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Supplementary data

Synthesis and properties of bis(pyrrolidino)fullerenes bridged by a flexible alkyl-tether

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Experimental Section

General: Dry-column flash chromatography (DCFC) was carried out with Merck silica gel 60 (15-40 μ m). Thin layer chromatography (TLC) was carried out on precoated silica gel 60 F₂₅₄ plates. IR spectra were recorded with a *Perkin-Elmer FTIR 1725X* spectrophotometer. UV spectra were recorded with a *GBC-Cintra 40* UV-vis spectrophotometer. NMR spectra were recorded with *Varian Gemini 200* (¹H at 200 MHz, ¹³C at 50 MHz) and *Brucker Avance 500* (¹H at 500 MHz, ¹³C at 125 MHz) spectrometers. Chemical shifts are measured in ppm, δ in Hz. Samples were dissolved in the indicated solvent system, and TMS was used as an internal reference (or DSS in D₂O solutions). The high-resolution MS spectra were obtained with an *Agilent Technologies 6210* TOF LC-MS spectrometer. Reactions induced by microwave irradiation were performed in a *Milestone MultiSynth* microwave multimode oven by using a *MonoPREP* kit.

Morphology investigations: Investigations of sample morphology were carried out with SEM, using a *JEOL JSM-840A* instrument, at an acceleration voltage of 30 kV. The samples for investigation of morphology of self-organized structures of **7** were prepared by dissolving in solution (PhMe, PhMe/*i*-PrOH (1:1), *i*-PrOH) at room temperature, 0 °C, and by heating (2 h) at 50 °C for PhMe/*i*-PrOH or 80 °C for PhMe, with (15 min) or without ultrasound stimuli. A drop of 1 mM solution of **7** in PhMe/*i*-PrOH (1:1, v/v), as well as their solution in individual solvents (PhMe or *i*-PrOH) were deposited on the surface of substrate (Si, Al foil and glass, 10x10 mm) and left during 24 h to slowly evaporate in a glass Petri dish (diameter 10 cm) under PhMe atmosphere at the room temperature. The remaining fullerene derivatives were investigated under the same conditions on a glass substrate by slow evaporation of a 1 mM solution (PhMe and 1:1 PhMe/*i*-PrOH mixture) at room temperature without ultrasonication. The investigated samples were gold sputtered in a JFC 1100 ion sputter and then subjected to SEM observations.

Antioxidant Activity in vitro: All experiments were performed in triplicate, and the average values were taken. *Preparation of liposomal gel of fullerene C₆₀ and fullerene bisadducts 4-15.* Liposomes were composed of tested compounds and soybean lecithin in a 1:4 ratio. Mesured fullerene or fullerene (0.1-1 mg) and fourfold mass of lecithin are solubilized in minimal volume of PhMe under the ultrasound for 1 minute. Solvent was evaporated and film of lipid-fullerene complex carefully diluted on vortex with deionized water to the concentration of the fullerenic component of 0.02 mg/mL. The final concentration of the pure compound of 0.002 mg/mL was obtained prior to use mixing the solution with water in 1:9 ratio.

FOX reagent preparation. Working FOX reagent was prepared by adding 10 mL of Reagent 2 (98 mg of (NH₄)₂Fe(SO₄)₂·x6H₂O (FAS) in 100 mL of 250mM H₂SO₄) to 900 mL of Reagent 1 (95 mg of XO-Na salt and 880 mg of 2,6-di-*t*-butyl-4-methylphenol (BHT) in 900 mL of MeOH) giving the final concentrations of 250 μ M FAS, 125 μ M of XO, 25 mM H₂SO₄, and 4 mM BHT. The reagent was consumed within 24 h. The absorbance was measured at 560 nm by UV-vis spectrophotometer *GBC-Cintra 40* with 90% MeOH as a zero probe. The applicability of the method in used range of peroxide concentration was confirmed by preparing standard calibration curve using increasing concentrations of TBHP (0-200 μ M) incubated with FOX reagent at room temperature for 30 min. Absorbances measured at 560 nm at the different concentrations confirmed linear correlation.

Sample preparation. The fullerenosomes and vitamin C solutions (0.02 mg/mL) were diluted by nine-fold volume of water to gain 0.002 mg/mL concentration prior to use (0.050 mL : 0.450 mL of water). The same volume of 200 μ M TBHP (obtained by diluting 0.050 mL of 2 mM TBHP with 0.450 mL of water) was added to the sample and vortexed for 1 min. After 10 min of incubation at room temperature, to an aliquot of 0.050 mL of the sample 0.950 mL of FOX reagent was added. Absorbance at 560 nm was determined for each sample after 80 min of incubation at room temperature.

Standard probe preparation. The standard probe of TBHP was prepared in the same manner, replacing the sample by the same volume of water. The absorbance of the standard probe refers to the starting (maximum) concentration of the peroxide in sample solution, prior to incubation. Difference of absorbances of the standard probe (A_s) and sample (A) is proportional to the quantity of the consumed peroxide by the sample compound.

Blank probe preparation. The blank probe contained 0.950 mL of FOX reagent and 0.050 mL of water. Absorbance of the blank probe measured at 560 nm (A₀) refers to the color of the reagent itself in the absence of the peroxide, and all absorbances of the samples and standards are diminished by the value of A₀ for the calculations of the peroxide concentration.

General procedures

a) Synthesis of dibenzyl esters of diglycines by direct *N,N'*-dialkylation of diamines by benzyl bromoacetate: To an ice-cooled solution of diamine (0.043 mol, 1 mol equiv) and TEA (8.70 g, 11.9 mL, 0.086 mol, 2 mol equiv) in DCM (250 mL), solution of BBA (17.9 g, 13.5 mL, 0.086 mol, 2 mol equiv) in DCM (100 mL), was added dropwise, during 4 h. After additional stirring for 24 h, mixture was washed with H₂O (3 x100 mL) and then with brine (2 x100 mL), and dried over anhydrous Na₂SO₄. The solvent was removed in *vacuo* and the remaining material was purified on a SiO₂ column by dry-flash chromatography using below mentioned solvents as eluents.

b) Benzyl groups removal by catalytic reduction. To a solution of dibenzyl ester of diglycine (1 mmol) in MeOH (50-100 mL) 10% Pd/C (10%, w/w) was added and the reaction mixture was hydrogenated at 40 psi H₂ over 24 h at room temperature. H₂ was evacuated from suspension with argon stream. The catalyst was removed by filtration and the solvent was evaporated to dryness, leaving the crude product, pure enough for further step.

- Dibenzyl-*N,N'*-(heptane-1,7-diyl)diglycinate (**2a**) was obtained as a colourless oil (1.77 g, 27%) from 1,7-heptanediamine **1a** (2.00 g, 0.015 mol, 1 mol equiv) and TEA (3.11 g, 4.26 mL, 0.031 mol, 2 mol equiv) in DCM (100 mL) and BBA solution (7.06 g, 4.83 mL, 0.31 mol, 2 mol equiv in DCM (50 mL)), according to general procedure (a): Eluent: EtOAc. ¹H NMR (200 MHz, CDCl₃): δ = 7.33 (s, 5H, CH^{Ar}), 5.14 (s, 2H, CH₂^{Bn}), 3.42 (s, 2H, CH₂^{Gly}), 2.57 (t, J=7.1 Hz, 2H, CH₂-NH), 1.90 (s, 1H, NH), 1.57-1.37 (m, 2H), 1.29 ppm (br s, 2H); ¹³C NMR (50 MHz, CDCl₃): δ = 172.12 (C=O), 135.37 (C^{Ar}), 128.27, 128.04 (CH^{Ar}), 66.11 (CH₂^{Bn}), 50.58 (CH₂^{Gly}), 49.20 (CH₂¹), 29.59, 28.97 (CH₂⁴), 26.77 ppm. ESI-TOF-MS: *m/z*: calc. for [C₂₅H₃₅N₂O₄+H]⁺: 427.25913, measured 427.25858; IR (ATR): $\tilde{\nu}$ = 3388, 3031, 2935, 2859, 1746, 1656, 1582, 1491, 1456, 1388, 1329, 1218, 1080, 1045, 740, 701 cm⁻¹.
- Dibenzyl-*N,N'*-(octane-1,8-diyl)diglycinate (**2b**) was obtained as a colourless oil (238 mg, 31%) from 1,8-octanediamine **1b** (250 mg, 1.733 mmol, 1 mol equiv) and TEA (350 mg, 0.48 mL, 3.466 mmol, 2 mol equiv) in DCM (12 mL) and BBA solution (793 mg, 0.54 mL, 3.466 mmol, 2 mol equiv in DCM (6 mL)), according to general procedure (a): Eluent: EtOAc; ¹H NMR (200 MHz, CDCl₃): δ = 7.30 (s,

- 5H, CH^{Ar}), 5.16 (s, 2H, CH_2^{Bn}), 3.44 (s, 2H, CH_2^{Gly}), 2.58 (t, $J=7.1$ Hz, 2H, CH_2-NH), 1.94 (s, 1H, NH), 1.58-1.38 (m, 2H), 1.28 ppm (br s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.41 (C=O), 135.57 (C_q^{Ar}), 128.53, 128.29 (CH^{Ar}), 66.40 (CH_2^{Bn}), 50.85 (CH_2^{Gly}), 49.49 (CH_2^1), 29.88, 29.28, 27.02 ppm; ESI-TOF-MS: m/z : calc. for $[C_{26}H_{36}N_2O_4+H]^+$: 441.27478, measured 441.27493; IR (ATR): $\tilde{\nu}$ = 3339, 3034, 2927, 2854, 1740, 1668, 1457, 1379, 1343, 1186, 1080, 740, 699 cm^{-1} .
3. Dibenzyl-*N,N'*-(nonane-1,9-diyl)diglycinate (**2c**) was obtained as a colourless oil (890 mg, 31%) from 1,9-nonanediamine **1c** (1.00 g, 6.000 mmol, 1 mol equiv) and TEA (1.21 g, 1.66 mL, 12.00 mmol, 2 mol equiv) in DCM (50 mL) and BBA solution (2.74 g, 1.90 mL, 12.00 mmol, 2 mol equiv in DCM (25 mL)), according to general procedure (a): Eluent: PhMe/EtOAc 1:1; 1H NMR (200 MHz, $CDCl_3$): δ = 7.35 (s, 5H, CH^{Ar}), 5.16 (s, 2H, CH_2^{Bn}), 3.43 (s, 2H, CH_2^{Gly}), 2.58 (t, $J=7.0$ Hz, 2H, CH_2-NH), 2.22 (s, 1H, NH), 1.58-1.38 (m, 2H), 1.27 (br s, 5H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.28 (C=O), 135.59 (C_q^{Ar}), 128.47, 128.22 (CH^{Ar}), 66.35 (CH_2^{Bn}), 50.78 (CH_2^{Gly}), 49.47 (CH_2-NH), 29.82, 29.30, 29.26, 27.02 ppm; IR (ATR): $\tilde{\nu}$ = 3325, 3062, 3033, 1223, 2852, 1737, 1657, 1578, 1491, 1459, 1393, 1329, 1182, 1023, 737, 699 cm^{-1} .
4. Dibenzyl-*N,N'*-(decane-1,10-diyl)diglycinate (**2d**) was obtained as a colourless oil (1.49 g, 21.6%) from 1,10-decanediamine **1d** (2.50 g, 0.0145 mol, 1 mol equiv) and TEA (2.93 g, 4.01 mL, 0.029 mol, 2 mol equiv) in DCM (90 mL) and BBA solution (6.65 g, 4.55 mL, 0.029 mol, 2 mol equiv in DCM (45 mL)), according to general procedure (a): Eluent: EtOAc; 1H NMR (200 MHz, $CDCl_3$): δ = 7.34 (s, 5H, CH^{Ar}), 5.15 (s, 2H, CH_2^{Bn}), 3.43 (s, 2H, CH_2^{Gly}), 2.58 (t, $J=7.0$ Hz, 2H, CH_2-NH), 1.89 (br s, 1H, NH), 1.60-1.40 (m, 2H), 1.26 ppm (br s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.22 (C=O), 135.48 (C_q^{Bn}), 128.36, 128.13 (CH^{Bn}), 66.20 (CH_2^{Bn}), 50.71 (CH_2^{Gly}), 49.36 (CH_2-NH), 29.77, 29.22 (2 CH_2), 26.93 ppm; IR (ATR): $\tilde{\nu}$ = 3444, 2976, 2939, 1748, 1473, 1434, 1399, 1217 cm^{-1} ; ESI-TOF-MS: m/z : calc. for $[C_{28}H_{42}N_2O_4+2H]^{2+}$: 235.15668, measured: 235.15656; calc. for $[C_{28}H_{41}N_2O_4+H]^+$: 469.30608, measured: 469.30540.
5. Dibenzyl-*N,N'*-(dodecane-1,12-diyl)diglycinate (**2e**) was obtained as a colourless oil (1.48 g, 20%) from 1,12-dodecanediamine **1e** (3.00 g, 0.015 mol, 1 mol equiv) and TEA (3.02 g, 4.14 mL, 0.030 mol, 2 mol equiv) in DCM (94 mL) and BBA solution (6.86 g, 4.70 mL, 0.030 mol, 2 mol equiv in DCM (47 mL)) according to general procedure (a): Eluent: PhMe/EtOAc 1:1; 1H NMR (200 MHz, $CDCl_3$): δ = 7.32 (s, 5H, CH^{Ar}), 5.16 (s, 2H, CH_2^{Bn}), 3.45 (s, 2H, CH_2^{Gly}), 2.59 (t, $J=7.0$ Hz, 2H, CH_2-NH), 1.71 (br s, 1H, NH), 1.58-1.38 (m, 2H), 1.26 ppm (br s, 8H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 172.41 (C=O), 135.54 (C_q^{Ar}), 128.49, 128.25 (CH^{Ar}), 66.35 (CH_2^{Bn}), 50.85 (CH_2^{Gly}), 49.51 (CH_2-NH), 29.92, 29.42 (2 CH_2), 29.37, 27.08 ppm; IR (ATR): $\tilde{\nu}$ = 3444, 2976, 2939, 1748, 1473, 1434, 1399, 1217 cm^{-1} ; ESI-TOF-MS: m/z : calc. for $[C_{28}H_{42}N_2O_4+2H]^{2+}$: 235.15668, measured: 235.15656; calc. for $[C_{28}H_{41}N_2O_4+H]^+$: 469.30608, measured: 469.30540. IR (ATR): $\tilde{\nu}$ = 3327, 3034, 2921, 2851, 1742, 1656, 1577, 1464, 1391, 1215, 1188, 994, 736, 699 cm^{-1} ; ESI-TOF-MS: m/z : calc. for $[C_{30}H_{46}N_2O_4+2H]^{2+}$: 249.17233, measured: 249.17317; calc. for $[C_{30}H_{45}N_2O_4+H]^+$: 497.33738, measured: 497.33723.
6. *N,N'*-(heptane-1,7-diyl)diglycine (**3a**). Catalytic reduction of dibenzyl ester **2a** (1.77 g, 4.15 mmol) yielded diglycine **3a** as oil (740 mg, 72.5%). 1H NMR (200 MHz, D_2O): δ = 3.62 (s, 2H, CH_2^{Gly}), 3.05 (t, $J=7.6$ Hz, 2H, CH_2-NH), 1.82-1.45 (m, 2H), 1.38 ppm (br s, 3H); ^{13}C NMR (50 MHz, D_2O): δ = 173.95 (C=O), 51.64 (CH_2^{Gly}), 50.11 (CH_2-NH), 30.26 (CH_2^4), 28.00, 27.97 ppm; IR (ATR): 2929, 2854, 2362, 1620, 1570, 1469, 1375, 1321 cm^{-1} ; ESI-TOF-MS: m/z : calc. for $[C_{11}H_{22}N_2O_4+H]^+$: 247.16523, measured 247.16401; calc. for $[C_{11}H_{22}N_2O_4+Na]^+$: 269.14718, measured 269.14642.
7. *N,N'*-(octane-1,8-diyl)diglycine (**3b**). Catalytic reduction of dibenzyl ester **2b** (238 mg, 0.54 mmol) yielded oilish diglycine **3b** (110 mg, 78%). 1H NMR (200 MHz, D_2O): δ = 3.58 (s, 2H, CH_2^{Gly}), 3.02 (t, $J=7.6$ Hz, 2H, CH_2-NH), 1.80-1.60 (m, 2H), 1.35 ppm (br s, 4H); ^{13}C NMR (50 MHz, D_2O): δ = 174.46 (C=O), 51.90 (CH_2^{Gly}), 50.24 (CH_2^1), 30.59, 28.22, 28.19 ppm; IR (KBr): $\tilde{\nu}$ = 3026, 2914, 2847, 2362, 1609, 1573, 1449, 1418, 1320, 1301 cm^{-1} . ESI-TOF-MS: m/z : calc. for $[C_{12}H_{25}N_2O_4+H]^+$: 261.18088, measured 261.17962; calc. for $[C_{12}H_{24}N_2O_4+Na]^+$: 283.16283, measured 283.16203.
8. *N,N'*-(nonane-1,9-diyl)diglycine (**3c**). Catalytic reduction of dibenzyl ester **2c** (820 mg, 1.80 mmol) yielded oilish diglycine **3c** (390 mg, 79%). 1H NMR (200 MHz, D_2O): δ = 3.58 (s, 2H, CH_2^{Gly}), 3.03 (t, $J=7.9$ Hz, 2H, CH_2-NH), 1.82-1.50 (m, 2H), 1.33 (br s, 5H) ppm; ^{13}C NMR (50 MHz, D_2O): δ = 174.20 (C=O), 51.79 (CH_2^{Gly}), 50.20 (CH_2^1), 30.79 (CH_2^5), 30.68, 28.24, 28.10 ppm; IR (ATR): $\tilde{\nu}$ = 3201, 3037, 2924, 2851, 1621, 1570, 1498, 1466, 1375, 1307, 597 cm^{-1} ; ESI-TOF-MS: m/z : calc. for $[C_{13}H_{28}N_2O_4+2H]^{2+}$: 138.10191, measured: 138.10095; calc. for $[C_{13}H_{27}N_2O_4+H]^+$: 275.19653, measured: 275.19530.
9. *N,N'*-(decane-1,10-diyl)diglycine (**3d**). Catalytic reduction of dibenzyl ester **2d** (1.02g, 2.18 mmol) yielded diglycine **3d** as a colourless oil (500 mg, 79%). 1H NMR (200 MHz, D_2O): δ = 3.58 (s, 2H, CH_2^{Gly}), 3.03 (t, $J=7.9$ Hz, 2H, CH_2-NH), 1.80-1.50 (m, 2H), 1.31 (br s, 6H) ppm; ^{13}C NMR (50 MHz, D_2O): δ = 174.26 (C=O), 51.82 (CH_2^{Gly}), 50.26 (CH_2^1), 30.99, 30.81, 28.32, 28.17 ppm; IR (ATR): $\tilde{\nu}$ = 2922, 2850, 1741, 1578, 1446, 1392, 1326, 1217 cm^{-1} ; ESI-TOF-MS: m/z : calc. for $[C_{14}H_{30}N_2O_4+2H]^{2+}$: 145.10973, measured: 145.10980; calc. for $[C_{14}H_{29}N_2O_4+H]^+$: 289.21218, measured: 289.21100.
10. *N,N'*-(dodecane-1,12-diyl)diglycine (**3e**). Catalytic reduction of dibenzyl ester **2e** (480 mg, 0.97 mmol) yielded diglycine **3e** as a colourless oil (290 mg, 95%). 1H NMR (200 MHz, D_2O -susp.): δ = 3.53 (s, 2H, CH_2^{Gly}), 2.97 (t, $J=7.6$ Hz, 2H, CH_2-NH , overlapped with DSS signal on 2.91 (t, $J=8.0$ Hz)), 1.90-1.52 (m, 2H), 1.29 (br s, 8H) ppm; ^{13}C NMR (50 MHz, D_2O -susp.): δ = 174.69 (C=O), 52.13 (CH_2^{Gly}), 50.36 (CH_2^1), 31.26, 31.14, 30.90, 28.42 (2 CH_2) ppm; IR (ATR): $\tilde{\nu}$ = 3066, 2920, 2851, 1617, 1576, 1496, 1465, 1440, 1381, 1321, 1305, 595, 569 cm^{-1} ; ESI-TOF-MS: m/z : calc. for $[C_{16}H_{34}N_2O_4+2H]^{2+}$: 159.112538, measured: 159.1258, calc. for $[C_{16}H_{33}N_2O_4+H]^+$: 317.24348, measured: 317.24275.

