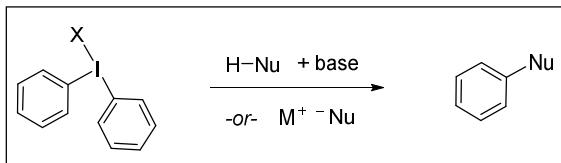
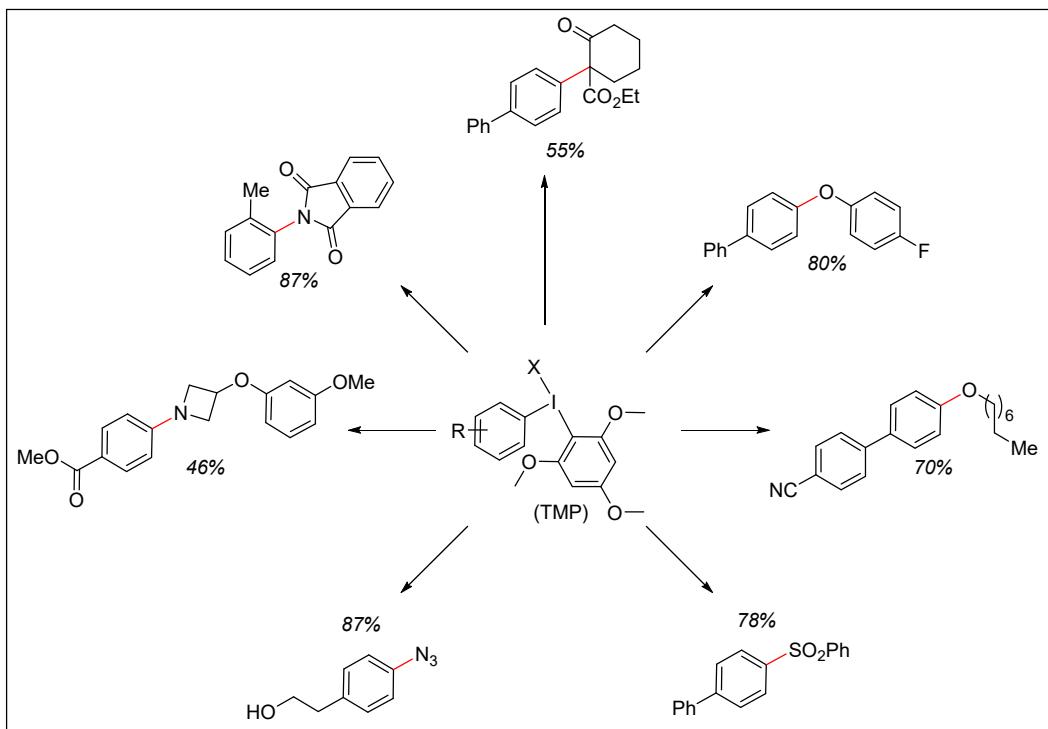


Unsymmetrical Diaryliodonium Salts

Diaryliodonium salts are well-known to transfer an aryl group to carbon and heteroatom nucleophiles, and in some cases, a base is required.^[1] However, transition metal catalysts and supporting ligands are not needed. Moreover, reactions conducted with diaryliodonium salts are operationally simple because they are non-toxic and are not sensitive to air or moisture. Therefore diaryliodonium salts offer an important alternative to metal-catalyzed arylation reactions. Despite these attractive characteristics, a major obstacle to their adoption in chemical synthesis and discovery chemistry has been commercial availability.



In collaboration with the Stuart Group at Portland State University, we now offer > 60 structurally distinct unsymmetrical diaryliodonium salts bearing a 2,4,6-trimethoxyphenyl (TMP) auxiliary that serves as a non-transferable “dummy” group. The aryl groups of the aryl(TMP)iodonium tosylates feature a diverse range of substituents, such as hydrocarbyl, halides, trifluoromethyl, nitro, nitrile, ester, amide, phenyl ether, hydroxyl(methyl), bromo(methyl), and substitution patterns. The use of unsymmetrical aryl(TMP)iodonium salts allows for exclusive aryl transfer selectivity and facilitates purification by easy removal of the iodo-2,4,6-trimethoxyphenyl group. Although method development for metal-free arylation reactions is continually expanding, the Stuart group has already demonstrated that they react with malonate, phenoxide and alkoxide, phenyl sulfinate, and azide, imide, and alicyclic amine nucleophiles.^[2] Others have also demonstrated that aryl(TMP)iodonium salts are useful reagents in radical arylations with visible light photoredox catalysis or under basic conditions, thus diversifying the reactivity profile of these reagents.^[3]



[1] Olofsson, B. Arylation with Diaryliodonium Salts. *Topics in Current Chemistry (in Hypervalent Iodine Chemistry)* 2016, Volume 373, 135-166.

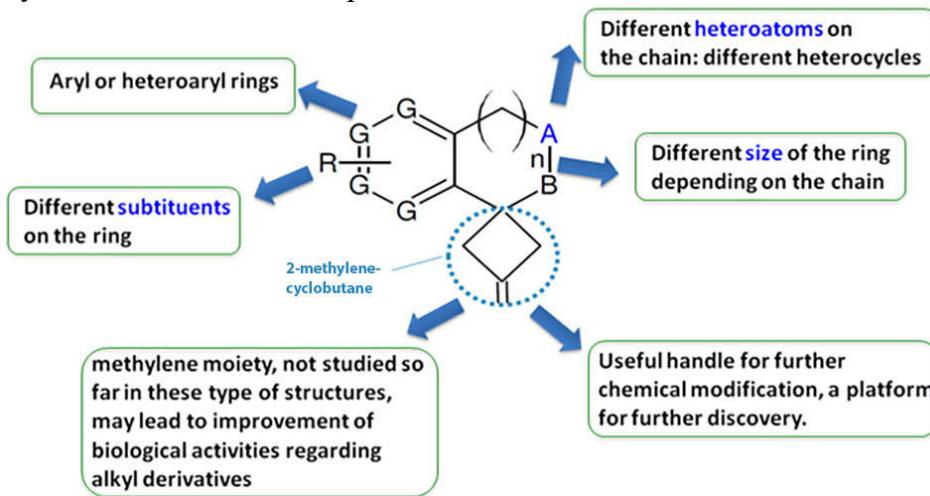
[2] (a) Seidl, T. L.; Sundalam, S. K.; McCullough, B.; Stuart, D. R. Unsymmetrical Aryl(2,4,6-trimethoxyphenyl)iodonium Salts: One-pot Synthesis, Scope, Stability, and Synthetic Studies. *Journal of Organic Chemistry* 2016, Volume 81, 1998 – 2009. (b) Sandtorv, A. H.; Stuart, D. R. Metal-free Synthesis of Aryl Amines: Beyond Nucleophilic Aromatic Substitution. *Angewandte Chemie International Edition* 2016, Volume 55, 15812-15815. (c) Seidl, T. L.; Stuart, D. R. An Admix Approach to Determine Counter Anion Effects on Metal-Free Arylation Reactions with Diaryliodonium Salts. *Journal of Organic Chemistry* 2017, Volume 82, 11765-11771. (d) Basu, S.; Sandtorv, A. H.; Stuart, D. R. Imide Arylation with Aryl(TMP)iodonium Tosylates. *Beilstein Journal of Organic Chemistry* 2018, Volume 14, 1034-1038.

