

Rhodium(III)-catalyzed directed amidation of unactivated C(sp³)-H bond to afford 1,2-amino alcohol derivatives

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General methods

Dried solvent, such as DCM, DCE, MeOH and THF were purchased from domestic corporations and used without purification. $[\text{RhCp}^*\text{Cl}_2]_2$ was purchased from TCI, AgSbF_6 , AgNtf_2 , AgOAc and AgOtf were purchased from Alfa. Analytical thin layer chromatography (TLC) plates, preparative TLC and the silica gel for column chromatography were phased from Qingdao Haiyang Chemical and Special Silica Gel Co, Ltd.

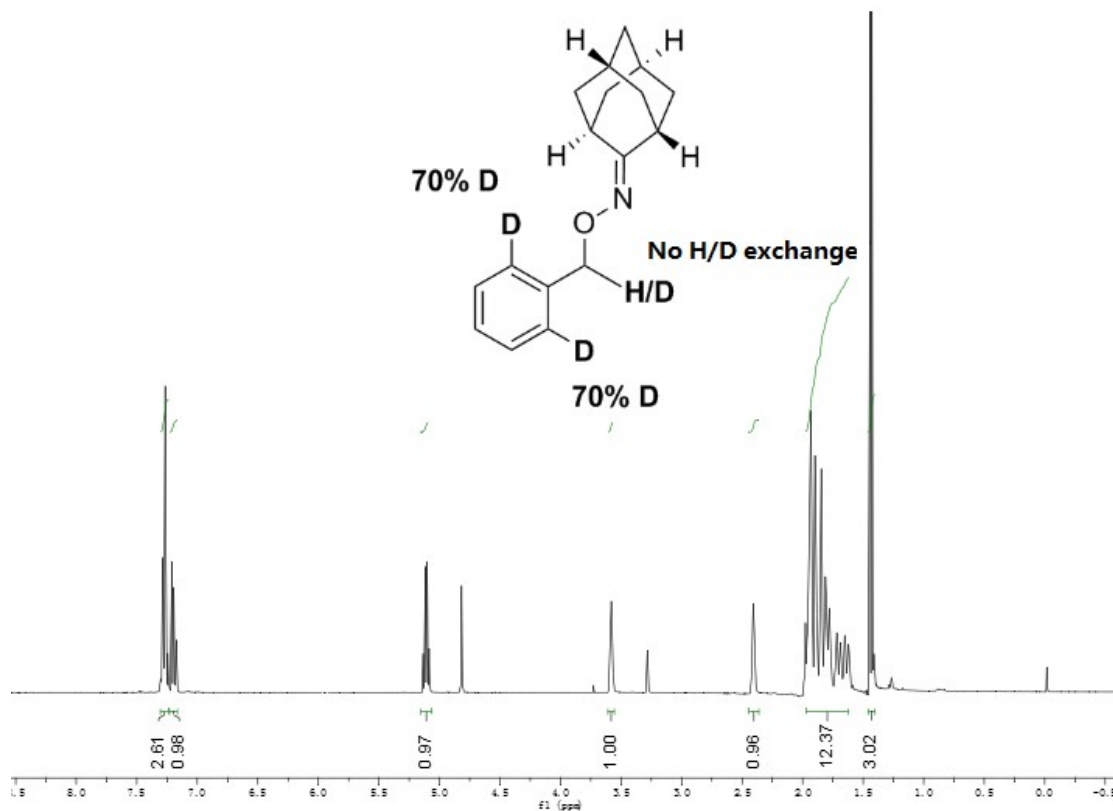
High-resolution LC-MS was carried out by Agilent LC/MSD TOF using a column of Agilent ZORBAX SB-C18 (rapid resolution, 3.5 μm , 2.1 \times 30 mm) at a flow of 0.40 mL/min. The solvent was MeOH/water (75:25 (v/v)), containing 5 mmol/L ammonium formate. The ion source is electrospray ionization (ESI).

Proton nuclear magnetic resonance (^1H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy were performed on Bruker Advance 400M NMR spectrometers. Chemical shifts of ^1H NMR spectra are reported as in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-*d* (δ = 7.260, singlet) and $\text{DMSO-}d_6$ (δ = 2.500, quintet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); m (multiplets), etc. The number of protons (n) for a given resonance is indicated by nH. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-*d* (δ = 77.230, triplet) and $\text{DMSO-}d_6$ (δ = 39.510, septet).

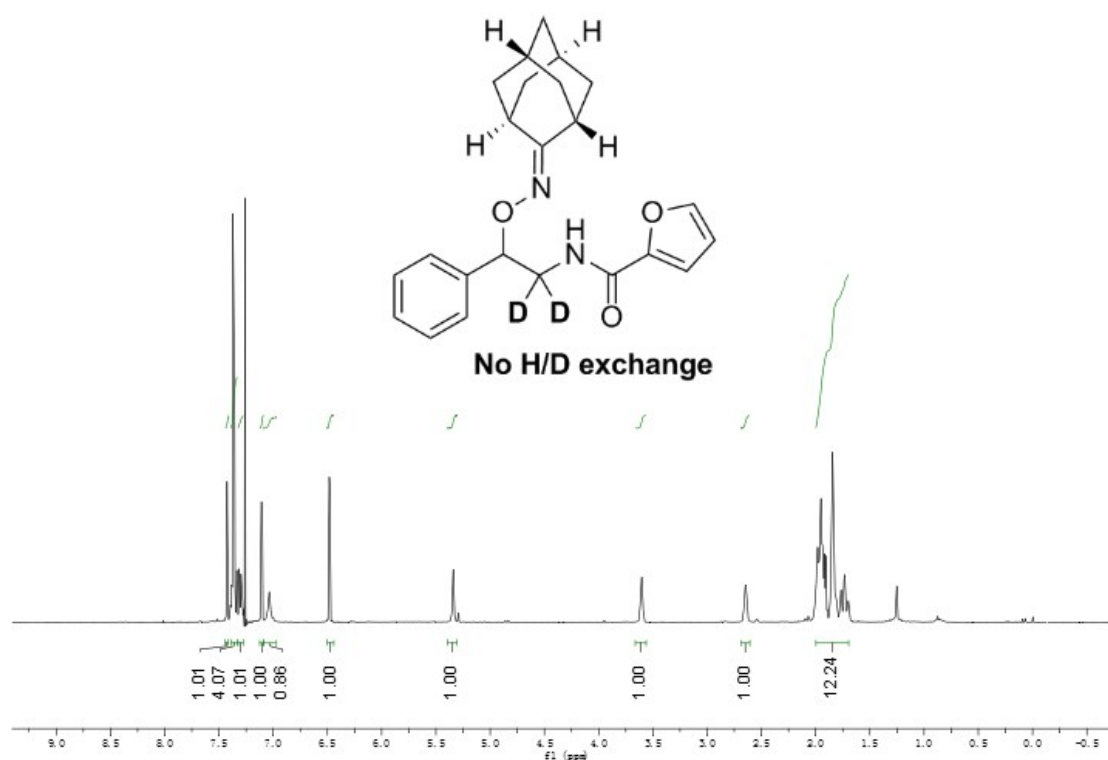
3-aryl-1,4,2-dioxazol-5-one, 3-(furan-2-yl)-5,5-dimethyl-1,4,2-dioxazole, AgOPiv and furan-2-carbonyl azide were synthesized according the previous literatures.¹⁻⁴

H/D exchange experiment

1) A mixture of $[\text{RhCp}^*\text{Cl}_2]_2$ (5.0 mol%), AgSbF_6 (20 mol%), AgOPiv (40 mol%) and ketoxime **1s** (0.5 mmol) in 2.0 mL DCE and 0.5 mL $[\text{D}_4]\text{MeOH}$ was heated to 80°C , and stirred overnight. Then the reaction mixture was cooled to room temperature and filtered, the filtrate was concentrated and the residue was purified with flash column chromatography. No H/D exchange at CH_3 was detected, and 70% deuteration on phenyl C-H was detected.

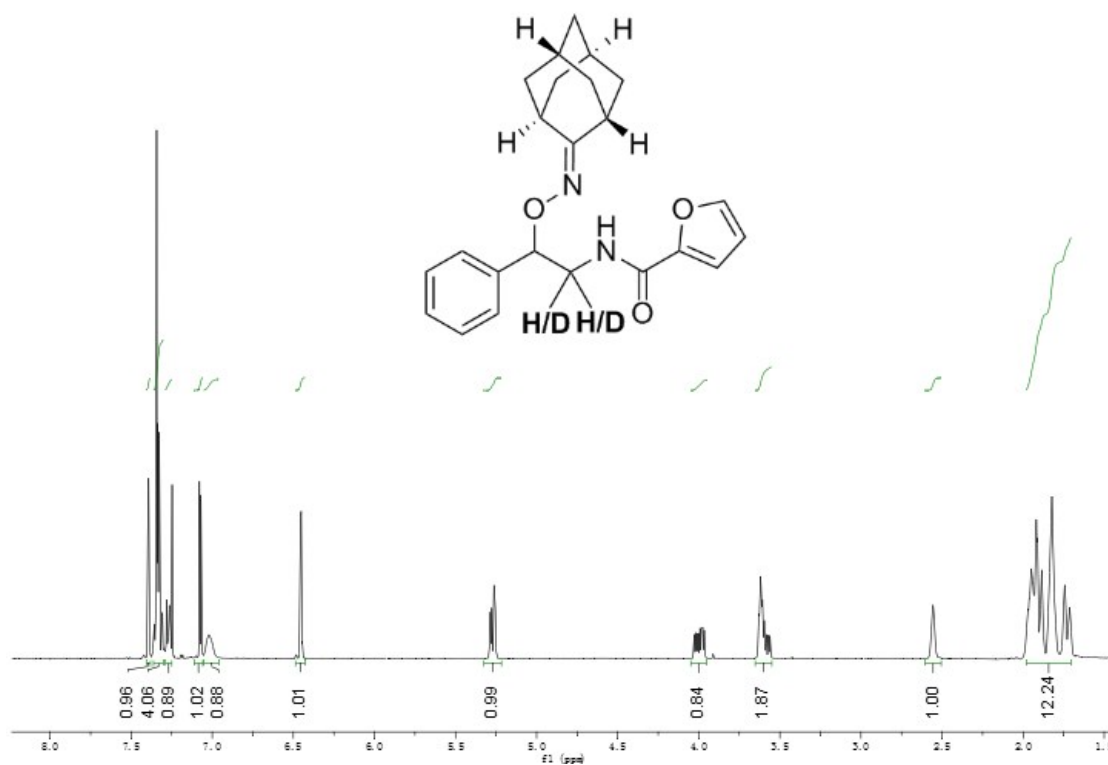


2) A mixture of [RhCp*Cl₂]₂ (5.0 mol%), AgSbF₆ (20 mol%), AgOPiv (40 mol%), ketoxime **1s-d₃** (0.5 mmol) and 3-(furan-2-yl)-1,4,2-dioxazol-5-one in 2.0 mL DCE was heated to 80°C, and stirred overnight. Then the reaction mixture was cooled to room temperature and filtered, the filtrate was concentrated and the residue was purified with flash column chromatography. No H/D exchange.

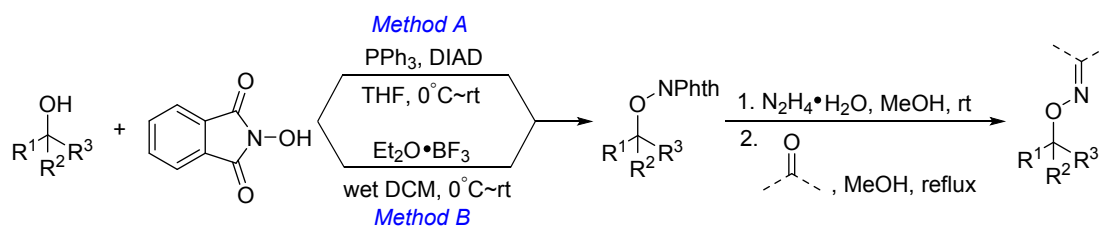


KIE experiment

A mixture of $[\text{RhCp}^*\text{Cl}_2]_2$ (5.0 mol%), AgSbF_6 (20 mol%), AgOPiv (40 mol%), ketoxime **1s**, **1s-d₃** (0.5 mmol) and 3-(furan-2-yl)-1,4,2-dioxazol-5-one in 2.0 mL DCE was heated to 80°C, and stirred overnight. Then the reaction mixture was cooled to room temperature and filtered, the filtrate was concentrated and the residue was purified with flash column chromatography. KIE value ($k_H/k_D = 5.2$) was determined by H NMR analysis.



