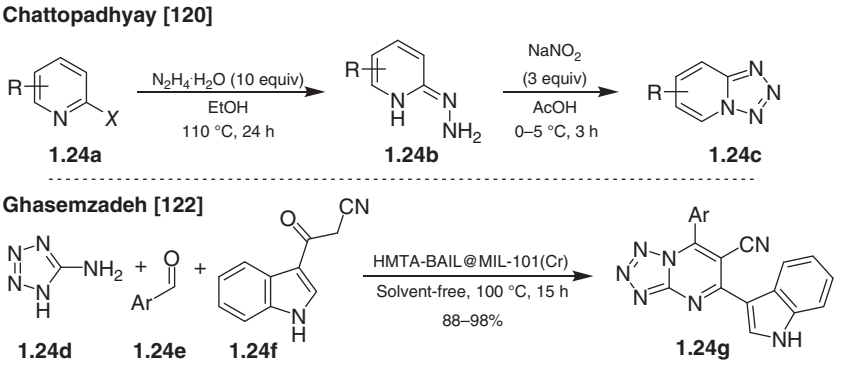
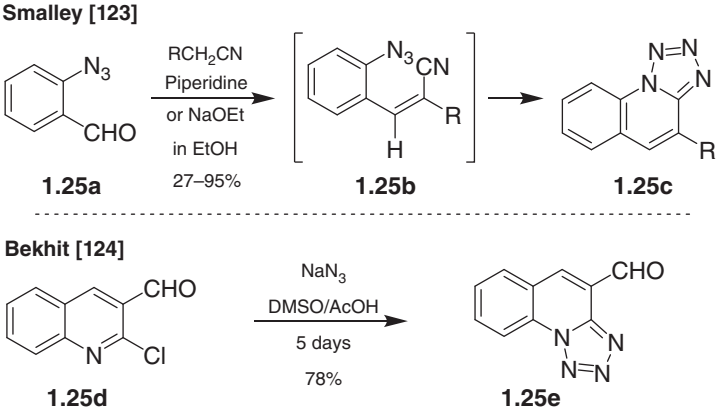


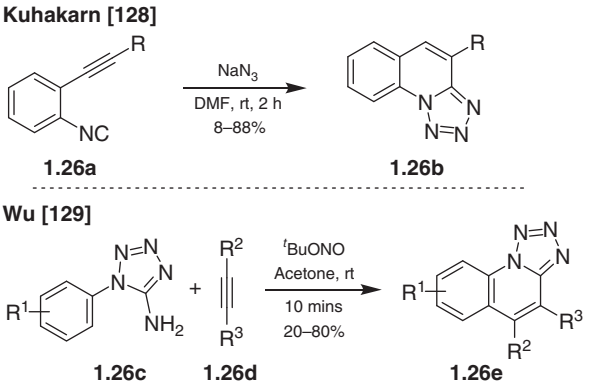
Scheme 1.24 Synthesis of diverse pyridotetrazoles.

1.4.3 Synthesis of Tetrazolo[1,5-*a*]quinolines

Tetrazolo[1,5-*a*]quinolines are largely found in natural products exhibiting biological activities. In 1997, Smalley and co-workers synthesized tetrazolo[1,5-*a*] quinolines **1.25c** by the reaction of 2-azidocarboxaldehyde **1.25a** with acetonitrile in the presence of piperidine or sodium ethoxide as base in ethanol (Scheme 1.25) [123]. The product formation could be rationalized through a Knoevenagel condensation of the acetonitrile with aldehyde **1.25a** followed by an intramolecular 1,3-dipolar cycloaddition reaction of azide with pendant cyano moiety present in **1.25b** intermediate. Later, Bekhit and co-workers reported the synthesis of tetrazolo[1,5-*a*]quinoline-4-carboxaldehyde **1.25e** from corresponding 2-chloroquinoline-3-carboxaldehyde **1.25d** by treating with sodium azide in DMSO/AcOH. [124–126] Recently, Chakroborty et al. modified the reaction conditions to attain a green and more efficient synthesis [127].



Scheme 1.25 Synthesis of tetrazolo[1,5-*a*]quinolines.



Scheme 1.26 Synthesis of various tetrazolo[1,5-*a*]quinolines.

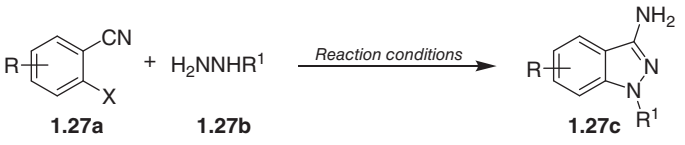
In 2019, Kuhakarn and co-workers [128] accomplished the synthesis of tetrazolo[1,5-*a*]quinolines **1.26b** from the reaction of *o*-alkynylisocyanobenzenes **1.26a** with sodium azide under metal- and base-free conditions (Scheme 1.26). This strategy involves nucleophilic addition of azide to isocyanide followed by 6-endo cyclization. On the other hand, Wu and co-workers [129] synthesized various tetrazolo[1,5-*a*]quinolines **1.26e** through *tert*-butylnitrite-mediated radical cyclization of 1*H*-tetrazol-5-amines **1.26c** with alkynes **1.26d**.

1.5 Synthesis of 3-Aminoindazoles

Interestingly, 3-aminoindazoles also has emerged as an efficient synthetic tool compatible with denitrogenative transformations. In 2002, Semple and co-workers [130–132] synthesized various 3-aminoindazoles from halobenzonitriles to access important non-covalent thrombin inhibitors. Later, the groups of Ma [133], Devkate [134], and Zhang and Hu [135] accomplished the synthesis of diverse 3-aminoindazoles **1.27c** from reaction of halobenzonitriles **1.27a** with hydrazines **1.27b** under the modified reaction conditions (Scheme 1.27). In 2010, Fabis and co-workers [136] reported a two-step synthesis of substituted 3-aminoindazoles **1.27g** from 2-bromobenzonitriles **1.27d** and hydrazones **1.27e**. This strategy involves *N*-arylation of hydrazone **1.27e** with *o*-bromobenzonitriles **1.27d** followed by deprotection of the hydrazone intermediate **1.27f** in methanol.

In 2011, Callot and co-workers [137] demonstrated a Buchwald–Hartwig C—N coupling reaction of various 3-haloindazoles **1.28a** to access 3-aminoindazoles **1.28b** in good to moderate yields (Scheme 1.28). Subsequently, Charrette and co-workers [138, 139] prepared 3-aminoindazoles from tertiary amides *via* the generation of aminohydrazones **1.28c** followed by intramolecular C—H amination.

Recently, Olmos and co-workers [140] reported the synthesis of 3-aminoindazoles **1.28g** from 3-(2-bromoaryl)-1,2,4-oxadiazol-5(4*H*)-ones **1.28e** and amines **1.28f** which involves an intramolecular N—N bond formation.



