Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2721695 A1 2009/11/12

(21) 2 721 695

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

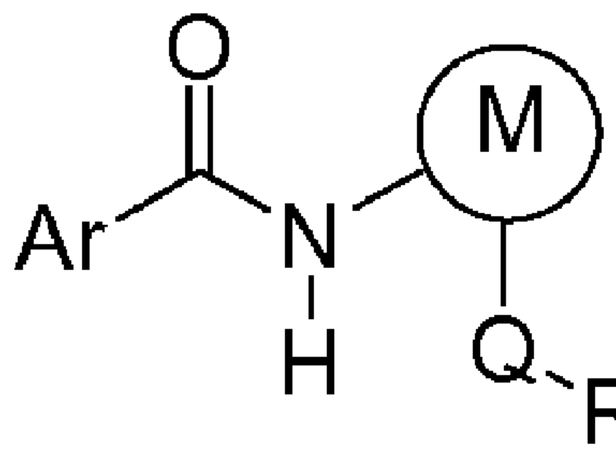
(86) Date de dépôt PCT/PCT Filing Date: 2009/05/06
(87) Date publication PCT/PCT Publication Date: 2009/11/12
(85) Entrée phase nationale/National Entry: 2010/10/15
(86) N° demande PCT/PCT Application No.: EP 2009/055446
(87) N° publication PCT/PCT Publication No.: 2009/135860
(30) Priorité/Priority: 2008/05/08 (EP08155888.4)

(51) Cl.Int./Int.Cl. *C07D 213/82* (2006.01), *C07C 231/02* (2006.01), *C07C 233/57* (2006.01), *C07C 233/64* (2006.01), *C07D 231/14* (2006.01), *C07D 231/16* (2006.01)

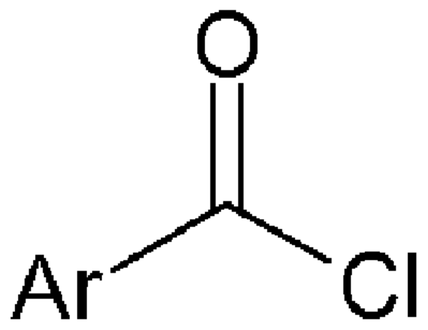
(71) Demandeur/Applicant:
BASF SE, DE

(72) Inventeurs/Inventors:
REICHERT, WOLFGANG, DE;
KORADIN, CHRISTOPHER, DE;
SMIDT, SEBASTIAN PEER, DE;
MAYWALD, VOLKER, DE;
WOLF, BERND, DE;
RACK, MICHAEL, DE; ...

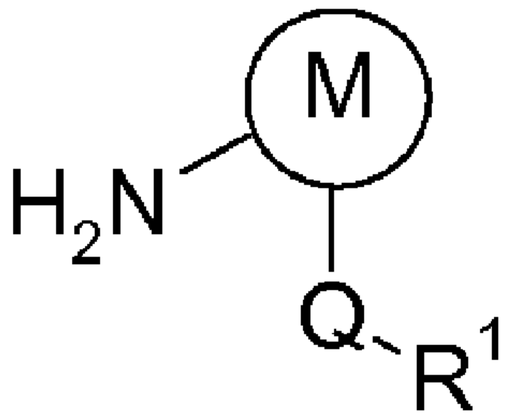
(54) Titre : PROCEDE DE PRODUCTION DE CARBOXAMIDES D'ARYLE
(54) Title: METHOD FOR MANUFACTURING ARYL CARBOXAMIDES




(I)




(II)




(III)

(57) Abrégé/Abstract:
Method for manufacturing aryl carboxamides of the formula (I), with Ar = singly to triply substituted phenyl , pyridyl or pyrazolyl rings, wherein the substituents are selected from halogen, $C_1$-$C_4$ alkyl and $C_1$-$C_4$ halogen alkyl; M = thienyl or phenyl, which can contain

CA 2721695 A1 2009/11/12

(21) 2 721 695

(13) A1

(72) Inventeurs(suite)/Inventors(continued): ZIERKE, THOMAS, DE; KEIL, MICHAEL, DE

(74) Agent: ROBIC

(57) Abrégé(suite)/Abstract(continued):
a halogen substituent; Q = direct bond, cyclopropylene, annulated bicyclo[2.2.1 ]heptane or bicyclo[2.2.1 ]heptene ring; $R^1$ = hydrogen, halogen, $C_1$-$C_6$ alkyl, $C_1$-$C_4$ alkoxy, Ci-C4 halogen alkoxy, singly to triply substituted phenyl, wherein the substituents are selected from halogen and trifluoromethylthio, or cyclopropyl; through reaction of an acid chloride of the formula (II) with an aryl amine (III) in a suitable non-aqueous solvent, wherein in the absence of an auxiliary base a) the acid chloride (II) is added, b) a pressure of 0 to 700 mbar is established, c) the aryl amine (III) is added in approximately stoichiometric amounts and d) the valuable product is isolated.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
Internationales Büro

(43) Internationales Veröffentlichungsdatum
12. November 2009 (12.11.2009)

PCT

(10) Internationale Veröffentlichungsnummer
WO 2009/135860 A1

(51) Internationale Patentklassifikation:
*C07D 213/82* (2006.01) *C07C 231/02* (2006.01)
*C07D 231/14* (2006.01) *C07C 233/57* (2006.01)
*C07D 231/16* (2006.01) *C07C 233/64* (2006.01)

(21) Internationales Aktenzeichen: PCT/EP2009/055446

(22) Internationales Anmeldedatum:
6. Mai 2009 (06.05.2009)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

(30) Angaben zur Priorität:
08155888.4 8. Mai 2008 (08.05.2008) EP

(71) Anmelder *(für alle Bestimmungsstaaten mit Ausnahme von US)*: **BASF SE** [DE/DE]; 67056 Ludwigshafen (DE).

