Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters
Tetrahedron Letters 47 (2006) 6641–6645

Regioselective synthesis of pentasubstituted benzene derivatives: TBAF as an effective catalyst for the sequential Michael addition-intramolecular aldolization

Da Yeon Park, Saravanan Gowrisankar and Jae Nyoung Kim*

Department of Chemistry and Institute of Basic Science, Chonnam National University, Gwangju 500-757, Republic of Korea

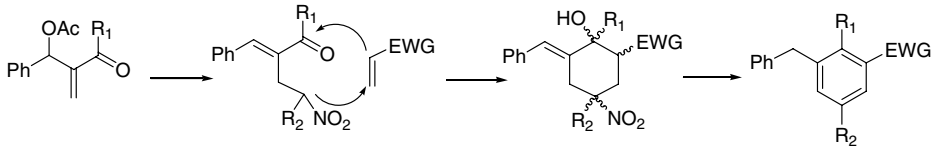
Received 1 June 2006; revised 27 June 2006; accepted 30 June 2006
Available online 28 July 2006

Abstract—Polysubstituted benzene derivatives were synthesized starting from the Baylis–Hillman adducts via the sequential introduction of primary nitroalkane at the primary position, Michael addition to β-branched Michael acceptor, aldol condensation, elimination of nitrous acid, and the final aromatization process.

Recently, we reported the synthesis of polysubstituted benzene and pyridine derivatives from Baylis–Hillman adducts.[1,2] The synthetic pathway for the benzene derivative, as an example, is depicted in Scheme 1.[1] As shown the reaction followed sequential introduction of primary nitroalkane at the primary position of the Baylis–Hillman adduct, Michael addition, aldol condensation, elimination of nitrous acid, and the final aromatization process.[1]

Based both on the importance and difficulties of regioselective synthesis of polysubstituted benzene derivatives,[1,3] we intended to extend our protocol to the synthesis of pentasubstituted benzene derivatives by using β-substituted Michael acceptors. We reasoned that if the sequential Michael addition-intramolecular aldolization steps could occur successfully with β-substituted Michael acceptor, other steps would proceed as before and pentasubstituted benzene derivatives (Scheme 2) could be synthesized easily including tetralone derivatives[4] (vide infra).

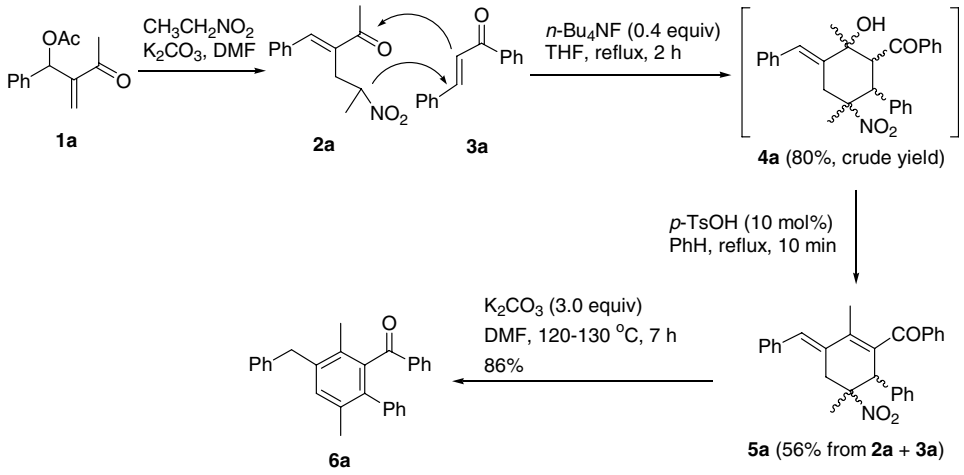
Thus, we examined the reaction of **2a** and chalcone (**3a**), as the representative β-substituted Michael acceptor, under various conditions. The reactions did not give appreciable yields of the Michael addition product nor the cyclized intermediate **4a** under the conditions including DBU/THF, DBU/CH_3CN, K_2CO_3/CH_3CN, K_2CO_3/DMF, and Cs_2CO_3/DMF.[5] Fortunately, we could obtain the cyclized intermediate **4a** as diastereomeric mixtures in 80% yield when we used TBAF (*n*-tetrabutylammonium fluoride) as the catalyst in THF.[6–8] Although we did not separate each isomer of **4a** in pure states, we could confirm the structure of **4a** by carrying out the next step (vide infra). The crude mixtures of **4a** under the influence of *p*-TsOH (10 mol %) in benzene at refluxing temperature for 10 min afforded **5a** as two isomeric mixtures (*syn*/*anti*) in 56% yield. The reaction



Scheme 1.

