# SUPPORTING INFORMATION

# Intramolecular hydride transfer onto arynes: redox-neutral and transition metal-free C(sp3)-H functionalization of amines

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## 1. General information

**General:** All chemicals including fluoride sources, activators and additives (KF, CsF, TBAF.3$H_2O$, TBAT, $Cs_2CO_3$ and 18-crown-6) were obtained from commercial sources and used as supplied without further purification. KF was dried under high vacumn with heating. Dry tetrahydrofuran (THF) and dichloromethane were obtained from the MB SPS-80 solvent purification machine. Reactions requiring anhydrous conditions were carried out in oven-dried apparatus under nitrogen. 3-Formyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **13** was prepared according to the reported procedure.[1] All aryne-generating reactions were homogenous at the specified reaction temperatures, with the exception of $Cs_2CO_3$.

**Chromatography**: Flash column chromatography was carried out using 40-63 μm silica gel or Biotage Isolera One flash purification system using KP-Sil or KP-NH (amine modified) Snap cartridges. Thin-layer chromatography (TLC) was performed on aluminium backed plates pre-coated with Silica Gel 60 $F_{254}$ and visualized using a UV lamp (254 nm) or Dragendorff reagent stain.

**Nuclear Magnetic Resonance Spectroscopy**: $^1H$, $^{13}C$ and $^{19}F$ NMR spectra were recorded on a Bruker Avance UltraShield AV400 or AV(III)400 (400 MHz, 376 MHz and 101 MHz). $^1H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ and referenced to the residual solvent peak at 7.26 ppm and solvent peak at 77.2 ppm. $^{19}F$ NMR spectra were recorded in $C_6F_6$ referenced to the solvent peak at -164.9 ppm. Chemical shifts are quoted in parts per million (ppm) to 2 dp for $^1H$ NMR spectra and 1 dp for the $^{13}C$ and $^{19}F$ NMR spectra. Coupling constants (*J*) were measured in Hertz (Hz) to 1 dp. Spectral data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sep = septet, dd = doublet of doublets, ddd = doublet of doublets of doublets, m = multiplet, br = broad) and coupling constant (*J*).

**Infrared (IR) spectroscopy**: IR spectra were recorded as solids or neat liquids on the PerkinElmer Spectrum 65 FT-IR spectrometer fitted with a Universal ATR sampling accessory and are reported in wavenumbers ($cm^{-1}$) to the nearest integer.

**Mass Spectroscopy**: High resolution mass spectra were acquired by nanospray ionization (NSI), time-of-flight (TOF) or atmospheric pressure chemical ionization (APCI) at the EPSRC UK National Mass Spectrometry Facility at Swansea University. Low resolution mass spectra were recorded on the Agilent 1100 series LC-MS (comprising a 6310 ion trap) under electrospray ionization (ESI) or on the Agilent GC-MS (comprising a 6890 GC and 5973 MSD) under electron ionization (EI).

**Optical rotation**: The optical rotation $[\alpha]_D$ was measured using a Bellingham Stanley ADP 220 Polarimeter and the values are given in $10^{-1}$ deg $cm^2$ $g^{-1}$. The measurements were recorded in $CHCl_3$ with the concentration given in parenthesis.

**Melting points**: Melting points determined in open glass capillaries and are uncorrected.

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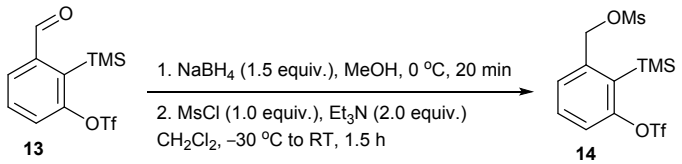
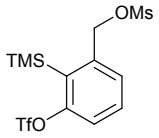
1 A. B. Smith III and W. S. Kim, *Proc. Natl. Acad. Sci. U.S.A.,* 2011, **108**, 6787–6792.

## 2. Synthesis and characterization of aryne precursor tether




**Scheme S1: Synthesis of mesylated aryne precursor**

**3-(((Methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 14:**




According to a modified literature procedure,[2] sodium borohydride (869 mg, 23.0 mmol) was added portion-wise to a solution of 3-formyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate[1] **13** (5.00 g, 15.3 mmol) in methanol (35 mL) at 0 °C and the reaction mixture was stirred for 20 minutes. A saturated aqueous solution of ammonium chloride (60 mL) was added to the reaction mixture and the aqueous layer was washed with ethyl acetate (3 × 50 mL). The combined organic layers were dried over magnesium sulphate, filtered and the solvent removed *in vacuo* to afford the crude 3-(hydroxymethyl)-2-(trimethylsilyl) phenyl trifluoromethanesulfonate as a white solid. Triethylamine (4.27 mL, 30.6 mmol) and methanesulfonyl chloride (1.18 mL, 15.3 mmol) were added to a solution of the crude 3-(hydroxymethyl)-2-(trimethylsilyl) phenyl trifluoromethanesulfonate in dichloromethane (91 mL) at –30 °C and the reaction mixture was stirred for 1.5 hours, while being allowed to warm to room temperature.[3] An aqueous solution of hydrochloric acid (2 M, 50 mL) and brine (50 mL) was added to the reaction mixture and the aqueous layer was washed with dichloromethane (3 × 75 mL). The combined organic layers were dried over magnesium sulphate, filtered and the solvent removed *in vacuo* to afford 3-(((methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (5.55 g, 89%) as a yellow oil which was used in subsequent steps without further purification. **$^{1}$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.51-7.47 (2H, m), 7.40-7.36 (1H, m), 5.36 (2H, s), 2.93 (3H, s), 0.49 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.5, 141.8, 133.0, 131.5, 130.1, 121.1, 118.7 (q, $J_{C-F}$ = 320), 70.3, 38.7, 1.9. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.5. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3035w, 2906w, 1600m, 1414s, 1356m, 1249m, 1207s, 1173s, 1135s, 922m, 832s, 597m. **HRMS (APCI)** calcd for $C_{12}H_{21}F_3NO_6S_2Si^+$ $[M+NH_4]^+$: 424.0526; found 424.0524.

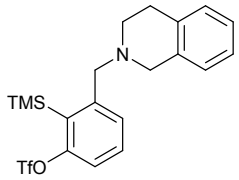
2 Merck and Co. Inc., US5047420A1, 1991.

3 J. Li, Z. Zhang, P. Xie, Q. Zhang, US288086A1, 2011.

## 3. Synthesis and characterization of hydride transfer precursors

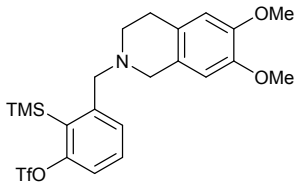
***General procedure for the synthesis of hydride transfer scaffolds:***

**3-((3,4-Dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 1a:**




According to a modified literature procedure,[4] 1,2,3,4-tetrahydroisoquinoline (127 μL, 1.00 mmol) and potassium carbonate (208 mg, 1.50 mmol) were added to a stirred solution of 3-(((methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (204 mg, 501 μmol) in acetonitrile (4.0 mL) at room temperature. The solution was stirred at room temperature, monitored by TLC, and then quenched with water (5 mL) upon completion. The organic layer was washed with brine (3 × 5 mL), dried over magnesium sulfate, filtered and concentrated *in vacuo*. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9:1) afforded 3-((3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (178 mg, 80%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.54-7.52 (1H, m), 7.40-7.36 (1H, m), 7.26-7.24 (1H, m), 7.16-7.09 (3H, m), 6.97-6.96 (1H, m), 3.76 (2H, s), 3.53 (2H, s), 2.88 (2H, t, *J* = 5.8), 2.69 (2H, t, *J* = 5.8), 0.41 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.8, 148.0, 134.8, 134.4, 132.3, 130.6, 129.3, 128.8, 126.7, 126.3, 125.8, 119.1, 118.7 (q, $J_{C-F}$ = 320), 63.2, 56.0, 50.8, 29.2, 2.1. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.6. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2953w, 2805w, 1598m, 1415s, 1247s, 1205s, 1136s, 930m, 829s, 739m, 598s. **HRMS (NSI)** calcd for $C_{20}H_{24}F_3NO_3SSi^+$ $[M+H]^+$: 444.1271; found 444.1259.

**3-((6,7-Dimethoxy-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 1b:**

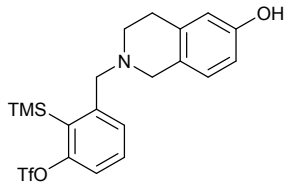



3-(((Methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (1.92 g, 4.72 mmol) and 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (1.30 g, 5.67 mmol) were subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 1:1) afforded 3-((6,7-dimethoxy-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl

4 S. H. Lim, J. Yi, C. S. Ra, K. Naham, D. W. Cho, G. Y. Lee, J. Kim, U. C. Yoon and P. S. Mariano, *Tetrahedron Lett.,* 2015, **56**, 3014–3018.

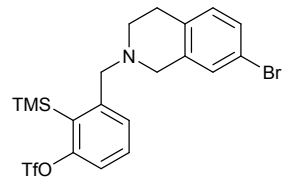
trifluoromethanesulfonate **1b** (1.56 g, 66%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.54-7.52 (1H, m), 7.40-7.36 (1H, m), 7.25-7.23 (1H, m), 6.60 (1H, s), 6.46 (1H, s), 3.85 (3H, s), 3.81 (3H, s), 3.75 (2H, s), 3.43 (2H, s), 2.80 (2H, t, *J* = 5.4), 2.67 (2H, t, *J* = 5.6), 0.41 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.8, 148.0, 147.6, 147.4, 132.3, 130.6, 129.3, 126.6, 126.2, 119.1, 118.7 (q, $J_{C-F}$ = 320), 111.5, 109.5, 63.1, 56.0 (2C), 55.5, 51.0, 28.7, 2.1. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.6. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2952w, 2836w, 1598m, 1414s, 1248s, 1206s, 1136s, 926m, 836s, 601m. **HRMS (NSI)** calcd for $C_{22}H_{29}F_3NO_5SSi^+$ $[M+H]^+$: 504.1482; found 504.1493.

**3-((7-Hydroxy-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 1c:**




3-(((Methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (214 mg, 526 μmol) and 6-hydroxy-1,2,3,4-tetrahydroisoquinoline (94.0 mg, 630 μmol) were subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 1:1) afforded 3-((7-hydroxy-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1c** (180 mg, 80%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.53-7.51 (1H, m), 7.39-7.35 (1H, m), 7.25-7.23 (1H, m), 6.83 (1H, d, *J* = 8.1), 6.61-6.58 (2H, m), 4.73 (1H, br s), 3.75 (2H, s), 3.44 (2H, s), 2.82 (2H, t, *J* = 5.9), 2.65 (2H, t, *J* = 5.9), 0.40 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.8, 154.0, 147.9, 135.9, 132.3, 130.6, 129.3, 127.8, 127.0, 119.0, 118.7 (q, $J_{C-F}$ = 321), 115.0, 113.3, 63.1, 55.4, 50.6, 29.2, 2.1. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.6. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3323w, 2930w, 2802w, 1597m, 1414m, 1206s, 1136s, 916m, 834s, 733m, 598m. **HRMS (NSI)** calcd for $C_{20}H_{25}F_3NO_4SSi^+$ $[M+H]^+$: 460.1220; found 460.1215.

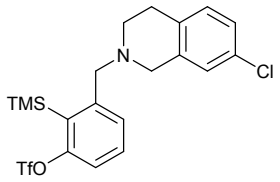
**3-((7-Bromo-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 1d:**




3-(((Methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (192 mg, 472 μmol) and 7-bromo-1,2,3,4-tetrahydroisoquinoline hydrochloride (176 mg, 708 μmol) were subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9.5:0.5) afforded 3-((7-bromo-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1d** (180 mg, 80%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.49-7.47 (1H, m), 7.40-7.36 (1H, m), 7.26-7.23 (2H, m), 7.11 (1H, d, *J* = 1.8), 6.97 (1H, d, *J* = 8.2), 3.75 (2H, s), 3.48 (2H, s), 2.80 (2H, t, *J* = 5.8), 2.66 (2H, t, *J* = 5.8),

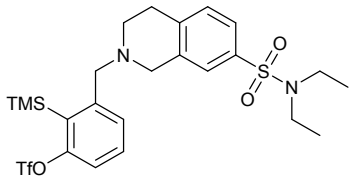
0.40 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.8, 147.6, 137.0, 133.5, 132.3, 130.7, 130.5, 129.5, 129.4, 129.3, 119.3, 119.2, 118.7 (q, $J_{C-F}$ = 320), 63.0, 55.4, 50.4, 28.6, 2.1. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.6. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2927w, 2805w, 1597m, 1413s, 1247m, 1205s, 1136s, 930m, 832s, 599s. **HRMS (NSI)** calcd for $C_{20}H_{24}BrF_3NO_3SSi^+$ $[M+H]^+$: 522.0367 ($^{79}$Br) & 524.0345 ($^{81}$Br); found 522.0366 ($^{79}$Br) & 524.0357 ($^{81}$Br).

