Palladium-Catalyzed Cross-Coupling Reaction of Sulfoxonium Ylides and Benzyl Bromides by Carbene Migratory Insertion

Kaichuan Yan, Maoyao He, Jianglian Li, Hua He, Ruizhi Lai, Yi Luo, Li Guo* and Yong Wu*

Key Laboratory of Drug-Targeting and Drug Delivery System of the Education Ministry, Sichuan Engineering Laboratory for Plant-Sourced Drug and Sichuan Research Center for Drug Precision Industrial Technology, West China School of Pharmacy, Sichuan University, Chengdu, 610041 (P.R. China)

Table of Contents

1. General Information……………………………………………………….…. S2

2. Experimental section .…………………………………………………  …….….…. S 2

  2.1. Synthesis of sulfoxonium ylides ….….….….…….….…….….…….….…. S2

  2.2. Typical procedure for Pd-catalyzed cross-coupling reaction …………S2

3. Characterization data for the products ………………………………………..…S3

4. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra of Products …………………… S14

5. HPLC Charts of 3a, 3c…………………………………………………..…..…….S44

6. References ……………………………………………………………………..…..…..… S46
1. General Information

Unless noted, all reactions were carried out in flame-dried glassware with magnetic stirring under an atmosphere of air. Solvents used were of analytical purity. All the reactions were monitored by thin-layer chromatography (TLC) and were visualized using UV light and Iodine. The product purification was done using silica gel column chromatography. Thin-layer chromatography (TLC) characterization was performed with precoated silica gel GF254 (0.2mm), while column chromatography characterization was performed with silica gel (100-200mesh). NMR spectra were recorded on a Varian spectrometer (400 MHz for $^1$H, 100 MHz for $^{13}$C, and 376 MHz for $^{19}$F). Chemical shifts are reported in δ ppm referenced to an internal SiMe$_4$ standard for $^1$HNMR and chloroform-d (δ 77.16) for $^{13}$C NMR. Chemical shifts are reported in δ ppm. Coupling constants were given in Hz. HRMS spectra were recorded on a Waters Q-TOF Premier. Melting points were measured with YRT-3 melting point apparatus (Shantou Keyi Instrument &Equipment Co., Ltd., Shantou, China).

2. Experimental section


The substrates of sulfoxonium ylides were prepared according to the procedure reported by Burtoloso $^1$. All the characteristic data are consistent with the data reported before $^{1,2}$.

2.2. Typical procedure for Pd-catalyzed cross-coupling reaction.

In an oven-dried Schlenk tube, equipped with a magnetic stir bar, 1a (0.1 mmol),
2a (1.2 eq), Pd(OAc)$_2$ (2.5 mol %), P(2-furyl)$_3$ (0.1 eq) and LiOtBu (2.0 eq)/Et$_3$N (0.5 eq) and 1 mL toluene were added. The tube was thoroughly flushed with argon, then the mixture was stirred for 24 hours at 80 °C. After completion of the reaction, the solvent was removed under vacuum, and the desired product was purified by column chromatography using PE/EA (40:1).

3. Characterization data for the products

**ethyl 2,3-diphenylacrylate (3a)**

Yield: 87% (22 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.84 (s, 1H), 7.41 – 7.33 (m, 3H), 7.25 – 7.13 (m, 5H), 7.08 – 7.03 (m, 2H), 4.28 (q, $J = 7.1$ Hz, 2H), 1.30 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 167.9, 140.2, 136.1, 134.9, 133.0, 130.7, 129.9, 129.0, 128.7, 128.3, 127.9, 61.3, 14.4; HRMS (ESI) $m/z$ calculated for [C$_{17}$H$_{17}$O$_2$, M + H]$^+$ : 253.1223; Found: 253.1224

