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Tetrahedron Letters 46 (2005) 8711–8714
Tetrahedron Letters

2-Nitrofurans as dienophiles in Diels–Alder reactions

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Received 6 September 2005; revised 5 October 2005; accepted 12 October 2005

Abstract—α-Nitrofuran derivatives are studied in Diels–Alder reactions under thermal conditions. In contrast to α-acylfurans, they proved to be efficient dienophiles.

1. Introduction

It has been known for some time that aromatic heterocycles, such as furan, thiophene and pyrrole undergo Diels–Alder (DA) reactions despite their aromaticity and hence expected inertness. In view of their electron-rich constitution and electron-donor properties, they have been mostly involved as the diene component in the cycloaddition process.[1] However, there exists a limited number of examples of five-membered, aromatic heterocycles acting as dienophiles in DA reactions with normal electron demand, for example, β-acylated furans have shown to be excellent dienophiles in interaction with isoprene. In contrast, α-acylfuran proved to be a very poor dienophile toward isoprene.[2,3] In view of our interest in cycloaddition chemistry of substituted aromatic heterocycles with electron withdrawing groups, we have reported studies on the dienophilic character of other aromatic systems such as nitroindoles[4] and nitronaphthalenes[5] in DA reactions with normal electron demand. More recently, we have shown that 2-nitrothiophene can act as dienophile in thermal DA reactions with Danishefsky's diene and isoprene leading to benzothiophenol or pyrrolyl-thiophene depending on the reaction conditions. Besides, the results demonstrate that α-nitro substituted thiophenes show higher dienophilicity than the β-nitro isomers.[6] The DA reactivity of thiophenes appears to be opposite to that reported for furans where the β-substituted bond was found to be more dienophilic.

Taking into account that the exposure of 2,5-dimethyl-3-nitrofuran to isoprene at elevated temperature yields the isomeric cycloadducts (with thermal extrusion of nitrous acid accompanying the DA reaction),[7] which is in agreement with the reactivity showed by pyrroles and furans β-substituted with electron-withdrawing groups, the purpose of the present work is to explore the behaviour of 2-nitrofuran, methyl 5-nitrofuran-3-carboxylate and methyl 5-nitrofuran-2-carboxylate in their exposure to dienes (strongly, moderately and poorly activated) under thermal conditions. The goal of this work is to determine if a strong electron-withdrawing group in α-position of furans induces reactivity at cycloaddition reactions like nitro-thiophenes.

2. Results and discussion

To test the efficacy of 2-nitrofurans as dienophile in DA reactions, the following compounds were used: 2-nitrofuran (**1a**), methyl 5-nitrofuran-3-carboxylate (**1b**) and methyl 5-nitrofuran-2-carboxylate (**1c**). Isoprene (**2**), 1-*N*-acetyl-*N*-propyl-1,3-butadiene (**3**), 1-diethylamino-3-*tert*-butyldimethyl-siloxy-1,3-butadiene (Rawal's diene) (**4**) and 1-methoxy-3-trimethysilyloxy-1,3-butadiene (Danishefsky's diene) (**5**) were chosen as the diene partners (Scheme 1).

When 2-nitrofurans were reacted with the above-mentioned dienes under different reaction conditions,[8] they showed their dienophilic character taking part in DA cycloaddition reactions. Treatment of **1a** with isoprene **2** gave a mixture of dihydrobenzofurans **6a** and **6b** (with thermal extrusion of nitro group as nitrous acid from

