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Rigid Axially Symmetrical C_{60}-BODIPY Triplet Photosensitizers: Effect of Bridge Length on Singlet Oxygen Generation

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Contents

1. Time-resolved fluorescence spectrum of R1

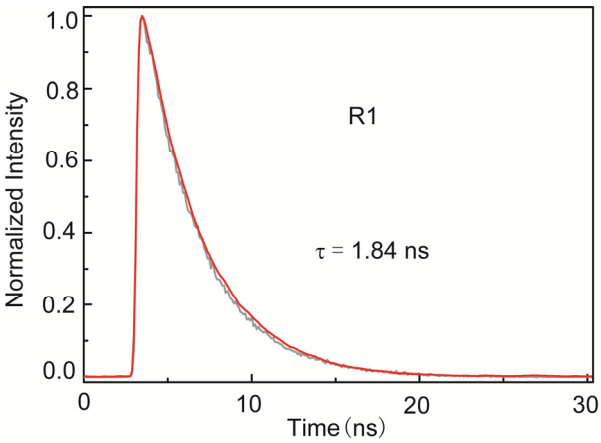


Figure S1. Fluorescence decay traces obtained with TCSPC of **R1** in toluene (1×10^{-6} mol/L) and the results of single exponential function fitting combining a deconvolution (ex 475 nm, em 520 nm).

2. Nanosecond time-resolved transient absorption spectra of R1 and R2

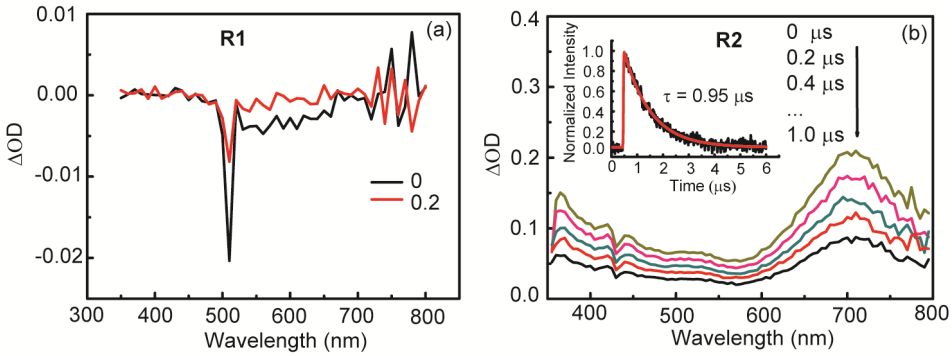


Figure S2. Nanosecond time-resolved transient absorption spectra of (a) **R1** and (b) **R2** in deaerated toluene upon excitation (532 nm, 7 ns fwhm, 2 mJ/pulse) at room temperature. Arrows indicate the spectral trend with time increasing. Inset shows the dynamic curves and transient absorption time profiles of **R2** at 710 nm.

The concentration of **R1** is the same with **C_{60}-B1** and **C_{60}-B2**, but no obvious triplet excited state was observed. The concentration of **R2** is higher than that of **C_{60}-B1** and **C_{60}-B2**. The data in Figure S17 (b) is to certificate the triplet excited state of C_{60}.

3. The spectral response of DHN and DHN with R1, R2 and MB as the sensitizers

As a control experiment, Figure S2a was the photo-oxidation of DHN without photosensitizer. Both **R1** and **R2** were also used as triplet photosensitizers for photocatalytic reaction, but nearly no product was observed.

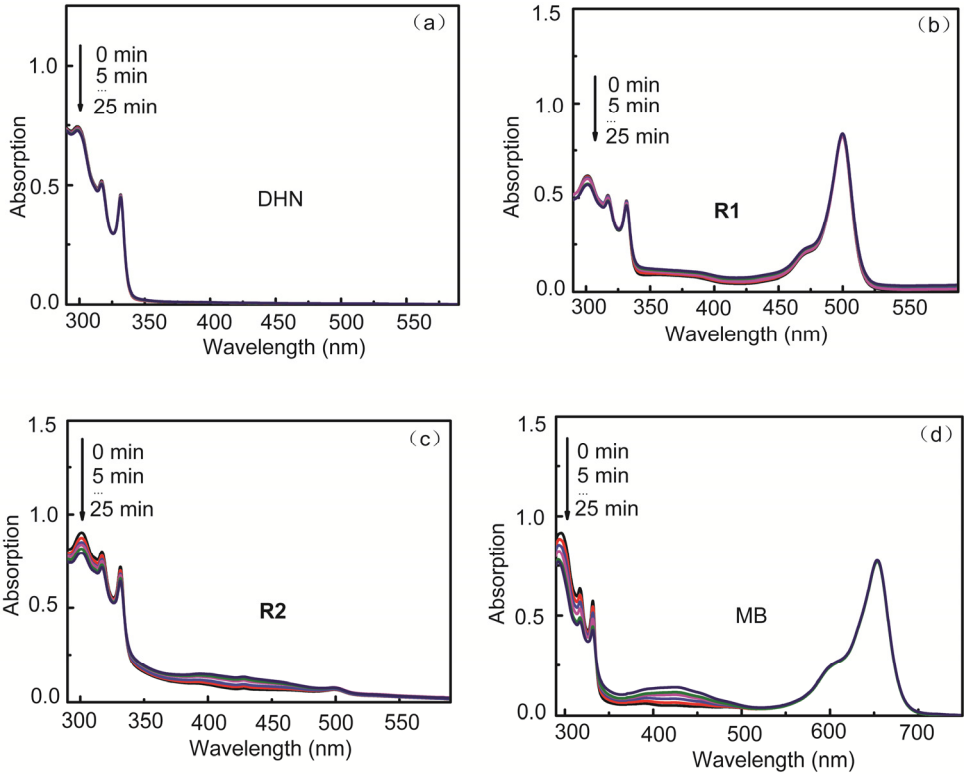


Figure S3. Absorption spectral changes for the photooxidation of DHN (a) without photosensitizer, (b) using **R1,** (c) **R2** and (d) **MB**. c[sensitizers] = 1.0×10^{-5} mol L^{-1}, c[DHN] = 1.0×10^{-4} mol L^{-1}. In CH_2Cl_2–MeOH (9/1, v/v).

4. The photostability of C_{60}-B1 and C_{60}-B2

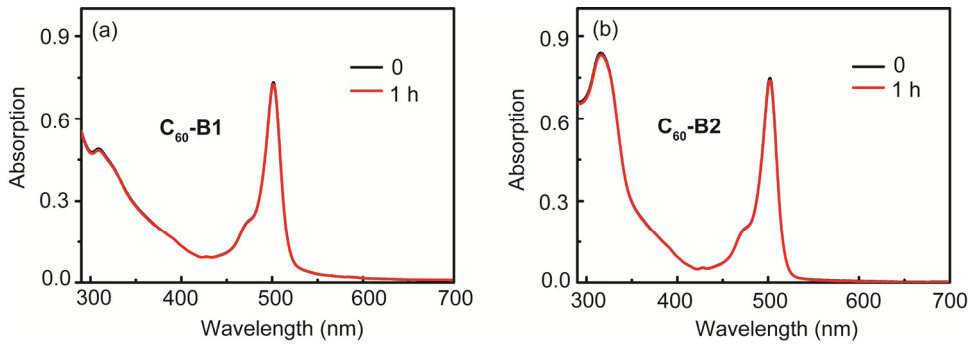
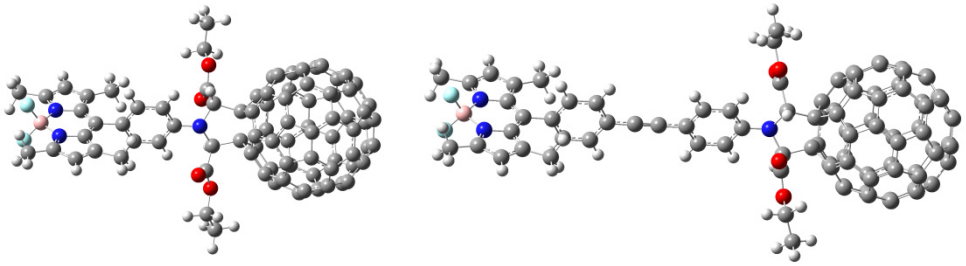


Figure S4. The stability of (a) **C_{60}-B1** and (b) **C_{60}-B2**. c[sensitizers] = 1.0×10^{-5} mol L^{-1} in CH_2Cl_2–MeOH (9/1, v/v). After being exposed to light for 1 h, no bleaching is observed for both **C_{60}-B1** and **C_{60}-B2**.

5. Calculation details.

The molecular structure optimization and excited state property calculation were performed at the CAM-B3LYP/3-21G level with the Gaussian 09 package.

5.1 The optimized structures of C_{60}-B1 and C_{60}-B2



C_{60}-B1 **C_{60}-B2**

Figure S5. The optimized structures of **C_{60}-B1** and **C_{60}-B2**.

5.2 Cartesian coordinate, the number of imaginary frequency and energy of C_{60}-B1 and C_{60}-B2

C_{60}-B1

0 1

The number of imaginary frequency = 0

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E = -4021.94626431 a.u.

C_{60}-B2

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The number of imaginary frequency = 0

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C	8.61972400	-0.83907100	2.85406500
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E = -4329.09008535 a.u.

6. High resolution mass spectra

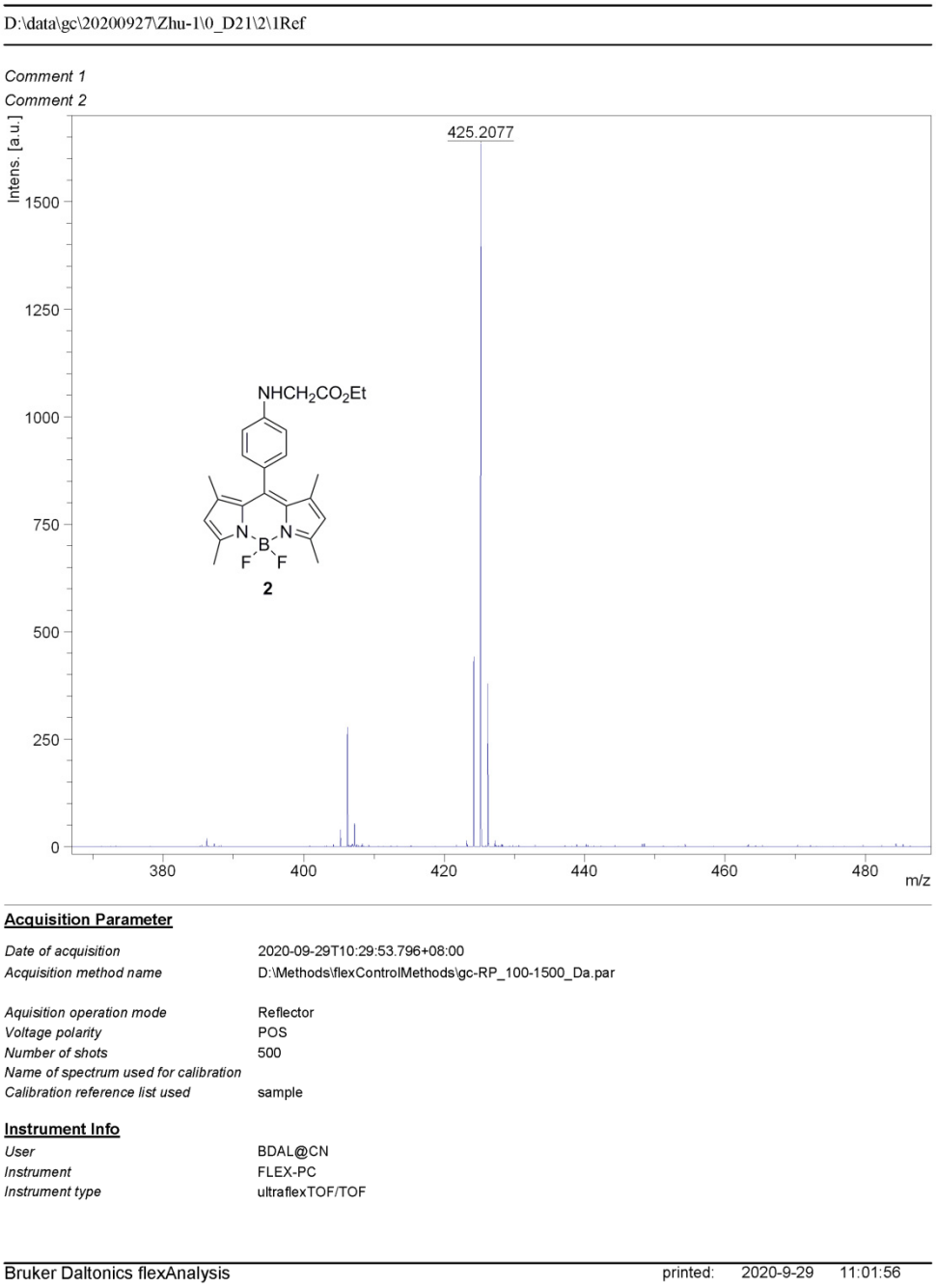


Figure S6. Expansion of the high resolution mass spectrum of **2**.

