Supplementary Information

Unraveling the Transient State of Photo-Induced Bond Cleavage Intramolecular Charge Transfer in Organoboron

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Table of Contents

1. Supporting Notes
2. Supporting Methods

    2.1 Synthetic procedure of BF-thio

    2.2 Time-resolved emission spectra (TRES)

    2.3 Transient absorption spectra (TA)

    2.4 Variable temperature transient absorption spectra

    2.5 Potential energy curves

3. Supporting Figures
4. Supporting References

1. Supporting Notes

All reagents and chemicals were purchased from commercial sources and used without further purification.

^{1}H NMR spectra, ^{11}B NMR spectra and ^{13}C NMR spectra were recorded with a Bruker Avance II-400 (400 MHz) and a Bruker Ascend 600 MHz spectrometers. High-resolution mass spectroscopy (HRMS) was performed by 9.4T Solarix Fourier Transform Ion Cytronic Resonance Mass Spectrometer (FT-ICR-MS). Gel permeation chromatography (GPC) measurements with THF as eluent at a flow rate of 1 mL·min^{-1} were performed at 30 °C using a Wyatt DAWN Series.

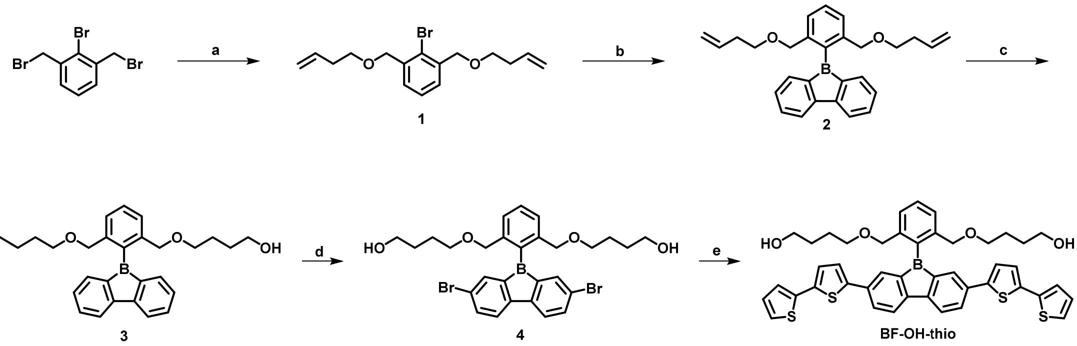
UV-visible absorption spectrum and emission spectra were recorded by using a Shimadzu UV-2550PC spectrophotometer and a Hitachi F-4600 spectrometer, respectively. All the emission spectra were corrected by an Avantes AvaSpec-2048TEC-USB2 spectrometer. Experiments with temperature changing from 223 K to 353 K were realized with the aid of Huber Ministat 230-CC and Unisoku CoolSpek CS-0411. The luminescence lifetimes were recorded by an Edinburgh FLS1000 spectrometer with a time correlated single photon counting (TCSPC) method. Photographs were taken with a mobile phone.

2. Supporting Methods

2.1 Synthetic procedure of BF-thio

The synthetic route used to prepare BF-thio is shown in Scheme S1. 5-Chloro-5*H*-dibenzoborole was prepared by reported procedures[1]. Structural characterization information for all compounds is shown in Figures S7 – S20.

Scheme S1



Condition：(a) 3-Buten-1-ol, NaH, THF, 0 °C; (b) 5-Chloro-5*H*-dibenzoborole, *n*-BuLi, THF, -78 °C; (c) 9-BBN dimer, NaOH, H_2O_2, THF, 0 °C; (d) NBS, DCM, r.t.; (e) 2,2′-Bithiophene-5-boronic acid pinacol ester, Cs_2CO_3, $Pd_2(dba)_3$, X-Phos, THF, 80 °C.

Compound 1: NaH (2.80 g, 116.7 mmol) was placed in a three-necked flask and a solution of 3-Buten-1-ol (4.20 g, 58.3 mmol) dissolved in 10 mL THF was added dropwise into the flask at 0 °C. The mixture was stirred for 10 min, followed by adding a solution of 2-Bromo-1,3-bis(bromomethyl)benzene (5.0 g, 14.6 mmol) dissolved in 20 mL THF to the mixture at 0 °C. The mixture was stirred at r.t. for 4 h. The mixture was quenched by adding water, followed by extracted with ethyl acetate, washed with water, dried over $MgSO_4$, and concentrated over the rotatory evaporator. The crude product was purified by the column chromatography on silica gel, providing the desired product **compound 1** as a colorless liquid (3.63 g, 76.4%).^{1}H NMR (400 MHz, DMSO-d_6,): δ (ppm) 7.40 (s, 3H), 5.89-5.79 (m, 2H), 5.13, 5.08 (d, 2H, J = 17.2 Hz), 5.04, 5.01 (d, 2H, J = 10.4 Hz), 4.52 (s, 4H), 3.56 (t, 4H, J = 6.4 Hz), 2.36-2.31 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$,): δ (ppm) 138.04, 135.08, 127.59, 127.06, 122.39, 116.39, 72.28, 70.19, 34.21. HRMS (EI, m/z): $[M-H]^+$ calcd. for $C_{16}H_{20}O_2Br^+$ 323.0641; found

323.0642.

Compound 2: *n*-BuLi (2.5 M，30.4 mmol) was added dropwise to a solution of **compound 1** (9.38 g, 28.8 mmol) dissolved in 50 mL THF at -78 °C under the protection of nitrogen, and the reaction mixture was stirred at -78 °C for 1 h. A solution of 5-Chloro-5*H*-dibenzoborole (5.71 g, 28.8 mmol) dissolved in 10 mL degassed toluene was added dropwise at -78 °C, followed by warming to r.t. and stirred for 16 h. The mixture was concentrated over the rotatory evaporator and the crude product was purified by the column chromatography on silica gel, providing the desired product **compound 2** as a light-yellow oil (5.76 g, 49.0%).^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.65, 7.63 (d, 2H, J = 7.6 Hz), 7.28-7.18 (m, 7H), 7.05 (t, 2H, J = 7.2 Hz), 5.56-5.46 (m, 2H), 4.95 (s, 2H), 4.91 (s, 2H), 4.58 (s, 4H), 3.27 (t, 4H, J = 6.8 Hz), 2.11-2.06 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$,): δ (ppm) 149.64, 148.84, 144.96, 138.53, 133.88, 131.41, 128.40, 126.68, 126.64, 122.56, 119.27, 117.09, 75.03, 70.70, 33.00. ^{11}B NMR (128 MHz, $CDCl_3$,): δ (ppm) 17.28. HRMS (EI, m/z): $[M]^+$ calcd. for $C_{28}H_{29}O_2B^+$ 408.2255; found 408.2254.

Compound 3: Under the protection of nitrogen, 9-BBN dimer (0.98 g, 4.0 mmol) was placed in a three-necked flask and a solution of **compound 2** (0.41 g, 1.0 mmol) dissolved in 10 mL degassed THF was added into the flask at 0 °C, followed by stirring at r.t. for 8 h. After cooled to 0 °C, 2 mL aqueous NaOH (2 M, 3.9 mmol) and 30% H_2O_2 (1.2 mL) were added carefully, and the mixture stirred for 15 min. The mixture was poured into water and extracted with ethyl acetate. The organic layer was separated and dried over Na_2SO_4, followed by concentrating over the rotatory evaporator. The crude product was purified by the column chromatography on silica gel, providing the desired product **compound 3** as a colorless oil (0.40 g，91.9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.65, 7.63 (d, 2H, J = 7.2 Hz), 7.31-7.27 (m, 3H), 7.21 (t, 4H, J = 6.8 Hz), 7.06 (t, 2H, J = 6.8 Hz), 4.59 (s, 4H), 3.37 (t, 4H, J = 6.0 Hz), 3.25 (t, 4H J = 6.0 Hz), 1.64 (s, 2 H), 1.44-1.34 (m ,8H). ^{13}C NMR (100 MHz, $CDCl_3$,): δ (ppm) 149.57, 149.05, 145.19, 138.33, 131.34, 128.37, 126.71, 126.64, 122.83, 119.29, 74.99, 71.59,

61.76, 28.64, 24.92. ^{11}B NMR (128 MHz, $CDCl_3$,): δ (ppm) 15.57. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{28}H_{33}BO_4Na^+$ 467.2364; found 467.2370.

Compound 4: In the absence of light, NBS (1.20 g, 6.8 mmol) was added to a solution of **compound 3** (1.50 g, 3.4 mmol) in 30 mL DCM, and the mixture stirred at r.t. for 4 h. The mixture was concentrated over the rotatory evaporator and the crude product was purified by the column chromatography on silica gel, providing the desired product **compound 4** as a colorless solid (0.92 g，44.9%). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.68, 7.66 (d, 2H, J = 8.0 Hz), 7.42, 7.40 (d, 2H, J = 8.0 Hz), 7.27-7.23 (m, 3H), 7.18, 7.16 (d, 2H J = 7.2 Hz), 4.59 (s, 4H), 4.28 (br, 2H), 3.19 (t, 8H J = 5.6 Hz), 1.36-1.33 (m ,4H), 1.21-1.18 (m ,4H). ^{13}C NMR (100 MHz, $CDCl_3$,): δ (ppm) 151.91, 147.22, 143.77, 138.32, 134.225, 131.42, 127.37, 123.32, 121.73, 121.21, 75.51, 72.10, 62.03, 28.86, 25.14. ^{11}B NMR (192 MHz, $CDCl_3$,): δ (ppm) 12.82. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{28}H_{31}BO_4Br_2Na^+$ 623.0574; found 623.0577.

