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Asymmetric oxidation of cyclobutanones: modification of the Sharpless catalyst

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Abstract

Oxidation of prochiral and racemic cyclobutanones with *t*-BuOOH and Ti–TADDOL-based complexes afforded lactones in up to 44% *ee*. The enantioselectivity of the reaction clearly depends on the amount of the reagent and the highest enantioselectivities were obtained with stoichiometric amounts of the complex. Modification of the TADDOL structure and use of the mixed complex derived from TADDOL and a tartaric ester led to more reactive but less selective oxidation systems.

1. Introduction

Chiral titanium complexes have been widely used in asymmetric synthesis.[1,2] Undoubtedly, the most popular chiral titanium reagent is the Sharpless catalyst used for the epoxidation of allylic alcohols.[3] This reagent is also used for other types of oxidation (e.g. to obtain sulfoxides from prochiral sulfides).[4,5] These reactions result in very high enantioselectivities and, therefore, only slight modifications have been made in the structure of the catalyst (use of cumyl hydroperoxide[6] and chiral hydroperoxides[7,8] instead of *t*-BuOOH). Our recent studies on the Baeyer–Villiger oxidation of cyclobutanones[9] (see also other asymmetric Baeyer–Villiger oxidations[10–13]), leading to lactones (*ee* up to 75%) and α-hydroxylation of α-hydroxyketones resulting in α,β-dihydroxyketones (*ee*s >95%),[14] broadened the scope of the use of the reagent.

Another widely used chiral titanium catalyst first reported by Seebach[15] is based on TADDOL (α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanols). These complexes catalyse various reactions, such as Diels–Alder cycloadditions[16,17] carbonyl–*ene* reactions,[18] 1,3-dipolar cycloadditions[19–22] and nucleophilic additions to carbonyl groups.[2] The enantioselectivity of the reaction may vary over a wide range

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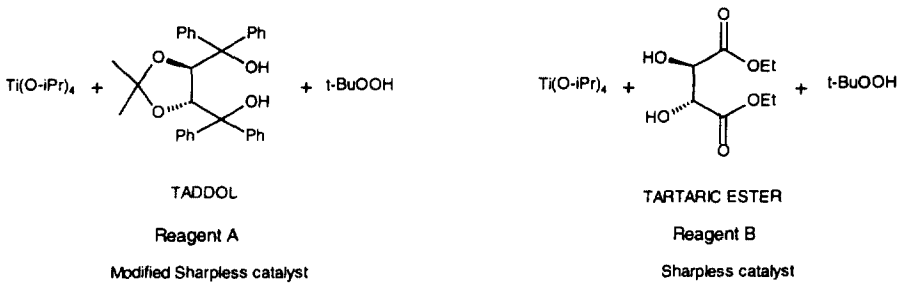


Figure 1.

and, therefore, attempts were made to modify the chiral auxiliary as well as the ligand to the metal in the catalyst.

The aim of the present study was to improve the rate and selectivity of the asymmetric oxidation of cyclobutanones by using a modified TADDOL-based catalyst (Fig. 1, reagent A) (using the traditional Sharpless catalyst (reagent B) the reaction times were up to 96 h, with *ee*s up to 75%).

2. Results and discussion

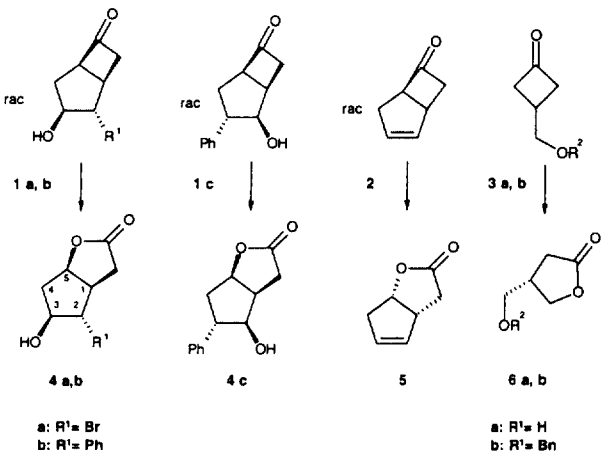
2.1. Oxidation of cyclobutanones with chiral titanium reagents; dependence of the enantioselectivity on the substrate structure

