Electronic Supplementary Material (ESI) for Dalton Transactions.

Revised Supporting information (DT-ART-03-2017-000895) for:

Achieving Yellow Emission by Varying Donor/Acceptor Units in Rod-shaped Fluorenyl-alkynyl Based π-Conjugated Oligomers and Their Binuclear Gold(I) Alkynyl Complexes

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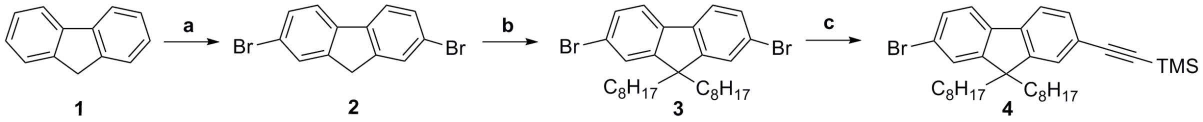
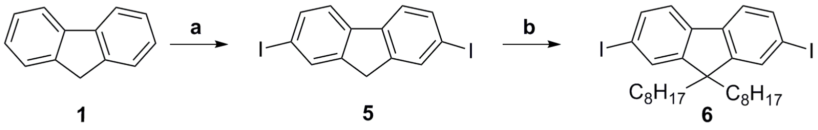
1. Synthesis and Characterization

1a. (i) Synthetic protocol



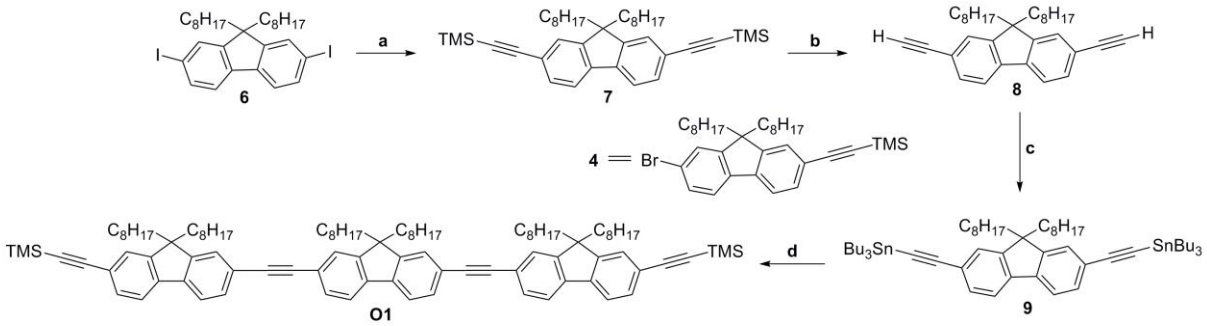
Scheme S1 Synthesis of **4**

Reagents and conditions: a) NBS, $FeCl_3$, DMF, 90 °C, 12 h; b) $C_8H_{17}Br$, TBAI, aq. NaOH, toluene, 60 °C, 12 h; c) 1.1 eqv. of ethynyltrimethylsilane, 3 mol% CuI, 3 mol% $Pd(PPh_3)_2Cl_2$, $^iPr_2NH$, THF, Reflux.



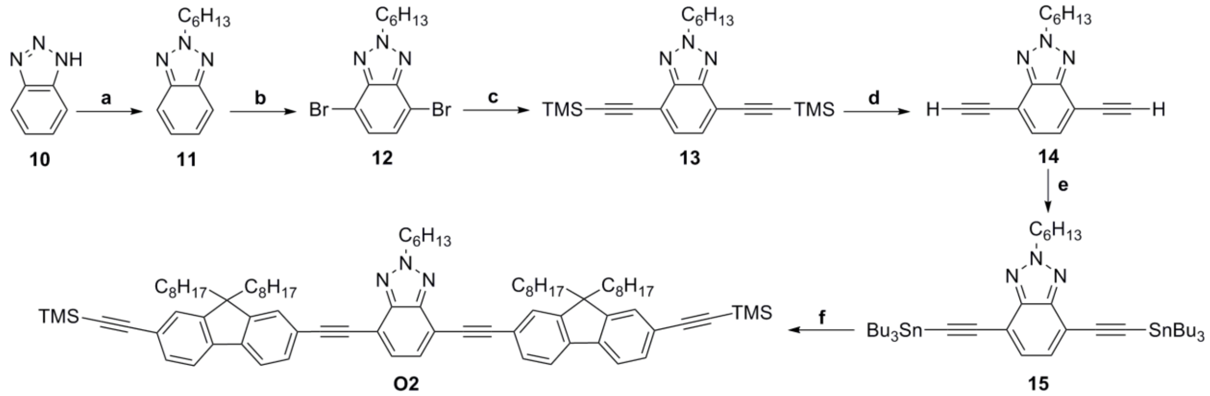
Scheme S2 Synthesis of **6**

Reagents and conditions: a) I_2, KIO_3, H_2SO_4, AcOH, 90 °C, 12 h; b) $C_8H_{17}Br$, TBAI, aq. NaOH, toluene, 60 °C, 12 h.



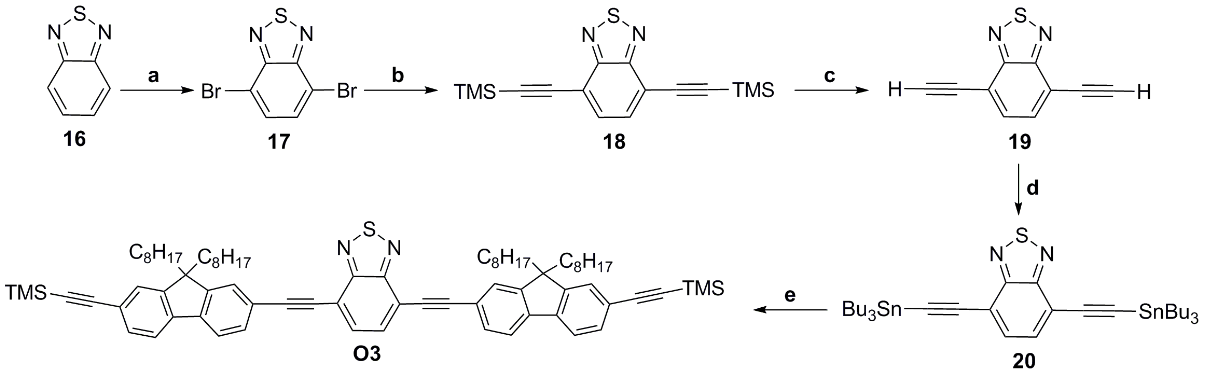
Scheme S3 Synthesis of **O1**

Reagents and conditions: a) 2.5 eqv. of ethynyltrimethylsilane, 3 mol% CuI, 3 mol% $Pd(PPh_3)_2Cl_2$, Et_3N, THF, Reflux, 24 h; b) K_2CO_3, DCM, MeOH, 28 °C, 4 h; c) 2.2 eqv. of Bu_3SnCl, LDA, THF, -20 °C to 28 °C, 4 h; d) 2.5 eqv. of **4**, 3 mol% $Pd(PPh_3)_4$, THF, Reflux, 24 h.



Scheme S4 Synthesis of **O2**

Reagents and conditions: a) $C_6H_{13}Br$, *t*-BuOK, MeOH, 28 °C, 4 days; b) HBr, Br_2, 100 °C, 8 h; c) 2.5 eqv. of ethynyltrimethylsilane, 3 mol% CuI, 3 mol% $Pd(PPh_3)_2Cl_2$, Et_3N, THF, Reflux, 24 h; d) K_2CO_3, DCM, MeOH, 28 °C, 4 h; e) 2.2 eqv. of Bu_3SnCl, LDA, THF, -20 °C to 28 °C, 4 h; f) 2.5 eqv. of **4**, 3 mol% $Pd(PPh_3)_4$, THF, Reflux, 24 h.



Scheme S5 Synthesis of **O3**

Reagents and conditions: a) HBr, Br_2, 100 °C, 8 h; b) 2.5 eqv. of ethynyltrimethylsilane, 3 mol% CuI, 3 mol% $Pd(PPh_3)_2Cl_2$, Et_3N, DCM, 28 °C, 24 h; c) K_2CO_3, DCM, MeOH, 28 °C, 4 h; d) 2.2 eqv. Bu_3SnCl, LDA, THF, -20 °C to 28 °C, 4 h; e) 2.5 eqv. of **4**, 3 mol% $Pd(PPh_3)_4$, THF, Reflux, 24 h.

1a. (ii) Synthesis and Characterization

2,7-Dibromfluorene (2). Fluorene (2.493 g, 15 mmol), NBS (10.68 g, 60 mmol), ferric chloride (0.1 g, 0.6 mmol), and dry DMF (60 mL) were taken in a 250 mL Schlenk flask and heated to 90 °C for 12 h under dark condition. The resulting mixture was then poured into water and extracted with DCM. The organic layer was washed extensively with dilute hydrochloric acid 1N, sodium bicarbonate, and finally with water. The DCM extract was dried over anhydrous magnesium sulfate and the solvent was evaporated using rotary evaporator. The product was recrystallized from dry ethanol to get analytically pure 2,7-

dibromofluorene (2). Yield: 3.6 g (75%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.68 (s, 2H), 7.60 (d, *J*=8.0 Hz, 2H), 7.50 (d, *J*=8.0 Hz, 2H), 3.88 (s, 2H, CH_2 at 9-position of fluorene unit). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 144.7, 139.6, 130.1, 128.3, 121.2, 120.9, 36.5 (Carbon at 9-position of fluorene unit).

2,7-Dibromo-9,9-dioctylfluorene (3). 2,7- Dibromofluorene (1.00 g, 3.08 mmol) was reacted with *n*-bromooctane (1.48 g, 1.32 mL, 7.7 mmol) in a two-phase system composed of toluene (25 mL) and aqueous sodium hydroxide (50 % w/w , 20 mL) solution using TBAI (0.1 g, 0.27 mmol) as the phase transfer catalyst at 60 °C for 10 h under argon atmosphere. After diluting the reaction mixture with ethyl acetate, the organic layer was washed with brine solution followed by water. The separated organic layer was dried over anhydrous magnesium sulfate, and the solvent was evaporated under vacuum. The crude product was purified by column chromatography using hexane as eluent. Yield: 1.35 g (80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.53-7.51 (m, 2H), 7.46-7.44 (m, 4H), 1.93-1.89 (m, 4H, octyl CH_2 attached to fluorene), 1.25-1.05 (m, 20H), 0.81 (t, *J*=8.0 Hz, 6H), 0.58-0.56 (m, 4H). ^{13}C {^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 152.4, 138.9, 130.0, 126.1, 121.4, 121.0, 55.6 (Carbon at 9-position of fluorene unit), 40.0, 31.6, 29.8, 29.0, 23.5, 22.5, 13.9.

2-Bromo-7-((trimethylsilyl)ethynyl)-9,9-dioctylfluorene (4). To a solution of 35 mL of dry THF and 20 mL of diisopropylamine in a 100 mL Schlenk flask, 2,7-dibromo-9,9-dioctylfluorene (2.19 g, 4.0 mmol) was added. After the addition of catalytic amount of CuI (0.02 g, 0.12 mmol), $Pd(PPh_3)_2Cl_2$ (0.08 g, 0.12 mmol) and trimethylsilylethyne (0.70 g, 7.2 mmol), the mixture was refluxed for 24 h under argon. After cooling to room temperature, the solvent was evaporated under reduced pressure. The residue was extracted with DCM and washed with water for two times. The combined organic layer after separation was then dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum to obtain the crude product. The crude product was purified by column chromatography (silica gel) using hexaness as an eluent to afford brown oil product. Yield: 1.35 g (60%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.60-7.51 (m, 2H, H_{Fl}), 7.47-7.41 (m, 4H, H_{Fl}), 1.96-1.88 (m, 4H, octyl CH_2 attached to fluorene), 1.15-1.01 (m, 20H, H_{octyl}), 0.86-0.79 (m, 6H, H_{octyl}), 0.58-0.51 (m, 4H, H_{octyl}), 0.28 (s, 9H, H_{TMS}). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 153.4, 150.4, 140.7, 139.6, 131.5, 130.3, 126.4, 126.3, 122.0, 121.8, 121.5, 119.7, 106.2, 94.4 (aromatic carbons), 55.6 (carbon at 9-position of Fl), 40.4, 31.9, 30.0, 29.4, 23.8, 22.8, 14.3 (alkyl carbons), 0.23 (C_{TMS}).

2,7-Diiodofluorene (5). A mixture of fluorene (0.5 g, 3 mmol), potassium iodate (0.32 g, 1.5 mmol) and iodine (1.90 g, 7.5 mmol) were stirred into a 250 mL Schlenk flask. Glacial acetic acid (30 mL) and 20 % aqueous sulfuric acid (3 mL) were added and the reaction mixture was heated at 90 °C under argon atmosphere. After 12 h, the reaction was cooled to 28 °C followed by addition of water (50 mL). The whole mixture was neutralized with 2M Na_2CO_3 solution and extracted with ether. The organic extract was washed with water and dried over anhydrous $MgSO_4$. After removal of solvent the product was purified by recrystallization from ethanol to obtain white solid product. Yield: 0.741 g (60%). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.87 (s, 2H), 7.72-7.68 (m, 2H), 7.51-7.47 (m, 2H), 3.84 (s, 2H, CH_2 at 9-position of fluorene unit). ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 145.0, 140.6, 136.2, 134.1, 121.8, 92.7, 36.5 (Carbon at 9-position of fluorene unit).

2,7-Diiodo-9,9-dioctylfluorene (6). 2,7- Diiodofluorene (0.84 g, 2.0 mmol) and catalytic amount of TBAI (0.07 g, 0.2 mmol) were dissolved in a solution of 35 mL DMSO and 12 mL of 50 % aqueous NaOH in a 100 mL Schlenk flask. After that, 1-bromooctane (0.97 g, 5 mmol) was added dropwise to the reaction mixture and was stirred at 60 °C for 12 h under argon atmosphere. The product was extracted with DCM and the organic layer washed with brine solution followed by water and dried over anhydrous $MgSO_4$. The product was purified by column chromatography using hexane as eluent. Yield: 0.98 g (77%). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.66-7.64 (m, 4H), 7.41-7.39 (m, 2H), 1.91-1.87 (m, 4H, octyl CH_2 attached to fluorene), 1.24-1.05 (m, 20H), 0.85-0.82 (m, 6H), 0.59-0.57 (m, 4H); ^{13}C {^1H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 152.7, 140.0, 136.3, 132.3, 121.8, 93.4, 55.8 (Carbon at 9-position of fluorene unit), 40.3, 32.0, 30.1, 29.5, 29.3, 23.9, 22.9, 14.4.

2,7-Bis((trimethylsilyl)ethynyl)-9,9-dioctylfluorene (7). 2,7-Diiodo-9,9-dioctylfluorene (0.64 g, 1.0 mmol), CuI (0.010 g, 0.06 mmol), $Pd(PPh_3)_2Cl_2$ (0.04 g, 0.06 mmol) and trimethylsilylethyne (0.37 g, 3.8 mmol) were added to a solution of 10 mL of dry THF and 8 mL of diisopropylamine in a 100 mL Schlenk flask. The reaction mixture was refluxed for 24 h under argon atmosphere. The solvent was evaporated under reduced pressure. The residue was extracted with DCM and washed with distilled water for two times. The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The crude product was passed through a silica gel column using hexanes as the eluent. Evaporation of the solvent led to a brownish oil, which crystallized upon standing. The yellow solid product was recrystallized from distilled absolute ethanol to afford analytically pure 7. Yield: 0.45 g (65%). ^1H

NMR ($CDCl_3$, 400 MHz): δ 7.60-7.58 (m, 2H, H_{Fl}), 7.46-7.41 (m, 4H, H_{Fl}), 1.94-1.90 (m, 4H, octyl CH_2 attached to fluorene), 1.10–1.01 (m, 20H, H_{octyl}), 0.84-0.80 (m, 6H, H_{octyl}), 0.54-0.51 (m, 4H, H_{octyl}), 0.28 (s, 18H, H_{TMS}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 150.9, 140.8, 131.2, 126.1, 121.7, 119.7 (aromatic carbons), 106.0 (-Fl-C≡$\underline{C}$-TMS), 94.2 (-Fl-$\underline{C}$≡C-TMS), 55.5 (carbon at 9-position of Fl), 40.3, 31.7, 22.6, 14.1 (alkyl carbons), 0.34 (C_{TMS}).

2,7-diethynyl-9,9-dioctylfluorene (8). In a 100 mL Schlenk flask compound **7** (0.25 g, 0.43 mmol) was dissolved in mixture of 10 mL of dry DCM and 6 mL of dry MeOH. To that K_2CO_3 (0.12 g, 0.86 mmol) was added and the reaction mixture was stirred at 28 ^oC for 4 h. The compound was extracted with DCM and the organic layer was washed with brine solution followed by distilled water. The organic part was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure to obtain pale yellow solid product. Yield: 0.17 g (90%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.64-7.62 (m, 2H, H_{Fl}), 7.49-7.46 (m, 4H, H_{Fl}), 3.15 (s, 2H, acetylene proton), 1.95-1.91 (m, 4H, octyl CH_2 attached to fluorene), 1.26–1.02 (m, 20H, H_{octyl}), 0.84-0.80 (m, 6H, H_{octyl}), 0.58-0.54 (m, 4H, H_{octyl}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 151.3, 141.2, 131.5, 126.8, 121.2, 120.2 (aromatic carbons), 84.8 (-Fl-$\underline{C}$≡C-H), 77.6 (C≡$\underline{C}$-H), 55.5 (carbon at 9-position of Fl), 40.5, 32.0, 30.2, 30.0, 29.4, 23.9, 22.8, 14.3 (alkyl carbons).

Synthesis of O1. In a 100 mL Schlenk flask diisopropylamine (0.15 mL, 1.08 mmol) and 3 mL of dry THF was taken and cooled to -78 ^oC. n-BuLi (0.60 mL, 0.90 mmol) was added dropwise and stirred at this temperature for 20 min. In another 100 mL Schlenk flask, $^nBu_3SnCl$ (0.25 g, 0.77 mmol) was added to a solution of compound **8** (0.15 g, 0.35 mmol) in 4 mL of dry THF at -20 ^oC. The freshly prepared LDA solution was added dropwise to the reaction mixture through a cannula at -20 ^oC. Then the reaction mixture was stirred for 4 h at 28 ^oC. In another 100 mL Schlenk flask compound **4** (0.416 g, 0.735 mmol) and $Pd(PPh_3)_4$ (0.014 g, 0.012mmol) were stirred in 5 mL of dry THF. To it, the stannylated derivative of compound **8** was added dropwise through a cannula and the reaction mixture was refluxed for 24 h under argon. The solvent was evaporated under reduced pressure and the compound was extracted with diethyl ether, followed by addition of 5% KF solution in water to remove the unreacted stannyl derivative. The organic part was dried over anhydrous $MgSO_4$ and purified by column chromatography using silica gel (60-120) and hexanes as an eluent to afford a yellow solid product. Yield: 0.305 g (62%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.70-7.44 (m, 18H, H_{Fl}), 2.02-1.95 (m, 12H, octyl CH_2 attached to fluorene), 1.21–1.01 (m, 60H, H_{octyl}), 0.86-0.81 (m, 18H, H_{octyl}), 0.62-0.55 (m, 12H, H_{octyl}), 0.29 (s, 18H, H_{TMS}); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) 151.2, 150.9, 141.0, 140.8, 131.3, 130.8, 130.7, 126.3, 125.9, 122.1, 122.0, 121.8, 120.1, 119.9 (aromatic carbons), 106.2 (-Fl-C≡$\underline{C}$-TMS), 94.3 (-Fl-$\underline{C}$≡C-TMS), 90.9 (-$\underline{C}$≡C-Fl-C≡C-TMS), 55.3 (carbon at 9-position of Fl), 40.5, 31.9, 30.1, 29.3, 23.7, 22.7, 14.1 (alkyl carbons), 1.08, 0.12 (C_{TMS}); FTIR (KBr, cm^{-1}): 2152 ($\upsilon_{C\equiv C}$ stretching); MALDI-TOF MS (m/z): $C_{101}H_{138}Si_2$ Calculated 1408.041 ($[M+H]^+$); Experimental 1408.088 ($[M+H]^+$); Anal. Calc. for $C_{101}H_{138}Si_2$: C, 86.14; H, 9.88. Found: C, 85.81, H, 10.09; UV-Vis λ_{max}: 386 nm ($\varepsilon = 12.46\times10^4$ $M^{-1}cm^{-1}$); $\lambda_{em}(\lambda_{ex})$: 413(386) nm.

2-Hexylbenzotriazole (11). In a 250 mL Schlenk flask 1,2,3-benzotriazole (5.0 g, 42.0 mmol), potassium tert-butoxide (4.94 g, 44.0 mmol), and hexylbromide (11.1 g, 67.0 mmol) were dissolved in anhydrous methanol (20 mL). The reaction mixture was stired for 4 days at 28 °C under argon. After removal of the solvent by evaporation, the residue was dissolved in DCM and the organic layer was washed with brine solution followed by distilled water. The organic part was dried over anhydrous $MgSO_4$ and the solvent was evaporated by rotary evaporator. The crude product was purified by silica gel (60-120) column chromatography using hexane as the eluent to obtain **11** as a light yellow liquid product. Yield: 3.16 g (37%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.89-7.82 (m, 2H, H_{Btz}), 7.42-7.33 (m, 2H, H_{Btz}), 4.76-4.68 (t, *J*= 8.0 Hz, 2H, (Btz)N-$\underline{CH_2}$-C_5H_{11}), 2.14-2.08 (m, 2H, (Btz)N-CH_2-$\underline{CH_2}$-C_4H_9), 1.39–1.28 (m, 6H, H_{hexyl}), 0.90-0.83 (m, 3H, H_{hexyl}). ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz): δ (ppm) 144.3, 126.0, 118.0, 56.6, 31.2, 30.0, 26.2, 22.4, 14.0.

4,7-Dibromo-2-hexylbenzotriazole (12). 2-Hexylbenzotriazole (1.02 g, 5.0 mmol) and 47 % aqueous HBr solution (6 mL) were added to a 100 mL two-necked round-bottomed flask, and the mixture was stirred for 1 h at 100 °C. Bromine (3.19 g, 20.0 mmol) was added very slowly to the mixture and it was heated to 135 °C for 12 h. After that, the reaction mixture was cooled to room temperature. Aqueous solution of $NaHCO_3$ was added and the product was extracted with DCM. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel (60-120) column chromatography using hexane as eluent to obtain yellow oil product. Yield: 1.38 g (76%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.50 (s, 2H, H_{Btz}), 4.80-4.76 (t, *J*= 8.0 Hz, 2H, (Btz)N-$\underline{CH_2}$-C_5H_{11}), 2.17-2.11 (m, 2H, (Btz)N-CH_2-$\underline{CH_2}$-C_4H_9), 1.55–1.34 (m, 6H, H_{hexyl}), 0.91-0.85 (m, 3H, H_{hexyl}). $^{13}C\{^1H\}$ NMR ($CDCl_3$**,** 50 MHz): δ (ppm) 143.6, 129.5, 110.0, 57.5, 31.2, 30.2, 26.3, 22.5, 14.1.

2-Hexyl-4,7-bis(trimethylsilyl)ethynyl)benzotriazole (13). 4,7-Dibromo-2-hexylbenzotriazole (1.08 g, 3.0 mmol) was dissolved in a mixture of 15 mL of dry THF and 10 mL of NEt_3 in a 100 mL Schlenk flask. Catalytic amount of CuI (0.02 g, 0.09 mmol), $Pd(PPh_3)_2Cl_2$ (0.06 g, 0.09 mmol) and trimethylsilylethyne (1.06 g, 10.8 mmol) were added to the solution. The reaction mixture was refluxed for 24 h under argon. After cooling to room temperature, the solvent was evaporated under reduced pressure and the compound was extracted with EtOAc. The organic part was washed with water and dried over anhydrous $MgSO_4$. The solvent was evaporated and the crude product was passed through a column of silica gel (60-120) using 2% EtOAc in hexanes as the eluent. Evaporation of the solvent led to a brown oil product. Yield: 0.77 g (65%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.46 (s, 2H, H_{Btz}), 4.78-4.74 (t, *J*= 8.0 Hz, 2H, (Btz)N-$\underline{CH_2}$-C_5H_{11}), 2.17-2.13 (m, 2H, (Btz)N-CH_2-$\underline{CH_2}$-C_4H_9), 1.38–1.34 (m, 6H, H_{hexyl}), 0.91-0.88 (m, 3H, H_{hexyl}), 0.31 (s, 18H, H_{TMS});. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 144.4, 130.8, 114.1 (aromatic carbons), 102.2 (Btz-C≡$\underline{C}$-TMS), 100.5 (Btz-$\underline{C}$≡C-TMS), 57.1 ((Btz)N-$\underline{C}H_2$-C_5H_{11}), 31.4, 30.2, 26.4, 22.6, 14.2 (alkyl carbons), 0.16 (C_{TMS}).

4,7-diethynyl-2-hexylbenzotriazole (14). In a 100 mL Schlenk flask compound **13** (0.19 g, 0.5 mmol) was dissolved in a solution of 10 mL of DCM and 6 mL of MeOH. The reaction mixture was stirred at 28 °C for 4 h after addition of K_2CO_3 (0.14 g, 1.0 mmol). The compound was extracted with DCM and the organic layer washed with brine solution followed by distilled water and dried over anhydrous $MgSO_4$. The crude product was purified by silica gel (60-120) column chromatography using hexanes as eluent. Yield: 0.11 g (91%). ^1H NMR ($CDCl_3$, 200 MHz): δ 7.50 (s, 2H, H_{Btz}), 4.81-4.73 (t, *J*= 8.0 Hz, 2H, (Btz)N-$\underline{CH_2}$-C_5H_{11}), 3.58 (s, 2H, -Btz-C≡C-$\underline{H}$), 2.15-2.05 (m, 2H, (Btz)N-CH_2-$\underline{CH_2}$-C_4H_9), 1.39–1.31 (m, 6H, H_{hexyl}), 0.93-0.85 (m, 3H, H_{hexyl}).; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz): δ (ppm) 144.7, 130.7, 113.5 (aromatic carbons), 84.4 (Btz-C≡$\underline{C}$-H), 79.3 (Btz-$\underline{C}$≡C-H), 57.4 ((Btz)N-$\underline{C}H_2$-C_5H_{11}), 31.4, 30.5, 26.4, 22.6, 14.1 (alkyl carbons).

Synthesis of O2. It was synthesized using a similar procedure as that for **O1** taking **14** (0.20 g, 0.8 mmol), $^nBu_3SnCl$ (0.57 g, 1.76 mmol), 4 (1.13 g, 2.0 mmol) and $Pd(PPh_3)_4$

(0.08 g, 0.07 mmol). The resulting crude product was purified by column chromatography using silica gel (60-120) and EtOAC/hexanes (5/95) to afford **O2** as a dark yellow solid product. Yield: 0.59 g (61%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.69-7.61 (m, 10H, $H_{Btz\ \&\ Fl}$), 7.48-7.44 (m, 4H, $H_{Btz\ \&\ Fl}$), 4.87-4.83 (t, *J*= 8Hz, 2H, (Btz)N-$\underline{CH_2}$-C_5H_{11}), 2.24-2.21 (m, 2H, (Btz)N-CH_2-$\underline{CH_2}$-C_4H_9), 2.05-1.96 (m, 8H, octyl CH_2 attached to fluorene), 1.29–1.04 (m, 46H, $H_{hexyl\ \&\ octyl}$), 0.84-0.80 (m, 15H, $H_{hexyl\ \&\ octyl}$), 0.62-0.58 (m, 8H, H_{octyl}), 0.29 (s, 18H, H_{TMS}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 151.3, 151.3, 144.6, 141.4, 141.1, 139.4,131.5, 131.4, 130.3, 126.5, 122.2, 121.9, 120.2, 120.1, 114.3, 114.1 (aromatic carbons), 106.3 (Fl-C≡$\underline{C}$-TMS), 97.7 (Btz-$\underline{C}$≡C-Fl), 94.6 (Btz-C≡$\underline{C}$-Fl), 86.0 (Fl-$\underline{C}$≡C-TMS), 57.4 ((Btz)N-$\underline{C}H_2$-C_5H_{11}), 55.6 (carbon at 9-position of Fl), 40.7, 34.1, 32.2, 31.9, 31.4, 30.5, 30.2, 29.9, 29.5, 29.2, 26.5, 23.9, 22.9, 22.7, 14.3 (alkyl carbons), 1.26, 0.29 (C_{TMS}); FTIR (KBr, cm^{-1}): 2151 ($\upsilon_{C\equiv C}$ stretching); MALDI-TOF MS (m/z): $C_{84}H_{113}N_3Si_2$ Calculated 1220.855 ($[M+H]^+$); Experimental 1220.905 ($[M+H]^+$); Anal. Calc. for $C_{84}H_{113}N_3Si_2$: C, 82.63; H, 9.33, N, 3.44. Found: C, 81.48, H, 9.58, N, 3.14; UV-Vis λ_{max}: 403 nm ($\varepsilon = 7.89\times10^4\ M^{-1}cm^{-1}$); $\lambda_{em}(\lambda_{ex})$: 449(403) nm.

4,7-Dibromobenzo-thiadiazole (17). Benzothiadiazole (1.0 g, 7.3 mmol) and 47 % aqueous HBr solution (15 mL) were added to a 100 mL two neck R.B flask, and the mixture was stirred for 1 h at 100 °C. Bromine (4.682 g, 29.2 mmol) was added very slowly and the mixture was refluxed for 12 h. After that, the reaction mixture was cooled to room temperature. Aqueous solution of $NaHCO_3$ was added and the product was extracted with $CHCl_3$. The organic layer was washed with water and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. . The crude product was purified by silica gel column chromatography using hexane as eluent to obtain light yellow solid product Yield: 1.98 g (92%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73(s, 2H, benzothiadiazole protons), $^{13}C\ \{^1H\}$ NMR ($CDCl_3$**,** 100 MHz): δ (ppm) 152.6, 132.1, 113.6.

4,7-bis(2(trimethylsilyl)ethynyl)benzothiadiazole (18). In a 100 mL Schlenk flask compound **17** (580 mg, 2.0 mmol), $Pd(PPh_3)_2Cl_2$ (42 mg, 0.06 mmol), CuI (12 mg, 0.06 mmol), trimethylsilylethyne (690 mg, 7.0 mmol) were treated in 8 mL of dry DCM and 5 mL of Et_3N stirred at 28 °C for 24 h. The compound was extracted with DCM and the organic layer washed with water and dried over anhydrous $MgSO_4$. The crude product was purified by silica gel (60-120) column chromatography using hexane as a eluent; Yield: 490 mg (74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.70 (s, 2H, H_{Btd}), 0.33 (s, 18H, H_{TMS});

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$**,** 100 MHz): *δ* (ppm) 154.5, 133.4, 117.6, 103.9 (Btd-C≡$\underline{C}$-TMS), 100.3 (Btd-$\underline{C}$≡C-TMS), 0.14 (-C_{TMS}).

4,7-diethynylbenzothiadiazole (19). In a 100 mL Schlenk flask compound **18** (0.20 g, 0.6 mmol) was dissolved in a mixture of 10 mL of dry DCM and 6 mL of dry MeOH. Then K_2CO_3 (0.17 g, 1.21 mmol) was added to it and the reaction mixture was stirred at 28 °C for 4 h. The compound was extracted with DCM and the organic layer washed with brine solution followed by distilled water and dried over anhydrous $MgSO_4$. The crude product was purified by silica gel (60-120) column chromatography using hexane as eluent. Yield: 0.10 g (90%). ^{1}H NMR ($CDCl_3$, 200 MHz): *δ* (ppm) 7.76 (s, 2H, H_{Btd}), 3.68 (s, 2H, Btd-C≡C-$\underline{H}$); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$**,** 100 MHz): *δ* (ppm) 153.6, 134.2, 114.5, 85.3 (Btd-C≡$\underline{C}$-H), 79.8 (Btd-$\underline{C}$≡C-H).

Synthesis of O3. It was synthesized analogously to **O1** using compound **19** (0.09 g, 0.5 mmol), $^{n}Bu_3SnCl$ (0.36 g, 1.1 mmol), 4 (0.71 g, 1.25 mmol) and $Pd(PPh_3)_4$ (0.05 g, 0.04 mmol). The resulting crude product was purified by column chromatography using silica gel (60-120) and EtOAC/hexanes (5/95) to afford red solid product. Yield: 0.37 g (64%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.85 (s, 2H, H_{Btd}), 7.69-7.63 (m, 8H, H_{Fl}), 7.49-7.45 (m, 4H, H_{Fl}), 2.05-1.91 (m, 8H, octyl CH_2 attached to fluorene), 1.25–1.04 (m, 40H, H_{octyl}), 0.83-0.80 (m, 12H, H_{octyl}), 0.64-0.51 (m, 8H, H_{octyl}), 0.31 (s, 18H, H_{TMS}); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ (ppm) 154.6, 151.4, 151.3, 141.7, 141.0, 132.7, 131.5, 126.5, 122.3, 121.4, 120.3, 120.2, 117.4 (aromatic carbons), 106.3 (Fl-C≡$\underline{C}$-TMS), 99.0 (Btd-$\underline{C}$≡C-Fl), 94.7 (Btd-C≡$\underline{C}$-Fl), 86.0 (Fl-$\underline{C}$≡C-TMS), 55.6 (carbon at 9-position of Fl), 40.6, 32.0, 30.2, 29.9, 29.5, 29.4, 23.9, 22.8, 14.3 (alkyl carbons), 1.24, 0.27 (C_{TMS}); FTIR (KBr, cm^{-1}): 2152 ($\upsilon_{C\equiv C}$ stretching); MALDI-TOF MS (m/z): $C_{78}H_{100}N_2SSi_2$; Calculated 1152.714 ($[M]^+$). Experimental 1152.766 ($[M]^+$); Anal. Calc. for $C_{78}H_{100}N_2SSi_2$: C, 81.19; H, 8.74, N, 2.43. Found: C, 80.36, H, 9.31, N, 2.25. UV-Vis λ_{max}: 445 nm ($\varepsilon = 4.8\times10^{4}$ $M^{-1}cm^{-1}$); $\lambda_{em}(\lambda_{ex})$: 547 (445) nm.

Synthesis of OH1. In a 100 mL Schlenk flask compound **O1** (0.17 g, 0.12 mmol) was added in a mixture of 8 mL of dry DCM and 5 mL of dry MeOH. K_2CO_3 (0.03 g, 0.24 mmol) was added and the reaction mixture was stirred at 28 °C for 4 h under argon. The compound was extracted with DCM and the organic layer was washed with brine solution followed by distilled water. The organic part was dried over anhydrous $MgSO_4$ and purified by silica gel (60-120) column chromatography using hexanes as eluent to obtain yellow solid product. Yield: 0.14 g (92%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.71-7.49 (m, 18H, H$_{\mathrm{Fl}}$), 3.17 (s, 2H, -C≡C-$\underline{\mathrm{H}}$), 2.00-1.97 (m, 12H, octyl CH$_2$ attached to fluorene), 1.30-1.06 (m, 60H, H$_{\mathrm{octyl}}$), 0.85-0.82 (m, 18H, H$_{\mathrm{octyl}}$), 0.66-0.58 (m, 12H, H$_{\mathrm{octyl}}$); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): 151.4, 151.2, 141.4, 140.9, 140.7, 131.8, 131.5, 131.0, 128.6, 126.7, 126.2, 122.4, 122.2, 120.9, 120.3, 120.1 (aromatic carbons), 91.1 (-Fl-C≡$\underline{\mathrm{C}}$-FL-$\underline{\mathrm{C}}$≡C-Fl-), 84.8 (-Fl-C≡$\underline{\mathrm{C}}$-H), 77.5 (-Fl-$\underline{\mathrm{C}}$≡C-H), 55.5 (carbon at 9-position of Fl), 40.6, 32.0, 30.2, 29.5, 23.9, 22.8, 14.3 (alkyl carbons); FTIR (KBr, cm^{-1}): 2102 ($\upsilon_{\mathrm{C≡C\ stretching}}$); MALDI-TOF MS (m/z): C$_{95}H_{122}$; Calculated 1263.954 ([M+H]$^{+}$); Experimental 1263.841 ([M+H]$^{+}$). UV-Vis $\lambda_{\max}$: 384 nm (ε = 9.25×10^{4} M^{-1}cm^{-1}); λ_{em}(λ_{ex}): 412, 433 (384) nm.

Synthesis of OH2. OH2 was prepared using a similar procedure as that for **OH1** using **O2** (0.19 g, 0.16 mmol) and K$_2$CO$_3$ (0.04 g, 0.32 mmol). It was purified by silica gel (60-120) column chromatography using EtOAc/ hexanes as eluent to afford dark yellow solid of **OH2.** Yield: 0.16 g (91%). ^{1}H NMR (CDCl$_3$, 400 MHz): *δ* (ppm) 7.71-7.48 (m, 14H, H$_{\mathrm{Btz,\ Fl}}$), 4.87- 4.83 (t, *J*= 8Hz, 2H, (Btz)N-$\underline{\mathrm{CH}}_2$-C$_5H_{11}$), 3.17 (s, 2H, -Fl-C≡C-$\underline{\mathrm{H}}$), 2.25- 2.21 (t, *J*= 8Hz, 2H, (Btz)N-CH$_2$-$\underline{\mathrm{CH}}_2$-C$_4H_9$) 2.00-1.99 (m, 8H, octyl CH$_2$ attached to fluorene), 1.43–1.05 (m, 46H, H$_{\mathrm{hexyl,\ octyl}}$), 0.83-0.80 (m, 15H, H$_{\mathrm{hexyl,\ octyl}}$), 0.62-0.56 (m, 8H, H$_{\mathrm{octyl}}$); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): 151.3, 144.5, 141.3, 141.2, 131.5, 131.4, 130.3, 126.6, 126.5, 121.9, 121.0, 120.3, 120.2, 114.0 (aromatic carbons), 97.6 (-Fl-C≡$\underline{\mathrm{C}}$-Btz-$\underline{\mathrm{C}}$≡C-Fl-), 86.0 (-Fl-$\underline{\mathrm{C}}$≡C-Btz-C≡$\underline{\mathrm{C}}$-Fl-), 84.8 (-Fl-C≡$\underline{\mathrm{C}}$-H), 77.6 (-Fl-$\underline{\mathrm{C}}$≡C-H), 57.4 ((Btz)N-$\underline{\mathrm{C}}$H$_2$-C$_5$H$_{11}$), 55.5 (carbon at 9-position of Fl), 40.6, 32.0, 30.4, 30.2, 29.4, 26.5, 23.9, 22.8, 14.3 (alkyl carbons); FTIR (KBr, cm^{-1}): 2106 ($\upsilon_{\mathrm{C≡C\ stretching}}$); MALDI-TOF MS (m/z): C$_{78}H_{97}N_3$; Calculated 1076.768 ([M+H]$^{+}$); Experimental 1076.585 ([M+H]$^{+}$). UV-Vis $\lambda_{\max}$: 401 nm (ε = 5.57×10^{4} M^{-1}cm^{-1}); λ_{em}(λ_{ex}): 441, 463 (401) nm.

Synthesis of OH3. OH3 was prepared analogously to **OH1** using **O3** (0.23 g, 0.2 mmol) and K$_2$CO$_3$ (0.05 g, 0.4 mmol). It was purified by silica gel (60-120) column chromatography using EtOAc/ hexanes as eluent to afford red solid of **OH3.** Yield: 0.18 g (92%). ^{1}H NMR (CDCl$_3$, 400 MHz): *δ* (ppm) 7.85 (s, 2H, H$_{\mathrm{Btd}}$), 7.73-7.46 (m, 12H, H$_{\mathrm{Fl}}$), 3.17 (s, 2H, -Fl-C≡C-$\underline{\mathrm{H}}$), 2.01-1.97 (m, 8H, octyl CH$_2$ attached to fluorene), 1.43–1.05 (m, 40H, H$_{\mathrm{octyl}}$), 0.83-0.80 (m, 12H, H$_{\mathrm{octyl}}$), 0.62-0.55 (m, 8H, H$_{\mathrm{octyl}}$),; ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): 154.6, 151.4, 141.6, 141.2, 132.7, 131.5, 126.8, 126.5, 121.5, 121.2, 120.4, 120.2, 117.4 (aromatic carbons), 98.9 (-Fl-C≡$\underline{\mathrm{C}}$-Btd-$\underline{\mathrm{C}}$≡C-

Fl-), 86.0 (-Fl-C≡C-Btd-C≡C-Fl-), 84.7 (-Fl-C≡C-H), 77.7 (-Fl-C≡C-H), 55.6 (carbon at 9-position of Fl), 40.5, 32.0, 30.2, 29.9, 29.4, 23.9, 22.8, 14.3 (alkyl carbons); FTIR (KBr, cm^{-1}): 2107 ($\upsilon_{C\equiv C\ \text{stretching}}$); MALDI-TOF MS (m/z): $C_{72}H_{84}N_2S$; Calculated 1009.635 ($[M+H]^+$); Experimental 1009.524 ($[M+H]^+$). UV-Vis λ_{max}: 445 nm ($\varepsilon = 2.6\times10^4\ M^{-1}cm^{-1}$); $\lambda_{em}(\lambda_{ex})$: 542 (445) nm.

