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Cesium fluoride-Celite: a solid base for efficient syntheses of aromatic esters and ethers

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Abstract—Coupling reactions of a number of aromatic and heteroaromatic phenols with alkyl, acyl or benzoyl halides in acetonitrile with cesium fluoride-Celite are described, demonstrating that this reagent provides an efficient, convenient and practical method for the syntheses of aromatic esters and ethers.

1. Introduction

Numerous naturally occurring as well as synthetically and biologically interesting compounds like nucleosides, carbohydrates, carbocycles, steroids, alkaloids etc. have hydroxyl functions as part of their structures. Several reactions, that is, oxidations, halogenations or dehydrations of these compounds need a protection of their hydroxyl groups to increase yields and reduce undesired side reactions. A wide variety of methods for the protection of alcohols are well documented, and their protection as esters or ethers are among the most used methods in organic synthesis for this purpose.[1] However, these procedures often suffer from serious limitations, especially, if acid or base labile moieties are an inherent part of the substrates.

A variety of organic reactions have recently been reported to be catalysed by cesium fluoride-Celite. The syntheses of carboxylic esters,[2] γ-lactones,[3] *N*-alkylation of anilines, carboxamides, and nitrogen heterocyclic compounds,[4] and ring opening of epoxides[5] are among the reactions which are facilitated. Moreover, in a recent publication, Kitaori[6] et al. reported the synthesis of enantiopure 2-hydroxymethyl-1,4-benzodioxane derivatives catalysed by cesium fluoride. In previous publications, Clark and Miller[7–9] recognized the importance of the fluoride ion as a catalyst for the promotion of various types of base-catalyzed reactions. Moreover, their work revealed,[10–12] that the fluoride ion effects the coupling reaction because of its high capability of hydrogen-bond formation. As reagents generating fluoride ions, potassium,[7] cesium[2,3] or tetraalkylammonium fluorides[13] were used so far. However, it is not easy to handle these hygroscopic reagents and the reproducibility of these reactions is invariably poor. In a recent communication,[2] poorly hygroscopic reagents generating fluoride ions were designed by allowing cesium fluoride to be absorbed on Celite. The effect of cesium fluoride-Celite might be twofold:[14] (a) activation of the hydroxyl group by the fluoride ion whose ionic character is large owing to the low charge/surface area ratio of the cesium cation[15] and (b) activation of the alkyl or acyl halide groups by the Lewis acid type effect.

We very recently described the syntheses of thioesters, thioethers, and symmetrical disulfides using CsF-Celite as a solid base.[16] In extension of our research on the reactivity of CsF-Celite, we wish to report on a practical and convenient method for the preparation of esters and ethers using the same reagent and demonstrate that our method overcomes various limitations which often occur during the formation of esters and ethers (see above).

2. Results and discussion

The CsF-Celite-assisted coupling of aromatic hydroxyl groups with various alkyl, acyl or benzoyl halides resulted in alkylation, acylation, benzylation and benzoylation

Keywords: Cesium fluoride-Celite; Alcohols; Esters; Ethers.
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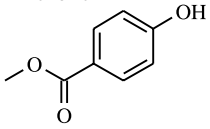
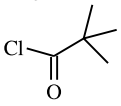
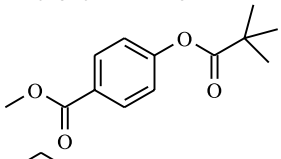
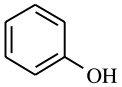
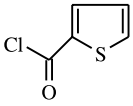
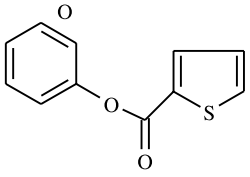
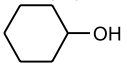
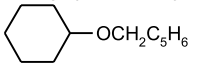
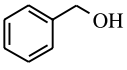
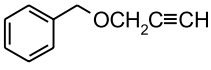
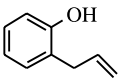
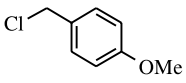
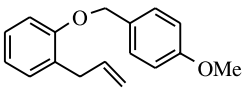
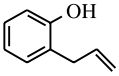
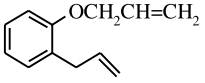
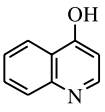
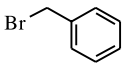
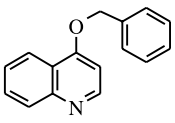
Table 1. *O*-Acylation of hydroxyl functions of selected phenols using CsF-Celite

