Tetrahedron Letters 50 (2009) 5322–5325

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Tetrahedron Letters

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An expedient synthesis of 2,4,5-trisubstituted 1,4-pentadienes from Baylis–Hillman adducts via the Pd-catalyzed decarboxylation–elimination protocol

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ARTICLE INFO

Article history:
Received 8 June 2009
Revised 29 June 2009
Accepted 30 June 2009
Available online 16 July 2009

Dedicated to the memory of the late Professor Eung Kul Ryu whose vision and passion in Organic and Medicinal Chemistry was an inspiration for all

Keywords:
Baylis–Hillman adducts
1,4-Pentadienes
Palladium
Decarboxylation–elimination.

ABSTRACT

We disclosed an efficient synthetic method of 2,4,5-trisubstituted 1,4-pentadienes from Baylis–Hillman adducts via the Pd-catalyzed decarboxylation–elimination protocol as the key step.

Recently Baylis–Hillman adducts have been used for the synthesis of many heterocyclic compounds and acyclic compounds.[1–3] Among them functionalized 1,4-pentadiene is one of the meaningful target structures due to the synthetic usefulness of this compound in organic synthesis.[2–4] Basavaiah and co-workers reported an elegant method for these compounds involving the combination of two polar intermediates.[2] As shown in Scheme 1, nucleophilic part is a zwitterion which is generated in situ from DABCO and acrylonitrile, and the electrophilic component is a DABCO salt of Baylis–Hillman bromide. The nucleophile attacked the electrophile in a S_N2' manner to produce 2,3,4-trisubstituted 1,4-pentadiene.[2]

During our recent studies on Pd-catalyzed decarboxylative protonation and allylations,[5] we reasoned out that 2,4,5-trisubstituted 1,4-pentadiene **5a** could be synthesized by using Pd-catalyzed decarboxylation–elimination strategy from modified Baylis–Hillman adduct such as **4a**, as shown in Scheme 2. Palladium-catalyzed decarboxylation–elimination was originally studied by Tsuji and has been used extensively in organic synthesis.[6] In order to check the feasibility of our rationale we prepared starting material **4a** by the reaction of Baylis–Hillman bromide **1a** and allyl acetoacetate (**2a**) to prepare **3a** and subsequent methylation with iodomethane to **4a**.[7]

With this compound **4a** we examined the reaction conditions as shown in Table 1 under the influence of $Pd(OAc)_2$ and PPh_3.[5,6] As shown in Table 1, the ratio of $Pd(OAc)_2/PPh_3$ was very important.[5d,6] High loading of PPh_3 [$PPh_3/Pd(OAc)_2 = 2.0$] increased the amounts of decarboxylative allylation product (**7a**, 63%) as in entry 1,[7] while low loading of PPh_3 [$PPh_3/Pd(OAc)_2 = 1.0–0.5$] produced decarboxylation–elimination product **5a** (78–83%) as the major product as in entries 2 and 3.[5d,6,7] The use of 5 mol % $Pd(OAc)_2$ showed a similar but slightly lower yield of **5a** (entry 4). As reported by Tsuji,[6] the use of non-polar solvent such as toluene lowered the yield of **5a** (65%), instead the yield of allylation product **7a** was increased to 20% (entry 5). The use of DMF did not show better results (entry 6). The use of $Pd(PPh_3)_4$ produced **7a** as the major product (60%) presumably due to high ratio of $PPh_3/Pd(OAc)_2$, and compound **5a** was not formed at all (entry 7). In all entries, decarboxylative protonation product **6a** was produced in variable amounts as a side product (4–25%).

