

## Supplementary Information

### Stable organic azides based on rigid tetrahedral methane and adamantane structures as high energetic materials

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Experimental procedures and spectral characterization for **3d**, **4a-d**, **5d**.

**General methods.** <sup>1</sup>H NMR: Bruker AC 250 (250 MHz), Bruker AM 400 (400 MHz);  $\delta$  = 7.26 ppm for CDCl<sub>3</sub>. The description of signals include: s = singlet, d = doublet, m = multiplet, dd = doublet of doublet. The spectra were analyzed according to first order. All coupling constants (*J*) are absolute values. The signal abbreviations include: Ar-H = aromatic proton. <sup>13</sup>C-NMR: Bruker AM 400 (400 MHz);  $\delta$  = 77.00 ppm for CDCl<sub>3</sub>. The signal structure was analyzed by DEPT and is described as follows: + = primary or tertiary C-atom (positive signal = secondary C-atom (negative signal and q = quaternary C-atom (no signal) MS (EI) (electron impact mass spectrometry): Finnigan MAT 90 (70 eV). The molecular fragments are quoted as the relation between mass and charge (m/z), the intensities as a percentage value relative to the intensity of the base signal (100%). The molecular ion obtains the abbreviation [M<sup>+</sup>]. IR (infrared spectroscopy): FT-IR Bruker IFS 88. IR spectra of solids were recorded in KBr. The deposit of the absorption band was given in wave numbers  $\tilde{\nu}$  in cm<sup>-1</sup>. The forms and intensities of the bands were characterized as follows: vs = very strong 0-10% T, s = strong 10-40% T, m = medium 40-70% T, w = weak 70-90% T, vw = very weak, 90-100% T, br = broad. Elemental analysis: Haraeus CHN-O-Rapid. Descriptions without nominated temperature were done at room temperature (rt), whereas there were used the following abbreviations: calc. (theoretical value), found (measured value). Information is given in mass percent. – TLC (Thin layer chromatography): Silica gel coated aluminum plates (Merck, silica gel 60, F254), detected under UV-light at 254 nm. Solvent mixtures are understood as volume/volume. Solid materials were powdered. Solvents, reagents and chemicals were purchased from Aldrich, Fluka, Janssen, and Merck. Ethyl acetate, diethyl ether and dichloromethane were distilled prior to use. All other solvents, reagents and chemicals were used as purchased.

**Tetrakis(4-azidophenyl)methane (3d).** Tetrakis(4-iodophenyl)methane (**1**) (84.0 mg, 0.10 mmol, 1.0 equiv.) was solved under argon in 15 mL DMSO at 100 °C and stirred rapidly. To the resulting clear solution, sodium azide (104 mg, 1.60 mmol, 16 equiv.), sodium ascorbate (7.92 mg, 0.04 mmol, 0.4 equiv.), CuI (15.2 mg, 0.08 mmol, 0.8 equiv.), *N,N'*-dimethylethylenediamine (13.1  $\mu$ L, 0.12 mmol, 1.2 equiv, solved in 6 mL DMSO/H<sub>2</sub>O (5:1) at 60 °C), were added *via* syringe pump (0.54 mL/h) to the prepared solution of **1** dropwise and stirred for 48 h at 100 °C.

