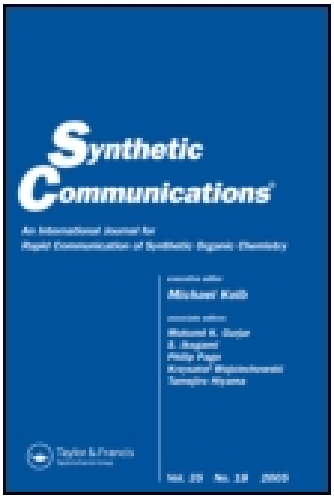

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Chlorotrimethylsilane: A Powerful Lewis Acidic Catalyst in Michael-Type Friedel-Crafts Reactions of Indoles and Enones

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Abstract: Catalytic amount of chlorotrimethylsilane (TMSCl) was found to be an effective silicon Lewis acid catalyst in catalyzing the Michael-type Friedel–Crafts reactions of indoles and chalcones to afford corresponding 3-substituted indole derivatives in good to excellent yields. The method is metal-free, has mild reaction conditions, and generates good yields of products with greater selectivity, which make it a useful and attractive process for the synthesis of different indole derivatives.

Keywords: dual activation, enone, Friedel–Crafts reaction, indole, silane

Among various synthetic applications of silane (organosilicon compounds),[1] the transformations utilizing derivatives containing leaving groups at the

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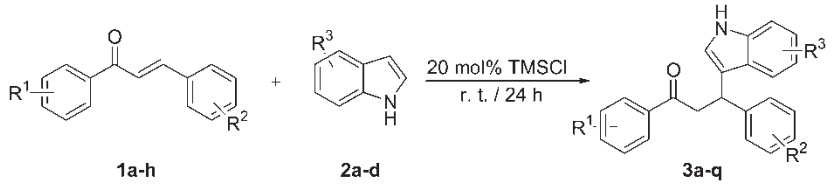
silicon atom have become especially widespread. The behavior of these compounds is determined primarily by the tendency of the silicon atom to expand its valence shell, giving rise to five- and six-coordinate intermediates.[2] This property allows one to consider silanes as Lewis acids, thereby justifying their use as mediators in carbon–carbon bond-forming reactions. The past four decades witnessed a tremendous development in the use of organosilicon compounds (silanes) for organic synthesis.[1b–e] The observation of the trialkylsilyl cation R_3Si^+, which is apparently the strongest silicon Lewis acid (SLA), has attracted considerable attention. Silicon Lewis acids (silanes) offer some advantages over traditional metal-centered activators. For example, silanes are compatible with many synthetically valuable C-nucleophiles and heteroatom, such as silyl enol ethers, allyl organometallic reagents, cuprates, phosphine, and carbamate.[3] Among the silane compounds, chlorotrimethylsilane (TMSCl) is one of the most useful reagents, is a highly reactive silylating agent, and has numerous applications in organic synthesis and catalysis.[4] TMSCl can facilitate the conjugate addition of organocopper and other organometallic reagents to different acceptors efficiently[5] and has been widely used as promoter or additive in several transition metal–or Lewis acid–catalyzed reaction transformations.[6] However, its direct use as a catalyst in organic reactions is rarely reported.[7] Herein, we report our findings, focusing on the TMSCl-catalyzed Michael-type Friedel–Crafts reactions of indoles and enones.

Among the Friedel–Crafts reactions, the Michael-type Friedel-Crafts addition of indoles to electron-deficient olefins and α,β-unsaturated enones is a very important process because it is involved in the total synthesis of a class of bioactive indole alkaloids such as the hapalindoles and other 3-substituted indoles derivatives, which are important substructures and building blocks for the synthesis of natural products and therapeutic agents.[8] During past years, a variety of transition metal salts, such as $Zr(OTf)_4$,[9] $Bi(OTf)_3$,[10] $CeCl_3{\cdot}7H_2O$-NaI,[11] $InBr_3$,[12] and other transition metal–based Lewis acid catalysts[13] or organic molecular catalysts (organocatalysis),[14] have been applied in this reaction for the preparation of 3-substituted indoles. However, some drawbacks still exist in previous synthetic methods (e.g., the use of expensive stoichiometric amounts of Lewis acidic catalysts and toxic heavy metals). Hence, searching for cheaper, simpler, and more efficient procedures (simple chemistry), including metal-free catalysts, is very attractive.

