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β-Peptide Coatings by Surface-Initiated Polymerization

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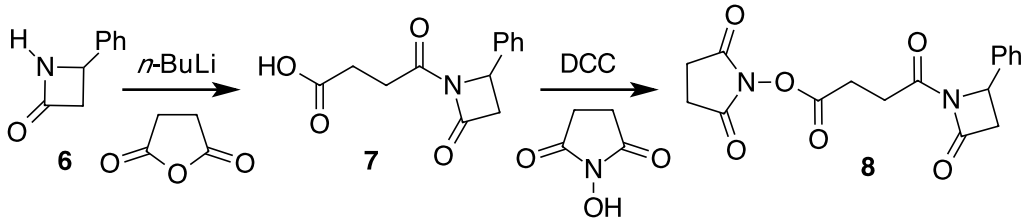
Supporting Information



Initiator reagent 8. To a -78 °C solution of **6**[1] (2.0 g, 13.6 mmol) in ether (360 mL) was added *n*-butyllithium (12 mL of a 1.28 M solution in hexanes, 16.3 mmol) and the resulting mixture was stirred for 30 min. A solution of succinic anhydride (1.50 g, 14.9 mmol) in THF (28 ml) was added dropwise over 10 min. After stirring for an additional 2 h at -78 °C, the mixture was diluted with 0.1 M HCl. The aqueous phase was extracted with dichloromethane (2 x 50 mL), the combined organics were washed with brine and dried over sodium sulfate. Concentration gave crude acid **7** as a thick slightly yellow solid which was used in next step without purification.

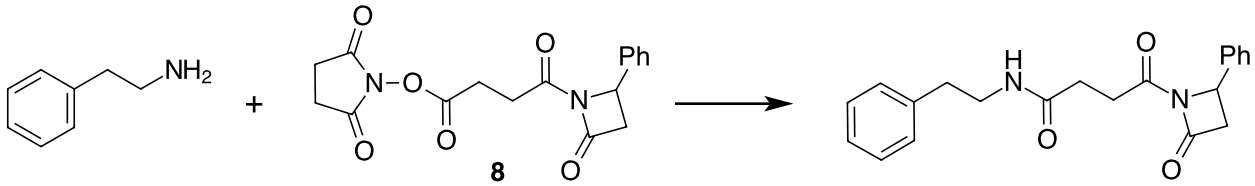
To a 0 °C solution of crude **7** (ca. 13.6 mmol) in dichloromethane (680 mL) was added DCC (3.34 g, 16.3 mmol). After 30 min at 0 °C, *N*-hydroxysuccinimide (1.87 g, 16.2 mmol) was added and the resulting mixture was allowed to warm to rt and then stirred overnight. The mixture was filtered, concentrated and purified by column chromatography (3:2 ethyl acetate/hexanes) to give **8** as colorless powder (1.45 g, 31% for two steps)

mp 312-133 °C

^{1}H NMR ($CDCl_3$) δ 7.4-7.3 (m, 5H), 5.04 (dd, J = 6.4, 3.6 Hz, 1H), 3.50 (dd, J = 16, 6.4 Hz, 1H), 3.07-3.15 (m, 2H), 2.89-3.04 (m, 2H), 2.79 (bs, 4H).

^{13}C NMR ($CDCl_3$) δ 168.8, 167.8, 167.6, 165.2, 137.4, 128.9, 128.5, 125.9, 52.6, 45.7, 31.1, 25.5, 25.1.

Exact mass, Calc. for $C_{17}H_{17}N_2O_5$ (M+H) 345.1081, found 345.1086.



4-Oxo-4-(2-oxo-4-phenylazetidin-1-yl)-*N*-phenethylbutanamide. To a 0° C solution of **8** (51.6 mg, 0.15 mmol) in dichloromethane (1 mL) under argon was added dropwise phenethylamine (22.7 µL, 0.18 mmol) and triethylamine (63 mL, 0.45 mmol). The mixture was stirred for 1 h at ambient temperature, concentrated and purified by flash chromatography over silica (ethyl acetate/hexanes,1:2) to give the title product (32.1 mg, 61%).

