

# *CrossFire databases*

- ◆ **Based on the most complete databases of organic and inorganic chemistry handbooks – the Beilstein and the Gmelin handbooks**

<b>Database</b>	<b>Content</b>
<b>CrossFire Beilstein</b>	Organic chemistry from key journals (1771-) and patent documents (1886-1980)
<b>CrossFire Gmelin</b>	Inorganic and Organometallic chemistry (1772-) from key journals



# Beilstein

- ◆ Based on the famous "*Beilstein's Handbuch der Organischen Chemie*"
- ◆ Covers the literature all the way to the beginning of organic chemistry (1771-)
- ◆ Original classification by compound class (System Numbers), includes physical data for all compounds
- ◆ The largest database for **experimental** physical, spectroscopic, chemical and biological activity data



# Gmelin

- ◆ Based on the famous "*Handbuch der Anorganischen Chemie*"
- ◆ Covers the literature all the way to the beginning of inorganic chemistry
- ◆ Originally organized by elements
- ◆ The largest database for **experimental** data for ceramics, nanocrystals, clusters, complexes
- ◆ Complementary to Beilstein



# Division of labor

	Ia	IIa	IIIb	IVb	Vb	VIb	VIIb	VIIIb	Ib	IIb	IIIa	IVa	Va	VIa	VIIa	VIIIa		
1	H															He		
2	Li	Be									B	C	N	O	F	Ne		
3	Na	Mg									Al	Si	P	S	Cl	Ar		
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra																
Lan			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Act			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

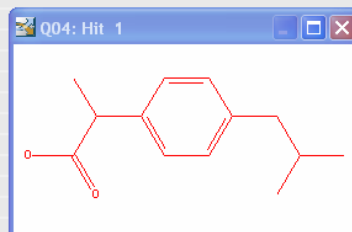
- ◆ Between 1771-1989, all elements of the periodic table were included in Beilstein. After 1979, only the elements in white are included – the remaining elements are covered in the Gmelin database.
- ◆ As such, organotransition metal compounds and complexes can be found in Gmelin.



# Data available on substances

## Field Availability List 1-10 of 52

Code	Field Name	Occ.
<a href="#">PHARM</a>	Bioactivity: Pharmacological Data	632
<a href="#">ECT</a>	Ecological Data: Ecotoxicology	29
<a href="#">ECA</a>	Ecological Data: Exposure Assessment	4
<a href="#">ECC</a>	Ecological Data: Concentration in the Environment	81
<a href="#">ECTD</a>	Ecological Data: Transport and Distribution	4
<a href="#">BIOD</a>	Ecological Data: Biodegradation	11
<a href="#">ECDH</a>	Ecological Data: Abiotic Degradation, Hydrolysis	2
<a href="#">RX</a>	Reaction	335
<a href="#">CDER</a>	Derivative	1
<a href="#">CNF</a>	Conformation	1



## Field Availability List 11-20 of 52

Code	Field Name	Occ.
<a href="#">IDA</a>	Interatomic Distances and Angles	2
<a href="#">MP</a>	Melting Point	46
<a href="#">CRYPH</a>	Crystal Phase	10
<a href="#">CSYS</a>	Crystal System	1
<a href="#">CSG</a>	Space Group	2
<a href="#">CDEI</a>	Density of the Crystal	3
<a href="#">BP</a>	Boiling Point	1
<a href="#">LIQPH</a>	Liquid Phase	1
<a href="#">CRT</a>	Critical Temperature	1
<a href="#">VP</a>	Vapour Pressure	1

## Field Availability List 21-30 of 52

Code	Field Name	Occ.
<a href="#">DEN</a>	Density of the Liquid	2
<a href="#">MEC</a>	Mechanical Properties	1
<a href="#">SDIF</a>	Self-diffusion	1
<a href="#">HFUS</a>	Enthalpy of Fusion	7
<a href="#">OTHE</a>	Other Thermochemical Data	1
<a href="#">OPT</a>	Optics	2
<a href="#">ORP</a>	Optical Rotatory Power	1
<a href="#">NMR</a>	NMR Spectroscopy	64
<a href="#">IR</a>	IR Spectroscopy	34
<a href="#">RAMAN</a>	Raman Spectroscopy	3

## Field Availability List 31-40 of 52

Code	Field Name	Occ.
<a href="#">UV</a>	UVVIS Spectroscopy	16
<a href="#">LUM</a>	Luminescence Spectroscopy	1
<a href="#">FLU</a>	Fluorescence Spectroscopy	4
<a href="#">MS</a>	Mass Spectrometry	10
<a href="#">ELCB</a>	Electrochemical Behaviour	1
<a href="#">DE</a>	Dissociation Exponent	15
<a href="#">POT</a>	Electrochemical Characteristics	1
<a href="#">FINFO</a>	Further Information	1
<a href="#">SLB</a>	Solubility (MCS)	111
<a href="#">SOLM</a>	Solution Behaviour (MCS)	44

## Field Availability List 41-50 of 52

Code	Field Name	Occ.
<a href="#">POW</a>	Partition octan-1-ol/water (MCS)	8
<a href="#">LVSM</a>	Liquid/Vapour Systems (MCS)	11
<a href="#">CPEM</a>	Complex Phase Equilibria (MCS)	1
<a href="#">LLSM</a>	Liquid/Liquid Systems (MCS)	36
<a href="#">LSSM</a>	Liquid/Solid Systems (MCS)	14
<a href="#">TRAM</a>	Transport Phenomena (MCS)	9
<a href="#">ENEM</a>	Energy Data (MCS)	7
<a href="#">ADSM</a>	Adsorption (MCS)	11
<a href="#">ASSM</a>	Association (MCS)	69
<a href="#">USE</a>	Use	5

## Field Availability List 51-52 of 52

Code	Field Name	Occ.
<a href="#">EXTID</a>	External Identifiers	1
<a href="#">CNR</a>	Reference	792

## Reaction 1 of 335

Reaction ID: 15R008 idle

# *Did you know that...*

- ◆ In Crossfire, you can search for
  - only crystalline substances
    - or only compounds that have a melting point above 100 °C
    - or for compounds for which X-ray structures have been obtained
  - compounds for which **both**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra have been obtained
  - compounds containing exactly one sulfur atom, or more than six carbon atoms, etc.
- ◆ and that it is possible to sort data by e.g. biological activity



# *Reaction searches*

- ◆ a very versatile tool in CrossFire
- ◆ allows user to define reactants, products, and atom connectivities between them
- ◆ results can be sorted according to
  - yield
  - solvent



# Example search 1: brominated arenes

MDL CrossFire Commander - [Query for Server default]

File Edit Task View Options Query Help

MDL CrossFire Commander Query Results Reports Alerts AutoNom

Query History | Open Query | Save Query | Print Query | Clear Query | Select Database | Draw Structure | Modify Alert | Create Alert | Start Search

Search Field Name in Hierarchy: ?

Predefined Search Forms | Hitsets

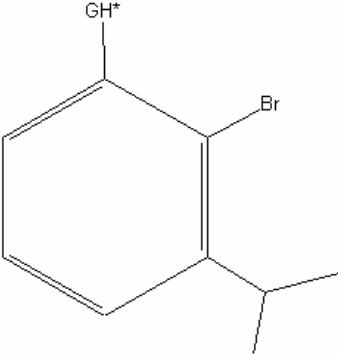
Search Fields | Queries

Beilstein(2008/04)

- Basic Indexes
- Bibliographic Information
- Substance Identification
- Chemical Properties
- Physical Properties
- Pharmacological and Ecologic
- External Identifiers

Query Builder ? Search in: Beilstein(2008/04)

total charge = 0, radicals = 0, components = 1, no impl. ring closures, no isotopes, no IST



Free Sites:  hetero atoms  all atoms

Stereo: off

Search:  as structure  as reactant  as product  as reagent/ as catalyst/ as solvent

Allow:  salts  addl. rings  isotopes  charges  radicals  mixtures  relat. Markush

Clear Structure Extended Options

and Search All Text ?  Truncate... Clear Text

and Search Fields ? Advanced Search Clear Table

<- Select (and edit) Search Form, Search Field, Query, or Hitset from left box and append to query

