## Supporting Information:

# Carbazole-based Compounds as Photoinitiators for Free Radical and Cationic Polymerization Upon near Visible Light Illumination.

Assi Al Mousawi[a,b], Ahmad Arar[a], Malika Ibrahim-Ouali[c], Sylvain Duval[d]

Frédéric Dumur*[e], Patxi Garra[a], Joumana Toufaily[b], Tayssir Hamieh[b], Bernadette Graff[a], Didier Gigmes[e], Jean Pierre Fouassier[a], Jacques Lalevée*[a]

[a] Institut de Science des Matériaux de Mulhouse IS2M – UMR CNRS 7361 – UHA, 15, rue Jean Starcky, 68057 Mulhouse Cedex, France.
[b] Laboratoire de Matériaux, Catalyse, Environnement et Méthodes analytiques (MCEMA-CHAMSI), EDST, Université Libanaise, Campus Hariri, Hadath, Beyrouth, Liban.
[c] Aix-Marseille Univ, CNRS, Centrale Marseille, iSm2, Marseille, France.
[d] Unité de Catalyse et Chimie du Solide (UCCS) – UMR CNRS 8181, Université de Lille, ENSCL, Bat C7, BP 90108, 59652 VilleneUVe d'Ascq, France.
[e] Aix Marseille Univ, CNRS, ICR UMR 7273, F-13397 Marseille, France.

***Corresponding authors:** jacques.lalevee@uha.fr; frederic.dumur@univ-amu.fr

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software. $^{1}H$ and $^{13}C$ NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: $^{1}H$ (400 MHz) and $^{13}C$ (100 MHz). The $^{1}H$ chemical shifts were referenced to the solvent peaks $CDCl_3$ (7.26 ppm), DMSO (2.49 ppm) and the $^{13}C$ chemical shifts were referenced to the solvent peak $CDCl_3$ (77 ppm), DMSO (49.5 ppm). All these carbazole photoinitiators were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis. 1,4-Dimethyl-carbazole **1** was synthesized as previously reported, without modifications and in similar yields. [B. Vehar, M. Hrast, A. Kovac, J. Konc, K. Mariner, I. Chopra, A. O'Neill, D. Janezic, S. Gobec, Bioorg. Med. Chem. 19 (2011) 5137-5146] X-ray analyses were performed at 100K under a nitrogen flow. X-ray intensity data were collected on a Bruker X8-APEX2 CCD area-detector diffractometer using Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) with an optical fiber as collimator. Several sets of narrow data frames (10 s per frame) were collected at different values of θ for two initial values of ϕ and ω, respectively, using 0.3° increments of ϕ or ω. Data reduction was accomplished using SAINT V8.34a.[1] The substantial redundancy in data allowed a semi-empirical absorption correction (SADABS V2014/5)[2] to be applied, on the basis of multiple measurements of equivalent reflections. The structure was solved by direct methods, developed by successive difference Fourier syntheses, and refined by full-matrix least-squares on all $F^2$ data using SHELX program suite.[3] Hydrogen atoms were included in calculated positions and allowed to ride on their parent atoms. The final refinements include anisotropic thermal parameters of all non-hydrogen atoms. The crystal data are given in Table S1. Supporting information is available in CIF format.

References

1 *SAINT Plus Version 7.53a; Brucker Analytical X-ray Systems: Madison, WI, 2008.*

2 G.M. Sheldrick, *SADABS, Brucker-Siemens Area detector Absorption and Other Correction, Version 2008/1; Brucker: Madison, WI, 2008.*

