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Methylbenzene-1-sulfonic Acids-catalyzed and Solvent-free Esterification of Benzoic Acid with Dodecan-1-ol for the Betterment of the Experiment in Cambodian High School

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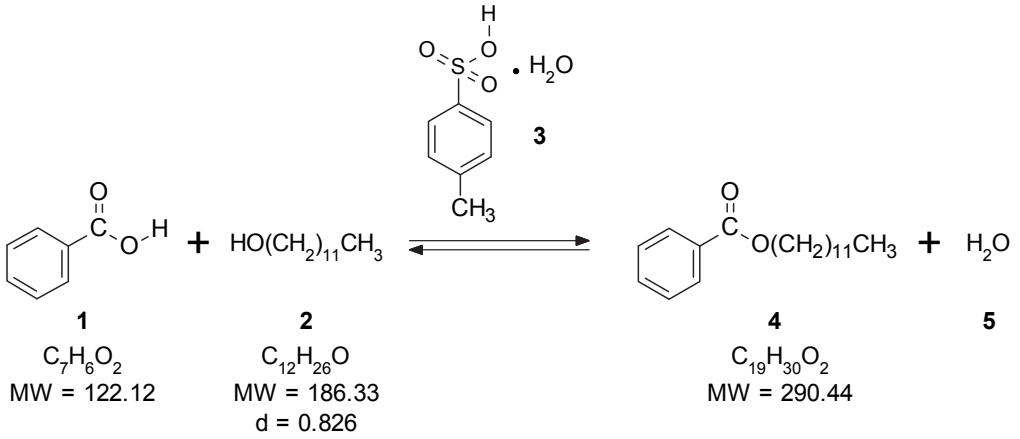
I. Introduction

Cambodian education system was abolished and intellects were purged from Cambodia by the policies of the Pol Pot regime in late 1970s. After the Pol Pot regime, the education system has been established by sudden improvements in the quantity of educational opportunities. However, the quality of education is still limited.[1]

To improve the quality of education, the Royal Government of Cambodia is working on new strategies to develop capacity and human resource.[2] Regarding to the aforementioned context, the Ministry of Education Youth and Sport (MoEYS) espoused a Policy on Science, Technology, Engineering, and Mathematics (STEM) with the intention to improve the capacities of students to develop highly qualified and responsible human resources in the areas of STEM for the country's sustainable and inclusive development. In this setting, MoEYS is working on reforming curriculum, promoting research of teachers and students and modernizing laboratories.[3]

The National Institute of Education (NIE, Cambodia) is responsible for producing master's degree in educational administration, high school teachers (bachelor degree + 1 year training), and junior high school French-Khmer teachers (high school-graduated degree + 2 years training) (pre-service training program). Moreover, NIE takes charge of upgrading leaders and staff of Provincial Offices of Education, Youth and Sport and high school teachers throughout the country, and training educational inspectors and high school principals. For high school teachers, NIE offers a variety of disciplines such as mathematics, physics, chemistry, biology, English, French, history, geography, earth sciences, informatics, morals, economics, agriculture, electricity, electronics, mechanics, animal husbandry, and hydrology.[4]

Recently, NIE has been encountering some difficulties such as lack of qualified science teachers, especially chemistry teachers, and lack of teaching materials. In order to participate in overcoming these difficulties, we have developed a new reaction conditions that could be applicable to chemistry teachers synthesizing methylbenzene-1-sulfonic acids as a catalyst for reactions such as esterifications and dehydrations which have been written in textbook of chemistry.[5]



Scheme 1. Synthesis of dodecyl benzoate (**4**).

The optimum reaction conditions for esterification of benzoic acid (**1**) with dodecan-1-ol (**2**) under the promotion of 4-methylbezene-1-sulfonic acid hydrate (**3**) as a catalyst to give dodecyl benzoate (**4**) was previously reported (Scheme 1).[6] However, the reaction was carried out in an oil bath at elevated temperature that could not be applicable in large classrooms (30 to 50 students); only few students actively participated in the experiments. Moreover, the recovery of **2** was still high (> 6.5%) that was required further purification using silica gel column chromatography, and commercial catalyst **3** was employed in the reaction. In order to solve the above mentioned problems, on one hand, we optimized the reaction conditions to decrease the recovery of **2** and developed a new experimental method that could be applicable to large classrooms so that all students can actively participate in the experiment. On another hand, we synthesized methylbenzene-1-sulfonic acids that could be used as a catalyst for the reaction.