Show Help for Search Fields

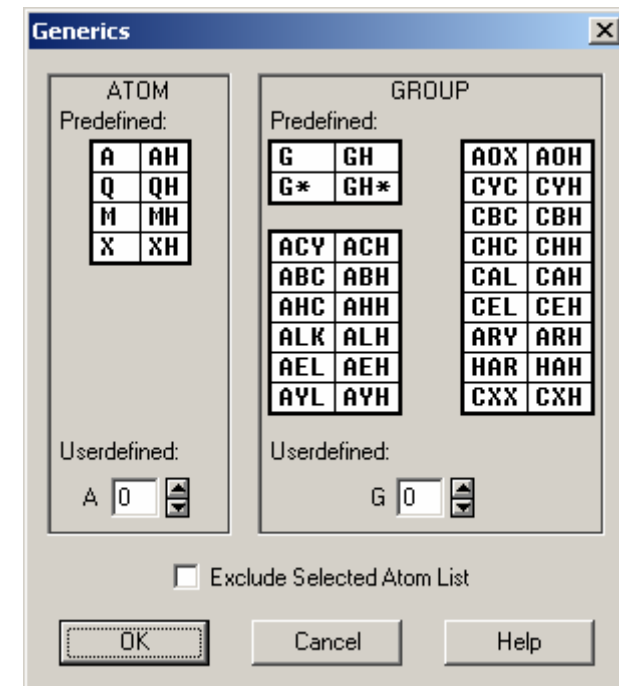
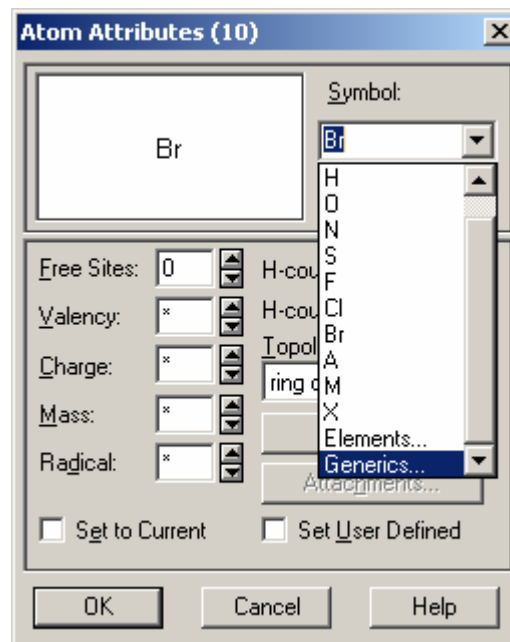
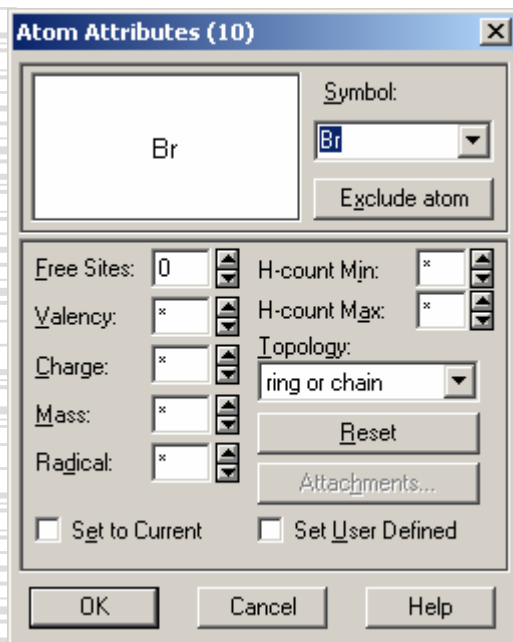
Search Context Substances Start Search

For Help, press F1

idle

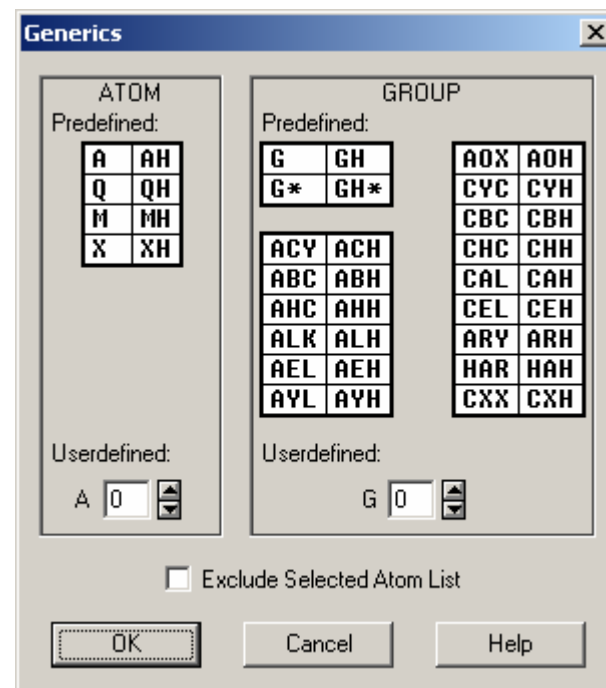
# Use of generic groups

- ◆ Click on atom in CrossFire editor
- ◆ Scroll down the list to Generics...
- ◆ A wide selection of different types of generics pops up



# Use of predefined groups

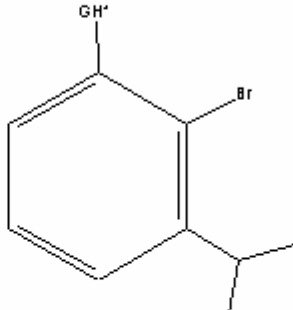
- ◆ Predefined group generics: G, GH: Any group (H: Hydrogen is also allowed)
- ◆ G\*, GH\*: Any group with ring closure
- ◆ Further refinements are possible, for example:
  - ACY, ACH: acyclic
    - ABC, ABH: carbon chain acyclic
    - AHC, AHH: heteroatom-containing acyclic
  - CYC, CYH: cyclic
    - CHC, CHH: heterocyclic
    - HAR, HAH: heteroaryl
    - ARY, ARH: Aryl
    - CAL, CAH: cycloalkyl
    - CBC, CBH: carbocyclic
    - CXX, CXH: cyclic, no C



# Example search 1: results

Search Status Report: Automatic Query Variation

Your recent search(es) had the following results: Hitset Family (2 of 2): Previous Next

No.	Select	Hitset	Hits	Context	Database	Query	Options
1	<input checked="" type="checkbox"/>	Q02	2 Substances		Beilstein(2008/04)	total charge = 0, radicals = 0, components = 1, no impl. ring closures, no isotopes, no IST 	original structure
2	<input type="checkbox"/>		stop after first result	Substances	Beilstein(2008/04)	same structure	free sites on hetero atoms
3	<input type="checkbox"/>		stop after first result	Substances	Beilstein(2008/04)	same structure	substructure search

Cancel To Report View

# Results in grid format

MDL CrossFire Commander - [Beilstein(2008/04):Q02 Substance 1 of 2]

File Edit Task View Options Window Help

MDL CrossFire Commander

Query Results Reports Alerts AutoNom

Substances: hit 1 of 2

History | Print Hits | View all | Show Grid | List | Get | Sort Hits | Copy | Export Hits | Copy to Report

[-] Gmelin(2008/03)  
[-] Beilstein(2008/04)  
    ... Saved Hitsets/Alert Hitsets  
    [-] Session Hitsets  
        [-] Q: Q01 (2 Substances)  
        [-] **Q: Q02 (2 Substances)**

Hit 1 BRN=1857014 C<sub>9</sub>H<sub>11</sub>Br

CC(C)C1=CC=CC=C1Br

Hit 2 BRN=2519179 C<sub>12</sub>H<sub>17</sub>Br

CC(C)C1=CC=C(C(C)C)C(Br)C1

# Hit #1

MDL CrossFire Commander - [Beilstein(2008/04):Q02 Substance 1 of 2]

File Edit Task View Options Window Help

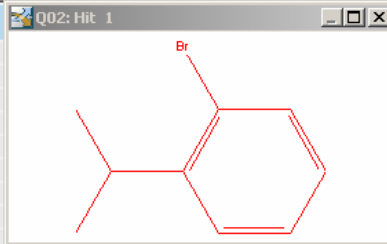
MDL CrossFire Commander Query Results Reports Alerts AutoNom Substances: hit 1 of 2

History Print Hits View all Show Grid List Get Sort Hits Copy Export Hits Copy to Report

- Gmelin(2008/03)
- Beilstein(2008/04)
  - Saved Hitsets/Alert Hitsets
  - Session Hitsets
    - Q: Q01 (2 Substances)
    - Q: Q02 (2 Substances)**

### Substance Identification

Beilstein Registry Number	<b>1857014</b>
Beilstein Preferred RN	7073-94-1
CAS Registry Number	7073-94-1
Chemical Name	1-bromo-2-(isopropyl)benzene
	1-bromo-2-isopropylbenzene
	1-bromo-2-iso-propylbenzene
	1-bromo-2-isopropyl benzene
	1-bromo-2-isopropylbenzene
	2-Bromo-1-isopropylbenzene
	2-bromo-iso-propylbenzene
Autoname	1-Bromo-2-isopropyl-benzene
Linear Structure Formula	C <sub>3</sub> H <sub>7</sub> C <sub>6</sub> H <sub>4</sub> Br
Molecular Formula	C <sub>9</sub> H <sub>11</sub> Br
Molecular Weight	199.09
Type of Substance	isocyclic
Beilstein Reference	5-05, 0-05-00-00395, 3-05-00-00887, 4-05-00-00994, 6-05



### Field Availability List 1-10 of 13

Code	Field Name	Occ.
<a href="#">RX</a>	Reaction	159
<a href="#">MP</a>	Melting Point	2
<a href="#">BP</a>	Boiling Point	20
<a href="#">DEN</a>	Density of the Liquid	3
<a href="#">HFUS</a>	Enthalpy of Fusion	1
<a href="#">OTHE</a>	Other Thermochemical Data	1
<a href="#">RI</a>	Refractive Index	5
<a href="#">NMR</a>	NMR Spectroscopy	6
<a href="#">IR</a>	IR Spectroscopy	1
<a href="#">MS</a>	Mass Spectrometry	2

### Field Availability List 11-13 of 13

Code	Field Name	Occ.
<a href="#">FINFO</a>	Further Information	1
<a href="#">EXTID</a>	External Identifiers	1
<a href="#">CNR</a>	Reference	85

For Help, press F1 idle ALL

# To view reaction schemes, tick "Structures included"

The screenshot shows the MDL CrossFire Commander interface. The 'View' menu is open, and the 'Structures included' option is checked and highlighted with a red box. The main window displays search results for 'Q02: Substance 1 of 2'. The results list includes:

- 108006**
- 1236613** isopropylbenzene
- 1857014** 1-bromo-2-(isopropyl)benzene
- 1858096** 4-isopropyl-1-bromobenzene

The 'Preparation' section lists: acetic acid, iron-powder, iodine, bromine, and a [click here](#) link. A citation is provided: **1740305**; Journal; Lamneck; JACSAT; Journal of the American Chemical Society; 76; 1954; 1106; DOI: 10.1021/ja01633a051; ISSN: 0002-7863.