Table S1. Visible region absorption bands 400–800 nm of *cis*-2 bisadducts.

Compound/R-	λ_1/ϵ	λ_2/ϵ	λ_3/ϵ	λ_4/ϵ	λ_5/ϵ
5 /(CH ₂) ₇ -	449 /4900	489 /3200	585 /1100	643 /520	682 /340
7 /(CH ₂) ₈ -	447 /4600	484 /2700	575 /860	645 /420	681 /250
9 /(CH ₂) ₉ -	442 /5100	484 /3100	570 /1000	643 /460	681/290
11 /(CH ₂) ₁₀ -	447 /4300	483 /2500	572 /830	640 /390	702 /250
13 /(CH ₂) ₁₂ -	446 /5000	483 /3000	570 /900	640 /420	683 /280

Table S2. Principal visible region absorption bands 400–800 nm of *cis*-3 bisadducts.

Compound/R-	λ_1/ϵ	λ_2/ϵ	λ_3/ϵ	λ_4/ϵ	λ_5/ϵ
6 /(CH ₂) ₇ -	435 /3800	469 /2300	554 /1300	657 /450	729 /310
8 /(CH ₂) ₈ -	434 /2900	465 /2000	555 /900	656 /480	731 /300
10 /(CH ₂) ₉ -	430 /3700	466 /2200	550 /1200	657 /410	727 /300
12 /(CH ₂) ₁₀ -	429 /3600	465 /2200	552 /1000	658 /410	724 /300

Table S3. ¹H/¹³C NMR chemical shifts (δ (ppm), multiplicity, *J* in Hz) of the non-fullerene moiety of regioisomers

Regioisomer	$\delta(sp^3-C^{full})$	$\delta(CH_2^{pyrr})$	$\delta(CH_2(1,n; 1',n'))$	$\delta(CH_2)$
<i>cis</i> -1 (C ₇) 4	67.68 65.36	4.74d(9.0); 4.55d(9.0); 3.95d(9.0); 3.43d(9.0) 66.28; 66.14	3.25dd(9.5; 13.5); 2.97dd(6.0; 13.5) 52.74	1.60-2.20 27.53; 26.04; 23.60
<i>cis</i> -2 (C ₇) 5	69.72 69.47	4.92dd(11.5; 2.7); 4.36dd(10.5; 2.7); 3.96d(10.5); 3.55d(11.5) 69.55; 66.71	3.83ddd(4.5; 8.5; 12.5); 2.84dt(11.0; 5.0) 52.14	1.70-2.30 29.60; 28.35; 27.92
<i>cis</i> -2 (C ₈) 7	67.36 67.00	4.54dd(9.0; 1.5); 4.20dd(8.5; 1.5); 3.44d(8.5); 3.04d(9.0) 67.33; 65.15	3.23dt(4.5; 7.0); 2.63br d(11.0) 51.94	1.35-2.37 27.85; 27.49; 22.96
<i>cis</i> -2 (C ₉) 9	68.67 67.77	4.68dd(9.5; 1.5); 4.27dd(9.5; 1.5); 3.54d(9.5); 3.23d(9.5) 67.77; 67.63	3.21dt(4.0; 12.0); 2.67dt(12.0; 4.0) 54.84	1.50-2.00 29.00; 28.78; 27.42; 27.07
<i>cis</i> -2 (C ₁₀) 11	67.47 67.13	4.44dd(9.0; 1.5); 4.22dd(9.0; 1.5); 3.44d(9.0); 3.37d(9.0) 68.25; 67.13	2.99ddd(4.5; 8.5; 12.5); 2.85ddd(4.5; 8.5; 13.0) 52.63	1.45-2.05 28.07; 27.83; 27.23; 25.89
<i>cis</i> -2 (C ₁₂) 13	66.89 66.71	4.04d(9.0); 3.99d(9.0); 3.69d(9.0); 3.67d(9.0) 67.69; 67.49	2.88dt(11.5; 7.0); 2.82dt(11.5; 7.0) 54.16	1.42-1.88 28.22; 28.20; 27.23; 26.96; 26.30
<i>cis</i> -3 (C ₇) 6	71.47 67.84	4.59dd(11.0; 2.5); 4.48dd(10.5; 2.5); 4.31d(10.5); 3.56d(11.0) 69.51; 65.08	3.50ddd(7.0; 8.5; 11.5); 2.81ddd(3.5; 7.5; 11.5) 51.58	1.53-1.95 28.37; 27.88; 24.38
<i>cis</i> -3 (C ₈) 8	69.09 65.58	4.28d(9.5); 4.27d(9.0); 3.88d(9.0); 3.18d(9.5) 68.41; 64.63	3.15q(6.0); 2.71br d(11.5) 51.90	1.01-2.35 29.56; 28.78; 25.23
<i>cis</i> -3 (C ₉) 10	69.29 65.62	4.37dd(9.5; 1.0); 4.36d(8.5); 3.81dd(8.5; 1.0); 3.26d(9.5) 69.07; 66.90	3.14dt(3.5; 11.5); 2.67dt(11.5; 4.0) 53.43	1.28-2.07 29.13; 28.89; 28.45; 25.13
<i>cis</i> -3 (C ₁₀) 12	69.26 65.79	4.36dd(9.5; 1.5); 4.35dd (9.5; 1.5); 3.79d(9.5); 3.36d (9.5) 68.48; 67.74	3.01ddd(11.5; 9.5; 4.0); 2.82ddd(11.5; 5.5; 4.5) 53.02	1.42-2.02 27.52; 27.05; 26.98; 25.73
<i>eq</i> (C ₁₂) 14	70.34 69.68 69.27	4.32dd(10.0; 1.5); 4.05s; 3.82s; 3.73dd(8.5; 1.5) 68.19; 66.75; 65.41	CH ₂ (1): 2.95t(5.5); CH ₂ (12): 2.94t(5.5) 53.34; 51.60	1.20-1.80 30.28; 30.25; 29.86; 29.61; 28.95; 28.37; 28.07; 27.27; 26.44; 25.33
<i>trans</i> -4 (C ₁₂) 15	70.25 70.03	4.55dd(9.0; 2.0); 4.53dd(9.0; 2.0); 4.09d(9.0); 3.70d(9.0) 68.88; 65.40	3.19-3.26m; 2.95dt(12.0; 5.0) 52.86	1.05-1.88 31.23; 30.65; 29.76; 28.53; 27.54
δ range	- 65-72	3.0-4.9 65-70	2.6-3.8 51-55	1.0-2.4 23-30

Table S4. ^{13}C NMR chemical shifts of the fullerene moiety of *cis*-2 bisadducts relative to literature values for the corresponding *N*-mTEG fulleropyrrolidine bisadduct [1].

5 (C ₇)	7 (C ₈)	9 (C ₉)	11 (C ₁₀)	13 (C ₁₂)	(-mTEG) ₂
160.18	160.12	159.65	159.82	159.02	158.67*
155.92	155.35	156.04	155.97	156.11	156.51*
149.06	149.14	149.15	149.22	149.20	149.28
148.83**	148.84**	148.85**	148.90**	148.82**	148.86**
148.80**	148.81**	148.80**	148.86**	148.75**	148.75**
147.29	147.57	147.49	147.60		147.84*
146.75		147.17	147.25	147.49****	147.73
146.61**	146.78***	147.73**	147.70**	147.69**	147.66**
146.50	146.70	147.03	147.06	147.42	147.49*
146.50	146.65	146.80	146.84	146.93	147.10
146.15	146.65	146.64	146.81	146.83	146.92
145.98	146.36	146.39	146.48	146.43	146.48
145.83	146.31	146.02	146.15	146.08	146.11
145.70	146.09	145.79	145.99	145.69	145.76
145.37	145.78	145.64	145.73	145.66	145.69
145.09	145.46	145.41	145.53	145.61	145.52
145.02	145.24	145.19	145.26	145.27	145.38
144.67	145.14	145.14	145.23	145.12	145.11
144.57	144.60	144.74	144.72	144.76	144.86
144.12	144.53	144.67	144.68	144.58	144.52
144.12	144.12	144.19	144.22	144.37	144.48
143.92	144.02	144.07	144.14	144.13	144.21
143.92	144.01	144.01	144.06	144.00	144.03
142.71	143.10	143.10	143.19	142.97	142.92
141.72	141.53	141.54	141.58	141.56	141.63
140.73	140.82	140.86	140.90	140.89	140.96
137.71	138.66	138.89	138.91	138.83	138.76
133.11	133.87	133.45	133.70	133.80	133.86
132.46	133.05	132.13	132.59	132.91	133.21
129.40**	130.68**	129.20**	130.08**	129.56**	129.34**

* Signals of the sp^2 fullerene carbons adjacent to functionalized 6,6-bond.

** Carbon signals of the relative intensity 1 (the others are the relative intensity 2).

*** Carbon signal of the relative intensity 3 (2+1).

**** Carbon signal of the relative intensity 4 (2+2).

mTEG - triethylene glycol mono methyl ether, $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$

1. K. Kordatos, S. Bosi, T. Da Ros, A. Zambon, V. Lucchini, M. Prato, *J. Org. Chem.* **2001**, *66*, 2802-2808.

Table S5. ^{13}C NMR chemical shifts of the fullerene moiety of bridged *cis*-1, *cis*-3, *eq* i *trans*-4 bisadducts relative to literature values for the corresponding *N*-mTEG fulleropyrrolidine bisadducts [1].

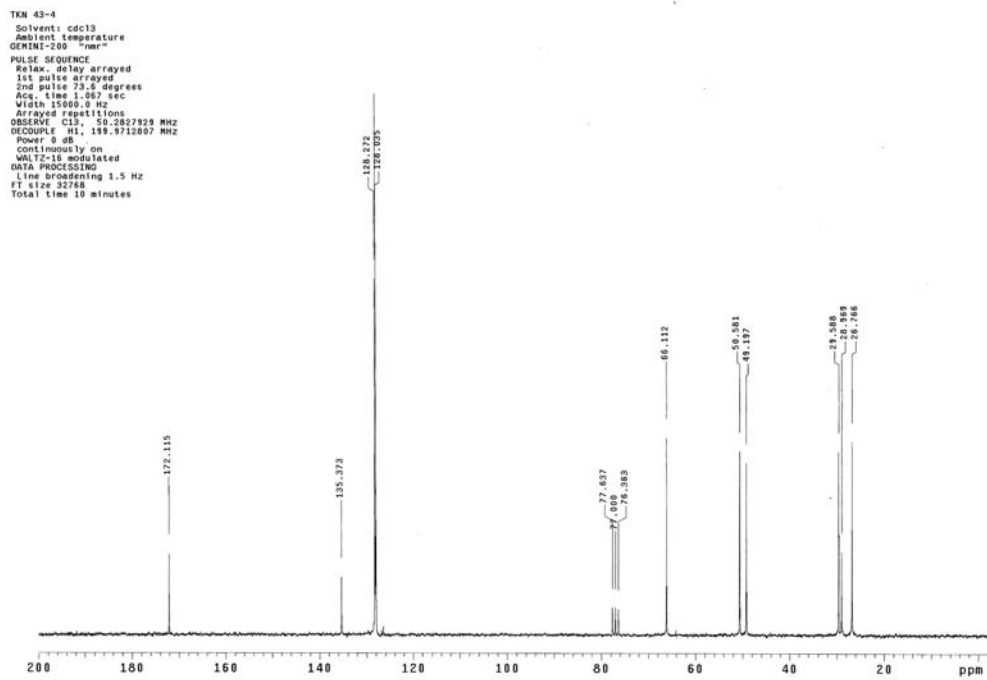
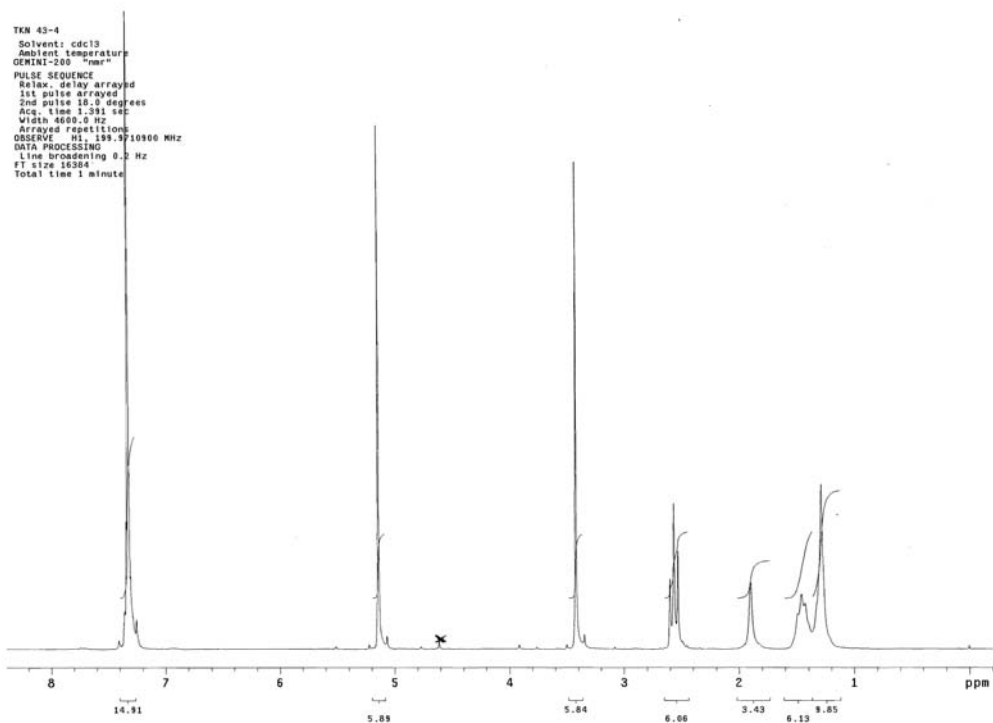
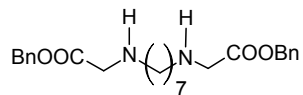
<i>cis</i> -1		<i>cis</i> -3				<i>eq</i>			<i>trans</i> -4	
4 (C ₇)	(-mTEG) ₂	6 (C ₇)	8 (C ₈)	10 (C ₉)	12 (C ₁₀)	(-mTEG) ₂ -	14 (C ₁₂)	(-mTEG) ₂ -	15 (C ₁₂)	(-mTEG) ₂ -
151.97	152.21*	154.70	153.89	153.78	153.68	152.00*	159.21	159.20*	154.14	154.85*
151.42	151.26*	150.10	149.14	149.67	149.81	150.18*	154.54	153.78*	153.43	152.79*
150.20	150.58*	148.85	148.93	149.01	149.03	149.12	153.36	153.23*	152.13	151.55*
149.01	149.08	148.21	148.45	148.53	148.56	148.94*	152.51	152.79*	150.64**	150.90*
148.10	148.20	148.13	148.10	148.25	148.27	148.75	149.60**	149.80**	150.03	150.85**
147.05	147.46	147.85	147.75	148.06	148.06	148.15	148.77	148.85	149.04**	149.52**
146.89	147.14	147.43	147.71	147.78	147.80	147.57	148.05	148.02	148.89	149.22
146.41	146.47	146.64	146.79	146.91	146.96	147.14	147.63**	147.75**	148.57	148.26
146.19**	146.22	146.46	146.52	146.43	146.28	146.29	147.49	147.75	148.17	147.97
146.15	146.14**	146.03	146.15	146.20	146.21	146.05	147.49	147.26	147.10**	147.64**
145.55	145.59	146.02	145.94	146.05	146.05	145.89	147.31	147.20	146.76	147.51
145.37	145.42	145.75	145.86	145.94	145.95	145.85	147.12	146.75	145.99	146.22
145.07	145.15	145.72	145.59	145.67	145.69	145.66	145.94	146.62	145.92	146.10
144.64	145.14	145.53	145.57	145.65	145.59	145.54	145.70	145.71	145.83	146.08
144.26	144.70	144.88	144.96	145.12	145.17	145.34	145.12	145.13	145.62	145.50
144.08	144.35	144.79	144.84	144.95	144.94	145.18	144.97	144.98	145.57	145.01
144.02	144.15	144.68	144.61	144.75	144.77	144.76	144.59	144.66	144.40	144.98
143.81	144.10	142.20	142.97	142.11	143.06	142.35	144.51	144.60	144.02	144.66
143.22	143.86	142.14	142.03	142.10	142.09	142.31	144.32	144.37	142.81**	142.84**
143.09	143.06	141.98	142.02	141.93	142.08	141.86	143.48	143.66	142.32	142.58
142.78**	142.82**	141.50	142.01	141.86	142.06	141.75	143.26	143.20	142.08	142.13
142.46	142.48	141.43	141.66	141.68	141.59	141.46	142.24	142.30	141.72	141.74
142.42**	142.48**	139.63	139.69	139.73	139.75	139.80	141.54	141.71	141.34	141.71
142.37	142.43	138.31	138.11	138.24	138.26	138.56	141.48	141.56	141.29	141.38
142.05	142.06	135.94	136.98	137.14	137.27	136.88	141.15	141.45	141.16	141.21
141.74	141.78	134.62	135.36	134.95	134.98	135.18	140.91	140.68	138.75	139.09
140.84	140.85	134.45	134.59	134.20	133.95	134.17	138.88	139.16	138.48	138.60
137.99**	137.96**	130.70	130.03	130.49	130.59	130.54*	136.58	136.73	136.09	136.07
135.18	135.30						135.70	135.52	135.49	135.41
134.96	135.15								131.19	131.18

* Signals of the sp^2 fullerene carbons adjacent to functionalized 6,6-bond.

