Supporting Information

BODIPY-phenylacetylene macrocycle dye motifs for enhanced light-harvesting and energy transfer applications

M. Yousaf, A. J. Lough, E. Schott and B. D. Koivisto*

Ryerson University, Toronto, Ontaraio M5B 2K3.

E-mail: bryan.koivisto@ryerson.ca

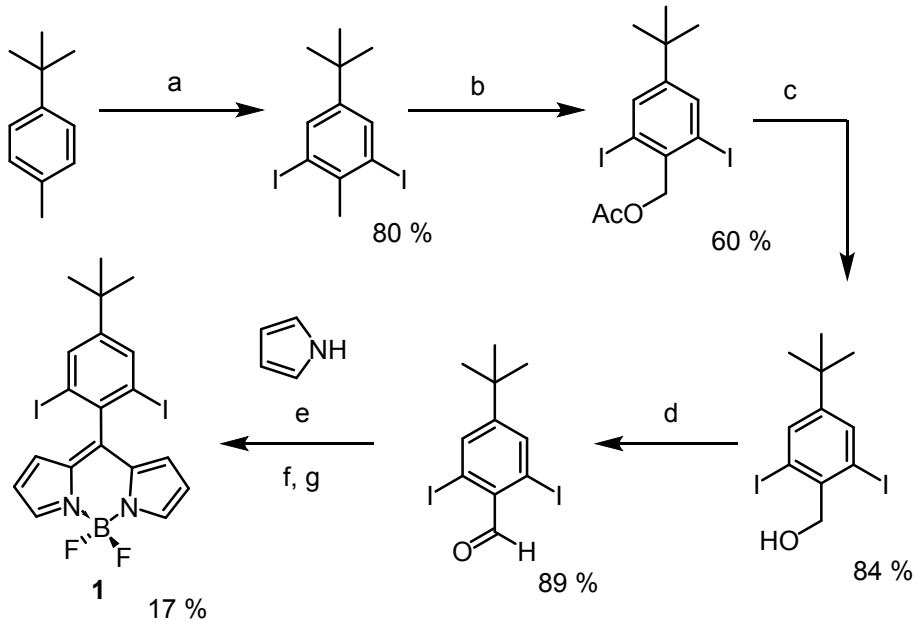
Tel: +1–416–979–5313; Fax: +1–416–979–5044

Table of Contents

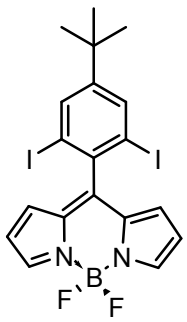
General Considerations

All reagents were purchased from Aldrich except $PdCl_2$ (Pressure Chemical Co., Pittsburg, PA). $PdCl_2$ was reacted with PPh_3 to make catalyst $PdCl_2(PPh_3)_2$. Purification by column chromatography was carried out using silica (Silicycle: ultrapure flash silica P60). Analytical thin-layer chromatography was performed on aluminum-backed sheets precoated with silica 60 F254 adsorbent (0.25 mm thick; Silicycle) and visualized under UV light. RT refers to room temperature. Routine ^{1}H, ^{13}C, $^{11}B\{^{1}H\}$ and ^{19}F NMR spectra were recorded at 400, 100, 128 and 376 MHz, respectively, on a Bruker AV 400 instrument at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) from low to high field and referenced to a residual non-deuterated solvent ($CHCl_3$) for ^{1}H and ^{13}C nuclei and BF_3•OEt_2 (^{11}B nucleus; δ = 0 ppm) C_6F_6 (^{19}F nucleus; δ = 0 ppm). Standard abbreviations indicating multiplicity are used as follows: s = singlet; d = doublet; q = quartet and br = broad. High resolution mass spectroscopy (HRMS) results were obtained from Queen University, Kingston Ontario. Electron impact (EI) mass spectrometry and Electrospray ionization (ESI) techniques were used for the ionization; time of flight (TOF) was used for analysis. UV-Vis data was taken using Cary Series UV-Vis-NIR Spectrophotometer from Agilent Technologies and dichloromethane (having the onset peak at 230 nm) was used as a solvent. The GAUSSIAN 09 computational package[1] was used to perform ground-state geometry optimization calculations employing Becke's three-parameter hybrid exchange functional and the Lee–Yang-Parr non-local correlation functional B3LYP[2] and 6-311G* basis set was used for all the atoms. Time-dependent density functional theory calculations were also performed using this methodology, and the first 200 singlet excited states were calculated. Calculations by the first-principles method were used to obtain accurate excitation energies and oscillator strengths. Solvent was modelled with the polarizable continuum model using acetonitrile as the solvent.[3]

Synthesis



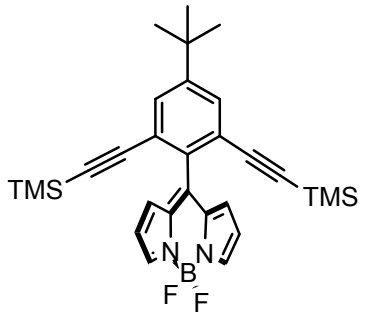
Scheme 1 – Synthesis of BODIPY **1.** Reaction conditions: a) KIO_4, I_2, $CHCl_3$, AcOH, H_2SO_4, H_2O, 90°C, 24 h.[4] b) $KMnO_4$, Ac_2O, AcOH, H_2SO_4, 40°C, 24 h.[2] c) K_2CO_3, MeOH, 25°C, 3 h.[5] d) PCC, 1, 2-dichloromethane, 25°C, 12 h.[5] e) TFA, 25°C, 12 h. f) DDQ, 25°C, 3 h. g) DiPEA, BF_3OEt_2, 25°C, 6 h.



1

Synthesis of BODIPY (1). 2,6-diiodo-4-*tert*-butylbenzaldehyde (1.0 g, 2.42 mmol, 1 eq) was added to a solution of pyrrole (0.36 g, 5.3 mmol, 2.2 eq) in dry DCM (100 mL); followed by a catalytic amount of trifluoroacetic acid (TFA). After stirring overnight 2,3-

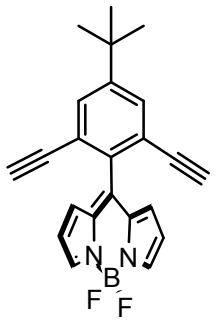
dichloro-5,6-dicyanobenzoquinone (0.82 g, 1.5 eq) was added to the resulting reddish solution, and the mixture was stirred for an addition 3 hours. Once TLC analysis revealed the completion of oxidation, *N,N*-diisopropylethylamine (DIPEA, 3 mL) and boron trifluoride diethyletherate (BF_3OEt_2, 3.5 mL) were added. After stirring for 6 hours, the mixture was concentrated in *vacuo*, redissolved in EtOAc and washed with water. The water layer was extracted with EtOAc and the combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography (toluene, R_f = 0.42) yielded the product as orange powder (237 mg, 17 %). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.96 (s, 2H), 7.95 (s, 2H), 6.71 (d, *J*=4.0 Hz, 2H), 6.52 (d, *J*=4.0 Hz, 2H), 1.36 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 156.1, 150.1, 145.2, 138.7, 136.6, 134.5, 130.0, 119.1, 96.1, 34.7, 31.0. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -145.85 (q). ^{11}B NMR ($CDCl_3$, 128 MHz): δ = 0.43 (t, J_{FB} = 28 Hz). HRMS (ESI-TOF): *m*/*z* 556.95364 ([M–F]$^-$), calcd for $C_{19}H_{17}BFI_2N_2$: *m*/*z* 556.95527.



