Supporting Information

Fullerene sugar balls

Jean-François Nierengarten,*[a] Julien Iehl,[a] Vincent Oerthel,[a] Michel Holler,[a] Beatriz M. Illescas,[b] Antonio Muñoz,[b] Nazario Martín,*[b] Javier Rojo,*[c] Macarena Sánchez-Navarro,[c] Samy Cecioni,[d] Sébastien Vidal,*[d] Kevin Buffet,[e] Maxime Durka,[e] Stéphane P. Vincent*[e]

[a] *Laboratoire de Chimie des Matériaux Moléculaires, Université de Strasbourg et CNRS (UMR 7509), Ecole Européenne de Chimie, Polymères et Matériaux (ECPM), 25 rue Becquerel, 67087 Strasbourg Cedex 2 (France). E-mail: nierengarten@chimie.u-strasbg.fr*

[b] *Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain. E-mail: nazmar@quim.ucm.es*

[c] *Grupo de Carbohidratos, Instituto de Investigaciones Químicas, CSIC-Universidad de Sevilla, Américo Vespucio, 49. Isla de la Cartuja 41092 Sevilla, Spain. E-mail: javier.rojo@iiq.csic.es*

[d] *Institut de Chimie et Biochimie Moléculaires et Supramoléculaires, Laboratoire de Chimie Organique 2 - Glycochimie, UMR5246, CNRS, Université Lyon 1, 43 Boulevard du 11 Novembre 1918, F-69622, Villeurbanne, France. E-mail: sebastien.vidal@univ-lyon1.fr*

[e] *University of Namur (FUNDP), Département de Chimie, Laboratoire de Chimie Bio-Organique, rue de Bruxelles 61, B-5000 Namur, Belgium; E-mail: stephane.vincent@fundp.ac.be*

Experimental section

General. Reagents and solvents were purchased as reagent grade and used without further purification. Compounds **1**,[1] **3b**[2] and **5**[3] were prepared according to previously reported procedures. It is worth noting that compound **5** is quite unstable in the solid state but reasonably stable in solution. Upon purification, the best is to use polyazide **5** for the click reactions within the next 12 hours to obtain good yields. Hydroxylated galactosides **3d** and **6a** were prepared from their acetylated precursors which were obtained from 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose by glycosylation under $SnCl_4/AgOCOCF_3$ activation.[4] Deprotection of the ester moieties afforded **3d**[5] and **6a**[6] in good yields. 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^{TM} matrix-assisted laser desorption time-of-flight mass spectrometer.

Synthesis of azide 3d[5]

A solution of 1-azido-3,6-dioxaoct-8-yl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside[3] (1.099 g, 2.2 mmol) and a catalytic amount of NaOMe (30 mg, 0.25 eq.) was stirred in dry methanol (50 mL) for 12 h at rt. The crude mixture was neutralized with Amberlite IR-120 resin (H^+), filtrated and evaporated to afford the pure compound **3c** as a colorless gum (662 mg, 90%).

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[1] J. Iehl and J.-F. Nierengarten, *Chem. Eur. J*. 2009, **15**, 7306.
[2] a) E. Arce, P. M. Nieto, V. Díaz, R. García-Castro, A. Bernad and J. Rojo, *Bioconjug. Chem.* 2003, **14**, 817. (b) T. K. Lindhorst, S. Kötter, U. Krallmann-Wenzel and S. Ehlers, *J. Chem. Soc*., *Perkin Trans. 1* 2001, 823.
[3] J. Iehl, R. Pereira de Freitas, B. Delavaux-Nicot and J.-F. Nierengarten, *Chem. Commun*. 2008, 2450.
[4] J. L. Xue, S. Cecioni, L. He, S. Vidal and J.-P. Praly, *Carbohydr. Res.* 2009, **344**, 1646.
[5] Z. Szurmai, L. Szabo and A. Liptak, *Acta Chim. Hung.* 1989, **126**, 259.
[6] S. Muthana, H. Yu, S. Huang and X. Chen, *J. Am. Chem. Soc.* 2007, **129**, 11918.

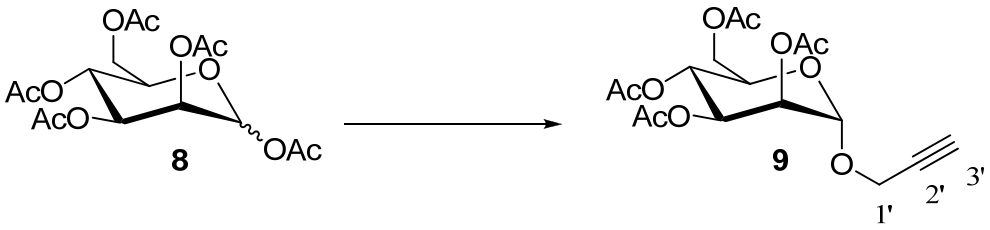
^{1}H NMR (300 MHz, D_2O): δ 3.34 (t, 1H, J = 5.1 Hz), 3.42 (dd, 1H, J = 3.0 Hz, J = 9.5 Hz), 3.46–3.51 (m, 2H), 3.59–3.64 (m, 6H), 3.66–3.74 (m, 6H), 3.78 (dd, 1H, J = 0.8 Hz, J = 3.0 Hz), 3.92–4.00 (m, 1H), 4.21 (d, 1H, J = 7.2 Hz).

Synthesis of alkyne 6a[6]

1-Propynyl-2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside[3] (1.252 g, 3.2 mmol) was stirred in a mixture of distilled methanol (50 mL), water (10 mL) and triethylamine (10 mL) for 16 h at rt. The crude mixture was evaporated then co-evaporated with toluene three times. Crystallization (MeOH/DCM) afforded the pure compound **6a** as a white solid (475 mg, 68%).

^{1}H NMR (300 MHz, D_2O): δ 2.90 (t, 1H, J = 2.4 Hz, C≡C*H*), 3.52 (dd, 1H, J = 7.8 Hz, J = 9.9 Hz), 3.65 (dd, 1H, J = 3.3 Hz, J = 9.9 Hz), 3.69–3.82 (m, 3H), 3.92 (d, 1H, J = 3.3 Hz), 4.46–4.48 (m, 2H), 4.57 (d, 1H, J = 7.8 Hz).

Synthesis of alkyne 6b

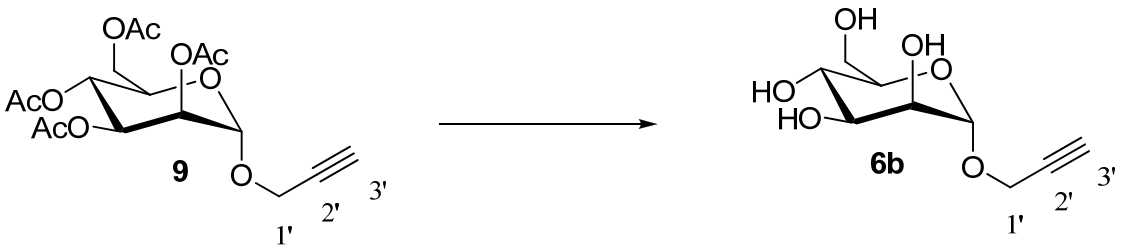


To an ice-cold (0°C) solution of D-mannose peracetate **8**[7] (1.00 g, 2.56 mmol, 1 eq) in dry DCM (25.00 mL) under argon atmosphere at 0°C was added dropwise propargyl alcohol (0.60 mL, 10.20 mmol, 4 eq) and boron trifluoride diethyl etherate (1.62 mL, 12.80 mmol, 5 eq). The reaction mixture was allowed to warm to room temperature then stirred for 48h. The solution was quenched with a saturated solution of $NaHCO_3$ (100 mL) and water (100 mL). The aqueous phase was then extracted with DCM (3x100 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure.

Purification of the residue by flash chromatography on silica gel (gradual elution: Cy/AcOEt 8/2 to Cy/AcOEt 7/3) afforded the desired mannoside **9** as a white crystalline powder (0.74 g, 75%).

[7] P.A Levene, *J. Biol. Chem.* 1924, **59**, 129.

The analytical data of **9** were in complete agreement with literature data.[8]



To a solution of **9** (0.800 g, 2.07 mmol, 1 eq) in dry methanol (4 mL) under argon atmosphere was added sodium methanolate (0.447 g, 8.27 mmol, 4 eq) at room temperature. A white precipitate immediately appeared. Methanol (4 mL) was added and the solution was stirred during a 5 minutes.

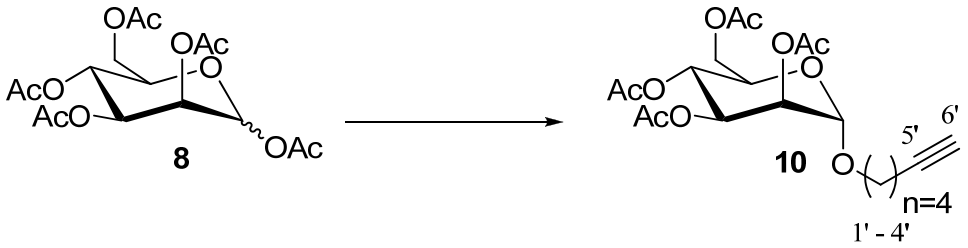
The reaction mixture was passed through a short column of dowex 50WX8-200 (H^+ form). The resin was washed with a solution of H_2O/MeOH 1/1 (50 mL). The fractions containing **6b** were concentrated under reduced pressure to afford the desired product **6b** (0.45 g, 99%).