Keywords: Polysubstituted benzenes; Baylis–Hillman adducts; TBAF; Michael acceptor.
* Corresponding author. Tel.: +82 62 530 3381; fax: +82 62 530 3389; e-mail: kimjn@chonnam.ac.kr

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.06.180

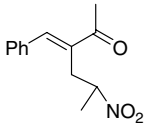
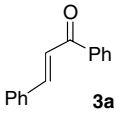
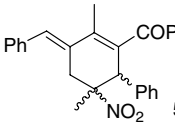
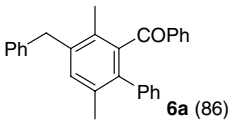
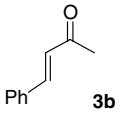
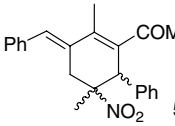
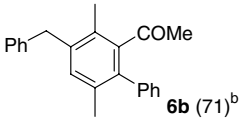
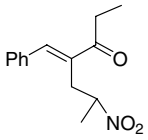
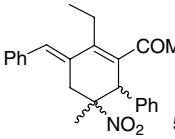
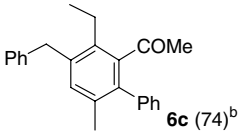
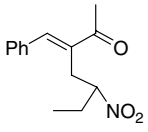
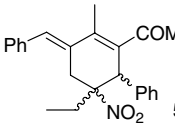
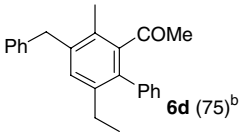
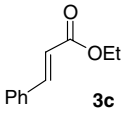
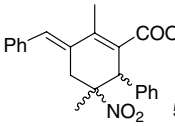
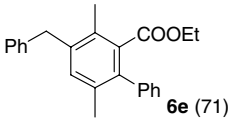


Scheme 2.

of **5a** and K_2CO_3 (3 equiv) in DMF at around 120–130 °C for 7 h gave the desired final pentasubstituted benzene **6a** in 86% yield (Scheme 2).[9]

Encouraged by the results we carried out the reactions of **2a–c** with chalcone (**3a**), 4-phenyl-3-buten-2-one (**3b**), and ethyl cinnamate (**3c**) and the results are summarized in Table 1. We observed in all cases the formation of variable ratios of diastereomeric mixtures **4**, which appeared just below the starting materials **2** on TLC. We separated the diastereomeric mixtures **4** altogether by column chromatography and used for the next dehydration step. After dehydration we could obtain the corresponding cyclohexene derivatives **5b–e** in 27–71%

