

Supporting Information

Bent-core compounds with two branched chains: Evidence of a new dark conglomerate mesophase

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Synthesis and analytical data

Materials: (S)-(-)-2-Methyl-1-butanol (Fluka, 95.0%, $[\alpha]_D^{20} -6.3 \pm 0.5^\circ$, $c = 10$ in EtOH), 3,7-Dimethyl-1-octanol (Aldrich, 99.0%) and 2-Ethyl-1-hexanol (Fluka, $\geq 99.0\%$) were purchased commercially.

3'-{4-[4-((S)-2-Methylbutoxy)benzoyloxy]benzoyloxy}-4-{4-[4-(2-ethylhexyloxy)benzoyloxy]benzoyloxy}biphenyl (1) ($C_{53}H_{52}O_{10}$; 848.99 g/mol):

1: Yield: 0.56 g (33%) of white crystals. ¹H-NMR (400 MHz, CDCl₃) δ (ppm) = 8.29 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.28 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.7$ Hz; 4 Ar-H), 7.66 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.36 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.30 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.22-7.19 (m, 1 Ar-H), 6.98 (d; $J \approx 8.7$ Hz; 4 Ar-H), 3.93 (d; $J \approx 5.4$ Hz; 2H, OCH₂), 3.90, 3.82 (2dd, $J \approx 9.3$ Hz ve $J \approx 6.2$ Hz each; 2H, OCH₂, (chiral alkyl chain)), 1.91-1.88 (m; 1H, CH), 1.77-1.74 (m, 1H, CH), 1.62-1.24 (m; 10H, 5 CH₂), 1.04 (d; $J \approx 6.6$ Hz; 3H, CH₃), 0.98-0.89 (m; 9H, 3 CH₃). ¹³C-NMR (100 MHz, CDCl₃) δ (ppm) = 164.38, 164.35, 164.23 (CO), 164.00, 163.92, 155.40, 151.31, 150.62, 142.04, 138.00, 126.86, 126.82, 120.97, 120.94 (Ar-C), 132.37, 131.87, 131.79, 129.82, 128.29, 124.67, 122.10, 122.06, 120.60, 120.44, 114.47 (Ar-CH), 73.27, 71.00 (OCH₂), 39.45, 34.80 (CH), 30.65, 29.23, 26.26, 24.02, 23.17 (CH₂), 16.65, 14.22, 11.46, 11.28 (CH₃). **MS (EI)** : m/z (%) = 848 (6) [M⁺], 353 (8) [M⁺-C₃₁H₂₇O₆], 311 (4) [M⁺-C₃₄H₃₃O₆], 233 (91) [M⁺-C₃₈H₃₁O₈], 191 (73) [M⁺-C₄₁H₃₇O₈], 121 (100) [C₇H₅O₂].

3'-{4-[4-((S)-2-Methylbutoxy)benzoyloxy]benzoyloxy}-4-{4-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy}biphenyl (2) ($C_{55}H_{56}O_{10}$; 877.04 g/mol):

2: Yield: 1.15 g (66%) of white crystals. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ (ppm) = 8.29 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.28 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d; $J \approx 9.0$ Hz; 4 Ar-H), 7.66 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.36 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.30 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.23-7.20 (m, 1 Ar-H), 6.98 (d; $J \approx 9.0$ Hz; 4 Ar-H), 4.10-4.06 (m; 2H, OCH_2), 3.91, 3.82 (2dd, $J \approx 9.1$ Hz and $J \approx 6.0$ Hz each; 2H, OCH_2 , (chiral alkyl chain)), 1.91-1.84 (m; 2H, 2 CH), 1.64-1.51, 1.34-1.15 (2m; 11H, CH, 5 CH_2), 1.03 (d; $J \approx 6.7$ Hz; 3H, CH_3), 0.97-0.94 (m, 6H, 2 CH_3), 0.86 (d, $J \approx 6.6$ Hz; 6H, 2 CH_3). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) = 164.38, 164.23 (CO), 163.92, 163.74, 155.39, 151.31, 150.62, 142.04, 138.00, 126.86, 126.83, 121.00, 120.97 (Ar-C), 132.38, 131.80, 129.83, 128.29, 124.67, 122.10, 122.06, 120.61, 120.43, 114.46 (Ar-CH), 73.26, 66.86 (OCH_2), 39.37, 37.40, 36.15, 26.26, 24.81 (CH_2), 34.80, 30.01, 28.13 (CH), 22.85, 22.75, 19.82, 16.65, 11.46 (CH_3). **MS (EI)** : m/z (%) = 381 (6) [$\text{M}^+ - \text{C}_{31}\text{H}_{27}\text{O}_6$], 311 (4) [$\text{M}^+ - \text{C}_{36}\text{H}_{37}\text{O}_6$], 261 (100) [$\text{M}^+ - \text{C}_{38}\text{H}_{31}\text{O}_8$], 191 (71) [$\text{M}^+ - \text{C}_{43}\text{H}_{41}\text{O}_8$], 121 (92) [$\text{C}_7\text{H}_5\text{O}_2$].

