Supporting Information
For

Enhancement of Two Photon Absorption Properties and Intersystem Crossing by Charge Transfer in Pentaaryl Boron Dipyrromethene (BODIPY) Derivatives

B. Küçüköz,[a] G. Sevinç,[b] E. Yildiz,[a] A. Karatay,[a] F. Zhong,[c] H. Yılmaz,[b] Y. Tutel,[a] M. Hayvalı[b*], J. Zhao,[c*] H. G. Yaglioglu[a*]

[a]*Department of Chemistry, Faculty of Science, Ankara University, 06100 Beşevler, Ankara, Turkey*
[b]*Department of Engineering Physics, Faculty of Engineering, Ankara University, 06100 Beşevler, Ankara, Turkey*

* Corresponding authors: Tel/Fax: +90 (312) 2127343 (G.Y.), Tel/Fax: +90 (312) 2232395 (M. H.)
E-mail addresses: yoglu@eng.ankara.edu.tr (H.G. Yaglioglu), hayvali@science.ankara.edu.tr (M. Hayvalı), zhaojzh@dlut.edu.cn (J. Zhao)

Contents **Page**

1. General Information 3
2. Characterization 3
3. Synthesis 3
3.1 Synthesis of Compound 4,4-difluoro-8-[4-(diphenylamino)phenyl]-1,7-[4-methoxyphenyl]-3,5-[4-bromophenyl]-4-bora-3a,4a-diaza-s-indacene (B1) 3
Scheme S5. Synthesis of Compound B1 3
3.2 Synthesis of Compound 4,4-difluoro-8-[4-(diphenylamino)phenyl]-1,7-[4-methoxyphenyl]-3,5-[4-methoxybiphenyl]-4-bora-3a,4a-diaza-s-indacene (B2) 4
Scheme S6. Synthesis of Compound B2 4
3.3 Synthesis of Compound 4,4-difluoro-8-[4-(diphenylamino)phenyl]-1,7-[4-methoxyphenyl]-3,5-[2,4-dimethoxybiphenyl]-4-bora-3a,4a-diaza-s-indacene (B3) 5

Scheme S7. Synthesis of Compound B3 5

3.4 Synthesis of Compound 4,4-difluoro-8-[4-(diphenylamino)phenyl]-1,7-[4-methoxyphenyl]-3,5-[4-N,N-diphenylaminobiphenyl]-4-bora-3a,4a-diaza-s-indacene (B4) 6

Scheme S8. Synthesis of Compound B4A 6

3.5 Synthesis of Compound 4,4-difluoro-8-[4-(diphenylamino)phenyl]-1,7-[4-methoxyphenyl]-3,5-[4-(1-pyrene)phenyl]-4-bora-3a,4a-diaza-s-indacene (B5) 7

Scheme S9. Synthesis of Compound B5 7

4. ADDITIONAL DATA 8

Figure S1. ^{1}H-NMR for compound B1 in $CDCl_3$ at 400 MHz 8

Figure S2. ^{13}C-NMR for compound B1 in $CDCl_3$ at 100 MHz 8

Figure S3. HRMS/TOF-ESI Spectrum of compound B1 9

Figure S4. ^{1}H-NMR for compound B2 in $CDCl_3$ at 400 MHz 9

Figure S5. ^{13}C-NMR for compound B2 in $CDCl_3$ at 100 MHz 10

Figure S6. HRMS/TOF-ESI Spectrum of compound B2 10

Figure S7. ^{1}H-NMR for compound B3 in $CDCl_3$ at 400 MHz 11

Figure S8. ^{13}C-NMR for compound B3 in $CDCl_3$ at 100 MHz 11

Figure S9. HRMS/TOF-ESI Spectrum of compound B3 12

Figure S10. ^{1}H-NMR for compound B4 in $CDCl_3$ at 400 MHz 12

Figure S11. ^{13}C-NMR for compound B4 in $CDCl_3$ at 100 MHz 13

Figure S12. HRMS/TOF-ESI Spectrum of compound B4 13

Figure S13. ^{1}H-NMR for compound B5 in $CDCl_3$ at 400 MHz 14

Figure S14. ^{13}C-NMR for compound B5 in $CDCl_3$ at 100 MHz 14

Figure S16. Femtosecond transient absorption spectra of B1 with different time delays 15

Figure S17. Experimental results (symbols) and theoretical fits (solid line) of open aperture Z-scan experiments for B2, B3, B4and B5 compounds at 76 GW/cm^2 input intensity in THF, using 800 nm femtosecond pulses. 16

1. General Information

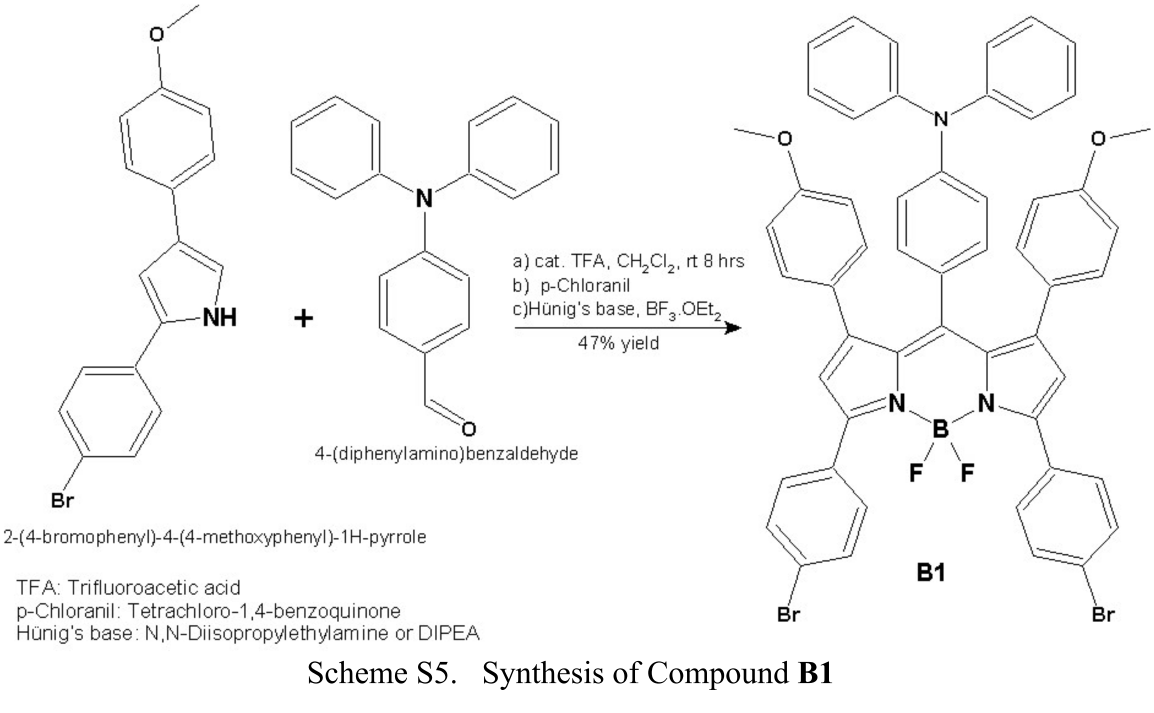
All solvents and reagents were purchased from Sigma-Aldrich Chemical Company and used as received without further purification. Reactions were monitored by thin layer chromatography using fluorescent coated aluminum sheets.

2. Characterization

Melting points were determined on a Barnstead Elechtrothermal 9100 platform. UV-Visible spectra were recorded on a SHIMADZU UV-1800 UV-vis spectrophotometer. Fluorescence spectra were recorded on a Perkin Elmer L5S55 Fluorescence Spectrometer. Mass spectral analyses were performed on a Agilent 6224 TOF LC/MS spectrometer.^{1}H NMR spectra were recorded on a VARIAN Mercury 400 MHz spectrometer. ^{1}H NMR chemical shifts (δ) are given in ppm downfield from Me_4Si, determined by chloroform ($\delta = 7.26$ ppm).^{13}C NMR spectra were recorded on a VARIAN Mercury 100 MHz spectrometer. ^{13}C NMR chemical shifts (δ) are reported in ppm with the internal $CDCl_3$ δ 77.0 ppm as standard.

