Electronic Supplementary Material (ESI) for Chemical Science

Supporting Information

3-Vinylborane Functionalized Oligothiophenes: Isomer-Dependent Electronic Structure and Fluorescence Enhancement Upon Anion Binding

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Contents

Experimental materials and methods: All reactions and manipulations of sensitive compounds were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (Innovative Technologies). Ether solvents were distilled from Na/benzophenone prior to use. Hydrocarbon solvents were purified using a solvent purification system (Innovative Technologies; alumina / copper columns for hydrocarbon solvents). Mes_2BH,[1] Mes_2BF[2] and **1**[3] were synthesized according to literature procedures. Other reagents were commercially available (Aldrich, Acros, Strem) and were either used as obtained or purified by standard procedures.[4] $^iPrMgCl•LiCl$ was generated *in situ* from ^iPrMgCl and LiCl. ^iPrMgCl was prepared from 2-chloropropane and Mg in Et_2O, insoluble components and metal flakes were filtered off, and the solvent was removed *in vacuo* to leave a homogeneous grey sludge of $^iPrMgCl•xEt_2O$, the Et_2O content of which was determined by ^1H-NMR. All 499.9 MHz ^1H, 125.7 MHz ^{13}C, and 160.4 MHz ^{11}B NMR spectra were recorded at ambient temperature on a Varian INOVA spectrometer equipped with a boron-free 5 mm dual broadband gradient probe (Nalorac, Varian Inc., Martinez, CA). Solution ^1H and ^{13}C NMR spectra were referenced internally to solvent signals.[5] If not stated otherwise, ^{11}B NMR spectra were acquired with boron-free quartz NMR tubes and referenced externally to $BF_3•Et_2O$ ($\delta = 0$). Individual signals are referred to as singlet (s), doublet (d), triplet (t), quintet (quint), multiplet (m), centro symmetrical multiplet (m_c) and broadened (br). GPC-RI/UV analyses were performed with THF (1 mL/min) as eluent on a Waters Empower GPC system equipped with a 717plus autosampler, a 1525 binary HPLC pump, a 2487 dual λ absorbance detector, a 2414 refractive index detector, and styragel columns (Polymer Laboratories; two columns 5 µm / Mixed-C). The columns were kept in a column heater at 35 °C and were calibrated with polystyrene standards (Polymer Laboratories). High resolution mass spectrometry measurements were performed on a Bruker 7-Tesla FT-MS using either APCI (Atmospheric Pressure Chemical Ionization) or MALDI (Matrix Assisted Laser Desorption Ionization) for sample ionization. Anthracene, 9,10-diphenylanthracene, benzo[*a*]pyrene or α-cyano-3-hydroxycinnamic acid were used as matrix in combination with silver(I) trifluoromethanesulphonate (AgOTf) as oxidant. EI-MS low resolution mass spectrometry data of volatile compounds were acquired using a Hewlett Packard GC/MS system consisting of a HP 5973 Mass Selective Detector and a HP 6890 Series GC system. UV-visible absorption data were acquired on a Varian Cary 500 UV-Vis / NIR spectrophotometer. The fluorescence data and integrated quantum yields were measured on a Varian Cary Eclipse fluorescence spectrophotometer with optically dilute solutions (A < 0.1). 9,10-Diphenylanthracene was used as the standard for determination of the quantum yields (ϕ); ϕ(9,10-diphenylanthracene) = 0.92.[6] Elemental analyses were obtained from Intertek / Quantitative Technologies Inc., Whitehouse, NJ.

Synthesis of 2α/ß: 2α/ß was synthesized from **1** (483 mg, 1.4 mmol) and Mes_2BH (385 mg, 1.5 mmol) by stirring in THF (10 ml) for 16 h at RT. The solvent was then removed *in vacuo*, the oily residue was redissolved and washed through a pad of Celite 454. The solvent was evaporated once more to give the crude product as yellow-green viscous oil in near quantitative yield. The isomers were separated by reversed-phase column chromatography (C_{18}, Acetonitrile/Et_2O, 9:1, v/v).

2α: Colorless oil, yield: 194 mg (331 μmol, 24 %). ^{1}H-NMR (500 MHz, C_6D_6): δ = 6.71 (s, 4 H, Mes-CH), 6.66-6.76 (m, 2 H, Th-H, vinyl-H), 2.30 (s, 12 H, *o*-Mes-CH_3), 2.12 (s, 6 H, *p*-Mes-CH_3), 2.10-2.20 (m, C=CH-CH_2), 1.13-1.21 (m, 2 H, C=CH-CH_2CH_2), 1.01-1.12 (m, 4 H, CH_2), 0.77 (t, $^3J_{HH}$ = 6.9 Hz, 3 H, CH_3) ppm. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.72 (s, 4 H, Mes-CH), 6.61 (t, 2 H, $^3J_{HH}$ = 7.2 Hz, vinyl-H), 6.54 (s, 1 H, Th-H), 2.25 (s, 6 H, *p*-Mes-CH_3), 2.20-2.30 (m, 2 H, C=CH-CH_2), 2.17 (s, 12 H, *p*-Mes-CH_3), 1.34-1.44 (m, 2 H, C=CH-CH_2CH_2), 1.20-1.30 (m, 4 H, CH_2), 0.77 (t, $^3J_{HH}$ = 5.8 Hz, 3 H, CH_3) ppm. ^{13}C-NMR (125 MHz, C_6D_6): δ = 160.3 (Mes), 144.7, 143.6, 142.1, 140.5 (Mes), 138.6 (Mes), 133.5 (vinyl-/Th-CH), 128.8 (Mes-CH), 109.6 (C-Br), 109.5 (C-Br), 32.7, 32.0, 28.5, 24.0 (*o*-Mes-CH_3), 22.8, 21.3 (*p*-Mes-CH_3), 14.2 (CH_3) ppm. ^{11}B-NMR (160.4 MHz, C_6D_6): δ = 74 ppm (half-width 2900 Hz). MALDI-MS for $[C_{29}H_{35}Br_2BS+Ag]^+$: calcd. [m/z] = 692.9956 Da, found [m/z] = 692.9972 Da. UV-vis (MeCN): λ_{max} = 313 nm. **2ß**: Colorless oil, yield: 209 mg (356 μmol, 25 %). ^{1}H-NMR (500 MHz, C_6D_6): δ = 7.02 (s, 1 H, Th-H/ vinyl-H), 6.96 (s, 1 H, Th-H/ vinyl-H), 6.79 (s, 4 H, Mes-CH), 2.54 (t, $^3J_{HH}$ = 8.1 Hz, 2 H, C=CH-CH_2), 2.31 (s, 12 H, *o*-Mes-CH_3), 2.17 (s, 6 H, *p*-Mes-CH_3), 1.43 (quint, 2 H, $^3J_{HH}$ = 6.9 Hz, C=CH-CH_2CH_2), 1.03-1.09 (m, 4 H, CH_2), 0.69 (t, $^3J_{HH}$ = 6.8 Hz, CH_3) ppm. ^{13}C-NMR (125 MHz, C_6D_6): δ = 157.5, 142.2, 140.5 (Mes), 139.9, 138.8 (Mes), 137.3 (vinyl-CH), 130.6 (Th-H), 128.9 (Mes-CH), 113.7 (C-Br), 111.7 (C-Br), 32.5, 32.5, 30.7, 23.5 (*p*-Mes-CH_3), 22.4, 21.3 (*o*-Mes-CH_3), 14.0 (CH_3) ppm. ^{11}B-NMR (160.4 MHz, C_6D_6): δ = 73 ppm (half-width

2250 Hz). MALDI-MS for $[C_{49}H_{67}BS_3+Ag]^+$: calcd. [m/z] = 692.9941 Da, found [m/z] = 692.9970 Da. UV-vis (MeCN): λ_{max} = 330 nm.

Synthesis of 3: 336 mg (1.0 mmol) of **1** were hydroborated with Mes_2BH (250 mg, 1.0 mmol) and the crude product was isolated as described for **2α/ß**. A solution of 1.0 mmol of $^iPrMgCl{\bullet}LiCl$ in 4 ml of THF, was then added to **2α/ß** and the mixture was stirred at ambient temperature for one hour. Subsequently 5 mL of dry toluene and $Ni(dppp)Cl_2$ (10 µmol, 5.4 mg) suspended in 1 mL of THF were added and the mixture was heated to 110 ˚C (oil bath temperature) for 16 h in a sealed flask. To isolate the product, the solvent was evaporated and the residue was taken up in a small amount of THF. Precipitation into 50 ml of cold MeOH yielded **3** as an orange-red solid that was recovered by centrifugation at 0 ˚C. Yield: 112.2 mg (263 µmol, 26 %). **3**: ^{1}H NMR (500 MHz, C_6D_6): δ = 7.20-7.50 (br, vinyl-/Th-H), 6.60-6.90 (br s, Mes H), 2.6-3.0 (br, CH=CB*CH*$_2$), 2.3-2.6 (br, *o*-Mes-CH_3), 2.0-2.3 (br, *p*-Mes-CH_3), 0.40-1.80 (br, 9-H, alkyl-H) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 142.53, 140.57, 138.55, 128.81 (Mes-CH), 32.78 (CH=CH*CH*$_2$), 32.06, 24.04, 23.48 (Mes-CH_3), 22.73, 21.29 (Mes-CH_3), 14.24 (CH_3) ppm. Only the 4 signals attributed to the mesityl groups could be resolved in the aromatic region. ^{11}B-NMR (160.4 MHz, C_6D_6): δ = 71 ppm (half-width 11500 Hz); 3.8 ppm (half-width 1600 Hz) after addition of 2 equiv. of TBAF. UV-vis (THF): λ_{max} = 327 nm, ε_{327} = 5575 $M^{-1}cm^{-1}$, none after addition 2 equiv. of TBACN. Elemental analysis ($C_{29}H_{35}BS{\bullet}0.3\ CHCl_3$): calcd. C 76.13 H 7.70 S 6.94; found C 76.27 H 7.26 S 6.72. GPC-UV: M_n = 1.72 kDa, M_w = 2.25 kDa, PDI = 1.31.

Synthesis of 3α: 3α was synthesized from **2α** (51.2 mg, 87.3 µmol) by the same method as **3**, with ^iPrMgCl (87.3 µmol) in 4 ml THF/toluene (1:1, v/v) with 1 % (0.47 mg, 0.87 µmol) of $Ni(dppp)Cl_2$. After 60 h of reflux the product was isolated by precipitation into MeOH, recovered by centrifugation and freeze dried from benzene. Yield: 10.1 mg (23.7 µmol, 27 %). ^{1}H NMR (500 MHz, C_6D_6): δ = 6.60-6.90 (Mes-H, Th-H, vinyl-H), 2.25-2.60 (o-Mes-CH_3), 1.95-2.25 (p-Mes-CH_3), 0.70-1.50 (alkyl). ^{13}C-NMR (125 MHz, C_6D_6): δ = 142.5, 140.6, 138.5, 128.8, 32.1 (br), 28.6 (br), 24.0 (br, *o*-Mes-CH_3), 22.8 (br, CH_2), 21.3 (br, *p*-Mes-CH_3), 14.3 (CH_3) ppm. Only the 4 signals attributed to the mesityl groups could be resolved in the aromatic region. ^{11}B-

NMR (160.4 MHz, C_6D_6): δ = 73.3 ppm (half-width 5400 Hz), -13.2 ppm (half-width 1400 Hz) after addition 2 equiv. of TBACN; 4.1 ppm (half-width 1900 Hz) after addition 2 equiv. of TBAF. UV-vis (THF): λ_{max} = 319 nm, none after addition 2 equiv. of TBACN.

