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Synthesis of gigantic macrocyclic polyketones through catalytic cyclometalation of cycloalkynes

Vladimir A. D'yakonov *, Aleksey A. Makarov, Usein M. Dzhemilev

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 141 Prospekt Oktyabrya, Ufa, 450075, Russia

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ABSTRACT

A new effective method for designing unique gigantic polyfunctional macrocarbocycles from cyclic acetylenes and Grignard reagents through the catalytic cyclometalation reaction in the presence of transition metal based complexes has been elaborated.

1. Introduction

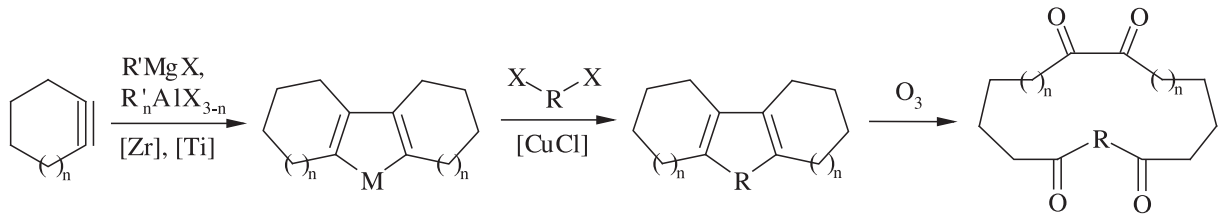
Natural macrocyclic antibiotics, ionophores, odours and other heteroatomic macrocyclic compounds are widely used in medicine, the fragrance industry, supramolecular and synthetic organic chemistry.

Among those known today, the synthetic methods of preparation macrocycles by marked scientists, such as Ruzichka, Ziegler, Blomquist, Prelog and Stoll as well as Sondheimer are worthy of note.[1] Unfortunately, these methods did not gain prominence because of low yields, multistage process, the necessity of hard-to-reach long-chain bifunctional precursors, the cyclization had to be carried out at high dilution, and difficulties in the separation of target macrocarbocycles from oligomeric byproducts.

Thermal rearrangements of organic peroxides[2a–c] as well as recently reported results on organometallic synthesis through the intermolecular cyclometalation reaction of unsaturated compounds, such as α,ω-dienes, α,ω-diynes and α,ω-diallenes assisted by stoichiometric and catalytic amounts of Co, Zr and Ti complexes,[2d–m] in our opinion, should be considered as promising research directions to synthesize macrocarbocycles.

Herein, we propose and discuss one pot synthesis to produce macrocarbocycles based on the new recently elaborated intermolecular cyclomagnesiation and cycloalumination reactions of cycloalkynes using BuMgX (X=Cl, Br) or $EtAlCl_2$ and Cp_2ZrCl_2 catalyst.[3]

We believed that the interaction between the obtained in situ alumina- or magnesacyclopentadienes and various organic α,ω-dihalogenides would afford macrocyclic polyketones via the oxidative cleavage of the corresponding unsaturated tri- and tetracyclic compounds (Scheme 1).



Scheme 1. Basic idea in the synthesis of macrocyclic polyketones.

* Corresponding author. Tel./fax: +7 347 2882750; e-mail address: DyakonovVA@rambler.ru (V.A. D'yakonov).

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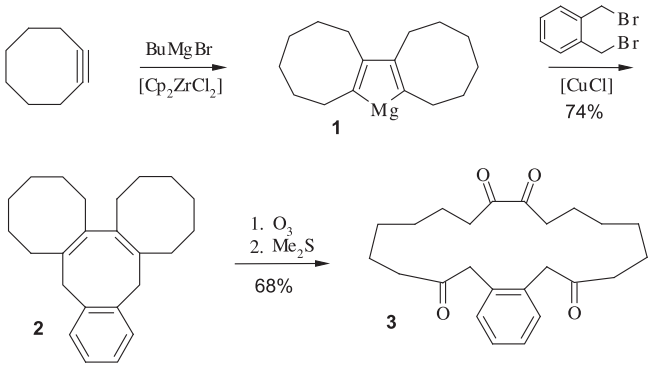
2. Results and discussion

As a result, the interaction between 2-magnesatricyclo[9.6.0^{1,11}.0^{3,10}]heptadeca-1(11),3(10)-diene **1**, generated in situ from cyclooctyne (as a model compound) and BuMgBr (THF, 20–23 °C, 4 h, 10 mol % Cp_2ZrCl_2)[3] and equimolar amounts of α,α′-dibromo-*o*-xylene in the presence of 20 mol % CuCl catalyst was shown to produce 3,4-benzotricyclo[12.6.0^{1,14}.0^{6,13}]eicosa-1(14),6(13)-diene **2** in 74% yield. Ozonolysis of the latter in CCl_4 and subsequent treatment with Me_2S led to macrocyclic C_{20} polyketone **3** in 68% yield (Scheme 2).



