Supporting Information

Transition Metal-Free Synthesis of α-Aryl Ketones via Oxyallyl

Cation Capture with Arylboronic Acids

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1. General Information

All the commercial reagents were used as such without further purification. All solvents were used as commercial anhydrous grade without further purification. The flash column chromatography was carried out over silica gel (230-400 mesh). ¹H and ¹³C NMR spectra were recorded on a Bruker Avance-400 MHz spectrometer or Bruker Avance-500 MHz spectrometer. Chemical shifts in ¹H NMR spectra were reported in parts per million (ppm, δ) downfield from the internal standard Me₄Si (TMS, $\delta = 0$ ppm). Chemical shifts in ¹³C NMR spectra were reported relative to the central line of the chloroform signal ($\delta = 77.0$ ppm). Peaks were labeled as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). High resolution mass spectra were obtained with a Shimadzu LCMS-IT-TOF mass spectrometer. Chemical yields refer to pure isolated substances.

2. General Procedure for the Synthesis of Substrates and Products

(a) Synthesis of product 3a



To a solution of 1 (0.2 mmol) and 2 (0.4 mmol) in mesitylene (2 mL), TEA (40.4 mg, 0.4 mmol) and (D)-tartaric acid (6 mg, 0.04 mmol) were added. The reaction mixture was then stirred at 110 °C for 24 hours. Upon completion, the reaction mixture was concentrated via rotary evaporation. The crude mixture was purified by flash column chromatography on silica gel to provide the desired product.

(b) Synthesis of α-tosyloxy ketones

$$\begin{array}{c} O \\ \hline \\ R^1 \\ R^2 \end{array} + \begin{array}{c} O \\ \hline \\ O \\ \hline \\ O \\ H \end{array} + \begin{array}{c} O \\ \hline \\ O \\ \hline \\ O \\ O \\ \hline \\ S0 \\ ^{\circ}C, 15-45 \\ min \end{array} + \begin{array}{c} O \\ \hline \\ R^1 \\ R^2 \end{array} + \begin{array}{c} O \\ O \\ \hline \\ R^1 \\ R^2 \end{array} + \begin{array}{c} O \\ O \\ R^1 \\ R^2 \end{array} + \begin{array}{c} O \\ R^1 \\ R^2 \\ R^2 \end{array} + \begin{array}{c} O \\ R^1 \\ R^2 \\ R^2 \\ R^2 \end{array} + \begin{array}{c} O \\ R^1 \\ R^2 \\ R^$$

The following procedure is adapted from the work of Tuncay *et al.*¹ To the ketone (15.3 mmol, 1.5 equiv.) dissolved in MeCN (20 mL, 0.5 M) was added [hydroxy(tosyloxy)iodo]benzene (4 g, 10.2 mmol, 1 equiv.), and the heterogeneous suspension was sonicated at 50 °C until a homogeneous solution was noted. The MeCN was removed under reduced pressure. The crude products were purified by flash column chromatography, affording the desired α -tosyloxyketone **1a-1f**.

(c) Synthesis of 2-bromocyclohexanone²



A solution of cyclohexanone (1.04 mL, 10.0 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of *n*-bromosuccinimide (NBS, 2.14 g, 12.0 mmol, 1.2 equiv.) and *p*-TsOH (190 mg, 1.0

mmol, 0.1 equiv.) in CH₂Cl₂ (10 mL) at 0 °C. The reaction mixture was then brought to reflux for 4 h. After addition of H₂O (10 mL), the organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (3×10 mL). The combined organic layers were washed with saturated aqueous NaHCO₃ (20 mL) and brine (20 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. Column chromatography on silica gel provided 2-bromocyclohexanone **1g** (1.6 g, 90% yield).

3. General Procedure for the Synthesis of Compounds 4-6

(a) Synthesis of 2-(4-bromophenyl)-cyclohexanol 4⁴



To a round bottom flask fitted with stirring bar was added 2-(4-bromophenyl)cyclohexanone **3am** (50.6 mg, 0.20 mmol) and methanol (1 mL) to a concentration of 0.2 M. The solution was treated with NaBH₄ (15.1 mg, 0.40 mmol) and stirred at room temperature for 2 hours. The reaction was then quenched with saturated NH₄Cl, and the aqueous layer was extracted with diethyl ether (3×5 mL). The organic layers were then combined, dried over anhydrous Na₂SO₄, filtered and concentrated. The crude mixture was purified on silica gel chromatography to give **4** as a while solid (40.8 mg, 80% yield).

