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Regioselective synthesis of polysubstituted benzenes from Baylis–Hillman adducts via [4+2] annulation protocol

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Abstract—A new and regioselective [4+2] benzannulation protocol toward polysubstituted benzenes was developed. A nitroalkane derivative, which was prepared from Baylis–Hillman adduct, served as the four-carbon unit and a Michael acceptor as a two-carbon unit. Vinyltriphenylphosphonium salt could also be used as a Michael acceptor efficiently.

1. Introduction

Polysubstituted aromatic compounds are highly useful entities, which are widely used in industry as well as in the laboratory. The synthesis of polysubstituted aromatic compounds in high yields in a regioselective manner is one of the challenging problems in organic synthesis.[1] Classical methods for the synthesis of polysubstituted aromatics are based on aromatic substitution, which introduces a substituent to the given arene. A variety of synthetic methodologies based on this route have been developed including the electrophilic or nucleophilic substitutions, catalyzed coupling reactions, and metalation–functionalization reactions. However, these methods suffer from a long multi-step reaction sequence, low yields of products, and production of regiochemical ambiguities originating from the activating or deactivating and orienting effects of the substituents.

Numerous approaches for the synthesis of aromatic compounds from acyclic precursors have received growing interest due to their short synthetic steps and the avoidance of regioisomeric problems. These general features are common in the most useful benzannulation reactions such as [3+2+1] Dötz reaction of Fisher carbene complexes,[2] Danheiser alkyne-cyclobutenone [4+2] cyclization,[3] [4+2] cycloaddition of metalacyclopentadienes and alkynes,[4] transition-metal-catalyzed [2+2+2] and [4+2] cycloadditions,[5] [4+2] Yamamoto benzannulation of *o*-alkynyl benzaldehyde and alkyne,[6] [3+3] cyclocondensation between bielectrophiles and binucleophiles,[7] and 1,6-electrocyclization reaction.[8] Recently, an efficient approach was developed for the synthesis of highly substituted phenols using a [5+1] benzannulation strategy by the reaction of α-alkenoyl ketene-(*S*,*S*)-acetals and nitroalkane.[9] Ballini and co-workers also reported an interesting synthetic approach for acetophenones and methyl benzoates via an anionic domino process from the reaction of primary 1,3-dinitroalkanes with 2-ene-1,4-dione or 2-ene-4-oxo ester derivatives.[10]

2. Results and discussion

The Baylis–Hillman reaction and chemical transformations of the Baylis–Hillman adducts have been investigated deeply by us and other groups.[11,12] Recently, we have reported an efficient regioselective construction method of polysubstituted pyridine ring starting from Baylis–Hillman adducts via sequential introduction of tosylamide, Michael reaction, aldol condensation, and elimination of TsH (Scheme 1).[12a] As an extension, we envisioned that we could prepare highly substituted benzene ring in a regiocontrolled manner if we used nitroalkane derivative **2** (Scheme 2) instead of the tosylamide derivative in Scheme 1. Appropriate Michael acceptor can serve as the remaining two-carbon unit for the purpose as depicted in Scheme 2.[13]

The synthesis of starting material **2** (four-carbon unit) was carried out by the addition–elimination protocol from the acetate of the Baylis–Hillman adduct of methyl (or ethyl) vinyl ketone **1** and primary nitroalkane in the presence of K_2CO_3.[14–16] The benzylidene moiety, which will be

Keywords: Polysubstituted benzenes; Baylis–Hillman adducts; Michael acceptor; Schweizer reagent.
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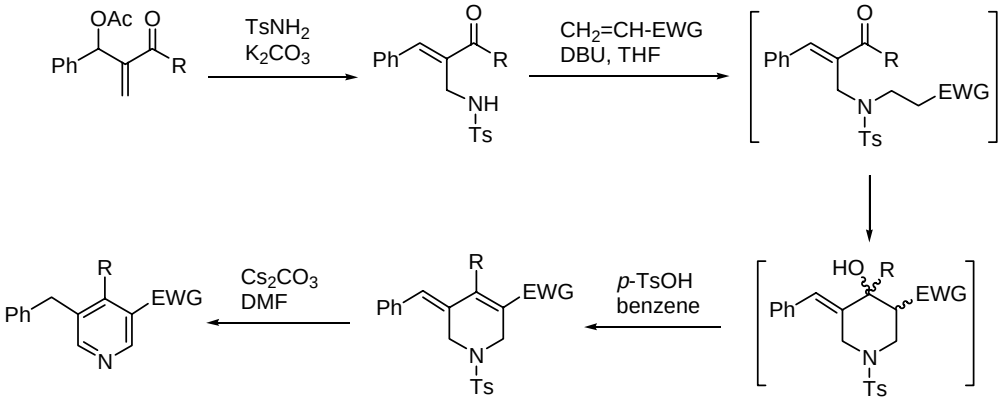
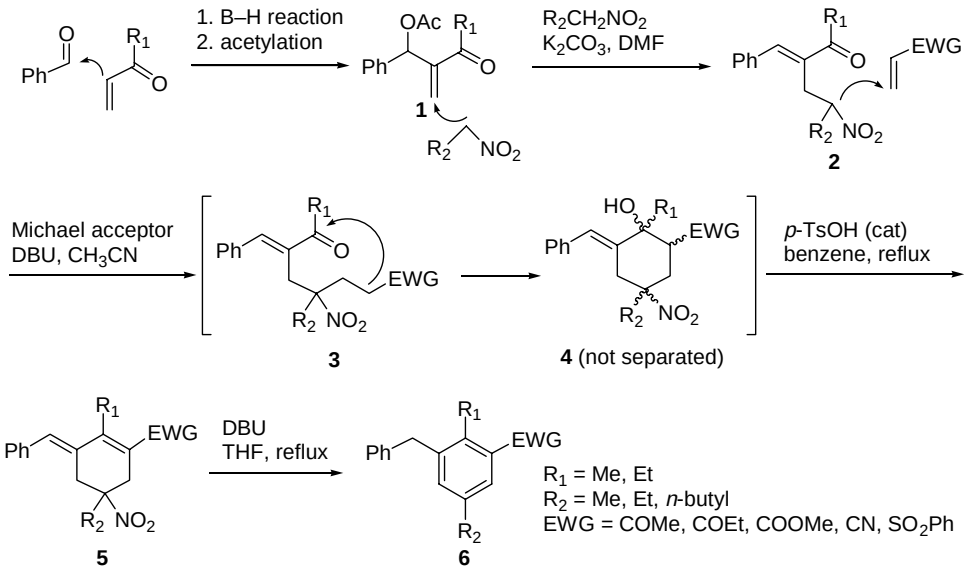