Synthesis of **3ß**: A solution of 145 µmol of ^{i}PrMgCl•LiCl dissolved in 3.5 ml of THF was added to **2ß** (85.5 mg, 146 µmol) and the mixture was stirred at ambient temperature for one hour. Subsequently Ni(dppp)Cl_2 (0.78 mg, 1.4 µmol) suspended in 145 µL of THF was added, and the reaction mixture was stirred for 18 h. The solution was then divided into two parts and one portion was heated to reflux for 16 h in a sealed flask, while the other was kept stirring at ambient temperature. Both reactions were worked up by precipitation into 20 ml of MeOH and the precipitate was recovered by centrifugation and freeze dried from benzene to give 20.7 mg (48.5 µmol, 33 %, RT) and 23.4 mg (54.9 µmol, 38 %, refluxed) of orange-red solids. Combined yield: 44.1 mg (103.4 µmol, 71 %).

3ß (RT): GPC-UV: M_n = 1.55 kDa, M_w = 1.84 kDa, PDI = 1.19. **3ß** (reflux): GPC-UV: M_n = 1.72 kDa, M_w = 2.19 kDa, PDI = 1.27. **3ß** (reflux): ^{1}H-NMR (500 MHz, C_6D_6): δ = 7.20-7.50 (br, vinyl-/Th-H), 6.60-6.90 (br s, Mes H), 2.70-3.00 (br, CH=CH*CH₂*), 2.25-2.70 (Mes-CH_3), 1.9-2.25 (Mes-CH_3), 1.55-1.9 (br, CH_2), 1.1-1.5 (br, CH_2), 0.7-1.0 (br, CH_3) ppm. ^{13}C-NMR (125 MHz, C_6D_6): δ = 142.5, 140.5, 139.7, 128.9, 33.2 (C=C-$\mathit{CH_2}$), 32.8 (CH_2), 31.3 (C=C-CH_2-$\mathit{CH_2}$), 23.4 (*p*-Mes-CH_3), 22.8 (CH_2), 21.3 (o-Mes-CH_3), 14.1 (CH_3) ppm. Only the 4 signals attributed to the mesityl groups could be resolved in the aromatic region. ^{11}B-NMR (160.4 MHz, C_6D_6): δ = 74.2 (half-width 5100 Hz), -12.9 (half-width 350 Hz) after addition 2 equiv. of TBACN, 3.5 ppm (half-width 1500 Hz) after addition 2 equiv. of TBAF. UV-vis λ_{max}(THF) = 332 nm, 424 after addition 2 equiv. of TBACN.

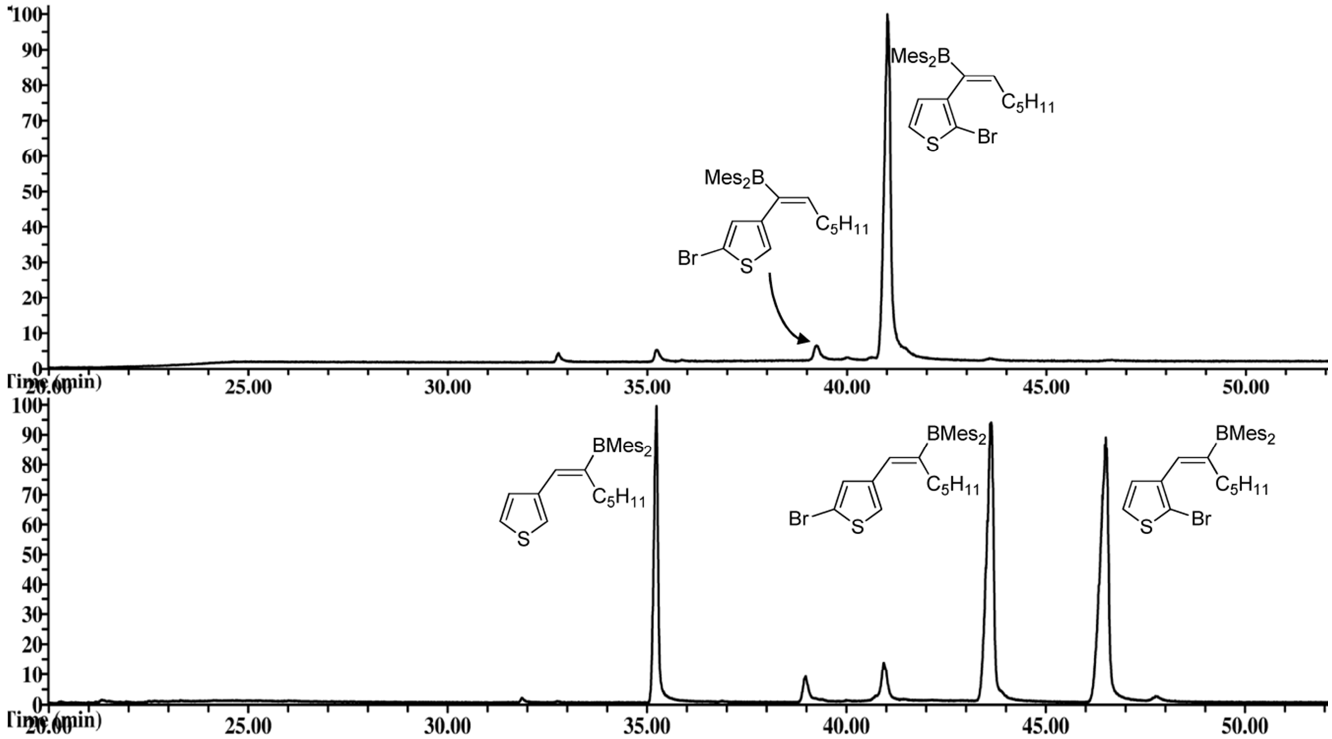

Figure S1. GC-chromatogram of the metathesis products of **2α** and **2ß**. Dehalogenated product is present due to excess of Grignard reagent.

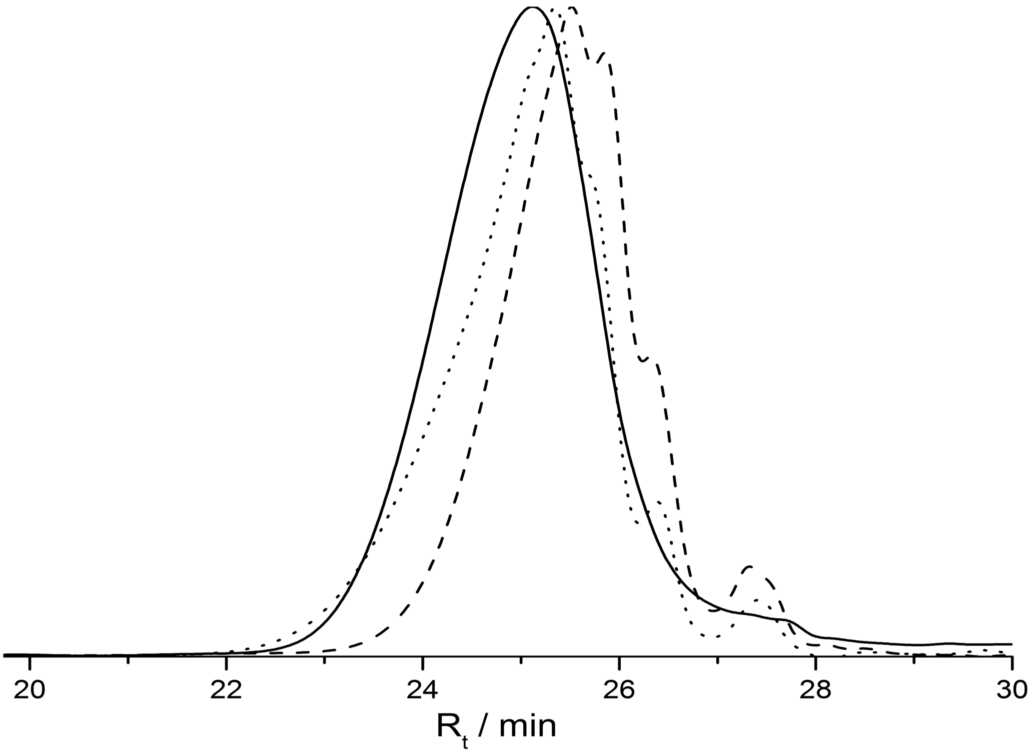

Figure S2. GPC-UV chromatograms of **3** (solid), **3α** (dashed), and **3ß** (dotted).

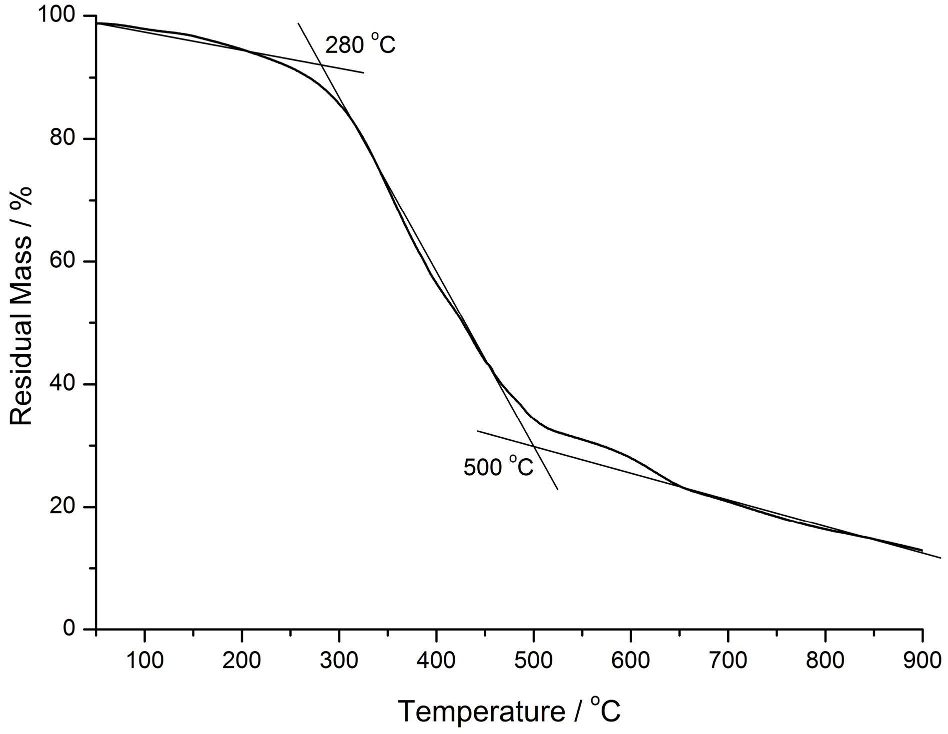

Figure S3. Thermogram of **3**. Scan rate 15 ˚C/min.