1b. NMR Spectra

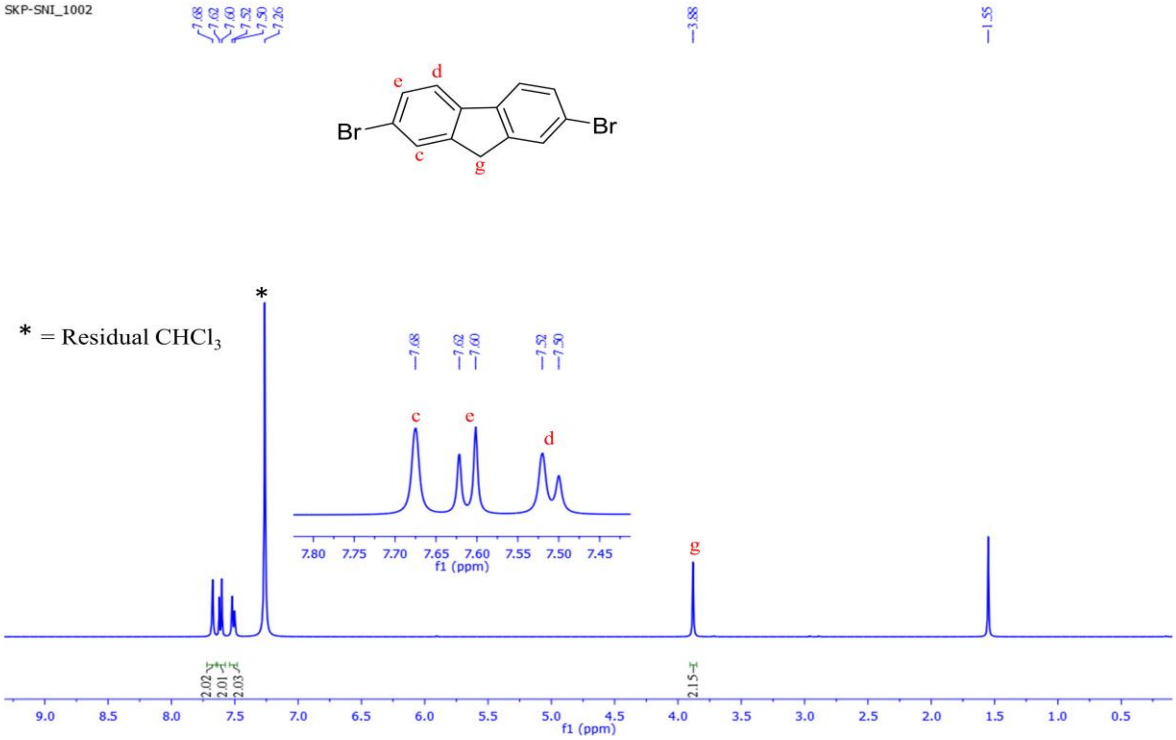


Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2**

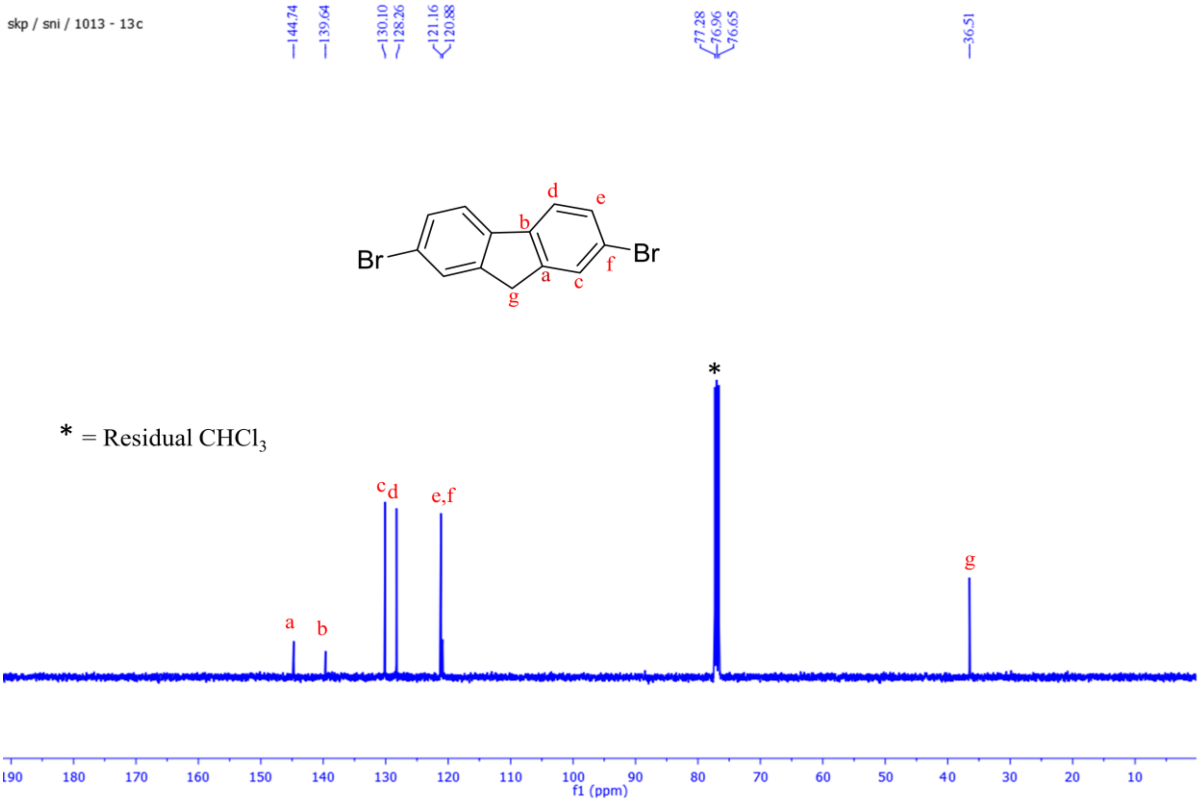


Fig. S2 $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2**

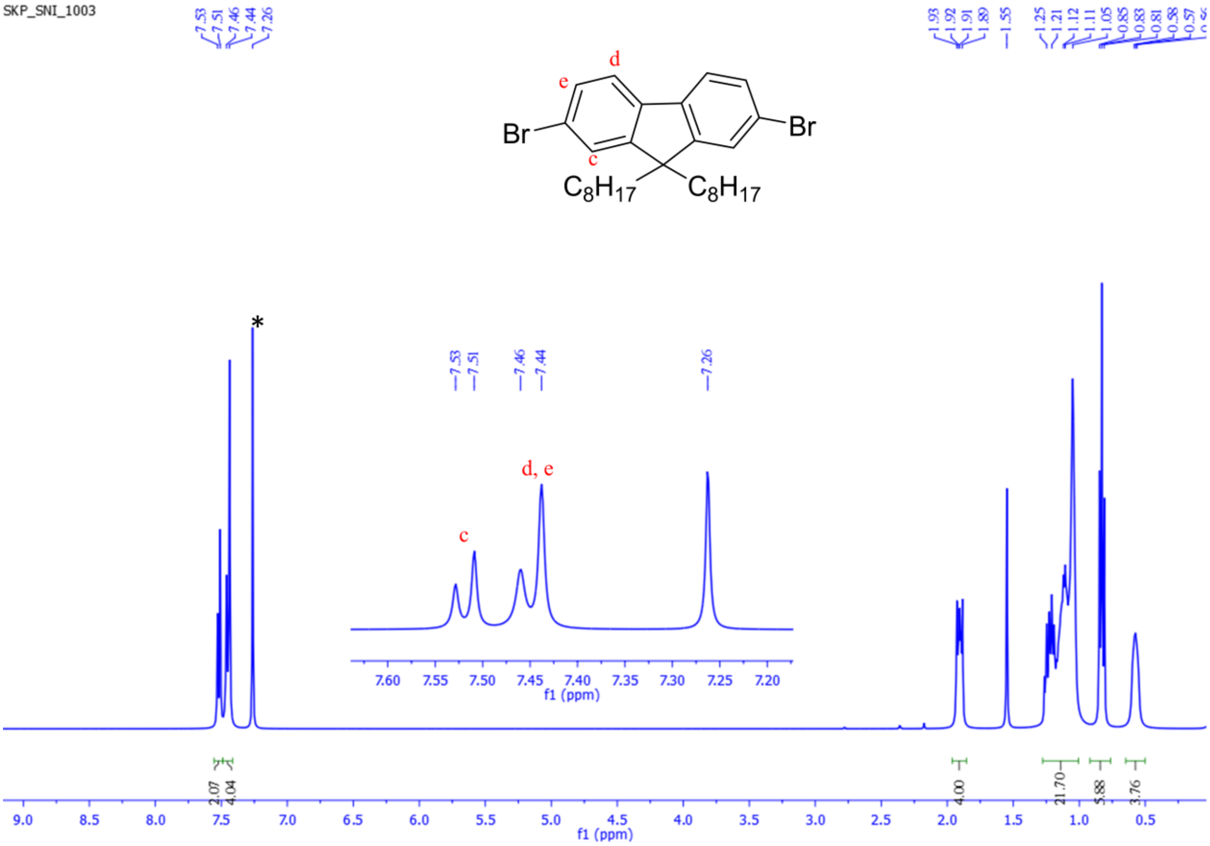


Fig. S3 ^1H NMR (400 MHz, $CDCl_3$) spectrum of **3**

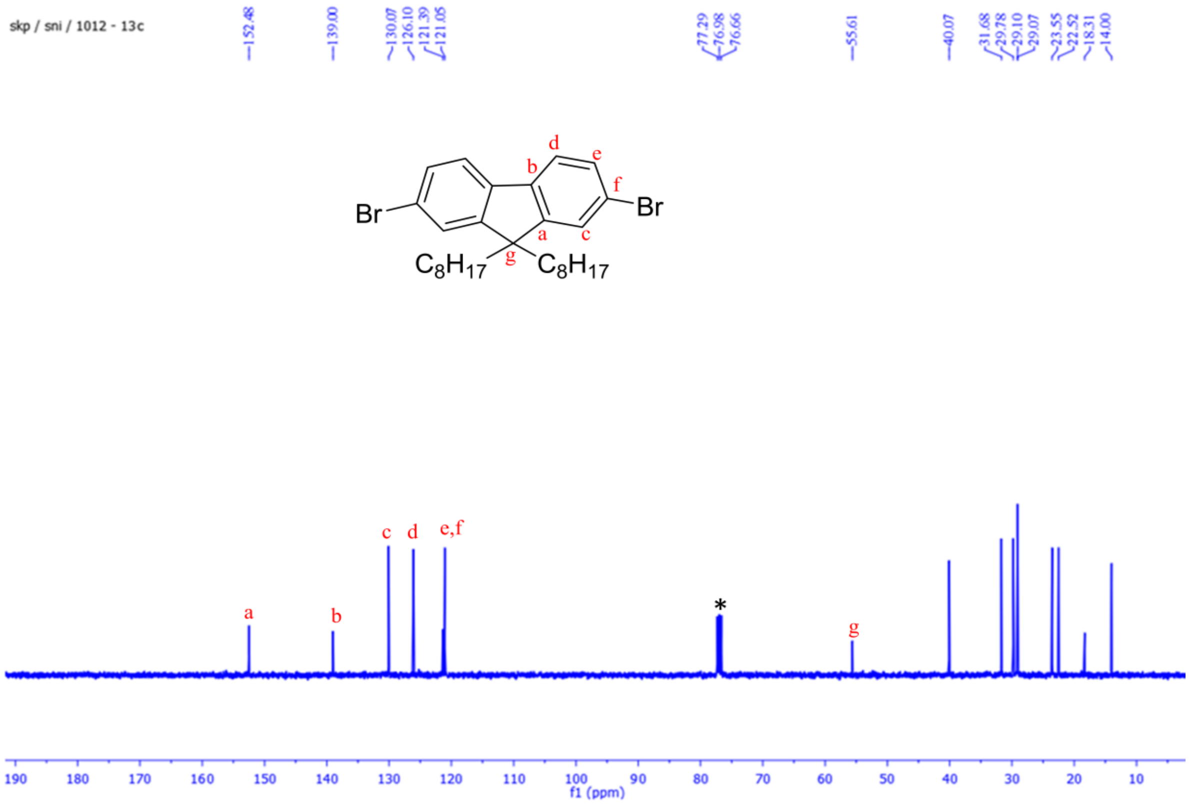


Fig. S4 $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3**

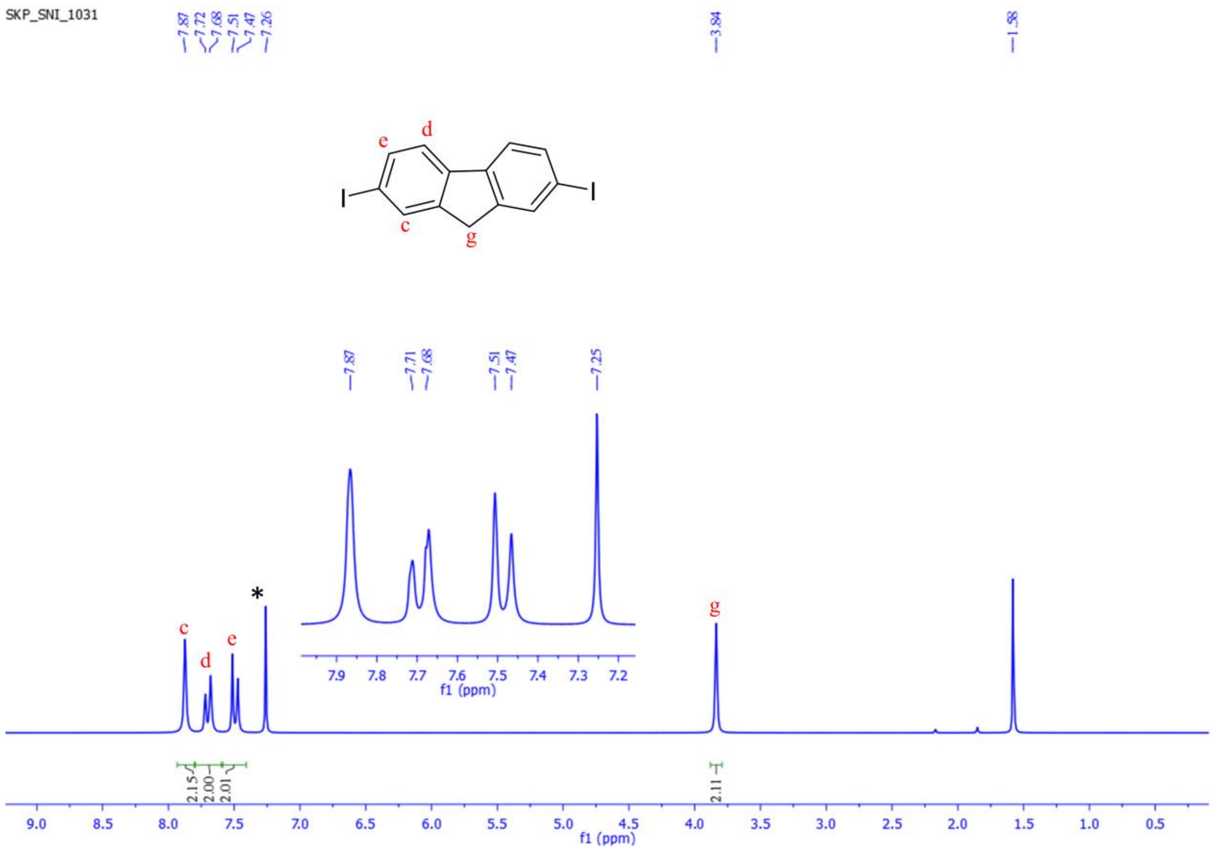


Fig. S5 ^1H NMR (400 MHz, $CDCl_3$) spectrum of **5**

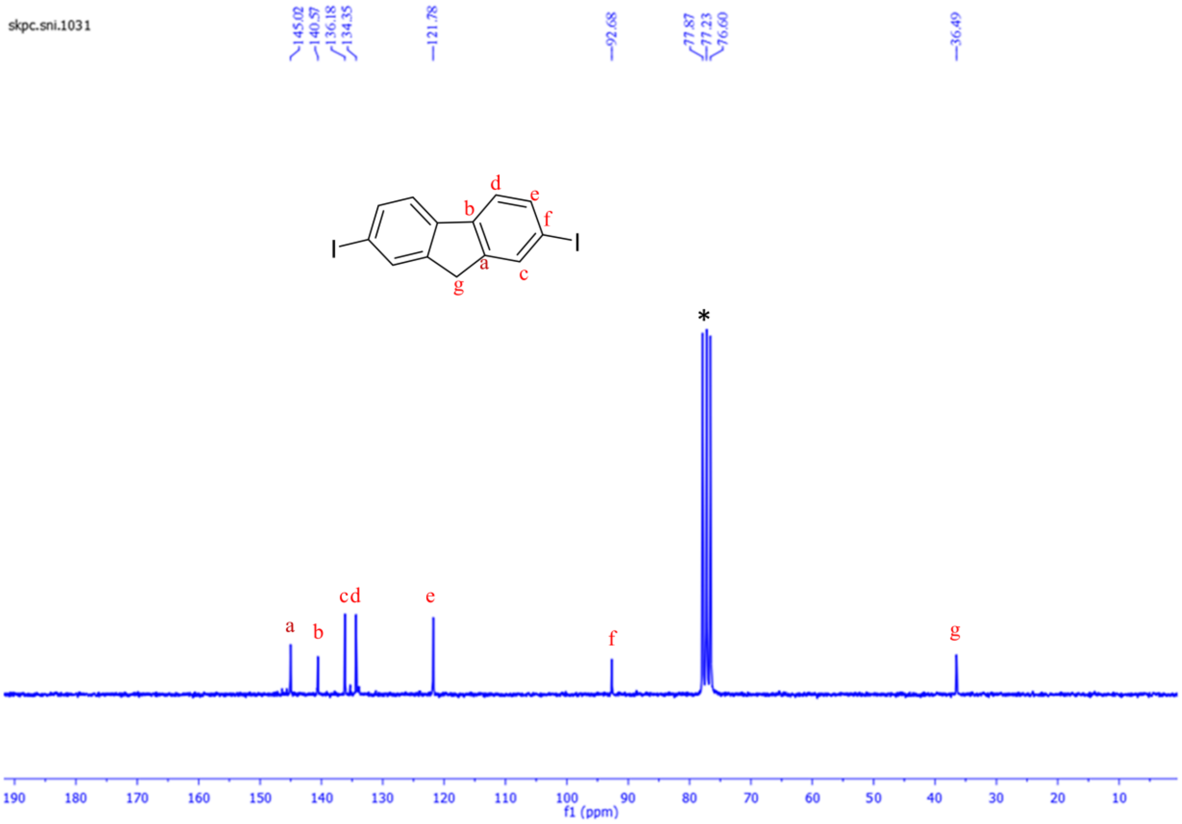


Fig. S6 $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **5**

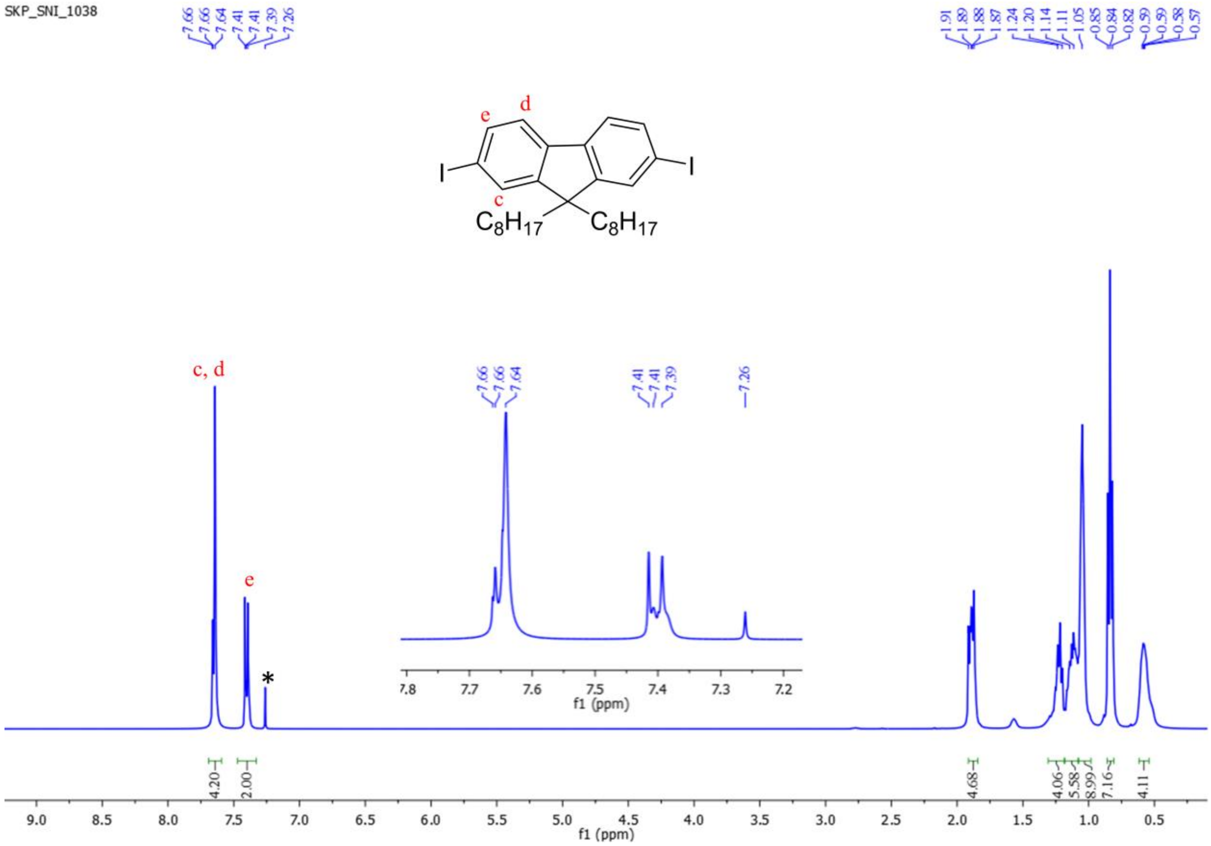


Fig. S7 ^1H NMR (400 MHz, $CDCl_3$) spectrum of **6**

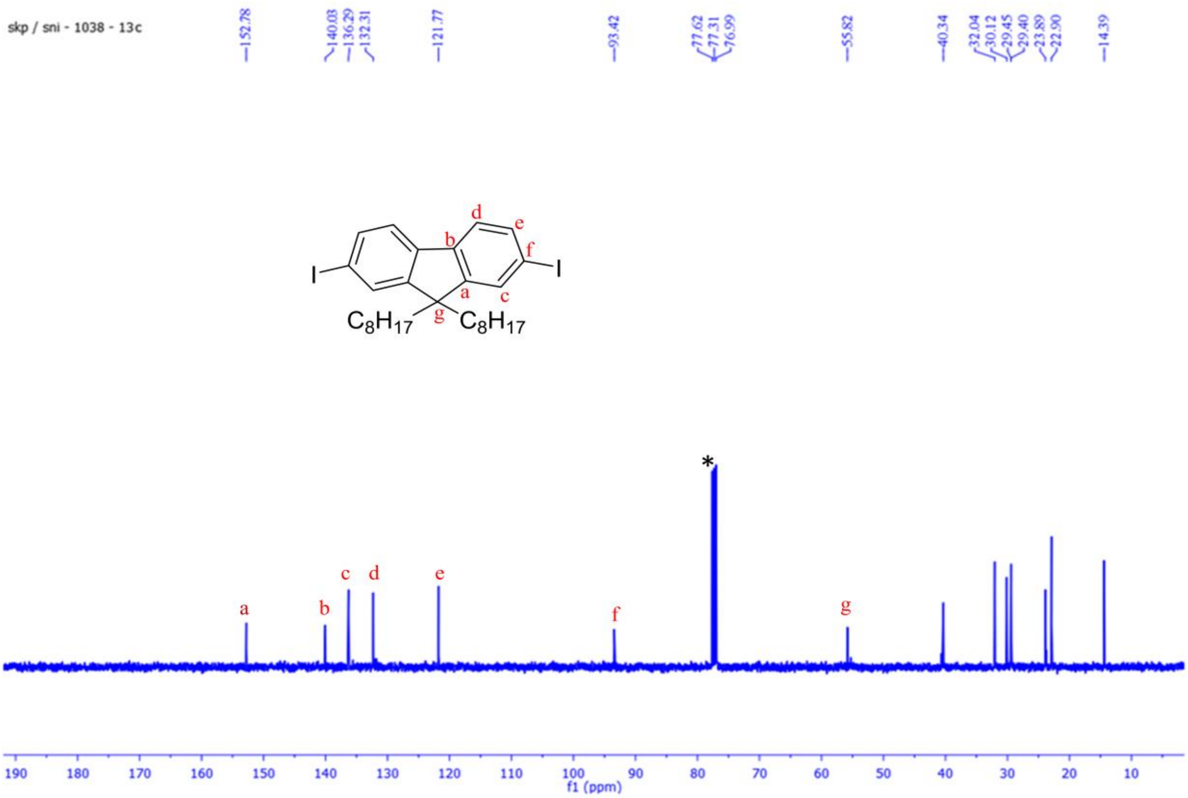


Fig. S8 $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **6**

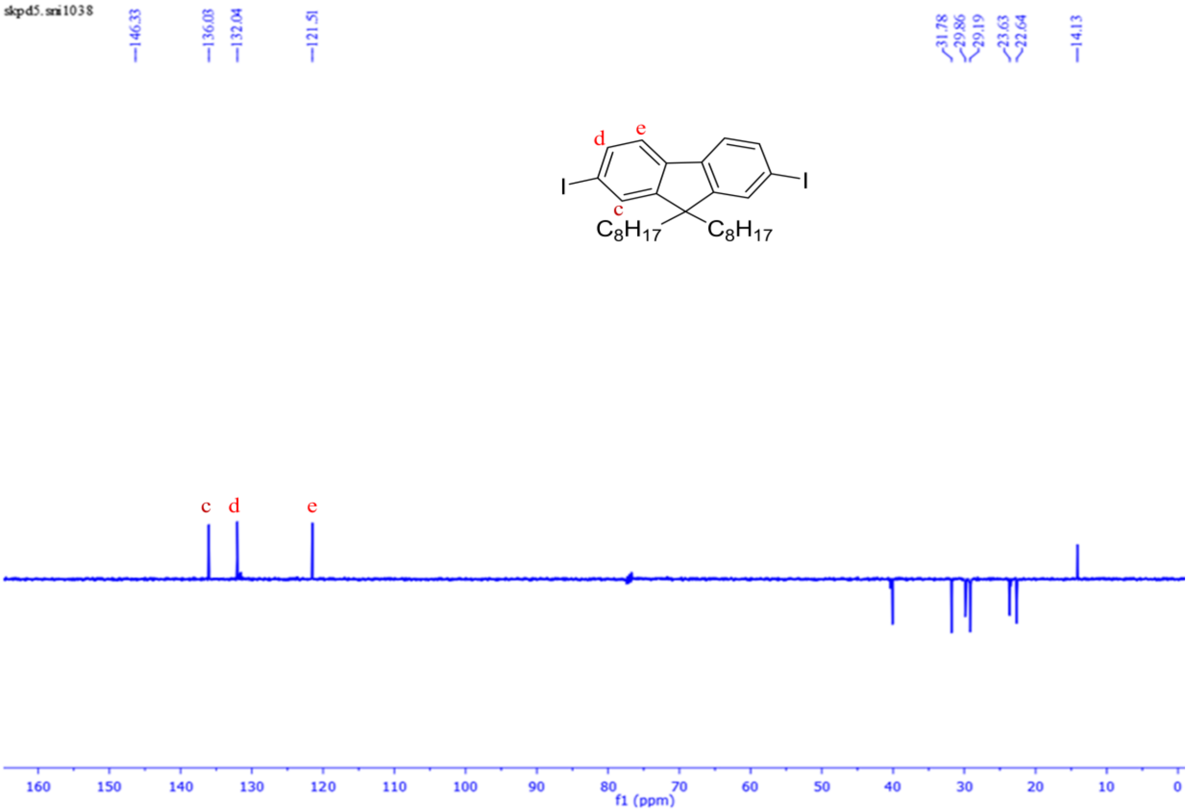


Fig. S9 DEPT-135 NMR (100 MHz, $CDCl_3$) spectrum of **6**

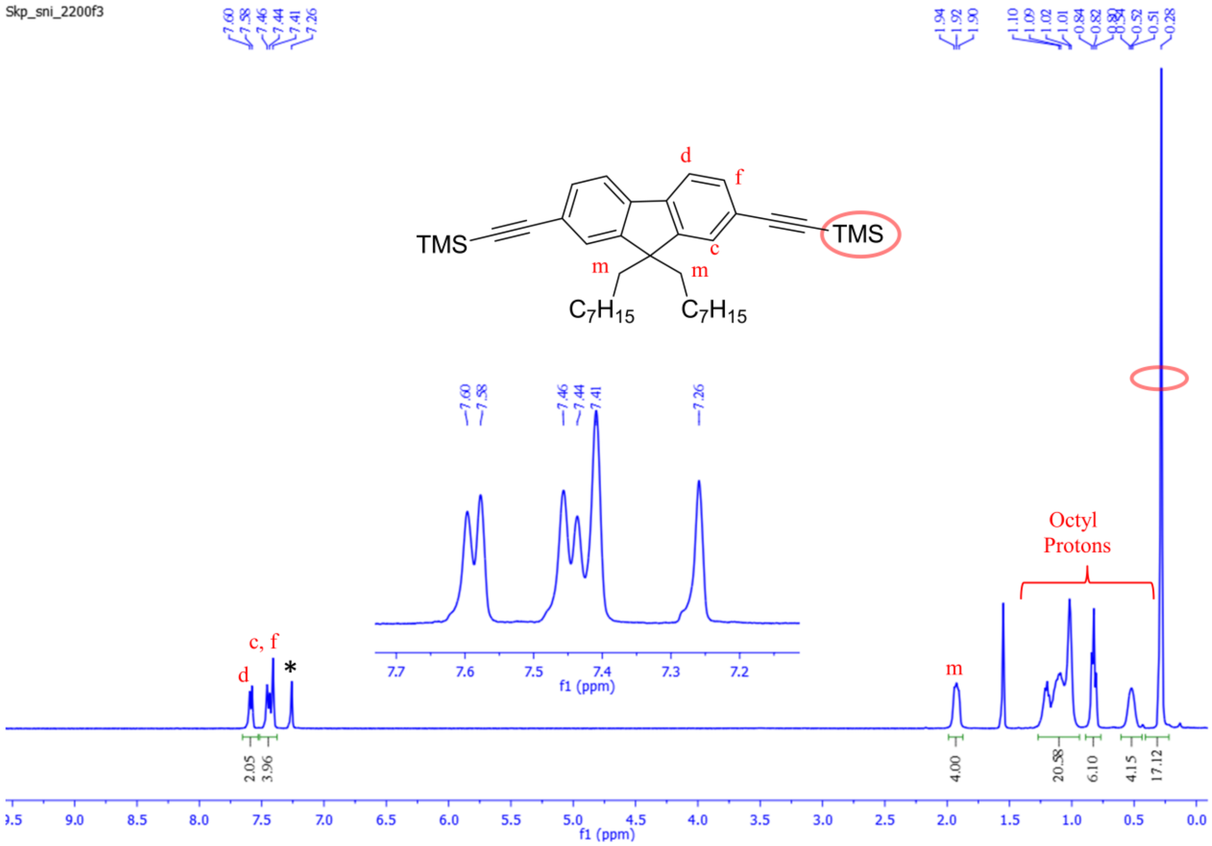


Fig. S10 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7**

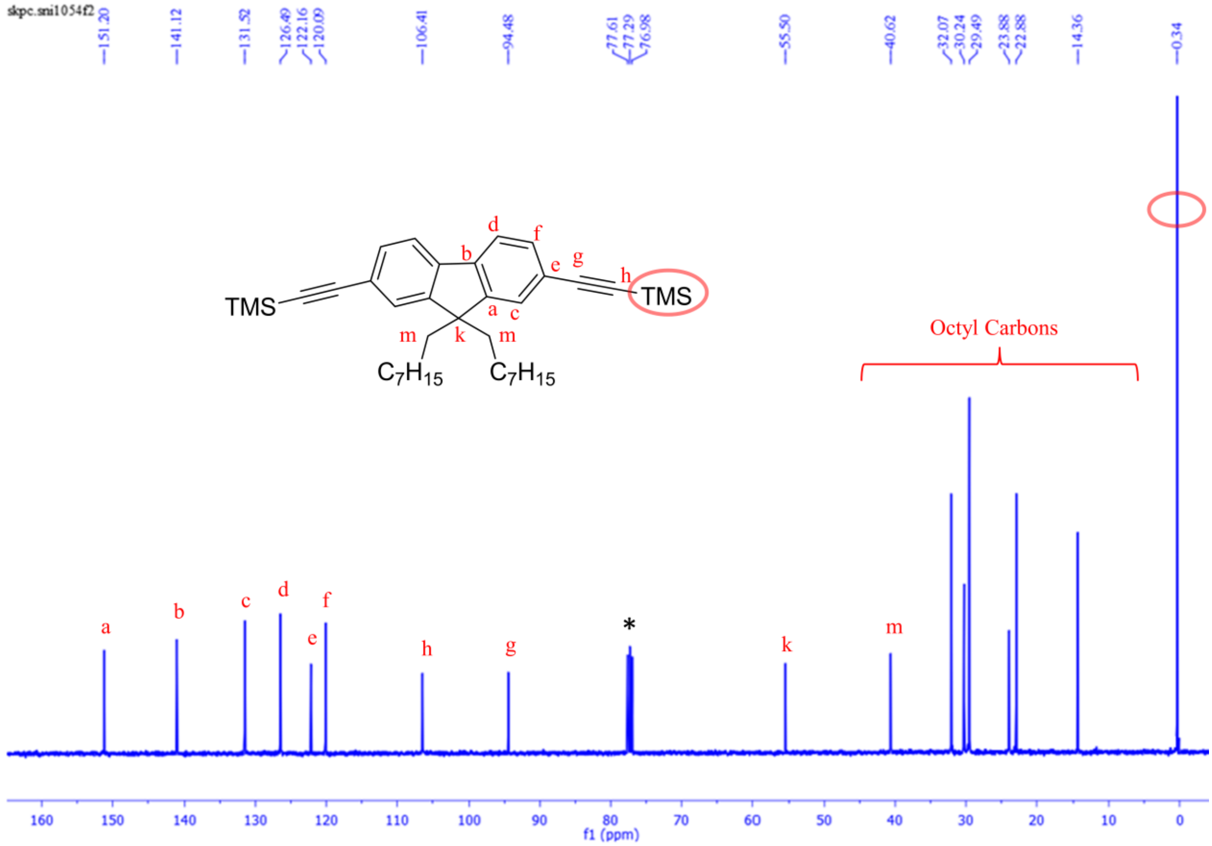


Fig. S11 $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **7**

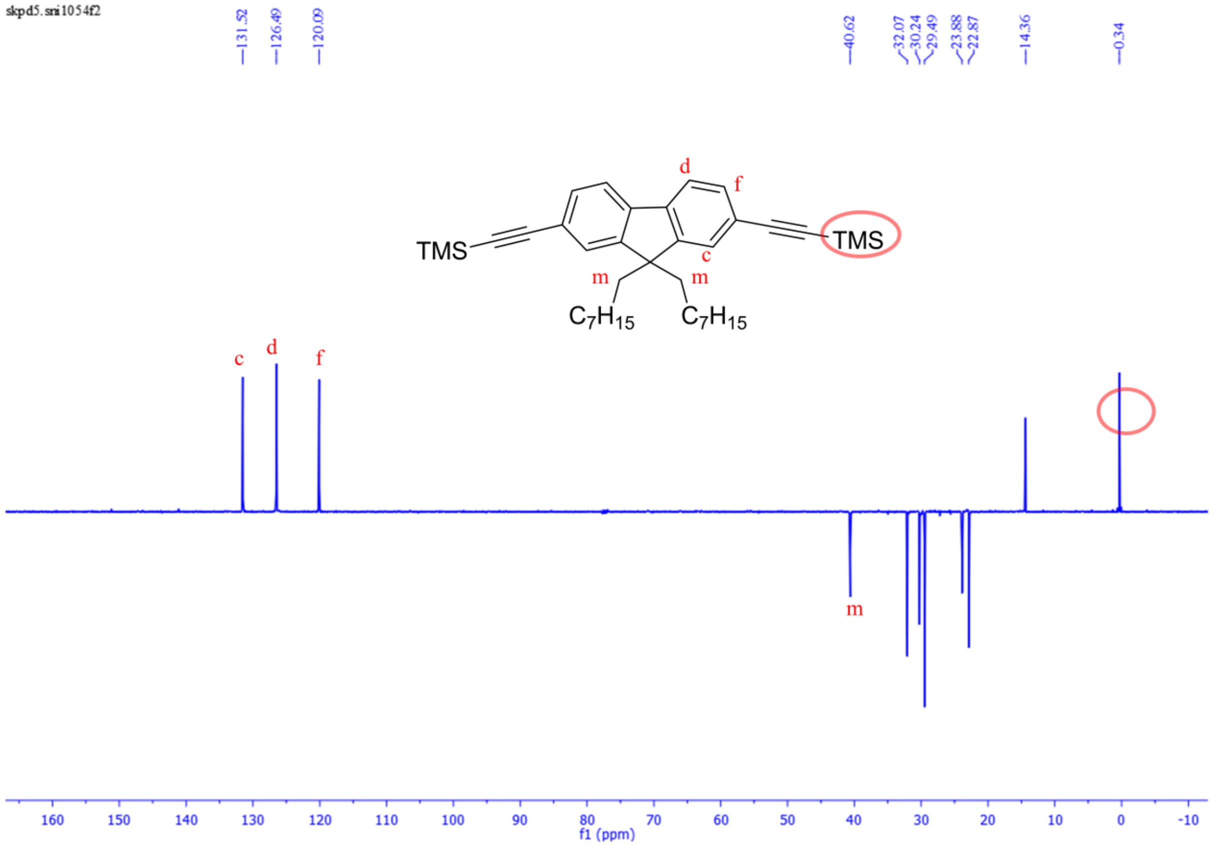


Fig. S12 DEPT-135 NMR (100 MHz, CDCl$_3$) spectrum of **7**

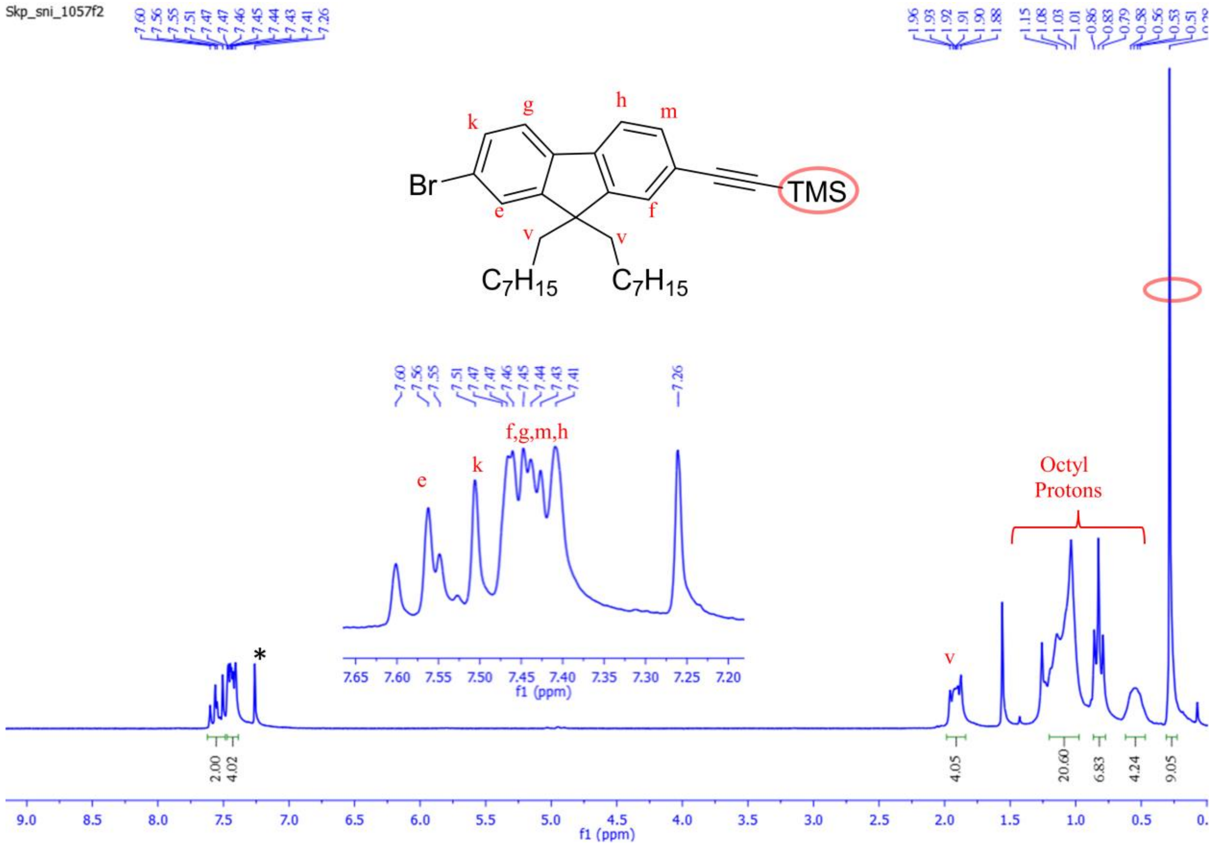


Fig. S13 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **4**

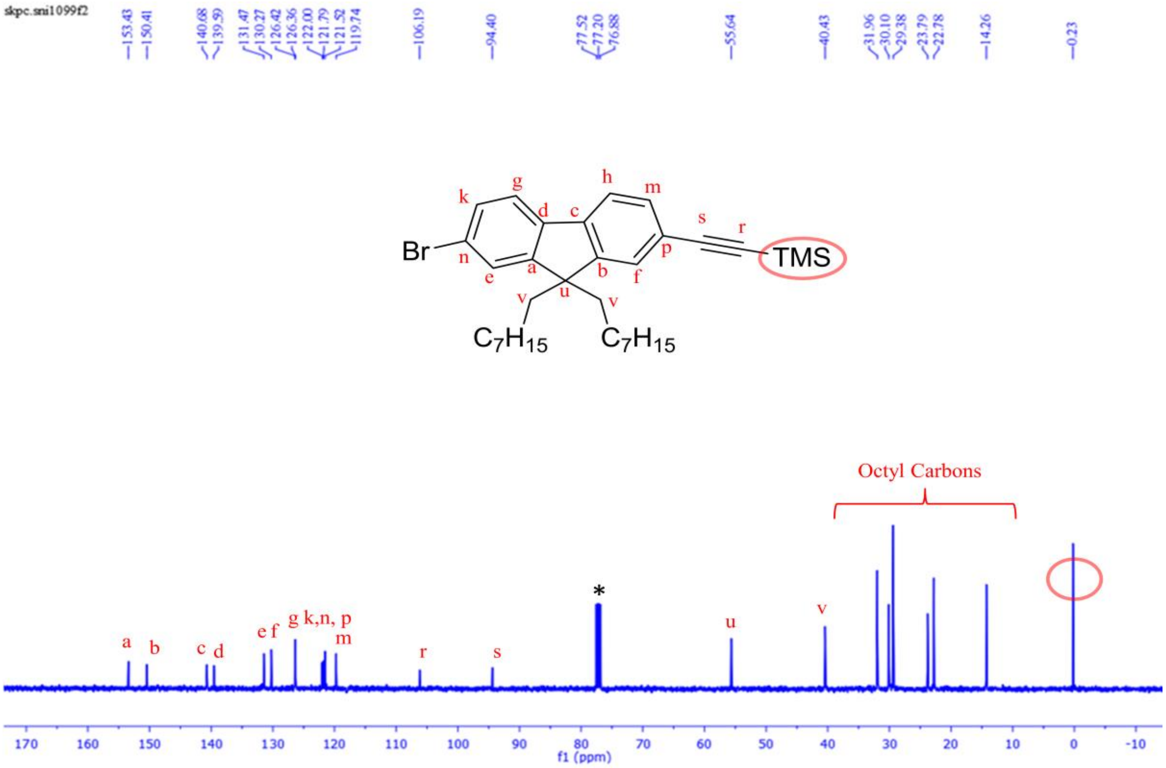


Fig. S14 $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4**