2

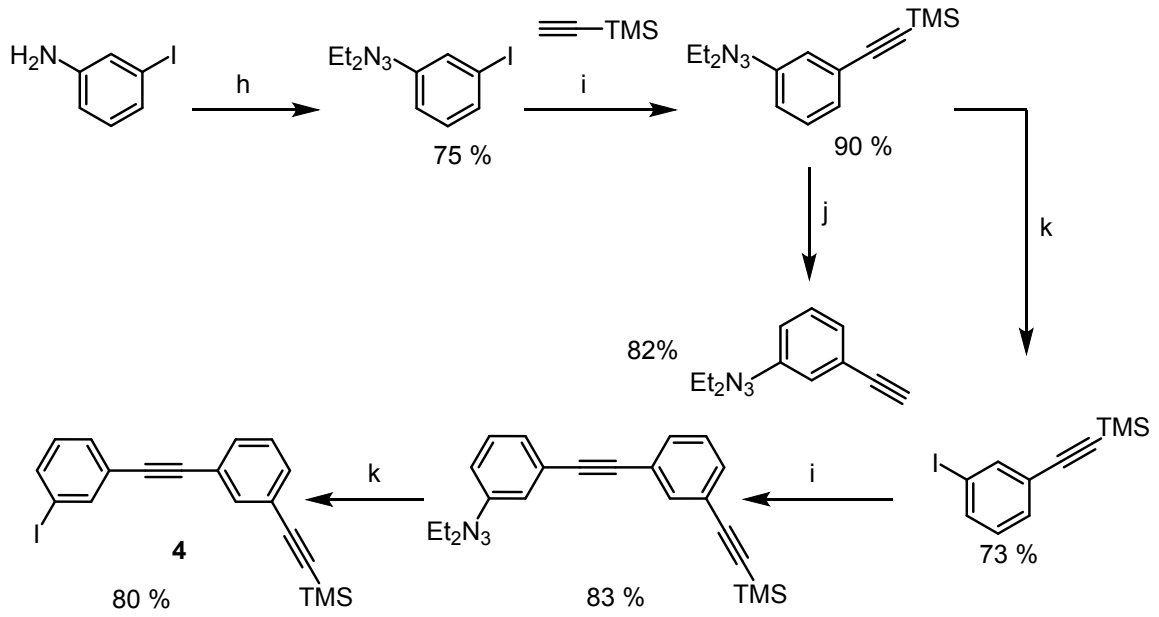
Synthesis of 2. In a 250 mL flask, BODIPY derivative **1** (440 mg, 0.700 mmol) was dissolved in THF:NEt_3 (4.5 mL, 2:1), followed by the addition of $PdCl_2(PPh_3)_2$ (48 mg, 0.070 mmol) and CuI (27 mg, 0.140 mmol) and TMS-acetylene (175 mg, 1.72 mmol). The mixture was stirred overnight at RT. The solution was filtered, the solvent removed, redissolved in EtOAc, and washed with NH_4Cl solution. The extract was then washed with brine, dried over $MgSO_4$, and refiltered. The solvent was evaporated in *vacuo*, and the residue was chromatographed using hex:DCM (2:1, R_f = 0.40) to yield the product as a greenish solid (282 mg, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.90 (s, 2H), 7.56 (s,

2H), 6.78 (d, *J*=4.0 Hz, 2H), 6.46 (d, *J*=4.0 Hz, 2H), 1.36 (s, 9H), -0.04 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.6, 144.9, 144.0, 136.4, 135.6, 131.0, 129.2, 123.6, 118.0,118.0, 102.4, 100.5, 34.8, 31.0, -0.6. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -145.45 (q). ^{11}B NMR ($CDCl_3$, 128 MHz): δ = 0.45 (t, J_{FB} = 28 Hz). HRMS (EI-TOF): *m*/*z* 516.2411 ([MH]$^+$), calcd for $C_{29}H_{35}BF_2N_2Si_2$: *m*/*z* 516.2400.

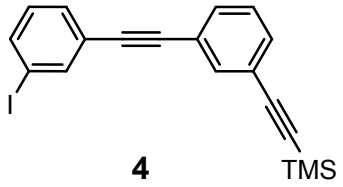


3

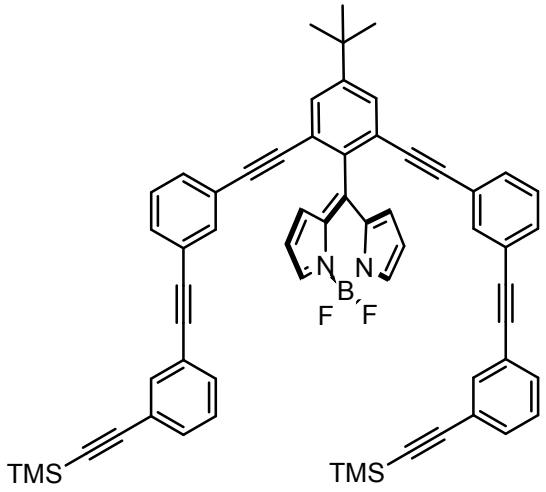
Synthesis of 3. BODIPY derivative **2** (0.16 g, 0.30 mmol) was dissolved in MeOH:THF (8 mL, 1:1) and stirred with excess KF (0.09 g, 5 eq). The reaction was left to stir overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and the solvent evaporated under reduced pressure. The residue was chromatographed using hex:DCM (2:1, R_f = 0.29) as eluent to give product as a red solid (82 mg, 73%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.92 (s, 2H), 7.65 (s, 2H), 6.75 (d, *J*=4.0 Hz, 2H), 6.48 (d, *J*=4.0 Hz, 2H), 2.99 (s, 2H), 1.38 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.8, 144.6, 143.9, 135.6, 130.7, 130.5, 122.7, 118.5, 82.1, 80.7, 34.8, 31.0. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -145.71 (q). ^{11}B NMR ($CDCl_3$, 128 MHz): δ = 0.48 (t, J_{FB} = 28 Hz). HRMS (EI-TOF): *m*/*z* 372.1605 ([MH]$^+$), calcd for $C_{23}H_{19}BF_2N_2$: *m*/*z* 372.1609.



Scheme 2 – Synthesis of **4.** Reaction conditions. h) $NaNO_2$, HCl, K_2CO_3, $HNEt_2$, 0°C, 30 min, 25°C, 1h.[6] i) CuI, $PdCl_2(PPh_3)_2$, THF, NEt_3, 25°C, 16 h.[6] j) KF, THF, MeOH, 25°C, 12 h. k) MeI, 120°C, 6 h.[6-7]

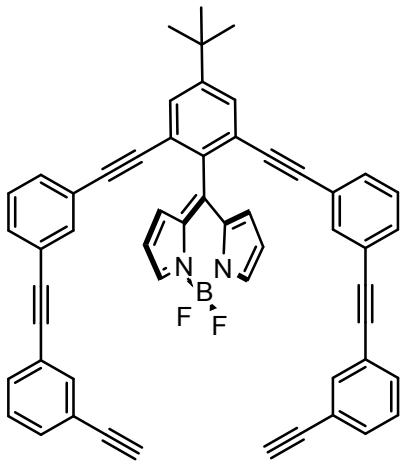


Synthesis of 4.[6] 1-[3-[2-(Trimethylsilyl)ethynyl]phenyl]-3,3-diethyltriazene (1.0 g, 2.68 mmol) and methyl iodide (5 mL) were sealed in a microwave tube under nitrogen and heated to 120°C for 12 hours. The reaction mixture was quenched with water; extracted with dichloromethane, dried with $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the pure product was isolated by column chromatography using pure hexanes (R_f = 0.40). The product was a yellow viscous liquid (858 mg, 80%). Spectroscopic data of **4** agreed with the previously reported literature. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.88 (t, 1H), 7.68-7.64 (m, 2H), 7.48-7.42 (m, 3H), 7.31-7.27 (m, 1H), 7.10-7.06 (m, 1H), 0.27 (s, 9H).



