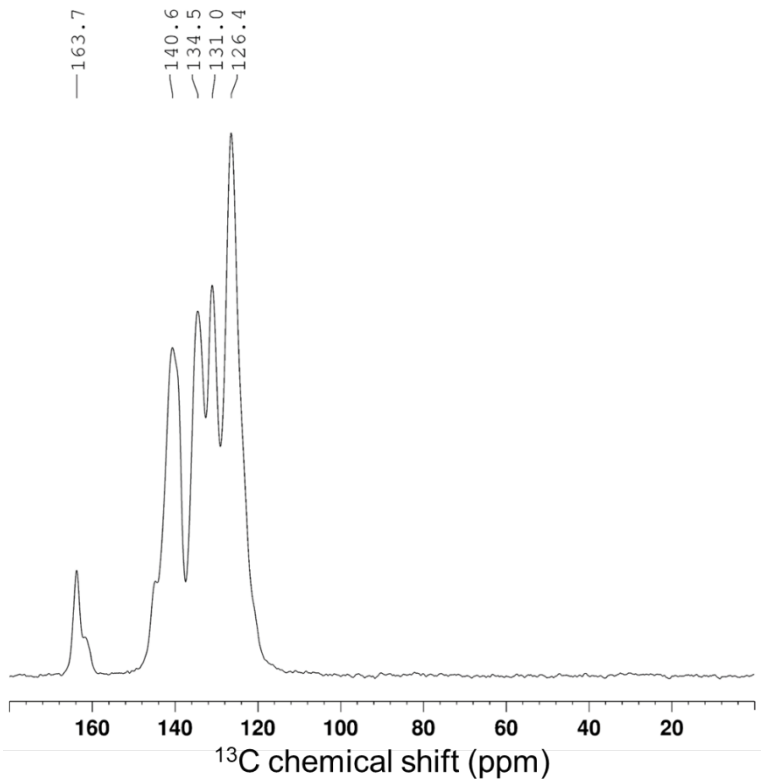


Figure S15: Solid-state $^{13}C\{^{1}H\}$ CPMAS NMR spectrum of compound **5c** (100.63 MHz, 298 K).

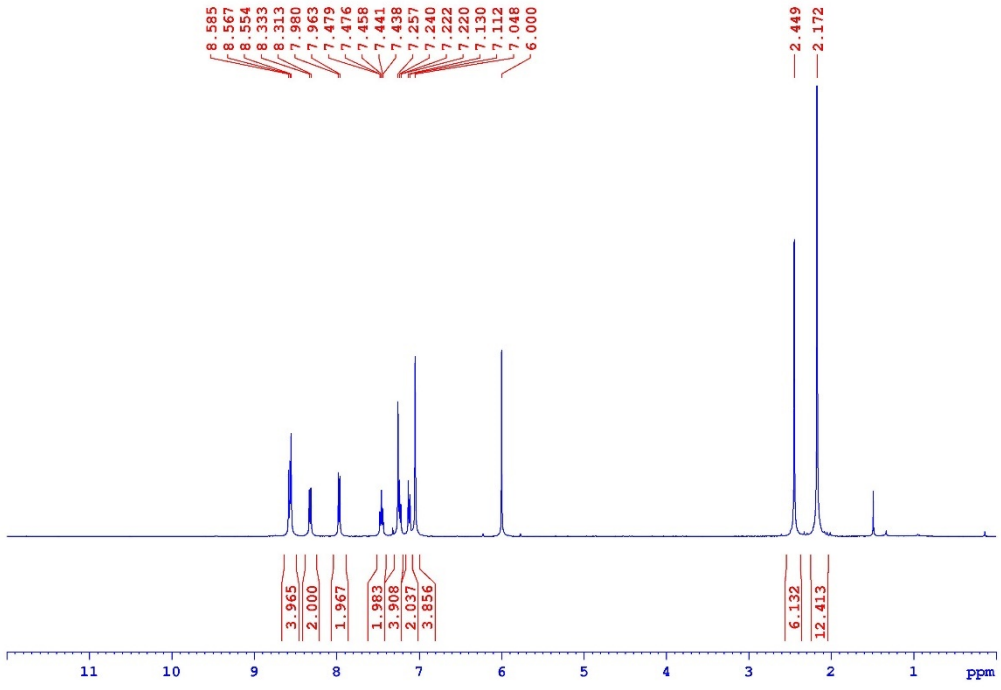


Figure S16: ^{1}H NMR Spectrum of compound **5d** (400 MHz, TCE-d2, 373 K).

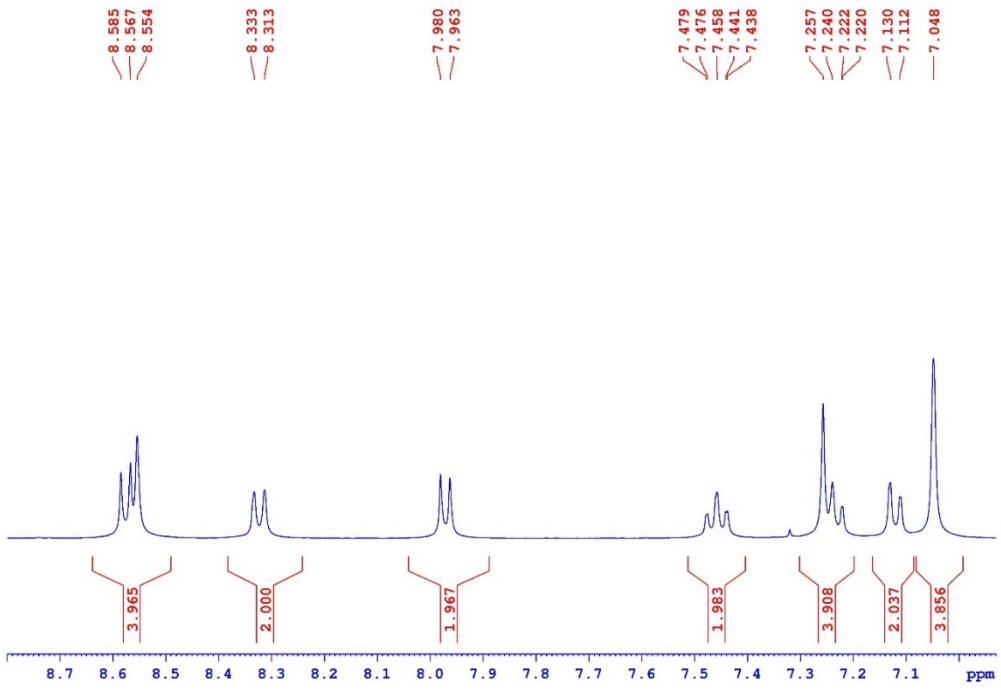


Figure S17: Magnified aromatic region of the ^{1}H NMR spectrum of compound **5d** (400 MHz, TCE-d2, 373 K).

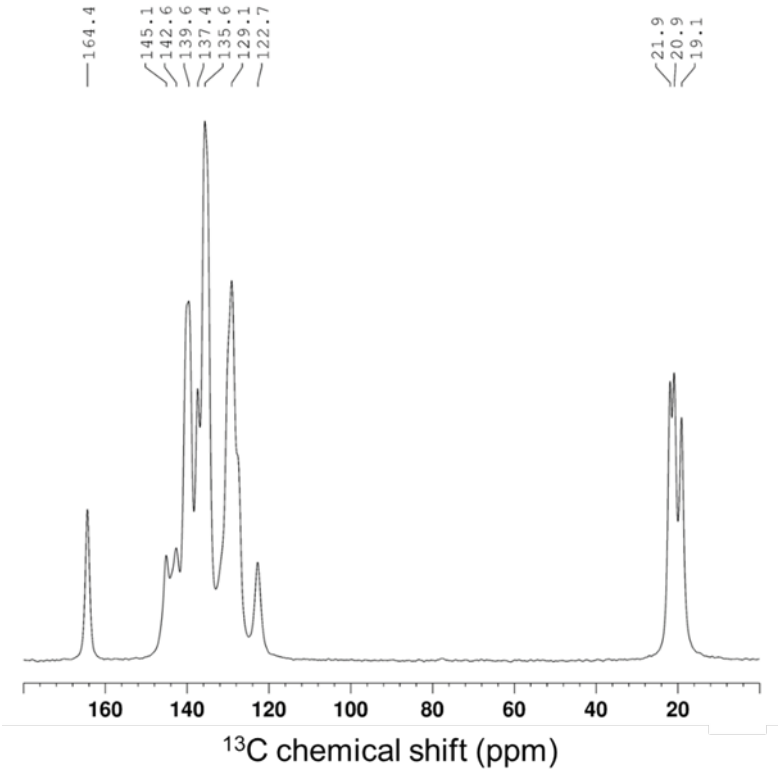


Figure S18: Solid-state ^{13}C{^{1}H} CPMAS NMR spectrum of compound **5d** (100.63 MHz, 298 K).

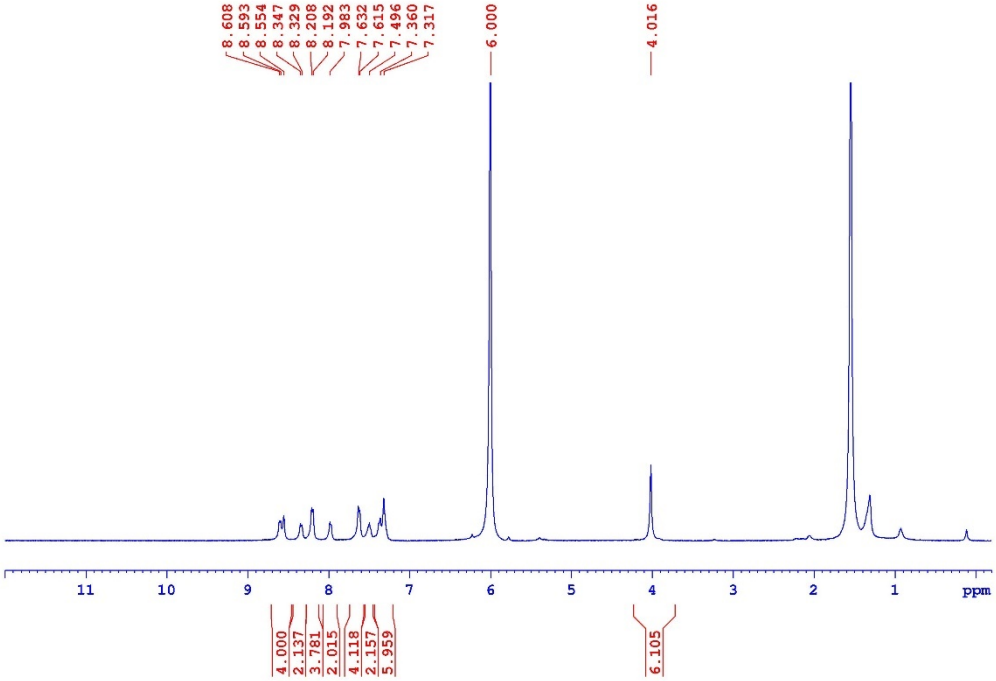


Figure S19: ^{1}H NMR Spectrum of compound **5e** (400 MHz, TCE-d2, 343K).

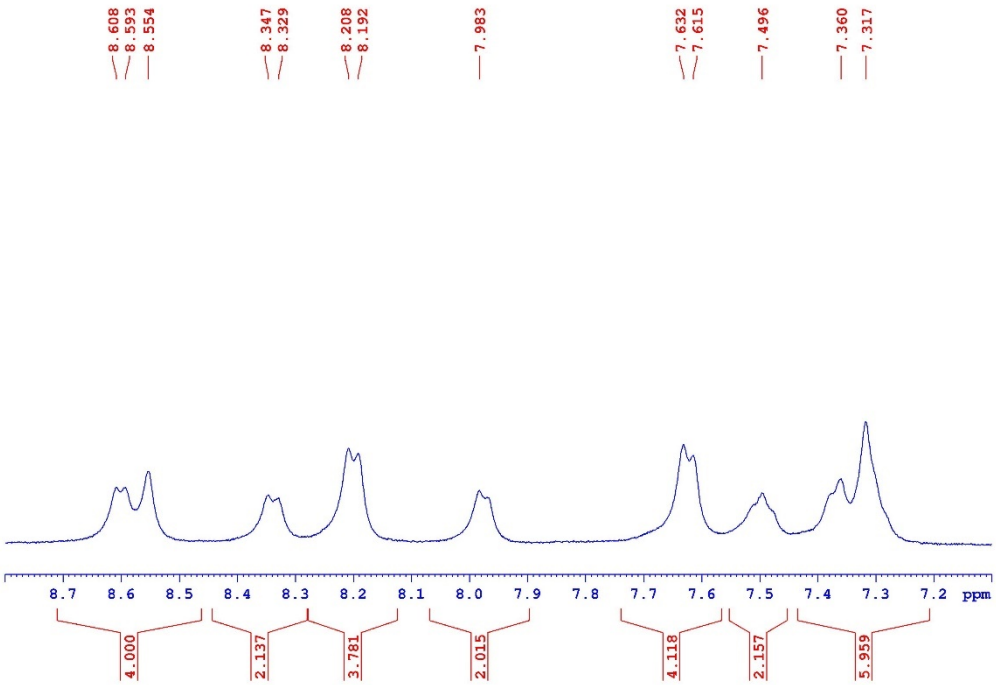


Figure S20: Magnified aromatic region of the ^{1}H NMR spectrum of compound **5e** (400 MHz, TCE-d2, 343K).

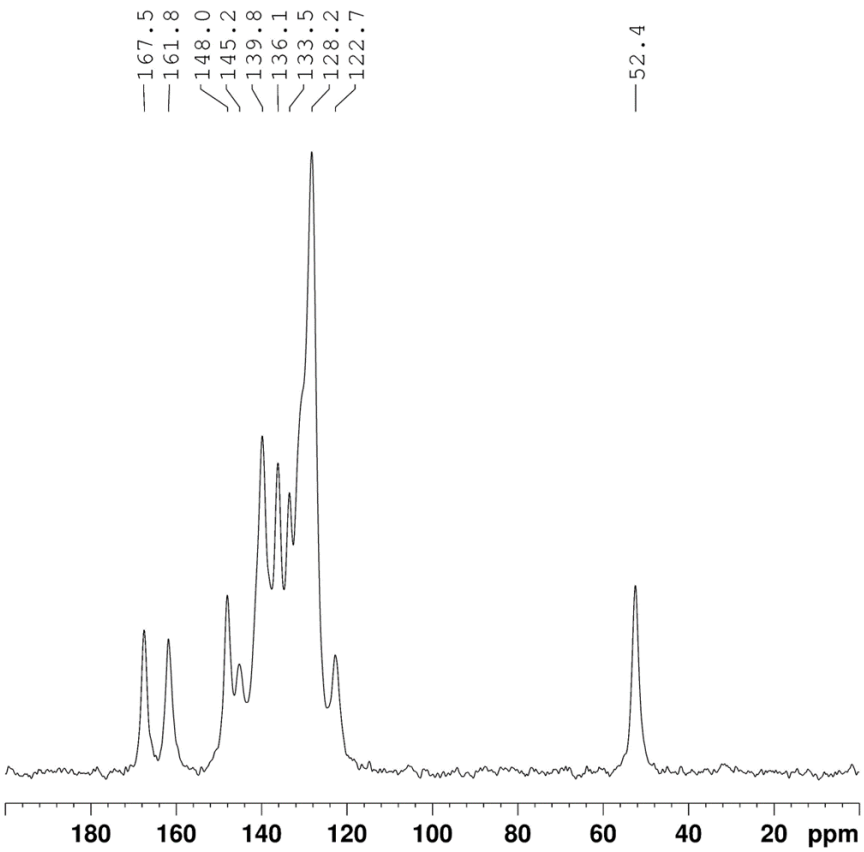


Figure S21: Solid-state $^{13}C\{^{1}H\}$ CPMAS NMR spectrum of compound **5e** (100.63 MHz, 298 K).

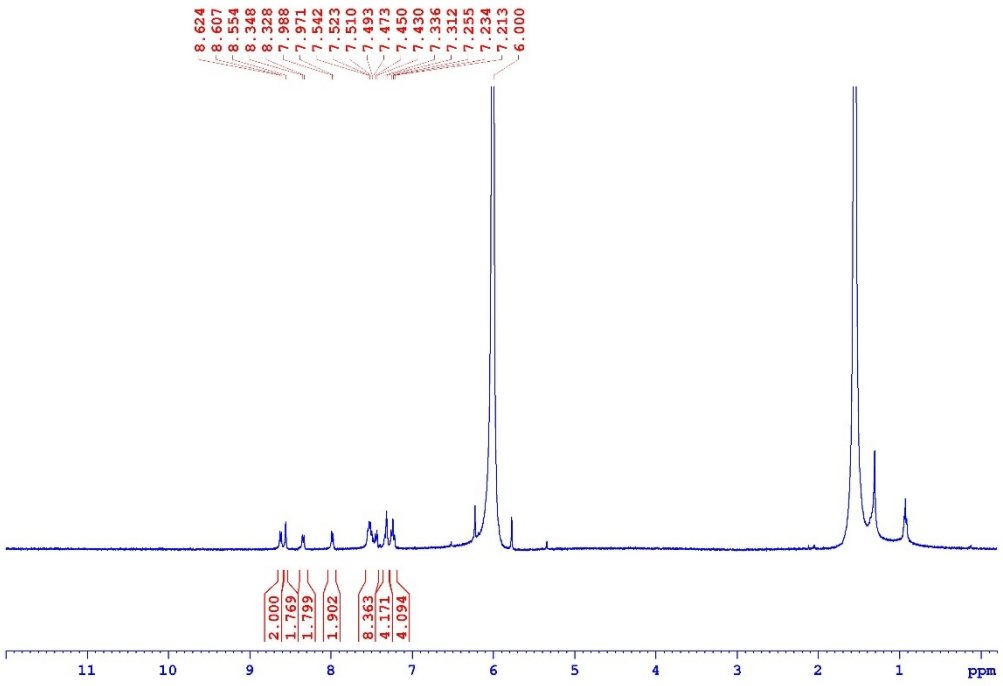


Figure S22: ^{1}H NMR Spectrum of compound **5f** (400 MHz, TCE-d2, 343 K).

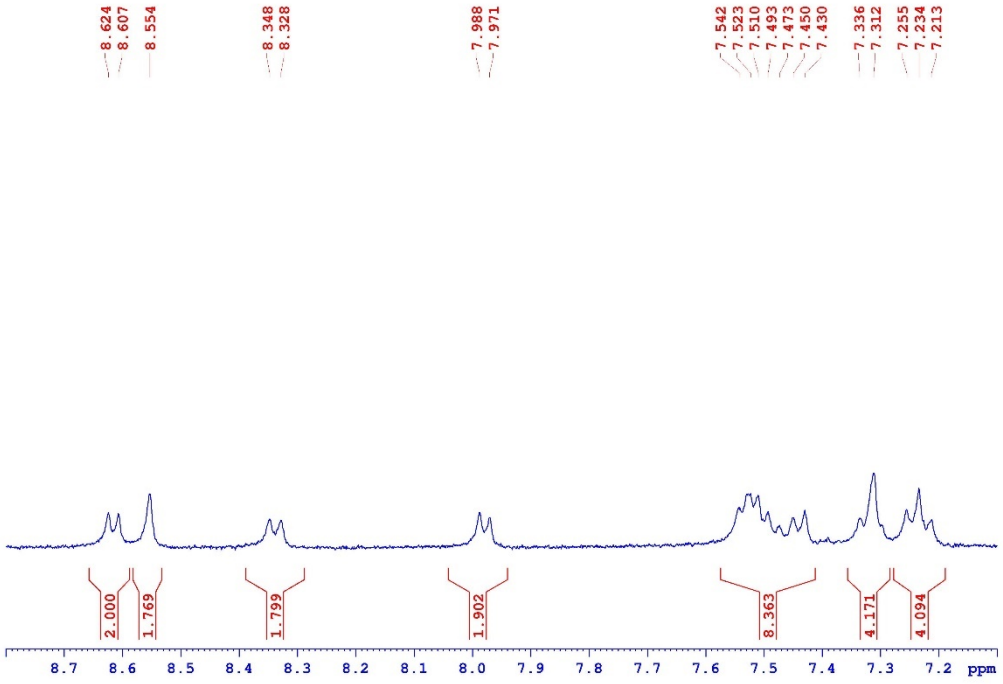


Figure S23: Magnified aromatic region of the ^{1}H NMR spectrum of compound **5f** (400 MHz, TCE-d2, 343 K).

