Supporting Information

Ruthenium-Catalyzed Alkenylation of Azoxybenzenes with Alkenes through *ortho*-Selective C–H Activation

Hongji Li,[†] Xiaoyu Xie,[†] and Lei Wang*^{†‡}

[†] Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P R China, Tel: +86-561-3802-069 Fax: +86-561-3090-518 E-mail: leiwang@chnu.edu.cn
[‡] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P R China

Table of Contents for Supporting Information

1. (General considerations	.1
2. 7	Typical procedure for the alkenylation of azoxybenzenes with alkenens	1
3.	Effect of solvent on the alkenylation reaction	2
4. 7	Typical procedure for the hydrolysis of product 3a 2	
5.	Ruthenium-catalyzed H/D exchange in DCE/D ₂ O	3
6. 7	Typical procedure for intermolecular competition experiments	4
7. 1	References	5
8. (Characterization data for the products	6
9. ¹	¹ H and ¹³ C NMR spectra of the products	14

1. General considerations

All ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz or 100 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument.

Azoxybenzenes were prepared from arylamines in SeO₂/H₂O₂/MeOH system,¹ and which must be recrystallized from ethanol before use. The chemicals and solvents were purchased from commercial suppliers either Shanghai Chemical Company, China, or from TCI, Japan. All the solvents were dried and freshly distilled in N₂ prior to use. Products were purified by flash chromatography on 200–300 mesh silica gels, SiO₂.

2. Typical procedure for the alkenylation of azoxybenzenes with alkenens

In glove-box, a 10 mL of Schlenk tube was charged with azoxybenzene (1a, 39.6 mg, 0.20 mmol), ethyl acrylate (2a, 30.0 mg, 0.30 mmol), [Cp*RuCl₂]_n (3.1 mg, containing 5.0 mol% Ru), AgSbF₆ (13.7 mg, 0.04 mmol), and Cu(OAc)₂ (36.3 mg, 0.20 mmol). Then anhydrous 1,2-dichloroethane (DCE, 1.0 mL) was injected into the Schlenk tube under N₂ atmosphere out of the glove-box. The reaction tube was placed in an oil bath. After the reaction was performed at 110 °C for 12 h, it was cooled to room temperature and detected by TLC, extracted with dichloromethane (DCM, 3×5.0 mL). The organic layers were combined, dried over MgSO₄, and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate $15:1\rightarrow9:1$, v/v), affording the desired product **3a** as a pale yellow liquid (40.3 mg, 68%).

3. Effect of solvent on the alkenylation reaction

· · · ·	<i>*</i>		
$ \begin{array}{c} $	+ OEt 2a	[Cp*RuCl ₂] _n (5.0 mol%) Cu(OAc) ₂ , Solvent, N ₂ , 110°	$ \begin{array}{c} $
entry		solvent	vield [%] ^b
1		DOE	
1		DCE	68
2		PhCH ₃	33
3		THF	trace
4		CH ₃ OH	NR
5		DMF	NR
6		DMSO	trace
7		CH ₃ CN	NR
8		diglyme	NR
^{<i>a</i>} Reaction conditions:	azoxybenzene (1a.	0.20 mmol), ethyl acrylate (2	a , 0.30 mmol), $[Cp*RuCl_2]_n$

Table S1 Effect of the solvent on the alkenylation reaction of azoxybenzene (1a) with ethyl acrylate $(2a)^a$

^{*a*} Reaction conditions: azoxybenzene (**1a**, 0.20 mmol), ethyl acrylate (**2a**, 0.30 mmol), $[Cp*RuCl_2]_n$ (containing 5.0 mol% Ru), AgSbF₆ (0.04 mmol), Cu(OAc)₂ (0.10 mmol), solvent (1.0 mL), 110 °C, Schlenk tube, N₂, 12 h. ^{*b*} Isolated yields.

4. Typical procedure for the hydrolysis of the product 3a

In open air, a reaction tube (5.0 mL) was charged with **3a** (59.2 mg, 0.20 mmol), NaOH (8.0 mg, 0.20 mmol) and MeOH (1.0 mL). The reaction mixture was stirred at 80 °C for 30 min. After starting material was completely disappeared, the resulting mixture was diluted with water and extracted with 1,2-dichloroethane (DCE, 3×5.0 mL). The organic layer was combined, dried over MgSO₄ and evaporated under reduced pressure. The residue was purified by flash chromatography (silica gel, pure ethyl acetate), affording the desired product **4a** as a white powder (51.5 mg, 96% yield).