Preparation of oximes from alcohol



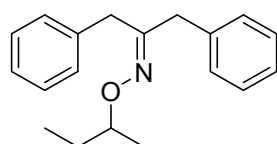
General procedure for synthesis of oximes:

1) **Method A:** The mixture of secondary alcohol (25 mmol), *N*-hydroxyphthalimide (30 mmol) and PPh_3 (30 mmol) in THF (50 mL) was cooled to $0^\circ C$, then DIAD (30 mmol) was added. The reaction mixture was stirred at room temperature for 5h. Solvent was removed in *vacuo*, and the residue was purified with flash column chromatography to afford the *PhthN* protected secondary alcohol.

Method B: The mixture of tertiary alcohol (25 mmol) and *N*-hydroxyphthalimide (50 mmol) in wet DCM (100 mL) was cooled to $0^\circ C$, then $Et_2O \cdot BF_3$ (25 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 2h, then sat. Na_2CO_3 solution was added. The mixture was extracted by EA, Solvent was removed in *vacuo*, and the residue was purified with flash column chromatography to afford the *PhthN* protected tertiary alcohol.

2) The *PhthN* protected alcohol (6 mmol) was dissolved in MeOH (30 mL), then hydrazine hydrate (360 μL) was added. The reaction mixture was stirred at room temperature for 1.5h, then ketone (6 mmol) was added, and the mixture was heat to reflux for 1.5h. Solvent was removed in *vacuo*, and the residue was purified with flash column chromatography to afford the oxime.

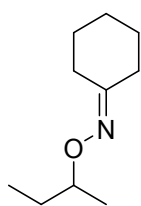
1,3-diphenylpropan-2-one O-(sec-butyl) oxime (1a)



Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). 1H NMR (400 MHz, DMSO- d_6) δ 7.37 – 7.08 (m, 10H), 4.17 – 4.10 (m, 1H), 3.48 (q, $J = 13.8$ Hz, 2H), 3.38 (s, 2H), 1.69 – 1.57 (m, 1H), 1.57 – 1.46 (m, 1H), 1.19 (d, $J = 6.3$ Hz, 3H), 0.87 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.1, 137.4,

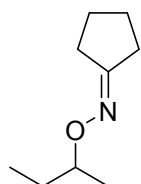
137.1, 129.4, 129.37, 129.3, 128.7, 128.6, 126.8, 126.4, 80.2, 39.9, 33.2, 28.7, 19.5, 10.0. HRMS (ESI): m/z ($M + H^+$) calcd for $C_{29}H_{24}ON$, 282.1852, found: 282.1846.

cyclohexanone O-(sec-butyl) oxime (1b)



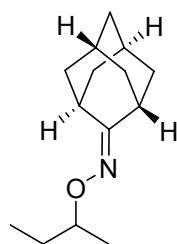
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.10 – 4.02 (m, 1H), 2.49 – 2.43 (m, 2H), 2.22 – 2.19 (m, 2H), 1.72 – 1.42 (m, 8H), 1.19 (d, $J = 6.3$ Hz, 3H), 0.91 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 159.8, 79.4, 32.5, 28.6, 27.3, 26.1, 26.0, 25.5, 19.3, 9.8. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{10}\text{H}_{20}\text{ON}$, 170.1539, found: 170.1536.

cyclopentanone O-(sec-butyl) oxime (1c)



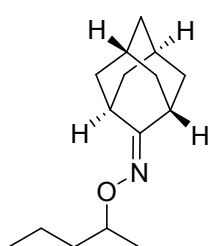
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.08 – 3.99 (m, 1H), 2.39 – 2.31 (m, 4H), 1.74 – 1.68 (m, 4H), 1.67 – 1.57 (m, 1H), 1.51 – 1.40 (m, 1H), 1.17 (d, $J = 6.3$ Hz, 3H), 0.88 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.7, 79.8, 31.1, 28.7, 27.8, 25.3, 24.8, 19.5, 9.8. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_9\text{H}_{18}\text{ON}$, 156.1383, found: 156.1382.

(1r,3r,5R,7S)-adamantan-2-one O-(sec-butyl) oxime (1d)



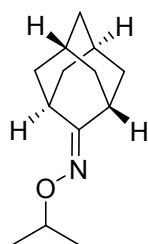
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.10 – 4.00 (m, 1H), 3.50 (s, 1H), 2.54 (s, 1H), 1.98 – 1.75 (m, 12H), 1.69 – 1.57 (m, 1H), 1.53 – 1.41 (m, 1H), 1.17 (d, $J = 6.3$ Hz, 3H), 0.89 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.5, 79.1, 39.3, 39.2, 37.8, 37.7, 36.7, 36.5, 29.8, 28.6, 28.1, 19.3, 9.7. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{14}\text{H}_{24}\text{ON}$, 222.1852, found: 222.1849.

(1r,3r,5R,7S)-adamantan-2-one O-pentan-2-yl oxime (1e)



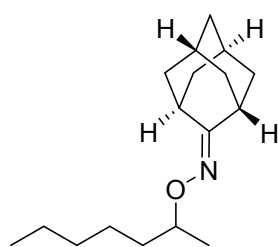
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.20 – 4.11 (m, 1H), 3.50 (s, 1H), 2.60 (s, 1H), 2.04 – 1.76 (m, 12H), 1.71 – 1.56 (m, 1H), 1.50 – 1.29 (m, 3H), 1.19 (d, $J = 6.2$ Hz, 3H), 0.91 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.3, 77.8, 39.2 (X2), 38.1, 37.8, 37.7, 36.7, 36.5, 29.8, 28.1, 19.9, 18.8, 14.4. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{15}\text{H}_{26}\text{ON}$, 236.2009, found: 236.2005.

(1r,3r,5R,7S)-adamantan-2-one O-isopropyl oxime (1f)



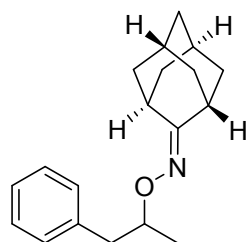
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.25 (hept, $J = 6.2$ Hz, 1H), 3.49 (s, 1H), 2.54 (s, 1H), 2.01 – 1.76 (m, 12H), 1.20 (d, $J = 6.2$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.7, 74.2, 39.3, 37.8, 36.7, 36.5, 29.8, 28.1, 21.9. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{13}\text{H}_{22}\text{ON}$, 208.1696, found: 208.1694.

(1r,3r,5R,7S)-adamantan-2-one O-heptan-2-yl oxime (1g)



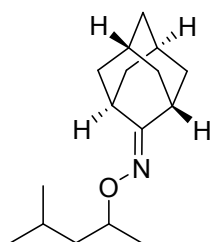
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.09 (h, $J = 6.2$ Hz, 1H), 3.49 (s, 1H), 2.54 (s, 1H), 1.98 – 1.75 (m, 12H), 1.64 – 1.56 (m, 1H), 1.44 – 1.25 (m, 7H), 1.18 (d, $J = 6.3$ Hz, 3H), 0.87 (t, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.2, 78.0, 39.2 (X2), 37.7 (X2), 36.7, 36.4, 35.8, 32.1, 29.7, 28.0, 25.2, 22.8, 19.8, 14.2. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{17}\text{H}_{30}\text{ON}$, 264.2322, found: 264.2323.

(1r,3r,5R,7S)-adamantan-2-one O-(1-phenylpropan-2-yl) oxime (1h)



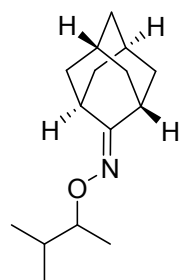
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.29 – 7.25 (m, 2H), 7.24 – 7.17 (m, 3H), 4.44 – 4.35 (m, 1H), 3.49 (s, 1H), 3.02 (dd, $J = 13.6, 5.7$ Hz, 1H), 2.76 (dd, $J = 13.6, 6.8$ Hz, 1H), 2.59 (s, 1H), 2.00 – 1.75 (m, 12H), 1.19 (d, $J = 6.3$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.7, 139.0, 129.8, 128.2, 126.1, 78.6, 42.1, 39.3, 39.2, 37.7, 37.7, 36.7, 36.5, 29.9, 28.0, 19.2. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{19}\text{H}_{26}\text{ON}$, 284.2009, found: 284.2006.

(1r,3r,5R,7S)-adamantan-2-one O-(4-methylpentan-2-yl) oxime (1i)



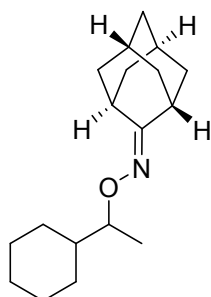
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.19 – 4.10 (m, 1H), 3.46 (s, 1H), 2.51 (s, 1H), 1.96 – 1.68 (m, 13H), 1.56 – 1.46 (m, 1H), 1.25 – 1.19 (m, 1H), 1.18 – 1.13 (m, 3H), 0.89 – 0.84 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.6, 76.3, 45.0, 39.1 (X2), 37.6, 37.5, 36.6, 36.3, 29.6, 28.0, 24.9, 23.0, 22.9, 20.4. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{16}\text{H}_{28}\text{ON}$, 250.2165, found: 250.2167.

(1r,3r,5R,7S)-adamantan-2-one O-(3-methylbutan-2-yl) oxime (1j)



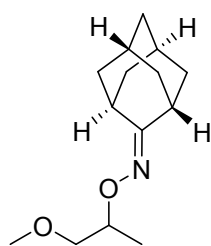
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.97 – 3.90 (m, 1H), 3.51 (s, 1H), 2.54 (s, 1H), 1.97 – 1.77 (m, 13H), 1.10 (d, $J = 6.4$ Hz, 3H), 0.89 (d, $J = 6.9$ Hz, 3H), 0.85 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.3, 82.4, 39.3, 39.1, 37.9, 37.7, 36.7, 36.5, 32.1, 29.8, 28.1, 28.1, 18.8, 17.3, 15.7. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{15}\text{H}_{26}\text{ON}$, 236.2009, found: 236.2008.

(1r,3r,5R,7S)-adamantan-2-one O-(1-cyclohexylethyl) oxime (1k)



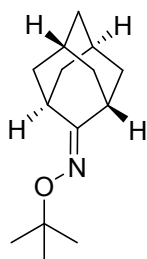
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.88 (p, $J = 6.2$ Hz, 1H), 3.48 (s, 1H), 2.51 (s, 1H), 1.97 – 1.59 (m, 17H), 1.55 – 1.45 (m, 1H), 1.25 – 1.07 (m, 6H), 1.05 – 0.90 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.1, 81.9, 42.5, 39.2, 39.1, 37.8, 37.6, 36.7, 36.4, 29.7, 29.2, 28.1 (X2), 28.0, 26.9, 26.5, 16.5. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{18}\text{H}_{30}\text{ON}$, 276.2322, found: 276.2321.

(1r,3r,5R,7S)-adamantan-2-one O-(1-methoxypropan-2-yl) oxime (1l)



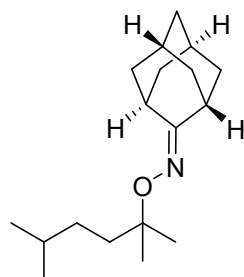
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.32 – 4.24 (m, 1H), 3.50 (dd, $J = 10.3, 5.3$ Hz, 2H), 3.40 (dd, $J = 10.3, 4.8$ Hz, 1H), 3.36 (s, 3H), 2.54 (s, 1H), 1.98 – 1.91 (m, 4H), 1.89 – 1.75 (m, 8H), 1.21 (d, $J = 6.5$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.3, 77.0, 75.4, 59.4, 39.2, 39.1, 37.8, 37.7, 36.7, 36.4, 29.8, 28.0, 16.9. **HRMS** (ESI): m/z ($M + \text{H}^+$) calcd for $\text{C}_{14}\text{H}_{24}\text{O}_2\text{N}$, 238.1802, found: 238.1799.