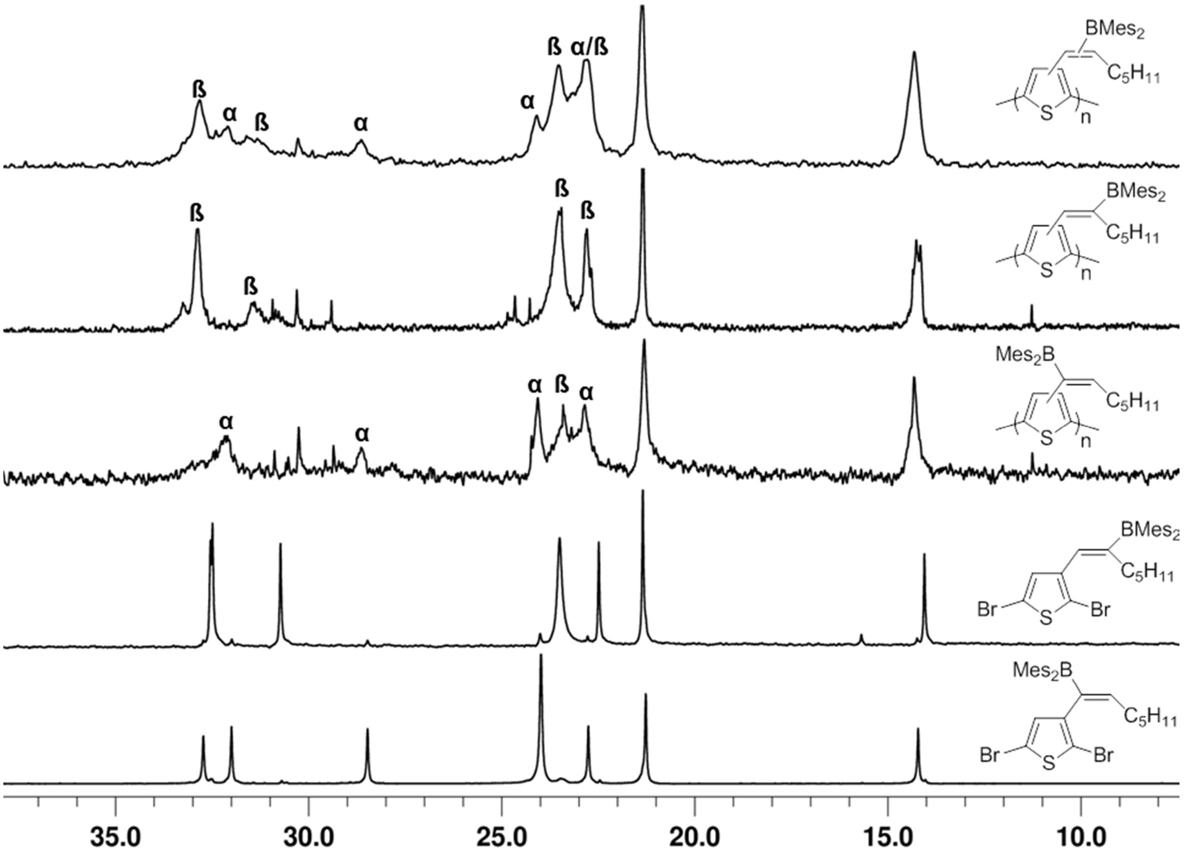

Figure S4. Comparison of the alkyl regions of ^{13}C NMR spectra of (top to bottom) **3**, **3ß**, **3α**, **2ß** and **2α** in C_6D_6.

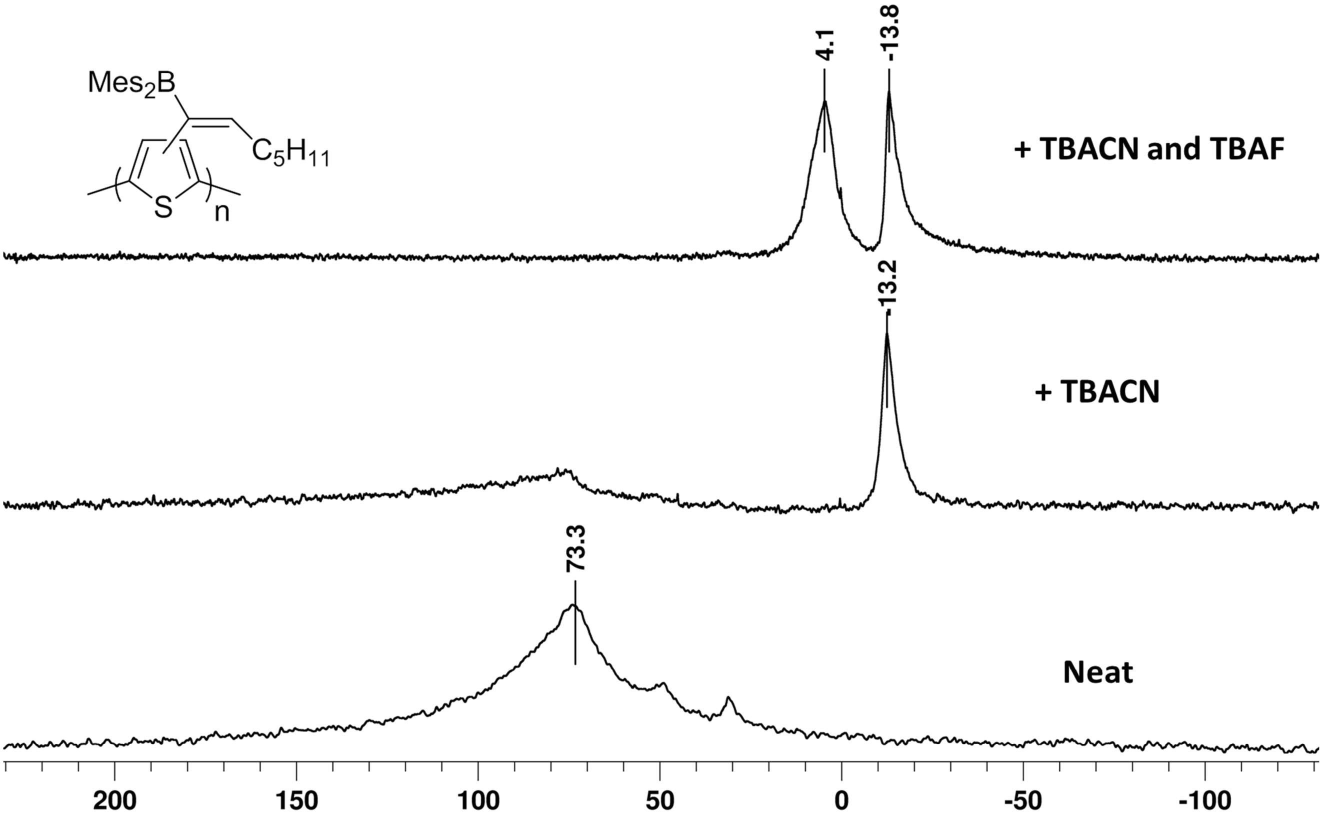

Figure S5. ^{11}B NMR spectrum of **3α** in C_6D_6; before (bottom) and after addition of TBACN (center) or TBACN / TBAF mixture (top).

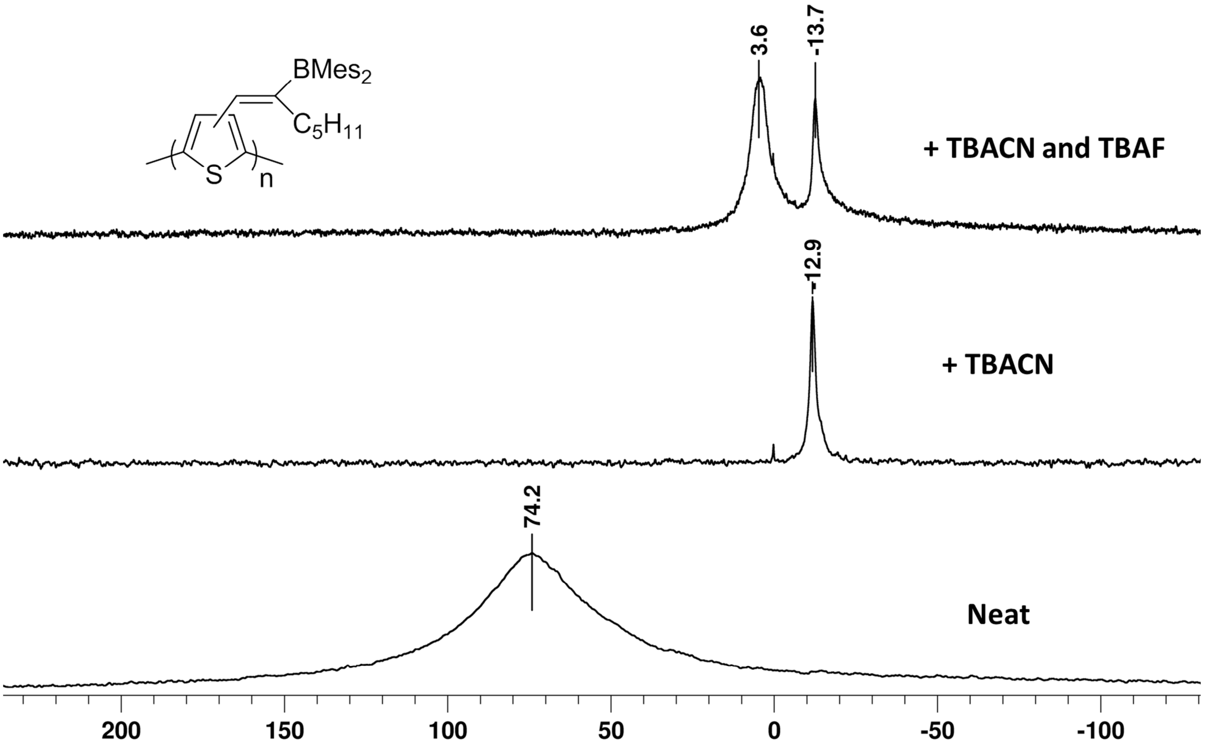

Figure S6. ^{11}B NMR spectrum of **3ß** in C_6D_6; before (bottom) and after addition of excess TBACN (center) or TBACN / TBAF mixture (top).

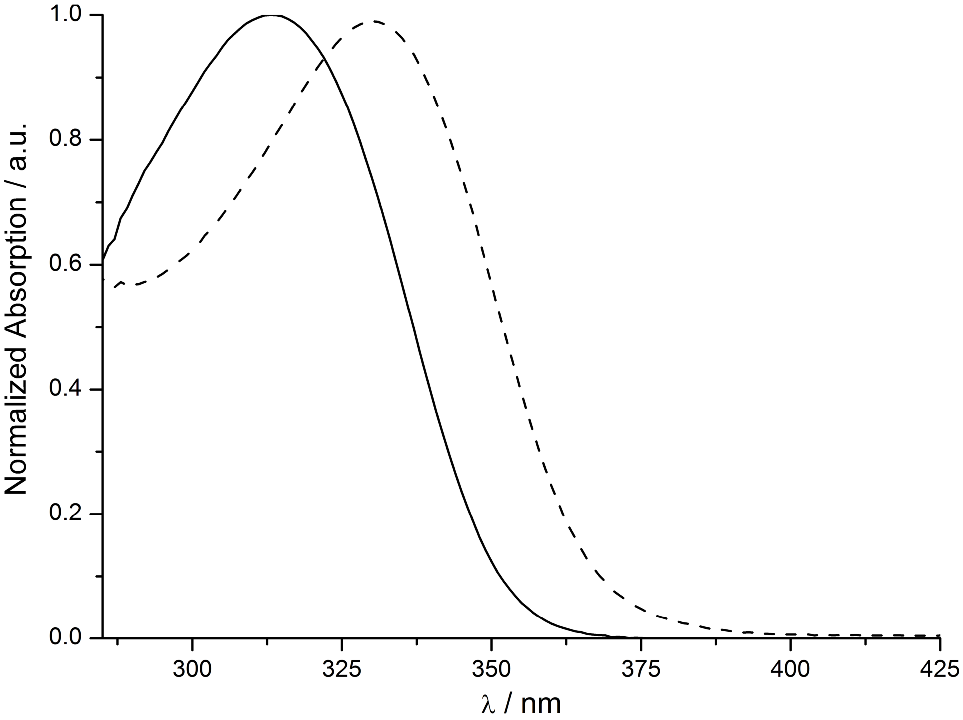

Figure S7. UV-vis spectra of **2α** (solid) and **2ß** (dashed) in MeCN.