5. Ruthenium-catalyzed H/D exchange in DCE/D₂O

In a nitrogen atmosphere, a dried Schlenk tube (10 mL) was charged with azoxybenzene (**1a**, 39.6 mg, 0.20 mmol), [Cp*RuCl₂]_n (3.1 mg, containing 5.0 mol% Ru), AgSbF₆ (13.8 mg, 0.04 mmol), Cu(OAc)₂ (36.3 mg, 0.20 mmol). Then anhydrous 1,2-dichloroethane (DCE, 0.50 mL) and D₂O (0.50 mL) were injected into the Schlenk tube. The reaction was performed in oil bath at 110 °C for 12 h, and it was cooled to room temperature. The reaction mixture was diluted with water and extracted with DCM (3×5 mL). The organic layers were combined, dried over MgSO₄, and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 9:1, v/v), affording the product **1a**-D₂ (38.9 mg). The deuterium incorporation was estimated by ¹H-NMR spectroscopy (See following ¹H NMR spectra).





6. Typical procedure for the intermolecular competition experiment

(1) In a glove-box, a Schlenk tube (10 mL) was charged with **1a** (158.4 mg, 0.80 mmol), **1h** (206.5 mg, 0.80 mmol), ethyl acrylate (**2a**, 40.0 mg, 0.40 mmol), [Cp*RuCl₂]_n (6.2 mg, containing 5.0 mol% Ru), AgSbF₆ (27.6 mg, 0.08 mmol), Cu(OAc)₂ (72.6 mg, 0.40 mmol). Then anhydrous 1,2-dichloroethane (DCE, 2.0 mL) was injected into the Schlenk tube under N₂ atmosphere. The reaction was performed in oil bath at 110 °C for 12 h and detected by TLC. The reaction mixture was diluted with water and extracted with DCM (3×10 mL). The organic layers were combined, dried over MgSO₄, and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 9:1→3:1, v/v), affording the desired product **3a** (31.2 mg, 0.104mmol) in 25% yield, and **3u** (63.0 mg , 0.176 mmol) in 44% yield. The calculated value for the molar ratio of products **3a:3u** was 1:1.6.

(2) The intermolecular competition experiment of **1b** and **1h** with ethyl acrylate **2a** was carried out under the above reaction conditions. The products **3o** and **3u** were isolated in 18.1 % yield (24.0 mg, 0.0722 mmol), and 40.5 % yield (57.7 mg, 0.162 mmol). The calculated value for the molar ratio of products **3o**:**3u** was 1:2.2.

7. References

1. Christin, G.; Beate, P.; Elisabeth, I., Karola, R.-B. Synthesis 2008, 1889.

8. Characterization data for the products



3a: ¹H NMR (400 MHz, CDCl₃): δ 8.16 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 15.6 Hz, 1H), 7.85–7.83 (m, 1H), 7.69–7.67 (m, 1H), 7.53–7.48 (m, 4H), 7.44–7.42 (m, 1H), 6.42 (d, *J* = 15.6 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.17, 143.84, 139.73, 130.53, 130.29, 130.16, 128.89, 128.75, 127.99, 125.40, 124.19, 121.56, 60.65, 14.21. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₁₇H₁₇N₂O₃: 297.1239, Found: 297.1238.



3b: ¹H NMR (400 MHz, CDCl₃): δ 8.16 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 16.0 Hz, 1H), 7.84–7.82 (m, 1H), 7.69–7.67 (m, 1H), 7.55–7.45 (m, 4H), 7.43–7.41 (m, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 3.78 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.65, 143.88, 140.03, 130.58, 130.39, 130.24, 128.84, 128.81, 128.07, 125.47, 124.26, 121.14, 51.85. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₁₆H₁₅N₂O₃: 283.1083, Found: 283.1083.



3c: ¹H NMR (400 MHz, CDCl₃): δ 8.20–8.14 (m, *J* = 8.0 Hz, 3H), 7.91–7.88 (m, 1H), 7.71–7.68 (m, 1H), 7.69–7.67 (m, 1H), 7.57–7.55 (m, 2H), 7.53–7.48 (m, 2H), 7.45–7.42 (m, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.57 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 164.42, 143.76, 142.67, 130.89, 130.70, 130.33, 128.82, 128.40, 128.16, 125.43, 124.36, 121.60, 119.05, 60.69, 60.32. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₁₇H₁₄F₃N₂O₃: 351.0957, Found: 351.0957.



