Supplementary Materials

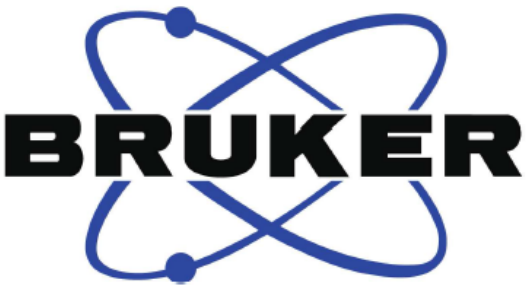
Table S1. Related 1-(arylsulfonyl)indole structures found in the Cambridge Structural Database.

CSD code	Reference	Ref. No.
ABURUK	Lutz, G.; Pindur, U.; Schollmeyer, D. Asymmetrische Diels-Alder-Reaktionen an 2- und 3- Vinylindolen. PhD Thesis, University of Mainz, Mainz, Germany, 1994.	[1]
ABUSAR	Lutz, G.; Pindur, U.; Schollmeyer, D. Asymmetrische Diels-Alder-Reaktionen an 2- und 3- Vinylindolen. PhD Thesis, University of Mainz, Mainz, Germany, 1994.	[1]
ABUSOF	Lutz, G.; Pindur, U.; Schollmeyer, D. Asymmetrische Diels-Alder-Reaktionen an 2- und 3- Vinylindolen. PhD Thesis, University of Mainz, Mainz, Germany, 1994.	[1]
ATOYAJ	Caballero, E.; Alonso, D.; Pelaez, R.; Alvarez, C.; Puebla, P.; Sanz, F.; Medarde, M.; Tome, F. 1-Phthalimido-4-(3-indolyl)-2-siloxy-1,3-butadienes: Synthesis and Diels–Alder reactivity. *Tetrahedron Lett.* **2004**, *45*, 1631–1634.	[2]
BANREO	Sankaranarayanan, R.; Yogavel, M.; Velmurugan, D.; Sekar, K.; Babu, G.; Perumal, P.T.; Raj, S.S.S.; Fun, H.-K. 8-Chloro-4-[1-(phenylsulfonyl)indol-3-yl]-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinoline. *Acta Crystallogr.* **2003**, *E59*, o49–o51.	[3]
BEHNAE	Kinsman, A.C.; Kerr, M.A. The Total Synthesis of (+) Hapalindole Q by an organomediated Diels Alder Reaction. *J. Am. Chem. Soc.* **2003**, *125*, 14120–14125.	[4]
BUJVUY	Jasinski, J.P.; Rinderspacher, A.; Gribble, G.W. Structures of three new (Phenylsulfonyl) indole derivatives. *J. Chem. Cryst.* **2010**, *40*, 40–47.	[5]
CIDBEX	Sonar, V.N.; Venkatraj, M.; Parkin, S.; Crooks, P.A. (*Z*)-2-[(1-Phenylsulfonyl-1H-indol-3-yl)methylene]-1-azabicyclo[2.2.2]octan-3-one semicarbazone. *Acta Crystallogr.* **2007**, *C63*, o277–o279.	[6]
