Supporting Information

Sequential copper catalyzed alkyne-azide and thiol-ene click reactions for the multiple functionalization of fullerene hexaadducts

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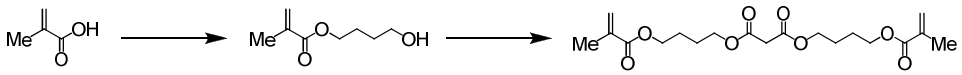
Experimental section

General. Reagents and solvents were purchased as reagent grade and used without further purification. Compound **7**[1] was prepared according to a previously reported procedure. All reactions were performed in standard glassware under an inert Ar or N_2 atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230-400 mesh, 0.040-0.063 mm) was purchased from E. Merck. Thin Layer Chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} purchased from E. Merck, visualization by UV light. IR spectra (cm^{-1}) were measured on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker AC 300 or AC 400 with solvent peaks as reference. MALDI-TOF-mass spectra were carried out on a Bruker BIFLEX™ matrix-assisted laser desorption time-of-flight mass spectrometer.

Preparation of compound 1

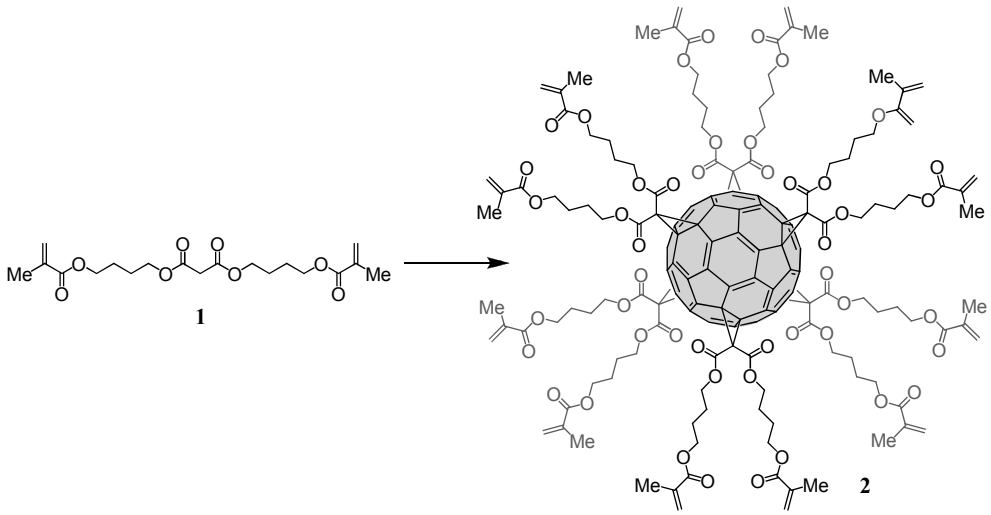


Compound 13. DCC (14.24 g, 69.69 mmol) was added to a solution of **12** (6 g, 69.69 mmol), 1,4-butanediol (9.32 mL, 104.54 mmol), HOBt (0.94 g, 6.97 mmol) and DMAP (1.70 g, 13.94 mmol) in CH_2Cl_2 (300 mL) at 0 °C under argon. The mixture was stirred for 48 h, filtered through a celite pad and concentrated. Column chromatography (SiO_2, CH_2Cl_2) yielded **13** (5.6 g, 51%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 6.06 (dq, *J* = 4 and 1.5 Hz, 1H), 5.51 (dq, *J* = 4 and 1.5 Hz, 1H), 4.14 (t, *J* = 6 Hz, 2H), 3.63 (t, *J* = 6 Hz, 2H), 2.25 (s, 1H), 1.90 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): 167.5, 136.3, 125.3, 64.4, 62.1, 29.0, 25.0, 18.2.

[1] J. Iehl, R. Pereira de Freitas, B. Delavaux-Nicot and J.-F. Nierengarten, *Chem. Commun*. 2008, 2450.

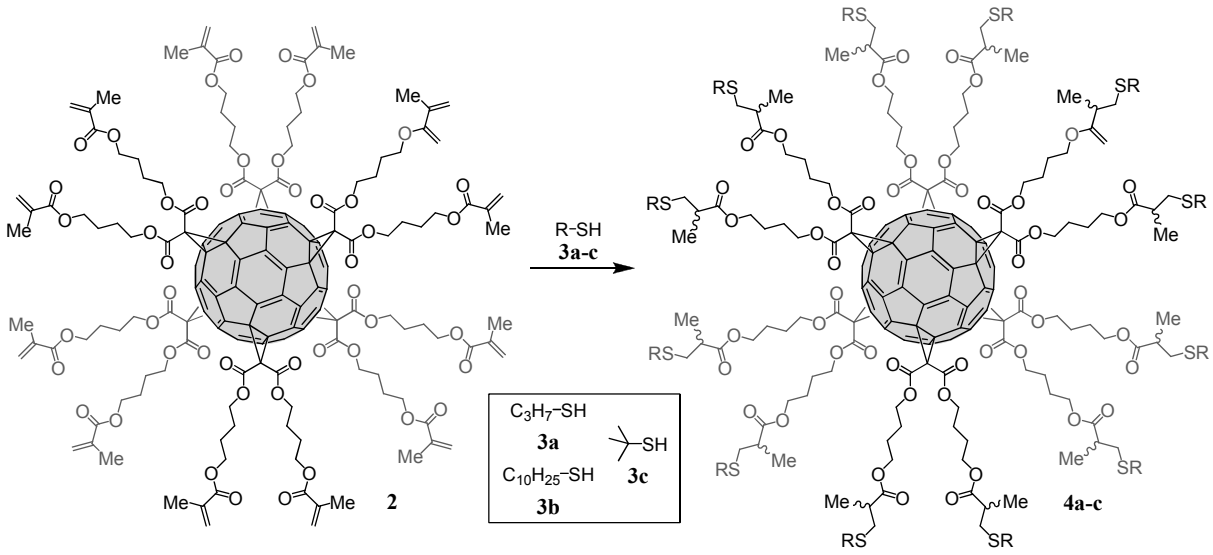
Compound 1. Malonyl dichloride (0.62 mL, 6.32 mmol) was added to a solution of **13** (2 g, 12.64 mmol) and pyridine (1.02 mL, 12.64 mmol) in CH_2Cl_2 (100 mL) at 0°C. After 1 h, the mixture was allowed to warm up to room temperature, then stirred for 18 h, filtered, and evaporated. Column chromatography (SiO_2, CH_2Cl_2/AcOEt 9:1) gave **1** (2.17 g, 89%) as a pale yellow oil. IR (neat): 1740 (C=O), 1714 (C=O), 1637 (C=C); ^{1}H NMR ($CDCl_3$, 300 MHz): 6.05 (m, 2H), 5.51 (m, 2H), 4.14 (m, 8H), 3.34 (s, 2H), 1.89 (m, 6H), 1.71 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz): 167.2, 166.3, 136.2, 125.3, 64.9, 63.9, 41.3, 25.1(x2), 18.1.

Preparation of compound 2



Compound 2. CBr_4 (12.64 g, 38.13 mmol), **1** (1.46 g, 3.81 mmol), and DBU (1.14 mL, 7.63 mmol) were added successively to a solution of C_{60} (0.27 g, 0.375 mmol) in ODCB (80 mL). The mixture was stirred for 72 h and evaporated. Column chromatography (SiO_2, CH_2Cl_2/AcOEt 8:2) gave **2** (0.47 g, 41%) as an orange glassy product. IR (neat): 1742 (C=O), 1713 (C=O), 1636 (C=C); UV/Vis (CH_2Cl_2): 245 (93500), 269 (68600), 283 (70000), 318 (sh, 42600), 338 (sh, 31100); ^{1}H NMR ($CDCl_3$, 300 MHz): 6.03 (m, 12H), 5.50 (m, 12H), 4.26 (t, J = 6 Hz, 24H), 4.10 (t, J = 6 Hz, 24H), 1.87 (m, 36H), 1.73 (m, 48H); ^{13}C NMR ($CDCl_3$, 75 MHz): 167.0, 163.4, 145.6, 140.9, 136.1, 125.3, 68.9, 66.2, 63.6, 45.1, 25.1(x2), 18.1; MALDI-TOF-MS: 3015 (M^+, calcd. for $C_{174}H_{156}O_{48}$: 3015.12).

