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# Cyclohepta[de]naphthalenes and the Rearranged Abietane Framework of Microstegiol via Nicholas Reaction Chemistry

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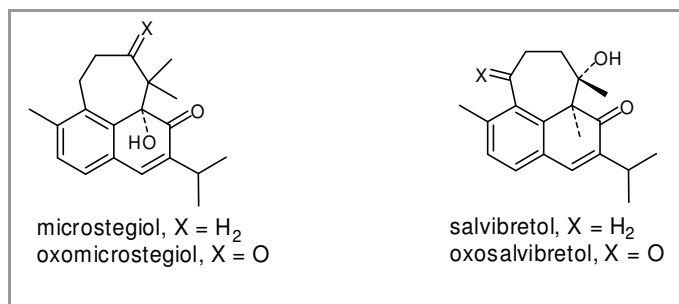
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**Abstract:** Nicholas reactions on 2,7-dioxygenated naphthalenes give C-1 monosubstitution and C-1/C-8 disubstitution in most cases. From  $\gamma$ -carbonyl cation monocondensation product **3b** or alkyne-unsubstituted dicondensation product **4a**, cyclohepta[de]naphthalenes bearing no substituents, gem-dimethyl substituents, and a ketone function, and the rearranged abietane framework of microstegiol may be prepared.

**Key words:** Carbocations, alkyne complexes, transition metals, electrophilic aromatic substitution, ring closure, tautomerism.

We have a long standing interest in the synthesis of seven membered ring systems, particularly involving the chemistry of alkyne dicobalt complexes and propargyldicobalt cations.<sup>1,2</sup> In particular, we have developed chemistry to incorporate nucleophiles, including electron rich arenes,  $\gamma$ -to electron withdrawing groups,<sup>3</sup> in an umpolung fashion,<sup>4-6</sup> and have used this chemistry to get access to seven membered ring systems.<sup>1a</sup>

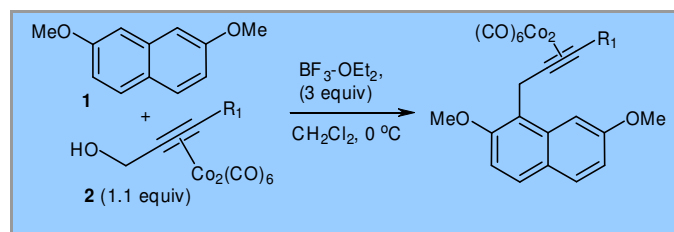
In this context we were drawn to cyclohepta[de]naphthalenes, featured in the rearranged abietanes such as microstegiol<sup>7</sup> and salvibretol,<sup>8</sup> and their oxygenated analogues (Figure 1).<sup>8,9</sup> These compounds are isolated from a number of plants of the *salvia* species that have long seen use as folk remedies and whose crude extracts have demonstrated antibacterial and anticancer activities;<sup>10</sup> microstegiol itself is known to possess antileukemic activity<sup>7,11</sup> and modest antibacterial activity.<sup>10b</sup> Surprisingly, these compounds have not received synthetic attention. Therefore we considered it worthy goal to investigate our Nicholas reaction- and  $\gamma$ -carbonyl cation chemistry towards the construction of the cyclohepta[de]naphthalene nucleus, with a particular view to the tautomerized 2-naphthol framework of microstegiol.



**Figure 1** Rearranged abietanes containing cyclohepta[de]naphthalene nucleus.

As a starting point to test reactivity, 2,7-dimethoxynaphthalene (**1**) was chosen, by virtue of its ready availability, its ability to direct monosubstitution to C-1 over C-3 in most cases<sup>12</sup> and disubstitution to C-1/C-8 over C-1/C-6 in many cases, and the potential for one alkoxy to serve as the masked version of the ketone function in microstegiol or salvibretol. Compound **1** showed sufficient nucleophilicity to react with propargyldicobalt cations; propargyl alcohol complex **2a** underwent BF<sub>3</sub>-OEt<sub>2</sub> mediated reaction to give **3a** in excellent yield (93%) (Table 1). Use of  $\gamma$ -carbonyl cation precursor **2b** (R<sub>1</sub> = CO<sub>2</sub>Me) gave good yields of condensation product **3b** (76%), while substitution on the remote alkyne carbon with methyl (**2c**) and trimethylsilyl (**2d**) functions also allowed formation of condensation products (**3c-d**) successfully (**3c**, 84%; **3d**, 71%).<sup>13</sup> Polyalkylation of the naphthalene nucleus did not appear to be a significant problem.<sup>14</sup>

