Research Article

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Synthesis and characterization of 1- and 2-cinnamoyloxyacetonaphthones

T. K. Venkatachalam,* G. K. Pierens and D. C. Reutens

The synthesis of 1- and 2-cinnamoyloxyacetonaphthones was achieved in one step using hydroxyl acetonaphthones and substituted cinnamic acids in the presence of a catalytic amount of phosphoroxychloride. Structural characterization was accomplished using high-resolution nuclear magnetic resonance (NMR) spectroscopy. Chemical shifts of the compounds were compared and the change in the chemical shifts relative to electron-donating and -withdrawing groups is presented. Introduction of a thiophene ring instead of phenyl-substituted analogs caused shielding of the olefinic proton. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: ^{1}H and ^{13}C NMR; cinnamoyloxyacetonaphthones; β-diketones

Introduction

Synthesis of **1** and **2**-cinnamoyloxyacetonaphthones constitutes the first step in the synthesis of β-diketones. Treatment of these acetonaphthones with alkali furnishes the required β-diketones. These β-diketones are versatile synthons for the preparation of chromones.[1–4] Various other procedures have been adopted to prepare **1,3**-diketones which involve the condensation of ketones with magnesium bromide etherate in the presence of *N*,*N*-diisopropylethylamine (DIPEA).[5] A mild and efficient pentafluorophenylammonium triflate-catalyzed alkylation of enol-silyl ethers has also been found to be suitable for the synthesis of diketones.[6] Using an α,β-unsaturated ketone, acid chlorides and a catalyst, Sato *et al*. successfully prepared diketones with substituted groups.[7] Rahn *et al*. synthesized ketones using silyl ethers and acyl/aryl chlorides in a two-step procedure.[8] These diketones have been widely used to form complexes with various metal ions.[9] For example, Graddon *et al*. synthesized cobalt complexes of *ortho*-hydroxyarylaldehydes and -ketones, and demonstrated a octahedral, cobalt (II) configuration in the complexes.[10] In contrast, Palaniandavar *et al*. prepared cobalt, nickel and copper complexes of **2**-hydroxychalcones which had a square-planar configuration.[11] Copper complexes of diketones may be useful as positron emission tomography (PET) imaging agents for the detection of amyloids. However, for diketones, the ligand field is not strong enough to complex copper ions due to the square-planar geometry of the complexes. To overcome this and to increase ligand field strength, Athappan *et al*. introduced extensive conjugation of diketones.[12,13] However, the structures of the initial precursor, cinnamoyloxyacetonaphthones and their nuclear magnetic resonance (NMR) characteristics have not been reported in the literature. The following communication describes the preparation of these cinnamoyloxyacetonaphthones and their full characterization including high-resolution NMR.

Results and Discussion

The synthesis of cinnamoyloxyacetonaphthones was achieved using Scheme 1. The compounds were synthesized following literature procedures.[12,13] The compounds were further purified by crystallization using methanol. Both 1- and 2-substituted acetonaphthone derivatives were prepared using appropriate hydroxynaphthones. Cinnamic acid containing electron-withdrawing and -donating groups were used for the synthesis of various cinnamoyl-substituted compounds.

The compounds were characterized using routine analytical techniques and the structural assignments were made using standard high-resolution NMR experiments (COSY, TOCSY, HSQC and HMBC). The UV spectra of the compounds in chloroform showed absorption corresponding to the aromatic conjugated system as expected. The infrared spectra showed strong absorption at wave-numbers 1712 and 1654 cm^{-1} indicative of the presence of C=O group in the structure. All other infrared spectral stretching frequencies were consistent with the structure of the compounds.

The ^{1}H NMR chemical shifts observed for all the synthesized compounds are shown in Table 1 and Fig. 1 shows the structure of compounds synthesized in the present study.

The unsubstituted acetonaphthones (**1** and **6**) showed all the aromatic signals belonging to the naphthyl moiety between δ = 8.07 and 7.11 ppm. The olefinic ^{1}H signals of the cinnamyl group of the molecules were found at δ = 8.02 and 7.11 ppm with a coupling constant of 15.0 Hz demonstrating the *trans*-configuration for the double bond. The other aromatic ^{1}H signals of the phenyl ring appeared between δ = 7.49 and 7.88 ppm. The methyl signal was observed at δ = 2.60 ppm consistent with the structure of the compound. All other compounds (**2**–**5, 7**–**10**) had substituents on the phenyl ring comprising both electron withdrawing and donating groups. As expected, the naphthyl hydrogens in these compounds did not show a significant change in their chemical shifts. However, there was marked change in the chemical shift values observed for the substituted phenyl ring in the structure of the compounds. For example, the observed

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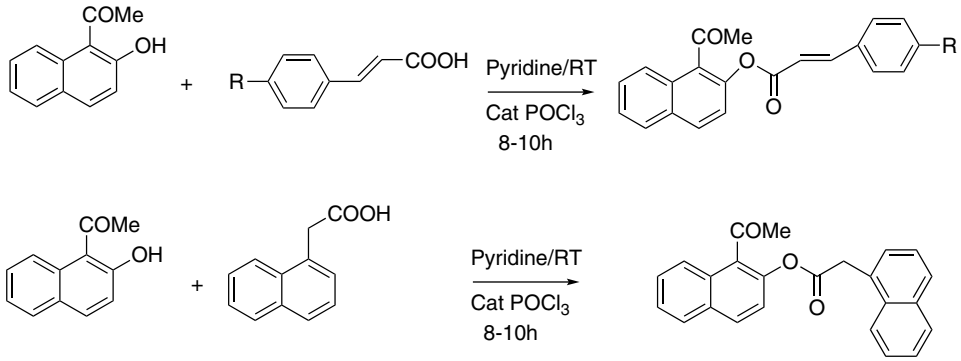


Scheme 1. Synthetic scheme showing the preparation of cinnamoyloxyacetonaphthones.

