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AYRIM AROMATIK ALDEGIDLARNI GRINYAR REAKTIVI YORDAMIDA ENANTIOSELEKTIV ALKINILLASH

ЭНАНТИОСЕЛЕКТИВНОЕ АЛКИНИЛИРОВАНИЕ НЕКОТОРЫХ АРОМАТИЧЕСКИХ АЛЬДЕГИДОВ С ИСПОЛЬЗОВАНИЕМ РЕАГЕНТА ГРИНЬЯРА

ENANTIOSELECTIVE ALKYNATION OF SOME AROMATIC ALDEHYDES USING A GRIGNARD REAGENT

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Annotatsiya

Molekulasida ftor, xlor, brom, kislorod, oltingugurt va azot atomlari saqlagan benzaldegid va uning turli xil hosilalarini etilmagniyxlorid, 2-(dibutilamin)-1-fenilpropanol-1 va triftoretanol asosida tayyorlangan katalitik sistemada siklopropiletin bilan alkinillash reaksiyasi bo'yicha yangi avlod aromatik atsetilen spirtlarini sintez qilish usuli tadqiq qilingan. Tanlangan aldegidlar molekulasidagi geteroatomlar, katalizator va erituvchilar tabiati, reaksiya davomiyligi va haroratning mahsulot unumiga ta'siri tizimli ravishda o'rganilgan. Alkinillash jarayonining yo'nalishi, bosqichlari hamda reaksiya mexanizmlari taklif qilingan.Sintez qilingan birikmalarning tarkibi, tozaligi va tuzilishi zamonaviy fizik-kimyoviy tadqiqot usullarda isbotlangan.

Аннотация

Изучен метод синтеза нового поколения ароматических ацетиленовых спиртов реакцией алкинилирования бензальдегида и его различных производных, содержащих в молекулах атомы фтора, хлора, брома, кислорода, серы и азота, циклопропилэтеном в каталитической системе, приготовленной на основе этилмагнийхлорида, 2-(дибутиламино)-1-фенилпропанола-1 и трифторэтанола. Систематически изучена природа гетероатомов в молекуле выбранных альдегидов, влияние катализатора и растворителей, продолжительности реакции и температуры на выход продуктов. Предложены направление, стадии и механизмы реакции процесса алкинилирования. Состав, чистота и строение синтезированных соединений доказаны современными физико-химическими методами исследования.

Abstract

A method for synthesizing a new generation of aromatic acetylenic alcohols by alkynylation of benzaldehyde and its various derivatives containing fluorine, chlorine, bromine, oxygen, sulfur, and nitrogen atoms in their molecules with cyclopropylethene in a catalytic system prepared on the basis of ethyl magnesium chloride, 2-(dibutylamino)-1-phenylpropanol-1, and trifluoroethanol has been studied. The nature of heteroatoms in the molecules of the selected aldehydes, the effect of the catalyst and solvents, reaction time, and temperature on the yield of the products have been systematically studied. The direction, stages, and mechanisms of the alkynylation reaction have been proposed. The composition, purity, and structure of the synthesized compounds have been proven by modern physicochemical methods of study.

Kalit so'zlar: *aromatik atsetilen spirtlari, benzaldegid va uning geteroatomli hosilalari, alkinillash reaksiyalari, katalitik sistema, Grinyar reaktivi, reaksiya mexanizmi, mahsulot unumi.*

Ключевые слова: *ароматические ацетиленовые спирты, бензальдегид и его гетероатомные производные, реакции алкинилирования, каталитическая система, реактив Гриньяра, механизм реакции, выход продуктов.*

Key words: *aromatic acetylenic alcohols, benzaldehyde and its heteroatom derivatives, alkynylation reactions, catalytic system, Grignard reagent, reaction mechanism, product yield.*

KIRISH

Bugungi kunda dunyoda innovatsion texnologiyalar va usullar orqali tabiiy xomashyolar va neft-gaz mahsulotlari asosida yuqori ehtiyojga ega bo'lgan yangi turdagi kimyoviy preparatlarni sintez qilish hamda ishlab chiqarish jadallik bilan rivojlanmoqda. Ayniqsa ilmiy va amaliy masalalarni hal qilishda tabiiy resurslar va neft-gazni qayta ishlashda yangi texnologiyalarni joriy etish dolzarb masalalardan biridir. Jumladan neft va gaz mahsulotlari asosida kimyoviy hamda biologik faollikga ega atsetilen spirtlarini olishning yangi usullarini topish, fizik-kimyoviy xususiyatlarini tadqiq qilish hamda ularning maqsadli qo'llanish sohalarini aniqlash ustida ilmiy izlanishlar olib borish talab qilinmoqda. Atsetilen spirtlaridan neft-gaz, kimyo, rezina-texnika, lok-bo'yoq va farmatsevtika sanoatida yuqori sifatli preparatlar olishda samarali erituvchilar sifatida qo'llanilayotganligi sababli bunday turkum moddalarni keng masshtabda sintez qilish muhim ahamiyatga ega.