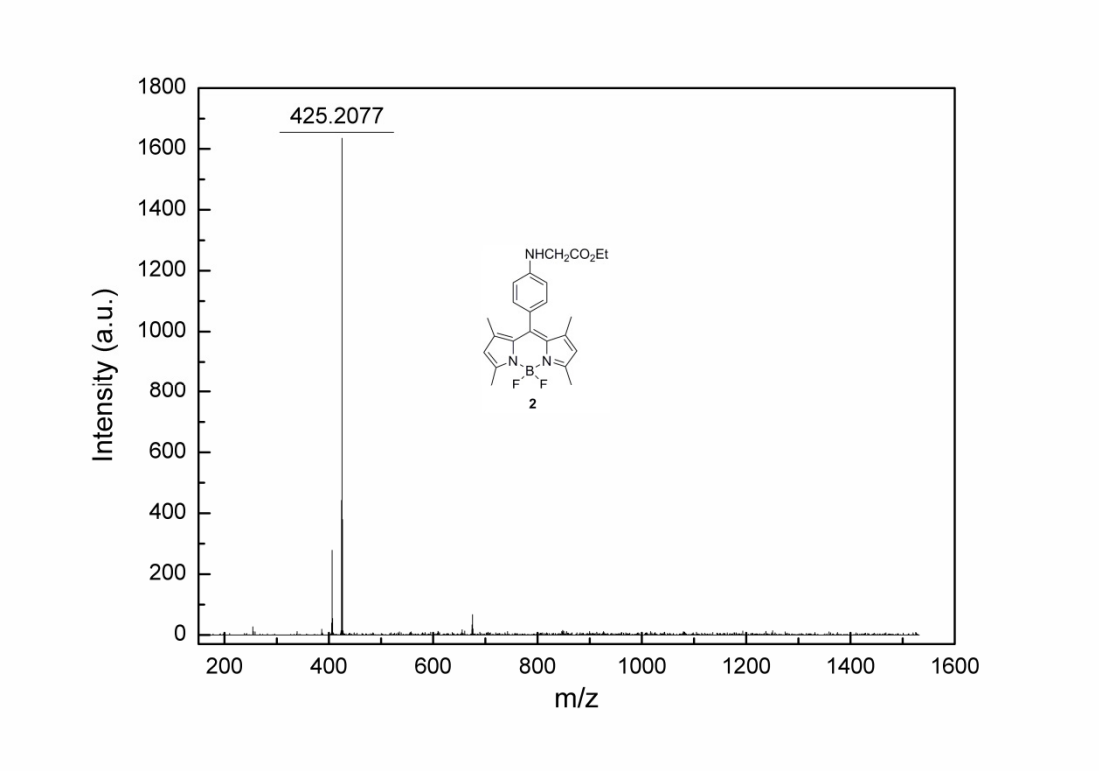


Figure S7. The high resolution mass spectrum of **2**.

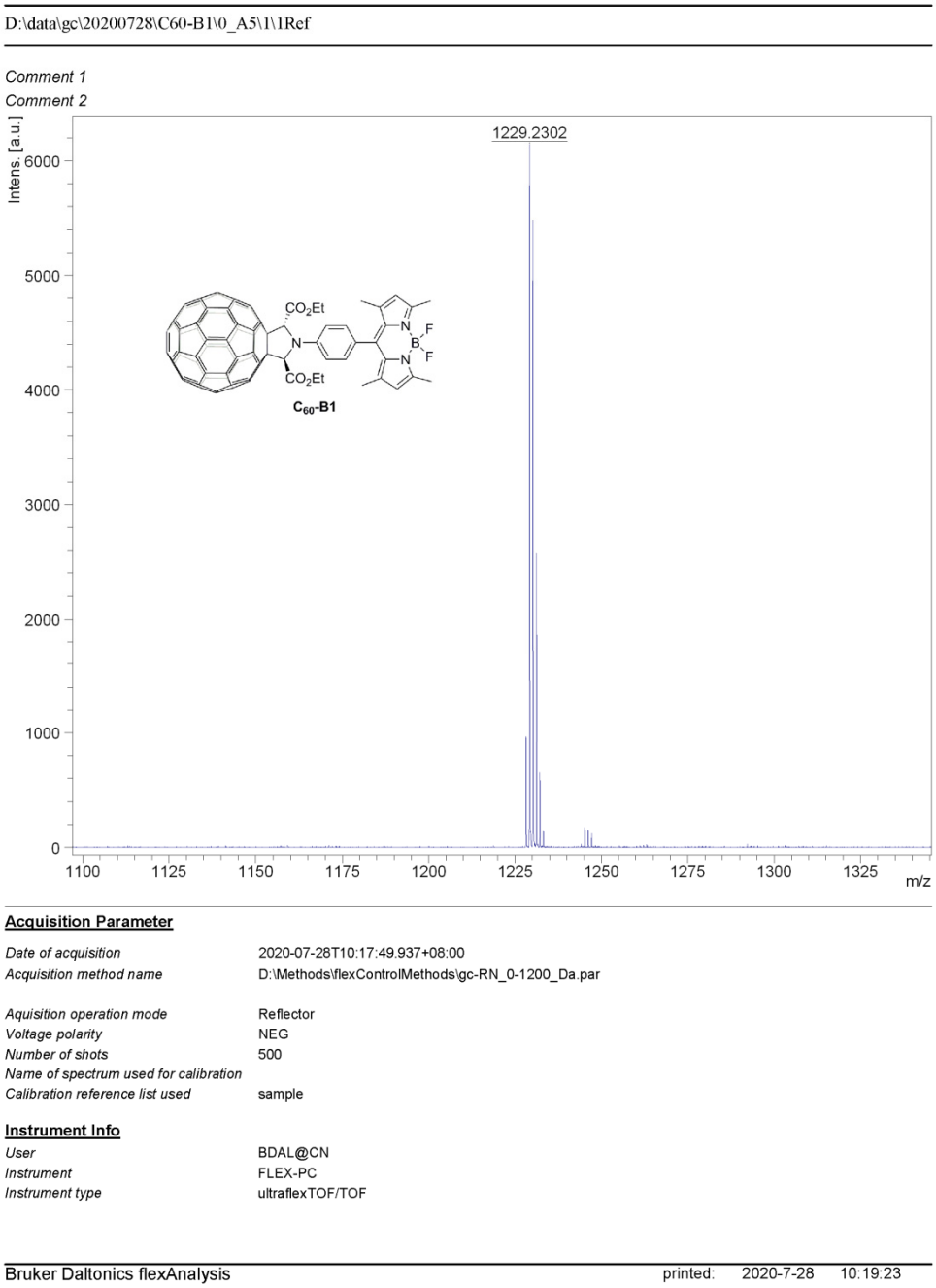


Figure S8. Expansion of the high resolution mass spectrum of **C_{60}-B1**.

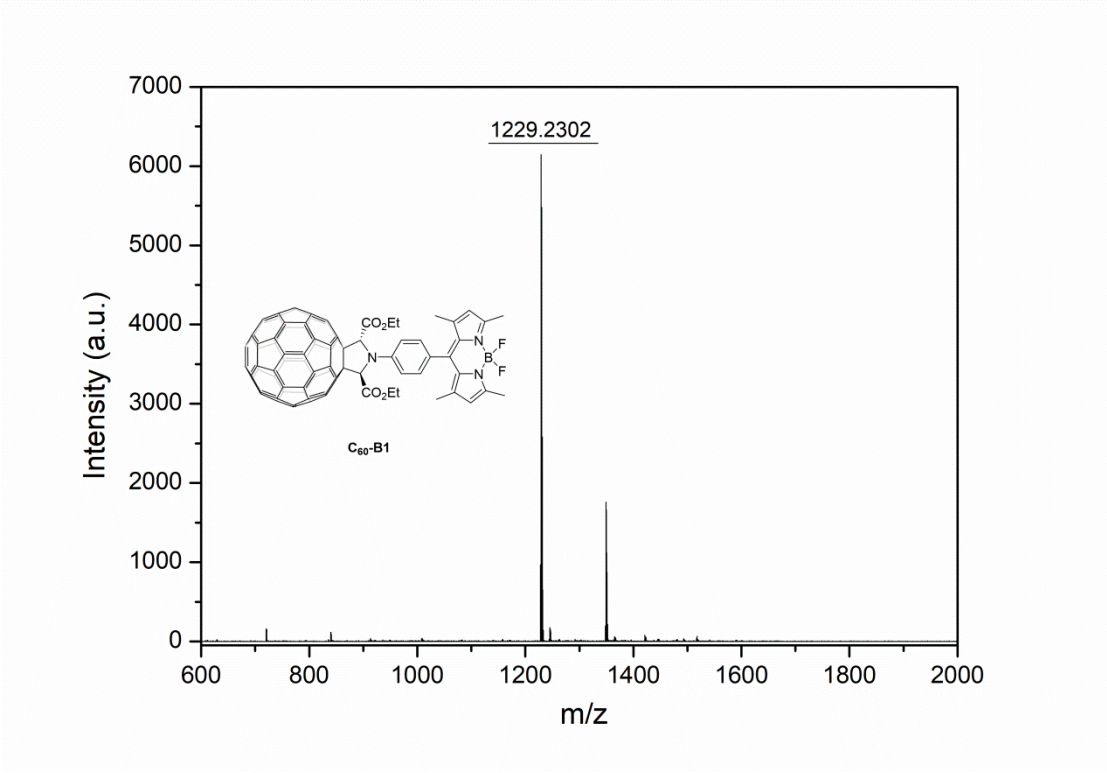


Figure S9. The high resolution mass spectrum of **C_{60}-B1**.

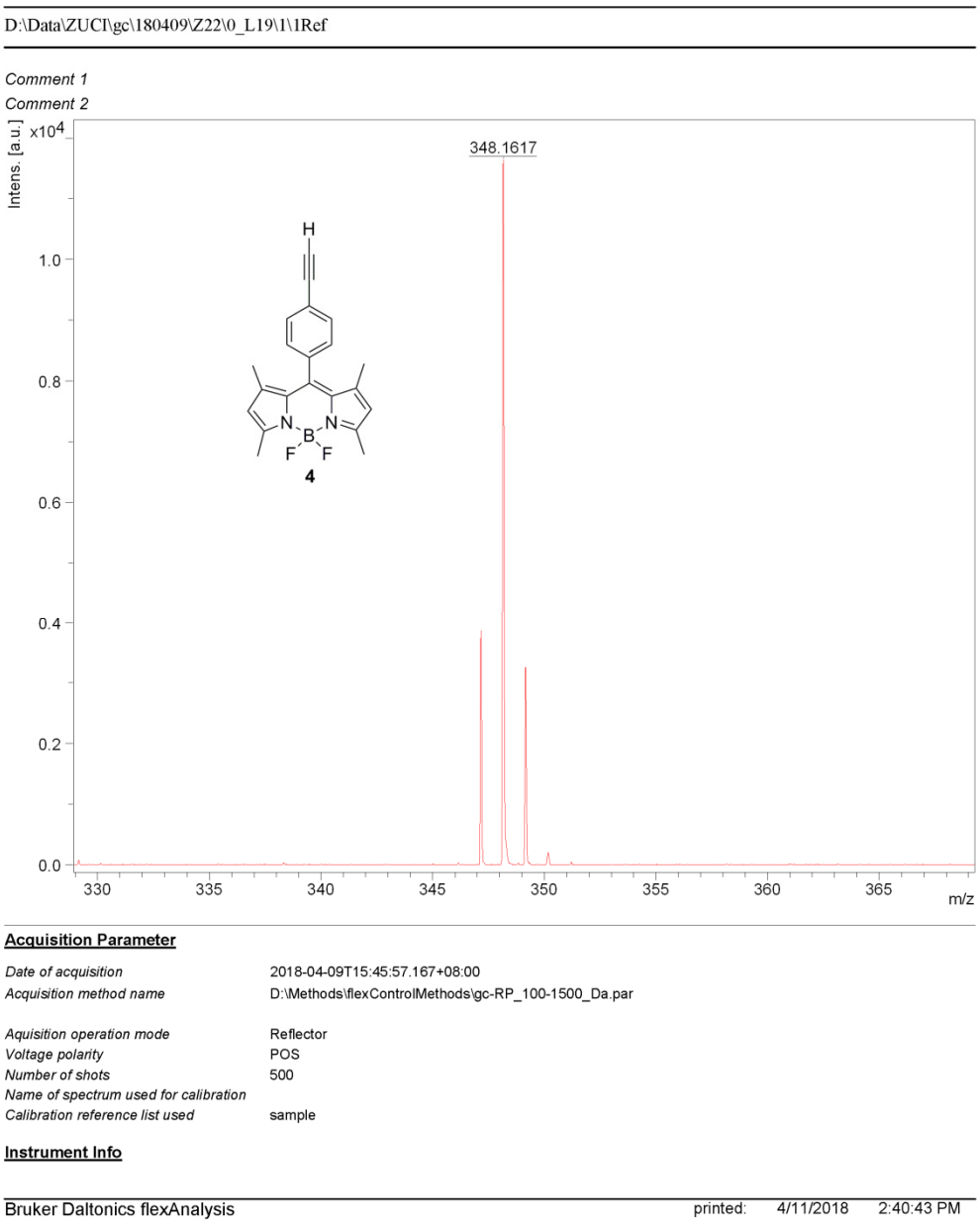


Figure S10. Expansion of the high resolution mass spectrum of **4**.

