Hypervalent Iodine(III)-Induced Intramolecular Cyclization of α-(Aryl)alkyl-β-dicarbonyl Compounds: A Convenient Synthesis of Benzannulated and Spirobenzannulated Compounds

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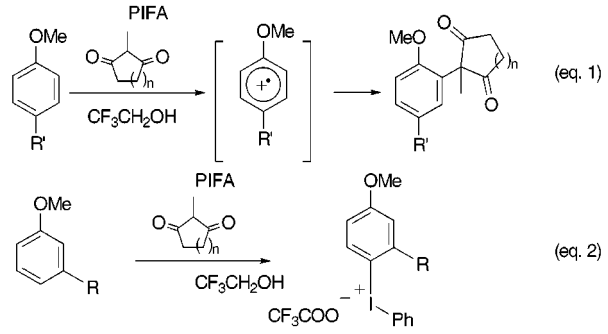
A novel hypervalent iodine(III)-induced direct intramolecular cyclization of α-(aryl)alkyl-β-dicarbonyl compounds has been described. Both meta- and para-substituted phenol ether derivatives containing acyclic or cyclic 1,3-dicarbonyl moieties at the side chain undergo this reaction in a facile manner. The reactions afford benzannulated and spirobenzannulated compounds that are of biological importance. The reaction is found to be general, mild, and high yielding. The mechanism of the reaction has been shown to involve a cation radical intermediate.

Introduction

In recent years, the use of hypervalent iodine(III) reagents in organic synthesis has gained popularity.[1] In particular, phenyliodine(III) diacetate (PIDA) and phenyliodine(III) bis(trifluoroacetate) (PIFA) have received much attention because of their similar reactivities to those of heavy metal reagents or anodic oxidation. Added advantages which render them synthetically more attractive are their low toxicity, ready availability, and easy handling. In our laboratory, we have been extensively utilizing these reagents to perform a variety of organic transformations. Recent research from our group using these reagents includes oxidative intramolecular phenolic coupling,[2] oxidative biaryl coupling reaction of phenol ethers,[3] α-azidation of cyclic sulfides,[4] synthesis of pyrroloiminoquinones,[5] intramolecular biaryl coupling reactions,[6] synthesis of indole derivatives,[7] oxidation reactions[8] etc. We had previously reported a hypervalent iodine-induced *intermolecular* substitution reaction of para-substituted phenol ethers using a variety of nucleophiles[9] (Scheme 1, eq 1). The reaction was shown to proceed through a cation radical intermediate. In contrast to the para-substituted phenol ethers, it has been observed by us[10] as well as others[11] that the reaction of meta-substituted phenol ethers with hypervalent

Scheme 1



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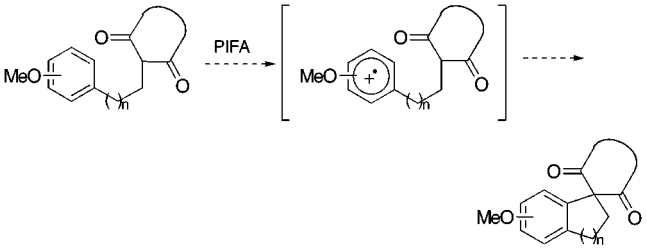
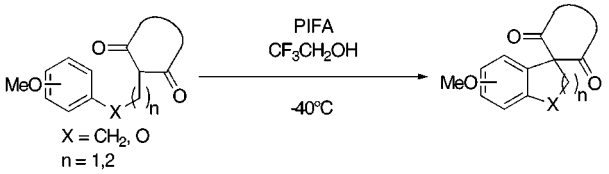
Scheme 2



iodine(III) reagent afforded exclusively the diaryliodonium salt (Scheme 1, eq 2).

As an extension of our previous work, we envisaged that a corresponding *intramolecular* nucleophilic substitution reaction of suitably functionalized phenol ether derivatives should provide access to benzannulated and spirobenzannulated compounds[12] (Scheme 2). Our synthetic interest in these compounds arose from the presence of such structural features in biologically active *cannabis* spironoids[13] as well as from their utilization in the synthesis of biologically important molecules.[14] Several routes are available for the synthesis of such compounds;[12−15] however, each method has its own merits and demerits. The recent photochemical electron-transfer arene cation radical route leading to these compounds sounds attractive,[12a] although its applicability to large-scale synthesis remains a question. Earlier, we had briefly communicated a two-step hypervalent iodine(III)-induced cyclization of meta-substituted α-(aryl)alkyl *β*-dicarbonyl derivatives to afford the benzannulated compounds by the treatment of a base.[10] The reaction has been shown to proceed via a diaryliodonium salt intermediate. In this paper, we report the full account of our research including a direct synthesis of spirobenzannulated compounds via a hypervalent iodine(III) induced *intramolecular* cyclization of both para- and meta-substituted phenol ether derivatives. Detailed mechanistic aspects are also discussed.

Scheme 3



Results and Discussion

Intramolecular Substitution Reaction of Para-Substituted Phenol Ether Derivatives. In a preliminary attempt, we examined the PIFA-induced intramolecular cyclization of para-substituted phenol ether derivative **1** containing a cyclic 1,3-dicarbonyl moiety at the side chain, which was prepared according to literature procedure.[16] As expected, upon exposure of compound **1** to PIFA in 2,2,2-trifluoroethanol (CF_3CH_2OH) at −40 °C it smoothly underwent intramolecular cyclization at the meta-position to afford the spirobenzannulated product **2** in 85% yield (Scheme 3, Table 1, entry 1).[12a] Encouraged by the result, a few more para-substituted phenol ether derivatives **3**, **5**, and **7** were prepared.[16] All these compounds were found to undergo the PIFA-induced cyclization to afford the respective products **4**, **6**, and **8** in fair yields (Table 1, entries 2 and 3). It is interesting to note that compounds **5** and **7** may have influence from para as well as meta substituents. Noteworthy is that the indanone derivative **9**[17] also afforded the cyclized product **10** in the presence of PIFA *albeit* in only modest yield (Table 1, entry 4). Thus, the PIFA-induced intramolecular cyclization of para-substituted phenol ether derivatives provides a convenient route to the synthesis of diversely substituted spirobenzannulated compounds. In contrast to the compounds **1**, **3**, **5**, **7**, and **9**, which contain cyclic 1,3-diones at the side chain, compounds **11a**−**c** with acyclic 1,3-diones did not undergo the expected cyclization. Instead, they were found to decompose or remain unaffected upon treatment with PIFA (Table 1, entry 5).

