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SYNTHESIS OF LACTAM ANALOG OF 4-EPI-BREFELDIN A

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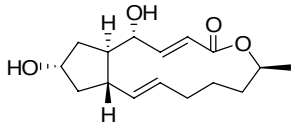
Abstract – A concise synthetic route to the lactam analog of 4-epi-brefeldin A is described. The key features of the synthesis involve cross metathesis of the bicyclic lactone intermediate and the side chain subunit readily available from an amino acid, and 13-membered macrolactam formation. Unlike the case of synthesis of natural (+)-brefeldin A, the introduction of C4-alcohol into the 13-membered lactam skeleton furnished the opposite configuration, which was confirmed by X-ray crystallographic analysis.

INTRODUCTION

Since a fungal metabolite, (+)-brefeldin A (BFA, **1**) was first isolated from *Penicillium decumbens* in 1958,[1] its unique structure and wide range of biological activities such as anticancer, antiviral, antimitotic and antifungal effect have attracted great interest of the synthetic chemists and biologists.[2, 3] In particular, the potent apoptotic effect of BFA induced by endoplasmic reticulum stress or other mechanisms makes it a promising molecule for development of an anticancer agent.[4] In addition, both the excellent biological activity of BFA and the limitations in its therapeutic applications have stimulated a resurgence of the synthetic medicinal chemistry[5] because the poor solubility and unsuitable pharmacokinetic features related to instability of BFA have hampered the progress toward its preclinical or clinical trial.[6] Thus, we have recently been interested in an improvement of both solubility and stability of BFA and worked on replacement of the lactone skeleton of BFA with lactam skeleton in an anticipation of improved solubility

and chemical stability on the basis of previous report.[7] In this connection, we have established an efficient synthetic approach providing us a readily access to the lactam analogs of BFA, which is quite attractive from the viewpoint of medicinal chemistry.

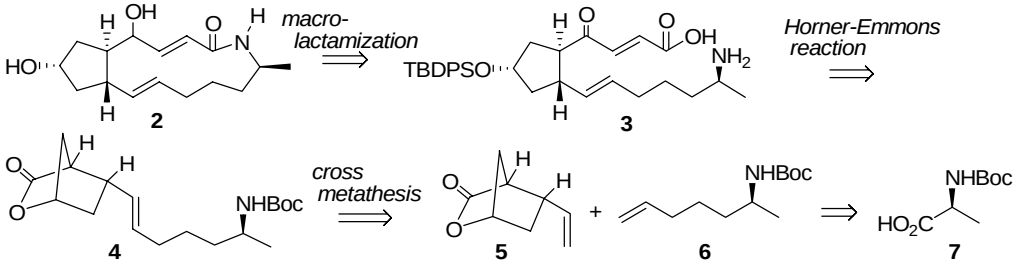


1 (+)-brefeldin A (BFA)

Fortunately our cross metathesis strategy, which was recently developed in our laboratory for the practical and convergent total synthesis of (+)-BFA,[8] permitted us to develop the more flexible and convergent synthetic route to the BFA lactam analog. We herein describe the synthesis of BFA lactam analogs via combination of cross metathesis and macrolactamization.