3'-{4-[4-(2-Ethylhexyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-((S)-2-Methylbutoxy)benzoyloxy]benzoyloxy}biphenyl (3) ($C_{53}\text{H}_{52}\text{O}_{10}$; 848.99 g/mol):

3: Yield: 0.59 g (35%) of white crystals. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ (ppm) = 8.29 (d; $J \approx 8.9$ Hz; 2 Ar-H), 8.28 (d; $J \approx 8.9$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.9$ Hz; 4 Ar-H), 7.66 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.45 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.9$ Hz; 2 Ar-H), 7.36 (d; $J \approx 8.9$ Hz; 2 Ar-H), 7.30 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.22-7.20 (m, 1 Ar-H), 6.98 (d; $J \approx 8.9$ Hz; 2 Ar-H), 6.97 (d; $J \approx 8.9$ Hz; 2 Ar-H), 3.93 (d; $J \approx 5.5$ Hz; 2H, OCH_2), 3.90, 3.82 (2dd, $J \approx 9.1$ Hz and $J \approx 6.5$ Hz each; 2H, OCH_2 , (chiral alkyl chain)), 1.91-1.89 (m; 1H, CH), 1.77-1.74 (m, 1H, CH), 1.61-1.24 (m; 5 CH_2), 1.03 (d; $J \approx 6.7$ Hz; 3H, CH_3), 0.96 (t; $J \approx 7.4$ Hz, 3H, CH_3), 0.94-0.89 (m; 6H, 2 CH_3). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) = 164.38, 164.24 (CO), 164.02, 163.92, 155.39, 151.31, 150.62, 142.05, 138.00, 126.86, 126.82, 120.94 (Ar-C), 132.37, 131.79, 129.83, 128.29, 124.66, 122.10, 122.06, 120.62, 120.44, 114.47 (Ar-CH), 73.27, 71.00 (OCH_2), 39.45, 34.80 (CH), 30.65, 29.23, 26.26, 24.02, 23.17 (CH_2), 16.65, 14.22, 11.46, 11.28 (CH_3). **MS (EI)** : m/z (%) = 353 (3) [$\text{M}^+ - \text{C}_{31}\text{H}_{27}\text{O}_6$], 311 (2) [$\text{M}^+ - \text{C}_{34}\text{H}_{33}\text{O}_6$], 233 (100) [$\text{M}^+ - \text{C}_{38}\text{H}_{31}\text{O}_8$], 191 (100) [$\text{M}^+ - \text{C}_{41}\text{H}_{37}\text{O}_8$], 121 (100) [$\text{C}_7\text{H}_5\text{O}_2$].

3'-{4-[4-(2-Ethylhexyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy}biphenyl (4) ($C_{58}H_{62}O_{10}$; 919.12 g/mol):

4: Yield: 0.48 g (26%) of white crystals. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ (ppm) = 8.29 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.28 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.9$ Hz; 4 Ar-H), 7.66 (d; $J \approx 8.5$ Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.36 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.30 (d; $J \approx 8.5$ Hz; 2 Ar-H), 7.22-7.21 (m, 1 Ar-H), 6.98 (d; $J \approx 8.9$ Hz; 2 Ar-H), 6.97 (d; $J \approx 8.9$ Hz; 2 Ar-H), 4.10-4.06 (m; 2H OCH_2), 3.93 (d; $J \approx 5.9$ Hz; 2H, OCH_2), 1.88-1.84 (m, 1H, CH), 1.77-1.73 (m, 1H, CH), 1.68-1.41, 1.33-1.15 (2m; 17H, CH, 8 CH_2), 0.96-0.90 (m; 9H, 3 CH_3), 0.86 (d; $J \approx 6.6$ Hz; 6H, 2 CH_3). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) = 164.35, 164.22 (CO), 164.00, 163.74, 155.39, 151.31, 150.62, 142.04, 138.00, 126.86, 126.83, 121.00, 120.94 (Ar-C), 132.37, 131.79, 129.83, 128.29, 124.67, 122.09, 122.06, 120.60, 120.44, 114.46 (Ar-CH), 71.00, 66.86 (OCH_2), 39.45, 30.01, 28.13 (CH), 39.37, 37.40, 36.15, 30.65, 29.23, 24.81, 24.02, 23.17 (CH_2), 22.85, 22.75, 19.82, 14.22, 11.28 (CH_3). **MS (EI)** : m/z (%) = 918 (4) [M^+], 381 (6) [$\text{M}^+ - \text{C}_{34}\text{H}_{33}\text{O}_6$], 353 (3) [$\text{M}^+ - \text{C}_{36}\text{H}_{37}\text{O}_6$], 261 (82) [$\text{M}^+ - \text{C}_{41}\text{H}_{37}\text{O}_8$], 233 (66) [$\text{M}^+ - \text{C}_{43}\text{H}_{41}\text{O}_8$], 121 (100) [$\text{C}_7\text{H}_5\text{O}_2$].