**Table 1** Monocondensation reactions of **1**



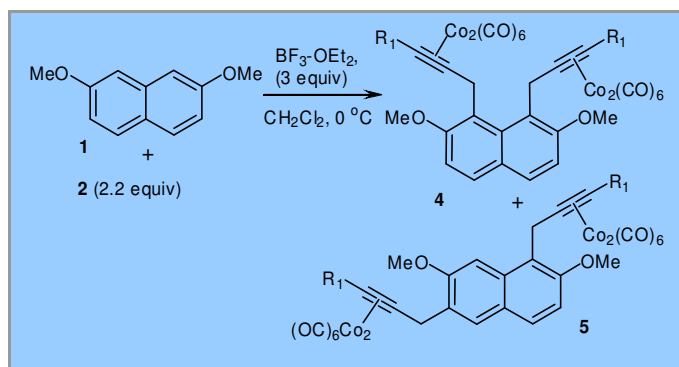
Complex	R <sub>1</sub>	Product	Yield (%)
<b>2a</b>	H	<b>3a</b>	93
<b>2b</b>	CO <sub>2</sub> Me <sup>a</sup>	<b>3b</b>	76
<b>2c</b>	Me	<b>3c</b>	84
<b>2d</b>	SiMe <sub>3</sub> <sup>b</sup>	<b>3d</b>	71

<sup>a</sup> Compound **2b** was employed as the methyl ether

<sup>b</sup> Reaction conducted at 0 °C – RT.

Disubstitution reactions on **1** could also be accomplished, by increasing the amount of propargyldicobalt cation precursors (**2**) to 2.2 equiv. For these reactions, the predominant 1,8-disubstitution pattern (**4**) was observed only for the unsubstituted (R<sub>1</sub> = H) and electron withdrawing group substituted (R<sub>1</sub> = CO<sub>2</sub>Me) propargyl cation complex precursors **2a** and **2b** (Table 2).<sup>15</sup> In the case of other R<sub>1</sub> substituents (R<sub>1</sub> = Me, Me<sub>3</sub>Si), the second substitution occurred at C-6, giving **5c** and **5d**. In the case of **2d** (R<sub>1</sub> = Me<sub>3</sub>Si), the second condensation was somewhat sluggish, and substantial amounts of **3d** were isolated in addition to **5d** despite allowing the reaction to warm to room temperature.

**Table 2** Dicondensation reactions of **1**

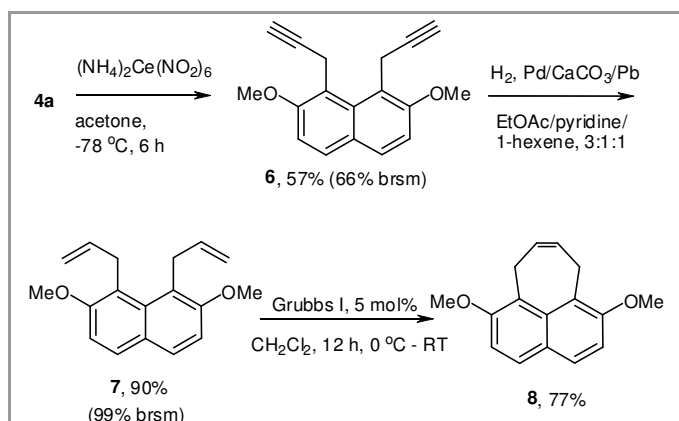


Complex	R <sub>1</sub>	Product	Yield (4,5) (%)
<b>2a</b>	H	<b>4a, 5a</b>	69, 9
<b>2b</b>	CO <sub>2</sub> Me <sup>a</sup>	<b>4b</b>	86, 0
<b>2c</b>	Me	<b>5c</b>	0, 86
<b>2d</b>	SiMe <sub>3</sub>	<b>3d, 5d</b>	0, 40 <sup>b</sup>

<sup>a</sup> Compound **2b** was employed as the methyl ether

<sup>b</sup> Reaction conducted at 0 °C – RT. In addition, 59 % of **3d** was isolated.