The resulting brown mixture was cooled down and taken-up in 50 mL of brine. After extraction with ethylacetate (2  $\times$  20 mL), the organic phase was dried over MgSO<sub>4</sub> and the solvent removed under reduced pressure afterwards. Tetrakis(4-azidophenyl)methane (**3d**) was purified by flash chromatography on silica gel (2  $\times$  20 cm, cyclohexane/CH<sub>2</sub>Cl<sub>2</sub>, 5:1) and isolated as a brown solid (20.0 mg, 0.04 mmol, 41%). – *R*<sub>f</sub> = 0.36 (cyclohexane/CH<sub>2</sub>Cl<sub>2</sub>, 5:1). – <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.9 (dd, <sup>3</sup>*J* = 8.8 Hz, <sup>4</sup>*J* = 4.9 Hz, 8 H, Ar<sub>o</sub>-H), 7.13 (dd, <sup>3</sup>*J* = 8.8 Hz, <sup>4</sup>*J* = 4.9 Hz, 8 H, Ar<sub>m</sub>-H) ppm. – <sup>13</sup>C-NMR (100 Hz, CDCl<sub>3</sub>):  $\delta$  = 142.9 (C<sub>q</sub>, Ar<sub>p</sub>-N<sub>3</sub>), 138.2 (C<sub>q</sub>, Ar-N<sub>3</sub>), 132.0 (+, C<sub>m</sub>, Ar-N<sub>3</sub>), 132.3 (+, C<sub>o</sub>, Ar-N<sub>3</sub>), 63.2 (C<sub>q</sub>, C(Ar-N<sub>3</sub>)<sub>4</sub>) ppm. – MS (70 eV, EI), m/z (%): 484 (100) [M<sup>+</sup>], 456 (56) [M<sup>+</sup>-N<sub>2</sub>, C<sub>25</sub>H<sub>16</sub>N<sub>10</sub>], 443 (26) [M<sup>+</sup>-N<sub>3</sub>, C<sub>25</sub>H<sub>16</sub>N<sub>9</sub>], 415 (16) [M<sup>+</sup>-N<sub>5</sub>, C<sub>25</sub>H<sub>16</sub>N<sub>7</sub>], 400 (1) [M<sup>+</sup>-N<sub>6</sub>, C<sub>25</sub>H<sub>16</sub>N<sub>5</sub>], 372 (8) [M<sup>+</sup>-N<sub>8</sub>, C<sub>25</sub>H<sub>16</sub>N<sub>4</sub>], 358 (19) [M<sup>+</sup>-N<sub>9</sub>, C<sub>25</sub>H<sub>16</sub>N<sub>3</sub>], 343 (56) [M<sup>+</sup>-N<sub>10</sub>, C<sub>25</sub>H<sub>16</sub>N<sub>2</sub>], 316 (34) [M<sup>+</sup>-N<sub>12</sub>, C<sub>25</sub>H<sub>16</sub>]. – IR (KBr):  $\tilde{\nu}$  = 3399 (br, vw), 3238 (vw), 3032 [w,  $\tilde{\nu}_{\text{Ar}}(\text{C-H})$ ], 2923 (vw), 2545 (vw), 2412 (w), 2923 (vw), 2545 (vw), 2412 (w), 2323 (vw), 2251 (w), 2137 [m,  $\tilde{\nu}_{\text{Ar}}(\text{N}_3)$ ], 1601 (w), 1577 (w), 1501 [m,  $\tilde{\nu}_{\text{Ar}}(\text{C=C})$ ], 1413 (w), 1290 (m), 1191 (m), 1130 (w), 1118 (w), 1017 (w), 945 (vw), 911 (vw), 829 [m,  $\tilde{\nu}_{\text{Ar}}(\text{p-subst.})$ ], 756 (w), 702 (w), 670 (w), 554 (w), 537 (m), 418 (vw) cm<sup>-1</sup>. – HRMS Calcd for C<sub>25</sub>H<sub>16</sub>N<sub>12</sub> 484.1620, found 484.1616. – UV/VIS (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 227 (4.4), 260 (4.7) nm.