3'-{4-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy}-4-{4-[4-((S)-2-Methylbutoxy)benzoyloxy]benzoyloxy}biphenyl (5) ($C_{55}\text{H}_{56}\text{O}_{10}$; 877.04 g/mol):

5: Yield: 0.52 g (30%) of white crystals. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ (ppm) = 8.29 (d; $J \approx 8.5$ Hz; 2 Ar-H), 8.28 (d; $J \approx 8.5$ Hz; 2 Ar-H), 8.15 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.66 (d; $J \approx 8.6$ Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.45 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.5$ Hz; 4 Ar-H), 7.30 (d; $J \approx 8.6$ Hz; 2 Ar-H), 7.22-7.19 (m, 1 Ar-H), 6.98 (d; $J \approx 8.7$ Hz; 4 Ar-H), 4.10-4.06 (m, 2H, OCH_2), 3.91, 3.82 (2dd, $J \approx 9.1$ Hz and $J \approx 6.0$ Hz each; 2H, OCH_2 , (chiral alkyl chain)), 1.91-1.84 (m; 2H, 2 CH), 1.69-1.51, 1.33-1.15 (2m; 11H, CH, 5 CH_2), 1.04 (d; $J \approx 6.7$ Hz; 3H, CH_3), 0.97-0.94 (m; 6H, 2 CH_3), 0.86 (d; $J \approx 6.6$ Hz; 6H, 2 CH_3). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ (ppm) = 164.34, 164.22 (CO), 164.00, 163.84, 155.44, 151.37, 150.66, 142.09, 138.04, 126.86, 126.82, 120.94 (Ar-C), 132.42, 131.84, 129.86, 128.33, 124.70, 122.13, 122.08, 120.62, 120.45, 114.45 (Ar-CH), 73.17, 66.75 (OCH_2), 39.22, 37.25, 35.99, 26.08, 24.64 (CH_2), 34.64, 29.83, 27.97 (CH), 22.69, 22.59, 19.64, 16.48, 11.29 (CH_3). **MS (EI)** : m/z (%) = 876 (5) [M^+], 381 (2) [$\text{M}^+ - \text{C}_{31}\text{H}_{27}\text{O}_6$], 311 (11) [$\text{M}^+ - \text{C}_{36}\text{H}_{37}\text{O}_6$], 261 (76) [$\text{M}^+ - \text{C}_{38}\text{H}_{31}\text{O}_8$], 191 (100) [$\text{M}^+ - \text{C}_{43}\text{H}_{41}\text{O}_8$], 121 (87) [$\text{C}_7\text{H}_5\text{O}_2$].

3,4'-Bis{4-[4-((S)-2-Methylbutoxy)benzoyloxy]benzoyloxy}biphenyl (7) ($C_{50}H_{46}O_{10}$; 806.90 g/mol):

7: Yield: 0.59 g (37%) of white crystals. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) = 8.29 (d; $J \approx 8.5$ Hz; 2 Ar-H), 8.28 (d; $J \approx 8.5$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.9$ Hz; 4 Ar-H), 7.65 (d; $J \approx 8.5$ Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.5$ Hz; 2 Ar-H), 7.36 (d; $J \approx 8.5$ Hz; 2 Ar-H), 7.29 (d; $J \approx 8.5$ Hz; 2 Ar-H), 7.23-7.19 (m, 1 Ar-H), 6.98 (d; $J \approx 8.9$ Hz; 4 Ar-H), 3.91, 3.82 (2dd, $J \approx 9.1$ Hz and $J \approx 6.0$ Hz each; 4H, 2 OCH_2 , (chiral alkyl chain)), 1.93-1.88 (m; 2H, 2 CH), 1.61-1.24 (m; 2 CH_2), 1.04 (d; $J \approx 6.9$ Hz; 6H, 2 CH_3), 0.96 (t; $J \approx 7.4$ Hz; 6H, 2 CH_3). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) = 164.35, 164.22 (CO), 163.92, 155.39, 151.31, 150.62, 142.06, 138.00, 126.86, 126.82, 120.96 (Ar-C), 132.37, 131.79, 129.83, 128.29, 124.67, 122.10, 122.06, 120.60, 120.43, 114.46 (Ar-CH), 73.26 (OCH_2), 34.79 (CH), 26.25 (CH_2), 16.65, 11.46 (CH_3). **MS (EI)** : m/z (%) = 806 (1) [M^+], 311 (7) [$\text{M}^+ - \text{C}_{31}\text{H}_{27}\text{O}_6$], 191 (100) [$\text{M}^+ - \text{C}_{38}\text{H}_{31}\text{O}_8$], 121 (89) [$\text{C}_7\text{H}_5\text{O}_2$].