3. Synthesis

3.1 Synthesis of Compound 4,4-difluoro-8-[4-(diphenylamino)phenyl]-1,7-[4-methoxyphenyl]-3,5-[4-bromophenyl]-4-bora-3a,4a-diaza-s-indacene (B1)



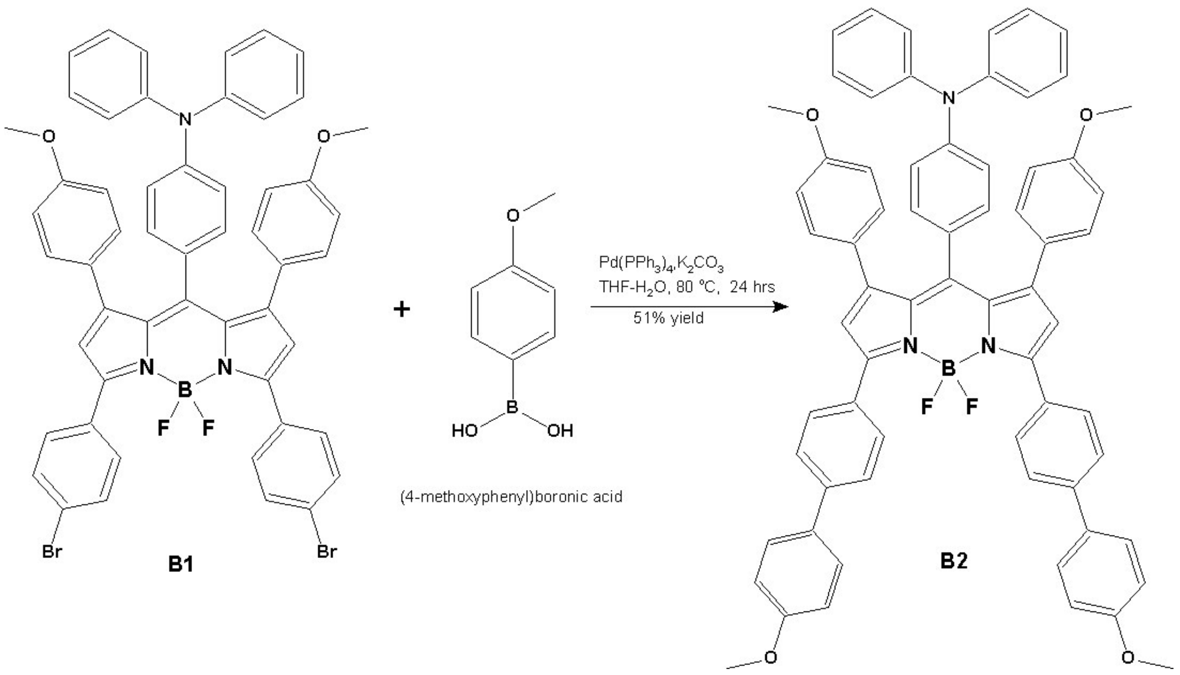
Scheme S5. Synthesis of Compound **B1**

2-(4-bromophenyl)-4-(4-methoxyphenyl)-1H-pyrrole (750 mg, 2.29 mmol) and 4-(diphenylamino)benzaldehyde (300 mg, 1.09 mmol) were dissolved in absolute CH_2Cl_2 (110 mL) under Ar atmosphere, one drop of Trifluoroacetic acid (TFA) and tetrachloro-1,4-benzoquinone (1.35 g. 5.49 mmol) was added, and the solution was stirred at room temperature for 10h. The reaction mixture was condensed to 30 mL and filtered to provide a green solid. Without purification, the green solid and hunig's base (1.27 mL, 7.68 mmol) were dissolved in 80 mL of CH_2CI_2, the mixture was stirred at room temperature for 10 min; $BF_3.OEt_2$ (1.53 mL, 12.07 mmol) were then added and stirring was continued overnight. The resulting solution was washed with water and dried over anhydrous Na_2SO_4, filtered, and evaporated. The residue was chromatographed on silica gel (elution: toluene) to afford 490 mg (yield: ~47%) Compound **B1** in the form of red powder.

Spectral data of Compound **B1** (mp = 306 ^oC)

^{1}H-NMR (400 MHz, $CDCl_3$):δ[ppm]: 3.81 (s, 6H), 6.23-6.25 (d, J=8.4 Hz, 2H), 6.48 (s, 2H), 6.64-6.66 (d, J=8.4 Hz, 4H), 6.76-6.78 (d, J=8.8 Hz, 2H), 6.82-6.84 (d, J=8.4 Hz, 4H), 6.85-6.87 (m, 4H), 7.07-7.11 (m, 2H), 7.27-7.31 (m, 4H), 7.55-7.57 (d, J=8.8 Hz, 4H), 7.72-7.75 (d, J=8.4 Hz, 4H). ^{13}C-NMR (100 MHz, $CDCI_3$) δ: 158.24, 155.11, 148.65, 147.82, 147.06, 146.60, 133.32, 132.60, 131.57, 131.40, 130.98, 130.13, 129.32, 128.61, 125.79, 124.25, 124.17, 124.01, 123.14, 118.35, 113.02, 55.24. HRMS/TOF-ESI: Calculated as 957.13715, found: 980.13117 $[M+Na]^+$, Δ=4.34 ppm

3.2 Synthesis of Compound 4,4-difluoro-8-[4-(diphenylamino)phenyl]-1,7-[4-methoxyphenyl]-3,5-[4-methoxybiphenyl]-4-bora-3a,4a-diaza-s-indacene (B2)



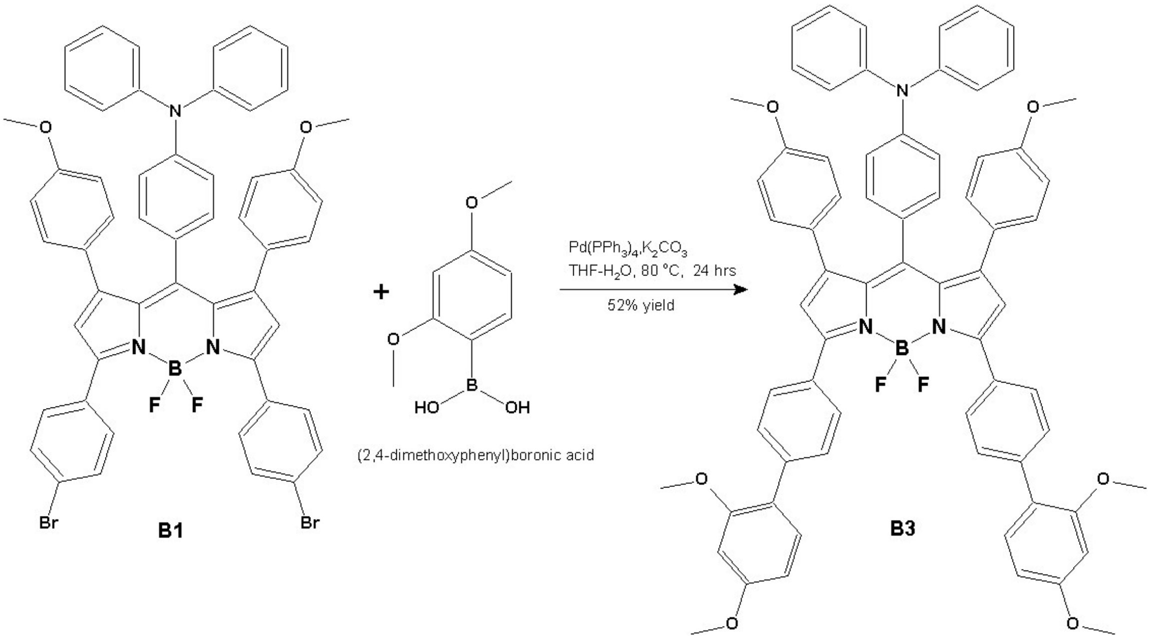
Scheme S6. Synthesis of Compound **B2**

In a schlenk flask, Compound **B1**(180 mg, 0.19 mmol), (4-methoxyphenyl)boronic acid (63 mg, 0.41 mmol), tetrakis(triphenylphosphine)palladium(0) (16 mg, 0,014 mmol) and K_2CO_3 (0.60 g, 4.51 mmol) were added to deaerated THF-H_2O (8 mL-2 mL) under an argon atmosphere. The reaction mixture was heated at 80 ºC for 24 h. After that, the reaction was quenched by adding water (30 mL) and the mixture was extracted with 30 mL of CH_2CI_2 three times. The solvent was dried using anhydrous Na_2SO_4 and than removed under vacuum. The crude product was chromatographed on silica gel with toluene as eluent to afford 195 mg (yield: ~51%) Compound **B2** in the form of blue solid.