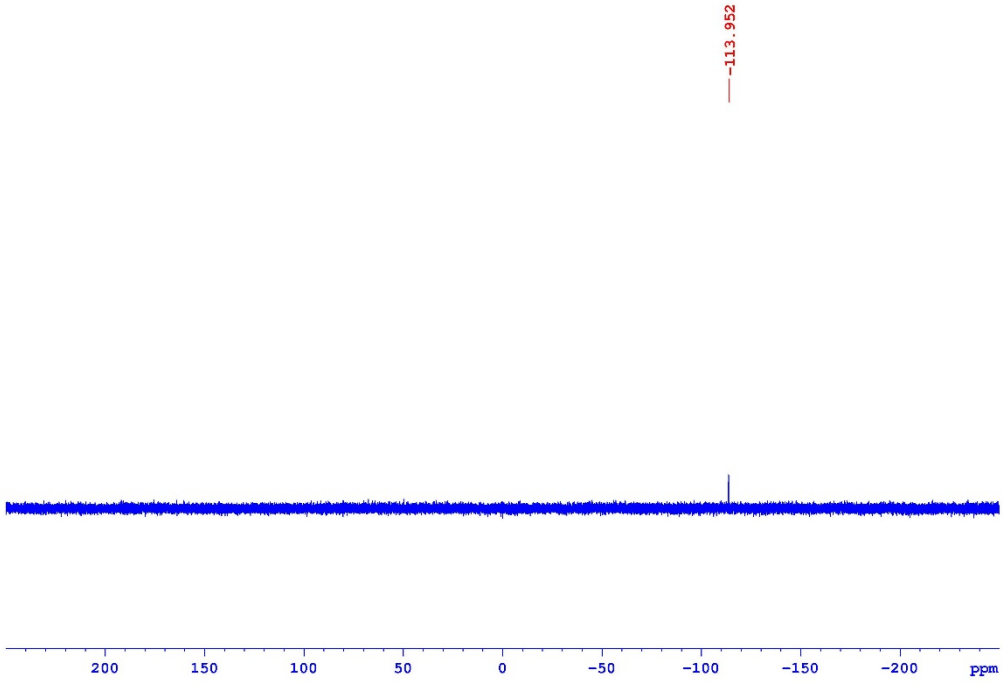


Figure S24: ^{19}F NMR spectrum of compound **5f** (376 MHz, TCE-d2, 343 K).

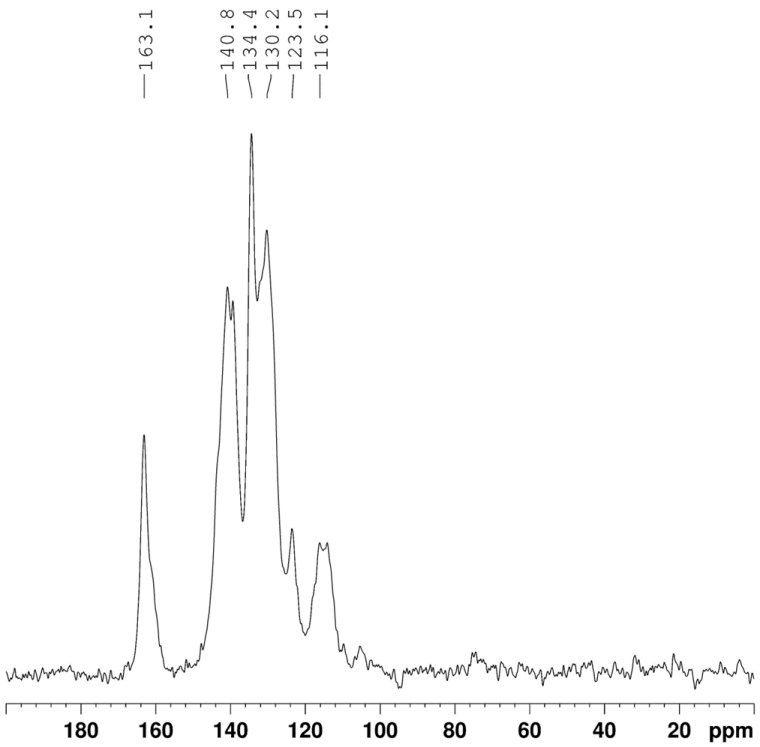


Figure S25: Solid-state $^{13}C\{^{1}H\}$ CPMAS NMR spectrum of compound **5f** (100.63 MHz, 298 K).

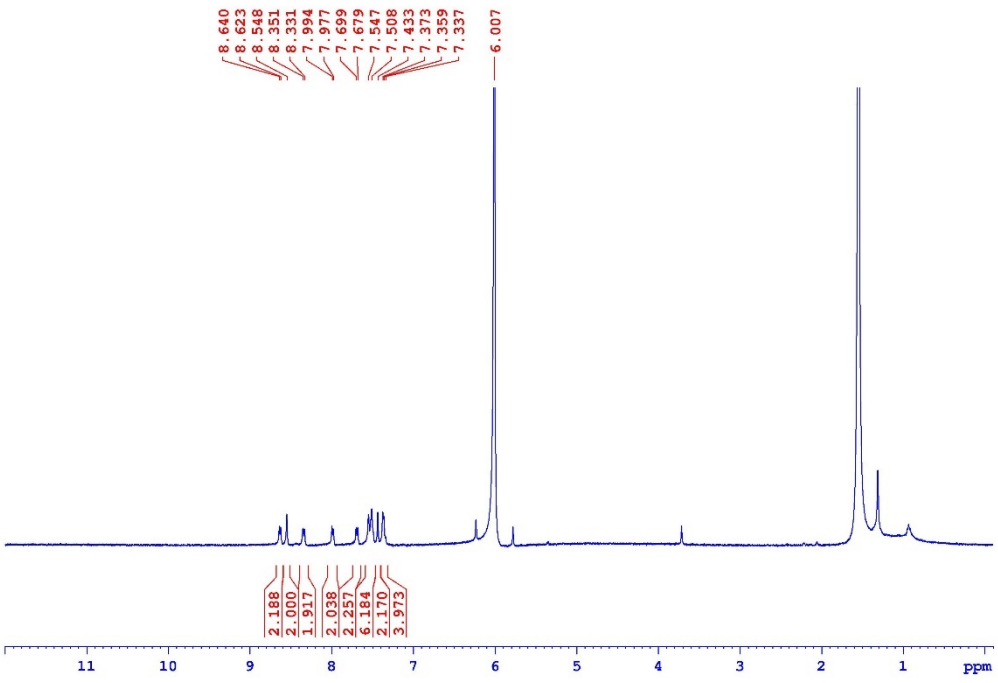


Figure S26: ^{1}H NMR Spectrum of compound **5g** (400 MHz, TCE-d2, 343 K).

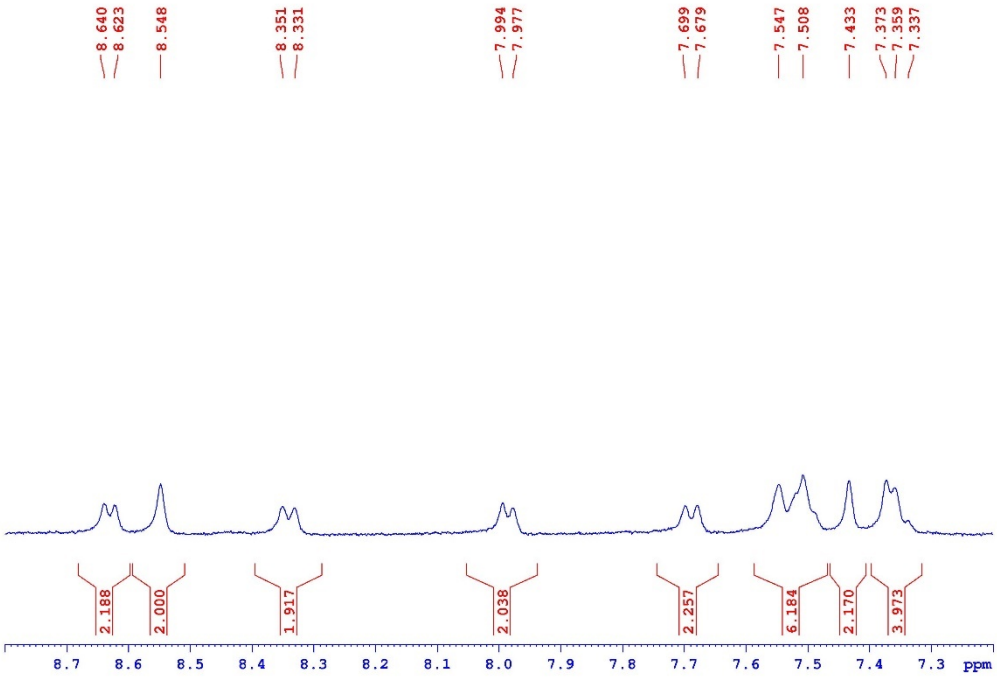


Figure S27: Magnified aromatic region of the ^{1}H NMR spectrum of compound **5g** (400 MHz, TCE-d2, 343 K).

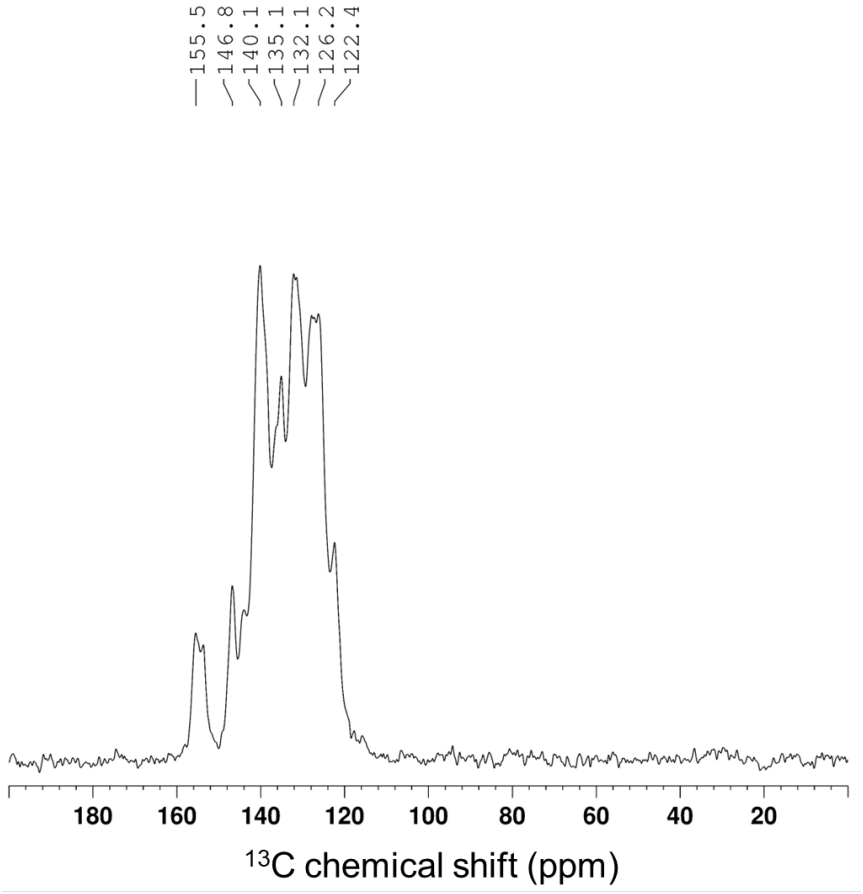


Figure S28: Solid-state ^{13}C{^{1}H} CPMAS NMR spectrum of compound **5g** (100.63 MHz, 298 K)

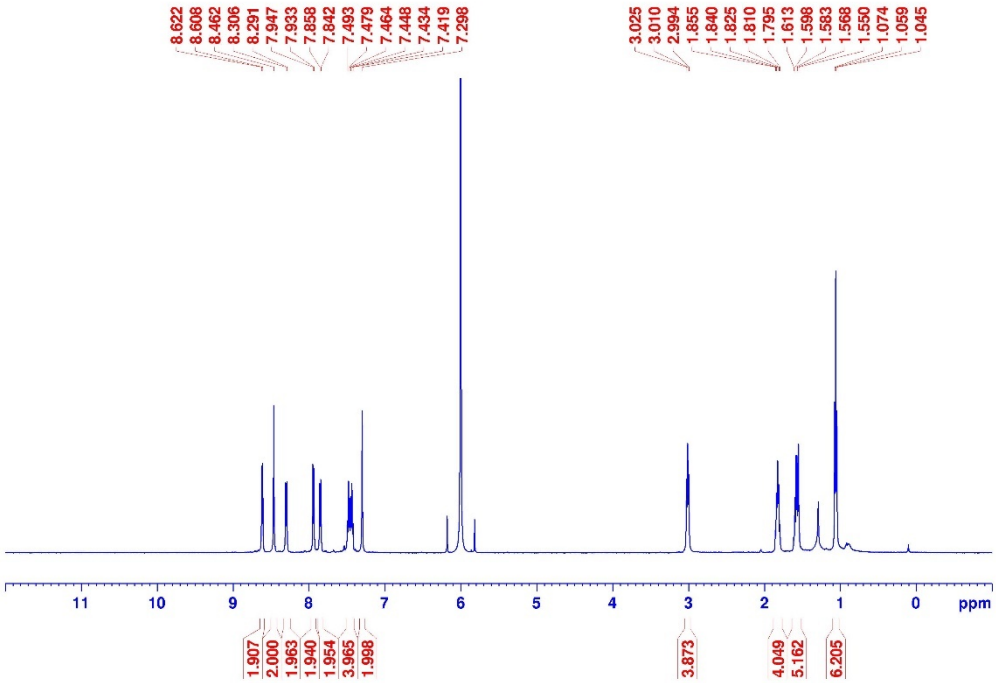


Figure S29: ^{1}H NMR Spectrum of compound **5h** (500 MHz, TCE-d2, 323 K).

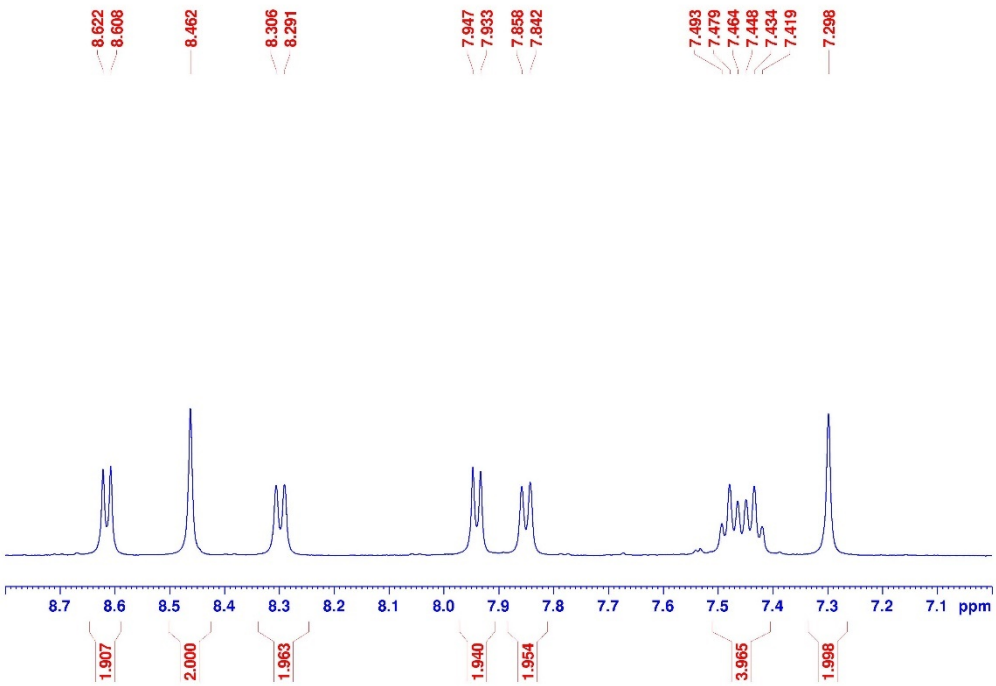


Figure S30: Magnified aromatic region of the ^{1}H NMR spectrum of compound **5h** (500 MHz, TCE-d2, 323 K).

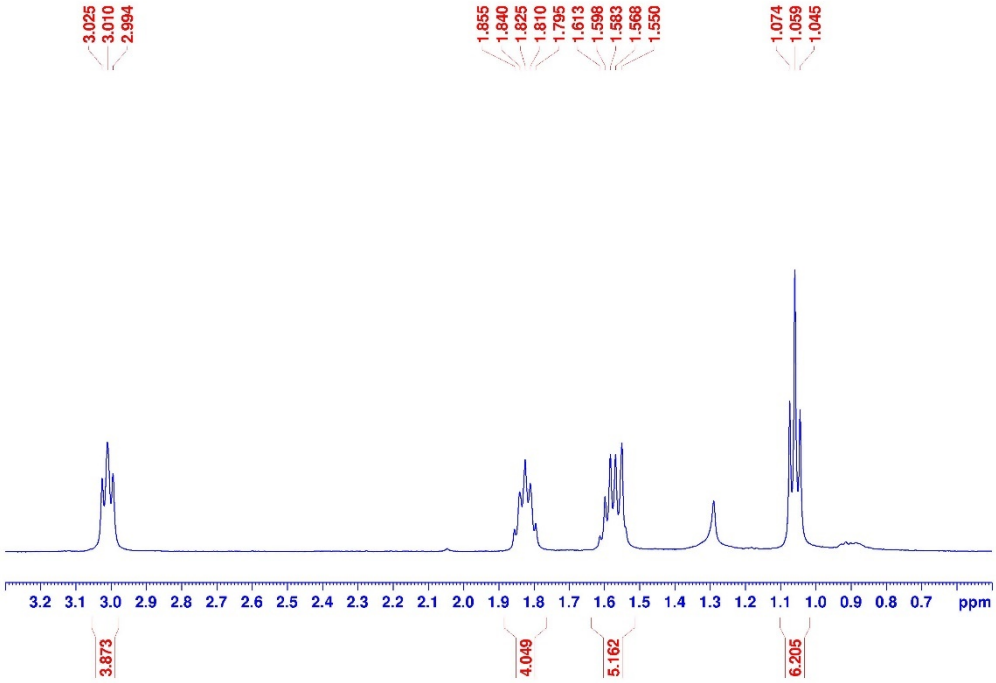


Figure S31: Magnified aliphatic region of the ^{1}H NMR spectrum of compound **5h** (500 MHz, TCE-d2, 323 K).