The reaction scheme at the bottom shows the conversion of isopropylbenzene (Reactant 1) to 1-bromo-2-(isopropyl)benzene (Reactant 2). The product is shown as a benzene ring with an isopropyl group and a bromine atom.

At the bottom of the window, the status bar indicates 'idle' and 'ALL: Substance as Product'.

# Scroll down or click in the Field Availability box to browse physical data

MDL CrossFire Commander - [Beilstein(2008/04):Q02 Substance 1 of 2]

File Edit Task View Options Window Help

MDL CrossFireCommander Query Results Reports Alerts AutoNom Substances: hit 1 of 2

History | Print Hits | View all | Show Grid | List | Get | Sort Hits | Copy | Export Hits | Copy to Report

Gmelin(2008/03)  
Beilstein(2008/04)  
  Saved Hitsets/Alert Hitsets  
  Session Hitsets  
    Q: Q01 (2 Substances)  
    Q: Q02 (2 Substances)

Ref. 2 [1142854](#); Journal; Dreisbach; Martin; IECHAD; Industrial and Engineering Chemistry; 41; 1949; 2876; ISSN: 0019-7866.

**Boiling Point 1-10 of 20**

VALUE (BP) C	Pressure (.P) Torr	Entry Date	Note	Ref.
210.32	760			1
90	15			2
71 - 72	3			3
210.2	760			4
131.7	75.9			5
145.1	123.8			5
175.8	315.5			5
193.7	507.5			5
205 - 207	740.6		1	6
210.5	746			7

Note 1 fluessig.

Ref. 1 [1740305](#); Journal; Lamneck; JACSAT; Journal of the American Chemical Society; 76; 1954; 1106; DOI: 10.1021/ja01633a051; ISSN: 0002-7863.  
 Ref. 2 [1740535](#); Journal; Crawford; Stewart; JCSOA9; Journal of the Chemical Society; 1952; 4443,4445; DOI: 10.1039/jr9520004443; ISSN: 0368-1769.  
 Ref. 3 [1625141](#); Journal; Brown et al.; JACSAT; Journal of the American Chemical Society; 79; 1957; 1897,1900; DOI: 10.1021/ja01565a035; ISSN: 0002-7863.  
 Ref. 4 [1142854](#); Journal; Dreisbach; Martin; IECHAD; Industrial and Engineering Chemistry; 41; 1949; 2876; ISSN: 0019-7866.  
 Ref. 5 [1142898](#); Journal; Dreisbach; Shrader; IECHAD; Industrial and Engineering Chemistry; 41; 1949; 2879; DOI: 10.1021/ie50480a054; ISSN: 0019-7866.  
 Ref. 6 [1517778](#); Journal; Fileti; GCITA9; Gazzetta Chimica Italiana; 16; 1886; 114; ISSN: 0016-5603.  
 Ref. 7 [4355447](#); Journal; Kiersznicki et al.; ZNSCAM; Zeszyty Naukowe Politechniki Slaskiej, Chemia; 40; 1967; 113,117,118; ISSN: 0372-9494.

**Boiling Point 11-20 of 20**

VALUE (BP) C	Pressure (.P) Torr	Entry Date	Note	Ref.
108 - 110	24			1
62	4			2
83 - 85	10			3
87	14			4
84 - 86	17			5
208 - 210	760			6
76 - 82	10			7
90 - 93	15			8
208 - 211	755			9
47	1.4			10

For Help, press F1      idle      ALL: Substance as Product

... e.g. NMR data

The screenshot displays the MDL CrossFire Commander interface. The window title is "MDL CrossFire Commander - [Beilstein(2008/04):Q02 Substance 1 of 2]". The menu bar includes File, Edit, Task, View, Options, Window, and Help. The main toolbar contains buttons for Query, Results, Reports, Alerts, and AutoHom. The status bar at the top right indicates "Substances: hit 1 of 2".

The left sidebar shows a tree view of the project structure:

- Gmelin(2008/03)
- Beilstein(2008/04)
  - Saved Hitsets/Alert Hitsets
  - Session Hitsets
    - Q: Q01 (2 Substances)
    - Q: Q02 (2 Substances)

The main content area displays five NMR spectroscopy entries, each with a title, description, and reference information:

### NMR Spectroscopy 1 of 6

Description	Chemical shifts
Nucleus	<sup>1</sup> H
Solvents	CDCl <sub>3</sub>
Frequency	300 MHz

Ref. 1 [6632244](#); Journal; Fey, Natalie; Howell, James A. S.; Lovatt, Jonatham D.; Yates, Paul C.; Cunningham, Desmond; McArdle, Patrick; Gottlieb, Hugo E.; Coles, Simon J.; DTARAF; Dalton Transactions; English; 46; 2006; 5464 - 5475; DOI: 10.1039/b610123b; ISSN: 1477-9226.

### NMR Spectroscopy 2 of 6

Nucleus	<sup>1</sup> H
Coupling Nuclei	<sup>1</sup> H
Solvents	CDCl <sub>3</sub>
Frequency	300 MHz

Ref. 1 [6632244](#); Journal; Fey, Natalie; Howell, James A. S.; Lovatt, Jonatham D.; Yates, Paul C.; Cunningham, Desmond; McArdle, Patrick; Gottlieb, Hugo E.; Coles, Simon J.; DTARAF; Dalton Transactions; English; 46; 2006; 5464 - 5475; DOI: 10.1039/b610123b; ISSN: 1477-9226.

### NMR Spectroscopy 3 of 6

Description	Chemical shifts
Nucleus	<sup>13</sup> C
Solvents	CDCl <sub>3</sub>
Frequency	75 MHz

Ref. 1 [6632244](#); Journal; Fey, Natalie; Howell, James A. S.; Lovatt, Jonatham D.; Yates, Paul C.; Cunningham, Desmond; McArdle, Patrick; Gottlieb, Hugo E.; Coles, Simon J.; DTARAF; Dalton Transactions; English; 46; 2006; 5464 - 5475; DOI: 10.1039/b610123b; ISSN: 1477-9226.

### NMR Spectroscopy 4 of 6

Description	Chemical shifts
Nucleus	<sup>13</sup> C
Solvents	CDCl <sub>3</sub>
Frequency	100 MHz

Ref. 1 [6633317](#); Journal; Sugiura, Hiroki; Sakai, Daisuke; Otani, Harunori; Teranishi, Kazuhiro; Takahira, Yusuke; Amemiya, Ryo; Yamaguchi, Masahiko; CMLTAG; Chemistry Letters; English; 36; 1; 2007; 72 - 73; DOI: 10.1246/cl.2007.72; ISSN: 0366-7022.

### NMR Spectroscopy 5 of 6

Description	Chemical shifts
Nucleus	<sup>1</sup> H
Solvents	benzene-d <sub>6</sub>
Frequency	400 MHz

For Help, press F1 | idle | ALL: Substance as Product

MDL CrossFire Commander - [Beilstein(2008/04):Q02 Substance 1 of 2]

File Edit Task View Options Window Help

MDL CrossFire Commander Query Results Reports Alerts AutoNom Substances: hit 1 of 2

History Print Hits View all Show Grid List Get Sort Hits Copy Export Hits Copy to Report

Gmelin(2008/03)  
 Beilstein(2008/04)  
 Saved Hitsets/Alert Hitsets  
 Session Hitsets  
 Q: Q01 (2 Substances)  
 Q: Q02 (2 Substances)

Frequency 400 MHz

Ref. 1 [6633317](#); Journal; Sugiura, Hiroki; Sakai, Daisuke; Otani, Harunori; Teranishi, Kazuhiro; Takahira, Yusuke; Amemiya, Ryo; Yamaguchi, Masahiko; CMLTAG; Chemistry Letters; English; 36; 1; 2007; 72 - 73; DOI: 10.1246/cl.2007.72; ISSN: 0366-7022.

**NMR Spectroscopy 6 of 6**

Nucleus 1H  
 Coupling Nuclei 1H  
 Solvents benzene-d6  
 Frequency 400 MHz

Ref. 1 [6633317](#); Journal; Sugiura, Hiroki; Sakai, Daisuke; Otani, Harunori; Teranishi, Kazuhiro; Takahira, Yusuke; Amemiya, Ryo; Yamaguchi, Masahiko; CMLTAG; Chemistry Letters; English; 36; 1; 2007; 72 - 73; DOI: 10.1246/cl.2007.72; ISSN: 0366-7022.

