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Supporting Information

Synthesis of Fumaramide Derived [3]Rotaxanes as Potential Precursors for Molecular Boxes

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General Methods

Reactions were carried out under dry N_2 using dry glassware. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Dichloromethane, diethyl ether, methanol and toluene were dried using a Pure Solv-MD Solvent Purification System. All other reagents and solvents were used as received from commercial suppliers unless otherwise indicated.

Liquid volumes less than 1 mL were measured and dispensed with Hamilton gastight syringes. Reaction temperatures refer to the temperature measured in an external bath. Progress of reactions was monitored by thin layer chromatography (TLC) using Merck Silica Gel 60 F_{254} aluminium or plastic backed plates that were visualized with UV light, *p*-anisaldehyde or potassium permanganate. Flash column chromatography was carried out using Davisil 60 Å Silica Gel in the solvent systems indicated. Melting points were recorded using a Gallenkamp melting point apparatus and are uncorrected.

HPLC was carried out on a DIONEX summit P580 quaternary low pressure gradient pump with a built-in vacuum degasser using a Summit UVD 170s UV/Vis multi-channel detector. Solvents were used as HPLC grade. Chromeleon software was used to visualise and process the obtained chromatograms. Analytical separations used a flow rate of 1 mL/min, and semi-preparative used a flow rate of 3 mL/min and preparative used a flow rate of 20 mL/min.

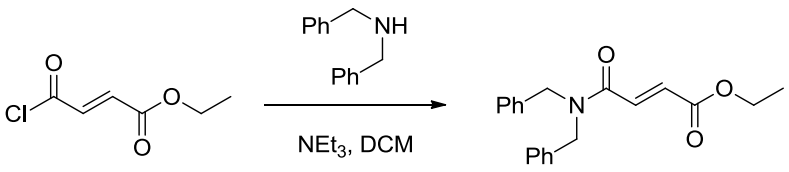
NMR data were recorded either on a Bruker AV300, AVIII300, AV400, AVIII400 or DRX500 spectrometers in the deuterated solvents indicated and the spectra were calibrated on residual solvent peaks. Chemical shifts (δ) are quoted in ppm and *J*

values are quoted in Hz. In reporting spectral data, the following abbreviations were used: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), br (broad). In the case of ambiguous assignments, 2-dimensional homonuclear (^{1}H - ^{1}H) and heteronuclear (^{1}H - ^{13}C) NMR experiments were used. All NMR spectra were processed using MestReNova. NH and OH protons were not reported when these were not observed.

Infrared spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer as neat films, wavelengths (ν) are quoted in cm^{-1}. Mass spectra were acquired on a Waters Micromass LCT TOF spectrometer using electrospray ionisation (ESI). Electron impact (EI) spectra were recorded on a Waters Micromass Zabspec/Magnetic sector mass spectrometer. Matrix-Assisted Laser Desorption Ionization (MALDI) spectra were either recorded on a Bruker Bi-flex MALDI Time of Flight mass spectrometer or a Waters Micromass MALDI mirco MX mass spectrometer.

Synthesis of rotaxane threads (Scheme 3)

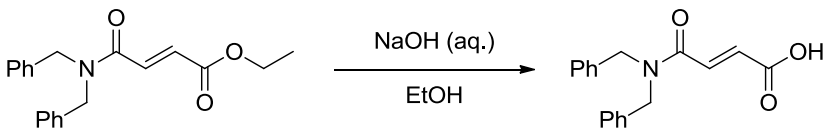
*(E)-ethyl 4-(dibenzylamino)-4-oxobut-2-enoate (**4**)*



4 98%

Ethyl fumaroyl chloride (400 mg, 2.5 mmol, 1.0 eq.) was dissolved in dry DCM (25 mL) at RT. A solution of dibenzylamine(0.47 mL, 2.5 mmol, 1.0 eq.) and NEt_3 (0.35 mL, 2.5 mmol, 1.0 eq.) in dry DCM (25 mL) was added using a syringe pump over a period of 2 h. The reaction was stirred overnight and the solvent was removed *in vacuo*. The crude product was purified by column chromatography with $CHCl_3$ / MeOH (98 / 2) as eluent to afford (*E*)-ethyl 4-(dibenzylamino)-4-oxobut-2-enoate (**4**) as a yellow solid (779 mg, 98%). m.p. 98 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, *J* = 15.2 Hz, 1H, C*H*), 7.23 – 6.96 (m, 10H, Ar, C*H*), 6.82 (d, *J* = 15.2 Hz, 1H, C*H*), 4.49 (s, 2H, CH_2), 4.36 (s, 2H, CH_2), 4.04 (q, *J* = 7.1 Hz, 2H, OCH_2), 1.11 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5 (*C*OO), 165.3 (*C*ONH), 136.7 (Ar, *C*), 136.0 (Ar, *C*), 133.8 (*C*H), 132.2 (*C*H), 129.0 (Ar, *C*H), 128.7 (Ar, *C*H), 128.4 (Ar, *C*H), 128.3 (Ar, *C*H), 128.0 (Ar, *C*H), 127.7 (Ar, *C*H), 127.6 (Ar, *C*H), 126.7 (Ar, *C*H), 61.1 (CH_2), 50.2 (CH_2), 48.5 (CH_2), 14.2 (CH_3); HRMS (ES+) calculated for $C_{20}H_{21}NO_3Na[M+Na]^+$ 346.1419, found 346.1429.

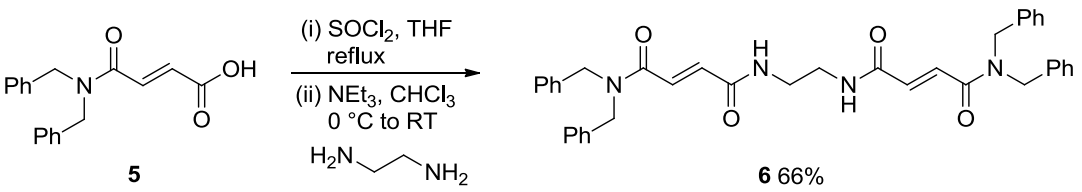
*(E)-4-(dibenzylamino)-4-oxobut-2-enoic acid (**5**)*



4 **5** 99%

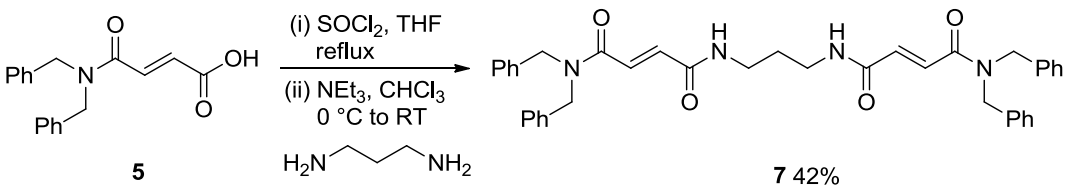
(*E*)-ethyl 4-(dibenzylamino)-4-oxobut-2-enoate (**4**) (468 mg, 1.45 mmol, 1.0 eq.) was dissolved in EtOH (50 mL). A solution of NaOH (70 mg, 1.74 mmol, 1.2 eq.) in water (2.5 mL) was added dropwise. The reaction mixture was stirred for 8 h at RT. The reaction mixture was then acidified with 1 M HCl (10 mL), extracted with DCM (3 x 20 mL) and washed with brine (20 mL). The organic layers were combined, dried over $MgSO_4$ and concentrated under reduced pressure to afford (*E*)-4-(dibenzylamino)-4-oxobut-2-enoic acid (**5**) (427 mg, 99%) as a white solid. m.p. 174 °C; ^{1}H NMR (300 MHz, d_6-DMSO) δ 7.36 – 7.14 (m, 10H, Ar, C*H*), 6.94 (d, *J* = 15.1 Hz, 1H, C*H*), 6.69 (d, *J* = 15.1 Hz, 1H, C*H*), 4.58 (s, 2H, CH_2), 4.52 (s, 2H, CH_2); ^{13}C NMR (100 MHz, d_6-DMSO) δ 169.7 (*C*OO), 167.3 (*C*ON), 143.2 (*C*H), 137.5 (Ar, *C*), 129.1 (Ar, *C*H), 128.7 (Ar, *C*H), 128.1 (Ar, *C*H), 127.8 (Ar, *C*H), 127.7 (Ar, *C*H), 127.6 (Ar, *C*H), 126.9 (Ar, *C*H), 126.0 (Ar, *C*H), 50.4 (*C*H_2), 48.8 (*C*H_2); HRMS (ES+) calculated for $C_{18}H_{17}NO_3Na_2$ $[M+2Na]^+$ 340.0926, found 340.0932.

*(E)-N^{1},N$^{1'}$-(ethane-1,2-diyl)bis(N^{6},N^{6}-dibenzylfumaramide) (**6**)*



(*E*)-4-(dibenzylamino)-4-oxobut-2-enoic acid (**5**) (300 mg, 1.0 mmol, 3.2 eq.) and thionyl chloride (1 mL) were dissolved in THF (10 mL) and heated at reflux for 3 h. The crude acid chloride formed was evaporated to dryness and the resulting residue was dissolved in $CHCl_3$ (10 mL) and cooled to 0°C. NEt_3 (0.26 mL, 1.9 mmol, 6.4 eq.) and ethylenediamine (32 μL, 0.3 mmol, 1.0 eq.) were added using a motor-driven syringe pump over a period of 2 h. The reaction mixture was stirred overnight and the solvent was then removed *in vacuo*. The crude product was purified by column chromatography with $CHCl_3$ / MeOH (95 / 5) as eluent to give the title product as a yellow solid (121 mg, 66%). m.p. 168 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 6.96 (m, 20H, Ar, C*H*, 4H, C*H*), 4.49 (s, 4H CH_2), 4.43 (s, 4H, CH_2), 3.17 (s, 4H, CH_2);^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2 (*C*ON), 165.1 (*C*ON), 136.6 (Ar, *C*), 135.9 (*C*H), 135.7 (*C*H), 129.8 (Ar, *C*H), 128.9 (Ar, *C*H), 128.1 (Ar, *C*H), 127.7 (Ar, *C*H), 126.9 (Ar, *C*H), 50.5 (CH_2), 48.7 (CH_2), 39.9 (CH_2); HRMS (ES+) calculated for $C_{38}H_{38}N_4O_4Na$ $[M+Na]^+$ 637.2791, found 637.2794.