3,4'-Bis{4-[4-(2-Ethylhexyloxy)benzoyloxy]benzoyloxy}biphenyl (8) ($C_{56}H_{58}O_{10}$; 891.07 g/mol):

8: Yield: 0.64 g (36%) of white crystals. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) = 8.29 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.28 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.9$ Hz; 4 Ar-H), 7.65 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.36 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.30 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.23-7.20 (m, 1 Ar-H), 6.98 (d; $J \approx 8.9$ Hz; 4 Ar-H), 3.93 (d; $J \approx 5.6$ Hz; 4H, 2 OCH_2), 1.79-1.73 (m; 2H, 2 CH), 1.55-1.24 (m; 8 CH_2), 0.97-0.89 (m; 12H, 4 CH_3). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ (ppm) = 164.37, 164.35, 164.23 (CO), 164.00, 155.40, 151.32, 150.63, 142.04, 138.00, 126.86, 126.83, 120.94 (Ar-C), 132.37, 131.80, 129.82, 128.29, 124.66, 122.10, 122.06, 120.60 120.44, 114.48 (Ar-CH), 71.00 (OCH_2), 39.46 (CH), 30.65, 29.23, 24.02, 23.17 (CH_2), 14.22, 11.28 (CH_3). **MS (EI)** : m/z (%) = 891 (1) [M^+], 353 (22) [$\text{M}^+ - \text{C}_{34}\text{H}_{33}\text{O}_6$], 233 (100) [$\text{M}^+ - \text{C}_{41}\text{H}_{37}\text{O}_8$], 121 (100) [$\text{C}_7\text{H}_5\text{O}_2$].

3,4'-Bis{4-[4-(3,7-Dimethyloctyloxy)benzoyloxy]benzoyloxy}biphenyl (9) ($C_{60}H_{66}O_{10}$; 947.18 g/mol):

9: Yield: 0.66 g (35%) of white crystals. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ (ppm) = 8.29 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.28 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.9$ Hz; 4 Ar-H), 7.65 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.36 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.30 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.22-7.19 (m; 1 Ar-H), 6.98 (d; $J \approx 8.9$

Hz; 4 Ar-H), 4.10-4.06 (m; 4H, 2 OCH₂), 1.88-1.82 (m; 2H, 2 CH), 1.68-1.46, 1.35-1.15 (2m; 18H, 2 CH, 8CH₂), 0.95 (d; $J \approx 6.4$ Hz; 6H, 2 CH₃), 0.87 (d; $J \approx 6.6$ Hz; 12H, 4 CH₃). **¹³C-NMR** (100 MHz, CDCl₃) δ (ppm) = 164.35, 164.21 (CO), 163.74, 155.39, 151.31, 150.62, 142.04, 138.00, 126.87, 126.83, 121.01 (Ar-C), 132.39, 131.80, 129.83, 128.29, 124.67, 122.09, 122.06, 120.60, 120.43, 114.46 (Ar-CH), 66.86 (OCH₂), 39.37, 37.40, 36.15, 24.81 (CH₂), 30.01, 28.13 (CH), 22.85, 22.75, 19.82 (CH₃). **MS (EI)** : m/z (%) = 947 (1) [M⁺], 381 (6) [M⁺-C₃₆H₃₇O₆], 261 (97) [M⁺-C₄₃H₄₁O₈], 121 (100) [C₇H₅O₂].