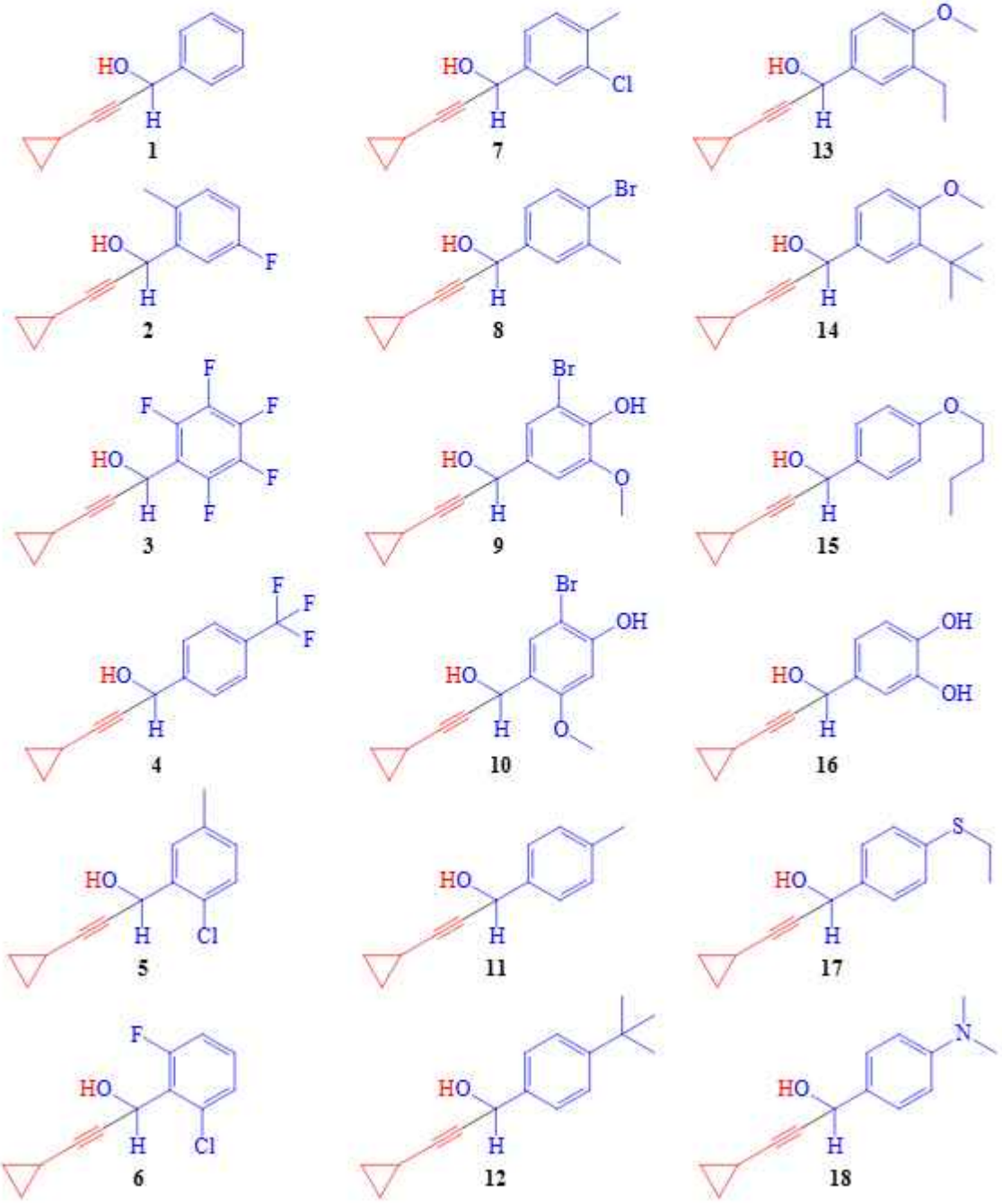
ADABIYOTLAR TAHLILI

Karbonil birikmalarining katalitik assimetrik alkinillanish jarayoni optik faol atsetilen spirtlarini sintez qilish uchun eng samarali usullardan biridir. Atsetilen spirtlari molekulalariga turli xil funktsional guruhlarni izolyatsiyalash orqali muhim xossalarga ega biologik faol birikmalar sintez qilish mumkin [1, 2]. Alifatik aldegidlarning ruh alkilalkinilidlar bilan tetragidrofuran-geksan eritmasida 24 soat davomida, 23 °C haroratda aminospirtlar katalizatorligida reaksiyalari o'rganilgan va 99% unumgacha atsetilen spirtlari sintez qilingan [3, 4]. Singh va Kamble fenilatsetilenning turli aldegidlar bilan anti-selektiv birikish reaksiyasini *Taddol, Quinidine, Cinchinidin* va *Cinchona* alkaloidlari ishtirokida amalga oshirgan. Katalizator sifatida $Ti(O^iPr)_4$ qo'llanilgan va 85% unum bilan atsetilen spirtlarini olishga erishgan. Kang va Wang jamoasi tomonidan katalizator sifatida bifunksional piridin bilan bog'langan aminospirtlar (β-sulfonamid) yordamida aldegidlarning rux alkilidlar bilan nukleofil birikish reaksiyalari 25 °C haroratda, 22 soat davomida olib borilgan. Dahmen va uning hamkasblari aldegidlarni salan, kinin, efedrin, prolinol va [2.2] parasiklofan kabi ligandlar yordamida katalitik alkinillash jarayonlari o'rganilgan [5-7]. Karbonil birikmalar (aldegid va ketonlar), iminlar, ketoefirlar, ketaminefirlar, oksikarbenlar, aldiminlarni turli xil alkinlar va ularning geteroatomli hosilalari yordamida og'ir metallar (Zn, Au, Ag, Cu, Ti) tuzlari hamda kuchli Lyuis kislotalari asosida tayyorlangan katalitik sistemalarda etinillash reaksiyalari o'rganilgan va yangi organik birikmalarni sintez qilish usullari ishlab chiqilgan [8-13]. Yuqorida keltirilgan atsetilen spirtlarini sintez qilish usullarining yutuqlari, ilmiy yangiligi bilan bir qatorda ayrim kamchiliklari ham mavjud, jumladan qo'llanilgan katalizator va erituvchilarning tan narxi qimmat, ularni ikkilamchi qayta ishlash deyarli imkonsiz, ekologik toza va resurs tejamkorlikga asoslanmagan.

