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Recyclable hafnium(IV) bis(perfluorooctanesulfonyl)amide complex for catalytic Friedel–Crafts acylation and Prins reaction in fluorous biphase system

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Abstract

In fluorous biphase system, hafnium(IV) bis(perfluorooctanesulfonyl)amide complex ($Hf[N(SO_2C_8F_{17})_2]_4$) was found to be a highly reactive and recyclable Lewis acid catalyst for Friedel–Crafts acylation and Prins reaction at significantly low catalyst loadings ($\leq$1 mol%). In these reactions, $Hf[N(SO_2C_8F_{17})_2]_4$ is selectively soluble in the lower fluorous phase and can be recovered simply by phase separation. Furthermore, the catalyst can be reused without decrease of activity.

Keywords: Fluorous biphase system; Bis(perfluorooctanesulfonyl)amide; Hafnium; Friedel–Crafts acylation; Prins reaction

1. Introduction

Recently, much interest has been devoted to the development of highly efficient Lewis acid catalyst for a variety of carbon–carbon bond forming reactions, and the pace of growth in this field of chemistry has been breathtaking [1]. However, the need for high loading and separation of the Lewis acid catalyst from the product are still the issues that need to be addressed in this area [2].

Fluorinated Lewis acid catalysts are a topic of growing interest because of their increasing Lewis acidity and fluorous solvent immobilization. In particular, the value of the phase separation and catalyst recyclability under fluorous biphase system (FBS) are well recognized [3], extended and developed for Green and Sustainable Chemistry (GSC), such as 3,5-bis(perfluorodecyl)phenylboronic acid-catalyzed FBS amide condensation and fluoroalkyldistannoxane-catalyzed FBS esterification [4,5].

We have recently introduced $Sn[N(SO_2C_8F_{17})_2]_4$ and $Hf[N(SO_2C_8F_{17})_2]_4$ as efficient FBS Lewis acid catalysts for several useful synthetic reactions such as Baeyer–Villiger oxidation [6], esterification [7], Friedel–Crafts acylation [8] and Prins reaction [9]. In these reactions, we have also demonstrated that these amide complexes are found to be far superior to the corresponding trifluoromethanesulfonate complexes, and that they can be easily recovered from the reaction mixture and can be reused in most cases. A key factor to accomplish the catalytic processes was ascribed to the use of long-enough perfluorinated $–N(SO_2C_8F_{17})_2$ ligand (not partially fluorinated ligand), whose structural characteristic can coordinate with a variety of metal cations to obtain the desired Lewis acid catalysts with appropriate catalytic activity, as well as the selective immobilization in the fluorous phase.

This paper reports our further results on Friedel–Crafts acylation and Prins reaction catalyzed by $Hf[N(SO_2C_8F_{17})_2]_4$ Lewis acid catalyst in FBS. Not only the fluorous activity comparison of $Hf[N(SO_2C_8F_{17})_2]_4$ and $Hf(OSO_2CF_3)_4$ for Friedel–Crafts acylation is first described, some mechanistic findings for Prins reaction are also presented.

2. Results and discussion

$Hf[N(SO_2C_8F_{17})_2]_4$ has been introduced as a highly active catalyst at low 1 mol% catalyst loadings for Friedel–Crafts acylation using anhydride as acylating agents [8]. During the course of our work in FBS, in addition to developing active

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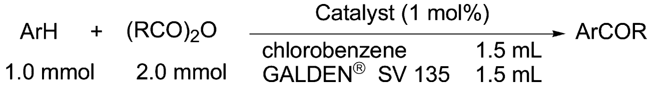
catalysts, we are more concerning the recyclability of catalysts. At first, $Hf[N(SO_2C_8F_{17})_2]_4$ was investigated using our previously described optimized conditions. As shown in Table 1, in all cases, $Hf[N(SO_2C_8F_{17})_2]_4$ can be reused simply by phase separation and showed a relatively better recyclability than $Hf(OSO_2CF_3)_4$, i.e., $Hf[N(SO_2C_8F_{17})_2]_4$ could be immobilized in the lower fluorous phase and directly reused more than three times, whereas $Hf(OSO_2CF_3)_4$ couldn't be recycled owing to its distribution in the upper chlorobenzene phase. This result can be attributed to the presence of the powerfully electron-withdrawing $–N(SO_2C_8F_{17})_2$ ligand bearing the higher fluorine loadings: the affinity with the fluorous solvent was increased so the fluorous phase immobilization was increased [10].