(1r,3r,5R,7S)-adamantan-2-one O-(tert-butyl) oxime (1m)



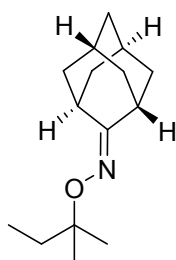
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.52 (s, 1H), 2.57 (s, 1H), 1.98 – 1.74 (m, 12H), 1.26 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.9, 76.7, 39.2, 37.7, 36.8, 36.5, 29.6, 28.1, 27.7. **HRMS** (ESI): m/z ($M + \text{H}^+$) calcd for $\text{C}_{14}\text{H}_{24}\text{ON}$, 222.1852, found: 222.1851.

(1r,3r,5R,7S)-adamantan-2-one O-(2,5-dimethylhexan-2-yl) oxime (1n)



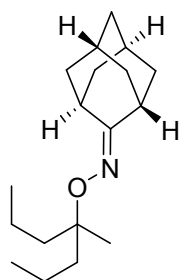
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.51 (s, 1H), 2.56 (s, 1H), 1.98 – 1.76 (m, 12H), 1.57 – 1.52 (m, 2H), 1.51 – 1.44 (m, 1H), 1.22 (s, 6H), 1.20 – 1.13 (m, 2H), 0.87 (d, $J = 6.6$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.0, 78.8, 39.3, 38.1, 37.8, 36.8, 36.6, 33.1, 29.7, 28.7, 28.2, 25.8, 23.0. **HRMS** (ESI): m/z ($M + \text{H}^+$) calcd for $\text{C}_{18}\text{H}_{32}\text{ON}$, 278.2478, found: 278.2476.

(1r,3r,5R,7S)-adamantan-2-one O-(tert-pentyl) oxime (1o)



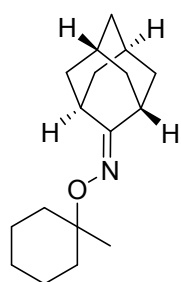
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.53 (s, 1H), 2.58 (s, 1H), 1.99 – 1.75 (m, 12H), 1.60 (q, $J = 7.5$ Hz, 2H), 1.22 (s, 6H), 0.84 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.8, 78.7, 39.3, 37.8, 36.8, 36.6, 32.8, 29.6, 28.2, 25.3, 8.4. **HRMS** (ESI): m/z ($M + \text{H}^+$) calcd for $\text{C}_{15}\text{H}_{26}\text{ON}$, 236.2009, found: 236.2006.

(1r,3r,5R,7S)-adamantan-2-one O-(4-methylheptan-4-yl) oxime (1p)



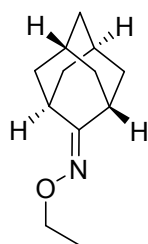
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.52 (s, 1H), 2.56 (s, 1H), 1.97 – 1.74 (m, 12H), 1.57 – 1.50 (m, 4H), 1.35 – 1.24 (m, 4H), 1.18 (s, 3H), 0.89 (t, $J = 7.3$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.7, 80.7, 40.7, 39.3, 37.9, 36.8, 36.6, 29.7, 28.2, 23.4, 17.1, 15.0. **HRMS** (ESI): m/z ($M + \text{H}^+$) calcd for $\text{C}_{18}\text{H}_{32}\text{ON}$, 278.2478, found: 278.2475.

(1r,3r,5R,7S)-adamantan-2-one O-(1-methylcyclohexyl) oxime (1q)



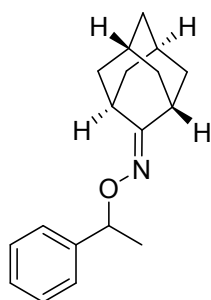
White solid, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.58 (s, 1H), 2.64 (s, 1H), 2.02 – 1.79 (m, 14H), 1.61 – 1.23 (m, 11H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.8, 39.2, 37.9, 36.6, 36.3, 36.2, 29.8, 27.9, 25.8, 25.7, 22.3. **HRMS** (ESI): m/z ($M + \text{H}^+$) calcd for $\text{C}_{17}\text{H}_{28}\text{ON}$, 262.2165, found: 262.2164.

(1r,3r,5R,7S)-adamantan-2-one O-ethyl oxime (1r)



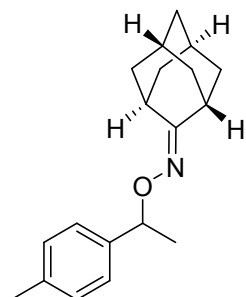
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 3.97 (q, $J = 7.0$ Hz, 2H), 3.42 (s, 1H), 2.47 (s, 1H), 2.03 – 1.70 (m, 12H), 1.16 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.8, 68.2, 38.9, 37.4, 36.4, 36.1, 29.3, 27.7, 14.4. **HRMS** (ESI): m/z ($M + \text{H}^+$) calcd for $\text{C}_{12}\text{H}_{20}\text{ON}$, 194.1539, found: 194.1541.

(1r,3r,5R,7S)-adamantan-2-one O-(1-phenylethyl) oxime (1s)



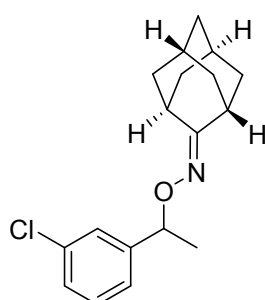
Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 – 7.30 (m, 4H), 7.27 – 7.21 (m, 1H), 5.22 (q, $J = 6.6$ Hz, 1H), 3.63 (s, 1H), 2.53 (s, 1H), 2.02 – 1.83 (m, 10H), 1.75 – 1.68 (m, 2H), 1.51 (d, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.5, 144.4, 128.3, 127.2, 126.2, 79.9, 39.2 (X2), 37.8, 37.7, 36.6, 36.3, 30.0, 28.0, 22.6. **HRMS** (ESI): m/z ($M + \text{H}^+$) calcd for $\text{C}_{18}\text{H}_{24}\text{ON}$, 270.1852, found: 270.1853.

(1r,3r,5R,7S)-adamantan-2-one O-(1-(p-tolyl)ethyl) oxime (1t)



White solid, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.22 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 7.8$ Hz, 2H), 5.18 (q, $J = 6.6$ Hz, 1H), 3.62 (s, 1H), 2.53 (s, 1H), 2.34 (s, 3H), 2.00 – 1.70 (m, 12H), 1.50 (d, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.8, 140.9, 129.1, 126.34, 80.1, 39.2, 39.2, 37.9, 36.6, 36.2, 30.2, 27.9, 27.9, 22.4, 21.3. **HRMS** (ESI): m/z ($M + \text{H}^+$) calcd for $\text{C}_{19}\text{H}_{26}\text{ON}$, 284.2009, found: 284.2004.

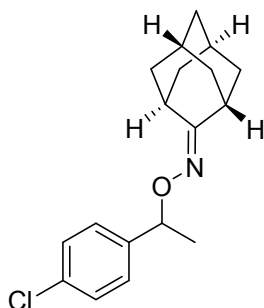
(1r,3r,5R,7S)-adamantan-2-one O-(1-(3-chlorophenyl)ethyl) oxime (1u)



White solid, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.29 (t, $J = 1.7$ Hz, 1H), 7.27 – 7.15 (m, 3H), 5.17 (q, $J = 6.6$ Hz, 1H), 3.62 (s, 1H), 2.50 (s, 1H), 2.00 – 1.69 (m, 12H), 1.48 (d, $J = 6.7$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.3, 146.7, 134.3, 129.7, 127.3, 126.4, 124.4.

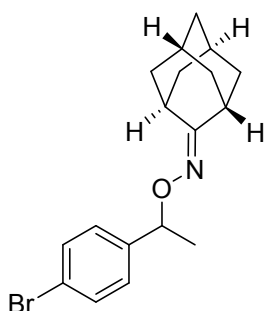
79.3, 39.3, 39.1, 37.8, 37.8, 36.6, 36.3, 30.1, 28.0, 22.6. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{18}H_{23}ONCl$, 304.1463, found: 304.1460.

(1r,3r,5R,7S)-adamantan-2-one O-(1-(4-chlorophenyl)ethyl) oxime (1v)



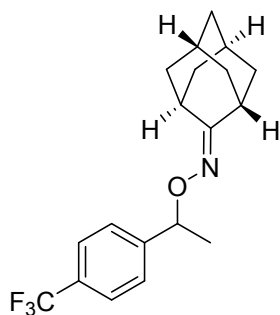
White solid, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). 1H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 4H), 5.15 (q, $J = 6.6$ Hz, 1H), 3.60 (s, 1H), 2.48 (s, 1H), 2.00 – 1.80 (m, 10H), 1.75 – 1.67 (m, 2H), 1.47 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 143.1, 132.8, 128.5, 127.6, 79.2, 39.2, 39.0, 37.8, 37.7, 36.6, 36.3, 29.9, 27.9, 22.6. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{18}H_{23}ONCl$, 304.1463, found: 304.1461.

(1r,3r,5R,7S)-adamantan-2-one O-(1-(4-bromophenyl)ethyl) oxime (1w)



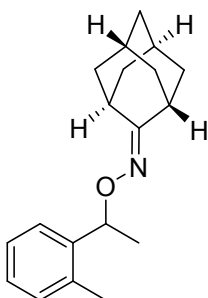
White solid, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). 1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, $J = 8.4$ Hz, 2H), 7.18 (d, $J = 8.4$ Hz, 2H), 5.16 (q, $J = 6.6$ Hz, 1H), 3.59 (s, 1H), 2.51 (s, 1H), 2.01 – 1.68 (m, 12H), 1.47 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 143.5, 131.5, 128.1, 121.1, 79.5, 39.3, 39.1, 37.9, 37.8, 36.6, 36.3, 30.1, 28.0, 27.9, 22.5. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{18}H_{23}ONBr$, 348.0958, found: 348.0951.

(1r,3r,5R,7S)-adamantan-2-one O-(1-(4-(trifluoromethyl)phenyl)ethyl) oxime (1x)



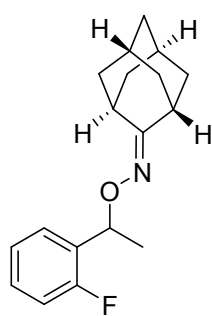
White solid, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). 1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 8.1$ Hz, 2H), 5.25 (q, $J = 6.6$ Hz, 1H), 3.63 (s, 1H), 2.49 (s, 1H), 2.02 – 1.84 (m, 10H), 1.78 – 1.68 (m, 2H), 1.50 (d, $J = 6.7$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.99, 148.75, 129.4 (q, $J = 32.3$ Hz), 126.43, 125.4 (q, $J = 3.8$ Hz), 124.5 (q, $J = 272.9$ Hz), 79.38, 39.24, 39.07, 37.88, 37.76, 36.59, 36.29, 30.02, 27.95, 22.60. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{19}H_{23}ONF_3$, 338.1726, found: 338.1721.

(1r,3r,5R,7S)-adamantan-2-one O-(1-(o-tolyl)ethyl) oxime (1y)



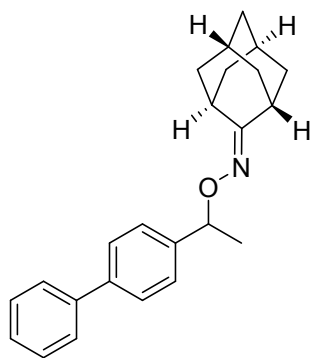
White solid, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). 1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.32 (m, 1H), 7.21 – 7.11 (m, 3H), 5.41 (q, $J = 6.5$ Hz, 1H), 3.64 (s, 1H), 2.53 (s, 1H), 2.37 (s, 3H), 2.02 – 1.72 (m, 12H), 1.49 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 141.3, 135.5, 130.7, 127.4, 126.1, 125.6, 77.7, 39.3, 38.0, 38.0, 36.5, 36.1, 30.5, 27.8, 27.8, 21.1, 19.3. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{19}H_{26}ON$, 284.2009, found: 284.2002.