Preparation of compounds 4a-c



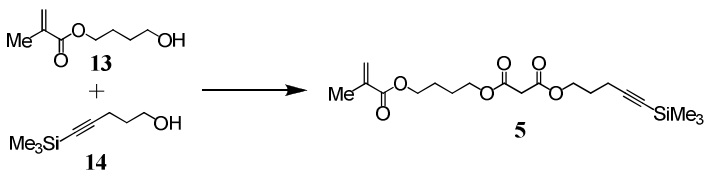
General procedure. AIBN (3 equiv.) was added to a mixture of **2** (1 equiv.) and the appropriate thiol (20 equiv.) in carefully degassed benzene. The resulting mixture was stirred for 1 h at 80°C. The mixture was then diluted with a small amount of CH_2Cl_2 and the product precipitated by addition of cyclohexane and filtered. The product was then purified as outlined in the following text.

Compound 4a. This compound was prepared from **2** (158 mg, 0.052 mmol), **3a** (80 mg, 1.04 mmol), AIBN (26 mg, 0.16 mmol) in benzene (5 mL). Column chromatography (SiO_2, CH_2Cl_2 containing 0.5% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **4a** (104 mg, 51%) as a red glassy product. IR (neat): 1728 (C=O); UV/Vis (CH_2Cl_2): 245 (115200), 269 (80200), 282 (77400), 320 (sh, 44500), 338 (sh, 33900); ^{1}H NMR ($CDCl_3$, 300 MHz): 4.30 (m, 24H), 4.12 (m, 24H), 2.81 (m, 12H), 2.67 (m, 12H), 2.57 (m, 12H), 2.49 (t, *J* = 7 Hz, 24H), 1.77 (m, 48H), 1.58 (q, *J* = 7 Hz, 24H), 1.25 (d, *J* = 7 Hz, 36H), 0.97 (t, *J* = 7 Hz, 36H); ^{13}C NMR ($CDCl_3$, 75 MHz): 175.0, 174.3, 163.5 (several peaks), 145.9 (several peaks), 140.9 (several peaks), 69.3 (several peaks), 64.2 (several peaks), 63.6 (several peaks), 45.2 (several peaks), 40.2, 32.7, 31.8, 25.0 (several peaks), 22.8, 16.8, 13.3 (several peaks); MALDI-TOF-MS: 3929 (M^+, calcd. for $C_{210}H_{252}O_{48}S_{12}$: 3929.0).

Compound 4b. This compound was prepared from **2** (133 mg, 0.04 mmol), **3b** (154 mg, 0.88 mmol), AIBN (22 mg, 0.13 mmol) in benzene (3 mL). Column chromatography (SiO_2, CH_2Cl_2 containing 1% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **4b** (79 mg, 35%) as a red glassy product. IR (neat): 1728 (C=O); UV/Vis (CH_2Cl_2): 246 (116200), 269 (88100), 283 (84300), 325 (sh, 48500), 337 (sh, 39600); ^{1}H NMR ($CDCl_3$, 300 MHz): 4.29 (m, 24H), 4.12 (m, 24H), 2.77 (m, 12H), 2.68 (m, 12H), 2.56 (m, 12H), 2.49 (t, *J* = 7 Hz, 24H), 1.76 (m, 48H), 1.53 (m, 24H), 1.24 (m, 216H), 0.86 (t, *J* = 7 Hz, 36H); ^{13}C NMR ($CDCl_3$, 75 MHz): 176.2 (several peaks), 175.0, 174.4, 163.6 (several peaks), 145.9 (several peaks), 140.9 (several peaks), 69.0 (several peaks), 64.3 (several peaks), 63.7 (several peaks), 45.2 (several peaks), 40.2, 32.7, 31.8, 29.8, 29.6, 29.5, 29.3, 29.25, 29.2, 28.8, 25.0 (several peaks), 16.9, 14.0; MALDI-TOF-MS: 5107 (M^+, calcd. for $C_{294}H_{420}O_{48}S_{12}$: 5107.26).

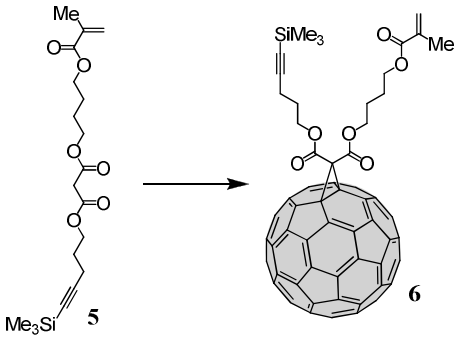
Compound 4c. This compound was prepared from **2** (200 mg, 0.06 mmol), **3c** (120 mg, 1.33 mmol), AIBN (33 mg, 0.2 mmol) in benzene (5 mL). Column chromatography (SiO_2, CH_2Cl_2 containing 1% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **4c** (140 mg, 52%) as a red glassy product. IR (neat): 1726 (C=O); UV/Vis (CH_2Cl_2): 245 (91200), 269 (69300), 283 (65100), 322 (sh, 38700), 339 (sh, 29400); ^{1}H NMR ($CDCl_3$, 300 MHz): 4.28 (m, 24H), 4.11 (m, 24H), 2.79 (m, 12H), 2.59 (m, 24H), 1.75 (m, 48H), 1.28 (m, 108H), 1.24 (m, 36H); ^{13}C NMR ($CDCl_3$, 75 MHz): ^{13}C NMR ($CDCl_3$, 75 MHz): 176.3 (several peaks), 175.0, 163.4 (several peaks), 146.0 (several peaks), 140.8 (several peaks), 68.9 (several peaks), 66.4 (several peaks), 63.6 (several peaks), 45.2 (several peaks), 40.3, 31.6, 30.8, 30.7, 25.1 (several peaks), 17.1; MALDI-TOF-MS: 4097 (M^+, calcd. for $C_{222}H_{276}O_{48}S_{12}$: 4097.32).

Preparation of compound 5.



Compound 5. Malonyl dichloride (0.92 mL, 9.48 mmol) was added to a solution of **13** (1.5 g, 9.48 mmol), **14** (1.48 g, 9.48 mmol) and pyridine (1.53 mL, 18.96 mmol) in CH_2Cl_2 (150 mL) at 0°C. After 1 h, the mixture was allowed to warm up to room temperature, then stirred for 16 h, filtered, and evaporated. Column chromatography (SiO_2, CH_2Cl_2/Hexane 9:1) gave **5** (1.35 g, 37%) as a colorless oil. IR (neat): 2175 (C≡C), 1742 (C=O), 1713 (C=O), 1636 (C=C); ^{1}H NMR ($CDCl_3$, 300 MHz): 6.07 (dq, *J* = 4 and 1.5 Hz, 1H), 5.53 (dq, *J* = 4 and 1.5 Hz, 1H), 4.21 (t, *J* = 6 Hz, 2H), 4.16 (m, 4H), 3.35 (s, 2H), 2.29 (t, *J* = 6 Hz, 2H), 1.91 (m, 3H), 1.83 (t, *J* = 6 Hz, 2H), 1.74 (m, 4H), 0.11 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): 167.2, 166.4, 166.3, 136.3, 125.3, 105.3, 85.4, 64.9, 64.1, 63.9, 41.4, 27.5, 25.2, 25.1, 18.2, 16.4, 0.0.

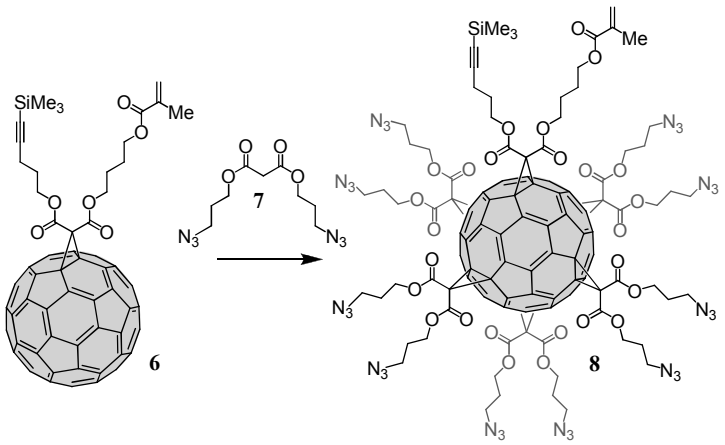
Preparation of compound 6.