BF-thio: To a Schlenk tube, **compound 4** (0.43 g, 0.71 mmol, 1 eq), 2,2′-Bithiophene-5-boronic acid pinacol ester (0.44 g, 1.5 mmol), 3 mL aqueous Cs_2CO_3 (0.92 g, 2.84 mmol), $Pd_2(dba)_3$ (3.2 mg, 0.5% eq), X-Phos (7 mg, 2% eq) and 10 mL THF were added under the protection of nitrogen. The mixture was stirred at 70 °C for 16 h. Cooling to r.t., the solvent in reaction mixture was removed by the rotatory evaporator and the mixture was dissolved in ethyl acetate, followed by washing with water and brine. The organic layer was separated, dried over Na_2SO_4, and concentrated over the rotatory evaporator. The crude product was purified by the column chromatography on silica gel, providing the desired product **BF-thio** as a yellow solid (0.33 g，60.2%). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.78, 7.76 (d, 2H, J = 8.0 Hz), 7.61, 7.59 (d, 2H, J = 8.0 Hz), 7.50, 7.49 (d, 2H, J = 3.6 Hz), 7.40 (s, 4H), 7.31-7.21 (m, 7H), 7.09-7.07 (m, 2H), 4.67 (s, 4H), 4.21 (t, 2H, J = 4.8 Hz), 3.23 (t, 4H, J = 6.0 Hz), 3.13-3.11 (m, 4H), 1.36-1.33 (m ,4H), 1.19-1.16 (m ,4H). ^{13}C NMR (100 MHz, $CDCl_3$,): δ (ppm) 150.40, 148.93, 144.66, 144.41, 138.61, 137.74, 135.94, 132.47, 128.53, 127.96, 127.21, 126.25, 124.66, 124.25, 123.46, 123.30, 123.11, 120.10, 75.43, 71.95, 62.16, 28.95, 25.17. ^{11}B NMR (192 MHz, $CDCl_3$,): δ (ppm) 13.14. HRMS (ESI, m/z): $[M+Na]^+$ calcd. for $C_{44}H_{41}BO_4S_4Br_2Na^+$ 795.1873; found 795.1875.

2.2 Time-resolved emission spectra (TRES)

TRES were recorded by an Edinburgh Instruments FLS1000 spectrophotometer, using single photon counting mode at different wavelengths, every 10 nm.

The fluorescence decay profiles are fitted by the following multiexponential function:

$$R(t) = A + \sum_{i=1}^{n} B_i e^{(-t/\tau_i)} \tag{1}$$

where R is the emission decay data, τ_i is the lifetime, and B_i is the pre-exponential factor. Relative concentration of component a (c_a) can be calculated by the following equation:

$$c_a = \frac{B_a}{\sum_{i=1}^{n} B_i} \times 100\% \tag{2}$$

2.3 Transient absorption spectra (TA)

TA was carried out by using a Helios pump-probe system (Ultrafast Systems) combined with a regenerative-amplified Ti: sapphire laser system (Legend Elite-1K-HE, 800 nm, 25 fs, 4 mJ/pulse, and 1 kHz repetition rate) and an optical parametric amplifier system. The output light of regenerative-amplified Ti: sapphire laser (800 nm) was split into two beams. The main part of the fundamental beam (800 nm) was sent to the optical parametric amplifiers (TOPAS-C), which generated a pump pulse with wavelength of 380 nm. A small part of the fundamental beam (800 nm) was introduced into the TA spectrometer in order to generate the probe light. After passing through a motorized optical delay line, the 800-nm light beam was attenuated with a neutral density filter and focused on a CaF_2 crystal, which was used to generate the white-light continuum (WLC) probe pulses with wavelength of 380 to 780 nm, respectively. The pump pulse was modulated such that the TA spectra with and without the pump pulses could be recorded alternately. The optical path difference between the pump light and the probe light, which was controlled by the motorized optical delay-line, was used to get the relative time delay between the probe light and the pump light. After sampling, the probe beam was collimated and then focused into a fiber-coupled spectrometer. The intensity of the pump pulse used in the experiment was controlled by a variable neutral-density filter wheel. The experiments were carried out at room temperature.

Data evaluation of the fs-TA was conducted by global analysis using Carpet View software. We applied global target analysis (GTA) using a sequential model (A→B→C→⋯) to adequately fit the data. The so-called evolution-associated difference spectra, which contain spectral information on the states contained in the kinetic model, are produced by global target analysis in addition to the decay-associated spectra usually acquired in global lifetime analysis.

2.4 Variable temperature transient absorption spectra

A cryostat (Unisoku, USP-203 Series) was placed in the optical path of fs-TA. Temperature range is from -80°C to +100°C by using liquid nitrogen as a coolant, and temperature accuracy is ±1°C. Two heating resistors in the main body: One to prevent frost on the optical viewing window and the other for internal temperature control. The cryostat has three sides of optical window, made of synthetic quartz. The pump and probe light pass through and focus on the cuvette in the cryostat.

2.5 Potential energy curves

Most of the discussion on potential energy surfaces has been described in the main text. Here we focused on the value of ω and the reasons for it. According to the density matrix theory, the expectation value of the coherent vibrational nucleus displacement can be calculated by the following equation[2]:

$$\langle Q_{AB} \rangle = \sum_{AB} \rho_{AB}(t) Q_{AB} \tag{6}$$

where ρ_{AB} is the density matrix element representing the degree of coherence of the quantum states A[(BF-thio)^{4}*] and B[(BF-thio)^{3}*] and decaying exponentially (dephasing) with time constant T_2. Q_{AB} is the vibrational matrix element between the quantum states A and B, viz:

$$Q_{AB} = \langle t_A | Q | t_B \rangle \tag{7}$$

In the above equation, the coherent vibrational motion of the nucleus displacement Q can be expressed in phenomenology as:

$$\frac{d^2}{dt^2} Q + \frac{2}{T_2} \frac{d}{dt} Q + \omega^2 Q = \frac{F(t)}{m} \tag{8}$$

where $F(t)$ is the driving force for the coherent vibrations, m is the reduced mass and ω is the frequency of the coherent oscillator. Based on transient spectroscopy, the two oscillators are completely coherent constructed by the breaking or not of the B-O bond, and therefore the ω can be expressed as the stretching vibration frequency of the bond. This frequency was determined by infrared absorption spectroscopy (as shown in Figure S5) to be 3.15×10^{13} Hz (1050 cm^{-1}), which is comparable to other B-O bonds of tetracoordinate boron compounds found in the literatures.[3-4] The generalized solution of the equation (8) is:

$$Q(t) = \frac{1}{\tilde{\omega}} \int_{-\infty}^{t} dt' F(t') e^{-\frac{t-t'}{T_2}} \sin\left[\tilde{\omega}(t-t')\right] \tag{9}$$

where $\widetilde{\omega} = \sqrt{\omega^2 - 1/T_2^2}$. The dephasing frequency is much larger than the vibrational frequency between the two oscillators, because of the high degree of electronic coupling of organic molecules and the large degree of coupling of the two states A and B. Therefore the $\widetilde{\omega}$ in the discussion of BF-thio can be simplified to the stretching vibration frequency ω of the B-O bond ($\widetilde{\omega} \approx \omega = 3.15\times10^{13}$ Hz). Eventually, the B-O bond length of the transition state is obtained by substituting the full physical quantities into Eq of r_T.

3. Supporting Figures

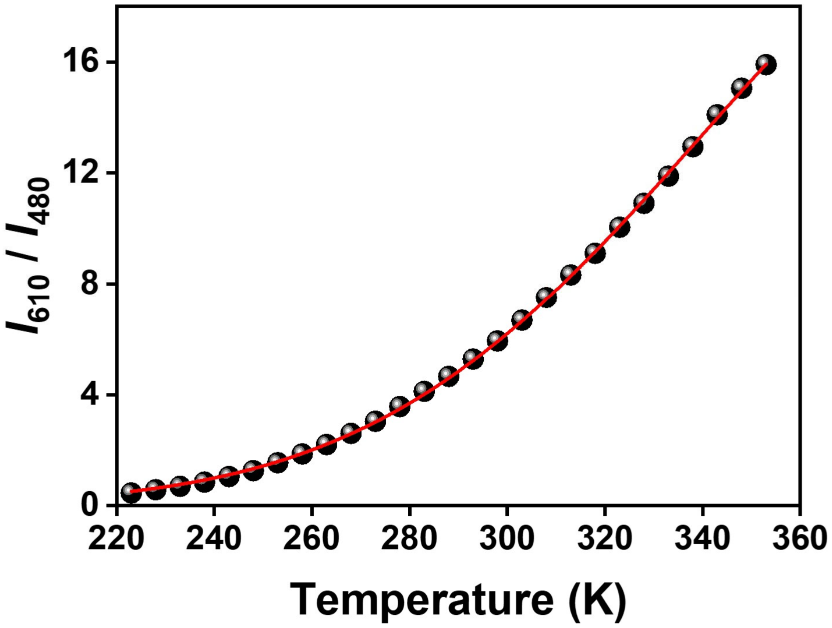


Figure S1. Plots of ratiometric fluorescence I_{610}/I_{480} as a function of temperature. I_{610}/I_{480} of BF-thio versus temperature varies from 253 to 353 K, which is fitted as $^{I_{610}}/_{I_{480}} = e^{(-15.3+9.08\times10^{-2}T-1.12\times10^{-4}T^2)}$, with the high correlation coefficient of 0.999.