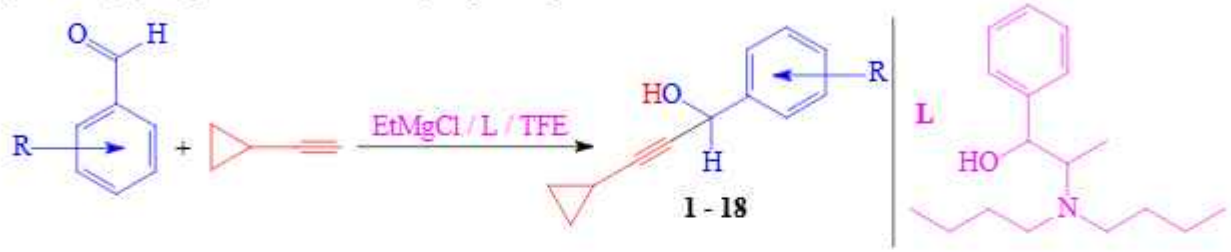
NATIJALAR VA MUHOKAMA

Tajriba qismi: Hajmi 25 ml bo'lgan vial flakonga dastlab 15 ml 2,2,2-triftoretanol ($C_2H_3F_3O$), 0,89 g (0,001 mol) etilmagniy xlorid (EtMgCl) va 1,32 g (0,02 mol) siklopropilatsetilen (C_5H_6) solindi va 60 minut davomida aralashtirildi. So'ngra ushbu aralashmaga promotor 0,53 g (0,002 mol) 2-(dibutilamin)-1-fenilpropanol-1 ($C_{17}H_{29}NO$) va 1,06 g (0,01 mol) benzaldegid (C_7H_6O) qo'shildi. Vial flakonidagi aralashma 4 soat davomida magnitli aralashtirgich yordamida muntazam aralashtirilib turildi. Jarayon xona haroratida olib borildi. Polimerlanishga qarshi gidroxinondan foydalanildi. Aralashma 4 soat davomida aralashtirilgandan keyin suv bilan gidroliz qilindi va yana 3 soat davomida aralashtirildi. Jarayonning keyingi bosqichida sistemadagi aralashma dixlormetan (CH_2Cl_2) bilan (3x10 ml) bilan ekstraksiya qilindi. Organik qatlam Na_2SO_4 yordamida quritildi, erituvchilar oddiy haydash yo'li bilan ajratib olindi. Mahsulot xromatografiya usuli yordamida tozalandi. Reaksiya natijasida (1,44 g) 84% unum bilan 3-siklopropil-1-fenilpropin-2-ol-1 (**1**) sintez qilindi.