Intramolecular Substitution Reaction of Meta-Substituted Phenol Ether Derivatives. Treatment of meta-substituted phenol ether derivatives bearing an acyclic 1,3-dicarbonyl moiety at the side chain, such as **12a**−**e** with PIFA, afforded the diaryliodonium salts **13a**−**e** and not the cyclized products (Table 1, entry 6). These diaryliodonium salts **13a**−**e** were isolated and characterized thoroughly. Further treatment of these diaryliodonium salts with a strong base such as KO^{t}Bu produced the cyclized products **14a**−**e** in good yields (Scheme 4). Three possible pathways can be envisioned for this substitution reaction as shown in Scheme 5. In the presence of a strong base, the iodonium salt may undergo elimination to form a benzyne intermediate or it may form a ligand-coupled intermediate, both of which can cyclize to the desired product. Alternatively, a direct nucleophilic substitution (SN Ar) on to the aromatic ring is also possible. The ligand-coupled intermediate formation may be more likely than the other two pathways,

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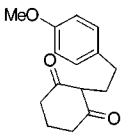
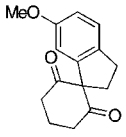
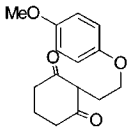
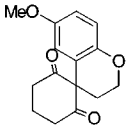
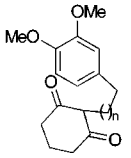
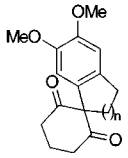
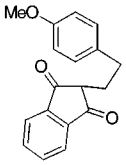
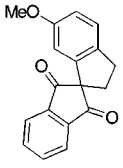
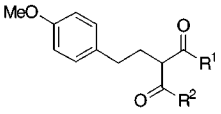
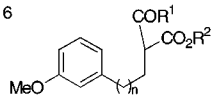
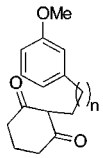
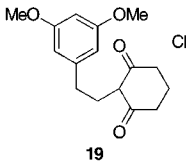
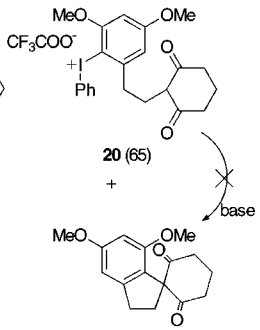
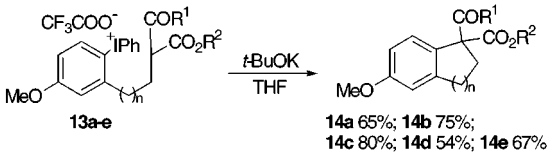
Table 1. PIFA-Induced Intramolecular Reaction of Para- and Meta-Substituted Phenol Ether Derivatives

Entry	Substrate	Product (Yield %)
	para-Substituted Phenol Ethers	
1		**1**  **2** (85)
2		**3**  **4** (65)
3		**5**: n = 1 **7**: n = 2  **6** (39) **8** (70)
4		**9**  **10** (34)
5		**11a**: R^1, R^2 = CH_3 a **11b**: R^1 = CH_3, R^2 = OCH_3 b **11c**: R^1, R^2 = OCH_3 a
	meta-Substituted Phenol Ethers	
6		**12a**: R^1 = OMe, R^2 = Me, n = 1 **13a** (64) **12b**: R^1 = Me, R^2 = Me, n = 1 **13b** (84) **12c**: R^1 = Me, R^2 = Et, n = 1 **13c** (69) **12d**: R^1 = Me, R^2 = Me, n = 2 **13d** (73) **12e**: R^1 = Me, R^2 = Et, n = 2 **13e** (96)
7		**15**: n = 1 **16** (70) **17**: n = 2 **18** (69)
8		**19**  **20** (65) + **21** (<3%)

[a] Decomposition. [b] No reaction.

Scheme 4



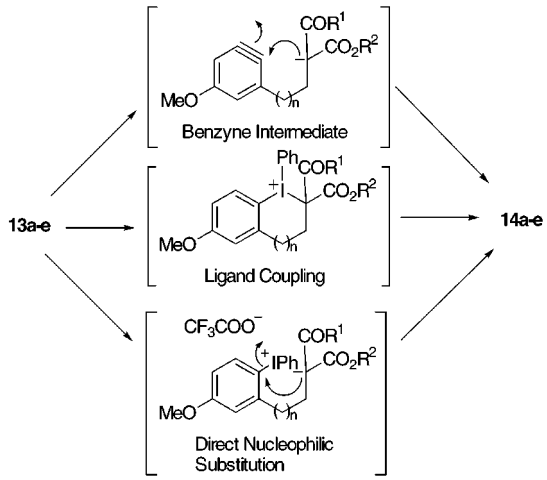
13a-e **14a** 65%; **14b** 75%; **14c** 80%; **14d** 54%; **14e** 67%

although there is no evidence to prove the mechanism. The two-step sequence can also be performed in one pot without the isolation of the diaryliodonium intermediate. The contrasting behavior of these meta-substituted acyclic 1,3-dicarbonyl compounds to that of the para-substituted ones is noteworthy.

On the basis of these observations, one would expect that reactions with substrates having cyclic 1,3-dicarbonyl moieties at the side chain (**15**, **17**)[16] would also lead to the diaryliodonium salts. To our surprise, compounds **15** and **17**, when subjected to the PIFA reaction conditions, did not give rise to the diaryliodonium salts. Instead, the cyclized products **16** and **18** were obtained directly in a single step in 70% and 69% yields, respectively (Table 1, entry 7).