The analytical data of **6b** were in complete agreement with literature data.[9]

Synthesis of alkyne 6c

[8] R. J. Kaufman and R. S. Sidhu et al. *J. Org. Chem.* 1982, **47***,* 4941; M. Touaibia, A. Wellens, T. C. Shiao, Q. Wang, S. Sirois, J. Bouckaert and R. Roy, *ChemMedChem*, 2007, **2**, 1190; P. van der Peet, C. T. Gannon, I. Walker, Z. Dinev, M. Angelin, S. Tam, J. E. Ralton, M. J. McConville and S. J. Williams, *ChemBioChem* 2006, **7**, 1384.

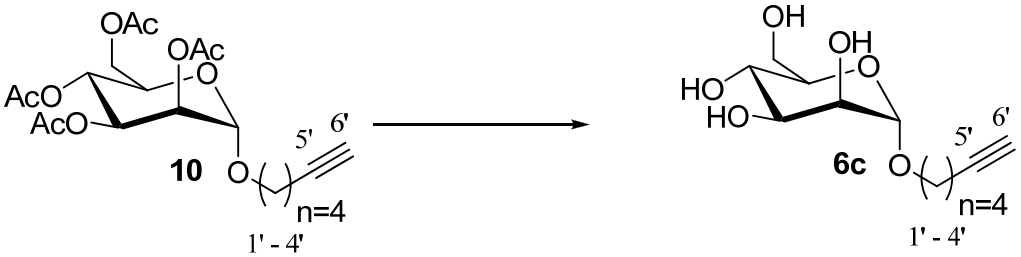
[9] C. Ferrandiz-Huertas, J. Isac-García, F. Pérez-Balderas and F. Santoyo-González, *Synthesis* 2005, **6**, 939.



To a solution of **8** (0.99 g, 2.56 mmol , 1 eq) in dry DCM (25.00 mL) under argon atmosphere at 0°C was added in quick dropwise 5-hexyn-1-ol (1.25 mL, 10.20 mmol, 4 eq) and boron trifluoride diethyl etherate (1.62 mL, 12.80 mmol, 5 eq). The reaction mixture was then stirred for 7 days at room temperature. The solution was quenched with a saturated solution of $NaHCO_3$ (2x150 mL) and water (1x150 mL). The aqueous phase was then extracted with DCM (3x100 mL), dried over $MgSO_4$, filtered and concentrated under vacuo.

Purification of the residue by flash chromatography on silica gel (gradual elution: Cy to Cy/AcOEt 9/1) afforded **10** as a colorless oil (0.59 g, 54%).

The analytical data of **10** were in complete agreement with literature data.[10]



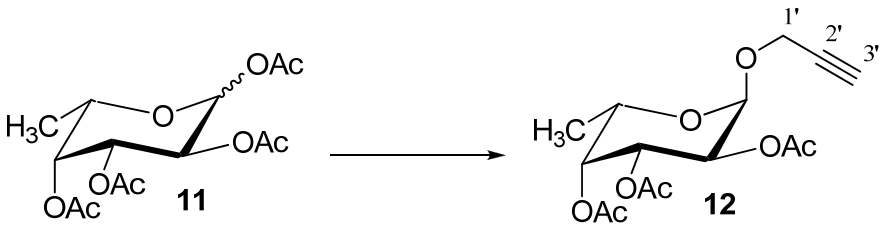
Under argon atmosphere was suspended **10** (500 mg, 1.17mmol, 1 eq) in distilled methanol (12 mL). Sodium (washed with cyclohexane, 95 mg) was added in one portion at 0°C. The reaction was stirred for 30 minutes at room temperature.

The reaction mixture was filtered over a short column of Dowex 50WX8-200 (H+ form). The resin was washed with MeOH / water (40mL) and finally evaporated under reduced pressure to yield **6c** as a colorless oil (300 mg, quantitative). ^{1}H NMR (21.4°C, 400 MHz, D_2O) δ = 4.72 (s, 1H, H-1), 3.79 (dd, $J_{1,2}$ = 1.6Hz, $J_{2,3}$ = 3.0Hz, 1H, H-2), 3.73 (d, $J_{6a,6b}$ = 11.9Hz, 1H, H-6a), 3.66-3.58 (m, 3H, H-3, H-1', H-6b), 3.53-3.48 (m, 2H, H-4, H-5), 3.41 (dt, J = 6.0Hz, J = 10.1Hz, 1H, H-1'), 2.20 (t, $J_{4',6'}$ = 2.5Hz, 1H, H-6'), 2.10 (dt, 2H, $J_{4',6'}$ = 2.3Hz, $J_{3',4'}$ = 6.8Hz, H-4'), 1.60-1.40 (m, 4H, H-2' H-3'); ^{13}C NMR (22.0°C, 100 MHz, D_2O) δ = 99.7 (C-1), 85.9 (C-6'), 72.7 (C-4), 70.6 (C-3), 70.1 (C-2), 69.3 (C-5'), 67.3 (C-1'), 66.8 (C-5), 60.9

[10] Y. Yamada, K. Matsuura and K. Kobayashi, *Bioorg. Med. Chem.* 2005, **13**, 1913.

(C-6), 27.7 (C-2'), 24.6 (C-3'), 17.4 (C-4'); $[\alpha]_D$ (MeOH, c=0.5, 20°C) = +30.0°; Mass (TOF-MS-ESI+): m/z: 283.11 (100%) $[M+Na]^+$, 543.24 (80%)$[2M+Na]^+$; HRMS (TOF-MS-ESI$^+$, m/z): calculated for $C_{12}H_{20}O_6Na^+$: 283.1152 $[M+Na]^+$ found: 283.1150

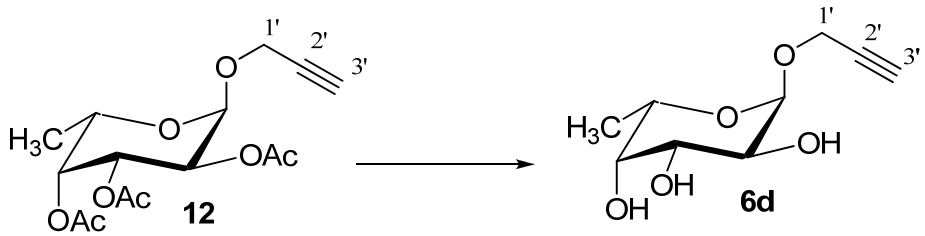
Synthesis of alkyne 6d



To a solution of **11**[11] (2.0 g, 6.02 mmol, 1 eq) in dry DCM (50.0 mL) was added dropwise propargyl alcohol (1.42 mL, 24.0 mmol, 4 eq) and boron trifluoride diethyl etherate (3.05 mL, 24.0 mmol, 4 eq) at 0°C under argon atmosphere and the solution was stirred overnight. The reaction mixture was then washed with a saturated solution of $NaHCO_3$ (50 mL) and water (50 mL), extracted with DCM (3x50 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure.

The residue was purified by flash chromatography on silica gel (gradual elution: Cy to Cy/AcOEt 6/4) to afford **12** (0.69 g, 35%) as a colorless oil and its beta-isomer (0.69 g, 35%) as a colorless oil.

The analytical data of **12** were in complete agreement with literature data.[12]



To a solution of **12** (1.00 g, 3.05 mmol, 1 eq) in dry MeOH (20 mL) was added sodium methanolate (0.29 g, 5.35 mmol, 1.5 eq) at 0°C. The solution was stirred during 15 minutes at room temperature then filtered over a short column of dowex 50WX8-200 (H^+ resin form).

[11] L. M. Wolfrom and J. A. Orsino, *J. Am. Chem. Soc.* 1934, **56**, 985.

[12] S. Béha, D. Giguère, R. Patnam and R. Roy, *Synlett* 2006, **11**, 1739.

The resin was washed with MeOH and water and finally solvents were evaporated under reduced pressure to afford the desired product **6d** as a white foam (0.54 g, 87%).
The analytical data of **6d** were in complete agreement with literature data.[13]

Compound 2.

A 1 M solution of TBAF in THF (1.17 mL, 1.17 mmol) was added to a solution of **2** (250 mg, 0.08 mmol) in CH_2Cl_2 (10 mL) at 0°C. After 1 h at 0°C, the organic layer was diluted with CH_2Cl_2, washed with water, dried ($MgSO_4$) and concentrated. Column chromatography (SiO_2, CH_2Cl_2/Cyclohexane 9:1) gave **2** (163 mg, 92%) as an orange glassy product. IR (neat): 3289 (C≡C-H), 2117 (C≡C), 1738 (C=O). UV/Vis (CH_2Cl_2): 249 (122700), 272 (90100), 283 (88300), 318 (sh, 49500), 338 (sh, 33800); ^{1}H NMR ($CDCl_3$, 300 MHz): 1.92 (m, 24H), 2.01 (s, 12H), 2.29 (t, J = 7 Hz, 24H), 4.39 (t, J = 7 Hz, 24H); ^{13}C NMR ($CDCl_3$, 75 MHz): 15.3, 27.3, 45.5, 65.5, 69.2, 70.0, 82.6, 141.2, 145.9, 163.8; MALDI-TOF-MS: 2124.4 ($[M]^+$, calcd. for $C_{138}H_{84}O_{24}$: 2124.535).

Compound 4a.