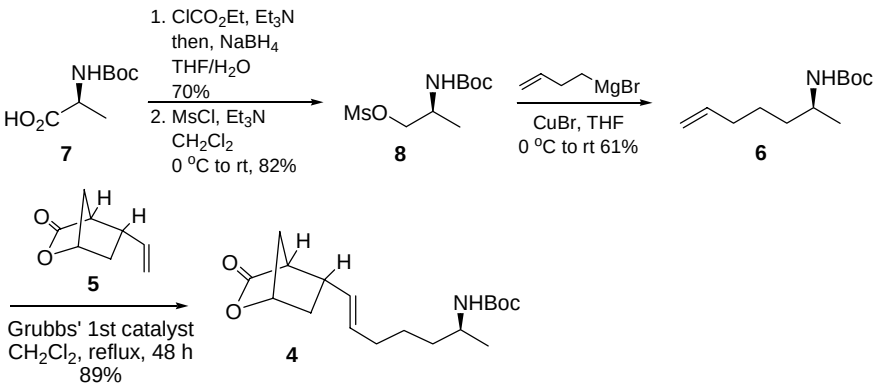
RESULTS AND DISCUSSION

Scheme 1. Retrosynthesis of the BFA lactam analog



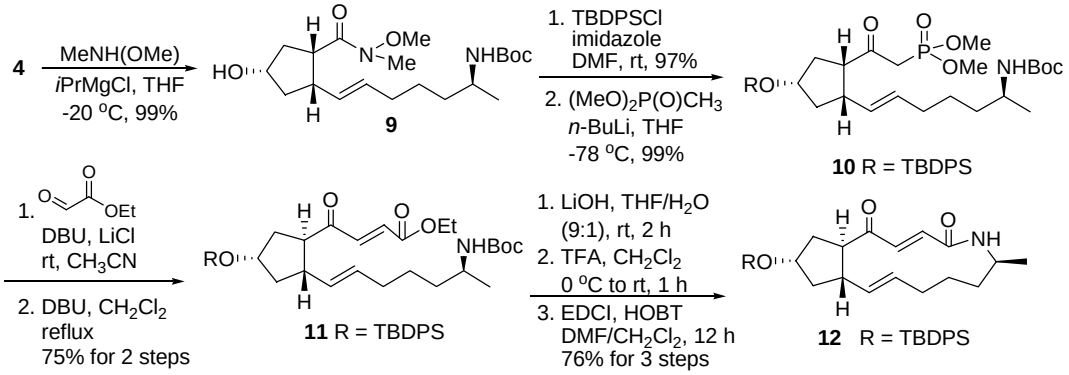
As summarized in scheme 1, we anticipated that the BFA lactam analog (**2**) could be obtained by macrolactamization of the amino acid **3** at the final stage, followed by ketone reduction. The amino acid **3** would be conveniently derived from the amino lactone **4** via three carbon extension using Horner-Emmons reaction. The requisite amino lactone **4** is efficiently prepared via cross metathesis of the bicyclic lactone **5**[8] and the side chain **6**, which is readily available from *N*-Boc-*L*-alanine **7**.

Scheme 2. Synthesis of the side chain **6** and cross metathesis reaction



Our synthesis commenced with the preparation of the side chain **6**. The commercially available *N*-Boc-L-alanine **7** was initially reduced and mesylated to afford the mesylate **8**,[9] which was then treated with 3-butenyl cuprate to give the side chain **6**. This simple 3-step procedure allowed us to secure a multigram quantity of the side chain **6**, which was subjected to the cross metathesis reaction. As expected, the cross metathesis of the bicyclic lactone **5** and the side chain **6** in the presence of the 1st-generation Grubbs catalyst afforded the desired product **4** having (*E*)-geometry along with a small amount of the (*Z*)-isomer (*E*:*Z* = ca 7: 1). It is noteworthy that any homodimer of the bicyclic lactone **5** was not detectable. Instead, the homodimer of the side chain **6** was the sole side product of this metathesis reaction. The homodimer was also reactive to the lactone **5** in the presence of 1st-generation Grubbs catalyst and more stable than **6**, which implies the storage benefit.

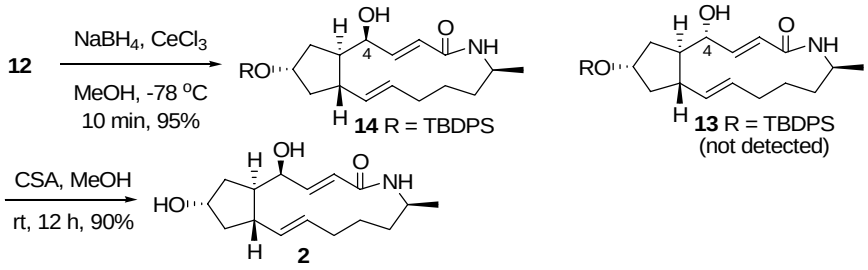
Scheme 3. Synthesis of macrolactam **12**



