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The facile one-pot synthesis of *N*-imidoylbenzotriazoles via a Beckmann rearrangement of ketoximes

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ABSTRACT

N-Imidoylbenzotriazoles **2a–m** were obtained in good to excellent yields (up to 97%) by the reaction of ketoximes **1a–m** with MsCl and subsequently with benzotriazole as a one-pot process in Toluene/CH_3CN at reflux temperature via a Beckmann rearrangement.

1. Introduction

Imidoylbenzotriazoles are chemically stable and versatile reagents, which have been employed as useful substitutes for imidoyl chlorides[1] in the synthesis biologically important functional groups or compounds (shown in Fig. 1) such as enaminones,[2] *N*-substituted β-enamino acid derivatives,[3] polysubstituted amidines,[4] 1,5-substituted tetrazoles,[5] amidrazones,[6] and triazoles.[6]

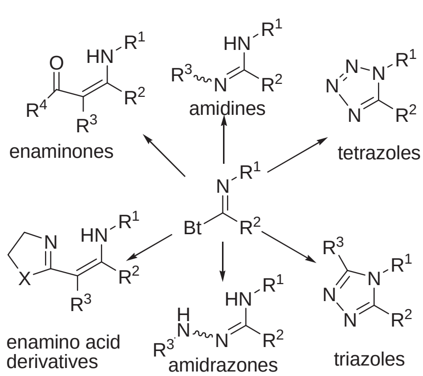

Figure 1.

Due to its synthetical importance, many efforts have been made to develop the synthetic methods by Katritzky[1–6] including the reaction of secondary amides under various reaction systems such as BtH/$POCl_3$/Et_3N,[1a] Bt_2SO,[1b] BtCl/PPh_3,[3] BtH/Pyridine/$(COCl)_2$,[4] and BtH/$SOCl_2$.[4] The reaction of isonitriles[7] with *N*-(aminoalkyl) benzotriazoles in the presence of $BF_3 \cdot Et_2O$ and the reaction of isocyanates[8] with *N*-acylbenzotriazoles have also been reported to produce the imidoylbenzotriazoles.

In 1999, Katritzky[9] reported a new synthesis of imidoylbenzotriazoles via BtTs mediated Beckmann Rearrangement of Ketoximes, in which a heterogeneous reaction system is required (*t*-BuOK or K_2CO_3/crown ether 18C6) and the yields of corresponding products are low to moderate in most cases. Considering the availability of various ketoximes, this new synthetic methodology obviously provides a potentially useful way to imidoylbenzotriazoles despite of the moderate yields and relatively harsh reaction condition.

As a part of research work in our group, we have developed a series of catalytic systems for the Beckmann Rearrangement of ketoximes including BOPCl,[10] TsCl,[11] TAPC,[12] $AlCl_3$.[13] According to the traditional reaction mechanism, the Beckmann Rearrangement of oxime sulfonates occurs smoothly to form a reactive iminocarbocation intermediate, which could be attacked by benzotriazole to form imidoylbenzotriazole as an excellent electrophile. In Katritzky's report,[9] the pre-prepared BtTs, containing both nucleophilic moiety Bt and Ts part serving for the formation of oxime sulfonates, was used for the synthesis of *N*-imidoylbenzotriazole. The relatively low yield of BtTs system is presumably caused by the low reactivity of BtTs in the formation of oxime sulfonates; therefore crown ether 18C6 and strong base *t*-BuOK instead of organic base such as triethylamine were employed to facilitate this process.

