Coupling of C(sp\(^3\))—H Bonds with C(sp\(^2\))—O Electrophiles: Mild, General and Selective

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General Considerations

All reactions were set up with glovebox and carried out under nitrogen atmosphere in Schlenk tubes. Reaction temperatures are reported as the temperature of the heat transfer medium surrounding the vessel unless otherwise stated. Anhydrous solvents were purchased from Acros Organics and used as received. Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Alfa Aesar, ABCR and TCI and used as received unless otherwise stated.

$^1$H and $^{13}$C NMR spectra were recorded on a Brüker Advance 400 spectrometer ($^1$H: 400 MHz, $^{13}$C: 101 MHz). Chemical shifts (δ) for $^1$H and $^{13}$C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for $^1$H and $^{13}$C NMR spectra and the chemical shifts converted to the TMS scale (CDCl$_3$: δH = 7.26 ppm, δC = 77.16 ppm; CD$_3$OD: δH = 3.31 ppm, δC = 49.00 ppm; (CD$_3$)$_2$SO: δH = 2.50 ppm, δC = 39.52 ppm).

GC-MS was obtained using electron ionization (SHIMADZU GCMS-QP 2010 SE). TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. Exact ESI mass spectra were recorded on a SHIMADZU LCMS-IT-TOF. ESI-MS were obtained on a Thermo LTQ mass spectrometer.
Synthesis of Substrates

2.1 General procedure for alkenyl tosylates 2 synthesis:

According to a procedure by Reeves et al \[1a\] without further optimization, in a 200 mL round-bottomed flask under magnetic stirring and nitrogen atmosphere was added appropriate ketones (19.02 mmol) in THF (47.6 mL) to give a pale yellow solution. The reaction mixture was cooled to -20 °C. Sodium tert-butoxide (2.01 g, 20.93 mmol) was added in one portion. The solution was stirred at -5 °C for 1 h then at room temperature for 30 min. The solution was cooled to -15°C. p-Toluenesulfonic anhydride (6.83 g, 20.93 mmol) was added in one portion. The resulting solution was stirred at -15 to -5 °C for 1.5 h, quenched with aq. NaHCO₃ (20 mL). MTBE was added (100 mL) and the organic phase was washed with water (4 x 100 mL), dried on MgSO₄ and concentrated, and purified by flash column chromatography.

3,4-dihydronaphthalen-2-yl 4-methylbenzenesulfonate (2a) The reaction of 3,4-dihydronaphthalen-2(1H)-one (2.78 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (2.86 g, 50%).

\(^1\)H NMR (400 MHz, CDCl₃) δ 7.88–7.80 (m, 2H), 7.38–7.31 (m, 2H), 7.15–7.09 (m, 2H), 7.09–7.05 (m, 1H), 6.91 (dd, J = 5.3, 3.5 Hz, 1H), 6.10 (s, 1H), 2.91–2.85 (m, 2H), 2.42 (dd, J = 8.1, 1.3 Hz, 5H).

6-phenyl-3,4-dihydronaphthalen-2-yl 4-methylbenzenesulfonate (2b) The reaction of 6-phenyl-3,4-dihydronaphthalen-2(1H)-one (4.20 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (4.15 g, 58%).

\(^1\)H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 8.3 Hz, 2H), 7.55 (dd, J = 8.3, 1.3 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.38–7.28 (m, 5H), 6.99 (d, J = 7.8 Hz, 1H), 6.15 (d, J = 1.4 Hz, 1H), 2.95 (t, J = 8.3 Hz, 2H), 2.59–2.33 (m, 5H).

6-fluoro-3,4-dihydronaphthalen-2-yl 4-methylbenzenesulfonate (2c) The reaction of 6-fluoro-3,4-dihydronaphthalen-2(1H)-one (3.17 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (2.98 g, 49%).

\(^1\)H NMR (400 MHz, CDCl₃) δ 7.95–7.75 (m, 2H), 7.43–7.31 (m, 2H), 6.92–6.82 (m, 1H), 6.86–6.75 (m, 2H), 6.09 (d, J = 1.2 Hz, 1H), 2.93–2.81 (m, 2H), 2.47 (s, 3H), 2.41 (tt, J = 8.1, 1.0 Hz, 2H).

6-bromo-3,4-dihydronaphthalen-2-yl 4-methylbenzenesulfonate (2d) The reaction of 6-bromo-3,4-dihydronaphthalen-2(1H)-one (4.28 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (4.59 g, 64%).

\(^1\)H NMR (400 MHz, CDCl₃) δ 7.88–7.79 (m, 2H), 7.41–7.31 (m, 2H), 7.26–7.20 (m, 2H), 6.79 (d, J = 8.0 Hz, 1H), 6.08 (d, J = 1.4 Hz, 1H), 2.85 (t, J = 8.4 Hz, 2H), 2.46 (s, 3H), 2.40 (ddd, J = 9.4, 8.0, 1.3 Hz, 2H).
6-methoxy-3,4-dihyronaphthalen-2-yl 4-methylbenzenesulfonate (2e) The 6-methoxy-3,4-dihyronaphthalen-2(1H)-one (3.36 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (4.56 g, 72%). \(^1\)H NMR (400 MHz, CDCl$_3$) δ 7.80 – 7.72 (m, 2H), 7.31 – 7.23 (m, 2H), 6.80 – 6.73 (m, 1H), 6.61 – 6.54 (m, 2H), 5.97 (t, J = 1.2 Hz, 1H), 3.70 (s, 3H), 2.78 (t, J = 8.3 Hz, 2H), 2.41 – 2.28 (m, 5H).

3,4-dihyronaphthalene-2,6-diyl bis(4-methylbenzenesulfonate) (2f) The reaction of 6-hydroxy-3,4-dihyronaphthalen-2(1H)-one (3.09 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (5.00 g, 56%). \(^1\)H NMR (400 MHz, CDCl$_3$) δ 7.86 – 7.72 (m, 2H), 7.70 – 7.57 (m, 2H), 7.27 (dd, J = 13.5, 8.1 Hz, 4H), 6.73 (d, J = 8.3 Hz, 2H), 6.57 (dd, J = 8.3, 2.5 Hz, 1H), 6.02 (d, J = 1.4 Hz, 1H), 2.75 (t, J = 8.4 Hz, 2H), 2.39 (d, J = 3.5 Hz, 5H), 2.32 (td, J = 8.4, 1.3 Hz, 2H).

cyclohex-1-en-1-yl 4-methylbenzenesulfonate (2g) The reaction of cyclohexanone (1.86 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (2.85 g, 59%). \(^1\)H NMR (400 MHz, CDCl$_3$) δ 7.82 – 7.75 (m, 2H), 7.36 – 7.30 (m, 2H), 5.35 (tt, J = 4.0, 1.5 Hz, 1H), 2.45 (s, 3H), 2.04 (ddt, J = 21.6, 6.2, 3.9, 2.2 Hz, 4H), 1.67 – 1.60 (m, 2H), 1.56 (td, J = 8.4, 1.3 Hz, 2H).

cyclohept-1-en-1-yl 4-methylbenzenesulfonate (2h) The reaction of cycloheptanone (2.13 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (3.20 g, 63%). \(^1\)H NMR (400 MHz, CDCl$_3$) δ 7.83 – 7.76 (m, 2H), 7.38 – 7.30 (m, 2H), 5.41 (t, J = 6.5 Hz, 1H), 2.45 (s, 3H), 2.37 – 2.27 (m, 2H), 2.03 – 1.93 (m, 2H), 1.64 (qd, J = 5.8, 5.0, 2.1 Hz, 2H), 1.56 – 1.47 (m, 4H), 6.5 Hz, 1H), 2.45 (s, 3H), 2.37 – 2.27 (m, 2H), 2.03 – 1.93 (m, 2H), 1.64 (qd, J = 5.8, 5.0, 2.1 Hz, 2H), 1.56 – 1.47 (m, 4H).

(E)-cyclooct-1-en-1-yl 4-methylbenzenesulfonate (2i) The reaction of cyclooctanone (2.40 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (2.51 g, 47%). \(^1\)H NMR (400 MHz, CDCl$_3$) δ 7.83 – 7.76 (m, 2H), 7.38 – 7.29 (m, 2H), 5.41 (t, J = 6.5 Hz, 1H), 2.45 (s, 3H), 2.35 – 2.30 (m, 2H), 2.02 – 1.94 (m, 2H), 1.64 (qd, J = 5.8, 5.0, 2.1 Hz, 2H), 1.55 – 1.46 (m, 4H).

4-methylcyclohex-1-en-1-yl 4-methylbenzenesulfonate (2j) The reaction of 4-methylcyclohexan-1-one (2.13 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (1.4 g, 18%). \(^1\)H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 5.30 (q, J = 2.5 Hz, 1H), 2.45 (s, 3H), 2.17 – 1.92 (m, 3H), 1.72 – 1.54 (m, 3H), 1.28 (dtd, J = 12.4, 9.9, 6.0 Hz, 1H), 0.91 (d, J = 6.2 Hz, 3H).
1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl 4-methylbenzenesulfonate (2k)\textsuperscript{[1b]} The reaction of 4-Phenylcyclohexanonee (3.3 g, 19.02 mmol) with p-Toluene sulfonic anhydride as outlined in the general procedure provided the title compound (3.0 g, 49%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.86 – 7.80 (m, 2H), 7.38 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.23 – 7.15 (m, 3H), 5.47 – 5.43 (m, 1H), 2.46 (s, 3H), 2.38 – 2.12 (m, 5H), 1.99 – 1.90 (m, 1H), 1.88 – 1.79 (m, 1H).

ethyl 4-(tosyloxy)cyclohex-3-enecarboxylate (2l) The reaction of ethyl 4-oxocyclohexanecarboxylate (3.23 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (3.2 g, 51%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.78 (d, \(J\) = 7.9 Hz, 2H), 7.32 (s, 2H), 5.32 (dd, \(J\) = 8.0, 3.4 Hz, 1H), 4.12 (q, \(J\) = 7.1 Hz, 2H), 2.53 – 2.39 (m, 4H), 2.28 – 2.12 (m, 2H), 2.22 – 2.10 (m, 2H), 2.05 – 1.95 (m, 1H), 1.83 – 1.65 (m, 1H), 1.24 (td, \(J\) = 7.1, 1.1 Hz, 3H).

3,6-dihydro-2H-pyran-4-yl 4-methylbenzenesulfonate (2m) The reaction of dihydro-2H-pyran-4(3H)-one (1.90 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (3.2 g, 51%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.82 (d, \(J\) = 8.4 Hz, 2H), 7.45 – 7.29 (m, 2H), 5.41 (d, \(J\) = 2.8, 1.4 Hz, 1H), 4.12 (q, \(J\) = 2.8 Hz, 2H), 3.76 (t, \(J\) = 5.5 Hz, 2H), 2.46 (s, 3H), 2.21 (dtd, \(J\) = 5.5, 2.7, 1.4 Hz, 2H).

tert-butyl 4-(tosyloxy)-5,6-dihydropyridine-1(2H)-carboxylate (2n) \textsuperscript{[1a]} The reaction of tert-butyl 4-oxopiperidine-1-carboxylate (3.79 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (3.2 g, 51%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.84 – 7.64 (m, 2H), 7.39 – 7.20 (m, 2H), 5.29 (s, 1H), 3.81 (q, \(J\) = 3.0 Hz, 2H), 3.42 (t, \(J\) = 5.8 Hz, 2H), 2.39 (s, 3H), 2.13 (s, 2H), 1.38 (s, 9H).

\((E)\)-styryl 4-methylbenzenesulfonate (\(E:Z = 2.2 : 1\)) (2s)\textsuperscript{[1a]} The reaction of 2-phenylacetaldehyde (2.28 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (3.2 g, 51%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, the major isomer) \(\delta\) 7.79 – 7.68 (m, 2H), 7.28 (d, \(J\) = 8.1 Hz, 2H), 7.25 – 7.09 (m, 5H), 7.00 (d, \(J\) = 12.3 Hz, 1H), 6.23 (d, \(J\) = 12.3 Hz, 1H), 2.37 (s, 3H),

2.2 General procedure for the synthesis of vinyl 4-methylbenzene sulfonate (2r)

According to a procedure by Skrydstrup et al \textsuperscript{[2]}, In a 500 mL round-bottomed flask under magnetic stirring and nitrogen atmosphere was added appropriate n-ButLi (100 mmol) in THF (150 mL) to give a pale yellow solution. The reaction mixture was stirred at 35 °C for 4h. Sodium tert-butoxide (15.25 g, 80 mmol, in 40 mL
anhydrous THF) was added dropwise in 30 min, then stirred for another 1h. The solution was poured into water, EtOAc was added (100 mL) and the organic phase was washed with brine (4 x 100 mL), dried on MgSO₄ and concentrated, and purified by flash column chromatography to get the desired product as colorless oil (6.9 g). ¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.74 (m, 2H), 7.39 – 7.33 (m, 2H), 6.60 (dd, J = 13.5, 5.9 Hz, 1H), 4.89 (dd, J = 13.5, 2.5 Hz, 1H), 4.68 (dd, J = 5.9, 2.5 Hz, 1H), 2.46 (s, 3H).