(1r,3r,5R,7S)-adamantan-2-one O-(1-(2-fluorophenyl)ethyl) oxime (1z)



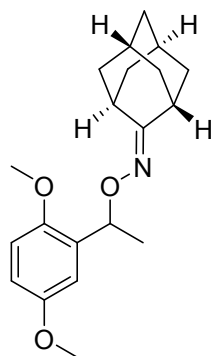
White solid, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.34 (td, $J = 7.5, 1.8$ Hz, 1H), 7.24 – 7.18 (m, 1H), 7.11 (td, $J = 7.5, 1.1$ Hz, 1H), 7.00 (ddd, $J = 10.4, 8.1, 1.2$ Hz, 1H), 5.53 (q, $J = 6.6$ Hz, 1H), 3.64 (s, 1H), 2.55 (s, 1H), 2.03 – 1.83 (m, 10H), 1.73 (dd, $J = 14.0, 13.5$ Hz, 2H), 1.52 (d, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.1, 160.3 (d, $J = 219.1$ Hz), 131.5 (d, $J = 13.8$ Hz), 128.5 (d, $J = 8.1$ Hz), 127.5 (d, $J = 4.6$ Hz), 124.1 (d, $J = 3.3$ Hz), 115.4 (d, $J = 21.8$ Hz), 74.3 (d, $J = 2.0$ Hz), 39.3, 39.1, 38.0, 37.8, 36.7, 36.3, 30.1, 28.0, 21.5. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{18}\text{H}_{23}\text{ONF}$, 288.1758, found: 288.1750.

(1r,3r,5R,7S)-adamantan-2-one O-(1-([1,1'-biphenyl]-4-yl)ethyl) oxime (1aa)



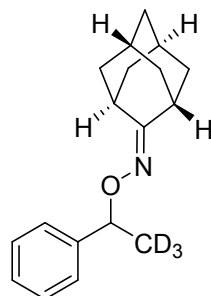
White solid, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.59 (ddt, $J = 8.4, 3.8, 1.6$ Hz, 4H), 7.46 – 7.38 (m, 4H), 7.36 – 7.31 (m, 1H), 5.27 (q, $J = 6.6$ Hz, 1H), 3.66 (s, 1H), 2.55 (s, 1H), 2.03 – 1.72 (m, 12H), 1.56 (d, $J = 6.6$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.8, 143.5, 141.3, 140.2, 128.9, 127.3, 127.2, 126.7, 79.7, 39.2, 39.2, 37.9, 37.8, 36.7, 36.4, 30.1, 28.0, 22.6. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{24}\text{H}_{28}\text{ON}$, 346.2165, found: 346.2163.

(1r,3r,5R,7S)-adamantan-2-one O-(1-(2,5-dimethoxyphenyl)ethyl) oxime (1ab)



White solid, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.88 (d, $J = 3.0$ Hz, 1H), 6.77 (d, $J = 8.8$ Hz, 1H), 6.72 (dd, $J = 8.8, 3.0$ Hz, 1H), 5.55 (q, $J = 6.5$ Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.68 (s, 1H), 2.56 (s, 1H), 2.00 – 1.72 (m, 12H), 1.44 (d, $J = 6.5$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.2, 153.9, 150.6, 134.4, 112.6, 112.1, 111.5, 74.7, 56.1, 55.9, 39.3, 39.1, 37.9, 37.8, 36.7, 36.3, 30.0, 28.0, 28.0, 21.5. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{20}\text{H}_{28}\text{O}_3\text{N}$, 330.2064, found: 330.2062.

(1r,3r,5R,7S)-adamantan-2-one O-(1-phenylethyl-2,2,2- d_3) oxime (1s- d_3)

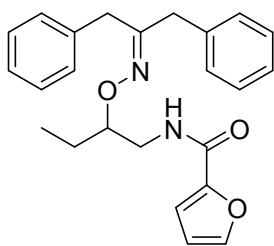


Colorless oil, $R_f = 0.5$ (EtOAc/Petroleum ether = 1:10). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.33 – 7.29 (m, 4H), 7.26 – 7.21 (m, 1H), 5.19 (s, 1H), 3.62 (s, 1H), 2.51 (s, 1H), 1.99 – 1.83 (m, 10H), 1.75 – 1.67 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.1, 144.2, 128.4, 127.3, 126.3, 79.9, 39.2, 39.1, 37.9, 37.8, 36.7, 36.3, 30.1, 28.0 (X2). **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{18}\text{H}_{21}\text{D}_3\text{ON}$, 273.2041, found: 273.2037.

General procedure for Rhodium catalyzed $\text{C}(\text{sp}^3)\text{-H}$ amidation of ketoximes to afford 1,2 amino

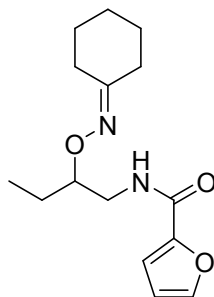
alcohol derivatives: a mixture of [RhCp*Cl₂]₂ (5.0 mol%), AgSbF₆ (20 mol%), AgOPiv (40 mol%), ketoxime (0.5 mmol) and 1,4,2-dioxazol-5-one (0.6 mmol) in 2.0 mL DCE was heated to 80°C, and stirred overnight. Then the reaction mixture was cooled to room temperature and filtered, the filtrate was concentrated and the residue was purified with flash column chromatography to afford 1,2 amino alcohol derivatives.

***N*-2-(((1,3-diphenylpropan-2-ylidene)amino)oxy)butyl)furan-2-carboxamide (3aa)**



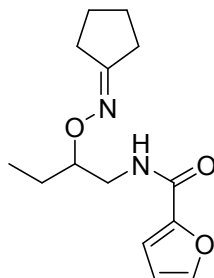
Colorless oil (105 mg, 54%), *R_f* = 0.4 (EtOAc/Petroleum ether = 1:3). ¹H NMR (400 MHz, CDCl₃) δ 7.36 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.31 – 7.16 (m, 8H), 7.14 – 7.11 (m, 2H), 7.09 (dd, *J* = 3.4, 0.8 Hz, 1H), 6.98 (s, 1H), 6.47 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.27 (tdd, *J* = 7.4, 5.9, 3.0 Hz, 1H), 3.87 (ddd, *J* = 14.1, 6.3, 3.0 Hz, 1H), 3.60 (s, 2H), 3.53 (ddd, *J* = 14.1, 7.5, 4.7 Hz, 1H), 3.46 (s, 2H), 1.84 – 1.59 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 158.7, 158.6, 148.3, 143.9, 136.8, 136.5, 129.2, 129.2, 128.8, 128.7, 127.0, 126.6, 114.2, 112.2, 82.7, 42.8, 40.0, 33.3, 24.9, 10.1. HRMS (ESI): *m/z* (*M* + *H*⁺) calcd for C₂₄H₂₇O₃N₂, 391.2016, found: 391.2010.

***N*-2-((cyclohexylideneamino)oxy)butyl)furan-2-carboxamide (3ba)**



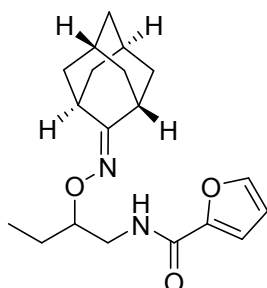
Colorless oil (90 mg, 65%), *R_f* = 0.4 (EtOAc/Petroleum ether = 1:3). ¹H NMR (400 MHz, CDCl₃) δ 7.40 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.09 (br s, 1H), 7.06 (dd, *J* = 3.5, 0.7 Hz, 1H), 6.47 – 6.45 (m, 1H), 4.12 – 4.06 (m, 1H), 3.77 (ddd, *J* = 14.1, 6.1, 2.9 Hz, 1H), 3.44 (ddd, *J* = 13.9, 7.4, 4.4 Hz, 1H), 2.48 (t, *J* = 6.1 Hz, 2H), 2.23 – 2.19 (m, 2H), 1.70 – 1.53 (m, 8H), 0.95 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 161.6, 158.5, 148.4, 143.9, 113.9, 112.2, 82.0, 42.9, 32.4, 27.2, 25.9, 25.9, 25.5, 24.8, 10.0. HRMS (ESI): *m/z* (*M* + *H*⁺) calcd for C₁₅H₂₃O₃N₂, 279.1703, found: 279.1698.

***N*-2-((cyclopentylideneamino)oxy)butyl)furan-2-carboxamide (3ca)**



Colorless oil (102 mg, 77%), *R_f* = 0.4 (EtOAc/Petroleum ether = 1:3). ¹H NMR (400 MHz, CDCl₃) δ 7.39 (dd, *J* = 2.5, 0.8 Hz, 1H), 7.03 (dd, *J* = 3.4, 0.9 Hz, 1H), 6.95 (br s, 1H), 6.44 – 6.42 (m, 1H), 4.08 – 4.01 (m, 1H), 3.77 – 3.70 (m, 1H), 3.47 – 3.39 (m, 1H), 2.41 – 2.30 (m, 4H), 1.74 – 1.49 (m, 6H), 0.92 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 158.5, 148.4, 143.9, 113.9, 112.1, 82.2, 42.6, 31.2, 27.9, 25.2, 24.8, 24.8, 10.0. HRMS (ESI): *m/z* (*M* + *H*⁺) calcd for C₁₄H₂₁O₃N₂, 265.1547, found: 265.1545.

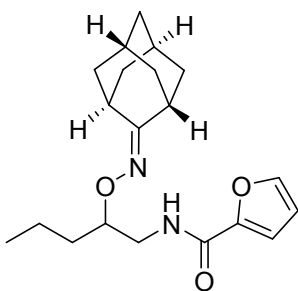
***N*-2-(((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)butyl)furan-2-carboxamide (3da)**



Colorless oil (150 mg, 91%), *R_f* = 0.4 (EtOAc/Petroleum ether = 1:3). ¹H NMR (400 MHz, CDCl₃) δ 7.38 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.08 (s, 1H), 7.05 (dd,

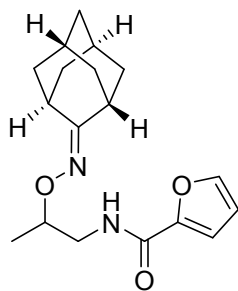
$J = 3.5, 0.8 \text{ Hz}, 1\text{H}$), 6.45 (dd, $J = 3.5, 1.8 \text{ Hz}, 1\text{H}$), 4.10 – 4.03 (m, 1H), 3.80 – 3.74 (m, 1H), 3.52 (s, 1H), 3.46 – 3.39 (m, 1H), 2.54 (s, 1H), 1.98 – 1.75 (m, 12H), 1.71 – 1.51 (m, 2H), 0.95 (t, $J = 7.5 \text{ Hz}, 3\text{H}$). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.7, 158.5, 148.5, 143.8, 113.9, 112.2, 81.6, 42.9, 39.2, 39.1, 37.8, 37.7, 36.6, 36.5, 29.8, 27.9, 24.9, 10.0. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{19}\text{H}_{27}\text{O}_3\text{N}_2$, 331.2016, found: 331.2010.