Based on above assumption, as depicted in Scheme 1, we further envisaged that the formation of oxime sulfonates **A** in situ by treating the oximes **1** with sulfonyl chloride in the presence of base, followed by smooth Beckmann Rearrangement of oxime sulfonates **A** to form the iminocarbocation species **B**, which is subjected to simultaneous nucleophilic attack by benzotriazole to afford the imidoylbenzotriazoles **2**. As a consequence, we would like to

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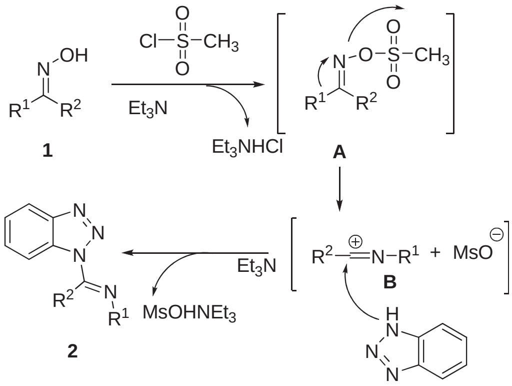


Scheme 1. Possible reaction pathway.

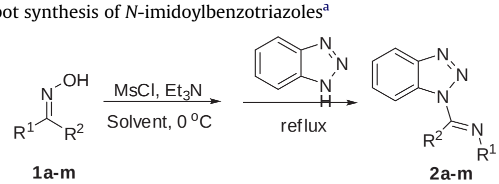
describe herein a highly efficient one-pot synthesis of imidoylbenzotriazoles by the reaction of ketoximes with MsCl and benzotriazoles in toluene or acetonitrile using triethylamine as base at reflux temperature.

2. Results and discussion

Initially, MsCl was used to react with acetophenone oxime **1a** in CH_3CN using Et_3N as base at 0 °C, without any workup, the resulting oxime sulfonate was then treated with benzotriazole at reflux temperature (Table 1). To our delight, as expected, the reaction proceeded very smoothly and generated the desired *N*-imidoylbenzotriazole in good yield (76% vs 60% in BtTs system,[9] entry 1). A simple solvent screening found that toluene gave the best result (95% yield, entry 1). Next, we examined the scope of substrates by using diarylketoxime **1b**, arylalkylketoximes **1a**, **c**–**h**, dialkylketoximes **1i**–**m**, and cyclohexanone oxime **1j**. All the arylalkylketoximes gave corresponding *N*-imidoylbenzotriazoles in excellent yields (91–97%) in toluene, regardless the electronic property of substituents on aromatic ring. The benzophenone oxime also proceeded smoothly affording product in 82% yield. Notably, the bulky oxime **1m** gave corresponding *N*-imidoylbenzotriazole **2m** as a 3:1 *E*/*Z* isomers in very good yield (entry 13, 77% yield), which is much better than that of Katritzky's result (77% vs 35% in BtTs system[9]). Interestingly, oximes **1i**, **1j**, and **1l** were not ideal for this process and afforded corresponding *N*-imidoylbenzotriazoles in low to moderate yields (40%, 37%, and 17%, respectively). We also tested the reaction of all substrates in acetonitrile, and found that the yields of *N*-imidoylbenzotriazoles for most cases were lower than that in toluene. However, for the cyclohexanone oxime **1j** and **1l**, the yields were increased to 53% from 37%, 73% from 17%, respectively(Table 1).

Compounds **2a**–**l** were determined as single *E*-isomers not only based on the NMR spectrum comparisons of our compounds to that of reported one,[9] but also the single crystal structure of X-ray diffraction of compound **2f**, the ORTEP plots with atom numbering scheme was shown in Figure 2. Compound **2m** was assigned as a 3:1 *E*/*Z* isomers based on the NMR spectrum comparison of our compound to that of reported one.[9]

Table 1
The one-pot synthesis of *N*-imidoylbenzotriazoles[a]