Spectral data of Compound **B2** (mp = 261 ^{o}C)

^{1}H-NMR (400 MHz, $CDCl_3$):δ[ppm]: 3.81 (s, 6H), 3.86 (s, 6H), 6.24-6.26 (d, J=8.4 Hz, 2H), 6.57 (s, 2H), 6.65-6.67 (d, J=8.4 Hz, 4H), 6.78-6.81 (d, J=8.4 Hz, 2H), 6.85-6.87 (m, 8H), 6.97-6.99 (d, J=8.8 Hz, 4H), 7.06-7.10 (m, 2H), 7.27-7.31 (m, 4H), 7.57-7.59 (d, J=8.4 Hz, 4H), 7.61-7.63 (d, J=8.0 Hz, 4H), 7.96-7.98 (d, J=8.4 Hz, 4H). ^{13}C-NMR (100 MHz, $CDCI_3$) δ: 159.35, 158.12, 156.01, 148.41, 147.33, 146.71, 145.93, 141.53, 133.35, 133.10, 131.04, 130.16, 129.96, 129.28, 129.02, 128.93, 128.19, 126.37, 125.73, 124.67, 124.01, 123.40, 118.44, 114.21, 112.96, 55.32, 55.22.HRMS/TOF-ESI: Calculated as 1011.40191, found: 1012.40840 $[M+H]^+$, Δ=1.32 ppm

3.3 Synthesis of Compound 4,4-difluoro-8-[4-(diphenylamino)phenyl]-1,7-[4-methoxyphenyl]-3,5-[2,4-dimethoxybiphenyl]-4-bora-3a,4a-diaza-s-indacene (B3)



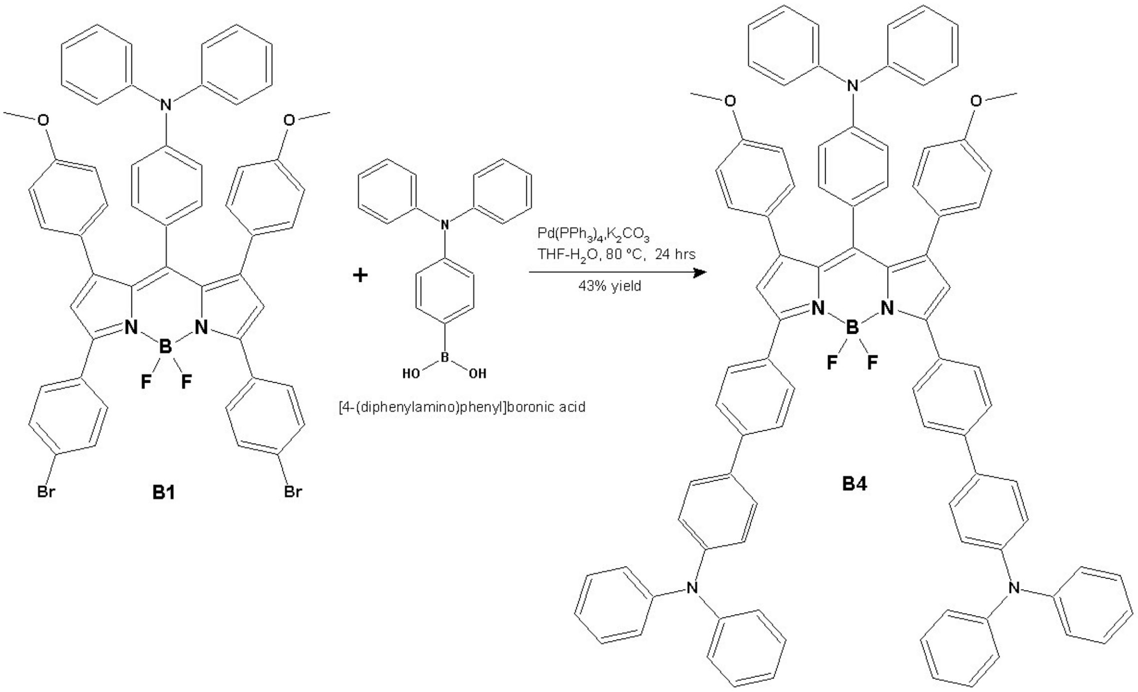
Scheme S7. Synthesis of Compound **B3**

In a schlenk flask, Compound **B1** (180 mg, 0.19 mmol), (2,4-dimethoxyphenyl)boronic acid (75 mg, 0.41 mmol), tetrakis(triphenylphosphine)palladium(0) (16 mg, 0,014 mmol) and K_2CO_3 (0.6 g, 4.51 mmol) were added to deaerated THF-H_2O (8 mL-2 mL) under an argon atmosphere. The reaction mixture was heated at 80 ºC for 24 h. After that, the reaction was quenched by adding water (30 mL) and the mixture was extracted with 30 mL of CH_2CI_2 three times. The solvent was dried using anhydrous Na_2SO_4 and than removed under vacuum. The crude product was chromatographed on silica gel with toluene as eluent to afford 210 mg (yield: ~52%) Compound **B3** in the form of blue solid.

Spectral data of Compound **B3** (mp = 267 ^{o}C)

^{1}H-NMR (400 MHz, $CDCl_3$):δ[ppm]: 3.80 (s, 6H), 3.81 (s, 6H), 3.85 (s, 6H), 6.26-6.24 (d, J=8.4 Hz, 2H), 6.59-6.56 (m, 6H), 6.66-6.64 (d, J=8.8 Hz, 4H), 6.81-6.79 (d, J=8.4 Hz, 2H), 6.87-6.84 (m, 8H), 7.09-7.06 (t, J=7.2 Hz, 2H), 7.29-7.27 (d, J=7.6 Hz, 3H), 7.33-7.31 (d, J=8.0 Hz, 3H), 7.59-7.57 (d, J=8.4 Hz, 4H), 7.94-7.92 (d, J=8.8 Hz, 4H). ^{13}C-NMR (100 MHz, $CDCI_3$) δ: 160.44, 158.08, 157.62, 156.34, 148.35, 147.15, 146.74, 145.75, 139.32, 123.97, 133.37, 132.66, 131.39, 130.76, 130.17, 129.28, 129.14, 129.03, 125.72, 124.79, 123.97, 123.57, 123.03, 118.45, 112.94, 104.68, 98.96, 55.51, 55.40, 55.21. HRMS/TOF-ESI: Calculated as 1071.42305, found: 1072.43046 $[M+H]^+$, Δ=3.39 ppm

3.4 Synthesis of Compound 4,4-difluoro-8-[4-(diphenylamino)phenyl]-1,7-[4-methoxyphenyl]-3,5-[4-N,N-diphenylaminobiphenyl]-4-bora-3a,4a-diaza-s-indacene (B4)



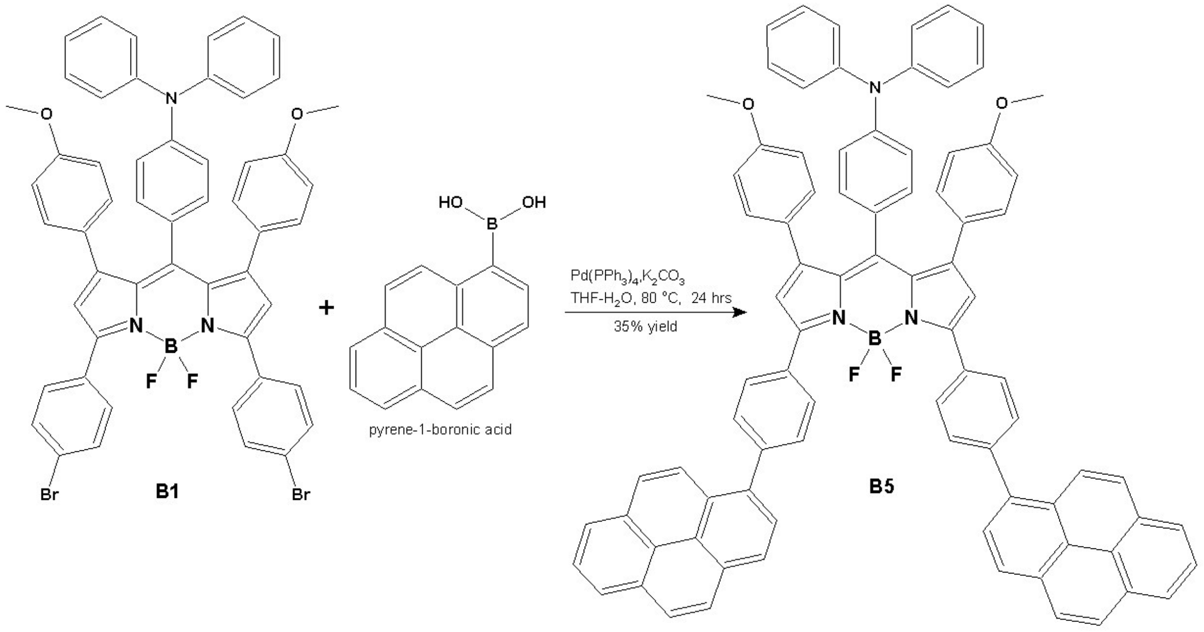
Scheme S8. Synthesis of Compound **B4A**

In a schlenk flask, Compound **B1** (150 mg, 0.16 mmol), [4-(diphenylamino)phenyl]boronic acid (100 mg, 0.35 mmol), tetrakis(triphenylphosphine)palladium(0) (14 mg, 0,012 mmol) and K_2CO_3 (0.52 g, 3.76 mmol) were added to deaerated THF-H_2O (8 mL-2 mL) under an argon atmosphere. The reaction mixture was heated at 80 ºC for 24 h. After that, the reaction was quenched by adding water (30 mL) and the mixture was extracted with 30 mL of CH_2CI_2 three times. The solvent was dried using anhydrous Na_2SO_4 and than removed under vacuum. The crude product was chromatographed on silica gel with toluene as eluent to afford 175 mg (yield: ~43%) Compound **B4** in the form of blue solid.