3 G.M. Sheldrick, *Acta Crystallogr. A* 2008, **64**, 112-122.

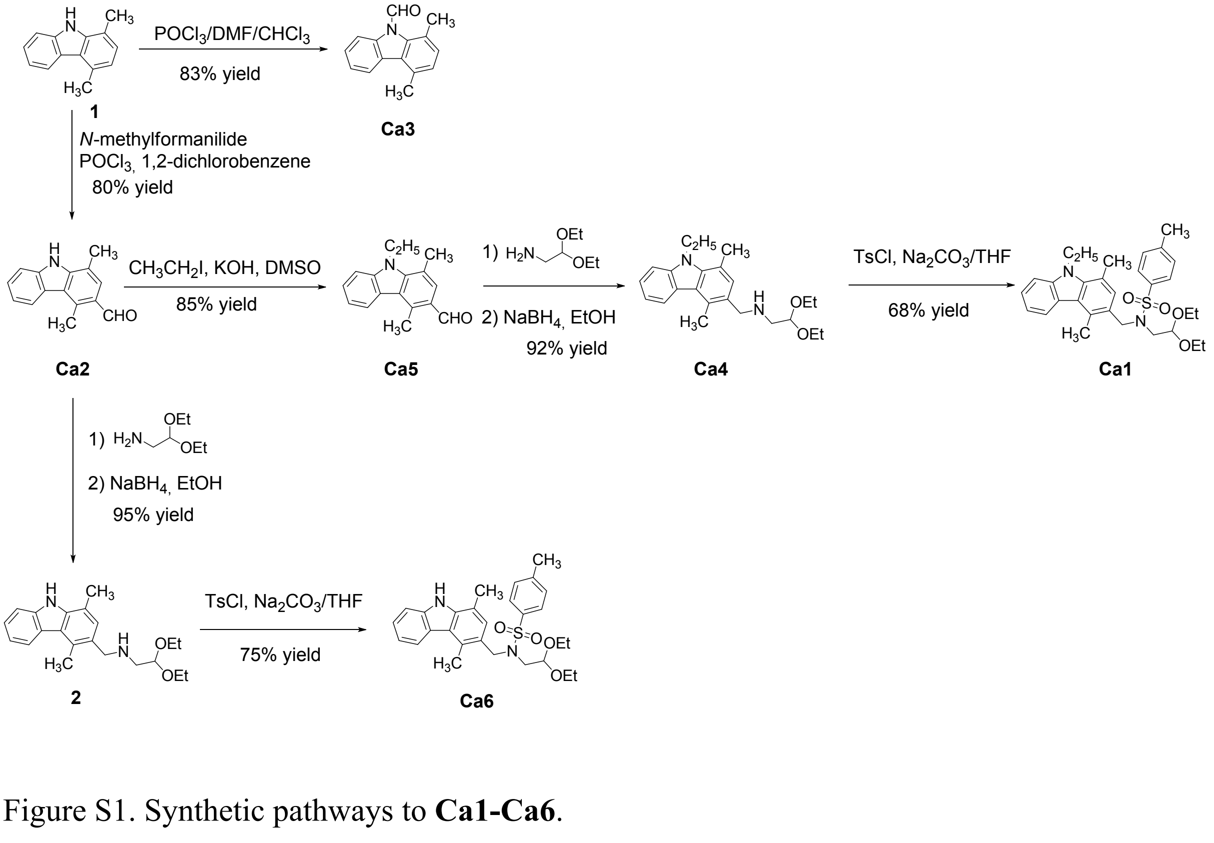
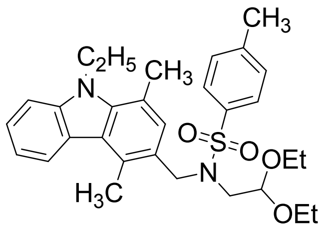


Figure S1. Synthetic pathways to **Ca1-Ca6**.

*Synthesis of N-(2,2-diethoxyethyl)-N-((9-ethyl-1,4-dimethyl-9H-carbazol-3-yl)methyl)-4-methylbenzenesulfonamide* ***Ca1***



To a mixture of *N*-((1,4-dimethyl-9-ethylcarbazol-3-yl)methyl)-2,2-diethoxy-ethanamine (2.5 g, 6.78 mmol) and $Na_2CO_3$ (0.84 g, 8.0 mmol, 1.2 eq.) in THF (35 mL) and water (18 mL), *p*-toluenesulfonyl chloride (1.64 g, 8.78 mmol) was added at room temperature. The reaction mixture was stirred for 2 h during which time a white precipitate formed. The reaction mixture was diluted with water. The white precipitate was filtered off, washed several times with pentane and dried under vacuum. The solid was purified by dissolution in a minimum of THF. Heptane was added until the solution became slightly turbid and the solution was cooled at -30°C overnight. During the night, a precipitate formed. It was filtered off, washed several times with pentane and dried under vacuum (2.41 g, 68% yield).