Scheme 1.



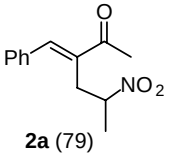
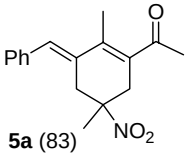
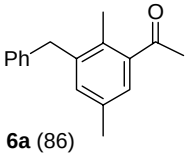
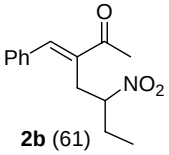
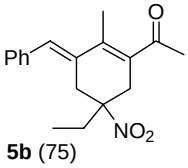
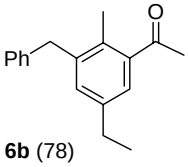
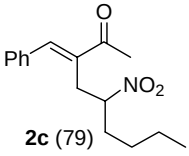
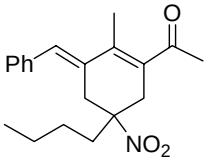
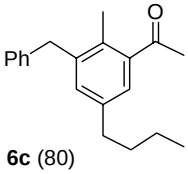
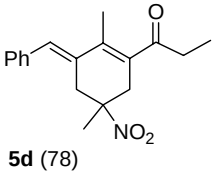
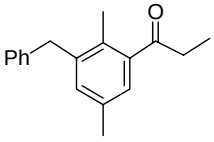
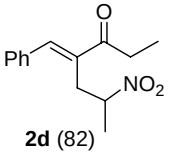
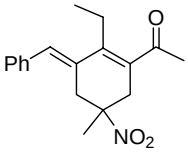
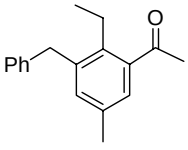
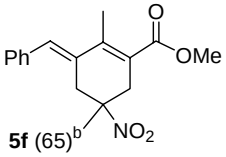
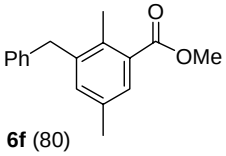
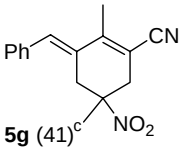
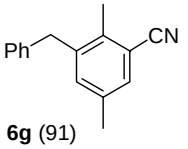
Scheme 2.

isomerized at the final stage to benzyl group, is essential for the construction of benzene ring at the final aromatization stage (vide infra). The next step was the construction of six-membered ring intermediate **4** via the consecutive Michael addition of **2** to the Michael acceptor and aldol-type cyclization, which occurred with the aid of DBU in CH_3CN in good yield. The intermediate **4** was not separated due to the complex nature of **4** by the formation of diasteroisomeric mixtures. Thus, we subjected the crude mixtures, after usual workup, in the dehydration conditions (*p*-TsOH, benzene, reflux) and obtained the dehydration product **5** in good overall yield. The final step was the elimination of HNO_2 and isomerization of the *exo*-double bond to the desired benzene ring. We expected that elimination of HNO_2 can occur with DBU and the isomerization will also occur simultaneously due to the favorable aromatization effect. As expected, the final step occurred in good yield with DBU in THF under refluxing conditions to our delight.

As shown in Table 1, variation of the substituents of the Baylis–Hillman adducts or of nitroalkanes did not alter the reactivity (entries 1–3 and 5). However, the reactivity was affected by the nature of the Michael acceptor. The reaction rates of the Michael addition of **2** to methyl vinyl ketone, ethyl vinyl ketone, phenyl vinyl sulfone, methyl acrylate, and acrylonitrile were similar (TLC monitoring). But, the reactivities of the next aldol cyclization reaction were found to be different depending on the nature of the electron-withdrawing group of the Michael acceptors presumably due to the different acidities of the α-protons nearby the EWG groups of the Michael acceptors. Fortunately, the following dehydration, elimination, and aromatization reactions from **4** to the final product **6** were all straightforward in these cases also (entries 4, 6, and 7). The use of acrylonitrile (entry 7) as the Michael acceptor required a long reaction time for the cyclization and gave low yield of **5g** (41%). Actually, we could isolate the Michael addition product **3g** in 41% after the whole reaction. This type of Michael addition product was also found in the cases of methyl acrylate (entry 6) and phenyl vinyl sulfone (Scheme 3). Especially, when we used phenyl vinyl sulfone as the Michael acceptor we found the formation of *exo*-methylene compound **5h′**, which showed the same reactivity to give **6h**.

