Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 84 (10) S303–S307 (2019) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

Studies on the [2+3] cycloaddition reaction of nitrile oxides to abietic acid esters

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J. Serb. Chem. Soc. 84 (10) (2019) 1073–1081

Benzyl abietate (**4**).[1] Yield: 40 %; yellowish wax; IR (KBr, cm^{-1}) 3097, 3080, 3040, 3000, 2960, 2928, 2860, 1724, 1680, 1610, 1497, 1456, 1386, 1240, 1200, 1144, 1100, 1090, 1050, 1020, 960, 820, 750, 697; ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 7.37–7.28 (5H, *m*, phenyl), 5.76 (1H, *s*, H14), 5.33 (1H, *m*, H7), 5.13 (1H, *d*, *J* = 12.6 Hz, H21a), 5.03 (1H, *d*, *J* = 12.6 Hz, H21b), 2.21 (1H, *septet*, *J* = 6.8 Hz, H15), 2.10–2.00 (3H, *m*, 11a, 12a & 12b), 1.99–1.87 (2H, *m*, H5 & 11b), 1.87–1.72 (4H, *m*, H1a, H3a, H9 & H6a), 1.72–1.52 (3H, *m*, H2a, H2b & H1b), 1.27–1.18 (2H, *m*, H6b & H3b), 1.28 (3H, *s*, H19), 1.01 (3H, *d*, *J* = 6.8 Hz, H16), 1.00 (3H, *d*, *J* = 6.8 Hz, H17), 0.82 (3H, *s*, H18); ^{13}C-NMR (125.8 MHz, $CDCl_3$, δ / ppm): 178.2 (C20), 145.1 (C13), 136.4 (C18), 135.4 (C8), 128.4 (C6′, C2′), 127.9 (C4′), 127.8 (C5′, C3′), 122.4 (C14), 120.6 (C7), 66.2 (C21), 50.8 (C9), 46.6 (C4), 45.1 (C5), 38.3 (C3), 37.1 (C1), 34.9 (C15), 34.5 (C10), 27.4 (C12), 25.6 (C11), 22.45 (C6), 21.4 (C16), 20.8 (C17), 18.1 (C2), 17.1 (C19), 14.1 (C18); EIMS *m/z* (rel. int): 392 (M^+, 18), 301 (M^+–CH_2Ar, 100), 257 (M^+ –O=$COCH_2Ar$, 14), 255 ((M^+ –O=$COCH_2Ar$)–2H, 19), 199 (M^+–O=COC–$H_2ArCH(CH_3)_2CH_3$, 10), 91 (CH_2Ar, 65).

*Perillyl abietate [4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)]-methyl(1*R*,4a*R*,10a*R*)--1,4a-dimethyl-7-(propan-2-yl)-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthrene--1-carboxylate (**5**)*. Yield: 35 %; colorless wax; Anal. Calcd. for $C_{30}H_{44}O_2$: C, 82.52; H, 10.16 %. Found: C, 82.43; H, 9.96 %; ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 5.77 (1H, *s*, H14), 5.72 (1H, *m*, H23), 5.36 (1H, *dd*, *J* = 2.7 & 2.1 Hz, H7), 4.72 (2H, *m*, H30), 4.49 (1H, *d*, *J* = 12.5 Hz, H21a), 4.37 (1H, *d*, *J* = 12.5 Hz, H21b), 2.23 (1H, *septet*, *J* = 6.6 Hz, H15), 2.17 (2H, *m*, H5 & H24a), 2.11 (1H, *m*, H12a), 2.07 (3H, *m*, H12b, H25 & H27a), 2.06 (1H, *m*, H3a), 1.97 (1H, *m*, H24b), 1.96 (1H, *m*, H9), 1.88 (1H, *m*, H1a), 1.86 (1H, *m*, H27b), 1.85 (1H,