From 1. A 1 M solution of TBAF in THF (0.4 mL, 0.4 mmol) was added to a mixture of **1** (76 mg, 0.025 mmol), **3a** (124 mg, 0.33 mmol), $CuSO_4.5H_2O$ (0.4 mg, 0.002 mmol) and sodium ascorbate (1.5 mg, 0.008 mmol) in CH_2Cl_2/H_2O (1:1, 1.5 mL). The resulting mixture was vigorously stirred at rt under N_2. 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 2% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **4a** (86 mg, 51%) as an orange glassy product. IR (neat): 1742 (C=O); UV/Vis (CH_2Cl_2): 247 (67100), 272 (48000), 285 (46000), 319 (sh, 27400), 337 (sh, 20400); ^{1}H NMR (CD_2Cl_2, 300 MHz): 1.76 (s, 36H), 1.94 (s, 36H), 1.96 (s, 36 H), 2.01 (s, 36H), 2.13 (m, 24H), 2.81 (m, 24H), 4.10 (m, 24H), 4.27 (m, 12H), 4.30 (m, 24 H), 4.82 (m, 12H), 5.57 (s, 12H), 5.98 (m, 12H), 7.92 (s, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz): 20.0, 20.5, 20.55, 20.6, 22.1, 27.8, 45.2, 61.5, 66.2, 67.7, 69.0, 70.3, 72.8, 74.7, 85.5, 119.9, 141.0, 145.8, 147.2, 163.6, 168.7, 169.5, 169.9, 170.5; MALDI-TOF-MS: 6606 ($[M]^+$, calcd. for $C_{306}H_{312}N_{36}O_{132}$: 6606.01).

[13] E. Fernandez-Megia, J. Correa, I. Rodríguez-Meizoso and R. Riguera, *Macromolecules* 2006, **39**, 2113.

From 2. A mixture of **2** (76 mg, 0.035 mmol), **3a** (173 mg, 0.45 mmol), $CuSO_4.5H_2O$ (0.6 mg, 0.004 mmol) and sodium ascorbate (2 mg, 0.001 mmol) in CH_2Cl_2/H_2O (1:1, 2 mL) was vigorously stirred at rt under N_2. 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 2% of methanol) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **4a** (215 mg, 91%) as an orange glassy product.

Compound 4b.

From 1. A 1 M solution of TBAF in THF (0.46 mL, 0.46 mmol) was added to a mixture of **1** (100 mg, 0.033 mmol), **3b** (89 mg, 0.43 mmol), $CuSO_4.5H_2O$ (0.5 mg, 0.003 mmol) and sodium ascorbate (2 mg, 0.01 mmol) in DMSO (0.6 mL). The resulting mixture was vigorously stirred at rt under N_2. After 60 h, methanol (15 mL) was added to the mixture and the resulting orange precipitate filtered, extensively washed with methanol then CH_2Cl_2 and dried under high vacuum to give **4b** (90 mg, 58%) as a red-orange powder. IR (neat): 3331 (O-H), 1740 (C=O); UV/Vis (H_2O): 269 (75200), 283 (73100), 319 (sh, 46100), 337 (sh, 34100); ^{1}H NMR (DMSO-d_6, 300 MHz): 1.96 (m, 24H), 2.65 (m, 24H), 3.75 (m, 24H), 4.24 (m, 24H), 4.71 (m, 12H), 5.19 (m, 12H), 5.30 (m, 12H), 5.39 (m, 12H), 5.46 (m, 12H), 8.03 (s, 12H); ^{13}C NMR (DMSO-d_6, 75 MHz): 21.4, 27.7, 45.6, 60.7, 66.7, 68.8, 69.5, 72.1, 76.9, 79.8, 87.5, 121.7, 140.7, 145.0, 145.8, 162.8.
From 2. A mixture of **2**(44 mg, 0.021 mmol), **3b** (55 mg, 0.27 mmol), $CuSO_4.5H_2O$ (0.3 mg, 0.002 mmol), sodium ascorbate (1.2 mg, 0.006 mmol) in DMSO (0.4 mL) was vigorously stirred at rt under N_2. After 60 h, methanol (15 mL) was added to the mixture and the resulting orange precipitate filtered, extensively washed with methanol and dried under high vacuum to give **4b** (74 mg, 74%) as a red-orange powder.

Compound 4c.

As described for **4b**, with **2** (40 mg, 0.019 mmol), **3c** (62 mg, 0.247 mmol), $CuSO_4.5H_2O$ (0.1 mg, 0.0006 mmol), sodium ascorbate (0.3 mg, 0.0017 mmol) in DMSO (0.4 mL). After 48 h, acetonitrile (6 mL) was added to the mixture and the resulting orange precipitate filtered, extensively washed with ethyl acetate and dried under high vacuum to give **4b** (87 mg, 90%) as a red-orange powder. IR (neat): 3428 (O-H), 1741.3 (C=O); UV/Vis (CH_2Cl_2): 219 (84165), 247 (73511), 282 (sh, 52094), 321 (sh, 33483), 341 (sh, 26085). ^{1}H NMR (DMSO-

d_6, 700 MHz: 1.97 (m, 24 H), 2.65 (m, 24H), 3.12 (m, 12H), , 3.54 (m, 24H), 3.61 (24H), 3.77, (m, 12H) 3.92 (m, 12H), 4.35-4.52 (m, 48H), 4.60 (m, 36H), 4.74(m, 24H), 7.83 (s, 12H); ^{13}C NMR (DMSO-d_6, 125 MHz): 22.0, 28.28, 46.0, 49.9, 61.5, 65.2, 67.1, 70.6, 71.5, 74.7, 100.2, 122.8, 141.2, 145.5, 146.4, 163.4.

Compound 4d.

As described for **4b**, with **2** (120 mg, 0.056 mmol), **3d** (250 mg, 0.73 mmol), $CuSO_4.5H_2O$ (0.3 mg, 0.0018 mmol), sodium ascorbate (1 mg, 0.005 mmol) in DMSO (0.5 mL). After 48 h, methanol (8 mL) and Et_2O (8 mL) were added to the mixture and the resulting orange precipitate filtered, extensively washed with methanol/Et_2O (1:1) then CH_2Cl_2 and dried under high vacuum to give **4d** (250 mg, 72%) as a red-orange powder. IR (neat): 3380 (O-H), 1739 (C=O); UV/Vis (H_2O): 247 (40500), 269 (30100), 283 (28800), 319 (sh, 17800), 339 (sh, 14000); ^{1}H NMR (DMSO-d_6, 300 MHz): 1.96 (m, 24H), 2.65 (m, 24H), 3.33 (m, 24H), 3.40 (m, 72H); 3.79 (m, 24H), 4.14 (m, 48H), 4.38 (m, 36H), 4.45 (m, 12H), 4.60 (m, 12H), 4.71 (m, 12 H), 4.85 (m, 12H), 7.82 (s, 12H); ^{13}C NMR (DMSO-d_6, 75 MHz): 21.4, 27.8, 45.7, 49.4, 60.6, 66.7, 67.8, 68.3, 68.8, 69.6, 69.8, 70.6, 73.6, 75.3, 103.7, 122.6, 140.9, 145.1, 145.8, 162.9.

Compound 7a.

As described for **4b**, with **5** (176 mg, 0.072 mmol), **6a** (203 mg, 0.93 mmol), $CuSO_4.5H_2O$ (1 mg, 0.0072 mmol) and sodium ascorbate (4 mg, 0.021 mmol) in CH_2Cl_2/H_2O/DMSO (1:1:1, 3 mL). After 48 h, methanol (15 mL) was added to the mixture and the resulting orange precipitate filtered, extensively washed with methanol then CH_2Cl_2 and dried under high vacuum to give **7a** (261 mg, 73%) as a red-orange powder. IR (neat): 3349 (O-H), 1739 (C=O); UV/Vis (H_2O): 246 (83900), 267 (65300), 284 (59100), 320 (sh, 35800), 343 (sh, 28000); ^{1}H NMR (DMSO-d_6, 300 MHz): 2.14 (m, 24H), 3.25-3.34 (m, 48H), 4.18-4.38 (48H), 4.54 (m, 12H), 4.70 (m, 36H), 4.91 (m, 12H), 8.04 (s, 12H); ^{13}C NMR (DMSO-d_6, 100 MHz): 28.7, 45.3, 46.2, 60.6, 61.5, 64.4, 68.2, 68.7, 70.5, 73.4, 75.3, 102.7, 124.3, 140.7, 144.3, 145.1, 162.8.

Compound 7b.

As described for **4b**, with **5** (295 mg, 0.127 mmol), **6b** (360 mg, 1.65 mmol), $CuSO_4.5H_2O$ (2 mg, 0.012 mmol) and sodium ascorbate (7 mg, 0.036 mmol) in CH_2Cl_2/H_2O/DMSO (1:1:1, 3 mL). After 48 h, methanol (15 mL) was added to the mixture and the resulting orange precipitate filtered, extensively washed with methanol then CH_2Cl_2 and dried under high vacuum to give **7b** (509 mg, 81%) as a red-orange powder. IR (neat): 3332 (O-H), 1740 (C=O); UV/Vis (H_2O): 245 (77700), 268 (62200), 282 (57500), 321 (sh, 35800), 341 (sh, 26400); ^{1}H NMR (DMSO-d_6, 300 MHz): 2.07 (m, 24H), 3.20 (m, 48H partially masked by the H_2O signal), 4.38 (m, 460H), 4.16 (m, 24H), 4.71 (m, 12H), 4.81 (m, 12H), 8.06 (s, 12H); ^{13}C NMR (DMSO-d_6, 75 MHz): 28.8, 46.0, 46.5, 59.3, 61.4, 64.6, 67.1, 68.9, 70.3, 71.0, 74.1, 99.3, 124.4, 140.8, 143.9, 145.3, 163.0.

Compound 7c.