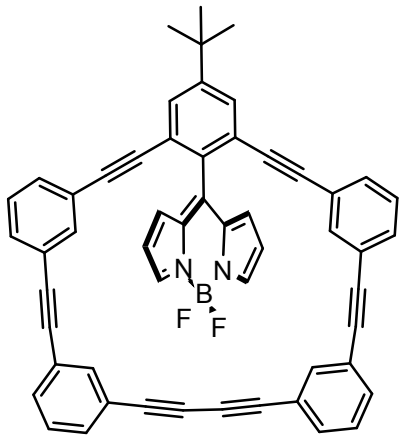
5

Synthesis of 5. To a solution of BODIPY derivative **3** (100 mg, 0.258 mmol) in THF:NEt_3 (30 mL; 2:1), $PdCl_2(PPh_3)_2$ (18 mg, 0.0258 mmol) and CuI (10 mg, 0.052 mmol) were added as catalysts followed by the addition of **4** (208 mg, 0.516 mmol). The mixture was stirred at RT overnight. The solution was filtered, the solvent removed from the filtrate, and dissolved in EtOAc and washed with NH_4Cl solution. The extract was then washed with brine, dried over $MgSO_4$, and filtered again. The solvent was evaporated in *vacuo*, and the residue was chromatographed using hex:DCM (1:1, R_f = 0.26) to give the product as a red solid (196 mg, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.98 (s, 2H), 7.71-7.64 (m, 4H), 7.48-7.37 (m, 8H), 7.31-7.29 (m, 2H), 7.24-7.20 (m, 2H), 7.09-7.06 (m, 2H), 6.92-6.91 (d, *J*=4.0 Hz, 2H), 6.51-6.50 (d, *J*=4.0 Hz, 2H), 1.45 (s, 9H), 0.26 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 153.0, 144.5, 135.6, 135.1, 134.7, 134.4, 131.7, 131.6, 131.5, 131.1, 129.3, 128.6, 128.5, 128.4, 123.7, 123.5, 123.5, 123.3, 123.3, 122.7, 118.5, 104.1, 95.0, 93.9, 89.1, 89.0, 87.8, 34.9, 31.1, -0.1. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -145.48 (q). ^{11}B NMR ($CDCl_3$, 128 MHz): δ = 0.65 (t, J_{FB} = 28 Hz). HRMS (ESI-TOF): *m*/*z* 897.3664 ([M–F]$^-$), calcd for $C_{61}H_{51}BFN_2Si_2$: *m*/*z* 897.3662.



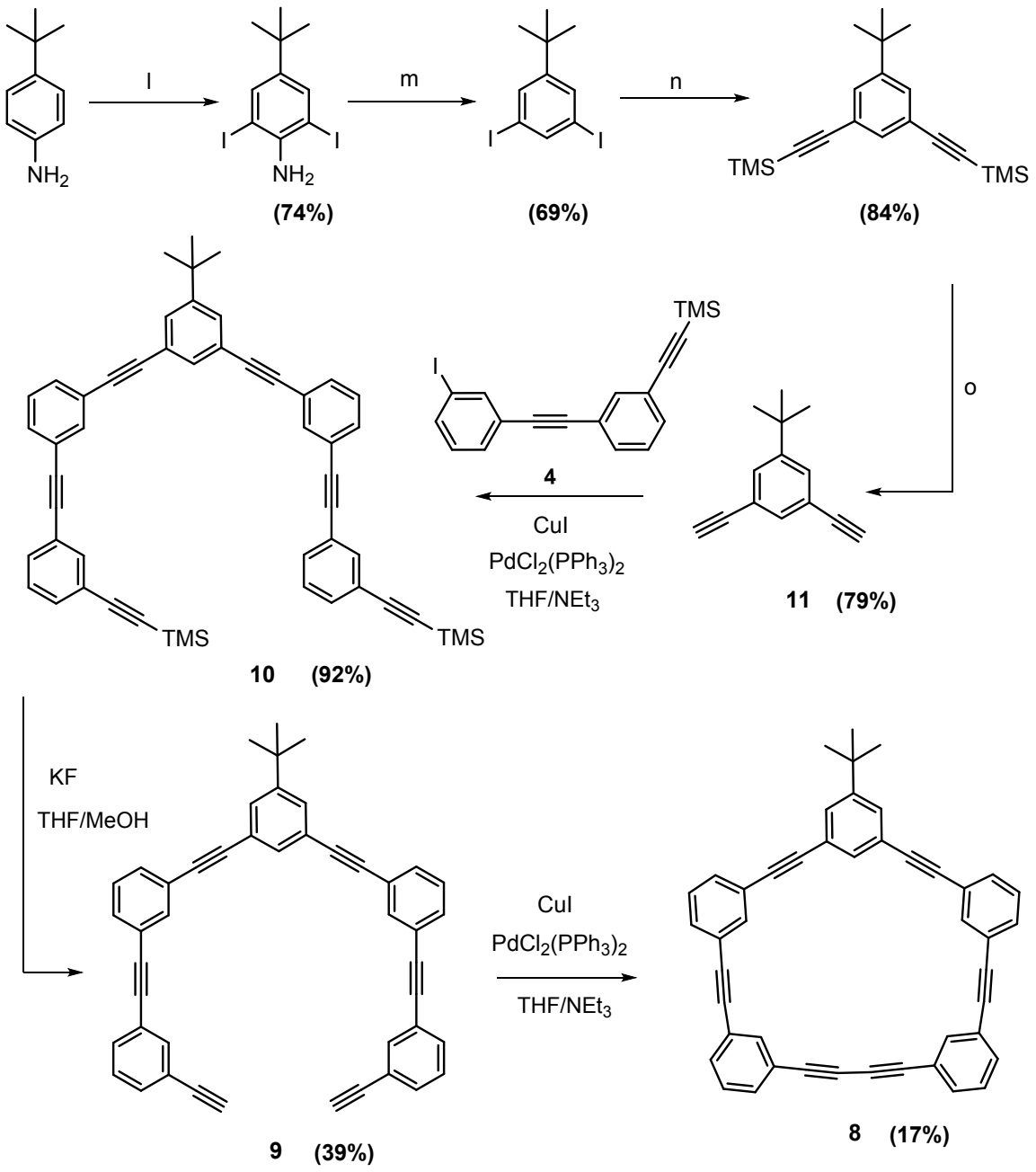
6

Synthesis of 6. Compound **5** (150 mg, 0.161 mmol) was dissolved in MeOH:THF (50 mL; 1:1) and reacted with excess KF (50 mg, 0.803 mmol). The reaction was left to stir overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and the solvent evaporated under reduced pressure. The residue was chromatographed using hex: DCM (1:1, R_f = 0.33) as an eluent to give product as a red viscous liquid (88 mg, 71%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.99 (s, 2H), 7.69-7.66 (m, 4H), 7.53-7.45 (m, 4H), 7.41-7.38 (m, 4H), 7.34-7.30 (m, 2H), 7.25-7.21 (m, 2H), 7.10-7.08 (m, 2H), 6.92-6.91 (d, *J*=4.0 Hz, 2H), 6.51-6.50 (d, *J*=4.0 Hz, 2H), 3.11 (s, 2H), 1.45 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 153.0, 144.5, 135.6, 135.1, 134.5, 132.0, 131.6, 131.1, 129.2, 128.6, 128.5, 128.5, 123.7, 123.5, 123.4, 123.2, 122.7, 122.5, 93.9, 89.1, 89.0, 87.9, 82.8, 77.9, 35.0, 31.1. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -145.44 (q). ^{11}B NMR ($CDCl_3$, 128 MHz): δ = 0.66 (t, J_{FB} = 28 Hz). HRMS (EI-TOF): *m*/*z* 772.2881 ([MH]$^+$), calcd for $C_{55}H_{35}BF_2N_2$: *m*/*z* 772.2861.