(72) Erfinder; und

(75) Erfinder/Anmelder *(nur für US)*: **REICHERT, Wolfgang** [DE/DE]; Hanns-Faystr. 3, 67227 Frankenthal (DE). **KORADIN, Christopher** [DE/DE]; Riedlangstr. 15, 67067 Ludwigshafen (DE). **SMIDT, Sebastian Peer** [DE/DE]; Ernst-Barlach-Str. 12, 68723 Oftersheim (DE). **MAYWALD, Volker** [DE/DE]; Christoph-Kröwerath-Str. 72, 67071 Ludwigshafen (DE). **WOLF, Bernd** [DE/DE]; Halbergstr. 4, 67136 Fußgönheim (DE). **RACK, Michael** [DE/DE]; Hildastr. 11/1, 69214 Eppelheim (DE). **ZIERKE, Thomas** [DE/DE]; Akazienstr. 12, 67459 Böhl-Iggelheim (DE). **KEIL, Michael** [DE/DE]; Fontanestr. 4, 67251 Freinsheim (DE).

(74) Gemeinsamer Vertreter: **BASF SE**; 67056 Ludwigshafen (DE).

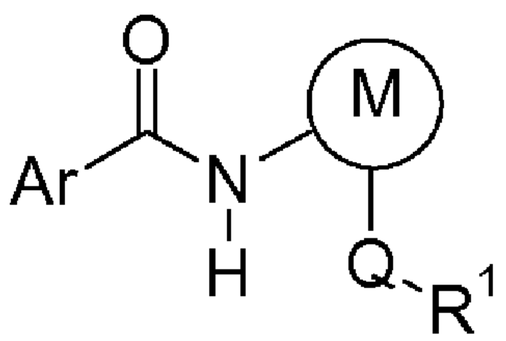
(81) Bestimmungsstaaten *(soweit nicht anders angegeben, für jede verfügbare nationale Schutzrechtsart)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Bestimmungsstaaten *(soweit nicht anders angegeben, für jede verfügbare regionale Schutzrechtsart)*: ARIPO (BW,

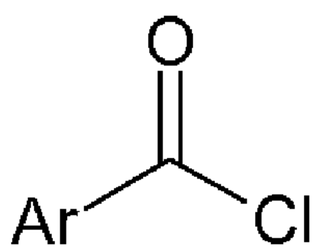
*[Fortsetzung auf der nächsten Seite]*

(54) Title: METHOD FOR MANUFACTURING ARYL CARBOXAMIDES

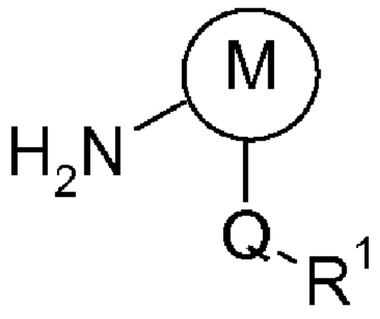
(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON ARYLCARBOXAMIDEN



(I)



(II)



(III)

(57) Abstract: Method for manufacturing aryl carboxamides of the formula (I), with Ar = singly to triply substituted phenyl , pyridyl or pyrazolyl rings, wherein the substituents are selected from halogen, $C_1$-$C_4$ alkyl and $C_1$-$C_4$ halogen alkyl; M = thienyl or phenyl, which can contain a halogen substituent; Q = direct bond, cyclopropylene, annulated bicyclo[2.2.1 ]heptane or bicyclo[2.2.1 ]heptene ring; $R^1$ = hydrogen, halogen, $C_1$-$C_6$ alkyl, $C_1$-$C_4$ alkoxy, Ci-C4 halogen alkoxy, singly to triply substituted phenyl, wherein the substituents are selected from halogen and trifluoromethylthio, or cyclopropyl; through reaction of an acid chloride of the formula (II) with an aryl amine (III) in a suitable non-aqueous solvent, wherein in the absence of an auxiliary base a) the acid chloride (II) is added, b) a pressure of 0 to 700 mbar is established, c) the aryl amine (III) is added in approximately stoichiometric amounts and d) the valuable product is isolated.

(57) Zusammenfassung: Verfahren zur Herstellung von Arylcarboxamiden der Formel (I) wobei Ar = ein- bis dreifach substituierter Phenyl-, Pyridyl- oder Pyrazolylring, wobei

*[Fortsetzung auf der nächsten Seite]*

WO 2009/135860 A1

WO 2009/135860 A1

GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), eurasisches (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Veröffentlicht**:

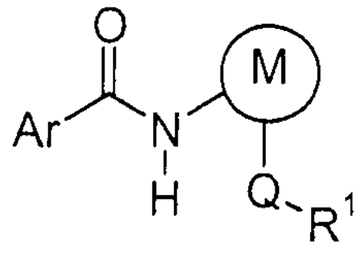
— *mit internationalem Recherchenbericht (Artikel 21 Absatz 3)*

die Substituenten ausgewählt sind aus Halogen, $C_1$-$C_4$-AIkyl und $C_1$-$C_4$-Halogenalkyl; M = Thienyl oder Phenyl, das einen Halogensubstituenten tragen kann; Q = direkte Bindung, Cyclopropylen, annellierter Bicyclo[2.2.1 ]heptan- oder BicycIo[2.2.1 ]hepten-Ring; $R^1$ = Wasserstoff, Halogen, $C_1$-$C_6$-Alkyl, $C_1$-$C_4$-AIkOXy, Ci-C4-Halogenalkoxy, ein- bis dreifach substituiertes Phenyl, wobei die Substituenten ausgewählt sind aus Halogen und Trifluormethylthio, oder Cyclopropyl; durch Umsetzung eines Säurechlorids der Formel (II) mit einem Arylamin (III) in einem geeigneten nicht-wässrigen Lösungsmittel, wobei man in Abwesenheit einer Hilfsbase a) das Säurechlorid (II) vorlegt, b) einen Druck von 0 bis 700 mbar einstellt, c) das Arylamin (III) in etwa stöchiometrischer Menge zudosiert und d) das Wertprodukt isoliert.

