Vicinal difunctionalization of carbon–carbon double bond for the platform synthesis of trifluoroalkyl amines

Béke, et al.
Supplementary Information
for
Vicinal difunctionalization of carbon–carbon double bond
for the platform synthesis of trifluoroalkyl amines
by
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General conditions

Analytical thin-layer chromatography (TLC) was performed on Merck DC pre coated TLC plates with 0.25 mm Kieselgel 60 F_{254}. Visualization was performed by fluorescence quenching under 254 nm irradiation, and staining with p-anisaldehyde or potassium-permanganate stains. Purification of the crude products was performed by medium pressure liquid chromatography (instrument: Biotage® Isolera™ Prime, stationary phase: Teledyne ISCO RediSep Rf® Normal phase silica, 24 g silica / cartridge, 20-40 μm particle size, 60 Å average pore size, mobile phase: according to TLC elution experiment, 15 mL/min). The $^1$H-, $^{13}$C-, $^{19}$F- and $^{31}$P-NMR spectra were recorded on a Bruker Avance-250 MHz or a Varian Inova 300 MHz or a Varian Inova 500 MHz spectrometer in CDCl$_3$, CD$_2$Cl$_2$, acetonitrile-$d_3$, methanol-$d_4$ or acetone-$d_6$. Chemical shifts are expressed in parts per million ($\delta$) and referenced to residual protiated solvent peaks as internal standards for $^1$H and $^{13}$C nuclei, while $^{19}$F and $^{31}$P chemical shifts are referenced to CFCl$_3$ and H$_3$PO$_4$ (40 w% aqueous solution) external standards, respectively. Coupling constants ($J$) are reported in Hertz (Hz) and splitting patterns are designated as s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), p (pentet), hept (heptet), dd (doublet of doublets), dt (doublet of triplets), td (triplet of doublets), tt (triplet of triplets), dq (doublet of quartets), qd (quartet of doublets), pd (pentet of doublets), ddt (doublet of doublet of triplets), ddq (doublet of doublet of quartets), dqd (doublet of quartet of doublets), tdq (triplet of doublet of quartets), dqdd (doublet of doublet of quartet of doublets), and m (multiplet). IR spectra were obtained on a Bruker IFS55 spectrometer on a single-reflection diamond ATR unit.

Conversions determined on an Agilent 6890N Gas Chromatograph (30 m x 0.25 mm column with 0.25 μm HP-5MS coating, He carrier gas) and low resolution mass spectrometry was obtained on an Agilent 5973 Mass Spectrometer (Ion source: EI+, 70eV, 230 °C, interface 300 °C). 4-Fluoroiodobenzene was used as internal standard, which formed upon decomposition of (4-fluorophenyl)(3,3,3-trifluoroprop-1-en-2-yl)iodonium trifluromethanesulfonate.

All melting points were measured on Büchi 510 apparatus and are uncorrected.

High-resolution mass spectra were acquired on an Agilent 6230 time-of-flight mass spectrometer equipped with a Jet Stream electrospray ion source in positive ion mode. Injections of 0.1-0.3 μl were directed to the mass spectrometer at a flow rate 0.5 ml/min (70% acetonitrile-water mixture, 0.1 % formic acid), using an Agilent 1260 Infinity HPLC system. Jet Stream parameters: drying
gas (N\textsubscript{2}) flow and temperature: 10.0 l/min and 325 °C, respectively; nebulizer gas (N\textsubscript{2}) pressure: 10 psi; capillary voltage: 4000V; sheath gas flow and temperature: 325°C and 7.5 l/min; TOFMS parameters: fragmentor voltage: 120 V; skimmer potential: 120 V; OCT 1 RF Vpp: 750 V. Full-scan mass spectra were acquired over the m/z range 100-2500 at an acquisition rate of 250 ms/spectrum and processed by Agilent MassHunter B.03.01 software.

Starting materials were obtained from commercial suppliers and were used without further purification. Liquid state amines (diisobutylamine, pyrrolidine, piperidine, 2-methyl-piperidine, 3-methyl-piperidine, 4-benzyl-piperidine, N-methyl-1-(naphthalen-1-yl)methanamine and N-methylaniline) were dried over and distilled from CaH\textsubscript{2}, under argon atmosphere or high vacuum. Solid state amines (3-hydroxy-piperidine, 3-hydroxymethylene-piperidine, 3-azabicyclo[3.2.2]nonane and adamant-1-ylamine) were sublimed under high vacuum. 4-Methoxybenzaldehyde was distilled under high vacuum. Dichloromethane was HPLC grade, while acetonitrile (contained <200 ppm water) and methanol were reagent grade, and used without further purification, tetrahydrofuran was distilled from benzophenone ketyl-sodium prior usage. Toluene was dried over activated 4Å molecular sieves and stored under argon.

**Preparation of starting materials**

*Synthesis of compound I*

(4-fluorophenyl)(3,3,3-trifluoroprop-1-en-2-yl)iodonium trifluoromethanesulfonate\textsuperscript{1}

\[
\begin{align*}
\text{F} & \quad \Theta \quad \text{OTf} \\
\text{CF}_3 & \\
\end{align*}
\]

A 40 mL screwed cap vial with a stirring bar was evacuated and refilled with argon 3 times. Trifluoroacetic anhydride (10 mL, 70.5 mmol, 7.2 equiv) and trifluoroacetic acid (77 \muL, 1 mmol, 10 mol\%) was added via syringe. The mixture was cooled to 0 °C, then hydrogen peroxide (980 \muL, 50 wt\% in water, 17 mmol, 1.7 equiv) was added dropwise within 2 minutes. 2-Iodo-3,3,3-trifluoropropene (1080 \muL, 10 mmol) was added dropwise via syringe. The off-white suspension was kept between 0 °C and 4 °C for 16 hours. After that, the mixture was cooled to -20°C, then dichloromethane (10 mL) was added slowly. Fluorobenzene (1.45 mL, 15.5 mmol, 1.55 equiv) was added dropwise to the suspension, followed by the addition of trifluoromethanesulfonic acid (880 \muL, 10 mmol, 1 equiv) to form an emerald green solution. Consider that the temperature is not allowed to reach more than -20 °C throughout the addition of triflic acid! δ

The reaction mixture was kept between 0 °C and 4 °C for 6 hours. After that, all volatiles were removed under reduced pressure at 0 °C, protected from light. The brownish green oil was shaken
with cold diethyl ether (20 mL, -20 °C), getting white precipitate. The suspension was kept at -20°C for 12 hours, then the white precipitate was filtered and washed with cold ether 3 times. Title compound was obtained as a white solid (4.37 g, 9.76 mmol, 97.6% yield).

M.p.= 144-147 °C. ¹H NMR (250 MHz, Acetonitrile-d₃) δ 8.20 (dd, J = 7.8, 4.2 Hz, 2H), 7.51 – 7.22 (m, 4H). ¹⁹F NMR (235 MHz, Acetonitrile-d₃) δ -64.53 (3F), -79.40 (3F), -105.44 (1F). ¹³C NMR (63 MHz, Acetonitrile-d₃) δ 166.4 (d, J = 254.6 Hz), 145.1 (q, J = 4.7 Hz), 139.9 (d, J = 9.5 Hz), 121.9 (q, J = 321.0 Hz), 121.2 (q, J = 273.8 Hz), 111.8 (q, J = 39.8 Hz), 108.3 (d, J = 3.2 Hz). IR (ATR, cm⁻¹) 3094, 3063, 3026, 2973, 2929, 2873, 1598, 1502, 1449, 1353, 1299, 1262, 1232, 1188, 1161, 1141, 1103, 1055, 1038, 973, 913, 888, 851, 795, 744, 692, 615, 579, 522, 468, 413.

General procedure for the synthesis of p-methoxybenzyl protected amines²

A 40 mL screwed cap vial was charged with stirring bar, 4 Å molecular sieves (1.5 g, beads), p-methoxybenzaldehyde (1.22 mL, 10 mmol) and dichloromethane (10 mL) at room temperature. Amine (12 mmol, 1.2 equiv) or amine hydrochloride (12 mmol, 1.2 equiv) and triethylamine (1.67 mL, 12 mmol, 1.2 equiv) were added and the reaction mixture was monitored by GC-MS. After complete conversion of p-methoxybenzaldehyde (5 min – 24 h) reaction mixture was filtered through a pad of Celite, filter cake was washed with diethylether. Filtrates were combined and evaporated to dryness under reduced pressure. Residue was dissolved in methanol (20 mL) and cooled to 0 °C, then sodium borohydride (454 mg, 12 mmol, 1.2 equiv) was added portionwise over 5 minutes to the stirred mixture. Reaction was allowed to warm room temperature over 16 hours, then concentrated onto Celite in vacuo. The obtained residue was purified by flash column chromatography (Hexanes:EtOAc = from 100:0 to 50:50).

N-(4-methoxybenzyl)prop-2-en-1-amine² (A1)

Amine A1 was synthesized according to general procedure from p-methoxybenzaldehyde (1.22 mL, 10 mmol), allylamine (900 uL, 12 mmol, 1.2 equiv) and sodium borohydride (454 mg, 12 mmol, 1.2 equiv) to afford the title compound as a pale yellow liquid (1.46 g, 8.24 mmol, 82% yield).

Rf= 0.30 (hexanes:ethyl acetate= 7:3). LRMS (EI, 70 eV): m/z (%): 121(100), 176(27), 122(18), 78(15), 56(15), 77(14), 135(12), 134(11), 177(10), 148(9), 91(9). ¹H NMR (250 MHz, CDCl₃) δ 7.15 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 8.6 Hz, 2H), 5.84 (ddt, J = 6.9, 5.9 Hz, 1H), 5.11 (dd, J = 17.2, 1.7 Hz, 1H), 5.02 (dd, J = 10.3, 1.2 Hz, 1H), 3.69 (s, 3H), 3.63 (s, 2H), 3.17 (bs, 2H), 1.52 (bs, 1H). ¹³C NMR (63 MHz, CDCl₃) δ 158.6, 136.8, 132.3, 129.3, 115.9, 113.7, 55.1, 52.6, 51.6.
IR (ATR, cm\(^{-1}\)) 3073, 3002, 2971, 2932, 2911, 2834, 1738, 1611, 1510, 1455, 1442, 1418, 1364, 1300, 1241, 1173, 1103, 1034, 994, 916, 811, 771, 702, 637, 561, 516.

Methyl (4-methoxybenzyl)-L-leucinate\(^3\) (A2)

Amine A2 was synthesized according to general procedure from \(p\)-methoxybenzaldehyde (1.22 mL, 10 mmol), methyl L-leucinate hydrochloride (2.18 g, 12 mmol, 1.2 equiv), triethylamine (1.67 mL, 12 mmol, 1.2 equiv) and sodium borohydride (454 mg, 12 mmol, 1.2 equiv) to afford the title compound as a pale yellow oil (2.28 g, 8.61 mmol, 86% yield).