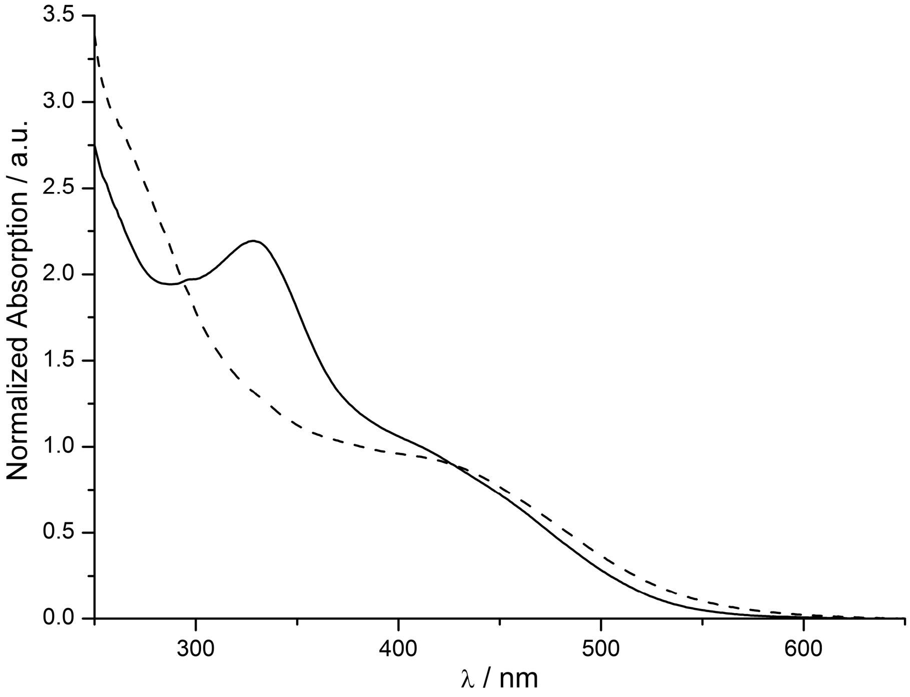

Figure S8. UV-vis spectrum of **3** in THF; before (solid) and after addition of excess TBACN (dashed). Spectra normalized to absorption at 420 nm.

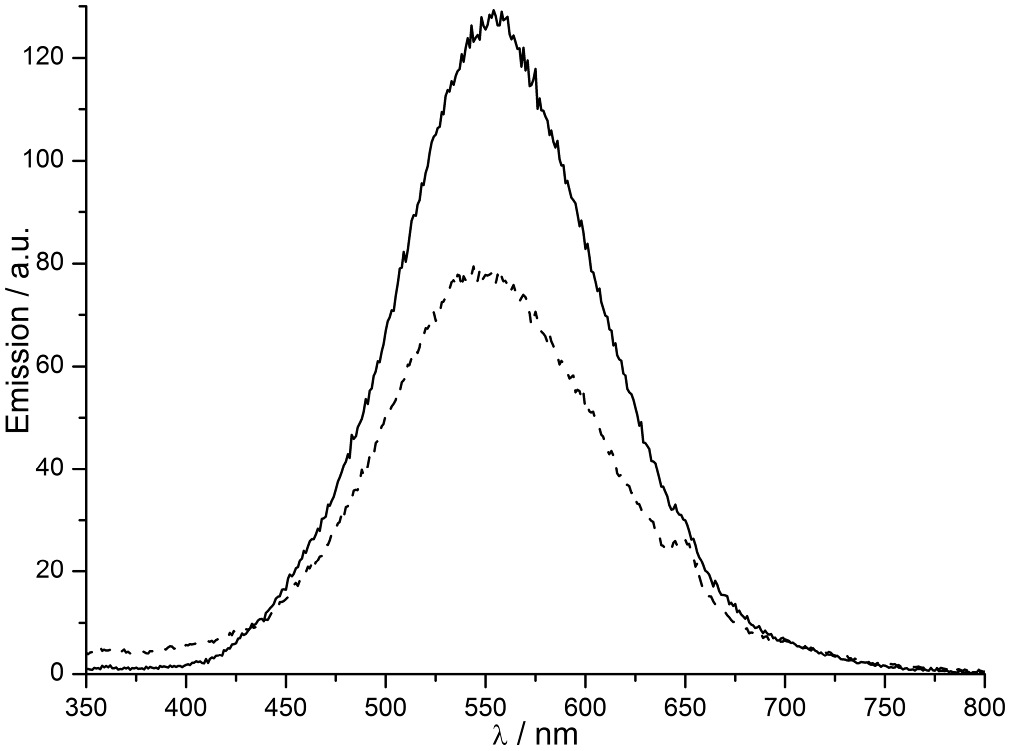

Figure S9. Fluorescence spectrum of **3** in THF, before (solid) and after addition of excess TBACN (dashed). Excitation at 325 nm.

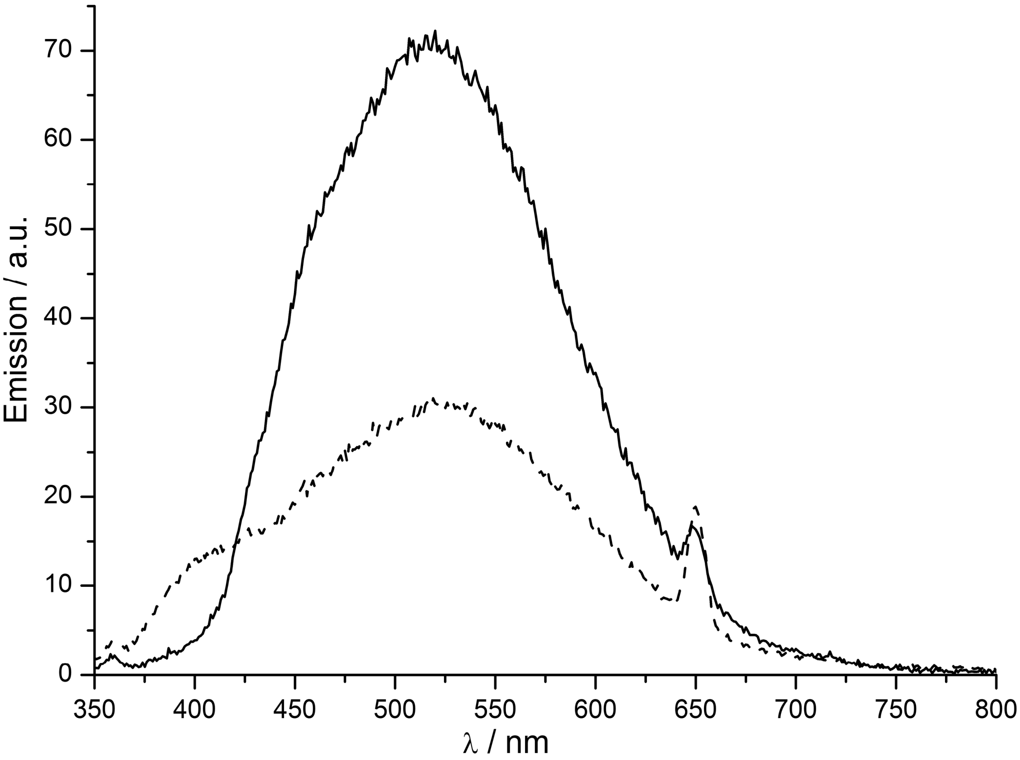

Figure S10. Fluorescence spectrum of **3α** in THF, before (solid) and after addition of excess TBACN (dashed). Excitation at 325 nm.

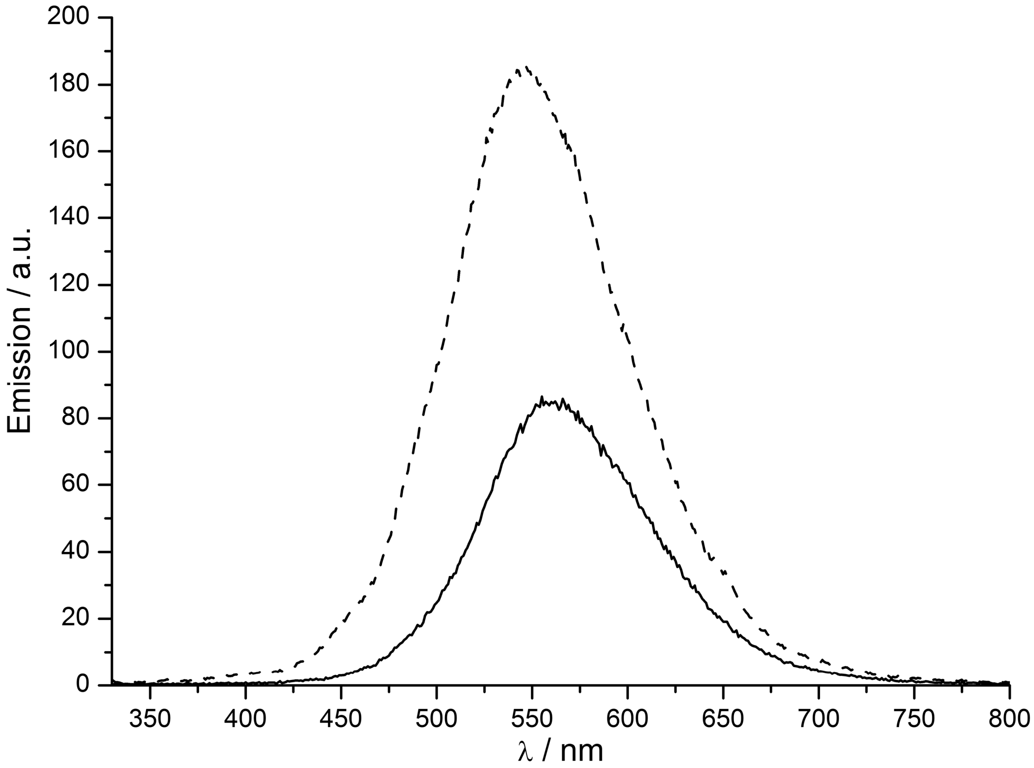

Figure S11. Fluorescence spectrum of **3ß** in THF, before (solid) and after addition of excess TBACN (dashed). Excitation at 325 nm.

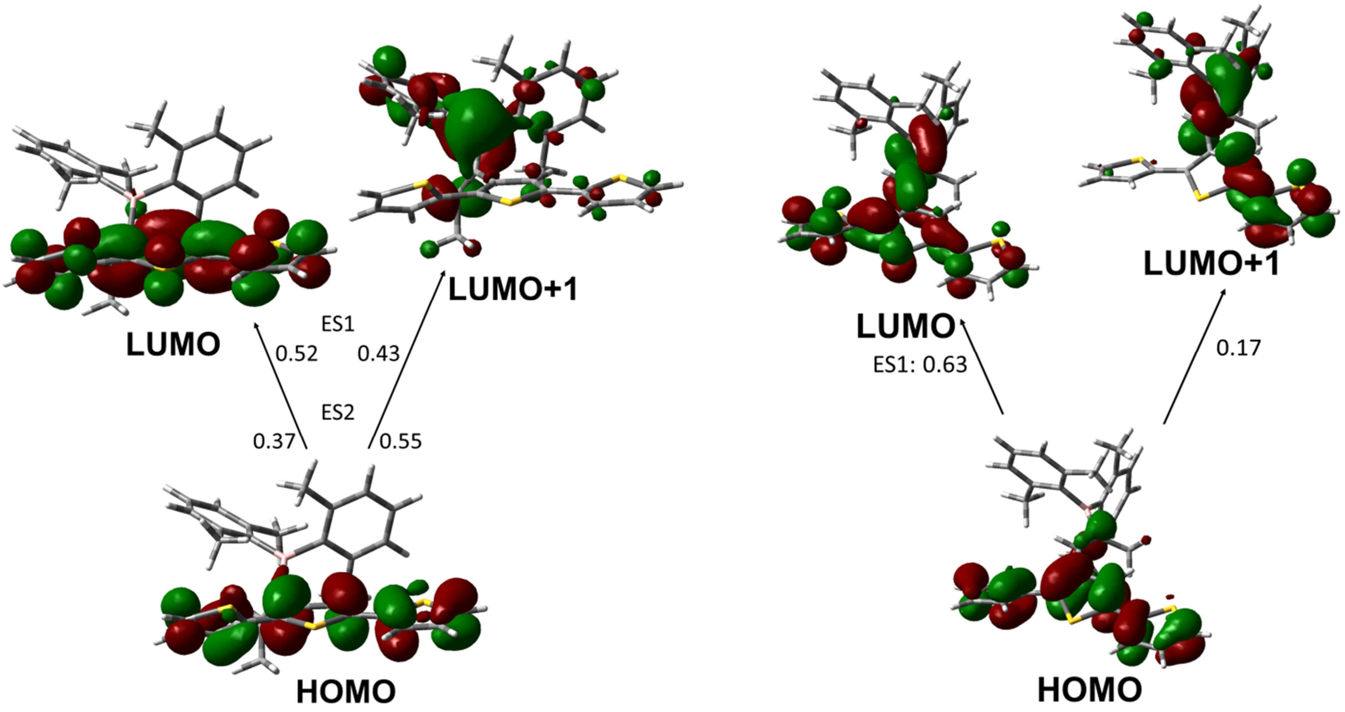

Figure S12. Depiction of the molecular orbitals involved in the lowest energy electronic transitions in **4α'** (left) and **4ß'** (right). **4α'**: ES1: 383 nm, f = 0.20; ES2: 369 nm, f = 0.37; **4ß'**. ES1: 422 nm, f = 0.29.

