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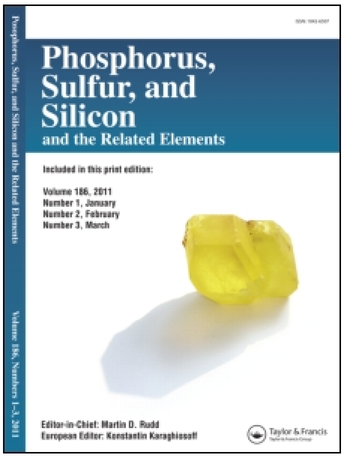

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Solid State S-Methylation of Thiols and O-Methylation of Phenols and Naphthols with Dimethyl Sulfate Under Microwave Irradiation

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Mild and efficient S-methylation of thiols and o-methylation of phenols and naphthols occurs with dimethyl sulfate (DMS) supported on basic alumina under microwave irradiation in solventless system.

Keywords Dimethyl sulfate; methylation; microwave irradiation; naphthals; phenols; thiols

INTRODUCTION

Protection of thio groups is important in many areas of organic synthesis especially in peptide, protein, and β-lactam synthesis.[1,2] A free SH-group can be protected as thioether, thioester, or after oxidation as disulfate, from which it can be regenerated by reduction.[3]

Aryl methyl sulfides are conveniently prepared by treatment of thiophenols with methyl iodide[4] or methyl p-toluenesulfonic acid.[5] The synthesis of alkyl sulfides catalyzed by the bis(diphenylphosphino) methane complex of platinum[6] and thiolate substitution of alkylhalides[7] by phase transfer catalysts,[8] palladium (0) catalytic alkyation,[9] bis(diphenylstannyl) telluride,[10] ligand transfer reaction of aryl thiocyanate,[11,12] and reaction of thiols with alkyl bromide in the presence of *n*-BuLi[13] have been reported.

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However, the inherent advantages of low cost and smoothness of reaction, high yields of pure products justify the use of dimethyl sulfate as the reagent of choice for replacing the mercapto hydrogen by methyl. Although dimethyl sulfate has its own merits for methylation of thiols, it shows some drawbacks regarding the relatively long reaction time and use of hazardous solvents.[14]

O-Methylation of phenols and naphthols is an important reaction in organic chemistry widely used in the synthesis of petrochemicals, fine chemicals, pharmaceuticals, fragrances, dyes and agrochemicals.[15]

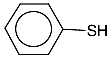
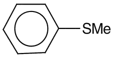
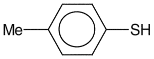
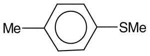
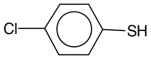
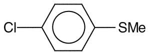
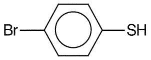
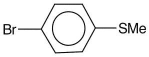
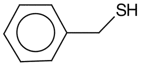
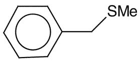
Protection and deprotection of functional groups is the inevitable operation for logic-centered multistage organic synthesis.[16] In this regard, the protection of phenols is amongst the most frequently desirable transformation. Regarding the ease of deprotection, it is convenient to protect phenols and naphthols as methyl ethers.[17]

Aryl methyl ethers are conventionally prepared by treatment of phenols and naphthols with DMS and MeI under classical heating[18] and sometimes under pressure.[19] Recently in organic synthesis, dimethyl carbonate has been also widely used as an alternative methylating reagent to replace hazardous compounds.[20] Vapor phase selective *o*-alkylation of phenols over alkali loaded silica has been recently reported.[21]

The use of microwave irradiation to deliver energy for organic reactions has increased in popularity in recent times. Microwave-assisted solvent-free reactions have been of growing interest as an efficient, economic, and clean procedure (green chemistry).[22] We[23] and others[24] have found that microwave irradiation facilitates numerous chemical transformation.