# Method for manufacturing aryl carboxamides

## Description

The present invention relates to a process for preparing arylcarboxamides of the formula (I)



(I),

where the substituents are each defined as follows:

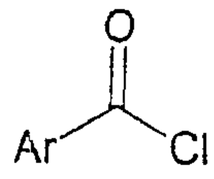
Ar is a mono- to trisubstituted phenyl, pyridyl or pyrazolyl ring, where the substituents are each independently selected from halogen, $C_1$-$C_4$-alkyl and $C_1$-$C_4$-haloalkyl;

M is thienyl or phenyl, which may bear a halogen substituent;

Q is a direct bond, cyclopropylene, a fused bicyclo[2.2.1]heptane or bicyclo[2.2.1]heptene ring;

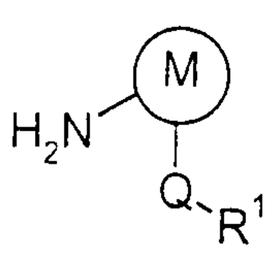
$R^1$ is hydrogen, halogen, $C_1$-$C_6$-alkyl, $C_1$-$C_4$-alkoxy, $C_1$-$C_4$-haloalkoxy, mono- to trisubstituted phenyl, where the substituents are each independently selected from halogen and trifluoromethylthio, or cyclopropyl;

by reacting an acid chloride of the formula (II)



(II)

with an arylamine (III)



(III),

in a suitable nonaqueous solvent.

JP-A 2001/172276 discloses that alkyl- or phenylcarbonyl chlorides can be reacted with

arylamines under reduced pressure. The reactions described are carried out without an auxiliary base, but in highly dilute solutions. For an industrial scale preparation of the arylcarboxamides (I), this process is, however, unsuitable owing to the large amounts of solvent. A more concentrated mode of operation is not possible, since this leads to lump formation and mixing problems, which greatly reduces the yield of product of value.

Other processes described in the literature for preparing carboxamides from acid chloride and arylamine without use of an auxiliary base (cf., for example, Journal of Combinatorial Chemistry (2003), 5(3), 253-259, Structural Chemistry (2006), 17(2), 241-247 and JP-A 1973/049217) are not usable on the industrial scale, because they afford the desired products of value only in poor yields.

It was accordingly an object of the present invention to provide a process usable on the industrial scale for preparing the arylcarboxamides (I).

Accordingly, it has been found that the arylcarboxamides (I) are obtainable in high yields by, in the absence of an auxiliary base,

a) initially charging the acid chloride (II),
b) establishing a pressure of from 0 to 700 mbar,
c) metering in the arylamine (III) in an approximately stoichiometric amount and
d) isolating the product of value.

The acid chlorides (II) are either commercially available or can be prepared, for example, according to R. C. Larock, Comprehensive Organic Transformations, Verlage Wiley-VCH, 2nd Edition 1999, pages 1929 ff.

The arylamines (III) are generally obtainable by hydrogenating the corresponding nitroaromatics. Further details can be found, for example, in R. C. Larock, Comprehensive Organic Transformations, Verlage Wiley-VCH, 2nd Edition 1999, pages 821 ff.

The term "**halogen**" in each case denotes fluorine, chlorine, bromine or iodine, preferably fluorine or chlorine;

"**$C_1$-$C_6$-alkyl**", as used herein, denotes a saturated straight-chain or branched hydrocarbon group comprising from 1 to 6 carbon atoms, especially from 1 to 4 carbon atoms, for example methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-

dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl, 1-ethyl-2-methylpropyl and isomers thereof. $C_1$-$C_4$-Alkyl comprises, for example, methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl or 1,1-dimethylethyl.

"**$C_1$-$C_4$-haloalkyl**" represents a partly or fully halogenated $C_1$-$C_4$-alkyl radical, where the halogen atom(s) is/are especially fluorine, chlorine and/or bromine, i.e., for example, chloromethyl, bromomethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 1-chloroethyl, 1-bromoethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2-chloro-2-fluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-1,1,2-trifluoroethyl, 2-chloro-2,2-difluoroethyl, 2-bromo-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl, 1,1,2,2-tetrafluoroethyl, 1,1,2,2-tetrachloroethyl, pentafluoroethyl, 2,2,3,3-tetrafluoro-1-propyl, 1,1,2,3,3,3-hexafluoro-1-propyl, 1,1,1,3,3,3-hexafluoro-2-propyl, heptafluoro-1-propyl, heptafluoro-2-propyl, 2,2,3,3,4,4,4-heptafluoro-1-butyl or nonafluoro-1-butyl, especially halomethyl, more preferably $CH(F)_2$ and $CF_3$;

"**$C_1$-$C_4$-alkoxy**" represents methoxy, ethoxy, n-propoxy, 1-methylethoxy, n-butoxy, 1-methylpropoxy, 2-methylpropoxy or 1,1-dimethylethoxy, especially 1-methylethoxy;

