

Supporting Information

Trifunctional Organolithium Initiator for Living Anionic Polymerization in Hydrocarbon Solvents in the Absence of Polar Additives

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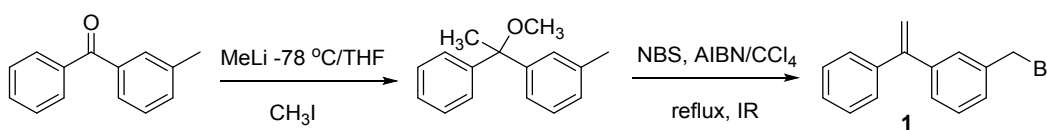
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Scheme S1: Schematics showing 3-bromomethyl DPE synthesis.

Synthesis of 1-(3-bromo-methylphenyl)-1-phenylethylene, 1. The bromide synthesis was completed by a two- step reaction, through an initial Wittig reaction and a subsequent Wohl-Ziegler bromination based on the reported procedure³³ with some modification as given below:

Synthesis of 1-(1-methoxy-1-phenyl)-3-methylbenzene. Commercially available 3-methylbenzophenone, (29 g, 147 mmol) was added to a round bottom flask and placed under N₂ atmosphere. Anhydrous THF (300 mL) was added through a double headed needle (cannula) in the flask. The solution was brought at -78 °C using mixture of isopropanol and dry ice, methyllithium solution (100 mL, 1.6M in diethylether) was added drop-wise in the solution under vigorous stirring. After the addition was completed the solution was slowly allowed to reach room

temperature. Iodomethane (40 mL, 642 mmol) was then added and the solution was left under stirring for three days. It was then poured in 5% w/v NaOH (500 mL) solution and stirred for an hour. The solution was then transferred into a separating funnel using hexane as the organic phase. The extraction on the aqueous solution was repeated for three more times. The hexane solution was then rotary evaporated down to a viscous liquid, hexane was added and the solution was dried with a small amount of magnesium sulfate. A color change was observed from a yellowish-greenish to a red-brown color. Purification of crude product by column chromatography (activated silica gel, 35-70 mesh, 300 g), with hexane as eluent gave 1-(1-methoxy-1-phenyl)-3-methylbenzene as yellow-green product, yield 91.7%. Thin layer chromatography TLC (silica gel F 254, hexane 95% and 5% ethylacetate) $R_f = 0.32$.

Synthesis of 1-(3-bromo-methylphenyl)-1-phenylethylene: Overall the synthesis of the unsaturated compound **1**, although it requires a three-step reaction, leads to high yields. Prudence and care was mandatory for the synthesis of the bromide **1** since the use of chemicals such as MeLi and AIBN is required. To prevent MeLi from reacting with THF, and forming a molecule of ethylene and the lithium enolate of acetaldehyde,^{1,2} the temperature was brought to -78 °C. The viscous 3-methylbenzophenone demands stirring in order to dilute in the THF solution. A small amount of AIBN was required, since its purpose was to create radicals to help the bromine substitution. If a large amount of radicals were present during the synthesis reaction that would result to a large number of side products. At temperatures above 60 °C AIBN decomposes and creates the necessary radicals and also releases N₂ gas. If the decomposition was done in a quick and uncontrollable manner the released gas might dismantle the reactor and cause NBS salt deposition on the reactor walls. Of great significance was the position of the lamp during the reaction, at first it must be placed at least 50 cm away from the flask. After 2 hours, once the bubbling in the solution was still mild, thus indication that the majority of the AIBN was disintegrated, the lamp was placed close to the flask so that the solvent could reflux. The purification of the bromide was challenging since the bromination reaction lead to the creation of five byproducts. After silica purification, the bromide maintained a yellow color and was of viscous substance, after recrystallization with methanol the bromide acquires the form of a white crystal.

Solvent CCl_4 was washed with saturated NaOH , freeze-degassed three times on the vacuum line, fractionally distilled keeping the middle fraction (one third of the total volume) in a round bottom flask, containing molecular sieves. In this first reaction 2 g of the precursor 1-(1-methoxy-1-phenyl)-3-methylbenzene (2 g, 8.84 mmol), where poured into a round bottom flask. N-Bromosuccinamide NBS (1.575 g, 8.85mmol) is quickly added in the flask, followed by a 2% molecular amount of AIBN (0.029 g, 0.177 mmol) compared to the precursor. The solvent, CCl_4 (25 mL) was transferred through a double pointed needle bridge, under constant nitrogen flow. For the reaction an IR lamp was used, as a heat source and also to help create the radicals trough the emitted radiation. The system is left under reflux for 24 hrs. The solution is chilled, filtered and the filtrate is then roto-vaporated. A red-brown viscous liquid is left. Purification of crude product by column chromatography with hexane as eluent, gave 3-bromomethyldiphenylethylene **3** as slightly yellow product, yield 68 % (Figure S1).