Several racemic (**1a–c**, **2**) and prochiral (**3a**, **b**) cyclobutanones (Scheme 1) were oxidised by reagent A. The reagent was prepared from Ti(O-*i*-Pr)$_4$ and TADDOL (ratio 1:1.2) by stirring them at room temperature for 1 h in CH_2Cl_2 in the presence of molecular sieves. The obtained mixture was cooled to −20°C, *t*-BuOOH was added to the mixture and the catalyst was allowed to age for 30 min. Finally, a ketone was added to the mixture and the reaction was run at −20°C for the appropriate time. The absolute configurations of the predominant enantiomers (obtained by the oxidation with reagent A) are depicted in Scheme 1. The results are presented in Table 1. The results shown in Table 1 indicate that the reagent derived from Ti(O-*i*-Pr)$_4$, TADDOL and *t*-BuOOH (reagent A) is characterised by a moderate enantioselectivity, affording lactones in up to 44% enantiomeric excess. The structure of the substrate has no significant influence on enantioselectivity. In the case of the sterically hindered phenyl-substituted cyclobutanones **1b** and **1c**, selectivity was only slightly lower (entries 3, 5) than in the case of the less hindered ketone **1a** (entry 1). It is noteworthy that, unlike Sharpless epoxidations, the existence of a hydroxy group in the substrate molecule is not essential.[9] Therefore, the unsaturated bicyclic ketone **2** was oxidised with a selectivity comparable to that of other substrates (entry 6).

For catalyst A, the influence of the reaction temperature on the enantioselectivity is not considerable. The reaction at −78°C afforded lactone **1a** with only a slight improvement of selectivity when compared with that from the experiment at −20°C (*ee* 44% and 41%, respectively; Table 1, entries 11 and 1).

All these above examples describe the kinetic discrimination of the substrate (racemic ketones). Prochiral ketones **3a** and **3b** were also oxidised under the same conditions (Table 1, entries 8–10). We found that the reaction is non-selective in the case of cyclobutanone **3b**, which has a protected OH-group. Oxidation of ketone **3a**, which bears an unprotected OH-group, with reagents A and B gave rather similar results (*ee* 33% and 40%, respectively). However, in both cases the obtained *ee* values are moderate.

We have not studied the structure of the catalyst in detail. However, in a separate experiment the catalyst was made from equimolar amounts of TADDOL and Ti(O-*i*-Pr)$_4$ in the presence of molecular sieves in toluene, followed by the evaporation of isopropanol and solvent to dryness. This procedure



Scheme 1. Oxidation of cyclobutanones **1a–c**, **2**, **3a**, **b** with *t*-BuOOH/Ti(O-*i*-Pr)$_4$/TADDOL complex

should exclude the possible formation of spirotitanate.[26] After adding *t*-BuOOH to the obtained Ti-complex, we performed the oxidation reaction of cyclobutanones, under identical conditions to those described earlier. In these experiments we got similar results to those reported earlier (Table 1). Thus, we can assume that in both cases we have the same TADDOL–titanate complex (the evaporation of isopropanol is not essential). The experimentally simpler route was chosen as a general method for the preparation of the catalyst.

As far as the rate of oxidation is concerned, the obtained results are an example of ligand accelerated catalysis[1] with reagent A (a new and more reactive catalyst is obtained via the replacement of a ligand at the metal centre). In our separate oxidation experiment (**1a** to lactone **2a**), where a mixture of *t*-BuOOH and Ti(O-*i*-Pr)$_4$ was used as a catalyst, we obtained 20% conversion of the substrate during 4 h at −20°C. The reaction of **1a** (under the same conditions and with the same reaction time) with the reagent that had TADDOL as a Ti-additive, afforded lactone in 33% yield. In the case of the same oxidation with reagent B, however, ligand deceleration takes place and a longer reaction time is needed. Also, the stereochemical behaviour of these reactions is opposite and enantiomeric lactones were obtained with reagents A and B (the only exception being compound **2**, which has no OH-group). It is known that Ti–TADDOL complexes may exist in monomeric or oligomeric forms.[27] As the result of a rapid exchange of the alkoxide ligands, an equilibrium mixture of various complexes is present in the reaction media. Each of these complexes is a potential oxidation catalyst, characterised by specific kinetic and stereochemical features. Moderate *ee* values of the product refer to the absence of a dominating asymmetric complex in these systems. In the case of the Sharpless catalyst, one of those complexes dominates from a kinetic as well as an equilibrium point of view.[28]