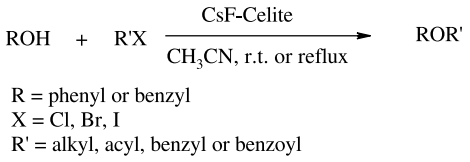
Entry	Substrate	Reagent	Product	Compound	% Yield	Physical state mp (mp, lit.) °C
1	C_6H_5OH	CH_3COCl	$C_6H_5O_2CCH_3$	**1**	89[a]	Liquid[17]
2	C_6H_5OH	C_6H_5COCl	$C_6H_5O_2CC_6H_5$	**2**	88[b]	68–70 (68–69)[18]
3	C_6H_5OH	4-$NO_2C_6H_4COCl$	4-$NO_2C_6H_4CO_2C_6H_5$	**3**	84[a]	128–129, (128–129)[19]
4	$C_6H_5CH_2OH$	C_6H_5COCl	$C_6H_5CH_2O_2CC_6H_5$	**4**	78[a]	Liquid[20]
5	$CH_3(CH_2)_4OH$	$CH_3(CH_2)_2COCl$	$CH_3(CH_2)_4O_2C(CH_2)_2CH_3$	**5**	5[b]	Liquid
6	2-$NO_2C_6H_4OH$	4-$CH_3OC_6H_4COCl$	2- $NO_2C_6H_4O_2CC_6H_4CH_3O$-4	**6**	76[b]	96–98, (96.5–97.5)[19]
7	4-$NO_2C_6H_4OH$	4-$CH_3OC_6H_4COCl$	4-$NO_2C_6H_4O_2CC_6H_4CH_3O$-4	**7**	81[b]	168–169, (165–166)[19]
8	4-$C_6H_5C_6H_4OH$	C_6H_5COCl	4-$C_6H_4C_6H_4O_2CC_6H_5$	**8**	63[b]	150–152, (149–150.5)[21]
9	2-$C_6H_5C_6H_4OH$	$CH_3O_2CCH_2CH_2$-COCl	2-$C_6H_5C_6H_4O_2CCH_2CH_2CO_2CH_3$	**9**	59[b]	Liquid[22]
10	4-$C_6H_5C_6H_4OH$	CH_3COCl	4-$C_6H_5C_6H_4O_2CCH_3$	**10**	78[b]	87–88, (87–88)[23]
11				**11**	82[b]	Liquid
12				**12**	73[b]	44–45, (44–46)[18]

[a] Room temp.
[b] Reflux at 82 °C.

Table 2. *O*-Alkylation of hydroxyl functions of selected phenols using CsF-Celite

Entry	Substrate	Reagent	Product	Compound	% Yield	Physical state mp (mp, lit.) °C
1	C_6H_5OH	$C_6H_5CH_2Br$	$C_6H_5OCH_2C_6H_5$	**13**	91[a]	39–40, (38)[24]
2	C_6H_5OH	CH_2=$CHCH_2Br$	$C_6H_5OCH_2CH$=CH_2	**14**	77[b]	Liquid[25]
3	C_6H_5OH	4-$NO_2C_6H_4CH_2Cl$	4-$NO_2C_6H_4CH_2OC_6H_5$	**15**	71[b]	90–91, (89–91)[26]
4	$C_6H_5CH_2OH$	4-$NO_2C_6H_4CH_2Br$	4-$NO_2C_6H_4CH_2OCH_2C_6H_5$	**16**	82	Liquid[27]
5	3,5-$(CH_3O)_2C_6H_3OH$	$CNCH_2CH_2Br$	3,5-$(CH_3O)_2C_6H_3OCH_2CH_2CN$	**17**	67[b]	Liquid
6	$CH_3(CH_2)_4OH$	$CH_3(CH_2)_3Cl$	$CH_3(CH_2)_4O(CH_2)_3CH_3$	**18**	9[b]	Liquid
7	2-$C_6H_5C_6H_4OH$	CH_2=$CHCH_2Br$	2-$C_6H_5C_6H_4OCH_2CH$=CH_2	**19**	62[b]	Liquid[28]
8	4-$C_6H_5C_6H_4OH$	$CH_3CH_2O_2CCH_2I$	4-$C_6H_5C_6H_4OCH_2CO_2CH_2CH_3$	**20**	89[b]	60–61, (60)[29]
9	4-$C_6H_5C_6H_4OH$	$C_2H_5O_2CCH$=$CHCH_2Br$	4-$C_6H_5C_6H_4OCH_2CH$=$CHCO_2C_2H_5$	**21**	64[b]	69–70
10	4-$NO_2C_6H_4OH$	4-$NO_2C_6H_4CH_2Br$	4-$NO_2C_6H_4OCH_2C_6H_4NO_2$-4	**22**	85[b]	187, (187.4)[30]
11	2,6-$(tbu)_2C_6H_3OH$	$C_6H_5CH_2Cl$	2,6-$(tbu)_2C_6H_3OCH_2C_6H_5$	**23**	88[b]	Liquid
12	4-$NO_2C_6H_4OH$	$C_6H_5CH_2Br$	4-$NO_2C_6H_4OCH_2C_6H_5$	**24**	75	102–105, (105–107)[26]
13	4-$CH_3C_6H_4OH$	4-$NO_2C_6H_4CH_2Cl$	4-$CH_3C_6H_4OCH_2C_6H_4NO_2$-4	**25**	92	92–94, (92–93)[26]
14		$C_6H_5CH_2Br$		**26**	18[b]	Liquid[31]
15		CH≡CCH_2Br		**27**	60	Liquid[32]
16				**28**	54[b]	Liquid
17		CH_2=$CHCH_2Br$		**29**	68[b]	Liquid[33]
18				**30**	81[b]	Liquid[34]