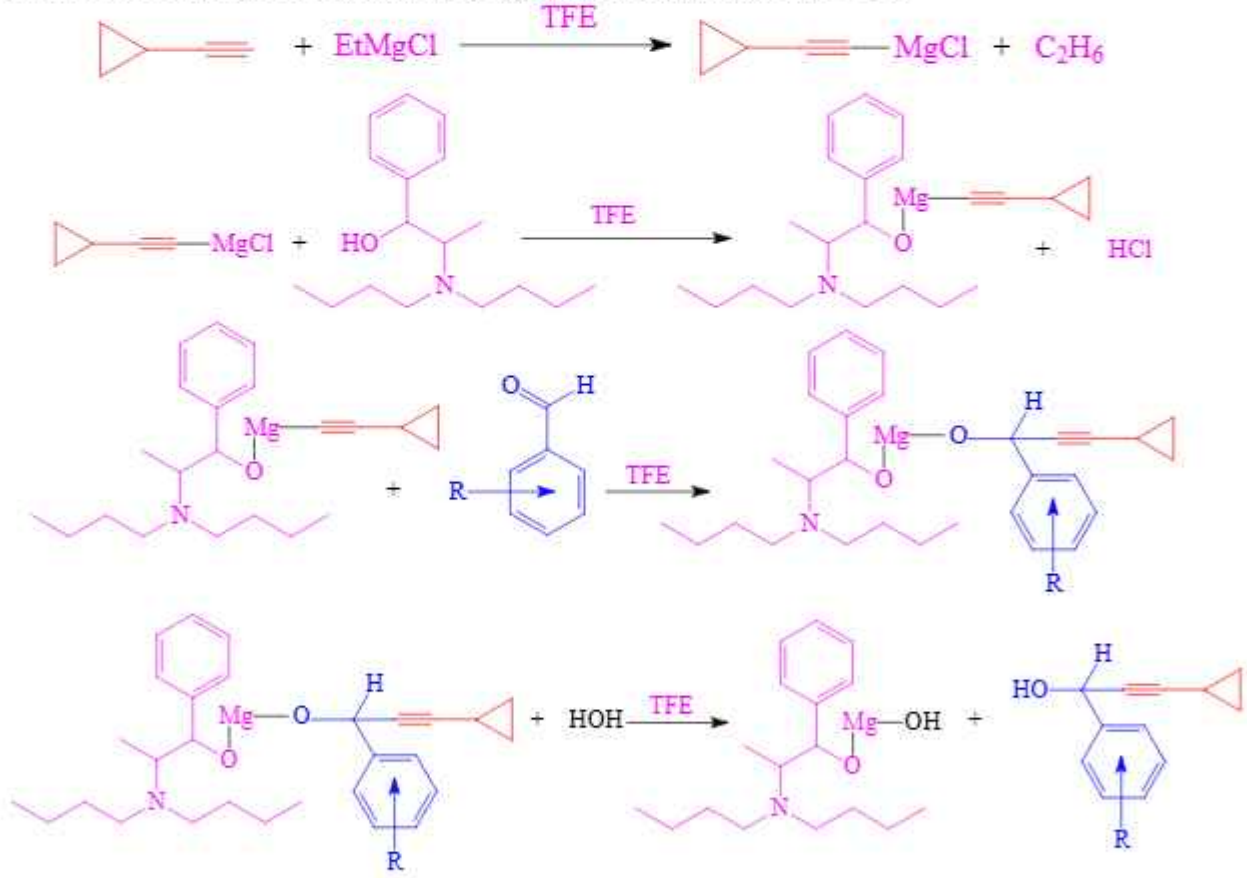
Ushbu usul bo'yicha quyidagi atsetilen spirtlari– 3-siklopropil-1-(5-ftor-2-metilfenil)propin-2-ol-1 (**2**, 83%), 3-siklopropil-1-(perftorfenil)propin-2-ol-1 (**3**, 81%), 3-siklopropil-1-(4-(triftormetil)fenil)propin-2-ol-1 (**4**, 71%), 1-(2-xlor-5-metilfenil)-3-siklopropilpropin-2-ol-1 (**5**, 87%), 1-(2-xlor-6-ftorfenil)-3-siklopropilpropin-2-ol-1 (**6**, 85%), 1-(3-xlor-4-metilfenil)-3-siklopropilpropin-2-ol-1 (**7**, 86%), 1-(4-brom-3-metilfenil)-3-siklopropilpropin-2-ol-1 (**8**, 89%), 2-brom-4-(3-siklopropil-1-gidroksipropin-2-il)-6-metoksifenol (**9**, 82%), 2-brom-4-(3-siklopropil-1-gidroksipropin-2-il)-5-metoksifenol (**10**, 79%), 3-siklopropil-1-p-tolilpropin-2-ol-1 (**11**, 87%), 1-(4-tret-butilfenil)-3-siklopropilpropin-2-ol-1 (**12**, 80%), 3-siklopropil-1-(3-etil-4-metoksifenil)propin-2-ol-1 (**13**, 83%), 1-(3-uchlamchi-butil-4-metoksifenil)-3-siklopropilpropin-2-ol-1 (**14**, 85%), 1-(4-butoksifenil)-3-siklopropilpropin-2-ol-1 (**15**, 90%), 4-(3-siklopropil-1-gidroksipropin-2-il)benzoldiol-1,2 (**16**, 75%), 3-siklopropil-1-(4-(etiltio)fenil)propin-2-ol-1 (**17**, 88%), 3-siklopropil-1-(4-(dimetilamino)fenil)propin-2-ol-1 (**18**, 87%) sintez qilindi. Sintez qilingan aromatik atsetilen spirtlarining tuzilish formulalari quyidagicha taklif etildi.

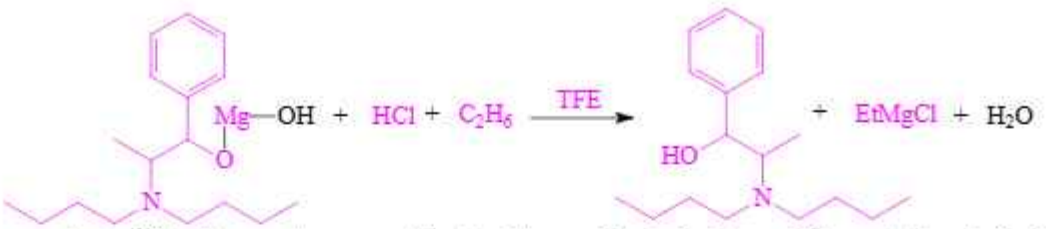


Jarayon ximizmi: Ushbu ishda tadqiqot obekti sifatida olingan benzaldegid va uning quyidagi R-almashgan hosilalari– 5-ftor-2-metilbenzaldegid, 2,3,4,5,6-pentaftorbenzaldegid, 4-(triftormetil)benzaldegid, 2-xlor-5-metilbenzaldegid, 2-xlor-6-ftorbenzaldegid, 3-xlor-4-metilbenzaldegid, 4-brom-3-metilbenzaldegid, 3-brom-4-gidroksi-5-metoksibenzaldegid, 5-brom-4-gidroksi-2-metoksibenzaldegid, 4-metilbenzaldegid, 4-uchlamchi-butilbenzaldegid, 3-etil-4-metoksibenzaldegid, 3-(uchlamchibutil)-4-metoksibenzaldegid, 4-butoksibenzaldegid, 3,4-digidroksibenzaldegid, 4-(tioetil)benzaldegid, 4-(dimetilamino) benzaldegidlarni $EtMgCl/C_{17}H_{29}NO/TFE$ katalitik sistemasida ilk bor siklopropilatsetilen bilan alkinillash orqali molekulasida alkil, oksialkil, tioalkil, aminoalkil, gidroksil va galogenlar kabi o'rinbosarlar, siklik va aromatik xalqa hamda uchbog' saqlagan saqlagan aromatik atsetilen spirtlari (**1-18**) sintezi tahlil qilingan. Adabiyot manbalari asosida tanlangan atsetilen spirtlarini sintez qilish reaksiyasi sxemasi va bosqichlari quyidagicha taklif etilmoqda [14-16].