(b) Synthesis of 2-(4-bromophenyl)-2-fluorocyclohexan-1-one 5⁴



Under argon atmosphere, to a 10 mL reaction tube charged with a magnetic stirring bar was added 2-(4-bromophenyl)cyclohexanone 4 (50.6 mg, 0.20 mmol), Selectfluor (141.8 mg, 0.40 mmol), *p*-TsOH (7.6 mg, 0.04 mmol), CH_2Cl_2 (0.2 mL) and MeCN (0.8 mL). The reaction mixture was stirred at 25 °C until the complete consumption of the starting material (monitored by TLC). The mixture was diluted with ethyl acetate, the resulting organic phase was washed successively with water and brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate) to give **5** as a while solid (46.0 mg, 83% yield).

(c) Synthesis of 7-(4-bromophenyl)oxepan-2-one 6¹⁷



To a solution of 2-(4-bromophenyl)cyclohexanone **4** (50.6 mg, 0.20 mmol) in 4 mL CH₂Cl₂ was added mCPBA (69 mg, 0.40 mmol) at 0°C. After stirring at rt overnight, the reaction mixture was quenched with 10% K₂CO₃ solution and a saturated aqueous solution of Na₂S₂O₃. The aqueous layer was separated and extracted with CH₂Cl₂. The combined organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure. The resulting crude product was purified by column chromatography (petroleum ether/ethyl acetate) to afford **6** as a colorless solid (47.9 mg, 89%).

4. Control Experiments^a

	1a $1a$ $1a$ $1a$ $1a$ $1a$ $1a$ $1a$	0(OH) ₂ additive Et ₃ N (2equiv.) solvent (0.1 M), 110 °C, 24 h	O Jaa	
Entry	Solvent	Additive	Add. Equiv.	Yield ^c
1	mesitylene	(D)-tartaric acid	0.2	74%
2	mesitylene	(D)-diethyl tartarate	0.2	54%
3	mesitylene	succinic acid	0.2	68%
4	mesitylene	HFIP ^b	-	70%
5	mesitylene	-	-	52%

^{*a*} Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), additive and Et₃N (2 equiv.) in mesitylene (2 mL) at 110 °C for 24 h; ^{*b*} mesitylene: HFIP (10:1, V/V); ^{*c*} Isolated yield.

5. Unsuccessful Results



^{*a*} Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), (*D*)-tartaric acid (0.04 mmol) and Et_3N (2 equiv.) in mesitylene (2 mL) at 110 °C for 24 h; ^{*b*} Pi system is necessary to engage the cationic electrophile.

6. Characterization of Substrates and Products



2-phenylcyclohexan-1-one (3aa)³

Colorless oil. R_F : 0.43 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (500 MHz, CDCl₃) δ : 7.36 (t, *J* = 7.5 Hz, 2H), 7.31-7.27 (m, 1H), 7.17 (d, *J* = 7.1 Hz, 2H), 3.64 (dd, *J* = 12.2, 5.4 Hz, 1H), 2.59-2.45 (m, 2H), 2.33-2.27 (m, 1H), 2.21-2.14 (m, 1H), 2.11-2.00 (m, 2H), 1.91-1.81 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ : 210.4, 138.8, 128.6, 128.4, 127.0, 57.5, 42.3, 35.2, 27.9, 25.4.



2-(2-fluorophenyl)cyclohexan-1-one (3ab)⁴

Colorless oil. R_F: 0.45 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.31-7.20 (m, 1H), 7.20-7.08 (m, 2H), 7.09-6.97 (m, 1H), 3.85 (dd, J = 9.3, 3.7 Hz, 1H), 2.71-2.37 (m, 2H), 2.33-2.12 (m, 2H), 2.13-1.93 (m, 2H), 1.94-1.69 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ : 208.4, 159.5 (d), 129.7 (d, J = 4.8 Hz), 128.5 (d, J = 8.3 Hz), 126.1 (d, J = 14.4 Hz), 123.9 (d, J = 3.3 Hz), 115.2 (d, J = 22.4 Hz), 51.0, 42.1, 33.7, 27.4, 25.5; ¹⁹F NMR (376 MHz, CDCl₃) δ : -109.56.



3ac

2-(2-chlorophenyl)cyclohexan-1-one (3ac)⁵

Colorless oil. R_F : 0.45 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.37 (d, *J* = 8.0 Hz, 1H), 7.29-7.17 (m, 3H), 4.10 (dd, *J* = 12.7, 5.3 Hz, 1H), 2.63-2.50 (m, 2H), 2.30-2.17 (m, 2H), 2.08-1.97 (m, 2H), 1.91-1.77 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ : 208.8, 136.7, 134.2, 129.4, 129.4, 128.1, 126.7, 54.0, 42.3, 33.9, 27.6, 25.6.