RESULTS AND DISCUSSION

To establish suitable Friedel–Crafts reaction conditions, we employed the reaction of indole with chalcone as a model in the presence of catalytic TMSCl (Scheme 1). The results of the TMSCl-catalyzed Friedel–Crafts reactions in various conditions are summarized in Table 1. Among these

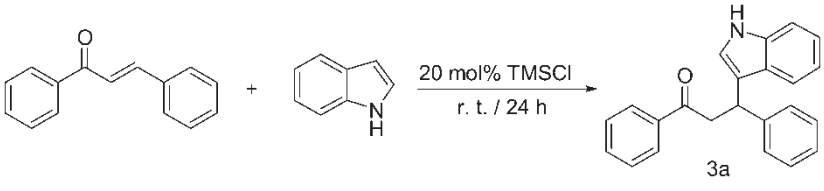


Scheme 1.

solvents, lower or nonpolar ones were proven to be effective for the reaction. CH_2Cl_2 provided the best result, but no reaction occurred in DMF probably because of the strong interaction between TMSCl and DMF. When the amount of TMSCl was reduced to 10 mol%, a slightly lower yield was obtained. Under the optimized mild condition (20 mol% of TMSCl, 1 equiv. chalcone, and 1.1 equiv. indole in CH_2Cl_2 at room temperature), the target compound **3a** was obtained in good yield (75%).

Under the optimized mild condition (20 mol% of TMSCl, 1 equiv. chalcone, and 1.1 equiv. indole in CH_2Cl_2 at room temperature), the target

Table 1. TMSCl-catalyzed Michael-type Friedel–Crafts reactions of indole with chalcone under different conditions



Entry	Solvent	Yield (%)[a]
1	CH_2Cl_2	75
2	Toluene	56
3	CH_3CN	62
4	Acetone	Trace
5	DMF	0
6	Et_2O	73
7	THF	15
8	CH_2Cl_2	54[b]
9	CH_2Cl_2	61[c]
10	CH_2Cl_2	70[d]

[a]Unless noted, all of the reactions were carried out with 20 mol% of TMSCl, and indole/chalcone = 1.1/1 at room temperature for 24 h.

[b]Using 10 mol% of TMSCl as catalyst.

[c]At reflux.

[d]Using 15 mol% of TMSCl as catalyst.

compound **3a** was obtained in good yield. Then we investigated various indoles and enones for Michael-type Friedel–Crafts reactions (Table 2). As shown in Table 2, the yields were very sensitive to the substrates employed. For the reactions of N-unsubstituted indoles (indole and 5-bromo-indole) with enones bearing an H- or Cl-group, good yields could be obtained (entries 2 to 3, 12); modest yields were obtained with enones bearing a methoxyl group (entry 5). This may be due to the strong interaction between TMSCl and N–H of indole, which disfavored the 1,4-counjugate addition to methoxyl-substituted enones. It should be emphasized that in the cases using N-substituted and C-2 substituted indoles, the corresponding yields with different enones were good to excellent (entries 6 to 11, up to almost quantitative conversion). Nearly all reactions are clean, and the target compounds are obtained in good yields with no formation of side products such as dimers or trimers, which are normally observed by the influence of strong acids. Judging from these findings, the mechanism of TMSCl-catalyzed Friedel–Crafts reaction of indole with chalcone proceeds possibly through the generation of silyl enol ether by the conjugate addition of indole to chalcone; then the Cl- would attack the TMS group of the silyl enol ether to regenerate TMSCl together with the formation of product **3a**.[15]

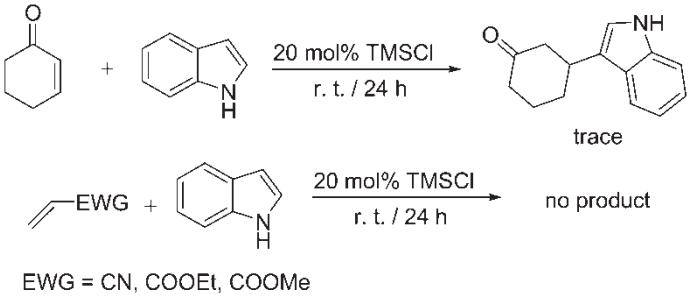
Encouraged by these results, we next evaluated this protocol for the reaction of 2-cyclohexen-1-one with indole. Unfortunately, the conversion is poor and only trace product was obtained (less than 10% of isolated