We have also investigated the dependence of the enantioselectivity of the Baeyer–Villiger oxidation reaction on the amount of reagent A. In order to obtain comparable results for the oxidation of the substrate **1a** at different substrate:reagent ratios, the reaction was quenched after approximately 40% conversion had been achieved. It was observed that the enantioselectivity of the reaction clearly depends on the amount of reagent A (Fig. 2). The highest *ee* value was obtained when stoichiometric amounts of the reagent were used. A low turnover number (close to 1, stoichiometric process) indicates that the mechanism is closer to that of the stoichiometric Sharpless epoxidation process rather than to that of the corresponding catalytic process.[3]

Table 1
Comparison of the oxidation of cyclobutanones with reagents A and B

Entry	Ketone	*t*-BuOOH (eq.)	Reagent	Reaction time (h)	Product	Yield (%)	*ee*[a] %	Abs. conf.[b]
1	**1a**	0.6	A	4	**4a**	33	41	(+)-1R, 2S, 3S, 5R[c]
2	**1a**	1.5	B	44	**4a**	40	75[9]	(-)-1S, 2R, 3R, 5S
3	**1b**	0.6	A	4	**4b**	20	39	(+)-1R, 2S, 3R, 5S
4	**1b**	1.5	B	46	**4b**	31	59	(-)-1S, 2R, 3S, 5R
5	**1c**	0.5	A	22	**4c**	35	31	(+)-1R, 2R, 3R, 5S
6	**2**	0.6	A	4	**5**	27	31	(-)-1S, 5R
7	**2**	1.5	B	44	**5**	7	53[9]	(-)-1S, 5R
8	**3a**	1.5	A	213	**6a**	23	33	(+)-S
9	**3a**	1.5	B	96[g]	**6a**	14	40[9]	(-)-R[9]
10	**3b**	1.0	A	72[f]	**6b**	26	0	-
11	**1a**	1.5	A	24[h]	**4a**	7	44	(+)-1R, 2S, 3S, 5R[c]

[a] Determined by HPLC on chiral column (Daicel Chiralcel ODH) or from the ratio of diastereoisomers of the corresponding (R)-O-methylmandelic acid esters by NMR spectroscopy [23]

[b] Sign of optical rotation and absolute configuration of the predominant enantiomer of lactone

[c] Determined by the (+)-sign of unreacted ketone **1a**, which reveals the excess of 1S, 2R, 3R, 5S enantiomer[24,25]. Consequently, lactone **4a** should have 1R, 2S, 3S, 5R configuration.

[g] Reaction at -5^0C

[f] Reaction at 0^0C

[h] Reaction at -78^0C

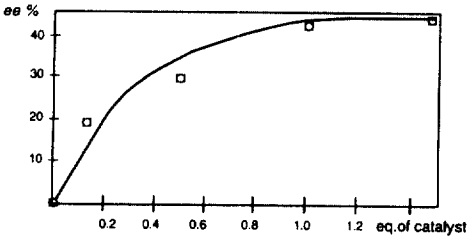
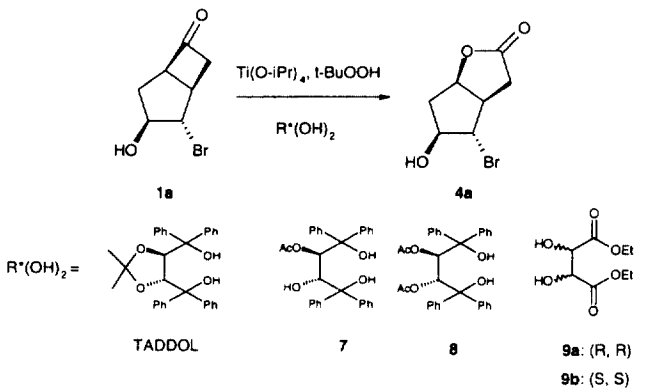


Figure 2. Dependence of the enantioselectivity of oxidation of cyclobutanone **1a** on the amount of reagent A