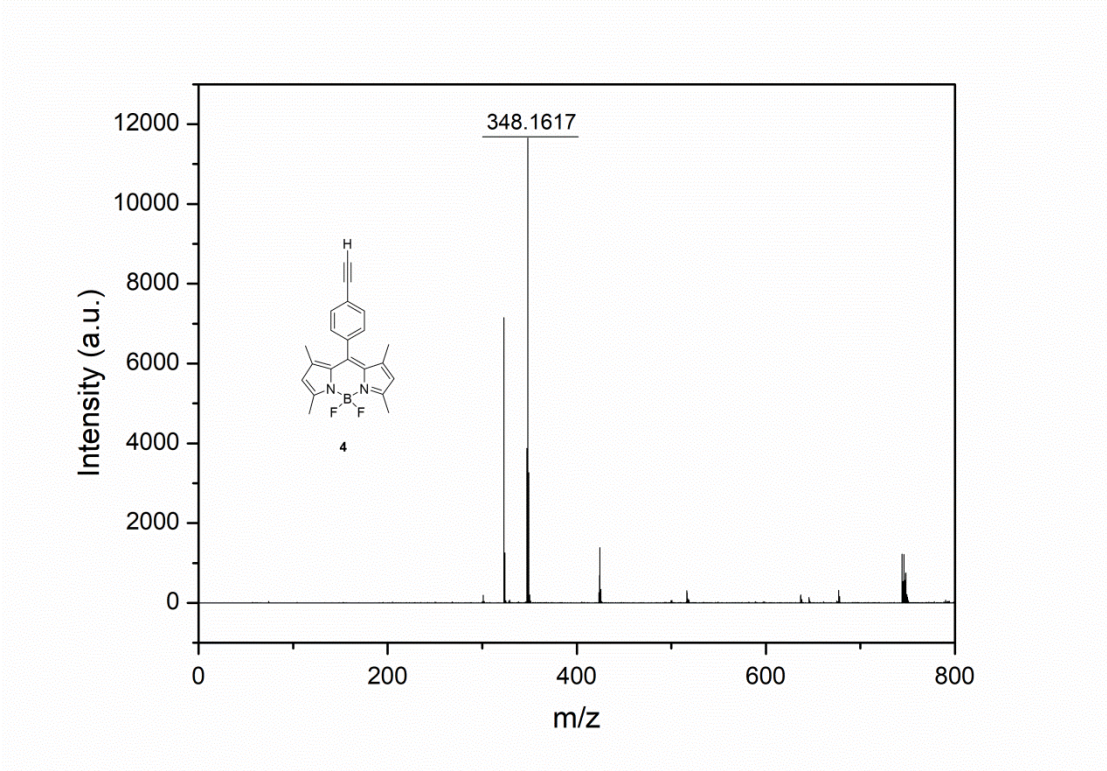


Figure S11. The high resolution mass spectrum of **4**.

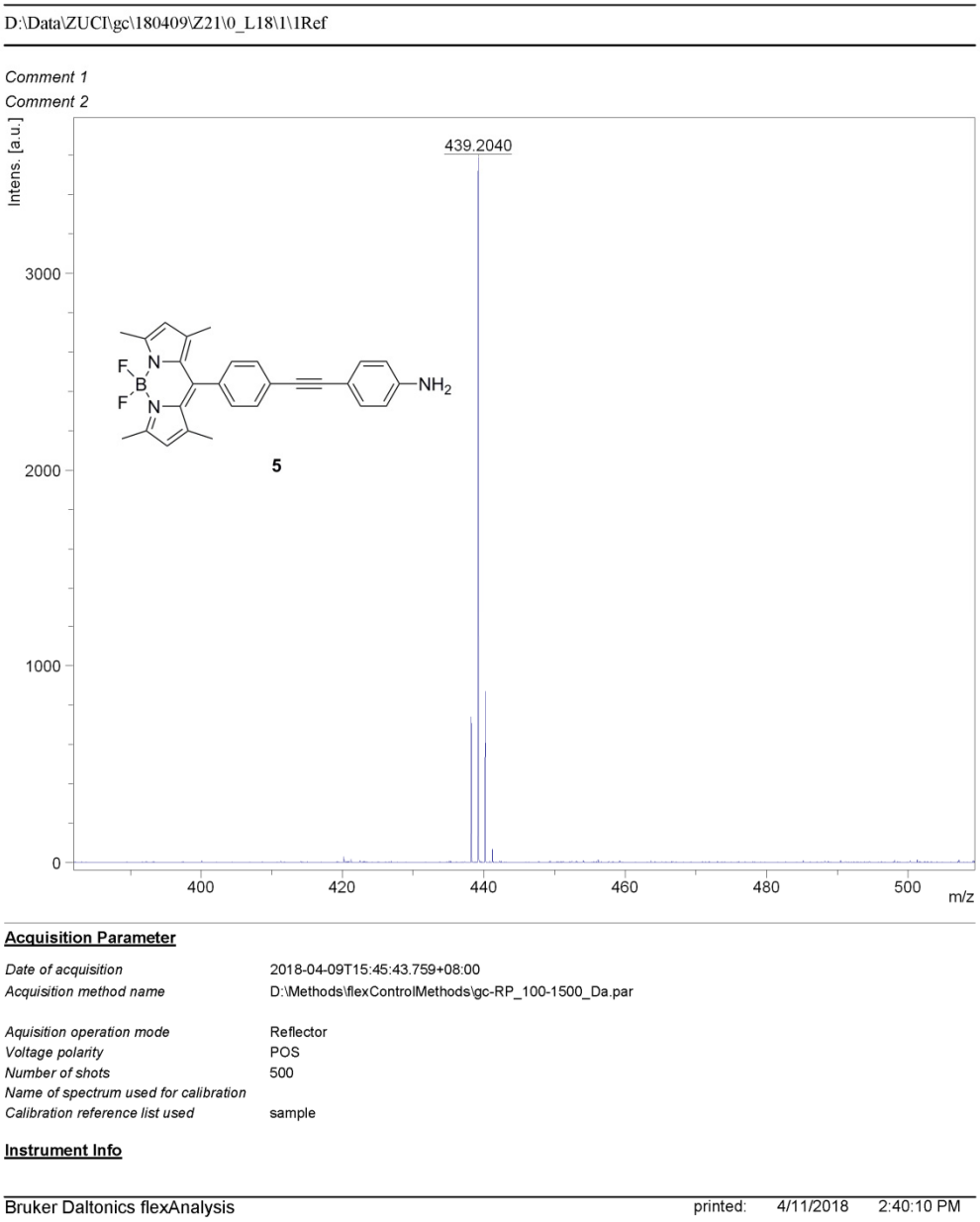


Figure S12. Expansion of the high resolution mass spectrum of **5**.

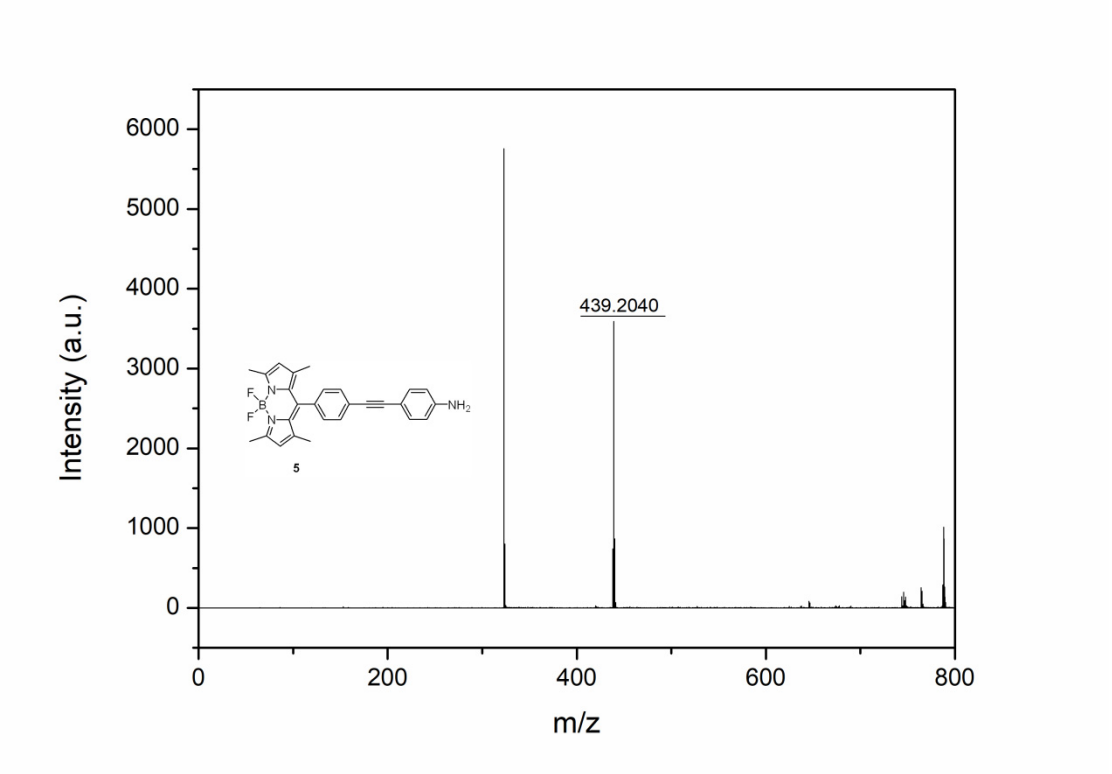


Figure S13. The high resolution mass spectrum of **5**.