**IR Spectroscopy**

Description Spectrum

Ref. 1 [5205031](#); Journal; Stoldt, Turk; JOCEAH; Journal of Organic Chemistry; 34; 1969; 2370; DOI: 10.1021/jo01260a026; ISSN: 0022-3263.

**Mass Spectrometry 1 of 2**

Ref. 1 [4462746](#); Journal; McLafferty, ANCHAM; Analytical Chemistry; 34; 1962; 16,23; DOI: 10.1021/ac60181a004; ISSN: 0003-2700.

**Mass Spectrometry 2 of 2**

Description electron impact (EI)  
 spectrum

Ref. 1 [6633317](#); Journal; Sugiura, Hiroki; Sakai, Daisuke; Otani, Harunori; Teranishi, Kazuhiro; Takahira, Yusuke; Amemiya, Ryo; Yamaguchi, Masahiko; CMLTAG; Chemistry Letters; English; 36; 1; 2007; 72 - 73; DOI: 10.1246/cl.2007.72; ISSN: 0366-7022.

**Further Information**

Description Further information

Ref. 1 [4462746](#); Journal; McLafferty, ANCHAM; Analytical Chemistry; 34; 1962; 16,23; DOI: 10.1021/ac60181a004; ISSN: 0003-2700.  
 Ref. 2 [4584513](#); Journal; Brown, Wirkkala; JACSAT; Journal of the American Chemical Society; 88; 1966; 1453,1455; DOI: 10.1021/ja00959a024; ISSN: 0002-7863.  
 Ref. 3 [4588102](#); Journal; Schwab, Mandre; ZPCFAX; Zeitschrift fuer Physikalische Chemie (Muenchen, Germany); 47; 1965; 337; ISSN: 0942-9352.

**External Identifiers**

CAS Registry Number 7073-94-1  
 INCHI Code LECYCYNAEJDSIL-UHFFFAOYAK

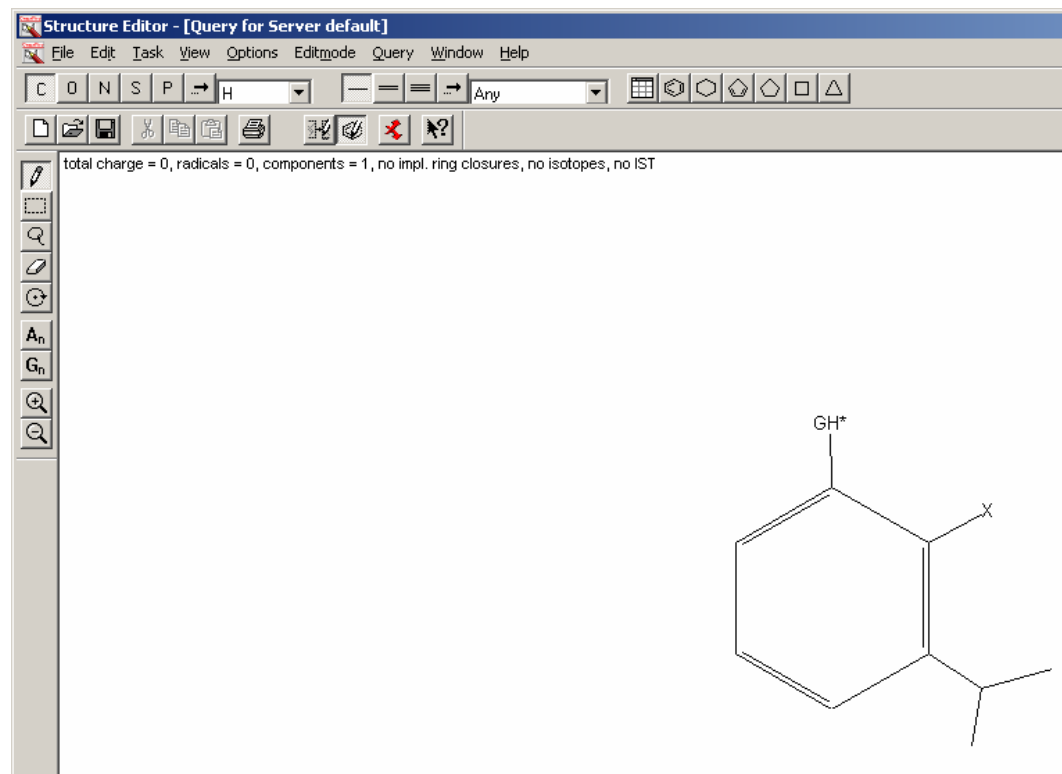
**Reference 1 of 85**

[68369](#); Journal; Whitesides, G.M. et al.; JACSAT; Journal of the American Chemical Society; English; 96; 17; 1974; 5398 - 5407; DOI: 10.1021/ja00824a014; ISSN: 0002-7863.

For Help, press F1 idle ALL: Substance as Product

# Expanding the query

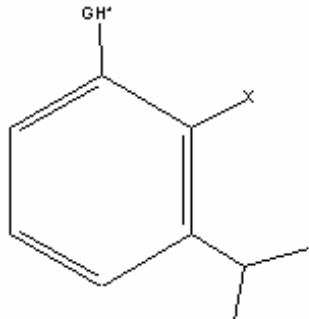
- ◆ If we are only interested in this specific structure, we can allow other halogens besides Br
- ◆ X defines any halogen



# Example search 2: More results this time

Search Status Report: Automatic Query Variation

Your recent search(es) had the following results: Hitset Family (3 of 3): [Previous](#) [Next](#)

No.	Select	Hitset	Hits	Context	Database	Query	Options
1	<input checked="" type="checkbox"/>	Q03	17	Substances	Beilstein(2008/04)	total charge = 0, radicals = 0, components = 1, no impl. ring closures, no isotopes, no IST 	original structure
2	<input type="checkbox"/>		stop after first result	Substances	Beilstein(2008/04)	same structure	free sites on hetero atoms
3	<input type="checkbox"/>		stop after first result	Substances	Beilstein(2008/04)	same structure	substructure search

Cancel To Report View

# Example search 2: results

MDL CrossFire Commander - [Beilstein(2008/04):Q03 Substance 1 of 17]

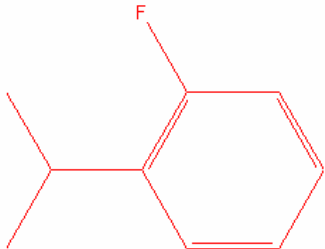
File Edit Task View Options Window Help

MDL CrossFire Commander Query Results Reports Alerts AutoNom Substances: hit 1 of 17

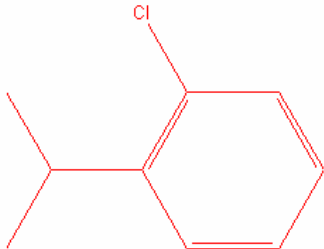
History | Print Hits | View all | Show | Grid | List | Get | Sort Hits | Copy | Export Hits | Copy to Report

- [-] Gmelin(2008/03)
- [-] Beilstein(2008/04)
  - [-] Saved Hitsets/Alert Hitsets
  - [-] Session Hitsets
    - [-] Q: Q01 (2 Substances)
    - [-] Q: Q02 (2 Substances)
    - [-] **Q: Q03 (17 Substance)**

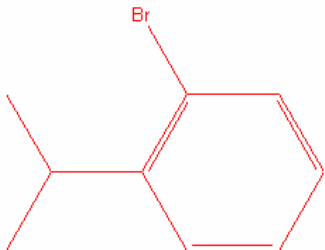
Hit 1 BRN=1857012 C<sub>9</sub>H<sub>11</sub>F



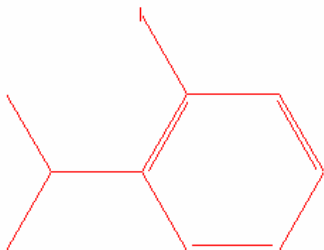
Hit 2 BRN=1857013 C<sub>9</sub>H<sub>11</sub>Cl



Hit 3 BRN=1857014 C<sub>9</sub>H<sub>11</sub>Br



Hit 4 BRN=2351872 C<sub>9</sub>H<sub>11</sub>I



For Help, press F1 | idle | GRID

# Example search 2: results

MDL CrossFire Commander - [Beilstein(2008/04):Q03 Substance 14 of 17]

File Edit Task View Options Window Help

MDL CrossFire Commander Query Results Reports Alerts AutoNom Substances: hit 14 of 17

History Print Hits View all Show Grid List Get Sort Hits Copy Export Hits Copy to Report

- Gmelin(2008/03)
- Beilstein(2008/04)
  - Saved Hitsets/Alert Hitsets
  - Session Hitsets
    - Q: Q01 (2 Substances)
    - Q: Q02 (2 Substances)
    - Q: Q03 (17 Substances)**

Hit 13 BRN=8832356 C<sub>11</sub>H<sub>15</sub>O

Hit 14 BRN=8832357 C<sub>11</sub>H<sub>13</sub>O

Hit 15 BRN=8832524 C<sub>12</sub>H<sub>17</sub>O

Hit 16 BRN=9388238 C<sub>12</sub>H<sub>17</sub>

For Help, press F1 idle GRID

# Expand the hit of an interesting compound...

MDL CrossFire Commander - [Beilstein(2008/04):Q03 Substance 14 of 17]