**ethyl 3-(3-methoxyphenyl)-2-phenylacrylate (3b)**

Yield: 90% (25.4 mg). Light yellow oil. $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.80 (s, 1H), 7.35 (dd, $J = 11.6, 7.1$ Hz, 3H), 7.27 – 7.21 (m, 2H), 7.10 (t, $J = 7.9$ Hz, 1H), 6.78 – 6.71 (m, 2H), 6.49 (s, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 3.46 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 167.9, 159.2, 140.1, 136.2, 136.0, 133.1, 129.9, 129.3, 128.7, 127.9, 123.9, 116.1, 114.4, 61.3, 54.9, 14.4; HRMS (ESI) $m/z$ calculated for [C$_{18}$H$_{19}$O$_3$, M + H]$^+$ : 283.1329; Found: 283.1327.
ethyl 3-(4-(tert-butyl) phenyl)-2-phenylacrylate (3c)

Yield: 94% (29 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.81 (s, 1H), 7.39 – 7.35 (m, 3H), 7.26 – 7.21 (m, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), 6.97 (d, $J = 8.4$ Hz, 2H), 4.25 (q, $J = 7.1$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.24 (s, 9H); $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 168.1, 152.6, 140.1, 136.5, 131.9, 130.7, 129.9, 128.7, 128.2, 127.8, 125.3, 61.2, 34.8, 31.2, 14.4; HRMS (ESI) m/z calculated for [C$_{21}$H$_{25}$O$_2$, M + H]$^+$: 309.1849; Found: 309.1852.

ethyl 3-(2-chlorophenyl)-2-phenylacrylate (3d)

Yield: 79% (22.7 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.03 (s, 1H), 7.43 – 7.33 (m, 2H), 7.29 – 7.26 (m, 2H), 7.16 (dd, $J = 6.7$, 3.0 Hz, 2H), 7.11 (td, $J = 7.8$, 1.7 Hz, 1H), 6.88 (t, $J = 7.9$ Hz, 1H), 6.73 (dd, $J = 7.9$, 1.7 Hz, 1H), 4.31 (q, $J = 7.1$ Hz, 2H), 1.33 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 167.5, 136.9, 135.2, 135.1, 135.0, 133.9, 131.3, 130.3, 129.7, 129.6, 128.4, 128.0, 126.2, 61.5, 14.4; HRMS (ESI) m/z calculated for [C$_{17}$H$_{16}$ClO$_2$, M + H]$^+$: 287.0833; Found: 287.0836.

ethyl 3-(3-chlorophenyl)-2-phenylacrylate (3e)

Yield: 75% (21.5 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.74 (s, 1H), 7.40 – 7.33 (m, 3H), 7.23 – 7.12 (m, 3H), 7.06 (t, $J = 7.9$ Hz, 1H), 7.01 (s, 1H), 6.89 (d, $J = 7.9$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.29 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 167.6, 138.6, 136.7, 135.4, 134.4, 134.2, 130.5, 129.8,
ethyl 3-(4-chlorophenyl)-2-phenylacrylate (3f)

Yield: 83% (23.8 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.78 (s, 1H), 7.41 – 7.31 (m, 3H), 7.23 – 7.17 (m, 2H), 7.13 (d, $J = 8.6$ Hz, 2H), 6.97 (d, $J = 8.6$ Hz, 2H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.30 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 167.7, 138.8, 135.7, 134.9, 133.6, 133.3, 131.8, 129.8, 128.8, 128.6, 128.1, 61.4, 14.4; HRMS (ESI) m/z calculated for $[C_{17}H_{16}ClO_2, M + H]^+$: 287.0833; Found: 287.0831.

ethyl 3-(2-cyanophenyl)-2-phenylacrylate (3g)

Yield: 64% (17.8 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.07 (s, 1H), 7.75 – 7.61 (m, 1H), 7.58 – 7.51 (m, 1H), 7.47 – 7.38 (m, 1H), 7.38 – 7.29 (m, 3H), 7.27 – 7.17 (m, 2H), 6.90 (d, $J = 7.9$ Hz, 1H), 4.33 (q, $J = 7.1$ Hz, 2H), 1.35 (t, $J = 7.1$ Hz, 2H), 1.15 (t, $J = 7.1$ Hz, 1H); $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 167.0, 138.8, 137.6, 135.0, 133.1, 132.1, 130.3, 130.1, 128.9, 128.7, 128.6, 128.4, 117.6, 113.6, 61.8, 14.4; HRMS (ESI) m/z calculated for $[C_{18}H_{16}NO_2, M + H]^+$: 278.1176; Found: 278.1177.

