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Comparison of the reactivity between 2- and 3-nitropyrroles in cycloaddition reactions. A simple indole synthesis

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Abstract—*N*-Tosyl-2-nitropyrroles react at high temperature with poorly and strongly activated dienes. They exhibit a dienophilic character similar to *N*-tosyl-3-nitropyrroles producing the corresponding indoles through a classical Diels–Alder process. A similar behaviour was observed in disubstituted *N*-tosyl-pyrroles.

1. Introduction

In view of their electron-rich constitution and electron-donor properties five-membered aromatic heterocycles have been involved in cycloaddition reactions mostly as the diene component.[1] However, only a limited number of them act as dienophiles in Diels–Alder (DA) reactions with normal electron demand, for example, aromatic heterocyclepentadienes holding an electron withdrawing group at β-position have shown to be excellent dienophiles in the interaction with isoprene at an elevated temperature. In contrast, α-acylheterocycles have proved to be very poor dienophiles towards isoprene.[2,3] Due to our interest in the cycloaddition chemistry of substituted aromatic heterocycles with electron-withdrawing groups, we have recently reported that 2-nitrofurans and 2-nitrothiophenes react with strong and poor dienes under different conditions. 2-Nitrofurans react with dienes strongly, moderately and poorly activated in normal electron demand DA reactions.[4] Instead 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.[5] Considering that there are fewer examples of tosyl-pyrrole reacting with dienes in normal electron demand DA reactions,[2] the purpose of the present work is to explore the behaviour of pyrroles substituted in 2-position with electron withdrawing groups (e.g., nitro or carboxylate) in their exposure to dienes under thermal conditions.

This allowed us to compare not only the relative reactivity of the 2- and 3-substitution of the aromatic ring but also the regioselectivities in the cases of successful cycloaddition. This study includes mono- and disubstituted tosyl-pyrroles.

2. Results and discussion

The study was carried out using 1-tosyl-2-nitropyrrole (**1a**), 1-tosyl-3-nitropyrrole (**1b**), methyl 5-nitro-1-tosyl-pyrrole-3-carboxylate (**1c**) and methyl 4-nitro-1-tosyl-pyrrole-2-carboxylate (**1d**). The diene components were isoprene (**2**), 1-*N*-acetyl-*N*-propylamino-1,3-butadiene (**3**) and 1-methoxy-3-trimethylsilyloxy-1,3-butadiene (Danishefsky's diene) (**4**) (Scheme 1).

When 2-nitropyrroles were reacted with the above mentioned dienes under different reaction conditions,[6] they showed their dienophilic character taking part in the DA cycloaddition reactions.

When **1a** was heated with less reactive isoprene **2**, it gave a mixture of dihydroindoles **5a** and **5b** (with thermal extrusion of nitrous acid accompanying the DA reaction) and indoles **6a** and **6b** as the principal products.[9]

The reactions of **1c** with isoprene proceeded to produce the mixture of isomeric cycloadducts **6c** and **6d** as the principal products (55%) and a mixture of double

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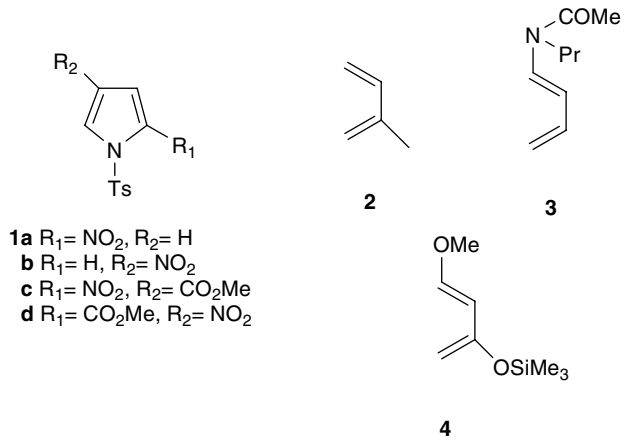