**3-((7-Chloro-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 1e:**




3-(((Methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (213 mg, 524 µmol) and 7-chloro-1,2,3,4-tetrahydroisoquinoline hydrochloride (128 mg, 627 µmol) were subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9:1) afforded 3-((7-chloro-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1e** (195 mg, 78%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.51-7.49 (1H, m), 7.40-7.36 (1H, m), 7.27-7.25 (1H, m), 7.10 (1H, dd, *J* = 8.2, 2.1), 7.03 (1H, d, *J* = 8.2), 6.96 (1H, d, *J* = 1.9), 3.76 (2H, s), 3.48 (2H, s), 2.83 (2H, t, *J* = 5.8), 2.67 (2H, t, *J* = 5.9), 0.41 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.8, 147.6, 136.5, 132.9, 132.3, 131.3, 130.7, 130.1, 129.3, 126.52, 126.50, 119.2, 118.7 (q, $J_{C-F}$ = 320), 62.9, 55.5, 50.5, 28.6, 2.1. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.6. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2930w, 2795w, 1599m, 1416s, 1249m, 1206s, 1136s, 931m, 833s, 740m, 719m, 598s. **HRMS (NSI)** calcd for $C_{20}H_{24}ClF_3NO_3SSi^+$ $[M+H]^+$: 478.0881 ($^{35}$Cl) & 480.0852 ($^{37}$Cl); found 478.0877 ($^{35}$Cl) & 480.0846 ($^{37}$Cl).

**3-((7-(*N*,*N*-Diethylsulfamoyl)-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 1f:**

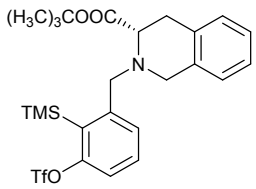



According to a literature procedure,[5] sodium hydride (66.0 mg, 2.75 mmol) was added portion-wise to a solution of diethylamine (0.28 mL, 2.75 mmol) in tetrahydrofuran (4 mL) at 0 °C. The reaction mixture was stirred for 15 minutes at 0 °C. 2-Trifluoroacetyl-1,2,3,4-tetrahydroisoquinoline-7-sulfonyl chloride (300 mg, 915 µmol) was added and the reaction was stirred overnight at room temperature. The reaction was then quenched with water (10 mL), extracted with ethyl acetate (2 × 10 mL), dried over magnesium sulfate, filtered and

5 C. Schneider, E. David, A. A. Toutov and V. Snieckus, *Angew. Chem. Int. Ed.,* 2012, **51**, 2722–2726.

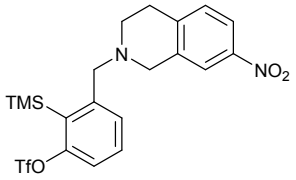
concentrated *in vacuo*. The crude thus obtained and 3-(((methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (186 mg, 456 μmol) were subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 3:2) afforded 3-((7-(*N*,*N*-diethylsulfamoyl)-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1f** (237 mg, 95%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.55 (1H, dd, *J* = 8.0, 1.9), 7.48-7.47 (1H, m), 7.40-7.37 (2H, m), 7.26-7.24 (1H, m), 7.21 (1H, d, *J* = 8.1), 3.78 (2H, s), 3.51 (2H, s), 3.20 (4H, q, *J* = 7.2), 2.92 (2H, t, *J* = 5.8), 2.72 (2H, t, *J* = 5.9), 1.10 (6H, t, *J* = 7.2), 0.38 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.9, 147.5, 139.4, 137.8, 135.8, 132.5, 130.8, 129.5, 129.4, 128.4, 124.9, 119.3, 118.7 (q, $J_{C-F}$ = 321), 63.0, 55.5, 50.3, 42.1, 29.2, 14.2, 2.0. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.6. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2957w, 2897w, 1598m, 1424m, 1327m, 1203s, 1135s, 943m, 835s, 708m, 599m. **HRMS (NSI)** calcd for $C_{24}H_{34}F_3N_2O_5S_2Si^+$ $[M+H]^+$: 579.1625; found 579.1610.

***tert*-Butyl (*S*)-2-(3-(((trifluoromethyl)sulfonyl)oxy)-2-(trimethylsilyl)benzyl)-1,2,3,4-tetrahydroisoquinoline-3-carboxylate 1g:**



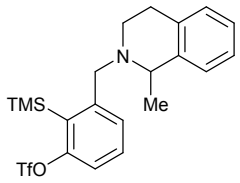

3-(((Methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (212 mg, 521 μmol) and *tert*-butyl (*S*)-1,2,3,4-tetrahydroisoquinoline-3-carboxylate hydrochloride (169 mg, 626 μmol) were subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9:1) afforded *tert*-butyl (*S*)-2-(3-(((trifluoromethyl)sulfonyl)oxy)-2-(trimethylsilyl)benzyl)-1,2,3,4-tetrahydroisoquinoline-3-carboxylate **1g** (198 mg, 70%) as a colourless oil. $[\alpha]^{22}_D$ = 28.7 ° (c = 0.0017, $CHCl_3$). **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.68-7.66 (1H, m), 7.39-7.36 (1H, m), 7.26-7.23 (1H, m), 7.15-7.09 (3H, m), 6.97-6.95 (1H, m), 4.12 & 4.07 (2H, ABq, $J_{AB}$ = 14.2), 3.99 (1H, d, *J* = 15.5), 3.73 (1H, d, *J* = 15.5), 3.60 (1H, dd, *J* = 6.0, 3.3), 3.19 (1H, dd, *J* = 16.1, 5.9), 3.19 (1H, dd, *J* = 16.1, 3.2), 1.36 (9H, s), 0.42 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 171.9, 155.6, 148.1, 134.2, 132.5, 131.7, 130.8, 128.8, 128.6, 126.4, 126.2, 126.0, 118.9, 118.7 (q, $J_{C-F}$ = 320), 81.3, 59.7, 59.5, 50.6, 32.2, 28.3, 2.1. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.5. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2978w, 2933w, 1726s, 1598m, 1417s, 1248m, 1209s, 1139s, 932m, 833s, 743m, 608m. **HRMS (NSI)** calcd for $C_{25}H_{33}F_3NO_5SSi^+$ **HRMS (NSI)** calcd for $C_{23}H_{27}N_2O_2^+$ $[M+H]^+$: 563.2067; found 563.2069.

**3-((7-Nitro-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 1h:**



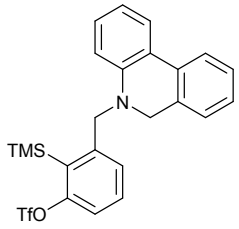

3-(((Methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (212 mg, 522 μmol) and 7-nitro-1,2,3,4-tetrahydroisoquinoline hydrochloride (134 mg, 626 μmol) were subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 4:1) afforded 3-((7'-nitro-3',4'-dihydroisoquinolin-2'(1'*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1h** (181 mg, 71%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.99 (1H, dd, *J* = 8.4, 2.2), 7.86 (1H, d, *J* = 2.0), 7.49-7.47 (1H, m), 7.42-7.38 (1H, m), 7.28-7.24 (2H, m), 3.79 (2H, s), 3.59 (2H, s), 2.96 (2H, t, *J* = 5.8), 2.71 (2H, t, *J* = 5.8), 0.40 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.9, 147.2, 146.3, 142.5, 136.3, 132.4, 130.8, 129.7, 129.4, 121.9, 121.4, 119.4, 118.7 (q, $J_{C-F}$ 320), 62.9, 55.5, 50.0, 29.4, 2.1. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.6. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2956w, 2805w, 1597m, 1416s, 1524s, 1344s, 1248s, 1211s, 1138s, 839s, 601s. **HRMS (TOF)** calcd for $C_{20}H_{24}F_3N_2O_5SSi^+$ $[M+H]^+$: 489.1127; found 489.1126.

**3-((1-Methyl-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 1i:**



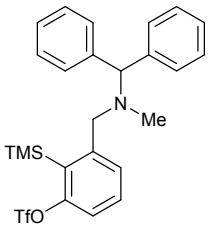

3-(((Methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (213 mg, 524 μmol), 1-methyl-1,2,3,4-tetrahydroisoquinoline (154 mg, 1.04 mmol) and potassium iodide (8.7 mg, 52 μmol) were subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9:1) afforded 3-((1-methyl-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1i** (196 mg, 82%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.66-7.64 (1H, m), 7.40-7.36 (1H, m), 7.24-7.22 (1H, m), 7.17-7.09 (3H, m), 7.06-7.02 (1H, m), 3.95 (1H, d, *J* = 14.1), 3.83 (1H, q, *J* = 6.7), 3.77 (1H, d, *J* = 14.1), 3.09-3.02 (1H, m), 2.95-2.87 (1H, m), 2.67-2.61 (2H, m), 1.36 (3H, d, *J* = 6.7), 0.40 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.5, 149.0, 140.2, 134.0, 131.9, 130.7, 129.1, 128.6, 127.6, 126.1, 125.9, 118.9, 118.8 (q, $J_{C-F}$ = 322), 58.5, 56.3, 42.7, 27.0, 19.7, 2.1. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.5. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2970w, 2837w, 1598m, 1415s, 1247m, 1206s, 1137s, 926m, 834s, 733m, 599s. **HRMS (NSI) calcd for $C_{21}H_{27}F_3NO_3SSi^+$ $[M+H]^+$:** 458.1428; found 458.1422.

**3-(Phenanthridin-5(6*H*)-ylmethyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 3a:**




According to a modified literature procedure,[6] sodium cyanoborohydride (631 mg, 10.0 mmol) was added portion-wise to a solution of phenanthridine (300 mg, 1.67 mmol) in acetic acid (6 mL) at 0 °C. The reaction mixture was stirred overnight at room temperature. Aqueous sodium hydroxide (1 M) was added to the reaction until the mixture reached pH 14. The reaction mixture was washed with dichloromethane (3 × 15 mL), dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude thus obtained and 3-(((methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (254 mg, 625 μmol) were then subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9:1) afforded 3-(phenanthridin-5(6*H*)-ylmethyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3a** (225 mg, 74%) as a white solid (**m.p**. 196-197 °C, recrystallized from $CH_2Cl_2$). **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.78-7.74 (2H, m), 7.46-7.44 (1H, m), 7.36-7.32 (2H, m), 7.27-7.15 (3H, m), 7.03-7.02 (1H, m), 6.92-6.88 (1H, m), 6.63-6.61 (1H, m), 4.60 (2H, s), 4.19 (2H, s), 0.45 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.8, 146.7, 146.0, 132.9, 132.2, 131.2, 131.0, 129.3, 127.9, 127.4, 127.3, 125.8, 124.0, 123.7, 122.7, 119.3 (2C), 118.8 (q, $J_{C-F}$ = 320), 113.1, 55.7, 52.5, 2.2. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.4. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3072w, 2957w, 2899w, 1600m, 1495m, 1420s, 1247m, 1205s, 1133s, 920m, 825s, 726s, 602s. **HRMS (NSI)** calcd for $C_{24}H_{25}F_3NO_3SSi^+$ $[M+H]^+$: 492.1271; found 492.1266.