***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)pentyl)furan-2-carboxamide (4)**



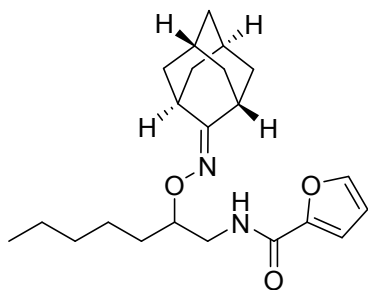
Colorless oil (155 mg, 90%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.39 (dd, $J = 1.7, 0.8 \text{ Hz}, 1\text{H}$), 7.13 (br s, 1H), 7.06 (dd, $J = 3.5, 0.8 \text{ Hz}, 1\text{H}$), 6.46 (dd, $J = 3.5, 1.7 \text{ Hz}, 1\text{H}$), 4.21 – 4.15 (m, 1H), 3.78 (ddd, $J = 14.0, 6.1, 3.0 \text{ Hz}, 1\text{H}$), 3.53 (s, 1H), 3.48 – 3.40 (m, 1H), 2.58 (s, 1H), 2.01 – 1.76 (m, 12H), 1.71 – 1.59 (m, 1H), 1.55 – 1.37 (m, 3H), 0.92 (t, $J = 7.2 \text{ Hz}, 3\text{H}$). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.7, 158.4, 148.4, 143.8, 113.9, 112.1, 80.1, 43.4, 39.2, 39.1, 37.8, 37.7, 36.5 (X2), 33.9, 29.8, 27.9, 18.9, 14.2. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{20}\text{H}_{29}\text{O}_3\text{N}_2$, 345.2173, found: 345.2171.

***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)propyl)furan-2-carboxamide (5)**



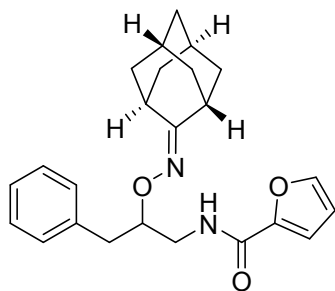
Colorless oil (112 mg, 71%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 (dd, $J = 1.6, 0.7 \text{ Hz}, 1\text{H}$), 7.26 (s, 1H), 7.05 – 7.01 (m, 1H), 6.44 (dd, $J = 3.5, 1.8 \text{ Hz}, 1\text{H}$), 4.30 (dq, $J = 9.6, 6.5, 3.2 \text{ Hz}, 1\text{H}$), 3.75 (ddd, $J = 14.0, 6.5, 3.2 \text{ Hz}, 1\text{H}$), 3.49 (s, 1H), 3.37 (ddd, $J = 14.0, 7.5, 4.6 \text{ Hz}, 1\text{H}$), 2.54 (s, 1H), 1.97 – 1.74 (m, 12H), 1.23 (d, $J = 6.4 \text{ Hz}, 3\text{H}$). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.8, 158.4, 148.3, 143.8, 113.9, 112.1, 76.4, 44.4, 39.1, 39.0, 37.7, 37.6, 36.5, 36.4, 29.7, 27.9, 17.6. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{18}\text{H}_{25}\text{O}_3\text{N}_2$, 317.1860, found: 317.1853.

***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)heptyl)furan-2-carboxamide (6)**



Colorless oil (166 mg, 89%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz,) δ 7.39 (dd, $J = 1.7, 0.7 \text{ Hz}, 1\text{H}$), 7.12 (br s, 1H), 7.06 (dd, $J = 3.5, 0.7 \text{ Hz}, 1\text{H}$), 6.46 (dd, $J = 3.5, 1.8 \text{ Hz}, 1\text{H}$), 4.20 – 4.12 (m, 1H), 3.78 (ddd, $J = 14.0, 6.2, 3.0 \text{ Hz}, 1\text{H}$), 3.53 (s, 1H), 3.43 (ddd, $J = 14.0, 7.5, 4.4 \text{ Hz}, 1\text{H}$), 2.57 (s, 1H), 2.00 – 1.76 (m, 12H), 1.69 – 1.60 (m, 1H), 1.54 – 1.25 (m, 7H), 0.86 (t, $J = 7.0 \text{ Hz}, 3\text{H}$). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.6, 158.4, 148.4, 143.7, 113.8, 112.1, 80.3, 43.3, 39.1, 39.0, 37.7, 37.6, 36.5, 36.4, 31.8, 31.7, 29.7, 27.9, 25.2, 22.6, 14.1. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{22}\text{H}_{23}\text{O}_3\text{N}_2$, 373.2486, found: 373.2485.

***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-3-phenylpropyl)furan-2-carboxamide (7)**

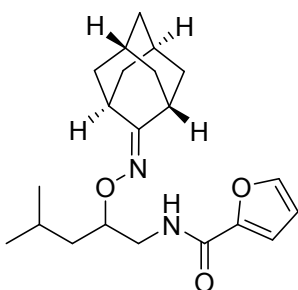


Colorless oil (167 mg, 85%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 (dd, $J = 1.7, 0.8$ Hz, 1H), 7.30 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 7.09 (dd, $J = 3.5, 0.7$ Hz, 1H), 7.07 (s, 1H), 6.48 (dd, $J = 3.5, 1.8$ Hz, 1H), 4.47 (qd, $J = 7.1, 3.2$ Hz, 1H), 3.79 (ddd, $J = 14.0, 5.7, 3.2$ Hz, 1H), 3.56 – 3.45 (m, 2H), 3.04 (dd, $J = 14.1, 6.9$ Hz, 1H), 2.88 (dd, $J = 14.1, 6.1$ Hz, 1H), 2.63 (s, 1H), 2.01 – 1.72 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.2, 158.6, 148.4, 144.0,

137.9, 129.7, 128.5, 126.6, 114.1, 112.2, 81.4, 42.7, 39.2, 39.2, 38.3, 37.8, 37.8, 36.6, 36.4, 30.1, 27.9.

HRMS (ESI): m/z ($M + H^+$) calcd for $\text{C}_{24}\text{H}_{29}\text{O}_3\text{N}_2$, 393.2173, found: 393.2163.

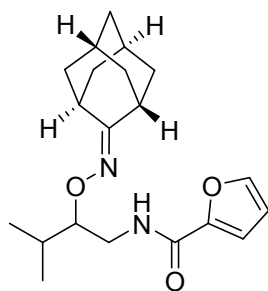
***N*-(2-((((1r,3r,5R,7S)-adamantan-2-ylidene)amino)oxy)-4-methylpentyl)furan-2-carboxamide (8)**



Colorless oil (149 mg, 83%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37 – 7.36 (m, 1H), 7.16 (br s, 1H), 7.03 – 7.01 (m, 1H), 6.43 (ddd, $J = 3.5, 1.6, 0.7$ Hz, 1H), 4.25 – 4.17 (m, 1H), 3.74 (ddd, $J = 14.0, 6.1, 3.0$ Hz, 1H), 3.48 (s, 1H), 3.40 (ddd, $J = 13.9, 7.3, 4.6$ Hz, 1H), 2.53 (s, 1H), 1.98 – 1.71 (m, 13H), 1.56 (ddd, $J = 14.8, 8.6, 6.3$ Hz, 1H), 1.27 (ddd, $J = 13.9, 7.8, 4.9$ Hz, 1H), 0.88 (d, $J = 6.4$ Hz). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.8, 158.4, 148.5, 143.8, 113.8, 112.1, 78.7, 43.8,

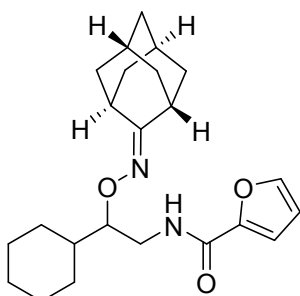
40.6, 39.1, 39.1, 37.7, 37.7, 36.5, 36.4, 29.8, 27.9, 24.9, 23.2, 22.6. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{21}\text{H}_{31}\text{O}_3\text{N}_2$, 359.2329, found: 359.2323.

***N*-(2-((((1r,3r,5R,7S)-adamantan-2-ylidene)amino)oxy)-3-methylbutyl)furan-2-carboxamide (9)**



Colorless oil (139 mg, 81%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 (dd, $J = 1.6, 0.8$ Hz, 1H), 7.13 (s, 1H), 7.01 (dd, $J = 4.4, 0.9$ Hz, 1H), 6.44 – 6.41 (m, 1H), 3.88 – 3.75 (m, 2H), 3.51 (s, 1H), 3.41 (ddd, $J = 13.8, 8.1, 4.2$ Hz, 1H), 2.52 (s, 1H), 1.96 – 1.73 (m, 13H), 0.94 (d, $J = 6.8$ Hz, 3H), 0.91 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.4, 158.4, 148.4, 143.7, 113.7, 112.0, 85.0, 41.1, 39.0, 37.7, 37.6, 36.5, 36.4, 30.0, 29.7, 27.8, 18.6, 18.6. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{20}\text{H}_{29}\text{O}_3\text{N}_2$, 345.2173, found: 345.2170.

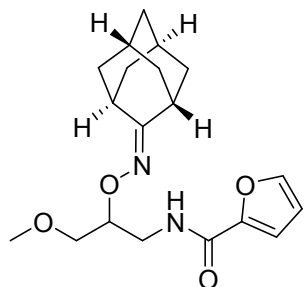
***N*-(2-((((1r,3r,5R,7S)-adamantan-2-ylidene)amino)oxy)-2-cyclohexylethyl)furan-2-carboxamide (10)**



Colorless oil (159 mg, 83%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 (d, $J = 1.4$ Hz, 1H), 7.15 (s, 1H), 7.02 (d, $J = 3.4$ Hz, 1H), 6.42 (dd, $J = 3.4, 1.7$ Hz, 1H), 3.92 – 3.87 (m, 1H), 3.79 (ddd, $J = 13.9, 6.1, 2.6$ Hz, 1H), 3.50 (s, 1H), 3.42 (ddd, $J = 13.7, 8.0, 4.2$ Hz, 1H), 2.53 (s, 1H), 1.97 – 1.57 (m, 18H), 1.22 – 1.00 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.5, 158.4, 148.5, 143.7, 113.7, 112.0, 84.3, 41.3,

39.7, 39.1, 39.0, 37.7 (X2), 36.5, 36.4, 29.7, 29.0, 28.9, 27.9, 26.5, 26.2, 26.1. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{23}H_{33}O_3N_2$, 385.2486, found: 385.2482.

***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-3-methoxypropyl)furan-2-carboxamide (11)**

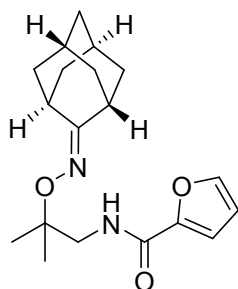


Colorless oil (104 mg, 60%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). 1H **NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.38 (m, 1H), 7.06 – 7.05 (m, 1H), 7.00 (s, 1H), 6.45 (dd, $J = 3.4, 1.8$ Hz, 1H), 4.31 (dq, $J = 7.2, 4.8$ Hz, 1H), 3.83 (ddd, $J = 14.1, 6.4, 4.0$ Hz, 1H), 3.64 – 3.50 (m, 4H), 3.37 (s, 3H), 2.55 (s, 1H), 1.97 – 1.74 (m, 12H). ^{13}C **NMR** (101 MHz, $CDCl_3$) δ 168.5, 158.5, 148.4, 143.9, 114.0, 112.2, 79.2, 72.6, 59.6, 40.9, 39.2, 39.0, 37.7, 37.6, 36.5, 36.4, 29.8, 27.9. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{19}H_{27}O_4N_2$,

347.1965, found: 347.1959.

***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-2-methylpropyl)furan-2-carboxamide**

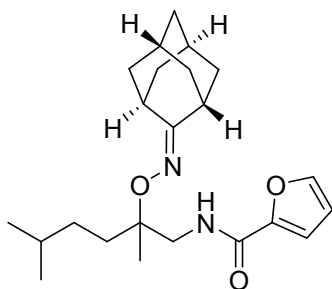
(12)



Colorless oil (117 mg, 71%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). 1H **NMR** (400 MHz, $CDCl_3$) δ 7.38 (dd, $J = 1.7, 0.8$ Hz, 1H), 7.26 (s, 1H), 7.10 (s, 1H), 7.04 (dd, $J = 3.5, 0.7$ Hz, 1H), 3.58 (d, $J = 5.8$ Hz, 2H), 3.50 (s, 1H), 2.55 (s, 1H), 1.99 – 1.73 (m, 13H), 1.24 (s, 6H). ^{13}C **NMR** (101 MHz, $CDCl_3$) δ 167.5, 158.4, 148.4, 143.8, 113.8, 112.1, 78.1, 47.2, 39.2, 37.7, 36.6, 36.5, 29.6, 27.9, 23.9. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{19}H_{27}O_3N_2$, 331.2016, found: 331.2016.