Scheme 2.

In order to establish the structure of macrocycle **3**, the NMR studies using 2D-techniques (COSY, HSQC, HMBC) have been accomplished. The ^{13}C 1D NMR spectrum of **3** gives 12 nonequivalent signals that meets requirements of symmetry in the molecule.

Two low field signals at δ 201.9 and δ 208.0 belong to carbonyl carbon atoms. The first one corresponds to 1,2-diketo conjugated group (C1, C2) and the second signal in a weaker field is assigned to the isolated carbonyl groups at the C9 and C14 carbon atoms. Three signals at δ 127.5, 131.2 and 133.6 are attributed to the aromatic ring carbon atoms.

Assignment of the other signals to methylene carbon atoms of macrocycle **3** were made from ^{1}H and ^{13}C NMR spectra on the basis of homonuclear H–H correlation (COSY) as well as direct heteronuclear ^{1}H–^{13}C interactions in the HSQC experiment. Molecular weight of compound **3** determined by means of MALDI TOF-TOF MS, was 384. These results allowed the identification of macrocyclic ketone **3** as 11,12-benzocycloeicosa-1,2,9,14-tetraone.

In continuation of these studies, we developed another effective approach to tetraketo macrocarbocycles using the one pot cyclomagnesiation reaction of cycloalkynes. The method is based on the Cp_2ZrCl_2 catalyzed intramolecular cyclomagnesiation reaction of 2,2′-diallyl-1,1′-bicycloalken-1-yls from the cross-coupling reaction of magnesacyclopenta-2,4-diene **1** or aluminacyclopenta-2,4-diene **4** with allylhalogenides,[3] which results in 8-magnesabicyclo[6.3.0^{6,10}]undeca-1,3-dienes with unsaturated annulated cyclic fragments. Acid hydrolysis of tetracyclic magnesacyclopentanes and subsequent cleavage of the double bonds with O_3 led to the target macrocyclic polyketones.

Thus, 2,2′-diallyl-1,1′-bicyclooct-1-ene-1-yl[3] **5** reacted with excess BuMgBr (Et_2O, 20–23 °C, 8 h) in the presence of the Cp_2ZrCl_2 catalyst (5 mol %) giving magnesabicyclo[6.3.0^{6,10}]undeca-1,3-diene **7**, which, after acid hydrolysis was converted to 3,4-dimetyltricyclo[12.6.0^{1,14}.0^{6,13}]eicosa-1 (14),6(13)-diene **7a** in 89% yield. Diene **7a** reacted with ozone under previously optimized conditions yielding macrocyclic tetraketone namely 11,12-dimethylcycloeicosa-1,2,9,14-tetraone **8a** (Scheme 3).

