Supplementary Material (ESI) for Chemical Communications
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*For Electronic Supplementary Information*

# Efficient Two- to Five-Photon Excited Violet Emission of Calix[4]arene-based Multiple Donor-Accepter Assembly

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**Experimental Section**

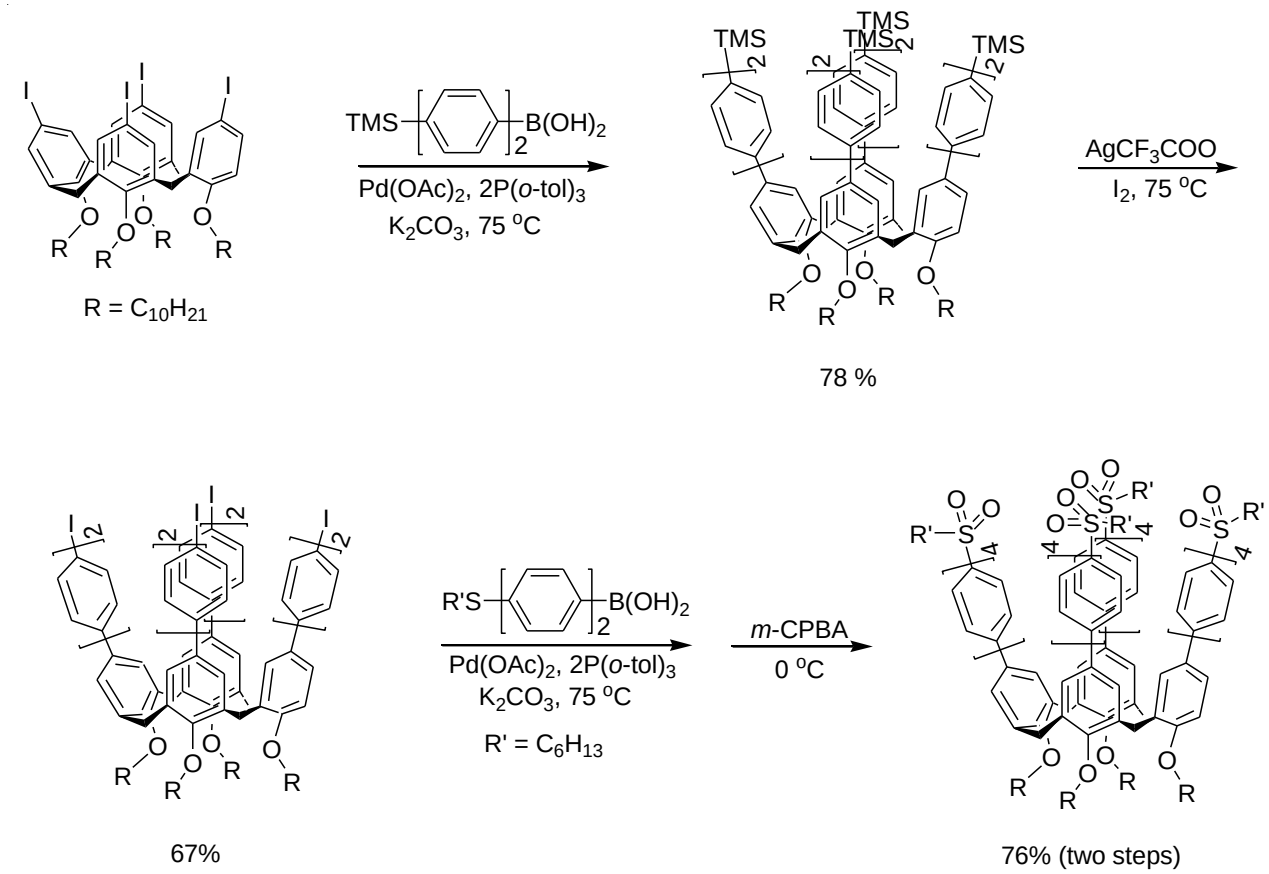
The TPA cross section was measured by the TPA induced fluorescence method .The TPA cross sections $\sigma_2$ was obtained by comparing their TPA induced up conversion fluorescence to that of Rhodamine 6G (both at the concentration of $5\times10^{-4}$ mol/l) according to(Appl .Opt, 37, 7352, 1998)

$$\sigma_2 = \frac{\sigma^{TPF}}{\Phi_F}$$

$$\sigma^{TPF} = \sigma_{cal}^{TPF}\frac{c_{cal}n_{cal}S}{cnS_{cal}}$$

Where $\Phi_F$ is the fluorescence quantum yield, $c$ is the concentration, $n$ is the refractive index, and S is the intensity of upconversed fluorescence. $\sigma^{TPF}$ is the two photon excitation cross section. The cal subscript refers to the standard reference solution. For the femto-second-pulse experiment, the excitation source is an optical parametric amplifier pumped by a mode-locked Ti:sapphire laser oscillator–amplifier system. The pulse width of the laser is 120 fs, and its repetition rate is 1 kHz. The fluorescence is collect by a telescope system which is consist of a lens f = 15 cm and a lens f = 30 cm. A monochromator connected with a GaAs PMT are used as the recorder for the MPA induced up-converted fluorescence.