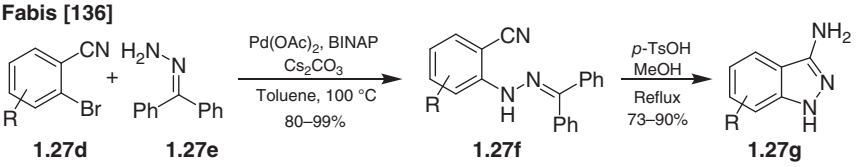
Reaction conditions:

Ma [133]: CuBr, K_2CO_3, DMSO, 80 °C [$R^1 = CO_2R^2$]

Devkate [134]: CAN, EtOH-H_2O,))))), 50–60 °C, 30–40 min

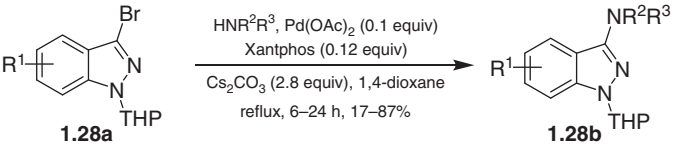
Zhang, Zhang and Wu [135]: ^{t}BuOK, diglyme

Fabis [136]

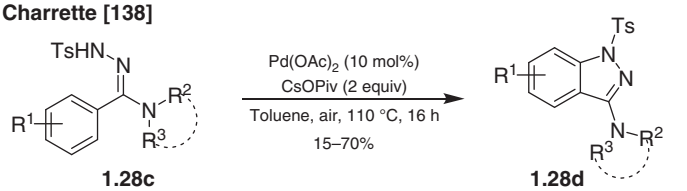


Scheme 1.27 Synthesis of 3-aminoindazoles from 2-halobenzonitriles.

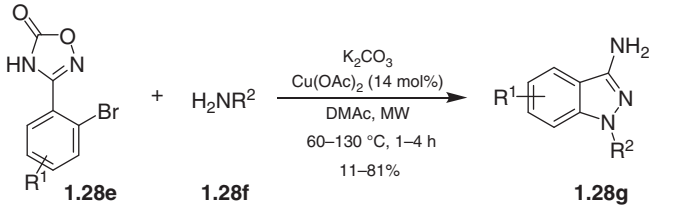
Callot [137]



Charrette [138]



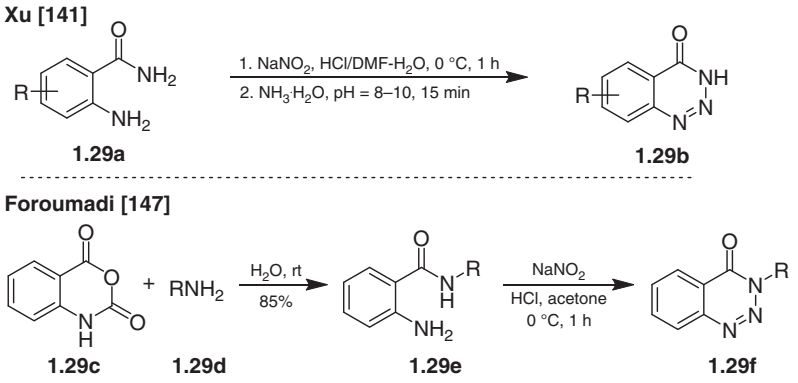
Olmos [140]



Scheme 1.28 Synthesis of various substituted 3-aminoindazoles.

1.6 Synthesis of Benzotriazinones

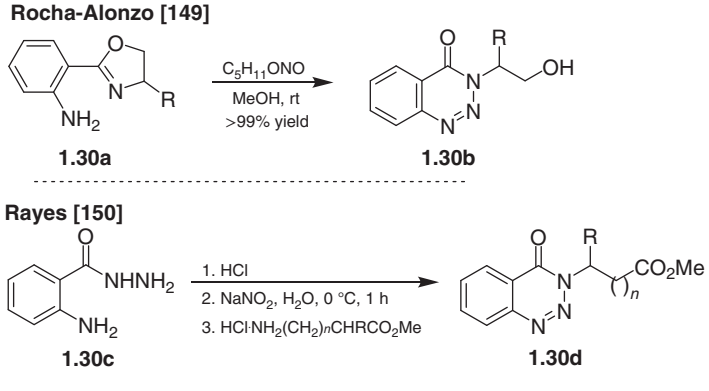
Another unique N-heterocycle, benzotriazinone, has been explored in several denitrogenative transformations. In 2015, Xu and co-workers [141–146] prepared several benzotriazinones **1.29b** from anthranilamides **1.29a** *via* diazotization, and cyclization reactions in one-pot (Scheme 1.29). They further derivatized these benzotriazinones by attaching spirocyclic indoline-2-one moieties, and studied



Scheme 1.29 Synthesis of benzotriazinones.

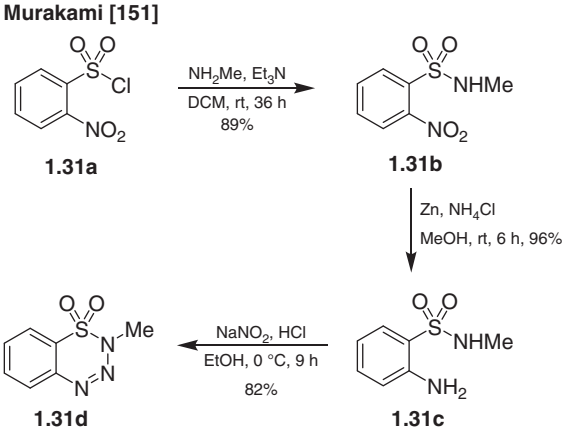
their nematicidal activities. Alternatively, the groups of Foroumadi [147], and Zhang and Li [148] prepared the benzotriazinones **1.29f** from isatoic anhydride **1.29c** and alkyl amines **1.29d** following the reaction sequence shown below. At first, isatoic anhydride **1.29c** and alkyl amines **1.29d** were stirred in water at room temperature to furnish 2-amino-*N*-(prop-2-yn-1-yl)benzamide **1.29e** as a white solid. Next, exposure of **1.29e** to acidic solution of sodium nitrite resulted in the formation of benzotriazinones **1.29f** *via* intramolecular nitrogen–nitrogen bond formation.

In 2017, Rocha-Alonzo and co-workers [149] developed a novel strategy to access 1,2,3-benzotriazinones **1.30b** from the reaction of 2-(*o*-aminophenyl)oxazolines **1.30a** with isoamyl nitrite in methanol (Scheme 1.30). Recently, Rayes and co-workers [150] reported the synthesis from anthranilhydrazide as well as methyl anthranilate.



Scheme 1.30 Synthesis of various N-substituted benzotriazinones.