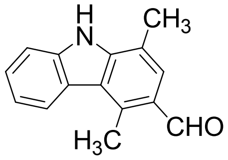
$^1$H NMR (DMSO-d$_6$) δ 0.91 (t, 6H, J = 7.0 Hz), 1.29 (t, 3H, J = 6.9 Hz), 2.39 (s, 3H), 2.68 (s, 3H), 2.75 (s, 3H), 3.04 (d, 2H, J = 5.3 Hz), 3.10-3.15 (m, 2H), 3.29-3.36 (m, 2H), 4.10 (t, 1H, J = 5.3 Hz), 4.51 (s, 2H), 4.60 (q, 2H, J = 6.8 Hz), 6.97 (s, 1H), 7.21 (t, 1H, J = 7.5 Hz), 7.42 (d, 2H, J = 8.1 Hz), 7.45 (t, 1H, J = 7.8 Hz), 7.61 (d, 2H, J = 8.3 Hz), 7.76 (d, 2H, J = 8.1 Hz), 8.20 (d, 1H, J = 7.9 Hz)

$^1$H NMR ($CDCl_3$) δ 1.10 (t, 6H, J = 7.0 Hz), 1.42 (t, 3H, J = 7.1 Hz), 2.41 (s, 3H), 2.71 (s, 3H), 2.83 (s, 3H), 3.23 (d, 2H, J = 5.4 Hz), 3.30-3.37 (m, 2H), 3.51-3.57 (m, 2H), 4.44 (t, 1H, J = 5.4 Hz), 4.60 (q, 2H, J = 7.1 Hz), 4.69 (s, 2H), 6.93 (s, 1H), 7.24-7.30 (m, 3H), 7.43-7.50 (m, 2H), 7.76 (d, 2H, J = 8.2 Hz), 8.25 (d, 1H, J = 7.9 Hz)

$^{13}$C NMR ($CDCl_3$) δ 15.2, 15.4, 16.1, 19.9, 21.4, 39.2, 49.5, 50.7, 63.1, 102.0, 108.4, 116.8, 119.0, 122.9, 123.0, 123.7, 123.9, 124.9, 127.3, 129.4, 131.1, 131.5, 137.5, 138.4, 140.9, 143.0

HRMS (ESI MS) m/z: theor: 522.2552 found: 522.2552 ($[M]^{+\cdot}$ detected)

*Synthesis of 1,4-dimethyl-9H-carbazole-3-carbaldehyde* ***Ca2***



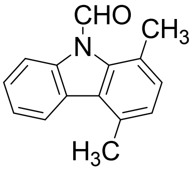
*N*-methylformanilide (2.4 mL, 19.2 mmol) and phosphorus oxychloride (1.45 mL, 16 mmol) in 1,2-dichlorobenzene (20 mL) were stirred for 0.5 h at room temperature. Then 1,4-dimethyl-carbazole (2.52 g, 11.3 mmol) in 1,2-dichlorobenzene (20 mL) was added and the reaction mixture was heated at 105 °C for 4 h. The reaction mixture was cooled to room temperature and sodium acetate (5 g) in water (50 mL) was added. The black solid was filtered off and the filtrate was concentrated under reduced pressure. Addition of THF and pentane precipitated a second black solid that was filtered off. The filtrate was once again concentrated under reduced pressure. Addition of THF and filtration on a plug of silicagel provided the title molecule as a light beige solid (2.02 g, 80% yield).

$^1$H NMR ($CDCl_3$) δ 2.57 (s, 3H, $CH_3$), 3.19 (s, 3H, $CH_3$), 7.32 (t, 1H, J = 7.3 Hz), 7.44-7.54 (m, 2H), 7.76 (s, 1H), 8.27 (d, 1H, J = 8.4 Hz), 8.31 (brs, 1H, NH), 10.46 (s, 1H, CHO)

$^{13}$C NMR ($CDCl_3$) δ 14.9, 16.8, 111.8, 118.3, 120.0, 121.5, 123.0, 123.8, 125.8, 125.9, 128.3, 135.9, 140.7, 142.5, 191.7

HRMS (ESI MS) m/z: theor: 223.0997 found: 223.0998 ($[M]^{+\cdot}$ detected)

*Synthesis of 1,4-dimethyl-9H-carbazole-9-carbaldehyde* ***Ca3***



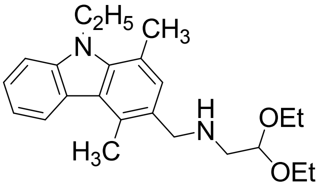
A solution of $CHCl_3$ (25 mL) containing 1,4-dimethyl-9*H*-carbazole (7.22 g, 37 mmol) and DMF (4 mL) was cooled to 0°C. $POC1_3$ (5 mL) was slowly added at 0°C and the solution was allowed to stir to room temperature for one hour. Then, the solution mixture was refluxed for 16 h. After cooling, the solution was poured into ice water. The resulting solution was extracted with chloroform several times. The organic phases were combined, dried over magnesium sulfate and the solvent removed under reduced pressure. Dissolution in a minimum of chloroform and addition of pentane precipitated a black solid which was filtered off, washed numerous times with pentane. The filtrate was concentrated under reduced pressure. Addition of ethanol precipitated a white solid that was filtered off, washed with ethanol and dried under reduced pressure (6.9 g, 83% yield).