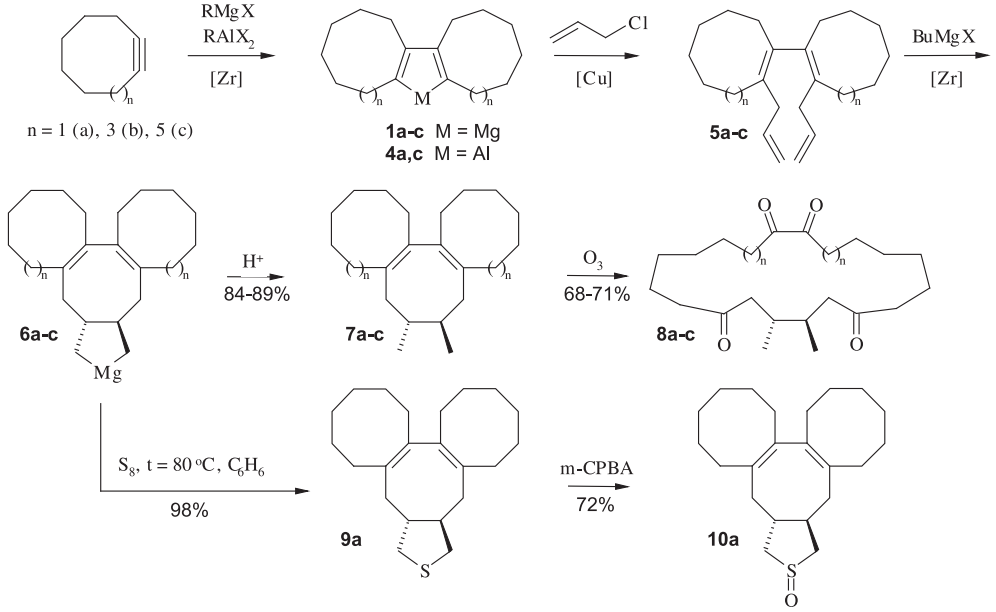
We found, surprisingly, that only the one isomer was obtained in all cases for **7a**–**c**, as judged by a combination of ^{1}H, ^{13}C NMR and GLC analysis.

It is known, that zirconocene generated from zirconocene dichloride and butyllithium have previously been shown[4] to be highly efficient stoichiometric reagents for the regio- and stereoselective reductive cyclization of nonconjugated dienes to give cycloalkanes and cycloalka-1,3-dienes with *trans*-configuration of 1,2-dimethyl groups.

For the evidence of the stereoconfiguration of dienes **7a**–**c** we performed the reaction of tetraenes **5a**–**c** obtained here with 1 equiv of Negishi reagent in THF at room temperature for 3 h[4c] that gave the same tricyclic dienes **7a**–**c**, as in the catalytic reaction in 89–95% yields after hydrolysis.

Based on the aforsaid we propose that compounds **7a**–**c**, obtained via catalytic cyclomagnesiation are in *trans*-configuration of *vic*-dimethyl groups.

Similar to cyclooctyne, cyclodecyne and cyclododecyne was found to participate in the above mentioned reaction to afford the



Scheme 3.

corresponding tricyclic dienes **7b**,**c** and macrocyclic teraketones C_{24} **8b** and C_{28} **8c** in high yields.

In our view, the developed method for a synthesis of macrocyclic ketones opens wide possibilities for interesting applications due to magnesa- and aluminacyclopentane fragments in initial tetracyclic metallacycles that create additional opportunities for the introduction of functional groups while exploiting, for example, the carbocyclization or demetallation reactions.[5] In particular, the organomagnesium compound **6a** was quantitatively converted to (*trans*)-13-thiatetracyclo[15.6.0^{1,17}.0^{2,9}.0^{11,15}] tricosa-1(17),2(9)-diene **9a** by the reaction with S_8, which was oxidized with *m*-CPBA to (*trans*)-13-thiatetracyclo[15.6.0^{1,17}.0^{2,9}.0^{11,15}]tricosa-1(17),2(9)-diene-13-oxide **10a** (Scheme 3). Splitting of signals at δ 45.1 (42.9) and δ 62.2 (58.9) belong to thiophane moiety of **10a** in ^{13}C NMR spectrum due to break the symmetry of molecule, also confirms a *trans*-configuration formed magnesacyclopentane.[6]

Our results obtained previously on catalytic cyclometalation of cycloalkynes (C_8–C_{16})[3] permit us to conclude that the elaborated approach to the synthesis of macrocarbocycles can be successfully extended further, to the other macrocyclic acetylenes of specified structure including those containing functional groups.

3. Conclusions

Thus, a new effective one pot method for the construction of macrocyclic ketones, based on Cp_2ZrCl_2 catalyzed successive intermolecular cyclometalation reaction of cycloalkynes followed by cross-coupling and oxidative splitting of double bonds in the three- and tetracyclic unsaturated compounds allows to produce macrocyclic C_{20}–C_{36} polyketones with high yields and selectivity.

In order to expand the range of monomers, which appeared to be precursors of gigantic polyfunctional macrocarbocycles, nowadays we extensively work on synthetic methods for carbocyclization of the said tricyclic magnesa- and aluminapenta-2,4-dienes using organic α,ω-dihalogenides as well as chloroanhydrides of different dicarboxylic acids.

