SUPPORTING INFORMATION FOR

Aromaticity Competition in Differentially-Fused Borepin Containing Polycyclic Aromatics

Reid E. Messersmith,[1] Maxime A. Siegler,[1] and John D. Tovar[1,2]*

[1] Department of Chemistry

[2] Department of Materials Science and Engineering

Johns Hopkins University

3400 North Charles Street

Baltimore, Maryland 21218

United States of America

*tovar@jhu.edu

1. NMR Spectra for new compounds **S-2**

2. Cyclic Voltammetry **S-37**

3. Single Crystal X-ray Crystallography **S-43**

4. Computational Details **S-75**

5. Photophysical Data **S-101**

6. Nomenclature **S-102**

7. Borepin Formation Information **S-103**

8. Proton NMR peak assignments **S-104**

9. Long Term storage of 8 **S-105**

8. References **S-106**

1. NMR Spectra for new compounds

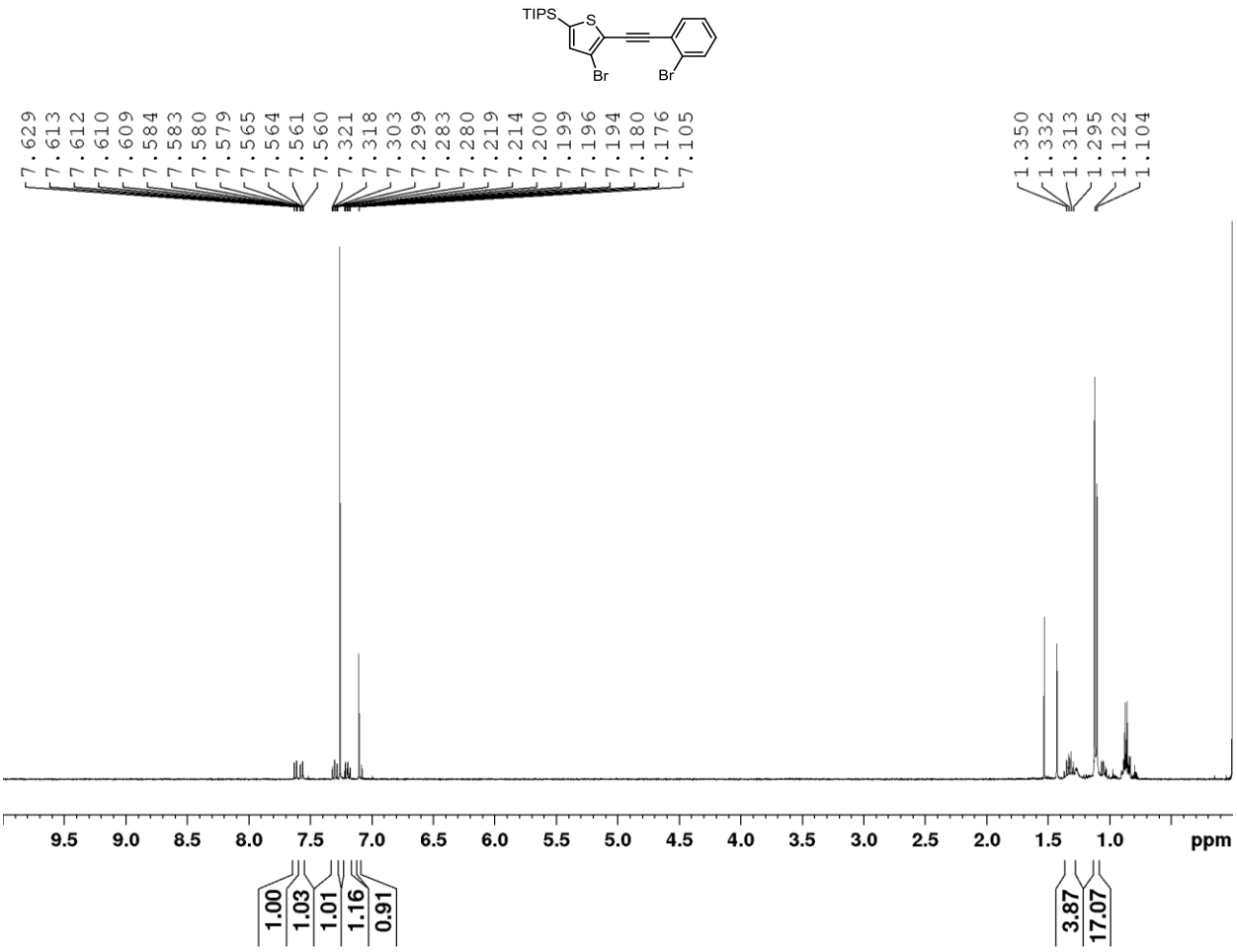


Figure S-1. ^{1}H NMR spectrum of **11** (400 MHz, $CDCl_3$).

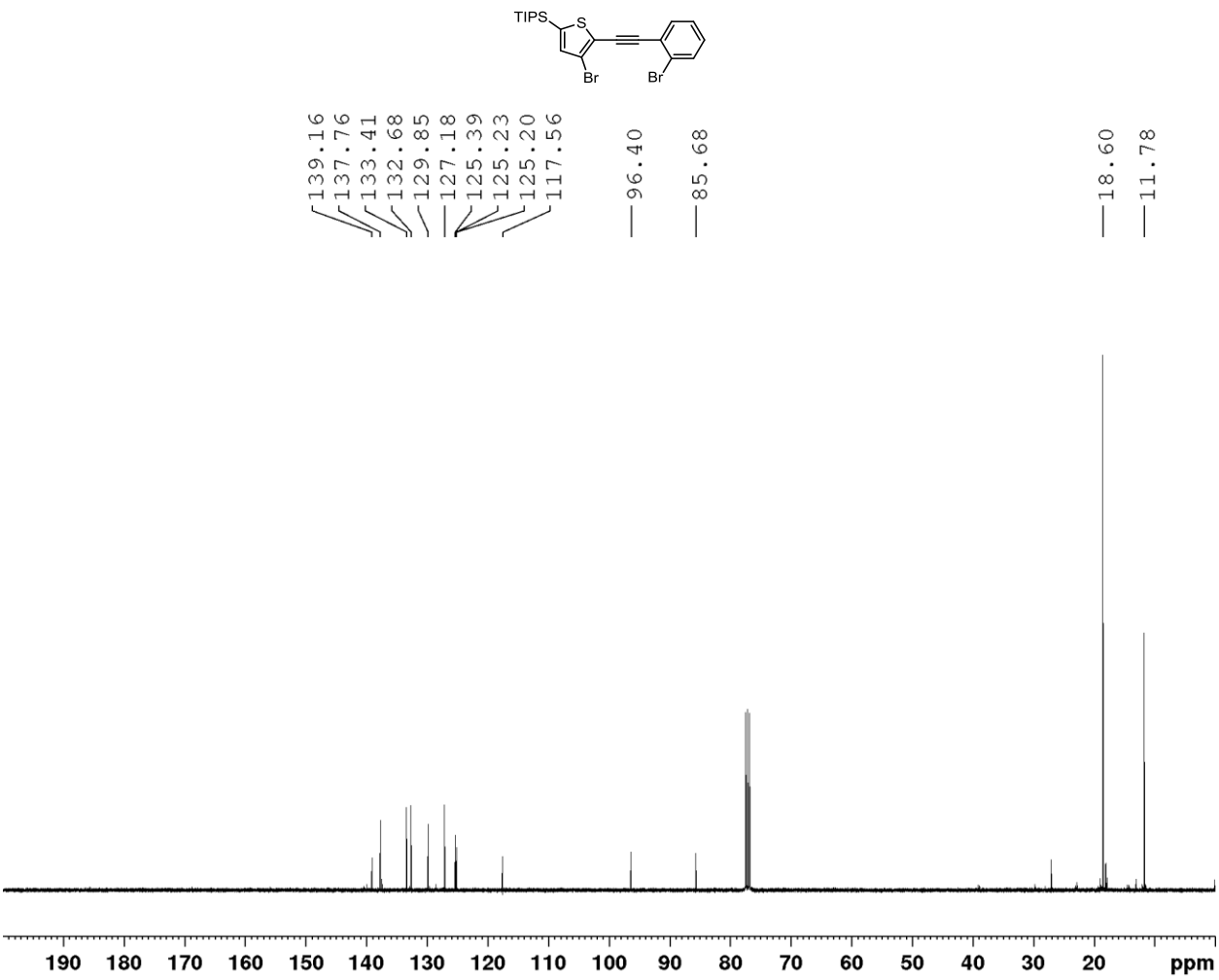


Figure S-2. ^{13}C {^{1}H} NMR spectrum of **11** (100 MHz, $CDCl_3$).

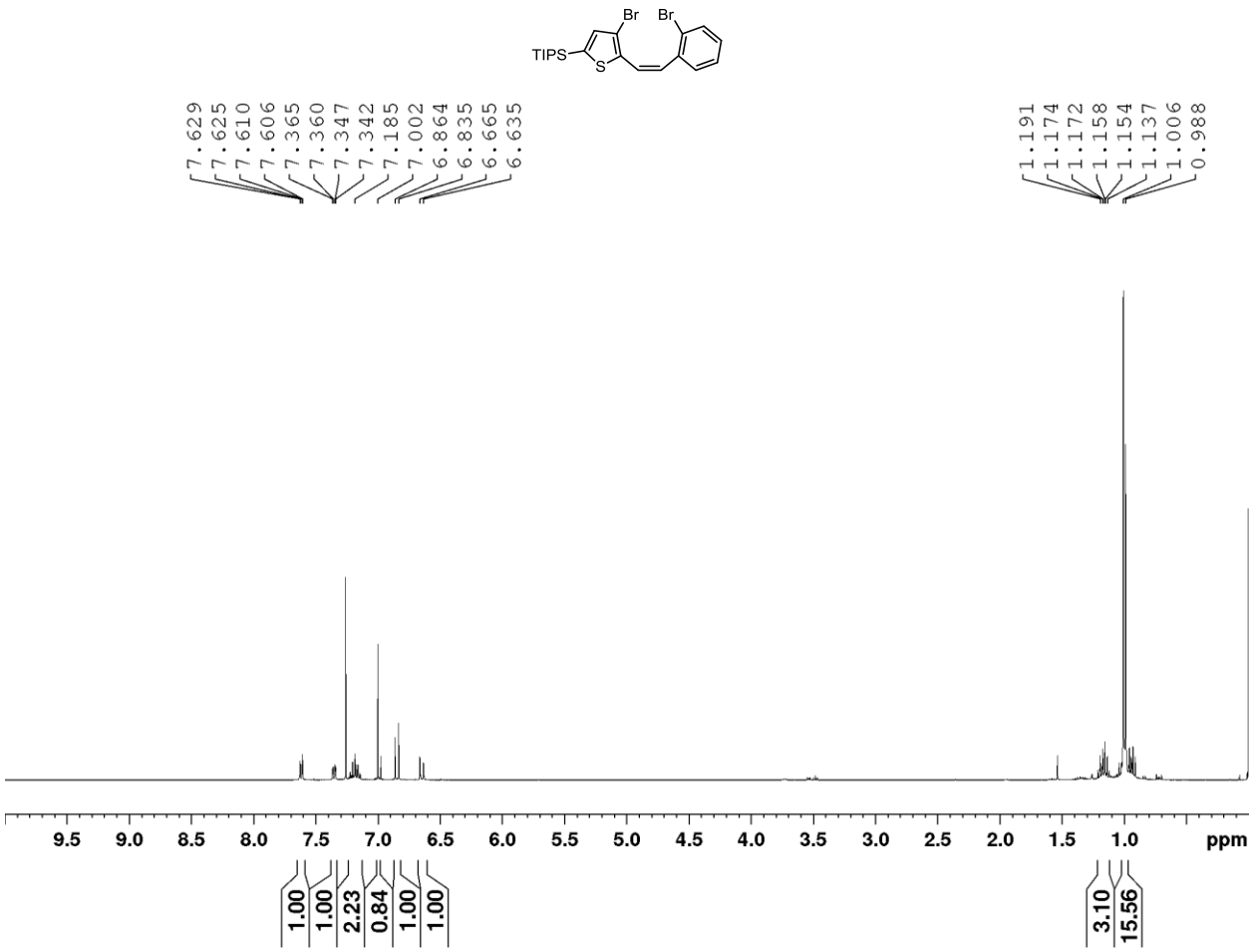


Figure S-3. ^{1}H NMR spectrum of **12** (400 MHz, $CDCl_3$).

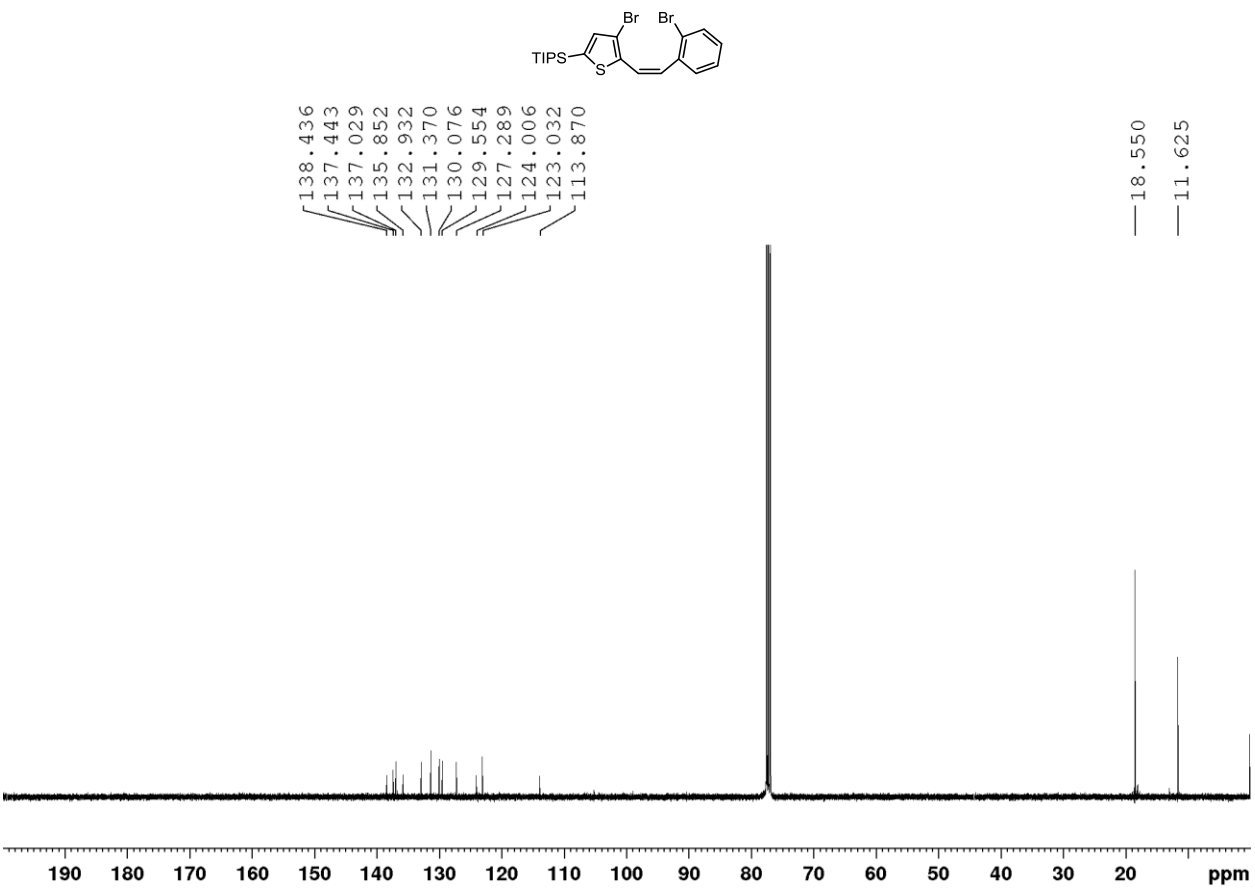


Figure S-4. ^{13}C {^{1}H} NMR spectrum of **12** (100 MHz, $CDCl_3$).

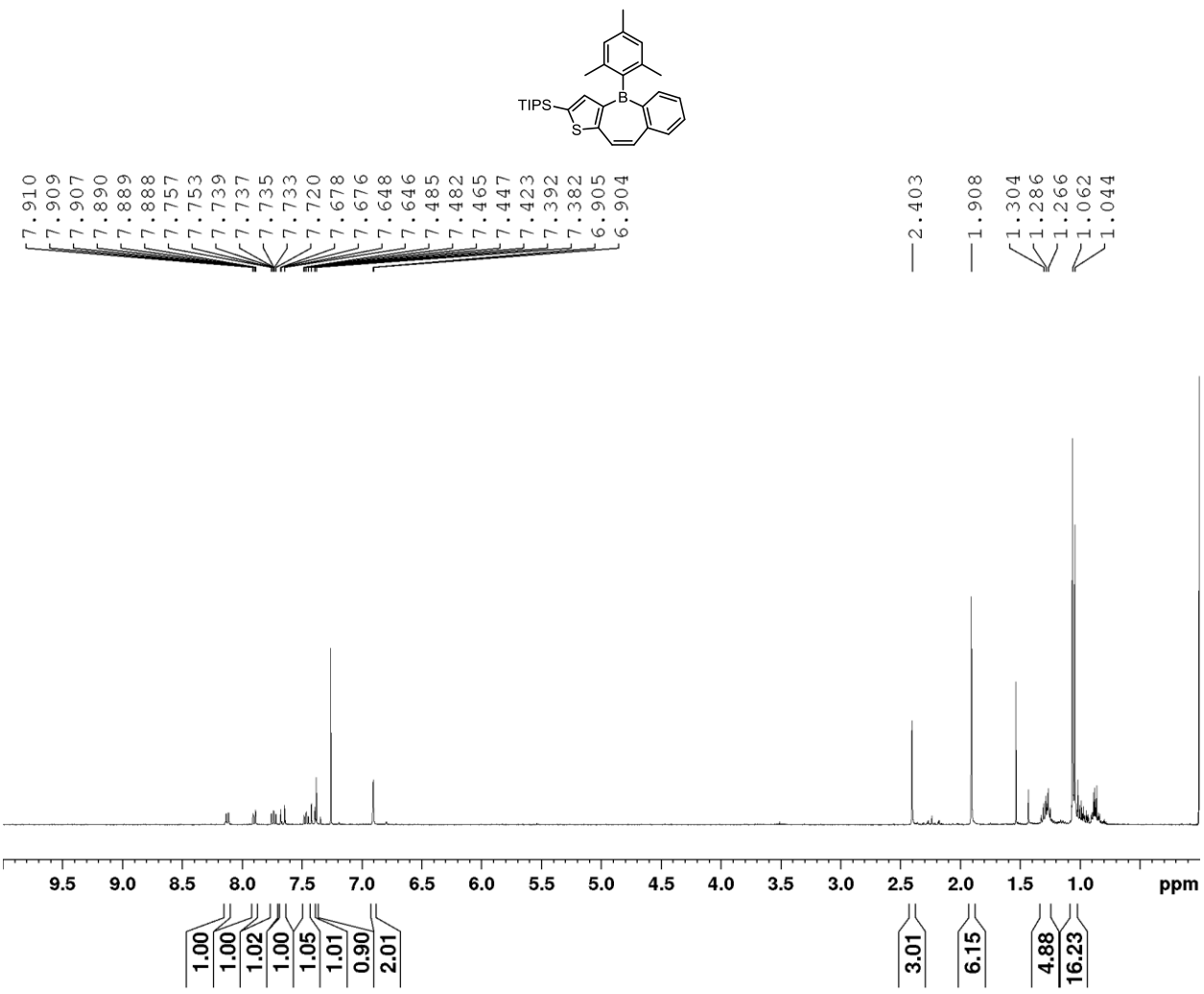


Figure S-5. ^{1}H NMR spectrum of **13** (400 MHz, $CDCl_3$).

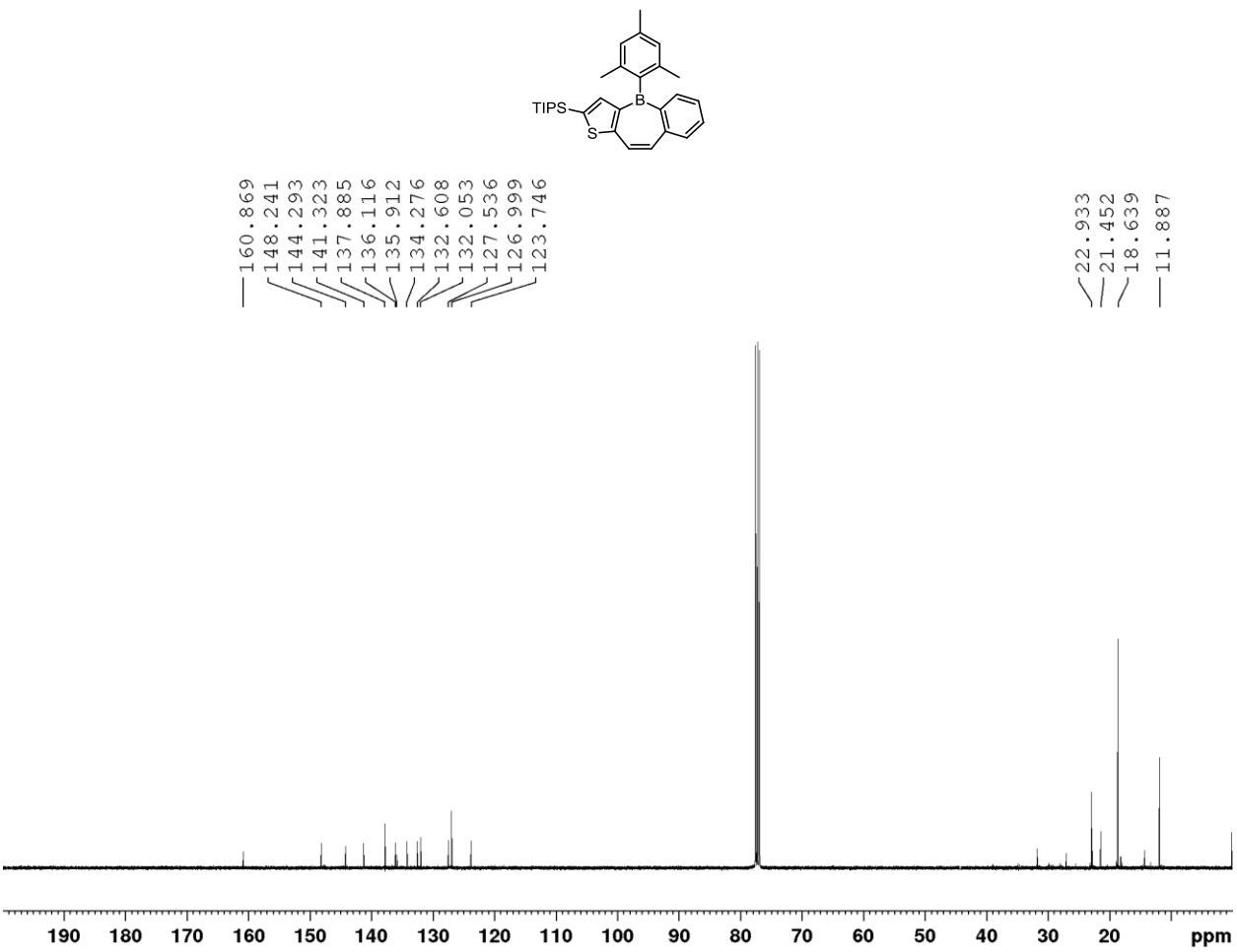


Figure S-6. ^{13}C {^{1}H} NMR spectrum of **13** (100 MHz, $CDCl_3$).

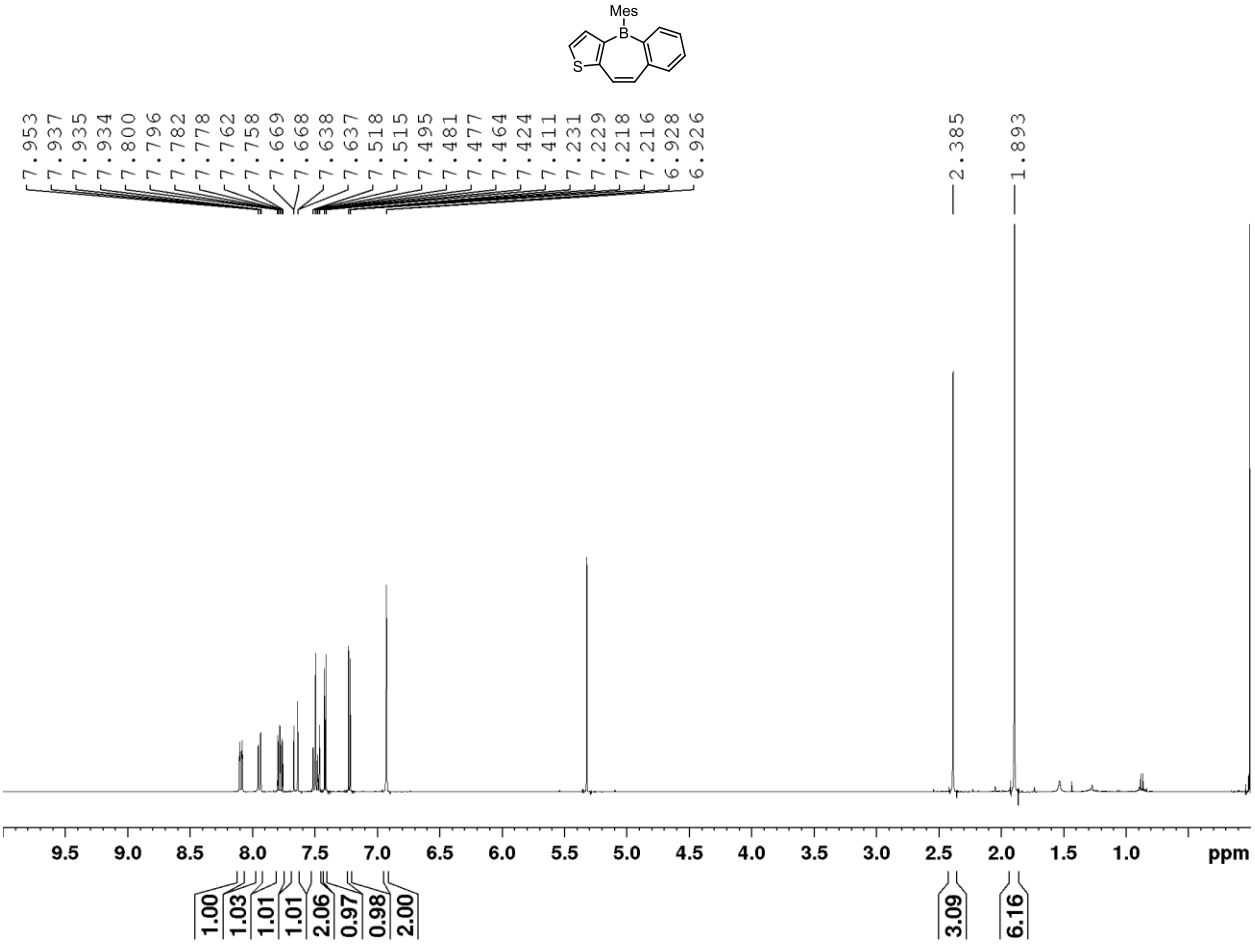


Figure S-7. ^{1}H NMR spectrum of **6** (400 MHz, CD_2Cl_2).

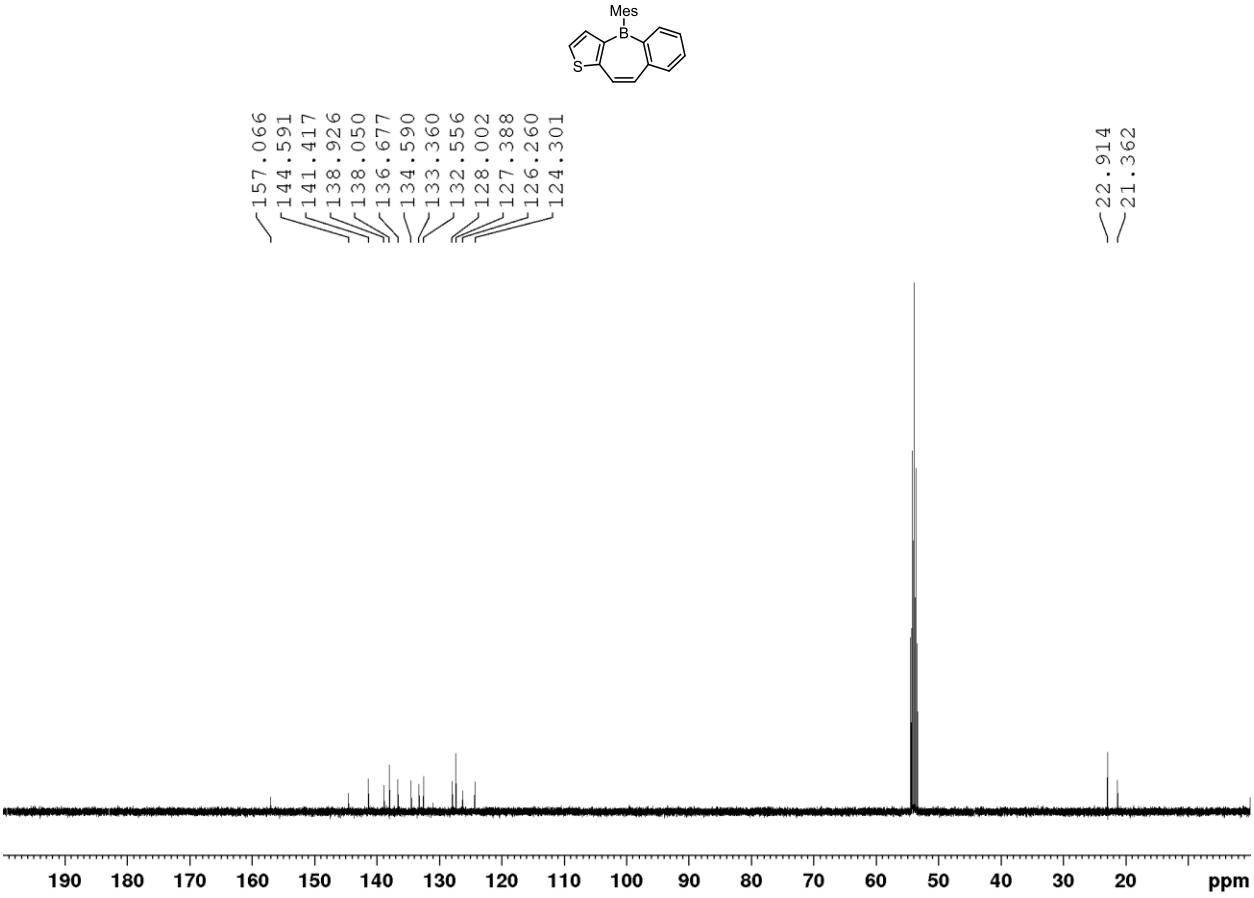


Figure S-8. ^{13}C {^{1}H} NMR spectrum of **6** (100 MHz, CD_2Cl_2).