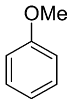
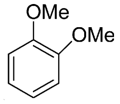
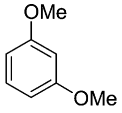
The fluorous biphase $Hf[N(SO_2C_8F_{17})_2]_4$ system was also evaluated and compared with $Hf(OSO_2CF_3)_4$, using the Prins reaction of α-methylstyrene with paraformaldehyde under the mild conditions of 35 °C for 0.5 h. As summarized in Table 2, a catalyst loading of 0.5 mol% turned out to be ideal. The use of a lower catalyst/α-methylstyrene ratio led to longer reaction time or to incomplete conversion. Unlike the above described Friedel–Crafts acylation, $Hf[N(SO_2C_8F_{17})_2]_4$ could no longer give higher activity than $Hf(OSO_2CF_3)_4$, but it gave significantly better recyclability than $Hf(OSO_2CF_3)_4$, i.e., $Hf[N(SO_2C_8F_{17})_2]_4$ could be immobilized in the lower fluorous phase and directly reused 17 times with yields consistently above 80%, whereas $Hf(OSO_2CF_3)_4$ could be reused only for 3 times owing to its distribution in the upper 1,2-dichloroethane phase.

Since the final aim of our ongoing studies was expected to apply this FBS to industrial process, using our fluorous biphase $Hf[N(SO_2C_8F_{17})_2]_4$ system we examined the Prins reaction between α-methylstyrene and paracetaldehyde to produce the corresponding industrial fragrance 2,4,6-trimethyl-4-phenyl-1,3-dioxanes, which has been employed for more than 20 years as an aromatic substance and sold under the names VERTACETAL® (manufacture: Symrise GmbH & Co. KG, Holzminden) [11]. The reaction optimization was first carried out. Fig. 1 shows the effect of $Hf[N(SO_2C_8F_{17})_2]_4$ amount. It was found a significant increase of yield was observed when the catalyst loadings was increased from 0.05 to 0.15 mol%, but further increase (over 0.15 mol%) resulted in gradual degrease. Fig. 2 shows the effect of reaction time. As can be seen, the long-time yield leveled off or increased slightly. In addition, the

Table 1
Fluorous biphase Friedel–Crafts acylation



$$\underset{1.0\text{ mmol}}{ArH} + \underset{2.0\text{ mmol}}{(RCO)_2O} \xrightarrow[\substack{\text{chlorobenzene 1.5 mL} \\ \text{GALDEN® SV 135 1.5 mL}}]{\text{Catalyst (1 mol\%)}} ArCOR$$

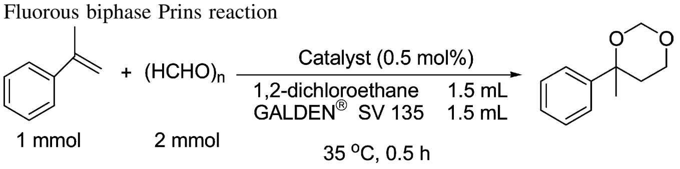
Entry	ArH	R	Conditions (°C, h)	Catalyst	Cycle[a]	Product[b] and yield (%)[c]
1		Me	100, 1	$Hf[N(SO_2C_8F_{17})_2]_4$	1	**1**, 80
					2	**1**, 81
					3	**1**, 79
					4	**1,** 78
					5	**1,** 80
				$Hf(OSO_2CF_3)_4$	1	**1**, 48
					2	**1**, 10
		n-C_3H_7	90, 1	$Hf[N(SO_2C_8F_{17})_2]_4$	1	**2**, 72
					2	**2**, 73
					3	**2**, 71
				$Hf(OSO_2CF_3)_4$	1	**2**, 44
					2	**2**, 6
		Ph	120, 2	$Hf[N(SO_2C_8F_{17})_2]_4$	1	**3**, 87
					2	**3**, 87
					3	**3**, 88
				$Hf(OSO_2CF_3)_4$	1	**3**, 30
					2	**3**, 8
2		Me	90, 1	$Hf[N(SO_2C_8F_{17})_2]_4$	1	**4**, 91
					2	**4**, 90
					3	**4**, 89
				$Hf(OSO_2CF_3)_4$	1	**4**, 39
					2	**4**, 4
3		Me	70, 1	$Hf[N(SO_2C_8F_{17})_2]_4$	1	**5**, 93
					2	**5**, 94
					3	**5**, 90
				$Hf(OSO_2CF_3)_4$	1	**5**, 35
					2	**5**, 8