[3] (a) Dohi, T.; Ueda, S.; Hirai, A.; Kojima, Y.; Morimoto, K.; Kita, Y. Selective Aryl Radical Transfers into Heteroaromatics from Diaryliodonium Salts with Trimethoxybenzene Auxiliary. *Heterocycles* 2017, Volume 95, 1272-1284. (b) Sun, D.; Yin, K.; Zhang, R. Visible-Light-Induced Multicomponent Cascade Cycloaddition Involving N-Propargyl Aromatic Amines, Diaryliodonium Salts, and Sulfur Dioxide: Rapid Access to 3-Arylsulfonylquinolines. *Chemical Communications* 2018, Volume 54, 1335-1338.

[3.4]-Spirooxindoles with a Methylenesubstituted Cyclobutyl Ring as Novel Chemical Building Blocks

Spirooxindoles are privileged scaffolds that are present in numerous pharmaceuticals and natural products[1–4]. Given the importance of [3.4]-spirooxindoles, a few studies were focused on their syntheses, and existing synthetic routes do not provide a versatile way of incorporating different substituents in the existing structures.

A *modular approach* to spiro-heterocycles bearing a methylene-substituted cyclobutyl ring is developed by Professor José-Antonio García-López and his colleagues [5, 6].The method allows an easy modification in several points at the scaffold:



The *reactive 2-methylene-cyclobutane group* was introduced as a useful handle for further chemical modification and a synthetic platform for further exploration of chemical space. This synthetic group provides an outstanding possibility to generate molecular libraries bearing the methylene-cyclobutyl ring as a building block.

These [3.4]-spirooxindoles with a methylene-substituted cyclobutyl ring provide a modular approach to get spiro-heterocycles where several parameters can easily be modified and utilized:

- Novel and easily accessible starting materials using simple catalytic system
- Aryl or heteroaryl rings bearing different substituents
- Different types of heterocycles depending on the nature of the chain (size and heteroatom substitution). For example, oxindole, indoline, dihydrobenzofuran, chromane, isochromane, dihydroisoquinoline, etc.
- Possibility to build up molecular complexity by exploiting the terminal olefin reactivity

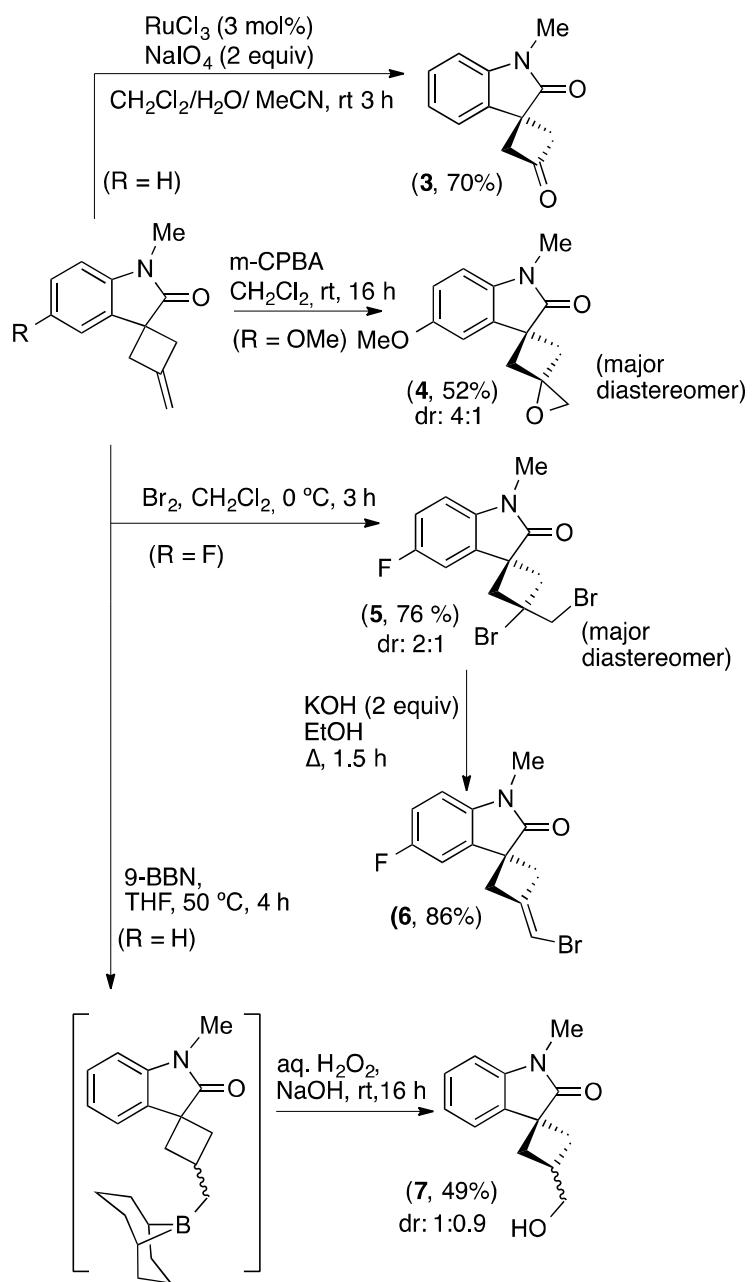
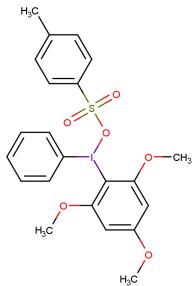