Entry	R^1	R^2	Yield(%) CH_3CN/Tol.	Yield[e] (%) Toluene
1(**2a**)	Ph	Me	76/95	60
1(**2a**)[b]	Ph	Me	46	—
1(**2a**)[c]	Ph	Me	Nd.	—
2(**2b**)	Ph	Ph	79/**82**	70
3(**2c**)	*p*-MeC_6H_4	Me	81/**97**	—
4(**2d**)	*p*-$MeOC_6H_4$	Me	67/**91**	—
5(**2e**)[d]	*o*-$MeOC_6H_4$	Me	81/**92**	—
6(**2f**)[d]	*m*-$MeOC_6H_4$	Me	82/**95**	—
7(**2g**)	Ph	Et	81/**90**	—
8(**2h**)[d]	*p*-ClC_6H_4	Me	85/**94**	—
9(**2i**)	Me	Me	31/**40**	20
10(**2j**)	$(CH_2)_5$		**53**/37	37
11(**2k**)	Bn	Bn	25/**47**	20
12(**2l**)	^{t}Bu	Me	**73**/17	60
13(**2m**)	^{i}Pr	^{i}Pr	46/**77**	35

[a] Reaction condition: (i) ketoxime (1.0 equiv), Et_3N (2.2 equiv), MsCl (1.1 equiv), Toluene/CH_3CN, ice bath, 30 min; (ii) benzotriazole (1.5 equiv), reflux, 2 h.
[b] THF was used instead of CH_3CN or toluene.
[c] Dioxane was used instead of CH_3CN or toluene, and no desired product was found.
[d] New compounds.
[e] Yields from Katritzky's result using toluene as solvent in Ref. 9.

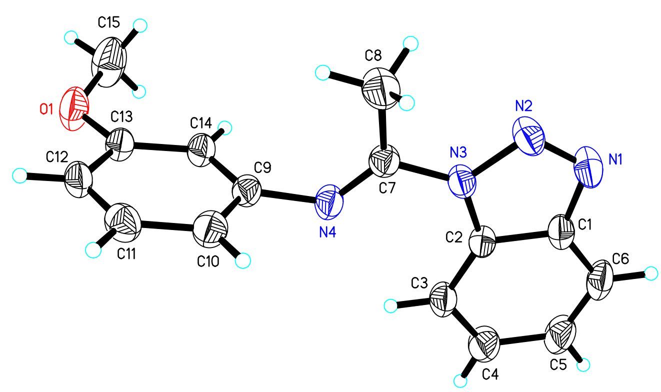


Figure 2. ORTEP view and atom numbering scheme for *N*-Imidoylbenzotriazole **2f**, and the thermal ellipsolids of the non-hydrogen atoms are drawn at the 50% probability level.

3. Conclusion

In conclusion, a new one-pot method for the synthesis of *N*-imidoylbenzotriazoles has been presented. This newly developed procedure would definitely provide an attractive way to make such compounds considering the excellent yields, simple operation, mild reaction condition, and easily available reagents.

4. Experimental

4.1. General methods

All solvents were distilled under standard procedures prior to use under nitrogen atmosphere. (For example: CH_3CN distilled from CaH_2; THF, dioxane, toluene distilled from Sodium). ^1H (400 MHz) and ^{13}C (100 MHz) NMR chemical shifts were reported in $CDCl_3$ 7.27 ppm for ^1H, 77 ppm for ^{13}C as standards and coupling constants (*J*) are reported in hertz (Hz). The following abbreviations are used to designate signal multiplicity: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad.

4.2. General procedure

To a solution of corresponding ketoxime (2 mmol) and triethylamine (0.62 mL, 4.4 mmol) in 4 mL of anhydrous toluene or acetonitrile under a nitrogen atmosphere was added MsCl (2.2 mmol) in an ice bath. After stirring for 30 min, benzotriazole (3 mmol) was then added and the resulting mixture was refluxed for 2 h. After completion of the reaction as monitored by TLC, the reaction was quenched with saturated aqueous sodium carbonate. The organic layer was extracted with ethyl acetate, dried over anhydrous sodium sulfate, and concentrated on rotary vacuum evaporator. The resulting crude product was purified by column chromatography on silica gel to give the corresponding *N*-aryl imidoylbenzotriazole in high yield with petroleum ether and ethyl acetate used as eluent. Other than, petroleum ether and ethyl acetate with triethylamine were chosen as eluent for *N*-alkyl substituted imidoylbenzotriazoles.