\(R_f = 0.38\) (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 207(15), 206(100), 137(7), 136(75), 122(62), 121(100), 106(5), 91(18), 90(8), 89(8), 78(26), 77(26), 65(6). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) 7.2 (d, \(J = 8.6\) Hz, 2H), 6.8 (d, \(J = 8.7\) Hz, 2H), 3.7 (s, 3H), 3.6 (s, 3H), 3.5 (d, \(J = 12.7\) Hz, 1H), 3.2 (t, \(J = 7.2\) Hz, 1H), 1.8 – 1.6 (m, 2H), 1.4 (dd, \(J = 7.5, 6.5\) Hz, 2H), 0.8 (d, \(J = 6.6\) Hz, 3H), 0.8 (d, \(J = 6.6\) Hz, 3H). \(^{13}\)C NMR (63 MHz, CDCl\(_3\)) \(\delta\) 176.5, 158.7, 132.0, 129.0, 128.2, 128.1, 126.5, 113.6, 61.8, 60.4, 55.0, 51.3, 39.7, 14.1. IR (ATR, cm\(^{-1}\)) 3063, 2997, 2953, 2870, 2836, 1733, 1612, 1511, 1463, 1367, 1300, 1244, 1195, 1170, 1150, 1106, 1035, 991, 824, 777, 577, 513.

Ethyl (4-methoxybenzyl)-L-phenylalaninate\(^4\) (A3)

Amine A3 was synthesized according to general procedure from \(p\)-methoxybenzaldehyde (1.22 mL, 10 mmol), L-phenylalanine ethyl ester hydrochloride (2.76 g, 12 mmol, 1.2 equiv), triethylamine (1.67 mL, 12 mmol, 1.2 equiv) and sodium borohydride (454 mg, 12 mmol, 1.2 equiv) to afford the title compound as a pale yellow oil (2.90 g, 9.27 mmol, 93% yield).

\(R_f = 0.28\) (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 121(100), 222(41), 122(25), 91(23), 77(14), 78(14), 240(12), 65(6), 136(6), 223(6), 92(5). \(^1\)H NMR (250 MHz, Chloroform-\(d\)) \(\delta\) 7.25 – 7.08 (m, 7H), 6.78 (d, \(J = 8.7\) Hz, 2H), 4.06 (q, \(J = 7.1\) Hz, 2H), 3.72 (d, \(J = 12.7\) Hz, 1H), 3.71 (s, 3H), 3.55 (d, \(J = 12.9\) Hz, 1H), 3.49 (t, \(J = 7.0\) Hz, 1H), 2.92 (d, \(J = 7.0\) Hz, 2H), 1.89 (s, 1H), 1.11 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (63 MHz, CDCl\(_3\)) \(\delta\) 174.4, 158.6, 137.3, 131.6, 129.2, 129.2, 128.2, 126.5, 113.6, 61.8, 60.4, 55.0, 51.3, 39.7, 14.1. IR (ATR, cm\(^{-1}\)) 3063, 3029, 2979, 2934, 2834, 1727, 1611, 1585, 1510, 1455, 1371, 1300, 1244, 1173, 1129, 1031, 811, 744, 699, 564, 513.
$N$-(4-methoxybenzyl)adamantan-1-amine$^5$ (A4)

Amine A3 was synthesized according to general procedure from $p$-methoxybenzaldehyde (1.22 mL, 10 mmol), adamantane-1-amine (900 µL, 12 mmol, 1.2 equiv) and sodium borohydride (454 mg, 12 mmol, 1.2 equiv) to afford the title compound as a colorless oil (1.71 g, 6.29 mmol, 63% yield).

$R_f = 0.30$ (hexanes:ethyl acetate= 7:3). **M.p.= 73-76 °C.** LRMS (EI, 70 eV): m/z (%): 272(8), 271(43), 270(7), 215(12), 214(64), 177(17), 136(5), 135(22), 122(21), 121(100), 107(11), 106(30), 93(11), 91(14), 79(12), 78(12), 77(18), 67(7), 65(5), 55(5). $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 7.25 (d, $J = 8.3$ Hz, 2H), 6.85 (d, $J = 8.7$ Hz, 2H), 3.79 (d, $J = 0.9$ Hz, 3H), 3.70 (s, 2H), 2.14 – 2.04 (m, 3H), 1.76 – 1.56 (m, 12H), 1.16 (s, 1H).

$^1$C NMR (63 MHz, CDCl$_3$) $\delta$ 158.5, 133.9, 129.5, 113.9, 77.7, 77.2, 76.7, 55.3, 50.9, 44.6, 43.0, 36.9, 29.8. **IR (ATR, cm$^{-1}$)** 3292, 2997, 2894, 2846, 1611, 1585, 1510, 1466, 1455, 1367, 1360, 1341, 1300, 1239, 1209, 1177, 1140, 1099, 1075, 1031, 1014, 973, 852, 831, 808, 787, 773, 760, 717, 706, 611, 523.

$N$-(4-methoxybenzyl)cyclopropanamine$^6$ (A5)

Amine A5 was synthesized according to general procedure from $p$-methoxybenzaldehyde (1.22 mL, 10 mmol), cyclopropylamine (840 µL, 12 mmol, 1.2 equiv) and sodium borohydride (454 mg, 12 mmol, 1.2 equiv) to afford the title compound as a pale yellow oil (1.41 g, 7.94 mmol, 79% yield).

$R_f = 0.39$ (hexanes:ethyl acetate= 10:1). **LRMS (EI, 70 eV):** m/z (%): 272(23), 176(14), 162(24), 135(5), 134(6), 122(27), 121(100), 91(15), 89(7), 78(23), 77(22), 65(6), 51(8). $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 7.14 (d, $J = 8.6$ Hz, 2H), 6.77 (d, $J = 8.6$ Hz, 2H), 3.68 (s, 2H), 3.67 (s, 2H), 2.05 (tt, $J = 6.3$, 3.8 Hz, 1H), 1.80 (s, 1H), 0.45 – 0.23 (m, 4H). $^1$C NMR (63 MHz, CDCl$_3$) $\delta$ 158.3, 132.6, 129.1, 113.5, 54.9, 52.9, 29.8, 6.2. **IR (ATR, cm$^{-1}$)** 3316, 3085, 3005, 2935, 2834, 1655, 1611, 1585, 1510, 1463, 1441, 1371, 1343, 1300, 1242, 1174, 1109, 1034, 1014, 926, 848, 817, 742, 700, 637, 581, 563, 519, 448, 417.
(R)-N-(4-methoxybenzyl)-1-phenylethan-1-amine\(^7\) (A6)

Amine A6 was synthesized according to general procedure from \(p\)-methoxybenzaldehyde (1.22 mL, 10 mmol), (R)-(+)-\(\alpha\)-methylbenzylamine (1.56 mL, 12 mmol, 1.2 equiv) and sodium borohydride (454 mg, 12 mmol, 1.2 equiv) to afford the title compound as a pale yellow oil (2.26 g, 9.35 mmol, 93% yield).

\(R_f = 0.31\) (hexanes:ethyl acetate= 10:1).

LRMS (EI, 70 eV): m/z (%): 121(100), 226(56), 105(24), 77(22), 136(19), 122(19), 78(14), 91(11), 227(9), 79(9), 104(6), 51(6), 241(6). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) 7.4 – 7.1 (m, 7H), 6.9 (d, \(J = 8.9\) Hz, 2H), 3.9 – 3.7 (m, 4H), 3.7 – 3.5 (m, 2H), 1.6 (s, 1H), 1.4 (d, \(J = 6.6\) Hz, 3H). \(^{13}\)C NMR (63 MHz, CDCl\(_3\)) \(\delta\) 158.6, 145.7, 132.8, 129.3, 128.5, 126.9, 126.7, 113.8, 57.4, 55.2, 51.0, 24.5. IR (ATR, cm\(^{-1}\)) 3061, 3026, 2999, 2959, 2931, 2833, 1738, 1611, 1584, 1510, 1492, 1451, 1368, 1300, 1242, 1173, 1113, 1075, 1034, 988, 820, 757, 699, 600, 570, 540, 520.

Ethyl (4-methoxybenzyl)glycinate\(^8\) (A7)

Amine A7 was synthesized according to general procedure from \(p\)-methoxybenzaldehyde (2.43 mL, 20 mmol), ethyl glycinate hydrochloride (3.35 g, 24 mmol, 1.2 equiv), triethylamine (3.35 mL, 24 mmol, 1.2 equiv), sodium borohydride (908 mg, 24 mmol, 1.2 equiv) and applied ethanol instead of methanol in the second step to afford the title compound as a pale yellow oil (3.07 g, 13.8 mmol, 69% yield).

\(R_f = 0.45\) (hexanes:ethyl acetate= 7:3). LRMS (EI, 70 eV): m/z (%): 223(6), 150(36), 148(11), 137(16), 136(100), 122(50), 121(100), 107(5), 106(8), 91(21), 90(8), 89(12), 79(6), 78(40), 77(30), 75(7), 65(7), 63(6), 52(8), 51(9). \(^1\)H NMR (250 MHz, CDCl\(_3\)) \(\delta\) 7.20 (d, \(J = 8.5\) Hz, 2H), 6.82 (d, \(J = 8.5\) Hz, 2H), 4.14 (q, \(J = 7.1\) Hz, 2H), 3.74 (s, 3H), 3.69 (s, 2H), 3.34 (s, 2H), 2.18 (s, 1H), 1.22 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (63 MHz, CDCl\(_3\)) \(\delta\) 158.8, 131.5, 129.4, 113.8, 60.6, 55.1, 52.6, 49.9, 14.1. IR (ATR, cm\(^{-1}\)) 2971, 2936, 2910, 2836, 1734, 1611, 1511, 1462, 1419, 1373, 1300, 1242, 1177, 1137, 1109, 1028, 812, 760, 571, 518.

\(N\)-(4-methoxybenzyl)hexan-1-amine\(^9\) (A8)

Amine A8 was synthesized according to general procedure from \(p\)-methoxybenzaldehyde (1.22 mL, 10 mmol), \(n\)-hexylamine (1.59 mL, 12 mmol, 1.2 equiv) and sodium borohydride (454 mg, 12 mmol, 1.2 equiv) to afford the title compound as a pale yellow oil (2.26 g, 9.35 mmol, 93% yield).
borohydride (454 mg, 12 mmol, 1.2 equiv) to afford the title compound as a pale yellow oil (1.40 g, 6.33 mmol, 63% yield).

Rf = 0.30 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 221(1), 150(9), 136(4), 122(9), 121(100), 91(2), 78(3), 77(3). ¹H NMR (250 MHz, CDCl₃) δ 7.14 (d, J = 8.5 Hz, 2H), 6.76 (d, J = 8.6 Hz, 2H), 3.69 (s, 3H), 3.63 (s, 2H), 2.52 (t, J = 7.2 Hz, 2H), 1.60 (s, 1H), 1.40 (q, J = 7.0, 6.4 Hz, 2H), 1.29 – 1.07 (m, 6H), 0.79 (t, J = 6.4 Hz, 3H). ¹³C NMR (63 MHz, CDCl₃) δ 158.6, 132.7, 129.3, 113.8, 55.2, 53.5, 49.4, 31.8, 30.1, 27.1, 22.7, 14.1. IR (ATR, cm⁻¹) 3064, 3029, 2999, 2899, 2955, 2854, 2834, 1738, 1611, 1585, 1510, 1456, 1377, 1300, 1244, 1173, 1105, 1036, 818, 751, 726, 699, 637, 574, 513, 418, 397.

N-(4-methoxybenzyl)heptan-2-amine (A9)

Amine A9 was synthesized according to general procedure from p-methoxybenzaldehyde (1.22 mL, 10 mmol), 2-aminoheptane (1.81 mL, 12 mmol, 1.2 equiv) and sodium borohydride (454 mg, 12 mmol, 1.2 equiv) to afford the title compound as a pale yellow oil (2.34 g, 9.93 mmol, 99% yield).

