# Classification of Synthetic Cannabinoids by Bridge Carbonyl Bands in Vapor Phase IR

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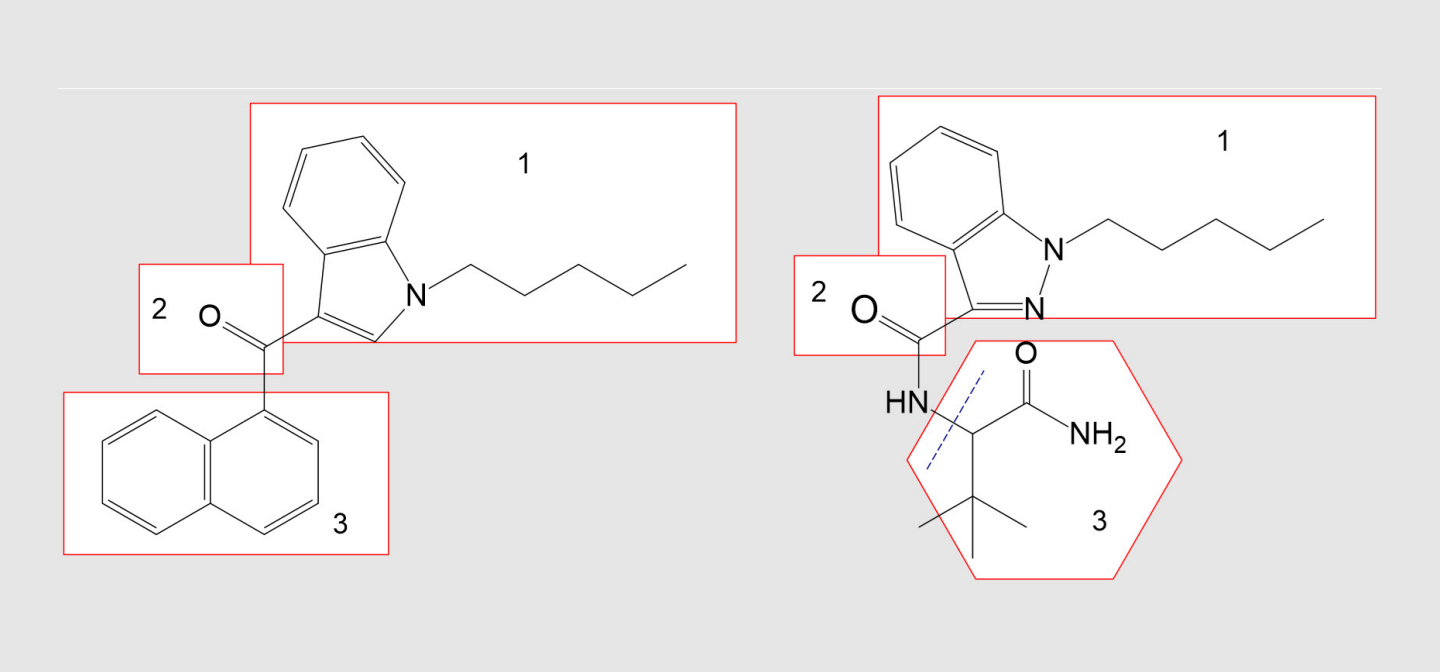
# Overview

Synthetic cannabinoids are a major category of designer drugs with such rapid growth that crime labs and chemical standards suppliers are in a constant race to identify them. Because of the implicit toxicity of these compounds, minimal handling of samples is desirable. GC-IR is a technology suitable for such a purpose. It requires a small amount of sample, is an easy IR process, and has a simple sample preparation procedure in which water and polymorphism affects are eliminated completely. Most importantly, vapor phase makes it possible to completely resolve and identify every single carbonyl band present within the molecule for all categories of synthetic cannabinoids (see **Background Information** section)[1-4]. This cannot be accomplished by using any other form of solid phase or deposit techniques because intermolecular hydrogen bonding can obscure these bands.

We have developed a unique application in KnowItAll[5] to classify synthetic cannabinoids using their distinct bridge carbonyl band patterns[6]. This new feature, along with Wiley's synthetic cannabinoids database[7] and other forensic databases[8-10], can help forensic, law enforcement, toxicology, pharmaceutical, and research communities accelerate their analyses.