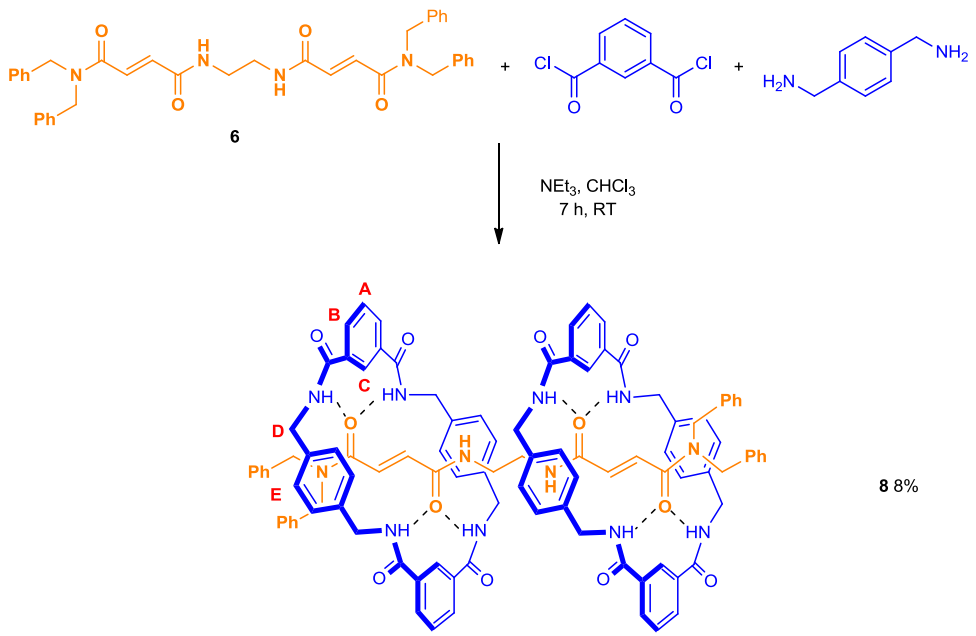
*(E)-N^1,N$^{1'}$-(propane-1,3-diyl)bis(N^6,N^6-dibenzylfumaramide) (**7**)*



(*E*)-4-(dibenzylamino)-4-oxobut-2-enoic acid (**5**) (300 mg, 1.0 mmol, 3.2 eq.) and thionyl chloride (1 mL) were dissolved in THF (10 mL) and heated at reflux for 3 h. The crude acid chloride formed was evaporated to dryness and the resulting residue was dissolved in $CHCl_3$ (10 mL) and cooled to 0 °C. NEt_3 (0.26 mL, 1.9 mmol, 6.4 eq.) and 1,3-diaminopropane (32 μL, 0.3 mmol, 1.0 eq.) were added using a motor-driven syringe pump over a period of 2 h. The reaction was stirred overnight and the solvent was removed *in vacuo*. The crude product was purified by column chromatography with $CHCl_3$ / MeOH (95 / 5) as eluent to give the title product (**7**) as a yellow solid (79 mg, 42%). m.p. 146 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.00 (m, 24H, 20 Ar, C*H*, 4 C*H*), 4.52 (m, 8H, CH_2), 3.22 (m, 4H, CH_2), 1.55 (s, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1 (*C*ON), 164.8 (*C*ON), 136.7 (Ar, *C*), 136.0 (*C*H), 129.9 (Ar, *C*H), 128. 9 (Ar, *C*H), 128.1 (Ar, *C*H), 127.8 (Ar, *C*H), 126.9 (Ar, *C*H), 50.4 (CH_2), 48.7 (CH_2), 36.4 (CH_2), 29.5 (CH_2); HRMS (ES+) calculated for $C_{39}H_{40}N_4O_4Na[M+Na]^+$ 651.2947, found 651.2946.

Synthesis of rotaxanes (Scheme 4)

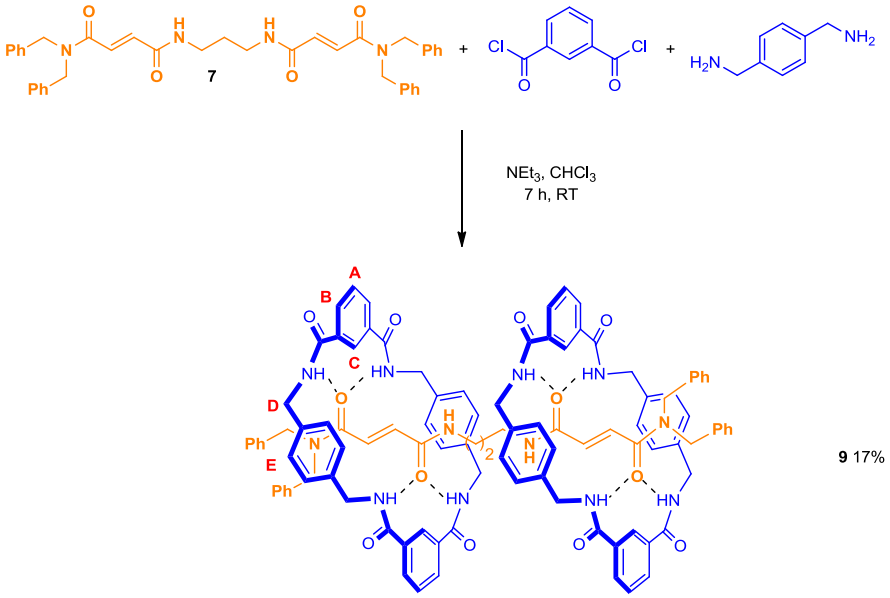
*(E)-N^1,N$^{1'}$-(ethane-1,2-diyl)bis(N^6,N^6-dibenzylfumaramide) [3]rotaxane (**8**)*



Et_3N (1.3 mL, 9.5 mmol, 48.0 eq.) was added to a stirred solution of (*E*)-*N*^{1},*N*$^{1'}$-(ethane-1,2-diyl)bis(*N*^{6},*N*^{6}-dibenzylfumaramide)(**6**) (121 mg, 0.2 mmol, 1.0 eq.) in anhydrous $CHCl_3$ (100 mL). The solution was stirred vigorously whilst solutions of *p*-xylylene diamine (643 mg, 4.7 mmol, 24.0 eq.) in anhydrous $CHCl_3$ (20 mL) and isophthaloyl dichloride (960 mg, 4.7 mmol, 24.0 eq.) in anhydrous $CHCl_3$ (20 mL) were simultaneously added over a period of 3 h using a motor-driven syringe pump. After a further 4 h period the resulting suspension was filtered through a Celite® pad and the solvent removed under reduced pressure.The crude product was purified by HPLC with H_2O / MeOH (15 / 85) as eluent to afford (*E*)-*N*^{1},*N*$^{1'}$-(ethane-1,2-diyl)bis(*N*^{6},*N*^{6}-dibenzylfumaramide) [3]rotaxane (**8**) as a white solid (25 mg, 8%).m.p. 176 °C; FTIR (film) ν_{max} 3300, 3064, 1637, 1601, 1529, 1464, 1423, 1353, 1274, 1079, 956, 818, 753, 729, 695; ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.69 (s, 2H, N*H*), 8.42 (s, 4H, Ar, C*H*, H_C), 8.01 – 7.92 (m, 16H, 8 Ar, C*H*, H_B, 8 N*H*), 7.54 (t, *J* = 7.7

Hz, 4H, Ar, C*H*, H_A), 7.30 – 7.25 (m, 6H, Ar, C*H*), 7.16 – 7.11 (m, 4H, Ar, C*H*), 6.98 – 6.91 (m, 6H, Ar, C*H*), 6.87 (s, 16H, Ar, C*H*, H_E), 6.69 (d, *J* = 7.2 Hz, 4H, Ar, C*H*), 6.00 – 5.88 (m, 4H, C*H*), 4.40 – 4.24 (m, 16H, CH_2, H_D), 4.08 (dd, *J* = 13.9, 4.0 Hz, 8H, CH_2), 3.10 (br s, 4H, CH_2);^{13}C NMR (100 MHz, d_6-DMSO) δ 165.3 (*C*ON), 165.2 (*C*ON), 164.9 (*C*ON), 136.9 (Ar, *C*), 136.0 (Ar, *C*), 133.7 (Ar, *C*), 132.9 (*C*H), 130.8 (*C*H), 128.5 (Ar, *C*H), 128.3 (Ar, *C*H), 127.5 (Ar, *C*H), 127.1 (Ar, *C*H), 126.0 (Ar, *C*H), 125.5 (Ar, *C*H), 124.0 (Ar, *C*H), 50.7 (CH_2), 50.3 (CH_2), 43.0 (CH_2), 37.7 (CH_2); HRMS (ES+) calculated for $C_{102}H_{94}N_{12}O_{12}Na$ $[M+Na]^+$ 1701.7012, found 1701.7054.

*(E)-N^1,N$^{1'}$-(propane-1,3-diyl)bis(N^6,N^6-dibenzylfumaramide) [3]rotaxane (**9**)*

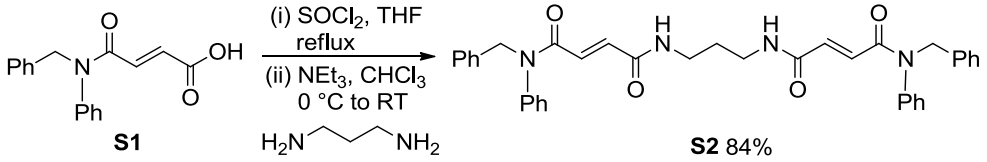


Et_3N (0.87 mL, 6.24 mmol, 48.0 eq.) was added to a stirred solution of (*E*)-*N*^{1},*N*$^{1'}$-(propane-1,3-diyl)bis(*N*^{6},*N*^{6}-dibenzylfumaramide)(**7**) (79 mg, 0.13 mmol, 1.0 eq.) in anhydrous $CHCl_3$ (100 mL). The solution was stirred vigorously whilst solutions of *p*-xylylene diamine (424 mg, 3.12 mmol, 24.0 eq.) in anhydrous $CHCl_3$ (20 mL) and isophthaloyl dichloride (633 mg, 3.12 mmol, 24.0 eq.) in anhydrous $CHCl_3$ (20 mL)

were simultaneously added over a period of 3 h using a motor-driven syringe pump. After a further 4 h period the resulting suspension was filtered through a Celite® pad and the solvent removed under reduced pressure.The crude product was purified by HPLC with H_2O / MeOH (15 / 85) as eluent to afford (*E*)-N^1,$N^{1'}$-(propane-1,3-diyl)bis(N^6,N^6-dibenzylfumaramide) [3]rotaxane (**9**) as a white solid (37 mg, 17%). m.p. 187 °C; FTIR (film) ν_{max} 3285, 3061, 2922, 1640, 1528, 1476, 1421, 1358, 1299, 1192, 1080, 1022, 959, 820, 695; ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.48 (s, 1H, N*H*), 8.38 (s, 4H, Ar, C*H*, H_C), 7.97 – 7.99 (m, 12H, 8 Ar, C*H*, H_B, 4 N*H*), 7.56 (t, *J* = 7.7 Hz, 4H, Ar, C*H*, H_A), 7.25 – 7.26 (m, 6H, Ar, C*H*), 7.11 – 7.12 (m, 4H, Ar, C*H*), 7.02 – 6.93 (m, 6H, Ar, C*H*), 6.86 (s, 16H, Ar, C*H*, H_E), 6.71 – 6.73 (m, 4H, Ar, C*H*), 6.00 – 5.82 (m, 4H, C*H*), 4.33 (dd, *J* = 21.1, 14.1 Hz, 16H, CH_2, H_D), 4.09 (d, *J* = 13.9 Hz, 8H, CH_2), 3.11 - 3.15 (m, 4H, CH_2), 1.71 – 1.62 (m, 2H, CH_2);^{13}C NMR (100 MHz, d_6-DMSO) δ 165.3 (*C*ON), 165.2 (*C*ON), 165.1 (*C*ON), 165.0 (*C*ON), 136.7 (Ar, *C*), 135.8 (Ar, *C*), 133.7 (Ar, *C*), 133.1 (*C*H), 130.7 (*C*H), 128.9 (Ar, *C*H), 128.5 (Ar, *C*H), 128.2 (Ar, *C*H), 127.5 (Ar, *C*H), 127.1 (Ar, *C*H), 125.6 (Ar, *C*H), 124.2 (Ar, *C*H), 50.7 (CH_2), 50.2 (CH_2), 43.1 (CH_2), 37.6 (CH_2), 28.4 (CH_2); HRMS (ES+) calculated for $C_{103}H_{96}N_{12}O_{12}Na$ $[M+Na]^+$ 1715.7168, found 1715.7144.