Compound 6. DBU (1.27 mL, 8.49 mmol) was added to a stirred solution of C_{60} (2.45 g, 3.39 mmol), I_2 (1.3 g, 5.09 mmol) and **5** (1.3 g, 3.39 mmol) in toluene (2.45 L) at room temperature. The resulting solution was stirred for 12 h, then filtered through a short plug of SiO_2 (CH_2Cl_2) and evaporated. Column chromatography (SiO_2, CH_2Cl_2/Hexane 6/4) gave **5** (1.87 g, 50%) as a dark red glassy product. IR (neat): 2174 (C≡C), 1742 (C=O), 1713 (C=O), 1636 (C=C); UV/Vis (CH_2Cl_2): 257 (123000), 227 (95400), 327 (36300), 360 (sh, 11000), 393 (3700), 414 (sh, 1700), 426 (1900); ^{1}H NMR ($CDCl_3$, 300 MHz): 6.12 (m, 1H), 5.57 (m, 1H), 4.59 (t, *J* = 6 Hz, 2H), 4.55 (t, *J* = 6 Hz, 2H), 4.23 (t, *J* = 6 Hz, 2H), 2.43 (t, *J* = 6 Hz, 2H), 2.05 (q, *J* = 6 Hz, 2H), 1.95 (m, 3H), 1.90 (m, 4H), 0.16 (s, 9H); ^{13}C NMR ($CDCl_3$, 75

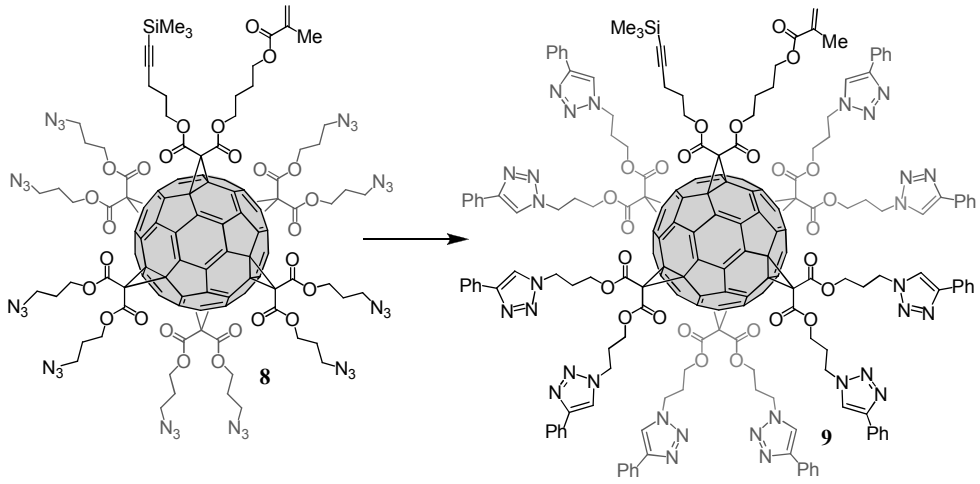
MHz): 167.3, 163.5(x2), 145.3, 145.2(x2), 145.1(x2), 144.9, 144.7, 144.6, 143.9, 143.1, 143.0(x2), 142.2, 141.9, 141.8, 141.0, 139.0(x2), 136.3, 125.6, 105.0, 86.0, 71.5, 66.8, 65.8, 63.9, 52.1, 27.6, 25.4, 25.3, 18.3, 16.6, 0.1; MALDI-TOF-MS: 1101 (M^+, calcd. for $C_{79}H_{28}O_6Si$: 1101.17).

Preparation of compound 8.



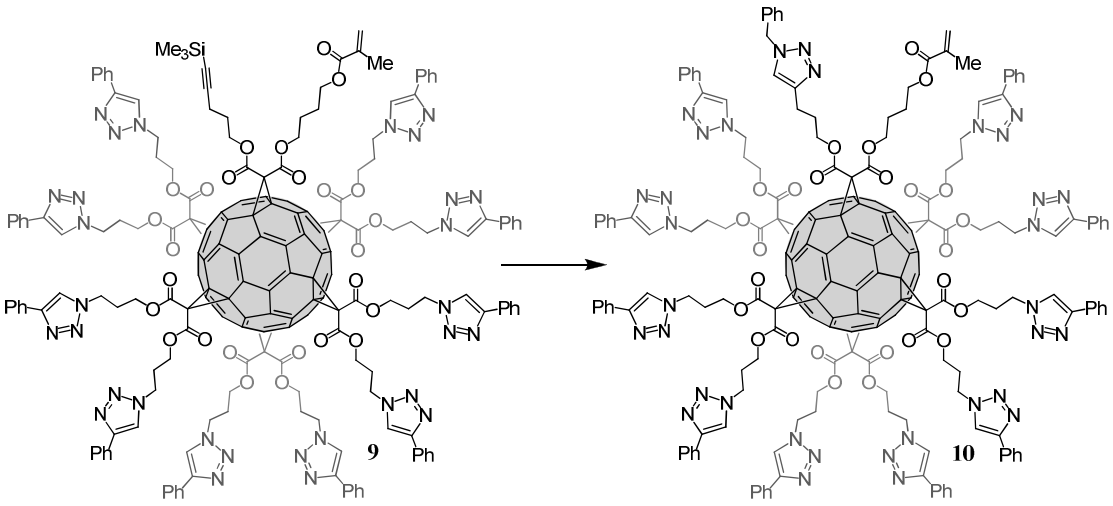
Compound 8. CBr_4 (15.05 g, 45.4 mmol), **7** (1.22 g, 4.54 mmol), and DBU (1.36 mL, 9.08 mmol) were added successively to a solution of **6** (0.5 g, 0.45 mmol) in ODCB (90 mL). The mixture was stirred for 72 h and evaporated. Column chromatography (SiO_2, CH_2Cl_2) gave **8** (0.62 g, 57%) as an orange glassy product. IR (neat): 2174 (C≡C), 2094 (N_3), 1742 (C=O), 1713 (C=O), 1636 (C=C); ^{1}H NMR ($CDCl_3$, 300 MHz): 6.08 (m, 1H), 5.55 (m, 1H), 4.35 (m, 24H), 4.16 (t, *J* = 6 Hz, 2H), 3.38 (t, *J* = 6 Hz, 20H), 2.30 (t, *J* = 6 Hz, 2H), 1.95 (m, 27H), 1.81 (q, *J* = 6 Hz, 2H), 0.12 (m, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): 166.7, 163.0 (several peaks), 161.5, 145.3 (several peaks), 140.6 (several peaks), 135.8, 125.0, 104.7, 85.2, 68.6, 66.1, 65.2, 63.7, 63.4 (several peaks), 62.6, 59.1, 47.9, 47.4 (several peaks), 47.1, 44.8, 31.1, 30.4, 27.5 (several peaks), 24.8, 24.7, 17.8, 16.0, -0.4.

Preparation of compound 9.