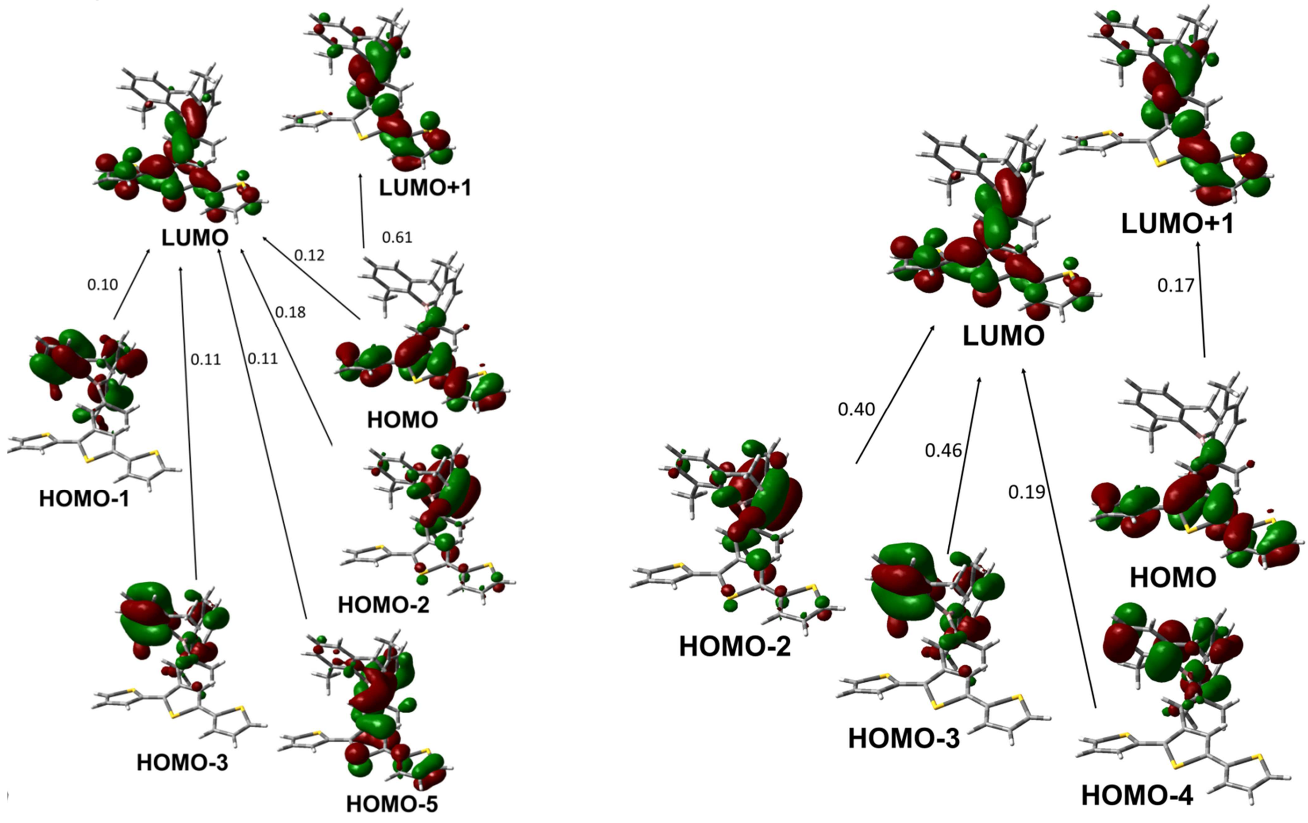

Figure S13. Depictions of the molecular orbitals involved in additional significantly populated higher energy electronic transitions in **4ß'**. ES2 (left): 369 nm, f = 0.28. ; ES5 (right): 348 nm, f = 0.33.

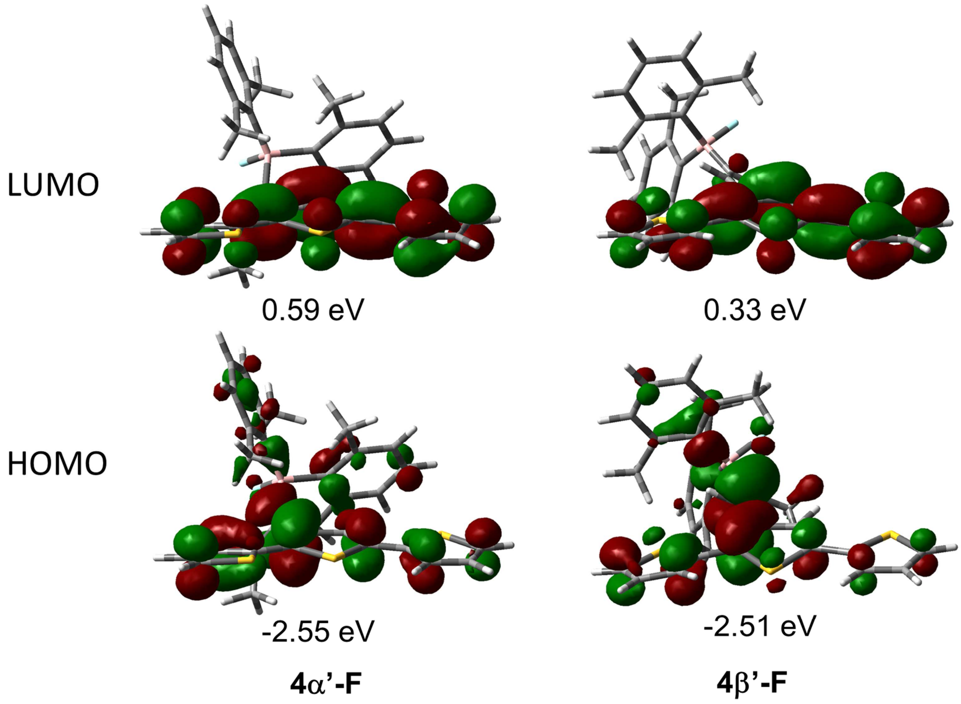

Figure S14. Frontier orbitals and relative energy levels of the fluoride complexes of **4α’/4ß’**. Generated using Gaussview (scaling radii 75%, isovalue 0.03).

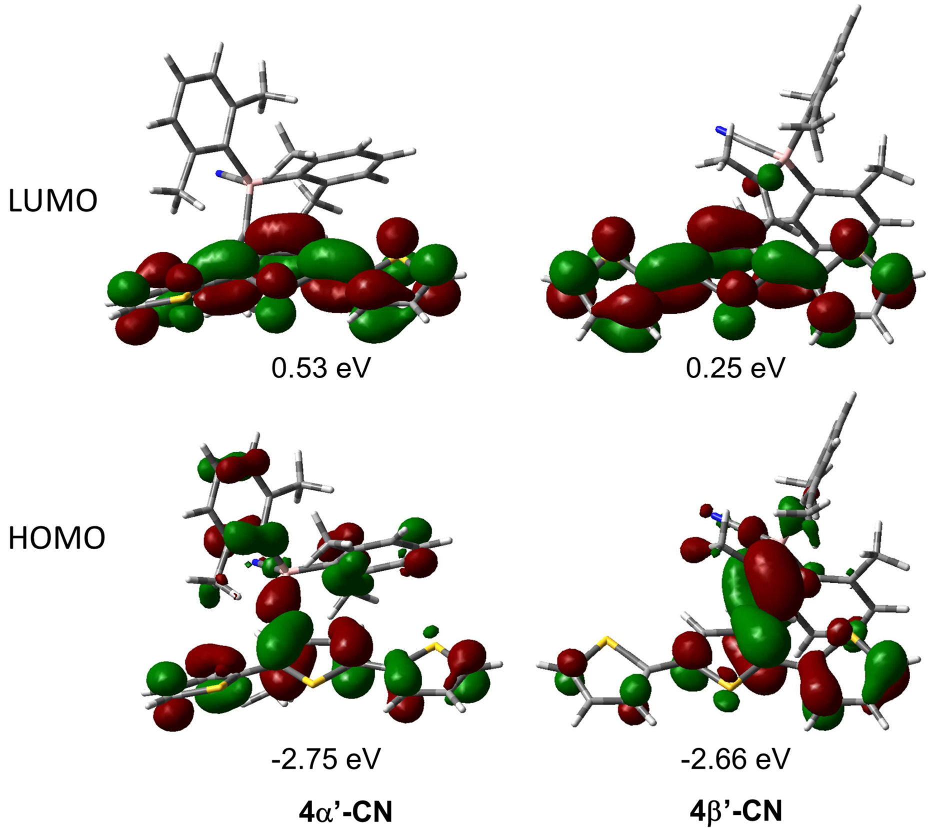

Figure S15. Frontier orbitals and relative energy levels of the cyanide complexes of **4α’/4ß’**. Generated using Gaussview (scaling radii 75%, isovalue 0.03).

Additional analytical data

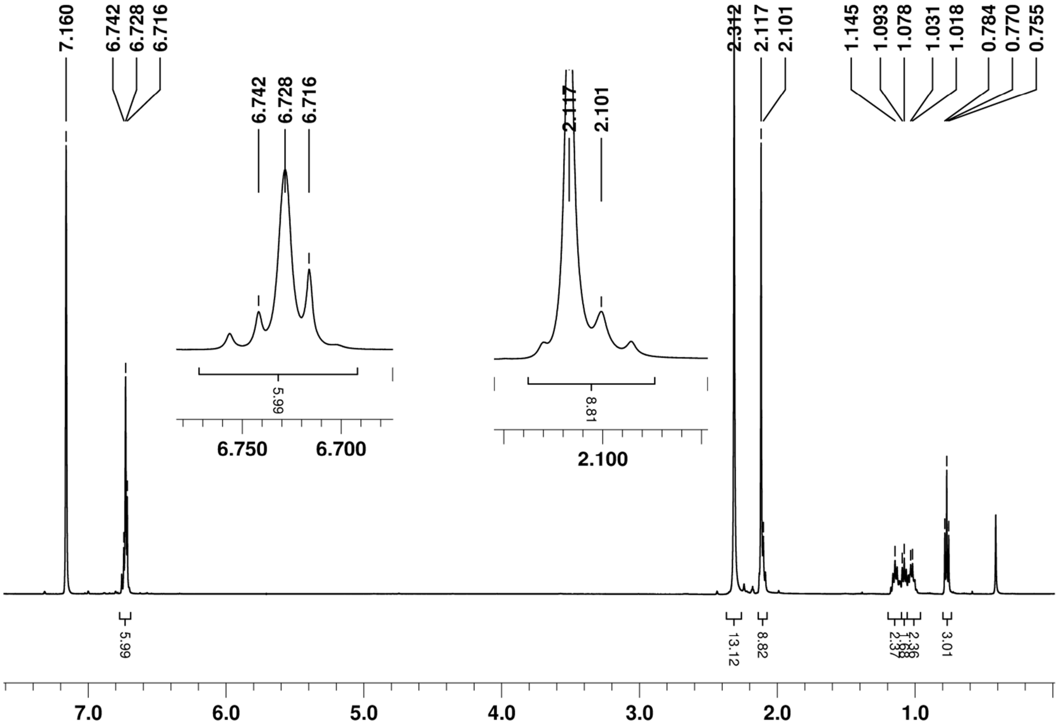

Figure S16. ^{1}H NMR spectrum of **2α** in C_6D_6.