Synthesis of rotaxane 10

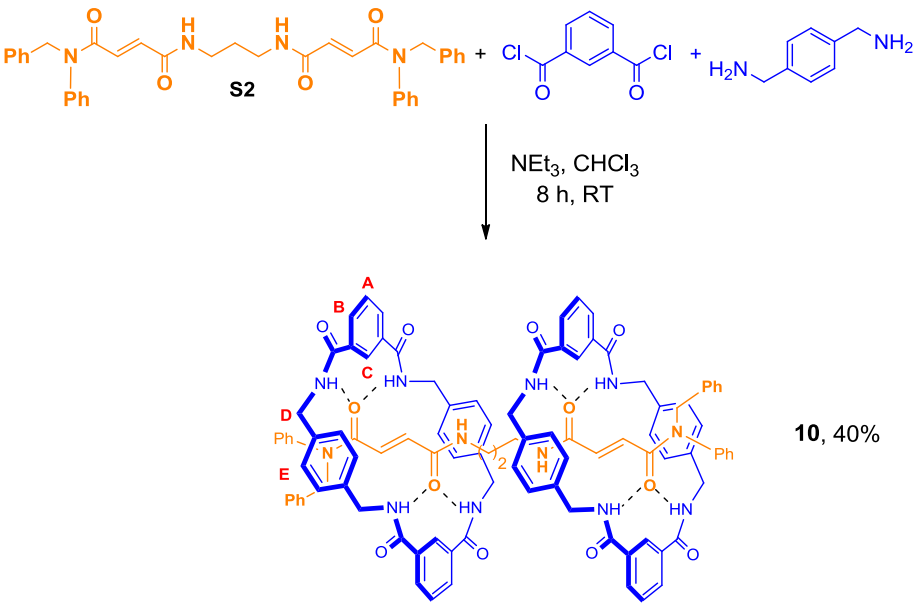
*(E)-N^{1},N$^{1'}$-(propane-1,3-diyl)bis(N^{6}-benzyl-N^{6}-phenylfumaramide) (**S2**)*



A mixture of the known acid (**S1**)[1] (2.7 g, 9.5 mmol, 4.8 eq.) and thionyl chloride (10 mL) were heated for 3 h at reflux. The crude acid chloride formed was evaporated to dryness and the resulting residue was dissolved in DCM (50 mL). The mixture was cooled to 0 °C. NEt_3 (1.32 mL, 9.5 mmol, 4.8 eq.) and 1,3-diaminopropane (290 μL, 2.0 mmol, 1.0 eq.) were added using a syringe pump over a period of 2 h. The reaction was stirred overnight and the solvent was removed *in vacuo.* The crude product was purified by column chromatography with EtOAc / pet (1 / 1) as eluent to give the title product (**S2**) as a white solid (1.0 g, 84%). m.p. 128 °C; FTIR (film) ν_{max} 3228, 3062, 2930, 1628, 1593, 1558, 1493, 1391, 1327, 1191, 970, 751, 694;^{1}H NMR (400 MHz, MeOD / $CDCl_3$) δ 7.37 – 7.30 (m, 6H, Ar, C*H*), 7.25 – 7.19 (m, 6H, Ar, C*H*), 7.17 – 7.13 (m, 4H, Ar, C*H*), 7.03 – 6.97 (m, 4H, Ar, C*H*), 6.89 (d, *J* = 15.0 Hz, 2H, C*H*), 6.71 (d, *J* = 15.0 Hz, 2H, C*H*), 4.97 (s, 4H, CH_2), 3.18 (t, *J* = 6.8 Hz, 4H, CH_2CH_2NH), 1.68 – 1.61 (m, 2H, CH_2); ^{13}C NMR (100 MHz, MeOD / $CDCl_3$) δ 166.5 (*C*O), 142.2 (Ar, *C*), 137.9 (Ar, *C*), 135.6 (*C*H), 131.8 (*C*H), 131.0 (Ar, *C*H), 129.9 (Ar, *C*H), 129.7 (Ar, *C*H), 129.4 (Ar, *C*H), 128.9 (Ar, *C*H), 54.8 (CH_2), 38.2 (CH_2), 29.9 (CH_2);HRMS (ES+) calculated for $C_{37}H_{36}N_4O_4Na$ $[M+Na]^+$ 623.2634, found 623.2629.

1. Alvarez-Pérez, M.; Goldup, S. M.; Leigh, D. A.; Slawin, A. M. Z., *J. Am. Chem. Soc.,* 2008, **130**, 1836.

(E)-N^1,N$^{1'}$-(propane-1,3-diyl)bis(N^6-benzyl-N^6-phenylfumaramide [3]rotaxane ***10***



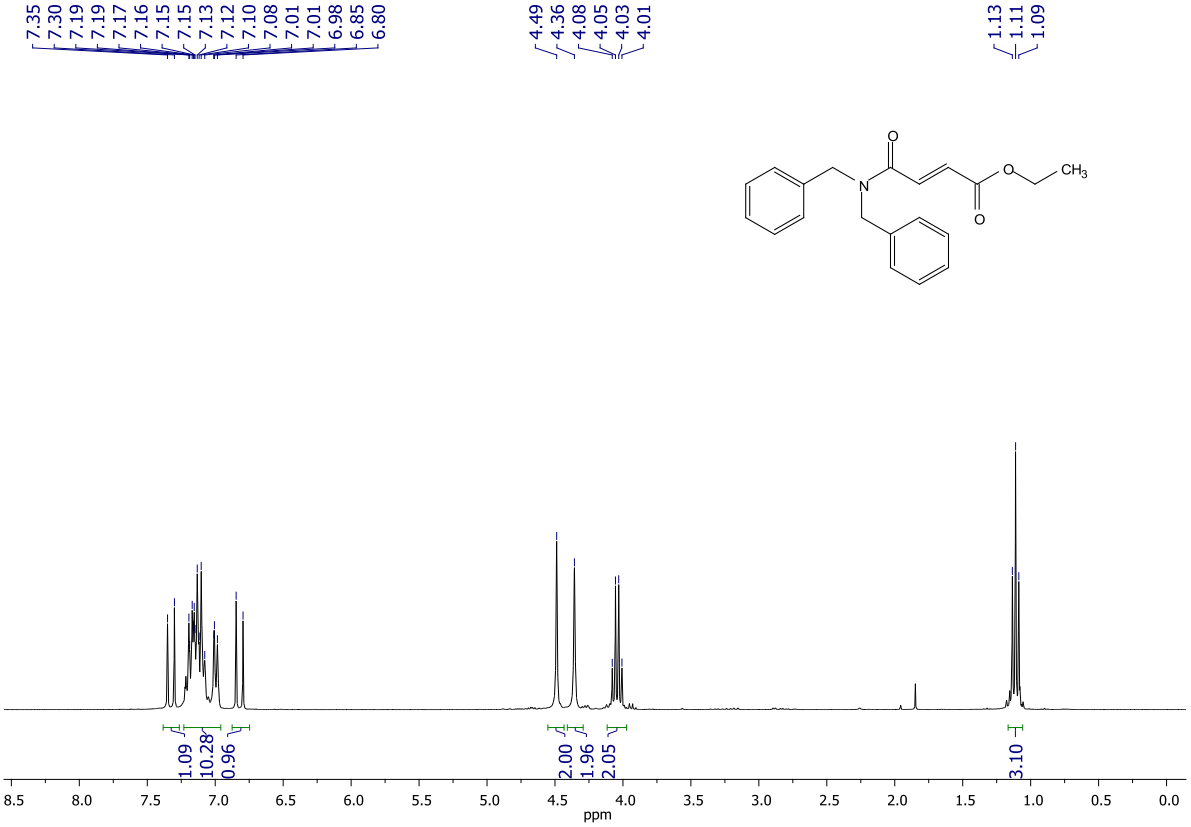
Et_3N (0.7 mL, 4.8 mmol, 48.0 eq.) was added to a stirred solution of (*E*)-*N*^{1},*N*$^{1'}$-(propane-1,3-diyl)bis(*N*^{6}-benzyl-*N*^{6}-phenylfumaramide) (**S2**) (60 mg, 0.1 mmol, 1.0 eq.) in anhydrous $CHCl_3$ (30 mL). The solution was stirred vigorously whilst solutions of *p*-xylylene diamine (327 mg, 2.4 mmol, 24.0 eq.) in anhydrous $CHCl_3$ (10 mL) and isophthaloyl dichloride (487 mg, 2.4 mmol, 24.0 eq.) in anhydrous $CHCl_3$ (10 mL) were simultaneously added over a period of 4 h using a motor-driven syringe pump. After a further 4 h period the resulting suspension was filtered through a Celite® pad and the solvent removed under reduced pressure.The crude product was purified by column chromatography with EtOAc / MeOH (9 / 1) as eluent to give the [3]rotaxane (**10**) as a white solid (67 mg, 40%) and the corresponding [2]rotaxane as a white solid (3 mg, 2%).

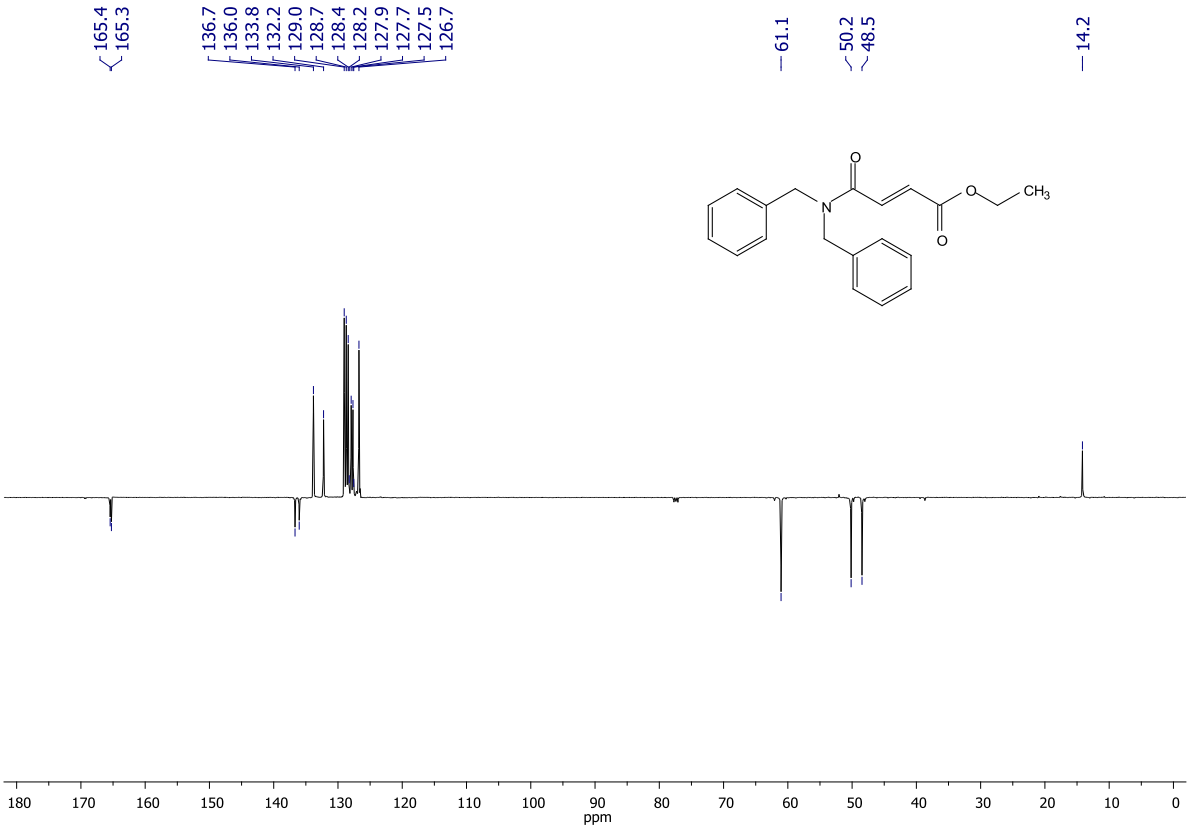
Data for rotaxane **10**: m.p. 178 °C; FTIR (film) ν_{max} 3283, 3066, 2926, 1639, 1609, 1588, 1530, 1495, 1415, 1305, 1272, 1174, 1079, 960, 698; ^{1}H NMR (400 MHz, CD_2Cl_2/ MeOD) δ 8.30 (br s, 4H, Ar, C*H*, H_C), 8.13 (dd, *J* = 7.8, 1.7 Hz, 8H, Ar, C*H*,