$^1$H NMR spectra were recorded using a Jeol JHM-EX270 FT NMR spectrometer or a Varian INOVA-400 FT NMR spectrometer and are referenced to the residual $CHCl_3$ 7.24 ppm. $^{13}$C NMR spectra were recorded using a Jeol JHM-EX270 FT NMR spectrometer or a Varian INOVA-400 FT NMR spectrometer and are referenced to the $CDCl_3$ 77 ppm. Mass spectroscopy (MS) measurements were carried using matrix-assisted laser desorption ionisation–time-of-flight (MALDI-TOF) technique. The decomposition temperatures ($T_{dec}$) as measured by thermal gravimetric analyser of these chromophores are very high $T_{dec}$ > 314 °C indicating that they are highly thermally stable.



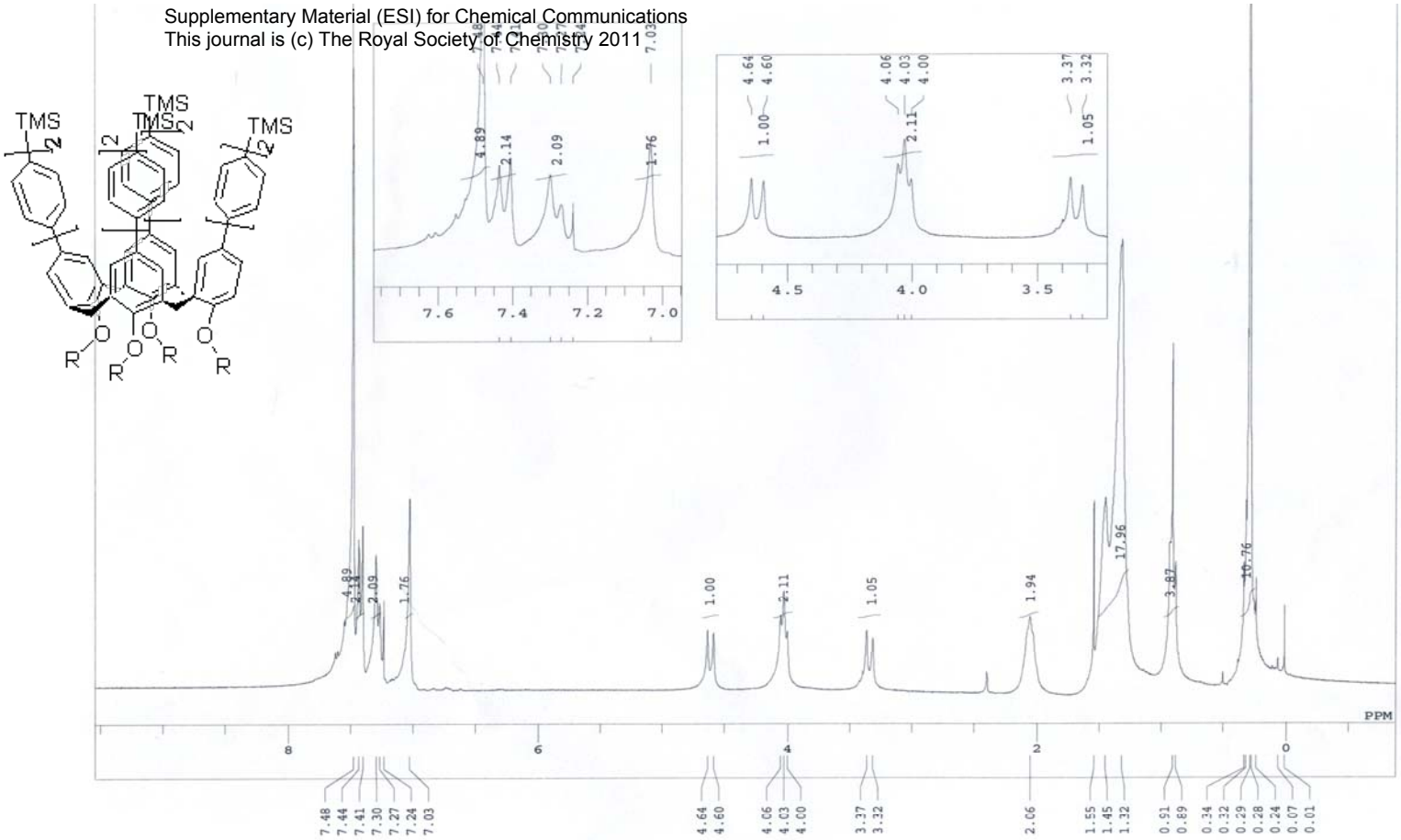

**5,11,17,23-Tetrakis[4'-(trimethylsilyl)biphenyl]-25,26,27,28-tetradecoxycalix[4]arene** To a stirred solution of 5,11,17,23-tetrakisiodo-25,26,27,28-tetradecoxycalix[4]arene (458 mg, 0.31 mmol), 4'-(trimethylsilyl)biphenyl-4-ylboronic acid (502 mg, 1.86 mmol), $Pd(OAc)_2$ (14 mg, 0.06 mmol) and P(*o*-tol)$_3$ (38 mg, 0.12 mmol) in 15 mL of toluene and 10 mL of methanol was added 5 mL of 2 M $K_2CO_3$ under $N_2$. After being heated to 75 °C for overnight, the reaction mixture was added with 50 mL of 2 M $Na_2CO_3$ and then extracted twice with $CH_2Cl_2$ (50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and evaporated to dryness. The crude product was purified by silica gel column chromatography using petroleum ether/$CH_2Cl_2$ (v/v 8:1) as eluent affording the target product (450 mg) in 78% yield. $^1$H NMR (400 MHz, $CDCl_3$, 25°C, δ) 7.48 (s, 16 H), 7.42 (d, *J* = 8.0 Hz, 8H), 7.26 (d, *J* = 7.6 Hz, 8H), 7.03 (s,

8H), 4.62 (d, $J$ = 13.2 Hz, 4H), 4.03 (t, $J$ = 7.4 Hz, 8H), 3.34 (d, $J$ = 13.2 Hz, 4H), 2.05 (bs, 8H), 1.27-1.44 (bs, 