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Quantitative Mass Balance Modelling for the Synthesis and Production of Ten High-Volume Insecticides

Ashok K. Rathoure[1,*], Anika Rathoure[2]

Abstract

This study presents a detailed quantitative mass balance analysis for the industrial synthesis and production of ten high-volume insecticides: acequinocyl, acetamiprid, acynonapyr, alpha-cypermethrin, benzpyrimoxan, bifenazate, bifenthrin, bistrifluron, broflanilide, and bromofos, focusing on material flows, process efficiencies, and environmental implications. These compounds, spanning diverse chemical classes like neonicotinoids, pyrethroids, and meta-diamides, are essential for crop protection but pose challenges due to resource-intensive syntheses and waste generation. For each insecticide, standardized manufacturing routes are modeled to yield 1 t of product, incorporating reaction chemistries (esterifications, nucleophilic substitutions, acid chloride activations), stoichiometric reactant quantities, byproducts (HCl, SO_2, salts), solvent usage (toluene, ethyl acetate), and waste streams. Calculations assume 1:1 molar ratios and near-theoretical yields, with inputs ranging from 5,444 kg (Benzpyrimoxan) to 17,803 kg (Broflanilide), dominated by solvents (up to 6,647 kg toluene) and water (up to 10,000 kg). Outputs include the target product, recovered solvents (e.g., 95% toluene recovery), losses (23–157 kg), effluents to treatment plants (up to 10,270 kg), and hazardous residues (6–613 kg) managed under regulatory frameworks like Rule 9. Key insights reveal solvent-heavy batch processes contributing 50–80% of inputs, halogenated byproducts (HCl: 30–544 kg; NaCl: up to 390 kg) amplifying toxicity risks, and multi-step syntheses (Broflanilide's four stages) exacerbating cumulative wastes. Efficiencies are evident in high mass conservation, but real-world losses from side reactions could inflate environmental footprints by 5–15%. Aligning with literature on pesticide persistence (e.g., neonicotinoid aquatic contamination), the models underscore opportunities for sustainability: catalytic alternatives to phosgene derivatives, continuous-flow reactors for solvent reduction, and waste valorization (HCl recycling). This analysis equips process engineers, regulators, and stakeholders with tools for life-cycle assessments, fostering greener agrochemical production to balance food security with ecological stewardship.

Keywords: Insecticides, mass balance, synthesis, production, agrochemicals, reaction chemistry, byproducts, environmental impact, sustainability, material flow

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INTRODUCTION

Insecticides play a crucial role in modern agriculture by protecting crops from pests, thereby ensuring food security for a growing global population. However, the production of these chemicals involves complex chemical syntheses that consume significant resources and generate byproducts, which can have environmental implications if not managed properly. Mass balance analysis is a key tool in chemical engineering to account for all materials entering and leaving a process, helping to identify inefficiencies, waste generation, and opportunities for improvement. This study focuses on ten high-volume insecticides, providing detailed quantitative mass balance models for their synthesis and production.

The selected insecticides represent a range of chemical classes and are widely used in agrochemical applications. For instance, neonicotinoids like Acetamiprid have been studied for their persistence in the environment and wastewater treatment systems. Understanding the mass balance in their production can aid in minimizing environmental releases. Similarly, pyrethroids such as Alpha-Cypermethrin and Bifenthrin require careful management of halogenated byproducts [1].

This study details the reaction chemistry, reactant quantities, product yields, and waste streams for producing 1 t of each insecticide, based on standard manufacturing processes. By quantifying inputs and outputs, including recovered solvents and effluents, the models support efforts toward sustainable production, reducing resource consumption and pollution. The analysis also draws on broader research into pesticide dynamics and environmental impacts to contextualize the findings shown in Table 1.

Table 1. The insecticide molecules considered for this research.

S.N.	Name of Insecticide	Formula	MW (g/mol)	CAS Number	Remarks
1	Acequinocyl	$C_{24}H_{32}O_4$	384.5	57960-19-7	Esterification reaction with acetyl chloride
2	Acetamiprid	$C_{10}H_{11}ClN_4$	222.67	135410-20-7	Two-step synthesis involving methylation and cyclization
3	Acynonapyr	$C_{24}H_{26}ClF_6N_2O_3$	505.93	1332838-17-1	Nucleophilic substitution with a pyridine derivative
4	Alpha-Cypermethrin	$C_{22}H_{19}Cl_2NO_3$	416.29	67375-30-8	Epimerization of cypermethrin via acid chloride intermediate
5	Benzpyrimoxan	$C_{16}H_{15}F_3N_2O_3$	340.29	1449021-97-9	Nucleophilic aromatic substitution with triethylamine
6	Bifenazate	$C_{17}H_{20}N_2O_3$	300.35	149877-41-8	Hydrazine carboxylate reaction with bromo-biphenyl
7	Bifenthrin	$C_{23}H_{22}ClF_3O_2$	422.87	82657-04-3	Esterification via acid chloride with biphenyl alcohol
8	Bistrifluron	$C_{16}H_7ClF_8N_2O_2$	446.68	201593-84-2	Urea formation via isocyanate intermediate
9	Broflanilide	$C_{25}H_{14}BrF_{11}N_2O_2$	663.28	1207727-04-5	Multi-step amide formation with multiple acid chloride steps
10	Bromofos	$C_8H_8BrCl_2O_3PS$	366.00	2104-96-3	Phosphorylation reaction with thiophosphate

ACEQUINOCYL CAS# 57960-19-7

Acequinocyl-Hydroxy reacts with Acetyl chloride to Acequinocyl.

Reaction Chemistry

Acequinocyl-Hydroxy (MF: $C_{22}H_{30}O_3$ MW: 342.5 g/mol) reacts with Acetyl chloride (MF: C_2H_3ClO MW: 78.5g/mol) to form Acequinocyl (MF: $C_{24}H_{32}O_4$ MW: 384.5 g/mol) and HCl as a byproduct, shown in Figure 1 [2].

$$C_{22}H_{30}O_3 + C_2H_3ClO \rightarrow C_{24}H_{32}O_4 + HCl$$

Reactants

Acequinocyl-Hydroxy:

- *Molecular Formula (MF):* $C_{22}H_{30}O_3$
- *Molecular Weight (MW):* 342.5 g/mol

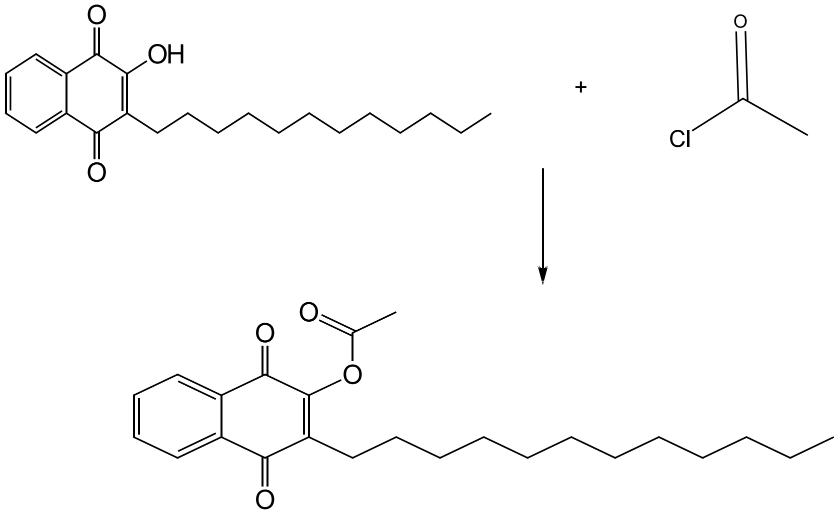


Figure 1. Acequinocyl-Hydroxy reacts with acetyl chloride to form acequinocyl.

Acetyl chloride:

- *Molecular formula (MF):* C_2H_3ClO
- *Molecular weight (MW):* 78.5 g/mol

Product

Acequinocyl:

- *Molecular formula (MF):* $C_{24}H_{32}O_4$
- *Molecular weight (MW):* 384.5 g/mol

Mass Balance

Calculate Moles of Acequinocyl:

$$Moles\ of\ acequinocyl = \frac{Mass}{Molecular\ weight} = \frac{1000g}{384.5g/mol} \times \frac{1000g}{1kg} = 2{,}605.3\ mol$$

Moles of Reactants Needed: 2,605.3 mol

Assuming a 1:1 molar ratio for the reaction.