H_B), 7.64 (t, *J* = 7.8 Hz, 4H, Ar, C*H*, H_A), 7.30 – 7.20 (m, 7H, Ar, C*H*), 7.04 – 6.95 (m, 21H, 16 Ar, C*H*, H_E, 5 m, Ar, C*H*), 6.88 (t, *J* = 7.8 Hz, 4H, Ar, C*H*), 6.81 – 6.75 (m, 4H, Ar, C*H*), 6.44 (m, 2H, N*H*), 5.86 (d, *J* = 14.9 Hz, 2H, C*H*), 5.46 (d, *J* = 14.9 Hz, 2H, C*H*), 4.66 (s, 4H, CH_2), 4.39 (d, *J* = 14.2 Hz, 8H, CH_2, H_D), 4.22 (d, *J* = 14.2 Hz, 8H, CH_2, H_D), 3.31 – 3.24 (m, 4H, CH_2CH_2NH), 1.91 – 1.75 (m, 2H, CH_2); ^{13}C NMR (100 MHz, CD_2Cl_2 / MeOD) δ 167.3 (*C*O), 166.5 (*C*O), 165.4 (*C*O), 140.8 (Ar, *C*), 137.9 (Ar, *C*), 136.8 (Ar, *C*), 134.3 (Ar, *C*), 133.0 (*C*H), 132.1 (*C*H), 130.0 (Ar, *C*H), 129.9 (Ar, *C*H), 129.8 (Ar, *C*H), 129.7 (Ar, *C*H), 129.1 (Ar, *C*H), 129.0 (Ar, *C*H), 128.7 (Ar, *C*H), 128.1 (Ar, *C*H), 127.7 (Ar, *C*H), 124.9 (Ar, *C*H), 55.0 (CH_2), 44.2 (CH_2), 38.6 (CH_2CH_2NH), 29.5 (CH_2); LRMS (ES+) 1688.8 ($[M+Na]^+$, 25%), 855.9 ($[M+2Na]^{2+}$, 100%).

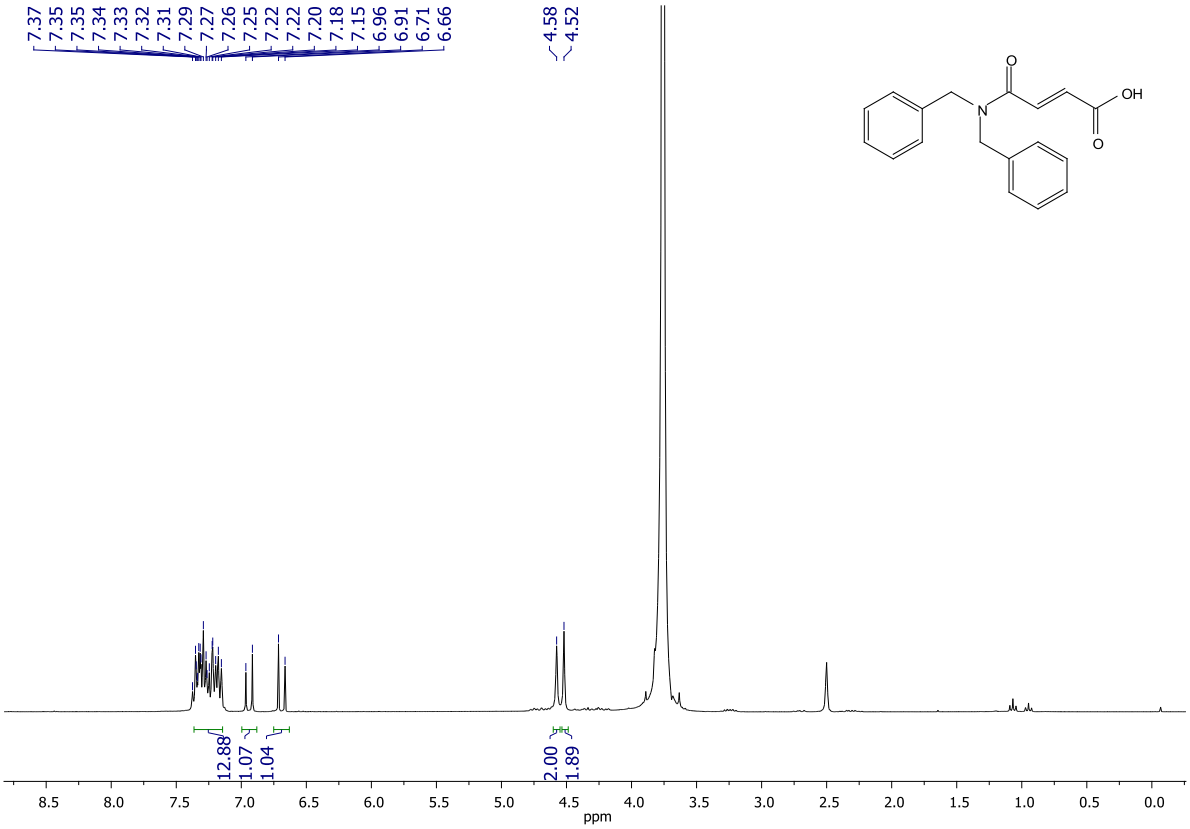
Data for the corresponding [2]rotaxane: m.p. 162 °C; FTIR (film) ν_{max} 3301, 3063, 2929, 1639, 1534, 1493, 1420, 1296, 1188, 1110, 1080, 967, 820, 696; ^1H NMR (400 MHz, MeOD / $CDCl_3$) δ 8.34 (br s, 2H, Ar, C*H*, H_C), 8.22 – 8.14 (m, 5H, 4 Ar, C*H*, H_B, 1 N*H*), 7.64 (t, *J* = 7.8 Hz, 2H, Ar, C*H*, H_A), 7.27 – 7.16 (m, 6H, Ar, C*H*), 7.09 – 7.00 (m, 8H, Ar, C*H*), 6.95 (s, 8H, Ar, C*H*, H_E), 6.84 (d, *J* = 8.0 Hz, 6H, Ar, C*H*), 6.31 (d, *J* = 14.8 Hz, 2H, C*H*), 6.04 (d, *J* = 14.8 Hz, 2H, C*H*), 4.77 (s, 4H, CH_2), 4.32 (s, 8H, CH_2, H_D), 3.21 (t, *J* = 6.8 Hz, 4H, CH_2CH_2NH), 1.74 – 1.66 (m, 2H, CH_2); ^{13}C NMR (100 MHz, MeOD / $CDCl_3$) δ 166.8 (*C*O), 165.7 (*C*O), 165.1 (*C*O), 140.6 (Ar, *C*), 137.4 (Ar, *C*), 136.4 (Ar, *C*), 134.2 (*C*H), 133.7 (Ar, *C*), 133.4 (*C*H), 131.9 (Ar, *C*H), 129.8 (Ar, *C*H), 129.6 (Ar, *C*H), 129.4 (Ar, *C*H), 129.2 (Ar, *C*H), 128.9 (Ar, *C*H), 128.7 (Ar, *C*H), 128.2 (Ar, *C*H), 127.9 (Ar, *C*H), 124.2 (Ar, *C*H), 54.3 (CH_2), 43.9 (CH_2), 37.3 (CH_2CH_2NH), 29.0 (CH_2); HRMS (ES+) calculated for $C_{69}H_{64}N_8O_8$ $[M+Na]^+$ 1155.4745, found 1155.4785.

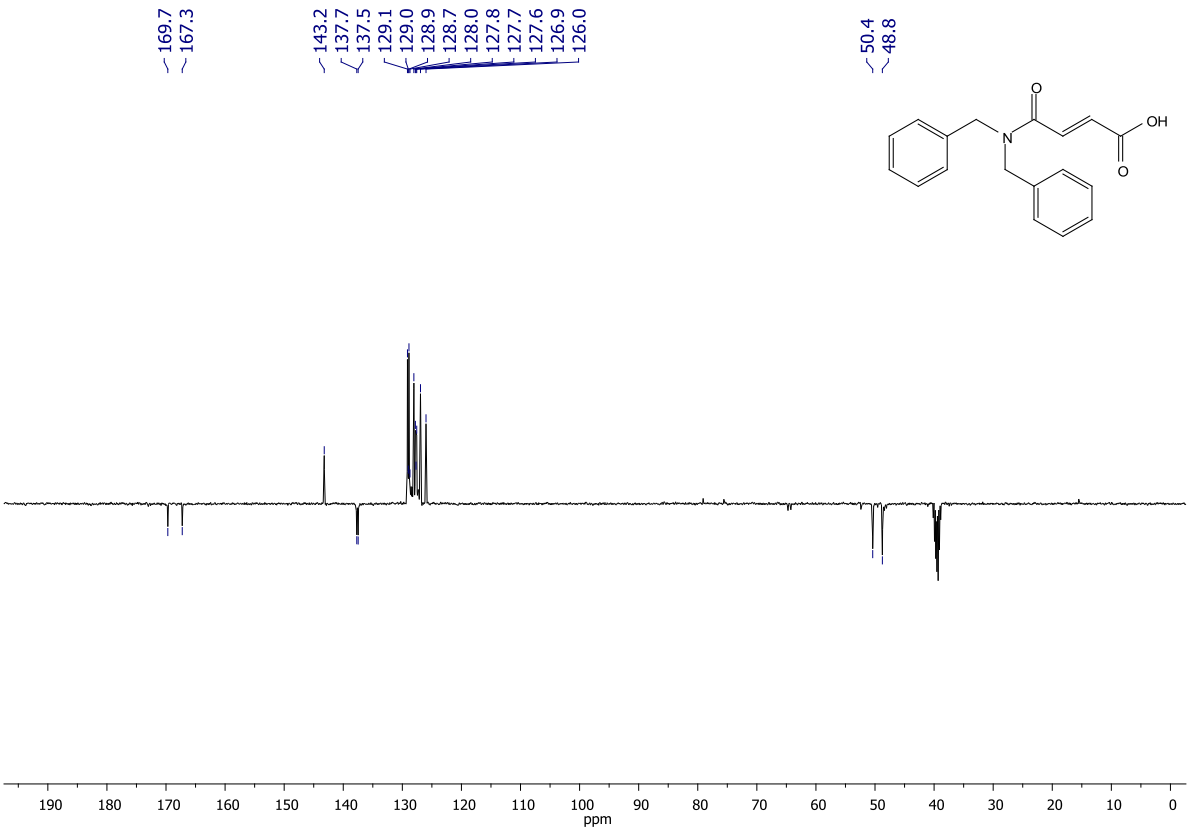
Compound **4**


7.35
7.30
7.19
7.19
7.17
7.16
7.15
7.15
7.13
7.12
7.10
7.08
7.01
7.01
6.98
6.85
6.80
4.49
4.36
4.08
4.05
4.03
4.01
1.13
1.11
1.09
1.09
10.28
0.96
2.00
1.96
2.05
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