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m, H26a), 1.80 (2H, *m*, H6a & H11a), 1.78 (1H, *m*, H3b), 1.74 (3H, *s*, H29), 1.64 (1H, *m*, H2a), 1.63 (1H, *m*, H6b), 1.58 (1H, *m*, H2b), 1.51 (1H, *m*, H26b), 1.26 (3H, *s*, H19), 1.21 (1H, *m*, H11b), 1.15 (1H, *m*, H1b), 1.02 (3H, *d*, J = 2.7 Hz, H16), 1.00 (3H, *d*, J = 2.4 Hz, H17), 0.83 (3H, *s*, H18); ^{13}C-NMR (75.5 MHz, $CDCl_3$, δ / ppm): 178.3 (C20), 149.6 (C28), 145.2 (C13), 135.4 (C8), 132.8 (C22), 125.1 (C23), 122.4 (C14), 120.6 (C7), 108.7 (C30), 68.4 (C21), 50.8 (C9), 46.7 (C4), 45.1 (C5), 40.8 (C25), 38.3 (C1), 37.5 (C6), 34.9 (C15), 34.5 (C10), 30.4 (C24), 27.4 (C12), 27.3 (C26), 26.4 (C27), 25.6 (C3), 22.5 (C11), 21.4 (C16), 20.8 (C17), 20.7 (C29), 18.1 (C2), 17.0 (C19), 14.0 (C18).

N-*Cyclohexyl*-N-*[(cyclohexylamino)carbonyl]-1-(1*R*,4a*R*,10a*R*)-1,4a--dimethyl-7-(propan-2-yl)-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthrene-1--carboxamide (**6**)*. Yield: 20 %; yellowish wax; Anal. Calcd. for $C_{33}H_{52}N_2O_2$: C, 77.90; H, 10.30; N, 5.51 %. Found: C, 78.18; H, 10.37; N, 5.40 %; IR (KBr, cm^{-1}) 3444, 3310, 2930, 2853, 1690, 1659, 1620, 1526, 1451, 1395, 1340, 1293, 1234, 1234, 1148, 1080, 1030, 1005, 893, 830; ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 7.33 (1H, *m*, HN), 5.74 (1H, *s*, H14), 5.32 (1H, *m*, H7), 4.16 (1H, *tt*, J = 11.7 & 2.8 Hz, H1′), 3.63 (1H, *m*, H1″), 2.38 (1H, *dd*, J = 12.0 & 4.6 Hz, H5), 2.21 (1H, *septet*, J = 6.8 Hz, H15), 2.09–1.89 (6H, *m*), 1.92 (1H, *m*, H10a), 1.89–1.70 (9H, *m*), 1.69–1.57 (3H, *m*), 1.57–1.44 (4H, *m*), 1.44–1.30 (2H, *m*), 1.33 (3H, *s*, H19), 1.30–1.05 (9H, *m*), 1.00 (3H, *d*, J = 6.8 Hz, H17), 0.99 (3H, *d*, J = 6.8 Hz, H16), 0.84 (3H, *s*, H18); ^{13}C-NMR (75.5 MHz, $CDCl_3$, δ / ppm): 179.8 (C20), 155.1 (C22), 145.0 (C13), 135.6 (C8), 122.4 (C14), 120.6 (C7), 56.3 (C1′), 51.4 (C9), 50.3 (C1″), 49.0 (C4), 45.4 (C5), 37.9 (C1), 37.7 (C3), 34.8 (C15), 34.7 (C10), 32.7 (C2″), 32.7 (C6″), 31.8 (C2′), 31.1 (C6′), 27.4 (C12), 26.1 (C4″), 25.5 (C), 25.5 (C), 25.4 (C), 24.9 (C), 24.8 (C), 24.7 (C), 23.9 (C19), 22.4 (C11), 21.3 (C16), 20.8 (C17), 18.3 (C2), 14.2 (C18); EIMS *m/z* (rel. int): 508 (M^+, 2), 383 ((M^+–$CH(CH_3)_2$–C_6H_{11})+H, 70), 256 ([M^+–O=CN C_6H_{11}C=ONC_6H_{11})–H], 100), 241 ([M^+–O=CNC_6H_{11}C=O$NC_6H_{11}CH_3$–H], 70), 213 ([M^+–O=CNC_6H_{11}C=O$NC_6H_{11}CH(CH_3)_2$)–H], 20), 185 ([M^+-O=CNC_6H_{11}C=O$NC_6H_{11}CH(CH_3)_2CH_3CH_3$)+H], 30), 97 ($NC_6H_{11}$), 83 ($C_6H_{11}$).