2-(2-bromophenyl)cyclohexan-1-one (3ad)⁵

Colorless oil. R_F : 0.45 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.56 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H),

4.12 (dd, J = 12.7, 5.1 Hz, 1H), 2.61-2.48 (m, 2H), 2.35-2.25 (m, 1H), 2.24-2.15 (m, 1H), 2.10-1.96 (m, 2H), 1.95-1.77 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ : 209.0, 138.5, 132.7, 129.6, 128.5, 127.5, 125.3, 56.7, 42.5, 34.3, 27.8, 25.8.



3ae

2-(o-tolyl)cyclohexan-1-one (3ae)³

Colorless oil. R_F : 0.43 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.27-7.11 (m, 4H), 3.80 (dd, J = 12.9, 4.9 Hz, 1H), 2.59-2.46 (m, 2H), 2.31-2.19 (m, 5H), 2.11-2.02 (m, 2H), 1.93-1.79 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ : 210.0, 137.3, 136.1, 130.3, 127.6, 126.8, 126.0, 53.8, 42.5, 34.2, 27.8, 25.9, 19.7.



3af

2-(2-methoxyphenyl)cyclohexan-1-one (3af)⁶

White solid. R_F : 0.40 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.23 (t, *J* = 9.1 Hz, 1H), 7.14-7.07 (m, 1H), 6.98-6.81 (m, 2H), 3.93 (m, 1H), 3.76 (s, 3H), 2.59-2.40 (m, 2H), 2.27-2.10 (m, 2H), 2.10-1.93 (m, 2H), 1.91-1.71 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ : 209.9, 156.9, 128.7, 127.9, 127.8, 120.5, 110.5, 55.4, 51.0, 42.3, 33.4, 27.5, 25.7.



3ag

2-(3-fluorophenyl)cyclohexan-1-one (3ag)³

Colorless oil. R_F : 0.45 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.33-7.26 (m, 1H), 7.01-6.78 (m, 3H), 3.61 (dd, J = 12.1, 5.5 Hz, 1H), 2.55-2.41 (m, 2H), 2.32-2.13 (m, 2H), 2.04-1.94 (m, 2H), 1.87-1.77 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ : 209.7, 162.9 (d, J = 245.2 Hz), 141.3 (d, J = 7.4 Hz), 129.8 (d, J = 8.3 Hz), 124.4 (d, J = 2.8 Hz), 115.6 (d, J = 21.6 Hz), 113.9 (d, J = 21.0 Hz), 57.2, 42.3, 35.1, 26.6, 25.4; ¹⁹F NMR (471 MHz, CDCl₃) δ : - 113.48.



3ah

2-(3-chlorophenyl)cyclohexan-1-one (3ah)⁴

Colorless oil. R_F: 0.45 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.25-7.18 (m, 2H), 7.11 (s, 1H), 7.02-6.96 (m, 1H), 3.56 (dd, J = 12.1, 5.4 Hz, 1H), 2.57-2.38 (m,

2H), 2.31-2.08 (m, 2H), 2.04-1.91 (m, 2H), 1.86-1.72 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ: 209.4, 140.7, 134.1, 129.5, 128.7, 127.0, 126.8, 57.0, 42.1, 35.0, 27.7, 25.3.



2-(m-tolyl)cyclohexan-1-one (3ai)7

Colorless oil. R_F: 0.42 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (500 MHz, CDCl₃) δ : 7.22 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 2H), 3.57 (dd, *J* = 12.0, 5.4 Hz, 1H), 2.57-2.39 (m, 2H), 2.34 (s, 3H), 2.29-2.11 (m, 2H), 2.10-1.96 (m, 2H), 1.89-1.75 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ : 210.3, 138.7, 137.8, 129.2, 128.2, 127.6, 125.5, 57.3, 42.1, 34.9, 27.7, 25.2, 21.4.



2-(3-methoxyphenyl)cyclohexan-1-one (3aj)8

Colorless oil. R_F : 0.43 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.28 (t, J = 3.9 Hz, 1H), 6.83 (dd, J = 8.0, 2.2 Hz, 1H), 6.76 (d, J = 7.6 Hz, 1H), 6.72 (d, J = 1.9 Hz, 1H), 3.82 (s, 3H), 3.61 (dd, J = 12.0, 5.4 Hz, 1H), 2.63-2.38 (m, 2H), 2.34-2.23 (m, 1H), 2.22-2.12 (m, 1H), 2.10-1.97 (m, 2H), 1.91-1.77 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ : 210.2, 159.5, 140.3, 129.3, 120.9, 114.5, 112.1, 57.3, 55.1, 42.1, 34.9, 27.7, 25.2.