II. Results and discussion

In this study, first, we synthesized ester **4** from acid **1** and alcohol **2** in the present of catalyst **3** with minimizing the recovery of alcohol **2** to 5% or less in order to obtain practical purity of ester **4**. Second, we modified the above experimental method of esterification by employing a shaker (Picture 1) and microwave instead of an oil bath, and separation using test tubes that gave students an opportunity of participating actively in the experiment. Moreover, we synthesized methylbenzene-1-sulfonic acids from toluene and concentrated sulfuric acid.

1. Minimization for the recovery of dodecan-1-ol

Initially, we reacted dodecan-1-ol (**2**) (9.75 mmol, 1.00 equiv) with benzoic acid (**1**) in different equivalents (1.00–4.00 equiv) in the presence of 4-methylbezene-1-sulfonic acid hydrate (**3**) (0.13 equiv) as a catalyst in a beaker (50 mL) at 110 °C for 40 min (the reaction temperature was controlled by an oil bath) to optimize the reaction conditions in order to decrease the recovery of dodecan-1-ol (**2**) (Table 1).[8,9,10,11,12,13] When the reaction was performed with 1.00 equivalent of benzoic acid (**1**), 12% of dodecan-1-ol (**2**) was recovered. To our satisfaction, by increasing benzoic acid (**1**) to 3.00 equivalents, dodecan-1-ol (**2**) was recovered in 3.7% (Table 1, Entry 5). There is an increase in recovery of dodecan-1-ol (**2**) was observed above that equivalent (Table 1, entry 6). So, minimum recovery of dodecan-1-ol (**2**) was obtained when 3.00 equivalents of **1** was employed.

2. Oil bath and test tube-assisted synthesis of dodecyl benzoate

4-Methylbenzene-1-sulfonic acid hydrate (**3**) was added to a mixture of benzoic acid (**1**) and dodecan-1-ol (**2**) in a beaker (50 mL). The mixture was then stirred at 110 °C for 40 min in an oil bath. After had been cooled with an ice-water bath, the mixture was transferred to a test tube and washed using saturated aq $NaHCO_3$ and saturated aq NaCl. After the aqueous layer had been removed using a Pasteur pipette, the organic layer was dried under reduced pressure to give ester **4**. The reaction was conducted repeatedly and a consistent yield of **4** (70–76%) and recovery of **2** (17–20%) was achieved. This experimental method could provide students with opportunity to take part in the experiment.

3. Shaker and test tube-assisted synthesis of dodecyl benzoate

4-Methylbenzene-1-sulfonic acid hydrate (**3**) was added to a mixture of benzoic acid (**1**) and dodecan-1-ol (**2**) in a beaker (50 mL). The mixture was then shaken at 80 °C for 1 h in a shaker (Picture 1). After had been cooled with an ice-water bath, the mixture was transferred to a test tube and washed using saturated aq $NaHCO_3$ and saturated aq NaCl. Then, the aqueous layer had been removed using a Pasteur pipette to give ester **4**. The results were shown in Table 2. Numerous conditions with difference in the equivalent of **1** and reaction time were performed. We found that when 4.00

Table 1. Minimization for the recovery of **2**.

Entry	**1** (equiv)	**2** (equiv)	**3** (equiv)	Time (min)	Temp. (°C)	Yield of **4** (%)	Recovery of **1** (%)[a]	Recovery of **2** (%)[b]
1	1.00	1.00	0.13	40	110	85	8.9	12
2	1.50	1.00	0.13	40	110	93	26	9.3
3	2.00	1.00	0.13	40	110	94	43	12
4	2.50	1.00	0.13	40	110	97	38	5.6
5	3.00	1.00	0.13	40	110	91	89	3.7
6	4.00	1.00	0.13	40	110	87	73	6.2