*Cycloadduct of methyl abietate (**2**) and 4-(trifluoromethyl)benzonitrile oxide (**7a**). Methyl (4a*S*,7a*S*,7*R*,9*R*,12a*S*,12b*R*)-3-isopropyl-9,12a-dimethyl-7-[4-(trifluoromethyl)phenyl]-1,7a,8,8a,9,10,11,12,12a,12b-decahydro-2*H*-phenanthro-[9,8a-d]-isoxazole-9-carboxylate (**8a**)*. Yield: 15 %; celadon oil; Anal. Calcd. for $C_{29}H_{36}F_3NO_3$: C, 69.16; H, 7.21; N, 2.78 %. Found: C, 69.33; H, 7.09; N, 2.89 %; ^{1}H-NMR (600 MHz, $CDCl_3$, δ / ppm): 7.69 (2H, *d*, J = 8.3 Hz, 2′ & 6′), 7.59 (2H, *d*, J = 8.3 Hz, 3′ & 5′), 5.60 (1H, *bs*, H14), 3.64 (3H, *s*, CH_3O), 3.53 (1H, *m*, H7), 2.30 (1H, *m*, H5), 2.17 (1H, *m*, H15), 2.10 (1H, *m*, H12b), 1.92 (2H, *m*, H1a & H3a), 1.90 (1H, *m*, H11a), 1.75 (1H, *m*, H6a), 1.65 (1H, *m*, H6b), 1.62–1.56 (2H, *m*, H2), 1.27 (1H, *m*, H11b), 1.24 (3H, *s*, H19), 1.20 (2H, *m*, H1b & H3b),

0.88 (6H, *d*, *J* = 6.2 Hz, H16 & H17), 0.86 (3H, *s*, H18); ^{13}C-NMR (125.8 MHz, $CDCl_3$, δ/ ppm): 178.7 (C20), 159.0 (C22), 149.0 (C13), 134.7 (C4′, *q*, *J* = 32.7 Hz), 131.2 (C1′), 126.9 (C2′ & C6′), 125.5 (C3′ & C5′), 118.9 (C14), 89.5 (C8), 51.9 (C7 & C21), 51.3 (C9), 44.6 (C5), 44.0 (C4), 38.2 (C1, C3), 37.3 (C6), 36.6 (C10), 35.2 (C15), 27.3 (C12), 22.7 (C11), 20.7 (C16 & C17), 18.1 (C2), 17.0 (C19), 14.1 (C18).

*Cycloadduct of methyl abietate (**2**) and 4-isopropylbenzonitrile oxide (**7b**). Methyl (4a*R*,7a*R*,8a*R*,9*R*,12a*S*,12b*R*)-3-isopropyl-7-(4-isopropylphenyl)-9,12a--dimethyl-1,7a,8,8a,9,10,11,12,12a,12b-decahydro-2*H*-phenantro[9,8a-d]-isoxazole-9-carboxylate (**8b**)*. Yield: 15 %; yellowish oil; Anal. Calcd. for $C_{31}H_{43}NO_3$: C, 77.95; H, 9.07; N, 2.93 %. Found: C, 77.87; H, 9.16; N, 3.08 %; ^{1}H-NMR (500 MHz, $CDCl_3$, δ / ppm): 7.75 (2H, *d*, *J* = 8.3 Hz, 2′ & 6′), 7.30 (2H, *d*, *J* = 8.3 Hz, 3′ & 5′), 5.29 (1H, *bs*, H14), 3.65 (3H, *s*, CH_3O), 2.96 (1H, *septet*, *J* = 7.0 Hz, H23), 2.92 (1H, *m*, H7), 2.82 (1H, *m*), 2.37 (1H, *dd*, *J* = 12.5 & 2.0 Hz, H5), 2.33 (1H, *bd*, *J* = 12.5 Hz), 1.98–1.73 (6H, *m*), 1.65 (1H, *m*), 1.62–1.56 (1H, *m*), 1.26 (6H, *d*, *J* = 7.0 Hz, H24 & H25), 1.25 (3H, *s*, H19), 1.24 (3H, *s*, H18), 1.22 (6H, *d*, *J* = 7.0 Hz, H16 & H17), 1.28–1.16 (4H, *m*); ^{13}C-NMR (125.8 MHz, $CDCl_3$, δ/ ppm): 177.5 (C20), 154.2 (C22), 151.7 (C4′), 145.8 (C13), 127.6 (C2′, C6′), 127.0 (C1′), 126.9 (C3′, C5′), 124.1 (C14), 90.0 (C8), 52.5 (C21), 50.9 (C9), 47.7 (C7), 44.9 (C5), 43.8 (C4), 37.8 (C10), 37.1 (C1), 36.8 (C3), 34.2 (C23), 33.5 (C15), 30.0 (C6), 25.3 (C12), 24.0 (C16 & C17), 23.7 (C24 & C25), 21.9 (C11), 18.4 (C2), 16.3 (C18 & C19).