56H), 0.89 (t, $J$ = 6.6 Hz, 12H), 0.29 (s, 36 H). $^{13}$C NMR (67.8 MHz, $CDCl_3$, 25°C, δ) 157.3, 141.2, 140.3, 138.9, 138.7, 135.1, 134.8, 133.7, 127.2, 127.1, 127.0, 126.3, 75.6, 32.0, 31.8, 30.4, 30.1, 29.9, 29.7, 29.5, 26.5, 22.7, 14.2, −1.0. HRMS (MALDI-TOF) Calcd for $C_{128}H_{168}O_4Si$, 1881.2020, Found: 1881.2117 $[M]^+$. mp: 195-197 °C.

**5,11,17,23-Tetrakis(4'-iodobiphenyl)-25,26,27,28-tetradecoxycalix[4]arene** To the solution of 5,11,17,23-tetrakis[4'-(trimethylsilyl)biphenyl]-25,26,27,28-tetradecoxy-calix[4]arene (450 mg, 0.24 mmol) in 25 mL $CHCl_3$, was added silver trifluoroacetate (318 mg, 1.44 mmol). After refluxing for 30 min under $N_2$, iodine (365 mg, 1.44 mmol) was added. The reaction mixture was allowed to reflux for another 2 h. After cooling down to room temperature, the crude mixture was filtered through a short silica gel column chromatography with celite. The filtrate was washed with water four times, dried over anhydrous $Na_2SO_4$ and evaporated to dryness. The crude product was purified by silica gel column chromatography using petroleum ether/$CH_2Cl_2$ (v/v 8:1) as eluent affording the target product (335 mg) in 67% yield. $^1$H NMR (400 MHz, $CDCl_3$, 25°C, δ) 7.59 (d, $J$ = 8.4 Hz, 8H), 7.27 (bs, 8H), 7.23 (bs, 8H), 7.10 (d, $J$ = 7.6 Hz, 8H), 6.99 (s, 8H), 4.60 (d, $J$ = 13.2 Hz, 4H), 4.00 (t, $J$ = 7.2 Hz, 8H), 3.32 (d, $J$ = 13.2 Hz, 4H), 1.96-2.04 (m, 8H), 1.29-1.44 (m, 56H), 0.90 (t, $J$ = 6.8 Hz, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C, δ) 156.5, 140.5, 139.9, 137.7, 137.6, 135.2, 134.3, 128.4, 127.1, 126.9, 126.7, 92.8, 75.6, 32.0, 31.4, 30.4, 30.0, 29.8, 29.5, 26.4, 22.7, 14.1. Anal. Calcd for $C_{116}H_{132}O_4I_4$: C, 66.41; H, 6.34. Found: C, 66.35; H, 6.17. mp: 130-131.5 °C.