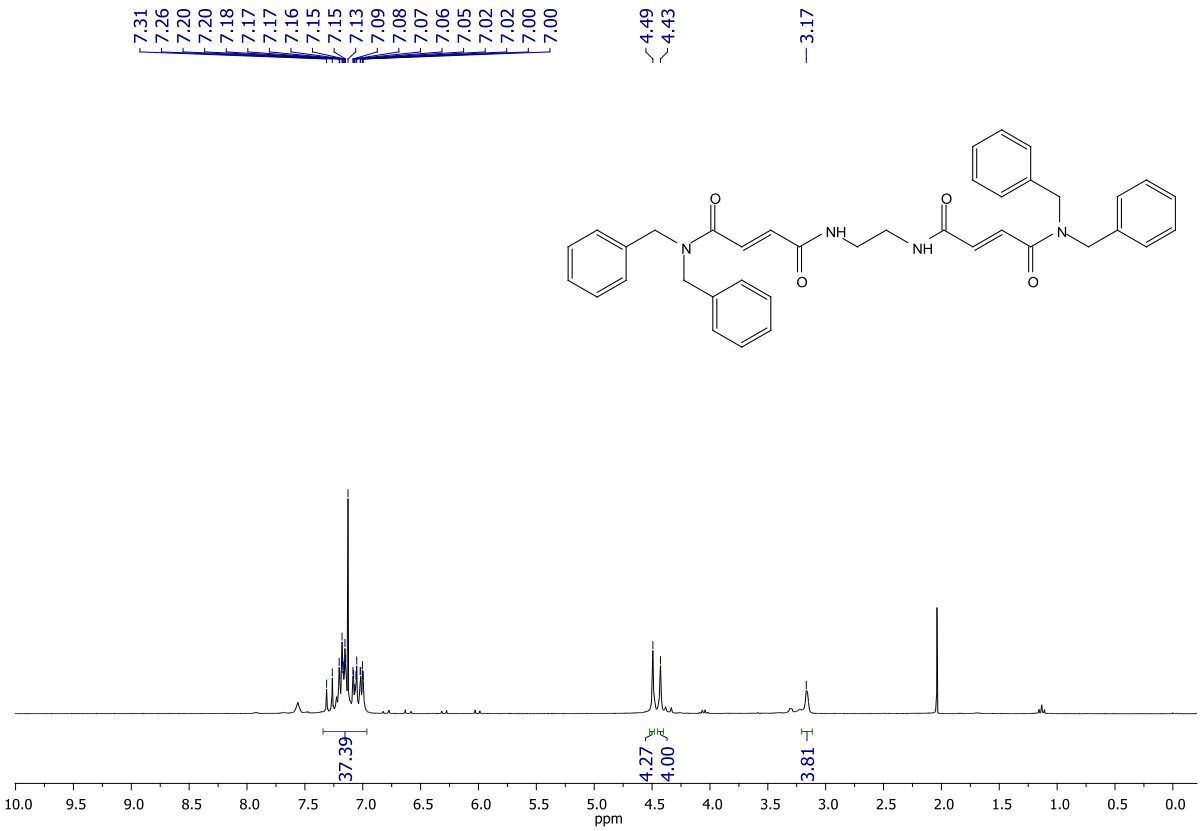

165.4
165.3
136.7
136.0
133.8
132.2
129.0
128.7
128.4
128.2
127.9
127.7
127.5
126.7
61.1
50.2
48.5
14.2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

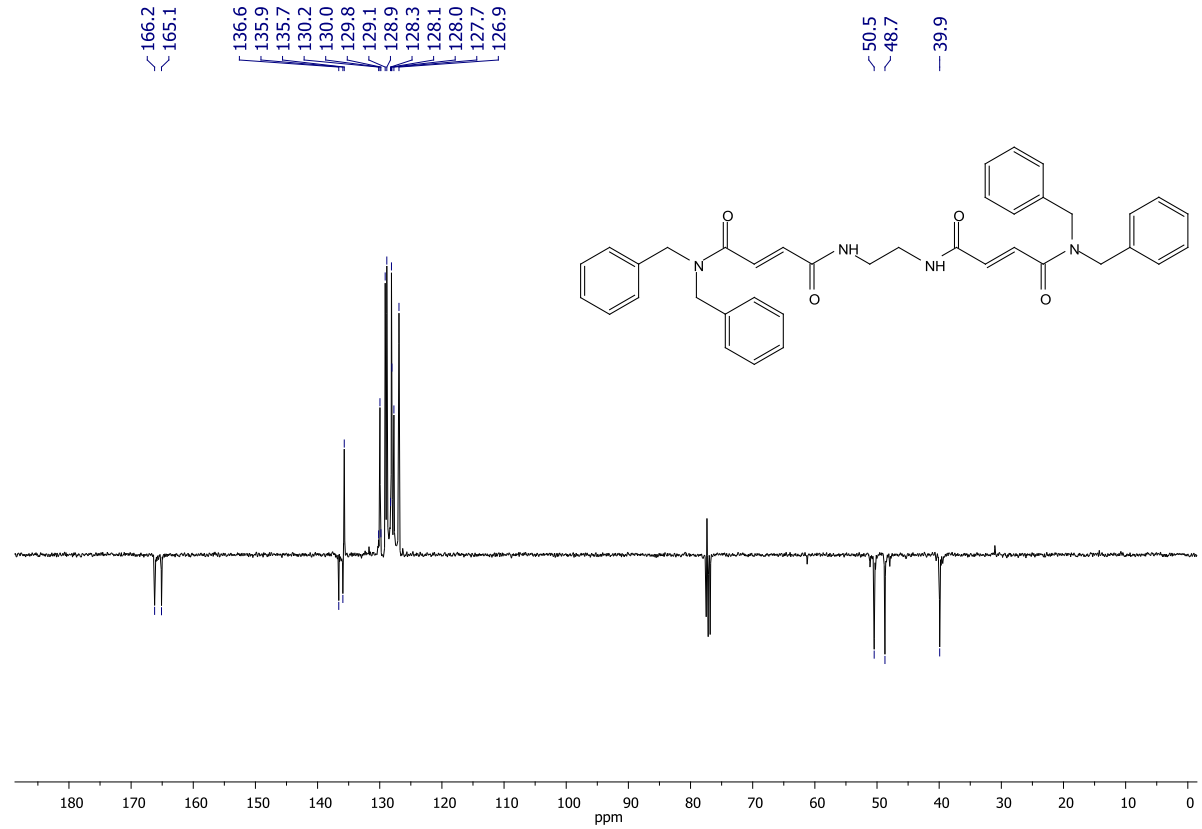
Compound 5


7.37
7.35
7.35
7.34
7.33
7.32
7.31
7.29
7.27
7.26
7.25
7.22
7.22
7.20
7.18
7.15
6.96
6.91
6.71
6.66
4.58
4.52
12.88
1.07
1.04
2.00
1.89
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
O
N
OH
O

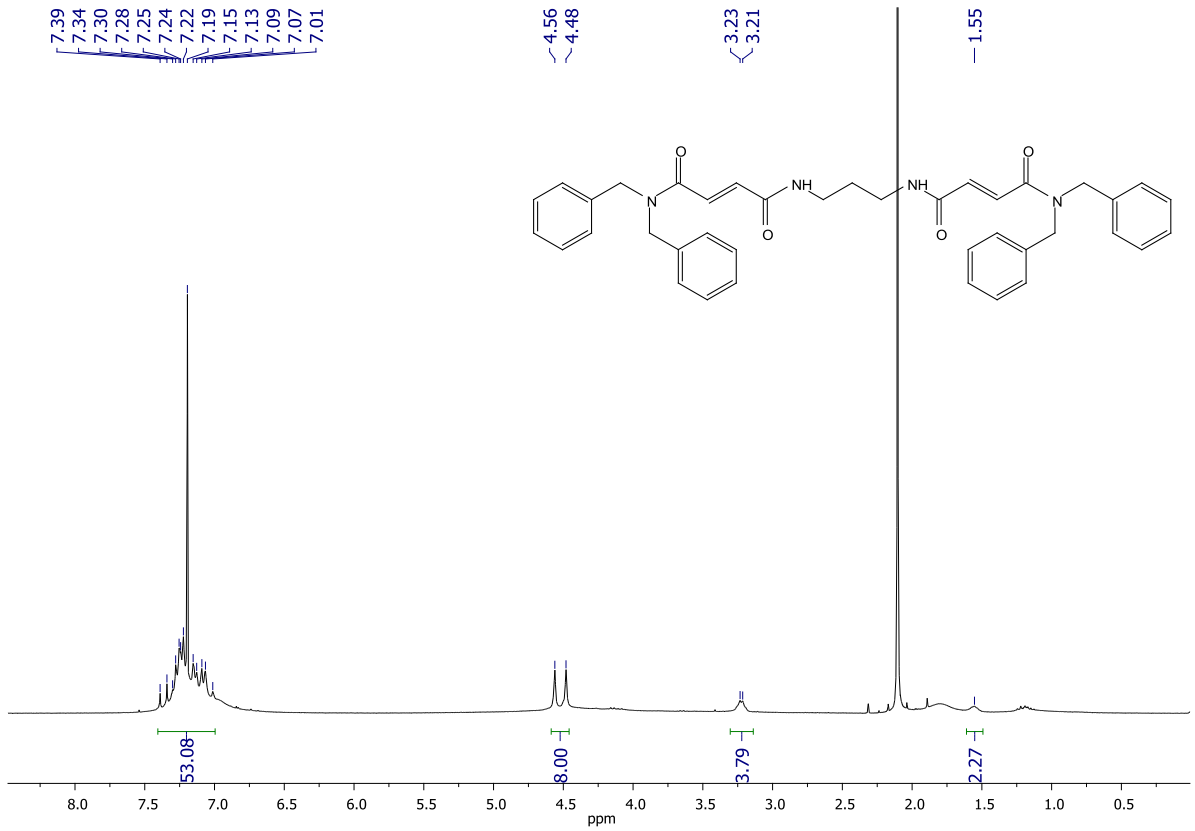

169.7
167.3
143.2
137.7
137.5
129.1
129.0
128.9
128.7
128.0
127.8
127.7
127.6
126.9
126.0
50.4
48.8
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
O
N
OH
O

