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Original article

# Microwave-assisted regioselective synthesis of substituted-9-bromo-9,10-dihydro-9,10-ethanoanthracenes via Diels-Alder cycloaddition

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## ABSTRACT

The substituted-9-bromo-9,10-dihydro-9,10-ethanoanthracenes *ortho* **8a-12a** and *meta* **8b-13b** have been synthesized via Diels-Alder reaction under microwave conditions. The cycloadduct isomers *ortho* **8a-11a** and *meta* **8b-11b**, with priority to *ortho* **8a-11a**, were obtained from the reaction of 9-bromoanthracene **1** with acrylonitrile **2**, 2-chloroacrylonitrile **3**, methacryloyl chloride **4** and acrylic acid **5**, while *ortho* **12a** and *meta* **12b**, with priority to *meta* **12b**, was obtained from the reaction of 9-bromoanthracene **1** with 1-cyano vinyl acetate **6**. Interestingly, the only isomer *meta* **13b** was obtained from the reaction of 9-bromoanthracene **1** with phenyl vinyl sulfone **7**. The results proved that the steric or/and electronic nature of the dienophile substituent is/are playing significant roles in the regioselectivity and isomers ratio.

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## 1. Introduction

Anthracene derivatives have been employed in versatile applications; for example in the organic electronics particularly organic light emitting diodes (OLED) as light-emitting materials (Varol et al., 2016; Peng et al., 2019; Chen et al., 2020) and in the chemotherapeutic field as antidepressants (Wilhelm and

Schmidt, 1969; Wadler et al., 1986; Huang et al., 2002), anti-proliferative agents (Cloonan et al., 2010; Cloonan and Williams, 2011; McNamara et al., 2014), antimalarial agents (Millet et al., 2004; Henry et al., 2008) and as glucocorticoid receptor modulators (Yang et al., 2009). 9-Bromoanthracene, which serve as a precursor for the synthesis of anthracene carboxyimides, has been considered as a promising candidate for bioimaging applications (Xu et al., 2017). These compounds are soluble and stable near-infrared (NIR) dyes (Yao et al., 2009). Many compounds have been reported and synthesized starting from 9-bromoanthracene, for example a series of bidentate bis-(pyridine) anthracene isomers (2,3-PyAn, 3,3-PyAn, 2,2-PyAn) were designed as nanocrystal photosensitizer (Li et al., 2017). Additionally, 9-bromoanthracene was incorporated into deoxyadenosine to prepare fluorescent nucleotide for biological applications (Le et al., 2017) indeed, it was hybridized with fluorescein to produce chemodosimeters for detection of singlet oxygen within the live cell (Chercheja et al., 2019).

Diels-Alder (DA) cycloaddition is one of the most efficient approach for the C–C bond formation. The catalysis is one the most

**Abbreviations:** OLED, organic light emitting diodes; NIR, near-infrared; DA, Diels-Alder; NMR, nuclear magnetic resonance; EWG, Electron Withdrawing Group; EDG, Electron Donating Group; Cl, chlorine atom; CN, nitrile group; OAc, acetoxy group; COOH, carboxyl group.

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important variables that affect the regioselectivity of DA cycloaddition, in particular, gold catalyst creates new opportunities for the regioselective cycloaddition (Praveen, 2019). Microwave-assisted organic synthesis has been gained significant attention better than conventional method because it makes reactions faster, safer, greener, more selective and more economic (Lidström et al., 2001; Wathey et al., 2002; Praveen et al., 2013; Gawande et al., 2014). The effect of substituents at the 9- or 10-position of the anthracene on the regioselectivity and photophysical properties have been investigated (Yang and Doweiko, 2005; Kim et al., 2008; Adel and Farooqui, 2013; Mallesham et al., 2014; Zhang et al., 2017). Based on the above findings, the substituents effect of the dienophiles on the DA regioselectivity has been reported through investigation the microwave-assisted reactions of 9-bromoanthracene **1** with six dienophiles individually; acrylonitrile **2**, 2-chloroacrylonitrile **3**, methacryloyl chloride **4**, acrylic acid **5**, 1-cyano vinyl acetate **6** and phenyl vinyl sulfone **7**.