**5,11,17,23-Tetrakis[4'''-(hexylsulfonyl)quaterphenyl]-25,26,27,28-tetradecoxy-calix[4]arene** To a stirred solution of

5,11,17,23-tetrakis(4'-iodobiphenyl)-25,26,27,28-tetradecoxycalix[4]arene (335 mg, 0.16 mmol), $Pd(OAc)_2$ (7 mg, 0.03 mmol) and P(*o*-tol)$_3$ (19 mg, 0.06 mmol) in 15 mL of toluene was added with 5 mL of 2 M $K_2CO_3$ under $N_2$ and 4'-(hexylthio)biphenyl-4-ylboronic acid (301 mg, 0.96 mmol) in 10 mL of methanol, respectively. After being heated to 75 °C for overnight, the reaction mixture was added with 50 mL of 2 M $Na_2CO_3$ and then extracted twice with $CH_2Cl_2$ (50 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$ and filtered. The filtrate was then cooled to $0^oC$ and added with MCPBA (248 mg, 1.44 mmol) in portion. After stirring for 2 h, the white suspension was filtered off and the filtrate was washed with $Na_2CO_3$ solution, dried over anhydrous $Na_2SO_4$ and evaporated to dryness. The crude product was then purified by silica gel chromatography using gradient elution technique with $CH_2Cl_2$/ethyl acetate as eluent affording the target product in 76% yield (340 mg). $^1$H NMR (400 MHz, $CDCl_3$, 25°C, δ) 7.91 (d, *J* = 8.4 Hz, 8H), 7.70 (d, *J* = 8.0 Hz, 8H), 7.62 (d, *J* = 8.0 Hz, 8H), 7.54-7.58 (m, 24H), 7.45 (bs, 8H), 7.31 (bs, 8H), 7.06 (bs, 8H), 4.64 (d, *J* = 13.2 Hz, 4H), 4.02 (bs, 8H), 3.37 (d, *J* = 13.2 Hz, 4H), 3.16 (t, *J* = 8.0 Hz, 8H), 2.05 (bs, 8 H), 1.72-1.80 (m, 8H), 1.25-1.46 (m, 80H), 0.85-0.93 (m, 