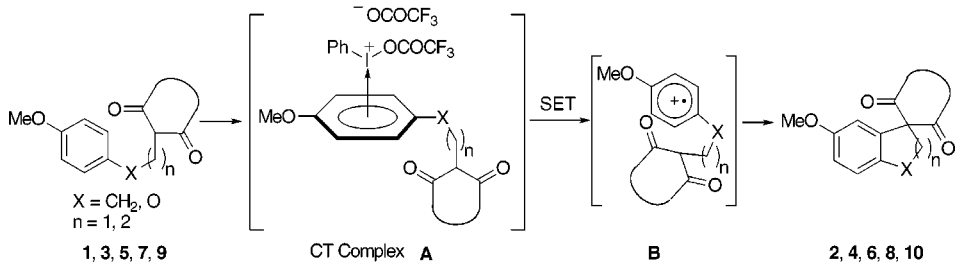
It is worth mentioning here that the cyclization occurred regiospecifically at the para position and not at

Scheme 5



the ortho position. The calculated electron spin densities of a model compound namely, *p-tert*-butyl anisole,[9] suggests that the cation radical is more concentrated on the ortho position, and hence, one might expect the substitution to occur at the ortho position preferentially. The most apparent explanation is steric hindrance. To get a further

Scheme 6



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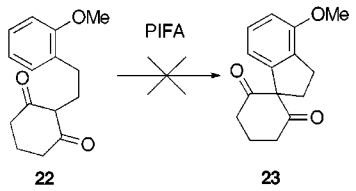
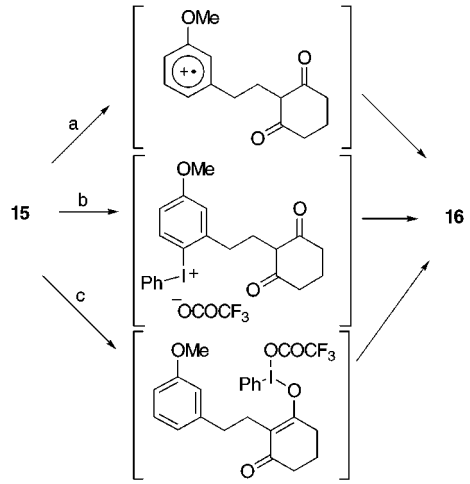
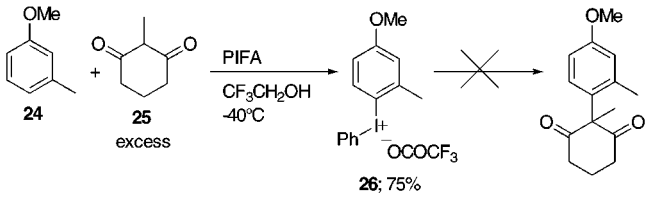


Scheme 8



Scheme 9



insight into this aspect, compound **19**, which has two methoxy groups at the meta position, was treated with PIFA under standard conditions. What we have observed is the predominant formation of the iodonium salt **20**, with only a trace amount of the cyclized product **21** (Table 1, entry 8). Attempted cyclization of the iodonium salt **20** with base failed also. This experiment provides additional evidence that the methoxy group present at the meta position prevents the nucleophile from cyclizing at the ortho position.

Mechanism. Mechanism of Cyclization of Para- and Meta-Substituted Phenol Ether Derivatives. As discussed in our previous paper,[9] the mechanism of reaction of para-substituted phenol ether derivatives (for example, **1**, **3**, **5**, **7**, and **9**) with PIFA involves the initial formation of charge-transfer complex **A** followed by single-electron transfer (SET) to afford the cation radical **B**, which then undergoes cyclization to give the products such as **2**, **4**, **6**, **8**, and **10** (Scheme 6). On the other hand, reaction of the ortho-substituted phenol ether derivative **22** with PIFA under usual conditions did not give rise to the expected cyclized product **23** (Scheme 7).

As has been described in Table 1 (entry 6), the PIFA-induced reaction of meta-substituted phenol ether derivatives **12**, containing acyclic 1,3-dione moieties at the side chain, proceeds through the formation of the diaryliodonium salts **13**. The isolation of the diaryliodonium salts **13** unambiguously proves the mechanistic pathway in these cases.

On the other hand, the mechanism of PIFA-induced reaction of meta-substituted phenol ether derivatives containing cyclic 1,3-dione moieties at the side chain, such as **15** and **17**, needs attention. Three different mechanistic pathways can be envisaged for this reaction as shown in Scheme 8. Path (a) involves the formation of cation radical intermediate which could directly cyclize at the activated para-position. Path (b) involves the formation of diaryliodonium salt, which might undergo cyclization under the reaction conditions probably without the need of a base, and path (c) involves the initial reaction of PIFA with the dicarbonyl moiety at the side chain, which can undergo intramolecular electrophilic aromatic substitution to afford the product.

Path (c) can be ruled out on the basis of the following reaction. On reacting 3-methylanisole **24** and a large excess of 2-methylcyclohexa-1,3-dione **25** with PIFA, it was observed that only the 3-methylanisole reacted with PIFA to give the diaryliodonium salt **26**, and the 2-methylcyclohexadione **25** remained intact in spite of it being in large excess (Scheme 9). This indicates that the aromatic ring is much more reactive than the dicarbonyl compound toward PIFA thereby ruling out the mechanistic pathway (c).

Path (b) may also be not probable for the following reasons. Unlike in the case of compound **12**, no diaryliodonium salt could be isolated in the reaction of **15** with PIFA. Second, according to entry 8 in Table 1, compound **21** was obtained in a trace amount. All efforts to cyclize the isolated diaryliodonium salt **20** were in vain, clearly suggesting that the cyclized product **21** was obtained directly and not through the diaryliodonium intermediate.

On the basis of these experiments and observations, it can be generalized that, in the presence of a strong nucleophile, the cation radical gives substituted compounds whereas in the absence of such a nucleophile, formation of the diaryliodonium salt (e.g., **13**) is preferred.