The plausible mechanism is depicted in Scheme 3 with **4a** as an example involving the sequential oxidative addition of *O*-allyl bond to Pd(0) to produce π-allylpalladium intermediate (**I**), decarboxylation to form a C-bound π-allylpalladium intermediate (**II**), and β-elimination to liberate **5a** and Pd(0). There can be present

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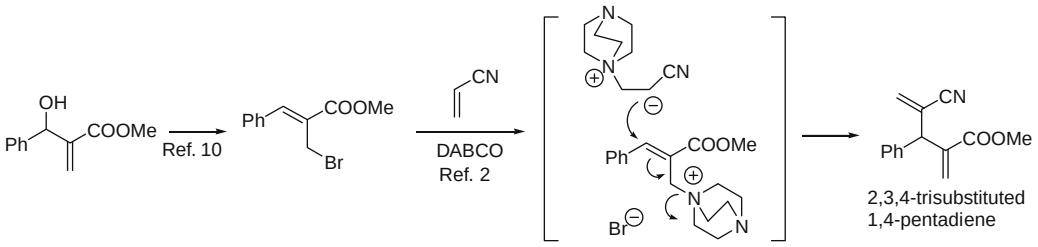
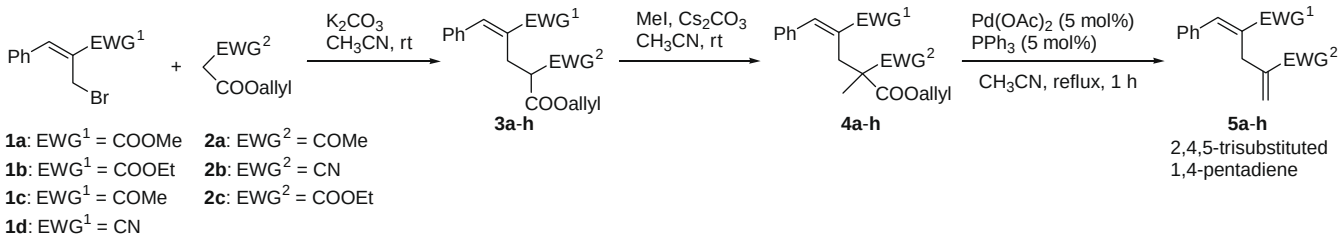
doi:10.1016/j.tetlet.2009.06.142



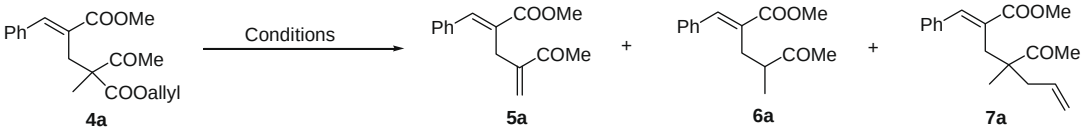
Scheme 1.



1a: EWG^1 = COOMe **2a**: EWG^2 = COMe
1b: EWG^1 = COOEt **2b**: EWG^2 = CN
1c: EWG^1 = COMe **2c**: EWG^2 = COOEt
1d: EWG^1 = CN

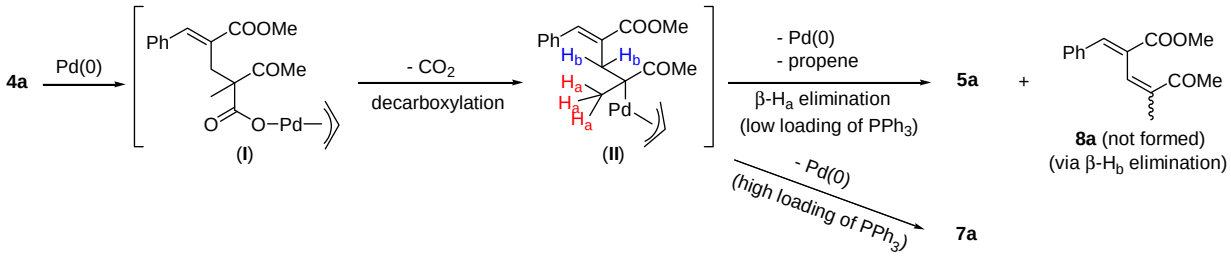
Scheme 2.

