Iridium-Catalyzed Arylation of Sulfoxonium Ylides and

Arylboronic Acid: A Straightforward Preparation of α-Aryl

Ketones.

Bing Shu,^{‡a, e} Xiao-Tong Wang,^{‡a, e} Zi-Xuan Shen,^e Tong Che,^a Mei Zhong,^e Jia-Lin Song,^e Hua-Jie Kang,^e Hui Xie,^a Luyong Zhang,^{*a, b, c, d} Shang-Shi Zhang,^{*a, c, d}

[‡]*These authors contributed equally.*

^aCenter for Drug Research and Development, Guangdong Pharmaceutical University, Guangzhou, 510006, China

^bJiangsu Key Laboratory of Drug Screening, China Pharmaceutical University, Nanjing 210009, PR China

^cGuangzhou Key Laboratory of Construction and Application of New Drug Screening Model Systems, Guangdong Pharmaceutical University, Guangzhou, 510006, China

^dKey Laboratory of New Drug Discovery and Evaluation of Ordinary Universities of Guangdong

Province, Guangdong Pharmaceutical University, Guangzhou, 510006, China

eSchool of Pharmacy, Guangdong Pharmaceutical University, Guangzhou, 510006, PR China

*Email: zhangshangshi@gdpu.edu.cn

*Email: lyzhang@cpu.edu.cn.

Supporting Information

Table of content

1. General information	2
2. Synthesis of substrates 1	3
3. General procedure and characterization of products	4
4. Synthetic application of the product 3aa	27
5. Mechanistic Studies	30
6. ¹ H NMR and ¹³ C NMR spectra	33
7. Reference	99

1. General information

Unless otherwise noted, all reactions were carried out at room temperature under an atmosphere of nitrogen with flame-dried glassware. If reaction was not conducted at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under nitrogen: THF (Na, benzophenone), Toluene (Na, benzophenone), Et₂O (Na, benzophenone), dichloromethane CaH₂). Anhydrous DMF was purchased from Acros Organics and stored under nitrogen atmosphere. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

Proton NMR (¹H) were recorded at 400 MHz, and Carbon NMR (¹³C) at 101 MHz NMR spectrometer unless otherwise stated. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with short wave UV light, or KMnO4 staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

No attempts were made to optimize yields for substrate synthesis.

2. Synthesis of substrates 1

The substrates of sulfoxonium ylides **1** were prepared accroding to the procedure reported by Burtoloso and Aïssa.^[1] All the characteristic data are consistent with the data reported before.^[2]

3. General procedure and characterization of products

General procedure A

In an oven-dried Schlenk tube under air, a mixture of the substrates **1** (0.2 mmol, 1.0 equiv), boronic acid **2** (0.3 mmol, 2.5 equiv), (Cp*IrCl₂)₂ (2.5 mol%), AgSbF₆ (10.0 mol%), DIPA (1.5 equiv) in PhMe (1.0 mL) at 60 °C. For synthesis of **3ca**, **3ja**, and **3ua**, the reaction mixture was stirred at 80 °C. For synthesis of **3fa**, 1.5 equiv of K₂HPO₄ was used and the reaction mixture was stirred at 80 °C. For synthesis of **3ta**, 1.5 equiv of K₂HPO₄ was used at 60 °C. The obtained solution was stirred for 12 h.

The reaction mixture was then diluted with EA (10.0 mL) and washed with H_2O . The aqueous phase was extracted with EA again. The organic layers were combined, washed with brine and dried over Na_2SO_4 . The pure product was purified by flash column chromatography on silica with an appropriate eluent to afford the pure product.

Characterization of products

1,2-diphenylethanone (3aa)^[3]

Following the general procedure A, the product **3aa** was obtained in 75% yield (29.8 mg, 0.15 mmol) as a colourless liquid after chromatography on silica gel (eluent = etroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.21. ¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.89 (m, 2H), 7.51 – 7.42 (m, 1H), 7.41 – 7.34 (m, 2H), 7.27 – 7.21 (m, 2H), 7.21 – 7.16 (m, 3H), 4.21 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 197.6, 136.6, 134.6, 133.1, 129.5, 128.7, 128.6, 128.6, 126.9, 45.5.

1-(4-fluorophenyl)-2-phenylethanone (3ba) [4]

Following the general procedure A, the product **3ba** was obtained in 58% yield (24.7 mg, 0.116 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.20. ¹H NMR (500 MHz, CDCl₃) δ 8.06 – 7.85 (m, 2H), 7.25 (t, *J* = 7.4 Hz, 2H), 7.18 - 7.17 (m, 3H), 7.04 (t, *J* = 8.4 Hz, 2H), 4.17 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 196.1, 165.8 (d, *J* = 255.0 Hz), 134.3, 133.0 (d, *J* = 2.9 Hz), 131.3 (d, *J* = 9.3 Hz), 129.4, 128.77, 127.0, 115.8 (d, *J* = 21.9 Hz), 45.5. ¹⁹F NMR (471 MHz, CDCl₃) δ -105.0.

1-(4-chlorophenyl)-2-phenylethanone (3ca)^[5]



Following the general procedure A, the product **3ca** was obtained in 81% yield (37.5 mg, 0.162 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.21. ¹H NMR (500 MHz, CDCl₃) δ 7.86 (d, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.19 - 7.16 (m, 3H), 4.17 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 196.5, 139.6, 134.9, 134.2, 130.1, 129.4, 123.0, 128.8, 127.1, 45.6.

1-(4-bromophenyl)-2-phenylethanone (3da)^[4]



Following the general procedure A, the product **3da** was obtained in 62% yield (34.0 mg, 0.124 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.23. ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 2H), 7.19 - 7.16 (m, 3H), 4.16 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 196.7, 135.3, 134.2, 132.0, 130.2, 129.4, 128.8, 128.4, 127.1, 45.6.

1-(4-iodophenyl)-2-phenylethanone (3ea) [6]



Following the general procedure A, the product **3ea** was obtained in 87% yield (56.2 mg, 0.174 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.18. ¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, *J* = 7.7 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.20 - 7.16 (m, 3H), 4.16 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 195.9, 136.9, 134.7, 133.1, 129.0, 128.3, 127.7, 126.0, 100.2, 44.4.