$^1$H NMR ($CDCl_3$) δ 2.72 (s, 3H), 2.80 (s, 3H), 7.09 (d, 1H, J = 7.6 Hz), 7.18 (d, 1H, J = 7.6 Hz), 7.44 (td, 1H, J = 7.5 Hz, J = 1.1 Hz), 7.51 (td, 1H, J = 7.5 Hz, J = 1.1 Hz), 8.09 (d, 1H, J = 7.5 Hz), 8.72 (d, 1H, J = 8.1 Hz), 9.97 (s, 1H)

$^{13}$C NMR ($CDCl_3$) δ 20.7, 22.6, 117.3, 119.6, 122.2, 124.7, 125.4, 126.0, 127.0, 127.3, 130.6, 131.6, 136.6, 137.8, 160.3

HRMS (ESI MS) m/z: theor: 223.0997 found: 223.0995 ($[M]^{+\cdot}$ detected)

*Synthesis of 2,2-diethoxy-N-((9-ethyl-1,4-dimethyl-9H-carbazol-3-yl)methyl) ethanamine **Ca4***



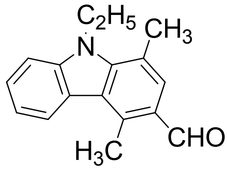
A mixture of 1,4-dimethyl-9-ethylcarbazole-3-carbaldehyde (3.5 g, 13.92 mmol, 1 eq.) and amino-acetaldehyde diethyl acetal (7.1 mL, 48.7 mmol, 3.5 eq.) was stirred at 115 °C under argon atmosphere for 3 h. The reaction mixture was cooled to room temperature. Anhydrous ethanol (50 mL) with activated molecular sieves was added. Sodium borohydride (2.10 g, 55.68 mmol, 4 eq., M = 37.83 g/mol) was added and the reaction mixture was stirred overnight and concentrated to dryness in vacuum. The residue was dissolved in ethyl acetate, washed with dil. HCl, water, saturated aqueous $NaHCO_3$, dried over magnesium sulfate and concentrated to give a light yellow oil that was purified by flash chromatography ($CHCl_3$) (4.72 g, 92% yield).

$^1$H NMR ($CDCl_3$) δ 1.31 (t, 6H, J = 7.0 Hz), 1.53 (t, 3H, J = 7.1 Hz), 1.76 (brs, 1H, NH), 2.91 (s, 3H), 2.97 (d, 2H, J = 5.6 Hz), 2.98 (s, 3H), 3.62-3.69 (m, 2H), 3.77-3.85 (m, 2H), 4.08 (s, 2H), 4.71 (q, 2H, J = 7.1 Hz), 4.78 (t, 1H, J = 5.6 Hz), 7.35 (td, 1H, J = 6.6 Hz, J = 1.5 Hz), 7.54 (d, 1H, J = 7.4 Hz), 7.58 (td, 2H, J = 8.1 Hz, J= 1.0 Hz), 8.38 (d, 1H, J = 7.9 Hz)

$^{13}$C NMR ($CDCl_3$) δ 15.4, 15.5, 16.1, 20.0, 39.2, 51.6, 51.9, 62.2, 102.3, 108.4, 116.8, 118.8, 123.0, 124.1, 124.8, 128.7, 129.7, 131.1, 138.1, 141.1

HRMS (ESI MS) m/z: theor: 368.2464 found: 368.2465 ($[M]^{+\cdot}$ detected)

*Synthesis of 9-ethyl-1,4-dimethyl-9H-carbazole-3-carbaldehyde **Ca5***



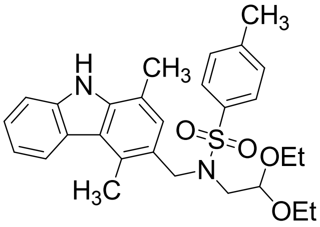
KOH (3.6 g, 64.1 mmol), 1,4-dimethyl-9*H*-carbazole-3-carbaldehyde (3.6 g, 16.1 mmol), and DMSO (20 mL) were mixed at room temperature for 30 min. Then, ethyl iodide (5.05 g, 2.60 mL, 32.4 mmol) was added and stirring was continued overnight. The reaction mixture was diluted with water (100 mL) and extracted with EtOAc several times. The organic phases were combined, dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was purified by filtration on a plug of silicagel using DCM as the eluent. Dissolution in a minimum of THF and addition of pentane precipitated a white solid that was filtered off, washed several times with pentane and dried under vacuum (3.44 g, 85% yield).