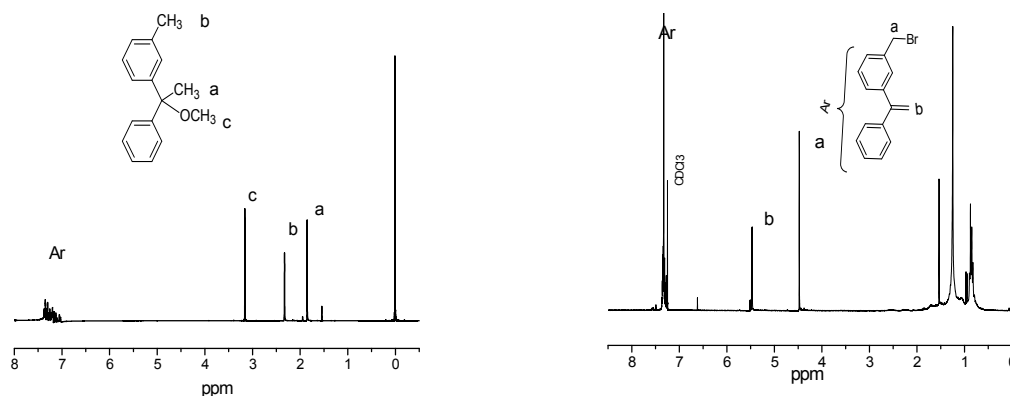


Figure S1. ^1H NMR of 1-(1-methoxy-1-phenyl-ethyl)-3-methylbenzene and 3-bromomethyl DPE

Polymerization of Isoprene by the Trifunctional Organolithium Initiator at Low Concentration.

The polymerization of isoprene using the trifunctional organolithium initiator at low concentration was performed using high vacuum technique according to standard protocol. The procedures for the preparation of purified monomer, solvents and the custom glass apparatuses have been previously described.^{31,32} A typical example for the polymerization of isoprene by the trifunctional organolithium initiator at low concentration is as follows (entry 1, Table 1): The polymerization was performed in a custom glass reactor containing ampoules of *sec*-butyllithium (0.36 mmol), the unsaturated compound **3** (0.113 mmol), isoprene (4.85 g, 71.2 mmol), methanol (~ 1 mL) and a purge flask with a solution of *n*-butyllithium in benzene. The main reactor for polymerization was washed with the purge solution to remove impurities from the glassware. The *n*-butyllithium was subsequently removed by repeated distillation of benzene from the purge flask. The unsaturated compound **3** and *sec*-BuLi were sequentially added to the reactor containing 300 mL of benzene by fracturing the break-seals which resulted in the immediate development of a pale yellow color, transitioning to red-orange after few hours. The isoprene added to the solution after aging the initiator solution (~15 h) by fracturing the break-seal and the color converted to a pale yellow. The polymerization was terminated by degassed methanol after 20 hours. The resulting polymer was of higher than expected molecular weight and broad molecular weight distribution.

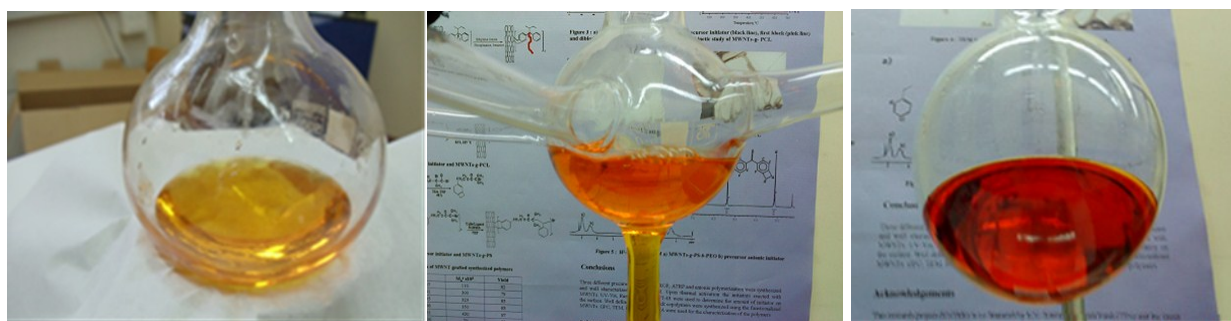


Figure S2: Photos during activation of 4,4,4-(ethane-1,1,1-triyl)tris(((3-(1-phenylvinyl)benzyl)oxy)benzene) with *sec*-BuLi. From left to right, a few seconds after *sec*-BuLi addition, 5 min and finally 15 min after addition.