3d: ¹H NMR (400 MHz, CDCl₃): δ 8.16 (d, *J* = 7.6 Hz, 2H), 8.02 (d, *J* = 16.0 Hz, 1H), 7.84–7.82 (m, 1H), 7.70–7.67 (m, 1H), 7.53–7.50 (m, 4H), 7.48–7.43 (m, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.18 (t, *J* = 6.8 Hz, 2H), 1.66–1.61 (m, 2H), 1.40–1.35 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.23, 143.81, 139.61, 130.50, 130.28, 130.15, 128.83, 128.74, 127.95, 125.39, 124.14, 121.57, 64.55, 30.65, 19.12, 13.66. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₁₉H₂₁N₂O₃: 325.1552, Found: 325.1553.



3e: ¹H NMR (400 MHz, CDCl₃): δ 8.16 (dd, *J* = 6.8 Hz, *J* = 4.8 Hz, 2H), 7.92 (d, *J* = 16.0 Hz, 1H), 7.82– 7.80 (m, 1H), 7.69–7.67 (m, 1H), 7.52–7.50 (m, 4H), 7.48–7.42 (m, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 1.49 (s, 2H), 1.66–1.61 (m, 2H), 1.40–1.35 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.43, 143.83, 138.48, 130.44, 130.12, 130.09, 128.97, 128.79, 128.74, 128.69, 127.87, 125.51, 125.38, 124.09, 123.47, 122.34, 80.78, 28.09. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₁₉H₂₁N₂O₃: 325.1552, Found: 325.1552.



3f: ¹H NMR (400 MHz, CDCl₃): δ 8.16 (d, *J* = 7.2 Hz, 2H), 8.00 (d, *J* = 16.0 Hz, 1H), 7.84–7.81 (m, 1H), 7.71–7.69 (m, 1H), 7.54–7.49 (m, 4H), 7.47–7.43 (m, 1H), 6.43 (d, *J* = 16.0 Hz, 1H), 4.11–4.08 (m, 2H), 1.35–1.21 (m, 10H), 0.89–0.84 (m, 7H); ¹³C NMR (100 MHz, CDCl₃): δ 166.34, 143.84, 139.47, 130.49, 130.32, 130.19, 128.83, 128.76, 127.96, 125.44, 124.12, 121.67, 67.08, 38.81, 30.40, 28.92, 23.81, 22.91, 14.01, 10.99. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₂₂H₂₇N₂O₃: 367.2022, Found: 367.2021.



3g: ¹H NMR (400 MHz, CDCl₃): δ 8.13 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 15.6 Hz, 1H), 7.83–7.81 (m, 1H), 7.67–7.64 (m, 1H), 7.52–7.49 (m, 2H), 7.46–7.39 (m, 3H), 7.28–7.24 (m, 1H), 6.96–6.87 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.52 (t, *J* = 4.8 Hz, 1H), 4.19 (t, *J* = 4.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 166.06, 158.45, 143.81, 140.59, 130.58, 130.44, 130.18, 129.50, 129.42, 128.77, 128.05, 125.41, 124.23, 121.17, 120.89, 114.66, 65.83, 63.06. HRMS (ESI) ([M+H]⁺) Calcd. for C₂₃H₂₁N₂O₄: 389.1501, Found: 389.1501.



3h: ¹H NMR (400 MHz, CDCl₃): δ 8.16–8.09 (m, 3H), 7.86–7.84 (m, 1H), 7.69–7.67 (m, 1H), 7.53–7.45 (m, 4H), 7.44–7.32 (m, 6H), 6.47 (d, *J* = 16.0 Hz, 1H), 5.24 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 165.92, 143.81, 140.34, 135.86, 130.52, 130.38, 130.13, 128.75, 128.52, 128.17, 128.10, 127.98, 125.39, 124.18, 121.13, 66.42. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₂₂H₁₉N₂O₃: 359.1396, Found: 359.1396.



3i: ¹H NMR (400 MHz, CDCl₃): δ 8.19–8.16 (m, 2H), 8.10 (d, *J* = 16.0 Hz, 1H), 7.85 (dd, *J* = 6.0 Hz, *J* = 3.2 Hz, 1H), 7.70–7.68 (m, 1H), 7.58–7.50 (m, 5H), 7.46–7.44 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 166.41, 140.66, 130.59, 130.47, 130.25, 128.81, 128.80, 128.04, 125.39, 124.25, 120.81, 66.36, 61.25. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₁₇H₁₇N₂O₄: 313.1188, Found: 313.1188.



3j: ¹H NMR (400 MHz, CDCl₃): δ 8.28 (d, *J* = 16.0 Hz, 1H), 8.19 (d, *J* = 7.6 Hz, 2H), 7.92–7.90 (m, 1H), 7.78–7.76 (m, 1H), 7.59–7.57 (m, 2H), 7.52–7.49 (m, 2H), 7.45–7.39 (m, 3H), 7.28–7.24 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.63 (d, *J* = 16.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 164.58, 150.68, 143.80, 141.88, 130.68, 130.66, 130.24, 129.38, 128.79, 128.66, 128.17, 125.81, 125.42, 124.32, 121.52, 120.54. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₂₁H₁₇N₂O₃: 345.1239, Found: 345.1239.