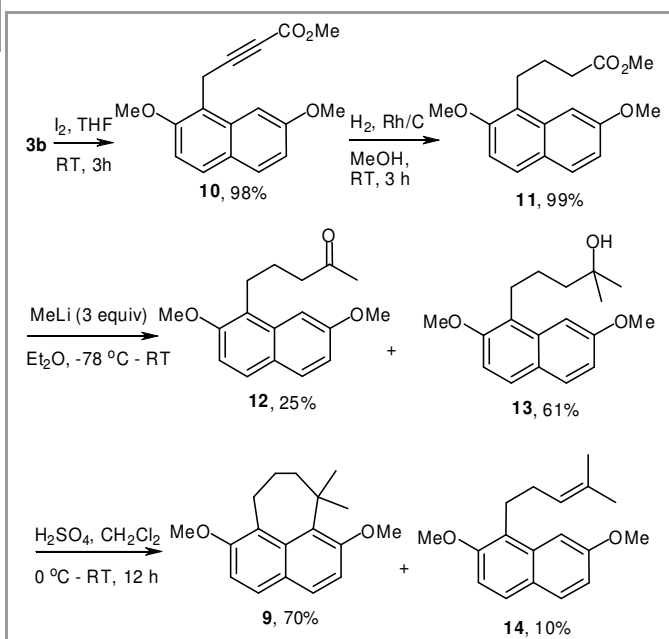
Given a basic understanding of the reactivity of 2,7-dioxygenated naphthalenes to propargyldicobalt cations, we considered  $\gamma$ -carbonyl cation adduct **3b** and 1,8-dicondensation product **4a** viable intermediates in the synthesis of cyclohepta[de]naphthalenes, and this possibility was explored. The unsubstituted cyclohepta[de]naphthalene nucleus was approached beginning with **4a** (Scheme 1). Decomplexation of the alkyne functions could be effected by (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>, affording diyne **6** in 57% yield (64% based on recovered starting **4a**). Hydrogenation of the alkynes using the Lindlar catalyst gave the diallylated naphthalene **7** (90% yield), and subsequent ring closing metathesis using (Cy<sub>3</sub>P)<sub>2</sub>Cl<sub>2</sub>Ru=CHPh (Grubbs 1 catalyst, 5 mol%) afforded **8** in 77% yield.<sup>16</sup> After the viability of this approach had been demonstrated, it was reported that the corresponding diacetoxy compound also has been prepared by ring closing metathesis chemistry.<sup>17</sup>



**Scheme 1** Dihydrocyclohepta[de]naphthalene preparation from **4a** via ring closing metathesis.

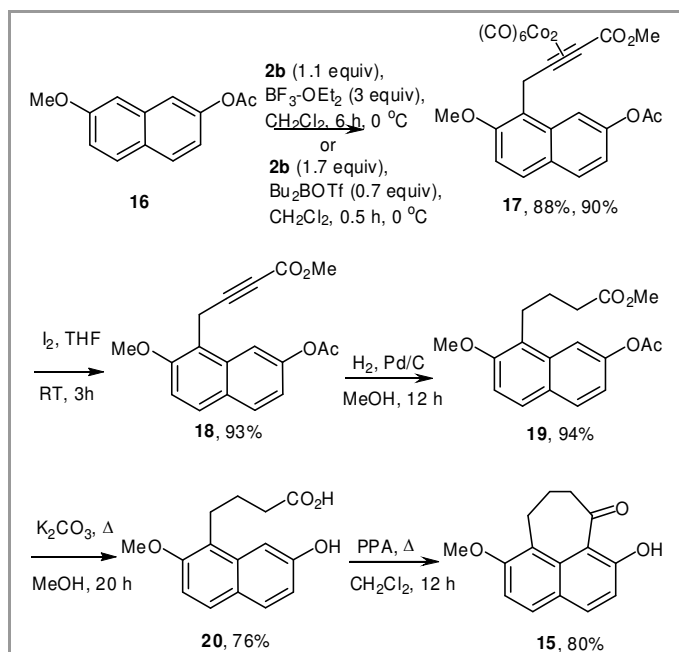
As opposed to **8**, other cyclohepta[de]naphthalene model systems were best approached from **3b**. For dimethyl substituted cyclohepta[de]naphthalene **9**, **3b** was readily decomplexed by I<sub>2</sub> in THF to give **10** in excellent yield

(98%) (Scheme 2). Catalytic hydrogenation of the alkyne function was sluggish over Pd/C, but proceeded well over Rh/C to afford **11** (99% yield). Subsequent addition of excess MeLi to the ester gave tertiary alcohol **13** (61% yield) along with an amount of methyl ketone **12** (25% yield). Finally, treatment of tertiary alcohol **13** with H<sub>2</sub>SO<sub>4</sub> (1 drop) gave cyclohepta[de]naphthalene **9** (70% yield), contaminated with a small amount (10%) of elimination product **14**.<sup>18</sup>