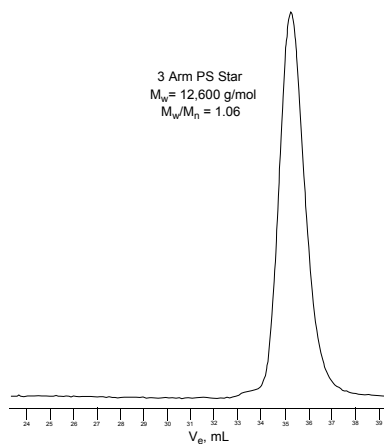


Figure S3: Size exclusion chromatography eluogram of the three-arm PS star (run 3, Table 1).

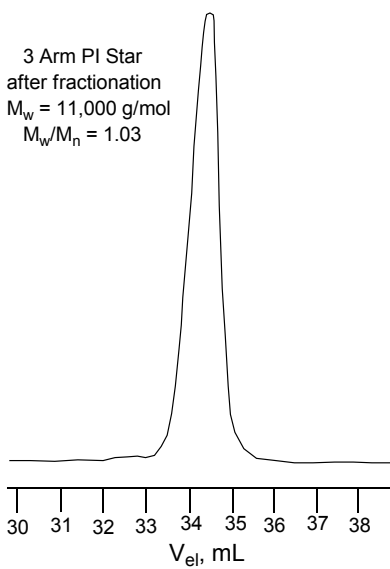


Figure S4: Size exclusion chromatography eluogram of the three arm PI star after fractionation (run 6, Table 1).

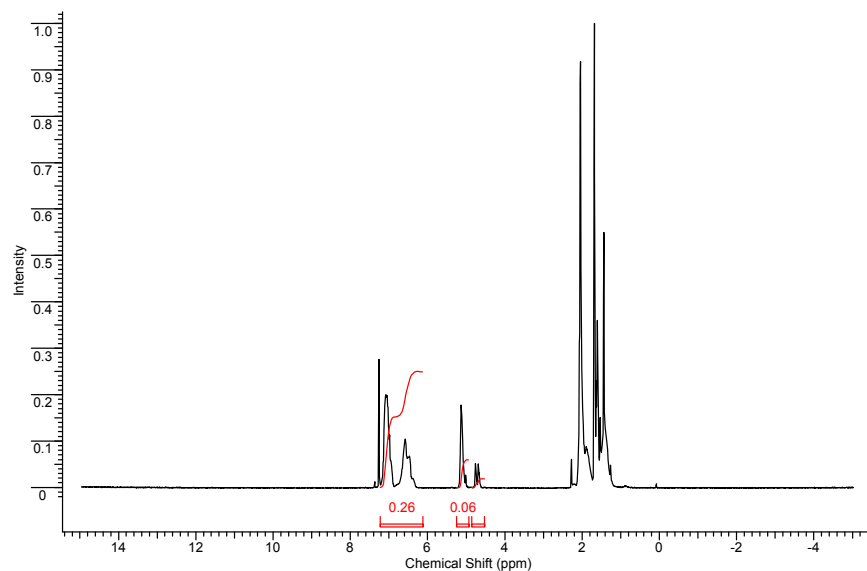


Figure S5: $^1\text{H-NMR}$ of PS-*b*-PI Star (run 7, Table 1).