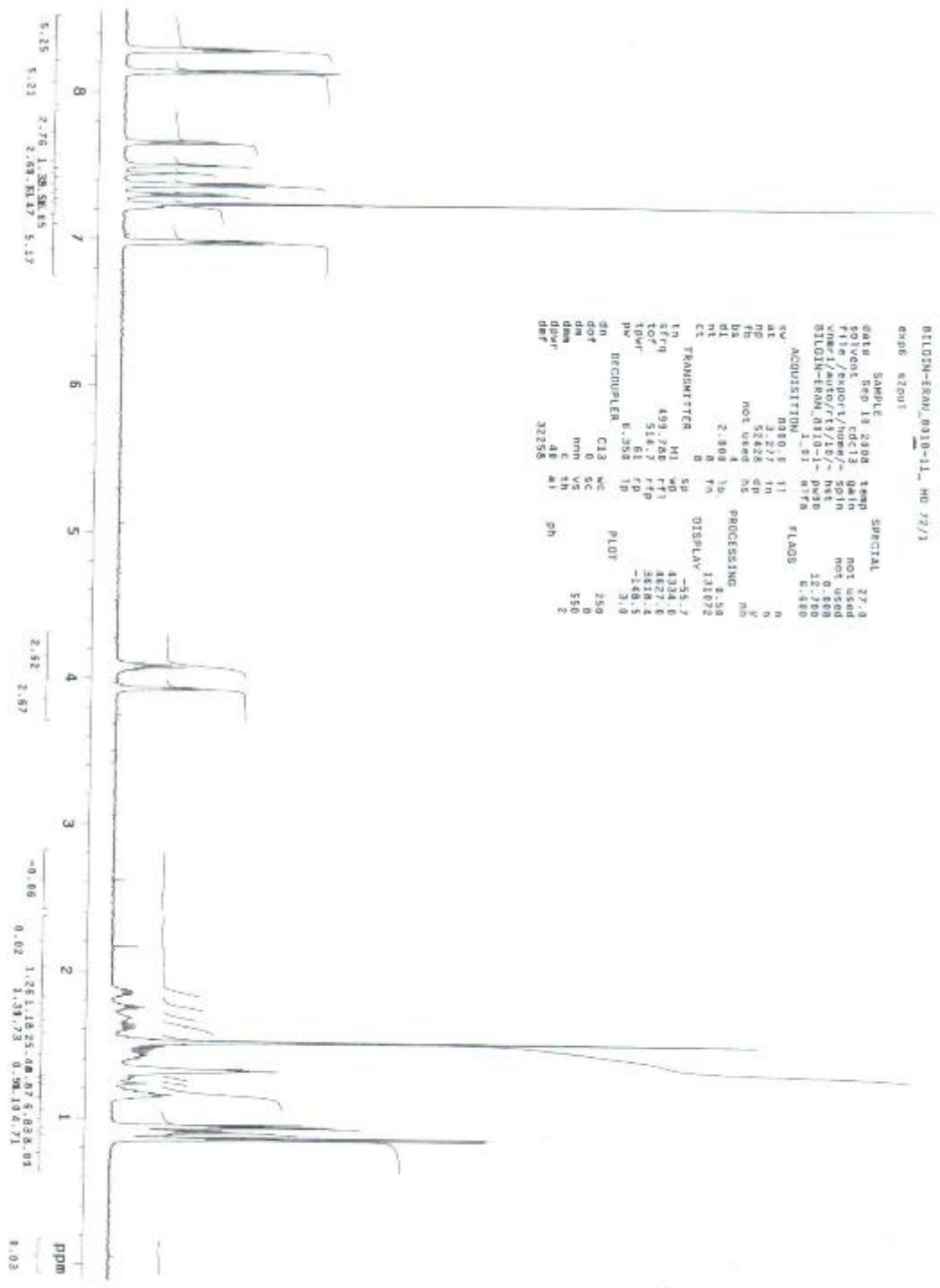


Figure S1. ¹H-NMR spectrum of compound 4.