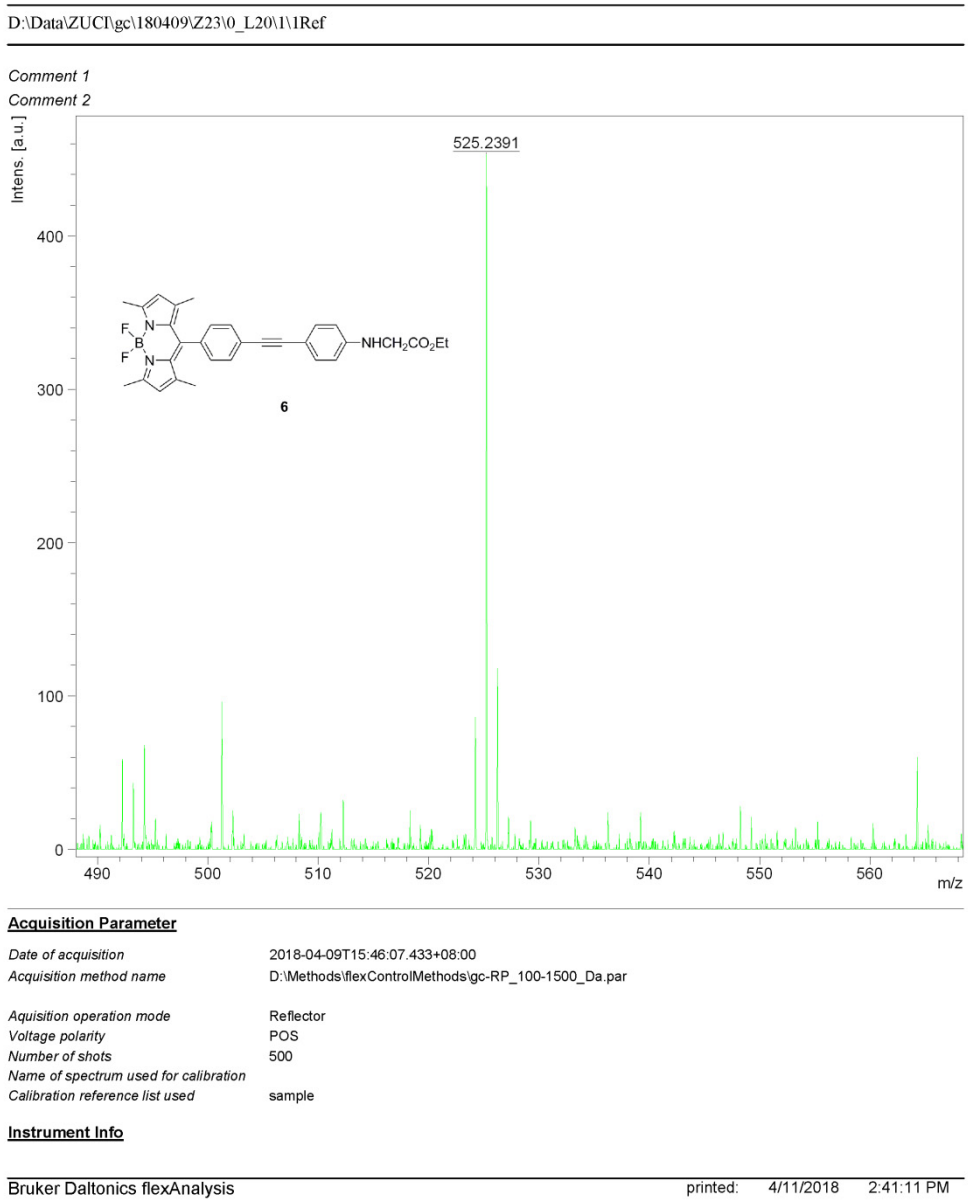


Figure S14. Expansion of the high resolution mass spectrum of **6**.

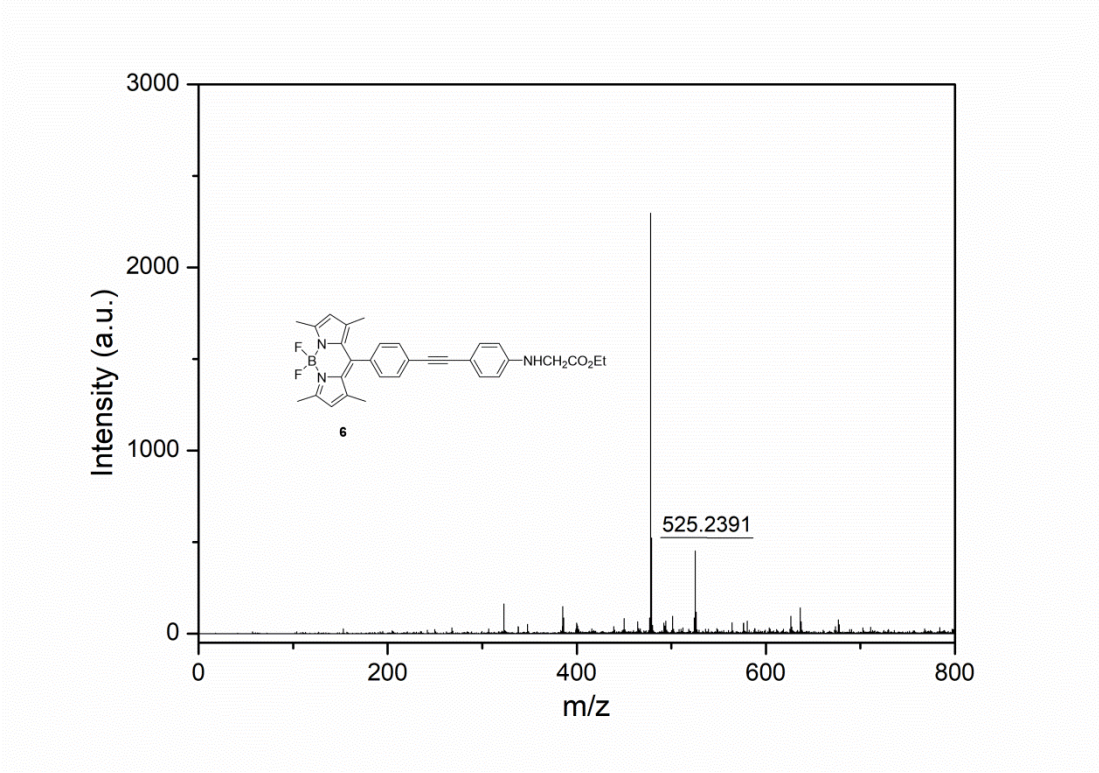
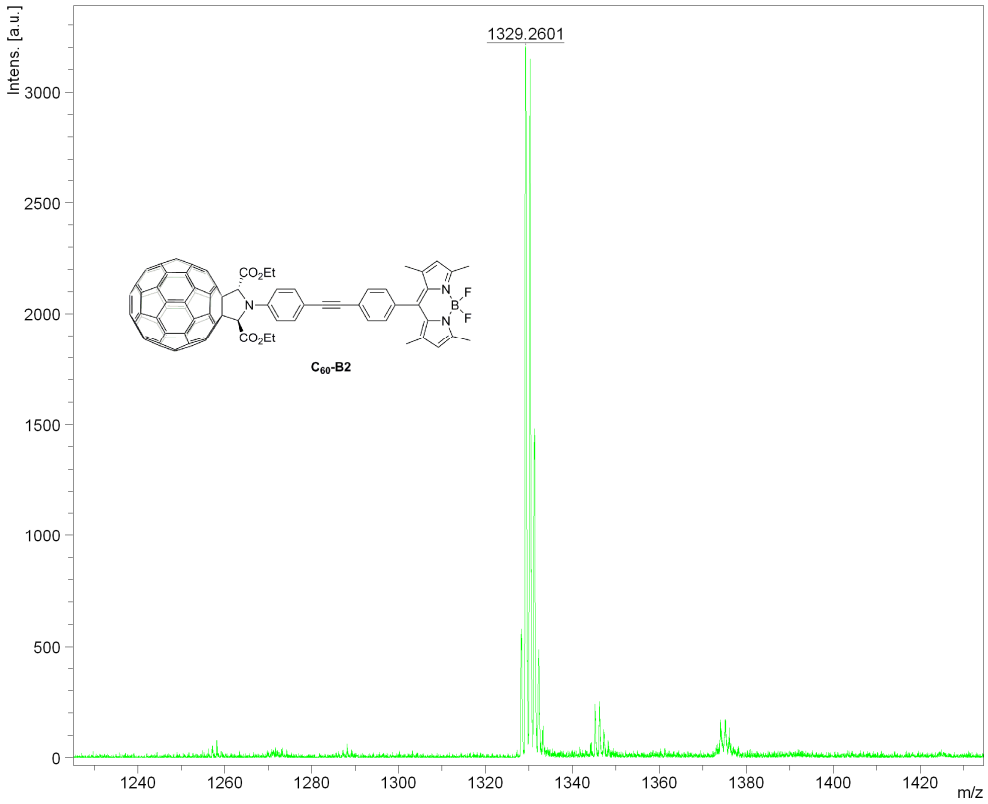


Figure S15. The high resolution mass spectrum of **6**.

D:\Data\ZUCI\gc\180131\17\0_N17\1\1Ref

Comment 1
Comment 2



Acquisition Parameter

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Acquisition method name	D:\Methods\flexControlMethods\gc-RN_0-1200_Da.par
Aquisition operation mode	Reflector
Voltage polarity	NEG
Number of shots	500
Name of spectrum used for calibration	
Calibration reference list used	sample

Instrument Info

Bruker Daltonics flexAnalysis printed: 1/31/2018 5:34:05 PM

Figure S16. Expansion of the high resolution mass spectrum of **C_{60}-B2**.

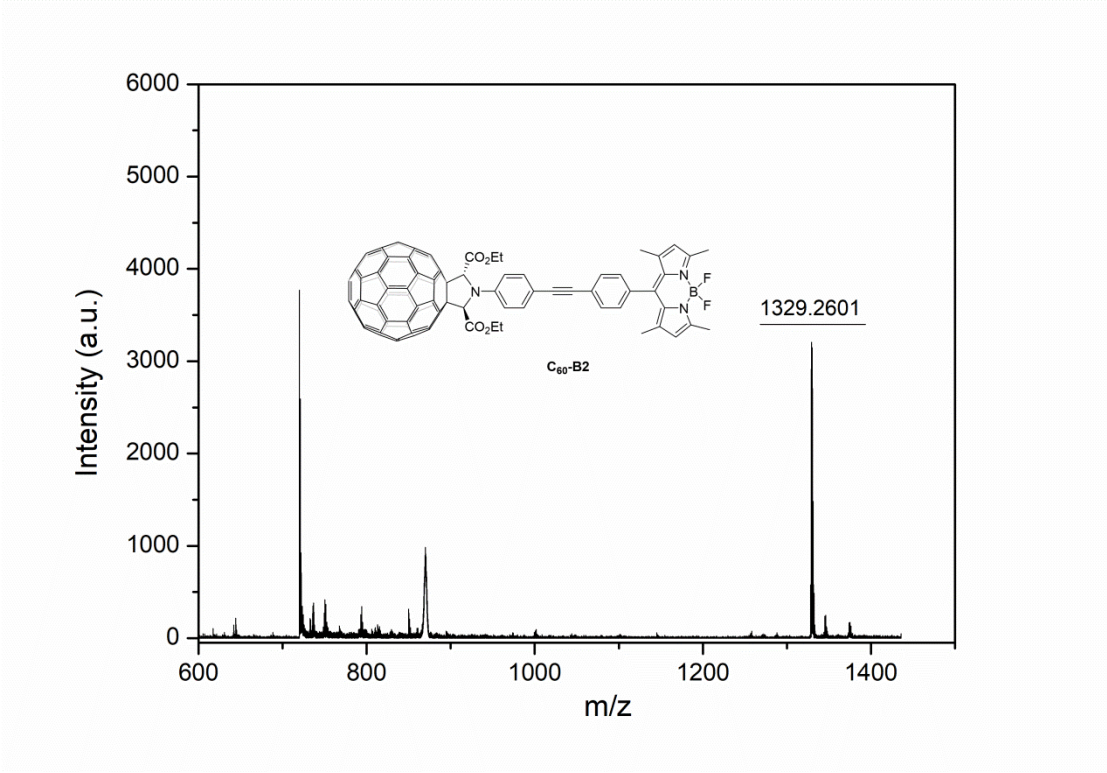

Figure S17. The high resolution mass spectrum of **C_{60}-B2**.

7. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra

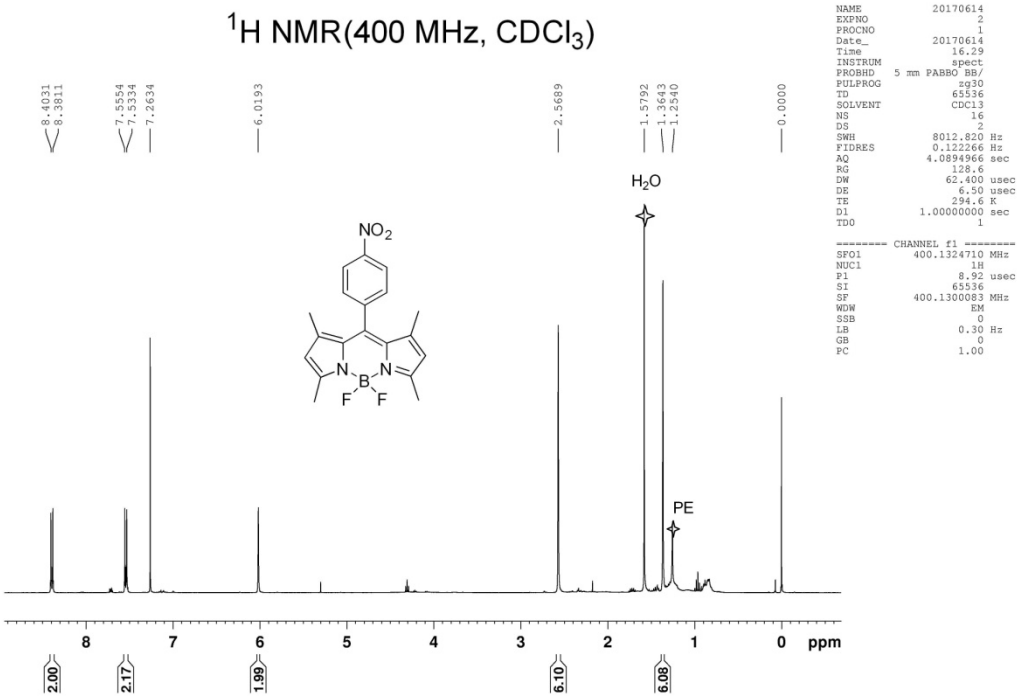

Figure S18. ^{1}H NMR of **1** in $CDCl_3$ (400 MHz).

