Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters
Tetrahedron Letters 47 (2006) 7343–7347

ortho Substituent effect on a 1,5-H shift reaction during thermal decomposition of aryltriazenes

Michael Harmata,* Xuechuan Hong and Pinguan Zheng

Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, United States

Received 27 June 2006; revised 4 August 2006; accepted 7 August 2006
Available online 1 September 2006

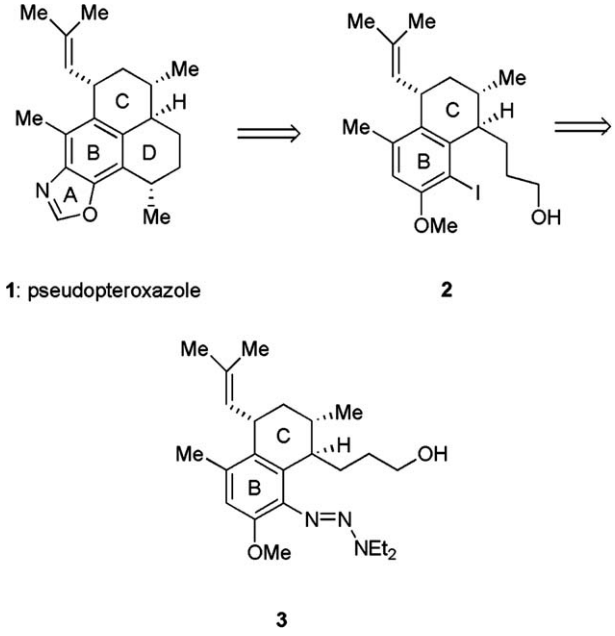
Abstract—An *ortho* substituent group has a significant effect on thermal decomposition of aryltriazenes. When the *ortho* methoxy-substituted phenyltriazenes were treated with methyl iodide at 110–130 °C, 1,5-H shift products were obtained in fair to moderate yields.

We have been investigating the synthesis of enantiomerically pure 2,1-benzothiazines as part of a program directed toward the synthesis of chiral ligands and natural products.[1] Most relevant here is the chemistry involving the stereoselective, intramolecular Michael addition of sulfoximine carbanions to α,β-unsaturated esters,[2] which provides a novel way to establish benzylic stereocenters with a high selectivity. This methodology was applied in the total syntheses of (+)-curcuphenol, (+)-curcumene,[3] erogorgiaene,[4] and pseudopteroxazole (**1**).[5]

During the course of our total synthesis of pseudopteroxazole (**1**),[5] we examined some aryltriazene chemistry as a method to introduce an iodide into the aromatic ring. In our initial approach toward pseudopteroxazole, we needed to install the iodide present in compound **2**, which would be obtained by the thermal decomposition of triazene **3** (Scheme 1).

Thus, a reductive desulfurization of **4** with Na/Hg provided aniline **5** in a 90% yield (Scheme 2).[6] Aniline **5** was then converted to 1-aryl-3,3-diethyltriazene **3** in 87% yield under standard conditions.[7] However, decomposition of **3** in neat methyl iodide in a sealed tube at 120–130 °C for 0.5 h generated 1,5-hydrogen atom transfer product **6** in a 61% yield and not the aryl iodide we desired (Scheme 2).[8,9]