In continuation of our program aimed at the study of microwave effects in organic chemistry under green conditions and due to the availability of dimethyl sulfate, we report here our study on solvent-free microwave-assisted methylation of thiols with DMS in the presence of KOH. As a first examination, thiophenol was thoroughly mixed with potassium hydroxide and DMS. The reaction mixture was placed in a household microwave oven. The reaction proceeded slowly and more seriously molten thiophenol was adhered to the wall of the beaker. Application of solid supports and microwave irradiation has been a field, which has shown excellent results leading to the development of many reaction procedures;[25] therefore, we decided to repeat the methylation using inorganic solid supports, which gave satisfactory results. Amongst the traditional solid supports used such as silica gel, zeolite, monmorillonite K-10, K_2CO_3, and basic alumina, the latter gave the best results in term of reaction time and yields. The reactions were simply conducted by mixing and grinding of thiophenol,

TABLE I Reaction of Thiols with DMS Supported onto Basic Alumina in Solventless System

Entry	Substrate	Reaction time (min)	Product	Yield[a] (%)
1		3		72
2		4		58
3		2		84
4		2		81
5		5		79

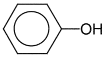
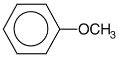
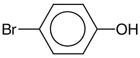
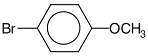
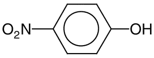
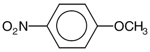
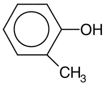
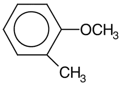
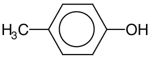
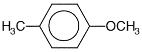
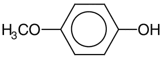
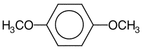
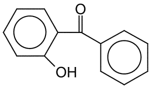
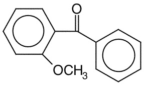
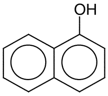
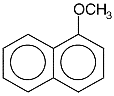
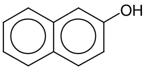
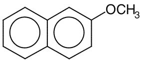
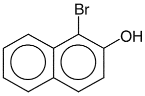
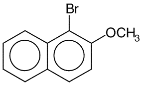
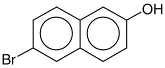
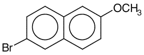
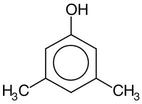
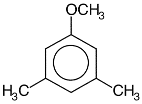
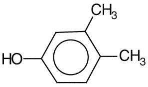
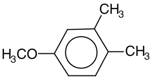
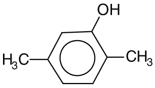
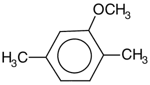
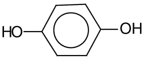
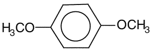
[a] Yields refer to isolated product.

basic alumina, DMS, and KOH, which gave methylthiophenol. To establish the generality of the method, substituted thiophenols were reacted in the same manner to obtain the corresponding methyl thioethers (Table I).

Solvent-free microwave-assisted methylation of phenols and naphthols with DMS in the presence of KOH was also investigated. As a first examination, phenol was thoroughly mixed with potassium hydroxide and DMS. The reaction mixture was placed in a household microwave oven. The progress of the reaction was monitored by TLC. The reaction proceeded slowly and more seriously molten phenol was adhered to the wall of the beaker. Coupling of application of solid support and microwave irradiation has been a field, which has shown excellent results leading to the development of many reaction procedures. Therefore, we decided to report the methylation using inorganic solid support, which gave satisfactory results. Amongst the traditional solid supports used such as silica gel, zeolite, montmorillonite K-10, K_2CO_3, and basic alumina, the latter gave the best results in term of reaction time and yields. The reactions were simply conducted by mixing and grinding of phenol, basic alumina, DMS, and KOH, which gave anisol as the product. To establish the generality of method, substituted phenols and naphthols were reacted in the same manner to obtain the corresponding methyl ethers (Table II). One of the main drawback of this procedure is lack of selectivity between phenolic-hydroxy group, alcoholic-hydroxy group, and hydroxy group of carboxylic acid. Thus when 2-hydroxy benzyl alcohol was reacted, a mixture of 2-methoxy benzyl alcohol and 2-methoxy benzyl methyl ether was obtained (entry 19). Reaction of 3-hydroxy

TABLE II Reaction of Phenols and Naphthols with DMS Supported onto Basic Alumina in Solventless System