Table 1. Synthesis of polysubstituted benzene derivatives

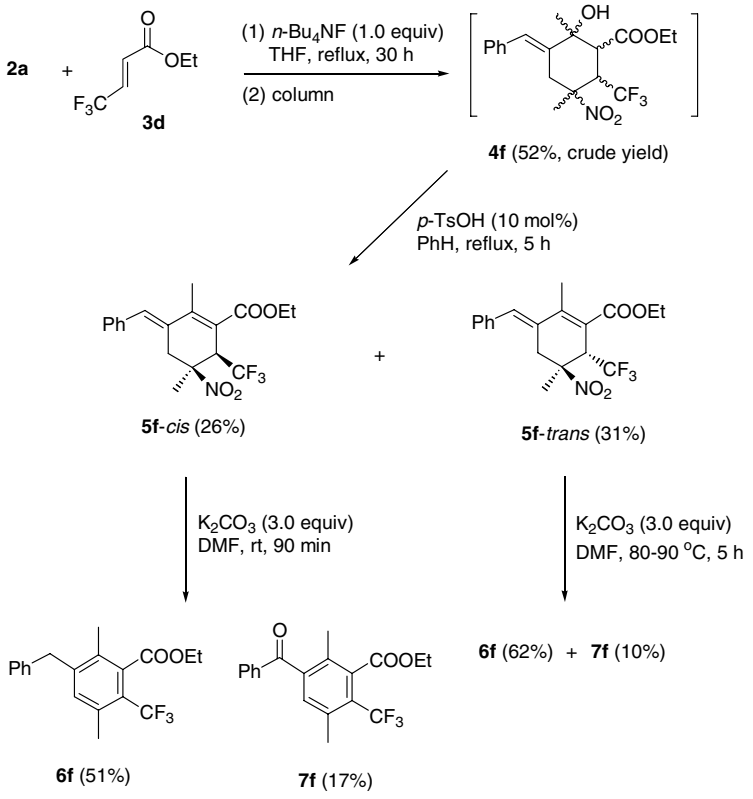
Entry	Substrate	Michael acceptor	Conditions	Cyclohexenone (%)[a]	Conditions	Product (%)
1	 **2a**	 **3a**	1. *n*-Bu_4NF (0.4 equiv) THF, reflux, 2 h; 2. column (**4a**, 80%); 3. *p*-TsOH (10 mol %) PhH, reflux, 10 min	 **5a** (70)	K_2CO_3 (3.0 equiv) DMF, 120–130 °C, 7 h	 **6a** (86)
2	**2a**	 **3b**	1. *n*-Bu_4NF (0.4 equiv) THF, reflux, 20 h; 2. column (**4b**, 87%); 3. *p*-TsOH (10 mol %) PhH, reflux, 10 min	 **5b** (71)	K_2CO_3 (3.0 equiv) DMF, 120–130 °C, 5 h	 **6b** (71)[b]
3	 **2b**	**3b**	1. *n*-Bu_4NF (0.4 equiv) THF, reflux, 8 h; 2. column (**4c**, 73%); 3. *p*-TsOH (10 mol %) PhH, reflux, 120 min	 **5c** (67)	K_2CO_3 (3.0 equiv) DMF, 120–130 °C, 3 h	 **6c** (74)[b]
4	 **2c**	**3b**	1. *n*-Bu_4NF (1.0 equiv) THF, rt, 48 h; 2. column (**4d**, 35%); 3. *p*-TsOH (10 mol %) PhH, reflux, 10 min	 **5d** (44)	K_2CO_3 (3.0 equiv) DMF, 120–130 °C, 4 h	 **6d** (75)[b]
5	**2a**	 **3c**	1. *n*-Bu_4NF (1.0 equiv) THF, reflux, 18 h; 2. column (**4e**, 46%); 3. *p*-TsOH (10 mol %) PhH, reflux, 24 h	 **5e** (27)	K_2CO_3 (3.0 equiv) DMF, 120–130 °C, 3 h	 **6e** (71)

[a] Mixtures of *syn*/*anti* were used in the next step without separation. We isolated one major isomer of **5a** and identified the structure.[8]
[b] The oxidized benzoyl derivatives were obtained in 3% (entry 2), 3% (entry 3), and 6% (entry 4), respectively.

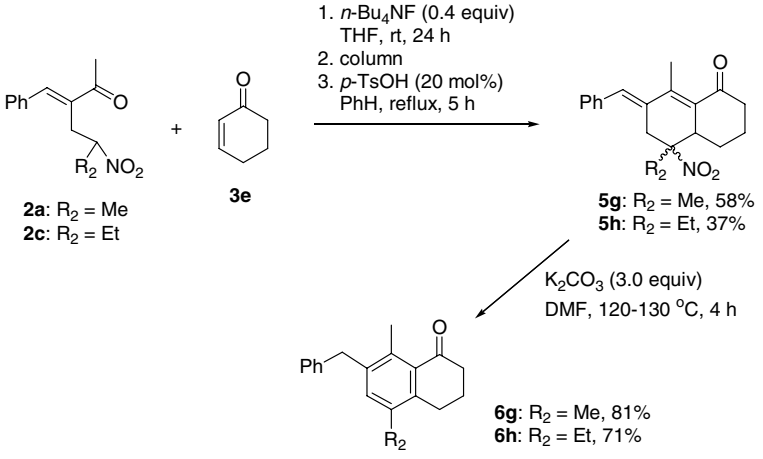
yields as cis/trans mixtures. The final step (elimination of HNO_2 and concomitant aromatization) proceeded effectively in all cases in good yields (71–75%). We elevated the reaction temperature sufficiently (120–130 °C) in order to convert both isomers (*syn*/*anti*) of **5b–e** into the final benzene derivatives **6b–e** (vide infra). In some cases, we observed the oxidized compounds **7b–d** (entries 2–4) in small amounts.