For the next trial, we examined the reaction of **2** and vinyltriphenylphosphonium bromide, which was known as Schweizer reagent,[17] as the other effective Michael acceptor (two-carbon unit). Our synthetic rationale is shown in

Table 1. Synthesis of regioselectively substituted benzenes

Entry	Substrate (%)	Conditions	Cyclohexene (%)	Product (%)[a]
1	 **2a** (79)	(1) DBU (1.0 equiv), MVK (1.5 equiv), CH_3CN, rt, 30 min; (2) aq workup; (3) *p*-TsOH (0.1 equiv), PhH, reflux, 1 h	 **5a** (83)	 **6a** (86)
2	 **2b** (61)	(1) DBU (1.0 equiv), MVK (1.5 equiv), CH_3CN, rt, 30 min; (2) aq workup; (3) *p*-TsOH (0.1 equiv), PhH, reflux, 1 h	 **5b** (75)	 **6b** (78)
3	 **2c** (79)	(1) DBU (1.0 equiv), MVK (1.8 equiv), CH_3CN, rt, 5 h; (2) aq workup; (3) *p*-TsOH (0.1 equiv), PhH, reflux, 1 h	 **5c** (71)	 **6c** (80)
4	**2a**	(1) DBU (1.0 equiv), EVK (1.5 equiv), CH_3CN, rt, 1 h; (2) aq workup; (3) *p*-TsOH (0.1 equiv), PhH, reflux, 3 h	 **5d** (78)	 **6d** (85)
5	 **2d** (82)	(1) DBU (1.0 equiv), MVK (1.5 equiv), CH_3CN, rt, 12 h; (2) aq workup; (3) *p*-TsOH (0.1 equiv), PhH, reflux, 3 h	 **5e** (73)	 **6e** (89)
6	**2a**	(1) DBU (2.0 equiv), methyl acrylate (1.8 equiv), CH_3CN, rt, 40 h; (2) aq workup; (3) *p*-TsOH (0.1 equiv), PhH, reflux, 4 h	 **5f** (65)[b]	 **6f** (80)
7	**2a**	(1) DBU (2.0 equiv), acrylonitrile (2.0 equiv), CH_3CN, rt, 4 days; (2) aq workup; (3) *p*-TsOH (0.1 equiv), PhH, reflux, 15 h	 **5g** (41)[c]	 **6g** (91)

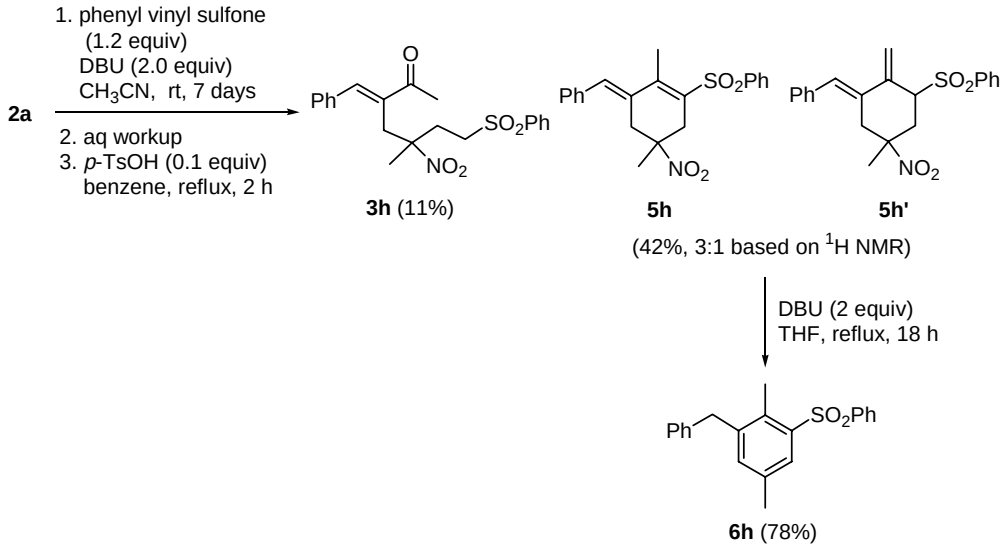
[a] DBU (2 equiv), THF, reflux, 5–96 h.
[b] Michael addition product **3f** was isolated in 7%.
[c] Michael addition product **3g** was isolated in 41% yield.

Scheme 4. The reaction of **2** and vinyltriphenylphosphonium bromide could provide benzylidene cyclohexene intermediate **7** via the successive Michael addition and Wittig reaction in the presence of appropriate base. The compound **7** could be converted into the aromatized product **8** under basic conditions via elimination of nitrous acid followed by isomerization of double bond.

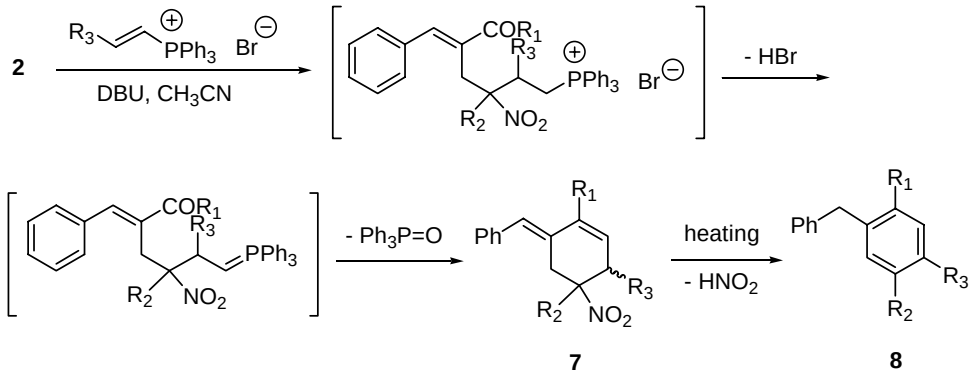
As expected, the reaction of **2a** and vinyltriphenylphosphonium bromide in the presence of DBU (3 equiv) in CH_3CN at refluxing temperature for 18 h gave desired **8a** in 86% yield. We were encouraged by the first successful results and extended the trial to the synthesis of a variety of polysubstituted benzene derivatives **8b–f** as summarized in Table 2. The synthesis of **8** was carried out without isolation of the corresponding intermediates **7** (see, Section 3). However, we could confirm the structure of corresponding intermediate **7a**, which was obtained in 48% yield when we carried out the reaction at around 40–50 °C for 3 h.