***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-2,5-dimethylhexyl)furan-2-carboxamide**

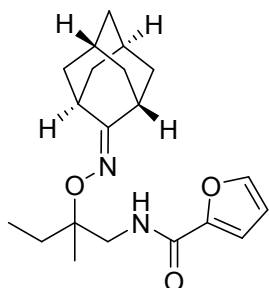
(13)



Colorless oil (152 mg, 79%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). 1H **NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.39 (m, 1H), 7.22 (s, 1H), 7.06 – 7.04 (m, 1H), 6.46 (dtd, $J = 4.2, 2.0, 1.2$ Hz, 1H), 3.67 – 3.56 (m, 2H), 3.52 (s, 1H), 2.58 (s, 1H), 2.00 – 1.65 (m, 13H), 1.54 – 1.42 (m, 2H), 1.24 – 1.16 (m, 5H), 0.87 – 0.83 (m, 6H). ^{13}C **NMR** (101 MHz, $CDCl_3$) δ 167.3, 158.5, 148.6, 143.8, 113.7, 112.1, 80.2, 46.5, 39.3, 39.2, 37.8 (X2), 36.7, 36.6, 34.4, 32.4, 29.6, 28.6, 28.0, 22.8, 22.7, 21.2. **HRMS**

(ESI): m/z ($M + H^+$) calcd for $C_{23}H_{35}O_3N_2$, 387.2642, found: 387.2636.

***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-2-methylbutyl)furan-2-carboxamide (14)**

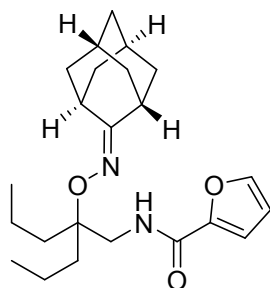


Colorless oil (126 mg, 73%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). 1H **NMR** (400 MHz, $CDCl_3$) δ 3.53 (s, 1H), 2.58 (s, 1H), 1.99 – 1.75 (m, 12H),

1.60 (q, $J = 7.5$ Hz, 2H), 1.22 (s, 6H), 0.84 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.8, 78.7, 39.3, 37.8, 36.8, 36.6, 32.8, 29.6, 28.2, 25.3, 8.4.

HRMS (ESI): m/z ($M + H^+$) calcd for $\text{C}_{20}\text{H}_{29}\text{O}_3\text{N}_2$, 345.2173, found: 345.2171.

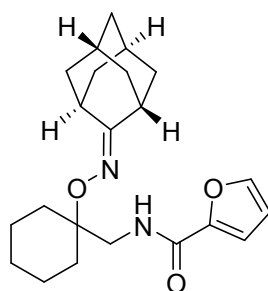
***N*-(2-(((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-2-propylpentyl)furan-2-carboxamide (15)**



Colorless oil (179 mg, 93%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). ^1H NMR (400 MHz, CDCl_3) δ 7.37 (dd, $J = 1.7, 0.8$ Hz, 1H), 7.28 (s, 1H), 7.02 – 7.01 (m, 1H), 6.43 (ddd, $J = 3.6, 1.8, 1.0$ Hz, 1H), 3.61 (d, $J = 5.6$ Hz, 2H), 3.50 (s, 1H), 2.55 (s, 1H), 1.96 – 1.72 (m, 12H), 1.59 – 1.42 (m, 4H), 1.33 – 1.21 (m, 4H), 0.85 (t, $J = 7.3$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.1, 158.2, 148.5, 143.7, 113.5, 112.0, 82.0, 44.9, 39.2, 37.7, 36.6, 36.5, 35.8, 29.5, 27.9, 16.6, 14.7. HRMS (ESI): m/z ($M + H^+$) calcd for $\text{C}_{23}\text{H}_{35}\text{O}_3\text{N}_2$,

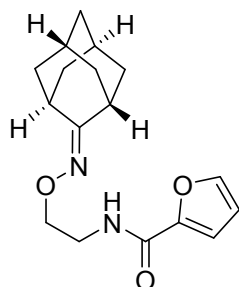
387.2642, found: 387.2637.

***N*-(1-(((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)cyclohexyl)methyl)furan-2-carboxamide (16)**



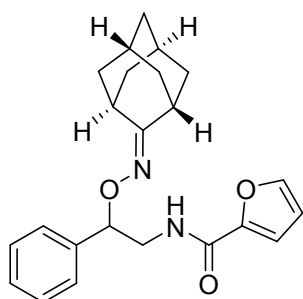
Colorless oil (181 mg, 98%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.37 (m, 1H), 7.25 (s, 1H), 7.02 (d, $J = 3.5$ Hz, 1H), 6.43 (dd, $J = 3.5, 1.8$ Hz, 1H), 3.60 (d, $J = 5.6$ Hz, 2H), 3.56 (s, 1H), 2.56 (s, 1H), 1.98 – 1.76 (m, 14H), 1.54 – 1.22 (m, 8H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.6, 158.5, 148.5, 143.7, 113.6, 112.0, 78.5, 46.6, 39.2, 37.9, 36.6, 36.5, 32.4, 29.6, 27.9, 25.8, 21.7. HRMS (ESI): m/z ($M + H^+$) calcd for $\text{C}_{22}\text{H}_{31}\text{O}_3\text{N}_2$, 371.2329, found: 371.2328.

***N*-(2-(((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)ethyl)furan-2-carboxamide (17)**



Colorless oil (63 mg, 42%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). ^1H NMR (400 MHz, CDCl_3) δ 7.37 (dd, $J = 1.7, 0.7$ Hz, 1H), 7.04 (dd, $J = 3.5, 0.6$ Hz, 1H), 6.96 (s, 1H), 6.43 (dd, $J = 3.5, 1.8$ Hz, 1H), 4.14 – 4.11 (m, 2H), 3.68 – 3.62 (m, 2H), 3.46 (s, 1H), 2.51 (s, 1H), 1.96 – 1.71 (m, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.0, 158.4, 148.3, 143.9, 114.0, 112.1, 71.2, 39.6, 39.1, 37.7, 36.5, 36.4, 29.7, 27.8. HRMS (ESI): m/z ($M + H^+$) calcd for $\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}_2$, 303.1703, found: 303.1700.

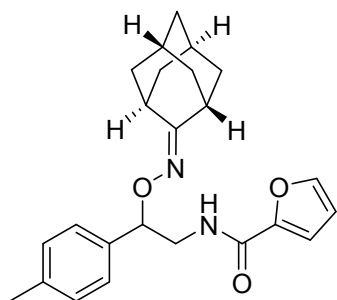
***N*-(2-(((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-2-phenylethyl)furan-2-carboxamide (18)**



Colorless oil (113 mg, 60%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.41 (m, 1H), 7.36 – 7.34 (m, 4H), 7.33 –

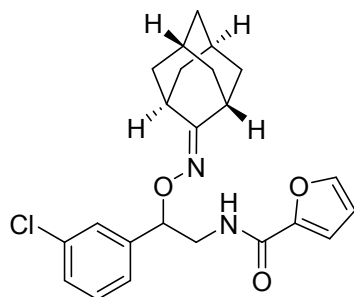
7.28 (m, 1H), 7.09 (dd, $J = 3.5, 0.7$ Hz, 1H), 7.01 (br s, 1H), 6.49 – 6.47 (m, 1H), 5.26 (dd, $J = 8.8, 3.5$ Hz, 1H), 4.02 (ddd, $J = 14.2, 7.2, 3.5$ Hz, 1H), 3.65 (s, 1H), 3.63 – 3.55 (m, 1H), 2.55 (s, 1H), 2.02 – 1.73 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.7, 158.4, 148.3, 143.9, 139.7, 128.6, 128.0, 126.6, 114.2, 112.2, 82.5, 44.8, 39.1, 37.8, 36.6, 36.3, 30.1, 29.9, 27.9 (X2). **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{23}\text{H}_{27}\text{O}_3\text{N}_2$, 379.2016, found: 379.2015.

***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-2-(*p*-tolyl)ethylfuran-2-carboxamide (19)**



Colorless oil (100 mg, 51%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 (dd, $J = 1.6, 0.5$ Hz, 1H), 7.24 (d, $J = 8.5$ Hz, 2H), 7.15 (d, $J = 7.9$ Hz, 2H), 7.08 (dd, $J = 3.5, 0.5$ Hz, 1H), 7.00 (s, 1H), 6.47 (dd, $J = 3.4, 1.7$ Hz, 1H), 5.20 (dd, $J = 8.7, 3.4$ Hz, 1H), 3.99 (ddd, $J = 14.1, 7.1, 3.5$ Hz, 1H), 3.63 (s, 1H), 3.57 (ddd, $J = 13.9, 8.7, 3.9$ Hz, 1H), 2.53 (s, 1H), 2.33 (s, 3H), 1.99 – 1.73 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.8, 158.4, 148.4, 143.9, 137.8, 136.6, 129.3, 126.6, 114.2, 112.2, 82.4, 44.8, 39.1, 37.8, 37.8, 36.6, 36.3, 30.1, 27.9, 27.9, 21.4. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{24}\text{H}_{29}\text{O}_3\text{N}_2$, 393.2173, found: 393.2164.

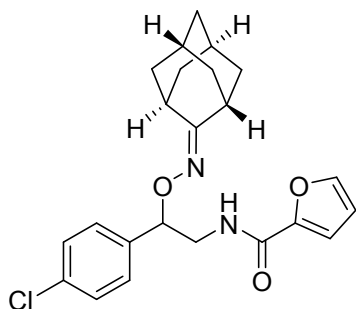
***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-2-(3-chlorophenyl)ethylfuran-2-carboxamide (20)**



Colorless oil (117 mg, 57%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 (dd, $J = 1.7, 0.8$ Hz, 1H), 7.32 (s, 1H), 7.28 – 7.20 (m, 3H), 7.08 (d, $J = 3.4$ Hz, 1H), 6.93 (s, 1H), 6.46 (dd, $J = 3.5, 1.8$ Hz, 1H), 5.20 (dd, $J = 8.9, 3.4$ Hz, 1H), 3.98 (ddd, $J = 14.2, 7.3, 3.5$ Hz, 1H), 3.62 (s, 1H), 3.51 (ddd, $J = 14.1, 8.9, 4.2$ Hz, 1H), 2.49 (s, 1H), 1.98 – 1.71 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.1, 158.4, 148.1, 144.0, 142.0, 134.5, 129.9, 128.1, 126.7, 124.8, 114.4, 112.3, 81.9, 44.5, 39.1, 39.0, 37.7, 36.5, 36.28, 30.1, 27.9.

HRMS (ESI): m/z ($M + H^+$) calcd for $\text{C}_{23}\text{H}_{26}\text{O}_3\text{N}_2\text{Cl}$, 413.1626, found: 413.1623.

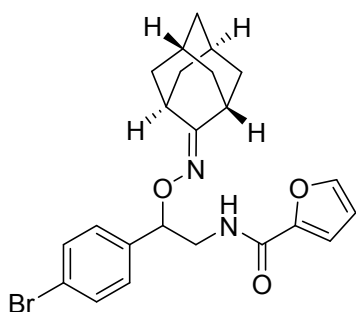
***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-2-(4-chlorophenyl)ethylfuran-2-carboxamide(21)**



Colorless oil (117 mg, 57%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 (dd, $J = 1.7, 0.7$ Hz, 1H), 7.32 – 7.26 (m, 4H), 7.08 (dd, $J = 3.4, 0.7$ Hz, 1H), 6.95 (s, 1H), 6.47 (dd, $J = 2.3, 1.2$ Hz, 1H), 5.21 (dd, $J = 8.7, 3.6$ Hz, 1H), 3.96 (ddd, $J = 14.2, 7.2, 3.6$ Hz, 1H), 3.61 (s, 1H), 3.55 (ddd, $J = 14.1, 8.7, 4.3$ Hz, 1H), 2.51 (s, 1H), 1.99 – 1.72 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.0, 158.4, 148.2, 144.0, 138.4, 133.7, 128.8, 128.0, 114.4, 112.3, 81.9, 44.5,

39.1, 39.0, 37.8, 37.7, 36.5, 36.3, 30.1, 27.9, 27.8. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{23}H_{26}O_3N_2Cl$, 413.1626, found: 413.1623.