Similarly, we could obtain **6f** from the reaction of **2a** and ethyl 4,4,4-trifluorocrotonate (**3d**) as in Scheme 3. In this case, we could separate the cis and trans isomers **5f**-*cis* and **5f**-*trans* in 26% and 31%, respectively.[9] The structures of **5f**-*cis* and **5f**-*trans* were supposed from the results of the next elimination step. The elimination of nitrous acid was fast (rt, <90 min) for **5f**-*cis*, while relatively slow for **5f**-*trans* (heating, 5 h). The elimination of HNO_2 for **5f**-*cis* must occur via the facile *anti*-periplanar state.[10] The elimination of HNO_2 from **5f**-*trans* must occur by following the difficult *syn*-elimination mode. It is noteworthy that an appreciable amount of oxidized benzoyl derivative **7f** was generated during the elimination stage.

As a next trial, we examined the reaction of **2a** and 2-cyclohexen-1-one (**3e**) for the synthesis of tetralone derivative. As shown in Scheme 4, we could synthesize desired compound **6g** in moderate yield by following



Scheme 3.



Scheme 4.

the same protocol. The reaction of **2c** and **3e** showed similar reactivity and we synthesized **6h** similarly.[9]

In summary, we disclosed the synthesis of pentasubstituted benzene derivatives regioselectively starting from the Baylis–Hillman adducts via the sequential introduction of primary nitroalkane at the primary position, Michael addition with TBAF, aldol condensation, elimination of nitrous acid, and the final aromatization process.

Acknowledgements

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2005-041-C00248). Spectroscopic data were obtained from the Korea Basic Science Institute, Gwangju branch.