^{1}H NMR ($CDCl_3$) δ 7.4-7.0 (m, 10H), 5.5 (bs, 1H), 4.94 (dd, J = 6.6, 3.8 Hz, 1H), 3.2-2.9 (m, 2H), 2.9 (dd, J = 16.4, 3.2 Hz 2H), 2.69 (t, J = 7.2 Hz, 2H), 2.38 (m, 2H).

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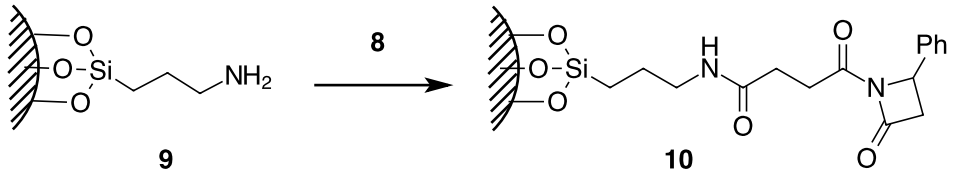
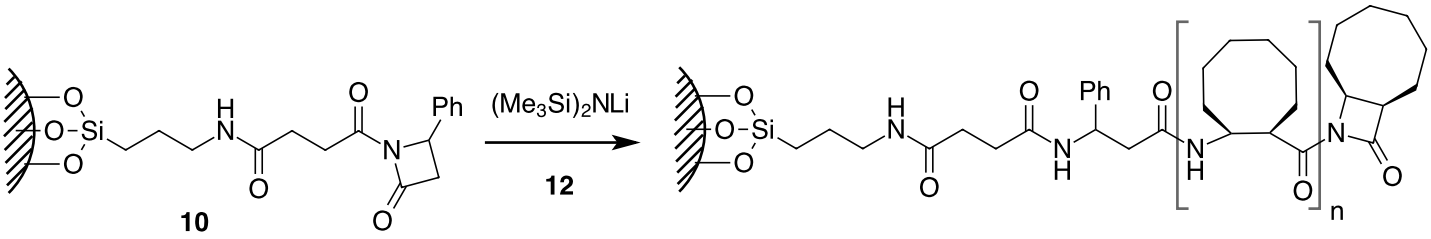


Attachment of polymerization initiator to glass particle surface. To a suspension of glass particles coated with aminopropylsilane (15 g, 7.8 μmol NH_2/g, 0.12 mmol amine[2]) in dichloromethane (30 mL) was added **8** (403 mg, 1.2 mmol) and the resulting mixture was stirred for 15 min at rt. After cooling the mixture to 0 °C, triethylamine (1.2 mL, 8.6 mmol) was added. After stirring for 20 min the mixture was allowed to warm to rt and stirred overnight. The mixture was filtered and the residue was washed three times each with chloroform, THF, methanol and acetone. The mixture was dried under vacuum to yield 13.4 g of **10**.



Surface Initiated Polymerization of β-Lactam 12. To a suspension of initiator-coated glass particles **10** (3.0 g, 7.8 μmol initiator/g, 23.4 μmol) in anhydrous DMF (15 mL) under argon was added *cis*-9-azabicyclo[6.2.0]decan-10-one **12**[3] (358 mg, 2.34 mmol) and the resulting mixture cooled to 0 °C. To this mixture was added dropwise a solution of lithium hexamethyldisilazide (0.36 mL of a 1.0 M soln in THF, 0.36 mmol). The mixture was allowed to warm to rt and stirred for 8 h. After dilution with sat. ammonium chloride the mixture was filtered and the residue was washed three times each with THF, water, acetone, chloroform, acetone and then dried under vacuum at rt overnight, yielding 2.5 g of the polymer-coated particles.

1. H. Huang, N. Iwasawa and T. Mukaiyama *Chem. Lett.* 1984, **13,** 1465.
2. R. K. Gaur and K. C. Gupta *Anal. Biochem.* 1989, **180,** 253.
3. H. Bestian, H. Biener, K. Clauss and H. Heyn *Liebigs Ann. Chem.* 1968, **718,** 94.