Fig. Further derivatization of the spirooxindole core made possible by 2-methylen-cyclobutane group

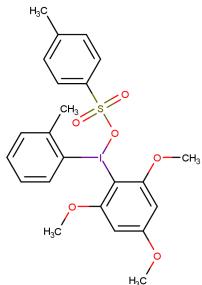
- [1] B. Yu, D. Q. Yu, H. M. Liu, *Eur. J. Med. Chem.* 2015, 97, 673–698.
 - [2] C. V. Galliford, K. A. Scheidt, *Angew. Chem. Int. Ed.* 2007, 46, 8778–8758; *Angew. Chem.* 2007, 119, 8934–8937.
 - [3] T. L. Pavlovska, R. G. Redkin, V. V. Lipson, D. V. Atamanuk, *Mol. Diversity*, 2016, 20, 299–344.
 - [4] N. Ye, H. Chen, E. A. Wold, P. Y. Shi, J. Zhou, *ACS Infect. Dis.* 2016, 2, 382–392.
 - [5] H. Azizollahi, M. Pérez-Gómez, V. P. Mehta, J.-A. García-López, *Adv. Synth. Catal.* 2020, 362, 1899–190
 - [6] H. Azizollahi, V. P. Mehta J.-A. García-López, *Chem. Commun.*, 2019, 55, 10281–10284

phenyl(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



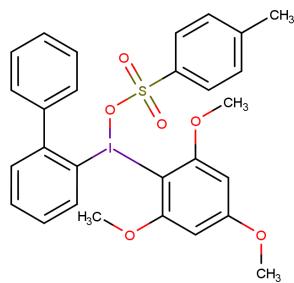
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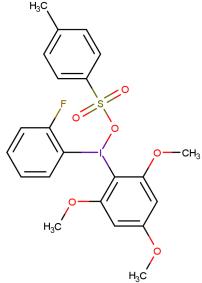
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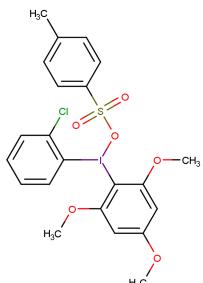
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CAS number NA

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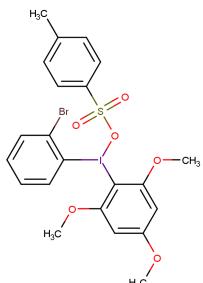
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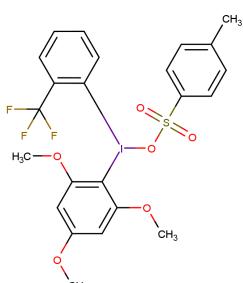
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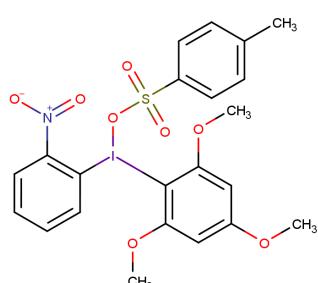
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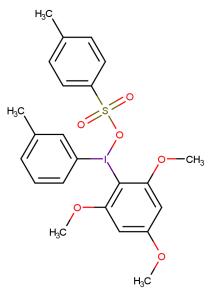
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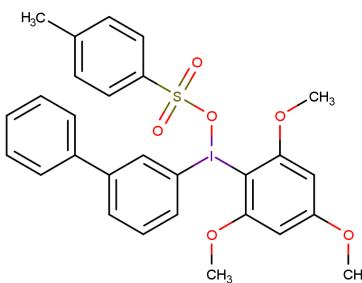
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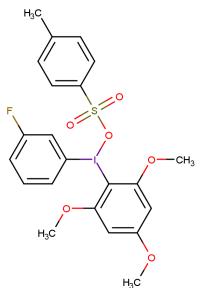
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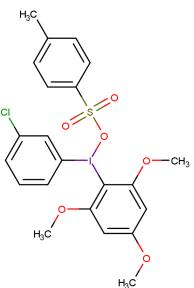
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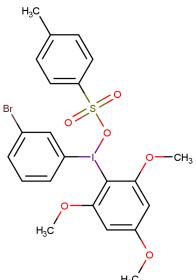
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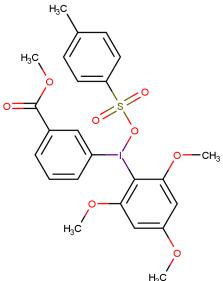
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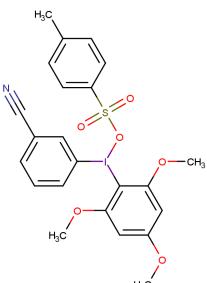
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Mol.fmla $C_{22}H_{22}BrIO_6S$
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methyl 3-((tosyloxy)(2,4,6-trimethoxyphenyl)-l3-iodaneyl)benzoate