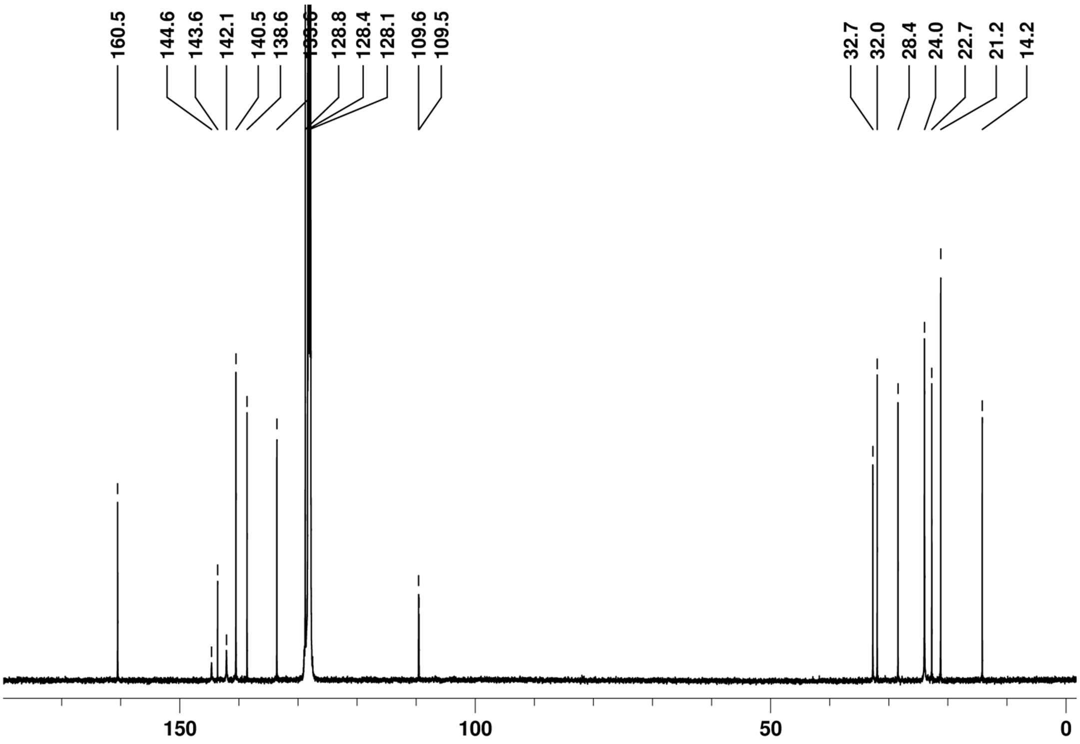

Figure S17. ^{13}C NMR spectrum of **2α** in C_6D_6.

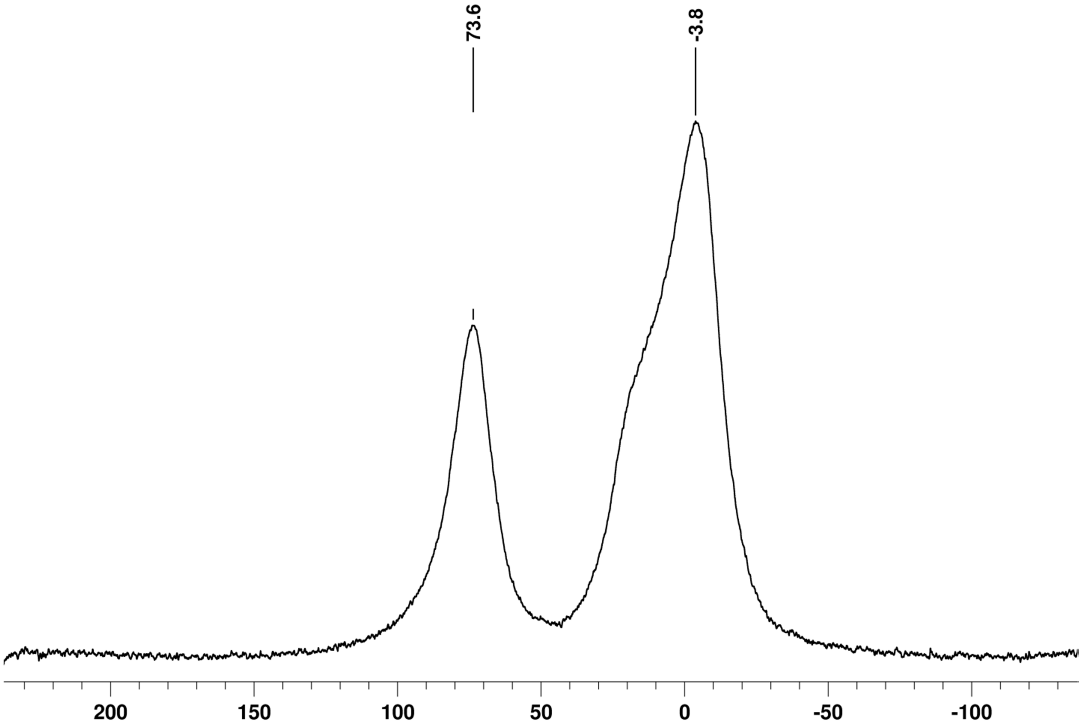

Figure S18. ^{11}B NMR spectrum of **2α** in C_6D_6. Non-boron-free NMR tube; peak at -3.8 ppm stems from glass.

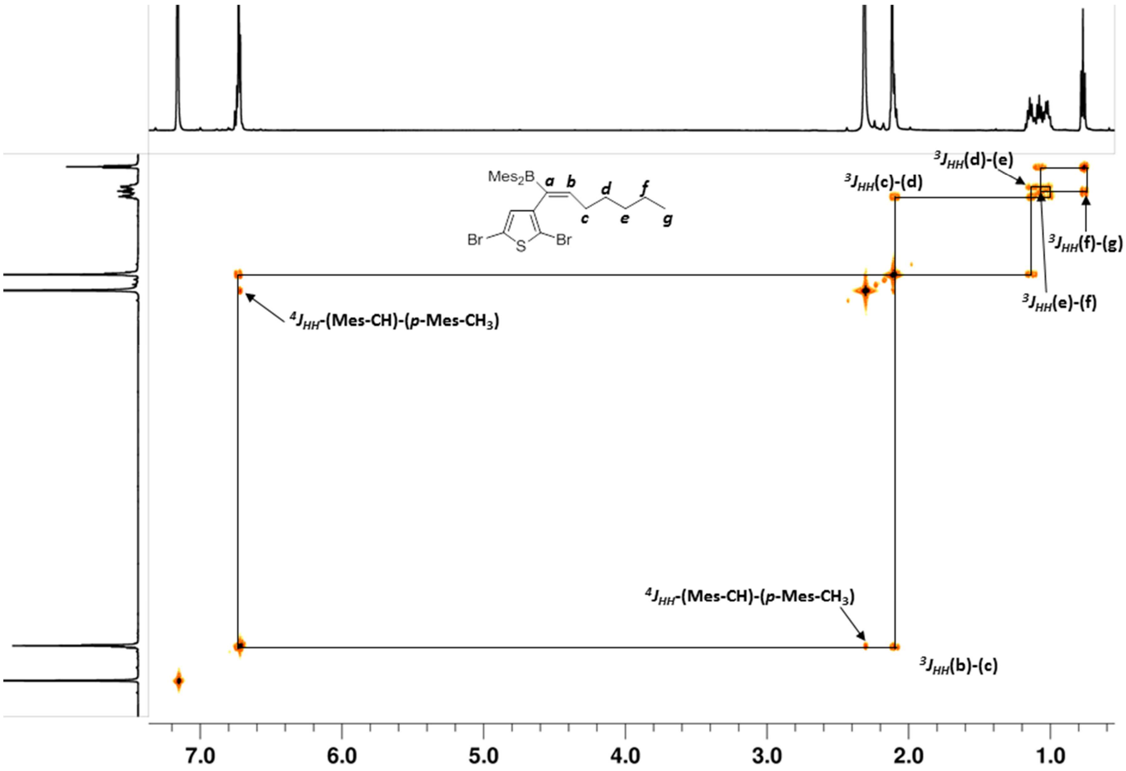

Figure S19. *HH-COSY* NMR spectrum of **2α** in C_6D_6.

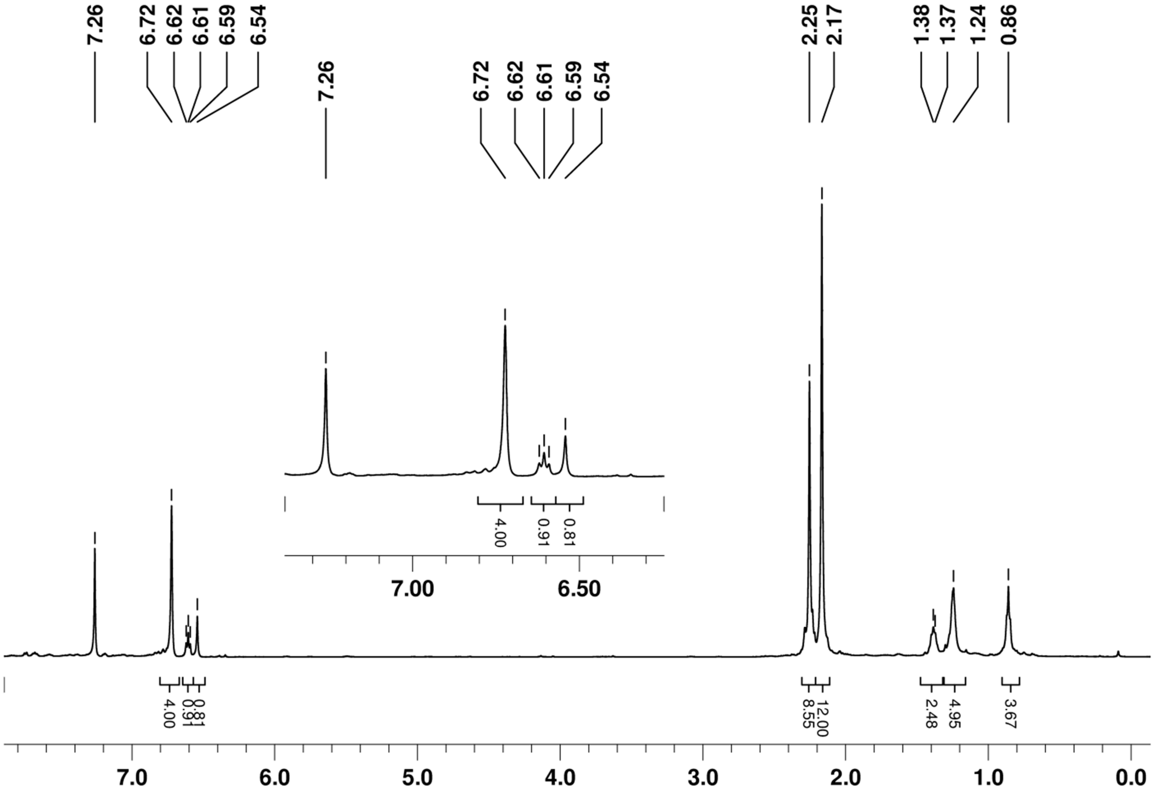

Figure S20. ^{1}H NMR spectrum of **2α** in $CDCl_3$.