$^1$H NMR ($CDCl_3$) δ 1.45 (t, 3H, J = 7.2 Hz), 2.81 (s, 3H), 3.14 (s, 3H), 4.58 (q, 2H, J = 7.1 Hz), 7.33 (td, 1H, J = 8.0 Hz, J= 1.1 Hz), 7.46 (d, 1H, J = 8.2 Hz), 7.52 (td, 1H, J = 8.2 Hz, J = 1.1 Hz), 7.68 (s, 1H), 8.27 (d, 1H, J = 8.0 Hz), 10.4 (s, 1H, CHO)

$^{13}$C NMR ($CDCl_3$) δ 15.1, 15.7, 20.2, 39.5, 109.1, 117.7, 120.3, 123.1, 123.4, 124.1, 125.8, 126.1, 131.6, 136.6, 141.2, 141.9, 191.4

HRMS (ESI MS) m/z: theor: 251.1310 found: 251.1308 ($[M]^{+\cdot}$ detected)

*Synthesis of N-(2,2-diethoxyethyl)-N-((1,4-dimethyl-9H-carbazol-3-yl)methyl)-4-methyl-benzenesulfonamide* ***Ca6***



To a mixture of *N*-((1,4-dimethyl-9*H*-carbazol-3-yl)methyl)-2,2-diethoxyethanamine **Ca4** (1.26 g, 3.7 mmol) and $Na_2CO_3$ (0.46 g, 4.4 mmol) in tetrahydrofuran (20 mL) and water (10 mL), *p*-toluenesulfonyl chloride (0.9 g, 4.8 mmol) was added at room temperature. The reaction mixture was stirred for 2 h, diluted with water and extracted with ethyl acetate. The combined organic layers were washed with 0.1 M HCl, water, saturated solution of $NaHCO_3$ and water. After drying over magnesium sulfate, the solvent was concentrated under reduced pressure. The residue was purified by filtration on a plug of silicagel using DCM as the eluent. Dissolution in a minimum of THF and addition of pentane precipitated a white solid that was filtered off, washed several times with pentane and dried under vacuum (1.37 g, 75% yield). Crystals suitable for single crystal X-ray diffraction were obtained from a concentrated dissolution in THF/pentane (1:1) $^1$H NMR (DMSO-$d_6$) δ 0.91 (t, 6H, J = 7.0 Hz), 2.41 (s, 3H), 2.44 (s, 3H), 2.76 (s, 3H), 3.04 (d, 2H, J = 5.4 Hz), 3.08-3.13 (m, 2H), 3.31-3.35 (m, 2H), 4.08 (t, 1H, J = 5.4 Hz), 4.51 (s, 2H), 6.98 (s, 1H), 7.17 (td, 1H, J = 8.0 Hz, J = 0.9 Hz), 7.38

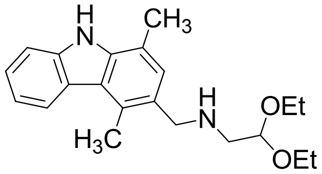
(td, 1H, J = 8.0 Hz, J = 0.9 Hz), 7.44 (d, 2H, J = 8.0 Hz), 7.52 (d, 1H, J = 8.0 Hz), 7.78 (d, 2H, J = 8.2 Hz), 8.17 (d, 1H, J = 8.0 Hz), 11.18 (brs, 1H, NH)

$^1$H NMR ($CDCl_3$) δ 1.00 (t, 6H, J = 7.0 Hz), 2.32 (s, 3H), 2.35 (s, 3H), 2.73 (s, 3H), 3.12 (d, 1H, J = 5.4 Hz), 3.19-3.27 (m, 2H), 3.41-3.48 (m, 2H), 4.35 (t, 1H, J = 5.4 Hz), 4.59 (s, 2H), 6.89 (s, 1H), 7.14-7.21 (m, 4H), 7.33 (td, 1H, J = 8.1 Hz, J = 1.1 Hz), 7.40 (d, 1H, J = 7.9 Hz), 7.66 (d, 2H, J = 8.3 Hz), 7.92 (s, 1H), 8.12 (d, 1H, J = 7.9 Hz)