*Cycloadduct of phenyl abietate (**3**) and 4-(trifluoromethyl)benzonitrile oxide (**7a**). Phenyl (4a*R*,7a*R*,8a*R*,9*R*,12a*S*,12b*R*)-3-isopropyl-9,12a-dimethyl-4--[(trifluoromethyl)phenyl]-1,7a,8,8a,9,10,11,12,12a,12b-decahydro-2*H*-phenantro-[9,8a-d]-isoxazole-9-carboxylate (**9**)*. Yield: 15 %; yellowish oil; Anal. Calcd. for $C_{34}H_{38}F_3NO_3$: C, 72.19; H, 6.77; N, 2.48 %. Found: C, 71.92; H, 6.82; N. 2.39 %. ^{1}H-NMR (500 MHz, $CDCl_3$, / ppm): 7.84 (2H, *d*, *J* = 8.5 Hz, 2′ & 6′), 7.58 (2H, *d*, *J* = 8.5 Hz, 3′ & 5′), 7.38 (2H, *m*, H3″ & H5″), 7.24–7.19 (1H, *m*, H4″), 7.02–6.99 (2H, *m*, H2″ & H6″), 5.59 (1H, *d*, *J* = 2.0 Hz, H14), 3.68 (1H, *m*, H7), 2.31–2.26 (1H, *m*, H15), 2.13–2.01 (2H, *m*), 1.98–1.79 (3H, *m*), 1.76–1.55 (3H, *m*), 1.44–1.26 (2H, *m*), 1.24 (3H, *s*, H19), 1.24–1.15 (3H, *m*), 1.11 (6H, *d*, *J* = 7.0 Hz, H16 & H17), 0.95–0.82 (1H, *m*), 0.81 (3H, *s*, H18); ^{13}C-NMR (125.8 MHz, $CDCl_3$, δ/ ppm): 176.5 (C20), 157.6 (C22), 151.9 (C1″), 151.0 (C13), 132.3 (C4′, *q*, *J* = 32.5 Hz), 130.5 (C1′), 129.9 (C3″ & C5″), 127.4 (C2′ & C6′), 126.6 (C14), 125.6 (C4″), 125.4 (C3′ & C5′), 121.5 (C2″ & C6″), 89.9 (C8), 49.7 (C9), 47.7 (C5), 45.1 (C7), 44.9, 39.1, 38.2, 36.6, 36.2 (C15), 29.7, 29.3, 24.1, 20.2 (C16 & C17), 17.1, 15.3.