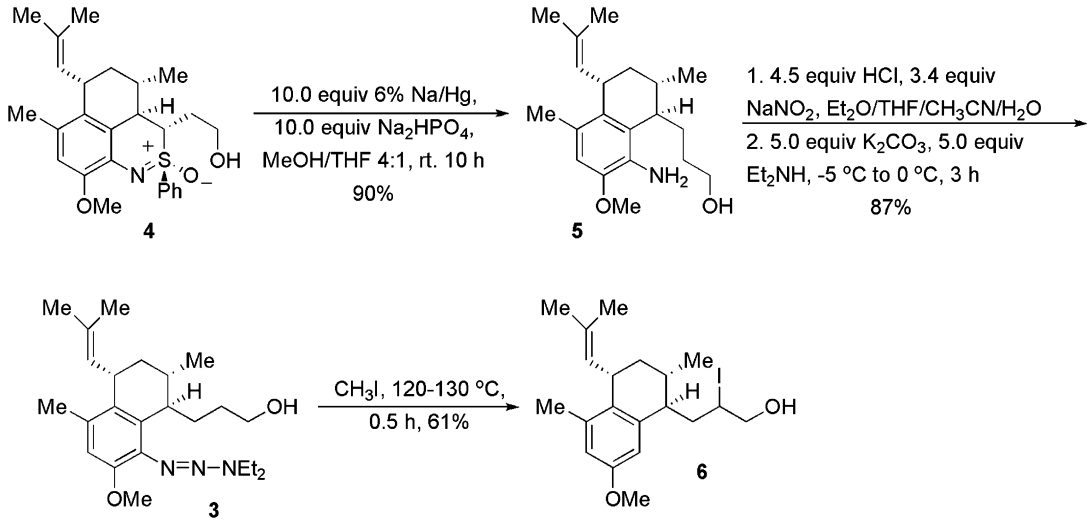
The formation of 1,5-hydrogen atom transfer product **6** prompted us to carry out a broader study of this reaction, since triazene derivatives are widely used in organic and medicinal chemistry. Triazenes have found use as metal complexes,[10] chelating agents,[11] hydrogenation catalysts,[12] iodo-masking groups in the preparation of N-containing heterocycles[13] and in the synthesis of macromolecules.[14] Triazine derivatives possess varied and strong biological and pharmacological activities[15] such as functioning as alkylating agents in tumor therapy.[16] While the 1,5-hydrogen atom transfer of several



Scheme 1.

* Corresponding author. Tel.: +1 573 882 1097; fax: +1 573 882 2754; e-mail: harmatam@missouri.edu

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.08.017



Scheme 2.

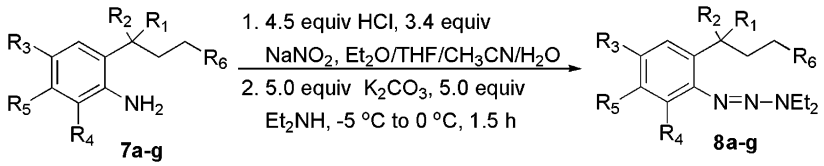
ortho-substituted aryl iodides has been achieved thermally,[17] to the best of our knowledge the related reaction using triazene chemistry has not been reported in the literature. Herein we report the *ortho* substituent effect on 1,5-H shift reactions by the thermal decomposition of aryltriazenes.

In most cases, synthesis of triazenes through the reaction of diazonium salts with secondary aliphatic amines like diethylamine is straightforward. 1-Aryl-3,3-diethyltriazenes **8a**–**g** were prepared by reacting salts **7a**–**g** with diethylamine in $Et_2O/THF/CH_3CN/H_2O$, in the presence of potassium carbonate at 0–5 °C (Table 1).[7] The reactions proceeded rapidly to completion and the yields of the triazenes were consistently high, usually greater than 90% (Table 1).[18]

Our initial evaluation of *ortho* substituent effects on 1,5-H shift reactions of aryltriazenes was carried out with hydrogen as an *ortho* substituent (Table 2, entries 1 and 2). The thermal decomposition of **8a**–**b** in neat methyl iodide in a sealed tube at 110–130 °C resulted in only aryl iodides **9a** and **9b** in 80% and 78% yields, respectively (Table 2, entries 1 and 2). Interestingly, no 1,5-H shift products were observed. However, the decomposition of *ortho*-methoxy-substituted aryltriazene **8c** provided not only aryl iodide **9c** in 45% yield, but 1,5-hydrogen atom transfer product **10c** as well in 40% yield (Table 2, entry 3). Thus, the replacement of an *ortho* hydrogen by a methoxy group has a great effect on the decomposition of triazene. Further studies showed this reaction to be very general. Treatment of various triazenes **8d**–**f** with methyl iodide in a sealed tube at 120–130 °C gave 1,5-hydrogen atom transfer products and aryl iodides in excellent yields and the yields of 1,5-hydrogen atom transfer products depended on the particular system. However, treatment of **8g** with similar conditions gave only decomposition (entry 7).[19]