As shown in Table 2, changes of the structure of starting materials **2** did not affect the reaction progress (entries 1–3). When we used **2e** and **2f**, which were made from ethyl nitroacetate, the reaction was completed in a short time at lower temperature (entries 4 and 6). However, when we used propenyltriphenylphosphonium bromide[17c] (entry 5) the yield of product **8e** was low.

We examined the reaction of nitroalkane derivative **2g**, which was made from the acetate of the Baylis–Hillman



Scheme 3.



Scheme 4.

adduct of *n*-hexanal and nitroethane.[15d] However, unfortunately, intractable complex mixtures were observed on TLC under the same reaction conditions of Scheme 2 with methyl vinyl ketone, as shown in Scheme 5. The reaction of **2a** and 2-cyclohexen-1-one also showed a complex nature and we could not obtain the desired product.

In summary, we disclosed a new route for the synthesis of polysubstituted benzene derivatives starting from Baylis–Hillman adducts via a regioselective [4+2] benzannulation protocol. Nitroalkane derivative, which was prepared from Baylis–Hillman adduct, served as the four-carbon unit and Michael acceptor including Schweizer reagent as a two-carbon unit.

3. Experimental

3.1. General procedure

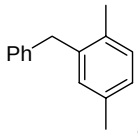
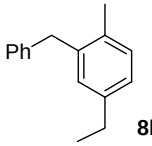
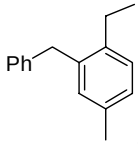
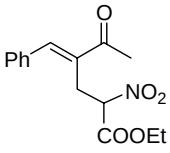
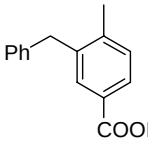
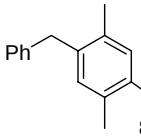
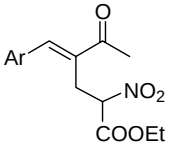
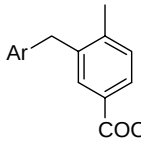
^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$. The signal positions are reported in ppm relative to TMS (δ scale) used as an internal standard. IR spectra are reported in cm^{-1}. Mass spectra were obtained from the Korea Basic Science Institute (Gwangju branch). Melting points are uncorrected. The elemental analyses were carried out at Korea Research Institute of Chemical Technology, Taejon, Korea. All reagents were purchased from commercial sources and used without further treatment. The separations were carried out by flash column chromatography over silica gel (230–400 mesh ASTM). Organic extracts were dried over anhydrous $MgSO_4$ and the solvents were evaporated on a rotary evaporator under water aspirator pressure.

3.2. Synthesis of starting material 2

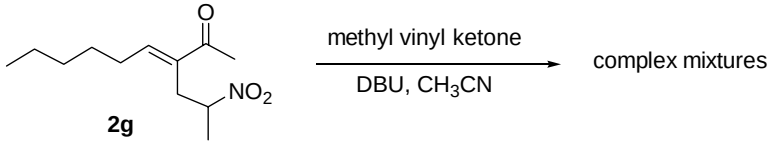
The starting materials **2a–d** and **2g** were prepared according to the previous paper.[14–16] Compounds **2e** and **2f** were synthesized analogously by using ethyl nitroacetate and the spectroscopic data are as follows.

3.2.1. Compound 2e. 73%; clear oil; IR (film) 1751, 1666, 1558, 1373, 1254, 1215 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.22 (t, J=7.2 Hz, 3H), 2.47 (s, 3H), 3.35 (dd, J=14.4, 6.6 Hz, 1H), 3.49 (dd, J=14.4, 9.3 Hz, 1H), 4.12–4.23 (m, 2H), 5.52 (dd, J=9.3, 6.6 Hz, 1H), 7.30–7.46 (m, 5H), 7.75 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.73, 25.76, 27.37, 62.89, 85.65, 128.72, 128.82, 129.27, 134.15, 135.04, 145.03, 164.01, 199.47; ESIMS *m/z* 292.1 (M^++H). Anal. Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81. Found: C, 61.97; H, 5.75; N, 4.96.

Table 2. Synthesis of regioselectively substituted benzenes

Entry	Substrate (%)	Conditions	Product (%)
1	**2a**	CH_2=$CHPPh_3Br$ (1.2 equiv), DBU (3.0 equiv), CH_3CN reflux, 18 h	 **8a** (86)
2	**2b**	CH_2=$CHPPh_3Br$ (1.2 equiv), DBU (3.0 equiv), CH_3CN reflux, 40 h	 **8b** (81)
3	**2d**	CH_2=$CHPPh_3Br$ (1.2 equiv), DBU (3.0 equiv), CH_3CN reflux, 28 h	 **8c** (74)
4	 **2e** (73)	CH_2=$CHPPh_3Br$ (1.2 equiv), DBU (3.0 equiv), CH_3CN 40–50 °C, 5 h	 **8d** (88)
5	**2a**	CH_2=$CHCH_2PPh_3Br$ (1.2 equiv), DBU (3.0 equiv), CH_3CN reflux, 40 h	 **8e** (40)
6[a]	 **2f** (79)	CH_2=$CHPPh_3Br$ (1.2 equiv), DBU (3.0 equiv), CH_3CN 40–50 °C, 3 h	 **8f** (86)

[a] Ar is 4-chlorophenyl.