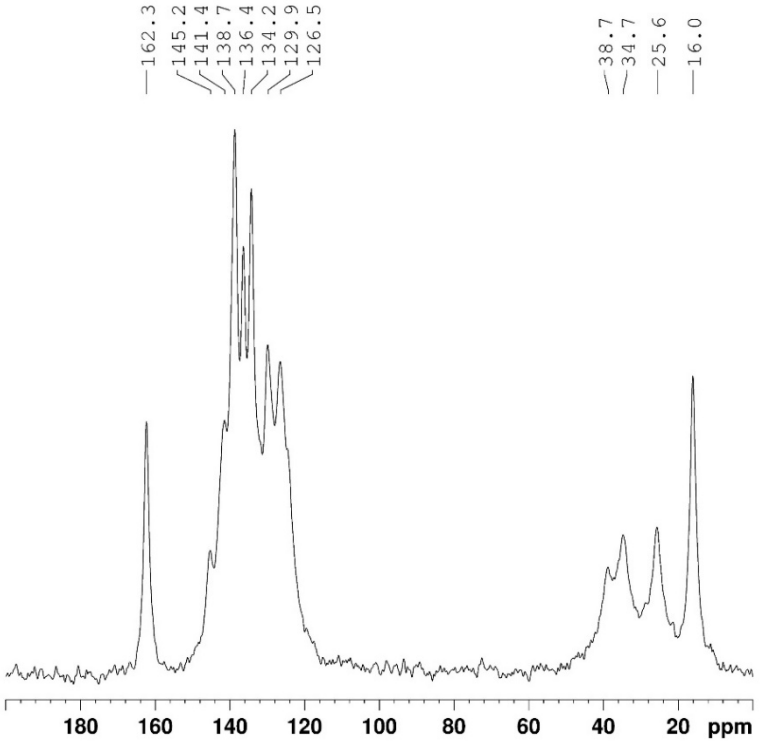


Figure S32: Solid-state ^{13}C{^{1}H} CPMAS NMR spectrum of compound **5h** (100.63 MHz, 298 K).

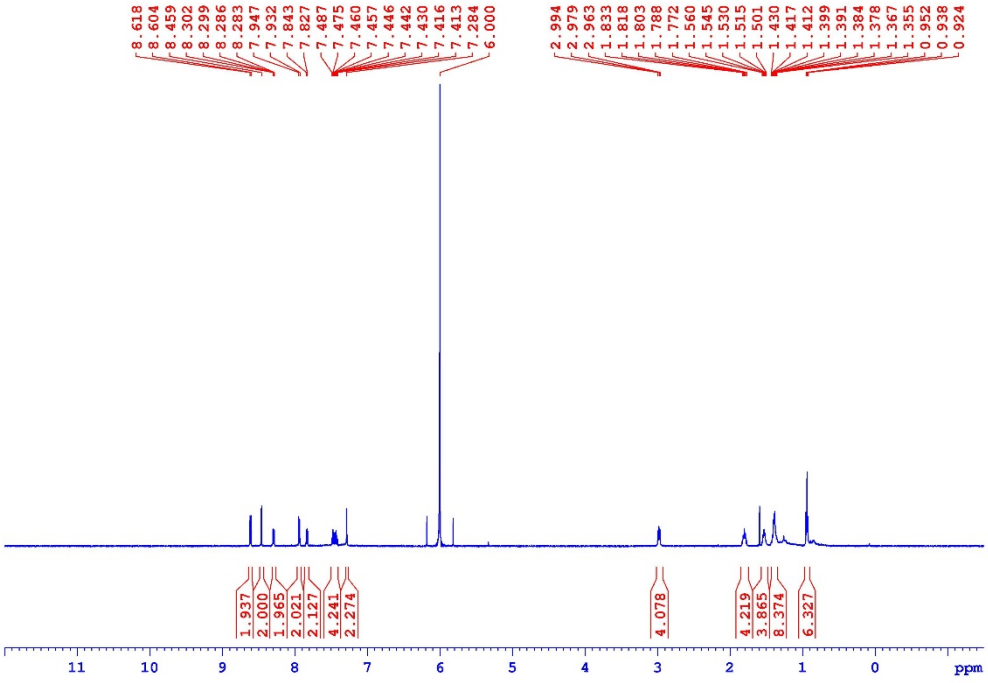


Figure S33: ^{1}H NMR Spectrum of compound **5i** (500 MHz, TCE-d2, 298 K).

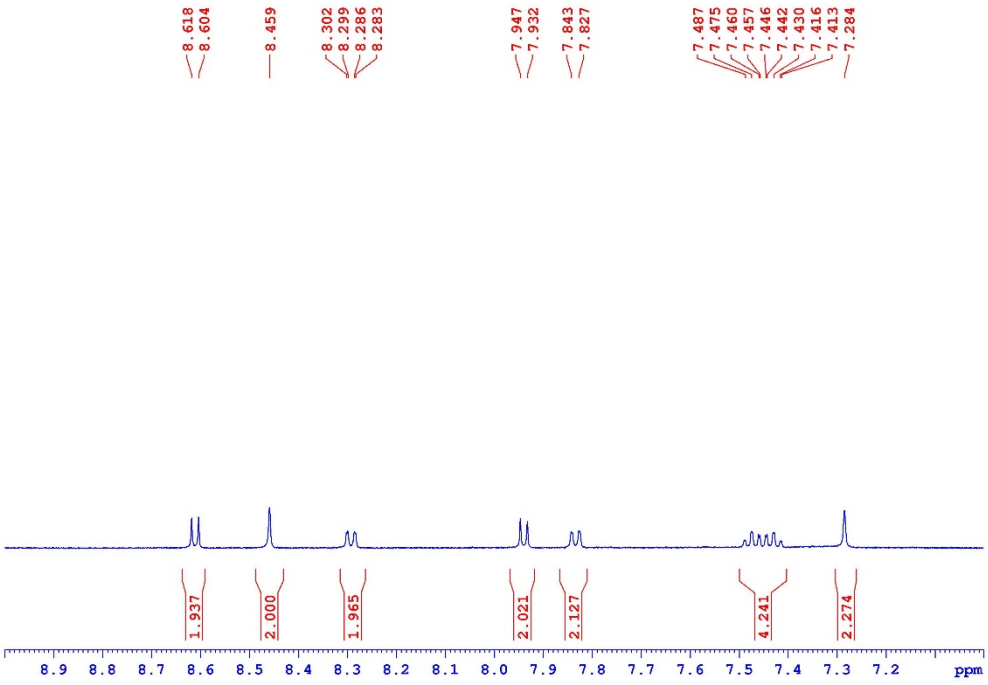


Figure S34: Magnified aromatic region of the ^{1}H NMR spectrum of compound **5i** (500 MHz, TCE-d2, 298 K).

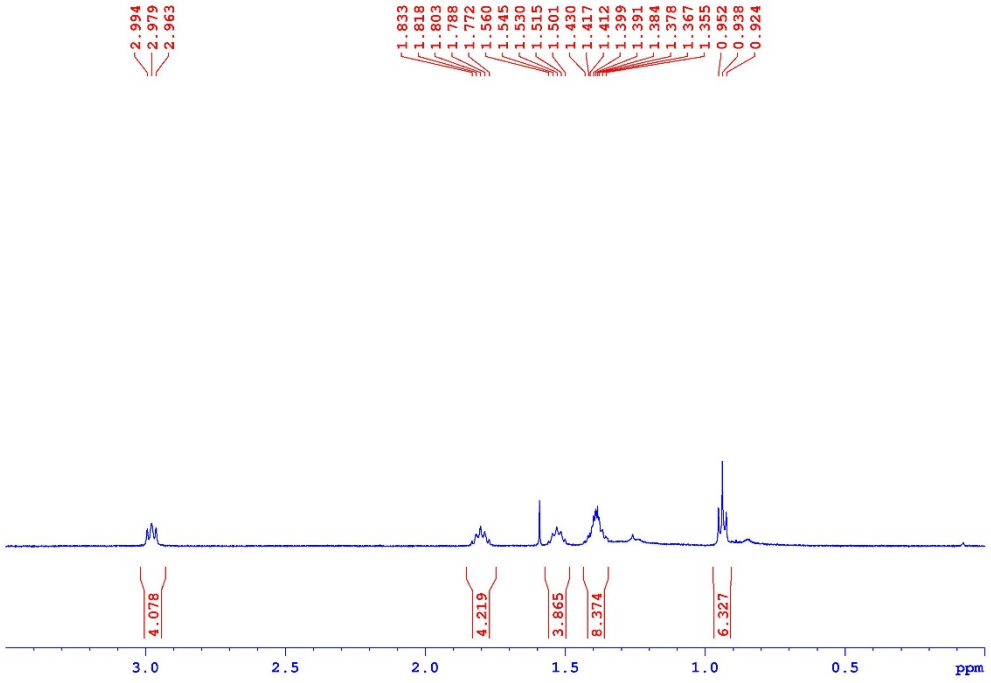


Figure S35: Magnified aliphatic region of the ^{1}H NMR spectrum of compound **5i** (500 MHz, TCE-d2, 298 K).

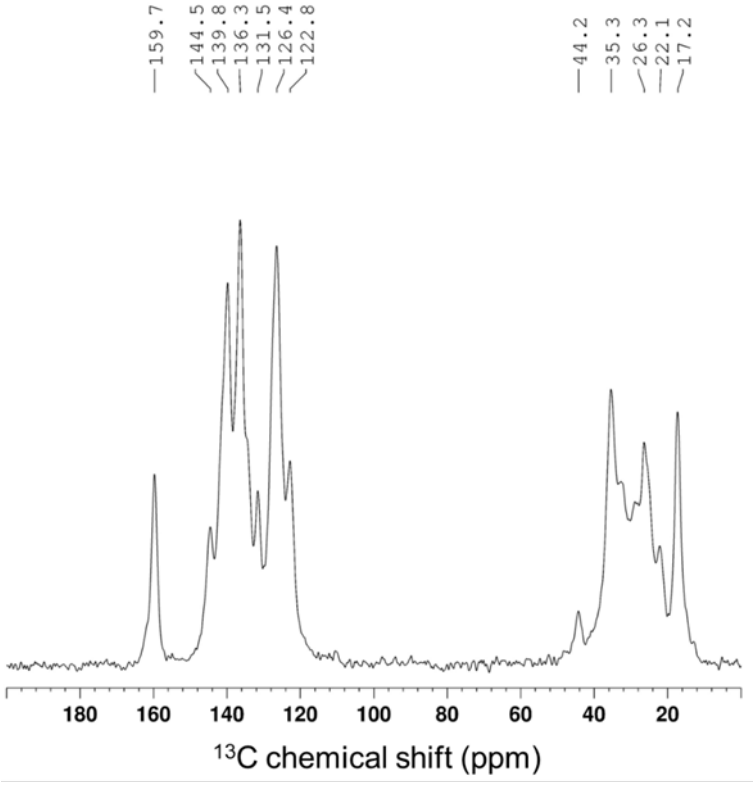


Figure S36: Solid-state ^{13}C{^{1}H} CPMAS NMR spectrum of compound **5i** (100.63 MHz, 298 K).

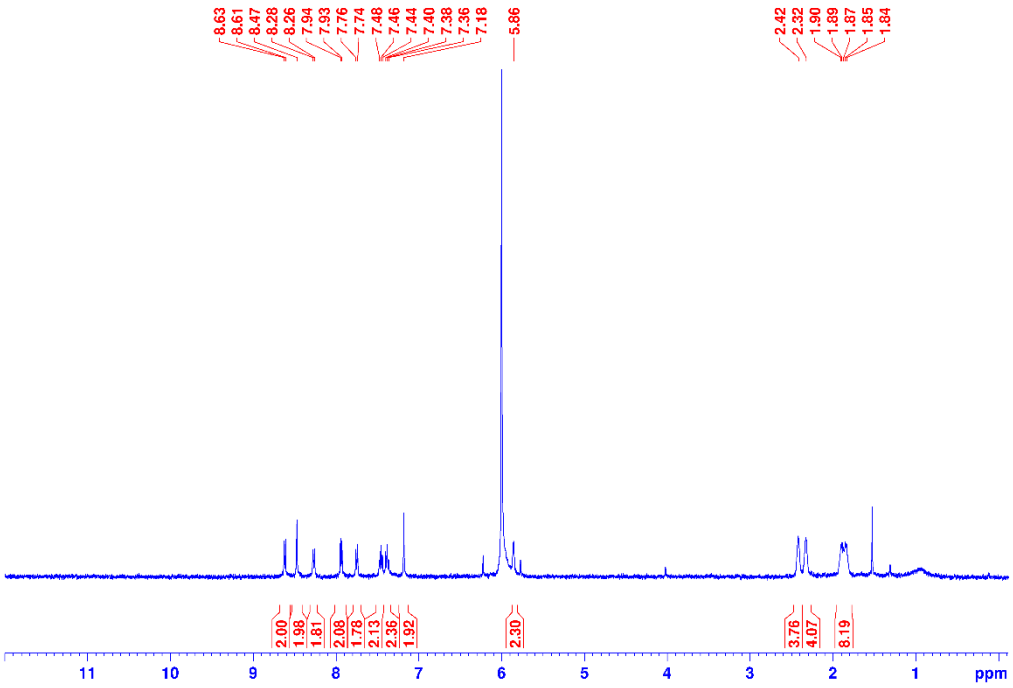


Figure S37: ^{1}H NMR Spectrum of compound **5j** (400 MHz, TCE-d2, 343 K).

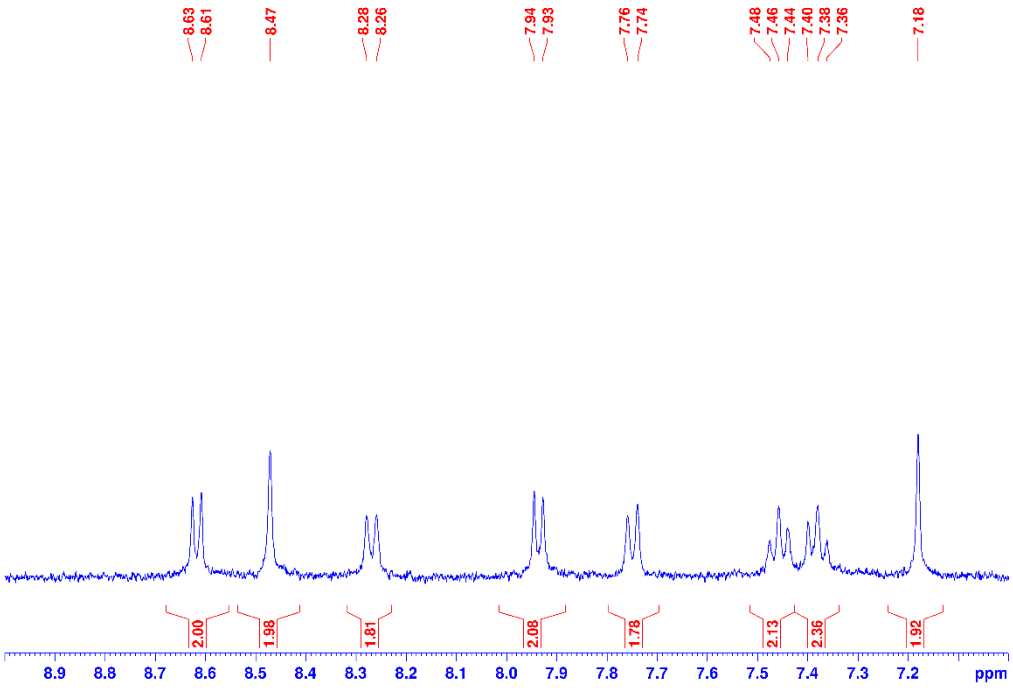


Figure S38: Magnified aromatic region of the ^{1}H NMR spectrum of compound **5j** (400 MHz, TCE-d2, 343 K).

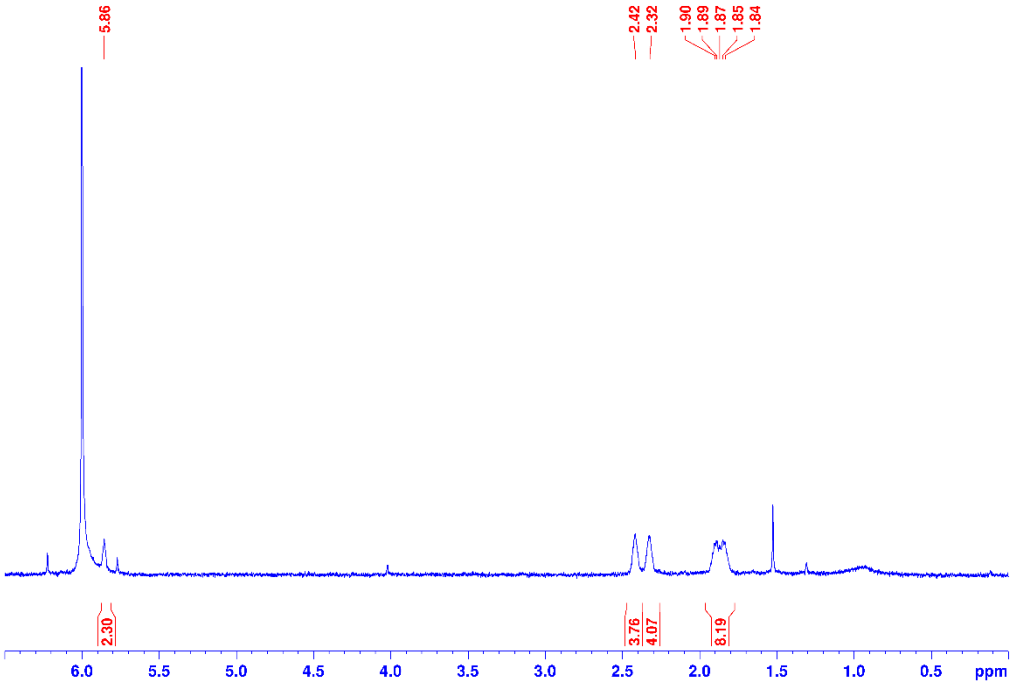


Figure S39: Magnified aliphatic region of the ^{1}H NMR spectrum of compound **5j** (400 MHz, TCE-d2, 343 K).

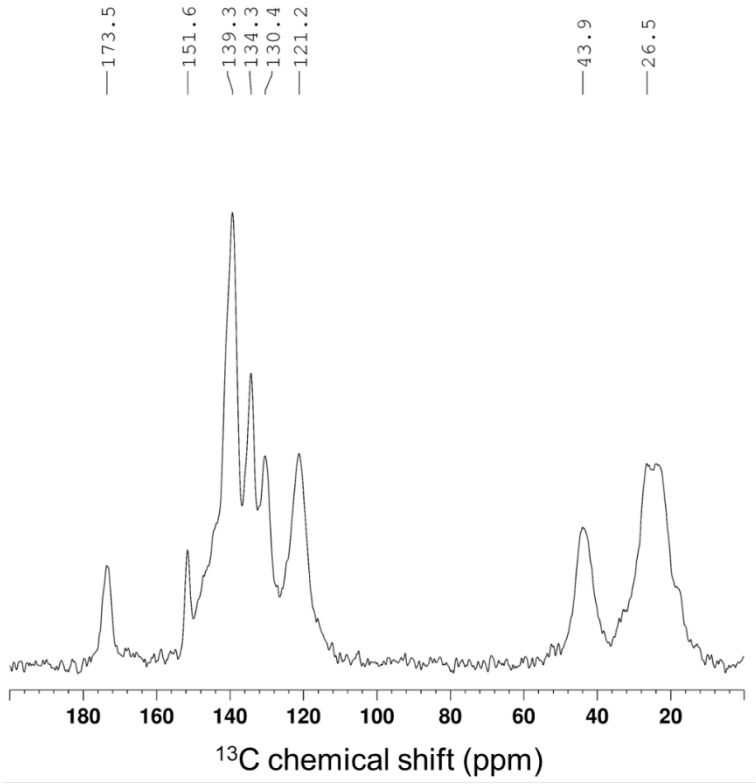


Figure S40: Solid-state ^{13}C{^{1}H} CPMAS NMR spectrum of compound **5j** (100.63 MHz, 298 K).