References and notes

1. (a) Lee, M. J.; Lee, K. Y.; Park, D. Y.; Kim, J. N. *Tetrahedron* **2006**, *62*, 3128; (b) Lee, M. J.; Lee, K. Y.; Gowrisankar, S.; Kim, J. N. *Tetrahedron Lett.* **2006**, *47*, 1355.
2. (a) Park, D. Y.; Lee, M. J.; Kim, T. H.; Kim, J. N. *Tetrahedron Lett.* **2005**, *46*, 8799; (b) Lee, M. J.; Kim, S. C.; Kim, J. N. *Bull. Korean Chem. Soc.* **2006**, *27*, 439.
3. (a) Bi, X.; Dong, D.; Liu, Q.; Pan, W.; Zhao, L.; Li, B. *J. Am. Chem. Soc.* **2005**, *127*, 4578; (b) Barun, O.; Nandi, S.; Panda, K.; Ila, H.; Junjappa, H. *J. Org. Chem.* **2002**, *67*, 5398; (c) Ballini, R.; Barboni, L.; Fiorini, D.; Giarlo, G.; Palmieri, A. *Chem. Commun.* **2005**, 2633; (d) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901; (e) Asao, N.; Nogami, T.; Lee, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 10921; (f) Asao, N.; Takahashi, K.; Lee, S.; Kasahara, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 12650; (g) Asao, N.; Aikawa, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 7458; (h) Langer, P.; Bose, G. *Angew. Chem., Int. Ed.* **2003**, *42*, 4033; (i) Katritzky, A. R.; Li, J.; Xie, L. *Tetrahedron* **1999**, *55*, 8263, and further references cited in Ref. 1a.
4. For the synthesis and synthetic applicability of tetralone derivatives, see: (a) Zhang, L.; Kozmin, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 10204; (b) Gray, A. D.; Smyth, T. P. *J. Org. Chem.* **2001**, *66*, 7113; (c) Nguyen, P.; Corpuz, E.; Heidelbaugh, T. M.; Chow, K.; Garst, M. E. *J. Org. Chem.* **2003**, *68*, 10195; (d) Uenoyama, Y.; Tsukida, M.; Doi, T.; Ryu, I.; Studer, A. *Org. Lett.* **2005**, *7*, 2985; (e) Vargas, A. C.; Quiclet-Sire, B.; Zard, S. Z. *Org. Lett.* **2003**, *5*, 3717; (f) Taber, D. F.; Neubert, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 12416.
5. We observed the formation of a diastereomeric mixture of **4a** in less than 20% in all cases.
6. For the usefulness of *n*-tetrabutylammonium fluoride as the catalyst of Michael reaction, see: (a) Ooi, T.; Doda, K.; Maruoka, K. *J. Am. Chem. Soc.* **2003**, *125*, 9022; (b) Sharma, G. V. M.; Reddy, V. G.; Chander, A. S.; Reddy, K. R. *Tetrahedron: Asymmetry* **2002**, *13*, 21; (c) Matsumoto, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 770; (d) Li, W.-S.; Thottathil, J.; Murphy, M. *Tetrahedron Lett.* **1994**, *35*, 6591; (e) Jenner, G. *New J. Chem.* **1999**, *23*, 525.
7. Yamamoto and co-workers reported the effective catalytic activity of *n*-tetrabutylammonium fluoride (TBAF) in their synthesis of bicyclo[3.3.1]nonenols by the sequential Michael addition-intramolecular aldolization process with TBAF: (a) Aoyagi, K.; Nakamura, H.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 4148; (b) Nakamura, H.; Aoyagi, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1167.
8. For the leading references on the Michael reaction involving β-substituted Michael acceptors, see: (a) Shankar, R.; Jha, A. K.; Singh, U. S.; Hajela, K. *Tetrahedron Lett.* **2006**, *47*, 3077; (b) Correc, O.; Guillou, K.; Hamelin, J.; Paquin, L.; Texier-Boullet, F.; Toupet, L. *Tetraheron Lett.* **2004**, *45*, 391; (c) Geirsson, J. K. F.; Arnadottir, L.; Jonsson, S. *Tetrahedron* **2004**, *60*, 9149; (d) Xuan, J. X.; Fry, A. J. *Tetrahedron Lett.* **2001**, *42*, 3275; (e) Hoashi, Y.; Yabuta, T.; Takemoto, Y. *Tetrahedron Lett.* **2004**, *45*, 9185.
9. Spectroscopic data of prepared compounds are as follows:
Compound **5a** (pure single isomer, unknown stereochemistry): yellow solid, mp 213–214 °C; IR (KBr) 3059, 1641, 1537, 1342, 1273 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.31 (s, 1H), 1.94 (d, $J = 1.2$ Hz, 3H), 2.53 (dd, $J = 16.8$ and 2.7 Hz, 1H) 3.64 (d, $J = 16.8$ Hz, 1H) 4.75 (s, 1H), 6.98 (d, $J = 2.7$ Hz, 1H), 7.25–7.73 (m, 15H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.29, 26.28, 32.76, 50.56, 89.87, 127.40, 128.06, 128.40, 128.60, 128.66, 129.20, 129.24, 129.99, 132.43, 133.26, 134.56, 135.49, 136.18, 136.81, 136.87, 198.10; LCMS *m*/*z* 376 (M^+-HNO_2).
Compound **5f**-*cis*: 26%; colorless oil; IR (film) 2985, 1716, 1554, 1350, 1246 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.37 (t, $J = 7.2$ Hz, 3H), 1.56 (s, 1H), 2.37 (s, 1H), 3.13 (d, $J = 17.0$ Hz, 1H), 3.56 (d, $J = 17.0$ Hz, 1H), 4.26–4.43 (m, 3H), 7.20 (d, $J = 2.4$ Hz, 1H), 7.33–7.47 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.12, 16.40, 26.51, 29.69, 32.53, 49.24 (q, $J = 26.9$ Hz, 1C), 61.61, 84.13, 124.56 (q, $J = 282.2$ Hz, 1C), 128.43, 128.68, 129.60, 132.54, 135.58, 135.70, 144.85, 167.17; LCMS *m*/*z* 383 (M^+).
Compound **5f**-*trans*: 31%; colorless oil; IR (film) 2985, 1716, 1551, 1342, 1250, 1152 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.35 (t, $J = 7.2$ Hz, 3H), 1.77 (d, $J = 1.8$ Hz, 3H), 2.29 (s, 3H), 2.95 (dd, $J = 18.0$ and 3.3 Hz, 1H), 3.71 (d, $J = 18.0$ Hz, 1H), 4.22–4.40 (m, 2H), 4.88 (q, $J = 11.0$ Hz, 1H), 4.88 (q, $J = 11.0$ Hz, 1H), 7.07 (s, 1H), 7.30–7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.07, 16.82, 25.74, 34.02, 46.76 (q, $J = 26.9$ Hz, 1C), 61.34, 87.28, 120.03, 125.05 (q, $J = 279.6$ Hz, 1C), 127.95, 128.56, 129.18, 131.93, 133.45, 136.30, 145.25, 167.01.
Compound **6a**: 86%; colorless oil; IR (film) 3059, 2924, 1670, 1450 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.05 (s, 6H), 4.05 (s, 2H), 7.05–7.55 (m, 16H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.23, 19.90, 39.25, 126.09, 126.75, 127.58, 128.11, 128.50, 128.74, 129.15, 130.20, 132.34, 132.71, 133.72, 137.89, 138.28, 138.46, 138.66, 140.19, 140.73, 200.22; LCMS *m*/*z* 376 (M^+). Anal. Calcd for $C_{28}H_{24}O$: C, 89.33; H, 6.43. Found: C, 89.42; H, 6.55.
Compound **6b**: 71%; white solid, mp 86–88 °C; IR (film) 3024, 1697, 1493, 1450 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.91 (s, 3H), 2.06 (s, 3H), 4.01 (s, 2H), 7.05 (s, 1H), 7.16–7.41 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.82, 19.95, 32.46, 39.39, 126.09, 127.34, 128.23, 128.42, 128.49, 128.74, 130.06, 132.07, 133.56, 135.42, 138.70, 138.87, 139.92, 143.58, 208.39.
Compound **7b** (2-acetyl-4-benzoyl-3,6-dimethylbiphenyl): 3%; colorless oil; IR (film) 2924, 1701, 1666, 1239 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.95 (s, 3H), 2.12 (s, 3H), 2.16 (s, 3H), 7.22–7.91 (m, 11H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.53, 19.97, 32.19, 127.85, 128.18, 128.45, 128.63, 129.51, 129.76, 130.21, 133.56, 133.67, 137.25, 138.14, 138.96, 139.14, 143.99, 198.41, 207.24.
Compound **6c**: 74%; colorless oil; IR (film) 3060, 2966, 1697, 1452 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.11 (t, $J = 7.5$ Hz, 3H), 1.90 (s, 2H), 2.04 (s, 2H), 2.54

