Supporting Information for

A Push–Pull Macrocycle With Both Linearly Conjugated and Cross-Conjugated Bridges

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Supplemental Figures

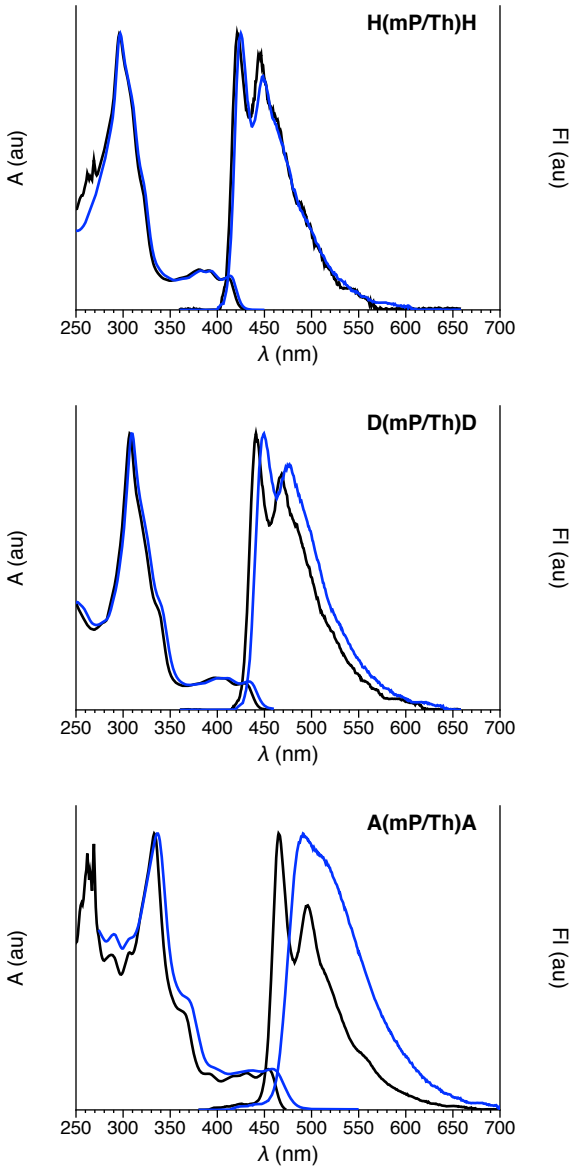


Figure S1. UV–vis and fluorescence spectra of **H(mP/Th)H**, **D(mP/Th)D**, and **A(mP/Th)A** in cyclohexane (black) and CH_2Cl_2 (blue).

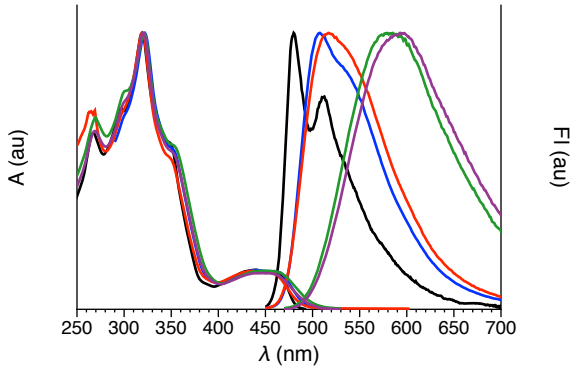


Figure S2. UV–vis and fluorescence spectra of **D(mP/Th)A** in in cyclohexane (black), toluene (blue), 1,4-dioxane (red), $CHCl_3$ (green) and CH_2Cl_2 (purple).

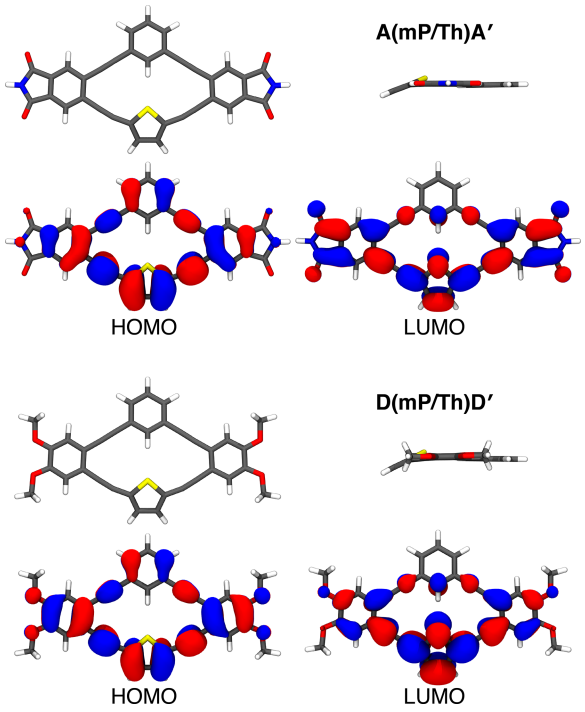


Figure S3. Optimized geometries and frontier molecular orbitals of **A(mP/Th)A′** and **D(mP/Th)D′**.

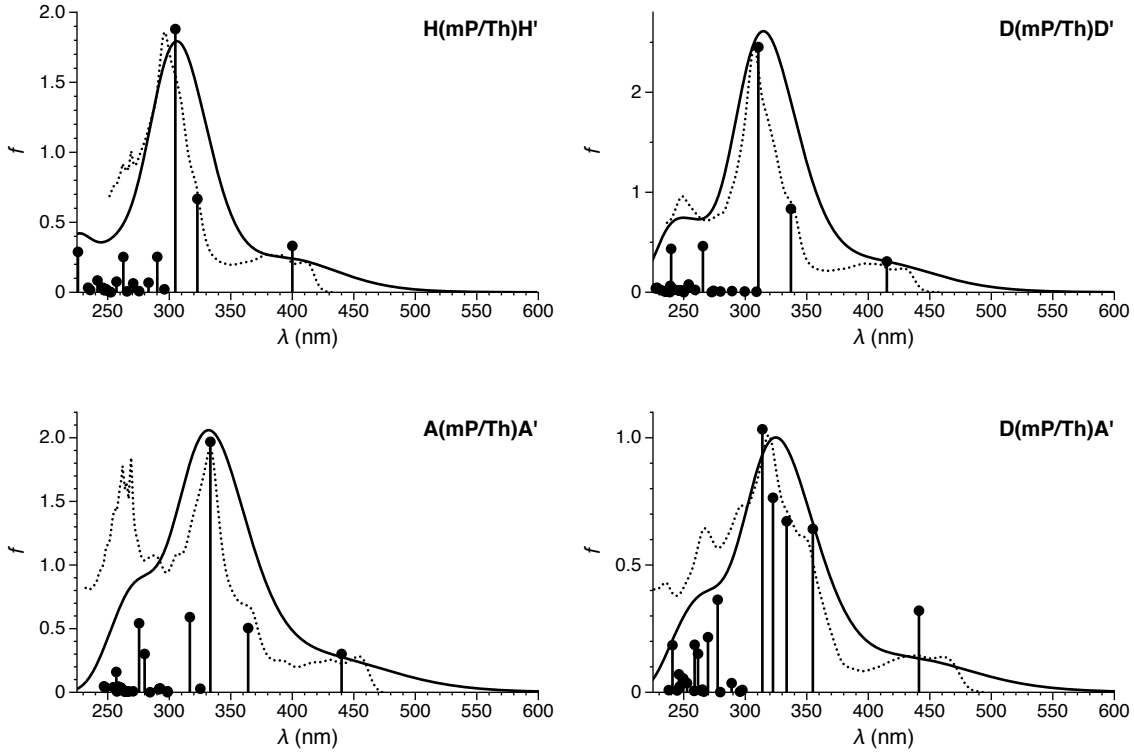


Figure S4. TD-DFT-calculated UV–vis transitions for **H(mP/Th)H′**, **D(mP/Th)D′**, **A(mP/Th)A′**, and **D(mP/Th)A′** at the TD/PCM(Cyclohexane)/CAM-B3LYP/6-311+G(2d,2p)//PCM/B3LYP/6-31+G(d,p) level. The solid lines are the simulated spectra based on the transitions with a 0.333 eV half-width at half-height. The dotted lines are the experimental spectra in cyclohexane (a.u.).

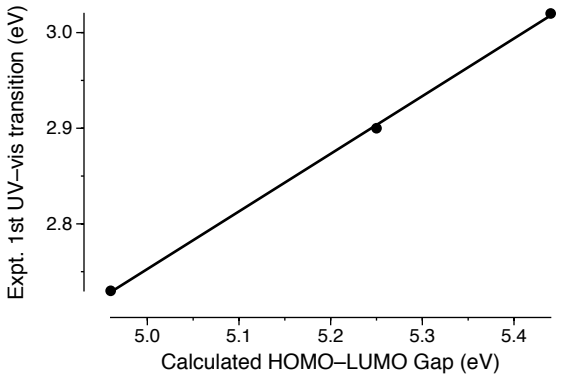


Figure S5. Lowest energy UV–vis transition (cyclohexane) vs PCM(cyclohexane)/CAM-B3LYP/6-311+G(2d,2p)//B3LYP/6-31+G(d) HOMO–LUMO gap for macrocycles **H(mP/Th)H**, **D(mP/Th)D**, and **A(mP/Th)A**.

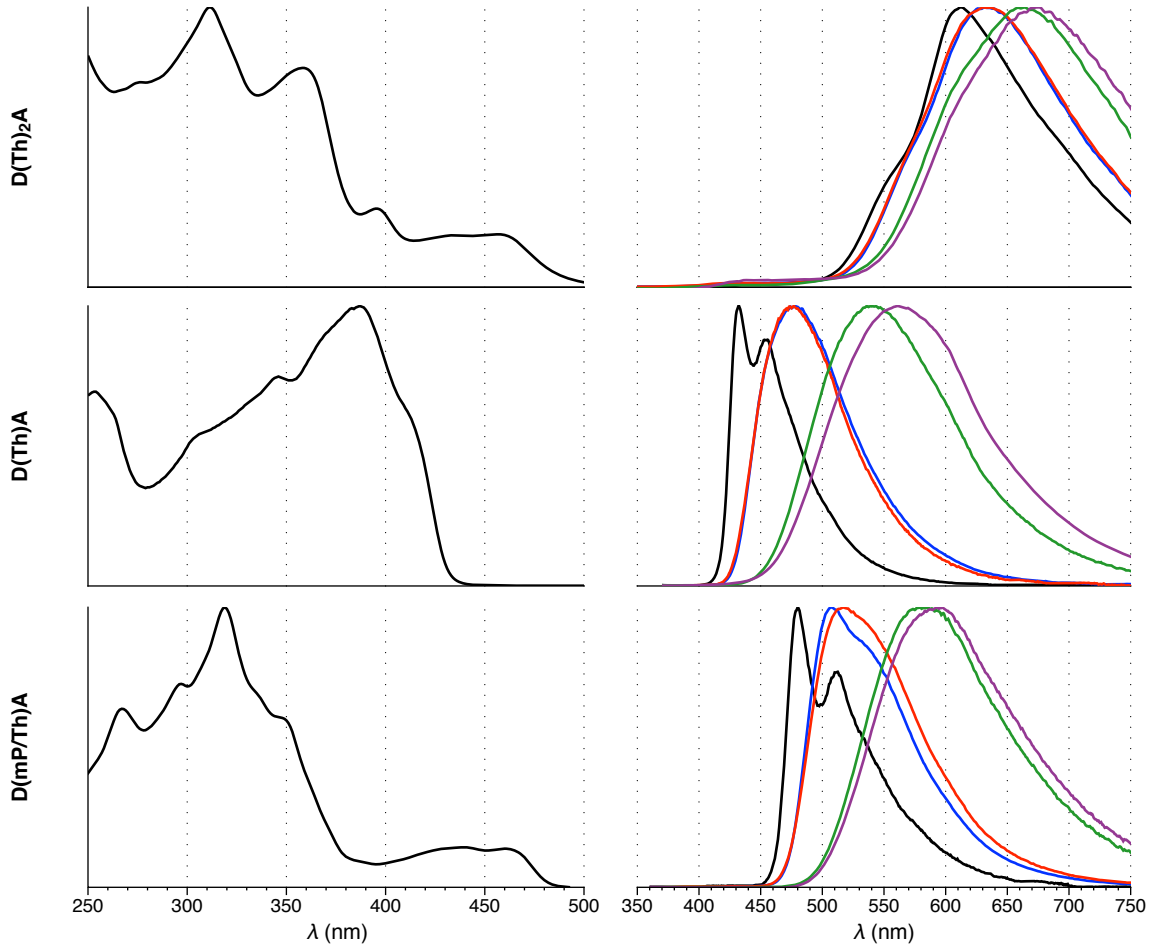


Figure S6. Comparison of the UV–vis (left) and fluorescence (right) spectra of **D(mP/Th)A**, **D(Th)A**, and **D(Th)$_2$A**. The spectra of the latter two compounds were previously reported.[1]

Lippert–Mataga Analysis

The fluorescence solvatochromism of **D(mP/Th)A** was analyzed using Weller's modification of the Lippert–Mataga equation:[2]

$$\bar{\nu}_f = -\frac{2\mu_e^2}{hca^3}\Delta f' + \bar{\nu}_0 \tag{1}$$

where $\bar{\nu}_f$ is the fluorescence emission maximum, $\bar{\nu}_0$ is the emission maximum in vacuum, a^3 is the volume of the Onsager cavity (estimated from the total volume of a PM3-minimized model of the structure), and $\Delta f'$ is a solvent-dependent parameter calculated from its dielectric constant (ε) and refractive index (n):

$$\Delta f' = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{4n^2 + 2} \tag{2}$$

Thus, $\bar{\nu}_f$ was plotted against $\Delta f'$ for both the five different solvents used (Figure 1) and for mixtures of

cyclohexane and CH_2Cl_2, shown in Figure S7. The plot in structurally different solvents yields a reasonably good linear fit given that eq 1 is an approximation that neglects second-order effects and solvent-specific interactions.[3]

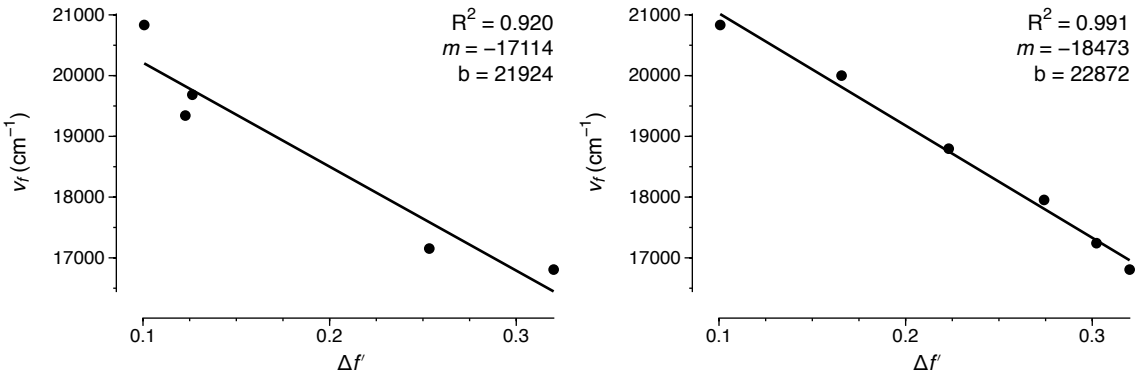


Figure S7. Lippert–Mataga plots of **D(mP/Th)A** fluorescence in cyclohexane, toluene, 1,4-dioxane, $CHCl_3$, and CH_2Cl_2 (left) and in mixtures of cyclohexane and CH_2Cl_2 (right).

Computational Data

Please note that Cartesian coordinates of optimized geometries are included in a separate, plain text SI file.

Table S1. Energies of optimized geometries (PCM(cyclohexane)/B3LYP/6-31+G(d,p))

Compound	Imag. Freq.	Energy (E_h)	ZPC (E_h)[a]	Total (E_h)
H(mP/Th)H′	0	−1549.665503	0.328147	−1549.337355
D(mP/Th)D′	0	−2007.776843	0.458046	−2007.318797
A(mP/Th)A′	0	−2111.381468	0.357865	−2111.023603
D(mP/Th)A′	0	−2059.579944	0.407916	−2059.172028

[a] Unscaled.

Fluorescence Lifetime Measurements

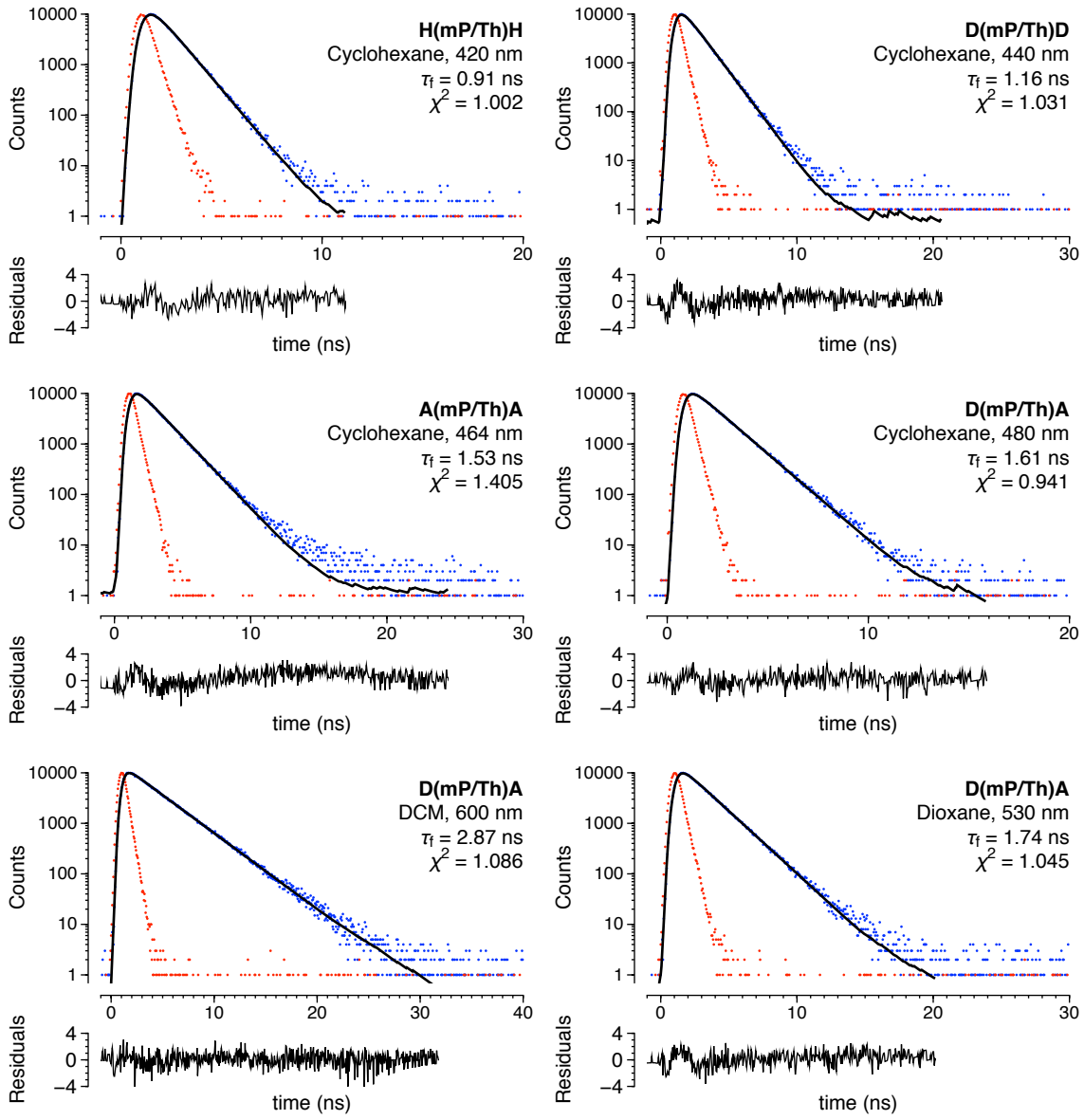


Figure S8. TCSPC measurements of new mixed-bridge macrocycles.