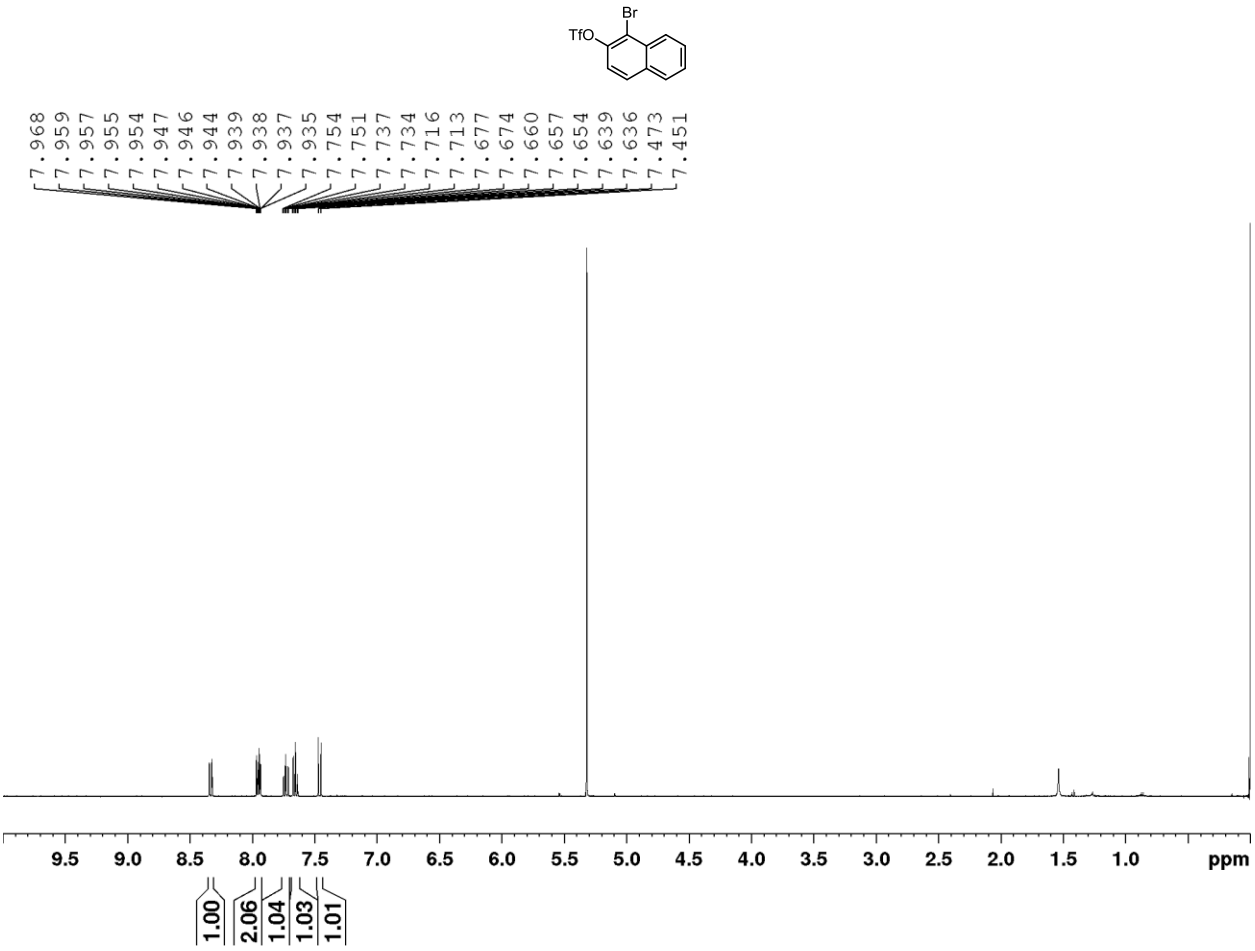


Figure S-9. ^{1}H NMR spectrum of **14** (400 MHz, CD_2Cl_2).

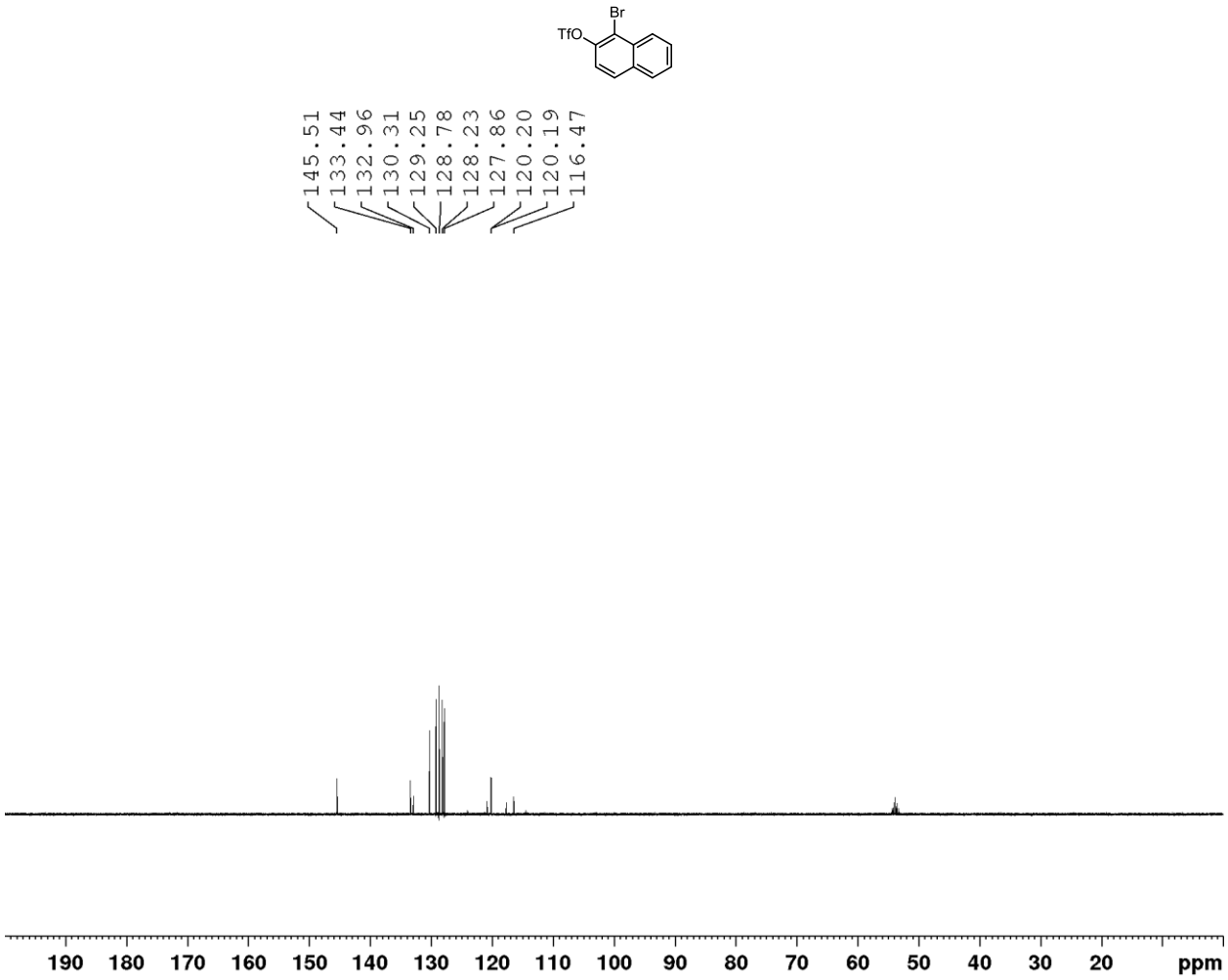


Figure S-10. ^{13}C {^{1}H} NMR spectrum of **14** (100 MHz, CD_2Cl_2).

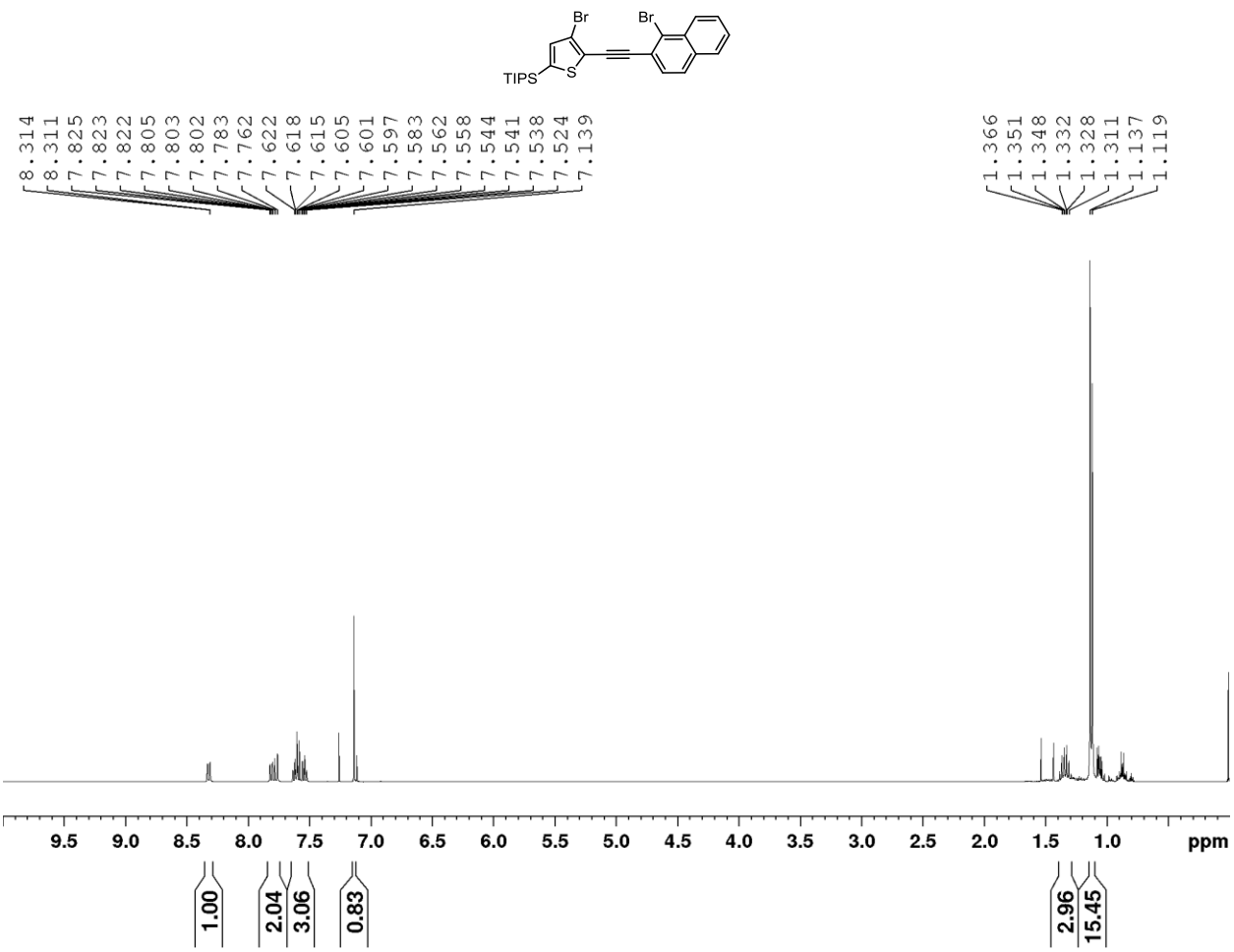


Figure S-11. ^{1}H NMR spectrum of **15** (400 MHz, $CDCl_3$).

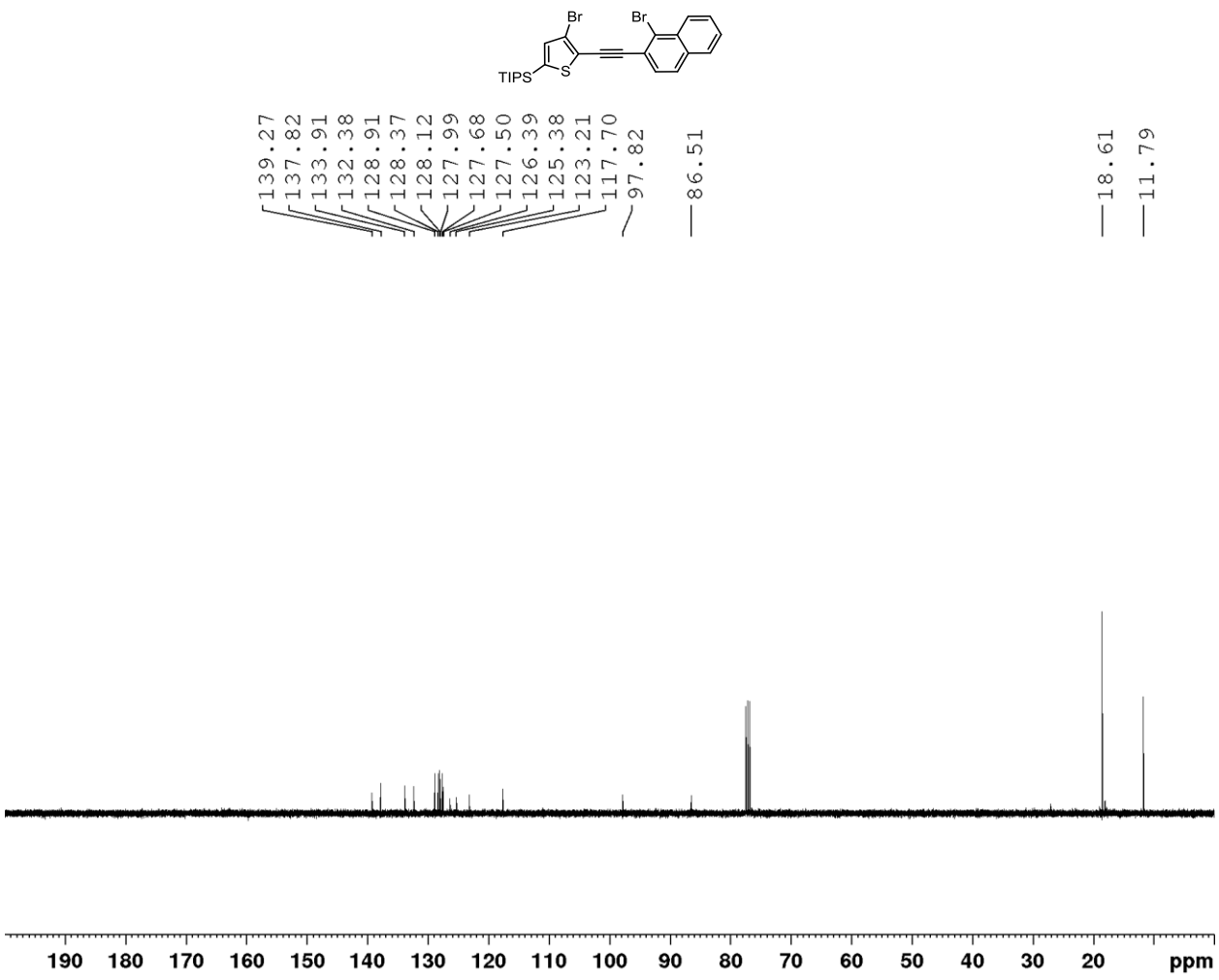


Figure S-12. ^{13}C {^{1}H} NMR spectrum of **15** (100 MHz, $CDCl_3$).

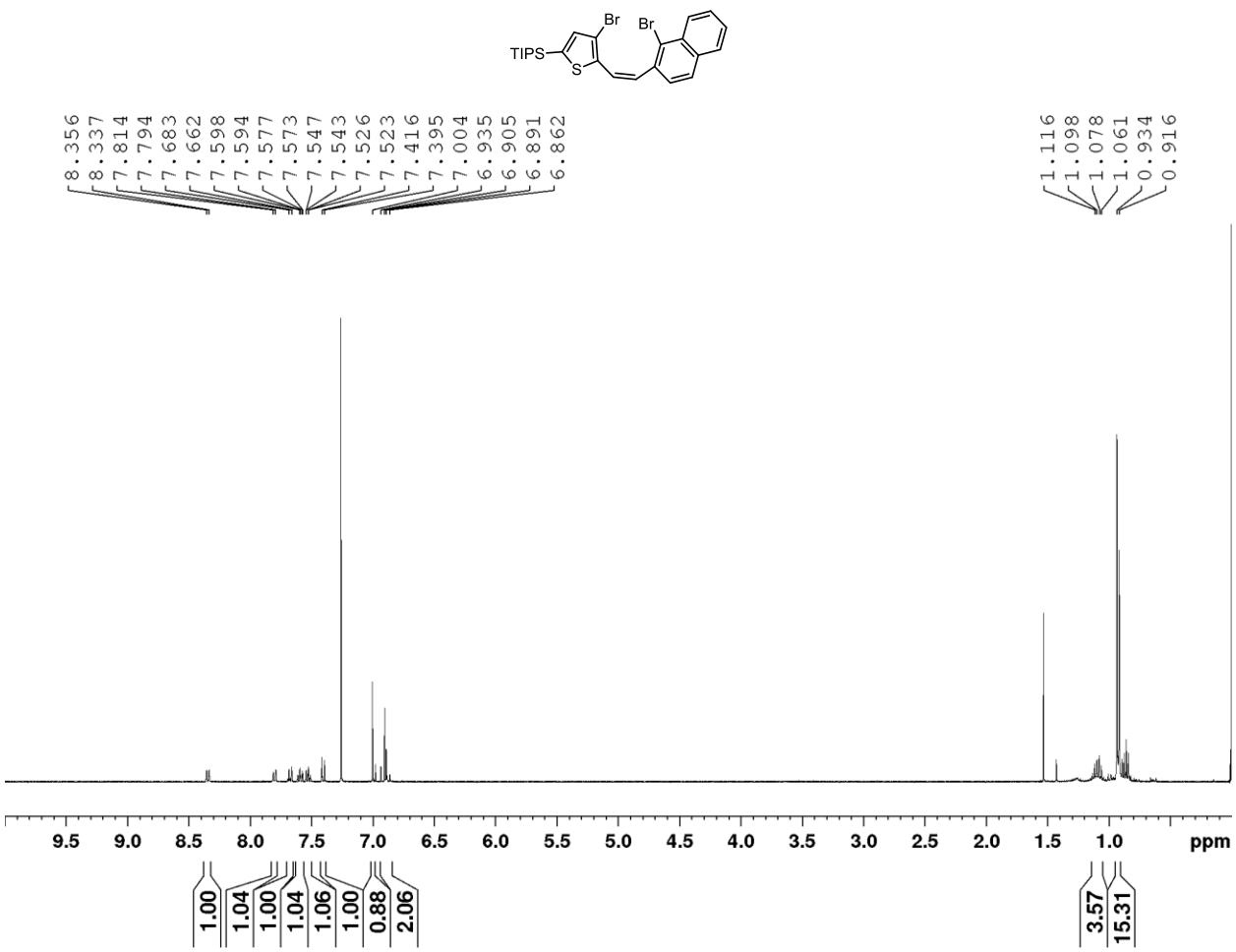


Figure S-13. ^{1}H NMR spectrum of **16** (400 MHz, $CDCl_3$).

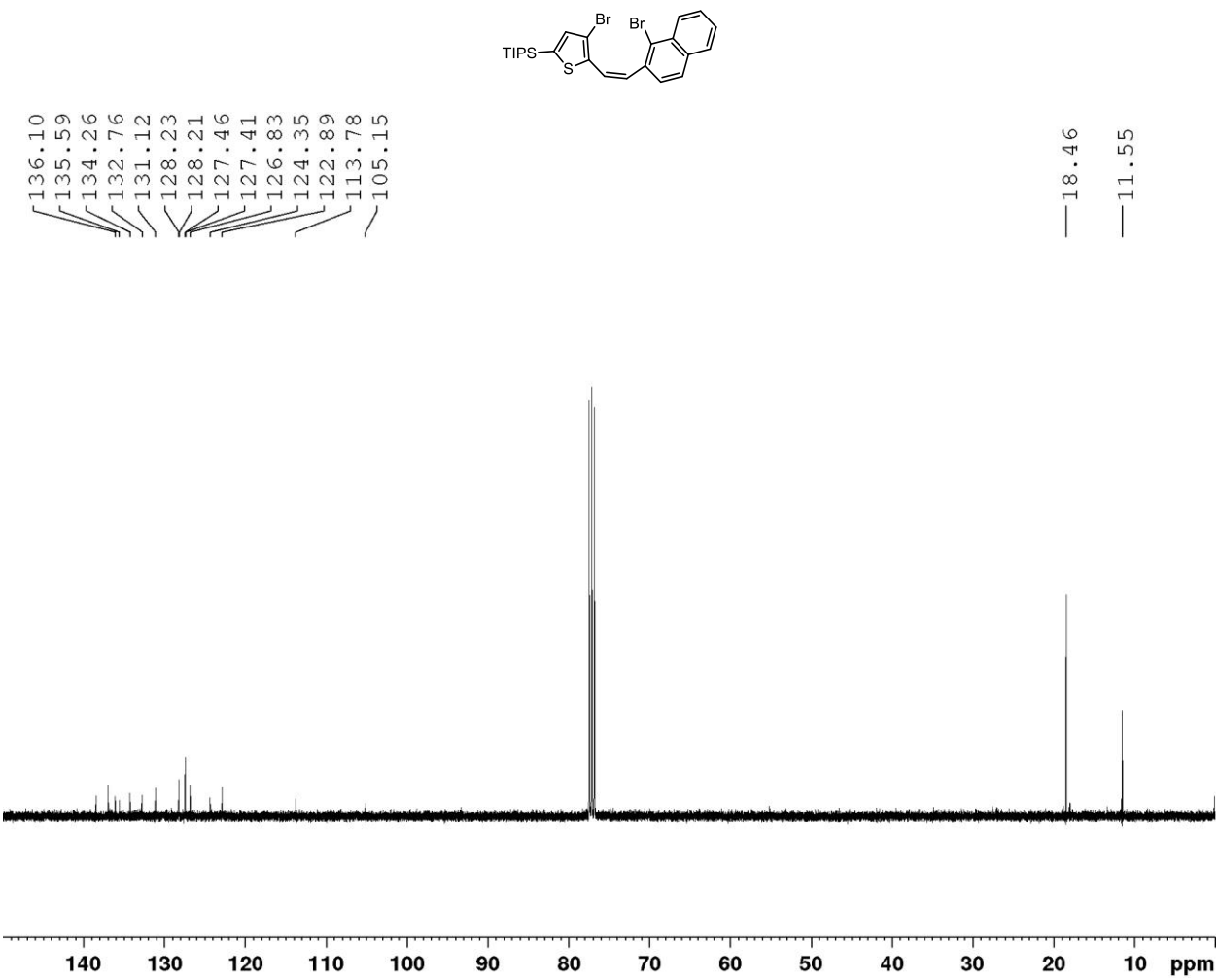


Figure S-14. ^{13}C {^{1}H} NMR spectrum of **16** (100 MHz, $CDCl_3$).

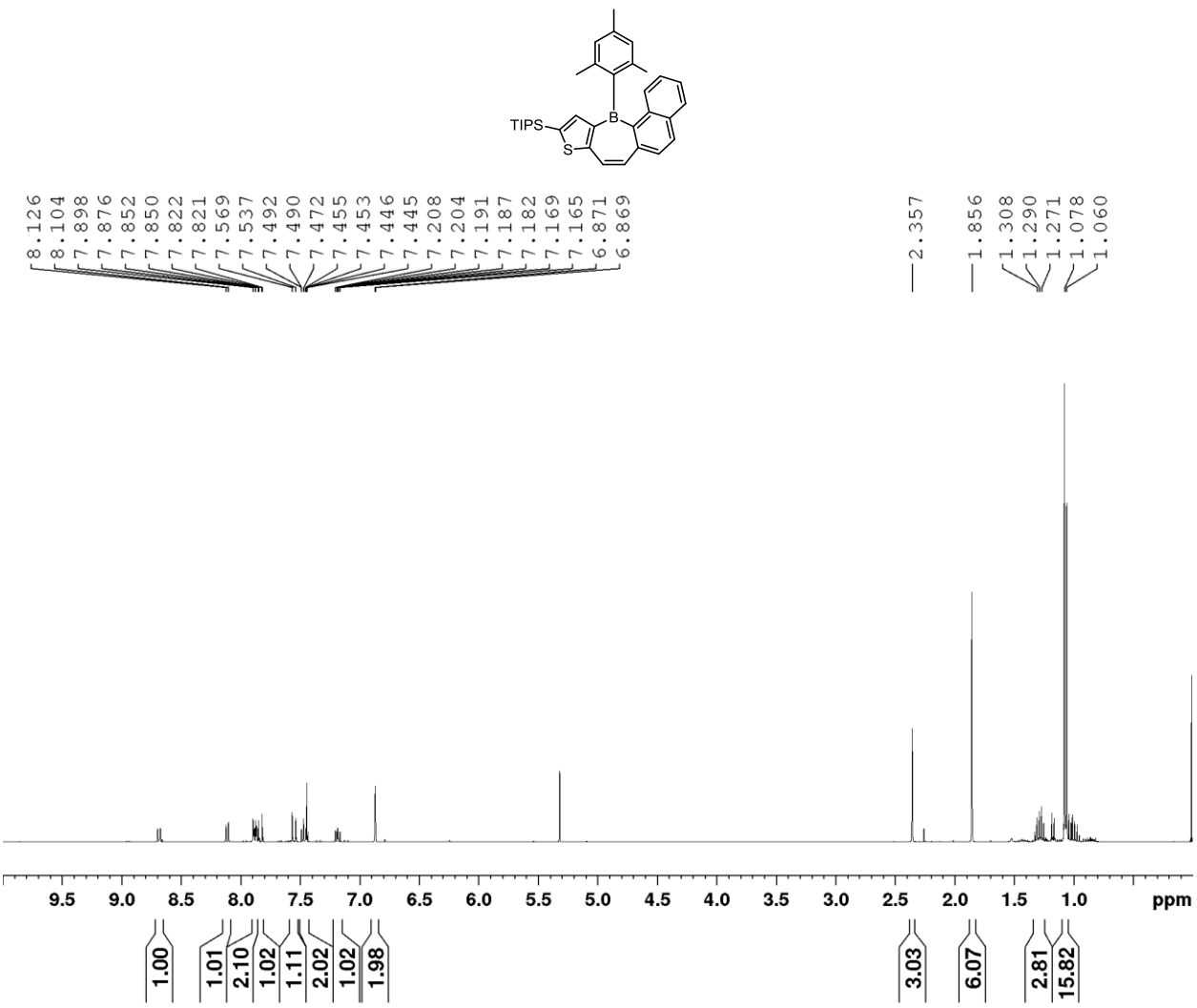


Figure S-15. ^{1}H NMR spectrum of **17** (400 MHz, CD_2Cl_2).

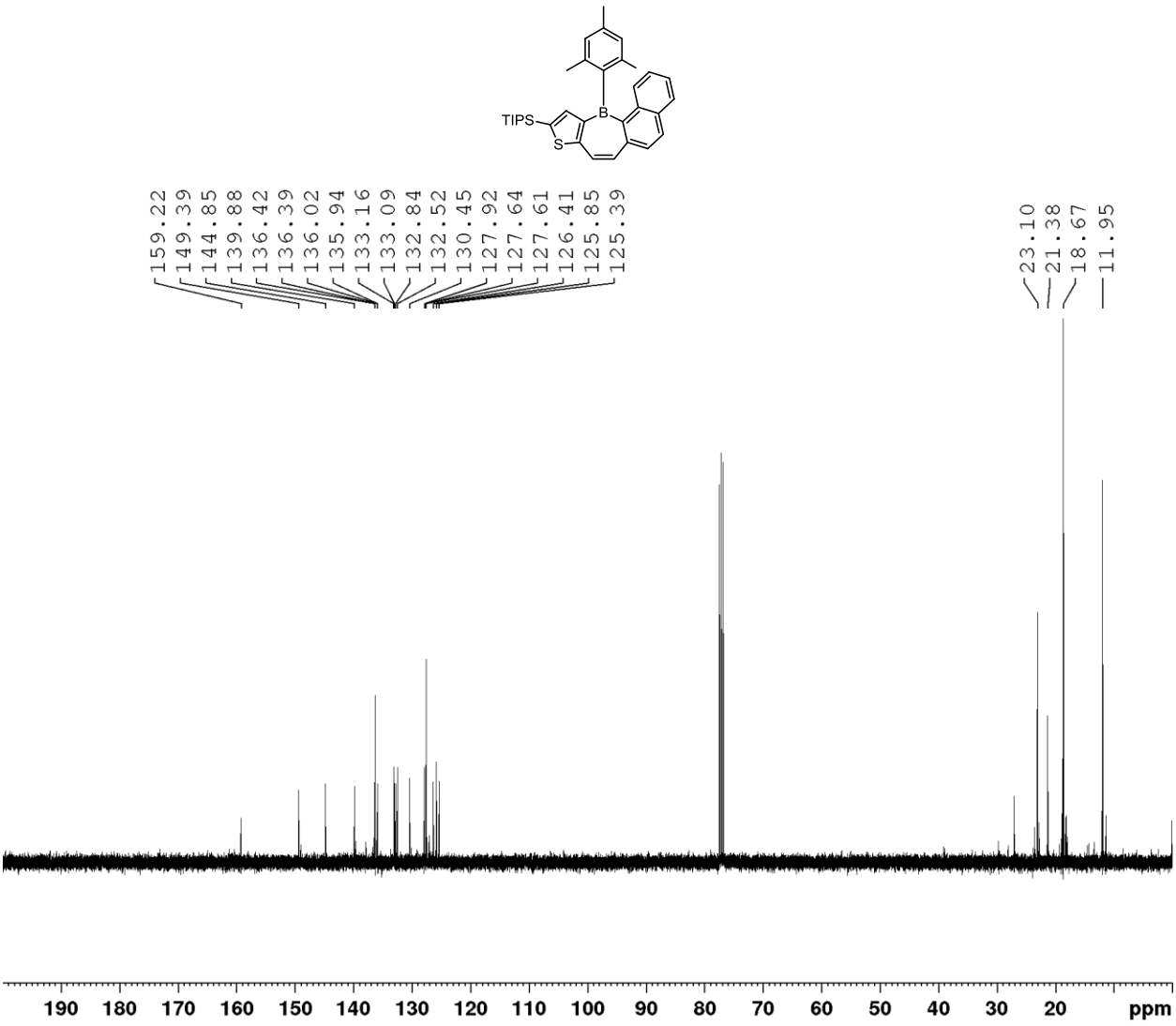


Figure S-16. ^{13}C {^{1}H} NMR spectrum of **17** (100 MHz, $CDCl_3$).