ethyl 3-(3-cyanophenyl)-2-phenylacrylate (3h)

Yield: 70% (19.4 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.76 (s, 1H), 7.50 – 7.43 (m, 1H), 7.41 – 7.34 (m, 2H), 6.93 (d, $J = 7.9$ Hz, 1H), 4.31 (q, $J = 7.1$ Hz, 2H), 1.33 (t, $J = 7.1$ Hz, 2H), 1.15 (t, $J = 7.1$ Hz, 1H); $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 167.0, 138.8, 137.6, 135.0, 133.1, 132.1, 130.3, 130.1, 128.9, 128.7, 128.6, 128.4, 117.6, 113.6, 61.8, 14.4; HRMS (ESI) m/z calculated for $[C_{18}H_{16}NO_2, M + H]^+$: 278.1176; Found: 278.1177.
ethyl 3-(4-cyanophenyl)-2-phenylacrylate (3i)

Yield: 73% (20.2 mg). White solid. m.p. 96.6-99.1°C. \( \text{\textit{H}} \) NMR (400 MHz, Chloroform-\( \text{d} \)) \( \delta \) 7.78 (s, 1H), 7.43 (d, \( J = 8.1 \) Hz, 2H), 7.37 (s, 3H), 7.21 – 7.15 (m, 2H), 7.11 (d, \( J = 8.0 \) Hz, 2H), 4.29 (q, \( J = 7.1 \) Hz, 2H), 1.30 (t, \( J = 7.1 \) Hz, 3H); \( \text{\textsuperscript{13}C} \) NMR (101 MHz, Chloroform-\( \text{d} \)) \( \delta \) 167.2, 139.5, 137.7, 136.3, 134.9, 132.0, 130.8, 129.7, 128.9, 128.5, 118.6, 112.1, 61.7, 14.4; HRMS (ESI) \( m/z \) calculated for \([C_{18}H_{16}NO_2, M + H]^+\) : 278.1176; Found: 278.1176.

ethyl 3-(4-bromophenyl)-2-phenylacrylate (3j)

Yield: 68% (22.5 mg). White solid. m.p. 69.2-81.5°C. \( \text{\textit{H}} \) NMR (400 MHz, Chloroform-\( \text{d} \)) \( \delta \) 7.74 (s, 1H), 7.36 (dd, \( J = 5.3, 2.0 \) Hz, 3H), 7.30 – 7.25 (m, 2H), 7.23 – 7.15 (m, 2H), 6.89 (d, \( J = 8.3 \) Hz, 2H), 4.26 (q, \( J = 7.1 \) Hz, 2H), 1.29 (t, \( J = 7.1 \) Hz, 3H); \( \text{\textsuperscript{13}C} \) NMR (101 MHz, Chloroform-\( \text{d} \)) \( \delta \) 167.7, 138.8, 135.6, 133.8, 133.8, 132.1, 131.6, 129.8, 128.8, 128.1, 123.3, 61.4, 14.4; HRMS (ESI) \( m/z \) calculated for \([C_{17}H_{16}BrO_2, M + H]^+\) : 331.0328; Found: 331.0331.
**ethyl 2-phenyl-3-(4-(trifluoromethyl) phenyl) acrylate (3k)**

![Chemical Structure](attachment:image.png)

Yield: 75% (24.0 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.82 (s, 1H), 7.40 (d, $J = 8.2$ Hz, 2H), 7.39 – 7.33 (m, 3H), 7.20 (dd, $J = 6.6$, 3.0 Hz, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 4.29 (q, $J = 7.1$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 167.5, 138.3, 135.4, 135.3, 130.7, 129.8, 129.0, 128.9, 128.8, 128.3, 125.2 (q, $J_{C\text{-}F} = 3.8$ Hz), 61.6, 14.4; $^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -62.88; HRMS (ESI) $m/z$ calculated for [C$_{18}$H$_{16}$F$_{3}$O$_{2}$, M + H]$^+$: 301.1097; Found: 301.1095.