Mass of Reactants

Acequinocyl-Hydroxy =2,605.3 mol×342.5 g/mol=892,340.25 g=892.34 kg
Acetyl chloride =2,605.3 mol×78.5 g/mol=204,717.05 g=204.72 kg
Molar mass of HCl is 36.5 g/mol
Mass of HCl=95,115.45 g=95.12 kg
30% HCl Solution =316.75 kg

Table 2. Mass balance of acequinocyl.

Input (kg)		**Output (kg)**		**Remarks**
Acequinocyl-Hydroxy	892.34	Acequinocyl	1000	Product
Acetyl chloride	204.72	TEA HCL	358	By-Product /Under rule 9
Triethyl amine (TEA)	286	Ethyl acetate	950	Recovered
Ethyl acetate	1000	Ethyl acetate	50	Loss
Water	5000	Salt	70.06	To TSDF
Water for HCl	252	Residue	35	Co-processing/Under Rule 9
-	-	Effluent	5172	To ETP
Total	*7635.06*	*Total*	*7635.06*	-

Table 2 shows the mass balance for the Acequinocyl manufacturing process, where total input and output are balanced at 7635.06 kg. The main product is Acequinocyl (1000 kg), with recovered materials, byproducts, and effluent managed as per environmental norms. This ensures efficient resource utilization and compliance with regulatory requirements.

ACETAMIPRID CAS# 135410-20-7

Manufacturing Process

2-Chloro-5-chloromethylpyridine reacts with methylamine under pressure and forms 6-chloro-N-methyl-3-pyridinemethanamine, as shown in Figure 2.

6-chloro-N-methyl-3-pyridinemethanamine reacts with Ethyl N-cyanoacetimidate and forms Acetamiprid, as shown in Figure 3 [3].

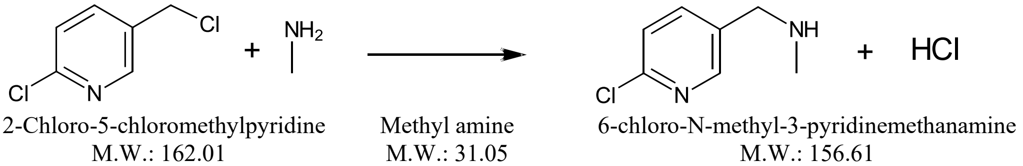


Figure 2. 2-Chloro-5-chloromethylpyridine reacts with Methyl amine under pressure and forms 6-chloro-N-methyl-3-pyridinemethanamine.

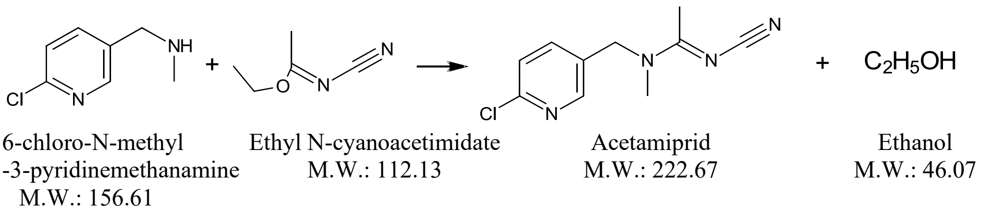


Figure 3. 6-chloro-N-methyl-3-pyridinemethanamine reacts with Ethyl N-cyanoacetimidate and forms Acetamiprid.

Step 1: Formation of 6-chloro-N-methyl-3-pyridinemethanamine

Reaction

- 2-Chloro-5-chloromethylpyridine (MW: 162.01) reacts with Methylamine (MW: 31.05) under pressure to form 6-chloro-N-methyl-3-pyridinemethanamine (MW: 156.61).

Equation:

$C_6H_5Cl_2N+CH_3NH_2$-------$\rightarrow C_7H_9ClN_2+HCl$

Byproduct: Hydrogen Chloride (HCl)

Step 2: Formation of Acetamiprid

Reaction

6-chloro-N-methyl-3-pyridinemethanamine (MW: 156.61) reacts with Ethyl N-cyanoacetimidate (MW: 112.13) to form Acetamiprid (MW: 222.67).

Equation

$C_7H_9ClN_2+C_5H_8N_2O$---------$\rightarrow C_{10}H_{11}ClN_4+C_2H_6O$

Byproduct: Ethanol (C_2H_6O)

Step 1:

Reactants

- 2-Chloro-5-chloromethylpyridine: 725 kg
- Methylamine: 138 kg

Conditions
- React under controlled pressure and temperature.
- Collect and neutralize the HCl byproduct.

Product
- 6-chloro-N-methyl-3-pyridinemethanamine: 707 kg

Mass of HCl=4475.95 moles×36.46 g/mol=163,177.08 g=163 kg

Step 2:
Reactants:
- 6-chloro-N-methyl-3-pyridinemethanamine: 707 kg
- Ethyl N-cyanoacetimidate: 505 kg

Conditions
- React under controlled temperature.
- Separate and collect ethanol byproduct.

Product: Acetamiprid: 1,000 kg

Table 3 shows the mass balance for Acetamiprid production, where total input and output are balanced at 11,748 kg. The process yields 1000 kg of Acetamiprid as the main product, with recoveries of Ethanol and Toluene for reuse. Byproducts like HCl solution and wastes such as effluent, salt, and residue are managed as per environmental regulations, ensuring efficient and controlled material utilization.

Table 3. Mass balance of Acetamiprid.

Input (kg)		**Output (kg)**		**Remarks**
2-Chloro-5-chloromethylpyridine	725	Acetamiprid	1000	Product
Methylamine	138	Ethanol	205	By-Product
Ethyl N-cyanoacetimidate	505	Ethanol	1450	Recovered
Ethanol	1500	Ethanol Loss	50	Loss
Toluene	2000	HCl (30%) soln	543	Under Rule 9
Water	5500	Toluene	1900	recovered
Water for HCl	380	Effluent	5500	To ETP
-	-	Salt	74	To TSDF
-	-	Residue	26	Under Rule 9
Total	11748	**Total**	11748	-

ACYNONAPYR CAS# 1332838-17-1

Manufacturing Process

(1R,5S)-3-[2-Propoxy-4-(trifluoromethyl)phenoxy]-9-azabicyclo[3.3.1]nonan-9-ol react with 2-chloro-5-(trifluoromethyl)pyridine to form Acynonapyr.

Basic Chemistry

(1R,5S)-3-[2-Propoxy-4-(trifluoromethyl)phenoxy]-9-azabicyclo [3.3.1]nonan-9-ol (MF:

$C_{18}H_{24}F_3NO_3$ MW: 359.38 g/mol) reacts with 2-chloro-5-(trifluoromethyl)pyridine (MF: $C_6H_3ClF_3N$ MW: 181.54 g/mol) to form Acynonapyr, as shown in Figure 4.