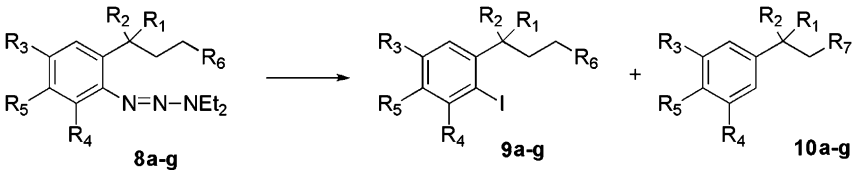
More than likely, 1,5-H shift reactions of the thermal decomposition of aryltriazenes can be attributed to a radical mechanism as outlined in Scheme 3. Accordingly, we formulated a possible mechanism for the reaction of triazene **8c**. Initial reaction of the nitrogen lone pair of triazene **8c** with methyl iodide gives intermediate **11**, which can follow one of two possible pathways: pathway 1 leads to the formation of product **9c** through nucleophilic attack by iodide, while pathway 2 is the radical pathway.[7a] For pathway 2, the formation of radical **13** occurs through diazonium cation formation

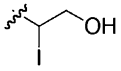
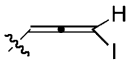
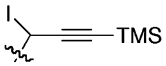
Table 1. Synthesis of 1-aryl-3,3-diethyltriazenes



Entry	Aniline	Yield (%)
1	**7a**: R_1 = Me (*S*), R_{2-4} = H, R_5 = Me, R_6 = OH	90
2	**7b**: R_1 = Me, R_{2-5} = H, R_6 = vinyl	87
3	**7c**: R_{1-3} = R_5 = H, R_4 = MeO, R_6 = vinyl	95
4	**7d**: R_{1-3} = R_5 = H, R_4 = MeO, R_6 = CH_2OH	92
5	**7e**: R_{1-3} = R_5 = H, R_4 = MeO, R_6 = ethynyl	94
6	**7f**: R_{1-3} = R_5 = H, R_4 = MeO, R_6 = TMSethynyl	96
7	**7g**: R_{1-3} = R_5 = H, R_4 = MeO, R_6 = $CHCHCO_2Et$	95