**ethyl 3-(3-nitrophenyl)-2-phenylacrylate (3l)**

![Chemical Structure](attachment:image.png)

Yield: 69% (20.5mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.07 – 8.01 (m, 1H), 7.90 (s, 1H), 7.84 (s, 1H), 7.44 – 7.36 (m, 3H), 7.32 (d, $J = 4.9$ Hz, 2H), 7.23 – 7.15 (m, 2H), 4.30 (q, $J = 7.1$ Hz, 2H), 1.32 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 167.2, 148.2, 137.2, 136.2, 136.1, 136.0, 134.8, 129.6, 129.2, 129.0, 128.6, 125.2, 123.4, 61.7, 14.4; HRMS (ESI) $m/z$ calculated for [C$_{17}$H$_{16}$NO$_{4}$, M + H]$^+$: 298.1074; Found: 298.1078.

**ethyl 3-(3,5-dimethylphenyl)-2-phenylacrylate (3m)**

![Chemical Structure](attachment:image.png)

Yield: 86% (24.1 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.77 (s, 1H), 7.38 – 7.31 (m, 3H), 7.21 (dd, $J = 7.3$, 2.3 Hz, 2H), 6.84 (s, 1H), 6.63 (s, 2H), 4.26 (q, $J = 7.1$ Hz,
2H), 2.11 (s, 6H), 1.29 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-d) δ 168.0, 140.6, 137.6, 136.4, 134.6, 132.5, 130.8, 129.9, 128.7, 128.6, 127.7, 61.2, 21.3, 14.4; HRMS (ESI) m/z calculated for [C$_{19}$H$_{21}$O$_2$, M + H] $^+$ : 281.1536; Found: 281.1540.

ethyl 3-(3,5-difluorophenyl)-2-phenylacrylate (3n)

Yield: 63% (18.1 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-d) δ 7.62 (s, 1H), 7.35 – 7.27 (m, 3H), 7.11 (dd, J = 6.6, 3.0 Hz, 2H), 6.62 – 6.52 (m, 1H), 6.46 (d, J = 6.7 Hz, 2H), 4.20 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-d) δ 167.3, 162.7 (dd, J$_{C-F}$ = 248.1 Hz, 12.8 Hz), 138.0 (t, J$_{C-F}$ = 9.8 Hz), 137.5 (t, J$_{C-F}$ = 2.8 Hz), 135.6, 134.9, 129.6, 128.9, 128.5, 113.2 (t, J$_{C-F}$ = 26.1 Hz), 104.4 (t, J$_{C-F}$ = 25.5 Hz), 61.7, 14.4; $^{19}$F NMR (376 MHz, Chloroform-d) δ -109.82 (t, J = 8.0 Hz, 2F); HRMS (ESI) m/z calculated for [C$_{17}$H$_{15}$F$_2$O$_2$, M + H] $^+$ : 289.1035; Found: 289.1031.

ethyl 3-(2,4-difluorophenyl)-2-phenylacrylate (3o)