# Theory

Synthetic cannabinoids can be represented by the following framework structure:




Where:

- "1" is the **CORE RING SYSTEM** – Most common are Indole and Indazole but can also be other ring systems such as Benzimidazole, Pyrrole, and Carbazole.
- "2" is the **BRIDGE** joining the **CORE RING SYSTEM** with another ring or functional group. Examples: Ketones, Esters, and Secondary Amides.
- "3" is the **SECONDARY SYSTEM** such as Naphthalene, Benzene, Quinoline, or another functional group such as an Ester or Primary Amide. If the third piece is a functional group, it begins on the opposite side of the dashed line from the **BRIDGE** ("2") functional group. In some cases, this secondary functional group may be bonded to another ring system. No matter how complex the third piece is, its functional group moiety is always bonded directly to the **BRIDGE** functional group.

All carbonyl absorptions are recorded from the unknown compound in the range of 1840-1640 $cm^{-1}$ and noted. The carbonyl band cluster can contain one single band to a maximum of three bands, and the **BRIDGE** frequency value is always the lowest in frequency of all (the band closest to 1640 $cm^{-1}$). If there is only one band present in this region, it is the **BRIDGE** frequency.

The numerous categories displayed in the software are defined by the three pieces given in this classification system and, when joined together, represent the entire molecular structure of a given synthetic cannabinoid variety. For more information, please see the **Background Information** section of this paper.

IR and Raman functional group analysis is already a feature of KnowItAll[5]. In the KnowItAll 2023 release, we expanded this application framework for vapor phase IR analysis.

## BRIDGE Carbonyl Bands in AnalyzeIt Vapor Phase IR Knowledgebase

Structure frameworks representing the essence of various synthetic carbonyl compound class were drawn and the corresponding primary band information is incorporated as shown in the **Figure 1** example. Sometimes, a functional group exhibits an extra band, which is unique to this type of cannabinoid. This band is incorporated into the **Knowledgebase**. When a secondary carbonyl group is in a structure, its band is also coded into the **Knowledgebase** as well. All three types of bands are used together to classify an unknown synthetic cannabinoid.

The **AnalyzeIt Vapor Phase IR Knowledgebase** is used with KnowItAll's manual band analysis tool, **AnalyzeIt**, and its automatic analysis tool, **ID Expert**.