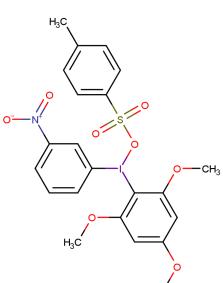
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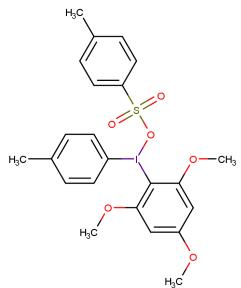
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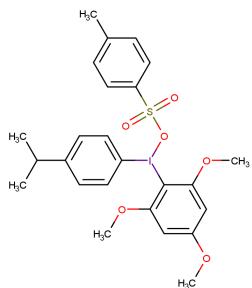
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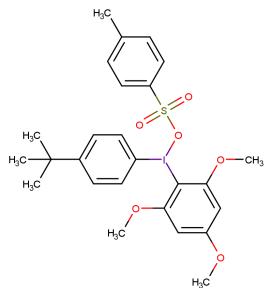
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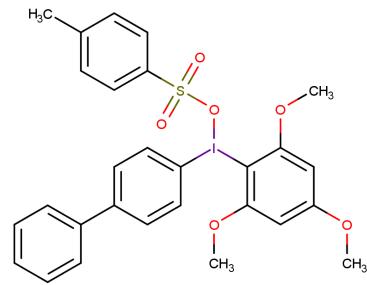
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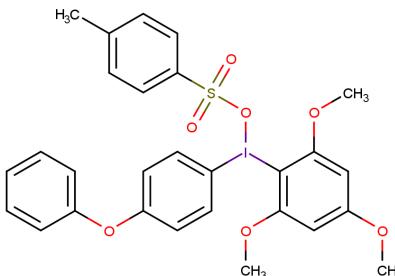
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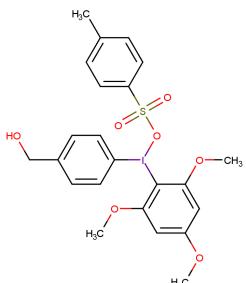
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Mol.fmla $C_{28}H_{27}IO_6S$
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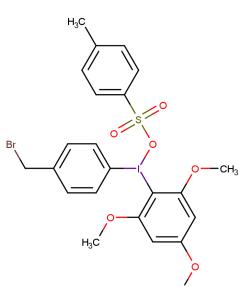
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CAS number NA

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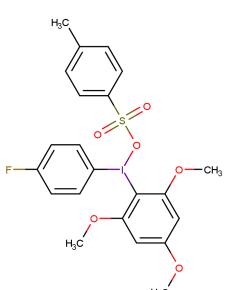
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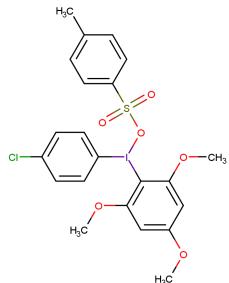
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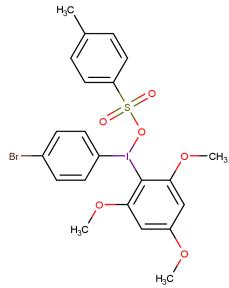
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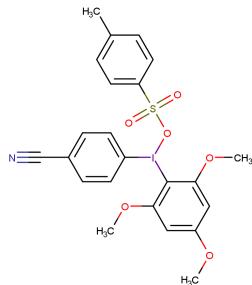
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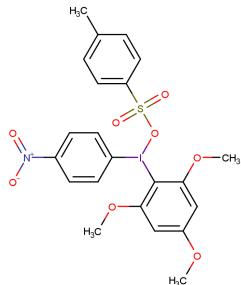
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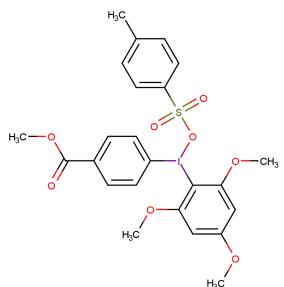
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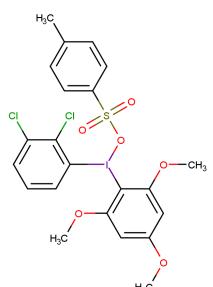
Catalog Number **RX-7098000032**
Mol.fmla *C₂₂H₂₂INO₈S*
Mol Weight 587.38
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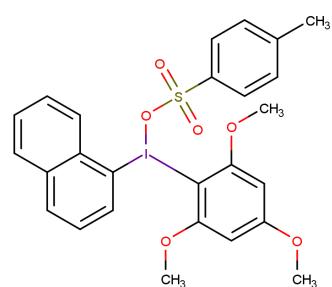
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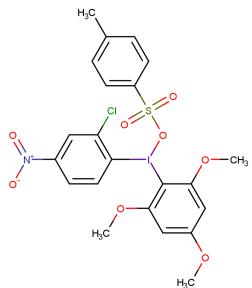
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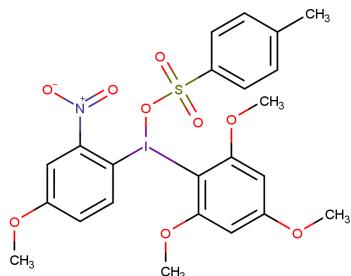
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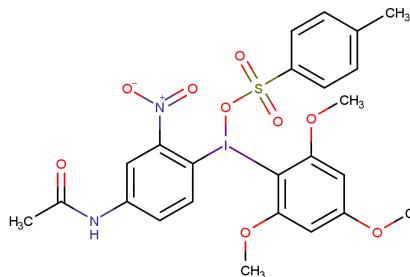
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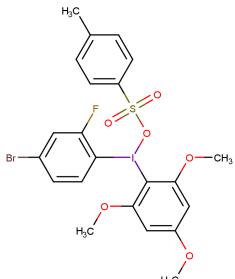
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Mol.fmla $C_{23}H_{24}INO_9S$
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CAS number NA

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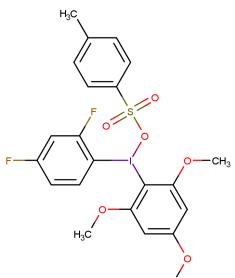
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CAS number NA

(4-bromo-2-fluorophenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



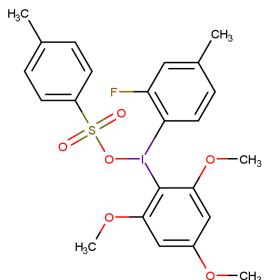
Catalog Number **RX-7098000039**
Mol.fmla $C_{22}H_{21}BrFIO_6S$
Mol Weight 639.27
CAS number NA