4. Simulated and measured HR-MS spectra

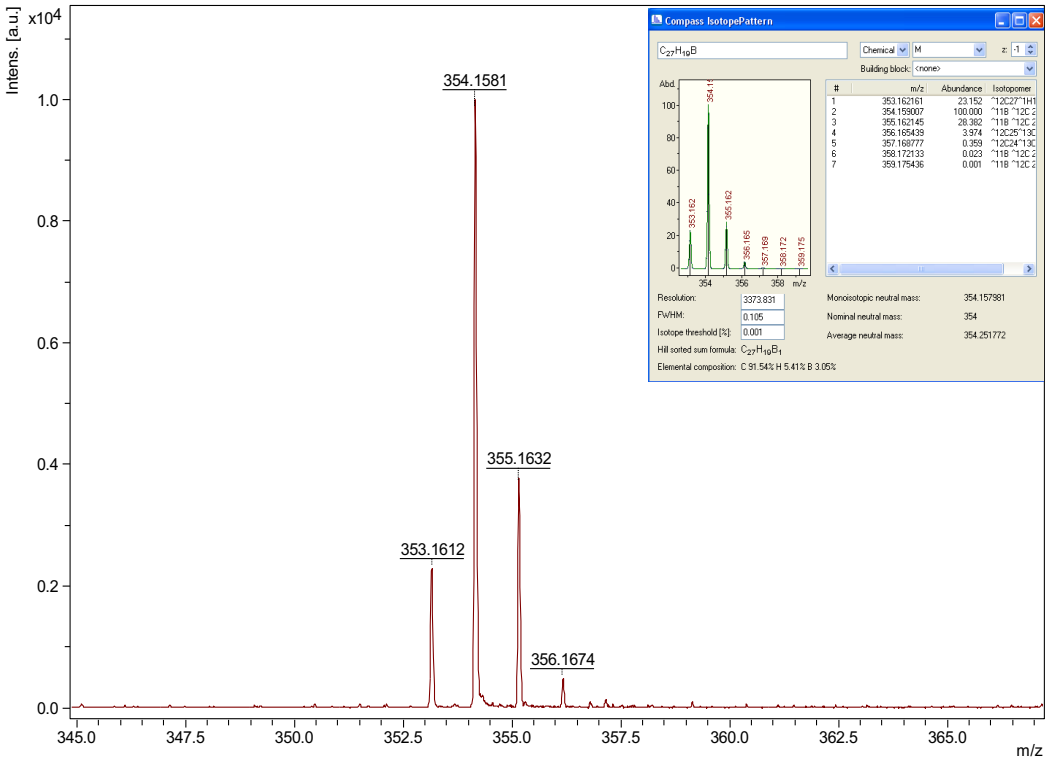


Figure S41. Simulated (right) and found (left) patterns of the high-resolution mass spectrum of **3a** (MALDI-TOF, positive mode) *m/z*: $[M]^+$ Calc'd for $C_{27}H_{19}B$.

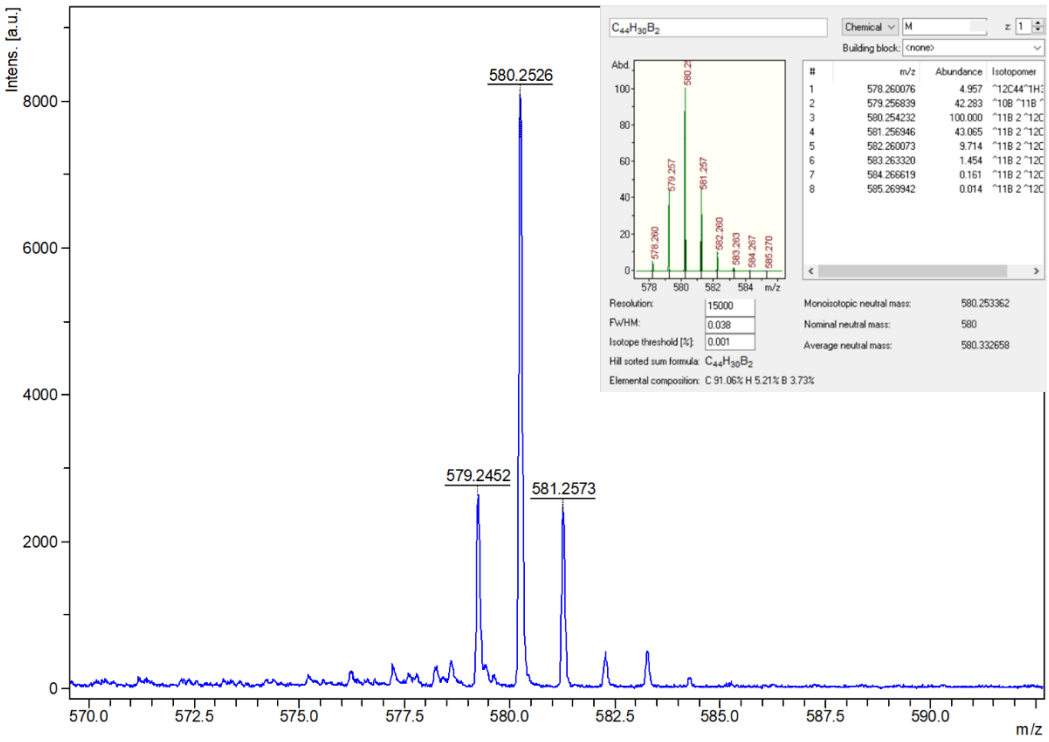


Figure S42. Simulated (right) and found (left) patterns of the high-resolution mass spectrum of **5a** (MALDI-TOF, negative mode) *m/z*: $[M]^-$ Calc'd for $C_{44}H_{30}B_2$.

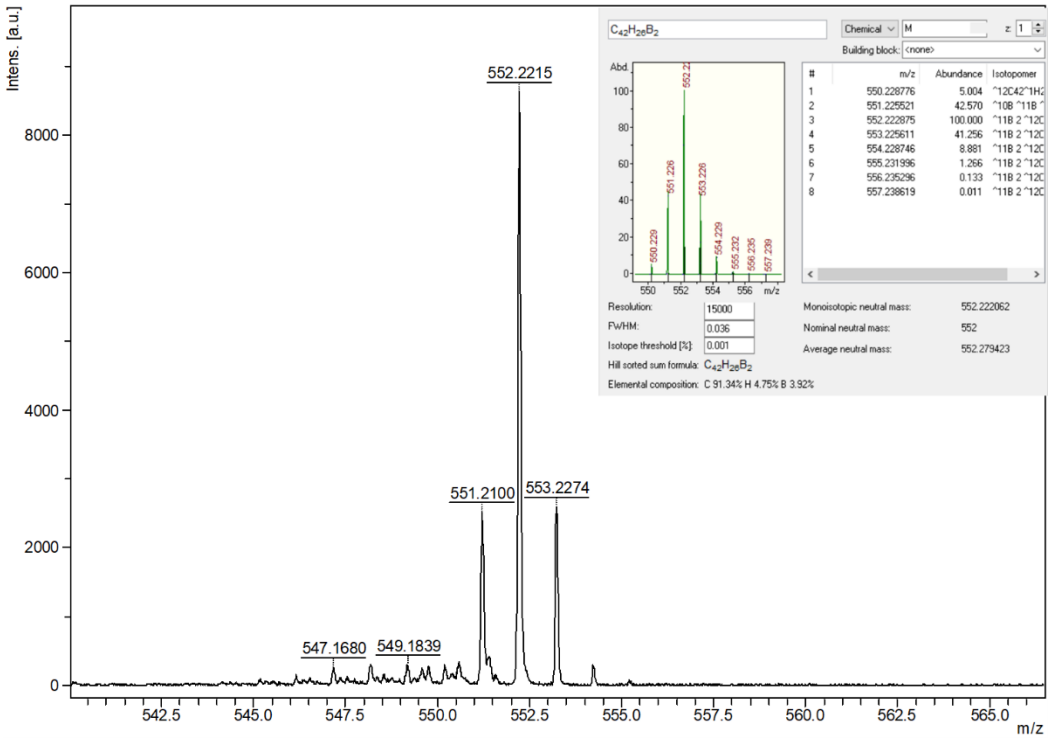


Figure S43. Simulated (right) and found (left) patterns of the high-resolution mass spectrum of **5b** (MALDI-TOF, positive mode) *m/z*: $[M]^+$ Calc'd for $C_{42}H_{26}B_2$.

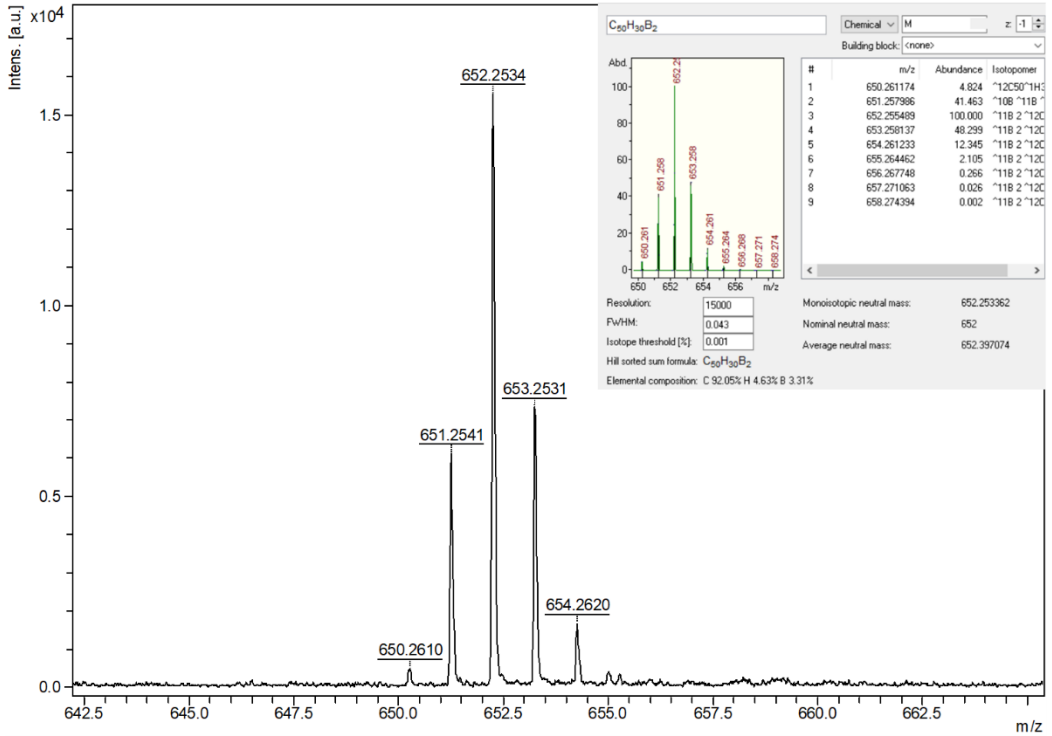


Figure S44. Simulated (right) and found (left) patterns of the high-resolution mass spectrum of **5c** (MALDI-TOF, negative mode) *m/z*: $[M]^-$ Calc'd for $C_{50}H_{30}B_2$

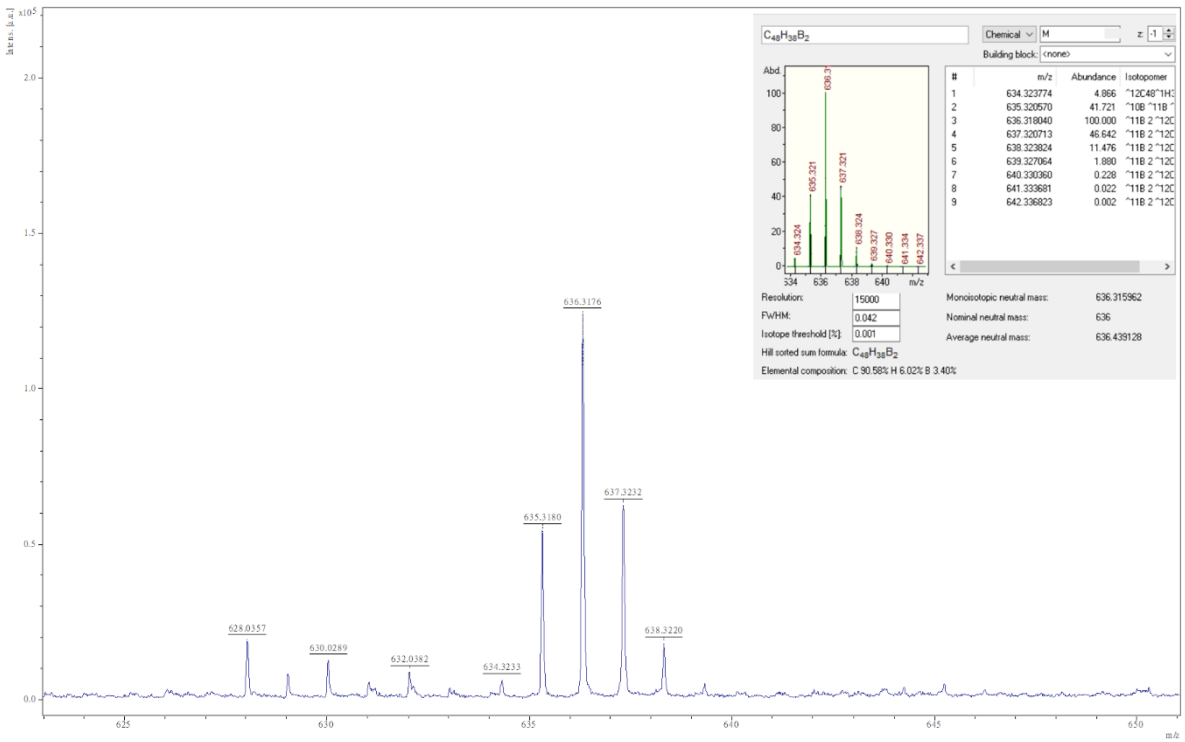


Figure S45. Simulated (right) and found (left) patterns of the high-resolution mass spectrum of **5d** (MALDI-TOF, negative mode) *m/z*: $[M]^-$ Calc'd for $C_{48}H_{38}B_2$

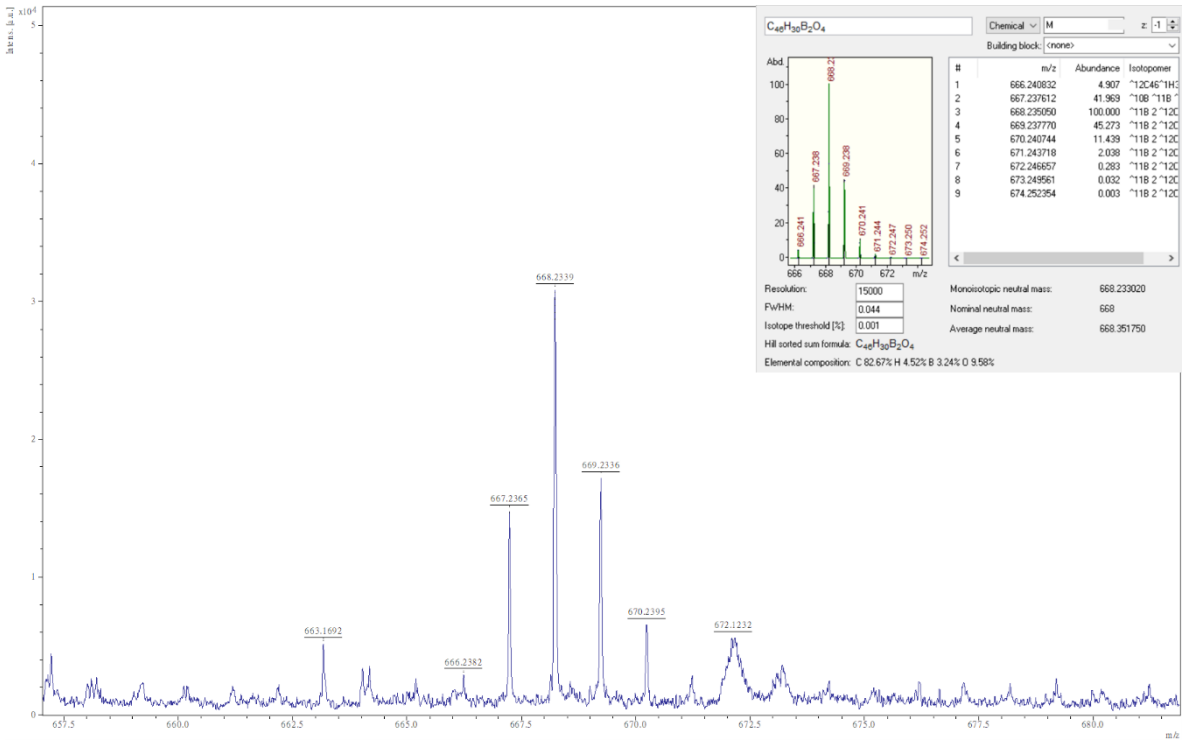


Figure S46. Simulated (right) and found (left) patterns of the high-resolution mass spectrum of **5e** (MALDI-TOF, negative mode) *m/z*: $[M]^-$ Calc'd for $C_{46}H_{30}B_2O_4$

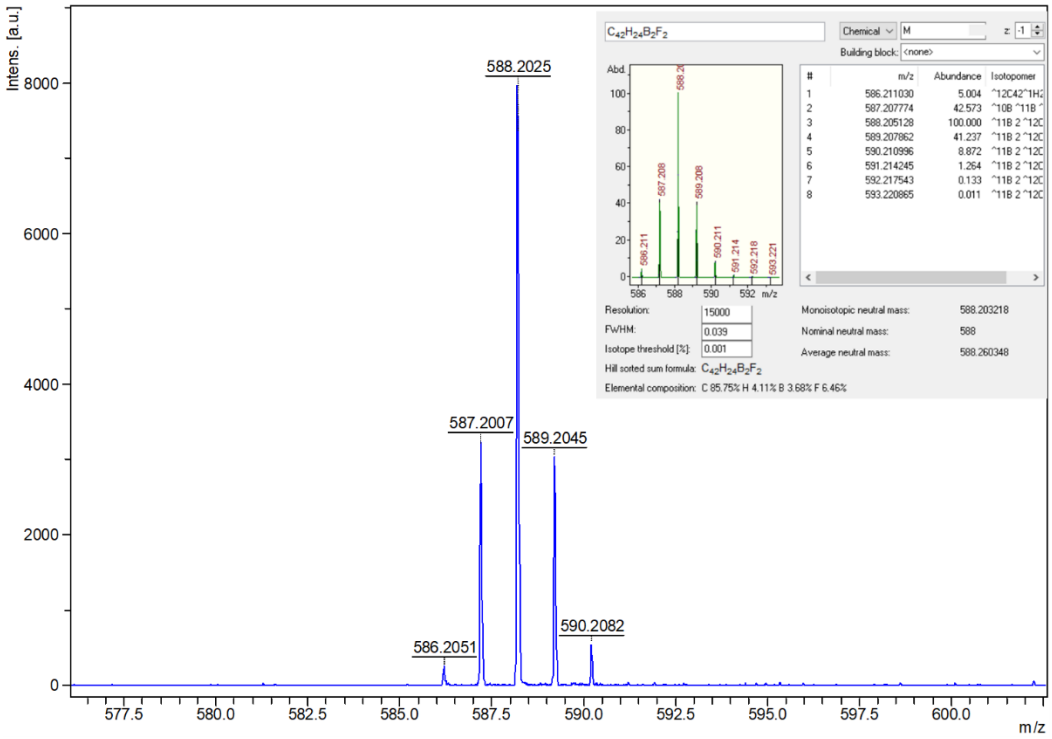


Figure S47. Simulated (right) and found (left) patterns of the high-resolution mass spectrum of **5f** (MALDI-TOF, negative mode) *m/z*: $[M]^-$ Calc'd for $C_{42}H_{24}B_2F_2$