[a] Cycle numbers of the lower fluorous catalyst phase.

[b] **1**, p-methoxyacetophenone; **2**, p-methoxybutyrophenone; **3**, p-methoxybenzophenone; **4**, 3,4-dimethoxyacetophenone; **5**, 2,4-dimethoxyacetophenone.

[c] Isolated yield after chromatography and determined by GC/MS and ^1H NMR analysis.

Table 2
Fluorous biphase Prins reaction



Entry	Catalyst	Cycle[a]	Conversion (%)[b]	Yield (%)[c]
1	$Hf[N(SO_2C_8F_{17})_2]_4$	1	95	87
		2	97	87
		3	97	85
		4	96	85
		5	100	86
		6–17	94–100	80–85
		18	94	73
		19	93	74
		20–25	80–86	60–66
2	$Hf(OSO_2CF_3)_4$	1	99	75
		2	92	84
		3	92	86
		4	85	58
		5	72	37
		6	51	10

Paraformaldehyde (60 mg, corresponding to 2 mmol equivalents of formaldehyde) was used as formaldehyde source.

[a] Cycle numbers of the lower fluorous catalyst phase.

[b] Conversion of α-methylstyrene.

[c] Yields were determined by calibrated quantitative GC and GC/MS analysis using *n*-tridecane as an internal standard.

yield was the highest at 10 °C and then decreased as the reaction temperature increased or decreased from 10 °C under the identical reaction conditions. These results manifested that, as the reaction proceeded, paracetaldehyde gradually decreased and acetaldehyde became the main acetaldehyde source (reacted for 2 h or over 0.15 mol% catalyst loadings was used), and the reaction became very slow. The generally accepted mechanism of the Prins reaction is that the reaction proceeds through the initially formed monomeric acetaldehyde by the interaction of paraldehyde with catalyst. This step is followed by the subsequent addition of the olefin to activated acetaldehyde and cyclization with another molecule of acetaldehyde. Here, we decided to present a different concept that involves initial activation of the paracetaldehyde, followed the direct reaction with α-methylstyrene. From this hypothesis, the slow rate observed in the increased catalyst amount or the prolonged time could become reasonable because paracetaldehyde almost disappeared to monomeric acetaldehyde. This was confirmed by the fact that a reaction conducted under identical conditions using acetaldehyde instead of paracetaldehyde led to much slow reaction rate.

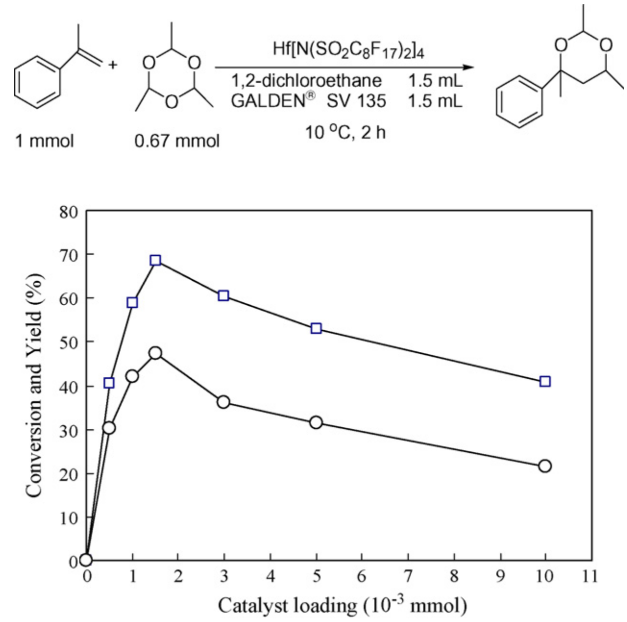


Fig. 1. Effect of $Hf[N(SO_2C_8F_{17})_2]_4$ catalyst loading on the conversion (□) of α-methylstyreneand and yield (○) in the reaction of α-methylstyrene with paracetaldehyde to VERTACETAL®.