Table 1
Optimized conditions for the synthesis of **5a** from **4a**



Entry	Conditions	Products (%)
1	$Pd(OAc)_2$ (10 mol %), PPh_3 (20 mol %), CH_3CN, reflux, 1 h	**5a** (0), **6a** (23), **7a** (63)
2[a]	$Pd(OAc)_2$ (10 mol %), PPh_3 (10 mol %), CH_3CN, reflux, 1 h	**5a** (83), **6a** (8), **7a** (0)
3	$Pd(OAc)_2$ (10 mol %), PPh_3 (5 mol %), CH_3CN, reflux, 1 h	**5a** (78), **6a** (5), **7a** (0)
4[a]	$Pd(OAc)_2$ (5 mol %), PPh_3 (5 mol %), CH_3CN, reflux, 1 h	**5a** (79), **6a** (4), **7a** (0)
5	$Pd(OAc)_2$ (10 mol %), PPh_3 (10 mol %), toluene, 80–90 °C, 1 h	**5a** (65), **6a** (5), **7a** (20)
6	$Pd(OAc)_2$ (10 mol %), PPh_3 (10 mol %), DMF, 80–90 °C, 1 h	**5a** (79), **6a** (5), **7a** (0)
7	$Pd(PPh_3)_4$ (10 mol %), CH_3CN, reflux, 1 h	**5a** (0), **6a** (25), **7a** (60

[a] Selected conditions for the entries in Table 2.

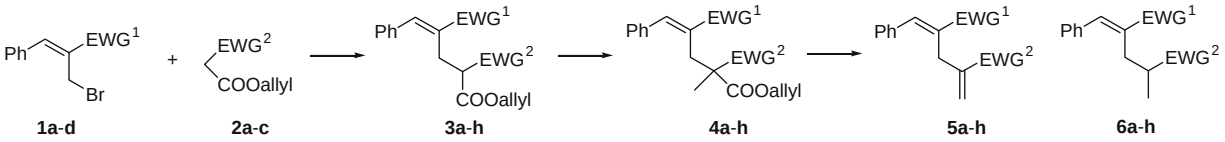


Scheme 3.

a competition between β-H elimination to alkene **5a** and reductive elimination of Pd(0) to allylated compound **7a** in the intermediate (**II**) stage. The competition could be controlled by changing the ratio of $Pd(OAc)_2/PPh_3$ as shown in Table 1 (entries 1–3). Low loading of PPh_3 increased the amounts of β-H elimination product **5a**. The regioselectivity between H_a and H_b during the β-H elimination of intermediate (**II**) was controlled completely and we obtained **5a** which was formed via the β-H_a elimination. We did not observe the formation of other alkene product **8a** at all in the reaction mixture.[6a,b,8] The selective β-H_a elimination may be attributed to the small steric hindrance during the elimination process of H_a.

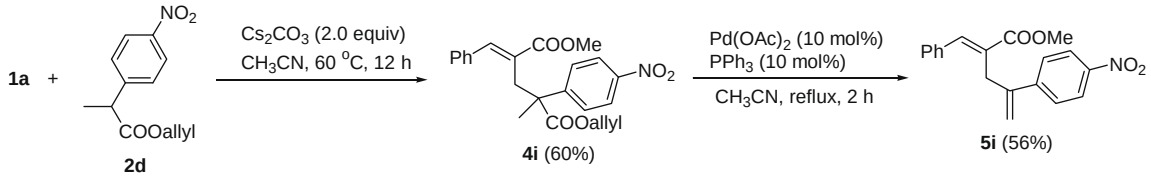
Encouraged by the successful results, we prepared starting materials **3b–h** by the reaction of Baylis–Hillman bromides **1a–d** and allyl esters **2a–c** (K_2CO_3, CH_3CN, rt) as summarized in Table 2.[5a] When the Baylis–Hillman bromide and allyl ester have nitrile functionality (entries 2, 7, and 8), the yield of compound **3** (**3b**, **3g**, and **3h**) was low because of the formation of dialkylation side product. Subsequent methylation of **3b–h** was carried out with iodomethane (Cs_2CO_3, CH_3CN, rt–60 °C) to make **4b–h** (74–92%). The next decarboxylation–elimination reactions of **4b–h** were carried out under the optimized conditions (entries 2 and 4 in Table 1), and the results are summarized in Table 2.