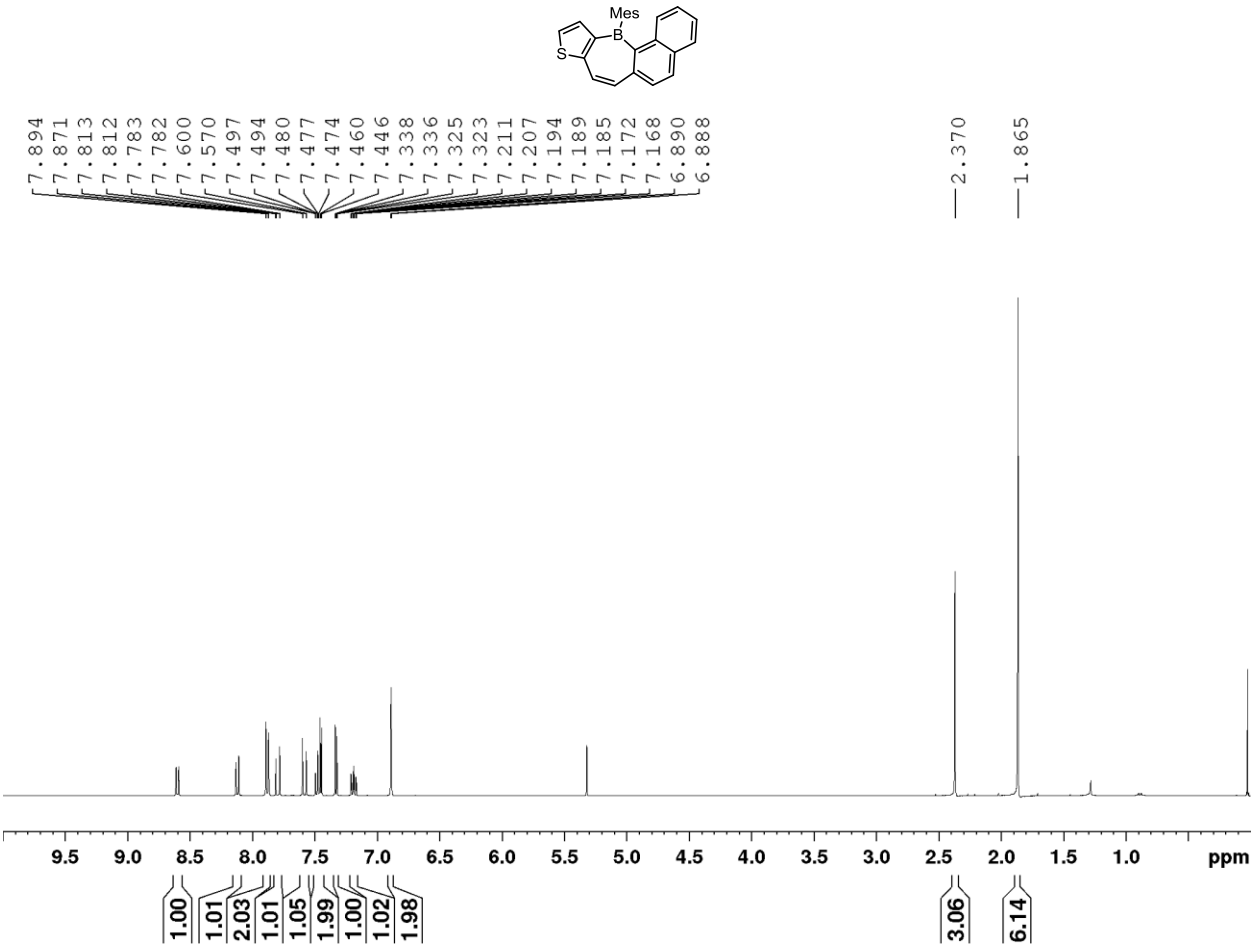


Figure S-17. ^{1}H NMR spectrum of **7** (400 MHz, CD_2Cl_2).

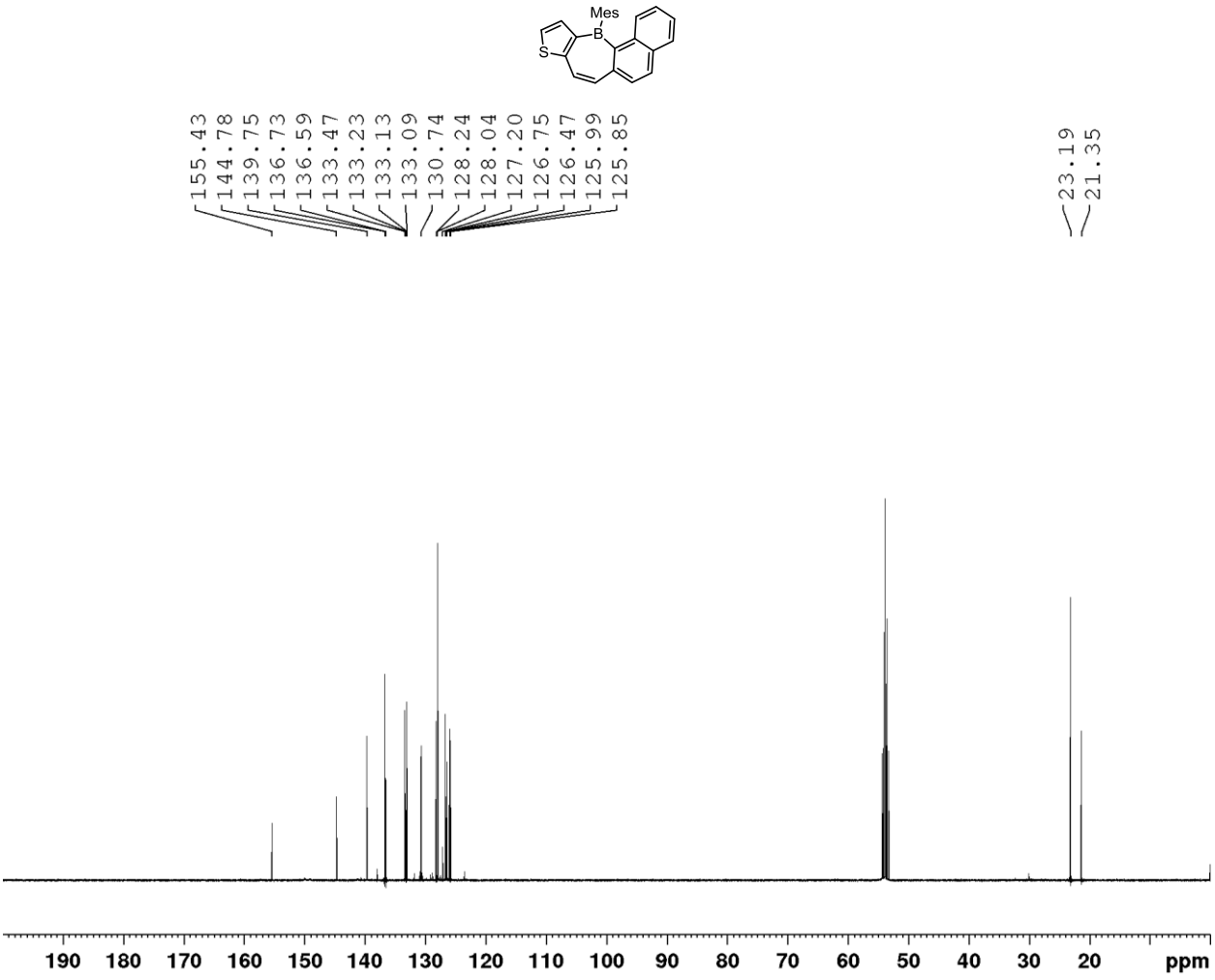


Figure S-18. ^{13}C {^{1}H} NMR spectrum of **7** (100 MHz, CD_2Cl_2).

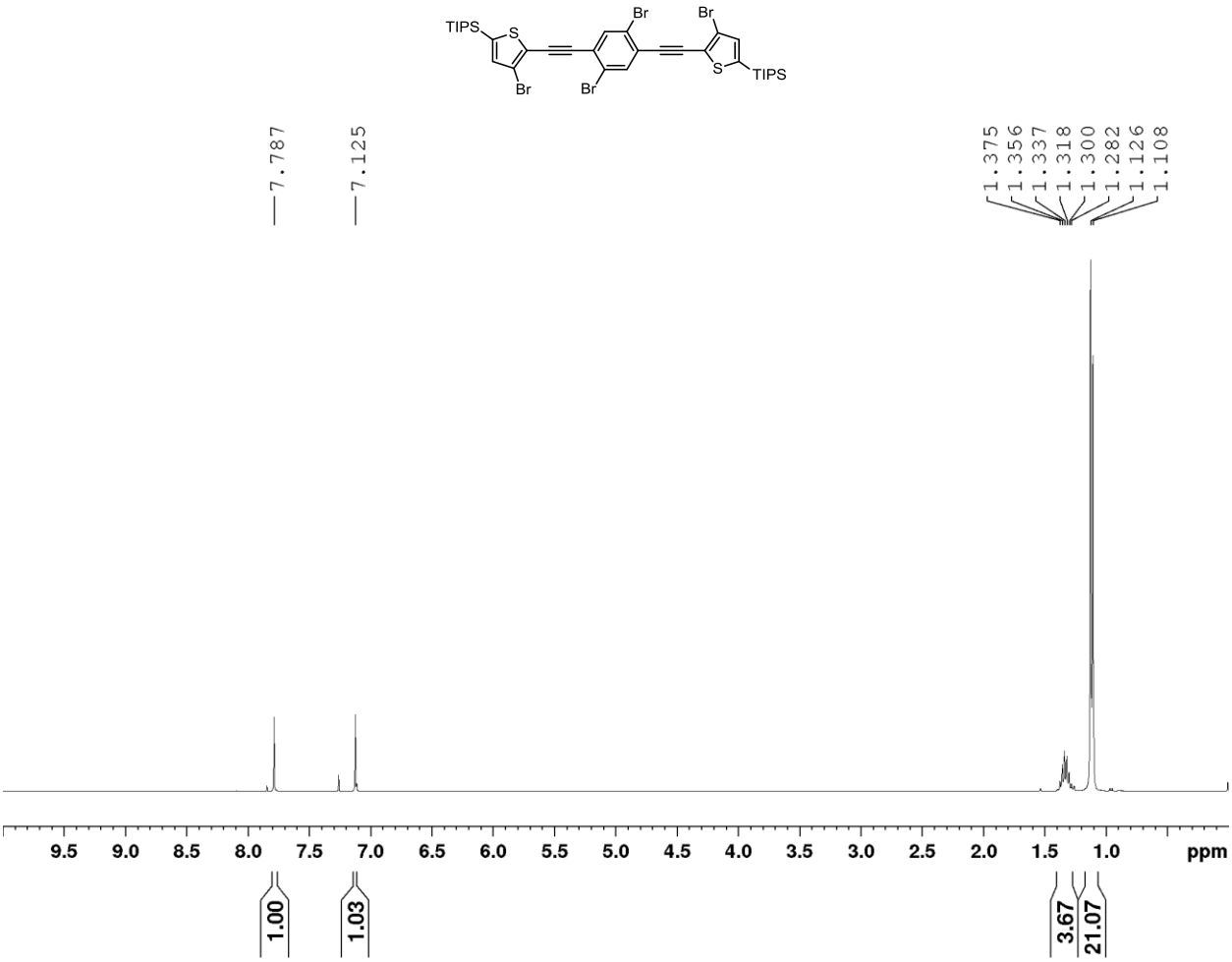


Figure S-19. ^{1}H NMR spectrum of **18** (400 MHz, $CDCl_3$).

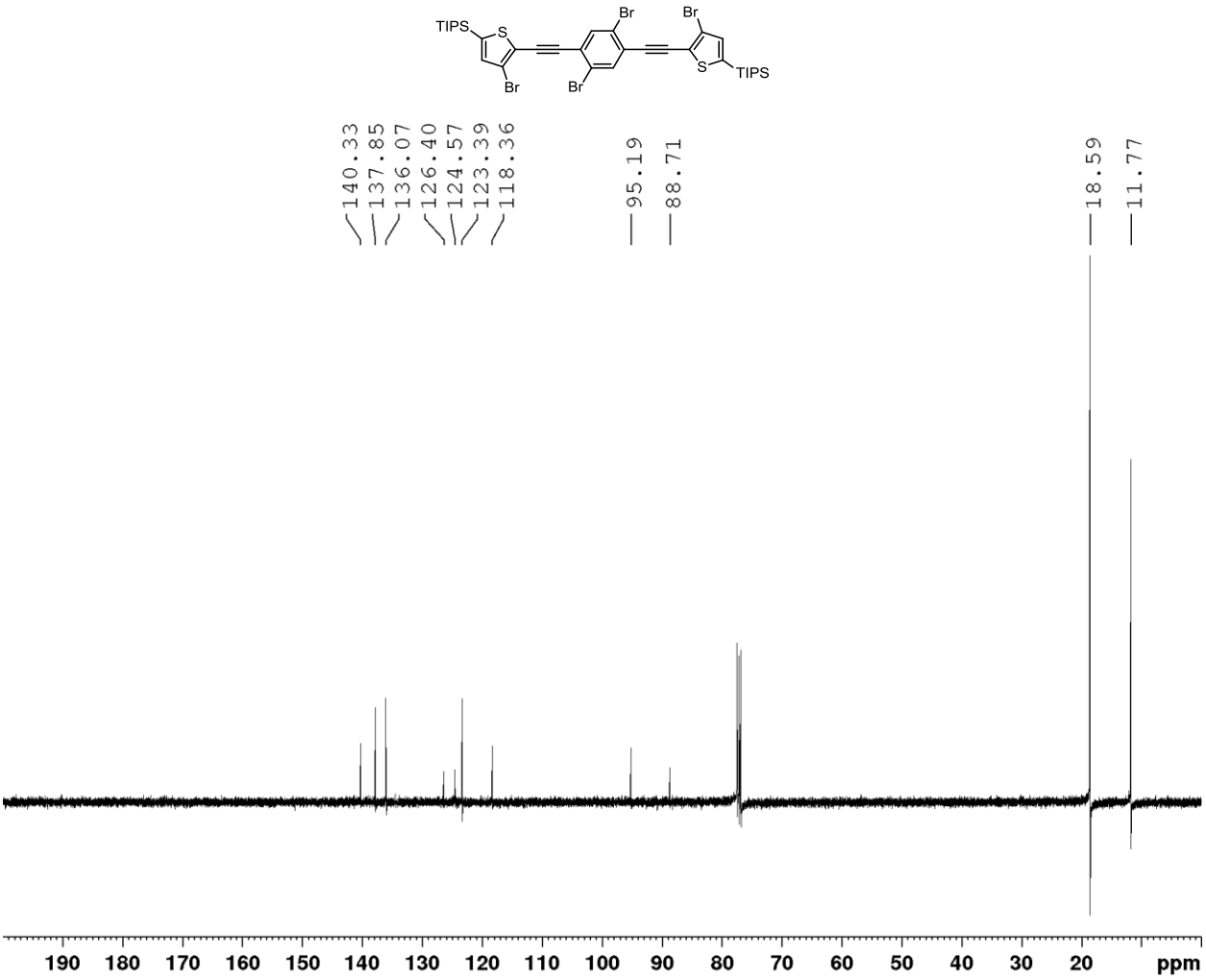


Figure S-20. ^{13}C {^{1}H} NMR spectrum of **18** (100 MHz, $CDCl_3$).

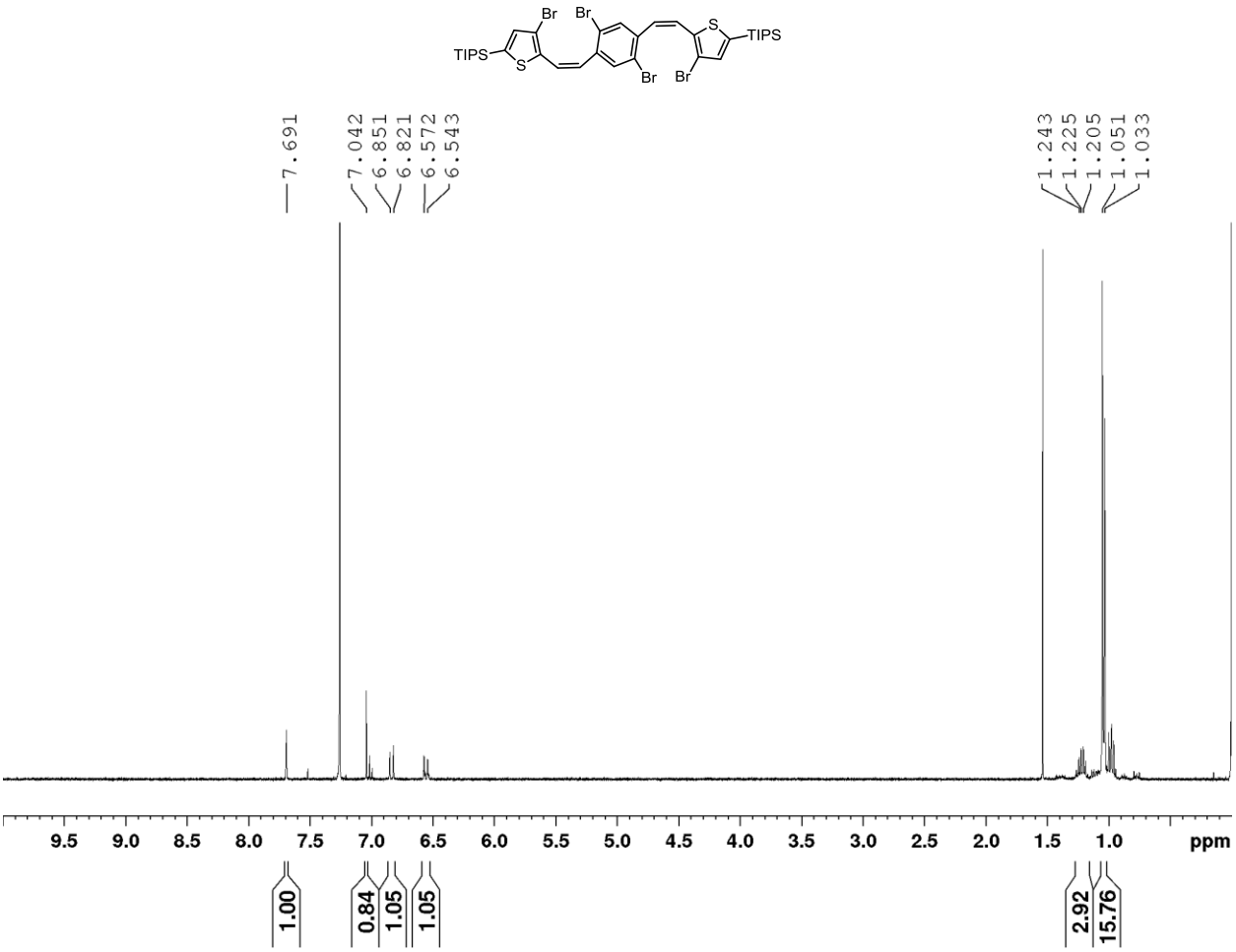


Figure S-21. ^{1}H NMR spectrum of **19** (400 MHz, $CDCl_3$).

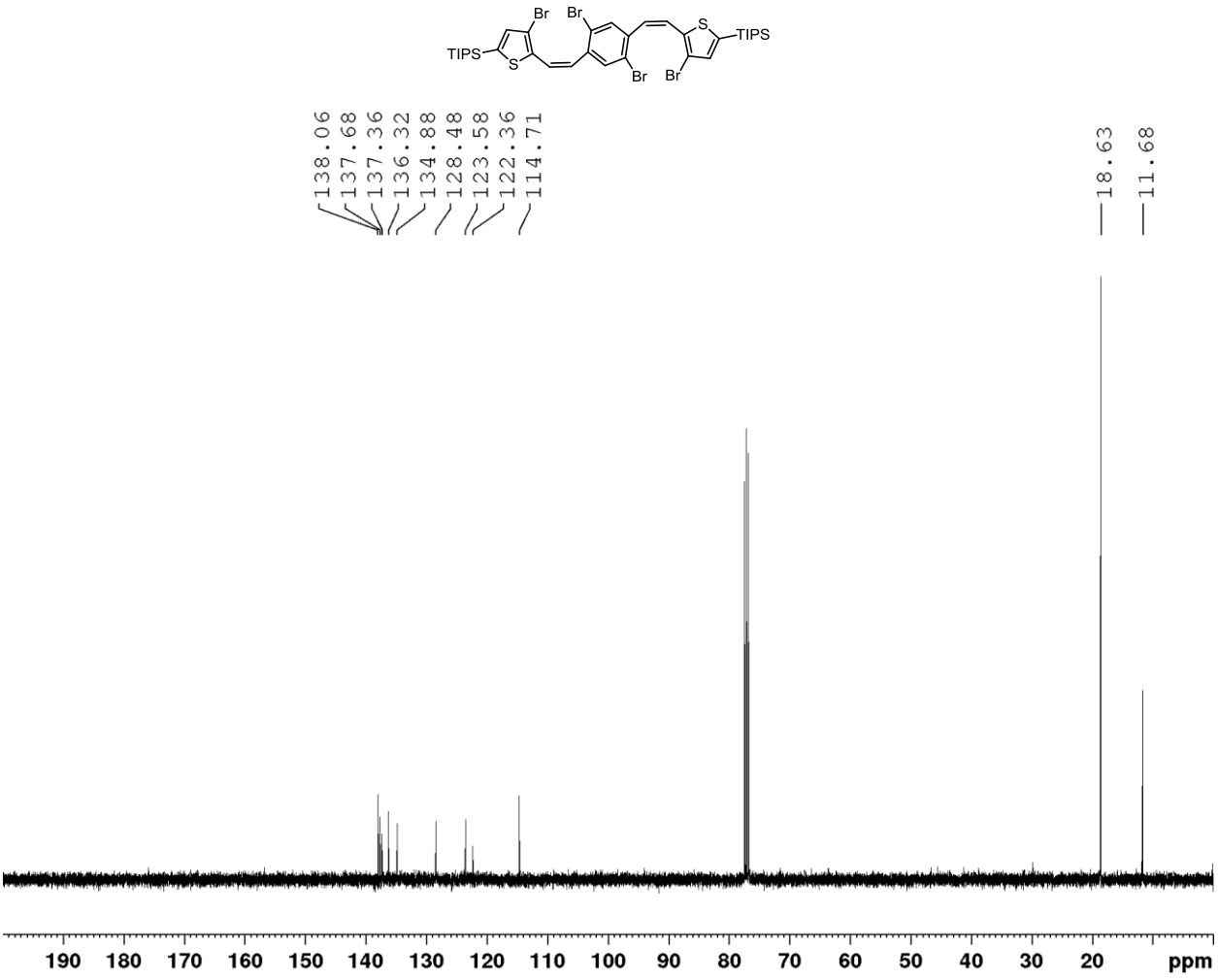


Figure S-22. ^{13}C {^{1}H} NMR spectrum of **19** (100 MHz, $CDCl_3$).

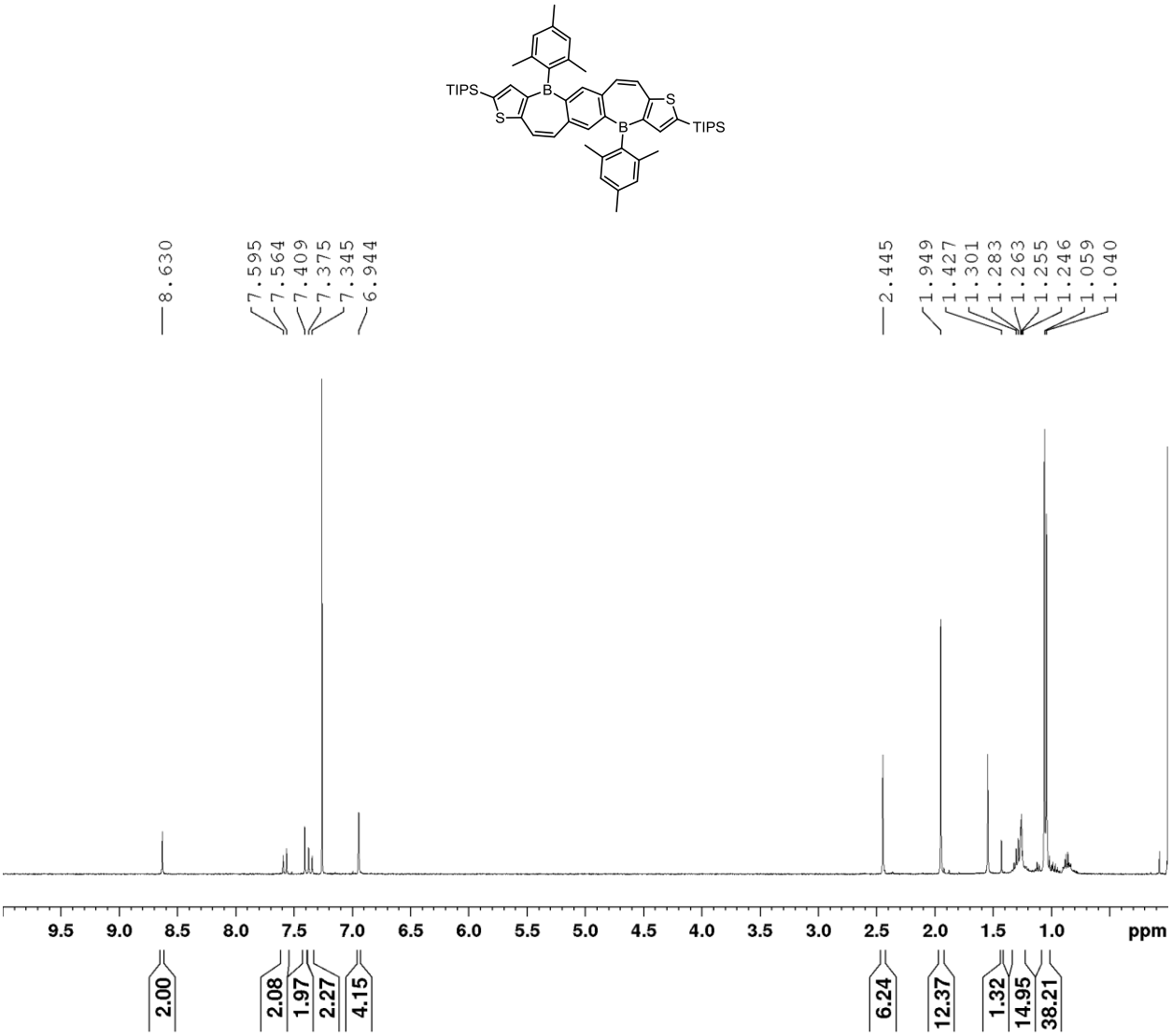


Figure S-23. ^{1}H NMR spectrum of **20** (400 MHz, $CDCl_3$).

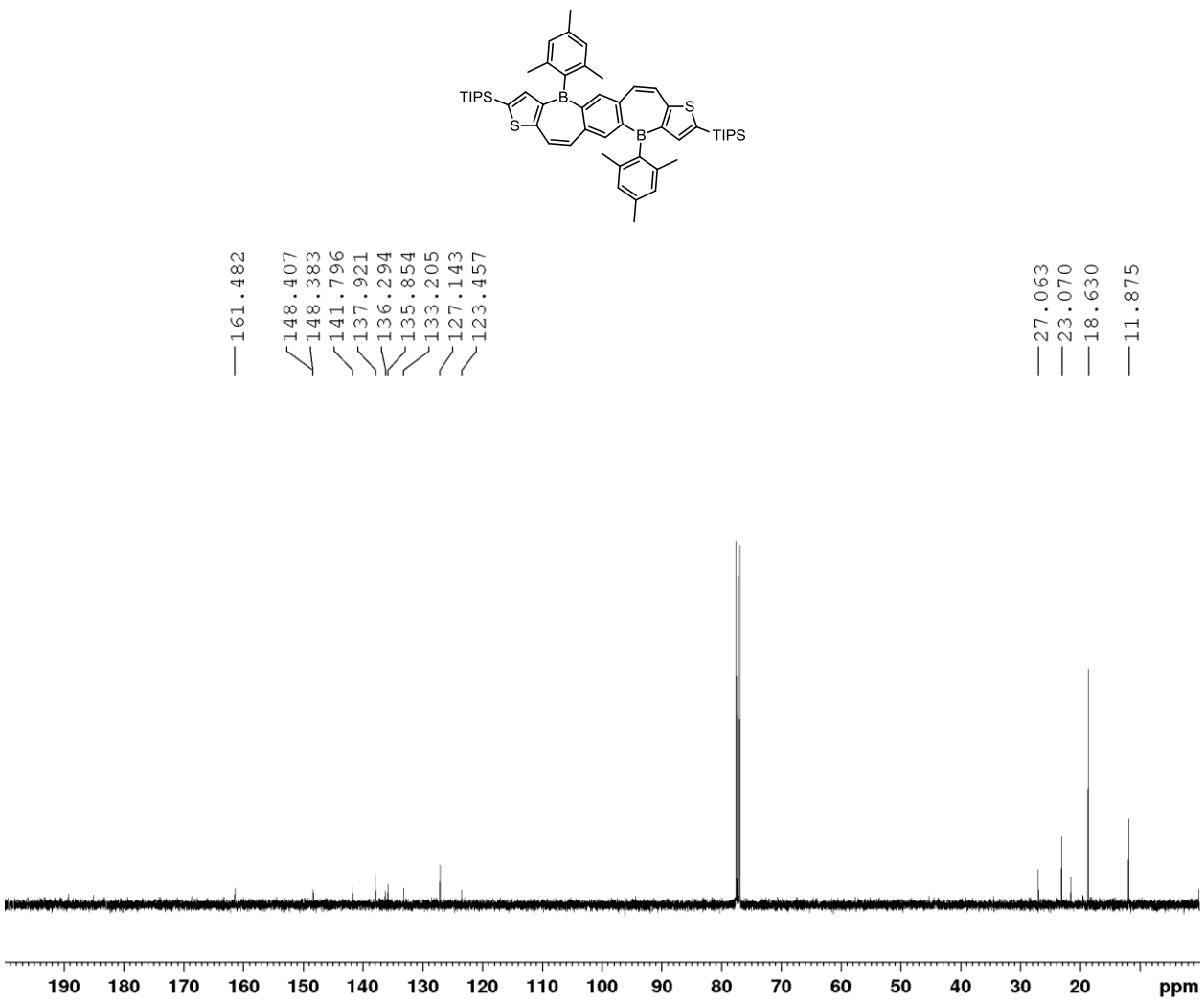


Figure S-24. ^{13}C {^{1}H} NMR spectrum of **20** (100 MHz, $CDCl_3$).

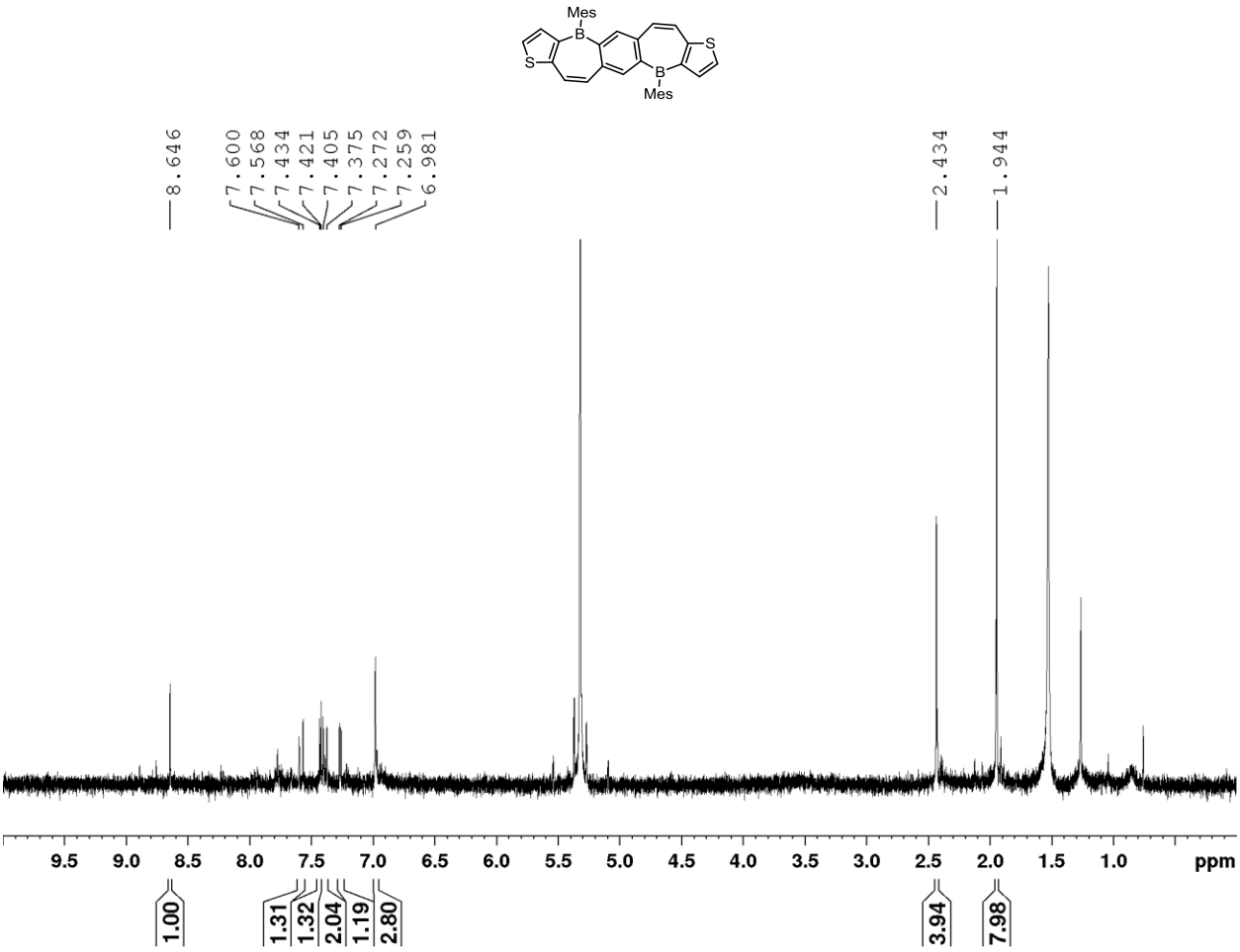


Figure S-25. ^{1}H NMR spectrum of **8** (100 MHz, CD_2Cl_2).