Keywords: Diels–Alder; Dienophiles; Nitrofurans.
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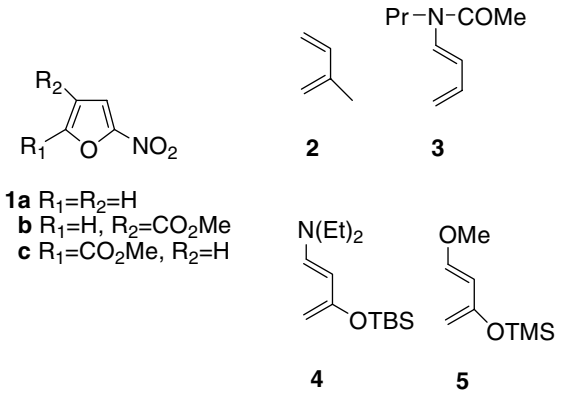
0040-4039/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.tetlet.2005.10.042



Scheme 1.

the initial DA adduct) and benzofurans **7a** and **7b** as principal products.[9]

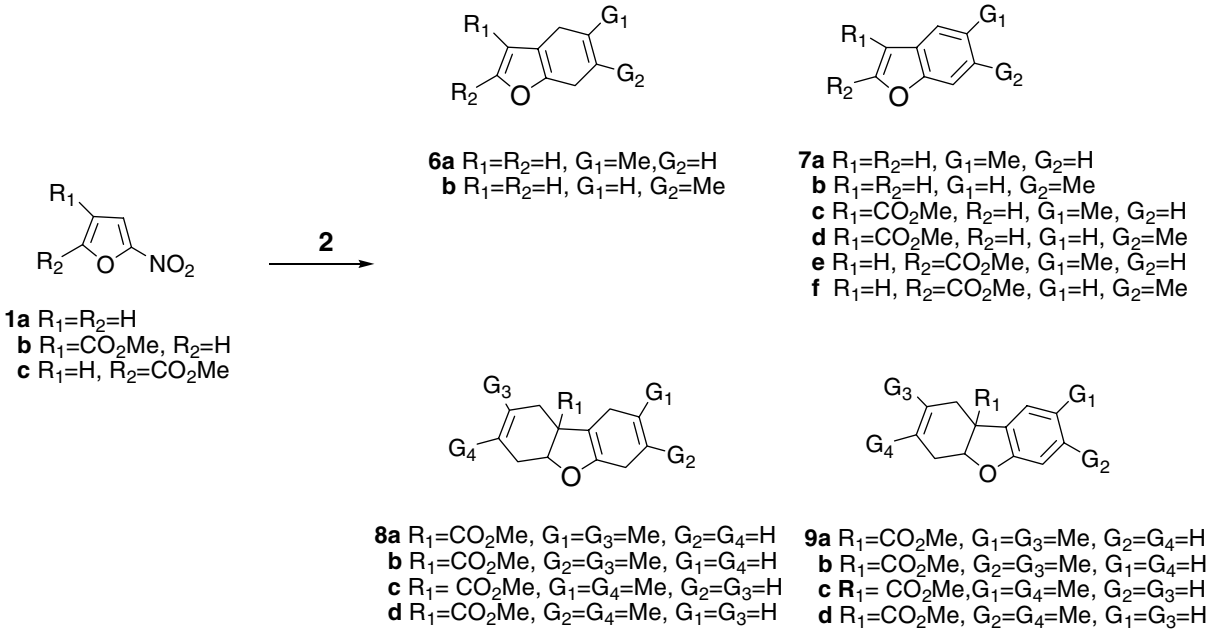
Exposure of **1b** to isoprene yielded the mixture of isomeric cycloadducts **7c** and **7d** as principal products (60%) and a mixture of double addition adducts **8a–d** (10%) and **9a–d** (30%), in both cases of regioisomer mixtures (Scheme 2, Table 1).[9]

On the other hand, reactions of **1c** with **2** gave a mixture of aromatic cycloadducts of simple addition **7e** and **7f** with moderate yields (Table 1, entries 5 and 6).[9] Table 1 shows that, in general, the yield increases with the increase of temperature in every experience.

It should be noted that the isolation of the primary nitroadduct was never achieved under these conditions.