2.3 General procedure for alkenyl triflates 2 synthesis: 2v as an example

According to a procedure by Occhiato et al.[³], to a solution of tert-butyl 2-oxopiperidine-1-carboxylate (2.0 g, 10.1 mmol), HMPA (2.62 mL) in THF (20 mL), cooled at -78°C and under nitrogen atmosphere, was added a solution of LiHMDS (18 mL of a 1 M solution in toluene, 18 mmol) in THF (20 mL), and the resulting mixture was stirred at -78°C for 1.5 h. Afterward, a solution of PhNTf₂ (3.88 g, 10.9 mmol) in THF (5 mL) was quickly added, leaving under stirring for 2 h at -78°C. Before allowing the temperature to rise to 0°C, then a 10% NaOH solution (20 mL) was added, the mixture was extracted with Et₂O (2 x 100 mL), and dried (K₂CO₃). After filtration and evaporation of the solvent, crude vinyl triflate 2v was obtained as a yellowish oil and purified by flash chromatography (petroleum ether, 1.33g, 40%). ¹H NMR (400 MHz, CDCl₃): δ 5.22 (t, J = 3.9 Hz, 1H), 3.56 – 3.49 (m, 2H), 2.19 (m, 2H), 1.73 – 1.64 (m, 2H), 1.42 (s, 9H). GCMS: calculated m/z for C₁₈H₁₉N: 331, found: 331.

(1S,4R)-bicyclo[2.2.1]hept-2-en-2-yl trifluoromethanesulfonate (2o) [⁴] The reaction of (1S,4R)-bicyclo[2.2.1]heptan-2-one (2.09 g, 19.02 mmol) with 1,1,1-trifluoro-N-phenyl-N-((trifluoromethyl)sulfonyl)methanesulfonamide as outlined in the general procedure provided the title compound (4.05 g, 57%). ¹H NMR (400 MHz, CDCl₃) ¹H δ 6.24 – 5.12 (m, 1H), 2.98 (dh, J = 4.8, 1.6 Hz, 2H), 1.86 – 1.71 (m, 2H), 1.66 (dp, J = 8.5, 2.2 Hz, 1H), 1.49 – 1.34 (m, 1H), 1.30 – 1.07 (m, 2H).

(1R,5S)-8-methyl-8-azabicyclo[3.2.1]oct-2-en-3-yl trifluoromethanesulfonate (2p) [⁴] The reaction of (1R,5S)-8-methyl-8-azabicyclo [3.2.1]octan-3- one ( 3.96 g, 19.02 mmol) with 1,1,1-trifluoro-N-phenyl-N-((trifluoromethyl) sulfonyl) methane sulfonamide as outlined in the general procedure provided the title compound (4.05 g, 57%). ¹H NMR (400 MHz, CDCl₃) δ 5.84 (dt, J = 5.6, 1.4 Hz, 1H), 3.67 – 3.33 (m, 2H), 2.92 – 2.72 (m, 1H), 2.41 (s, 3H), 2.27 – 2.14 (m, 1H), 2.07 (tt, J = 11.6, 6.0 Hz, 1H), 1.98 – 1.88 (m, 2H), 1.69 – 1.58 (m, 1H).

(1R,5S)-9-methyl-9-azabicyclo[3.3.1]non-2-en-3-yl trifluoromethanesulfonate (2q) [⁴] The reaction of (1R,5S)-9-methyl-9-azabicyclo[3.3.1]nonan-3-one (2.91 g, 19.02...
mmol) with 1,1,1-trifluoro-N-phenyl-N-((trifluoromethyl)sulfonyl)methane sulfonamide as outlined in the general procedure provided the title compound (2.90 g, 27%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.69 (dt, $J$ = 5.4, 1.7 Hz, 1H), 3.47 (ddd, $J$ = 5.6, 4.0, 2.2 Hz, 1H), 3.20 (ddd, $J$ = 7.0, 4.6, 2.1 Hz, 1H), 2.74 (dd, $J$ = 18.2, 7.2 Hz, 1H), 2.38 (s, 3H), 2.00 (dd, $J$ = 18.2, 1.4 Hz, 1H), 1.86 (td, $J$ = 14.4, 13.2, 7.2, 4.0 Hz, 2H), 1.67 – 1.47 (m, 4H).

1H-isochromen-3-yl trifluoromethanesulfonate (2t) The reaction of isochroman-3-one (2.81 g, 19.02 mmol) with 1,1,1-trifluoro-N-phenyl-N-((trifluoromethyl)sulfonyl)methanesulfonamide as outlined in the general procedure provided the title compound (2.60 g, 50%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.2 (m, 4H), 5.81 (s, 1H), 5.37 (s, 2H).

(1H-isochromen-3-yl)diphenylphosphine oxide (2u) The synthesis of 2u was as the same as the synthesis of alkenyl triflates except adding diphenylphosphinic chloride instead of PhNTf$_2$. The reaction of isochroman-3-one (2.81 g, 19.02 mmol) with diphenylphosphinic chloride as outlined in the general procedure provided the title compound (2.40 g, 38%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.42 – 7.31 (m, 2H), 7.29 – 7.14 (m, 8H), 7.00 – 6.89 (m, 3H), 6.87 – 6.78 (m, 2H), 5.35 (s, 2H). GCMS: calculated m/z for $C_{21}H_{17}O_3P$: 348, found: 348.

2.4 General procedure for aryl tosylates 4 synthesis

According to a procedure by Gooßen et al$^{[6]}$, a solution of tosyl chloride (11.5 g, 120.0 mmol) in CH$_2$Cl$_2$ (100.0 mL) was added dropwise to a solution of appropriate phenol (100.0 mmol) and DABCO (22.4 g, 200.0 mmol) in anhydrous CH$_2$Cl$_2$ (200 mL) at 0 °C. After complete addition, the mixture was warmed to room temperature and allowed to stir until completion following the reaction by TLC. The mixture was then diluted with Et$_2$O (200 mL), quenched with 10% aq. HCl and washed successively with aqueous solution of NaHCO$_3$ and brine. After drying over MgSO$_4$, the solvent was removed under reduced pressure to give a solid. Recrystallization from chloroform-hexane gave the corresponding aryl tosylates.

4-acetylphenyl 4-methylbenzenesulfonate (4a) The reaction of 1-(4-hydroxyphenyl)ethanone (13.6 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (27.3 g, 94%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 – 7.79 (m, 2H), 7.68 – 7.61 (m, 2H), 7.29 – 7.14 (m, 8H), 7.00 – 6.89 (m, 3H), 6.87 – 6.78 (m, 2H), 5.35 (s, 2H).

4-(trifluoromethyl)phenyl 4-methylbenzenesulfonate (4b) The reaction of 4-(trifluoromethyl)phenol (16.2 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (16.4 g, 52%). $^1$H
NMR (400 MHz, CDCl₃) δ 7.76 – 7.68 (m, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.17 – 7.08 (m, 2H), 2.46 (s, 3H).

4-(methylsulfonyl)phenyl 4-methylbenzenesulfonate (4c) The reaction of 4-(methylsulfonyl)phenol (17.2 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (26.1 g, 81%). ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.87 (m, 2H), 7.77 – 7.70 (m, 2H), 7.39 – 7.32 (m, 2H), 7.10 – 7.02 (m, 2H), 2.39 (s, 3H).

4-cyanophenyl 4-methylbenzenesulfonate (4d) The reaction of 4-cyanobenzonitrile (17.2 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (26.1 g, 81%). ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.60 (m, 2H), 7.58 – 7.50 (m, 2H), 7.31 – 7.23 (m, 2H), 7.10 – 7.02 (m, 2H), 2.39 (s, 3H).

ethyl 4-(tosyloxy)benzoate (4e) The reaction of ethyl 4-hydroxybenzoate (16.6 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (27.8 g, 87%). ¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.86 (m, 2H), 7.66 – 7.59 (m, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.02 – 6.94 (m, 2H), 4.28 (q, J = 7.1 Hz, 2H), 2.37 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H).

4-benzoylphenyl 4-methylbenzenesulfonate (4f) The reaction of (4-hydroxyphenyl)(phenyl)methanone (19.8 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (24.3 g, 70%). ¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.63 (m, 6H), 7.57 – 7.48 (m, 1H), 7.45 – 7.36 (m, 2H), 7.30 – 7.22 (m, 2H), 7.08 – 7.00 (m, 2H), 2.38 (s, 3H).

3-methoxyphenyl 4-methylbenzenesulfonate (4g) The reaction of 3-methoxyphenol (12.4 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (22.1 g, 79%). ¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.61 (m, 2H), 7.27 – 7.20 (m, 2H), 7.13 – 7.03 (m, 1H), 6.71 (ddd, J = 8.4, 2.4, 1.1 Hz, 1H), 6.52 – 6.43 (m, 2H), 3.65 (s, 3H), 2.37 (s, 3H).

naphthalen-2-yl 4-methylbenzenesulfonate (4k) The reaction of naphthalen-2-ol (14.4 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (26.2 g, 88%). ¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.78 (m, 1H), 7.78 – 7.69 (m, 4H), 7.52 – 7.45 (m, 3H), 7.33 – 7.27 (m, 2H), 7.09 (dd, J = 8.9, 2.4 Hz, 1H), 2.44 (s, 3H).

naphthalen-1-yl 4-methylbenzenesulfonate (4l) The reaction of naphthalen-1-ol (14.4 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (27.3 g, 92%). ¹H NMR (400 MHz, CDCl₃) δ
quinolin-8-yl 4-methylbenzenesulfonate (4m) The reaction of quinolin-8-ol (14.5 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (24.5 g, 82%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.75 (dd, $J = 4.2, 1.7$ Hz, 1H), 8.06 (dd, $J = 8.3, 1.7$ Hz, 1H), 7.86 – 7.76 (m, 2H), 7.67 (dd, $J = 8.1, 1.4$ Hz, 1H), 7.51 (dd, $J = 7.6, 1.4$ Hz, 1H), 7.46 – 7.39 (m, 1H), 7.32 (dd, $J = 8.3, 4.2$ Hz, 1H), 7.22 – 7.16 (m, 2H), 2.34 (s, 3H).

pyridin-2-yl 4-methylbenzenesulfonate (4n) The reaction of pyridin-2-ol (9.5 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (20.2 g, 81%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.18 (ddd, $J = 4.9, 2.1, 0.8$ Hz, 1H), 7.85 – 7.78 (m, 2H), 7.30 – 7.23 (m, 2H), 7.14 (ddd, $J = 7.3, 4.9, 1.0$ Hz, 1H), 7.04 (dt, $J = 8.1, 0.9$ Hz, 1H), 2.37 (s, 3H).

pyridin-3-yl 4-methylbenzenesulfonate (4o) The reaction of pyridin-2-ol (9.5 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (20.2 g, 81%).

pyridin-4-yl 4-methylbenzenesulfonate (4p) The reaction of pyridin-2-ol (9.5 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (20.2 g, 81%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.62 – 8.54 (m, 2H), 7.79 – 7.71 (m, 2H), 7.38 – 7.31 (m, 2H), 7.06 – 6.99 (m, 2H), 2.46 (s, 3H).

2.5 General procedure for aryl triflates 4 synthesis

According to a procedure by Goossen et al. [7], a flame-dried flask was successively charged with appropriate phenol (10.6 mmol, 1.00 equiv), CH$_2$Cl$_2$ (10 mL), and pyridine (1.80 mL, 21.3 mmol, 2.00 equiv) at 0°C. After dropwise addition of a solution of triflic anhydride (2.15 mL, 3.61 g, 12.8mmol, 1.20 equiv) in CH$_2$Cl$_2$ (5 mL), the reaction mixture was stirred at room temperature for 1.5 h and quenched with the addition of Et$_2$O (15 mL) and aqueous HCl (10%, 5 mL). The reaction mixture was washed successively with aqueous saturated NaHCO$_3$ (10 mL) and brine (10 mL). Drying over MgSO$_4$, evaporation of the solvents under reduced pressure and purification by flash column chromatography afforded the desired product.

4-fluorophenyl trifluoromethanesulfonate (4h) The reaction of 4-fluorophenol (1.19 g, 10.6 mmol) with triflic anhydride as outlined in the general procedure provided the title compound as colorless oil (1.60 g, 71%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 – 7.41 (m, 2H), 7.23 – 7.15 (m, 2H).
[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (4i) The reaction of [1,1'-biphenyl]-4-ol (1.80 g, 10.6 mmol) with triflic anhydride as outlined in the general procedure provided the title compound as colorless oil (1.57 g, 49%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.67 – 7.61 (m, 2H), 7.58 – 7.53 (m, 2H), 7.50 – 7.43 (m, 2H), 7.42 – 7.32 (m, 3H).

phenyl trifluoromethanesulfonate (4j) The reaction of phenol (1.00 g, 10.6 mmol) with triflic anhydride as outlined in the general procedure provided the title compound as colorless oil (0.73 g, 30%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.50 – 7.42 (m, 2H), 7.41 – 7.36 (m, 1H), 7.32 – 7.24 (m, 2H).
Screening reaction conditions and Characterization of Products.

Table SI1 Screening reaction conditions

<table>
<thead>
<tr>
<th>entry</th>
<th>variation from the standard conditions</th>
<th>yield (%)&lt;sup&gt;[b]&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>88</td>
</tr>
<tr>
<td>2</td>
<td>Ru(bpy)&lt;sub&gt;3&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; as photocatalyst</td>
<td>83</td>
</tr>
<tr>
<td>3</td>
<td>Ru(bpy)&lt;sub&gt;3&lt;/sub&gt;(PF&lt;sub&gt;6&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt; as photocatalyst</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>Ir(DF(CF&lt;sub&gt;3&lt;/sub&gt;)ppy)&lt;sub&gt;2&lt;/sub&gt;(dtbbpy)(PF&lt;sub&gt;6&lt;/sub&gt;) as photocatalyst</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>Ni(cod)&lt;sub&gt;2&lt;/sub&gt; as Ni catalyst</td>
<td>87</td>
</tr>
<tr>
<td>6</td>
<td>no light</td>
<td>N.D.</td>
</tr>
<tr>
<td>7</td>
<td>no photocatalyst</td>
<td>N.D.</td>
</tr>
<tr>
<td>8</td>
<td>no Ni catalyst</td>
<td>N.D.</td>
</tr>
<tr>
<td>9</td>
<td>no base</td>
<td>trace</td>
</tr>
</tbody>
</table>

<sup>a</sup> 1a (0.9 mmol), 2a (0.3 mmol).<sup>b</sup> Isolated yield. bpy = 2,2'-bipyridine, dtbbpy = 4,4'-di-tert-butyl-2,2'-bipyridyl, cod = 1,5-cyclooctadiene, LED = light-emitting diode. N.D. = Not detected.