Synthesis of the 13-membered macrolactam **12** from **4** is described in Scheme 3. Initial lactone ring opening with *N*-methoxymethylamine gave the Weinreb amide **9**,[10] which was converted to the phosphonate **10** via TBDPS protection, followed by phosphorylation with dimethyl methyl phosphonate. Horner-Emmons reaction according to Masamune-Roush protocol[11] and epimerization of the stereogenic center adjacent to carbonyl provided exclusively the (*E)*-isomer **11** of a 1, 2-*anti*-substituted alkoxycyclopentane. Subsequent hydrolysis of the ester **11**, followed by Boc-deprotection afforded the amino acid **3** (shown in Scheme 1) as the macrolactamization precursor. Gratifyingly, macrolactamization of **3** using EDCI and HOBT under dilution condition (0.5 μM) gave the desired macrolactam **12** in good yield.

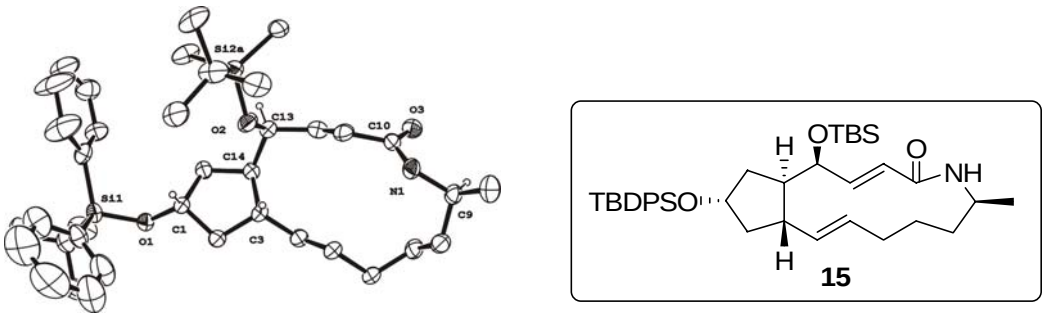
We previously revealed that $NaBH_4$ reduction of the C4 carbonyl group of the macrolactone skeleton provides the desired C4 (*R*)-hydroxy group as a major product.[8] Thus, it was envisioned that subjection of the ketone **12** to the same reduction condition would also produce the alcohol **13** with the same C4-configuration as the natural one. Reduction of the lactam **12** with $NaBH_4$ in MeOH afforded the

Scheme 4. Stereoselective reduction of the macrolactam **12** and completion of synthesis



corresponding alcohol as a single isomer in 95% isolated yield. In order to determine the C4 stereochemistry using X-ray crystallography, we obtained the TBS ether **15**. Unexpectedly, the X-ray crystal structure analysis revealed the opposite configuration, which implies that reduction of **12** furnished the undesired alcohol **14** instead of **13**. Although it is difficult to explain this result at present, the opposite diastereoselectivity is likely due to the conformational change induced by an introduction of the amide moiety.[12]

Figure 1. Crystal structure of **15** (other hydrogens were omitted for simplicity.)



In summary, we have achieved synthesis of 4-*epi*-BFA lactam analog **2** via the highly practical and efficient transformations in 14% overall yield for 14 steps. Interestingly, in case of macrolactam architecture, the conversion of ketone to alcohol at C4 resulted in inversion of the C4-stereochemistry, which was confirmed by X-ray crystallographic analysis. Our new findings as well as the established synthetic route would be widely applicable for the future synthetic work related to the medicinal chemistry of BFA. Our continuing studies on the BFA analogs and their biological evaluations are in progress and will be reported in due courses.

EXPERIMENTAL

Unless noted otherwise, all starting materials were obtained from commercial suppliers and were used without further purification. Air and moisture sensitive reactions were performed under an argon

atmosphere. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck) with indicated solvents. Thin-layer chromatography was performed using 0.25 mm silica gel F254 plates (Merck). Optical rotations were measured using sodium light (D line 589.3 nm)

tert-Butyl *N*-[(1*S*)-1-methyl-5-hexenyl]carbamate (**6**)