Alkinillash reaksiyasi bosqichlari esa quyidagicha taklif qilindi [17-23].





Tanlangan katalitik sistemada aromatik atsetilen spirtlarini sintez qilish reaksiyalari -10 ÷ 40 °C harorat intervallarida, 4-12 soat vaqt oralig'ida olib borildi. Tadqiqot natijalari asosida tadqiqot obyekti bo'lgan aldegidlarni EtMgCl/$C_{17}H_{29}NO$/TFE katalitik sistemasida alkinillash reaksiyalarining eng muqobil sharoitlari topildi. Jumladan reaksiyalar 8 soat davomida, 20 °C haroratda olib borilganda mahsulot unumining maksimum chiqishi aniqlandi. Tadqiqotlarimiz natijalariga ko'ra ushbu reaksiyalarni olib borishda bir qator oraliq va qo'shimcha mahsulotlar hosil bo'lishi, ularning reaksiya yo'nalishi va borishiga ta'sirlari o'rganildi. Reaksiyalarning faollanish energiyalari hisoblandi.

Fizik-kimyoviy tadqiqot natijalari: Sintez qilingan aromatik atsetilen diollarining tuzilishi zamonaviy ^{1}H-YaMR, ^{13}C-YaMR spektroskopiya usullari yordamida tahlil qilndi. Olingan natijalar quyidagicha bayon qilinmoqda.

3-siklopropil-1-fenilpropin-2-ol-1 (**1**). ^{1}H YaMR (400 MHz, xloroform-*d*) δ 7.56 – 7.23 (m, 5H), 5.77 – 5.41 (m, 2H), 2.62 (m, *J* = 7.1, 2.6 Hz, 1H), 1.50 – 1.24 (m, 4H).

3-siklopropil-1-(5-ftor-2-metilfenil)propin-2-ol-1 (2). ^{1}H YaMR (400 MHz, xloroform-*d*) δ 6.07 (dd, *J* = 6.9, 2.5 Hz, 1H), 5.30 (d, *J* = 6.8 Hz, 1H), 2.52 (pd, *J* = 7.0, 2.5 Hz, 1H), 1.50 – 1.14 (m, 4H).

3-siklopropil-1-(perftorfenil)propin-2-ol-1 (3). ^{1}H YaMR (400 MHz, xloroform-*d*) δ 7.79 – 7.65 (m, 2H), 7.51 – 7.33 (m, 2H), 5.70 (d, *J* = 6.5 Hz, 1H), 5.65 – 5.54 (m, 1H), 2.58 (m, *J* = 7.0, 2.4 Hz, 1H), 1.55 – 1.32 (m, 4H).

3-siklopropil-1-(4-(triftormetil)fenil)propin-2-ol-1 (4). ^{1}H YaMR (400 MHz, DMSO-*d*) δ 6.04 (dd, *J* = 6.9, 2.5 Hz, 1H), 5.26 (d, *J* = 6.8 Hz, 1H), 2.48 (m, *J* = 7.0, 2.5 Hz, 1H), 1.34 – 1.19 (m, 4H).

1-(2-xlor-5-metilfenil)-3-siklopropilpropin-2-ol-1 (5). ^{1}H YaMR (400 MHz, xloroform-*d*) δ 7.47 (d, *J* = 7.5 Hz, 1H), 7.29 – 7.18 (m, 1H), 7.07 – 6.96 (m, 1H), 5.89 (dd, *J* = 7.0, 2.6 Hz, 1H), 5.56 (d, *J* = 7.0 Hz, 1H), 2.68 (m, *J* = 7.1, 2.6 Hz, 1H), 2.39 (d, *J* = 0.9 Hz, 3H), 1.52 (dd, *J* = 7.0, 2.4 Hz, 4H). ^{13}C YaMR (125 MHz, xloroform-*d*) δ 126.93, 124.01, 120.63, 119.21, 82.54, 77.16, 55.34, 45.33, 12.24, 12.21, 4.87.

1-(2-xlor-6-ftorfenil)-3-siklopropilpropin-2-ol-1 (6). ^{1}H YaMR (400 MHz, benzol-d) δ 7.46 (dd, J = 7.5, 1.6 Hz, 1H), 7.40 (td, J = 7.4, 4.9 Hz, 1H), 7.19 – 7.12 (m, 1H), 6.07 (dd, J = 7.0, 2.6 Hz, 1H), 5.64 (d, J = 7.1 Hz, 1H), 2.62 (m, J = 7.1, 2.6 Hz, 1H), 1.58 – 1.41 (m, 4H). ^{13}C YaMR (125 MHz, benzol-*d*) δ 162.78, 160.73, 135.32, 130.95, 128.08, 126.23, 115.61, 92.02, 91.97, 89.07, 63.59, 14.74.