Reactant ID Verified

Internal calibrated

$[\text{C}_{65}\text{H}_{54}\text{O}_3 + \text{H-CH}_4]^+$ Fragment is dominant

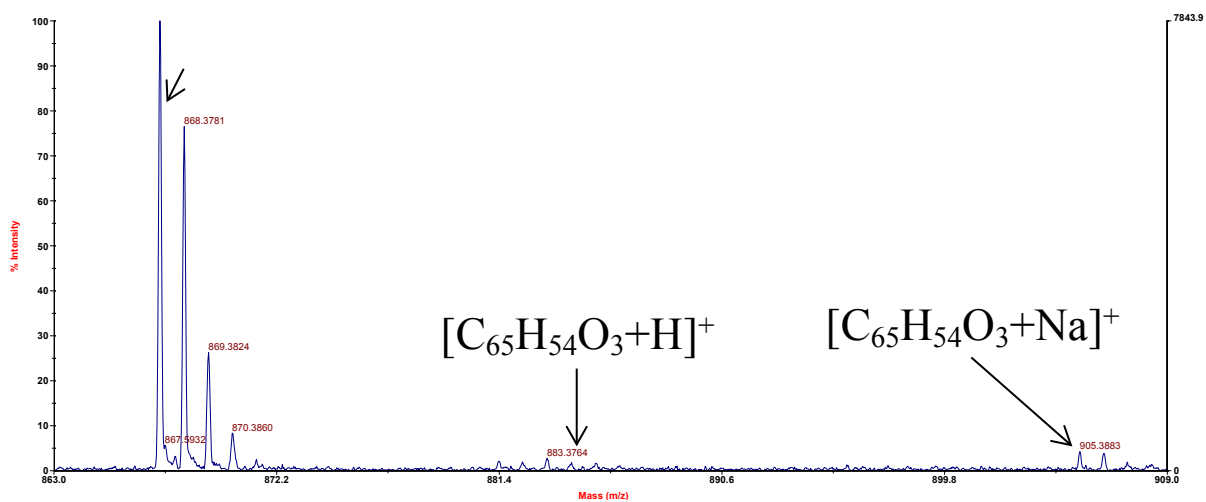
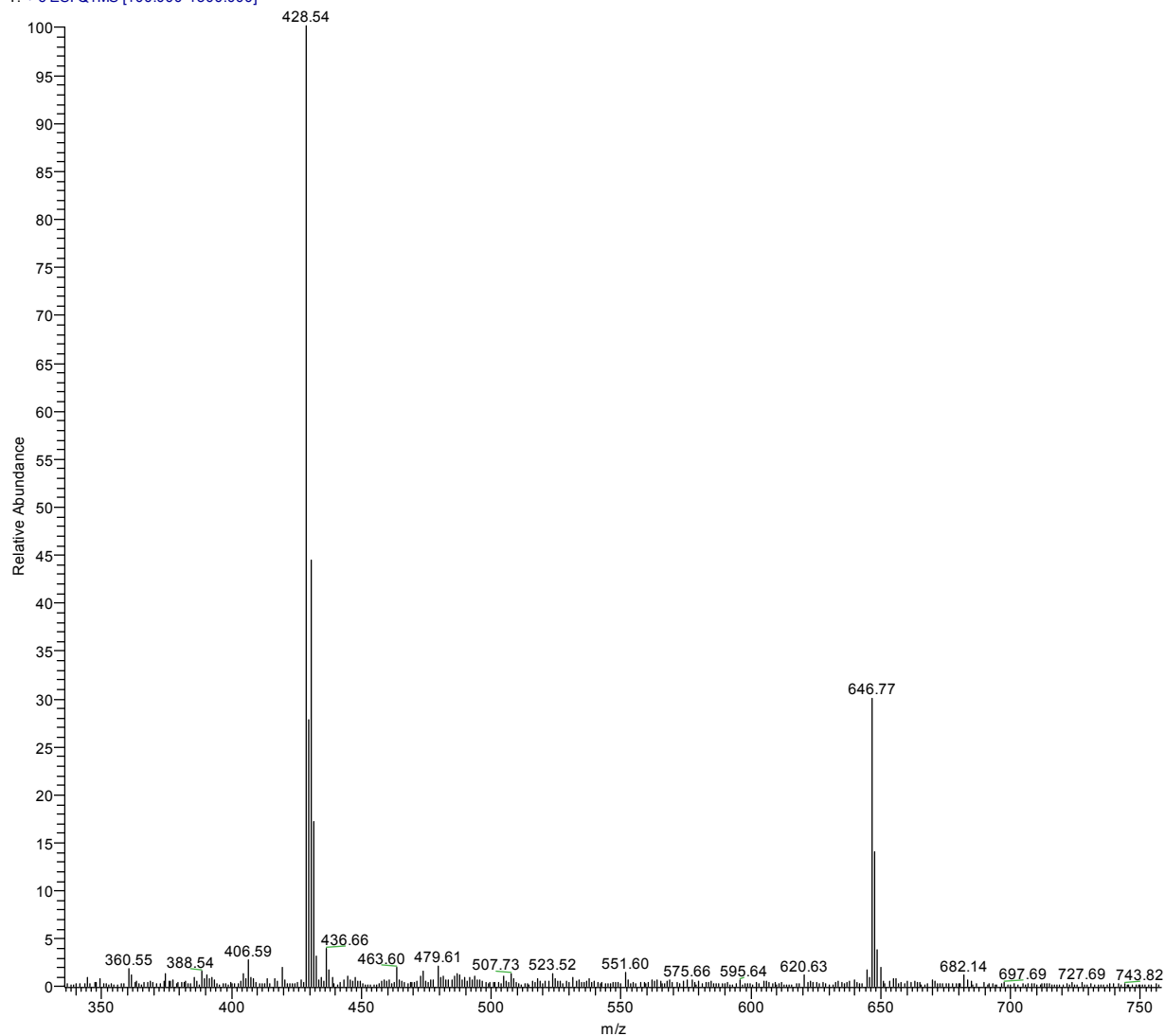