General procedure for the synthesis of 3

To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added Ru(bpy)<sub>3</sub>Cl<sub>2</sub>·6H<sub>2</sub>O (0.003 mmol), 2a (0.3 mmol) and dtbbpy (0.006 mmol). The tube was evacuated and filled N<sub>2</sub> for three times before being transferred into a glovebox. NiCl<sub>2</sub>·glyme (0.006 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (0.6 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N<sub>2</sub>. Dry DMF (3.0 mL) were added to the tube, followed by 1a (0.9 mmol). The resulting mixture was degassed by using a “freeze–pump–thaw” procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from a 30 W blue LED and stirred at
room temperature for 4 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 500:1 to 300:1) to provide the pure product 3aa as a pale yellow oil in 88% yield (65.7 mg, 0.264 mmol).

**General procedure for the synthesis of 5**

To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added Ru(bpy)$_3$Cl$_2$·6H$_2$O (0.003 mmol), 4a (0.3 mmol). The tube was evacuated and filled N$_2$ for three times before being transferred into a glovebox. NiBr$_2$·glyme (0.006 mmol), Me$_4$Phen (0.006 mmol) and DABCO (0.6 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N$_2$. Dry DMF (3.0 mL) were added to the tube, followed by 1a (0.9 mmol). The resulting mixture was degassed by using a “freeze–pump–thaw” procedure (3 times). Afterwards, the solution was placed at a distance of 3–5 cm from a 30 W blue LED and stirred at room temperature for 12 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 50:1 to 30:1) to provide the pure product 5aa as a pale white solid in 78% yield (56.2 mg, 0.235 mmol).

**General procedure for the synthesis of 5ma**

To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)(PF$_6$) (0.003 mmol, 0.01 equiv.), 4a (0.3 mmol, 1.0 equiv.). The tube was evacuated and filled N$_2$ for three times before being transferred into a glovebox. NiBr$_2$·glyme (0.015 mmol, 0.05 equiv.), Me$_4$Phen (0.015 mmol, 0.05 equiv.) was added to the tube before transferring out of the glovebox and placing
under an atmosphere of $\text{N}_2$. Dry DMSO (3.0 mL) were added to the tube, followed by $3\text{m}$ (0.9 mmol, 3.0 equiv.) and 3-acetoxyquinuclidine (0.33 mmol, 1.1 equiv.). The resulting mixture was degassed by using a “freeze–pump–thaw” procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from a 30 W blue LED and stirred at room temperature for 24 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 20:1 to 10:1) to provide the pure product $5\text{aa}$ as a pale white solid in 72% yield (62.3 mg, 0.215 mmol).

**General procedure for the synthesis of $5\text{na}$**

To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added $\text{Ir[dF(CF}_3\text{ppy})_2(\text{dtbbpy})(\text{PF}_6)}$ (0.003 mmol, 0.01 equiv.), $4\text{a}$ (0.3 mmol, 1.0 equiv.). The tube was evacuated and filled $\text{N}_2$ for three times before being transferred into a glovebox. $\text{NiBr}_2$·glyme (0.015 mmol, 0.05 equiv.), $\text{Me}_4\text{Phen}$ (0.015 mmol, 0.05 equiv.) was added to the tube before transferring out of the glovebox and placing under an atmosphere of $\text{N}_2$. Dry DMSO (3.0 mL) were added to the tube, followed by $3\text{n}$ (3.0 mmol, 10.0 equiv.) and 3-acetoxyquinuclidine (0.33 mmol, 1.1 equiv.). The resulting mixture was degassed by using a “freeze–pump–thaw” procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from a 30 W blue LED and stirred at room temperature for 36 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 20:1 to 15:1) to provide the pure product $5\text{aa}$ as a pale white solid in 59% yield (33.5 mg, 0.176 mmol).

**Tips:**
2. Avoid other light source irradiation.
3. For the reaction of $2\text{n}$, $4\text{a}$ in gram scale, the reaction mixture was degassed by purging nitrogen (30 min).
N-((3,4-dihyronaphthalen-2-yl)methyl)-N-methylaniline (3aa)

Yellow oil;

Rf (PE:EA=50:1): 0.5;

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.14 (dd, \(J = 8.8, 7.3\) Hz, 2H), 7.08 – 6.96 (m, 3H), 6.88 (d, \(J = 6.4\) Hz, 1H), 6.76 – 6.47 (m, 3H), 6.21 (s, 1H), 3.89 (s, 2H), 2.90 (s, 3H), 2.75 (t, \(J = 8.2\) Hz, 2H), 2.15 (t, \(J = 8.2\) Hz, 2H);

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 149.90, 137.92, 134.79, 134.27, 129.12, 127.27, 126.58, 126.49, 125.84, 122.72, 116.39, 112.27, 58.27, 38.21, 27.93, 25.16;

ESI-MS: calculated m/z for \([C_{18}H_{20}N]\)^+: 250.1, found: 250.1.

N-methyl-N-((6-phenyl-3,4-dihyronaphthalen-2-yl)methyl)aniline (3ab)

80.9 mg, 0.249 mmol, 83%;

Colorless oil;

Rf (PE:EA=50:1): 0.5;

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.58 (m, 2H), 7.37 (m, 5H), 7.27 – 7.20 (m, 2H), 7.05 (d, \(J = 7.6\) Hz, 1H), 6.82 – 6.67 (m, 3H), 6.35 (t, \(J = 1.8\) Hz, 1H), 4.02 (s, 2H), 3.01 (s, 3H), 2.97 – 2.87 (t, \(J = 8.1\) Hz, 2H), 2.37 – 2.20 (t, \(J = 8.1\) Hz, 2H);

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 148.80, 140.07, 138.36, 137.12, 134.17, 132.39, 128.08, 127.65, 125.97, 125.83, 125.16, 125.08, 124.16, 121.26, 115.34, 111.19, 57.24, 37.20, 27.07, 24.17;

Exact Mass ESI-MS: calculated m/z for \([C_{24}H_{23}N+H]^+\): 326.1903, found: 326.1909.

N-((6-fluoro-3,4-dihyronaphthalen-2-yl)methyl)-N-methylaniline (3ac)

63.1 mg, 0.236 mmol, 79%;

Yellow oil;

Rf (PE:EA=50:1): 0.5;

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.24 – 7.05 (m, 2H), 6.81 (m, 1H), 6.77 – 6.52 (m, 5H), 6.17 (t, \(J = 1.7\) Hz, 1H), 3.88 (s, 2H), 2.89 (s, 3H), 2.72 (t, \(J = 8.1\) Hz, 2H), 2.21 – 2.03 (t, \(J = 8.1\) Hz, 2H);
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.44 (d, $J = 245.2$ Hz), 148.74, 136.01 (d, $J = 7.5$ Hz), 135.86 (d, $J = 2.5$ Hz), 129.32 (d, $J = 3.0$ Hz), 128.07, 125.89 (d, $J = 8.1$ Hz), 120.58, 115.36, 113.37 (d, $J = 21.7$ Hz), 111.76 (d, $J = 21.3$ Hz), 111.15, 57.06, 37.16, 27.03 (d, $J = 1.8$ Hz), 23.61;

ESI-MS: calculated m/z for [C$_{18}$H$_{19}$FN+H]$^+$: 268.15, found: 268.10.

N-((6-bromo-3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3ad)

\[
\text{Exact Mass ESI-MS: calculated m/z for [C}_{18}\text{H}_{18}\text{BrN+H]}^+: 328.0695 (100 \%), 330.0675 (98 \%), \text{ found: 328.0625.}
\]

N-((6-methoxy-3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3ae)

\[
\text{Exact Mass ESI-MS: calculated m/z for [C}_{19}\text{H}_{21}\text{NO+H]}^+: 280.1696, \text{ found: 280.1701.}
\]
6-((methyl(phenyl)amino)methyl)-7,8-dihydronaphthalen-2-yl 4-methylbenzene sulfonate (3af)

71.7 mg, 0.171 mmol, 57 %; White solid;

$R_f$ (PE:EA=10:1): 0.5;

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.76 – 7.65 (m, 2H), 7.33 – 7.16 (m, 4H), 6.88 – 6.78 (m, 2H), 6.77 – 6.66 (m, 3H), 6.60 (dd, $J = 8.2, 2.5$ Hz, 1H), 6.22 (t, $J = 1.7$ Hz, 1H), 3.96 (s, 2H), 2.97 (s, 3H), 2.76 (t, $J = 8.2$ Hz, 2H), 2.43 (s, 3H), 2.20 (t, $J = 8.2$ Hz, 2H);

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 149.70, 147.86, 145.25, 138.78, 136.53, 133.27, 132.58, 129.73, 129.16, 128.53, 126.47, 121.45, 121.42, 119.96, 116.48, 112.17, 58.14, 38.37, 27.83, 24.68, 21.75;

Exact Mass ESI-MS: calculated m/z for [C$_{25}$H$_{25}$NO$_3$S+Na]$^+$: 442.1447, found: 442.1452.

N-(cyclohex-1-en-1-ylmethyl)-N-methylaniline (3ag)

51.3 mg, 0.255 mmol, 85 %; Colorless oil;

$R_f$ (PE:EA=100:1): 0.5;

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.12 (m, 2H), 6.80 – 6.24 (m, 3H), 5.43 (t, $J = 3.5$, 1H), 3.65 (s, 2H), 2.82 (s, 3H), 2.05 – 1.66 (m, 4H), 1.52 (m, 4H);

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 150.06, 134.01, 129.02, 122.20, 115.89, 112.07, 58.98, 37.98, 26.44, 25.01, 22.73, 22.68;

Exact Mass ESI-MS: calculated m/z for [C$_{14}$H$_{19}$N+H]$^+$: 202.1590, found: 202.1596.

N-(cyclohept-1-en-1-ylmethyl)-N-methylaniline (3ah)

46.0 mg, 0.213 mmol, 71 %; Colorless oil;

$R_f$ (PE:EA=100:1): 0.5;
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.24 – 7.17 (m, 2H), 6.68 (m, 3H), 5.61 (t, $J = 6.3$ Hz, 1H), 3.74 (s, 2H), 2.90 (s, 3H), 2.08 (m, 4H), 1.78 – 1.70 (m, 2H), 1.48 (m, 4H);

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 148.92, 138.73, 127.95, 125.64, 114.85, 110.98, 58.86, 36.62, 31.45, 29.43, 27.07, 26.21, 25.58;

**Exact Mass ESI-MS:*** calculated m/z for [C$_{15}$H$_{21}$N+H]$^+$: 216.1747, found: 216.1752.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.19 – 7.10 (m, 2H), 6.60 (m, 3H), 5.33 (t, $J = 8.2$ Hz, 1H), 3.72 (s, 2H), 2.84 (s, 3H), 2.13 – 1.98 (m, 4H), 1.49 – 1.36 (m, 8H);

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 149.92, 136.43, 129.04, 124.36, 115.78, 111.81, 58.17, 38.00, 29.81, 28.77, 27.13, 26.52, 26.49, 25.9;

**ESI-MS:*** calculated m/z for [C$_{16}$H$_{23}$N+H]$^+$: 230.19, found: 230.12.

N-methyl-N-((4-methylcyclohex-1-en-1-yl)methyl)aniline (3aj)

47.1 mg, 0.219 mmol, 73%;

Colorless oil;

R$_f$(PE:EA=100:1): 0.5;

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.06 (m, 2H), 6.79 – 6.49 (m, 3H), 5.47 (m, 1H), 3.74 (s, 2H), 2.89 (s, 3H), 2.20 – 1.86 (m, 3H), 1.78 – 1.56 (m, 3H), 1.36 – 1.12 (m, 1H), 0.94 (d, $J = 6.0$ Hz, 3H);

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 150.01, 133.66, 129.00, 121.81, 115.85, 112.03, 58.71, 37.96, 33.57, 30.92, 28.64, 26.48, 21.76;

**Exact Mass ESI-MS:*** calculated m/z for [C$_{15}$H$_{21}$N+H]$^+$: 216.1747, found: 216.1752.

N-((4-(tert-butyl)cyclohex-1-en-1-yl)methyl)-N-methylaniline (3ak)

53.5 mg, 0.207 mmol, 69%
colorless oil;

\[ R_f \text{ (PE:EA}=100:1): 0.6; \]

\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.42 – 7.03 (m, 2H), 6.84 – 6.59 (m, 3H), 5.51 (m, 1H), 3.93 – 3.60 (m, 2H), 2.90 (s, 3H), 2.08 – 1.90 (m, 3H), 1.88 – 1.67 (m, 2H), 1.32 – 1.09 (m, 2H), 0.86 (s, 9H).

\( ^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 150.00, 133.80, 129.00, 122.44, 115.83, 112.02, 77.36, 58.52, 44.32, 37.97, 32.25, 27.88, 27.27, 26.56, 24.00.

**Exact Mass ESI-MS:** calculated m/z for \([\text{C}_{18}\text{H}_{27}\text{N}+\text{H}]^+\): 258.2216; found: 258.2218.