In 2010, Murakami and co-workers reported a Ni-catalyzed annulation of 1,2,3,4-benzothiatriazine-1,1(2*H*)-dioxides **1.31d** with allenes (Scheme 1.31) [151]. Herein, benzothiazinone **1.31d** was synthesized from *ortho*-nitrobenzenesulfonyl chloride **1.31a**. Coupling of **1.31a** with methylamine followed by reduction of



Scheme 1.31 Synthesis of benzothiazinones. Source: Murakami [151]/John Wiley & Sons.

1.31b using Zn gives *ortho*-amino-*N*-methylbenzenesulfonamide **1.31c**. Finally, HONO-mediated ring closing of **1.31c** provides **1.31d** in 82% yield.

1.7 Summary and Outlook

Owing to the remarkable footprints left by various nitrogen heterocycles in the advancement of drugs, and total synthesis of natural products of biological importance, the development of methodologies to access such N-heterocycles has caught significant attention of synthetic chemists in past years. Wherein, atom and cost economy, green approach, and sustainability of the strategy were utmost priorities among other parameters. This chapter highlights the important modifications encountered over the years to accomplish the synthesis of diverse N-heterocycles, for example, triazoles, tetrazoles, 3-aminoindazoles, benzotriazinones, etc. with better yields and selectivity, specifically, which undergo various denitrogenative transformations. Delightfully, many synthetic routes have been developed in a metal-free manner and using milder conditions, some of which are even sustained in a water medium. In recent times, various metal nanoparticles have also been exploited in the advancement of synthesis of these N-heterocycles. Nonetheless, the synthesis of triazoloindoles, pyridotriazoles, thiadiazoles, and benzotriazinones has not received much attention. Hence, further development of synthetic methodologies to attain better accessibility is desirable due to the growing demand for these heterocycles as synthetic tools.

References

1 Anbarasan, P., Yadagiri, D., and Rajasekar, S. (2014). Recent advances in transition-metal-catalyzed denitrogenative transformations of 1,2,3-triazoles and related compounds. *Synthesis* 46: 3004–3023.

2 Akter, M., Rupa, K., and Anbarasan, P. (2022). 1,2,3-Triazole and its analogues: new surrogates for diazo compounds. *Chem. Rev.* 122: 13108–13205.

3 Kadhim, M.M., Mahmood, E.A., Heravi, M.R.P. et al. (2022). The synthesis of biologically active 1-sulfonyl-1,2,3-triazoles from sulfonyl azides and alkynes: a focus review. *J. Sulfur Chem.* 44: 377–391.

4 Bahadorikhalili, S., Divar, M., Damghani, T. et al. (2021). *N*-Sulfonyl ketenimine as a versatile intermediate for the synthesis of heteroatom containing compounds. *J. Org. Chem.* 939: 121773–121812.

5 Danilkina, N.A., Govdi, A.I., and Balova, I.A. (2020). 5-Iodo-1*H*-1,2,3-triazoles as versatile building blocks. *Synthesis* 52: 1874–1896.

6 Kumar, A.S., Kommu, N., Ghule, V.D., and Sahoo, A.K. (2014). Synthesis of trifluoromethyl-substituted *N*-aryl-poly-1,2,3-triazole derivatives. *J. Mater. Chem. A* 2: 7917–7926.

7 Niedermann, K., Früh, N., Senn, R. et al. (2012). Direct electrophilic *N*-trifluoromethylation of azoles by a hypervalent iodine reagent. *Angew. Chem. Int. Ed.* 51: 6511–6515.

8 Usachev, B.I. (2018). Chemistry of fluoroalkyl-substituted 1,2,3-triazoles. *J. Fluor. Chem.* 210: 6–45.

9 Neochoritis, C.G., Zhao, T., and Dömling, A. (2019). Tetrazoles via multicomponent reactions. *Chem. Rev.* 119: 1970–2042.

10 Verma, A., Kaur, B., Venugopal, S. et al. (2022). Tetrazole: a privileged scaffold for the discovery of anticancer agents. *Chem. Biol. Drug Des.* 100: 419–442.

11 Das, S.K., Roy, S., and Chattopadhyay, B. (2023). Transition-metal-catalyzed denitrogenative annulation to access high-valued N-heterocycles. *Angew. Chem. Int. Ed.* 62: e202210912.

12 Guo, Y. and Gao, Q. (2022). Recent advances in 3-aminoindazoles as versatile synthons for the synthesis of nitrogen heterocycles. *Org. Biomol. Chem.* 20: 7138–7150.

13 Wiley, R.H., Hussung, K.F., and Moffat, J. (1956). The preparation of 1,2,3-triazole. *J. Org. Chem.* 21: 190–192.

14 Looker, J.J. (1965). Preparation of 1,2,3-triazoles from 7-azido-l,3, 5-cycloheptatriene. A displacement from nitrogen. *J. Org. Chem.* 30: 638–639.

15 Birkofer, L., Ritter, A., and Richter, P. (1963). Thermolyse silylierter tetrazole. *Chem. Ber.* 96: 2750–2757.

16 Birkofer, L. and Wegner, P. (1966). 1.3-Cycloadditionen mit trimethylsilyl-azid; uber isomere *N*-acetyl-1.2.3-triazole. *Chem. Ber.* 99: 2512–2517.

17 Huisgen, R., Knorr, R., Möbius, L., and Szeimies, G. (1965). Einige Beobachtungen zur Addition organischer Azide an CC-Dreifachbindungen. *Chem. Ber.* 98: 4014–4021.

18 Harvey, G.R. (1966). A new synthesis of 1,2,3-triazoles and diazo esters from phosphorus ylids and azides. *J. Org. Chem.* 31: 1587–1590.

19 Holzer, W. and Ruso, K. (1992). Functionalisation of 1,2,3-triazole via lithiation of 1-[2-(trimethylsilyl)ethoxy]methyl-1*H*-1,2,3-triazole. *J. Heterocyclic Chem.* 29: 1203–1207.

20 Buckle, B.D.R. and Rockell, C.J.M. (1982). The 4-methoxybenzyl group, a versatile N-protecting group for the synthesis of N-unsubstituted v-triazoles. *J. Chem. Soc. Perkin Trans.* 1: 627–630.

21 Tanaka, Y., Velen, S.R., and Miller, S.I. (1973). Syntheses and properties of *H*-1,2,3-triazoles. *Tetrahedron* 29: 3271–3283.

22 Jankovič, D., Virant, M., and Gazvoda, M. (2022). Copper-catalyzed azide-alkyne cycloaddition of hydrazoic acid formed in situ from sodium azide affords 4-monosubstituted-1,2,3-triazoles. *J. Org. Chem.* 87: 4018–4028.

23 Loren, J.C., Krasiński, A., Fokin, V.V., and Sharpless, K.B. (2005). *NH*-1,2,3-triazoles from azidomethyl pivalate and carbamates: base-labile N-protecting groups. *Synlett* 18: 2847–2850.