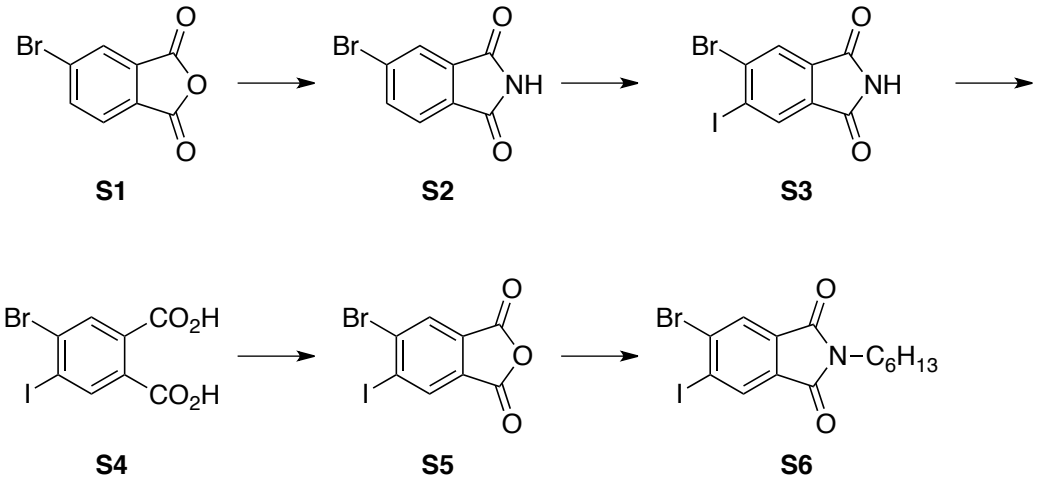
Experimental

General methods

Unless otherwise noted, all reagents and solvents were purchased from commercial sources and used without further purification. Anhydrous THF was obtained by distillation from sodium/benzophenone. Flash column chromatography was performed using Silicycle SiliaFlash P60 (40-63 μm, 230-400 mesh). Gel permeation chromatography was performed using a Waters Breeze 2 HPLC equipped with a 19×300 mm Ultrastyragel 500 Å GPC column with THF as the eluent. Melting points were determined using a Thermal Analysis Q20 differential scanning calorimeter at a heating rate of 10 °C/min or by a polarized optical microscope with a Linkam LTS 350 variable temperature stage. NMR spectra were measured in

deuterated solvents ($CDCl_3$ or DMSO-d_6) using Bruker Avance 300 or 500 MHz spectrometers. Chemical shifts are reported in δ (ppm) relative to TMS, with the residual solvent protons used as internal standards ($CDCl_3$: 7.26 for ^1H, 77.16 for ^{13}C; DMSO-d_6: 2.50 for ^1H, 39.52 for ^{13}C). Low resolution mass spectra were performed using a Shimadzu LC-MS in ESI or APCI modes and MALDI-MS samples were recorded using a Bruker Ultraflex MALDI spectrometer in reflectron mode with dithranol as the matrix. In many cases, the MALDI samples were doped with CuI to promote formation of Cu^+ adducts. High resolution mass spectra were obtained from Ohio State University microanalyses group and University of Cincinnati mass spectrometry facility.

Synthesis of N-hexyl-4-bromo-5-iodophthalimide



S1 **S2** **S3**

S4 **S5** **S6**

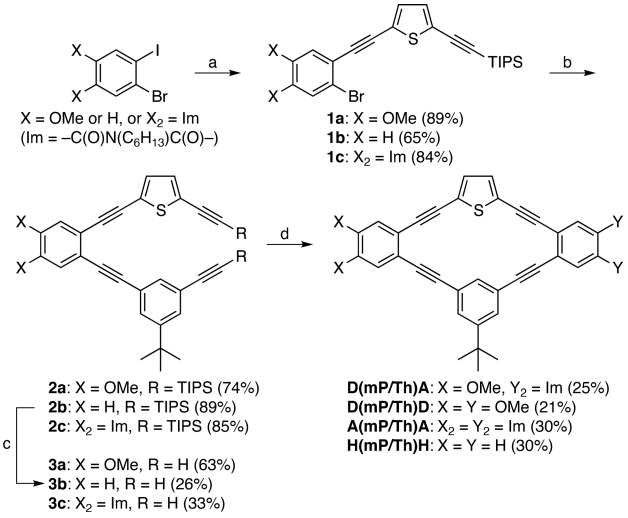
4-Bromo-5-iodophthalimide (S3). 4-Bromophthalimide **S2**[4] (10.75 g, 0.047 mol) in 20% oleum (28.6 mL, 54.9 g, 0.308 mol) and I_2 (12.05 g, 0.047 mmol) was vigorously stirred at 80–85 °C for 40 h. The dark viscous solution was poured into ice (100 g) and the white precipitate was collected by vacuum filtration. The precipitate was washed in the following order: 2% (w/v) K_2CO_3(aq), satd $Na_2S_2O_3$(aq), and water to give a yellow precipitate. The crude solid was dried under high vacuum for 18 h to give a pale yellow solid in quantitative yield. The solid **S3** was used in the next step without further purification: mp 200 °C dec; ^1H NMR (300 MHz, DMSO-d_6) δ 8.08 (s, 1H), 8.28 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 110.3, 126.9, 132.8, 134.2, 134.4, 135.8, 167.8, 168.1; MS (ESI, negative ion mode) calcd for $C_8H_2BrINO_2$ ($[M-H]^-$) 349.8, found 349.8; HRMS (ESI) calcd for $C_8H_3BrINO_2Na$ ($[M+Na]^+$) 373.8290, found 373.8253.

4-Bromo-5-iodobenzoic acid (S4). A suspension of **S3** (16.70 g, 0.047 mol) in 10% (w/v) KOH(aq) (50 mL) was heated under reflux for 18 h. The clear dark solution was acidified with aqueous 6 M HCl solution to pH 2 and the resulting precipitate was collected by vacuum filtration. The precipitate was

washed with several volumes of water and the solid was dried under high vacuum to give a **S4** as a yellow solid (7.74 g, 44% over 2 steps): mp >300 °C dec; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.12 (s, 1H), 8.37 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 105.8, 132.2, 133.9, 134.2, 135.3, 135.3, 166.6, 166.9; MS (ESI, negative ion mode) calcd for $C_8H_3BrIO_4$ (M^-) 368.8, found 368.7.

***N*-Hexyl-4-bromo-5-iodophthalimide (S6).** To a round bottom flask containing **S4** (7.74 g, 0.0208 mol) was added $SOCl_2$ (13 mL, 21.3 g, 0.179 mol) at 60 °C and the yellow suspension was heated to 90 °C for 16 h. The excess $SOCl_2$ was removed under reduced pressure and the crude yellow solid was dried under high vacuum to give 4-bromo-5-iodophthalic anhydride **S5** which was used in the next step without further purification: ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.94 (s, 1H), 8.16 (s, 1H). A suspension of **S5** (7.34 g, 0.0208 mol) and hexylamine (2.75 mL, 2.10 g, 0.0208 mol) in toluene (40 mL) was heated under reflux for 18 h. The reaction mixture was concentrated under reduced pressure. Purification by flash chromatography (19:1 hexanes/Et_2O then Et_2O) followed by trituration (Et_2O) gave **S6** as a beige solid (4.83 g, 53% over 2 steps): mp 102–103 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (t, J = 6.8 Hz, 3H), 1.28 (br s, 6H), 1.63 (m, 2H), 3.63 (t, J = 7.3 Hz, 2H), 8.02 (s, 1H), 8.28 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.5, 26.5, 28.4, 31.3, 38.5, 108.1, 126.9, 131.3, 132.9, 134.8, 136.1, 166.3, 166.6.

Synthesis of mixed bridged intermediates and macrocycles



Compound 1a. A Schlenk tube containing $Pd(OAc)_2$ (26 mg, 0.116 mmol), CuI (19 mg, 0.099 mmol), PPh_3 (169 mg, 0.64 mmol) and 1-bromo-2-iodoveratrole[5] (1.00 g, 2.91 mmol) was evacuated and backfilled with argon (3×). To this solid mixture was added a solution of 2-ethynyl-5-(triisopropylsilylethynyl)thiophene (1.00 g, 3.5 mmol) in HN^iPr_2 (25 mL). The suspension was degassed by three freeze-pump-thaw cycles and heated with stirring at 75 °C for 18 h. The resulting suspension was diluted with CH_2Cl_2 (30 mL), washed with water (2 × 15 mL), dried ($MgSO_4$), filtered, and

concentrated. Purification by flash chromatography (9:1 hexanes/CH_2Cl_2 then CH_2Cl_2) gave **1a** as a brown oil (1.30 g, 89 %, contains ~15% 1-bromo-2-iodoveratrole): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (s, 21H), 3.88 (s, 3H), 3.89 (s, 3H), 6.99 (s, 1H), 7.04 (s, 1H), 7.10 (d, *J* = 3.8 Hz, 1H), 7.12 (d, *J* = 3.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.3, 18.6, 56.1, 56.2, 85.1, 92.5, 97.1, 98.8, 114.9, 115.2, 116.8, 124.1, 125.2, 131.6, 132.3, 148.2, 150.1; MS (APCI) calcd for $C_{25}H_{31}BrO_2SSi$ (M^+) 502.09, found 502.2; HRMS (ESI) calcd for $C_{25}H_{31}BrNaO_2SSi$ ($[M+Na]^+$) 525.0895, found 525.0915.

Compound 2a. A Schlenk tube containing $Pd(P^tBu_3)_2$ (44 mg, 0.086 mmol), CuI (16 mg, 0.084 mmol), and DABCO (2.2 g) was evacuated and backfilled with argon (3×). To this solid mixture was added a solution of **1a** (1.00 g, 2.0 mmol) and 1-*tert*-butyl-3-ethynyl-5-(triisopropylsilylethynyl)benzene (1.80 g, 5.3 mmol) in toluene (45 mL). The suspension was degassed by three freeze-pump-thaw cycles and stirred at room temperature for 18 h. The resulting suspension was concentrated and diluted with CH_2Cl_2 (30 mL), washed with water (2 × 15 mL), dried ($MgSO_4$), filtered, and concentrated. Purification by flash chromatography (hexanes then 2:8 hexanes/toluene) gave **2a** as a brown gummy solid (1.13 g, 74%): mp 64–65 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (s, 21H), 1.15 (s, 21H), 1.32 (s, 9H), 3.93 (s, 3H), 3.93 (s, 3H), 7.00 (s, 1H), 7.03 (s, 1H), 7.08 (d, *J* = 3.8 Hz, 1H), 7.12 (d, *J* = 3.8 Hz, 1H), 7.44 (t, *J* = 1.7 Hz, 1H), 7.51 (t, *J* = 1.3 Hz, 1H), 7.56 (t, *J* = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.3, 11.4, 18.6, 18.7, 31.2, 34.7, 56.1, 85.1, 87.9, 90.5, 92.4, 92.8, 96.9, 98.8, 106.8, 113.6, 114.0, 118.3, 118.9, 123.1, 123.5, 124.5, 124.9, 128.8, 128.9, 131.3, 132.2, 132.5, 149.2, 149.4, 151.5; MALDI-TOF-MS (dithranol) calcd for $C_{48}H_{65}O_2SSi_2$ ($[M+H]^+$) 761.4, found 761.2; HRMS (ESI) calcd for $C_{48}H_{64}NaO_2SSi_2$ ($[M+Na]^+$) 783.4063, found 783.4079.

Compound 3a. To solution of **2a** (1.75 g, 2.3 mmol) in THF (15 mL) was added dropwise a 1.0 M solution of TBAF in THF (5.0 mL, 5.0 mmol). The mixture was stirred at room temperature for 2 h under an argon atmosphere. The resulting solution was diluted with CH_2Cl_2 (20 mL), washed with brine, water, dried ($MgSO_4$), filtered, and concentrated. Purification by flash chromatography (9:1 hexanes/EtOAc) gave **3a** as a brown oil (0.65 g, 63%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (s, 9H), 3.07 (s, 1H), 3.37 (s, 1H), 3.92 (s, 3H), 3.93 (s, 3H), 6.99 (s, 1H), 7.02 (s, 1H), 7.13 (d, *J* = 3.9 Hz, 1H), 7.15 (d, *J* = 3.8 Hz, 1H), 7.48 (t, *J* = 1.4 Hz, 1H), 7.54 (t, *J* = 1.4 Hz, 1H), 7.57 (t, *J* = 1.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.1, 34.7, 56.1, 76.5, 77.2, 82.2, 83.3, 84.8, 88.2, 92.3, 93.1, 113.6, 113.9, 118.2, 118.9, 122.1, 123.2, 125.2, 129.1, 131.2, 132.3, 133.0, 149.2, 149.5, 151.7; MALDI-TOF-MS (dithranol) calcd for $C_{30}H_{24}O_2S$ (M^+) 448.1, found 448.0; HRMS (ESI) calcd for $C_{30}H_{24}NaO_2S$ ($[M+Na]^+$) 471.1395, found 471.1411.

Macrocycle D(Th/mP)A. A Schlenk tube containing $Pd(P^tBu_3)_2$ (2.5 mg, 5 μmol) and *N*-hexyl-4,5-diiodophthalimide[1] (58 mg, 0.12 mmol) was evacuated and backfilled with argon (3×). To this solid mixture was added a solution of **3a** (44 mg, 0.098 mmol) in Et_3N/toluene (3:7, 50 mL). The suspension was degassed by three freeze-pump-thaw cycles and stirred at room temperature for 18 h. The resulting suspension was concentrated and diluted with CH_2Cl_2 (30 mL), washed with water (3 × 20 mL), dried ($MgSO_4$), filtered, and concentrated. Purification by gel permeation chromatography gave **D(Th/mP)A** as a light orange solid (16.5 mg, 25 %): mp >300 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.4 Hz, 3H), 1.31 (br s, 6H), 1.36 (s, 9H), 1.63 (m, 2H), 3.60 (t, *J* = 7.8 Hz, 2H), 3.88 (s, 3H), 3.93 (s, 3H), 6.77 (s, 1H), 6.94-6.95 (m, 3H), 7.43 (t, 1H), 7.54 (t, 1H), 7.70 (s, 1H), 7.89 (s, 1H), 8.50 (t, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.5, 26.5, 28.5, 31.2, 31.3, 34.8, 38.2, 55.9, 56.0, 85.3, 87.8, 88.6, 90.5, 92.1, 95.7, 97.6, 112.3, 114.6, 117.7, 119.9, 122.3, 123.5, 123.8, 124.5, 126.9, 127.2, 128.3, 129.0, 129.4, 130.1, 130.3, 131.8, 134.1, 148.9, 149.3, 151.5, 167.1, 167.2; MALDI-TOF-MS (dithranol) calcd for $C_{44}H_{37}NO_4S$ (M^+) 675.2, found 675.0; HRMS (ESI) calcd for $C_{44}H_{37}NNaO_4S$ ($[M+Na]^+$) 698.2341, found 698.2333. Prior to UV–vis and fluorescence spectroscopy, the compound was recrystallized from hexanes/CH_2Cl_2.

Macrocycle D(Th/mP)D. A Schlenk tube containing $Pd(P^tBu_3)_2$ (2.7 mg, 5.3 μmol), 1,2-diiodoveratrole[6,7] (43 mg, 0.11 mmol) and DABCO (2.2 g) was evacuated and backfilled with argon (3×). To this solid mixture was added a solution of **3a** (41 mg, 0.091 mmol) in toluene (45 mL). The suspension was degassed by three freeze-pump-thaw cycles and stirred at room temperature for 18 h. The resulting suspension was concentrated and diluted with CH_2Cl_2 (30 mL), washed with water (3 × 20 mL), dried ($MgSO_4$), filtered, and concentrated. Purification by gel permeation chromatography followed by flash chromatography (2:8 hexanes/CH_2Cl_2) gave **D(Th/mP)D** as a yellow solid (11.3 mg, 21%): mp >300 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (s, 9H), 3.91 (s, 6H), 3.95 (s, 6H), 6.91 (s, 2H), 7.01 (s, 2H), 7.08 (s, 2H), 7.52 (t, *J* = 1.4 Hz, 2H), 8.52 (t, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.2, 34.8, 56.0, 56.1, 85.4, 88.4, 92.2, 96.7, 112.4, 114.8, 118.0, 120.0, 123.3, 125.4, 128.5, 128.6, 133.7, 149.1, 149.4, 151.4; MALDI-TOF-MS (dithranol) calcd for $C_{38}H_{30}O_4S$ (M^+) 582.2, found 581.9; HRMS (ESI) calcd for $C_{38}H_{30}NaO_4S$ ($[M+Na]^+$) 605.1763, found 605.1750.

Compound 1b. A Schlenk tube containing $Pd(OAc)_2$ (35 mg, 0.16 mmol), CuI (20 mg, 0.10 mmol) and PPh_3 (203 mg, 0.77 mmol) was evacuated and backfilled with argon (3×). To this solid mixture was added a solution of 1-bromo-2-iodobenzene (0.454 mL, 1.00 g, 3.53 mmol) and 2-ethynyl-5-(triisopropylsilylethynyl)thiophene[8] (1.22 g, 4.23 mmol) in HN^iPr_2 (25 mL). The suspension was degassed by three freeze-pump-thaw cycles and heated with stirring at 75 °C for 18 h. The resulting

suspension was diluted with CH_2Cl_2 (30 mL), washed with water (2 × 15 mL), dried ($MgSO_4$), filtered, and concentrated. Purification by flash chromatography (hexanes, then 19:1 hexanes/Et_2O, then 1:1 hexanes/Et_2O) gave **1b** as a clear yellow oil (0.99 g, 65%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (s, 21H), 7.11 (d, *J* = 3.9 Hz, 1H), 7.16 (d, *J* = 3.9 Hz, 1H), 7.19 (td, *J* = 7.8, 1.6 Hz, 1H), 7.29 (td, *J* = 7.6, 1.2 Hz, 1H), 7.52 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.61 (dd, *J* = 8.0, 1.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.3, 18.6, 86.7, 92.2, 97.3, 98.7, 107.6, 108.6, 111.4, 113.3, 124.9, 125.4, 125.6, 127.1, 129.7, 131.9, 132.3, 132.5, 133.1; MS (APCI) calcd for $C_{23}H_{27}BrSSi$ (M^+) 442.1, found 442.2; HRMS (ESI) calcd for $C_{23}H_{27}BrNaSSi$ ($[M+Na]^+$) 465.0684, found 465.0664.

Compound 2b. A Schlenk tube containing $Pd(P^tBu_3)_2$ (48 mg, 0.094 mmol), CuI (18 mg, 0.095 mmol) and DABCO (2 g) was evacuated and backfilled with argon (3×). To this solid mixture was added a solution of **1b** (1.00 g, 2.3 mmol) and 1-*tert*-butyl-3-ethynyl-5-(triisopropylsilylethynyl)benzene[9,10] (0.920 g, 2.7 mmol) in toluene (50 mL). The suspension was degassed by three freeze-pump-thaw cycles and stirred at room temperature for 18 h. The resulting suspension was concentrated and diluted with CH_2Cl_2 (30 mL), washed with water (2 × 15 mL), dried ($MgSO_4$), filtered, and concentrated. Purification by flash chromatography (hexanes then Et_2O) gave **2b** as a brown gummy solid (1.44 g, 89%): mp 43–44 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (s, 21H), 1.15 (s, 21H), 1.32 (s, 9H), 7.09 (d, *J* = 3.9 Hz, 1H), 7.14 (d, *J* = 3.8 Hz, 1H), 7.32 (m, 2H), 7.45 (t, *J* = 1.4, 1H), 7.52–7.57 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.3, 18.6, 18.7, 31.1, 34.7, 86.4, 87.8, 90.6, 92.6, 93.7, 112.4, 113.3, 122.9, 123.5, 124.1, 125.3, 125.7, 128.1, 128.3, 129.0, 129.1, 131.5, 131.7, 131.8, 132.4, 132.5, 151.6; MS (APCI) calcd for $C_{46}H_{60}SSi_2$ (M^+) 700.4, found 700.5; HRMS (ESI) calcd for $C_{46}H_{60}NaSSi_2$ ($[M+Na]^+$) 723.3852, found 723.3862.