**N-methyl-N-((1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)methyl)aniline (3al)**

\[
\begin{array}{c}
\text{Ph} \\
\text{N}
\end{array}
\]

61.6 mg, 0.222 mmol, 74%;

Colorless oil;

\[ R_f \text{ (PE:EA}=100:1): 0.5; \]

\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.26 – 7.07 (m, 7H), 6.74 – 6.54 (m, 3H), 5.52 (dt, \( J = 5.2, 1.8 \text{ Hz}, 1\text{H} \)), 3.71 (d, \( J = 2.2 \text{ Hz}, 2\text{H} \)), 2.85 (s, 3H), 2.77 – 2.61 (m, 1H), 2.32 – 2.17 (m, 1H), 2.14 – 1.94 (m, 3H), 1.89 (m, 1H), 1.78 – 1.62 (m, 1H);

\( ^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 149.94, 147.04, 147.04, 134.05, 129.11, 128.43, 126.97, 126.08, 121.79, 116.04, 112.10, 58.67, 40.31, 38.21, 33.21, 29.85, 27.03;

**Exact Mass ESI-MS:** calculated m/z for \([\text{C}_{20}\text{H}_{21}\text{N}+\text{H}]^+\): 278.1903, found: 278.1909.

**ethyl 4-((methyl(phenyl)amino)methyl)cyclohex-3-enecarboxylate (3am)**

\[
\begin{array}{c}
\text{COOEt} \\
\text{N}
\end{array}
\]

63.9 mg, 0.234 mmol, 78%;

Colorless oil;

\[ R_f \text{ (PE:EA}=20:1): 0.3; \]

\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.20 – 7.08 (m, 2H), 6.71 – 6.51 (m, 3H), 5.44 (m, 1H), 4.05 (q, \( J = 7.1 \text{ Hz}, 2\text{H} \)), 3.75 – 3.59 (m, 2H), 2.82 (s, 3H), 2.51 – 2.36 (m, 1H), 2.18 (m, 2H), 2.05 – 1.81 (m, 3H), 1.73 – 1.54 (m, 1H), 1.17 (t, \( J = 7.1 \text{ Hz}, 3\text{H} \));

\( ^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 174.76, 148.80, 132.80, 127.97, 119.29, 115.04, 111.04, 59.24, 57.49, 38.45, 36.95, 26.33, 24.59, 24.15, 13.21;
**Exact Mass ESI-MS:** calculated m/z for \([C_{17}H_{23}NO_2+H]^+\): 274.1802, found: 274.1807.

**N-((3,6-dihydro-2H-pyran-4-yl)methyl)-N-methylaniline (3an)**

\[
\begin{array}{c}
\text{51.1 mg, 0.252 mmol, 84\%;} \\
\text{Colorless oil;}
\end{array}
\]

\[
R_f (PE:EA=10:1): 0.5;
\]

\[\text{^1H NMR (400 MHz, CDCl}_3\text{)} \delta 7.31 – 7.12 (m, 2H), 6.83 – 6.59 (m, 3H), 5.52 (dt, } J = 2.9, 1.3 \text{ Hz, 1H), 4.12 (q, } J = 2.5 \text{ Hz, 2H), 3.99 – 3.70 (m, 4H), 2.93 (s, 3H), 2.03 (m, 2H);} \]

\[\text{^13C NMR (101 MHz, CDCl}_3\text{)} \delta 148.62, 130.99, 128.03, 119.62, 115.23, 111.01, 64.32, 63.07, 57.01, 37.17, 25.48;\]

**Exact Mass ESI-MS:** calculated m/z for \([C_{13}H_{17}NO+H]^+\): 204.1383, found: 204.1383.

**tert-butyl 4-((methyl(phenyl)amino)methyl)-5,6-dihydro pyridine-1(2H)-carboxylate (3ao)**

\[
\begin{array}{c}
\text{81.5 mg, 0.270 mmol, 90\%;} \\
\text{Colorless oil;}
\end{array}
\]

\[
R_f (PE:EA=10:1): 0.5;
\]

\[\text{^1H NMR (400 MHz, CDCl}_3\text{)} \delta 7.21 (dd, } J = 8.9, 7.1 \text{ Hz, 2H), 6.68 (d, } J = 7.9 \text{ Hz, 3H), 5.46 (s, 1H), 4.03 – 3.66 (m, 4H), 3.50 (t, } J = 5.8 \text{ Hz, 2H), 2.92 (s, 3H), 2.03 (d, } J = 6.4 \text{ Hz, 2H), 1.46 (s, 9H);} \]

\[\text{^13C NMR (101 MHz, CDCl}_3\text{)} \delta 154.95, 149.67, 133.04, 129.11, 118.48, 116.33, 112.09, 79.56, 58.12, 42.86, 39.66, 38.24, 28.51, 26.38;\]

**Exact Mass ESI-MS:** calculated m/z for \([C_{18}H_{26}N_2O_2+H]^+\): 303.2067, found: 303.2073.

**N-(bicyclo[2.2.1]hept-2-en-2-ylmethyl)-N-methylaniline (3ap)**
47.9 mg, 0.225 mmol, 75 %;  
colorless oil;  
\( R_f \) (PE:EA=100:1): 0.6;  

**\( ^1\)H NMR** (400 MHz, CDCl\(_3\)) δ 7.12 (m, 2H), 6.66 – 6.55 (m, 3H), 5.57 (s, 1H), 3.95 (dd, \( J = 17.1, 1.9 \text{ Hz}, 1\)H), 3.76 (dd, \( J = 17.1, 1.6 \text{ Hz}, 1\)H), 2.83 (s, 3H), 2.72 (m, 1H), 2.63 (s, 1H), 1.55 (m, 2H), 1.32 (m, 1H), 1.09 – 0.87 (m, 3H);  

**\( ^{13}\)C NMR** (101 MHz, CDCl\(_3\)) δ 148.78, 144.73, 129.22, 127.92, 114.94, 111.09, 50.86, 47.27, 42.31, 41.15, 37.03, 25.51, 23.40;  

**Exact Mass ESI-MS:** calculated m/z for \([C_{15}H_{19}N+H]^+\): 214.1590, found: 214.1580.

**N-methyl-N-((8-methyl-8-azabicyclo[3.2.1]oct-2-en-3-yl)methyl)aniline (3aq)**

47.2 mg, 0.195 mmol, 65 %;  
colorless oil;  
\( R_f \) (EA:methol=0.3): 0.6;  

**\( ^1\)H NMR** (400 MHz, CDCl\(_3\)) δ 7.25 – 7.16 (m, 2H), 6.77 – 6.60 (m, 3H), 5.65 (m, 1H), 3.78 – 3.68 (m, 2H), 3.36 – 3.21 (m, 2H), 2.91 (s, 3H), 2.46 (dd, \( J = 17.5, 4.4 \text{ Hz}, 1\)H), 2.36 (s, 3H), 2.16 (m, 1H), 2.04 (m, 1H), 1.81 (m, 1H), 1.61 – 1.44 (m, 2H);  

**\( ^{13}\)C NMR** (101 MHz, CDCl\(_3\)) δ 148.64, 129.94, 127.99, 124.53, 115.17, 111.08, 57.97, 56.74, 56.61, 37.21, 35.58, 32.54, 31.89, 28.45;  

**Exact Mass ESI-MS:** calculated m/z for \([C_{16}H_{22}N_2+H]^+\): 243.1856, found: 243.1861.

**N-methyl-N-((9-methyl-9-azabicyclo[3.3.1]non-3-en-3-yl)methyl)aniline (3ar)**

47.6 mg, 0.186 mmol, 62 %;  
colorless oil;  
\( R_f \) (EA:methol=0.3): 0.6;  

**\( ^1\)H NMR** (400 MHz, CDCl\(_3\)) δ 7.33 – 7.15 (m, 2H), 6.71 (m, 3H), 5.45 (t, \( J = 5.2, 1\)H), 3.98 – 3.74 (m, 2H), 3.40 (d, \( J = 4.9 \text{ Hz}, 1\)H), 3.21 (t, \( J = 5.9 \text{ Hz}, 1\)H), 2.97 (s, 3H), 2.46 (s, 3H), 2.45 – 2.37 (m, 1H), 2.14 – 1.92 (m, 2H), 1.83 – 1.66 (m, 1H), 1.61 – 1.41 (m, 4H);
**13C NMR** (101 MHz, CDCl₃) δ 149.55, 135.11, 129.13, 120.05, 116.48, 112.13, 58.05, 55.11, 52.89, 41.08, 38.47, 31.95, 27.64, 26.69, 14.81;

**Exact Mass ESI-MS:** calculated m/z for [C₁₇H₂₅N₂]+: 257.2012, found: 257.2002.

**N-methyl-N-(3-phenylallyl)aniline (3as)**

\[
\begin{align*}
\text{64.2 mg, 0.288 mmol, 96 %, (E : Z = 2.2 : 1);} \\
\text{colorless oil;}
\end{align*}
\]

Rₕ (PE:EA=100:1): 0.6;

**1H NMR** (400 MHz, CDCl₃, the major isomer) δ 7.45 – 6.80 (m, 7H), 6.75 – 6.56 (m, 3H), 6.56 – 5.54 (m, 2H), 4.06 (2H), 2.86 (3H);

**13C NMR** (101 MHz, CDCl₃, the major isomer) δ 148.54, 135.87, 130.23, 128.14, 127.89, 127.48, 126.35, 125.27, 115.56, 111.60, 53.87, 36.98.

**ESI-MS:** calculated m/z for [C₁₆H₁₇N]+: 224.14, found: 224.10.

**N-allyl-N-methylaniline (3at)**

\[
\begin{align*}
\text{21.6 mg, 0.147 mmol, 49 %;} \\
\text{colorless oil;}
\end{align*}
\]

Rₕ (PE:EA=100:1): 0.6;

**1H NMR** (400 MHz, CDCl₃) δ 7.21 (m, 2H), 6.76 – 6.63 (m, 3H), 5.89 – 5.76 (m, 1H), 5.20 – 5.08 (m, 2H), 3.89 (dt, \(J = 5.4, 1.8\) Hz, 2H), 2.91 (s, 3H);

**13C NMR** (101 MHz, CDCl₃) δ 149.55, 133.88, 129.15, 116.47, 116.18, 112.51, 55.32, 38.04;

**Exact Mass ESI-MS:** calculated m/z for [C₁₀H₁₃N]+: 148.1121, found: 148.1126.

**N-((1H-isochroman-3-yl)methyl)-N-methylaniline(3au)**

\[
\begin{align*}
\text{30.6 mg, 0.122 mmol, 61 % (2u), (0.2 mmol scale);} \\
\text{37.7 mg, 0.100 mmol, 50 % (2v);} \\
\text{White solid;}
\end{align*}
\]

Rₕ (PE:EA=100:1): 0.6;
$^{1}\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 7.31 – 7.20 (m, 2H), 7.14 (m, 2H), 6.98 (d, $J$ = 7.3 Hz, 1H), 6.89 (dd, $J$ = 7.4, 1.3 Hz, 1H), 6.83 – 6.65 (m, 3H), 5.74 (d, $J$ = 1.3 Hz, 1H), 5.08 (s, 2H), 3.98 (s, 2H), 3.04 (s, 3H);

$^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) $\delta$ 154.41, 149.36, 131.28, 129.13, 128.17, 127.48, 126.20, 123.73, 122.91, 116.79, 112.45, 101.42, 68.88, 54.61, 38.69;

**Exact Mass ESI-MS:** calculated m/z for [C$_{17}$H$_{17}$NO+H]$^+$: 252.1383, found: 252.1388.

tert-butyl 6-((methyl(phenyl)amino)methyl)-3,4-dihydropyridine-1(2H)-carboxylate (3aw)

- 40.8 mg, 0.135 mmol, 45 % ;
- Colorless oil;
- $R_t$ (PE:EA=10:1): 0.6;

$^{1}\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 7.25 – 7.17 (m, 2H), 6.89 – 6.51 (m, 3H), 5.08 (tt, $J$ = 3.8, 1.5 Hz, 1H), 4.23 (m, 2H), 3.62 – 3.39 (m, 2H), 2.97 (s, 3H), 2.15 – 1.97 (m, 2H), 1.86 – 1.68 (m, 2H), 1.50 (s, 9H);

$^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) $\delta$ 152.83, 148.30, 134.61, 127.94, 114.96, 110.96, 110.79, 79.70, 55.33, 43.73, 37.52, 27.37, 22.37, 21.72;

**Exact Mass ESI-MS:** calculated m/z for [C$_{18}$H$_{26}$N$_2$O$_2$+H]$^+$: 303.2067, found: 303.2073.

N-((3,4-dihydronaphthalen-2-yl)methyl)-N-ethylaniline (3ba)

- 59.1 mg, 0.225 mmol, 75 % ;
- colorless oil;
- $R_t$ (PE:EA=100:1): 0.4;

$^{1}\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 7.20 (td, $J$ = 7.2, 1.9 Hz, 2H), 7.14 – 7.05 (m, 3H), 6.95 (dt, $J$ = 6.5, 1.6 Hz, 1H), 6.76 – 6.61 (m, 3H), 6.29 (m, $J$ = 1.6 Hz, 1H), 3.95 (s, 2H), 3.44 (q, $J$ = 7.1 Hz, 2H), 2.84 (t, $J$ = 8.2 Hz, 2H), 2.25 (t, $J$ = 8.2 Hz, 2H), 1.19 (t, $J$ = 7.0 Hz, 3H);
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.61, 137.94, 134.79, 134.38, 129.21, 127.28, 126.53, 126.51, 125.87, 122.36, 115.92, 112.11, 55.53, 44.78, 28.01, 25.21, 12.04;

Exact Mass ESI-MS: calculated m/z for [C$_{19}$H$_{21}$N+H]$^+$: 264.1747, found: 264.1752.