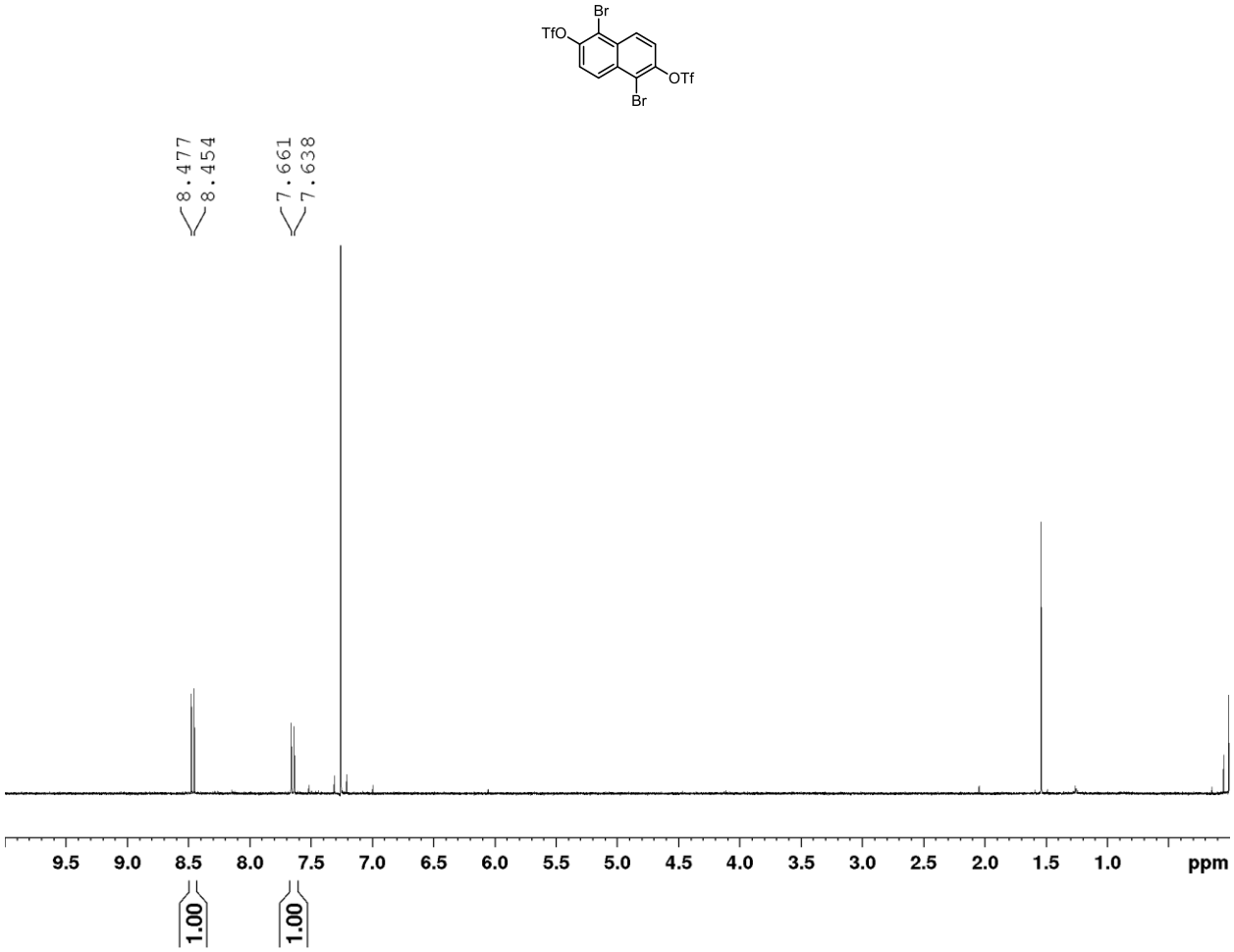


Figure S-28. ^{1}H NMR spectrum of **21** (400 MHz, $CDCl_3$).

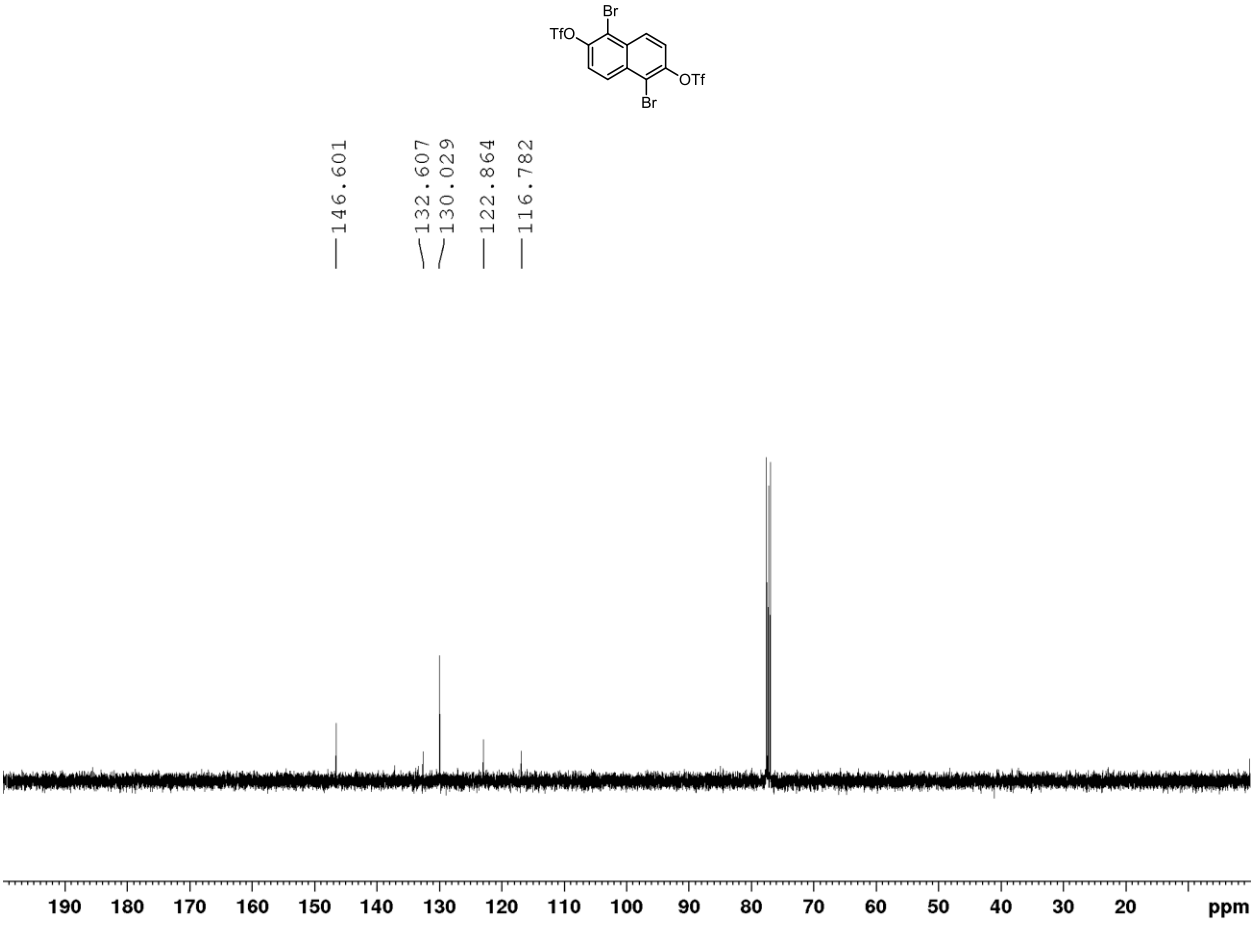


Figure S-29. ^{13}C {^{1}H} NMR spectrum of **21** (100 MHz, $CDCl_3$).

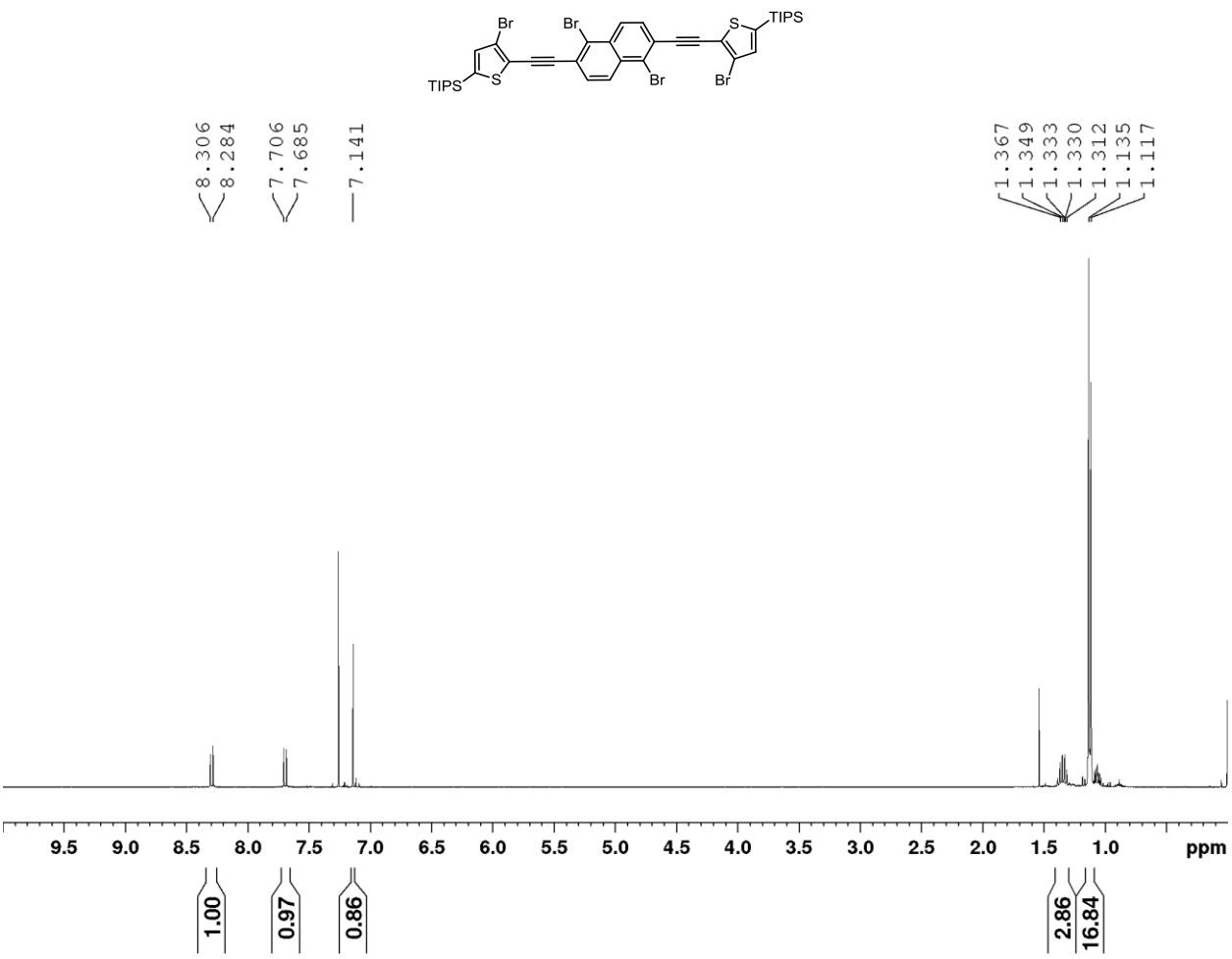


Figure S-30. ^{1}H NMR spectrum of **22** (400 MHz, $CDCl_3$).

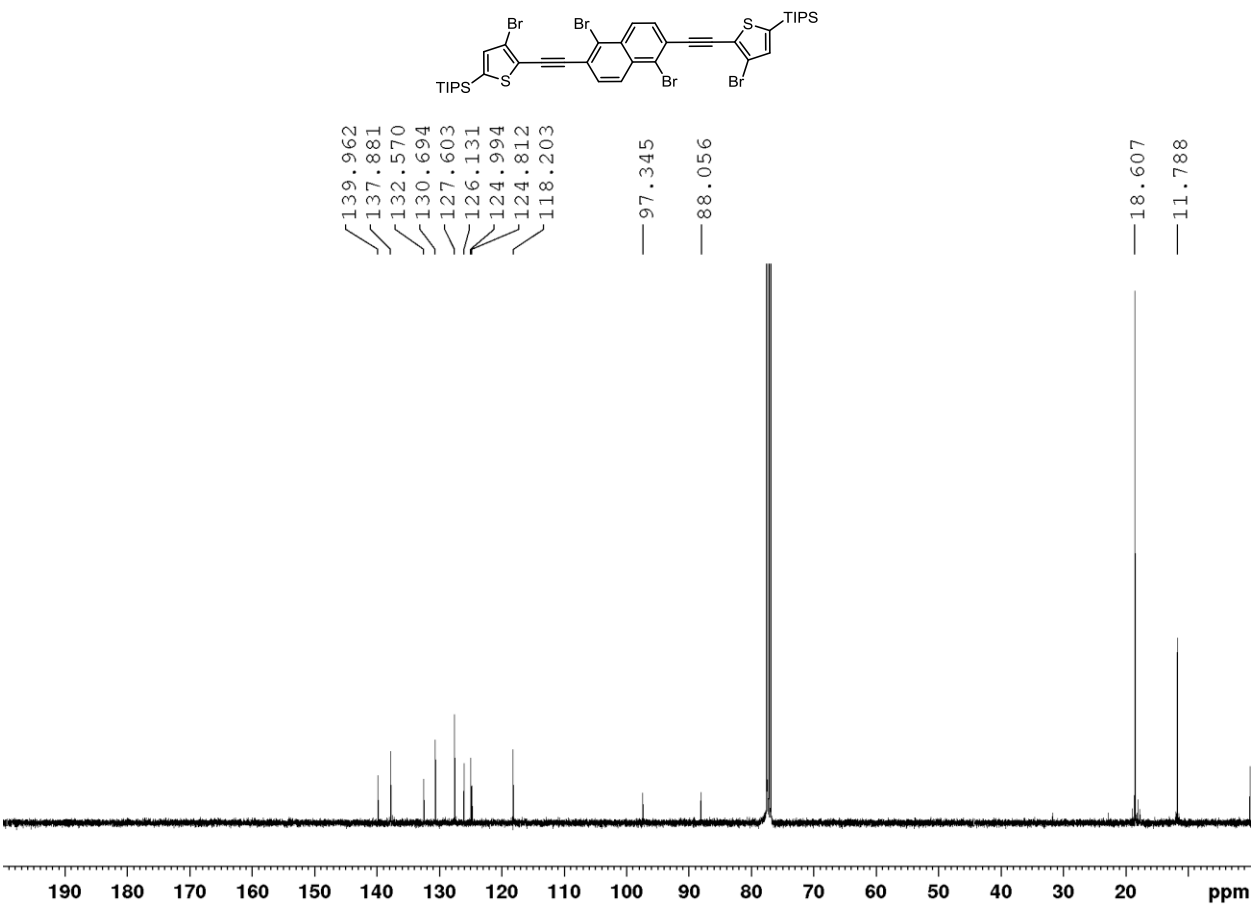


Figure S-31. ^{13}C {^{1}H} NMR spectrum of **22** (100 MHz, $CDCl_3$).

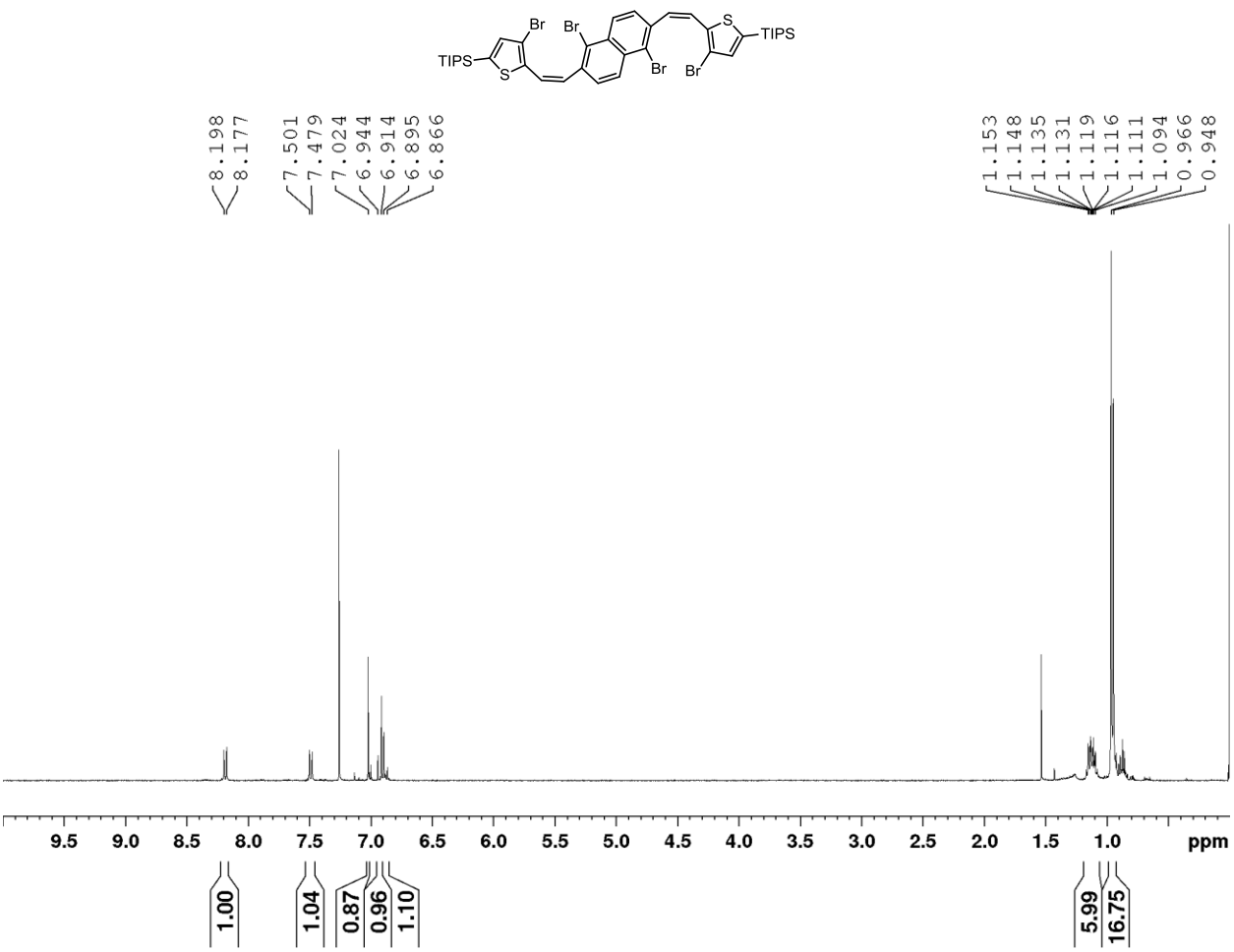


Figure S-32. ^{1}H NMR spectrum of **23** (400 MHz, $CDCl_3$).

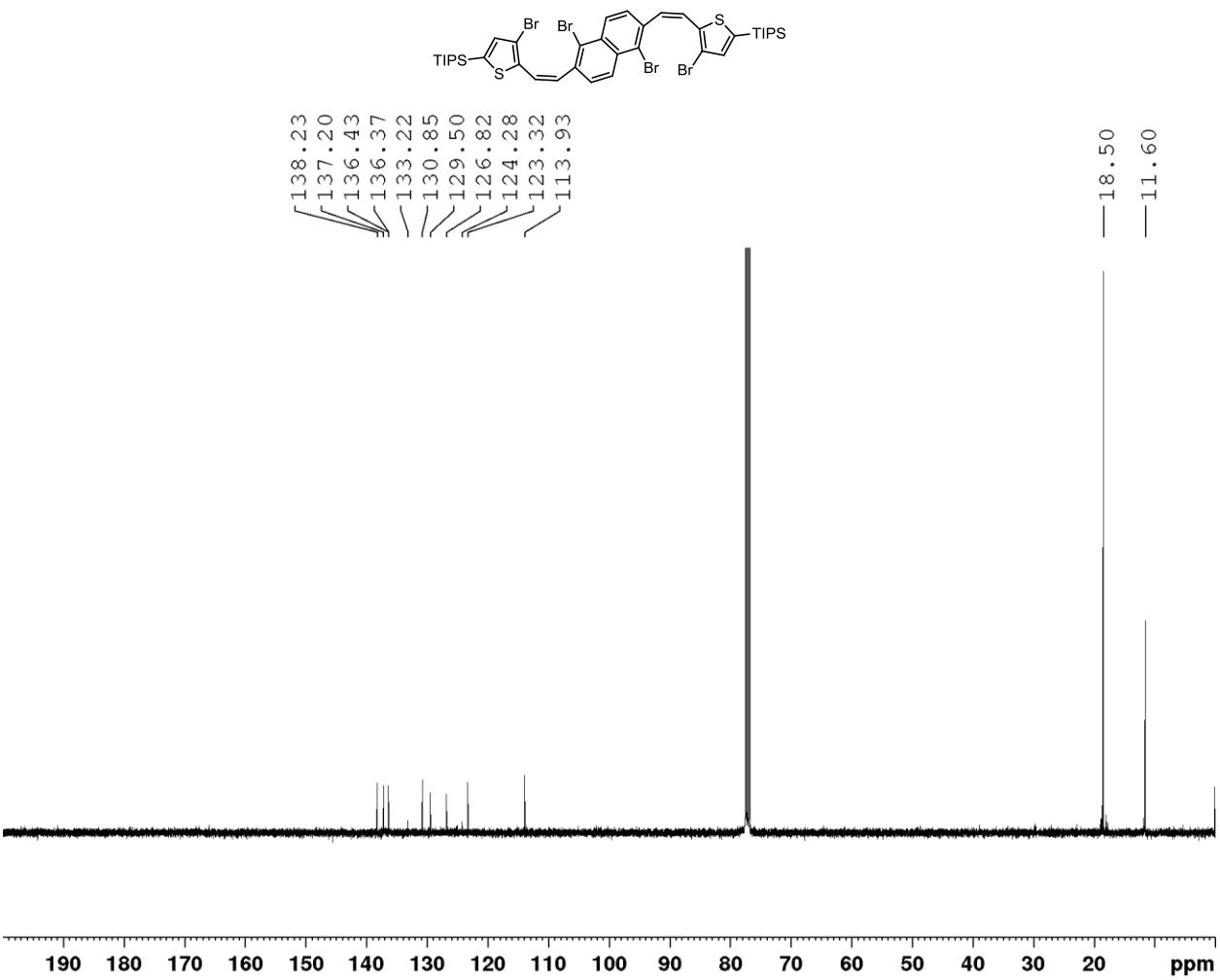


Figure S-33. ^{13}C {^{1}H} NMR spectrum of **23** (100 MHz, $CDCl_3$).

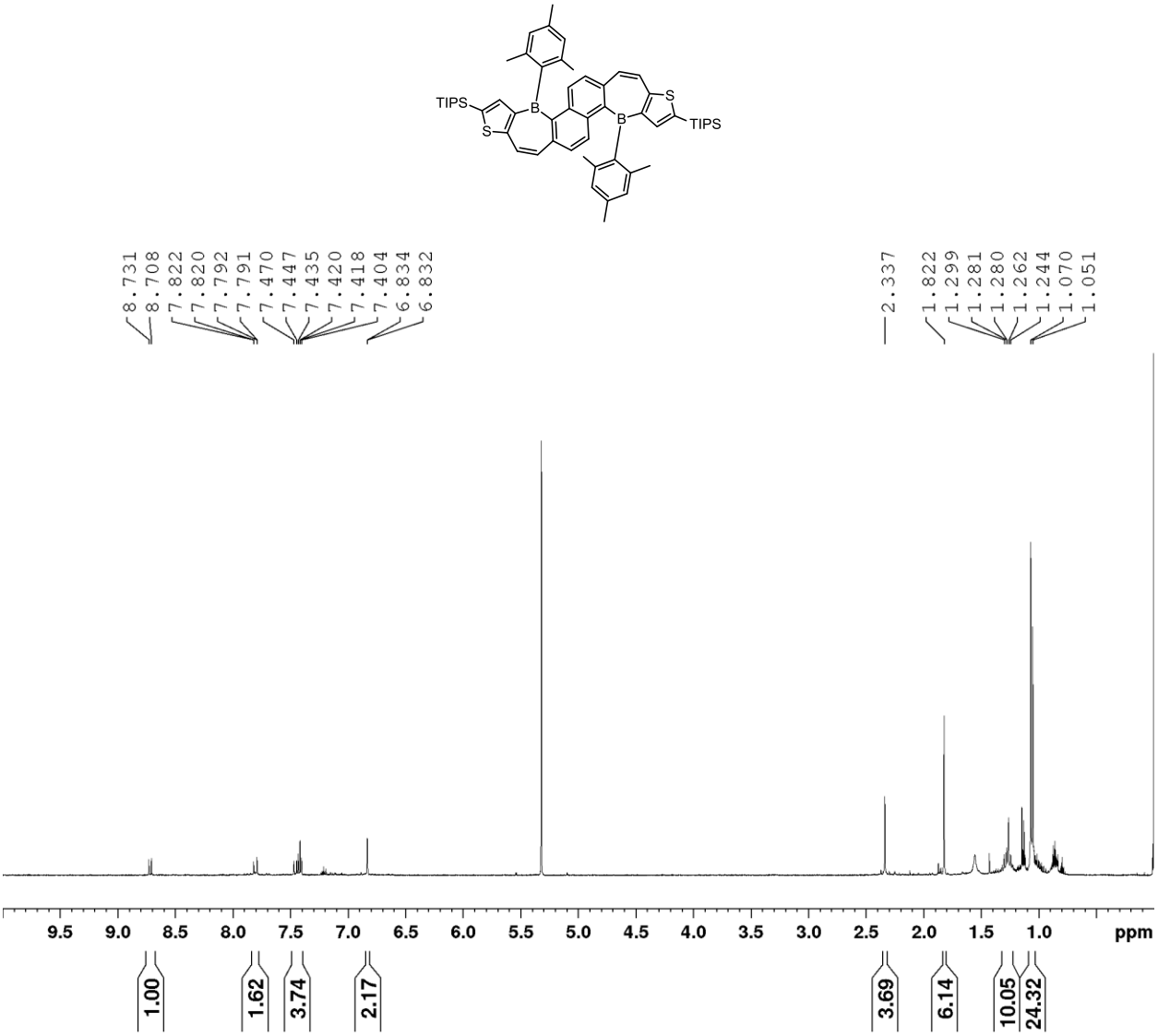


Figure S-34. ^{1}H NMR spectrum of **24** (400 MHz, CD_2Cl_2).

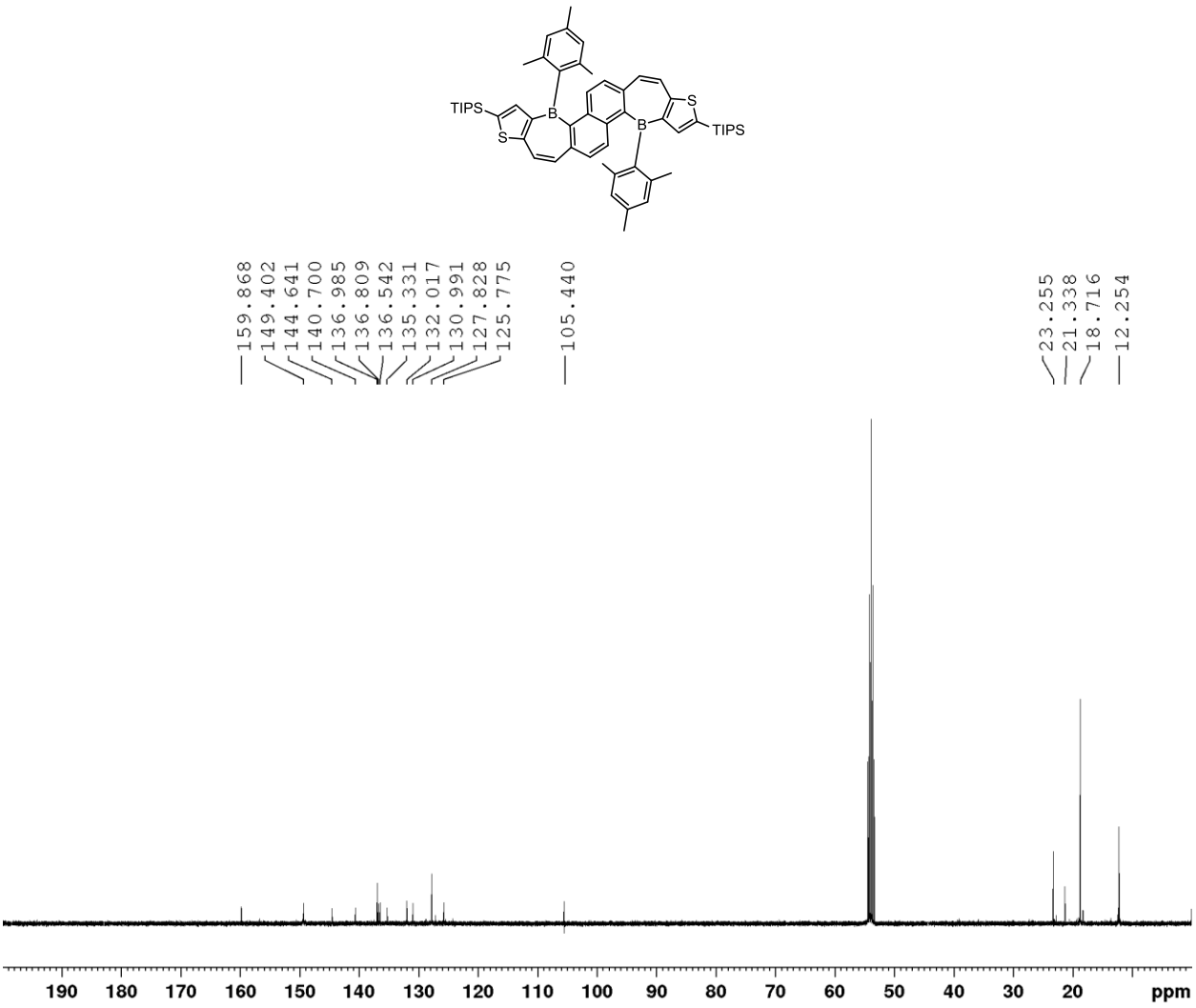


Figure S-35. ^{13}C {^{1}H} NMR spectrum of **24** (100 MHz, CD_2Cl_2).