4. Experimental section

4.1. General

All solvents were dried (hexane over $LiAlH_4$, Et_2O and THF over Na) and freshly distilled before use. All reactions were carried out under a dry argon atmosphere. The reaction products were analyzed using chromatography on a 'Shimadzu GS-9A' instrument (2000×2 mm column packed with 5% of SE-30 and 15% PEG-6000 on Chromaton N-AW, carrier gas—He). The IR-spectra were recorded on Bruker 'Vertex 70V'. Mass spectral measurements were performed on a Finnigan-4021 spectrometer at 70 eV and working temperature 200 °C and Bruker MALDI TOF-TOF. Elemental analysis of samples was determined on Carlo Erba, model 1106. The ^{1}H and ^{13}C NMR spectra were recorded as $CDCl_3$ solutions on spectrometer 'Bruker Avance-400' (100 MHz for ^{13}C and 400 MHz for ^{1}H). The chemical shifts are reported as δ values in parts per million relative to internal standard Me_4Si. ^{13}C NMR spectra were edited by *J*-modulation (JMOD) on CH constants. Individuality and purity of the synthesized compounds were controlled with the use of TLC on Silufol UV-254 plates, I_2 was used as a developer.

*4.1.1. 3,4-Benzotricyclo[12.6.0^{1,14}.0^{6,13}]eicosa-1(14),6(13)-diene (**2**).* A 50 mL glass reactor was charged with BuMgBr (2 M solution in diethyl ether, 22 mmol), Cp_2ZrCl_2 (292 mg, 1.0 mmol) and cyclic alkyne (10 mmol) under a dried argon atmosphere at 0 °C. The resulting solution was allowed to warm to rt and stirred for 8 h. At −20 °C CuCl (99 mg, 1 mmol) and α,α′-dibromo-*o*-xylene (1.32 g, 5 mmol) were added. The reaction mixture was allowed to warm to 20 °C and stirred for 6 h. The reaction mixture was quenched with an 8–10% (aq) solution of HCl. The layers were separated and the aqueous phase was extracted with Et_2O or hexane. The organic layer was diluted with hexane, dried over $MgSO_4$ and concentrated in vacuo. The product was isolated by column chromatography on silica gel (40–100 mesh grade) with hexane as eluent affording the product **2**. Yield 1.6 g (74%), as a colourless solid. Mp 54–56 °C. IR: 3050, 1625, 1460, 1380, 720 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11–7.16 (m, 2H), 7.07–7.10 (m, 2H), 3.76–3.78 (m, 2H), 3.01–3.03 (m, 2H), 2.25–3.28 (m, 8H), 1.54–1.61 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.1, 136.7, 130.6, 129.0, 126.3, 41.6, 30.9, 30.4, 28.8, 28.7, 26.9, 26.8. MS, *m*/*z*: 320 (M^+). Anal. Calcd for $C_{24}H_{32}$: C, 89.94; H, 10.06%. Found: C, 89.81; H, 10.01%.

*4.1.2. 11,12-Benzocycloeicosa-1,2,9,14-tetraone (**3**).* A stream of O_2 containing 3–4% O_3 was passed through a cold (−10 °C) solution of 1.6 g (5 mmol) of diene **2** in 20 mL of $CC1_4$ for 25 min. After the solution had been purged with N_2, 1.1 mL (15 mmol) of Me_2S was added and the solution was allowed to warm to 25 °C with stirring for 4 h. The solvent was removed under reduced pressure and the residual solid was dissolved in CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. After the organic solution had been dried and concentrated, and the product **3** was isolated by column chromatography on silica gel (40–100 mesh grade) with hexane–ethylacetate (20:1) as eluent. Yield: 1.3 g (68%), as a light yellow oil, R_f=0.33. IR: 3040, 1600, 1460, 1380 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.27 (m, 2H), 7.13–7.16 (m, 2H), 3.65 (s, 4H), 2.70 (t, *J*=7 Hz, 4H), 2.41 (t, *J*=7 Hz, 4H), 1.59–1.60 (m, 4H), 1.48–1.49 (m, 4H), 1.20–1.34 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.0, 201.9, 133.6, 131.3, 127.6, 48.2, 41.4, 36.1, 28.5, 28.3, 23.2, 23.1. MALDI TOF-TOF: 384. Anal. Calcd for $C_{24}H_{32}O_4$: C, 74.97; H, 8.39; O, 16.64%. Found: C, 74.83; H, 8.37; O, 16.59%.