N-((3,4-dihyronaphthalen-2-yl)methyl)-N-isopropylaniline (3ca)

\[\begin{align*}
\text{62.3 mg, 0.225 mmol, 75%;} \\
\text{colorless oil;} \\
R_f (\text{PE:EA}=100:1): 0.4; \\
^1H \text{ NMR (400 MHz, CDCl}_3\text{)} \delta 7.15 – 6.95 (m, 5H), 6.93 – 6.80 (m, 1H), 6.72 – 6.56 (m, 3H), 6.29 (t, 1H), 4.12 (p, J = 6.6 Hz, 1H), 3.73 (s, 2H), 2.79 (t, J = 8.1 Hz, 2H), 2.20 (t, J = 8.2 Hz, 2H), 1.13 (d, J = 6.6 Hz, 6H);
\end{align*}\]

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.39, 138.25, 133.61, 128.03, 126.16, 125.43, 125.27, 124.71, 121.03, 115.20, 111.99, 49.09, 46.80, 27.04, 24.21, 18.64;

Exact Mass ESI-MS: calculated m/z for [C$_{20}$H$_{23}$N+H]$^+$: 278.1903, found: 278.1890.

N-((3,4-dihyronaphthalen-2-yl)methyl)-N-phenylaniline (3da)

\[\begin{align*}
\text{60.7 mg, 0.195 mmol, 85%;} \\
\text{colorless oil;} \\
R_f (\text{PE:EA}=100:1): 0.4; \\
^1H \text{ NMR (400 MHz, CDCl}_3\text{)} \delta 7.30 – 7.21 (m, 5H), 7.10 – 7.03 (m, 6H), 6.94 (td, J = 7.3, 1.0 Hz, 3H), 6.45 (m, 1H), 4.45 (s, 2H), 2.81 (t, J = 8.1 Hz, 2H), 2.28 (t, J = 8.1 Hz, 2H);
\end{align*}\]

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.14, 137.82, 134.70, 134.26, 129.35, 129.22, 129.18, 127.22, 126.56, 126.45, 125.90, 123.03, 121.31, 120.67, 57.75, 27.89, 25.20;

Exact Mass ESI-MS: calculated m/z for [C$_{23}$H$_{21}$N+H]$^+$: 312.1747, found: 312.1752.

N-((3,4-dihyronaphthalen-2-yl)methyl)-N,4-dimethylaniline (3ea)

\[\begin{align*}
\text{68.6 mg, 0.261 mmol, 87%;} \\
\text{86.2 mg, 0.230 mmol, 80%;}
\end{align*}\]
colorless oil;

**R**$_f$(PE:EA=100:1): 0.4;

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.07 – 6.86 (m, 6H), 6.60 (d, $J = 8.6$ Hz, 2H), 6.23 (t, $J = 1.6$ Hz, 1H), 3.86 (s, 2H), 2.87 (s, 3H), 2.75 (t, $J = 8.2$ Hz, 2H), 2.24 – 2.08 (m, 5H);

**$^{13}$C NMR** (101 MHz, CDCl$_3$) $\delta$ 146.89, 137.20, 133.75, 133.26, 128.57, 126.20, 125.47, 125.41, 124.76, 124.55, 121.71, 111.52, 57.59, 37.27, 26.88, 24.11, 19.20;

**Exact Mass ESI-MS:** calculated m/z for [C$_{19}$H$_{21}$N+H]$^+$: 264.1747, found: 264.1752.

4-chloro-N-((3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3fa)

![Chemical Structure](image)

72.4 mg, 0.255 mmol, 85%

colorless oil;

**R**$_f$(PE:EA=20:1): 0.8;

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.23 – 7.04 (m, 5H), 7.02 – 6.91 (m, 1H), 6.57 (d, $J = 9$ Hz, 2H), 6.25 (t, $J = 1.6$ Hz, 1H), 3.96 (s, 2H), 2.98 (s, 3H), 2.83 (t, $J = 8.2$ Hz, 2H), 2.14(t, $J = 8.2$ Hz, 2H);

**$^{13}$C NMR** (101 MHz, CDCl$_3$) $\delta$ 148.33, 137.23,134.72, 134.07, 128.87, 127.31, 126.73, 126.54, 125.89, 122.88, 121.16, 113.33, 58.29, 38.56, 27.86, 25.13;

**Exact Mass ESI-MS:** calculated m/z for [C$_{18}$H$_{18}$ClN+H]$^+$: 284.1206, found: 284.1205.

1-(4-(((3,4-dihydronaphthalen-2-yl)methyl)(methyl)amino)phenyl)ethanone (3ga)

![Chemical Structure](image)

72.0 mg, 0.246 mmol, 82%

White solid;

**R**$_f$(PE:EA=10:1): 0.3;

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 8.00 – 7.76 (m, 2H), 7.21 – 7.05 (m, 3H), 6.95 (d, $J = 4.6$ Hz, 1H), 6.66 – 6.59 (m, 2H), 6.21 (t, $J = 1.6$ Hz, 1H), 4.09 (q, $J = 1.3$ Hz, 2H), 3.10 (s, 3H), 2.85 (t, $J = 8.1$ Hz, 2H), 2.50 (s, 3H), 2.23 (m, 2H);
**13C NMR** (101 MHz, CDCl₃) δ 196.32, 152.94, 136.11, 134.62, 133.84, 130.61, 127.33, 126.89, 126.57, 125.97, 125.67, 122.98, 110.74, 57.44, 38.47, 27.79, 26.01, 25.09;

**Exact Mass ESI-MS:** calculated m/z for [C₂₀H₂₁NO+H]⁺: 292.1696, found: 292.1692.

N-((3,4-dihydronaphthalen-2-yl)methyl)-4-(4-(dimethylamino)benzyl)-N-methylaniline (3ha)

![Chemical Structure](image)

73.2 mg, 0.192 mmol, 63%;
colorless oil;

**Rf (PE:EA=5:1): 0.5;**

**1H NMR** (400 MHz, CDCl₃) δ 7.07 – 6.92 (m, 7H), 6.89 (dd, J = 6.6, 1.6 Hz, 1H), 6.65 – 6.57 (m, 4H), 6.22 (t, J = 1.6 Hz, 1H), 3.86 (s, 2H), 3.72 (s, 2H), 2.86 (s, 3H), 2.81 (s, 6H), 2.75 (t, J = 8.2 Hz, 2H), 2.15 (t, J = 8.2 Hz, 2H);

**13C NMR** (101 MHz, CDCl₃) δ 149.08, 148.29,138.29, 134.85, 134.35, 130.42, 130.03, 129.45, 127.28, 126.56, 126.49, 125.86, 122.82, 113.12, 112.54, 58.60, 40.99, 39.93, 38.30, 27.97, 25.19;

**ESI-MS:** calculated m/z for [C₂₇H₃₀N₂+H]⁺: 383.2, found: 383.1.

N-((3,4-dihydronaphthalen-2-yl)methyl)-3-methoxy-N-methylaniline (3ia)

![Chemical Structure](image)

68.6 mg, 0.246 mmol, 82 %;
colorless oil;

**Rf (PE): 0.5;**

**1H NMR** (400 MHz, CDCl₃) δ 7.09 – 6.99 (m, 4H), 6.90 (d, J = 6.4 Hz, 1H), 6.33 – 6.16 (m, 4H), 3.91 (s, 2H), 3.71 (s, 3H), 2.91 (s, 3H), 2.76 (t, J = 8.1 Hz, 2H), 2.16 (t, J = 7.8 Hz, 2H);

**13C NMR** (101 MHz, CDCl₃) δ 160.72, 151.26, 137.82, 134.79, 134.26, 129.80, 127.28, 126.60, 126.50, 125.86, 122.71, 105.46, 101.04, 98.83, 58.19, 55.13, 38.33, 27.93, 25.13;
**Exact Mass ESI-MS:** calculated m/z for [C\(_{19}\)H\(_{21}\)NO+H]\(^+\): 280.1696, found: 280.1701.

N-((3,4-dihydronaphthalen-2-yl)methyl)-N,3-dimethylaniline (3ja)

\[\begin{align*}
\text{Me} & \\
\text{N} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\end{align*}\]

63.2 mg, 0.240 mmol, 80%;

colorless oil;

\(R_f (\text{PE:EA}=100:1): 0.5;\)

\(\text{\(^1\)H NMR (400 MHz, CDCl}_3\) \delta 7.17 – 7.05 (m, 4H), 6.97 (d, \(J = 6.4\) Hz, 1H), 6.61 – 6.49 (m, 3H), 6.30 (t, \(J = 1.6\) Hz, 1H), 3.96 (s, 2H), 2.96 (s, 3H), 2.83 (t, \(J = 8.1\) Hz, 2H), 2.30 (s, 3H), 2.24 (t, \(J = 8.1\) Hz, 2H);\)

\(\text{\(^{13}\)C NMR (101 MHz, CDCl}_3\) \delta 150.08, 138.81, 138.11, 134.84, 134.35, 129.02, 127.30, 126.59, 126.51, 125.88, 122.72, 117.44, 113.05, 109.61, 58.33, 38.18, 27.98, 25.21, 21.99;\)

**Exact Mass ESI-MS:** calculated m/z for [C\(_{19}\)H\(_{21}\)N+H]\(^+\): 264.1747, found: 264.1752.

3-chloro-N-((3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3ka)

\[\begin{align*}
\text{Cl} & \\
\text{N} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\end{align*}\]

67.2 mg, 0.237 mmol, 79%;

colorless oil;

\(R_f (\text{PE}): 0.5;\)

\(\text{\(^1\)H NMR (400 MHz, CDCl}_3\) \delta 7.16 – 7.04 (m, 4H), 7.01 – 6.92 (m, 1H), 6.72 – 6.62 (m, 2H), 6.58 (m, 1H), 6.24 (t, \(J = 1.6\) Hz, 1H), 3.96 (s, 2H), 2.98 (s, 3H), 2.83 (t, \(J = 8.2\) Hz, 2H), 2.21 (t, \(J = 8.7\) Hz, 2H);\)

\(\text{\(^{13}\)C NMR (101 MHz, CDCl}_3\) \delta 150.83 , 137.03 , 135.06 , 134.75 , 134.09 , 130.05 , 127.34 , 126.76 , 126.57 , 125.95 , 122.89 , 116.18 , 111.96 , 110.36 , 57.94 , 38.33 , 27.89 , 25.14;\)

**ESI-MS:** calculated m/z for [C\(_{18}\)H\(_{17}\)NCl+H]\(^+\): 284.1, found: 284.0.

N-((3,4-dihydronaphthalen-2-yl)methyl)-N,3,5-trimethylaniline (3la)

\[\begin{align*}
\text{Me} & \\
\text{N} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\text{C} & \\
\end{align*}\]

69.8 mg, 0.252 mmol, 84%;
colorless oil;
Rf (PE:EA=100:1): 0.6;
\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.09 – 6.98 (m, 3H), 6.90 (d, \(J = 6.8\) Hz, 1H), 6.32 (s, 3H), 6.24 (t, \(J = 1.6\) Hz, 1H), 3.87 (s, 2H), 2.87 (s, 3H), 2.77 (t, \(J = 8.2\) Hz, 2H), 2.19 – 2.10 (m, 8H);
\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 149.18, 137.62, 137.19, 133.79, 133.33, 126.21, 125.47, 125.43, 124.79, 121.55, 117.51, 109.26, 57.26, 37.04, 26.91, 24.14, 20.77;
**Exact Mass ESI-MS:** calculated m/z for \([\text{C}_{20}\text{H}_{23}\text{N}+\text{H}]^+\): 278.1903, found: 278.1909.

1-(4-((methyl(phenyl)amino)methyl)phenyl)ethanone (5aa)

\[
\begin{array}{c}
\text{N} \\
\text{Ac}
\end{array}
\]

56.2 mg, 0.235 mmol, 78%;
White solid;
R\(_f\) (PE:EA = 20:1): 0.5;
\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.91 (d, \(J = 8.2\) Hz, 2H), 7.41 – 7.29 (m, 2H), 7.29 – 7.14 (m, 2H), 6.72 (dt, \(J = 7.7, 1.0\) Hz, 3H), 4.58 (s, 2H), 3.04 (s, 3H), 2.58 (s, 3H).
\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 197.76, 149.42, 144.93, 136.06, 129.27, 128.76, 126.83, 116.94, 112.40, 56.65, 38.79, 26.63.
**Exact Mass ESI-MS:** calculated m/z for \([\text{C}_{16}\text{H}_{17}\text{NO}+\text{H}]^+\): 240.1388, found: 240.1376.

N-methyl-N-(4-(trifluoromethyl)benzyl)aniline (5ab)

\[
\begin{array}{c}
\text{N} \\
\text{CF}_3
\end{array}
\]

64.5 mg, 0.243 mmol, 81%;
Yellow solid;
R\(_f\) (PE): 0.5;
\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.56 (d, \(J = 8.1\) Hz, 2H), 7.34 (d, \(J = 7.9\) Hz, 2H), 7.27 – 7.18 (m, 2H), 6.78 – 6.66 (m, 3H), 4.58 (s, 2H), 3.03 (s, 3H).
\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 149.40, 143.37, 129.29, 129.26 (q, \(J = 32.3\) Hz), 126.94, 125.55 (q, \(J = 3.8\) Hz), 124.24 (q, \(J = 272.2\) Hz), 117.02, 112.41, 56.49, 38.72.
\(^1\text{H NMR}\) (376 MHz, CDCl\(_3\)) \(\delta\) -62.35.
**Exact Mass ESI-MS:** calculated m/z for \([\text{C}_{15}\text{H}_{15}\text{F}_3\text{N}]^+\): 266.1151, found: 266.1153.
N-methyl-N-(4-(methylsulfonyl)benzyl)aniline (5ac)

\[
\begin{align*}
\text{77.5 mg, 0.281 mmol, 94%;} \\
\text{Colorless oil;} \\
\text{R}_f (\text{PE:EA = 1:1}): 0.8;
\end{align*}
\]

\[^1H\text{ NMR (400 MHz, CDCl}_3\text{)} \delta 7.88 - 7.74 (m, 2H), 7.43 - 7.30 (m, 2H), 7.24 - 7.08 (m, 2H), 6.78 - 6.53 (m, 3H), 4.53 (s, 2H), 2.98 (s, 3H), 2.96 (s, 3H).
\]

\[^{13}C\text{ NMR (101 MHz, CDCl}_3\text{)} \delta 148.15, 144.96, 138.11, 128.28, 126.72, 126.50, 116.16, 111.37, 55.50, 43.50, 37.85.
\]

**Exact Mass ESI-MS**: calculated m/z for [C\textsubscript{15}H\textsubscript{17}NO\textsubscript{2}S+H]\textsuperscript{+}: 276.1058, found: 276.1056.