^{1}H chemical shift of proton H17 for **2** and **3** was $\delta = 7.92$ and 7.69 ppm, respectively.

The change in the chemical shift values were consistent with the nature of substituents present in the phenyl ring.[14] In **5**, the change in chemical shift was more marked ($\delta = 7.87$ ppm) due to the presence of the highly electron withdrawing CF_3 group in *ortho*-position of the phenyl ring. The chemical shift of this proton was $\delta = 7.05$ ppm for **4**, which has a methoxy (electron donating) group in its structure.

In the case of compounds **6**–**9** which are the **1**-acetonaphthone derivatives, the chemical shift for H17 was affected marginally ($\delta = 7.84, 7.55, 7.68$ and 7.81 ppm, respectively). For H18, a similar trend was observed as described above for **2**-acetonaphthone derivatives.

For the ^{13}C NMR chemical shifts (Table 2), the C═O carbon of the ketone was observed at $\delta \sim 198$ ppm for the 2-substituted ketones followed by a peak at $\delta \sim 165$ ppm corresponding to the ester carbon in their structures. On the other hand, the C═O carbon in **1**-substituted acetonaphthones was observed at $\delta \sim 202$ ppm. The ester carbon showed similar shift values to those of the 2-substituted acetonaphthones. The methyl group signal was also shifted down field for the 1-substituted acetonaphthone compared to the 2-substituted acetonaphthone ($\delta = 32.5$ vs 30.0 ppm). The 1-substituted acetonaphthone always show more deshielded methyl signal than 2-substituted acetonaphthones due to the effect of hydrogen atom in *peri*-position. In similar fashion, the chemical shifts for the C1 and C2 carbons were different due to the interchange of the substituents in the naphthyl moiety.

Supporting evidence confirming the structure of the compounds was obtained using COSY TOCSY, HSQC and HMBC techniques. The structural elucidation of compound **4** was chosen as an example. The COSY and TOCSY spectra of **4** showed four-spin-systems, one containing four protons and the other three containing two protons. The spin-system containing four protons are associated with the naphthalene ring (H6–H9). The peak at $\delta = 8.06$ ppm is connected to a peak at $\delta = 7.71$ ppm which in turn is connected to a peak at $\delta = 7.66$ followed by another peak at $\delta = 8.0$ ppm. The exact positions could not be assigned using this information. The peak at $\delta = 6.95$ ppm is connected to a peak at $\delta = 7.97$ ppm with a coupling constant value of 15.8 Hz confirming these protons which are associated with the double bond. Furthermore, the coupling constant value of this magnitude indicates a *trans*-configuration of the protons. Another spin-system in the molecule is the connection between protons at $\delta = 7.84$ and 7.05 ppm with integrals corresponding to two protons. This represents a *para*-substituted aromatic core. Finally, peaks at $\delta = 7.93$ and 7.97 ppm shows the remaining two protons of the naphthalene ring (H3 and H4). The other protons at $\delta = 2.62$ and 3.83 are easily assignable for the presence of methyl and methoxy groups.

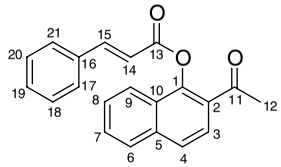
In HSQC spectrum of **4**, the protons directly bonded to carbons were found. There were 12 cross peaks observed in the spectrum which is consistent with the number of protonated carbons. The ^{13}C NMR spectrum showed 20 peaks, 12 found previously in the HSQC spectrum and the remaining 8 carbons were quaternary carbons. Among those eight quaternary carbons, two are carbonyl carbons, one of which resonated at $\delta = 197.7$ ppm indicating a ketone (C11) while the other at $\delta = 165.2$ ppm, an ester (C13).

The HMBC spectrum was used to connect the spin systems resulting in a complete confirmation of the structure. The C2 carbon was assigned due to a cross peak from H12 (CO–Me). H3 ($\delta = 7.93$ ppm) showed cross peaks to C2 and C1. Therefore, H4 could be assigned as $\delta = 7.97$ ppm. The signal at $\delta = 7.71$ (H8) ppm showed cross peaks to $\delta = 135.7$ ppm (C10) and a second cross peak to $\delta = 122.7$ ppm (C6). From the above data, the four-spin-system consisting of H6/H7/H8/H9 can easily be assigned.

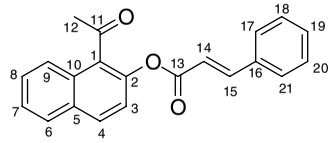
Focusing our attention towards the vinylic protons of the double bond, the HMBC spectrum showed a cross peak between $\delta = 7.97$ and 165.2 (C13) confirming the H15 chemical shift. Furthermore, the peak at $\delta = 6.95$ ppm showed a cross peak to $\delta = 126.5$ ppm confirming the quaternary carbon C16. Additionally, the peak at $\delta = 7.84$ showed a cross peak with $\delta = 147.3$ ppm representing the position of H17/H21 being *ortho* to the vinylic double bond protons in the molecule. The methoxy ^{1}H signal at $\delta = 3.85$ ppm was shown to have a cross peak with another quaternary carbon at $\delta = 161.7$ ppm. Based on this, the C19 signal was assigned. This leaves only one carbon at $\delta = 126.8$ ppm which was assigned to C5, indirectly. The results obtained from the above studies provide irrefutable experimental evidences for the proposed assignment of all the compounds in the present study. A similar technique was adopted to assign protons/carbons in all the remaining compounds in the present study.