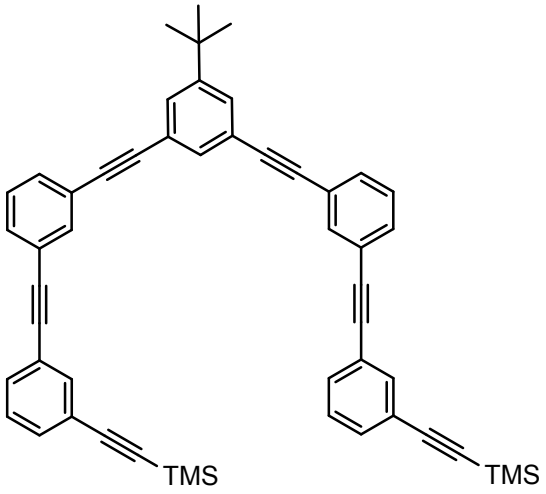


7

Synthesis of 7. BODIPY pre-macrocycle **6** (93 mg, 0.118 mmol) was dissolved in THF:NEt_3 (120 mL, 2:1) and sparged with N_2 for 15 minutes. $PdCl_2(PPh_3)_2$ (8.3 mg, 0.012 mmol) and CuI (4.5 mg, 0.024 mmol) were added as catalysts and the mixture was stirred at RT overnight. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc, and washed with NH_4Cl solution. The extract was then washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in *vacuo*, and the residue was chromatographed using hex:DCM (2:1, R_f = 0.30) to give the product as a dark red solid (14 mg, 15%). ^{1}H NMR $CDCl_3$, 400 MHz): δ = 8.15 (s, 2H), 8.12 (s, 2H), 7.69 (s, 2H), 7.44- 7.39 (m, 4H), 7.36-7.29 (m, 6H), 7.24-7.22 (m, 2H), 7.14 (s, 2H), 6.95-6.94 (d, *J*=4.0 Hz, 2H), 6.50-6.49 (d, *J*=4.0 Hz, 2H), 1.46 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.9, 144.7, 140.2, 137.4, 135.6, 131.1, 130.3, 130.2, 130.0, 129.7, 129.1, 128.4, 128.2, 123.8, 123.8, 123.6, 122.8, 122.7, 118.6, 118.6, 93.9, 89.8, 89.7, 88.2, 82.4, 75.3, 34.9, 31.1. ^{19}F NMR ($CDCl_3$, 376.5 MHz,): δ = -145.86 (q). ^{11}B NMR ($CDCl_3$, 128 MHz): δ = 0.83 (t, J_{FB} = 28 Hz). HRMS (EI-TOF): *m*/*z* 770.2701 ($[MH]^+$), calcd for $C_{55}H_{33}BF_2N_2$: *m*/*z* 770.2705.

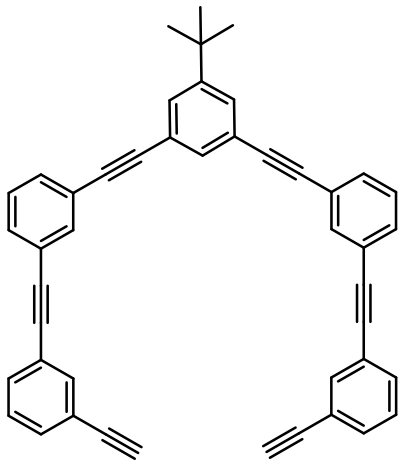


Scheme 4 – Synthesis of controlled macrocycle **8.** Reaction conditions. l) KI, H_2O_2, H_2SO_4, MeOH, 25°C, 12 h.[8] m) $NaNO_2$, H_2SO_4, EtOH, Reflux, 8 h.[9] n) Ethynyltrimethylsilane, CuI, $PdCl_2(PPh_3)_2$, THF/NEt_3 (2:1), 25°C, 12 h.[9] o) KF, THF/MeOH (1:1), 25°C, 12 h.[9]



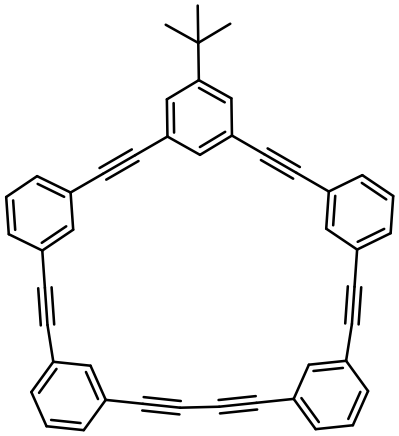
10

Synthesis of 10. To a solution of **11** (0.307 g, 1.684 mmol) in THF:NEt_3 (20 mL; 2:1), $PdCl_2(PPh_3)_2$ (18 mg, 0.0258 mmol) and CuI (10 mg, 0.052 mmol) were added, followed by the addition of **4** (1.30 g, 3.536 mmol). The mixture was stirred at RT overnight. The solution was filtered, the solvent removed from the filtrate, and dissolved in EtOAc and washed with NH_4Cl solution. The extract was then washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using hex:EtOAc (19:1, R_f = 0.6) to give the product as a light-yellow solid (1.144 g, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73 (t, *J*=1.2 Hz, 2H), 7.68 (t, *J*=1.2 Hz, 2H), 7.55-7.43 (m, 11H), 7.37-7.33 (t, *J*=7.6 Hz, 2H), 7.32-7.28 (t, *J*=7.6 Hz, 2H),1.37 (s, 9H), 0.27 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.7, 134.7, 131.8, 131.7, 131.5, 131.5, 131.4, 129.0, 128.5, 128.4, 123.6, 123.6, 123.5, 123.3, 123.0, 104.1, 95.1, 89.7, 89.1, 89.1, 88.5, 34.7, 31.1, -0.1. HRMS (ESI-TOF): *m*/*z* 727.3257 ($[M+H]^+$), calcd for $C_{52}H_{47}Si_2$: *m*/*z* 727.3222.



9

Synthesis of 9. Compound **10** (1.144 g, 1.573 mmol) was dissolved in MeOH:THF (20, mL, 1:1) and reacted with excess KF (0.75 g, 7.866 mmol). The reaction was left to stir overnight at RT. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was dried over $MgSO_4$, filtered and the solvent evaporated under reduced pressure. The residue was chromatographed using hex: EtOAc (15:1, R_f = 0.4) as an eluent to give product as an off-white solid (232 mg, 25%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73 (s, 2H), 7.68 (s, 2H), 7.55-7.46 (m, 11H), 7.37-7.30 (m, 4H), 3.11 (s, 2H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.8, 135.2, 134.7, 132.0, 131.9, 131.9, 131.5, 131.4, 129.0, 128.6, 128.5, 123.6, 123.4, 123.4, 123.0, 122.6, 89.8, 89.2, 89.0, 88.5, 82.7, 77.9, 34.8, 31.1. HRMS (ESI-TOF): *m*/*z* 583.2454 ($[M+H]^+$), calcd for $C_{46}H_{31}$: *m*/*z* 583.2426.



8

Synthesis of 8. Pre-macrocycle **9** (78 mg, 0.134 mmol) was dissolved in THF:NEt_3 (130 mL, 2:1) and sparged with N_2 for 15 minutes. $PdCl_2(PPh_3)_2$ (9.0 mg, 0.013 mmol) and CuI (5.0 mg, 0.027 mmol) were added as catalysts and the mixture was stirred at RT overnight. The solution was filtered, the solvent removed from the filtrate, dissolved in EtOAc, and washed with NH_4Cl solution. The extract was then washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated *in vacuo*, and the residue was chromatographed using hex:Et_2O (9:1, R_f = 0.63) to give the product as a pink solid (13.5 mg, 17%). ^{1}H NMR $CDCl_3$, 400 MHz): δ = 7.97 (s, 2H), 7.85 (s, 2H), 7.69 (s, 1H), 7.54-7.44 (m, 8H), 7.37-7.30 (m, 6H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.8, 139.5, 136.8, 133.0, 130.8, 130.6, 130.1, 129.8, 128.7, 128.6, 128.5, 123.8, 123.7, 123.3, 123.1, 122.3, 90.2, 90.0, 89.4, 88.6, 82.5, 75.2, 34.8, 31.2. HRMS (EI-TOF): *m*/*z* 580.2187 ($[MH]^+$), calcd for $C_{46}H_{28}$: *m*/*z* 580.2191.