"**$C_1$-$C_4$-haloalkoxy**" represents a partly or fully halogenated $C_1$-$C_4$-alkoxy radical, where the halogen atom(s) is/are especially fluorine, chlorine and/or bromine, i.e., for example, $OCH_2Cl$, $OCH_2Br$, $OCHCl_2$, $OC(Cl)_3$, $OCH_2F$, $OCHF_2$, $OCF_3$, OCHFCl, $OCFCl_2$, $OCF_2Cl$, $OCHCl\text{-}CH_3$, $OCHBr\text{-}CH_3$, $OCHF\text{-}CH_3$, $OCH_2\text{-}CH_2F$, $OCH_2\text{-}CHF_2$, $OCH_2\text{-}CHFCl$, $OCH_2\text{-}CF_3$, $OCF_2\text{-}CHFCl$, $OCH_2\text{-}CF_2Cl$, $OCH_2\text{-}CF_2Br$, $OCH_2\text{-}CFCl_2$, $OCH_2\text{-}C(Cl)_3$, $OCF_2\text{-}CHF_2$, $OC(Cl)_2\text{-}CHCl_2$, $OC_2F_5$, $OCH_2\text{-}CF_2\text{-}CHF_2$, $OCF_2\text{-}CHF\text{-}CF_3$, $OCH(CF_3)_2$, $O(n\text{-}C_3F_7)$, $OCF(CF_3)_2$, 2,2,3,3,4,4,4-heptafluoro-1-butoxy or nonafluoro-1-butoxy, especially $OCF_2\text{-}CHF\text{-}CF_3$.

The preparation of the following arylcarboxamides (I) is preferred:
benodanil, bixafen, boscalid, flutolanil, mepronil, penthiopyrad,
N-(2-bicyclopropyl-2-ylphenyl)-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethylpyrazol-4-ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethyl-5-fluoropyrazol-4-ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-5-chloro-1,3-dimethylpyrazol-4-ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-3-fluoromethyl-1-methylpyrazol-4-ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-3-(chlorofluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-5-fluoro-1-methylpyrazol-4-

ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-5-chloro-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-3-(chlorodifluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-5-fluoro-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-5-chloro-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethyl-5-fluoropyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-5-chloro-1,3-dimethylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-3-fluoromethyl-1-methylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-3-(chlorofluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-5-fluoro-1-methylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-5-chloro-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-3-(chlorodifluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-5-fluoro-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-5-chloro-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide,
N-(3',4'-dichloro-3-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-dichloro-3-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-difluoro-3-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-carboxamide,
N-(3',4'-difluoro-3-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3'-chloro-4'-fluoro-3-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-dichloro-4-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-difluoro-4-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-

ylcarboxamide,
N-(3',4'-dichloro-4-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-difluoro-4-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3'-chloro-4'-fluoro-4-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-difluoro-5-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-difluoro-5-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-1,3-dimethyl-1H-pyrazol-4-ylcarboxamide,
N-(3'-chloro-4'-fluoro-5-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-fluoro-4-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-fluoro-5-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-chloro-5-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-methyl-5-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-fluoro-5-fluorobiphenyl-2-yl)-1,3-dimethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-chloro-5-fluorobiphenyl-2-yl)-1,3-dimethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-methyl-5-fluorobiphenyl-2-yl)-1,3-dimethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-fluoro-6-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-[2-(1,1,2,3,3,3-hexafluoropropoxy)phenyl]-3-difluoromethyl-1-methyl-1H-pyrazol-4-ylcarboxamide,
N-[4'-(trifluoromethylthio)biphenyl-2-yl]-3-difluoromethyl-1-methyl-1H-pyrazol-4-ylcarboxamide,
N-[4'-(trifluoromethylthio)biphenyl-2-yl]-1-methyl-3-trifluoromethyl-1-methyl-1H-pyrazol-4-ylcarboxamide,
3-(difluoromethyl)-1-methyl-N-[1,2,3,4-tetrahydro-9-(1-methylethyl)-1,4-methanonaphthalen-5-yl]-1H-pyrazol-4-ylcarboxamide,
N-(3'-chloro-5-fluorobiphenyl-2-yl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(4'-chloro-5-fluorobiphenyl-2-yl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,

N-(4'-chlorobiphenyl-2-yl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(4'-bromobiphenyl-2-yl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(4'-iodobiphenyl-2-yl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(3',5'-difluorobiphenyl-2-yl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(2-chloro-4-fluorophenyl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(2-bromo-4-fluorophenyl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(2-iodo-4-fluorophenyl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide or
N-[2-(1,3-dimethylbutyl)phenyl]-1,3-dimethyl-5-fluoro-1H-pyrazol-4-ylcarboxamide.

Particular preference is given to those carboxamides (I) in which
Ar is a mono- to trisubstituted pyridyl or pyrazolyl ring, where the substituents are each independently selected from halogen, $C_1$-$C_4$-alkyl and $C_1$-$C_4$-haloalkyl. Very particular preference is given to those carboxamides (I) in which Ar is a di- or trisubstituted pyrazolyl ring, where the substituents are each independently selected from halogen, $C_1$-$C_4$-alkyl and $C_1$-$C_4$-haloalkyl, especially fluorine, chlorine, methyl, difluoromethyl and trifluoromethyl.

According to the invention, the reaction is conducted without an auxiliary base in an organic solvent which is substantially anhydrous. A low water content is understood to mean from about 0.5 g to 5 g of water per mole of acid chloride (II) used. Larger amounts of water should be avoided, since the water would lead to an increased consumption of feedstocks.