The reaction of **1a** with 1-*N*-acetyl-*N*-propyl-1,3-butadiene **3** afforded benzofuran **10a** with loss of *N*-acetyl-*N*-propylamino and nitro groups. In the same way, in the reactions with Rawal's and Danishefsky's diene cycloadducts **11a** and **12a** were obtained with moderate to high yield and complete regioselectivity (Table 2).[9]

When **3**, **4** and **5** reacted with **1b**, they yielded **10b**, **11b** and **12b**, respectively. In the reactions with **1c**, **10c**, **11c** and **12c** were obtained.[9] These reactions proceeded by addition of the diene selectively to the nitro-substituted double bond of the furan. All addition products showed extrusion of the nitro group as nitrous acid. It is noteworthy that only 1:1 adducts whose structure revealed site selectivity and regioselectivity were obtained (Scheme 3).



Scheme 2. Diels–Alder reactions of 2-nitrofurans derivatives and isoprene.

Table 1.

Entry	Dienophile	Conditions[a]	Product	Product ratio	Yield[b] (%)
1	**1a**	200 °C, 72 h	**6a**,**b**; **7a**,**b**	**1**:**1**:**3**:**3**	62
2		150 °C, 72 h	**6a**,**b**; **7a**,**b**	**1**:**1**:**3**:**3**	53
3	**1b**	200 °C, 72 h	**7c**,**d**; **8a**,**b**,**c**,**d**; **9a**,**b**,**c**,**d**	**1**:**3**; **1**:**3**:**1**:**2**; **1**:**3**:**1**:**2**	70
4		150 °C, 72 h	**7c**,**d**; **8a**,**b**,**c**,**d**; **9a**,**b**,**c**,**d**	**1**:**3**; **1**:**3**:**1**:**2**; **1**:**3**:**1**:**2**	60
5	**1c**	200 °C, 72 h	**7e**,**f**	**1**:**3**	55
6		150 °C, 72 h	**7e**,**f**	**1**:**3**	51

[a] 12 equiv of isoprene in benzene.
[b] Based on consumed dienophile.

Table 2.

Entry	Diene	Dienophile	D/D[a]	Condition	Product, yield[b]
1	**3**	**1a**	3:1	120 °C, 72 h	**10a**, 58%
2	**3**	**1b**	3:1	120 °C, 72 h	**10b**, 51%
3	**3**	**1c**	3:1	120 °C, 72 h	**10c**, 28%
4	**4**	**1a**	3:1	RefluxTol. 120 h	**11a**, 82%
5	**4**	**1b**	3:1	RefluxTol. 120 h	**11b**, 45%
6	**4**	**1c**	3:1	RefluxTol. 120 h	**11c**, 32%
7	**5**	**1a**	2:1	120 °C, 72 h	**12a**, 50%
8	**5**	**1b**	2:1	120 °C, 72 h	**12b**, 55%
9	**5**	**1c**	2:1	120 °C, 72 h	**12c**, 43%

[a] Diene/dienophile ratio.
[b] Based on consumed nitrofuran.

3. Conclusions

It has been demonstrated that in contrast to the 2-acylated furans, 2-nitrofurans react efficiently with the above-mentioned dienes in normal electron demand Diels–Alder reactions, with the nitro group inducing side selectivity. This substituent is easily extrused under thermal conditions, giving cycloadducts of high interest as intermediaries in the synthesis of some alkaloid families as morphine, kreysiginine and codeine. Selecting the appropriate reagents (diene-dienophile), the DA adducts for the total synthesis of these natural products could be obtained in a simple way.

The reactions of **1b** with isoprene underwent cycloaddition with the formation of 1:1 and 2:1 adducts. With the same diene, **1c** gave only 1:1 adducts. The behaviour of 2-nitrofurans with carbomethoxy group substituent at β′ position is in agreement with the difference between β-acylfurans and their α-acyl isomers.