**3-((Benzhydryl(methyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 3b:**

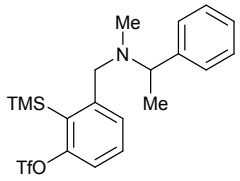



3-(((Methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (277 mg, 681 μmol) and *N*-(diphenylmethyl)methylamine (175 mg, 887 μmol) were subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9:1) afforded 3-((benzhydryl(methyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (227 mg, 80%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 8.07-8.05 (1H, m), 7.50-7.46 (5H, m), 7.31-7.29 (4H, m), 7.24-7.20 (3H, m), 4.60 (1H, s), 3.62 (2H, s), 2.08 (3H,

6 L. Matesic, J. M. Locke, K. L. Vine, M. Ranson, J. B. Bremmer and D. Skropeta, *Tetrahedron,* 2012, **68**, 6810–6819.

s), 0.33 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.0, 149.6, 142.6 (2C), 130.9, 130.8, 128.7 (4C), 128.1 (4C), 127.4, 127.3 (2C), 118.8 (q, $J_{C-F}$ = 321), 118.4, 75.9, 59.5, 40.4, 2.4 (3C). **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.3. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3032w, 2958w, 1597m, 1414s, 1248m, 1206s, 1136s, 920m, 837s, 760m, 704m, 599m. **HRMS (NSI)** calcd for $C_{25}H_{29}F_3NO_3SSi^+$ $[M+H]^+$: 508.1584; found 508.1573.

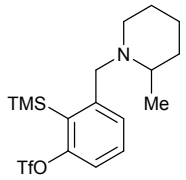
**3-((Methyl(1-phenylethyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 3c:**




According to a literature procedure,[7] a mixture of α-methylbenzylamine (319 μL, 2.48 mmol) and methyl trifluoromethanesulfonate (406 μL, 3.71 mmol) in hexafluoroisopropanol (2.5 mL) were stirred for 1 hour at room temperature. The reaction was quenched by the addition of aqueous hydrogen chloride (2 M, 2.5 mL) and the reaction mixture was concentrated *in vacuo*. The reaction mixture was then dissolved in dichloromethane (15 mL), washed with sodium bicarbonate (2 × 10 mL), dried over magnesium sulfate, filtered and concentrated *in vacuo*. The crude thus obtained, 3-(((methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (375 mg, 923 μmol) and potassium iodide (14.9 mg, 92.3 μmol) were then subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9:1) afforded 3-((methyl(1-phenylethyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3c** (213 mg, 52%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.77-7.76 (1H, m), 7.40-7.32 (5H, m), 7.27-7.23 (1H, m), 7.18-7.16 (1H, m), 3.73 (1H, q, $J$ = 6.8), 3.60 & 3.55 (2H, ABq, $J_{AB}$ = 14.3), 2.06 (3H, s), 1.45 (3H, d, $J$ = 6.8), 0.38 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.1, 149.8, 143.4, 131.0, 130.7, 128.4, 128.1, 127.8, 127.1, 118.8 (q, $J_{C-F}$ = 320), 118.5, 63.7, 58.9, 38.0, 18.2, 2.4. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.3. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3026w, 2973w, 1599m, 1413s, 1248m, 1207s, 1137s, 922m, 834s, 701m, 600m. **HRMS (NSI)** calcd for $C_{20}H_{27}F_3NO_3SSi^+$ $[M+H]^+$: 446.1428; found 446.1423.

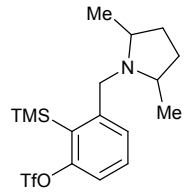
**3-((2-Methylpiperidin-1-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 3d:**

7 T. Lebleu, X. Ma, J. Maddaluno and J. Legros, *Chem. Commun.,* 2014, **50**, 1836–1838.




3-(((Methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (211 mg, 519 μmol) and 2-methylpiperidine (122 μL, 1.04 mmol) were subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9:1) afforded 3-((2-methylpiperidin-1-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3d** (151 mg, 84%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.76-7.74 (1H, m), 7.74-7.34 (1H, m), 7.18-7.16 (1H, m), 3.98 (1H, d, *J* = 14.4), 3.33 (1H, d, *J* = 14.4), 2.60-2.57 (1H, m), 2.46-2.44 (1H, m), 2.03-1.98 (1H, m), 1.68-1.63 (2H, m), 1.49-1.46 (2H, m), 1.37-1.35 (2H, m), 1.06 (3H, d, *J* = 6.2), 0.45 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.2, 150.3, 130.9, 130.6, 128.2, 118.8 (q, $J_{C-F}$ = 320), 118.3, 58.9, 56.4, 51.6, 34.5, 26.3, 23.3, 18.0, 2.5. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.3. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2934m, 2857w, 1598m, 1416s, 1248m, 1205s, 1136s, 920m, 836s, 599s. **HRMS (NSI)** calcd for $C_{17}H_{27}F_3NO_3SSi^+$ $[M+H]^+$: 410.1428; found 410.1424.

**3-((2,5-Dimethylpyrrolidin-1-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 3e:**

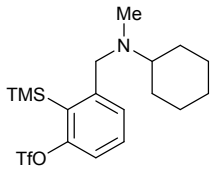



According to a literature procedure,[8] a mixture of sodium cyanoborohydride (688 mg, 62.8 mmol), ammonium acetate (844 mg, 77.1 mmol), potassium hydroxide (148 mg, 55.7 mmol) and 2,5-hexanedione (1.00 mL, 8.52 mmol) in methanol (6 mL) were stirred overnight at room temperature. Sodium borohydride (500 mg, 37.8 mmol) was added portion-wise at 0 °C and the reaction mixture was stirred for 3 hours at room temperature. Aqueous sodium hydroxide (1 M) was added to the reaction until pH 14 was reached. The reaction mixture was extracted with diethyl ether (10 mL × 3), dried over magnesium sulfate, filtered and concentrated *in vacuo* to a reduced volume of 2 mL. The crude thus obtained and 3-(((methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (207 mg, 505 μmol) were then subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9:1) afforded 3-((2,5-dimethylpyrrolidin-1-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3e** (174 mg, 83%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.93-7.91 (1H, m), 7.36-7.32 (1H, m), 7.16-7.14 (1H, m), 3.76 (2H, s), 2.68-2.61 (2H, m), 1.91-1.82 (2H, m), 1.46-1.36 (2H, m), 0.90 (6H, d, *J* = 6.1), 0.45 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 154.8, 152.3, 130.1, 129.4, 129.0, 118.8 (q, $J_{C-F}$ = 320),

8 T. H. Jones, J. Franko, M. S. Blum and H. M. Fales, *Tetrahedron Lett.,* 1980, **21**, 789–792.

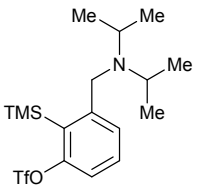
118.1, 62.8, 57.9, 31.8, 21.3, 2.6. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.0. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2961m, 2872w, 1599m, 1418s, 1248m, 1207s, 1138s, 925m, 830s, 601s. **HRMS (TOF)** calcd for $C_{17}H_{27}F_3NO_3SSi^+$ $[M+H]^+$: 410.1430; found 410.1433.

**3-((Cyclohexyl(methyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 3f:**



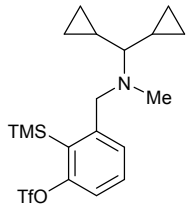

3-(((Methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (134 mg, 330 μmol) and *N*-methylcyclohexylamine (86 μL, 0.66 mmol) were subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9:1) afforded 3-((cyclohexyl(methyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3f** (96.0 mg, 69%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.66-7.63 (1H, m), 7.38-7.34 (1H, m), 7.19-7.17 (1H, m), 3.70 (2H, s), 2.44-2.40 (1H, m), 2.08 (3H, s), 1.85-1.79 (4H, m), 1.66-1.62 (1H, m), 1.33-1.19 (4H, m), 1.16-1.08 (1H, m), 0.43 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.3, 150.2, 131.3, 130.6, 128.4, 118.8 (q, $J_{C–F}$ = 320), 118.5, 62.9, 58.7, 36.7, 28.8, 26.6, 26.2, 2.3. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.4. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2929m, 2855w, 1598m, 1416s, 1247m, 1206s, 1137s, 927m, 830s, 599s. **HRMS (NSI)** calcd for $C_{18}H_{29}F_3NO_3SSi^+$ $[M+H]^+$: 424.1584; found 424.1582.

**3-((Diisopropylamino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 3g:**



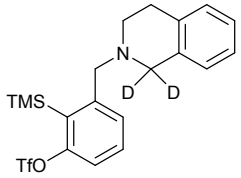

3-(((Methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (193 mg, 475 μmol) and *N,N*-diisopropylamine (133 μL, 949 μmol) were subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9:1) afforded 3-((diisopropylamino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3g** (164 mg, 85%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.94-7.92 (1H, m), 7.38-7.34 (1H, m), 7.16-7.14 (1H, m), 3.73 (2H, s), 3.00 (2H, sep, $J$ = 6.6), 1.02 (12H, d, $J$ = 6.6), 0.46 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 154.9, 152.9, 130.6, 129.7, 127.1, 118.8 (q, $J_{C–F}$ = 320), 118.0, 49.9, 48.3, 21.0, 2.5. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.3. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2966m, 2906w, 1599m, 1417s, 1250m, 1204s, 1137s, 922m, 827s, 599m. **HRMS (NSI)** calcd for $C_{17}H_{29}F_3NO_3SSi^+$ $[M+H]^+$: 412.1584; found 412.1582.

**3-(((Dicyclopropylmethyl)(methyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 3h:**




3-(((Methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (270 mg, 664 μmol) and (dicyclopropylmethyl)methylamine (100 mg, 799 μmol) were subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9:1) afforded 3-(((dicyclopropylmethyl)(methyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3h** (204 mg, 70%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.79-7.77 (1H, m), 7.40-7.36 (1H, m), 7.19-7.17 (1H, m), 3.89 (2H, s), 2.23 (3H, s), 1.44 (1H, t, *J* = 8.3), 0.98-0.89 (2H, m), 0.56-0.49 (4H, m), 0.45 (9H, s), 0.35-0.23 (4H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.4, 150.4, 131.1, 130.7, 128.1, 118.8 (q, $J_{C–F}$ = 320), 118.4, 72.3, 58.9, 37.4, 12.1, 3.4, 3.0, 2.4. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.3. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3080w, 2954w, 1598m, 1415s, 1248m, 1206s, 1137s, 923m, 830s, 600s. **HRMS (NSI)** calcd for $C_{19}H_{29}F_3NO_3SSi^+$ $[M+H]^+$: 436.1584; found 436.1584.

**3-((3,4-Dihydroisoquinolin-2(1*H*)-yl-1,1-*d*$_2$)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 1a-*d*$_2$:**




According to modified a literature procedure,[9] paraformaldehyde-$d_2$ (100 mg, 3.35 mmol) was added to a stirred solution of *N*-phenethylformamide (476 μL, 3.35 mmol) in formic acid (1.4 mL) and the resulting mixture was heated at 50 °C for 24 hours. Aqueous sodium hydroxide (1 M) was added to the solution until pH = 14 was reached. Dichloromethane (20 mL) was added and the organic layer was washed with saturated aqueous sodium carbonate (2 × 20 mL) then dried over magnesium sulphate, filtered and concentrated *in vacuo*. Potassium hydroxide (350 mg, 6.26 mmol) was added to the crude mixture in a 1:1 mixture of ethanol (10 mL) and water (10 mL). The reaction mixture was stirred for 2 hours at 100 °C then quenched with saturated aqueous sodium bicarbonate (20 mL) and extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried over magnesium sulphate, filtered and concentrated *in vacuo*. The crude product thus obtained and 3-(((methylsulfonyl)oxy)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **14** (512 mg, 1.26 mmol) were then subjected to the general procedure for the synthesis of hydride transfer scaffolds. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9:1) afforded 3-((3,4-dihydroisoquinolin-2(1*H*)-yl-1,1-$d_2$)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a-*d*$_2$** (511 mg, 91%) as a colourless oil. **$^1$H**

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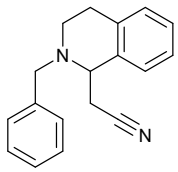
**NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.57-7.55 (1H, m), 7.42-7.38 (1H, m), 7.28-7.26 (1H, m), 7.18-7.11 (3H, m), 7.00-6.97 (1H, m), 3.79 (2H, s), 2.91 (2H, t, $J$ = 5.9), 2.71 (2H, t, $J$ = 5.9), 0.44 (9H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 155.8, 148.0, 134.6, 134.5, 132.3, 130.6, 129.3, 128.8, 126.7, 126.3, 125.8, 119.0, 118.7 (q, $J_{C–F}$ = 321), 63.1, 55.2 (quint, $J_{C–D}$ = 21.2), 50.7, 29.1, 2.1. **$^{19}$F NMR (376 MHz, $C_6F_6$):** $\delta_F$ = –76.6. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2951w, 2906w, 1598m, 1414m, 1247m, 1205s, 1136s, 932m, 915m, 833s, 739m, 598m. **HRMS (NSI)** calcd for $C_{20}H_{23}D_2F_3NO_3SSi^+$ $[M+H]^+$: 446.1397; found 446.1393.