3ak

2-(4-fluorophenyl)cyclohexan-1-one (3ak)³

Colorless oil. R_F : 0.45 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.20-6.93 (m, 4H), 3.60 (dd, J = 11.8, 5.3 Hz, 1H), 2.64-2.36 (m, 2H), 2.33-2.09 (m, 2H), 2.08-1.91 (m, 2H), 1.90-1.70 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ : 210.1, 161.8 (d, J = 244.7 Hz), 134.4 (d, J = 2.4 Hz), 130.0 (d, J = 7.9 Hz), 115.1 (d, J = 21.3 Hz), 56.6, 42.2, 35.4, 27.8, 25.4; ¹⁹F NMR (376 MHz, CDCl₃) δ : -116.20.



3al

2-(4-chlorophenyl)cyclohexan-1-one (3al)7

Colorless oil. R_F : 0.45 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.35-7.24 (m, 2H), 7.11-7.01 (m, 2H), 3.65-3.55 (m, 1H), 2.61-2.38 (m, 2H), 2.34-2.09 (m, 2H),

2.09-1.90 (m, 2H), 1.91-1.68 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ: 209.8, 137.2, 132.7, 129.9, 128.5, 56.8, 42.2, 35.2, 27.8, 25.3.



2-(4-bromophenyl)cyclohexan-1-one (3am)9

White solid. R_F : 0.45 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.45 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 3.57 (dd, *J* = 12.1, 5.3 Hz, 1H), 2.56-2.39 (m, 2H), 2.29-2.11 (m, 2H), 2.04-1.91 (m, 2H), 1.88-1.75 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ : 209.7, 137.7, 131.4, 130.3, 120.8, 56.8, 42.2, 35.2, 27.7, 25.3.



2-(4-methoxyphenyl)cyclohexan-1-one (3an)³

White solid. R_F : 0.43 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.15-7.00 (m, 2H), 6.94-6.85 (m, 2H), 3.79 (s, 3H), 3.57 (dd, J = 12.2, 5.4 Hz, 1H), 2.59-2.37 (m, 2H), 2.34-2.08 (m, 2H), 2.07-1.91 (m, 2H), 1.90-1.72 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ : 210.7, 158.4, 130.8, 129.4, 113.8, 56.5, 55.2, 42.2, 35.3, 27.9, 25.4.



2-(4-(tert-butyl)phenyl)cyclohexan-1-one (3ao)³

White solid. R_F : 0.40 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.36 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.65-3.54 (m, 1H), 2.57-2.42 (m, 2H), 2.31-2.13 (m, 2H), 2.03 (dd, *J* = 18.7, 6.7 Hz, 2H), 1.88-1.77 (m, 2H), 1.32 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ : 210.7, 149.6, 135.7, 128.2, 125.4, 57.0, 42.3, 35.2, 34.5, 31.5, 28.0, 25.4.



2-(p-tolyl)cyclohexan-1-one (3ap)³

Colorless oil. R_F : 0.45 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (500 MHz, CDCl₃) δ : 7.15 (d, *J* = 7.9 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 3.58 (dd, *J* = 12.1, 5.4 Hz, 1H), 2.57-2.39 (m, 2H), 2.34 (s, 3H), 2.31-2.11 (m, 2H), 2.10-1.94 (m, 2H), 1.94-1.74 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ : 210.4, 136.4, 135.7, 129.0, 128.3, 57.0, 42.1, 35.0, 27.8, 25.3, 21.0



2-(4-phenoxyphenyl)cyclohexan-1-one (3aq)

Colorless oil. R_F : 0.50 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 35:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.45-7.28 (m, 2H), 7.18-6.92 (m, 7H), 3.59 (dd, J = 12.2, 5.5 Hz, 1H), 2.61-2.38 (m, 2H), 2.35-2.11 (m, 2H), 2.06-1.91 (m, 2H), 1.89-1.74 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ : 210.4, 157.2, 156.1, 133.5, 129.7, 129.7, 123.2, 119.0, 118.6, 56.7, 42.2, 35.4, 27.9, 25.4. HRMS (ESI): *m/z* [M+H]⁺ calcd. for [C₁₈H₁₉O₂]⁺: 267.1380, found: 267.1380.