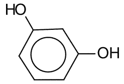
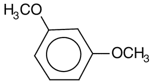
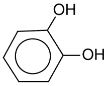
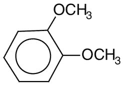
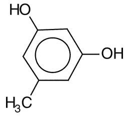
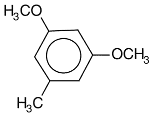
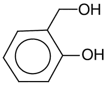
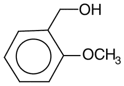
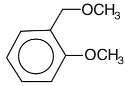
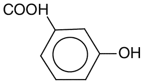
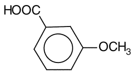
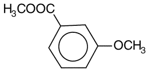
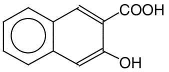
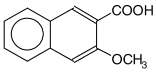
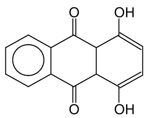
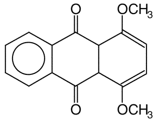
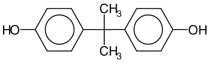
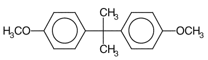
$$\mathrm{ArOH} + \mathrm{Me_2SO_4} \xrightarrow{\text{KOH, basic alumina}} \mathrm{ArOMe}$$

Entry	Substrate	Reaction time (min)	Product[a]	Yield[b] (%)
1		7		56
2		6		87
3		5		89
4		7		81
5		7		82
6		7		68
7		3		92
8		6		78
9		5		89
10		7		75
11		6		88
12		10		76
13		10		75
14		10		75
15		5		87

(Continued on next page)

TABLE II Reaction of Phenols and Naphthols with DMS Supported onto Basic Alumina in Solventless System *(Continued)*

$$\mathrm{ArOH} + \mathrm{Me_2SO_4} \xrightarrow{\text{KOH, basic alumina}} \mathrm{ArOMe}$$

Entry	Substrate	Reaction time (min)	Product[a]	Yield[b] (%)
16		6		89
17		7		78
18		7		79
19		3		42
				31
20		5		37
				34
21		7		77
22		12		21
23		7		89

[a] The products were identified by comparison of their physical and spectroscopic data (Table IV); with authentic samples.

[b] Yields refer to isolated products.

benzoic acid gave a mixture of methyl ether and methyl ether methyl ester (entry 20).

It should be noted that with a domestic microwave oven, realistic power and temperature controls during the reaction could not be achieved. In this way, the comparison of ease of methylation on various substituted thiophenols by comparison of their yield seems not to be reliable.

In conclusion, methylation of thiophenols, phenols, and naphthols with DSM in solventless system under microwave irradiation are rapid and manipulatively simple protocol when compared to the conventional solution phase reaction.

EXPERIMENTAL SECTION

All thiophenols, phenols, and naphthols were commercially available and purchased from Aldrich. All products were known and their physical and spectroscopic data were compared with those of authentic compounds. ^{1}HNMR spectra were recorded on Bruker 90 MHz. Mass spectra were measured on Agileni 5973 Network Mass spectrometer. Although we did not observe any accident using KOH and DMS under microwave irradiation, use of the oven in an efficient hood is highly recommended.

Synthesis of Methylthiophenols

In a beaker an appropriate thiol (1 mmol) potassium hydroxide (1 mmol) and basic alumina (1 g) were thoroughly mixed. To this mixture DMS (0.5 mmol) was added. This mixture was grinded thoroughly and placed in a household microwave oven. The progress of reaction was monitored by TLC using petroleum ether as eluent. After the completion of reaction, the mixture was allowed to cool and then extracted with petroleum ether. The extract was dried over $MgSO_4$, filtered, and evaporated to dryness. The product was purified by vacuum distillation to afford the desired products. Yields and reaction times are given in Table I. Selected spectroscopic data are listed in Table III.

$$\text{ArSH} \xrightarrow[\text{basic alumina, MW}]{\text{DSM, KOH}} \text{ArSMe}$$

SYNTHESIS OF AROMATIC METHYL ETHERS. GENERAL PROCEDURE

An appropriate aromatic phenol or naphthol (1 mmol), potassium hydroxide (1 mmol) [for dihydroxy compounds 2 mmol], and dimethyl sulfate (0.5 mmol) [for dihydroxy compounds (1 mmol)] were thoroughly mixed with basic alumina. The mixture was heated in a domestic microwave oven in an open beaker for an appropriate time. The reaction mixture was allowed to cool and then extracted with acetone. The extract then was dried over $MgSO_4$. The mixture was filtered and the