Usable solvents are, for example, aromatic hydrocarbons such as toluene, o-, m-, p-xylene, mesitylene, ethylbenzene and chlorobenzene, halogenated aliphatic hydrocarbons such as tetrachloroethane and dichloroethylene, ethers such as methyl tert-butyl ethyl, tetrahydrofuran and dioxane or mixtures of the solvents mentioned. Particularly preferred solvents are the aromatic hydrocarbons, especially toluene and o-, m-, p-xylene.

According to the invention, the acid chloride (II) is initially charged, the desired pressure is established and the arylamine (III) is metered in. Metered addition is understood to mean both the addition of (III) in portions and the continuous addition of (III)

a) to the surface of the solution of (II) or
b) directly into the solution of (II), as an “immersed mode of reaction”.

The pressure is generally selected such that the reaction mixture boils.

It is normal to work at a pressure between 0 and 700 mbar and a reaction temperature of from 20 to 120°C, preferably at from 200 to 600 mbar and from 70 to 100°C,

especially at from 350 to 450 mbar and 80 to 90°C.

Acid chloride (II) and arylamine (III) are used in about equimolar amounts, or one of the components is used in a slight excess of up to 10 mol%. The molar ratio of (III) to (II) is thus generally from 0.9 : 1 to 1.1 : 1, preferably from about 1.0 to 1.1.

The metered addition of (III), preferably dissolved in the organic solvent in which (II) has also been initially charged, is effected typically over the course of from 0.5 to 20 hours, especially from 2 to 10 hours, more preferably from 3 to 5 hours.

The carboxamide (I) is released from the reaction mixture preferably by direct crystallization or by treatment of the reaction mixture with a suitable base and subsequent crystallization, for example at from (-20) to 20°C.

Suitable bases for this purpose are alkali metal hydroxides such as sodium and potassium hydroxide, alkali metal carbonates such as sodium and potassium carbonate, alkali metal hydrogencarbonates such as sodium and potassium hydrogencarbonate, alkali metal phosphates such as sodium and potassium phosphate, alkali metal hydrogenphosphates such as sodium and potassium hydrogen-phosphate, alkali metal dihydrogenphosphates such as sodium and potassium dihydrogenphosphate, and also nitrogen bases such as ammonia.
Particular preference is given to the alkali metal hydroxides such as sodium and potassium hydroxide, alkali metal carbonates such as sodium and potassium carbonate, and also to the alkali metal hydrogencarbonates such as sodium and potassium hydrogencarbonate.

The base can be used in solid form or in the form of its commercial aqueous solutions. Preference is given to using a from 1 to 20% by weight aqueous solution, the amount preferably being such that the pH of the solution is from 3 to 12, preferably from 7 to 10.

The crystalline product of value can finally be removed by means of customary methods, for example filtration.

The process products (I) are valuable active ingredients in crop protection.

Working examples:

Example 1

Synthesis of N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide

100.0 g (0.504 mol, 98% pure) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl chloride were dissolved at 25°C in 257.2 g of toluene. The solution was evacuated to 400 mbar and heated to 85°C. Subsequently, within 3 hours, 492.8 g (0.499 mol, 23% strength) of toluenic 3',4',5'-trifluorobiphenyl-2-ylamine solution were metered in, after which stirring was continued for another 1 hour. After venting and cooling to 25°C with a ramp of 10°C/h, the mixture was stirred overnight. Subsequently, the mixture was cooled to 0°C, and the solid constituents were filtered off, washed with cold toluene and dried at 80°C under reduced pressure. The yield (without further processing of the mother liquor) was 177.7 g (92%).

Example 1a (comparative test)

Synthesis of N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide (analogous mode of reaction to example 1 from JP-A 2001/172276, p. 10)

19.0 g (0.085 mol, 99.8% pure) of 3',4',5'-trifluorobiphenyl-2-ylamine were dissolved in 400.0 g of toluene. Within 1 min, 17.7 g (0.089 mol, 98.1% pure) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl chloride were added at 25°C. Subsequently, the reaction mixture was evacuated to 72 mbar and heated to 40°C for 3 hours. After 15 min, a white solid formed, which was later converted to a viscous, gel-like suspension. After cooling to 0°C, the mixture was filtered through a glass frit (very slow, blockages) and the filtercake was washed with cold toluene. The residue was dried under reduced pressure and afforded 15.0 g of a mixture of 3',4',5'-trifluorobiphenyl-2-ylamine hydrochloride (40% by weight) and N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide (48% by weight). The mother liquor (375.0 g) comprised 2.8% by weight of N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide. Purely theoretically, the yield was thus approx. 54%.

Example 2

Synthesis of N-(3',5'-difluorobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide

38.9 g (0.196 mol, 98% pure) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl chloride were dissolved at 25°C in 100.0 g of toluene. The solution was evacuated to 400 mbar and heated to 85°C. Subsequently, within 1.5 hours, 173.0 g (0.194 mol, 23% strength) of toluenic 3',4'-difluorobiphenyl-2-ylamine solution were metered in and the reaction mixture was stirred for a further 1 hour. After venting and cooling to room temperature, the mixture was concentrated to volume approx. 100 ml under reduced pressure. The solids were filtered off, washed with n-hexane and dried at 85°C under reduced pressure. The yield (without further processing of the mother liquor) was

46.5 g (66%).