*Cycloadduct **10** of benzyl abietate (**4**) and 4-(trifluoromethyl)benzonitrile oxide (**7a**). Benzyl (4a*R*,7a*R*,8a*R*,9*R*,12a*S*,12b*R*)-3-isopropyl-9,12a-dimethyl-7--[4-(trifluoromethyl)phenyl]-1,7a,8,8a,9,10,11,12,12a,12b-decahydro-2*H*-phen-*

*antro[9,8a-d]-isoxazole-9-carboxylate (**10**)*. Yield: 15 %; yellowish oil; Anal. Calcd. for $C_{35}H_{40}F_3NO_3$: C, 72.52; H, 6.96; N, 2.42 %. Found: C, 72.41; H, 7.08; N, 2.51 %; ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 7.90 (2H, *d*, *J* = 8.3 Hz, H2′ & H6′), 7.62 (2H, *d*, *J* = 8.3 Hz, H3′ & H5′), 7.37–7.28 (5H, *m*, phenyl), 6.13 (1H, *d*, *J* = 2.1 Hz, H14), 5.20 (1H, *d*, *J* = 12.6 Hz, H21a), 4.87 (1H, *d*, *J* = 12.6 Hz, H21b), 3.14 (1H, *m*, H7), 2.35–2.22 (1H, *m*, H15), 2.11–1.97 (2H, *m*), 1.88––1.67 (2H, *m*), 1.66–1.45 (1H, *m*), 1.35–1.12 (5H, *m*), 1.12–1.10 (2H, *m*), 1.11 (6H, *d*, *J* = 6.9 Hz, H16 & H17), 0.91 (3H, *s*, H19), 0.83 (3H, *s*, H18); ^{13}C-NMR (125.8 MHz, $CDCl_3$, δ/ ppm): 178.2 (C20), 160.0 (C22), 148.8 (C13), 138.2 (C1′), 131.0 (*q*, *J* = 32.7 Hz, C4′), 130.2 (C14), 128.4 (C4″), 127.8 (2C, C2″ & C6″), 127.5 (2C, C3″ & C5″), 127.2 (2C, C2′ & C6′), 125.4 (2C, *m*, C5′ & C3′), 94.0 (C8), 66.4 (C21), 52.3 (C9), 51.7 (C7), 47.4 (C5), 46.4 (C4), 37.0 (C1), 36.6 (C10), 36.1 (C3), 35.0 (C15), 27.0 (C12), 23.7 (C6), 22.4 (C11), 18.3 (C17 & C16), 15.2 (C19), 14.1 (C18); EIMS *m*/*z* (rel. int): 580 (M^++ H, 1), 530 ((M^+–F–2×(CH_3), 2), 365 (30), 145 ($C_6H_4CF_3$, 12), 91 ($C_6H_5CH_2$, 100).

*Dicycloadduct **11** of perillyl abietate (**5**) and 4-(trifluoromethyl)benzonitrile oxide(**7a**)*. ((R)-*4*-((R)-*5-Methyl-3-(4(trifluoromethyl)phenyl)-4,5-dihydroisoxazol--5-yl)cyclohex-1-en-1-yl)-methyl (*4a*R,*7a*R,*8a*R,*9*R,*12a*S,*12b*R)-*3-isopropyl-9,12a--dimethyl-7-(4-trifluoromethyl)phenyl)-1,7a,8,8a,9,10,11,12,12a,12b-decahydro--2H-phenantro[9,8a-d]-isoxazole-9-carboxylate* Yield: 25 %; celadon oil; Anal. Calcd. for $C_{46}H_{52}F_6N_2O_4$: C, 68.13; H, 6.46; N, 3.45 %. Found: C, 67.98; H, 6.57, N, 3.59 %; ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 7.76 (4H, *d*, *J* = 8.5 Hz, 2′, 2″, 6′ & 6″), 7.65 (4H, *d*, *J* = 8.5 Hz, 3′, 3″, 5′ & 5″), 5.72 (2H, *m*, H14 & H24), 4.48 (2H, *m*, H21), 3.23 (1H, *d*, *J* = 16.5 Hz, H30a), 2.95 (1H, *d*, *J* = 16.5 Hz, H30b), 2.94 (1H, *m*, H7), 2.32–2.18 (3H, *m*), 2.11–1.99 (4H, *m*), 1.98–1.84 (5H, *m*), 1.84–1.61 (2H, *m*), 1.60–1.45 (1H, *m*, H6a), 1.44 (3H, *s*, H32), 1.43––1.30 (3H, *m*), 1.27 (3H, *s*, H19), 1.26 (3H, *s*, H18), 1.25 (6H, *d*, *J* = 7.0 Hz, H16 & H17), 1.25–0.83 (4H, m); ^{13}C-NMR (125.8 MHz, $CDCl_3$, δ/ ppm): 178.0 (C20), 154.9 (C22 & C31), 146.5 (C13), 133.5 (C4′ & C4″), 132.9 (C23), 130.7 (C1″), 130.0 (C1′), 126.7 (C2′, C2″, C6′ & C6″), 125.7 (C3′, C3″, C5′ & C5″), 124.8 (C24), 124.6 (C14), 90.5 (C8 & C29), 68.8 (C21), 46.9 (C4), 42.8 (C30), 42.7 (C9), 42.0 (C5 & C7), 41.8 (C26), 37.4 (C1), 37.0 (C3), 34.9 (C10), 30.0 (C15), 27.2 (C25), 27.0 (C28), 26.7 (C12), 24.0 (C6, C19 & C32), 23.7 (C27), 22.2 (C11), 20.9 (C16 & C17), 18.1 (C2), 17.3 (C18).