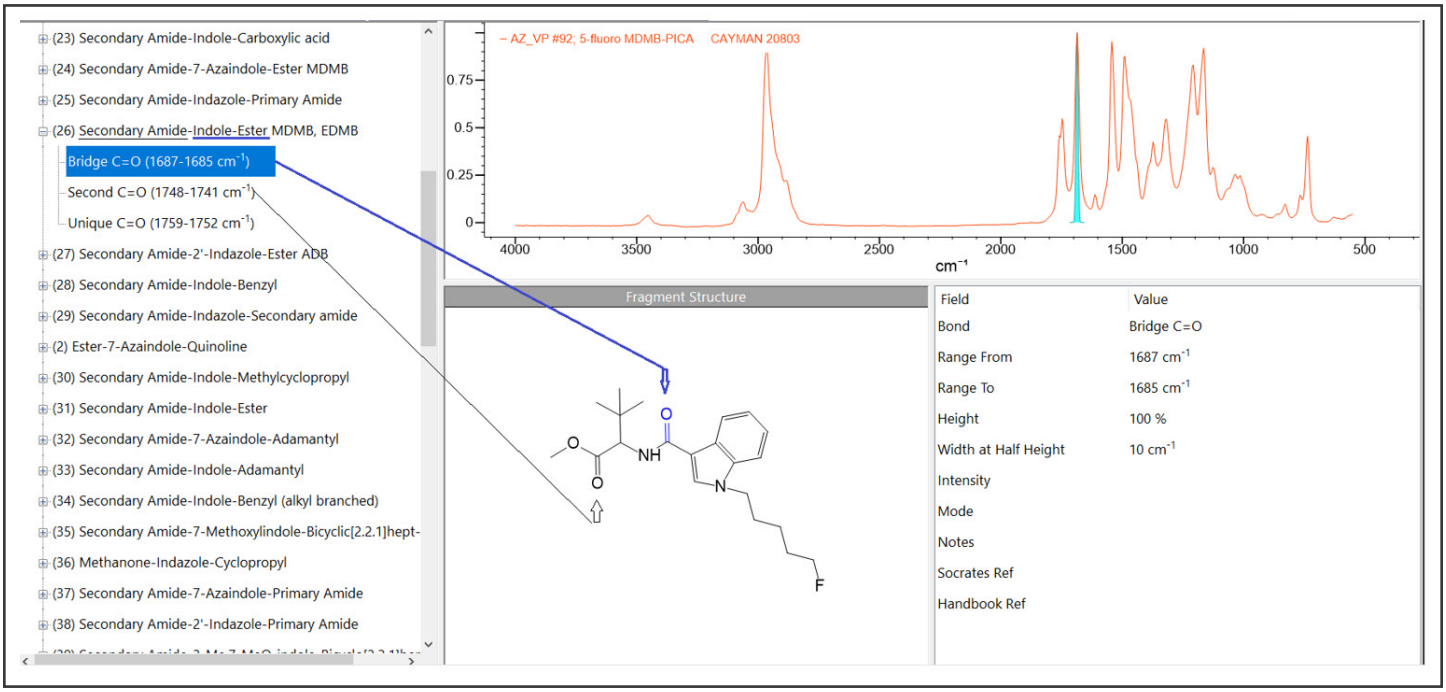



**Figure 1.** An example representation of a carbonyl band cluster. The selected band is highlighted in blue.

## AnalyzeIt Vapor Phase IR Application

After an unknown spectrum is read into the application, the user can click on peaks in the 1840-1640 $cm^{-1}$ region, and the application will show matching functional groups listed in alphabetical order. Individual band information is available for more specific analysis (**Figure 2**).

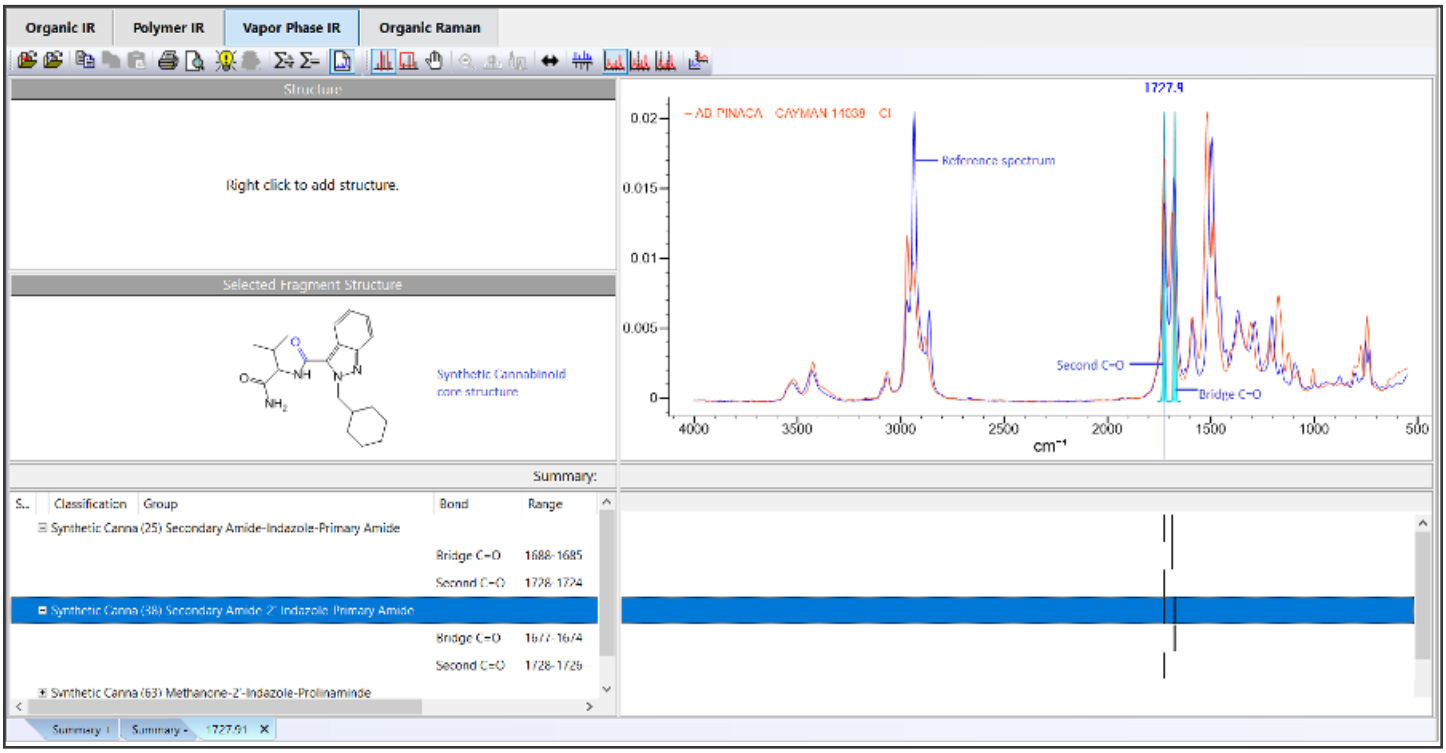



**Figure 2. AnalyzeIt Vapor Phase IR** application interface.

## ID Expert Synthetic Cannabinoid Classification

Automatic functional group analysis has always been a feature of the **KnowItAll ID Expert** application. When an unknown IR or Raman spectrum is read, **ID Expert** performs functional group analysis and lists relevant matches in a hit list tab. The **KnowItAll** 2023 release expanded this feature to use a proprietary **Vapor Phase IR Knowledgebase** for synthetic cannabinoid classification (**Figure 3**).