[a] Room temp.
[b] Reflux at 82 °C.



Scheme 1.

(Tables 1 and 2). A mixture of phenol (1.0 mol), CsF-Celite (1.5 mol) and alkyl halide (2.0 mol) in acetonitrile is stirred at room temperature or under reflux, and after completion of the reaction (monitored through TLC), it afforded alkylated products in good yields (Scheme 1). Coupling of 3,5-dimethoxyphenol with 3-bromopropionitrile in DMF or acetonitrile resulted in the formation of 3-(3,5-dimethyoxy-phenoxy)propionitrile (**17**) in equally good yields, clearly indicating that the activity of CsF-Celite is not solvent-dependent. Similarly, a variety of phenols underwent efficient and clean coupling reactions at room temperature or under reflux with acyl or benzoyl halides in the presence of CsF-Celite as a solid base.

To generalize our synthetic methodology, we have synthesized twelve esters and 18 ethers (Tables 1 and 2) under the present reaction conditions (given in the Section 3). All synthesized compounds were characterized through different spectroscopic techniques and their elemental analyses.

The reactions catalyzed by cesium fluoride-Celite are usually carried out under mild conditions with good yields and simple work up: only filtration is required to remove the catalyst and evaporation of the filtrate affords the pure products. In a previous short communication[2] esters of acids were prepared from carboxylic acids and alkyl halides via CsF-Celite catalysis, however, the utility of this solid base under the same reaction conditions for the protection of an alcohol as an ether was overlooked. Besides, we investigated the CsF-Celite-mediated reaction of 4-hydroxybenzoic acid with benzyl bromide to compare the reactivity of the hydroxyl functions of phenols and carboxylic acids and found that due to the higher acidity of the carboxyl group it afforded benzyl 4-hydroxybenzoate in 95%, whereas benzyl 4-benzyloxy-benzoate was obtained in less than 5% yield only. Furthermore, when aliphatic alcohols and ordinary alkyl halides were reacted, unsatisfactory results were obtained (Table 1 entry 5, Table 2 entry 6 and 14). This might be due to less activity of aliphatic alcohols as compared to aromatic hydroxyls, as the phenyl residues excert electron-withdrawing properties due to its mesomeric effect. Similarly, ordinary alkyl halides were less active than allylic, benzylic, and vinylic alkyl halides due to their resonance effects. However, as described in our recent communication, very good results were obtained in case of etherification and esterification of aliphatic thiols by reacting with alkyl halides via the present reaction conditions.[16] In this way, we extended the utility of CsF-Celite as an efficient, inexpensive, non-corrosive and environmentally friendly reagent for the protection of hydroxyl functions by ethers as well as esters.

3. Experimental

3.1. General information

Melting points were determined with a Büchi SMP-20 apparatus and are uncorrected. IR spectra (KBr discs) were recorded on a Bruker FT-IR IFS 48 spectrometer and EI mass spectral data on a Varian MAT 711 (70 eV) spectrometer (data are tabulated as *m/z*). ^{1}H and ^{13}C NMR spectra were performed in $CDCl_3$ containing ca. 1% tetramethylsilane as internal standard on a Bruker AC 250 (250 and 62.9 MHz) spectrometer. Chemical shifts are reported in δ (ppm) and coupling constants are given in Hz. The progress of all reactions was monitored by TLC on 2.0×5.0 cm aluminum sheets, precoated with silica gel $60F_{254}$ to a thickness of 0.25 mm (Merck, Germany). The chromatograms were visualized under ultraviolet light (254–366 nm).