From Table 1, it is evident that the **1**- and **2**-substitutions changed the chemical shifts according to the substituent on the naphthyl ring. The H3 atoms of 1- and 2-substituted acetonaphthones varied by 0.45 ppm. The electron-withdrawing group (COMe) shifted this proton resonance to higher frequency for **2**-acetonaphthone compared to **1**-acetonaphthone derivatives. The H4 signals also showed a change of 0.1 ppm. The other protons in the aromatic system showed only slight variation in their chemical shifts (Table 1). However, considering the H14 and H15 in the

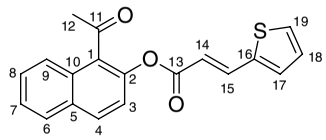
Table 1. Proton chemical shifts of cinnamoyloxyacetonaphthones in DMSO-d_6 at 298 K



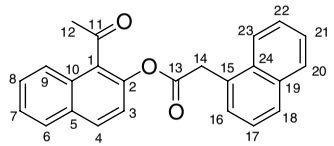
Compounds 1-5, 11



Compounds 6-10, 12



Compound 13



Compound 14

Compound	3	4	6	7	8	9	12	14	15	17	18	19	20	21
1	7.95 (d, 8.5)	7.99 (d, 8.6)	8.02 (d, 7.5)	7.66 (t, 7.9)	7.71 (t, 7.4)	8.07 (d, 8.2)	2.61	7.11 (d, 16.0)	8.02 (d, 15.0)	7.88 (m)	7.49 (m)	7.50 (m)	7.49 (m)	7.88 (m)
2	7.96 (d, 8.5)	8.00 (d, 8.2)	8.01 (d, 8.3)	7.67 (t, 7.7)	7.72 (t, 7.5)	8.07 (d, 8.3)	2.62	7.14 (d, 16.0)	8.01 (d, 16.8)	7.92 (d, 8.3)	7.56 (d, 8.3)	(Cl)	7.56 (d, 8.3)	7.92 (d, 8.3)
3	7.95 (d, 8.6)	7.98 (t, 8.2)	8.01 (d, 8.3)	7.66 (t, 7.5)	7.71 (t, 7.2)	8.07 (d, 8.3)	2.62	7.15 (d, 16.2)	7.99 (d, 16.0)	7.69 (d, 8.3)	7.84 (d, 8.3)	(Br)	7.84 (d, 8.3)	7.69 (d, 8.3)
4[a]	7.93 (d, 8.6)	7.97 (d, 8.6)	8.00 (d, 8.4)	7.66 (t, 7.3) Hz	7.71 (t, 7.3)	8.06 (d, 8.2)	2.62	6.95 (d, 15.8)	7.97 (d, 15.0)	7.84 (d, 8.6)	7.05 (d, 8.4)	(OMe)	7.05 (d, 8.4)	7.84 (d, 8.6)
5	7.97 (d, 8.5)	8.01 (d, 8.7)	8.02 (d, 8.3)	7.68 (t, 7.7)	7.72 (t, 6.7)	8.08 (d, 8.3)	2.62	7.23 (d, 15.7)	8.15 (d, 15.7)	(CF_3)	7.87 (d, 7.8)	7.71 (t, 6.7)	7.82 (t, 7.4)	8.27 (d, 7.6)
6	7.50 (m)	8.11 (d, 8.6)	7.78 (d, 8.1)	7.63 (t, 7.3)	7.60 (t, 8.0)	8.05 (d, 7.9)	2.61	6.97 (d, 16.0)	7.94(d) (d, 16.0)	7.84 (m)	7.48 (m)	7.46 (m)	7.48 (m)	7.84 (m)
7	7.48 (d, 8.8)	8.11 (d, 8.9)	7.78 (d, 8.4)	7.60 (t, 7.8)	7.62 (t, 7.0)	8.05 (d, 8.0)	2.60	6.99 (d, 15.9)	7.93 (d, 15.9)	7.55 (d, 8.4)	7.88 (d, 8.4)	(Cl)	7.88 (d, 8.4)	7.55 (d, 8.4)
8	7.48 (d, 8.9)	8.11 (d, 8.8)	7.78 (d, 8.1)	7.63 (t, 6.8)	7.61 (t, 7.6)	8.05 (d, 7.9)	2.60	7.01 (d, 16.1)	7.94 (d, 16.1)	7.68 (d, 8.1)	7.81 (d, 8.3)	(Br)	7.81 (d, 8.3)	7.68 (d, 8.1)
9[a]	7.47 (d, 8.6)	8.10 (d, 8.9)	7.78 (d, 8.2)	7.62 (t, 6.9)	7.60 (t, 7.8)	8.04 (d, 8.2)	2.61	6.81 (d, 15.9)	7.88 (d, 16.0)	7.81 (d, 8.6)	7.02 (d, 8.6)	(OMe)	7.02 (d, 8.6)	7.81 (d, 8.6)
10	7.53 (d, 8.9)	8.11 (d, 8.8)	7.78 (d, 7.5)	7.63 (t, 6.7)	7.60 (t, 7.7)	8.05 (d, 8.2)	2.62	7.09 (d, 15.0)	8.08 (d, 15.0)	(CF_3)	7.79 (t, 8.2)	7.69 (t, 7.8)	7.85 (d, 8.0)	8.21 (d, 7.7)
11[b]	7.29 (d, 8.8)	8.05 (d, 8.6)	7.74 (d, 8.2)	7.60 (t, 6.8)	7.58 (t, 7.8)	8.01 (d, 8.1)	2.99	2.99	3.00	7.16 (m)	7.16 (m)	7.23 (m)	7.16 (m)	7.16 (m)
12[b]	7.92 (d, 8.6)	7.91 (d, 8.6)	7.67 (m)	7.53 (t, 7.5)	7.67 (m)	8.02 (d, 8.3)	2.56	3.19	3.06	7.36 (d, 7.0)	7.35 (m)	7.27 (t, 7.0)	7.35 (m)	7.36 (d,7.0)
13	7.44 (d, 8.6)	8.08 (m)	7.76 (d, 8.2)	7.61 (t, 6.7)	7.59 (t, 7.5)	8.03 (d, 8.2)	2.60	6.55 (d, 16.0)	8.08 (m)	7.67 (d, 3.0)	7.19 (t, 4.0)	7.81 (d, 5.0)	–	–
14[c]	7.44 (d, 8.8)	8.08 (d, 8.8)	7.71 (d, 8.5)	7.59 (t, 6.5)	7.58 (t, 6.5)	8.01 (d, 7.8)	2.40	4.23	–	–	–	–		