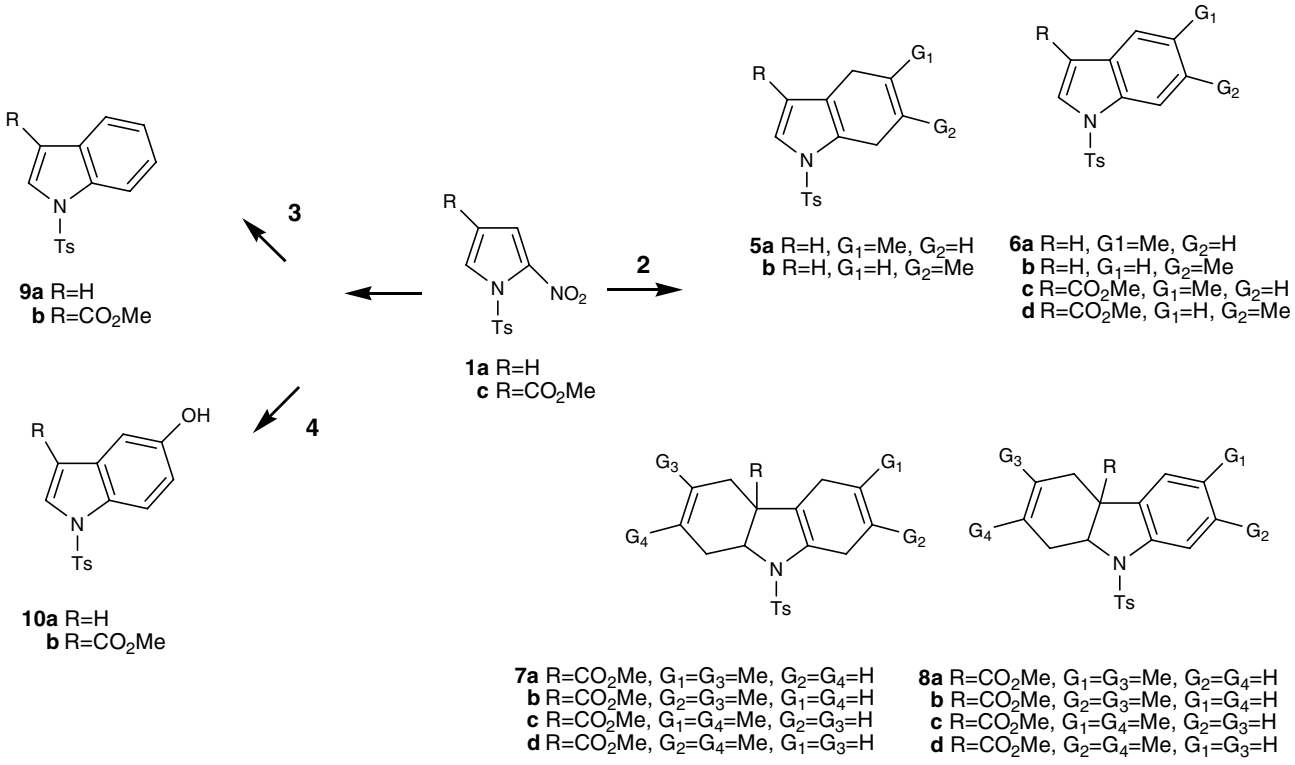
Scheme 1.

addition adducts **7a**–**d** (15%) and **8a**–**d** (35%), in both cases of regioisomer mixtures (Scheme 2, Table 1).[9]

Similarly, the reactions of **1b** with isoprene yielded a mixture of isomeric cycloadducts **5a**, **5b**, **6a** and **6b** (Scheme 3, Table 1).

On the other hand, the treatment of **1d** with **2** afforded a mixture of isomeric indoles **11a** and **11b**. These reactions proceeded by the addition of the diene selectively to the nitro-substituted double bond of the pyrrole. No bis-adduct from the double cycloaddition of the diene was detected.