## 2. Results and discussion

As a part of our ongoing interest in DA cycloaddition, in particular reaction of anthracene derivatives with many dienophiles (Sultan et al., 2016, 2017a, 2017b), our group has recently reported the DA cycloaddition and tested the cycloadducts in *in vitro* as antidepressants (Karama et al., 2016a) and anticancer agents (Karama et al., 2016b). More recently, we reported the regioselective DA reactions between 10-allyl-1,8-dichloroanthracene and three substituted dienophiles (Sultan and Karama, 2016). Unfortunately we failed to obtain the cycloadducts in dichloromethane or toluene at room temperature. In fact, from our experiences, we can say; chlorinated anthracenes are not reactive enough for DA reactions at room temperature and even under conventional heating. In this line, the DA reaction of phenyl vinyl with sulfoxide 1,8-dichloroanthracene afford cycloadduct in 30% yield after 8 days (del Rosario Benites et al., 1999), in comparison, the reaction of phenyl vinyl sulfoxide with anthracene afford 83% of the cycloadduct (Paquette et al., 1978). So in this work, 9-bromoanthracene **1** was subjected to react with six dienophiles **2–7** separately under microwave conditions affording *ortho/meta* cycloadducts with variable regioselectivity (Scheme 1, Table 1).

The DA reaction of 9-bromoanthracene **1** with acrylonitrile **2** was successfully carried out in xylene affording two isomers *ortho* **8a**: *meta* **8b** in a ratio 3.5:1 respectively as deduced from nuclear magnetic resonance spectrum (NMR) of the cycloadduct crude. It looks that nitrile group as a strong EWG on the dienophile **2** exerted an electronic effect and may a slightly steric effect also leading to the formation *meta* **8b** as a minor isomer. Meek et al, reported the DA cycloaddition of various ethylene equivalents with 9-Nitroanthracene and 9-Anthramide affording either or both isomer, the authors indicated that the negativity of the 9-substituent on the anthracene as a diene may play a significant role in determining the isomer ratio, but the negativity of the substituent on the dienophile do not (Meek et al., 1960). In a communication study, bicyclic amino acids were obtained in highly regioselectivity from DA cycloaddition of 2-acetamidoacrylate with 9-substituted anthracenes (Yang and Doweiko, 2005). This study observed that the *ortho* isomer was not formed at high temperatures, on the other hand, the DA cycloaddition of 2-acetamidoacrylate with 9-chloroanthracene or 9-methylanthracene were not sufficiently regioselective (Yang and Doweiko, 2005). The configuration assignment and regioselectivity of Diels-Alder cycloadducts could be clear in help of understanding the nature of the substituent (Verma and Singh, 1976, 1977). The NMR spectra of the isomer *ortho* **8a** showed the bridge-head proton H-10 at chemical shift ( $\delta$ ) 4.37 ppm as triplet with coupling constants (*J*) 2 Hz while the

corresponding bridge-head proton H-10' of the isomer *meta* **8b** appeared at chemical shift ( $\delta$ ) 4.55 ppm as doublet with coupling constants (*J*) 2 Hz. The slight downfield shifting of the H-10' in the isomer *meta* **8b**, in compare to isomer *ortho* **8a**, could be attributed to the deshielding effect of the nitrile group (CN), since its position on C-11' is close to <sup>1</sup>H-10 of the isomer *meta* **8b**.