Yield: 72% (20.8 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-d) δ 7.92 (s, 1H), 7.44 – 7.30 (m, 3H), 7.24 – 7.10 (m, 2H), 6.77 (ddd, J = 10.8, 8.7, 2.6 Hz, 1H), 6.68 (td, J = 8.6, 6.4 Hz, 1H), 6.51 (td, J = 8.5, 2.6 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-d) δ 167.4, 163.7 (dd, J$_{C-F}$ = 150.4 Hz, 12.1 Hz), 161.2 (dd, J$_{C-F}$ = 152.0 Hz, 12.1 Hz), 135.4, 131.7 (dd, J$_{C-F}$ = 9.7 Hz, 3.8 Hz), 130.9 (dd, J$_{C-F}$ = 5.2 Hz, 1.5 Hz), 129.9, 128.7, 128.2, 126.9, 119.3 (dd, J$_{C-F}$ =
12.1 Hz, 4.0 Hz), 111.2 (dd, $J_{C-F} = 21.3$ Hz, 3.7 Hz), 104.0 (t, $J_{C-F} = 25.7$ Hz), 61.5, 14.4; $^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -107.46 (dt, $J = 16.0$, 8.3 Hz, 1F), -109.45 (q, $J = 9.2$ Hz, 1F); HRMS (ESI) $m/z$ calculated for [C$_{17}$H$_{15}$F$_2$O$_2$, M + H]$^+$: 289.1035; Found: 289.1037.

**ethyl 3-(2-chloro-4-fluorophenyl)-2-phenylacrylate (3p)**

![3p structure]

Yield: 65% (19.8 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.96 (s, 1H), 7.44 – 7.33 (m, 1H), 7.31 – 7.27 (m, 2H), 7.20 – 7.08 (m, 3H), 6.71 (dd, $J = 8.9$, 6.1 Hz, 1H), 6.61 (td, $J = 8.4$, 2.6 Hz, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 1.32 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 167.4, 162.2 (d, $J = 252.7$ Hz), 136.0 (d, $J = 10.3$ Hz), 135.7, 135.0, 132.5 (d, $J = 8.8$ Hz), 130.2, 130.0 (d, $J = 3.9$ Hz), 128.8, 128.5, 128.1, 117.0 (d, $J = 24.7$ Hz), 113.9 (d, $J = 21.2$ Hz), 61.6, 14.4; $^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -110.15 (q, $J = 8.0$ Hz); HRMS (ESI) $m/z$ calculated for [C$_{17}$H$_{15}$ClFO$_2$, M + H]$^+$: 305.0735; Found: 305.0737.

**ethyl 3-(2-cyano-5-fluorophenyl)-2-phenylacrylate (3q)**

![3q structure]

Yield: 42% (19.8 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.99 (s, 1H), 7.64 (dd, $J = 8.6$, 5.4 Hz, 1H), 7.35 (dd, $J = 5.1$, 2.0 Hz, 3H), 7.17 (dd, $J = 6.5$, 2.9 Hz, 2H), 6.99 (td, $J = 8.1$, 2.6 Hz, 1H), 6.54 (dd, $J = 9.9$, 2.6 Hz, 1H), 4.32 (q, $J = 7.1$ Hz, 2H), 1.35 (d, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 166.6, 164.2 (d, $J =$...
256.2 Hz), 141.8 (d, J = 9.6 Hz), 138.8, 135.3 (d, J = 9.6 Hz), 134.1, 133.7 (d, J = 2.3 Hz), 129.8, 128.9, 128.8, 117.6 (d, J = 24.5 Hz), 116.8, 116.6 (d, J = 23.1 Hz), 109.8 (d, J = 3.4 Hz), 62.0, 14.3; \(^{19}\)F NMR (376 MHz, Chloroform-d) δ -102.54; HRMS (ESI) m/z calculated for \([C_{18}H_{15}FNO_2, M + H]^+\): 296.1081; Found: 296.1083.

**ethyl 3-(naphthalen-2-yl)-2-phenylacrylate (3r)**

![Structure](image_url)

Yield: 85% (25.7 mg). Colorless oil. \(^1\)H NMR (400 MHz, Chloroform-d) δ 8.00 (s, 1H), 7.70 (d, J = 6.6 Hz, 1H), 7.65 (s, 2H), 7.53 (d, J = 8.7 Hz, 1H), 7.42 (t, J = 6.2 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.29 – 7.22 (m, 2H), 6.99 (d, J = 8.6 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H); \(^{13}\)C NMR (101 MHz, Chloroform-d) δ 168.0, 140.3, 136.1, 133.4, 133.1, 132.5, 131.6, 130.1, 128.9, 128.7, 128.6, 128.0, 127.6, 127.1, 126.6, 125.6, 61.4, 14.4; HRMS (ESI) m/z calculated for \([C_{21}H_{19}O_2, M + H]^+\): 303.1380; Found: 303.1385.