3.2. Materials

Pentanol, cyclohexanol, benzyl alcohol, phenol, 4-methyl-phenol, 2-allylphenol, 2,6-di-*tert*-butylphenol, 3,5-dimeth-oxyphenol, 2-phenylphenol, 4-phenylphenol, 2-nitrophenol, 4-nitrophenol, 8-hydroxyquinoline, methyl 4-hydroxy-benzoate, acetyl chloride, 2,2-dimethylpropanoyl chloride, butanoyl chloride, benzoyl chloride, 4-methoxybenzoyl chloride, 4-nitrobenzoylchloride, methyl 4-chloro-4-oxo-butanoate, 2-thiophenecarbonyl chloride, allyl bromide, ethyl iodoactate, butyl chloride, benzyl chloride, 4-methoxy-benzyl chloride, 4-nitrobenzyl chloride, 3-bromopropio-nitrile, propargyl bromide, benzyl bromide, 4-nitrobenzyl bromide, CsF, Celite 521 and other chemicals were commercially available (Fluka, Aldrich, Germany). Anhydrous acetonitrile was purchased from Merck and used without purification. The CsF-Celite was prepared by stirring an aqueous solution of CsF with Celite 521 at room temperature for 20 min.[2]

3.3. General procedure for syntheses of ethers and esters

To a stirred solution of the hydroxyl compound (1.0 mol) and CsF-Celite (1.5 mol) in 20 ml of acetonitrile, the alkyl, acyl, benzyl, or benzoyl halides (2.0 mol) were added. Then, the mixture was continued for stirring at room temperature or reflux up to completion of the reaction, indicated by TLC monitoring. The reaction mixture was filtered, the solvent evaporated and the residue dissolved in ethyl acetate. Precipitates were filtered off, washed with ethyl acetate (20 ml) and the filtrate evaporated under reduced pressure. The product was purified, whenever necessary, by column chromatography on silicagel using various solvent systems like dichloromethane, petroleum ether etc. as eluents, to afford the pure ester or ether products.

Physical properties like melting points, physical states and NMR spectroscopic data of the compounds agreed with those reported in the literature[17–33] and were furthermore confirmed by comparing the data with those of authentic samples. Unknown compounds or compounds for which incomplete physical data were reported in the literature were characterized by their mass spectra, NMR spectra and elemental analyses.

3.3.1. Phenyl benzoate (2). Solid; mp 68–70 °C, (lit.[18] 68–69 °C); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.12–8.22 (m, 10H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 121.2, 125.7, 126.5, 129.5, 129.7, 131.1, 134.4, 151.5, 164.0; EI MS (*m*/*z*): 198.29; Anal. Calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09. Found: C, 78.73; H, 5.17.

3.3.2. Phenyl 4-nitrobenzoate (3). Solid; mp 128–129 °C, (lit.[19] 128–129 °C); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.25–8.42 (m, 9H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 121.2, 123.5, 126.5, 129.6, 130.1, 134,4, 150.5, 150.7, 165.0; EI MS (*m*/*z*): 243.42; Anal. Calcd for $C_{13}H_9NO_4$: C, 64.20; H, 3.73. Found: C, 64.13; H, 3.75.

3.3.3. Benzyl benzoate (4). Liquid;[20] ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.20 (s, 2H), 7.25–8.15 (m, 10H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 67.4, 126.8, 129.1, 130.5, 130.8, 133.4, 135.2, 165.1; EI MS (*m*/*z*): 212.29; Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.34; H, 5.55.

3.3.4. 4-Phenylphenyl benzoate (8). Solid; mp 150–152 °C, (lit.[21] 149–150.5 °C); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.10–7.38 (m, 9H), 7.41–8.15 (m, 5H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 118.2, 121.5, 126.7, 127.5, 129.8, 130.2, 130.6, 131.9, 134.1, 138.4, 152.5, 167.0; EI MS (*m*/*z*): 274.20; Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.74. Found: C, 83.20; H, 5.75.

3.3.5. Methyl 4-[(2,2-dimethylpropanoyl)oxy]benzoate (11). Liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.15 (m, 2H), 8.05 (m, 2H), 4.1 (s, 3H), 1.64 (s, 9H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 25.6, 39.4, 51.5, 120.4, 127.7, 130.8, 157.8, 165.2, 174.1; EI MS (*m*/*z*): 236.27; Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.12; H, 6.85.