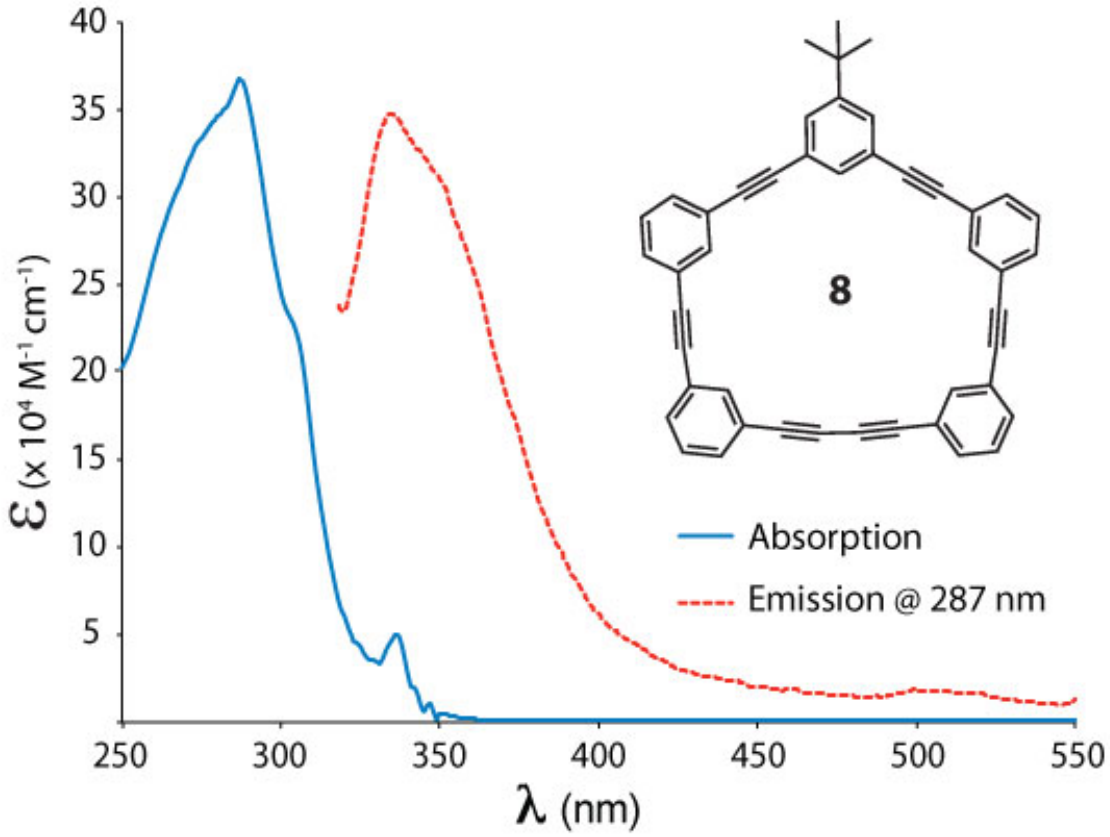


Figure S1. Absorption and emission of controlled macrocycle **8.**

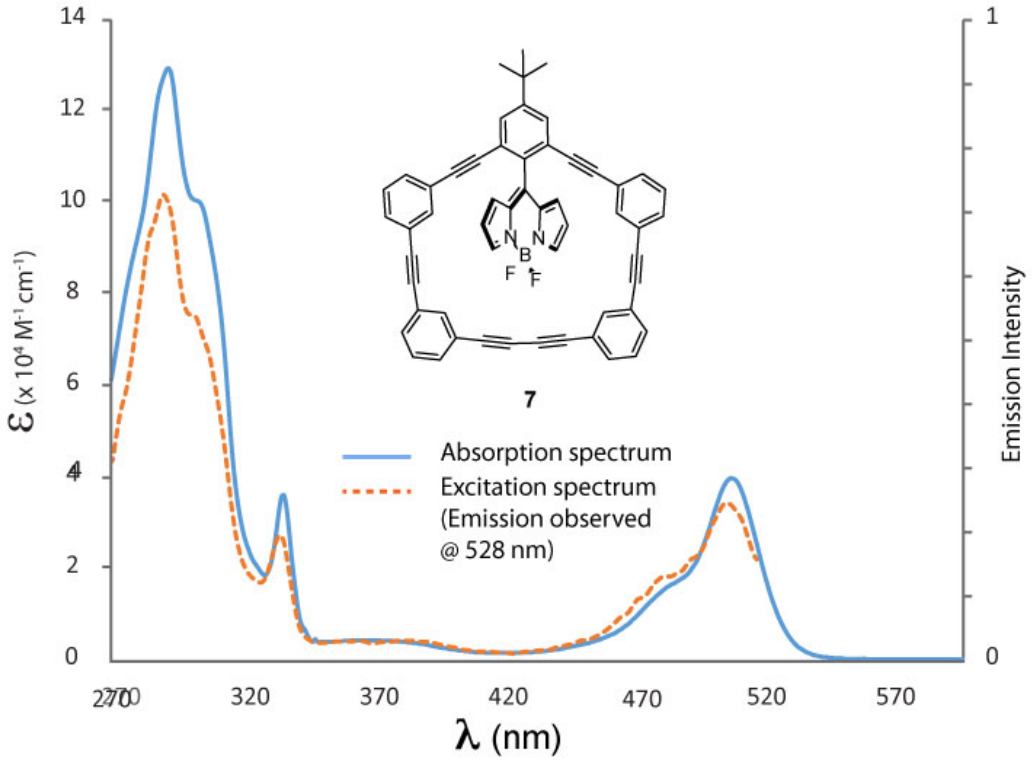


Figure S2. Absorption and excitation (emission observed @ 528nm) spectra of **7** in DCM.

Table S1. Absorption and Emission Data for the BODIPY fluorophore in benchmark molecule **1** and macrocycle derivative **7**.

Compound	***Absorption*[a]**		***Fluorescence*[b]**	
	λ_{max} *(nm)*	*(ε×10⁴ M⁻¹cm⁻¹)*	λ_{em} *(nm)*	Quantum Yield[c]
1	515	3.5	533	0.12
7	510	4.0	528	0.89

[a] Low energy absorptions of BODIPY in DCM from UV-Vis. [b] Measurements were made in DCM (dichloromethane). [c] Quantum yield for BODIPY (**1**) and BODIPY-macrocycle (**7**), were determined at 22°C relative to Rhodamine 6G in ethanol (QY = 0.95) using a Luminescence Spectrophotometer LS50B (Perkin Elmer).