24 Banert, K. (1989). Synthesis of 1,2,3-triazoles from propargyl azides by rearrangement of the azido group. Indication of short-lived allenyl azides and triazafulvenes. *Chem. Ber.* 122: 911–918.

25 Loren, J.C. and Sharpless, K.B. (2005). The Banert cascade: a synthetic sequence to polyfunctional *NH*-1,2,3-triazoles. *Synthesis* 9: 1514–1520.

26 Alexander, J.R., Kevorkian, P.V., and Topczewski, J.J. (2021). Intercepting the Banert cascade with nucleophilic fluorine: direct access to α-fluorinated *NH*-1,2,3-triazoles. *Chem. Commun.* 57: 5024–5027.

27 Thomas, J., Jana, S., Liekens, S., and Dehaen, W. (2016). A single-step acid catalyzed reaction for rapid assembly of *NH*-1,2,3-triazoles. *Chem. Commun.* 52: 9236–9239.

28 Medvedeva, A.S., Demina, M.M., Vu, T.D. et al. (2016). β-Cyclodextrin-catalyzed three-component synthesis of 4,5-disubstituted 1,2,3-(*NH*)-triazoles from propynals, trimethylsilyl azide and malononitrile in water. *Mendeleev Commun.* 26: 326–328.

29 Medvedeva, A.S., Demina, M.M., Kon'kova, T.V. et al. (2017). Microwave assisted solvent- and catalyst-free three-component synthesis of *NH*-1,2,3-triazoloimines. *Tetrahedron* 73: 3979–3985.

30 Hui, R., Zhao, M., Chen, M. et al. (2017). One-pot synthesis of 4-aryl-*NH*-1,2,3-triazoles through three-component reaction of aldehydes, nitroalkanes and NaN3. *Chin. J. Chem.* 35: 1808–1812.

31 Quan, X.-J., Ren, Z.-H., Wang, Y.-Y., and Guan, Z.-H. (2014). p-Toluenesulfonic acid mediated 1,3-dipolar cycloaddition of nitroolefins with NaN3 for synthesis of 4-Aryl-*NH*-1,2,3-triazoles. *Org. Lett.* 16: 5728–5731.

32 Efimov, I.V. (2019). Recent methods for the synthesis of *NH*-1,2,3-triazoles. *Chem. Heterocycl. Compd.* 55: 28–30.

33 Dutta, B., Hazarika, P.K., Saika, P. et al. (2023). [DDQM][TFSI]: a room temperature ionic liquid as an active electrode material for supercapacitor devices and a catalyst for rapid synthesis of 4-aryl-*NH*-1,2,3-triazoles under microwave irradiation. *New J. Chem.* https://doi.org/10.1039/D3NJ00862B.

34 Vergara-Arenas, B.I., Lomas-Romero, L., Ángeles-Beltrán, D. et al. (2017). Multicomponent synthesis of 4-aryl-*NH*-1,2,3-triazoles in the presence of Al-MCM-41 and sulfated zirconia. *Tetrahedron Lett.* 58: 2690–2694.

35 Shu, W.-M., Zhang, X.-F., Zhang, X.-X. et al. (2019). Metal-free cascade [4 + 1] cyclization access to 4-aryl-*NH*-1,2,3-triazoles from *N*-tosylhydrazones and sodium azide. *J. Org. Chem.* 84: 14919–14925.

36 Ren, M.-T., Li, M., Wang, A.-J. et al. (2020). Iodine-mediated condensation–cyclization of α-azido ketones with p-toluenesulfonyl hydrazide for synthesis of 4-aryl-*NH*-1,2,3-triazoles. *Eur. J. Org. Chem.* 2020: 2233–2236.

37 Huang, C., Geng, X., Zhao, P. et al. (2021). Direct synthesis of 4-aryl-1,2,3-triazoles via I2-promoted cyclization under metal- and azide-free conditions. *J. Org. Chem.* 86: 13664–13672.

38 Ishihara, K., Ishihara, K., Kato, Y. et al. (2022). A solvent-free synthesis of 4-aryl-*NH*-1,2,3-triazoles from ketones utilizing diphenyl phosphorazidate. *Synth. Commun.* 52: 1326–1335.

39 Yang, L., Wu, Y., Yang, Y. et al. (2018). Catalyst-free synthesis of 4-acyl-*NH*-1,2,3-triazoles by water-mediated cycloaddition reactions of enaminones and tosyl azide. *Beilstein J. Org. Chem.* 14: 2348–2353.

40 Opsomer, T. and Dehaen, W. (2021). Metal-free syntheses of N-functionalized and *NH*-1,2,3-triazoles: an update on recent developments. *Chem. Commun.* 57: 1568–1590.

41 Gribanov, P.S., Atoian, E.M., Philippova, A.N. et al. (2021). One-pot synthesis of 5-amino-1,2,3-triazole derivatives via dipolar azide−nitrile cycloaddition and Dimroth rearrangement under solvent-free conditions. *Eur. J. Org. Chem.* 2021: 1378–1384.

42 Beryozkina, T.V., Efimov, I.V., Fabian, W.M.F. et al. (2015). Reactivity of 1,2,3-triazoles towards sulfonyl chlorides. A novel approach to 1- and 2-sulfonyl-4-azolyl-1,2,3-triazoles. *Tetrahedron* 71: 6189–6195.

43 Rostovtsev, V.V., Green, L.G., Fokin, V.V., and Sharpless, K.B. (2002). A stepwise Huisgen cycloaddition process: copper(I)-catalyzed regioselective "ligation" of azides and terminal alkynes. *Angew. Chem. Int. Ed.* 41: 2596–2599.

44 Tornøe, C.W., Christensen, C., and Meldal, M. (2002). Peptidotriazoles on solid phase: [1,2,3]-triazoles by regiospecific copper(I)-catalyzed 1,3-dipolar cycloadditions of terminal alkynes to azides. *J. Org. Chem.* 67: 3057–3064.

45 De Nino, A., Maiuolo, L., Costanzo, P. et al. (2021). Recent progress in catalytic synthesis of 1,2,3-triazoles. *Catalysts* 11: 1120–1167.

46 Meldal, M. and Tornøe, C.W. (2008). Cu-Catalyzed azide-alkyne cycloaddition. *Chem. Rev.* 108: 2952–3015.

47 Hein, J.E. and Fokin, V.V. (2010). Copper-catalyzed azide-alkyne cycloaddition (CuAAC) and beyond: new reactivity of copper(I) acetylides. *Chem. Soc. Rev.* 39: 1302–1315.

48 Yoo, E.J., Ahlquist, M., Kim, S.H. et al. (2007). Copper-catalyzed synthesis of *N*-sulfonyl-1,2,3-triazoles: controlling selectivity. *Angew. Chem. Int. Ed.* 46: 1730–1733.