Table 2. Reaction of aryltriazenes with methyl iodide

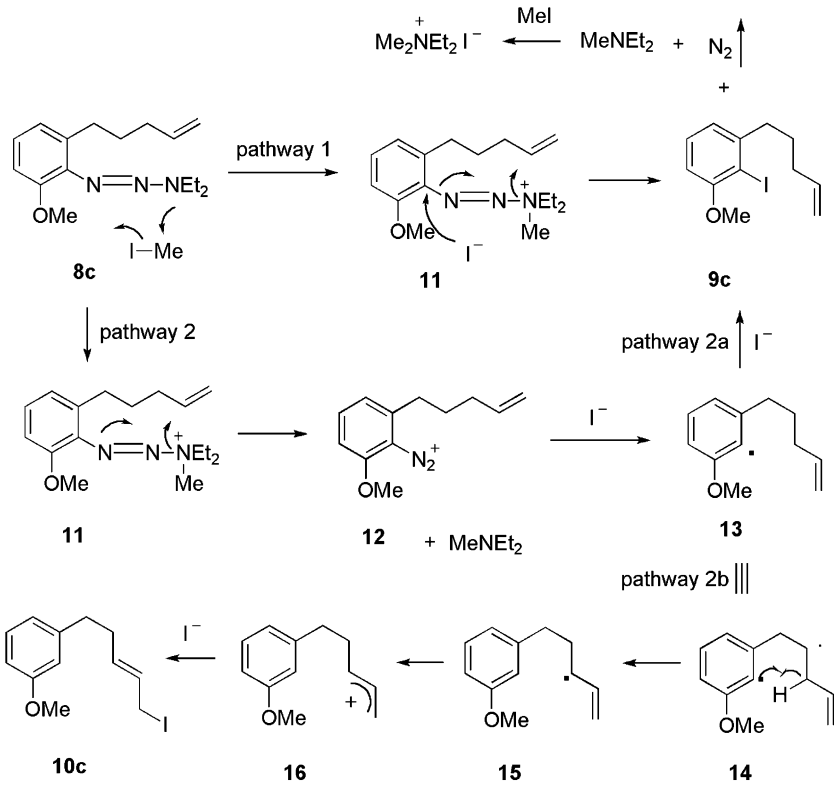


Entry	Triazene	Reaction conditions	R_7	**9** Yield (%)	**10** Yield (%)
1	**8a**	CH_3I, 130 °C, 0.5 h	—	80	0
2	**8b**	CH_3I, 110–120 °C, 24 h	—	78	0
3	**8c**	CH_3I, 120–130 °C, 24 h	–CH=CHCH$_2$I	45	40
4	**8d**	CH_3I, 120–130 °C, 0.5 h		59	14
5	**8e**	CH_3I, 120–130 °C, 1 h		74 (41/59)[a]	—
6	**8f**	CH_3I, 120–130 °C, 0.5 h		79 (42/58)[a]	—
7	**8g**	CH_3I, 110–120 °C, 1 h	—	[b]	[b]

[a] Mixture of **9**:**10** in ratio shown.
[b] Decomposition observed.

and single electron transfer. 1,5-Hydrogen atom transfer of **13** and subsequent reaction of the allyl radical with iodine anion at the terminus affords **10c** (pathway 2b); another route is that of the formation of iodide **9c** via radical **13** and iodine anion (pathway 2a).

In summary, we have studied the thermal decomposition of triazenes with and without *ortho* substituents. The results obviously showed that the *ortho* methoxy group has a significant effect on 1,5-H shift reactions and iodination. 1,5-H shift products were obtained in moderate yields when the *ortho* methoxy-substituted triazenes were treated with methyl iodide at 110–130 °C. Further investigations regarding the scope and application of benzothiazine chemistry will be reported in due course.



Scheme 3.

Acknowledgments

This work was supported by the NIH (1R01-AI59000-01A1), to whom we are grateful.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.08.017.