The multiplicity and the coupling constants (in Hz) are given for all the signals in parenthesis. The substituted groups are represented in parenthesis.
[a] Compounds **4** and **9** had a methoxy groups and the methyl signal appeared as singlets at 3.80 and 3.82 ppm, respectively.
[b] In compounds **11** and **12**, C14–C15 is a single bond. These two compounds had saturated methylene groups instead of unsaturated double bond.
[c] Compound **14**, the naphthyl protons in the structure was not resolvable. It showed two multiplets, one between 7.95 and 7.91 ppm (4H) and another between 7.55 and 7.50 ppm (3H).

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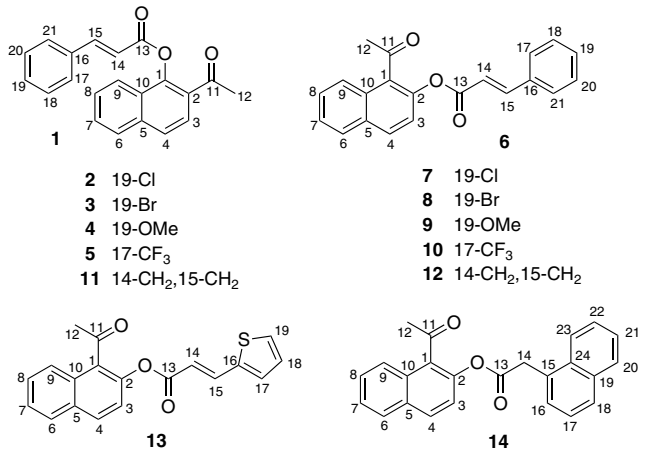


Figure 1. Structures of cinnamoyloxyacetonaphthones synthesized.

double bond, **5** and **10** showed a distinctive behaviour. These signals appeared at $\delta = 7.23$ and 8.15 ppm for **5**. Similarly, the above two ^{1}H signals appeared in **10** at $\delta = 7.09$ and 8.08 ppm, respectively. Since CF_3 is an electron withdrawing group which is in the *ortho*-position of the phenyl ring, it pulls the electron density from the double bond causing a shift of these ^{1}H signals to higher frequency. In other words, these two protons are deshielded compared to other compounds in the series. Additionally, the steric factor associated with trifluoromethyl group at the *ortho*-position may also account for such a trend observed in these two compounds. Considering the chemical shift value of H14 for **4**, the signal appeared at $\delta = 6.95$ ppm which is approximately 0.2 ppm to lower frequency and this is expected due to the electron donating nature of methoxy group. A similar trend was seen for **9**, wherein this proton was shifted to lower frequency ($\delta = 6.81$ ppm). The chemical shift of H15 was shifted slightly to lower frequency for both these compounds (**4** and **9**).

The chemical shift values observed for the naphthyl moiety were almost identical for most of the compounds, as expected. However, the electron-withdrawing groups in the phenyl ring of the molecule affected the chemical shift of C19 considerably, consistent with the notion that electron-donating and -withdrawing groups should produce opposite effects. The unsubstituted compounds **1** and **6** showed chemical shift values of $\delta = 131.1$ and 130.9 ppm for C19, while the bromo-substituted derivatives gave values of $\delta = 124.6$ and 124.8 ppm, respectively. A similar trend was seen for the chloro-substituted compounds albeit with a shift to lower frequency ($\delta = 126.3$ ppm). Considering **4** and **9**, we found that the chemical shift for C19 shifted dramatically to a higher frequency of $\delta = 161.7$ ppm in both compounds demonstrating the influence of electron-donating groups.