File Edit Task View Options Window Help

MDL CrossFire Commander Query Results Reports Alerts AutoNom Substances: hit 14 of 17

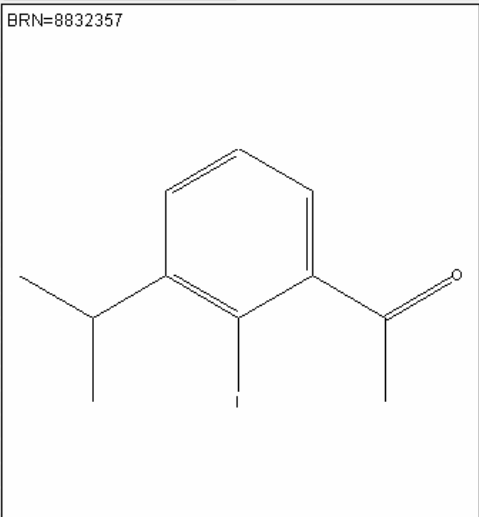
History Print Hits View all Show Grid List Get Sort Hits Copy Export Hits Copy to Report

Beilstein(2008/03)  
Beilstein(2008/04)  
Saved Hitsets/Alert Hitsets  
Session Hitsets  
Q: Q01 (2 Substances)  
Q: Q02 (2 Substances)  
Q: Q03 (17 Substances)

### Substance Identification

Beilstein Registry Number **8832357**  
Chemical Name 2-iodo-3-(1-methylethyl)acetophenone  
Autoname 1-(2-iodo-3-isopropyl-phenyl)-ethanone  
Linear Structure Formula C<sub>11</sub>H<sub>13</sub>IO  
Molecular Formula C<sub>11</sub>H<sub>13</sub>IO  
Molecular Weight 288.128  
Type of Substance isocyclic

BRN=8832357



Field Availability List 1-7

Code	Field Name	Occ.
<a href="#">RX</a>	Reaction	1
<a href="#">CPD</a>	Crystal Property Description	1
<a href="#">NMR</a>	NMR Spectroscopy	3
<a href="#">IR</a>	IR Spectroscopy	1
<a href="#">MS</a>	Mass Spectrometry	1
<a href="#">EXTID</a>	External Identifiers	1

For Help, press F1 idle

... to see how the compound was made

MDL CrossFire Commander - [Beilstein(2008/04):Q03 Substance 14 of 17]

File Edit Task View Options Window Help

MDL CrossFire Commander Query Results Reports Alerts AutoHom Substances: hit 1 of 2

History Print Hits View all Show Grid List Get Sort Hits Copy Export Hits Copy to Report

Gmelin(2008/03)  
Beilstein(2008/04)  
  Saved Hits/Alert Hits  
  Session Hits  
    Q: Q01 (2 Substances)  
    Q: Q02 (2 Substances)  
    **Q: Q03 (17 Substances)**

### Reaction

Reaction ID	<b>8834132</b>
Reactant BRN	<b>1857014</b> 1-bromo-2-(isopropyl)benzene
	<b>741857</b> AN
Product BRN	<b>8832357</b> 2-iodo-3-(1-methylethyl)acetophenone
No. of Reaction Details	1
Reaction Classification	Preparation
Product BRN	<b>8832357</b> 2-iodo-3-(1-methylethyl)acetophenone
Yield	31 percent
Find similar reactions	<a href="#">click here</a>

Note 1 Multistep reaction.  
Ref. 1 **6288716**; Journal; Hirt, Urs H.; Schuster, Martin F. H.; French, Andrew N.; Wiest, Olaf G.; Wirth, Thomas; EJOCFK; European Journal of Organic Chemistry; English; 2001; 1569 - 1580; ISSN: 1434-193X.

RX.ID=8834132

The reaction scheme shows the conversion of 1-bromo-2-(isopropyl)benzene (Reactant 1) to 2-iodo-3-(1-methylethyl)acetophenone (Product). The reactant is a benzene ring with a bromine atom at the 1-position and an isopropyl group at the 2-position. The product is a benzene ring with an iodine atom at the 2-position, an isopropyl group at the 3-position, and an acetyl group at the 1-position. The reaction is indicated by a dashed arrow pointing from the reactant to the product.

For Help, press F1      idle      ALL: Substance as Product

# Avoid overexpansion

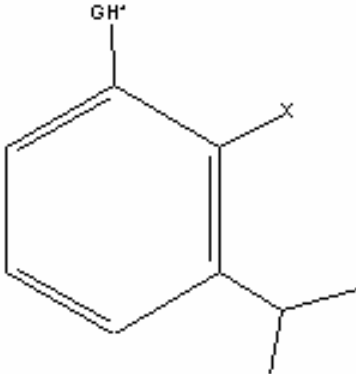
<b>Free Sites:</b> ?		<b>Stereo:</b> ?	
<input type="checkbox"/> hetero atoms		off	
<input checked="" type="checkbox"/> all atoms			
<b>Search:</b> ?		<b>Allow:</b> ?	
<input checked="" type="radio"/> as structure		<input checked="" type="checkbox"/> salts	
<input type="radio"/> as reactant		<input checked="" type="checkbox"/> addl. rings	
<input type="radio"/> as product		<input checked="" type="checkbox"/> isotopes	
<input type="radio"/> as reagent/ as catalyst/ as solvent		<input checked="" type="checkbox"/> charges	
		<input checked="" type="checkbox"/> radicals	
		<input type="checkbox"/> mixtures	
		<input type="checkbox"/> relat. Markush	



# The search program and the database can handle 23235 hits – but can you?

Search Status Report

Your recent search(es) had the following results: Hitset Family (4 of 4):

No.	Select	Hitset	Hits	Context	Database	Query	Options
1	<input checked="" type="checkbox"/>	Q04	23235	Substances	Beilstein(2008/04)	impl. free sites 	original structure

# *Restricting the compound by data*

- ◆ CrossFire allows users to search for compounds that fulfill specific search criteria:
  - Only compounds for which pharmacological or bioactivity data has been obtained
  - Only crystalline compounds
  - Compounds with only one nitrogen
  - etc.



# Search Fields

The screenshot shows the MDL CrossFire Commander interface. On the left, a tree view under 'Beilstein(2008/04)' lists search fields: Basic Indexes, Bibliographic Information, Substance Identification, Chemical Properties, Physical Properties, Pharmacological and Ecologic., and External Identifiers. A red arrow points to the '+' icon next to 'Basic Indexes'.

1. Click on + to expand the Search Field selection

The main window displays a chemical structure of a substituted benzene ring with a  $\text{GH}^+$  group at the top, an 'X' at the 2-position, and an isopropyl group at the 3-position. The text 'impl. free sites' is visible above the structure.

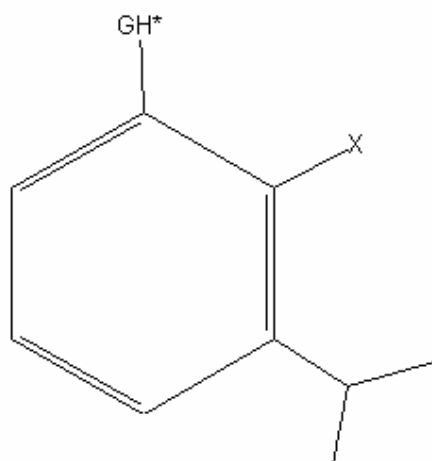
2. Create a search table using the Search Fields - add restrictions, create combinations of them, etc.

The bottom section shows a search table with the following structure:

	Operator	(	Field name	Relation	Field content	List	)
1				is			
2	and			is			
3	and			is			

Additional interface elements include a 'Search Field Name in Hierarchy' search box, 'Predefined Search Forms' and 'Hitsets' tabs, 'Free Sites' and 'Stereo' options, 'Search' and 'Allow' radio buttons, 'Clear Structure' and 'Extended Options' buttons, and a 'Search Context' dropdown set to 'Substances' with a 'Start Search' button.

# Example search 3



Free Sites: [?](#)

hetero atoms  
 all atoms

Stereo: [?](#)

off

Search: [?](#)

as structure  
 as reactant  
 as product  
 as reagent/  
as catalyst/  
as solvent

Allow: [?](#)

salts  
 addl. rings  
 isotopes  
 charges  
 radicals  
 mixtures  
 relat. Markush

Clear Structure    Extended Options

and [?](#) Search Fields [?](#)

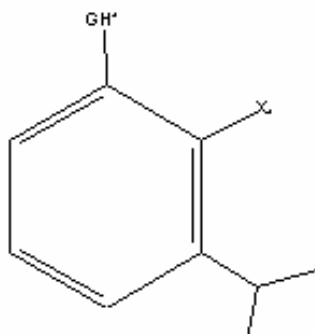
	Operator	(	Field name	Relation	
1			Pharmacological Data(PHARM)	exists	
2	and			is	
3	and			is	



# Results

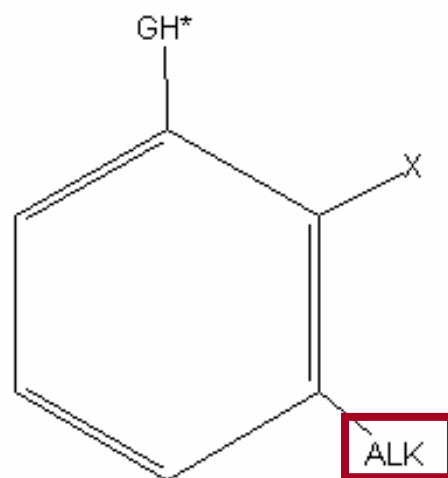
Search Status Report: Automatic Query Variation