**Scheme 2** Conversion of **3b** to 7,7-dimethyltetrahydrocyclohepta[de]naphthalene.

Similarly, cyclohepta[de]naphthalenone **15** was best approached via a monocondensation route employing  $\gamma$ -carbonyl cation precursor **2b**. In this case, unsymmetrically substituted **16**, bearing a more readily deprotected acetate function, was chosen as the starting point (Scheme 3). Lewis acid mediated (either BF<sub>3</sub>·OEt<sub>2</sub> (88%) or Bu<sub>2</sub>BOTf (90%)) reaction of **16** with propargyl methyl ether complex **2b** gave monocondensation product **17** in excellent yield. After removal of the hexacarbonyldicobalt unit (I<sub>2</sub>, THF, 93%) to give **18**, catalytic hydrogenation (H<sub>2</sub>, Pd/C) of the alkyne function afforded **19** (94%). Hydrolysis of both the methyl ester and acetate functions was rather sluggish, but in K<sub>2</sub>CO<sub>3</sub>/MeOH at reflux, **19** gradually was converted to phenolic acid **20** (76%). Subjecting **20** to polyphosphoric acid (CH<sub>2</sub>Cl<sub>2</sub>, reflux, 12h) then resulted in closure of the seven-membered ring to give **15** in good yield (80%).<sup>19</sup> The phenolic ring of compound **15** existed entirely in the enolic/phenolic tautomer, as expected based on the existence of 1-hydroxy-7,12-pleiadenedione in its phenolic form.<sup>20</sup>



**Scheme 3** Preparation of tetrahydrocyclohepta[de]naphthalene-7-one.

Finally, we deemed it important to determine whether the combination of the seven-membered ring system and latent carbonyl function would be sufficient to drive the naphthol ring tautomer to the keto form. To this end, decomplexed and reduced adduct **19** was subjected to reaction with MeLi, affording tertiary alcohol **21** in 70%

## Experimental Section

To a solution of 2,7-dimethoxynaphthalene **1** in  $\text{CH}_2\text{Cl}_2$  (0.05 M) at  $0^\circ\text{C}$  was added propargyl alcohol complex **2** (1.1 equiv for monocondensations, 2.2 equiv for dicondensations) and  $\text{BF}_3\cdot\text{OEt}_2$  (3 equiv). After 3 h of stirring at  $0^\circ\text{C}$ ,  $\text{NH}_4\text{Cl}_{(\text{aq})}$  was added, and the mixture subjected to a conventional extractive workup. Purification by flash chromatography afforded **3** (monocondensation) or **4/5** (dicondensation).

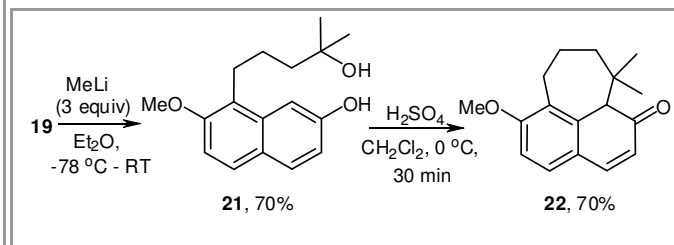
## Acknowledgment

We are grateful to NSERC (Canada), the Canada Foundation for Innovation (CFI) and Ontario Innovation Trust (OIT) for support of this research.

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yield (Scheme 4). Exposure of **21** to a single drop of  $\text{H}_2\text{SO}_4$  in  $\text{CH}_2\text{Cl}_2$  promoted rapid cyclization at  $0^\circ\text{C}$ , giving **22** in 70% yield. Compound **22** existed entirely in the dehydro- $\beta$ -tetralone tautomeric structure present in microstegiol; no evidence of the enol tautomer could be observed spectroscopically.<sup>21</sup> To our knowledge, this constitutes the first preparation of this ring system.



**Scheme 4** Preparation of rearranged abietane framework of microstegiol.

In conclusion, we have demonstrated the viability of Nicholas reaction chemistry in the assembly of cyclohepta[de]naphthalene rings, and in the construction of the rearranged abietane framework of microstegiol. Future work, which involves installation of the  $\gamma$ -carbonyl cation equivalent ortho- to a less donating (methyl) substituent, and introduction of a hydroxyl function  $\alpha$ - to the keto function, is in progress and will be reported in due course.