3k: ¹H NMR (400 MHz, CDCl₃): δ 8.24 (d, *J* = 16.0 Hz, 1H), 8.18–8.16 (m, 2H), 7.89–7.87 (m, 1H), 7.75–7.41 (m, 1H), 7.58–7.53 (m, 2H), 7.50–7.46 (m, 2H), 7.43–7.39 (m, 1H), 7.18–7.17 (m, 2H), 7.03–6.57 (m, 2H), 6.59 (d, *J* = 16.0 Hz, 1H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 164.82, 148.39, 143.76, 141.69, 135.45, 130.66, 130.64, 130.24, 129.89, 128.78, 128.67, 128.15, 125.42, 124.30, 121.17, 120.61, 115.02, 20.84. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₂₂H₁₉N₂O₃: 359.1396, Found: 359.1396.



31: ¹H NMR (400 MHz, CDCl₃): δ 8.27 (d, *J* = 16.0 Hz, 1H), 8.18 (d, *J* = 7.2 Hz, 2H), 7.92–7.90 (m, 1H), 7.76–7.74 (m, 1H), 7.59–7.57 (m, 2H), 7.52–7.48 (m, 3H), 7.45–7.44 (m, 1H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.12–7.09 (m, 2H), 6.59 (d, *J* = 16.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 164.34, 149.11, 143.77, 142.36, 131.19, 130.84, 130.72, 130.33, 129.44, 128.82, 128.53, 128.18, 125.43, 124.38, 122.91, 120.06. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₂₁H₁₆N₂O₃: 379.0849, Found: 379.0849.



3m: ¹H NMR (400 MHz, CDCl₃): δ 8.14 (d, J = 8.4 Hz, 2H), 7.82–7.76 (m, 2H), 7.72–7.62 (m, 1H), 7.53–7.42 (m, 4H), 7.41–7.27 (m, 1H), 6.26 (t, J = 4.4 Hz, 1H), 4.12–4.05 (m, 4H), 1.34–1.21 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 143.74, 143.35(d, J = 7.7 Hz), 130.45, 130.12 (d, J = 6.3 Hz), 129.51, 128.65, 127.84, (d, J = 1.6 Hz), 125.29, 123.96 (d, J = 0.9 Hz), 119.04, 117.15 (d, J = 3.4 Hz), 61.97 (d, J = 5.6 Hz), 16.19 (d, J = 6.4 Hz). HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₁₈H₂₂N₂O₄P: 361.1317, Found: 361.1317.



3n: ¹H NMR (400 MHz, CDCl₃): δ 8.17–8.15 (m, 2H), 7.87–7.78 (m, 2H), 7.66–7.64 (m, 1H), 7.54–7.48 (m, 4H), 7.44–7.42 (m, 1H), 6.23 (d, *J* = 4.4 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 144.52 (d, *J* = 7.7 Hz), 130.58, 130.34, 130.18, 129.53, 129.29, 128.74, 127.98, 127.97, 125.34, 124.13, 124.11, 117.57, 115.67, 52.58, 52.55 (d, *J* = 5.9 Hz). HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₁₆H₁₈N₂O₄P: 333.1004, Found: 333.1002.



30: ¹H NMR (400 MHz, CDCl₃): δ 8.26–8.23 (m, 2H), 8.01 (d, *J* = 16.0 Hz, 1H), 7.89 (dd, *J* = 8.8 Hz, *J* = 5.2 Hz, 1H), 7.22–7.14 (m, 3H), 6.38 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 6.8 Hz, 2H), 1.31 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.85, 164.24 (d, *J*_{C-F} = 15.5 Hz), 161.81, 161.65, 140.27 (d, *J*_{C-F} = 3.4 Hz), 139.05 (d, *J*_{C-F} = 2.0 Hz), 131.64 (d, *J*_{C-F} = 8.3 Hz), 128.01 (d, *J*_{C-F} = 8.6 Hz), 126.63, 126.54, 122.57, 117.10 (d, *J*_{C-F} = 23.0 Hz), 115.73 (d, *J*_{C-F} = 22.4 Hz), 114.64 (d, *J*_{C-F} = 23.9 Hz), 60.85, 14.21. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₁₇H₁₅F₂N₂O₃: 333.1051 , Found: 333.1050.