Your recent search(es) had the following results: Hitset Family (6 of 6): [Previous](#) [Next](#)

No.	Select	Hitset	Hits	Context	Database	Query	Options
1	<input type="checkbox"/>		0	Substances	Beilstein(2008/04)	total charge = 0, radicals = 0, components = 1, no impl. ring closures, no isotopes, no IST  and "PHARM"	original structure
2	<input checked="" type="checkbox"/>	Q06	3415	Substances	Beilstein(2008/04)	same structure and "PHARM"	substructure search

[Cancel](#) [To Report](#) [View](#)

# Example search 3 – second attempt



Free Sites: [?](#)

hetero atoms  
 all atoms

Stereo: [?](#)

off

Search: [?](#)

as structure  
 as reactant  
 as product  
 as reagent/  
as catalyst/  
as solvent

Allow: [?](#)

salts  
 addl. rings  
 isotopes  
 charges  
 radicals  
 mixtures  
 relat. Markush

Clear Structure    Extended Options

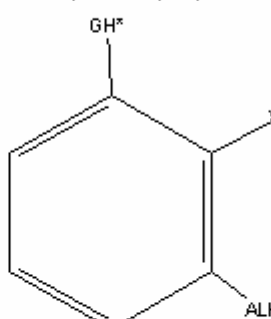
and [?](#) Search Fields [?](#)

	Operator	(	Field name	Relation	
1			Pharmacological Data(PHARM)	exists	
2	and			is	
3	and			is	

# Results

Search Status Report: Automatic Query Variation

Your recent search(es) had the following results: Hitset Family (8 of 8): Previous Next

No.	Select	Hitset	Hits	Context	Database	Query	Options
1	<input checked="" type="checkbox"/>	Q08	28	Substances	Beilstein(2008/04)	<p>total charge = 0, radicals = 0, components = 1, no impl. ring closures, no isotopes, no IST</p>  <p>and "PHARM"</p>	original structure
2	<input type="checkbox"/>		stop after first result	Substances	Beilstein(2008/04)	same structure and "PHARM"	free sites on hetero atoms
3	<input type="checkbox"/>		stop after first result	Substances	Beilstein(2008/04)	same structure and "PHARM"	substructure search

Cancel To Report View

# Sort results

**Sort or Group the Hitset** [X]

Hitset: Q08  
Database: Beilstein(2008/04)  
Current Status: sorted

Sort by    Group by

Effect (PHARM.E)    Ascending  
 Descending

Then sort by: [ ]    Ascending  
 Descending

Then sort by: [ ]    Ascending  
 Descending

Cancel   Help   OK

# Search results: the most pharmacologically active compounds bearing this structural unit

MDL CrossFire Commander - [Beilstein(2008/04):Q08 Substance 1 of 84]

File Edit Task View Options Window Help

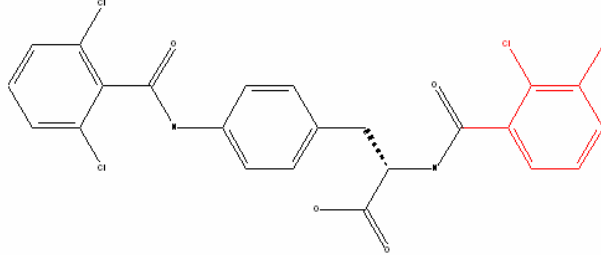
MDL CrossFire Commander Query Results Reports Alerts AutoNom Substances: hit 1 of 84

History | Print Hits | View all | Show Grid | List | Get | Sort Hits | Copy | Export Hits | Copy to Report

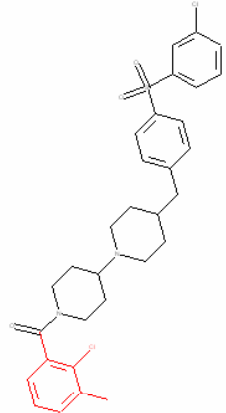
Beilstein(2008/04)

- Saved Hitsets/Alert Hitsets
- Session Hitsets
  - Q: Q06 (3415 Substances)
  - Q: Q07 (8941 Substances)
  - Q: Q08 (84 Substance):**
    - 1: (S)-2-(2-Chloro-3-methyl-5-chlorophenyl)propanoic acid
    - 2: 1-(2-chloro-3-methylphenyl)ethanone
    - 3: 8-(1-(2-fluoro-3-methylphenyl)ethoxy)octane
    - 4: 2-chloro-3-methylbenzamide
    - 5: 2-bromo-N-((1S,2R)-2-iodoethyl)ethanamine
    - 6: C13H12ClNO2S
    - 7: o-chlorotoluene
    - 8: 1,3-diethyl-2-bromobenzene
    - 9: C13H12ClNO2S
    - 10: C13H12ClNO2S
    - 11: 2-iodotoluene
    - 12: ortho-chloro-ethylbenzene
    - 13: 2-iodotoluene
    - 14: ortho-chloro-ethylbenzene
    - 15: 2-(2-bromo-3-methylphenyl)ethanone
    - 16: o-chlorotoluene
    - 17: o-chlorotoluene
    - 18: 2-iodotoluene
    - 19: (S)-2-(2-Chloro-3-methylphenyl)propanoic acid
    - 20: 1-(2-chloro-3-methylphenyl)ethanone
    - More...

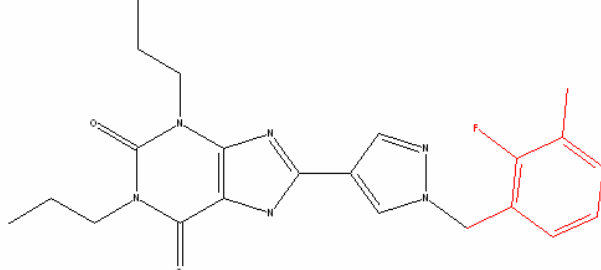
Hit 1 BRN=9235484 C<sub>24</sub>H<sub>19</sub>Cl<sub>3</sub>N<sub>2</sub>O<sub>4</sub>;Bio(2)



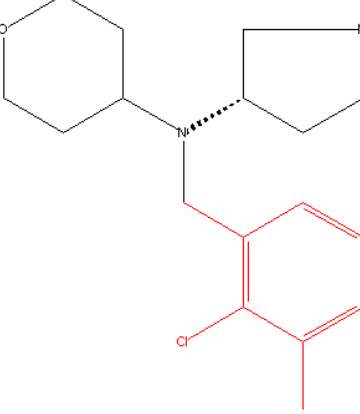
Hit 2 BRN=9885062 C<sub>31</sub>H<sub>34</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>3</sub>S;Bio(2)



Hit 3 BRN=10607318 C<sub>22</sub>H<sub>25</sub>FN<sub>6</sub>O<sub>2</sub>;Bio(3)



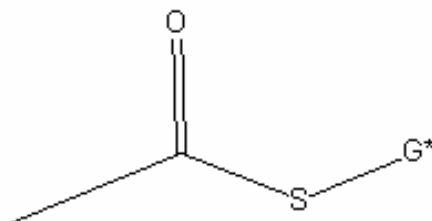
Hit 4 BRN=10695114 C<sub>17</sub>H<sub>25</sub>ClN<sub>2</sub>O;Bio(6)



For Help, press F1 | idle | GRID: sorted by Effect (PHARM.E)

# Example search 4

- ◆ How many thioesters that have a melting point are there?



and  Search Fields ?

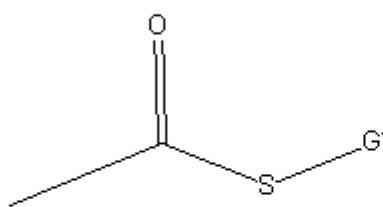
	Operator	(	Field name	Relation	
1			Melting Point(MP)	exists <input type="button" value="v"/>	
2	and <input type="button" value="v"/>			is <input type="button" value="v"/>	
3	and <input type="button" value="v"/>			is <input type="button" value="v"/>	



# Results: without restrictions, there are 1849

Search Status Report: Automatic Query Variation

Your recent search(es) had the following results: Hitset Family (10 of 10): Previous Next

No.	Select	Hitset	Hits	Context	Database	Query	Options
1	<input checked="" type="checkbox"/>	Q10	1849	Substances	Beilstein(2008/04)	total charge = 0, radicals = 0, components = 1, no impl. ring closures, no isotopes, no IST  and "MP"	original structure
2	<input type="checkbox"/>		stop after first result	Substances	Beilstein(2008/04)	same structure and "MP"	free sites on hetero atoms
3	<input type="checkbox"/>		stop after first result	Substances	Beilstein(2008/04)	same structure and "MP"	substructure search

Cancel To Report View

# Some of the results contain two sulfur atoms

Fire Commander - [Beilstein(2008/04):Q10 Substance 1 of 1849]