Table 2. TMSCl-catalyzed Michael-type Friedel–Crafts reactions of indoles with chalcones[a]

Entry	R^1	R^2	R^3	Product	Yield (%)[b]
1	H	H	*N*-CH_3	**3b**	97
2	H	*p*-Cl	H	**3c**	71
3	H	*o*-Cl	H	**3d**	90
4	H	*p*-OCH_3	H	**3e**	65
5	*p*-OCH_3	H	H	**3f**	55
6	H	*p*-Cl	*N*-CH_3	**3 g**	97
7	H	*p*-OCH_3	*N*-CH_3	**3 h**	94
8	*p*-OCH_3	H	*N*-CH_3	**3i**	88
9	H	H	2-CH_3	**3j**	99
10	H	*p*-Cl	2-CH_3	**3 k**	99
11	H	*p*-OCH_3	2-CH_3	**3l**	95
12	H	H	5-Br	**3 m**	68
13	H	*p*-Cl	5-Br	**3n**	55

[a]Unless noted, all of the reactions were carried out with 20 mol% of TMSCl and indole/chalcone = 1.1/1 at room temperature for 24 h.

[b]Isolated yield.



Scheme 2.

yield). We also tried to explore the catalytic activities of TMSCl in the aza-Michael reaction of α,β-ethylenic compounds with indoles; as shown in Scheme 2, no any products was detected after 24 h. This clearly showed chlorotrimethylsilane (TMSCl) is suitable only to activate chalcones and failed in the case of cyclic enones, α,β-unsaturated esters, and acrylonitrile for this Friedel–Crafts reaction. This selectivity could be useful for complex molecules with the existence of these blocks in synthetic applications.

In summary, we have demonstrated that simple TMSCl is an effective and promising catalyst for the Michael-type Friedel–Crafts reactions of indoles with chalcones. This novel entry has the advantages of being metal-free, using mild reaction conditions, and generating good yields of products with greater selectivity, which make it a useful and attractive process for the synthesis of indole derivates. This work offers good examples for the application of Lewis acidic silane catalyst for novel Friedel–Crafts reactions of indoles with chalcones. Application to enantio-selective variants with chiral silane in asymmetric Michael-type Friedel–Crafts reactions on the basis of these new findings is in progress in our laboratories.

EXPERIMENTAL

All reaction flasks and solvents were dried according to standard methods prior to use. Flash-column chromatography was performed over silica (100–200 mesh). NMR spectra were recorded on a 400-MHz spectrometer. ^{13}C NMR spectra were obtained with broadband proton decoupling. For spectra recorded in $CDCl_3$, unless noted, chemical shifts were recorded relative to the internal TMS (tetramethylsilane) reference signal. IR spectra were recorded using a FTIR apparatus. Thin-layer chromatography was performed using silica. TMSCl was distilled with Mg prior to use.

Typical Michael-Type Friedel–Crafts Reaction Procedure (3a–3n)

TMSCl (0.1 mmol) was added into a solution of enone (0.5 mmol) and indol (0.55 mmol) in freshly distilled CH_2Cl_2 (3 mL). After stirring at room temperature for 24 h, the mixture was diluted with H_2O (10 mL) and extracted with EtOAc (3 × 15 mL). The combined organic layers were dried (Na_2SO_4), concentrated in vacuo, and purified by column chromatography on silica gel (EtOAc–pet. ether, 1:5) to gain the pure product.