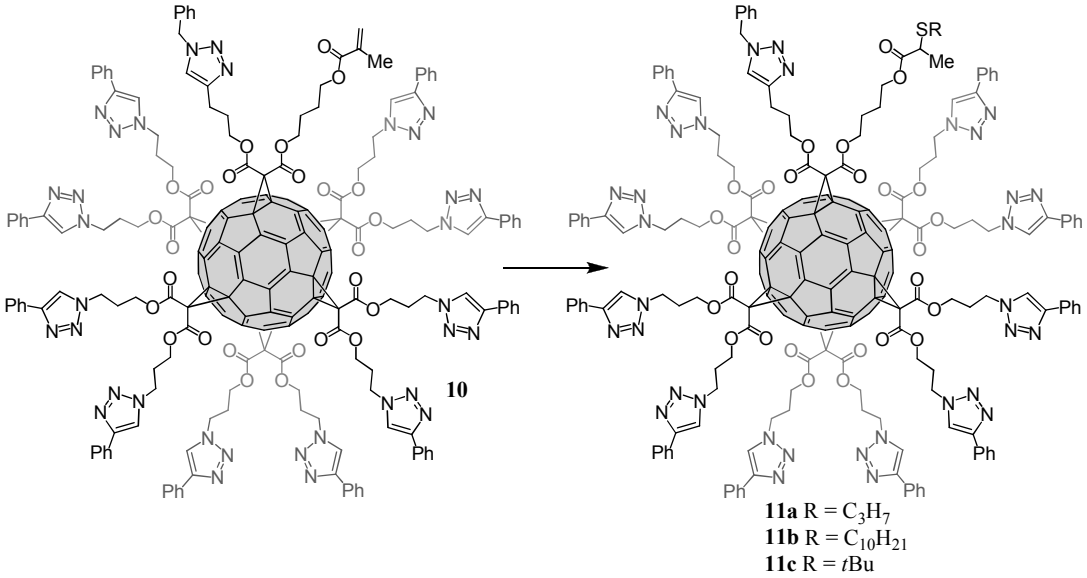
Compound 9. A mixture of **8** (0.62 mg, 0.25 mmol), phenylacetylene (315 mg, 3.08 mmol), $CuSO_4.5H_2O$ (4 mg, 0.025 mmol) and sodium ascorbate (15 mg, 0.077 mmol) in CH_2Cl_2/H_2O (1:1, 10 mL) was vigorously stirred at rt. After 24 h, the organic layer was diluted with CH_2Cl_2, washed with water, dried ($MgSO_4$) and concentrated. Column chromatography (SiO_2, CH_2Cl_2 containing 2% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **9** (588 mg, 66%) as an orange glassy product. IR (neat): 2173 (C≡C), 1740 (C=O), 1713 (C=O), 1636 (C=C); UV/Vis (CH_2Cl_2): 246 (234800), 270 (117400), 283 (67500), 319 (sh, 36100), 340 (sh, 25200);): 8.00-7.75 (m, 30H), 7.45-7.25 (m, 30H), 6.12 (m, 1H), 5.58 (m, 1H), 4.47 (m, 20H), 4.39 (m, 24H), 4.16 (t, J = 6 Hz, 2H), 2.34 (m, 22H), 1.96 (m, 3H), 1.90 (m, 4H), 1.78 (m, 2H), 0.12 (m, 9H);^{13}C NMR ($CDCl_3$, 75 MHz): 167.0, 163.2 (several peaks), 147.6, 145.6 (several peaks), 141.0 (several peaks), 136.0, 130.3, 128.6, 127.9, 125.4, 120.0, 104.8, 85.6, 69.1, 69.0, 68.9, 66.5, 65.6, 63.6 (several peaks), 46.6 (several peaks), 45.1, 29.0 (several peaks), 27.2, 24.9, 24.8, 18.1, 16.2, -0.1; MALDI-TOF-MS: 3464 (M^+, calcd. for $C_{204}H_{148}N_{30}O_{26}Si$: 3463.69).

Preparation of compound 10.



Compound 10. A 1 M solution of TBAF in THF (0.12 mL, 0.12 mmol) was added to a mixture of **9** (200 mg, 0.057 mmol), benzyl azide (23 mg, 0.17 mmol), $CuSO_4.5H_2O$ (3.4 mg, 0.0057 mmol) and sodium ascorbate (3.4 mg, 0.017 mmol) in CH_2Cl_2/H_2O (1:1, 3 mL). The resulting mixture was vigorously stirred at rt. After 12 h, the organic layer was diluted with CH_2Cl_2, washed with water, dried ($MgSO_4$) and concentrated. Column chromatography (SiO_2, CH_2Cl_2 containing 3% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **10** (178 mg, 87 %) as an orange glassy product. IR (neat): 1739 (C=O), 1713 (C=O), 1636 (C=C); UV/Vis (CH_2Cl_2): 246 (213600), 265 (115200), 286 (40300), 318 (sh, 21900), 337 (sh, 15800); ^{1}H NMR ($CDCl_3$, 300 MHz): 8.00-7.75 (m, 33H), 7.45-7.25 (m, 33H), 6.04 (m, 1H), 5.51 (m, 1H), 5.44 (s, 2H), 4.41 (m, 20H), 4.33 (m, 26H), 4.08 (t, J = 6 Hz, 2H), 2.68 (m, 2H), 2.30 (m, 20H), 1.89 (m, 3H), 1.69 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): 167.1, 163.3 (several peaks), 161.8, 147.7, 146.5, 145.7 (several peaks), 141.0 (several peaks), 136.0, 134.8, 130.3, 128.9, 128.7, 128.0, 125.5, 120.9, 120.3, 120.0, 69.2, 69.0, 66.6, 66.3 (several peaks), 63.8, 63.6, 63.1, 53.8, 46.7 (several peaks), 46.3, 45.3, 29.5, 29.1 (several peaks), 28.8, 27.9, 25.0, 24.9, 21.9, 18.2; MALDI-TOF-MS: 3524 (M^+, calcd. for $C_{208}H_{146}N_{33}O_{26}$: 3523.65).

Preparation of compounds 11a-c.



General procedure. AIBN (3 equiv.) was added to a mixture of **10** (1 equiv.) and the appropriate thiol (20 equiv.) in carefully degassed THF. The resulting mixture was refluxed for 1 h. The mixture was then diluted with a small amount of CH_2Cl_2 and the product precipitated by addition of cyclohexane and filtered. The product was then purified as outlined in the following text.

Compound 11a. This compound was prepared from **10** (100 mg, 0.003 mmol), **3b** (42 mg, 0.56 mmol), AIBN (14 mg, 0.084 mmol) in THF (2 mL). Column chromatography (SiO_2, CH_2Cl_2 containing 2% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **11a** (72 mg, 70%) as a red glassy product. IR (neat): 1740 (C=O); UV/Vis (CH_2Cl_2): 247 (196100), 265 (110100), 286 (46600), 318 (sh, 26400), 335 (sh, 20100); ^{1}H NMR ($CDCl_3$, 300 MHz): 8.00-7.75 (m, 33H), 7.45-7.25 (m, 33H), 5.44 (s, 2H), 4.43 (m, 20H), 4.33 (m, 26H), 4.05 (m, 2H), 2.72 (m, 3H), 2.34 (m, 24H), 1.64 (m, 6H), 1.20 (m, 3H), 0.94 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): 163.3 (several peaks), 161.9, 147.8, 146.6, 145.8 (several peaks), 141.1 (several peaks), 134.8, 130.4, 128.9, 128.8, 128.5, 128.1, 127.9, 125.6, 121.0, 120.3, 120.0, 69.1 (several peaks), 66.5 (several peaks), 63.8, 63.6, 63.1, 53.8, 46.7 (several peaks), 46.4, 45.4, 40.2, 32.6, 31.8, 29.2 (several peaks), 25.0 (several

peaks), 22.0, 16.8, 13.3 (several peaks); MALDI-TOF-MS: 3600 (M^+, calcd. for $C_{211}H_{155}N_{33}O_{26}S$: 3600.82).

Compound 11b. This compound was prepared from **10** (54 mg, 0.015 mmol), **3b** (53 mg, 0.3 mmol), AIBN (8 mg, 0.045 mmol) in THF (1 mL). Column chromatography (SiO_2, CH_2Cl_2 containing 2% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **11b** (51 mg, 91%) as a red glassy product. IR (neat): 1739 (C=O); UV/Vis (CH_2Cl_2): 246 (204800), 256 (170200), 284 (63600), 318 (sh, 37400), 339 (sh, 27800); ^{1}H NMR ($CDCl_3$, 300 MHz): 8.00-7.75 (m, 33H), 7.45-7.25 (m, 33H), 5.44 (s, 2H), 4.43 (m, 20H), 4.35 (m, 26H), 4.07 (m, 2H), 2.68 (m, 3H), 2.31 (m, 24H), 1.71 (m, 6H), 1.23 (m, 17H), 0.86 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): 163.4 (several peaks), 147.8 (several peaks), 145.8 (several peaks), 141.1 (several peaks), 134.8, 130.4, 128.9, 128.8, 128.5, 128.1, 127.9, 125.6, 121.0, 120.1, 120.0, 69.1 (several peaks), 66.4 (several peaks), 63.8, 63.7, 63.1, 53.8, 46.8 (several peaks), 46.4, 45.4, 40.2, 32.6, 31.8, 29.2, 28.0, 26.7, 25.0 (several peaks), 22.6, 22.0, 20.6, 16.8, 14.1 (several peaks); MALDI-TOF-MS: 3698 (M^+, calcd. for $C_{218}H_{169}N_{33}O_{26}S$: 3699.01).