$^{13}$C NMR ($CDCl_3$) δ 15.2, 15.9, 16.4, 21.4, 49.5, 50.8, 63.1, 102.0, 110.6, 116.6, 119.5, 122.0, 122.8, 124.2, 124.5, 125.0, 127.3, 128.9, 129.5, 130.6, 137.4, 138.5, 139.7, 143.1

HRMS (ESI MS) m/z: theor: 494.2239 found: 494.2241 ([M]$^{+\cdot}$ detected)

*Synthesis of N-((1,4-dimethyl-9H-carbazol-3-yl)methyl)-2,2-diethoxyethanamine* ***2***



A mixture of 1,4-dimethyl-9*H*-carbazole-3-carbaldehyde (1.0 g, 4.5 mmol) and amino-acetaldehyde diethyl acetal (2.3 mL, 15.7 mmol) was stirred at 115 °C under argon atmosphere for 3 h. The reaction mixture was cooled to room temperature. Anhydrous ethanol (50 mL) with activated molecular sieves was added. Sodium borohydride (0.68 g, 18 mmol) was added and the reaction mixture was stirred for 1 h and concentrated to dryness in vacuum. The residue was dissolved in ethyl acetate, washed with water, dried and concentrated to give a brown viscous gum that was purified by flash chromatography (ethyl acetate:hexane 4:1) to give a yellowish product (1.45 g, 95% yield).

$^1$H NMR ($CDCl_3$) δ 1.24 (t, 6H, J = 7.1 Hz, $\underline{CH_3}$-$CH_2$), 1.58 (brs, 1H, NH), 2.51 (s, 3H, $CH_{3arom}$), 2.87-2.89 (m, 5H, $CH_{3arom}$ + NH–$\underline{CH_2}$–CH), 3.51-3.61 (m, 2H, $\underline{CH_2}$-$CH_3$), 3.66-3.76 (m, 2H, $\underline{CH_2}$-$CH_3$), 4.00 (s, 2H, NH-$\underline{CH_2}$-Ar), 4.69 (t, 1H, J = 5.7 Hz, CH), 7.20 (s, 1H), 7.23-7.26 (m, 1H), 7.42-7,45 (m, 1H), 7.48 (d, 1H, J = 7.5 Hz), 8.14 (brs, 1H, NH), 8.26 (d, 1H, J = 7.9 Hz)

$^{13}$C NMR ($CDCl_3$) δ 15.4, 15.8, 16.5, 25.6, 51.7, 62.3, 67.9, 102.1, 110.5, 116.7, 119.3, 122.1, 122.8, 124.6, 124.9, 128.5, 129.2, 138.3, 139.9

Table S1. Selected crystallographic data for **Ca6**

| | |
|---|---|
| Formula | $C_{28}H_{34}N_2O_4S$ |
| Formula weight | 494.55 |
| Temperature/K | 100 |

| | |
|---|---|
| Crystal color | colorless |
| Crystal size/mm | 0.1 x 0.02 x 0.02 |
| Crystal system | Triclinic |
| Space group | *P-1* |
| $a$/Å | 10.0007(10) |
| $b$/Å | 10.5374(11) |
| $c$/Å | 12.7404(13) |
| $\alpha$/° | 102.821(4) |
| $\beta$/° | 90.215(4) |
| $\gamma$° | 102.546(2) |
| Volume/Å$^3$ | 1275.9(2) |
| Z, $\rho_{calculated}$/g.cm$^{-3}$ | 2, 1.287 |
| $\mu$/mm$^{-1}$ | 0.164 |
| $\Theta$ range/° | 1.642-26.4 |
| Limiting indices | $-12 \leq h \leq 12$<br>$-13 \leq k \leq 9$<br>$-15 \leq l \leq 15$ |
| Collected reflections | 23651 |
| Unique reflections | 5138<br>[R(int) = 0.0378] |
| Parameters | 322 |
| Goodness-of-fit on F$^2$ | 1.041 |
| Final R indices [I>2$\sigma$(I)] | R1 = 0.0519<br>wR2 = 0.1223 |
| R indices (all data) | R1 = 0.0687<br>wR2 = 0.1328 |
| Largest diff. peak and hole/e.Å$^{-3}$ | 1.15 and -0.51 |

Figure S2. Single crystal X-ray structure of **Ca6**