(q, $J = 7.5$ Hz, 2H), 4.05 (s, 2H), 7.02 (s, 1H), 7.17–7.39 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.71, 19.95, 23.15, 32.57, 38.25, 126.05, 127.29, 128.86, 128.77, 130.12, 132.48, 133.61, 134.80, 135.51, 138.08, 138.86, 140.51, 143.32, 207.82; LCMS m/z 328 (M^+).

Compound **7c** (2-acetyl-4-benzoyl-3-ethyl-6-methylbiphenyl): 3%; colorless oil; IR (film) 2925, 1699, 1667, 1447 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.07 (t, $J =$ 4.5 Hz, 3H), 1.95 (s, 3H), 2.10 (s, 3H), 2.57 (q, $J = 4.5$ Hz, 2H), 7.17 (s, 1H), 7.23–7.63 (m, 9H), 7.89 (d, $J = 4.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.66, 20.02, 23.48, 32.55, 127.82, 128.44, 128.54, 129.74, 129.87, 130.31, 133.51, 135.35, 137.37, 138.23, 138.74, 139.01, 143.71, 198.31, 206.93.

Compound **6d**: 75%; colorless oil; IR (film) 3059, 2966, 1697, 1454 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.99 (t, $J = 7.5$ Hz, 3H), 1.92 (s, 3H), 2.11 (s, 3H), 2.40 (q, $J = 7.5$ Hz, 2H), 4.03 (s, 2H), 7.08 (s, 1H), 7.16–7.40 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.59, 15.82, 25.83, 32.48, 39.54, 126.06, 127.32, 128.08, 128.25, 128.45, 128.70, 130.26, 130.58, 134.90, 138.55, 138.86, 139.92, 142.72, 208.47.

Compound **7d** (2-acetyl-4-benzoyl-6-ethyl-3-methylbiphenyl): 6%; colorless oil; IR (film) 3062, 2962, 1701, 1666, 1450 cm^{-1}; ^{1}H NMR($CDCl_3$, 300 MHz) δ 1.01 (t, $J = 7.5$ Hz, 3H), 1.95 (s, 3H), 2.16 (s, 3H), 2.44 (q, $J = 7.5$ Hz, 2H), 7.23–7.90 (m, 11H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.33, 16.53, 25.82, 32.23, 127.82, 127.97, 128.13, 128.31, 128.63, 129.97, 130.25, 133.55, 137.28, 137.83, 138.47, 139.29, 139.80, 144.16, 198.47, 207.39.