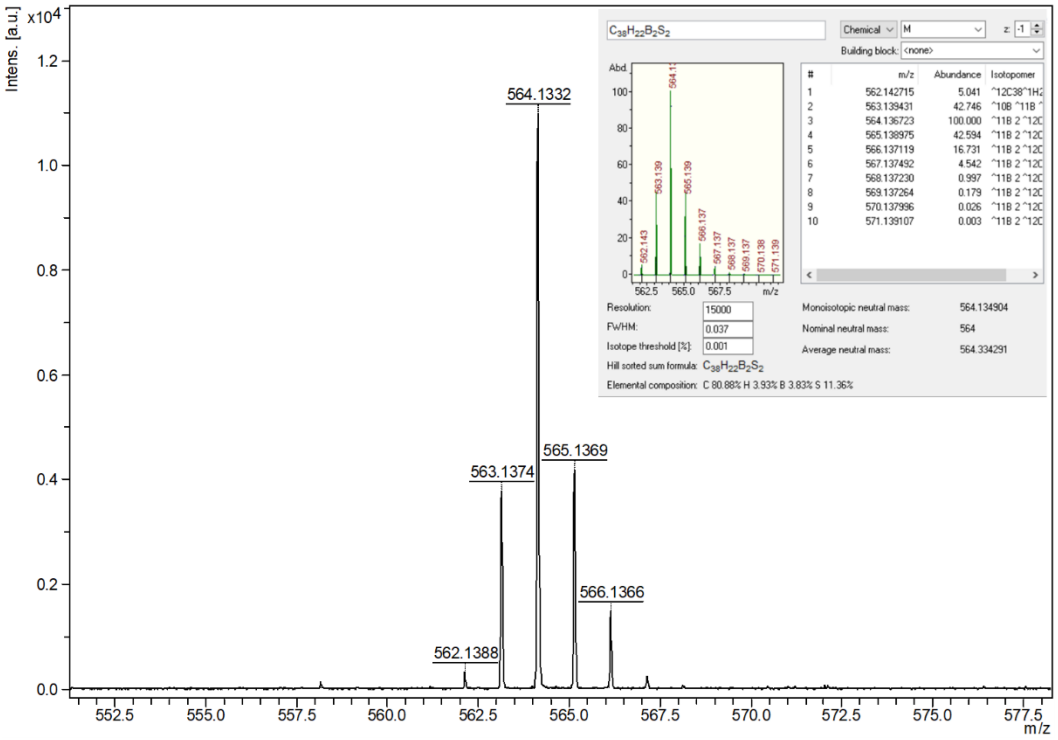


Figure S48. Simulated (right) and found (left) patterns of the high-resolution mass spectrum of **5g** (MALDI-TOF, negative mode) *m/z*: $[M]^-$ Calc'd for $C_{38}H_{22}B_2S_2$

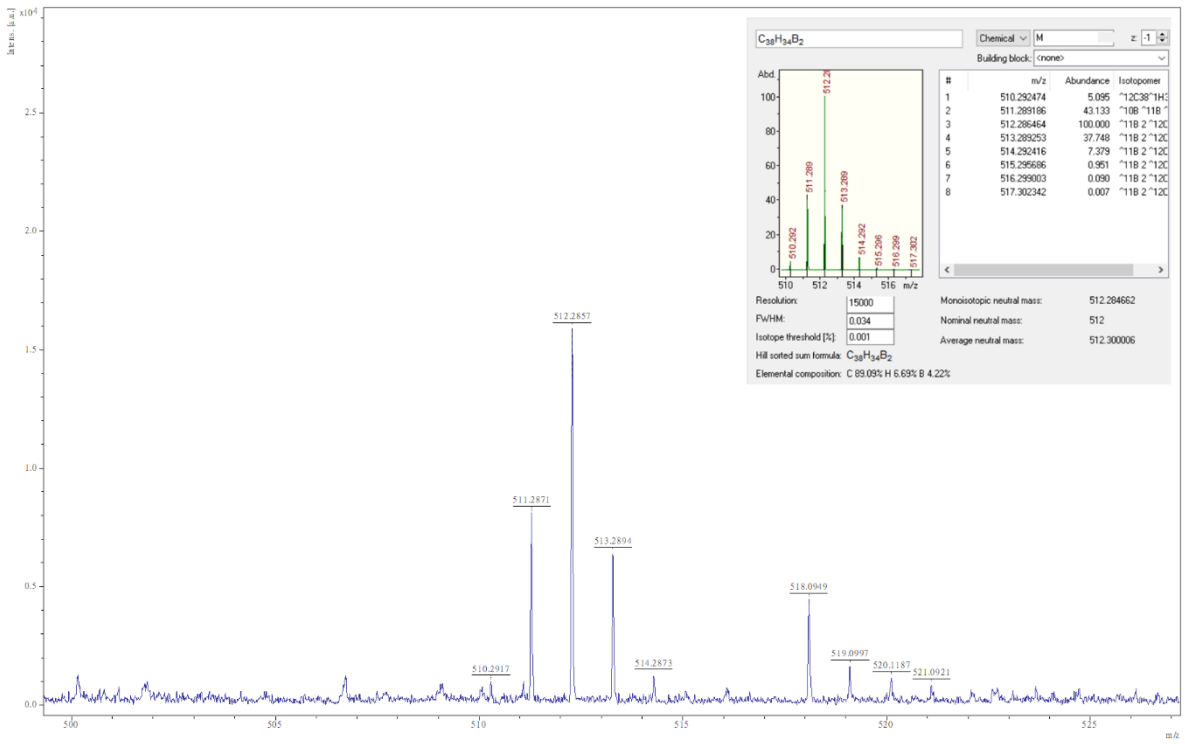


Figure S49. Simulated (right) and found (left) patterns of the high-resolution mass spectrum of **5h** (MALDI-TOF, negative mode) *m/z*: $[M]^-$ Calc'd for $C_{38}H_{34}B_2$

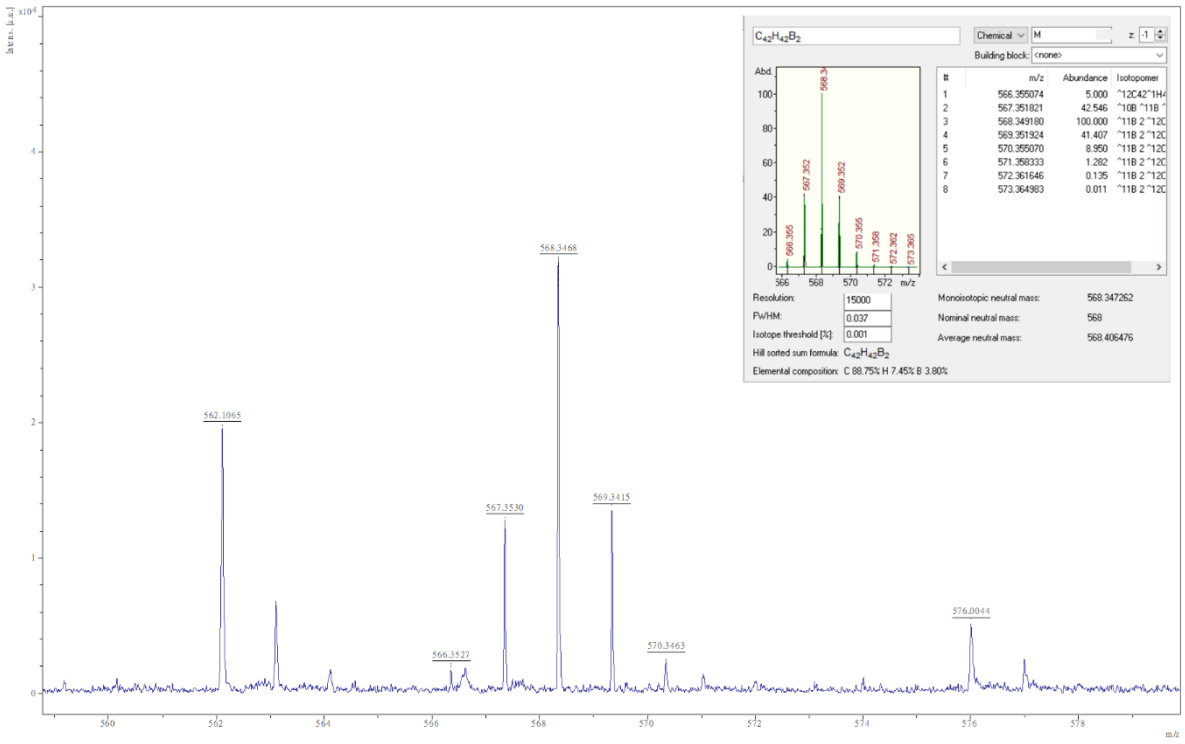


Figure S50. Simulated (right) and found (left) patterns of the high-resolution mass spectrum of **5i** (MALDI-TOF, negative mode) *m/z*: $[M]^-$ Calc'd for $C_{42}H_{42}B_2$

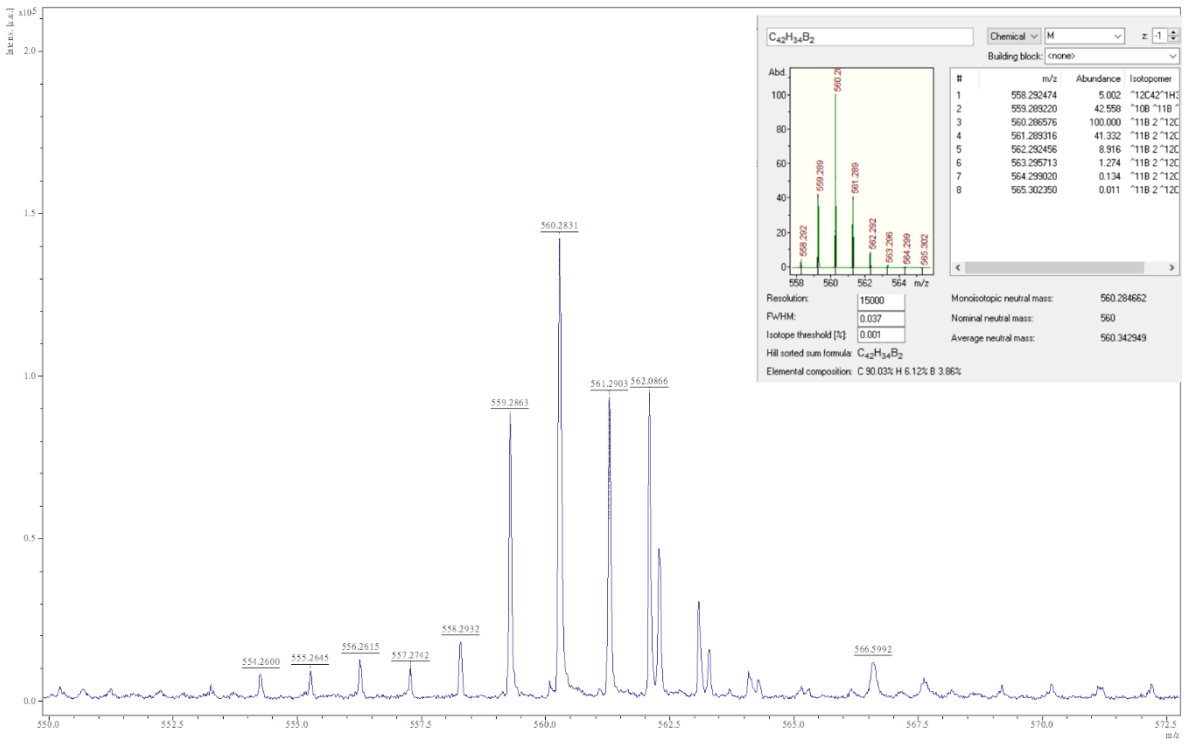


Figure S51. Simulated (right) and found (left) patterns of the high-resolution mass spectrum of **5j** (MALDI-TOF, negative mode) *m/z*: $[M]^-$ Calc'd for $C_{42}H_{34}B_2$

5. Cyclic Voltammetry

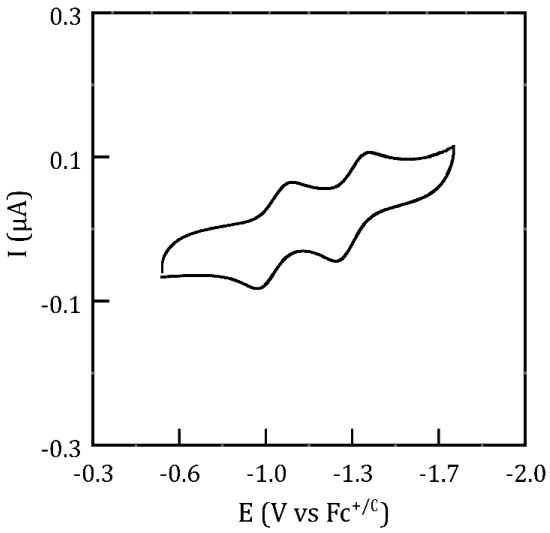


Figure S52. Cyclic Voltammogram of **5a** (1.0 x 10^{-3} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K).

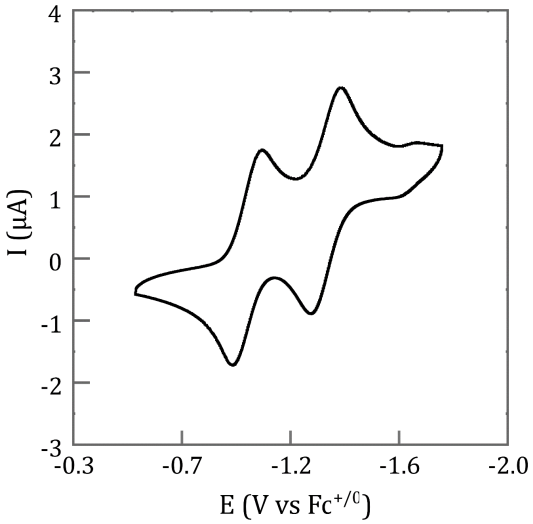


Figure S53. Cyclic Voltammogram of **5b** (8.3 x 10^{-4} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K).

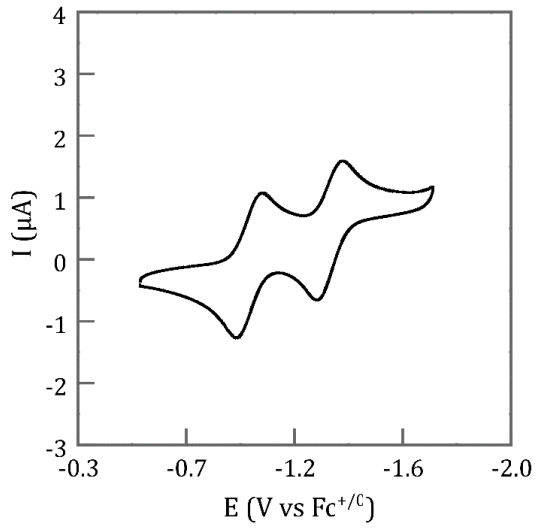


Figure S54. Cyclic Voltammogram of **5c** (8.7 x 10^{-4} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K).

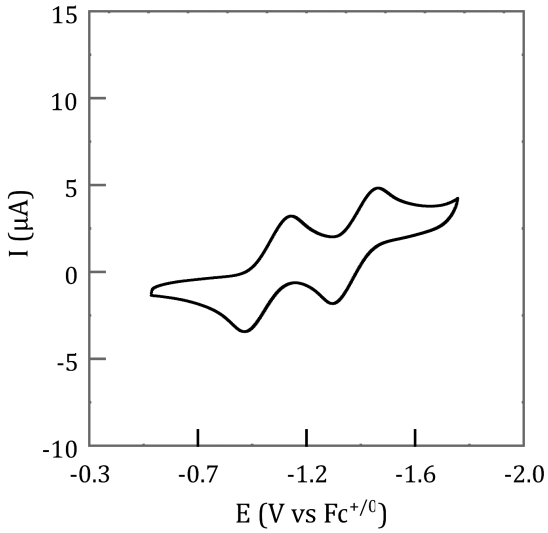


Figure S55. Cyclic Voltammogram of **5d** (1.1 x 10^{-3} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K).

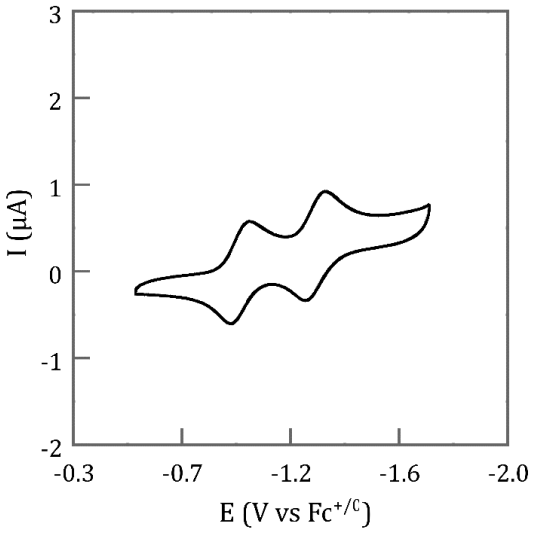


Figure S56. Cyclic Voltammogram of **5e** (9.0 x 10^{-4} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K).

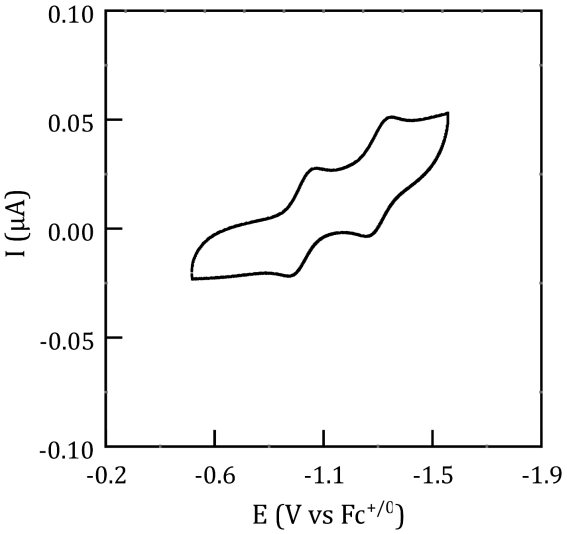


Figure S57. Cyclic Voltammogram of **5f** (5.3 x 10^{-4} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K).

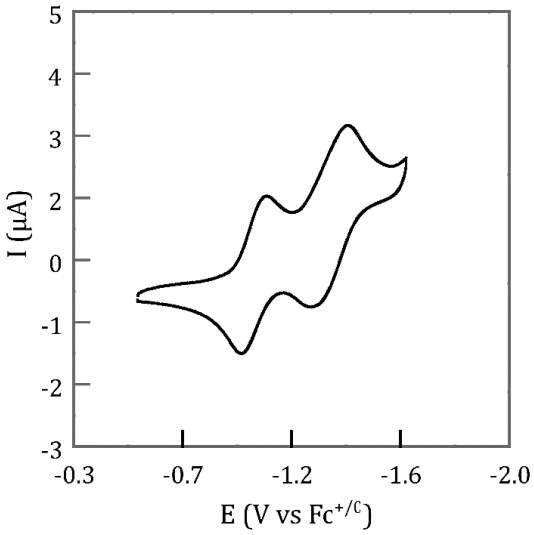


Figure S58. Cyclic Voltammogram of **5g** (1.2 x 10^{-3} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K).

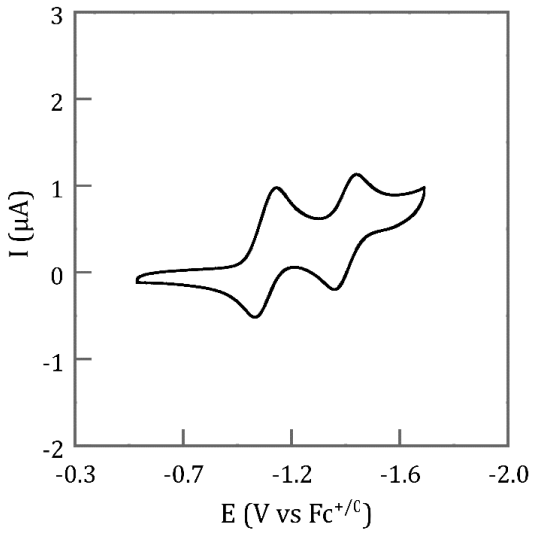


Figure S59. Cyclic Voltammogram of **5h** (8.2 x 10^{-4} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K).