49 Yoo, E.J., Ahlquist, M., Bae, I. et al. (2008). Mechanistic studies on the Cu-catalyzed three-component reactions of sulfonyl azides, 1-alkynes and amines, alcohols, or water: dichotomy via a common pathway. *J. Org. Chem.* 73: 5520–5528.

50 Wang, F., Fu, H., Jiang, Y., and Zhao, Y. (2008). Copper-catalyzed cycloaddition of sulfonyl azides with alkynes to synthesize *N*-sulfonyltriazoles "on water" at room temperature. *Adv. Synth. Catal.* 350: 1830–1834.

51 Cano, I., Nicasio, M.C., and Pérez, P.J. (2010). Copper(I) complexes as catalysts for the synthesis of *N*-sulfonyl-1,2,3-triazoles from *N*-sulfonylazides and alkynes. *Org. Biomol. Chem.* 8: 536–538.

52 Raushel, J. and Fokin, V.V. (2010). Efficient synthesis of 1-sulfonyl-1,2,3-triazoles. *Org. Lett.* 12: 4952–4955.

53 Liu, Y., Wang, X., Xu, J. et al. (2011). Highly controlling selectivity of copper(I)-catalyzed azide/alkyne cycloaddition (CuAAC) between sulfonyl azids and normal alkynes or propynoates. *Tetrahedron* 67: 6294–6299.

54 Lazreg, F. and Cazin, C.S.J. (2018). Copper(I)-NHC complexes as efficient catalysts for the synthesis of 1,4-disubstituted 1,2,3-sulfonyltriazoles in air. *Organometallics* 37: 679–683.

55 Meza-Avina, M.E., Patel, M.K., Lee, C.B. et al. (2011). Selective formation of 1,5-substituted sulfonyl triazoles using acetylides and sulfonyl azides. *Org. Lett.* 13: 2984–2987.

56 Ramachary, D.B., Ramakumar, K., and Narayana, V.V. (2008). Amino acid-catalyzed cascade [3 + 2]-cycloaddition/hydrolysis reactions based on the push-pull dienamine platform: Synthesis of highly functionalized *NH*-1,2,3-triazoles. *Chem. Eur. J.* 14: 9143–9147.

57 Rajasekar, S. and Anbarasan, P. (2019). A general proline-catalyzed synthesis of 4,5-disubstituted *N*-sulfonyl-1,2,3-triazoles from 1,3-dicarbonyl compounds and sulfonyl azide. *Chem. Asian J.* 14: 4563–4567.

58 Zhang, W. and Xu, W. (2016). Synthesis of 1-arylsulfonyl-1,2,3-triazoles from (*Z*)-arylvinyl bromides by sequential elimination–cycloaddition reaction. *Chem. Heterocycl. Compd.* 52: 192–195.

59 Zheng, X., Wan, Y., Ling, F., and Ma, C. (2017). Copper-catalyzed tandem reaction of terminal alkynes and sulfonyl azides for the assembly of substituted aminotriazoles. *Org. Lett.* 19: 3859–3862.

60 Kwon, Y.-J., Lee, S.-G., and Kim, W.-S. (2023). Continuous flow synthesis of *N*-sulfonyl-1,2,3-triazoles for tandem relay Cu/Rh dual catalysis. *J. Org. Chem.* 88: 1200–1214.

61 Coe, P.L. and Holton, A.G. (1977). Some reactions of diazomethane with polyfluoroazaolefins. *J. Fluor. Chem.* 10: 553–564.

62 Zhang, R.Z., Zhang, R.X., Wang, S. et al. (2022). An *N*-trifluoromethylation/cyclization strategy for accessing diverse *N*-trifluoromethyl azoles from nitriles and 1,3-dipoles. *Angew. Chem. Int. Ed.* 61: e202110749.

63 Blastik, Z.E., Voltrová, S., Matoušek, V. et al. (2017). Azidoperfluoroalkanes: synthesis and application in copper(I)-catalyzed azide–alkyne cycloaddition. *Angew. Chem. Int. Ed.* 56: 346–349.

64 Wu, Y.-M., Deng, J., Li, Y., and Chen, Q.-Y. (2005). Regiospecific synthesis of 1,4,5-trisubstituted-1,2,3-triazole via one-pot reaction promoted by copper(I) salt. *Synthesis* 8: 1314–1318.

65 Li, L., Zhang, G., Zhu, A., and Zhang, L. (2008). A convenient preparation of 5-iodo-1,4-disubstituted-1,2,3-triazole: multicomponent one-pot reaction of azide and alkyne mediated by CuI-NBS. *J. Org. Chem.* 73: 3630–3633.

66 Li, L., Li, Y., Li, R. et al. (2011). A new synthetic protocol for one-pot preparations of 5-halo-1,4-disubstituted-1,2,3-triazoles. *Aust. J. Chem.* 64: 1383–1389.

67 Bogdan, A.R. and James, K. (2011). Synthesis of 5-iodo-1,2,3-triazole-containing macrocycles using copper flow reactor technology. *Org. Lett.* 13: 4060–4063.

68 Li, L., Ding, S., Yang, Y. et al. (2017). Multicomponent aqueous synthesis of iodo-1,2,3-triazoles: single-step models for dual modification of free peptide and radioactive iodo labeling. *Chem. Eur. J.* 23: 1166–1172.

69 Li, L., Xing, X., Zhang, C. et al. (2018). Novel synthesis of 5-iodo-1,2,3-triazoles using an aqueous iodination system under air. *Tetrahedron Lett.* 59: 3563–3566.

70 Hein, J.E., Tripp, J.C., Krasnova, L.B. et al. (2009). Copper(I)-catalyzed cycloaddition of organic azides and 1-iodoalkynes. *Angew. Chem. Int. Ed.* 48: 8018–8021.

71 Brotherton, W.S., Clark, R.J., and Zhu, L. (2012). Synthesis of 5-iodo-1,4-disubstituted-1,2,3-triazoles mediated by in situ generated copper(I) catalyst and electrophilic triiodide ion. *J. Org. Chem.* 77: 6443–6455.

72 Barsoum, D.N., Brassard, C.J., Deeb, J.H.A. et al. (2013). Synthesis of 5-iodo-1,2,3-triazoles from organic azides and terminal alkynes: ligand acceleration effect, substrate scope, and mechanistic insights. *Synthesis* 45: 2372–2386.

73 Barsoum, D.N., Okashah, N., Zhang, X., and Zhu, L. (2015). Mechanism of copper(I)-catalyzed 5-iodo-1,2,3-triazole formation from azide and terminal alkyne. *J. Org. Chem.* 80: 9542–9551.