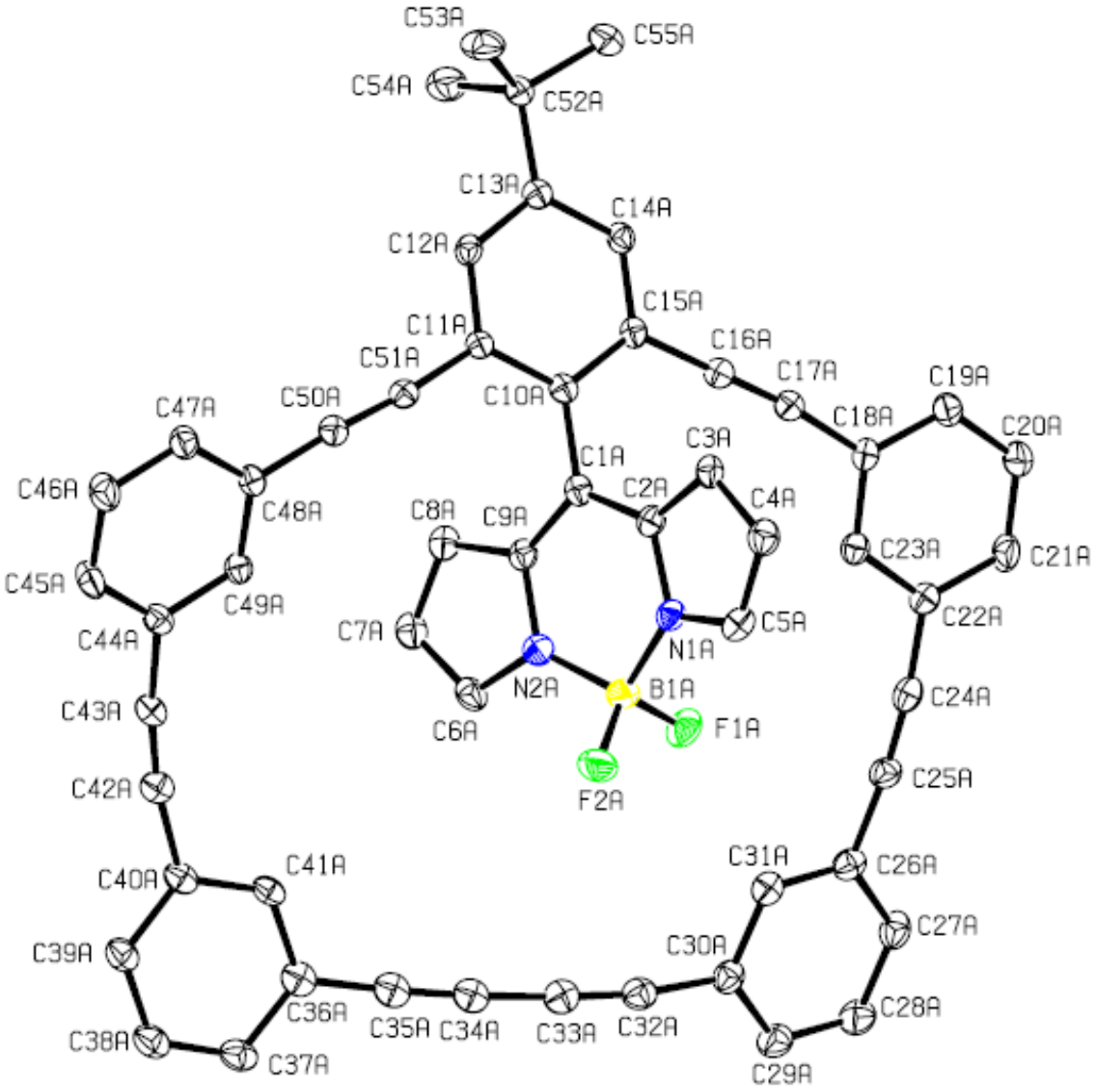
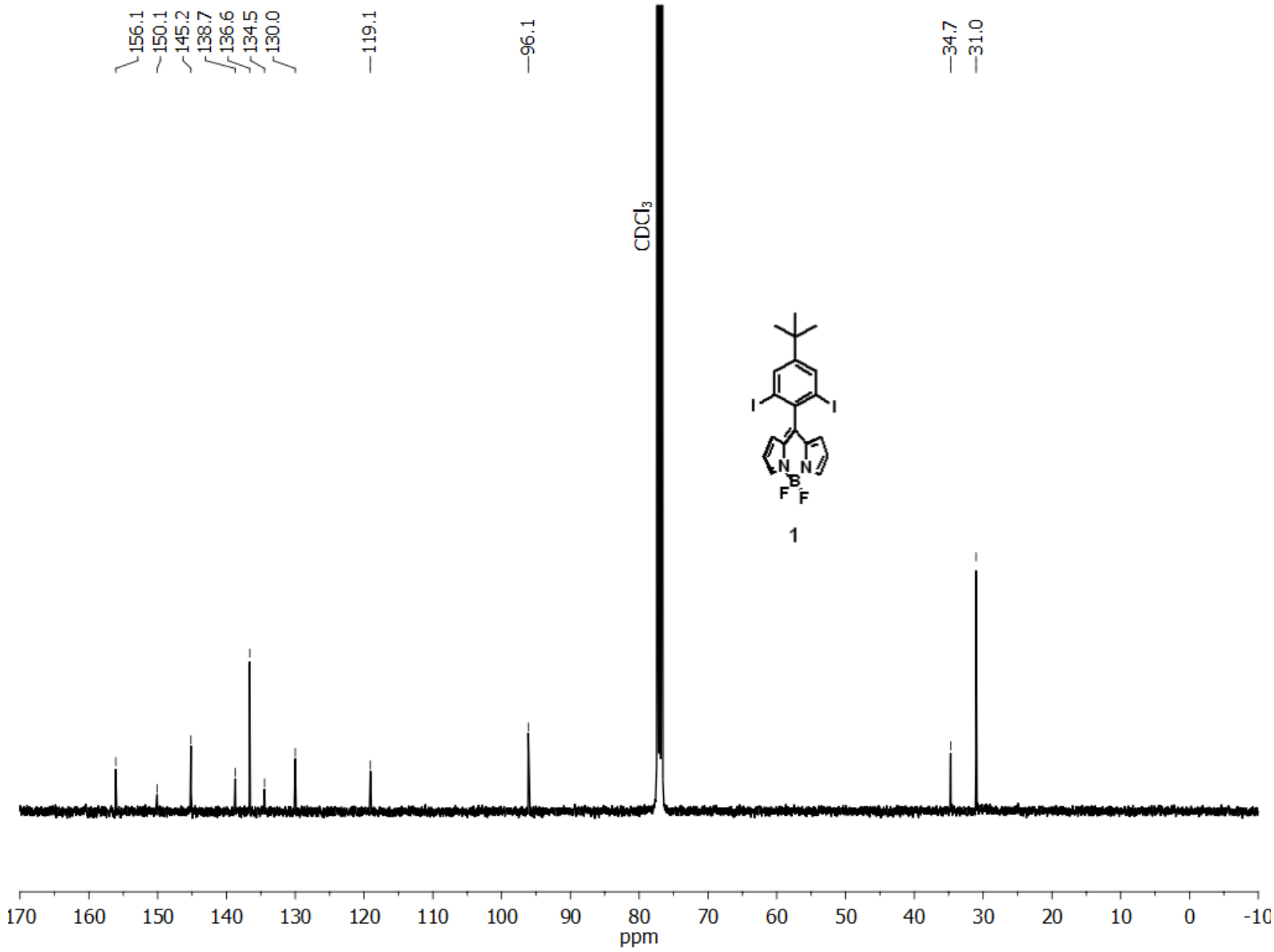
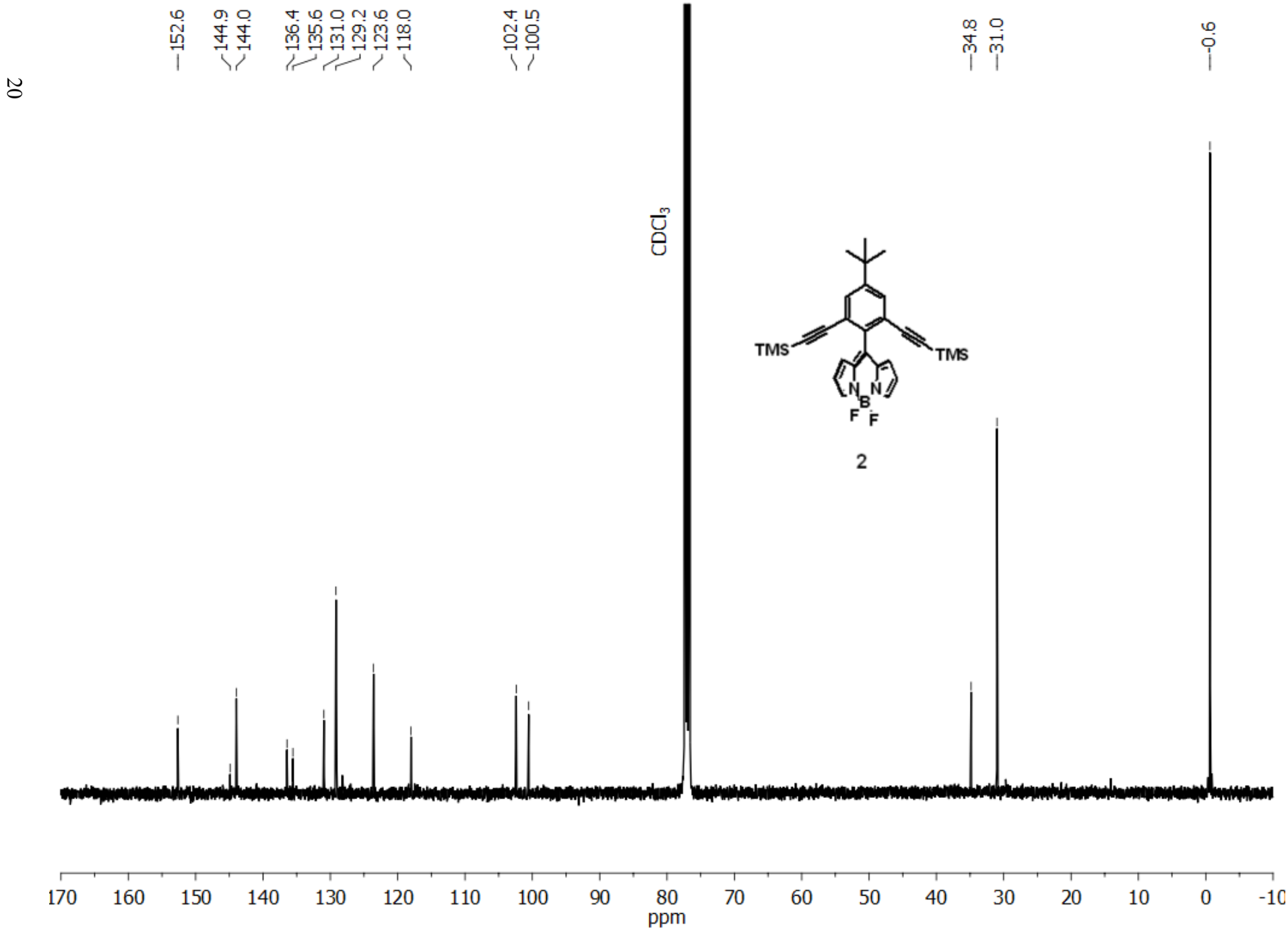