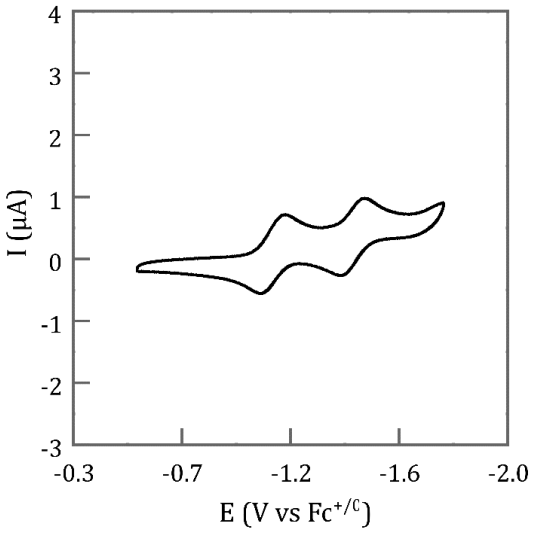


Figure S60. Cyclic Voltammogram of **5i** (8.2 x 10^{-4} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K).

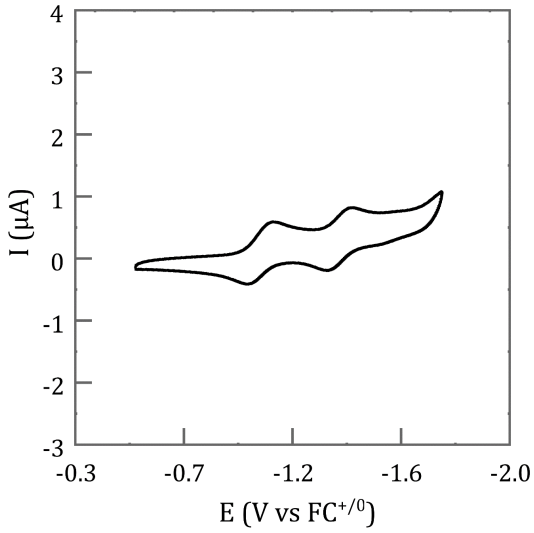


Figure S61. Cyclic Voltammogram of **5j** (5.0 x 10^{-4} M, 0.1 M n-Bu_4NPF_6, in *o*-$C_6H_4Cl_2$, vs. $Fc^{+/0}$, 298 K).

6. UV-Vis and FluorescenceSpectroscopy

Table S2. Optoelectronic Properties of 3a and 5a-j.

	λ_{abs} [nm] (ε [M^{-1} cm^{-1}])	λ_{emi} [nm]	Stokes shift [cm^{-1}]	First $E_{1/2\ red}$ [V]	Second $E_{1/2\ red}$ [V]	Φ [%]
3a	365 (4500), 445 (8300)	587	-	-1.62	-	14
5a	429 (5700), 525 (17500), 561 (21800)	608	1222	-1.01	-1.33	3
5b	431 (2600), 521 (14400), 559 (19400)	603	1306	-0.98	-1.29	1
5c	432 (3600), 519 (16300), 556 (21900)	607	1511	-0.97	-1.29	1
5d	430 (3900), 515 (21100), 553 (29000)	610	1690	-1.00	-1.49	1
5e	433 (8500), 521 (23600), 558 (28800)	607	1446	-0.95	-1.24	<1
5f	431 (5500), 520 (19400), 559 (25000)	616	1656	-0.97	-1.26	<1
5g	430 (8700), 527 (28700), 563 (36200)	616	1528	-0.99	-1.30	<1
5h	425 (4700), 510 (19500), 546 (25400)	604	1759	-1.05	-1.36	<1
5i	426 (6500), 509 (23700), 546 (29400)	601	1677	-1.08	-1.39	<1
5j	427 (6400), 516 (16600), 551 (20300)	607	1674	-1.02	-1.33	<1

Optical measurements were performed at 10^{-6}-10^{-5} M in *o*-$C_6H_4Cl_2$ at 298 K. Cyclic voltammetry experiments were performed at 10^{-4}-10^{-3} M in *o*-$C_6H_4Cl_2$ at 298 K. Reduction potentials are cited with respect to $Fc^{+/0}$ using ferrocene as an internal standard.

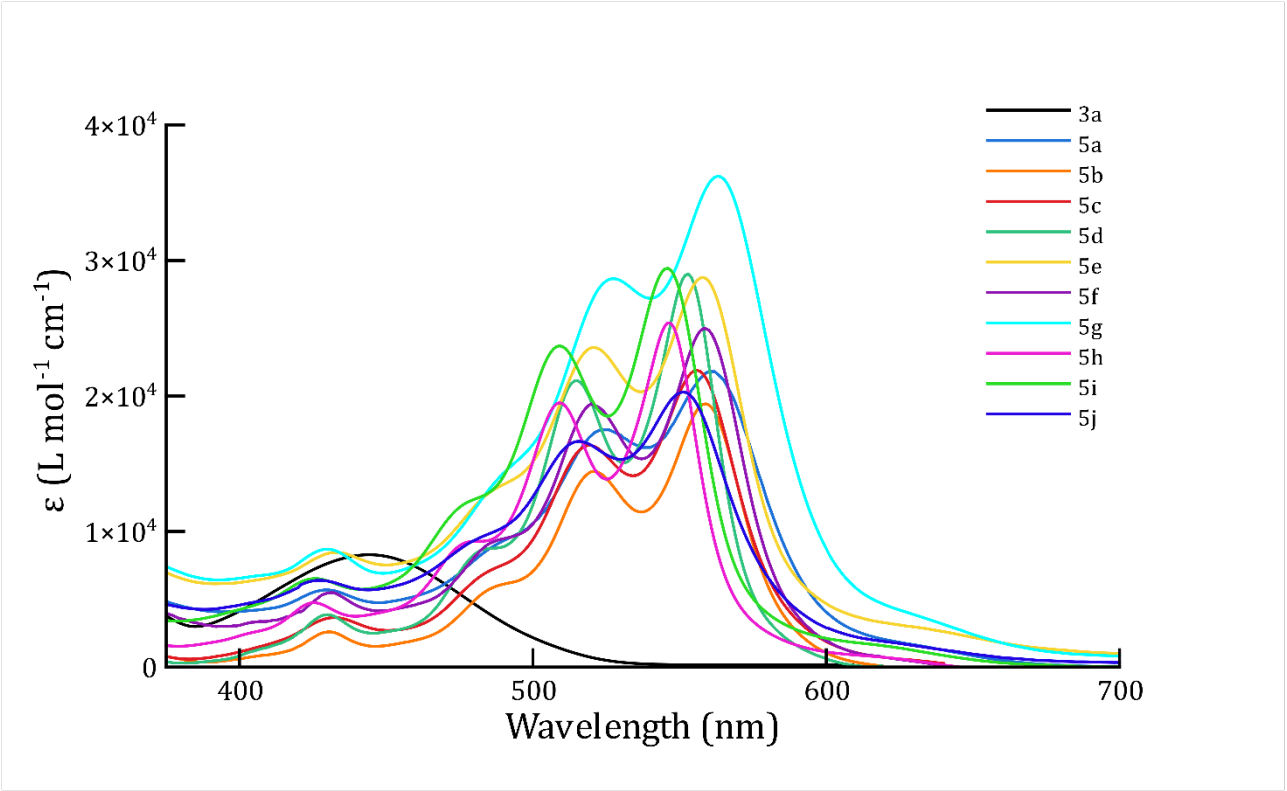


Figure S62. UV-Vis absorption spectra of boron-containing PAHs **3a** and **5a-j** (10^{-6} - 10^{-5} M in *o*-$C_6H_4Cl_2$, 298 K).

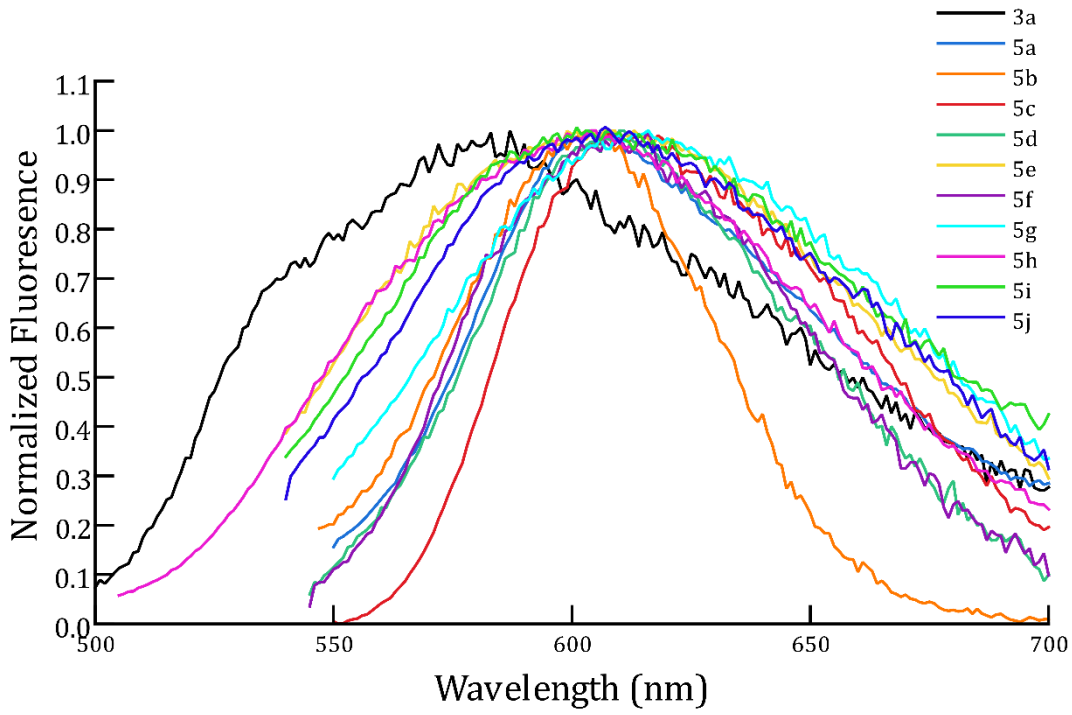


Figure S63. Fluorescence spectra of boron-containing PAHs **3a** and **5a-j** (10^{-6} - 10^{-5} M in *o*-$C_6H_4Cl_2$, 298 K).

7. X-ray Crystallography

Crystal Data for 5-(p-tolyl)benzo[3,4]borinino[1,2-a]naphtho[1,8-de]borinine 3a ($C_{27}H_{19}B$)：*M*r = 354.23, 0.200x0.150x0.100 mm^3, Monoclinic space group $P2_1/c$, *a* = 15.6381(8) Å, α = 90°, *b* = 14.3429(6) Å, β = 98.268(2)°, *c* = 8.1555(4) Å, γ = 90°, *V* = 1810.23(15) $Å^3$, *Z* = 4, ρ(*calcd*) = 1.300 Mg/m^3, μ = 0.073 mm^{-1}, $F_{(000)}$ = 744, *GooF*(F^2) = 1.052, R_1 = 0.0436, wR^2 = 0.1184 for I>2σ(I), R_1 = 0.0490, wR^2 = 0.1243 for all data, 4680 unique reflections [θ ≤ 25.242°] with a completeness of 99.9% and 254 parameters, 0 restraints.

Crystal Data for 5a ($C_{44}H_{30}B_2$): *M*r = 580.30, 0.120x0.075x0.020 mm^3, Triclinic space group P-1, *a* = 9.0920(3) Å, α = 92.2249(14)°, *b* = 10.7481(3) Å, β = 103.0066(13)°, *c* = 15.4529(5) Å, γ = 95.7954(12)°, *V* = 1460.87(8) $Å^3$, *Z* = 2, ρ(*calcd*) = 1.319 Mg/m^3, μ = 0.556 mm^{-1}, $F_{(000)}$ = 608, *GooF*(F^2) = 1.065, R_1 = 0.0523, wR^2 = 0.1408 for I>2σ(I), R_1 = 0.0679, wR^2 = 0.1488 for all data, 5491 unique reflections [θ ≤ 67.679°] with a completeness of 99.4% and 417 parameters, 0 restraints.

Crystal Data for 5c ($C_{50}H_{30}B_2$): *M*r = 652.36, 0.090x0.050x0.040 mm^3, Monoclinic space group C2/c, *a* = 43.961(2) Å, α = 90°, *b* = 9.5533(4) Å, β = 95.191(3)°, *c* = 7.9022(4) Å, γ = 90°, *V* = 3305.1(3) $Å^3$, *Z* = 4, ρ(*calcd*) = 1.311 Mg/m^3, μ = 0.556 mm^{-1}, $F_{(000)}$ = 1360, *GooF*(F^2) = 1.030, R_1 = 0.0507, wR^2 = 0.1375 for I>2σ(I), R_1 = 0.0669, wR^2 = 0.1491 for all data, 3236 unique reflections [θ ≤ 67.679°] with a completeness of 99.6% and 236 parameters, 0 restraints.

Crystal Data for 5d ($C_{48}H_{38}B_2$): *M*r = 636.40, 0.150 x 0.110 x 0.080 mm^3, Monoclinic space group $P2_1/c$, *a* = 19.8935(12) Å, α = 90°, *b* = 7.5081(4) Å, β = 92.113(2)°, *c* = 11.7916(7) Å, γ = 90°, *V* = 1760.02(18) $Å^3$, *Z* = 2, ρ(*calcd*) = 1.201 Mg/m^3, μ = 0.503 mm^{-1}, $F_{(000)}$ = 672, *GooF*(F^2) = 1.038, R_1 = 0.0427, wR^2 = 0.1176 for I>2σ(I), R_1 = 0.0462, wR^2 = 0.1221 for all data, 27436 unique reflections [θ ≤ 67.679°] with a completeness of 99.7% and 229 parameters, 0 restraints.

Crystal Data for 5f ($C_{42}H_{24}B_2F_2$): *M*r = 588.23, 0.070x0.060x0.040 mm^3, Orthorhombic space group Pbca, *a* = 8.1524(2) Å, α = 90°, *b* = 8.4349(2) Å, β = 90°, *c* = 40.5242(11) Å, γ = 90°, *V* = 2786.63(12) $Å^3$, *Z* = 4, ρ(*calcd*) = 1.402 Mg/m^3, μ = 0.699 mm^{-1}, $F_{(000)}$ = 1216, *GooF*(F^2) = 1.106, R_1 = 0.0524, wR^2 = 0.1507 for I>2σ(I), R_1 = 0.0587, wR^2 = 0.1550 for all data, 2723 unique reflections [θ ≤ 67.679°] with

a completeness of 99.6% and 208 parameters, 0 restraints.

Crystal Data for 5g ($C_{38}H_{22}B_2S_2$): *M*r = 564.29, 0.100x0.030x0.030 mm^3, Triclinic space group P-1, *a* = 9.3575(2) Å, α = 96.4677(12)°, *b* = 12.6004(3) Å, β = 98.9712(13)°, *c* = 17.5852(5) Å, γ = 104.1357(12)°, *V* = 1961.32(8) $Å^3$, *Z* = 3, ρ(*calcd*) = 1.433 Mg/m^3, μ = 2.058 mm^{-1}, $F_{(000)}$ = 876, *GooF*(F^2) = 1.023, R_1 = 0.0393, wR^2 = 0.1020 for I>2σ(I), R_1 = 0.0510, wR^2 = 0.1123 for all data, 7622 unique reflections [θ ≤ 67.679°] with a completeness of 99.3% and 706 parameters, 1073 restraints.

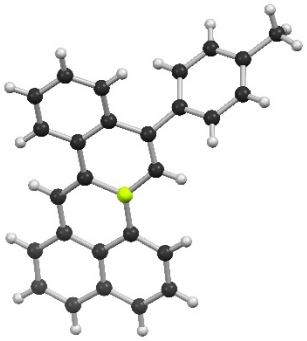


Figure S64: Solid-state structure of **3a**. C: black, B: yellow-green, H: grey.

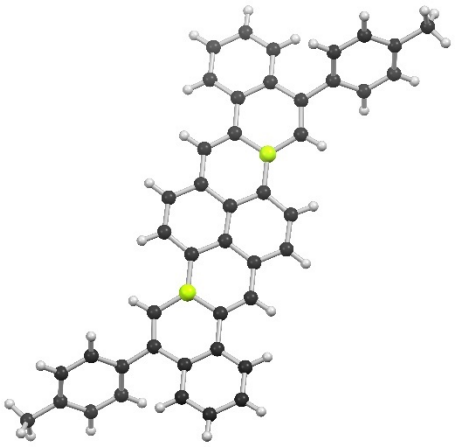


Figure S65: Solid-state structure of **5a**. C: black, B: yellow-green, H: grey.

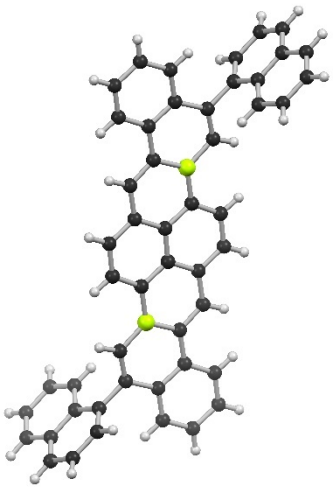


Figure S66: Solid-state structure of **5c**. C: black, B: yellow-green, H: grey

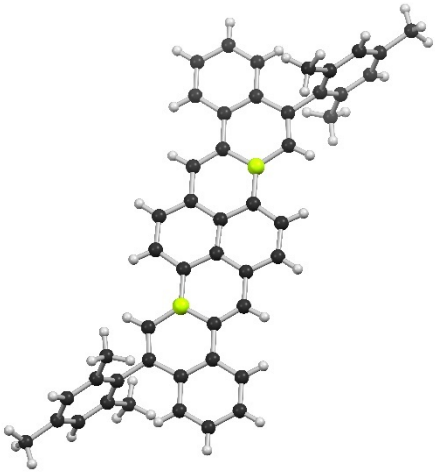


Figure S67: Solid-state structure of **5d**. C: black, B: yellow-green, H: grey

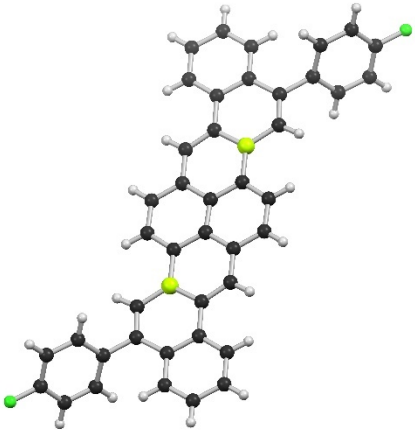


Figure S68: Solid-state structure of **5f**. C: black, B: yellow-green, H: grey, F: green

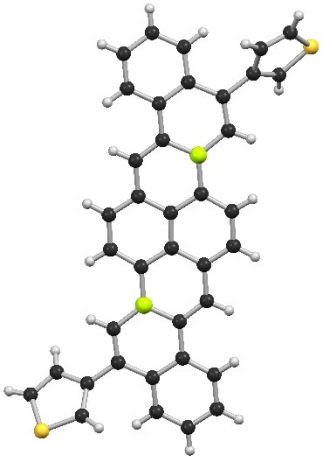


Figure S69: Solid-state structure of **5g**. C: black, B: yellow-green, H: grey, S: yellow.

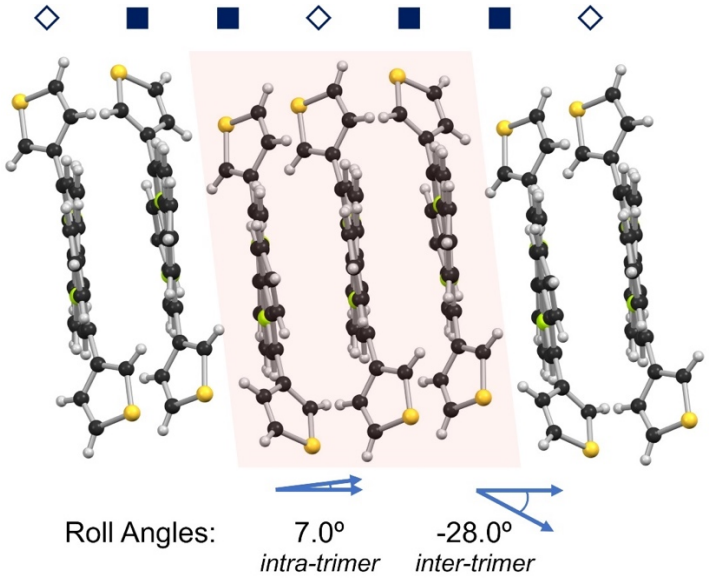


Figure S70: Intra-trimer and inter-trimer roll angles in π-stacks of compound **5g**.