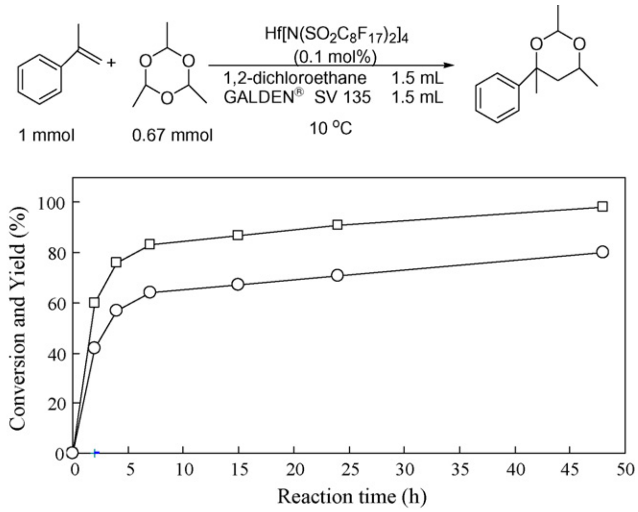
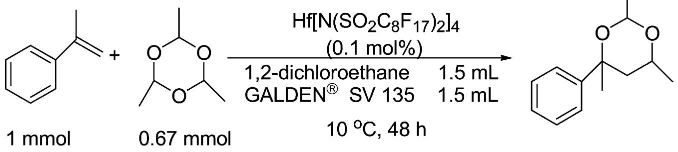


Fig. 2. Effect of reaction time on the conversion (□) of α-methylstyrene and yield (○) in the reaction of α-methylstyrene with paracetaldehyde to VERTACETAL®.

The possibility of recycling $Hf[N(SO_2C_8F_{17})_2]_4$ catalyst for the synthesis of VERTACETAL® was also investigated. As shown in Table 3, even after $Hf[N(SO_2C_8F_{17})_2]_4$ catalyst was recycled eight times, the GC conversion and GC yield remained at a constant level, giving the eighth reaction cycle's turnover numbers (TONs, calculated using the yield of 2,4,6-trimethyl-4-phenyl-1,3-dioxanes) of 6220 [12], which was a relatively high result of the use of Lewis acid as catalysts. In addition, the product was obtained as a mixture of isomers 2,4,6-trimethyl-4-phenyl-1,3-dioxanes, which contains the isomer (2*RS*,4*SR*,6*RS*)-2,4,6-trimethyl-4-phenyl-1,3-dioxane, (2*RS*,4*RS*,6*RS*)-2,4,6-trimethyl-4-phenyl-1,3-dioxane and (2*RS*,4*SR*,6*SR*)-2,4,6-trimethyl-4-phenyl-1,3-dioxane, and there is no considerable difference for ratio of isomers in each cycle. For example, the product obtained in the sixth reaction cycle was characterized by GC/MS, ^1H and ^{13}C NMR and also by comparison with authentic sample, which exhibited the following compositional distribution: 52.5% (2*RS*,4*SR*,6*RS*)-2,4,6-trimethyl-4-phenyl-1,3-dioxane, 45.9% (2*RS*,4*RS*,6*RS*)-2,4,6-trimethyl-4-phenyl-1,3-dioxane and 1.6% (2*RS*,4*SR*,6*SR*)-2,4,6-trimethyl-4-phenyl-1,3-dioxane.

Table 3
Prins reaction of α-methylstyrene with paracetaldehyde to VERTACETAL®



Cycle[a]	Conversion (%)[b]	Yield (%)[c,d]
1	97	80
2	96	80
3	94	79
4	96	79
5	95	80
6	93	79
7	94	78
8	85	67

[a] Cycle numbers of the lower fluorous catalyst phase.