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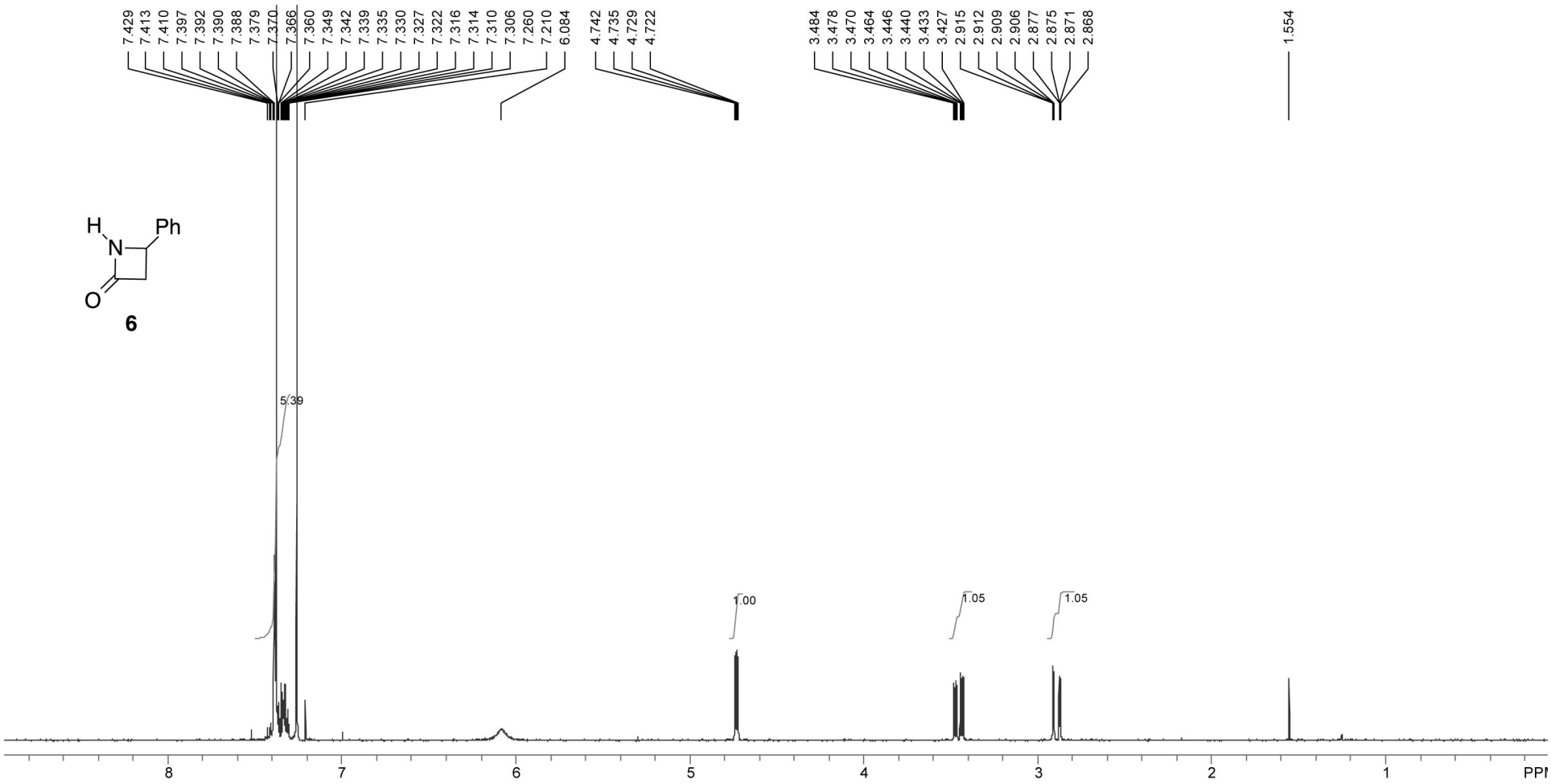