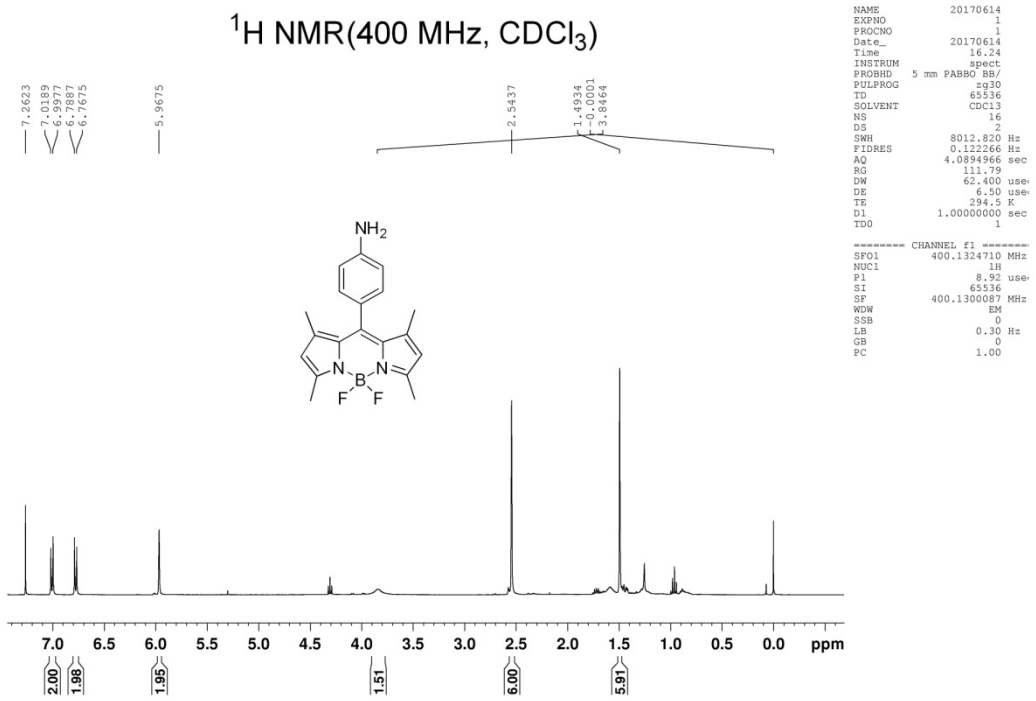

Figure S19. ^{1}H NMR of **R1** in $CDCl_3$ (400 MHz).

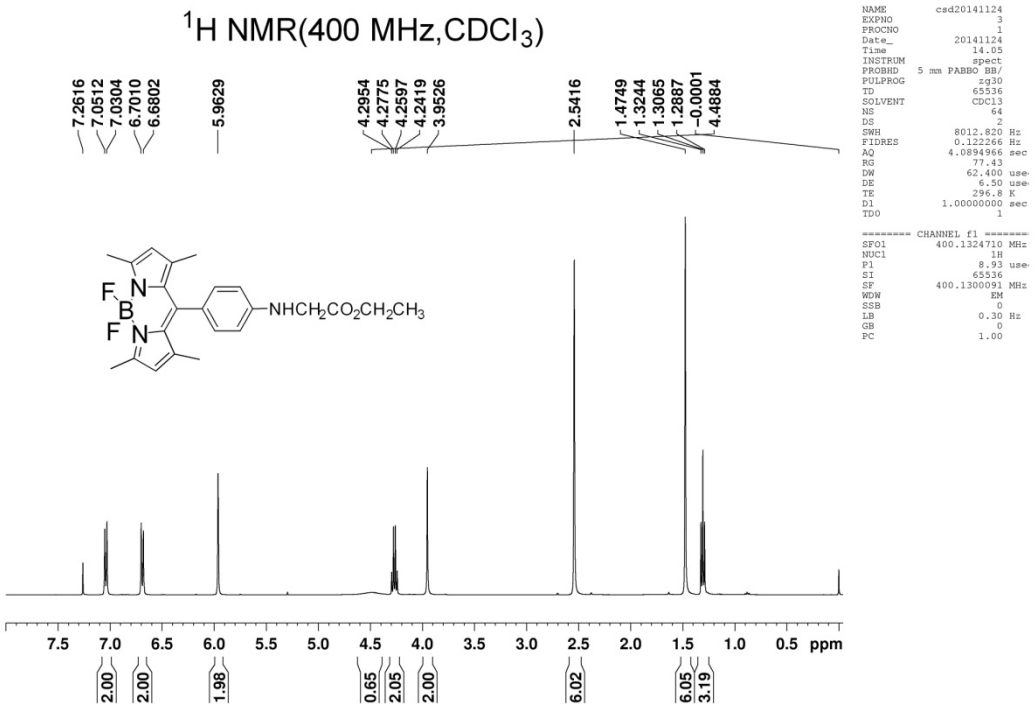

Figure S20. ^{1}H NMR of **2** in $CDCl_3$ (400 MHz).

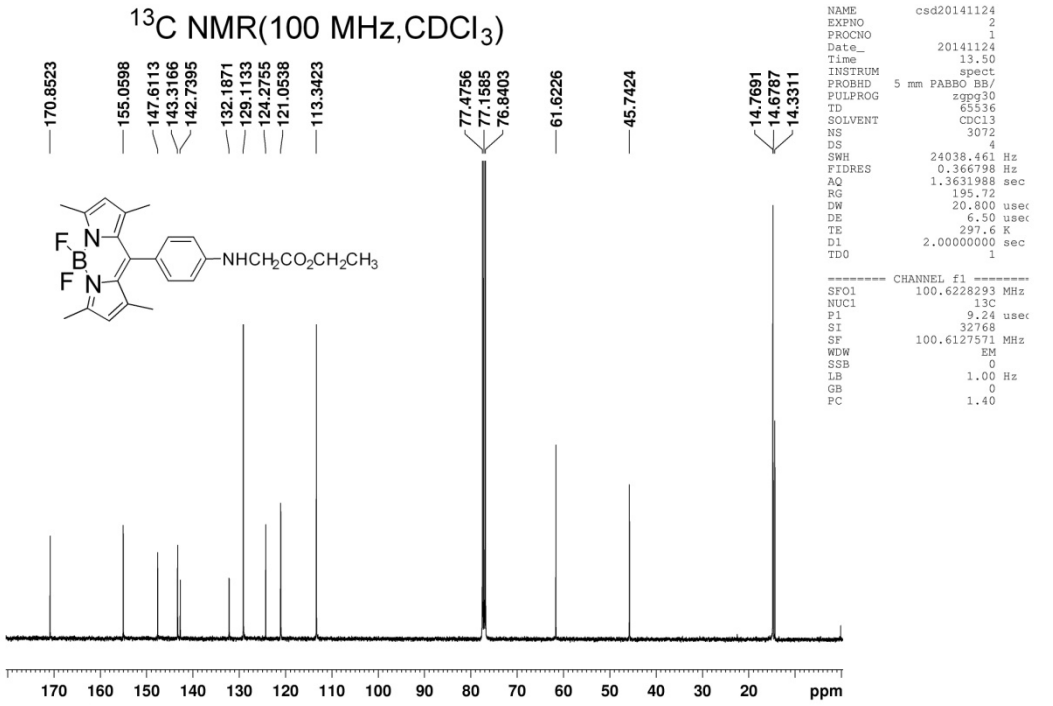

Figure S21. ^{13}C NMR of **2** in $CDCl_3$ (100 MHz).

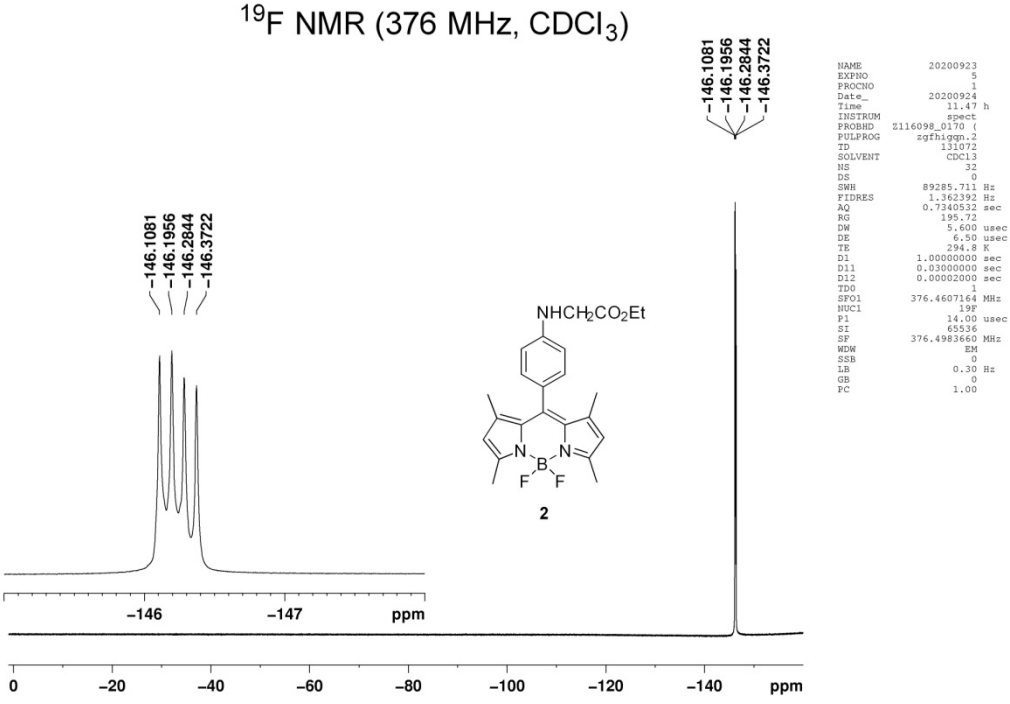

Figure S22. ^{19}F NMR of **2** in $CDCl_3$ (376 MHz).

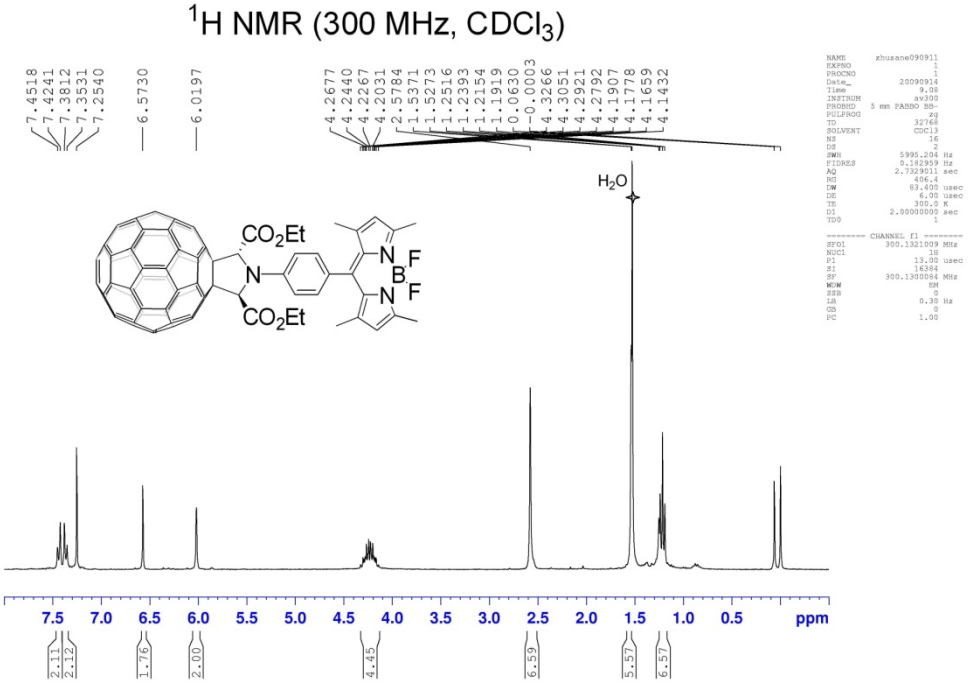

Figure S23. ^{1}H NMR of **C_{60}-B1** in $CDCl_3$ (300 MHz).