(2,4-difluorophenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



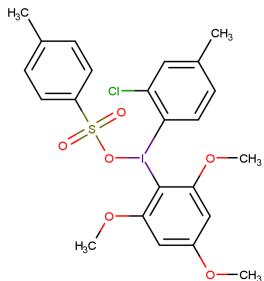
Catalog Number **RX-7098000040**
Mol.fmla $C_{22}H_{21}F_2IO_6S$
Mol Weight 578.37
CAS number NA

(2-fluoro-4-methylphenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



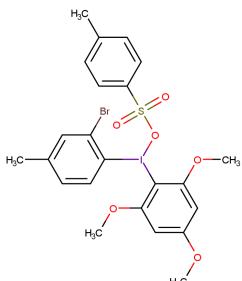
Catalog Number **RX-7098000041**
Mol.fmla *C₂₃H₂₄FI₃O₆S*
Mol Weight 574.4
CAS number NA

(2-chloro-4-methylphenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



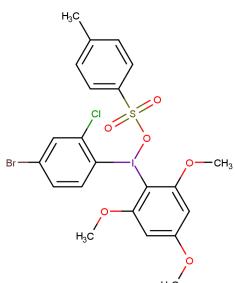
Catalog Number **RX-7098000042**
Mol.fmla *C₂₃H₂₄ClI₃O₆S*
Mol Weight 590.85
CAS number NA

(2-bromo-4-methylphenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



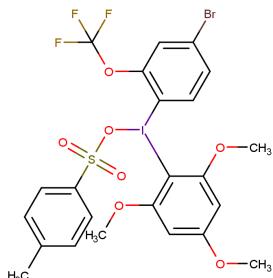
Catalog Number **RX-7098000043**
Mol.fmla *C₂₃H₂₄BrI₃O₆S*
Mol Weight 635.31
CAS number NA

(4-bromo-2-chlorophenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



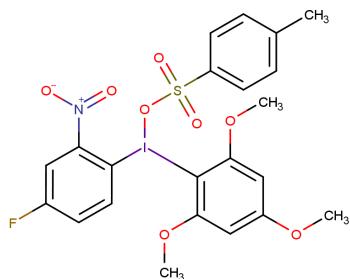
Catalog Number **RX-7098000044**
Mol.fmla *C₂₂H₂₁BrClI₃O₆S*
Mol Weight 655.72
CAS number NA

(4-bromo-2-(trifluoromethoxy)phenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



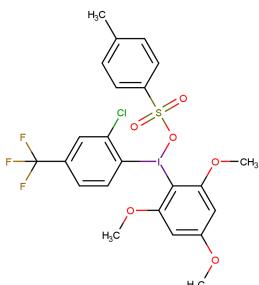
Catalog Number	RX-7098000045
Mol.fmla	<i>C</i> ₂₃ <i>H</i> ₂₁ <i>BrF</i> ₃ <i>IO</i> ₇ <i>S</i>
Mol Weight	705.28
CAS number	NA

(4-fluoro-2-nitrophenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



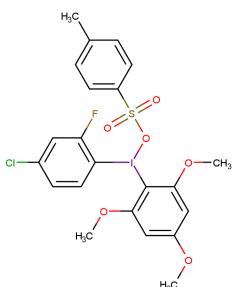
Catalog Number	RX-7098000046
Mol.fmla	<i>C</i> ₂₂ <i>H</i> ₂₁ <i>FNO</i> ₈ <i>S</i>
Mol Weight	605.37
CAS number	NA

(2-chloro-4-(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



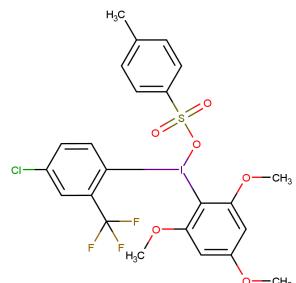
Catalog Number	RX-7098000047
Mol.fmla	<i>C</i> ₂₃ <i>H</i> ₂₁ <i>ClF</i> ₃ <i>IO</i> ₆ <i>S</i>
Mol Weight	644.82
CAS number	NA

(4-chloro-2-fluorophenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



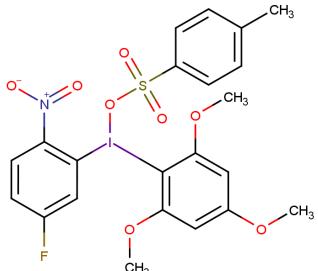
Catalog Number	RX-7098000048
Mol.fmla	<i>C</i> ₂₂ <i>H</i> ₂₁ <i>ClFI</i> ₆ <i>S</i>
Mol Weight	594.82
CAS number	NA

(4-chloro-2-(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



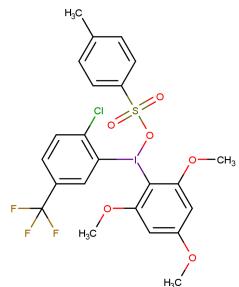
Catalog Number	RX-7098000049
Mol.fmla	<i>C</i> ₂₃ <i>H</i> ₂₁ <i>ClF</i> ₃ <i>IO</i> ₆ <i>S</i>
Mol Weight	644.82
CAS number	NA

(5-fluoro-2-nitrophenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



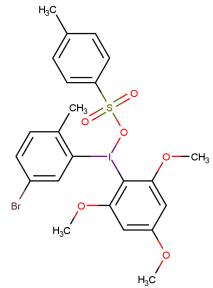
Catalog Number	RX-7098000050
Mol.fmla	<i>C</i> ₂₂ <i>H</i> ₂₁ <i>FNO</i> ₈ <i>S</i>
Mol Weight	605.37
CAS number	1868173-33-4

(2-chloro-5-(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



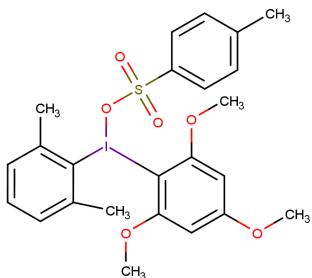
Catalog Number	RX-7098000051
Mol.fmla	<i>C</i> ₂₃ <i>H</i> ₂₁ <i>ClF</i> ₃ <i>IO</i> ₆ <i>S</i>
Mol Weight	644.82
CAS number	1868173-35-6