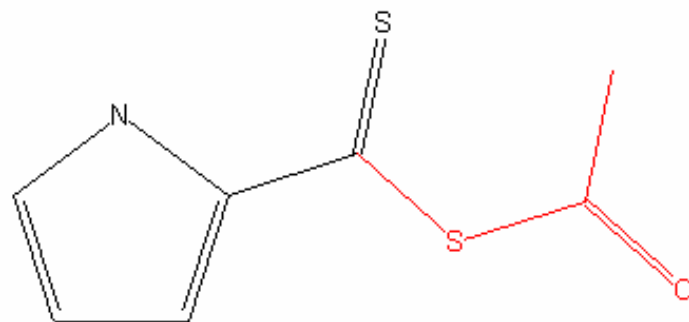
File Options Window Help

Query Results Reports Alerts

View all Show Grid List Get Sort Hits Copy Export Hits Copy to Rep

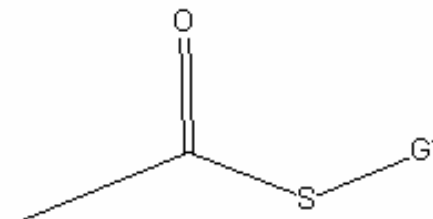
Hit 1 BRN=4186 C7H7NOS2

rt Hitsets



# Redefine search: only one S

- ◆ Element count (ELC): first element symbol, then number
- ◆ i.e. S1: only one sulfur atom



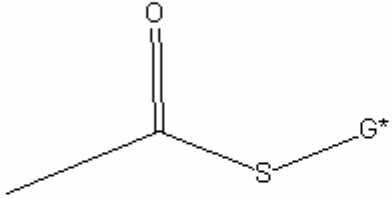
	Operator	(	Field name	Relation	
1			Melting Point(MP)	exists	
2	and		Element Counts(ELC)	is	S1
3	and			is	



# Now there are only 1249

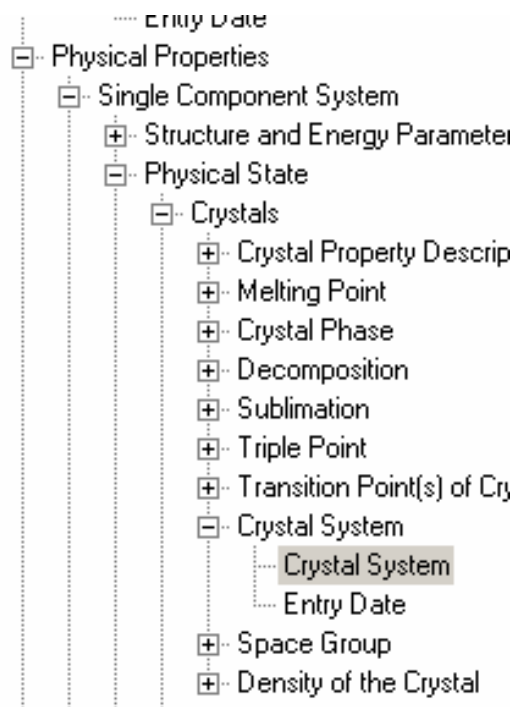
Search Status Report: Automatic Query Variation

Your recent search(es) had the following results: Hitset Family (13 of 13): Previous Next

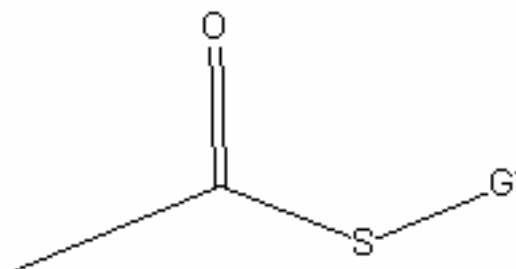
No.	Select	Hitset	Hits	Context	Database	Query	Options
1	<input checked="" type="checkbox"/>	Q13	1249	Substances	Beilstein(2008/04)	total charge = 0, radicals = 0, components = 1, no impl. ring closures, no isotopes, no IST  and "MP and ELC=""S1""	original structure
2	<input type="checkbox"/>		stop after first result	Substances	Beilstein(2008/04)	same structure and "MP and ELC=""S1""	free sites on hetero atoms
3	<input type="checkbox"/>		stop after first result	Substances	Beilstein(2008/04)	same structure and "MP and ELC=""S1""	substructure search

Cancel To Report View

# Adding further restrictions 2



- ◆ Only rhombic crystals allowed
- ◆ Crystal system typically determined for compounds for which single crystal X-ray diffraction data has been obtained



and  **Search Fields** [?](#)

	Operator	(	Field name	Relation		Field content
1			Melting Point(MP)	exists <input type="button" value="▼"/>		
2	and <input type="button" value="▼"/>		Element Counts(ELC)	is <input type="button" value="▼"/>	S1	
3	and <input type="button" value="▼"/>		Crystal System(CSYS)	is <input type="button" value="▼"/>	rhombic	

# Now we are down to two structures

n(2008/04):Q14 Substance 1 of 2

ow Help

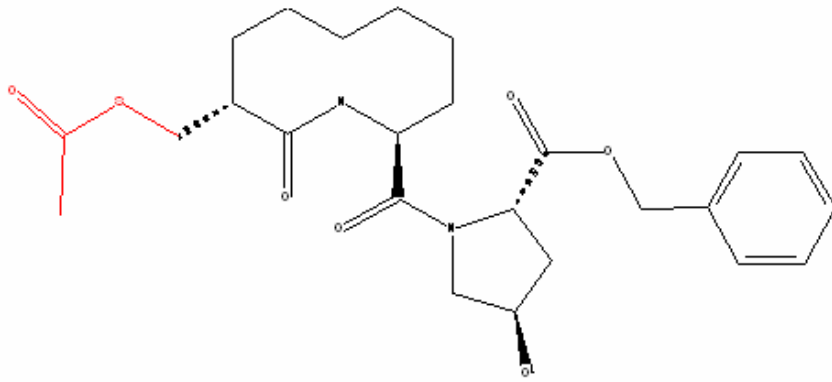
er

Query Results Reports Alerts AutoNom

Substances: hit 1 of 2

View all Show Grid List Get Sort Hits Copy Export Hits Copy to Report

Hit 1 BRN=6674307 C<sub>25</sub>H<sub>34</sub>N<sub>2</sub>O<sub>6</sub>S ;Bio(1)

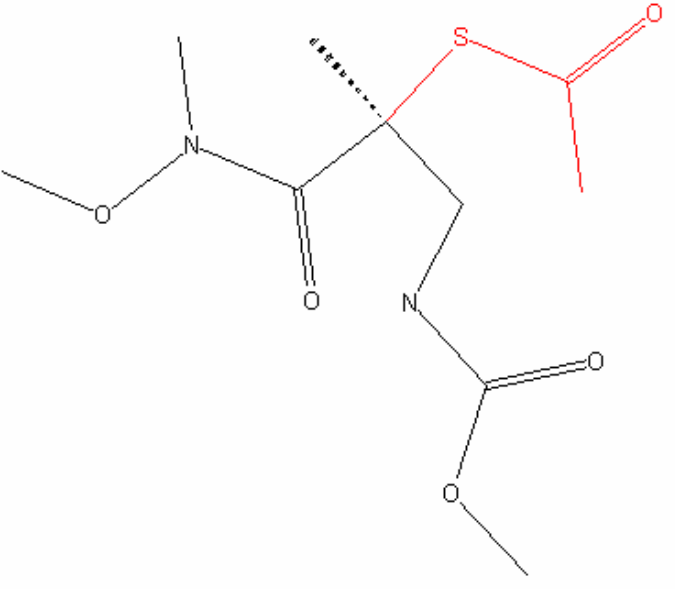


PHAF  
zoylar  
-4-[4-  
-1H-  
trolidi  
sulfon

ulfan

zoyle

Hit 2 BRN=10256731 C<sub>10</sub>H<sub>18</sub>N<sub>2</sub>O<sub>5</sub>S



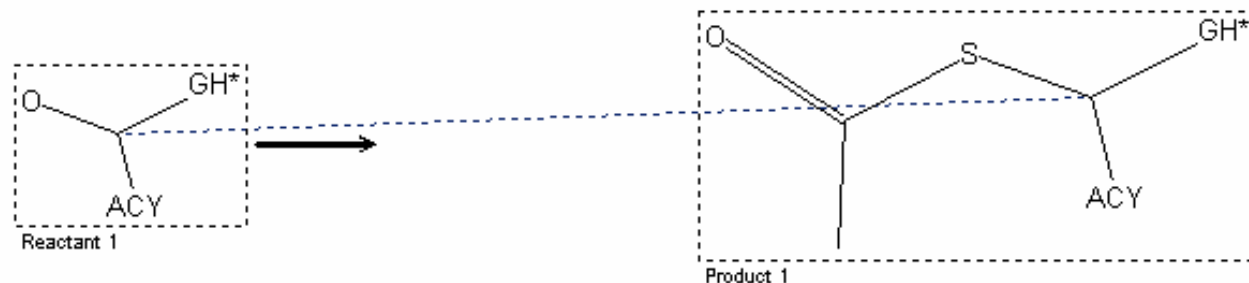
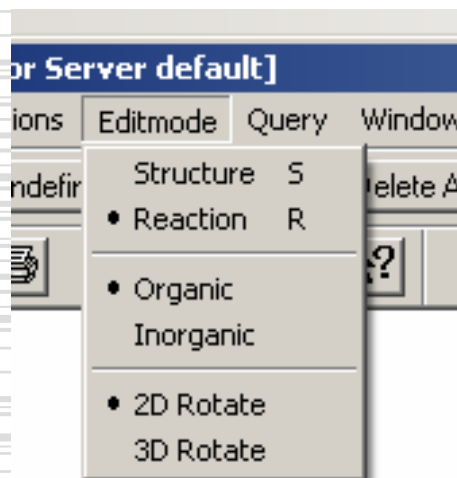
# Reaction searches in CrossFire

- ◆ The wide selection of generic groups allows easy search for literature precedent
- ◆ Typical scenario: You need to do a reaction for a new compound but preferably with known, reliable chemistry
- ◆ Questions to be addressed:
  - What are the typical conditions people have used for this type of reaction?
  - Does the reaction work with various substituents and steric demands?
  - Which conditions typically afford the best yields and selectivities?