Compound 11c. This compound was prepared from **10** (100 mg, 0.003 mmol), **3c** (51 mg, 0.56 mmol), AIBN (14 mg, 0.084 mmol) in THF (2 mL). Column chromatography (SiO_2, CH_2Cl_2 containing 3% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **11c** (64 mg, 62%) as a red glassy product. IR (neat): 1740 (C=O); UV/Vis (CH_2Cl_2): 246 (188400), 263 (120300), 285 (60200), 320 (sh, 36600), 338 (sh, 28700); ^{1}H NMR ($CDCl_3$, 300 MHz): 8.00-7.75 (m, 33H), 7.45-7.25 (m, 33H), 5.43 (s, 2H), 4.41 (m, 20H), 4.34 (m, 26H), 4.07 (m, 2H), 2.68 (m, 3H), 2.30 (m, 22H), 1.70 (m, 4H), 1.26 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz): 163.4 (several peaks), 147.8, 146.6, 145.8 (several peaks), 141.1 (several peaks), 134.8, 130.4, 128.9, 128.8, 128.5, 128.1, 127.9, 125.6, 121.0, 120.1, 120.0, 69.1 (several peaks), 66.4 (several peaks), 63.7 (several peaks), 53.9, 46.7 (several peaks), 45.4, 40.2, 32.3, 29.2 (several peaks), 28.0, 25.0 (several peaks), 22.6, 22.0, 20.6; MALDI-TOF-MS: 3614 (M^+, calcd. for $C_{212}H_{157}N_{33}O_{26}S$: 3614.84).

Fig. S1. ^{1}H NMR spectra (300 MHz, $CDCl_3$) of **1** (top), **2** (middle) and **4a** (bottom).

Fig. S2. ^{13}C NMR spectra (75 MHz, $CDCl_3$) of **2** (top) and **4b** (bottom); unambiguous assignment was achieved with the help of the corresponding DEPT spectra. As the thiol-ene click reaction generates an asymetric center, compounds **4b** is indeed obtained as a mixture of diastereoisomers. As a result, its ^{13}C NMR spectrum is quite broad.

Fig. S3. Partial view of the ^{1}H NMR spectra (300 MHz, $CDCl_3$) of **9** (top), **10** (middle) and **11a** (bottom) highlighting the appearance of typical benzylic CH_2 resonance when going from **9** to **10** as well as the disappearance of the vinylic signals when going from **10** to **11a**.

Fig. S4. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **9**; unambiguous assignment was achieved with the help of the corresponding DEPT spectrum.

Fig. S5. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **10**; unambiguous assignment was achieved with the help of the corresponding DEPT spectrum.

Fig. S6. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **11c**; unambiguous assignment was achieved with the help of the corresponding DEPT spectrum.

Fig. S7. MALDI-TOF mass spectrum of compound **9** showing the expected molecular ion peak at 3464 (calcd. for $C_{204}H_{148}N_{30}O_{26}Si$: 3463.69); characteristic fragments are also highlighted.

Fig. S8. MALDI-TOF mass spectrum of compound **10** showing the expected molecular ion peak at 3524 (calcd. for $C_{208}H_{146}N_{33}O_{26}$: 3523.65); characteristic fragments are also highlighted.

Fig. S9. MALDI-TOF mass spectrum of compound **11b** showing the expected molecular ion peak at 3698 (calcd. for $C_{218}H_{169}N_{33}O_{26}S$: 3699.01); characteristic fragments are also highlighted.

Fig. S1.

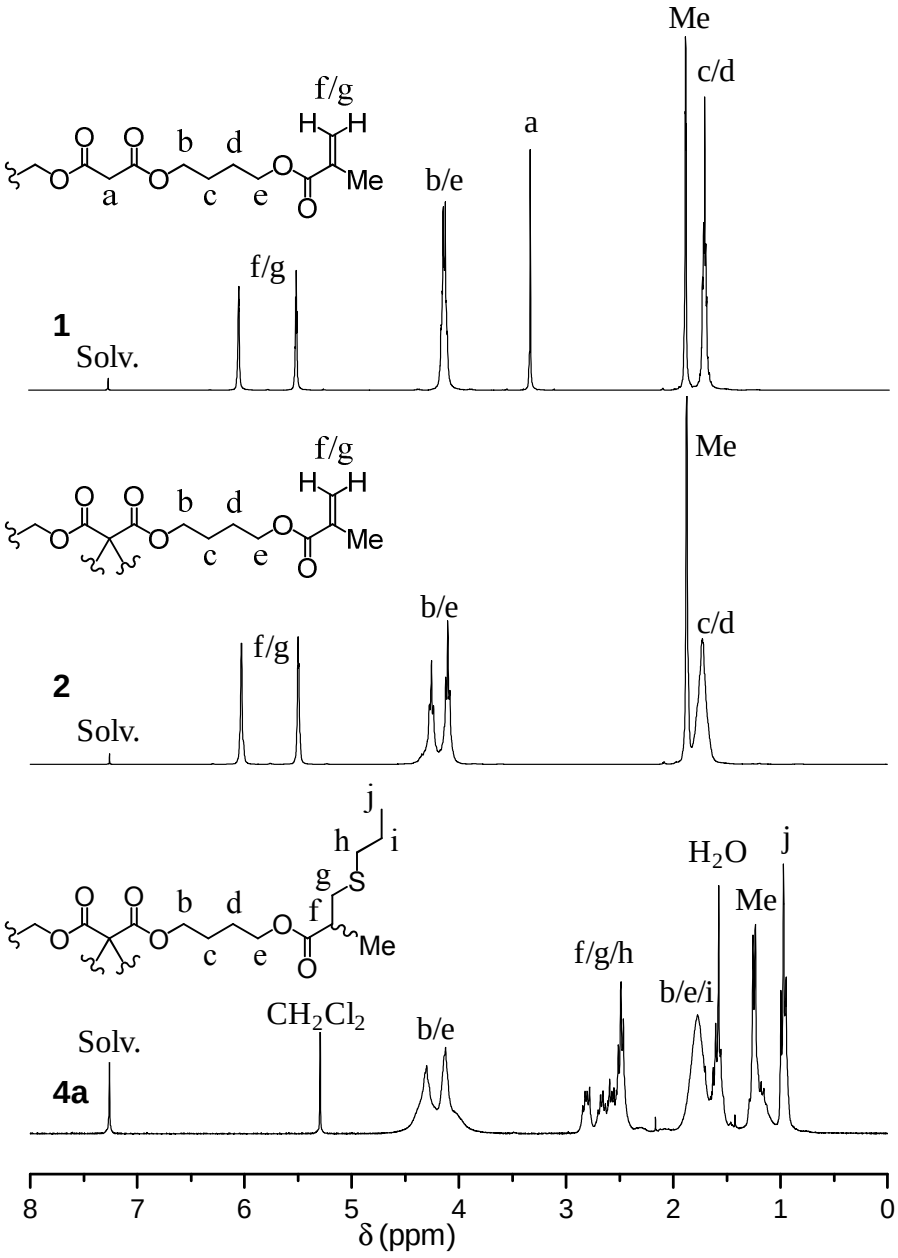

Me
c/d
f/g
a
b/e
f/g
1
Solv.
f/g
Me
b/e
c/d
f/g
2
Solv.
j
h
i
g
S
f
H_2O
j
Me
f/g/h
b/e/i
CH_2Cl_2
b/e
Solv.
4a
8
7
6
5
4
3
2
1
0
δ (ppm)

Fig. S2.