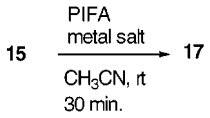
The most likely mechanism through which these reactions proceed is via path (a), which involves the formation of cation radical intermediate. Additional evidence for the cation radical intermediate was obtained

Table 2. Oxidation Potential of Methylanisole[a]

entry	substrate	E_p (V vs SCE)
1	*p*-methylanisole	1.29
2	*m*-methylanisole	1.32
3	*o*-methylanisole	1.31

[a] Values under the concentration of 5.0×10^{-3} mol dm^{-3} in $(CF_3)_2CHOH$; 0.1 mol dm^{-3} [N^{n}Bu$_4$][ClO$_4$], sweep rate 100 mV s^{-1}.

Table 3. Effect of Added Metal Salts



entry	metal salt	yield (%)
1	none	27
2	$LiBF_4$	29
3	$Mg(ClO_4)_2$	46

from the following experiment. It is well-known that the presence of some metal salts in the reaction medium accelerates the formation of the cation radical.[16] We have also carried out our reaction in the presence of metal salts. As the cation radical can be formed effectively in CF_3CH_2OH without adding metal salts, we have chosen CH_3CN as the solvent medium in this reaction. The results of these experiments are presented in Table 3. Clearly, addition of metal salts increase the rate of the reaction.

Conclusions

In conclusion, we have reported a facile and convenient synthesis of benzannulated and spirobenzannulated compounds via an intramolecular substitution reaction of phenol ether derivatives induced by a hypervalent iodine(III) reagent, namely PIFA. The reaction conditions are mild, and the products are obtained in good yields. This method involves nontoxic and convenient reagents, and the reaction is amenable to large-scale synthesis. Hence, we believe that this methodology will be quite attractive for the synthesis of the title compounds. Applications of this method to other substrates are currently in progress.

Experimental Section

All compounds were fully characterized (^{1}H, ^{13}C, IR, mass). IR spectra (cm^{-1}) were recorded using a KBr pellet. ^{1}H NMR (and ^{13}C NMR) spectra were recorded in $CDCl_3$, unless otherwise mentioned, at 270, 300, or 500 MHz with TMS as an internal standard. E. Merck silica gel 60 for column chromatography and E. Merck precoated TLC plates, silica gel F_{254}, for preparative thin-layer chromatography were used. The organic layers were dried over anhydrous $MgSO_4$ or Na_2SO_4. Commercially available PIFA, $(CF_3)_2CHOH$, and CF_3CH_2OH were used without further purification.

General Procedure for the Preparation of Coupling Precursor Bearing Cyclohexanedione (1, 3, 5, 7, 15, 17, and 19).[17] Under an argon atmosphere, to a stirring solution of sodium (2.53 g, 110 mmol) in liquid ammonia (360 mL), a solution of 1,3-dimethoxybenzene (2.76 g, 20.0 mmol) in ethanol (6.74 mL) and Et_2O (8.46 mL) was added dropwise at −78 °C. The reaction mixture was stirred at −78 °C for 2 h and subsequently quenched by the addition of ethanol (40.0 mL) at −78 °C, H_2O (20.0 mL)−ethanol (20.0 mL) at −50 °C, and H_2O (20.0 mL) at the ambient temperature seqentially. Ammonia was removed by standing at room temperature to give crude residue which was extracted with petroleum ether/ether (1:1) and the organic layer was washed with brine. After evaporation, 1,5-dimethoxy-1,4-cyclohexadiene (2.14 g, 75%) was obtained.

To a solution of the corresponding alcohol (6.00 mmol) (methoxyphenethyl alcohol or methoxyphenylpropyl alcohol as the case may be) in CH_2Cl_2 (20.0 mL), triphenylphosphine (1.68 g, 6.60 mmol), imidazole (449 mg, 6.60 mmol), and iodine (1.57 g, 6.00 mmol) were added at room temperature. The reaction mixture was stirred for 1 h, then saturated aqueous sodium thiosulfate was added, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The crude residue was subjected to column chromatography to give the corresponding iodo compound.

tert-Butyllithium (1.7 M, 1.94 mL, 3.30 mmol) was added to THF (17.0 mL) under argon atmosphere at −78 °C followed by the addition of a solution of 1,5-dimethoxy-1,4-cyclohexadiene (421 mg, 3.00 mmol) in THF (3.00 mL), and the reaction mixture was stirred at ambient temperature for 1 h. Hexamethylphosphoric triamide (0.640 mL, 3.51 mmol) was added to the mixture, and it was stirred for 30 min. A solution of the previously prepared iodo compound (3.93 mmol) in THF (3.00 mL) was added to the above mixture at −78 °C, and it was stirred for 1 h and at 0 °C for 30 min. The reaction mixture was then quenched with brine and extracted with pentane. The organic layer was washed with water, dried over Na_2SO_4, and concentrated. Acetone and 1 N HCl (6.00 mL) were added to the residue, and the mixture was stirred at room temperature for 1 h. Acetone was removed under reduced pressure, and the targeted compound was extracted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, and evaporated to give crude residue which was subjected to column chromatography to give the desired product.

General Procedure: PIFA-Induced Intramolecular Coupling Reaction. To a solution of coupling precursor in CF_3CH_2OH was added a solution of PIFA in CF_3CH_2OH, and the reaction mixture was stirred at the same temperature for 30 min. The solvent was removed to give crude product, which was subjected to preparative thin-layer or column chromatography to give the coupling compounds.