Compound 3b. To solution of **2b** (1.47 g, 2.1 mmol) in THF (10 mL) was added dropwise a 1.0 M solution of TBAF in THF (4.6 mL, 4.6 mmol). The mixture was stirred at room temperature for 2 h under an argon atmosphere. The resulting solution was diluted with CH_2Cl_2 (20 mL), washed with brine and water, then dried ($MgSO_4$), filtered, and concentrated. Purification by flash chromatography (9:1 hexanes/EtOAc) gave **3b** as a clear pale brown oil (0.23 g, 26%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (s, 9H), 3.08 (s, 1H), 3.38 (s, 1H), 7.16 (s, 2H), 7.30–7.35 (m, 2H), 7.50–7.58 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.1, 34.7, 76.5, 77.3, 82.3, 83.3, 86.1, 88.1, 92.9, 93.6, 122.2, 123.1, 123.6, 124.9, 125.2, 125.7, 128.2, 128.5, 129.3, 129.5, 131.5, 131.6, 131.8, 132.5, 133.0, 151.7; MALDI-TOF-MS (dithranol) calcd for $C_{56}H_{40}S_2$ ($2M^+$) 776.25, found 776.1; HRMS (ESI) calcd for $C_{28}H_{20}NaS$ ($[M+Na]^+$) 411.1183, found 411.1184.

Macrocycle H(mP/Th)H. A Schlenk tube containing $Pd(P^tBu_3)_2$ (3.6 mg, 7.0 μmol) and DABCO

(0.8 g) was evacuated and backfilled with argon (3×). To this solid mixture was added a solution of **3b** (42 mg, 0.108 mmol) and 1,2-diiodobenzene (17 μL, 43 mg, 0.130 mmol) in toluene (55 mL). The suspension was degassed by three freeze-pump-thaw cycles and stirred at room temperature for 18 h. The resulting suspension was concentrated and diluted with CH_2Cl_2 (30 mL), washed with water (3 × 20 mL), dried ($MgSO_4$), filtered, and concentrated. Purification by gel permeation chromatography gave **H(mP/Th)H** as a yellow solid (15.0 mg, 30%): mp >300 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.37 (s, 9H), 7.06 (s, 2H), 7.29–7.34 (m, 4H), 7.44–7.46 (m, 2H), 7.55 (d, *J* = 1.5 Hz, 2H), 7.60–7.62 (m, 2H), 8.54 (t, *J* = 1.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.2, 34.8, 86.5, 88.4, 93.4, 96.6, 123.1, 124.9, 125.5, 126.8, 128.1, 128.4, 129.08, 129.1, 130.3, 132.6, 133.9, 151.5; MALDI-TOF-MS (dithranol) calcd for $C_{34}H_{22}S$ (M^+) 462.14, found 461.84; HRMS (ESI) calcd for $C_{34}H_{22}NaS$ ($[M+Na]^+$) 485.1340, found 485.1357.

Compound 1c. A Schlenk tube containing $Pd(OAc)_2$ (23 mg, 0.102 mmol), CuI (13 mg, 0.068 mmol), PPh_3 (129 mg, 0.49 mmol) and *N*-hexyl-4-bromo-5-iodophthalimide (1.00 g, 2.3 mmol) was evacuated and backfilled with argon (3×). To this solid mixture was added a solution of 2-ethynyl-5-(triisopropylsilylethynyl)thiophene (0.790 g, 2.7 mmol) in HN^iPr_2 (25 mL). The suspension was degassed by three freeze-pump-thaw cycles and heated with stirring at 75 °C for 18 h. The resulting suspension was diluted with CH_2Cl_2 (30 mL), washed with water (2 × 15 mL), dried ($MgSO_4$), filtered, and concentrated. Purification by flash chromatography (1:1 hexanes/CH_2Cl_2) gave **1c** as a light brown solid (1.15 g, 84%): mp 96–97 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.21 (s, 21H), 1.31 (br s, 6H), 1.63 (m, 2H), 3.66 (t, *J* = 7.4 Hz, 2H), 7.14 (d, *J* = 3.8 Hz, 1H), 7.23 (d, *J* = 3.8 Hz, 1H), 7.91 (s, 1H), 8.05 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.3, 14.0, 18.6, 22.5, 26.5, 28.4, 31.3, 38.5, 91.4, 91.5, 98.4, 98.5, 122.4, 126.9, 127.1, 127.4, 130.5, 130.8, 131.2, 131.8, 132.4, 133.3, 166.6, 167.0; MS (APCI) calcd for $C_{31}H_{38}BrNO_2SSi$ (M^+) 595.15, found 595.3; HRMS (ESI) calcd for $C_{31}H_{38}BrNNaO_2SSi$ ($[M+Na]^+$) 618.1474, found 618.1481.

Compound 2c. A Schlenk tube containing $Pd(P^tBu_3)_2$ (39 mg, 0.076 mmol), CuI (14 mg, 0.074 mmol), and DABCO (2.1 g) was evacuated and backfilled with argon (3×). To this solid mixture was added a solution of **1c** (1.15 g, 1.9 mmol) and 1-*tert*-butyl-3-ethynyl-5-(triisopropylsilylethynyl)benzene (0.78 g, 2.3 mmol) in toluene (50 mL). The suspension was degassed by three freeze-pump-thaw cycles and stirred at room temperature for 18 h. The resulting suspension was concentrated and diluted with CH_2Cl_2 (30 mL), washed with water (2 × 15 mL), dried ($MgSO_4$), filtered, and concentrated. Purification by flash chromatography (8:2 hexanes/CH_2Cl_2 then 1:1 hexanes/CH_2Cl_2) gave **2c** as a light brown solid

(1.40 g, 85%): mp 54–55 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.13 (s, 21H), 1.15 (s, 21H), 1.33 (s, 15H), 1.68 (m, 2H), 3.68 (t, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 3.8 Hz, 1H), 7.21 (d, *J* = 3.8 Hz, 1H), 7.50 (t, *J* = 1.7 Hz, 1H), 7.54 (t, *J* = 1.4 Hz, 1H), 7.58 (t, *J* = 1.6 Hz, 1H), 7.95 (d, *J* = 0.6 Hz, 1H), 7.98 (d, *J* = 0.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.3, 14.0, 18.7, 22.5, 26.5, 28.5, 31.1, 31.3, 34.7, 38.4, 86.9, 90.7, 91.1, 91.7, 98.0, 98.4, 106.4, 122.0, 122.9, 123.8, 125.8, 126.2, 126.7, 129.1, 129.9, 130.6, 130.8, 130.9, 130.9, 132.6, 132.7, 132.9, 151.8, 167.1; MALDI-TOF-MS (dithranol) calcd for $C_{54}H_{72}NO_2SSi_2$ ($M+H^+$) 854.5, found 854.3; HRMS (ESI) calcd for $C_{54}H_{71}NNaO_2SSi_2$ ($[M+Na]^+$) 876.4642, found 876.4639.

Compound 3c. To solution of **2c** (0.250 g, 0.29 mmol) in THF (15 mL) was added glacial AcOH (36.5 μL, 0.64 mmol) followed by a 1.0 M solution of TBAF in THF (0.64 mL, 0.64 mmol). The mixture was stirred at room temperature for 2 h under an argon atmosphere. The resulting solution was diluted with CH_2Cl_2 (10 mL), washed with brine and water, then dried ($MgSO_4$), filtered, and concentrated. Purification by flash chromatography (19:1 hexanes/EtOAc) gave **3c** as a brown solid (52 mg, 33%): mp 150–151 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.33 (s, 15H), 1.68 (m, 2H), 3.11 (s, 1H), 3.42 (s, 1H), 3.67 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 3.8 Hz, 1H), 7.22 (d, *J* = 3.8 Hz, 1H), 7.54 (t, *J* = 1.7 Hz, 1H), 7.57 (t, *J* = 1.4 Hz, 1H), 7.59 (t, *J* = 1.6 Hz, 1H), 7.93 (d, *J* = 0.6 Hz, 1H), 7.95 (d, *J* = 0.6 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.5, 26.5, 28.5, 31.0, 31.2, 34.8, 38.4, 76.1, 77.6, 82.9, 83.0, 87.1, 90.3, 91.9, 97.8, 122.1, 122.4, 123.6, 125.0, 125.8, 126.2, 129.4, 130.3, 130.5, 130.8, 131.0, 132.8, 133.2, 151.9, 167.1, 167.2; MALDI-TOF-MS (dithranol) calcd for $C_{36}H_{31}NO_2S$ (M^+) 541.20, found 541.91; HRMS (ESI) calcd for $C_{36}H_{31}NNaO_2S$ ($[M+Na]^+$) 564.1973, found 564.1965.

Macrocycle A(mP/Th)A. A Schlenk tube containing $Pd(P^tBu_3)_2$ (5.0 mg, 9.8 μmol), *N*-hexyl-4,5-diiodophthalimide[1] (47 mg, 0.097 mmol) and DABCO (1.00 g) was evacuated and backfilled with argon (3×). To this solid mixture was added a solution of **3c** (44 mg, 0.081 mmol) in toluene (40 mL). The suspension was degassed by three freeze-pump-thaw cycles and stirred at room temperature for 18 h. The resulting suspension was concentrated and diluted with CH_2Cl_2 (30 mL), washed with water (3 × 20 mL), dried ($MgSO_4$), filtered, and concentrated. Purification by gel permeation chromatography gave **A(mP/Th)A** as a light orange solid (18.7 mg, 30%); mp >300 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.3 Hz, 6H), 1.32 (br s, 12H), 1.39 (s, 9H), 1.67 (m, 4H), 3.65 (t, *J* = 7.5 Hz, 4H), 7.12 (s, 2H), 7.59 (s, 2H), 7.77 (s, 2H), 7.95 (s, 2H), 8.54 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.5, 26.5, 28.5, 31.2, 31.4, 34.9, 38.4, 87.8, 90.1, 96.1, 97.4, 122.4, 124.7, 125.6, 127.0, 129.9, 130.2, 130.5, 130.8, 130.9, 131.9, 134.3, 152.1, 167.0; MALDI-TOF-MS (dithranol) calcd for $C_{50}H_{44}CuN_2O_4S$ ($[M+Cu]^+$) 831.2, found

831.0; HRMS (ESI) calcd for $C_{100}H_{88}N_4NaO_8S_2$ ($[2M+Na]^+$) 1559.5941, found 1559.5936. Prior to UV–vis and fluorescence spectroscopy, the compound was recrystallized from hexanes/CH_2Cl_2.

UV–vis and Fluorescence Spectroscopy

UV–vis and fluorescence spectroscopy were obtained for solutions in commercial spectrophotometric-grade solvents. Spectra were obtained in 10 mm quartz cuvettes. Emission spectra are corrected.[11] Quantum yields were determined using standard methods for nitrogen-sparged solutions relative to quinine bisulfate in 0.5 M H_2SO_4 (Φ_f = 0.54) (emission between 350 and 600 nm) or rhodamine 101 in EtOH (Φ_f = 0.91) (emission above 550 nm). The absorbance of the solutions was kept below 0.10 to avoid the inner filter effect. The quinine bisulfate was cross-checked against 9,10-diphenylanthracene in cyclohexane (Φ_f = 0.91) and the rhodamine 101 with cresyl violet in MeOH (Φ_f = 0.54); in both cases the measured quantum yields agreed with literature values to within 10%. Fluorescence lifetimes were determined for nitrogen-sparged solutions.

Computational Chemistry

All calculations were performed using Gaussian 09, rev. B.01.[12] Geometries were visualized using VMD 1.9.1.[13]

NMR Spectra

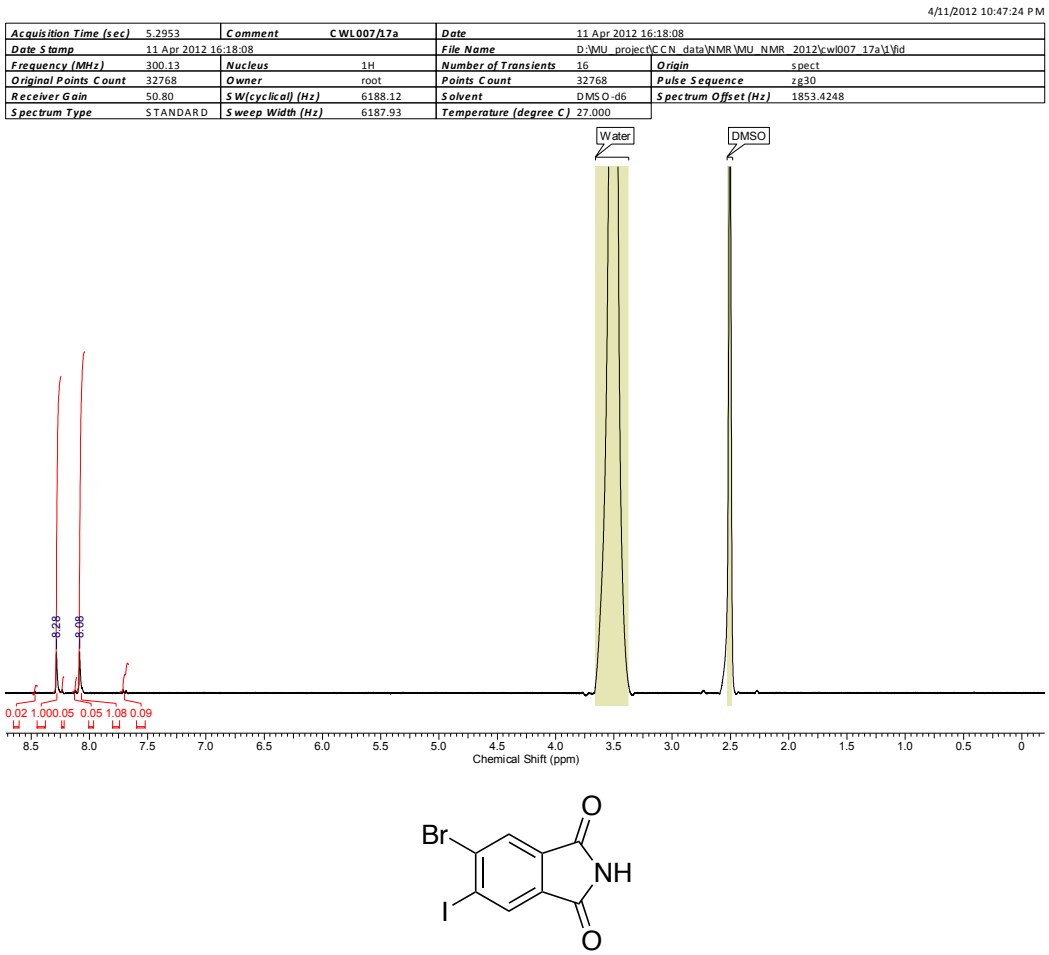


Figure S9. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of compound **S3**.

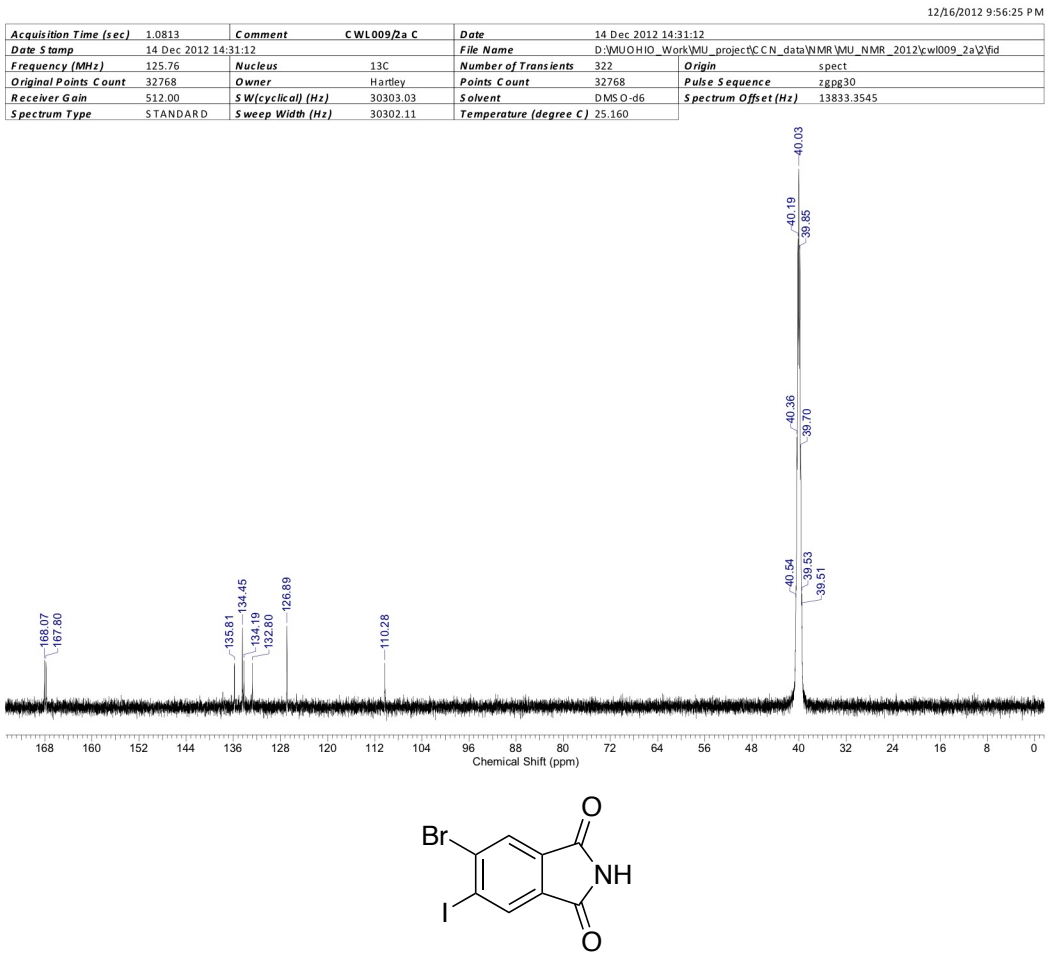
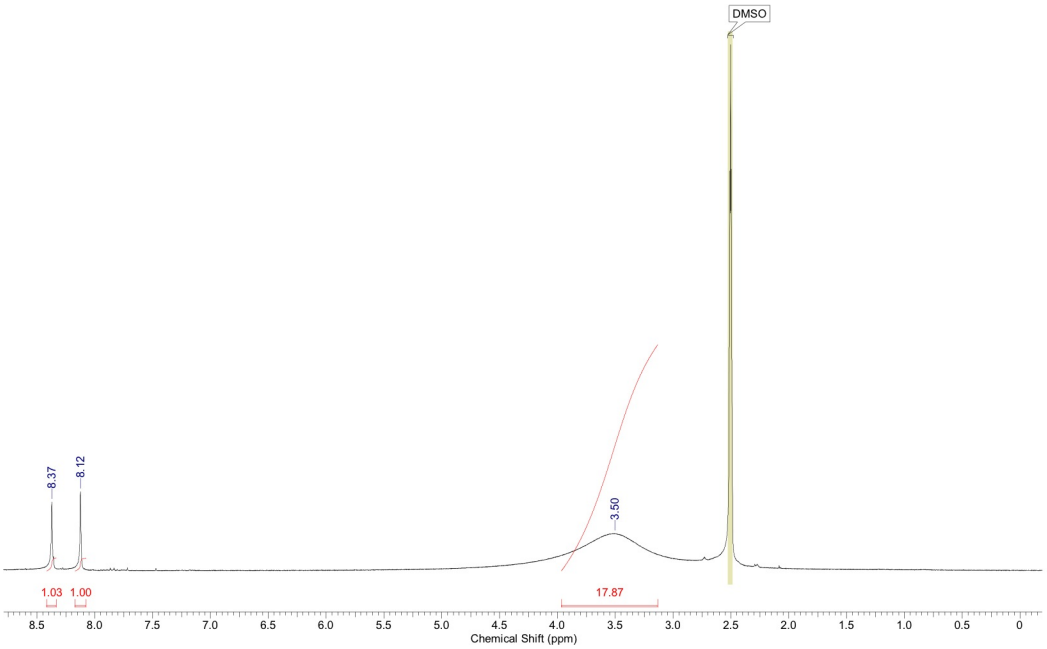


Figure S10. ^{13}C NMR spectrum (125 MHz, DMSO-d_6) of compound **S3**.