Data

3a: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.97$ (bs, 1H), 7.93 (d, $J = 7.2$ Hz, 2H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.40–7.44 (m, 3H), 7.35 (d, $J = 7.2$ Hz, 2H), 7.23–7.31 (m, 3H), 7.14 (q, $J = 7.2$, 7.2 Hz, 2H), 7.01 (t, $J = 7.4$ Hz, 1H), 6.96 (s, 1H), 5.07 (t, $J = 7.2$ Hz, 1H), 3.81 (dd, $J = 6.8$, 6.8 Hz, 1H), 3.72 (dd, $J = 7.6$, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 198.6$, 144.2, 137.0, 136.6, 133.0, 128.6, 128.4, 128.1, 127.8, 126.6, 126.3, 122.1, 121.4, 119.5, 119.4, 119.2, 111.1, 45.2, 38.1; IR (KBr): 3462, 3078, 3056, 3024, 1669, 1597, 1580, 1490, 758, 746, 703, 692 cm^{-1}; MS (EI): m/z = 325.

3b: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.93$ (d, $J = 7.2$ Hz, 2H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.40–7.45 (m, 3H), 7.36 (d, $J = 7.6$ Hz, 2H), 7.24–7.28 (m, 3H), 7.16 (q, $J = 7.2$, 7.2 Hz, 2H), 7.00 (t, $J = 7.4$ Hz, 1H), 6.83 (s, 1H), 5.06 (t, $J = 7.2$ Hz, 1H), 3.80 (dd, $J = 6.8$, 6.8 Hz, 1H), 3.74 (dd, $J = 7.6$, 6.0 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 198.5$, 144.4, 137.3, 137.2, 132.9, 128.5, 128.4, 128.1, 127.8, 127.0, 126.2, 121.7, 119.6, 118.8, 117.8, 109.2, 45.3, 38.1, 33.8, 32.6; IR (KBr): 3431, 1674, 1596, 1488, 1448, 1247, 740, 749 cm^{-1}; MS (EI): m/z = 339.

3c: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.00$ (bs, 1H), 7.92 (d, $J = 7.6$ Hz, 2H), 7.54 (t, $J = 7.0$ Hz, 1H), 7.42 (t, $J = 6.8$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.24–7.28 (m, 2H), 7.18–7.22 (m, 2H), 7.15 (t, $J = 7.6$ Hz, 1H), 7.01 (t, $J = 7.4$ Hz, 1H), 6.97 (s, 1H), 5.03 (t, $J = 7.2$ Hz, 1H), 3.79 (dd, $J = 6.8$, 6.4 Hz, 1H), 3.68 (dd, $J = 8.0$, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 198.2$, 142.7, 136.9, 136.6, 133.2, 131.9, 129.2, 128.6, 128.5, 128.0, 126.4, 122.3, 121.3, 119.5, 119.4, 118.9, 111.2, 44.9, 37.5; IR (KBr): 3398, 3084, 3056, 3026, 1681, 1596, 1579, 1489, 820, 768, 746, 689 cm^{-1}; MS (EI): m/z = 359.

3d: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.99$ (s, 1H), 7.97 (s, 2H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.38–7.46 (m, 3H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.26 (s, 1H), 7.20–7.24 (m, 1H), 7.08–7.17 (m, 3H), 7.02 (t, $J = 7.6$ Hz, 2H), 5.54 (t, $J = 7.4$ Hz, 1H), 3.80 (dd, $J = 8.8$, 8.8 Hz, 1H), 3.68 (dd, $J = 6.4$, 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 198.0$, 141.6, 136.9, 136.6, 133.6, 133.0, 129.8, 129.0, 128.6, 128.2, 127.6, 126.9, 126.7, 122.2, 122.0,

119.5, 119.5, 117.8, 111.1, 44.2, 34.9; IR (KBr): 3375, 3056, 1677, 1619, 1595, 1577, 768, 754, 742, 685 cm^{-1}; MS (EI): m/z = 359.

3e: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.97$ (bs, 1H), 7.92 (d, $J = 8.0$ Hz, 2H), 7.52 (t, $J = 7.2$ Hz, 1H), 7.39–7.44 (m, 3H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.25 (s, 1H), 7.22–7.24 (m, 1H), 7.13 (t, $J = 7.6$ Hz, 1H), 7.00 (t, $J = 7.6$ Hz, 1H), 6.96 (s, 1H), 6.78 (d, $J = 7.2$ Hz, 2H), 5.00 (t, $J = 7.4$ Hz, 1H), 3.78 (dd, $J = 6.8$, 6.4 Hz, 1H), 3.73 (s, 3H), 3.68 (dd, $J = 8.0$, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 198.7$, 158.0, 137.2, 136.7, 136.3, 132.9, 128.7, 128.5, 128.1, 126.6, 122.1, 121.3, 119.7, 119.6, 119.4, 113.8, 111.1, 55.2, 45.4, 37.5; IR (KBr): 3422, 1670, 1250, 1032 cm^{-1}; MS (EI): m/z = 355.