Example 3

Synthesis of N-(3',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethyl-1H-pyrazole-4-carboxamide

79.1 g (0.494 mol, 99% pure) of 1,3-dimethyl-1H-pyrazole-4-carbonyl chloride were dissolved at 25°C in 257.2 g of toluene. The solution was evacuated to 400 mbar and heated to 85°C. Subsequently, within 3 hours, 483.0 g (0.489 mol, 23% strength) of toluenic 3',4',5'-trifluorobiphenyl-2-ylamine solution were metered in and the reaction mixture was stirred for a further 1 hour. After venting and cooling to 70°C, the mixture was cooled to 20°C with a cooling ramp of 5°C/h and stirred overnight. Subsequently, the mixture was cooled to 0°C, and the solids were filtered off, washed with cold toluene and dried at 80°C under reduced pressure. The yield (without further processing of the mother liquor) was 155.4 g (92%).

Example 4

Synthesis of N-(2-chlorophenyl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide

80.0 g (0.403 mol, 98% pure) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl chloride were dissolved at 25°C in 257.2 g of toluene. The solution was evacuated to 400 mbar and heated to 85°C. Subsequently, within 3 hours, 221.3 g (0.399 mol, 23% strength) of toluenic 2-chloroaniline solution were metered in and the reaction mixture was stirred for a further 1 hour. After venting and cooling to 20°C with a ramp of 10°C/h, the mixture was stirred overnight. Subsequently, the mixture was cooled to 0°C, and the solids were filtered off, washed with cold toluene and dried at 80°C under reduced pressure. The yield (without further processing of the mother liquor) was 105 g (92%).

Example 5

Synthesis of N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide

5.6 g (0.029 mol, 98% pure) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl chloride were dissolved at 25°C in 10.4 g of toluene. The solution was evacuated to 400 mbar and heated to 85°C. Subsequently, within 5 minutes, 7.8 g (0.030 mol, approx. 92% pure) of 3',4'-dichloro-5-fluorobiphenyl-2-ylamine, dissolved in 28 g of toluene, were metered in and the reaction mixture was stirred for a further 1 hour. After venting and cooling to 25°C overnight, the mixture was cooled further to 0°C, and the solids were filtered off, washed with cold toluene and dried at 80°C under reduced pressure. The yield (without further processing of the mother liquor) was 8.1 g (71%).

Example 6

Synthesis of N-(2-bicyclopropyl-2-ylphenyl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide

16.7 g (0.086 mol, 98% pure) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl chloride were dissolved at 25°C in 48.0 g of toluene. The solution was evacuated to 400 mbar and heated to 85°C. Subsequently, within 45 min, 15.0 g (0.087 mol) of 2-bicyclopropyl-2-ylphenylamine, dissolved in 51.6 g of toluene, were metered in and the reaction mixture was stirred for another 1 h. After venting and cooling to 25°C, the mixture was stirred overnight. Subsequently, the mixture was concentrated under reduced pressure and dried. The yield was 27.3 g (96%).

Example 7

Synthesis of N-(9-isopropyl-1,2,3,4-tetrahydro-1,4-methanonaphthalen-5-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide

15.1 g (0.0752 mol, 96.5% pure) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl chloride were dissolved at 25°C in 100 ml of toluene. The solution was evacuated to 350 mbar and heated to 85°C. Subsequently, within 60 min, 20 g (0.074 mol, 75%; 65:10 syn/anti isomer mixture) of 9-isopropyl-1,2,3,4-tetrahydro-1,4-methano-naphthalen-5-ylamine, dissolved in 100 ml of toluene, were metered in and the reaction mixture was stirred for another 1 hour. After venting and cooling to 25°C, the mixture was stirred overnight. Subsequently, the mixture was concentrated under reduced pressure and dried. The yield was 31.3 g; according to 1H NMR 70% pure (82%).

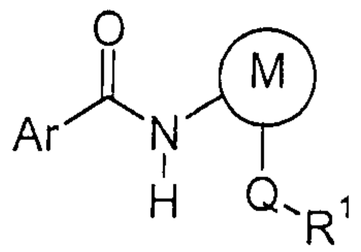
Example 8

Synthesis of 2-chloro-N-(4'-chlorobiphenyl-2-yl)nicotinamide

100.0 g (0.557 mol, 98% pure) of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carbonyl chloride were dissolved at 25°C in 80.0 g of toluene. The solution was evacuated to 200 mbar and heated to 95°C. Subsequently, within 2.5 hours, 396.8 g (0.541 mol, 28% strength) of xylenic 4'-chlorobiphenyl-2-ylamine solution were metered in and the reaction mixture was stirred for a further 1 hour. After venting and cooling to 87°C, the mixture was seeded with 1 g of 2-chloro-N-(4'-chlorobiphenyl-2-yl)nicotinamide and the temperature was maintained for 1 hour. Subsequently, the mixture was cooled to 25°C with a ramp of 5°C/h. After further cooling to 10-15°C, the solids were filtered off, washed with cold xylene and dried at 80°C under reduced pressure. The yield (without further processing of the mother liquor) was 166.4 g (73%). HPLC shows the desired product and the diacylated product in a ratio of 85:15 area%.