**1,3,5,7-tetrakis(4-azidophenyl)adamantane (4d). A. From 2.** 1,3,5,7-tetrakis(4-iodophenyl)adamantane (**2**) (400 mg, 0.42 mmol, 1.0 equiv.) was solved in 10 mL DMSO under argon while heating at 100 °C and stirring rapidly. Sodium azide (474 mg, 6.72 mmol, 16 equiv.), sodium ascorbate (33.3 mg, 0.17 mmol, 0.4 equiv.), CuI (64.0 mg, 0.34 mmol, 0.8 equiv.), *N,N'*-dimethylethylenediamine (55.0  $\mu$ L 0.50 mmol, 1.2 equiv.) were solved in 23 mL DMSO/H<sub>2</sub>O (20:3) at 60 °C. The resulting green solution was added *via* syringe pump (0.5 mL/hr) to the clear solution of compound **2** in DMSO and stirred at 100 °C. After 48 h, the mixture was cooled down and taken-up in a saturated NaCl/ethylacetate-mixture (50 mL, 1:1). A brown precipitate was filtered, the solution extracted with ethylacetate (2  $\times$  20 mL) and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and 1,3,5,7-tetrakis(4-azidophenyl)adamantane (**4d**) was isolated as a white solid after purification by flash chromatography on silica gel (4  $\times$  20 cm, cyclohexane/CH<sub>2</sub>Cl<sub>2</sub>, 1:1) in 34 % yield (85.0 mg, 0.14 mmol). –  $R_f$  = 0.28 (cyclohexane/ CH<sub>2</sub>Cl<sub>2</sub> 1:1). – <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.10 (s, 12 H, Ad-CH<sub>2</sub>), 7.02 (d, <sup>3</sup>*J* = 8.64, 8 H, Ar<sub>o</sub>-H), 7.45 (d, <sup>3</sup>*J* = 8.64, 8 H, Ar<sub>m</sub>-H) ppm. – <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 145.5 (C<sub>q</sub>, Ar<sub>p</sub>-N<sub>3</sub>), 137.8 (C<sub>q</sub>, Ar-Ad), 126.1(+, C<sub>o</sub>-Ar), 118.7 (+, C<sub>m</sub>-Ar), 46.9 (–, C<sub>s</sub>-Ad), 26.6 (C<sub>q</sub>-Ad) ppm. – IR (KBr):  $\tilde{\nu}$  = 3395 (vw), 3244 (vw), 3033 [w,  $\tilde{\nu}_{\text{Ar}}(\text{C-H})$ ], 2929 (w), 2851 [w,  $\tilde{\nu}_{\text{Ad}}(\text{CH}_2)$ ], 2574 (vw), 2419 (w), 2326 (vw), 2259 (w), 2127 [m,  $\tilde{\nu}_{\text{Ar}}(\text{N}_3)$ ], 1953 (vw), 1893 (vw), 1768 (vw), 1604 (w), 1575 [w,  $\tilde{\nu}_{\text{Ar}}(\text{C=C})$ ], 1508 (m), 1445 (w), 1413 (w), 1356 (w), 1296 (m), 1190 (w), 1130 (w), 1014 (w), 892 (vw), 822 [m,  $\tilde{\nu}_{\text{Ar}}(\text{p-subst.})$ ], 770 (w), 671 (w), 561 (w), 532 (w) cm<sup>-1</sup>. – UV/VIS (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 256 (4.8) nm.

**1,3,5,7-tetrakis(4-azidophenyl)adamantane (4d). B. From 2.** 1,3,5,7-tetrakis(4-iodophenyl)adamantane (**2**) (400 mg, 0.42 mmol, 1.0 equiv.), sodium azide (220 mg, 3.39 mmol, 8.0 equiv.), sodium ascorbate (17.0 mg, 0.08 mmol, 0.2 equiv.), CuI (32.0 mg, 0.17 mmol, 0.4 equiv.) and *L*-proline (29 mg, 0.25 mmol, 0.6 equiv.) were solved in 6 mL DMSO/H<sub>2</sub>O and stirred for 48 h under argon at 100 °C.

The mixture was cooled down and taken-up in a saturated NaCl/ethylacetate-mixture (30 mL, 1:1). A brown precipitate was filtered, the solution extracted with ethylacetate (2  $\times$  10 mL) and dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure and 1,3,5,7-tetrakis(4-azidophenyl)adamantane (**4d**) (18.0 mg, 0.03 mmol, 7%) and its lower derivatives **4a-c** were isolated after purification by flash chromatography over silica gel (4  $\times$  20 cm, cyclohexane/ CH<sub>2</sub>Cl<sub>2</sub>, 5:1).

–  $R_f$  = 0.28 (cyclohexane/ CH<sub>2</sub>Cl<sub>2</sub>, 1:1).