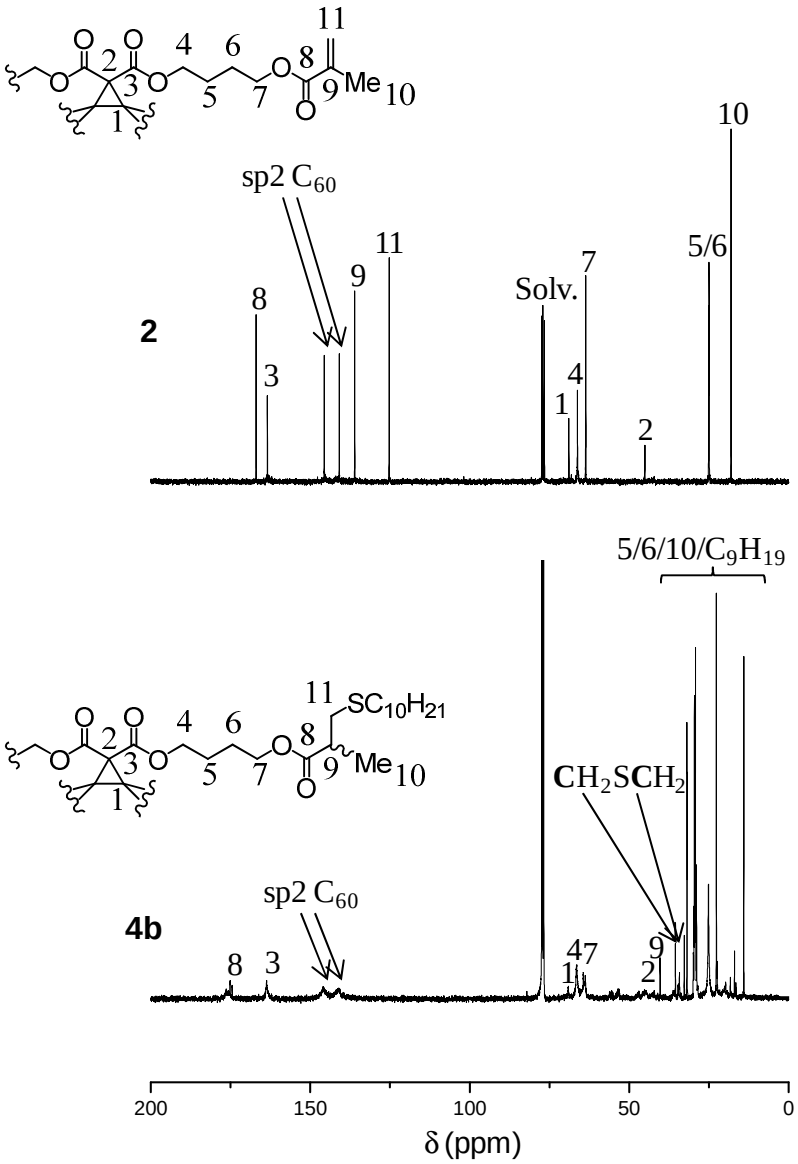

11
2
4
6
8
3
5
7
9
Me
10
1
10
sp2 C60
11
9
8
2
Solv.
7
5/6
3
4
1
2
5/6/10/C9H19
11
SC10H21
CH2SCH2
sp2 C60
4b
8
3
4
7
1
9
2
200
150
100
50
0
δ (ppm)

Fig. S3.

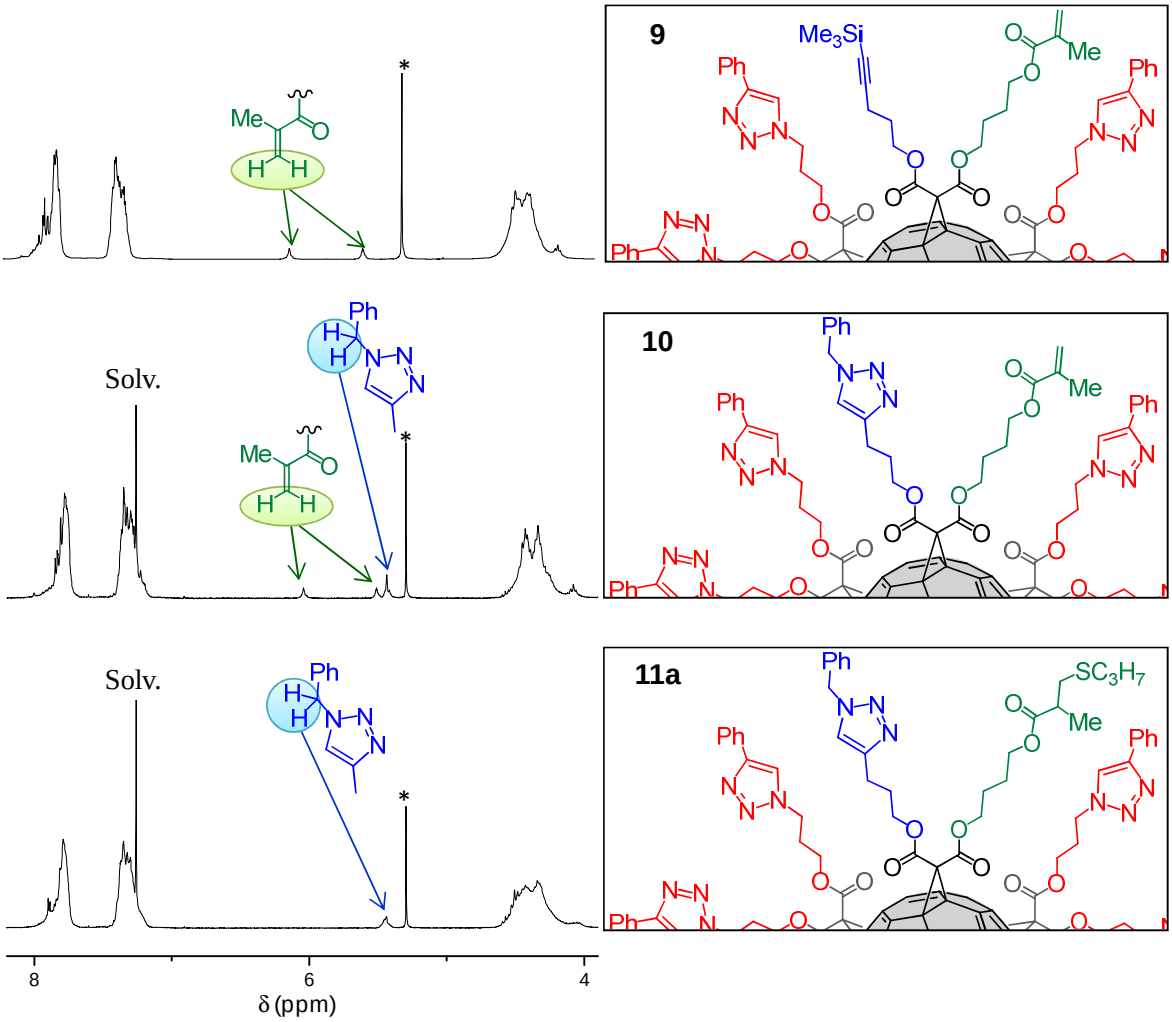


Fig. S4.

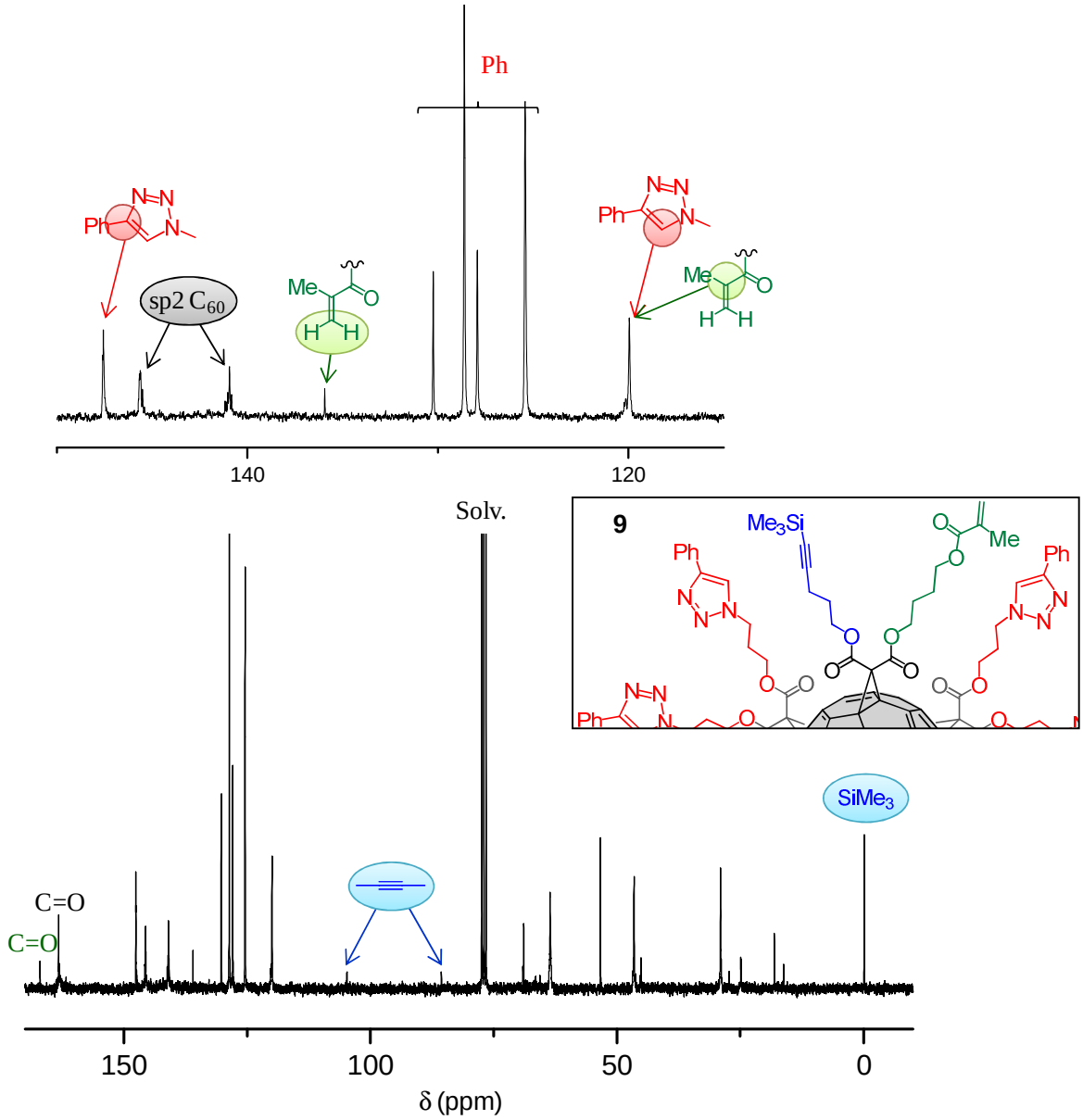

Ph
sp2 C60
Me
H H
Ph
Me
H H
140
120
Solv.
9
Me3Si
Ph
Me
Ph
SiMe3
C=O
C=O
150
100
50
0
δ (ppm)