FAKZOI	Mandal, D.; Yamaguchi, A.D.; Yamaguchi, J.; Itami, K. Synthesis of dragmacidin D via direct C-H couplings. *J. Am. Chem. Soc.* **2011**, *133*, 19660–19663.	[7]
FAKZUO	Mandal, D.; Yamaguchi, A.D.; Yamaguchi, J.; Itami, K. Synthesis of dragmacidin D via direct C-H couplings. *J. Am. Chem. Soc.* **2011**, *133*, 19660–19663.	[7]
HIZHEE	Zhu, J.; Zhang, X.Z.; Chen, S.Q.; Huang, X.H.; Zhang, Q.F. *J. Anhui Univ. Technol.* **2007**, *24*, 273.	[8]
IRIFAR	Zhao, F.; Fu, C.; Ma, S. Studies on the Intermolecular Hydroarylation of N-Ts- or N-Ac-Protected Indoles and 2,3-Allenoates. *Eur. J. Org. Chem.* **2011**, *2011*, 1227–1231.	[9]
IRIFEV	Zhao, F.; Fu, C.; Ma, S. Studies on the Intermolecular Hydroarylation of N-Ts- or N-Ac-Protected Indoles and 2,3-Allenoates. *Eur. J. Org. Chem.* **2011**, *2011*, 1227–1231.	[9]
IZEBEU	Sonar, V.N.; Parkin, S.; Crooks, P.A. (*Z*)-2-(1-Phenylsulfonyl-1H-indol-3-ylmethylene)-1-azabicyclo[2.2.2]octan-3-one and (*Z*)-(S)-2-(1-phenylsulfonyl-1H-indol-3-ylmethylene)-1-azabicyclo[2.2.2]octan-3-ol. *Acta Crystallogr.* **2004**, *C60***,** o659–o661.	[10]
IZEBIY	Sonar, V.N.; Parkin, S.; Crooks, P.A. (*Z*)-2-(1-Phenylsulfonyl-1H-indol-3-ylmethylene)-1-azabicyclo[2.2.2]octan-3-one and (*Z*)-(S)-2-(1-phenylsulfonyl-1H-indol-3-ylmethylene)-1-azabicyclo[2.2.2]octan-3-ol. *Acta Crystallogr.* **2004**, *C60***,** o659–o661.	[10]
IZUNAS	Meza-Leon, R.L.; Crich, D.; Bernes, S.; Quintero, L. Endo-selective quenching of hexahydropyrrolo[2,3-b]indole-based N-acyliminium ions. *J. Org. Chem.* **2004**, *69*, 3976–3978.	[11].
IZUNIA	Meza-Leon, R.L.; Crich, D.; Bernes, S.; Quintero, L. Endo-selective quenching of hexahydropyrrolo[2,3-b]indole-based N-acyliminium ions. *J. Org. Chem.* **2004**, *69*, 3976–3978.	[11]