2.2. *Variation of the chiral ligand of the catalyst*

It has been suggested that in the Sharpless complex the carbonyl functions play an important role for the rigidity and activity of the catalyst through reversible ligation.[28] Therefore, acylated derivatives of TADDOL **7** and **8** were synthesised and the oxidation of cyclobutanone **1a** was carried out with their

corresponding titanium complexes (**7**, **8**, TADDOL, tartaric acid ethyl ester **9a** and **9b**, Scheme 2). The obtained results are presented in Table 2. Any derivatisation of TADDOL led to a lower enantioselectivity of the reaction. Thus, the reagent derived from diacylated derivative **8** afforded lactone in 6.5% *ee*, while the reaction with monoacylated derivative **7** led to a racemic product (entries 3 and 2). Carbonyl groups in the acylated TADDOL derivatives **7** and **8** are in the β-position relative to the stereogenic centre of the substrate, and in the δ-position relative to the hydroxy group. We suppose that they are located too far from the metal atom of the complex to have an appreciable enantio-differentiating effect on the complexation of the substrate to the catalyst and, therefore, their asymmetric induction is low.



Scheme 2. Oxidation of cyclobutanone **1a** with chirally modified complexes

The mixed complexes derived from TADDOL and tartaric ester in the oxidation of **1a** had low enantioselectivity (Table 2, entry 5) or did not have any (Table 2, entry 4). It has already been mentioned that reagents A and B have different enantio-preferences, affording lactones **4a** with opposite absolute configurations. The same phenomenon can be clearly observed in the experiments with mixed TADDOL and *R,R* or *S,S*-tartaric ester catalysts. In the case of the TADDOL–*R,R*-tartaric ester mixture, a racemic lactone was obtained (Table 2, entry 4, the catalysts in the mixture have opposite selectivities). The mixed TADDOL and *S,S*-tartaric ester catalyst resulted in a certain enantioselectivity (Table 2, entry 5). Surprisingly enough, the *ee* value of the product was lower (19%) than the *ee* value of the product from the experiments when both components were separately used in unmixed complexes (see Table 1, entries 1 and 2). It can be assumed that in the mixture a new complex(-es) is formed which may be less selective than both alone.

Table 2
Oxidation of cyclobutanone **1a** with the catalyst produced from Ti(O-*i*-Pr)$_4$ and R*(OH)$_2$

Entry	R*(OH)$_2$	t-BuOOH (eq.)	Reaction time (h)	Yield (%)	*ee* %
1	TADDOL	0.6	4	33	41
2	**7**	1	6	30	0
3	**8**	1	1.5	10	6.5
4	TADDOL + **9a**	0.6	42	20	0
5	TADDOL +**9b**	0.6	42	18	19
6	**9a**	1.5	42	40	75

3. Conclusions

The asymmetric oxidation of cyclobutanones with *t*-BuOOH and Ti-TADDOL-based chiral complexes proceeds with a moderate enantioselectivity (up to 44%). The reaction is faster than in the case of the Sharpless catalyst. The modification of the TADDOL structure as well as the combination of two chiral auxiliaries in the chiral catalyst lead to even lower values of *ee*.

4. Experimental

4.1. General data

1D and 2D FT NMR spectra were obtained on a Bruker AMX-500 spectrometer in $CDCl_3$ solution. The chemical shifts are reported relative to the TMS signal. Mass spectra were recorded on a Hitachi M80B spectrometer at an ionising potential of 70 eV. Optical rotations were obtained using a Polamat A polarimeter. Cyclobutanones **1a**, **3a**, **3b** were synthesised via known methods (according to Roberts[29] and Oehlschlager,[30] respectively.) Cyclobutanone **2** is commercially available.

*4.2. 3-Hydroxy-2-phenyl-bicyclo[3.2.0]heptane-6-one **1b** and 2-hydroxy-3-phenyl-bicyclo[3.2.0]heptane-6-one **1c***