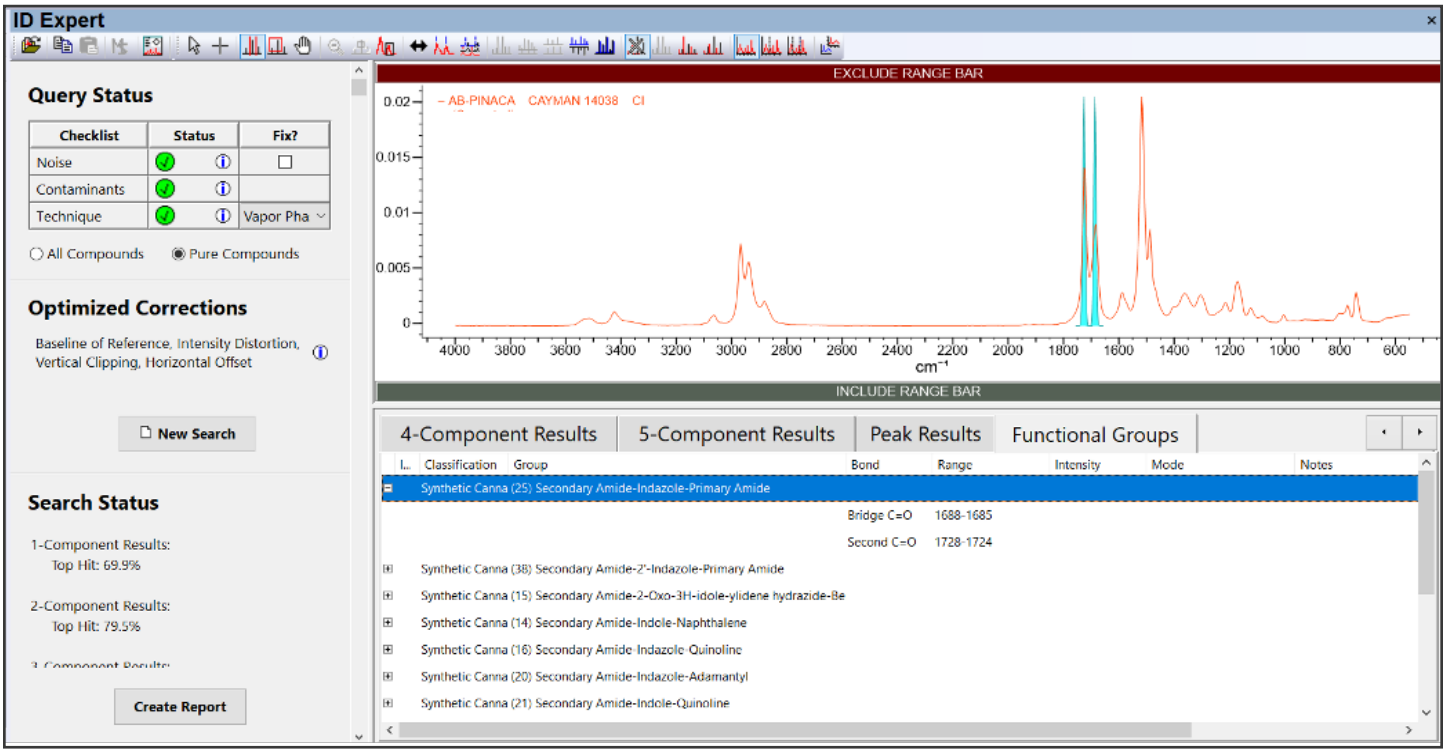



**Figure 3.** KnowItAll ID Expert performs automatic vapor phase IR synthetic cannabinoid classification.

# Other Relevant Material

The KnowItAll software has a long track record of providing data and tools to support forensic, law enforcement, and drug research communities. Over time, a set of digital solutions have been developed for this purpose.

## IR – Vapor Phase FT-IR Library of Synthetic Cannabinoids – Wiley - Wiley Science Solutions[7]

This database has been designed in conjunction with forensics experts to enable chemists and toxicologists to identify in this ever-growing class of novel psychoactive substances. It has over 200 entries and is growing quickly.