1-(3-xlor-4-metilfenil)-3-siklopropilpropin-2-ol-1 (7). ^{1}H YaMR (400 MHz, xloroform-*d*) δ 7.45 – 7.29 (m, 1H), 7.26 (d, *J* = 1.4 Hz, 2H), 5.79 (dd, *J* = 6.7, 2.5 Hz, 1H), 5.68 (d, *J* = 6.8 Hz, 1H), 2.61 (m, *J* = 7.1, 2.6 Hz, 1H), 2.23 (d, *J* = 0.7 Hz, 3H), 1.51 – 1.35 (m, 4H). ^{13}C YaMR (125 MHz, xloroform-*d*) δ 138.00, 129.86, 127.20, 125.92, 91.15, 81.03, 80.99, 66.38, 19.34, 13.86, 13.81, 11.82.

1-(4-brom-3-metilfenil)-3-siklopropilpropin-2-ol-1 (8). ^{1}H YaMR (400 MHz, xloroform-*d*) δ 7.50 (d, *J* = 7.5 Hz, 1H), 7.27 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.15 (dd, *J* = 1.4, 0.7 Hz, 1H), 5.78 – 5.54 (m, 2H), 2.55 (m, *J* = 7.0, 1.6, 0.7 Hz, 1H), 2.27 (s, 3H), 1.48 – 1.25 (m, 4H). ^{13}C YaMR (125 MHz, xloroform) δ 148.50, 146.36, 142.06, 140.04, 138.58, 136.72, 130.91, 130.86, 101.46, 91.49, 32.63, 24.37, 24.33, 12.20.

2-brom-4-(3-siklopropil-1-gidroksipropin-2-il)-6-metoksifenol (9). ^{1}H YaMR (400 MHz, xloroform-d) δ 8.67 (s, 1H), 7.25 (d, J = 1.4 Hz, 1H), 7.00 (d, J = 1.4 Hz, 1H), 5.83 – 5.67 (m, 2H), 3.88 (s, 3H), 2.59 (m, J = 7.0, 2.2 Hz, 1H), 1.52 – 1.25 (m, 4H). ^{13}C YaMR (125 MHz, xloroform-d) δ 159.25, 154.53, 143.98, 136.50, 121.17, 117.06, 101.93, 92.18, 77.16, 67.69, 25.03, 24.79, 12.93.

2-brom-4-(3-siklopropil-1-gidroksipropin-2-il)-5-metoksifenol (10). ^{1}H YaMR (400 MHz, benzol-*d*) δ 7.87 (s, 1H), 7.16 (s, 1H), 6.78 (s, 1H), 6.10 (dd, *J* = 7.0, 2.6 Hz, 1H), 5.82 (d, *J* = 7.0 Hz, 1H), 4.11 (s, 3H), 2.85 (pd, *J* = 7.0, 2.5 Hz, 1H), 1.78 – 1.51 (m, 4H). ^{13}C YaMR (125 MHz, benzol-*d*) δ 158.35, 154.64, 130.49, 122.29, 108.80, 100.75, 91.32, 86.10, 62.38, 55.85, 13.95, 1.79.

3-siklopropil-1-p-tolilpropin-2-ol-1 (11). ^{1}H YaMR (400 MHz, xloroform-*d*) δ 7.49 – 7.32 (m, 2H), 7.30 – 7.13 (m, 2H), 5.95 – 5.59 (m, 2H), 2.83 (m, *J* = 7.1, 2.5 Hz, 1H), 2.48 (d, *J* = 1.0 Hz, 3H), 1.71 – 1.42 (m, 4H). ^{13}C YaMR (125 MHz, xloroform-*d*) δ 133.50, 132.95, 125.47, 122.99, 87.05, 77.16, 61.84, 17.10, 9.95, 2.07.

1-(4-tret-butilfenil)-3-siklopropilpropin-2-ol-1 (12). ^{1}H YaMR (400 MHz, xloroform-*d*) δ 7.38 – 7.19 (m, 4H), 5.73 – 5.48 (m, 2H), 2.59 (m, *J* = 7.1, 2.5 Hz, 1H), 1.52 – 1.36 (m, 4H), 1.34 (s, 9H). ^{13}C YaMR (125 MHz, xloroform-*d*) δ 150.42, 150.35, 137.45, 127.02, 125.20, 125.18, 91.15, 81.03, 65.97, 34.66, 31.20, 13.87.

3-siklopropil-1-(3-etil-4-metoksifenil)propin-2-ol-1 (13). ^{1}H YaMR (400 MHz, xloroform-*d*) δ 7.32 (k, *J* = 1.1 Hz, 1H), 7.27 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 1H), 5.74 (d, *J* = 6.7 Hz, 1H), 5.62 (dd, *J* = 6.7, 2.5 Hz, 1H), 3.85 (s, 3H), 2.71 – 2.54 (m, 3H), 1.52 – 1.35 (m, 4H), 1.20 (t, *J* = 8.0 Hz, 3H). ^{13}C YaMR (125 MHz, xloroform) δ 157.30, 150.25, 132.39, 126.82, 125.77, 112.27, 91.09, 81.03, 66.60, 55.56, 21.96, 21.91, 15.59, 13.81.

1-(3-uchlamchi-butil-4-metoksifenil)-3-siklopropilpropin-2-ol-1 (14). ^{1}H YaMR (400 MHz, xloroform-*d*) δ 7.37 (dd, *J* = 1.5, 0.6 Hz, 1H), 7.27 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 5.76 (d, *J* = 6.6 Hz, 1H), 5.70 – 5.61 (m, 1H), 3.85 (s, 3H), 2.60 (m, *J* = 7.0, 2.4 Hz, 1H), 1.60 – 0.89 (m, 13H). ^{13}C YaMR (125 MHz, xloroform-*d*) δ 157.03, 137.76, 131.22, 126.10, 126.09, 125.39, 112.65, 91.14, 81.00, 66.12, 55.78, 35.05, 29.82, 13.87.