Figure S3. Crystal structure of BODIPY-macrocycle **7**.

7.96
7.95
7.26
6.71
6.70
6.52
6.51
2.17
1.57
1.36
1.25
1.02
0.96
0.98
1.00
4.46
CDCl3
Acetone
H2O
Hexanes
1
ppm


156.1
150.1
145.2
138.7
136.6
134.5
130.0
119.1
96.1
CDCl3
34.7
31.0
I
I
N
N
B
F
F
1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

7.90
7.56
7.26
6.78
6.77
6.46
6.45
2.36
2.17
1.54
1.36
1.26
0.88
0.04
CDCl3
Toluene
Acetone
H2O
Hexanes
Hexanes
1.02
1.01
1.02
1.00
4.53
8.81
TMS
TMS
B
F
F
N
N
2
ppm

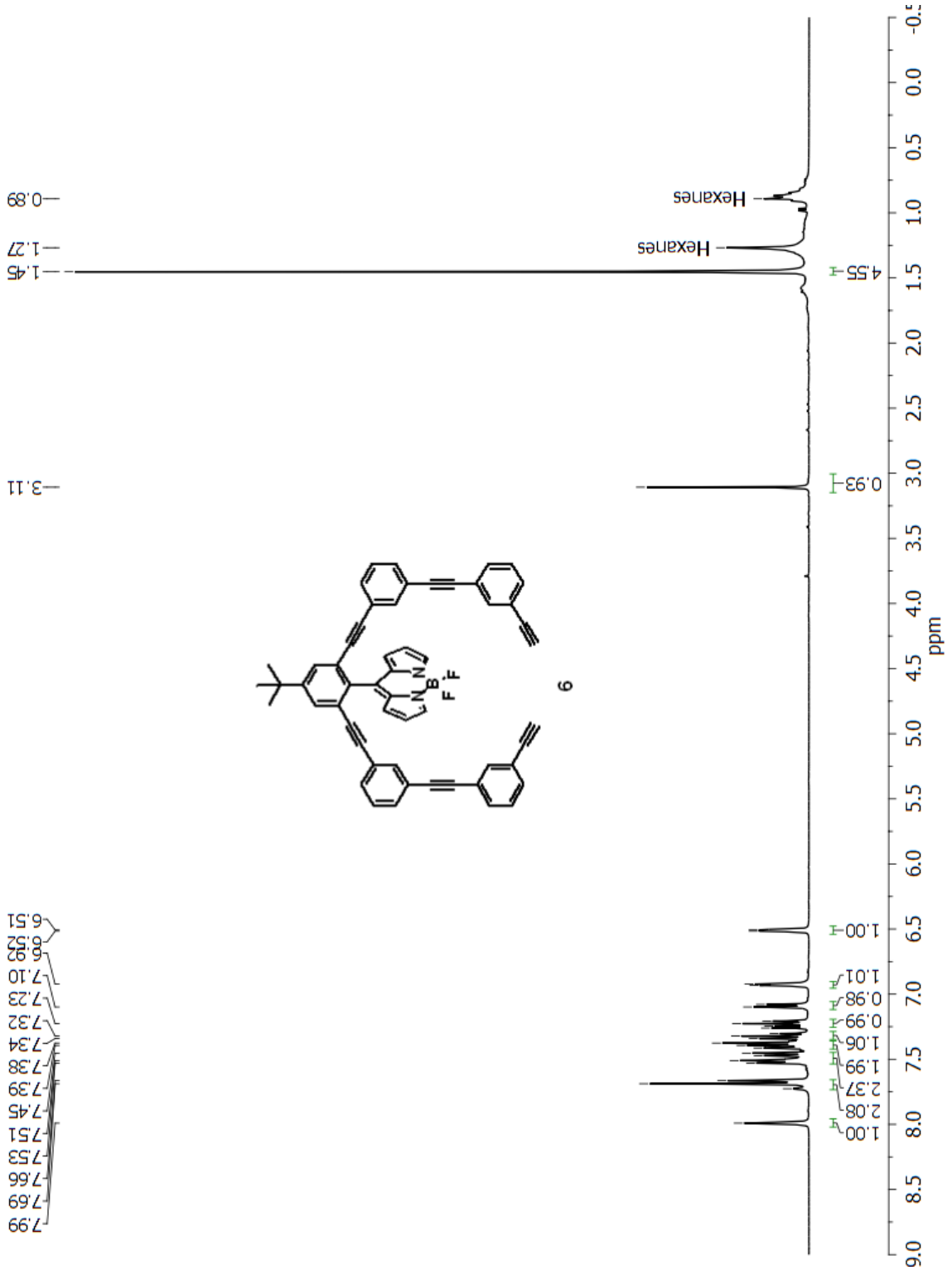

152.6
144.9
144.0
136.4
135.6
131.0
129.2
123.6
118.0
102.4
100.5
CDCl3
34.8
31.0
0.6
TMS
TMS
N
B
N
F
F
2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

7.92
7.65
7.26
6.75
6.74
6.48
6.48
2.99
1.56
1.38
1.36
0.88
CDCl3
H2O
Hexanes
Hexanes
1.01
0.99
1.01
1.00
0.94
4.52
ppm
3

152.8
144.6
143.9
135.6
130.7
130.5
122.7
118.5
82.1
80.7
CDCl3
Grease
34.8
31.0
29.7
3
ppm

7.98
7.68
7.64
7.48
7.37
7.31
7.29
7.26
7.22
7.08
7.06
6.92
6.91
6.51
6.50
1.58
1.45
1.26
0.26
1.00
2.09
4.35
1.09
1.00
1.01
1.00
1.00
4.52
8.96
Dichloromethane
H2O
Hexanes
TMS
TMS
5
ppm