Scheme 5.

3.2.2. Compound 2f. 79%; clear oil; IR (film) 2985, 1751, 1670, 1562, 1377, 1250, 1215 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.24 (t, J=7.2 Hz, 3H), 2.46 (s, 3H), 3.30 (dd, J=14.4, 6.3 Hz, 1H), 3.44 (dd, J=14.4, 9.3 Hz, 1H), 4.16–4.26 (m, 2H), 5.53 (dd, J=9.3, 6.3 Hz, 1H), 7.27 (d, J=8.4 Hz, 2H), 7.41 (d, J=8.4 Hz, 2H), 7.68 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.74, 25.75, 27.42, 62.99, 85.61, 129.10, 130.06, 132.55, 135.33, 135.55, 143.65, 163.90, 199.21. Anal. Calcd for $C_{15}H_{16}ClNO_5$: C, 55.31; H, 4.95; N, 10.88. Found: C, 55.26; H, 4.92; N, 10.67.

3.3. Synthesis of the intermediate 5

Typical procedure for the synthesis of cyclohexene intermediate **5a**: to a stirred solution of **2a** (233 mg, 1.0 mmol) and methyl vinyl ketone (105 mg, 1.5 mmol) in CH_3CN (5 mL) was added DBU (153 mg, 1.0 mmol) and stirred at rt for 30 min. TLC observation showed complete disappearance of starting material **2a** and the formation of diastereomeric mixtures of **4a**. After aq workup the crude diastereomeric mixtures were dissolved in benzene (5 mL), added *p*-TsOH (20 mg, 0.1 mmol), and heated to reflux for 1 h. After the usual workup and column chromatographic purification process (hexanes/ether, 5:1) we obtained desired **5a** as a white solid, 237 mg (83%). The other compounds **5b–h** were synthesized analogously and the spectroscopic data of prepared compounds are as follows.

3.3.1. Compound 5a.[13] 83%; white solid, mp 81–83 °C; IR (KBr) 1685, 1539, 1350, 1234 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.58 (s, 3H), 2.03 (t, J=1.8 Hz, 3H), 2.37 (s, 3H), 2.66 (dd, J=17.7, 1.8 Hz, 1H), 2.82 (dd, J=15.3, 1.8 Hz, 1H), 3.28 (d, J=17.7 Hz, 1H), 3.43 (d, J=15.3 Hz, 1H), 6.92 (s, 1H), 7.25–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$,

75 MHz) δ 15.78, 25.74, 29.82, 36.34, 36.62, 86.01, 127.36, 128.34, 128.98, 131.18, 133.09, 133.66, 133.83, 136.60, 204.25. Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.76; H, 6.83; N, 4.87.

3.3.2. Compound 5b. 75%; clear oil; IR (film) 2974, 1685, 1539, 1442, 1354, 1234 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.83 (t, J=7.5 Hz, 3H), 1.81–1.99 (m, 2H), 2.01 (t, J=1.8 Hz, 3H), 2.38 (s, 3H), 2.65 (d, J=17.4 Hz, 1H), 2.78 (dd, J=15.6, 1.8 Hz, 1H), 3.25 (d, J=17.4 Hz, 1H), 3.46 (d, J=15.6 Hz, 1H), 6.89 (s, 1H), 7.24–7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.76, 15.83, 29.87, 32.17, 34.46, 34.61, 89.68, 127.33, 128.36, 128.95, 130.97, 132.98, 133.69, 133.96, 136.67, 204.60. Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68. Found: C, 72.16; H, 7.19; N, 4.65.

3.3.3. Compound 5c. 71%; clear oil; IR (film) 2958, 1685, 1539, 1442, 1354, 1234 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.83 (t, J=6.9 Hz, 3H), 1.04–1.29 (m, 4H), 1.77–1.90 (m, 2H), 2.02 (t, J=1.5 Hz, 3H), 2.38 (s, 3H), 2.65 (dd, J=18.0, 1.8 Hz, 1H), 2.78 (dd, J=15.6, 1.8 Hz, 1H), 3.25 (d, J=18.0 Hz, 1H), 3.46 (d, J=15.6 Hz, 1H), 6.89 (s, 1H), 7.26–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.63, 15.84, 22.31, 25.31, 29.87, 34.86, 35.00, 38.88, 89.37, 127.32, 128.36, 128.94, 130.96, 133.04, 133.70, 133.98, 136.70, 204.59. Anal. Calcd for $C_{20}H_{25}NO_3$: C, 73.37; H, 7.70; N, 4.28. Found: C, 73.51; H, 7.69; N, 4.31.

3.3.4. Compound 5d. 78%; clear oil; IR (film) 2931, 1689, 1539, 1450, 1346, 1261 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.15 (t, J=7.2 Hz, 3H), 1.58 (s, 3H), 1.97 (t, J=1.8 Hz, 3H), 2.60–2.70 (m, 3H), 2.82 (dd, J=15.3, 1.8 Hz, 1H), 3.25 (d, J=17.7 Hz, 1H), 3.43 (d, J=15.3 Hz, 1H), 6.87 (s, 1H), 7.25–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 7.83, 15.84, 25.80, 35.23, 36.39, 36.73, 86.09, 127.34, 128.39, 129.02, 130.55, 132.20, 132.98, 134.21, 136.70, 208.10. Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68. Found: C, 72.18; H, 7.19; N, 4.51.