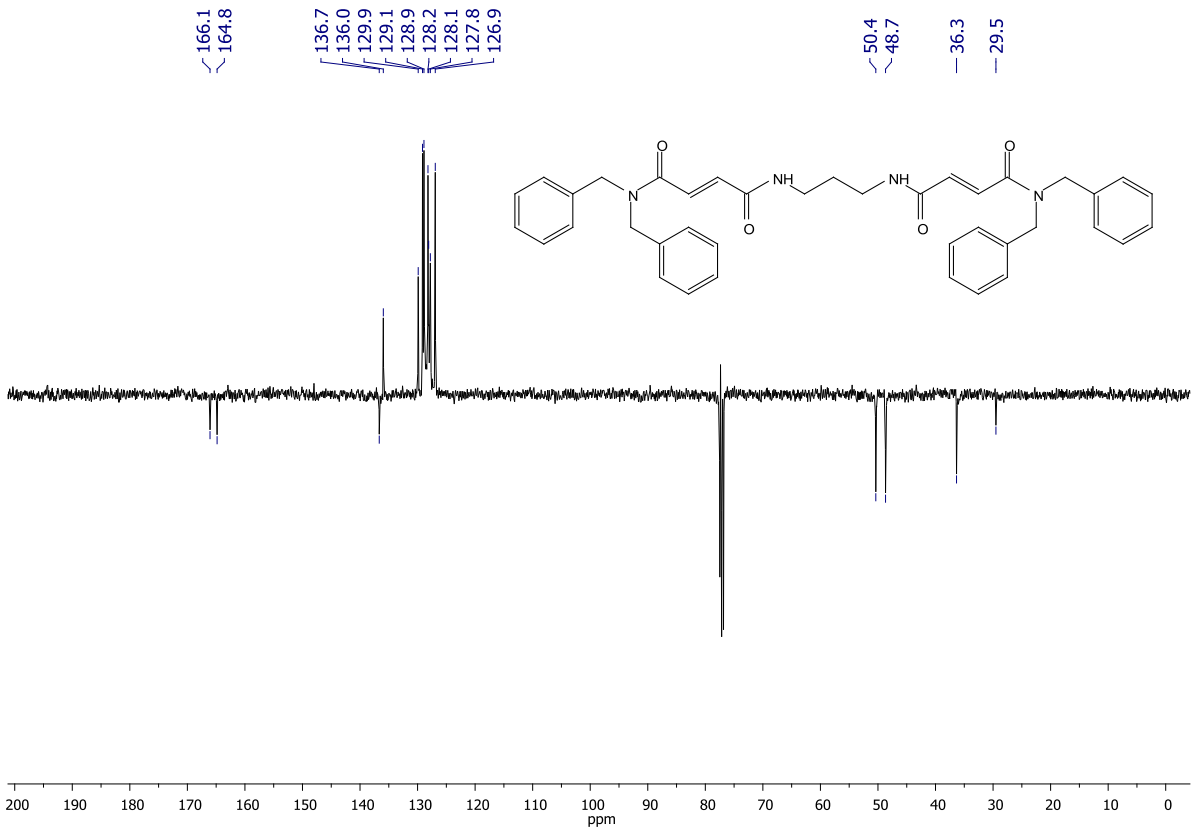
Compound 6


7.31
7.26
7.20
7.20
7.18
7.17
7.17
7.16
7.15
7.15
7.13
7.09
7.08
7.07
7.06
7.05
7.02
7.02
7.00
7.00
4.49
4.43
3.17
37.39
4.27
4.00
3.81
ppm

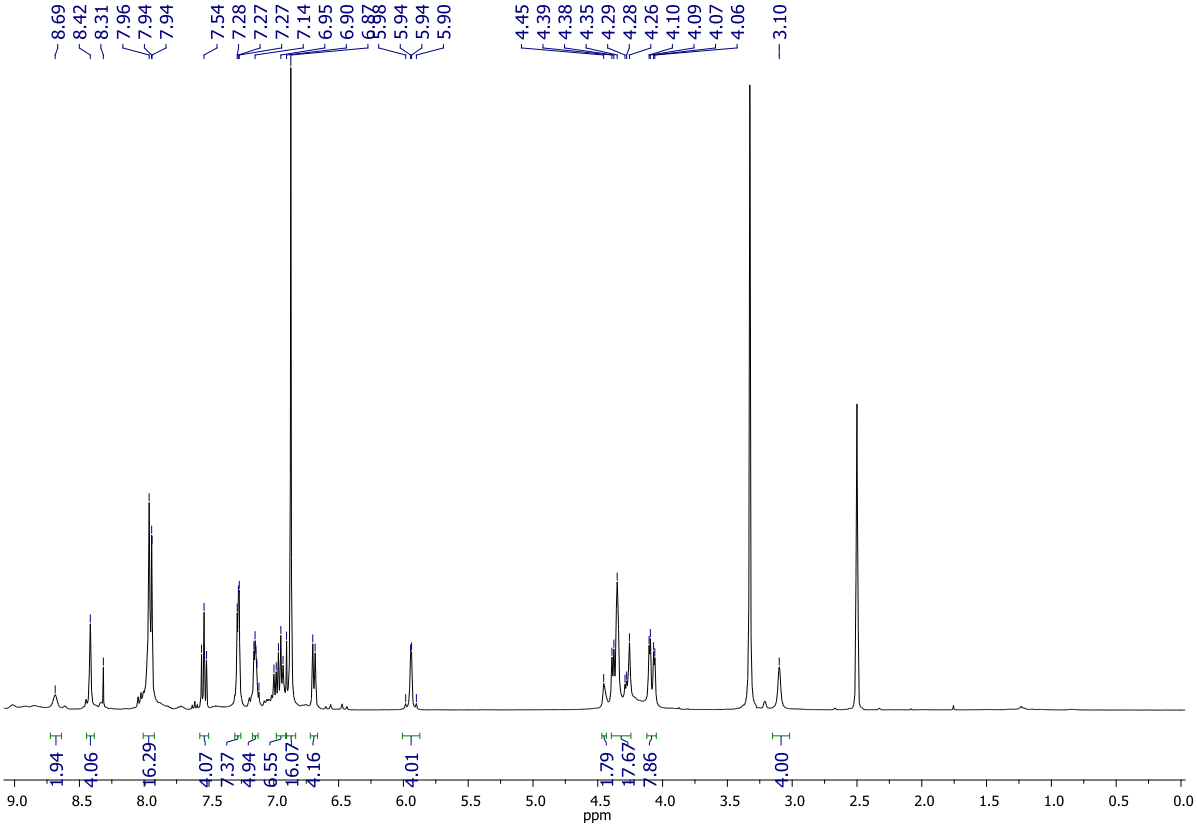

166.2
165.1
136.6
135.9
135.7
130.2
130.0
129.8
129.1
128.9
128.3
128.1
128.0
127.7
126.9
50.5
48.7
39.9
ppm

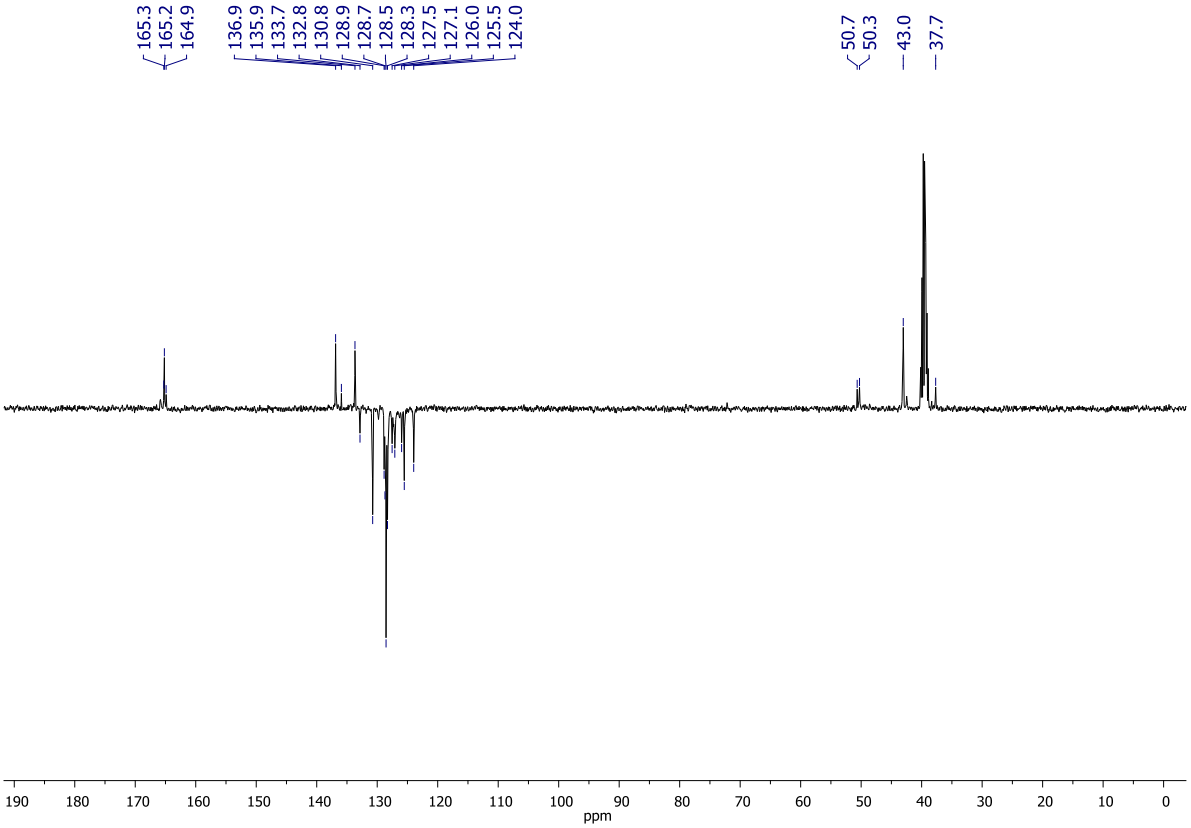
Compound 7


7.39
7.34
7.30
7.28
7.25
7.24
7.22
7.19
7.15
7.13
7.09
7.07
7.01
4.56
4.48
3.23
3.21
1.55
53.08
8.00
3.79
2.27
ppm