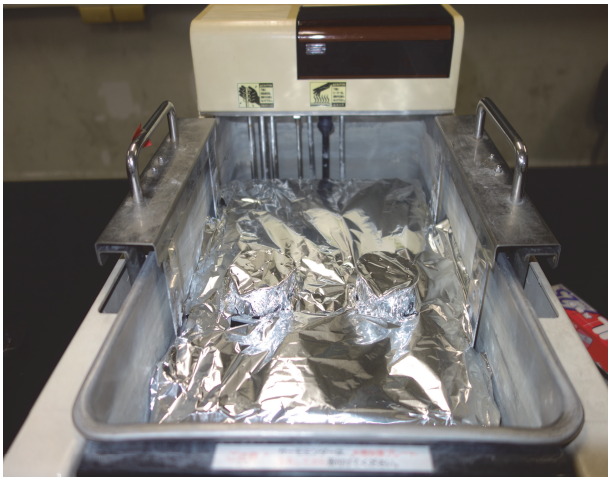
[a] Recovery of **1** was calculated from starting material of **1**.

[b] Recovery of **2** was calculated form starting material of **2**.

Table 2. Preliminary reaction conditions investigation for student experiments.

Entry	**1** (equiv)	**2** (equiv)	**3** (equiv)	Time (h)	Temp. (°C)	Yield of **4** (%)	Recovery of **2** (%)[a]
1	1.50	1.00	0.10	2	80	69	30
2	2.00	1.00	0.10	1	80	39	48
3	2.50	1.00	0.10	1	80	35	37
4	3.00	1.00	0.10	1	80	47	55
5	4.00	1.00	0.10	1	80	–[b]	–[b]

[a] Recovery of **2** was calculated form starting material of **2**. [b] Not determined.



Picture 1. Shaker-assisted esterification. Beakers were covered with holed aluminum foil for releasing water vapor and preventing water from returning to the beakers.

equivalents of **1** was reacted with 1.00 equivalent of **2** for 1 h, the yield of **4** and recovery of **2** could not be determined because a large amount of **1** remained in the mixture. A good yield of **4** was obtained when 1.50 equivalents of **1** was reacted with 1.00 equivalent of **2** for 2 h.

4. Application of shaker and test tube-assisted synthesis of dodecyl benzoate

After had been modified, the experimental method was applicable to large classrooms. The experiment was then conducted by students. Benzoic acid (**1**) and 4-methylbenzene-1-sulfonic acid hydrate (**3**) was added to dodecan-1-ol (**2**) in a beaker (50 mL). After had been shaken for 120 min at 80 °C in a shaker, the mixture was cooled to room temperature and added saturated aq $NaHCO_3$. The mixture was then transferred to a test tube and manually shaken for 1 min. After the aqueous layer had been removed using a Pasteur pipette, saturated aq NaCl was added to the test tube and thence manually shaken for 1 min. The aqueous layer was removed from the test tube using the Pasteur pipette to give ester **4**. As shown in Table 3 (Entries 1 and 2), a consistent yield of **4** was accomplished even though the reaction was conducted by the students.

5. Synthesis of methylbenzene-1-sulfonic acids hydrate

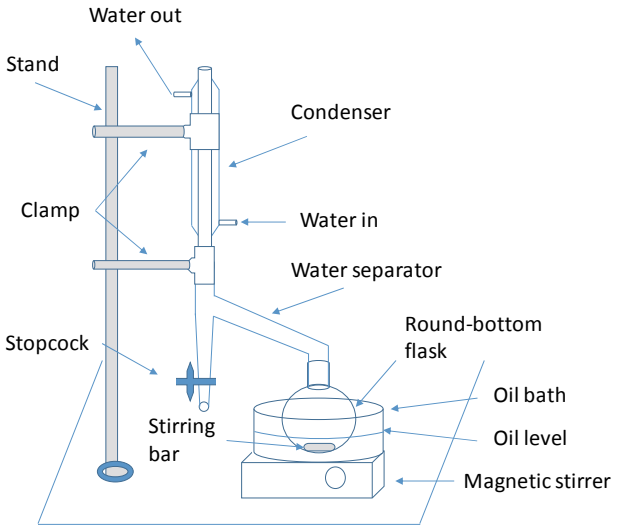
A lack of chemicals is commonly encountered in schools that are located in rural area due to the high price and some chemicals are commercially unavailable. In order to solve this problem, we developed an experimental method of synthesizing methylbenzene-1-sulfonic acids hydrate that can be used as a catalyst in esterifications. Methylbenzene-1-sulfonic acids hydrate were synthesized using a method that had been modified from previously described method.[7] Concentrated sulfuric acid was added to excessive toluene in a round bottom flask. The reaction mixture was refluxed for 1 h at 175 °C (oil bath temperature) with a return flow at the water separator (Picture 2) and then let the mixture cool to room temperature. Two drops of water were added to the mixture and thence the precipitate was collected by filtration

Table 3. Reaction conditions for the student experiments.