24H). $^{13}$C NMR (100 MHz, $CDCl_3$, 25°C, δ) 156.4, 145.7, 140.8, 140.3, 140.0, 138.4, 138.0, 137.6, 135.2, 134.5, 128.6, 127.6, 127.4, 127.2, 127.1, 127.1, 126.9, 75.6, 56.2, 32.0, 31.6, 31.2, 30.4, 30.0, 29.8, 29.7, 29.5, 27.9, 26.4, 22.7, 22.5, 22.3, 14.1, 13.9. MS (MALDI-TOF) m/z Calcd for $C_{188}H_{215}O_{12}S_4Na$, 2818.03, Found: 2818.10 $[M - H + Na]^+$. mp: 314 °C (dec).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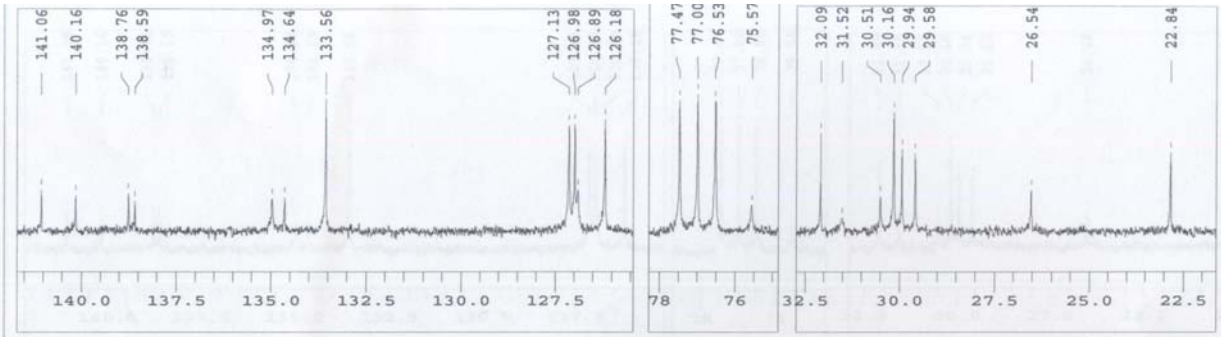