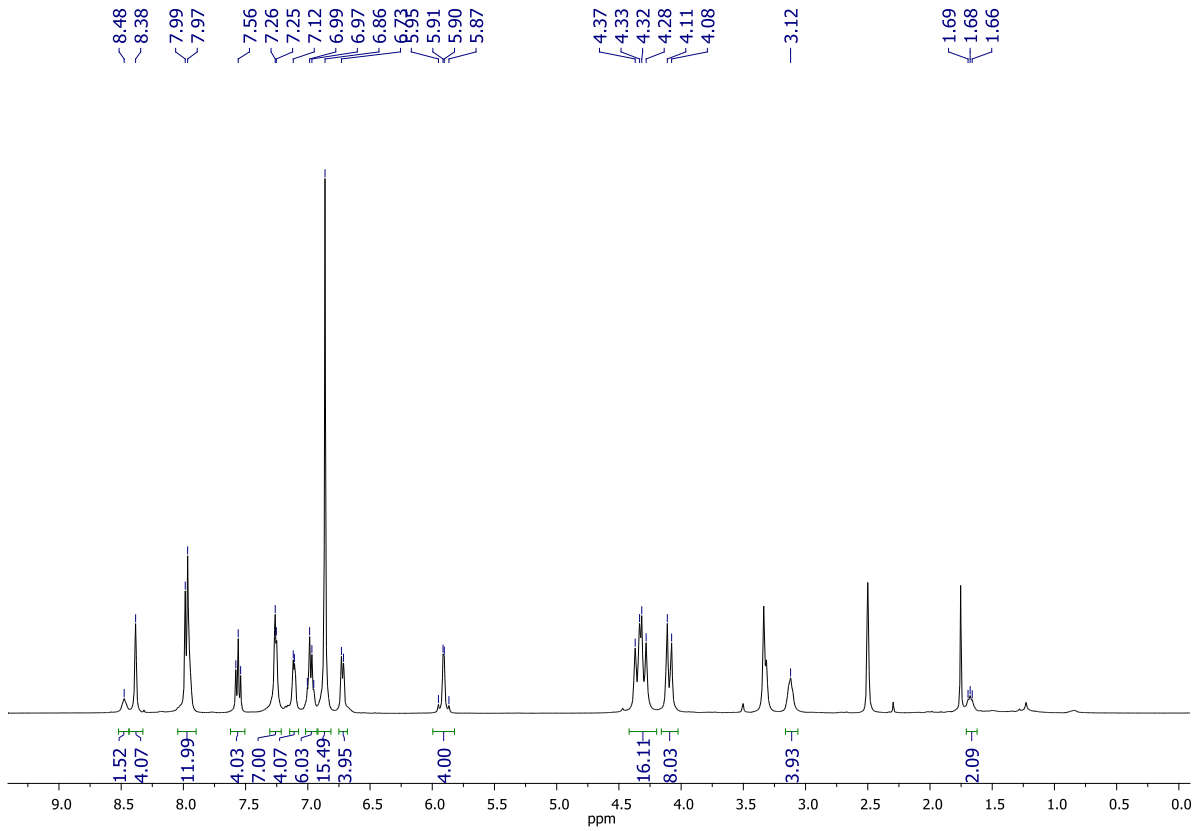

166.1
164.8
136.7
136.0
129.9
129.1
128.9
128.2
128.1
127.8
126.9
50.4
48.7
36.3
29.5
ppm

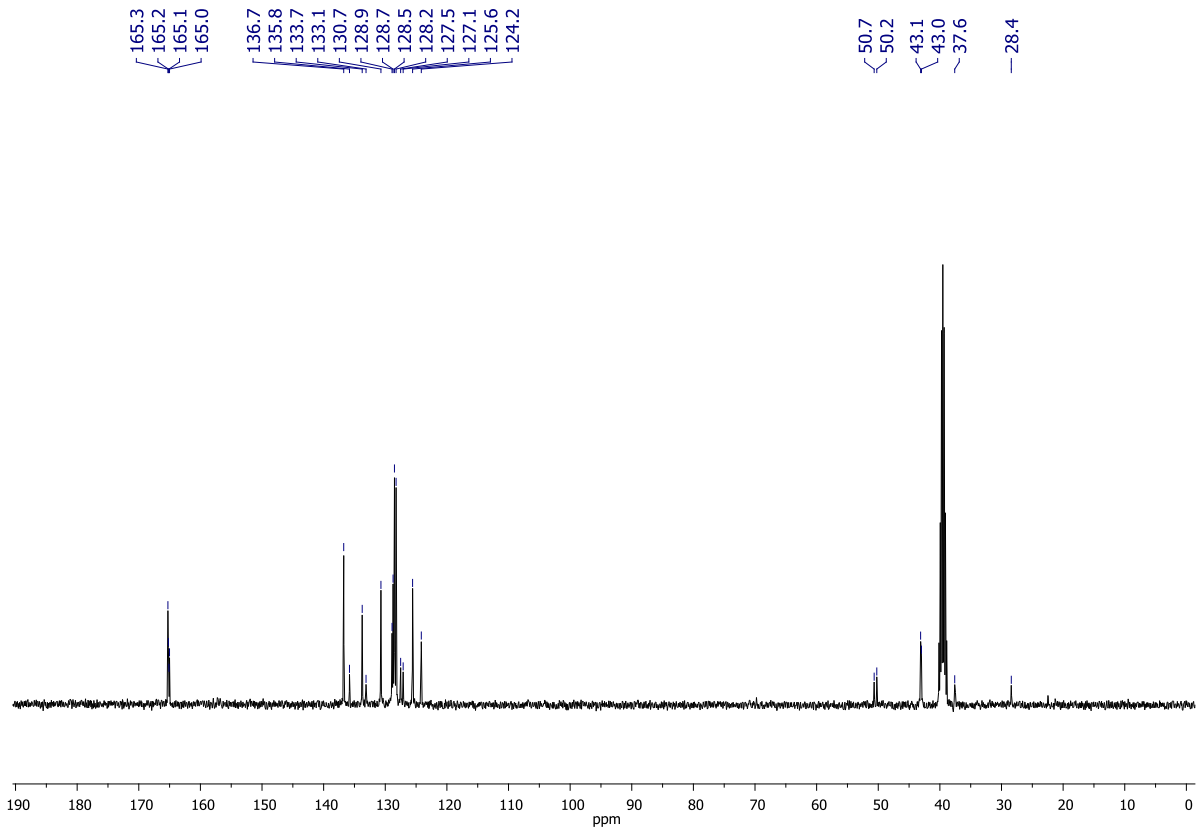
Compound 8


8.69
8.42
8.31
7.96
7.94
7.94
7.54
7.28
7.27
7.27
7.14
6.95
6.90
5.94
5.94
5.90
4.45
4.39
4.38
4.35
4.29
4.28
4.26
4.10
4.09
4.07
4.06
3.10
1.94
4.06
16.29
4.07
7.37
4.94
6.55
16.07
4.16
4.01
1.79
17.67
7.86
4.00
ppm

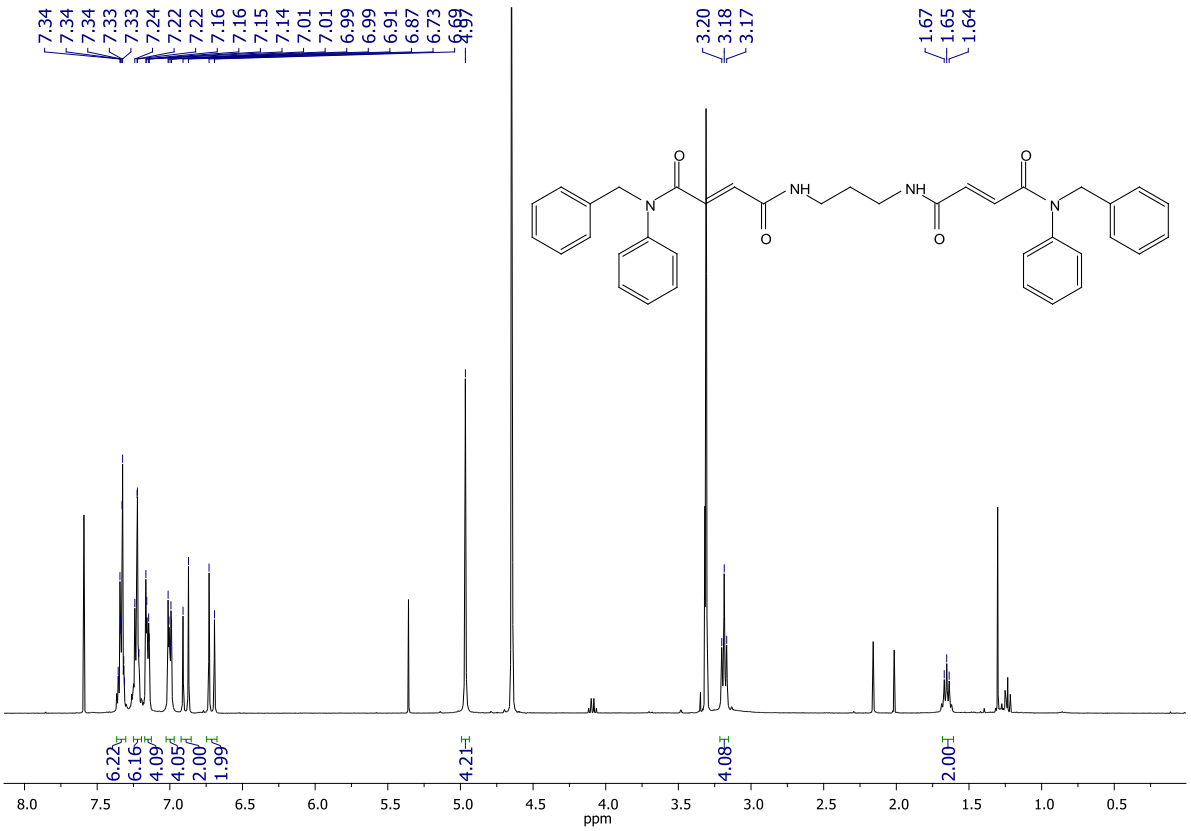

165.3
165.2
164.9
136.9
135.9
133.7
132.8
130.8
128.9
128.7
128.5
128.3
127.5
127.1
126.0
125.5
124.0
50.7
50.3
43.0
37.7
ppm

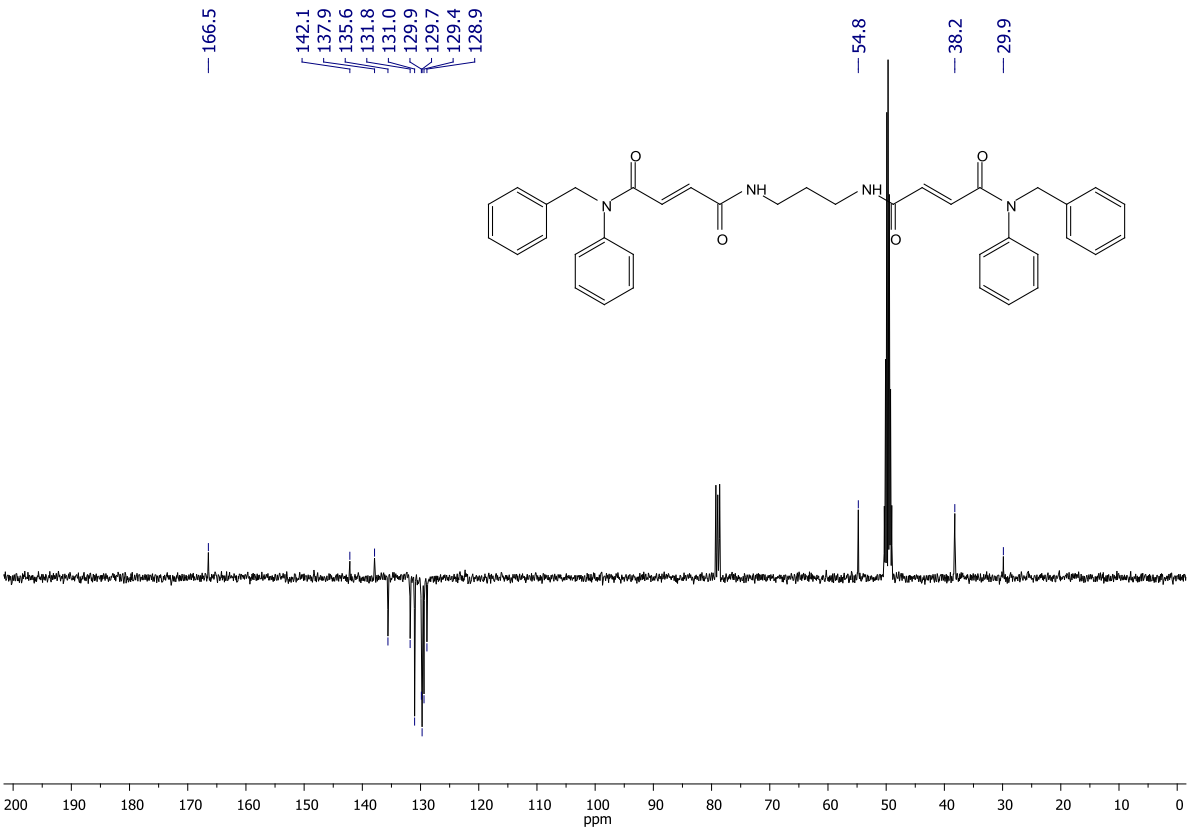
Compound 9


8.48
8.38
7.99
7.97
7.56
7.26
7.25
7.12
6.99
6.97
6.86
6.73
6.55
5.91
5.90
5.87
4.37
4.33
4.32
4.28
4.11
4.08
3.12
1.69
1.68
1.66
1.52
4.07
11.99
4.03
7.00
4.07
6.03
15.49
3.95
4.00
16.11
8.03
3.93
2.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