References and notes

1. (a) Harmata, M.; Ghosh, S. K. *Org. Lett.* **2001**, *3*, 3321; (b) Harmata, M. *Chemtracts* **2003**, *16*, 660; (c) Harmata, M.; Pavri, N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2419.
2. Harmata, M.; Hong, X. *J. Am. Chem. Soc.* **2003**, *125*, 5754.
3. Harmata, M.; Hong, X.; Barnes, C. L. *Tetrahedron Lett.* **2003**, *44*, 7261.
4. Harmata, M.; Hong, X. *Tetrahedron Lett.* **2005**, *46*, 3847.
5. (a) Harmata, M.; Hong, X.; Barnes, C. L. *Org. Lett.* **2004**, *6*, 2201; (b) Harmata, M.; Hong, X. *Org. Lett.* **2005**, *7*, 3581.
6. Harmata, M.; Kahraman, M. *Synthesis* **1994**, 142.
7. (a) Ku, H.; Barrio, J. R. *J. Org. Chem.* **1981**, *46*, 5239; (b) Satyamurthy, N.; Barrio, J. R. *J. Org. Chem.* **1983**, *43*, 4394.
8. Cary, J. M.; Moore, J. S. *Org. Lett.* **2002**, *4*, 4663.
9. Moore, J. S.; Weinstein, E. J.; Wu, Z. *Tetrahedron Lett.* **1991**, *32*, 2465.
10. Paul, P.; Tyagi, B.; Bilakhiya, A. K.; Dastidar, P.; Suresh, E. *Inorg. Chem.* **2000**, *39*, 14.
11. Lee, C. H.; Yamamoto, T. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 615.
12. Santra, P. K.; Sagar, P. *J. Mol. Catal. A: Chem.* **2003**, *197*, 37.
13. Wirshun, M.; Winkler, K. L.; Jochims, J. C. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1755.
14. (a) Young, J. K.; Nelson, J. C.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 10841; (b) Jones, L.; Schumm, J. S.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1388; (c) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402; (d) Bräse, S.; Enders, D.; Köbberling, J.; Avemaria, F. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 3413; (e) Nicolaou, K. C.; Boddy, C. N. C.; Li, H.; Koumbis, A. E.; Hughes, R.; Natarajan, S.; Jain, N. F.; Ramanjulu, J. M.; Bräse, S.; Soloman, M. E. *Chem. Eur. J.* **1999**, *5*, 2602; (f) Nicolaou, K. C.; Boddy, C. N. C.; Bräse, S.; Winssinger, N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2097.
15. (a) Iino, Y.; Karakida, T.; Sugamata, N.; Andoh, T.; Takei, H.; Takahashi, M.; Yaguchi, S.; Matsumo, Y.; Takehara, M.; Sakato, M.; Kawashina, S.; Morishita, Y. *Anticancer Res.* **1998**, *18*, 171; (b) Burkhard, K.; Steward, M.; Barret, M. P.; Brun, R.; Gilbert, I. H. *J. Med. Chem.* **2001**, *44*, 3440; (c) Nishimura, N.; Kato, A.; Maeba, I. *Carbohydr. Res.* **2001**, *331*, 77.
16. Rouzer, C. A.; Sabourin, M.; Skinner, T. L.; Thompson, E. J.; Wood, T. O.; Chmurny, G. N.; Klose, J. R.; Roman, J. M.; Smith, R. H., Jr.; Michejda, C. J. *Chem. Res. Toxicol.* **1996**, *9*, 172.
17. (a) Curran, D. P.; Fairweather, N. *J. Org. Chem.* **2003**, *68*, 2972; (b) Beckwith, A. L. J.; Meijs, G. F. *J. Org. Chem.* **1987**, *52*, 1922; (c) Abeywickrema, A. N.; Beckwith, A. L. J. *J. Chem. Soc., Chem. Commun.* **1986**, 464.
18. *Triazene synthesis*. General procedure: To a 50 mL round bottomed flask was added aniline (0.9 mmol), 4.5 M aq HCl (0.9 mL), and Et_2O/THF/CH_3CN 7:6:1 (5 mL). The mixture was chilled to 5 °C in an ice bath. A solution of $NaNO_2$ (211 mg, 3.06 mmol) in CH_3CN/H_2O 2:3 (4 mL) was added and the reaction mixture was stirred at 0–5 °C for 1 h. A second 50 mL round bottomed flask was charged with diethylamine (464 μL, 4.5 mmol), K_2CO_3 (621 mg, 4.5 mmol), and CH_3CN/H_2O 2:1 (5 mL), which was chilled to 0–5 °C in an ice bath. The solution of aniline was transferred over 15 min to the first flask, and stirred for an additional 1 h at 0–5 °C. The solution was extracted with 3×10 mL Et_2O. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuo, to give a brown oil. Purification of the product by basic aluminum oxide chromatography (5% Et_2O/pentane) afforded a colorless oil in excellent yield. Compound **8b**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.32–7.36 (m, 2H), 7.20–7.24 (m, 1H), 7.08–7.15 (m, 2H), 5.74–5.81 (m, 1H), 4.94 (d, $J = 18.7$ Hz, 1H), 4.88 (d, $J = 12.1$ Hz, 1H), 3.73 (q, $J = 7.1$ Hz, 4H), 3.60 (q, $J = 7.1$ Hz, 1H), 1.95–2.03 (m, 2H), 1.60–1.80 (m, 2H), 1.18–1.27 (m, 9H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 148.2, 139.2, 126.2, 126.0, 125.3, 116.5, 113.8, 37.0, 32.2, 32.0, 21.1. Compound **8c**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.05 (t, $J = 7.9$ Hz, 1H), 6.81–6.85 (m, 2H), 5.81–5.87 (m, 1H), 5.03 (dt, $J = 17.2$, 1.7 Hz, 1H), 4.97 (dt, $J = 10.2$, 0.9 Hz, 1H), 3.77–3.81 (m, 7H), 2.59 (dd, $J = 7.7$, 7.7 Hz, 2H), 2.09 (q, $J = 7.4$ Hz, 2H), 1.63–1.69 (m, 2H), 1.31 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.8, 139.9, 138.7, 136.3, 124.9, 122.1, 114.2, 109.9, 56.0, 33.6, 31.2, 29.8. Compound **8d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00 (t, $J = 7.9$ Hz, 1H), 6.74–6.79 (m, 2H), 3.71–3.76 (m, 7H), 3.52–3.54 (m, 2H), 2.53 (t, $J = 7.2$ Hz, 2H), 1.99 (s, 1H), 1.48–1.57 (m, 4H), 1.25 (t, $J = 7.1$ Hz, 6H). Compound **8e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.02 (t, $J = 7.9$ Hz, 1H), 6.79 (td, $J = 7.3$, 1.1 Hz, 2H), 3.76 (s, 3H), 3.75 (q, $J = 7.1$ Hz, 4H), 2.66 (t, $J = 7.6$ Hz, 2H), 2.16 (td, $J = 7.1$, 2.6 Hz, 2H), 1.94 (t, $J = 2.6$ Hz, 1H), 1.76 (dt, $J = 7.6$, 7.3 Hz, 2H), 1.27 (t, $J = 7.1$, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.8, 139.9, 135.3, 124.9, 122.2, 110.1, 84.3, 68.2, 56.0, 30.6, 29.1, 18.0. Compound **8f**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.00 (t, $J = 7.8$ Hz, 1H), 6.78–6.83 (m, 2H), 3.75 (s, 3H), 3.76 (q, $J = 7.1$ Hz, 4H), 2.65 (t, $J = 7.5$ Hz, 2H), 2.20 (t, $J = 7.2$ Hz, 2H), 1.75 (dt, $J = 14.9$, 7.5 Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 6H), 0.16 (s, 9H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 151.9, 140.0, 135.5, 125.0, 122.3, 110.3, 107.5, 84.4, 56.1, 30.8, 29.3, 19.5, 0.14. Compound **8g**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.88–7.05 (m, 2H), 6.76–6.80 (m, 2H), 5.78 (dt, $J = 15.6$, 1.4 Hz, 1H), 4.16 (q, $J = 7.1$ Hz, 2 H), 3.70–3.79 (m, 7H), 2.56 (dd, $J = 6.9$, 6.9 Hz, 2H), 2.17 (q, $J = 7.2$ Hz, 2H), 1.68 (td, $J = 15.1$, 7.6 Hz, 2H), 1.23–1.30 (m, 9H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 166.6, 151.9, 149.1, 140.0, 135.7, 125.0, 122.1, 121.3, 110.3, 60.0, 56.1, 31.9, 31.1, 28.8, 14.2.
19. *General procedure for decomposition of triazenes*: A 10 mL sealed tube under Ar was charged with triazene (0.076 mmol) in methyl iodide (2 mL). The solution was degassed, sealed, and stirred at 110–130 °C for 20 h. The methyl iodide was removed under reduced pressure and the red residue was dissolved in Et_2O (10 mL), washed with saturated $Na_2S_2O_3$ solution, water, and dried over $MgSO_4$. Removal of the solvent gave a crude product. Purification of the product by flash chromatography (20% EtOAc/pentanes) afforded two colorless oils. However, the products were not always separable. Compound **9b**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (dd, $J = 7.9$, 1.2 Hz, 1H), 7.30 (td, $J = 7.4$, 1.2 Hz, 1H), 7.18 (dd, $J = 7.8$, 1.6 Hz, 1H), 6.88 (td, $J = 7.5$, 1.8 Hz, 1H), 5.80–5.81 (m, 1H),