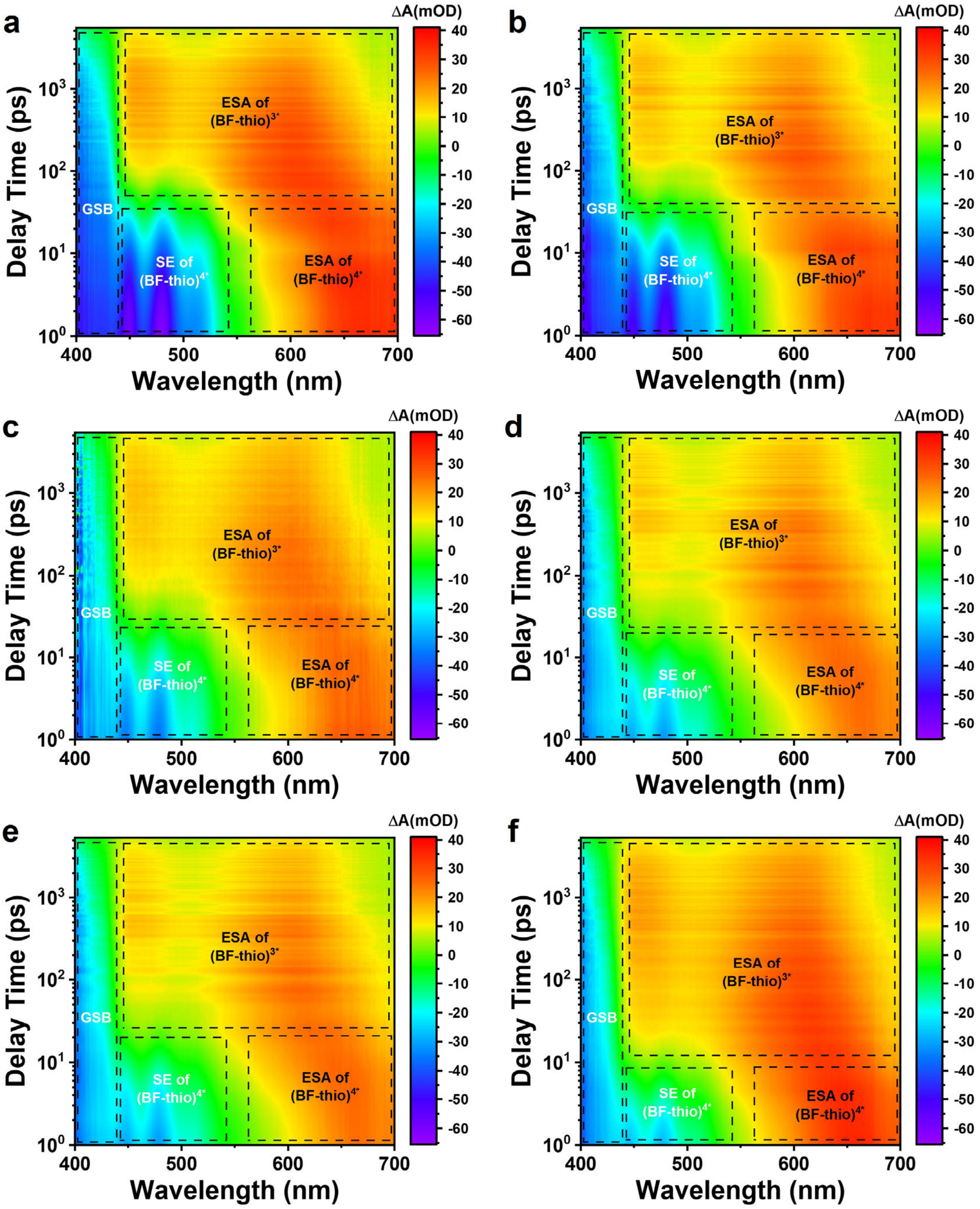


Figure S2. 2D pseudocolor fs-TA plots of BF-thio in toluene at (a) 253 K, (b) 263 K, (c) 273 K, (d) 283 K, (e) 293 K, (f) 323 K.

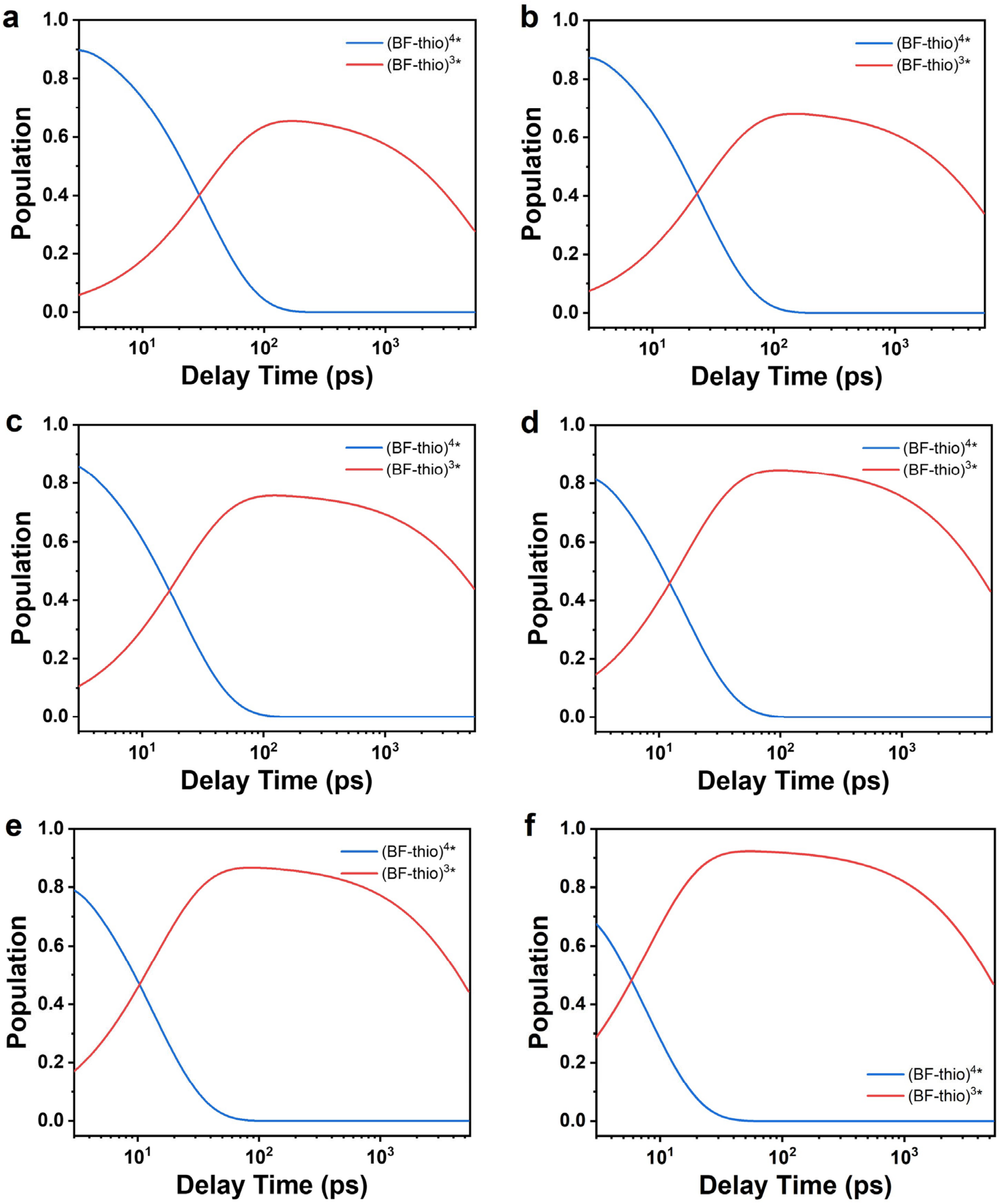


Figure S3. Relative populations of the respective species with colors correlating with the evolution-associated spectra of BF-thio in toluene at (a) 253 K, (b) 263 K, (c) 273 K, (d) 283 K, (e) 293 K, (f) 323 K.