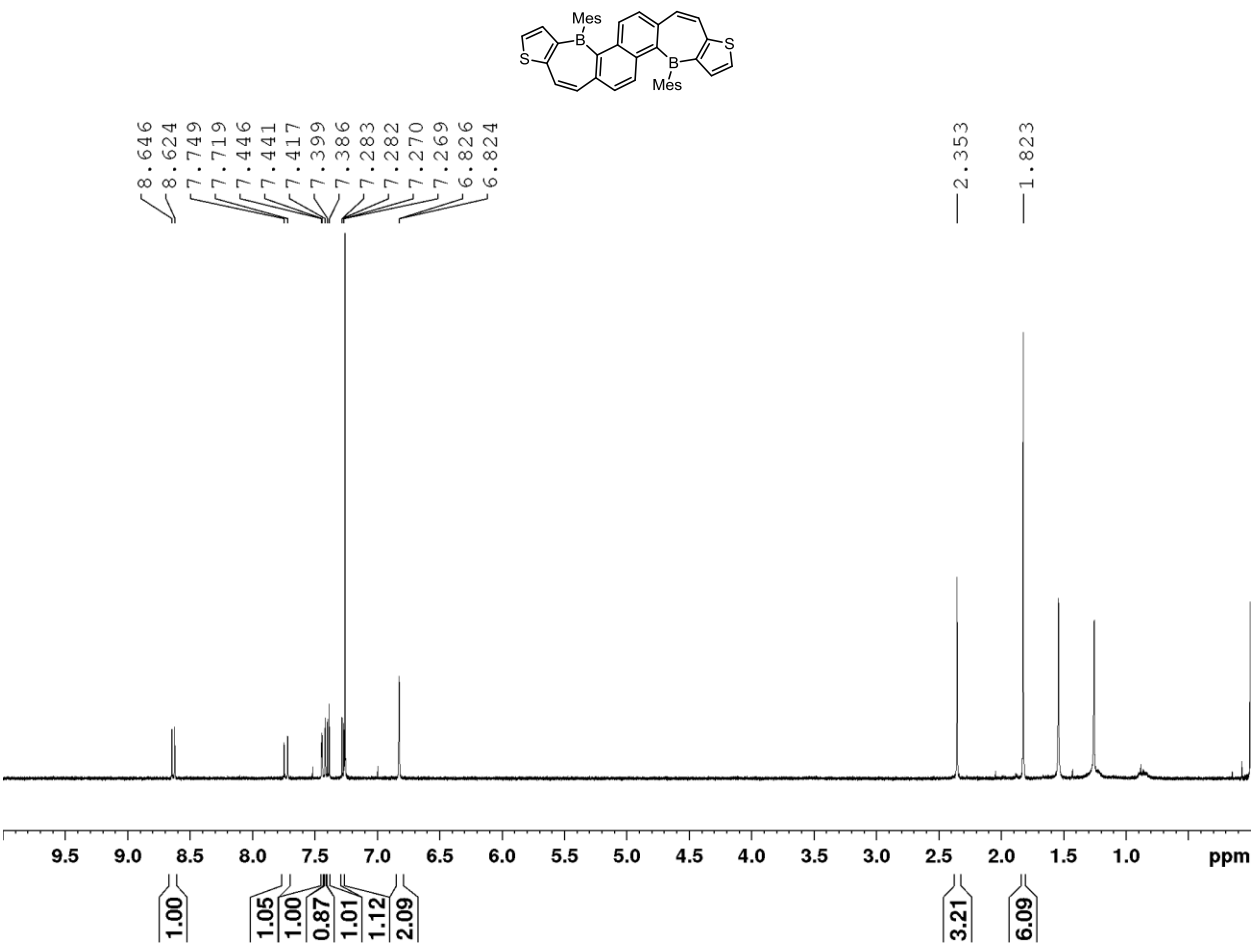


Figure S-36. ^{1}H NMR spectrum of **9** (400 MHz, $CDCl_3$).

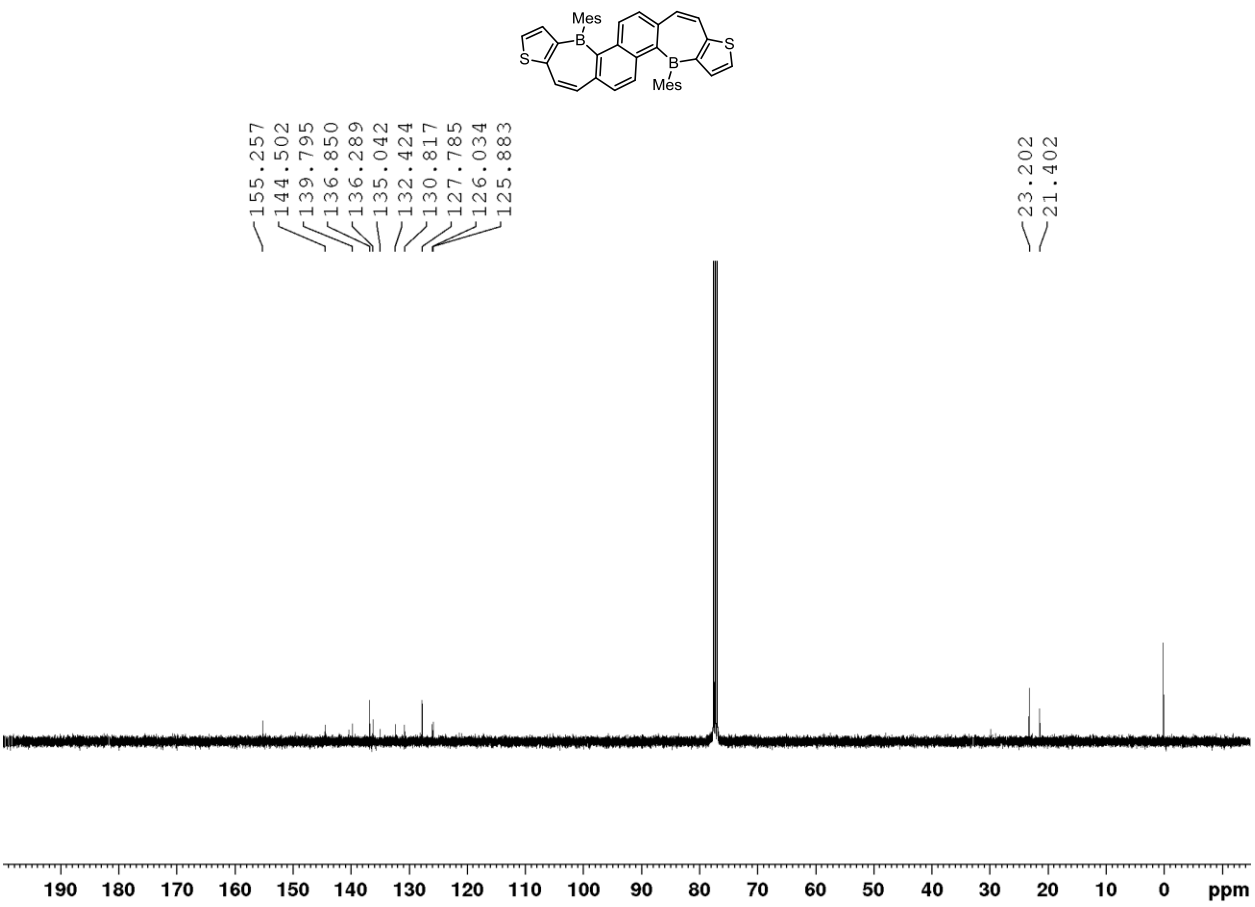


Figure S-37. ^{13}C {^{1}H} NMR spectrum of **9** (100 MHz, $CDCl_3$).

2. Cyclic Voltammetry

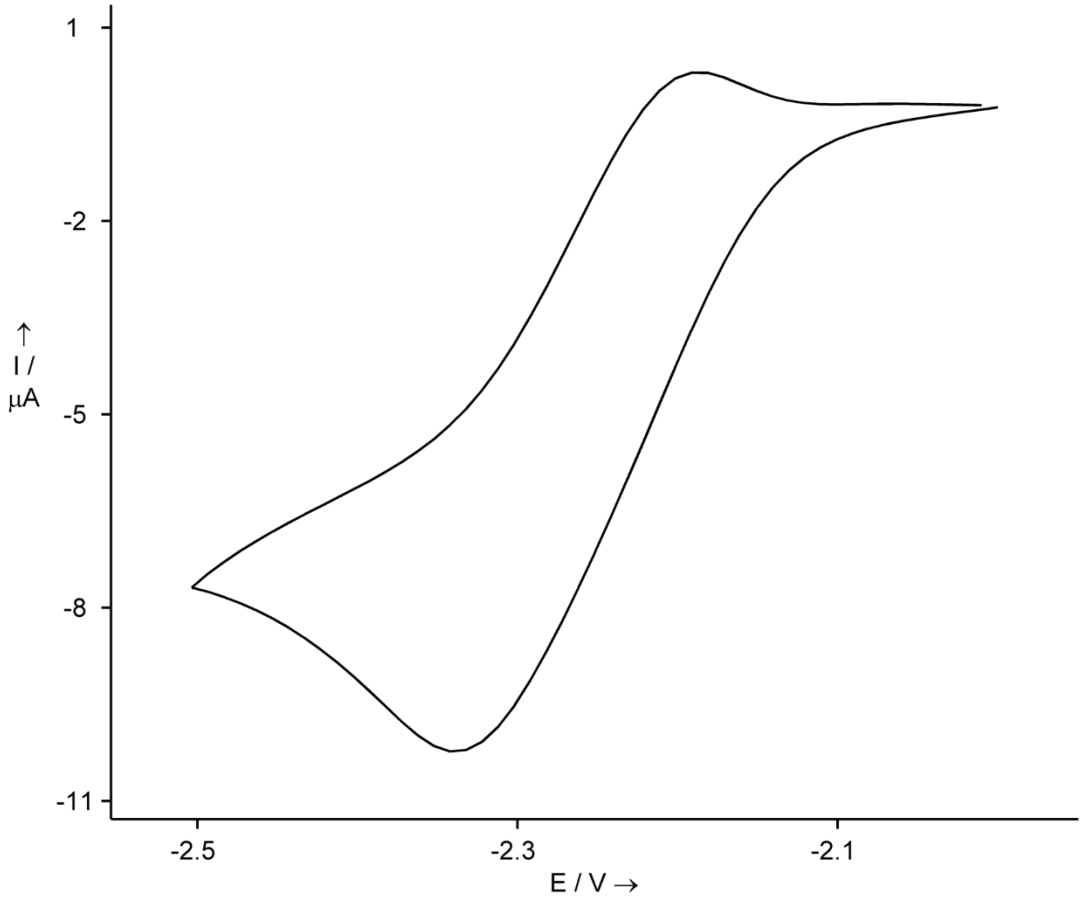


Figure S-38. Cyclic voltammogram obtained for **6** (3.2 mM) in dry and de-oxygenated THF with 0.1 M $TBAPF_6$ and a potential sweep rate of 100 mV/s (Ag/Ag^+).

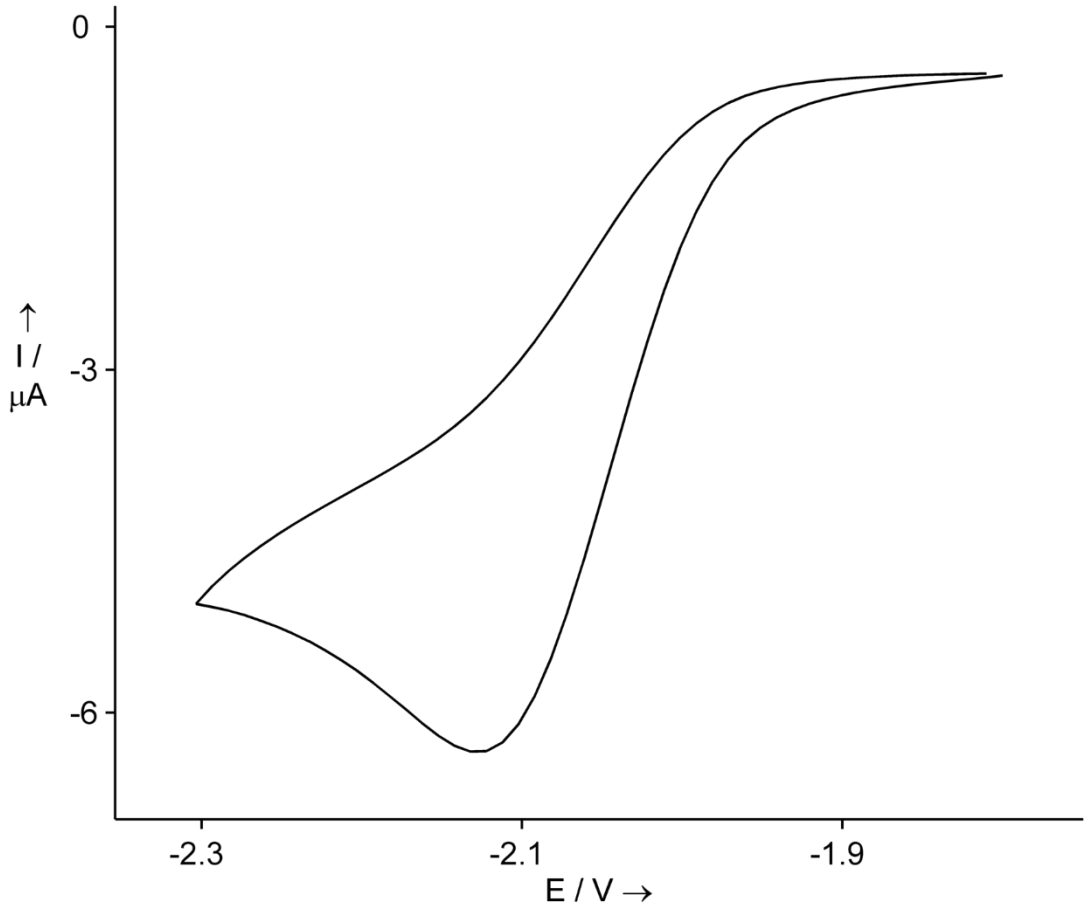


Figure S-39. Cyclic voltammogram obtained for **7** (1.8 mM) in dry and de-oxygenated THF with 0.1 M $TBAPF_6$ and a potential sweep rate of 100 mV/s (Ag/Ag^+).

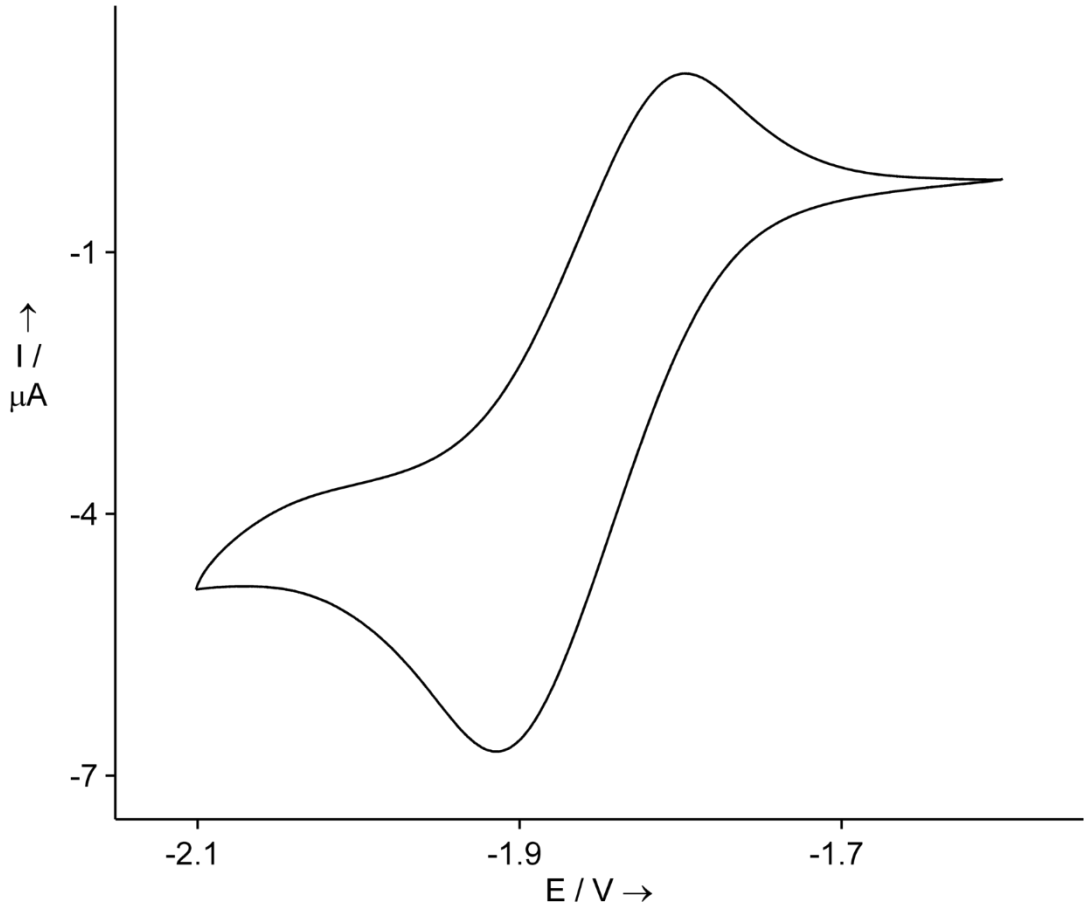


Figure S-40. Cyclic voltammogram obtained for **8** (2.9 mM) in dry and de-oxygenated THF with 0.1 M $TBAPF_6$ and a potential sweep rate of 100 mV/s (Ag/Ag^+).

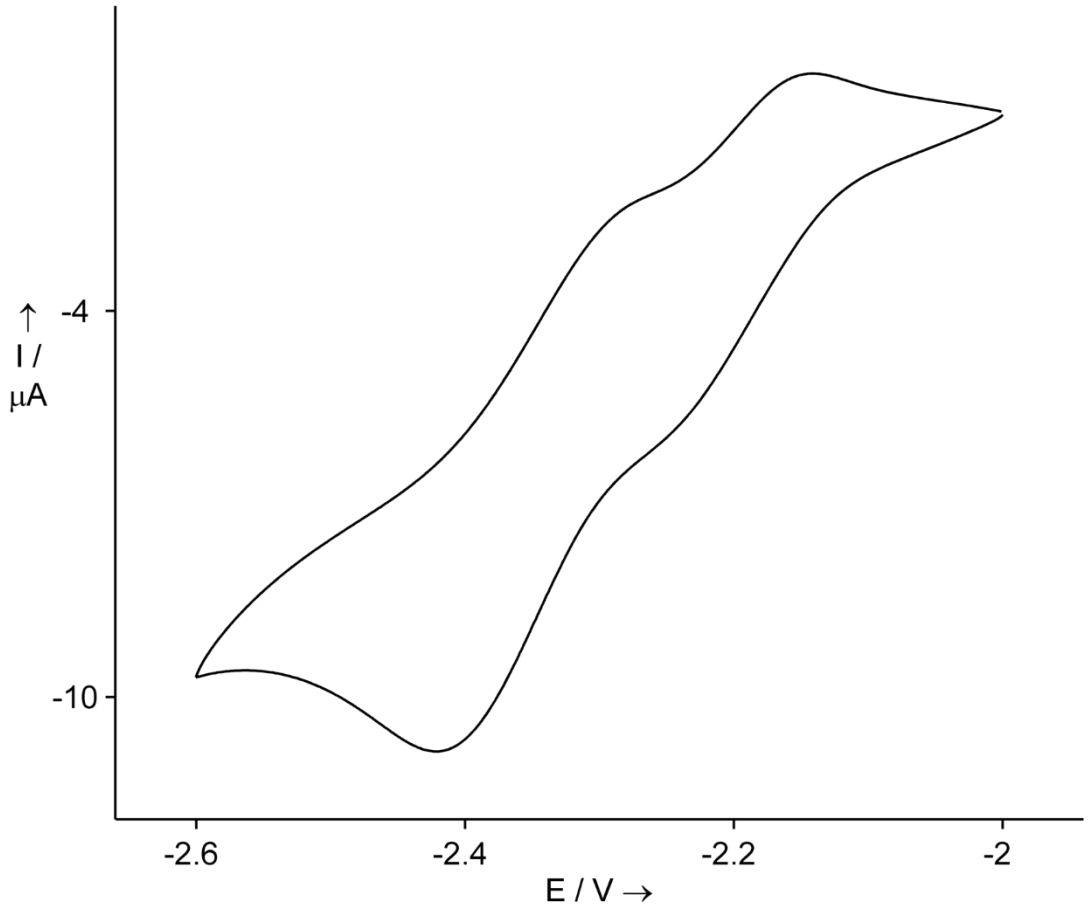


Figure S-41. Cyclic voltammogram obtained for **8** (2.9 mM) in dry and de-oxygenated THF with 0.1 M $TBAPF_6$ and a potential sweep rate of 100 mV/s (Ag/Ag^+).

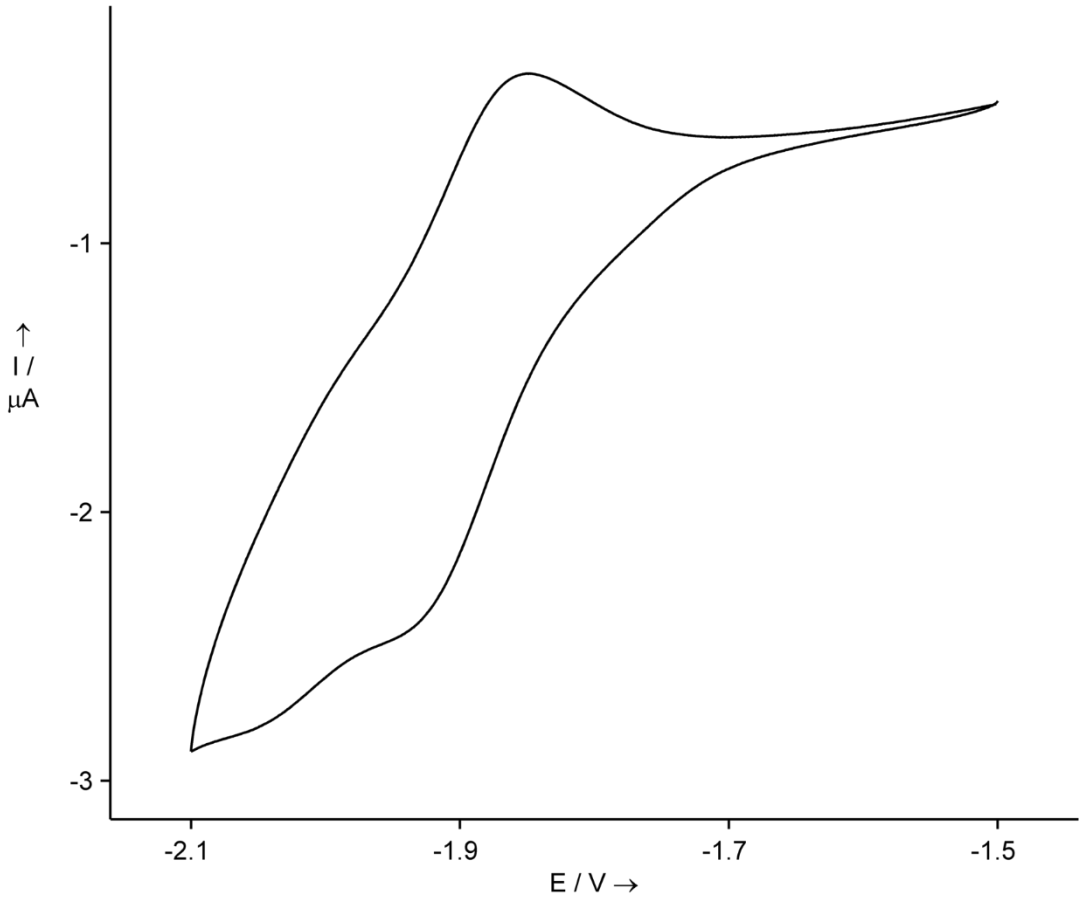


Figure S-42. Cyclic voltammogram obtained for **9** (1.4 mM) in dry and de-oxygenated THF with 0.1 M $TBAPF_6$ and a potential sweep rate of 100 mV/s (Ag/Ag^+).

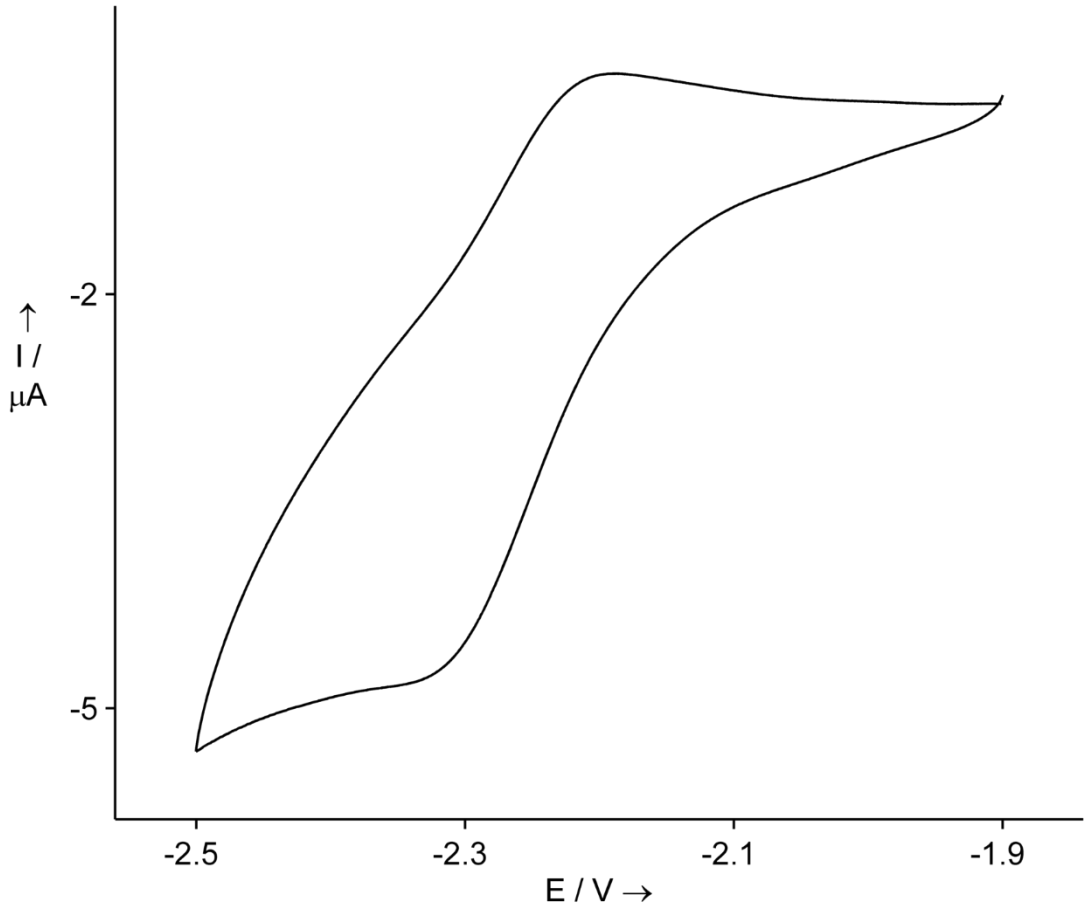
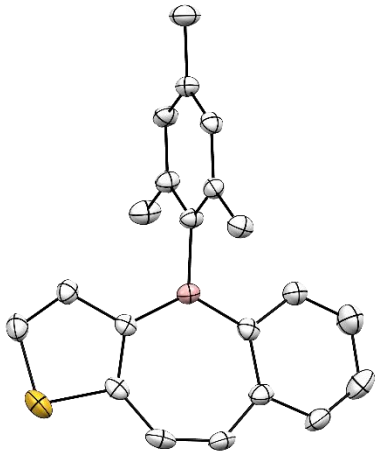


Figure S-43. Cyclic voltammogram obtained for **9** (1.4 mM) in dry and de-oxygenated THF with 0.1 M $TBAPF_6$ and a potential sweep rate of 100 mV/s (Ag/Ag^+).

3. Single Crystal X-ray Crystallography

Compound 6



All reflection intensities were measured at 110(2) K using a diffractometer (equipped with Atlas detector) with Mo *K*α radiation (λ = 0.71073 Å) under the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2014/7 (Sheldrick, 2015) and was refined on F^2 with SHELXL-2014/7 (Sheldrick, 2015). Numerical absorption correction based on gaussian integration over a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 *U*eq of the attached C atoms. The structure is disordered.

Additional Note:

(i) The part C1→C12 (including B1 and S1) is found to be disordered over two orientations. The major and minor components of the disorder are related by a pseudo twofold axis. The occupancy factor of the major component of the disorder refines to 0.6966(18).

Crystal data	
Chemical formula	$C_{21}H_{19}BS$
M_r	314.23
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	110
a, b, c (Å)	9.3963 (5), 7.9827 (4), 23.0568 (16)
β (°)	93.800 (6)
V (Å^3)	1725.64 (17)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.18
Crystal size (mm)	0.58 × 0.39 × 0.13
Data collection	
Diffractometer	Dual, Cu at zero, Atlas diffractometer
Absorption correction	Gaussian *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013,16:46:58) Numerical absorption correction based on gaussian integration over a multifaceted crystal model
T_{min}, T_{max}	0.477, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14327, 3956, 3183
R_{int}	0.034
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.121, 1.07
No. of reflections	3956
No. of parameters	326
No. of restraints	531
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, -0.20

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013, 16:46:58), *SHELXS2014*/7 (Sheldrick, 2015), *SHELXL2014*/7 (Sheldrick, 2015), *SHELXTL* v6.10 (Sheldrick, 2008).[1]

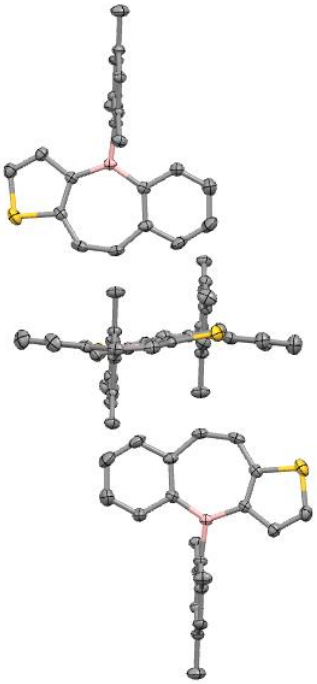
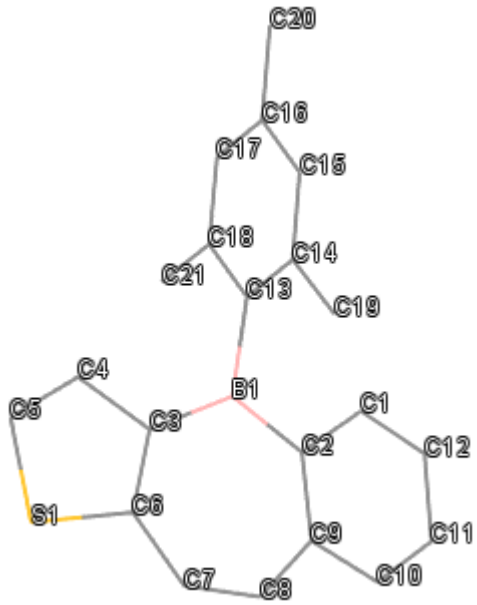


Figure S-44. Displacement ellipsoid plots (50% probability level) showing crystal packing of **6**. Disorder and H atoms are omitted for clarity.