[b] Conversion of α-methylstyrene.

[c] Yields were determined by calibrated quantitative GC and GC/MS analysis using *n*-tridecane as an internal standard.

[d] Combined yields of isomers.

3. Conclusion

Fluorous biphase $Hf[N(SO_2C_8F_{17})_2]_4$ complex is an extremely effective and recyclable Lewis acid catalyst for Friedel–Crafts acylation and Prins reaction. Easy recycle and reuse of this FBS technique is expected to contribute to the development of industrial application process, e.g., the manufacture of 1,3-dioxanes.

4. Experimental

4.1. General

^1H, ^{13}C and ^{19}F NMR spectra were recorded on a JEOL JNM-ECA600 (600 MHz) instrument using tetramethylsilane (δ 0.00), chloroform-*d* (δ 77.0) and α,α,α-trifluorotoluene (δ −63.20) as internal standards, respectively. GC analysis was carried out on a SHIMADZU GC-1700AF. GC/MS measurement was performed on a Hewlett-Packard G1800A GLS. Atomic emission spectra were taken on IRIS/AP (Nippon Jarrell Ash Co.). Products after isolation were qualitatively identified by GC/MS, ^1H and ^{13}C NMR, and quantitatively analyzed by GC.

$$CF_3\{[O{-}CF(CF_3){-}CF_2]_n{-}(O{-}CF_2)_m\}{-}O{-}CF_3$$

Structure of GALDEN® SV 135 (Solvay Solexis K.K.).

All products listed in Table 1 are commercially available.

4.2. Synthesis of bis(perfluorooctanesulfonyl)amine

The preparation of $(C_8F_{17}SO_2)_2NH$ was performed in three steps.

- *Step 1: preparation of perfluorooctanesulfonamide*. To liquid NH_3 (ca. 130 ml) was added perfluorooctanesulfonyl fluoride (36.7 g, 73 mmol) at −78 °C. After the stirring was held at the constant temperature (−78 °C) for about 1.5 h, it was then continued at room temperature for 1.5 h. The resulting white slurry was acidified to pH of about 2 with 1 M H_2SO_4 and then extracted into diisopropyl ether (100 ml). The diisopropyl ether layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and dried in vacuum at 80 °C/0.01 mmHg for 16 h to give the cream residue of $C_8F_{17}SO_2NH_2$ (94% yield).
- *Step 2: preparation of triethylammonium bis(perfluorooctanesulfonyl)amide*. To a mixture of perfluorooctanesulfonamide (34.4 g, 69 mmol) and Et_3N (60 ml) was added perfluorooctanesulfonyl fluoride (36.0 g, 72 mmol). This mixture was refluxed for 23 h, cooled to room temperature, and the resulting biphase system was separated. After the upper Et_3N layer was removed, the lower brown fluorous layer was washed with 10% HCl to yield the brown solid, which was finally dried in vacuum at 70 °C/0.01 mmHg for 6 h to afford $(C_8F_{17}SO_2)_2N\ HNEt_3$ as crude form.
- *Step 3: preparation of bis(perfluorooctanesulfonyl)amine*. A mixture of the above crude $(C_8F_{17}SO_2)_2N\ HNEt_3$, EtOH (612 ml) and H_2O (68 ml) was introduced into ion exchange resins column (Amberlite IR-120B), and the eluate was concentrated under reduced pressure to give a white solid, which was finally sublimed in vacuum at 120–160 °C/0.02 mmHg to give white powders of $(C_8F_{17}SO_2)_2NH$ in 62% yield (42.8 g). ^{19}F NMR: δ −126.2 (s, 4F), −119.8 to −124.2 (m, 20F), −114.0 (s, 4F), −81.2 (s, 6F); IR (KBr) 3374, 1371, 1334, 1221, 1150, 1089, 987, 943, 815, 745, 648 cm^{-1}. Calcd. for $(C_8F_{17}SO_2)_2NH$: C, 19.58; F, 65.83; N, 1.43; Found: C, 19.60; F, 65.91; N, 1.39.