Rf = 0.36 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 204(1), 165(2), 164(18), 164(3), 162(2), 136(3), 135(2), 134(1), 122(11), 121(100), 91(3), 90(1), 89(1), 82(1), 78(4), 77(4), 57(1). ¹H NMR (250 MHz, CDCl₃) δ 7.16 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 8.6 Hz, 2H), 3.70 (s, 3H), 3.61 (q, J = 12.8 Hz, 2H), 2.56 (dq, J = 12.2, 7.4, 6.5 Hz, 1H), 1.39 (s, 2H), 1.33 – 1.10 (m, 7H), 0.99 (d, J = 6.3 Hz, 3H), 0.81 (t, J = 6.6 Hz, 3H). ¹³C NMR (63 MHz, CDCl₃) δ 158.6, 133.0, 129.3, 113.8, 55.2, 52.5, 50.8, 37.1, 32.1, 25.7, 22.7, 20.3, 14.1. IR (ATR, cm⁻¹) 3063, 2996, 2955, 2955, 2856, 1738, 1612, 1585, 1510, 1463, 1374, 1300, 1244, 1171, 1106, 1036, 822, 808, 750, 727, 696, 574, 515.

N-(4-methoxybenzyl)octan-1-amine (A10)

Amine A10 was synthesized according to general procedure from p-methoxybenzaldehyde (1.22 mL, 10 mmol), 2-aminoheptane (1.81 mL, 12 mmol, 1.2 equiv) and sodium borohydride (454 mg, 12 mmol, 1.2 equiv) to afford the title compound as a pale yellow oil (2.34 g, 9.93 mmol, 99% yield).
**R**f = 0.39 (hexanes:ethyl acetate = 10:1). LRMS (EI, 70 eV): m/z (%): 249(3), 248(4), 150(33), 137(11), 136(12), 128(7), 122(33), 121(100), 106(3), 91(7), 78(9), 77(9), 75(3). **1H NMR** (250 MHz, CDCl$_3$) δ 7.14 (d, $J = 8.5$ Hz, 2H), 6.76 (d, $J = 8.5$ Hz, 2H), 3.68 (s, 3H), 3.62 (s, 2H), 2.51 (t, $J = 7.2$ Hz, 2H), 1.67 (s, 1H), 1.49 – 1.32 (m, 2H), 1.18 (s, 10H), 0.79 (t, $J = 6.1$ Hz, 3H). **13C NMR** (63 MHz, CDCl$_3$) δ 158.6, 132.6, 129.3, 113.7, 55.2, 53.5, 49.4, 31.9, 30.1, 29.6, 29.3, 27.4, 22.7, 14.1. IR (ATR, cm$^{-1}$) 3063, 2953, 2922, 2853, 1738, 1612, 1585, 1510, 1456, 1365, 1300, 1244, 1173, 1106, 1036, 820, 754, 723, 700, 573, 515.

**N-(4-methoxybenzyl)aniline**$^{11}$ (A11)

Amine A11 was synthesized according to general procedure from $p$-methoxybenzaldehyde (1.22 mL, 10 mmol), aniline (1.09 mL, 12 mmol, 1.2 equiv) and sodium borohydride (454 mg, 12 mmol, 1.2 equiv) to afford the title compound as an off-white solid (1.34 g, 6.29 mmol, 63% yield).

**R**f = 0.31 (hexanes:ethyl acetate = 10:1). M. p. = 54-58 °C. LRMS (EI, 70 eV): m/z (%): 212(12), 211(89), 210(100), 196(4), 195(5), 168(4), 167(13), 166(2), 139(2), 104(3), 92(2), 91(2), 78(4), 77(31), 76(3), 65(5), 64(2), 63(3), 51(10), 50(3). **1H NMR** (250 MHz, CDCl$_3$) δ 7.19 (t, $J = 7.9$ Hz, 2H), 6.89 (d, $J = 8.6$ Hz, 2H), 6.74 (t, $J = 7.3$ Hz, 1H), 6.64 (d, $J = 7.7$ Hz, 2H), 4.24 (s, 2H), 3.93 (s, 1H), 3.79 (s, 3H). **13C NMR** (63 MHz, CDCl$_3$) δ 158.9, 148.2, 131.4, 129.3, 128.9, 117.6, 114.1, 113.0, 55.3, 47.8. IR (ATR, cm$^{-1}$) 3075, 3047, 3020, 3002, 2961, 2934, 2907, 2856, 2836, 1599, 1582, 1511, 1499, 1470, 1460, 1438, 1424, 1300, 1246, 1171, 1153, 1110, 1095, 1068, 1032, 872, 835, 818, 746, 692, 544, 523, 513.

**N-(4-methoxybenzyl)-3-nitroaniline**$^{12}$ (A12)

Amine A12 was synthesized according to general procedure from $p$-methoxybenzaldehyde (1.22 mL, 10 mmol), 3-nitroaniline (1.09 mL, 12 mmol, 1.2 equiv) and sodium borohydride (454 mg, 12 mmol, 1.2 equiv) to afford the title compound as an orange solid (1.34 g, 6.29 mmol, 63% yield).

**R**f = 0.59 (hexanes:ethyl acetate = 7:3). M. p. = 98-102 °C. LRMS (EI, 70 eV): m/z (%): 257(15), 256(100), 255(50), 210(7), 209(21), 195(10), 168(6), 167(20), 166(11), 140(7), 139(9), 77(9), 76(10), 51(7). **1H NMR** (250 MHz, CDCl$_3$) δ 7.51 – 7.39 (m, 1H), 7.35 (t, $J = 2.1$ Hz, 1H), 7.27 – 7.11 (m, 3H), 6.83 (dd, $J = 6.4$, 2.1 Hz, 3H), 4.44 (d, $J = 26.7$ Hz, 1H), 4.22 (s, 2H), 3.73 (s, 3H).
$^{13}$C NMR (63 MHz, CDCl$_3$) $\delta$ 159.2, 149.4, 148.8, 130.0, 128.9, 118.9, 114.3, 112.1, 106.6, 55.3, 47.6. IR (ATR, cm$^{-1}$) 3406, 3098, 3075, 3033, 3012, 2952, 2928, 2900, 2853, 2836, 1611, 1582, 1536, 1509, 1341, 1275, 1241, 1170, 1097, 1031, 844, 812, 787, 733, 669, 506, 468.

3-phenylprop-2-yn-1-ol$^{13}$

A 250 mL round bottom flask was charged with stirring bar, Pd(PPh$_3$)$_2$Cl$_2$ (140 mg, 0.2 mmol, 1 mol%) and CuI (76.2 mg, 0.04 mmol, 2 mol%), then the sealed flask was purged with argon for 5 minutes. Triethylamine (80 mL, purged with argon) followed by iodobenzene (2.28 mL, 20 mmol) was added under argon atmosphere and stirred for 5 minutes at room temperature. Propargyl alcohol (1.31 mL, 22 mmol, 1.1 equiv) was added dropwise over 5 minutes, then the mixture was stirred for 16 hours at room temperature. Reaction mixture was filtered through a pad of Celite, solids were washed with EtOAc and the combined filtrates were concentrated in vacuo. Solid residue was purified by flash column chromatography (eluent: hexanes:ethyl acetate= 7:3) to afford the title compound as a colorless liquid (2.64 g, 20 mmol, 99% yield).

$R_f$ = 0.41 (hexanes:ethyl acetate= 7:3). LRMS (EI, 70 eV): m/z (%): 132(58), 131(100), 115(25), 104(28), 103(53), 102(14), 89(7), 78(28), 77(38), 76(7), 75(9), 74(10), 63(13), 62(7), 51(17). $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 7.38 (dd, $J$ = 6.8, 2.8 Hz, 2H), 7.23 (dd, $J$ = 5.1, 1.8 Hz, 3H), 4.44 (s, 2H), 2.77 (s, 1H).

3-Phenylprop-2-yn-1-yl 4-methylbenzenesulphonate$^{14}$

A 50 mL round bottom flask was charged with stirring bar, 3-phenylprop-2-yn-1-ol (2.78 g, 21 mmol), tosyl chloride (4.80 g, 25.2 mmol, 1.2 equiv) and diethyl ether (33 mL), then cooled to 0 °C. Pulverized potassium hydroxide (6.6 g, 118 mmol, 5.6 equiv) was added in one portion to the vigorously stirred mixture and stirring was continued for 1 hour at the same temperature. Reaction mixture was quenched by pouring cold water, extracted with diethyl ether. Combined organic layers were washed with brine, dried over Na$_2$SO$_4$ and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography (eluent: hexanes:ethyl acetate= 7:3). The title compound was obtained as a white solid (2.67 g, 9.32 mmol, 44% yield).

$R_f$ = 0.55 (hexanes:ethyl acetate= 7:3). LRMS (EI, 70 eV): m/z (%): 192(7), 139(41), 131(41), 116(7), 115(100), 114(55), 105(14), 103(10), 103(8), 102(7), 92(11), 91(12), 91(12), 89(15), 77(8), 77(7), 65(18). $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J$ = 8.4 Hz, 2H), 7.31 – 7.09 (m, 7H), 4.87
13C NMR (63 MHz, CDCl₃) δ 145.1, 133.5, 131.8, 129.9, 129.1, 128.3, 128.2, 121.5, 89.0, 80.7, 58.7, 21.6.

**General procedure for the synthesis of propargyl amines**

A 20 mL vial was charged with stirring bar, appropriate amine (12 mmol, 4 equiv), potassium carbonate (419 mg, 3 mmol, 1 equiv) and acetonitrile (9 mL). 3-Phenylprop-2-yn-1-yl 4-methylbenzenesulfonate (859 mg, 3 mmol) was added in one portion, then the mixture was heated to 70°C and stirred for 16 hours. Reaction mixture was concentrated onto Celite and the residue was purified by flash column chromatography (hexanes:EtOAc = 100:0 -> 50:50).

**N-isobutyl-3-phenylprop-2-yn-1-amine** (A13)

Amine A13 was synthesized according to general procedure from isobutylamine (1.19 mL, 12 mmol, 4 equiv), potassium carbonate (419 mg, 3 mmol, 1 equiv) and 3-phenylprop-2-yn-1-yl 4-methylbenzenesulfonate (859 mg, 3 mmol) to afford the title compound as a brown liquid (425 mg, 2.27 mmol, 76% yield).

**IR** (ATR, cm⁻¹) 3057, 3023, 2953, 2870, 2815, 1792, 1738, 1598, 1489, 1466, 1442, 1365, 1330, 1252, 1217, 1112, 1069, 1028, 950, 913, 753, 689, 525.

1H NMR (250 MHz, Methylene Chloride-d₂) δ 7.3 – 7.2 (m, 2H), 7.2 – 7.1 (m, 3H), 3.4 (s, 2H), 2.4 (d, J = 6.7 Hz, 2H), 1.6 (dp, J = 13.3, 6.7 Hz, 1H), 1.2 (s, 1H), 0.8 (s, 3H), 0.8 (s, 3H).

13C NMR (63 MHz, Methylene Chloride-d₂) δ 133.9, 130.6, 130.2, 125.9, 90.8, 85.2, 59.4, 41.5, 30.8, 22.9.

**Rf** = 0.52 (hexanes:ethyl acetate= 7:3). LRMS (EI, 70 eV): m/z (%): 115(100), 144(78), 116(15), 89(10), 145(9), 63(6), 65(4), 114(4), 130(4), 187(4), 77(3).