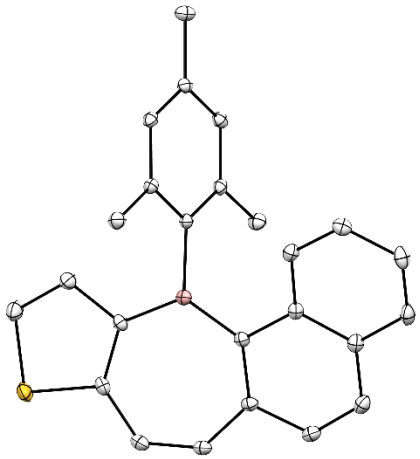
Selected geometric parameters (Å, º)

C1—C12	1.387 (5)	C13—C18	1.407 (2)
C1—C2	1.414 (4)	C14—C15	1.3933 (19)
C2—C9	1.418 (4)	C14—C19	1.5091 (19)
C2—B1	1.545 (4)	C15—C16	1.387 (2)
B1—C3	1.542 (5)	C16—C17	1.390 (2)
B1—C13	1.595 (3)	C16—C20	1.5107 (19)
C3—C6	1.397 (4)	C17—C18	1.3919 (19)
C3—C4	1.427 (4)	C18—C21	1.5112 (19)
C4—C5	1.347 (4)	C1'—H1'	0.9500
C5—S1	1.716 (4)	C1—H1	0.9500
S1—C6	1.740 (3)	C4'—H4'	0.9500
C6—C7	1.423 (4)	C4—H4	0.9500
C7—C8	1.371 (5)	C5'—H5'	0.9500
C8—C9	1.440 (6)	C5—H5	0.9500
C9—C10	1.409 (4)	C7'—H7'	0.9500
C10—C11	1.318 (13)	C7—H7	0.9500
C11—C12	1.408 (13)	C8'—H8'	0.9500
C1'—C12'	1.387 (10)	C8—H8	0.9500
C1'—C2'	1.400 (8)	C10'—H10'	0.9500
C2'—C9'	1.456 (9)	C10—H10	0.9500
C2'—B1'	1.538 (10)	C11'—H11'	0.9500

B1'—C3'	1.529 (10)	C11—H11	0.9500
B1'—C13	1.605 (7)	C12'—H12'	0.9500
C3'—C6'	1.400 (8)	C12—H12	0.9500
C3'—C4'	1.422 (8)	C15—H15	0.9500
C4'—C5'	1.325 (11)	C17—H17	0.9500
C5'—S1'	1.695 (10)	C19—H19C	0.9800
S1'—C6'	1.755 (9)	C19—H19B	0.9800
C6'—C7'	1.412 (8)	C19—H19A	0.9800
C7'—C8'	1.381 (12)	C20—H20C	0.9800
C8'—C9'	1.425 (12)	C20—H20B	0.9800
C9'—C10'	1.400 (8)	C20—H20A	0.9800
C10'—C11'	1.321 (19)	C21—H21C	0.9800
C11'—C12'	1.409 (19)	C21—H21B	0.9800
C13—C14	1.4038 (18)	C21—H21A	0.9800
C12—C1—C2	122.7 (3)	C17—C16—C20	120.74 (14)
C1—C2—C9	116.3 (3)	C16—C17—C18	121.69 (14)
C1—C2—B1	116.2 (3)	C17—C18—C13	119.84 (13)
C9—C2—B1	127.5 (3)	C17—C18—C21	119.85 (13)
C3—B1—C2	124.8 (3)	C13—C18—C21	120.30 (12)
C3—B1—C13	118.0 (3)	C2'—C1'—H1'	118.4
C2—B1—C13	117.2 (3)	C12'—C1'—H1'	118.4
C6—C3—C4	110.7 (3)	C2—C1—H1	118.6
C6—C3—B1	126.1 (3)	C12—C1—H1	118.6
C4—C3—B1	123.2 (3)	C3'—C4'—H4'	122.5
C5—C4—C3	114.8 (3)	C5'—C4'—H4'	122.5
C4—C5—S1	111.5 (2)	C3—C4—H4	122.6
C5—S1—C6	92.10 (16)	C5—C4—H4	122.6
C3—C6—C7	131.0 (3)	S1'—C5'—H5'	123.4
C3—C6—S1	110.9 (2)	C4'—C5'—H5'	123.4
C7—C6—S1	118.07 (18)	S1—C5—H5	124.3
C8—C7—C6	128.4 (3)	C4—C5—H5	124.3
C7—C8—C9	132.1 (4)	C6'—C7'—H7'	114.9
C10—C9—C2	119.6 (3)	C8'—C7'—H7'	114.9
C10—C9—C8	113.3 (3)	C6—C7—H7	115.8
C2—C9—C8	127.1 (3)	C8—C7—H7	115.8
C11—C10—C9	122.4 (7)	C7'—C8'—H8'	114.0

C10—C11—C12	120.8 (10)	C9'—C8'—H8'	114.0
C1—C12—C11	118.2 (6)	C7—C8—H8	114.0
C12'—C1'—C2'	123.3 (7)	C9—C8—H8	114.0
C1'—C2'—C9'	115.7 (6)	C9'—C10'—H10'	118.7
C1'—C2'—B1'	117.8 (7)	C11'—C10'—H10'	118.7
C9'—C2'—B1'	126.5 (6)	C9—C10—H10	118.8
C3'—B1'—C2'	125.7 (6)	C11—C10—H10	118.8
C3'—B1'—C13	121.9 (6)	C10'—C11'—H11'	119.7
C2'—B1'—C13	112.3 (6)	C12'—C11'—H11'	119.7
C6'—C3'—C4'	110.0 (6)	C10—C11—H11	119.6
C6'—C3'—B1'	127.2 (7)	C12—C11—H11	119.6
C4'—C3'—B1'	122.7 (6)	C1'—C12'—H12'	120.8
C5'—C4'—C3'	115.0 (7)	C11'—C12'—H12'	120.8
C4'—C5'—S1'	113.1 (6)	C1—C12—H12	120.9
C5'—S1'—C6'	91.1 (5)	C11—C12—H12	120.9
C3'—C6'—C7'	129.2 (6)	C14—C15—H15	119.3
C3'—C6'—S1'	110.8 (6)	C16—C15—H15	119.3
C7'—C6'—S1'	120.0 (5)	C16—C17—H17	119.2
C8'—C7'—C6'	130.2 (8)	C18—C17—H17	119.2
C7'—C8'—C9'	132.0 (11)	H19B—C19—H19C	109.5
C10'—C9'—C8'	114.4 (8)	H19A—C19—H19C	109.5
C10'—C9'—C2'	119.1 (6)	H19A—C19—H19B	109.5
C8'—C9'—C2'	126.4 (7)	C14—C19—H19C	109.5
C11'—C10'—C9'	122.6 (11)	C14—C19—H19B	109.5
C10'—C11'—C12'	120.6 (17)	C14—C19—H19A	109.5
C1'—C12'—C11'	118.3 (11)	H20B—C20—H20C	109.5
C14—C13—C18	118.62 (12)	H20A—C20—H20C	109.5
C14—C13—B1	118.2 (3)	H20A—C20—H20B	109.5
C18—C13—B1	122.9 (3)	C16—C20—H20C	109.5
C14—C13—B1'	117.9 (6)	C16—C20—H20B	109.5
C18—C13—B1'	122.6 (6)	C16—C20—H20A	109.5
C15—C14—C13	120.13 (13)	H21B—C21—H21C	109.5
C15—C14—C19	119.88 (12)	H21A—C21—H21C	109.5
C13—C14—C19	119.99 (12)	H21A—C21—H21B	109.5
C16—C15—C14	121.47 (13)	C18—C21—H21C	109.5
C15—C16—C17	118.24 (13)	C18—C21—H21B	109.5
C15—C16—C20	121.01 (14)	C18—C21—H21A	109.5

Compound 7



All reflection intensities were measured at 110(2) K using a diffractometer (equipped with Atlas detector) with Mo *K*α radiation (λ = 0.71073 Å) under the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2014/7 (Sheldrick, 2015) and was refined on F^2 with SHELXL-2014/7 (Sheldrick, 2015). Numerical absorption correction based on gaussian integration over a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 *U*eq of the attached C atoms. The structure was modelled as ordered.

Additional notes:

(i) The structure might be slightly disordered, but the amount of disorder is minimal as the residual electron density peaks are minimal ($\Delta\rho_{max}$ and $\Delta\rho_{min}$ are 0.67, -0.34 e Å^{-3}, respectively).

Crystal data	
Chemical formula	$C_{25}H_{21}BS$
M_r	364.29
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	110

a, *b*, *c* (Å)	7.7856 (3), 11.4781 (4), 12.1000 (4)
α, β, γ (°)	115.871 (3), 100.097 (3), 94.798 (3)
V (Å^3)	942.08 (6)
Z	2
Radiation type	Mo *Kα*
μ (mm^{-1})	0.18
Crystal size (mm)	0.52 × 0.41 × 0.36
Data collection	
Diffractometer	Dual, Cu at zero, Atlas
Absorption correction	Gaussian *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013,16:46:58) Numerical absorption correction based on gaussian integration over a multifaceted crystal model
T_{min}, T_{max}	0.362, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15297, 4325, 3912
R_{int}	0.021
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.116, 1.03
No. of reflections	4325
No. of parameters	247
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.67, -0.34

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013, 16:46:58), *SHELXS2014*/7 (Sheldrick, 2015), *SHELXL2014*/7 (Sheldrick, 2015), *SHELXTL* v6.10 (Sheldrick, 2008).[1]

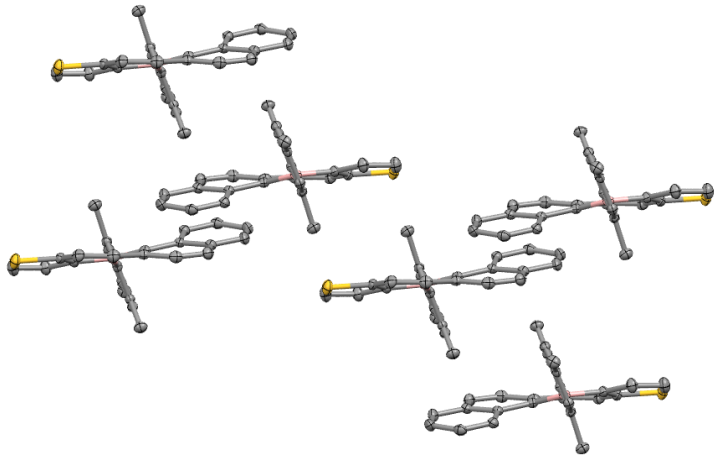
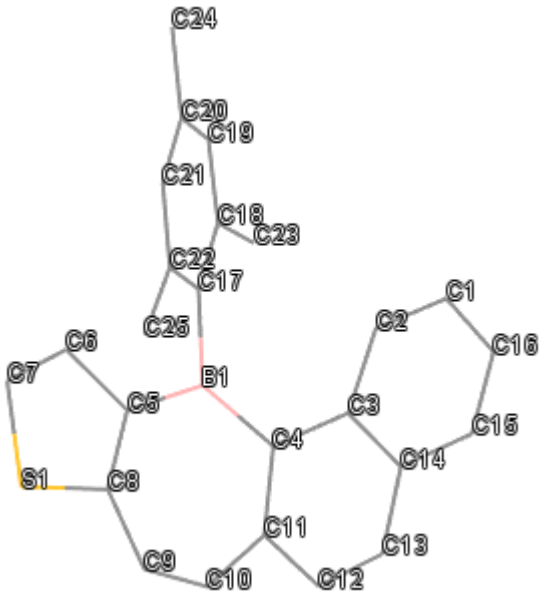


Figure S-45. Displacement ellipsoid plots (50% probability level) showing crystal packing of **7**. H atoms are omitted for clarity.



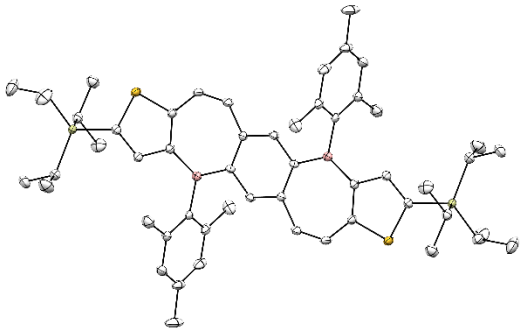
Selected geometric parameters (Å, º)

C1—C2	1.377 (2)	C19—C20	1.393 (2)
C1—C16	1.405 (2)	C20—C21	1.394 (2)
C2—C3	1.419 (2)	C20—C24	1.510 (2)
C3—C14	1.425 (2)	C21—C22	1.399 (2)
C3—C4	1.4690 (19)	C22—C25	1.514 (2)
C4—C11	1.421 (2)	C1—H1	0.9500
C4—B1	1.563 (2)	C2—H2	0.9500
C5—C8	1.399 (2)	C6—H6	0.9500
C5—C6	1.442 (2)	C7—H7	0.9500
C5—B1	1.546 (2)	C9—H9	0.9500
C6—C7	1.354 (2)	C10—H10	0.9500
C7—S1	1.7146 (18)	C12—H12	0.9500
C8—C9	1.419 (2)	C13—H13	0.9500
C8—S1	1.7280 (15)	C15—H15	0.9500
C9—C10	1.348 (2)	C16—H16	0.9500
C10—C11	1.447 (2)	C19—H19	0.9500
C11—C12	1.437 (2)	C21—H21	0.9500
C12—C13	1.349 (2)	C23—H23C	0.9800
C13—C14	1.414 (2)	C23—H23B	0.9800

C14—C15	1.422 (2)	C23—H23A	0.9800
C15—C16	1.348 (2)	C24—H24C	0.9800
C17—C22	1.405 (2)	C24—H24B	0.9800
C17—C18	1.414 (2)	C24—H24A	0.9800
C17—B1	1.599 (2)	C25—H25C	0.9800
C18—C19	1.393 (2)	C25—H25B	0.9800
C18—C23	1.510 (2)	C25—H25A	0.9800
C2—C1—C16	120.41 (15)	C4—B1—C17	121.96 (13)
C1—C2—C3	122.23 (14)	C7—S1—C8	91.92 (8)
C2—C3—C14	115.86 (13)	C2—C1—H1	119.8
C2—C3—C4	123.14 (13)	C16—C1—H1	119.8
C14—C3—C4	120.89 (13)	C1—C2—H2	118.9
C11—C4—C3	116.17 (13)	C3—C2—H2	118.9
C11—C4—B1	122.77 (13)	C5—C6—H6	122.6
C3—C4—B1	120.60 (12)	C7—C6—H6	122.6
C8—C5—C6	109.31 (13)	S1—C7—H7	124.2
C8—C5—B1	128.31 (14)	C6—C7—H7	124.2
C6—C5—B1	122.33 (13)	C8—C9—H9	116.2
C7—C6—C5	114.80 (15)	C10—C9—H9	116.2
C6—C7—S1	111.56 (13)	C9—C10—H10	113.1
C5—C8—C9	129.58 (14)	C11—C10—H10	113.1
C5—C8—S1	112.38 (12)	C11—C12—H12	118.7
C9—C8—S1	117.82 (11)	C13—C12—H12	118.7
C10—C9—C8	127.65 (14)	C12—C13—H13	119.9
C9—C10—C11	133.84 (14)	C14—C13—H13	119.9
C4—C11—C12	119.79 (14)	C14—C15—H15	119.4
C4—C11—C10	128.89 (14)	C16—C15—H15	119.4
C12—C11—C10	111.29 (13)	C1—C16—H16	120.2
C13—C12—C11	122.68 (14)	C15—C16—H16	120.2
C12—C13—C14	120.15 (14)	C18—C19—H19	119.1
C13—C14—C15	120.12 (14)	C20—C19—H19	119.1
C13—C14—C3	119.41 (14)	C20—C21—H21	119.2
C15—C14—C3	120.46 (14)	C22—C21—H21	119.2
C16—C15—C14	121.26 (15)	H23B—C23—H23C	109.5
C15—C16—C1	119.53 (15)	H23A—C23—H23C	109.5
C22—C17—C18	118.24 (13)	H23A—C23—H23B	109.5

C22—C17—B1	120.55 (13)	C18—C23—H23C	109.5
C18—C17—B1	121.09 (13)	C18—C23—H23B	109.5
C19—C18—C17	120.15 (14)	C18—C23—H23A	109.5
C19—C18—C23	119.64 (13)	H24B—C24—H24C	109.5
C17—C18—C23	120.11 (13)	H24A—C24—H24C	109.5
C20—C19—C18	121.80 (13)	H24A—C24—H24B	109.5
C19—C20—C21	117.95 (13)	C20—C24—H24C	109.5
C19—C20—C24	121.73 (14)	C20—C24—H24B	109.5
C21—C20—C24	120.32 (14)	C20—C24—H24A	109.5
C20—C21—C22	121.52 (14)	H25B—C25—H25C	109.5
C21—C22—C17	120.31 (13)	H25A—C25—H25C	109.5
C21—C22—C25	118.83 (13)	H25A—C25—H25B	109.5
C17—C22—C25	120.86 (13)	C22—C25—H25C	109.5
C5—B1—C4	125.73 (13)	C22—C25—H25B	109.5
C5—B1—C17	112.20 (12)	C22—C25—H25A	109.5

Compound 20



All reflection intensities were measured at 110(2) K using a diffractometer (equipped with Atlas detector) with Mo *K*α radiation (λ = 0.71073 Å) under the program CrysAlisPro (Version 1.171.37.31 Agilent Technologies, 2014). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2013 (Sheldrick, 2013) and was refined on F^2 with SHELXL-2013 (Sheldrick, 2013). Analytical numeric absorption corrections based on a multifaceted crystal model were applied using CrysAlisPro (Version 1.171.37.31 Agilent Technologies, 2014). The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times *U*eq of the attached C atoms.

The asymmetric unit contains ½ molecule of the target compound (the molecule is found at sites of inversion symmetry, and hence only one half of the molecule is crystallographically independent) and one disordered lattice dichloromethane solvent molecule. The structure is mostly ordered. The solvent molecule is disordered over three orientations, and the occupancy factors of the three components refine to 0.367(3), 0.483(3) and 0.150(2). The SUMP instruction was used so that the sum of the three occupancy factors equals one.

Crystal data	
Chemical formula	$C_{54}H_{72}B_2S_2Si_2 \cdot 2(CHCl_3)$
M_r	1101.77
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	110
a, *b*, *c* (Å)	7.60896 (18), 12.9290 (3), 15.5388 (3)

α, β, γ (°)	80.6046 (19), 89.3364 (19), 79.1474 (19)
V (Å^3)	1480.88 (6)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.44
Crystal size (mm)	0.41 × 0.33 × 0.28
Data collection	
Diffractometer	Dual, Cu at zero, Atlas
Absorption correction	Analytical *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.31 (release 14-01-2014 CrysAlis171 .NET) (compiled Jan 14 2014,18:38:05) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.925, 0.945
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22578, 6781, 5841
R_{int}	0.029
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.101, 1.03
No. of reflections	6781
No. of parameters	379
No. of restraints	247
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.56, -0.29

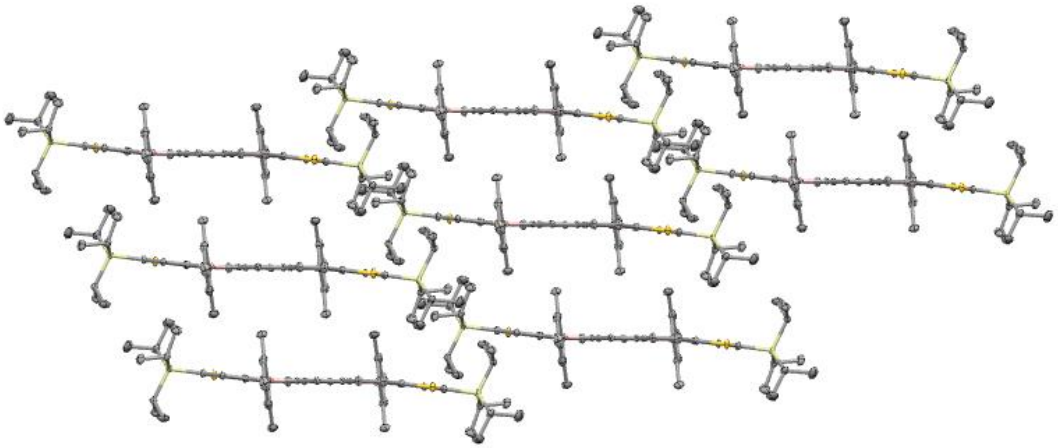
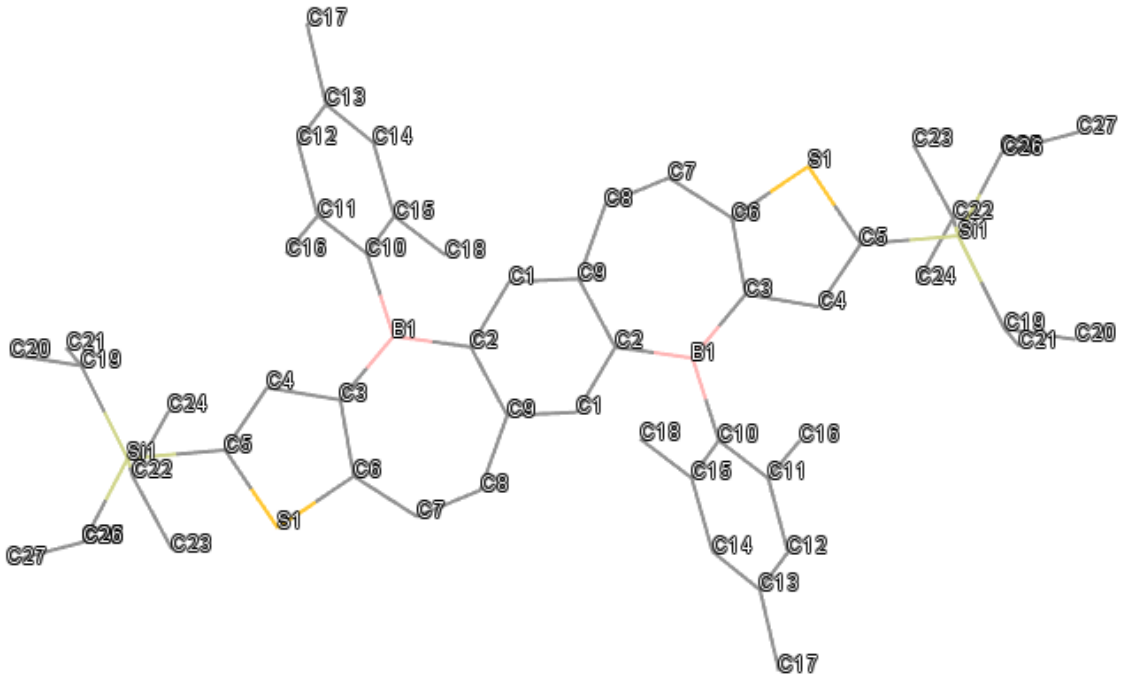


Figure S-46. Displacement ellipsoid plots (50% probability level) showing crystal packing of **8-TIPS**. H atoms and solvent molecules are omitted for clarity.



Selected geometric parameters (Å, º)

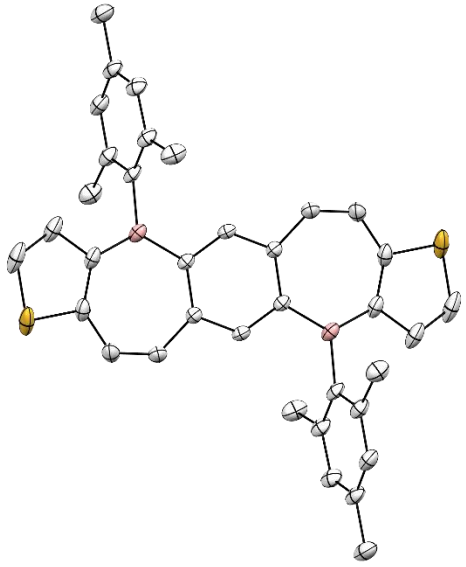
C1—C2	1.4007 (19)	C1C—Cl2C	1.747 (12)
C1—C9^{i}	1.4065 (19)	C1C—Cl3C	1.867 (12)
C2—C9	1.4317 (19)	C1S—H1S	1.0000
C2—B1	1.564 (2)	C1C—H1C	1.0000
C3—C6	1.397 (2)	C1'—H1'	1.0000
C3—C4	1.4352 (19)	C1—H1	0.9500
C3—B1	1.537 (2)	C4—H4	0.9500
C4—C5	1.373 (2)	C7—H7	0.9500
C5—S1	1.7299 (15)	C8—H8	0.9500
C5—Si1	1.8761 (15)	C12—H12	0.9500
C6—C7	1.428 (2)	C14—H14	0.9500
C6—S1	1.7279 (14)	C16—H16C	0.9800
C7—C8	1.350 (2)	C16—H16B	0.9800
C8—C9	1.448 (2)	C16—H16A	0.9800
C9—C1^{i}	1.4065 (19)	C17—H17C	0.9800
C10—C11	1.406 (2)	C17—H17B	0.9800
C10—C15	1.408 (2)	C17—H17A	0.9800
C10—B1	1.586 (2)	C18—H18C	0.9800
C11—C12	1.402 (2)	C18—H18B	0.9800

C11—C16	1.506 (2)	C18—H18A	0.9800
C12—C13	1.386 (2)	C19—H19	1.0000
C13—C14	1.387 (3)	C20—H20C	0.9800
C13—C17	1.513 (2)	C20—H20B	0.9800
C14—C15	1.395 (2)	C20—H20A	0.9800
C15—C18	1.506 (2)	C21—H21C	0.9800
C19—C21	1.531 (2)	C21—H21B	0.9800
C19—C20	1.536 (2)	C21—H21A	0.9800
C19—Si1	1.8855 (16)	C22—H22	1.0000
C22—C24	1.533 (2)	C23—H23C	0.9800
C22—C23	1.535 (2)	C23—H23B	0.9800
C22—Si1	1.8895 (15)	C23—H23A	0.9800
C25—C27	1.529 (2)	C24—H24C	0.9800
C25—C26	1.532 (2)	C24—H24B	0.9800
C25—Si1	1.8889 (15)	C24—H24A	0.9800
C1S—Cl3	1.745 (10)	C25—H25	1.0000
C1S—Cl2	1.745 (12)	C26—H26C	0.9800
C1S—Cl1	1.773 (11)	C26—H26B	0.9800
C1'—Cl2'	1.738 (8)	C26—H26A	0.9800
C1'—Cl3'	1.776 (10)	C27—H27C	0.9800
C1'—Cl1'	1.779 (9)	C27—H27B	0.9800
C1C—Cl1C	1.718 (12)	C27—H27A	0.9800
C2—C1—C9^{i}	125.89 (13)	C5—C4—H4	121.9
C1—C2—C9	115.50 (12)	C6—C7—H7	115.4
C1—C2—B1	116.50 (12)	C8—C7—H7	115.4
C9—C2—B1	128.00 (12)	C7—C8—H8	113.8
C6—C3—C4	110.08 (12)	C9—C8—H8	113.8
C6—C3—B1	126.78 (13)	C11—C12—H12	119.0
C4—C3—B1	123.13 (13)	C13—C12—H12	119.0
C5—C4—C3	116.28 (13)	C13—C14—H14	119.2
C4—C5—S1	108.64 (11)	C15—C14—H14	119.2
C4—C5—Si1	129.70 (12)	H16B—C16—H16C	109.5
S1—C5—Si1	121.66 (8)	H16A—C16—H16C	109.5
C3—C6—C7	131.63 (13)	H16A—C16—H16B	109.5
C3—C6—S1	111.23 (11)	C11—C16—H16C	109.5
C7—C6—S1	117.13 (11)	C11—C16—H16B	109.5

C8—C7—C6	129.13 (14)	C11—C16—H16A	109.5
C7—C8—C9	132.50 (14)	H17B—C17—H17C	109.5
C1^{i}—C9—C2	118.61 (12)	H17A—C17—H17C	109.5
C1^{i}—C9—C8	114.39 (13)	H17A—C17—H17B	109.5
C2—C9—C8	127.00 (13)	C13—C17—H17C	109.5
C11—C10—C15	118.52 (13)	C13—C17—H17B	109.5
C11—C10—B1	121.24 (13)	C13—C17—H17A	109.5
C15—C10—B1	120.23 (13)	H18B—C18—H18C	109.5
C12—C11—C10	119.58 (14)	H18A—C18—H18C	109.5
C12—C11—C16	119.59 (14)	H18A—C18—H18B	109.5
C10—C11—C16	120.83 (13)	C15—C18—H18C	109.5
C13—C12—C11	121.97 (15)	C15—C18—H18B	109.5
C12—C13—C14	118.11 (14)	C15—C18—H18A	109.5
C12—C13—C17	121.30 (17)	Si1—C19—H19	106.0
C14—C13—C17	120.58 (17)	C20—C19—H19	106.0
C13—C14—C15	121.58 (15)	C21—C19—H19	106.0
C14—C15—C10	120.21 (15)	H20B—C20—H20C	109.5
C14—C15—C18	119.52 (14)	H20A—C20—H20C	109.5
C10—C15—C18	120.28 (13)	H20A—C20—H20B	109.5
C21—C19—C20	110.30 (14)	C19—C20—H20C	109.5
C21—C19—Si1	114.43 (12)	C19—C20—H20B	109.5
C20—C19—Si1	113.34 (11)	C19—C20—H20A	109.5
C24—C22—C23	110.63 (13)	H21B—C21—H21C	109.5
C24—C22—Si1	111.34 (11)	H21A—C21—H21C	109.5
C23—C22—Si1	112.80 (11)	H21A—C21—H21B	109.5
C27—C25—C26	111.71 (15)	C19—C21—H21C	109.5
C27—C25—Si1	113.05 (12)	C19—C21—H21B	109.5
C26—C25—Si1	116.22 (12)	C19—C21—H21A	109.5
C3—B1—C2	124.73 (13)	Si1—C22—H22	107.3
C3—B1—C10	117.29 (12)	C23—C22—H22	107.3
C2—B1—C10	117.97 (12)	C24—C22—H22	107.3
C5—Si1—C19	106.73 (7)	H23B—C23—H23C	109.5
C5—Si1—C25	107.23 (7)	H23A—C23—H23C	109.5
C19—Si1—C25	116.52 (7)	H23A—C23—H23B	109.5
C5—Si1—C22	108.25 (7)	C22—C23—H23C	109.5
C19—Si1—C22	109.09 (7)	C22—C23—H23B	109.5
C25—Si1—C22	108.73 (7)	C22—C23—H23A	109.5

C6—S1—C5	93.76 (7)	H24B—C24—H24C	109.5
Cl3—C1S—Cl2	112.2 (7)	H24A—C24—H24C	109.5
Cl3—C1S—Cl1	114.0 (7)	H24A—C24—H24B	109.5
Cl2—C1S—Cl1	111.1 (9)	C22—C24—H24C	109.5
Cl2'—C1'—Cl3'	107.3 (6)	C22—C24—H24B	109.5
Cl2'—C1'—Cl1'	111.8 (6)	C22—C24—H24A	109.5
Cl3'—C1'—Cl1'	106.9 (7)	Si1—C25—H25	104.9
Cl1C—C1C—Cl2C	106.1 (9)	C26—C25—H25	104.9
Cl1C—C1C—Cl3C	103.5 (8)	C27—C25—H25	104.9
Cl2C—C1C—Cl3C	108.3 (9)	H26B—C26—H26C	109.5
Cl1—C1S—H1S	106.3	H26A—C26—H26C	109.5
Cl2—C1S—H1S	106.3	H26A—C26—H26B	109.5
Cl3—C1S—H1S	106.3	C25—C26—H26C	109.5
Cl1C—C1C—H1C	112.8	C25—C26—H26B	109.5
Cl2C—C1C—H1C	112.8	C25—C26—H26A	109.5
Cl3C—C1C—H1C	112.8	H27B—C27—H27C	109.5
Cl1'—C1'—H1'	110.3	H27A—C27—H27C	109.5
Cl2'—C1'—H1'	110.3	H27A—C27—H27B	109.5
Cl3'—C1'—H1'	110.3	C25—C27—H27C	109.5
C2—C1—H1	117.1	C25—C27—H27B	109.5
$C9^{i}$—C1—H1	117.1	C25—C27—H27A	109.5
C3—C4—H4	121.9		

Compound 8



All reflection intensities were measured at 110(2) K using a diffractometer (equipped with Atlas detector) with Cu *K*α radiation (λ = 1.54178 Å) under the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2013 (Sheldrick, 2008) and was refined on F^2 with SHELXL-2013 (Sheldrick, 2008). Analytical numeric absorption correction based on a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions (unless otherwise specified) using the instructions AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 *U*eq of the attached C atoms.