All products gave satisfactory analytical data, which were listed as follows.

*4.2.1. (E)-N-(1-(1H-Benzo[d][1,2,3]triazol-1-yl)ethylidene)aniline (**2a**).* Light yellow solid (EtOAc-*n*-hexane); mp 109–110 °C, (lit.[4] mp 106–108 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J=8.3 Hz, 1H), 8.13 (d, J=8.3 Hz, 1H), 7.59 (t, J=7.7 Hz, 1H), 7.48 (t, J=7.7 Hz, 1H), 7.42 (t, J=7.8 Hz, 2H), 7.19 (t, J=7.4 Hz, 1H), 6.95 (d, J=7.4 Hz, 2H), 2.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 147.4, 146.6, 131.3, 129.3, 129.2, 125.4, 124.4, 120.3, 119.7, 115.7, 16.3.

*4.2.2. (E)-N-((1H-Benzo[d][1,2,3]triazol-1-yl)(phenyl)methylene) aniline (**2b**).* Yellow needles (EtOAc-*n*-hexane); mp 131–132 °C, (lit.[4] mp 129–131 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J=8.4 Hz, 1H), 8.17 (d, J=8.3 Hz, 1H), 7.65 (t, J=7.7 Hz, 1H), 7.52 (t, J=7.7 Hz, 1H), 7.45–7.35 (m, 5H), 7.23 (t, J=7.8 Hz, 2H), 7.04 (t, J=7.4 Hz, 1H), 6.88 (dd, J=8.4, 1.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 147.1, 146.5, 132.1, 130.4(4), 130.3(8), 130.2(8), 129.4, 129.0, 128.3, 125.7, 124.3, 121.6, 120.1, 115.5.

*4.2.3. (E)-N-(1-(1H-Benzo[d][1,2,3]triazol-1-yl)ethylidene)-4-methylaniline (**2c**).* Light yellow solid (EtOAc-*n*-hexane); mp 117–118 °C, (lit.[4] mp 113–115 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J=8.2 Hz, 1H), 8.05 (d, J=8.2 Hz, 1H), 7.49 (t, J=7.5 Hz, 1H), 7.38 (t, J=7.5 Hz, 1H), 7.17 (d, J=7.8 Hz, 2H), 6.84 (d, J=7.9 Hz, 2H), 2.70 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 146.6, 144.8, 133.8, 131.3, 129.8, 129.1, 125.3, 120.4, 119.7, 115.8, 21.0, 16.2.

*4.2.4. (E)-N-(1-(1H-Benzo[d][1,2,3]triazol-1-yl)ethylidene)-4-methoxyaniline (**2d**).* Light yellow solid (EtOAc-*n*-hexane); mp 135–136 °C, (lit.[2] mp 128–129 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J=8.3 Hz, 1H), 8.13 (d, J=8.3 Hz, 1H), 7.60 (t, J=7.5 Hz, 1H), 7.48 (t, J=7.5 Hz, 1H), 6.99–6.90 (m, 4H), 3.85 (s, 3H), 2.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 154.0, 146.6, 140.5, 131.3, 129.1, 125.3, 121.7, 119.7, 115.8, 114.5, 55.5, 16.2.

*4.2.5. (E)-N-(1-(1H-Benzo[d][1,2,3]triazol-1-yl)ethylidene)-2-methoxyaniline (**2e**).* Colorless needles (EtOAc-*n*-hexane); mp 131–132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J=8.3 Hz, 1H), 8.12 (d, J=8.3 Hz, 1H), 7.59 (t, J=7.5 Hz, 1H), 7.47 (t, J=7.7 Hz, 1H), 7.17 (td, J=8.0, 1.6 Hz, 1H), 7.06–6.97 (m, 2H), 6.94 (dd, J=7.6, 1.5 Hz, 1H), 3.83 (s, 3H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 149.3, 146.7, 136.4, 131.5, 129.2, 125.3, 121.6, 121.1, 119.7, 116.0, 111.8, 55.7, 16.8; HRMS (EI) calcd for $C_{15}H_{14}N_4O$ [M^+] 266.1168, found 266.1166; IR(KBr), cm^{-1}: 3070, 2961, 2934, 2832, 1684, 1490, 1443, 1396, 1248, 1085, 1031, 972.