Acquisition Time (sec)	5.2953	*Comment*	CWL007/17b	*Date*	18 Apr 2012 14:08:00		
Date Stamp	18 Apr 2012 14:08:00			*File Name*	D:\MU_project\CCN_data\NMR\MU_NMR_2012\cwl007_17b\1\fid		
Frequency (MHz)	300.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect
Original Points Count	32768	*Owner*	root	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	128.00	*SW(cyclical) (Hz)*	6188.12	*Solvent*	DMSO-d6	*Spectrum Offset (Hz)*	1853.4248
Spectrum Type	STANDARD	*Sweep Width (Hz)*	6187.93	*Temperature (degree C)*	27.000		



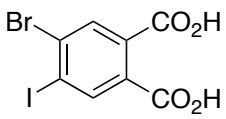


Figure S11. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of compound **S4**.

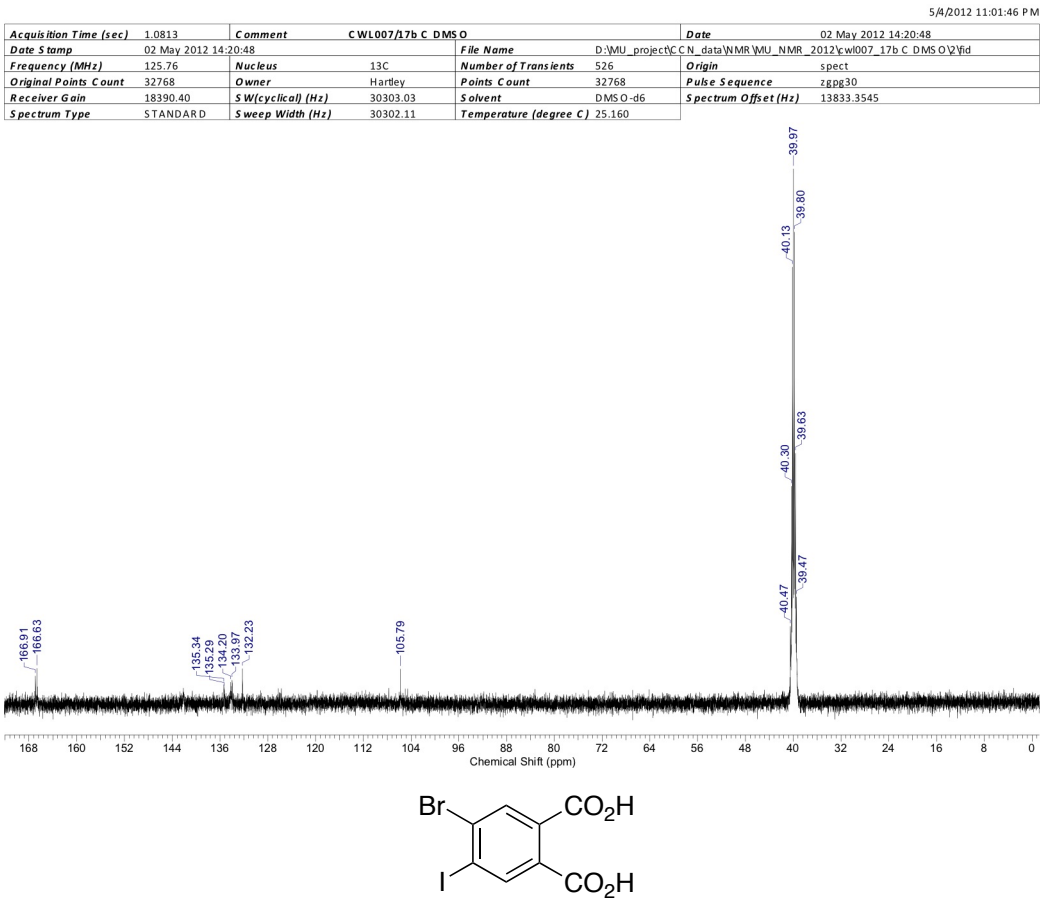
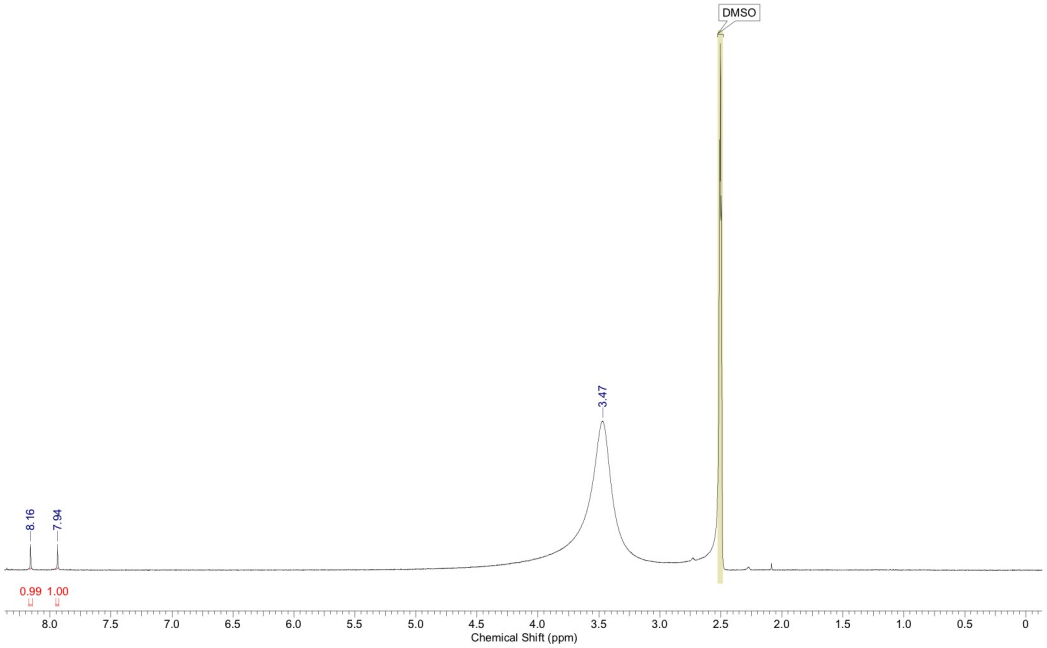


Figure S12. ^{13}C NMR spectrum (125 MHz, DMSO-d_6) of compound **S4**.

Acquisition Time (sec)	6.9730	*Comment*	CWL007/44a DMSO			*Date*	03 May 2012 17:11:28
Date Stamp	03 May 2012 17:11:28			*File Name*	F:\cwl007_44a DMSO\1\PDATA\1\1r		
Frequency (MHz)	300.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect
Original Points Count	32768	*Owner*	root	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	4.00	*SW(cyclical) (Hz)*	4699.25	*Solvent*	DMSO-d6	*Spectrum Offset (Hz)*	1853.4265
Spectrum Type	STANDARD			*Sweep Width (Hz)*	4699.10	*Temperature (degree C)*	27.000



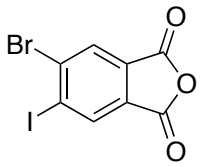


Figure S13. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of compound **S5**.

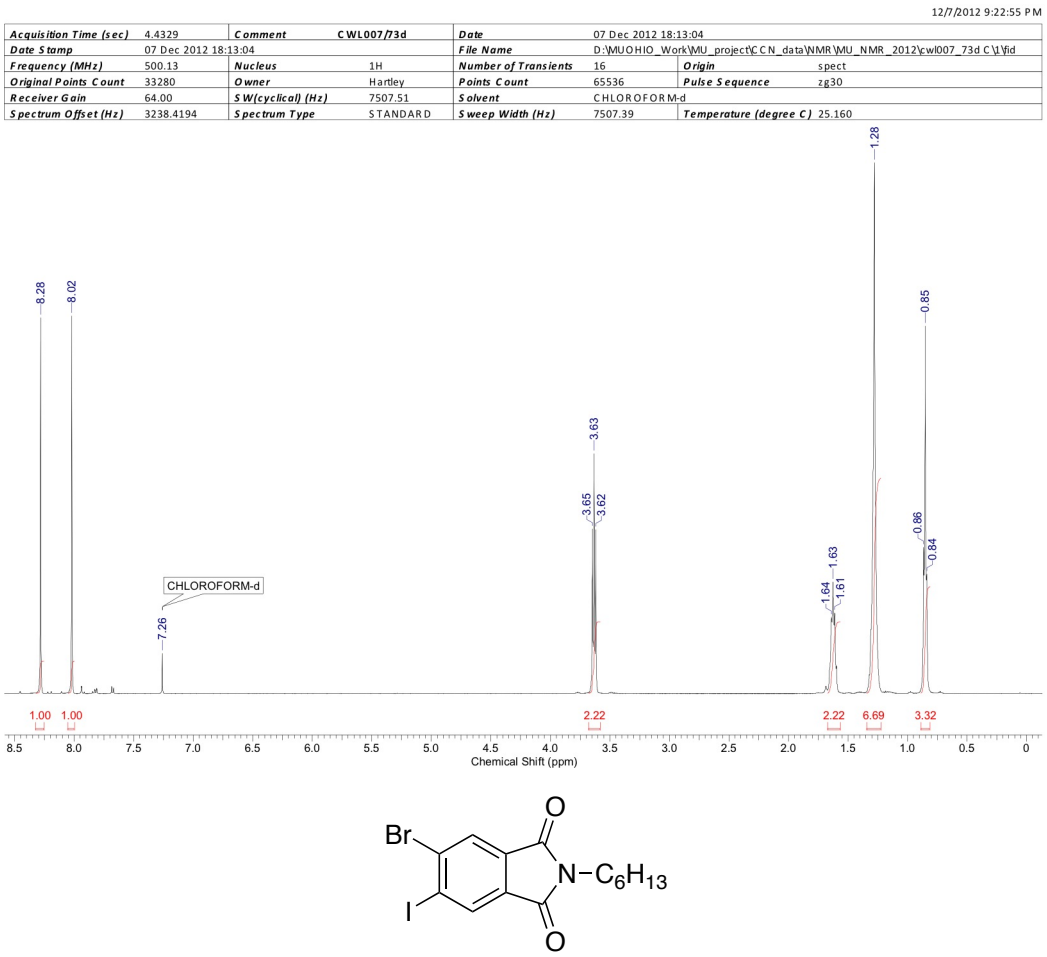
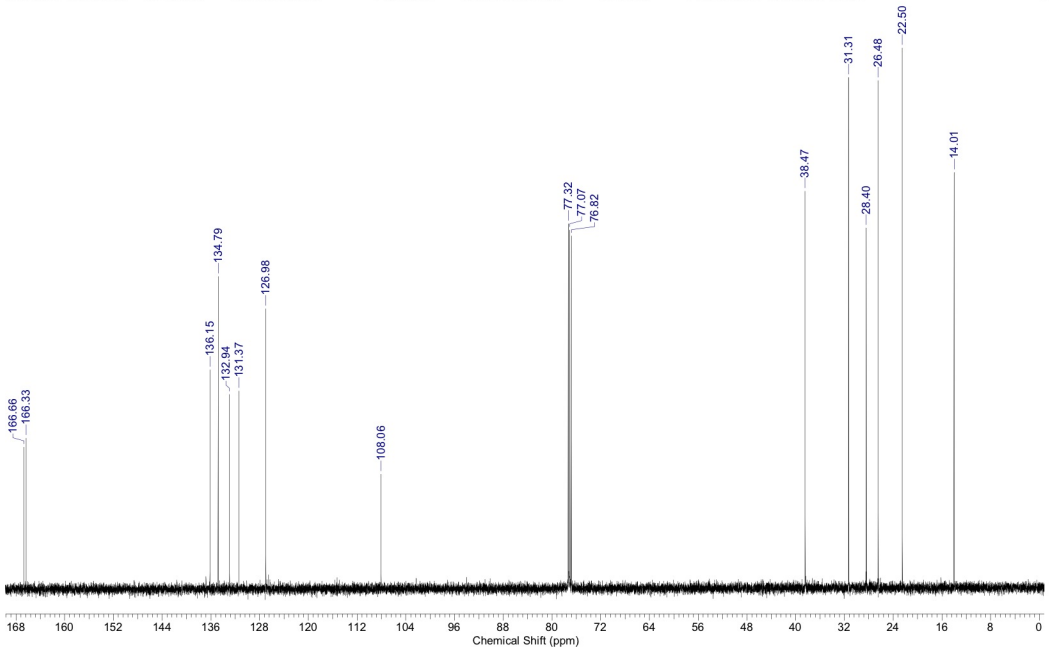


Figure S14. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **S6**.

12/7/2012 9:27:48 PM

Acquisition Time (sec)	1.0813	*Comment*	CWL007/73d C	*Date*	07 Dec 2012 18:17:20		
Date Stamp	07 Dec 2012 18:17:20			*File Name*	D:\MUOHIO_Work\MU_project\CCN_data\NMR\MU_NMR_2012\cwl007_73d C\2\fid		
Frequency (MHz)	125.76	*Nucleus*	13C	*Number of Transients*	126	*Origin*	spect
Original Points Count	32768	*Owner*	Hartley	*Points Count*	32768	*Pulse Sequence*	zgpg30
Receiver Gain	512.00	*SW(cyclical) (Hz)*	30303.03	*Solvent*	CHLOROFORM-d		
Spectrum Offset (Hz)	13833.3545	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	30302.11	*Temperature (degree C)*	25.160



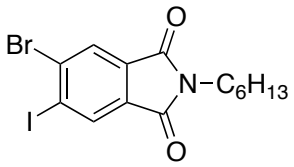


Figure S15. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **S6**.

Acquisition Time (sec)	4.4329	*Comment*	CWL005/119c			*Date*	27 Aug 2012 09:05:04
Date Stamp	27 Aug 2012 09:05:04			*File Name*	D:\MU_project\CCN_data\NMR\MU_NMR_2011\cwl005_119c 500\1\fid		
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect
Original Points Count	33280	*Owner*	Hartley	*Points Count*	65536	*Pulse Sequence*	zg30
Receiver Gain	40.30	*SW(cyclical) (Hz)*	7507.51	*Solvent*	CHLOROFORM-d		
Spectrum Offset (Hz)	3237.3884	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	7507.39	*Temperature (degree C)*	25.160

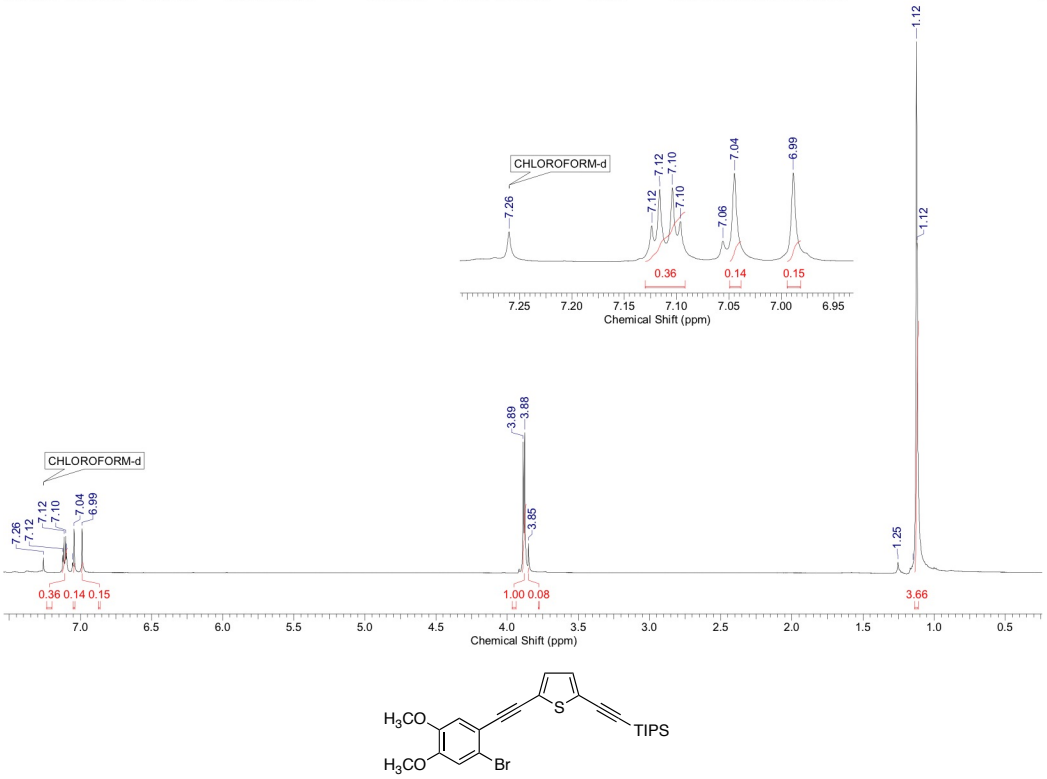


Figure S16. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **1a**.

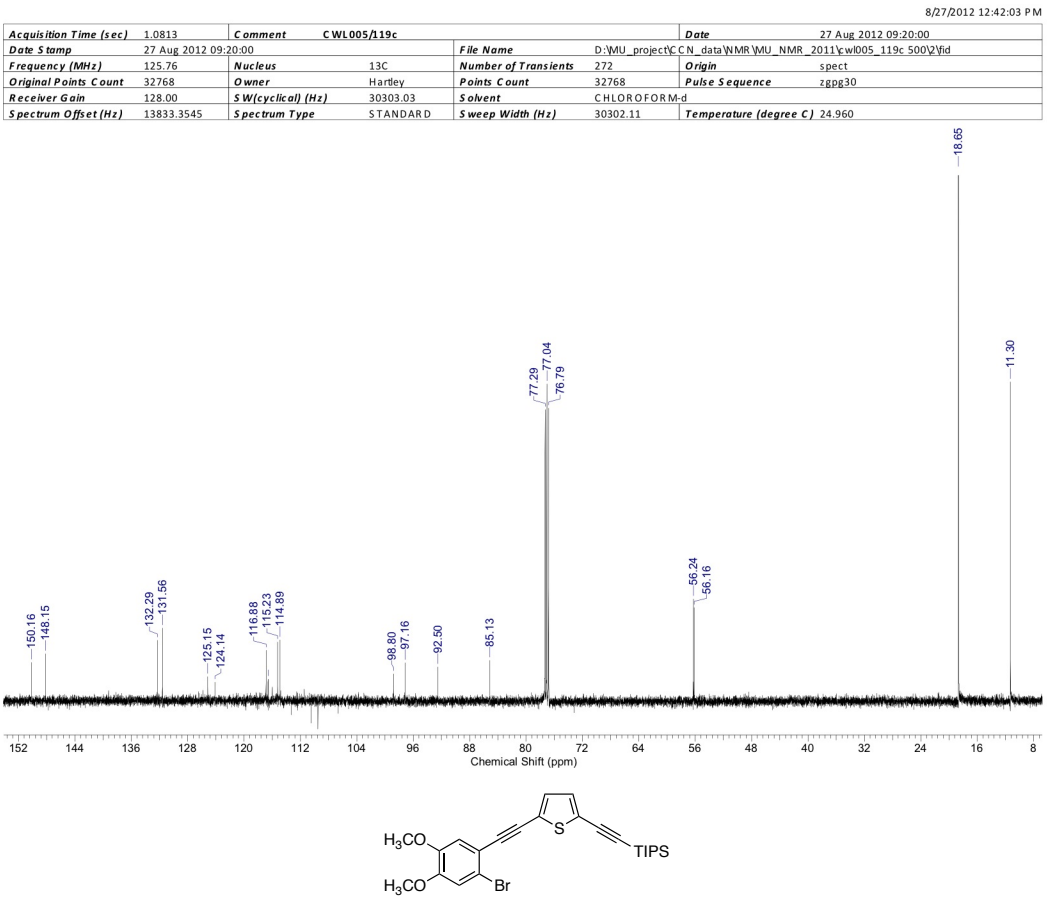


Figure S17. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **1a**.