Spectral data of Compound **B4** (mp = 247 °C)

^{1}H-NMR (400 MHz, $CDCl_3$):δ[ppm]: 3.80 (s, 6H), 6.23-6.25 (d, J=8.4 Hz, 2H), 6.57 (s, 2H), 6.64-6.66 (d, 8.4 Hz, 4H), 6.78-6.80 (d, J=8.4 Hz, 2H), 6.84-6.86 (m, 8H), 6.99-7.15 (m, 18H), 7.25-7.30 (m, 12H), 7.50-7.52 (d, J=8.8 Hz, 4H), 7.61-7.64 (d, J=8.4 Hz, 4H), 7.95-7.97 (d, J=8.4 Hz, 4H). ^{13}C-NMR (100 MHz, $CDCI_3$) δ: 158.12, 148.40, 147.60, 147.41, 147.28, 146.71, 145.83, 141.35, 134.29, 133.35, 132.16, 131.11, 130.15, 129.98, 129.29, 129.26, 128.93, 127.75, 126.26, 125.73, 124.86, 124.53, 124.00, 123.61, 122.98, 118.43, 118.11, 116.70, 112.96, 55.21. HRMS/TOF-ESI: Calculated as 1285.52777, found: 1324.49030 $[M+K]^+$, Δ=0.89 ppm

3.5 Synthesis of Compound 4,4-difluoro-8-[4-(diphenylamino)phenyl]-1,7-[4-methoxyphenyl]-3,5-[4-(1-pyrene)phenyl]-4-bora-3a,4a-diaza-s-indacene (B5)



Scheme S9. Synthesis of Compound **B5**

In a schlenk flask, Compound **B1** (180 mg, 0.16 mmol), pyrene-1-boronic acid (102 mg, 0.41 mmol), tetrakis(triphenylphosphine)palladium(0) (16 mg, 0,014 mmol) and K_2CO_3 (0.62 g, 4.51 mmol) were added to deaerated THF-H_2O (8 mL-2 mL) under an argon atmosphere. The reaction mixture was heated at 80 ºC for 24 h. After that, the reaction was quenched by adding water (30 mL) and the mixture was extracted with 30 mL of CH_2CI_2 three times. The solvent was dried using anhydrous Na_2SO_4 and than removed under vacuum. The crude product was chromatographed on silica gel with toluene as eluent to afford 160 mg (yield: ~35%) Compound **B5** in the form of blue solid.

Spectral data of Compound **B5** (mp = 226-229 ºC)

^{1}H-NMR (400 MHz, $CDCl_3$):δ[ppm]: 3.84 (s, 6H), 6.28-6.30 (d, J=8.4 Hz, 2H), 6.69-6.71 (m, 6H), 6.85-6.93 (m, 10H), 7.09-7.12 (m, 2H), 7.29-7.31 (m, 4H), 7.75-7.77 (d, J=8.4 Hz, 4H), 7.98-8.25 (m, 20H), 8.34-8.31 (d, J=8.8 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCI_3$) δ: 158.19, 156.11, 148.54, 147.56, 146.70, 142.15, 137.21, 135.75, 133.70, 133.44, 131.73, 131.46, 131.00, 130.70, 130.50, 130.22, 129.61, 129.32, 128.92, 128.45, 127.68, 127.57, 127.48, 127.40, 125.96, 125.78, 125.51, 125.40, 125.07, 124.97, 124.87, 124.70, 124.62, 124.08, 123.68, 118.45, 113.02, 55.24. HRMS/TOF-ESI: Calculated as 1201.45902, found: 1200.45069 $[M-H]^+$, Δ=0.43 ppm