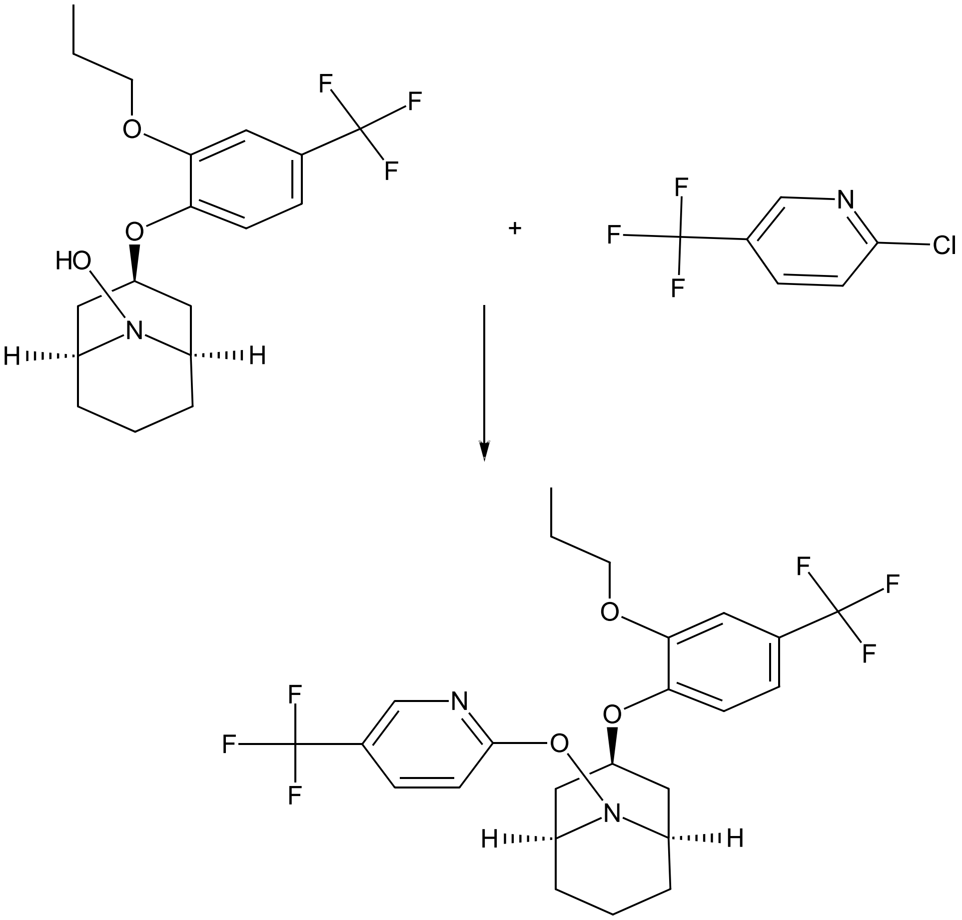


Figure 4. Basic manufacturing chemistry of acynonapyr.

Reaction
$C_{18}H_{24}F_3NO_3+C_6H_3ClF_3N$---------→$C_{24}H_{26}ClF_6N_2O_3$
Molecular Weights:
(1R,5S)-3-[2-Propoxy-4-(trifluoromethyl)phenoxy]-9-azabicyclo[3.3.1]nonan-9-ol: 359.38 g/mol
2-chloro-5-(trifluoromethyl)pyridine: 181.54 g/mol
Acynonapyr: 505.93 g/mol

Mass Balance

Calculate the moles of Acynonapyr

$$Moles\ of\ Acynonapyr = \frac{1ton\times10^6 g/ton}{505.93\ g/mol} = 1{,}976.59\ mol$$

Required starting materials

(1R,5S)-3-[2-Propoxy-4-(trifluoromethyl)phenoxy]-9-azabicyclo[3.3.1]nonan-9-ol: 1,976.59 mol×359.38 g/mol=710,107.54 g≈710.11 kg

2-chloro-5-(trifluoromethyl)pyridine: 1,976.59 mol×181.54 g/mol=358,737.65 g≈358.74 kg
Toluene is used to dissolve the reactants.
Recovery of Toluene: 1,976.59 mol×2×92.14 g/mol=364,125.17 g≈364.13 kg
95% recovery: 364.13 kg×0.95=345.92 kg

Table 4 presents the mass balance for Acynonapyr production, showing a total input and output of 9404.85 kg, confirming process equilibrium. The reaction yields 1000 kg of Acynonapyr as the main product, with Toluene (2400 kg) recovered for reuse. Waste streams such as effluent, salts, and residues are properly disposed of through TSDF and ETP as per regulatory guidelines, ensuring efficient material management and minimal losses.

Table 4. Mass balance of acynonapyr.

Input (kg)		**Output (kg)**		**Remarks**
(1R,5S)-3-[2-Propoxy-4-(trifluoromethyl) phenoxy]-9-azabicyclo [3.3.1] nonan-9-ol	710.11	Acynonapyr	1000	Product
2-chloro-5-(trifluoromethyl)pyridine	358.74	Toluene	2400	Recovered
K_2CO_3	286	Toluene	100	Loss
Toluene	2500	Salt	47.85	To TSDF
KBr	50	Effluent	5500	To ETP
Water	5500	KCl	50	To TSDF
	-	$KHCO_3$	286	To TSDF
	-	Residue	21	Rule 9
Total	*9404.85*	*Total*	*9404.85*	-

ALPHA-CYPERMETHRIN CAS# 67375-30-8

Cis-DVA reacts with Thionyl chloride to form acid chloride, and this acid chloride reacts with m-phemoxybenzaldehyde and sodium cyanide to form Cypermethrin. Cypermethrin undergoes an epimerization reaction to form Alpha Cypermethrin, as shown in Figure 5 [4].

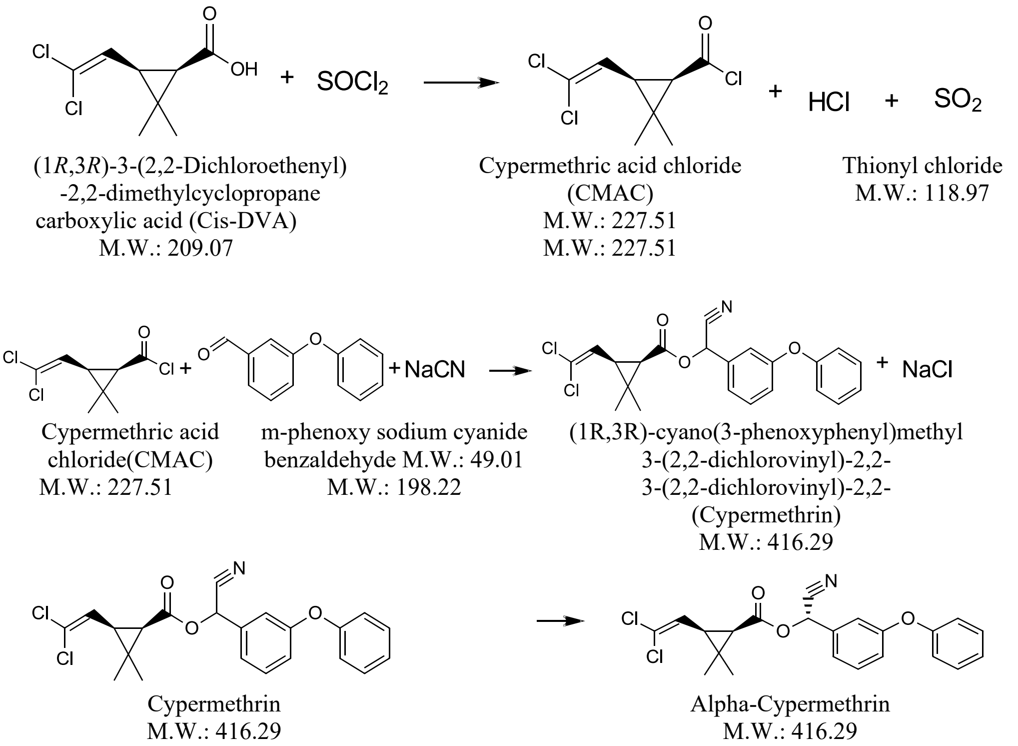


Figure 5. Route of synthesis of alpha-cypermethrin.