CDCl3
Dichloromethane
Grease
Hexanes
Hexanes
5
TMS
TMS
N
B
F
F
-0.1
14.1
22.7
29.7
31.1
34.9
53.4
87.8
88.9
89.1
93.9
95.0
104.1
123.3
123.3
123.5
128.4
128.5
131.5
131.6
131.6
131.7
134.4
135.0
144.5
153.0
ppm


9
Hexanes
Hexanes
ppm

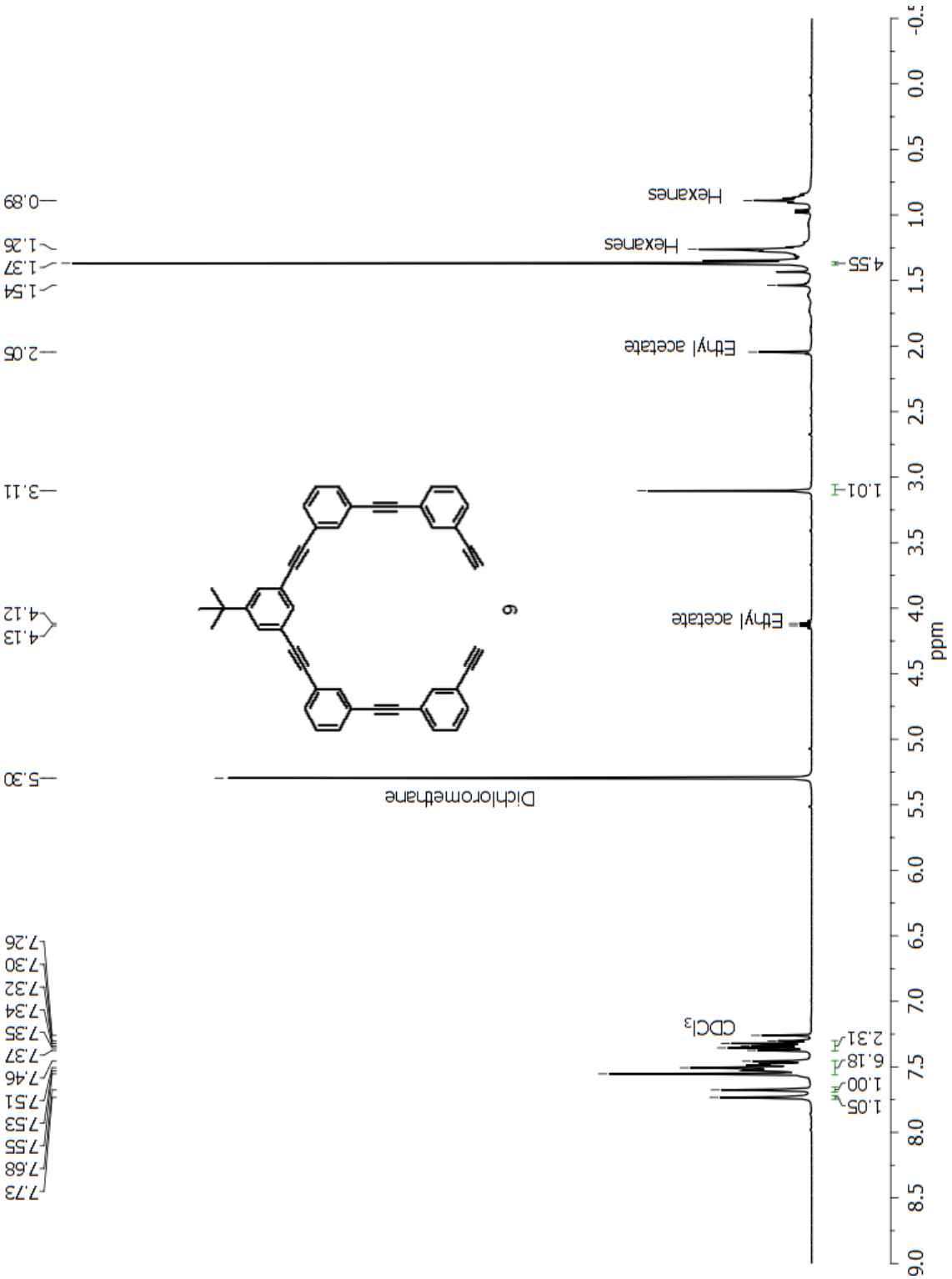
153.0
144.5
135.1
134.5
132.0
131.7
131.6
131.1
129.2
128.5
128.5
123.7
123.4
123.2
122.7
122.5
93.9
89.1
89.0
87.9
82.8
77.9
CDCl3
35.0
31.1
29.7
14.1
Grease
Hexanes
ppm
9

8.15
8.12
7.69
7.42
7.39
7.36
7.34
7.26
7.13
6.50
6.49
1.55
1.46
1.26
0.88
H2O
Hexanes
Hexanes
7
1.00
1.01
1.01
2.14
3.12
0.99
1.01
1.00
1.00
4.71
ppm

14.1
22.7
29.7
31.1
34.9
Hexanes
Hexanes
Grease
CDCl3
75.3
82.4
88.2
89.7
89.8
93.9
122.7
122.8
123.6
123.8
123.8
128.2
128.4
129.1
129.7
130.0
130.2
130.3
131.1
137.4
140.2
144.7
152.9
7
ppm

7.971
7.849
7.686
7.539
7.440
7.366
7.303
7.259
1.547
1.374
1.258
0.883
Hexanes
H2O
Hexanes
1.00
0.99
0.52
4.49
2.99
4.54
8
ppm

Hexanes
Hexanes
Grease
Hexanes
Hexanes
CDCl3
8
ppm


9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.05
1.00
6.18
2.31
4.55
1.01
CDCl3
Ethyl acetate
Ethyl acetate
Hexanes
Hexanes
Dichloromethane
5.30
4.13
4.12
3.11
2.05
1.54
1.37
1.26
0.89
7.73
7.68
7.55
7.53
7.51
7.46
7.37
7.35
7.34
7.32
7.30
7.26

151.8
135.2
134.7
132.0
131.9
131.9
131.5
131.4
129.0
128.6
128.5
123.6
123.4
123.4
123.0
122.6
89.8
89.2
89.0
88.5
82.7
77.9
CDCl3
53.4
34.7
31.1
29.7
22.7
14.1
Dichloromethane
Grease
Hexanes
Hexanes
6
ppm

TMS
TMS
10
Hexanes
Hexanes
0.27
0.89
1.37
1.27
9.19
4.42
1.00
1.01
6.03
1.10
1.06
7.73
7.67
7.55
7.53
7.50
7.48
7.46
7.45
7.43
7.37
7.35
7.33
7.31
7.30
7.28
7.26
ppm

ppm
CDCl3
Grease
THF
Hexanes
Hexanes
TMS
TMS
10

References

1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, A. Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03*; Gaussian Inc., Wallingford, CT, 2009.

2(a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; (b) *J. Chem. Phys.*, 1993, **98**, 1372; (c) C. T. Lee, W. T. Yang and R. G. Parr, *Physical Review B*, 1988, **37**, 785.

3 M. Cossi, G. Scalmani, N. Rega and V. Barone, *J. Chem. Phys.*, 2002, **117**, 43.

4 G. Brizius and U. H. F. Bunz, *Org. Lett.*, 2002, **4**, 2829.

5 K. Hirai, K. Bessho, T. Kitagawa and H. Tomioka, *J. Phys. Org. Chem.*, 2010, **23**, 347.

6 A. Orita, D. An, T. Nakano, J. Yaruva, N. C. Ma and J. Otera, *Chem.-Eur. J.*, 2002, **8**, 2005.

7 B. T. Holmes, W. T. Pennington and T. W. Hanks, *Synth. Commun.*, 2003, **33**, 2447.

8 J. Iskra, S. Stavber and M. Zupan, *Synthesis-Stuttgart*, 2004, 1869.

9 Y. Hua, R. O. Ramabhadran, E. O. Uduehi, J. A. Karty, K. Raghavachari and A. H. Flood, *Chem.-Eur. J.*, 2011, **17**, 312.