TABLE III Spectroscopic and Physical Data

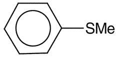
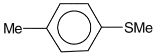
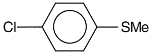
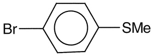
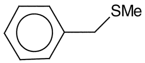
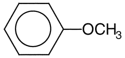
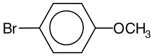
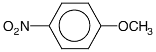
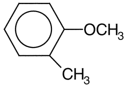
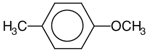
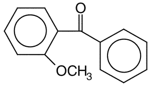
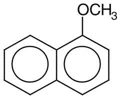
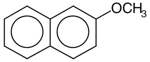
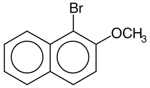
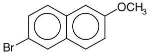
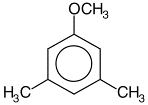
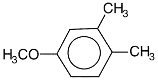
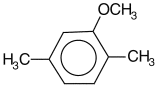
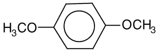
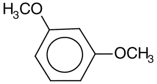
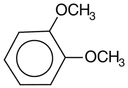
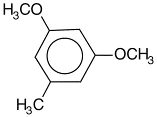
Entry	Product	^{1}H-NMR δ cm^{-1}	IR $\tilde{\upsilon}$ (KBr disc) cm^{-1}	MS	Mp, Bp °C	
					Meas.	Lit.
1		7.1 (m, 5H, benzene) 2.5 (s, 3H, Me)	3060, 3019, 3003, 1940, 1864, 1791, 1723, 1481, 1441, 1334, 1090, 1026, 739, 691	124 (100), 123 (8.3), 109 (34.3), 91 (26.04), 78 (32.3), 68 (6.2), 65 (12.5), 51 (10.5), 45 (10.5), 39 (7.3)	Oil	−15, 188
2		7 (dd, 4H, benzene) 2.5 (s, 3H, S-Me) 2.3 (s, 3H, Me)	2983, 2920, 1493, 1438, 1427, 1399, 1378, 1270, 1186, 1120, 1040, 1017, 800, 625, 500	138 (100), 137 (11.4), 123 (27.08), 122 (5.2), 121 (10.4), 91 (53.12), 79 (11.4), 78 (5.2), 77 (93), 45 (21.8), 39 (10.4)	Oil	—, 94 (31)
3		7.1 (dd, 4H, benzene) 2.5 (s, 3H, Me)	3949, 3079, 3068, 2987, 1883, 1562, 1477, 1428, 1389, 1320, 1113, 1097, 1011, 967, 810, 747, 539, 487	160 (36.45), 158 (100), 145 (16.6), 143 (45.8), 125 (12.5), 108 (31.25), 75 (6.25), 45 (12.5)	Oil	—, 170
4		7.2 (dd, 4H, benzene) 2.5 (s, 3H, Me)	3013, 2973, 1889, 1632, 1557, 1447, 1431, 1384, 1186, 1186, 1118, 1093, 1000, 800, 500	204 (100), 202 (99), 189 (23), 187 (23), 171 (6.25), 169 (6.25), 158 (6.25), 156 (6.25), 123 (6.25), 122 (7.3), 108 (35.4)	34	35, 255
5		7.1 (m, 5H, benzene) 2 (s, 3H, Me) 3.7 (s, 2H, CH$_2$)	3084, 3062, 3028, 2942, 2866, 1494, 1436, 1425, 1318, 1072, 1029, 979, 968, 913, 771, 725, 700, 472	138 (31.25), 92 (8.2), 91 (100), 65 (10.41), 45 (5.2), 39 (5.2)	Oil	—, 195-8

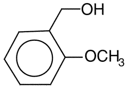
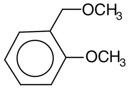
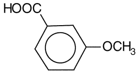
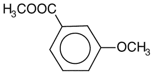
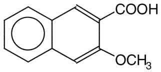
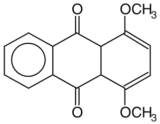
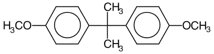
TABLE IV Selected Spectroscopic Data of the Products