*4.2.6. (E)-N-(1-(1H-Benzo[d][1,2,3]triazol-1-yl)ethylidene)-3-methoxyaniline (**2f**).* Colorless crystals (EtOAc-*n*-hexane); mp 84–85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J=8.3 Hz, 1H), 8.13 (d, J=8.3 Hz, 1H), 7.60 (t, J=7.7 Hz, 1H), 7.49 (t, J=7.7 Hz, 1H), 7.33 (t, J=8.0 Hz, 1H), 6.75 (dd, J=8.3, 1.8 Hz, 1H), 6.56–6.44 (m, 2H), 3.85 (s, 3H), 2.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 154.2, 148.8, 146.7, 131.3, 130.1, 129.2, 125.4, 119.7, 115.7, 112.5, 109.8, 106.2, 55.3, 16.3; HRMS (EI) calcd for $C_{15}H_{14}N_4O$ [M^+] 266.1168, found 266.1164; IR(KBr), cm^{-1}: 3096, 3073, 3017, 1674, 1485, 1449, 1390, 1283, 1083, 968. Crystals of **2f** were triclinic, space group *P*-1; empirical formula $C_{15}H_{14}N_4O$, formula weight, 266.30; a=9.5140 (11) Å, b=12.7073(15) Å, c=13.2828(15) Å, α=62.272(2)°, β=86.659 (2)°, γ=74.863(2)°, V=1368.4(3) Å^3; T=293(2) K; λ=0.71073 Å; Z=4, D_{calc}=1.293 g cm^{-3}; F(000)=560, μ=0.085 mm^{-1}; crystal size=0.420×0.381×0.207 mm; reflections collected, 7267; unique reflections (R_{int}=0.0709), 5029; $wR2$=0.1437(all data), $R1$=0.0527 ($I>2\sigma(I)$); Data in the θ range 1.87–25.50° were collected at 293(2) K on a Bruker Apex CCD diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares using all F^2 data. The hydrogen atoms were placed in calculated positions and allowed to ride on the parent atom.

*4.2.7. (E)-N-(1-(1H-Benzo[d][1,2,3]triazol-1-yl)propylidene) aniline (**2g**).* White solid (EtOAc-*n*-hexane); mp 101–102 °C, (lit.[1a] mp 99 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J=8.3 Hz, 1H), 8.11 (d, J=8.3 Hz, 1H), 7.55 (t, J=7.6 Hz, 1H), 7.48–7.36 (m, 3H), 7.16 (t, J=7.4 Hz, 1H), 6.94 (d, J=7.6 Hz, 2H), 3.14 (q, J=7.5 Hz, 2H), 1.35 (t, J=7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 147.4, 146.6, 131.5, 129.3(2), 129.2(7), 125.4, 124.2, 119.9, 119.7, 115.8, 23.0, 12.9.

*4.2.8. (E)-N-(1-(1H-Benzo[d][1,2,3]triazol-1-yl)ethylidene)-4-chloroaniline (**2h**).* Colorless needles (EtOAc-*n*-hexane); mp 148–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J=8.2 Hz, 1H), 8.10 (d, J=8.2 Hz, 1H), 7.57 (t, J=7.6 Hz, 1H), 7.46 (t, J=7.6 Hz, 1H), 7.37 (d, J=8.3 Hz, 2H), 6.89 (d, J=8.5 Hz, 2H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 146.6, 145.9, 131.2, 129.8, 129.4, 129.3, 125.5, 121.8, 119.8, 115.6, 16.4; HRMS (EI) calcd for $C_{14}H_{11}{}^{35}ClN_4$ [M^+] 270.0672, found 270.0671; IR(KBr), cm^{-1}: 3112, 3067, 2832, 1682, 1595, 1485, 1390, 1207, 1075, 1038, 977.