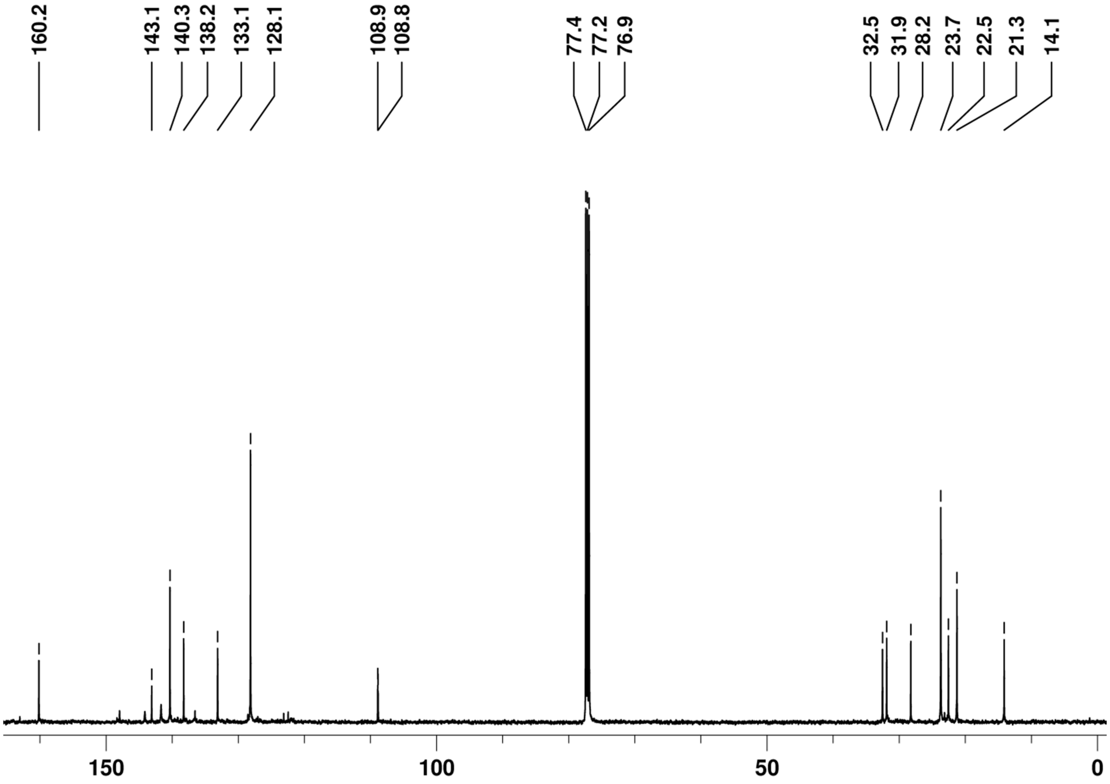

Figure S21. ^{13}C NMR spectrum of **2α** in $CDCl_3$.

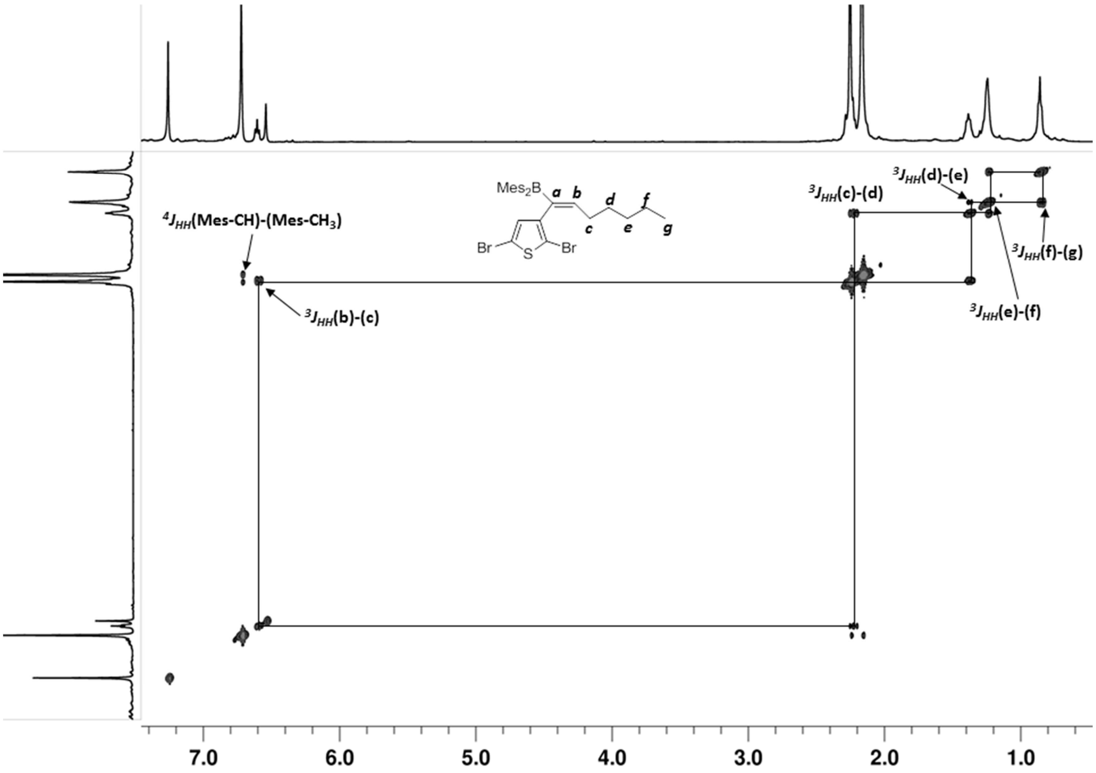

Figure S22. *HH-COSY* NMR spectrum of **2α** in CDCl$_3$.

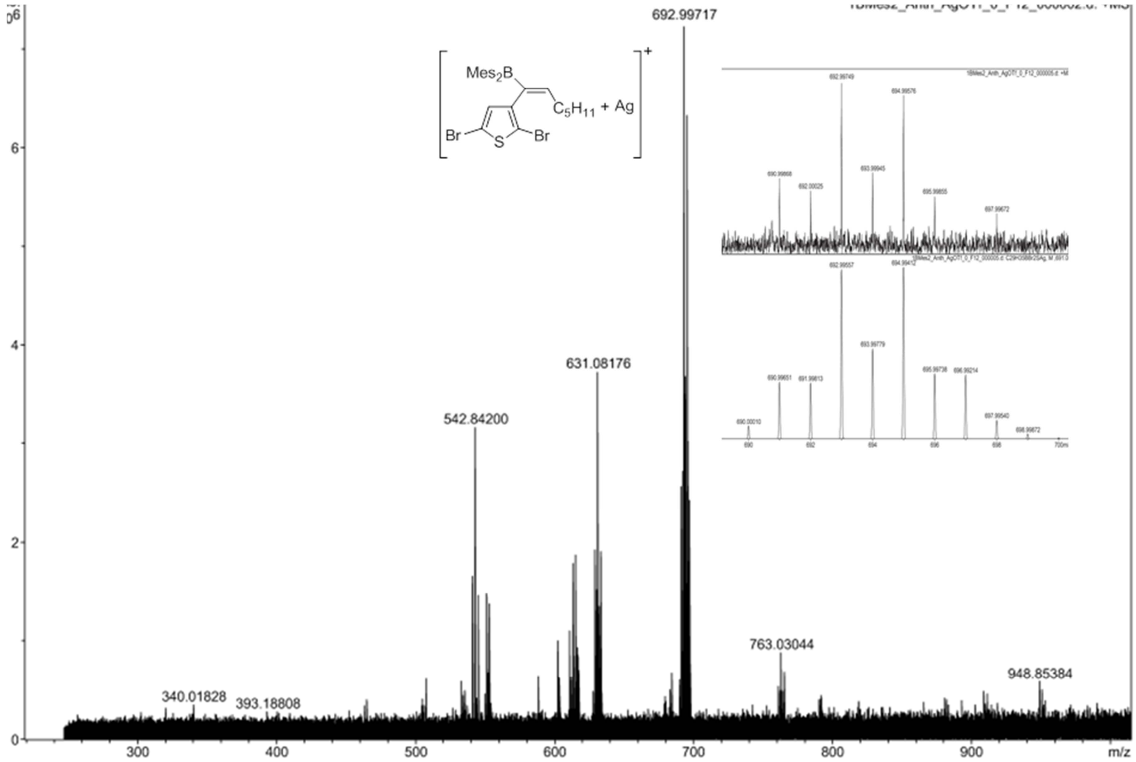

Figure S23. MALDI-MS spectrum of **2α**.

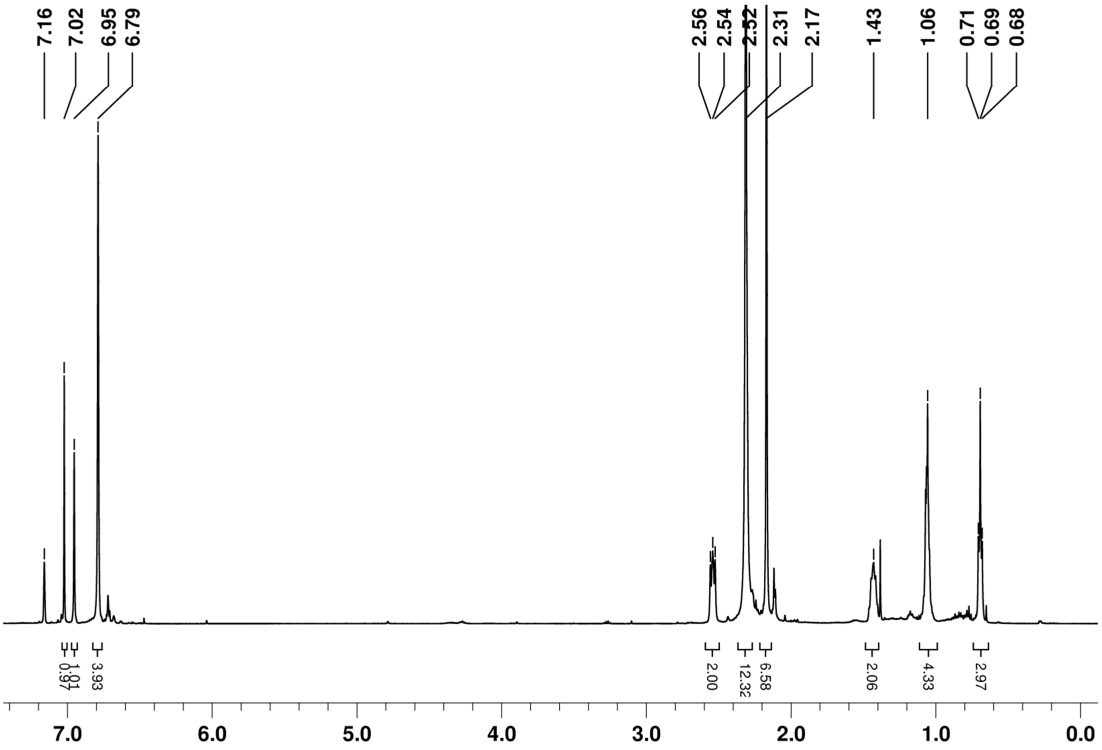

Figure S24. ^{1}H NMR spectrum of **2ß** in C_6D_6.