Route of Synthesis

1. Formation of Cypermethric Acid Chloride (CMAC):
   Cis-DVA+Thionyl chloride ($SOCl_2$)→Cypermethric Acid Chloride (CMAC)+HCl+SO_2
   $C_8H_{10}Cl_2O_2+SOCl_2 \rightarrow C_8H_8Cl_2OCl+HCl+SO_2$
   Molecular Weights:

- Cis-DVA: 209.07 g/mol
- Thionyl Chloride ($SOCl_2$): 118.97 g/mol
- CMAC: 227.51 g/mol

2. Formation of Cypermethrin:
   CMAC+m-Phenoxybenzaldehyde+Sodium Cyanide (NaCN)→Cypermethrin+NaCl
   $C_8H_9Cl_3O+C_{13}H_{10}O_2+NaCN\rightarrow C_{22}H_{19}Cl_2NO_3+NaCl$
   Molecular Weights:
   - CMAC: 227.51 g/mol
   - m-Phenoxybenzaldehyde: 198.22 g/mol
   - Sodium Cyanide (NaCN): 49.01 g/mol
   - Cypermethrin: 416.29 g/mol
3. Epimerization to Alpha-Cypermethrin:
   $$Cypermethrin \xrightarrow{Epimerization} Alpha - Cypermethrin$$
   No change in molecular weight (416.29 g/mol).
   Moles of Alpha-Cypermethrin (1000 kg×1000 g/kg)/416.29 g/mol =2401.63 moles

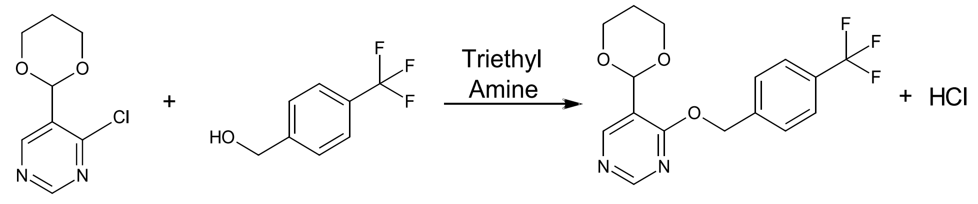
i. *Cis-DVA: MW: 209.07 g/mol*
   Required for 1 t of Alpha-Cypermethrin:
   $$\frac{1000kg \times 209.07}{416.29} = 501.86\ kg$$
ii. *Thionyl Chloride ($SOCl_2$): MW: 118.97 g/mol*
   Required for 1 t of Alpha-Cypermethrin:
   $$\frac{501.86\ kg \times 118.97}{209.07} = 285.77\ kg$$
iii. *m-Phenoxybenzaldehyde: MW: 198.22 g/mol*
   Required for 1 t of Alpha-Cypermethrin:
   $$\frac{1000\ kg \times 198.22}{416.29} = 475.97\ kg$$
4. Sodium Cyanide (NaCN): MW: 49.01 g/mol
   Required for 1 t of Alpha-Cypermethrin:
   $$\frac{1000\ kg \times 49.01}{416.29} = 117.63\ kg$$

Mass of NaCl=2401.63 moles×58.44 g/mol=140,289.97 g=140.29 kg
Mass of HCl=2401.63 moles×36.46 g/mol=87,503.47 g=87.50 kg
Mass of SO_2=2401.63 moles×64.07 g/mol=153,883.37 g=153.88 kg

Table 5 shows the mass balance for Alpha-Cypermethrin production, where total input and output are balanced at 15,913.23 kg. The process produces 1000 kg of Alpha-Cypermethrin as the main product, with Hexane (1950 kg) recovered for reuse. Byproducts and wastes such as HCl solution, $NaHSO_3$, salts, and residues are safely managed under Rule 9 or sent to TSDF/ETP, ensuring efficient material utilization and environmental compliance.

BENZPYRIMOXAN CAS #1449021-97-9

4-(Trifluoromethyl)benzyl alcohol reacts with the intermediate in the presence of triethylamine to form Benzpyrimoxan, as shown in Figure 6 [5].



4-chloro-5-(1,3-dioxan-2-yl)
Pyrimidine (Intermediate)

4-(Trifluoromethyl)benzyl
alcohol
M.W.-176.14

Benzpyrimoxan
M.W.- 340.29

Figure 6. Route of synthesis of benzpyrimoxan.

Table 5. Mass balance of alpha cypermethrin.

Input (kg)		**Output (kg)**		**Remarks**
Cis-DVA	501.86	Alpha-Cypermethrin	1000	Product
Thionyl Chloride	285.77	HCl $_{30\%}$ Soln	292	Under Rule 9
m-Phenoxybenzaldehyde	475.97	$NaHSO_{3\ (25\%)}$	997	Under Rule 9
Sodium Cyanide	117.63	Hexane	1950	Recovered
Hexane	2000	Hexane	50	Loss
NaOCl	1000	TEA Salt	487.5	To TSDF
TEA (triethylamine)	400	Effluent	10270	To ETP
TEBAcl	25	Residue	157	Under Rule 9
Water	10000	Salt	319.73	To TSDF
Acetic acid	10	NaCl	390	To TSDF
Water for HCl	204	-	-	-
NaOH	200	-	-	
Water for NaHSO3	643	-	-	-
Na_2CO_3	50	-	-	-
Total	**15913.23**	**Total**	**15913.23**	-

Starting Materials

- 4-(Trifluoromethyl)benzyl alcohol ($C_8H_7F_3O$, MW: 176.14)
- 4-chloro-5-(1,3-dioxan-2-yl)pyrimidine (Intermediate)
- Triethylamine ($C_6H_{15}N$, MW: 101.19)

Reaction

- 4-(Trifluoromethyl)benzyl alcohol reacts with 4-chloro-5-(1,3-dioxan-2-yl)pyrimidine in the presence of Triethylamine.
- The reaction results in the formation of Benzpyrimoxan ($C_{16}H_{15}F_3N_2O_3$, MW: 340.29) and a byproduct of HCl.

Formation of Benzpyrimoxan

$C_8H_7F_3O+C_7H_7ClN_2O_2+C_6H_{15}N \rightarrow C_{16}H_{15}F_3N_2O_3+C_6H_{15}NHCl$

- $C_8H_7F_3O$: 4-(Trifluoromethyl)benzyl alcohol
- $C_7H_7ClN_2O_2$: 4-chloro-5-(1,3-dioxan-2-yl)pyrimidine
- $C_6H_{15}N$: Triethylamine
- $C_{16}H_{15}F_3N_2O_3$: Benzpyrimoxan
- $C_6H_{15}NHCl$: Triethylammonium chloride(TEA chloride) (byproduct)

Manufacturing Process

1. Preparation:
   - Equip the reactor with a stirrer, thermometer, and nitrogen inlet.
   - Charge the reactor with 4-(Trifluoromethyl)benzyl alcohol and 4-chloro-5-(1,3-dioxan-2-yl)pyrimidine.
   - Add Triethylamine gradually while stirring under a nitrogen atmosphere.
2. Reaction:
   - Maintain the reaction temperature between 60 and 80°C.
   - Stir the mixture for 6–8 h, monitoring the reaction progress by TLC or HPLC.
   - Once the reaction is complete, cool the mixture to room temperature.
3. Work-up:
   - Add water to the reaction mixture to precipitate the product.

  - Extract the organic layer using a suitable solvent (e.g., dichloromethane).
  - Wash the organic layer with brine, dry over anhydrous sodium sulfate, and evaporate the solvent under reduced pressure.
4. Purification:
  - Purify the crude product by recrystallization or column chromatography to obtain pure Benzpyrimoxan [6].

Raw Material Requirement

4-(Trifluoromethyl)benzyl alcohol: Molecular Weight: 176.14 g/mol

$$\frac{1000kg}{340.29g\ /\ mol} \times 176.14g/mol = 517kg$$

4-chloro-5-(1,3-dioxan-2-yl)pyrimidine: Molecular Weight: ~214 g/mol

$$\frac{1000kg}{340.29g\ /\ mol} \times 214g/mol = 628.88kg$$

Triethylamine: Molecular Weight: 101.19 g/mol

$$\frac{1000kg}{340.29g\ /\ mol} \times 101.19g/mol = 297.25kg$$

Table 6. Mass balance of benzpyrimoxan.

Input (kg)		Output (kg)		Remarks
4-(Trifluoromethyl)benzyl alcohol	517.63	Benzpyrimoxan	1000	Product
4-chloro-5-(1,3-dioxan-2-yl) pyrimidine	628.88	TEA chloride	404.46	By-Product
Triethylamine	297.25	Effluent	2039.3	To ETP
Toluene	2000	Toluene	1950	Recovered
Water	2000	Toluene	50	Loss
Total	*5443.76*	*Total*	*5443.76*	-

Table 6 presents the mass balance for benzpyrimoxan production, with total input and output balanced at 5443.76 kg. The process yields 1000 kg of benzpyrimoxan as the main product, while TEA chloride (404.46 kg) is generated as a byproduct. Toluene (1950 kg) is efficiently recovered for reuse, and effluent (2039.3 kg) is directed to the ETP, indicating effective resource recovery and controlled waste management.

BIFENAZATE CAS# 149877-41-8

Manufacturing Process

3-Bromo-4-methoxybiphenyl reacts with propan-2-yl hydrazinecarboxylate to form bifenazate, as shown in Figure 7.