4. ADDITIONAL DATA

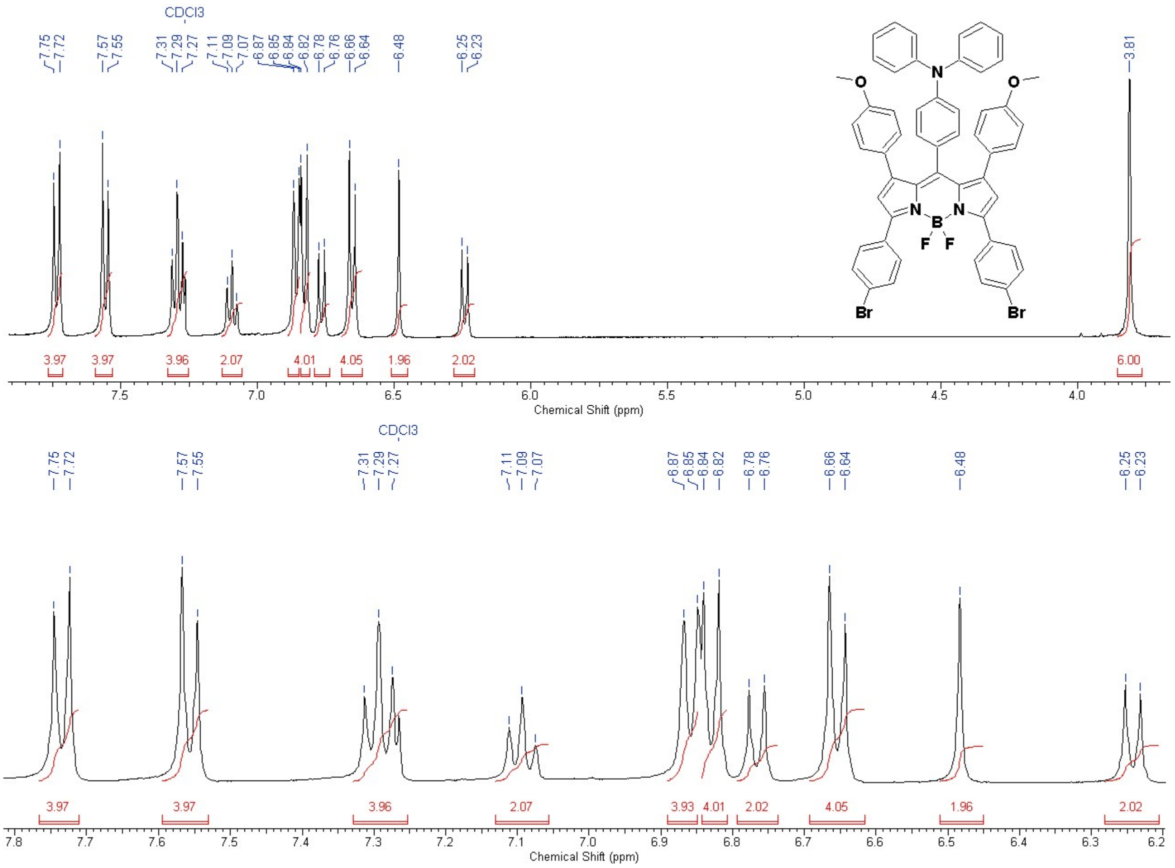


Figure S1. ^{1}H-NMR for compound **B1** in $CDCl_3$ at 400 MHz

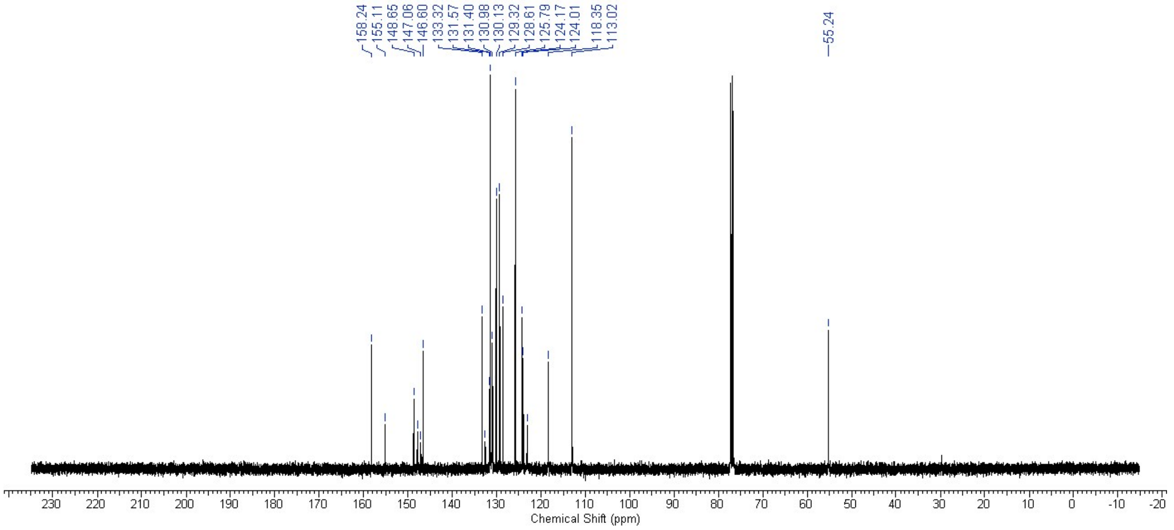


Figure S2. ^{13}C-NMR for compound **B1** in $CDCl_3$ at 100 MHz

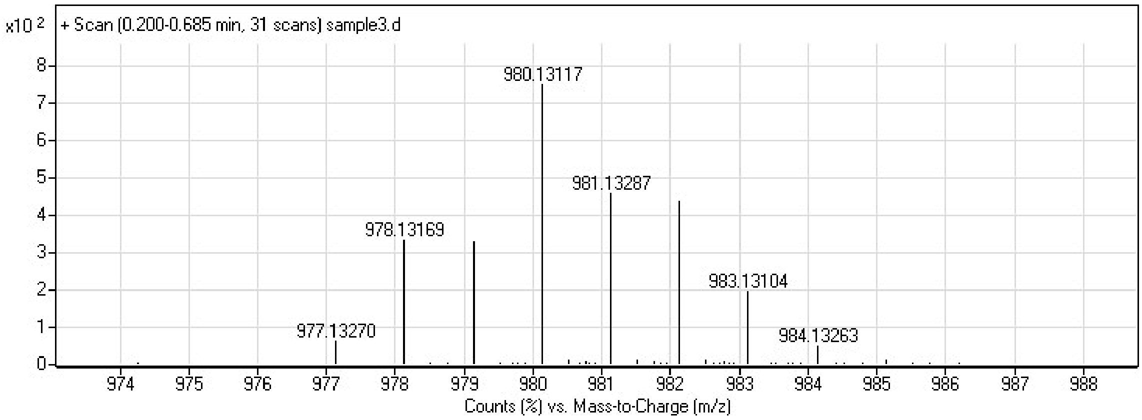


Figure S3. HRMS/TOF-ESI Spectrum of compound **B1**

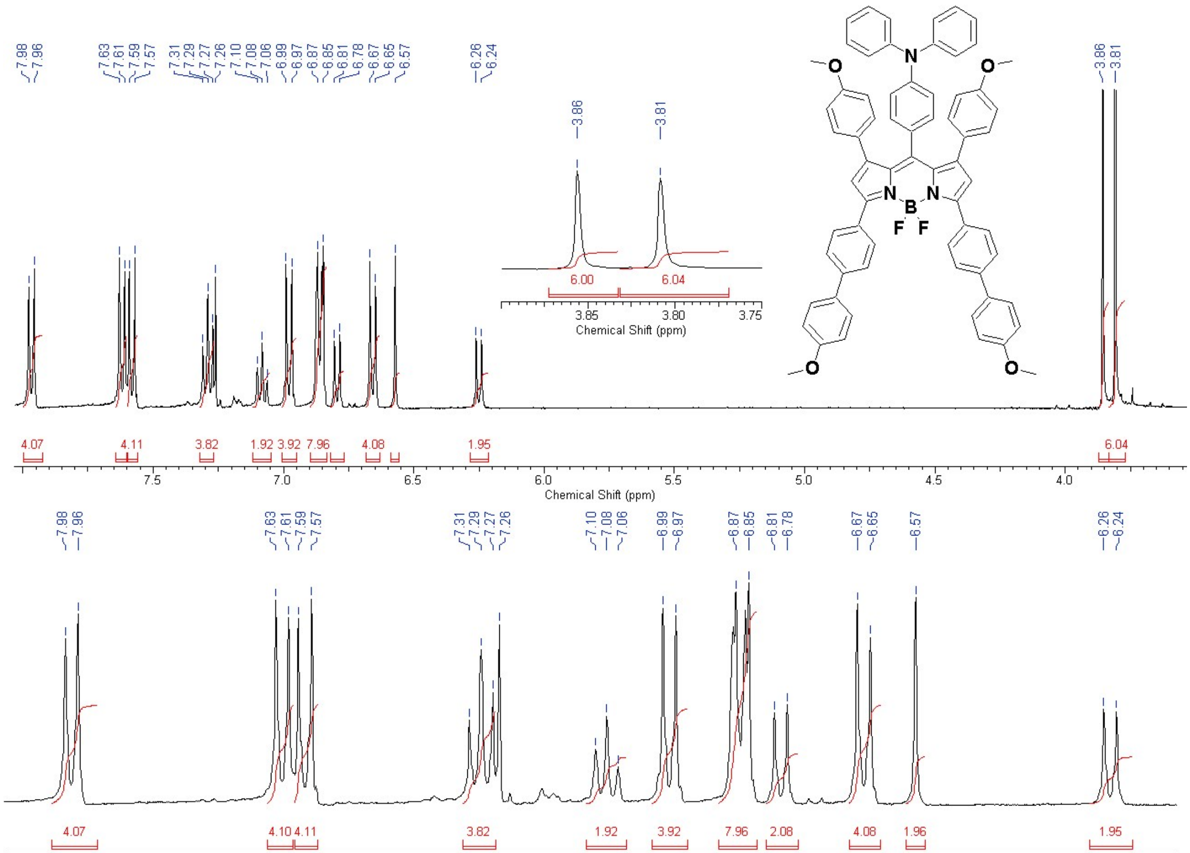


Figure S4. ^{1}H-NMR for compound **B2** in $CDCl_3$ at 400 MHz

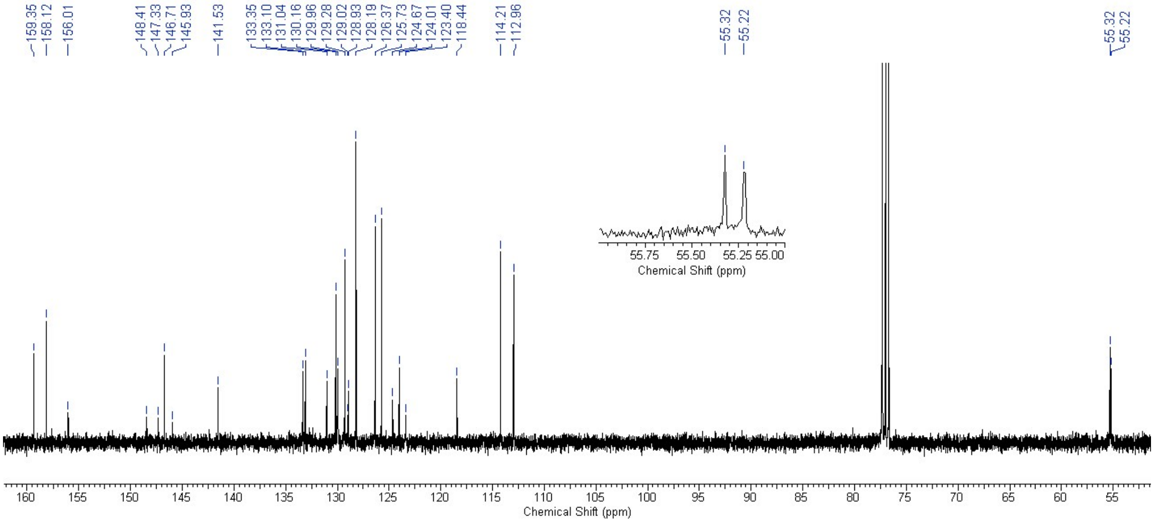


Figure S5. ^{13}C-NMR for compound **B2** in $CDCl_3$ at 100 MHz

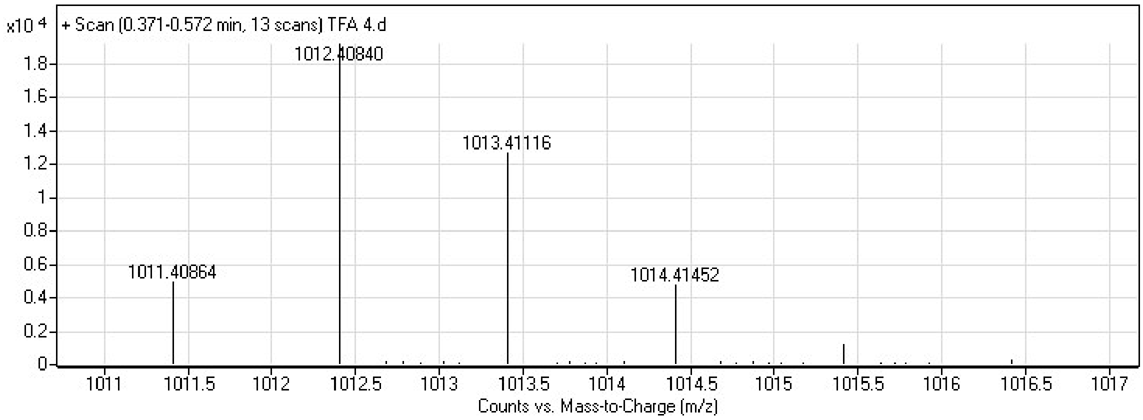


Figure S6. HRMS/TOF-ESI Spectrum of compound **B2**