*4.2.9. (E)-N-(1-(1H-Benzo[d][1,2,3]triazol-1-yl)ethylidene) methanamine (**2i**).* Yellow needles (EtOAc-*n*-hexane); mp 64–65 °C, (lit.[9] mp 52.0–53.0 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J=8.3 Hz, 1H), 8.10 (d, J=8.2 Hz, 1H), 7.53 (t, J=7.6 Hz, 1H), 7.42 (t, J=7.5 Hz, 1H), 3.38 (s, 3H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 146.2, 131.0, 128.4, 124.7, 119.1, 115.4, 37.0, 13.5.

*4.2.10. 1-(3,4,5,6-Tetrahydro-2H-azepin-7-yl)-1H-benzo[d][1,2,3] triazole (**2j**).* Colorless needles (EtOAc-*n*-hexane); mp 110–111 °C, (lit.[9] mp 101.0 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J=8.3 Hz, 1H), 8.08 (d, J=8.2 Hz, 1H), 7.55 (t, J=7.6 Hz, 1H), 7.42 (t, J=7.6 Hz, 1H), 3.91–3.88 (m, 2H), 3.53–3.50 (m, 2H), 1.99–1.90 (m, 2H), 1.81–1.71 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 146.8, 131.3, 128.7, 125.0, 119.5, 115.8, 50.5, 31.1, 29.5, 26.5, 23.3.

*4.2.11. (E)-N-(1-(1H-Benzo[d][1,2,3]triazol-1-yl)-2-phenylethylidene)-1-phenylmethanamine (**2k**)*[9]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J=8.2 Hz, 1H), 8.02 (d, J=8.2 Hz, 1H), 7.47 (t, J=7.5 Hz, 1H), 7.42–7.32 (m, 5H), 7.30–7.13 (m, 6H), 4.91 (s, 2H), 4.72 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 146.9, 139.6, 134.8, 131.7, 129.2, 129.1, 128.8, 128.7, 127.8, 127.2(2), 127.1(5), 125.4, 119.8, 115.9, 54.1, 34.1.

*4.2.12. (E)-N-(1-(1H-Benzo[d][1,2,3]triazol-1-yl)ethylidene)-2 methylpropan-2-amine (**2l**)*[9]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J=8.4 Hz, 1H), 8.06 (d, J=8.3 Hz, 1H), 7.53 (t, J=7.5 Hz, 1H), 7.41 (t, J=7.4 Hz, 1H), 2.86 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 146.5, 131.3, 128.3, 124.6, 119.3, 116.0, 54.5, 30.5, 18.1.

*4.2.13. N-[(E,Z)-1-(1H-Benzo[d][1,2,3]triazol-1-yl)-2-methylpropylidene]propan-2-amine(**2m**)*[9]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J=8.3 Hz, 1H), 8.13 (d, J=8.6 Hz, 1H), 8.07 (d, J=8.3 Hz, 1H), 7.57–7.49 (m, 2H), 7.46–7.37 (m, 3H), 4.19–4.09 (m, 1H), 3.87–3.76

(m, 1H), 3.26–3.02 (m, 2H), 1.53 (d, J=7.1 Hz, 6H), 1.34 (d, J=6.2 Hz, 6H), 1.17 (d, J=6.8 Hz, 6H), 1.11 (d, J=6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 151.7, 145.6, 144.6, 132.6, 132.1, 128.4, 128.3, 124.6, 124.2, 120.0, 119.2, 115.6, 109.5, 51.2, 49.6, 36.8, 29.0, 24.4, 23.7, 19.7, 19.4.

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Supplementary data

Supplementary data for this article can be found in the online version, at doi:10.1016/j.tet.2010.06.001. The ^{1}H NMR and ^{13}C NMR copies of all compounds were attached as supplementary material. These data include MOL files and InChIKeys of the most important compounds described in this article.

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