Figure S6: MALDI-TOF MS of compound **3**, before the addition of *sec*-BuLi.

Trif_unsat#25 RT: 0.42 AV: 1 NL: 2.51E7
T: + c ESI Q1MS [100.000-1500.000]



Trif_unsat#11 RT: 0.18 AV: 1 NL: 2.20E7
T: +c ESI Q1MS [100.000-1500.000]

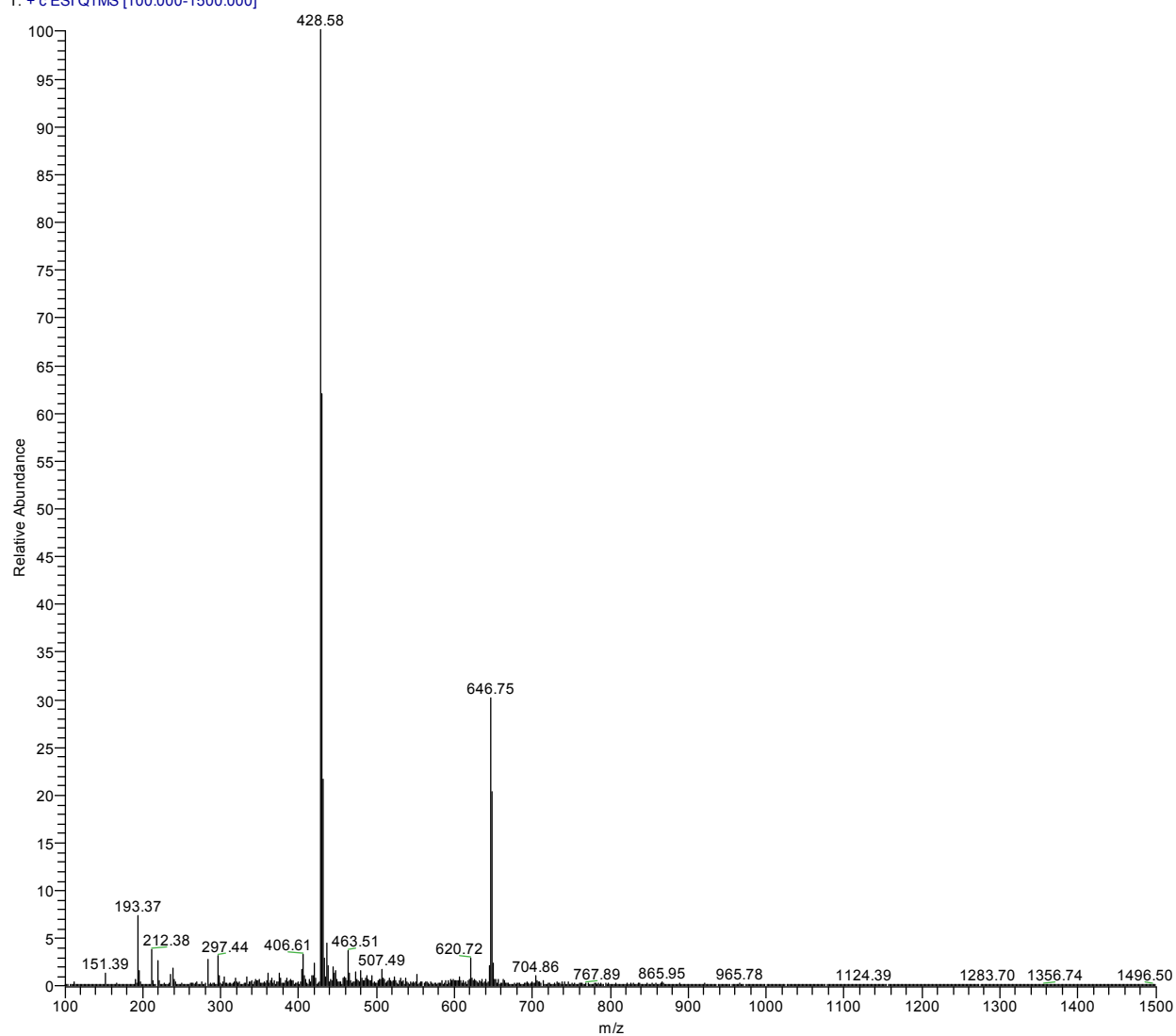


Figure S7: LC MS of compound **3**, before the addition of *sec*-BuLi.