$[\alpha]_D^{20}$ +4.1 (c 0.5, acetone); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.83 – 5.70 (m, 1H), 5.01 – 4.91 (m, 1H), 4.26 (bs, 1H), 3.61 (bs, 1H), 2.03 (d, 1H, *J* = 6.9 Hz), 1.41 (s, 9H), 1.41 – 1.37 (m, 4H), 1.08 (d, 1H, *J* = 6.6 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 155.3, 138.5, 114.5, 78.8, 46.3, 36.7, 33.5, 28.3, 25.2, 21.2; IR (KBr) ν_{max} 3339, 2976, 2932, 1696, 1521, 1455, 1391 cm^{-1}; LRMS (FAB) *m/z* 214 ($M+H^+$); HR-MS (FAB) Calcd for $C_{12}H_{24}NO_2$ ($M+H^+$): 214.1807, Found 214.1798.

tert-Butyl *N*-(1*S*,5*E*)-1-methyl-6-[(1*S*,4*R*,5*S*)-3-oxo-2-oxabicyclo[2.2.1]hept-5-yl]-5-hexenylcarbamate (**4**)

To a solution of bicyclic lactone **5** (17 mg, 0.12 mmol) and side chain **6** (91 mg, 0.43 mmol) in CH_2Cl_2 (3 mL) was added 1st Grubbs' catalyst (10 mg, 0.01 mmol) at rt. After stirring for 48 h at reflux, the reaction mixture was cooled to an ambient temperature and 5 drops of DMSO were added. After stirring for 10 h at rt, the reaction mixture was concentrated *in vacuo* and purified by column chromatography on silica gel (EtOAc : *n*-hexane = 1 : 2) to afford 35 mg (89%) of cross metathesis adduct **4** as a colorless oil.; $[\alpha]_D^{20}$ –23.6 (c 2.8, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 5.57 – 5.48 (m, 1H), 5.31 – 5.21 (m, 1H), 4.83 (s, 1H), 4.30 (bs, 1H), 3.58 (bs, 1H) 2.89 – 2.75 (m, 2H), 2.20 (d, 1H, *J* = 10.2 Hz), 2.14 –1.97 (m, 2H), 1.71 (t, 2H, *J* = 10.2 Hz), 1.62 – 1.56 (m, 1H), 1.41 (s, 9H), 1.41 – 1.35 (m, 4H), 1.07 (d, 1H, *J* = 6.6 Hz); IR (KBr) ν_{max} 2970, 1786, 1698, 1520, 1404, 1248, 1174cm^{-1}; LRMS (FAB) *m/z* 324 ($M+H^+$); HR-MS (FAB) Calcd for $C_{18}H_{30}NO_4$ ($M+H^+$): 324.2175, Found 324.2171.

(6*S*,11a*S*,13*S*,14a*R*)-13-[*tert*-Butyl(diphenyl)silyl]oxy-6-methyl-5,6,7,8,9,11a,12,13,14,14a-decahydrocyclopenta[*f*]azacyclotridecine-1,4-dione (**12**)

To a solution of enone ester **11** (8 mg, 0.01 mmol) in THF (1 mL) and H_2O (0.5 mL) was added $LiOH{\cdot}H_2O$ (5 mg, 0.21 mmol) at rt. Reaction mixture was stirred for 3 h and quenched by 2 N HCl (0.5 mL). The mixture was extracted with EtOAc 3 times, dried over $MgSO_4$ and concentrated *in vacuo*. This crude mixture (8 mg) in 1 mL CH_2Cl_2 was treated with 0.2 mL TFA at rt and stirred for 1 h at rt. The reaction mixture was concentrated under the reduced pressure and dried *in vacuo* for about 3 h. These crude mixture (7 mg) in DMF (10 mL) and CH_2Cl_2 (10 mL) was treated with HOBT (16 mg, 0.12 mmol) and EDCI (23 mg, 0.12 mmol) at 0 ^oC and warmed up to rt immediately. After stirring for 24 h at rt, the reaction mixture was quenched by H_2O and concentrated under the reduced pressure. The mixture was