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- (13) Selected compounds: **(3a)** IR (KBr)  $\nu_{\max}$  3003, 2960, 2090, 2055  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$   $\delta$  7.71 (d, J = 8.9, 1H), 7.70 (d, J = 8.9, 1H), 7.22 (d, J = 2.4, 1H), 7.10 (d, J = 8.9, 1H), 7.04 (dd, J = 8.9, 2.4, 1H), 5.95 (s, 1H), 4.60 (s, 2H), 3.97 (s, 3H), 3.94 (s, 3H);  $^{13}\text{C NMR}$  199.6, 158.4, 154.7, 133.9, 130.2, 128.6, 124.6, 120.1, 116.1, 109.7, 101.6, 96.1, 73.5, 55.4, 55.1, 29.5; MS m/e 484 ( $\text{M}^+$ -CO), 456 ( $\text{M}^+$ -2CO), 428 ( $\text{M}^+$ -3CO), 372 ( $\text{M}^+$ -5CO); HRMS m/e for  $\text{C}_{21}\text{H}_{14}\text{Co}_2\text{O}_8$  calcd ( $\text{M}^+$ -2CO) 455.9454, found 455.9441. **(3b)** IR (KBr)  $\nu_{\max}$  3003, 2951, 2097, 2063, 2028, 1708;  $^1\text{H NMR}$   $\delta$  7.72 (d, J = 8.9, 1H), 7.68 (d, J = 8.9, 1H), 7.18 (d, J = 2.3, 1H), 7.10 (d, J = 8.9, 1H), 7.02 (dd, J = 8.9, 2.3, 1H), 4.64 (s, 2H), 3.96 (s, 3H), 3.95 (s, 3H), 3.53 (s, 3H);  $^{13}\text{C NMR}$  198.4, 171.7, 158.5, 154.7, 133.9, 130.1, 128.8, 124.4, 119.1, 116.2, 109.3, 101.1, 99.4, 79.3, 55.2, 54.9, 52.4, 29.0; MS m/e 570 ( $\text{M}^+$ ), 542 ( $\text{M}^+$ -1CO), 514 ( $\text{M}^+$ -2CO), 486 ( $\text{M}^+$ -3CO), 458 ( $\text{M}^+$ -4CO), 430 ( $\text{M}^+$ -5CO), 402 ( $\text{M}^+$ -6CO); HRMS m/e for  $\text{C}_{23}\text{H}_{16}\text{Co}_2\text{O}_{10}$  calcd ( $\text{M}^+$ -CO) 541.9458, found 541.9455.
- (14) However, substitution at the propargylic site in **2** resulted in condensation reactions at C-3 in preference to C-1.
- (15) Selected compounds: **(4a)**. IR (KBr)  $\nu_{\max}$  2917, 2090, 2051, 2021;  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$   $\delta$  7.70 (d, J = 8.9, 2H), 7.12 (d, J = 8.9, 2H), 5.83 (s, 2H), 5.22 (d, J = 16.4, 2H), 4.50 (d, J = 16.4, 2H), 3.99 (s, 6H);  $^{13}\text{C NMR}$  199.6, 156.1, 131.9, 130.7, 126.5, 121.3, 110.1, 97.5, 73.8, 55.9, 30.6; MS m/e 808 ( $\text{M}^+$ -1CO), 780 ( $\text{M}^+$ -2CO), 752 ( $\text{M}^+$ -3CO), 724 ( $\text{M}^+$ -4CO), 696 ( $\text{M}^+$ -5CO), 668 ( $\text{M}^+$ -6CO), 640 ( $\text{M}^+$ -7CO), 612 ( $\text{M}^+$ -8CO); HRMS m/e for  $\text{C}_{30}\text{H}_{16}\text{Co}_4\text{O}_{14}$  calcd. ( $\text{M}^+$ -CO) 807.7917, found 807.7904. **(4b)** IR (KBr)  $\nu_{\max}$  3004, 2950, 2097, 2067, 1710  $\text{cm}^{-1}$ ; 7.71 (d, J = 9.0, 2H), 7.10 (d, J = 9.0, 2H), 5.19 (d, J = 16.5, 2H), 4.69 (d, J = 16.5, 2H), 3.40 (s, 6H), 3.46 (s, 6H);  $^{13}\text{C NMR}$  198.2, 170.6, 156.1, 132.1, 131.0, 126.3, 120.3, 109.8, 99.9, 80.3, 55.7, 52.4, 30.9; MS m/e 896 ( $\text{M}^+$ -2CO), 840 ( $\text{M}^+$ -4CO), 784 ( $\text{M}^+$ -6CO), 728 ( $\text{M}^+$ -8CO), 700 ( $\text{M}^+$ -9CO).