2-([1,1'-biphenyl]-4-yl)cyclohexan-1-one (3ar)¹¹

White solid. R_F : 0.55 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 35:1). ¹H NMR (500 MHz, CDCl₃) δ : 7.61-7.55 (m, 4H), 7.43 (t, J = 7.7 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 8.2 Hz, 2H), 3.67 (dd, J = 12.3, 5.4 Hz, 1H), 2.59-2.46 (m, 2H), 2.36-2.29 (m, 1H), 2.22-2.15 (m, 1H), 2.11-2.02 (m, 2H), 1.90-1.82 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ : 210.4, 141.0, 139.8, 137.8, 128.9, 128.7, 127.1, 127.1, 57.1, 42.2, 35.2, 27.8, 25.4.



methyl 4-(2-oxocyclohexyl)benzoate (3as)⁶

Colorless oil. R_F : 0.43 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 8.00 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 3.67 (dd, *J* = 12.3, 5.5 Hz, 1H), 2.57-2.42 (m, 2H), 2.31-2.14 (m, 2H), 2.08-1.97 (m, 2H), 1.90-1.79 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ : 209.4, 166.9, 144.0, 129.6, 128.7, 128.6, 57.4, 52.0, 42.2, 35.0, 27.7, 25.3.



3at

2-(2-isopropylphenyl)cyclohexan-1-one (3at)

Colorless oil. R_F : 0.40 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.33 (dd, J = 7.7, 1.3 Hz, 1H), 7.31-7.25 (m, 1H), 7.25-7.18 (m, 1H), 7.14 (d, J = 7.6 Hz, 1H), 3.92 (dd, J = 12.7, 5.4 Hz, 1H), 3.00-2.84 (m, 1H), 2.67-2.45 (m, 2H), 2.37-2.17 (m, 2H), 2.19-2.01 (m, 2H), 1.97-1.80 (m, 2H), 1.32-1.15 (m, 6H); ¹³C NMR (126 MHz, CDCl₃) δ : 210.2, 146.4,

136.0, 128.3, 127.1, 125.6, 125.3, 53.2, 42.5, 35.3, 29.3, 27.6, 25.9, 24.0, 23.8. HRMS (ESI): *m/z* [M+H]⁺ calcd. for [C₁₅H₂₁O]⁺: 217.1587, found: 217.1584.



2-(naphthalen-1-yl)cyclohexan-1-one (3au)¹²

White solid. R_F : 0.39 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.90-7.84 (m, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.75-7.68 (m, 1H), 7.51-7.42 (m, 3H), 7.36 (d, J = 7.1 Hz, 1H), 4.36 (dd, J = 12.5, 5.3 Hz, 1H), 2.71-2.60 (m, 2H), 2.47-2.38 (m, 1H), 2.36-2.23 (m, 2H), 2.18-2.10 (m, 1H), 2.02-1.88 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ : 210.0, 135.2, 133.8, 131.8, 129.0, 127.6, 125.9, 125.3, 125.3, 125.3, 123.2, 53.3, 42.6, 34.3, 27.9, 25.9.



3av

2-(anthracen-9-yl)cyclohexan-1-one (3av)³

White solid. R_F : 0.55 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 35:1). ¹H NMR (400 MHz, CDCl₃) δ : 8.42 (s, 1H), 8.11-7.98 (m, 2H), 7.98-7.82 (m, 2H), 7.56-7.37 (m, 4H), 4.88 (dd, J = 12.3, 6.7 Hz, 1H), 2.98-2.77 (m, 1H), 2.80-2.46 (m, 2H), 2.41-2.28 (m, 2H), 2.26-2.10 (m, 2H), 2.08-1.86 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ : 209.3, 132.5, 132.0, 130.0, 129.5, 127.5, 125.5, 124.6, 51.3, 41.9, 33.4, 25.7, 25.5.



2-(benzo[d][1,3]dioxol-5-yl)cyclohexan-1-one (3aw)³

Colorless oil. R_F : 0.40 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 6.77 (d, *J* = 7.9 Hz, 1H), 6.64 (d, *J* = 1.4 Hz, 1H), 6.58 (dd, *J* = 7.9, 1.4 Hz, 1H), 5.93 (s, 2H), 3.53 (dd, *J* = 12.0, 5.3 Hz, 1H), 2.59-2.38 (m, 2H), 2.30-2.08 (m, 2H), 2.03-1.92 (m, 2H), 1.88-1.75 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ : 210.5, 147.7, 146.5, 132.7, 121.6, 109.1, 108.3, 101.0, 57.2, 42.3, 35.5, 27.9, 25.5.



2-(thiophen-2-yl)cyclohexan-1-one (3ax)¹⁰

Colorless oil. R_F : 0.30 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1). ¹H NMR (400 MHz, CDCl₃) δ :

7.24 (d, J = 5.1 Hz, 1H), 6.99-6.90 (m, 1H), 6.86 (d, J = 3.2 Hz, 1H), 3.92 (dd, J = 11.1, 5.4 Hz, 1H), 2.60-2.53 (m, 1H), 2.50-2.36 (m, 2H), 2.18-1.92 (m, 3H), 1.94-1.73 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ : 208.9, 141.1, 126.5, 125.1, 124.4, 52.0, 41.6, 36.2, 27.7, 25.0.