1-([1,1'-biphenyl]-4-yl)-2-phenylethanone (3fa) ^[7]



Following the general procedure A, the product **3fa** was obtained in 76% yield (41.5 mg, 0.152 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.25. ¹H NMR (500 MHz, CDCl₃) δ 8.00 (d, *J* = 7.3 Hz, 2H), 7.58 (d, *J* = 7.3 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.23 – 7.14 (m, 3H), 4.22 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 196.2, 144.8, 138.8, 134.2, 133.6, 128.4, 128.2, 127.9, 127.7, 127.2, 126.2, 126.2, 125.9, 44.5.

4-(2-phenylacetyl)benzonitrile (3ga) [6]



Following the general procedure A, the product **3ga** was obtained in 37% yield (16.6 mg, 0.074 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.20. ¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 7.3 Hz, 2H), 7.68 (d, *J* = 7.3 Hz, 2H), 7.27 (t, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 7.0 Hz, 1H), 7.18 (t, *J* = 6.5 Hz, 2H), 4.22 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 196.3, 139.5, 133.5, 132.6, 129.4, 129.0,

128.9, 127.3, 117.9, 116.4, 45.9.

2-phenyl-1-(p-tolyl)ethanone (3ha) [7]

Following the general procedure A, the product **3ha** was obtained in 98% yield (41.3 mg, 0.196 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.22. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.38-7.32 (m, 2H), 7.30-7.25 (m, 5H), 4.28 (s, 2H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.3, 144.0, 134.8, 134.2, 129.4, 129.3, 128.8, 128.6, 126.8, 45.4, 21.7.

1-(4-methoxyphenyl)-2-phenylethanone (3ia) [7]



Following the general procedure A, the product **3ia** was obtained in 80% yield (36.3 mg, 0.16 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.26. ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 2H), 7.20 - 7.15 (m, 3H), 6.85 (d, *J* = 7.7 Hz, 2H), 4.16 (s, 2H), 3.78 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 196.3, 163.5, 134.0, 131.0, 129.6, 129.4, 128.7, 126.8, 113.8, 55.5, 45.3.

1-(4-nitrophenyl)-2-phenylethanone (3ja)^[8]



Following the general procedure A, the product **3ja** was obtained in 63% yield (30.3 mg, 0.126 mmol) as a yellow solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.22. ¹H NMR (500 MHz, CDCl₃) δ 8.22 (d, *J* = 7.7 Hz, 2H), 8.07 (d, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.22 (d, *J* = 7.0 Hz, 1H), 7.18 (d, *J* =

7.4 Hz, 2H), 4.26 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 196.1, 150.3, 141.0, 133.4, 129.7, 129.4, 129.0, 127.4, 123.9, 46.1.

2-phenyl-1-(4-(trifluoromethyl)phenyl)ethanone (3ka)^[7]



Following the general procedure A, the product **3ka** was obtained in 78% yield (41.4 mg, 0.156 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.21. ¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.1 Hz, 2H), 7.22 - 7.18 (m, 3H), 4.24 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 196.6, 139.2, 134.5 (*J* = 32.7 Hz), 133.8, 129.4, 128.9, 128.9, 127.2, 125.7 (*J* = 3.7 Hz), 123.6 (d, *J* = 272.8 Hz), 45.9. ¹⁹F NMR (471 MHz, CDCl₃) δ -63.2.

methyl 4-(2-phenylacetyl)benzoate (3la)^[9]



Following the general procedure A, the product **3la** was obtained in 83% yield (42.4 mg, 0.166 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.23. ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 8.5 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.32 – 7.26 (m, 3H), 4.33 (s, 2H), 3.96 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 197.2, 166.2, 139.8, 134.0, 133.9, 129.9, 129.5, 128.8, 128.5, 127.1, 52.5, 45.9.

1-(3-chlorophenyl)-2-phenylethanone (3ma)^[10]

CL

Following the general procedure A, the product **3ma** was obtained in 61% yield (28.1 mg,

0.124 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.21. ¹H NMR (400 MHz, CDCl₃) δ 8.00 (t, *J* = 1.8 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.56 - 7.54 (m, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.39 - 7.33 (m, 2H), 7.32 - 7.26 (m, 3H), 4.28 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 196.4, 138.2, 135.0, 134.0, 133.1, 130.0, 129.5, 128.8, 128.7, 127.1, 126.7, 45.6.

2-phenyl-1-(m-tolyl)ethan-1-one (3na) [6]



Following the general procedure A, the product **3na** was obtained in 73% yield (30.5 mg, 0.146 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.24. ¹H NMR (400 MHz, CDCl₃) δ 7.86 - 7.83 (m, 2H), 7.42 - 7.33 (m, 4H), 7.32 - 7.27 (m, 3H), 4.30 (s, 2H), 2.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.9, 138.5, 136.7, 134.7, 133.9, 129.5, 129.1, 128.7, 128.5, 126.9, 125.9, 45.5, 21.4.

1-(3-methoxyphenyl)-2-phenylethan-1-one (3oa) [6]



Following the general procedure A, the product **30a** was obtained in 77% yield (35.1 mg, 0.154 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.20. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.57 – 7.54 (m, 1H), 7.43 – 7.32 (m, 3H), 7.32 – 7.25 (m, 4H), 7.15 – 7.10 (m, 1H), 4.30 (s, 2H), 3.86 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.5, 159.9, 138.0, 134.6, 129.6, 129.4, 128.7, 126.9, 121.3, 119.7, 112.9, 55.4, 45.6.

2-phenyl-1-(o-tolyl)ethanone (3pa) [11]



Following the general procedure A, the product **3pa** was obtained in 70% yield (29.6 mg, 0.146 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.20. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.29 (m, 3H), 7.28 - 7.27 (m, 1H), 7.24 - 7.22 (m, 4H), 4.21 (s, 2H), 2.44 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 201.5, 138.6, 137.6, 134.5, 132.0, 131.4, 129.6, 128.6, 128.6, 126.9, 125.6, 48.5, 21.3.

1-(2-iodophenyl)-2-phenylethan-1-one (3qa) [7]



Following the general procedure A, the product **3qa** was obtained in 41% yield (26.6 mg, 0.082 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.21. ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.21 (m, 4H), 7.21 – 7.14 (m, 3H), 7.02 (t, *J* = 7.6 Hz, 1H), 4.13 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 202.1, 144.4, 140.4, 133.3, 131.5, 129.7, 128.6, 127.9, 127.9, 127.1, 91.2, 48.8.