4-((methyl(phenyl)amino)methyl)benzonitrile (5ad)

\[
\begin{align*}
\text{57.9 mg, 0.261 mmol, 87%;} \\
\text{Yellow oil;} \\
\text{R}_f (\text{PE:EA=20:1}): 0.5;
\end{align*}
\]

\[^1H\text{ NMR (400 MHz, CDCl}_3\text{)} \delta 7.60 (d, J = 8.3 Hz, 2H), 7.35–7.20 m, 4H), 6.80 – 6.65 (m, 3H), 4.57 (s, 2H), 3.04 (s, 3H).
\]

\[^{13}C\text{ NMR (101 MHz, CDCl}_3\text{)} \delta 149.21, 145.02, 132.49, 129.35, 127.37, 118.93, 117.25, 112.43, 110.82, 56.67, 38.88.
\]

**Exact Mass ESI-MS**: calculated m/z for [C\textsubscript{15}H\textsubscript{14}N\textsubscript{2}+H]\textsuperscript{+}: 223.1235, found: 223.1229.

ethyl 4-((methyl(phenyl)amino)methyl)benzoate (5ae)

\[
\begin{align*}
\text{70.7 mg, 0.264 mmol, 88%;} \\
\text{Yellow oil;} \\
\text{R}_f (\text{PE:EA=20:1}): 0.5;
\end{align*}
\]

\[^1H\text{ NMR (400 MHz, CDCl}_3\text{)} \delta 8.04 – 7.92 (m, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.25 – 7.19 (m, 2H), 6.77 – 6.68 (m, 3H), 4.57 (s, 2H), 4.36 (q, J = 7.1 Hz, 2H), 3.03 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H).
\]

\[^{13}C\text{ NMR (101 MHz, CDCl}_3\text{)} \delta 166.51, 149.48, 144.53, 129.91, 129.27, 129.25, 126.61, 116.89, 112.42, 60.89, 56.68, 38.73, 14.36.
\]
Exact Mass ESI-MS: calculated m/z for [C\textsubscript{17}H\textsubscript{19}NO\textsubscript{2}+H]\textsuperscript{+}: 270.1494, found: 270.1481.

(4-((methyl(phenyl)amino)methyl)phenyl)(phenyl)methanone (5af)

\[
\begin{align*}
\text{63.2 mg, 0.210 mmol, 70%;} \\
\text{Pale yellow oil;} \\
R_f (\text{PE:EA = 20:1}): 0.1;
\end{align*}
\]

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.69 (td, \(J = 8.2, 1.6\) Hz, 4H), 7.56 – 7.44 (m, 1H), 7.45 – 7.32 (m, 2H), 7.26 (m, 2H), 7.20 – 7.06 (m, 2H), 6.77 – 6.54 (m, 3H), 4.52 (s, 2H), 2.97 (s, 3H).

\textbf{\textsuperscript{13}C NMR} (101 MHz, CDCl\textsubscript{3}) \(\delta\) 195.28, 148.38, 143.21, 136.64, 135.27, 131.28, 129.50, 128.93, 128.21, 127.20, 125.49, 115.84, 111.34, 55.58, 37.73.

Exact Mass ESI-MS: calculated m/z for [C\textsubscript{21}H\textsubscript{19}NO+H]\textsuperscript{+}: 302.1545, found: 302.1545.

N-(3-methoxybenzyl)-N-methylaniline (5ag)

\[
\begin{align*}
\text{36.1 mg, 0.159 mmol, 53%;} \\
\text{Colorless oil;} \\
R_f (\text{PE:EA = 100:1}): 0.5;
\end{align*}
\]

\textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.29 – 7.14 (m, 3H), 6.89 – 6.61 (m, 6H), 4.49 (s, 2H), 3.75 (s, 3H), 3.00 (s, 3H).

\textbf{\textsuperscript{13}C NMR} (101 MHz,) \(\delta\) 159.96, 149.81, 140.93, 129.61, 129.18, 119.05, 116.60, 112.43, 112.40, 112.12, 56.72, 55.19, 38.57.

Exact Mass ESI-MS: calculated m/z for [C\textsubscript{15}H\textsubscript{17}NO+H]\textsuperscript{+}: 228.1388, found: 228.1374.

N-(4-fluorobenzyl)-N-methylaniline (5ah)

\[
\begin{align*}
\text{31.0 mg, 0.144 mmol, 48%;} \\
\text{Yellow oil;} \\
R_f (\text{PE:EA = 100:1}): 0.5;
\end{align*}
\]
\[ ^1\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 7.27 - 7.13 (\text{m, 4H}), 7.04 - 6.94 (\text{m, 2H}), 6.73 (\text{m, 3H}), 4.48 (\text{d, } J = 1.1 \text{ Hz, 2H}), 2.99 (\text{s, 3H}). \]

\[ ^{13}\text{C NMR} (101 \text{ MHz, CDCl}_3) \delta 161.90 (J = 152 \text{ Hz}), 149.63, 134.61, 129.23, 128.27 (J = 5 \text{ Hz}), 116.80, 115.39 (J = 13 \text{ Hz}), 112.51, 56.09, 38.47. \]

**LRMS**: calculated m/z for \([C_{14}H_{14}FN+H]^+\): 216.12, found: 216.15.

**N-[(1,1'-biphenyl)-4-ylmethyl)-N-methylaniline (5ai)**

\[
\begin{align*}
\text{N} & \quad \text{41.4 mg, 0.151 mmol, 75\%;} \\
\text{White solid;} & \quad \text{Rf (PE:EA = 20:1): 0.5;} \\
\text{1H NMR} & \quad (400 \text{ MHz, CDCl}_3) \delta 7.57 (\text{m, 4H}), 7.49 - 7.40 (\text{m, 2H}), 7.38 - 7.21 (\text{m, 5H}), 6.88 - 6.64 (\text{m, 3H}), 4.59 (\text{d, } J = 6.5 \text{ Hz, 2H}), 3.13 - 3.00 (\text{m, 3H}).
\end{align*}
\]

**13C NMR** (101 MHz, CDCl$_3$) δ 149.76, 140.95, 139.90, 138.15, 129.25, 128.78, 127.35, 127.20, 127.07, 121.66, 116.61, 112.42, 56.42, 38.60.

**Exact Mass ESI-MS**: calculated m/z for \([C_{18}H_{17}N+H]^+\): 248.1439, found: 248.1432.

**N-benzyl-N-methylaniline (5aj)**

\[
\begin{align*}
\text{N} & \quad \text{39.6 mg, 0.202 mmol, 67\%;} \\
\text{Yellow oil;} & \quad \text{Rf (PE:EA): 0.5;} \\
\text{1H NMR} & \quad (400 \text{ MHz, CDCl}_3) \delta 7.30 (\text{m, 2H}), 7.27 - 7.15 (\text{m, 5H}), 6.81 - 6.66 (\text{m, 3H}), 4.53 (\text{s, 2H}), 3.01 (\text{s, 3H}).
\end{align*}
\]

**13C NMR** (101 MHz, CDCl$_3$) δ 149.82, 139.10, 129.26, 128.63, 126.93, 126.82, 116.62, 112.45, 56.71, 38.58.

**Exact Mass ESI-MS**: calculated m/z for \([C_{14}H_{13}N+H]^+\): 198.1283, found: 198.1279.

**N-methyl-N-(naphthalen-2-ylmethyl)aniline (5ak)**

\[
\begin{align*}
\text{N} & \quad \text{60.0 mg, 0.243 mmol, 81\%;} \\
\text{Yellow solid;} & \quad \text{Rf (PE): 0.5;} \\
\end{align*}
\]
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 – 7.74 (m, 3H), 7.67 (s, 1H), 7.49 – 7.34 (m, 3H), 7.26 – 7.20 (m, 2H), 6.86 – 6.69 (m, 3H), 4.68 (s, 2H), 3.06 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.90, 136.62, 133.53, 132.70, 129.24, 128.36, 127.73, 127.70, 126.10, 125.56, 125.21, 125.13, 116.67, 112.49, 57.01, 38.54.

**Exact Mass ESI-MS:** calculated m/z for [C$_{18}$H$_{17}$N+H]$^+$: 248.1439, found: 248.1432.

N-methyl-N-(naphthalen-1-ylmethyl)aniline (5a)

48.8 mg, 0.198 mmol, 66%;

Pale yellow oil;

$\text{R}_f$ (PE:EA = 50:1): 0.8;

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99 – 7.94 (m, 1H), 7.92 – 7.86 (m, 1H), 7.79 – 7.73 (m, 1H), 7.57 – 7.47 (m, 2H), 7.38 (dd, $J = 8.1, 7.1$ Hz, 1H), 7.30 (dq, $J = 7.0, 1.2$ Hz, 1H), 7.25 – 7.18 (m, 2H), 6.82 – 6.75 (m, 3H) 4.96 (s, 2H), 3.07 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.77, 133.90, 133.25, 131.23, 129.27, 128.93, 127.48, 126.10, 125.72, 125.67, 123.95, 122.75, 116.52, 112.20, 54.60, 38.49.

**Exact Mass ESI-MS:** calculated m/z for [C$_{18}$H$_{17}$N+H]$^+$: 248.1439, found: 248.1426.

N-methyl-N-(quinolin-8-ylmethyl)aniline (5am)

35.4 mg, 0.144 mmol, 48%;

Pale yellow oil;

$\text{R}_f$ (PE:EA = 50:1): 0.5;

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.95 (dd, $J = 4.2, 1.8$ Hz, 1H), 8.17 (dd, $J = 8.3, 1.8$ Hz, 1H), 7.70 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.52 – 7.39 (m, 3H), 7.26 – 7.14 (m, 2H), 6.74 (dt, $J = 7.8, 1.1$ Hz, 2H), 6.72 – 6.64 (m, 1H), 5.27 (s, 2H), 3.18 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.53, 148.16, 145.37, 135.30, 135.04, 128.10, 127.34, 125.49, 125.42, 125.40, 119.98, 114.93, 110.77, 52.34, 37.93.

**Exact Mass ESI-MS:** calculated m/z for [C$_{17}$H$_{16}$N$_2$+H]$^+$: 249.1392, found: 249.1387.
N-methyl-N-(pyridin-2-ylmethyl)aniline (5an)

28.4 mg, 0.144 mmol, 48%;
Pale yellow oil;
\( R_f (\text{PE:EA} = 100:1): 0.5; \)

\( ^1H \text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta 8.59 \ (m, 1H), 7.59 \ (td, J = 7.7, 1.8 \text{ Hz, } 1H), 7.39 – 7.03 \ (m, 4H), 6.84 – 6.60 \ (m, 3H), 4.65 \ (s, 2H), 3.12 \ (s, 3H). \)

\( ^{13}C \text{ NMR} \ (101 \text{ MHz, CDCl}_3) \delta 159.41, 150.55, 149.24, 136.75, 129.22, 121.90, 120.75, 116.71, 112.21, 58.88, 39.08. \)

**Exact Mass ESI-MS:** calculated m/z for \([C_{13}H_{14}N_2+H]^+\): 199.1235, found: 199.1232.

N-methyl-N-(pyridin-3-ylmethyl)aniline (5ao)

29.0 mg, 0.147 mmol, 49%;
Pale yellow oil;
\( R_f (\text{PE:EA} = 100:1): 0.5; \)

\( ^1H \text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta 8.53 \ (s, 2H), 7.73 – 7.43 \ (m, 1H), 7.33 – 7.13 \ (m, 3H), 6.89 – 6.56 \ (m, 3H), 4.54 \ (s, 2H), 3.01 \ (s, 3H). \)

\( ^{13}C \text{ NMR} \ (101 \text{ MHz, CDCl}_3) \delta 159.41, 149.55, 149.24, 136.75, 129.22, 121.90, 120.75, 116.71, 112.21, 53.47, 37.58. \)

**Exact Mass ESI-MS:** calculated m/z for \([C_{13}H_{14}N_2+H]^+\): 199.1235, found: 199.1230.

N-methyl-N-(pyridin-4-ylmethyl)aniline (5ap)

40.2 mg, 0.204 mmol, 68%;
Pale yellow oil;
\( R_f (\text{PE:EA} = 50:1): 0.8; \)

\( ^1H \text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta 8.54 \ (s, 2H), 7.28 – 7.11 \ (m, 4H), 6.74 \ (tt, J = 7.2, 1.1 \text{ Hz, } 1H), 6.69 \ (dt, J = 7.2, 1.1 \text{ Hz, } 2H), 4.51 \ (s, 2H), 3.05 \ (s, 3H). \)

\( ^{13}C \text{ NMR} \ (101 \text{ MHz, CDCl}_3) \delta 159.41, 150.55, 149.24, 136.75, 129.22, 121.90, 120.75, 116.19, 111.67, 53.47, 37.86. \)