Sample_2 #46-103 RT: 0.81-1.78 AV: 58 NL: 4.67E6
T: + c ESI Q1MS [400.000-800.000]

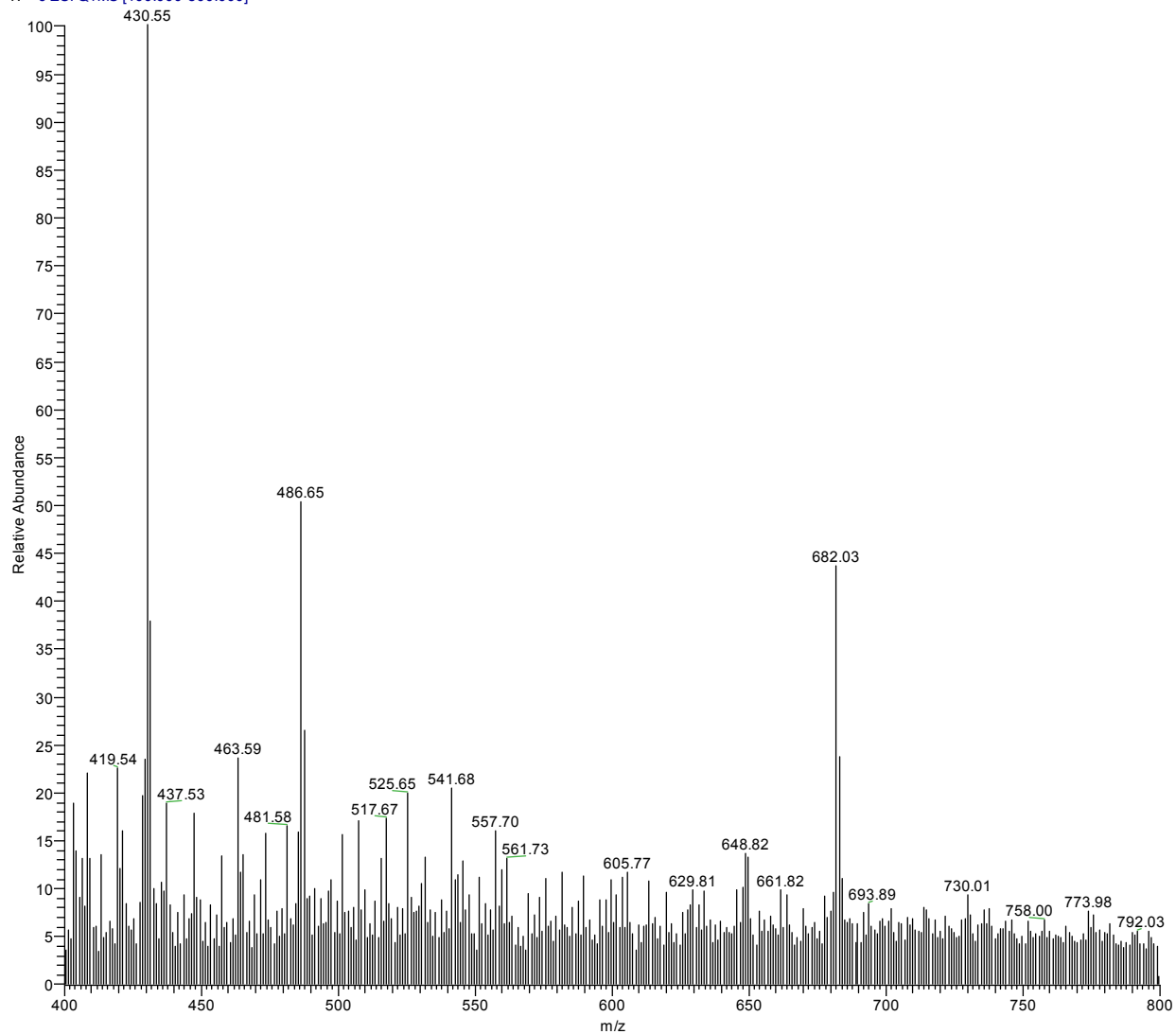


Figure S8: LC MS of compound **3**, 2.5 h after the addition of 1/3 of the stoichiometric amount of *sec*-BuLi.