The structure is ordered. The molecule is found at sites of inversion symmetry, and thus only one half of the molecule is crystallographically independent.

Crystal data	
Chemical formula	$C_{36}H_{32}B_2S_2$
M_r	550.35
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	110

a, *b*, *c* (Å)	12.9336 (2), 7.95419 (16), 15.2850 (3)
β (°)	111.401 (2)
V (Å^3)	1464.04 (5)
Z	2
Radiation type	Cu *K*α
μ (mm^{-1})	1.81
Crystal size (mm)	0.49 × 0.26 × 0.03
Data collection	
Diffractometer	Dual, Cu at zero, Atlas diffractometer
Absorption correction	Analytical *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013,16:46:58) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897)
T_{min}, T_{max}	0.608, 0.943
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9753, 2871, 2576
R_{int}	0.028
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.616
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.100, 1.04
No. of reflections	2871
No. of parameters	184
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.31, -0.57

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET) (compiled Aug 13 2014,18:06:01), *SHELXS2013* (Sheldrick, 2013), *SHELXL2013* (Sheldrick, 2013), *SHELXTL* v6.10 (Sheldrick, 2008).[1]

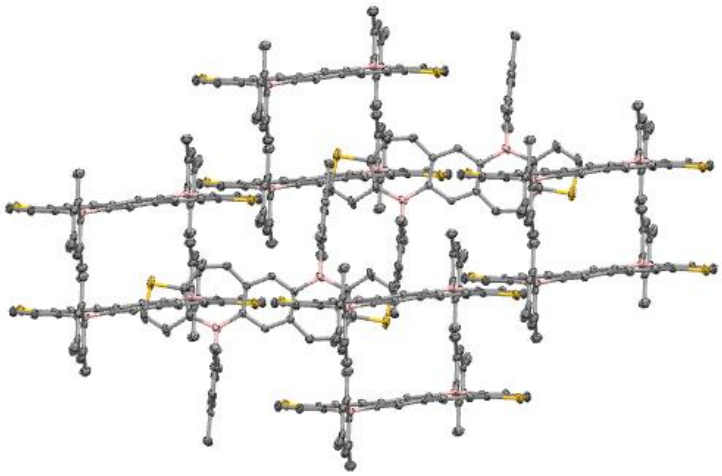
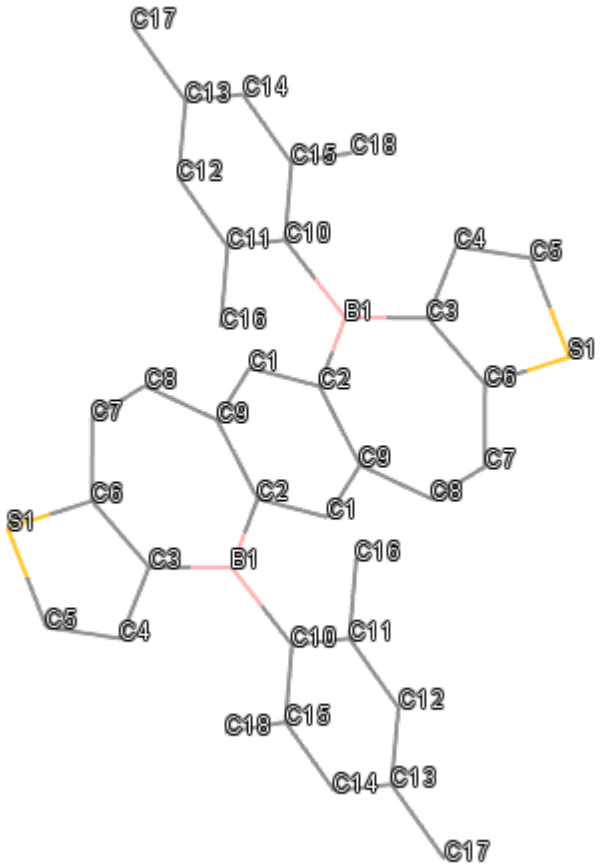


Figure S-47. Displacement ellipsoid plots (50% probability level) showing crystal packing of **8**. H atoms are omitted for clarity.



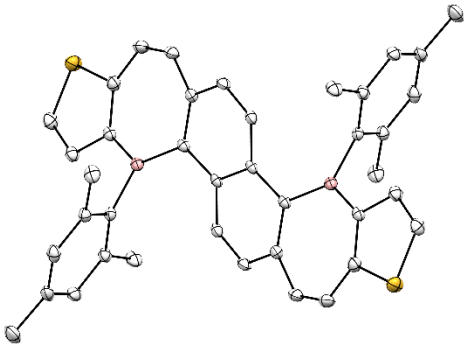
Selected geometric parameters (Å, º)

C1—C2	1.3970 (19)	C13—C14	1.393 (2)
C1—C9^{i}	1.4044 (18)	C13—C17	1.511 (2)
C2—C9	1.4333 (18)	C14—C15	1.395 (2)
C2—B1	1.5594 (19)	C15—C18	1.510 (2)
C3—C6	1.393 (2)	C1—H1	0.9500
C3—C4	1.4380 (19)	C4—H4	0.9500
C3—B1	1.536 (2)	C5—H5	0.9500
C4—C5	1.353 (2)	C7—H7	0.9500
C5—S1	1.710 (2)	C8—H8	0.9500
C6—C7	1.429 (2)	C12—H12	0.9500
C6—S1	1.7395 (14)	C14—H14	0.9500
C7—C8	1.352 (2)	C16—H16C	0.9800
C8—C9	1.4494 (19)	C16—H16B	0.9800

C9—C1^{i}	1.4044 (18)	C16—H16A	0.9800
C10—C15	1.405 (2)	C17—H17C	0.9800
C10—C11	1.408 (2)	C17—H17B	0.9800
C10—B1	1.588 (2)	C17—H17A	0.9800
C11—C12	1.396 (2)	C18—H18C	0.9800
C11—C16	1.507 (2)	C18—H18B	0.9800
C12—C13	1.382 (2)	C18—H18A	0.9800
C2—C1—C9^{i}	125.55 (12)	C5—S1—C6	91.98 (8)
C1—C2—C9	116.28 (12)	C2—C1—H1	117.2
C1—C2—B1	116.45 (12)	C9^{i}—C1—H1	117.2
C9—C2—B1	127.26 (12)	C3—C4—H4	122.8
C6—C3—C4	110.30 (13)	C5—C4—H4	122.8
C6—C3—B1	127.23 (13)	S1—C5—H5	124.1
C4—C3—B1	122.47 (14)	C4—C5—H5	124.1
C5—C4—C3	114.39 (16)	C6—C7—H7	115.6
C4—C5—S1	111.78 (12)	C8—C7—H7	115.6
C3—C6—C7	131.01 (13)	C7—C8—H8	113.6
C3—C6—S1	111.52 (11)	C9—C8—H8	113.6
C7—C6—S1	117.47 (11)	C11—C12—H12	119.1
C8—C7—C6	128.70 (14)	C13—C12—H12	119.1
C7—C8—C9	132.73 (14)	C13—C14—H14	119.1
C1^{i}—C9—C2	118.17 (12)	C15—C14—H14	119.1
C1^{i}—C9—C8	114.80 (12)	H16B—C16—H16C	109.5
C2—C9—C8	127.03 (12)	H16A—C16—H16C	109.5
C15—C10—C11	118.27 (13)	H16A—C16—H16B	109.5
C15—C10—B1	122.94 (12)	C11—C16—H16C	109.5
C11—C10—B1	118.54 (13)	C11—C16—H16B	109.5
C12—C11—C10	120.22 (14)	C11—C16—H16A	109.5
C12—C11—C16	119.57 (14)	H17B—C17—H17C	109.5
C10—C11—C16	120.18 (13)	H17A—C17—H17C	109.5
C13—C12—C11	121.75 (14)	H17A—C17—H17B	109.5
C12—C13—C14	117.89 (13)	C13—C17—H17C	109.5
C12—C13—C17	121.15 (15)	C13—C17—H17B	109.5
C14—C13—C17	120.96 (15)	C13—C17—H17A	109.5
C13—C14—C15	121.85 (15)	H18B—C18—H18C	109.5
C14—C15—C10	120.00 (13)	H18A—C18—H18C	109.5

C14—C15—C18	119.57 (14)	H18A—C18—H18B	109.5
C10—C15—C18	120.43 (13)	C15—C18—H18C	109.5
C3—B1—C2	124.60 (13)	C15—C18—H18B	109.5
C3—B1—C10	115.16 (12)	C15—C18—H18A	109.5
C2—B1—C10	120.24 (12)		

Compound 9



All reflection intensities were measured at 110(2) K using a diffractometer (equipped with Atlas detector) with Mo *K*α radiation (λ = 0.71073 Å) under the program CrysAlisPro (Version 1.171.36.32 Agilent Technologies, 2013). The same program was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-2014/7 (Sheldrick, 2008) and was refined on F^2 with SHELXL-2014/7 (Sheldrick, 2008). Analytical numeric absorption correction based on a multifaceted crystal model was applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 *U*eq of the attached C atoms.

The structure is ordered. The molecule is found at sites of inversion symmetry, and thus only one half of the molecule is crystallographically independent.

Crystal data	
Chemical formula	$C_{40}H_{34}B_2S_2$
M_r	600.41
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	110
a, *b*, *c* (Å)	7.7053 (3), 10.2275 (4), 10.5360 (5)
α, β, γ (°)	109.999 (4), 103.639 (4), 92.088 (3)
V (Å^3)	751.97 (6)
Z	1

Radiation type	Mo *Kα*
μ (mm^{-1})	0.21
Crystal size (mm)	0.30 × 0.19 × 0.05
Data collection	
Diffractometer	Dual, Cu at zero, Atlas diffractometer
Absorption correction	Analytical *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013,16:46:58) Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. (Clark, R. C. & Reid, J. S. (1995). Acta Cryst. A51, 887-897)
T_{min}, T_{max}	0.956, 0.991
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10548, 3449, 3034
R_{int}	0.027
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.105, 1.04
No. of reflections	3449
No. of parameters	202
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.37, -0.28

Computer programs: *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.32 (release 02-08-2013 CrysAlis171 .NET) (compiled Aug 2 2013, 16:46:58), *SHELXS2014*/7 (Sheldrick, 2014), *SHELXL2014*/7 (Sheldrick, 2014), *SHELXTL* v6.10 (Sheldrick, 2008).[1]

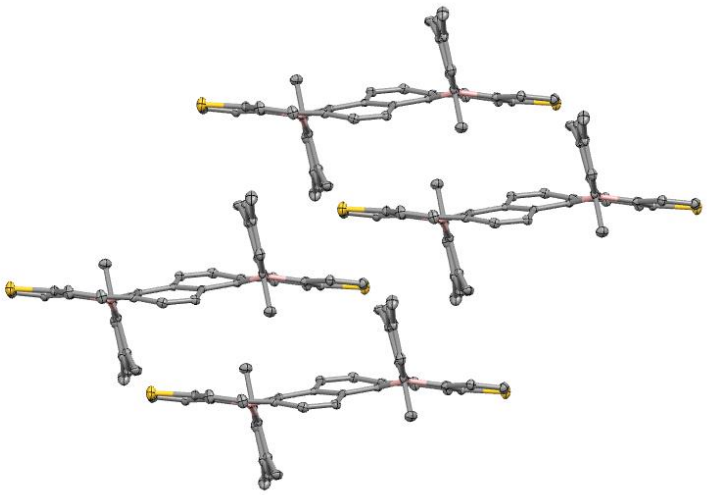
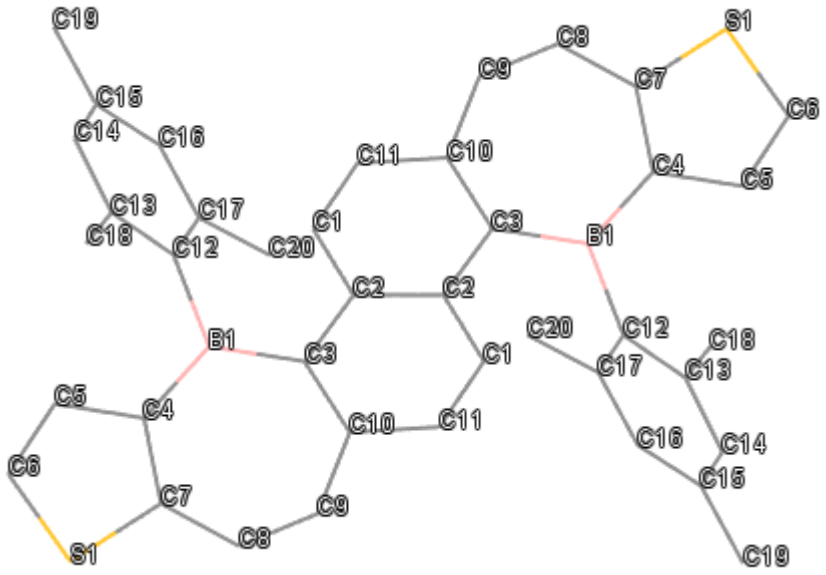


Figure S-48. Displacement ellipsoid plots (50% probability level) showing crystal packing of **9**. H atoms are omitted for clarity.



Selected geometric parameters (Å, º)

C1—C11^{i}	1.353 (2)	C14—C15	1.388 (2)
C1—C2	1.420 (2)	C15—C16	1.392 (2)
C2—C2^{i}	1.426 (3)	C15—C19	1.510 (2)
C2—C3	1.451 (2)	C16—C17	1.395 (2)
C3—C10	1.413 (2)	C17—C20	1.508 (2)
C3—B1	1.566 (2)	C1—H1	0.9500
C4—C7	1.400 (2)	C5—H5	0.9500
C4—C5	1.440 (2)	C6—H6	0.9500
C4—B1	1.550 (2)	C8—H8	0.9500
C5—C6	1.360 (2)	C9—H9	0.9500
C6—S1	1.7071 (16)	C11—H11	0.9500
C7—C8	1.422 (2)	C14—H14	0.9500
C7—S1	1.7310 (16)	C16—H16	0.9500
C8—C9	1.349 (2)	C18—H18C	0.9800
C9—C10	1.444 (2)	C18—H18B	0.9800
C10—C11	1.428 (2)	C18—H18A	0.9800
C11—C1^{i}	1.353 (2)	C19—H19C	0.9800
C12—C13	1.409 (2)	C19—H19B	0.9800
C12—C17	1.415 (2)	C19—H19A	0.9800
C12—B1	1.595 (2)	C20—H20C	0.9800

C13—C14	1.399 (2)	C20—H20B	0.9800
C13—C18	1.512 (2)	C20—H20A	0.9800
C11^{i}—C1—C2	120.84 (14)	C3—B1—C12	121.61 (13)
C1—C2—C2^{i}	116.50 (16)	C6—S1—C7	91.96 (7)
C1—C2—C3	120.46 (13)	C2—C1—H1	119.6
C2^{i}—C2—C3	122.94 (16)	C11^{i}—C1—H1	119.6
C10—C3—C2	116.49 (13)	C4—C5—H5	122.7
C10—C3—B1	122.92 (13)	C6—C5—H5	122.7
C2—C3—B1	119.92 (13)	S1—C6—H6	124.2
C7—C4—C5	109.35 (13)	C5—C6—H6	124.2
C7—C4—B1	127.13 (14)	C7—C8—H8	115.9
C5—C4—B1	123.42 (13)	C9—C8—H8	115.9
C6—C5—C4	114.65 (14)	C8—C9—H9	113.5
C5—C6—S1	111.70 (12)	C10—C9—H9	113.5
C4—C7—C8	130.21 (14)	C1^{i}—C11—H11	118.5
C4—C7—S1	112.33 (11)	C10—C11—H11	118.5
C8—C7—S1	117.02 (12)	C13—C14—H14	119.2
C9—C8—C7	128.18 (15)	C15—C14—H14	119.2
C8—C9—C10	133.00 (15)	C15—C16—H16	119.0
C3—C10—C11	118.63 (13)	C17—C16—H16	119.0
C3—C10—C9	128.43 (14)	H18B—C18—H18C	109.5
C11—C10—C9	112.93 (13)	H18A—C18—H18C	109.5
C1^{i}—C11—C10	123.07 (14)	H18A—C18—H18B	109.5
C13—C12—C17	117.67 (13)	C13—C18—H18C	109.5
C13—C12—B1	124.82 (13)	C13—C18—H18B	109.5
C17—C12—B1	117.11 (13)	C13—C18—H18A	109.5
C14—C13—C12	120.62 (14)	H19B—C19—H19C	109.5
C14—C13—C18	118.38 (14)	H19A—C19—H19C	109.5
C12—C13—C18	120.96 (13)	H19A—C19—H19B	109.5
C15—C14—C13	121.61 (14)	C15—C19—H19C	109.5
C14—C15—C16	117.76 (14)	C15—C19—H19B	109.5
C14—C15—C19	121.83 (15)	C15—C19—H19A	109.5
C16—C15—C19	120.42 (15)	H20B—C20—H20C	109.5
C15—C16—C17	122.08 (14)	H20A—C20—H20C	109.5
C16—C17—C12	120.10 (14)	H20A—C20—H20B	109.5
C16—C17—C20	118.90 (14)	C17—C20—H20C	109.5

C12—C17—C20	120.99 (13)	C17—C20—H20B	109.5
C4—B1—C3	124.24 (13)	C17—C20—H20A	109.5
C4—B1—C12	113.66 (12)		

4. Computational Details

Compound 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.922686	3.002433	0.000069
2	6	0	2.050833	4.077455	-0.000029
3	6	0	0.672287	3.841015	-0.000203
4	6	0	0.206619	2.534053	-0.000233
5	6	0	1.058910	1.399066	-0.000095
6	6	0	2.465879	1.661933	0.000024
7	1	0	3.993932	3.184852	0.000176
8	1	0	2.437760	5.092636	0.000016
9	1	0	-0.028804	4.670487	-0.000313
10	1	0	-0.864370	2.367254	-0.000366
11	6	0	3.520195	0.668711	0.000022
12	1	0	4.516016	1.109027	0.000045
13	6	0	3.516705	-0.686634	-0.000044
14	1	0	4.510230	-1.132096	-0.000096
15	6	0	2.457241	-1.674355	-0.000020
16	6	0	2.906977	-3.017235	-0.000073
17	6	0	1.051674	-1.404113	0.000104
18	6	0	2.029463	-4.087649	0.000049
19	1	0	3.977246	-3.205306	-0.000199
20	6	0	0.193415	-2.534585	0.000245
21	6	0	0.652172	-3.843978	0.000233

22	1	0	2.411055	-5.104848	0.000000
23	1	0	-0.876651	-2.361985	0.000357
24	1	0	-0.053242	-4.669781	0.000356
25	5	0	0.360682	-0.000740	-0.000026
26	6	0	-1.235844	0.003177	-0.000017
27	6	0	-1.960313	0.007237	-1.214142
28	6	0	-1.960280	0.007540	1.214120
29	6	0	-3.359394	0.014439	-1.196665
30	6	0	-3.359374	0.014739	1.196675
31	6	0	-4.080939	0.015153	0.000017
32	1	0	-3.898704	0.021267	-2.142187
33	1	0	-3.898648	0.021811	2.142215
34	6	0	-1.232018	0.008767	2.542005
35	1	0	-1.933311	0.012379	3.381182
36	1	0	-0.589294	-0.873042	2.648370
37	1	0	-0.584367	0.887382	2.644697
38	6	0	-1.232065	0.008137	-2.542038
39	1	0	-0.589172	-0.873582	-2.648106
40	1	0	-0.584606	0.886855	-2.645053
41	1	0	-1.933376	0.011312	-3.381206
42	6	0	-5.591527	-0.010656	0.000024
43	1	0	-6.000829	0.485119	-0.885633
44	1	0	-5.973253	-1.039671	0.000381
45	1	0	-6.000838	0.485726	0.885340

Compound 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.334526	3.679618	-0.000219
2	6	0	0.951472	3.255932	-0.000305
3	6	0	1.565926	1.942164	-0.000174
4	6	0	-1.611825	2.989174	-0.000045
5	6	0	0.854230	0.678874	-0.000073
6	6	0	-1.807749	1.571997	-0.000056
7	1	0	-0.442733	4.762997	-0.000304
8	1	0	1.683505	4.062023	-0.000449
9	6	0	-2.738958	3.843811	0.000082
10	1	0	-2.575618	4.918125	0.000063
11	6	0	-4.035793	3.355380	0.000188
12	1	0	-4.876219	4.043943	0.000280
13	6	0	-4.247350	1.974353	0.000170
14	1	0	-5.255413	1.570312	0.000257
15	6	0	-3.152058	1.120524	0.000029
16	1	0	-3.330869	0.051436	-0.000012
17	6	0	2.961501	1.947820	-0.000141
18	1	0	3.481876	2.902732	-0.000233
19	6	0	3.736194	0.771748	0.000018
20	6	0	3.051168	-0.484116	0.000144
21	6	0	1.639109	-0.478598	0.000078
22	5	0	-0.698063	0.467532	-0.000109
23	6	0	-1.205743	-1.046360	-0.000105

24	6	0	-1.435746	-1.733168	-1.214304
25	6	0	-1.436123	-1.732994	1.214134
26	6	0	-1.879465	-3.060017	-1.196852
27	6	0	-1.879838	-3.059841	1.196735
28	6	0	-2.111327	-3.743329	-0.000045
29	1	0	-2.046551	-3.572379	-2.142589
30	1	0	-2.047235	-3.572056	2.142498
31	6	0	-1.203944	-1.041873	-2.541678
32	1	0	-1.844784	-0.158876	-2.650276
33	1	0	-0.168356	-0.695923	-2.639357
34	1	0	-1.413137	-1.710298	-3.381580
35	6	0	-1.204775	-1.041477	2.541470
36	1	0	-1.845778	-0.158561	2.649781
37	1	0	-1.414058	-1.709820	3.381411
38	1	0	-0.169267	-0.695337	2.639352
39	6	0	-2.621110	-5.165482	-0.000014
40	1	0	-3.718207	-5.196547	-0.000046
41	1	0	-2.282825	-5.712566	-0.885443
42	1	0	-2.282880	-5.712509	0.885471
43	1	0	1.139652	-1.441802	0.000154
44	6	0	3.810194	-1.687187	0.000347
45	1	0	3.283300	-2.637635	0.000448
46	6	0	5.184645	-1.647086	0.000378
47	1	0	5.758425	-2.568957	0.000517
48	6	0	5.863888	-0.400056	0.000224
49	1	0	6.949933	-0.384164	0.000224
50	6	0	5.159338	0.780738	0.000081
51	1	0	5.679554	1.734919	-0.000025

Compound 3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.496784	-1.378786	-0.031344
2	6	0	5.453094	-2.275064	-0.008814
3	6	0	4.107453	-1.814693	-0.004314
4	6	0	3.857261	-0.407282	-0.023663
5	6	0	4.957558	0.492495	-0.046574
6	6	0	6.249054	0.018409	-0.050305
7	1	0	3.188326	-3.754640	0.034013
8	1	0	7.521468	-1.739097	-0.034698
9	1	0	5.643377	-3.344938	0.005753
10	6	0	2.997547	-2.684103	0.018835
11	6	0	2.515120	0.035422	-0.019315
12	1	0	4.759304	1.560934	-0.060902
13	1	0	7.085580	0.710505	-0.067796
14	6	0	1.404818	-0.812398	0.002821
15	6	0	1.677285	-2.236528	0.022468
16	1	0	2.348637	1.107227	-0.035350
17	6	0	0.675995	-3.289134	0.047018
18	1	0	1.117279	-4.284332	0.067205
19	6	0	-0.677055	-3.288955	0.046970
20	1	0	-1.118598	-4.284038	0.067157
21	6	0	-1.678080	-2.236097	0.022456
22	6	0	-2.998437	-2.683390	0.018719
23	6	0	-1.405278	-0.812021	0.003012

24	6	0	-4.108161	-1.813747	-0.004270
25	1	0	-3.189438	-3.753890	0.033702
26	6	0	-2.515422	0.036027	-0.018889
27	6	0	-3.857659	-0.406391	-0.023285
28	6	0	-5.453900	-2.273825	-0.008893
29	1	0	-2.348756	1.107797	-0.034728
30	6	0	-4.957758	0.493633	-0.045974
31	6	0	-6.497394	-1.377314	-0.031211
32	1	0	-5.644417	-3.343661	0.005411
33	6	0	-6.249359	0.019831	-0.049827
34	1	0	-4.759269	1.562033	-0.060045
35	1	0	-7.522157	-1.737401	-0.034666
36	1	0	-7.085734	0.712114	-0.067153
37	5	0	-0.000112	-0.117445	0.000546
38	6	0	0.000246	1.479930	0.003365
39	6	0	-0.000104	2.214358	-1.198730
40	6	0	0.000813	2.194810	1.229090
41	6	0	-0.000019	3.617439	-1.167264
42	6	0	0.000904	3.590051	1.225537
43	6	0	0.000654	4.325431	0.032516
44	1	0	-0.000556	4.165824	-2.107999
45	1	0	0.001052	4.120431	2.176307
46	6	0	0.000952	1.451609	2.548434
47	1	0	-0.879412	0.805619	2.645355
48	1	0	0.880773	0.804785	2.644655
49	1	0	0.001605	2.143527	3.395308
50	6	0	-0.000778	1.527631	-2.550990
51	1	0	-0.881413	1.811625	-3.139128

52	1	0	0.880659	1.809524	-3.138947
53	1	0	-0.002092	0.438093	-2.467027
54	6	0	0.002769	5.836102	0.056974
55	1	0	-0.866119	6.229422	0.597498
56	1	0	0.894744	6.227416	0.560384
57	1	0	-0.017687	6.251641	-0.954347

Compound 4

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.221708	-0.605698	-0.015082
2	6	0	1.257133	0.797632	-0.012681
3	6	0	-1.183176	0.652181	-0.025390
4	6	0	-1.218306	-0.751034	-0.023824
5	6	0	0.055478	-1.398708	-0.021648
6	1	0	2.169373	-1.132444	-0.010517
7	1	0	-2.131580	1.178047	-0.026162
8	6	0	0.289919	-2.827686	-0.026252
9	1	0	1.348276	-3.082511	-0.026787
10	6	0	-0.538128	-3.900770	-0.030640
11	1	0	-0.020086	-4.858343	-0.034477
12	6	0	-1.982011	-4.044913	-0.028752
13	6	0	-2.939046	-2.982633	-0.025274
14	5	0	-2.639594	-1.438142	-0.024477
15	6	0	-2.435779	-5.386415	-0.028913
16	1	0	-1.696329	-6.182681	-0.032803
17	6	0	-3.781767	-5.711167	-0.023924
18	1	0	-4.091358	-6.752477	-0.024039
19	6	0	-4.731385	-4.685328	-0.019239
20	1	0	-5.792684	-4.916037	-0.015837
21	6	0	-4.304643	-3.363931	-0.020009
22	1	0	-5.054016	-2.580895	-0.020275
23	5	0	2.678229	1.486955	0.001255

24	6	0	-0.017427	1.445394	-0.020605
25	6	0	-0.252493	2.874290	-0.022408
26	1	0	-1.310972	3.128527	-0.028177
27	6	0	0.575156	3.947674	-0.018750
28	1	0	0.056652	4.905025	-0.022818
29	6	0	2.018855	4.092317	-0.010000
30	6	0	2.472438	5.433982	-0.010401
31	6	0	2.975610	3.030662	-0.000224
32	6	0	3.818358	5.758673	-0.001782
33	1	0	1.732982	6.230233	-0.017701
34	6	0	4.341111	3.411582	0.008960
35	6	0	4.768045	4.732676	0.008109
36	1	0	4.128043	6.799959	-0.002507
37	1	0	5.089769	2.627634	0.017145
38	1	0	5.829321	4.963480	0.015235
39	6	0	3.941315	0.500254	0.018291
40	6	0	4.496513	0.032489	1.249331
41	6	0	4.523326	0.022648	-1.201765
42	6	0	5.564837	-0.881119	1.222580
43	6	0	5.586135	-0.888087	-1.141656
44	6	0	6.129914	-1.366120	0.049482
45	1	0	5.960798	-1.229679	2.166301
46	1	0	6.006851	-1.249669	-2.072554
47	6	0	-3.907704	-0.458013	-0.021259
48	6	0	-4.496453	-0.015013	1.208915
49	6	0	-4.485757	0.007668	-1.242486
50	6	0	-5.611879	0.830941	1.166579
51	6	0	-5.585592	0.882502	-1.197041

52	6	0	-6.177701	1.308545	-0.014486
53	1	0	-6.061439	1.135587	2.103977
54	1	0	-5.992308	1.239248	-2.133071
55	6	0	-4.021332	-0.317577	-2.702688
56	6	0	-4.064513	-0.398389	2.665169
57	6	0	-7.391830	2.255305	0.033114
58	6	0	-3.500816	0.988316	-3.356391
59	1	0	-2.616847	1.359916	-2.827998
60	1	0	-3.216678	0.804277	-4.398938
61	1	0	-4.251573	1.782851	-3.350338
62	6	0	-2.909664	-1.370466	-2.867211
63	1	0	-2.674181	-1.464492	-3.933168
64	1	0	-1.980950	-1.091060	-2.367261
65	1	0	-3.215151	-2.357298	-2.517030
66	6	0	-5.225782	-0.857685	-3.519519
67	1	0	-5.626100	-1.768454	-3.061967
68	1	0	-6.044704	-0.140022	-3.604721
69	1	0	-4.903444	-1.106577	-4.536757
70	6	0	-2.753968	-1.192007	2.820885
71	1	0	-2.777713	-2.159192	2.316821
72	1	0	-1.885593	-0.633042	2.469325
73	1	0	-2.595845	-1.398547	3.885323
74	6	0	-3.866460	0.890438	3.506908
75	1	0	-4.775006	1.489744	3.601620
76	1	0	-3.545592	0.625473	4.520452
77	1	0	-3.091917	1.526011	3.065314
78	6	0	-5.188960	-1.257607	3.298314
79	1	0	-4.938952	-1.506272	4.336287

80	1	0	-6.152116	-0.739965	3.301377
81	1	0	-5.315236	-2.196289	2.748997
82	6	0	-7.865328	2.675684	-1.371108
83	1	0	-8.177319	1.814459	-1.970759
84	1	0	-8.726460	3.346320	-1.284320
85	1	0	-7.085323	3.211480	-1.922056
86	6	0	-8.569920	1.548846	0.744724
87	1	0	-8.312951	1.258284	1.767619
88	1	0	-9.439841	2.213542	0.796362
89	1	0	-8.866060	0.643352	0.205066
90	6	0	-7.016770	3.535941	0.815946
91	1	0	-6.710154	3.311009	1.841579
92	1	0	-6.189819	4.063246	0.329085
93	1	0	-7.872855	4.218546	0.866047
94	6	0	4.092009	0.372745	-2.666720
95	6	0	4.035299	0.391420	2.702639
96	6	0	2.935816	1.459697	2.848014
97	1	0	3.253920	2.438185	2.486717
98	1	0	2.006016	1.184036	2.347258
99	1	0	2.696651	1.570076	3.911620
100	6	0	5.247612	0.930226	3.508013
101	1	0	5.655644	1.830326	3.036373
102	1	0	4.931980	1.196436	4.523019
103	1	0	6.059237	0.204842	3.598944
104	6	0	3.496397	-0.894653	3.380994
105	1	0	4.236265	-1.699018	3.395048
106	1	0	3.210485	-0.685269	4.418209
107	1	0	2.609892	-1.265722	2.856444