8. Computations

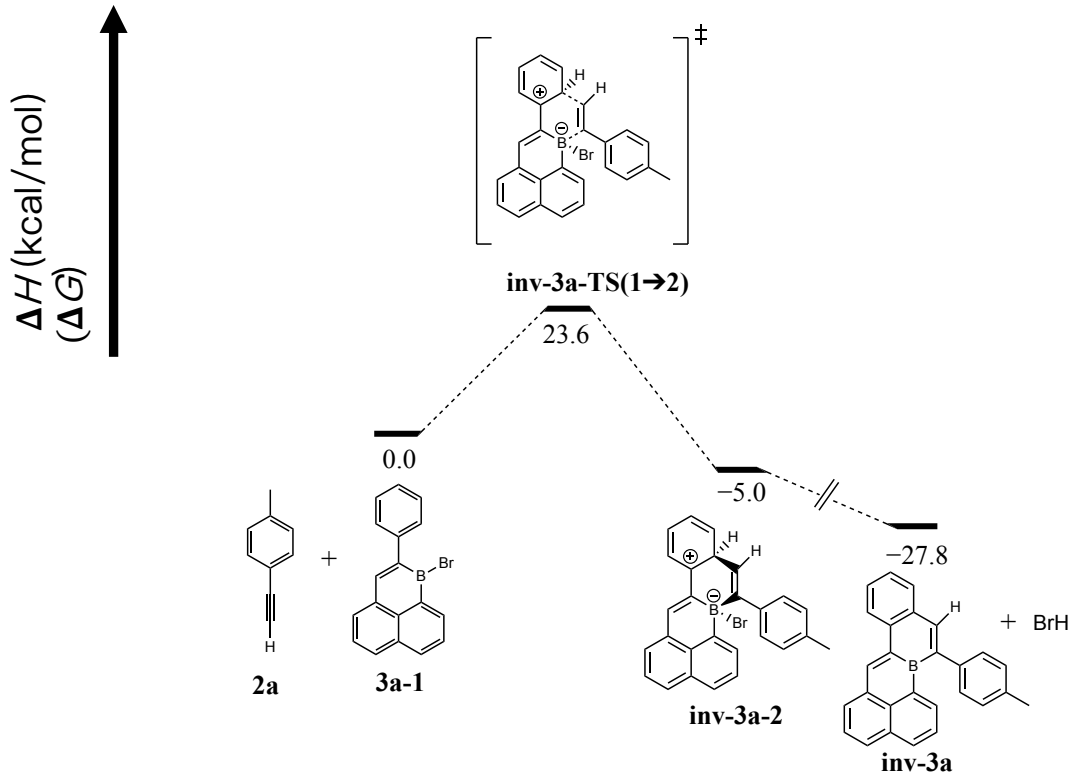


Figure S71: DFT-calculated enthalpy and free energy profile of the formation of the regioisomer (**inv-3a**) of **3a** with inverted orientation of alkyne **2a** (optimized in CPCM solvation model, solvent: CH_2Cl_2, B3LYP-D3(BJ)/def2-TZVP//B3LYP-D3(BJ)/def2-SVP).

Table S3: Enthalpies and Gibbs free energies of all species in energy diagrams.

Species	E_{elec}	ZPE + H_{vib} + 4RT	H(Eh)	ZPE + H_{vib} + 4RT - TS	G(Eh)
2a	-347.8769	0.1460	-347.7309	0.1025	-347.7744
3a-1	-3292.5959	0.2632	-3292.3327	0.2036	-3292.3923
3a-TS(1➔2)	-3640.4685	0.4093	-3640.0592	0.3268	-3640.1417
3a-2	-3640.4711	0.4104	-3640.0607	0.3283	-3640.1427
3a-TS(2➔3)	-3640.4591	0.4095	-3640.0495	0.3299	-3640.1291
3a-3	-3640.4821	0.4113	-3640.0708	0.3314	-3640.1508
3a	-1065.7241	0.3995	-1065.3246	0.3266	-1065.3975
HBr	-2574.7918	0.0093	-2574.7825	-0.0133	-2574.8051
inv-3a-TS(1➔2)	-3640.4348	0.4089	-3640.0259	0.3284	-3640.1064
inv-3a-2	-3640.4827	0.4112	-3640.0715	0.3319	-3640.1508
inv-3a	-1065.7249	0.3995	-1065.3254	0.3262	-1065.3987

Coordinates of optimized structures in CPCM solvation model (CH_2Cl_2)

17
2a
C -1.468873 0.327747 2.071533
H -2.285661 -0.333656 2.296519
C -0.545965 1.077109 1.819245
C 0.541076 1.960270 1.520847
C 1.700550 1.972427 2.322259
H 1.766770 1.298468 3.178560
C 2.755494 2.832171 2.024608
H 3.647308 2.823416 2.656744
C 2.696531 3.707679 0.927551
C 1.540070 3.688444 0.130482
H 1.472137 4.355688 -0.732753
C 0.477615 2.833804 0.416643
H -0.411825 2.833162 -0.216401
C 3.827570 4.657583 0.631872
H 3.688201 5.610674 1.171324
H 4.795765 4.242708 0.949579
H 3.884337 4.895517 -0.440702

32
3a-1
C -1.593607 0.045492 -1.770468
C -0.232939 0.429888 -1.997499
C 0.066462 1.286757 -3.058446
H 1.106475 1.577379 -3.227154
C -0.940100 1.782211 -3.911797
H -0.672718 2.449831 -4.733242
C -2.257983 1.422276 -3.705850
H -3.046011 1.800390 -4.361551
C -2.611940 0.551897 -2.637177
C -3.960003 0.169482 -2.409696
H -4.737382 0.558474 -3.072134
C -4.287231 -0.681476 -1.369031
H -5.327013 -0.970313 -1.202033
C -3.277414 -1.178474 -0.522904
H -3.551687 -1.851434 0.292627
C -1.932180 -0.835746 -0.694109
5 0 -0.788409 -1.350368 0.206990
C 1.870754 -1.197659 2.130604
C 3.009979 -1.554239 2.854740
H 3.008363 -1.462846 3.943773
C 4.149319 -2.024525 2.192994
H 5.037889 -2.309661 2.761293
C 4.140658 -2.128855 0.798916
H 5.022399 -2.500840 0.271165
C 3.002789 -1.764303 0.074800
H 2.998764 -1.863293 -1.013301
C 1.848103 -1.291858 0.726527
C 0.653911 -0.879616 -0.055940

C 0.826508 -0.050346 -1.135967
H 1.832885 0.308020 -1.381227
35 0 -1.182778 -2.651492 1.617325
H 0.990688 -0.826046 2.657676

49

3a-TS(1➔2)

C -1.610306 0.080315 -1.742369
C -0.235108 0.403501 -2.004588
C 0.081530 1.184817 -3.112332
H 1.129251 1.429366 -3.305837
C -0.917561 1.656700 -3.992204
H -0.634350 2.270786 -4.850295
C -2.240728 1.331360 -3.776827
H -3.019084 1.679390 -4.460599
C -2.616264 0.533617 -2.658089
C -3.970973 0.175012 -2.424874
H -4.736865 0.521204 -3.123744
C -4.310098 -0.601989 -1.335000
H -5.352300 -0.883381 -1.164830
C -3.314175 -1.027303 -0.428767
H -3.607976 -1.632366 0.432971
C -1.973067 -0.697436 -0.597196
5 0 -0.846709 -1.047448 0.472625
C -1.333095 0.157128 1.809721
H -2.275198 -0.112467 2.272976
C -0.495596 1.087500 1.823997
C 1.833121 -1.381650 2.152393
C 2.978643 -1.745168 2.862399
H 2.938901 -1.805925 3.953013
C 4.169164 -2.033201 2.187962
H 5.063785 -2.323915 2.743808
C 4.195810 -1.958715 0.791492
H 5.112346 -2.200060 0.247050
C 3.050949 -1.588128 0.084593
H 3.085315 -1.561041 -1.006275
C 1.844990 -1.273918 0.746279
C 0.650158 -0.826565 -0.010704
C 0.828457 -0.101663 -1.148598
H 1.840385 0.163380 -1.473303
C 0.535240 1.998516 1.581707
C 1.707854 2.012381 2.379552
H 1.783572 1.336441 3.231040
C 2.749860 2.866903 2.060212
H 3.653826 2.868802 2.673342
C 2.668976 3.727990 0.945744
C 1.502488 3.711963 0.157571
H 1.433565 4.367749 -0.712805
C 0.446094 2.867401 0.465136
H -0.448187 2.842892 -0.158406
C 3.808978 4.649853 0.622530
H 3.882555 5.446025 1.382959

H 4.768245 4.109206 0.634823
H 3.682995 5.126868 -0.358803
35 0 -1.159334 -2.846894 1.428177
H 0.917570 -1.165922 2.700192

49
3a-2
C -2.245613 -0.465532 -2.288034
C -0.988400 -0.871939 -2.857325
C -0.911598 -1.142971 -4.220104
H 0.048203 -1.447320 -4.646049
C -2.040244 -1.025329 -5.061917
H -1.944782 -1.249189 -6.127100
C -3.252014 -0.622507 -4.541850
H -4.129478 -0.521434 -5.185752
C -3.382815 -0.329301 -3.153591
C -4.620564 0.097951 -2.604934
H -5.484100 0.203923 -3.266795
C -4.725971 0.376831 -1.256547
H -5.679064 0.708690 -0.836945
C -3.603518 0.228237 -0.413749
H -3.730955 0.431813 0.653829
C -2.366040 -0.195235 -0.888174
5 0 -1.113734 -0.445569 0.074470
C -0.949124 0.812645 1.175581
H -1.900532 1.177049 1.583527
C 0.137270 1.376031 1.529601
C 1.787709 -1.364573 1.227944
C 3.005372 -1.229588 1.893957
H 3.162390 -1.747874 2.843226
C 4.015857 -0.419388 1.365594
H 4.958648 -0.293038 1.902709
C 3.806662 0.233458 0.146096
H 4.585121 0.876418 -0.271624
C 2.596605 0.081268 -0.530211
H 2.427131 0.620854 -1.464346
C 1.554964 -0.708577 0.001053
C 0.245769 -0.762386 -0.689926
C 0.210269 -0.955669 -2.033637
H 1.135877 -1.182424 -2.576977
C 1.302016 2.034185 1.885534
C 2.030942 1.653199 3.046072
H 1.676035 0.813302 3.642742
C 3.167740 2.355333 3.411206
H 3.718389 2.062875 4.307474
C 3.634445 3.433017 2.634920
C 2.917127 3.804603 1.475476
H 3.274729 4.640565 0.870644
C 1.773214 3.127013 1.101324
H 1.218761 3.413027 0.206483
C 4.894477 4.155073 3.006924
H 5.742848 3.738015 2.435636
H 4.833521 5.224795 2.758546

H 5.127897 4.043601 4.074861
35 0 -1.662931 -2.078849 1.372272
H 0.996392 -1.979605 1.655480

49

3a-TS(2➔3)

C 7.445113 5.575287 0.906173
C 8.606768 5.077186 0.212384
C 8.498861 4.693572 -1.123037
H 9.387178 4.322657 -1.640985
C 7.275203 4.787487 -1.819417
H 7.221663 4.473797 -2.864357
C 6.157172 5.288185 -1.184131
H 5.208427 5.378191 -1.719542
C 6.215236 5.700900 0.178103
C 5.076061 6.239683 0.833362
H 4.141286 6.336324 0.275114
C 5.156483 6.639516 2.152590
H 4.280925 7.062282 2.651960
C 6.367162 6.492652 2.864918
H 6.391591 6.790731 3.917337
C 7.511561 5.956347 2.283240
5 0 8.846345 5.686993 3.108586
C 9.324796 6.837856 4.146395
H 8.611024 7.615130 4.456742
C 10.540093 7.013299 4.594093
C 11.607405 5.272085 4.163453
C 12.907641 5.382539 4.740269
H 13.036093 5.152909 5.799679
C 13.968282 5.827238 3.987649
H 14.956423 5.954832 4.433405
C 13.772321 6.114470 2.611781
H 14.612031 6.484943 2.018778
C 12.541583 5.928281 2.005490
H 12.415697 6.161026 0.946957
C 11.427774 5.469110 2.751911
C 10.097021 5.332034 2.180999
C 9.903485 5.041310 0.863662
H 10.746674 4.757391 0.222974
C 11.451507 7.903838 5.252535
C 11.703270 7.804531 6.638222
H 11.179496 7.046348 7.223624
C 12.607041 8.664276 7.247170
H 12.784328 8.585504 8.322840
C 13.305175 9.636421 6.502153
C 13.059538 9.721803 5.123480
H 13.591679 10.467702 4.528273
C 12.149404 8.869154 4.500360
H 11.970781 8.938970 3.426144
C 14.281702 10.556966 7.182246
H 15.028827 9.985716 7.756452
H 14.811832 11.192146 6.458989

H 13.763465 11.215002 7.899720
35 0 8.387774 3.953299 4.371442
H 10.854712 4.683863 4.693966

49
3a-3
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C -1.259333 -0.880144 -3.100594
C -1.542761 -1.221605 -4.429605
H -0.722349 -1.531915 -5.081376
C -2.852463 -1.168389 -4.935059
H -3.047099 -1.444294 -5.973268
C -3.889093 -0.756873 -4.115439
H -4.909268 -0.704307 -4.504436
C -3.658037 -0.391564 -2.760377
C -4.719933 0.047337 -1.925324
H -5.730673 0.099046 -2.337436
C -4.468980 0.408065 -0.615969
H -5.285492 0.752561 0.023413
C -3.157665 0.329326 -0.098722
H -2.987849 0.607662 0.945158
C -2.080332 -0.111752 -0.863564
5 0 -0.616813 -0.250684 -0.275865
C -0.056261 0.811322 0.747864
H -0.678384 1.616878 1.153974
C 1.254166 0.813332 1.064939
C 2.116130 -0.331628 0.493122
C 3.513057 -0.433305 0.952792
H 3.715960 -0.206572 2.000347
C 4.514622 -0.842585 0.126362
H 5.536141 -0.950541 0.494472
C 4.224648 -1.122511 -1.242361
H 5.040313 -1.429115 -1.901893
C 2.945203 -1.031498 -1.757086
H 2.783500 -1.269488 -2.808490
C 1.854304 -0.652902 -0.945613
C 0.484490 -0.628840 -1.356977
C 0.102751 -0.924454 -2.649374
H 0.838289 -1.205748 -3.410065
C 1.881635 1.816650 1.957110
C 1.260415 2.190066 3.160256
H 0.338199 1.687771 3.460034
C 1.812538 3.178006 3.979420
H 1.308893 3.442898 4.913089
C 3.004978 3.828253 3.632126
C 3.625952 3.455054 2.427095
H 4.551591 3.952378 2.123784
C 3.080547 2.468771 1.608441
H 3.580878 2.214584 0.670953
C 3.617424 4.881290 4.519635
H 2.943331 5.156727 5.343527
H 4.562896 4.525639 4.963282
H 3.855685 5.794324 3.950510

35 0 -0.676721 -2.214804 0.973423
H 1.605628 -1.225991 0.980958

47
3a
C -2.318254 -0.376733 -2.304461
C -1.327422 -1.100954 -3.050310
C -1.716653 -1.802406 -4.195659
H -0.960235 -2.352352 -4.761617
C -3.055464 -1.817057 -4.632442
H -3.325531 -2.375568 -5.530965
C -4.021259 -1.126467 -3.923537
H -5.062715 -1.132545 -4.254623
C -3.676302 -0.396448 -2.752737
C -4.654332 0.320185 -2.011986
H -5.692004 0.304224 -2.355003
C -4.300626 1.026641 -0.876873
H -5.059236 1.574632 -0.313503
C -2.957380 1.040741 -0.446837
H -2.701687 1.607195 0.452364
C -1.951155 0.354539 -1.132762
5 0 -0.464015 0.349597 -0.682828
C 0.107470 1.128973 0.499065
H -0.496163 1.798174 1.121689
C 1.449231 1.089981 0.779435
C 2.381519 0.227095 0.026680
C 3.724463 0.101256 0.448014
H 4.054971 0.640858 1.334600
C 4.634747 -0.703657 -0.227621
H 5.665025 -0.779002 0.127551
C 4.218306 -1.419172 -1.357223
H 4.922052 -2.054523 -1.900269
C 2.895946 -1.331466 -1.777859
H 2.587140 -1.915790 -2.645572
C 1.948363 -0.528426 -1.109533
C 0.538501 -0.471521 -1.525047
C 0.058219 -1.121230 -2.636816
H 0.719087 -1.703792 -3.287197
C 1.977813 1.949173 1.877918
C 1.437379 1.863845 3.170092
H 0.662223 1.122230 3.376109
C 1.885845 2.702064 4.194262
H 1.453459 2.606095 5.193928
C 2.879816 3.663100 3.963220
C 3.411064 3.756037 2.665111
H 4.178680 4.505238 2.451618
C 2.975596 2.913974 1.643722
H 3.402324 3.013814 0.643233
C 3.377255 4.563851 5.064601
H 2.767244 4.464366 5.974021
H 4.420594 4.324338 5.331422
H 3.361891 5.620929 4.753918

2
HBr
H 0.000000 0.000000 -0.114882
35 0 0.000000 0.000000 1.314882

49
inv-3a-TS(1➔2)
C 0.474601 2.368065 -0.086546
C -0.846560 2.775288 -0.481903
C -1.064497 4.081233 -0.914125
H -2.073191 4.377787 -1.213553
C -0.015152 5.022755 -0.977013
H -0.219636 6.039449 -1.320061
C 1.261357 4.655834 -0.603871
H 2.081599 5.377190 -0.643056
C 1.535205 3.333654 -0.152164
C 2.842085 2.953589 0.250274
H 3.648438 3.689154 0.190569
C 3.081417 1.678508 0.722411
H 4.085058 1.390032 1.044057
C 2.030296 0.741460 0.795086
H 2.247507 -0.249926 1.193300
C 0.731632 1.041803 0.385901
5 0 -0.466482 0.000280 0.477313
C -0.179667 -1.503391 -0.486271
C -1.199490 -2.129025 -0.894402
C -3.300193 -1.455125 0.540066
C -4.290259 -2.387883 0.207210
H -4.544529 -3.178524 0.916359
C -4.937113 -2.315087 -1.024707
H -5.698224 -3.051521 -1.292152
C -4.604822 -1.288624 -1.925134
H -5.102204 -1.233549 -2.896095
C -3.636549 -0.349673 -1.591589
H -3.366185 0.427704 -2.308266
C -2.951908 -0.407722 -0.349735
C -1.858266 0.537745 -0.059732
C -1.947352 1.827438 -0.480208
H -2.893206 2.209208 -0.881688
35 0 -0.478485 -0.802467 2.421228
H -2.800231 -1.515877 1.505187
H -1.947321 -2.778080 -1.322159
C 1.250789 -1.875361 -0.676100
C 2.014480 -1.252410 -1.671916
C 1.850691 -2.808047 0.175090
C 3.364837 -1.567303 -1.810663
H 1.551773 -0.510749 -2.325140
C 3.209858 -3.103824 0.033823
H 1.260065 -3.280613 0.961242
C 3.990376 -2.491792 -0.956974
H 3.949923 -1.074434 -2.591800
H 3.670725 -3.827210 0.711486