Compound **6e**: 71%; colorless oil; IR (film) 2978, 1725, 1282, 1188 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, $J = 7.2$ Hz, 3H), 2.05 (s, 3H), 2.20 (s, 3H), 3.91 (q, $J = 7.2$ Hz, 2H), 4.01 (s, 2H), 7.06 (s, 1H), 7.16–7.38 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.63, 16.14, 20.02, 39.37, 60.67, 126.06, 127.06, 127.87, 128.46, 128.75, 129.46, 130.13, 132.57, 133.63, 135.60, 137.25, 138.33, 139.34, 139.93, 170.01. Anal. Calcd for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02. Found: C, 83.61; H, 7.24.

Compound **6f**: 51%; colorless oil; IR (film) 2985, 1736, 1454, 1304, 1203, 1122 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.36 (t, $J = 7.2$ Hz, 3H), 2.15 (s, 3H), 2.42 (d, $J = 2.4$ Hz, 3H), 3.99 (s, 2H), 4.39 (q, $J = 7.2$ Hz, 2H), 7.07–7.32 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.95, 15.72, 19.91 (q, $J = 3.1$ Hz, 1 C), 39.44, 61.74, 122.47, 123.77, 124.94 (q, $J = 277.0$ Hz, 1C), 126.41, 128.64, 131.33, 133.75, 134.50, 134.97, 138.74, 143.09, 168.99. Anal. Calcd for $C_{19}H_{19}F_3O_2$: C, 67.85; H, 5.69. Found: C, 67.59; H, 5.88.

Compound **7f**: 17%; colorless oil; IR (film) 2987, 1736, 1674, 1450, 1369, 1246, 1130 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.38 (t, $J = 7.2$ Hz, 3H), 2.18 (s, 3H), 2.50 (s, 3H), 4.41 (q, $J = 7.2$ Hz, 2H), 7.22 (s, 1H), 7.46–7.51 (m, 2H), 7.60–7.66 (m, 1H), 7.78–7.81 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.94, 16.31, 19.97 (q, $J = 2.9$ Hz, 1C), 62.04, 123.84 (q, $J = 273.8$ Hz, 1C), 126.58 (q, $J = 29.7$ Hz, 1C), 128.84, 130.08, 130.69, 131.29, 134.07, 134.52 (q, $J = 2.9$ Hz, 1C), 135.14 (q, $J = 1.7$ Hz, 1C), 136.37, 142.91, 167.97, 196.88.

Compound **6g**: 81%; white solid, mp 68–70 °C; IR (film) 2939, 1678, 1454 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.09 (q, $J = 6.3$ Hz, 2H), 2.24 (s, 3H), 2.46 (s, 3H), 2.63(t, $J = 6.3$ Hz, 2H), 2.81 (t, $J = 6.3$ Hz, 2H), 4.00 (s, 2H), 7.07–7.28 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.34, 19.61, 22.50, 27.19, 39.48, 40.88, 125.90, 128.36, 128.44, 132.95, 133.04, 136.01, 136.71, 137.79, 140.34, 141.80, 201.59; LCMS m/z 264 (M^+). Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.20; H, 7.78.

Compound **6h**: 71%; colorless oil; IR (film) 2962, 1677, 1453 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.18 (t, $J = 7.8$ Hz, 3H), 2.08 (q, $J = 6.3$ Hz, 2H), 2.44 (s, 3H), 2.62 (q, $J = 7.8$ Hz, 2H), 2.64 (t, $J = 6.3$ Hz, 2H), 2.87 (t, $J = 6.3$ Hz, 2H), 4.03 (s, 2H), 7.08–7.29 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.63, 17.43, 22.60, 25.98, 26.45, 39.71, 40.86, 125.93, 128.40, 128.47, 133.31, 134.51, 136.81, 138.08, 138.86, 140.38, 141.22, 201.68.

10. Smith, M. B.; March, J. In *March's Advanced Organic Chemistry*, 5th ed.; John Wiley & Sons: New York, 2001; pp 1300–1306.