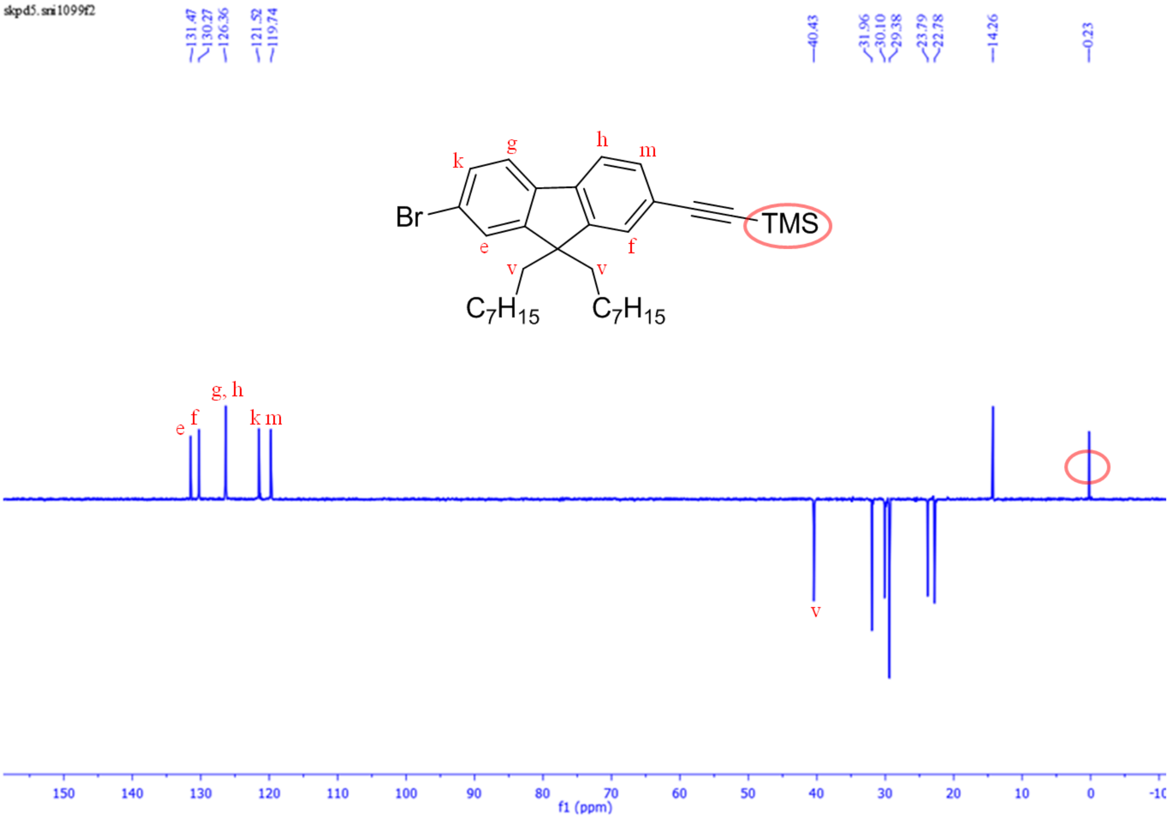


Fig. S15 DEPT-135 NMR (100 MHz, $CDCl_3$) spectrum of **4**

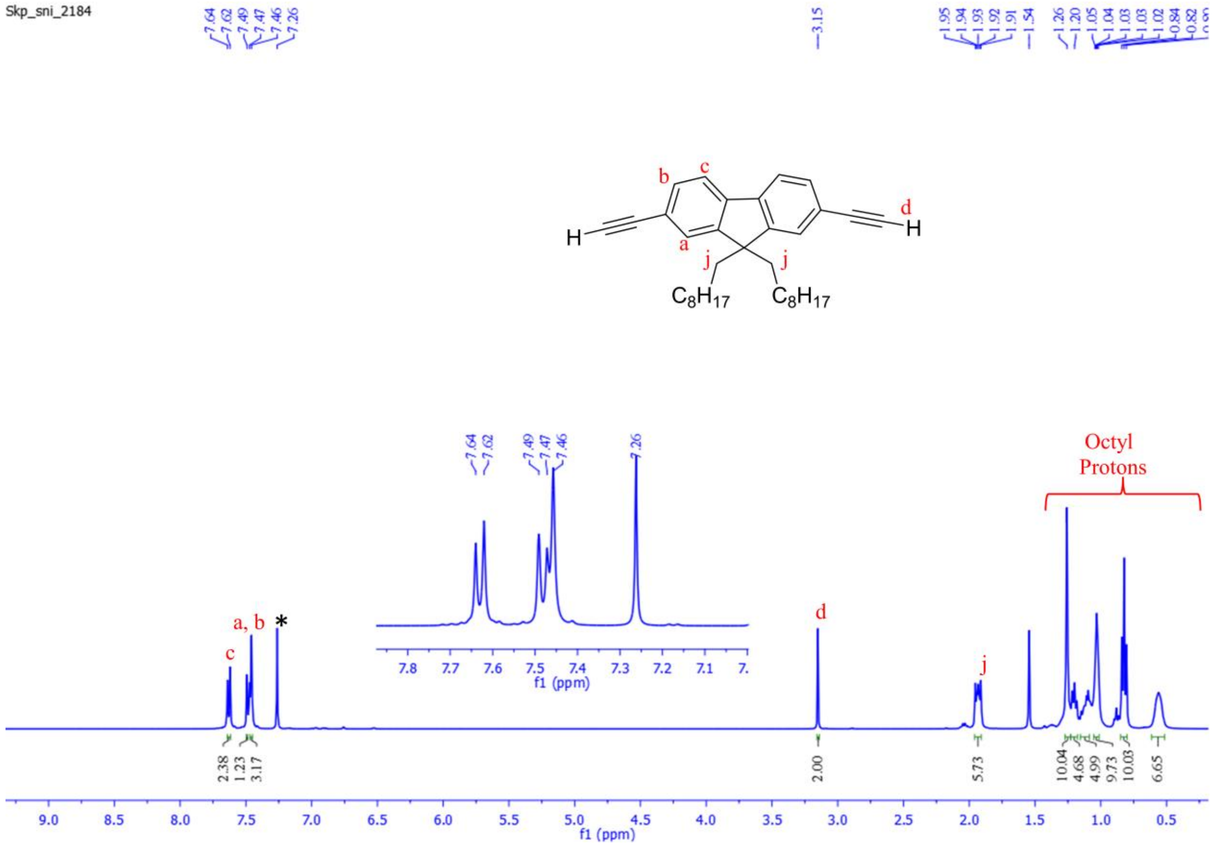


Fig. S16 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **8**

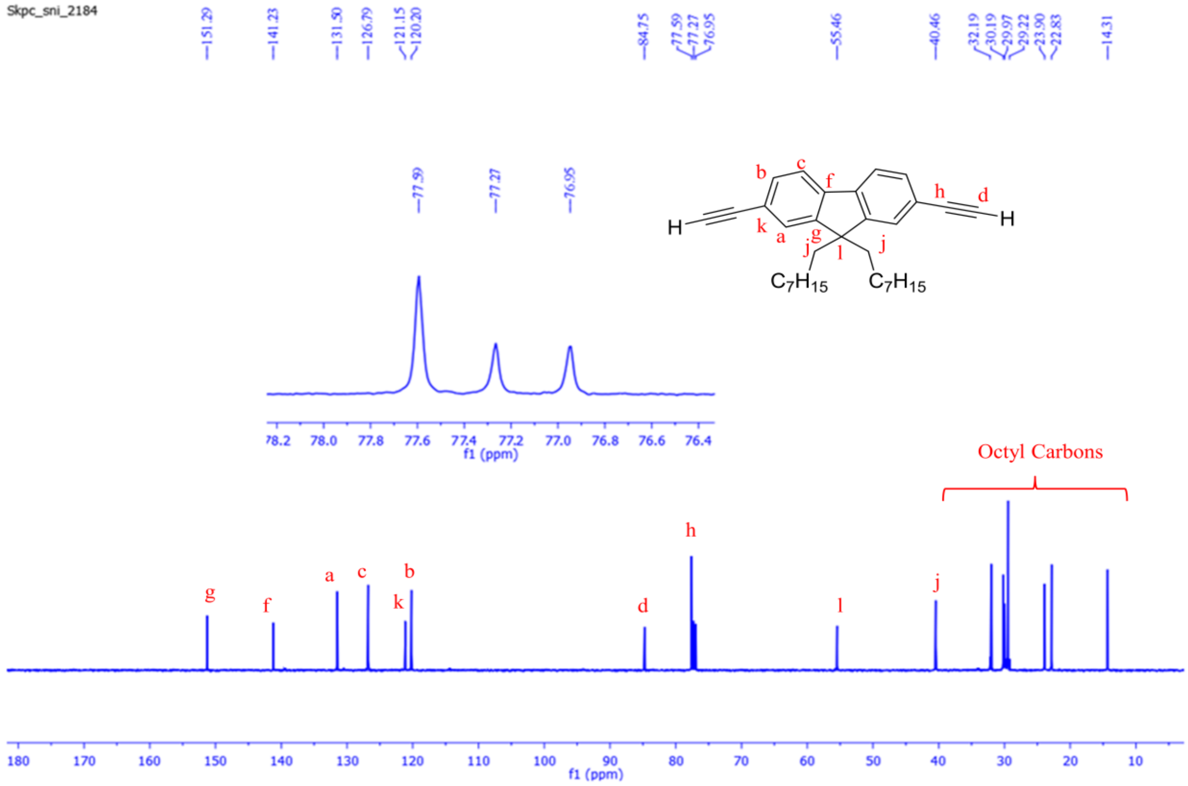


Fig. S17 ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of **8**

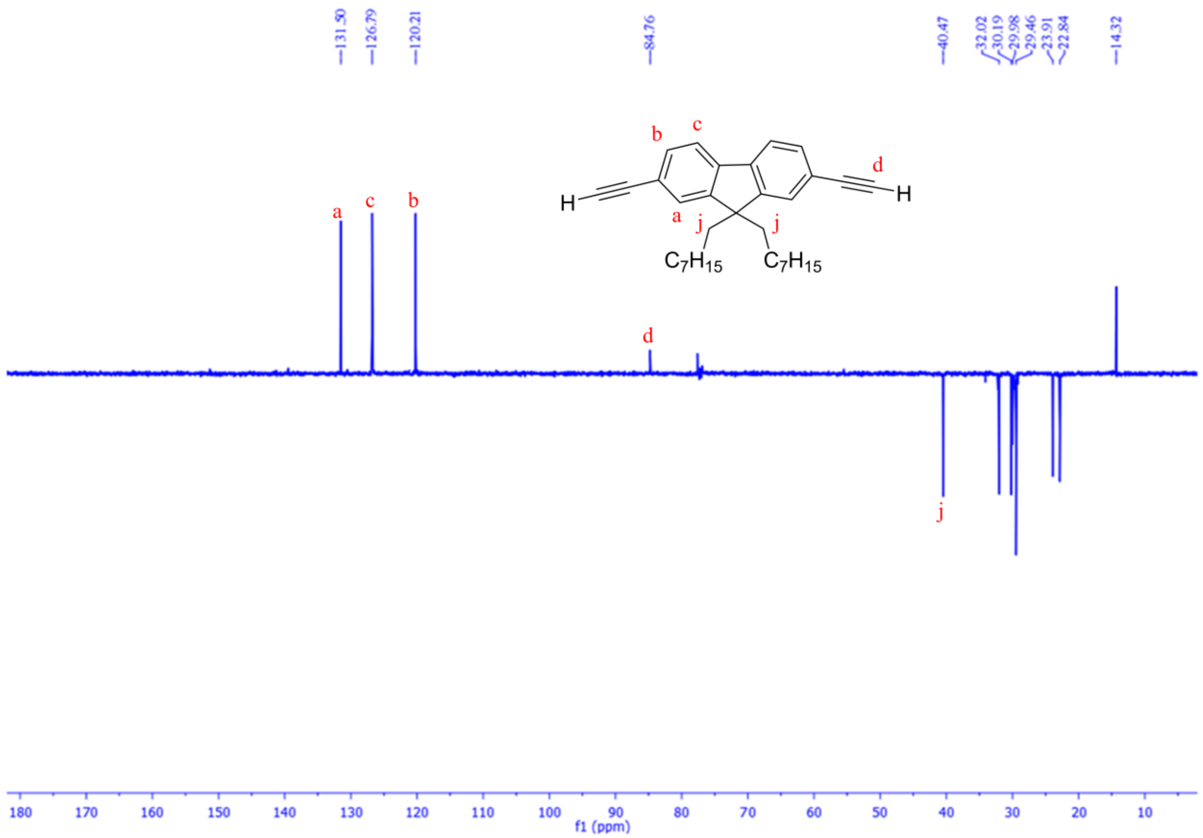


Fig. S18 DEPT-135 NMR (100 MHz, $CDCl_3$) spectrum of **8**

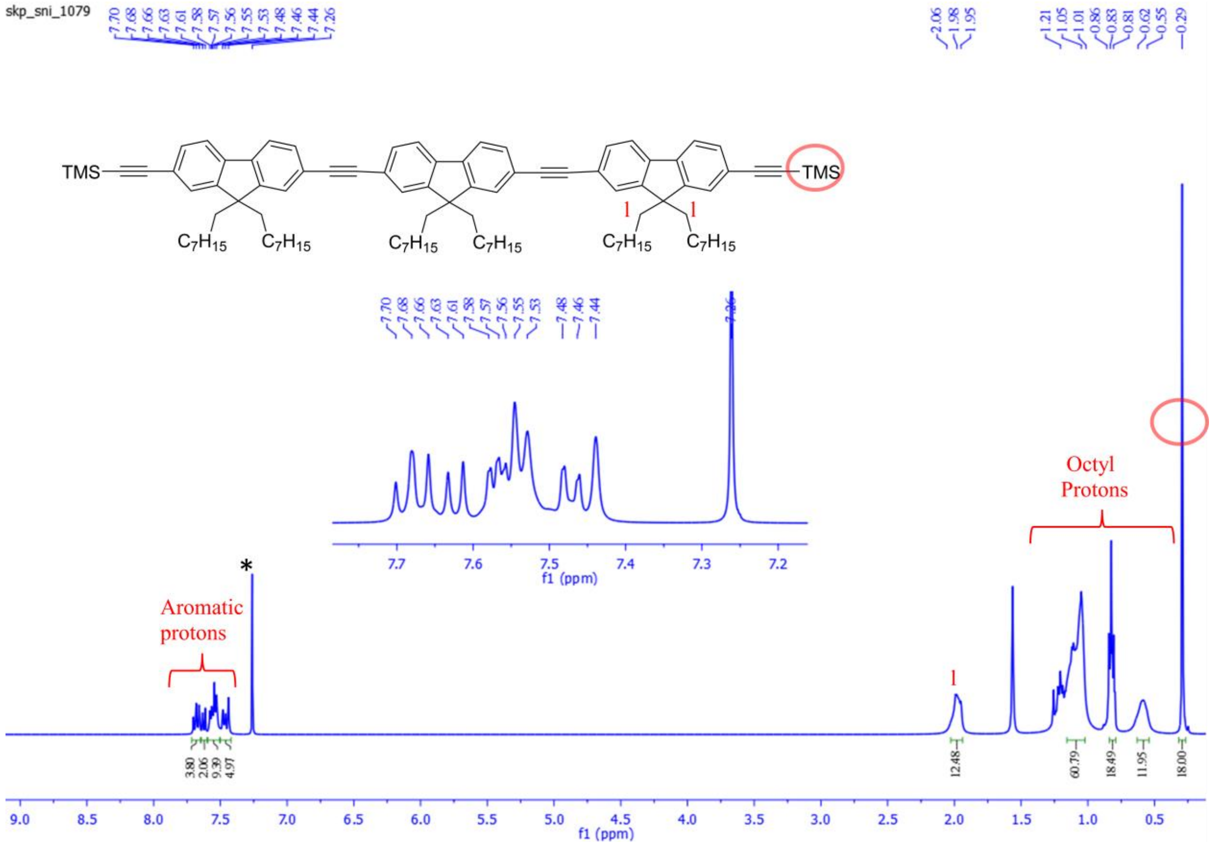


Fig. S19 ^1H NMR (400 MHz, $CDCl_3$) spectrum of **O1**

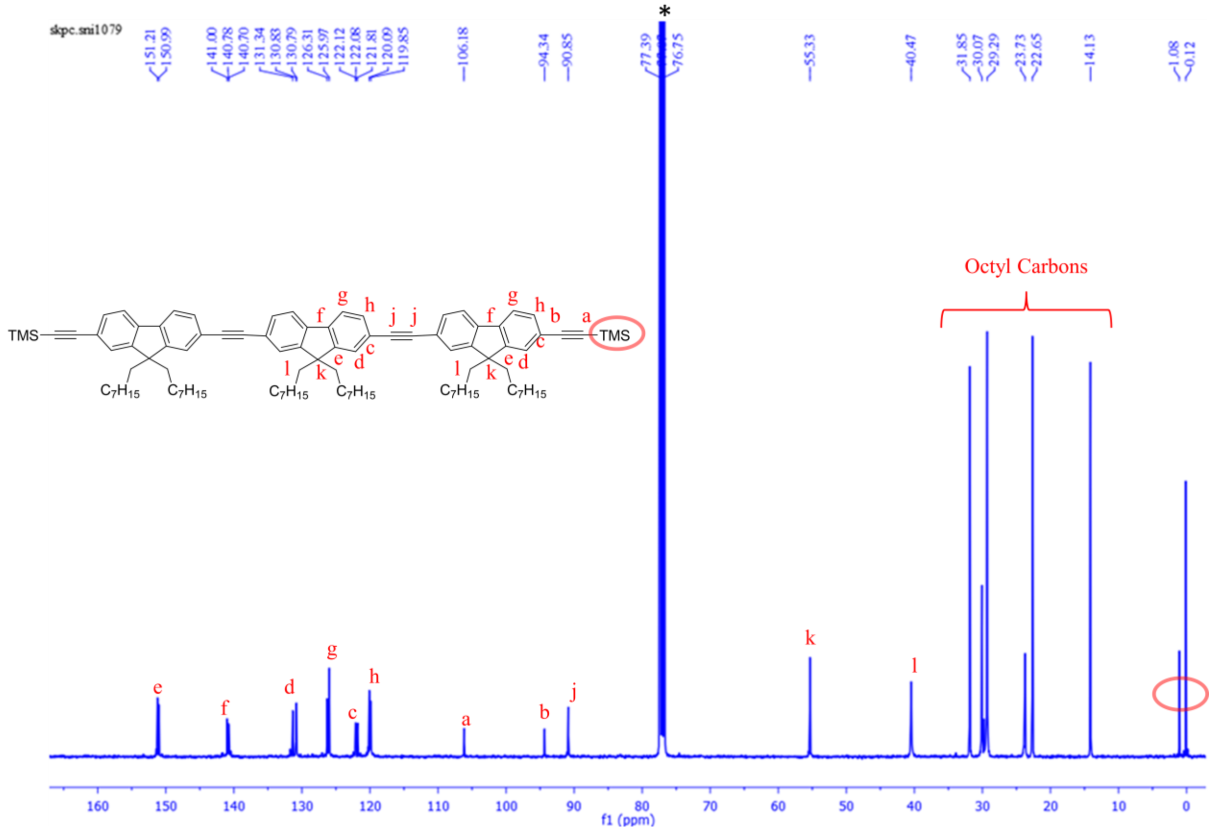


Fig. S20 $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **O1**

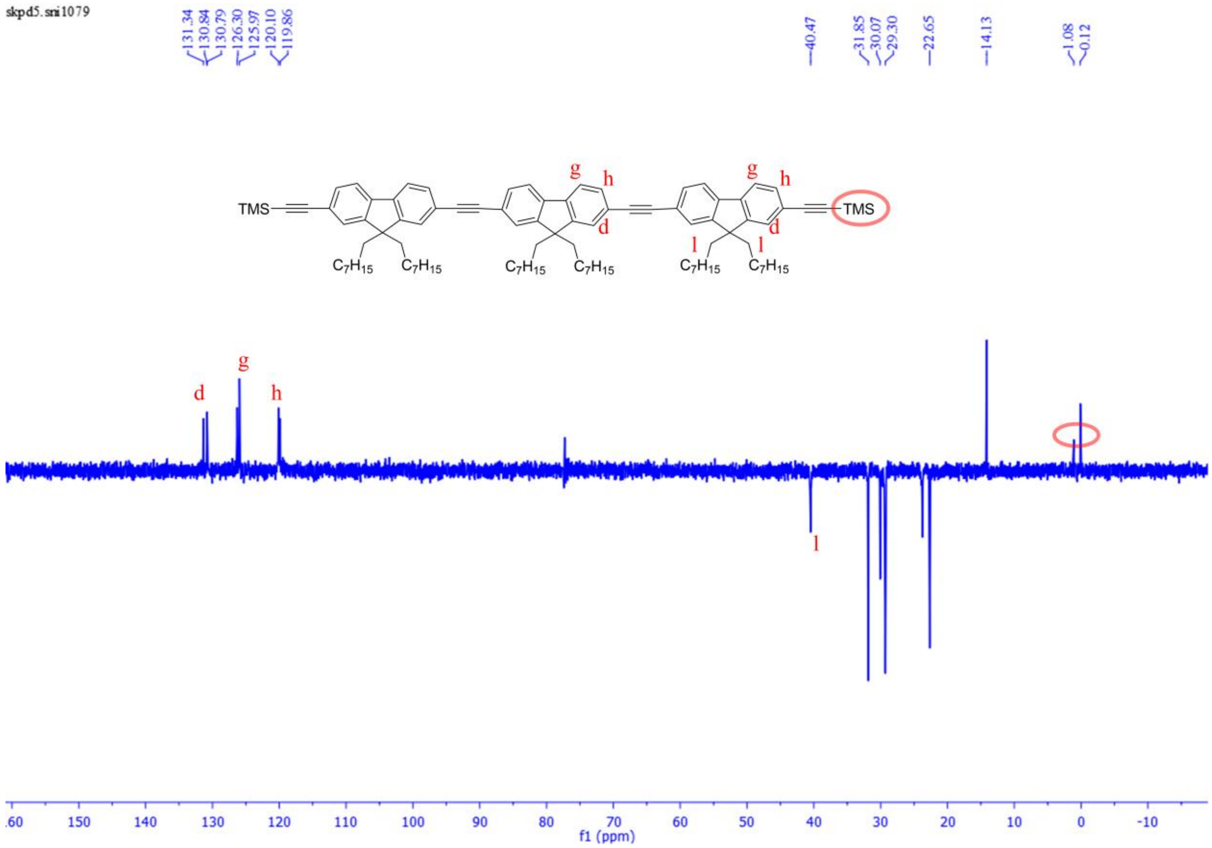


Fig. S21 DEPT-135 NMR (100 MHz, $CDCl_3$) spectrum of **O1**

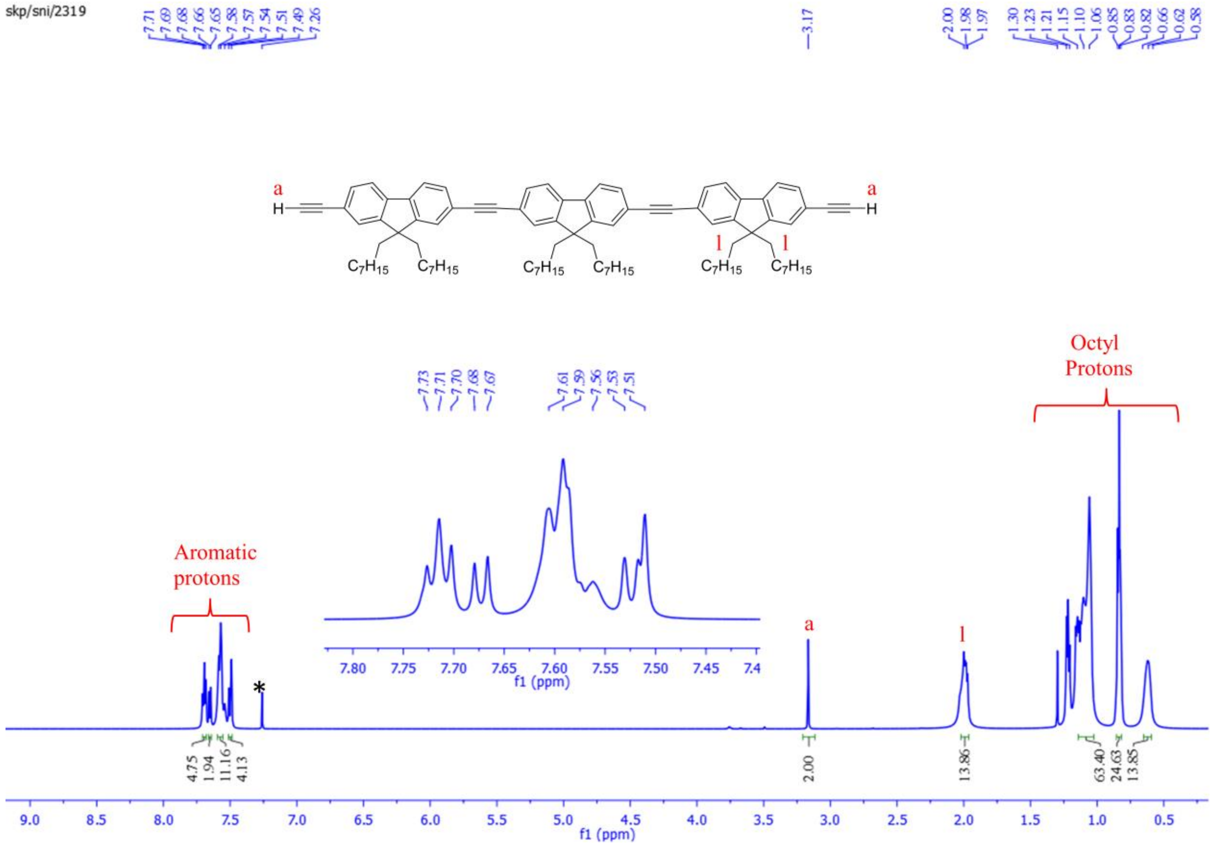


Fig. S22 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **OH1**

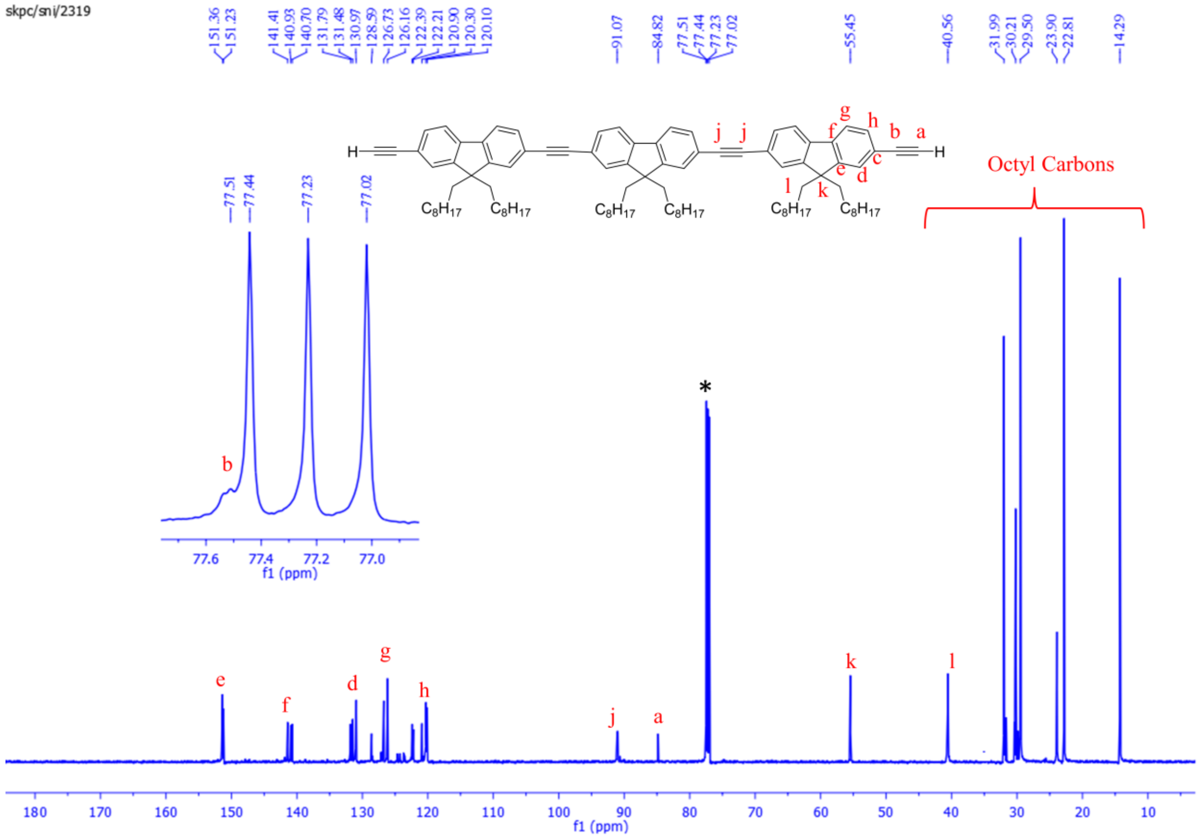


Fig. S23 ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of **OH1**

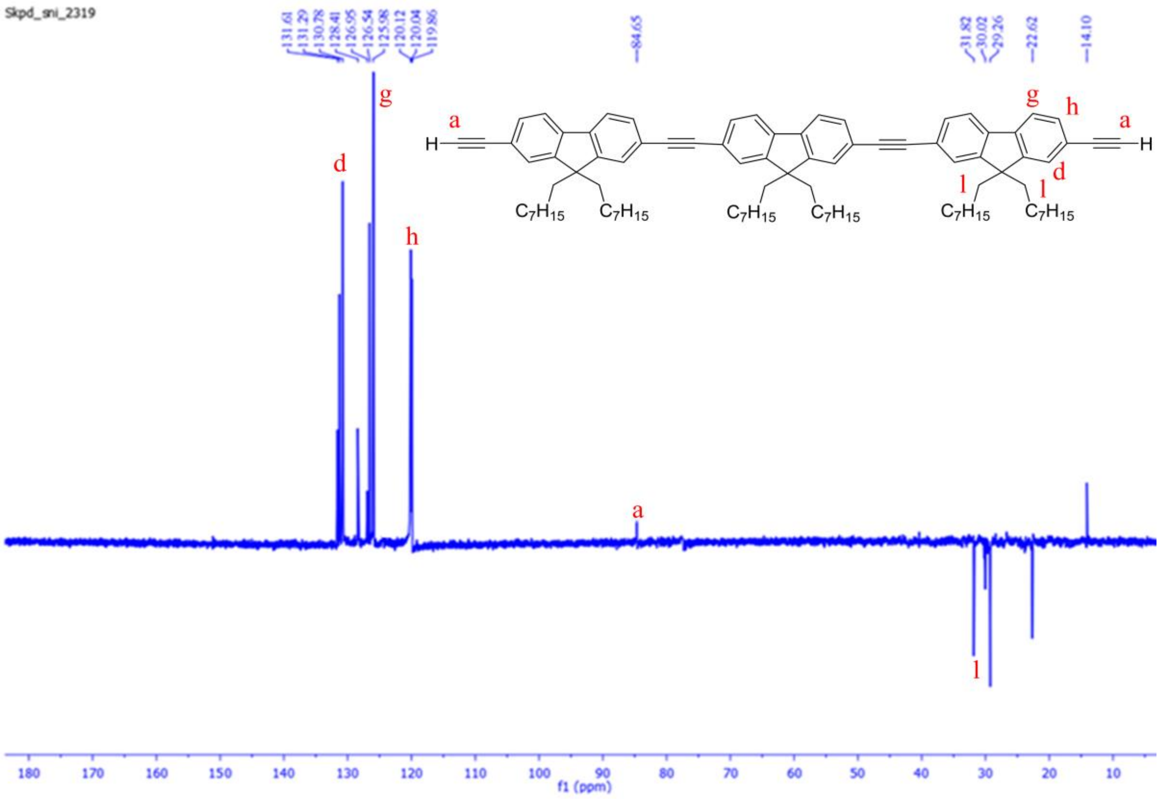


Fig. S24 DEPT-135 NMR (100 MHz, $CDCl_3$) spectrum of **OH1**

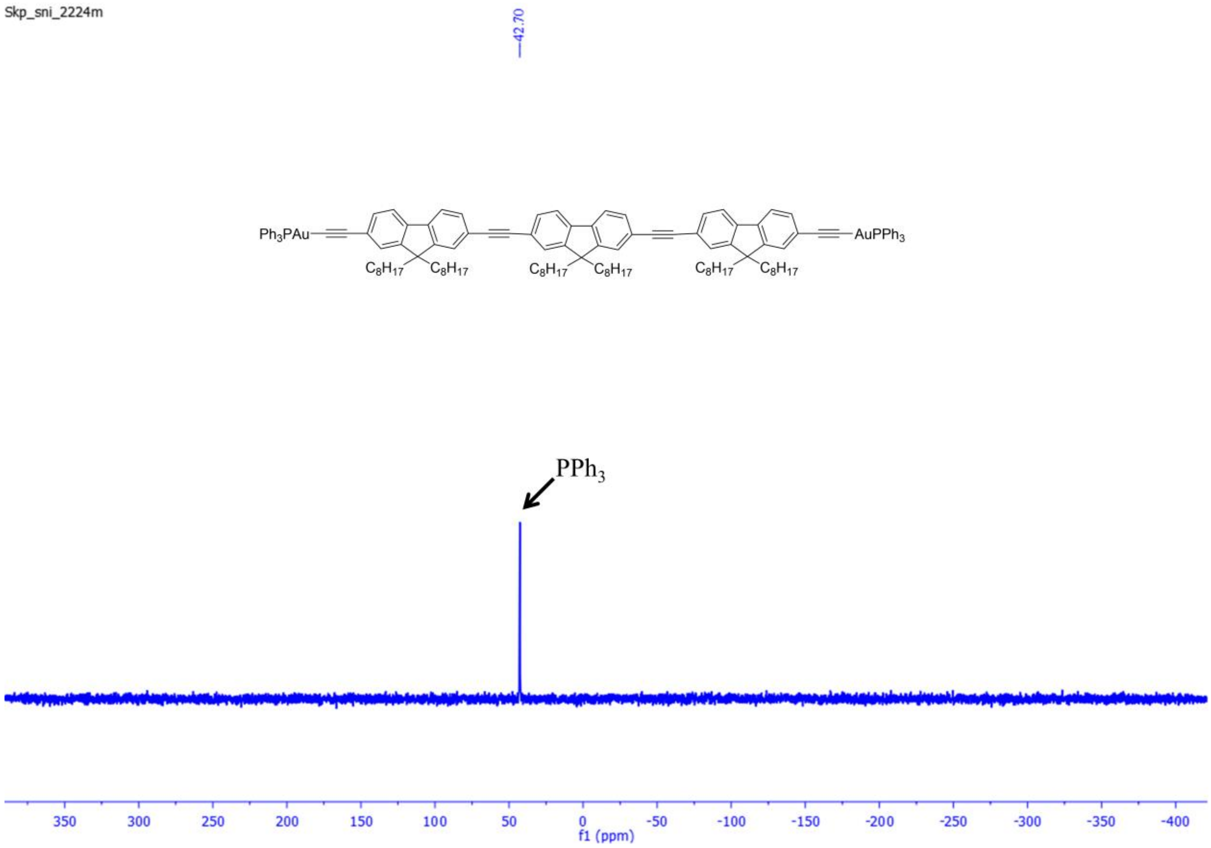


Fig. S25 $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) spectrum of **OM1**

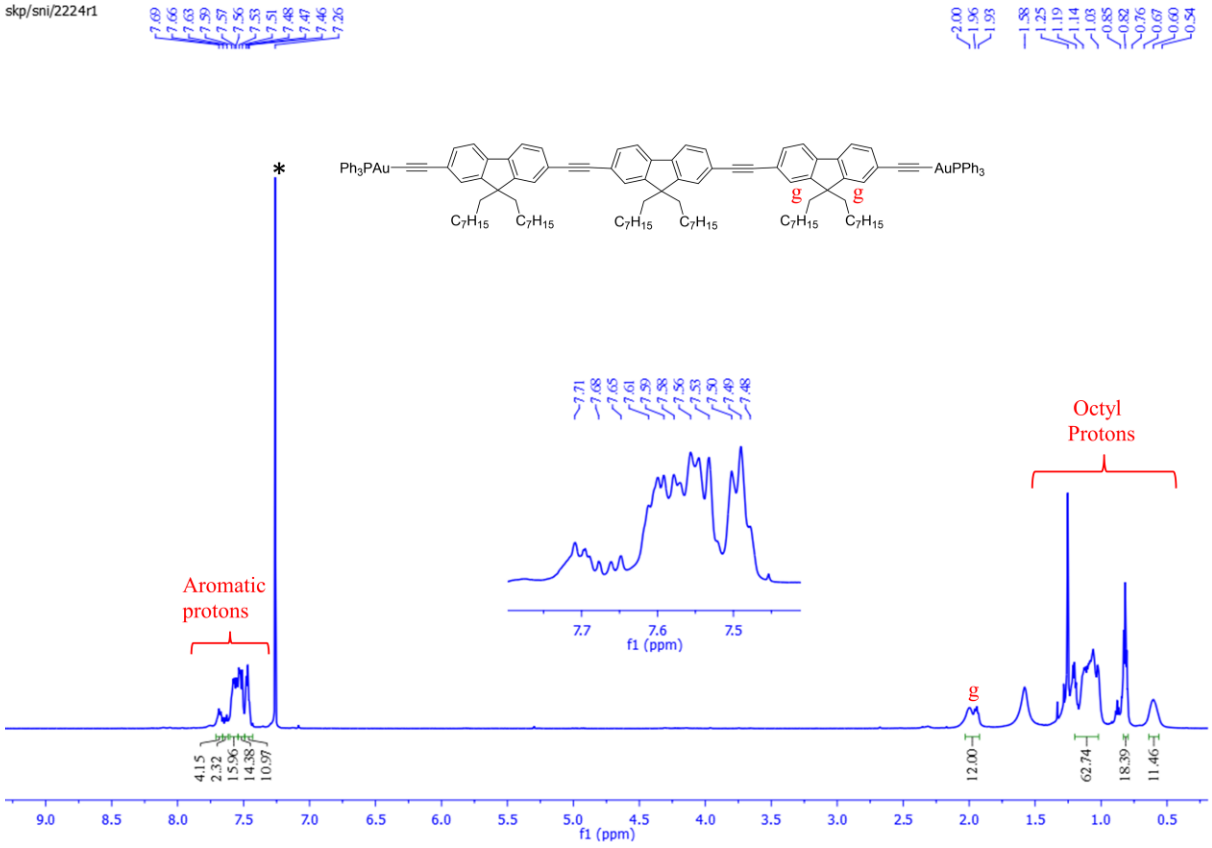


Fig. S26 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **OM1**

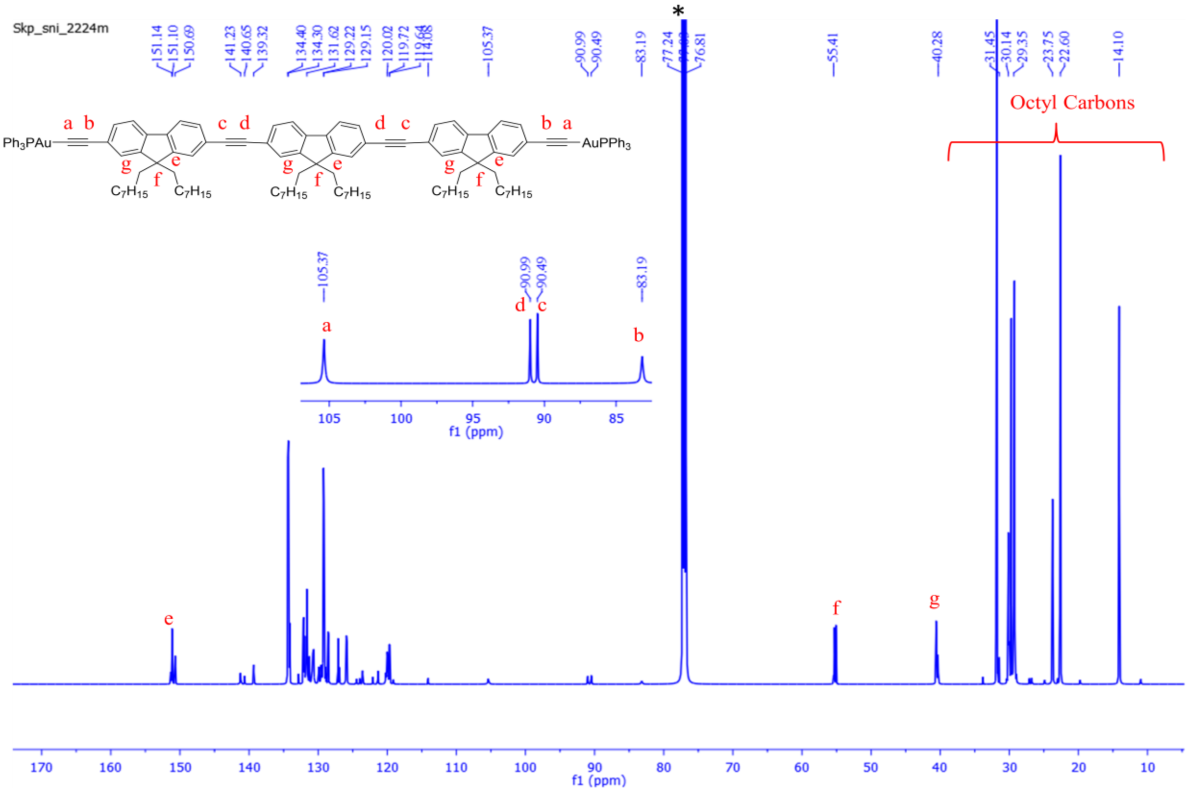


Fig. S27 $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) spectrum of **OM1**