## KnowItAll IR and Raman Spectral Database Collections - Wiley Science Solutions[8]

This database collection provides access to the world's largest collection of high-quality infrared and Raman spectra including the renowned Sadtler™ databases. Along with spectra, records contain physical properties and structures, when available. These collections are an essential tool for the identification, classification, and verification of unknown compounds in a wide range of applications such as forensics/toxicology, polymer/materials, environmental, pharmaceutical, biotech, automotive/aerospace, food/cosmetics, and many more.

## KnowItAll Mass Spectra of Designer Drugs - Wiley Science Solutions[9]

This database is a comprehensive GCMS collection of designer drugs, pharmaceuticals, chemical warfare agents, and related substances annually updated. Data related to these compounds has been sourced from both peer-reviewed literature as well as law enforcement sources, providing the most comprehensive global picture of these compounds. Data are carefully compiled in cooperation with the Regional Departments of Criminal Investigation as well as other partners worldwide. As much as possible, spectra are verified by standard mass spectra libraries and checked by mass spectral interpretations.

## KnowItAll DEA Controlled Substance Regulation System[10]

Finally, the CSRS expert system built into KnowItAll predicts the DEA controlled substance status through structural characteristics.

# Summary

The rate of synthetic cannabinoids creation is often faster than databases and forensics chemical suppliers can cover immediately. As a result of this gap, many samples encountered in analysis are true unknowns. Machine-assisted classification and positive identification of these unknowns can help law enforcement and forensic organizations stay ahead of curve.

**KnowItAll AnalyzeIt Vapor Phase IR** for classification of synthetic cannabinoids offers a solution that has broad and profound implications. This feature, combined with the expansion of the synthetic cannabinoids database and other forensic databases, provides significant assistance and support to forensic, law enforcement, toxicology, pharmaceutical, and research communities.

# Background Information

**Categorical Examples (Controlled Substances)**

| Category | | Examples (Compound ID) |
|---|---|---|
| **(1)** | ESTER -Indazole – Quinoline | NPB-22 (15535), 5-fluoro NPB-22 (15536), FUB-NPB-22 (16883) |
| **(2)** | ESTER –7-Azaindole –Quinoline | 5-fluoro 7-QUPAIC (23011) |
| **(3)** | ESTER –Índole –Quinoline or Isoquinoline | BB-22 "QUCHIC" (14099), FUB-PB-22 (14949), PB-22 (14096), 5-fluoro PB-22 (14095), 5-fluoro PB-22 3-Hydroxyquinoline isomer (14511), 5-fluoro PB-22 4-Hydroxyquinoline isomer (14512), 5-fluoro PB-22 5-Hydroxyquinoline isomer (14513), 5-fluoro PB-22 6-Hydroxyquinoline isomer (14514), 5-fluoro PB-22 7-Hydroxyquinoline isomer (14515) |
| **(4)** | ESTER –Índole –Naphthalene | NM2201 (15334), FDU-PB-22 (14968) |
| **(5)** | ESTER – Indazole –Naphthalene | SDB-005 (15389), 5-fluoro SDB-005 (15353), 3-CAF (15962) |
| **(6)** | ESTER – Indazole –Ester | MO-CHMINACA (17136) |
| **(7)** | ESTER – Indazole –Adamantyl | APINAC (18589), 5-fluoro APINAC (18592) |
| **(8)** | SECONDARY AMIDE – Indazole – Naphthalene | MN-18 (14817), 5-fluoro MN-018 (14816) |
| **(9)** | SECONDARY AMIDE -Tetrahydrobenzo[b]thieno – Naphthalene | JNK Inhibitor IX (15624) |
| **(10)** | METHANONE – 2-methyl-Indole – 2,3-dichloro-Benzene | GW 405833 (20219) |
| **(11)** | SECONDARY AMIDE – 2-oxo-3H-Indol-ylidene hydrazide – Cyclopropyl | Azidoindolene 1 (17083) |
| **(12)** | SECONDARY AMIDE – Indazole – Naphthalene | NNEI-2'-indazole isomer (14738) |
| **(13)** | SECONDARY AMIDE – Indole – Benzene | 5-fluoro Phenyl-PICA (23924), SDB-006 N-phenyl analog (16044) |