4.3. Synthesis of hafnium(IV) bis(perfluorooctanesulfonyl)amide

To a solution of $HN(SO_2C_8F_{17})_2$ (5.9 g, 6.0 mmol) in anhydrous methanol (10 ml) was added hafnium(IV) chloride (0.5 g, 1.5 mmol). This mixture was stirred continuously at 50 °C for 15 h. After being cooled to room temperature, the mixture was evaporated and dried at 80 °C/0.01 mmHg for 16 h to give white powders of hafnium(IV) bis(perfluorooctanesulfonyl)amide complex in 97% yield (6.0 g). ^{19}F NMR: δ −126.2 (s, 8F), −120.1 to −124.0 (m, 40F), −114.2 (s, 8F), −81.5 (s, 12F); IR (KBr) 3401, 1641, 1333, 1206, 1152, 1088, 987, 945, 816, 736, 627 cm^{-1}. Calcd. for $Hf[N(SO_2C_8F_{17})_2]_4$: C, 18.75; Hf, 4.35, F, 43.03; N, 1.37; Found: C, 18.65; Hf, 4.33, F, 44.06; N, 1.34.

4.4. Typical procedure for $Hf[N(SO_2C_8F_{17})_2]_4$-catalyzed Friedel–Crafts acylation

To a mixture of GALDEN® SV 135 (1.5 ml) and chlorobenzene (1.5 ml) were added $Hf[N(SO_2C_8F_{17})_2]_4$ (41.0 mg, 0.01 mmol), anisole (108.1 mg, 1.0 mmol) and acetic anhydride (204.2 mg, 2.0 mmol). The reaction mixture was stirred continuously at 100 °C for 1 h. Once the stirring was stopped, the reaction mixture settled down at room temperature and turned into two liquid phases within 5 min, i.e., an upper chlorobenzene and a lower SV 135 phase. Pure *p*-methoxyacetophenone was obtained from the upper phase after silica gel chromatography (120.1 mg, 80% isolated yield). The lower fluorous phase containing the catalyst was reused in the subsequent recycling reactions, to which chlorobenzene (1.5 ml), anisole (108.1 mg, 1.0 mmol) and acetic anhydride (204.2 mg, 2.0 mmol) were added, respectively. The other operations and procedure (e.g., stirring at 100 °C for 1 h, product separation) were the same as described above for the first cycle. Such a procedure was repeated further four times. Substantially, the yields of *p*-methoxyacetophenone were 81%, 79%, 78% and 80% in the succeeding four times, respectively. In addition, about 1.0 wt.% leaching of $Hf[N(SO_2C_8F_{17})_2]_4$ catalyst into the chlorobenzene phase was observed (determined by atomic emission spectrometry) on each cycle, and 94% of $Hf[N(SO_2C_8F_{17})_2]_4$ remained in the flask after the fifth run.

4.5. Typical procedure for $Hf[N(SO_2C_8F_{17})_2]_4$-catalyzed Prins reaction

To a mixture of GALDEN® SV 135 (1.5 ml) and 1,2-dichloroethane (1.5 ml) were added $Hf[N(SO_2C_8F_{17})_2]_4$ (20.5 mg, 0.005 mmol), α-methylstyrene (118.2 mg, 1.0 mmol), paraformaldehyde (60.0 mg, corresponding to 2 mmol equivalents of formaldehyde). The mixture was stirred at 35 °C for 0.5 h. Once the stirring was stopped, the mixture settled down at room temperature and turned into two liquid phases, i.e., an upper 1,2-dichloroethane and a lower SV 135 phase. The upper 1,2-dichloroethane phase was evaporated to give a crude oil. The crude product was purified by commercially available TLC (silica gel) to afford pure 4-methyl-4-phenyl-1,3-dioxane product (153.9 mg, 0.86 mmol), which was characterized by GC/MS, ^{1}H and ^{13}C NMR. The lower fluorous phase containing the catalyst was reused in the subsequent recycling reactions, to which 1,2-dichloroethane (1.5 ml), α-methylstyrene (118.2 mg, 1.0 mmol), paraformaldehyde (60.0 mg, 2.0 mmol) were added, respectively. The other operations and procedure (e.g., stirring at 35 °C for 0.5 h, product separation) were the same as described above for the first cycle. Such a procedure was repeated further 25 times, and the yields were as described above in Table 2. In addition, a 0.8 wt.% leaching of $Hf[N(SO_2C_8F_{17})_2]_4$ catalyst into 1,2-dichloroethane phase was observed (determined by atomic emission spectrometry) in the first cycle, and 85% of $Hf[N(SO_2C_8F_{17})_2]_4$ remained in the flask after the 15th cycle. The catalyst recover studies are still under progress.