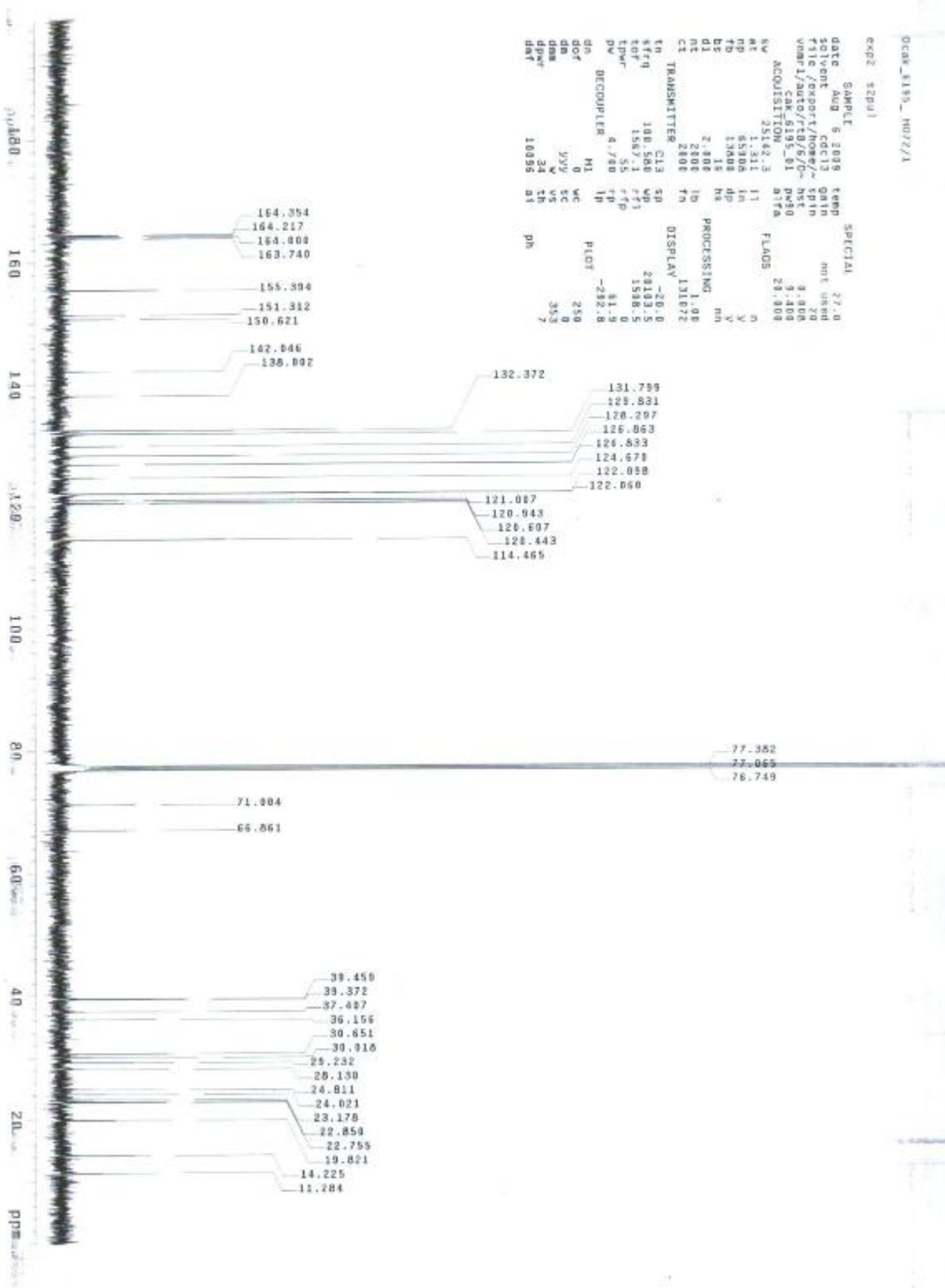


Figure S2. ^{13}C -NMR spectrum of compound **4**.