*4.1.3. (trans)-3,4-Dimetyltricyclo[12.6.0^{1,14}.0^{6,13}]eicosa-1(14),6(13)-diene (**7a**).* A 50 mL glass reactor was charged with BuMgBr (2 M solution in diethyl ether, 22 mmol), Cp_2ZrCl_2 (292 mg, 1.0 mmol) and 2,2′-diallyl-1,1′-bicyclooct-1-ene-1-yl (**5a**) (2.98 g, 10 mmol) under a dried argon atmosphere at 0 °C. The resulting solution was allowed to warm to rt and stirred for 8 h. The reaction mixture was quenched with an 8–10% (aq) solution of HCl. The layers were separated and the aqueous phase was extracted with Et_2O or hexane. The organic layer was diluted with hexane, separated and dried over $MgSO_4$. Evaporation and vacuum distillation gave **7a**. Yield 2.67 g (89%), as a colourless oil. Bp 189–191 °C (1 Torr). IR: 1620, 1450, 1370 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.85 (m, 4H), 2.11–2.32 (m, 8H), 1.70–1.73 (m, 2H), 1.53–1.61 (m, 16H), 0.95 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.6, 134.9, 42.2, 36.2, 31.4, 30.4, 29.2, 29.0, 27.0, 26.9, 23.5. MS, *m*/*z*: 300 (M^+). Anal. Calcd for $C_{22}H_{36}$: C, 87.93; H, 12.07%. Found: C, 87.79; H, 12.05%.

*4.1.4. (trans)-3,4-Dimetyltricyclo[14.8.0^{1,16}.0^{6,15}]tetracosa-1(16),6(15)-diene (**7b**).* R_f=0.65 (hexane). IR: 1625, 1450, 1360 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.87 (m, 4H), 2.10–2.32 (m, 8H), 1.69–1.71 (m, 2H), 1.55–1.60 (m, 24H), 0.94 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3, 134.7, 42.2, 36.2, 31.5, 30.4, 29.2, 29.1, 28.9, 27.0, 26.9, 23.4. MS, *m*/*z*: 356 (M^+). Anal. Calcd for $C_{24}H_{44}$: C, 87.56; H, 12.44%. Found: C, 87.48; H, 12.45%. Yield 88%.

*4.1.5. (trans)-3,4-Dimetyltricyclo[16.10.0^{1,18}.0^{6,17}]octacosa-1(18),6(17)-diene (**7c**).* R_f=0.63 (hexane). IR: 1620, 1460, 1370 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.84–2.87 (m, 4H), 2.08–2.30 (m, 8H), 1.70–1.71 (m, 2H), 1.52–1.55 (m, 32H), 0.95 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.4, 134.9, 42.1, 36.2, 31.4, 30.4, 30.3, 29.5,

29.3, 29.1, 27.1, 26.9, 23.1. MS, *m*/*z*: 412 (M^+). Anal. Calcd for $C_{30}H_{52}$: C, 87.30; H, 12.70%. Found: C, 87.19; H, 12.68%. Yield 84%.

*4.1.6. (trans)-11,12-Dimethylcycloeicosane-1,2,9,14-tetraone (**8a**).* The procedure described for ozonolysis of diene **2** was applied to the dienes **7a**–**c**. R_f=0.35. IR: 2920, 2850, 1600, 1460, 1455, 1340 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.70–2.74 (m, 4H), 2.30–2.31 (m, 4H), 2.37–2.38 (m, 2H), 2.22 (d, *J*=6.4 Hz, 2H), 1.99–2.00 (m, 2H), 1.64–1.66 (m, 4H), 1.53–1.56 (m, 4H), 1.25–1.41 (m, 8H), 0.81 (d, *J*=6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.8, 201.3, 48.8, 42.0, 35.9, 32.5, 28.2, 28.1, 23.1, 22.8, 14.6. MALDI TOF-TOF: 364. Anal. Calcd for $C_{22}H_{36}O_4$: C, 72.49; H, 9.95; O, 17.56%. Found: C, 72.23; H, 9.97; O, 17.53%.Yield 1.29 g (71%), as a light yellow oil.

