

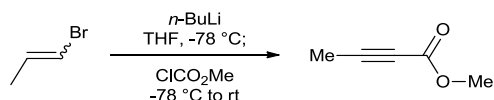
Supporting information: Facile multi-decagram synthesis of methyl but-2-ynoate

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Procedure:



An oven-dried 3-L round-bottomed flask equipped with a magnetic stirring bar, a rubber septum, an electronic thermometer and flushed with nitrogen was charged with (*Z/E*)-1-bromo-1-propene (81.5 mL, 952 mmol) (Note 1), 1 L of anhydrous tetrahydrofuran (THF) (Note 2) and maintained under a nitrogen atmosphere. The flask was cooled to $-78\text{ }^\circ\text{C}$ with a dry ice-acetone bath, and after 10 minutes *n*-butyllithium 2.5M (800 mL, 2.00 mol) (Note 3) was added slowly to maintain the internal temperature below $-60\text{ }^\circ\text{C}$. Following the end of the addition, the off-white mixture was stirred for 1.5 hours at $-78\text{ }^\circ\text{C}$ before methyl chloroformate (96.0 mL, 1.24 mol) (Note 4) was added dropwise over 40 minutes in order to maintain the internal temperature between $-70\text{ }^\circ\text{C}$ and $-60\text{ }^\circ\text{C}$. The mixture was stirred for 2 hours at $-78\text{ }^\circ\text{C}$ before the cooling bath was removed allowing the mixture to warm to room temperature over 1.5 hours. 500 mL of water were subsequently added and the organic layer was decanted. The aqueous fraction was extracted twice with 400 mL of diethyl ether and the combined organic fractions were dried over anhydrous sodium sulfate, filtered, and the filtrate was concentrated under reduced pressure ($40\text{ }^\circ\text{C}$, 100 mbar) (Note 5) to afford an orange brown liquid (Note 6). After distillation through a 5 cm long vigreux column (Bp = $64\text{--}67\text{ }^\circ\text{C}$, 60 mbar) (Note 7) methyl but-2-ynoate (74.7g, 80%) (Note 8) was obtained as a colourless oil (Note 9).