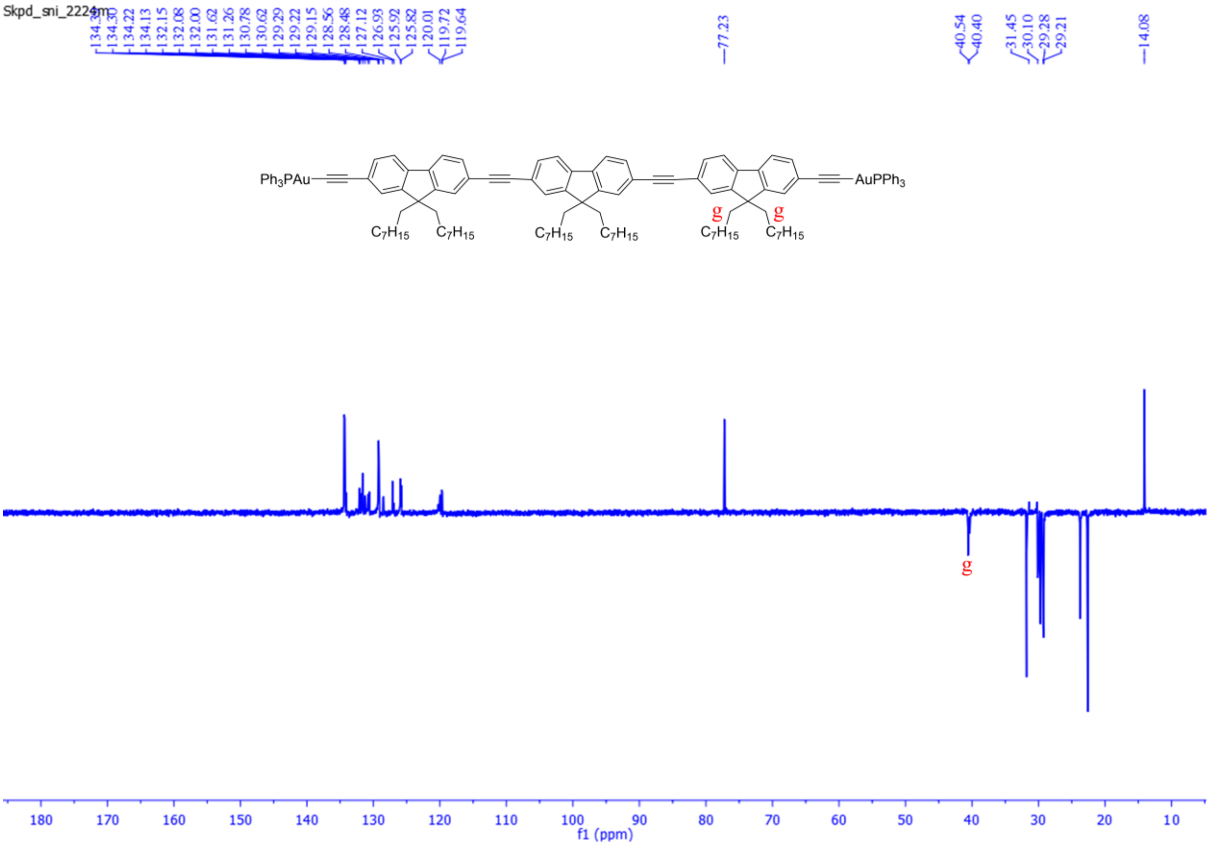


Fig. S28 DEPT-135 NMR (150 MHz, CDCl$_3$) spectrum of **OM1**

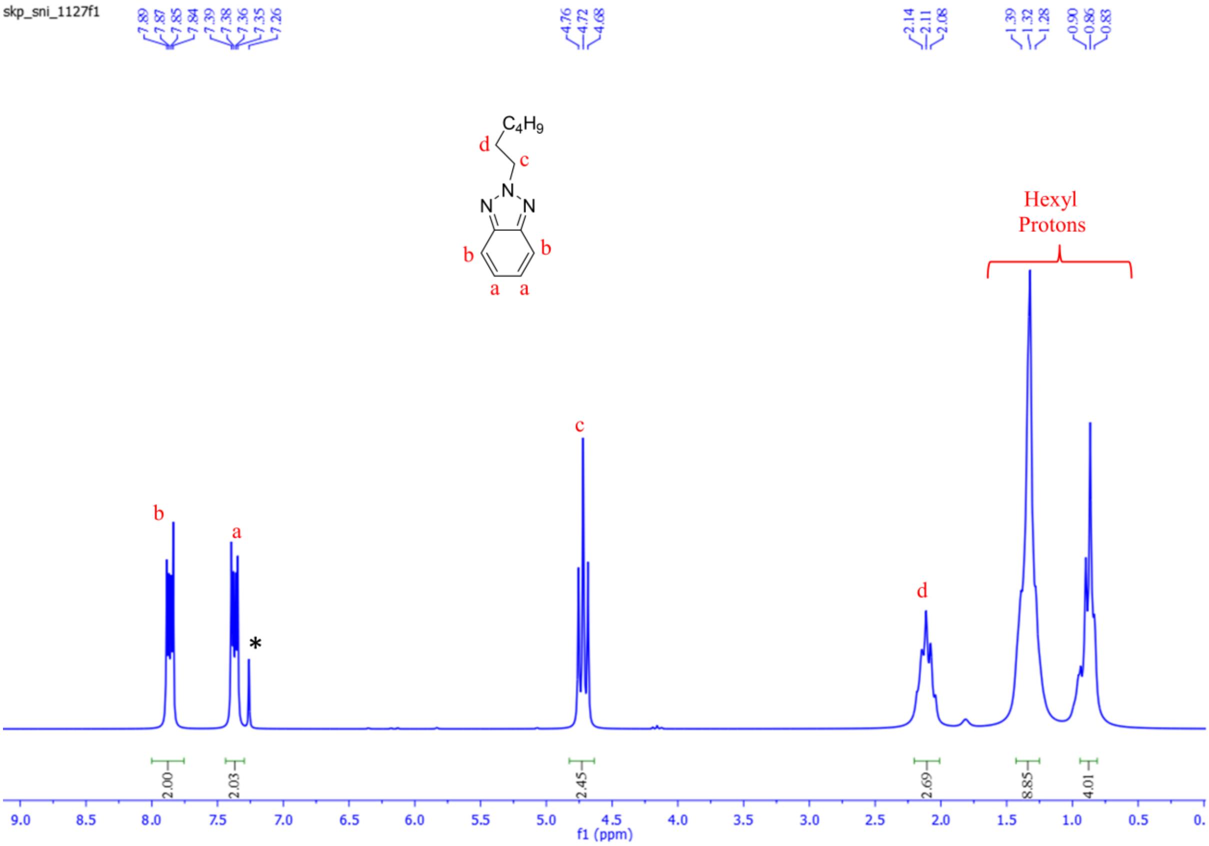


Fig. S29 ^{1}H NMR (200 MHz, CDCl$_3$) spectrum of **11**

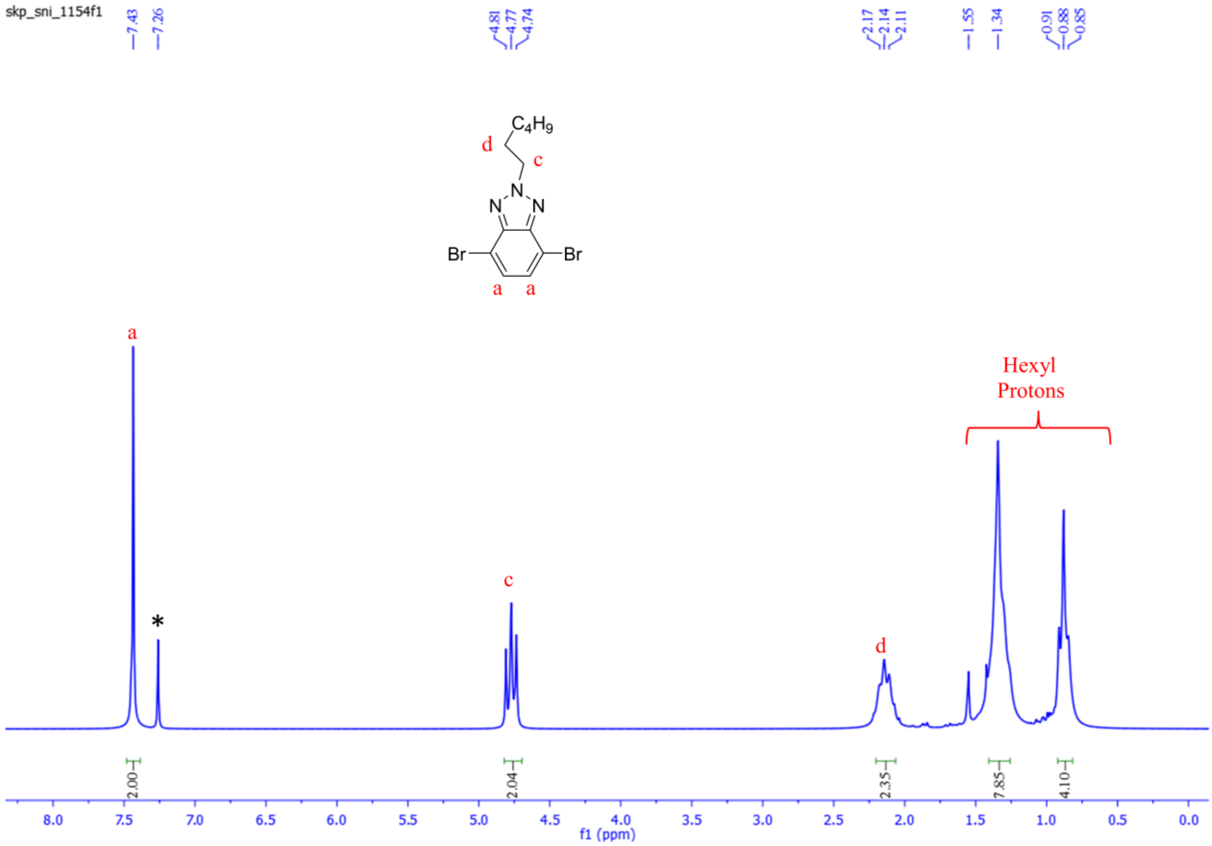


Fig. S30 ^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **12**

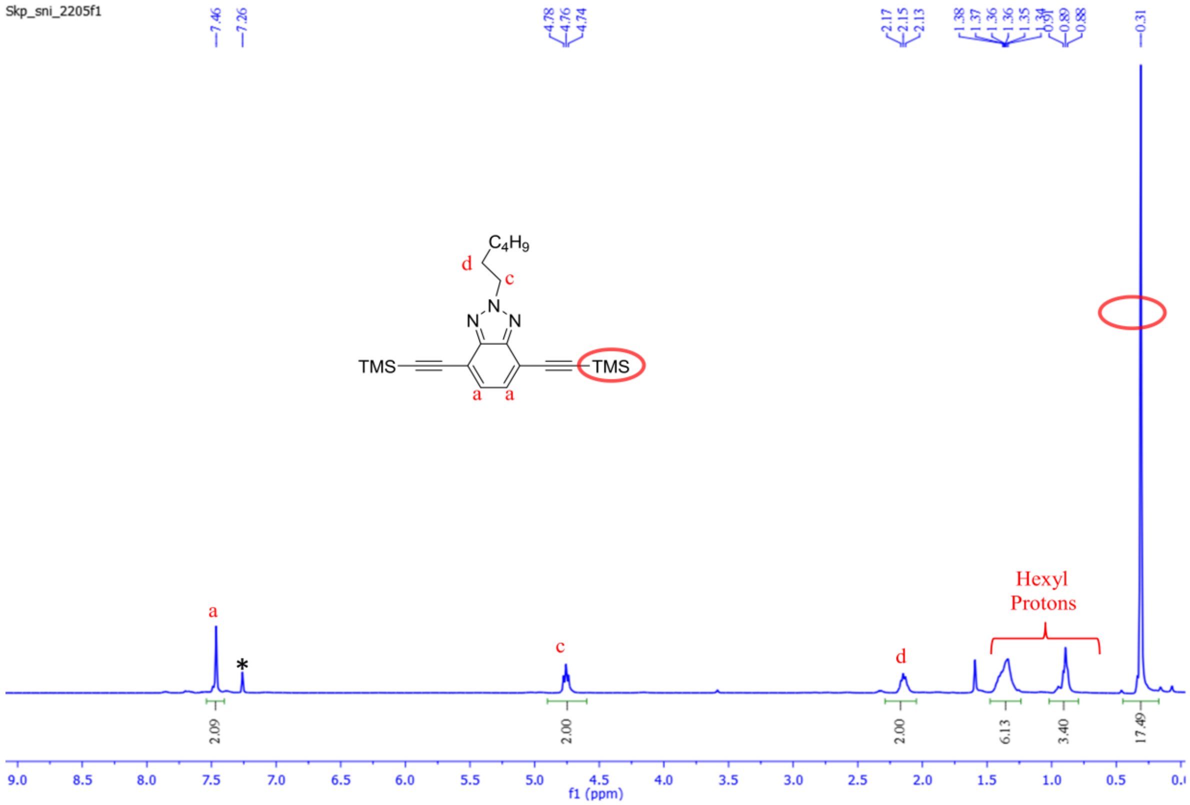


Fig. S31 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13**

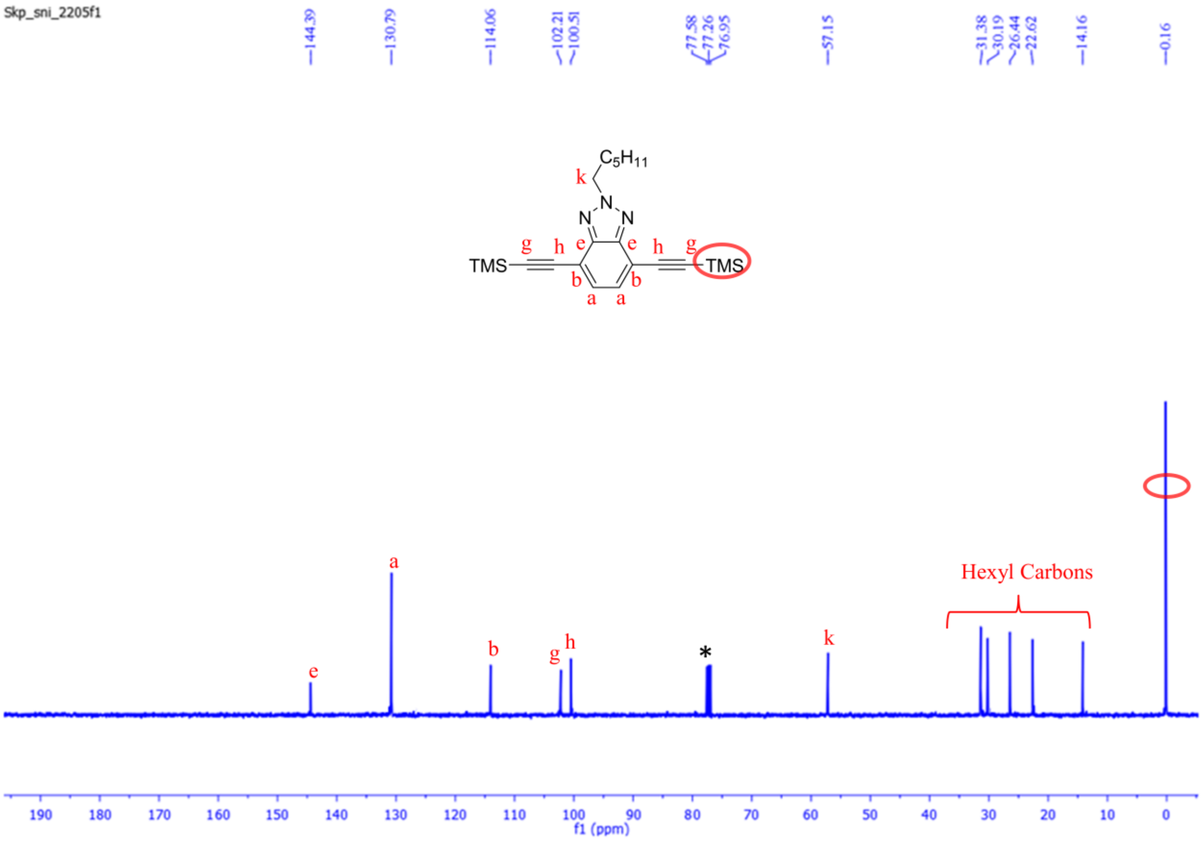


Fig. S32 ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) spectrum of **13**

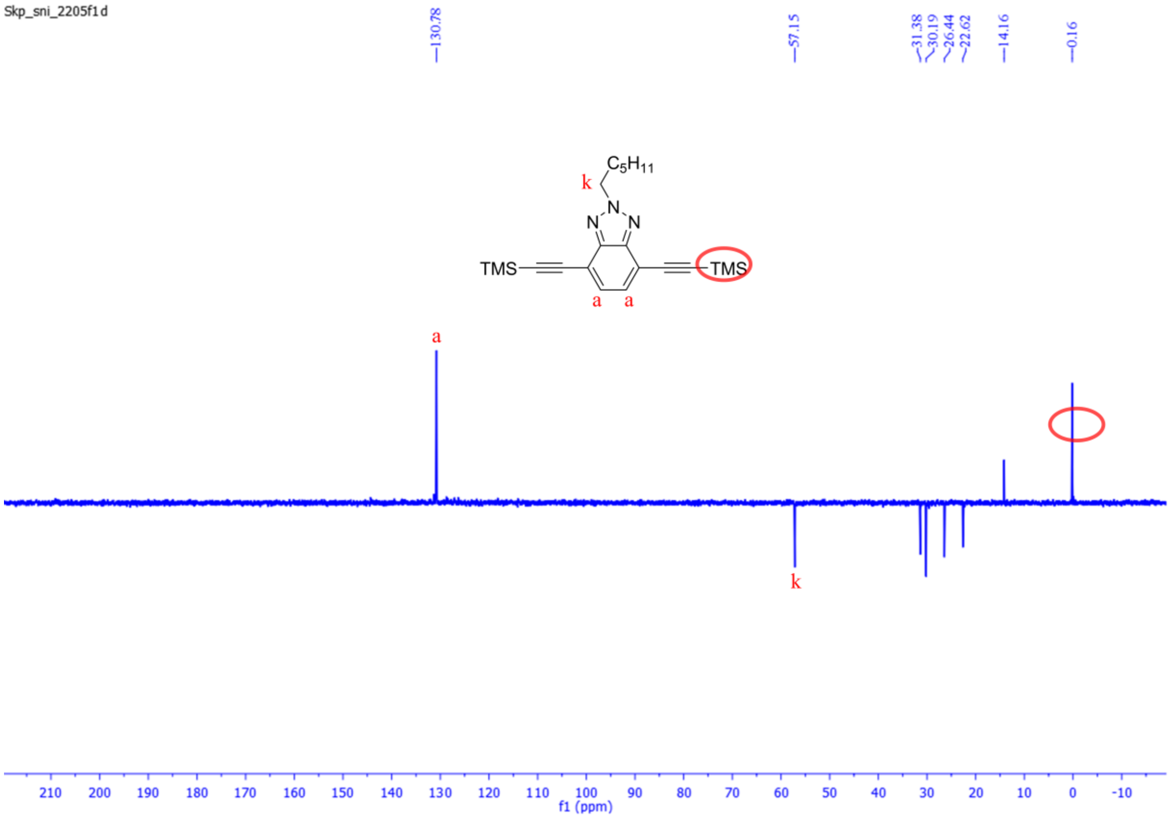


Fig. S33 DEPT-135 NMR (100 MHz, CDCl$_3$) spectrum of **13**

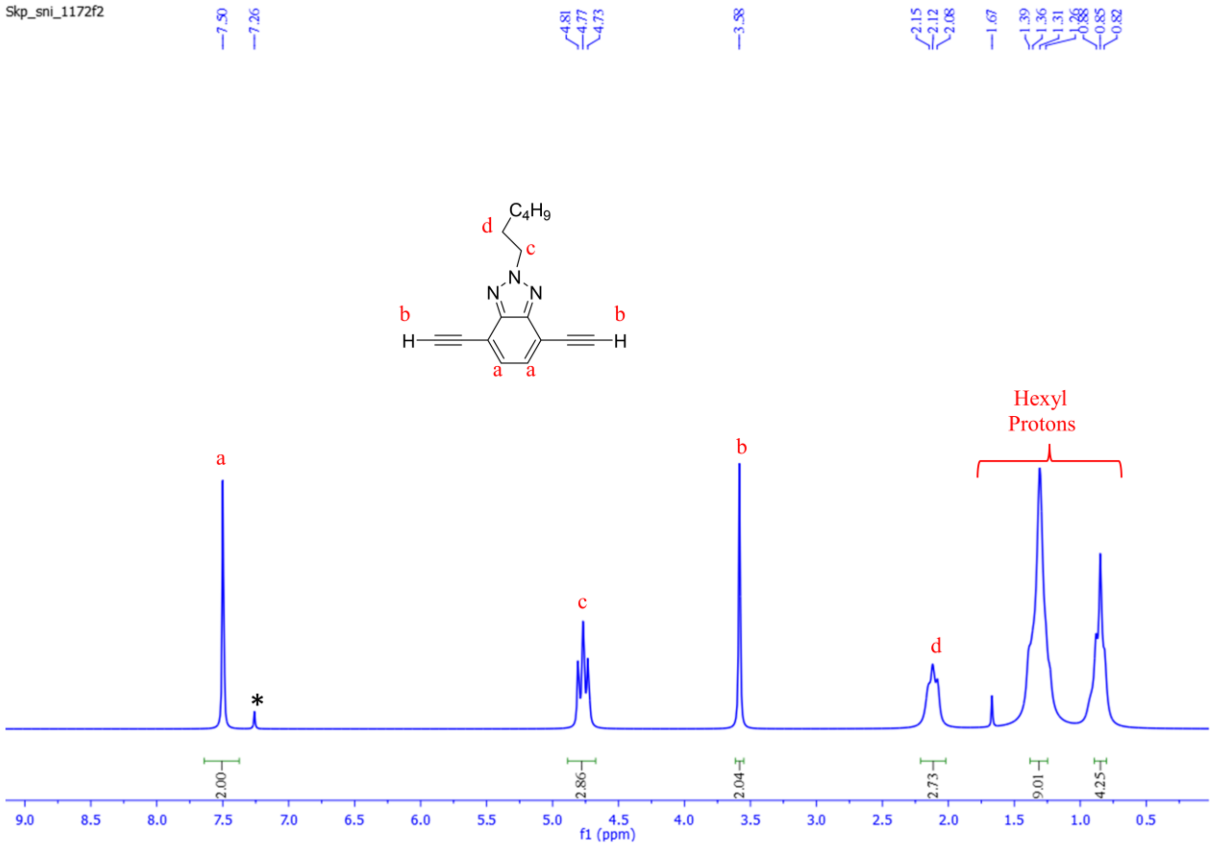


Fig. S34 ^{1}H NMR (200 MHz, $CDCl_3$) spectrum of **14**

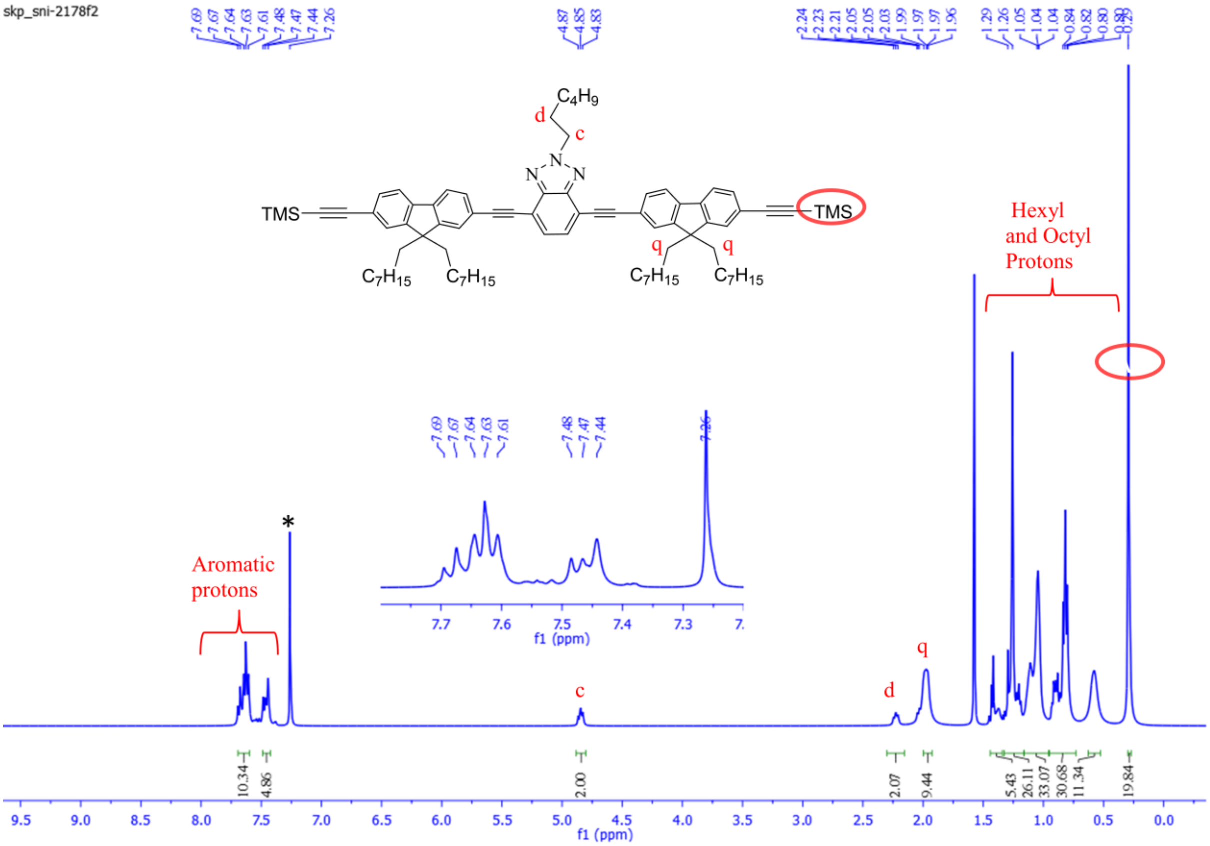


Fig. S35 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **O2**

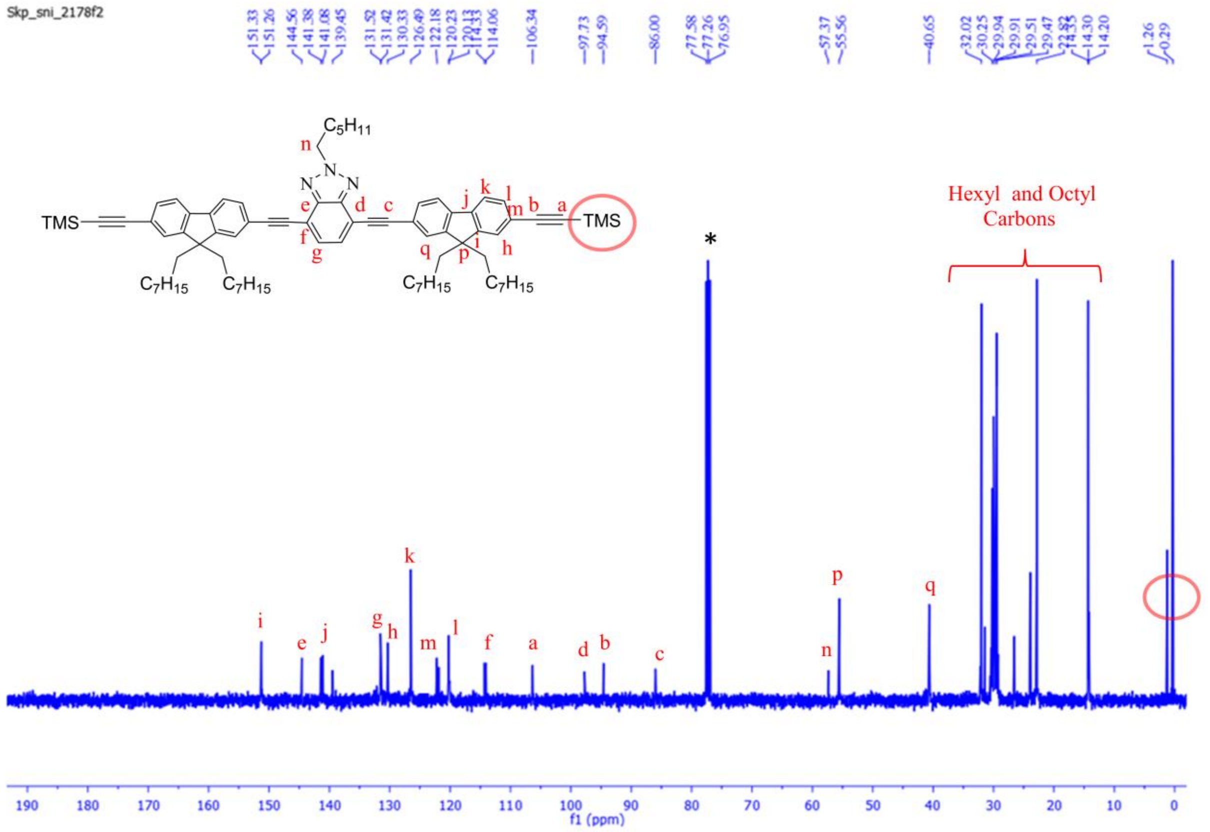


Fig. S36 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **O2**

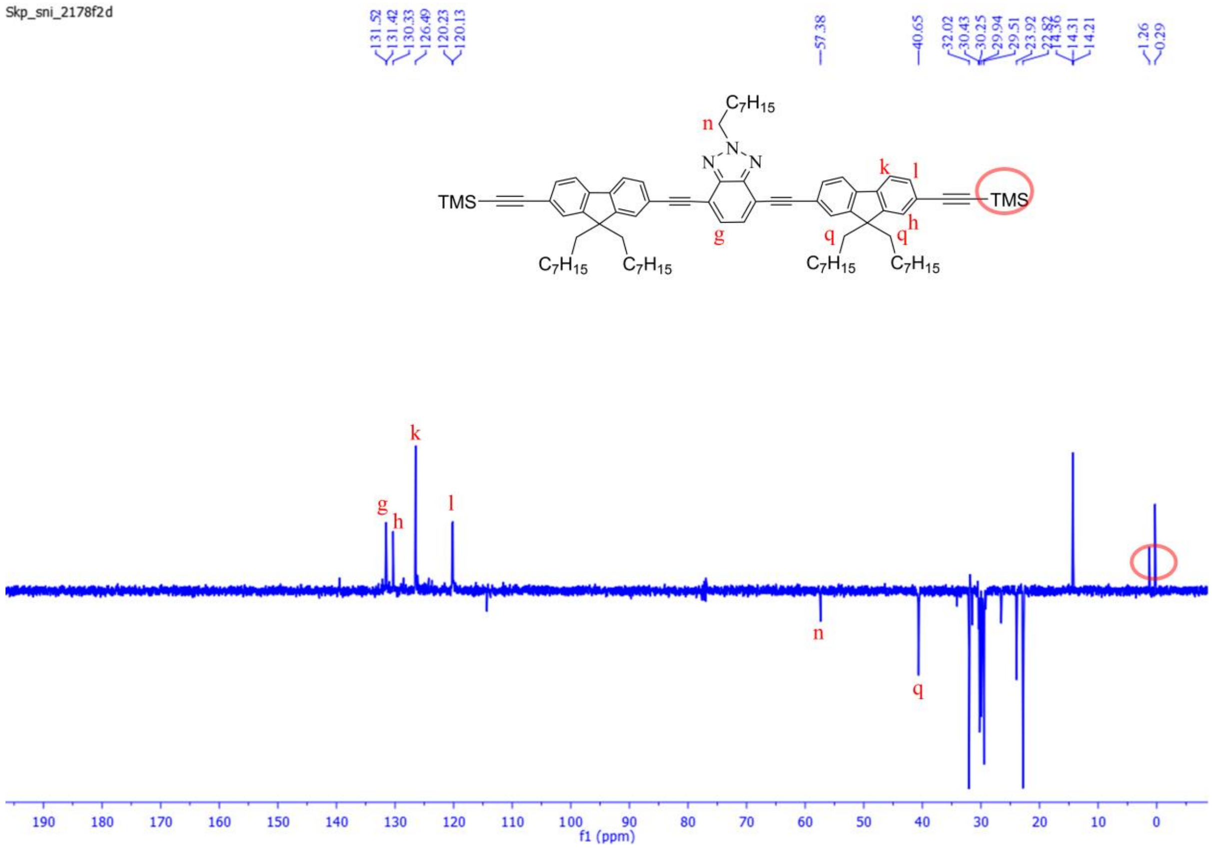


Fig. S37 DEPT-135 NMR (100 MHz, $CDCl_3$) spectrum of **O2**

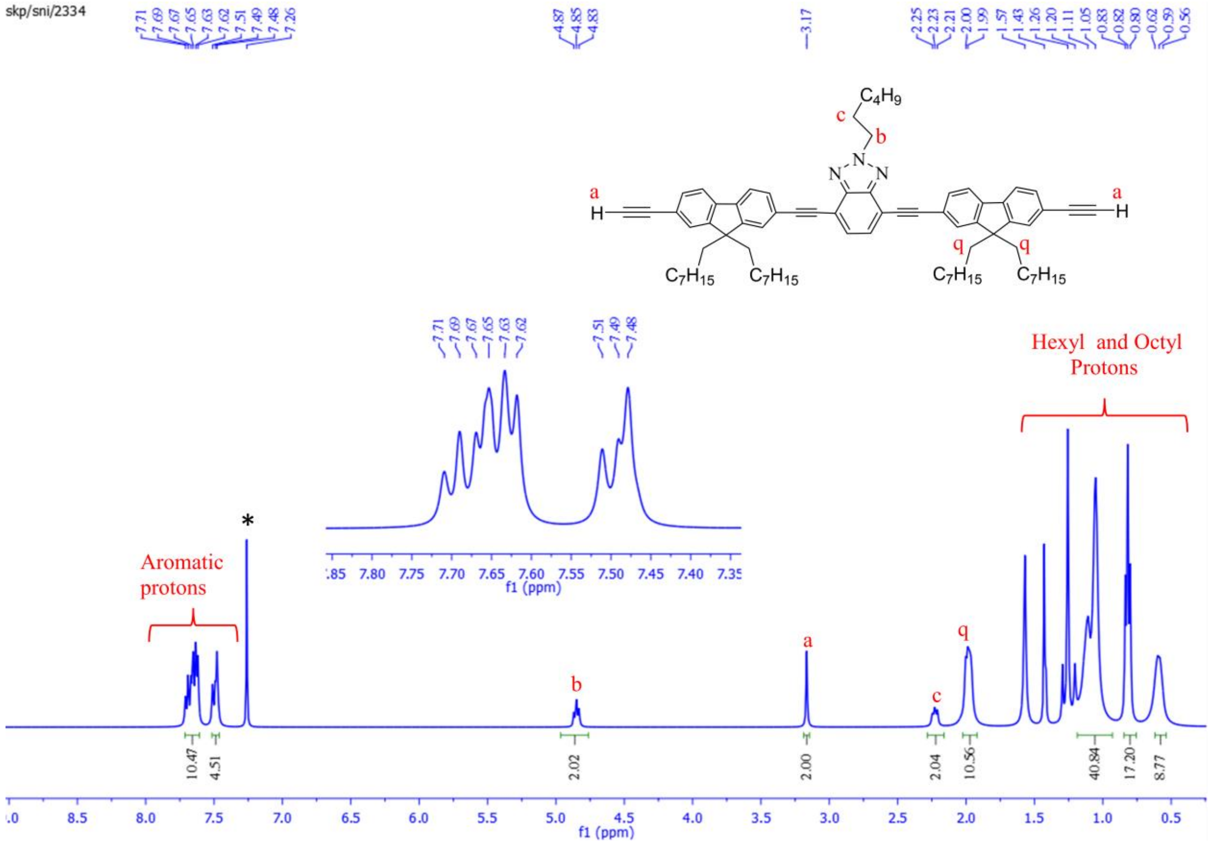


Fig. S38 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **OH2**

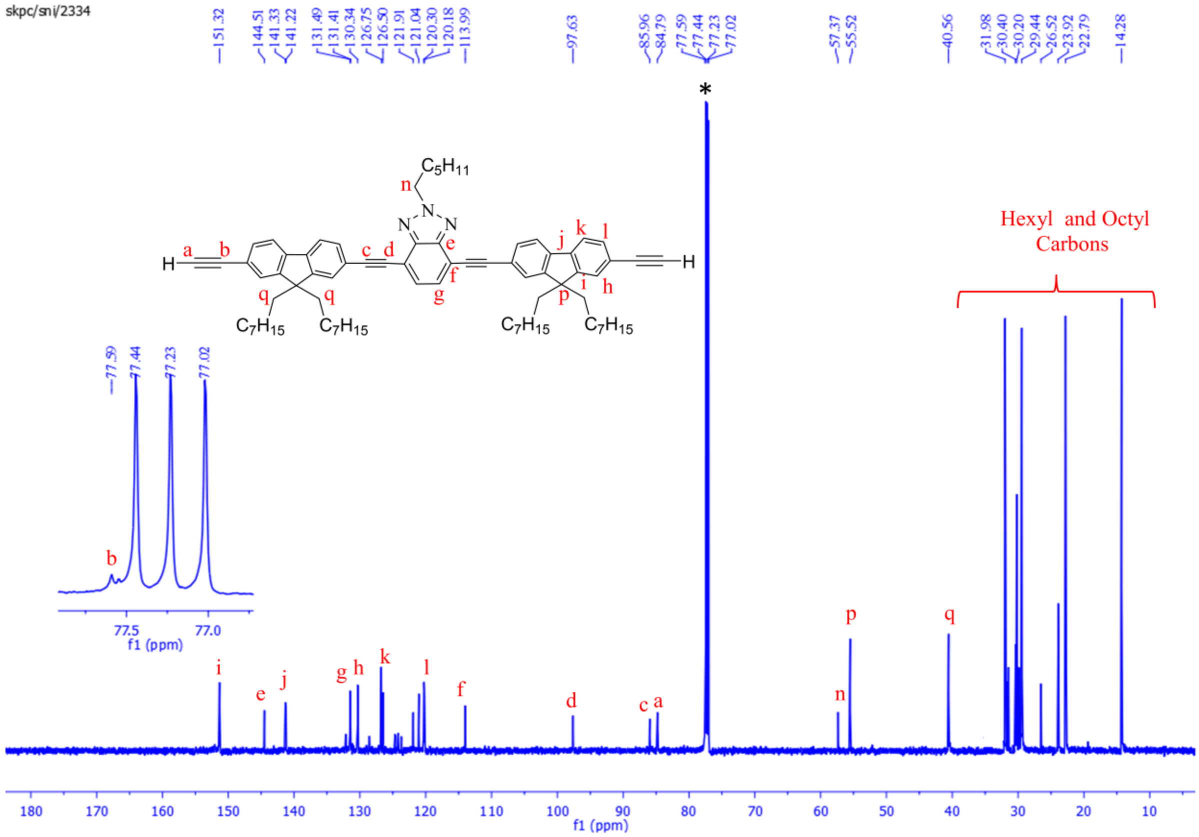


Fig. S39 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **OH2**

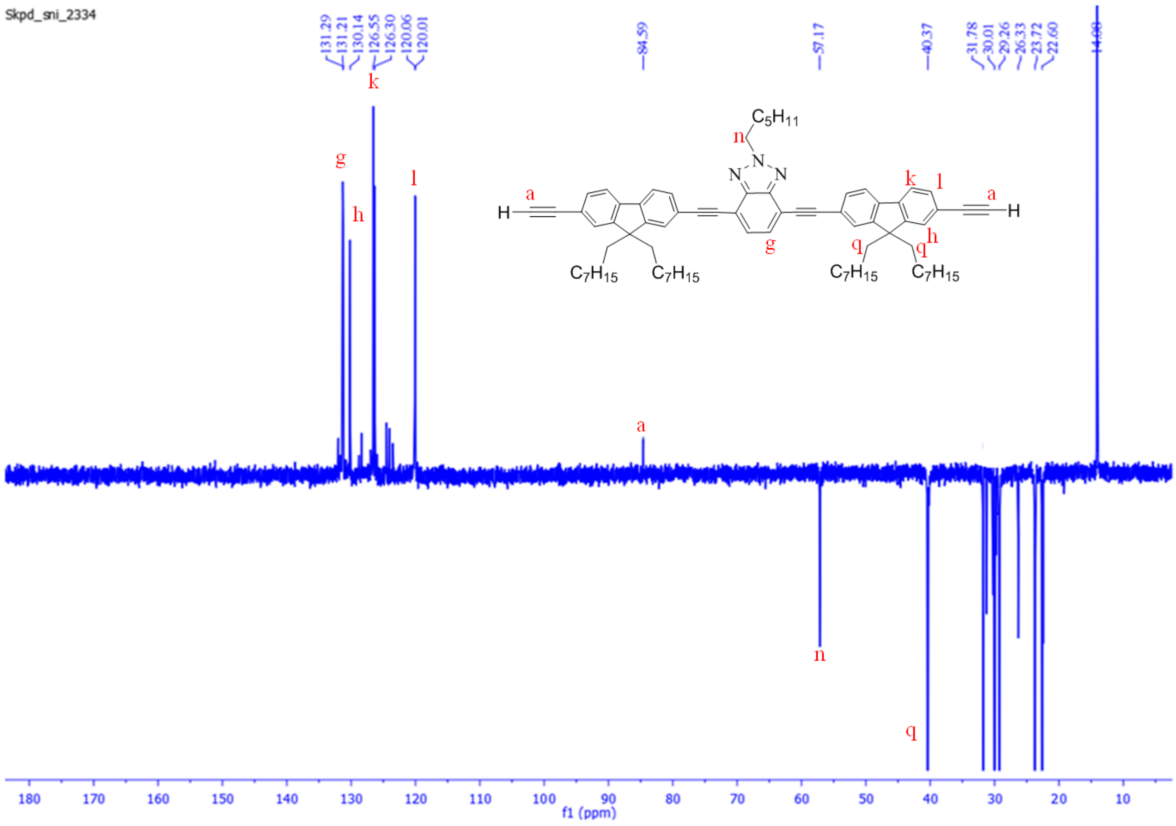


Fig. S40 DEPT-135 NMR (100 MHz, CDCl3) spectrum of **OH2**

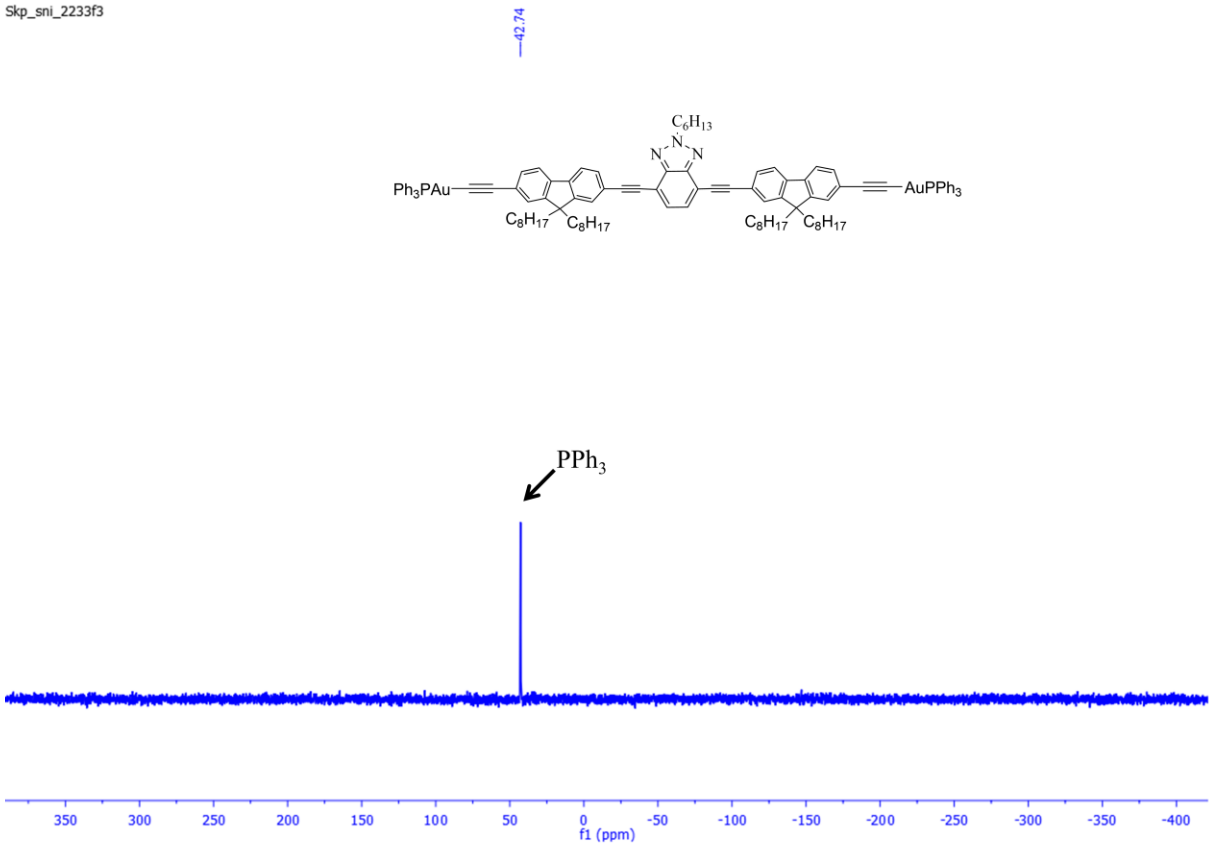


Fig. S41 $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) spectrum of **OM2**

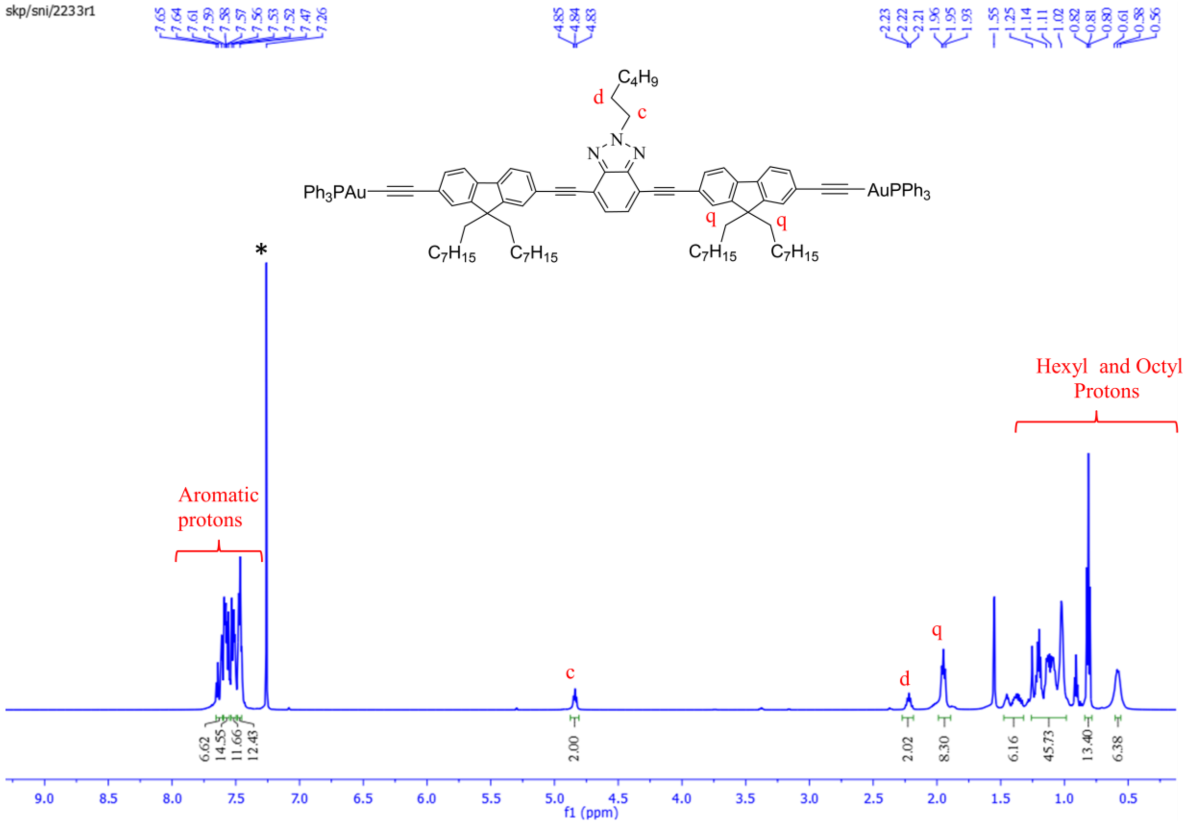


Fig. S42 ^{1}H NMR (600 MHz, CDCl$_3$) spectrum of **OM2**

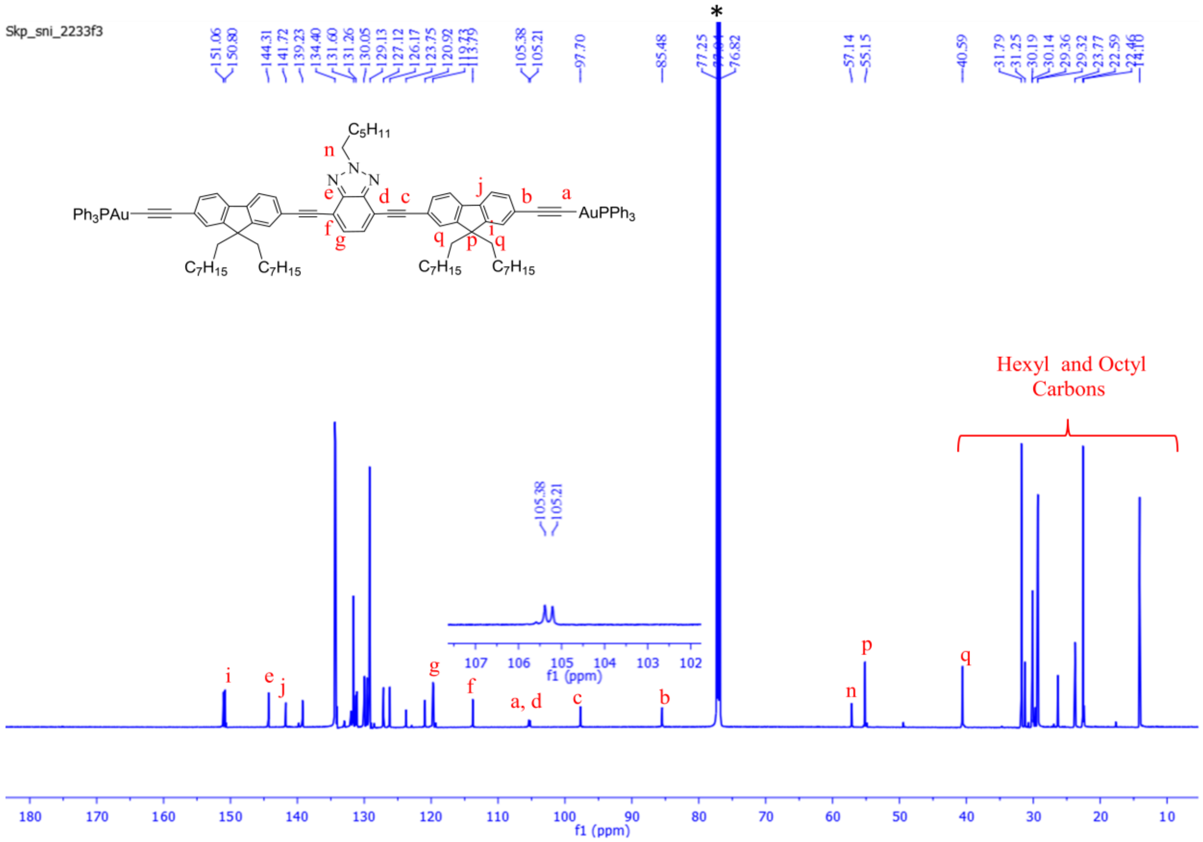


Fig. S43 ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) spectrum of **OM2**