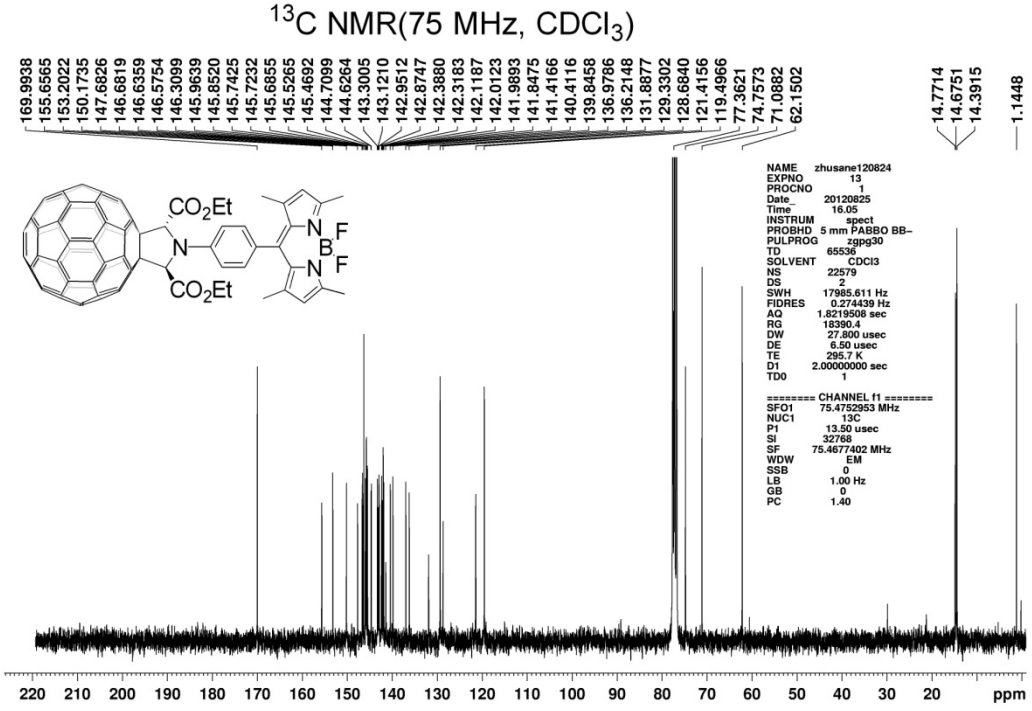

Figure S24. ^{13}C NMR of **C_{60}-B1** in $CDCl_3$ (75 MHz).

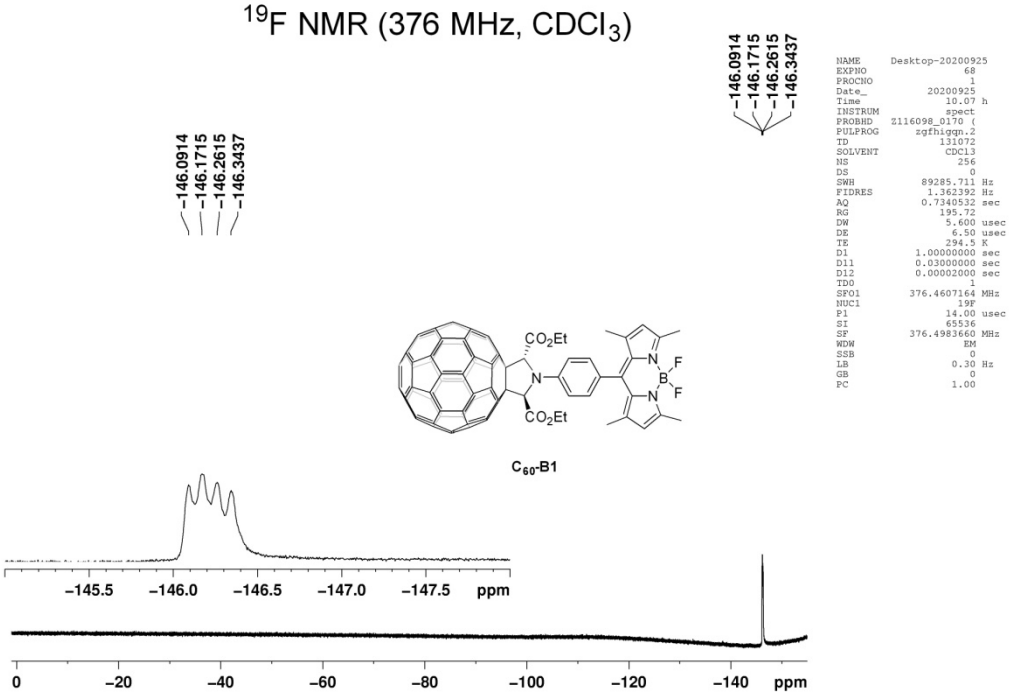

Figure S25. ^{19}F NMR of **C_{60}-B1** in $CDCl_3$ (376 MHz).

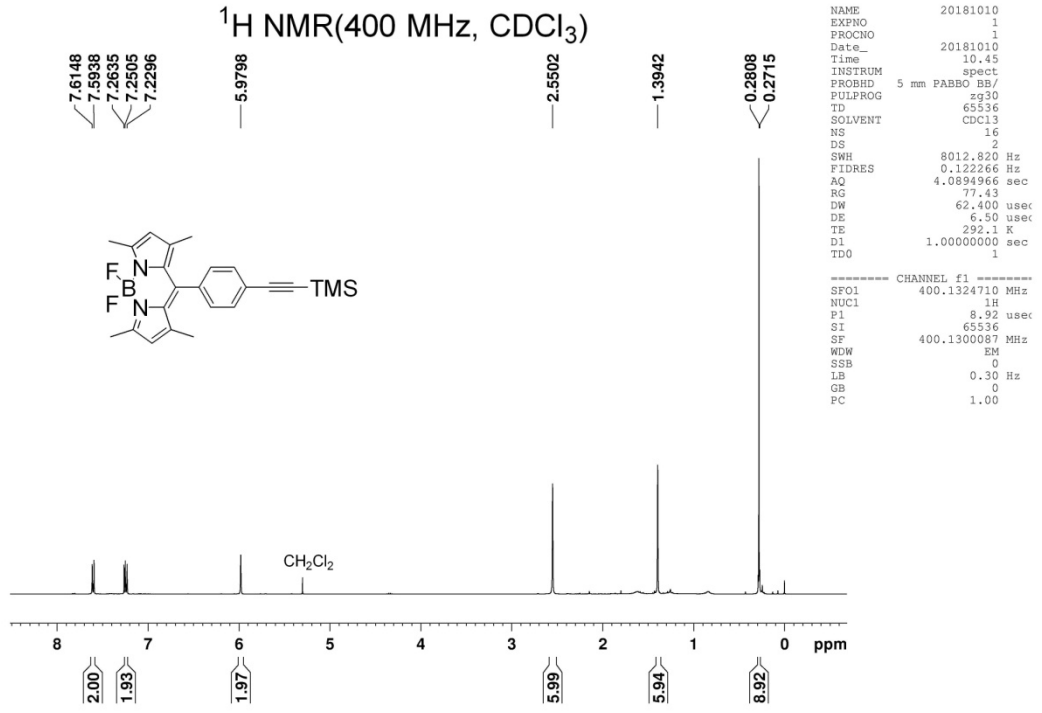

Figure S26. ^{1}H NMR of **3** in $CDCl_3$ (400 MHz).

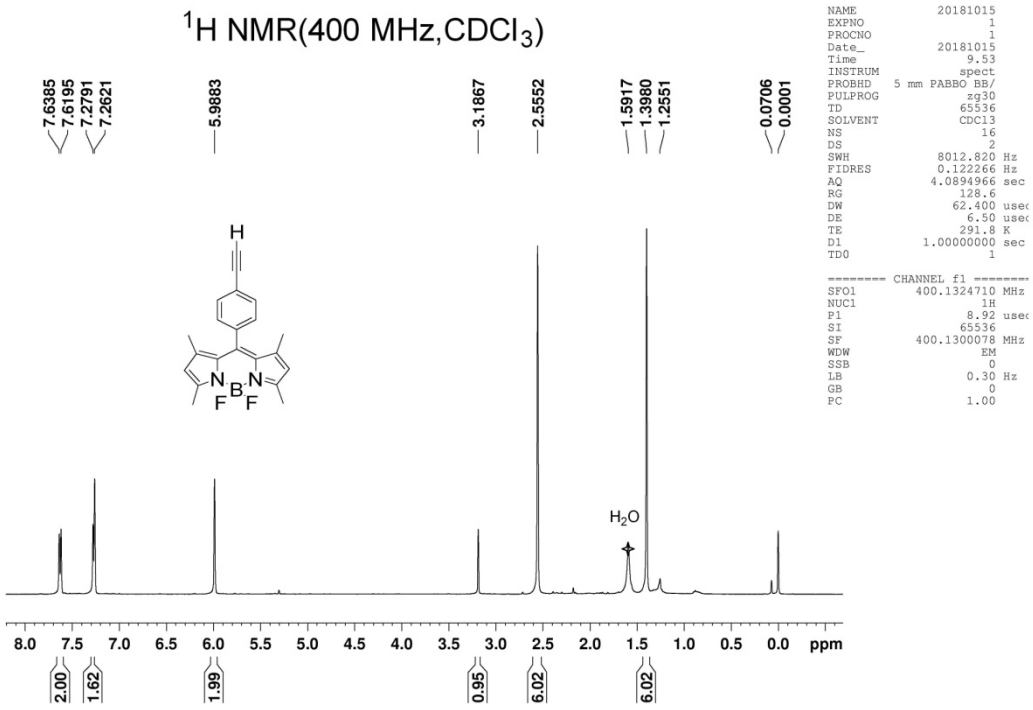

Figure S27. ^{1}H NMR of **4** in $CDCl_3$ (400 MHz).

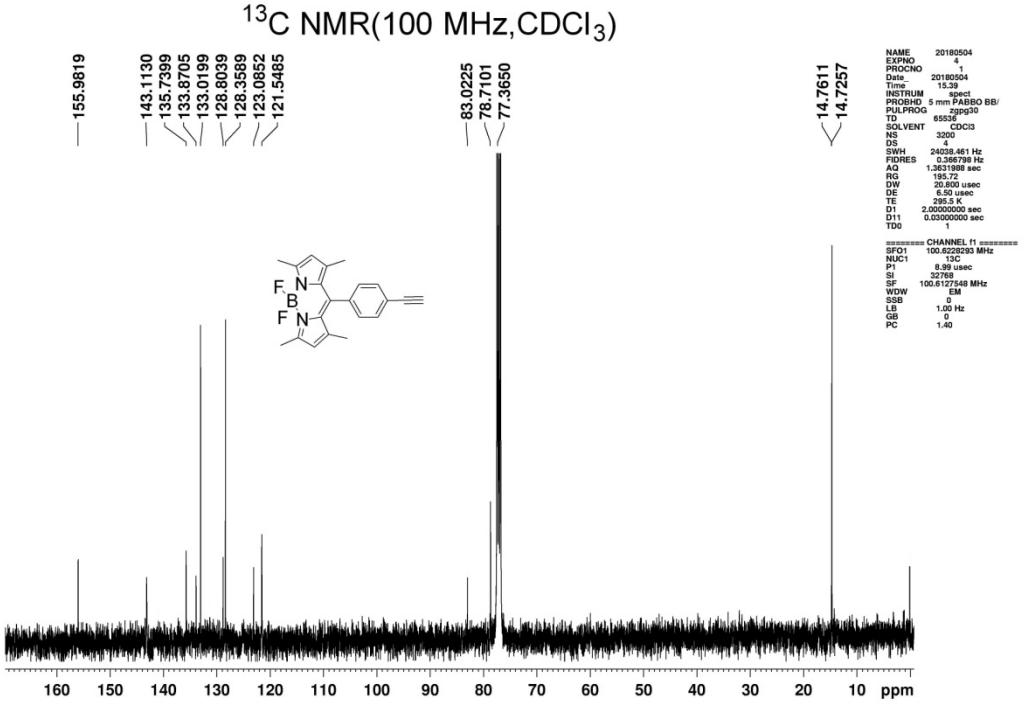

Figure S28. ^{13}C NMR of **4** in $CDCl_3$ (100 MHz).