1-(4-butoksifenil)-3- siklopropilpropin-2-ol-1 (15). ^{1}H YaMR (400 MHz, xloroform-*d*) δ 7.35 – 7.19 (m, 2H), 6.86 – 6.73 (m, 2H), 5.68 – 5.49 (m, 2H), 4.03 – 3.75 (m, 2H), 2.48 (m, *J* = 7.0, 2.5 Hz, 1H), 1.67 (m, *J* = 7.1, 1.6 Hz, 2H), 1.50 – 1.17 (m, 6H), 0.87 (t, *J* = 8.0 Hz, 3H). ^{13}C YaMR (125 MHz, xloroform-*d*) δ 141.96, 135.50, 122.93, 99.05, 88.93, 77.16, 74.28, 38.60, 38.58, 26.79, 21.75, 9.76.

4-(3-siklopropil-1-gidroksipropin-2-il)benzoldiol-1,2 (16). ^{1}H YaMR (400 MHz, xloroform-*d*). δ 9.25 (s, 1H), 9.17 (s, 1H), 7.25 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.15 – 6.94 (m, 2H), 5.98 (d, *J* = 6.7 Hz, 1H), 5.91 – 5.79 (m, 1H), 2.95 (pd, *J* = 7.1, 2.6 Hz, 1H), 1.91 – 1.26 (m, 4H). ^{13}C YaMR (125 MHz, xloroform-*d*) δ 141.70, 141.25, 126.88, 116.08, 111.54, 109.67, 109.65, 87.04, 77.16, 62.40, 62.38, 62.35, 9.92.

3-siklopropil-1-(4-(etiltio)fenil)propin-2-ol-1 (17). ^{1}H YaMR (400 MHz, xloroform-*d*). δ 7.36 – 7.30 (m, 2H), 7.28 – 7.22 (m, 2H), 5.68 (d, *J* = 6.7 Hz, 1H), 5.65 – 5.59 (m, 1H), 2.96 – 2.82 (m, 2H), 2.58 (m, *J* = 7.1, 2.5 Hz, 1H), 1.51 – 1.33 (m, 4H), 1.27 (t, *J* = 8.0 Hz, 3H). ^{13}C YaMR (125 MHz, xloroform-*d*). δ 132.85, 132.84, 124.91, 124.90, 123.86, 123.84, 123.80, 123.77, 123.75, 87.27, 77.16, 62.59, 23.46, 23.44, 10.59, 9.98.

3-siklopropil-1-(4-(dimetilamino)fenil)propin-2-ol-1 (18). ^{1}H YaMR (400 MHz, xloroform-*d*). δ 7.30 – 7.24 (m, 2H), 6.88 – 6.82 (m, 2H), 5.70 (d, *J* = 6.7 Hz, 1H), 5.67 – 5.62 (m, 1H), 2.99 (s, 4H), 2.61 (m, *J* = 7.0, 2.5 Hz, 1H), 1.51 – 1.38 (m, 4H). ^{13}C YaMR (125 MHz, xloroform-*d*). δ 132.88, 128.57, 121.42, 92.00, 81.89, 66.71, 41.15, 14.72, 14.70, 12.71.

Kvant-kimyoviy tadqiqot natijalari: Sintez qilingan aromatik atsetilen spirtlari kvant-kimyoviy ko'rsatkichlari zamonaviy dasturlar asosida hisoblandi.