(*E*)-2-styrylcyclohexanone (*3ay*) and (*E*)-2-(2-phenylethylidene)cyclohexanone (*3ay*') as a mixture (3ay:3ay' = 3.7:1)

White solid. R_F : 0.65 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 40:1). ¹H NMR (500 MHz, CDCl₃) δ : 7.38 (d, J = 7.5 Hz, 7.4H), 7.32-7.15 (m, 16.1H), 6.78 (t, J = 7.6 Hz, 1H), 6.47-6.35 (m, 7.4H), 3.45 (d, J = 7.6 Hz, 2H), 3.19 (dt, J = 10.4, 6.4 Hz, 3.7H), 2.61 (t, J = 6.0 Hz, 2H), 2.50-2.43 (m, 5.7H), 2.40-2.32 (m, 3.7H), 2.22-2.16 (m, 3.7H), 2.09-2.03 (m, 3.7H), 1.97-1.85 (m, 6.7H), 1.82-1.72 (m, 12.1H); ¹³C NMR (101 MHz, CDCl₃) δ : 211.2, 137.1, 136.6, 131.4, 128.6, 128.5, 127.5, 127.3, 126.3, 126.3, 54.0, 41.7, 40.2, 34.4, 33.9, 27.6, 26.8, 24.4, 23.6, 23.3.



4-methyl-2-phenylcyclohexan-1-one (3ba)

Colorless oil. R_F : 0.45 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.37-7.29 (m, 2H), 7.28-7.21 (m, 1H), 7.15-7.07 (m, 2H), 3.64 (dt, J = 13.4, 4.5 Hz, 1H), 2.59-2.45 (m, 2H), 2.26-2.04 (m, 3H), 1.80-1.66 (m, 1H), 1.62-1.46 (m, 1H), 1.11-1.01 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ : 210.3, 138.8, 128.7, 128.3, 126.9, 56.7, 43.7, 41.6, 35.7, 32.4, 21.3. HRMS (ESI): m/z [M+H]⁺ calcd. for [C₁₃H₁₇O]⁺: 189.1274, found: 189.1289.



3-phenyltetrahydro-4*H*-pyran-4-one (3ca)¹³

White solid. R_F: 0.25 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1). ¹H NMR (500 MHz, CDCl₃) δ : 7.35 (t, *J* = 7.4 Hz, 2H), 7.32-7.27 (m, 1H), 7.27-7.21 (m, 2H), 4.30-4.20 (m, 2H), 4.03-3.93 (m, 2H), 3.79 (dd, *J* = 8.7, 6.1 Hz, 1H), 2.71-2.63 (m, 1H), 2.63-2.54 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ : 205.7, 134.9, 128.9, 128.6, 127.5, 73.1, 68.5, 58.0, 41.9.



2-phenylcycloheptan-1-one (3da)¹⁴

White solid. R_F : 0.50 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 30:1). ¹H NMR (500 MHz, CDCl₃) δ : 7.34-7.28 (m, 2H), 7.27-7.19 (m, 3H), 3.80-3.65 (m, 1H), 2.69 (t, J = 12.7 Hz, 1H), 2.52 (d, J = 12.1 Hz, 1H), 2.21-2.09 (m, 1H), 2.08-1.90 (m, 4H), 1.71-1.55 (m, 1H), 1.53-1.40 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ : 213.4, 140.4, 128.5, 127.8, 126.9, 58.8, 42.7, 32.0, 30.0, 28.5, 25.3.



2-phenylcyclopentadecan-1-one (3ea)¹⁵

Colorless oil. R_F : 0.40 in 20% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 45:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.38-7.16 (m, 5H), 3.77 (dd, J = 9.3, 5.3 Hz, 1H), 2.55-2.38 (m, 1H), 2.33-2.13 (m, 2H), 1.78-1.66 (m, 1H), 1.66-1.50 (m, 3H), 1.42-1.19 (m, 19H); ¹³C NMR (101 MHz, CDCl₃) δ : 211.9, 139.5, 128.8, 128.2, 127.1, 58.1, 41.6, 32.3, 27.6, 27.1, 26.9, 26.9, 26.5, 26.5, 26.3, 23.6.