1-(3-fluoro-4-methylphenyl)-2-phenylethanone (3ra)



Following the general procedure A, the product **3ra** was obtained in 46% yield (30.1 mg, 0.092 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.19. Mp 83-84 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 10.3 Hz, 1H), 7.25 (t, *J* = 7.3 Hz, 2H), 7.20 - 7.17 (m, 4H), 4.16 (s, 2H), 2.25 (s, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ -116.1. ¹³C NMR (126 MHz, CDCl₃) δ 196.3, 161.3 (d, *J* = 246.5 Hz), 136.3 (d, *J* = 6.3 Hz), 134.3, 131.6 (d, *J* = 4.8 Hz), 131.0 (d, *J* = 17.7 Hz), 129.4, 128.7, 127.0, 124.3 (d, *J* = 3.2 Hz), 115.0 (d, *J* = 23.2 Hz), 45.5, 14.9 (d, *J* = 3.5 Hz). ESI-MS: calculated C₁₅H₁₄FO [M+H]⁺ 229.1023; Found 229.1001.

2-(3-oxo-4-phenylbutyl)isoindoline-1,3-dione (3sa)



Following the general procedure A, the product **3sa** was obtained in 66% yield (39.0 mg, 0.132 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.23. Mp 115-116 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.82-7.79 (m, 2H), 7.75 – 7.67 (m, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 4.9 Hz, 1H), 7.21 – 7.16 (m, 2H), 3.94 (t, *J* = 7.3 Hz, 2H), 3.73 (s, 2H), 2.88 (t, *J* = 7.3 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 205.5, 168.0, 133.9, 133.6, 132.0, 129.4, 128.8, 127.1, 123.2, 50.2, 39.8, 33.1. ESI-MS: calculated C₁₈H₁₆NO₃ [M+H]⁺ 294.1125; Found 294.1134.

1-(naphthalen-2-yloxy)-3-phenylpropan-2-one (3ta)



Following the general procedure A, the product **3ta** was obtained in 61% yield (33.7 mg, 0.122 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.22. Mp 101-102 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.30 - 7.25 (m, 3H), 7.23 - 7.12 (m, 4H), 6.86 (s, 1H), 4.64 (s, 2H), 3.85 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 204.9, 155.6, 134.3, 133.1, 129.9, 129.6, 129.4, 128.9, 127.7, 127.4, 126.9, 126.7, 124.2, 118.5, 106.9, 72.1, 46.4. ESI-MS: calculated C₁₉H₁₆O₂Na [M+Na]⁺ 299.1043; Found 299.1007.

1-(4-chloro-2-methylphenoxy)-3-phenylpropan-2-one (3ua)



Following the general procedure A, the product **3ua** was obtained in 76% yield (41.5 mg,

0.152 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.21. Mp 101-102 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.26 (t, *J* = 7.2 Hz, 2H), 7.22 - 7.18 (m, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.07 (s, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.42 (d, *J* = 8.6 Hz, 1H), 4.51 (s, 2H), 3.83 (s, 2H), 2.21 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 204.7, 154.4, 132.9, 130.9, 129.5, 128.9, 127.4, 126.5, 126.2, 111.9, 72.4, 46.2, 16.3. ESI-MS: calculated C₁₆H₁₅ClO₂Na [M+Na]⁺ 297.0653; Found 297.0645.

1-(naphthalen-2-yl)-2-phenylethanone (3va) [7]



Following the general procedure A, the product **3va** was obtained in 75% yield (37.1 mg, 0.15 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.21. ¹H NMR (500 MHz, CDCl₃) δ 8.45 (s, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.78 (t, *J* = 9.0 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.21 (m, 4H), 7.20 – 7.13 (m, 1H), 4.32 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 197.7, 135.6, 134.7, 134.0, 132.5, 130.5, 129.7, 129.5, 128.8, 128.6, 128.6, 127.8, 126.9, 126.8, 124.3, 45.6.

1-(2,3-dihydrobenzo[b][1,4]dioxin-2-yl)-2-phenylethanone (3wa)



Following the general procedure A, the product **3wa** was obtained in 30% yield (15.4 mg, 0.06 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.24. Mp 86-87 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.24 (t, *J* = 7.3 Hz, 2H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.87 - 6.79 (m, 3H), 4.68 - 4.57 (m, 1H), 4.25 (d, *J* = 11.4 Hz, 1H), 4.14 (dd, *J* = 11.4, 5.9 Hz, 1H), 3.96 (d, *J* = 15.9 Hz, 1H), 3.80 (d, *J* = 15.9 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 205.2, 143.3, 142.2, 132.7, 129.7, 128.7, 127.3, 122.2, 122.2, 117.6, 117.4, 64.6, 45.8. ESI-MS:

calculated C₁₆H₁₄O₃Na [M+Na]⁺ 277.0835; Found 277.0845.

2-phenyl-1-(thiophen-2-yl)ethanone (3xa) ^[12]



Following the general procedure A, the product **3xa** was obtained in 64% yield (25.8 mg, 0.128 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.19. ¹H NMR (400 MHz, CDCl₃) δ 7.79 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.66 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.36 (dd, *J* = 5.1, 3.2 Hz, 1H), 7.35 – 7.32 (m, 3H), 7.30 (d, *J* = 2.0 Hz, 1H), 7.14 (dd, *J* = 4.9, 3.8 Hz, 1H), 4.22 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 190.5, 143.9, 134.3, 134.1, 132.7, 129.4, 128.7, 128.2, 127.1, 46.4.

(*R*)-3-(6-methoxynaphthalen-2-yl)-1-phenylbutan-2-one (3ya)



Following the general procedure A, the product **3ya** was obtained in 32% yield (19.7 mg, 0.064 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.20. Mp 78-79 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.63 (t, *J* = 9.2 Hz, 2H), 7.50 (s, 1H), 7.22 – 7.11 (m, 4H), 7.09 (d, *J* = 8.9 Hz, 1H), 7.05 (s, 1H), 6.96 (d, *J* = 7.4 Hz, 2H), 3.90 (q, *J* = 6.8 Hz, 1H), 3.84 (s, 3H), 3.57 (s, 2H), 1.36 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 208.3, 157.8, 135.5, 134.4, 133.8, 129.5, 129.2, 129.2, 128.6, 127.7, 126.9, 126.8, 126.5, 119.2, 105.6, 55.4, 52.0, 48.1, 17.7. ESI-MS: calculated C₂₁H₂₁O₂ [M+H]⁺ 305.1536; Found 305.1519.