4.5.1. 4-Methyl-4-phenyl-1,3-dioxane

^{1}H NMR ($CDCl_3$): δ 1.45 (s, 3H), 2.10–2.30 (m, 2H), 3.65 (dt, 1H, $J = 2.4$, 11.0 Hz), 3.90–3.95 (m, 1H), 4.75 (d, 1H, $J = 6.5$ Hz), 4.90 (d, 1H, $J = 6.5$ Hz), 7.21–7.30 (m, 1H), 7.29–7.37 (m, 2H), 7.42–7.46 (m, 2H).

^{13}C NMR ($CDCl_3$): δ 32.1, 35.0, 63.5, 75.7, 89.1, 125.7, 127.0, 128.6, 144.1.

4.5.2. (2RS,4SR,6RS)-2,4,6-Trimethyl-4-phenyl-1,3-dioxane

^{1}H NMR ($CDCl_3$): δ 1.21 (d, $J = 6.5$ Hz, 3H), 1.33 (d, $J = 5$ Hz, 3H), 1.40 (s, 3H), 1.67 (dd, $J = 11.5$ Hz, $J = 14$ Hz, 1H), 2.32 (dd, $J = 2$ Hz, $J = 14$ Hz, 1H), 3.65 (ddq (12 lines), $J = 2$ Hz, $J = 11.5$ Hz, $J = 6.5$ Hz, 1H), 4.70 (q, $J = 5$ Hz, 1H), 7.19–7.26 (m, 1H), 7.31-7.37 (m, 4H).

^{13}C NMR ($CDCl_3$): δ 21.1, 21.6, 34.3, 41.0, 68.9, 76.4, 93.6, 125.8, 126.8, 128.6, 144.4.

4.5.3. (2RS,4RS,6RS)-2,4,6-Trimethyl-4-phenyl-1,3-dioxane

^{1}H NMR ($CDCl_3$): δ 1.22 (d, $J = 6$ Hz, 3H), 1.41 (d, $J = 5$ Hz, 3H), 1.58 (s, 3H), 1.60 (dd, $J = 11.5$ Hz, $J = 13$ Hz, 1H), 1.79 (dd, J = 2.5 Hz, $J = 13$ Hz, 1H), 4.00 (ddq [12 lines], $J = 2.5$ Hz, $J = 11.5$ Hz, $J = 6$ Hz, 1H), 5.18 (q, $J = 5$ Hz, 1H), 7.18–7.25 (m, 1H), 7.29–7.37 (m, 2H), 7.42–7.46 (m, 2H).

^{13}C NMR ($CDCl_3$): δ 21.6, 21.8, 23.2, 43.6, 68.5, 74.5, 92.2, 123.9, 126.6, 128.1, 148.9.

4.5.4. (2RS,4SR,6SR)-2,4,6-Trimethyl-4-phenyl-1,3-dioxane

^{1}H NMR ($CDCl_3$): δ 1.15 (d, $J = 6.5$ Hz, 3H), 1.37 (d, $J = 5$ Hz, 3H), 1.48 (s, 3H), 2.16 (dd, [B-part of an AB Specturm]), $J = 8$ Hz, $J = 14$ Hz, 1H), 2.19 (dd [A-part of an AB Specturm]), $J = 5$ Hz, $J = 14$ Hz, 1H), 4.26 (ddq [14 lines]), $J = 5$ Hz, $J = 8$ Hz, $J = 14$ Hz, 1H), 5.01 (q, $J = 5$ Hz, 1H), 7.22–7.29 (m, 1H), 7.33–7.38 (m, 4H).

^{13}C NMR ($CDCl_3$): δ 21.4, 21.9, 29.3, 42.2, 68.6, 75.3, 92.9, 124.5, 126.8, 128.4, 147.9.

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