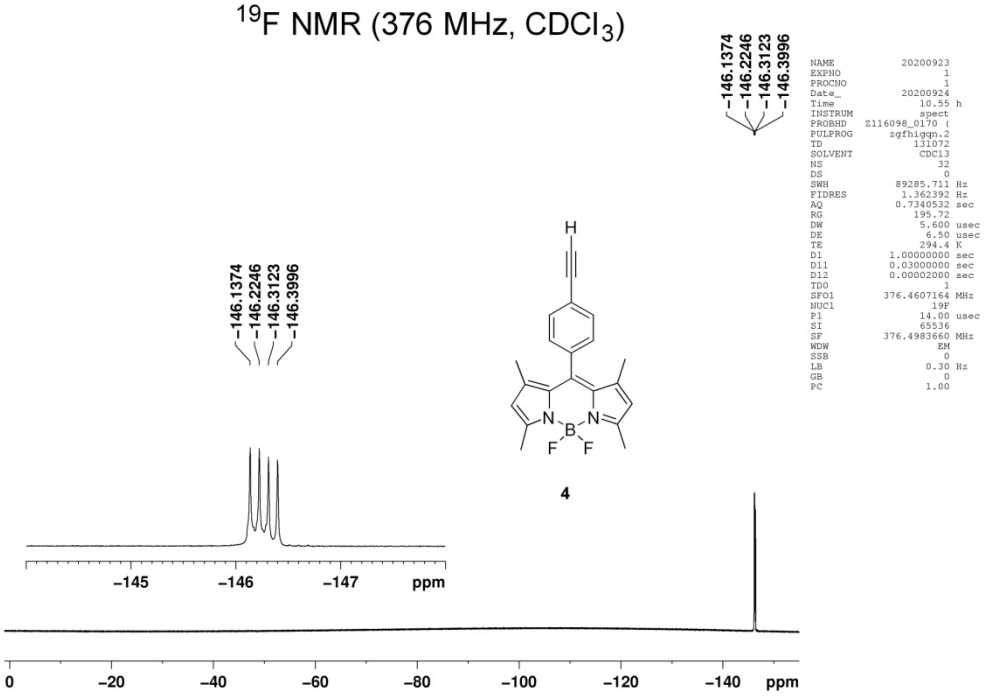

Figure S29. ^{19}F NMR of **4** in $CDCl_3$ (376 MHz).

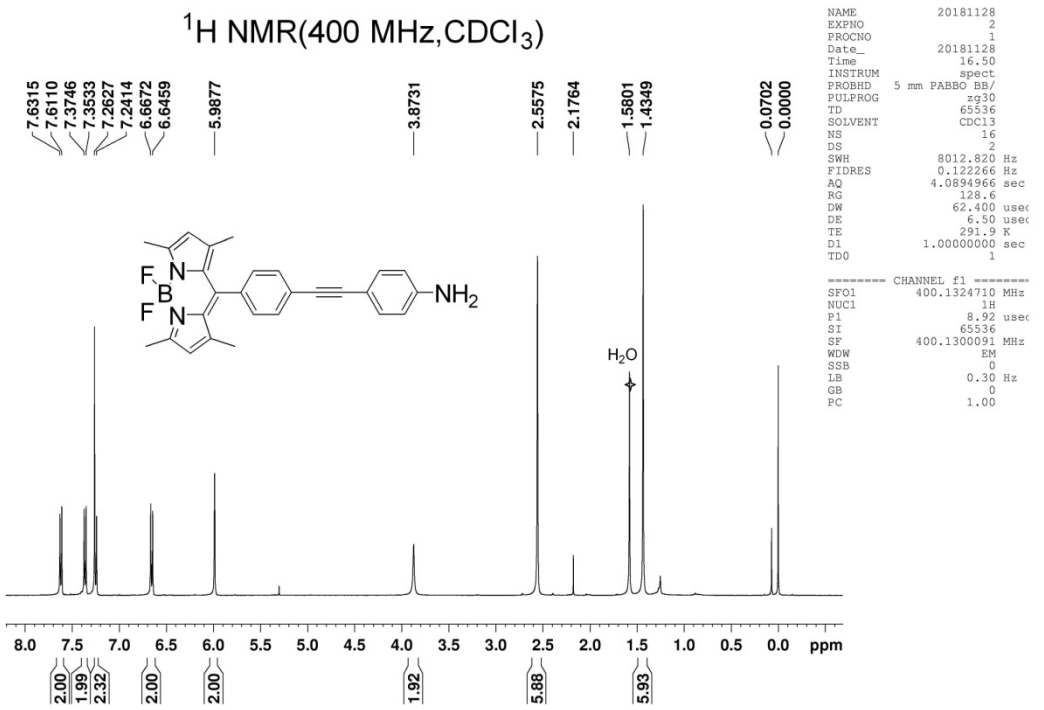

Figure S30. ^{1}H NMR of **5** in $CDCl_3$ (400 MHz).

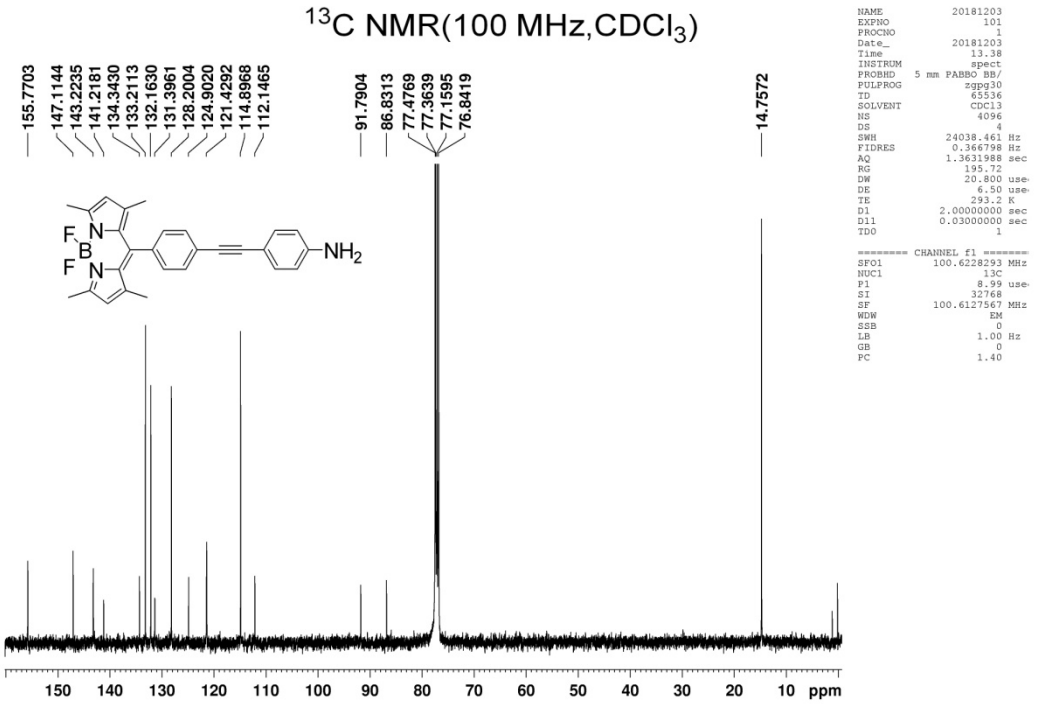

Figure S31. ^{13}C NMR of **5** in $CDCl_3$ (100 MHz).

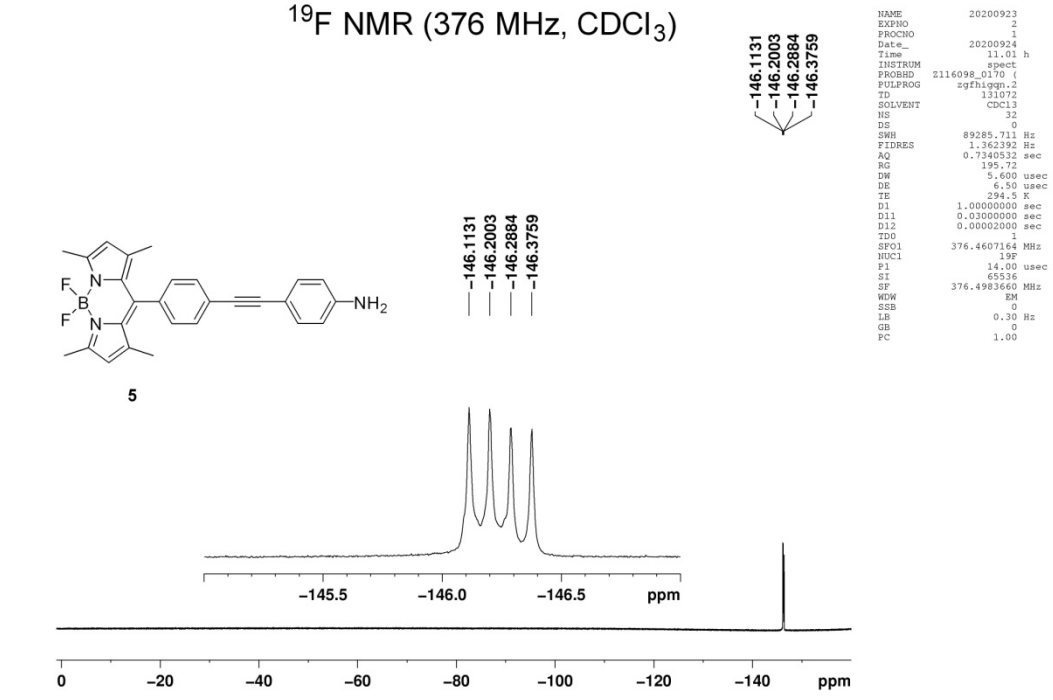

Figure S32. ^{19}F NMR of **5** in $CDCl_3$ (376 MHz).

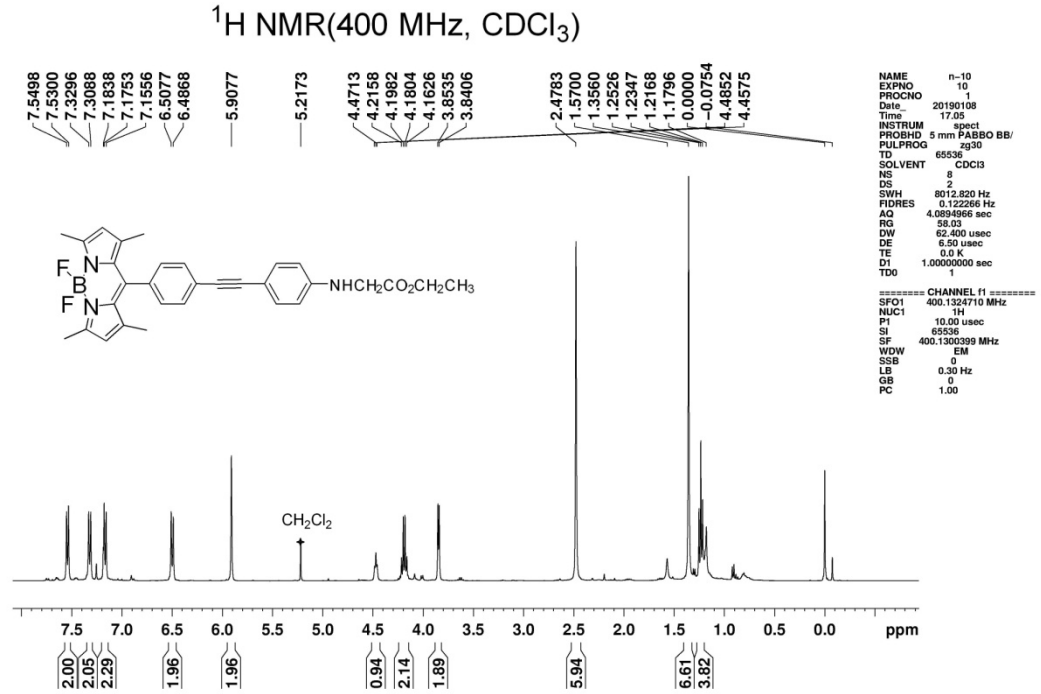

Figure S33. ^{1}H NMR of **6** in $CDCl_3$ (400 MHz).