Table 2
Synthesis of 2,4,5-trisubstituted 1,4-pentadienes **5**



Entry	**1** + **2** (EWG^1/EWG^2)	**3** (%)[a]	Conditions[b]	**4** (%)	Conditions[c]	**5** (%), **6** (%)
1	**1a** + **2a** (COOMe/COMe)	**3a** (79)	rt, 6 h	**4a** (86)	A, 1 h	**5a** (83), **6a** (8)
2	**1a** + **2b** (COOMe/CN)	**3b** (68)[d]	rt, 12 h	**4b** (88)	B, 1 h	**5b** (68), **6b** (13)
3	**1a** + **2c** (COOMe/COOEt)	**3c** (97	60 °C, 12 h	**4c** (91)	DMF, 2 h[e]	**5c** + **6c** (55, 3:2)[f]
4	**1b** + **2a** (COOEt/COMe)	**3d** (81)	rt, 6 h	**4d** (91)	A, 1 h	**5d** (72), **6d** (–)
5	**1c** + **2a** (COMe/COMe)	**3e** (75)	rt, 48 h	**4e** (74)	A, 1 h	**5e** (72), **6e** (10)
6	**1c** + **2b** (COMe/CN)	**3f** (65)	rt, 12 h	**4f** (92)	A, 1 h	**5f** (54), **6f** (17)
7	**1d** + **2a** (CN/COMe)	**3g** (55)[g,i]	rt, 12 h	**4g** (85)[i]	A, 1 h	**5g** (73),[i] **6g** (–)
8	**1d** + **2b** (CN/CN)	**3h** (26)[h,i]	rt, 12 h	**4h** (75)[i]	B, 1 h	**5h** (62),[i] **6h** (15)[i]

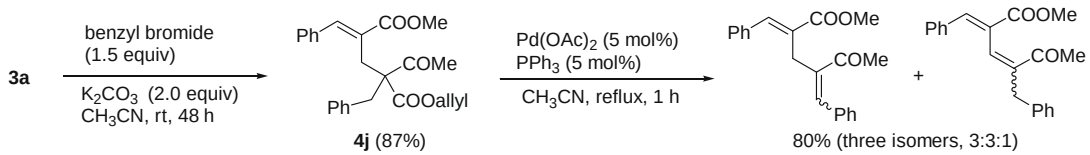
[a] Conditions: **1** (1.5 mmol), **2** (1.2 equiv), K_2CO_3 (2.0 equiv), CH_3CN, rt, 12 h.
[b] Conditions: MeI (5.0 equiv), Cs_2CO_3 (2.0 equiv), CH_3CN.
[c] Conditions A (entry 2 in Table 1), conditions B (entry 4 in Table 1).
[d] Bis adduct (**1a**:**2b** = 2:1) was isolated in 18% even with 2.5 equiv of **2b**.
[e] Run at 140–150 °C.
[f] Mixed together and the ratio of **5c**/**6c** was calculated from ^{1}H NMR.
[g] Bis adduct (**1d**:**2a** = 2:1) was isolated in 16% even with 10 equiv of **2a**.
[h] Bis adduct (**1d**:**2b** = 2:1) was isolated in 69% even with 10 equiv of **2b**.
[i] The geometry of benzylidene part is *Z* when EWG1 is nitrile.



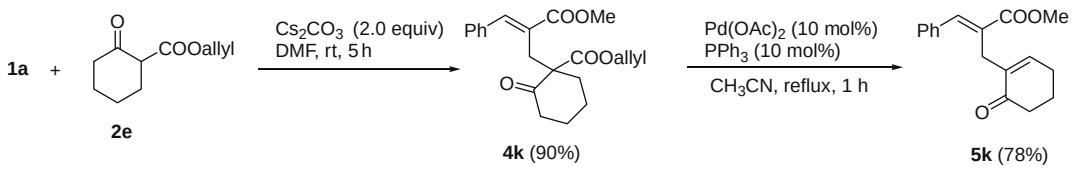
Scheme 4.