Basic Chemistry

3-Bromo-4-methoxybiphenyl (MF: $C_{13}H_{11}BrO$ MW: 263.13 g/mol) reacts with propan-2-yl hydrazinecarboxylate (MF: $C_4H_{10}N_2O_2$ MW: 118.13 g/mol) to form bifenazate (MF: $C_{17}H_{20}N_2O_3$ MW: 300.35 g/mol) [7].

Synthesis Reaction

$$C_{13}H_{11}BrO + C_4H_{10}N_2O_2 \rightarrow C_{17}H_{20}N_2O_3 + HBr$$

Reactants

- 3-Bromo-4-methoxybiphenyl ($C_{13}H_{11}BrO$, MW: 263.13 g/mol)
- Propan-2-yl hydrazinecarboxylate ($C_4H_{10}N_2O_2$, MW: 118.13 g/mol)
- The reaction may be carried out in a suitable organic solvent such as ethanol or acetonitrile under reflux conditions.

- A base like sodium carbonate or potassium carbonate is often used to neutralize the hydrogen bromide (HBr) byproduct.

Product: Bifenazate ($C_{17}H_{20}N_2O_3$, MW: 300.35 g/mol)
Byproduct: Hydrogen bromide (HBr)

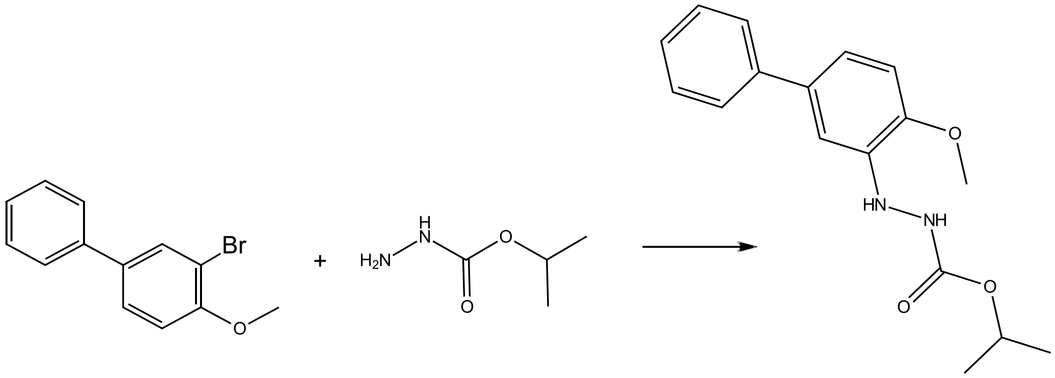


Figure 7. Route of synthesis of bifenazate.

Molecular Weights

3-Bromo-4-methoxybiphenyl ($C_{13}H_{11}BrO$): 263.13 g/mol
Propan-2-yl hydrazinecarboxylate ($C_4H_{10}N_2O_2$): 118.13 g/mol
Bifenazate ($C_{17}H_{20}N_2O_3$): 300.35 g/mol

Moles of Bifenazate Needed:

$$Moles\ of\ bifenazate = \frac{1000kg}{300.35g/mol} \times 1000g/kg \approx 3329.59mol$$

1 mol of 3-Bromo-4-methoxybiphenyl reacts with 1 mol of propan-2-yl hydrazinecarboxylate to produce 1 mol of Bifenazate.

Mass of 3-Bromo-4-methoxybiphenyl=3329.59 mol×263.13 g/mol≈875.63 kg

Mass of Propan-2-yl hydrazinecarboxylate=3329.59 mol×118.13 g/mol≈393.30 kg

Table 7 shows the mass balance for Bifenazate production, with total input and output balanced at 5768.93 kg. The process produces 1000 kg of Bifenazate as the main product, while KBr (400 kg) is formed as a byproduct. Ethyl acetate (1450 kg) is recovered for reuse, and waste materials such as effluent, salt, and residue are managed through ETP and TSDF, ensuring efficient recovery and safe disposal.

Table 7. Mass balance of bifenazate.

Input (kg)		**Output (kg)**		**Remarks**
3-Bromo-4-methoxybiphenyl	875.63	Bifenazate	1000	Product
Propan-2-yl hydrazinecarboxylate	393.30	KBr	400	Byproduct
K_2CO_3	500	Ethyl acetate	1450	Recovered
Ethyl acetate	1500	Ethyl acetate	50	Loss
Water	2500	$KHCO_3$	235	-
-	-	Salt	100.93	To TSDF
-	-	Residue	33	Rule 9
-	-	Effluent	2500	To ETP
Total	*5768.93*	*Total*	*5768.93*	-

BIFENTHRIN CAS# 82657-04-3

λ-cyhalothric acid reacts with thionyl chloride to form an acid chloride, and this acid chloride reacts with 3-hydroxymethyl-2-methyl-biphenyl to form bifenthrin in Figure 8 [8].

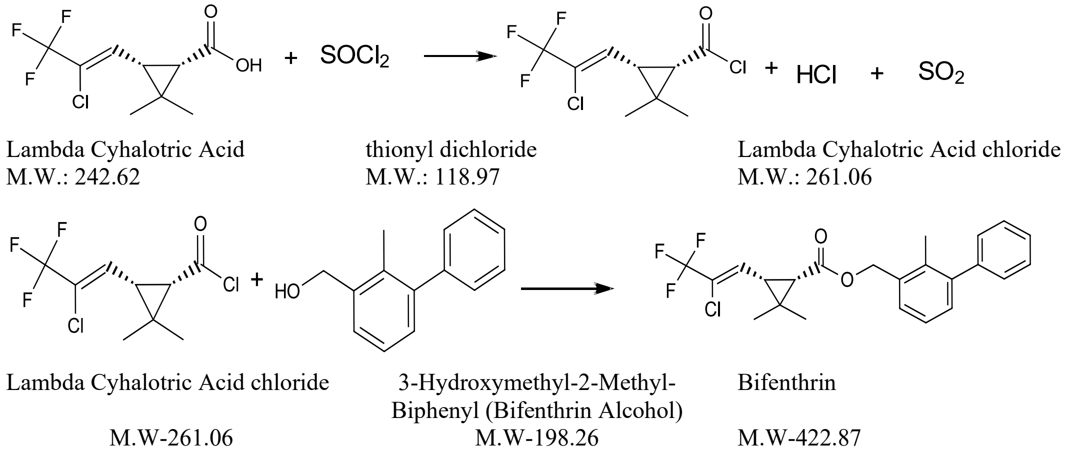


Figure 8. Route of synthesis of bifenthrin.

Step 1: Formation of Lambda Cyhalothric Acid Chloride

λ-Cyhalothric Acid ($C_9H_{10}ClF_3O_2$)+Thionyl Chloride ($SOCl_2$)-----→Lambda Cyhalotric Acid Chloride ($C_9H_9Cl_2F_3O$)+HCl+SO_2

Molecular Weights:

- λ-Cyhalothric Acid: 242.62 g/mol
- Thionyl Chloride ($SOCl_2$): 118.97 g/mol
- Lambda Cyhalotric Acid Chloride: 261.06 g/mol
- Byproducts: HCl (36.46 g/mol), SO_2 (64.06 g/mol)

Step 2: Formation of Bifenthrin

Lambda Cyhalotric Acid Chloride ($C_9H_9Cl_2F_3O$)+Bifenthrin Alcohol ($C_{14}H_{14}O$)→Bifenthrin ($C_{23}H_{22}ClF_3O_2$)

Molecular Weights:

- Lambda Cyhalotric Acid Chloride: 261.06 g/mol
- Bifenthrin Alcohol: 198.26 g/mol
- Bifenthrin: 422.87 g/mol

Manufacturing Process

Step 1: Preparation of Lambda Cyhalotric Acid Chloride

- λ-Cyhalothric Acid is charged into a reactor.
- Thionyl Chloride is added gradually with stirring.
- The reaction is maintained at a suitable temperature (typically around 60–80°C) until completion.
- The reaction mixture is then cooled, and the byproducts (HCl and SO_2) are removed, yielding Lambda Cyhalotric Acid Chloride.