**N-(3-phenylprop-2-yn-1-yl)cyclohexanamine** (A14)

Amine A14 was synthesized according to general procedure from cyclohexylamine (1.37 mL, 12 mmol, 4 equiv), potassium carbonate (419 mg, 3 mmol, 1 equiv) and 3-phenylprop-2-yn-1-yl 4-methylbenzenesulfonate (859 mg, 3 mmol) to afford the title compound as a brown liquid (269 mg, 1.26 mmol, 42% yield).

**Rf** = 0.24 (hexanes:ethyl acetate= 7:3). LRMS (EI, 70 eV): m/z (%): 115(100), 170(34), 156(33), 157(23), 130(13), 80(12), 116(11), 89(10), 213(9), 55(8), 128(6), 212(5), 85(5).

1H NMR (250 MHz, Methylene Chloride-d₂) δ 7.4 (dq, J = 8.3, 3.4, 2.6 Hz, 2H), 7.4 – 7.3 (m, 3H), 3.7 (s, 2H), 2.7 (tt, J = 10.0, 3.8 Hz, 1H), 2.0 – 1.6 (m, 5H), 1.5 – 1.0 (m, 6H).

13C NMR (63 MHz, Methylene
Chloride-$d_2$ δ 133.8, 130.6, 130.2, 125.9, 91.0, 84.9, 57.6, 38.3, 35.5, 28.6, 27.2. IR (ATR, cm$^{-1}$) 3080, 3057, 3020, 2924, 2851, 1738, 1489, 1443, 1368, 1326, 1253, 1229, 1217, 1119, 1069, 1028, 951, 913, 889, 753, 689, 596, 540, 525, 509, 459, 424.

$N$-hexyl-1-((phenylethynyl)cyclohexan-1-amine$^{17}$ (A15)

A 10 mL microwave instrument vial was charged with stirring bar, phenylacetylene (336 uL, 3 mmol, 1 equiv), cyclohexanone (311 uL, 3 mmol, 1 equiv), hexylamine (396 uL, 3 mmol, 1 equiv) and copper(I) iodide (114 mg, 0.6 mmol, 20 mol%), then sealed with Teflon septa. Vial was evacuated and backfilled with argon (repeated three times), then placed in the microwave cavity and irradiated at ceiling temperature 100°C for 25 minutes. After completion of reaction, the mixture was cooled to room temperature, diluted with methanol and concentrated onto Celite under reduced pressure. Residue was purified by flash column chromatography (eluent: hexanes:ethyl acetate= 7:3) to afford the title compound as a brown liquid (531 mg, 1.87 mmol, 62% yield). 

$^1$H NMR (250 MHz, CDCl$_3$) δ 7.42–7.30 (m, 2H), 7.26–7.15 (m, 3H), 2.73 (t, $J$ = 6.8 Hz, 2H), 1.87 (d, $J$ = 11.9 Hz, 2H), 1.70–1.51 (m, 5H), 1.52–0.92 (m, 12H), 0.92–0.70 (m, 3H).

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 131.6, 128.2, 127.7, 123.8, 93.6, 84.5, 55.1, 43.3, 38.3, 31.8, 30.7, 27.2, 26.0, 23.1, 22.7, 14.1. IR (ATR, cm$^{-1}$) 3080, 3056, 3020, 2927, 2854, 1738, 1489, 1443, 1375, 1365, 1290, 1265, 1228, 1217, 1158, 1120, 1069, 951, 909, 753, 689, 658, 637, 559, 536, 516, 491.

$N$-(4-methoxybenzyl)prop-2-yn-1-amine$^{18}$ (A16)

A 250 mL round bottom flask was charged with stirring bar, $p$-methoxybenzaldehyde (1.84 mL, 15.1 mmol) and methanol (100 mL), followed by propargylamine (1.16 mL, 18.2 mmol, 1.2 equiv). The mixture was stirred for 4 hours, then cooled to 0°C and sodium borohydride (1.00 g, 26.5 mmol, 1.75 equiv) was added portionwise. Reaction mixture was allowed to warm room temperature over 16 hours, then concentrated onto Celite under reduced pressure. The obtained residue was purified by flash column chromatography (eluent: hexanes:ethyl acetate= 7:3) to afford the title compound as a colorless liquid (2.01 g, 11.5 mmol, 76% yield).
RF = 0.41 (hexanes:ethyl acetate= 7:3). **LRMS** (EI, 70 eV): m/z (%): 121(100), 174(68), 146(45), 134(26), 122(24), 77(22), 78(21), 144(15), 135(14), 91(14), 175(12), 68(12). \textbf{1H NMR} (250 MHz, CDCl$_3$) $\delta$ 7.18 (d, $J = 8.4$ Hz, 2H), 6.78 (d, $J = 8.5$ Hz, 2H), 3.73 (s, 2H), 3.70 (s, 3H), 3.32 (d, $J = 2.3$ Hz, 2H), 2.19 (t, $J = 2.0$ Hz, 1H), 1.43 (s, 1H).

**IR** (ATR, cm$^{-1}$) 3288, 3030, 3002, 2934, 2912, 2834, 1738, 1611, 1585, 1510, 1455, 1364, 1300, 1241, 1174, 1102, 1032, 811, 776, 759, 702, 635, 580, 560, 515.

**HRMS** m/z [M+H]$^+$ calculated for C$_{16}$H$_{25}$N$_2$O$_2$+: 277.1916, found: 277.1910.

**tert-butyl 3-(phenethylamino)azetidine-1-carboxylate (A17)**

A 100 mL round bottom flask was charged with stirring bar, tert-butyl 3-oxoazetidine-1-carboxylate (873 mg, 5.0 mmol) and dichloromethane (50 mL). To the stirred mixture, acetic acid (28.6 µL, 0.5 mmol, 10 mol%), followed by phenylethylamine (882 µL, 7.0 mmol, 1.4 equiv) was added at room temperature and stirred for 3 hours. Then the reaction mixture was cooled to 0°C and sodium triacetoxyborohydride (4.45 g, 21 mmol, 4.2 equiv) was added portionwise. The mixture was allowed to warm room temperature over 16 hours, then volatiles were evaporated under reduced pressure. The obtained residue was purified by flash column chromatography (eluent: hexanes:ethyl acetate= 7:3) to afford the title compound as a yellow syrup (539 mg, 1.95 mmol, 39% yield).

RF = 0.31 (hexanes:ethyl acetate= 7:3). **LRMS** (EI, 70 eV): m/z (%): 203(3), 148(3), 147(28), 129(2), 129(2), 105(12), 104(23), 103(2), 91(4), 79(2), 77(3), 57(18), 56(23), 55(2), 91(4), 79(2), 77(3), 57(18), 56(100), 55(4). \textbf{1H NMR} (250 MHz, Methanol-d$_4$) $\delta$ 7.23 (ddt, $J = 14.8$, 10.4, 7.0 Hz, 5H), 4.04 (dd, $J = 8.8$, 7.0 Hz, 2H), 3.78 – 3.47 (m, 3H), 2.74 (d, $J = 2.9$ Hz, 4H), 1.43 (s, 9H). \textbf{13C NMR} (63 MHz, Methanol-d$_4$) $\delta$ 158.1, 140.9, 129.6, 127.3, 80.8, 49.5, 48.6, 37.0, 28.7. **IR** (ATR, cm$^{-1}$) 3307, 3061, 3026, 2973, 2877, 2863, 1692, 1604, 1476, 1455, 1399, 1364, 1292, 1252, 1156, 1126, 1109, 1029, 936, 861, 771, 747, 699, 564, 499, 464. **HRMS** m/z [M+H]$^+$ calculated for C$_{16}$H$_{25}$N$_2$O$_2$+: 277.1916, found: 277.1910.

**3-((tert-butyldimethylsilyl)oxy)azetidine (A18)**

A 40 mL vial was charged with stirring bar and 3-hydroxyazetidin-1-ium chloride (657 mg, 6.0 mmol), vial was sealed with Teflon septa and screw cap, then evacuated and backfilled with argon (three cycles). Solution of imidazole (1.23 g, 18 mmol, 3 equiv) and dimethylformamide (23 µL, 0.3 mmol, 5 mol%) in dichloromethane (10
mL) was added under argon atmosphere and stirred at room temperature. Solution of tert-butylidimethylsilyl chloride (1.03 g, 6.6 mmol, 1.1 equiv) in dichloromethane (10 mL) was added dropwise under argon atmosphere. Reaction mixture was stirred for 3 hours, then concentrated under reduced pressure. Residue was suspended in diisopropyl ether and filtered through a pad of Celite. Solids were washed with diisopropyl ether two times and combined filtrates concentrated under reduced pressure to afford the title compound as a colorless (689 mg, 3.68 mmol, 61% yield).

R<sub>f</sub> = 0.45 (hexanes:ethyl acetate= 7:3). LRMS (EI, 70 eV): m/z (%): 186(1), 174(5), 173(20), 172(100), 98(16), 97(6), 96(28), 89(17), 84(10), 82(15), 75(17), 74(4), 73(13), 70(7), 59(11), 57(4).

<sup>1</sup>H NMR (250 MHz, Chloroform-<sup>d</sup>) δ 4.45 (s, 1H), 3.89 – 2.80 (m, 4H), 2.53 (bs, 1H), 0.83 (s, 9H), -0.01 (s, 6H).

<sup>13</sup>C NMR (63 MHz, Chloroform-d) δ 71.4, 58.1, 25.9, 18.1, -4.9. IR (ATR, cm<sup>−1</sup>) 2952, 2929, 2856, 1738, 1472, 1463, 1371, 1252, 1229, 1217, 1202, 1158, 1068, 1005, 879, 834, 774, 736, 671, 398.

3-(methoxycarbonyl)azetidin-1-ium trifluoromethanesulfonate (A19)

A 30 mL vial was charged with stirring bar, 1-(tert-butoxycarbonyl)azetidine-3-carboxylic acid (402 mg, 2.0 mmol), methanol (10 mL) and trifluoromethanesulfonic acid (186 µL, 2.1 mmol, 1.05 equiv) then vial was sealed with Teflon septa and screw cap. Reaction mixture was stirred for 16 hours at room temperature, then volatiles were evaporated under reduced pressure. Residues were dissolved in dry diethylether and volatiles were evaporated under reduced pressure (repeated three times), then the residue was dried under high vacuum. Title compound was obtained as a hygroscopic, colorless solid (522 mg, 1.97 mmol, 98% yield).

R<sub>f</sub> = 0.36 (toluene:ethyl acetate:acetic acid= 7:2:1). LRMS (EI, 70 eV): m/z (%): 57(100), 55(20), 56(20), 87(18), 142(13), 160(9), 55(5), 58(5), 59(4), 115(4). <sup>1</sup>H NMR (250 MHz, Acetonitrile-d<sub>3</sub>) δ 7.32 (bs, 2H), 4.34 – 4.18 (m, 1H), 3.70 (dd, J = 16.6, 8.7 Hz, 1H), 3.70 (s, 3H). <sup>19</sup>F NMR (235 MHz, Acetonitrile-d<sub>3</sub>) δ -79.28. <sup>13</sup>C NMR (63 MHz, Acetonitrile-d<sub>3</sub>) δ 172.1, 121.5 (q, J = 318.7 Hz), 53.3, 50.0, 35.4. IR (ATR, cm<sup>−1</sup>) 3238, 3085, 3046, 2969, 2895, 1736, 1700, 1441, 1384, 1365, 1320, 1265, 1242, 1226, 1207, 1158, 1080, 1065, 1029, 922, 878, 852, 838, 773, 753, 734, 637, 573, 513.