As described for **4b**, with **5** (100 mg, 0.043 mmol), **6c** (145 mg, 0.56 mmol), $CuSO_4.5H_2O$ (0.7 mg, 0.004 mmol) and sodium ascorbate (3 mg, 0.003 mmol) in CH_2Cl_2/H_20/DMSO (1:1:1, 3 mL). The dark red solution was stirred at ambient temperature for 48 h. After 48 h, methanol (15 mL) was added to the mixture and the resulting orange precipitate filtered and extensively washed with methanol. The resulting compound was dissolved in DMSO and precipitated by addition of MeOH and filtered (2 x), then extensively washed with methanol then CH_2Cl_2 and dried under high vacuum to give **7c** (93 mg, 40%) as a red-orange solid. IR (neat): 3332 (O-H), 1740 (C=O); UV/Vis (H_2O): 247 (79700), 269 (64300), 283 (58700), 320 (sh, 37200), 337 (sh, 29200); ^{1}H NMR (DMSO-d_6, 300 MHz): 1.55 (m, 48H), 2.19 (m, 24H), 2.59 (m, 24H), 3.40 (m, 24H partially masked by the H_2O signal), 3.62 (m, 24H), 4.33 (m, 60H), 4.43 (m, 12H), 4.55 (m, 12H), 4.70 (m, 24H), 7.81 (s, 12H); ^{13}C NMR (DMSO-d_6, 75 MHz): 24.7, 25.7, 28.5, 45.2, 45.9, 48.5, 61.2, 64.3, 65.9, 67.0, 68.6, 70.3, 71.0, 73.8, 99.7, 121.7, 140.6, 145.0, 146.9, 162.6.

Compound 7d.

As described for **4b**, with **5** (100 mg, 0.043 mmol), **6d** (113 mg, 0.56 mmol), $CuSO_4.5H_2O$ (07 mg, 0.004 mmol) and sodium ascorbate (2.6 mg, 0.0.012 mmol) in CH_2Cl_2/H_2O/DMSO (1:1:1, 3 mL). After 48 h, methanol (15 mL) was added to the mixture and the resulting orange precipitate filtered, extensively washed with methanol then CH_2Cl_2 and dried under high vacuum to give **7d** (110 mg, 54%) as a red-orange powder. IR (neat): 3332 (O-H), 1740

(C=O); UV/Vis (H_2O): 246 (49800), 269 (38500), 284 (33900), 322 (sh, 20400), 343 (sh, 14700); ^{1}H NMR (DMSO-d_6, 300 MHz): 1.01 (m, 36H), 2.16 (m, 24H), 3.47 (m, 36H), 3.74 (m, 12H), 4.36 (m, 48H), 4.53 (m, 24H), 4.69 (m, 12H), 8.05 (s, 12H); ^{13}C NMR (DMSO-d_6, 75 MHz): 16.2, 28.5, 46.0, 60.0, 64.2, 65.9, 67.8, 69.4 (x2), 71.4, 98.4, 124.1, 140.5, 144.9 (x2), 162.5.

Fig. S1. ^{13}C NMR (top) and DEPT (bottom) spectra of compound **4a** recorded in $CDCl_3$.

Fig. S2. ^{13}C NMR (top) and DEPT (bottom) spectra of compound **4b** recorded in DMSO-d_6.

Fig. S3. ^{13}C NMR (top) and DEPT (bottom) spectra of compound **4c** recorded in DMSO-d_6.

Fig. S4. ^{13}C NMR (top) and DEPT (bottom) spectra of compound **4d** recorded in DMSO-d_6.

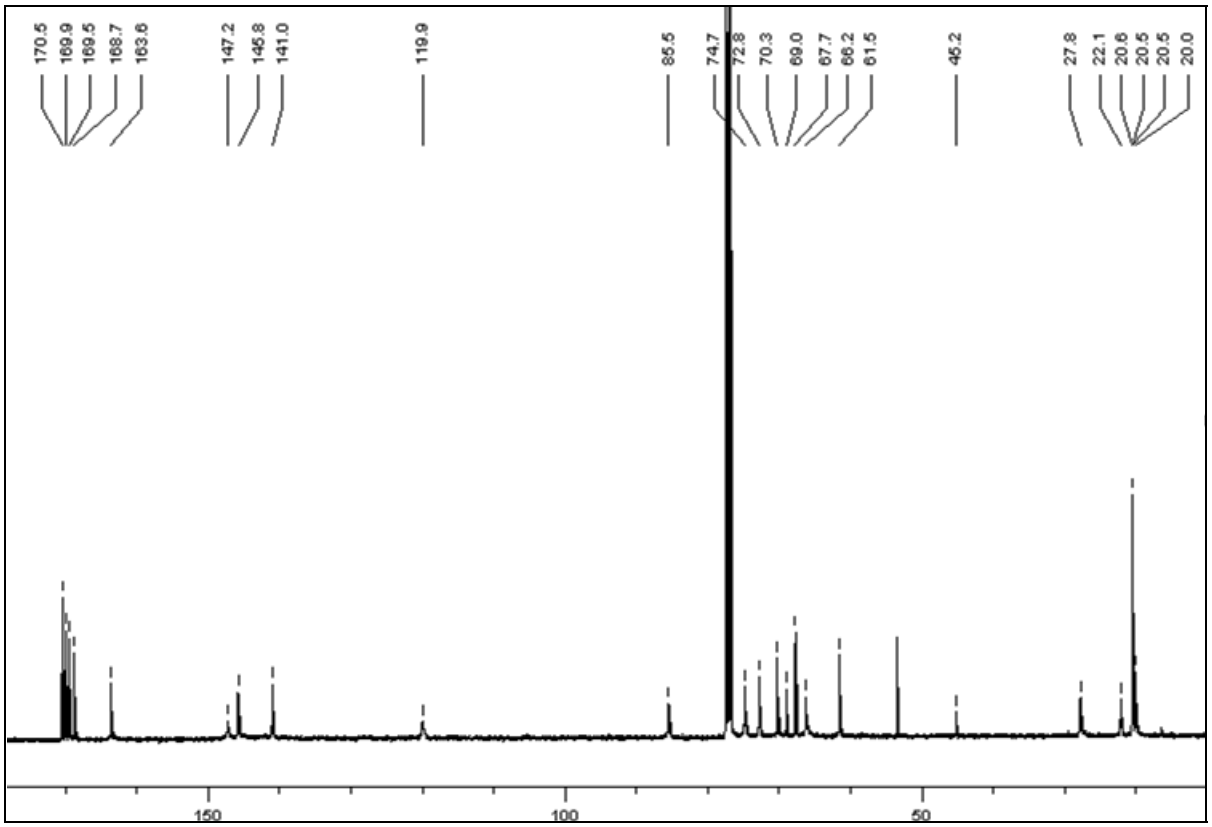
Fig. S5. ^{13}C NMR (top) and DEPT (bottom) spectra of compound **7a** recorded in DMSO-d_6.

Fig. S6. ^{13}C NMR (top) and DEPT (bottom) spectra of compound **7b** recorded in DMSO-d_6.

Fig. S7. ^{13}C NMR (top) and DEPT (bottom) spectra of compound **7c** recorded in DMSO-d_6.

Fig. S8. ^{13}C NMR (top) and DEPT (bottom) spectra of compound **7d** recorded in DMSO-d_6.