- (16) **(6)** IR (KBr)  $\nu_{\max}$  3291, 2932, 2107, 1618  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$   $\delta$  7.72 (d, J = 9.0, 2H), 7.18 (d, J = 9.0, 2H), 4.31 (d, J = 2.6, 4H), 4.03 (s, 6H), 2.16 (t, J = 2.6, 2H);  $^{13}\text{C NMR}$  156.7, 133.5, 130.1, 126.2, 117.3, 111.0, 84.7, 69.1, 56.9, 17.3; MS m/e 264 ( $\text{M}^+$ ); HRMS m/e for  $\text{C}_{18}\text{H}_{16}\text{O}_2$ , calcd ( $\text{M}^+$ ) 264.1150, found 264.1153. **(7)** IR (KBr)  $\nu_{\max}$  3077, 2934, 1614  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$   $\delta$  7.72 (d, J = 8.9, 2H), 7.18 (d, J = 8.9, 2H), 6.23 (m, 2H), 5.09 (dd, J = 10.3, 1.9, 2H), 4.84 (dd, J = 17.3, 1.9, 2H), 3.93 (s, 6H), 3.91 (m, 4H);  $^{13}\text{C NMR}$  156.7, 139.0, 134.9, 129.4, 126.3, 120.4, 114.5, 111.0, 56.8, 30.9; MS m/e 268 ( $\text{M}^+$ ); HRMS m/e for  $\text{C}_{18}\text{H}_{20}\text{O}_2$  calcd ( $\text{M}^+$ ) 268.1463, found 268.1466. **(8)** IR (KBr)  $\nu_{\max}$  3033, 2934, 1616  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$   $\delta$  7.59 (d, J = 9.0, 2H), 7.11 (d, J = 9.0, 2H), 6.19 (m, 2H), 4.02 (d, J = 5.6, 4H), 3.92 (s, 6H);  $^{13}\text{C NMR}$  153.9, 134.8, 130.9, 128.3, 126.8, 120.2, 111.9, 57.2, 24.2; MS m/e 240 ( $\text{M}^+$ ), HRMS m/e for  $\text{C}_{16}\text{H}_{16}\text{O}_2$  calcd ( $\text{M}^+$ ) 240.1150, found 240.1150.
- (17) (a) Kotha, S.; Mandal, K.; Tiwari, A.; Mobin, S. M. *Chem. Eur. J.* **2006**, *12*, 8024. (b) Chattopadhyay, S. K.; Ghosh, D.; Neogi, K. *Synth. Commun.* **2007**, *37*, 1535.
- (18) **(10)** IR (KBr)  $\nu_{\max}$  2956, 2233, 1712, 1628;  $^1\text{H NMR}$   $\delta$  7.72 (d, J = 9.0, 1H), 7.69 (d, J = 8.9, 1H), 7.22 (d, J = 2.4, 1H), 7.11 (d, J = 9.0, 1H), 7.05 (dd, J = 8.9, 2.4, 1H), 4.11 (s, 2H), 3.97 (s, 3H), 3.96 (s, 3H), 3.70 (s, 3H);  $^{13}\text{C NMR}$  158.4, 154.6, 154.0, 133.7, 129.9, 128.9, 124.3, 116.1, 113.6, 110.1, 101.2, 87.7, 71.9, 56.1, 55.0, 52.2, 14.5; MS m/e 284 ( $\text{M}^+$ ); HRMS m/e for  $\text{C}_{17}\text{H}_{16}\text{O}_4$  calcd ( $\text{M}^+$ ) 284.1049, found 284.1033. **(11)** IR (KBr)  $\nu_{\max}$  2954, 1740, 1628;  $^1\text{H NMR}$   $\delta$  7.69 (d, J = 8.9, 1H), 7.66 (d, J = 8.9, 1H), 7.32 (d, J = 2.0, 1H), 7.12 (d, J = 8.9, 1H), 7.03 (dd, J = 8.9, 2.0, 1H), 3.98 (s, 3H), 3.93 (s, 3H), 3.70 (s, 3H), 3.11 (t, J = 7.6, 2H), 2.44 (t, J = 7.1, 2H), 2.00 (m, 2H);  $^{13}\text{C NMR}$  174.0, 158.1, 154.8, 134.1, 129.8, 127.3, 124.5, 121.2, 115.7, 110.2, 101.6, 55.9, 55.1, 51.2, 33.4, 24.2, 24.1; MS m/e 288 ( $\text{M}^+$ ); HRMS m/e for  $\text{C}_{17}\text{H}_{20}\text{O}_4$  calcd ( $\text{M}^+$ ) 288.1362, found 288.1360. **(13)** IR (KBr)  $\nu_{\max}$  3422 br, 2966, 1627;  $^1\text{H NMR}$   $\delta$  7.70 (d, J = 8.9, 1H), 7.66 (d, J = 8.9, 1H), 7.24 (d, J = 2.3, 1H), 7.13 (d, J = 8.9, 1H), 7.05 (dd, J = 8.9, 2.3, 1H), 3.952 (s, 3H), 3.945 (s, 3H), 3.09 (t, J = 7.6, 2H), 1.75 (m, 2H), 1.69 (m, 2H) 1.38 (br s, 1H), 1.23 (s, 6H);  $^{13}\text{C NMR}$  158.0, 154.8, 134.1, 130.0, 127.1, 124.7, 122.6, 115.5, 110.8, 102.0, 70.9, 56.3, 55.1, 43.8, 29.1, 25.4, 24.4; MS m/e 288 ( $\text{M}^+$ ), HRMS m/e for  $\text{C}_{18}\text{H}_{24}\text{O}_3$  calcd ( $\text{M}^+$ ) 288.1725, found 288.1713. **(9)** IR (KBr)  $\nu_{\max}$  2929, 1612;  $^1\text{H NMR}$   $\delta$  7.54 (d, J = 8.9, 1H), 7.52 (d, J = 8.8, 1H), 7.09 (d, J = 8.9, 1H), 7.07 (d, J = 8.8, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.00 (br m, 2H), 1.96 (m, 2H), 1.70 (m, 2H), 1.52 (s, 6H);  $^{13}\text{C NMR}$  158.8, 154.5, 137.6, 131.7, 127.3, 126.9, 125.4, 122.9, 112.1, 111.6, 84.6, 57.4, 56.0, 41.1, 39.4, 25.5, 22.1; MS m/e 270 ( $\text{M}^+$ ); HRMS m/e for  $\text{C}_{18}\text{H}_{22}\text{O}_2$  calcd ( $\text{M}^+$ ) 270.1620, found 270.1614.