(8S,9S,10R,13S,14S,17S)-10,13-dimethyl-17-(2-phenylacetyl)-6,7,8,9,10,11,12,13,14,15,16,17dodecahydro-1H-cyclopenta[a]phenanthren-3(2H)-one (3za)



Following the general procedure A, the product **3za** was obtained in 66% yield (51.8 mg, 0.132 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.17. Mp 133-134 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.23 (d, *J* = 7.2 Hz, 2H), 7.19 – 7.15 (m, 1H), 7.10 (d, *J* = 7.4 Hz, 2H), 5.99 (s, 1H), 3.66 - 3.57 (m, 2H), 2.60 - 2.57 (m, 1H), 2.47 - 2.41 (m, 1H), 2.28 - 2.23 (m, 1H), 2.15 - 2.11 (m, 2H), 2.04 - 1.99 (m, 1H), 1.80 - 1.77 (m, 1H), 1.63 – 1.53 (m, 6H), 1.45 – 1.35 (m, 2H), 1.29 – 1.16 (m, 3H), 1.14 - 1.09 (m, 1H), 1.00 - 0.96 (m, 1H), 0.89 (s, 3H), 0.63 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 208.6, 140.5, 134.4, 130.4, 129.6, 128.6, 127.0, 126.9, 123.9, 61.9, 57.0, 51.2, 47.8, 44.6, 39.0, 34.8, 34.5, 31.7, 31.6, 30.7, 24.5, 23.5, 21.2, 18.9, 13.7. ESI-MS: calculated C₂₇H₃₅O₂ [M+H]⁺ 391.2553; Found 391.2549.

4-(2-phenylacetyl)-N,N-dipropylbenzenesulfonamide (3aaa)



Following the general procedure A, the product **3aaa** was obtained in 55% yield (39.5 mg, 0.11 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.26. Mp 63-64 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.27 (t, *J* = 7.2 Hz, 2H), 7.21 - 7.17 (m, 3H), 4.23 (s, 2H), 3.04 - 2.98 (m, 4H), 1.52 - 1.42 (m, 4H), 0.79 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 196.6, 144.2, 139.2, 133.7, 129.4, 129.2, 128.9, 127.3, 127.2, 50.0, 45.9, 22.0, 11.2. ESI-MS: calculated C₂₀H₂₆NO₃S [M+H]⁺ 360.1628; Found 360.1630.

2-([1,1'-biphenyl]-4-yl)-1-phenylethanone (3ab) ^[13]



Following the general procedure A, the product **3ab** was obtained in 76% yield (41.4 mg, 0.152 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.21. ¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.91 (m, 2H), 7.52 – 7.42 (m, 5H), 7.40 – 7.29 (m, 4H), 7.28 – 7.20 (m, 3H), 4.23 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 197.6, 140.9, 139.9, 136.7, 133.6, 133.3, 130.0, 128.8, 128.7, 128.7, 127.5, 127.3, 127.1, 45.1.

2-(4-phenoxyphenyl)-1-phenylethanone (3ac) [14]



Following the general procedure A, the product **3ac** was obtained in 90% yield (52.1 mg, 0.18 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.27. ¹H NMR (400 MHz, CDCl₃) δ 8.07 - 8.05 (m, 2H), 7.64 - 7.56 (m, 1H), 7.52 - 7.49 (m, 2H), 7.40 - 7.32 (m, 2H), 7.30 - 7.23 (m, 2H), 7.17 - 7.09 (m, 1H), 7.08 - 6.96 (m, 4H), 4.30 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 197.6, 157.2, 156.3, 136.6, 133.2, 130.8, 129.7, 129.3, 128.7, 128.6, 123.3, 119.0, 118.9, 44.7.

1-phenyl-2-(4-vinylphenyl)ethanone (3ad) [15]



Following the general procedure A, the product **3ad** was obtained in 98% yield (43.5 mg, 0.196 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.22. ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 8.03 (m, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.22 (m, 2H), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.75 (d, *J* = 17.6 Hz, 1H), 5.25 (d, *J* = 10.9 Hz, 1H), 4.30 (s,

2H). ¹³C NMR (101 MHz, CDCl₃) δ 197.5, 136.6, 136.5, 136.3, 134.1, 133.2, 129.6, 128.7, 128.6, 126.5, 113.7, 45.3.

1-phenyl-2-(4-(trimethylsilyl)phenyl)ethan-1-one (3ae) [16]



Following the general procedure A, the product **3ae** was obtained in 77% yield (41.4 mg, 0.154 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.19. ¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, J = 7.2 Hz, 2H), 7.54 (d, J = 7.1 Hz, 1H), 7.49 - 7.44 (m, 4H), 7.26 (d, J = 8.7 Hz, 2H), 4.28 (s, 2H), 0.25 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 197.7, 138.9, 136.7, 135.2, 133.7, 133.3, 129.0, 128.8, 128.8, 45.6, -1.0.

2-(4-fluorophenyl)-1-phenylethanone (3af)^[13]



Following the general procedure A, the product **3af** was obtained in 86% yield (37.0 mg, 0.176 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.21. ¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.22 (m, 2H), 7.03 (t, *J* = 8.3 Hz, 2H), 4.27 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 197.4, 161.9 (d, *J* = 245.2 Hz), 136.5, 133.33, 131.1 (d, *J* = 8.0 Hz), 130.2 (d, *J* = 3.3 Hz), 128.7, 128.53, 115.5 (d, *J* = 21.4 Hz), 44.5. ¹⁹F NMR (471 MHz, CDCl₃) δ -116.0.

2-(4-bromophenyl)-1-phenylethanone (3ag) [13]



Following the general procedure A, the product 3ag was obtained in 65% yield (35.7 mg,

0.13 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.23. ¹H NMR (400 MHz, CDCl₃) δ 8.06 – 7.97 (m, 2H), 7.64 – 7.55 (m, 1H), 7.53 – 7.42 (m, 4H), 7.16 (d, *J* = 8.4 Hz, 2H), 4.27 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 197.0, 136.4, 133.4 (d, *J* = 10.5 Hz), 131.8, 131.3, 128.7, 128.5, 121.0, 44.8.