Entry	**1** (equiv)	**2** (equiv)	**3** (equiv)	Time (h)	Temp. (°C)	Yield of **4** (%)	Recovery of **2** (%)[a]
1	1.50	1.00	0.10	2	80	64	25
2	1.50	1.00	0.10	2	80	58	28
3	2.00	1.00	0.10	2	80	48	17
4	2.50	1.00	0.10	2	80	56	31
5	3.00	1.00	0.10	2	80	49	21

[a] Recovery of **2** was calculated from starting material of **2**.

with suction washing with toluene. The precipitate was dried in a desiccator under reduced pressure to give a crude product (5.705g, 29.99 mmol, 80%) as pale pink solid. The product was analyzed for specific compounds by ^{1}H NMR



Picture 2. Water separator-assisted sulfonation of toluene in fume hood.

(400.13 MHz, D_2O). The spectra showed that three compounds were expected to form: 4-methylbenzene-1-sulfonic acid, 2-methylbenzene-1-sulfonic acid, 3-methylbenzene-1-sulfonic acid (trace).[14] According to the spectra, it was likely that the amount of each compound decreased in the pattern: 4-methylbenzene-1-sulfonic acid > 2-methylbenzene-1-sulfonic acid > 3-methylbenzene-1-sulfonic acid. The ratio of 4-methylbenzene-1-sulfonic acid to 2-methylbenzene-1-sulfonic acid to 3-methylbenzene-1-sulfonic acid was 3:0.38:0.02.

6. Application of laboratory synthesized methylbenzene-1-sulfonic acids hydrate

After had been synthesized, a solid mixture of methylbenzene-1-sulfonic acids hydrate was used as a catalyst for esterification of benzoic acid (**1**) and dodecan-1-ol (**2**). Methylbenzene-1-sulfonic acids hydrate was added to a mixture of benzoic acid (**1**) and dodecan-1-ol (**2**) in a beaker (50 mL). The mixture was then stirred for 40 min at 110 °C in an oil bath. After had been cooled with an ice-water bath, the organic layer was washed using saturated aq $NaHCO_3$ and saturated aq NaCl, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated under reduce pressure to give dodecyl benzoate (**4**) (94%) with the recovery of **1** (67%) and **2** (5.1%).

7. Microwave-assisted synthesis of dodecyl benzoate

Conventional heating usually involves the use of an oil bath that takes longer time to achieve the target temperature. Microwave heating can have certain benefit over oil bath heating such as short reaction time, mild reaction conditions, lower energy usage, higher chemical yield.[15] Because of the above-mentioned benefits, microwave was employed in the following esterification. 4-Methylbenzene-1-sulfonic acid hydrate (**3**) (0.2511g, 1.320 mmol, 0.130 equiv) was added to a mixture of benzoic acid (**1**) (1.8601 g, 15.231 mmol, 1.500 equiv) and dodecan-1-ol (**2**) (2.20 mL, 1.8920 g, 10.154 mmol, 1.000 equiv) in a glass vial with a silicone cap. The vial with stirring bar was then placed in a Monowave 50 for 40 min at 110 °C. After had been allowed to reach room temperature, the organic layer was washed with saturated aq $NaHCO_3$ (30 mL x 3) and saturated aq NaCl (30 mL x 2), dried over anhydrous Na_2SO_4, and filtered. The filtrate was dried under reduced pressure to give a crude product. We observed some water remaining in the vial. The reaction is reversible, so removing water from the reaction mixture is extremely important to increase yield of ester **4**. Our objective was to investigate if water could be removed from the reaction mixture by addition of desiccants. Three different desiccants were explored for their ability to absorb water from the mixture (Na_2SO_4, $MgSO_4$, MS4A). As seen from Table 4, addition of desiccants into the reaction mixture afforded ester **4** in good yield except for MS4A. This could be caused by the basicity of MS4A that neutralized the acid catalyst and by release water from adsorbed water on MA4A at high temperature. The results (Table 4, Entry 3) suggested that sufficient yield of ester **4** was obtained when magnesium

Table 4. Optimization of microwave-assisted reaction conditions.