**ethyl 3-(naphthalen-1-yl)-2-phenylacrylate (3s)**

![Structure](image_url)

Yield: 83% (25.1 mg). Colorless oil. \(^1\)H NMR (400 MHz, Chloroform-d) δ 8.46 (s, 1H), 8.12 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.2 Hz, 1H), 7.61 – 7.48 (m, 3H), 7.21 – 7.12 (m, 5H), 6.96 (d, J = 7.2 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H); \(^{13}\)C NMR (101 MHz, Chloroform-d) δ 167.8, 138.6, 135.5, 135.4, 133.5, 132.5, 132.2, 130.4, 128.8, 128.8, 128.2, 128.1, 127.6, 126.6, 126.2,
ethyl 2,3,3-triphenylacrylate (3t)

![Structural formula](image)

Yield: 18% (5.9 mg). White solid. m.p. 105.9-107.2°C. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.35 – 7.29 (m, 5H), 7.22 – 7.10 (m, 8H), 7.02 (dd, $J = 7.8$, 1.9 Hz, 2H), 4.03 (q, $J = 7.1$ Hz, 2H), 0.98 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 170.7, 146.1, 142.6, 140.7, 137.6, 133.9, 131.0, 130.0, 129.3, 128.3, 128.2, 128.0, 127.8, 127.5, 61.1, 13.8; HRMS (ESI) m/z calculated for [C$_{23}$H$_{21}$O$_2$, M + H]$^+$ : 329.1536; Found: 329.1533.

ethyl 2-phenylpenta-2,4-dienoate (3u)

Yield: 24% (4.9 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.44 (d, $J = 11.4$ Hz, 1H), 7.42 – 7.29 (m, 3H), 7.23 (d, $J = 6.5$ Hz, 2H), 6.45 – 6.34 (m, 1H), 5.66 (dd, $J = 17.0$, 1.8 Hz, 1H), 5.41 (dd, $J = 10.0$, 1.8 Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 1.29 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 167.5, 140.5, 135.1, 133.7, 133.4, 130.3, 128.0, 127.8, 125.6, 61.2, 14.4; HRMS (ESI) m/z calculated for [C$_{13}$H$_{15}$O$_2$, M + H]$^+$ : 203.1067; Found: 203.1068.

ethyl 2-(4-chlorophenyl)-3-phenylacrylate (3v)
Yield: 66% (18.9 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.85 (s, 1H), 7.33 (d, $J = 8.2$ Hz, 2H), 7.25 – 7.11 (m, 5H), 7.05 (d, $J = 7.0$ Hz, 2H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.30 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 167.6, 140.8, 134.5, 134.5, 133.9, 131.7, 131.5, 130.6, 129.3, 129.0, 128.4, 61.5, 14.4; HRMS (ESI) $m/z$ calculated for [C$_{17}$H$_{16}$ClO$_2$, M + H]$^+$: 287.0833; Found: 287.0835.

**ethyl 3-phenyl-2-(p-tolyl) acrylate (3w)**

Yield: 61% (16.2 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.80 (s, 1H), 7.22 – 7.13 (m, 5H), 7.12 – 7.04 (m, 4H), 4.26 (q, $J = 7.1$ Hz, 2H), 2.38 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 168.2, 140.0, 137.6, 135.0, 133.0, 132.9, 130.7, 129.8, 129.4, 129.0, 128.3, 61.3, 21.5, 14.4; HRMS (ESI) $m/z$ calculated for [C$_{18}$H$_{19}$O$_2$, M + H]$^+$: 267.1380; Found: 267.1385.