- (19) **(17)** IR (KBr)  $\nu_{\max}$  3004, 2952, 2099, 2063, 2029, 1765, 1709;  $^1\text{H NMR}$   $\delta$  7.82 (d, J = 9.0, 1H), 7.81 (d, J = 8.8, 1H) 7.61 (d, J = 2.2, 1H), 7.26 (d, J = 9.0, 1H), 7.11 (dd, J = 8.8, 2.2, 1H), 4.60 (s, 2H), 3.96 (s, 3H), 3.75 (s, 3H), 2.33 (s, 3H);  $^{13}\text{C NMR}$  198.0, 170.5, 169.4, 154.7, 149.3, 133.2, 130.0, 128.8, 126.8, 120.0, 118.6, 114.1, 111.8, 98.5, 93.9, 55.2, 52.5, 28.2, 20.8; MS m/e 542 ( $\text{M}^+$ -2CO), 514 ( $\text{M}^+$ -3CO), 486 ( $\text{M}^+$ -4CO), 458 ( $\text{M}^+$ -5CO), 430 ( $\text{M}^+$ -6CO); HRMS m/e for  $\text{C}_{24}\text{H}_{16}\text{Co}_2\text{O}_{11}$  calcd ( $\text{M}^+$ -3CO) 513.9509, found 513.9511. **(18)** IR (KBr)  $\nu_{\max}$  2917, 2234, 1761, 1712;  $^1\text{H NMR}$   $\delta$  7.81 (d, J = 8.9, 2H), 7.62 (d, J = 2.1, 1H), 7.26 (d, J = 8.9, 1H), 7.15 (dd, J = 8.8, 2.1, 1H), 4.08 (s, 2H), 3.99 (s, 3H), 3.71 (s, 3H), 2.38 (s, 3H);  $^{13}\text{C NMR}$  169.4, 154.7, 154.0, 149.4, 133.1, 129.9, 129.2, 126.9, 118.8, 114.8, 113.7, 112.7, 87.4, 72.0, 56.3, 52.3, 21.0, 14.6; MS m/e 312 ( $\text{M}^+$ ); HRMS m/e for  $\text{C}_{18}\text{H}_{16}\text{O}_5$  calcd ( $\text{M}^+$ ) 312.0998, found 312.0991. **(19)** IR (KBr)  $\nu_{\max}$  3067, 2950, 1759, 1734;  $^1\text{H NMR}$   $\delta$  7.75 (d, J = 8.8, 1H), 7.67 (d, J = 1.9, 1H), 7.65 (d, J = 9.0, 1H), 7.16 (d, J = 9.0, 1H), 7.09 (dd, J = 8.8, 1.9, 1H), 3.85 (s, 3H), 3.64 (s, 3H), 3.08 (t, J = 17.6, 2H), 2.39 (t, J = 7.4, 2H), 2.33 (s, 3H), 1.99 (m, 2H);  $^{13}\text{C NMR}$  173.9, 169.5, 154.9, 149.1, 133.6, 129.9, 127.6, 127.1, 122.3, 118.4, 114.0, 112.7, 56.1, 51.2, 33.5, 24.7, 24.0, 21.1; MS m/e 316 ( $\text{M}^+$ ); HRMS m/e for  $\text{C}_{18}\text{H}_{20}\text{O}_5$  calcd ( $\text{M}^+$ ) 316.1311, found 316.1316. **(20)** IR (KBr)  $\nu_{\max}$  3385 br, 2924, 1703, 1626;  $^1\text{H NMR}$  (acetone- $d_6$ )  $\delta$  7.63 (d, J = 8.8, 1H), 7.62 (d, J = 9.0, 1H), 7.28 (br s, 1H), 7.11 (d, J = 9.0, 1H), 6.93 (dd, J = 8.8, 2.1, 1H), 3.87 (s, 3H), 2.99 (t, J = 7.7, 2H), 2.35 (m, 2H), 1.85 (m, 2H);  $^{13}\text{C NMR}$  (acetone- $d_6$ ) 174.5, 156.0, 155.1, 134.8, 130.2, 127.7, 124.5, 120.7, 115.7, 110.3, 104.8, 55.8, 33.3, 24.8, 24.1; MS m/e 260 ( $\text{M}^+$ ); HRMS m/e for  $\text{C}_{15}\text{H}_{16}\text{O}_4$  calcd ( $\text{M}^+$ ) 260.1049, found 260.1045. **(15)** IR (KBr)  $\nu_{\max}$  3009, 2970, 1616  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$   $\delta$  12.73 (s, 1H), 7.71 (d, J = 8.9, 1H), 7.63 (d, J = 8.8, 1H), 7.12 (d, J = 8.8, 1H), 6.93 (d, J = 8.9, 1H), 3.95 (s, 3H), 3.01 (t, J = 7.1, 2H), 2.71 (t, J = 7.4, 2H), 2.39 (m, 2H);  $^{13}\text{C NMR}$  207.4, 162.5, 157.3, 136.2, 135.7, 128.6, 123.2, 122.3, 116.5, 115.2, 110.3, 56.2, 42.3, 29.5, 25.4; MS m/e 242 ( $\text{M}^+$ ); HRMS for  $\text{C}_{15}\text{H}_{14}\text{O}_3$  calcd ( $\text{M}^+$ ) 242.0943, found 242.0931.
- (20) a) Rieche, A.; Fruhwald, E. *Chem. Ber.* **1931**, *64B*, 1603.; b) Moghaddam, F. M.; Porkaleh, H.; Zali-Boeini, H. *Lett. Org. Chem.* **2006**, *3*, 123.