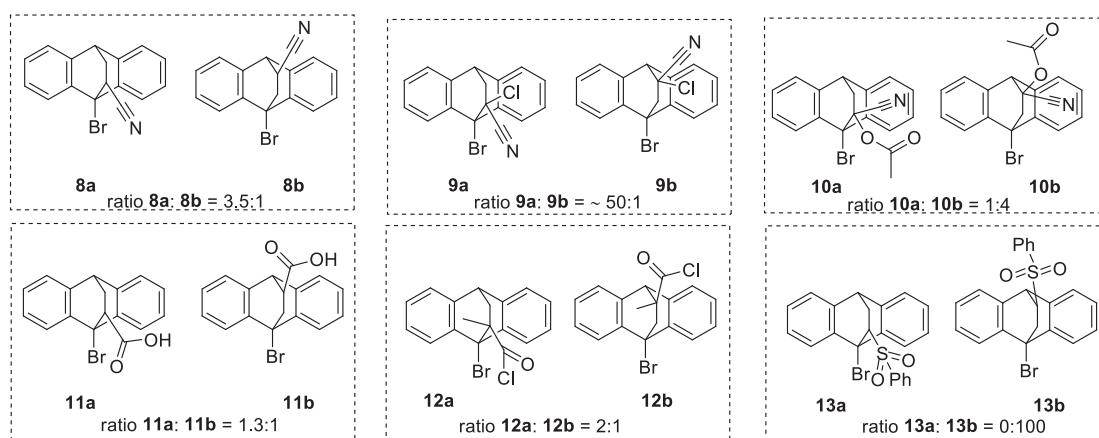
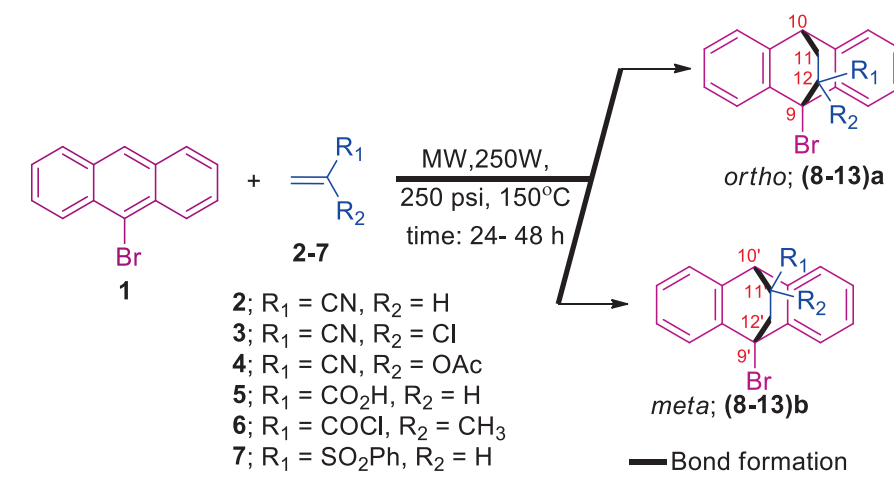
The reaction of 9-bromoanthracene **1** with 2-chloroacrylonitrile **3** afforded almost isomer *ortho* **9a** with insignificant amount of the isomer *meta* **9b**. The presence chlorine atom as EWG on this dienophile **3**, compare to dienophile acrylonitrile **2**, exhibited an electronic effect but not steric effect, since the ratio of the isomer *ortho* **9a** is increased. Sultan and Karama reported that chlorine atom on 2-chloroacrylonitrile had no steric effect in the DA cycloaddition of 2-chloroacrylonitrile and 10-allyl-1,8-dichloroanthracene.

The bridge-head proton H-10 of isomer *ortho* **9a** appeared at chemical shift ( $\delta$ ) 4.36 ppm as a triplet with coupling constant (*J*) 2.4 Hz. However the amount of the isomer *meta* **9b** was insignificant, the assignment of this isomer was scientifically valuable; the bridge-head proton H-10' of the isomer *meta* **9b** appeared at chemical shift ( $\delta$ ) 4.72 ppm as a singlet signal. The shifting of H-10' of the isomer *meta* **9b**, in relative to H-10 of the isomer *ortho* **9a**, could be attributed to the deshielding effect of the chlorine (Cl) atom and nitrile group (CN), since their positions on C-11' are very close to H-10'.

In contrast, the isomer *meta* **10b** was the major resulting from the reaction of 9-bromoanthracene **1** with 1-cyano vinyl acetate **4**. NMR assignment was recruited to understand the regioselectivity and then identify the isomers and their ratio. It's clear that acetate group on the dienophile exerted a significant steric or/and electronic effects leading to the formation isomer *meta* **10b** as a major in a ratio 1:4 for *ortho* **10a**: *meta* **10b** respectively as deduced from NMR spectrum of the cycloadduct crude. For these cycloadducts; the bridge-head proton H-10' of isomer *meta* **10b** appeared at chemical shift ( $\delta$ ) 5.07 ppm as a singlet while the bridge-head proton H-10 of the isomer *ortho* **10a** appeared at chemical shift ( $\delta$ ) 4.37 ppm as triplet with coupling constants (*J*) 2.8 Hz. The downfield shifting of the H-10' in the isomer *meta* **10b**, in compare to isomer *ortho* **10a**, could be attributed to the deshielding effect of the nitrile (CN) and acetoxy (OAc) groups, since their positions on C-11 are close to H-10' of the isomer *meta* **10b**.