The cycloaddition between 1-*N*-acetyl-*N*-propylamino-1,3-butadiene **3** with **1a** and **1b** yielded only 1-tosyl-indol with moderate to a high yield. The results of this type of DA reactions involving the *N*-tosyl-2-nitropyrrole indicate a possible sequential pathway where the ease of thermal extrusion of nitrous acid accompanying the DA reaction would lead to the 4-substituted-*N*-tosyl-dihydroindol adduct, which would undergo thermal aromatization by losing the *N*-acetyl-*N*-alkylamino substituent.[7]

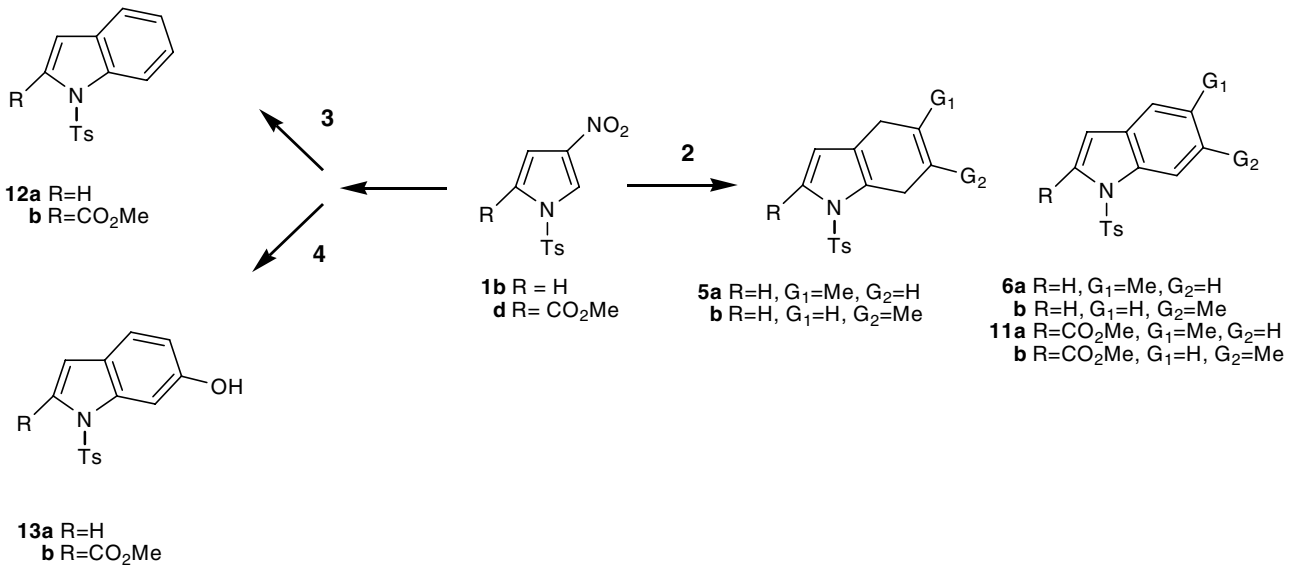


Scheme 2. Reactivity of *N*-tosyl-2-nitropyrroles with different dienes.

Table 1. Thermal reactions of *N*-tosyl-nitropyrroles with isoprene

Entry	Dienophile	Conditions[a]	Products	Product ratio	Yield[b] (%)
1	**1a**	200 °C, 72 h	**5a**, **5b**, **6a**, **6b**	1:1:5:5	50
2		150 °C, 72 h	**5a**, **5b**, **6a**, **6b**	1:1:5:5	45
3	**1b**	200 °C, 72 h	**5a**, **5b**, **6a**, **6b**	5:5:1:1	50
4		150 °C, 72 h	**5a**, **5b**, **6a**, **6b**	5:5:1:1	44
5	**1c**	200 °C, 72 h	**6c**, **6d**, **7a**, **7b**, **7c**, **7d**, **8a**, **8b**, **8c**, **8d**	1:5; 1:3:1:2; 1:3:1:2	60
6		150 °C, 72 h	**6c**, **6d**, **7a**, **7b**, **7c**, **7d**, **8a**, **8b**, **8c**, **8d**	1:5; 1:3:1:2; 1:3:1:2	55
7	**1d**	200 °C, 72 h	**11a**, **11b**	5:1	45
8		150 °C, 72 h	**11a**, **11b**	5:1	44

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



Scheme 3. Reactivity of *N*-tosyl-3-nitropyrroles with different dienes.