3f: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.98$ (bs, 1H), 7.92 (d, $J = 8.8$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 1H), 7.29–7.35 (m, 3H), 7.24 (t, $J = 7.4$ Hz, 2H), 7.14 (q, $J = 6.8$, 8.0 Hz 2H), 6.97–7.03 (m, 2H), 6.89 (d, $J = 8.8$ Hz, 2H), 5.06 (t, $J = 7.4$ Hz, 1H), 3.84 (s, 3H), 3.76 (dd, $J = 7.2$, 6.8 Hz, 1H), 3.66 (dd, $J = 8.0$, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.0$, 163.4, 144.4, 136.6, 130.4, 128.4, 127.8, 126.7, 126.2, 122.1, 121.4, 119.6, 119.3, 113.7, 111.1, 55.4, 44.8, 38.4; IR (KBr): 3432, 1665, 1265, 1023 cm^{-1}; MS (EI): m/z = 355.

3g: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.93$ (d, $J = 8.0$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.39–7.46 (m, 3H), 7.28 (t, $J = 8.2$ Hz, 3H), 7.17–7.23 (m, 3H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.82 (s, 1H), 5.03 (t, $J = 7.2$ Hz, 1H), 3.79 (dd, $J = 6.0$, 6.4 Hz, 1H), 3.70 (dd, $J = 8.4$, 8.4 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 198.2$, 142.9, 137.4, 137.0, 133.1, 131.9, 129.2, 128.6, 128.1, 126.8, 126.2, 121.8, 119.4, 119.0, 117.4, 109.3, 45.1, 37.5, 33.8, 32.7; IR (KBr): 3432, 1673, 1594, 1486, 1469, 1247, 745, 690 cm^{-1}; MS (EI): m/z = 373.

3h: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.93$ (d, $J = 8.0$ Hz, 2H), 7.53 (t, $J = 7.2$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 3H), 7.24–7.28 (m, 3H), 7.18 (t, $J = 7.6$ Hz, 1H), 7.01 (t, $J = 7.2$ Hz, 1H), 6.78–6.82 (m, 3H), 5.00 (t, $J = 7.2$ Hz, 1H), 3.78 (dd, $J = 6.4$, 6.4 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 3.70 (dd, $J = 6.8$, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 198.6$, 158.0, 137.4, 137.2, 136.5, 132.9, 128.7, 128.5, 128.1, 127.0, 126.1, 121.6, 119.6, 118.8, 118.2, 113.8, 109.2, 55.2, 45.5, 37.4, 32.7; IR (KBr): 3426, 1676, 1611, 1510, 1466, 1252, 740, 691 cm^{-1}; MS (EI): m/z = 369.

3i: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.92$ (d, $J = 9.2$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 1H), 7.35 (d, $J = 7.6$ Hz, 2H), 7.23–7.27 (m, 3H), 7.16 (q, $J = 7.6$, 7.6 Hz, 2H), 7.00 (t, $J = 7.4$ Hz, 1H), 6.89 (d, $J = 8.8$ Hz, 2H), 6.82 (s, 1H), 5.05 (t, $J = 7.0$ Hz, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 3.70 (dd, $J = 10.0$, 8.8 Hz, 1H), 3.69 (dd, $J = 8.8$, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 197.0$, 163.4, 144.5, 137.3, 130.3, 130.3, 128.4, 127.8, 127.0,

126.2, 126.1, 121.6, 119.6, 118.8, 117.9, 113.6, 109.1, 55.4, 44.9, 38.2, 32.6; IR (KBr): 3433, 1667, 1601, 1575, 1484, 1418, 1247, 1185, 1024, 747, 701 cm^{-1}; MS (EI): m/z = 369.