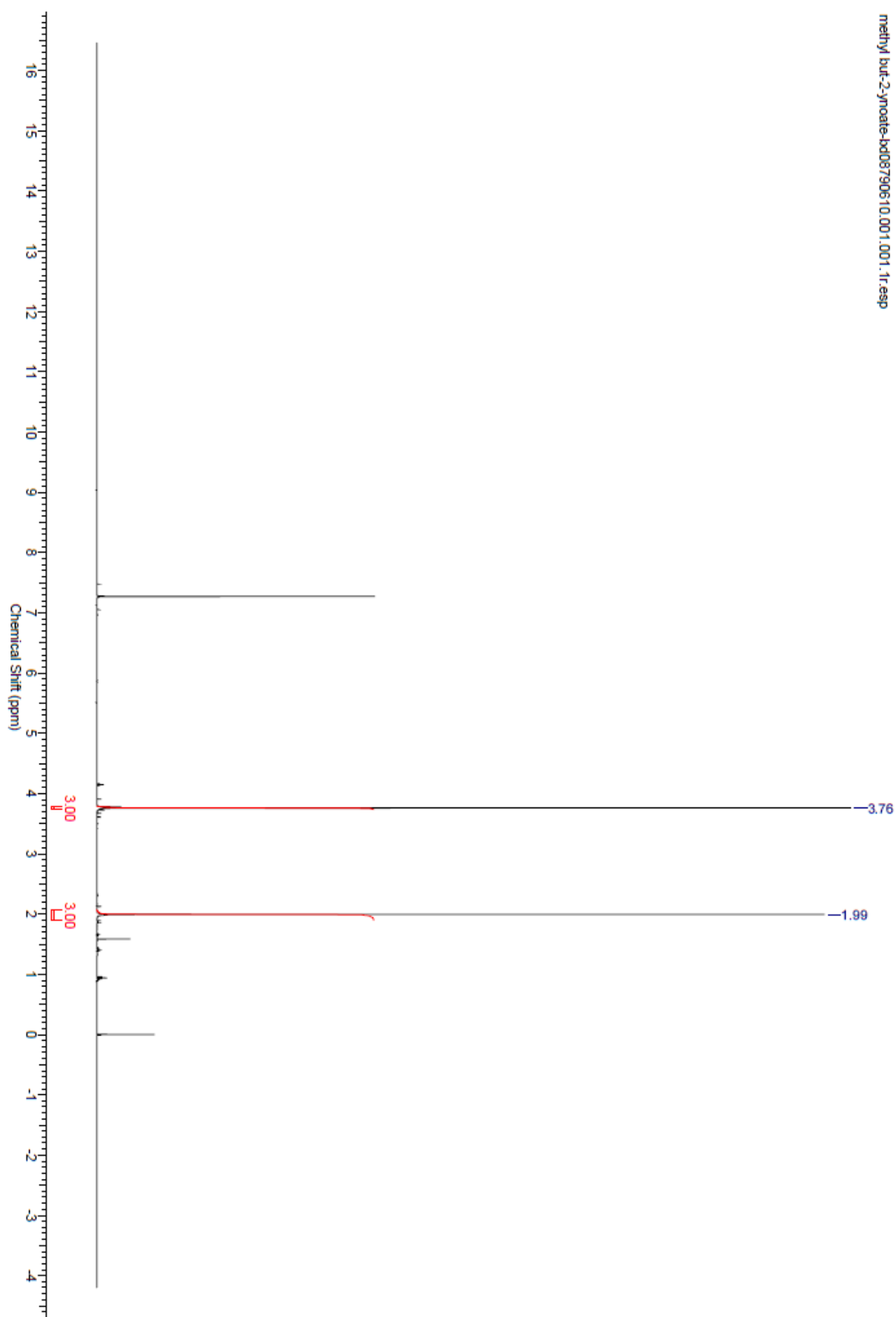
Notes

1. 1-Bromo-1-propene (*cis* and *trans*, 98%) (CAS 590-14-7) was purchased from Sigma-Aldrich Chemical Company, Inc. (Cat. No. B78203) and used as received.
2. Anhydrous tetrahydrofuran was obtained by filtration through activated alumina (powder ~150 mesh, pore size 58 \AA , basic, Sigma-Aldrich) columns.
3. *n*-Butyllithium 2.5M solution in hexanes, AcroSeal was purchased from Acros Organics and used as received.
4. Methyl chloroformate (99%) was purchased from Sigma-Aldrich Chemical Company, Inc. and used as received.
5. Employing these conditions for concentrating *in vacuo* minimized product loss on the rotary evaporator.
6. Depending on the scale, the colour of the crude product may change from pale yellow to brown; however, this has no significant effect on the yield.
7. Towards the end of the distillation, the residue was transferred to a smaller flask and the distillation was continued to recover the maximum amount of product.
8. Similar results were obtained starting with 40 mL and 10 mL of 1-bromo-1-propene: methyl but-2-ynoate was afforded in 84% and 77% yields respectively.
9. The product is stable at $-20\text{ }^\circ\text{C}$ for at least three months.