extracted with EtOAc and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (EtOAc / *n*-hexane 3 : 2) to afford 5 mg (76% for 3 steps) of **12** as a colorless oil.; $[\alpha]_D^{20}$ +58.4 (c 0.76, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 7.63 – 7.61 (m, 4H), 7.42 – 7.34 (m, 6H), 6.78 (d, 1H, *J* = 16.5 Hz), 6.74 (d, 1H, *J* = 16.5 Hz), 5.71 (d, 1H, *J* = 8.5 Hz), 5.63 – 5.58 (m, 1H), 5.20 – 5.14 (m, 1H), 4.39 – 4.36 (m, 1H), 3.70 – 3.68 (m, 1H), 3.48 (q, 1H, *J* = 9.0 Hz), 2.39 – 2.32 (m, 1H), 2.26 – 2.23 (m, 1H), 2.20 – 1.96 (m, 3H), 1.75 – 1.71 (m, 1H), 1.64 – 1.58 (m, 2H), 1.53 – 1.50 (m, 2H), 1.21 (d, 3H, *J* = 6.5 Hz), 1.32 – 1.27 (m, 1H), 1.05 (s, 9H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 202.4, 167.1, 139.3, 136.4, 135.7, 134.0, 130.6, 129.6, 127.6, 74.3, 50.9, 48.0, 45.5, 44.1, 38.4, 36.1, 28.9, 27.0, 23.0, 19.1, 18.4, 1.0; IR (KBr) ν_{max} 2931, 2856, 1661, 1393, 1108 cm^{-1}; LRMS (EI+) *m/z* 515 (M^+); HR-MS (FAB) Calcd for $C_{32}H_{42}NO_3Si$ ($M+H^+$): 516.2934, Found 516.2938.

(1*R*,6*S*,11a*S*,13*S*,14a*R*)-13-[*tert*-Butyl(diphenyl)silyl]oxy-1-hydroxy-6-methyl-5,6,7,8,9,11a,12,13,14,14a-decahydrocyclopenta[*f*]azacyclotridecin-4(1*H*)-one (**14**)

To a solution of lactam **12** (40 mg, 0.08 mmol) and $CeCl_3 \cdot 7H_2O$ (90 mg, 0.24 mmol) in 2 mL of MeOH was added $NaBH_4$ (7.5 mg, 0.20 mmol) at –78 °C. After stirring for 10 min at –78 °C, the reaction was quenched by saturated aqueous NH_4Cl. The reaction mixture was extracted with EtOAc and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (EtOAc / *n*-hexane / MeOH = 25 : 15 : 1) to afford 38 mg (95%) of alcohol **14** as a colorless oil.; ^{1}H-NMR (CD_3OD, 500 MHz) δ 7.66 – 7.62 (m, 4H), 7.42 – 7.36 (m, 6H), 6.45 (dd, 1H, *J* = 4.1, 15.8 Hz), 6.04 (dd, 1H, *J* = 1.25, 15.8 Hz), 5.43 (m, 1H), 5.26 (dd, 1H, *J* = 9.6, 14.7 Hz), 4.34 (m, 1H), 4.25 (m, 1H), 3.94 (dd, 1H, *J* = 6.6, 16.7 Hz), 2.51 (t, 1H, *J* = 8.5 Hz), 2.27 (m, 1H), 2.13 (q, 1H, *J* = 7.4 Hz), 2.03 (m, 1H), 1.91 (t, 1H, *J* = 10.9 Hz), 1.85 – 1.77 (m, 7H), 1.11 (d, 3H, *J* = 6.8 Hz), 1.03 (s, 9H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 135.7, 135.6, 134.4, 134.3, 129.5, 129.4, 129.1, 127.5, 127.4, 74.3, 71.0, 60.3, 48.5, 46.2, 39.2, 38.7, 32.9, 26.9, 25.5, 21.1, 19.0, 14.1; IR (KBr) ν_{max} 3294, 2931, 2857, 1597, 1544, 1456, 1363 cm^{-1}; LRMS (FAB) *m/z* 518 ($M+H^+$); HR-MS (FAB) Calcd for $C_{32}H_{44}NO_3Si$ ($M+H^+$): 518.3090, Found 518.3097.