Claims

1. A process for preparing arylcarboxamides of the formula (I)



(I),

where the substituents are each defined as follows:

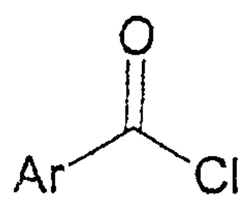
Ar is a mono- to trisubstituted phenyl, pyridyl or pyrazolyl ring, where the substituents are each independently selected from halogen, $C_1$-$C_4$-alkyl and $C_1$-$C_4$-haloalkyl;

M is thienyl or phenyl, which may bear a halogen substituent;

Q is a direct bond, cyclopropylene, a fused bicyclo[2.2.1]heptane or bicyclo[2.2.1]heptene ring;

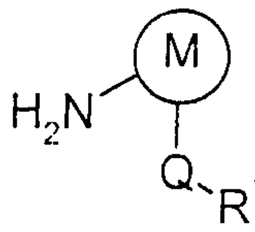
$R^1$ is hydrogen, halogen, $C_1$-$C_6$-alkyl, $C_1$-$C_4$-alkoxy, $C_1$-$C_4$-haloalkoxy, mono- to trisubstituted phenyl, where the substituents are each independently selected from halogen and trifluoromethylthio, or cyclopropyl;

by reacting an acid chloride of the formula (II)



(II)

with an arylamine (III)



(III),

in a suitable nonaqueous solvent,

which comprises, in the absence of an auxiliary base,

a) initially charging the acid chloride (II),

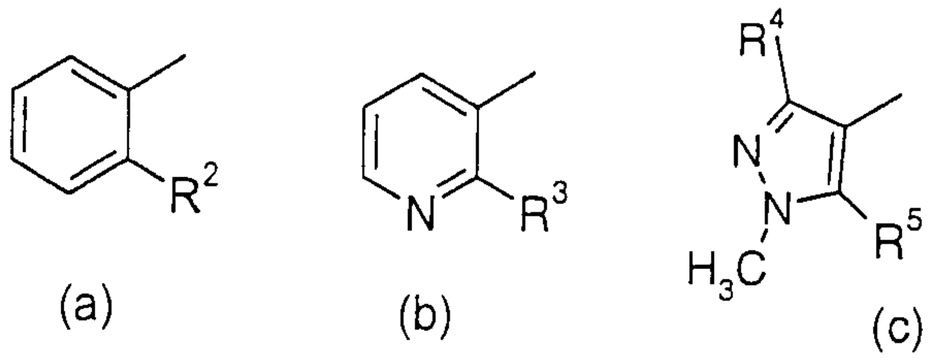
b) establishing a pressure of from 0 to 700 mbar,

c) metering in the arylamine (III) in an approximately stoichiometric amount

and

d) isolating the product of value.

2. The process according to claim 1, wherein Ar is a phenyl, pyridyl or pyrazolyl ring



(a) (b) (c)

and

$R^2$ is halogen, methyl or trifluoromethyl;

$R^3$ is halogen;

$R^4$ is $C_1$-$C_4$-alkyl or $C_1$-$C_4$-haloalkyl and

$R^5$ is hydrogen or halogen.

3. The process according to claim 1, wherein M is phenyl, Q is cyclopropylene and $R^1$ is cyclopropyl.

4. The process according to claim 1, wherein M is phenyl, Q is a bond and $R^1$ is isopropoxy or mono- to trisubstituted phenyl, where the substituents are each independently selected from halogen and trifluoromethylthio.

5. The process according to claim 1, wherein M is phenyl substituted by one halogen, Q is a bond and $R^1$ is hydrogen or mono- to tri-halogen-substituted phenyl.

6. The process according to claim 1, wherein the arylcarboxamide is benodanil, bixafen, boscalid, flutolanil, mepronil, penthiopyrad, N-(2-bicyclopropyl-2-ylphenyl)-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethyl-5-fluoropyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-5-chloro-1,3-dimethylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-3-fluoromethyl-1-methylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-3-(chlorofluoromethyl)-1-methylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide, N-(3',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-5-fluoro-1-methylpyrazol-4-ylcarboxamide,

N-(3',4',5'-trifluorobiphenyl-2-yl)-5-chloro-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-3-(chlorodifluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-5-fluoro-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide,
N-(3',4',5'-trifluorobiphenyl-2-yl)-5-chloro-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-1,3-dimethyl-5-fluoropyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-5-chloro-1,3-dimethylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-3-fluoromethyl-1-methylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-3-(chlorofluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-3-difluoromethyl-5-fluoro-1-methylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-5-chloro-3-difluoromethyl-1-methylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-3-(chlorodifluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-5-fluoro-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide,
N-(2',4',5'-trifluorobiphenyl-2-yl)-5-chloro-1-methyl-3-trifluoromethylpyrazol-4-ylcarboxamide,
N-(3',4'-dichloro-3-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-dichloro-3-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-difluoro-3-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-carboxamide,
N-(3',4'-difluoro-3-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3'-chloro-4'-fluoro-3-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-dichloro-4-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-

ylcarboxamide,
N-(3',4'-difluoro-4-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-dichloro-4-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-difluoro-4-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3'-chloro-4'-fluoro-4-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-difluoro-5-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-difluoro-5-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(3',4'-dichloro-5-fluorobiphenyl-2-yl)-1,3-dimethyl-1H-pyrazol-4-ylcarboxamide,
N-(3'-chloro-4'-fluoro-5-fluorobiphenyl-2-yl)-1-methyl-3-difluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-fluoro-4-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-fluoro-5-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-chloro-5-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-methyl-5-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-fluoro-5-fluorobiphenyl-2-yl)-1,3-dimethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-chloro-5-fluorobiphenyl-2-yl)-1,3-dimethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-methyl-5-fluorobiphenyl-2-yl)-1,3-dimethyl-1H-pyrazol-4-ylcarboxamide,
N-(4'-fluoro-6-fluorobiphenyl-2-yl)-1-methyl-3-trifluoromethyl-1H-pyrazol-4-ylcarboxamide,
N-[2-(1,1,2,3,3,3-hexafluoropropoxy)phenyl]-3-difluoromethyl-1-methyl-1H-pyrazol-4-ylcarboxamide,
N-[4'-(trifluoromethylthio)biphenyl-2-yl]-3-difluoromethyl-1-methyl-1H-pyrazol-4-ylcarboxamide,
N-[4'-(trifluoromethylthio)biphenyl-2-yl]-1-methyl-3-trifluoromethyl-1-methyl-1H-pyrazol-4-ylcarboxamide,
3-(difluoromethyl)-1-methyl-N-[1,2,3,4-tetrahydro-9-(1-methylethyl)-1,4-methanonaphthalen-5-yl]-1H-pyrazol-4-ylcarboxamide,