6′-Methoxyspiro[cyclohexane-1,1′-indan]-2,6-dione (2). Prepared from **1** (13.0 mg, 0.0500 mmol), PIFA (21.5 mg, 0.0500 mmol), and CF_3CH_2OH (1.00 + 2.00 mL) (11.0 mg, 85%, column chromatography, SiO_2; *n*-hexane/EtOAc = 1:2): pale yellow oil; IR (KBr) 2950, 1725, 1695, 1605 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (1H, d, J = 8.4 Hz), 6.79 (1H, d, J = 2.1 Hz), 6.75 (1H, dd, J = 8.4, 2.1 Hz), 3.78 (3H, s), 3.02 (2H, t, J = 7.3 Hz), 2.95−2.74 (4H, m), 2.60 (2H, t, J = 7.3 Hz), 2.21−1.79 (2H, m); ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 207.2, 160.0, 146.6, 132.2, 125.2, 112.8, 110.3, 77.8, 55.3, 38.3, 33.5, 31.5, 17.7; HRMS (EI) calcd for $C_{15}H_{16}O_3$ (M^+) 244.1099, found 244.1076.

6-Methoxyspiro[chroman-4,1′-cyclohexane]-2′,6′-dione (4). Prepared from **3** (131 mg, 0.500 mmol), PIFA (237 mg, 0.550 mmol), and CF_3CH_2OH (10.0 + 15.0 mL) (86.0 mg, 66%, column chromatography, SiO_2; CH_2Cl_2/MeOH = 200:1): colorless crystal; mp 129−130 °C (EtOAc); IR (KBr) 2965, 2880, 1725, 1695, 1505 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.80 (1H, d, J = 8.8 Hz), 6.79 (1H, dd, J = 8.8, 2.6 Hz), 6.13 (1H, d, J = 2.6 Hz), 4.08 (2H, d, J = 5.3 Hz), 3.70 (3H, s), 2.96−2.85 (2H, m), 2.81−2.72 (2H, m), 2.30−2.19 (3H, m), 2.09−1.95 (1H, m); ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 208.1, 153.1, 149.9, 118.9, 118.1, 115.3, 114.9, 66.7, 61.1, 55.6, 38.0, 32.2, 17.3; HRMS (EI) calcd for $C_{15}H_{16}O_4$ (M^+) 260.1048, found 260.1069. Anal. calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20. Found: C, 69.14; H, 6.16.

5′,6′-Dimethoxyspiro[cyclohexane-1,1′-indan]-2,6-dione (6). Prepared from **5** (28.0 mg, 0.100 mmol), PIFA (43.0 mg, 0.100 mmol), and CF_3CH_2OH (2.00 + 2.00 mL) (10.0 mg, 39%, preparative thin-layer chromatography, SiO_2; *n*-hexane/EtOAc = 1:2): pale yellow oil; IR (KBr) 2940, 2855, 1720, 1605 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.77 (1H, s), 6.61 (1H, s), 3.86 (3H, s), 3.84 (3H, s), 2.97 (2H, t, J = 7.2 Hz), 2.92−2.73 (4H, m), 2.56 (2H, t, J = 7.2 Hz), 2.22−2.03 (2H, m); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 207.6, 149.7, 148.0, 136.9, 130.8, 108.2,

107.5, 78.4, 56.2, 55.8, 38.4, 35.7, 31.1, 17.7; HRMS (EI) calcd for $C_{16}H_{18}O_4$ (M^+) 274.1205, found 274.1205.

3′,4′-Dihydro-6′,7′-dimethoxyspiro[cyclohexane-1,1′-2′*H*-naphthalene]-2,6-dione (8). Prepared from **7** (87.0 mg, 0.300 mmol), PIFA (129 mg, 0.300 mmol), and CF_3CH_2OH (6.00 + 6.00 mL) (60.0 mg, 70%, column chromatography, SiO_2; *n*-hexane/EtOAc = 1:1): colorless crystal; mp 139−140 °C (EtOAc); IR (KBr) 2940, 1725, 1695, 1520 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.60 (1H, s), 5.98 (1H, s), 3.84 (3H, s), 3.75 (3H, s), 2.99−2.92 (2H, m), 2.74−2.69 (4H, m), 2.30−2.22 (1H, m), 2.18−2.16 (2H, m), 2.03−1.93 (1H, m), 1.78−1.73 (2H, m); ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 209.7, 148.5, 147.1, 130.9, 124.1, 113.0, 111.5, 71.3, 56.0, 55.6, 38.0, 34.4, 28.8, 18.9, 17.7; HRMS (EI) calcd for $C_{17}H_{20}O_4$ (M^+) 288.1361, found 288.1351. Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.69; H, 6.90.

6′-Methoxyspiro[indan-2,1′-indan]-1,3-dione (10). Prepared from **5** (24.0 mg, 0.0860 mmol), PIFA (37.0 mg, 0.0860 mmol), and CF_3CH_2OH (2.00 + 2.00 mL) (8.00 mg, 33%, preparative thin-layer chromatography, SiO_2; CH_2Cl_2/MeOH = 100:1): yellow crystal; mp 164−165 °C (EtOAc); IR (KBr) 1745, 1705, 1595, 1490 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 8.08−8.04 (2H, m), 7.92−7.88 (2H, m), 6.87 (1H, d, J = 2.5 Hz), 6.61 (1H, dd, J = 8.4, 2.5 Hz), 6.52 (1H, d, J = 8.4 Hz), 3.76 (3H, s), 3.28 (2H, t, J = 7.4 Hz), 2.56 (2H, t, J = 7.4 Hz); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 201.7, 160.2, 147.3, 142.5, 135.8, 123.8, 123.3, 113.1, 110.4, 55.4, 33.2, 32.2; HRMS (EI) calcd for $C_{18}H_{14}O_3$ (M^+) 278.0943, found 278.0943. Anal. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.90; H, 5.14.

General Procedure for the Synthesis of Dicarbonyl Compounds 12. A slurry of 2-(3-methoxyphenyl)-1-iodoethane or 3-(3methoxyphenyl)-1-iodopropane (1.00 equiv), dicarbonyl compound (0.900 or 1.00 equiv) and potassium carbonate (2.50 equiv) in dry acetone (10.0 mL for 1 mmol of starting material) was refluxed (bath temperature 70 °C), and the progress of the reaction was monitored by TLC. When TLC indicated the disappearance of starting material the reaction was stopped. The reaction mixture was then cooled to room temperature, quenched with water, and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification by column chromatography over silica gel (*n*-hexane/EtOAc = 4:1) afforded the corresponding products **12**.