(1*R*,6*S*,11a*S*,13*S*,14a*R*)-1,13-Dihydroxy-6-methyl-5,6,7,8,9,11a,12,13,14,14a-decahydrocyclopenta[*f*]-azacyclotridecin-4(1*H*)-one (**2**)

To a solution of alcohol **14** (5 mg, 0.10 mmol) in MeOH (1 mL) was added CSA (20 mg) at 0 °C and warmed up to rt. After stirring for 12 h at rt, the reaction mixture was quenched by saturated aqueous $NaHCO_3$, extracted with EtOAc and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica

gel (EtOAc / MeOH = 15:1) to afford 2.5 mg (90%) of BFA lactam analog **2** as a white solid.; ^{1}H-NMR (CD_3OD, 500 MHz) δ 6.46 (dd, 1H, *J* = 4.0, 15.8 Hz), 6.08 (dd, 1H, *J* = 1.25, 15.8 Hz), 5.48 (t, 1H, *J* = 11.2 Hz), 5.34 – 5.33 (m, 1H), 5.21 (dd, 1H, *J* = 9.7, 14.8 Hz), 4.38 (s, 1H), 4.16 (t, 1H, *J* = 5.6 Hz), 3.94 (m, 1H), 2.63 (m, 1H), 2.25 (t, 1H, *J* = 7.2 Hz), 2.10 – 1.93 (m, 4H), 1.80 – 1.74 (m, 4H), 1.60 – 1.59 (m, 1H), 1.13 (d, 3H, *J* = 6.7 Hz); IR (KBr) ν_{max} 3290, 2922, 2852, 1709, 1608, 1538, 1454 cm^{-1}; LRMS (FAB) *m/z* 280 ($M+H^+$); HR-MS (FAB) Calcd for $C_{16}H_{26}NO_3$ ($M+H^+$): 280.1913, Found 280.1916

(1*R*,6*S*,11a*S*,13*S*,14a*R*)-13-[*tert*-Butyl(diphenyl)silyl]oxy-6-methyl-1-[(*tert*-butyl(dimethyl)silyl)oxy]-5,6,7,8,9,11a,12,13,14,14a-decahydrocyclopenta[*f*]azacyclotridecin-4(1*H*)-one (**15**)

To a solution of alcohol **14** (12 mg, 0.02 mmol) in CH_2Cl_2 (1 mL) were added Et_3N (96 μL, 0.69 mmol) and TBSOTf (0.14 mL, 0.46 mmol) at 0 °C and warmed up to rt. After stirring for 12 h at rt, the reaction mixture was quenched by H_2O, extracted with EtOAc and the combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (EtOAc / *n*-hexane = 1:3) to afford 11 mg (75%) of TBS ether **15** as a colorless oil.; ^{1}H-NMR (CD_3OD, 300 MHz) δ 7.74 – 7.71 (m, 4H), 7.51 – 7.42 (m, 6H), 6.51 (dd, 1H, *J* = 3.9, 15.6 Hz), 6.16 (dd, 1H, *J* = 1.2, 15.6 Hz), 5.49 – 5.44 (m, 1H), 5.29 (dd, 1H, *J* = 9.6, 14.7 Hz), 4.50 (s, 1H), 4.28 (t, 1H, *J* = 5.8 Hz), 4.06 – 4.01 (m, 1H), 2.69 – 2.57 (m, 1H), 2.16 (q, 1H, *J* = 7.4 Hz), 1.97 – 1.76 (m, 6H), 1.19 (d, 3H, *J* = 6.6 Hz), 1.09 (s, 9H), 0.87 (s, 9H), 0.01 (d, 6H, *J* = 6 Hz); ^{13}C-NMR (CD_3OD, 75 MHz) δ 170.9, 147.7, 139.2, 137.7, 137.6, 136.2, 131.7, 131.5, 129.4, 125.6, 76.4, 74.3, 48.4, 46.2, 41.1, 40.9, 38.6, 35.4, 28.2, 27.3, 21.9, 20.6, 19.7, -3.2, -4.0; IR (KBr) ν_{max} 3273, 2930, 2856, 1634, 1542, 1460, 1363 cm^{-1}; LRMS (FAB) *m/z* 632 ($M+H^+$); HR-MS (FAB) Calcd for $C_{38}H_{58}NO_3Si_2$ ($M+H^+$): 632.3955, Found 632.3961.

ACKNOWLEDGEMENTS

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