2-(4-iodophenyl)-1-phenylethanone (3ah)^[17]



Following the general procedure A, the product **3ah** was obtained in 57% yield (36.8 mg, 0.114 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.21. ¹H NMR (400 MHz, CDCl₃) δ 8.05 – 7.95 (m, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.64 – 7.56 (m, 1H), 7.51 - 7.47 (m, 2H), 7.04 (d, *J* = 8.3 Hz, 2H), 4.25 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 196.9, 137.7, 136.4, 134.1, 133.4, 131.6, 128.7, 128.5, 92.4, 44.9.

methyl 4-(2-oxo-2-phenylethyl)benzoate (3ai) [17]



Following the general procedure A, the product **3ai** was obtained in 49% yield (25.1 mg, 0.10 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.22. ¹H NMR (400 MHz, CDCl₃) δ 8.04 - 8.01 (m, 4H), 7.63 - 7.56 (m, 1H), 7.51 - 7.47 (m, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 4.37 (s, 2H), 3.92 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 196.8, 166.9, 139.8, 136.4, 133.4, 129.9, 129.6, 128.8, 128.7, 128.5, 77.3, 77.3, 77.1, 76.8, 52.1, 45.4.

1-phenyl-2-(4-(trifluoromethoxy)phenyl)ethanone (3aj) [18]



Following the general procedure A, the product **3aj** was obtained in 66% yield (37.0 mg, 0.132 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.22. ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.92 (m, 2H), 7.53 - 7.49 (m, 1H), 7.42 - 7.38 (m, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.22 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 197.0, 148.2, 136.5, 133.4, 133.2, 131.0, 128.6 (d, *J* = 26.1 Hz), 120.5 (d, J = 256.9 Hz), 44.5. ¹⁹F NMR (471 MHz, CDCl₃) δ -57.9.

1-phenyl-2-(4-(trifluoromethyl)phenyl)ethanone (3ak) [18]



Following the general procedure A, the product 3ak was obtained in 47% yield (24.7 mg, 0.092 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.23. ¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, J = 7.8 Hz, 2H), 7.63 – 7.56 (m, 3H), 7.49 (t, J = 7.4 Hz, 2H), 7.39 (d, J = 7.8 Hz, 2H), 4.36 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 196.7, 138.6, 136.3, 133.5, 130.0, 129.3 (q, J = 32.4 Hz), 128.8, 128.5, 125.6 (q, J = 3.8 Hz), 124.2 (q, J = 272.0 Hz), 45.1. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.5.

2-(4-nitrophenyl)-1-phenylethanone (3al) [6]



Following the general procedure A, the product **3al** was obtained in 52% yield (25.2 mg, 0.102 mmol) as a light yellow solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.21. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 8.7 Hz, 2H), 8.08 – 7.99 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 4.44 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 196.0, 147.1, 142.0, 136.2,

133.8, 130.7, 128.9, 128.5, 123.8, 45.0.

2-(3-acetylphenyl)-1-phenylethanone (3am) [16]



Following the general procedure A, the product **3am** was obtained in 50% yield (23.8 mg, 0.10 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.19. ¹H NMR (400 MHz, CDCl₃) δ 8.09 – 8.01 (m, 2H), 7.88 (d, *J* = 6.6 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.42 (m, 4H), 4.38 (s, 2H), 2.62 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 198.0, 197.0, 137.5, 136.4, 135.1, 134.4, 133.4, 129.4, 128.9, 128.8, 128.5, 127.1, 45.1, 26.7.

1-phenyl-2-(m-tolyl)ethanone (3an)^[16]



Following the general procedure A, the product **3an** was obtained in 53% yield (22.4 mg, 0.10 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.20. ¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.13 – 7.05 (m, 3H), 4.26 (s, 2H), 2.34 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 197.8, 138.3, 136.7, 134.5, 133.2, 130.2, 128.7, 128.6, 127.7, 126.5, 45.5, 21.4.

2-(3,5-dimethoxyphenyl)-1-phenylethanone (3ao) [19]



Following the general procedure A, the product **3ao** was obtained in 61% yield (31.2 mg, 0.122 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.18. ¹H NMR (400 MHz, CDCl₃) δ 8.06 – 7.98 (m, 2H), 7.62 – 7.52 (m, 1H), 7.52 – 7.43 (m, 2H), 6.45 (d, *J* = 2.2 Hz, 2H), 6.38 (t, *J* = 2.2 Hz, 1H), 4.23 (s, 2H), 3.78 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 197.4, 161.0, 136.7, 136.6, 133.2, 128.7, 128.6, 107.5, 99.0, 55.3, 45.8.

2-fluoro-5-(2-oxo-2-phenylethyl)benzaldehyde (3ap)



Following the general procedure A, the product **3ap** was obtained in 43% yield (21.0 mg, 0.088 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.22. Mp 107-108 °C. ¹H NMR (500 MHz, CDCl₃) δ 10.35 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.75 (d, *J* = 6.4 Hz, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.55 – 7.46 (m, 3H), 7.16 (t, *J* = 9.3 Hz, 1H), 4.33 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 196.6, 187.1 (d, *J* = 6.4 Hz), 163.9 (d, *J* = 258.4 Hz), 137.7 (d, *J* = 9.1 Hz), 136.2, 133.6, 131.2 (d, *J* = 3.7 Hz), 129.6 (d, *J* = 1.9 Hz), 128.9, 128.4, 124.0 (d, *J* = 8.4 Hz), 116.8 (d, *J* = 20.9 Hz), 44.1. ESI-MS: calculated C₁₅H₁₂FO₂ [M+H]⁺ 243.0816; Found 243.0787. ¹⁹F NMR (471 MHz, CDCl₃) δ -124.6.

2-(4-chloro-3-methoxyphenyl)-1-phenylethanone (3aq)



Following the general procedure A, the product **3aq** was obtained in 70% yield (36.6 mg, 0.14 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.21. Mp 93-94 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 1H),

6.76 (s, 1H), 6.72 (d, J = 7.9 Hz, 1H), 4.18 (s, 2H), 3.79 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 197.2, 155.0, 136.4, 134.5, 133.4, 130.2, 128.8, 128.6, 122.4, 121.2, 113.3, 56.1, 45.2. ESI-MS: calculated C₁₅H₁₄ClO₂ [M+H]⁺ 261.0677; Found 261.0666.

2-(3-chloro-4-methylphenyl)-1-phenylethanone (3ar)



Following the general procedure A, the product **3ar** was obtained in 78% yield (38.3 mg, 0.15 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.23. Mp 61-62 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.04 – 8.01 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.28 (s, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.08 (dd, *J* = 7.7, 1.3 Hz, 1H), 4.25 (s, 2H), 2.37 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 197.1, 136.4, 134.6, 134.5, 133.6, 133.4, 131.1, 130.0, 128.7, 128.6, 127.8, 44.6, 19.7. ESI-MS: calculated C₁₅H₁₄ClO [M+H]⁺ 245.0728; Found 245.0726.