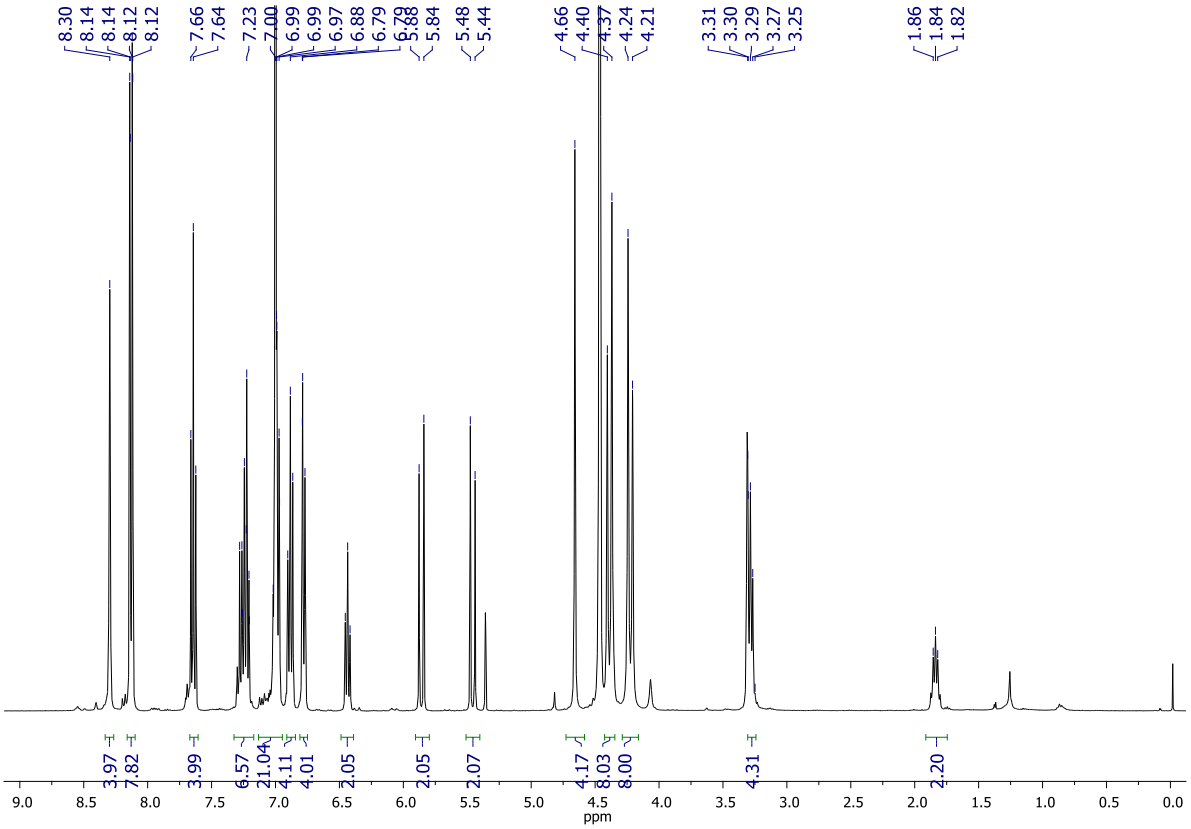

165.3
165.2
165.1
165.0
136.7
135.8
133.7
133.1
130.7
128.9
128.7
128.5
128.2
127.5
127.1
125.6
124.2
50.7
50.2
43.1
43.0
37.6
28.4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

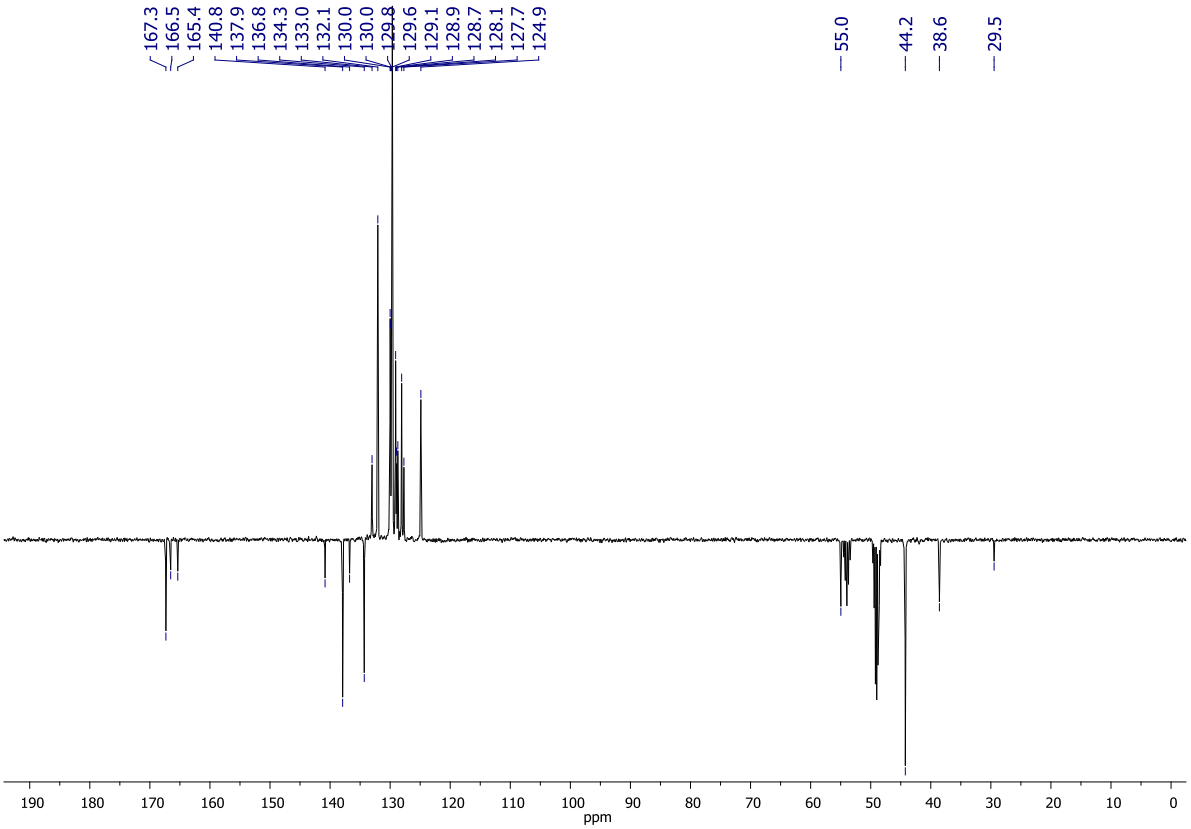
Compound S2


7.34
7.34
7.34
7.33
7.33
7.24
7.22
7.22
7.16
7.16
7.15
7.14
7.01
7.01
6.99
6.99
6.91
6.87
6.73
6.69
4.97
3.20
3.18
3.17
1.67
1.65
1.64
6.22
6.16
4.09
4.05
2.00
1.99
4.21
4.08
2.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm


166.5
142.1
137.9
135.6
131.8
131.0
129.9
129.7
129.4
128.9
54.8
38.2
29.9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

Compound 10


8.30
8.14
8.14
8.12
8.12
7.66
7.64
7.23
7.00
6.99
6.99
6.97
6.88
6.79
6.79
5.88
5.84
5.48
5.44
4.66
4.40
4.37
4.24
4.21
3.31
3.30
3.29
3.27
3.25
1.86
1.84
1.82
3.97
7.82
3.99
6.57
21.04
4.11
4.01
2.05
2.05
2.07
4.17
8.03
8.00
4.31
2.20
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


167.3
166.5
165.4
140.8
137.9
136.8
134.3
133.0
132.1
130.0
130.0
129.8
129.6
129.1
128.9
128.7
128.1
127.7
124.9
55.0
44.2
38.6
29.5
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

X-Ray Crystallography

Suitable crystals of **9** were selected and datasets were measured on a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating anode generator ($\lambda_{Mo\text{-}K\alpha}$ = 0.71075 Å) with HF Varimax optics and for **10** on a Bruker SMART 6000 diffractometer ($\lambda_{Cu\text{-}K\alpha}$ = 1.54184 Å). The data collections were driven and processed by CrystalClear-SM Expert 2.0 r7[1] for **9** and were driven by SMART[2] and processed by SAINTPLUS[3] for **10**. Absorption corrections were applied using CrystalClear-SM Expert 2.0 r7[1] for **9** and using SADABS[4] for **10**. The structure of **9** was solved using ShelXS-97[5] and of **10** by SIR2004[6] and both structures were refined by a full-matrix least-squares procedure on F^2 in ShelXL-97.[5]

In **9** two phenyl rings and a solvent ethanol molecule are disordered while in **10** an ethanol molecule and methanol molecule are present on the same site at 50 % occupancy each and one water molecule is disordered over three positions while another is not disordered. All non-hydrogen atoms were refined with anisotropic displacement parameters apart from the disordered ethanol molecule in **9** and one part of the disordered water molecule in **10**. All hydrogen atoms in **9** and those not belonging to water molecules in **10** were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (U_{eq}) of the parent atom. In **10** the hydrogen atoms belonging to one water molecule were refined subject to bond distance and angle restraints while it was not possible to refine hydrogen atom positions belonging to the disordered water molecule and methanol molecule. As a result not all the hydrogen bonding could be tabulated for **10**.

(1) *CrystalClear-SM Expert 2.0 r7*, 2011, Rigaku.

(2) *SMART, program for instrument control and data acquisition*, 1997, Bruker AXS, Inc. 5465 East Cheryl Parkway, Madison, Wisconsin 53711-5373, USA.

(3) *SAINTPLUS, program suite for data processing*, 1997, Bruker AXS, Inc. 5465 East Cheryl Parkway, Madison, Wisconsin 53711-5373, USA.

(4) Sheldrick, G. M. 2007, *SADABS,* Bruker AXS Inc., Madison, Wisconsin, USA.

(5) Sheldrick, G. M. *Acta Cryst.*, 2008, **A64**, 112-122.

(6) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.*, 1994, **27**, 435-388.