The DA cycloaddition of 9-bromoanthracene **1** with acrylic acid **5** was carried out under the same condition to its reaction with acrylonitrile **2** and the ratio isomers *ortho* **11a**: *meta* **11b** was in the same direction where isomer *ortho* **11a** is the major. But the amount of isomer *ortho* **11a** is less and vice versa regarding amount of isomer *meta* **11b**. This is could be referred to the steric effect exerted by carboxyl group (COOH) that is more than nitrile group (CN) do. The isomers *ortho* **11a**: *meta* **11b** ratio is 1.3:1 while it was 3.5:1 in case of acrylonitrile. The NMR spectra of the isomer *ortho* **11a** exhibited the bridge-head proton H-10 at chemical shift ( $\delta$ ) 4.39 ppm as broad singlet and after enlarge the spectra it appears as triplet with coupling constants (*J*) 2.4 Hz while the bridge-head proton H-10' of the isomer *meta* **11b** appeared at chemical shift ( $\delta$ ) 4.74 ppm as doublet with coupling constants (*J*) 2 Hz. The slight downfield shifting of the H-10' in the isomer *meta* **11b**, in compare to isomer *ortho* **11a**, is may due to the deshielding effect of the carboxyl group (COOH), since its position on C-11' is close to H-10' of the isomer *meta* **11b**.

The effect of methyl group as an electron donating group (EDG) beside to an electron withdrawing group (EWG) on the dienophile, as in methacryloyl chloride **6**, is studied. The DA cycloaddition of 9-bromoanthracene **1** with methacryloyl chloride **6** led to the formation isomers *ortho* **12a** and *meta* **12b** in a ratio 2:1 respectively. The <sup>1</sup>H NMR spectrum was employed to distinguish between the



**Scheme 1.** The DA cycloaddition of 9-bromoanthracene **1** with six dienophiles **2-7**.

**Table 1**

The ratio of *ortho* (**8a-13a**)/*meta* (**8b-13b**) cycloadducts.

Entry	Dienophile	Substituent Nature	Cycloadducts Ratio <i>ortho</i> ( <b>8-13a</b> ): <i>meta</i> ( <b>8-13b</b> )
<b>1</b>	H <sub>2</sub> C = CHCN, <b>2</b>	EWG	<b>8a</b> : <b>8b</b> = 3.5:1
<b>2</b>	H <sub>2</sub> C = CClCN, <b>3</b>	EWG, EWG	<b>9a</b> : <b>9b</b> = ~50:1
<b>3</b>	H <sub>2</sub> C = C(OCOCH <sub>3</sub> )CN, <b>4</b>	EDG, EWG	<b>10a</b> : <b>10b</b> = 1:4
<b>4</b>	H <sub>2</sub> C = CHCOOH, <b>5</b>	EWG	<b>11a</b> : <b>11b</b> = 1.3:1
<b>5</b>	H <sub>2</sub> C = C(COCl)CH <sub>3</sub> , <b>6</b>	EWG, EDG	<b>12a</b> : <b>12b</b> = 2:1
<b>6</b>	H <sub>2</sub> C = CHSO <sub>2</sub> Ph, <b>7</b>	EWG	<b>13a</b> : <b>13b</b> = 0: 100

EWG: Electron Withdrawing Group; EDG: Electron Donating Group.

isomers *ortho* **12a** and *meta* **12b**; the bridge-head proton H-10 of the isomer *ortho* **12a** appeared as a triplet at chemical shift ( $\delta$ ) 4.29 ppm with coupling constants (*J*) 2.4 Hz whereas the corresponding bridge-head proton H-10' of isomer *meta* **12b** appeared as singlet signal at chemical shift ( $\delta$ ) 4.42 ppm.