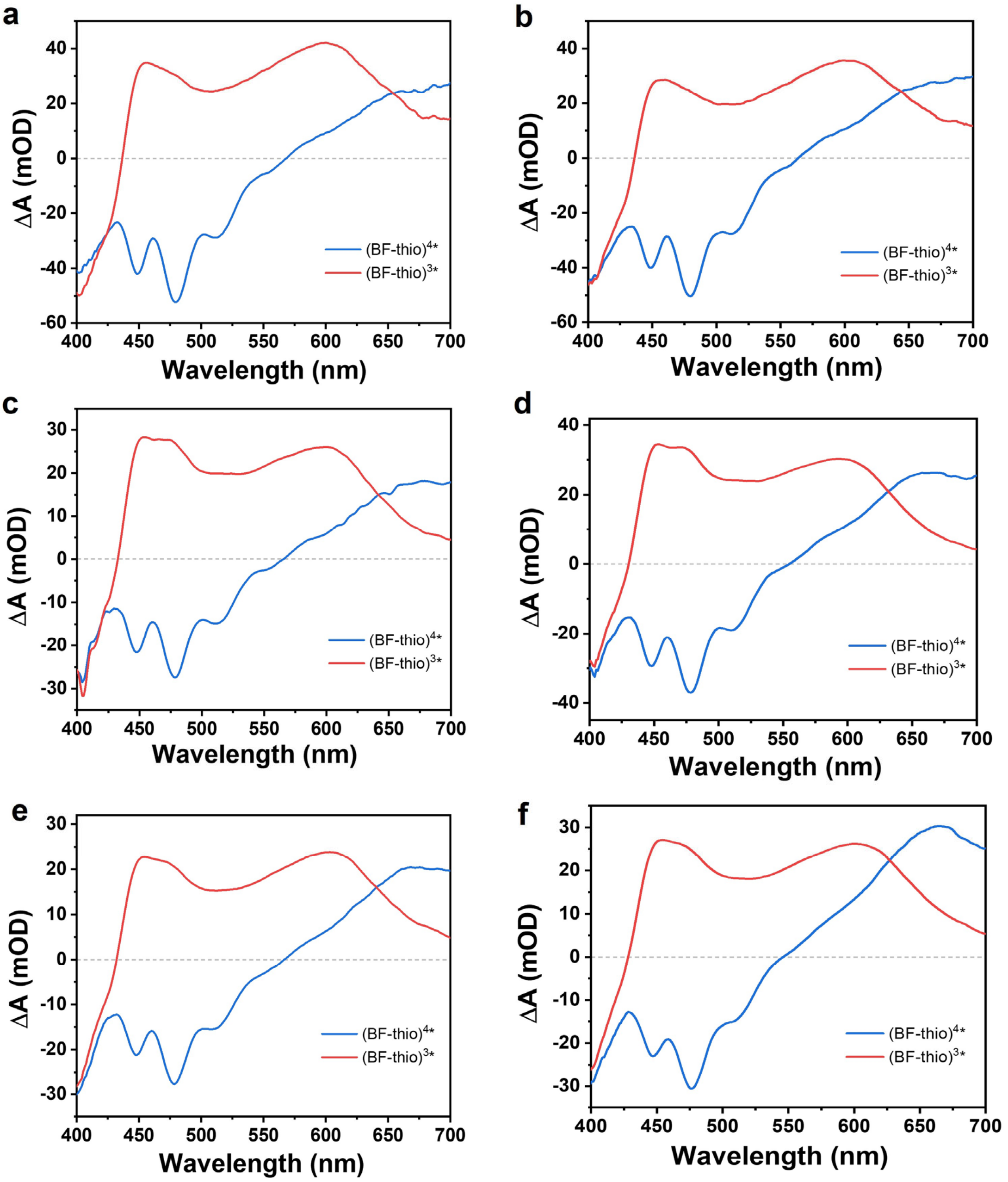


Figure S4. Evolution-associated spectra of BF-thio in toluene at (a) 253 K, (b) 263 K, (c) 273 K, (d) 283 K, (e) 293 K, (f) 323 K.

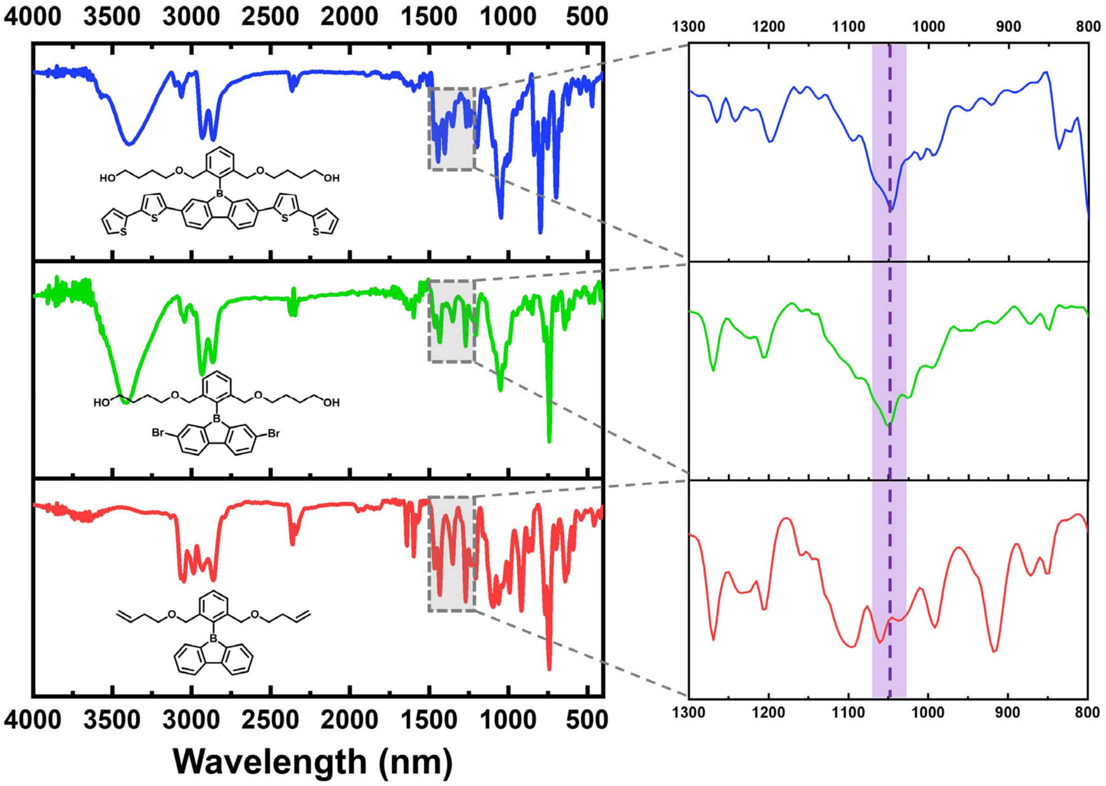


Figure S5. IR spectra of BF-thio, Compound 4 and Compound 2.

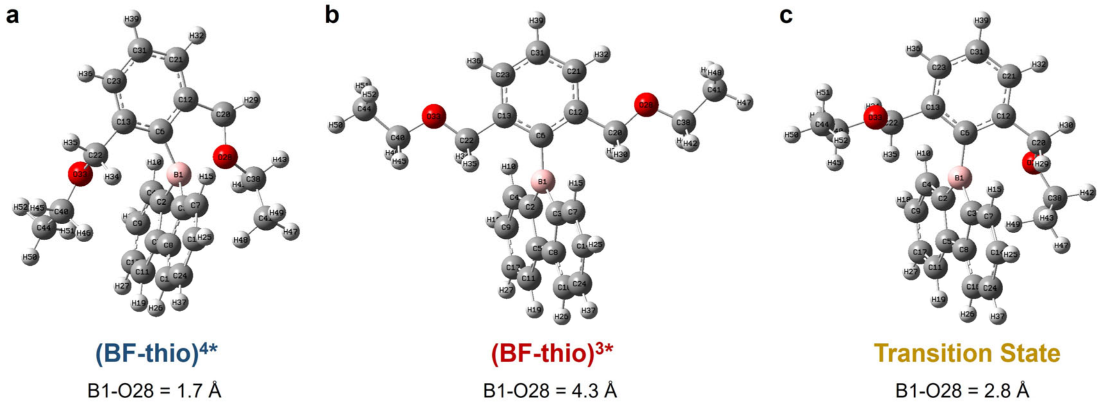


Figure S6. DFT result. The optimized structures of (a) (BF-thio)^{4}* and (b) (BF-thio)^{3}*. (c) The structures of transition state during the progress of B←O bond cleavage. Unfortunately, we were unable to obtain the crystal data for BF-thio. According to the literature[5-6], the O–B bond length in 4-coordinate boron compounds typically ranges from 1.5 to 1.6 Å.

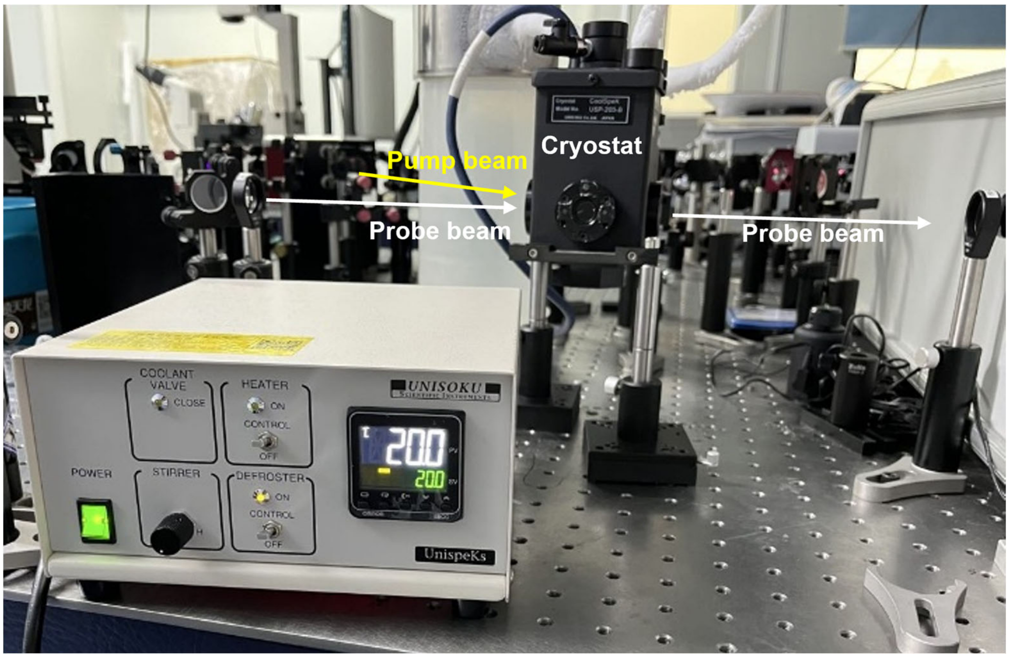


Figure S7. Photograph of the cryostat setup used for variable-temperature TA measurements.