Surprisingly, exposure of every 2-nitrofuran to electron-rich dienes yielded 1:1 adducts with the cycloaddition taking place on the nitrated bond. These results would show that dienes with strong electron-donor substituents induce the Diels–Alder cycloaddition selectively. Generally, the more powerful the electronic effect of the substituents, the more regioselective the reaction.

Moreover, a very strong electron-acceptor group, such as nitro group induces in the furan ring similar reactivity at α- and β-positions.

Acknowledgements

This work received financial support from the Science and Technology Secretariat-UNL-CAI+D Program and Doctoral Grant Programs at Universidad Nacional del Litoral.

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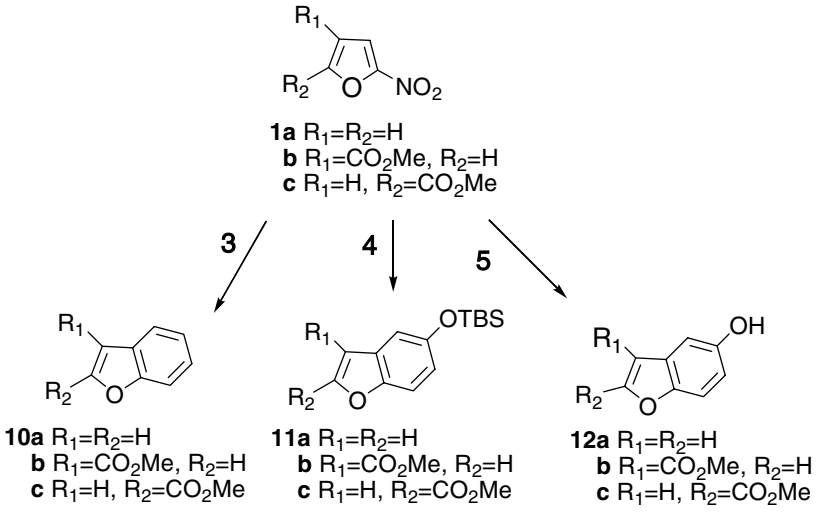
8. General procedure. The temperature, the length of the reaction and the diene/dienophile ratio are given in Tables 1 and 2. An ampoule containing 1.0 mmol of the dienophile and the required amount of diene in 0.5 ml of dry benzene was cooled in liquid nitrogen, sealed and then heated in an oil bath. After the reaction time was completed, it was cooled once more in liquid nitrogen and opened. The



Scheme 3.

solution was evaporated and the residue purified by column chromatography in silica gel or alumina using hexane/ethyl acetate mixtures as eluent. Biolatto, B.; Kneeteman, M.; Paredes, E.; Mancini, P. *J. Org. Chem.* **2001**, *66*, 3906–3912.