**Exact Mass ESI-MS:** calculated m/z for \([C_{13}H_{14}N_2+H]^+\): 199.1235, found: 199.1233.
tert-butyl 2-(4-acetylphenyl)pyrrolidine-1-carboxylate (5ma)

\[
\text{\textbf{R}}_f (\text{PE:EA} = 5:1): 0.3;
\]

\[
\text{\textbf{H}}\text{ NMR} (400 MHz, CDCl}_3) \delta 8.06 - 7.77 (m, 2H), 7.41 - 7.01 (m, 2H), 5.08 - 4.71 (m, 1H), 3.65 (t, J = 6.8 Hz, 2H), 2.59 (d, J = 8.6 Hz, 3H), 2.36 (dt, J = 14.2, 7.9 Hz, 1H), 2.00 - 1.72 (m, 3H), 1.46 (s, 3H), 1.18 (s, 6H).
\]

\[
\text{\textbf{C}}\text{ NMR} (101 MHz, CDCl}_3) \delta 197.81, 154.43, 150.81, 135.72, 128.64, 128.44, 125.64, 79.54, 61.17, 60.67, 47.40, 47.15, 35.90, 34.75, 28.49, 28.16, 26.62, 23.66, 23.26. \textbf{CGMS}: \text{calculated m/z for C}_{17}H_{23}NO_3: 289.2, found: 289.2.
\]

1-(4-(tetrahydrofuran-2-yl)phenyl)ethanone (5na)

\[
\text{\textbf{R}}_f (\text{PE:EA} = 10:1): 0.2;
\]

\[
\text{\textbf{H}}\text{ NMR} (400 MHz, CDCl}_3) \delta 7.86 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.88 (t, J = 7.2 Hz, 1H), 4.16 - 3.95 (m, 1H), 3.95 - 3.82 (m, 1H), 2.52 (s, 3H), 2.30 (dd, J = 12.5, 6.4 Hz, 1H), 2.07 - 1.88 (m, 2H), 1.78 - 1.62 (m, 1H).
\]

\[
\text{\textbf{C}}\text{ NMR} (101 MHz, CDCl}_3) \delta 196.82, 148.17, 135.04, 127.44, 124.57, 79.11, 67.85, 33.68, 25.60, 24.94. \textbf{CGMS}: \text{calculated m/z for C}_{12}H_{14}O_2: 190.1, found: 190.1.
\]

(8R,9S,13S,14S)-13-methyl-3-((methyl(phenyl)amino)methyl)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (5aq)

\[
\text{\textbf{R}}_f (\text{PE:EA}=20:1): 0.2;
\]

\[
\text{\textbf{H}}\text{ NMR} (400 MHz, CDCl}_3) \delta 7.22 - 7.08 (m, 3H), 6.97 - 6.86 (m, 2H), 6.72 - 6.57 (m, 3H), 4.39 (s, 2H), 2.92 (s, 3H), 2.80 (dd, J = 8.7, 4.0 Hz, 2H), 2.49 - 2.27 (m, 2H), 2.21 (td, J = 10.7, 4.2 Hz, 1H), 2.12 - 1.84 (m, 4H),
\]
1.62 – 1.29 (m, 6H), 0.82 (s, 3H).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11 (d, $J = 8.2$ Hz, 1H), 7.86 – 7.77 (m, 2H), 7.43 (dd, $J = 5.3, 4.2, 2.3$ Hz, 3H), 7.36 (d, $J = 1.4$ Hz, 1H), 7.23 (dd, $J = 8.2, 1.5$ Hz, 1H), 7.21 – 7.12 (m, 2H), 6.73 (s, 1H), 6.72 – 6.62 (m, 3H), 4.57 (s, 2H), 3.03 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.23, 162.29, 155.74, 148.26, 145.61, 130.69, 130.52, 128.30, 127.97, 125.27, 125.06, 122.75, 121.87, 116.14, 114.54, 111.35, 106.56, 55.79, 37.87.

LRMS: calculated m/z for [C$_{23}$H$_{19}$NO$_2$+H]$^+$: 342.15, found: 342.20

2-((methyl(phenyl)amino)methyl)cyclohexan-1-ol (7ag)

60.0 mg, 0.272 mmol, 68 %;

Yellow oil;

$R_f$ (PE:EA=1:1): 0.5;

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.27 (m, 2H), 6.98 – 6.81 (m, 3H), 4.13 (s, 1H), 3.58 – 3.38 (m, 2H), 3.01 (dd, $J = 14.0, 5.4$ Hz, 1H), 2.89 (s, 3H), 2.04 – 1.94 (m, 1H), 1.78 – 1.63 (m, 4H), 1.32 – 1.15 (m, 3H), 1.01 – 0.90 (m, 1H);

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.00, 129.17, 119.24, 115.84, 76.14, 61.36, 42.29, 40.38, 35.07, 29.12, 25.42, 24.41;

Exact Mass ESI-MS: calculated m/z for [C$_{14}$H$_{22}$NO]+: 220.1696, found: 220.1704.
N-methyl-O-(2-methylene cyclohexyl)-N-phenyl hydroxylamine. (8ag)

30.4 mg, 0.140 mmol, 70%;

Yellow oil;

$R_f$ (PE): 0.5;

$^{1}\text{H NMR}$ (400 MHz, CHCl$_3$) $\delta$ 7.25 – 7.15 (m, 2H), 7.04 – 6.93 (m, 2H), 6.87 (tt, $J = 7.3$, 1.1 Hz, 1H), 4.92 – 4.86 (m, 1H), 4.76 (dt, $J = 2.2$, 1.1 Hz, 1H), 4.13 – 4.05 (m, 1H), 3.00 (s, 3H), 2.33 (m, 1H), 2.05 (m, 1H), 1.80 (m, 2H), 1.78 – 1.65 (m, 1H), 1.60 – 1.42 (m, 1H), 1.47 – 1.35 (m, 1H), 1.19 (m, 1H);

$^{13}\text{C NMR}$ (101 MHz, CHCl$_3$) $\delta$ 152.37, 146.94, 127.72, 120.61, 114.96, 107.81, 80.86, 44.85, 32.13, 31.77, 26.80, 21.56;

ESI-MS: calculated m/z for [C$_{14}$H$_{20}$NO]$^+$: 218.15, found: 218.10.

N-methyl-O-(4-methylene tetrahydro-2H-pyran-3-yl)-N-phenyl hydroxylamine

(8an)

35.5 mg, 0.162 mmol, 81%;

Yellow oil;

$R_f$ (PE): 0.5;

$^{1}\text{H NMR}$ (400 MHz, CHCl$_3$) $\delta$ 7.26 – 7.15 (m, 2H), 7.10 – 6.97 (m, 2H), 6.90 (t, $J = 7.3$ Hz, 1H), 5.02 (s, 1H), 4.90 (s, 1H), 4.04 (d, $J = 3.4$ Hz, 1H), 3.95 (dd, $J = 11.7$, 4.1 Hz, 1H), 3.81 (dt, $J = 9.9$, 4.7 Hz, 1H), 3.65 (dd, $J = 11.7$, 2.8 Hz, 1H), 3.50 (ddd, $J = 10.8$, 9.2, 3.4 Hz, 1H), 3.02 (s, 3H), 2.57 (ddd, $J = 13.8$, 9.2, 4.7 Hz, 1H), 2.15 (dt, $J = 13.7$, 4.0 Hz, 1H);

$^{13}\text{C NMR}$ (101 MHz, CHCl$_3$) $\delta$ 153.02, 142.68, 128.82, 122.02, 116.13, 111.67, 79.84, 70.90, 69.13, 45.73, 33.21;

Exact Mass ESI-MS: calculated m/z for [C$_{13}$H$_{18}$NO$_2$]$^+$: 220.1332, found: 220.1341.

4-bromo-N-(cyclohex-1-en-1-ylmethyl)-N-methylaniline (9ag)

54.0 mg, 0.193 mmol, 97%;

Yellow oil;

$R_f$ (PE): 0.5;
$^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 7.23–7.14 (m, 2H), 6.51–6.43 (m, 2H), 5.39 (m, $J = 5.3, 3.6, 1.7$ Hz, 1H), 3.64 (s, 2H), 2.82 (s, 3H), 1.97–1.87 (m, 2H), 1.79 (t, 2H), 1.58–1.47 (m, 4H);

$^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) $\delta$ 147.82, 132.36, 130.56, 121.34, 112.55, 106.59, 57.83, 37.20, 25.32, 23.88, 21.57, 21.52;

**Exact Mass ESI MS**: calculated m/z for [C$_{14}$H$_{19}$BrN]$^+$: 282.0675, found: 282.0665.
The Application of the Reaction

(A) functionalization of natural products

(B) product diversification

Synthesis of 5aq

A 100 mL round-bottom flask containing a magnetic stir bar was charged with 4q\(^+\) (0.61 g, 2.26 mmol), and DMAP (30 mg, 0.25 mmol). Under a positive flow of nitrogen, CH\(_2\)Cl\(_2\) (10 mL) and Et\(_3\)N (6.0 mL, 43 mmol) were each introduced via syringe, and the clear solution was cooled on a water/ice bath. N-phenyl bis(trifluoromethylsulfon)imide (0.93 g, 2.6 mmol) dissolved in CH\(_2\)Cl\(_2\) (5 mL) was added via cannula and the reaction was allowed to stir at rt for 22 h. The mixture was diluted with EtO\(_2\), washed once with water, twice with saturated aqueous ammonium chloride, twice with saturated aqueous sodium bicarbonate, and once with brine. The solution obtained was dried over anhydrous MgSO\(_4\), filtered, and concentrated by rotary evaporation. The oily residue was purified by flash chromatography eluting with 10/90 ethyl acetate/petroleum ether to afford the triflate as a white solid (0.86 g, 94%).

\((8R,9S,13S,14S)-13\)-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yltrifluoro methanesulfonate. \(^1\)H NMR (400 MHz, CDCl\(_3\))
δ 7.34 (dd, J = 8.7, 1.1 Hz, 1H), 7.08 – 6.97 (m, 2H), 2.95 (dd, J = 8.8, 4.1 Hz, 2H), 2.58 – 2.46 (m, 1H), 2.46 – 2.36 (m, 1H), 2.30 (td, J = 10.6, 4.4 Hz, 1H), 2.25 – 2.10 (m, 1H), 2.10 – 2.02 (m, 2H), 2.02 – 1.92 (m, 1H), 1.72 – 1.39 (m, 6H), 0.92 (s, 3H). All spectroscopic data is in agreement with those previously reported.[8]

To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added \text{Ir}[\text{dF(CF}_3\text{ppy})_2(\text{dtbbpy})(\text{PF}_6)] (0.0075 mmol), the above solid (0.3 mmol). The tube was triple evacuated/N$_2$ filled before being transferred into a glovebox. Ni(cod)$_2$ (0.03 mmol), Me$_4$Phen (0.03 mmol) and DABCO (0.6 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N$_2$. Dry DMF (3.0 mL) were added to the tube, followed by 1a (0.9 mmol). The resulting mixture was degassed by using a “freeze–pump–thaw” procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from a 30 W blue LED and stirred at room temperature for 12 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 50:1 to 30:1) to provide the pure product 5aq as a pale white solid in 68% yield (76.0 mg, 0.204 mmol).

**Synthesis of 5ar**

To a solution of tosyl chloride (1.8 g, 6.3 mmol) in CH$_2$Cl$_2$ (10.0 mL) was added dropwise to a solution of 4r' (1.5 g, 9.5 mmol) and DABCO (2.1 g, 18.9 mmol) in anhydrous CH$_2$Cl$_2$ (20 mL) at 0 °C. After complete addition, the mixture was warmed to room temperature and allowed to stir until completion following the reaction by TLC. The mixture was then diluted with Et$_2$O (20 mL), quenched with 10 % aq. HCl and washed successively with aqueous solution of NaHCO$_3$ and brine. After drying over MgSO$_4$, the solvent was removed under reduced pressure to give the tosylate as a white solid (2.03 g, 82%). 4-oxo-2-phenyl-4H-chromen-7-yl 4-methylbenzenesulfonate $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, J = 8.7 Hz, 1H), 7.89 – 7.79 (m, 2H), 7.73 – 7.65 (m, 2H), 7.54 – 7.42 (m, 3H), 7.38 (d, J = 2.2 Hz, 1H), 7.32 – 7.24 (m, 2H), 6.85 (dd, J = 8.7, 2.2 Hz, 1H), 6.74 (s, 1H), 2.39 (s, 3H). All
spectroscopic data is in agreement with those previously reported.\textsuperscript{[9]}

To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added Ru(bpy)$_3$Cl$_2$·6H$_2$O (0.003 mmol), the above solid (0.3 mmol). The tube was triple evacuated/N$_2$ filled before being transferred into a glovebox. NiBr$_2$-glyme (0.006 mmol), Me$_4$Phen (0.006 mmol) and DABCO (0.6 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N$_2$. Dry DMF (3.0 mL) were added to the tube, followed by 1a (0.9 mmol). The resulting mixture was degassed by using a “freeze–pump–thaw” procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from a 30 W blue LED and stirred at room temperature for 12 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 50:1 to 30:1) to provide the pure product 5aa as a pale white solid in 64% yield (65.9 mg, 0.193 mmol).

**Synthesis of 2-((methyl(phenyl)amino)methyl)cyclohexan-1-ol (7ag)\textsuperscript{[10]}**

![Chemical structure of 2-((methyl(phenyl)amino)methyl)cyclohexan-1-ol (7ag)](attachment)

To a solution of alkene N-(cyclohex-1-en-1-ylmethyl)-N-methylaniline (0.4 mmol 80.4 mg) in THF (2 mL) was added NaBH$_4$ (0.8 mmol, 30.4 mg) at room temperature under N$_2$. The slurry was cooled to 0°C, and BF$_3$·OEt$_2$ (120 μL) in THF (1 mL) was slowly added. The addition was kept slow enough to keep the temperature of the reaction mixture below 0°C. After the addition the reaction mixture was stirred at 0°C for 1 h and at room temperature for 1.5 h. The reaction was re-cooled to 0°C and water (1 mL) was added slowly to destroy the excess borane. The reaction was stirred at rt for 2 h, followed by the addition of Oxone® (0.8 g) in water (1 mL) at 0°C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by adding NaHSO$_3$ (solid) until all excess oxidant was
destroyed (KI/starch test paper). The pH of the reaction mixture was 1 - 2. The reaction mixture was extracted with ethyl acetate (2 mL), and the aqueous layer was adjusted to pH 12 with 6 N NaOH and extracted with ethyl acetate (4* 2 mL). The organic layer was washed with brine, dried over NaSO$_4$, and concentrated in vacuo. The residue obtained is pure alcohol (60.0 mg, 68%).