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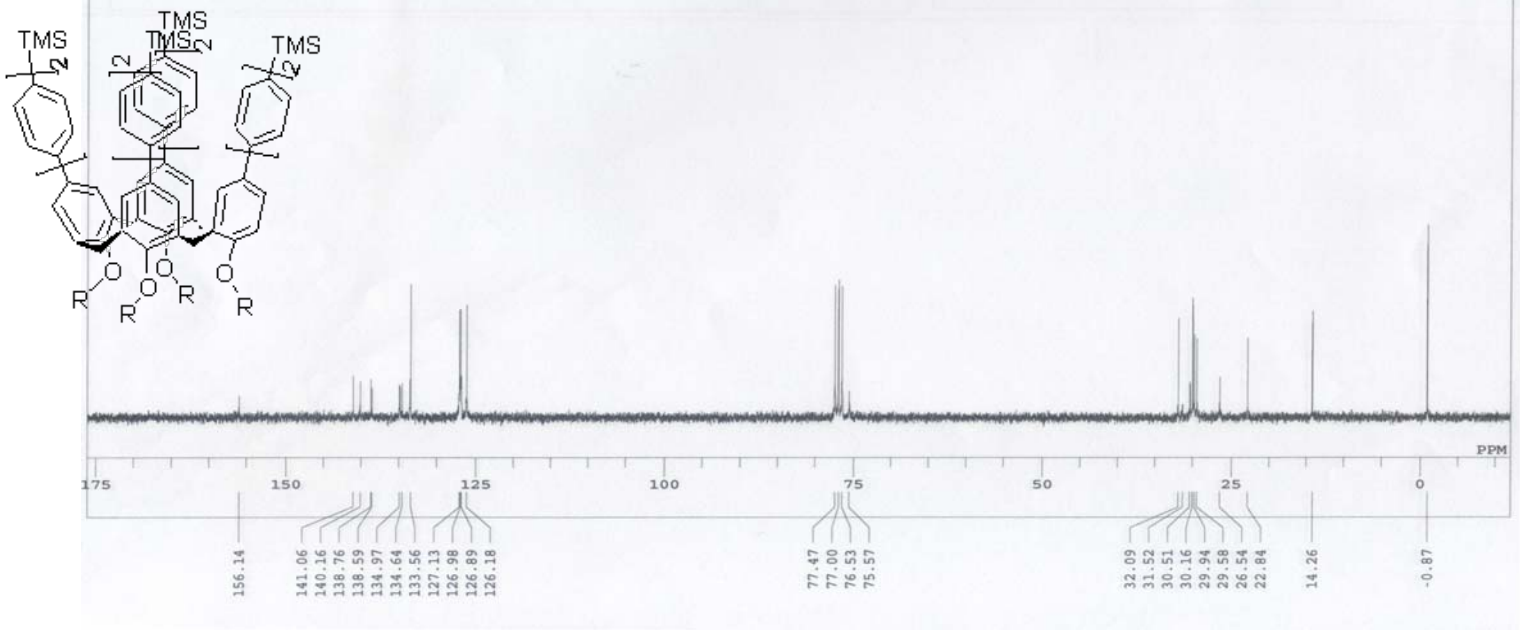
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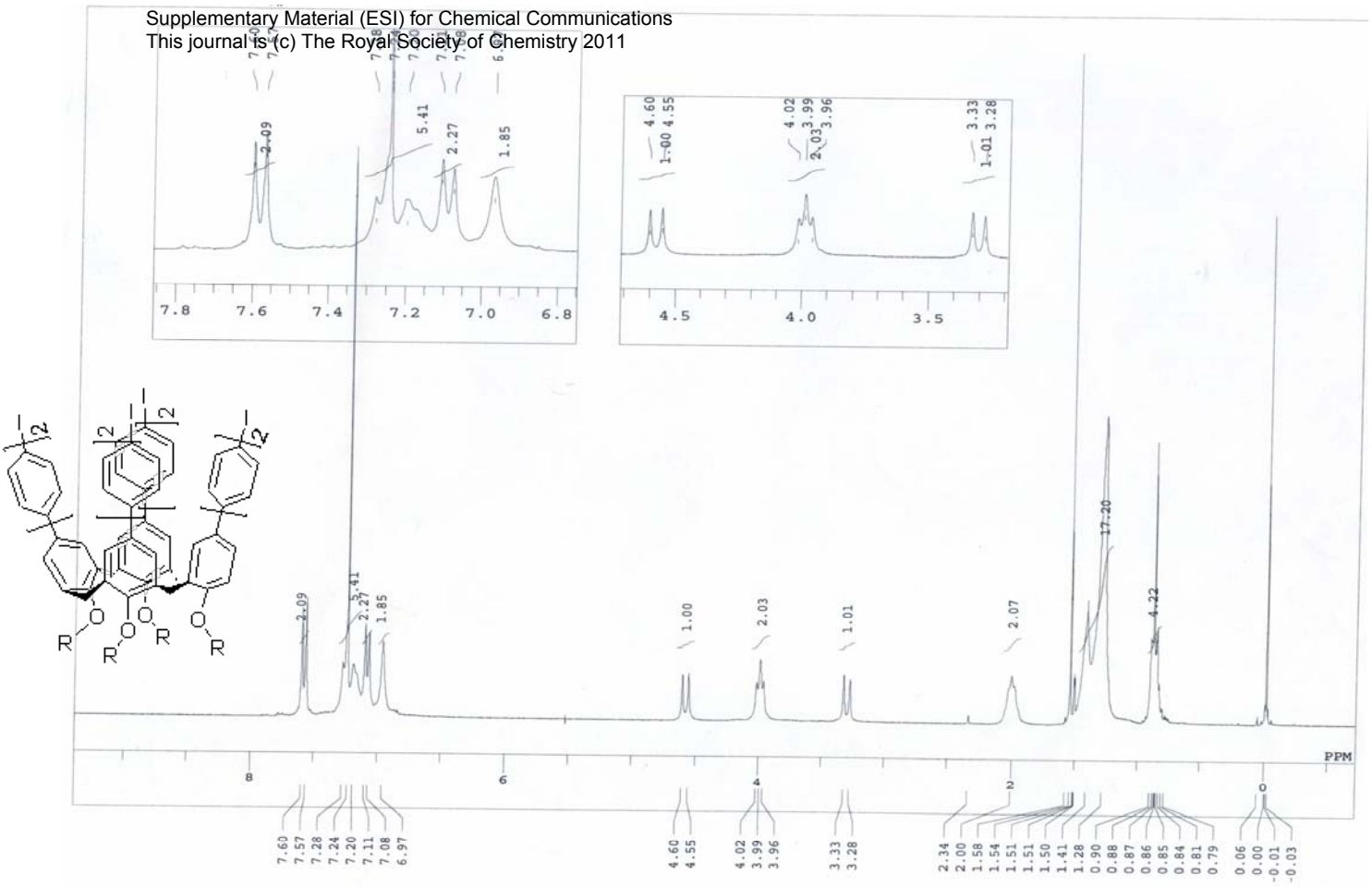
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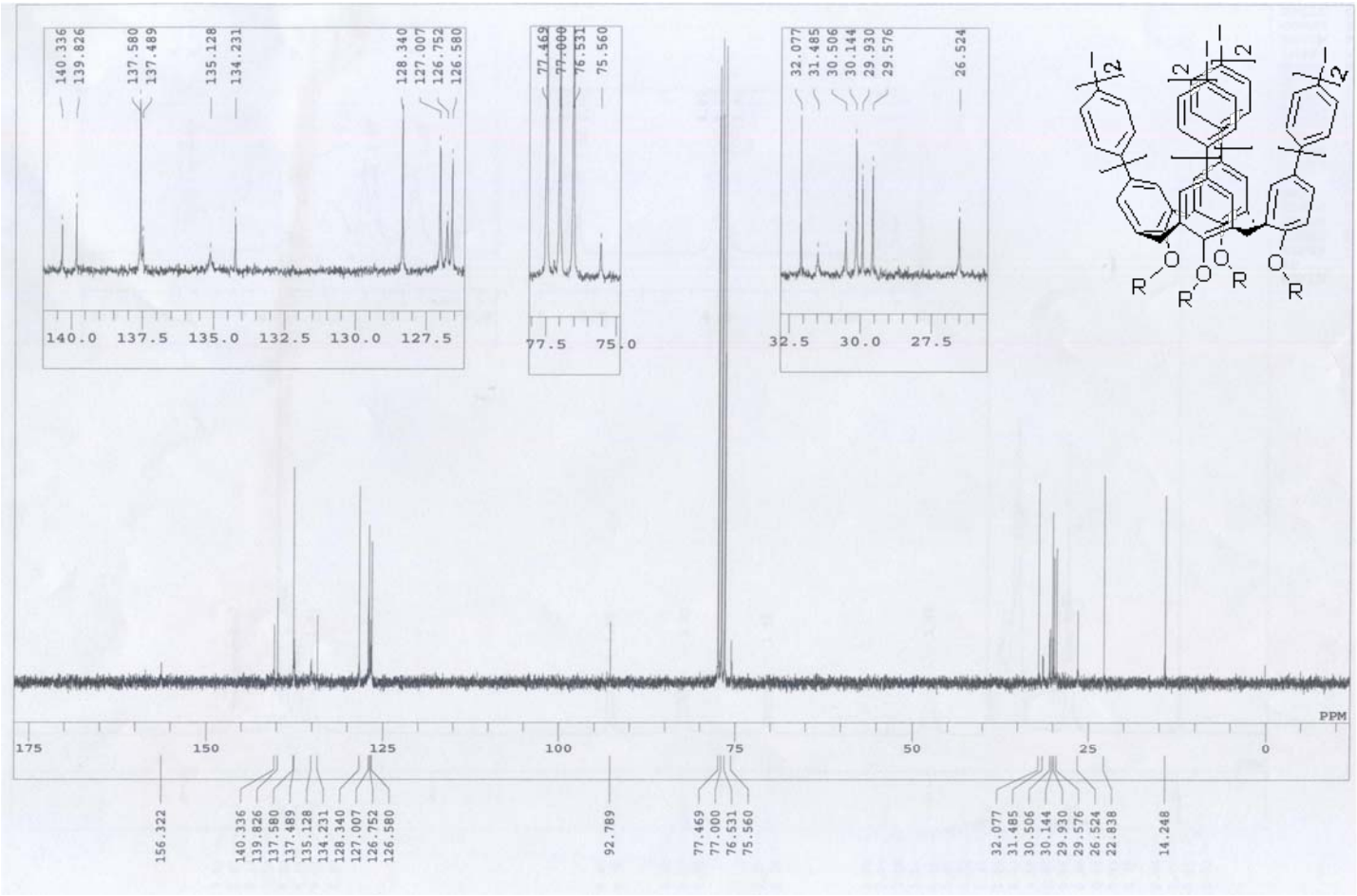
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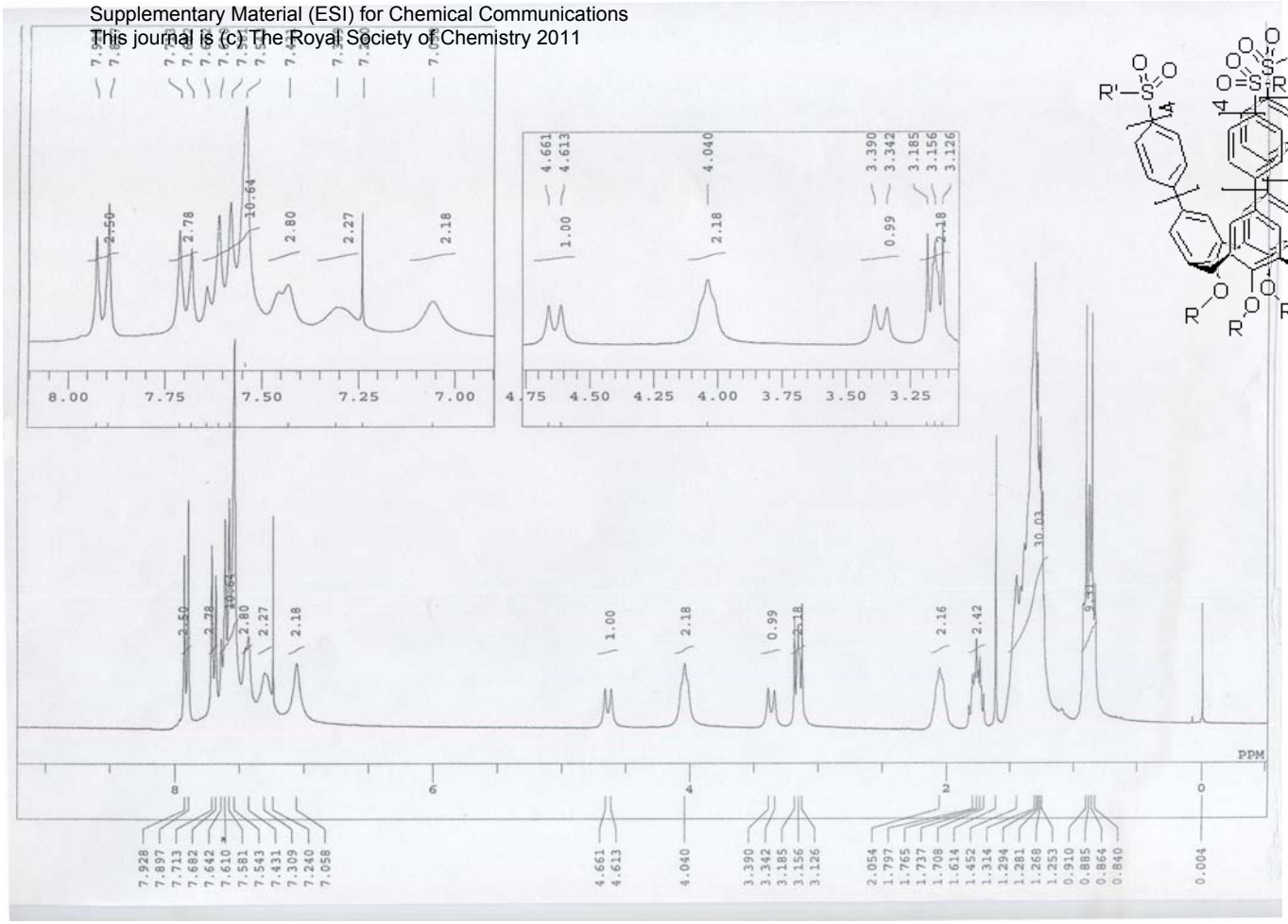
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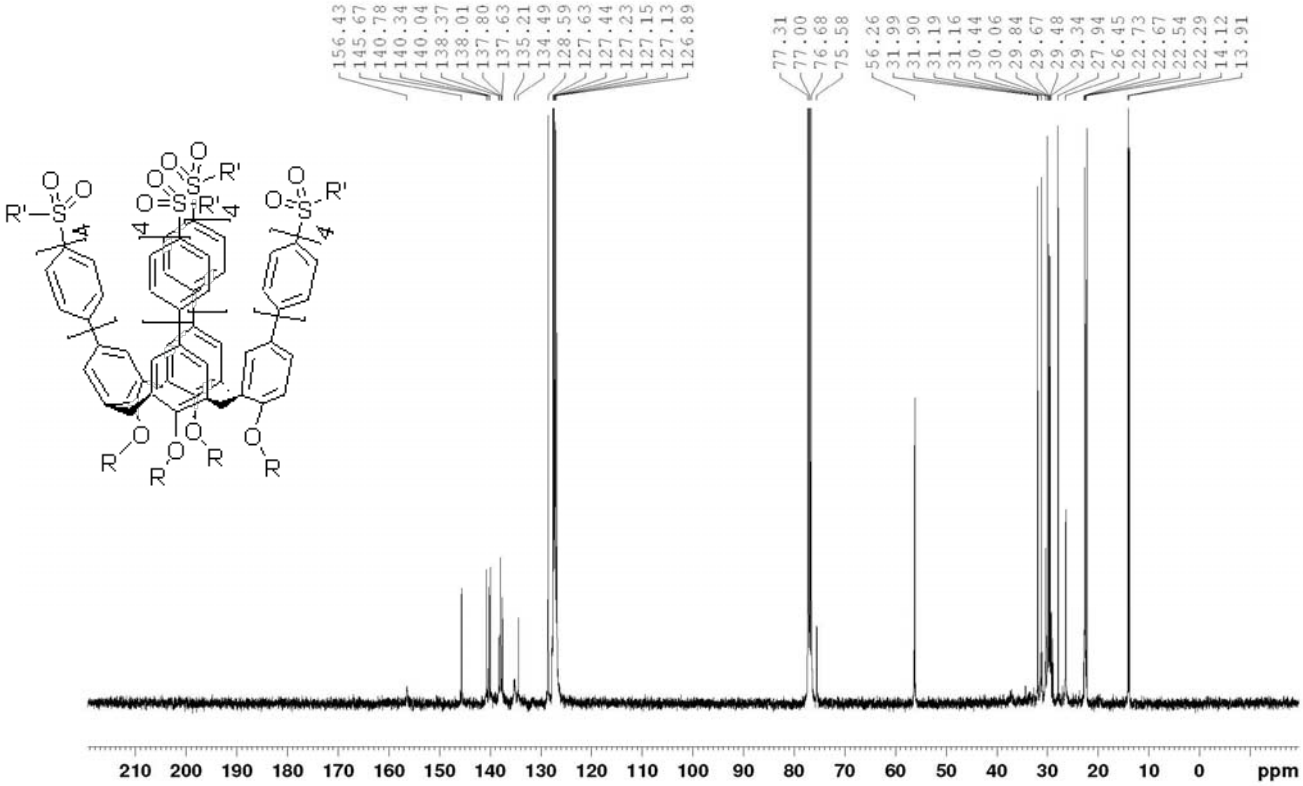
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