9. Spectral data: **6a** δ ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.86 (s, 3H), 3.15 (m, 2H), 3.35 (m, 2H), 5.56 (m, 1H), 6.25 (d, 1H, $J = 3.1$ Hz), 7.05 (d, 1H, $J = 3.1$Hz); ^{13}C NMR (500 MHz) δ: 22.6, 24.5, 27.3, 110.7, 114.4, 122.5, 134.6, 140.6, 153.0. **6b** ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.88 (s, 3H), 3.16 (m, 2H), 3.35 (m, 2H), 5.54 (m, 1H), 6.25 (d, 1H, $J = 3.1$Hz), 7.5 (d, 1H, $J = 3.1$ Hz); ^{13}C NMR (500 MHz) δ: 20.1, 23.0, 31.8, 110.9, 114.6, 122.4, 135.1, 140.6, 153.0. **7a** ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.48 (s, 3H), 6.68 (d, 1H, $J = 3.5$Hz), 7.01 (dd, 1H, $J = 8.6$; 2.4 Hz), 7.27 (d, 1H, $J = 2.4$ Hz), 7.31 (d, 1H, $J = 8.6$ Hz), 7.52 (d, 1H, $J = 3.5$ Hz); ^{13}C NMR (500 MHz) δ: 24.9, 107.1, 112.0, 121.0, 125.2, 128.8, 131.8, 146.2, 153.8. **7b** ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.52 (s, 3H), 6.67 (d, 1H, $J = 3.3$ Hz), 6.89 (dd, 1H, $J = 8.7$; 2.4 Hz), 7.25 (d, 1H, $J = 3.5$ Hz), 7.38 (d, 1H, $J = 8.6$ Hz), 7.50 (d, 1H, $J = 3.5$Hz); ^{13}C NMR (500 MHz) δ: 24.7, 106.5, 111.8, 121.1, 124.1, 126.0, 132.5, 145.2, 156.5. **7c** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.33 (s, 3H), 3.89 (s, 3H), 6.97 (dd, 1H, $J = 8.6$ Hz; $J = 2.3$ Hz), 7.28 (d, 1H, $J = 2.3$ Hz), 7.31 (d, 1H; $J = 8.6$ Hz), 8.05 (s, 1H); IR (C=O) 1729 cm^{-1}; ^{13}C NMR (300 MHz) δ: 24.8, 52.5, 109.5, 111.2, 119.8, 125.2, 125.7, 129.5, 153.2, 155.8, 160.2; IR (C=O) 1728 cm^{-1}. **7d** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.33 (s, 3H), 3.88 (s, 3H), 6.94 (dd, 1H, $J = 8.6$; 2.4 Hz), 7.20 (d, 1H, $J = 2.4$ Hz), 7.41 (d, 1H, $J = 8.6$ Hz), 8.01 (s, 1H); ^{13}C NMR (300 MHz) δ: 24.7, 52.5, 109.9, 112.3, 120.1, 122.5, 124.1, 132.1, 157.0, 157.7, 160.3; IR (C=O) 1728 cm^{-1}. **7e** ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.45 (s, 3H), 3.89 (s, 3H), 7.03 (dd, 1H, $J = 8.7$, 2.3 Hz), 7.34 (m, 2H), 7.62 (s, 1H); ^{13}C NMR (500 MHz, $CDCl_3$) δ: 24.6, 50.0, 112.4, 113.6, 121.2, 126.3, 129.4, 132.3, 146.1, 157.6, 160.3; IR (C=O) 1739 cm^{-1}. **7f** ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.48 (s, 3H), 3.89 (s, 3H), 6.98 (dd, 1H, $J = 8.7$, 2.3 Hz), 7.23 (d, 1H, $J = 2.3$ Hz), 7.40 (d, 1H, $J = 8.6$ Hz), 7.61 (s, 1H); IR (C=O) 1739 cm^{-1}. **8a** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.71 (s, 6H), 2.34 –2.61 (m, 4H), 3.15 (m, 2H), 3.30 (m, 2H), 3.66 (s, 3H), 4.76 (m, 1H), 5.54 (m, 1H), 5.61 (br s, 1H); ^{13}C NMR (300 