Sample_3 #76-133 RT: 1.33-2.30 AV: 58 NL: 1.19E6
T: + c ESI Q1MS [400.000-800.000]

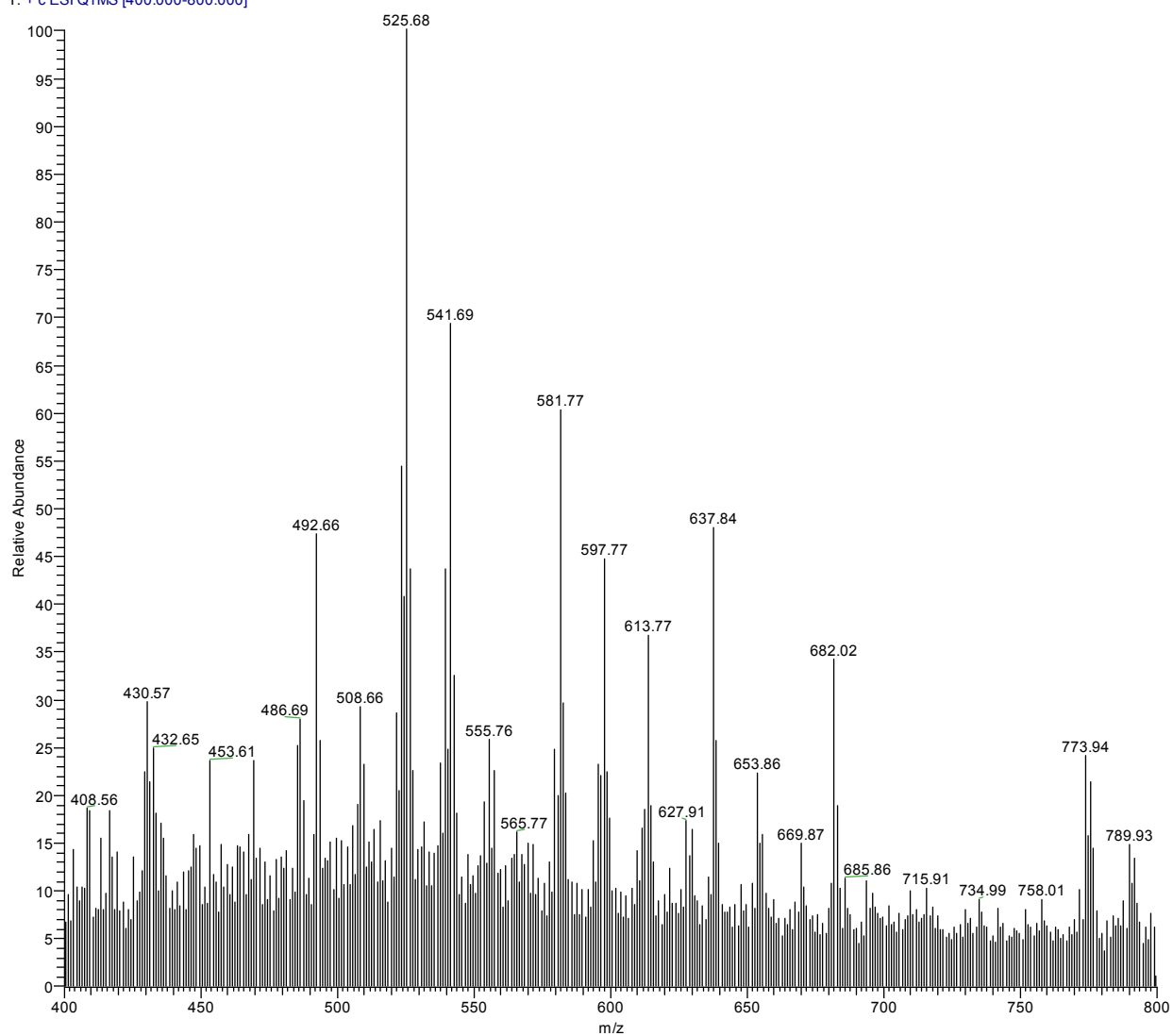


Figure S9: LC MS of compound **3**, 2.5 h after the addition of 2/3 of the stoichiometric amount of *sec*-BuLi.