***N*-(2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-2-(4-bromophenyl)ethyl)furan-2-carboxamide(22)**

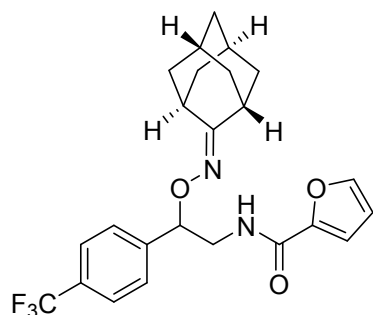


Colorless oil (132 mg, 58%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3).

1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, $J = 8.4$ Hz, 2H), 7.42 (dd, $J = 1.7$, 0.7 Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 2H), 7.10 (dd, $J = 3.5$, 0.7 Hz, 1H), 6.94 (s, 1H), 6.48 (dd, $J = 3.4$, 1.7 Hz, 1H), 5.20 (dd, $J = 8.7$, 3.5 Hz, 1H), 3.97 (ddd, $J = 14.2$, 7.2, 3.6 Hz, 1H), 3.62 (s, 1H), 3.55 (ddd, $J = 14.1$, 8.7, 4.2 Hz, 1H), 2.52 (s, 1H), 2.00 – 1.73 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.9, 158.4, 148.1, 144.0, 138.9, 131.7, 128.3,

121.9, 114.3, 112.2, 81.9, 44.4, 39.1, 39.0, 37.8, 37.7, 36.5, 36.2, 30.0, 27.8, 27.8. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{23}H_{26}O_3N_2Br$, 457.1121, found: 457.1120.

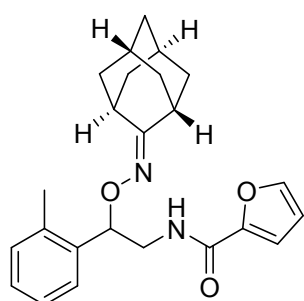
***N*-(2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-2-(4-(trifluoromethyl)phenyl)ethyl)furan-2-carboxamide (23)**



Colorless oil (107 mg, 48%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). **1H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, $J = 8.1$ Hz, 2H), 7.48 (d, $J = 8.2$ Hz, 2H), 7.44 – 7.42 (m, 1H), 7.11 (d, $J = 3.5$ Hz, 1H), 6.94 (s, 1H), 6.50 (dd, $J = 3.5$, 1.8 Hz, 1H), 5.31 (dd, $J = 8.7$, 3.4 Hz, 1H), 4.02 (ddd, $J = 14.2$, 7.2, 3.5 Hz, 1H), 3.65 (s, 1H), 3.61 – 3.53 (m, 1H), 2.53 (s, 1H), 2.01 – 1.73 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 158.5, 148.1, 144.1, 143.9, 130.3 (q, $J = 32.4$ Hz), 127.0,

125.6 (q, $J = 3.7$ Hz), 124.3 (q, $J = 273.1$ Hz), 114.5, 112.4, 82.1, 44.4, 39.1, 39.1, 37.9, 37.8, 36.5, 36.3, 30.2, 27.9, 27.9. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{24}H_{26}O_3N_2F_3$, 447.1890, found: 447.1882.

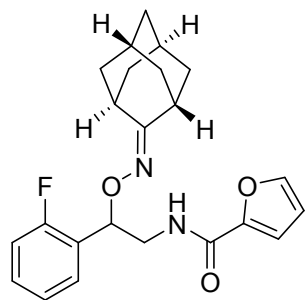
***N*-(2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-2-(*o*-tolyl)ethyl)furan-2-carboxamide (24)**



Colorless oil (104 mg, 53%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). **1H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 1H), 7.36 – 7.26 (m, 1H), 7.21 – 7.13 (m, 4H), 7.09 (d, $J = 3.4$ Hz, 1H), 6.47 (dd, $J = 3.4$, 1.8 Hz, 1H), 5.48 (dd, $J = 9.0$, 2.9 Hz, 1H), 4.05 (ddd, $J = 14.3$, 7.5, 2.9 Hz, 1H), 3.66 (s, 1H), 3.46 (ddd, $J = 14.2$, 9.1, 3.7 Hz, 1H), 2.54 (s, 1H), 2.42 (s, 3H), 2.00 – 1.73 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 158.4, 148.3, 143.9, 137.6, 135.5, 130.7, 127.8, 126.0, 125.9, 114.1, 112.2, 80.0, 43.9, 39.0, 37.8

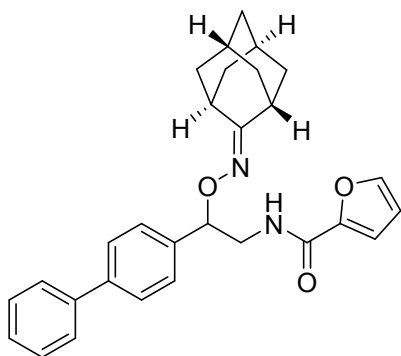
(X2), 36.5, 36.3, 30.1, 27.8, 19.3. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{24}H_{29}O_3N_2$, 393.2173, found: 393.2163.

***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-2-(2-fluorophenyl)ethyl)furan-2-carboxamide (25)**



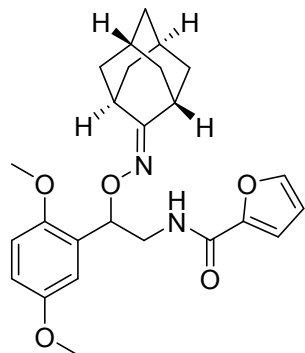
Colorless oil (103 mg, 52%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 (dd, $J = 1.7, 0.7$ Hz, 1H), 7.38 (td, $J = 7.4, 1.7$ Hz, 1H), 7.30 – 7.24 (m, 1H), 7.13 (td, $J = 7.5, 1.1$ Hz, 1H), 7.09 (dd, $J = 3.5, 0.6$ Hz, 1H), 7.07 – 7.02 (m, 1H), 6.97 (s, 1H), 6.48 (dd, $J = 3.5, 1.8$ Hz, 1H), 5.57 (dd, $J = 8.5, 3.5$ Hz, 1H), 4.03 (ddd, $J = 14.1, 6.8, 3.5$ Hz, 1H), 3.71 – 3.62 (m, 2H), 2.56 (s, 1H), 1.99 – 1.74 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.9, 160.2 (d, $J = 247.7$ Hz), 158.40, 148.3, 144.0, 129.6 (d, $J = 8.3$ Hz), 128.1 (d, $J = 4.1$ Hz), 126.9 (d, $J = 13.7$ Hz), 124.2 (d, $J = 3.4$ Hz), 115.7 (d, $J = 21.7$ Hz), 114.2, 112.3, 43.6, 39.1, 39.1, 37.8, 37.8, 36.6, 36.3, 30.1, 27.9. HRMS (ESI): m/z ($M + H^+$) calcd for $\text{C}_{23}\text{H}_{26}\text{O}_3\text{N}_2\text{F}$, 397.1922, found: 397.1917.

***N*-2-([1,1'-biphenyl]-4-yl)-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)ethyl)furan-2-carboxamide (26)**



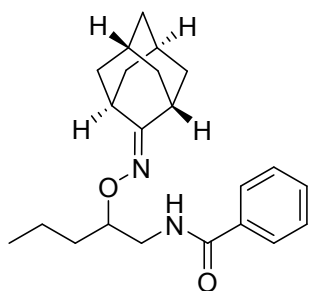
Colorless oil (111 mg, 49%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.60 (d, $J = 8.1$ Hz, 4H), 7.48 – 7.41 (m, 5H), 7.34 (t, $J = 7.3$ Hz, 1H), 7.12 (d, $J = 3.4$ Hz, 1H), 7.06 (s, 1H), 6.51 – 6.47 (m, 1H), 5.33 (dd, $J = 8.7, 3.4$ Hz, 1H), 4.07 (ddd, $J = 14.0, 7.1, 3.5$ Hz, 1H), 3.71 – 3.62 (m, 2H), 2.58 (s, 1H), 2.02 – 1.76 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.1, 158.4, 148.3, 144.0, 140.9, 138.7, 128.9, 127.5, 127.3, 127.2, 127.1, 114.3, 112.2, 82.3, 44.7, 39.1(X2), 37.8, 36.5, 36.3, 30.1, 27.9(X2). HRMS (ESI): m/z ($M + H^+$) calcd for $\text{C}_{29}\text{H}_{31}\text{O}_3\text{N}_2$, 455.2329, found: 455.2322.

***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-2-(2,5-dimethoxyphenyl)ethyl)furan-2-carboxamide (27)**



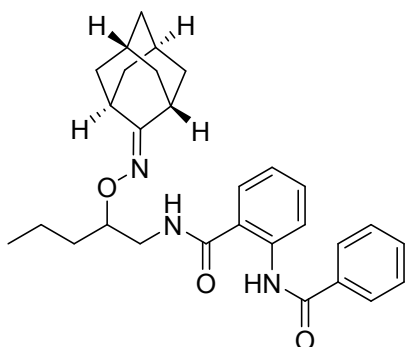
Colorless oil (109 mg, 50%), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.41 (dd, $J = 1.7, 0.7$ Hz, 1H), 7.07 (dd, $J = 3.5, 0.7$ Hz, 1H), 7.04 (s, 1H), 6.91 (d, $J = 2.6$ Hz, 1H), 6.80 – 6.75 (m, 2H), 6.47 (dd, $J = 3.5, 1.8$ Hz, 1H), 5.61 (dd, $J = 8.0, 3.8$ Hz, 1H), 3.97 (ddd, $J = 13.8, 6.6, 3.9$ Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.67 (s, 1H), 3.54 (ddd, $J = 13.8, 8.0, 4.1$ Hz, 1H), 2.56 (s, 1H), 2.00 – 1.76 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.2, 158.3, 153.7, 150.6, 148.4, 143.8, 129.2, 113.9, 113.4, 112.9, 112.1, 111.3, 77.1, 55.9, 55.8, 43.8, 39.0, 37.8, 37.7, 36.5, 36.2, 30.0, 27.9. HRMS (ESI): m/z ($M + H^+$) calcd for $\text{C}_{25}\text{H}_{31}\text{O}_5\text{N}_2$, 439.2227, found: 439.2221.

***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)pentyl)benzamide (28)**



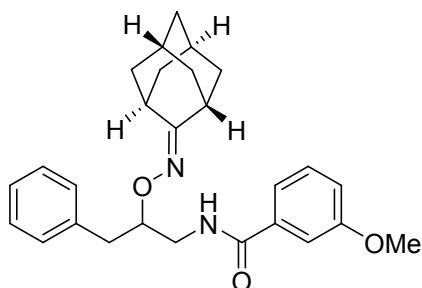
Colorless oil (88 mg, 50%), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.77 – 7.74 (m, 2H), 7.48 – 7.42 (m, 1H), 7.42 – 7.36 (m, 2H), 7.23 (s, 1H), 4.23 – 4.15 (m, 1H), 3.82 (ddd, $J = 13.9, 6.1, 2.8$ Hz, 1H), 3.52 (s, 1H), 3.45 (ddd, $J = 14.0, 8.0, 4.1$ Hz, 1H), 2.54 (s, 1H), 2.00 – 1.72 (m, 12H), 1.69 – 1.60 (m, 1H), 1.55 – 1.38 (m, 3H), 0.91 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.6, 167.2, 134.9, 131.3, 128.6, 127.0, 80.1, 44.9, 39.1, 37.7, 37.7, 36.6, 36.5, 34.0, 29.7, 27.9, 27.9, 19.0, 14.2. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{22}\text{H}_{31}\text{O}_2\text{N}_2$, 355.2380, found: 355.2372.