Fig. S1.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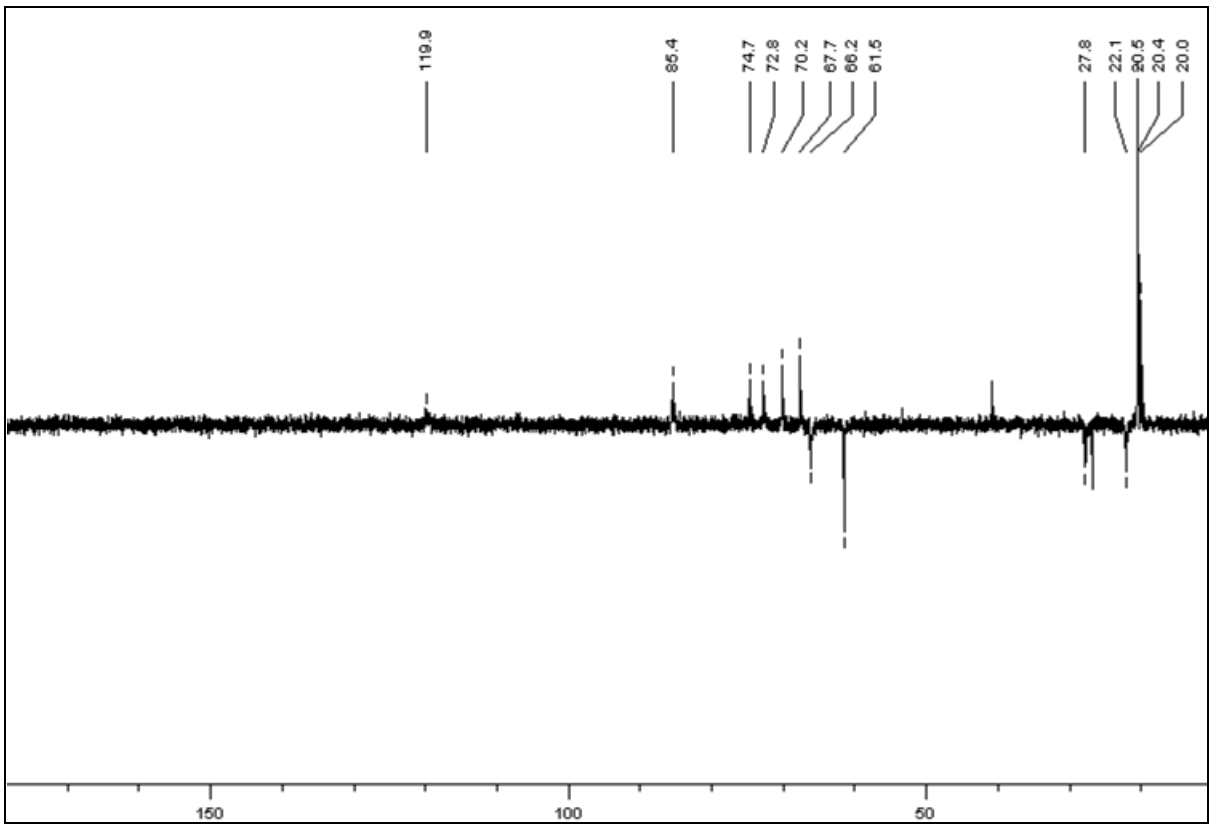
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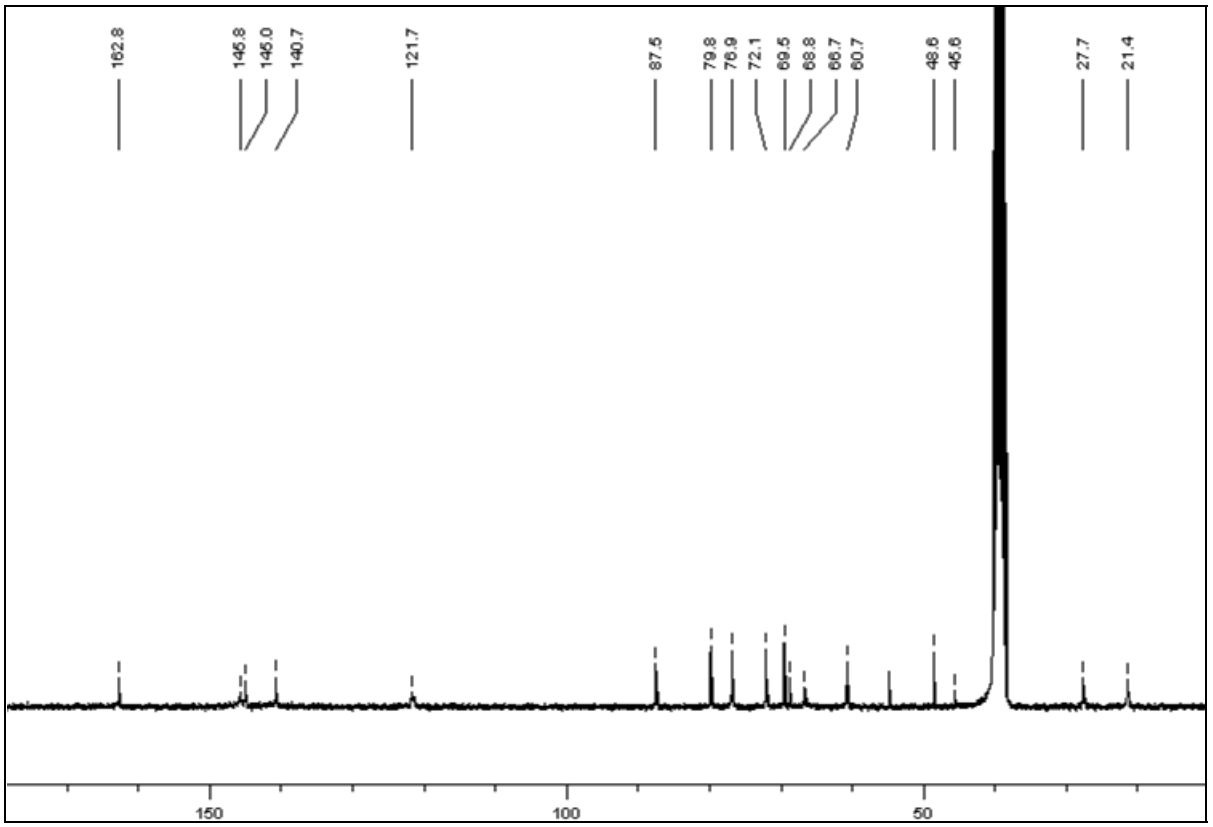
Fig. S2.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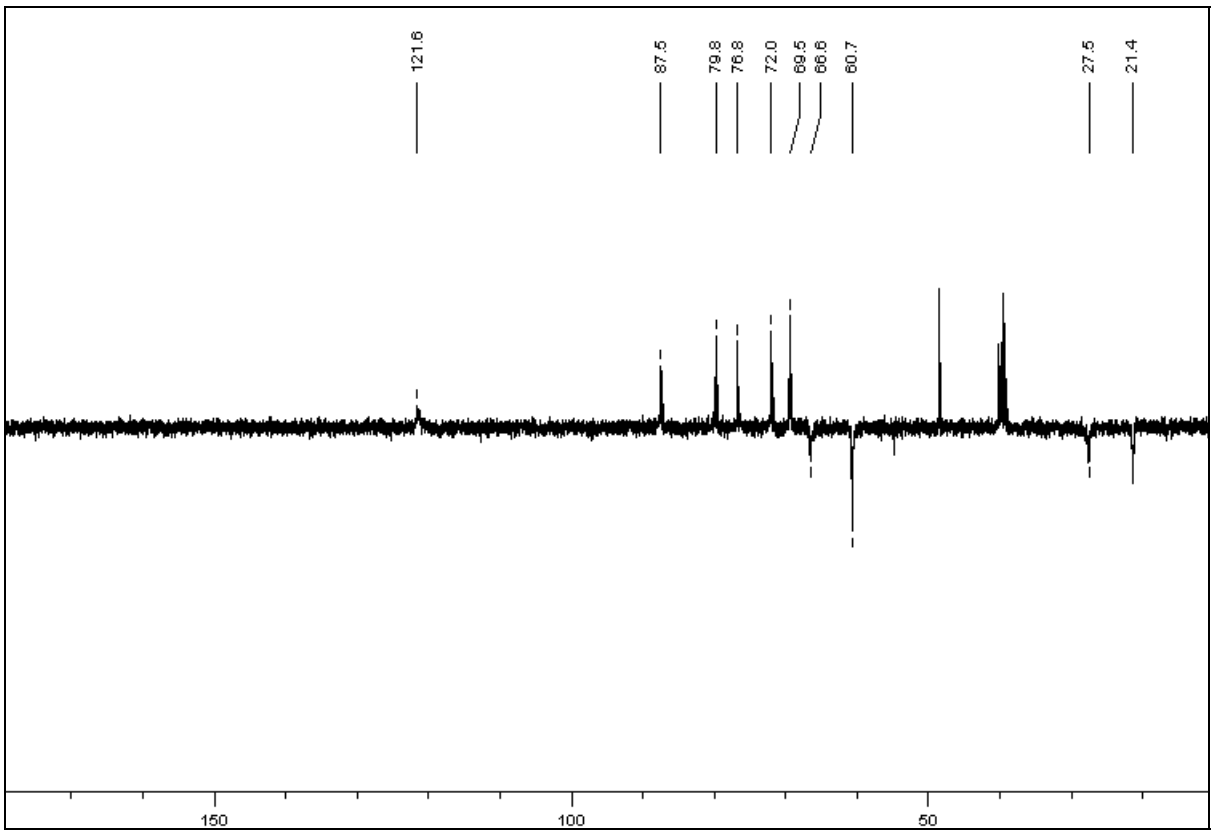