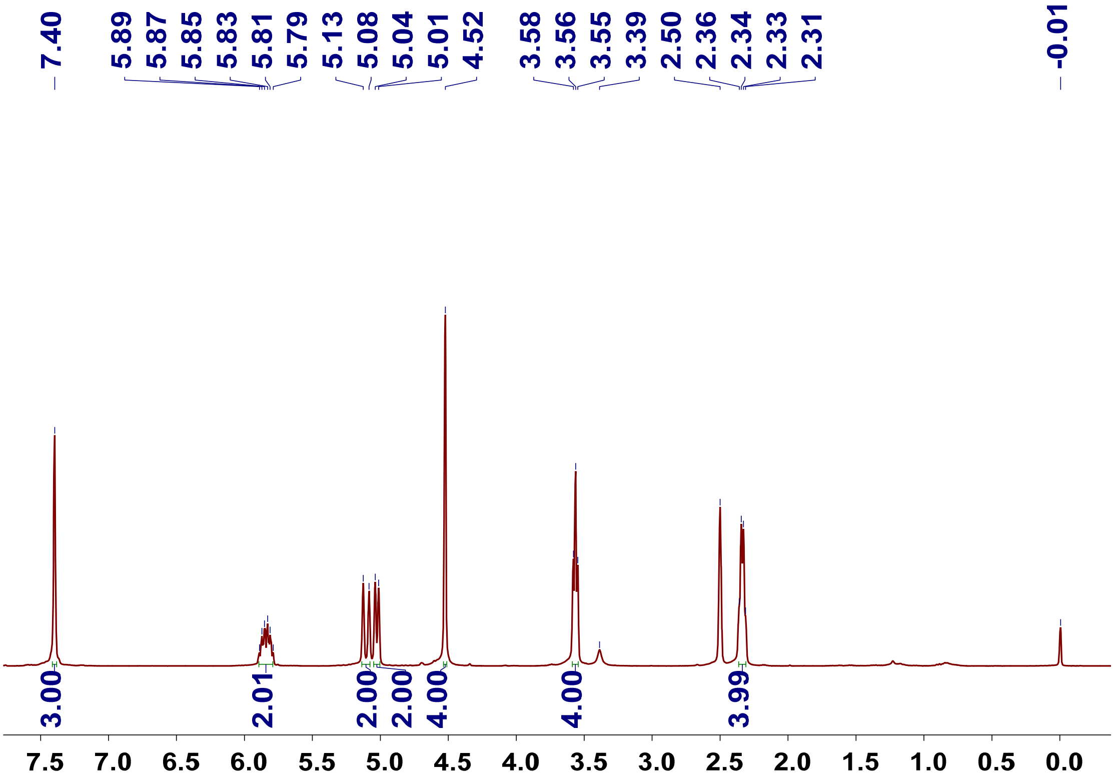


Figure S8. ^{1}H NMR of compound 1 (DMSO-d_6)

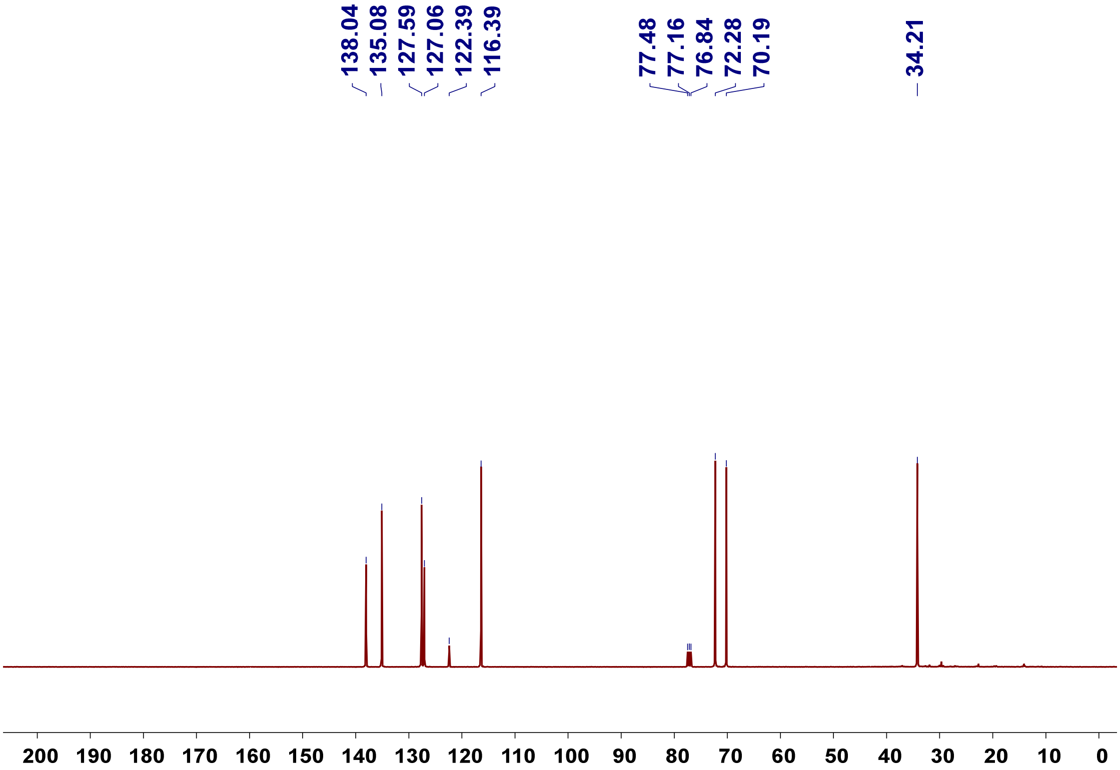


Figure S9. ^{13}C NMR of compound 1 ($CDCl_3$)

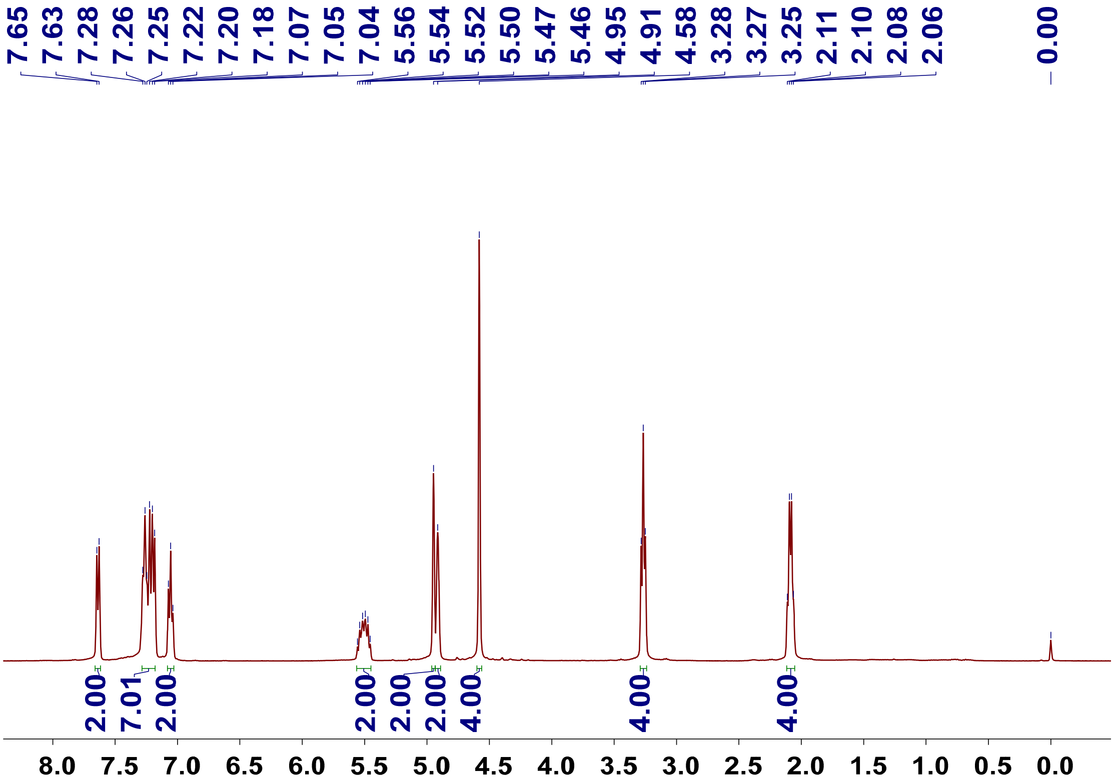


Figure S10. ^{1}H NMR of compound 2 ($CDCl_3$)

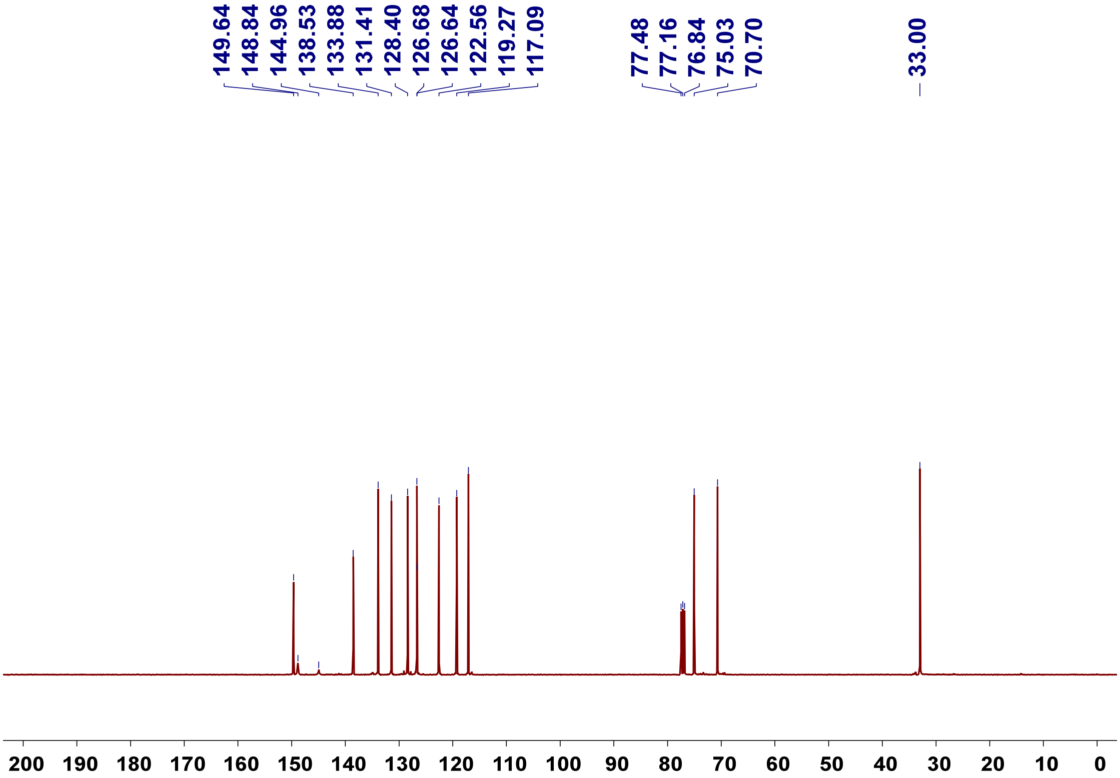


Figure S11. ^{13}C NMR of compound 2 ($CDCl_3$)