3.3.5. Compound 5e. 73%; white solid, mp 79–81 °C; IR (KBr) 2974, 1689, 1539, 1350, 1238 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.14 (t, J=7.5 Hz, 3H), 1.58 (s, 3H), 2.36 (s, 3H), 2.40–2.50 (m, 2H), 2.64 (d, J=17.4 Hz, 1H), 2.81 (dd, J=15.3, 1.8 Hz, 1H), 3.27 (d, J=17.4 Hz, 1H), 3.41 (d, J=15.3 Hz, 1H), 6.95 (s, 1H), 7.26–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.68, 22.12, 25.60, 29.59, 36.47, 36.58, 85.96, 127.34, 128.34, 128.99, 130.93 (2C), 133.09, 136.66, 139.41, 203.95. Anal. Calcd for $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68. Found: C, 72.43; H, 7.12; N, 4.69.

3.3.6. Compound 5f. 65%; white solid, mp 74–76 °C; IR (KBr) 2951, 1716, 1539, 1435, 1242 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.55 (s, 3H), 2.26 (t, J=1.8 Hz, 3H), 2.76 (dd, J=18.3, 1.8 Hz, 1H), 2.85 (dd, J=14.7, 1.5 Hz, 1H), 3.36 (d, J=14.7 Hz, 1H), 3.37 (d, J=18.3 Hz, 1H), 3.80 (s, 3H), 7.02 (s, 1H), 7.02–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.00, 25.49, 36.22, 37.23, 51.78, 85.84, 124.20, 127.49, 128.36, 129.03, 132.41, 133.64, 136.56, 140.52, 168.45. Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.94; H, 6.44; N, 4.58.

3.3.7. Compound 5g. 41%; white solid, mp 83–85 °C; IR (KBr) 2206, 1543, 1450, 1346, 1265 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.59 (s, 3H), 2.29 (t, J=1.5 Hz, 3H), 2.70 (dd, J=17.7, 1.8 Hz, 1H), 2.80 (dd, J=15.6, 1.8 Hz, 1H), 3.31 (d, J=17.7 Hz, 1H), 3.49 (d, J=15.6 Hz, 1H), 7.01 (s, 1H), 7.27–7.44 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.28, 25.81, 35.91, 36.92, 85.07, 105.45, 118.50, 128.15, 128.52, 129.10, 130.89, 134.25, 135.43, 148.07. Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.77; H, 6.25; N, 10.26.

3.3.8. Compound 5h. 42%; clear oil; IR (film) 2927, 1539, 1300, 1146 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.59 (s, 3H), 2.32 (s, 3H), 2.67 (d, J=15.3 Hz, 1H), 2.97 (d, J=18.9 Hz, 1H), 3.51 (d, J=15.3 Hz, 1H), 3.66 (d, J=18.9 Hz, 1H), 7.07 (s, 1H), 7.21–7.96 (m, 10H). In the ^1H NMR spectrum of **5h** small amounts (25%) of **5h′** was mixed: 1.66 (s, 3H), 2.38–2.50 (m, 1H), 2.81–2.88 (m, 1H), 3.06–3.16 (m, 1H), 3.44–3.70 (m, 1H), 4.16–4.22 (m, 1H), 4.66 (s, 1H), 5.41 (s, 1H), 6.60 (s, 1H), 7.21–7.96 (m, 10H). We did not take ^{13}C NMR due to the lack of pure **5h**.

3.4. Synthesis of benzene derivatives 6a–h

Typical procedure for the synthesis of cyclohexene intermediate **6a**: to a stirred solution of **5a** (143 mg, 0.5 mmol) in THF (3 mL) was added DBU (152 mg, 1.0 mmol) and heated to reflux for 6 h. After the usual workup and column chromatographic purification process (hexanes/ether, 10:1) we obtained desired **6a** as a white solid, 103 mg (86%). The other compounds **6b–h** were synthesized analogously and the spectroscopic data of prepared compounds are as follows (reaction time was noted in the parenthesis).

3.4.1. Compound 6a.[13] 86% (6 h); white solid, mp 40–41 °C; IR (KBr) 2924, 1685 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.26 (s, 3H), 2.32 (s, 3H), 2.54 (s, 3H), 3.99 (s, 2H), 7.05–7.29 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.97, 20.86, 30.45, 39.57, 126.01, 126.80, 128.41, 128.55, 132.06, 133.65, 134.84, 139.96, 140.34, 140.53, 204.00; ESIMS m/z 239.1 (M^++H). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.71; H, 7.75.

3.4.2. Compound 6b. 78% (48 h); clear oil; IR (film) 2966, 1685, 1454, 1354, 1281 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.22 (t, J=7.5 Hz, 3H), 2.26 (s, 3H), 2.55 (s, 3H), 2.61 (q, J=7.5 Hz, 2H), 4.01 (s, 2H), 7.07–7.29 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.52, 15.03, 27.27, 29.48, 38.70, 124.59, 125.01, 127.41, 127.54, 131.35, 131.55, 138.98, 139.36, 139.67, 140.28, 203.09; ESIMS m/z 253.1 (M^++H). Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.59; H, 7.81.