# Background Information

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| **(14)** | SECONDARY AMIDE – Indole – Naphthalene | NNEI (15001), NNEI 2'-naphthyl isomer (14738), 5-fluoro NNEI (14147), 5-fluoro NNEI 2'-naphthyl isomer (14318) |
| **(15)** | SECONDARY AMIDE – 2-oxo-3H-Indol-ylidene hydrazide – Benzene | MDA-19 (10563), MDA-77 (10639), BZO-POXIZID (34795), BZO-4en-POXIZID (35503), 5-fluoro BZO-POXIZID (34586) |
| **(16)** | SECONDARY AMIDE – Indazole – Quinoline | THJ (14889), 5-fluoro THJ (14890) |
| **(17)** | SECONDARY AMIDE – Indazole – Ester | (S)-5-fluoro ADB (23631), MDMB-BUTINACA (28739), MMB-4en-PINACA (29750), 4-fluoro EDMB-BUTINACA (33374), MDMB-3en-BUTINACA (28508), 5-fluoro ADB (16603), MDMB-4en-PINACA (26097), iPDMB-FUBINACA (28930), MEP-FUBINACA (21654), Methyl (S)-2-(1H-indazole-3-carboxamido)-3,3-dimethylbutanoate (27248), EMB-FUBINACA (17449), MDMB-FUBINACA (16966), 4-fluoro MDMB-BUTINACA (26645), AMB (15488), 4-fluoro AMB (9002738), 5-fluoro AMB (15489), 4-cyano MMB-BUTINACA (33334), FUB-AMB (9001960), EMB-FUBINACA (17449), MDMB-CHMINACA (16200), MA-CHMINACA (16421) |
| **(18)** | SECONDARY AMIDE – Indazole – Benzyl (including alkyl branched) | 4-fluoro-CUMYL-5-fluoro-PINACA (26134), CUMYL-CBMICA (31325), CUMYL PIPETINACA (27331), 4-chloro-CUMYL-PINACA (26132), Benzyl-4-cyano BUTINACA (31313), CUMYL CBMINACA (31325), 4-cyano CUMYL-BUTINACA (20194), 5-fluoro-tert-Butylbenzyl-PINACA (23351), Ethylbenzyl CYBINACA (24431), 4-chloro CUMYL-PINACA (26132) |
| **(19)** | SECONDARY AMIDE – Carbazole – Ester "MDMB" | MDMB-CHMCZCA (19295) |
| **(20)** | SECONDARY AMIDE – Indazole – Adamantyl | 4-fluoro ABUTINACA (30724), ATHPINACA isomer 1 (18365), ATHPINACA isomer 2 (19040), ACHMINACA (25006), AKB-48 (11566), 5-chloro AKB-48 (18166), AKB-48 N-4-(fluorobenzyl) analog (15937), 5-bromo APINACA (25209) |
| **(21)** | SECONDARY AMIDE – Indole – Quinoline | AM2201 8-quinolinyl carboxamide (14892) |
| **(22)** | SECONDARY AMIDE – 7-Azaindole – Ester "MMB" | 5-fluoro MMB-P7AICA (31189), MMB-CHM7AICA (31188) |
| **(23)** | SECONDARY AMIDE – Indole – Carboxylic Acid | MMB-4en-PICA butanoic acid metabolite (31275) |

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| **(24)** | SECONDARY AMIDE – 7-Azaindole – Ester "MDMB" | MDMB-CHM7AICA (31186), MDMB-FUB7AICA (31187), 5-fluoro MDMB-7-PAICA (25286) |
| **(25)** | SECONDARY AMIDE – Indazole – Primary Amide | AMP-4en-PINACA (33818), AB-PINACA (14038), 5-chloro AB-PINACA (9001857), 5-fluoro AB-PINACA (14755), ADB-PHENITACA (33194), ADB-4en-PINACA (33205), ADB-PINACA (14763), ADB-PINACA isomer 1 (9001525), ADB-PINACA isomer 2 (9001526), ADB-PINACA isomer 3 (9001527), ADB-PINACA isomer 4 (9001994), 5-fluoro ADB-PINACA (14764), APP-BUTINACA (26905), PX2 (16434), ADB-BUTINACA (29350), ADB-BUTINACA N-(4-Hydroxybutyl) metabolite, 4-cyano ADB-BUTINACA (26506), AB-FUBINACA (14039), ADB-BINACA (18757), ADB-FUBINACA (14292), AB-FUBINACA isomer 1 (9001528), AB-FUBINACA isomer 2 (9001529), |
| **(26)** | SECONDARY AMIDE – Indole – Ester "MDMB", "EDMB" | 5-fluoro EDMB-PICA (30725), 5-fluoro MDMB-PICA metabolite 9 (27587), 4-chloro MDMB-BUTICA (31805), 4-fluoro MDMB-BUTICA (31075), 5-fluoro MDMB-PICA (20803), MDMB-FUBICA (18364) |
| **(27)** | SECONDARY AMIDE – 2'-Indazole – Ester "ADB" | 5-fluoro ADB 2'-indazole isomer (28962) |
| **(28)** | SECONDARY AMIDE –Indole – Benzyl | 4-fluoro-CUMYL-5-fluoro-PICA (26131), SDB-006 (15156), 5-fluoro SDB-006 (15390), CUMYL-PICA (17211), 5-fluoro CUMYL-PICA (17212), CUMYL-CBMICA (30207) |
| **(29)** | SECONDARY AMIDE –Indazole – Secondary Amide | EADB-FUBINACA (23345) |
| **(30)** | SECONDARY AMIDE –Indole – methyl-Cyclopropyl | 5-fluoro CYPPICA (17615) |
| **(31)** | SECONDARY AMIDE –Indole – Ester | 5-fluoro EMB-PICA (30769), 5-chloro AMB-PICA (29751), MMB-022 (25906), 5-fluoro EMB-PICA N-(5-Hydroxypentyl) metabolite (31540), 4-fluoro EMB-BUTICA (31298), MPP-PICA (31268), 5-bromo AMB-PICA (29752), MEP-CHMICA (21652), MMB-FUBICA (20182), MEP-FUBICA (21653), MMP-PICA (31268), 5-fluoro MMP-PICA (25916), MMB-018 (15970), MMB-CHMICA (17984), MMB-2201 (15971) |
| **(32)** | SECONDARY AMIDE –7-Azaindole – Adamantyl | AFUB7AICA (31185), 5-fluoro 7-APAICA (23021) |