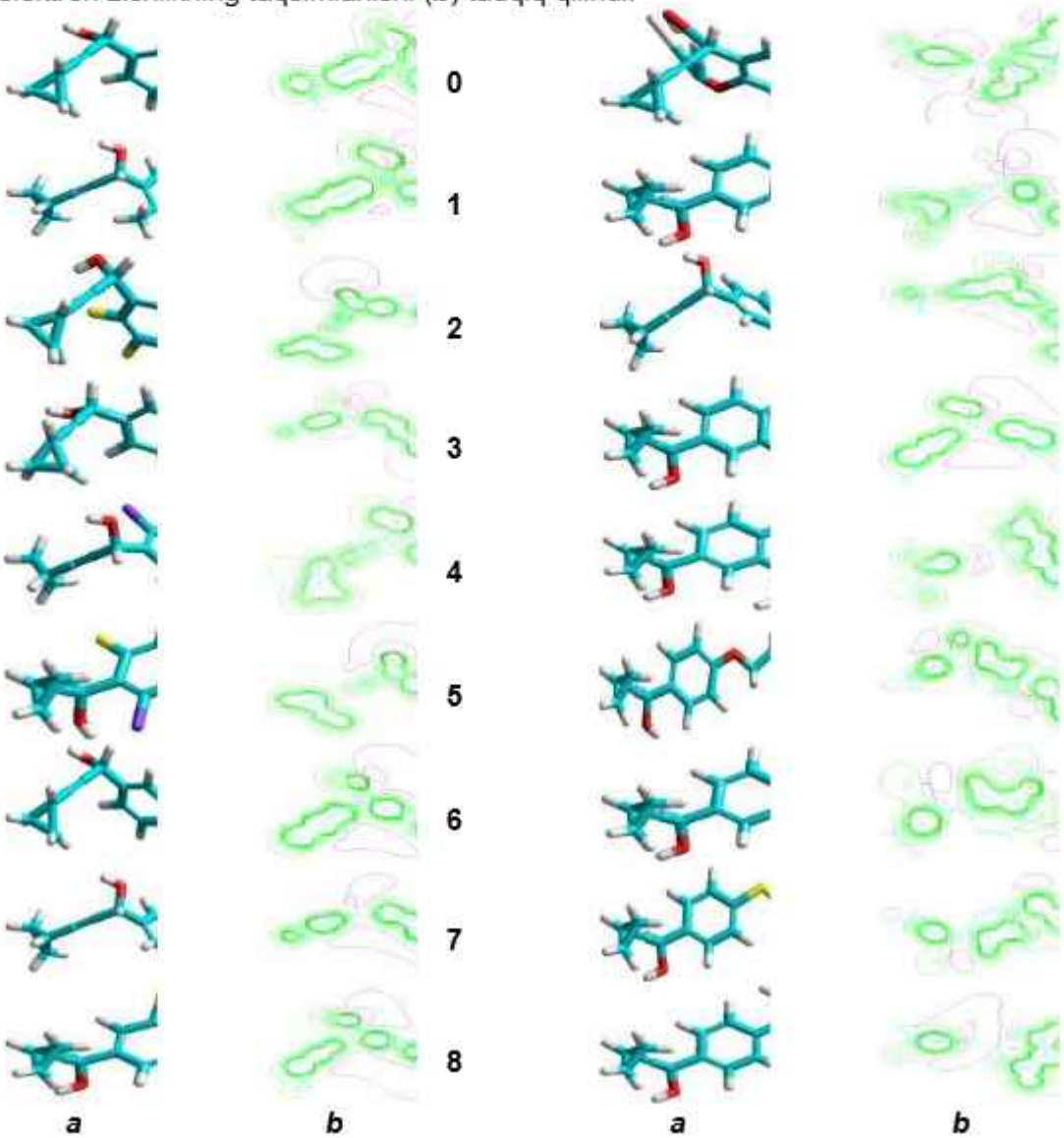
1-jadval

Sintez qilingan aromatik atsetilen spirtlarining kvant-kimyoviy hisoblashlari

Aromatik atsetilen spirtlari	Issiqlik energiyasi, kkal/mol	Van-der-Vaals energiyasi, kkal/mol	Kulon energiyasi, kkal/mol	Torsion energiyasi, kkal/mol	Valent burchak energiyasi, kkal/mol	Bog' energiyasi, kkal/mol
1	4,5147	6,0312	0,2554	-3,1905	0,388	1,2859
2	3,0203	4,1868	0,6771	-4,7234	0,5546	2,3352
3	3,1595	6,0655	-1,1633	-5,5676	0,9256	2,8993

4	8,0519	6,2329	0,9879	-3,4769	1,1253	3,0303
5	3,0216	4,1708	0,6764	-4,7231	0,5541	2,3435
6	4,1726	2,4487	0,3260	-3,5781	0,9109	4,0651
7	3,7384	4,4794	1,0391	-4,6415	0,5603	2,3012
8	1,3635	2,0247	1,1422	-5,0186	0,4076	2,8076
9	6,5343	6,2971	1,1262	-5,0738	1,0026	3,1798
10	5,5101	5,5668	0,8743	-5,0186	0,9072	3,1530
11	3,0355	3,5194	0,9865	-3,8222	0,3557	1,9960
12	8,0537	6,2341	0,9881	-3,4774	1,2787	3,0302
13	6,8003	5,6261	1,0433	-4,3734	0,9881	3,5162
14	15,6650	10,6136	0,7443	-4,2552	2,4828	6,0794
15	11,9322	7,7509	1,1262	-2,6518	0,9692	4,7378
16	1,3625	2,0218	1,1428	-5,0200	0,407	2,8107
17	9,8656	6,7876	1,1219	-3,1014	0,7487	4,3088
18	-1,8033	1,7708	1,0676	-7,1672	0,3292	2,1963

Sintez qilingan aromatik atsetilen spirtlari molekulalarining fazoviy struktura tuzilishi (***a***), molekulalarda elektron zichlikning taqsimlanishi (***b***) tadqiq qilindi.



1-Rasm. Sintez qilingan aromatik atsetilen spirtlarining ayrim fazoviy tuzilishlari

XULOSA

Ilk bor $EtMgCl/C_{17}H_{29}NO/TFE$ kompleks katalitik sistemada benzaldegid va uning turli xil xosilalarini siklopropilatsetilen ishtirokida enentioselektiv alkinillash orqali 18 turdagi yangi aromatik atsetilen spirtlari sintez qilindi.

Tanlangan aldegidlar molekulasining fazoviy tuzilishi, molekuladagi o'rinbosarlar tabiati, ularning faolligi va stabilligining mahsulot unumi va reaksiyaning borishiga ta'siri o'rganildi va yangi ilmiy qonuniyatlar taklif qilindi.

Sintez qilingan aromatik atsetilen spirtlari identifikatsiyalandi, ularning tozaligi, tuzilishi va tarkibi zamonaviy fizik-kimyoviy tadqiqot usullari yordamida isbotlandi, xususiy konstantalari aniqlandi, reaksiya mexanizmlari taklif qilindi, energetik, kvant-kimyoviy va xususiy kattaliklari hisoblandi.

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