Herein, we also report the DA cycloaddition, where the only isomer *meta* **13b** was formed. The DA cycloaddition of 9-bromoanthracene **1** with phenyl vinyl sulfone **7** gave only isomer *meta* **13b**. However, the phenyl sulfone group is EWG, the big significant volume of the phenyl sulfone group exhibited a significant steric effect leading to no formation of the isomer *ortho* **13a** but only isomer *meta* **13b**. The assignment of the isomer *meta* **13b** by <sup>1</sup>H NMR analysis was clear. The bridge-head proton H-10' of the isomer *meta* **13b** exhibited as a doublet signal and appeared at chemical shift ( $\delta$ ) 4.91 ppm with coupling constants (*J*) 1.6 Hz.

### 3. Conclusion

In conclusion, microwave-assisted DA cycloadditions of 9-Bromoanthracene **1** with six different-substituted dienophiles **2-7** have been reported. The *ortho* **8a-13a** and *meta* **8b-13b** cycloadducts were obtained in different ratios. The dienophiles; acrylonitrile **2**, 2-chloroacrylonitrile **3**, methacryloyl chloride **4** and acrylic acid **5** were independently reacted with 9-bromoanthracene **1** affording *ortho* **8a-11a** as major isomers while dienophile 1-cyano vinyl acetate **6** was reacted with 9-bromoanthracene **1** affording *meta* **12b** as a major isomer. In contrast, the dienophile phenyl vinyl sulfone **7** was reacted with 9-bromoanthracene **1** affording only isomer *meta* **13b**. It is noteworthy to mention that the steric or/and electronic nature of the dienophile substituent is/are playing significant roles in the regioselectivity and isomers ratio.

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### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jksus.2020.10.002>.

## References

- Adel, A.-S., Farooqui, M., 2013. (4+ 2) Cycloaddition Reactions of 9-Substituted Anthracene Compounds. *Orient. J. Chem.* 29 (3), 1033–1039.
- Chen, L.-Y., Shiu, Y.-J., Wu, Y.-J., Huang, W.-Y., 2020. Simple structured color tunable white organic light-emitting diodes utilizing an ambipolar anthracene derivative with low-lying LUMO. *Org. Electron.* 76, 105454.
- Chercheja, S., Daum, S., Xu, H.-G., Beierlein, F., Mokhir, A., 2019. Hybrids of a 9-anthracenyl moiety and fluorescein as chemodosimeters for the detection of singlet oxygen in live cells. *Org. Biomol. Chem.* 17 (46), 9883–9891.
- Cloonan, S.M., Drozowska, A., Fayne, D., Williams, D.C., 2010. The antidepressants maprotiline and fluoxetine have potent selective antiproliferative effects against Burkitt lymphoma independently of the norepinephrine and serotonin transporters. *Leukemia & lymphoma* 51 (3), 523–539.
- Cloonan, S.M., Williams, D.C., 2011. The antidepressants maprotiline and fluoxetine induce Type II autophagic cell death in drug-resistant Burkitt's lymphoma. *Int. J. Cancer* 128 (7), 1712–1723.
- del Rosario Benites, M.a., Fronczek, F.R., Maverick, A.W., 1999. Intermolecular hydrogenation of a C C bond during  $\pi$ -cyclopentadienyliron complexation of 1, 8-dichloro-9, 10-dihydro-9, 10-ethanoanthracene. *J. Organomet. Chem.* 577 (1), 24–30.
- Gawande, M.B., Shelke, S.N., Zboril, R., Varma, R.S., 2014. Microwave-assisted chemistry: synthetic applications for rapid assembly of nanomaterials and organics. *Acc. Chem. Res.* 47 (4), 1338–1348.
- Henry, M., Alibert, S., Baragatti, M., Mosnier, J., Baret, E., Amalvict, R., Legrand, E., Fusai, T., Barbe, J., Rogier, C., 2008. Dihydroethanoanthracene derivatives reverse in vitro quinoline resistance in *Plasmodium falciparum* malaria. *Med. Chem.* 4 (5), 426–437.
- Huang, H.-S., Lee, K.-Y., Shi, C.-H., Hsu, H.-C., 2002. Synthesis and pharmaceuticals of novel 9-substituted-1, 5-dichloroanthracene analogs. Google Patents.
- Karama, U., Sultan, M.A., Almansour, A.I., El-Taher, K.E., 2016a. Synthesis of chlorinated tetracyclic compounds and testing for their potential antidepressant effect in mice. *Molecules* 21 (1), 61.
- Karama, U.S.E., Sultan, M.A.S., Almansour, A.I., Tahir, K.E.H.E., Elnakady, Y.A., Mohaya, T.A.A., 2016b. Halogenated tetracyclic compounds. Google Patents.
- Kim, S.-K., Yang, B., Ma, Y., Lee, J.-H., Park, J.-W., 2008. Exceedingly efficient deep-blue electroluminescence from new anthracenes obtained using rational molecular design. *J. Mater. Chem.* 18 (28), 3376–3384.
- Le, B.H., Koo, J.C., Joo, H.N., Seo, Y.J., 2017. Diverse size approach to incorporate and extend highly fluorescent unnatural nucleotides into DNA. *Bioorg. Med. Chem.* 25 (14), 3591–3596.
- Li, X., Fast, A., Huang, Z., Fishman, D.A., Tang, M.L., 2017. Complementary Lock-and-Key Ligand Binding of a Triplet Transmitter to a Nanocrystal Photosensitizer. *Angew. Chem. Int. Ed.* 56 (20), 5598–5602.
- Lidström, P., Tierney, J., Wathey, B., Westman, J., 2001. Microwave assisted organic synthesis—a review. *Tetrahedron* 57 (45), 9225–9283.
- Malleshham, G., Balaiah, S., Reddy, M.A., Sridhar, B., Singh, P., Srivastava, R., Bhanuprakash, K., Rao, V.J., 2014. Design and synthesis of novel anthracene derivatives as n-type emitters for electroluminescent devices: a combined experimental and DFT study. *Photochem. Photobiol. Sci.* 13 (2), 342–357.
- McNamara, Y., Bright, S., Byrne, A., Cloonan, S., McCabe, T., Williams, D., Meegan, M., 2014. Synthesis and antiproliferative action of a novel series of maprotiline analogues. *Eur. J. Med. Chem.* 71, 333–353.