# Background Information

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| **(33)** | SECONDARY AMIDE – Indole – Adamantyl | JWH-018 Adamantyl Carboxamide "APICA" (9001193), STS-135 "5-fluoro APICA" (11564) |
| **(34)** | SECONDARY AMIDE – Indole – Benzyl (alkyl branched) | Ethylphenethyl FUBICA (23764), 5-fluoro Ethylbenzyl-PICA (24430) |
| **(35)** | SECONDARY AMIDE –7-methoxy-Indole – Bicyclo[2.2.1]hept-2-yl | MN-25 (14249) |
| **(36)** | METHANONE – Indazole – Cyclopropyl | FAB-144 (15155) |
| **(37)** | SECONDARY AMIDE – 7-Azaindole – Primary Amide | 5-fluoro AB-7-PAICA (26646) |
| **(38)** | ECONDARY AMIDE –2'-Indazole – Primary Amide | AB-CHMINACA 2'-indazole isomer (17521), APP-BUTINACA 2'indazole isomer (synthesized) |
| **(39)** | SECONDARY AMIDE – 2-methyl-7-methoxy-Indole – Bicyclo[2.2.1] hept-2-yl | MN-25-2-methyl derivative (9001455) |
| **(40)** | METHANONE – Carbazole – Naphthalene | EG2201 (16884) |
| **(41)** | ETHANONE – Indole – Benzene | JWH-167 (13979), JWH-201 (10721), JWH-203 (15669), JWH-203 3-chlorophenyl isomer (10868), JWH-203 4-chlorophenyl isomer (10867), JWH-203 N-(4-Hydroxypentyl) metabolite (14227), JWH-25 (10722), JWH-251 3-methylphenyl isomer (9001022), RCS-8 "SR18" (10636), RCS-8 4-methoxy isomer (10863), RCS-8 3-methoxy isomer (10864), Cannabipiperidiethanone (11655) |
| **(42)** | METHANONE – Indazole – Naphthalene | THJ-2201 (14789), THJ-018 (11962) |
| **(43)** | ETHANONE – Indole – 2-bromo or 2-methyl BENZENE | JWH-251 (10578), JWH-249 (11153) |

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| **(44)** | ETHANONE – Indole – Naphthalene | 7'-methoxy NABUTIE (22630), NAMIE (22631), NAPIE (22632) |
| **(45)** | METHANONE – Benzamidazole – Napthalene | JWH-018 Benzimidazole analog (15074), AM-2201 Benzimidazole analog (15202) |
| **(46)** | SECONDARY AMIDE – Indole – Primary Amide | AB-FUBICA (18758), ADB-FUBICA (18756), AB-BICA (18759), ADB-BICA (19729), APP-PICA (17613), ADB-CHMICA (17213), 5-fluoro ADBICA (14766), PX-1 (16201) |
| **(47)** | METHANONE – Pyrrole – Naphthalene | JWH-030 (10831), JWH-031 (10824), JWH-145 (10825), JWH-146 (14232), JWH-147 (10826), JWH-307 (10797), JWH-309 5-isomer (11483), JWH-368 (10829), JWH-370 (10827) |
| **(48)** | METHANONE – Indole – 8-methoxy or chloro NAPHTHALENE | JWH-398 8-chloronaphthyl isomer (9001028), JWH-081 8 -methoxynaphthyl isomer (9001049) |
| **(49)** | METHANONE – Indazole – 1,2,3,4-Tetrahydroquinoline | THQ-PINACA (27081) |
| **(50)** | METHANONE – Indole-Cyclopropyl | XLR-11 (11565), UR-144 (11502), UR-144 N-(5-chloropentyl) analog (11951), (1H-Indol-3-yl) (2,2,3,3-tetramethylcyclopropyl) Methanone (9001966) |
| **(51)** | METHANONE – Indole – 2 or 8 halogen substituted NAPHTHALENE | JWH-398 2-chloronaphthyl isomer (9001023), JWH-424 (9001203) |
| **(52)** | METHANONE – Indole – 2 or 8 halogen substituted BENZENE | AM679 (11504), AM2233 (11008) |
| **(53)** | SECONDARY AMIDE – Imidazo[1,2-c]quinazoline – 3-PYRIDINE | PIK-90 (10010749) |
| **(54)** | METHANONE – Indole – Piperazine | Mepirapim (15388) |
| **(55)** | METHANONE – Indole – 2, 3 or 8 substituted NAPHTHALENE | JWH-081 2-methoxynaphthyl isomer (9001044), JWH-081 3-methoxynaphthyl isomer (9001045), JWH-122 2-methylnaphthyl isomer (9001032), JWH-122 8-methylnaphthyl isomer (9001037) |