Fig. S5.

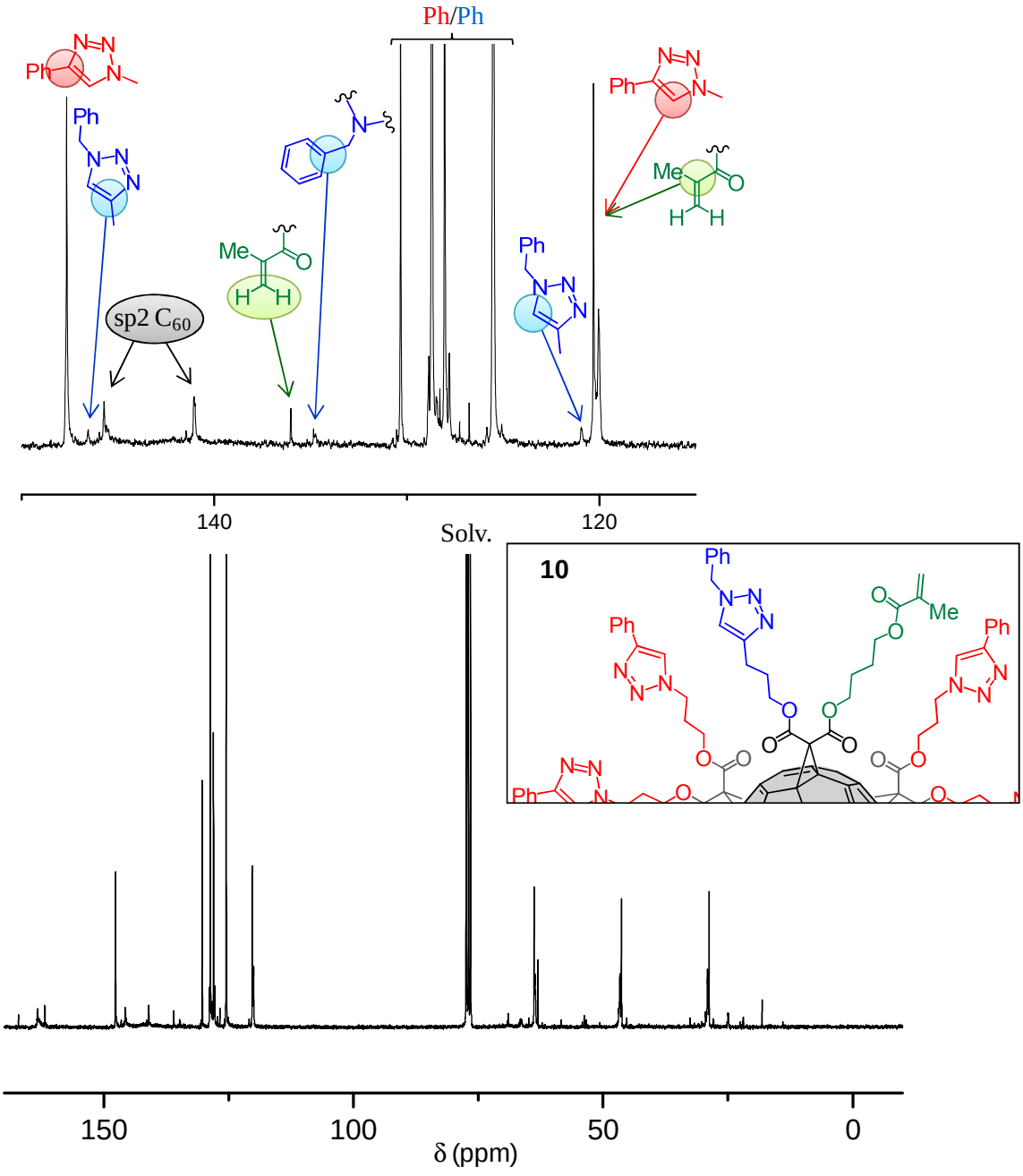


Fig S6.

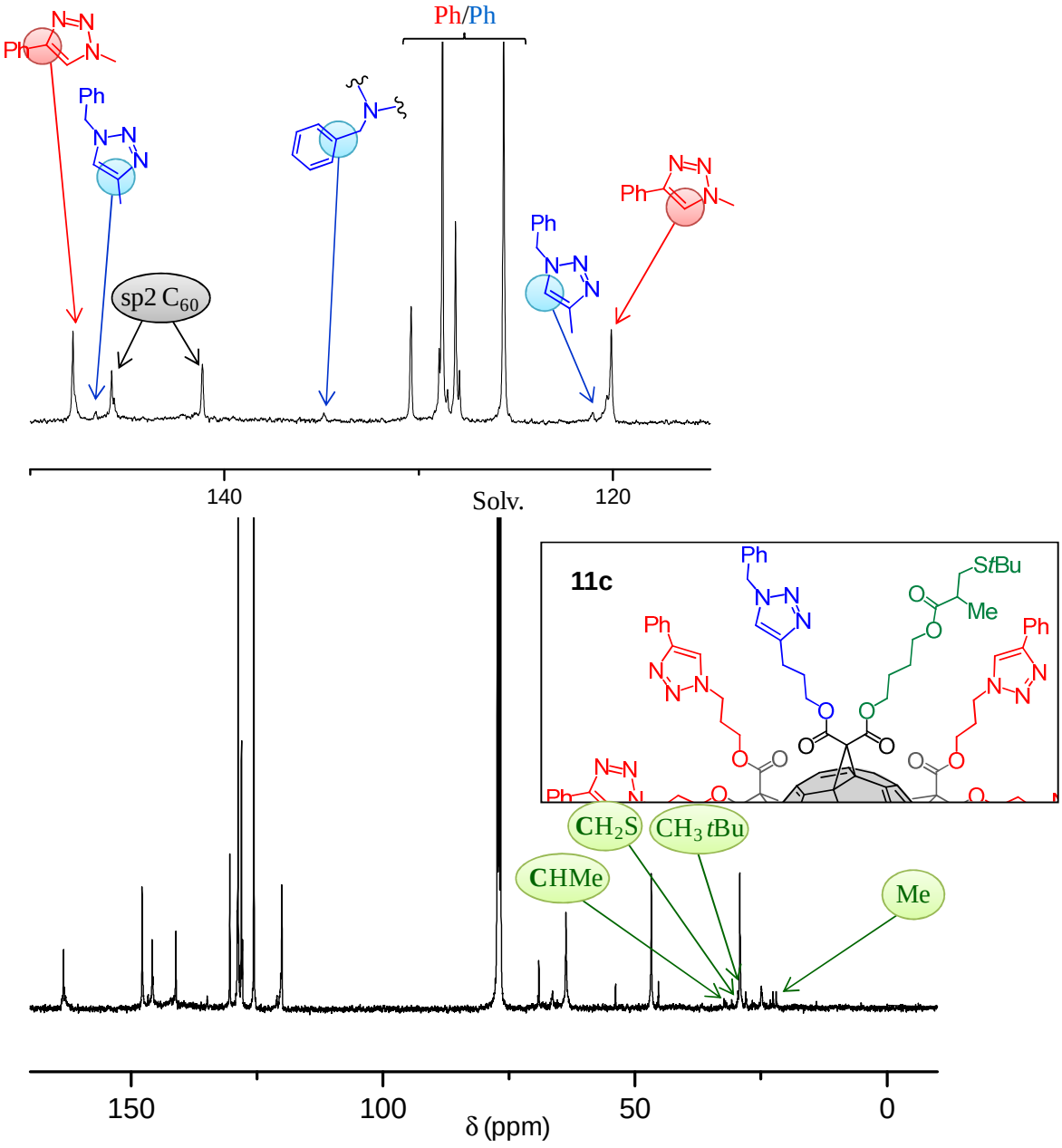

Ph/Ph
sp2 C60
140
Solv.
120
11c
StBu
Me
CH2S
CH3 tBu
CHMe
Me
150
100
50
0
δ (ppm)

Fig. S7.