**General procedure for the synthesis of piperidine derivatives**

A 40 mL vial was charged with stirring bar, appropriate alcohol (10.0 mmol), imidazole (1.02 g, 15.0 mmol), dimethylformamide (77 µL, 1 mmol, 10 mol%) and dichloromethane (20 mL). To the
stirred reaction mixture, tert-butyldimethylsilyl chloride (1.71 g, 11 mmol, 1.1 equiv) was added at room temperature and stirring was continued for 16 hours. Reaction mixture was diluted with diethylether (120 mL) and washed with water (3 × 50 mL) and brine (1 × 20 mL). Organic phase was separated, dried over anh. MgSO₄, filtered and the filtrate was concentrated in vacuo.

3-((tert-butyldimethylsilyl)oxy)piperidine (A20)

Compound A20 was prepared according to general procedure from piperidine-3-ol (1.01 g, 10 mmol) to afford a pale yellow oil (1.99 g, 9.26 mmol, 93% yield).

Rf = 0.52 (hexanes:ethyl acetate= 7:3). LRMS (EI, 70 eV): m/z (%): 158(100), 84(44), 82(32), 75(26), 73(21), 159(14), 59(12), 56(11), 57(9), 55(9), 156(8), 101(7), 58(4), 200(3). ¹H NMR (250 MHz, CDCl₃) δ 3.52 (dt, J = 7.3, 3.7 Hz, 1H), 2.83 (d, J = 12.2 Hz, 1H), 2.75 – 2.62 (m, 1H), 2.60 – 2.34 (m, 2H), 2.20 (bs, 1H), 1.81 – 1.54 (m, 2H), 1.33 (tt, J = 12.0, 7.5 Hz, 2H), 0.88 – 0.68 (m, 9H), 0.01 – 0.13 (m, 6H). ¹³C NMR (63 MHz, CDCl₃) δ 67.9, 54.0, 46.1, 33.8, 25.8, 24.4, 18.1, -4.7, -4.8. IR (ATR, cm⁻¹) 2929, 2911, 2894, 2856, 2809, 1738, 1472, 1462, 1439, 1363, 1251, 1229, 1217, 1149, 1093, 1066, 1046, 1029, 1005, 879, 851, 832, 804, 771, 668.

3-((tert-butyldimethylsilyl)oxy)methyl)piperidine (A21)

Compound A21 was prepared according to general procedure from piperidin-3-ylmethanol (1.15 g, 10 mmol) to afford a pale yellow oil (1.47 g, 6.4 mmol, 64% yield).

Rf = 0.23 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 172(100), 96(36), 75(26), 89(24), 73(22), 82(22), 59(21), 98(19), 173(19), 84(15), 70(12), 57(8), 214(6), 229(3). ¹H NMR (250 MHz, CDCl₃) δ 3.47 – 3.21 (m, 2H), 3.06 (d, J = 11.5 Hz, 1H), 2.93 (d, J = 12.1 Hz, 1H), 2.46 (td, J = 11.8, 2.7 Hz, 1H), 2.34 – 2.13 (m, 1H), 1.91 (s, 1H), 1.76 – 1.48 (m, 3H), 1.48 – 1.24 (m, 1H), 1.01 (qd, J = 11.9, 3.9 Hz, 1H), 0.82 (s, 9H), -0.03 (d, J = 3.7 Hz, 6H). ¹³C NMR (63 MHz, CDCl₃) δ 66.6, 50.2, 47.2, 40.0, 27.8, 26.3, 26.0, 18.3, -5.4, -5.4. IR (ATR, cm⁻¹) 2928, 2854, 2802, 2734, 1738, 1470, 1442, 1385, 1361, 1252, 1217, 1078, 1005, 939, 832, 773, 665, 567.
Synthesis of compound 6
1-(naphthalen-1-ylmethyl)-2-(trifluoromethyl)aziridine

To a stirred suspension of sodium carbonate (63.6 mg, 0.60 mmol), 1-naphthylmethylamine (64.2 mg, 0.4 mmol) and dichloromethane (4 ml) 4-fluorophenyl)(3,3,3-trifluoroprop-1-en-2-yl)iodonium trifluoromethanesulfonate (196 mg, 0.42 mmol) was added in one portion. Reaction was monitored by TLC and after completion the mixture was concentrated onto Celite and purified by flash chromatography (eluent: hexanes:ethyl acetate= 10:1). Title compound was obtained as a colorless syrup (91.6 mg, 0.365 mmol, 91% yield).

Rf = 0.33 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 141(100), 115(27), 251(17), 142(14), 139(10), 127(6), 128(5), 154(3), 126(3), 63(3), 140(3), 60(3), 252(3), 116(3). ¹H NMR 1H NMR (250 MHz, Acetonitrile-d₃) δ 8.29 – 8.07 (m, 1H), 8.03 – 7.76 (m, 2H), 7.67 – 7.32 (m, 4H), 3.97 (s, 2H), 2.49 (pd, J = 5.6, 3.0 Hz, 1H), 2.12 (d, J = 3.1 Hz, 1H), 1.87 (d, J = 6.4 Hz, 1H). ¹⁹F NMR (235 MHz, Acetonitrile-d₃) δ -71.67. ¹³C NMR (63 MHz, Acetonitrile-d₃) δ 135.1, 134.6, 132.5, 129.4, 129.0, 127.0, 126.8, 126.4, 125.7 (d, J = 271.3 Hz), 125.0, 37.9 (q, J = 39.0 Hz), 30.8 (q, J = 1.9 Hz). IR (ATR, cm⁻¹) 3041, 2988, 2971, 2901, 1738, 1598, 1510, 1475, 1429, 1283, 1232, 1131, 1072, 1058, 1028, 957, 865, 835, 793, 771, 734, 655, 537, 408.
Optimization of reaction conditions of homodiamination
A 4 mL screwed cap vial was charged with stirring bar, sodium carbonate (0-3.0 equiv), solvent (2 mL) and \( N \)-methyl-1-(naphthalen-1-yl)methanamine (1.0-3.0 equiv). To the vigorously stirred mixture, (4-fluorophenyl)(3,3,3-trifluoroprop-1-en-2-yl)iodonium trifluoromethanesulfonate (93.2 mg, 0.20 mmol) was added portionwise within one minute. Reaction mixture was stirred for the indicated time, diluted with the corresponding solvent and concentrated onto Celite under reduced pressure. Residue was purified by flash column chromatography.

Supplementary Table 1: Optimization of reaction conditions of homodiamination

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Reaction monitoring by $^{19}$F-NMR

A 5 mm O.D. NMR tube was charged with (4-fluorophenyl)(3,3,3-trifluoroprop-1-en-2-yl)iodonium trifluoromethanesulfonate (23.3 mg, 0.05 mmol) acetonitrile-$d_3$ (500 µL) and sealed with a hollow cap. An LDPE tube was filled with five layers of substances in a following sequence: acetonitrile (100 µL), air (100 µL), appropriate secondary amine (0.20 mmol, 4 equiv), air (100 µL) and acetonitrile (100 µL), then was placed in the NMR tube. These substances were added in one portion to the reaction mixture at $t=0$ second. Recording of $^{19}$F-NMR spectra (proton decoupled, No. dummy scan = 0, No. scan = 1) was started at $t=-60$ seconds and 15 seconds time intervals were applied between experiments.

Supplementary Figure 1: Reaction scheme and monitoring of homodiamination reaction with of $N$-methyl-1-(naphthalen-1-yl)methanamine
Supplementary Figure 2: Reaction monitoring of homodiamination reaction with N-methylaniline by $^{19}$F-NMR-spectroscopy
Supplementary Figure 3: Reaction monitoring of homodiamination reaction with N-ethylaniline by $^{19}$F-NMR-spectroscopy
Supplementary Figure 4: GC-MS TIC of homodiamination reaction with N-ethylaniline
Supplementary Figure 5: Reaction monitoring of homodiamination reaction with indoline by $^{19}$F-NMR-spectroscopy
General procedure for the synthesis of homofunctionalized diamines

Vial was charged with stirring bar, appropriate amine (2.5 equiv) and acetonitrile (1 mL / 0.1 mmol). To the vigorously stirred mixture, sodium carbonate (1.5 equiv) was added, then (4-fluorophenyl)(3,3,3-trifluoroprop-1-en-2-yl)iodonium trifluoromethanesulfonate (1) (1 equiv) was added portionwise. Reaction mixture was stirred for 3 hours, diluted with dichloromethane and concentrated onto Celite under reduced pressure. Residue was purified by flash column chromatography (hexanes:ethyl acetate = 100:0 → 50:50).

Synthesis of compound 7
3,3,3-trifluoro-N<sup>1</sup>,N<sup>2</sup>-dimethyl-N<sup>1</sup>,N<sup>2</sup>-diphenylpropane-1,2-diamine

Compound 7 was prepared according to general procedure from N-methylaniline (54 µL, 0.5 mmol, 2.5 equiv), sodium carbonate (31.8 mg, 0.3 mmol, 1.5 equiv) and 1 (92.3 mg, 0.2 mmol, 1 equiv) to afford a pale yellow oil (47.1 mg, 0.153 mmol, 76%). R<sub>f</sub> = 0.53 (hexanes:ethyl acetate= 10:1).

LRMS (EI, 70 eV): m/z (%): 308(5), 188(3), 132(2), 121(9), 120(100), 119(2), 118(3), 105(6), 104(9), 91(4), 79(2), 78(2), 77(14), 51(3).

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 7.2 (t, J = 8.6, 7.5 Hz, 2H), 7.1 (t, J = 8.6, 7.4 Hz, 2H), 6.8 – 6.6 (m, 6H), 4.5 (pd, J = 8.4, 4.0 Hz, 1H), 3.9 (dd, J = 15.4, 4.0 Hz, 1H), 3.7 (dd, J = 15.4, 8.5 Hz, 1H), 2.9 (s, 6H).

<sup>19</sup>F NMR (235 MHz, CDCl<sub>3</sub>) δ -70.01.

<sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>) δ 149.9, 148.2, 129.7, 129.3, 126.0 (q, J = 288.8 Hz), 119.0, 117.5, 114.5, 112.6, 59.2 (q, J = 26.3 Hz), 49.4 (d, J = 0.9 Hz), 39.5, 32.3 (d, J = 1.6 Hz).

IR (ATR, cm<sup>-1</sup>) 3095, 3063, 3029, 2910, 2827, 1598, 1503, 1451, 1363, 1314, 1272, 1239, 1207, 1166, 1141, 1117, 1095, 1034, 1000, 963, 895, 858, 746, 691, 516.

HRMS m/z [M+H]<sup>+</sup> calculated for C<sub>17</sub>H<sub>20</sub>N<sub>2</sub>F<sub>3</sub>: 309.1579, found: 309.1579.

Synthesis of compound 8
N<sup>1</sup>,N<sup>2</sup>-diethyl-3,3,3-trifluoro-N<sup>1</sup>,N<sup>2</sup>-diphenylpropane-1,2-diamine

Compound 8 was prepared according to general procedure from N-ethylaniline (96 µL, 0.75 mmol, 2.5 equiv), sodium carbonate (47.7 mg, 0.45 mmol, 1.5 equiv) and 1 (140 mg, 0.3 mmol, 1 equiv) to afford a pale yellow oil (13.3 mg, 0.0395 mmol, 13% yield). R<sub>f</sub> = 0.55 (hexanes:ethyl acetate= 10:1).