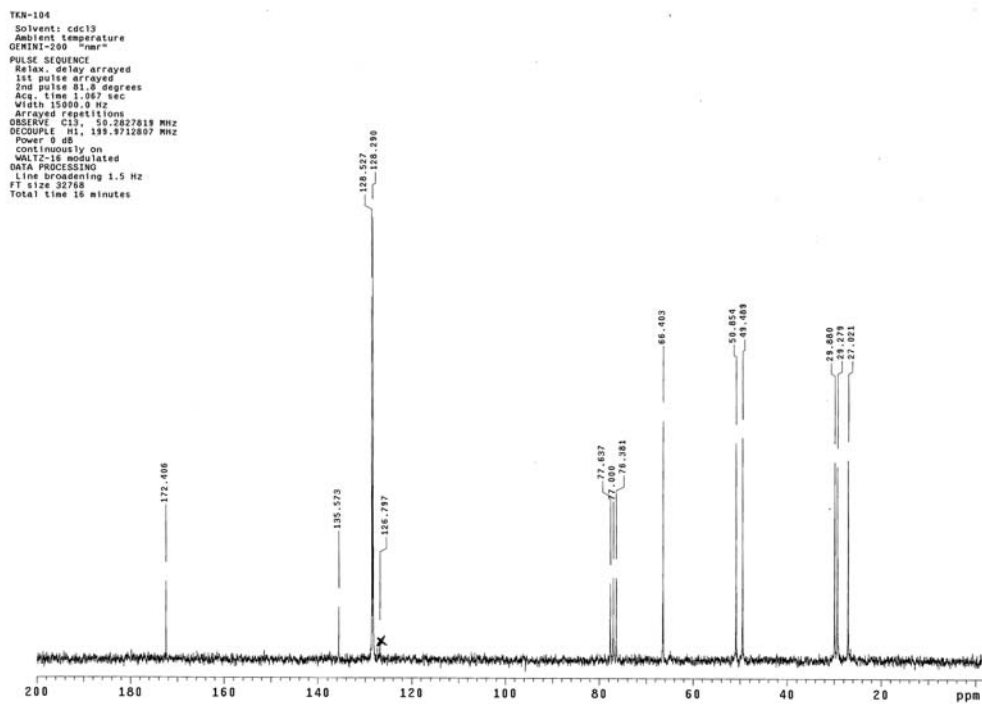
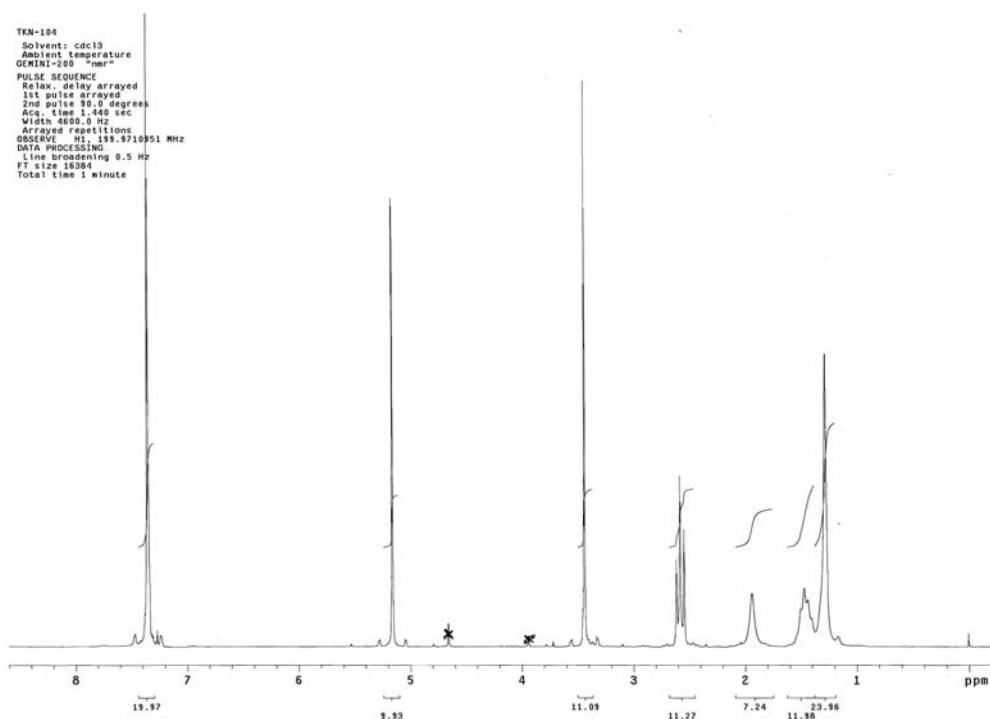
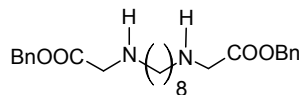
** Carbon signals of the relative intensity 1 (the others are the relative intensity 2).

mTEG - triethylene glycol mono methyl ether, $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$ 1. K. Kordatos, S. Bosi, T. Da Ros, A. Zambon, V. Lucchini, M. Prato, *J. Org. Chem.* **2001**, *66*, 2802-2808.

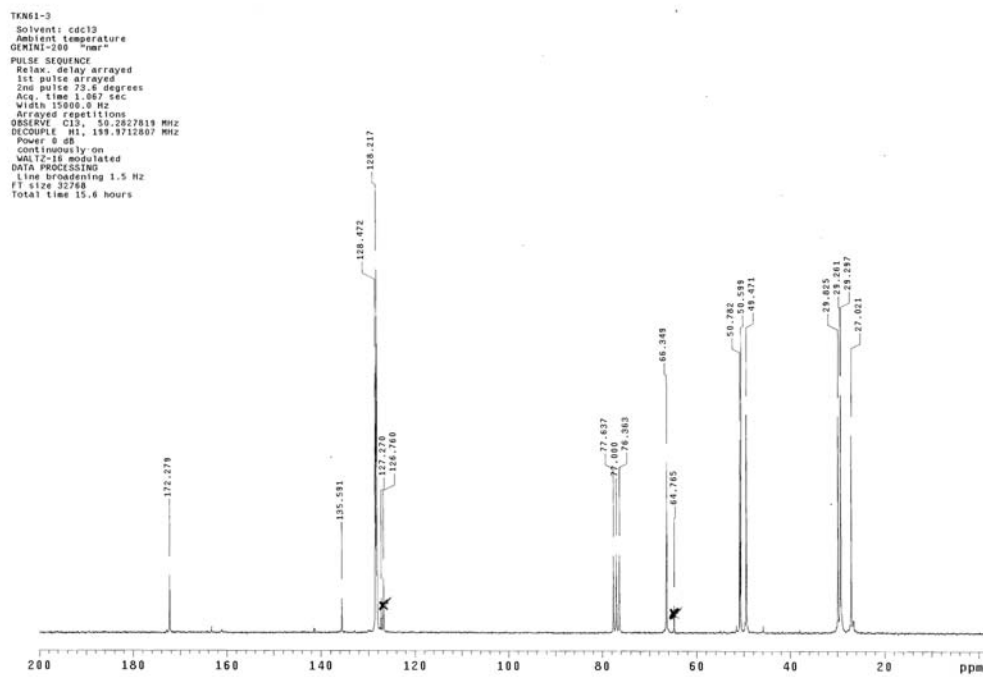
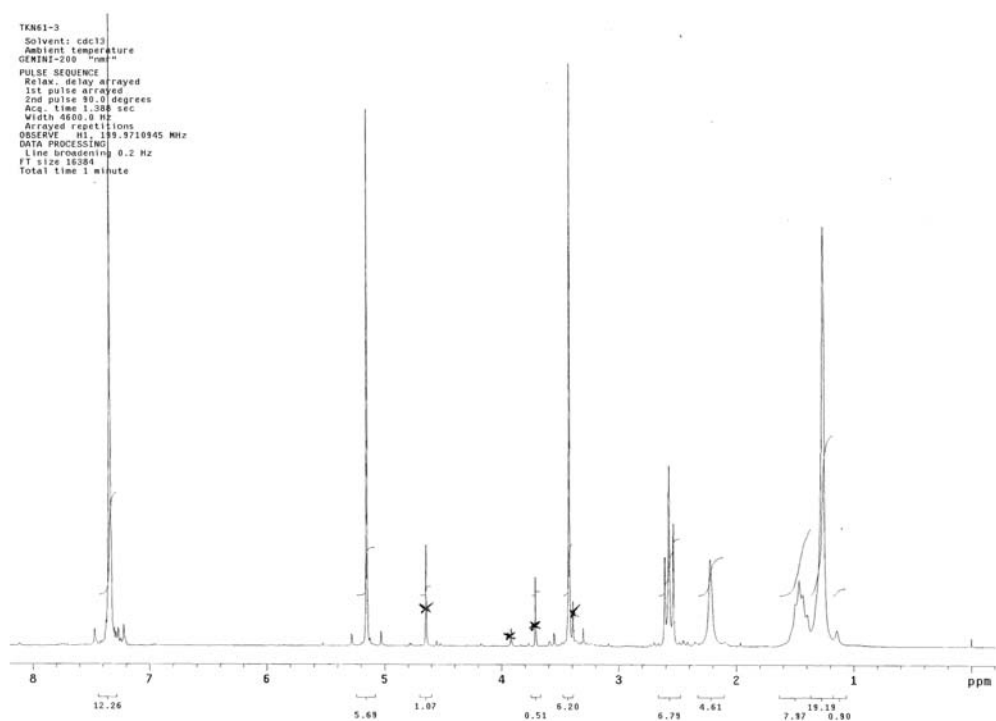
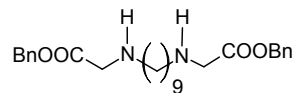
NMR spectra of compound 2a.



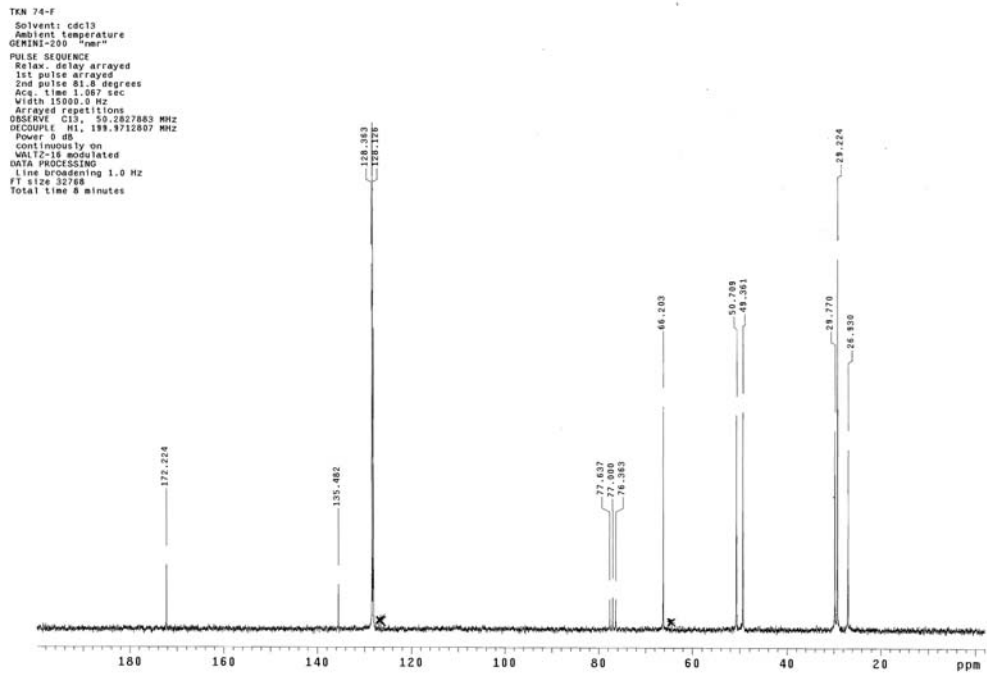
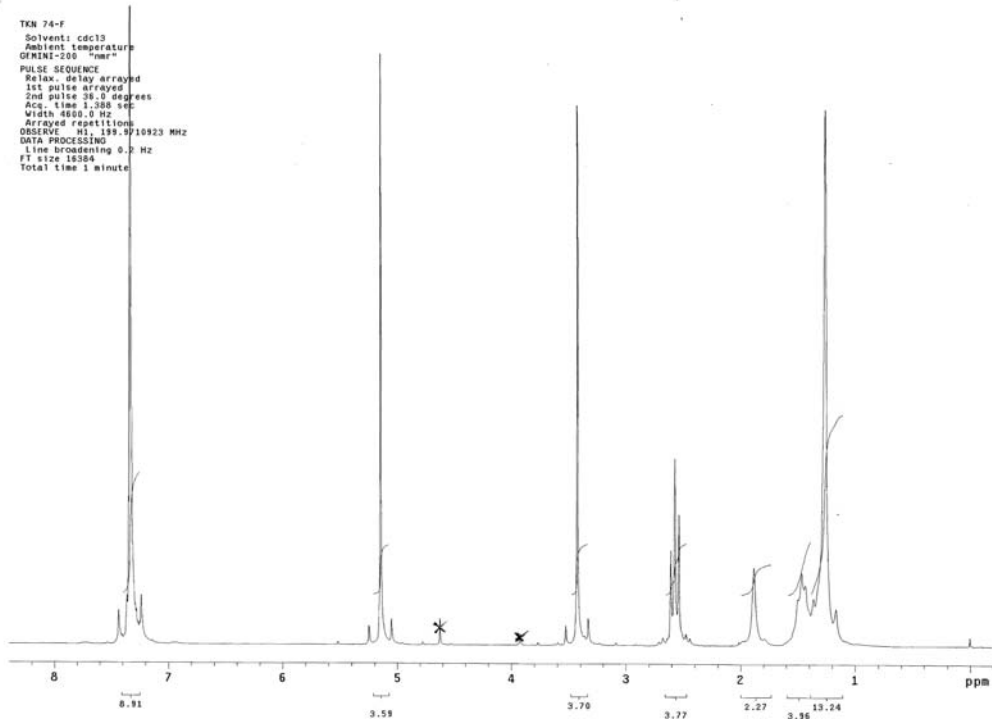
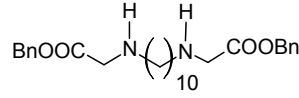
NMR spectra of compound 2b.



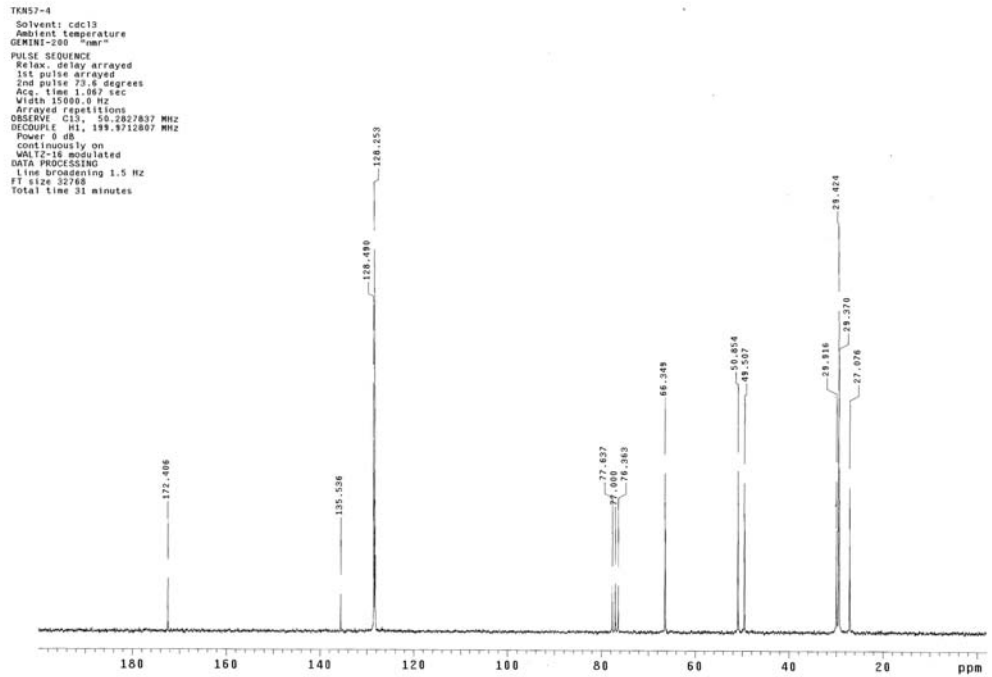
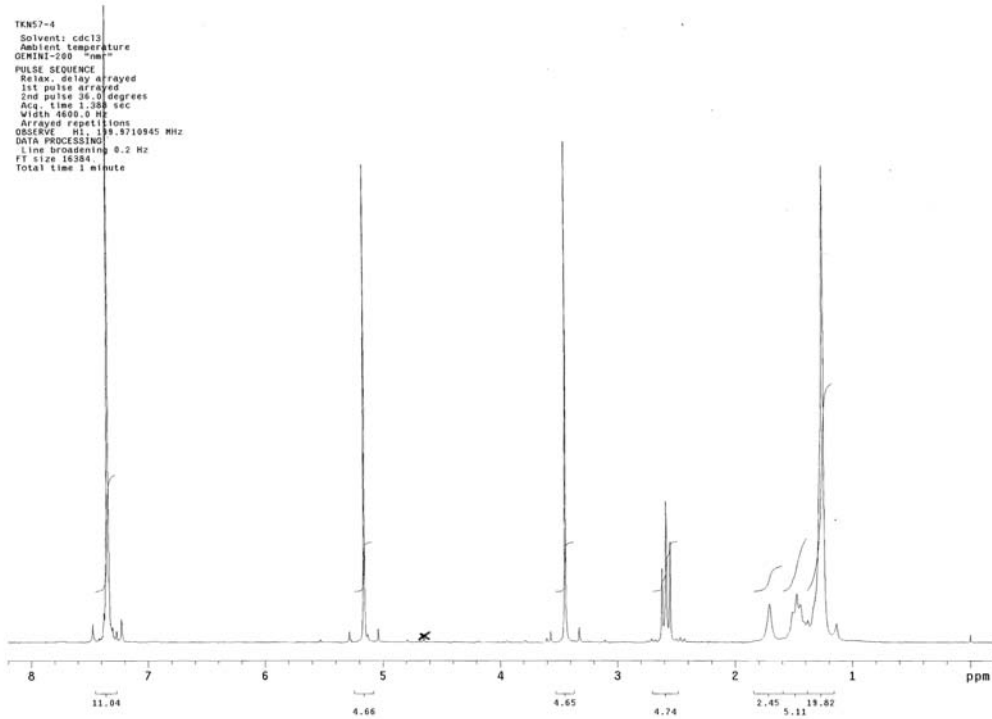
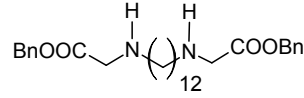
NMR spectra of compound 2c