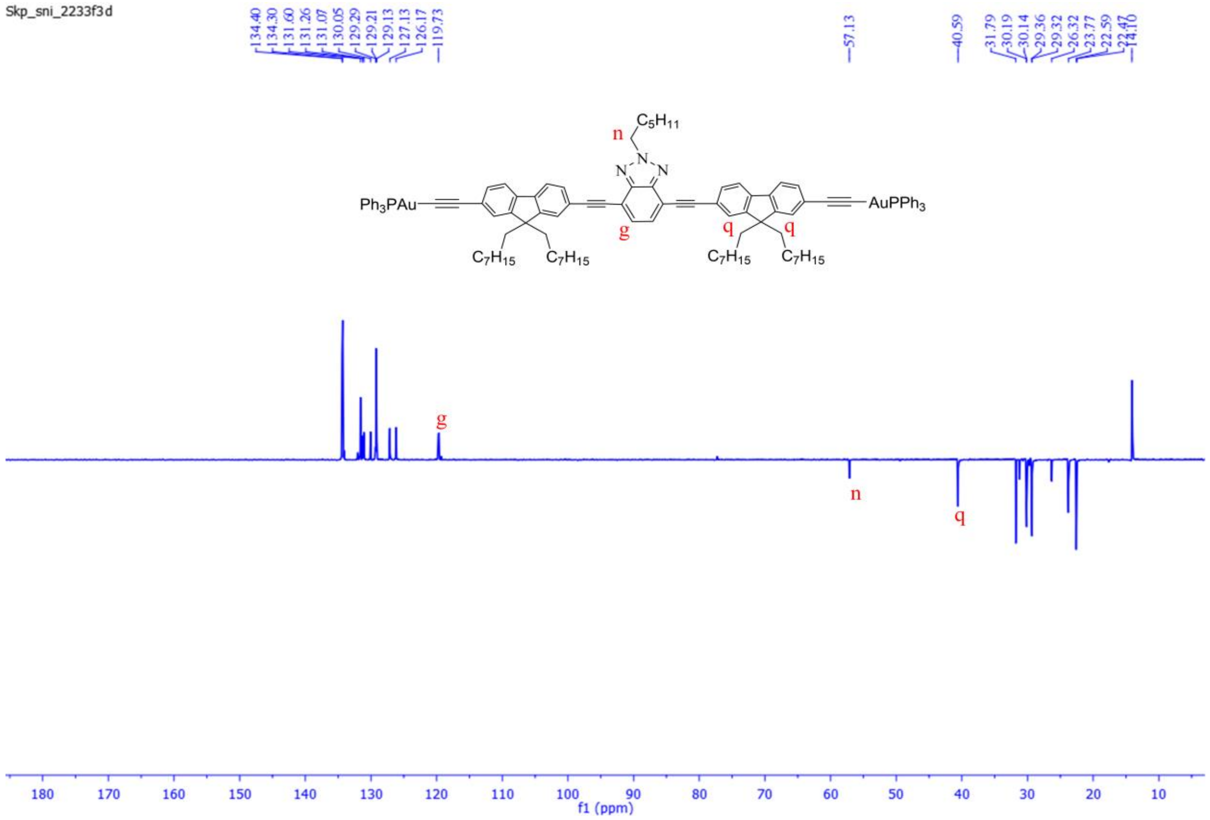


Fig. S44 DEPT-135 NMR (150 MHz, $CDCl_3$) spectrum of **OM2**

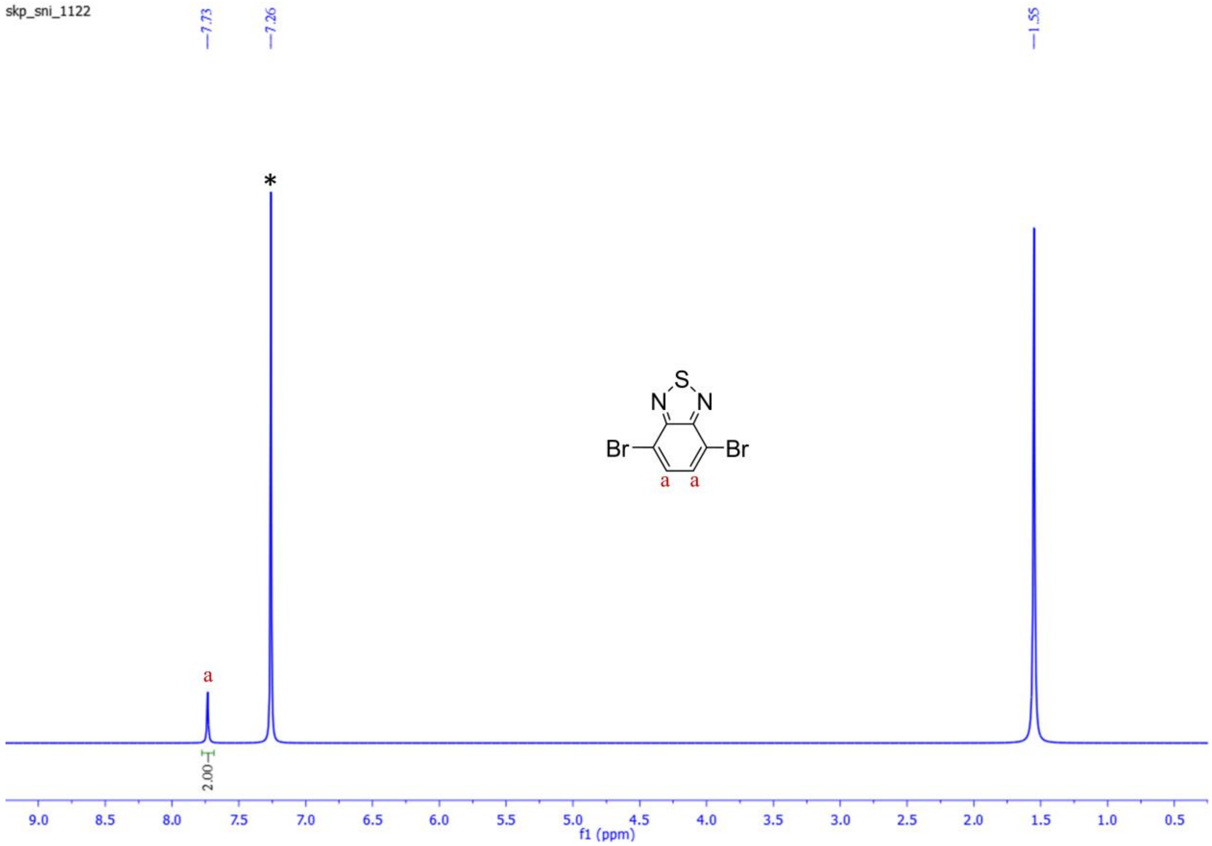


Fig. S45 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **17**

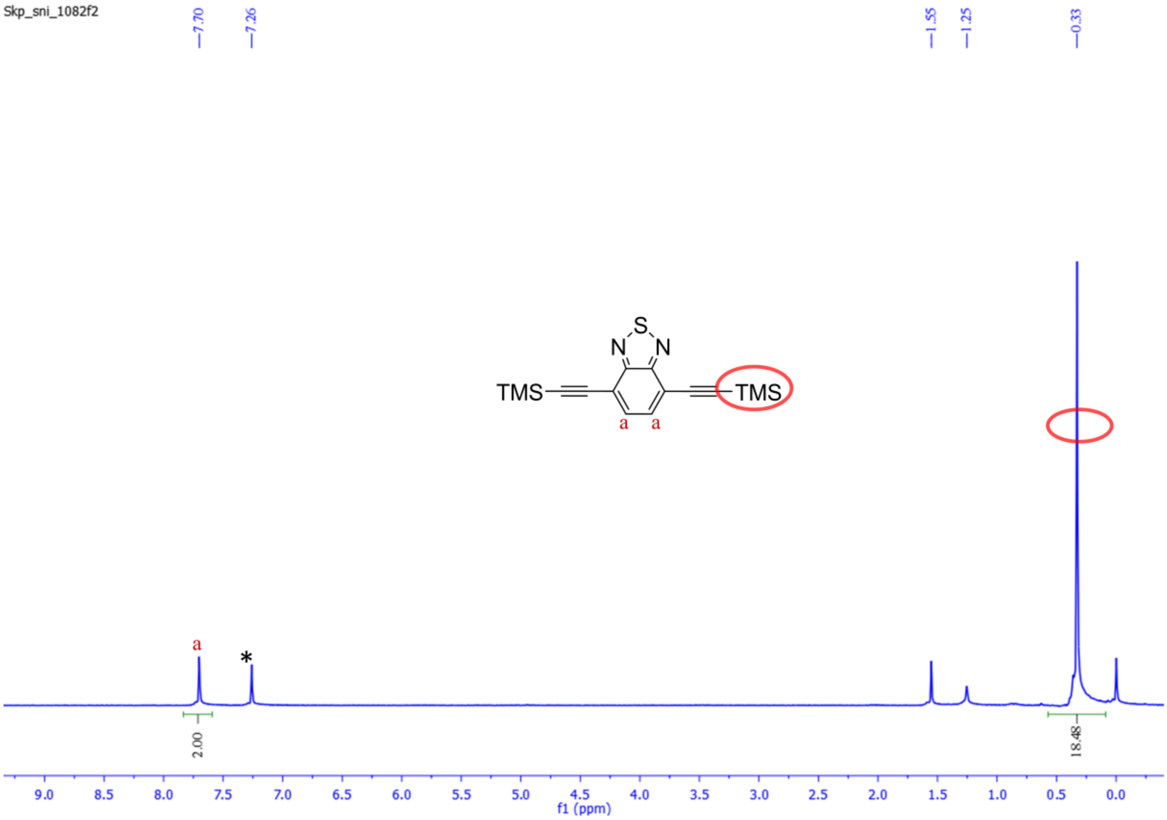


Fig. S46 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **18**

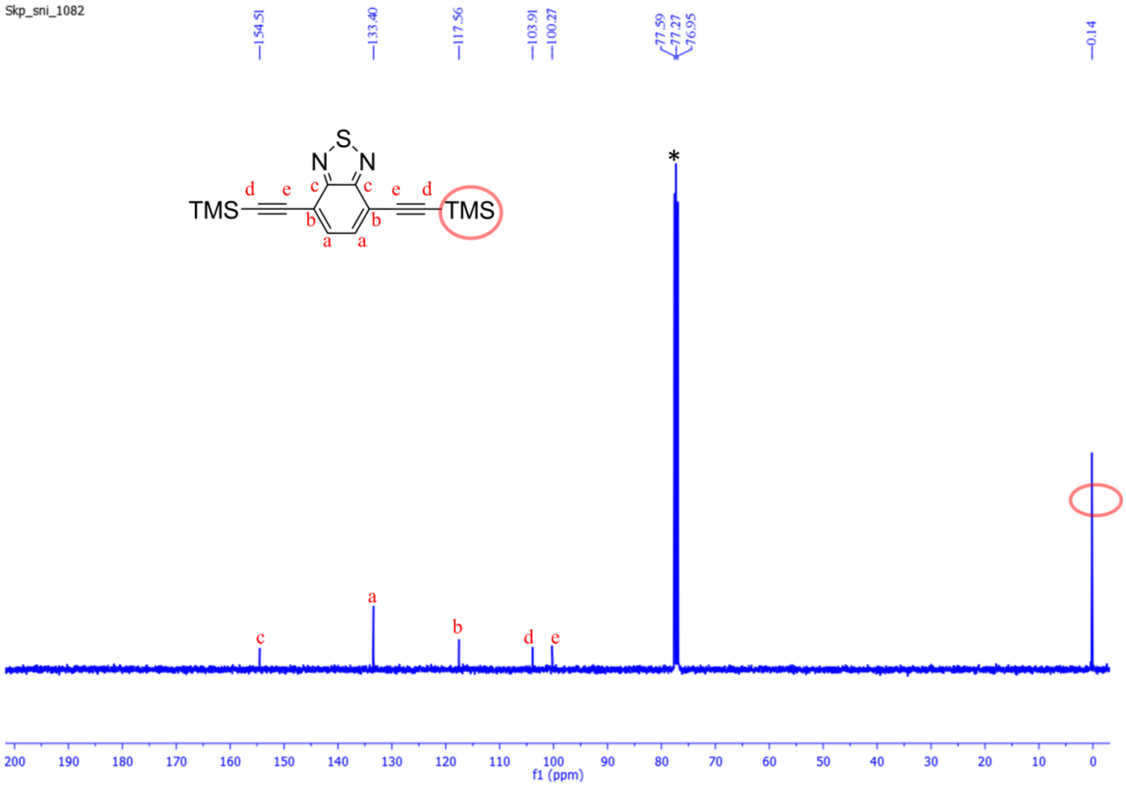


Fig. S47 $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **18**

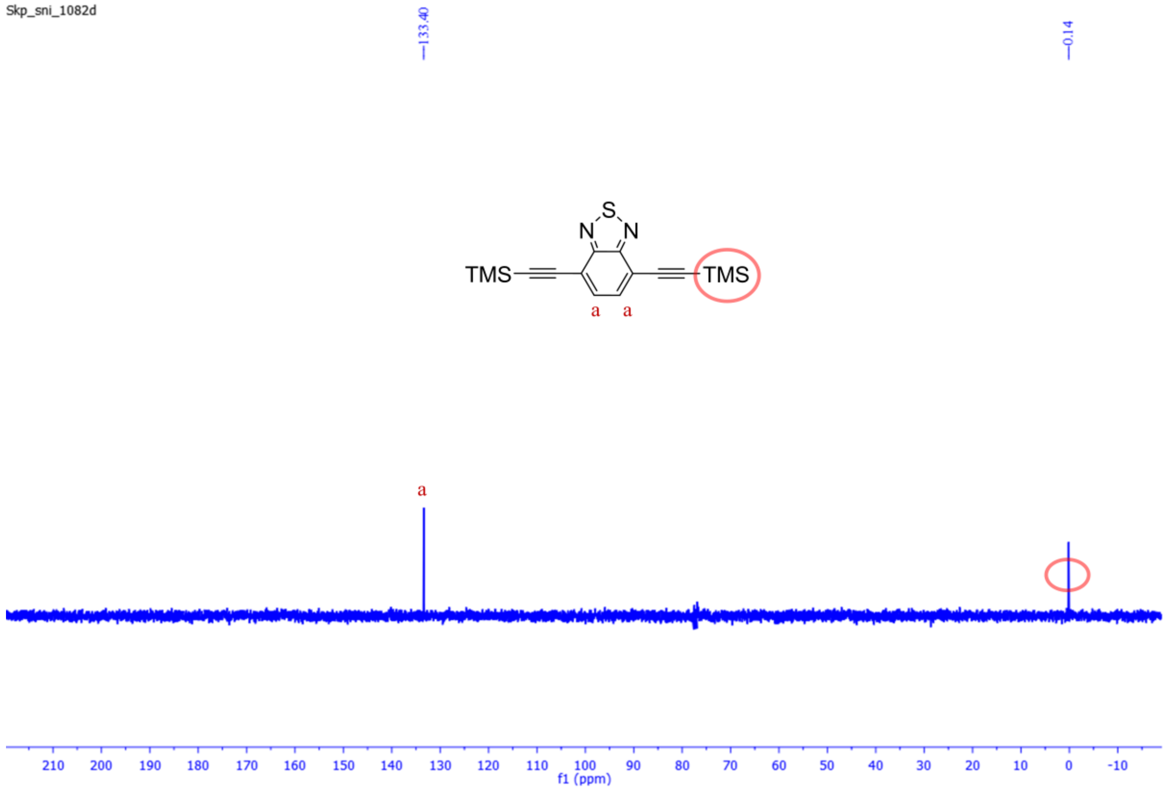


Fig. S48 DEPT-135 NMR (100 MHz, $CDCl_3$) spectrum of **18**

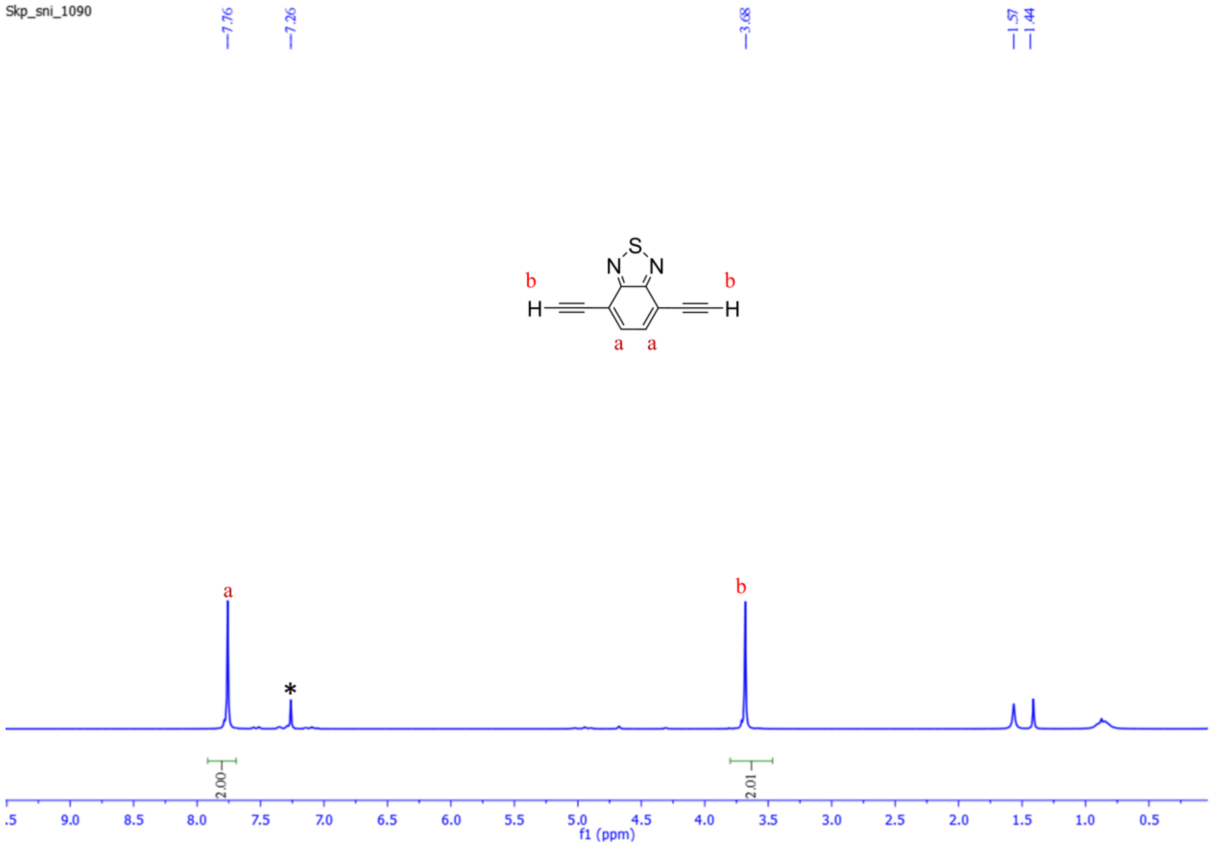


Fig. S49 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **19**

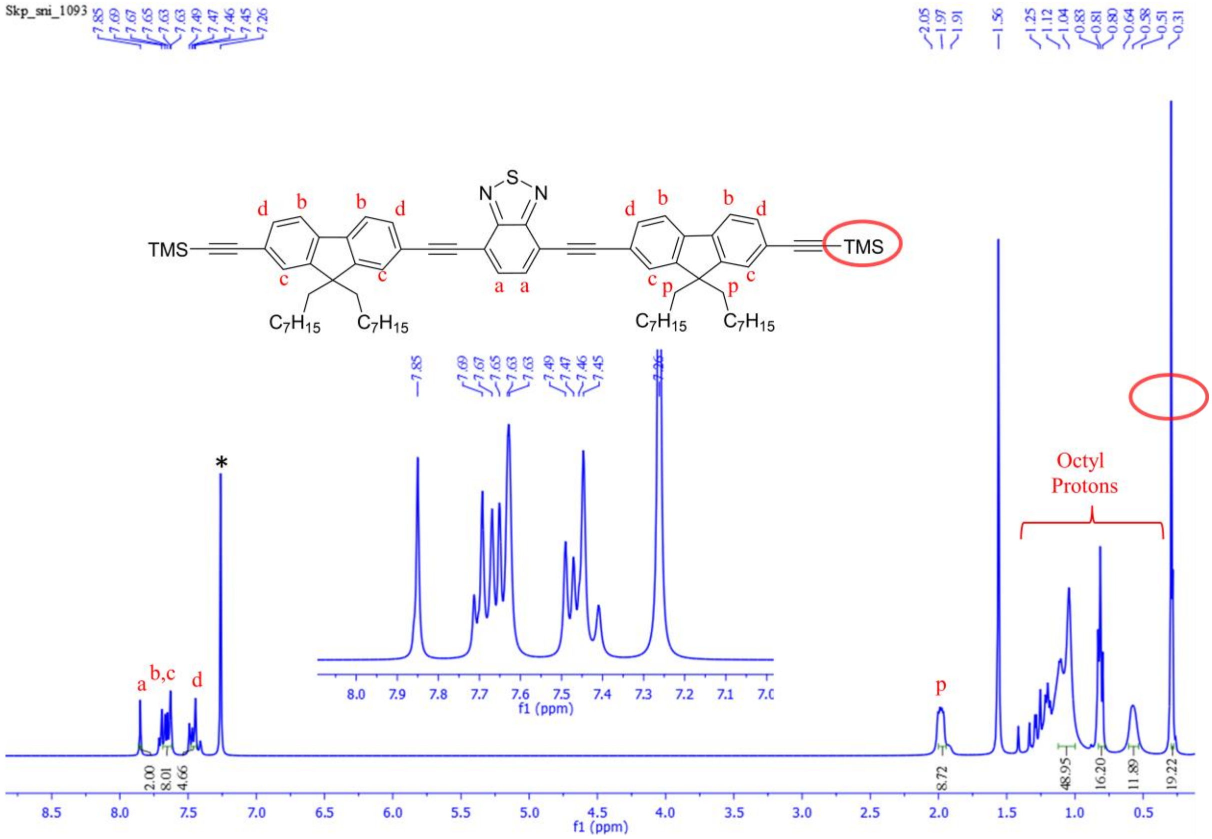


Fig. S50 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **O3**

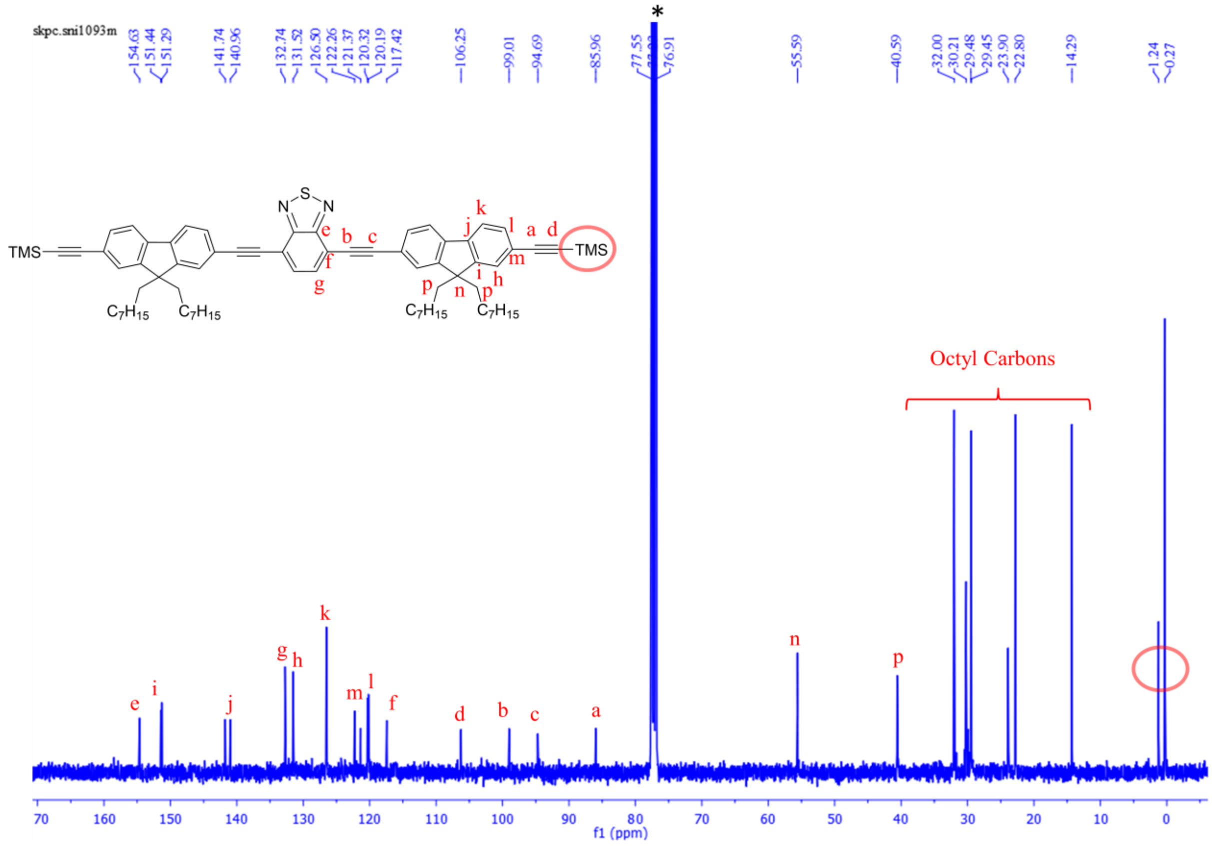


Fig. S51 $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **O3**

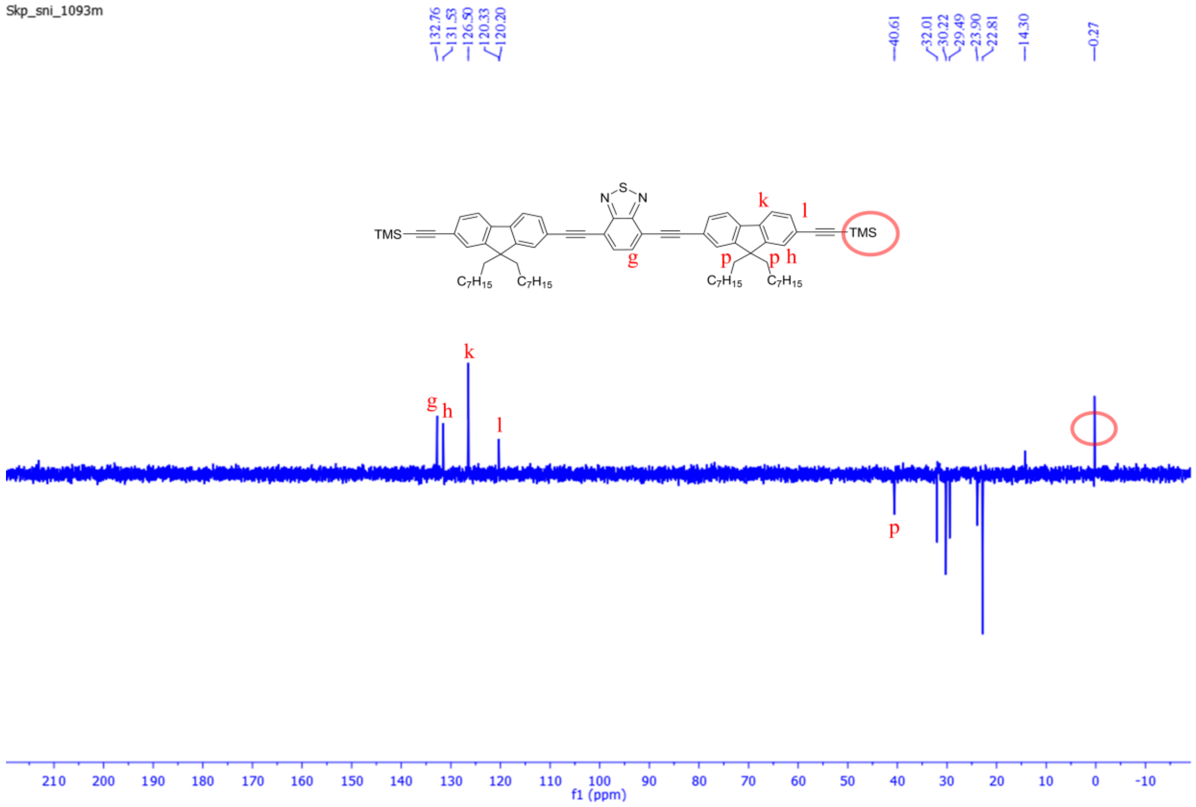


Fig. S52 DEPT-135 NMR (100 MHz, $CDCl_3$) spectrum of **O3**

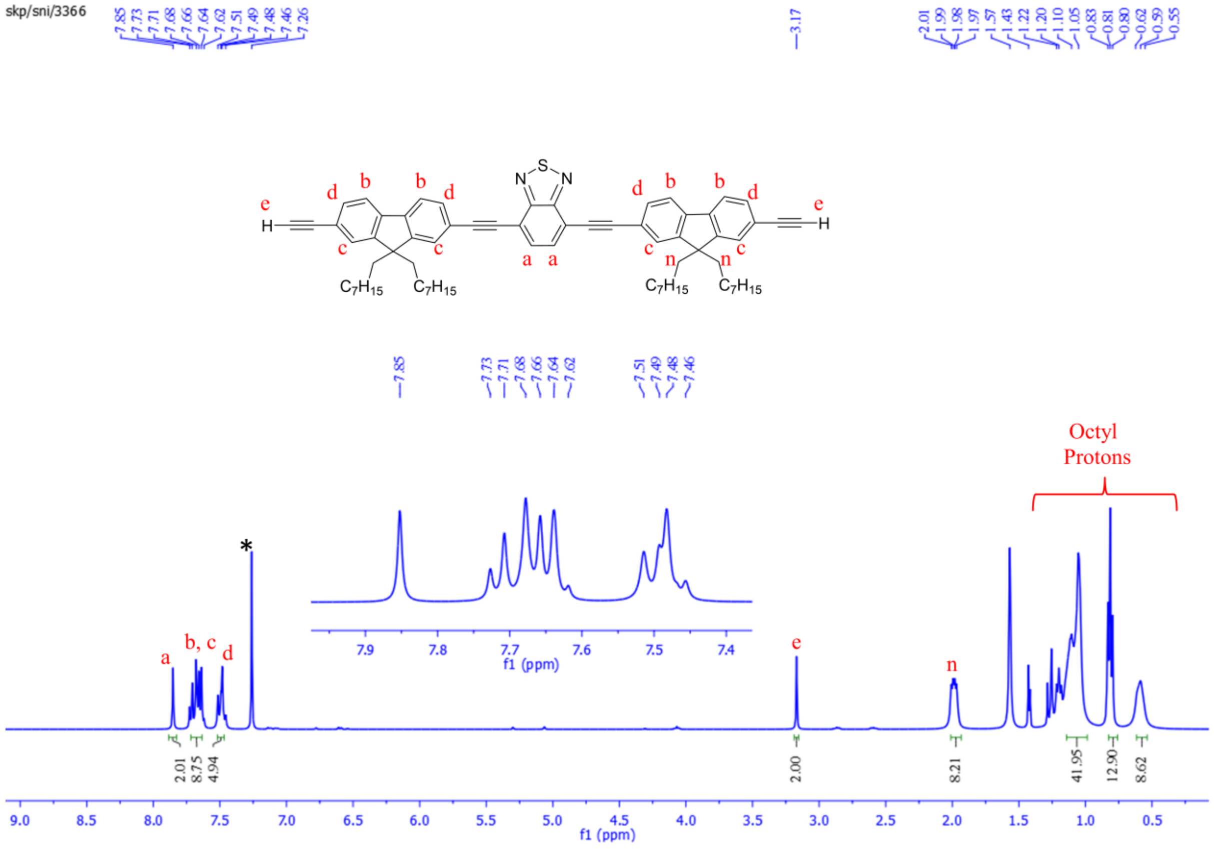


Fig. S53 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **OH3**

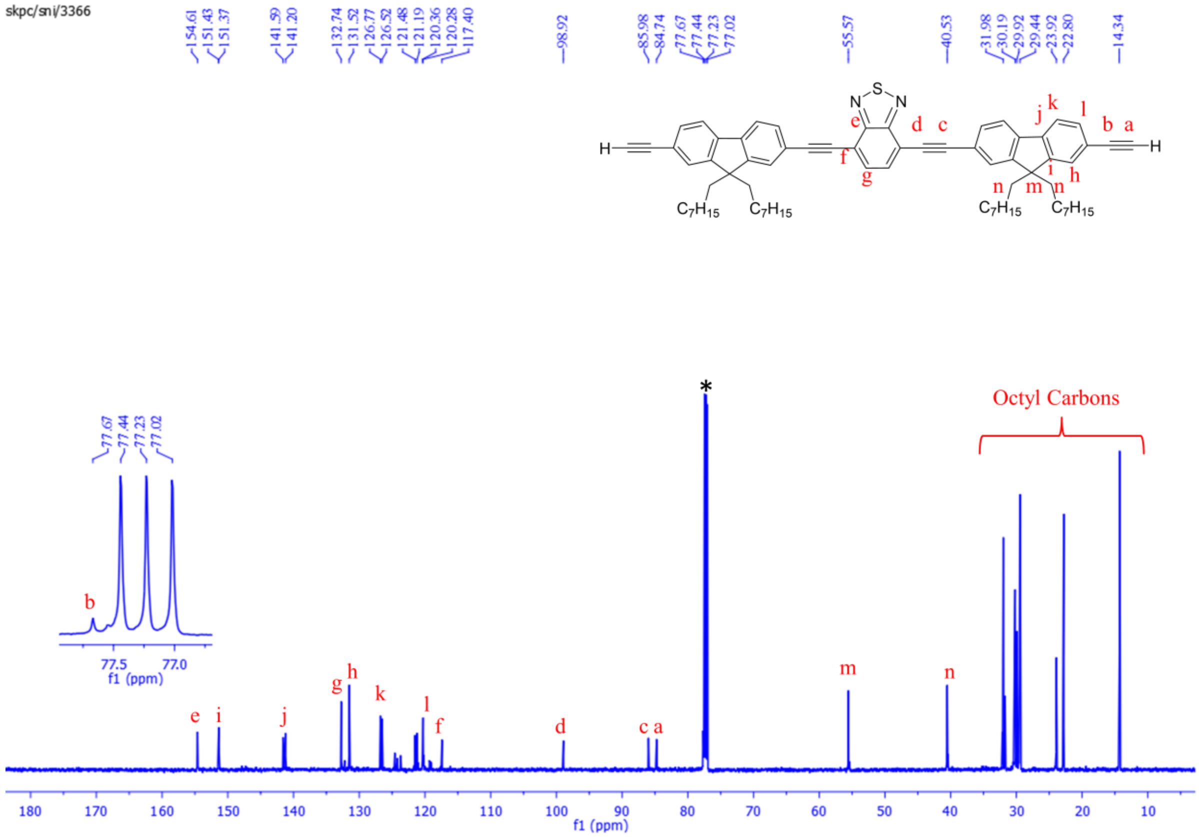


Fig. S54 $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **OH3**

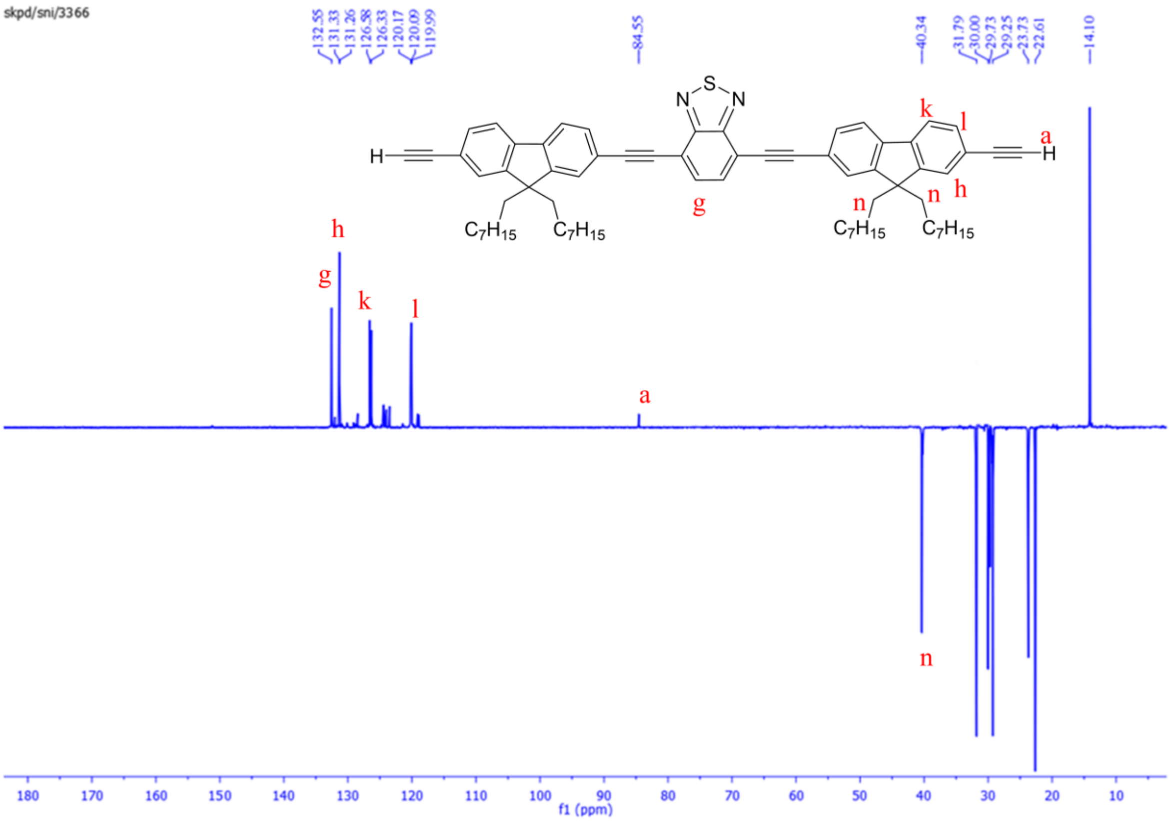


Fig. S55 DEPT-135 NMR (100 MHz, $CDCl_3$) spectrum of **OH3**

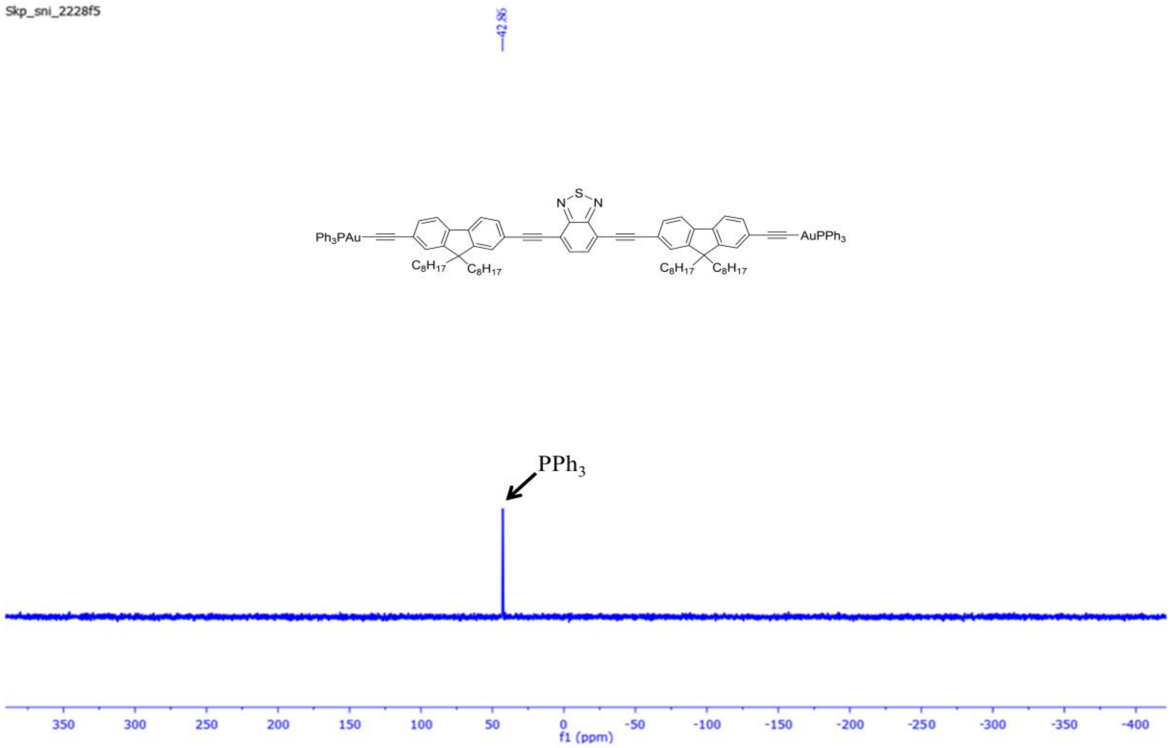


Fig. S56 $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) spectrum of **OM3**