**1,3,5-tris(4-iodophenyl)-7-(4-azidophenyl)adamantane (4a). First fraction.** The product was isolated as a white crystalline solid (9.00 mg, 0.01 mmol, 3% yield). –  $R_f$  = 0.40 (cyclohexane/ CH<sub>2</sub>Cl<sub>2</sub>, 5:1). – <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.07 (s, 12 H, Ad-CH<sub>2</sub>), 7.01 (dd, <sup>3</sup>*J* = 8.7 Hz, <sup>4</sup>*J* = 4.2 Hz, 2 H, Ar<sub>o</sub>(I)-H), 7.19 (dd, <sup>3</sup>*J* = 8.6 Hz, <sup>4</sup>*J* = 4.7 Hz, 6 H, Ar<sub>o</sub>(N<sub>3</sub>)-H), 7.42 (dd, <sup>3</sup>*J* = 8.7 Hz, <sup>4</sup>*J* = 4.2 Hz, 2 H, Ar<sub>m</sub>(I)-H), 7.67 (dd, <sup>3</sup>*J* = 8.6 Hz, <sup>4</sup>*J* = 4.7 Hz, 6 H, Ar<sub>m</sub>(N<sub>3</sub>)-H). – <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 148.5 (C<sub>q</sub>, Ar-I), 145.5 (C<sub>q</sub>, Ar-N<sub>3</sub>), 138.1 (C<sub>q</sub>, Ar<sub>p</sub>-N<sub>3</sub>), 137.5 (+, C<sub>m</sub>, Ar-I), 127.1 (+, C<sub>o</sub>, Ar-I), 126.4 (+, C<sub>o</sub>, Ar-N<sub>3</sub>), 119.0 (+, C<sub>m</sub>, Ar-N<sub>3</sub>), 91.7 (C<sub>q</sub>, Ar<sub>p</sub>-I), 46.8 (–, C<sub>s</sub>, Ad), 39.9 (C<sub>q</sub>, Ad) ppm. – IR (KBr):  $\tilde{\nu}$  = 3434 (br, vw), 3029 [vw,  $\tilde{\nu}_{\text{Ar}}(\text{C-H})$ ], 2929 (w), 2898 (vw), 2851 [vw,  $\tilde{\nu}_{\text{Ad}}(\text{CH}_2)$ ], 2415 (vw), 2125 [w,  $\tilde{\nu}_{\text{Ar}}(\text{N}_3)$ ], 1901 (vw), 1605 (vw), 1508 [w,  $\tilde{\nu}_{\text{Ar}}(\text{C=C})$ ], 1485 (w), 1444 (vw), 1391 (w), 1357 (w), 1187 (w), 1118 (w), 1066 [w,  $\tilde{\nu}_{\text{Ar}}(\text{C-I})$ ], 1002 (w), 891 (vw), 819 [w,  $\tilde{\nu}_{\text{Ar}}(\text{p-subst.})$ ], 779 (w), 668 (vw), 526 (w) cm<sup>-1</sup>. – MS (FAB, 3-NBA) *m/z* (%): 859 (42) [M<sup>+</sup>], 831 (78) [M<sup>+</sup>-N<sub>2</sub>, C<sub>34</sub>H<sub>28</sub>I<sub>3</sub>N<sub>3</sub>], 766 (100), 733 (49) [(M+H)<sup>+</sup>-I, C<sub>34</sub>H<sub>28</sub>I<sub>2</sub>N<sub>3</sub>], 723 (33), 705 (34). – UV/VIS (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (A) = 238 (0.8960) nm.

**1,3-bis(4-iodophenyl)-5,7-bis(4-azidophenyl)adamantane (4b). Second fraction.** It was received as a bright yellow solid (29.0 mg, 0.04 mmol, 9% yield). –  $R_f$  = 0.29 (cyclohexane/CH<sub>2</sub>Cl<sub>2</sub>, 5:1). – <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.08 (s, 12 H, Ad-CH<sub>2</sub>), 7.12 (dd, <sup>3</sup>*J* = 8.7 Hz, <sup>4</sup>*J* = 4.7 Hz, 4 H, Ar<sub>o</sub>(N<sub>3</sub>)-H), 7.20 (dd, <sup>3</sup>*J* = 8.6 Hz, <sup>4</sup>*J* = 4.2 Hz, 4 H, Ar<sub>o</sub>(I)-H), 7.43 (dd, <sup>3</sup>*J* = 8.7 Hz, <sup>4</sup>*J* = 4.7 Hz, 4 H, Ar<sub>m</sub>(N<sub>3</sub>)-H), 7.67 (dd, <sup>3</sup>*J* = 8.6 Hz, <sup>4</sup>*J* = 4.2 Hz, 4 H, Ar<sub>m</sub>(I)-H) ppm. – <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 148.5 (C<sub>q</sub>, Ar-I), 145.6 (C<sub>q</sub>, Ar-N<sub>3</sub>), 138.1 (C<sub>q</sub>, Ar<sub>p</sub>-N<sub>3</sub>), 137.5 (+, C<sub>m</sub>, Ar-I), 127.1 (+, C<sub>o</sub>, Ar-I), 126.4 (+, C<sub>o</sub>, Ar-N<sub>3</sub>), 119.0 (+, C<sub>m</sub>, Ar-N<sub>3</sub>), 91.7 (C<sub>q</sub>, Ar<sub>p</sub>-I), 46.8 (–, C<sub>s</sub>, Ad), 39.9 (C<sub>q</sub>, Ad) ppm. – IR (KBr):  $\tilde{\nu}$  = 3396 (br, vw), 3239 (vw), 3031 [w,  $\tilde{\nu}_{\text{Ar}}(\text{C-H})$ ], 2930 (w), 2851 [w,  $\tilde{\nu}_{\text{Ad}}(\text{CH}_2)$ ], 2575 (vw), 2415 (w), 2258 (w), 2123 [m,  $\tilde{\nu}_{\text{Ar}}(\text{N}_3)$ ], 1948 (w), 1901 (w), 1734 (w), 1654 (vw), 1605 (w), 1575 (w), 1508 [m,  $\tilde{\nu}_{\text{Ar}}(\text{C=C})$ ], 1486 (w), 1444 (w), 1412 (vw), 1390 (w), 1357 (w), 1286 (w), 1189 (w), 1116 (w), 1055 [w,  $\tilde{\nu}_{\text{Ar}}(\text{C-I})$ ], 1002 (w), 962 (w), 921 (vw), 891 (w), 819 [w,  $\tilde{\nu}_{\text{Ar}}(\text{p-subst.})$ ]. – UV/VIS (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (A) = 238 (0.2538), 254 (0.1581) nm.