Entry	**1** (equiv)	**2** (equiv)	**3** (equiv)	Desiccant	Time (min)	Temp. (°C)	Yield of **4** (%)	Recovery of **2** (%)[a]
1	1.50	1.00	0.13	Not used	40	110	89	15
2	1.50	1.00	0.13	Na_2SO_4	40	110	85	12
3	1.50	1.00	0.13	$MgSO_4$	40	110	92	7.3
4	1.50	1.00	0.13	MS4A	40	110	8.6	105
5	1.50	1.00	0.13	Not used	5	180	94	15

[a] Recovery of **2** was calculated from starting material of **2**.

sulfate was employed as desiccant. Moreover, when we performed the reaction without using desiccant in short reaction time at 180 °C (Table 4, Entry 5), brown color of the reaction mixture was observed and there is no significant different in yield of the product was obtained.

III. Conclusion

We found the reaction conditions that can be used to synthesize practical purity of **4** with high yield and low recovery of **2** (< 5%). In addition, we have developed new experimental methods that can be applicable to large classroom and to synthesis of methylbenzene-1-sulfonic acids hydrate that can be used as a catalyst in esterification. This finding can give benefits chemistry teachers who are struggling with the experimental methods of esterification and the lack of methylbenzene-1-sulfonic acids hydrate as a catalyst.

IV. Experimental section

1. General

All reagents and solvents were of reagents grade quality and purchased commercially. Structure of synthetic compounds were confirmed by ^{1}H and ^{13}C NMR spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AVANCE III instrument operating at 400.13 and 100.62 MHz, respectively. Chemical shifts were referenced to TMS in $CDCl_3$ as internal standard. Benzoic acid (16.6 mg, 0.136 mmol) was used for the reference substance of ERETIC2.[16] The yield of dodecyl benzoate and recovery of dodecan-1-ol were calculated from their concentrations. Thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Microwave-assisted synthesis was carried out using a Monowave 50 (Anton Paar, Austria) and a water bath shaker (TAITEC PERSONAL-11EX, Japan) was used in shaker-assisted synthesis.

2. Determinations for yield of dodecyl benzoate and for recovery of dodecan-1-ol

Benzoic acid (1.240–4.960 g, 10.154–40.616 mmol, 1.00–4.00 equiv) and 4-methylbenzene-1-sulfonic acid hydrate (0.251 g, 1.320 mmol, 0.13 equiv) was added to dodecan-1-ol (2.20 mL, 1.8920 g, 10.154 mmol, 1.00 equiv) in a beaker (50 mL). After had been stirred for 40 min at 110 °C in an oil bath, the mixture was cooled with an ice-water bath and dissolved with chloroform (90 mL) and thence washed with saturated aqueous solution of sodium hydrogen carbonate (30 mL x 3) and saturated aqueous solution of sodium chloride (30 mL x 3), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give a crude product. The product (16.4 mg–16.7 mg) was transferred to a volumetric flask (1 mL) and diluted with $CDCl_3$ until the solution became 1 mL. The solution was transferred to a NMR tube. The concentration of **1**, **2**, **3**, and **4** were determined from integral value of ^{1}H NMR spectra by ERETIC2 with using the reference substance (benzoic acid).

3. Oil bath and test tube-assisted synthesis of dodecyl benzoate

4-Methylbenzene-1-sulfonic acid hydrate (0.19 g, 0.98 mmol, 0.10 equiv) was added to a mixture of benzoic acid (1.19 g, 9.75 mmol, 1.00 equiv) and dodecan-1-ol (2.20 mL, 1.83 g, 9.82 mmol, 1.00 equiv) in a beaker (50 mL). The mixture was then stirred at 110 °C for 40 min in an oil bath. After had been cooled with an ice-water bath, the mixture was transferred to a test tube (20 mL) and washed using saturated aq $NaHCO_3$ (5 mL x 3) and saturated aq NaCl (5 mL x 3). After the aqueous layer had been removed using a Pasteur pipette, the organic layer was dried under reduced pressure to give a crude product. The product (16.4 mg–16.7 mg) was transferred to a volumetric flask (1 mL) and diluted with $CDCl_3$ until the solution became 1 mL. The solution was transferred to a NMR tube. The concentration of **2** and **4** were determined from integral value of ^{1}H NMR spectra by ERETIC2 with using the reference substance (benzoic acid).