- Meek, J.S., Wilgus, D.R., Dann, J.R., 1960. Diels-Alder Reactions of 9-Substituted Anthracens. I IV. 9-Nitroanthracene and 9-Anthramide. *J. Am. Chem. Soc.* 82 (10), 2566–2569.
- Millet, J., Torrentino-Madamet, M., Alibert, S., Rogier, C., Santelli-Rouvier, C., Mosnier, J., Baret, E., Barbe, J., Parzy, D., Pradines, B., 2004. Dihydroethanoanthracene derivatives as in vitro malarial chloroquine resistance reversal agents. *Antimicrob. Agents Chemother.* 48 (7), 2753–2756.
- Paquette, L.A., Moerck, R.E., Harirchian, B., Magnus, P.D., 1978. Use of phenyl vinyl sulfoxide as an acetylene equivalent in Diels-Alder cycloadditions. *J. Am. Chem. Soc.* 100 (5), 1597–1599.
- Peng, L., Yao, J.-W., Wang, M., Wang, L.-Y., Huang, X.-L., Wei, X.-F., Ma, D.-G., Cao, Y., Zhu, X.-H., 2019. Efficient soluble deep blue electroluminescent dianthracenyl/phenylene emitters with CIE  $y$  ( $y \leq 0.08$ ) based on triplet-triplet annihilation. *Sci. Bull.* 64 (11), 774–781.
- Praveen, C., 2019. Dexterity of gold catalysis in controlling the regioselectivity of cycloaddition reactions. *Catalysis Rev.* 61 (3), 406–446.
- Praveen, C., Dheenkumar, P., Perumal, P., 2013. Super acid catalysed sequential hydrolysis/cycloisomerization of o-(acetylenic) benzamides under microwave condition: Synthesis, antinociceptive and antiinflammatory activity of substituted isocoumarins. *J. Chem. Sci.* 125 (1), 71–83.
- Sultan, M.A., Almansour, A.I., Pillai, R.R., Kumar, R.S., Arumugam, N., Armaković, S., Armaković, S.J., Soliman, S.M., 2017a. Synthesis, theoretical studies and molecular docking of a novel chlorinated tetracyclic:(Z/E)-3-(1, 8-dichloro-9, 10-dihydro-9, 10-ethanoanthracen-11-yl) acrylaldehyde. *J. Mol. Struct.* 1150, 358–365.
- Sultan, M.A., U. Karama, 2016. Substituent effects on regioselectivity of the Diels-Alder reactions: Reactions of 10-allyl-1, 8-dichloroanthracene with 2-chloroacrylonitrile, 1-cyanovinyl acetate and phenyl vinyl sulfone. *J. Chem.* 2016.
- Sultan, M.A., Karama, U., Almansour, A.I., Soliman, S.M., 2016. Theoretical Study on Regioselectivity of the Diels-Alder Reaction between 1, 8-Dichloroanthracene and Acrolein. *Molecules* 21 (10), 1277.
- Sultan, M.A., Karama, U., Almansour, A.I., Soliman, S.M., Ghabbour, H.A., Mabkhot, Y. N., 2017b. Synthesis, Characterization and DFT Calculations of 4, 5, 12-and 1, 8, 12-trichloro-9, 10-dihydro-9, 10-ethanoanthracene-12-carbonitriles. *Crystals* 7 (9), 259.