Entry	Product	^{1}HNMR ($CDCl_3$) δ (ppm)	IR (KBr disc) $\tilde{\upsilon}$ (cm^{-1})	Ms	Mp, Bp (°C)	
					Measured	Lit.
1		3.7 (s, 3H, Me) 6.5–7.5 (m, 5H, benzene)	2750, 1600, 1500, 1300, 1050, 750	108 (100), 93 (14), 78 (50), 65 (54), 51 (14), 39 (25)	Liquid	—, 155.5[26]
2		3.7 (s, 3H, CH_3) 6.5–7.5 (ddd, 4H, benzene)	2900, 1600, 1500, 1250, 1050, 900	188 (100), 186 (100), 158 (19), 156 (19), 145 (32), 143 (32), 107 (6), 92 (25), 77 (78), 63 (51), 50 (23), 39 (16)	Liquid	9–10, 223[26]
3		3.8 (s, 3H, CH_3) 6.5–7.5 (dd, 4H, benzene)	3080, 2970, 1590, 1500, 1340, 1270, 1170, 1120, 1030, 850, 750, 700, 630, 620	153 (100), 123 (48), 107 (12), 95 (15), 92 (56), 77 (56), 64 (34), 63 (26), 50 (17)	54–5	54, 260[26]
4		2.3 (s, 3H, CH_3) 3.7 (s, 3H, CH_3) 6–8 (m, 4H, benzene)	2750, 1600, 1500, 1300, 1290, 1150, 1100, 1050, 760, 700	122 (100), 121 (38), 107 (28), 91 (17), 79 (21), 77 (25), 51 (7)	Liquid	−34, 171[27]
5		2.3 (s, 3H, CH_3) 3.7 (s, 3H, CH_3) 6.5–7.5 (dd, 3H, benzene)	2850, 1600, 1500, 1250, 1100, 800, 700	122 (100), 121 (39), 107 (27), 91 (180, 79 (20), 77 (24), 51 (8)	Liquid	−32, 175[27]
6		3.7 (s, 6H, CH_3) 6.6 (dd, 4H, benzene)	2900, 1500, 1300, 1250, 1050, 800, 700	138 (100), 123 (93), 94 (38), 63 (9), 41 (20)	58–60	59, 212[27]
7		3.9 (s, 3H, CH_3) 6.5–7.5 (dd, 9H, benzene)	3060, 3000, 2900, 2800, 1650, 1600, 1500, 1420, 1310, 1290, 1250, 1170, 1150, 1200, 1020, 1000, 930, 850, 790, 750, 700, 600	212 (51), 195 (18), 181 (5), 107 (4), 135 (100), 121 (22), 105 (38), 92 (16), 77 (64), 51 (17)	39–41	41, 195[27]
8		3.8 (s, 3H, CH_3) 6.5–7.5 (m, 7H, naphthalene)	3000, 1600, 1500, 1350, 1250, 1100, 1000, 800, 700	158 (100), 143 (52), 115 (99), 89 (10)	Liquid	−10, 269[27]

9		3.7 (s, 3H, CH_3) 6.5–7.5 (m, 7H, naphthalene)	2800, 1600, 1500, 1350, 1250, 1050, 850, 750	158 (100), 143 (9), 128 (12), 115 (95), 89 (60), 63 (8)	71–3	73, 274[27]
10		3.7 (s, 3H, CH_3) 6.5–7.5 (m, 6H, naphthalene)	3000, 2950, 2900, 2850, 1610, 1500, 1350, 1250, 1220, 1150, 1050, 1000, 900, 800, 780, 750, 700, 650, 600, 520	238 (100), 236 (100), 223 (19), 221 (190, 195 (48), 193 (48), 127 (12), 114 (14)	83–4	84–5, —[28]
11		3.8 (s, 3H, CH_3) 6.5–7.5 (m, 6H, naphthalene)	3000, 1700, 1450, 1250, 1200, 1050, 900, 850	236 (100), 221 (19), 193 (76), 142 (70, 126 (24), 114 (82), 88 (19), 74 (160, 63 (30), 50 (13)	103–5	105, –[28]
12		2.35 (s, 6H, CH_3) 3.7 (s, 3H, CH_3) 6–6.5 (m, 3H, benzene)	3000, 1550, 1400, 1300, 1200, 1050, 900, 680	136 (100), 121 (35), 107 (9), 105 (12), 93 (12), 91 (50), 77 (20)	Liquid	—, 194[27]
13		2.35 (s, 6H, CH_3) 3.9 (s, 3H, CH_3) 6–6.5 (m, 3H, benzene)	3150, 1600, 1500, 1300, 1100, 1050, 800	136 (100), 121 (59), 105 (18), 91 (29), 77 (22)	Liquid	—, 202[27]
14		2.35 (s, 6H, CH_3) 3.9 (s, 3H, CH_3) 6.5–7.5 (m, 3H, benzene)	3150, 1600, 1500, 1300, 1150, 1050, 800	136 (100), 121 (59), 105 (18), 91 (29), 77 (22)	Liquid	—, 194[27]
15		3.7 (s, 6H, CH_3) 6.6 (dd, 4H, benzene)	2900, 1500, 1300, 1250, 1050, 800, 700	138 (100), 123 (93), 94 (37), 63 (9), 41 (20)	58–9	59, 212[27]
16		3.7 (s, 6H, CH_3) 6–7 (m, 4H, benzene)	3000, 2900, 1600, 1450, 1300, 1200, 1050, 900, 850, 750	138 (100), 109 (29), 95 (22), 78 (22), 65 (15), 63 (9)	Liquid	–52, 217[27]
17		3.7 (s, 6H, CH_3) 6.5–7 (m, 4H, benzene)	3100, 3050, 3000, 2850, 1600, 1500, 1480, 1320, 1250, 1150, 1120, 1000, 750	138 (100), 123 (42), 95 (48), 77 (29), 65 (15), 63 (70), 52 (18), 51 (12), 41 (12)	Oil	22–3, 206–7[27]
18		2.35 (s, 6H, CH_3) 3.8 (s, 6H, CH_3) 6 (m, 3H, benzene)	3000, 2990, 2850, 1600, 1460, 1410, 1340, 1320, 1300, 1250, 1200, 1150, 1070, 910, 830, 680, 610, 580	152 (100), 123 (52), 109 (16), 91 (23), 79 (15), 77 (17), 66 (8), 65 (7), 51 (8), 39 (12)	Liquid	–, 244[29]