The C14 chemical shift for most of the compounds was between $\delta = 116$ and 117 ppm. Only the trifluoro-substituted compounds **5** and **10** showed a shift to higher frequency for this carbon ($\delta = 121.2$ ppm). Similarly, C15 chemical shifts values were found at $\delta = 141$ ppm for both the compounds. If we compare the change in the chemical shift for C14 carbon in these two compounds with others, a 4 ppm shift to higher frequency is experienced due to the introduction of trifluoromethyl group in the phenyl ring. On the other hand, the C15 chemical shift for these two compounds showed a value of $\delta = 141$ ppm which is a 6 ppm shift to lower frequency compared to the chemical shift observed for all other compounds. The change in the chemical shift values observed for these carbons can be accounted by considering both electronic and steric effect associated with the trifluoromethyl group. Since the trifluoromethyl group is highly electron-withdrawing in nature, it reduces electron density from the double bond due to its resonance effect. Additionally, we propose that steric constraints of the bulky CF_3 group may also influence the electron density associated with the double bond causing a change in their chemical shift values compared to other compounds in the series. On the contrary, the introduction of methoxy group on the phenyl ring altered the chemical shift of this carbon (C14) to $\delta = 113.5$ ppm. This is a shift to lower frequency of nearly 4 ppm compared to the other compounds in the series due to the electron-donating nature of the methoxy group. In contrast, the C15 chemical shift did not change drastically when compared to the other compounds ($\delta = 147$ ppm). Since the methoxy group is positioned at the *para*-position of the phenyl moiety, the steric factors seems to play only a minor role unlike the trifluoromethyl group which is at the *ortho*-position in compound **5** and **10**. All other carbon chemical shifts were similar with marginal differences between the compounds.

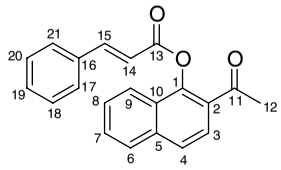
We examined the ^{1}H chemical shifts for **13** and **14** to understand the effect of saturation of the double bond and of introducing a heterocyclic ring. Both compounds selected for this purpose had a **1**-acetonaphthone substitution in the naphthyl ring. For **13**, which has a thiophene ring, the naphthyl moiety showed chemical shift values in the range of $\delta = 8.08$–7.67 ppm. The double bond proton signal appeared at $\delta = 6.55$ ppm which is shift to lower frequency compared to location of the peak in phenyl-substituted analogs. The effects on carbon chemical shifts followed a similar trend to the ^{1}H chemical shifts.

We next examined the effect of saturation of the double bond in the structure of cinnamoyloxyacetonaphthone for which we compared the chemical shift values for **11** and **12**. The chemical shifts of the naphthyl moiety did not change drastically compared to other compounds with the unsaturation. However, the aromatic ring proton signals were shifted to lower frequency by 0.2 ppm in the saturated compound compared to the unsaturated analogs. Additionally, the introduction of saturation automatically shifted the H14 and H15 signals to $\delta = 3.0$ ppm which is expected due to free CH_2 groups. In an identical fashion, the carbon chemical shift values of the saturated compounds **11** and **12** were shifted slightly towards lower frequency by 0.2 ppm for the phenyl ring carbons consistent with the result observed for ^{1}H chemical shifts. Interestingly, the C19 signal showed significant shift to lower frequency ($\delta = 126.3$ vs 131.1 ppm) for the saturated compounds **11** and **12** compared to the unsaturated analogs. It appears from the above result that the CH_2 group behaved similar to that of a methyl group and therefore one would expect an electron-donating ability of the methylene group which is expected to increase the electron density at the *para*-position (C19) of the phenyl ring. On the other hand, in the unsaturated analogs showed an opposite trend which is consistent with the electron donating and electron withdrawing groups.

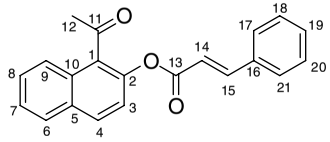
We also synthesized a thiophene-substituted compound to compare the chemical shift values. Accordingly, we present the data for compound **13** which is a 1-substituted acetonaphthone. Most of the chemical shifts were similar for the naphthyl moiety in the structure of the compound. However, the H14 signal in the unsaturated bond was shifted to lower frequency ($\delta = 6.55$ ppm) compared to the phenyl-substituted analogs. The ^{13}C chemical shifts were in accordance with the structure of the compound.

Concerning compound **14** which has a single bond instead of a double bond, most of the protons could not be resolved due to

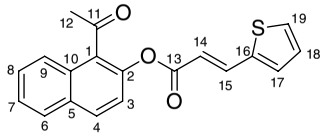
Table 2. ^{13}C NMR chemical shifts of cinnamoyloxyacetonaphthones in DMSO-d_6 at 298 K