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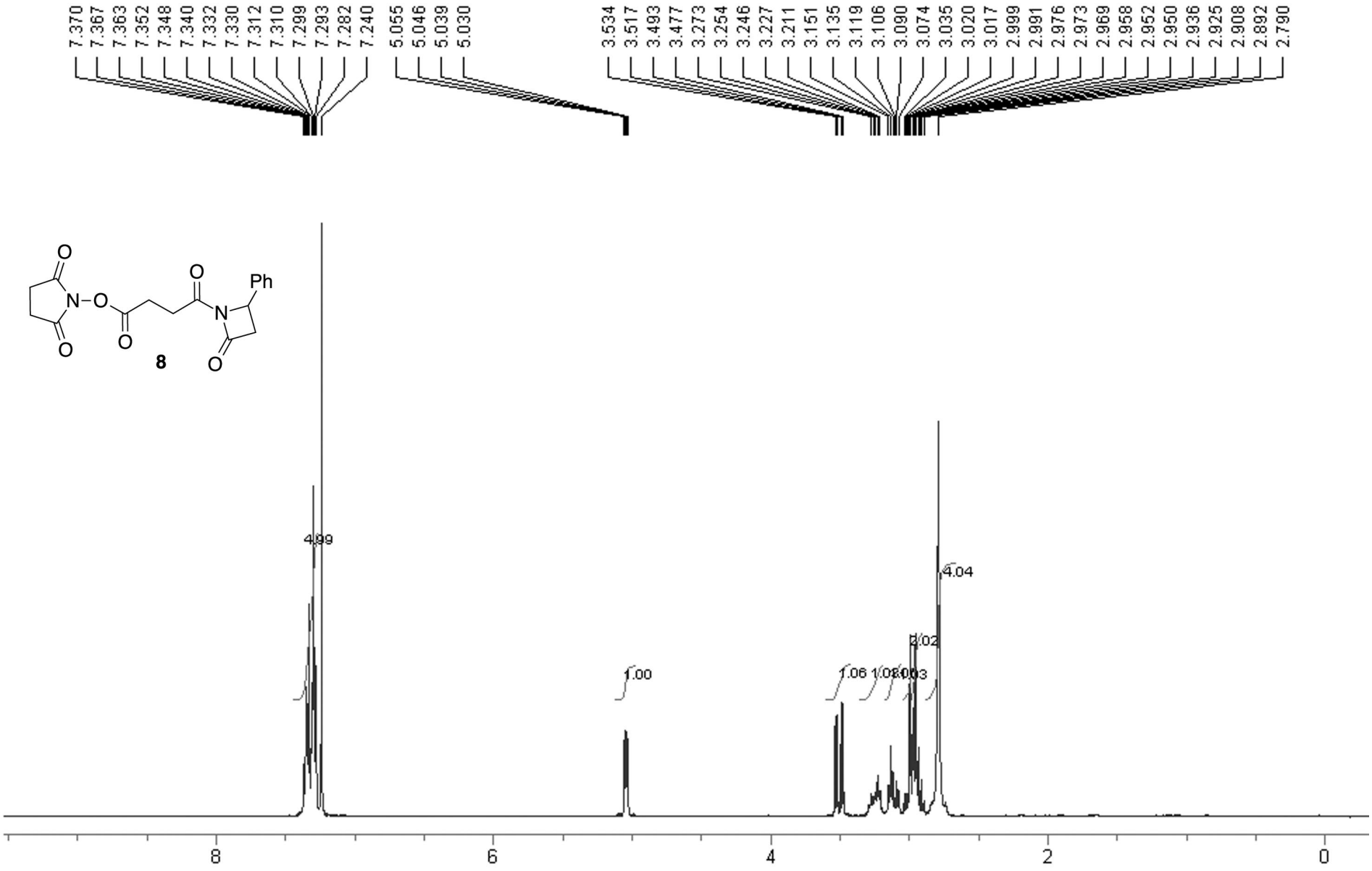