(Continued on next page)

TABLE IV Selected Spectroscopic Data of the Products *(Continued)*

					Mp, Bp (°C)	
Entry	Product	^{1}HNMR ($CDCl_3$) δ(ppm)	IR (KBr disc) $\tilde{\upsilon}$ (cm^{-1})	Ms	Measured	Lit.
19		2 (s, 1H, OH) 3.7 (s, 3H, CH_3) 4.8 (s, 2H, CH_2) 6–7 (m, 4H, benzene)	3500, 3000, 1600, 1400, 1250, 1100, 1050, 750	138 (100), 137 (29), 123 (19), 121 (19), 109 (33), 107 (38), 106 (21), 105 (52), 91 (35), 77 (47), 65 (12), 51 (18), 39 (14)	Liquid	—, 247[30]
		3.2 (s, 3H, CH_3) 3.7 (s, 3H, CH_3) 4.6 (s, 2H, CH_2) 6.5–7 (m, 4H, benzene)			Liquid	—, 229–30[30]
20		^{a}3.7 (s, 3H, CH_3) 7–8 (m, 4H, benzene) 11 (s, 1H, OH)	2700, 1700, 1800, 1300, 1050, 950, 750	152 (100), 121 (99), 93 (68), 39 (10)	103–4	105[31]
		^{a}2.5 (s, 3H, CH_3) 3.7 (s, 3H, CH_3) 6–8 (m, 4H, benzene)	107 (63), 92 (36), 77 (42), 64 (15.7), 50 (5)	107 (63), 92 (36), 77 (42), 64 (15), 50 (5)	Liquid	—, 236–8[32]
21		4 (s, 3H, CH_3) 7–8 (m, 6H, naphthalene) 11 (s, 1H, OH)	3070, 3000, 2850, 2650, 1700, 1900, 1620, 1600, 1510, 1500, 1350, 1290, 1250, 1200, 1050, 1000, 820, 750, 700	202 (100), 185 (50), 155 (14), 143 (15), 127 (12), 115 (10), 114 (11)	132–134	133, —[33]
22		4.2 (s, 6H, CH_3) 7–8 (m, 6H, anthraquinone)	—	268 (42), 253 (100), 236 (10), 209 (100), 159 (19), 139 (15)	169–171	170–1, —[34]
23		1.5 (s, 6H, CH_3) 3.7 (s, 6H, CH_3) 7–8 (m, 8H, benzene)	—	—	59–62	60.5, 371[35]

^{a}(in C_2D_6O).

filtrate was evaporated to dryness. Liquid compounds were purified by distillation and solid compounds were either purified or separated by column chromatography to afford the desired aromatic ether. Yields, reaction times, and products are given in Table II. Selected spectroscopic data are given in Table IV.

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