3fa

2-phenylpentan-3-one (3fa)¹⁶

Colorless oil. R_F : 0.50 in 20% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 50:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.35-7.29 (m, 2H), 7.27-7.24 (m, 1H), 7.24-7.19 (m, 2H), 3.81-3.71 (m, 1H), 2.45-2.28 (m, 2H), 1.39 (d, *J* = 7.0 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ : 211.5, 140.9, 128.8, 127.8, 127.0, 52.7, 34.2, 17.5, 7.9.





cis-2-methyl-6-phenylcyclohexanone (3ha)

Colorless oil. R_F : 0.43 in 15% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.29 (m, 2H), 7.26-7.22 (m, 1H), 7.15-7.11 (m, 2H), 3.62 (dd, J = 12.4, 5.1 Hz, 1H), 2.64-2.53 (m, 1H), 2.33-2.16 (m, 2H), 2.03-1.86 (m, 3H), 1.56-1.46 (m, 1H), 1.06 (d, J = 6.5 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ : 211.2, 138.8, 128.7, 128.2, 126.8, 57.7, 45.8, 37.2, 36.3, 25.8, 14.7. HRMS (ESI): m/z [M+H]⁺ calcd. for [C₁₃H₁₇O]⁺: 189.1274, found: 189.1295.



2-(4-bromophenyl)cyclohexan-1-ol (4)⁴

White solid. R_F : 0.45 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.48-7.42 (m, 2H), 7.16-7.11 (m, 2H), 3.69-3.54 (m, 1H), 2.46-2.33 (m, 1H), 2.14-2.04 (m, 1H), 1.91-1.70 (m, 3H), 1.61-1.22 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ : 142.5, 131.7, 129.6, 120.4, 74.2, 52.6, 34.6, 33.3, 25.9, 25.0.



2-(4-bromophenyl)-2-fluorocyclohexan-1-one (5)⁴

White solid. R_F : 0.48 in 20% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 30:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.53 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 2.87-2.72 (m, 1H), 2.51-2.27 (m, 3H), 2.13-1.97 (m, 2H), 1.93-1.75 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ : 205.6 (d, J = 23.5 Hz), 135.5 (d, J = 22.0 Hz), 131.6, 127.9 (d, J = 7.1 Hz), 123.1 (d, J = 2.7 Hz), 97.8 (d, J = 183.3 Hz), 39.6, 38.4 (d, J = 22.8 Hz), 27.4, 21.7 (d, J = 5.8 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ : -146.45.



7-(4-bromophenyl)oxepan-2-one (6)¹⁷

White solid. R_F : 0.36 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 20:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.44-7.40 (m, 2H), 7.22-7.18 (m, 2H), 5.20 (d, J = 9.4 Hz, 1H), 2.81-2.71 (m, 2H), 2.11-1.95 (m, 4H), 1.82-1.68 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ : 174.5, 139.8, 131.6, 127.5, 121.9, 81.2, 37.5, 34.9, 28.5, 22.7.



5-methyl-2-oxocyclohexyl 4-methylbenzenesulfonate (1b)

Colorless liquid. R_F : 0.20 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.83 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.01 (dd, *J* = 12.6, 6.5 Hz, 1H), 2.53-2.26 (m, 6H), 2.16-1.92 (m, 2H), 1.77-1.53 (m, 1H), 1.45-1.20 (m, 1H), 1.12-0.95 (m, 3H); ¹³C NMR (126 MHz, CDCl₃) δ : 202.4, 144.8, 133.8, 129.7, 127.9, 80.7, 42.3, 39.7, 34.6, 31.0, 21.6, 20.7. HRMS (ESI): *m/z* [M+H]⁺ calcd. for [C₁₄H₁₉O₄S]⁺: 283.0999, found: 283.0938.



4-oxotetrahydro-2*H*-pyran-3-yl 4-methylbenzenesulfonate (1c)¹⁸

White solid. R_F : 0.20 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.84 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.92 (dd, *J* = 9.2, 6.7 Hz, 1H), 4.30 (ddd, *J* = 11.1, 6.6, 1.3 Hz, 1H), 4.23-4.10 (m, 1H), 3.73-3.56 (m, 2H), 2.72-2.53 (m, 2H), 2.45 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ : 198.4, 145.3, 133.0, 129.8, 128.0, 77.9, 71.0, 68.2, 42.3, 21.7.



2-tosyloxycycloheptanone (1d)¹⁸

White solid. R_F : 0.20 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.83 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 5.11-4.93 (m, 1H), 2.65-2.39 (m, 5H), 1.97-1.48 (m, 8H); ¹³C NMR (126 MHz, CDCl₃) δ : 206.3, 145.0, 133.4, 129.8, 127.9, 84.0, 40.3, 31.2, 27.8, 25.1, 22.6, 21.6.



2-tosyloxycyclopentadecanone (1e)¹⁹

White solid. R_F : 0.30 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 15:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.80 (d, *J* = 7.3 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 4.72-4.65 (m, 1H), 2.78-2.61 (m, 1H), 2.53-2.30 (m, 4H), 1.87-1.65 (m, 3H), 1.59-1.44 (m, 1H), 1.44-1.01 (m, 20H); ¹³C NMR (101 MHz, CDCl₃) δ : 207.5, 145.2, 133.1, 129.9, 127.9, 84.1, 37.7, 31.5, 27.3, 26.9, 26.6, 26.5, 26.5, 26.4, 26.1, 26.1, 25.9, 22.5, 21.7, 21.7.