3.3.6. Benzyl phenyl ether (13). Solid; mp 39–40 °C (lit.[24] 38 °C); ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.20 (s, 2H, CH_2), 6.77–6.19 (m, 10H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 70.10, 114.1, 123.8, 127.5, 127.9, 128.4, 129.5, 137.6, 158.1; EI MS (*m*/*z*): 184.24; Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.59; H, 6.65.

3.3.7. 4-Nitrobenzyl phenyl ether (15). Solid; mp 90–91 °C (lit.[26] 89–91 °C); ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.22 (s, 2H), 7.05 (m, 3H), 7.50 (m, 2H), 7.24 (d, J=9 Hz, 2H), 7.95 (d, J=9 Hz, 2H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 70.1, 114.9, 121.8, 124.1, 126.5, 129.8, 138.1, 146.7, 158.2; EI MS (*m*/*z*): 229.55; Anal. Calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84. Found: C, 67.97; H, 4.96.

3.3.8. 3,5-Dimethoxyphenyl propionitrile ether (17). Liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.82 (t, J=6.2 Hz, 2H), 3.58 (s, 6H), 4.22 (t, J=6.7 Hz, 2H) 6.24–6.32 (m, 3H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 18.5, 55.2, 64.1, 92.6, 100.7, 118.1, 161.4, 164.6; EI MS (*m*/*z*): 207.24; Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32. Found: C, 63.78; H, 6.41.

3.3.9. Ethyl 4-phenylphenoxy acetate (20). Solid; mp 60–61 °C, (lit.[29] 60 °C); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.36 (t, J=6.7 Hz, 3H), 4.24 (q, J=6.9 Hz, 2H), 4.85 (s, 2H), 6.75–7.52 (m, 9H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 14.2, 61.1, 65.0, 115.8, 127.6, 128.2, 128.8, 129.4, 130.4, 142.5, 157.6, 169.5; EI MS (*m*/*z*): 256.30; Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.09; H, 6.31.

3.3.10. Ethyl 4-phenylphenyloxy butenoate (21). Solid; mp 69–70 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.26 (t, J=7.1 Hz, 3H), 4.24 (q, J=6.9 Hz, 2H), 4.75 (d, J=4.10 Hz, 2H), 6.15–6.8 (m, 2H), 7.15–7.52 (m, 9H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 14.8, 60.0, 66.8, 114.1, 118.5, 128.5, 128.8, 129.6, 131.2, 142.0, 142.1, 160.4, 166.5; EIMS, *m*/*z*=282.34; Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.75; H, 6.35.

3.3.11. 2,6-di-*tert*-Butylphenyl benzyl ether (23). Liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.46 (s, 18H), 7.10–7.15 (m, 3H), 7.25–7.29 (m, 5H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 29.5, 34.8, 70.7, 122.5, 126.5, 127.4, 128.8, 132.6, 147.1, 152.8; EI MS (*m*/*z*): 296.51; Anal. Calcd for $C_{21}H_{28}O$: C, 85.08; H, 9.52. Found: C, 85.12; H, 9.40.

3.3.12. 4-Nitrophenyl benzyl ether (24). Solid; mp 102–105 °C (lit.[26] 105–107 °C); ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.25 (s, 2H), 7.04 (d, J=9 Hz, 2H), 7.50 (s, 5H), 8.10 (d, J=9 Hz, 2H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 69.1, 116.9, 124.8, 126.1, 128.5, 128.8, 140.2, 141.2, 164.5; EI MS (*m*/*z*): 229.42; Anal. Calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 67.99; H, 4.88; N, 6.12.

3.3.13. Benzyl propargyl ether (27). Liquid;[31] ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.45 (t, J=2.7 Hz, 2H) 4.12 (s, 1H), 4.5 (s, 2H), 7.10–7.22 (m, 5H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 57.5, 72.2, 75.7, 81.4, 124.5, 127.8, 128.2, 140.2; EI MS (*m*/*z*): 146.21; Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 81.95; H, 6.75.

3.3.14. 2-Allylphenyl 4-methoxybenzyl ether (28). Liquid; ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.05 (m, 2H), 3.74 (s, 3H), 5.12 (s, 2H), 5.22–5.28 (m, 2H), 6.20–6.25 (m, 1H), 6.80–7.45 (m, 8H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 36.5, 54.01, 70.1, 112.8, 114.9, 115.4, 121.8, 126.1, 127.4, 129.8, 138.2, 157.5, 159.2; EI MS (*m*/*z*): 254.28; Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.24; H, 7.15.

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