(5-bromo-2-methylphenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



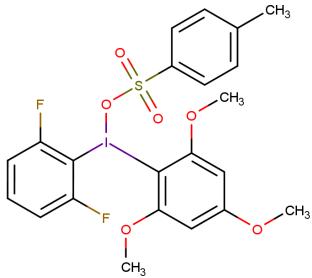
Catalog Number	RX-7098000052
Mol.fmla	<i>C</i> ₂₃ <i>H</i> ₂₄ <i>BrIO</i> ₆ <i>S</i>
Mol Weight	635.31
CAS number	NA

(2,6-dimethylphenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



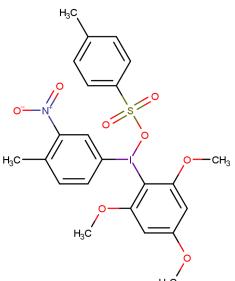
Catalog Number **RX-7098000053**
Mol.fmla $C_{24}H_{27}IO_6S$
Mol Weight 570.44
CAS number NA

(2,6-difluorophenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



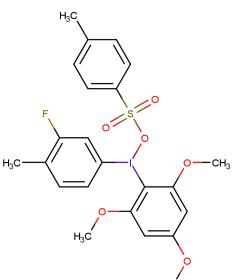
Catalog Number **RX-7098000054**
Mol.fmla $C_{22}H_{21}F_2IO_6S$
Mol Weight 578.37
CAS number NA

(4-methyl-3-nitrophenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



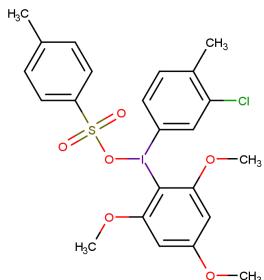
Catalog Number **RX-7098000055**
Mol.fmla $C_{23}H_{24}INO_8S$
Mol Weight 601.41
CAS number 1868173-31-2

(3-fluoro-4-methylphenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



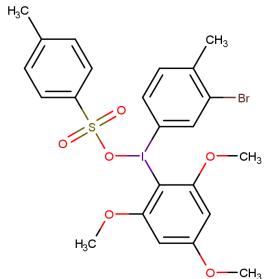
Catalog Number **RX-7098000056**
Mol.fmla $C_{23}H_{24}FIO_6S$
Mol Weight 574.4
CAS number NA

(3-chloro-4-methylphenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



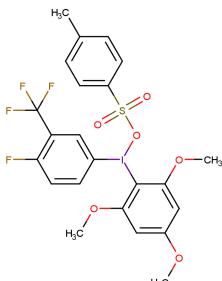
Catalog Number **RX-7098000057**
Mol.fmla $C_{23}H_{24}ClIO_6S$
Mol Weight 590.85
CAS number 1868173-27-6

(3-bromo-4-methylphenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



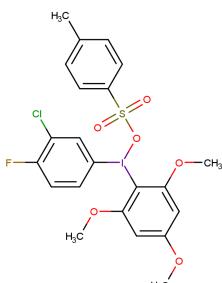
Catalog Number **RX-7098000058**
Mol.fmla $C_{23}H_{24}BrIO_6S$
Mol Weight 635.31
CAS number NA

(4-fluoro-3-(trifluoromethyl)phenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



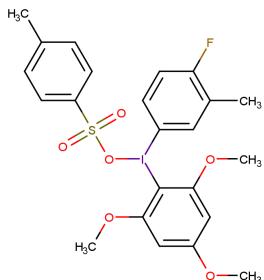
Catalog Number **RX-7098000059**
Mol.fmla $C_{23}H_{21}F_4IO_6S$
Mol Weight 628.37
CAS number 1868173-29-8

(3-chloro-4-fluorophenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



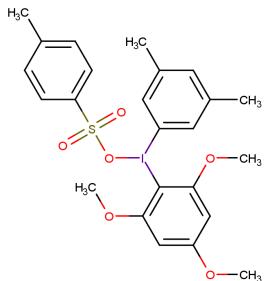
Catalog Number **RX-7098000060**
Mol.fmla $C_{22}H_{21}ClFO_6S$
Mol Weight 594.82
CAS number NA

(4-fluoro-3-methylphenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



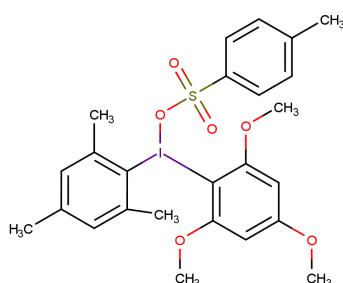
Catalog Number **RX-7098000061**
Mol.fmla *C₂₃H₂₄FI₃O₆S*
Mol Weight 574.4
CAS number NA

(3,5-dimethylphenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



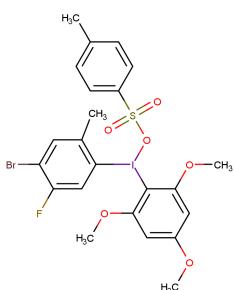
Catalog Number **RX-7098000062**
Mol.fmla *C₂₄H₂₇IO₆S*
Mol Weight 570.44
CAS number 1868173-23-2

mesityl(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate



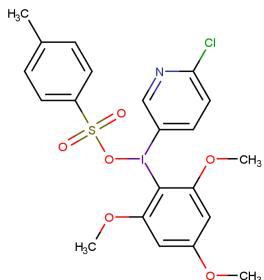
Catalog Number **RX-7098000063**
Mol.fmla *C₂₅H₂₉IO₆S*
Mol Weight 584.47
CAS number 1817741-05-1

(4-bromo-5-fluoro-2-methylphenyl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate

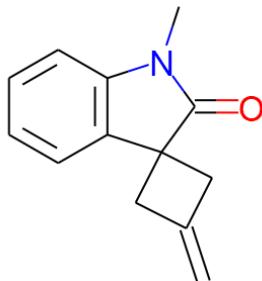


Catalog Number **RX-7098000064**
Mol.fmla *C₂₃H₂₃BrFI₃O₆S*
Mol Weight 653.3
CAS number NA