74 Wang, D., Chen, S., and Chen, B. (2014). "Green" synthesis of 1,4-disubstituted 5-iodo-1,2,3-triazoles under neat conditions, and an efficient approach of construction of 1,4,5-trisubstituted 1,2,3-triazoles in one pot. *Tetrahedron Lett.* 55: 7026–7028.

75 Lal, S., Rzepa, H.S., and Díez-González, S. (2014). Catalytic and computational studies of N-heterocyclic carbene or phosphine-containing copper(I) complexes for the synthesis of 5-iodo-1,2,3-triazoles. *ACS Catal.* 4: 2274–2287.

76 Zhang, J., Chen, W., Wang, B. et al. (2015). One-pot three-component synthesis of 1,4,5-trisubstituted 5-iodo-1,2,3-triazoles from 1-copper(I) alkyne, azide and molecular iodine. *RSC Adv.* 5: 14561–14566.

77 Gribanov, P.S., Topchiy, M.A., Karsakova, I.V. et al. (2017). General method for the synthesis of 1,4-disubstituted 5-halo-1,2,3-triazoles. *Eur. J. Org. Chem.* 2017: 5225–5230.

78 Govdi, A.I., Danilkina, N.A., Ponomarev, A.V., and Balova, I.A. (2019). 1-Iodobuta-1,3-diynes in copper-catalyzed azide-alkyne cycloaddition: a one-step route to 4-ethynyl-5-iodo-1,2,3-triazoles. *J. Org. Chem.* 84: 1925–1940.

79 Gharpure, S.J., Naveen, S., Chavan, R.S., and Padmaja (2020). Regioselective synthesis of halotriazoles and their utility in metal catalyzed coupling reactions. *Eur. J. Org. Chem.* 2020: 6870–6886.

80 Arenas, J.L. and Crousse, B. (2021). An overview of 4- and 5-halo-1,2,3-triazoles from cycloaddition reactions. *Eur. J. Org. Chem.* 2021: 2665–2679.

81 Jones, G. (2002). The chemistry of the triazolopyridines: an update. *Adv. Heterocycl. Chem.* 83: 1–70.

82 Jones, G. and Abarca, B. (2010). The chemistry of the [1,2,3]triazolo[1,5-*a*] pyridines: an update. *Adv. Heterocycl. Chem.* 100: 195–252.

83 Deady, L.W. and Devine, S.M. (2006). Novel annulated products from aminonaphthyridinones. *Tetrahedron* 62: 2313–2320.

84 Xing, Y., Sheng, G., Wang, J. et al. (2014). Preparation of triazoloindoles via tandem copper catalysis and their utility as α-imino rhodium carbene precursors. *Org. Lett.* 16: 1244–1247.

85 Sheng, G., Huang, K., Chi, Z. et al. (2014). Preparation of 3-diazoindolin-2-imines via cascade reaction between indoles and sulfonylazides and their extensions to 2,3-diaminoindoles and imidazo[4,5-*b*]indoles. *Org. Lett.* 16: 5096–5099.

86 Katritzky, A.R., Lan, X., Yang, J.Z., and Denisko, O.V. (1998). Properties and synthetic utility of N-substituted benzotriazoles. *Chem. Rev.* 98: 409–548.

87 Hurd, C.D. and Mori, R.I. (1955). On acylhydrazones and 1,2,3-thiadiazoles. *J. Am. Chem. Soc.* 77: 5359–5364.

88 Kurandina, D. and Gevorgyan, V. (2016). Rhodium thiavinyl carbenes from 1,2,3-thiadiazoles enable modular synthesis of multisubstituted thiophenes. *Org. Lett.* 18: 1804–1807.

89 Duncia, J.V., Pierce, M.E., and Santella, J.B. III, (1991). Three synthetic routes to a sterically hindered tetrazole. A new one-step mild conversion of an amide into a tetrazole. *J. Org. Chem.* 56: 2395–2400.

90 Huff, B.E. and Staszak, M.A. (1993). A new method for the preparation of tetrazoles from nitriles using trimethylsilylazide/trimethylaluminum. *Tetrahedron Lett.* 34: 8011–8014.

91 Wittenberger, S.J. and Donner, B.G. (1993). Dialkyltin oxide mediated addition of trimethylsilyl azide to nitriles. A novel preparation of 5-substituted tetrazoles. *J. Org. Chem.* 58: 4139–4141.

92 Koguro, K., Oga, T., Mitsui, S., and Orita, R. (1998). Novel synthesis of 5-substituted tetrazoles from nitriles. *Synthesis* 1998: 910–914.

93 Curran, D.P., Hadida, S., and Kim, S.-Y. (1999). Tris(2-perfluorohexylethyl)tin azide: A new reagent for preparation of 5-substituted tetrazoles from nitriles with purification by fluorous/organic liquid-liquid extraction. *Tetrahedron* 55: 8997–9006.

94 Demko, Z.P. and Sharpless, K.B. (2001). Preparation of 5-substituted 1*H*-tetrazoles from nitriles in water. *J. Org. Chem.* 66: 7945–7950.

95 Himo, F., Demko, Z.P., Noodleman, L., and Sharpless, K.B. (2002). Mechanisms of tetrazole formation by addition of azide to nitriles. *J. Am. Chem. Soc.* 124: 12210–12216.

96 Demko, Z.P. and Sharpless, K.B. (2002). An expedient route to the tetrazole analogues of α-amino acids. *Org. Lett.* 4: 2525–2527.

97 Himo, F., Demko, Z.P., Noodleman, L., and Sharpless, K.B. (2003). Why is tetrazole formation by addition of azide to organic nitriles catalyzed by zinc(II) salts? *J. Am. Chem. Soc.* 125: 9983–9987.

98 Amantini, D., Beleggia, R., Fringuelli, F. et al. (2004). TBAF-Catalyzed synthesis of 5-substituted 1*H*-tetrazoles under solventless conditions. *J. Org. Chem.* 69: 2896–2898.

99 Ek, F., Manner, S., Wistrand, L.-G., and Frejd, T. (2004). Synthesis of fused tetrazole derivatives via a tandem cycloaddition and N-allylation reaction and parallel synthesis of fused tetrazole amines. *J. Org. Chem.* 69: 1346–1352.

100 Kantam, M.L., Kumar, K.B.S., and Sridhar, C. (2005). Nanocrystalline ZnO as an efficient heterogeneous catalyst for the synthesis of 5-substituted 1*H*-tetrazoles. *Adv. Synth. Catal.* 347: 1212–1214.

101 Kantam, M.L., Balasubrahmanyam, V., and Kumar, K.B.S. (2006). Zinc hydroxyapatite-catalyzed efficient synthesis of 5-substituted 1*H*-tetrazoles. *Synth. Commun.* 36: 1809–1814.

102 Jin, T., Kitahara, F., Kamijo, S., and Yamamoto, Y. (2008). Copper-catalyzed synthesis of 5-substituted 1*H*-tetrazoles via the [3 + 2] cycloaddition of nitriles and trimethylsilyl azide. *Tetrahedron Lett.* 49: 2824–2827.