As in Table 2, all entries produced the corresponding 1,4-pentadienes **5b**–**h** in moderate to good yields (33–73%) and decarboxylative protonation products were generated together in low yields (10–22%) as side products. The yields of products were good when EWG^2 is acetyl (**5d**, **5e**, and **5g**) while low to moderate when EWG^2 is ester or nitrile (**5b**, **5c**, **5f**, and **5h**). It is interesting to note that ester derivative **4c** did not produce **5c** in CH_3CN or in toluene even at refluxing temperature for a long time. When we used DMF as a solvent at high temperature (140–150 °C) we could obtain **5c** fortunately, although in low yield as a mixture with **6c** (entry 3 in Table 2).

As another entry, we examined the reaction of **4i** having *p*-nitrophenyl group.[5b,9] Synthesis of **4i** was performed by the reaction of **1a** and allyl arylacetate **2d** according to our recent Letter.[5b] The reaction of **4i** produced decarboxylation–elimination product **5i** in moderate yield (56%) as shown in Scheme 4. In order to synthesize more complex 1,4-diene, we prepared compound **4j** by benzylation of **3a**. Under the same conditions (entry 4 in Table 1) three types of compounds (3:3:1) were isolated as a mixture in 80%, which states that stereo- and regiochemistry could not be controlled in this case (Scheme 5).[6a,b,8] The reaction of cyclohexanone derivative **4k**, prepared from **1a** and allyl 2-oxocyclohexane-



Scheme 5.



Scheme 6.

carboxylate (**2e**), showed decarboxylation–elimination product **5k** in good yield (78%) regioselectively, as shown in Scheme 6.

In summary, we disclosed an efficient method for the synthesis of various 2,4,5-trisubstituted 1,4-pentadienes by using the Pd-catalyzed decarboxylation–elimination protocol as the key step under the conditions of low loading of PPh_3.

Acknowledgements

This study was financially supported by Special Research Program of Chonnam National University, 2009. Spectroscopic data were obtained from the Korea Basic Science Institute, Gwangju branch.