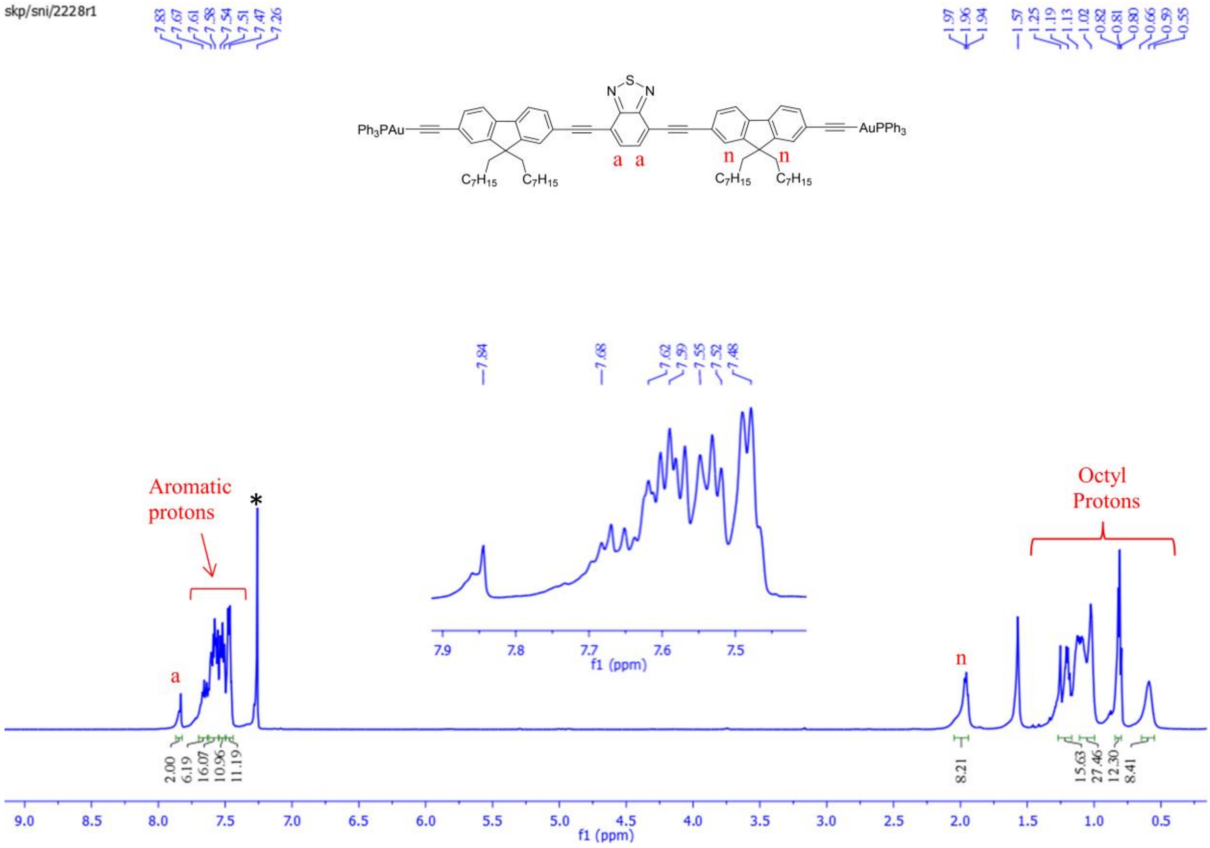


Fig. S57 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **OM3**

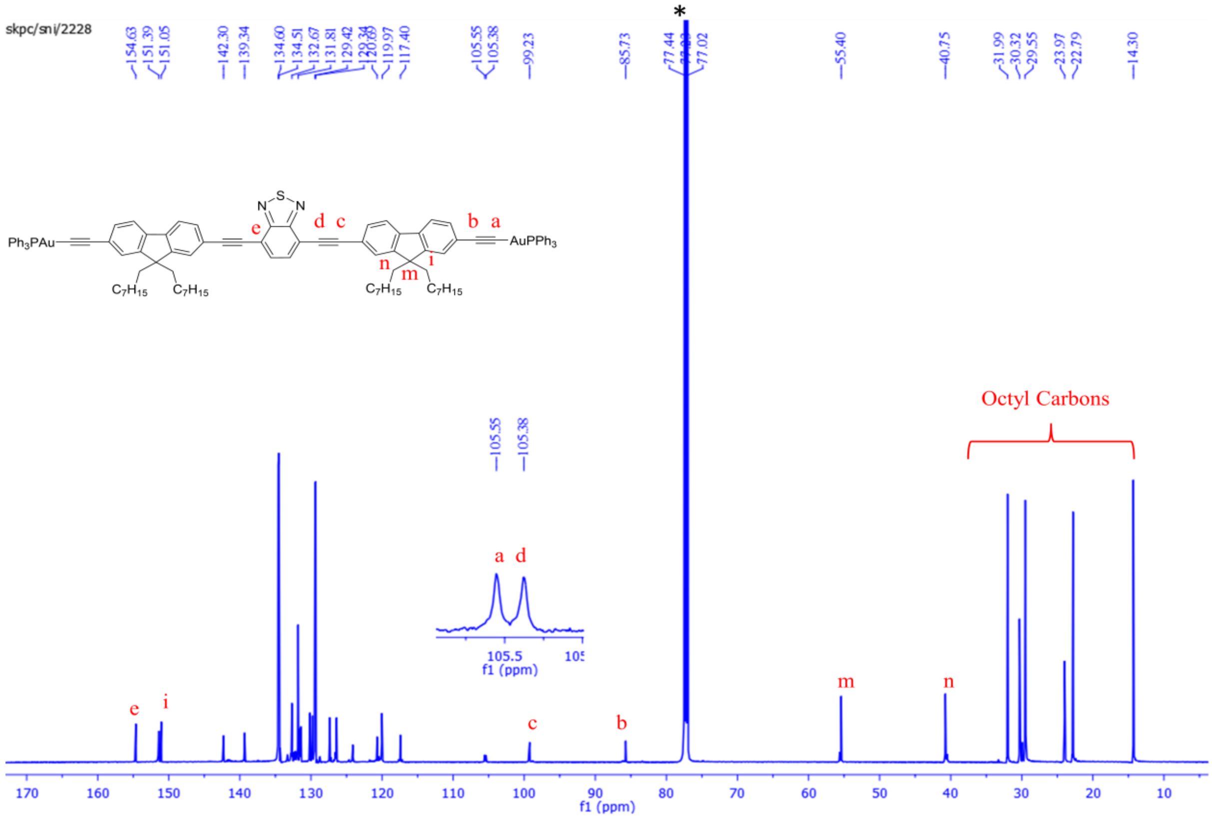


Fig. S58 $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) spectrum of **OM3**