3-oxopentan-2-yl 4-methylbenzenesulfonate (1f)¹⁸

White solid. R_F : 0.45 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 25:1). ¹H NMR (500 MHz, CDCl₃) δ : 7.81 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.85-4.77 (m, 1H), 2.67-2.53 (m, 2H), 2.46 (s, 3H), 1.35 (d, *J* = 7.0 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ : 207.7, 145.3, 133.2, 130.0, 127.9, 80.7, 31.2, 21.6, 17.6, 7.0.



3-methyl-2-oxocyclohexyl 4-methylbenzenesulfonate (1h)

White solid. R_F: 0.18 in 10% ethyl acetate in hexane. The crude mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1). ¹H NMR (400 MHz, CDCl₃) δ : 7.84 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.99 (dd, *J* = 11.3, 6.7 Hz, 1H), 2.45-2.33 (m, 5H), 2.09-2.02 (m, 1H), 1.93-1.87 (m, 1H), 1.83-1.74 (m, 2H), 1.34-1.24 (m, 1H), 1.02 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ : 203.8, 144.7, 134.0, 129.6, 127.8, 81.8, 44.6, 35.6, 35.1, 23.1, 21.6, 13.8. HRMS (ESI): *m/z* [M+H]⁺ calcd. for [C₁₄H₁₉O₄S]⁺: 283.0999, found: 283.1015.

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¹H NMR spectrum of 3ab in CDCl₃



¹H NMR spectrum of 3ac in CDCl₃



¹H NMR spectrum of 3ad in CDCl₃



¹H NMR spectrum of 3ae in CDCl₃



¹H NMR spectrum of 3af in CDCl₃



¹H NMR spectrum of 3ag in CDCl₃



¹H NMR spectrum of 3ah in CDCl₃



¹H NMR spectrum of 3ai in CDCl₃







¹H NMR spectrum of 3ak in CDCl₃



¹H NMR spectrum of 3al in CDCl₃



¹H NMR spectrum of 3am in CDCl₃



¹H NMR spectrum of 3an in CDCl₃



¹H NMR spectrum of 3ao in CDCl₃



¹H NMR spectrum of 3ap in CDCl₃



¹H NMR spectrum of 3aq in CDCl₃



¹H NMR spectrum of 3ar in CDCl₃





S35

¹H NMR spectrum of 3at in CDCl₃



¹H NMR spectrum of 3au in CDCl₃



¹H NMR spectrum of 3av in CDCl₃



¹H NMR spectrum of 3aw in CDCl₃



¹H NMR spectrum of 3ax in CDCl₃





¹H NMR spectrum of 3ba in CDCl₃



¹H NMR spectrum of 3ca in CDCl₃



¹H NMR spectrum of 3da in CDCl₃





¹H NMR spectrum of 3ea in CDCl₃

¹H NMR spectrum of 3fa in CDCl₃



¹H NMR spectrum of 3ha in CDCl₃



¹H NMR spectrum of 4 in CDCl₃



¹H NMR spectrum of 5 in CDCl₃



¹H NMR spectrum of 6 in CDCl₃



¹H NMR spectrum of 1b in CDCl₃



¹H NMR spectrum of 1c in CDCl₃



¹H NMR spectrum of 1d in CDCl₃



¹H NMR spectrum of 1e in CDCl₃



¹H NMR spectrum of 1f in CDCl₃



-80000 75000 -70000 OTs -65000 60000 -55000 1h 50000 45000 40000 -35000 30000 -25000 -20000 -15000 10000 -5000 -0 1.00-J $1.03 \pm$ 3.00-F -86.1 2.00H 5.00-I 1.00 --5000 5.0 1. 0 8.5 8.0 7.0 6.5 6.0 4.5 4.0 fl (ppm) 3.5 2.0 7.5 5.5 3. 0 2.5 1.5 0.5 0.0 ¹³C NMR spectrum of 1h in CDCl₃ -203.8 -144.8 ~134.0 ~129.7 ~127.9 -81.8 -44.735.635.123.1 21.7 -13.8 -9000 -8000 OTs 7000 1h 6000 -5000 4000 3000 -2000 -1000 -- 1000 0 150 140 130 120 110 100 fl (ppm) 70 60 50 40 10 210 200 190 180 170 160 90 80 30 20

¹H NMR spectrum of 1h in CDCl₃