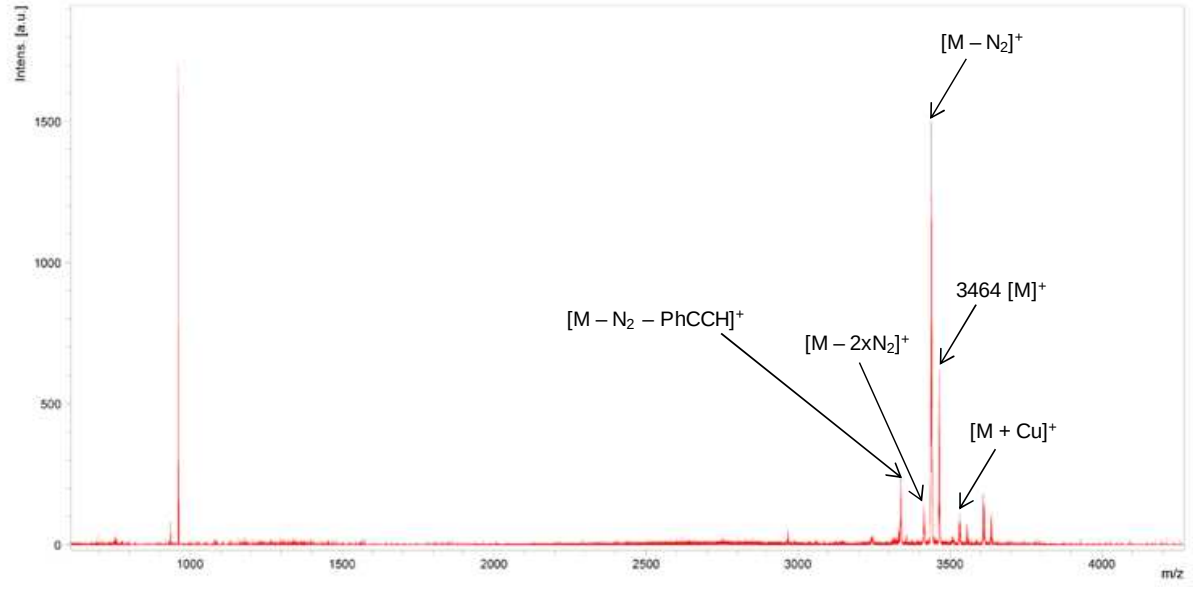

Intens. [a.u.]
1500
1000
500
0
1000
1500
2000
2500
3000
3500
4000
m/z
[M – N2]+
3464 [M]+
[M – N2 – PhCCH]+
[M – 2xN2]+
[M + Cu]+

Fig. S8.

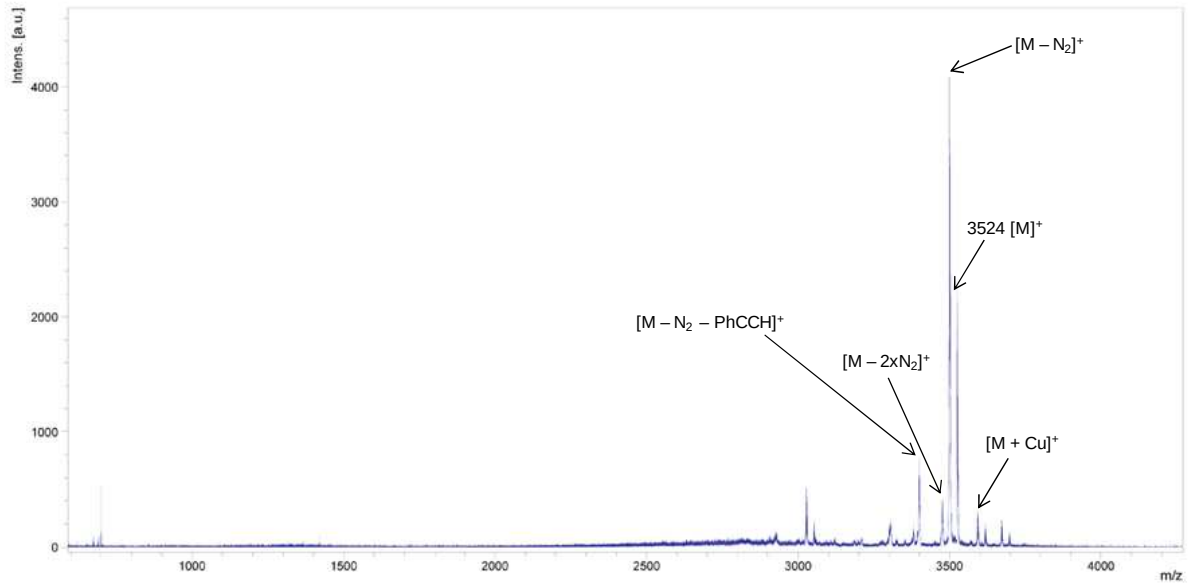
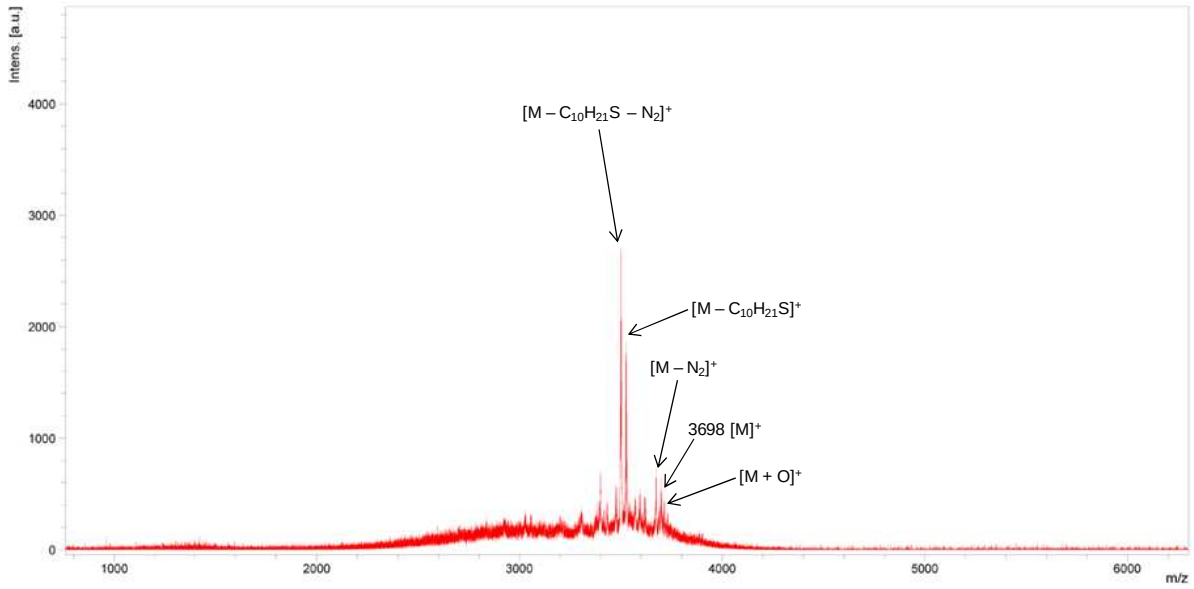

Intens. [a.u.]
4000
3000
2000
1000
0
1000
1500
2000
2500
3000
3500
4000
m/z
[M – N2]+
3524 [M]+
[M – N2 – PhCCH]+
[M – 2xN2]+
[M + Cu]+

Fig. S9.


Intens. [a.u.]
4000
3000
2000
1000
0
1000
2000
3000
4000
5000
6000
m/z
[M – C10H21S – N2]+
[M – C10H21S]+
[M – N2]+
3698 [M]+
[M + O]+