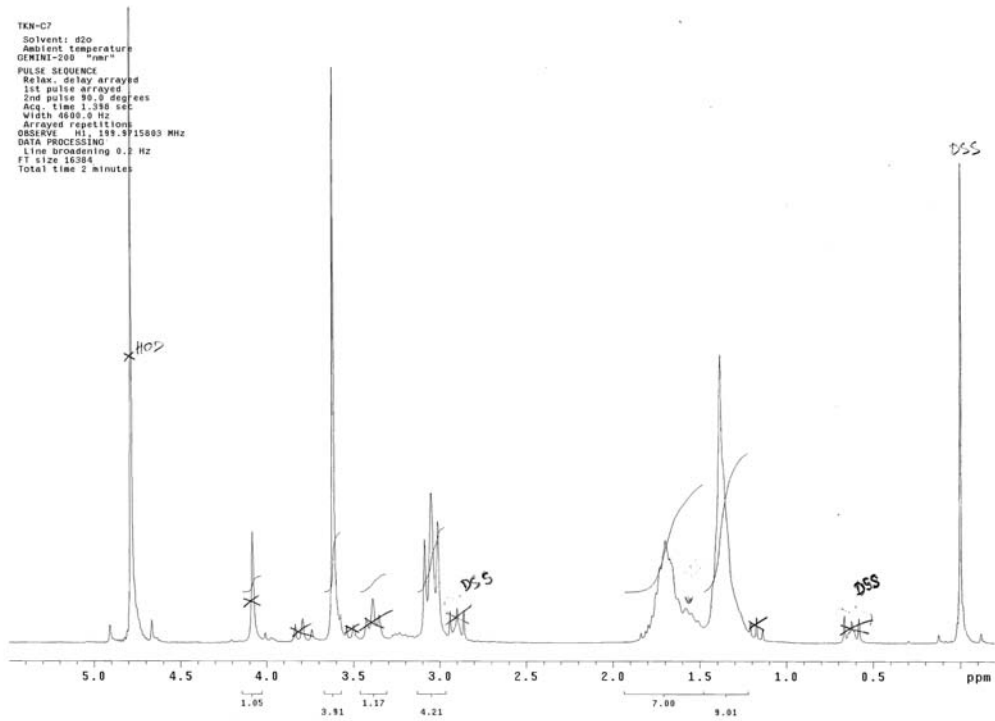
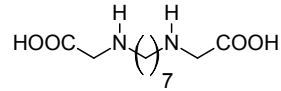
NMR spectra of compound 2d



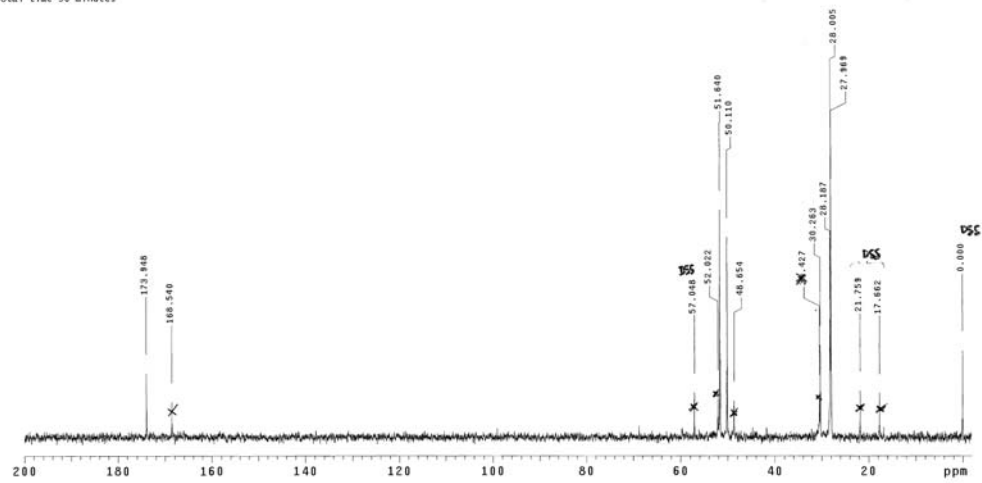
NMR spectra of compound 2e



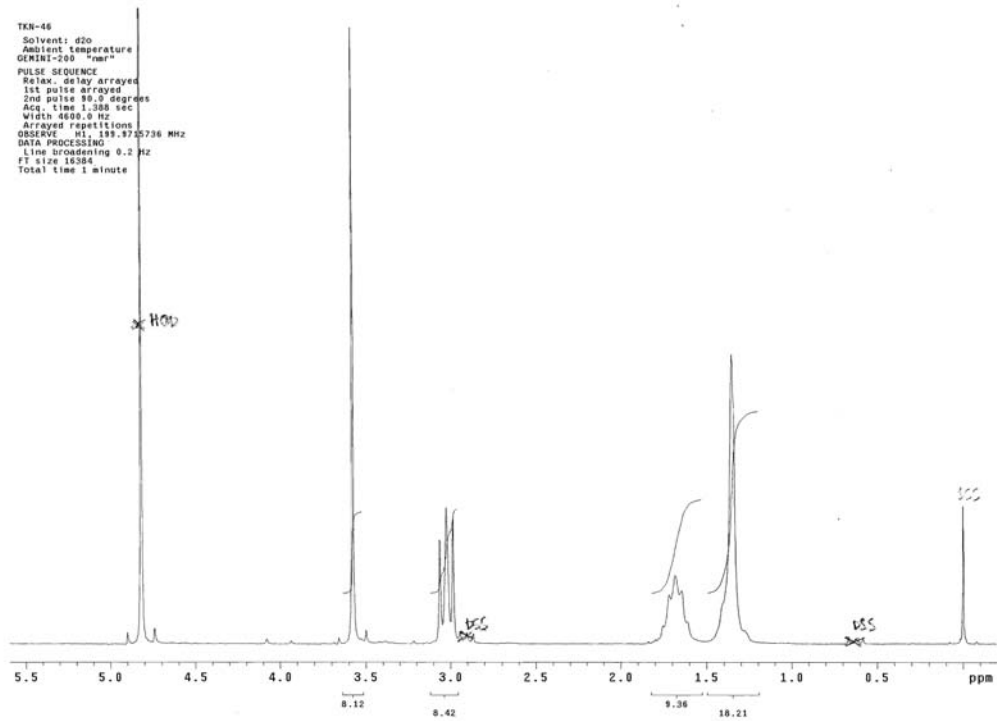
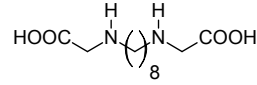
NMR spectra of compound 3a



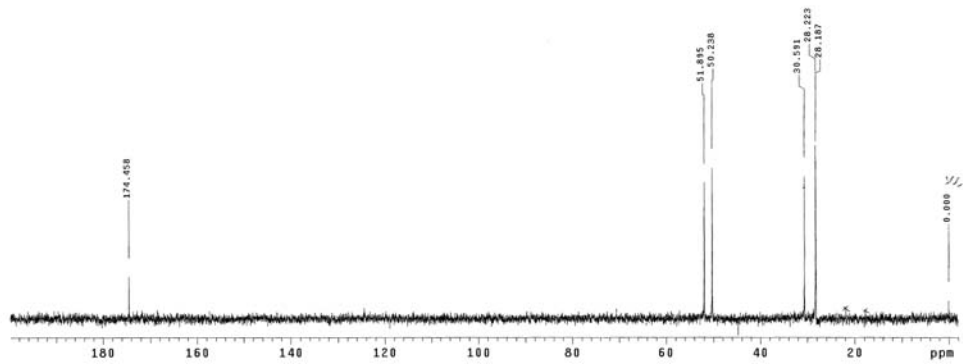
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1st pulse arrayed
2nd pulse 75.0 degrees
Acq. time 1.067 sec
Width 15990.0 Hz
Arrayed repetitions
OBSERVE C13, 50.2827437 MHz
DECOUPLE H1, 199.9717946 MHz
Power 0 db
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 32768
Total time 50 minutes



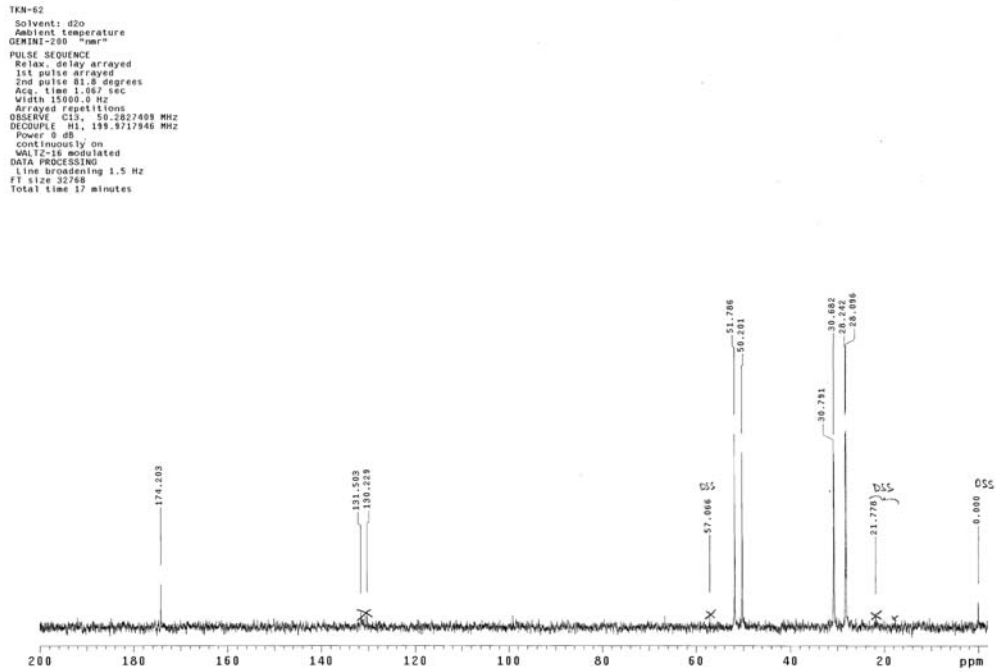
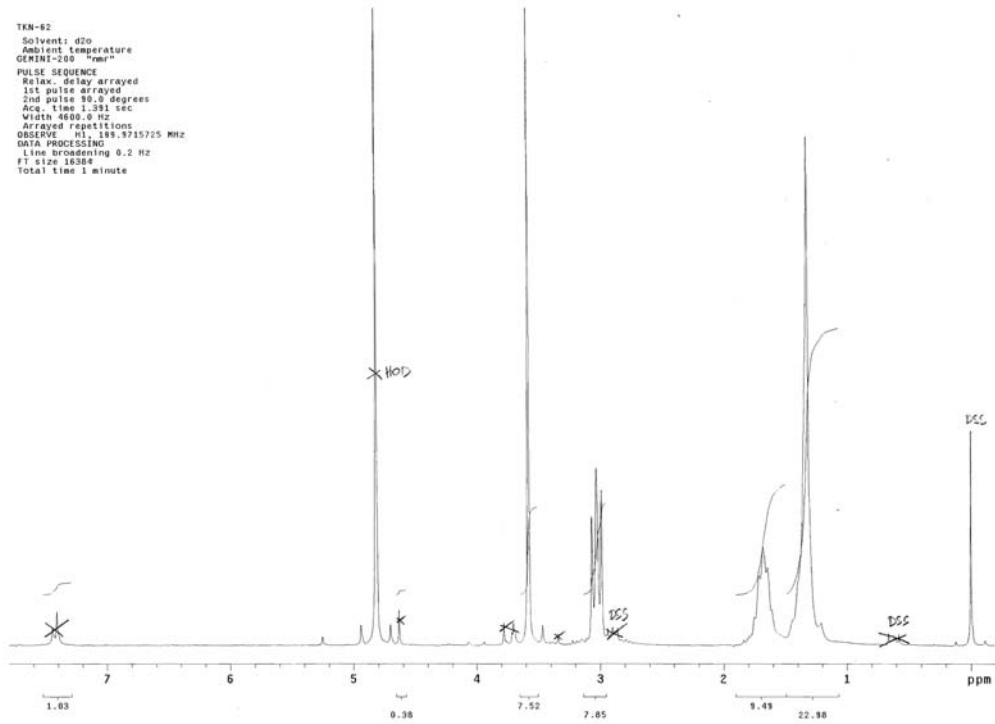
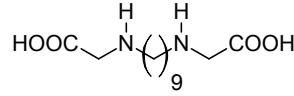
NMR spectra of compound 3b



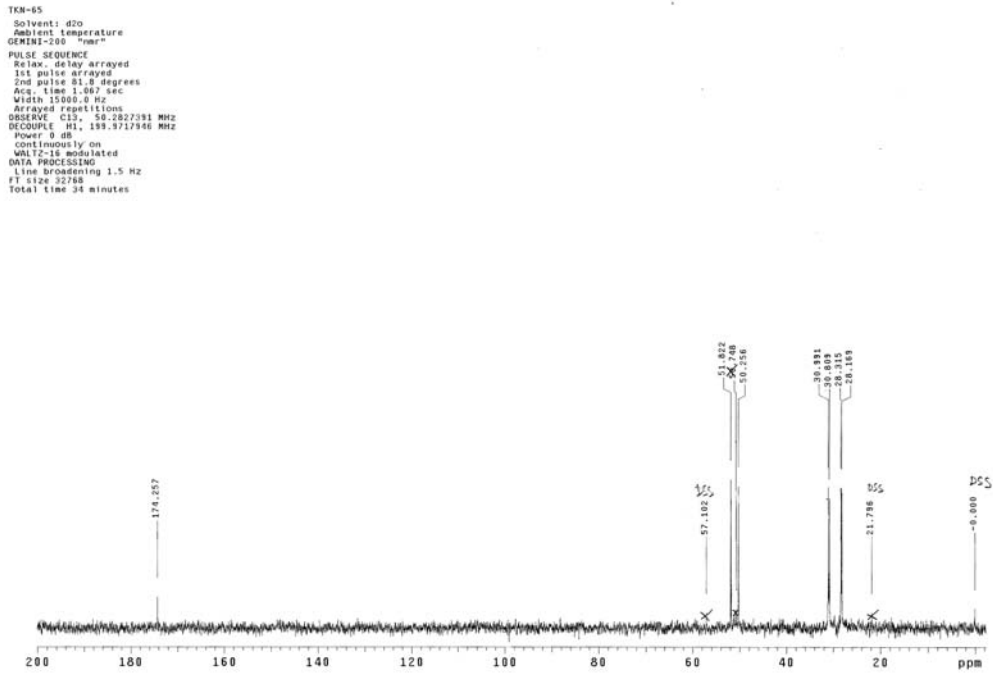
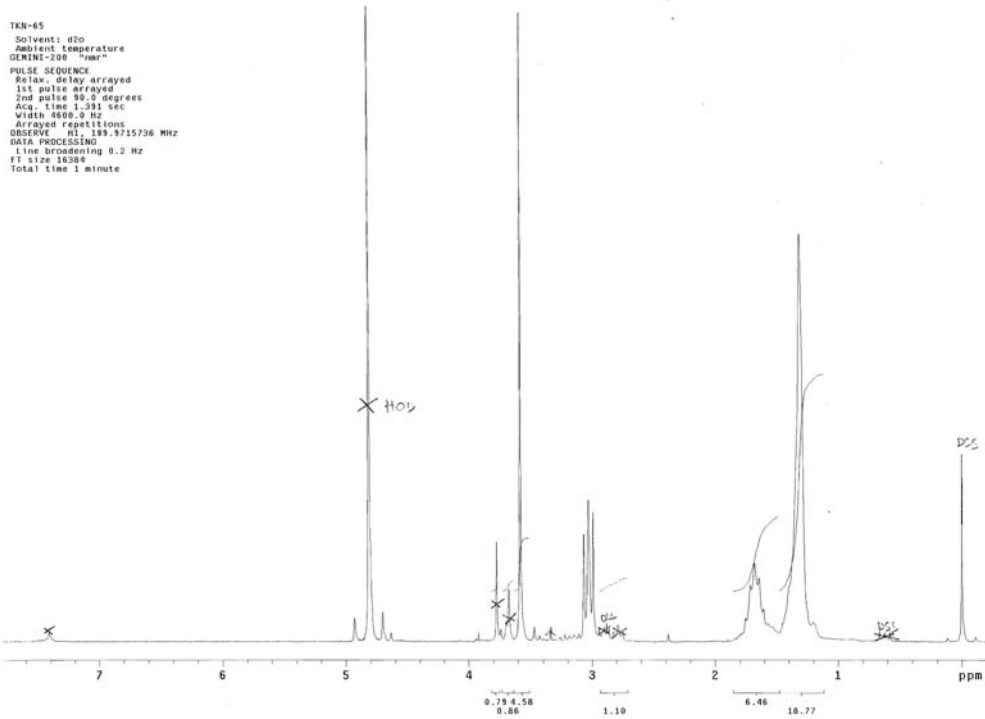
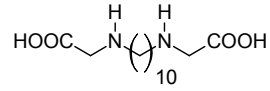
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2nd pulse 75.6 degrees
Acq. time 1.067 sec
Width 15000.0 Hz
Arrayed repetitions
OBSERVE C13, 50.2827382 MHz
DECUPLE n1, 199.9717946 MHz
Power 0 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.8 Hz
FT size 32768
Total time 32 minutes