*4.1.7. (trans)-13,14-Dimethylcyclotetracosane-1,2,11,16-tetraone (**8b**).* R_f=0.37. IR: 2930, 2850, 1600, 1465, 1455, 1320 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.72–2.75 (m, 4H), 2.39–2.42 (m, 4H), 2.37–2.39 (m, 2H), 2.20 (d, *J*=6.4 Hz, 2H), 2.01–2.03 (m, 2H), 1.63–1.66 (m, 4H), 1.53–1.57 (m, 4H), 1.29–1.37 (m, 16H), 0.82 (d, *J*=6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.7, 201.3, 48.6, 42.0, 35.8, 32.6, 29.1, 28.7, 28.2, 28.1, 23.1, 22.8, 14.6. MALDI TOF-TOF: 420. Anal. Calcd for $C_{26}H_{44}O_4$: C, 74.24; H, 10.54; O, 15.22%. Found: C, 74.13; H, 10.55; O, 15.18%.Yield 69%, as a light yellow oil.

*4.1.8. (trans)-15,16-Dimethylcyclooctacosane-1,2,13,18-tetraone (**8c**).* R_f=0.38. IR: 2920, 2860, 1610, 1460, 1455, 1330 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.68–2.74 (m, 4H), 2.39–2.42 (m, 4H), 2.37–2.38 (m, 2H), 2.21 (d, *J*=6.8 Hz, 2H), 1.95–1.97 (m, 2H), 1.65–1.69 (m, 4H), 1.50–1.53 (m, 4H), 1.31–1.42 (m, 24H), 0.84 (d, *J*=7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.5, 201.2, 48.8, 41.9, 35.9, 32.4, 29.0, 28.5, 28.2, 28.4, 23.2, 22.6, 14.0. MALDI TOF-TOF: 476. Anal. Calcd for $C_{30}H_{52}O_4$: C, 75.58; H, 10.99; O, 13.43%. Found: C, 75.44; H, 10.95; O, 13.45%.Yield 71%, as a light yellow oil.

*4.1.9. The procedure described.[7] (trans)-13-Thiatetracyclo[15.6.0^{1,17}.0^{2,9}.0^{11,15}]tricosa-1(17),2(9)-diene (**9a**).* IR: 2915, 2845, 1435 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.80 (dd, *J*=5.2, 10 Hz, 2H), 2.52 (t, *J*=10 Hz, 2H), 2.35–2.38 (m, 2H), 2.31–2.34 (m, 2H), 2.16–2.18 (m, 2H), 2.13–2.15 (m, 2H), 2.10–2.12 (m, 2H), 1.95 (d, *J*=12 Hz, 2H), 1.6–1.61 (m, 4H), 1.53–1.56 (m, 2H), 1.46–1.63 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7, 133.2, 47.3, 36.9, 36.4, 31.7, 30.4, 30.1, 28.6, 26.9, 26.7. MS, *m*/*z*: 330 (M^+). Anal. Calcd for $C_{22}H_{34}S$: C, 79.93; H, 10.37; S, 9.70%. Found: C, 79.85; H, 10.35; S, 9.72%. Yield 98%, as a yellow solid. Mp 71–72 °C.

*4.1.10. The procedure described.[8] (trans)-13-Thiatetracyclo[15.6.0^{1,17}.0^{2,9}.0^{11,15}]tricosa-1(17),2(9)-diene-13-oxide (**10a**).* IR: 2930, 2840, 1455, 1050 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.11–3.84 (m, 2H), 2.31–2.34 (m, 2H), 2.31–2.34 (m, 3H), 2.16–2.19 (m, 2H), 2.13–2.17 (m, 2H), 2.01–2.12 (m, 4H), 1.44–1.65 (m, 19H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.3, 133.0, 45.1, 42.9, 62.2, 58.9, 36.0, 35.9, 31.6, 30.1, 29.9, 28.5, 26.8, 26.5. MS, *m*/*z*: 346 (M^+). Anal. Calcd for $C_{22}H_{34}SO$: C, 76.24; H, 9.89; O, 4.62%; S, 9.25%. Found: C, 76.01; H, 9.85; O, 4.64%; S, 9.27%. Yield 72%, as a white solid. Mp 165–167 °C.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.06.054.

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