2-fluoro-4-(2-oxo-2-phenylethyl)benzonitrile (3as)



Following the general procedure A, the product **3as** was obtained in 32% yield (15.2 mg, 0.06 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.24. Mp 91-92 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.02 – 8.00 (m, 2H), 7.66 - 7.59 (m, 2H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.19 - 7.16 (m, 2H), 4.39 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 195.5, 163.1 (d, *J* = 259.2 Hz), 143.0 (d, *J* = 8.1 Hz), 136.0, 133.9, 133.4, 129.0, 128.4, 126.4 (d, *J* = 3.4 Hz), 117.9 (d, *J* = 19.9 Hz), 113.9, 100.1 (d, *J* = 15.5 Hz), 45.0 (d, *J* = 1.5 Hz). ESI-MS: calculated C₁₅H₁₁FNO [M+H]⁺ 240.0819; Found 240.0839. ¹⁹F NMR (471 MHz, CDCl₃) δ -106.4.

2-(2-fluoro-5-methylphenyl)-1-phenylethanone (3at) [16]



Following the general procedure A, the product **3at** was obtained in 21% yield (9.5 mg, 0.042 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.22. ¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.1 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.03 (d, *J* = 6.4 Hz, 2H), 6.96 (t, *J* = 8.8 Hz, 1H), 4.28 (s, 2H), 2.29 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 196.6, 159.1 (d, *J* = 242.7 Hz), 136.4, 133.6 (d, *J* = 3.5 Hz), 133.3, 132.0 (d, *J* = 4.1 Hz), 129.3 (d, *J* = 8.0 Hz), 128.7, 128.5, 121.3 (d, *J* = 16.2 Hz), 115.0 (d, *J* = 22.0 Hz), 38.6, 20.7.

2-(2,3-dihydrobenzofuran-5-yl)-1-phenylethanone (3au) [20]



Following the general procedure A, the product **3au** was obtained in 62% yield (29.6 mg, 0.124 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.28. ¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 7.4 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.09 (s, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.53 (t, *J* = 8.6 Hz, 2H), 4.20 (s, 2H), 3.17 (t, *J* = 8.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 198.2, 159.1, 136.7, 133.1, 129.1, 128.6, 128.6, 127.6, 126.3, 126.0, 109.3, 71.3, 44.9, 29.7.

2-(benzo[d][1,3]dioxol-5-yl)-1-phenylethanone (3av) [20]



Following the general procedure A, the product **3av** was obtained in 62% yield (40.4 mg, 0.124 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.23. ¹H NMR (500 MHz, CDCl₃) δ 8.04 – 7.97 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 6.76 (d, *J* = 7.9 Hz, 2H), 6.71 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.93 (s, 2H), 4.20 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 197.7, 147.9, 146.6, 136.5, 133.2, 128.7, 128.6, 128.1, 122.6, 109.9, 108.5, 101.0, 45.1.

1-phenyl-2-(thiophen-3-yl)ethanone (3aw) ^[20]



Following the general procedure A, the product **3aw** was obtained in 48% yield (19.5 mg, 0.098 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.25. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.32 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.05 (d, *J* = 4.8 Hz, 1H), 4.33 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 197.1, 136.5, 134.2, 133.3, 128.7, 128.7, 128.6, 125.8, 122.9, 40.1.

2-(benzofuran-2-yl)-1-phenylethanone (3ax)



Following the general procedure A, the product **3ax** was obtained in 71% yield (33.7 mg, 0.14 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.22. Mp 86-87 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.07 (dd, J = 5.2, 3.3 Hz, 2H), 7.67 – 7.58 (m, 1H), 7.54 - 7.50 (m, 3H), 7.49 – 7.44 (m, 1H), 7.28 – 7.18 (m, 2H), 6.67 (s, 1H), 4.48 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 194.5, 155.0, 151.4, 136.1, 133.6, 128.8, 128.7, 123.8, 122.7, 120.7, 111.0, 105.4, 38.9. ESI-MS: calculated C₁₆H₁₃O₂ [M+H]⁺ 237.0910; Found 237.0903.

2-(dibenzo[b,d]furan-4-yl)-1-phenylethanone (3ay)



Following the general procedure A, the product **3ay** was obtained in 45% yield (26.1 mg, 0.094 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.19. Mp 95-96 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, *J* = 7.4 Hz, 2H), 7.85 (d, *J* = 7.4 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.39 - 7.34 (m, 3H), 7.26 - 7.20 (m, 3H), 4.56 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 196.6, 156.1, 154.7, 136.6, 133.3, 128.7, 128.6, 128.4, 127.1, 124.6, 124.2, 123.0, 122.8, 120.8, 119.6, 118.8, 111.7, 39.4. ESI-MS: calculated C₂₀H₁₅O₂ [M+H]⁺ 287.1067; Found 287.1059.

2-(dibenzo[b,d]thiophen-2-yl)-1-phenylethanone (3az)



Following the general procedure A, the product **3az** was obtained in 75% yield (45.4 mg, 0.15 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.21. Mp 96-97 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.05 – 7.99 (m, 1H), 7.96 - 7.94 (m, 3H), 7.79 – 7.64 (m, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.40 – 7.29 (m, 4H), 7.25 (d, *J* = 8.1 Hz, 1H), 4.34 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 197.7, 139.8, 138.1, 136.6, 136.0, 135.3, 133.3, 130.9, 128.7, 128.7, 128.3, 126.8, 124.4, 123.0, 122.9, 122.5, 121.7, 45.5. ESI-MS: calculated C₂₀H₁₅OS [M+H]⁺ 303.0838; Found 303.0839.

2-(naphthalen-1-yl)-1-phenylethanone (4aa) [7]



Following the general procedure A, the product **4aa** was obtained in 40% yield (19.9 mg, 0.080 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.21. ¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.08 (m, 2H), 7.93 – 7.87 (m, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.63 - 7.59 (m, 1H), 7.56 – 7.48 (m, 4H), 7.48 – 7.42 (m, 1H), 7.39 (d, *J* = 6.7 Hz, 1H), 4.77 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 197.7, 136.7, 133.9, 133.3, 132.3, 131.4, 128.8, 128.7, 128.5, 128.0, 127.9, 126.3, 125.8, 125.5, 123.9, 43.1.