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7. Typical procedure for the synthesis of **3a**, **4a**, and **5a**. Compound **1a** was prepared from Baylis–Hillman adduct by treatment with HBr as reported.[10] A stirred mixture of **1a** (383 mg, 1.5 mmol), **2a** (256 mg, 1.8 mmol), and K_2CO_3 (415 mg, 3.0 mmol) in CH_3CN (2 mL) was stirred at room temperature for 12 h. After the usual aqueous workup and column chromatographic purification process (hexanes/ether, 10:1) compound **3a** was isolated as colorless oil, 375 mg (79%).[5a] A mixture of **3a** (316 mg, 1.0 mmol), MeI (705 mg, 5.0 mmol), and Cs_2CO_3 (650 mg, 2.0 mmol) in CH_3CN (2 mL) was stirred at room temperature for 6 h. After the usual aqueous workup and column chromatographic purification process (hexanes/ether, 10:1) compound **4a** was isolated as colorless oil, 284 mg (86%). A mixture of compound **4a** (165 mg, 0.5 mmol), $Pd(OAc)_2$ (11 mg, 10 mol %), and PPh_3 (13 mg, 10 mol %) in CH_3CN (1 mL) was heated to reflux for 1 h under nitrogen atmosphere. After filtering through a Celite pad, removal of solvent, and the residue was purified by column chromatographic purification process (hexanes/CH_2Cl_2, 1:9) to afford compound **5a** (101 mg, 83%) and **6a** (9 mg, 8%). Selected spectroscopic data of compounds **4a**, **5a**, **5b**, **5g**, **5i**, **6a**, and **7a** are as follows.
Compound **4a**: 86%; colorless oil; IR (film) 2950, 1741, 1714 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.11 (s, 3H), 2.07 (s, 3H), 3.31 (d, J = 14.4 Hz, 1H), 3.37 (d, J = 14.4 Hz, 1H), 3.76 (s, 3H), 4.34–4.42 (m, 1H), 4.52–4.59 (m, 1H), 5.20–5.31 (m, 2H), 5.77–5.90 (m, 1H), 7.26–7.41 (m, 5H), 7.82 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.14, 25.95, 29.71, 51.95, 59.26, 65.96, 118.89, 128.37, 128.59, 128.78, 128.97, 131.35, 135.36, 142.60, 168.48, 172.23, 204.12; ESIMS m/z 331 (M^++1).
Compound **5a**: 83%; colorless oil; IR (film) 2951, 1714, 1676 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.42 (s, 3H), 3.53 (t, J = 1.5 Hz, 2H), 3.79 (s, 3H), 5.70 (t, J = 1.8 Hz, 1H), 6.11 (t, J = 1.8 Hz, 1H), 7.25–7.38 (m, 5H), 7.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.92, 28.52, 52.11, 124.79, 128.56, 128.91, 129.03, 129.21, 134.93, 141.79, 146.32, 168.30, 199.01; ESIMS m/z 245 (M^++1). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.89; H, 6.75.
Compound **5b**: 68%; colorless oil; IR (film) 2952, 2223, 1714 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.49 (t, J = 1.5 Hz, 2H), 3.83 (s, 3H), 5,75 (t, J = 1.8 Hz, 1H), 5.97 (t, J = 1.5 Hz, 1H), 7.30–7.45 (m, 5H) 7.98 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.15, 52.34, 118.50, 120.66, 126.36, 128.80, 128.91, 129.36, 131.03, 134.38, 143.61, 167.39; ESIMS m/z 228 (M^++1). Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 74.11; H, 5.97; N, 6.03.
Compound **5g**: 73%; colorless oil; IR (film) 2209, 1678 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.39 (s, 3H), 3.36 (s, 2H), 6.08 (t, J = 1.2 Hz, 1H), 6.25 (s, 1H), 7.07 (s, 1H), 7.35–7.44 (m, 3H), 7.70–7.75 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.68, 36.86, 108.08, 118.39, 128.24, 128.68, 128.77, 130.19, 133.47, 144.06, 145.77, 198.24; ESIMS m/z 212 (M^++1). Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.84; H, 6.13; N, 6.47.
Compound **5i**: 56%; colorless oil; IR (film) 1713, 1516, 1345 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.69 (t, J = 1.2 Hz, 2H), 3.82 (s, 3H), 5.24 (t, J = 1.8 Hz, 1H), 5.56 (t, J = 1.5 Hz, 1H), 7.34–7.39 (m, 5H), 7.60 (dt, J = 9.0 and 2.7 Hz, 2H), 7.95 (s, 1H), 8.19 (dt, J = 9.0 and 2.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.96, 52.25, 115.93, 123.65, 126.79, 128.67, 128.97, 129.06, 129.15, 135.01, 141.83, 144.13, 147.19, 147.78, 168.24; ESIMS m/z 324 (M^++1). Anal. Calcd for $C_{19}H_{17}NO_4$: C, 70.58; H, 5.30; N, 4.33. Found: C, 70.46; H, 5.54; N, 4.30.
Compound **6a**: 8%; colorless oil; IR (film) 2951, 1710 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.99 (d, J = 6.9 Hz, 3H), 2.10 (s, 3H), 2.63–2.69 (m, 1H), 2.76–2.91 (m, 2H), 3.82 (s, 3H), 7.27–7.42 (m, 5H), 7.78 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.66, 28.10, 29.66, 46.10, 52.05, 128.46, 128.55, 129.03, 130.82, 135.39, 141.14, 168.52, 211.63; ESIMS m/z 247 (M^++1).
Compound **7a**: 63%; colorless oil; IR (film) 2977, 1712, 1707 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.92 (s, 3H), 1.88–1.96 (m, 1H), 2.02 (s, 3H), 2.33–2.40 (m, 1H), 2.93 (s, 2H), 3.76 (s, 3H), 4.90–4.96 (m, 2H), 5.39–5.52 (m, 1H), 7.26–7.41 (m, 5H), 7.76 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.09, 25.76, 33.86, 42.75, 51.82, 51.86, 118.14, 128.14, 128.50, 128.79, 130.21, 133.58, 135.74, 141.63, 168.90, 211.75; ESIMS m/z 287 (M^++1).
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