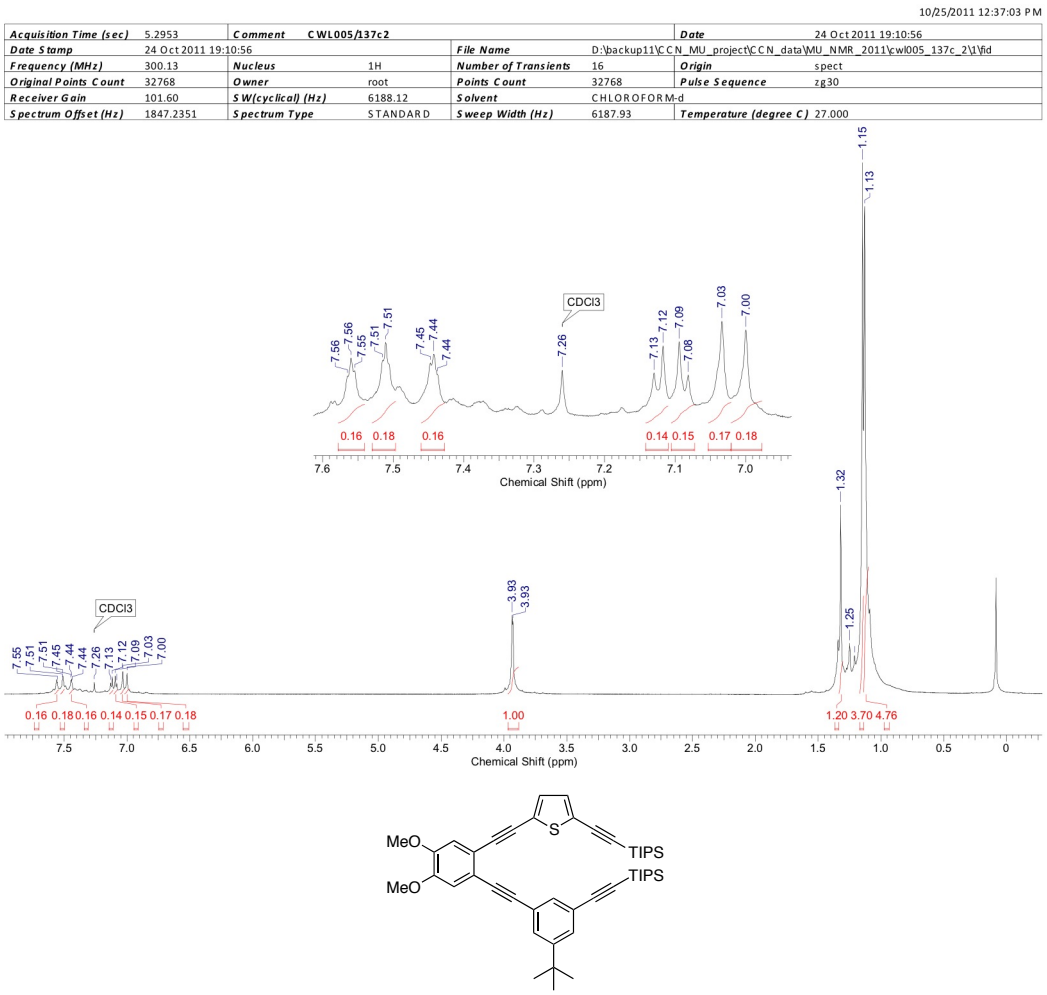


Figure S18. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **2a**.

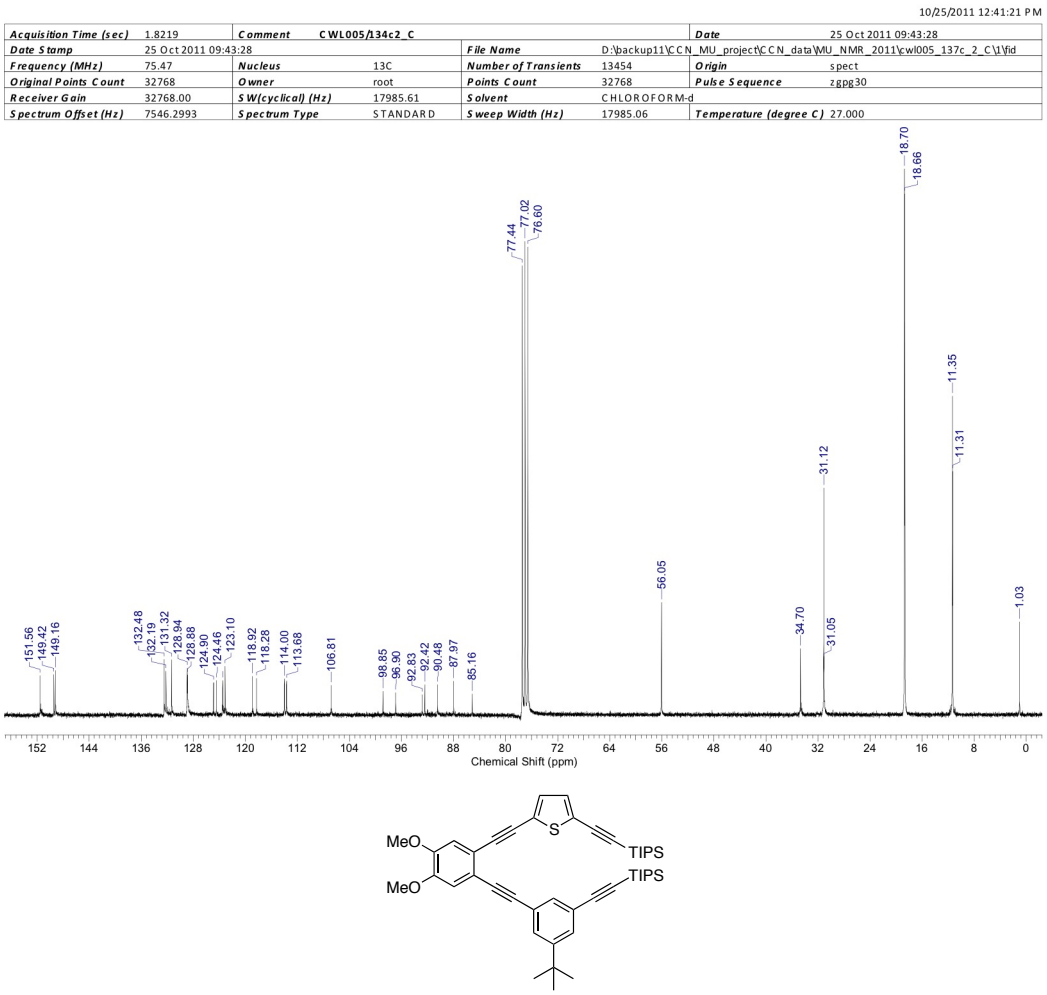
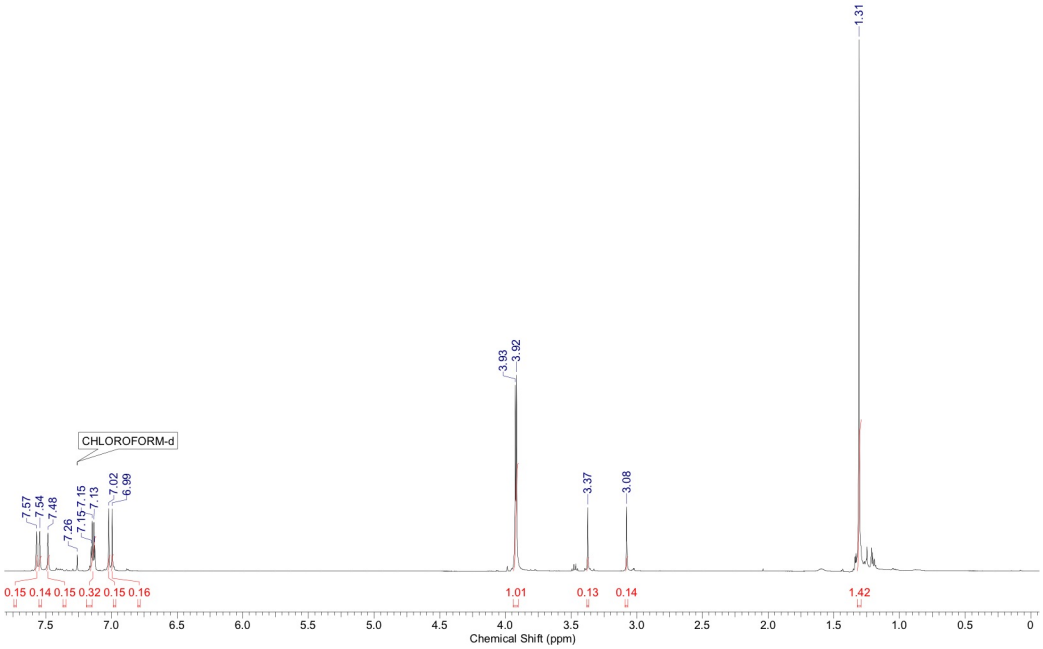


Figure S19. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **2a**.

Acquisition Time (sec)	2.1823	*Comment*	CWL006/69f C	*Date*	26 Apr 2012 13:06:08		
Date Stamp	26 Apr 2012 13:06:08			*File Name*	D:\MU_project\CCN_data\NMR\MU_NMR_2012\cwl006_69f C\1\fid		
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect
Original Points Count	16384	*Owner*	Hartley	*Points Count*	16384	*Pulse Sequence*	zg30
Receiver Gain	40.30	*SW(cyclical) (Hz)*	7507.51	*Solvent*	CHLOROFORM-d		
Spectrum Offset (Hz)	3237.5605	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	7507.05	*Temperature (degree C)*	25.100



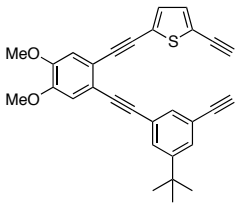


Figure S20. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3a**.

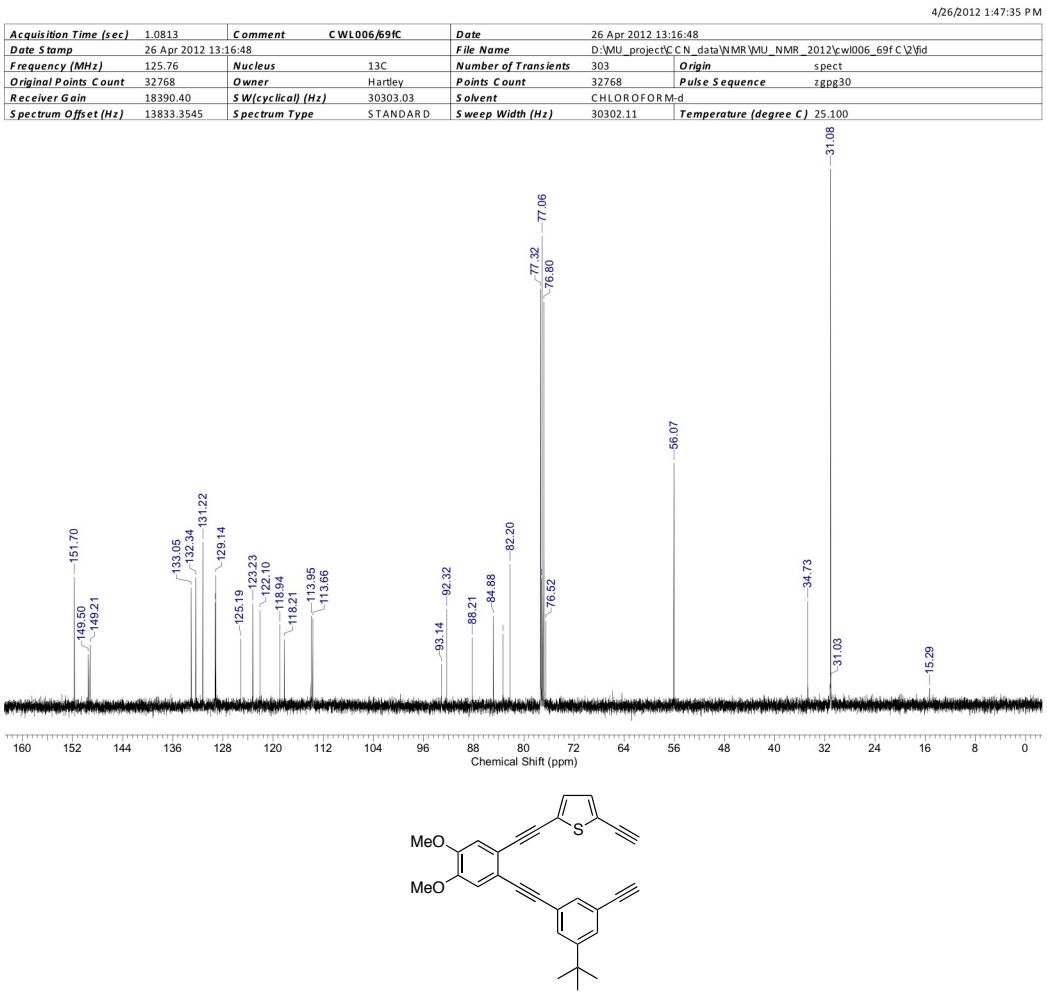
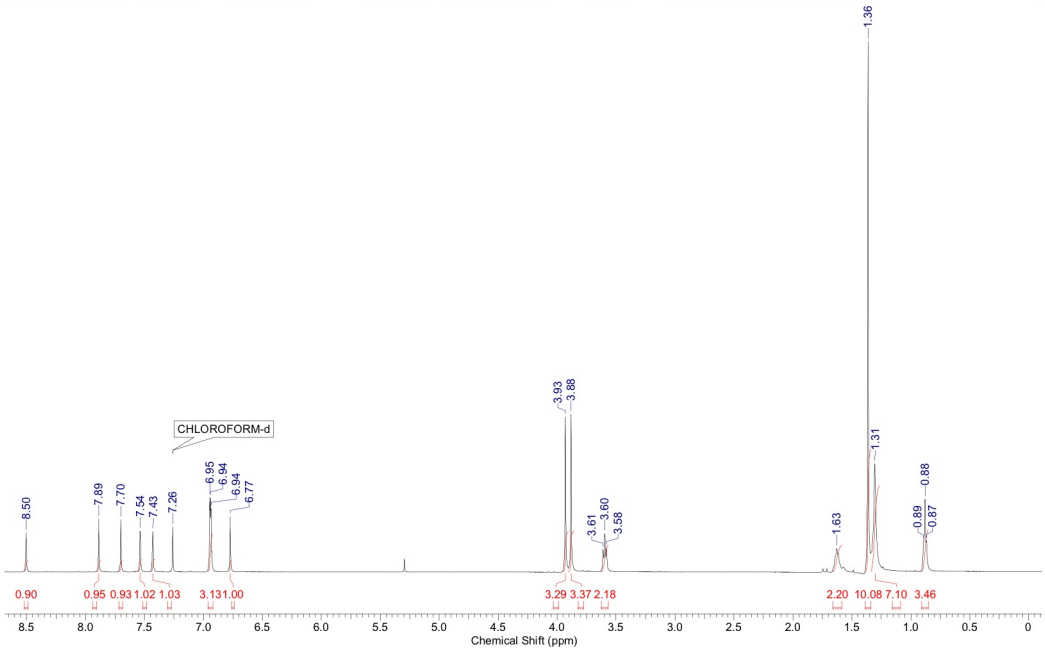


Figure S21. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3a**.

Acquisition Time (sec)	2.1823	*Comment*	CWL006/121e C_1			*Date*	19 Mar 2012 14:12:16
Date Stamp	19 Mar 2012 14:12:16			*File Name*	D:\MU_project\C CN_data\NMR\MU_NMR_2012\cwl006_121e C\1\fid		
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect
Original Points Count	16384	*Owner*	Hartley	*Points Count*	16384	*Pulse Sequence*	zg30
Receiver Gain	114.00	*SW(cyclical) (Hz)*	7507.51	*Solvent*	CHLOROFORM-d		
Spectrum Offset (Hz)	3237.5605	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	7507.05	*Temperature (degree C)*	25.000



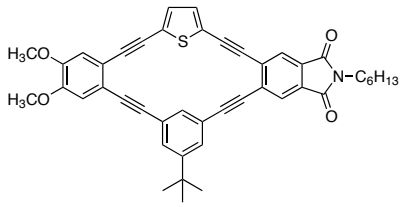


Figure S22. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **D(mP/Th)A**.

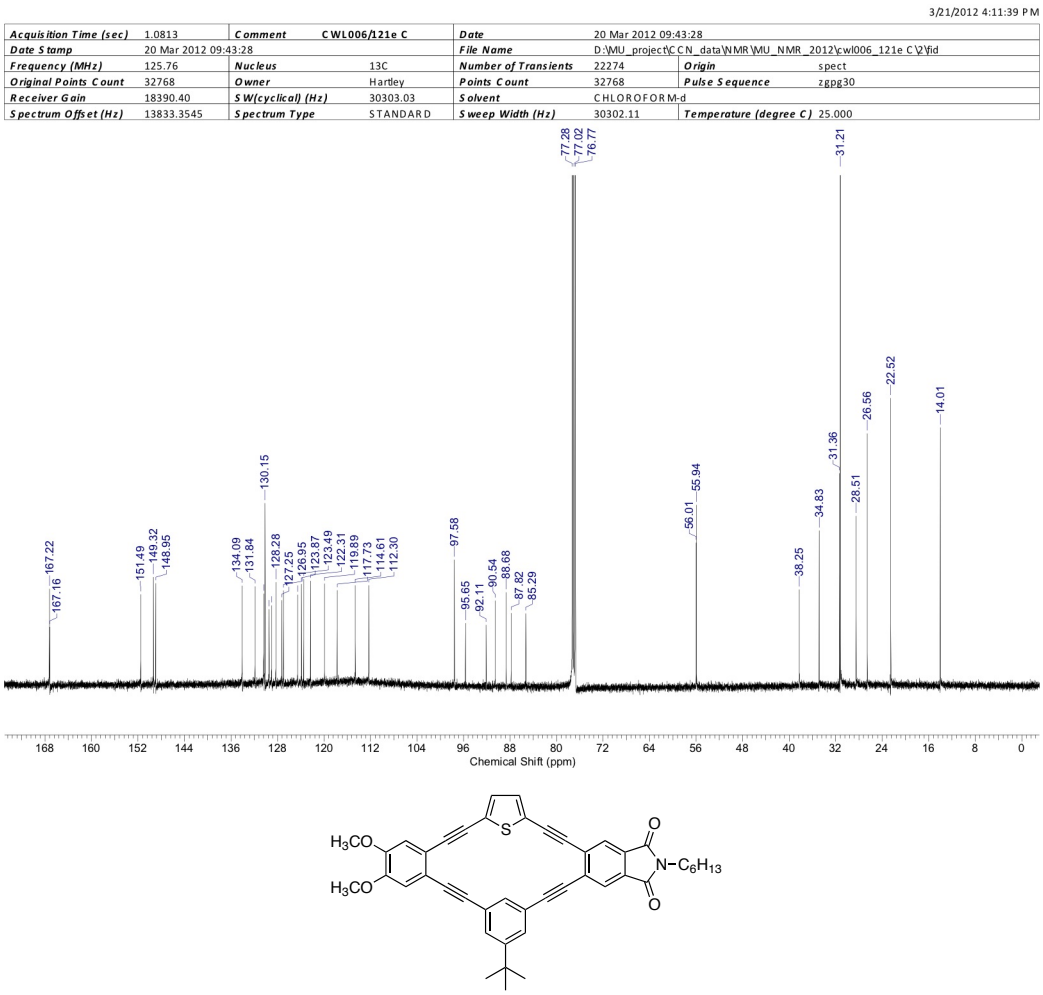
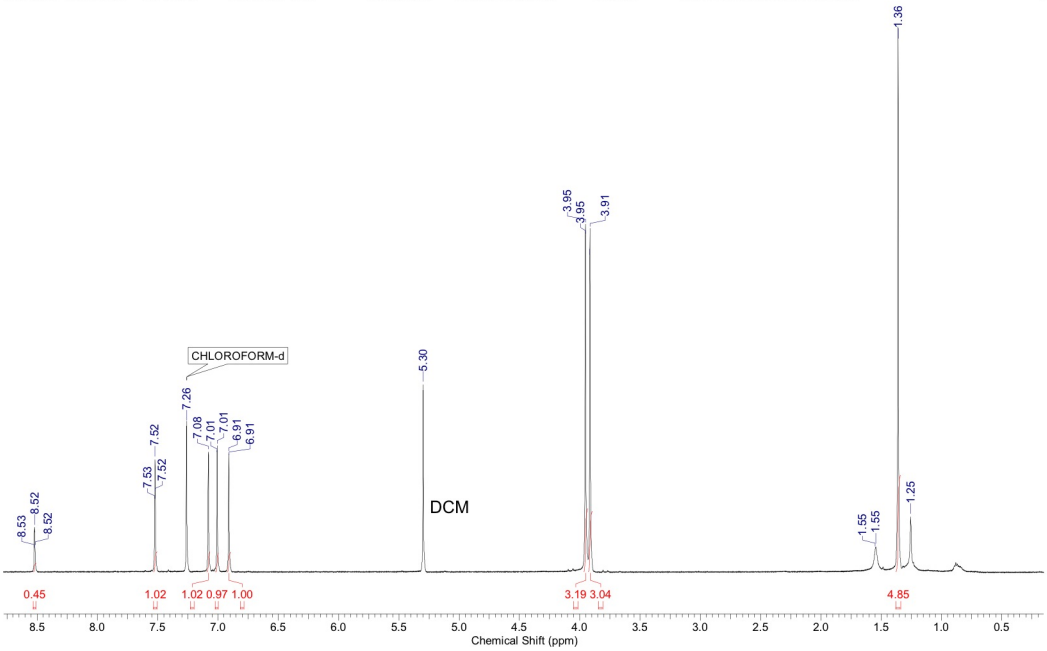


Figure S23. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **D(mP/Th)A**.