**1-(4-iodophenyl)-3,5,7-tris(4-azidophenyl)adamantane (4c). Third fraction.** The product was purified by flash chromatography and isolated as a yellow solid (34.0 mg, 0.05 mmol, 12% yield). –  $R_f$  = 0.23 (cyclohexane/CH<sub>2</sub>Cl<sub>2</sub>, 5:1). – <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.08 (s, 12 H, Ad-CH<sub>2</sub>), 7.00 (dd, <sup>3</sup>*J* = 8.7 Hz, <sup>4</sup>*J* = 4.7 Hz, 6 H, Ar<sub>o</sub>(N<sub>3</sub>)-H), 7.21 (dd, <sup>3</sup>*J* = 8.6 Hz, <sup>4</sup>*J* = 4.3 Hz, 2 H, Ar<sub>o</sub>(I)-H), 7.44 (dd, <sup>3</sup>*J* = 8.7 Hz, <sup>4</sup>*J* = 4.7 Hz, 6 H, Ar<sub>m</sub>(N<sub>3</sub>)-H), 7.67 (dd, <sup>3</sup>*J* = 8.6 Hz, <sup>4</sup>*J* = 4.2 Hz, 2 H, Ar<sub>m</sub>(I)-H) ppm. – <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 148.5 (C<sub>q</sub>, Ar-I), 145.6 (C<sub>q</sub>, Ar-N<sub>3</sub>), 138.0 (C<sub>q</sub>, Ar<sub>p</sub>-N<sub>3</sub>), 137.4 (+, C<sub>m</sub>, Ar-I), 127.1 (+, C<sub>o</sub>, Ar-I), 126.3 (+, C<sub>o</sub>, Ar-N<sub>3</sub>), 119.0 (+, C<sub>m</sub>, Ar-N<sub>3</sub>), 91.5 (C<sub>q</sub>, Ar<sub>p</sub>-I), 46.9 (–, C<sub>s</sub>, Ad), 38.9 (C<sub>q</sub>, Ad) ppm. – IR (KBr):  $\tilde{\nu}$  = 3390 (br, vw), 3242 (w), 3032 [w,  $\tilde{\nu}_{\text{Ar}}(\text{C-H})$ ], 2929 (m), 2851 [m,  $\tilde{\nu}_{\text{Ad}}(\text{CH}_2)$ ], 2572 (vw), 2415 (w), 2324 (w), 2259 (w), 2125

[s,  $\tilde{\nu}_{\text{Ar}}(\text{N}_3)$ ], 1952 (w), 1894 (w), 1604 (m), 1575 (w), 1508 [s,  $\tilde{\nu}_{\text{Ar}}(\text{C}=\text{C})$ ], 1445 (w), 1412 (w), 1392 (w), 1357 (m), 1292 (m), 1190 (m), 1116 (m), 1014 (m), 891 (w), 831 [m,  $\tilde{\nu}_{\text{Ar}}(\text{p-subst.})$ ], 772 (m), 699 (w), 671 (w), 557 (w), 533 (m). – UV/VIS ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  (A) = 239 (0.5623), 254 (0.4408) nm.