## 4. Synthesis and characterization of hydride transfer products

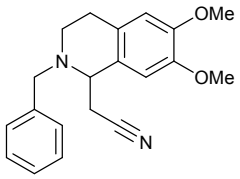
***General procedure for hydride transfer onto aryne:***

**2-(2-Benzyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile 2a:**



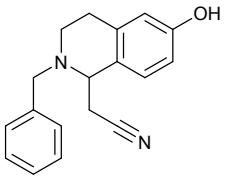
A stirred solution of potassium fluoride (13.9 mg, 239 μmol) and 18-crown-6 (63.4 mg, 240 μmol) in 1,2-dimethoxyethane (9.0 mL) was heated at 90 °C for 10 minutes. A solution of 3-((3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (53.2 mg, 120 μmol) in acetonitrile (3.0 mL) was added and the reaction mixture was left to stir at 90 °C. The reaction was monitored by LC-MS and once complete, the mixture was allowed to cool to room temperature and the solvent then removed *in vacuo*. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 7:3) afforded 2-(2-benzyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile **2a** (24.2 mg, 77%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.45-7.43 (2H, m), 7.37-7.34 (2H, m), 7.31-7.27 (1H, m), 7.24-7.19 (2H, m), 7.17-7.14 (1H, m), 7.12-7.09 (1H, m), 4.10-4.07 (1H, m), 3.86 & 3.81 (2H, ABq, $J_{AB}$ = 13.6), 3.18-3.12 (1H, m), 2.99-2.91 (1H, m), 2.88-2.78 (2H, m), 2.74-2.68 (2H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 138.6, 135.2, 135.1, 129.5, 128.9, 128.6, 127.6, 127.5, 127.4, 126.5, 118.6, 58.5, 58.0, 43.9, 25.5, 25.2. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3026w, 2923w, 2247m, 1603m, 1494m, 1452m, 738s, 698m. **HRMS (NSI)** calcd for $C_{18}H_{19}N_2^+$ $[M+H]^+$: 263.1543; found 263.1546.

**2-(2-Benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile 2b:**



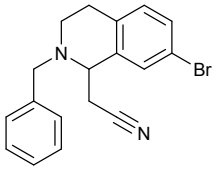
3-((6,7-Dimethoxy-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1b** (73.0 mg, 145 μmol) was subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 1:1) afforded 2-(2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile **2b** (41.1 mg, 88%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.43-7.42 (2H, m), 7.37-7.33 (2H, m), 7.30-7.28 (1H, m), 6.62 (1H, s), 6.60 (1H, s), 4.01-3.98 (1H, m), 3.87 (3H, s), 3.85 (3H, s), 3.81 (2H, br s apparent), 3.16-3.09 (1H, m), 2.92-2.77 (3H, m), 2.68 (1H, dd, *J* = 16.8, 5.6), 2.60-2.54 (1H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 148.5, 147.7, 138.6, 128.9, 128.6, 127.5, 127.0, 126.7, 118.8, 111.8, 110.3, 58.2, 57.6, 56.2, 56.0, 43.7, 25.0, 24.8. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3001w, 2935w, 2245m, 1610m, 1453m, 1357m, 1255s, 1226s, 1116s, 1101s, 1018m, 733s, 698s. **HRMS (TOF)** calcd for $C_{20}H_{23}N_2O_2^+$ $[M+H]^+$: 323.1760; found 323.1751.

**2-(2-Benzyl-7-hydroxy-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile 2c:**



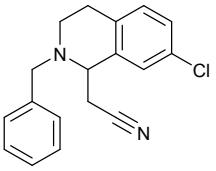

3-((7-Hydroxy-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1c** (54.0 mg, 11.7 μmol) was subjected to the general procedure for hydride transfer. The crude was dissolved in dichloromethane (15 mL) and washed with potassium chloride (3 × 10 mL), dried over magnesium sulfate, filtered and concentrated *in vacuo* affording 2-(2-benzyl-7-hydroxy-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile **2c** (20.6 mg, 63%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.43-7.41 (2H, m), 7.36-7.33 (2H, m), 7.30-7.28 (1H, m), 6.97 (1H, d, *J* = 8.3), 6.68 (1H, dd, *J* = 8.3, 2.5), 6.62 (1H, d, *J* = 2.2), 5.35 (1H, br s), 4.03 (1H, m), 3.84 & 3.78 (2H, ABq, $J_{AB}$ = 13.5), 3.14-3.07 (1H, m), 2.90-2.75 (3H, m), 2.71-2.63 (2H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 154.8, 138.6, 136.8, 128.9 (2C), 128.6, 127.5, 127.2, 118.7, 115.5, 114.0, 58.5, 57.6, 43.8, 25.8, 25.2. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3363w, 3027w, 2922m, 2250m, 1610m, 1497m, 1453m, 1365m, 1154m, 736s, 699m. **HRMS (NSI)** calcd for $C_{18}H_{19}N_2O^+$ $[M+H]^+$: 279.1496; found 279.1492.

**2-(2-Benzyl-7-bromo-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile 2d:**



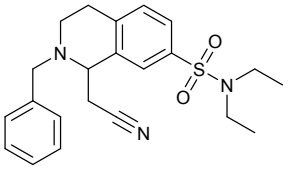

3-((7-Bromo-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1d** (41.0 mg, 78.5 μmol) was subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 4:1) afforded 2-(2-benzyl-7-bromo-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile **2d** (12.0 mg, 45%) as a white solid (**m.p.** 119-120 °C, recrystallized from $CH_2Cl_2$). **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.42-7.41 (2H, m), 7.37-7.32 (3H, m), 7.31-7.27 (1H, m), 7.23 (1H, d, *J* = 1.9), 7.03 (1H, d, *J* = 8.2), 4.04-4.01 (1H, m), 3.82 & 3.78 (2H, ABq, $J_{AB}$ = 13.6), 3.19-3.10 (1H, m), 2.91-2.61 (5H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 138.2, 137.2, 134.2, 131.2, 130.6, 130.4, 128.9, 128.7, 127.6, 119.9, 118.1, 58.3, 57.5, 43.6, 25.2, 24.9. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3061w, 2925w, 2247m, 1592m, 1484m, 1454m, 738s, 699s. **HRMS (NSI)** calcd for $C_{18}H_{18}BrN_2^+$ $[M+H]^+$: 341.0648 ($^{79}$Br) & 343.0627 ($^{81}$Br); found 341.0654 ($^{79}$Br) & 343.0631 ($^{81}$Br).

**2-(2-Benzyl-7-chloro-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile 2e:**



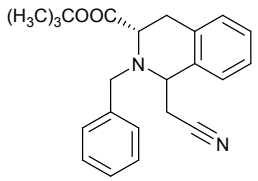

3-((7-Chloro-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1e** (65.0 mg, 136 μmol) was subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane) afforded 2-(2-benzyl-7-chloro-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile **2e** (16.5 mg, 41%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.42-7.41 (2H, m), 7.37-7.33 (2H, m), 7.31-7.27 (1H, m), 7.19 (1H, dd, *J* = 8.2, 2.1), 7.10-7.08 (2H, m), 4.04-4.01 (1H, m), 3.83 & 3.78 (2H, ABq, $J_{AB}$ = 13.5), 3.19-3.12 (1H, m), 2.93-2.63 (5H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 138.2, 136.7, 133.7, 132.0, 130.9, 128.9, 128.7, 127.7, 127.6, 127.4, 118.1, 58.4, 57.6, 43.7, 25.2, 24.9. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3063w, 3027w, 2925m, 2248m, 1600m, 1487s, 1454m, 1429m, 1365m, 1180m, 1092m, 740s, 700s. **HRMS (NSI)** calcd for $C_{18}H_{18}ClN_2^+$ $[M+H]^+$: 297.1153; found 297.1158.

**2-Benzyl-1-(cyanomethyl)-*N*,*N*-diethyl-1,2,3,4-tetrahydroisoquinoline-7-sulfonamide 2f:**



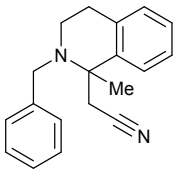

3-((7-(*N*,*N*-Diethylsulfamoyl)-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1f** (71.0 mg, 123 μmol) was subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 3:2) afforded 2-benzyl-1-(cyanomethyl)-*N*,*N*-diethyl-1,2,3,4-tetrahydroisoquinoline-7-sulfonamide **2f** (16.1 mg, 33%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.66-7.63 (1H, m), 7.58-7.57 (1H, m), 7.40-7.33 (4H, m), 7.31-7.27 (2H, m), 4.14-4.11 (1H, m), 3.84 & 3.79 (2H, ABq, $J_{AB}$ = 13.5), 3.25 (4H, q, *J* = 7.2), 3.20-3.13 (1H, m), 3.00-2.92 (1H, m), 2.87-2.73 (4H, m), 1.13 (6H, t, *J* = 7.1). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 140.4, 138.7, 138.0, 136.1, 130.3, 128.8, 128.7, 127.7, 126.3, 125.8, 117.9, 58.7, 57.7, 43.8, 42.3, 26.2, 24.8, 14.4. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2977w, 2933w, 2248m, 1600m, 1455m, 1331s, 1200m, 1150s, 1117m, 934m, 706s. **HRMS (NSI)** calcd for $C_{22}H_{28}N_3O_2S^+$ $[M+H]^+$: 398.1897; found 398.1894.

***tert*-Butyl 2-benzyl-1-(cyanomethyl)-1,2,3,4-tetrahydroisoquinoline-3-carboxylate 2g:**



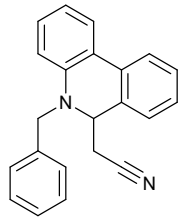

*tert*-Butyl (*S*)-2-(3-(((trifluoromethyl)sulfonyl)oxy)-2-(trimethylsilyl)benzyl)-1,2,3,4-tetrahydroisoquinoline-3-carboxylate **1g** (48.0 mg, 88.3 μmol) was subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 4:1) afforded *tert*-butyl 2-benzyl-1-(cyanomethyl)-1,2,3,4-tetrahydroisoquinoline-3-carboxylate **2g** (10.0 mg, 31%) as a yellow oil and an inseparable 2:1 mixture of diastereoisomers. **Major diastereoisomer $^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.45-7.42 (2H, m), 7.38-7.35 (2H, m), 7.31-7.29 (1H, m), 7.26-7.23 (1H, m), 7.22-7.07 (3H, m), 4.51-4.49 (1H, m), 4.09 (1H, d, *J* = 14.4), 3.98 (1H, d, *J* = 14.3), 3.74-3.72 (1H, m), 3.32 (1H, dd, *J* = 15.5, 5.0), 3.02-2.96 (1H, m), 2.84 (1H, dd, *J* = 16.6, 5.0), 2.68 (1H, dd, *J* = 16.6, 3.8), 1.23 (9H, s). **Minor diastereoisomer $^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.45-7.42 (2H, m), 7.38-7.33 (2H, m), 7.31-7.29 (1H, m), 7.26-7.23 (1H, m), 7.22-7.07 (3H, m), 4.17-4.13 (1H, m), 4.00 (1H, d, *J* = 13.7), 3.82 (1H, d, *J* = 13.7), 3.45 (1H, dd, *J* = 9.3, 5.7), 3.08 (1H, dd, *J* = 15.7, 9.4), 3.02-2.96 (1H, m), 2.72-2.65 (1H, m), 2.46 (1H, dd, *J* = 16.7, 7.6), 1.49 (9H, s). **Major diastereoisomer $^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 172.3, 138.9, 135.9, 133.3, 129.1, 128.8, 128.5, 127.6, 127.2, 127.0, 126.6, 118.1, 81.2, 58.8, 57.6, 56.5, 33.2, 28.1, 27.8. **Minor diastereoisomer $^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 173.1, 138.5, 135.3, 133.8, 129.0, 128.7, 128.4, 128.0, 127.8, 127.1, 126.9, 118.6, 81.5, 61.5, 60.7, 58.9, 30.5, 28.0, 26.8. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3975m, 2925m, 2247m, 1603m, 1494m, 1455s, 1367s, 1252m, 1151m, 744s, 700s. **HRMS (NSI)** calcd for $C_{23}H_{27}N_2O_2^+$ $[M+H]^+$: 363.2067; found 363.2069.