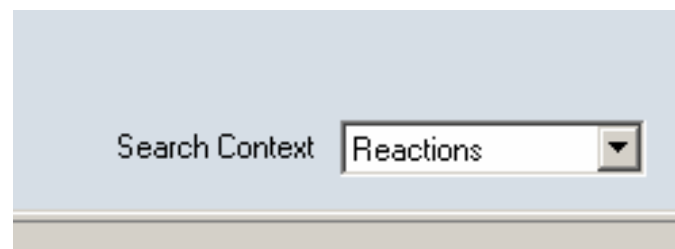
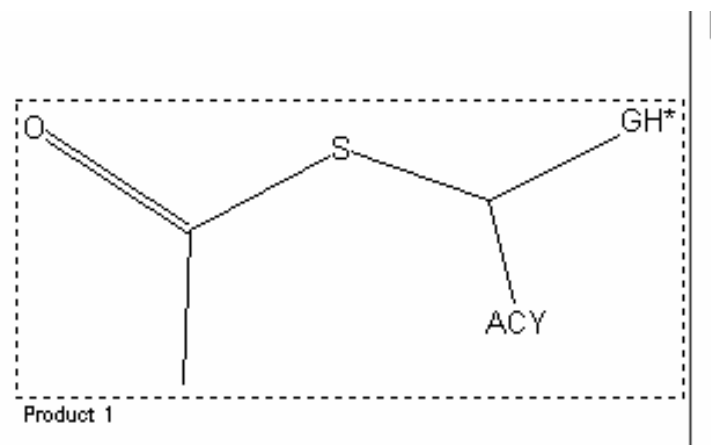
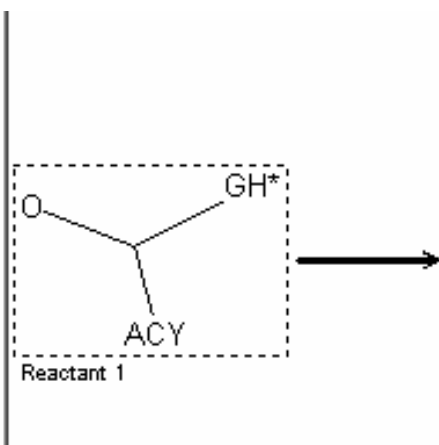


# Search strategy: use generic groups to expand the search

- ◆ Too many G\* groups will slow down the search
- ◆ Connect the atoms common in reactant and product



# Setting up the search



# Results


## Search Status Report: Automatic Query Variation

Your recent search(es) had the following results:

Hitset Family (1 of 1):

Previous

Next

No.	Select	Hitset	Hits	Context	Database	Query	Options
1	<input checked="" type="checkbox"/>	Q15	396	Reactions	Beilstein(2008/04)	<p>total charge = 0, radicals = 0, no impl. ring closures, no isotopes</p>  <p>The diagram shows a chemical reaction. On the left, a cyclic structure is enclosed in a dashed box. An arrow points to the right, where an open-chain structure is also enclosed in a dashed box. The structures appear to be related to a specific chemical transformation.</p>	original structure
2	<input type="checkbox"/>		stop after first result	Reactions	Beilstein(2008/04)	same structure	free sites on hetero atoms
3	<input type="checkbox"/>		stop after first result	Reactions	Beilstein(2008/04)	same structure	substructure search

Cancel

To Report

View

# Instead of browsing through 386 results...

MDL CrossFire Commander - [Beilstein(2008/04):Q15 Reaction 1 of 396]

File Edit Task View Options Window Help

MDL CrossFire Commander Query Results Reports Alerts AutoHom Reactions: hit 1 of 396

History Print Hits View all Show Grid List Get Sort Hits Copy Export Hits Copy to Report

Gmelin(2008/03)  
Beilstein(2008/04)  
Saved Hitsets/Alert Hitsets  
Session Hitsets  
Q: Q15 (396 Reactions)

Hit 1 RX.ID=224765

Reactant 1 Product 1

Hit 2 RX.ID=224766

Reactant 1 Product 1

Hit 3 RX.ID=230707

Reactant 1 Product 1

Hit 4 RX.ID=231772

Reactant 1 Product 1

For Help, press F1 idle GRID Reactions

*... you can sort the results by  
yield!*

The dialog box is titled "Sort or Group the Hitset" and contains the following fields and controls:

- Hitset: Q15
- Database: Beilstein(2008/04)
- Current Status: sorted
- Sort by:  Sort by,  Group by
- Sort by dropdown: Yield (numerical) [RX.NYD]
- Sort direction:  Ascending,  Descending
- Then sort by: [Empty dropdown]
- Then sort direction:  Ascending,  Descending
- Then sort by: [Empty dropdown]
- Then sort direction:  Ascending,  Descending
- Buttons: Cancel, Help, OK

... And even export the  
results to Excel!

The dialog box is titled "Export data from the following hits:" and contains the following fields and controls:

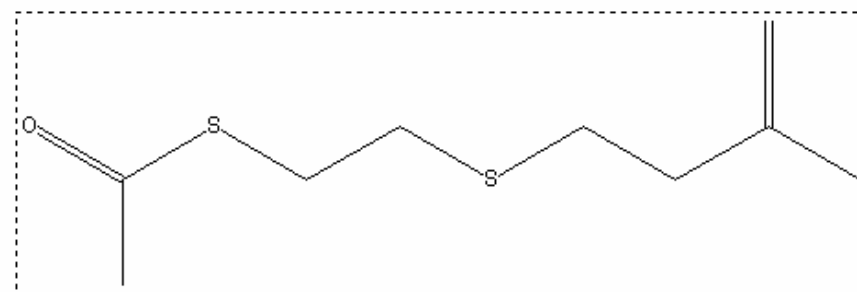
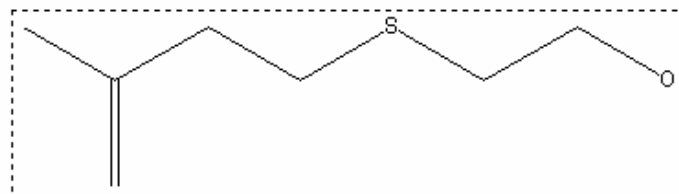
- Export Setting: Reactions to Excel(Reactions\_to\_Excel\_AE8.exs)
- Export options:  All,  Current,  Selected Hits Only,  Range
- Range: from: 1 to: 50
- Buttons: Close, Help, Start

# The best result

## Reaction

Reaction ID	<b>3088043</b>
Reactant BRN	<a href="#">5422726</a> 2--(3-Methyl-3-butenyl)thio>ethanol
Product BRN	<a href="#">5424009</a> 2--(3-Methyl-3-butenyl)thio>ethylthioacetate
No. of Reaction Details	1
Find similar reactions	<a href="#">click here</a>

RX.ID=3088043



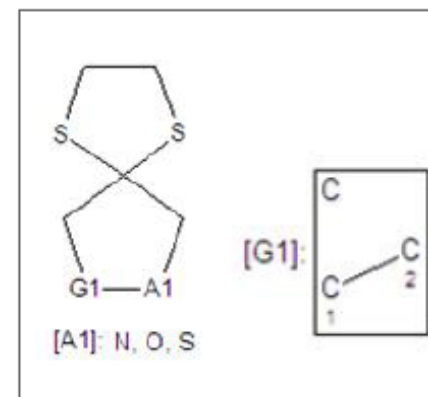
## Reaction Details

Reaction Classification	Preparation
Product BRN	<a href="#">5424009</a> 2--(3-Methyl-3-butenyl)thio>ethylthioacetate
Yield	99 percent

Ref. 1 [5660137](#); Journal; Krafft, Marie E.; Juliano, Carmelinda A.; JOCEAH; Journal of Organic Chemistry; English; 57; 19; 1992; 5106 - 5115; [

# Hints for successful reaction searches

- ◆ Use the generic substituents creatively
  - You can also generate user-defined generic groups!
  - These are extremely useful within ring systems. For example, creating G1 with one or two carbons allows variability in ring size
- ◆ Use atom connectivities between reagents and products to restrict search results
- ◆ Restrict your search by reagent or catalyst (if you know what they should be)



# ***What to do with reaction search results***

- ◆ Identify the **typical** method used in the literature and then **consult the original literature**
  - **In other words, find out who invented the reaction and read their papers first**
  - NEVER rely on a single preparatory method from someone who did not even invent the chemistry! Very often in the chemical literature, people who simply reproduced a method did not write down all the details.
- ◆ CrossFire does not tell you which method to use but it will tell you where others have been successful!