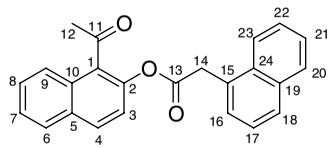
Compounds 1-5, 11



Compounds 6-10, 12



Compound 13



Compound 14

Compound	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
1	145.4	126.7	125.2	126.0	126.7	122.7	127.7	128.7	127.9	135.7	197.7	30.0	164.9	116.7	147.4	133.8	128.9	129.0	131.1	129.0	128.9
2	145.3	127.0	125.3	126.1	126.7	122.7	127.8	128.8	128.0	135.6	197.7	30.0	164.8	117.5	146.0	132.8	130.6	129.1	135.7 (Cl)	129.1	130.6
3	145.3	127.0	125.3	126.1	126.7	122.7	127.7	128.8	128.0	135.7	197.7	30.1	164.8	117.6	146.1	133.1	132.0	130.8	124.6 (Br)	130.8	132.0
4	145.6	127.3	125.2	125.9	126.8	122.7	127.7	128.7	127.9	135.7	197.7	30.1	165.2	113.7	147.3	126.5	130.8	114.5	161.7 55.4(OMe)	114.5	130.8
5	145.1	126.8	125.4	126.3	126.6	122.6	127.9	128.9	128.1	135.7	197.7	30.0	164.4	121.5	141.1	131.8	127.4(29.5) 124.1(CF_3,273.3)	126.4 (5.3)	131.1	133.2	128.9
6	131.1	144.4	122.0	130.2	129.1	124.3	127.8	126.3	128.4	131.1	202.0	32.3	164.8	116.5	147.4	133.3	128.8	129.0	130.9	129.0	128.8
7	130.4	144.5	131.1	122.1	128.6	124.5	126.5	128.0	128.6	131.3	202.6	32.5	164.9	117.5	146.2	132.9	129.3	124.5	135.9 (Cl)	124.5	129.3
8	130.4	144.5	122.1	131.3	129.2	124.5	128.0	126.5	128.6	131.1	202.6	32.5	164.9	117.6	146.3	133.2	132.2	130.9	124.8 (Br)	130.9	132.2
9	130.3	144.5	122.1	130.8	129.1	124.3	127.8	126.4	128.4	131.1	202.5	32.3	165.1	113.5	147.3	126.2	130.9	114.5	161.7 55.4(OMe)	114.5	130.9
10	130.2	144.1	121.8	131.1	129.0	124.3	127.8	126.4	128.5	130.9	202.3	32.3	164.1	121.2	141.0	131.6	127.4(29.6) 124.1(CF_3,279.5)	126.3 (5.4)	131.2	133.1	128.8
11[a]	144.2	130.1	121.8	130.8	129.0	124.3	127.8	126.3	128.4	131.1	202.4	29.9	171.6	29.9	32.2	140.0	128.4	128.4	126.3	128.4	128.4
12[a]	126.7	145.5	126.0	125.4	126.5	128.7	127.5	122.8	127.8	135.0	197.7	29.9	171.2	35.0	30.0	135.7	128.5	128.5	126.3	128.5	128.5
13	130.4	144.5	122.2	131.1	129.2	124.4	128.0	126.5	128.6	131.2	202.7	32.5	164.8	114.4	140.2	138.6	133.5	129.0	131.4	–	–
14[b]	130.2	144.2	121.8	130.8	129.0	124.2	127,7	126.3	128.4	131.1	202.0	32.2	170.0	40.3	–	–	–	–	–	–	–

The substituted groups are represented in parenthesis.

[a] In compounds **11** and **12**, C14–C15 is a single bond, where in all other compounds it is a double bond.

[b] Compound **14** showed ten more carbon signals corresponding to additional naphthyl ring which are unresolvable (126.0–133.0 ppm).

overlapping signals. This is due to the presence of two naphthyl rings in the structure of these compounds as shown in the table. The protons showed chemical shift values in the range of $\delta = 8.08-7.44$ ppm. The methylene ^{1}H signal was observed at $\delta = 4.23$ ppm as a singlet followed by the methyl signal at $2.\delta = 40$ ppm.

In summary, we have synthesized cinnamoyloxy-substituted acetonaphthones and examined their structure with a number of analytical techniques. The chemical shifts associated with naphthyl protons varied marginally. In contrast, substitution of the phenyl ring in the cinnamoyl moiety resulted in significant changes in chemical shifts corresponding to the electron donating/withdrawing groups attached to the ring. The trifluoromethyl-substituted compound showed the highest influence for the *trans*-double bond protons (H15) compared to other substituted groups on the phenyl ring. Introduction of a thiophene ring in the structure shifted the *trans*-double bond ^{1}H signal to lower frequency ($\delta = 6.55$ ppm) compared to the phenyl-substituted compounds.

Experimental

All the chemicals were obtained from Aldrich Sigma and were used without further purification. NMR spectra were recorded in dimethyl sulfoxide and the chemical shifts are reported relative to residual DMSO-d_6 at $\delta = 2.54$ ppm. For the NMR, samples were prepared by dissolving approximately 10 mg of compound in 0.5 ml of DMSO-d_6. The NMR data was acquired on a Bruker 900 MHz NMR spectrometer equipped with a cryoprobe. The ^{1}H NMR spectra were acquired with a sw = 10 ppm with a 90° pulse of 9 μs, number of points = 64 K, acquisition time = 3.6 s and 32 scans. The carbon spectra were acquired with a sweep width of 230 ppm. The 90° pulse width was 12 μs, number of points = 128 K, acquisition time = 1.5 s, number of scans = 128. The COSY spectra were run using similar parameters as stated for ^{1}H NMR spectra and the number of indirect increment in indirect dimension (td1) was set at 256 and the size was 4 K. The TOCSY spectra had similar parameters as described above with a mixing time of 80 ms. For the HSQC, the ^{1}H spectral parameters were used. Additionally, the sweep width for the carbon dimension was 160 ppm, number of point = 2 K, number of scans = 4 and 128 increments, the $^1J_{CH}$ coupling constant set to 145 Hz. The HMBC spectrum was also set with ^{1}H parameters and the carbon sweep width used was 230 ppm, number of scans = 8, multibond coupling set at 8.0 Hz. The raw data was usually multiplied by an exponential or shifted sine squared function before performing the Fourier transform. The ^{1}H signal splitting patterns were designated as follows: s, singlet; d, doublets; t, triplets and m, multiplets. UV/Vis spectra were obtained from a Lambda UV spectrometer using either methanol or chloroform as solvent. Infrared spectra were taken as KBr disc on a Lambda FTIR spectrometer. The infrared frequencies are designated as follows: vw, very weak; w, weak; m, medium; s, strong and vs, very strong. Elemental analysis was performed at the elemental analysis facility of the School of Molecular Biosciences, University of Queensland.