**2-(2-Benzyl-1-methyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile 2i:**



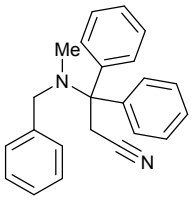

3-((1-Methyl-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1i** (70.0 mg, 153 μmol) was subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 4:1) afforded 2-(2-benzyl-1-methyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile **2i** (26.6 mg, 63%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.51-7.49 (2H, m), 7.37-7.34 (2H, m), 7.29-7.23 (3H, m), 7.22-7.18 (1H, m), 7.12-7.10 (1H, m), 3.96 (1H, d, *J* = 14.0), 3.62 (1H, d, *J* = 14.0), 3.03-2.81 (4H, m), 2.73-2.64 (2H, m), 1.60 (3H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 140.1, 139.8, 134.0, 129.4, 128.6, 128.4, 127.2, 126.9, 126.5, 126.2, 118.0, 59.9, 53.6, 43.0, 30.2, 29.8, 23.2. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3062w, 3026w, 2930w, 2245m, 1602m, 1493s, 1452s, 1373m, 1135m, 761s, 734s, 700s. **HRMS (NSI)** calcd for $C_{19}H_{21}N_2^+$ $[M+H]^+$: 277.1699; found 277.1701.

**2-(5-Benzyl-5,6-dihydrophenanthridin-6-yl)acetonitrile 4a:**



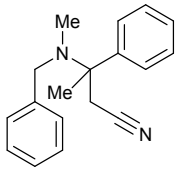
3-(Phenanthridin-5(6*H*)-ylmethyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3a** (48.0 mg, 97.6 μmol) was subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 7:3) afforded 2-(5'-benzyl-5',6'-dihydrophenanthridin-6'-yl)acetonitrile **4a** (21.8 mg, 72%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.78-7.76 (2H, m), 7.41-7.36 (1H, m), 7.28-7.16 (7H, m), 7.13-7.12 (1H, m), 6.93-6.89 (1H, m), 6.82-6.80 (1H, m), 4.79 (1H, d, *J* = 15.2), 4.68-4.64 (1H, m), 4.52 (1H, d, *J* = 15.2), 2.55 (1H, dd, *J* = 16.5, 6.6), 2.35 (1H, dd, *J* = 16.5, 7.1). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 142.0, 137.1, 132.8, 130.8, 129.7, 128.93, 128.87, 127.74, 127.73, 127.6, 126.2, 123.9, 123.3, 123.0, 119.8, 118.2, 115.6, 58.6, 54.5, 20.9. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3065w, 3032w, 2919w, 2247m, 1603m, 1492s, 1442s, 756m, 730s. **HRMS (NSI)** calcd for $C_{22}H_{19}N_2^+$ $[M+H]^+$: 311.1543; found 311.1546.

**3-(Benzyl(methyl)amino)-3,3-diphenylpropanenitrile 4b:**



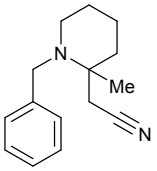
3-((Benzhydryl(methyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3b** (71.0 mg, 140 μmol) was subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 4:1) afforded 3-(benzyl(methyl)amino)-3,3-diphenylpropanenitrile **4b** (24.2 mg, 53%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.49-7.46 (6H, m), 7.42-7.38 (4H, m), 7.37-7.32 (4H, m), 7.28-7.24 (1H, m), 3.52 (2H, s), 3.40 (2H, s), 2.11 (3H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 139.9, 139.6, 128.6, 128.5, 128.2, 128.1, 127.8, 127.0, 117.8, 70.0, 56.2, 35.9, 29.5. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3058w, 2921w, 2250m, 1603m, 1494s, 1446s, 1265m, 1028m, 735s, 700s. **HRMS (NSI)** calcd for $C_{23}H_{23}N_2^+$ $[M+H]^+$: 327.1856; found 327.1858.

**3-(Benzyl(methyl)amino)-3-phenylbutanenitrile 4c:**



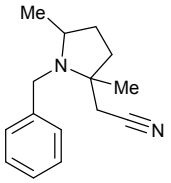

3-((Methyl(1-phenylethyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3c** (42.0 mg, 94.3 μmol) was subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 4:1) afforded 3-(benzyl(methyl)amino)-3-phenylbutanenitrile **4c** (8.00 mg, 32%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.69-7.67 (2H, m), 7.41-7.38 (2H, m), 7.33-7.28 (5H, m), 7.26-7.21 (1H, m), 3.50 & 3.41 (2H, ABq, $J_{AB}$ = 13.5), 2.90 & 2.83 (2H, ABq, $J_{AB}$ = 16.6), 2.18 (3H, s), 1.66 (3H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 144.7, 139.8, 128.7, 128.4, 128.3, 127.8, 127.0, 126.4, 118.3, 62.3, 56.5, 34.8, 29.1, 19.6. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3027w, 2929w, 2246m, 1602m, 1494s, 1452s, 1375s, 1217s, 765m, 742m, 699s. **HRMS (NSI)** calcd for $C_{18}H_{21}N_2^+$ $[M+H]^+$: 265.1699; found 265.1702.

**2-(1-Benzyl-2-methylpiperidin-2-yl)acetonitrile 4d:**




3-((2-Methylpiperidin-1-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3d** (75.0 mg, 183 μmol) was subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 4:1) afforded 2-(1-benzyl-2-methylpiperidin-2-yl)acetonitrile **4d** (21.3 mg, 51%) as a pale green oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.38-7.36 (2H, m), 7.32-7.30 (2H, m), 7.25-7.21 (1H, m), 3.58 & 3.47 (2H, ABq, $J_{AB}$ = 13.8), 2.74 (1H, d, $J$ = 16.7), 2.45 (1H, d, $J$ = 16.7), 2.40-2.36 (2H, m), 1.90-1.85 (1H, m), 1.64-1.46 (5H, m), 1.30 (3H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 140.0, 128.41, 128.40, 127.0, 118.7, 55.7, 54.0, 47.0, 37.8, 26.0, 25.0, 21.1, 20.9. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3027w, 2934m, 2247m, 1604m, 1495m, 1452s, 1376m, 1127s, 1068m, 738s, 713s, 696s. **HRMS (NSI)** calcd for $C_{15}H_{21}N_2^+$ $[M+H]^+$: 229.1699; found 229.1701.

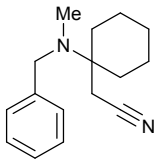
**2-(1-Benzyl-2,5-dimethylpyrrolidin-2-yl)acetonitrile 4e:**




3-((2,5-Dimethylpyrrolidin-1-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3e** (94.0 mg, 229 μmol) was subjected to the general procedure for hydride transfer. Silica gel

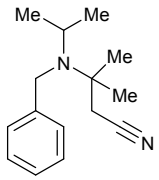
flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 4:1) afforded a 2:1 mixture of diastereoisomers of 2-(1-benzyl-2,5-dimethylpyrrolidin-2-yl)acetonitrile **4e** (24.1 mg, 46%) as a brown oil. **Major diastereoisomer $^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.41-7.35 (2H, m), 7.31-7.27 (2H, m), 7.23-7.22 (1H, m), 3.87 (1H, d, *J* = 14.8), 3.57 (1H, d, *J* = 14.8), 3.12-3.04 (1H, m), 2.44 & 2.34 (2H, ABq, $J_{AB}$ = 16.4), 2.10-1.83 (3H, m), 1.57-1.42 (1H, m), 1.29 (3H, s), 0.86 (3H, d, *J* = 6.2). **Major diastereoisomer $^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 141.4, 128.40 or 128.35, 128.27 or 128.0, 126.8, 119.4, 63.3, 58.5, 50.2, 36.9, 30.2, 26.4, 24.7, 21.0. **Minor diastereoisomer $^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.41-7.35 (2H, m), 7.31-7.27 (2H, m), 7.23-7.22 (1H, m), 3.76 (1H, d, *J* = 14.8), 3.63 (1H, d, *J* = 14.8), 2.98-2.90 (1H, m), 2.23-2.15 (2H, m), 2.10-1.83 (1H, m), 1.74-1.67 (1H, m), 1.57-1.42 (2H, m), 1.19 (3H, s), 0.97 (3H, d, *J* = 6.1). **Minor diastereoisomer $^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 141.5, 128.40 or 128.35, 128.27 or 128.0, 127.0, 118.9, 63.0, 60.0, 51.5, 37.7, 31.2, 30.9, 22.0, 20.8. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3027m, 2928m, 2245m, 1605m, 1495m, 1454s, 1378s, 1209m, 1146m, 727s, 697s. **HRMS (NSI)** calcd for $C_{15}H_{21}N_2^+$ $[M+H]^+$: 229.1699; found 229.1700.

**2-(1-(Benzyl(methyl)amino)cyclohexyl)acetonitrile 4f:**




3-((Cyclohexyl(methyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3f** (74.0 mg, 175 μmol) was subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 4:1) afforded 2-(1-(benzyl(methyl)amino)cyclohexyl)acetonitrile **4f** (16.5 mg, 39%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.36-7.30 (4H, m), 7.26-7.20 (1H, m), 3.66 (2H, s), 2.45 (2H, s), 2.14 (3H, s), 2.02-1.99 (2H, m), 1.84-1.74 (2H, m), 1.71-1.58 (3H, m), 1.51-1.33 (3H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 140.5, 128.5, 128.2, 126.9, 119.2, 57.9, 53.5, 34.2, 33.4, 25.8, 21.8, 21.4. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3030w, 2934m, 2240m, 1603m, 1494m, 1454s, 1365s, 1229m, 1217s, 739m, 697m. **HRMS (NSI)** calcd for $C_{16}H_{23}N_2^+$ $[M+H]^+$: 243.1856; found 243.1858.

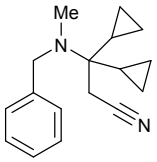
**3-(Benzyl(isopropyl)amino)-3-methylbutanenitrile 4g:**




3-((Diisopropylamino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3g** (89.0 mg, 216 μmol) was subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9:1) afforded 3-(benzyl(isopropyl)amino)-3-methylbutanenitrile **4g** (18.4 mg, 37%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.43-7.41 (2H, m), 7.31-7.27 (2H, m), 7.20-7.16 (1H, m), 3.83 (2H, s), 2.43 (1H, sep, *J* = 6.6), 2.44 (2H, s), 1.25 (6H, s), 1.08 (6H, d, *J* = 6.6). **$^{13}$C**

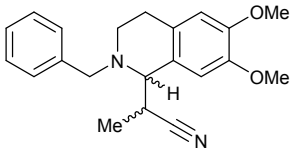
**NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 144.8, 128.3, 126.9, 126.3, 118.9, 58.1, 47.5, 46.0, 30.5, 26.8, 22.4. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3062w, 3027w, 2973m, 2245m, 1601m, 1493m, 1451s, 1387s, 1368s, 1238m, 1043m, 1026m, 939m, 745m, 712s, 696s. **HRMS (NSI)** calcd for $C_{15}H_{23}N_2^+$ $[M+H]^+$: 231.1856; found 231.1858.

**3-(Benzyl(methyl)amino)-3,3-dicyclopropylpropanenitrile 4h:**



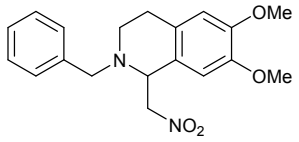

3-(((Dicyclopropylmethyl)(methyl)amino)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **3h** (70.0 mg, 161 μmol) was subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 4:1) afforded 3-(benzyl(methyl)amino)-3,3-dicyclopropylpropanenitrile **4h** (15.0 mg, 39%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.46-7.44 (2H, m), 7.34-7.31 (2H, m), 7.25-7.21 (1H, m), 3.87 (2H, s), 2.33 (2H, s), 2.32 (3H, s), 1.08-1.01 (2H, m), 0.56-0.50 (4H, m), 0.49-0.40 (4H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 140.8, 128.43, 128.37, 126.8, 118.4, 59.1, 55.3, 35.6, 23.7, 14.7, 1.9, 0.9. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3007w, 2850m, 2253m, 1494m, 1454m, 1365m, 1217m, 1048m, 1027m, 735s, 699m. **HRMS (NSI)** calcd for $C_{17}H_{23}N_2^+$ $[M+H]^+$: 255.1856; found 255.1859.