Acquisition Time (sec)	4.4329	*Comment*	CWL008/57c	*Date*	08 Dec 2012 18:34:24		
Date Stamp	08 Dec 2012 18:34:24			*File Name*	D:\MUOHIO_Work\MU_project\CCN_data\NMR\MU_NMR_2012\cwl008_57c C\1\fid		
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect
Original Points Count	33280	*Owner*	Hartley	*Points Count*	65536	*Pulse Sequence*	zg30
Receiver Gain	456.10	*SW(cyclical) (Hz)*	7507.51	*Solvent*	CHLOROFORM-d		
Spectrum Offset (Hz)	3238.5342	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	7507.39	*Temperature (degree C)*	25.160



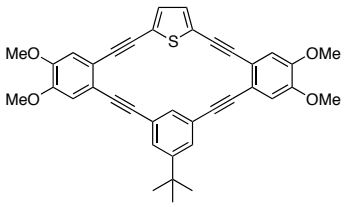


Figure S24. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **D(mP/Th)D**.

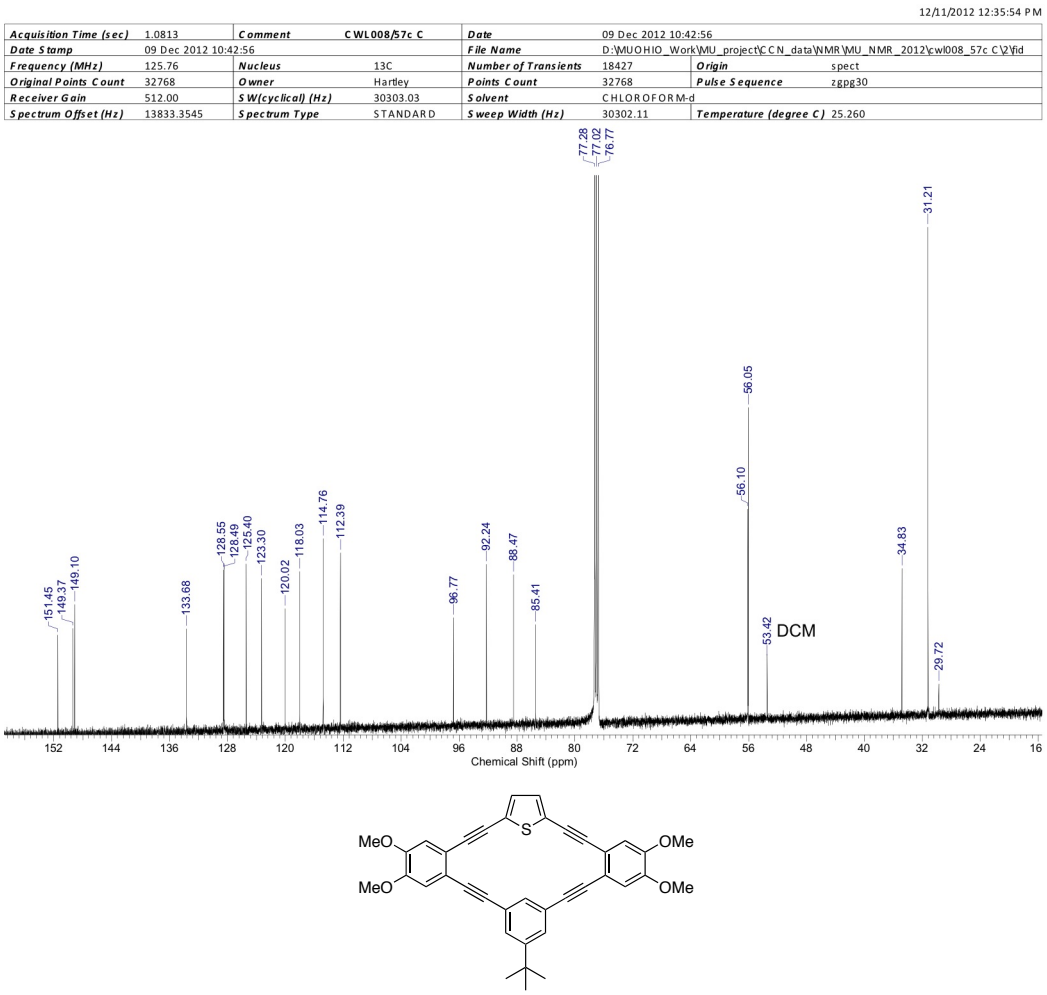


Figure S25. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **D(mP/Th)D**.

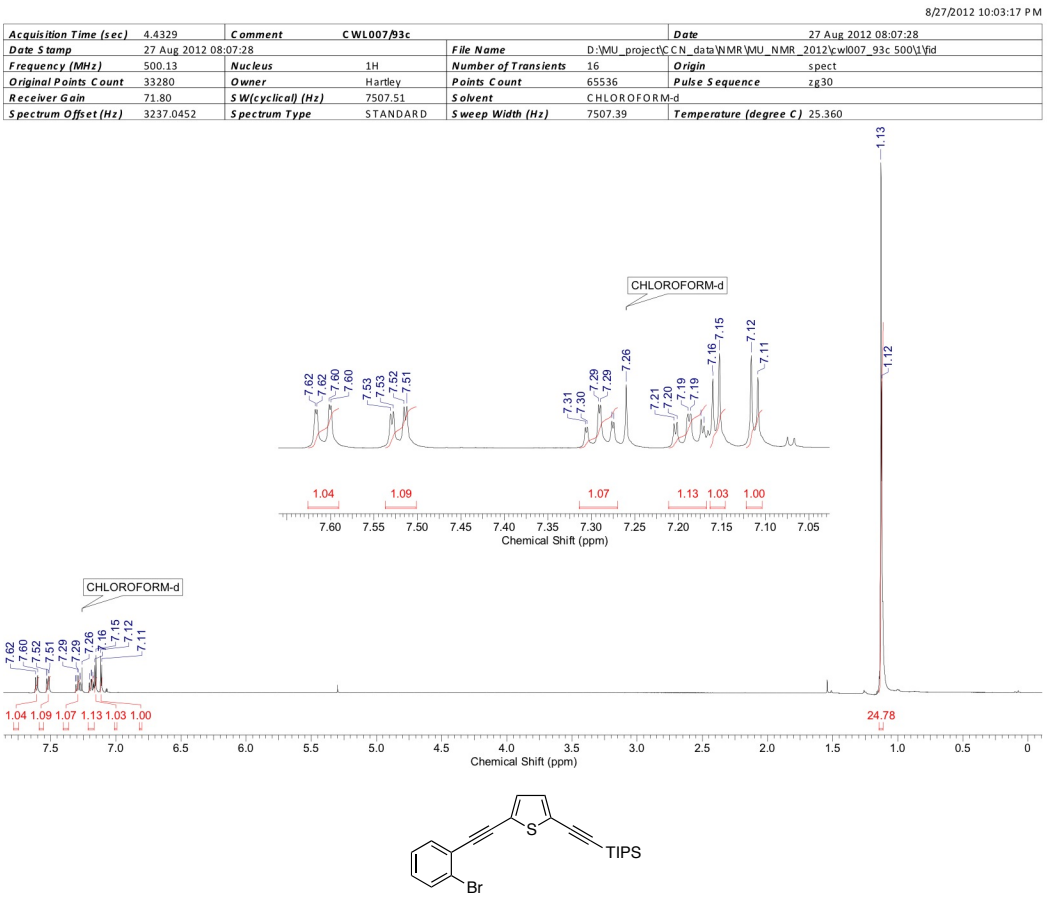


Figure S26. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **1b**.

Acquisition Time (sec)	1.0813	*Comment*	CWL007/93c C			*Date*	27 Aug 2012 08:18:08
Date Stamp	27 Aug 2012 08:18:08			*File Name*	D:\MU_project\CCN_data\NMR\MU_NMR_2012\cwl007_93c 500\2\fid		
Frequency (MHz)	125.76	*Nucleus*	13C	*Number of Transients*	280	*Origin*	spect
Original Points Count	32768	*Owner*	Hartley	*Points Count*	32768	*Pulse Sequence*	zgpg30
Receiver Gain	90.50	*SW(cyclical) (Hz)*	30303.03	*Solvent*	CHLOROFORM-d		
Spectrum Offset (Hz)	13833.3545	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	30302.11	*Temperature (degree C)*	24.860

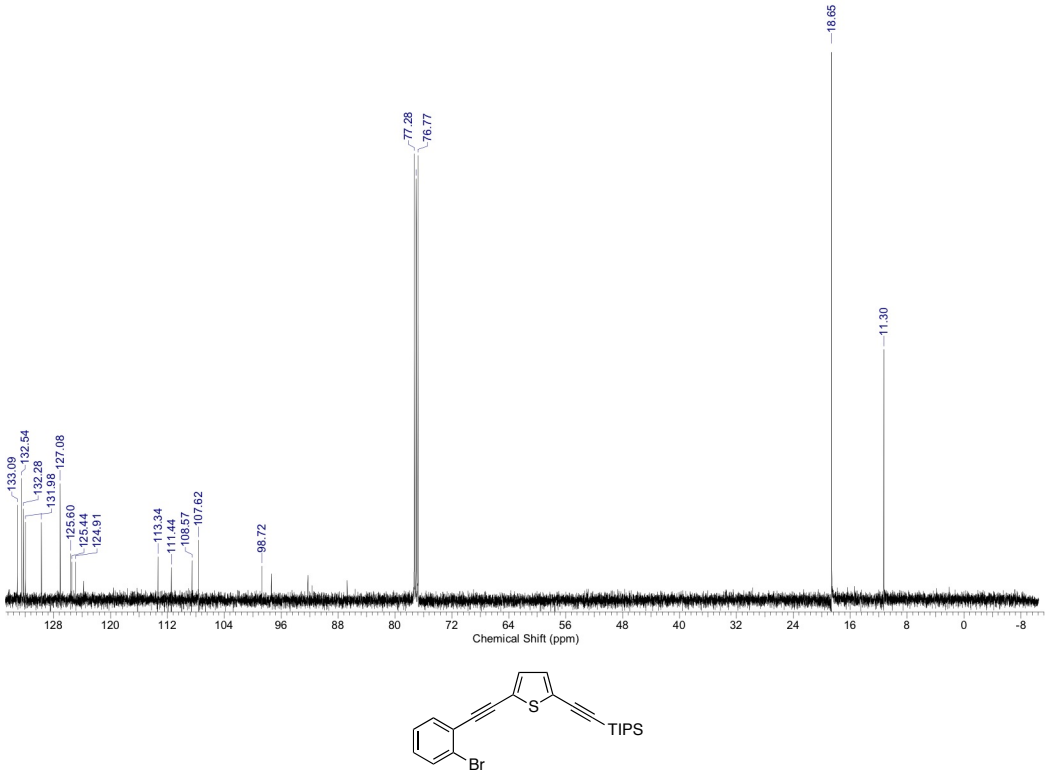


Figure S27. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **1b**.

Acquisition Time (sec)	4.4329	*Comment*	CWL007/111e			*Date*	27 Aug 2012 09:26:24
Date Stamp	27 Aug 2012 09:26:24			*File Name*	D:\MU_project\CCN_data\NMR\MU_NMR_2012\cwl007_111e 500\1\fid		
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect
Original Points Count	33280	*Owner*	Hartley	*Points Count*	65536	*Pulse Sequence*	zg30
Receiver Gain	40.30	*SW(cyclical) (Hz)*	7507.51	*Solvent*	CHLOROFORM-d		
Spectrum Offset (Hz)	3237.3884	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	7507.39	*Temperature (degree C)*	25.160

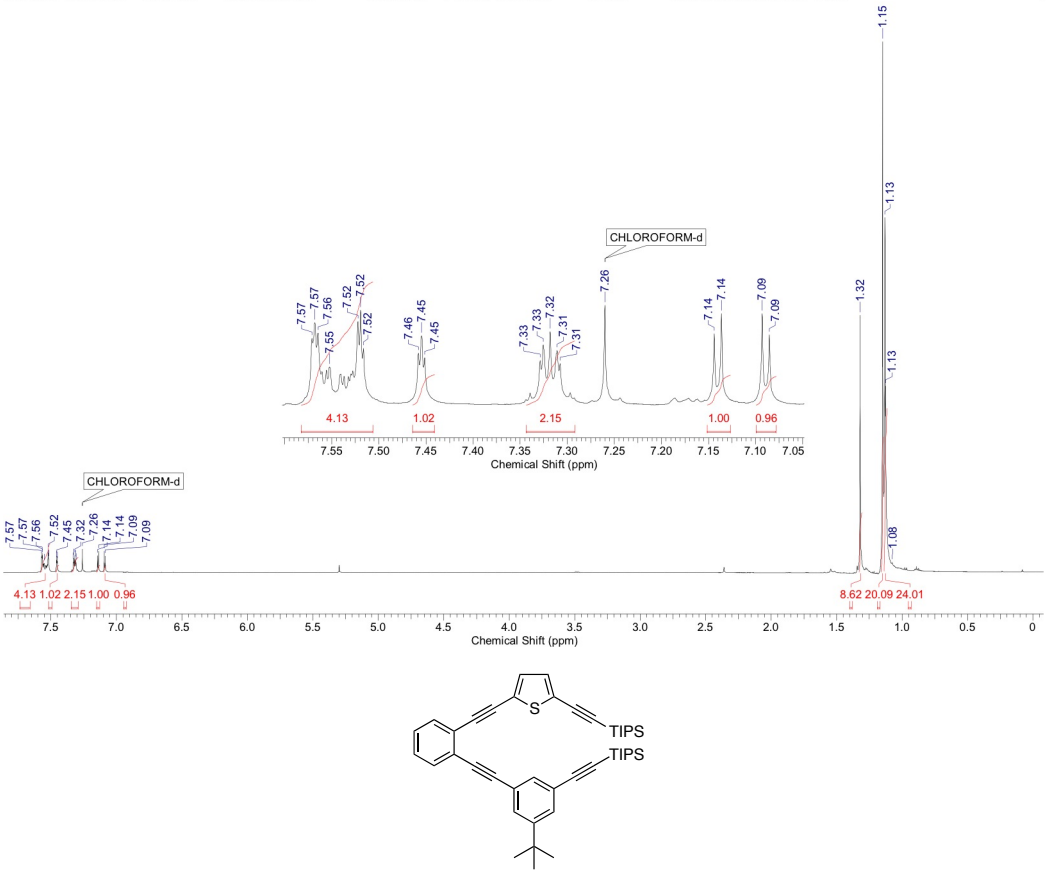


Figure S28. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **2b**.

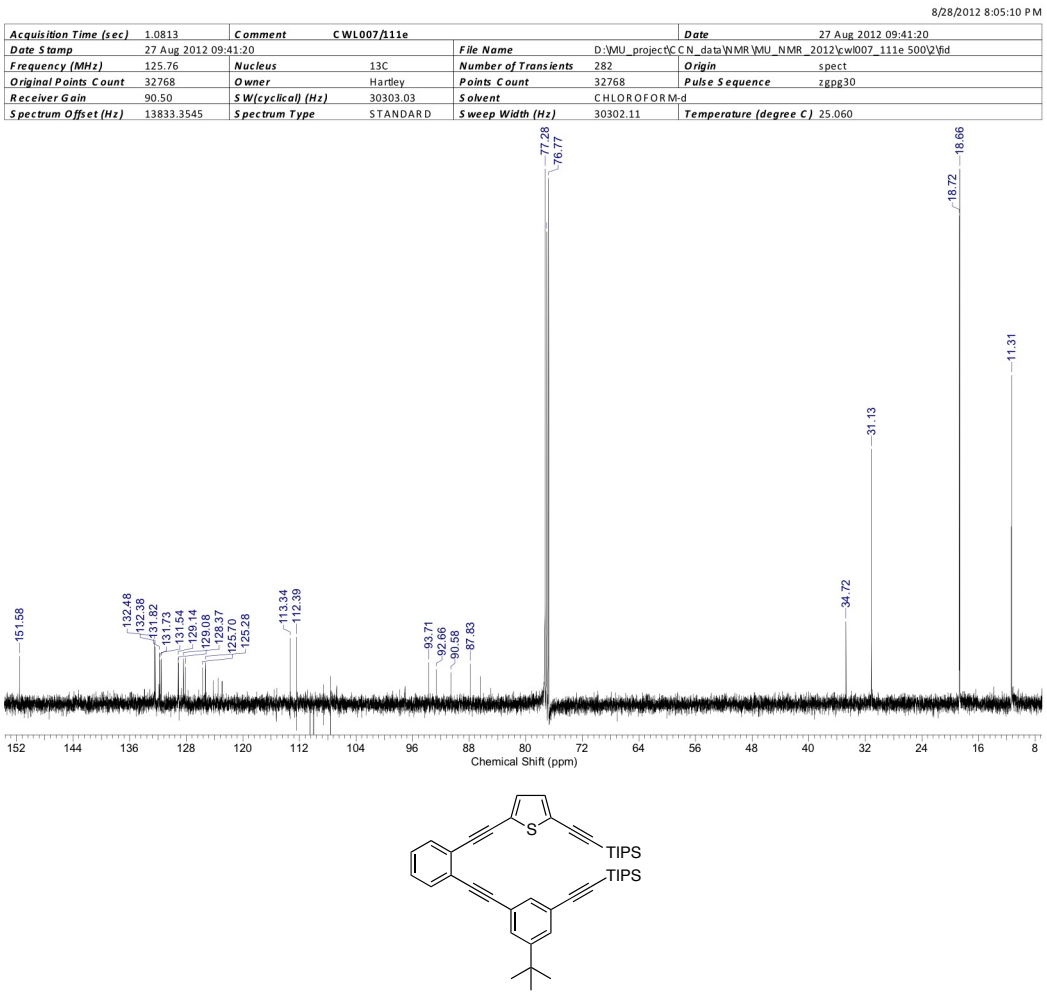


Figure S29. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **2b**.