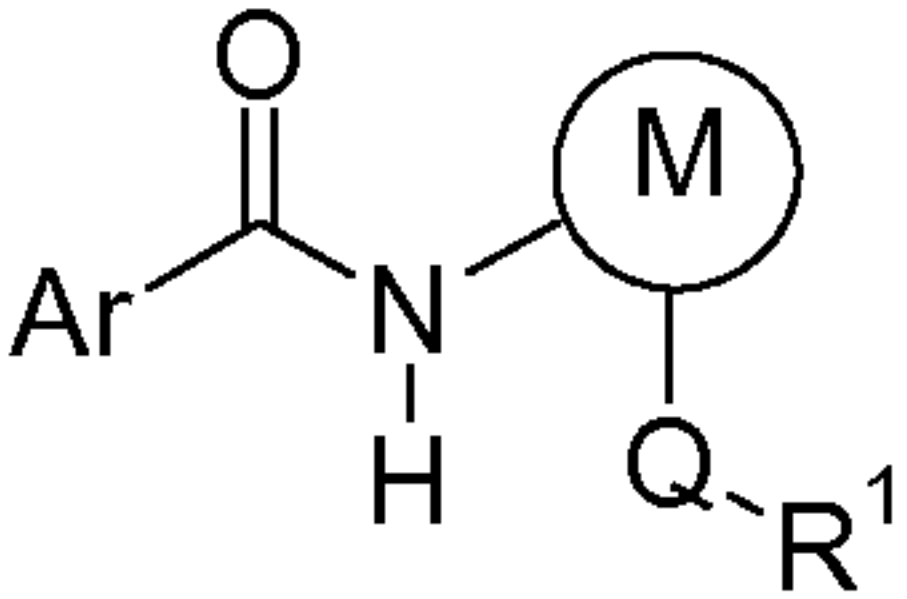
N-(3'-chloro-5-fluorobiphenyl-2-yl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(4'-chloro-5-fluorobiphenyl-2-yl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(4'-chlorobiphenyl-2-yl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(4'-bromobiphenyl-2-yl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(4'-iodobiphenyl-2-yl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(3',5'-difluorobiphenyl-2-yl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(2-chloro-4-fluorophenyl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(2-bromo-4-fluorophenyl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide,
N-(2-iodo-4-fluorophenyl)-3-(difluoromethyl)-1-methylpyrazol-4-ylcarboxamide or
N-[2-(1,3-dimethylbutyl)phenyl]-1,3-dimethyl-5-fluoro-1H-pyrazol-4-ylcarboxamide.

7. The process according to claim 1, wherein the reaction of II with III is undertaken at a pressure of from 200 to 600 mbar.

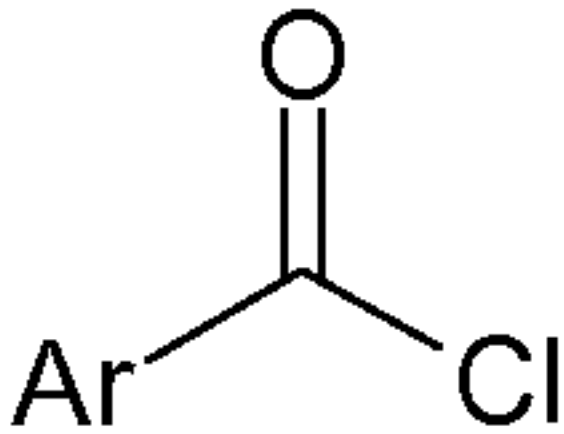
8. The process according to claim 1, wherein the reaction of II with III is undertaken at from 20 to 120°C.

9. The process according to claim 1, wherein the molar ratio of II to III is from 0.9 : 1 to 1.1 : 1.

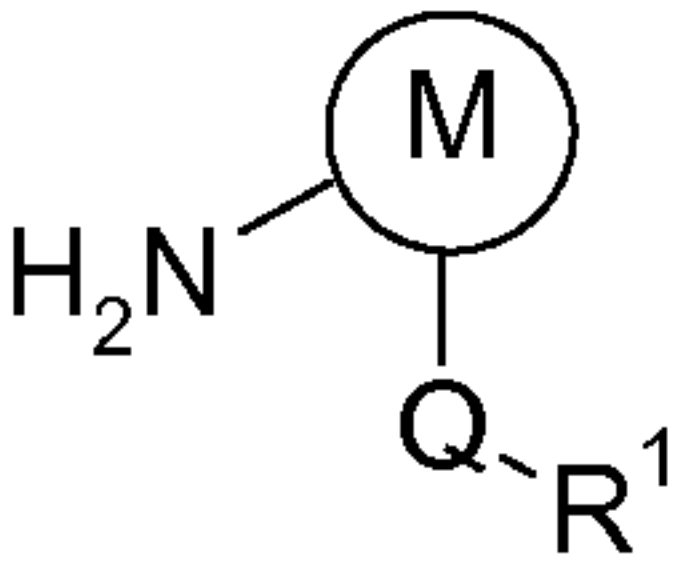
10. The process according to claim 1, wherein the starting material is an arylamine III which has been obtained by hydrogenating the corresponding nitroaryl.




(I)




(II)




(III)