3.4.3. Compound 6c. 80% (72 h); clear oil; IR (film) 2927, 1685, 1454, 1354, 1284 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.92 (t, J=7.2 Hz, 3H), 1.23–1.43 (m, 2H), 1.52–1.76 (m, 2H), 2.26 (s, 3H), 2.54 (s, 3H), 2.58 (t, J=7.8 Hz, 2H), 4.01 (s, 2H), 7.06–7.28 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.88, 16.02, 22.29, 30.47, 33.54, 35.04, 39.69, 125.99, 126.17, 128.40, 128.52, 132.34, 133.11, 139.94, 140.00, 140.25, 140.56, 204.08; ESIMS m/z 281.2 (M^++H).

Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.91; H, 8.61.

3.4.4. Compound 6d. 85% (5 h); clear oil; IR (film) 2931, 1693, 1454, 1342, 1161 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.17 (t, $J=7.5$ Hz, 3H), 2.20 (s, 3H), 2.30 (s, 3H), 2.83 (q, $J=7.5$ Hz, 2H), 3.98 (s, 2H), 7.02 (s, 1H), 7.07–7.29 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 8.29, 15.86, 20.86, 35.99, 39.54, 125.78, 125.99, 128.39, 128.57, 131.34, 133.05, 134.85, 139.97, 140.16, 141.14, 207.62; ESIMS *m/z* 253.2 ($M^+ + H$). Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.73; H, 7.89.

3.4.5. Compound 6e. 89% (12 h); clear oil; IR (film) 2966, 1689 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.09 (t, $J=7.5$ Hz, 3H), 2.30 (s, 3H), 2.55 (s, 3H), 2.74 (q, $J=7.5$ Hz, 2H), 4.03 (s, 2H), 7.02 (s, 1H), 7.08–7.29 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.64, 20.86, 22.30, 30.61, 38.45, 126.00, 127.07, 128.38, 128.61, 134.06, 134.91, 138.28, 139.69, 140.06, 140.61, 203.79; ESIMS *m/z* 253.1 ($M^+ + H$). Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.47; H, 8.08.

3.4.6. Compound 6f. 80% (96 h); clear oil; IR (film) 2924, 1724, 1454, 1308, 1207 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.30 (s, 3H), 2.36 (s, 3H), 3.87 (s, 3H), 4.01 (s, 2H), 7.06–7.09 (m, 3H), 7.15–7.29 (m, 3H), 7.48 (d, $J=1.2$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.15, 20.75, 39.70, 51.88, 126.00, 128.41, 128.52, 128.74, 131.50, 134.45 (2C), 134.87, 140.00, 140.05, 169.21; ESIMS *m/z* 255.1 ($M^+ + H$). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.19; H, 7.27.

3.4.7. Compound 6g. 91% (9 h); clear oil; IR (film) 2924, 2225, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.30 (s, 3H), 2.39 (s, 3H), 3.98 (s, 2H), 7.04–7.08 (m, 2H), 7.14 (s, 1H), 7.16–7.32 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.32, 20.61, 39.40, 113.51, 118.74, 126.36, 128.52, 128.59, 131.15, 135.36, 136.18, 137.45, 139.05, 140.12; ESIMS *m/z* 222.1 ($M^+ + H$). Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.87; H, 6.95; N, 6.18.

3.4.8. Compound 6h. 78% (18 h); white solid, mp 113–114 °C; IR (KBr) 2924, 1450, 1304, 1149 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.26 (s, 3H), 2.38 (s, 3H), 3.94 (s, 2H), 6.98–7.86 (m, 11H), 8.00 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.39, 20.92, 39.35, 126.24, 127.34, 128.39, 128.47, 128.52, 128.94, 132.80, 133.43, 135.86, 136.40, 139.18, 139.25, 141.52, 141.79; ESIMS *m/z* 337.1 ($M^+ + H$). Anal. Calcd for $C_{21}H_{20}O_2S$: C, 74.97; H, 5.99. Found: C, 75.07; H, 5.93.

3.5. Analytical data of Michael addition products 3f–h

3.5.1. Compound 3f. 7%; clear oil; IR (film) 1739, 1674, 1539 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.30 (s, 3H), 1.83–1.95 (m, 1H), 2.02–2.34 (m, 3H), 2.48 (s, 3H), 3.24 (d, $J=14.1$ Hz, 1H), 3.36 (d, $J=14.1$ Hz, 1H), 3.63 (s, 3H), 7.26–7.45 (m, 5H), 7.74 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.82, 25.77, 28.72, 33.95, 34.00, 51.80, 90.07, 128.44, 128.83, 128.85, 134.95, 137.43, 143.67, 172.51, 199.54; ESIMS *m/z* 320.1 ($M^+ + H$). Anal. Calcd for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.39. Found: C, 64.02; H, 6.61; N, 4.45.

3.5.2. Compound 3g. 41%; white solid, mp 93–95 °C; IR (KBr) 2249, 1670, 1543 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.36 (s, 3H), 1.85–1.95 (m, 1H), 2.15–2.35 (m, 3H), 2.49 (s, 3H), 3.25 (d, $J=13.8$ Hz, 1H), 3.34 (d, $J=13.8$ Hz, 1H), 7.14–7.48 (m, 5H), 7.80 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.50, 22.10, 25.70, 33.51, 34.23, 89.53, 118.31, 128.32, 129.02, 129.13, 134.69, 136.68, 144.56, 199.36; ESIMS *m/z* 287.1 ($M^+ + H$). Anal. Calcd for $C_{16}H_{18}N_2O_3$: C, 67.12; H, 6.34; N, 9.78. Found: C, 67.35; H, 6.19; N, 9.73.