- Varol, S.F., Sayin, S., Eymur, S., Merdan, Z., Ünal, D., 2016. Optical performance of efficient blue/near UV nitropyridine-conjugated anthracene (NAMA) based light emitting diode. *Org. Electron.* 31, 25–30.
- Verma, S., Singh, R., 1976. Assignment of configurations to adducts of 2-substituted anthracene with maleic anhydride by NMR spectroscopy. *Aust. J. Chem.* 29 (6), 1215–1222.
- Verma, S.M., Singh, M.D., 1977. Structural elucidation with nuclear magnetic resonance spectroscopy. Diels-Alder adducts of 1-aminoanthracene and maleic anhydride: restricted rotation about the aryl C (1)-N bond and intrinsic asymmetry about the imide (Nsp<sup>2</sup>-Csp<sup>3</sup>) system. *J. Organic Chem.* 42 (23), 3736–3740.
- Wadler, S., Fuks, J.Z., Wiernik, P.H., 1986. Phase I and II agents in cancer therapy: I. Anthracylidines and related compounds. *J. Clinical Pharmacol.* 26 (7), 491–509.
- Wathey, B., Tierney, J., Lidström, P., Westman, J., 2002. The impact of microwave-assisted organic chemistry on drug discovery. *Drug Discovery Today* 7 (6), 373–380.
- Wilhelm, M., Schmidt, P., 1969. Synthese und Eigenschaften von 1-Aminoalkyl-dibenzo [b, e] bicyclo [2.2. 2] octadienen. *Helv. Chim. Acta* 52 (6), 1385–1395.
- Xu, J., Niu, G., Wei, X., Lan, M., Zeng, L., Kinsella, J.M., Sheng, R., 2017. A family of multi-color anthracene carboximides: synthesis, spectroscopic properties, solvatochromic fluorescence and bio-imaging application. *Dyes Pigm.* 139, 166–173.
- Yang, B.V., Doweiko, L.M., 2005. Highly regioselective Diels-Alder reactions of 9-substituted anthracenes and 2-acetamidoacrylate: synthesis of conformationally constrained  $\alpha$ -amino acids. *Tetrahedron Lett.* 46 (16), 2857–2860.
- Yang, B.V., Vaccaro, W., Doweiko, A.M., Doweiko, L.M., Huynh, T., Tortolani, D., Nadler, S.G., McKay, L., Somerville, J., Holloway, D.A., 2009. Discovery of novel dihydro-9, 10-ethano-anthracene carboxamides as glucocorticoid receptor modulators. *Bioorg. Med. Chem. Lett.* 19 (8), 2139–2143.
- Yao, J.H., Chi, C., Wu, J., Loh, K.P., 2009. Bisanthracene bis (dicarboxylic imide) s as soluble and stable NIR dyes. *Chem. Eur. J.* 15 (37), 9299–9302.
- Zhang, W., Wang, Q., Feng, X., Yang, L., Wu, Y., Wei, X., 2017. Anthracene-based derivatives: Synthesis, photophysical properties and electrochemical properties. *Chem. Res. Chin. Univ.* 33 (4), 603–610.