Step 2: Synthesis of Bifenthrin

- Lambda Cyhalotric Acid Chloride is reacted with Bifenthrin Alcohol.
- The reaction is carried out at a controlled temperature, typically in the range of 50–70°C, under an inert atmosphere (e.g., nitrogen).
- After completion, the mixture is cooled, and Bifenthrin is isolated through standard purification techniques such as crystallization or distillation [9].

Raw Material Requirement

Lambda Cyhalotric Acid Calculation:

$$Required\ amount = \frac{1000kg \times 242.62g/mol}{422.87g/mol} \approx 573.64kg$$

Thionyl Chloride Calculation:

$$Required\ amount = \frac{573.64kg \times 118.97g/mol}{242.62g/mol} \approx 281.47kg$$

Required amount =

Bifenthrin Alcohol Calculation:

$$Required\ amount = \frac{1000kg \times 198.26g/mol}{422.87g/mol} \approx 468.82kg$$

Weight of SO_2=2,364.81 moles×64.06 g/Mol=151,477.04 g=151.48 kg

Weight of HCl=2,364.81 moles×36.46 g/Mol=86,214.44 g=86.21 kg

NaCl produced: 150.93 kg

Table 8 presents the mass balance for Bifenthrin production, with total input and output balanced at 15,863.93 kg. The process yields 1000 kg of Bifenthrin as the main product, while Hexane (2900 kg) is recovered for reuse. Byproducts such as HCl and $NaHSO_3$ solutions and wastes, including effluent, salt, and residue, are managed under Rule 9, ETP, and TSDF, ensuring efficient material utilization and compliance with environmental standards.

Table 8. Mass balance of bifenthrin.

Input (kg)		***Output (kg)***		***Remarks***
λ-Cyhalothric Acid	573.64	Bifenthrin	1000	Product
Thionyl Chloride	281.47	HCl 30% solution	287	Under Rule 9
Bifenthrin Alcohol	468.82	$NaHSO_3$ 25% soln	981	Under Rule 9
Water	10000	Hexane	2900	Recovered
Water for HCl	200	Hexane	100	Loss
TEBAcl	25	Catalyst	50	-
Sodium Carbonate	50	Effluent	10000	To ETP
NaOCl	100	NaCl	150.93	-
Acetic Acid	10	Residue	264	Under Rule 9
Hexane	3000	Salt	131	To TSDF
Sodium carbonate	275	-	-	-
Catalyst	50	-	-	-
Water for $NaHSO_3$	633	-	-	-
NaOH	197	-	-	-
Total	*15863.93*	*Total*	*15863.93*	-

BISTRIFLURON CAS# 201593-84-2

2,6-difluorobenzamide react with Triphosgene to from 2,6-difluorobenzoyl isocyanate then 2,6-difluorobenzoyl isocyanates react with 2-chloro-3,5-bis(trifluoromethyl)aniline to from Bistrifluron [10].

Basic Chemistry

Step 1: 2,6-difluorobenzamide (MF: $C_7H_5F_2NO$; MW: 157.12 g/mol) reacts with Triphosgene (MF: $C_3Cl_6O_3$; MW: 296.7 g/mol) to form 2,6-difluorobenzoyl isocyanate (MF: $C_8H_3F_2NO_2$; MW: 183.11 g/mol) and HCl as a byproduct.

2,6-Difluorobenzamide + Triphosgene--------→2,6-Difluorobenzoyl Isocyanate + HCl

$C_7H_5F_2NO + C_3Cl_6O_3 \rightarrow C_8H_3F_2NO_2 + 2HCl + 2COCl_2$

STEP 2: 2,6-difluorobenzoyl isocyanate (MF: $C_8H_3F_2NO_2$; MW: 183.11 g/mol) reacts with 2-chloro-3,5-bis(trifluoromethyl)aniline (MF: $C_8H_4ClF_6N$; MW: 263.57 g/mol) to form Bistrifluron (MF: $C_{16}H_7ClF_8N_2O_2$; MW: 446.68 g/mol) in Figure 9.

$C_8H_3F_2NO_2 + C_8H_4ClF_6N \rightarrow C_{16}H_7ClF_8N_2O_2$

2,6-Difluorobenzoyl Isocyanate +2-Chloro-3,5-bis(trifluoromethyl)aniline ----→Bistrifluron

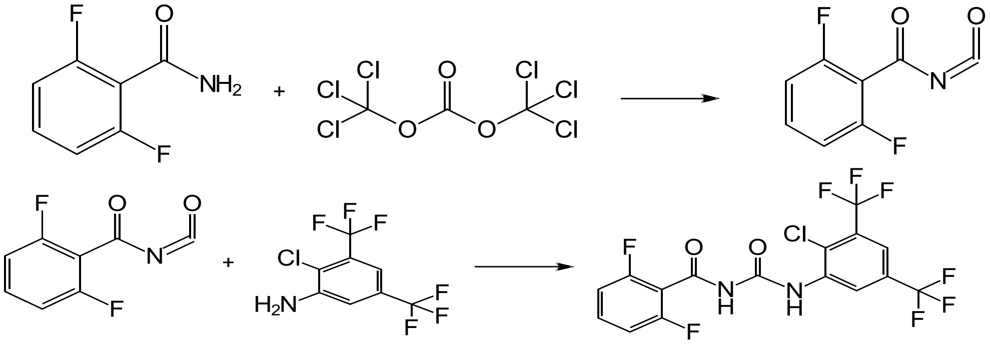


Figure 9. Route of synthesis bistrifluron.

Step 1: Synthesis of 2,6-Difluorobenzoyl Isocyanate

Molar Masses:

2,6-Difluorobenzamide: 157.12 g/mol

Triphosgene: 296.7 g/mol

2,6-Difluorobenzoyl Isocyanate: 183.11 g/mol

Step 2: Synthesis of Bistrifluron

Molar Masses:

- *2,6-Difluorobenzoyl Isocyanate:* 183.11 g/mol
- *2-Chloro-3,5-bis(trifluoromethyl)aniline:* 263.57 g/mol
- *Bistrifluron:* 446.68 g/mol

Required Moles of Bistrifluron

The required moles of Bistrifluron are calculated by converting 1000 kg to grams (1,000 kg = 1×10^6 g) and dividing by its molecular weight (446.68 g/mol). Thus, producing 1000 kg of Bistrifluron requires about 2240 moles.

$$Moles\ of\ bistrifluron = \frac{1000kg}{446.68g/mol} \times \frac{10^6 g}{1kg} \approx 2239.89\, mol$$

Reactant Quantities

2,6-Difluorobenzamide: 2239.89 mol×157.12 g/mol≈352 kg

Triphosgene (1/3 moles): 1/3×2239.89 mol×296.7 g/mol≈1/3×664.68 kg=221.56 kg

2-Chloro-3,5-bis(trifluoromethyl)aniline: 2239.89 mol×263.57 g/mol≈590.56 kg

Solvent *(Toluene):* Toluene is typically used in excess to ensure the dissolution of intermediates and reaction completion. 5:1 ratio by mass to the limiting reactant (Triphosgene):

Mass of Toluene required≈664.68×10=6646.8 kg=6647 kg

Byproducts

Moles of HCl=2239.89 mol×2=4479.78 mol

Molar mass of HCl =36.46 g/mol
Mass of HCl=4479.78 mol×36.46 g/mol=163,326.67 g=163.33 kg (2 Moles)