Sample_4 #57-85 RT: 0.98-1.47 AV: 29 NL: 2.12E6
T: +c ESI Q1MS [400.000-800.000]

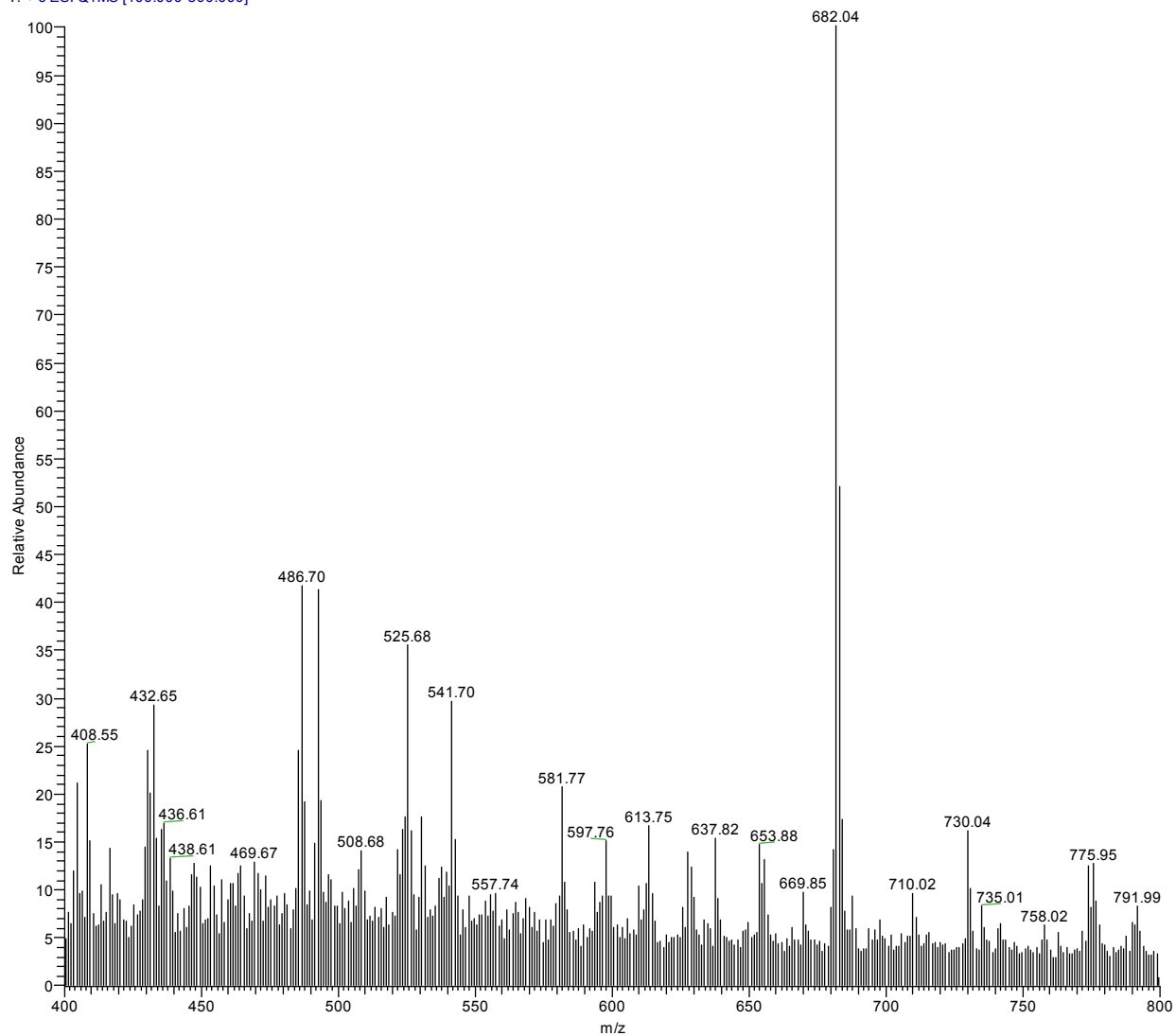


Figure S10: LC MS of compound **3**, 2.5 h after the addition of stoichiometric amount of *sec*-BuLi.

References

- (1) Wakefield, B. J. *The Chemistry of Organolithium Compounds*, Pergamon Press: Elmsford, NY, 1974.
- (2) Ogle, C. A.; Strickler, F. H.; Gordon, G. *Macromolecules* **1993**, *26*, 5803-5805.