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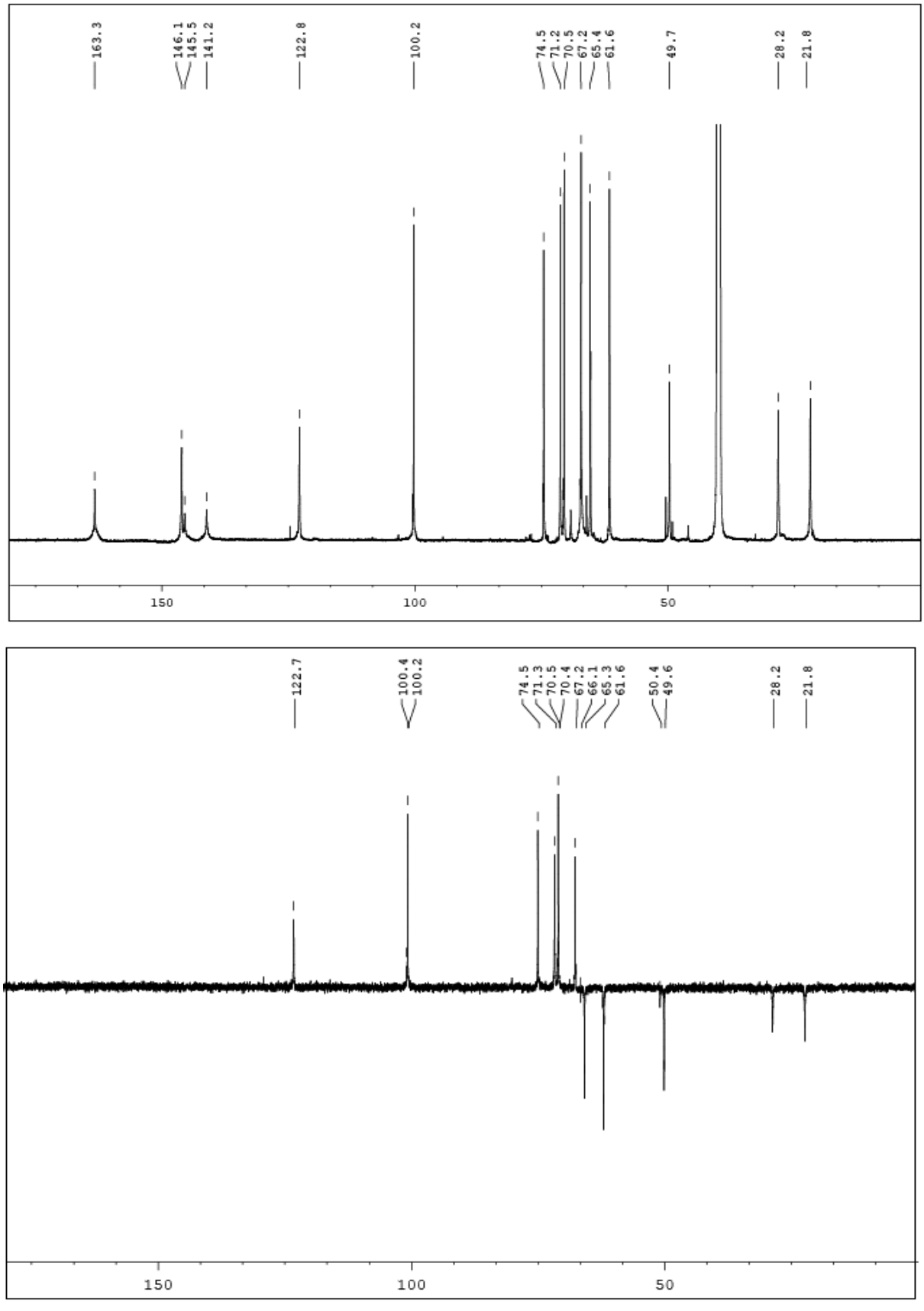
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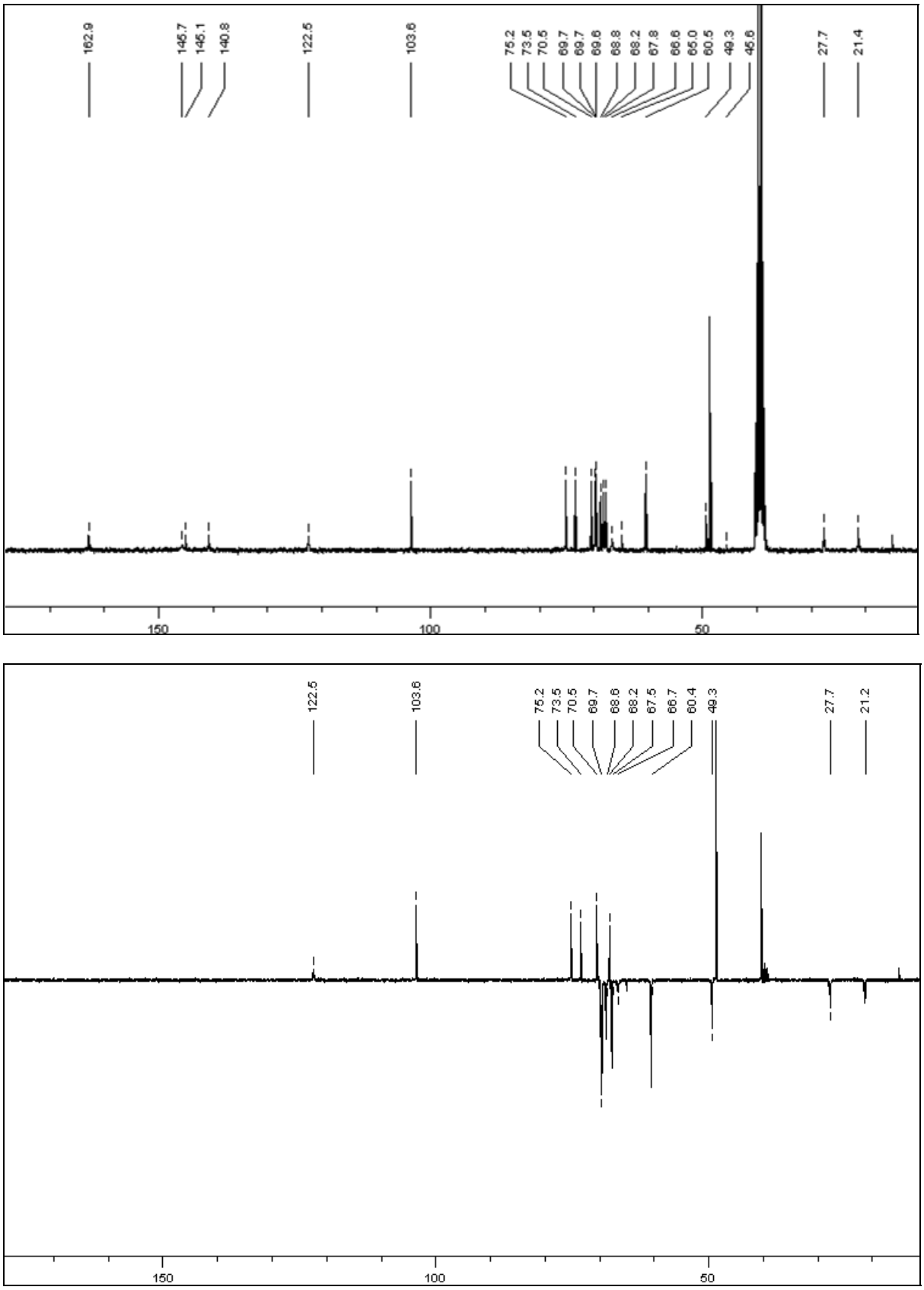
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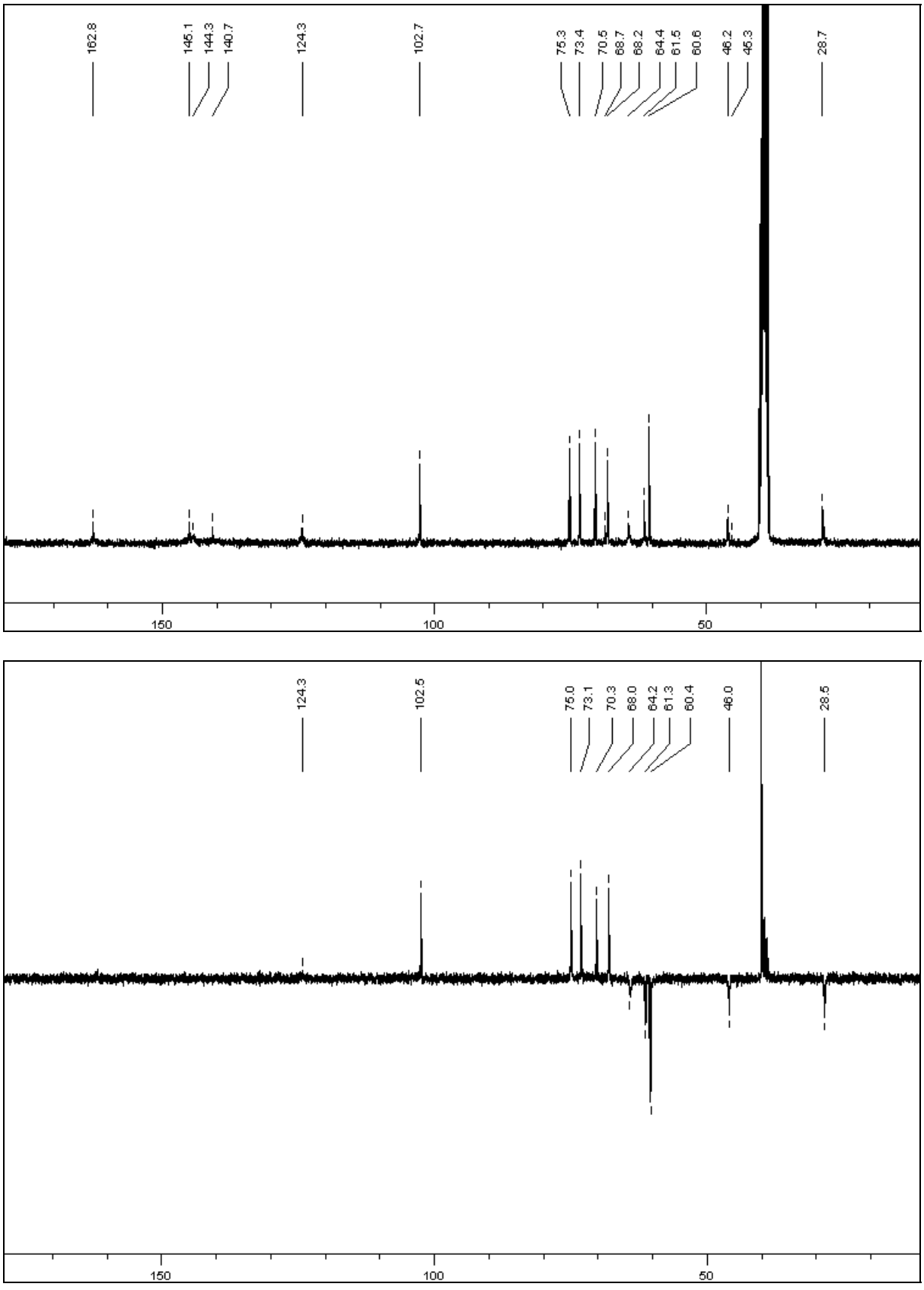