**Synthesis of N-methyl-O-(4-methylene tetrahydro-2H-pyran-3-yl)-N-phenylhydroxylamine (8an)**

\[
\text{N-((3,6-dihydro-2H-pyran-4-yl)methyl)-N-methylaniline (0.2 mmol, 40.6 mg) in methylenechloride (2 mL) and 0.5 M aqueous sodium hydrogencarbonate (0.3 mmol, 1.5 eq.,) was added 70% m-chlorperbenzoic acid (0.2 mmol, 49.3 mg, 1.0 eq.) with stirring. After stirring at rt for 3 h. The organic layer was washed with 1N sodium solution, water, brine, dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue obtained is pure (35.5mg, 81 %).}
\]

**Synthesis of N-methyl-O-(2-methylene cyclohexyl)-N-phenylhydroxylamine (8ag)**

The procedure is the same to the Synthesis of 8an.

**Synthesis of 4-bromo-N-(cyclohex-1-en-1-ylmethyl)-N-methylaniline (9ag)\textsuperscript{[11]}**
A mixture of 40.2 mg (0.200 mmol, 1.0 eq.) of N-(cyclohex-1-en-1-ylmethyl)-N-methylaniline and 38.9 mg (0.220 mmol, 1.1 eq.) of NBS was dissolved in 3 mL of DMF. The reaction mixture was stirred for overnight at room temperature and the resulting solvent was concentrated in vacuo. The residue was purified by silica gel flash chromatography (pure petroleum) to give the pure desired product 4-bromo-N-(cyclohex-1-en-1-ylmethyl)-N-methylaniline 54.0 mg (yield, 97%).
Mechanistic studies

![Scheme SI-1 Trapping of free radical](image)

(1) **Trapping of free radical with TEMPO**

To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added Ru(bpy)$_3$Cl$_2$·6H$_2$O (0.003 mmol), 2a (0.3 mmol) and dtbbpy (0.006 mmol), 2,2,6,6-tetramethylpiperding-1-oxyl (TEMPO, 0.6 mmol). The tube was evacuated and refilled with N$_2$ 3 times before being transferred into a glovebox. NiCl$_2$·glyme (0.006 mmol) and Cs$_2$CO$_3$ (0.6 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N$_2$. Dry DMF (3.0 mL) were added to the tube, followed by 1a (0.9 mmol). The resulting mixture was degassed by using a “freeze–pump–thaw” procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from a 30 W blue LED and stirred at room temperature for 4 h. No desired product 3aa was detected by TLC plate or GCMS.

(2) **Trapping of free radical with tert-butyl acrylate**

To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added Ru(bpy)$_3$Cl$_2$·6H$_2$O (0.003 mmol), 2a (0.3 mmol) and dtbbpy (0.006 mmol). The tube was evacuated and refilled with N$_2$ 3 times before being transferred into a glovebox. NiCl$_2$·glyme (0.006 mmol) and Cs$_2$CO$_3$ (0.6 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N$_2$. Dry DMF (3.0 mL) were added to the tube, followed by 1a (0.9 mmol) and tert-butyl acrylate (0.6 mmol). The resulting mixture was degassed by using a “freeze–pump–thaw” procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from
a 30 W blue LED and stirred at room temperature for 4 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 500:1 to 300:1 to 100:1) to provide the pure product 3aa as a pale white solid in 28% yield (with 67% of 2a recovered), 6aa and 6ab as colorless oil in 23% yield (the ratio of 6aa:6ab is 3:2, which are inseparable from each other).

(3) Stoichiometric reactions of Ni(0) complex with alkenyl/aryl tosylates
In order to get more insights to this reaction, stoichiometric reactions of Ni(0) complex with alkenyl/aryl tosylates were carried out (Scheme SI-2). The procedure for Scheme S2 ia as following: to a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added 2 (0.1 mmol) and dtbbpy (0.1 mmol). Ni(cod)2 (0.1 mmol) and Cs2CO3 (0.2 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N2. Dry DMF (1.0 mL) were added to the tube, and then stirred at room temperature for 12 h. Afterwards, 1N HCl solution(2 mL) was added and stirred for 1h. The reaction mixture was extracted with EtOAc, dried.
with MgSO$_4$. Then, the solvent was removed in vacuum. The yield of deoxyprotonation product was determined by $^1$H NMR and/or GC.

All of such reactions showed low conversion and gave less than 10% of deoxyprotonation byproducts arising from C─O activation$^{[12]}$ and further protonation (Scheme SI-2 Eqs 1-6). Compared to the high efficiency of the catalytic reaction (83%, Scheme SI-2 Eq 1,3), these low yields indicated the direct oxidative addition to Ni(0) was inefficient and less favored in this reaction. Based on the above information and previous seminar works$^{[13]}$, we then proposed a possible pathway for the coupling of 1a with 2 (Figure SI-1). Firstly, Ru-photocatalyst A is excited to generate B, which undergoes single-electron oxidation with 1a to give Ru-photocatalyst C and, after deprotonation of the intermediate $N$-centered radical cation with the carbonate base, carbon-centered radical 1a$^\circ$. Combination of 1a$^\circ$ with Ni(0) complex D might form the highly electron-rich Ni(I) complex E, which could undergo oxidative addition into the C(sp$^2$)─O bond of 2 at room temperature to generate the highly reactive Ni(III) species F. The following reductive elimination would give the desired product 3 and the Ni(I) complex G. Lastly, both A and D are regenerated to complete the dual catalytic cycle through reduction of G by the reduced form of Ru-photocatalyst C.
However, at present stage, we cannot rule out the other catalytic cycle present in Figure SI-2\textsuperscript{13}. Firstly, Ru-photocatalyst \textbf{A} is excited to generate \textbf{B}, which undergoes single-electron oxidation with 1\textit{a} to give Ru-photocatalyst \textbf{C} and, after deprotonation of the intermediate \textit{N}-centered radical cation with the carbonate base, carbon-centered radical 1\textit{a}'. Concurrent with this photoredox mechanism, Ni(0) complex \textbf{D} could undergo oxidative addition into the C(sp\textsuperscript{2})─O bond of 2 at room temperature to generate the Ni(II) species \textbf{E}. Interception of radical 1\textit{a}' by \textbf{E} would then generate organometallic Ni(III) adduct \textbf{F}. The following reductive elimination would give the desired product 3 and the Ni(I) complex \textbf{G}. Lastly, both \textbf{A} and \textbf{D} are regenerated to complete the dual catalytic cycle through reduction of \textbf{G} by the reduced form of Ru-photocatalyst \textbf{C}.

\textbf{(4) Proposed catalytic cycle for coupling of aryl tosylate 4a with 1m and 1n}

Firstly, Ir-photocatalyst \textbf{A} is excited to generate \textbf{B}, which undergoes single-electron oxidation with 4\textit{a} to give Ir-photocatalyst \textbf{C} and \textit{N}-centered radical cation 4\textit{b}, Hydrogen atom transfer (HAT) between 4\textit{b} and 1 gave a carbon-centered radical 1'. Concurrent with this photoredox mechanism, Ni(0) complex \textbf{D} could undergo oxidative addition into the C(sp\textsuperscript{2})─O bond of 2 at room temperature to generate the Ni(II) species \textbf{E}. Interception of radical 1' by \textbf{E} would
then generate organometallic Ni(III) adduct F (Interception of radical 1′ with Ni(0) to form Ni(I) and subsequent oxidation to C(sp³)–O bond of 2 to form Ni(III) adduct F is also possible). The following reductive elimination would give the desired product 3 and the Ni(I) complex G. Lastly, both A and D are regenerated to complete the dual catalytic cycle through reduction of G by the reduced form of Ir-photocatalyst C.

![Figure SI-3 Proposed catalytic cycle III](image-url)
References


Copies of NMR spectra

N-((3,4-dihyronaphthalen-2-yl)methyl)-N-methylaniline (3aa)
N-methyl-N-((6-phenyl-3,4-dihyronaphalen-2-yl)methyl)aniline (3ab)
N-((6-fluoro-3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3ac)
N-((6-bromo-3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3ad)
N-((6-methoxy-3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3ae)
6-((methyl(phenyl)amino)methyl)-7,8-dihydronaphthalen-2-yl 4-methylbenzene sulfonate (3af)
N-(cyclohex-1-en-1-ylmethyl)-N-methylaniline (3ag)
N-(cyclohept-1-en-1-ylmethyl)-N-methylaniline (3ah)
(E)-N-(cyclooct-1-en-1-ylmethyl)-N-methylaniline (3ai)
N-methyl-N-((4-methylcyclohex-1-en-1-yl)methyl)aniline (3aj)
N-((4-(tert-butyl)cyclohex-1-en-1-yl)methyl)-N-methylaniline (3ak)
N-methyl-N-((1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)methyl)aniline (3aI)
ethyl 4-((methyl(phenyl)amino)methyl)cyclohex-3-enecarboxylate (3am)
N-((3,6-dihydro-2H-pyran-4-yl)methyl)-N-methylaniline (3an)
tert-butyl
4-((methyl(phenyl)amino)methyl)-5,6-dihydropyridine-1(2H)-carboxylate (3ao)
N-(bicyclo[2.2.1]hept-2-en-2-ylmethyl)-N-methylaniline (3ap)
N-methyl-N-((8-methyl-8-azabicyclo[3.2.1]oct-2-en-3-yl)methyl)aniline (3aq)
N-methyl-N-((9-methyl-9-azabicyclo[3.3.1]non-3-en-3-yl)methyl)aniline (3ar)
N-methyl-N-(3-phenylallyl)aniline (3as)
N-((1H-isochromen-3-yl)methyl)-N-methylaniline(3au)
tert-butyl 6-((methyl(phenyl)amino)methyl)-3,4-dihydropyridine-1(2H)-carboxylate (3aw)
N-((3,4-dihyronaphthalen-2-yl)methyl)-N-ethylaniline (3ba)
N-((3,4-dihyronaphthalen-2-yl)methyl)-N-isopropylaniline (3ca)
N-((3,4-dihydronaphthalen-2-yl)methyl)-N-phenylaniline (3da)
N-((3,4-dihyronaphthalen-2-yl)methyl)-N,4-dimethylaniline (3ea)
4-chloro-N-((3,4-dihyronaphthalen-2-yl)methyl)-N-methylaniline (3fa)
1-(4-(((3,4-dihyronaphthalen-2-yl)methyl)(methyl)amino)phenyl)ethanone (3ga)
N-((3,4-dihydronaphthalen-2-yl)methyl)-4-(4-(dimethylamino)benzyl)-N-methylaniline (3ha)
N-((3,4-dihyronaphthalen-2-yl)methyl)-3-methoxy-N-methylaniline (3ia)
3-chloro-N-((3,4-dihyronaphthalen-2-yl)methyl)-N-methylaniline (3ja)
3-chloro-N-((3,4-dihyronaphthalen-2-yl)methyl)-N-methylaniline (3ka)
N-((3,4-dihydonaphthalen-2-yl)methyl)-N,3,5-trimethylaniline (3la)
1-(4-((methyl(phenyl)amino)methyl)phenyl)ethanone (5aa)
N-methyl-N-(4-(trifluoromethyl)benzyl)aniline (5ab)
N-methyl-N-(4-(methylsulfonyl)benzyl)aniline (5ac)
4-((methyl(phenyl)amino)methyl)benzonitrile (5ad)
ethyl 4-((methyl(phenyl)amino)methyl)benzoate (5ae)
(4-((methyl(phenyl)amino)methyl)phenyl)(phenyl)methanone  (5af)
N-(3-methoxybenzyl)-N-methylaniline (5ag)
N-(4-fluorobenzyl)-N-methylaniline (5ah)
N-[[1,1'-biphenyl]-4-ylmethyl]-N-methylaniline (5ai)
N-benzyl-N-methylaniline (5aj)
N-methyl-N-(naphthalen-2-ylmethyl)aniline (5ak)
N-methyl-N-(naphthalen-1-ylmethyl)aniline (5al)
N-methyl-N-(quinolin-8-ylmethyl)aniline (5am)
N-methyl-N-(pyridin-2-ylmethyl)aniline (5an)
N-methyl-N-(pyridin-3-ylmethyl)aniline (5ao)
N-methyl-N-(pyridin-4-ylmethyl)aniline (5ap)
tert-butyl 2-(4-acetylphenyl)pyrrolidine-1-carboxylate (5ma)
1-(4-(tetrahydrofuran-2-yl)phenyl)ethanone (5na)
(8R,9S,13S,14S)-13-methyl-3-((methyl(phenyl)amino)methyl)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (5aq)
7-((methyl(phenyl)amino)methyl)-2-phenyl-4H-chromen-4-one (5ar)
2-((methyl(phenyl)amino)methyl)cyclohexan-1-ol (7ag)
N-methyl-O-(2-methylenecyclohexyl)-N-phenylhydroxylamine (8ag)
N-methyl-O-(4-methylenetetrahydro-2H-pyran-3-yl)-N-phenylhydroxylamine (8an)
4-bromo-N-(cyclohex-1-en-1-ylmethyl)-N-methylaniline(9ag)