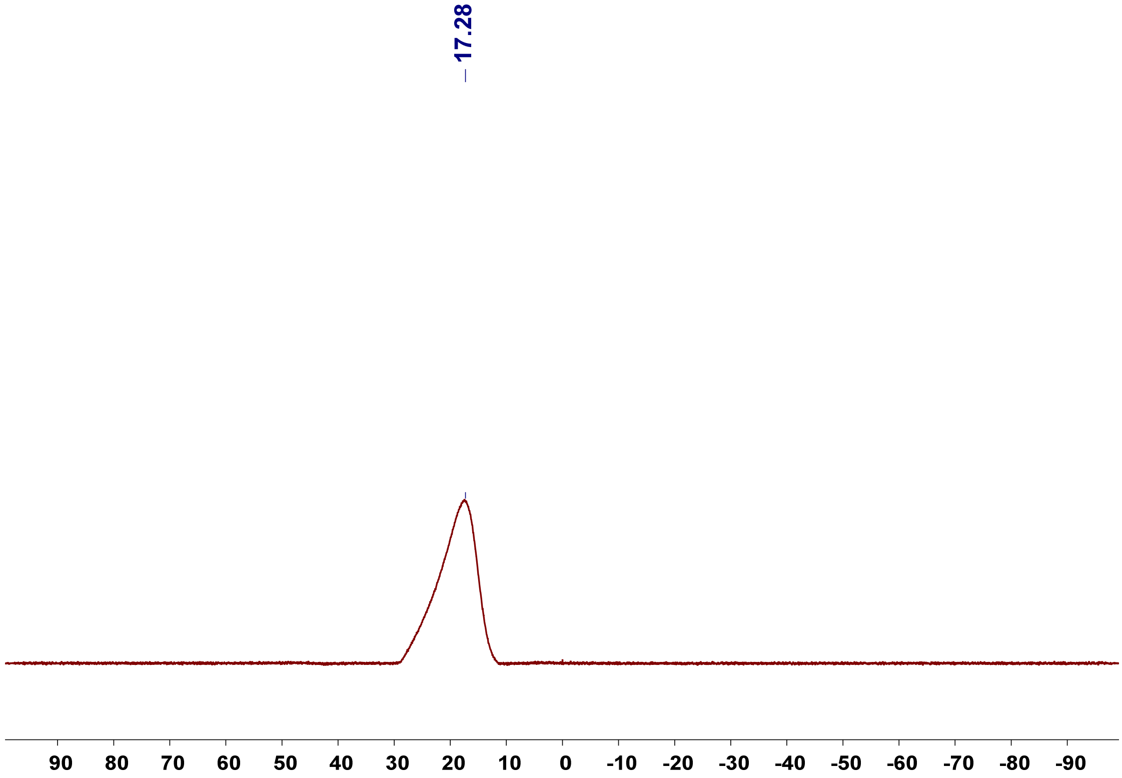


Figure S12. ^{11}B NMR of compound 2 ($CDCl_3$)

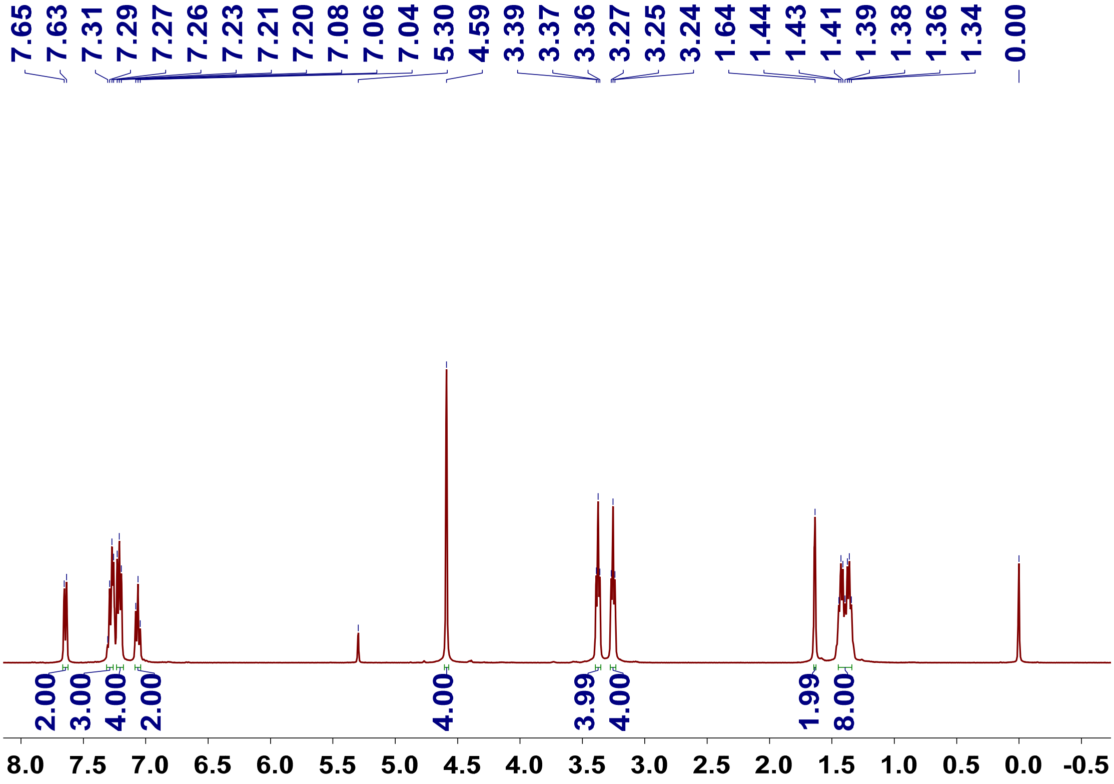


Figure S13. ^{1}H NMR of compound 3 ($CDCl_3$)

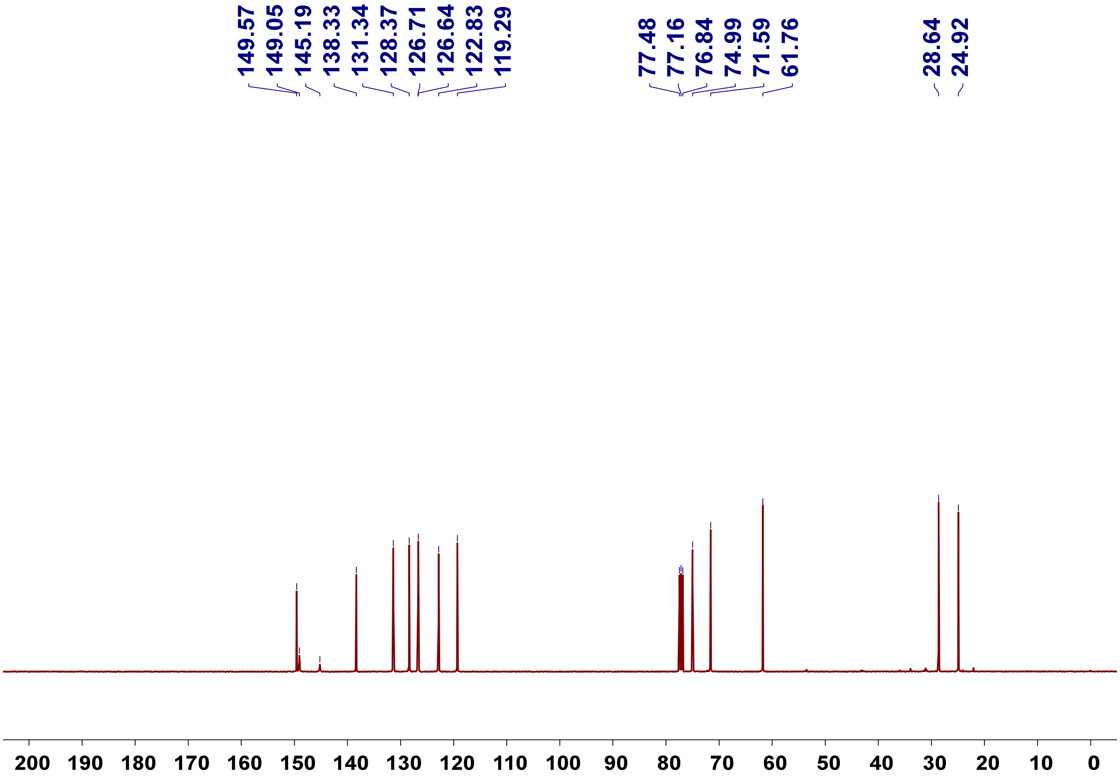


Figure S14. ^{13}C NMR of compound 3 ($CDCl_3$)