108	6	0	2.999673	1.444170	-2.840617
109	1	0	2.782899	1.549508	-3.909472
110	1	0	2.058511	1.174699	-2.357954
111	1	0	3.313951	2.423375	-2.477938
112	6	0	3.561919	-0.916093	-3.346418
113	1	0	2.663763	-1.280286	-2.837169
114	1	0	3.297475	-0.713330	-4.390638
115	1	0	4.298990	-1.723191	-3.339833
116	6	0	5.321865	0.901453	-3.451620
117	1	0	5.722404	1.804798	-2.979830
118	1	0	6.133282	0.173306	-3.518596
119	1	0	5.028486	1.158940	-4.475522
120	6	0	7.289060	-2.380318	0.023756
121	6	0	8.497529	-1.768129	-0.722986
122	1	0	8.851190	-0.863277	-0.218034
123	1	0	9.327037	-2.483535	-0.759366
124	1	0	8.246222	-1.498124	-1.752839
125	6	0	6.832002	-3.663341	-0.710417
126	1	0	5.981259	-4.124608	-0.198085
127	1	0	6.527776	-3.455967	-1.740513
128	1	0	7.646184	-4.396356	-0.744431
129	6	0	7.753116	-2.778388	1.437421
130	1	0	8.119147	-1.915781	2.003694
131	1	0	6.949818	-3.249404	2.013479
132	1	0	8.574068	-3.499385	1.366873

Compound 5

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.990178	3.717145	-0.000147
2	6	0	0.195960	2.610301	-0.000145
3	6	0	0.904716	1.356417	-0.000069
4	6	0	2.296537	1.577805	0.000002
5	16	0	2.672685	3.298823	-0.000045
6	1	0	0.691489	4.756631	-0.000195
7	1	0	-0.886461	2.660463	-0.000183
8	6	0	3.399686	0.678393	0.000081
9	1	0	4.382782	1.143857	0.000143
10	6	0	3.397333	-0.690084	0.000110
11	1	0	4.378816	-1.158935	0.000154
12	6	0	2.291083	-1.585681	0.000051
13	6	0	0.900045	-1.359471	-0.000003
14	16	0	2.661264	-3.307987	0.000051
15	6	0	0.186950	-2.610896	-0.000051
16	6	0	0.977302	-3.720496	-0.000026
17	1	0	-0.895635	-2.657195	-0.000080
18	1	0	0.675034	-4.758946	-0.000047
19	5	0	0.172214	-0.000277	-0.000043
20	6	0	-1.417794	0.002254	-0.000060
21	6	0	-2.141097	0.006116	1.214367
22	6	0	-2.141212	0.005997	-1.214386
23	6	0	-3.540106	0.012379	1.197139

24	6	0	-3.540234	0.012280	-1.197043
25	6	0	-4.261180	0.012379	0.000077
26	1	0	-4.079820	0.019061	2.142412
27	1	0	-4.080008	0.018908	-2.142281
28	6	0	-1.411782	0.008008	2.541792
29	1	0	-2.112554	0.010311	3.381434
30	1	0	-0.767221	-0.872523	2.647818
31	1	0	-0.765009	0.887283	2.644693
32	6	0	-1.412002	0.007634	-2.541876
33	1	0	-0.764621	0.886468	-2.644680
34	1	0	-0.768061	-0.873336	-2.648073
35	1	0	-2.112825	0.010535	-3.381471
36	6	0	-5.771799	-0.014403	0.000171
37	1	0	-6.152720	-1.043709	0.000034
38	1	0	-6.181412	0.481201	0.885770
39	1	0	-6.181529	0.481467	-0.885228

Compound 6

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.781999	3.110038	-0.000293
2	6	0	1.889160	4.165390	-0.000485
3	6	0	0.514052	3.901329	-0.000472
4	6	0	0.075126	2.586635	-0.000250
5	6	0	0.949027	1.467688	-0.000041
6	6	0	2.356193	1.756086	-0.000079
7	1	0	3.848868	3.316501	-0.000294
8	1	0	2.255288	5.188165	-0.000671
9	1	0	-0.202777	4.717264	-0.000652
10	1	0	-0.992286	2.394917	-0.000221
11	6	0	3.440309	0.797986	0.000023
12	1	0	4.423416	1.264687	-0.000275
13	6	0	3.472336	-0.563015	0.000067
14	1	0	4.465739	-1.007005	0.000013
15	6	0	2.390634	-1.493354	0.000127
16	6	0	1.002369	-1.290531	0.000118
17	16	0	2.795290	-3.203239	0.000269
18	6	0	0.308885	-2.554277	0.000110
19	6	0	1.118795	-3.649612	0.000102
20	1	0	-0.772368	-2.621432	0.000078
21	1	0	0.836436	-4.693541	0.000062
22	5	0	0.264543	0.064673	0.000107
23	6	0	-1.326800	-0.010603	0.000181

24	6	0	-2.049189	-0.058019	-1.214202
25	6	0	-2.049050	-0.057171	1.214359
26	6	0	-3.445384	-0.145994	-1.196841
27	6	0	-3.445504	-0.145183	1.196964
28	6	0	-4.165099	-0.193122	0.000196
29	1	0	-3.984096	-0.176854	-2.142232
30	1	0	-3.984280	-0.175405	2.142307
31	6	0	-5.670675	-0.319401	-0.000236
32	1	0	-6.113654	0.170134	-0.873152
33	1	0	-5.983691	-1.371081	-0.025875
34	1	0	-6.110222	0.126736	0.897149
35	6	0	-1.322005	-0.005523	2.541974
36	1	0	-2.020744	-0.061271	3.381433
37	1	0	-0.611460	-0.834281	2.643760
38	1	0	-0.745180	0.920687	2.648988
39	6	0	-1.321814	-0.007420	-2.541677
40	1	0	-0.744550	0.918478	-2.649008
41	1	0	-0.611613	-0.836541	-2.642837
42	1	0	-2.020381	-0.063274	-3.381278

Compound 7

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.894496	-0.469932	0.000035
2	6	0	-5.187453	0.708336	-0.000187
3	6	0	-3.763212	0.695865	-0.000054
4	6	0	-3.080703	-0.562369	0.000318
5	6	0	-3.843798	-1.763623	0.000549
6	6	0	-5.217496	-1.719249	0.000405
7	1	0	-3.509931	2.824117	-0.000566
8	1	0	-6.980452	-0.451850	-0.000074
9	1	0	-5.704936	1.663998	-0.000466
10	6	0	-2.988685	1.869706	-0.000283
11	6	0	-1.670022	-0.559148	0.000417
12	1	0	-3.319732	-2.715577	0.000838
13	1	0	-5.793882	-2.639504	0.000577
14	6	0	-0.881814	0.596375	0.000183
15	6	0	-1.589985	1.866965	-0.000167
16	1	0	-1.168780	-1.522136	0.000697
17	6	0	-0.990690	3.187168	-0.000426
18	1	0	-1.727668	3.987971	-0.000639
19	6	0	0.298093	3.619456	-0.000415
20	1	0	0.428245	4.699662	-0.000618
21	6	0	1.512168	2.862160	-0.000169
22	6	0	1.736685	1.479115	0.000132
23	6	0	3.150173	1.196380	0.000313

24	6	0	3.952543	2.297447	0.000150
25	16	0	3.020258	3.760726	-0.000223
26	1	0	3.538028	0.184846	0.000552
27	1	0	5.032923	2.342664	0.000244
28	5	0	0.665297	0.367200	0.000258
29	6	0	1.215947	-1.127777	0.000359
30	6	0	1.481317	-1.800936	1.214529
31	6	0	1.480847	-1.801283	-1.214300
32	6	0	1.992765	-3.103402	1.197003
33	6	0	1.992102	-3.103316	-1.197002
34	6	0	2.258830	-3.773650	0.000179
35	1	0	2.186728	-3.606499	2.142551
36	1	0	2.185588	-3.606466	-2.142678
37	6	0	1.209982	-1.123545	-2.541347
38	1	0	0.154603	-0.844541	-2.641773
39	1	0	1.792744	-0.200887	-2.647096
40	1	0	1.463997	-1.775852	-3.381602
41	6	0	1.211308	-1.123396	2.541868
42	1	0	1.795323	-0.201565	2.648038
43	1	0	0.156310	-0.843041	2.642467
44	1	0	1.464495	-1.776376	3.381851
45	6	0	2.841276	-5.167616	-0.001073
46	1	0	2.490221	-5.748116	-0.860049
47	1	0	3.937219	-5.142638	-0.054588
48	1	0	2.574257	-5.714216	0.908513

Compound 8

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.415310	-0.357452	0.000096
2	6	0	-0.954213	0.968012	0.000055
3	6	0	0.397408	1.372759	0.000066
4	6	0	1.415308	0.357451	0.000047
5	6	0	0.954211	-0.968013	0.000075
6	6	0	-0.397410	-1.372760	0.000121
7	1	0	-1.704145	1.752352	0.000023
8	1	0	1.704143	-1.752353	0.000073
9	6	0	0.593931	2.804127	0.000060
10	1	0	-0.338374	3.364913	0.000004
11	6	0	1.714044	3.579199	0.000152
12	1	0	1.539308	4.653050	0.000124
13	6	0	3.087020	3.187123	0.000272
14	6	0	3.687027	1.917746	0.000245
15	16	0	4.288527	4.468205	0.000453
16	6	0	5.123234	2.038499	0.000473
17	6	0	5.588314	3.318891	0.000565
18	1	0	5.776653	1.174460	0.000518
19	1	0	6.614092	3.661209	0.000722
20	5	0	2.968331	0.554057	0.000023
21	6	0	3.904006	-0.733605	-0.000180
22	6	0	4.341123	-1.310437	1.214286
23	6	0	4.340747	-1.310292	-1.214844

24	6	0	5.184473	-2.426710	1.196493
25	6	0	5.184138	-2.426545	-1.197451
26	6	0	5.621869	-3.000041	-0.000582
27	1	0	5.506726	-2.859274	2.141910
28	1	0	5.506147	-2.858956	-2.143020
29	6	0	-0.593933	-2.804128	0.000218
30	1	0	0.338372	-3.364914	0.000170
31	6	0	-1.714046	-3.579200	0.000361
32	1	0	-1.539310	-4.653051	0.000430
33	6	0	-3.087022	-3.187124	0.000423
34	6	0	-3.687029	-1.917748	0.000281
35	16	0	-4.288529	-4.468206	0.000616
36	6	0	-5.123235	-2.038501	0.000363
37	6	0	-5.588316	-3.318893	0.000547
38	1	0	-5.776655	-1.174461	0.000312
39	1	0	-6.614094	-3.661210	0.000638
40	5	0	-2.968333	-0.554059	0.000094
41	6	0	-3.904008	0.733603	-0.000116
42	6	0	-4.340878	1.310179	-1.214793
43	6	0	-4.340991	1.310550	1.214337
44	6	0	-5.184235	2.426452	-1.197409
45	6	0	-5.184362	2.426813	1.196535
46	6	0	-5.621859	3.000049	-0.000542
47	1	0	-5.506303	2.858810	-2.142983
48	1	0	-5.506547	2.859436	2.141947
49	6	0	3.897776	-0.731253	-2.542422
50	1	0	2.806586	-0.751927	-2.646890
51	1	0	4.206235	0.315617	-2.647747

52	1	0	4.322597	-1.288796	-3.381812
53	6	0	3.898745	-0.731430	2.542076
54	1	0	2.807514	-0.750418	2.646329
55	1	0	4.322546	-1.290070	3.381254
56	1	0	4.208860	0.314895	2.648019
57	6	0	6.558676	-4.185371	-0.000780
58	1	0	6.412494	-4.811195	-0.886503
59	1	0	7.608266	-3.864590	-0.000588
60	1	0	6.412315	-4.811627	0.884610
61	6	0	-3.898182	0.730930	-2.542373
62	1	0	-4.322262	1.289051	-3.381754
63	1	0	-2.806957	0.750470	-2.646613
64	1	0	-4.207729	-0.315597	-2.647951
65	6	0	-3.898358	0.731739	2.542127
66	1	0	-4.207537	-0.314878	2.647872
67	1	0	-2.807154	0.751702	2.646554
68	1	0	-4.322779	1.289897	3.381310
69	6	0	-6.558656	4.185386	-0.000791
70	1	0	-7.608249	3.864612	-0.001300
71	1	0	-6.412765	4.811308	0.884909
72	1	0	-6.411996	4.811541	-0.886203

Compound 9

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.349037	-2.153905	-0.451488
2	6	0	-1.762742	-0.852237	-0.034634
3	6	0	-0.687628	0.121328	0.174185
4	6	0	0.688685	-0.118108	-0.176005
5	6	0	0.953518	-1.371657	-0.792103
6	6	0	0.001363	-2.341722	-0.875020
7	1	0	-1.932513	1.590087	1.175236
8	6	0	-0.952905	1.375781	0.788223
9	6	0	1.764125	0.854836	0.034281
10	1	0	1.932649	-1.585036	-1.180899
11	1	0	0.275973	-3.304338	-1.296739
12	6	0	1.350539	2.156728	0.450608
13	6	0	-0.000621	2.345715	0.871189
14	1	0	-0.275707	3.308979	1.291075
15	5	0	-3.278202	-0.427255	0.024277
16	5	0	3.279272	0.428608	-0.022850
17	6	0	-2.104878	-3.384154	-0.502430
18	1	0	-1.486499	-4.243200	-0.752548
19	6	0	-3.407433	-3.695284	-0.265081
20	1	0	-3.664867	-4.750209	-0.329107
21	6	0	-4.482413	-2.803788	-0.014347
22	6	0	-4.491886	-1.402290	0.050993
23	16	0	-6.093333	-3.491539	0.118188

24	6	0	-5.853370	-0.934278	0.177742
25	6	0	-6.798319	-1.912960	0.238518
26	1	0	-6.107459	0.116607	0.218704
27	1	0	-7.869261	-1.802129	0.339741
28	6	0	2.107296	3.386348	0.503490
29	1	0	1.488770	4.246037	0.751009
30	6	0	3.411148	3.696158	0.271556
31	1	0	3.669359	4.750824	0.336745
32	6	0	4.486276	2.803605	0.025327
33	6	0	4.494228	1.402209	-0.042170
34	16	0	6.098690	3.489428	-0.098692
35	6	0	5.855648	0.932544	-0.163576
36	6	0	6.802154	1.910092	-0.218186
37	1	0	6.108549	-0.118612	-0.205432
38	1	0	7.873416	1.797997	-0.314519
39	6	0	3.751478	-1.098973	0.054694
40	6	0	4.284053	-1.784839	-1.065862
41	6	0	3.744940	-1.763363	1.302297
42	6	0	4.764738	-3.090828	-0.927652
43	6	0	4.243220	-3.067707	1.406008
44	6	0	4.753392	-3.754718	0.302940
45	1	0	5.160838	-3.602021	-1.803306
46	1	0	4.233371	-3.558065	2.377690
47	6	0	-3.752477	1.099350	-0.058982
48	6	0	-3.741410	1.761043	-1.308164
49	6	0	-4.283169	1.790050	1.059386
50	6	0	-4.235706	3.066429	-1.415717
51	6	0	-4.759851	3.097251	0.917248

52	6	0	-4.751087	3.755454	-0.316234
53	1	0	-4.215903	3.557245	-2.387011
54	1	0	-5.147706	3.615008	1.792691
55	6	0	3.205998	-1.082976	2.543537
56	1	0	3.672843	-0.104896	2.706771
57	1	0	2.126044	-0.911711	2.470273
58	1	0	3.386245	-1.689917	3.435298
59	6	0	4.322169	-1.129633	-2.432779
60	1	0	5.032920	-0.296361	-2.464648
61	1	0	4.615499	-1.845628	-3.205658
62	1	0	3.346092	-0.717845	-2.717418
63	6	0	-4.316044	1.142261	2.430031
64	1	0	-3.339391	0.731077	2.713499
65	1	0	-4.606193	1.862546	3.200125
66	1	0	-5.027395	0.309794	2.468957
67	6	0	-3.194493	1.079612	-2.545363
68	1	0	-2.114509	0.911030	-2.466877
69	1	0	-3.658339	0.100130	-2.708700
70	1	0	-3.372300	1.684228	-3.439192
71	6	0	-5.306105	5.153177	-0.458377
72	1	0	-4.823478	5.694539	-1.277748
73	1	0	-6.382610	5.135317	-0.671399
74	1	0	-5.168678	5.734341	0.458828
75	6	0	5.252910	-5.174849	0.427016
76	1	0	5.606821	-5.387542	1.440292
77	1	0	4.459092	-5.898626	0.202108
78	1	0	6.075422	-5.372867	-0.267477

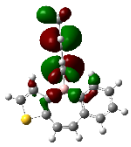
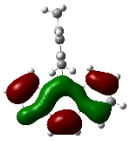
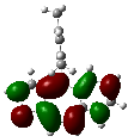
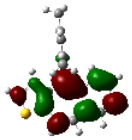
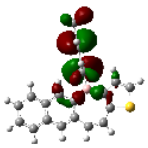
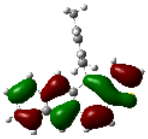
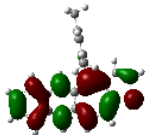
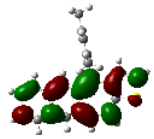
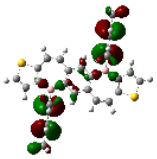
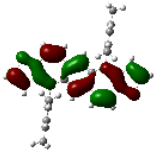
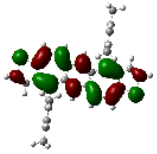
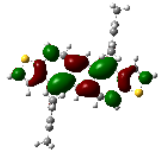
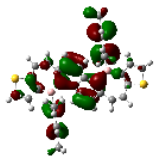
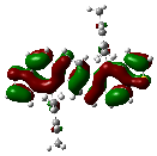
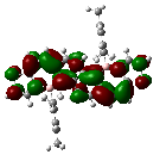
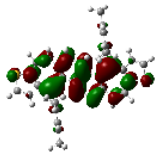
	HOMO -1	HOMO	LUMO	LUMO +1
6				
7				
8				
9				

Figure S-49. Molecular Orbital Contour Plots

	HOMO -1	HOMO	LUMO	LUMO +1
6	-5.87	-5.68	-1.71	-1.40
7	-5.81	-5.60	-1.83	-1.58
8	-5.92	-5.39	-2.19	-1.94
9	-5.81	-5.46	-2.11	-1.79

Figure S-50. Calculated energy levels (eV)

5. Photophysical Data

	λ_{abs} (nm)	logε (cm^{-1} M^{-1})	λ_{em} (nm)	QY (%)
1 [a]	262	5.09	400	70
2 [a]	280	4.89	445	39
3 [a]	314	4.19	477	1
4 [b]	286	4.54	456	71
5 [c]	266	5.40	392	6
6 ■	256	4.45	384	6
7 ■	308	4.33	431	6
8 ■	302	4.56	469	8
9 ■	337	4.53	452	19

[a] Ref[2] [b] Ref[3] [c] Ref[4] [d] Ferrocene as common reference potential

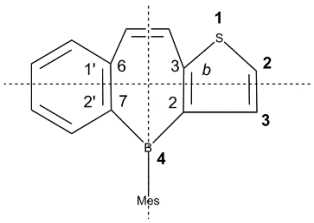
Figure S-51. Full photophysical data

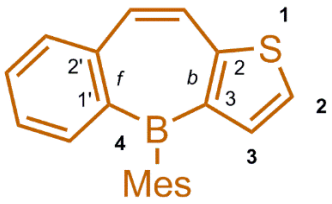
6. Nomenclature

Below are our best interpretations of the 'Preferred IUPAC Name' for each of the compounds along with the 'Borepin Focused Name.'

6 – IUPAC: 4-mesitylbenzo[1',2':6,7]borepino[3,2-*b*]thiophene

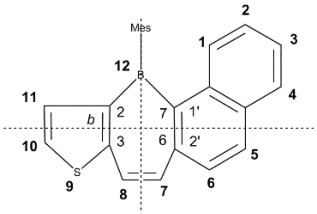
6 – Borepin: *B*-mesitylbenzo[1',2'-*f*]thieno[3,2-*b*]borepin

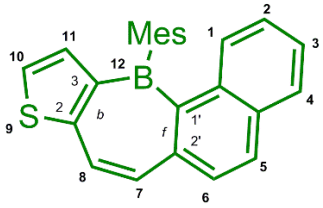




7 – IUPAC: 12-mesitylnaphtho[2',1':6,7]borepino[3,2-*b*]thiophene

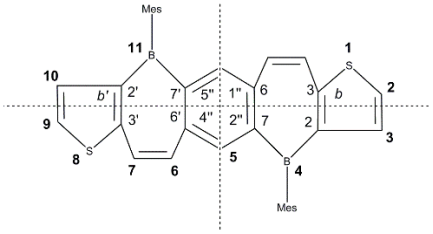
7 – Borepin: *B*-mesitylnaphtho[1',2'-*f*]thieno[3,2-*b*]borepin

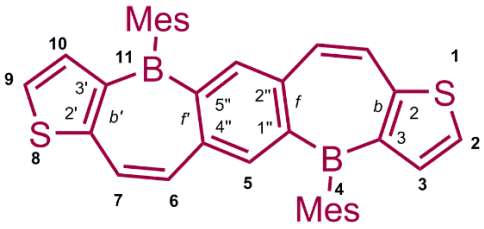




8 – IUPAC: 4,11-dimesitylbenzo[1'',2'':6,7;4'',5'':6',7']diborepino[3,2-*b*:3',2'-*b*']dithiophene

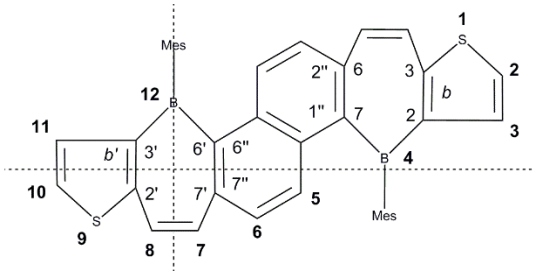
8 – Borepin: *B*,*B'*-dimesitylbenzo[1'',2''-*f*;5'',4''-*f'*]dithieno[3,2-*b*;3',2'-*b'*]diborepin

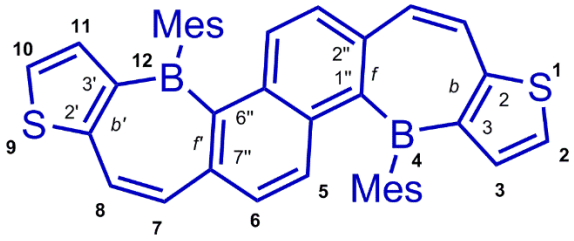




9 – IUPAC: 4,12-dimesitylnaphtho[1'',2'':7,6;6'',7'':6',7']diborepino[3,2-*b*:3',2'-*b*']dithiophene

9 – Borepin: *B*,*B'*-dimesitylnaphtho[1'',2''-*f*;6'',7''-*f'*]dithieno[3,2-*b*,3',2'-*b'*]diborepin

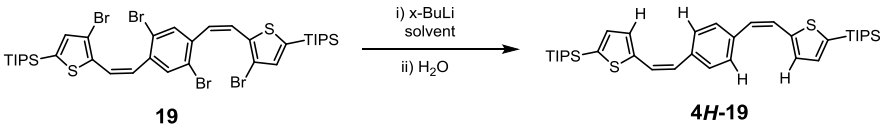




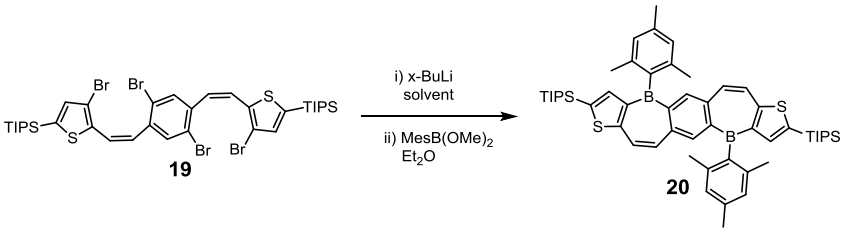
7. Borepin Formation Information

Quenching with H_2O was an effective method for evaluating lithium-halogen exchange. A series of *t*-BuLi exchanges followed by quenching with H_2O demonstrated the need for a majority inert solvent (hexane, benzene) with minority lithiate solubilizing solvent (THF, Et_2O). Despite successful protonation of **19** in hexane:Et_2O (95:5), formation of **20** only occurred in benzene:Et_2O (95:5) possibly due to the complex nature of the mixed aggregate. Et_2O as the minority solvent led to the desired product but THF did not, which could be due to the difference in solubility of the byproduct LiOMe in those two solvents.[5]

H_2O quench:



Borepin formation:



Solvent(s)	x-BuLi	Temp (° C)	H_2O quench (**4*H*-19**)	Borepin Formation (**20**)
THF	tert	-78	no	
THF	sec	-78	no	
THF	normal	-78	no	
Et_2O	tert	-78	some	
Hexane/Et_2O	tert	-78	Yes	No
Hexane/THF	tert	-78	no	
Hexane/Et_2O	tert	Reflux	no	
Benzene/Et_2O	tert	5	Yes	Yes

Figure S-52. Lithium-halogen exchange trails

8. Proton NMR peak assignments

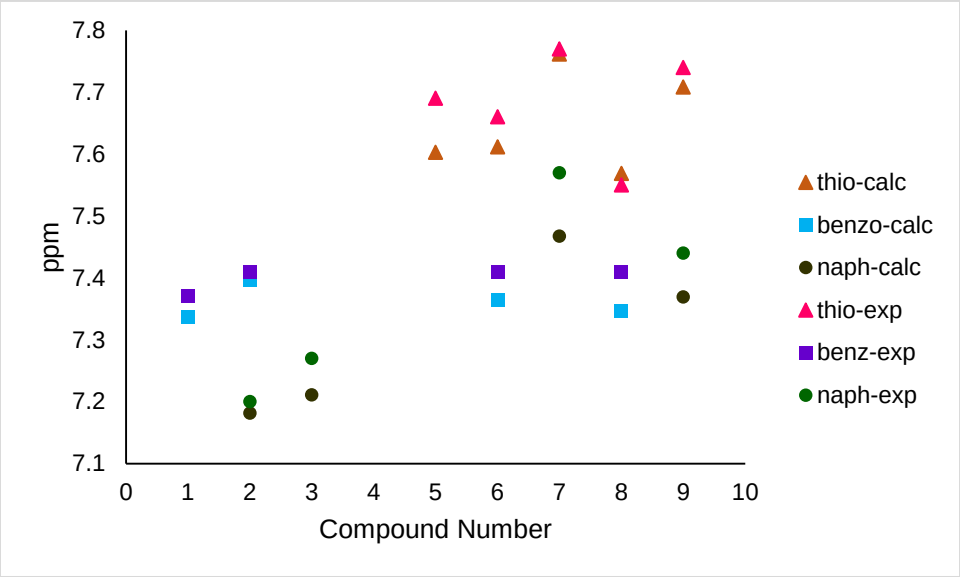


Figure S-53. Comparison between DFT calculated and experimental $^{1}H_{\gamma}$ NMR resonances. Isotropic values were subtracted from an average of the tetramethylsilane proton NMR values (calculated at the same level of theory on a geometry optimized structure) to give the "ppm-calc" values.

9. Long Term storage of 8

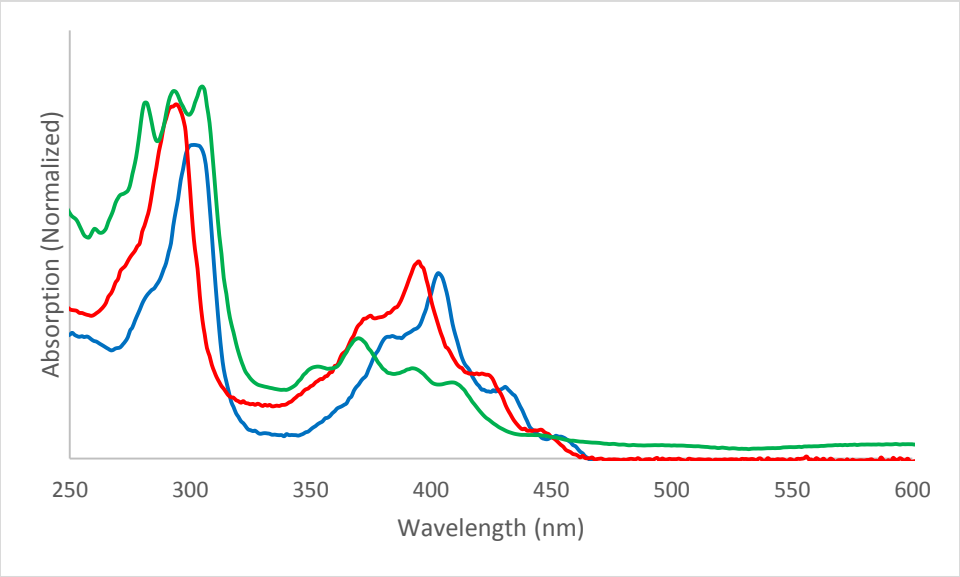


Figure S-54. UV-vis spectra of compound **8** freshly prepared (blue), stored as a solid for 6 months (red), or stored dissolved in $CHCl_3$ for 6 months (green).

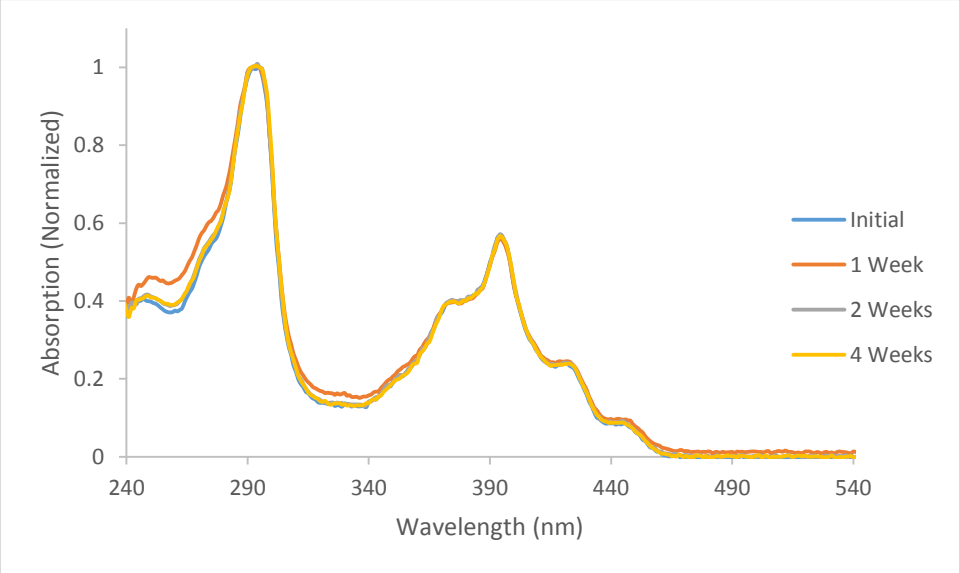


Figure S-55. UV-vis spectra of compound **8** freshly prepared and sequential samples stored in the solid state, suspended in $CHCl_3$.

8. References

1. Sheldrick, G., *Acta Crystallographica Section A* **2008,** *64* (1), 112-122.
2. Mercier, L. G.; Piers, W. E.; Parvez, M., *Angew. Chem. Int. Ed.* **2009,** *48* (33), 6108-6111.
3. Caruso, A.; Tovar, J. D., *Org. Lett.* **2011,** *13* (12), 3106-3109.
4. Levine, D. R.; Siegler, M. A.; Tovar, J. D., *J. Am. Chem. Soc.* **2014,** *136* (19), 7132-7139.
5. Wang, X.-Y.; Narita, A.; Feng, X.; Müllen, K., *J. Am. Chem. Soc.* **2015,** *137* (24), 7668-7671.