(6-chloropyridin-3-yl)(2,4,6-trimethoxyphenyl)-l3-iodaneyl 4-methylbenzenesulfonate

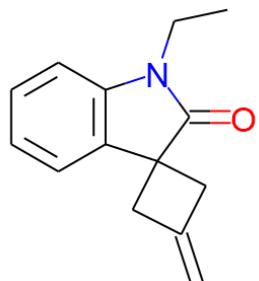


1'-methyl-3-methylenespiro[cyclobutane-1,3'-indolin]-2'-one



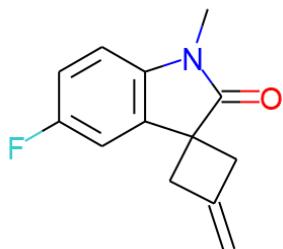
Catalog Number **RX-S01**
Mol.fmla *C₁₃H₁₃NO*
Mol Weight 199.25
CAS number NA

1'-ethyl-3-methylenespiro[cyclobutane-1,3'-indolin]-2'-one



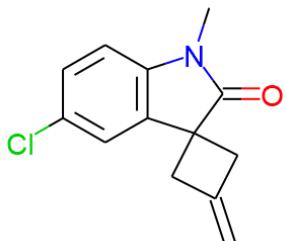
Catalog Number **RX-S02**
Mol.fmla *C₁₄H₁₅NO*
Mol Weight 213.28
CAS number NA

5'-fluoro-1'-methyl-3-methylenespiro[cyclobutane-1,3'-indolin]-2'-one



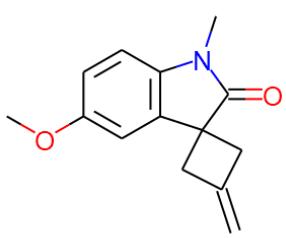
Catalog Number **RX-S03**
Mol.fmla *C₁₃H₁₂FNO*
Mol Weight 217.24
CAS number NA

5'-chloro-1'-methyl-3-methylenespiro[cyclobutane-1,3'-indolin]-2'-one



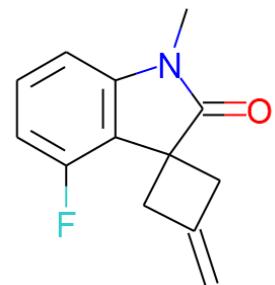
Catalog Number **RX-S04**
Mol.fmla *C₁₃H₁₂ClNO*
Mol Weight 233.70
CAS number NA

5'-methoxy-1'-methyl-3-methylenespiro[cyclobutane-1,3'-indolin]-2'-one



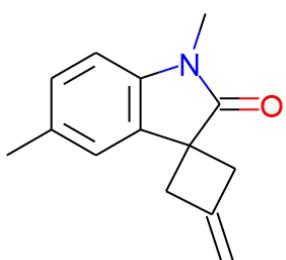
Catalog Number **RX-S05**
Mol.fmla *C₁₄H₁₅NO₂*
Mol Weight 229.28
CAS number NA

4'-fluoro-1'-methyl-3-methylenespiro[cyclobutane-1,3'-indolin]-2'-one



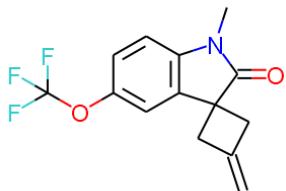
Catalog Number **RX-S06**
Mol.fmla *C₁₃H₁₂FNO*
Mol Weight 217.24
CAS number NA

1',5'-dimethyl-3-methylenespiro[cyclobutane-1,3'-indolin]-2'-one



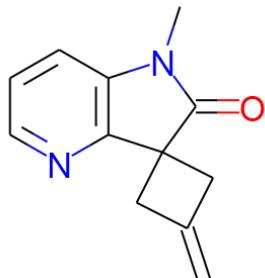
Catalog Number **RX-S07**
Mol.fmla *C₁₄H₁₅NO*
Mol Weight 213.28
CAS number NA

1'-methyl-3-methylene-5'-(trifluoromethoxy)spiro[cyclobutane-1,3'-indolin]-2'-one



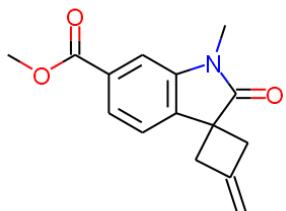
Catalog Number **RX-S08**
Mol.fmla $C_{14}H_{12}F_3NO_2$
Mol Weight 283.25
CAS number NA

1'-methyl-3-methylenespiro[cyclobutane-1,3'-pyrrolo[3,2-b]pyridin]-2'(1'H)-one



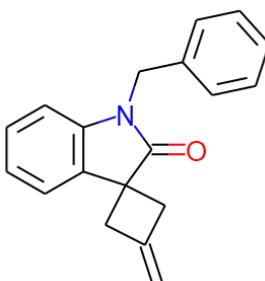
Catalog Number **RX-S09**
Mol.fmla $C_{12}H_{12}N_2O$
Mol Weight 200.24
CAS number NA

methyl 1'-methyl-3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-6'-carboxylate



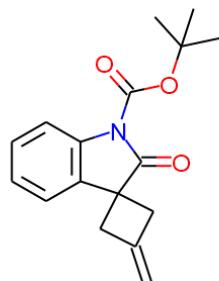
Catalog Number **RX-S10**
Mol.fmla $C_{15}H_{15}NO_3$
Mol Weight 257.29
CAS number NA

1'-benzyl-3-methylenespiro[cyclobutane-1,3'-indolin]-2'-one



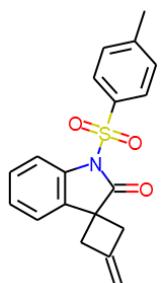
Catalog Number **RX-V11**
Mol.fmla $C_{19}H_{17}NO$
Mol Weight 275.35
CAS number NA

tert-butyl 3-methylene-2'-oxospiro[cyclobutane-1,3'-indoline]-1'-carboxylate



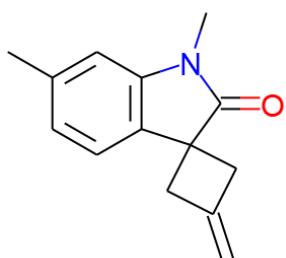
Catalog Number **RX-V12**
Mol.fmla *C₁₇H₁₉NO₃*
Mol Weight 285.34
CAS number NA