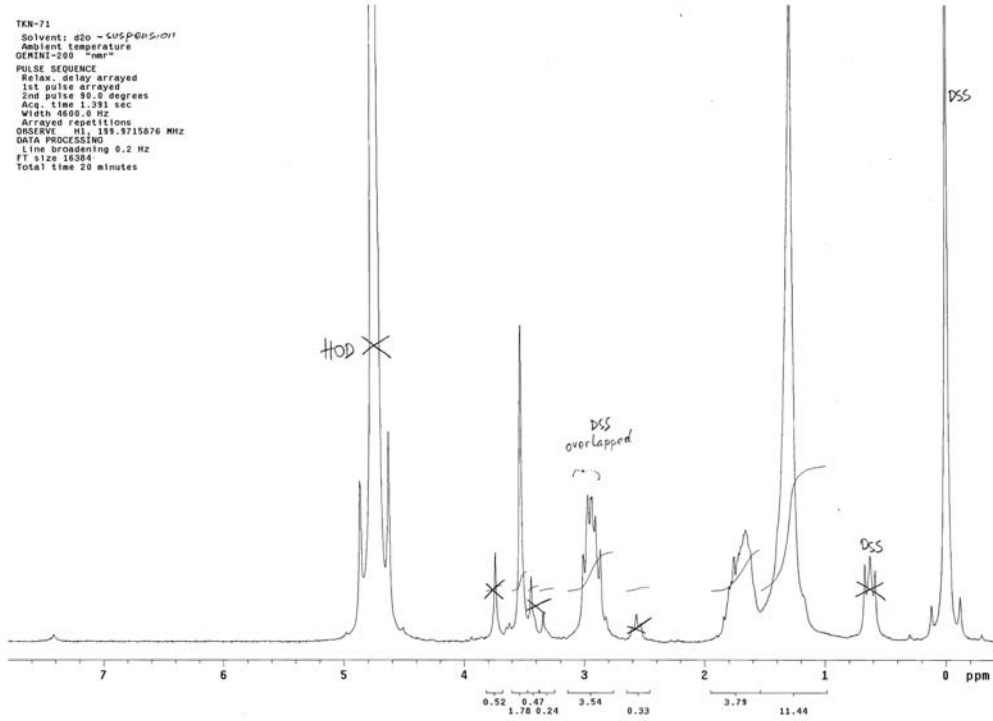
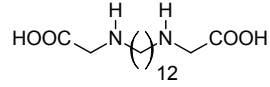
NMR spectra of compound 3c



NMR spectra of compound 3d

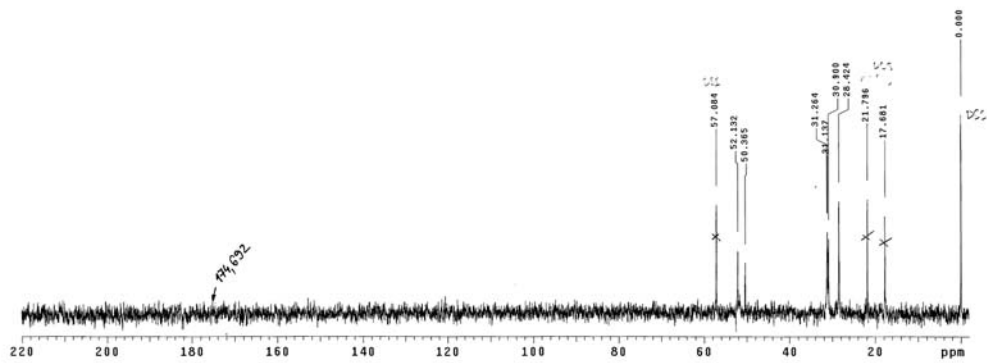


NMR spectra of compound 3e

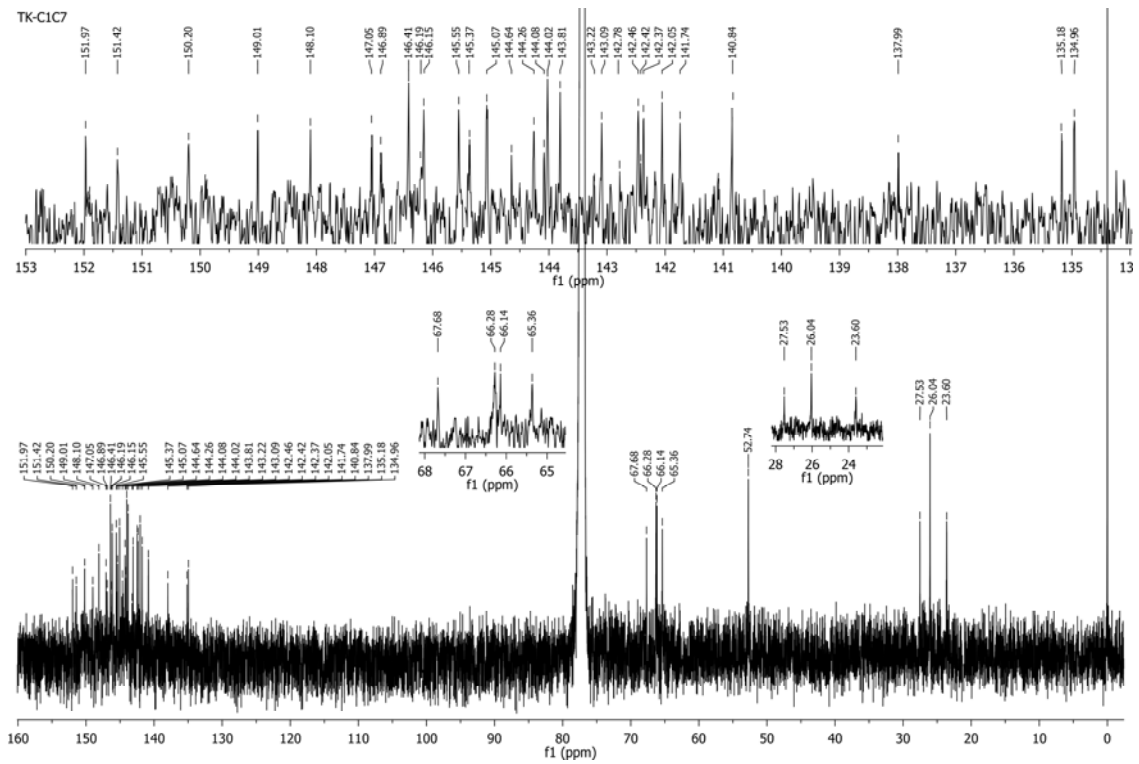
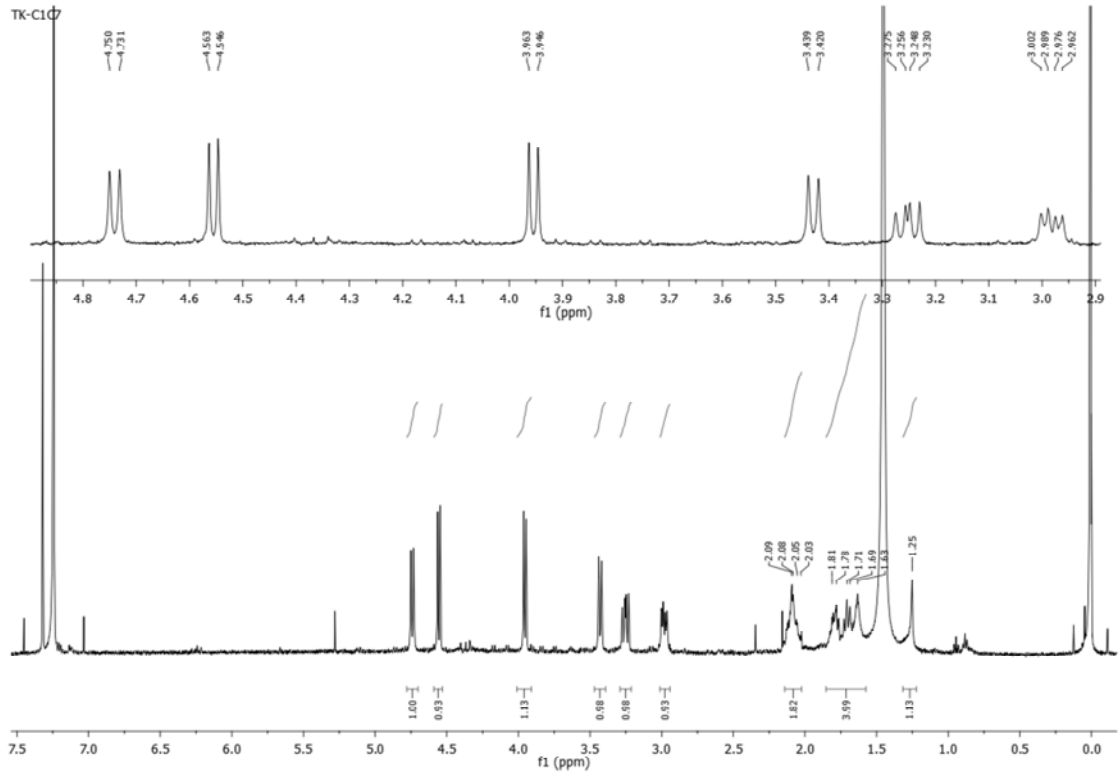


TKN-71
Solvent: d2o - SUSPENSION
Ambient temperature
GEMINI-200 "nmr"

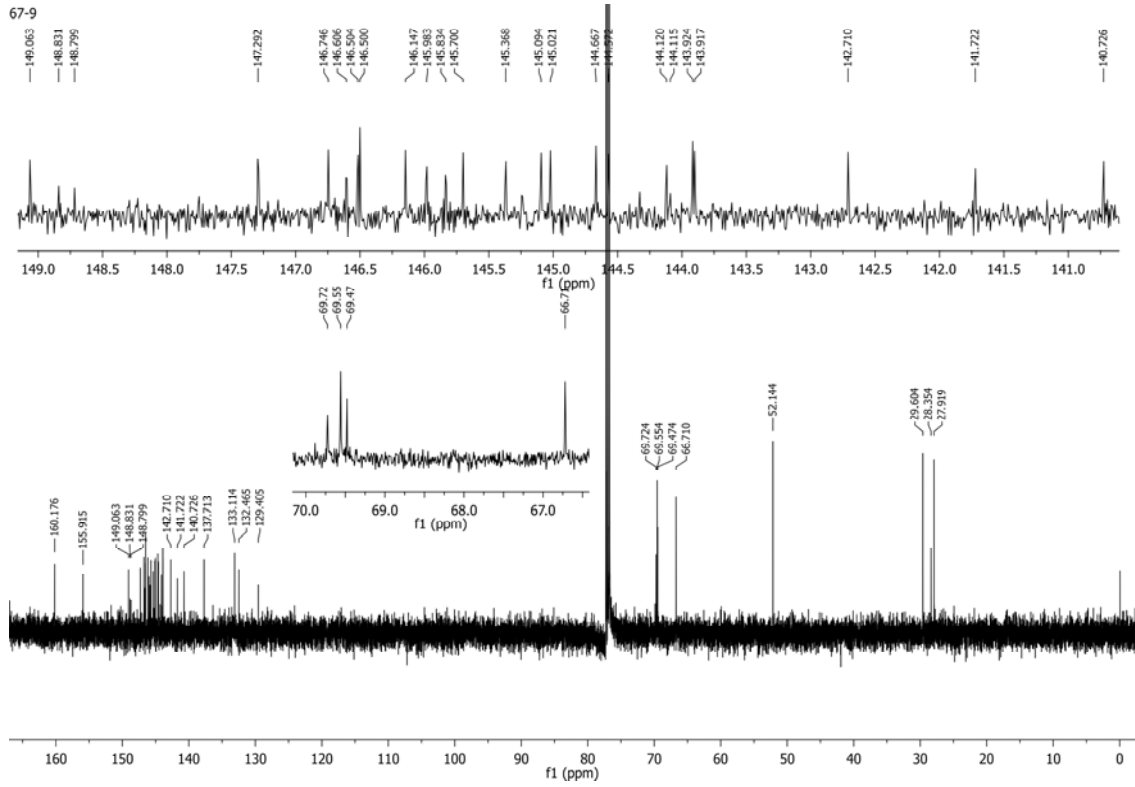
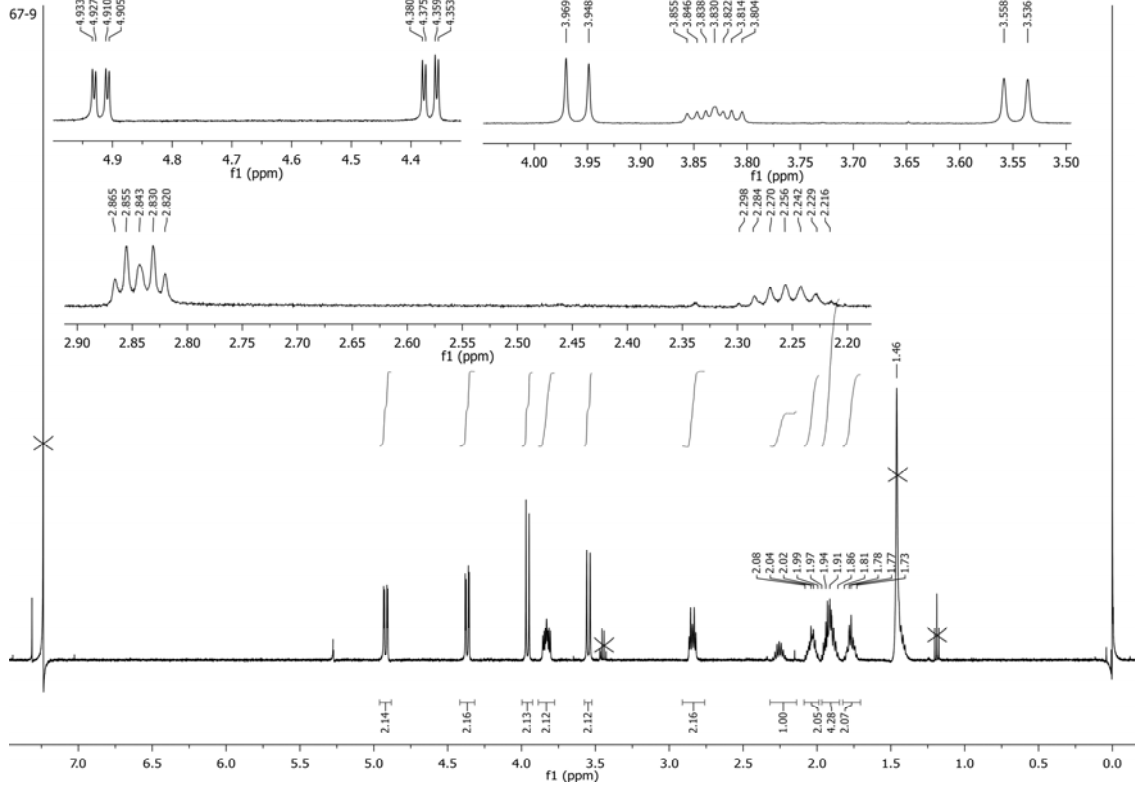
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2nd pulse 91.0 degrees
Acq. time 1.067 sec
Width 15000.0 Hz
Arrayed repetitions
OBSERVE C13, 50.2827409 MHz
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Power 0 db
continuously on
WALTZ-16 modulated
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FT size 32768
Total time 14.9 hours



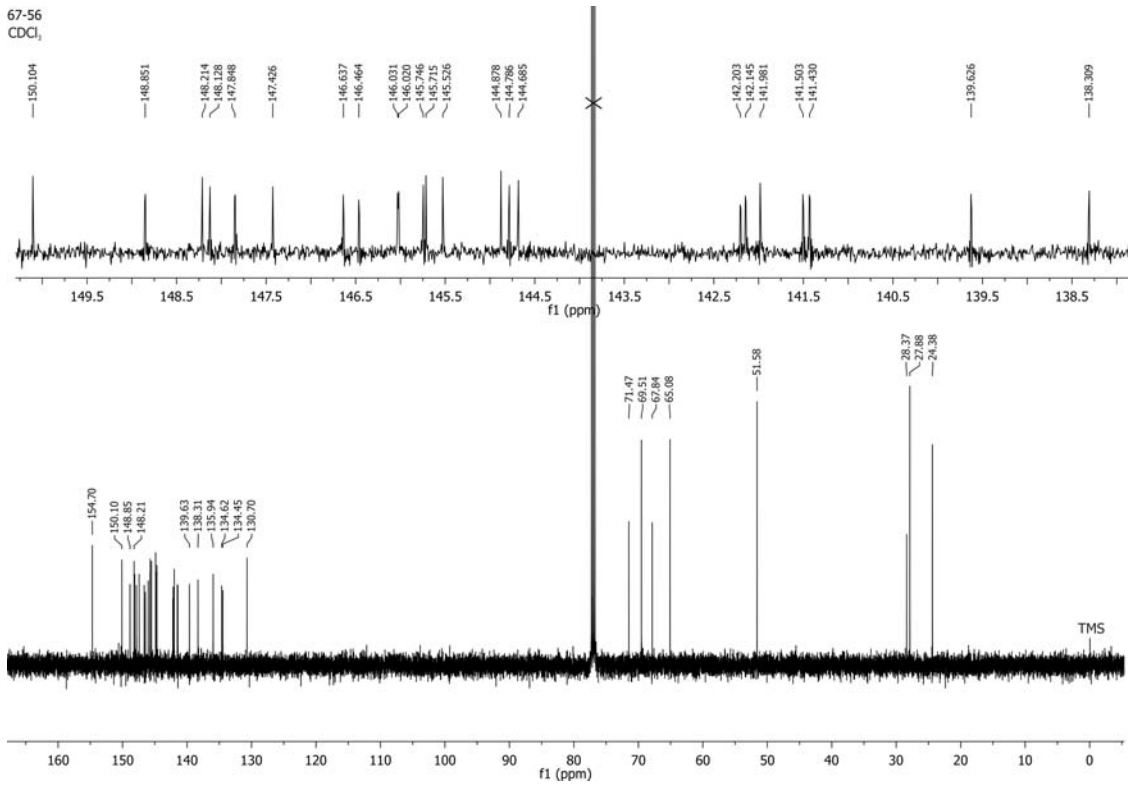
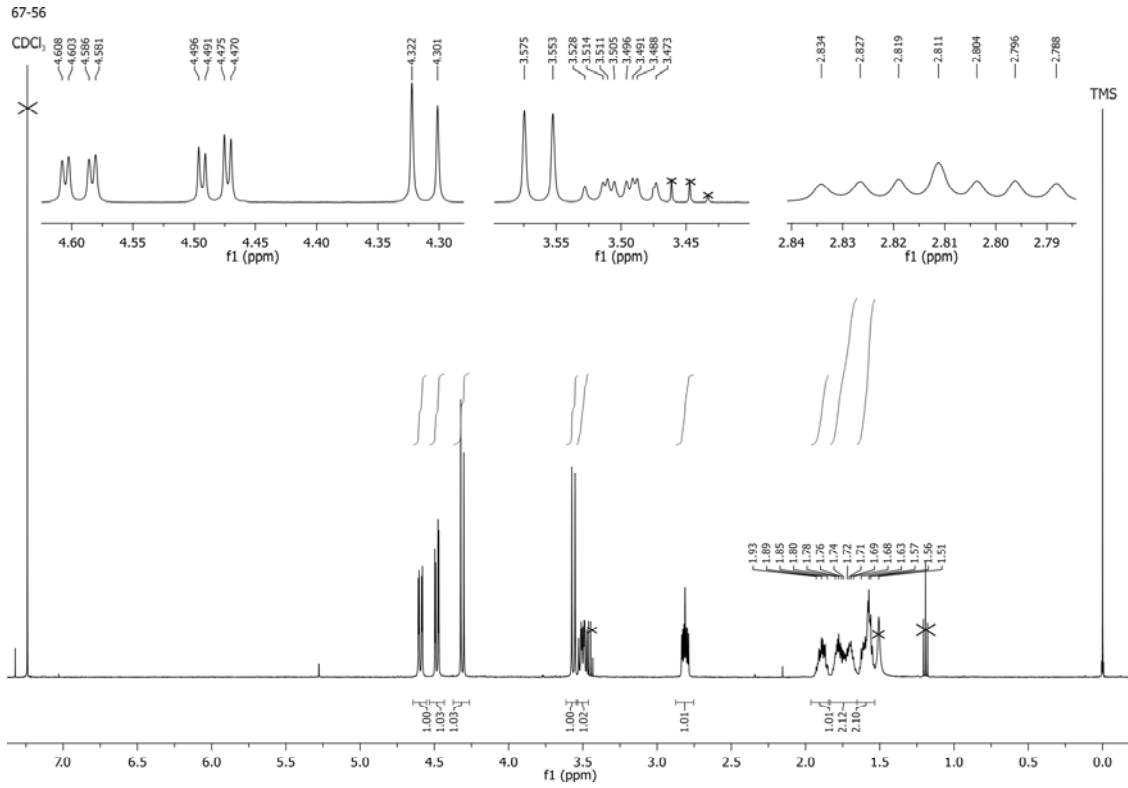
NMR spectra of compound 4