Similarly, in the reactions with Danishefsky's diene cycloadduct **10a** and **13a** were obtained with a high yield and complete regioselectivity, which is controlled by the nitro and methoxy groups (Table 2). This products resulted from the expected aromatization of the nitro-adducts promoted by the loss of the nitro and methoxyl groups as nitrous acid and methanol, respectively.[8]

The isolation of the intermediate cycloadduct was never achieved under these conditions.

Exposure of **1c** and **1d** to **3** and **4** afforded indoles **9b**, **12b**, **10b** and **13b**, respectively.[9] All addition products showed extrusion of the nitro group as nitrous acid. In these reactions, only 1:1 adducts whose structure revealed site selectivity and regioselectivity were obtained. The nitro group orients the cycloaddition selectively towards the double bond to which it is directly attached (Scheme 3, Table 2).

Table 2. Thermal reactions of *N*-tosyl-nitropyrroles with dienes **3** and **4**

Entry	Dienophile	Diene	Condition[c] (°C)	Product	Yield[d] (%)
1	**1a**	**3**[a]	140	**9a**	45
2			120	**9a**	53
3	**1b**		140	**12a**	44
4			120	**12a**	52
5	**1c**		140	**9b**	40
6			120	**9b**	41
7	**1d**		140	**12b**	44
8			120	**12b**	48
9	**1a**	**4**[b]	140	**10a**	48
10			120	**10a**	46
11	**1b**		140	**13a**	47
12			120	**13a**	48
13	**1c**		140	**10b**	50
14			120	**10b**	52
15	**1d**		140	**13b**	44
16			120	**13b**	43

[a] Diene/dienophile ratio 3:1.
[b] Diene/dienophile ratio 2:1.
[c] Reaction's time 72 h.
[d] Based on consumed dienophile.

3. Conclusions

It has been demonstrated that 1-tosyl-2-nitropyrrole reacts efficiently with the above-mentioned dienes in normal electron demand Diels–Alder reactions, with the nitro group inducing side selectivity.

A very strong electron-acceptor group, such as a nitro group, induces a similar reactivity at 2- and 3-positions in the pyrrole ring. The ease of thermal extrusion of nitrous acid accompanying the DA reaction of 2- and 3-nitropyrroles followed by the further aromatization makes this reaction sequence a simple method of indole preparation, direct intermediate in the synthesis of some alkaloids as serotonine, trytamine and gramine.