General Procedure for the Reaction of Dicarbonyl Compounds 12 with PIFA. To a solution of the dicarbonyl compound **12** (1 equiv) in $(CF_3)_2CHOH$ at room temperature under N_2 atmosphere was added slowly PIFA (1.1 equiv) over a period of 10 to 15 min. The reaction mixture was then stirred at room temperature until TLC indicated the absence of starting material (approximately 10 min). The solvent evaporated, and product was purified by column chromatography over silica (CH_2Cl_2/MeOH = 10:1) to give the diaryliodonium salts **13**.

Iodonium Salt 13a. Iodonium salt **13a** was obtained in 64% (146 mg) yield by the reaction of **12a** (0.39 mmol, 105 mg) with PIFA (0.43 mmol, 186 mg) in $(CF_3)_2CHOH$ (1.00 mL): pale yellow oil; IR (KBr) 3500, 2950, 1730, 1680, 1590, 1570 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 (1H, d, J = 8.5 Hz), 7.81 (2H, dd, J = 8.2, 1.0 Hz), 7.43−7.38 (1H, m), 7.38−7.25 (2H, m), 6.83 (1H, d, J = 3.0 Hz), 6.70 (1H, dd, J = 8.8, 3.0 Hz), 3.73 (3H, s), 3.66 (6H, s), 3.37 (1H, t, J = 7.3 Hz), 2.83−2.78 (2H, m), 2.09−2.01 (2H, m); ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 169.1, 162.9, 145.2, 139.5, 133.5, 131.4, 131.1, 116.8, 116.6, 115.2, 109.9, 55.5, 52.6, 50.5, 36.1, 29.3; HRMS (FAB) calcd for $C_{20}H_{22}IO_5$ ($M^+ - CF_3COO^-$) 469.0512, found 469.0537; HRMS (FAB) calcd for $C_2F_3O_2$ (CF_3COO^-) 112.9850, found 112.9877. Anal. Calcd for $C_{22}H_{22}F_3IO_7$: C, 45.38; H, 3.81. Found: C, 45.40; H, 4.09.

Iodonium Salt 13b. Iodonium salt **13b** was obtained as a pale yellow viscous liquid by the reaction of **12b** (0.8 mmol, 200 mg) with PIFA (0.88 mmol, 379 mg) in $(CF_3)_2CHOH$ (1.5 mL) in 84% (382 mg) yield: pale yellow viscous liquid; IR (KBr) 2950, 1750, 1720, 1570 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (1H, d, J = 9.1 Hz), 7.85 (2H, d, J = 7.3 Hz), 7.50 (1H, t, J = 7.7 Hz), 7.37 (2H, t, J = 8.1 Hz), 6.91 (1H, d, J = 2.9 Hz), 6.77 (1H, dd, J = 8.1, 2.9 Hz), 3.83 (3H, s), 3.76 (3H, s), 3.57 (1H, t, J = 7.0 Hz), 2.87−2.80 (2H, m), 2.24 (3H, s), 2.15−2.05 (2H, m); ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 202.5, 169.7, 163.1, 145.6, 139.5, 133.5, 131.6, 131.4, 116.8, 116.6, 115.5, 109.8, 58.2, 55.6, 52.6, 36.4, 29.3, 28.6; HRMS (FAB) calcd for $C_{20}H_{22}IO_4$ ($M^+ - CF_3COO^-$) 453.0563, found 453.0571.

Iodonium Salt 13c. Compound **13c** was obtained in 69% (161 mg) as a pale yellow oil by the reaction of compound **12c** (0.4 mmol, 106 mg) with PIFA (0.44 mmol, 190 mg) in $(CF_3)_2CHOH$ (1.5 mL): IR (KBr) 3500(br), 3000, 2950, 1740, 1710, 1680, 1560 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.99 (1H, d, J = 8.8 Hz), 7.87 (2H, d, J = 7.9 Hz), 7.47−7.43 (1H, m), 7.37−7.31 (2H, m), 6.91 (1H, d, J = 3.0 Hz), 6.78−6.74 (1H, dd, J = 8.5, 2.7 Hz), 4.25−4.17 (2H, q, J = 7.0 Hz), 3.82 (3H, s), 3.54 (1H, t, J = 7.0 Hz), 2.89−2.82 (2H, m), 2.24 (3H, s), 2.15−2.04 (2H, m), 1.28 (3H, t, J = 7.0 Hz); ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 202.6, 169.2, 162.9, 145.5, 139.4, 133.2, 131.4, 130.9, 118.5, 116.7, 115.4, 111.6, 61.7, 58.5, 55.6, 36.4, 29.3, 28.5, 14.1; HRMS (EI) calcd for $C_{21}H_{24}IO_4$ ($M^+ - CF_3COO^-$) 467.0719, found 467.0722.

Iodonium Salt 13d. Compound **13d** was obtained in 73% (225 mg) yield as a pale yellow oil by the reaction of compound **12d** (0.53 mmol, 140 mg) with PIFA (0.64 mmol, 274 mg) in $(CF_3)_2CHOH$ (1.5 mL): IR (KBr) 2900, 1740, 1710, 1680, 1580, 1560, 1470, 1440 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (1H, d, J = 8.8 Hz), 7.82 (2H, d, J = 7.6 Hz), 7.50 (1H, t, J = 7.3 Hz), 7.38 (2H, t, J = 7.3 Hz), 6.90 (1H, d, J = 2.7 Hz), 6.78−6.74 (1H, dd, J = 8.8, 3.0 Hz), 3.83 (3H, s), 3.72 (3H, s), 3.44 (1H, t, J = 7.0 Hz), 2.82 (2H, t, J = 7.6 Hz), 2.21 (3H, s), 1.85−1.83 (2H, m), 1.62−1.52 (2H, m); ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 202.8, 169.9, 163.2, 146.1, 139.5, 133.3, 131.7, 131.3, 116.8, 116.2, 115.1, 109.2, 58.9, 55.6, 52.4, 38.5, 29.1, 28.0, 27.3; HRMS (EI) calcd for $C_{21}H_{24}IO_4$ ($M^+ - CF_3COO^-$) 467.0719, found 467.0710.