MHz) δ: 24.5, 28.9, 30.3, 32.4, 35.7, 52.5, 60.2, 73.5, 121.6, 123.8, 131.8, 134.2, 141.3, 173.0; IR (C=O) 1730 cm^{-1}. **8b** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.69 (s, 3H), 1.72 (s, 3H), 2.37–2.65 (m, 4H), 3.16 (m, 2H), 3.32 (m, 2H), 3.68 (s, 3H), 4.86 (m, 1H), 5.44 (m, 1H), 5.60 (br s, 1H); ^{13}C NMR (300 MHz) δ: 22.4, 22.7, 24.5, 30.8, 36.4, 52.2, 59.9, 75.3, 105.7, 120.1, 122.0, 130.7, 133.4, 144.2, 173.1; IR (C=O) 1730 cm^{-1}. **8c** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.69 (s, 3H), 1.71 (s, 3H), 2.37–2.65 (m, 4H), 3.16 (m, 2H), 3.32 (m, 2H), 3.68 (s, 3H), 4.86 (m, 1H), 5.44 (m, 1H), 5.60 (br s, 1H); ^{13}C NMR (300 MHz) δ: 22.5, 22.7, 29.7, 32.5, 34.7, 39.8, 54.7, 63.8, 72.6, 105.7, 122.0, 124.1, 132.3, 136.3, 142.1, 172.1; IR (C=O) 1731 cm^{-1}. **8d** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.72 (s, 6H), 2.06–2.36 (m, 4H), 3.24 (m, 2H), 3.41 (m, 2H), 3.67 (s, 3H), 4.60 (m, 1H), 5.83 (m, 1H), 6.10 (m, 1H); ^{13}C NMR (300 MHz) δ: 22.4, 23.5, 26.0, 30.1, 38.5, 38.8, 52.8, 63.1, 71.0, 103.5, 121.2, 123.5, 131.9, 134.2, 141.5, 171.1; IR (C=O) 1730 cm^{-1}. **9a** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.68 (s, 3H), 2.22 (s, 3H), 2.31–2.63 (m, 4H), 3.66 (s, 3H), 4.75 (m, 1H), 5.35 (br s, 1H), 6.58 (d, 1H, $J = 8.6$ Hz), 6.79 (dd, 1H, $J = 8.6$ Hz, $J =$ 2.2 Hz), 6.82 (d, 1H, $J = 2.2$ Hz); ^{13}C NMR (300 MHz) δ: 23.4, 24.5, 28.1, 37.5, 53.1, 61.6, 78.0, 114.5, 123.5, 124.5, 127.1, 130.5, 134.1, 158.1, 173.1; IR (C=O) 1729 cm^{-1}. **9b** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.68 (s, 3H), 2.24 (s, 3H), 2.33–2.65 (m, 4H), 3.65 (s, 3H), 4.77 (m, 1H), 5.40 (br s, 1H), 6.51 (d, 1H, $J = 2.2$ Hz), 6.54 (dd, 1H, $J = 8.7$ Hz, $J = 2.2$ Hz), 7.01 (d, 1H, $J = 8.7$ Hz); ^{13}C NMR (300 MHz) δ: 23.5, 24.6, 29.1, 35.4, 52.7, 59.0, 80.8, 113.1, 120.7; 121.6, 123.5, 128.9, 134.1, 136.5, 160.9, 172.6; IR (C=O) 1729 cm^{-1}. **9c** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.71 (s, 3H), 2.21–2.46 (m, 2H), 2.35 (s, 3H), 2.47–2.72 (m, 2H), 3.67 (s, 3H), 4.86 (m, 1H), 5.39 (br s, 1H), 6.50 (d, 1H, $J = 2.4$ Hz), 6.53 (dd, 1H, $J = 8.7$ Hz, $J = 2.4$ Hz), 7.00 (d, 1H, $J = 8.7$ Hz); ^{13}C NMR (300 MHz) δ: 24.4, 25.6, 29.2, 35.2, 52.5, 58.7, 80.7, 113.2, 120.7, 121.5, 123.4, 128.8, 134.0, 136.2, 160.8, 172.5; IR (C=O) 1730 cm^{-1}. **9d** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.71 (s, 3H), 2.25 (s, 3H), 2.32–2.63 (m, 4H), 3.65 (s, 3H), 4.88 (m, 1H), 5.40 (br