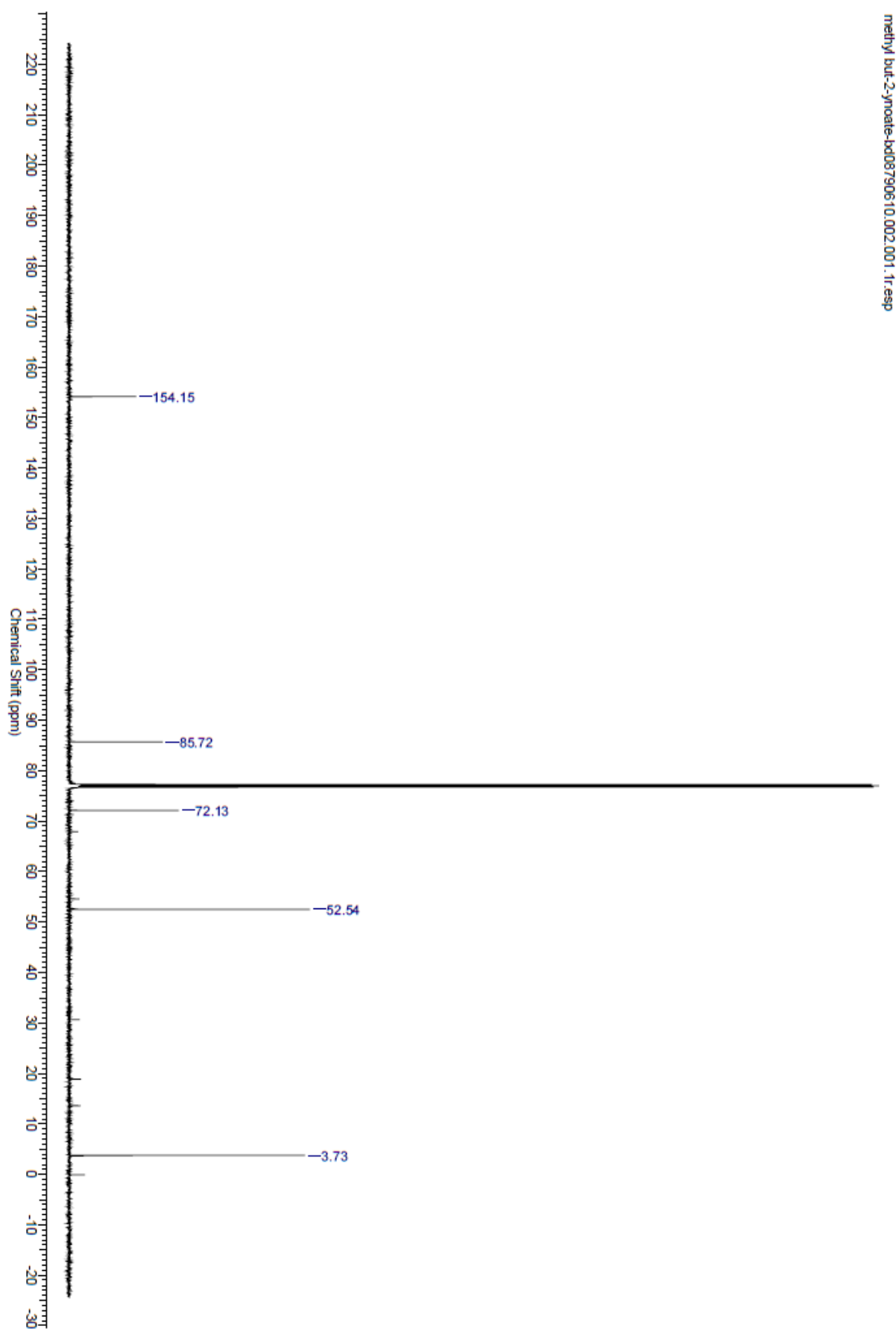
The elemental analysis and the spectral analysis of the product are as follows: Anal. Calcd for $C_5H_6O_2$: C, 61.22; H, 6.16. Found: C, 61.12; H, 6.00%. 1H NMR ($CDCl_3$, 500 MHz) δ_H 3.76 (s, 3H, CH_3-O), 1.99 (s, 3H, $CH_3-C\equiv$). ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 154.2 (C- $\underline{C}O_2Me$), 85.7 ($CH_3-\underline{C}\equiv$), 72.1 ($C\equiv\underline{C}-CO_2Me$), 52.5 ($\underline{C}H_3-O$), 3.7 ($\underline{C}H_3-C\equiv$). IR (film)/ cm^{-1} ν_{max} 2957, 2247, 1714, 1436, 1263, 1075.

^1H , ^{13}C NMR and elemental analysis of *methyl but-2-ynoate*:

^1H NMR (CDCl_3 , 500 MHz)



^{13}C NMR (CDCl_3 , 125 MHz)



Elemental analysis



Elemental Analysis Service

Please send completed form and samples to:


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Science Centre
London Metropolitan University
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Sample submitted by: Iacovos Neal Michaelides
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Date Submitted: 12-01-11

Please submit ca. 5 mg of sample.

Sample Reference No.: IAMI-BEDA-036H.1
Name of Compound: METHYL BUT-2-YNOATE
Molecular Formula: $C_5H_8O_2$
Stability: Unknown, keep in dry place
Hazards: XN= Harmful; R: 10, 20/21/22, 36/37/38
Other Remarks: Malodorous

Element	Expected %	Found (1)	Found (2)	
Carbon	61.22	61.13	61.12	
Hydrogen	6.16	6.00	6.00	
Nitrogen	N/A	-	-	

Authorising Signature: 

Date Completed: 130111	Signature: 
Comments:	