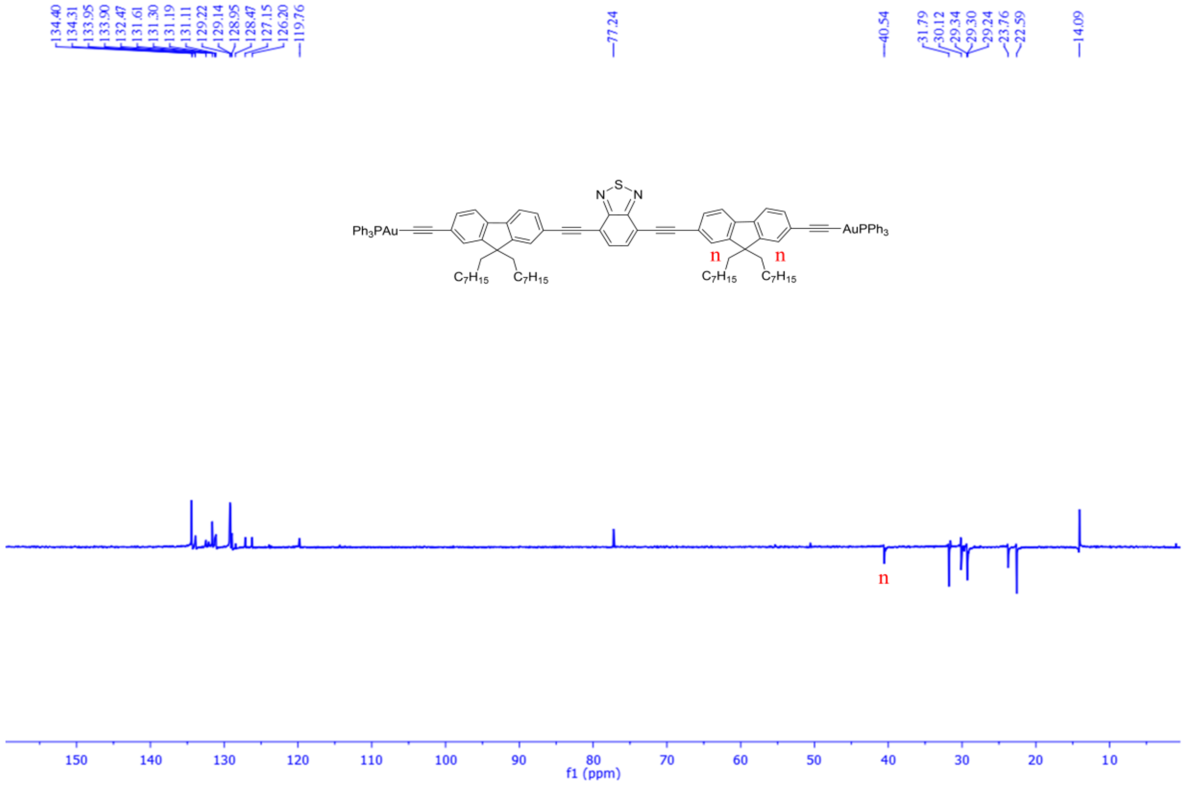


Fig. S59 DEPT-135 NMR (150 MHz, $CDCl_3$) spectrum of **OM3**

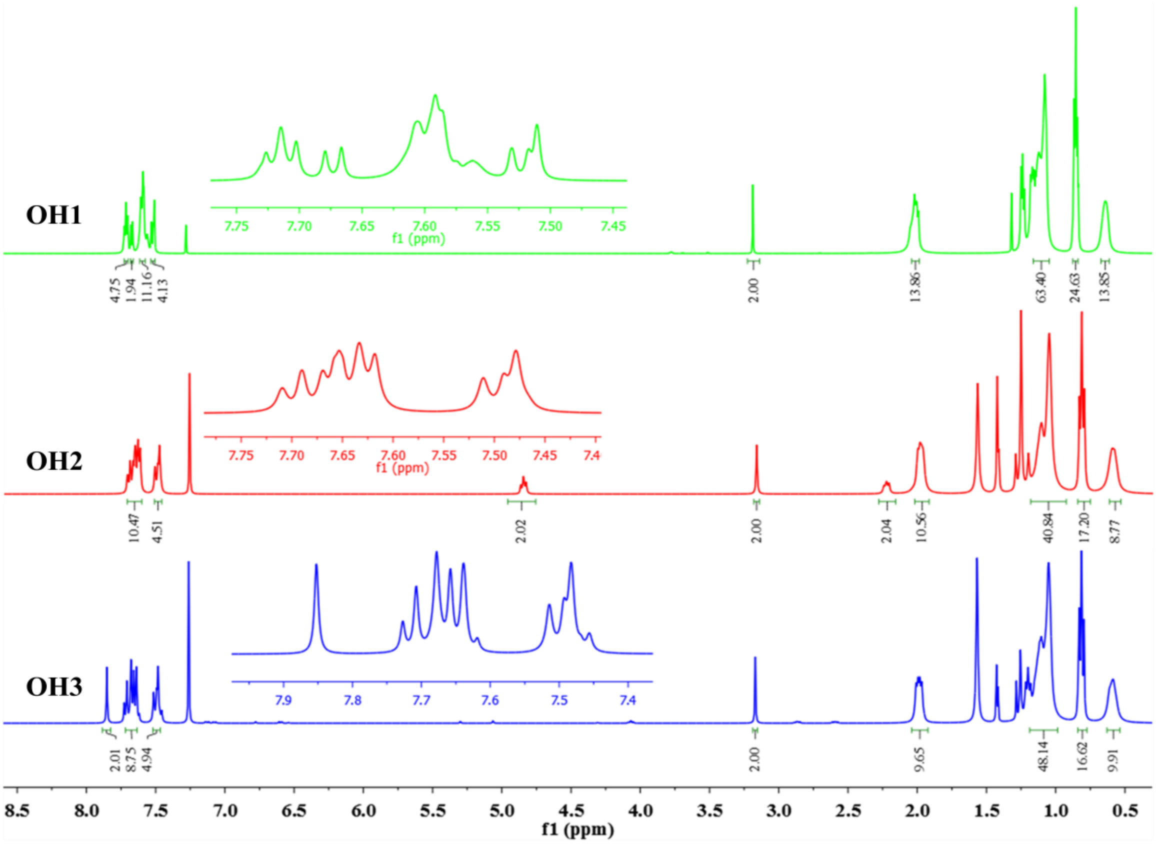


Fig. S60 ^{1}H NMR (400 MHz, $CDCl_3$) spectra of **OH1**, **OH2** and **OH3**

1c. FTIR Spectra

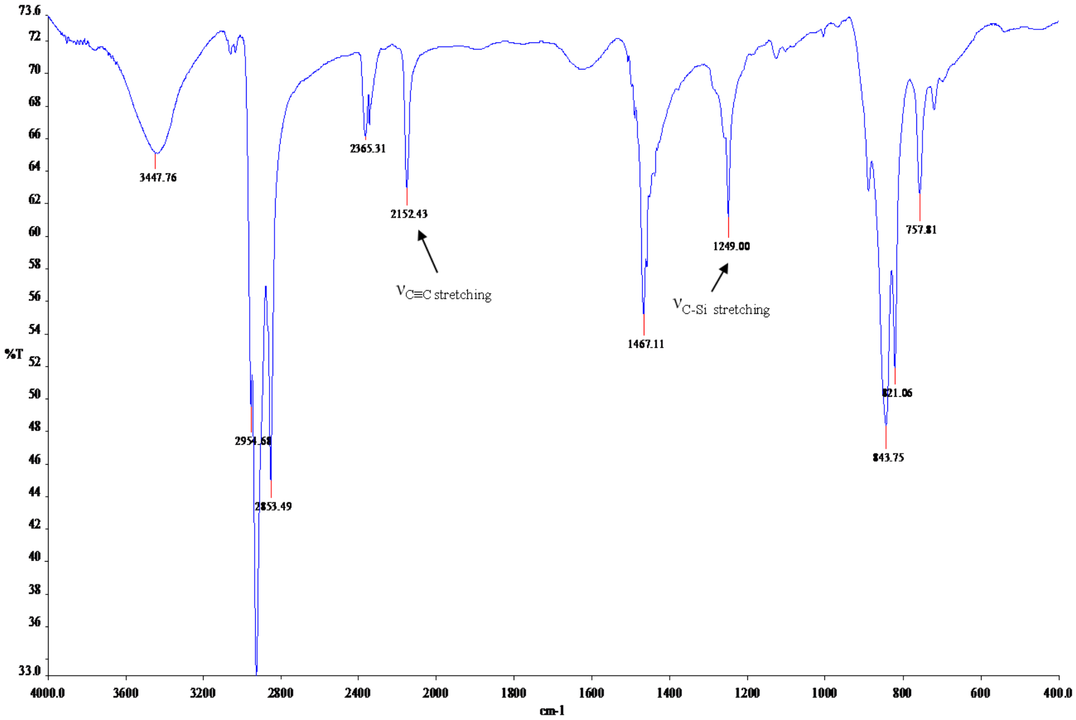


Fig. S61 FTIR spectrum of **O1**

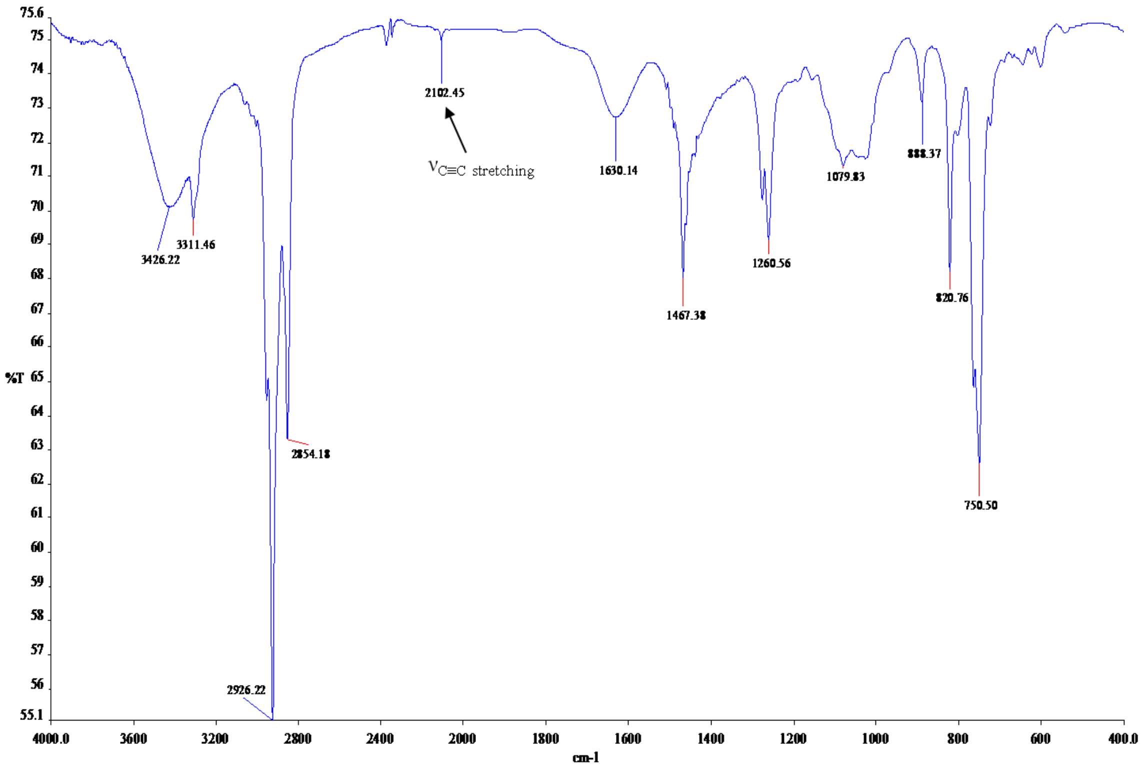


Fig. S62 FTIR spectrum of **OH1**

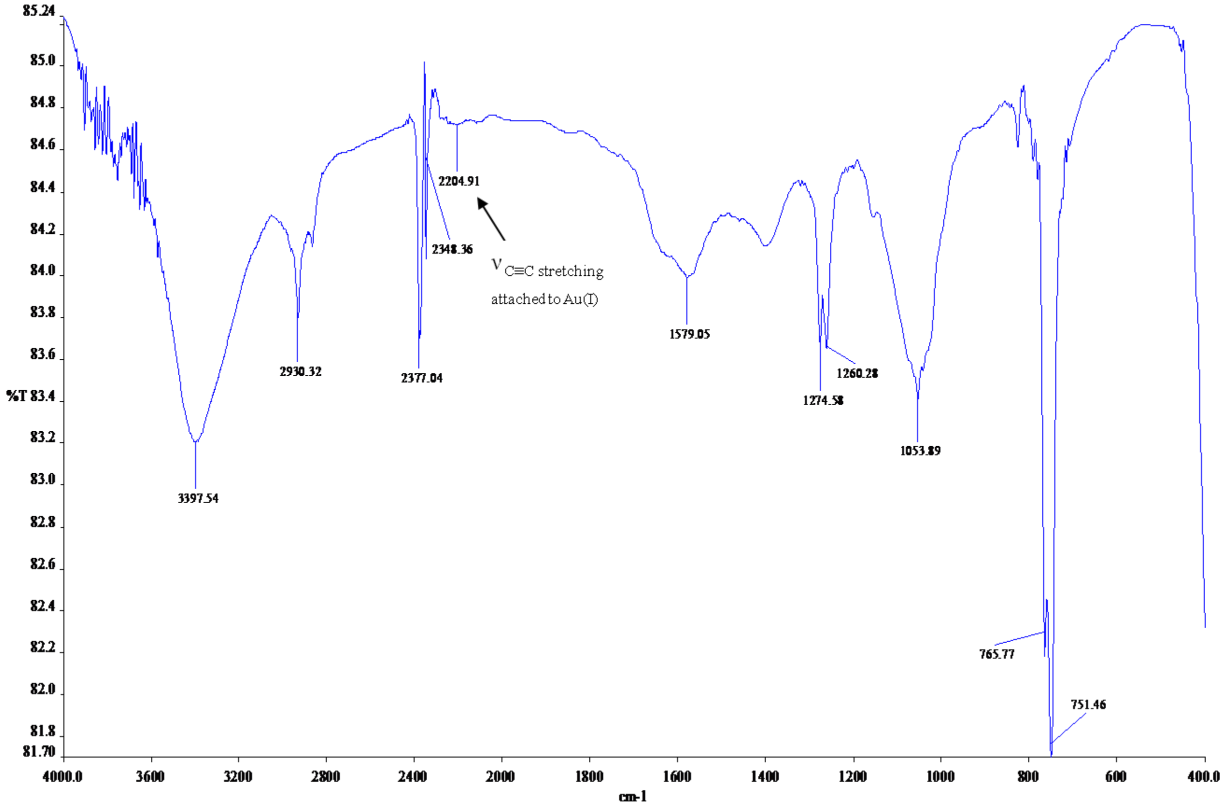


Fig. S63 FTIR spectrum of **OM1**

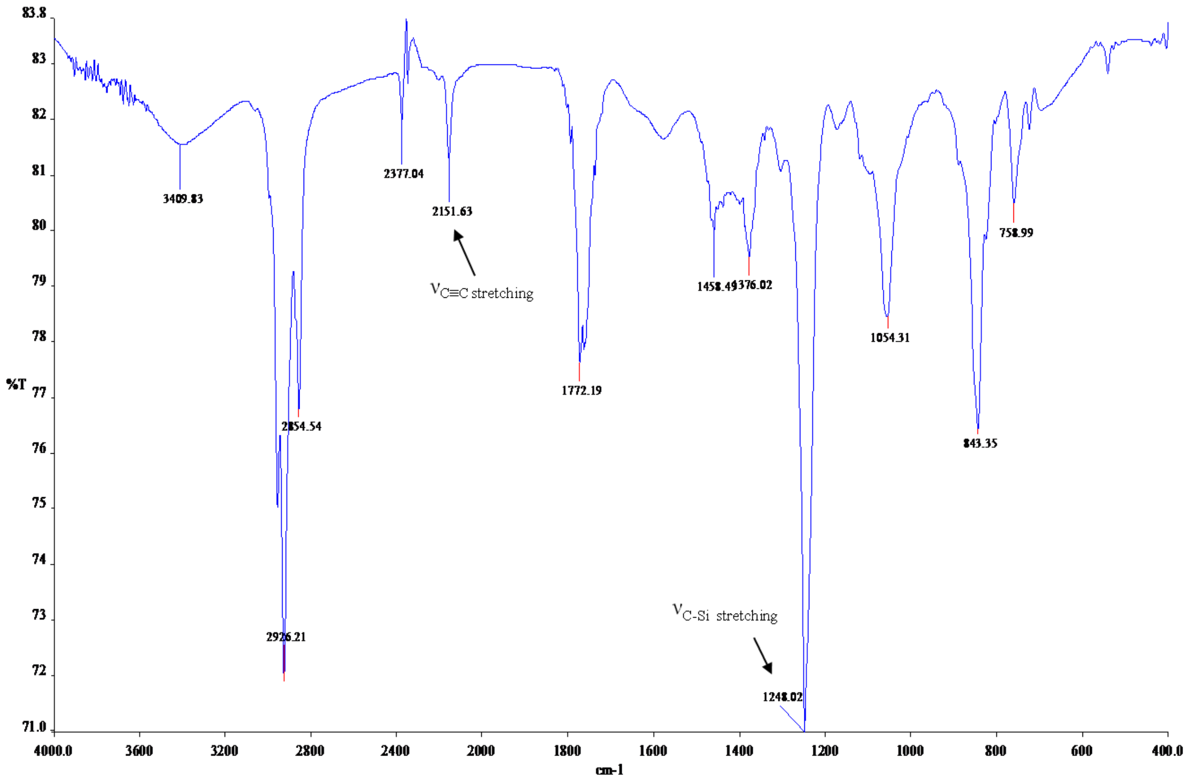


Fig. S64 FTIR spectrum of **O2**

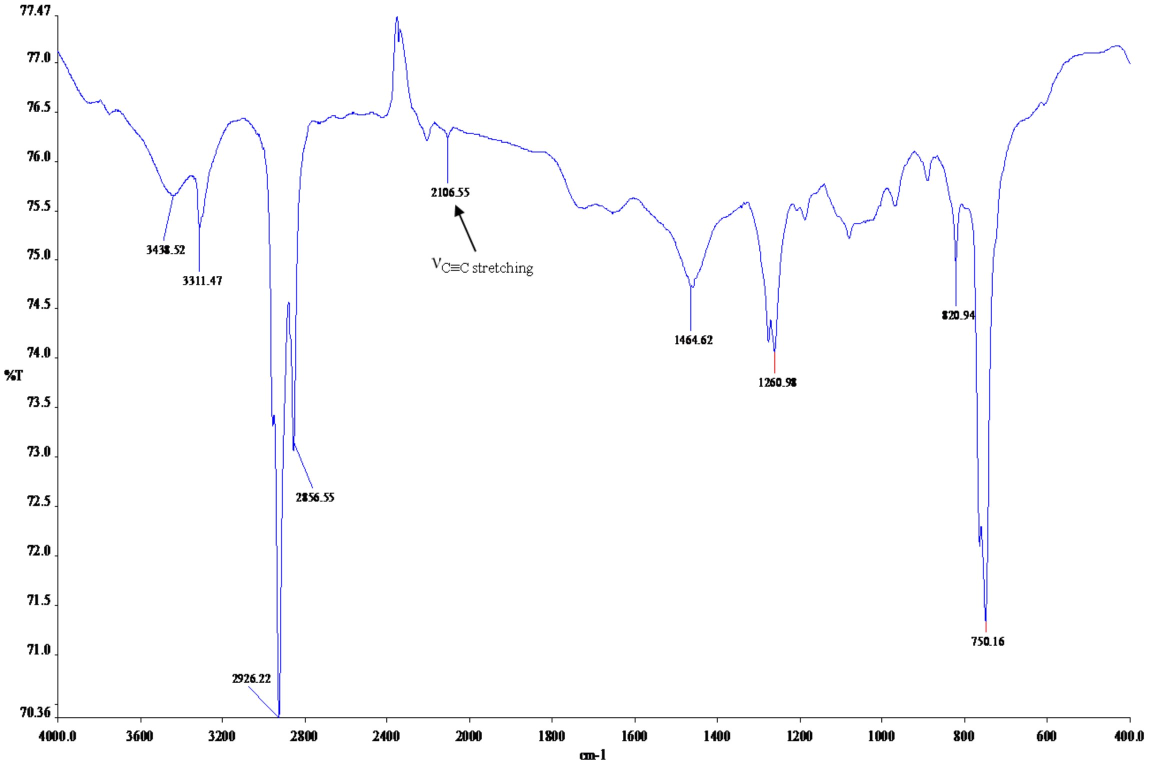


Fig. S65 FTIR spectrum of **OH2**

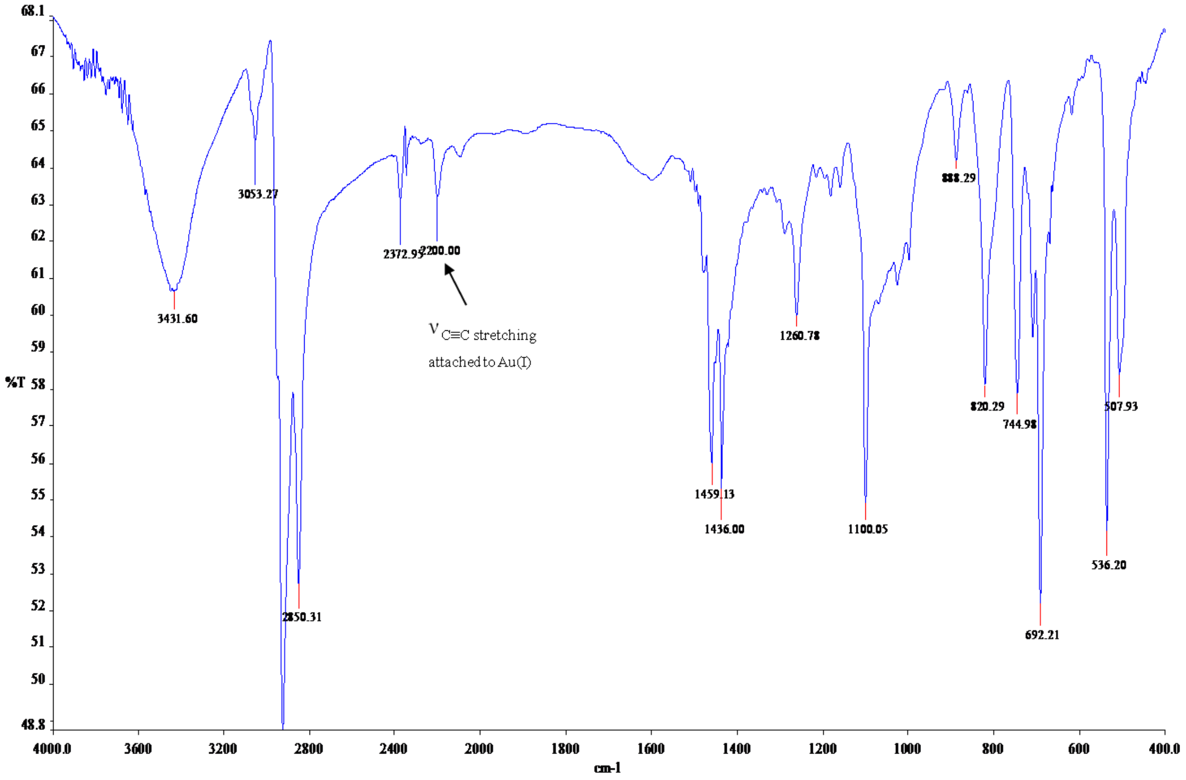


Fig. S66 FTIR spectrum of **OM2**

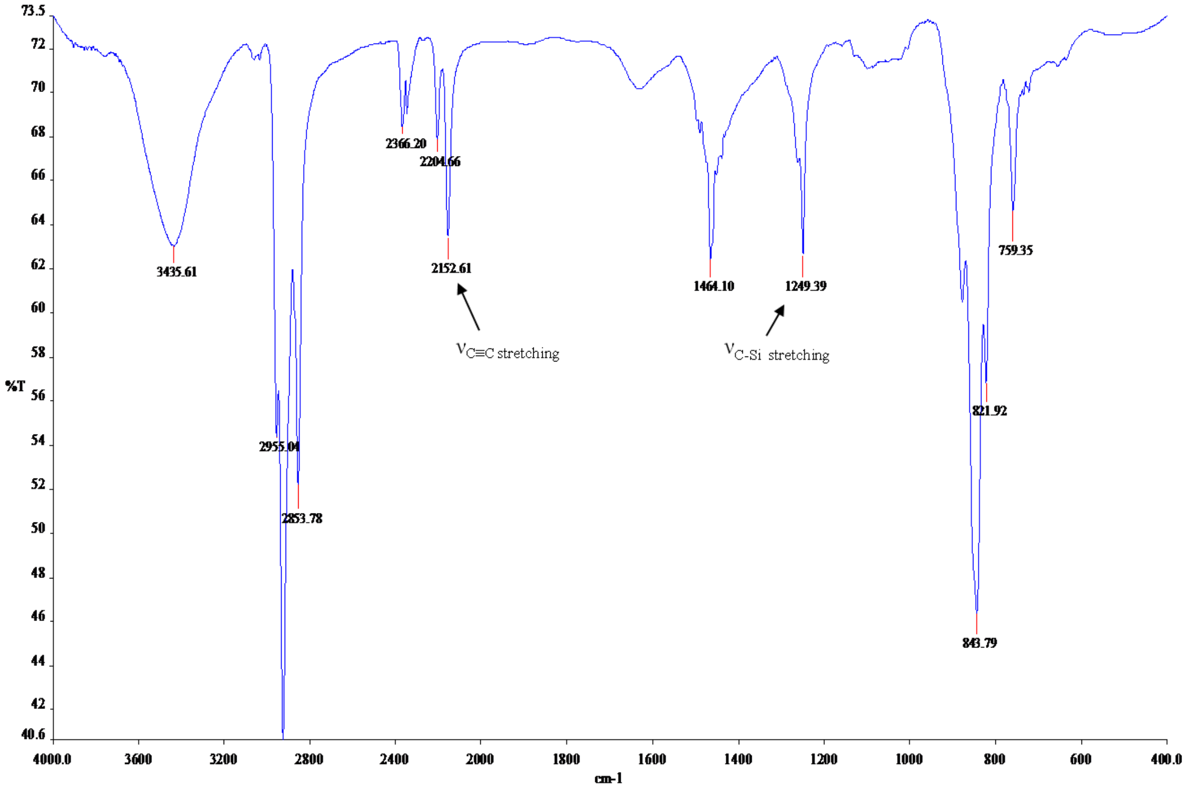


Fig. S67 FTIR spectrum of **O3**

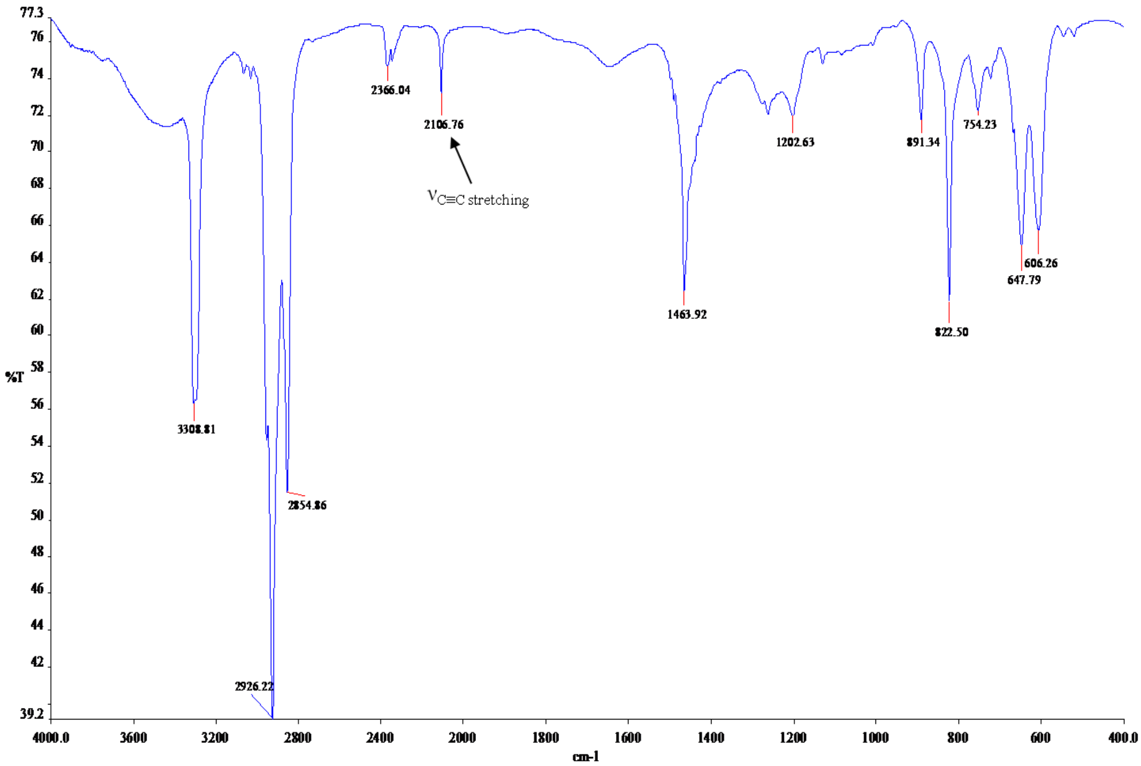


Fig. S68 FTIR spectrum of **OH3**

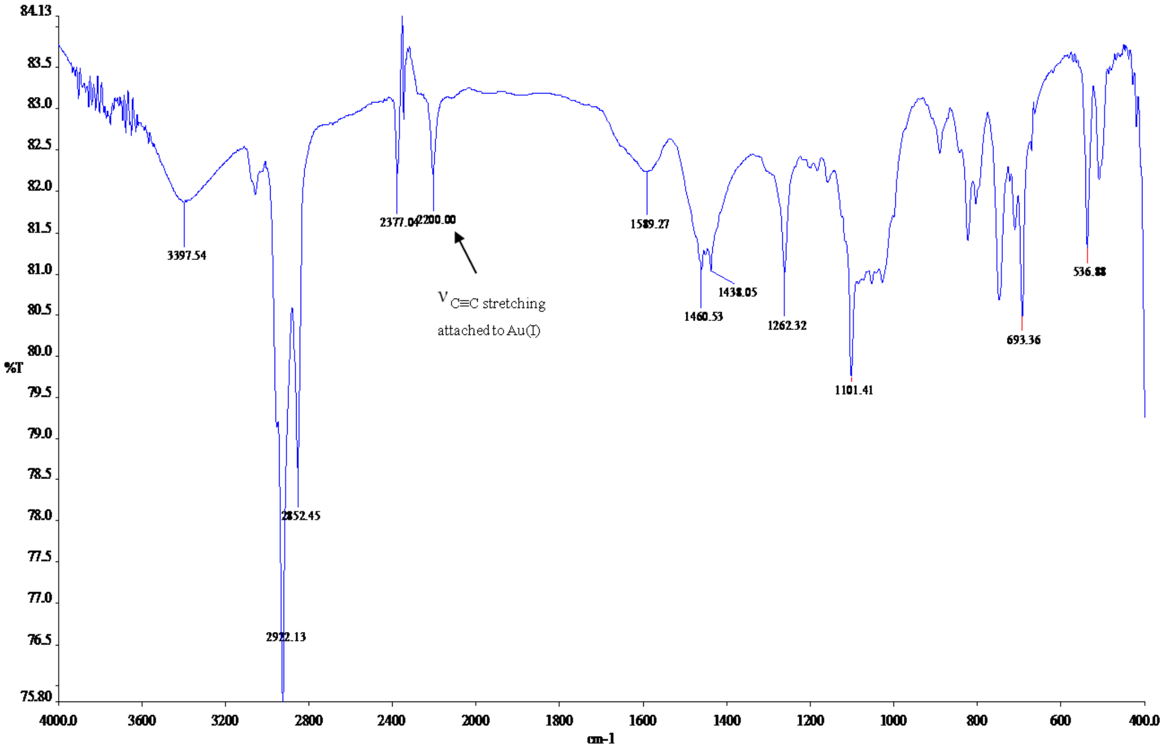


Fig. S69 FTIR spectrum of **OM3**

1d. MALDI-TOF MS spectrometry

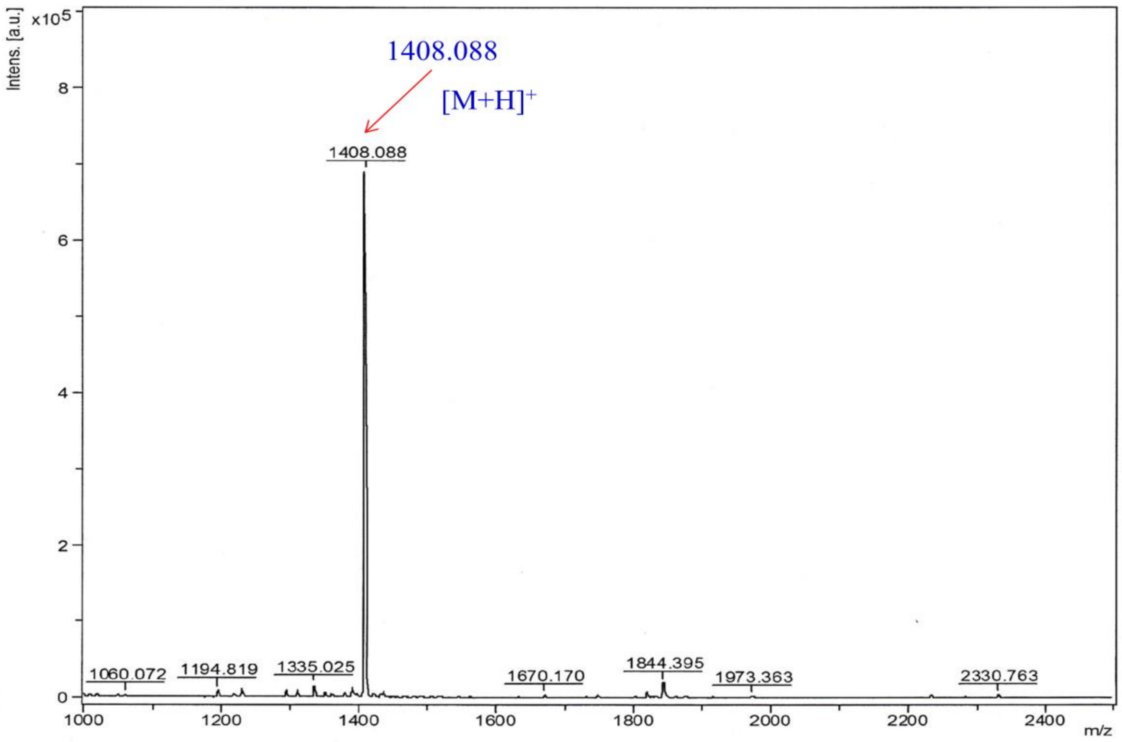


Fig. S70 MALDI-TOF mass spectrometry of **O1**

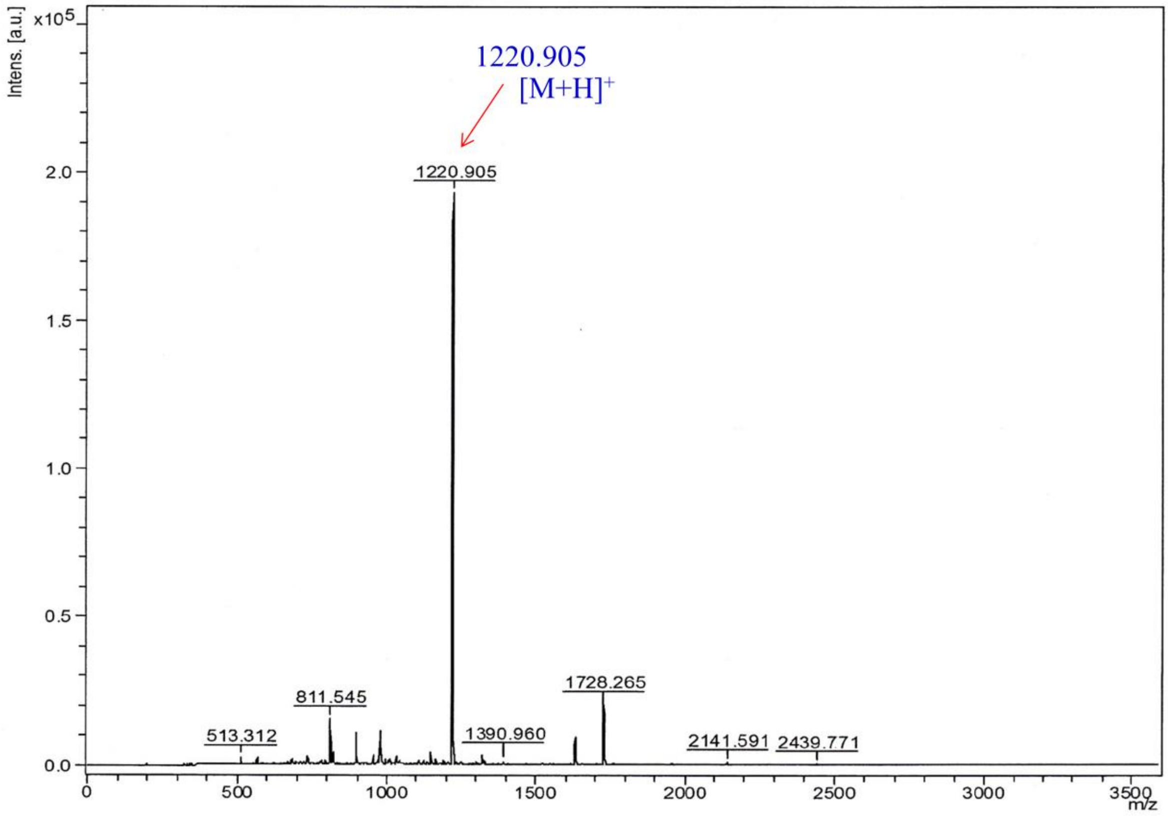


Fig. S71 MALDI-TOF mass spectrometry of **O2**

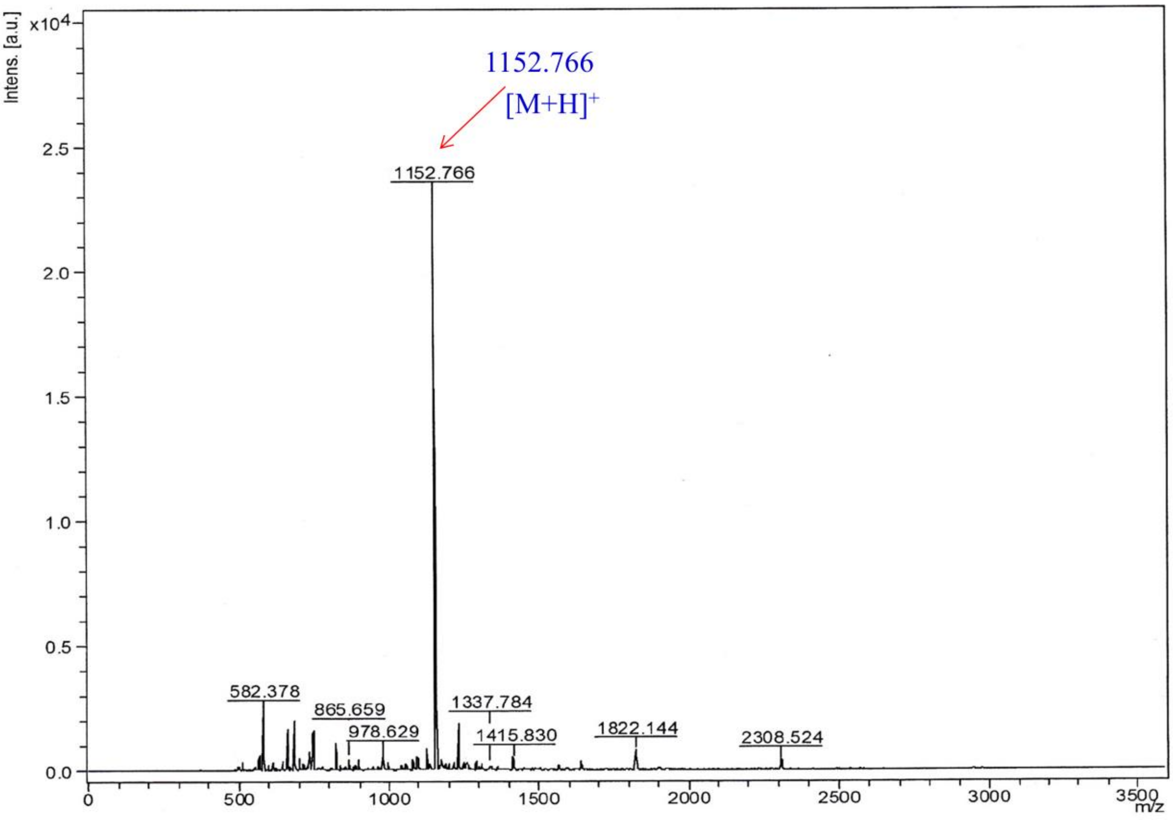


Fig. S72 MALDI-TOF mass spectrometry of **O3**

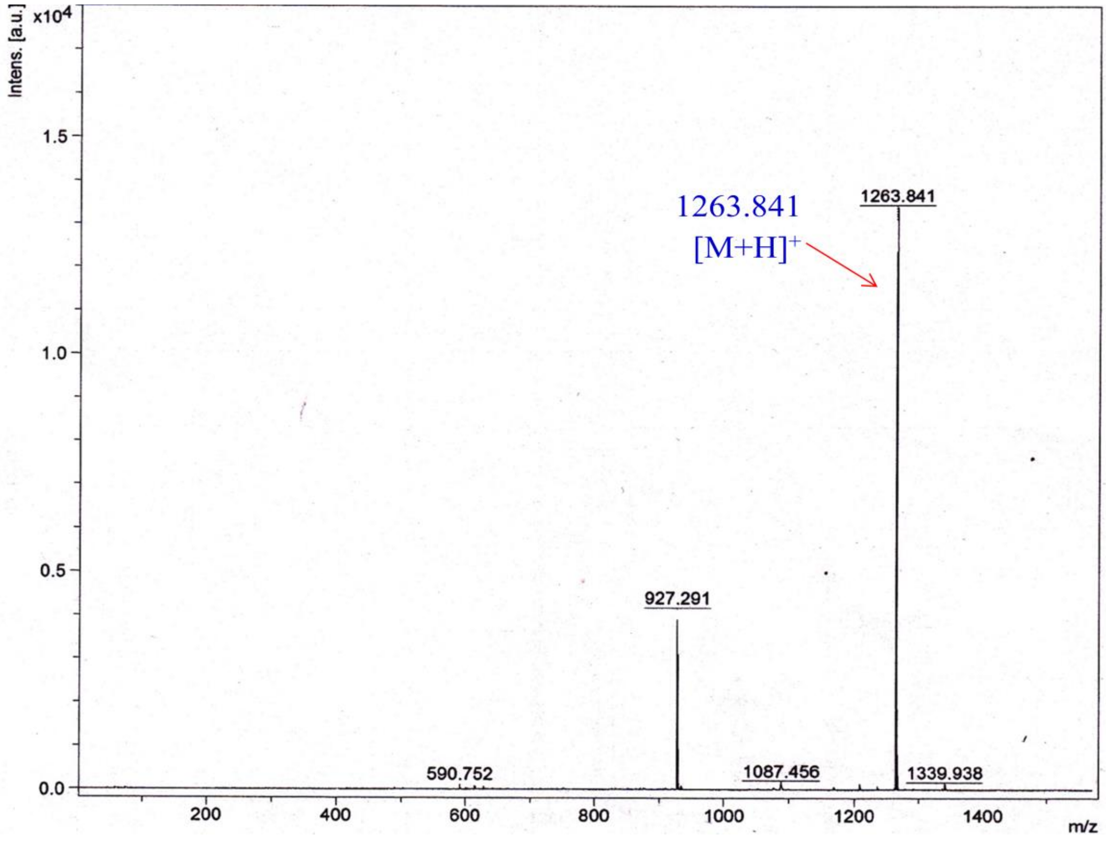


Fig. S73 MALDI-TOF mass spectrometry of **OH1**

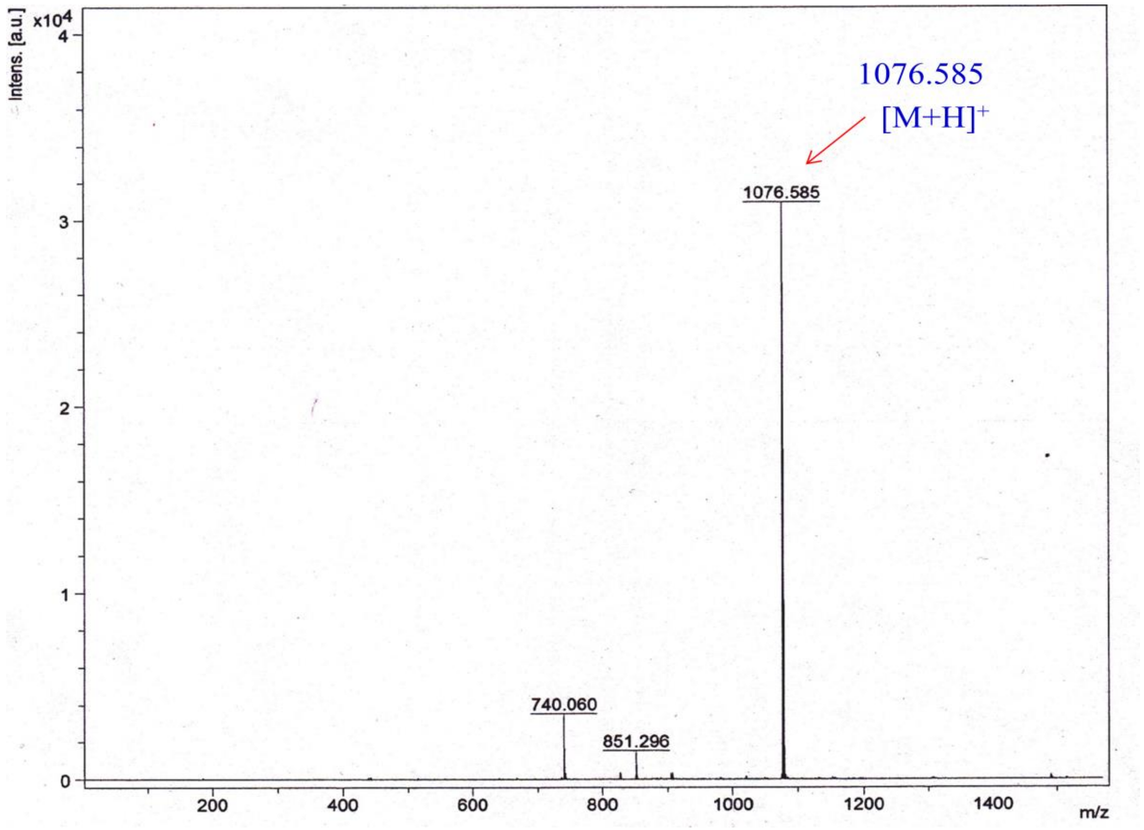


Fig. S74 MALDI-TOF mass spectrometry of **OH2**

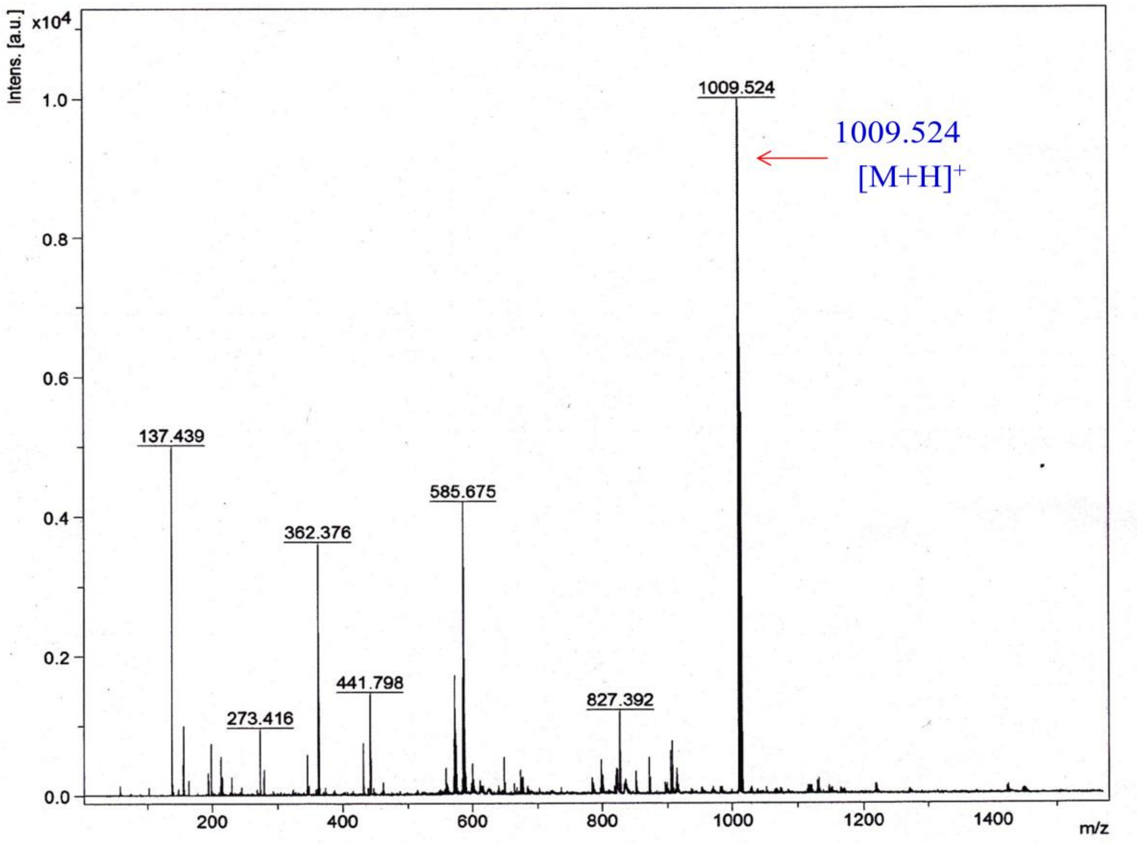


Fig. S75 MALDI-TOF mass spectrometry of **OH3**

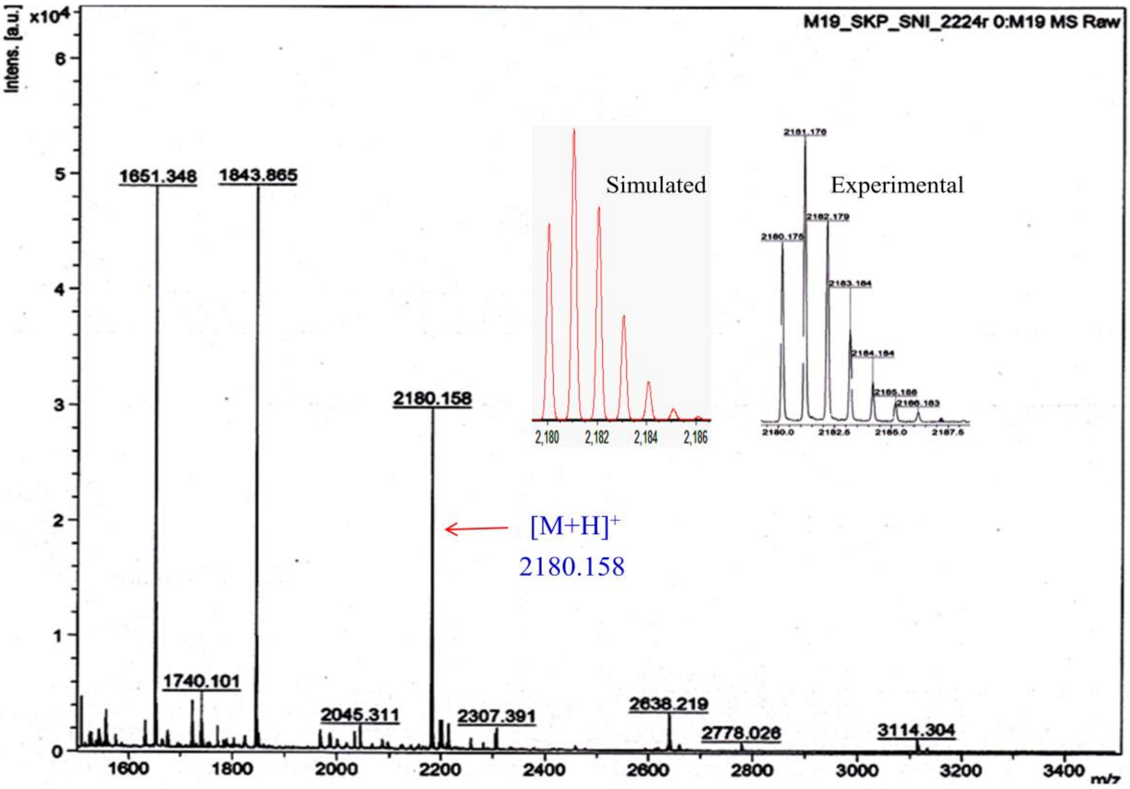


Fig. S76 MALDI-TOF mass spectrometry of **OM1**

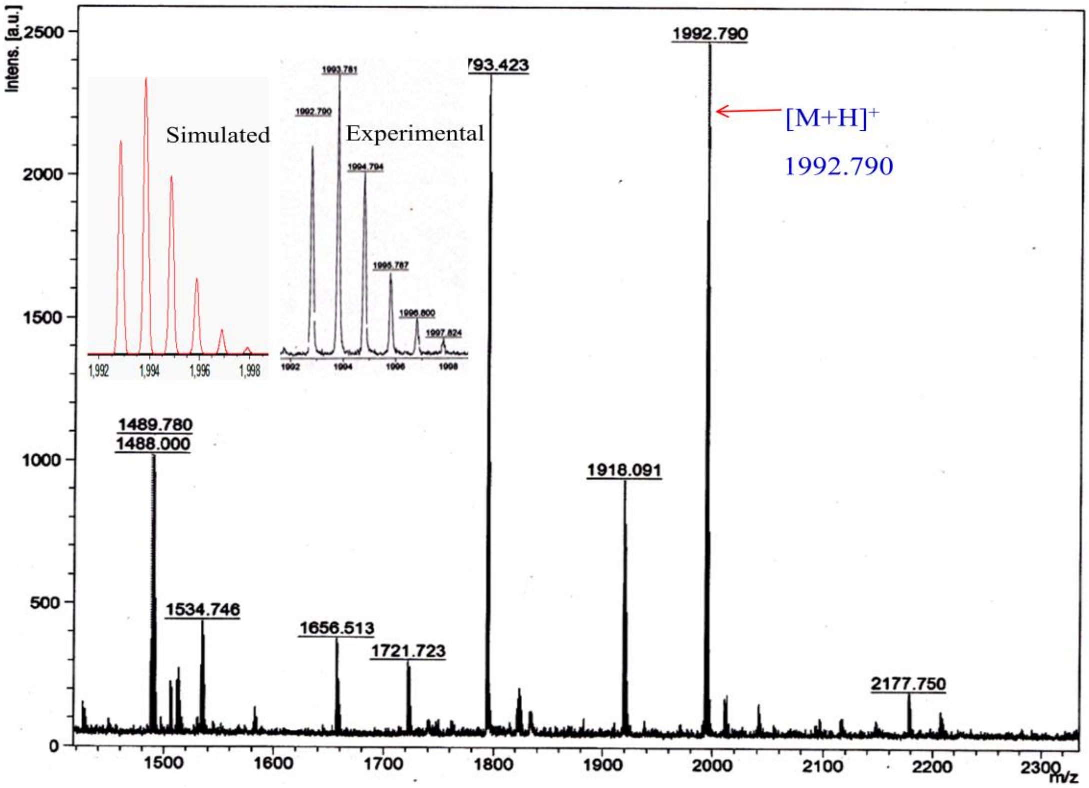


Fig. S77 MALDI-TOF mass spectrometry of **OM2**

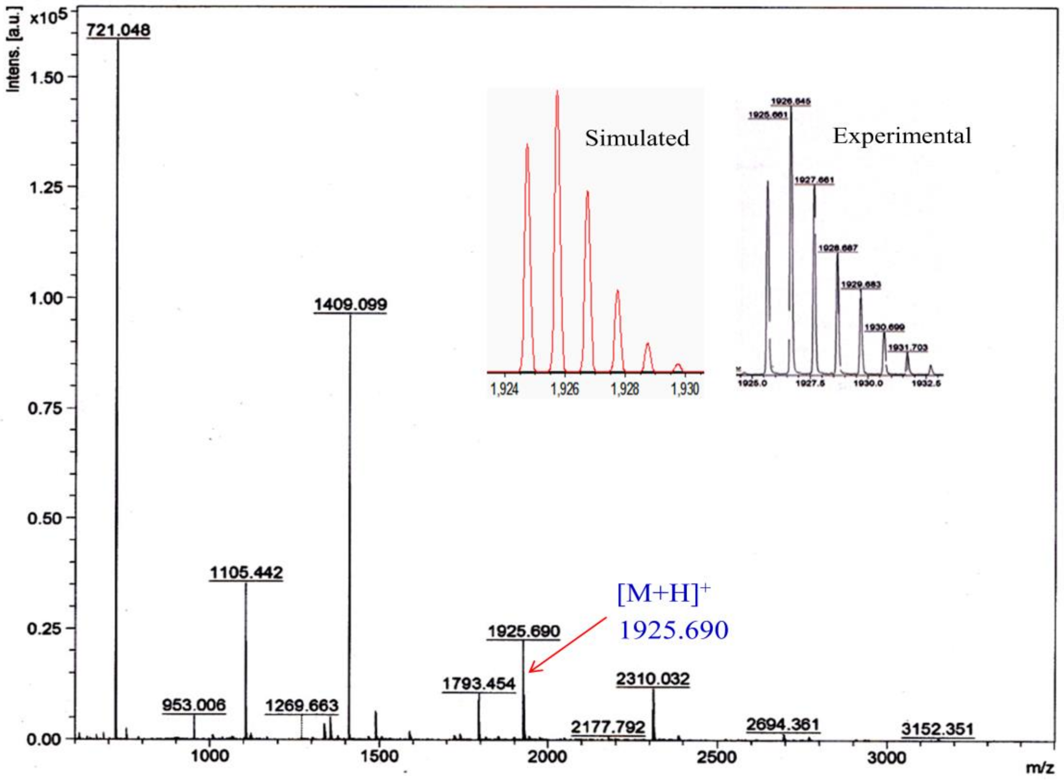
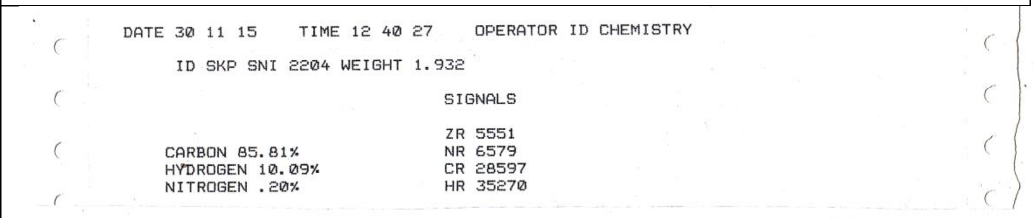
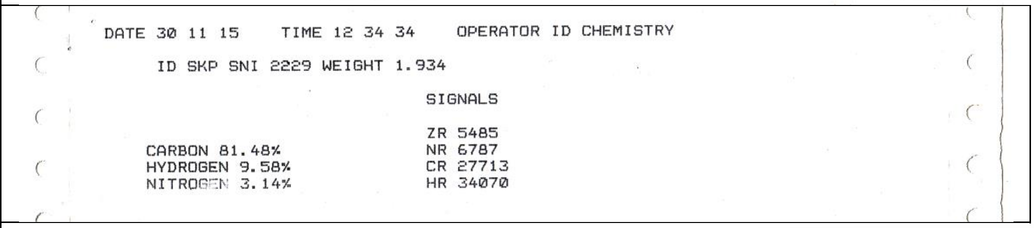
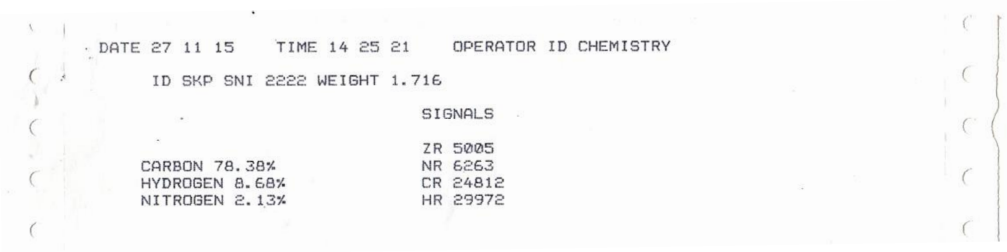
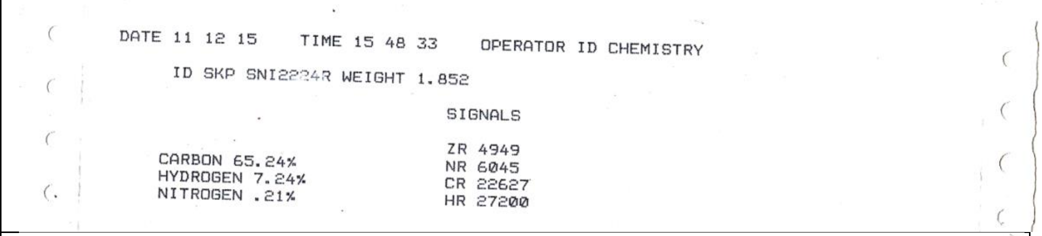
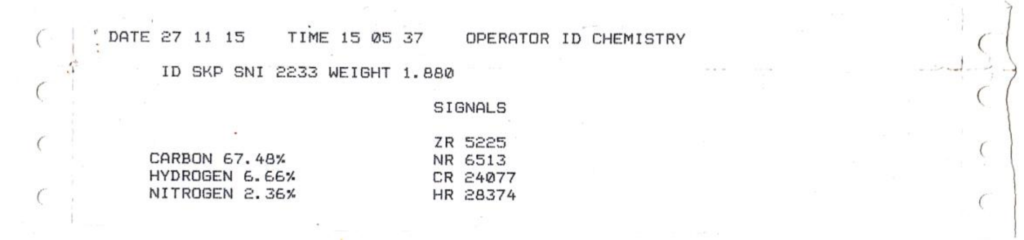
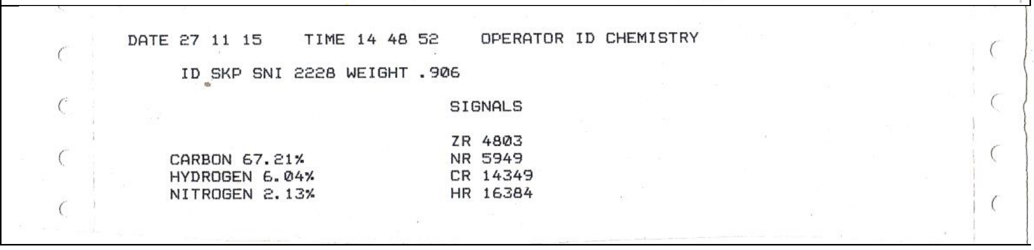


Fig. S78 MALDI-TOF mass spectrometry of **OM3**

1e. CHN analysis

Compound	CHN data
O1	 DATE 30 11 15 TIME 12 40 27 OPERATOR ID CHEMISTRY ID SKP SNI 2204 WEIGHT 1.932 SIGNALS ZR 5551 CARBON 85.81% NR 6579 HYDROGEN 10.09% CR 28597 NITROGEN .20% HR 35270
O2	 DATE 30 11 15 TIME 12 34 34 OPERATOR ID CHEMISTRY ID SKP SNI 2229 WEIGHT 1.934 SIGNALS ZR 5485 CARBON 81.48% NR 6787 HYDROGEN 9.58% CR 27713 NITROGEN 3.14% HR 34070
O3	 DATE 27 11 15 TIME 14 25 21 OPERATOR ID CHEMISTRY ID SKP SNI 2222 WEIGHT 1.716 SIGNALS ZR 5005 CARBON 78.38% NR 6263 HYDROGEN 8.68% CR 24812 NITROGEN 2.13% HR 29972
OM1	 DATE 11 12 15 TIME 15 48 33 OPERATOR ID CHEMISTRY ID SKP SNI2224R WEIGHT 1.852 SIGNALS ZR 4949 CARBON 65.24% NR 6045 HYDROGEN 7.24% CR 22627 NITROGEN .21% HR 27200
OM2	 DATE 27 11 15 TIME 15 05 37 OPERATOR ID CHEMISTRY ID SKP SNI 2233 WEIGHT 1.880 SIGNALS ZR 5225 CARBON 67.48% NR 6513 HYDROGEN 6.66% CR 24077 NITROGEN 2.36% HR 28374
OM3	 DATE 27 11 15 TIME 14 48 52 OPERATOR ID CHEMISTRY ID SKP SNI 2228 WEIGHT .906 SIGNALS ZR 4803 CARBON 67.21% NR 5949 HYDROGEN 6.04% CR 14349 NITROGEN 2.13% HR 16384

In elemental analysis of **OM1,** even after repeated attempt, identical result was observed with 6.9% less in ‘C’. This is presumably due to the formation of Au particles embedded in the carbon matrix (generated from fluorenyl-alkynyl moieties). It is also supported by the formation of residual in crucible after TGA analysis (as depicted in Fig S79) while heating **OM1** from RT to 700 °C (at 5 °C/ min). Formation of Au particle was confirmed by SEM and Energy Dispersive X-ray (EDX) analyses.

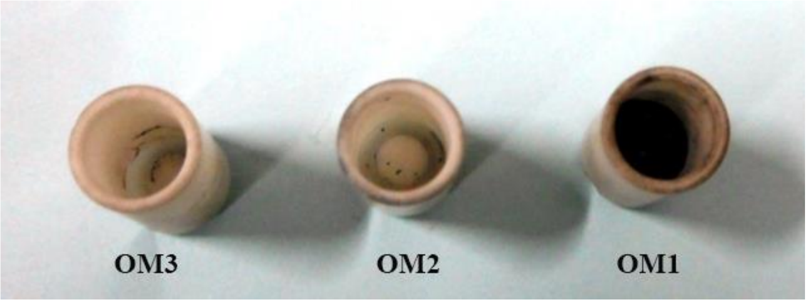


Fig. S79 Images of crucibles after thermal analyses

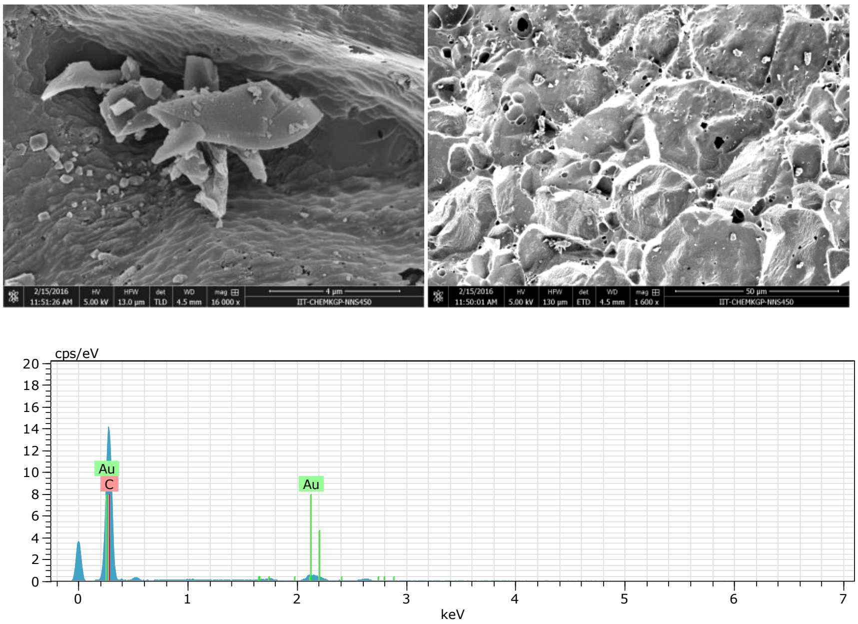


Fig. S80 SEM and EDX analyses of the residual part after TGA analysis of **OM1.**

2. Photophysical studies

Determination of Quantum yield:

All the UV−vis absorption and fluorescence emission spectra were collected using a Shimadzu UV−vis spectrophotometer (model UV 2450 and a Spex Fluorolog-3 spectrofluorimeter (model FL3−11) respectively. Throughout all the measurements, the concentration were maintained at (~1 × 10^{-5}) M. The PL quantum yields were calculated by using the absolutely measured quantum yield of quinine sulphate in 0.1 M H_2SO_4 solution as reference at 298 K. The phosphorescence quantum yields were calculated by using the absolutely measured quantum yield of 9,10-diphenylanthracene in degassed CH_2Cl_2 at 77 K. In both the cases, the sample and standard concentrations were adjusted to obtain an absorbance of 0.1 or less. The following equation was used to calculate the quantum yields[1]:

$$\frac{\Phi_S}{\Phi_R} = \frac{A_S}{A_R} \times \frac{(Abs)_R}{(Abs)_S} \times \frac{\eta_S^2}{\eta_R^2}$$

Here Φ represents the quantum yield, (Abs) represents the absorbance, A represents the area under the fluorescence curve, and η is the refractive index of the medium. The subscript S and R denote the corresponding parameters for the sample and reference respectively.

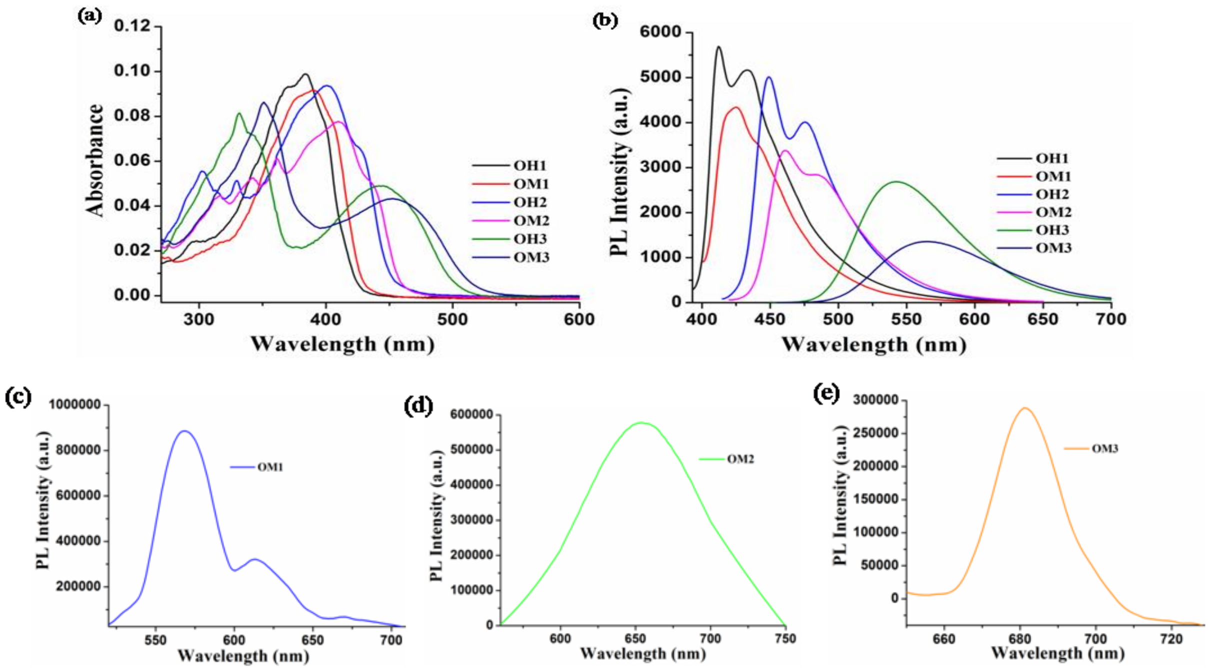


Fig. S81 (a) Absorption and (b) emission spectra of **OH1-OH3** and **OM1-OM3** in degassed 1,2-DCE at 298 K. (c), (d) and (e) emission spectra of **OM1-OM3** in degassed DCM at 77 K.

Preparation of thin film for solid state absorption measurement:

The quartz substrates (17 x 15 x 1 mm^3) were cleaned in a fresh piranha solution (7:3 mixture of 98% $H_2SO_4$and 30% H_2O_2), washed with Milli-Q water, and followed by ultrasonication in alkaline isopropanol and 0.1 M aqueous HCl at 60 °C for 1 h each. After careful washing with Milli-Q water, thin film of the compounds was prepared by spin coating on quartz plate. Compound solution in toluene (~10^{-3}M) was dropped on quartz plate and it was spin coated at 1000 rpm for 60 second.

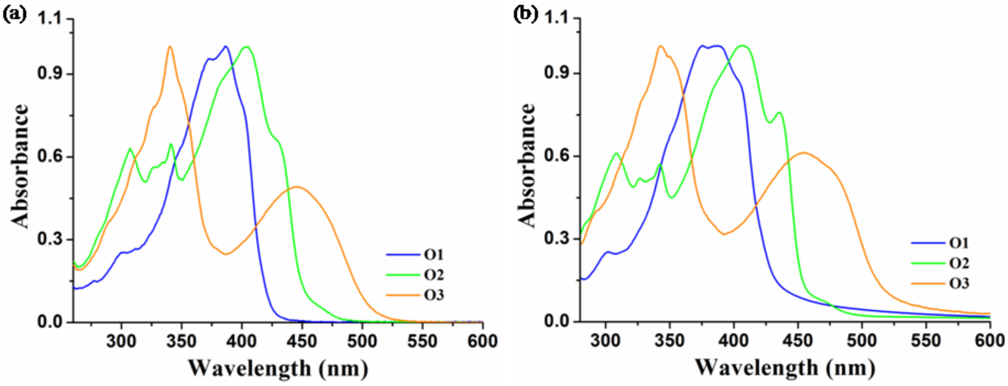


Fig. S82 Normalized absorption spectra of **O1-O3** (a) in degassed 1,2-DCE (b) in Thin film (coated on quartz plate)

Table S1. Absorbance data of O1-O3

Compound	Absorption			
	Solution	Thin flim		
	λ_{max} in nm ($\varepsilon \times 10^4$ L.mol^{-1}cm^{-1})	λ_{max}, nm	λ_{max} cut off	E_g in eV (Optical)
O1	302 (3.83), 374 (11.99), 386 (12.46)	300, 375, 389, 404 (sh)	437	2.83
O2	307 (4.94), 341 (5.14), 403 (7.89), 430 (sh)	308, 342, 408, 435	459	2.70
O3	326 (sh), 340 (9.29), 445 (4.80)	292 (sh), 343, 456	521	2.38

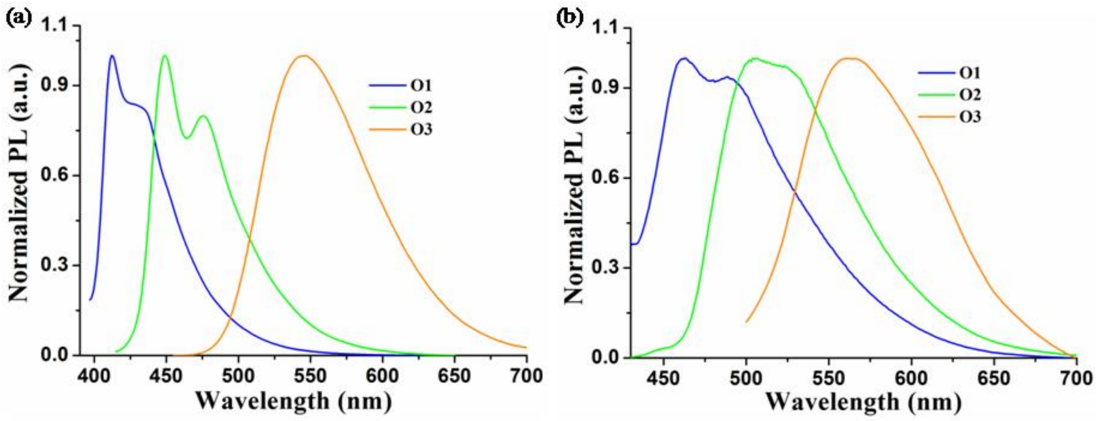


Fig. S83 Normalized PL spectra of **O1-O3** (a) in degassed 1,2-DCE (b) in Thin film (coated on quartz plate)

Table S2. Fluorescence data of O1-O3

	Fluorescence			
	Solution			Thin flim
Compound	λ_{em} (λ_{ex}), nm	Quantum Yield (Φ)	Stokes Shift, nm	λ_{em} (λ_{ex}), nm
O1	412, 434 (sh) (386)	0.39	26	462, 489 (389)
O2	441, 463 (403)	0.37	38	505 (408)
O3	545 (445)	0.24	100	563 (456)

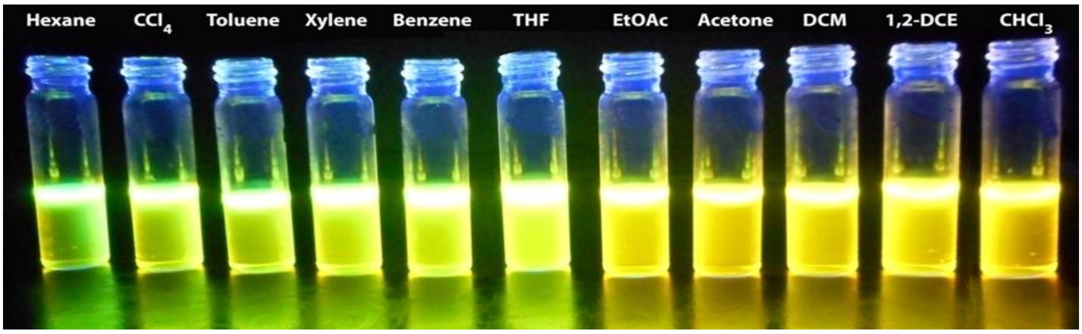


Fig. S84 Visual appearance of **OH3** in presence of different polar solvent under UV illumination at 365 nm.

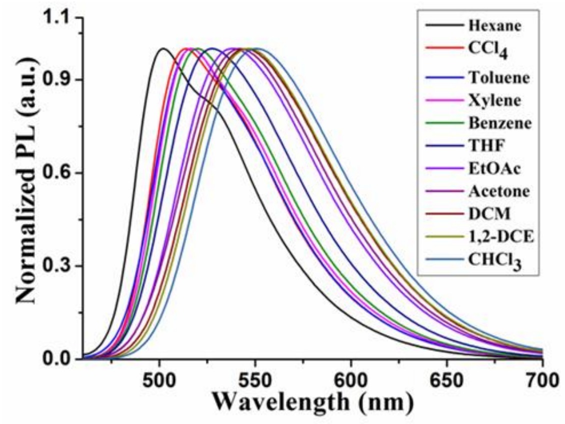


Fig. S85 Normalized PL spectra of **OH3** in solvent with different polarity

Table S3. Photophysical properties of OH3 in different solvents (~1x10^{-5} M**)**

Solvent	λ_{max}, nm	λ_{em} (λ_{ex}), nm	Quantum Yield (Φ)	Stokes Shift, cm^{-1}	FWHM, nm
Hexane	444	502 (444)	0.32	2602	66
CCl_4	447	514 (447)	0.31	2916	71
Toluene	446	517 (446)	0.31	3079	72
Xylene	443	517 (443)	0.30	3231	72
Benzene	445	520 (445)	0.30	3241	74
DCM	445	545 (445)	0.26	4123	88
1,2-DCE	445	547 (445)	0.26	4190	89
THF	442	528 (442)	0.28	3685	80
Chloroform	450	551 (450)	0.25	4073	91
EtOAc	440	539 (440)	0.26	4174	84
Acetone	439	542 (439)	0.25	4328	86

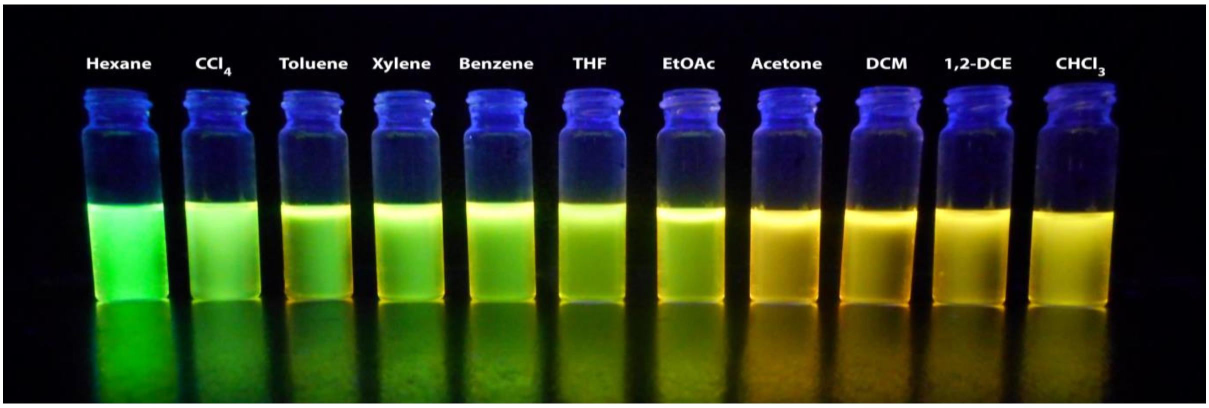


Fig. S86 Visual appearance of **OM3** in presence of different polar solvent under UV illumination at 365 nm.

Table S4. Photophysical properties of OM3 in different solvents (~1x10^{-5} M)

Solvent	λ_{max}, nm	λ_{em} (λ_{ex}), nm	Quantum Yield (Φ)	Stokes Shift, cm^{-1}	FWHM, nm
Hexane	446	508 (446)	0.21	2736	67
CCl_4	451	526 (451)	0.19	3161	76
Toluene	448	529 (448)	0.20	3417	78
Xylene	447	531 (447)	0.18	3538	79
Benzene	449	532 (449)	0.17	3474	80
DCM	452	562 (452)	0.14	4330	97
1,2-DCE	453	564 (453)	0.13	4344	100
THF	449	544 (449)	0.16	3889	88
Chloroform	455	568 (455)	0.13	4372	105
EtOAc	447	550 (447)	0.16	4189	90
Acetone	451	561 (451)	0.12	4347	95

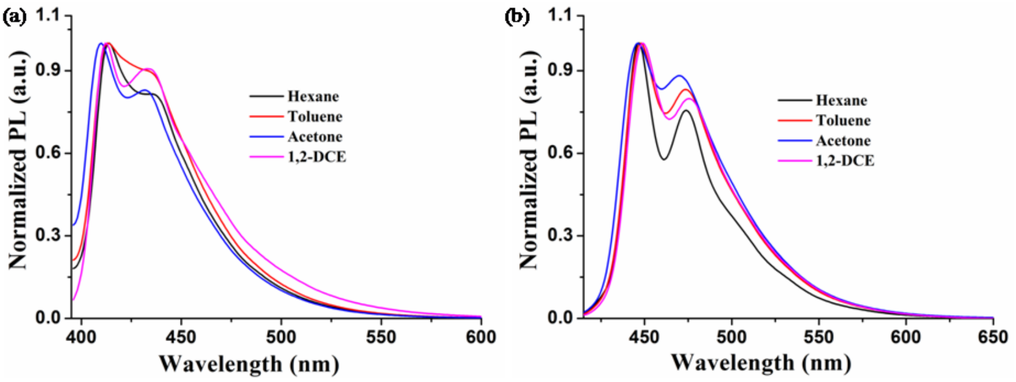


Fig. S87 Normalized PL spectra of (a) **OH1** and (b) **OH2** in solvent with different polarity

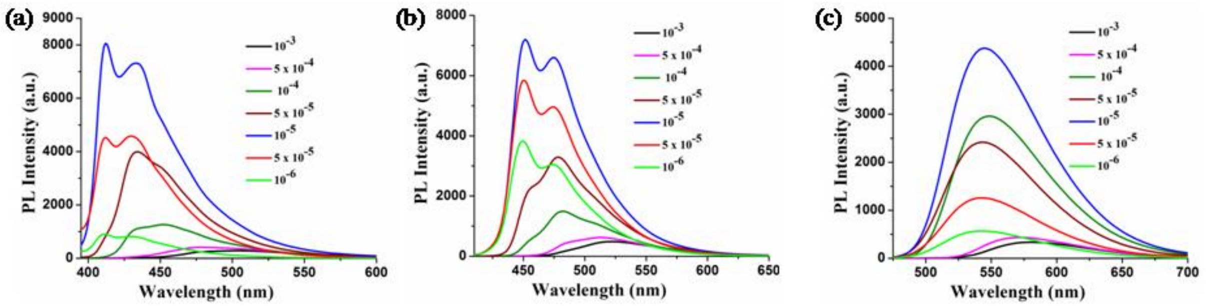


Fig. S88 Concentration dependent PL spectra of (a) **OH1 (b) OH2 (c) OH3** in 1,2-DCE (1 x 10^{-3} M to 1 x 10^{-6} M).