s, 1H), 6.51 (d, 1H, $J = 2.2$ Hz), 6.54 (dd, 1H, $J = 8.7$ Hz, $J = 2.2$ Hz), 7.01 (d, 1H, $J = 8.7$ Hz); ^{13}C NMR (300 MHz) δ: 24.4, 26.1, 29.4, 38.8, 53.1, 63.2, 78.5, 115.0, 122.1, 123.9, 124.6, 131.4, 136.2, 137.8, 162.3, 173.0; IR (C=O) 1729 cm^{-1}. **10b** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.86 (s, 3H), 7.28–7.32 (m, 2H), 7.43–7.46 (m, 1H), 7.86–7.90 (m, 1H), 8.03 (s, 1H); ^{13}C NMR (300 MHz) δ: 52.8, 112.5; 118.2, 123.1, 124.6, 125.3, 127.1, 157.8, 158.3, 160.2; IR (C=O) 1729 cm^{-1}. **10c** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.85 (s, 3H), 7.25–7.29 (m, 2H), 7.41–7.46 (m, 1H), 7.84–7.90 (m, 1H), 8.01 (s, 1H); ^{13}C NMR (300 MHz) δ: 52.8, 113.5, 119.0, 123.1, 124.7, 126.1, 127.1, 157.9, 158.4, 160.2; IR (C=O) 1726 cm^{-1}. **11a** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.20 (s, 6H), 1.05 (s, 9H), 6.90 (dd, 1H, $J = 8.8$ Hz, $J = 2.4$Hz), 6.93 (d, 1H; $J = 3.8$Hz), 7.07 (d, 1H, $J = 2.4$Hz), 7.39 (d, 1H, $J = 8.8$Hz), 7.45 (d, 1H, $J = 3.8$Hz); ^{13}C NMR (300 MHz) δ: −4.4, 18.7, 25.7, 109.3, 111.6, 112.0, 119.1, 130.1, 145.5, 149.2, 150.1; IR (C=O) 1730 cm^{-1}. **11b** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.20 (s, 6H), 1.05 (s, 9H), 3.89 (s, 3H), 6.90 (dd, 1H, $J = 8.8$ Hz, $J = 2.4$Hz), 7.12 (d, 1H, $J = 2.4$Hz), 7.39 (d, 1H, $J = 8.8$Hz), 8.01 (s, 1H); ^{13}C NMR (300 MHz) δ: −4.6, 18.8, 25.7, 53.4, 109.3, 112.2, 116.7, 119.6, 130.1, 151.3, 151.8, 157.3, 161.1; IR (C=O) 1729 cm^{-1}. **11c** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.90 (s, 3H), 6.87 (dd, 1H, $J = 8.7$, 2.4 Hz), 7.10 (d, 1H, $J = 2.4$ Hz), 7.36 (d, 1H, $J = 8.7$ Hz), 7.61 (s, 1H); IR (C=O) 1726 cm^{-1}. **12a** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.21 (br s, 1H), 6.82 (dd, 1H, $J = 8.8$ Hz, $J = 2.4$ Hz), 6.85 (d, 1H, $J = 3.8$ Hz), 7.07 (d, 1H, $J = 2.4$ Hz), 7.40 (d, 1H, $J = 8.8$ Hz), 7.62 (d, 1H, $J = 3.8$ Hz); ^{13}C NMR (300 MHz) δ: 105.5, 106.1, 115.2, 116.8, 131.4, 147.8, 150.2, 152.5. **12b** ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.90 (s, 3H), 5.18 (br s, 1H), 6.75 (dd, 1H, $J = 8.4$ Hz, $J = 2.4$ Hz), 7.05 (d, 1H, $J = 2.4$ Hz), 7.75 (d, 1H, $J = 8.4$ Hz), 8.15 (s, 1H); ^{13}C NMR (300 MHz) δ: 51.6, 105.9, 113.1, 114.5, 116.3, 127.4, 150.2, 153.8, 156.9, 160.1; IR (C=O) 1730 cm^{-1}. **12c** δ: 3.85 (s, 3H), 5.20 (br s, 1H), 6.73 (dd, 1H, $J = 8.8$, 2.4 Hz), 7.01 (d, 1H, $J = 2.4$ Hz), 7.33 (d, 1H, $J = 8.8$ Hz), 7.65 (s, 1H); IR (C=O) 1726 cm^{-1}.