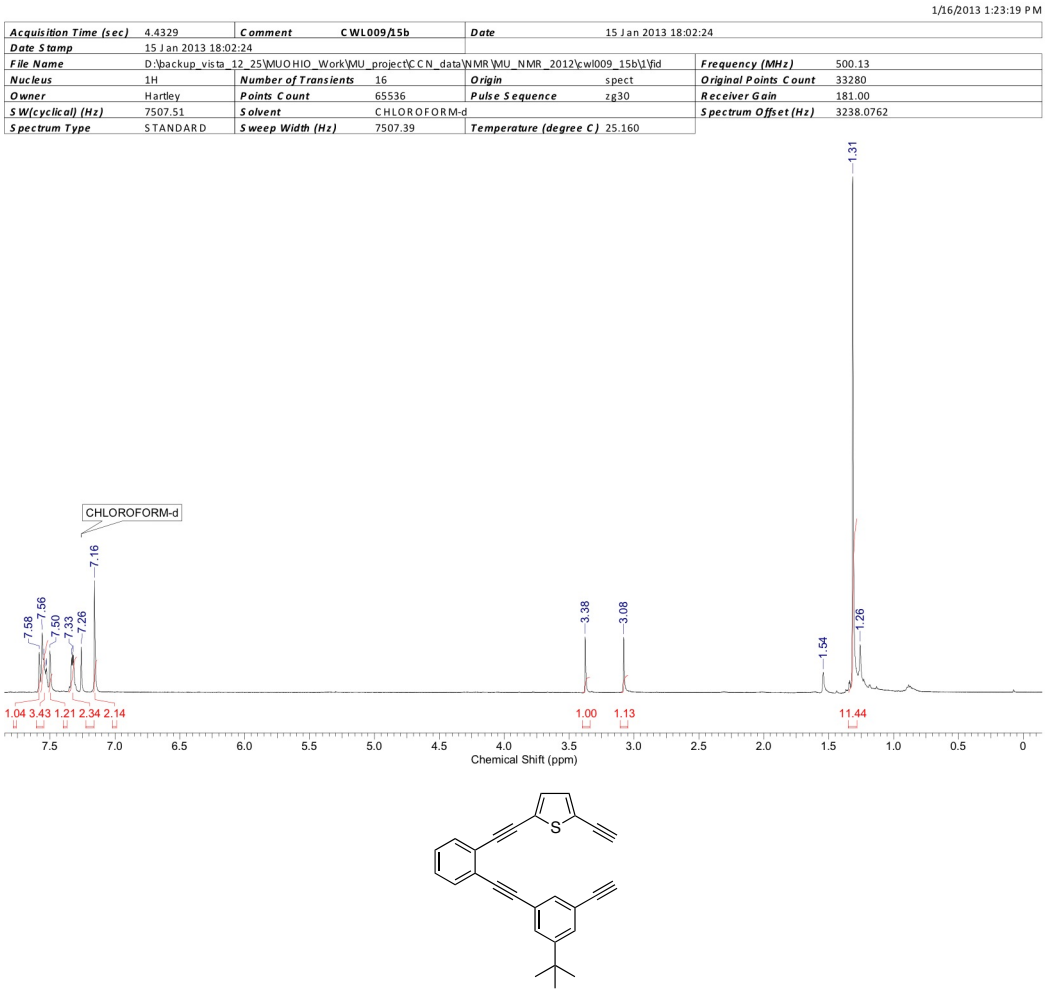


Figure S30. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3b**.

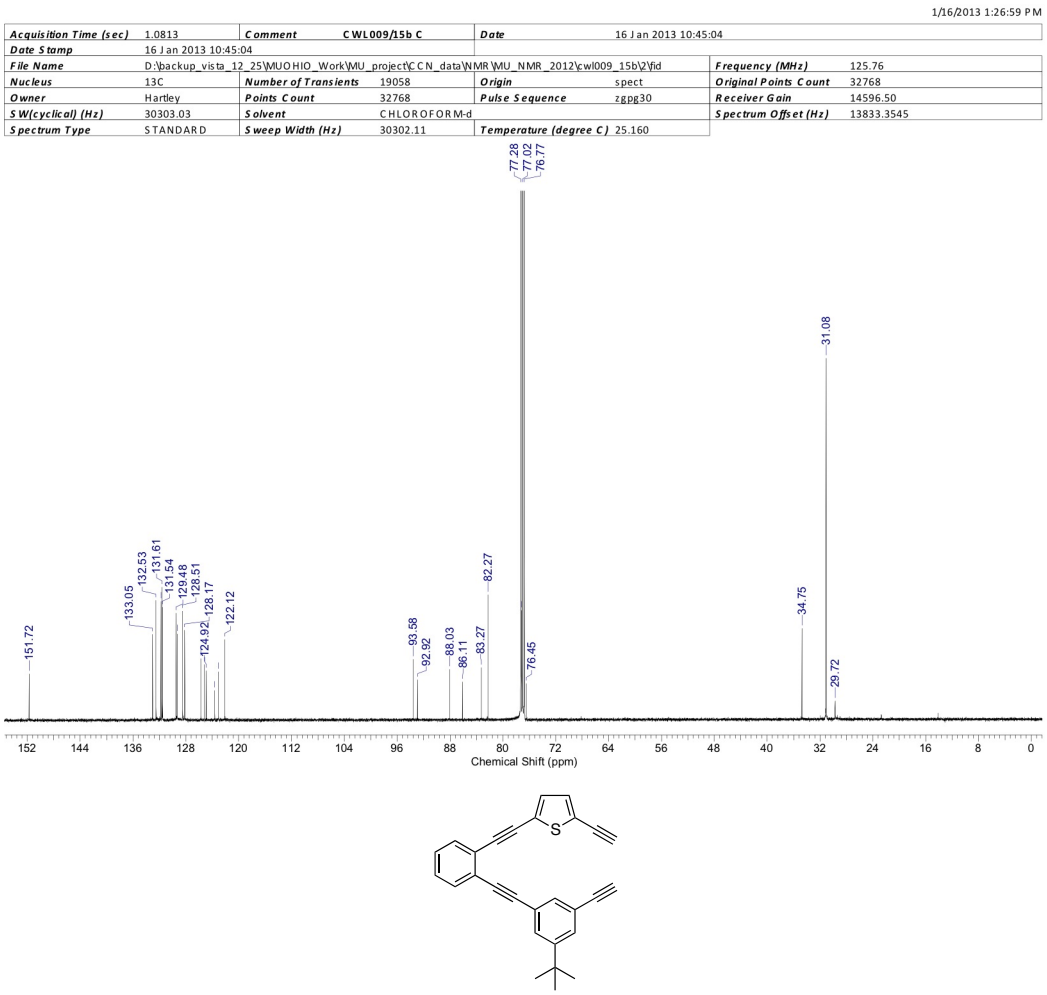


Figure S31. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3b**.

12/8/2012 10:48:23 AM

Acquisition Time (sec)	4.4329	*Comment*	CWL008/24c	*Date*	07 Dec 2012 19:08:32		
Date Stamp	07 Dec 2012 19:08:32			*File Name*	D:\MUOHIO_Work\MU_project\CCN_data\NMR\MU_NMR_2012\cwl008_24c C\1\fid		
Frequency (MHz)	500.13	*Nucleus*	1H	*Number of Transients*	128	*Origin*	spect
Original Points Count	33280	*Owner*	Hartley	*Points Count*	65536	*Pulse Sequence*	zg30
Receiver Gain	574.70	*SW(cyclical) (Hz)*	7507.51	*Solvent*	CHLOROFORM-d		
Spectrum Offset (Hz)	3238.0762	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	7507.39	*Temperature (degree C)*	25.160

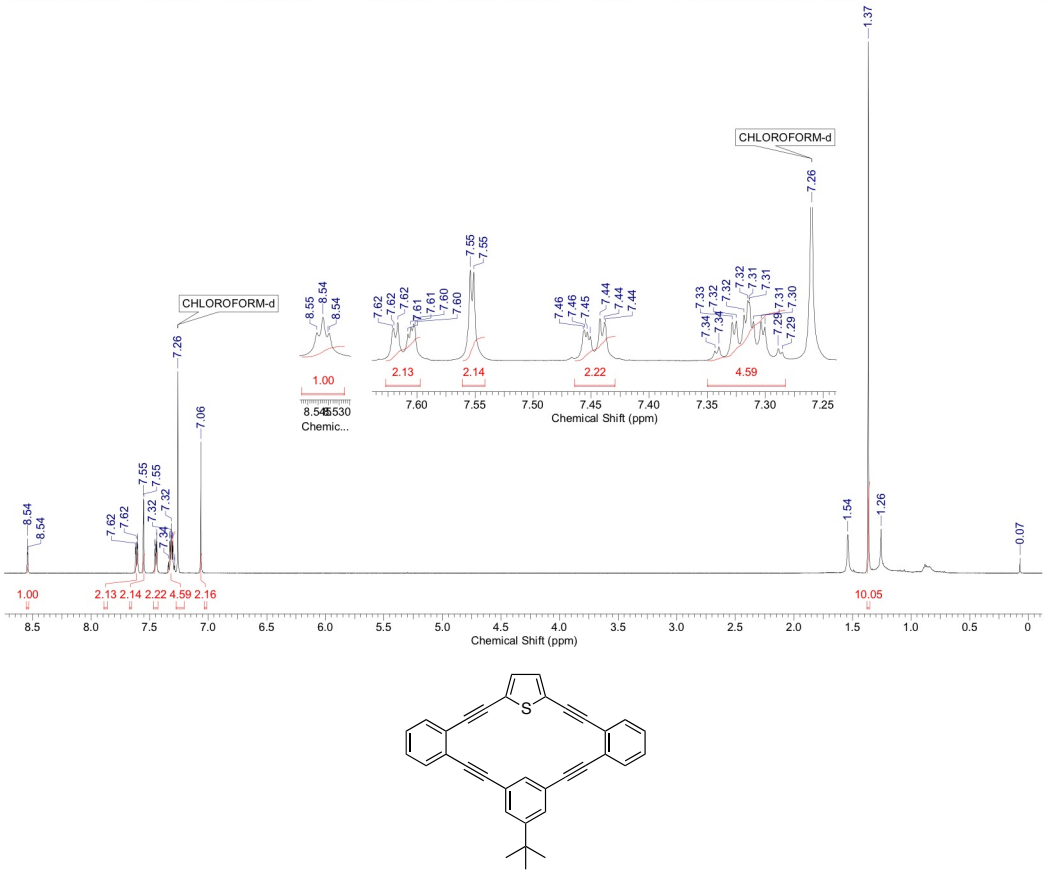


Figure S32. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **H(mP/Th)H**.

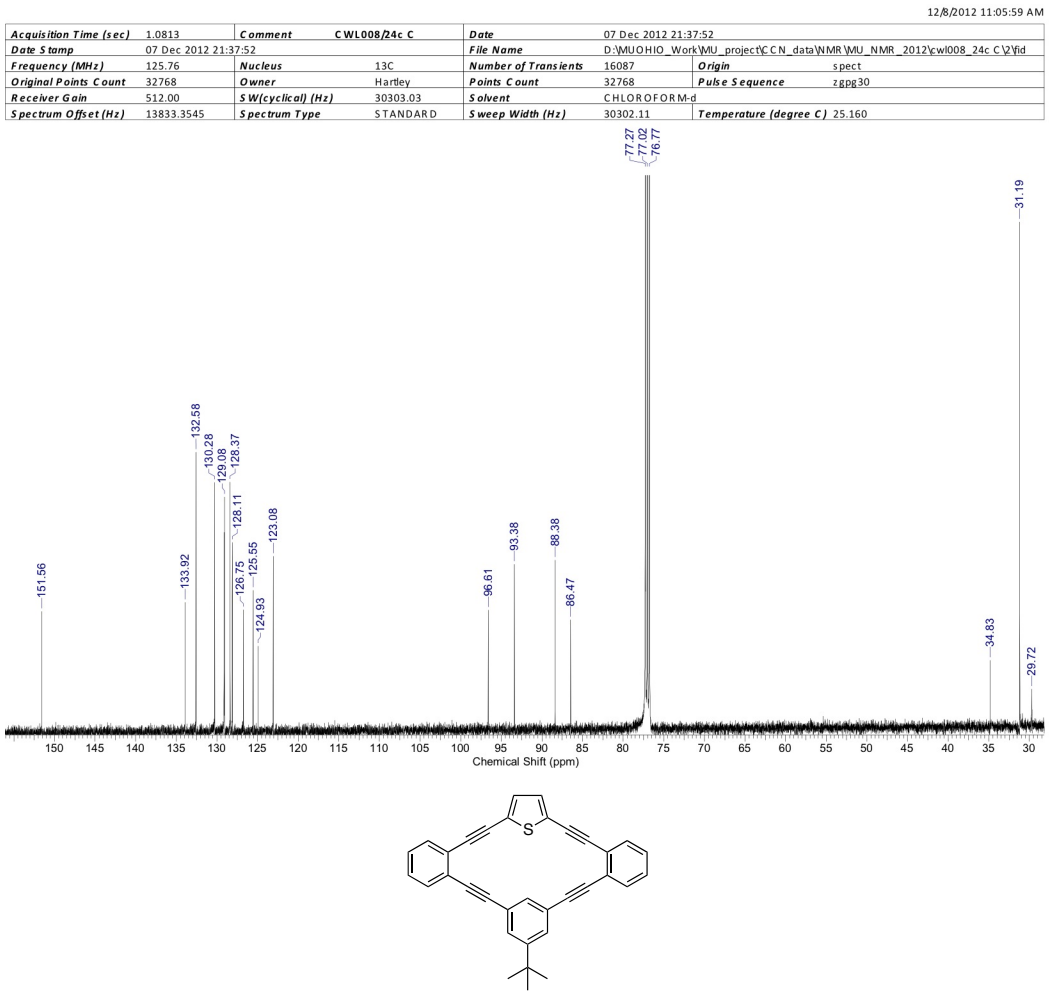
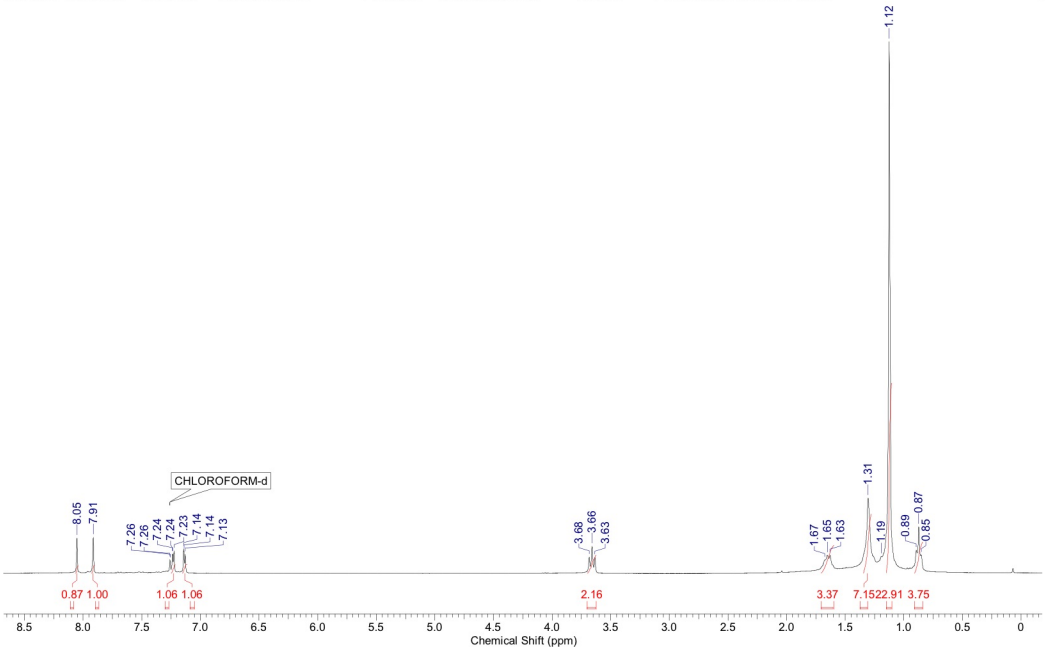


Figure S33. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **H(mP/Th)H**.

Acquisition Time (sec)	5.2953	*Comment*	CWL007/76c	*Date*	06 Aug 2012 16:16:00		
Date Stamp	06 Aug 2012 16:16:00			*File Name*	D:\WU_project\CCN_data\NMR\WU_NMR_2012\cwl007_76c\1\fid		
Frequency (MHz)	300.13	*Nucleus*	1H	*Number of Transients*	16	*Origin*	spect
Original Points Count	32768	*Owner*	root	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	64.00	*SW(cyclical) (Hz)*	6188.12	*Solvent*	CHLOROFORM-d		
Spectrum Offset (Hz)	1846.2910	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	6187.93	*Temperature (degree C)*	27.000



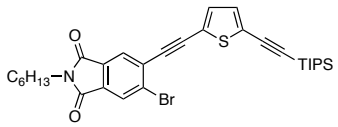


Figure S34. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **1c**.

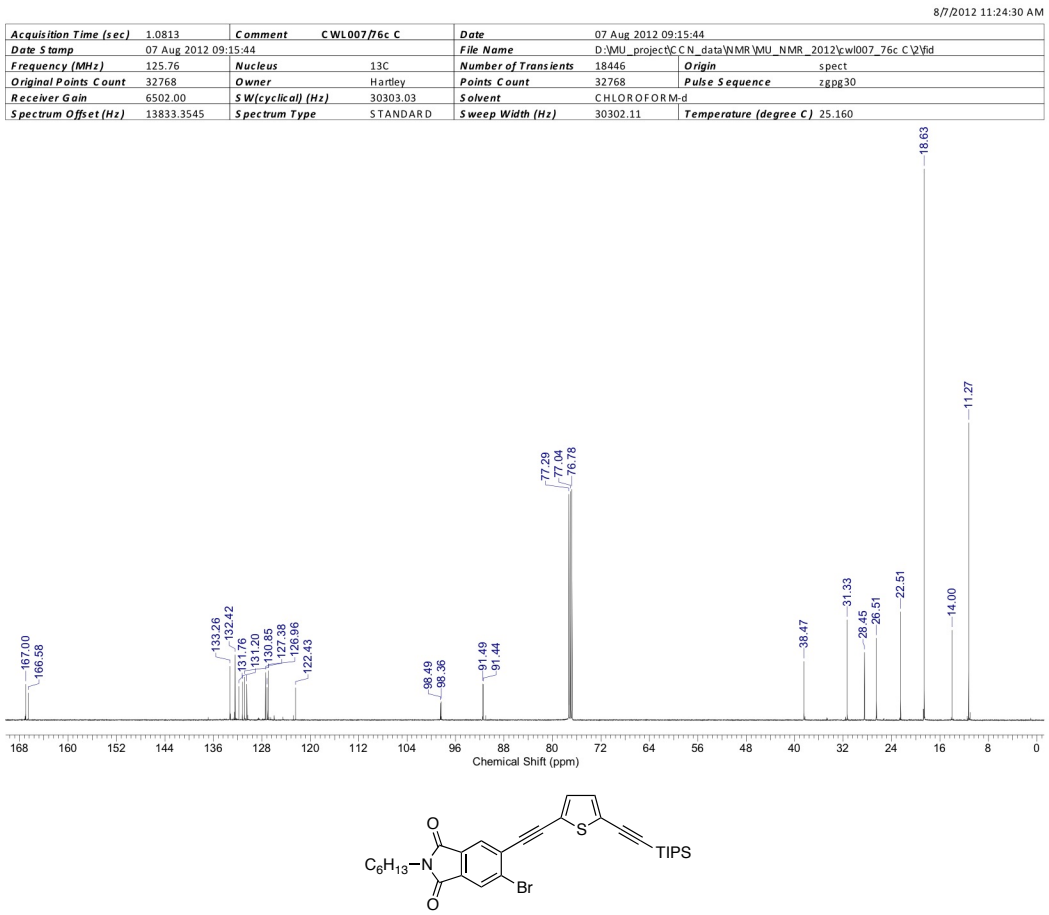


Figure S35. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **1c**.