4. Shaker and test tube-assisted synthesis of dodecyl benzoate

4-Methylbenzene-1-sulfonic acid hydrate (0.17g, 0.98 mmol, 0.10 equiv) was added to a mixture of benzoic acid (2.40 g, 19.64 mmol, 2.00 equiv) and dodecan-1-ol (2.2 mL, 1.83 g, 9.82 mmol, 1.00 equiv) in a beaker (50 mL). The mixture was then shaken at 80 °C for 1 h in a shaker. After had been cooled with an ice-water bath, the mixture was transferred to a test tube and washed using saturated aq $NaHCO_3$ (5 mL x 8) and saturated aq NaCl (5 mL x 2). Then, the aqueous layer had been removed using a Pasteur pipette to give a crude product.

5. Application of shaker and test tube-assisted synthesis of dodecyl benzoate

Benzoic acid (1.80–3.60 g, 14.7–29.5 mmol, 1.50–3.00 equiv) and 4-methylbenzene-1-sulfonic acid hydrate (0.17 g, 0.98 mmol, 0.10 equiv) was added to dodecan-1-ol (2.20 mL, 1.83 g, 9.82 mmol, 1.00 equiv) in a beaker (50 mL). After had been shaken for 2 h at 80 °C in a shaker, the mixture was cooled to room temperature and added saturated aq $NaHCO_3$

(5 mL). The mixture was then transferred to a test tube and manually shaken for 1min. After the aqueous layer had been removed using a Pasteur pipette, saturated aq NaCl (5 mL) was added to the test tube and thence manually shaken for 1 min. The aqueous layer was removed from the test tube using the Pasteur pipette leaving the organic layer that was a crude product.

6. Synthesis of methylbenzene-1-sulfonic acids hydrate

To a round bottom flask (200 mL) were added toluene (15 mL) and concentrated sulfuric acid (2 mL). The reaction mixture was refluxed with a return flow at the water separator for 1 h at 175 °C (oil bath temperature) and then let the mixture cool to room temperature. Two drops of water were added to the mixture and thence the precipitate was collected by filtration with suction washing with toluene. The precipitate was dried in a desiccator under reduced pressure to give a crude product (5.705g, 29.99 mmol, 80%) as pale pink solid.

7. Application of laboratory synthesized methylbenzene-1-sulfonic acids hydrate

Methylbenzene-1-sulfonic acids hydrate (0.2511g, 1.320 mmol, 0.130 equiv) was added to a mixture of benzoic acid (1.860 g, 15.231 mmol, 1.500 equiv) and dodecan-1-ol (2.20 mL, 1.89 g, 10.15 mmol, 1.00 equiv) in a beaker (50 mL). The mixture was then stirred for 40 min at 110 °C in an oil bath. After had been cooled with an ice-water bath, the organic layer was washed using saturated aq $NaHCO_3$ (30 mL x 3) and saturated aq NaCl (30 mL x 2), dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure to give a crude product (94%) as colorless oil.

8. Microwave-assisted synthesis of dodecyl benzoate

4-Methylbenzene-1-sulfonic acid hydrate (0.2511g, 1.320 mmol, 0.130 equiv) was added to a mixture of benzoic acid (1.8601 g, 15.231 mmol, 1.500 equiv) and dodecan-1-ol (2.20 mL, 1.8920 g, 10.154 mmol, 1.000 equiv) in a glass vial with a silicone cap. The vial with stirring bar was then placed in a Monowave 50 for 5–40 min at 110–180 °C. After had been allowed to reach room temperature, the organic layer was washed with saturated aq $NaHCO_3$ (30 mL x 3) and saturated aq NaCl (30 mL x 2), dried over anhydrous Na_2SO_4, and filtered. The filtrate was dried under reduced pressure to give a crude product.

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