A solution of PhLi (1.2 M in Et_2O, 1.5 mmol) and $BF_3 \cdot Et_2O$ (185 μl, 1.5 mmol) was added to a solution of ethylene acetal of 2,3-epoxy-bicyclo[3.2.0]heptane-6-one[29] (260 mg, 1.5 mmol) in anhydrous THF (5 ml) at −78°C under Ar atmosphere. The reaction mixture was stirred at −78°C for 4.5 h. The mixture was allowed to warm up to −15°C and was quenched with a saturated solution of $NaHCO_3$ (5 ml). The phases were separated, the aqueous layer was extracted with EtOAc (5×20 ml), and the combined organic phases were washed with brine, dried with $MgSO_4$ and evaporated. The crude product was used without purification in the deprotection of ketone, with 0.5 N H_2SO_4 in acetonitrile. Obtained products were separated by column chromatography on silica gel affording a less polar regioisomer **1b** (107 mg) and more polar isomer **1c** (60 mg, total yield 55%). MS: m/z=202, 160, 142, 104,91. ^1H and ^{13}C NMR. **1b**: δ_{TMS} from C-1 to C-7, δ^1H: 3.11, 3.35, 4.33, 2.19(x)/2.14(n), 3.83, 3.34(x)/3.25(n), 2-Ph: 7.18(o), 7.33(m), 7.24(p); $\delta^{13}C$: 34.57, 58.99, 82.34, 37.85, 63.30, 213.80, 53.09, 2-Ph: 142.55(s), 127.13(o), 128.51(m), 126.53(p). **1c:** δ_{TMS} from C-1 to C-7, δ^1H: 3.06, 4.38, 2.99, 2.23(x)/1.95(n), 3.59, 3.27/3.10, 3-Ph: 7.26(o), 7.34(m), 7.26(p); $\delta^{13}C$: 31.93, 79.50, 49.19, 32.58, 61.42, 212.60, 46.09, 3-Ph: 140.31(s), 127.42(o), 128.74(m), 127.10(p).

4.3. (2R,3R)-1,1,4,4-Tetraphenyl-2-acetoxy-1,2,4-butanetriol 7

To a solution of (2*R*,3*R*)-1,1,4,4-tetraphenyl-1,2,3,4-butanetetraol (405 mg, 0.95 mmol) in acetonitrile (2 ml), was added acetic anhydride (380 μl, 4 mmol) and trimethylchlorosilane (6 μl, 0.05 mmol). The reaction mixture was stirred for 48 h at room temperature. The solvent was evaporated in vacuum and the crude product was purified by column chromatography on silica gel, affording 292 mg (60%) of the target compound as an oil. It was recrystallized from Et_2O:petroleum ether (m.p. 83–86°C). $[\alpha]_{578}$ −141 (c 3.10, $CHCl_3$). ^1H and ^{13}C NMR **7:** δ^1H: 2.01(CH_3CO), 4.92(CHOH), 6.03(CHOAc), 7.1–7.7(Ph); $\delta^{13}C$: 20.96 and 170.81(CH_3CO), 78.71(C-2), 79.19(C-3), 85.43 and 86.32 (C-1 and C-4), 141.53, 142.93, 144.64 and 145.42(s), 126.23, 126.44, 127.53 and 127.99(o), 127.29, 127.49, 128.19 and 128.40(m), 126.86, 127.27, 127.32 and 127.64(p).

4.4. (2R,3R)-1,1,4,4-Tetraphenyl-2,3-diacetoxy-1,4-butanediol 8

The diacylated derivative **8** was prepared in an analogous way from the monoacylated compound **7**. $[\alpha]_{578}$ −131 (c 1.46,$CHCl_3$). ^1H and ^{13}C NMR **8**: δ^1H: 1.62(CH_3CO), 6.31(HCO), 7.25 and 7.60(o and o′), 7.17 and 7.33(m and m′), 7.15 and 7.25(p and p′); $\delta^{13}C$: 20.42 and 169.57(CH_3CO), 78.70(HCO), 88.97(Ph_2CO), 142.66 and 144.59(s and s′), 126.27 and 127.09(o and o′), 127.49 and 128.01(m and m′), 126.78 and 127.14(p and p′).

4.5. General procedure for oxidation of cyclobutanones under conditions of kinetic resolution

The mixture of TADDOL (0.6 mmol), Ti(O-*i*-Pr)$_4$ (0.5 mmol) and 4A powdered molecular sieves (100 mg) in CH_2Cl_2 (3 ml) was stirred at room temperature for 1 h under Ar atmosphere. The mixture was cooled to −20°C and *t*-BuOOH (0.3 mmol in toluene, 4.6 M solution) was added. Cyclobutanone (0.5 mmol) in CH_2Cl_2 (1.5 ml) was added after 30 min and the mixture was stirred at −20°C for the appropriate time. The reaction was quenched with a solution of citric acid monohydrate (0.5 mmol in a mixture of 10% acetone in ether, 15 ml) by stirring at room temperature for 1 h. The heterogeneous mixture obtained was filtered through a path of Celite and purified by column chromatography on silica gel.