Iodonium Salt 13e. Compound **13e** was obtained in a yield of 96% (178 mg) by the reaction of compound **12e** (0.64 mmol, 178 mg) with PIFA (0.7 mmol, 302 mg) in $(CF_3)_2CHOH$ (2.5 mL) as a pale yellow viscous liquid: IR (KBr) 2900, 1710, 1680, 1580, 1560 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.99 (1H, d, J = 8.5 Hz), 7.80 (2H, d, J = 7.3 Hz), 7.53−7.50 (1H, m), 7.41−7.36 (2H, m), 6.90 (1H, d, J = 2.7 Hz), 6.79−6.75 (1H, dd, J = 11.9, 3.0 Hz), 4.19 (2H, q, J = 7.3 Hz), 3.83 (3H, s), 3.42 (1H, t, J = 7.0 Hz), 2.82 (2H, t, J = 7.6 Hz), 2.21 (3H, s), 1.88−1.82 (2H, m), 1.60−1.54 (2H, m), 1.26 (3H, t, J = 7.3 Hz); ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 202.9, 169.4, 163.2, 146.1, 139.5, 133.3, 131.7, 131.4, 116.8, 116.3, 115.1, 109.2, 61.5, 59.1, 55.6, 38.5, 29.1, 28.0, 27.3, 14.0; HRMS (EI) calcd for $C_{22}H_{26}IO_4$ ($M^+ - CF_3COO^-$) 481.0876, found 481.0876.

General Procedure for the Base-Induced Cyclization of the Diaryliodonium Salts 13. To a flame-dried two-necked flask, cooled under nitrogen atmosphere, were added KO^{t}Bu (1.2 equiv) and dry THF (1.00 mL for 1.00 mmol scale). A solution of the iodonium salt (1 equiv) in THF (2.00 mL for 1 mmol scale) was then added dropwise through a cannula over a period of 15 min. The reaction mixture was then stirred at room temperature for 30 min, after which time TLC indicated the disappearance of starting material. The solvent was evaporated, and the residue was purified by column chromatography over silica (*n*-hexane/EtOAc = 4:1) to afford the cyclized products **14**.

1,1-Dimethoxycarbonyl-5-methoxyindane (14a). The cyclized product **14a** was obtained in 65% (32 mg) yield by the reaction of iodonium salt **13a** (0.19 mmol, 108 mg) with KO^{t}Bu (0.22 mmol, 25 mg) as a colorless oil: IR (KBr) 2900, 1740, 1600, 1580, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45 (1H, d, J = 8.5 Hz), 6.81−6.75 (2H, m), 3.80 (3H, s), 3.74 (6H, s), 3.00 (2H, t, J = 7.0 Hz), 2.70 (2H, t, J = 7.0 Hz); ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 171.4, 160.3, 146.0, 131.1, 127.3, 113.0, 109.4, 64.7, 55.3, 52.8, 34.6, 31.0; HRMS (EI) calcd for $C_{14}H_{16}O_5$ (M^+) 264.0998, found 264.1033.

1-Acetyl-1-methoxycarbonyl-5-methoxyindane (14b). Compound **14b** was obtained as a colorless oil in 75% (56 mg) yield by the reaction of iodonium salt **13b** (0.3 mmol, 172 mg) with KO^{t}Bu (0.36 mmol, 41 mg): IR (KBr) 2900, 1740, 1710, 1600, 1500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38(1H, d, J

= 8.2 Hz), 6.79−6.75(2H, m), 3.77(3H, s), 3.73(3H, s), 2.99−2.92(2H, m), 2.75−2.66(1H, m), 2.57−2.48(1H, m), 2.14(3H, s); ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 203.5, 171.9, 160.3, 146.3, 131.1, 127.1, 113.0, 109.8, 71.5, 55.3, 52.7, 33.4, 31.0, 26.2; HRMS (EI) calcd for $C_{14}H_{16}O_4$ (M^+) 248.1048, found 248.1066.

1-Acetyl-1-ethoxycarbonyl-5-methoxyindane (14c). Compound **14c** was obtained as a colorless oil in 80% (26 mg) yield by the reaction of iodonium salt **13c** (0.12 mmol, 72 mg) with KO^{t}Bu (0.15 mmol, 17 mg): colorless oil; IR (KBr) 2900, 1740, 1710, 1600, 1580, 1500 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (1H, d, J = 8.2 Hz), 6.88−6.77 (2H, m), 4.26−4.18 (2H, dq, J = 7.3, 1.8 Hz), 3.79 (3H, s), 3.01−2.94 (2H, m), 2.77−2.68 (1H, m), 2.58−2.56 (1H, m), 2.17 (3H, s), 1.27 (3H, t, J = 7.3 Hz); ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 203.4, 171.3, 160.2, 146.3, 131.2, 127.1, 112.9, 109.7, 71.5, 61.5, 55.3, 33.3, 30.9, 26.2, 14.0; HRMS (EI) calcd for $C_{15}H_{18}O_4$ (M^+) 262.1205, found 262.1211. Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.24; H, 7.01.

1-Acetyl-1-methoxycarbonyl-6-methoxy-1,2,3,4-tetrahydronaphthalene (14d). Compound **14d** was obtained as a colorless oil in 54% (41 mg) yield by the reaction of iodonium salt **13d** (0.29 mmol, 170 mg) with KO^{t}Bu (0.35 mmol, 40 mg): IR (KBr) 2950, 1740, 1710, 1600, 1570, 1500 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (1H, d, J = 8.5 Hz), 6.75−6.63 (2H, m), 3.77 (3H, s), 3.70 (3H, s), 2.78 (2H, t, J = 6.2 Hz), 2.58−2.50 (1H, ddd, J = 9.9, 6.9, 3.1 Hz), 2.07 (3H, s), 2.04−1.97 (1H, m), 1.84−1.76 (2H, m); HRMS (EI) calcd for $C_{15}H_{18}O_4$ (M^+) 262.1205, found 262.1208.