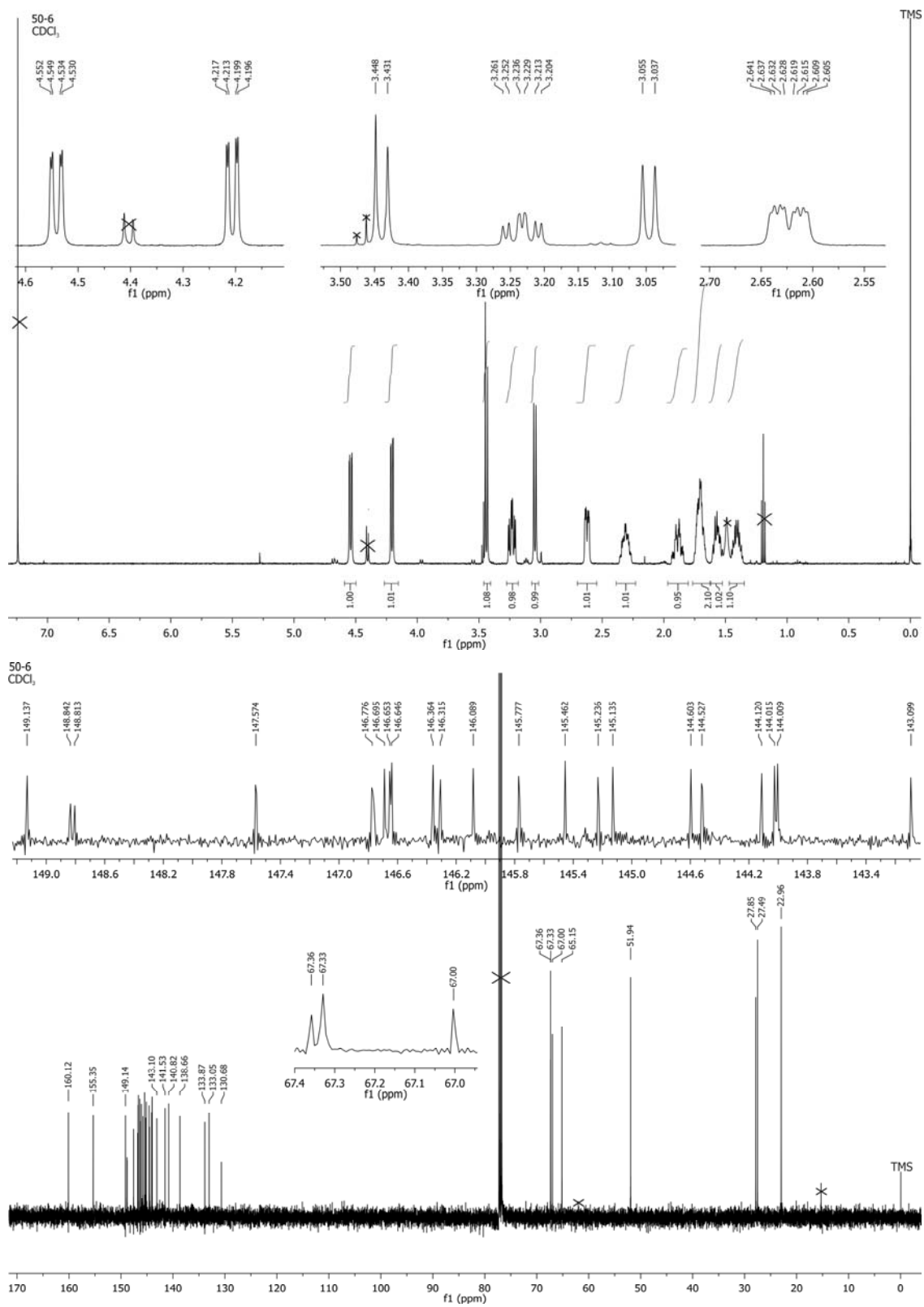
NMR spectra of compound 5



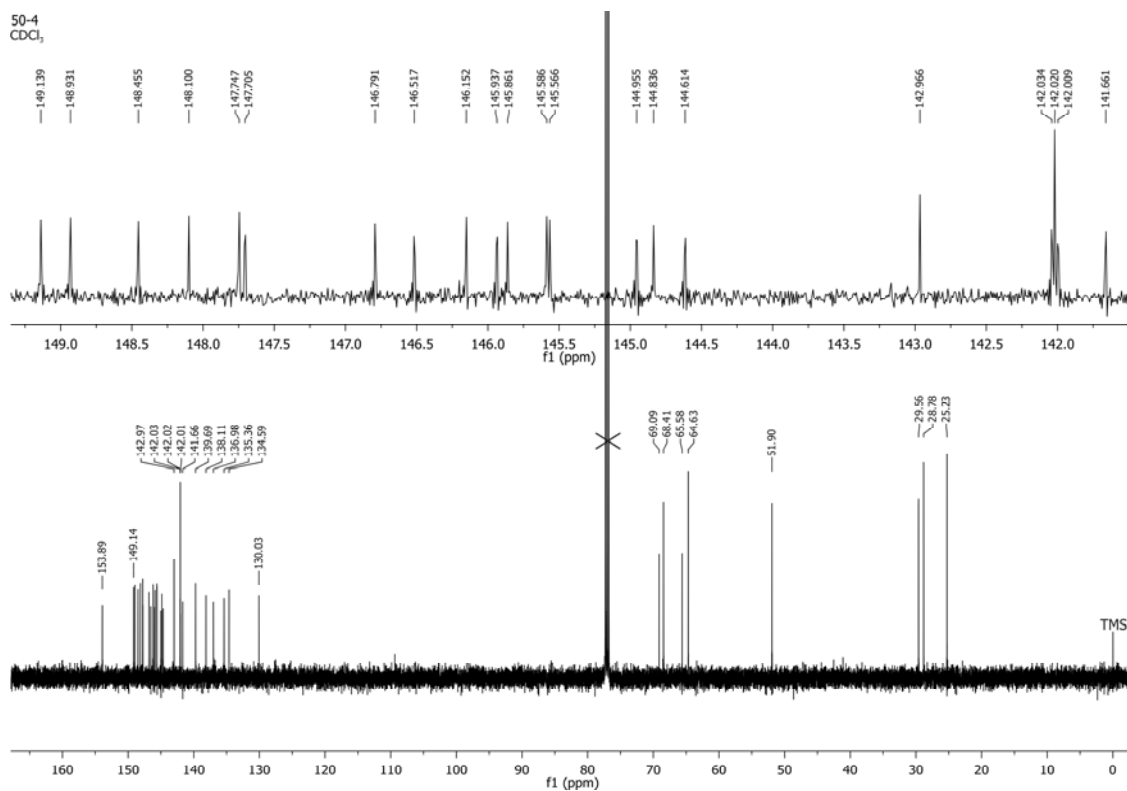
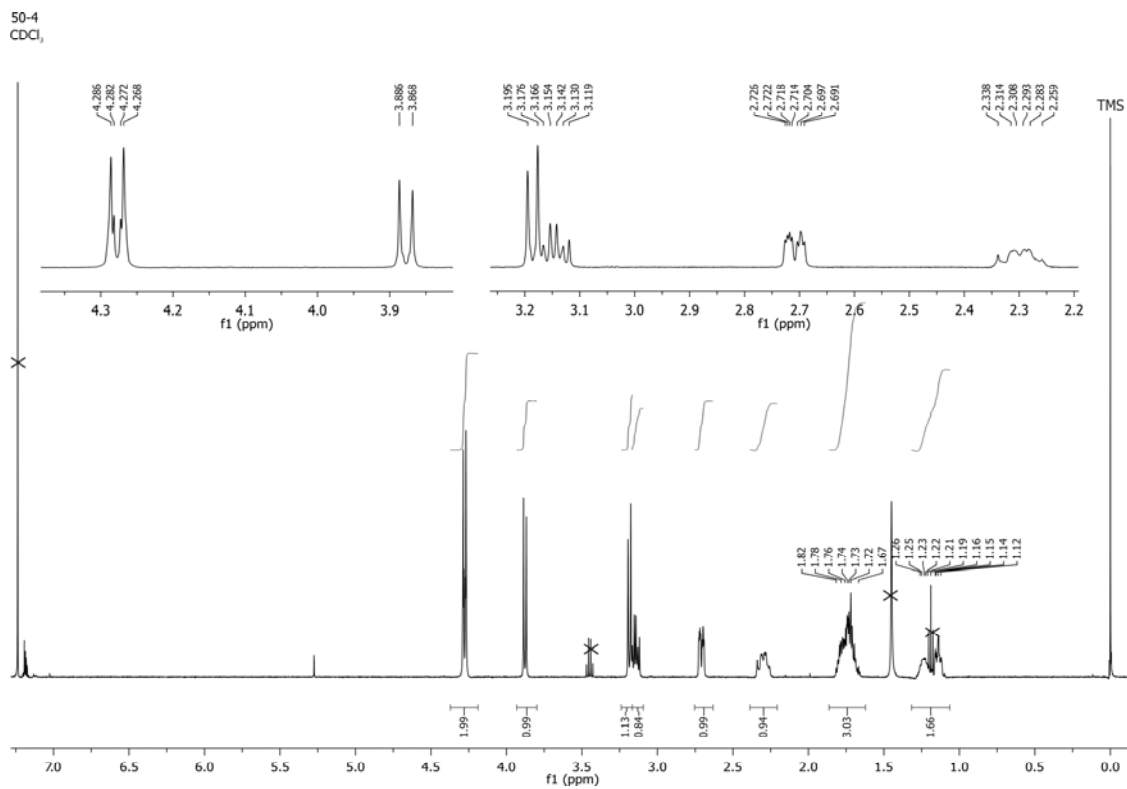
NMR spectra of compound 6



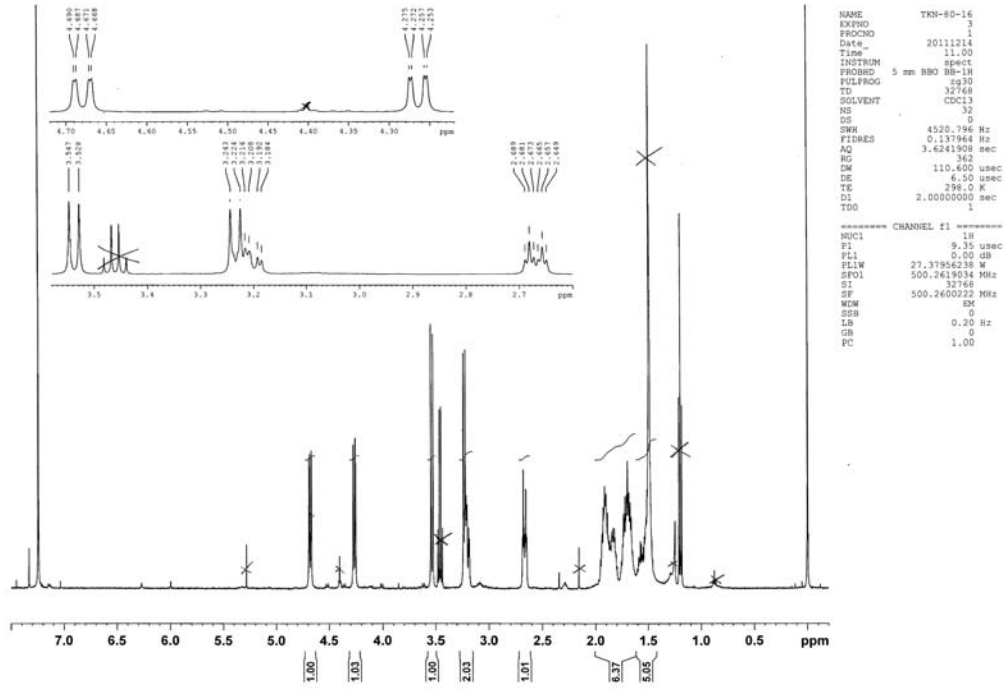
NMR spectra of compound 7



NMR spectra of compound 8

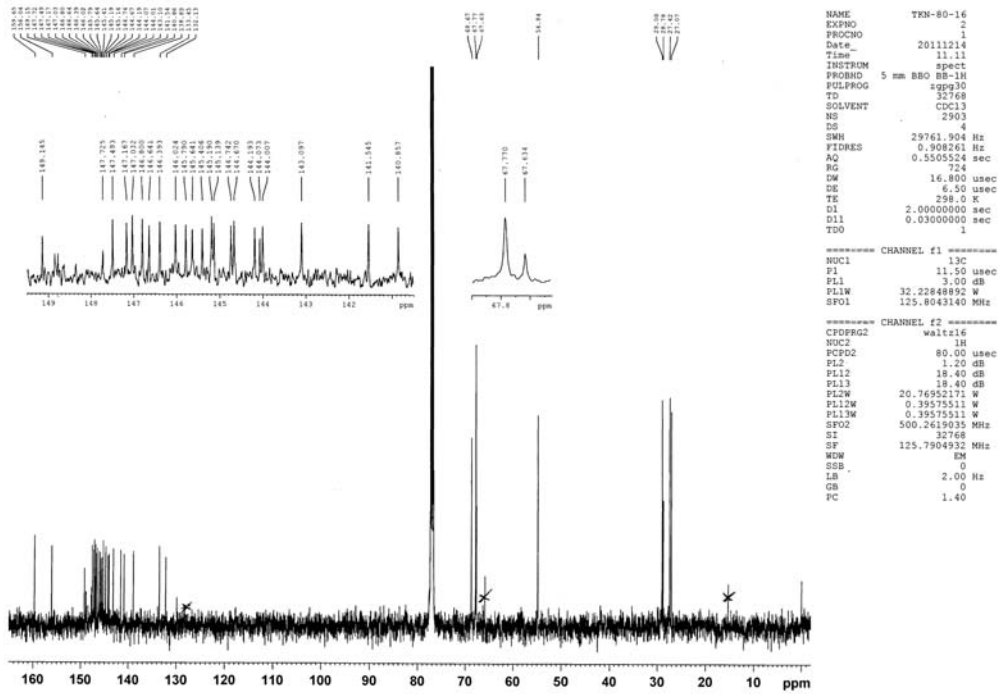


NMR spectra of compound 9



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NS        32
DS        4
SWH       4520.796 Hz
FIDRES   0.137966 Hz
AQ        3.6241908 sec
RG        362
DM        110.400 usec
DE        6.50 usec
TE        298.0 K
D1        2.0000000 sec
D11       1
TDO       1