2-(naphthalen-2-yl)-1-phenylethanone (4ab) [16]



Following the general procedure A, the product **4ab** was obtained in 67% yield (33.2 mg, 0.134 mmol) as a white solid after chromatography on silica gel (eluent = etroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.20. ¹H NMR (400 MHz, CDCl₃) δ 8.12 – 8.05 (m, 2H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 6.9 Hz, 1H), 7.76 (s, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.46 (m, 4H), 7.44 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.48 (s, 2H).¹³C NMR (126 MHz, CDCl₃) δ 197.7, 136.6, 133.6, 133.3, 132.4, 132.2, 128.7, 128.7, 128.4, 128.1, 127.7, 127.7, 127.6, 126.2, 125.8, 45.7.

Note: In order to verify the reliability and repeatability of the product yield in the article, we selectively repeated experiments on some substrates. The specific reaction results are shown in the following table:



Number	Yield (original)	Yield (repeat)	Yield (average)
3ga	37%	38%	37%
3ma	62%	60%	61%
Зра	73%	68%	70%
3xa	66%	63%	64%
3af	88%	85%	86%
3ak	46%	49%	47%
3al	51%	54%	52%
3an	50%	57%	53%
3 ap	44%	43%	43%
3ar	75%	81%	78%
3as	30%	34%	32%
3aw	49%	47%	48%
3ax	70%	73%	71%
3ay	47%	44%	45%
3ai	50%	49%	49%

4. Synthetic application of the product 3aa

4.1 Gram Scale Synthesis



In an oven-dried Schlenk tube under air, a mixture of the substrates **1a** (3 mmol, 1.0 equiv), boronic acid **2a** (4.5 mmol, 1.5 equiv), (Cp*IrCl₂)₂ (2.5 mol%), AgSbF₆ (10.0 mol%), DIPA (1.5 equiv) and PhMe (0.2 M) was stirred at 60 °C for 12 h. Then the reaction mixture was then diluted with EA (30.0 mL) and washed with H₂O. The aqueous phase was extracted with EA again. The organic layers were combined, washed with brine and dried over Na₂SO₄. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product (petroleum ether : ethyl acetate = 100:1) to give **3aa** (0.4 g, 68%).

4.2 Synthesis of benzil (5) and benzoin (6)



In an oven-dried Schlenk tube under air, a mixture of the substrates **3aa** (0.5 mmol, 1.0 equiv), KHCO₃ (25.0 mol%), DMSO (0.05M) was stirred at 80 °C overnight. Then the reaction mixture was then diluted with EA (10.0 mL) and washed with H₂O. The aqueous phase was extracted with EA again. The organic layers were combined, washed with brine and dried over Na₂SO₄. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product (petroleum ether : ethyl acetate = 32:1-8:1) to give **5** (78.7 mg, 75%) and **6** (19.0 mg, 18%). Compound **5**, light yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.86 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 7.91 (d, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.36 – MHz, CDCl₃) δ 7.91 (d, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.36 –

7.25 (m, 5H), 5.95 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 199.0, 139.1, 134.0, 133.6, 129.2, 129.3, 128.8, 128.7, 127.9, 76.3.



4.3 Synthesis of 2-(naphthalen-2-yl)-4,5-diphenyl-1H-imidazole (7)

In an oven-dried Schlenk tube, a mixture of the substrates **5** (0.2 mmol, 1.0 equiv), 2-Naphthaldehyde (1.2 eq), NH₄Ac (3.0 eq), HAc (0.04M) was stirred at 120 °C overnight. Then the reaction mixture was then diluted with EA (10.0 mL) and washed with saturated sodium hydrogencarbonate to adjust pH to 7-8. The aqueous phase was extracted with EA again. The organic layers were combined, washed with brine and dried over Na₂SO₄. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product (petroleum ether : ethyl acetate = 4:1-1:1) to give **7** (52.0 mg, 75%) as a white solid. ¹H NMR (400 MHz, DMSO) δ 12.87 (s, 1H), 8.63 (s, 1H), 8.27 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 8.00 – 7.93 (m, 2H), 7.60 (d, *J* = 7.2 Hz, 2H), 7.58 – 7.51 (m, 4H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H). ¹³C NMR (101 MHz, DMSO) δ 146.0, 137.9, 135.6, 133.5, 133.2, 131.5, 129.2, 129.0, 129.0, 128.9, 128.7, 128.6, 128.3, 128.2, 127.6, 127.2, 127.1, 126.8, 124.4, 124.0.

4.4 Synthesis of 5,5-diphenylimidazolidine-2,4-dione (phenytoin, 8)



In an oven-dried Schlenk tube, a mixture of the substrates **5** (0.2 mmol, 1.0 equiv), urea (2.0 eq), 20% NaOH (0.2 mL), EtOH (0.02 M) was stirred at 70 °C for 2 h. Then the reaction mixture

was then diluted with EA (10.0 mL) and washed with 10% hydrochloric acid to adjust pH to 5-6. The aqueous phase was extracted with EA again. The organic layers were combined, washed with brine and dried over Na₂SO₄. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product (petroleum ether : ethyl acetate = 2:1-1:2) to give **8** (44.3 mg, 88%) as a white solid. ¹H NMR (500 MHz, DMSO) δ 11.08 (s, 1H), 9.31 (s, 1H), 7.40 - 7.39 (m, 4H), 7.36 - 7.35 (m, 6H). ¹³C NMR (126 MHz, DMSO) δ 175.3, 156.4, 140.4, 129.0, 128.5, 127.0, 70.7.

5. Mechanistic Studies

5.1 Deuterated experiment



In an oven-dried Schlenk tube under air, a mixture of the substrates **1i** (0.2 mmol), boronic acid **2a** (0.5 mmol, 2.5 equiv), (Cp*IrCl₂)₂ (2.5 mol%), AgSbF₆ (10.0 mol%), D₂O (0.8 mmol, 4.0 equiv) and PhMe (0.2 M) was stirred at 60 °C for 2 h. Then the reaction mixture was then diluted with EA (30.0 mL) and washed with H₂O. The aqueous phase was extracted with EA again. The organic layers were combined, washed with brine and dried over Na₂SO₄. The pure product was purified by flash column chromatography on silica with an appropriate solvent (petroleum ether : ethyl acetate = 16:1) to afford the mixture product **3ia** and **3ia'** (12.7 mg, 28%). The spectra of the products are shown in the following figure.