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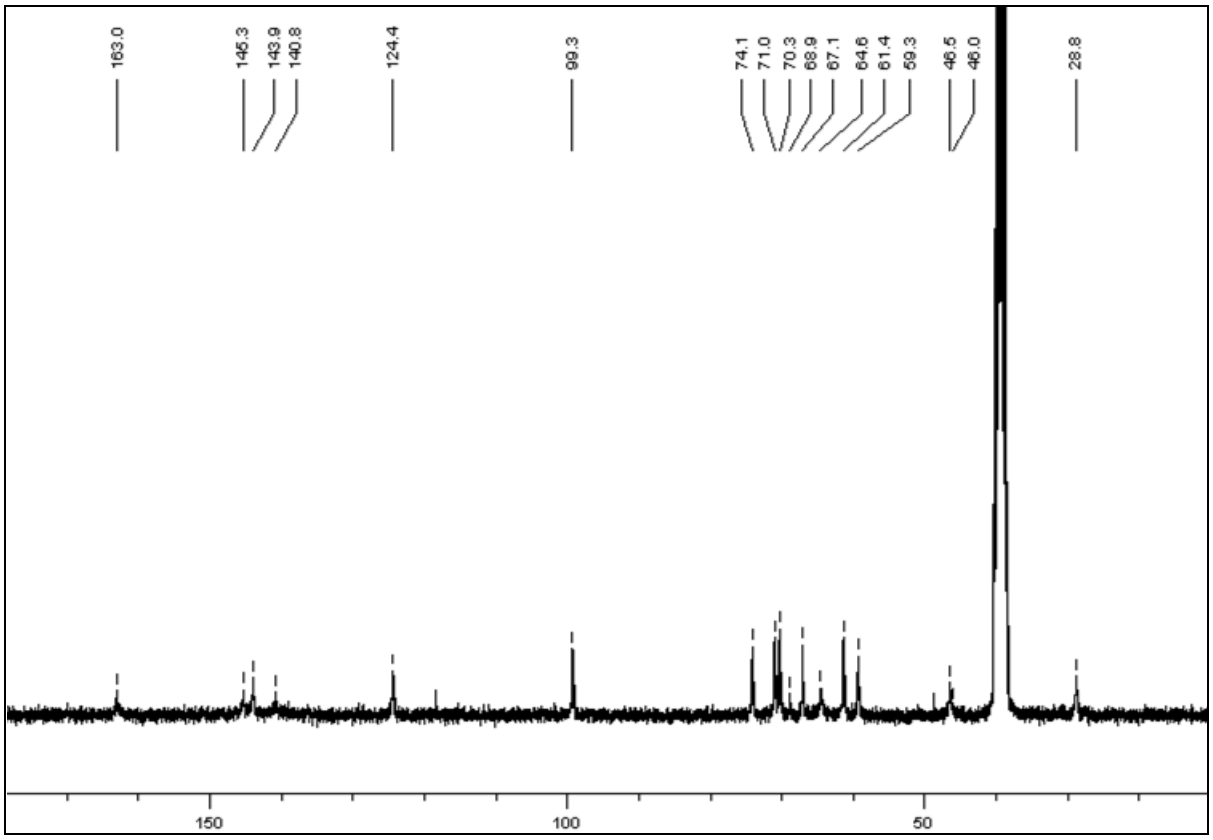
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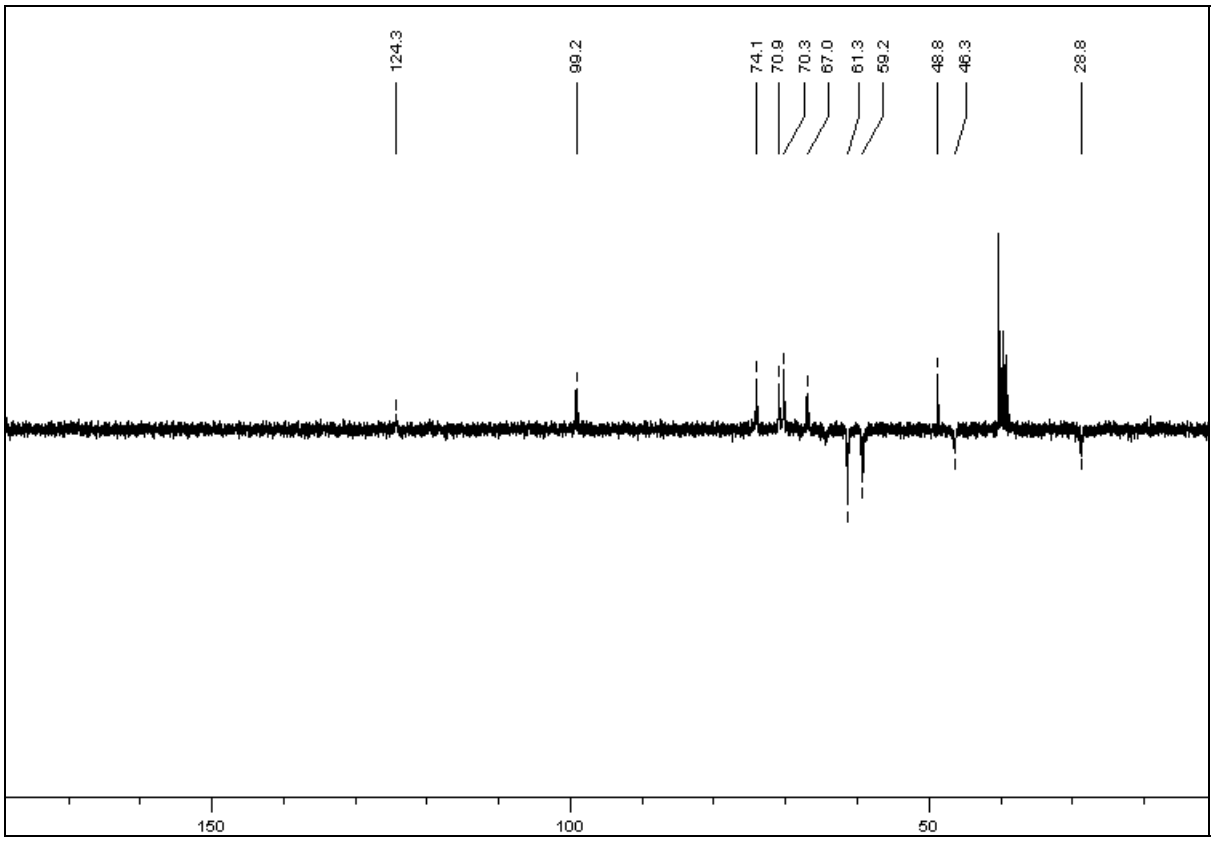
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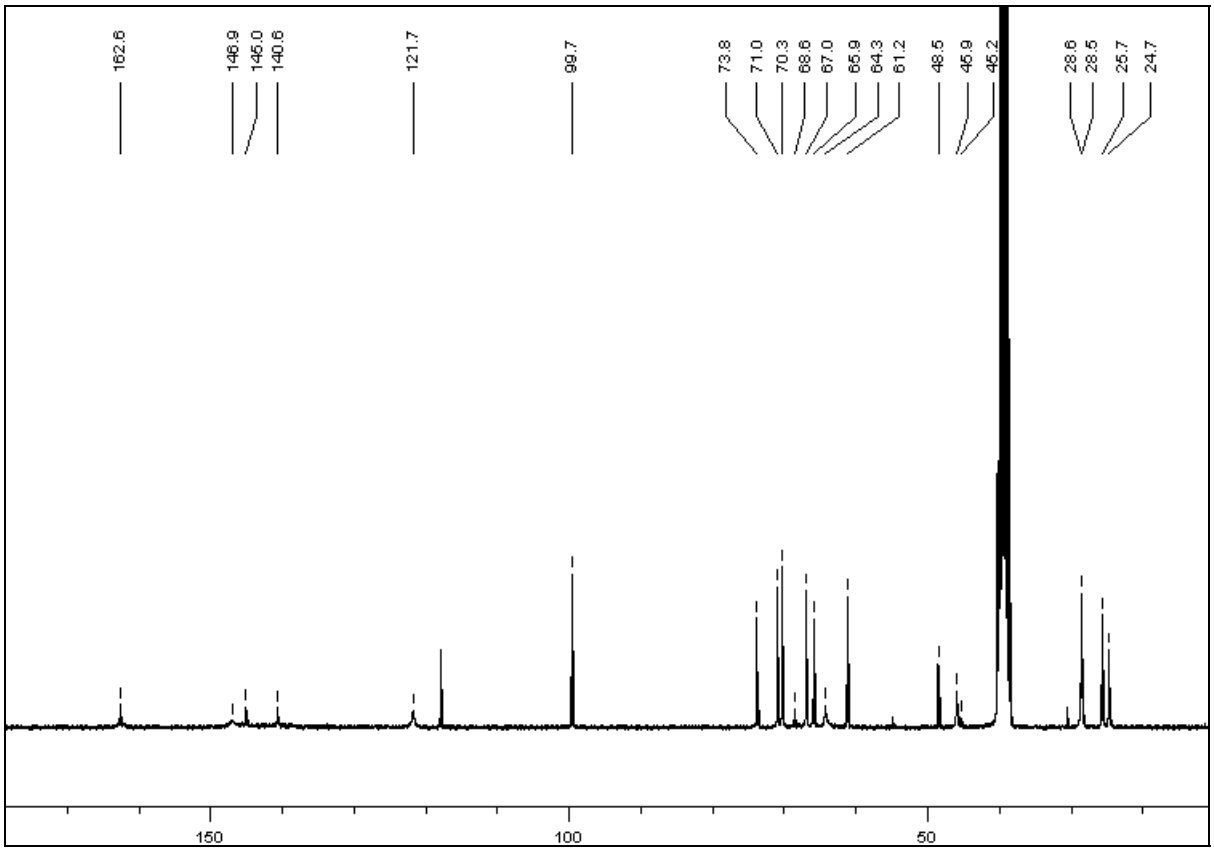