**2-(2-Benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolin-1-yl)propanenitrile 5b:**



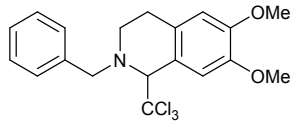

3-((6,7-Dimethoxy-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1b** (74.6 mg, 0.148 mmol) and propionitrile (3.70 mL) were subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (*n*-hexane:ethyl acetate 9:1 to 4:1, NH silica) afforded 2-(2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolin-1-yl)propanenitrile **5b** (33.0 mg, 66%) as a colourless oil and an inseparable 1:1 mixture of diastereoisomers. The data presented is for the 1:1 mixture of diastereoisomers. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.39-7.26 (10H, m), 6.80 (1H, s), 6.70 (1H, s), 6.63 (1H, s), 6.62 (1H, s), 3.88-3.86 (12H, m), 3.84-3.72 (6H, m), 3.63 (1H, d, *J* = 8.3), 3.33-3.26 (1H, m), 2.99-2.71 (6H, m), 2.66-2.52 (2H, m), 1.40 (3H d, *J* = 7.2), 1.24 (3H, d, *J* = 7.1). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 148.1, 148.0, 147.1, 146.9, 138.7, 138.6, 128.7, 128.5, 128.2, 128.1, 127.9, 127.1, 127.1, 126.6, 125.3, 124.9, 122.7, 122.5, 111.9, 111.3, 111.3, 110.6, 62.5, 62.0, 59.2, 58.0, 55.8, 55.8, 55.6, 55.6, 44.9, 43.0, 32.5, 32.2, 24.9, 23.3, 15.8, 14.4. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3027w, 2995w, 2935w, 1517s, 1453m, 1118s, 737s, 700s. **HRMS (NSI)** calcd for $C_{21}H_{25}N_2O_2^+$ $[M+H]^+$: 337.1911, found 337.1909.

**2-Benzyl-6,7-dimethoxy-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline 6b:**



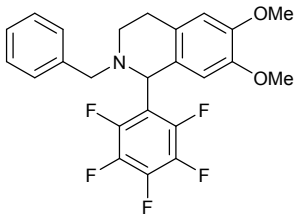

3-((6,7-Dimethoxy-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1b** (75.5 mg, 0.150 mmol) and nitromethane (3.75 mL) were subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (*n*-hexane:ethyl acetate 93:7 to 11:9, NH silica) afforded 2-benzyl-6,7-dimethoxy-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline **6b** (35.7 mg, 70%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.34-7.25 (5H, m), 6.63 (1H, s), 6.54 (1H, s) 4.72 (1H, m), 4.49-4.45 (2H, m), 3.87 (3H, s), 3.84 (3H, s), 3.83 (1H, d, *J* = 13.3), 3.74 (1H, d, *J* = 13.3), 3.24-3.14 (1H, m), 3.05-2.85 (2H, m), 2.45-2.39 (1H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 148.6, 147.8, 138.3, 128.7, 128.3, 127.3, 127.2, 123.6, 111.9, 110.0, 79.4, 59.3, 57.3, 56.0, 55.8, 41.8, 22.3. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3016w, 2936w, 1549s, 1379s, 1119s, 737s, 699m. **HRMS (NSI)** calcd for $C_{19}H_{23}N_2O_4^+$ $[M+H]^+$: 343.1652, found 343.1654.

**2-Benzyl-6,7-dimethoxy-1-(trichloromethyl)-1,2,3,4-tetrahydroisoquinoline 7b:**




3-((6,7-Dimethoxy-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1b** (70.7 mg, 0.140 mmol) and chloroform (1.40 mL) were subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (*n*-hexane:ethyl acetate 9:1, NH silica) afforded 2-benzyl-6,7-dimethoxy-1-(trichloromethyl)-1,2,3,4-tetrahydroisoquinoline **7b** (23.1 mg, 41%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.48-7.47 (2H, m), 7.36-7.32 (2H, m), 7.29-7.26 (1H, m), 7.06 (1H, s), 6.67 (1H, s), 4.57 (1H, s), 4.51 (1H, d, *J* = 14.1), 3.94 (1H, d, *J* =14.1), 3.89 (3H, s), 3.89 (3H, s), 3.31-3.26 (1H, m), 3.19-3.11 (1H, m), 2.61-2.55 (1H, m), 2.43-2.37 (1H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 148.9, 146.2, 138.8, 131.5, 128.2, 128.1, 127.0, 122.0, 115.1, 110.6, 107.2, 77.9, 63.6, 56.0, 55.7, 47.9, 28.2. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2958w, 2920w, 1514s, 1465m, 1276s, 727s, 680s. **HRMS (ASAP)** calcd for $C_{19}H_{21}Cl_3NO_2^+$ $[M+H]^+$: 400.0638, found 400.0643.

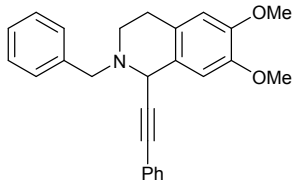
**2-Benzyl-6,7-dimethoxy-1-(perfluorophenyl)-1,2,3,4-tetrahydroisoquinoline 8b:**




3-((6,7-Dimethoxy-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1b** (69.8 mg, 0.139 mmol) and pentafluorobenzene (3.46 mL) were

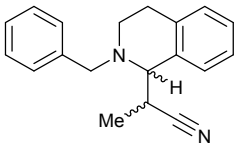
subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (*n*-hexane:ethyl acetate 19:1 to 7:1) afforded 2-Benzyl-6,7-dimethoxy-1-(perfluorophenyl)-1,2,3,4-tetrahydroisoquinoline **8b (**38.3 mg, 62%) as a colourless oil. **$^{1}$H NMR (400 MHz, CDCl$_3$):** $\delta_H$ = 7.28-7.26 (4H, m), 7.24-7.23 (1H, m), 6.63 (1H, s), 6.20 (1H, s), 5.15 (1H, s), 3.86 (3H, s), 3.70 (3H, s), 3.72 (1H, d, *J* = 13.7), 3.51 (1H, d, *J* = 13.7), 3.06-3.00 (2H, m), 2.68-2.64 (1H, m), 2.55-2.50 (1H, m). **$^{13}$C NMR (101 MHz, CDCl$_3$):** $\delta_C$ = 147.8, 147.3, 138.5, 128.2, 128.1, 127.9, 126.9, 126.6, 110.9, 109.6, 59.6, 58.1, 55.9, 55.7, 47.9, 28.7. **$^{19}$F NMR (376 MHz, CDCl$_3$):** $\delta_F$ = –162.2 - –162.1 (3F, m) -155.4 - –155.3 (2F, m). **IR (neat): $\nu_{max}$/cm$^{-1}$** 2935w, 2835w, 1519s, 1454m, 1333m, 1229m, 992s. **HRMS (ASAP)** calcd for $C_{24}H_{21}F_5NO_2^+$ $[M+H]^+$: 450.1492, found 450.1497.

**2-Benzyl-6,7-dimethoxy-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline 9b:**




3-((6,7-Dimethoxy-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1b** (74.9 mg, 0.149 mmol) and phenylacetylene (3.72 mL) were subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (*n*-hexane:ethyl acetate 93:7 to 11:9, NH Silica) afforded 2-benzyl-6,7-dimethoxy-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline **9b** (27.2 mg, 48%) as a colourless oil. **$^{1}$H NMR (400 MHz, CDCl$_3$):** $\delta_H$ = 7.49-7.44 (4H, m), 7.37-7.27 (6H, m), 6.75 (1H, s), 6.61 (1H, s), 4.70 (1H, s), 3.94 (2H, ABq, $J_{AB}$ = 13.1), 3.85 (3H, s), 3.84 (3H, s), 3.10-3.07 (1H, m), 3.01-2.93 (1H, m), 2.85-2.80 (1H, m), 2.74-2.69 (1H, m). **$^{13}$C NMR (101 MHz, CDCl$_3$):** $\delta_C$ = 148.0, 147.2, 138.2, 131.6, 129.1, 128.1, 128.1, 127.9, 127.2, 127.0, 125.9, 123.1, 111.2, 110.3, 87.4, 86.5, 59.4, 55.8, 55.7, 53.7, 45.8, 28.5. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3060w, 3028w, 2911m, 2831m, 1518s, 1452s, 1225s, 757s, 699s. **HRMS (NSI)** calcd for $C_{26}H_{26}NO_2^+$ $[M+H]^+$:384.1958, found 384.1955.

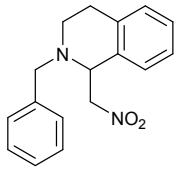
**2-(2-Benzyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propanenitrile 5a:**




3-((3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (50.0 mg, 0.113 mmol) and propionitrile (2.82 mL) were subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (*n*-hexane:ethyl acetate 4:1, NH silica) afforded 2-(2-benzyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propanenitrile **5a** (13.0 mg, 42%) as a colourless oil and an inseparable 1:1.2 mixture of diastereoisomers. **Major diastereoisomer $^{1}$H NMR (400 MHz, CDCl$_3$):** $\delta_H$ = 7.43-7.27 (5H, m), 7.24-7.12 (4H, m), 3.95-3.75 (3H, m), 3.15-2.67 (5H, m), 1.26 (3H, d, *J* = 7.1). **Minor diastereoisomers $^{1}$H NMR (400 MHz, CDCl$_3$):** $\delta_H$ = 7.43-7.27 (5H, m), 7.24-7.12 (4H, m), 3.95-3.75 (3H, m), 3.38-3.31 (1H, m), 3.15-2.67 (4H, m), 1.38 (3H, d, *J* = 7.2). **Major and Minor diastereoisomers $^{13}$C NMR (101 MHz, CDCl$_3$):** $\delta_C$ =

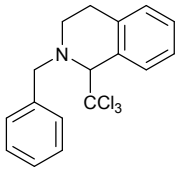
138.7, 138.6, 135.7, 134.3, 133.5, 129.2, 128.9, 128.9, 128.7, 128.6, 128.5, 128.2, 128.1, 127.6, 127.3, 127.2, 127.1, 126.3, 125.9, 125.8, 122.4, 122.3, 62.8, 62.7, 59.3, 58.8, 44.7, 43.8, 32.7, 32.6, 25.0, 24.7, 15.5, 14.9. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3066w, 3022w, 2937m, 2239w, 1604w, 1454s, 747s, 700s. **HRMS (NSI)** calcd for $C_{19}H_{21}N_2^+$ $[M+H]^+$: 277.1699, found 277.1700.

**2-Benzyl-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline 6a:**



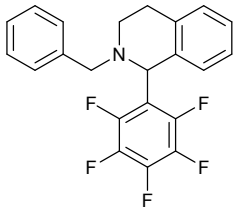

3-((3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (72.6 mg, 0.164 mmol) and nitromethane (4.10 mL) were subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (*n*-hexane:ethyl acetate 4:1, NH silica) afforded 2-benzyl-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline **6a** (32.5 mg, 70%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.44-7.29 (4H, m), 7.27-7.08 (5H, m), 4.74 (1H, dd, *J* = 11.6, 10.2), 4.56 (1H, dd, *J* = 10.2, 4.5), 4.48 (1H, dd, *J* = 11.6, 4.5), 3.84 (1H, d, *J* = 13.2), 3.76 (1H, d, *J* = 13.2), 3.25-3.18 (1H, m), 3.08-3.00 (1H, m), 2.96-2.91 (1H, m), 2.56-2.51 (1H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 138.0, 135.0, 131.8, 129.4, 128.5, 128.0, 127.4, 127.2, 127.1, 126.2, 79.1, 59.3, 57.2, 41.4, 22.5. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3027w, 2924m, 1552s, 1380m, 741m, 700m. **HRMS (NSI)** calcd for $C_{17}H_{19}N_2O_2^+$ $[M+H]^+$: 283.1441, found 283.1442.