----- CHANNEL f1 -----
NUC1      1H
P1        9.35 usec
PL1       0.00 dB
PL1W      27.37956238 W
SFO1      500.2619034 MHz
SI        32768
SF        500.2600222 MHz
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PC        1.00
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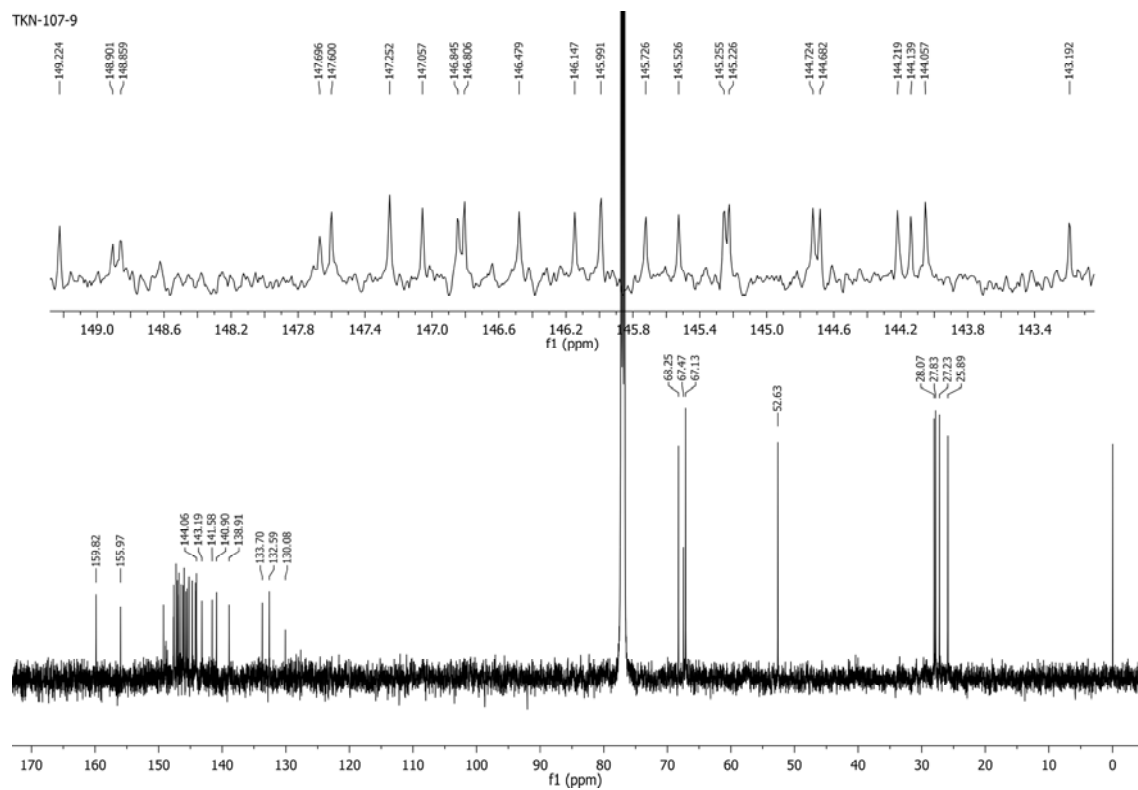
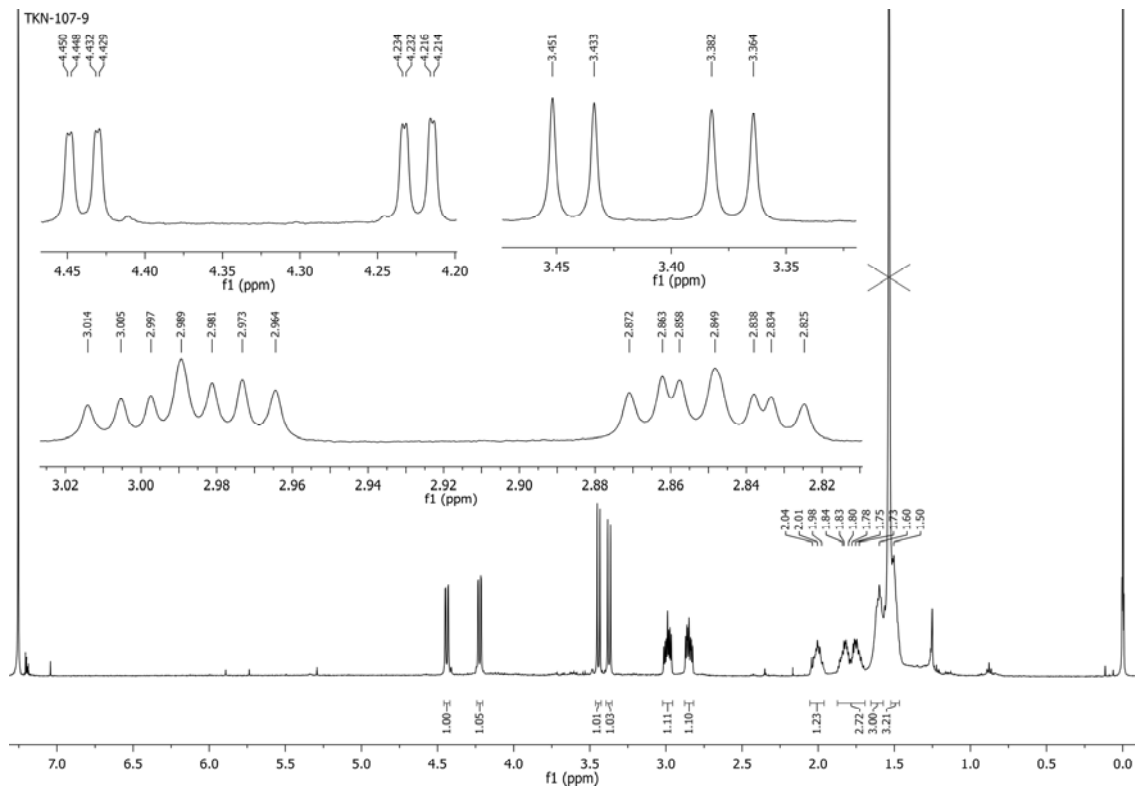


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PROCNO   1
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PULPROG  zgpg30
TD        32768
SOLVENT  CDCl3
NS        2503
DS        4
SWH       29761.904 Hz
FIDRES   0.908261 Hz
AQ        0.5505524 sec
RG        724
DM        16.800 usec
DE        6.50 usec
TE        298.0 K
D1        2.0000000 sec
D11       0.0300000 sec
TDO       1

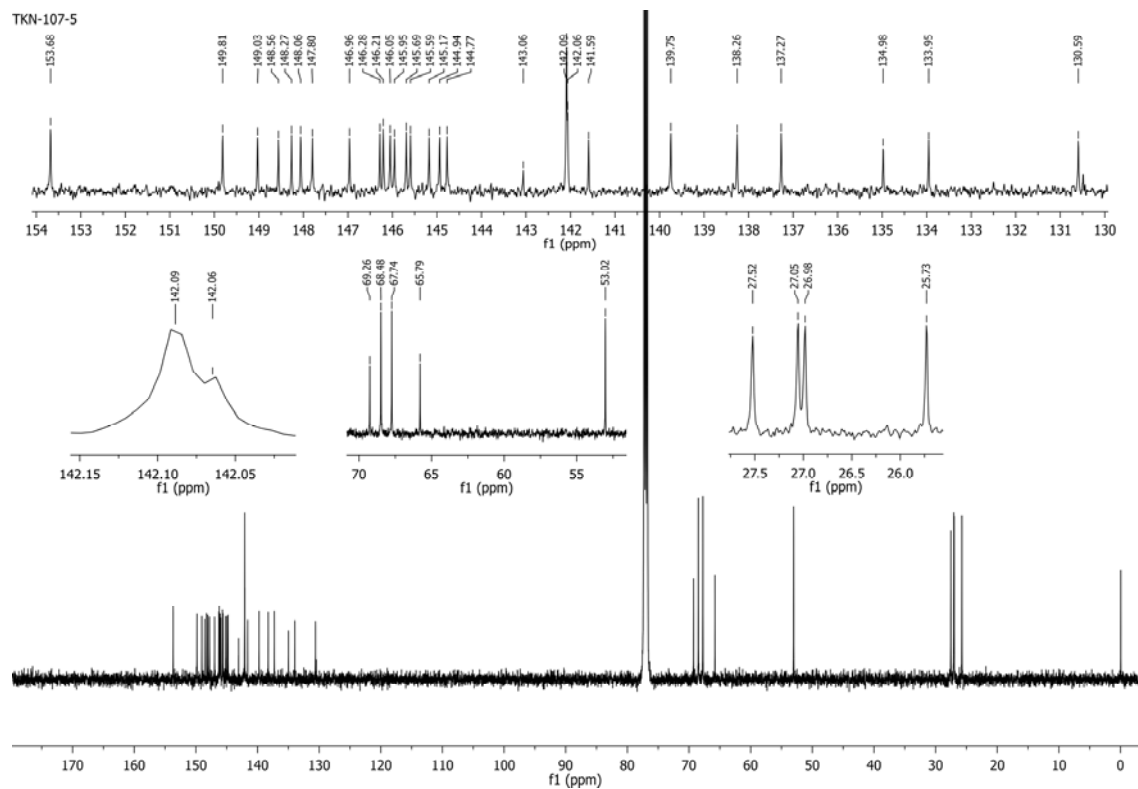
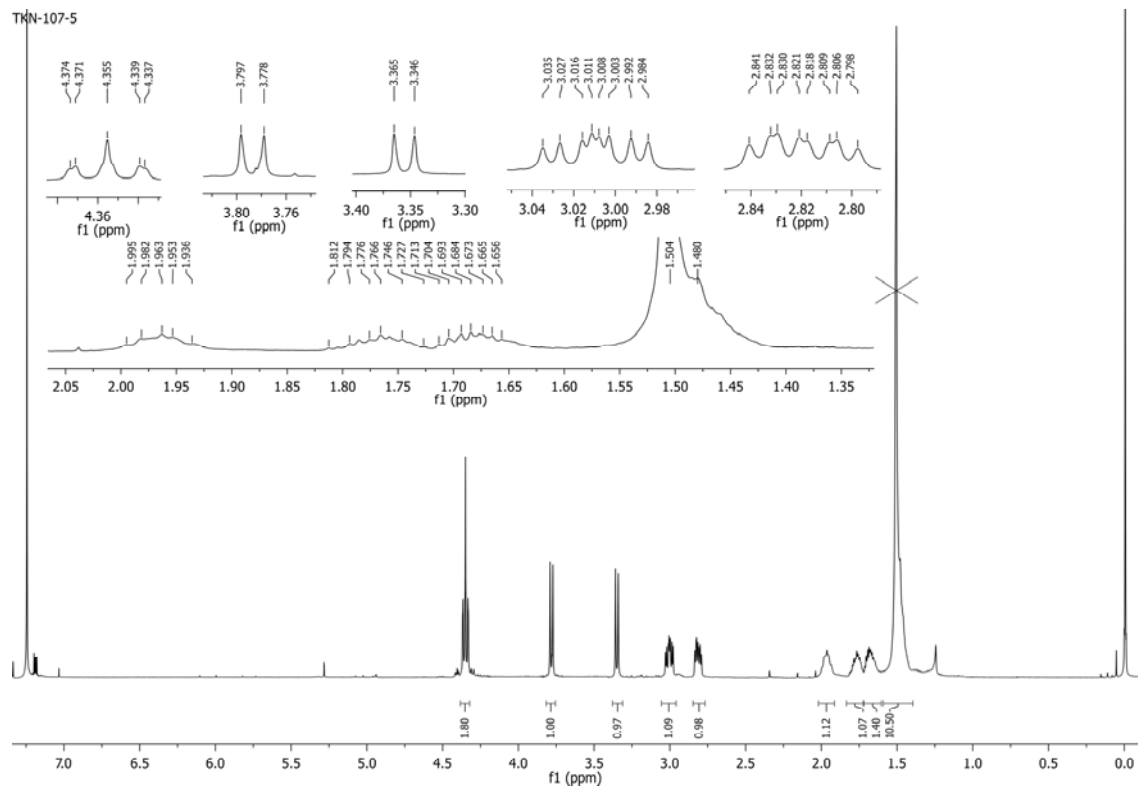
----- CHANNEL f1 -----
NUC1      13C
P1        11.50 usec
PL1       3.00 dB
PL1W      32.22848992 W
SFO1      125.8043140 MHz