3j: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.90$ (d, $J = 7.6$ Hz, 2H), 7.78 (bs, 1H), 7.50 (d, $J = 7.2$ Hz, 2H), 7.37–7.41 (m, 4H), 7.14–7.29 (m, 4H), 6.99–7.10 (m, 2H), 5.12 (t, $J = 6.8$ Hz, 1H), 3.99 (dd, $J = 7.6$, 8.4 Hz, 1H), 3.92 (dd, $J = 7.6$, 6.8 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 199.1$, 144.2, 137.1, 135.4, 132.8, 131.7, 128.4, 128.2, 128.0, 127.5, 125.9, 120.7, 119.1, 119.1, 113.6, 110.4, 43.5, 36.8, 12.1; IR (KBr): 3410, 3350, 1671, 1459, 1448, 1261, 1206, 753, 740, 691 cm^{-1}; MS (EI): m/z = 339.

3k: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.86$ (d, $J = 7.6$ Hz, 2H), 7.79 (bs, 1H), 7.48 (t, $J = 7.2$ Hz, 1H), 7.34–7.43 (m, 3H), 7.16–7.27 (m, 5H), 6.97–7.08 (m, 2H), 5.04 (t, $J = 7.0$ Hz, 1H), 3.89 (m, 1H), 3.87 (m, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 198.8$, 142.7, 137.0, 135.4, 133.0, 131.7, 131.5, 128.9, 128.5, 128.3, 128.0, 127.2, 120.8, 119.3, 118.9, 113.2, 110.5, 43.4, 36.2, 12.0; IR (KBr): 3410, 3350, 1671, 1597, 1456, 1261, 1206, 740, 692 cm^{-1}; MS (EI): m/z = 373.

3l: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.87$ (d, $J = 7.6$ Hz, 2H), 7.76 (bs, 1H), 7.45–7.50 (m, 2H), 7.36 (t, $J = 7.8$ Hz, 2H), 7.22–7.27 (m, 2H), 7.19 (d, $J = 7.6$ Hz, 1H), 6.96–7.07 (m, 2H), 6.77 (d, $J = 8.8$ Hz, 2H), 5.02 (t, $J = 7.0$ Hz, 1H), 3.89 (m, 1H), 3.87 (m, 1H), 3.72 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 199.2$, 157.7, 137.2, 136.3, 135.5, 132.8, 131.5, 128.4, 128.0, 127.4, 120.7, 119.1, 113.8, 113.6, 110.4, 55.2, 43.8, 36.0, 12.1; IR (KBr): 3378, 1673, 1509, 1461, 1448, 1299, 1257, 1244, 1176, 1034, 744, 706 cm^{-1}; MS (EI): m/z = 369.

3m: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.01$ (bs, 1H), 7.93 (d, $J = 7.2$ Hz, 2H), 7.53–7.57 (m, 2H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.25–7.34 (m, 4H), 7.16–7.25 (m, 3H), 7.01 (s, 1H), 5.00 (t, $J = 7.2$ Hz, 1H), 3.78 (dd, $J = 6.8$, 6.8 Hz, 1H), 3.70 (dd, $J = 6.8$, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 198.3$, 143.8, 137.1, 135.2, 133.1, 128.6, 128.6, 128.4, 128.1, 127.7, 126.5, 125.1, 122.6, 122.1, 119.0, 112.8, 112.5, 45.2, 38.0; IR (KBr): 3427, 1666, 1598, 1454, 1286, 1102, 798, 750 cm^{-1}; MS (EI): m/z = 404.

3n: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.15$ (bs, 1H), 7.92 (d, $J = 8.0$ Hz, 2H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.50 (s, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.14–7.26 (m, 6H), 6.96 (s, 1H), 4.97 (t, $J = 7.4$ Hz, 1H), 3.75 (dd, $J = 7.2$, 6.8 Hz, 1H), 3.66 (dd, $J = 7.2$, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 198.0$, 142.3, 136.8, 135.2, 133.2, 132.1, 129.1, 128.7, 128.2, 128.0, 125.2, 122.5, 121.8, 118.5, 112.8, 112.6, 44.9, 37.3, 33.8; IR (KBr): 3455, 3350, 1678, 1595, 1487, 1458, 1446, 808, 689 cm^{-1}; MS (EI): m/z = 438.

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