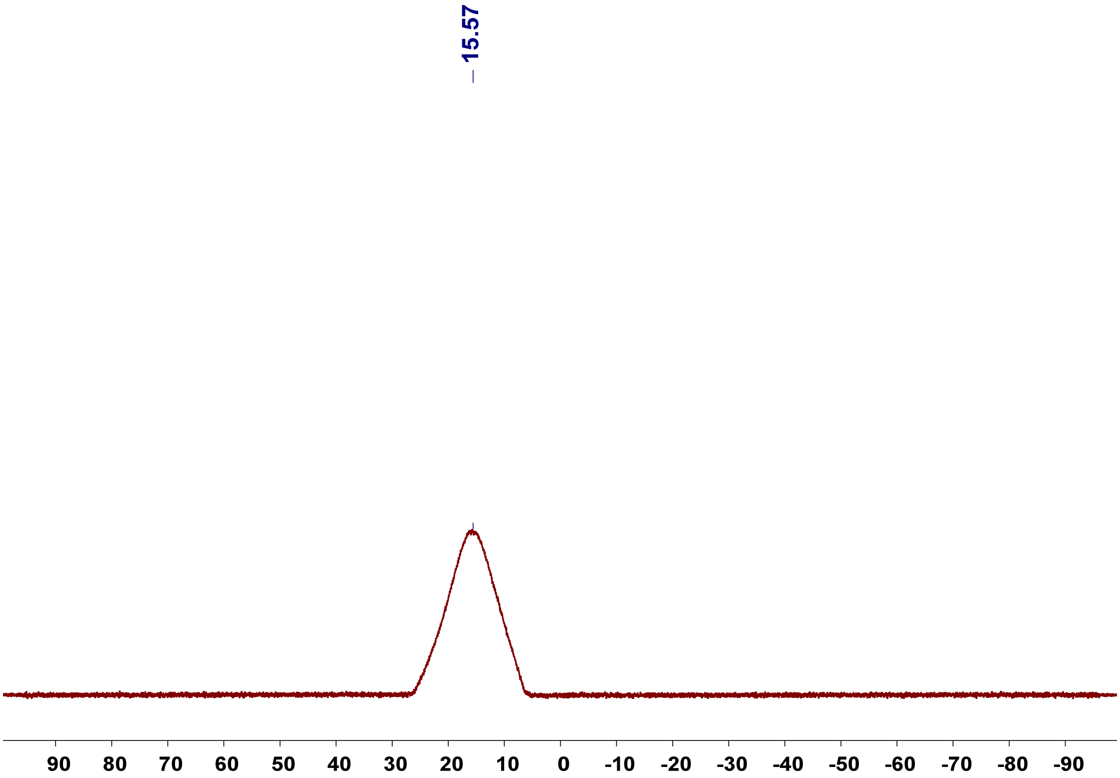


Figure S15. ^{11}B NMR of compound 3 ($CDCl_3$)

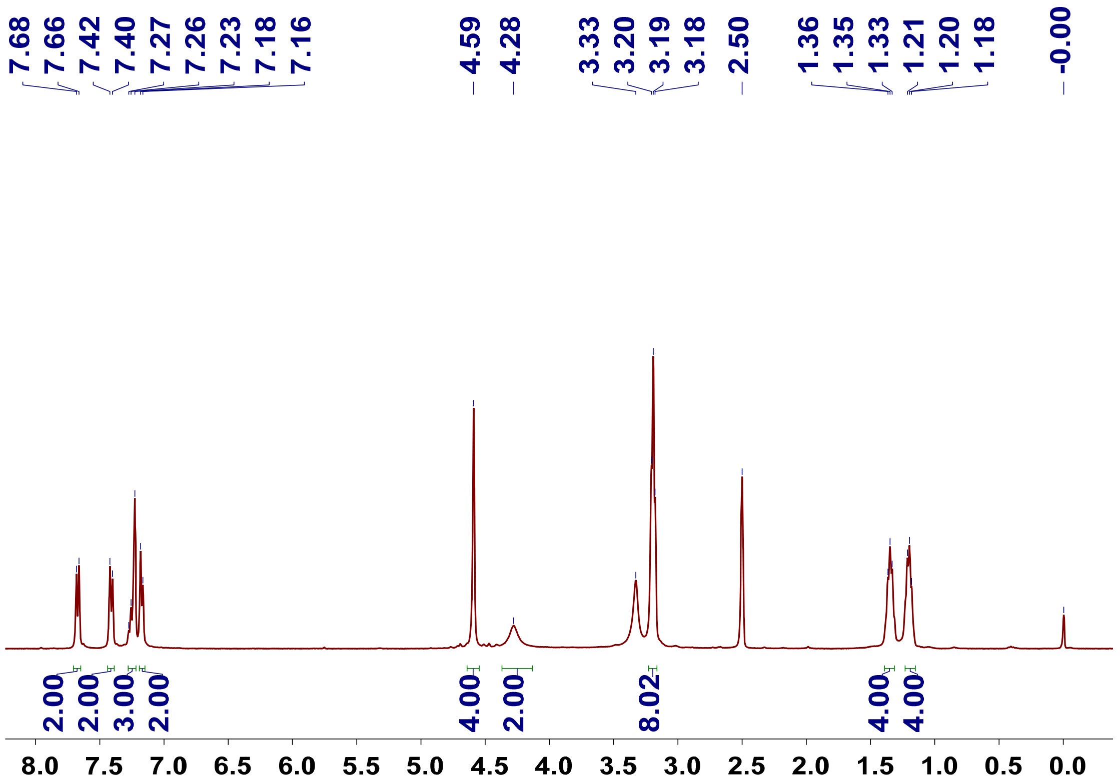


Figure S16. ^{1}H NMR of compound 4 (DMSO-d_6)

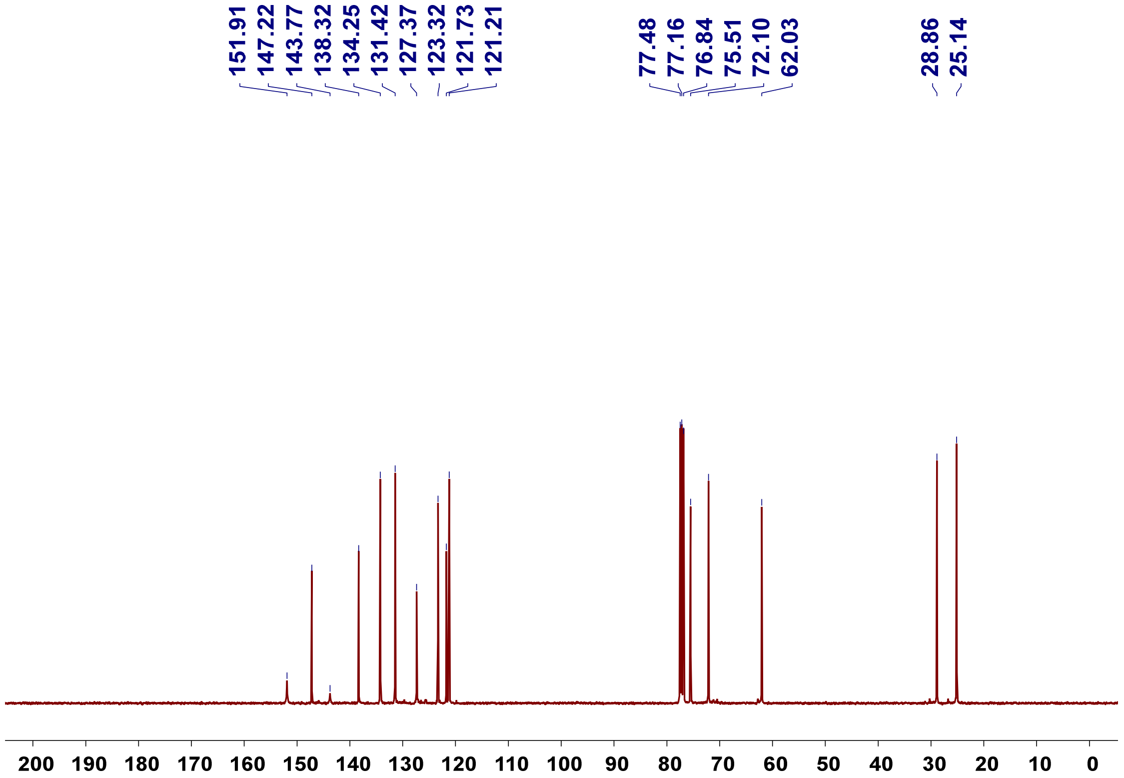


Figure S17. ^{13}C NMR of compound 4 (CDCl$_3$)

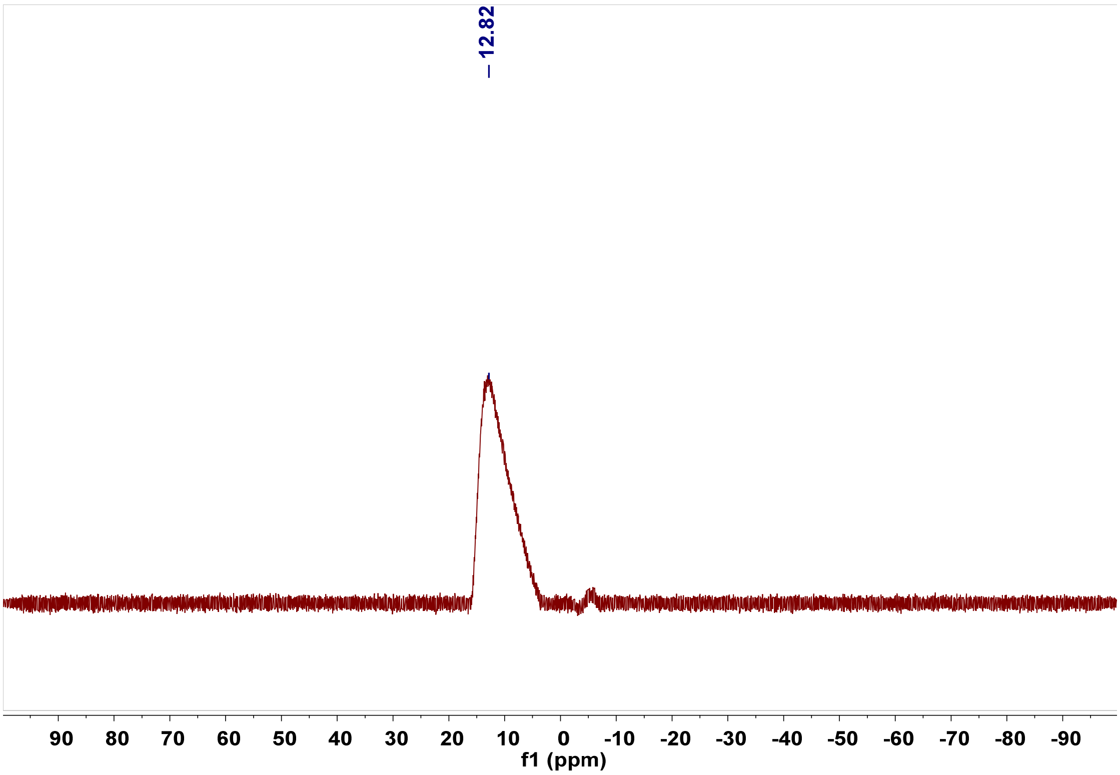


Figure S18. ^{11}B NMR of compound 4 ($CDCl_3$)