4.92–5.00 (m, 2H), 3.08 (q, $J = 7.0$ Hz, 1H), 2.06 (m, 1H), 1.98 (m, 1H), 1.73–1.75 (m, 1H), 1.43–1.63 (m, 1H), 1.19 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.2, 139.5, 138.5, 128.5, 127.7, 126.5, 114.5, 101.8, 42.8, 36.7, 31.6, 21.3. Compound **9c**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.20 (t, $J = 7.8$ Hz, 1H), 6.83 (dd, $J = 7.6$, 1.1 Hz, 1H), 6.64 (dd, $J = 8.1$, 1.1 Hz, 1H), 5.81–5.92 (m, 1H), 5.05 (dd, $J = 8.1$, 1.1 Hz, 1H), 5.00 (d, $J = 11.8$ Hz, 1H), 3.87 (s, 3H), 2.78 (dd, $J = 7.8$, 7.8 Hz, 2H), 2.14 (q, $J = 7.1$ Hz, 2H), 1.63–1.75 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 158.1, 147.0, 138.4, 128.8, 121.9, 114.8, 108.2, 92.8, 56.4, 40.6, 33.3, 29.2. Compound **10c**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.16–7.25 (m, 1H), 6.71–6.77 (m, 3H), 5.71–5.76 (m, 2H), 3.84–3.87 (m, 2H), 3.79 (s, 3H), 2.63–2.71 (m, 2H), 2.31–2.43 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 159.5, 142.9, 133.9, 129.2, 128.4, 120.7, 114.1, 111.1, 55.1, 35.1, 33.5, 6.40. Compound **9d**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.19 (t, $J = 7.8$ Hz, 1H), 6.83 (dd, $J = 7.6$, 1.2 Hz, 1H), 6.64 (dd, $J = 8.1$, 1.2 Hz, 1H), 3.86 (s, 3H), 3.67 (t, $J = 5.8$ Hz, 2H), 2.77–2.83 (m, 2H), 1.63–1.71 (m, 4H), 1.59 (s, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 158.0, 146.8, 128.8, 121.8, 108.3, 92.7, 62.6, 56.4, 40.7, 32.2, 26.2. Compound **10d**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.17–7.25 (m, 1H), 6.73–6.81 (m, 3H), 4.11–4.14 (m, 1H), 3.79 (s, 3H), 3.70–3.77 (m, 2H), 2.82–2.88 (m, 1H), 2.66–2.74 (m, 1H), 1.97–2.19 (m, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 159.7, 142.0, 129.5, 120.8, 114.3, 111.5, 68.5, 55.1, 40.6, 37.5, 35.3. Compound **9e**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.17–7.24 (m, 1H), 6.86 (dd, $J = 7.5$, 1.1 Hz, 1H), 6.65 (dd, $J = 7.7$, 0.9 Hz, 1H), 3.87 (s, 3H), 2.90 (dd, $J = 7.9$, 7.5 Hz, 2H), 2.24 (td, $J = 7.0$, 2.6 Hz, 2H), 2.00 (t, $J = 2.6$ Hz, 1H), 1.84 (q, $J = 7.5$ Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 158.2, 146.1, 128.8, 122.1, 108.5, 92.0, 84.0, 68.8, 56.4, 29.0, 28.6, 17.9. Compound **10e**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.20 (t, $J = 8.0$ Hz, 1H), 6.73–6.80 (m, 3H), 5.69 (dt, $J =$ 5.7, 2.5 Hz, 1H), 5.12 (td, $J = 6.4$, 5.9 Hz, 1H), 3.80 (s, 3H), 2.74 (t, $J = 7.6$ Hz, 2H), 2.40–2.49 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 205.3, 159.6, 142.6, 129.3, 120.7, 114.4, 111.4, 95.5, 55.1, 39.9, 35.9, 34.6. Compound **9f**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.20–7.27 (m, 1H), 6.90 (dd, $J = 7.6$, 1.2 Hz, 1H), 6.67 (dd, $J = 8.1$, 1.1 Hz, 1H), 3.89 (s, 3H), 2.75–2.95 (m, 2H), 2.21–2.34 (m, 2H), 1.85 (dt, $J = 15.2$, 7.6 Hz, 2H), 0.21 (s, 9H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 158.1, 146.2, 128.8, 122.1, 108.4, 106.9, 92.7, 85.1, 56.4, 40.0. Compound **10f**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.23 (td, $J = 7.6$, 1.8 Hz, 1H), 6.78–6.83 (m, 3H), 4.47 (t, $J = 6.9$ Hz, 1H), 3.82 (s, 3H), 2.75–2.95 (m, 2H), 2.21–2.34 (m, 2H), 0.21 (s, 9H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 159.7, 141.5, 129.5, 120.8, 114.3, 111.5, 106.0, 91.7, 55.1, 42.3, 35.1, 9.8, −0.29.