Acknowledgements

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6. *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 solution was evaporated and the residue purified by column chromatography in silica gel or alumina using hexane/ethyl acetate mixtures as the eluent. Biolatto, B.; Kneeteman, M.; Paredes, E.; Mancini, P. *J. Org. Chem.* **2001**, *66*, 3906–3912.
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9. *Spectral data*. Compounds **5a**, **5b**, **6a** and **6b**, both of the homologous benzenesulfonylated derivatives were reported by Wenkert et al.[2] Compound **6c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.35 (s, 3H); 2.40 (s, 3H); 3.89 (s, 3H); 7.20 (d, 1H, $J = 8.1$ Hz); 7.32 (d, 2H, $J = 8$ Hz); 7.41 (d, 1H, $J = 8.1$ Hz); 7.71 (s, 1H); 7.82 (d, 2H, $J = 8$ Hz); 7.95 (s, 1H). ^{13}C NMR (75 MHz) δ: 24.4; 24.7; 51.6; 108.9; 118.8; 120.7; 126.7; 128.3; 129.2; 131.2; 133.2; 135.2; 144.1; 165.0. HRMS *m/z* 343.4063 (calcd $C_{18}H_{17}O_4NS$, 343.4059). Compound **6d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.35 (s, 3H); 2.40 (s, 3H); 3.89 (s, 3H); 7.1–7.30 (m, 2H); 7.32 (d, 2H, $J = 8$ Hz); 7.82 (d, 2H, $J = 8$ Hz); 7.95 (s, 1H); 8.15 (d, 1H, $J = 8.1$ Hz). ^{13}C NMR (75 MHz) δ: 24.3; 51.5; 108.9; 111.5; 119.3; 121.6; 123.8; 128.4; 126.9; 127.6; 128.8; 130.5; 135.3; 136.0; 143.8; 165.0. Compound **7a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.85 (s, 6H); 2.1–2.5 (m, 4H); 2.32 (s, 3H); 3.1–3.5 (m, 6H); 3.68 (s, 3H); 5.2 (br s, 1 H); 5.41 (m, 1H); 7.32 (d, 2H, $J = 8$ Hz); 7.82 (d, 2H, $J = 8$ Hz). ^{13}C NMR (75 MHz) δ: 23.5; 24.6; 28.1; 32.6; 33.7; 37.1; 46.6; 52.9; 59.2; 116.7; 121.6; 123.7; 127.6; 129.7; 132.5; 135.1; 134.6; 137.7; 170.0. HRMS *m/z* 412.5335 (calcd $C_{23}H_{26}O_4NS$, 412.5331). Compound **7b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.70 (s, 3H); 1.72 (s, 3H); 2.05–2.45 (m, 4H); 2.35 (s, 3H); 2.7 (m, 4H); 3.5 (m, 1H); 3.68 (s, 3H); 5.1 (br s, 1H); 5.4 (m, 1H); 7.32 (d, 2H, $J = 8$ Hz); 7.82 (d, 2H, $J = 8$ Hz). ^{13}C NMR (75 MHz) δ: 23.3; 23.6; 24.6; 27.5; 28.6; 37.2; 40.3; 47.8; 53.2; 58.6; 116.4; 121.6; 123.7; 128.4; 130.2; 131.6; 135.1; 135.8; 137.6; 143.5; 171.0. Compound **7c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.70 (s, 3H); 1.72 (s, 3H); 2.05–2.45 (m, 4H); 2.35 (s, 3H); 2.8 (m, 4H); 3.4 (m, 1H); 3.68 (s, 3H); 5.0 (br s, 1H); 5.5 (m, 1H); 7.32 (d, 2H, $J = 8$ Hz); 7.82 (d, 2H, $J = 8$ Hz). ^{13}C NMR (75 MHz) δ: 23.1; 23.6; 24.7; 32.1; 32.6; 34.1; 35.6; 44.4; 53.5; 61.4; 116.7; 121.6; 124.5; 128.2; 130.3; 132.2; 134.7; 135.0; 137.6; 142.7; 171.0. Compound **7d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.72 (s, 6H); 2.06–2.41 (m, 4H); 2.35 (s, 3H); 2.7 (m, 4H); 3.4 (m, 1H); 3.68 (s, 3H); 5.1 (br s, 1H); 5.4 (m, 1H); 7.32 (d, 2H, $J = 8$ Hz); 7.82 (d, 2H, $J = 8$ Hz). ^{13}C NMR (75 MHz)δ: 23.1; 23.3; 24.6; 27.3; 32.5; 36.6; 40.5; 44.7; 52.4; 61.4; 116.9; 121.3; 124.5; 128.0; 130.2; 132.4; 134.8; 135.2; 137.8; 142.6; 171.0. Compound **8a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.69 (s, 3H); 2.21 (s, 3H); 2.35 (s, 3H); 2.1–2.6 (m, 4H); 3.68 (s, 3H); 3.81 (m, 1H); 5.35 (br s, 1H); 6.25 (d, 1H, $J = 8.1$ Hz); 6.60 (dd, 1H, $J = 8.1$–1.5 Hz); 6.90 (d, 1H, $J = 1.5$ Hz); 7.32 (d, 2H, $J = 8$ Hz); 7.82 (d, 2H, $J = 8$ Hz). ^{13}C NMR (75 MHz) δ: 23.7; 24.7; 25.4; 27.1; 37.2; 53.7; 54.8; 56.5; 114.6; 124.2; 127.5; 128.4; 130.4; 130.9; 131.1; 135; 137.7; 141.6; 142.3; 172.1. HRMS *m/z* 410.5227 (calcd $C_{23}H_{24}O_4SN$, 410.5223). Compound **8b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.71 (s, 3H); 2.24 (s, 3H); 2.35 (s, 3H); 2.05–2.7 (m, 4H); 3.69 (s, 3H); 3.79 (m, 1H); 5.40 (br s, 1H); 6.20 (d, 1H, $J = 2.1$ Hz); 6.35 (dd, 1H, $J = 8.1$–2.1 Hz); 7.1 (d, 1H, $J = 8.1$ Hz); 7.32 (d, 2H, $J = 8$ Hz); 7.82 (d, 2H, $J = 8$ Hz). ^{13}C NMR (75 MHz) δ: 23.6; 24.7; 27.1; 37.2; 52.5; 53.6; 56.6; 114.2; 117.8; 124.3; 127.0; 128.7; 129.2; 130.2; 135.9; 137.3; 141.7; 144.1; 172.0. Compound **8c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.71 (s, 3H); 2.22 (s, 3H); 2.35 (s, 3H); 2.1–2.7 (m, 4H); 3.68 (s, 3H); 3.82 (m, 1H); 5.41 (br s, 1H); 6.24 (d, 1H, $J = 8.1$ Hz); 6.60 (dd, 1H, $J = 8.1$–1.5 Hz); 6.90 (d, 1H, $J = 1.5$ Hz); 7.32 (d, 2H, $J = 8$ Hz); 7.82 (d, 2H, $J = 8$ Hz). ^{13}C NMR (75 MHz) δ: 23.2; 24.5; 25.4; 30.2; 34.5; 51.5; 53.4; 60.0; 113.6; 123.7; 127.4; 128.4; 129.8; 131.4; 131.6; 135.7; 137.3; 140.5; 142.6; 172.0. Compound **8d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.69 (s, 3H); 2.22 (s, 3H); 2.35 (s, 3H); 2.1–2.7 (m, 4H); 3.68 (s, 3H); 3.81 (m, 1H); 5.35 (br s, 1H); 6.20 (d, 1H, $J = 8.1$ Hz); 6.35 (dd, 1H, $J = 8.1$–2.1 Hz); 7.1 (d, 1H, $J = 2.1$ Hz); 7.32 (d, 2H, $J = 8$ Hz); 7.82 (d, 2H, $J = 8$ Hz). ^{13}C NMR (75 MHz) δ: 23.7; 24.7; 30.2; 34.7; 51.2; 53.6; 59.3; 113.6; 118.1; 124.0; 127.6; 128.5; 130.1; 131.0; 134.2; 137.1; 137.8; 142.1; 144.6; 172.0. Compound **9b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.35 (s, 3H); 3.89 (s, 3H); 7.31–7.34 (m, 3H); 7.65 (m, 2H); 7.82 (d, 2H, $J = 8$ Hz); 8.1 (s, 1H); 8.3 (dd, 1H, $J = 8.1$–2.1 Hz). ^{13}C NMR (75 MHz) δ: 24.6; 51.7; 109.3; 111.4; 119.6; 121.1; 123.6; 126.5; 128.4; 129.3; 131.0; 135.2; 137.8; 144.2; 167. HRMS *m/z* 329.3796 (calcd $C_{17}H_{15}O_4NS$, 329.3789). Compound **10a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.37 (s, 3H); 5.0 (br s, 1H); 6.45 (d, 1H, $J = 3.1$ Hz); 6.85 (dd, 1H, $J = 8.1$–1.2 Hz); 7.21 (d, 1H, $J = 1.2$ Hz), 7.27 (d, 1H, $J = 8.1$ Hz); 7.32 (d, 2H, $J = 8$ Hz); 7.82 (d, 2H, $J = 8$ Hz). ^{13}C NMR (75 MHz) δ: 24.5; 102.5; 104.4; 110.9; 112.5; 118.6; 127.6; 128.7; 129.7; 130.3; 135.2; 143.6; 152.7. HRMS *m/z* 311.3642 (calcd $C_{15}H_{13}O_3SN$, 311.3636). Compound **10b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.35 (s, 3H); 3.90 (s, 3H); 5.20 (br s, 1H); 6.74 (dd, 1H, $J = 8.4$–2.2 Hz); 7.05 (d, 1H, $J = 8.4$ Hz); 7.32 (d, 2H, $J = 8$ Hz); 7.75 (d, 1H, $J = 2.2$ Hz); 7.82 (d, 2H, J= 8 Hz); 8.20 (s, 1H). ^{13}C NMR (75 MHz) δ: 24.5; 52.0; 104.2; 109.1; 112.6; 113.8; 128.5; 128.8; 129.1; 129.7; 131.4; 135.0; 144.4; 153.1; 167.1. HRMS *m/z* 345.3790 (calcd $C_{17}H_{15}O_5NS$, 345.3783). Compound **11a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.45 (s, 6H); 3.89 (s, 3H); 7.05 (d, 1H, $J = 8.6$ Hz); 7.32 (d, 2H, $J = 8$ Hz); 7.40 (m, 2H); 7.61 (d, 1H, $J = 2.1$ Hz); 7.82 (d, 2H, $J = 8$ Hz). ^{13}C NMR (75 MHz) δ: 24.5; 24.8; 52.1; 109.6; 112.3; 119.5; 121.7; 129.5; 130.5; 131.7; 132.4; 135.8; 140.5; 144.6; 160.1. Compound **11b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.35 (s, 3H); 2.40 (s, 3H); 3.89 (s, 3H); 7.04 (s, 1H); 7.2–7.40 (m, 2H); 7.32 (d, 2H, $J = 8$ Hz); 7.7 (d, 1H, $J = 8.4$ Hz); 7.82 (d, 2H, $J = 8$ Hz). ^{13}C NMR (75 MHz) δ: 24.5; 52.1; 109.7; 112.4; 119.5; 121.7; 129.6; 130.5; 131.7; 132.4; 135.9; 140.5; 145.2, 160.1. Compound **12b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.35 (s, 3H); 3.90 (s, 3H); 7.1–7.25 (m, 2H); 7.32 (d, 2H, $J = 8$ Hz); 7.5–7.7 (m, 3H); 7.82 (d, 2H, $J = 8$ Hz). ^{13}C NMR (75 MHz) δ: 24.5; 52.1; 109.7; 112.1; 119.8; 121.3; 123.6; 128.5; 130.6; 130.8; 135.7; 142.4; 144.5; 160.1. Compound **13a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.35 (s, 3H); 5.0 (br s 1H); 6.21 (d, 1H, $J = 3.0$ Hz); 6.63 (dd, 1H, $J = 8.1$–1.1 Hz); 7.0 (d, 1H, $J = 1.1$ Hz); 7.25 (d, 1H, $J = 3.0$ Hz); 7.32 (d, 2H, $J = 8$ Hz); 7.38 (d, 1H, $J = 8.1$ Hz); 7.82 (d, 2H, $J = 8$ Hz). ^{13}C NMR (75 MHz) δ: 24.5; 97.3; 102.6; 113.6; 118.4; 120.5; 120.8; 128.4; 130.7; 135.8; 137.7; 143.8; 150.6. Compound **13b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.35 (s, 3H); 3.90 (s, 3H); 5.12 (br s, 1H); 6.95 (s, 1H); 7.1–7.28 (m, 2H); 7.32 (d, 2H, $J = 8$ Hz); 7.80 (d, 1H, $J = 8.4$ Hz); 7.82 (d, 2H, $J = 8$ Hz). ^{13}C NMR (75 MHz) δ: 24.5; 52.6; 97.9; 110.4; 115.7; 121.6; 123.9; 130.5; 131.8; 133.7; 135.9; 143.8; 151.2.