----- CHANNEL f2 -----
CFPRG2    waltz16
NUC2      1H
PCPD2     80.00 usec
PL2       1.20 dB
PL12      18.40 dB
PL13      18.40 dB
PL1W      20.76952171 W
SFO2      0.39575511 W
SFO2      500.2619035 MHz
SI        32768
SF        125.7904932 MHz
MEM       EM
SSB       0
LB        2.00 Hz
GB        0
PC        1.40
```

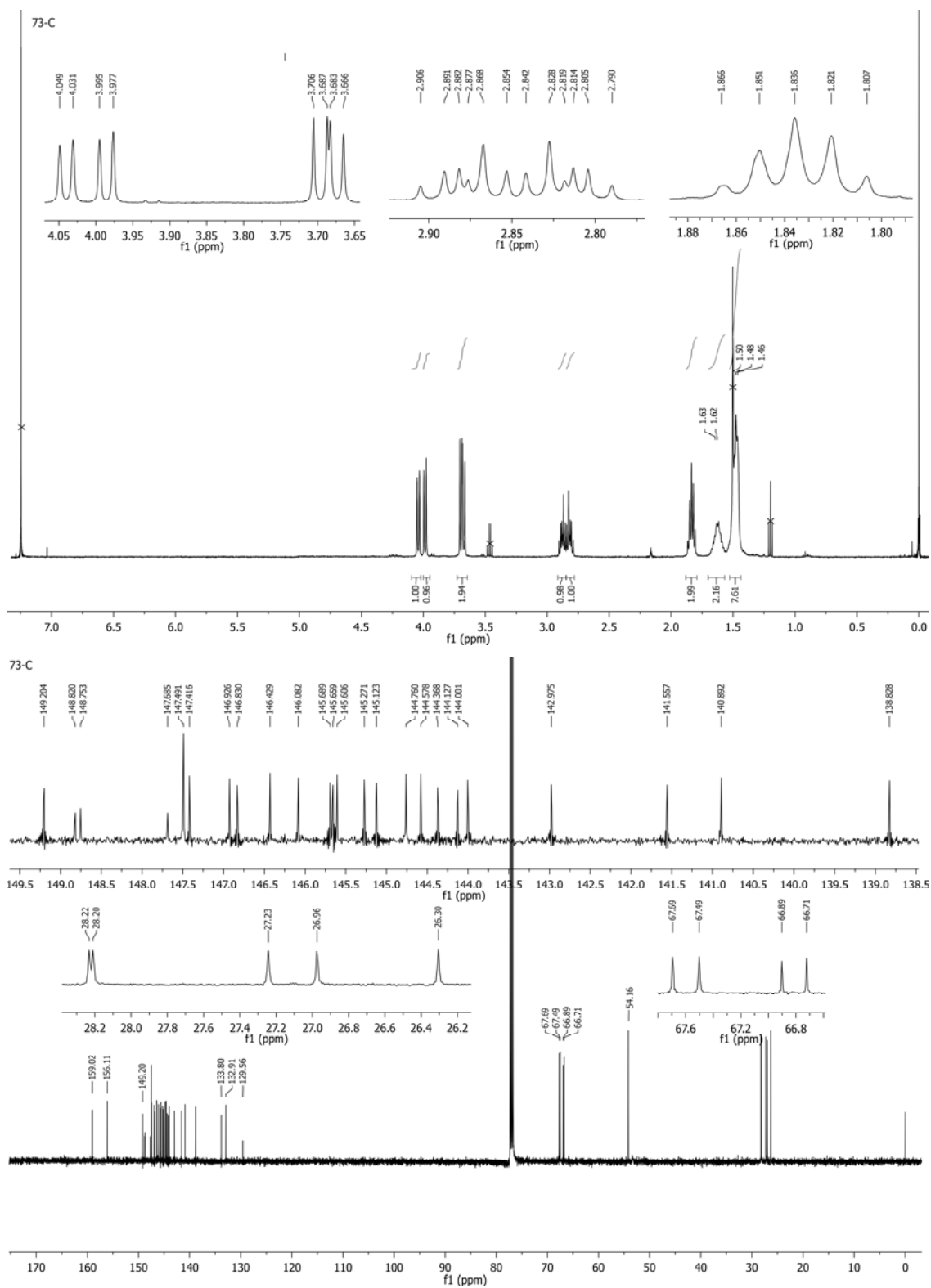

NMR spectra of compound 11



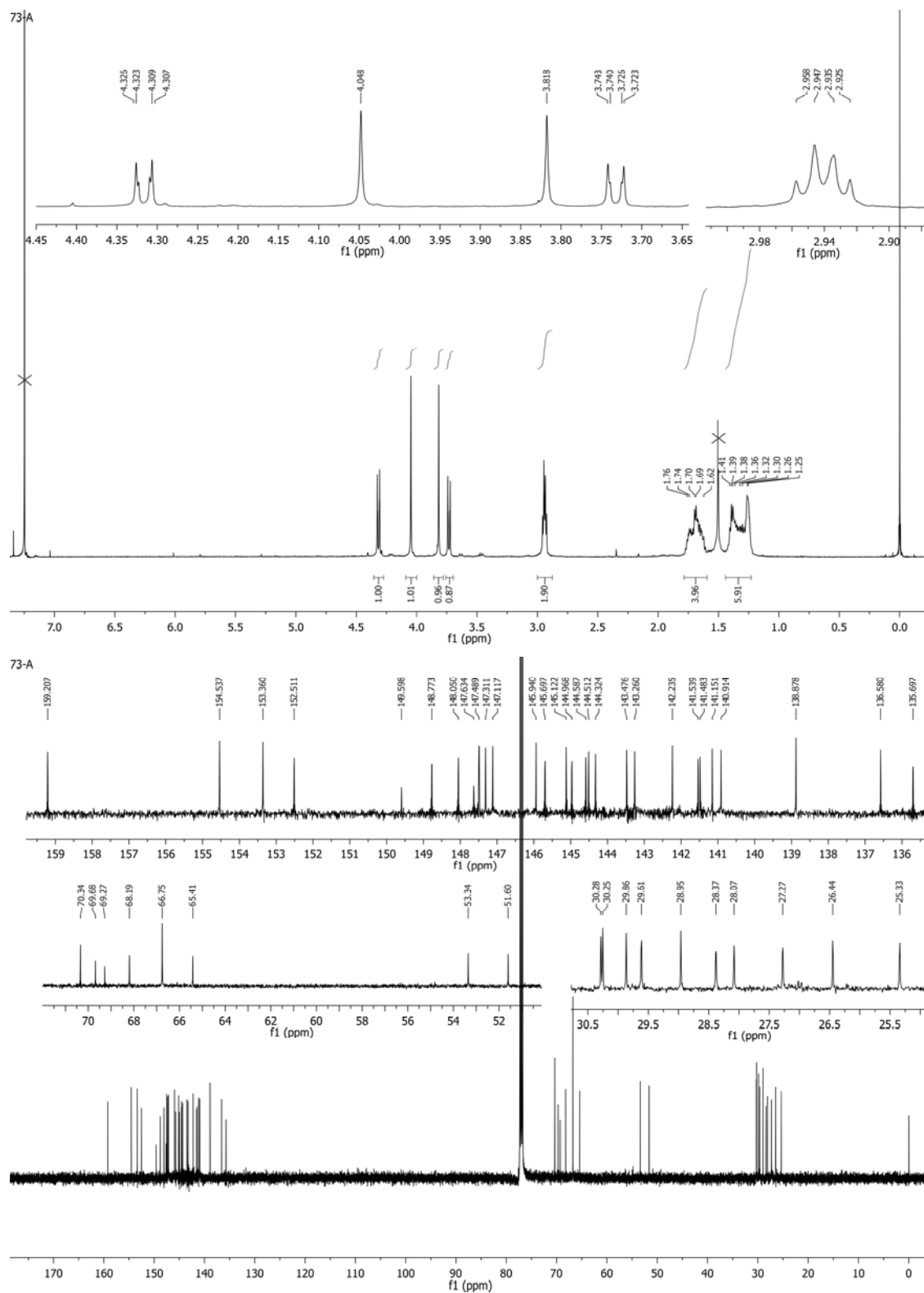
NMR spectra of compound 12



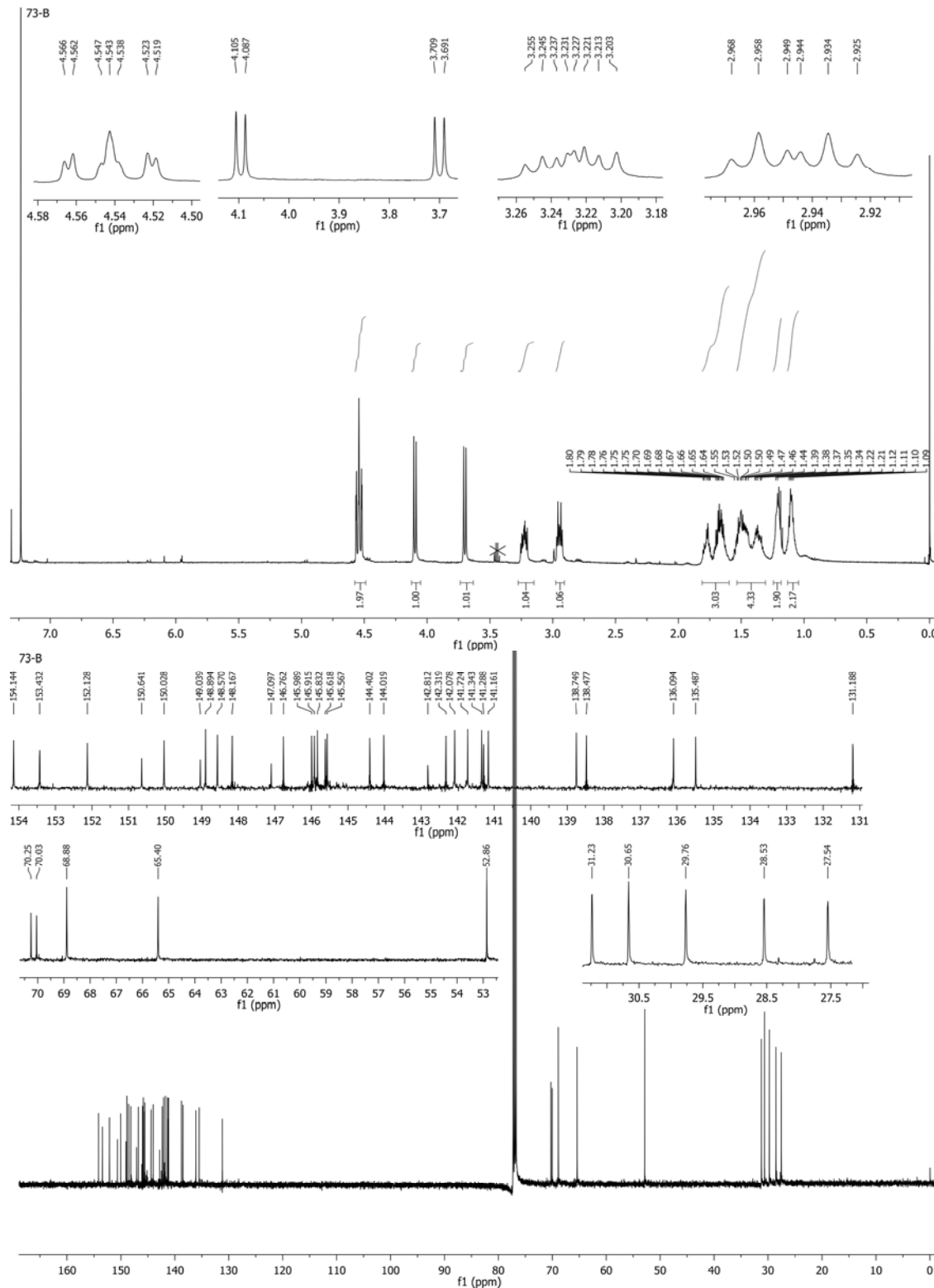
NMR spectra of compound 13



NMR spectra of compound 14



NMR spectra of compound 15.



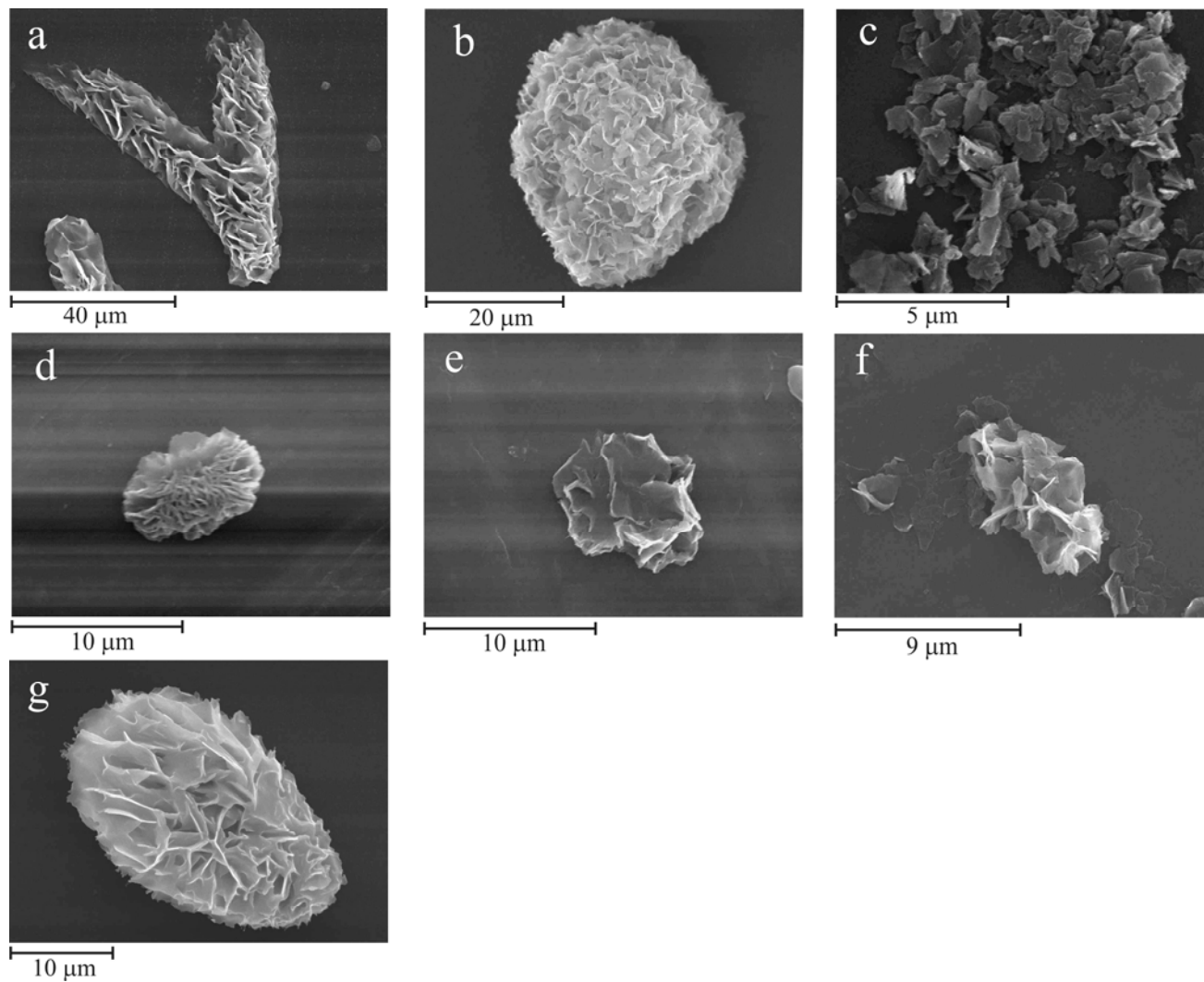


Figure S1: SEM images of the self-organized particles of **7** prepared from different solvents on various substrates at room temperature: PhMe (**a**: glass substrate, **d**: Al foil, **g**: Si wafer), PhMe/*i*-PrOH (**b**: glass substrate, **e**: Al foil) and *i*-PrOH (**c**: glass substrate, **f**: Al foil)

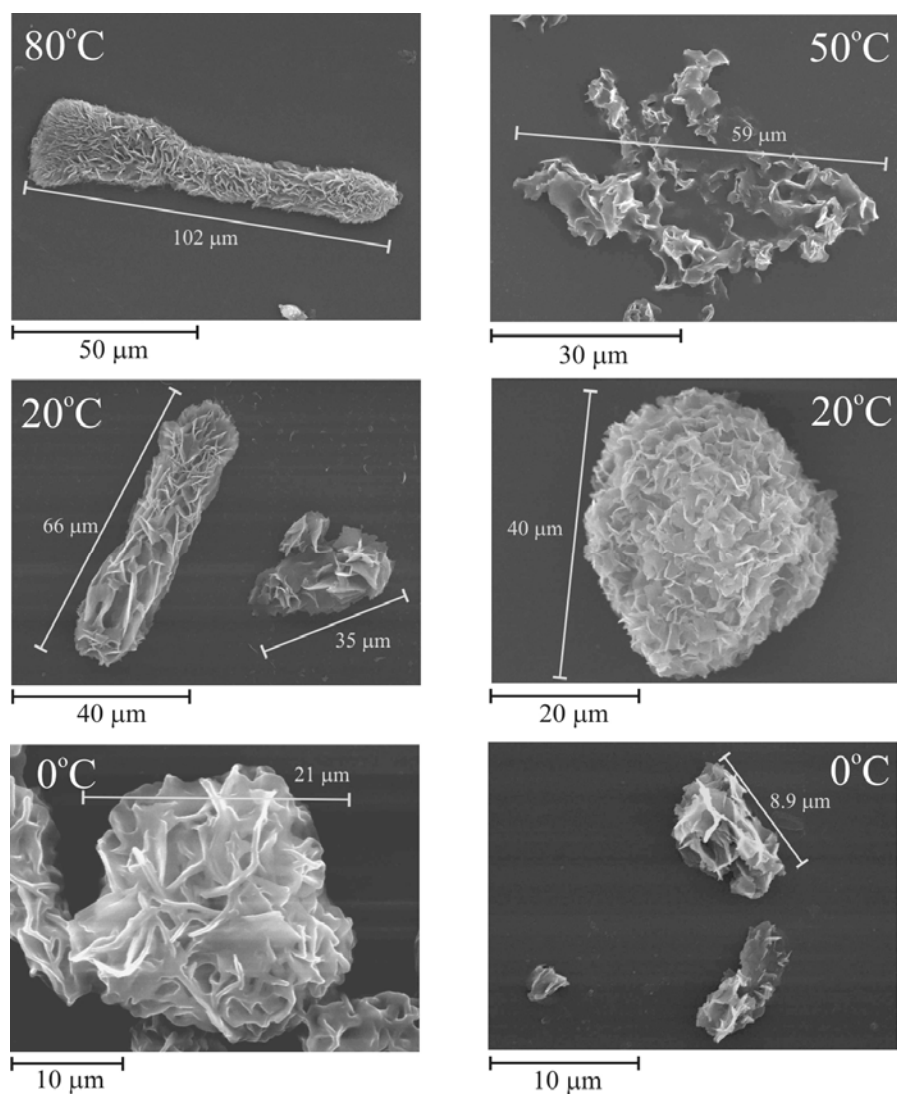


Figure S2. Self-organized particles of **7** obtained from PhMe solution (left) and from PhMe/*i*-PrOH (1:1) mixture (right) at different temperatures.

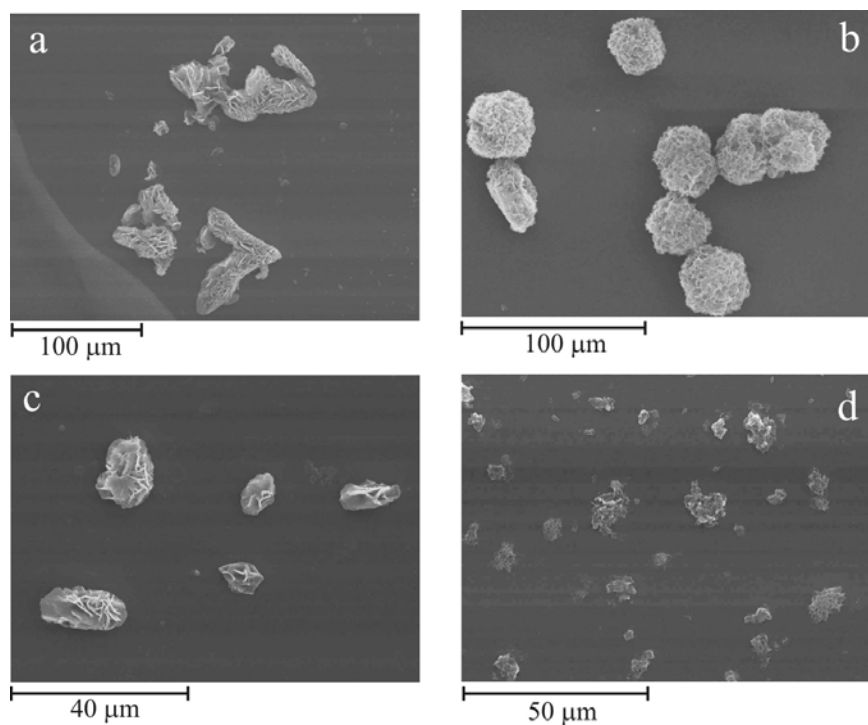


Figure S3. SEM images of flaked microparticles of **7** obtained from PhMe solution (left) and from PhMe/*i*-PrOH (1:1) mixture (right) without (**a**, **b**) or with (**c**, **d**) ultrasound stimuli.

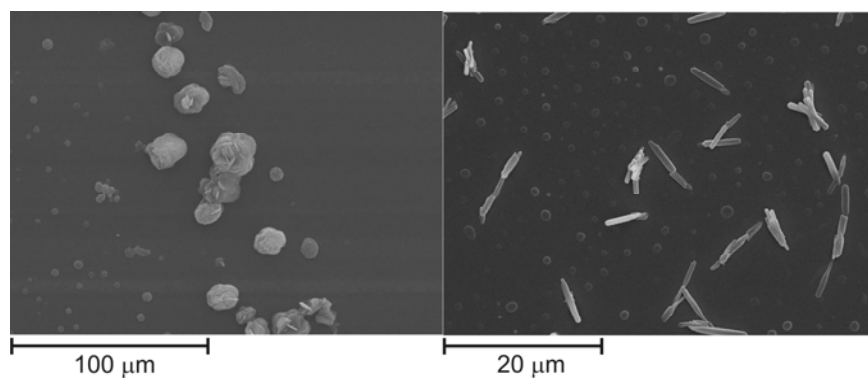


Figure S4. SEM images of *cis*-2 bisadduct **9** (left) and *cis*-3 bisadduct **12** prepared from PhMe solution on glass substrate.

Table S6: Antioxidant capacity of bisadducts **4-15** determined as a percentage of scavenged peroxide. Results are also presented relative to vitamin C and pristine C₆₀ as standards. The last two columns present efficiencies relative to vitamin C and C₆₀ recalculated to the molar ratio 1:1.

Compound	H ₂ O ₂					TBHP				
	Δ (%)	$\Delta/\Delta_{\text{vitC}}$	$\Delta/\Delta_{\text{C60}}$	$\frac{\Delta/\Delta_{\text{vitC}}}{M/M_{\text{vit}}}$ ×	$\frac{\Delta/\Delta_{\text{C60}}}{M/M_{\text{C60}}}$ ×	Δ (%)	$\Delta/\Delta_{\text{vitC}}$	$\Delta/\Delta_{\text{C60}}$	$\frac{\Delta/\Delta_{\text{vitC}}}{M/M_{\text{vit}}}$ ×	$\frac{\Delta/\Delta_{\text{C60}}}{M/M_{\text{C60}}}$ ×
4 , <i>cis</i> -1, <i>n</i> =7	-17.3	1.3	0.9	6.6	1.1	-16.7	1.4	1.0	7.2	1.2
5 , <i>cis</i> -2, <i>n</i> =7	-22.5	1.6	1.2	8.2	1.5	-19.3	1.6	1.2	8.2	1.5
6 , <i>cis</i> -3, <i>n</i> =7	-17.5	1.3	0.9	6.6	1.1	-16.7	1.4	1.0	7.2	1.2
7 , <i>cis</i> -2, <i>n</i> =8	-22.4	1.7	1.2	8.5	1.5	-22.3	1.9	1.3	9.9	1.6
8 , <i>cis</i> -3, <i>n</i> =8	-18.7	1.4	1.0	7.1	1.3	-20.6	1.8	1.2	9.2	1.5
9 , <i>cis</i> -2, <i>n</i> =9	-17.7	1.3	0.9	6.9	1.2	-16.1	1.4	1.0	7.3	1.3
10 , <i>cis</i> -3, <i>n</i> =9	-13.5	1.0	0.7	5.2	0.9	-11.0	0.9	0.7	5.0	0.9
11 , <i>cis</i> -2, <i>n</i> =10	-16.8	1.2	0.9	6.6	1.2	-14.9	1.3	0.9	6.8	1.2
12 , <i>cis</i> -3, <i>n</i> =10	-11.2	0.8	0.6	4.3	0.8	-10.2	0.9	0.6	4.8	0.8
13 , <i>cis</i> -2, <i>n</i> =12	-16.3	1.2	0.8	6.6	1.1	-15.6	1.1	0.7	6.0	1.0
14 , <i>eq</i> , <i>n</i> =12	-12.0	0.9	0.6	5.0	0.8	-11.5	1.0	0.6	5.4	0.9
15 , <i>trans</i> -4, <i>n</i> =12	-11.3	0.8	0.6	4.4	0.8	-8.94	0.8	0.5	4.2	0.7
C ₆₀	-19.0	1.4	1.0	5.7	1	-16.7	1.4	1	5.8	1
Vitamin C	-13.7	1.0	0.7	1	0.2	-11.7	1	0.7	1	0.2