- (21) **(21)** IR (KBr)  $\nu_{\max}$  3358, 2967  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  8.10 (br s, 1H), 7.65 (d,  $J = 8.8$ , 1H), 7.61 (d,  $J = 8.9$ , 1H), 7.33 (d,  $J = 2.2$ , 1H), 7.08 (d,  $J = 8.9$ , 1H), 7.01 (dd,  $J = 8.8, 2.2$ , 1H), 3.91 (s, 3H), 2.95 (br t,  $J = 7.0$ , 2H), 2.60 (br s, 1H), 1.65 (m, 4H), 1.21 (s, 6H);  $^{13}\text{C}$  NMR 154.6, 154.5, 134.4, 130.3, 127.3, 124.5, 122.1, 115.6, 110.7, 105.3, 72.0, 56.4, 43.5, 29.1, 25.4, 24.3; MS  $m/e$  274 ( $M^+$ ); HRMS  $m/e$  for  $\text{C}_{17}\text{H}_{22}\text{O}_3$  calcd 274.1569, found 274.1574. **(22)** IR (KBr)  $\nu_{\max}$  2934, 1653, 1615  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.29 (d,  $J = 9.7$ , 1H), 7.13 (d,  $J = 8.4$ , 1H), 6.79 (d,  $J = 8.4$ , 1H), 5.97 (d,  $J = 9.7$ , 1H), 3.84 (s, 3H), 3.63 (s, 1H), 3.36 (m, 1H), 2.42 (m, 1H), 1.84 (m, 1H), 1.51 (m, 1H), 1.38 (m, 1H), 1.27 (m, 1H), 1.17 (s, 3H), 0.66 (s, 3H);  $^{13}\text{C}$  NMR 203.2, 157.7, 145.5, 140.8, 129.4, 127.9, 124.4, 123.5, 108.9, 58.3, 55.7, 43.2, 37.0, 27.4, 24.2, 21.5, 20.2; MS  $m/e$  256 ( $M^+$ ); HRMS  $m/e$  for  $\text{C}_{17}\text{H}_{20}\text{O}_2$  calcd 256.1463, found 256.1457.