**1,3,5,7-tetrakis(4-(4-hydroxymethyl-1,2,3-triazol-1-yl)-phenyl)adamantane (5d).**

1,3,5,7-tetrakis(4-azidophenyl)adamantane (**4d**) (40.0 mg, 0.07 mmol, 1.0 equiv.) were solved in 20 mL DMSO under argon at 100 °C. After that,  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  (3.60 mg, 0.01 mmol, 0.2 equiv.), sodium ascorbate (5.20 mg, 0.03 mmol, 0.4 equiv.), solved in 1 mL  $\text{H}_2\text{O}$ , and prop-2-yn-1-ol 46.1  $\mu\text{L}$  (44.4 mg, 0.79 mmol, 12 equiv.) were added slowly. It was stirred for 48 h at 100 °C, taken-up in 20 mL ethylacetate and washed with  $2 \times 20 \text{ mL H}_2\text{O}$ ,  $2 \times 20 \text{ mL brine}$  and  $2 \times 20 \text{ mL H}_2\text{O}$ . The solvent was removed under reduced pressure. The crude product was taken-up in 30 mL  $\text{CHCl}_3$  and dried over  $\text{MgSO}_4$ . Compound **5d** was purified by flash chromatography on silica gel ( $2 \times 20 \text{ cm}$ ;  $\text{CH}_2\text{Cl}_2/\text{methanol}$ , 5:1) after removing the solvent. The 1,2,3-triazole **5d** was isolated as a bright yellow solid (6.00 mg, 7.20  $\mu\text{mol}$ , 11%). –  $R_f = 0.40$  ( $\text{CH}_2\text{Cl}_2/\text{methanol}$ , 5:1). –  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 2.15$  (s, 12 H, Ad- $\text{CH}_2$ ), 4.61 (s, 6 H, - $\text{CH}_2\text{OH}$ ), 7.53 (d,  $^3J = 8.8 \text{ Hz}$ , 8 H, Ar<sub>o</sub>-H), 7.60 (d,  $^3J = 8.7 \text{ Hz}$ , 8 H, Ar<sub>m</sub>-H), 7.98 (s, 4 H, - $\text{HC}=\text{CCH}_2\text{OH}$ ) ppm. –  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 39.1$  (C<sub>q</sub>, Ad), 46.5 (–, C<sub>s</sub>, Ad- $\text{CH}_2$ ), 55.3 (–, C<sub>s</sub>, - $\text{CH}_2\text{OH}$ ), 120.2 (C<sub>t</sub>, - $\text{CH}=\text{CCH}_2\text{OH}$ ), 120.3 (+, C<sub>m</sub>, Ar), 126.3 (+, C<sub>o</sub>, Ar), 135.0 (C<sub>q</sub>, Ar<sub>p</sub>), 148.4 (C<sub>q</sub>, Ar-Ad), 149.3 (- $\text{CH}=\text{CCH}_2\text{OH}$ ) ppm. – MS (FAB, 3-NBA),  $m/z$  (%): 829 (100)  $[\text{M}+\text{H}]^+$ , 733 (10), 731 (22), 573 (26), 529 (32), 485 (30), 419 (100). – IR (KBr):  $\tilde{\nu} = 3365$  [br, w,  $\tilde{\nu}(\text{OH})$ ], 2923 (w), 2853 [w,  $\tilde{\nu}_{\text{Ad}}(\text{CH}_2)$ ], 1609 (vw), 1519 [w,  $\tilde{\nu}_{\text{Ar}}(\text{C}=\text{C})$ ], 1378 (w), 1262 (w), 1238 (w), 1184 (w), 1040 (w), 836 [w,  $\tilde{\nu}_{\text{Ar}}(\text{p-subst.})$ ], 788 (w), 761 (vw), 700 (vw), 560 (w)  $\text{cm}^{-1}$ . – HRMS Calcd for  $\text{C}_{46}\text{H}_{45}\text{O}_4\text{N}_{12}$  ( $\text{M}^+$ ) 829.3687, found 829.3694. – UV/VIS ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  (A) = 227 (0.015), 255 (0.028), 472 (0.011) nm.