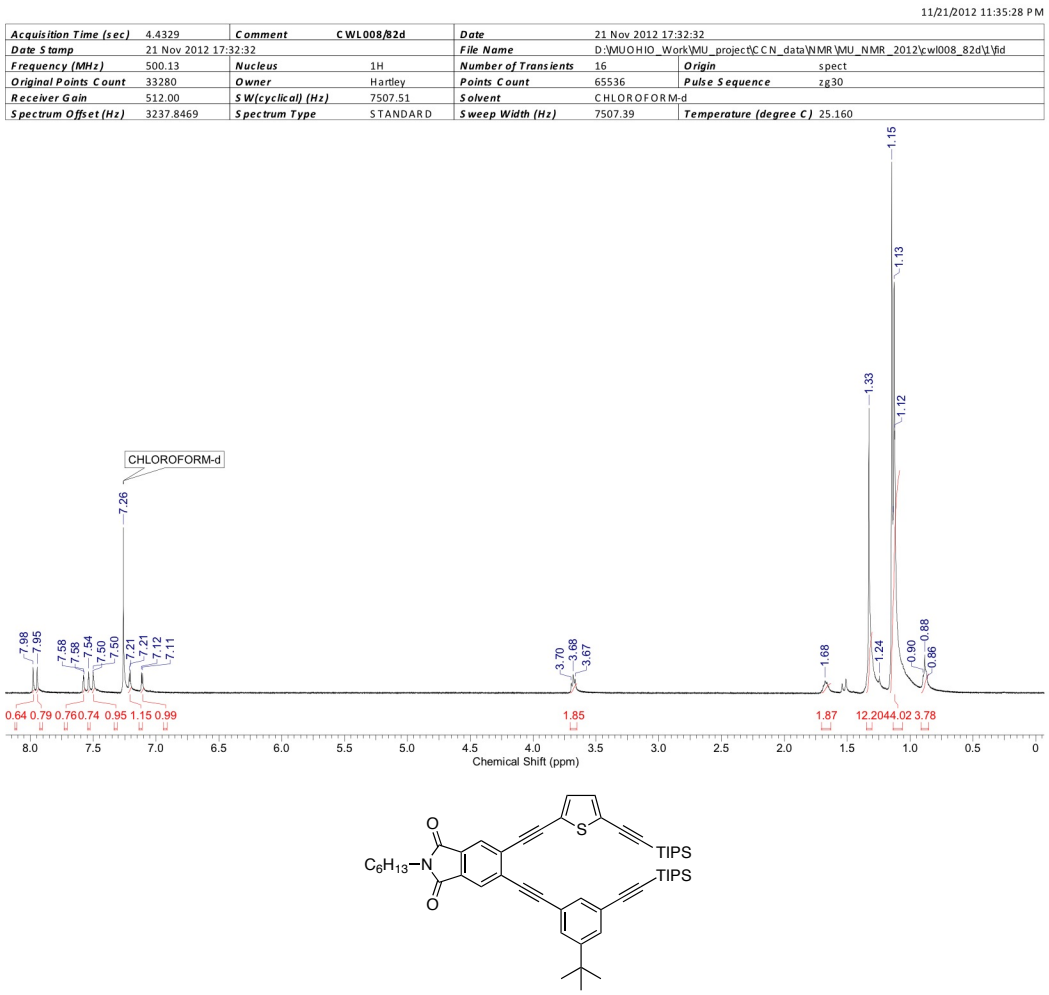


Figure S36. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **2c**.

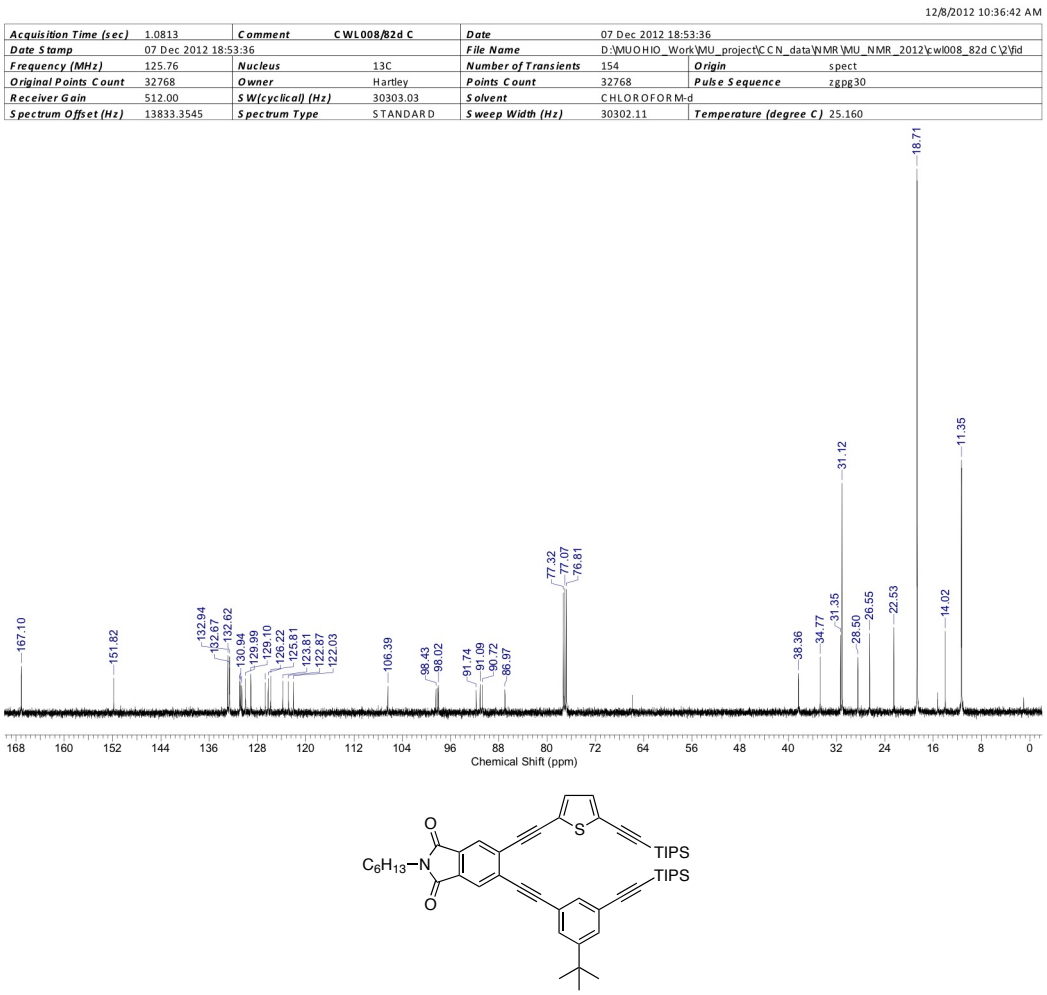


Figure S37. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **2c**.

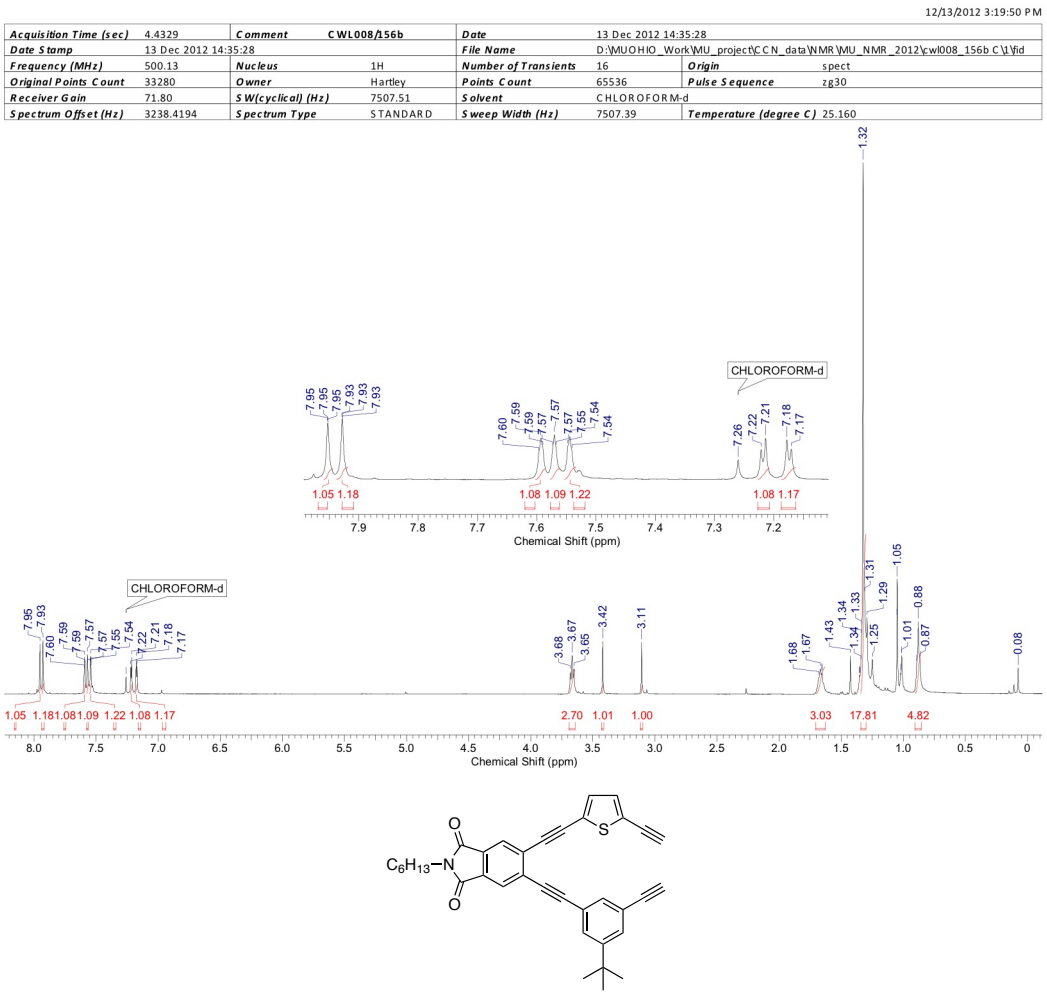


Figure S38. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **3c** (small amount of grease impurity).

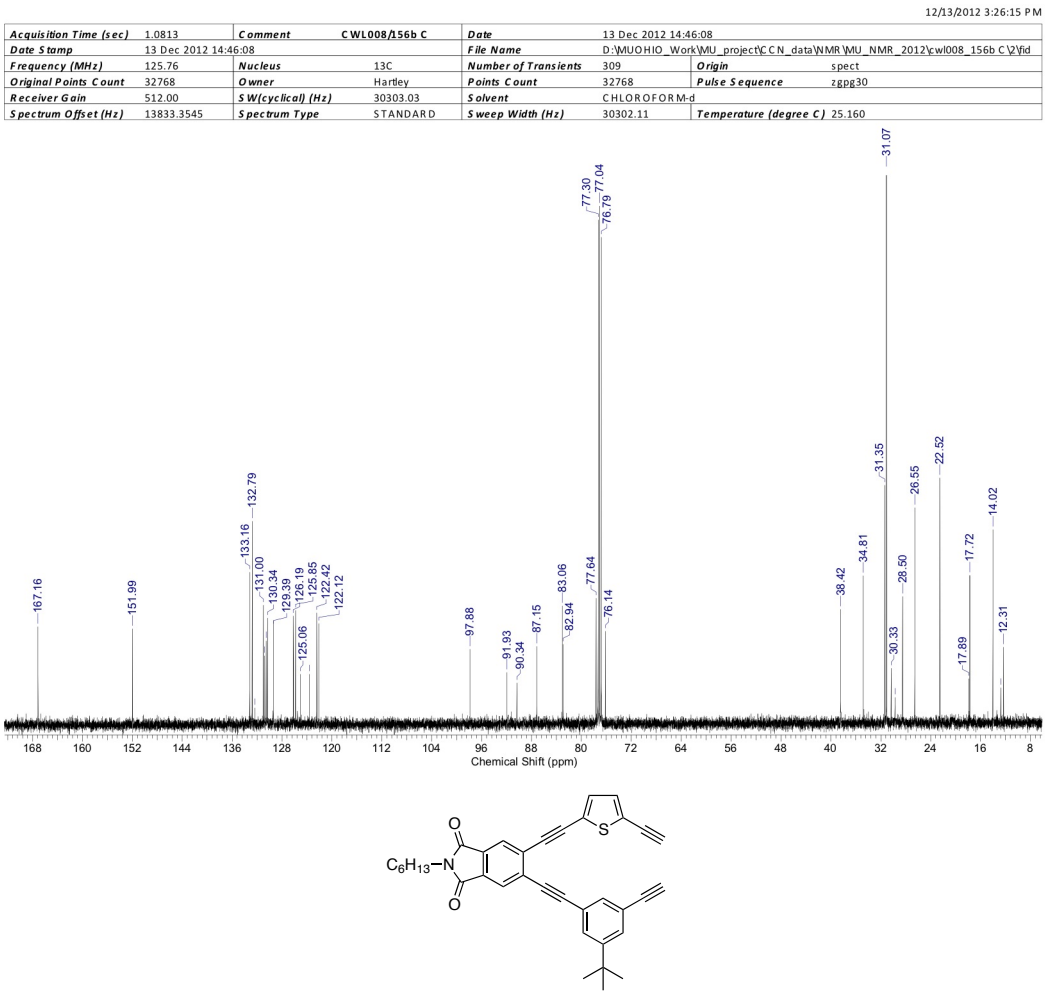


Figure S39. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **3c** (small amount of grease impurity).

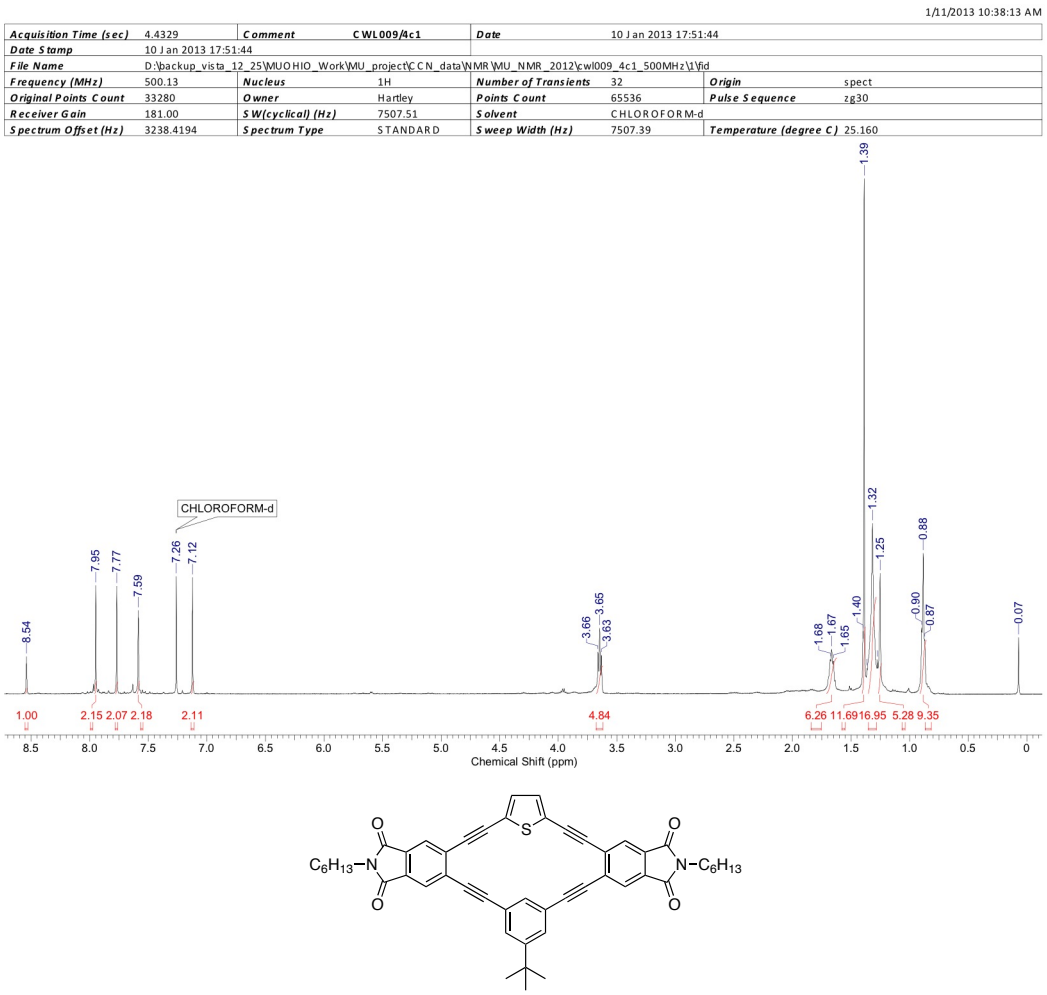


Figure S40. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **A(mP/Th)A**.

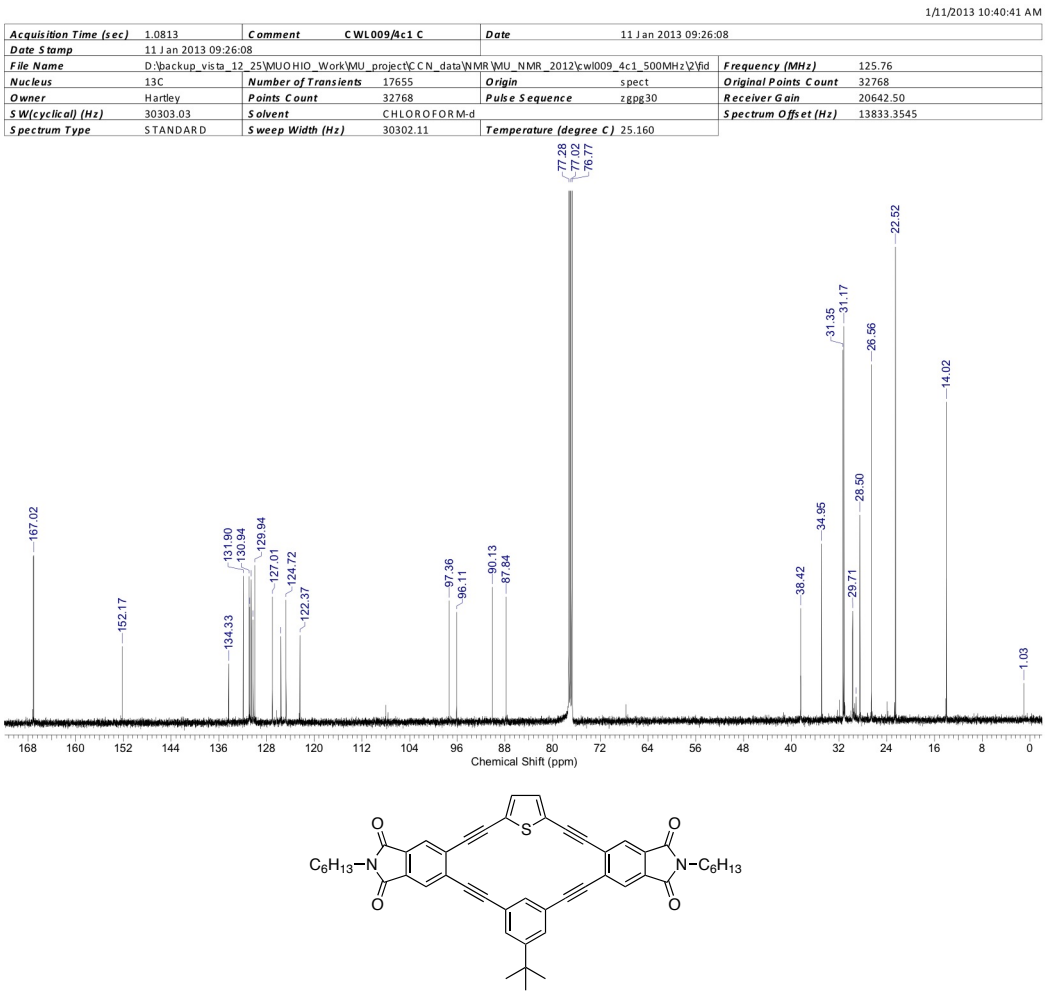


Figure S41. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of compound **A(mP/Th)A**.

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