Physical constants of compounds

*(E)-2-Acetylnaphthalen-1-yl-3-phenylacrylate (**1**)*

UV ($CHCl_3$): 332 (sh), 283 nm; IR(KBr): 3429 (w), 3065 (w), 3028 (w), 2922 (w), 1732 (vs), 1706 (vs), 1634 (vs), 1594 (s), 1505 (m), 1447 (m), 1428 (w), 1411 (w), 1382 (m), 1353 (w), 1303 (m), 1235 (s), 1209 (s), 1136 (vs), 1063 (m), 1022 (w), 996 (m), 919 (w), 865 (w), 817 (s), 764 (vs) cm^{-1}; elemental analysis: calcd for $C_{21}H_{16}O_3$: C: 79.73, H:5.10, found: C:79.97, H:4.91.

*(E)-2-Acetylnaphthalen-1-yl-3-(4-chlorophenyl)acrylate (**2**)*

UV ($CHCl_3$): 327 (sh),280 nm; IR (KBr): 3423 (w), 3354 (w), 3086 (w), 3007 (w), 1730 (vs) 1715 (vs), 1682 (vs), 1621 (s), 1590 (s), 1489 (s), 1466 (s), 1404 (s), 1350 (m), 1325 (m), 1276 (m), 1212 (s), 1196 (m), 1150 (m), 1073 (m), 1008 (w), 988 (m), 923 (w), 828 (w), 754 (vs) cm^{-1}; elemental analysis: calcd for $C_{21}H_{15}ClO_3$: C: 71.90, H: 4.31, Cl: 10.11; found : C: 72.13, H: 4.24.

*(E)-2-Acetylnaphthalen-1-yl-3-(4-bromophenyl)acrylate (**3**)*

UV ($CHCl_3$): 322 (sh), 290 nm; IR (KBr): 3441 (w), 3086 (w), 3066 (w),3010 (w), 1730 (vs), 1715 (vs), 1682 (vs), 1594 (s), 1508 (m), 1489 (s), 1465 (s), 1403 (s), 1387 (w), 1349 (m), 1325 (m), 1276 (m), 1232 (s), 1196 (m), 1150 (m), 1073 (m), 1009 (w), 923 (w), 828 (w), 755 (vs), 729 (m) cm^{-1}; elemental analysis: calcd for $C_{21}H_{15}BrO_3$: C: 63.81, H: 3.83, found: C: 63.70, H: 3.73.

*(E)-2-Acetylnaphthalen-1-yl-3-(4-methoxyphenyl)acrylate (**4**)*

UV ($CHCl_3$): 315, 295 (sh)nm; IR (KBr): 3442 (w), 3361 (w),3020 (s), 2973 (vw), 1731 (vs), 1683 (vs), 1631 (vs), 1603 (vs), 1574 (m), 1514 (s), 1465 (m), 1424 (m), 1360 (w), 1216 (m), 1172 (s), 1122 (vs), 1065 (m), 1028 (m), 984 (m), 828 (s), 754 (vs) cm^{-1}.

*(E)-2-Acetylnaphthalen-1-yl-3-(2-(trifluoromethyl)phenyl)acrylate (**5**)*

UV ($CHCl_3$): 320 (sh), 286 nm; IR: (KBr): 3430, (vs) 3065 (w), 3028 (w), 2922 (vw), 1733 (vs), 1707 (vs), 1690 (vs), 1634 (m), 1594 (m), 1505 (m), 1466 (m), 1447 (m), 1428 (m), 1411 (m), 1381 (m), 1352 (w), 1312 (vs), 1273 (vs), 1235 (s), 1209 (w), 1136 (vs), 1062 (m), 1095 (s), 977 (m), 920 (vw), 865 (w), 817 (m), 764 (vs), 741 (vs) cm^{-1}; elemental analysis: calcd for $C_{22}H_{15}F_3O_3$: :68.75, H: 3.93, F: 14.83, Found: C: 68.57, H:4.01.

*1-Acetylnaphthalen-2-yl-cinnamate (**6**)*

UV ($CHCl_3$): 333 (sh), 286 nm; IR: 3442 (vw), 3404 (vw), 3075 (s), 2924 (vw), 1732 (vs), 1637 (s), 1579 (s), 1511 (m), 1464 (m), 1433 (m), 1417 (m), 1387 (m), 1354 (s), 1306 (s), 1276 (m), 1211 (vs), 1144 (vs), 1076 (w), 1018 (m), 996 (vs), 925, (w) 866 (s), 849 (s), 826 (s), 765 (vs), 742 (vs) cm^{-1}; elemental analysis: calcd for $C_{21}H_{16}O_3$: C: 79.73, H:5.10, found: C: 79.88, H:4.86.