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| **(56)** | METHANONE – Indole – Naphthalene | NE-CHMIMO (29301), JWH-018 (10900), JWH-018 2'-naphthyl isomer (9001004), JWH-018 N-(1,2-dimethylpropyl) isomer (9001003), JWH-018 N-(1,1-dimethylpropyl) isomer (9001000), JWH-018 2'-naphthyl-N-(1,1-dimethylpropyl) isomer (9001007), JWH-018 N-(1ethylpropyl) isomer (11585), JWH-018 2-naphthyl-N-(1-ethylpropyl) isomer (11586), JWH-018 N-(2-methylbutyl) isomer (10690), JWH-018 N-(1-methylbutyl) isomer (9001002), JWH-018 N-(2,2-dimethylpropyl) isomer (9001001), JWH-018 6-methoxyindole analog (10697), FUB-JWH 018 (17332), AM2201 (10707), AM2201 2'-naphthyl isomer (10862), MAM2201 (9001219), F2201 (9001580), AM2232 (11503), JWH-019 (15664), JWH-202 (10850), JWH-071 (13890), JWH-072 (9001201), JWH-073 (10904), JWH-073 6-methoxyindole (14084), JWH-073 2'-naphthyl isomer (9001014), JWH-073 2-methylnaphthyl analog (10848), JWH-073 4-methylnaphthyl analog (9001076), JWH-080 (14013), JWH-081 (10579), JWH-081 4-hydroxynaphthyl metabolite (14347), JWH-081 5-methoxynaphthyl isomer (9001046), JWH-081 6-methoxynaphthyl isomer (9001047), JWH-081 7-methoxynaphthyl isomer (9001048), JWH-122 (15667), JWH-122 3-methylnaphthyl isomer (9001033), JWH-122 5-methylnaphthyl isomer (9001034), JWH-122 6-methylnaphthyl isomer (9001035), JWH-122 7-methylnaphthyl isomer (9001036), JWH-122 N-(4-pentyl) analog (11611), CHM-122 (22043), JWH-180 |
| **(57)** | METHANONE – Indole – Adamantyl | JWH-018 Adamantyl (9000799), 5-fluoro JWH-018 Adamantyl (14432) |
| **(58)** | METHANONE – Indole – 4-methoxy BENZENE | RCS-4 C4 homolog (10798), RCS-4 "SR-19" (10645), AM-2233 (11008), AM-679 (11504) |
| **(59)** | METHANONE – 2-methyl-INDOLE – Cyclopropyl | M-144 (16084), XLR-12 (14935) |
| **(60)** | METHANONE – Indazole – Prolinamide | 1(N)-Butylindazole-3-(L)-prolinamide (synthesized) |
| **(61)** | METHANONE – 2'-Pyrrole-Naphthalene | JWH-031 2'-isomer (11631), JWH-030 2'-naphthoyl isomer (11632) |
| **(62)** | METHANONE – 2-methyl-INDOLE-Naphthalene | JWH-007 (10266), JWH-011 (9001058), JWH-015 (10009018), JWH-016 (10849), JWH-149 (13978) |
| **(63)** | METHANONE – 2'-Indazole – Prolinamide | 2(N)-Butylindazole-3-(L)-prolinamide (synthesized) |
| **(64)** | METHANONE - 2-methyl-INDOLE – 4-methoxy or methyl substituted NAPHTHALENE | JWH-098 (10680), JWH-213 (11659) |

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