Table S1. *Cont.*

CSD code	Reference	Ref. No.
KEGCUV	Dockendorff, C.; Lautens, M.; Lough, A.J. 2-(1-Phenylsulfonyl-1H-indol-3-yl)-1,2-dihydronaphthalen-1-ol. *Acta Crystallogr.* **2006**, *E62*, o1030–o1032.	[12]
KERKIC	Kumar, G.S.; Chinnakali, K.; Balamurugan, R.; Mohanakrishnan, A.K.; Fun, H.-K. Ethyl 2-bromo-3-(1-phenylsulfonyl-1H-indol-3-yl)acrylate. *Acta Crystallogr.* **2006**, *E62*, o4972–o4974.	[13]
KIXTUG	Sankaranarayanan, R.; Velmurugan, D.; Raj, S.S.S.; Fun, H.-K.; Babu, G.; Perumal, P.T. 4-[1-(Phenylsulfonyl)indol-3-yl]-3a,4,5,9b-tetrahydro-3H-cyclopenta[c]quinolone. *Acta Crystallogr.* **2000**, *C56*, 475–476.	[14]
LAPBIP	Paramasivam, S.; Bhaskar, G.; Seshadri, P.R.; Perumal, P.T. (E)-3-Phenyl-2-(1-tosyl-1H-indol-3-ylcarbonyl)acrylonitrile. *Acta Crystallogr.* **2012**, *E68*, o683–o684.	[15]
LOXDOR	Jiang, B.; Yang, C.G.; Gu, X.H. A highly stereoselective synthesis of indolyl N-substituted glycines. *Tetrahedron Lett.* **2001**, *42*, 2545–2547.	[16]
LUDKUR	Mizoguchi, H.; Oguri, H.; Tsuge, K.; Oikawa, H. Divergent and expeditious access to fused skeletons inspired by indole alkaloids and transtaganolides. *Org. Lett.* **2009**, *11*, 3016–3019.	[17]
MORJUY	Jiang, B.; Yang, C.G.; Xiong, W.N.; Wang, J. Synthesis and cytotoxicity evaluation of novel indolylpyrimidines and indolylpyrazines as potential antitumor agents. *Bioorg. Med. Chem.* **2001**, *9*, 1149–1154.	[18]
PAWVIU	Zukerman-Schpector, J.; Wulf, G.D.; Stefani, H.A.; Vasconcelos, S.N.S.; Ng, S.W.; Tiekink, E.R.T. 3-Ethenyl-1-(4-methylphenylsulfonyl)-1H-indole. *Acta Crystallogr.* **2012**, *E68*, o1829–o1830.	[19]
QASXAK	Caballero, E.; Alonso, D.; Pelaez, R.; Alvarez, C.; Puebla, P.; Sanz, F.; Medarde, M.; Tome, F. Diels–alder reactivity of 4-aryl-1-phthalimido-2-siloxy-1,3-butadienes. *Tetrahedron* **2005**, *61*, 6871–6878.	[20]
QITMOV	Nieger, M. University of Bonn, Bonn, Germany, Personal communication, 2000.	[21]
ROCLIF	Forke, R.; Jager, A.; Knolker, H.-J. First total synthesis of clausine L and pityriazole, a metabolite of the human pathogenic yeast *Malassezia furfur*. *Org. Biomol. Chem.* **2008**, *6*, 2481–2483.	[22]
TEKTAE	Mohialdin-Khaffaf, S.; Persaud, K.C.; Pritchard, R.G. 3-Hexanoyl-1-tosylindole. A highly stereospecific preparation of 3-alkyl-substituted indoles. *Acta Crystallogr.* **1996**, *C52*, 2607–2609.	[23]
UBEBOU	Li, L.; Han, M.; Xiao, M.; Xie, Z. Proline-catalyzed enantioselective synthesis of aza-quaternary carbon derivatives. *Synlett* **2011**, *12*, 1727–1730.	[24]
VACKUH	Chakkaravarthi, G.; Panchatcharam, R.; Dhayalan, V.; Mohanakrishnan, A.K.; Manivannan, V. (Phenyl)(1-phenylsulfonyl-1H-indol-3-yl)methanone. *Acta Crystallogr.* **2010**, *E66*, o2895.	[25]
YEDYAI	Sonar, V.N.; Parkin, S.; Crooks, P.A. (Z)-2-[1-(4-Methylphenylsulfonyl)-1H-indol-3-ylmethylene]-1-azabicyclo[2.2.2]octan-3-one. *Acta Crystallogr.* **2006**, *E62*, o623–o625.	[26]
ZIKKAF	Schollmeyer, D.; Fischer, G.; Pindur, U. Dimeric 3-vinylindoles as potential antitumor active compounds: 1,1,3,4-Tetramethyl-3-(1-methyl-1H-indol-3-yl)-1,2,3,4-tetrahydrocyclopenta[b]indole and 1,1,3-Trimethyl-4-phenylsulfonyl-3-(1-phenylsulfonyl-1H-indol-3-yl)-1,2,3,4-tetrahydrocyclopenta[b]indole. *Acta Crystallogr.* **1995**, *C51*, 2572–2575.	[27]
ZILPAL	Vangveravong, S.; Nichols, D.E. Stereoselective synthesis of trans-2-(Indol-3-yl)cyclopropylamines: Rigid tryptamine analogs. *J. Org. Chem.* **1995**, *60*, 3409–3413.	[28]

Figure S1. NMR acquisition parameters.

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Current Data Parameters
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EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
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PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH            7878.151 Hz
FIDRES         0.240422 Hz
AQ             2.0797257 sec
RG                   57
DW                63.467 use
DE                 6.50 use
TE                272.9 K
D1           1.00000000 sec
TD0                   1

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SFO1        600.1730171 MHz
NUC1                 1H
P1                 7.38 use
PLW1          9.00000000 W

F2 - Processing parameters
SI                65536
SF          600.1700293 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
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Figure S2. NMR spectra at different temperatures.