1-Acetyl-1-ethoxycarbonyl-6-methoxy-1,2,3,4-tetrahydronaphthalene (14e). Compound **14e** was obtained as a colorless oil in 67% (36 mg) yield by the reaction of iodonium salt **13e** (0.19 mmol, 115 mg) with KO^{t}Bu (0.21 mmol, 24 mg): IR (KBr) 2900, 1730, 1710, 1610, 1570, 1500 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (1H, d, J = 8.8 Hz), 6.77−6.73 (1H, dd, J = 8.8, 2.4 Hz), 6.65 (1H, d, J = 2.4 Hz), 4.27−4.10 (2H, m), 3.78 (3H, s), 2.80 (2H, t, J = 6.4 Hz), 2.59−2.51 (1H, m), 2.10 (3H, s), 2.08−2.00 (1H, m), 1.84−1.76 (2H, m), 1.26 (3H, t, J = 7.1 Hz); ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 206.4, 171.8, 158.7, 138.7, 131.6, 124.0, 113.7, 112.2, 64.7, 61.5, 55.1, 29.8, 29.6, 26.7, 19.7, 14.0; HRMS (EI) calcd for $C_{16}H_{20}O_4$ (M^+) 276.1361, found 276.1385.

5′-Methoxyspiro[cyclohexane-1,1′-indan]-2,6-dione (16). Prepared from **15** (100 mg, 0.400 mmol), PIFA (172 mg, 0.400 mmol), and CF_3CH_2OH (10.0 + 10.0 mL). (70.0 mg, 66%, column chromatography, SiO_2; n-hexane/EtOAc = 5:1) following the general procedure as described earlier: colorless oil; IR (KBr) 2957, 1725, 1696, 1605, 1584, 1495, 1489, 1464, 1456, 1435, 1314, 1258, 1213, 1169, 1148, 1103, 1092, 1026, 904, 866, 849, 833, 814 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.10 (1H, d, J = 8.4 Hz), 6.79−6.73 (2H, m), 3.77 (3H, s), 3.01 (2H, t, J = 7.3 Hz), 2.94−2.72 (4H, m), 2.60 (2H, t, J = 7.3 Hz), 2.17−1.97 (2H, m); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 207.2, 160.0, 146.5, 132.2, 125.1, 112.7, 110.2, 77.7, 55.3, 38.2, 33.4, 31.4, 17.7; HRMS (EI) calcd for $C_{15}H_{16}O_3$ (M^+) 244.1099, found 244.1103.

3′,4′-Dihydro-7′-methoxyspiro[cyclohexane-1,1′-2′*H*-naphthalene]-2,6-dione (18). Prepared from **17** (26.0 mg, 0.100 mmol), PIFA (43.0 mg, 0.100 mmol), and CF_3CH_2OH (2.00 + 2.00 mL) (17.0 mg, 65%, preparative thin-layer chromatography, SiO_2; n-hexane/EtOAc = 2:1) following the general procedure as described earlier: colorless oil; IR (KBr) 2940, 1725, 1695, 1610, 1505 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.71 (1H, dd, J = 8.6, 2.6 Hz), 6.65 (1H, d, J = 2.6 Hz), 6.50 (1H, d, J = 8.6 Hz), 3.84 (3H, s), 2.94−2.88 (2H, m), 2.78−2.66 (4H, m), 2.31−2.15 (3H, m), 2.06−1.87 (1H, m), 1.80−1.71 (2H, m); ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 209.9, 158.3, 139.5, 131.3, 124.9, 113.4, 112.7, 70.9, 55.0, 38.0, 34.3, 29.4, 18.9, 17.6; HRMS (EI) calcd for $C_{16}H_{18}O_3$ (M^+) 258.1256, found 258.1273.

5′,7′-Dimethoxyspiro[cyclohexane-1,1′-indan]-2,6-dione (21). Prepared from **19** (28.0 mg, 0.100 mmol), PIFA (43.0 mg, 0.100 mmol), and CF_3CH_2OH (2.00 + 2.00 mL) (<1 mg, <3%, preparative thin-layer column chromatography, SiO_2; n-hexane/EtOAc = 1:2): pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.36 (1H, d, J = 3.0 Hz), 6.25 (1H, d, J = 3.0 Hz), 3.82 (3H, s), 3.78(3H, s), 2.95−2.91 (2H, m), 2.73−2.69 (2H, m), 2.60−2.56 (2H, m), 2.36−2.32 (2H, m), 2.01−1.92 (2H, m); HRMS (EI) calcd for $C_{16}H_{18}O_4$ (M^+) 274.1205, found 274.1224.

[2-[2-(2,6-Dioxocyclohexyl)ethyl]-4,6-dimethoxyphenyl](phenyl)iodonium trifluoroacetate (20). Isolated from the above reaction together with **21**. Colorless crystal: mp 171−173 °C (EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (2H, d, J = 7.7 Hz), 7.56 (1H, t, J = 7.7 Hz), 7.41 (2H, t, J = 7.7 Hz), 6.67 (1H, d, J = 2.7 Hz), 6.40 (1H, d, J = 2.7 Hz), 3.87 (6H, s), 2.99−2.93 (2H, m), 2.62−2.56 (3H, m), 2.49−2.44 (5H, m), 1.94−1.86 (2H, m).

Supporting Information Available: Experimental details and data for **1**, **3**, **5**, **7**, **9**, **12a**−**e**, **15**, **17**, and **19**. ^{1}H and ^{13}C NMR spectra of all compounds lacking elemental analysis (**2**, **6**, **7**, **9**, **12b**−**e**, **13b**−**e**, **14a**,**b**,**d**,**e**, **16**, **18**, **20**, and **21**). This material is available free of charge via the Internet at http://pubs.acs.org.

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