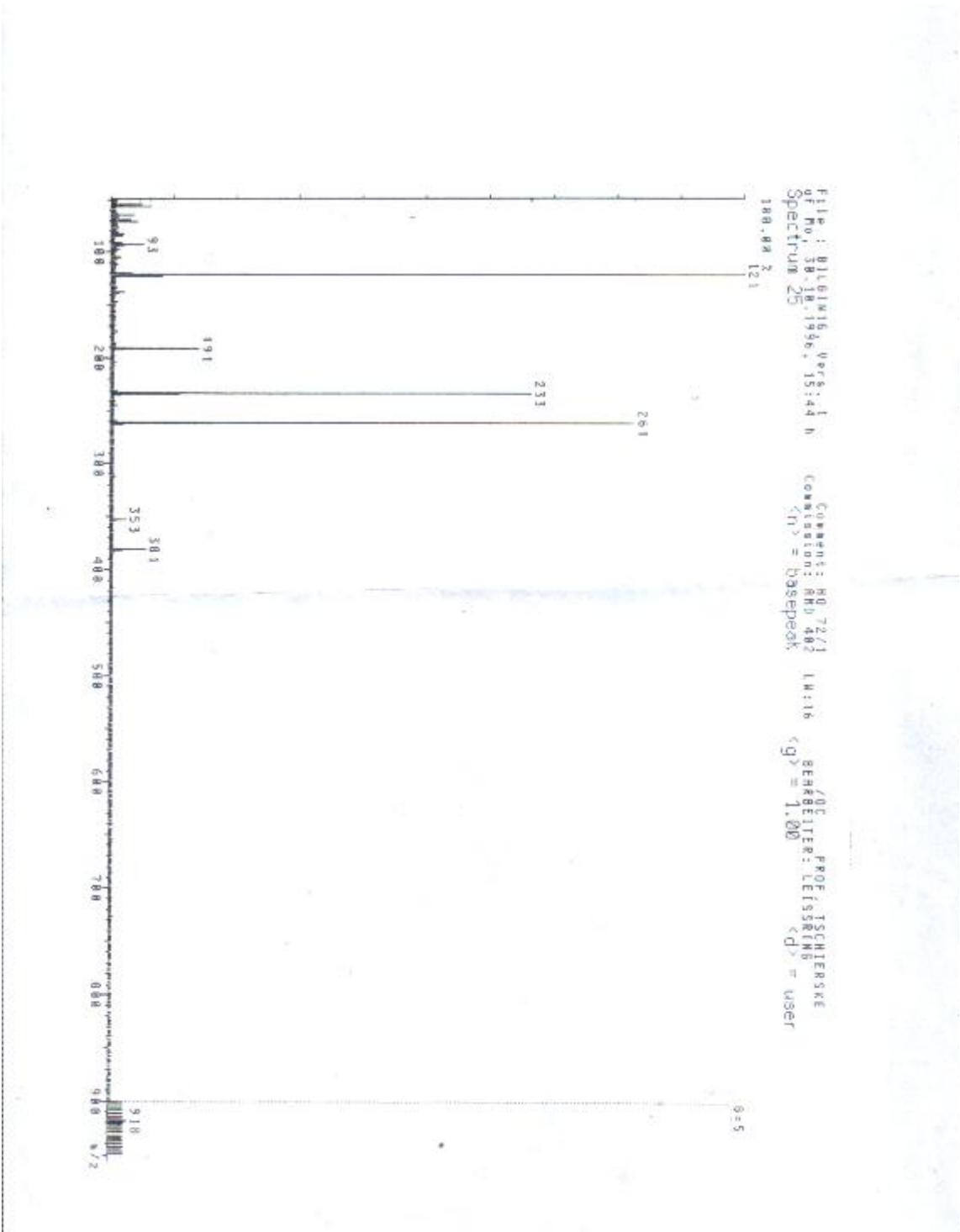


Figure S3. MS spectrum of compound 4.