LRMS (EI, 70 eV): m/z (%): 336(1), 214(1), 202(1), 174(1), 135(10), 134(100), 132(1), 118(1), 107(1), 106(9), 106(6), 105(2), 105(1), 104(7), 91(3), 79(3), 78(1), 77(11), 65(1), 51(2).

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 7.22 – 7.02 (m, 4H), 6.78 – 6.54 (m, 6H), 4.36 (td, J = 7.9, 4.6 Hz, 1H), 3.77 – 3.53 (m, 2H), 3.42 – 3.16 (m, 4H), 1.08 (t, J = 6.9 Hz, 3H), 1.01 (t, J = 6.9 Hz, 3H).
(t, J = 7.1 Hz, 3H). 19F NMR (235 MHz, Chloroform- d) δ -69.86. 13C NMR (63 MHz, Chloroform- d) δ 147.9, 129.7, 129.2, 126.4 (q, J = 288.3 Hz), 119.4, 117.7, 116.6, 113.6, 60.6 (q, J = 25.5 Hz), 48.6, 46.5, 39.1, 13.1, 12.1. IR (ATR, cm-1) 3094, 3063, 3026, 2973, 2929, 2873, 1598, 1502, 1449, 1353, 1299, 1262, 1232, 1188, 1161, 1141, 1103, 1055, 1038, 973, 913, 888, 851, 795, 744, 692, 615, 579, 522, 468, 413. HRMS m/z [M+H]+ calculated for C19H24N2F3+: 337.1892, found: 337.1893.

**Synthesis of compound 9**

1,1’-(3,3,3-trifluoropropane-1,2-diyldiindoline

Compound 9 was prepared according to general procedure from indoline (57 µL, 0.5 mmol, 2.5 equiv), sodium carbonate (31.8 mg, 0.3 mmol, 1.5 equiv) and 1 (93.2 mg, 0.2 mmol, 1 equiv) to afford a brown oil (62.1 mg, 0.187 mmol, 93% yield). Rf = 0.55 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 332(17), 200(8), 133(15), 133(8), 132(100), 132(49), 131(8), 130(20), 130(9), 118(6), 117(18), 117(10), 103(6), 91(7), 91(18), 117(10), 116(6), 115(7), 115(7), 115(10), 114(6), 113(8), 113(20), 113(10), 112(8), 111(7), 110(6), 91(7), 90(8), 77(10), 77(5). 1H NMR (250 MHz, Methanol- d4) δ 7.15 – 6.92 (m, 4H), 6.74 – 6.41 (m, 4H), 4.57 (ddt, J = 16.7, 8.5, 4.2 Hz, 1H), 3.78 (dd, J = 14.0, 9.5 Hz, 2H), 3.61 (q, J = 8.7 Hz, 1H), 3.48 – 3.32 (m, 2H), 3.26 (q, J = 8.9 Hz, 1H), 2.95 (t, J = 8.7 Hz, 2H), 2.89 – 2.65 (m, 2H). 19F NMR (235 MHz, Methanol- d4) δ -72.00. 13C NMR (63 MHz, Methanol- d4) δ 152.8, 151.7, 131.0, 129.8, 128.3, 128.2, 127.5 (q, J = 287.1 Hz), 125.6, 125.5, 119.2, 118.9, 107.5, 106.9, 56.6 (q, J = 27.0 Hz), 54.5, 48.1, 46.3 (q, J = 19 Hz), 29.3, 29.1. IR (ATR, cm-1) 3048, 3029, 2952, 2873, 1598, 1502, 1449, 1475, 1460, 1263, 1242, 1192, 1157, 1146, 1120, 1090, 1054, 1025, 991, 868, 739, 713, 700, 630, 577, 417. HRMS m/z [M+H]+ calculated for C19H20N2F3+: 333.1579, found: 333.1579.

**Synthesis of compound 10**

1,1’-(3,3,3-trifluoropropane-1,2-diyldi)bis(1,2,3,4-tetrahydroquinoline)

Compound 10 was prepared according to general procedure from 1,2,3,4-tetrahydroquinoline (64 µL, 0.5 mmol, 2.5 equiv), sodium carbonate (31.8 mg, 0.3 mmol, 1.5 equiv) and 1 (93.2 mg, 0.2 mmol, 1 equiv) to afford a brown oil (36.1 mg, 0.10 mmol, 50% yield). Rf = 0.55 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 360(3), 147(11), 146(100), 144(4), 131(7), 130(11), 118(8), 117(9), 115(3), 91(11), 77(3). 1H NMR (250 MHz, Chloroform- d) δ 7.14 (t, J = 7.8 Hz, 1H), 7.07 – 6.90 (m, 3H), 6.76 – 6.57 (m, 3H), 6.52 (d, J = 8.3 Hz, 1H), 4.76 (tt, J = 12.9, 6.3 Hz, 1H), 3.88 (dd, J = 15.3, 4.4 Hz, 1H), 3.71 (dd, J = 15.3, 7.6 Hz,
1H), 3.39 (dt, $J = 16.3$, 5.5 Hz, 4H), 2.84 (h, $J = 9.8$ Hz, 2H), 2.72 (t, $J = 6.4$ Hz, 2H), 2.14 – 1.74 (m, 4H). $^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -69.3. $^{13}$C NMR (63 MHz, Chloroform-d) $\delta$ 144.8, 144.2, 129.9, 129.6, 127.5, 127.2, 124.8 (q, $J = 289.1$ Hz), 123.7, 123.2, 117.7, 116.6, 112.0, 110.0, 56.3 (q, $J = 25.2$ Hz), 50.8, 48.3, 43.6, 28.2, 28.1, 22.2, 22.1. IR (ATR, cm$^{-1}$) 3067, 3022, 2932, 2890, 2846, 1713, 1602, 1575, 1496, 1458, 1348, 1302, 1275, 1235, 1218, 1188, 1157, 1129, 1107, 1061, 742, 689, 529. HRMS m/z [M+H]$^+$ calculated for C$_{21}$H$_{24}$N$_2$F$_3$: 361.1892, found: 361.1906.

Synthesis of compound 11
3,3,3-trifluoro-$N^1,N^2$-bis(2-methoxyphenyl)-$N^1,N^2$-dimethylpropane-1,2-diamine

Compound 11 was prepared according to general procedure from 2-methoxy-$N$-methylaniline (70.7 mg, 0.5 mmol, 2.5 equiv), sodium carbonate (31.8 mg, 0.3 mmol, 1.5 equiv) and 1 (93.2 mg, 0.2 mmol, 1 equiv) to afford a brown oil (32.2 mg, 0.087 mmol, 44% yield). $R_f$ = 0.28 (hexanes:ethyl acetate= 10:1).

LRMS (EI, 70 eV): m/z (%): 368 (1), 218 (1), 151 (10), 150 (100), 148 (1), 136 (2), 135 (20), 134 (28), 121 (2), 120 (5), 107 (1), 106 (1), 104 (1), 93 (2), 92 (2), 91 (2), 79 (2), 78 (2), 77 (5), 65 (3), 51 (1). $^1$H NMR (250 MHz, Chloroform-d) $\delta$ 7.04 – 6.72 (m, 8H), 4.60 (h, $J = 8.5$ Hz, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 3.66 (s, 1H), 3.63 (s, 1H), 2.87 (s, 6H).

$^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -68.26.

$^{13}$C NMR (63 MHz, Chloroform-d) $\delta$ 152.7, 151.5, 140.5, 129.3 (q, $J = 290.6$ Hz), 122.5, 122.1, 121.1, 121.0, 120.4, 111.8, 111.7, 60.1 (q, $J = 25.3$ Hz), 55.4 (d, $J = 2.4$ Hz), 51.1, 41.1, 34.0 (d, $J = 1.1$ Hz). IR (ATR, cm$^{-1}$) 3063, 2997, 2956, 2904, 2836, 1594, 1500, 1456, 1438, 1235, 1160, 1110, 1090, 1055, 1027, 991, 961, 855, 733, 689, 591, 530, 488, 451. HRMS m/z [M+H]$^+$ calculated for C$_{19}$H$_{24}$N$_2$O$_2$F$_3$: 369.179, found: 369.1789.

Synthesis of compound 12
3,3,3-trifluoro-$N^1,N^2$-dimethyl-$N^1,N^2$-di-m-tolylpropane-1,2-diamine

Compound 12 was prepared according to general procedure from N-methyl-3-toluidine (77.3 mg, 0.625 mmol, 2.5 equiv), sodium carbonate (39.7 mg, 0.375 mmol, 1.5 equiv) and 1 (117 mg, 0.25 mmol, 1 equiv) to afford a colorless oil (54.6 mg, 0.162 mmol, 65% yield). $R_f$ = 0.65 (hexanes:ethyl acetate= 10:1).

LRMS (EI, 70 eV): m/z (%): 337 (2), 336 (11), 202 (3), 146 (2), 135 (17), 134 (100), 133 (3), 132 (2), 120 (2), 119 (11), 118 (12), 105 (3), 92 (3), 91 (19), 90 (2), 89 (2), 77 (3), 65 (6). $^1$H NMR (250 MHz, Chloroform-d) $\delta$ 7.14 – 7.01 (m, 1H), 6.96 (t, $J = 7.8$ Hz, 1H), 6.56 – 6.49 (m, 2H), 6.47 – 6.36 (m, 3H), 6.31 – 6.27 (m, 1H), 4.47 (pd, $J = 8.4$, 4.1 Hz, 1H), 3.82 (dd, $J = 15.4$, 4.1 Hz, 1H), 3.59 (dd, $J = 15.4$, 4.1 Hz, 1H), 3.50 – 3.40 (m, 5H).
8.4 Hz, 1H), 2.83 (s, 6H), 2.20 (s, 3H), 2.10 (s, 3H). \textsuperscript{19}F NMR (235 MHz, Chloroform-\textit{d}) \(\delta\) -69.99.

\textsuperscript{13}C NMR (63 MHz, Chloroform-\textit{d}) \(\delta\) 150.0, 148.1, 139.4, 139.0, 129.5, 129.1, 126.0 (q, \(J = 288.8\) Hz), 119.9, 118.4, 115.4, 113.5, 111.6, 109.9, 58.9 (q, \(J = 26.2\) Hz), 49.4, 39.8, 32.3 (q, \(J = 1.6\) Hz), 22.0, 21.8. IR (ATR, cm\(^{-1}\)) 3046, 2945, 2918, 2826, 1602, 1582, 1496, 1449, 1360, 1302, 1273, 1245, 1181, 1163, 1139, 1119, 1099, 1046, 1017, 995, 968, 909, 839, 766, 757, 732, 691, 576, 478, 441. HRMS m/z [M+H]\(^+\) calculated for \(C_{19}H_{24}N_2F_3\): 337.1892, found: 337.1897.

**Synthesis of compound 13**

3,3,3-trifluoro- \(N^1\),\(N^2\)-bis(3-fluorophenyl)- \(N^1\),\(N^2\)-dimethylpropane-1,2-diamine

Compound 13 was prepared according to general procedure from 3-fluoro-\(N\)-methylaniline (58 \(\mu\)L, 0.5 mmol, 2.5 equiv), sodium carbonate (31.8 mg, 0.3 mmol, 1.5 equiv) and 1 (93.2 mg, 0.2 mmol, 1 equiv) to afford a pale yellow oil (30.2 mg, 0.088 mmol, 44% yield). \textit{Rf} = 0.56 (hexanes:ethyl acetate= 10:1).