103 Aali, E., Gholizadeh, M., and Noroozi-Shad, N. (2022). 1-Disulfo-[2,2-bipyridine]-1,1-diium chloride ionic liquid as an efficient catalyst for the green synthesis of 5-substituted 1*H*-tetrazoles. *J. Mol. Struct.* 1247: 131289–131295.

104 Abdollahi-Alibeik, M. and Moaddeli, A. (2015). Multi-component one-pot reaction of aldehyde, hydroxylamine and sodium azide catalyzed by Cu-MCM-41 nanoparticles: a novel method for the synthesis of 5-substituted 1*H*-tetrazole derivatives. *New J. Chem.* 39: 2116–2122.

105 Abadi, S.S.A.D.M. and Zarchi, M.A.K. (2017). A novel route for the synthesis of 5-substituted 1-*H* tetrazoles in the presence of polymer-supported palladium nanoparticles. *New J. Chem.* 41: 10397–10406.

106 Halder, M., Islam, M.M., Singh, P. et al. (2018). Sustainable generation of $Ni(OH)_2$ nanoparticles for the green synthesis of 5-substituted 1*H*-tetrazoles: a competent turn on fluorescence sensing of H_2O_2. *ACS Omega* 3: 8169–8180.

107 Swami, S., Sahu, S.N., and Shrivastava, R. (2021). Nanomaterial catalyzed green synthesis of tetrazoles and its derivatives: a review on recent advancements. *RSC Adv.* 11: 39058–39086.

108 Ghorbani-Choghamarani, A., Shiri, L., and Azadi, G. (2016). The first report on the eco-friendly synthesis of 5-substituted 1*H*-tetrazoles in PEG catalyzed by Cu(II) immobilized on Fe^3O^4@SiO^2@l-arginine as a novel, recyclable and non-corrosive catalyst. *RSC Adv.* 6: 32653–32660.

109 Movaheditabar, P., Javaherian, M., and Nobakht, V. (2022). Igneous rock powder as a heterogeneous multi-oxide nano-catalyst for the synthesis of 5-substituted-1*H*-tetrazoles in polyethylene glycol. *J. Iran. Chem. Soc.* 19: 1805–1816.

110 Mashhoori, M.-S. and Sandaroos, R. (2022). New ecofriendly heterogeneous nano-catalyst for the synthesis of 1-substituted and 5-substituted 1*H*-tetrazole derivatives. *Sci. Rep.* 12: 15364–15379.

111 Sajjadi, M., Nasrollahzadeh, M., Ghafuri, H. et al. (2022). Modified chitosan-zeolite supported Pd nanoparticles: a reusable catalyst for the synthesis of 5-substituted-1*H*-tetrazoles from aryl halides. *Int. J. Biol. Macromol.* 209: 1573–1585.

112 Bharathi, M., Indira, S., Vinoth, G. et al. (2022). A green one-pot three-component syntheses of tetrazole under microwave irradiation using Ni Schiff base complex of mixed ligands on MCM-41 as an efficient heterogeneous catalyst. *J. Porous. Mater.* 30: 691–703.

113 Reddy, K.S., Iyengar, D.S., and Bhalerao, U.T. (1983). The reaction of pyridine N-oxide and its benzoanalogues with arenesulfonyl azides: novel synthesis of tetrazoloazines. *Chem. Lett.* 1983: 1745–1748.

114 Boyer, J.H. and Schoen, W. (1956). 2,3-Ψ-Dinitrosopyridines. *J. Am. Chem. Soc.* 78: 423–425.

115 Keith, J.M. (2006). One-step conversion of pyridine N-oxides to tetrazolo [1,5-*a*]pyridines. *J. Org. Chem.* 71: 9540–9543.

116 Tamba, S., Nitani, M., Seo, T. et al. (2022). Tetrazolo[1,5-*a*]pyridine-containing π-conjugated systems: synthesis, properties, and semiconducting characteristics. *Org. Lett.* 24: 3792–3796.

117 Liu, S., Lentz, D., and Tzschucke, C.C. (2014). Conversion of pyridine N-oxides to tetrazolopyridines. *J. Org. Chem.* 79: 3249–3254.

118 Paronikyan, E.G., Sirakanyan, S.N., and Noravyan, A.S. (1997). Synthesis of derivatives of tetrazolo[1,5-*a*]- and oxazolo[4,5-*b*]pyrano(thiopyrano) [3,4-c]pyridines. *Chem. Heterocycl. Compd.* 33: 1101–1103.

119 Laha, J.K. and Cuny, G.D. (2008). Synthesis of tetrazolo[1,5-*a*]pyridines utilizing trimethylsilyl azide and tetrabutylammonium fluoride hydrate. *Synthesis* 2008: 4002–4006.

120 Roy, S., Khatua, H., Das, S.K., and Chattopadhyay, B. (2019). Iron(II)-based metalloradical activation: switch from traditional click chemistry to denitrogenative annulation. *Angew. Chem. Int. Ed.* 58: 11439–11443.

121 Khatua, H., Das, S.K., Roy, S., and Chattopadhyay, B. (2021). Dual reactivity of 1,2,3,4-tetrazole: manganese-catalyzed click reaction and denitrogenative annulation. *Angew. Chem. Int. Ed.* 60: 304–312.

122 Abdollahi-Basir, M.H., Mirhosseini-Eshkevari, B., Zamani, F., and Ghasemzadeh, M.A. (2021). Synthesis of tetrazolo[1,5-*a*]pyrimidine-6-carbonitriles using HMTA-BAIL@MIL-101(Cr) as a superior heterogeneous catalyst. *Sci. Rep.* 11: 5109–5120.

123 Porter, T.C., Smalley, R.K., Teguiche, M., and Purwono, B. (1997). Tetrazolo[1,5-*a*]quinolines and 1,2,3-triazolo[1,5-*a*]quinazolines by the action of cyanocarbanions on 2-azidoarylcarbonyl compounds. *Synthesis* 1997: 773–777.

124 Bekhit, A.A., El-Sayed, O.A., Aboulmagd, E., and Park, J.Y. (2004). Tetrazolo[1,5-*a*]quinoline as a potential promising new scaffold for the synthesis of novel anti-inflammatory and antibacterial agents. *Eur. J. Med. Chem.* 39: 249–255.

125 Meth-Cohn, O., Narine, B., and Tarnowski, B. (1981). A versatile new synthesis of quinolines and related fused pyridines. Part 5. The synthesis of 2-chloroquinoline-3-carbaldehydes. *J. C. S. Perkin I. Perkin* I: 1520–1530.