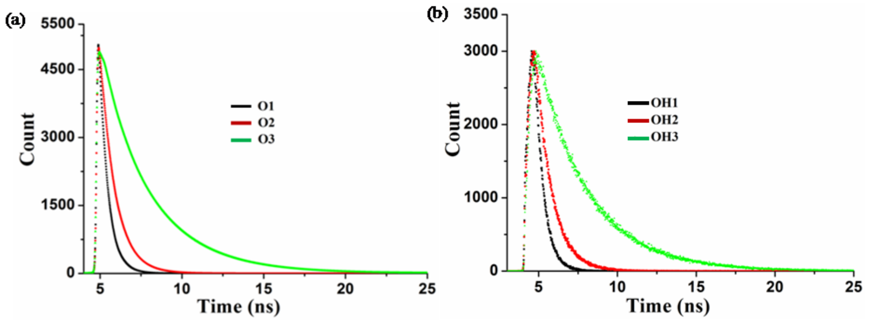


Fig. S89 Time resolved fluorescence spectra of (a) **O1-O3** and (b) **OH1-OH3**

Table S5. Fluorescence lifetimes of O1-O3, OH1-OH3 and OM1-OM3

Compound	Lifetime				
	τ_1 (A_1), ns	τ_2 (A_2), ns	$\langle\tau_{av}\rangle$, ns	k_r^a($\times10^8$), S^{-1}	k_{nr}^b($\times10^9$), S^{-1}
O1	0.46 (97%)	1.0 (3%)	0.48	8.13	1.27
O2	0.74 (63%)	1.05(37%)	0.85	4.35	0.74
O3	1.04 (15%)	3.16 (85%)	2.84	0.85	0.70
OH1	0.51 (100%)	-		8.23	1.14
OH2	0.98 (100%)	-		3.98	0.62
OH3	3.18 (100%)	-		0.82	0.23
OM1	0.42 (98%)	0.99 (2%)	0.43	6.28	1.69
OM2	0.73 (70%)	1.05 (30%)	0.83	2.53	0.95
OM3	0.85 (19%)	3.12 (81%)	2.69	0.48	0.32

$^{a}k_r=\Phi/\tau$, $^{b}k_{nr}=(1-\Phi)/\tau$ and $\tau_{av}=(A_1/A_1+A_2)\,\tau_1+(A_2/A_1+A_2)\,\tau_2$

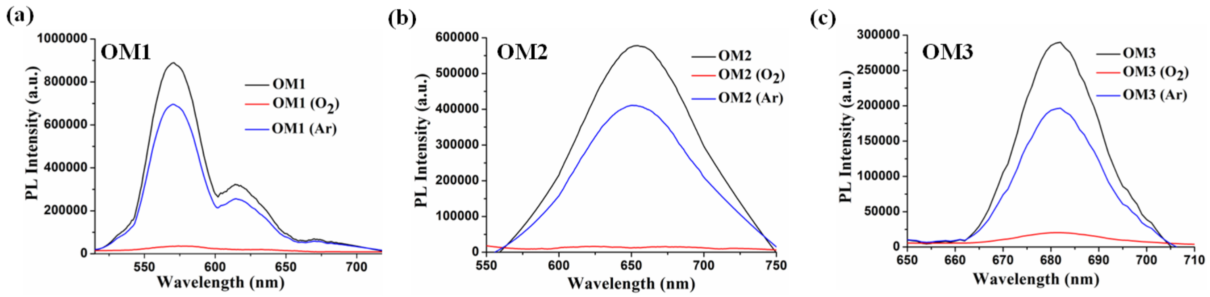


Fig. S90 The emission spectra of (a) **OM1** (b) **OM2** and (c) **OM3** at 77 K. (Black line : In degassed DCM solution; Red line: after saturation of the DCM solution with oxygen; Blue line : after deoxygenating the DCM solution with argon gas).

3. Electrochemical characterization

Cyclic Voltammetry (CV) and Differntial Pulse Voltammetry (DPV) analyses for the oligomers and the Au(I) complexes as film were carried out in CH_3CN using $^{n}Bu_4NPF_6$ (0.1 M) as supporting electrolyte, Pt wire counter electrode and Ag/AgCl reference electrode. The film of the oligomers **(OH1-OH3)** and their Au(I) complexes (**OM1-OM3**) were prepared by drop casting the corresponding DCM solution on GC-disc electrode.

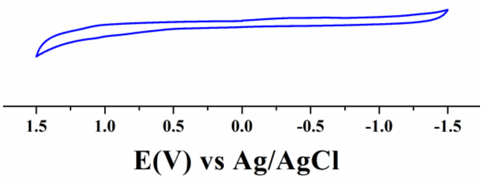


Fig. S91 Cyclic Voltamogram of acetonitrile (blank run) using $^{n}Bu_4NPF_6$ as supporting electrolyte, GC disc working electrode, Pt wire auxiliary electrode and Ag/AgCl reference electrode. Scan rate: 100 mV/s.

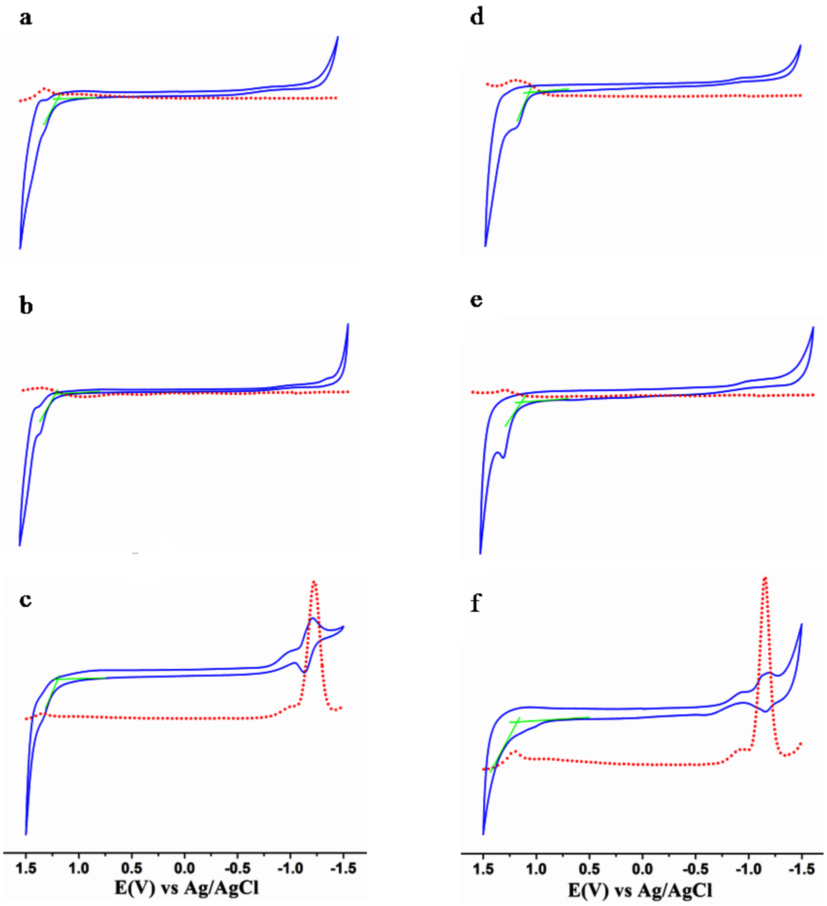


Fig. S92 Cyclic Voltamogram (blue line) and Differntial Pulse Voltammetry (dotted red line) of films (drop casted on GC disc working electrode) of a) **OH1** b) **OH2** c) **OH3** d) **OM1** e) **OM2** and f) **OM3.**

Table S6. Electrochemical data of **OH1-OH3** and **OM1-OM3**[a] carried out in CH_3CN as film on GC disc working electrode.[a]

Compound	E_{ox} (V)	E_{ox}^{onset} (V)	E_{red} (V)
OH1	1.26	1.16	
OH2	1.29	1.14	
OH3	1.33	1.19	$E_{1/2}$ = -1.17(80)[b] (reversible)
OM1	1.19	1.09	
OM2	1.25	1.08	
OM3	1.31	1.17	$E_{1/2}$ = -1.17 (quasi-reversible)

[a] Cyclic Voltamogram of film of the samples, drop casted on GC disc working electrode using, $^nBu_4NPF_6$ as supporting electrolyte in CH_3CN, Pt wire auxiliary electrode and Ag/AgCl reference electrode. Scan rate 100 mV/s. [b] Half-wave potentials evaluated from cyclic voltammetry as $E_{1/2} = (E_{pa} + E_{pc})/2$, peak potential difference in mV in parentheses.

Table S7. Electrochemical data of **OH1-OH3** and **OM1-OM3** in DCM solution.[a]

Compound	E_{ox}, V	E_{red}
OH1	1.27	
OH2	1.31	
OH3	1.34	$E_{1/2}$ = -1.17(90) (reversible)
OM1	1.21	
OM2	1.26	
OM3	1.29	$E_{1/2}$ = -1.16 (quasi-reversible)

[a] CV measurement was carried in DCM using Pt disc working electrode, $TBAPF_6$ (0.1 M) as supporting electrolytes, Pt wire auxiliary electrode and Ag/AgCl reference electrode.

4. Thermal analysis

4a. DSC data

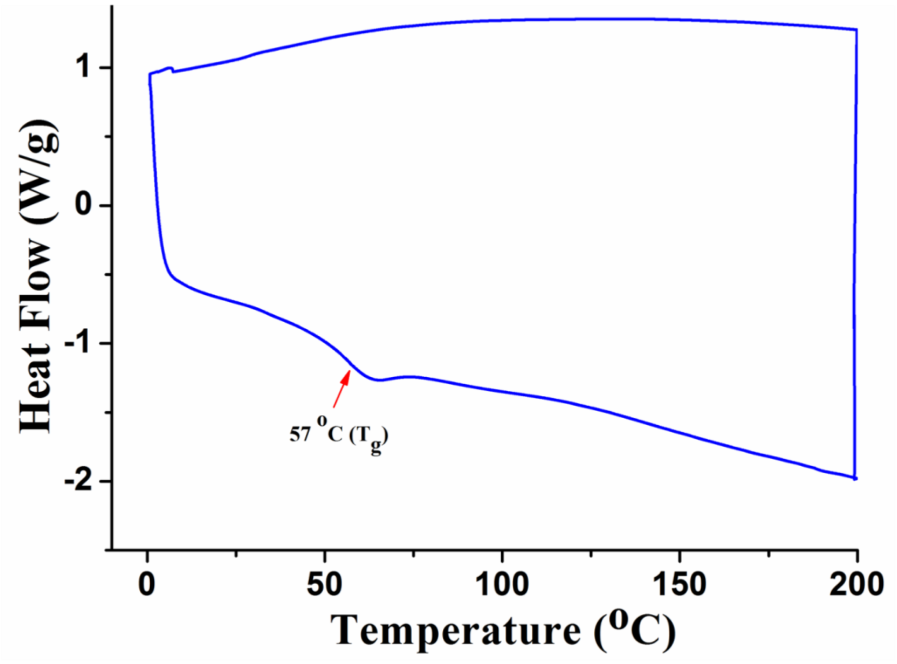


Fig. S93 DSC Thermogram of **O1** recorded at a rate of 10 °C/min

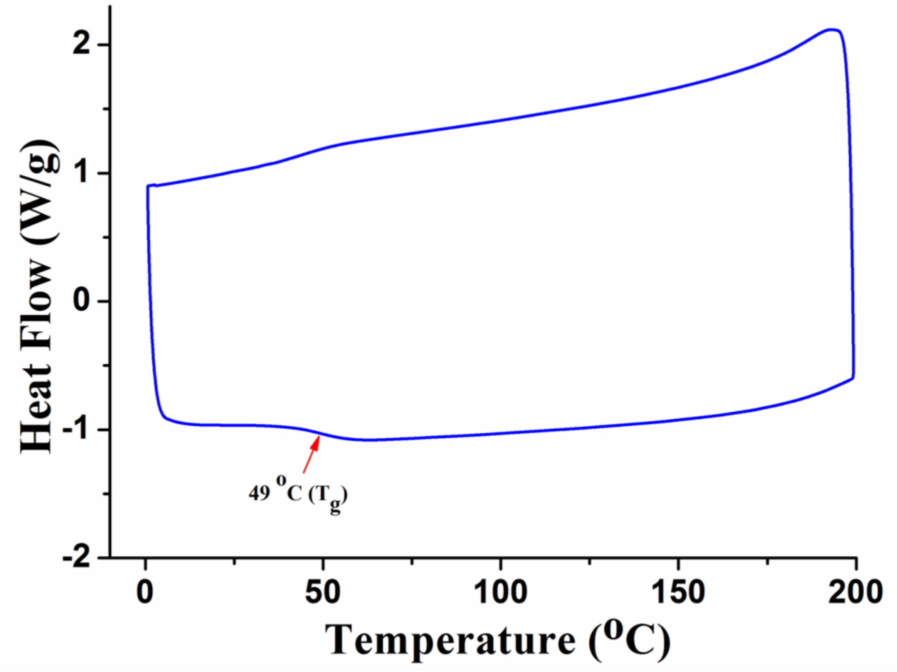


Fig. S94 DSC Thermogram of **O2** recorded at a rate of 10 °C/min

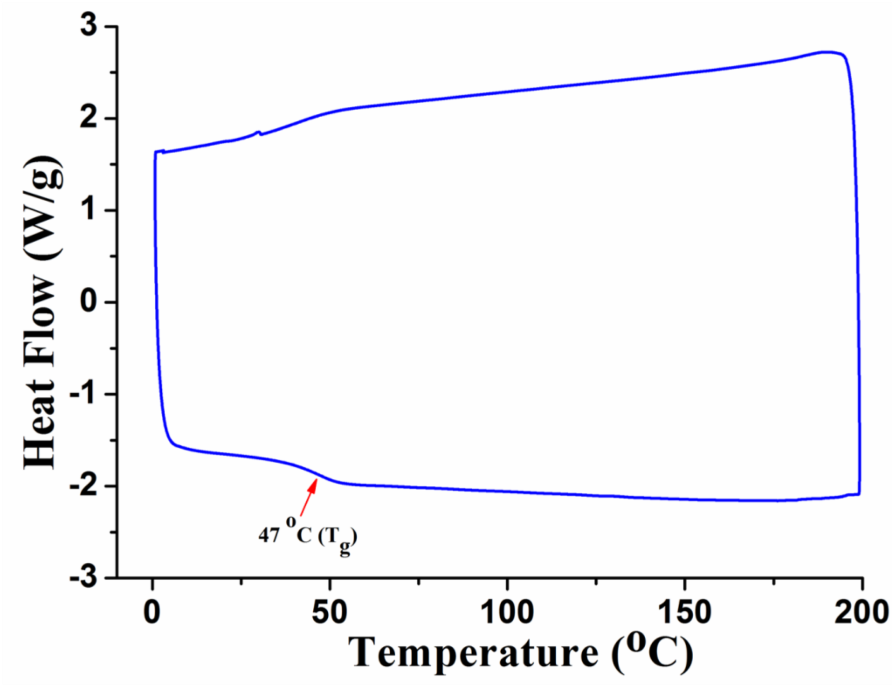


Fig. S95 DSC Thermogram of **O3** recorded at a rate of 10 ^{o}C/min

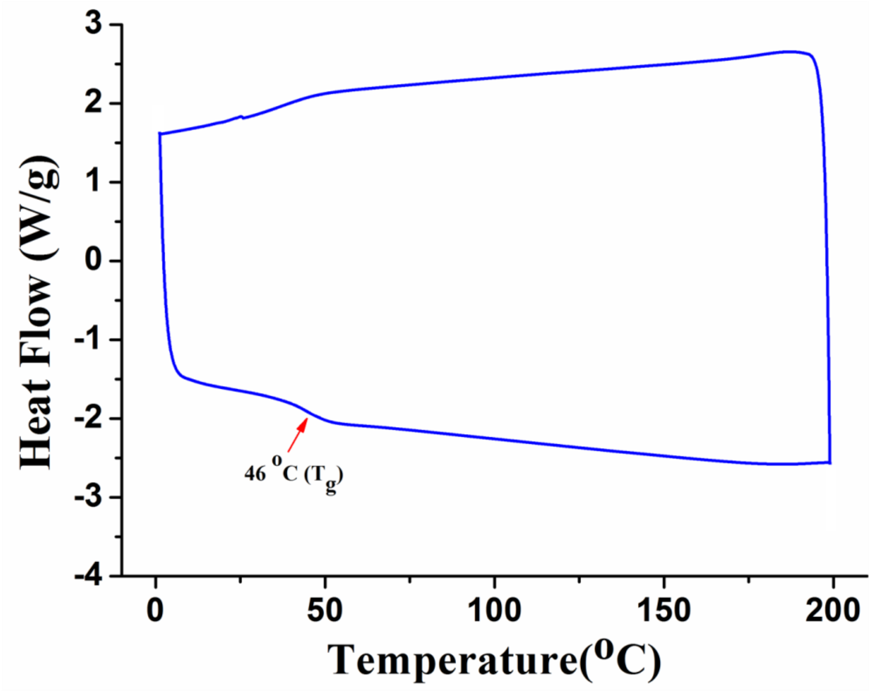


Fig. S96 DSC Thermogram of **OM1** recorded at a rate of 10 ^{o}C/min

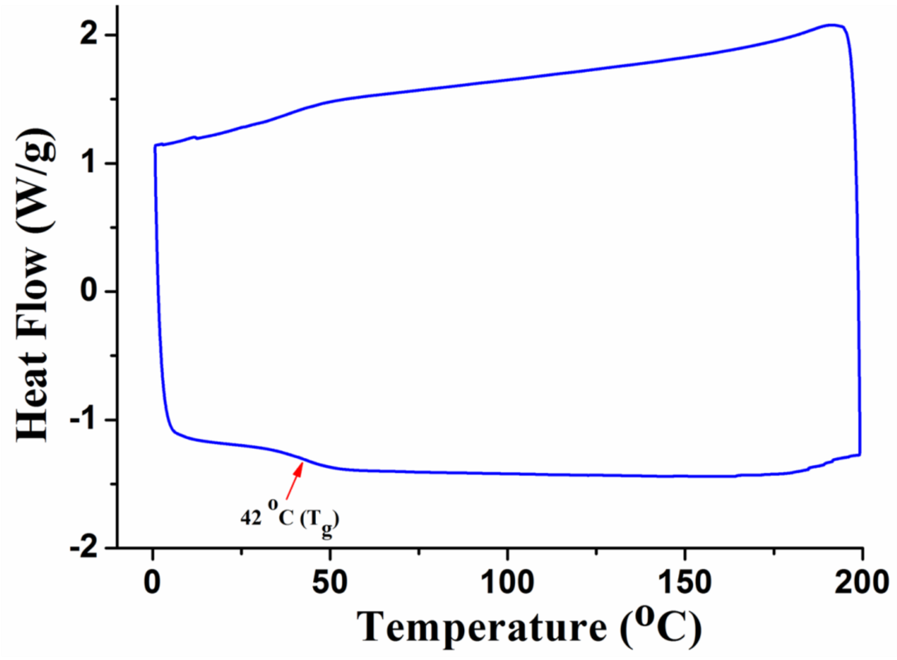


Fig. S97 DSC Thermogram of **OM2** recorded at a rate of 10 °C/min

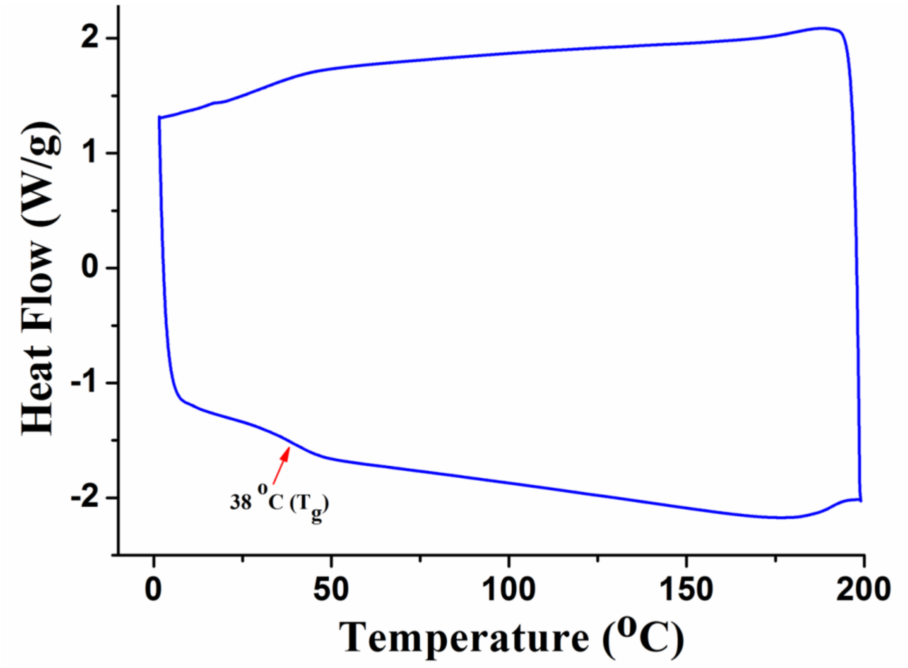


Fig. S98 DSC Thermogram of **OM3** recorded at a rate of 10 °C/min

4b. TGA Data

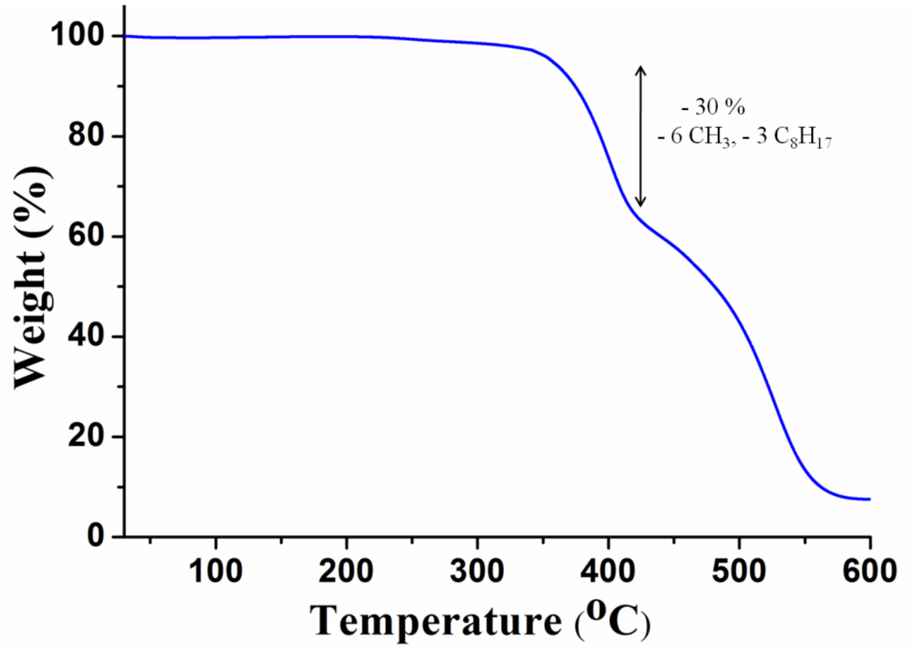


Fig. S99 TGA Thermogram of **O1** recorded at a rate of 5 ^oC/min under N_2

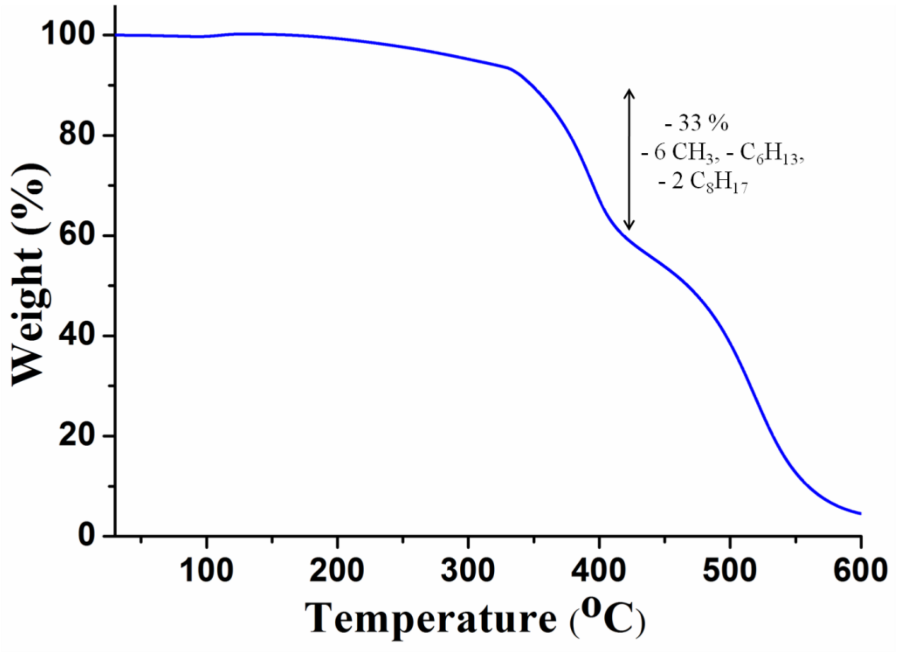


Fig. S100 TGA Thermogram of **O2** recorded at a rate of 5 ^oC/min under N_2

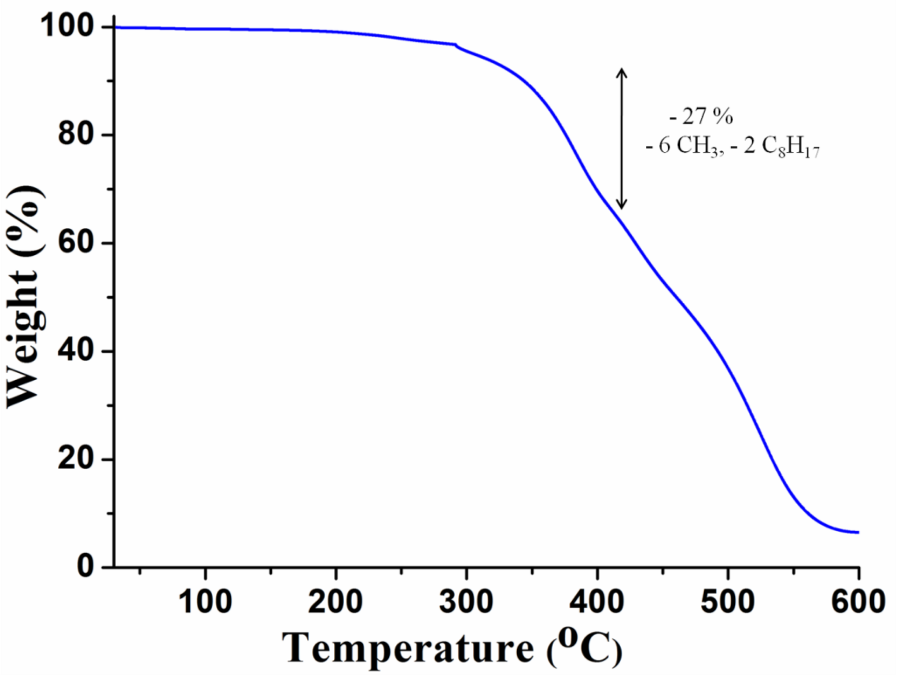


Fig. S101 TGA Thermogram of **O3** recorded at a rate of 5 ^{o}C/min under N_2

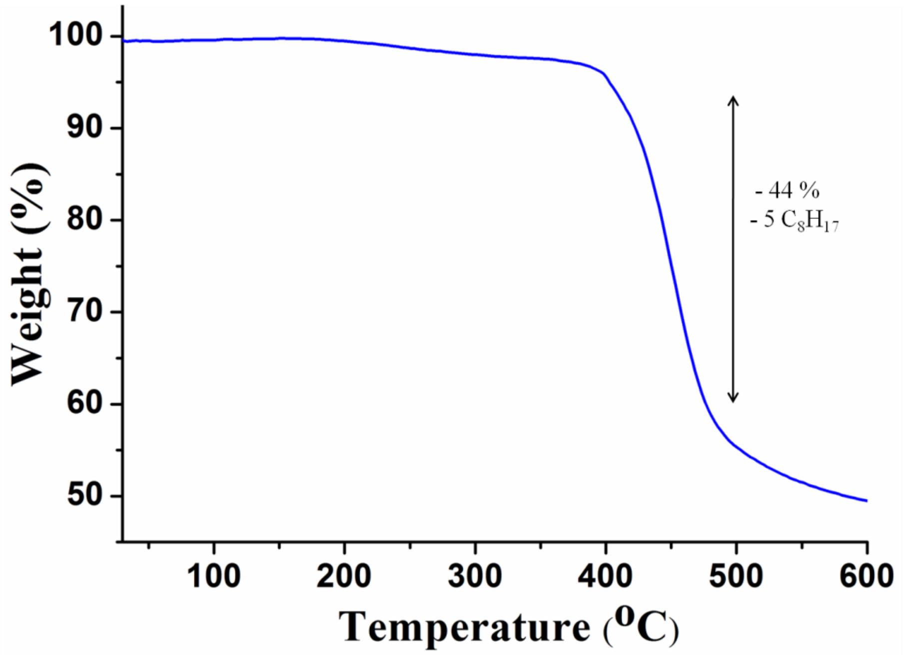


Fig. S102 TGA Thermogram of **OH1** recorded at a rate of 5 ^{o}C/min under N_2

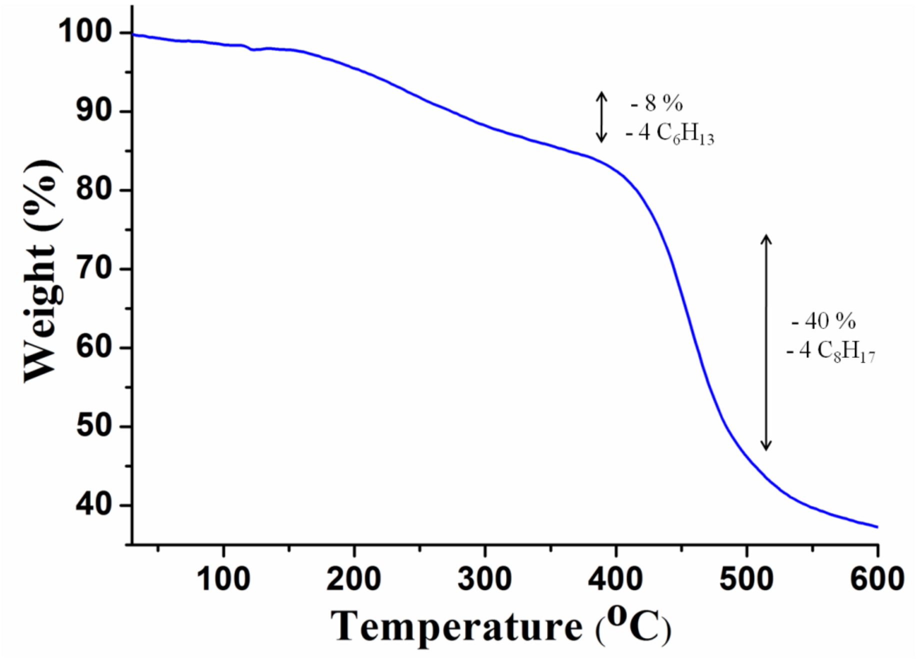


Fig. S103 TGA Thermogram of **OH2** recorded at a rate of 5 °C/min under N_2

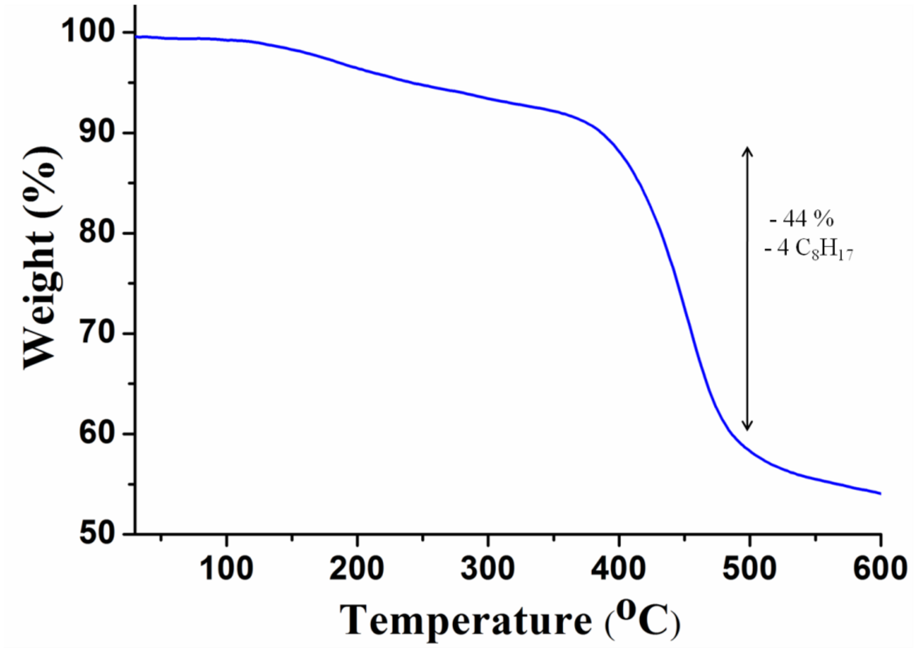


Fig. S104 TGA Thermogram of **OH3** recorded at a rate of 5 °C/min under N_2

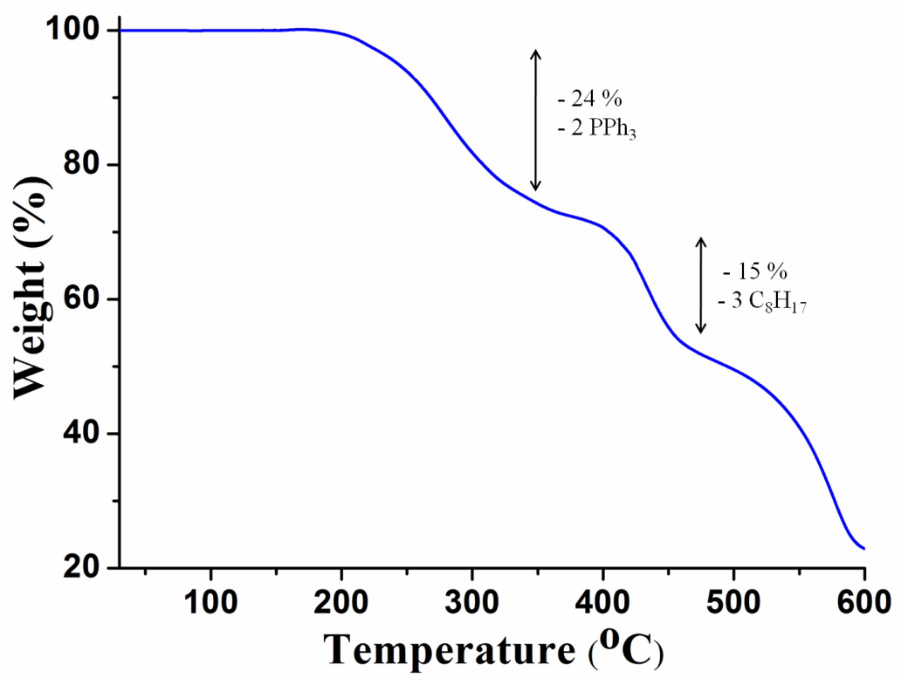


Fig. S105 TGA Thermogram of **OM1** recorded at a rate of 5 ^{o}C/min under N_2

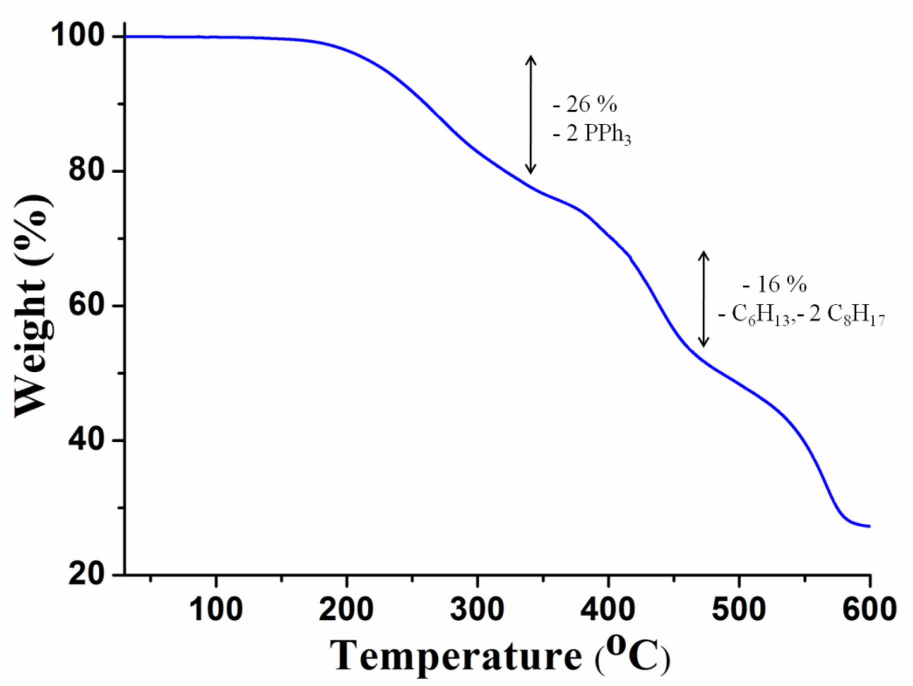


Fig. S106 TGA Thermogram of **OM2** recorded at a rate of 5 ^{o}C/min under N_2

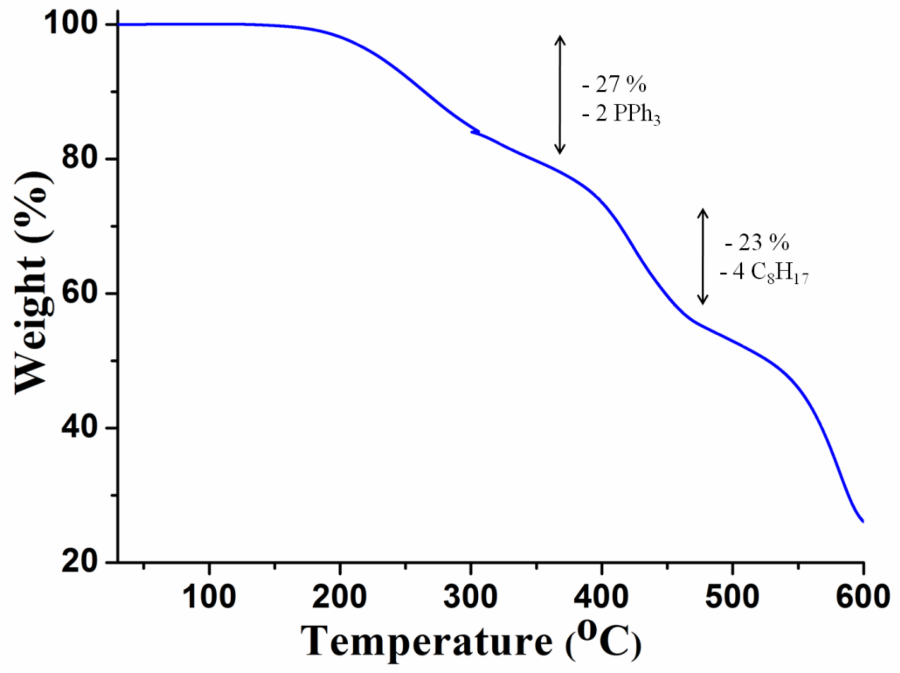


Fig. S107 TGA Thermogram of **OM3** recorded at a rate of 5 °C/min under N_2

5. Crystallographic data

X-ray data collections and refinement. The orange needle-like single crystals of **O3** suitable for X-ray crystallography, were obtained by layering MeOH on DCM solution of **O3**. Single-crystal X-ray structural study was performed on a Bruker-APEX-II CCD X-ray diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 100(2) K using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). The frames were indexed, integrated, and scaled using the SMART and SAINT software package,[2] and the data were corrected for absorption using the SADABS program.[3] Pertinent crystallographic data for **O3** is summarized in Table S5. The title compound crystallizes in the triclinic space group, P-1. Two independent molecules of O3 were located in the asymmetric unit with negligible differences in their metrical parameters. CCDC 1512387 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The structure was solved and refined using the SHELX suite of programs.[4] The molecular structure was generated by using ORTEP-3 for Windows Version 2.02.[5] The hydrogen atoms were included in geometrically calculated positions in the final stages of the refinement and were refined according to the typical riding model. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Table S8. Crystallographic data and refinement parameters for **O3.**

	O3
Empirical formula	$C_{78}H_{100}N_2SSi_2$
Formula weight	1153.83
Crystal system	Triclinic
Space group	P-1
a, Å	15.523(9)
b, Å	17.690(11)
c, Å	28.487(17)
α, deg	99.08(2)
β, deg	102.73(2)
γ, deg	103.53(2)
V, Å^3	7235(8)
Z	4
ρ_{calcd}, g cm^{-3}	1.059
μ, mm^{-1}	1.19
F(000)	2504
Reflections	
Collected	85829
independent	25388
observed [I > 2σ(I)]	5020
No. of variables	1732
Goodness-of-fit	0.986
Final R indices [I>2σ(I)][a]	$R_1 = 0.1749$
	$wR_2 = 0.3995$
R indices (all data)[a]	$R_1 = 0.4700$
	$wR_2 = 0.5827$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma|F_o^2|^2]$

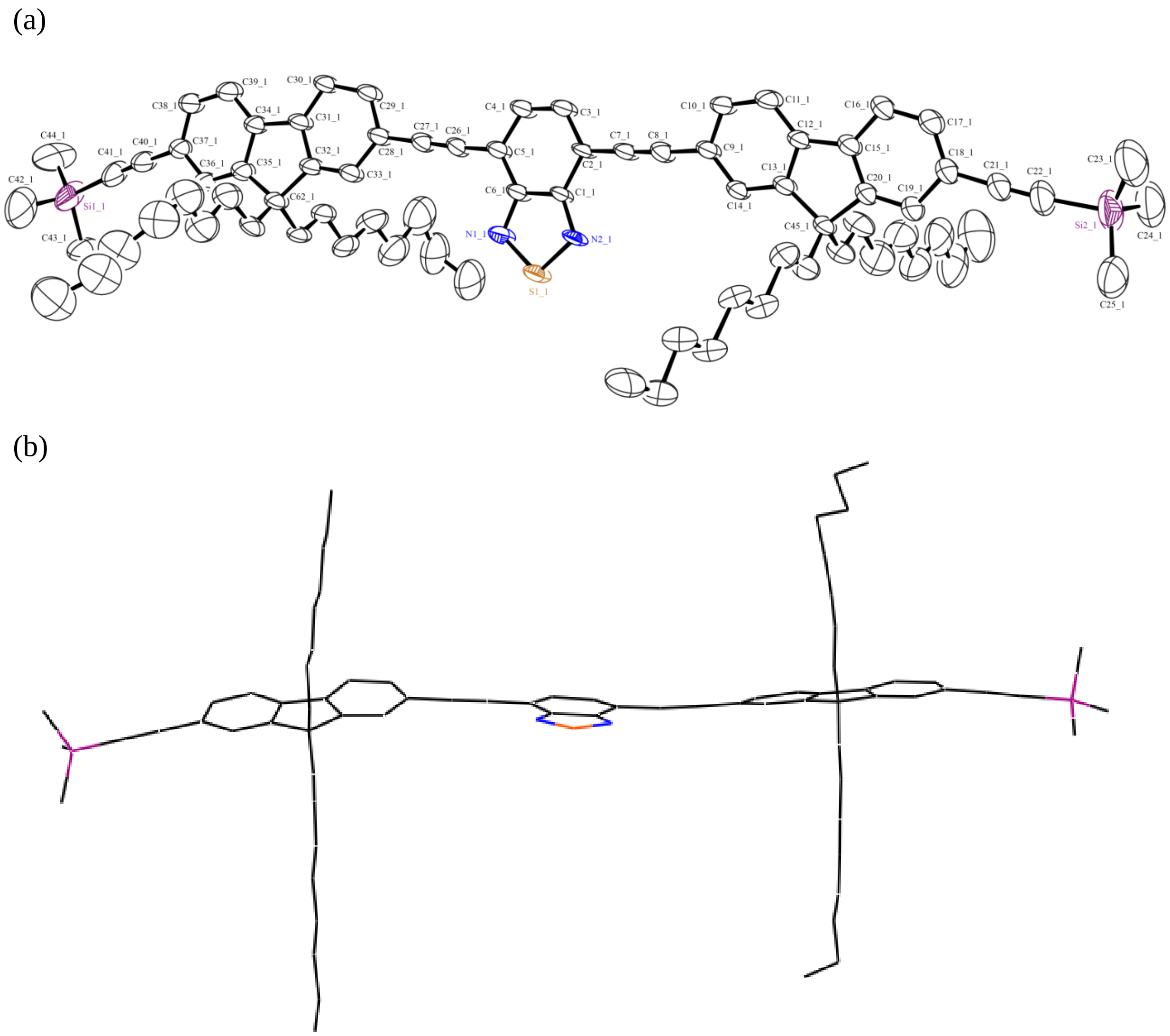


Fig. S108 (a) ORTEP representation of **O3** with atoms labelled. For the sake of clarity, the carbon atoms of octyl groups are not labelled, and the hydrogen atoms have been omitted. The thermal ellipsoids are drawn at 30% of probability. (b) Side view as a stick model. Hydrogen atoms have been omitted for the sake of clarity.

6. Reference

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5. L. J. Farrugia, ORTEP-3 for windows-A version of ORTEP-III with a graphical user interface (GUI) *J. Appl. Cryst*., 1997, **30**, 565.