**ethyl 2-(3-methoxyphenyl)-3-phenylacrylate (3x)**

Yield: 63% (17.8 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.81 (s, 1H), 7.28 (d, $J = 7.9$ Hz, 1H), 7.22 – 7.13 (m, 3H), 7.07 (d, $J = 6.6$ Hz, 2H), 6.89 (dd, $J = 7.8$, 2.2 Hz, 1H), 6.80 (d, $J = 7.6$ Hz, 1H), 6.77 (dd, $J = 2.7$, 1.5 Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 3.76 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 167.9, 159.8, 140.3, 137.4, 134.8, 132.8, 130.7, 129.8, 129.2, 128.3, 122.3, 115.2, 113.8, 61.3, 55.4, 14.4; HRMS (ESI) $m/z$ calculated for [C$_{18}$H$_{19}$O$_3$, M + H]$^+$: 283.1329; Found: 283.1325.
**isobutyl 2,3-diphenylacrylate (3z)**

Yield: 75% (21.1 mg). Colorless oil. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.86 (s, 1H), 7.42 – 7.28 (m, 4H), 7.25 – 7.12 (m, 4H), 7.07 (d, \(J = 7.1\) Hz, 2H), 3.99 (d, \(J = 6.4\) Hz, 2H), 2.02 – 1.88 (m, 1H), 0.9 (d, \(J = 6.8\) Hz, 6H); \(^1\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 168.0, 140.2, 136.1, 134.8, 133.0, 130.7, 129.8, 129.1, 128.6, 128.3, 127.8, 71.3, 27.9, 19.2; HRMS (ESI) \(m/z\) calculated for \(\text{[C}_{19}\text{H}_{21}\text{O}_{2}, M + H]^+\) : 281.1536; Found: 281.1537.

**\((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)\) 2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H cyclopenta[a]phenanthren-3-yl 2,3-diphenylacrylate (4)**

Yield: 34% (20.1 mg). Colorless oil. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.80 (s, 1H), 7.38 – 7.30 (m, 3H), 7.25 – 7.09 (m, 5H), 7.08 – 6.98 (m, 2H), 5.38 (dd, \(J = 5.0\), 2.4 Hz, 1H), 4.74 (tt, \(J = 11.1\), 4.9 Hz, 1H), 2.44 – 2.31 (m, 2H), 2.05 – 1.81 (m, 6H), 1.66 – 1.41 (m, 11H), 1.19 – 1.04 (m, 8H), 1.02 (s, 3H), 0.98 – 0.92 (m, 1H), 0.92 (d, \(J = 6.5\) Hz, 3H), 0.87 (dd, \(J = 6.6\), 1.8 Hz, 6H), 0.68 (s, 3H); \(^1\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 167.4, 139.9, 139.9, 136.1,
ethyl 2-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-3-phenylacrylate (5)

Yield: 78% (20.1 mg). Colorless oil. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.78 (s, 1H), 7.41 – 7.29 (m, 1H), 7.26 – 7.06 (m, 5H), 7.05 – 6.86 (m, 2H), 4.28 (q, $J = 7.3$ Hz, 2H), 2.99 – 2.81 (m, 2H), 2.52 (dd, $J = 18.8$, 8.6 Hz, 1H), 2.47 – 2.30 (m, 2H), 2.22 – 2.11 (m, 1H), 2.13 – 1.94 (m, 3H), 1.69 – 1.48 (m, 6H), 1.32 (t, $J = 7.1$ Hz, 2H), 1.20 (t, $J = 7.1$ Hz, 1H), 0.94 (s, 3H); $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 221.2, 168.2, 139.7, 139.4, 136.7, 135.0, 133.2, 132.8, 130.7, 130.3, 129.0, 128.3, 127.3, 125.6, 61.3, 50.8, 48.2, 44.6, 38.2, 36.0, 31.8, 29.4, 26.7, 25.7, 21.7, 14.5, 14.1; HRMS (ESI) $m/z$ calculated for [C$_{29}$H$_{33}$O$_3$, M + H]$^+$: 429.2424; Found: 429.2421.