LRMS (EI, 70 eV): m/z (%): 344(2), 206(3), 150(2), 139(9), 138(100), 136(3), 123(5), 122(10), 110(2), 109(5), 96(3), 95(11), 75(3). \textsuperscript{1}H NMR (250 MHz, Chloroform-\textit{d}) \(\delta\) 7.21 (dd, \(J = 8.2, 7.1\) Hz, 1H), 7.09 (dd, \(J = 8.2, 7.6\) Hz, 1H), 6.56 – 6.27 (m, 6H), 4.51 (pd, \(J = 8.3, 4.0\) Hz, 1H), 3.90 (dd, \(J = 15.5, 3.9\) Hz, 1H), 3.71 (dd, \(J = 15.5, 8.6\) Hz, 1H), 2.93 (s, 3H), 2.92 (s, 3H). \textsuperscript{19}F NMR (235 MHz, Chloroform-\textit{d}) \(\delta\) -70.20 (s, 3F), -111.62 (s, 1F), -111.91 (s, 1F). \textsuperscript{13}C NMR (63 MHz, Chloroform-\textit{d}) \(\delta\) 164.5 (d, \(J = 243.1\) Hz), 164.0 (d, \(J = 243.6\) Hz), 151.5 (d, \(J = 10.2\) Hz), 149.8 (d, \(J = 10.5\) Hz), 130.8 (d, \(J = 10.3\) Hz), 130.4 (d, \(J = 10.1\) Hz), 125.7 (q, \(J = 288.2\) Hz), 109.8 (d, \(J = 2.5\) Hz), 107.9 (d, \(J = 2.4\) Hz), 105.7 (d, \(J = 21.4\) Hz), 104.1 (d, \(J = 21.6\) Hz), 101.6 (d, \(J = 26.0\) Hz), 99.7 (d, \(J = 26.2\) Hz), 58.9 (q, \(J = 26.9\) Hz), 49.2, 39.6, 32.5 (q, \(J = 1.7\) Hz). IR (ATR, cm\(^{-1}\)) 3078, 3043, 2917, 2830, 1616, 1580, 1497, 1452, 1297, 1272, 1234, 1157, 1130, 1117, 1097, 1076, 1048, 1014, 1004, 978, 903, 822, 754, 681, 496, 451. HRMS m/z [M+H]\(^+\) calculated for \(C_{17}H_{18}N_2F_3\): 345.139, found: 345.1396.
Synthesis of compound 14

$N^1,N^2$-bis(3-chlorophenyl)-3,3,3-trifluoro- $N^1,N^2$-dimethylpropane-1,2-diamine

Compound 14 was prepared according to general procedure from 3-chloro-$N$-methylaniline (63 µL, 0.50 mmol, 2.5 equiv), sodium carbonate (31.8 mg, 0.30 mmol, 1.5 equiv) and 1 (93.2 mg, 0.20 mmol, 1 equiv) to afford a pale yellow oil (29.7 mg, 0.079 mmol, 39% yield). $R_f$ = 0.50 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 376(1), 222(2), 157(3), 156(32), 155(9), 154(100), 141(2), 140(3), 139(4), 138(7), 125(2), 119(4), 118(6), 111(4), 91(2), 77(3), 76(2), 75(4). $^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 7.18 (t, $J$ = 8.1 Hz, 1H), 7.07 (t, $J$ = 8.1 Hz, 1H), 6.77 – 6.52 (m, 3H), 6.48 (dd, $J$ = 8.4, 2.6 Hz, 1H), 4.47 (qd, $J$ = 8.3, 4.0 Hz, 1H), 3.88 (dd, $J$ = 15.5, 4.0 Hz, 1H), 3.71 (dd, $J$ = 15.5, 8.6 Hz, 1H), 2.91 (s, 6H). $^{19}$F NMR (235 MHz, Chloroform-$d$) $\delta$ -70.13. $^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 150.8, 148.9, 135.7, 135.3, 130.7, 130.3, 125.6 (q, $J$ = 288.2 Hz), 119.2, 117.9, 114.5, 112.9, 112.5, 110.8, 58.8 (q, $J$ = 26.9 Hz), 49.4, 39.8, 32.5. IR (ATR, cm$^{-1}$) 3077, 2951, 2912, 2829, 1592, 1563, 1489, 1435, 1364, 1293, 1270, 1239, 1212, 1167, 1147, 1097, 1046, 1002, 987, 971, 913, 832, 814, 759, 716, 681, 571, 491, 441, 410. HRMS m/z [M+H]$^+$ calculated for C$_{17}$H$_{18}$N$_2$F$_3$Cl$_2$+: 377.0799, found: 377.0804.

Synthesis of compound 15

3,3,3-trifluoro- $N^1,N^2$-dimethyl- $N^1,N^2$-di-p-tolylpropane-1,2-diamine

Compound 15 was prepared according to general procedure from $N$-methyl-4-toluidine (75.7 mg, 0.625 mmol, 2.5 equiv), sodium carbonate (39.7 mg, 0.375 mmol, 1.5 equiv) and 1 (117 mg, 0.25 mmol, 1 equiv) to afford a colorless oil (51.2 mg, 0.152 mmol, 61% yield). $R_f$ = 0.55 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 336(3), 202(2), 135(10), 134(100), 119(7), 118(8), 105(2), 91(10), 77(2), 65(3). $^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 7.13 (d, $J$ = 8.5 Hz, 2H), 7.03 (d, $J$ = 8.5 Hz, 2H), 6.69 (d, $J$ = 8.5 Hz, 2H), 6.62 (d, $J$ = 8.6 Hz, 2H), 4.54 (pd, $J$ = 8.4, 4.0 Hz, 1H), 3.91 (dd, $J$ = 15.3, 8.6 Hz, 1H), 3.72 (dd, $J$ = 15.3, 8.6 Hz, 1H), 3.04 – 2.86 (m, 6H), 2.34 (s, 3H), 2.28 (s, 3H). $^{19}$F NMR (235 MHz, Chloroform-$d$) $\delta$ -69.96. $^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 147.8, 146.1, 130.2, 129.8, 128.2, 126.7, 126.1 (q, $J$ = 289.4 Hz), 114.8, 112.9, 59.5 (q, $J$ = 25.9 Hz), 49.6, 39.7, 32.3 (q, $J$ = 1.4 Hz), 20.4. IR (ATR, cm$^{-1}$) 3012, 2951, 2866, 2824, 1618, 1517, 1363, 1310, 1270, 1238, 1205,
1164, 1140, 1116, 1095, 1046, 998, 964, 909, 800, 732, 678, 518. **HRMS** m/z [M+H]^+ calculated for C_{19}H_{24}N_{2}F_{3}^+: 337.1892, found: 337.1889.

**Synthesis of compound 16**
\[ \text{N}^1,\text{N}^2\text{-bis(4-chlorophenyl)-3,3,3-trifluoro- N}^1,\text{N}^2\text{-dimethylpropane-1,2-diamine} \]

Compound 16 was prepared according to general procedure from 4-chloro-N-methylaniline (94 µL, 0.75 mmol, 2.5 equiv), sodium carbonate (47.7 mg, 0.45 mmol, 1.5 equiv) and 1 (140 mg, 0.3 mmol, 1 equiv) to afford a pale yellow oil (56.4 mg, 0.15 mmol, 50% yield). **Rf** = 0.53 (hexanes:ethyl acetate= 10:1). **LRMS** (EI, 70 eV): m/z (%): 378(2), 376(2), 222(2), 157(3), 156(32), 155(9), 154(100), 141(2), 140(2), 140(2), 139(6), 138(9), 125(2), 119(5), 118(5), 113(2), 111(6), 77(2), 75(2). **1H NMR** (250 MHz, Chloroform-d) δ 7.27 – 7.17 (m, 2H), 7.17 – 7.07 (m, 2H), 6.61 (d, \( J = 9.1 \) Hz, 2H), 6.55 (d, \( J = 9.1 \) Hz, 2H), 4.44 (ddq, \( J = 12.1, 8.3, 4.2 \) Hz, 1H), 3.88 (dd, \( J = 15.5, 3.8 \) Hz, 1H), 3.70 (dd, \( J = 15.5, 8.7 \) Hz, 1H), 2.91 (s, 6H). **19F NMR** (235 MHz, Chloroform-d) δ -70.13. **13C NMR** (63 MHz, Chloroform-d) δ 148.4, 146.6, 129.5, 129.2, 125.7 (q, \( J = 288.4 \) Hz), 124.1, 122.7, 115.6, 113.8, 59.1 (q, \( J = 26.6 \) Hz), 49.3, 39.7, 32.4 (q, \( J = 1.4 \) Hz). **IR** (ATR, cm\(^{-1}\)) 3078, 3047, 2990, 2945, 2904, 2829, 1597, 1496, 1364, 1309, 1269, 1238, 1207, 1166, 1141, 1117, 1095, 1046, 997, 964, 807, 763, 710, 621, 510, 411. **HRMS** m/z [M+H]^+ calculated for C_{17}H_{18}N_{2}F_{3}Cl_{2}^+: 377.0799, found: 377.0797.

**Synthesis of compound 17**
\[ \text{N}^1,\text{N}^2\text{-bis(4-bromophenyl)-3,3,3-trifluoro- N}^1,\text{N}^2\text{-dimethylpropane-1,2-diamine} \]

Compound 17 was prepared according to general procedure from 3-bromo-N-methylaniline (95.9 mg, 0.5 mmol, 2.5 equiv), sodium carbonate (31.8 mg, 0.3 mmol, 1.5 equiv) and 1 (93.2 mg, 0.2 mmol, 1 equiv) to afford a pale yellow oil (53.7 mg, 0.115 mmol, 58% yield). **Rf** = 0.43 (hexanes:ethyl acetate= 10:1). **LRMS** (EI, 70 eV): m/z (%): 468(1), 466(2), 464(1), 201(9), 200(96), 199(10), 198(100), 185(6), 184(9), 183(6), 182(8), 157(6), 155(6), 119(14), 118(16), 105(3), 104(5), 91(3), 77(4), 76(5). **1H NMR** (250 MHz, Chloroform-d) δ \( J = 8.8 \) Hz, 2H), 7.16 (d, \( J = 8.7 \) Hz, 2H), 6.46 (d, \( J = 8.9 \) Hz, 2H), 6.40 (d, \( J = 8.9 \) Hz, 2H), 4.34 (td, \( J = 8.2, 3.7 \) Hz, 1H), 3.78 (dd, \( J = 15.4, 3.7 \) Hz, 1H), 3.60 (dd, \( J = 15.5, 8.7 \) Hz, 1H), 2.80 (s, 6H). **19F NMR** (235 MHz, Chloroform-d) δ \( J = 289.3 \) Hz, 2H), 7.16 (d, \( J = 8.7 \) Hz, 2H), 6.46 (d, \( J = 8.9 \) Hz, 2H), 6.40 (d, \( J = 8.9 \) Hz, 2H), 4.34 (td, \( J = 8.2, 3.7 \) Hz, 1H), 3.78 (dd, \( J = 15.4, 3.7 \) Hz, 1H), 3.60 (dd, \( J = 15.5, 8.7 \) Hz, 1H), 2.80 (s, 6H). **13C NMR** (63 MHz, Chloroform-d) δ 148.8, 146.8, 132.4, 132.1, 123.3 (q, \( J = 289.3 \) Hz, 2H), 116.0, 114.2, 111.4, 109.9, 58.9 (q, \( J = 26.7 \) Hz), 49.3, 39.7, 32.4.
IR (ATR, cm⁻¹) 3078, 3044, 2989, 2946, 2829, 2989, 2946, 2902, 2829, 1866, 1741, 1589, 1493, 1373, 1312, 1269, 1238, 1205, 1167, 1141, 1117, 1096, 1046, 994, 963, 906, 861, 804, 756, 730, 705, 688, 648, 638, 628, 596, 566, 540, 510, 481, 461.