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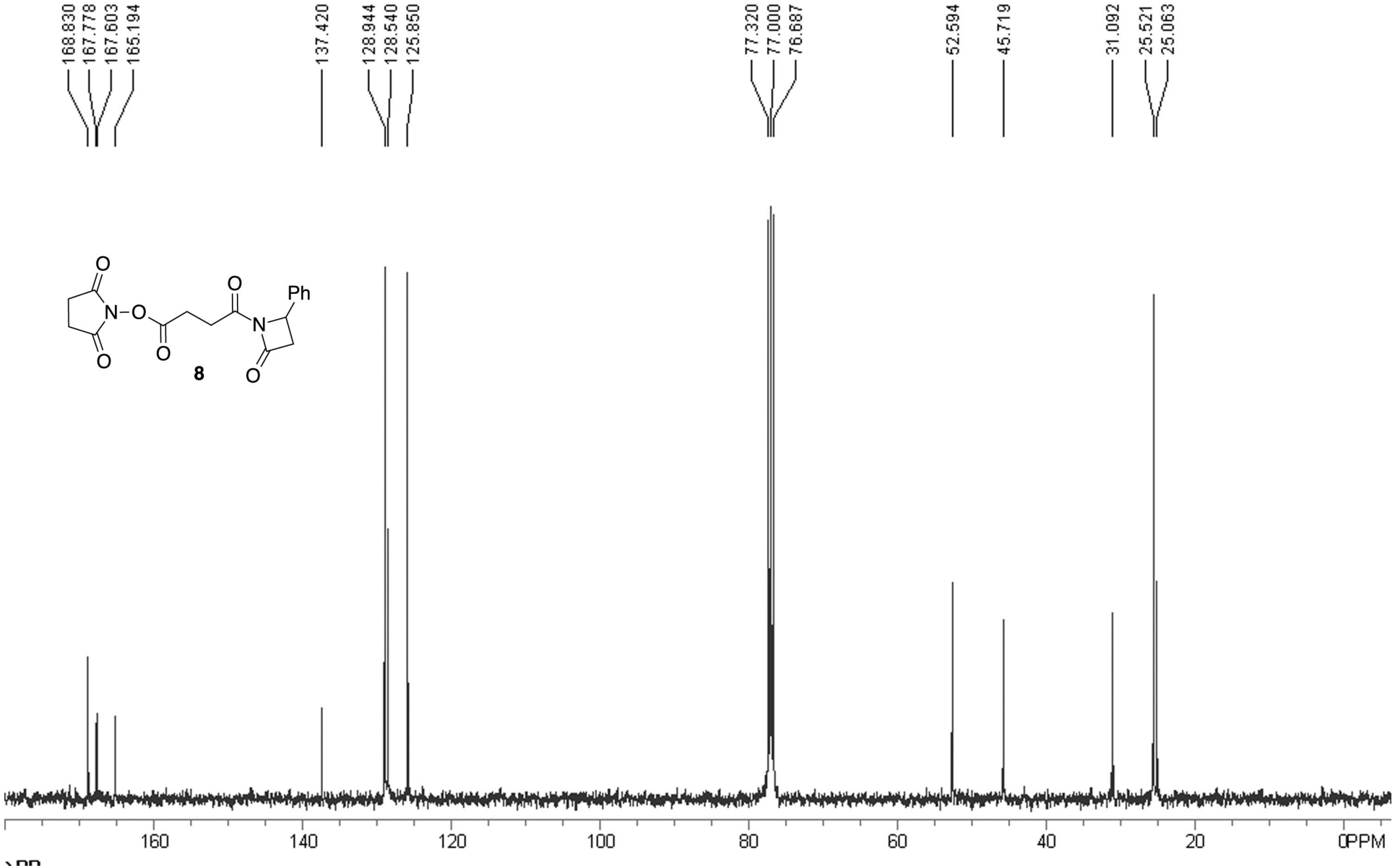

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