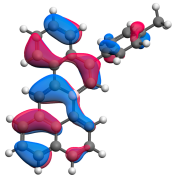
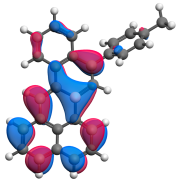
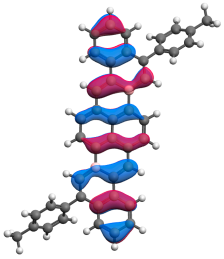
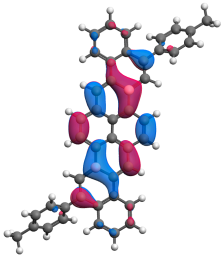
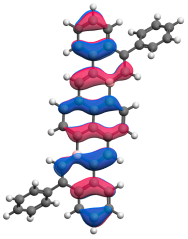
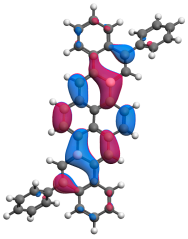
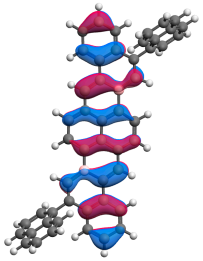
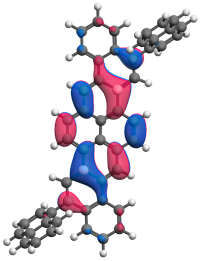
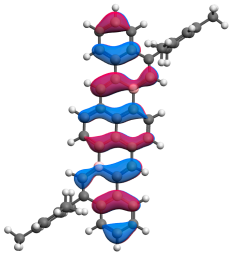
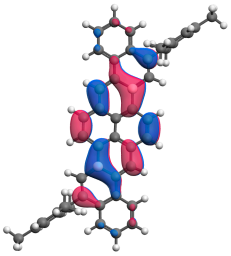
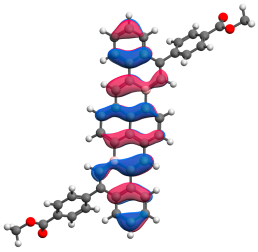
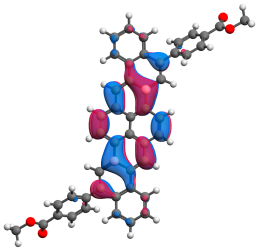
C 5.455565 -2.810024 -1.113096
H 5.660583 -3.264990 -2.096409
H 6.069734 -1.897081 -1.048855
H 5.801399 -3.508897 -0.338071

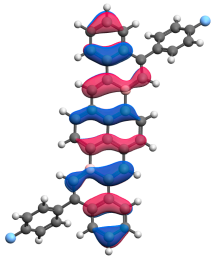
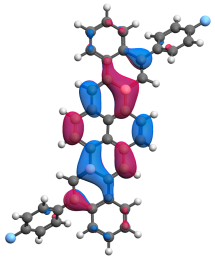
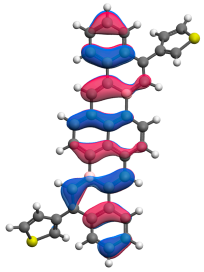
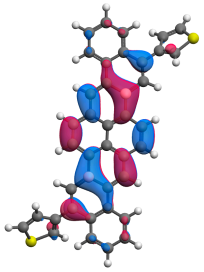
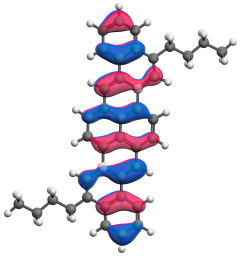
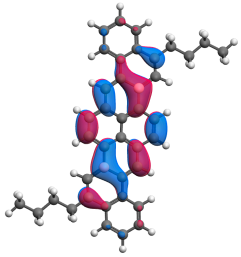
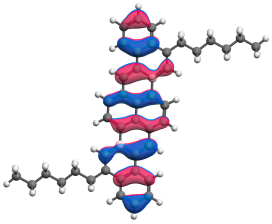
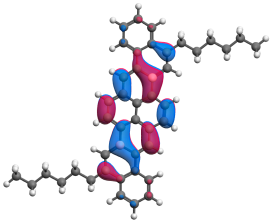
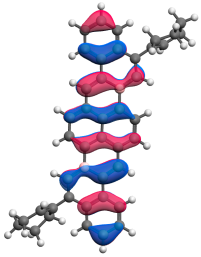
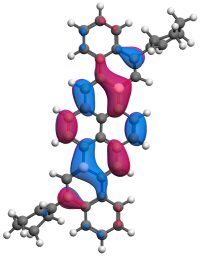
49
inv-3a-2
C 0.454847 2.600234 -0.242445
C -0.822162 2.942520 -0.827813
C -1.049159 4.243135 -1.297517
H -2.020531 4.483285 -1.736763
C -0.058727 5.234991 -1.211336
H -0.260819 6.241261 -1.583381
C 1.170254 4.929721 -0.652372
H 1.945983 5.696487 -0.579924
C 1.455583 3.626722 -0.159646
C 2.714873 3.322149 0.420164
H 3.474305 4.105585 0.480140
C 2.963826 2.052957 0.904539
H 3.929966 1.818864 1.358310
C 1.973597 1.052800 0.813918
H 2.193825 0.062313 1.215618
C 0.722073 1.287222 0.244978
5 0 -0.400114 0.167194 0.148341
C -0.056691 -1.322912 -0.342995
C -1.100692 -2.146480 -0.551488
C -2.523269 -1.683335 -0.293033
C -3.581151 -2.682512 -0.530299
H -3.353217 -3.722543 -0.283795
C -4.809316 -2.328974 -0.996637
H -5.595479 -3.073388 -1.132995
C -5.067590 -0.962206 -1.323657
H -6.057345 -0.688941 -1.697937
C -4.108257 0.022792 -1.189159
H -4.364026 1.046100 -1.464706
C -2.813735 -0.276189 -0.708720
C -1.757045 0.667011 -0.516721
C -1.872872 1.974073 -0.944091
H -2.788448 2.333182 -1.424789
35 0 -1.036419 -0.157260 2.332964
H -2.515548 -1.537144 0.837646
H -0.979865 -3.186061 -0.873250
C 1.322286 -1.815400 -0.572353
C 2.200209 -1.145335 -1.446387
C 1.800701 -2.964203 0.078450
C 3.493921 -1.613579 -1.664269
H 1.855303 -0.248612 -1.964733
C 3.104411 -3.423849 -0.133151
H 1.144526 -3.492004 0.774580
C 3.975789 -2.759323 -1.006833
H 4.149428 -1.077410 -2.356768
H 3.451515 -4.316338 0.395189
C 5.386569 -3.240887 -1.233440

H 5.591073 -3.390457 -2.306291
H 6.122719 -2.504800 -0.868425
H 5.576657 -4.191675 -0.714493

47
inv-3a
C 0.410728 2.767358 -0.416204
C -0.935390 3.097098 -0.789158
C -1.294238 4.438914 -0.952803
H -2.322714 4.679890 -1.233867
C -0.367544 5.479079 -0.752648
H -0.676947 6.516641 -0.893414
C 0.925618 5.181509 -0.363761
H 1.650525 5.980835 -0.190952
C 1.335506 3.832807 -0.176272
C 2.650659 3.519427 0.258367
H 3.354842 4.334721 0.442810
C 3.025427 2.204793 0.458781
H 4.030538 1.967505 0.814526
C 2.114275 1.161934 0.192952
H 2.443340 0.136808 0.357838
C 0.813147 1.400950 -0.266331
5 0 -0.222168 0.276515 -0.580159
C 0.063031 -1.245822 -0.695242
C -1.022983 -2.074271 -0.793210
C -2.409803 -1.654073 -0.870111
C -3.420245 -2.636216 -0.953845
H -3.130146 -3.690148 -0.937071
C -4.760943 -2.284666 -1.056002
H -5.530323 -3.057794 -1.115979
C -5.116718 -0.927425 -1.078553
H -6.167527 -0.637310 -1.152865
C -4.133228 0.054674 -1.000579
H -4.440119 1.101796 -1.006411
C -2.766091 -0.274257 -0.897661
C -1.692759 0.724531 -0.797815
C -1.936387 2.069402 -0.943203
H -2.938737 2.437114 -1.186216
H -0.862809 -3.158232 -0.851990
C 1.413833 -1.867439 -0.715075
C 2.373376 -1.472205 -1.667554
C 1.772709 -2.882232 0.186372
C 3.632624 -2.065888 -1.711419
H 2.121250 -0.684735 -2.381597
C 3.041079 -3.470279 0.145513
H 1.053288 -3.202310 0.944168
C 3.994997 -3.075455 -0.802037
H 4.354104 -1.739795 -2.466236
H 3.294277 -4.250247 0.869092
C 5.363562 -3.705653 -0.856609
H 5.525174 -4.224638 -1.816322
H 6.157648 -2.946059 -0.767742
H 5.502660 -4.438908 -0.049003

Table S4: Frontier molecular orbitals of **3a** and **5a-j** calculated at the B3LYP-D3(BJ)/def2-TZVP//B3LYP-D3(BJ)/def2-SVP level of theory (isosurface = 0.07 $Å^{-3}$).

compound	HOMO[a]	LUMO[a]	HOMO E (eV)	LUMO E (eV)
3a			-5.871	-2.854
5a			-5.847	-3.509
5b			-5.895	-3.563
5c			-5.915	-3.595
5d			-5.900	-3.566
5e			-6.025	-3.711

5f			-5.983	-3.651
5g			-5.905	-3.571
5h			-5.828	-3.466
5i			-5.823	-3.462
5j			-5.834	-3.481

[a] isosurface = 0.07 Å^{-3}

Coordinates of optimized structures in gas phase

47
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C 7.549992 5.660206 0.892206
C 8.444404 4.716637 0.282803
C 7.984301 3.935259 -0.779717
H 8.667222 3.217036 -1.241541
C 6.668336 4.052270 -1.267607
H 6.341749 3.425741 -2.100450
C 5.796988 4.957520 -0.692568

H 4.773763 5.055793 -1.064441
C 6.215466 5.775476 0.392277
C 5.335071 6.711035 0.998430
H 4.314784 6.799345 0.615528
C 5.758944 7.495771 2.053912
H 5.074513 8.212536 2.513842
C 7.077267 7.369767 2.539476
H 7.391174 7.998966 3.376295
C 7.988694 6.469597 1.984469
5 0 9.447421 6.310142 2.498088
C 10.050962 7.042357 3.692796
H 9.480684 7.732406 4.323831
C 11.337569 6.787148 4.089196
C 12.226680 5.881821 3.334656
C 13.588113 5.770738 3.692591
H 13.968006 6.367470 4.520946
C 14.461531 4.933983 3.007647
H 15.509597 4.874256 3.310110
C 13.990278 4.179821 1.927190
H 14.664173 3.516536 1.379459
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C 12.309760 6.691399 6.421653
H 12.326174 5.601462 6.352853
C 12.724239 7.316712 7.595093
H 13.065587 6.706438 8.436336
C 12.708532 8.716052 7.720109
C 12.252390 9.463602 6.626976
H 12.232166 10.554867 6.693892
C 11.824551 8.840536 5.452220
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C 13.167252 9.378948 8.993943
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H 12.554794 9.058760 9.853394
H 14.211874 9.115002 9.228703

76
5a
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C 8.126181 4.661949 0.576799
C 7.612662 3.833721 -0.425504
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C 6.255333 3.871312 -0.778317
H 5.897769 3.204826 -1.566905
C 5.356789 4.736618 -0.150273
C 5.862015 5.591969 0.876911
C 4.974360 6.496511 1.551185
C 5.485931 7.317868 2.560121

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C 6.841188 7.272980 2.919979
H 7.196758 7.932391 3.715387
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C 9.920415 7.113198 3.790574
H 9.372654 7.770984 4.473539
C 11.251629 6.931079 4.066808
C 12.118517 6.077280 3.229369
C 13.512198 6.054917 3.450885
H 13.934067 6.680055 4.236809
C 14.365279 5.270456 2.681920
H 15.439706 5.279061 2.879074
C 13.838683 4.482548 1.653242
H 14.495815 3.860582 1.040649
C 12.471536 4.507668 1.399246
H 12.083689 3.907151 0.575266
C 11.584200 5.295279 2.157851
C 10.145393 5.360996 1.860705
C 9.537785 4.592275 0.903593
H 10.103140 3.859599 0.317483
C 11.836429 7.616140 5.253553
C 12.456637 6.892389 6.288901
H 12.544189 5.806956 6.205438
C 12.939058 7.539664 7.423640
H 13.405086 6.951181 8.219255
C 12.835068 8.933458 7.567496
C 12.218990 9.652037 6.534841
H 12.126971 10.738451 6.617524
C 11.721446 9.006236 5.400857
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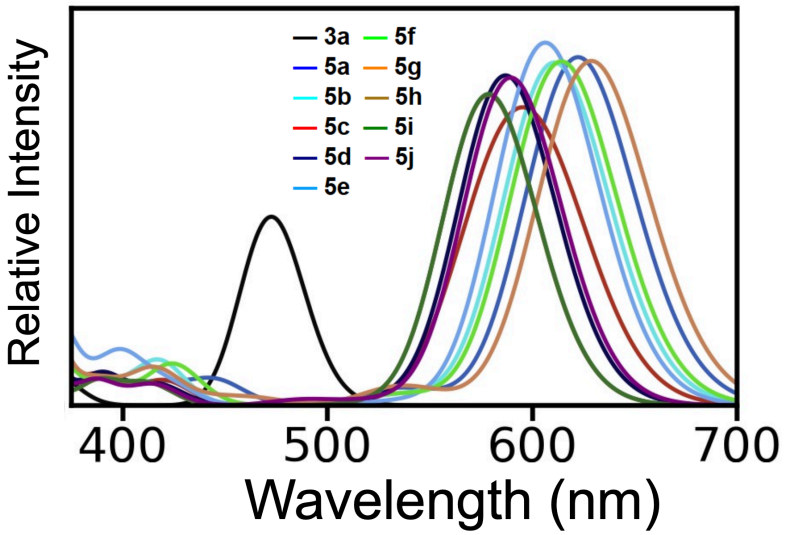

Figure S72: TD-DFT-simulated absorption spectra of **3a** and **5a-j** in $C_6H_4Cl_2$ calculated at the B3LYP-D3(BJ)/def2-TZVP//B3LYP-D3(BJ)/def2-SVP level of theory.

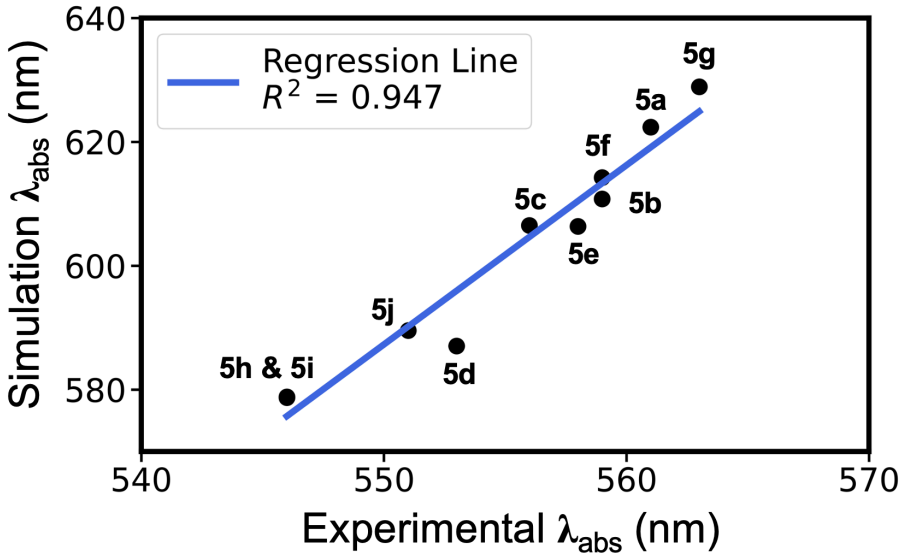

Figure S73: Correlation graph comparing the lowest energy absorption maxima measured for compounds **5a**-**j** (solvent: *o*-$C_6H_4Cl_2$) to those calculated for **5a-j** using TD-DFT at the level of B3LYP-D3(BJ)/def2-TZVP//B3LYP-D3(BJ)/def2-SVP, solvent: *o*-$C_6H_4Cl_2$).

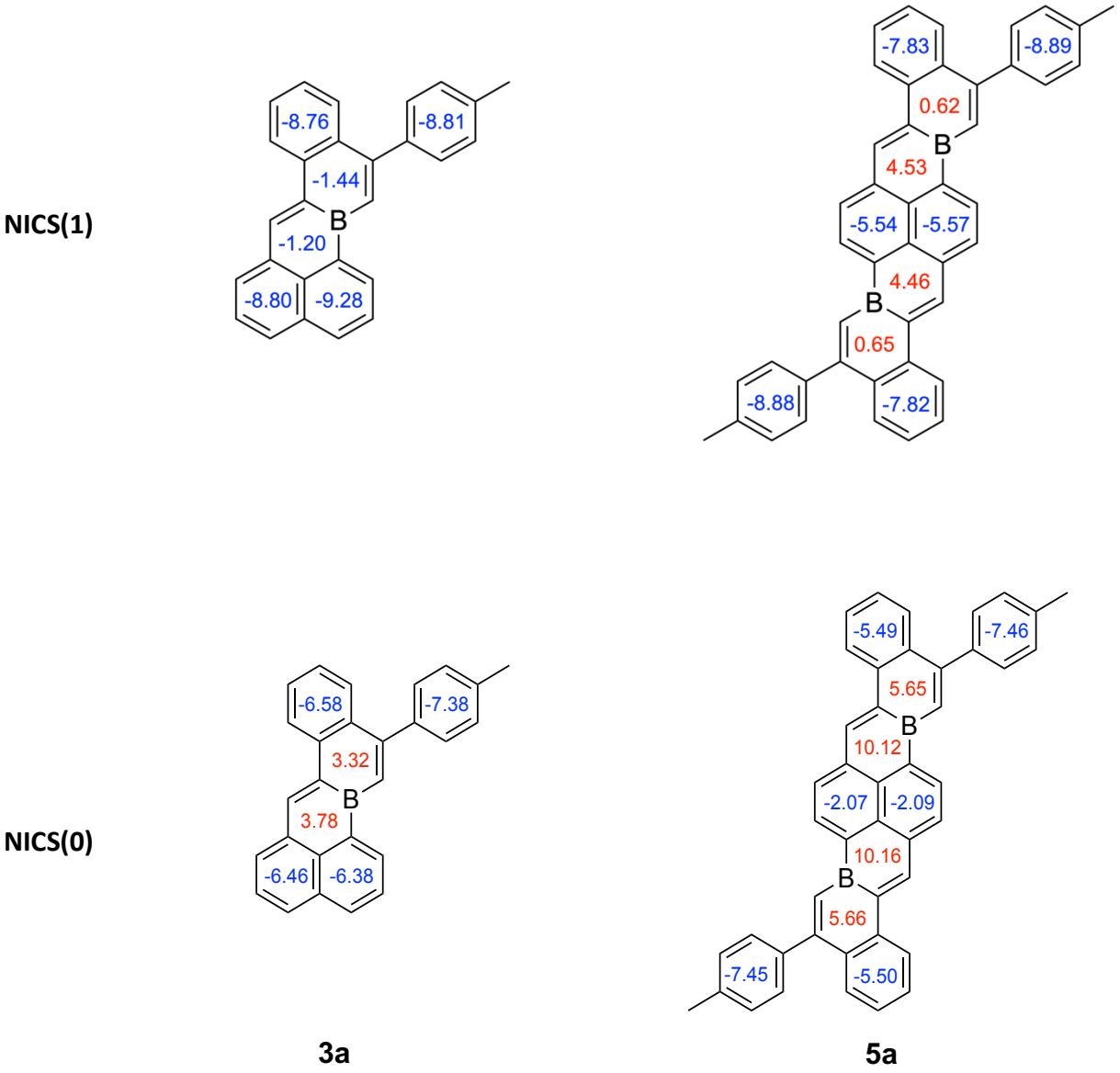

Figure S74: Nucleus-independent chemical shift calculations (NICS(1), NICS(0)) of representative boron-containing compounds **3a** and **5a** (B3LYP-D3(BJ)/def2-TZVP//B3LYP-D3(BJ)/def2-SVP).

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