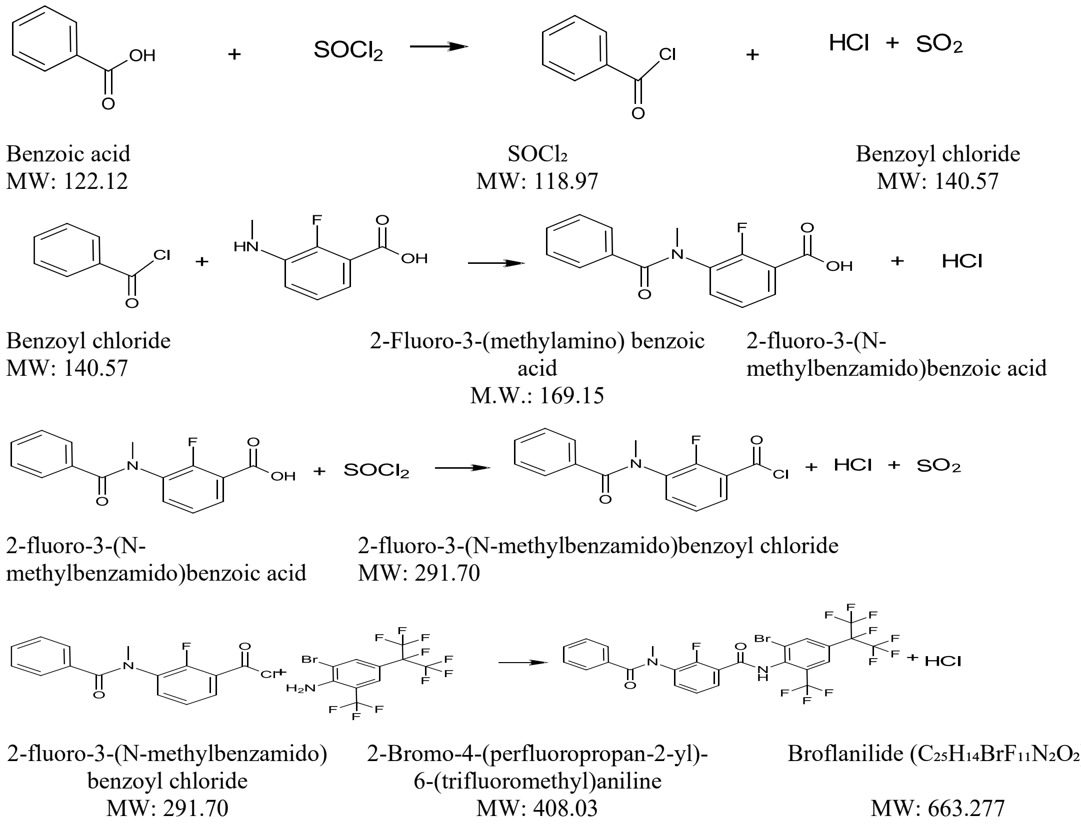
Table 9 shows the mass balance for Bistrifluron production, where total input and output are balanced at 11,191.12 kg. The process yields 1000 kg of Bistrifluron as the final product, with Toluene (6540 kg) efficiently recovered for reuse. HCl solution and residue are managed under Rule 9, while effluent (3000 kg) is sent to the ETP, ensuring proper waste treatment and resource recovery.

Table 9. Mass balance of bistrifluron.

Input (kg)		**Output (kg)**		**Remarks**
2,6-Difluorobenzamide	352	Bistrifluron	1000	Product
Tri-phosgene	221.56	HCl $_{30\%}$ Soln	544	Under Rule 9
2-Chloro-3,5-bis (trifluoromethyl)aniline	590.56	Toluene	6540	Recovered
Toluene	6647	Toluene	101	Loss
Water	3000	Residue	6.12	Under Rule 9
Water for HCl	380	Effluent	3000	To ETP
Total	*11191.12*	*Total*	*11191.12*	-

BROFLANILIDE CAS# 1207727-04-5

Benzoic acid reacts with thionyl chloride and forms its acid chloride in Figure 10. This acid chloride reacts with 2-Fluoro3-(methylamino) benzoic acid to form 2-fluoro-3-(N-methylbenzamido)benzoic acid, 2-fluoro-3-(N-methylbenzamido)benzoic acid further react with Thionyl chloride to form its acid chloride, and this acid chloride reacts with 2-Bromo-4-(perfluoropropan-2-yl)-6-(trifluoromethyl) aniline to form Broflanilid [11].



Benzoic acid
MW: 122.12

$SOCl_2$
MW: 118.97

Benzoyl chloride
MW: 140.57

Benzoyl chloride
MW: 140.57

2-Fluoro-3-(methylamino) benzoic acid
M.W.: 169.15

2-fluoro-3-(N-methylbenzamido)benzoic acid

2-fluoro-3-(N-methylbenzamido)benzoic acid

2-fluoro-3-(N-methylbenzamido)benzoyl chloride
MW: 291.70

2-fluoro-3-(N-methylbenzamido) benzoyl chloride
MW: 291.70

2-Bromo-4-(perfluoropropan-2-yl)-6-(trifluoromethyl)aniline
MW: 408.03

Broflanilide ($C_{25}H_{14}BrF_{11}N_2O_2$)
MW: 663.277

Figure 10. Route of synthesis of broflanilide.

Formation of Benzoyl Chloride

Reaction: Benzoic acid ($C_7H_6O_2$, MW: 122.12) reacts with Thionyl chloride ($SOCl_2$, MW: 118.97) to form Benzoyl chloride (C_7H_5ClO, MW: 140.57).

$C_7H_6O_2+SOCl_2 \rightarrow C_7H_5ClO+HCl+SO_2$

Formation of 2-fluoro-3-(N-methylbenzamido)Benzoic Acid

Reaction: Benzoyl chloride (C_7H_5ClO, MW: 140.57) reacts with 2-Fluoro-3-(methylamino)benzoic acid ($C_8H_8FNO_2$, MW: 169.15) to form 2-fluoro-3-(N-methylbenzamido)benzoic acid.

$C_7H_5ClO+C_8H_8FNO_2 \rightarrow C_{15}H_{13}FNO_3+HCl$

Formation of 2-fluoro-3-(N-methylbenzamido)Benzoyl Chloride

Reaction: 2-fluoro-3-(N-methylbenzamido)benzoic acid reacts with Thionyl chloride ($SOCl_2$) to form 2-fluoro-3-(N-methylbenzamido)benzoyl chloride ($C_{15}H_{11}ClFNO_2$, MW: 291.70).

$C_{15}H_{13}FNO_3+SOCl_2 \rightarrow C_{15}H_{11}ClFNO_2+HCl+SO_2$

Formation of Broflanilide

Reaction: 2-fluoro-3-(N-methylbenzamido)benzoyl chloride ($C_{15}H_{11}ClFNO_2$) reacts with 2-Bromo-4-(perfluoropropan-2-yl)-6-(trifluoromethyl)aniline ($C_{10}H_4BrF_{10}N$, MW: 408.03) to form Broflanilide ($C_{25}H_{14}BrF_{11}N_2O_2$, MW: 663.277).

$C_{15}H_{11}ClFNO_2+C_{10}H_4BrF_{10}N \rightarrow C_{25}H_{14}BrF_{11}N_2O_2+HCl$

Manufacturing Process

Stage 1: Production of Benzoyl Chloride

- Mix Benzoic acid with Thionyl chloride in a reaction vessel.
- Maintain the temperature to control the exothermic reaction.
- Collect the Benzoyl chloride after the completion of the reaction.

Stage 2: Formation of 2-fluoro-3-(N-methylbenzamido) benzoic acid

- Add Benzoyl chloride to 2-Fluoro-3-(methylamino)benzoic acid in a reactor.
- Allow the reaction to proceed under controlled conditions.
- Isolate the 2-fluoro-3-(N-methylbenzamido)benzoic acid.

Stage 3: Conversion to 2-fluoro-3-(N-methylbenzamido)benzoyl chloride

- React the 2-fluoro-3-(N-methylbenzamido)benzoic acid with Thionyl chloride in a reactor.
- Control the reaction temperature and pressure.
- Collect the 2-fluoro-3-(N-methylbenzamido)benzoyl chloride.

Stage 4: Synthesis of Broflanilide

- React 2-fluoro-3-(N-methylbenzamido)benzoyl chloride with 2-Bromo-4-(perfluoropropan-2-yl)-6-(trifluoromethyl)aniline.
- Carry out the reaction under controlled conditions.
- Purify and isolate Broflanilide.