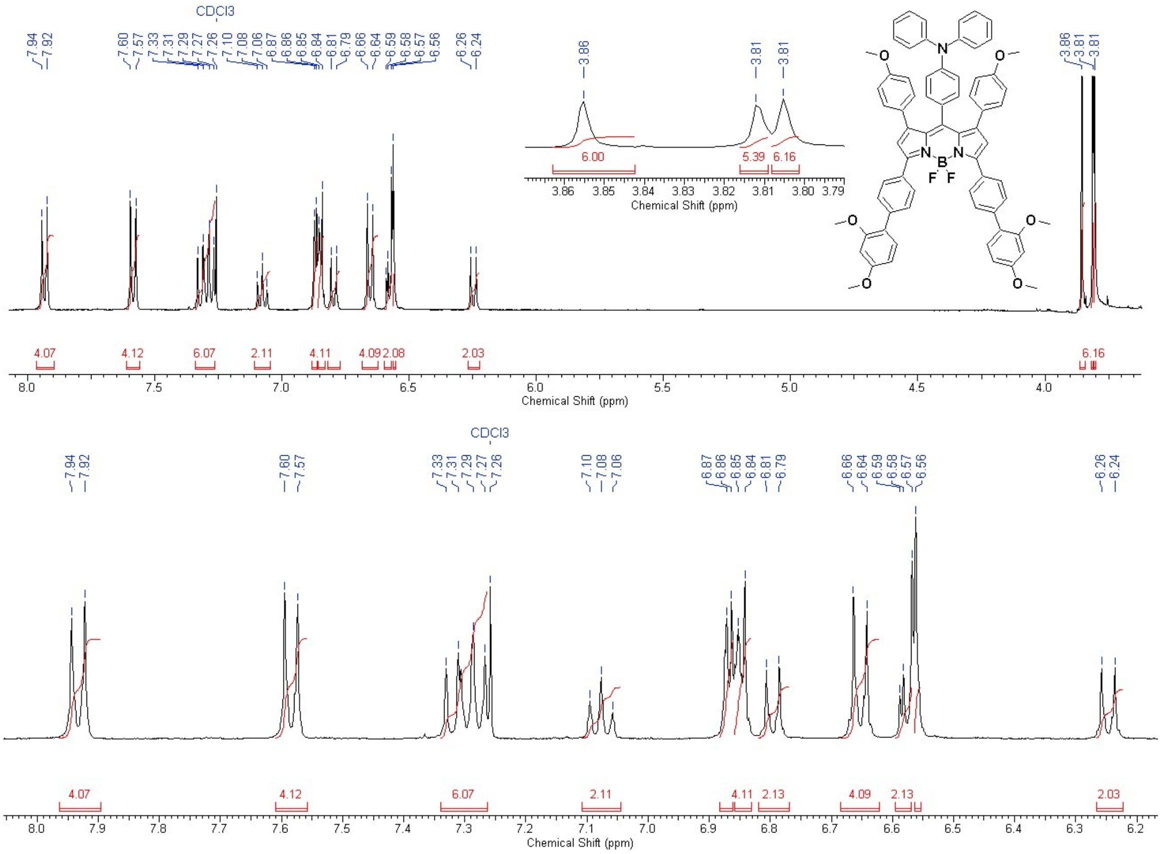


Figure S7. ^{1}H-NMR for compound **B3** in $CDCl_3$ at 400 MHz

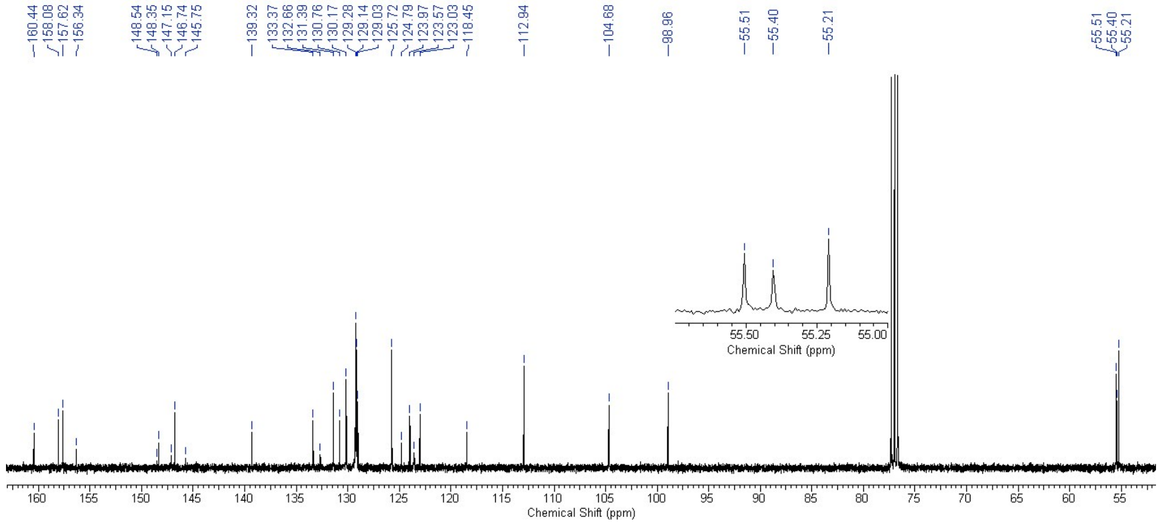


Figure S8. ^{13}C-NMR for compound **B3** in $CDCl_3$ at 100 MHz

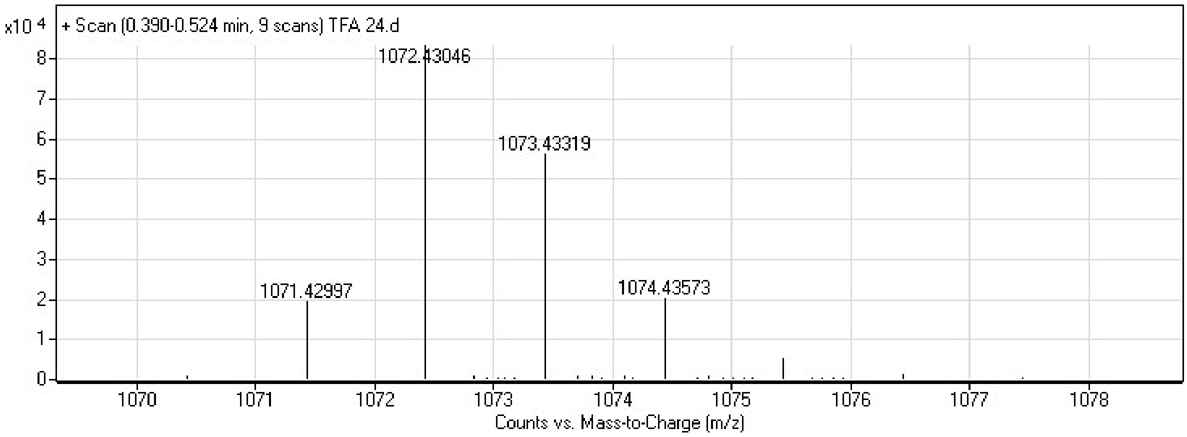


Figure S9. HRMS/TOF-ESI Spectrum of compound **B3**

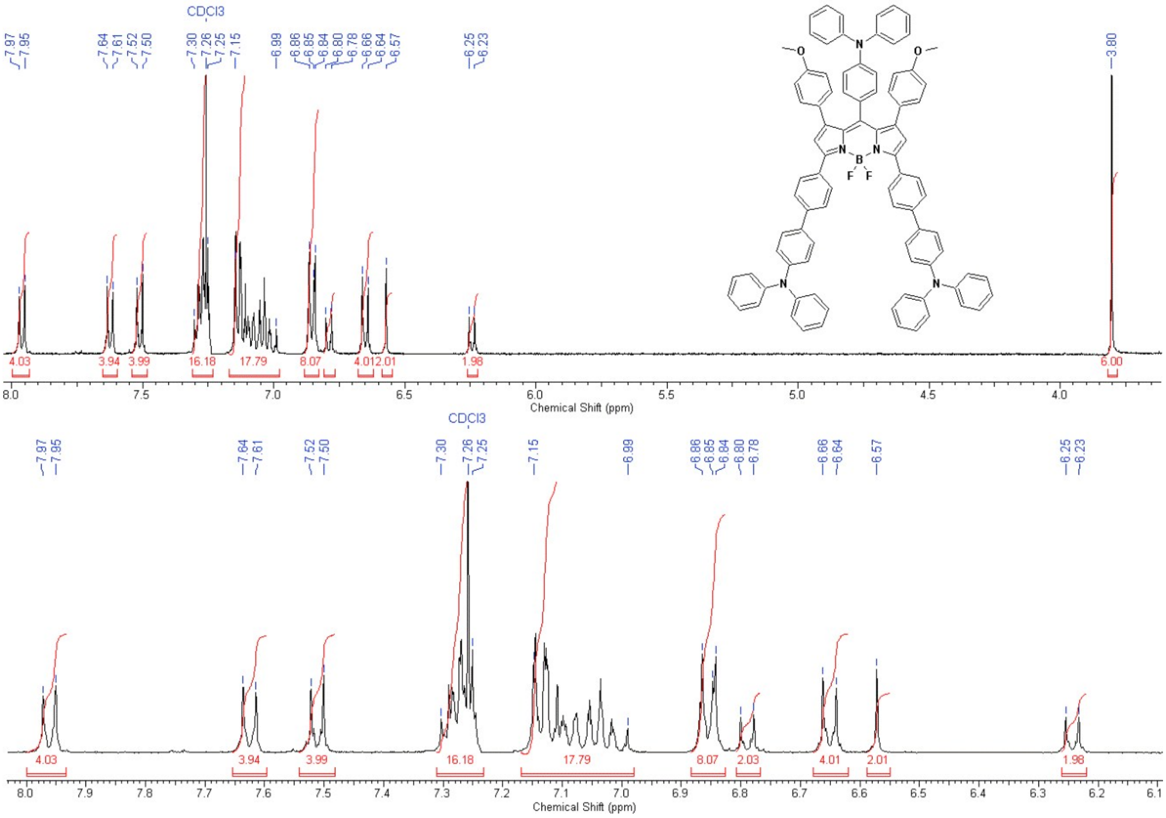


Figure S10. ^{1}H-NMR for compound **B4** in $CDCl_3$ at 400 MHz

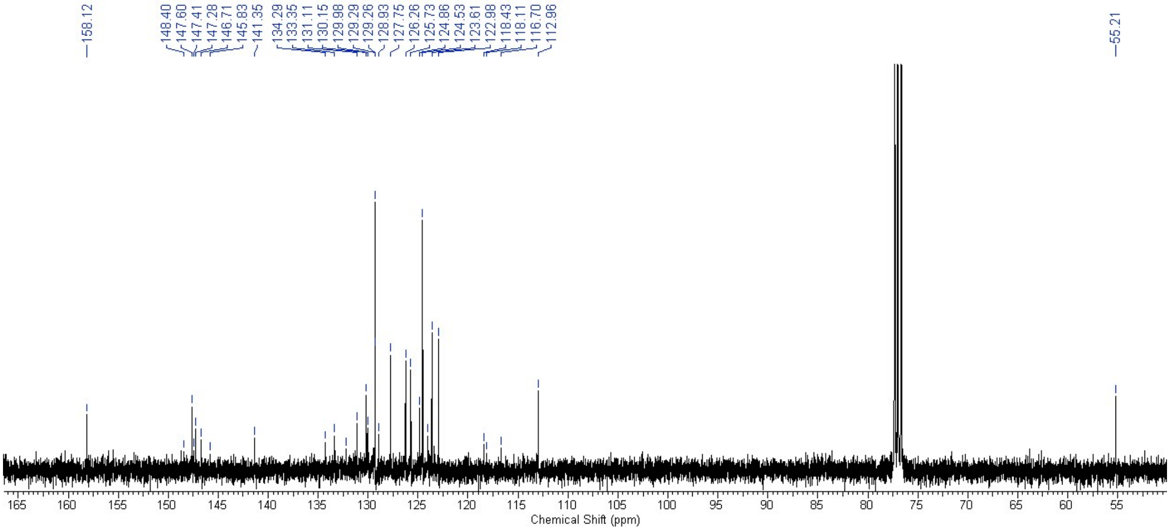


Figure S11. ^{13}C-NMR for compound **B4** in $CDCl_3$ at 100 MHz

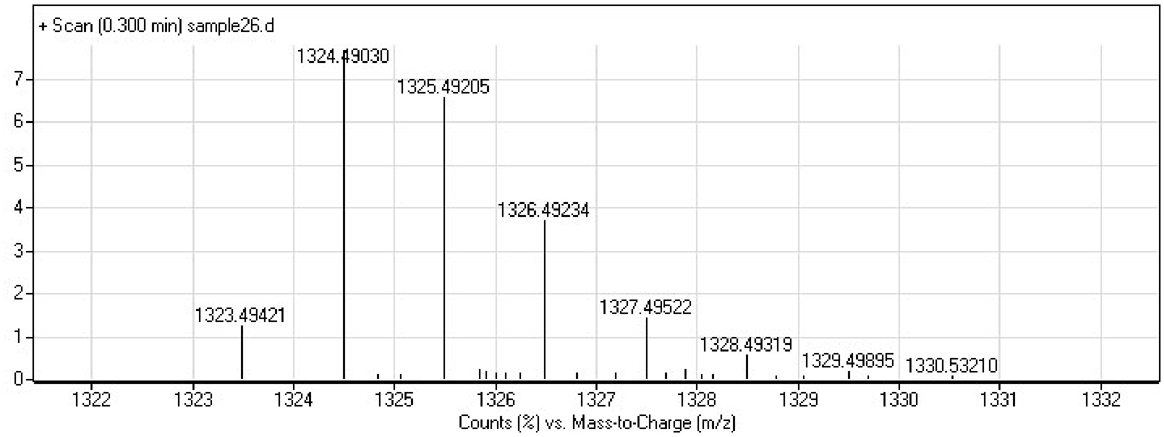


Figure S12. HRMS/TOF-ESI Spectrum of compound **B4**

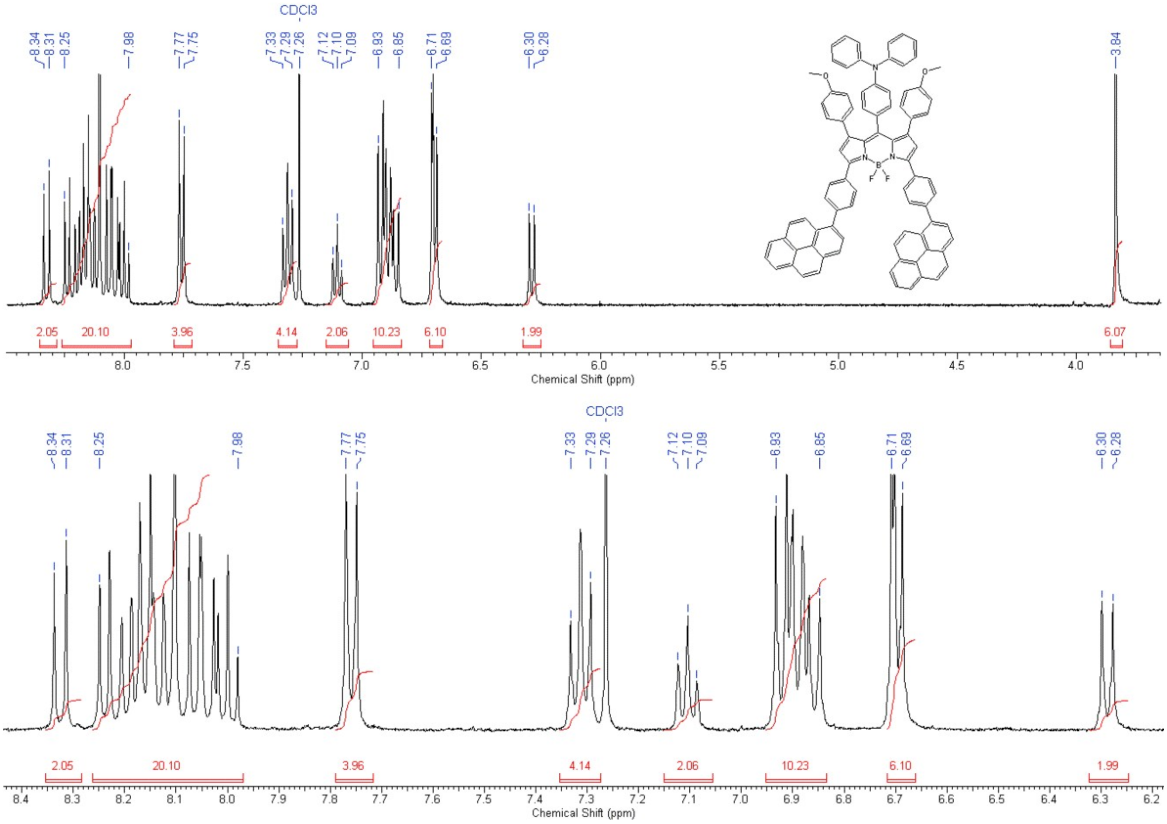