**2-Benzyl-1-(trichloromethyl)-1,2,3,4-tetrahydroisoquinoline 7a:**



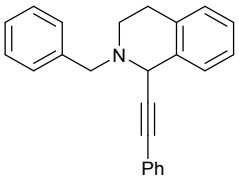

3-((3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (53.1 mg, 0.120 mmol) and chloroform (1.20 mL) were subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (*n*-hexane:ethyl acetate 9:1, NH silica) afforded 2-benzyl-1-(trichloromethyl)-1,2,3,4-tetrahydroisoquinoline **7a** (16.5 mg, 41%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.55 (1H, br d, *J* = 7.5), 7.49 (2H, br d, *J* = 7.5), 7.37-7.22 (5H, m), 7.19 (1H, br d, *J* = 7.5), 4.67 (1H, s), 4.57 (1H, d, *J* = 13.7), 3.95 (1H, d, *J* =13.7), 3.33-3.25 (2H, m), 2.68-2.62 (1H, m), 2.43-2.36 (1H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 139.0, 138.8, 131.9, 130.4, 128.3, 128.2, 128.1, 127.8, 127.0, 125.1, 106.9, 78.4, 63.9, 48.1, 29.0. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3029w, 2927w, 1494m, 1454m, 725s, 698s. **HRMS (NSI)** calcd for $C_{17}H_{17}Cl_3N^+$ $[M+H]^+$: 340.0421, found 340.0424.

**2-Benzyl-1-(perfluorophenyl)-1,2,3,4-tetrahydroisoquinoline 8a:**



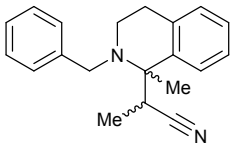
3-((3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (62.6 mg, 0.141 mmol) and pentafluorobenzene (3.53 mL) were subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (*n*-hexane:ethyl acetate 19:1 to 2:3, NH silica) afforded 2-benzyl-1-(perfluorophenyl)-1,2,3,4-tetrahydroisoquinoline **8a** (26.3 mg, 48%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.28-7.19 (5H, m), 7.16-7.05 (3H, m), 6.73 (1H, br d, $J$ = 7.7), 5.21 (1H, s), 3.74 (1H, d, $J$ = 13.6) 3.49 (1H, d, $J$ = 13.6), 3.17-3.06 (2H, m), 2.76-2.71 (1H, m), 2.56-2.50 (1H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 138.5, 135.5, 135.1, 128.4, 128.1, 128.1, 126.9, 126.9, 126.5, 125.9, 59.6, 58.5, 48.1, 29.2. **$^{19}$F NMR (376 MHz, $CDCl_3$):** $\delta_F$ = –162.4 - –162.2 (3F, m), –155.5 - –155.4 (2F, m). **IR (neat): $\nu_{max}$/cm$^{-1}$** 3028w, 2970w, 2947w, 1500s, 1455m, 1367s, 994s, 699s. **HRMS (NSI)** calcd for $C_{22}H_{17}F_5N^+$ $[M+H]^+$: 390.1276, found 390.1270.

**2-Benzyl-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline 9a:**



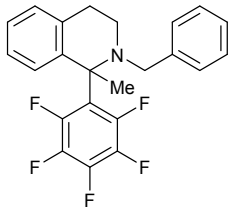
3-((3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (74.7 mg, 0.168 mmol) and phenylacetylene (4.21 mL) were subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 9:1) afforded 2-benzyl-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline **9a** (16.5 mg, 30%) as a colourless oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.53-7.33 (7H, m), 7.32-7.27 (4H, m), 7.21-7.13 (3H, m), 4.80 (1H, s), 3.95 (2H, ABq, $J_{AB}$ = 13.2), 3.13-3.00 (2H, m), 2.87-2.78 (2H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 138.2, 135.3, 133.9, 131.6, 129.1, 128.8, 128.1, 128.0, 127.9, 127.6, 127.0, 126.7, 125.6, 123.1, 87.4, 86.6, 59.4, 54.2, 45.6, 28.9. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3063w, 3030w, 2916w, 1489s, 1453m, 747s, 692s. **HRMS (NSI)** calcd for $C_{24}H_{22}N^+$ $[M+H]^+$: 324.1747, found 324.1747.

**2-(2-Benzyl-1-methyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propanenitrile 5i:**



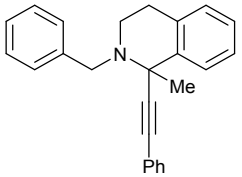

3-((1-Methyl-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1i** (78.4 mg, 0.171 mmol) and propionitrile (4.28 mL) were subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (*n*-hexane:ethyl acetate 9:1 to 4:1, NH silica) afforded 2-(2-benzyl-1-methyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propanenitrile **5i** (10.0 mg, 20%) as a yellow oil and an inseparable 1:1 mixture of diastereoisomers. The data presented is for the 1:1 mixture of diastereoisomers.. **$^{1}$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.69 (1H, br d, *J* = 7.9), 7.37-7.27 (6H, m), 7.21-6.99 (11H, m), 4.41 (1H, d, *J* = 14.3), 4.01 (1H, d, *J* = 14.3), 3.45 (1H, d, *J* = 14.3), 3.35 (1H, d, *J* = 14.3), 3.15 (1H, q, *J* = 7.1), 3.10 (1H, q, *J* 7.1), 2.85-2.72 (4H, m), 2.63-2.46 (4H, m), 1.70 (3H, s), 1.66 (3H, s), 1.22 (3H, d, *J* = 7.1), 1.03 (3H, d, *J* = 7.1). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 139.9, 139.7, 139.7, 138.6, 136.5, 136.4, 128.9, 128.6, 128.3, 128.2, 127.9, 127.7, 126.9, 126.7, 126.6, 126.5, 126.4, 126.3, 126.2, 126.0, 122.9, 122.7, 62.0, 61.6, 53.7, 53.5, 43.2, 42.7, 37.4, 34.1, 29.8, 28.6, 21.1, 20.9, 13.7, 13.4. **IR (neat): $\nu_{max}$/cm$^{-1}$** 2980w, 2937w, 2237w, 1603w, 1452s, 737s, 702s. **HRMS (NSI)** calcd for $C_{20}H_{23}N_2^+$ $[M+H]^+$: 291.1856, found 291.1858.

**2-Benzyl-1-methyl-1-(perfluorophenyl)-1,2,3,4-tetrahydroisoquinoline 8i:**



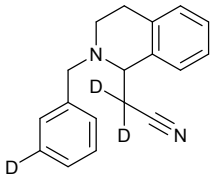

3-((1-Methyl-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1i** (71.8 mg, 0.157 mmol) and pentafluorobenzene (3.93 mL) were subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (*n*-hexane:ethyl acetate 19:1 to 7:3, NH silica) afforded 2-benzyl-1-methyl-1-(perfluorophenyl)-1,2,3,4-tetrahydroisoquinoline **8i** (31.7 mg, 50%) as a yellow oil. **$^{1}$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.34-7.26 (4H, m), 7.23-7.08 (4H, m), 6.87-6.85 (1H, m), 3.76 (1H, d, *J* = 14.2) 3.59 (1H, d, *J* = 14.2), 3.18-3.10 (1H, m), 2.89-2.83 (2H, m), 2.72-2.67 (1H, m), 1.94 (3H, t, $J_{H\text{-}F}$ = 4.3). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 142.9, 139.6, 133.8, 128.3, 128.2, 127.6, 126.8, 126.7, 126.1, 125.8, 65.1, 55.3, 42.0, 29.6, 21.5 (1C, t, $J_{C\text{-}F}$ = 5.9). **$^{19}$F NMR (376 MHz, $CDCl_3$):** $\delta_F$ = –162.9 - –162.8 (3F, m) –156.1 - –156.0 (2F, m). **IR (neat): $\nu_{max}$/cm$^{-1}$** 3016m, 2970m, 2947m, 1521s, 1480s, 1366s, 973s, 739s. **HRMS (NSI)** calcd for $C_{23}H_{19}F_5N^+$ $[M+H]^+$: 404.1432, found 404.1431.

**2-Benzyl-1-methyl-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline 9i:**



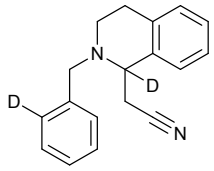

3-((1-Methyl-3,4-dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1i** (74.2 mg, 0.162 mmol) and phenylacetylene (4.05 mL) were subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (*n*-hexane:ethyl acetate 9:1, NH silica) afforded 2-benzyl-1-methyl-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline **9i** (29.8 mg, 55%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.59-7.56 (1H, m), 7.47-7.42 (4H, m), 7.35-7.31 (2H, m), 7.29-7.20 (5H, m), 7.17-7.13 (1H, m), 7.07-7.06 (1H, m), 4.13 (1H, d, $J$ = 14.4), 3.76 (1H, d, $J$ = 14.4), 2.92-2.79 (3H, m), 2.69-2.64 (1H, m), 1.87 (3H, s). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 140.8, 140.4, 133.9, 131.6, 128.6, 128.3, 128.0, 128.0, 127.7, 127.7, 126.6, 126.2, 125.8, 123.2, 92.3, 84.2, 58.1, 55.5, 44.1, 29.8, 28.6. **IR (neat): $\nu_{max}$/cm$^{-1}$** 3059w, 2921w, 2247w, 1490m, 1453m, 725s, 691s. **HRMS (NSI)** calcd for $C_{25}H_{24}N^+$ $[M+H]^+$: 338.1903, found 338.1903.

**2-(2-((Phenyl-3-*d*)methyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile-*$d_2$* 2a-*$d_3$*:**




3-((3,4-Dihydroisoquinolin-2(1*H*)-yl)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (222 mg, 500 µmol) was subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 7:3) afforded 2-(2-((phenyl-3-*d*)methyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acetonitrile-*$d_2$* **2a-*$d_3$*** (99.6 mg, 75%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.47-7.46 (2H, m), 7.40-7.36 (1H, m), 7.32-7.30 (1H, m), 7.25-7.20 (2H, m), 7.18-7.16 (1H, m), 7.13-7.11 (1H, m), 4.09 (1H, s), 3.87 & 3.82 (2H, ABq, $J_{AB}$ = 13.6), 3.16 (1H, ddd, $J$ = 13.0, 9.2, 4.7), 3.00-2.92 (1H, m), 2.90-2.84 (1H, m), 2.76-2.70 (1H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 138.5, 135.1, 135.0, 129.4, 128.8, 128.7, 128.5, 128.2 (t, $J_{C-D}$ = 24), 127.5, 127.3 (2C), 126.4, 118.5, 58.4, 57.8, 43.8, 25.5, 24.7 (quint, $J_{C-D}$ = 20). **IR (neat): $\nu_{max}$/cm$^{-1}$** 3060w, 3021w, 2923w, 2832w, 2248m, 1600m, 1452m, 1428m, 1365m, 1095m, 909m, 730s, 697m, 653m. **HRMS (NSI)** calcd for $C_{18}H_{16}D_3N_2^+$ $[M+H]^+$: 266.1731; found 266.1732.