3p: ¹H NMR (400 MHz, CDCl₃): δ 8.14 (d, *J* = 8.8 Hz, 2H), 8.01 (d *J* = 16.0 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 1.6 Hz, 1H), 7.48–7.44 (m, 4H), 6.38 (d, *J* = 16.0 Hz, 1H), 4.25 (d, *J* = 6.8 Hz, 2H), 1.31 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.80, 142.13, 138.91, 136.85, 135.82, 130.90, 130.03, 129.01, 128.09, 126.94, 125.72, 123.69, 122.62, 60.84. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₁₇H₁₅Cl₂N₂O₃: 365.0460, Found: 365.0460.



3q: ¹H NMR (400 MHz, CDCl₃): δ 8.28 (s, 1H), 8.11–8.09 (m, 5H), 7.94 (d, *J* = 16.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.38–4.31 (m, 4H), 4.21–4.18 (m, 2H), 1.38–1.33 (m, 6H), 1.24 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.87, 165.61, 164.66, 150.78, 146.64, 138.71, 132.73, 131.49, 131.14, 130.17, 129.57, 129.34, 125.12, 124.50, 122.79, 61.83, 61.25, 60.83. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₂₃H₂₅N₂O₇: 441.1662, Found: 441.1662.



3r: ¹H NMR (400 MHz, CDCl₃): δ 8.07–7.99 (m, 3H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.41 (s, 1H), 7.25–7.22 (m, 3H), 6.34 (d, *J* = 16.0 Hz, 1H), 4.20 (q, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 2.38 (s, 3H), 1.26 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.29, 141.74, 140.79, 140.66, 140.38, 130.84, 129.30, 128.73, 128.41, 125.51, 124.12, 121.03, 60.56, 21.57, 21.22, 14.23. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₁₉H₂₁N₂O₃: 325.1552, Found: 325.1552.



3s: ¹H NMR (400 MHz, CDCl₃): δ 8.02–7.96 (m, 3H), 7.62 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 1H), 6.39 (d, *J* = 15.6 Hz, 1H), 4.24 (q, *J* = 6.8 Hz, 2H), 2.45 (s, 3H), 2.44 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.26, 148.71, 143.84, 141.16, 139.46, 138.47, 131.16, 130.83, 128.48, 127.67, 125.85, 125.75, 124.50,122.38, 120.59, 60.48, 21.37, 21.13, 14.17. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₁₉H₂₁N₂O₃: 325.1552, Found: 325.1552.



3t: ¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 15.6 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.31–7.27 (m, 1H), 7.25–7.20 (m, 4H), 6.40 (d, *J* = 15.6 Hz, 1H), 4.17–4.11 (m, 2H), 2.35 (s, 3H), 2.30 (s, 3H), 1.21 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.96, 142.23, 137.90, 134.49, 132.65, 131.11, 130.90, 129.23, 128.96, 127.71, 125.99, 124.68, 122.21, 121.44, 60.64, 18.35, 16.82, 14.17. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₁₉H₂₁N₂O₃: 325.1552, Found: 325.1552.



3u: ¹H NMR (400 MHz, CDCl₃): δ 8.27 (d, *J* = 8.8 Hz, 2H), 8.12 (d, *J* = 15.6 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.08 (d, *J* = 3.2 Hz, 1H), 7.00–6.97 (m, 1H), 6.35 (d, *J* = 15.6 Hz, 1H), 4.25 (q, *J* = 7.6 Hz, 2H), 3.89 (s, 3H), 3.88 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 166.25, 160.60, 160.57, 141.01, 137.91, 130.65, 127.73, 125.86, 121.01, 115.32, 113.70, 112.62, 60.59, 55.73, 55.46. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₁₉H₂₁N₂O₅: 357.1450, Found: 357.1451.



4a: ¹H NMR (DMSO- d_6 , 400 MHz): δ 8.03 (d, J = 8.0 Hz, 2H), 7.98–7.95 (m, 1H), 7.84–7.82 (m, 1H), 7.68 (d, J = 15.2 Hz, 1H), 7.61–7.60 (m, 2H), 7.57–7.55 (m, 2H), 7.53–7.48 (m, 1H), 6.59 (d, J = 16.0 Hz, 1H); ¹³C NMR (DMSO- d_6 , 100 MHz): δ 167.40, 148.72, 143.71, 137.96, 131.25, 131.19, 130.66, 129.41, 128.35, 127.75, 125.10, 124.25, 123.07. HRMS (MALDI-DHB) ([M+H]⁺) Calcd. for C₁₅H₁₃N₂O₃: 269.0926, Found: 269.0926.

9. ¹H and ¹³C NMR spectra of the products





























