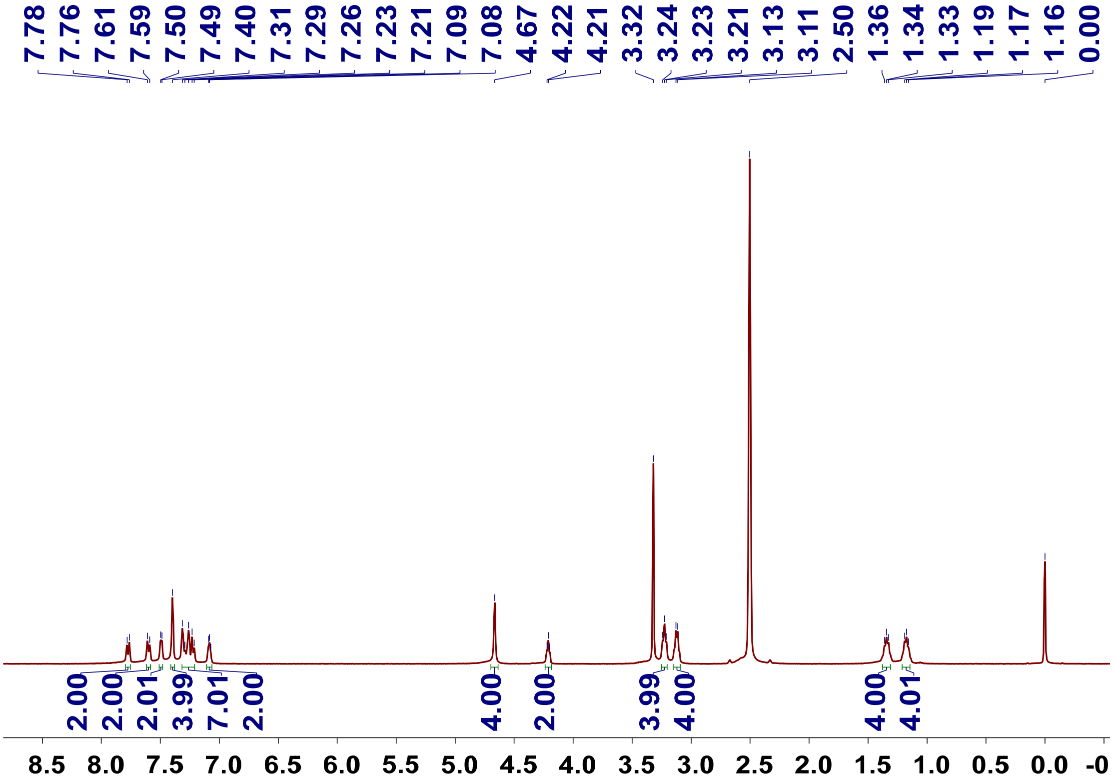


Figure S19. ^{1}H NMR of BF-OH-thio (DMSO-d_6)

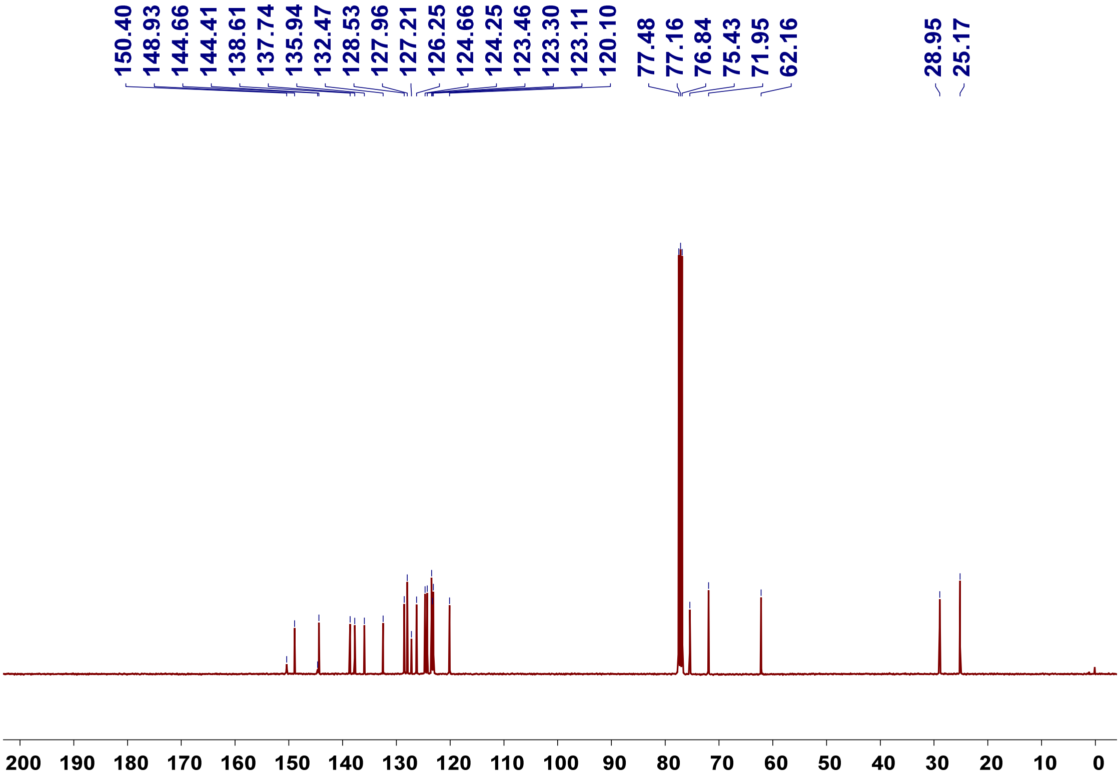


Figure S20. ^{13}C NMR of BF-OH-thio (CDCl$_3$)

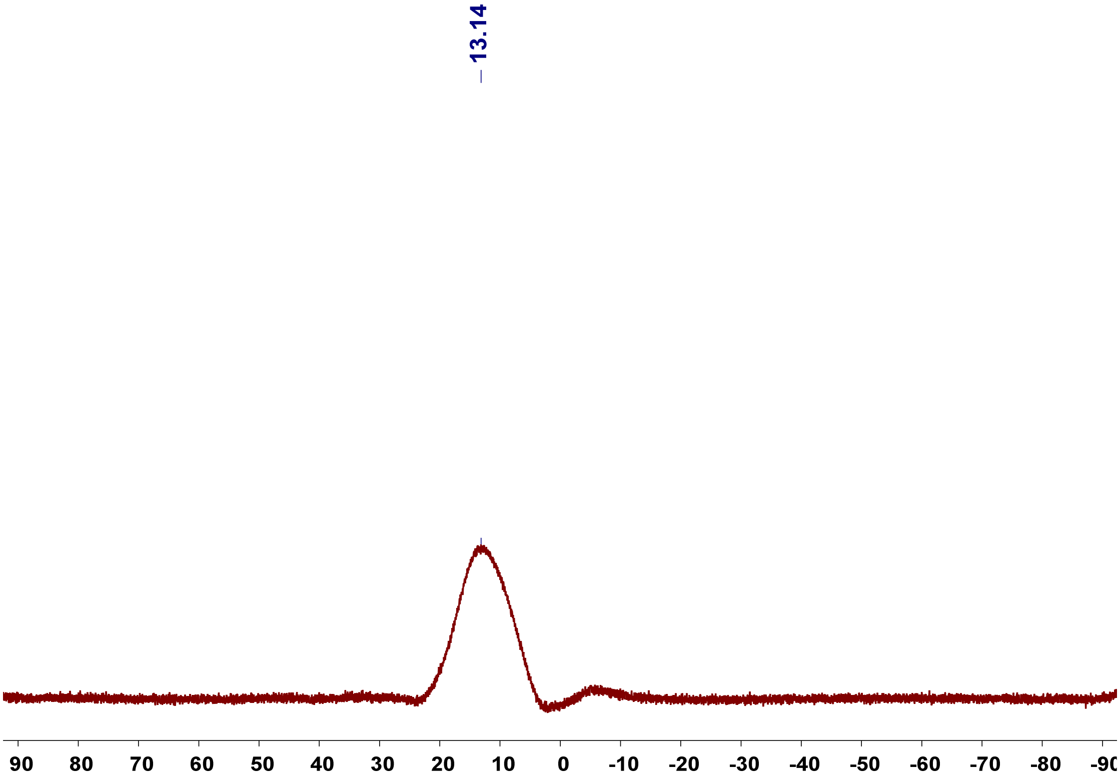


Figure S21. ^{11}B NMR of BF-OH-thio (CDCl$_3$)

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