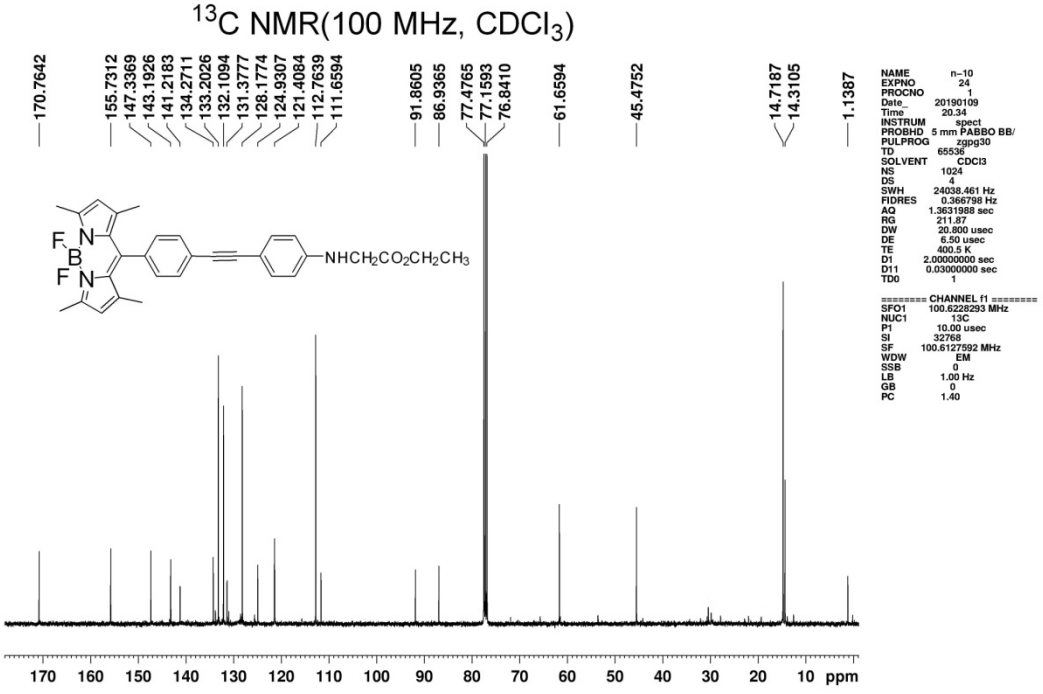

Figure S34. ^{13}C NMR of **6** in $CDCl_3$ (100 MHz).

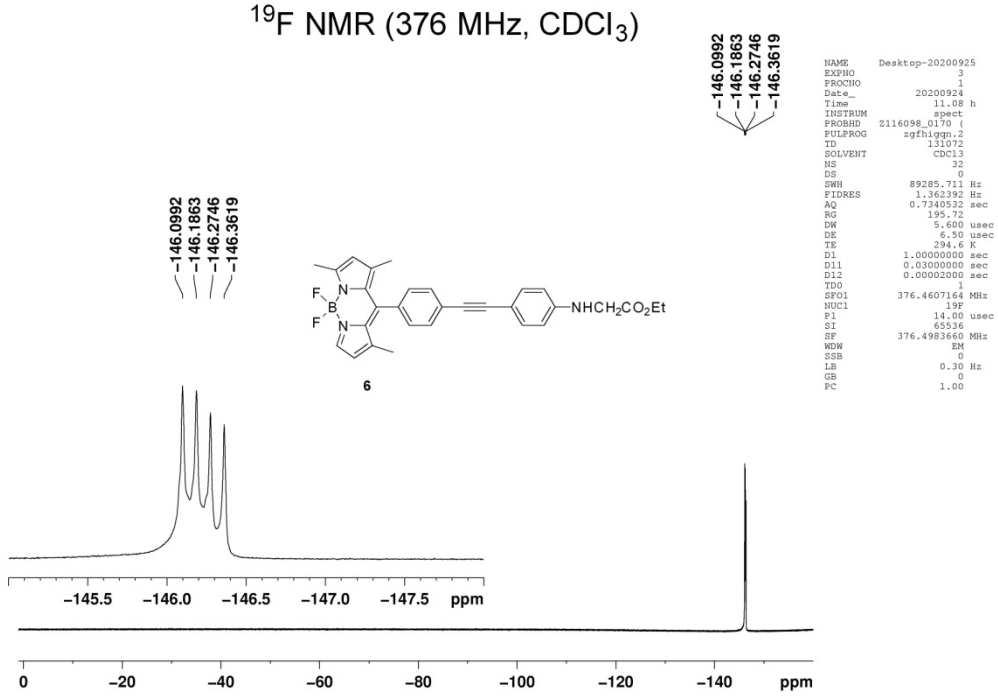

Figure S35. ^{19}F NMR of **6** in $CDCl_3$ (376 MHz).

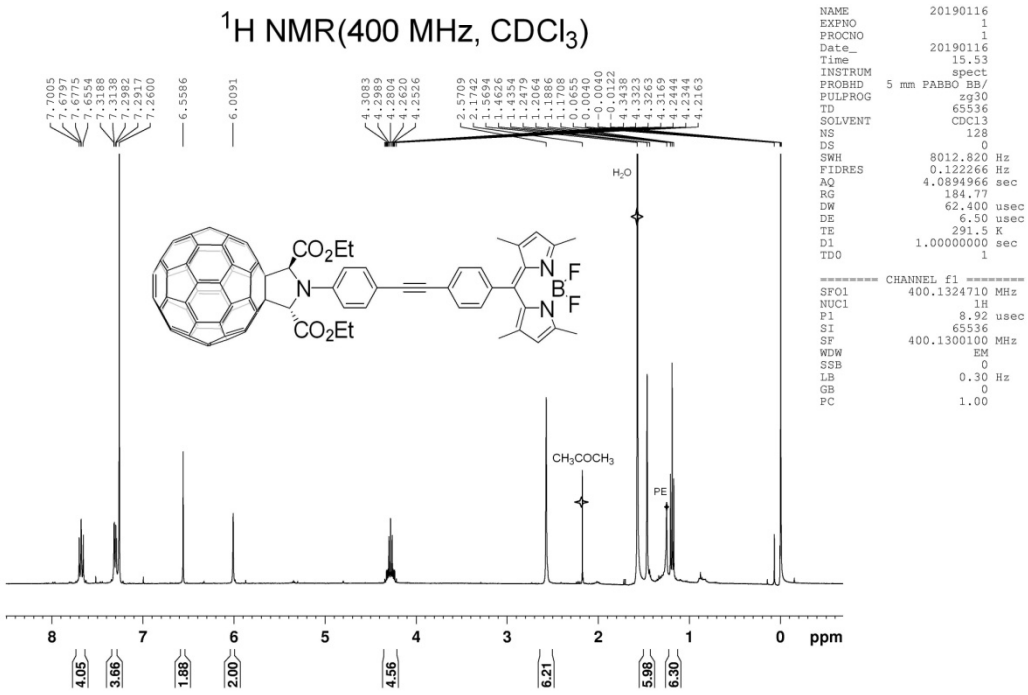

Figure S36. ^{1}H NMR of **C_{60}-B2** in $CDCl_3$ (400 MHz).

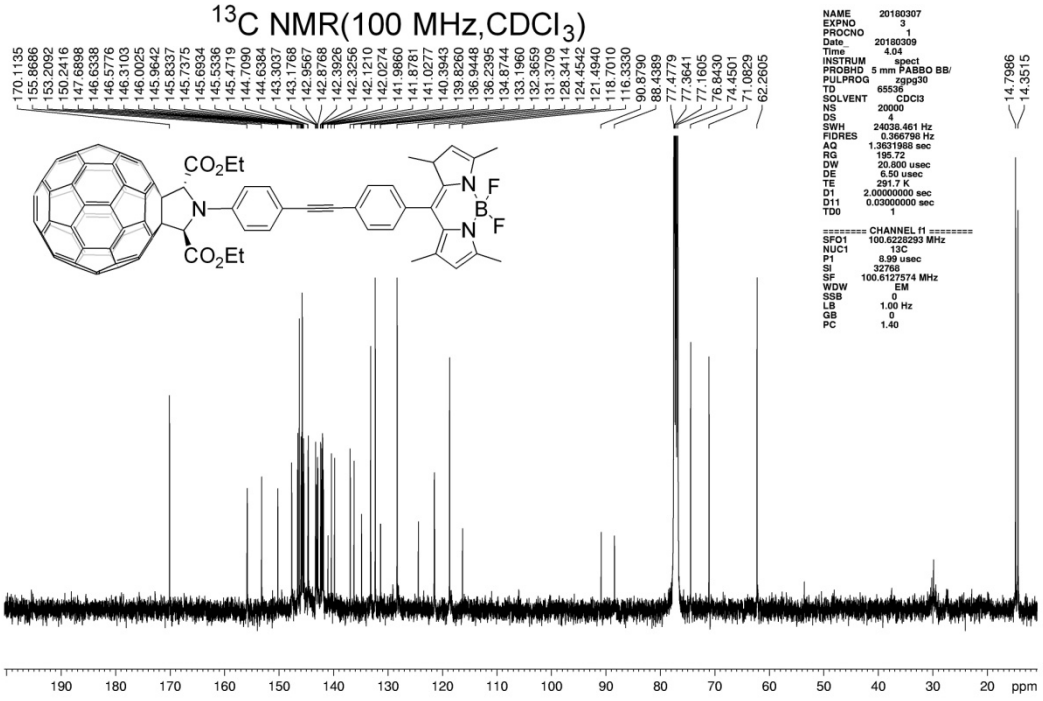

Figure S37. ^{13}C NMR of **C_{60}-B2** in $CDCl_3$ (100 MHz)

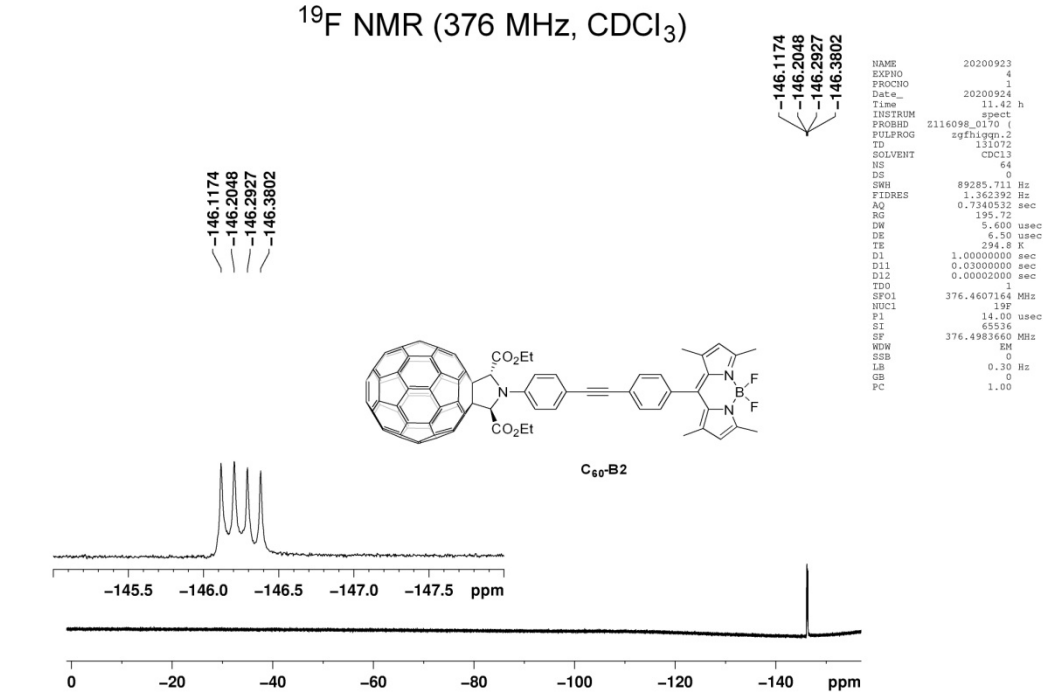

Figure S38. ^{19}F NMR of **C_{60}-B2** in $CDCl_3$ (376 MHz).