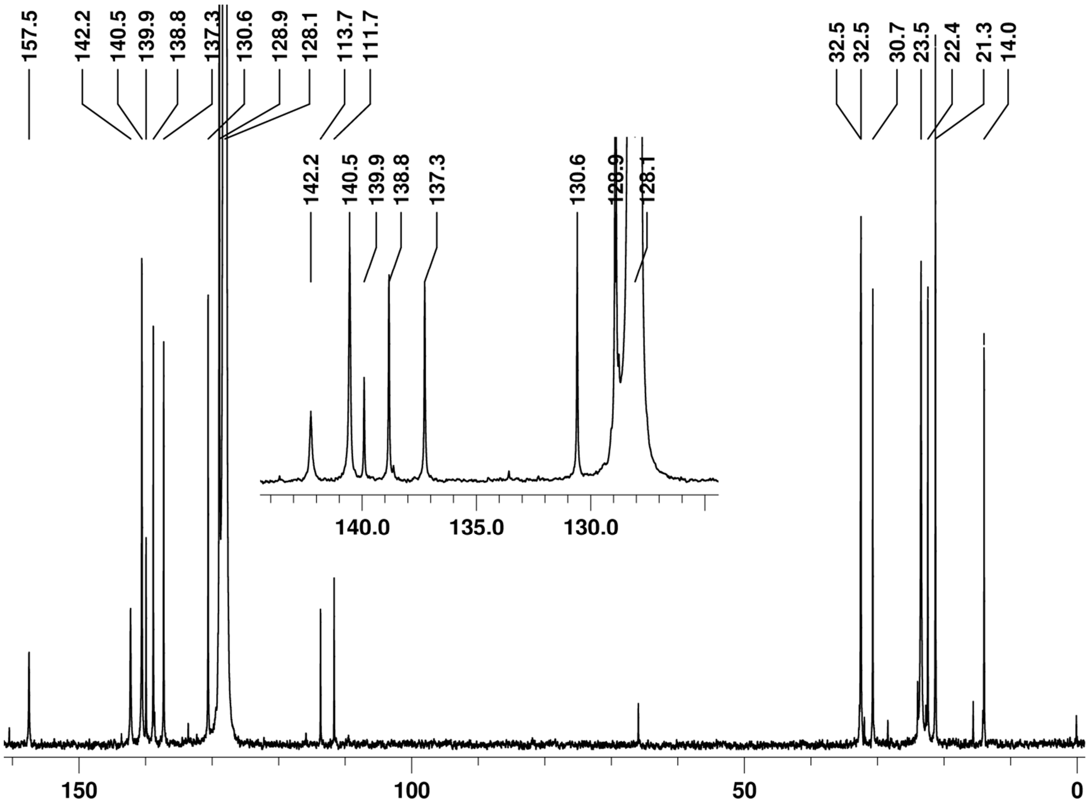

Figure S25. ^{13}C NMR spectrum of **2ß** in C_6D_6.

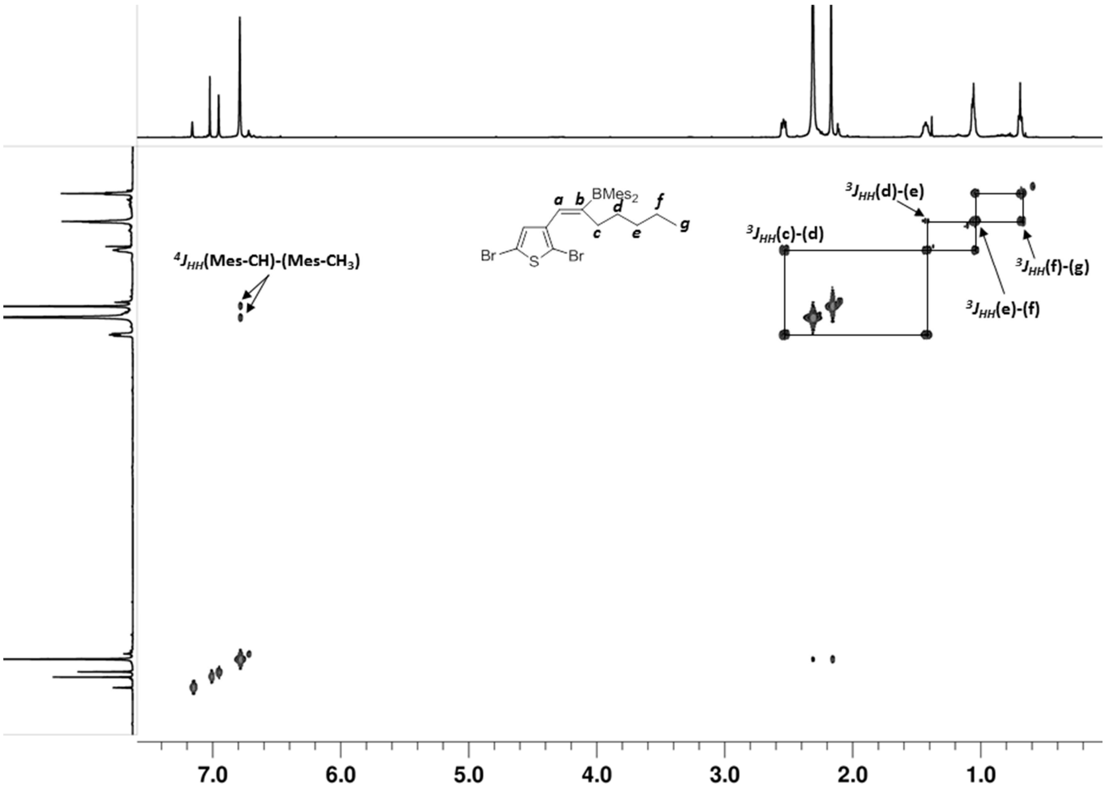

Figure S26. *HH-COSY* NMR spectrum of **2ß** in C_6D_6.

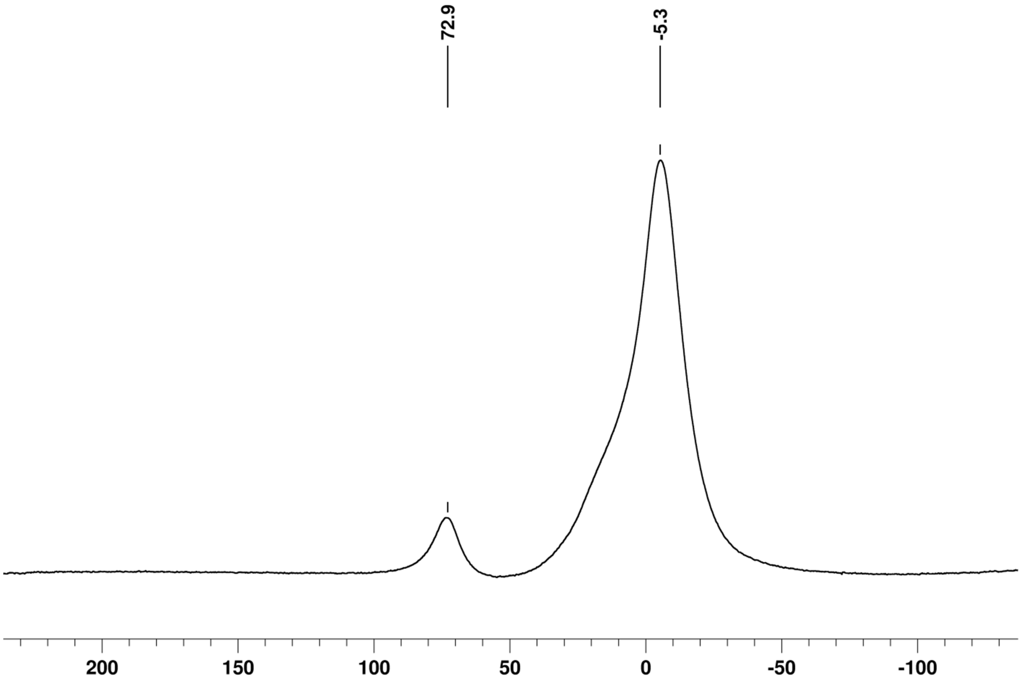

Figure S27. ^{11}B NMR spectrum of **2ß** in C_6D_6. Non-boron-free NMR tube; peak at -5.3 ppm stems from glass.

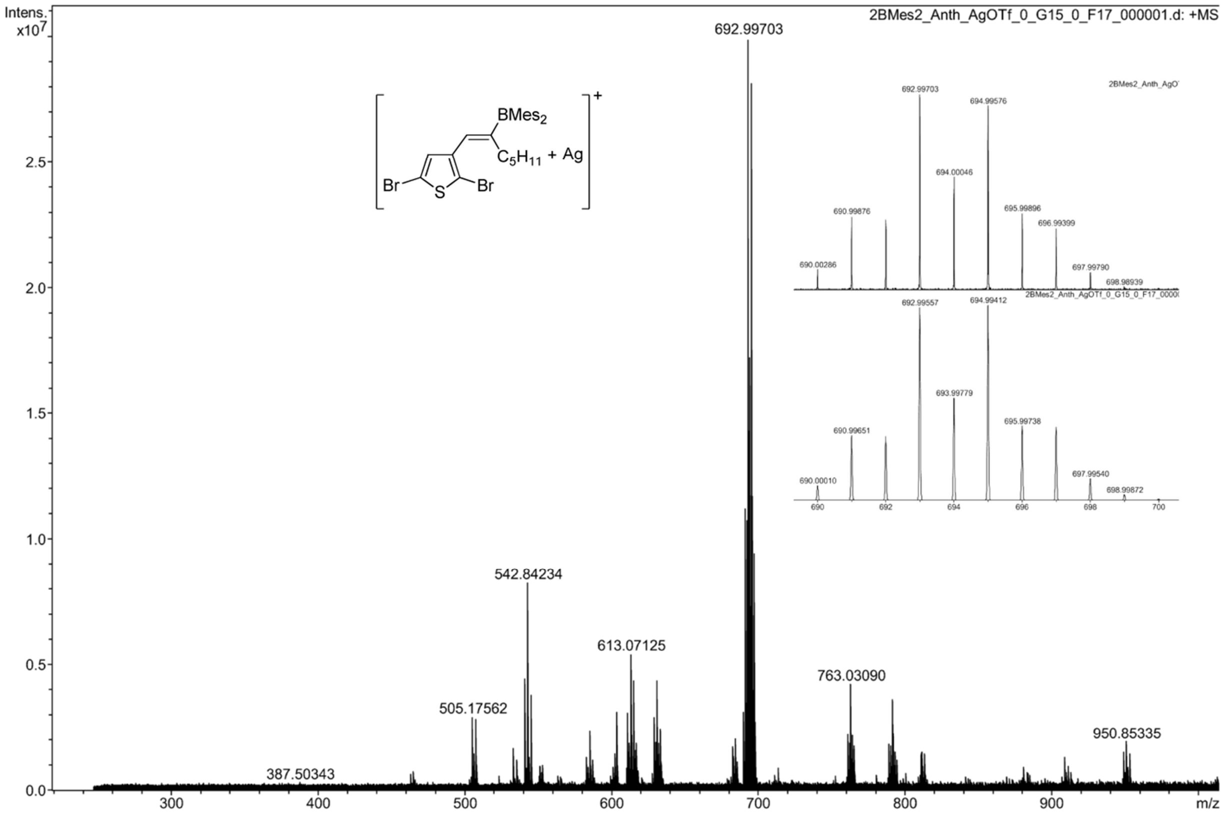

Figure S28. MALDI-MS spectrum of **2ß**.

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