In an oven-dried Schlenk tube under air, a mixture of the product **3ia** (0.2 mmol), $(Cp*IrCl_2)_2$ (2.5 mol%), AgSbF₆ (10.0 mol%), D₂O (0.8 mmol, 4.0 equiv) and PhMe (0.2 M) was stirred at 60 °C for 2 h. Then the reaction mixture was then diluted with EA (30.0 mL) and washed with H₂O. The aqueous phase was extracted with EA again. The organic layers were combined, washed with brine and dried over Na₂SO₄. The pure product was purified by flash column chromatography on silica with an appropriate solvent (petroleum ether : ethyl acetate = 16:1) to afford the product **3ia** (40.1 mg, 88%). The spectra of the products are shown in the following figure.



5.2 Competitive experiment



In an oven-dried Schlenk tube under air, a mixture of the substrates **1i** (0.1 mmol), **1k** (0.1 mmol), boronic acid **2a** (0.5 mmol, 2.5 equiv), (Cp*IrCl₂)₂ (2.5 mol%), AgSbF₆ (10.0 mol%), DIAP (0.3 mmol, 1.5 equiv) and PhMe (0.2 M) was stirred at 60 °C for 2 h. Then the reaction mixture was then diluted with EA (30.0 mL) and washed with H₂O. The aqueous phase was extracted with EA again. The organic layers were combined, washed with brine and dried over Na₂SO₄. The pure product was purified by flash column chromatography on silica with an appropriate solvent (petroleum ether : ethyl acetate = 16:1) to afford the product **3ia** (14.2 mg, 31%) and **3ka** (9.2 mg, 17%).



In an oven-dried Schlenk tube under air, a mixture of the substrates **1a** (0.2 mmol), boronic acid **2c** (0.25 mmol, 1.25 equiv), boronic acid **2k** (0.25 mmol, 1.25 equiv), (Cp*IrCl₂)₂ (2.5 mol%), AgSbF₆ (10.0 mol%), DIAP (0.3 mmol, 1.5 equiv) and PhMe (0.2 M) was stirred at 60 °C for 2 h. Then the reaction mixture was then diluted with EA (30.0 mL) and washed with H₂O. The aqueous phase was extracted with EA again. The organic layers were combined, washed with brine and dried over Na₂SO₄. The pure product was purified by flash column chromatography on silica with an appropriate solvent (petroleum ether : ethyl acetate = 16:1) to afford the product **3ac** (23.9 mg, 41%) and **3ak** (10.1 mg, 19%).

6. ¹H NMR and ¹³C NMR spectra



¹³C NMR spectrum of **3aa**



¹³C NMR spectrum of **3ba**



¹⁹F NMR spectrum of **3ba**






¹³C NMR spectrum of **3da**































¹⁹F NMR spectrum of **3ka**



















¹³C NMR spectrum of **3pa**



¹³C NMR spectrum of **3qa**







¹⁹F NMR spectrum of **3ra**







¹³C NMR spectrum of **3sa**



¹³C NMR spectrum of **3ta**























¹³C NMR spectrum of **3za**











¹⁹F NMR spectrum of **3af**

8.04 8.03 8.03 8.01 8.01 8.01 7.162 7.160 7.150 7.150 7.150 7.150 7.150 7.151 7.155 7



¹⁹F NMR spectrum of **3aj**







¹⁹F NMR spectrum of **3ak**







¹³C NMR spectrum of **3am**















¹⁹F NMR spectrum of **3ap**



¹³C NMR spectrum of **3aq**















¹³C NMR spectrum of **3at**











¹³C NMR spectrum of **3aw**











¹³C NMR spectrum of **3az**

























7. Reference

- [1] Talero, A. G.; Martins, B. S.; Burtoloso, A. C. B. Org. Lett. 2018, 20, 7206-7211.
- [2] Janot, C.; Palamini, P.; Dobson, B. C.; Muir, J.; Aïssa, C. Org. Lett., 2019, 21, 296-299.
- [3] Lei, C.; Zhu, D.; Tangcueco, V. T.; Zhou, J. S. Org. Lett. 2019, 21, 5817-5822.
- [4] Moustafa, D.; Sweet, C.; Lim, H.; Calalp, B.; Kaur, P. *Tetrahedron Letters*. **2018**, *59*, 3816–3820.
- [5] Miao, T.; Wang, G.-W. Chem. Commun., 2011, 47, 9501-9503.
- [6] Rao, B.; Tang, J.; Zeng, X. Org. Lett. 2016, 18, 1678-1681.
- [7] Chen, X.; Chen, Z.; So, C. M. J. Org. Chem. 2019, 84, 6337–6346.
- [8] Moustafa, D.; Sweet, C.; Lim, H.; Calalp, B.; Kaur, P. *Tetrahedron Letters*. 2018, 59, 3816–3820.
- [9] Davies, A. V.; Fitzpatrick, K. P.; Betori, R. C.; Scheidt, K. A.; Angew. Chem. Int. Ed. 10.1002/anie.202001824.
- [10] Wong, Y.-C.; Parthasarathy, K.; Cheng, C.-H. Org. Lett. 2010, 12, 1736-1739.
- [11] Huang, K.; Li, G.; Huang, W.-P.; Yu, D.-G.; Shi, Z.-J. Chem. Commun., 2011, 47, 7224–7226.
- [12] Zhang, J.; Yang, M.; Liu, J.-B.; He, F.-S.; Wu, J. Chem. Commun., 2020, 56, 3225-3228.
- [13] Chen, T.; Li, Y.-F.; An, Y.; Zhang, F.-M.; Org. Lett. 2016, 18, 4754–4757.
- [14] Labadie, J. W.; Stille, J. K. J. Am. Chem. Soc. 1983, 105, 6129-6137.
- [15] Greenhalgh, M. D.; Frank, D. J.; Thomas, S. P.; Adv. Synth. Catal. 2014, 356, 584-590.
- [16] Gao, K.; Yorimitsu, H.; Osuka, A. Angew. Chem. Int. Ed. 2016, 55, 4573-4576.
- [17] Ye, C.; Twamley, B.; Shreeve, J. M. Org. Lett. 2005, 7, 3961-3964.
- [18] Su, Y.; Sun, X.; Wu, G.; Jiao, N. Angew. Chem. Int. Ed. 2013, 52, 9808-9812.
- [19] Yu, Z.; Qiu, H.; Liu, L.; Zhang, J. Chem. Commun., 2016, 52, 2257-2260.
- [20] Hu, F.; Yang, J.; Xia, Y.; Ma, C.; Xia, H.; Zhang, Y.; Wang, J. Org. Chem. Front., 2015, 2, 1450-1456.