***N*-(2-(((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)pentyl)-2-benzamidobenzamide (28')**



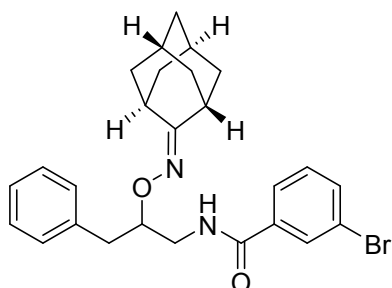
Colorless oil (50 mg, 21%), $R_f = 0.4$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 12.37 (s, 1H), 8.84 (d, $J = 8.4$ Hz, 1H), 8.05 (dd, $J = 7.9, 1.7$ Hz, 2H), 7.62 (s, 1H), 7.56 – 7.48 (m, 5H), 7.08 (td, $J = 7.7, 1.1$ Hz, 1H), 4.28 – 4.20 (m, 1H), 3.83 (ddd, $J = 13.9, 5.9, 2.4$ Hz, 1H), 3.54 – 3.43 (m, 2H), 2.56 (s, 1H), 2.02 – 1.74 (m, 12H), 1.72 – 1.64 (m, 1H), 1.57 – 1.42 (m, 3H), 0.94 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.1, 168.3, 165.8, 140.4, 135.1, 132.8, 131.9, 128.9, 127.6, 126.7, 122.8, 121.7, 120.6, 79.8, 45.5, 39.2, 39.2, 37.8, 37.8, 36.7, 36.5, 34.1, 29.9, 29.8, 27.9, 27.9, 19.1, 14.2. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{29}\text{H}_{36}\text{O}_3\text{N}_3$, 474.2751, found: 474.2745.

***N*-(2-(((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-3-phenylpropyl)-3-methoxybenzamide (29)**



Colorless oil (136 mg, 63%), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:2). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 (dd, $J = 2.5, 1.6$ Hz, 1H), 7.32 – 7.18 (m, 7H), 7.08 (s, 1H), 7.01 (ddd, $J = 8.1, 2.6, 1.1$ Hz, 1H), 4.47 – 4.40 (m, 1H), 3.88 – 3.82 (m, 4H), 3.56 – 3.46 (m, 2H), 3.04 (dd, $J = 14.1, 7.1$ Hz, 1H), 2.88 (dd, $J = 14.0, 5.9$ Hz, 1H), 2.56 (s, 1H), 1.99 – 1.69 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.1, 167.2, 156.0, 138.0, 136.5, 129.6, 129.6, 128.4, 126.5, 118.7, 117.7, 112.4, 80.9, 55.6, 44.3, 39.2, 39.1, 38.4, 37.7, 36.6, 29.9, 27.9. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{27}\text{H}_{33}\text{O}_3\text{N}_2$, 433.2486, found: 433.2480.

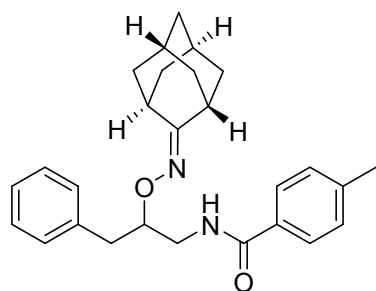
***N*-(2-(((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-3-phenylpropyl)-3-bromobenzamide (30)**



Colorless oil (146 mg, 61%), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.85 (t, $J = 1.8$ Hz, 1H), 7.70 – 7.67 (m, 1H), 7.58 (ddd, $J = 8.0, 1.9, 1.0$ Hz, 1H), 7.30 – 7.18 (m,

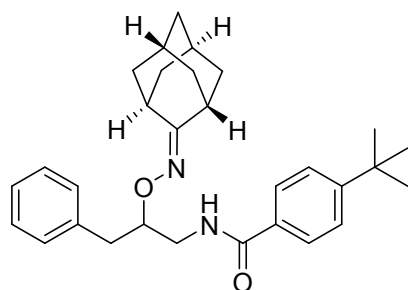
6H), 4.48 – 4.40 (m, 1H), 3.84 (ddd, $J = 13.9, 6.0, 3.0$ Hz, 1H), 3.55 – 3.45 (m, 2H), 3.03 (dd, $J = 14.1, 7.2$ Hz, 1H), 2.87 (dd, $J = 14.1, 5.9$ Hz, 1H), 2.59 (s, 1H), 2.02 – 1.68 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.3, 165.6, 137.9, 136.8, 134.3, 130.2, 130.1, 129.6, 128.4, 126.5, 125.8, 122.7, 80.7, 44.7, 39.2, 39.2, 38.4, 37.7, 37.6, 36.5, 36.5, 29.9, 27.8. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{26}\text{H}_{30}\text{O}_2\text{N}_2\text{Br}$, 481.1485, found: 481.1479.

***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-3-phenylpropyl)-4-methylbenzamide (31)**



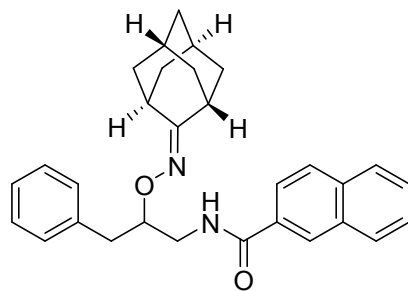
Colorless oil (108 mg, 52%), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64 (d, $J = 8.2$ Hz, 2H), 7.31 – 7.18 (m, 7H), 7.05 (s, 1H), 4.48 – 4.40 (m, 1H), 3.85 (ddd, $J = 14.0, 5.9, 3.0$ Hz, 1H), 3.57 – 3.47 (m, 2H), 3.04 (dd, $J = 14.1, 7.1$ Hz, 1H), 2.89 (dd, $J = 14.1, 5.9$ Hz, 1H), 2.57 (s, 1H), 2.38 (s, 3H), 1.99 – 1.69 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.1, 167.3, 141.8, 138.1, 132.1, 129.7, 129.3, 128.4, 127.0, 126.5, 81.0, 44.2, 39.2, 39.2, 38.4, 37.7, 36.6, 29.9, 27.9, 21.6. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{27}\text{H}_{33}\text{O}_2\text{N}_2$, 417.2537, found: 417.2527.

***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-3-phenylpropyl)-4-(tert-butyl)benzamide(32)**



Colorless oil (114 mg, 50%), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (d, $J = 8.4$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H), 7.31 – 7.18 (m, 5H), 7.05 (s, 1H), 4.48 – 4.40 (m, 1H), 3.86 (ddd, $J = 13.9, 5.8, 3.0$ Hz, 1H), 3.59 – 3.47 (m, 2H), 3.04 (dd, $J = 14.0, 7.1$ Hz, 1H), 2.89 (dd, $J = 14.0, 5.9$ Hz, 1H), 2.58 (s, 1H), 2.01 – 1.70 (m, 12H), 1.33 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.1, 167.2, 154.8, 138.1, 132.0, 129.6, 128.4, 126.8, 126.4, 125.5, 81.0, 44.0, 39.2, 39.1, 38.4, 37.7, 36.5, 36.5, 35.0, 31.3, 29.9, 27.9. **HRMS** (ESI): m/z ($M + H^+$) calcd for $\text{C}_{30}\text{H}_{39}\text{O}_2\text{N}_2$, 459.3006, found: 459.2999.

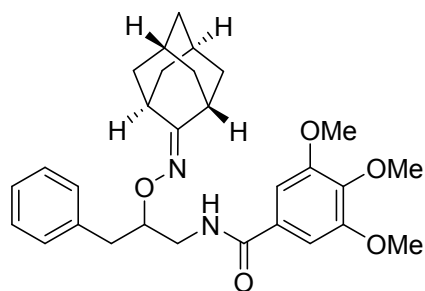
***N*-2-((((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-3-phenylpropyl)-2-naphthamide (33)**



Colorless oil (131 mg, 58%), $R_f = 0.3$ (EtOAc/Petroleum ether = 1:2). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.25 (s, 1H), 7.90 – 7.81 (m, 4H), 7.58 – 7.49 (m, 2H), 7.38 – 7.20 (m, 6H), 4.50 (ddd, $J = 10.0, 8.9, 3.0$ Hz, 1H), 3.92 (ddd, $J = 13.9, 6.0, 3.0$ Hz, 1H), 3.59 (ddd, $J = 13.9, 8.1, 4.1$ Hz, 1H), 3.52 (s, 1H), 3.07 (dd, $J = 14.0, 7.1$ Hz, 1H), 2.92 (dd, $J = 14.0, 5.9$ Hz, 1H), 2.62 (s, 1H), 2.01 – 1.70 (m, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.1, 167.3,

138.0, 134.8, 132.8, 132.1, 129.7, 129.0, 128.5, 127.9, 127.6, 127.4, 126.8, 126.5, 123.8, 80.9, 44.5, 39.2, 38.5, 37.7, 37.7, 36.6, 36.5, 29.9, 27.9. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{30}H_{33}O_2N_2$, 453.2537, found: 453.2530.

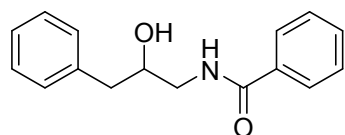
***N*-(2-(((1*r*,3*r*,5*R*,7*S*)-adamantan-2-ylidene)amino)oxy)-3-phenylpropyl)-3,4,5-trimethoxybenzamide(34)**



Colorless oil (138 mg, 56%), R_f = 0.3 (EtOAc/Petroleum ether = 1:1). **¹H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.16 (m, 6H), 7.11 (s, 1H), 4.54 – 4.37 (m, 1H), 3.87 (s, 3H), 3.87 (s, 6H), 3.57 – 3.45 (m, 2H), 3.02 (dd, J = 14.0, 7.2 Hz, 1H), 2.89 (dd, J = 14.1, 5.7 Hz, 1H), 2.53 (s, 1H), 2.05 – 1.65 (m, 12H). **¹³C NMR** (101 MHz, $CDCl_3$) δ 168.1, 166.9, 153.2, 140.9, 138.0, 130.3, 129.5, 128.4, 126.4, 104.4, 81.0, 61.0, 56.3, 44.4, 39.1, 39.1, 38.4,

37.6, 37.6, 36.6, 36.4, 29.8, 27.8. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{29}H_{37}O_5N_2$, 493.2697, found: 493.2690.

***N*-(2-hydroxy-3-phenylpropyl)benzamide (36)**



35 (0.1 mmol, 40 mg) was dissolved in 2.0 mL ethyl acetate, and 400 mg Pd/C was added. The reaction mixture was stirred at room temperature under H_2 atmosphere for 1h, then filtered and the filtrate was concentrated, and the residue was purified with flash

column chromatography to afford **36** as colorless oil (24 mg, 95%), R_f = 0.4 (EtOAc/Petroleum ether = 1:1). **¹H NMR** (400 MHz, CD_3OD) δ 7.81 (dt, J = 3.5, 2.3 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.48 – 7.42 (m, 2H), 7.30 – 7.24 (m, 4H), 7.21 – 7.15 (m, 1H), 4.09 – 4.00 (m, 1H), 3.53 (dd, J = 13.6, 4.4 Hz, 1H), 3.36 (dd, J = 13.6, 7.5 Hz, 1H), 2.85 (dd, J = 13.8, 5.4 Hz, 1H), 2.76 (dd, J = 13.8, 7.6 Hz, 1H). **¹³C NMR** (101 MHz, MeOD) δ 170.7, 140.0, 135.8, 132.8, 130.6, 129.7, 129.5, 128.4, 127.4, 72.7, 47.0, 42.7. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{16}H_{18}O_2N$, 256.1332, found: 256.1329.

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