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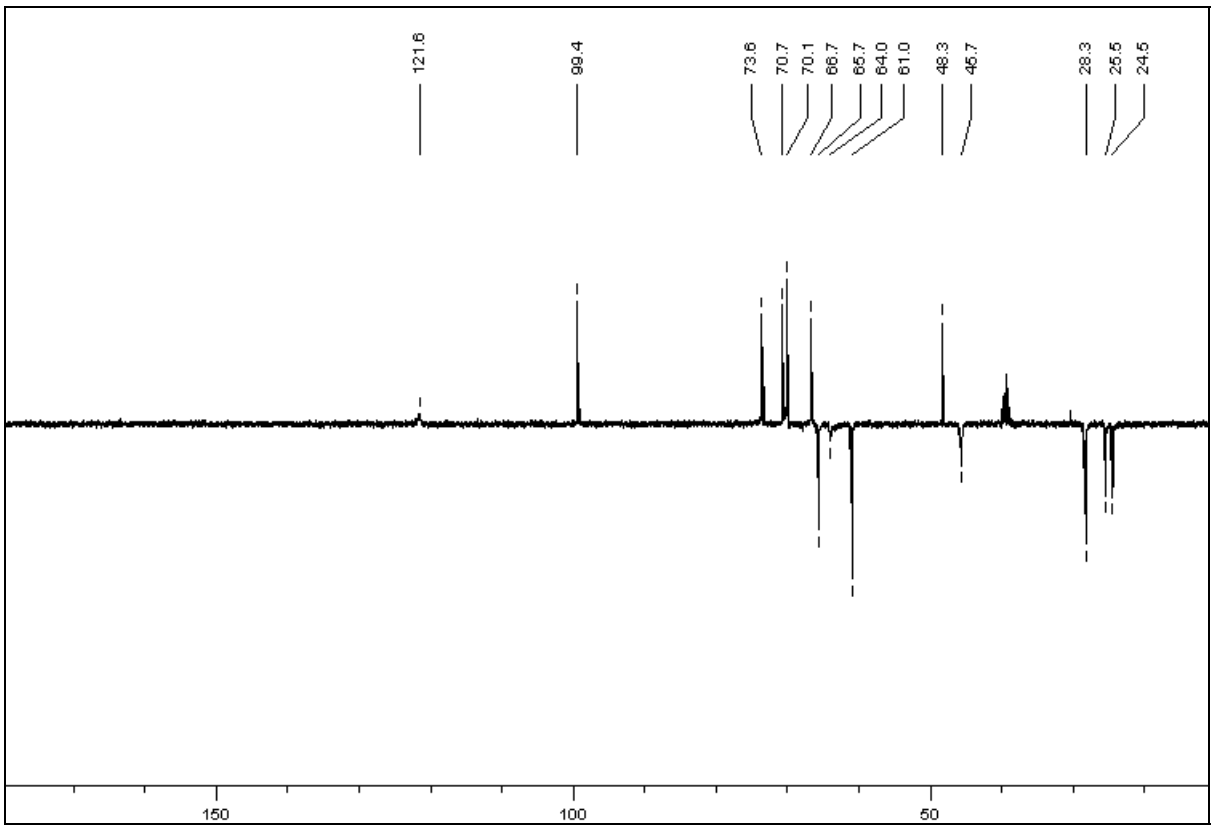
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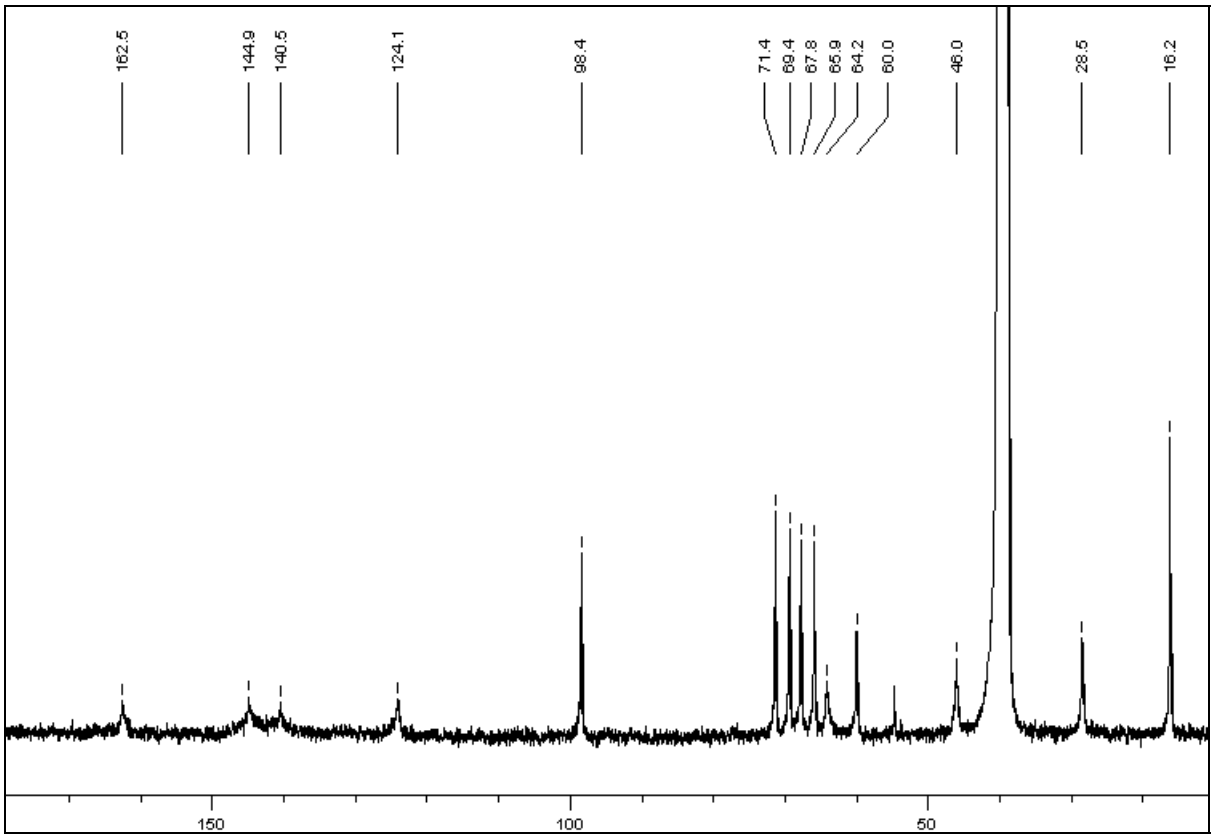
Fig. S8.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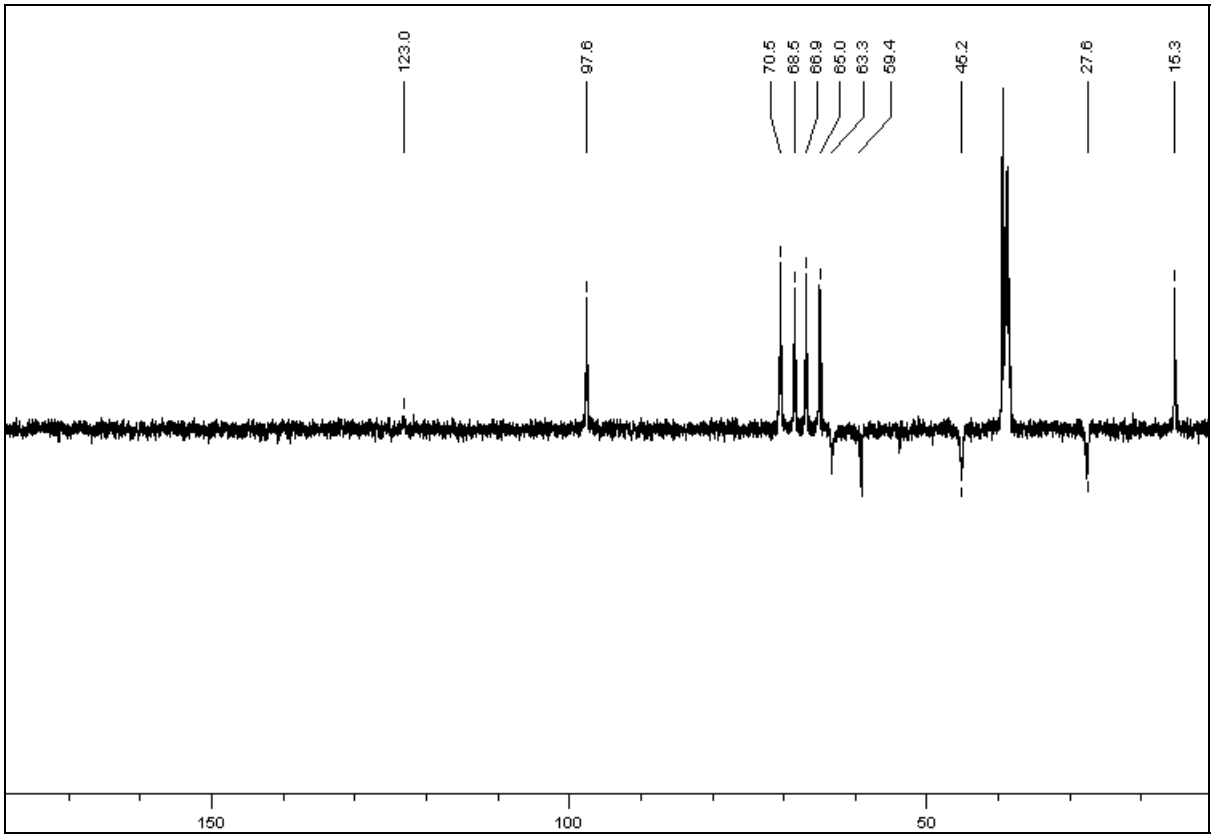
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