*(E)-1-Acetylnaphthalen-2-yl-3-(4-chlorophenyl)acrylate (**7**)*

UV ($CHCl_3$); 310, 281 nm; IR (KBr): 3443 (m), 3067 (w), 2919 (w), 1730 (vs), 1708 (vs), 1630 (m), 1589 (w), 1490 (w), 1403 (w), 1384 (vw), 1302 (s), 1217 (s), 1134 (s), 1117 (s), 1084 (m), 986 (s), 967 (m), 866 (w), 819 (vs), 765 (s), 743 (s) cm^{-1}.

*(E)-1-acetylnaphthalen-2-yl-3-(4-bromophenyl)acrylate (**8**)*

UV ($CHCl_3$): 330 (sh),303; IR (KBr): 3456 (m), 3065 (w), 2919 (vw), 1732 (vs), 1708 (vs), 1637 (m), 1583 (w), 1487 (w), 1403 (m), 1352 (s), 1306 (s), 1273 (vw), 1218 (s), 1135 (s), 1119 (s), 1105 (m), 1072 (w), 1009 (w), 988 (s), 869 (m), 848(m0, 817 (vs), 768 (s), 743 (vs) cm^{-1}; elemental analysis: calcd for $C_{21}H_{15}BrO_3$, C: 63.81, H: 3.83, found: C: 64.15, H: 3.74

*(E)-1-Acetylnaphthalen-2-yl-3-(4-methoxyphenyl)acrylate (**9**)*

UV ($CHCl_3$): 303, 276 (sh) nm; IR (KBr): 3442 (vw), 3401 (vw), 3075 (w), 2924, (w) 1733 (vs), 1705 (vs), 1637 (vs), 1602 (s), 1579 (m), 1511 (s), 1464 (m), 1447 (w), 1432 (m), 1417 (m), 1387 (w), 1354 (m), 1306 (w), 1276 (w), 1211 (s), 1144 (vs), 1117 (m), 1018 (s), 996 (s), 925 (w), 865 (w), 826 (s), 742 (vs) cm^{-1}; elemental analysis: calcd for $C_{22}H_{18}O_4$, C: 76.29, H: 5.24; found: C: 76.25, H: 5.16.

*(E)-1-Acetylnaphthalen-2-yl-3-(2-(trifluoromethyl)phenyl)acrylate (**10**)*

UV ($CHCl_3$): 320 (sh),285 nm; IR (KBr): 3340 (vw), 3065 (vw), 2919 (vw), 1741 (vs), 1703 (vs), 1633 (vs), 1600 (s), 1575 (s), 1512 (s), 1487 (s), 1462 (m), 1432 (m), 1390 (m), 1352 (m), 1310 (vs), 1273 (vs), 1205 (vs), 1119 (vs), 1090 (w), 1037 (m), 981 (vs), 888 (m), 863 (s), 847 (m), 822 (s), 791 (m), 770 (vs) cm^{-1};

*1-Acetylnaphthalen-2-yl-3-phenylpropanoate (**11**)*

UV($CHCl_3$): 322, 274 nm; IR(KBr): 3443 (w), 3067 (vw), 2919 (vw), 1764 (vs), 1731 (vw), 1709 (vs), 1702, 1629 (vw), 1589 (vw), 1516 (m), 1491 (w), 1403 (w), 1384 (m), 1302 (w), 1218 (vs), 1134 (vs), 1117 (s), 1085 (w), 1014 (w), 986 (vw), 967 (vw), 866 (w), 819 (m), 765 (m), cm^{-1}.

*2-Acetylnaphthalen-1-yl-3-phenylpropanoate (**12**)*

UV ($CHCl_3$): 281, 339 nm; IR: 3409 (w), 3061 (vw), 3026 (vw), 2925 (vw), 2854 (vw),1764 (vs), 1686 (vs), 1626 (m), 1598 (m), 1570 (m), 1497 (m), 1467 (m), 1425 (m), 1359 (s), 1274 (s), 1237 (s), 1193(m0, 1119 (vs), 1078 (w), 1025 (w), 981 (w), 872 (w), 815 (s), 749 (s) cm^{-1}.

*(E)-1-Acetylnaphthalen-2-yl-3-(thiophen-2-yl)acrylate (**13**)*

UV ($CHCl_3$): 315, 275 (sh) nm; IR(KBr): 3430 (vw), 3065 (vw), 3027 (vw), 2922 (vw), 1728 Vs), 1699 (vs), 1690 (vs), 1619 (vs), 1594 (w), 1511 (w), 1466 (w), 1447 (w), 1422 (m), 1411 (w), 1381 (w), 1281 (m), 1272 (m), 1237 w), 1201 (vs), 1135 (vs), 1117 (vs), 1062 (w), 1031 (w), 1022 (w), 975 (s), 919 (w), 868 (m), 817 (m), 731 (s) cm^{-1}; elemental analysis: calcd for $C_{19}H_{14}O_3S$, C: 70.79, H:4.38, S: 9.95, found: C: 70.93, H: 4.22 S: 9.55.

*1-Acetylnaphthalen-2-yl-2-(naphthalene-1-yl)acetate (**14**)*

UV ($CHCl_3$): 330 (sh), 275 nm; IR (KBr): 3418 (w), 3056 (w), 1757 (vs), 1703 (vs), 1577 (w), 1506 (m),1435 (w), 1354 (w), 1351 (w), 1205 (vs), 1160 (w), 1133 (s), 1109 (vs), 1020 (w), 996 (vw), 815 (m), 759 (m) cm^{-1}.

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