RAW MATERIAL REQUIREMENT

Benzoic acid ($C_7H_6O_2$, MW: 122.12)

$$Amount\ required = \frac{1000\ kg}{663.277 g/mol} \times 122.12 g/mol$$

Amount required ≈184.17 kg

Thionyl chloride ($SOCl_2$, MW: 118.97)

- For converting Benzoic acid: ≈154.88 kg
- For converting 2-fluoro-3-(N-methylbenzamido)benzoic acid: ≈113.36 kg

2-Fluoro-3-(methylamino)benzoic acid ($C_8H_8FNO_2$, MW: 169.15)
Amount required ≈255.14 kg

2-Bromo-4-(perfluoropropan-2-yl)-6-(trifluoromethyl)aniline ($C_{10}H_4BrF_{10}N$, MW: 408.03)
Amount required ≈615.32 kg

Total HCl produced =1,301.43+1,301.43+952.77+952.77=4,508.40 moles
Weight of HCl produced: 4,508.40 moles×36.46 g/mol=164,394.90 g=164.39 kg
Total SO_2 produced =1,301.43+952.77=2,254.20 moles
Weight of SO_2 produced: 2,254.20 moles×64.06 g/mol=144,432.85 g=144.43 kg

Table 10 represents a material balance for the synthesis of broflanilide, showing both the input (raw materials and reagents) and output (products, by-products, recovered solvents, effluents, and residues) in kilograms. It ensures that the total input equals the total output (17802.63 kg), confirming process consistency and compliance with Rule 9 of the hazardous and other wastes (management and transboundary movement) Rules, 2016, regarding proper waste handling and reporting (CPCB, 2016).

Table 10. Mass balance of broflanilide.

Input (kg)		**Output (kg)**		**Remarks**
Benzoic acid	184.17	Broflanilide	1000	Product
Thionyl chloride	268.24	HCl 30%	547	Rule 9
2-Fluoro-3-(methylamino)benzoic acid	255.14	$NaHSO_3$ 25%	934	Rule 9
2-Bromo-4-(perfluoropropan-2-yl)-6-(trifluoromethyl)aniline	615.32	Salt	208.63	To TSDF
Toluene	2000	Effluent	10000	To ETP
Triethyl amine	250	Toluene	1900	Recovered
Acetonitrile	2500	Toluene	100	Loss
Water	10000	Acetonitrile	2400	Recovered
Water for HCl	383	Acetonitrile	100	Loss
Water for $NaHSO_3$	604	Residue	613	Rule 9
TEBAcl	75	-	-	-
Sodium Carbonate	150	-	-	-
NaOCl	300	-	-	-
Acetic Acid	30	-	-	-
NaOH	187.76	-	-	-
Total	*17802.63*	*Total*	*17802.63*	-

BROMOFOS CAS# 2104-96-3

4-bromo-2,5-dichlorophenol reacts with Dimethyl chlorothiophosphate to form Bromofos.

Synthesis Route for Bromofos

To synthesize 1 t of Bromofos ($C_8H_8BrCl_2O_3PS$, MW: 366 g/mol) from 4-bromo-2,5-dichlorophenol ($C_6H_3BrCl_2O$, MW: 241.89 g/mol) and dimethyl chlorothiophosphate ($C_2H_6ClO_2PS$, MW: 160.56 g/mol), as shown in Figure 11.

$$C_6H_3BrCl_2O + C_2H_6ClO_2PS \rightarrow C_8H_8BrCl_2O_3PS + HCl$$

Step-by-Step Calculation

Molar Requirements

To produce 1 t (1,000,000 g) of Bromofos:

$$Moles\ of\ bromofos\ needed = \frac{1{,}000{,}000g}{366g/mol} \approx 2732.24\ moles$$

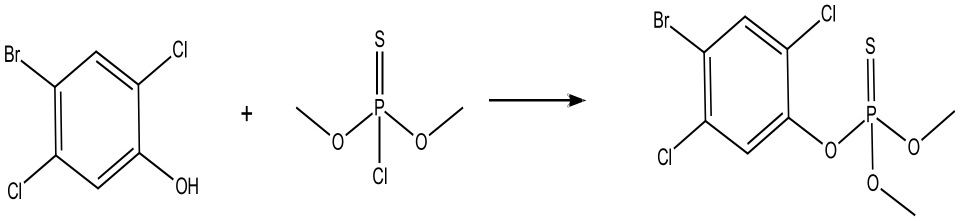
Reactants Calculation

4-bromo-2,5-dichlorophenol:

- Mass required=2732.24 moles×241.89 g/mol≈660,875.29 g≈660.88 kg
- Dimethyl chlorothiophosphate:
- Mass required=2732.24 moles×160.56 g/mol≈438,663.85 g≈438.66 kg

Byproduct: HCl:

- Mass produced=2732.24 moles×36.46 g/mol≈99,579.71 g≈99.54 kg
- 30% Soln =331 kg



4-bromo-2,5-dichlorophenol Dimethyl chlorothiophosphate Bromofos
M.Wt.:241.89 M.Wt.: 160.56 M.Wt. 366

$C_6H_3BrCl_2O$ (241.89 g/mol)+$C_2H_6ClO_2PS$ (160.56 g/mol)→$C_8H_8BrCl_2O_3PS$ (366 g/mol)+HCl

Figure 11. Route of synthesis of bromofos.

Table 11 presents the mass balance for the synthesis of Bromofos, detailing the total input and output materials (6218.54 kg each) to ensure process accountability. It includes raw materials, recovered solvents, and waste such as effluent, impurities, and residues managed as per Rule 9 of the Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016 (CPCB, 2016).

Table 11. Mass balance of bromofos.

Input (kg)		**Output (kg)**		**Remarks**
4-bromo-2,5-dichlorophenol	660.88	Bromofos	1000	Product
Dimethyl chlorothiophosphate	438.66	NaCl	274	
Toluene	654	Toluene	621	Recovered
Water	4000	Toluene	23	Loss
Water for HCl	231	Impurities	165.54	To TSDF
NaOH 48%	234	Residue	135	Under Rule 9
-	-	Effluent	4000	To ETP
Total	*6218.54*	*Total*	*6218.54*	-

This comprehensive quantitative mass balance analysis of the synthesis and production of ten high-volume insecticides: acequinocyl, acetamiprid, acynonapyr, alpha-cypermethrin, benzpyrimoxan, bifenazate, bifenthrin, bistrifluron, broflanilide, and bromofos, provides critical insights into the material flows, resource utilization, and waste generation inherent in these agrochemical manufacturing processes. By modeling the production of 1 t of each insecticide, the study reveals consistent patterns across diverse chemical classes: esterifications, nucleophilic substitutions, acid chloride formations, and urea syntheses dominate the reaction chemistries, with thionyl chloride, acetyl chloride, and triphosgene frequently employed as activating agents.

Key observations include:

- *Resource Intensity:* Total input masses ranged from approximately 5,444 kg (Benzpyrimoxan) to 17,803 kg (Broflanilide), driven largely by solvents like toluene (up to 6,647 kg) and water (up to 10,000 kg). Reactants typically constitute 20–50% of inputs, underscoring the solvent-heavy nature of these batch processes.

- *Byproduct and waste profiles:* Halogenated byproducts such as HCl (30–544 kg across processes), NaCl (up to 390 kg), and salts (up to 319 kg) are ubiquitous, often managed under regulatory frameworks like Rule 9 for hazardous waste. Effluents to effluent treatment plants (ETP) dominate outputs (up to 10,270 kg), while residues (6–613 kg) and losses (23–157 kg) highlight opportunities for recovery. Solvent recovery rates, such as 95% for toluene in Acynonapyr production, demonstrate feasible efficiency gains.
- *Efficiency and yield considerations:* Assuming 1:1 molar stoichiometries and near-theoretical yields, the models indicate strong mass conservation (total inputs equaling outputs), but real-world deviations due to side reactions or purification losses could inflate waste by 5–15%. Multi-step processes like those for Broflanilide and Alpha-Cypermethrin exhibit cumulative byproduct accumulation, amplifying environmental footprints.

These findings align with broader literature on pesticide manufacturing, where neonicotinoids like Acetamiprid contribute to aquatic contamination through incomplete treatment of process streams, and pyrethroids like Bifenthrin generate persistent halogenated residues. The analysis emphasizes the need for greener alternatives, such as catalytic activation to replace phosgene derivatives or continuous-flow reactors to minimize solvent use [12]. Implementing life-cycle assessments could further quantify carbon footprints and toxicity potentials, guiding regulatory compliance and corporate sustainability goals.

CONCLUSION

While these insecticides are vital for agricultural productivity, their production demands optimized material balances to mitigate ecological risks. Future research should explore integrated waste valorization (e.g., HCl recycling) and bio-based feedstocks, fostering a transition toward circular agrochemical economies. This work serves as a foundational tool for process engineers, policymakers, and industry stakeholders committed to balancing efficacy with environmental stewardship.

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