**2-(2-((Phenyl-2-*d*)methyl)-1,2,3,4-tetrahydroisoquinolin-1-yl-1-*d*)acetonitrile 2a-$d_2$:**

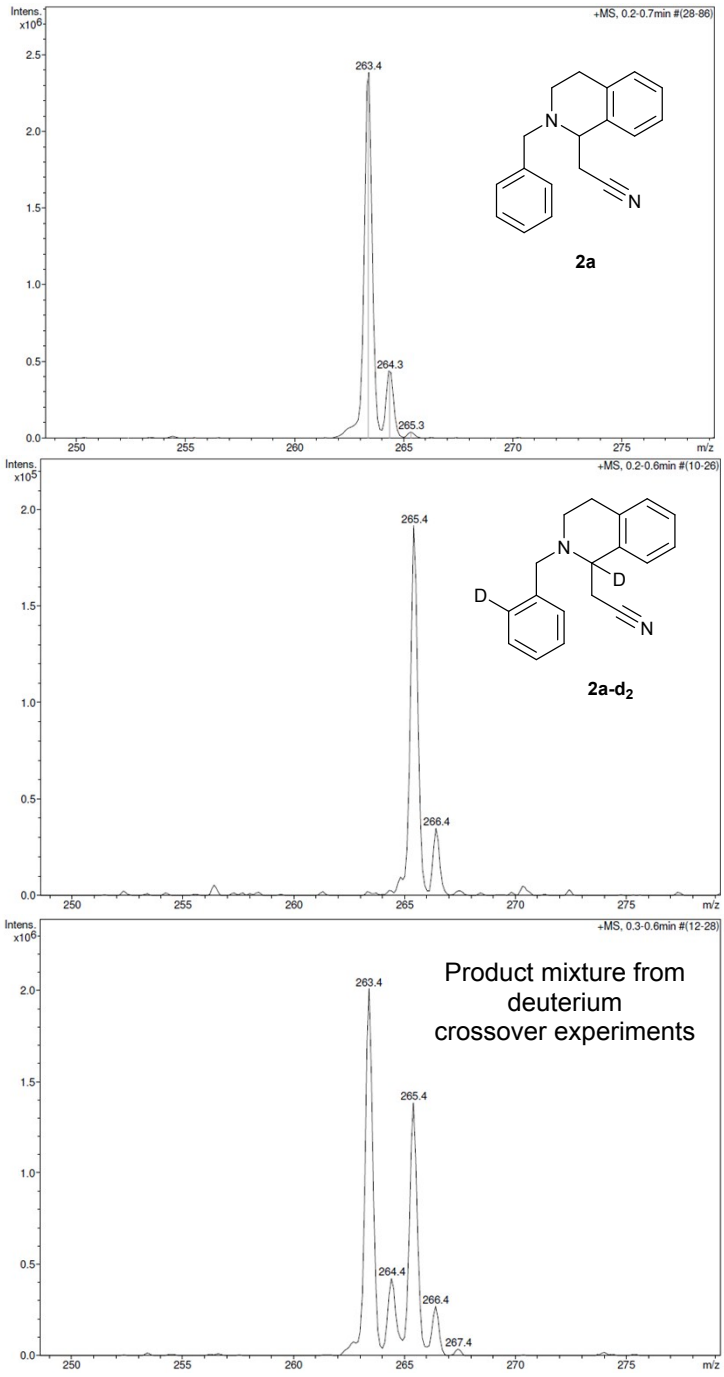



3-((3,4-Dihydroisoquinolin-2(1*H*)-yl-1,1-$d_2$)methyl)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a-*d*$_2$** (44.0 mg, 98.7 μmol) was subjected to the general procedure for hydride transfer. Silica gel flash column chromatography (1% $Et_3N$ in *n*-hexane:ethyl acetate 7:3) afforded 2-(2-((phenyl-2-*d*)methyl)-1,2,3,4-tetrahydroisoquinolin-1-yl-1-*d*)acetonitrile **2a-*d*$_2$** (14.9 mg, 57%) as a yellow oil. **$^1$H NMR (400 MHz, $CDCl_3$):** $\delta_H$ = 7.44-7.43 (1H, m), 7.38-7.34 (2H, m), 7.31-7.27 (1H, m), 7.24-7.18 (2H, m), 7.16-7.14 (1H, m), 7.11-7.09 (1H, m), 3.86 & 3.81 (2H, ABq, $J_{AB}$ = 13.6), 3.19-3.12 (1H, m), 2.99-2.91 (1H, m), 2.89-2.79 (2H, m), 2.73-2.68 (2H, m). **$^{13}$C NMR (101 MHz, $CDCl_3$):** $\delta_C$ = 138.5, 135.1, 135.0, 129.5, 128.9, 128.6, 128.5, 127.6, 127.5, 127.4, 126.5, 118.6, 58.3, 57.5 (t, $J_{C-D}$ = 22.1), 43.8, 25.4, 25.0.*** IR (neat): $\nu_{max}$/cm$^{-1}$** 3066w, 2925m, 2250m, 1596m, 1489m, 1453m, 780m, 746m. **HRMS (NSI)** calcd for $C_{18}H_{17}D_2N_2^+$ $[M+H]^+$: 265.1671; found 265.1668.

* $C^{3''}$–D signal cannot be located. Comparison with analogous protonated compound **2a** suggests this signal might be obscure by the additional signal at 128.5 ppm.

## 5. Isotope distribution for deuterium crossover experiments & 2D NMR spectroscopic experiments to support deuterium incorporation

***Isotope distribution (LC-MS)***




$C_{18}H_{18}N_2$ (MW = 262)

Calculated isotope distribution:

| | |
|---|---|
| 263 $(M+H)^+$ | 100.0% |
| 264 (M+H)+1 | 20.5% |

Found isotope distribution:

| | |
|---|---|
| 263 $(M+H)^+$ | 100.0% |
| 264 (M+H)+1 | 18.5% |

$C_{18}H_{16}D_2N_2$ (MW = 264)

Calculated isotope distribution:

| | |
|---|---|
| 265 $(M+H)^+$ | 100.0% |
| 266 (M+H)+1 | 20.4% |

Found isotope distribution:

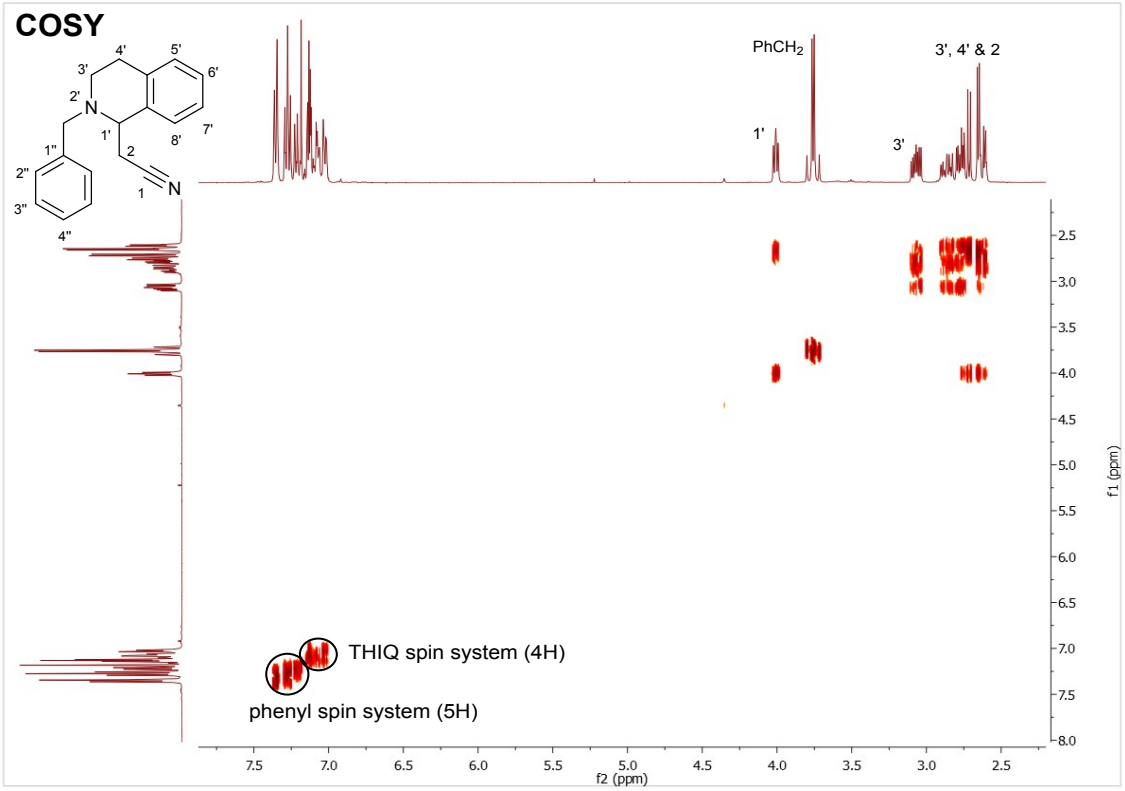
| | |
|---|---|
| 265 $(M+H)^+$ | 100.0% |
| 266 (M+H)+1 | 18.2% |

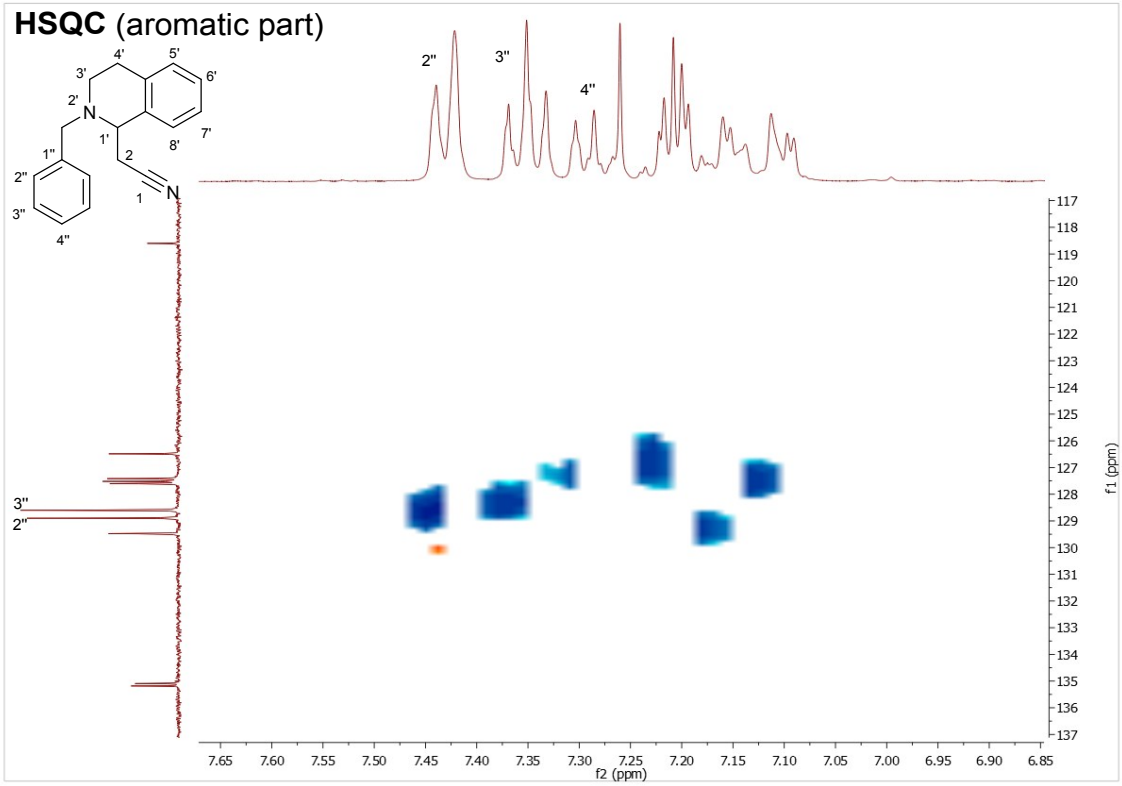
Found isotope distribution:

| | |
|---|---|
| 263 | 100% |
| 264 | 21.1% |
| 265 | 68.9% |
| 266 | 13.5% |

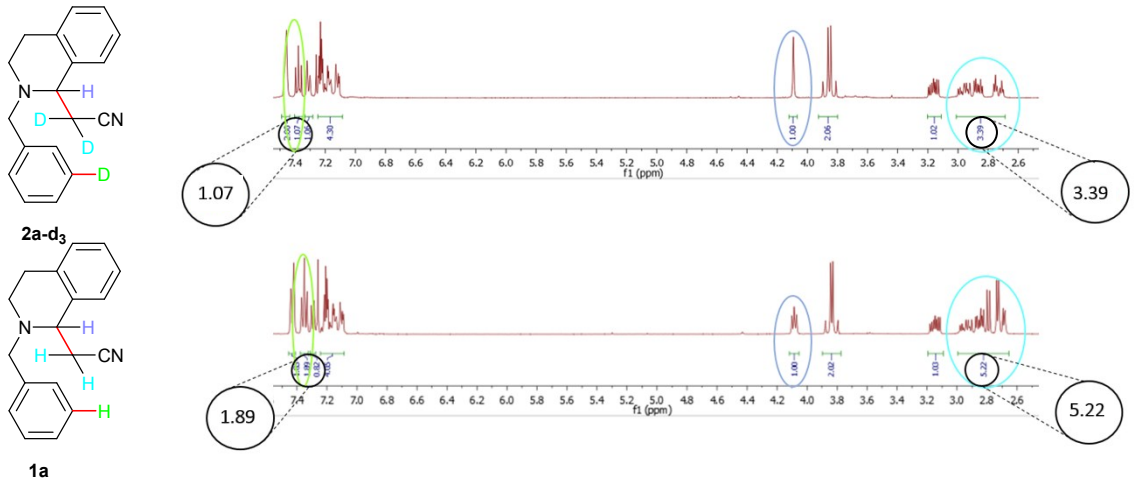
The isotope distribution of peak 264 (i.e. potential monodeuterated cross-product) in the crossover experiment is equivalent to (within error of peak integration) the value of peak 264 for isolated compound **2a**, revealing the absence of crossover products and thus supporting intramolecular process.

*2D NMR spectra for atomic attribution*



## *Deuterium incorporation ($^1$H NMR spectra)*




## *Deuteride transfer ($^1$H NMR spectra)*