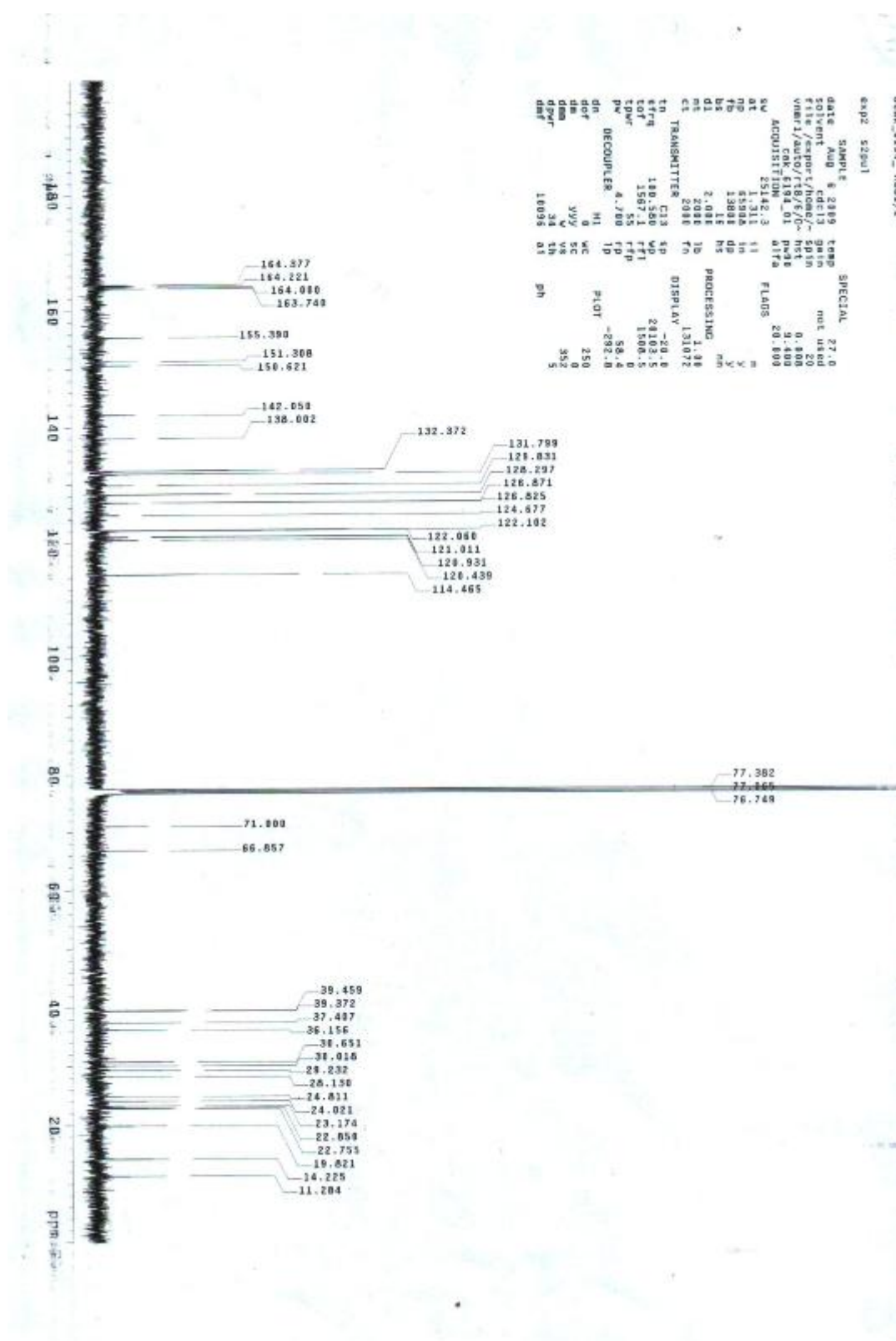


Figure S5. ^{13}C -NMR spectrum of compound 6.

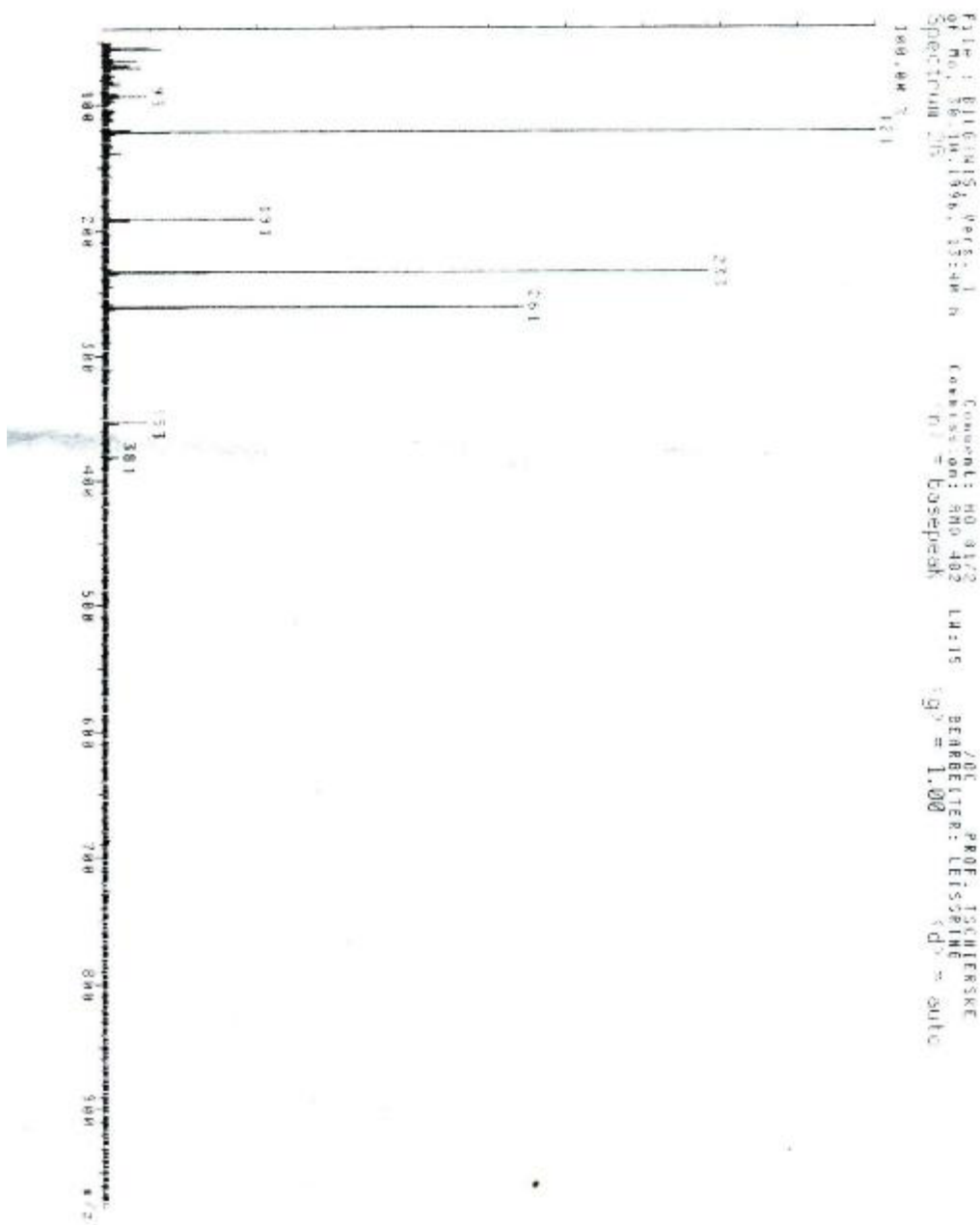


Figure S6. MS spectrum of compound 6.