126 Kategaonkar, A.H., Labade, V.B., Shinde, P.V. et al. (2010). Synthesis and antimicrobial activity of tetrazolo[1,5-*a*]-quinoline-4-carbonitrile derivatives. *Monatsh. Chem.* 141: 787–791.

127 Chakroborty, S., Ramírez-Lopez, S.C., and Unnamatla, M.V.B. (2022). Synthesis of alkoxy-alkyl- tetrazolo[1,5-*a*] quinoline & tetrazolo[1,5-*a*] quinoline-4-carbaldehyde derivatives under green conditions. *Mater. Today Proc.* 57: 2423–2427.

128 Khaikate, O., Soorukram, D., Leowanawat, P. et al. (2019). Azide-triggered bicyclization of o-alkynylisocyanobenzenes: synthesis of tetrazolo[1,5-*a*]quinolines. *Eur. J. Org. Chem.* 2019: 7050–7057.

129 Liu, T., Ji, Y.-G., and Wu, L. (2019). tert-Butyl nitrite-mediated radical cyclization of tetrazole amines and alkynes toward tetrazolo[1,5-*a*]quinolines. *Org. Biomol. Chem.* 17: 2619–2623.

130 Cui, J.J., Araldi, G.L., Reiner, J.E. et al. (2002). Non-covalent thrombin inhibitors featuring P3-heterocycles with P1-bicyclic arginine surrogates. *Bioorg. Med. Chem. Lett.* 12: 2925–2930.

131 Halley, F. and Sava, X. (1997). Synthesis of 5-cyanoindazole and 1-methyl and 1-aryl-5-cyanoindazoles. *Synth. Commun.* 27: 1199–1207.

132 Orsini, P., Menichincheri, M., Vanotti, E., and Panzeri, A. (2009). Highly efficient synthesis of 5-benzyl-3-aminoindazoles. *Tetrahedron Lett.* 50: 3098–3100.

133 Xu, L., Peng, Y., Pan, Q. et al. (2013). Assembly of substituted 3-aminoindazoles from 2-bromobenzonitrile via a CuBr-catalyzed coupling/condensation cascade process. *J. Org. Chem.* 78: 3400–3404.

134 Devkate, C.G., Patil, A.M., Warad, K.D. et al. (2017). Ceric(IV) ammonium nitrate catalyzed highly efficient synthesis of 3-aminoindazole and their antibacterial screening. *Int. J. Res. Pharm. Chem.* 7: 513–517.

135 Zhang, C., Zhao, H., Li, Z. et al. (2020). Rapid access to 3-aminoindazoles from nitriles with hydrazines: a strategy to overcome the basicity barrier imparted by hydrazines. *Chem. Commun.* 56: 9521–9524.

136 Lefebvre, V., Cailly, T., Fabis, F., and Rault, S. (2010). Two-step synthesis of substituted 3-aminoindazoles from 2-bromobenzonitriles. *J. Org. Chem.* 75: 2730–2732.

137 Lohou, E., Collot, V., Stiebing, S., and Rault, S. (2011). Direct access to 3-aminoindazoles by Buchwald–Hartwig C—N coupling reaction. *Synthesis* 16: 2651–2663.

138 Cyr, P., Régnier, S., Bechara, W.S., and Charette, A.B. (2015). Rapid access to 3-aminoindazoles from tertiary amides. *Org. Lett.* 17: 3386–3389.

139 Sajadi, M.S., Darehkordi, A., and Hosseini, S.M.S. (2021). Synthesis of *N*-aryl-3*H*-indazol-3-imine and *N*-aryl-1*H*-indazol-3-amine via Na_2WO_4/H_2O_2 mediated by intramolecular N—N coupling. *Tetrahedron* 84: 132023–132028.

140 Zhu, W.F., Krämer, A., Knapp, S. et al. (2022). Cascade synthesis of kinase-privileged 3-aminoindazoles via intramolecular N—N bond formation. *J. Org. Chem.* 87: 3856–3862.

141 Wang, G.-L., Chen, X., Chang, Y.-N. et al. (2015). Synthesis of 1,2,3-benzotriazin-4-one derivatives containing spirocyclic indoline-2-one moieties and their nematicidal evaluation. *Chin. Chem. Lett.* 26: 1502–1506.

142 Fiorino, F., Caliendo, G., Perissutti, E. et al. (2005). Synthesis by microwave irradiation and antidiarrhoeal activity of benzotriazinone and saccharine derivatives. *Arch. Pharm. Chem. Life Sci.* 338: 548–555.

143 Chen, X., Jia, H., Li, Z., and Xu, X. (2019). Synthesis and nematicidal evaluation of 1,2,3-benzotriazin-4-one derivatives containing piperazine as linker against Meloidogyne incognita. *Chin. Chem. Lett.* 30: 1207–1213.

144 Chang, Y., Zhang, J., Chen, X. et al. (2017). Synthesis and nematicidal activities of 1,2,3-benzotriazin-4-one derivatives containing thiourea and acylthiourea against Meloidogyne incognita. *Bioorg. Med. Chem. Lett.* 27: 2641–2644.

145 Zhang, R., Guo, W., Wang, G. et al. (2020). Synthesis and nematicidal activities of 1,2,3-benzotriazin-4-one derivatives containing benzo[d][1,2,3]thiadiazole against Meloidogyne incognita. *Bioorg. Med. Chem. Lett.* 30: 127369–127372.

146 Caliendo, G., Fiorino, F., Grieco, P. et al. (1999). Preparation and local anaesthetic activity of benzotriazinone and benzoyltriazole derivatives. *Eur. J. Med. Chem.* 34: 1043–1051.

147 Moghimi, S., Goli-Garmroodi, F., Pilali, H. et al. (2016). Synthesis and anti-acetylcholinesterase activity of benzotriazinone-triazole systems. *J. Chem. Sci.* 128: 1445–1449.

148 Liu, C., Li, X., Zhang, J. et al. (2023). DNA-compatible benzotriazinone formation through aryl diazonium intermediates. *J. Org. Chem.* 88: 6565–6572.

149 Rocha-Alonzo, F., Chávez, D., Ochoa-Terán, A. et al. (2017). A novel synthesis of 1,2,3-benzotriazinones from 2-(o-aminophenyl)oxazolines. *J. Chemother.* 2017: https://doi.org/10.1155/2017/2384780.

150 El Rayes, S.M., Ali, I.A.I., Fathalla, W., and Mahmoud, M.A.A. (2020). Synthesis and biological activities of some new benzotriazinone derivatives based on molecular docking; promising HepG2 liver carcinoma inhibitors. *ACS Omega* 5: 6781–6791.

151 Miura, T., Yamauchi, M., Kosaka, A., and Murakami, M. (2010). Nickel-catalyzed regio- and enantioselective annulation reactions of 1,2,3,4-benzothiatriazine-1,1(2*H*)-dioxides with allenes. *Angew. Chem. Int. Ed.* 49: 4955–4957.