4. $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR Spectra of Products.
1H NMR of 3a

13C NMR of 3a
$^{1}H$ NMR of 3c

$^{13}C$ NMR of 3c
$^{1}H$ NMR of 3d

$^{13}C$ NMR of 3d
$^1$H NMR of 3e

$^{13}$C NMR of 3e
$^{1}H$ NMR of $3f$

$^{13}C$ NMR of $3f$
\(^1\)H NMR of 3g

\(^{13}\)C NMR of 3g
$^1\text{H NMR of 3h}$

$^{13}\text{C NMR of 3h}$
$^{1}H$ NMR of 3i

$^{13}C$ NMR of 3i
$^{1}$H NMR of 3j

$^{13}$C NMR of 3j
\( ^1H \) NMR of 3k

\( ^13C \) NMR of 3k
$^{19}\text{F NMR of 3k}$

$^{1}\text{H NMR of 3l}$
$^{13}$C NMR of 3l

$^1$H NMR of 3m
$^{13}$C NMR of 3m

NOESY of 3m
$^{1}H$ NMR of 3n

$^{13}C$ NMR of 3n

Z/E > 20:1
$^{19}$F NMR of 3n

$^1$H NMR of 3o
$^{13}$C NMR of 3o

$^{19}$F NMR of 3o
\textbf{\textsuperscript{1}H NMR of 3p}

\textbf{\textsuperscript{13}C NMR of 3p}
$\text{Cl}-\text{F}$

$\text{COOEt}$

$^1\text{H}$ NMR of 3p

$^1\text{F}$ NMR of 3p

$\text{NC}$

$\text{COOEt}$

$Z/E > 20:1$

$^1\text{H}$ NMR of 3q
\[ 1^3\text{C NMR of } 3q \]

\[ 1^9\text{F NMR of } 3q \]
$2E : 1Z = 10 : 1$

$^1$H NMR of 3r

$^{13}$C NMR of 3r
$^1$H NMR of 3s

$^{13}$C NMR of 3s
$^1$H NMR of 3t

$^{13}$C NMR of 3t
$^1$H NMR of 3u

$^{13}$C NMR of 3u
\( ^1H \text{NMR of } 3v \)

\( ^13C \text{NMR of } 3v \)
\(^1\)H NMR of 3w

\(^{13}\)C NMR of 3w
$^1$H NMR of 3x

$^{13}$C NMR of 3x
$^1$H NMR of 4

$^{13}$C NMR of 4
$^1$H NMR of 5

$^{13}$C NMR of 5
5. HPLC Charts of 3a, 3c

<table>
<thead>
<tr>
<th>峰保留时间</th>
<th>类型</th>
<th>峰宽</th>
<th>峰面积</th>
<th>峰高</th>
<th>峰面积</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>mAU</td>
<td>*s</td>
<td>[mAU]</td>
</tr>
<tr>
<td>4</td>
<td>3.415</td>
<td>VV</td>
<td>0.1397</td>
<td>16.91923</td>
<td>1.78534</td>
</tr>
<tr>
<td>5</td>
<td>40.651</td>
<td>MM</td>
<td>2.0277</td>
<td>5472.85059</td>
<td>44.98375</td>
</tr>
<tr>
<td>6</td>
<td>44.981</td>
<td>MM</td>
<td>2.1613</td>
<td>6.63197e4</td>
<td>511.41574</td>
</tr>
</tbody>
</table>

总量： 7.18610e4 564.75053
6. references.


<table>
<thead>
<tr>
<th>峰</th>
<th>保留时间</th>
<th>类型</th>
<th>峰宽</th>
<th>峰面积</th>
<th>峰高</th>
<th>峰面积</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.810 BB</td>
<td>1.1892</td>
<td>1745.13696</td>
<td>21.35743</td>
<td>17.2812</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>34.065 BB</td>
<td>1.4287</td>
<td>8353.35840</td>
<td>85.34573</td>
<td>82.7188</td>
<td></td>
</tr>
</tbody>
</table>

总量：1.00985e4 106.70315