*Dicycloadduct **12** of perillyl abietate (**5**) and 4-trifluoromethylbenzonitrile oxide (**7a**)*. ((R)-*4*-((S)-*5-Methyl-3-(4(trifluoromethyl)phenyl)-4,5-dihydroisoxazol--5-yl)cyclohex-1-en-1-yl)-methyl (*4a*R,*7a*R,*8a*R,*9*R,*12a*S,*12b*R)-*3-isopropyl--9,12a-dimethyl-7-(4-trifluoromethyl)phenyl)-1,7a,8,8a,9,10,11,12,12a,12b-deca-hydro-2H-phenantro[9,8a-d]-isoxazole-9-carboxylate* Yield: 25 %; celadon oil, Anal. Calcd. for $C_{46}H_{52}F_6N_2O_4$: C, 68.13; H, 6.46; N, 3.45 %. Found: C, 68.35; H, 6.29; N, 3.38 %; ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 7.76 (4H, *d*, *J* = 8.3

Hz, 2′, 2″, 6′ & 6″), 7.64 (4H, *d*, *J* = 8.3 Hz, 3′, 3″, 5′ & 5″), 5.72 (2H, *m*, H14 & H24), 4.45 (2H, *m*, H21), 3.23 (1H, *d*, *J* = 16.5 Hz, H30a), 2.93 (1H, *d*, *J* = 16.5 Hz, H30b), 2.86 (1H, *m*, H7), 2.32–2.18 (3H, *m*), 2.11–1.99 (4H, *m*), 1.98–1.85 (5H, *m*), 1.85–1.65 (2H, *m*), 1.60–1.44 (3H, *m*), 1.44 (3H, *s*, H32), 1.43–1.28 (3H, *m*), 1.27 (3H, *s*, H19), 1.25 (3H, *s*, H18), 1.22 (6H, *d*, *J* = 7.0 Hz, H16 & H17), 1.08–0.81 (3H, *m*); ^{13}C-NMR (125.8 MHz, $CDCl_3$, δ / ppm): 178.5 (C20), 154.7 (C22), 154.5 (C31), 145.8 (C13), 134.0 (C4′ & C4″), 133.3 (C23), 131.5 (C1′ & C1″), 126.7 (C2′, C2″, C6′ & C6″), 125.6 (C3′ & C5′), 125.0 (C3″ & C5″), 124.5 (C14 & C24), 90.8 (C8), 90.4 (C29), 68.3 (C21), 48.0 (C9), 43.7 (C4), 43.0 (C7 & C30), 42.3 (C5), 42.3 (C1, C26), 37.8 (C15), 36.8 (C10), 36.5 (C3), 26.6 (C12, C25 & C28), 24.2 (C6, C19 & C32), 24.2 (C11, C16, C17 & C27), 23.4 (C2), 16.7 (C18 & C19).

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