3-methylene-1'-tosylspiro[cyclobutane-1,3'-indolin]-2'-one



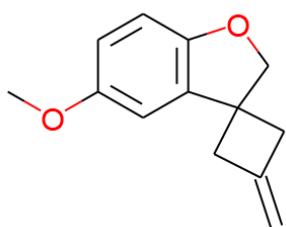
Catalog Number **RX-V13**
Mol.fmla *C₁₉H₁₇NO₃S*
Mol Weight 339.41
CAS number NA

1',6'-dimethyl-3-methylenespiro[cyclobutane-1,3'-indolin]-2'-one



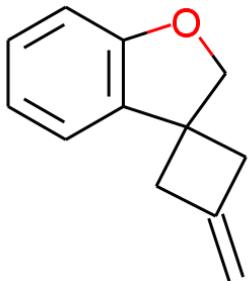
Catalog Number **RX-V14**
Mol.fmla *C₁₄H₁₅NO*
Mol Weight 213.28
CAS number NA

5-methoxy-3'-methylene-2H-spiro[benzofuran-3,1'-cyclobutane]



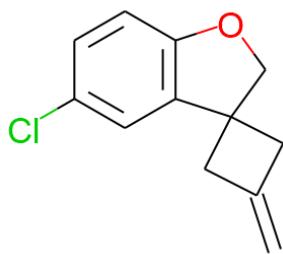
Catalog Number **RX-V15**
Mol.fmla *C₁₃H₁₄O₂*
Mol Weight 202.25
CAS number NA

3'-methylene-2H-spiro[benzofuran-3,1'-cyclobutane]



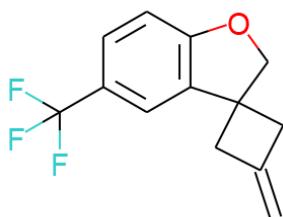
Catalog Number **RX-V16**
Mol.fmla *C₁₂H₁₂O*
Mol Weight 172.23
CAS number NA

5-chloro-3'-methylene-2H-spiro[benzofuran-3,1'-cyclobutane]



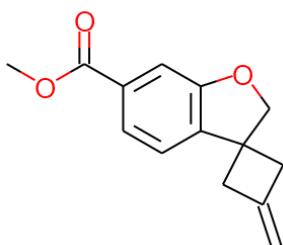
Catalog Number **RX-V17**
Mol.fmla *C₁₂H₁₁ClO*
Mol Weight 206.67
CAS number NA

3'-methylene-5-(trifluoromethyl)-2H-spiro[benzofuran-3,1'-cyclobutane]



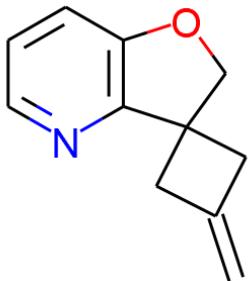
Catalog Number **RX-V18**
Mol.fmla *C₁₃H₁₁F₃O*
Mol Weight 240.23
CAS number NA

methyl 3'-methylene-2H-spiro[benzofuran-3,1'-cyclobutane]-6-carboxylate



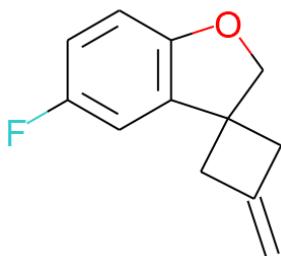
Catalog Number **RX-V19**
Mol.fmla *C₁₄H₁₄O₃*
Mol Weight 230.26
CAS number NA

3-methylene-2'H-spiro[cyclobutane-1,3'-furo[3,2-b]pyridine]



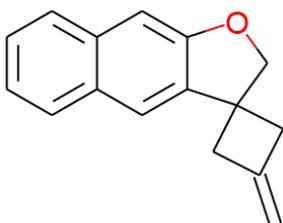
Catalog Number **RX-V20**
Mol.fmla *C₁₁H₁₁NO*
Mol Weight 173.22
CAS number NA

5-fluoro-3'-methylene-2H-spiro[benzofuran-3,1'-cyclobutane]



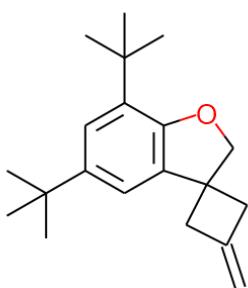
Catalog Number **RX-V21**
Mol.fmla *C₁₂H₁₁FO*
Mol Weight 190.22
CAS number NA

3-methylene-2'H-spiro[cyclobutane-1,3'-naphtho[2,3-b]furan]



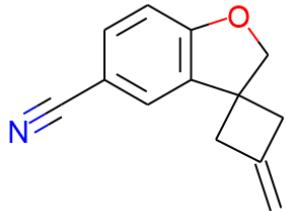
Catalog Number **RX-V22**
Mol.fmla *C₁₆H₁₄O*
Mol Weight 222.29
CAS number NA

5,7-di-tert-butyl-3'-methylene-2H-spiro[benzofuran-3,1'-cyclobutane]



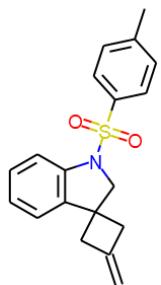
Catalog Number **RX-V23**
Mol.fmla *C₂₀H₂₈O*
Mol Weight 284.44
CAS number NA

3'-methylene-2H-spiro[benzofuran-3,1'-cyclobutane]-5-carbonitrile



Catalog Number **RX-V24**
Mol.fmla *C₁₃H₁₁NO*
Mol Weight 197.24
CAS number NA

3-methylene-1'-tosylspiro[cyclobutane-1,3'-indoline]



Catalog Number **RX-V25**
Mol.fmla *C₁₉H₁₉NO₂S*
Mol Weight 325.43
CAS number NA