Figure S13. ¹H-NMR for compound **B5** in $CDCl_3$ at 400 MHz

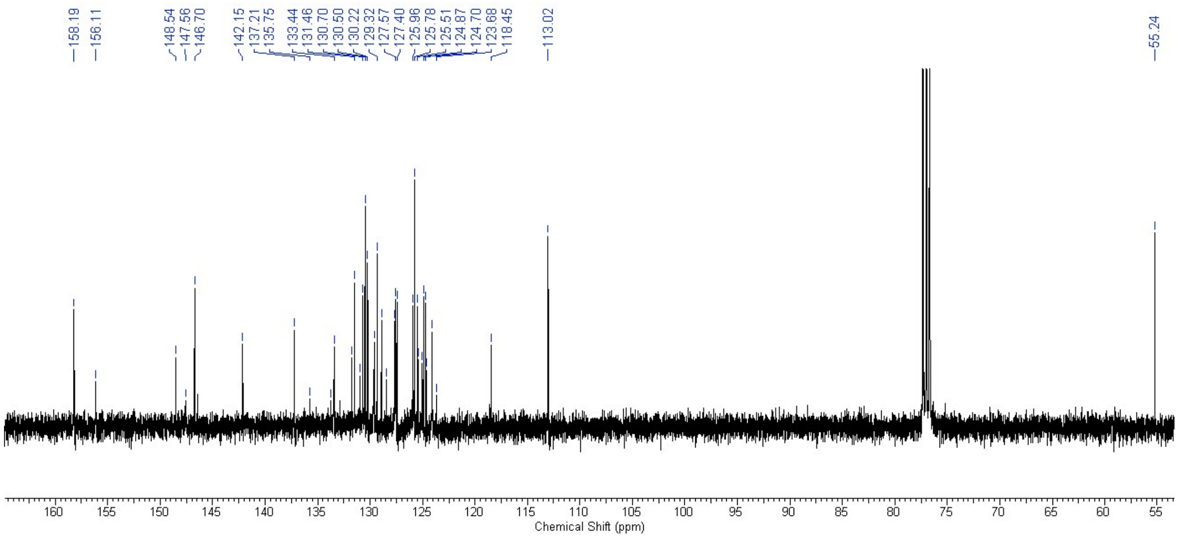


Figure S14. ¹³C-NMR for compound **B5** in $CDCl_3$ at 100 MHz

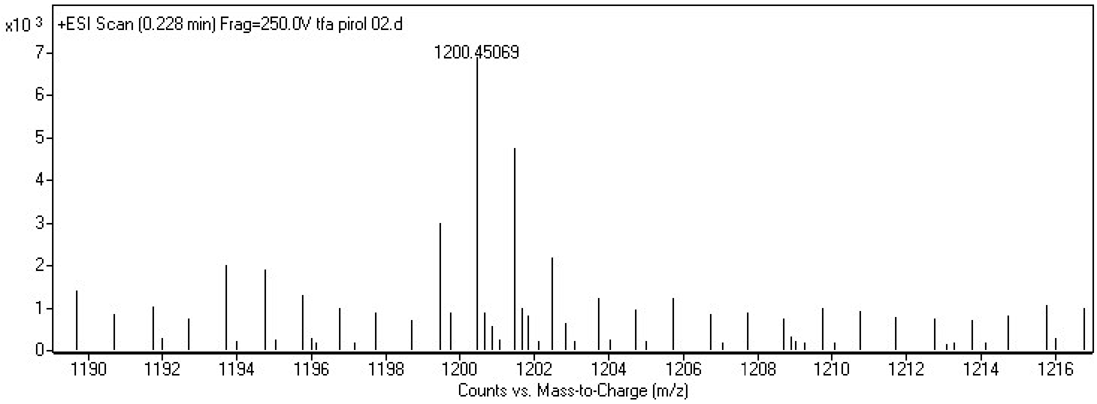


Figure S15. HRMS/TOF-ESI Spectrum of compound **B5**

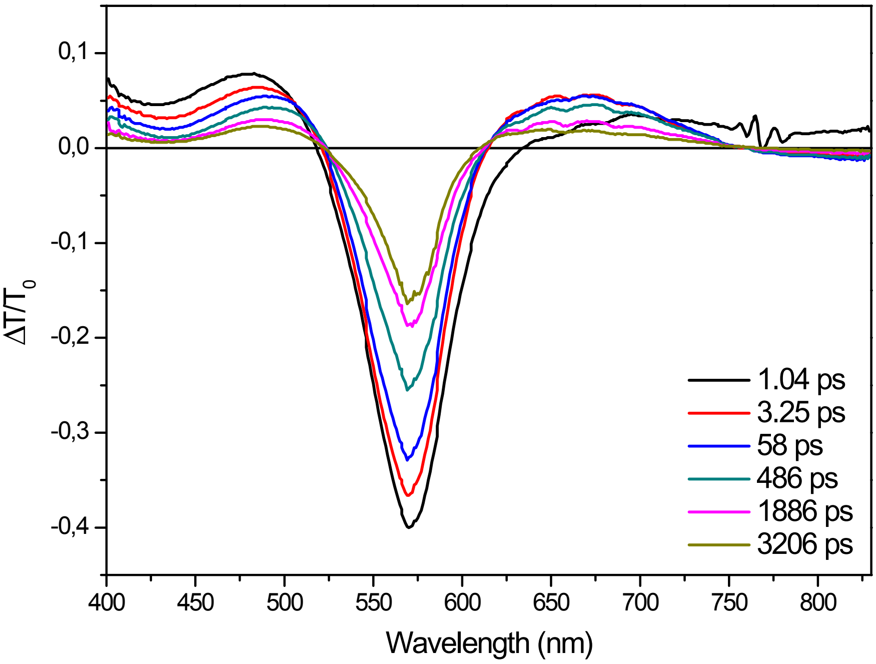


Figure S16. Femtosecond transient absorption spectra of **B1** with different time delays

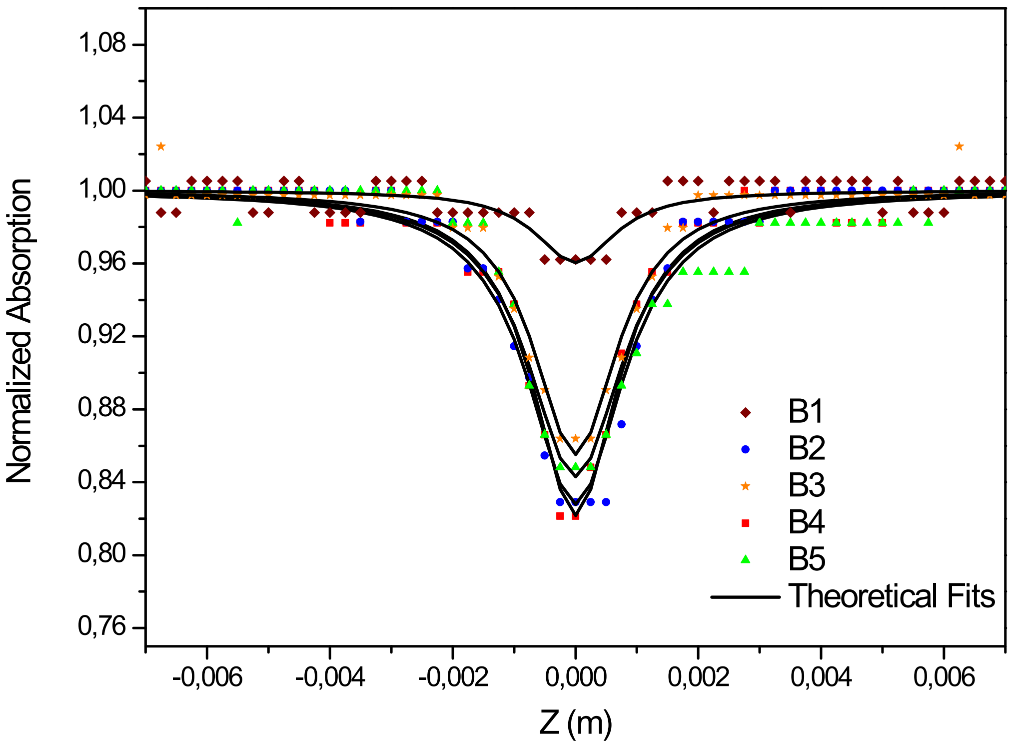


Figure S17. Experimental results (symbols) and theoretical fits (solid line) of open aperture Z-scan experiments for **B2**, **B3**, **B4**and **B5** compounds at 76 GW/cm^2 input intensity in THF, using 800 nm femtosecond pulses.

Triplet Quantum Yield Calculation

We calculated triplet state quantum yield by using following equation [1],

$$\Phi_{sam} = \Phi_{sam}\left(\frac{\varepsilon_{std}}{\varepsilon_{sam}}\right)\left(\frac{\Delta A_{sam}}{\Delta A_{std}}\right)$$

In this equation, *sam* and *std* represents the sample and the standard. Φ represents triplet quantum yield, ε represents molar absorption coefficient and A represents optical intensity of bleaching signal in femtosecond absorption spectroscopy.

References:

[1] Carmichael, I.; Hug, G. L. Triplet–Triplet Absorption Spectra of Organic Molecules in Condensed Phases. J. Phys. Chem. Ref. Data 1986, 15, 1−250.