3.5.3. Compound 3h. 11%; clear oil; IR (film) 2927, 1670, 1539, 1308, 1149 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.28 (s, 3H), 1.90–2.01 (m, 1H), 2.22–2.38 (m, 1H), 2.44 (s, 3H), 2.85–3.01 (m, 2H), 3.22 (d, $J=14.1$ Hz, 1H), 3.31 (d, $J=14.1$ Hz, 1H), 7.25–7.71 (m, 8H), 7.75 (s, 1H), 7.80–7.84 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.27, 25.65, 31.62, 33.80, 51.30, 89.28, 128.02, 128.41, 128.97, 129.04, 129.37, 133.98, 134.70, 136.71, 138.44, 144.26, 199.31; ESIMS *m/z* 402.1 ($M^+ + H$). Anal. Calcd for $C_{21}H_{23}NO_5S$: C, 62.82; H, 5.77; N, 3.49. Found: C, 62.98; H, 5.65; N, 3.47.

3.6. Synthesis of 7a and 8a–f

Typical procedure for the synthesis of intermediate **7a** and benzene derivative **8a**: to a stirred solution of **2a** (233 mg, 1.0 mmol) and vinyltriphenylphosphonium bromide (443 mg, 1.2 mmol) in CH_3CN (5 mL) was added DUB (456 mg, 3 mmol) and heated to reflux for 18 h. After usual workup and column chromatographic purification process (hexanes/ether, 40:1) we obtained the desired benzene derivative **8a** (169 mg, 86%). We could obtain the corresponding intermediate **7a** in 48% yield when we carried out the reaction at around 40–50 °C for 3 h. We synthesized other benzene derivatives **8b–f** analogously without isolation of the corresponding intermediates. The spectroscopic data of prepared compounds are as follows.

3.6.1. Compound 7a. 48%; clear oil; IR (film) 1539, 1450, 1346 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.54 (s, 3H), 1.93 (s, 3H), 2.49 (d, $J=18.0$ Hz, 1H), 2.89 (d, $J=15.3$ Hz, 1H), 3.07 (d, $J=18.0$ Hz, 1H), 3.33 (d, $J=15.3$ Hz, 1H), 5.63–5.67 (m, 1H), 6.62 (s, 1H), 7.21–7.39 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.60, 25.43, 36.16, 36.56, 86.91, 123.30, 126.81, 126.97, 128.25, 129.05, 133.27, 133.37, 137.03. Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.03; H, 7.21; N, 5.71.

3.6.2. Compound 8a.[18a] 86%; clear oil; IR (film) 2920, 1496, 1450 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.28 (s, 3H), 2.78 (s, 3H), 3.94 (s, 2H), 6.92–7.28 (m, 8H); ESIMS *m/z* 197.1 ($M^+ + H$).

3.6.3. Compound 8b.[18b] 81%; clear oil; IR (film) 2962, 2927, 1496, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.20 (t, $J=7.5$ Hz, 3H), 2.18 (s, 3H), 2.57 (q, $J=7.5$ Hz,

2H), 3.95 (s, 2H), 6.94–7.27 (m, 8H); ESIMS *m/z* 211.1 ($M^+ + H$).

3.6.4. Compound 8c. 74%; clear oil; IR (film) 2962, 2924, 1496, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.11 (t, $J=7.5$ Hz, 3H), 2.27 (s, 3H), 2.56 (q, $J=7.5$ Hz, 2H), 3.98 (s, 2H), 6.92 (s, 1H), 6.98–7.28 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.98, 20.94, 25.33, 38.72, 125.81, 127.32, 128.31, 128.39, 128.67, 131.09, 135.22, 137.91, 139.38, 141.05; ESIMS *m/z* 211.1 ($M^+ + H$). Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.29; H, 8.71.

3.6.5. Compound 8d. 86%; clear oil; IR (film) 1720, 1265 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.36 (t, $J=7.2$ Hz, 3H), 2.52 (s, 3H), 4.02 (s, 2H), 4.34 (q, $J=7.2$ Hz, 2H), 7.06–7.28 (m, 6H), 7.81–7.85 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.28, 19.83, 39.39, 60.69, 126.04, 127.73, 128.31, 128.40, 128.48, 130.37, 131.13, 138.95, 139.67, 142.28, 166.72; ESIMS *m/z* 255.1 ($M^+ + H$). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.34; H, 7.29.

3.6.6. Compound 8e.[18c] 40%; clear oil; IR (film) 2920, 1496, 1454 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.16 (s, 3H), 2.19 (s, 3H), 2.21 (s, 3H), 3.91 (s, 2H), 6.88 (s, 1H), 6.93 (s, 1H), 7.09–7.27 (m, 5H); ESIMS *m/z* 211.1 ($M^+ + H$).

3.6.7. Compound 8f. 86%; clear oil; IR (film) 1716, 1269 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.38 (t, $J=7.2$ Hz, 3H), 2.24 (s, 3H), 3.98 (s, 2H), 4.35 (q, $J=7.2$ Hz, 2H), 7.02 (d, $J=8.1$ Hz, 2H), 7.22 (d, $J=8.1$ Hz, 2H+1H), 7.82 (s, 1H), 7.84 (d, $J=8.1$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.31, 19.81, 38.77, 60.78, 127.95, 128.45, 128.54, 129.82, 130.51, 131.05, 131.88, 138.19, 138.44, 142.18, 166.64; ESIMS *m/z* 255.1 ($M^+ + H$). Anal. Calcd for $C_{17}H_{17}ClO_2$: C, 70.71; H, 5.93. Found: C, 70.58; H, 5.89.

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