4.6. Determination of ee and absolute configuration

Enantiomeric excesses of bicyclic hydroxylactones (**4a–c**, **5**) were determined on isolated products by HPLC analyses on a chiral column (Daicel Chiralcel ODH, 4.6×250 mm, hexane:*i*-PrOH, 9:1). Lactone **6a** was derivatised with (*R*)-O-methylphenylacetic acid and the diastereomeric esters obtained were analysed by NMR. The absolute configuration of lactone **6a** was suggested to be *S* for the (+)-isomer (according to our previous work).[9]

The absolute configuration of the predominant enantiomer of lactone **4a** was determined by the optical rotation of the unreacted ketone **1a**. According to the conformational model of the (*R*)-O-methylphenylacetic acid ester of lactone **4b**, its phenyl ring must, in the 1*R*,2*S*,3*R*,5*S* isomer, shield atoms 1, 2 and 8 and deshield atoms 4 and 5.[23] This is confirmed by the chemical shifts of C-1, C-4 and C-5 and H-2, H-8x, H-8n, H-4x, H-4n and H-5. In the case of the (*R*)-O-methylphenylacetic acid ester of the lactone, the **4c** phenyl ring of MPA is oriented in the 1*R*,2*R*,3*R*,5*S* isomer towards C-1 and C-8, which are shifted together with their H-atoms to high field. In another enantiomeric lactone the characteristic mutual influence of two phenyl rings is observed: all ^{13}C and ^1H atoms are shifted to high field, thus giving additional confirmation for the assignment of the absolute configurations of the enantiomers of **4c**.

4.7. ^1H and ^{13}C NMR spectra of (R)-O-methylphenylacetic acid ester of lactones 4b and 4c

4b: *R*-MPA ester of 1*R*,2*S*,3*R*,5*S* isomer, from C-1 to C-8, δ^1H: 3.07, 2.95, 5.24, 2.60(x)/2.17(n), 5.13, 2.71(x)/2.18(n); $\delta^{13}C$: 43.17, 56.70, 80.69, 37.29, 83.18, 176.14, 34.88, 2-Ph: 138.42(s), 127.26(o), 128.69(m), 127.36(p), MPA: 170.00, 82.24, 57.18, 135.73, 127.15, 128.81, 128.94. *R*-MPA ester of 1*S*,2*R*,3*S*,5*R* isomer, from C-1 to C-8, δ^1H: 3.06, 3.15, 5.23, 2.59/1.89, 5.08, 2.80/2.48; $\delta^{13}C$: 43.52, 56.39, 80.35, 37.09, 82.84, 175.99, 33.91, 2-Ph: 137.86, 127.33, 128.64, 127.56, MPA: 170.17, 82.41, 57.18, 135.65, 127.10, 128.75, 128.77.

4c: *R*-MPA ester of 1*R*,2*R*,3*R*,5*S* isomer, from C-1 to C-8, δ^1H: 3.29, 5.15, 3.26, 2.03(x)/2.33(n), 5.01, 2.09(x)/1.93(n), 3-Ph: 7.21(o), 7.33(m), 7.28(p); $\delta^{13}C$: 39.30, 79.03, 45.19, 36.75, 81.99, 176.43,

27.74, 3-Ph: 138.22, 127.16, 128.78, 127.38, MPA: 170.01, 82.09, 57.06, 135.75, 127.18, 128.92, 129.25. *R*-MPA ester of 1*S*,2*S*,3*S*,5*R* isomer, from C-1 to C-8, δ^1H: 3.39, 5.04, 3.22, 2.04(x)/2.33(n), 5.09, 2.55(x,n), 3-Ph: 6.97(o), 7.17(m), 7.18(p); δ^{13}C: 39.62, 79.75, 45.36, 36.03, 82.45, 176.48. 28.70, 3-Ph: 138.05, 126.98, 128.57, 127.12, MPA: 170.18, 82.24, 57.27, 135.54, 126.85, 128.65, 128.78.

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