Synthesis of compound 18

3,3,3-trifluoro-N¹,N²-bis(4-methoxyphenyl)-N¹,N²-dimethylpropane-1,2-diamine

Compound 18 was prepared according to general procedure from 4-methoxy-N-methylaniline (70 mg, 0.75 mmol, 2.5 equiv), sodium carbonate (31.8 mg, 0.45 mmol, 1.5 equiv) and 1 (93.2 mg, 0.2 mmol, 1 equiv) to afford a pale yellow oil (57.5 mg, 0.166 mmol, 78% yield). Rf = 0.60 (hexanes:ethyl acetate = 7:3). LRMS (EI, 70 eV): m/z (%): 368(8), 218(3), 151(14), 150(100), 136(3), 135(13), 134(5), 121(3), 120(9), 92(3), 77(3). ¹H NMR (250 MHz, Chloroform-d) δ 6.89 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 9.1 Hz, 2H), 6.73 (d, J = 8.4 Hz, 2H), 6.65 (d, J = 8.9 Hz, 2H), 4.39 (td, J = 8.2, 3.7 Hz, 1H), 3.80 (s, 3H), 3.78–3.60 (m, 5H), 2.91 (bs, 6H). ¹³C NMR (63 MHz, Chloroform-d) δ 153.1, 152.5, 144.5, 142.9, 126.2 (q, J = 289.4 Hz), 116.6, 115.2, 114.9, 114.6, 60.5 (q, J = 25.7 Hz), 55.8, 55.7, 50.2, 40.2, 32.6 (q, J = 1.1 Hz). IR (ATR, cm⁻¹) 3078, 3044, 2989, 2946, 2829, 1866, 1741, 1589, 1493, 1373, 1312, 1269, 1238, 1205, 1167, 1141, 1117, 1096, 1046, 994, 963, 906, 861, 804, 756, 730, 705, 688, 648, 638, 628, 596, 566, 540, 510, 481, 461. HRMS m/z [M+H]⁺ calculated for C₁₉H₂₄N₂O₂F₃⁺: 369.1790, found: 369.1790.

Synthesis of compound 19

3,3,3-trifluoro-N¹,N²-dimethyl-N¹,N²-bis(naphthalen-1-ylmethyl)propane-1,2-diamine

Compound 19 was prepared according to general procedure from N-methyl-1-(naphthalen-1-yl)methanamine (85.6 mg, 0.5 mmol, 2.5 equiv), sodium carbonate (31.8 mg, 0.3 mmol, 1.5 equiv) and 1 (93.2 mg, 0.2 mmol, 1 equiv) to afford a colorless oil (78.8 mg, 0.180 mmol, 90% yield). Rf = 0.55 (hexanes:ethyl acetate = 10:1). LRMS (EI, 70 eV): m/z (%): 185(7), 184(51), 182(1), 170(1), 168(1), 167(1), 143(1), 142(13), 141(100), 139(3), 127(1), 116(1), 115(14), 89(1). ¹H NMR (250 MHz, Chloroform-d) δ 8.04–7.88 (m, 1H), 7.79 (d, J = 7.7 Hz, 1H), 7.54–7.29 (m, 4H), 7.18–6.85 (m, 8H), 3.81 (s, 2H), 3.64 (d, J = 13.0 Hz, 1H), 3.41 (d, J = 12.9 Hz, 1H), 3.20–2.98 (m, 1H), 2.76–2.55 (m, 1H), 2.25 (dd, J = 13.6, 3.1 Hz, 1H), 1.85 (s, 3H), 1.79 (s, 3H). ¹⁹F NMR (235 MHz, Chloroform-d) δ -67.95. ¹³C NMR (63 MHz,
Chloroform-\(d\) \(\delta\) 134.5, 134.0, 134.0, 132.6, 132.4, 128.5, 128.4, 128.2, 128.1, 127.6, 127.4 (\(q, J = 290.4\) Hz), 127.2, 125.8, 125.8, 125.7, 125.3, 125.2, 125.1, 124.7, 61.7 (\(q, J = 24.3\) Hz), 61.5, 58.0, 53.6, 42.5, 36.5. \textbf{IR (ATR, cm}^{-1}) 3047, 2946, 2849, 2807, 1597, 1509, 1462, 1367, 1310, 1253, 1158, 1100, 1051, 1008, 907, 790, 773, 730, 703, 649, 520, 454, 414. \textbf{HRMS} \(m/z\) [M+H]+ calculated for C_{27}H_{28}N_{2}F_{3}+: 437.2205, found: 437.2198.

\textit{Synthesis of compound 20}

3,3,3-trifluoro-\(N^{1},N^{1},N^{2},N^{2}\)-tetraisobutylpropane-1,2-diamine

Compound 20 was prepared according to general procedure from diisobutylamine (130 \(\mu\)L, 0.75 mmol, 2.5 equiv), sodium carbonate (47.7 mg, 0.45 mmol, 1.5 equiv) and 1 (140 mg, 0.3 mmol, 1 equiv) to afford a pale yellow oil (70.8 mg, 0.201 mmol, 67% yield). \(R_f = 0.75\) (hexanes:ethyl acetate= 10:1). \textbf{LRMS} (EI, 70 eV): \(m/z\) (%): 309(1), 209(2), 190(2), 143(11), 142(100), 140(2), 126(1), 124(1), 100(4), 98(2), 86(7), 84(2), 57(10), 56(1), 55(1). \textbf{\(^1\)H NMR} (250 MHz, Chloroform-\(d\)) \(\delta\) 3.16 (\(qt, J = 8.9, 5.2\) Hz, 1H), 2.74 – 2.48 (m, 2H), 2.46 – 2.21 (m, 4H), 2.06 (\(h, J = 7.9, 6.9\) Hz, 4H), 1.69 (\(tp, J = 13.3, 6.6\) Hz, 4H), 1.06 – 0.68 (m, 24H). \textbf{\(^1\)F NMR} (235 MHz, Chloroform-\(d\)) \(\delta\) -68.12. \textbf{\(^{13}\)C NMR} (63 MHz, Chloroform-\(d\)) \(\delta\) 127.7 (\(q, J = 289.1\) Hz), 64.6, 60.8, 60.8 (\(q, J = 23.8\) Hz), 53.9, 27.3, 26.5, 21.2, 21.1, 20.8, 20.7. \textbf{IR (ATR, cm}^{-1}) 2953, 2907, 2870, 2824, 2805, 2749, 2722, 1469, 1388, 1365, 1278, 1248, 1170, 1153, 1117, 1082, 1035, 990, 959, 927, 849, 824, 710, 620, 598, 484. \textbf{HRMS} \(m/z\) [M+H]+ calculated for C_{17}H_{40}N_{2}F_{3}+: 353.3144, found: 353.3148.

\textit{Synthesis of compound 21}

\(N^{1},N^{1},N^{2},N^{2}\)-tetrabenzyl-3,3,3-trifluoropropane-1,2-diamine

Compound 21 was prepared according to general procedure from dibenzylamine (100 \(\mu\)L, 0.5 mmol, 2.5 equiv), sodium carbonate (31.8 mg, 0.3 mmol, 1.5 equiv) and 1 (93.2 mg, 0.2 mmol, 1 equiv) to afford a white solid (65.2 mg, 0.133 mmol, 67% yield). \(R_f = 0.63\) (hexanes:ethyl acetate= 10:1). \textbf{M.p. = 102-105 °C. LRMS} (EI, 70 eV): \(m/z\) (%): 91(100), 210(79), 211(13), 92(8), 65(8), 181(4), 118(2), 89(2), 212(1), 208(1), 73(1), 109(1), 63(1), 207(1), 397(1), 51(1), 182(1), 165(1), 77(1). \textbf{\(^1\)H NMR} (250 MHz, Chloroform-\(d\)) \(\delta\) 7.76 – 6.93 (m, 20H), 3.87 – 3.62 (m, 6H), 3.54 (\(tt, J = 12.8, 6.4\) Hz, 1H), 3.35 (\(d, J = 13.5\) Hz, 2H), 3.03 (\(dd, J = 13.6, 7.2\) Hz, 1H), 2.74 (\(dd, J = 13.6, 4.2\) Hz, 1H). \textbf{\(^{19}\)F NMR} (235 MHz, Chloroform-\(d\)) \(\delta\) -67.32. \textbf{\(^{13}\)C NMR} (63 MHz, Chloroform-\(d\)) \(\delta\) 139.2, 138.7, 129.3, 129.1, 128.4, 128.4, 127.6 (\(d, J = 290.1\) Hz), 127.3, 127.2, 58.7, 57.5 (\(q, J = 24.5\) Hz), 54.5, 51.6.
**IR** (ATR, cm\(^{-1}\)) 3083, 3063, 3026, 3005, 2981, 2910, 2821, 1738, 1599, 1493, 1452, 1370, 1280, 1262, 1239, 1196, 1163, 1134, 1109, 1096, 1069, 1045, 1028, 973, 959, 913, 746, 734, 695, 588, 547, 516, 482, 471, 403. **HRMS** m/z [M+H]\(^+\) calculated for C\(_{31}\)H\(_{32}\)N\(_2\)F\(_3\): 489.2518, found: 489.2516.

**Synthesis of compound 22**

Tetramethyl 2,2',2'',2'''-((3,3,3-trifluoropropane-1,2-diyl)bis(azanetriyl))tetraacetate

Compound 22 was prepared according to general procedure from dimethyl 2,2'-azanediyldiacetate (121 mg, 0.75 mmol, 2.5 equiv), sodium carbonate (47.7 mg, 0.45 mmol, 1.5 equiv) and I (140 mg, 0.3 mmol, 1 equiv) to afford a colorless liquid (122 mg, 0.293 mmol, 98% yield). **Rf** = 0.30 (hexanes:ethyl acetate= 7:3). **LRMS** (EI, 70 eV): m/z (%): 416(1), 358(3), 357(20), 256(3), 256(3), 225(4), 198(3), 196(4), 175(8), 174(100), 147(2), 146(17), 146(14), 116(13), 74(2), 56(2). **\(^1\)H NMR** (250 MHz, Chloroform-\(d\)) \(\delta\) 3.64 (s, 21H), 3.11 (dd, \(J\) = 14.3, 8.1 Hz, 1H), 2.97 (dd, \(J\) = 14.3, 4.2 Hz, 1H). **\(^{19}\)F NMR** (235 MHz, Chloroform-\(d\)) \(\delta\) -70.72. **\(^{13}\)C NMR** (63 MHz, Chloroform-\(d\)) \(\delta\) 171.8, 171.5, 126.5 (q, \(J\) = 290.2, 289.6, 289.1 Hz), 63.1 (q, \(J\) = 25.3 Hz), 55.1, 52.6, 51.7, 51.5, 50.7. **IR** (ATR, cm\(^{-1}\)) 3063, 2968, 2885, 2863, 2812, 1721, 1601, 1510, 1451, 1395, 1314, 1270, 1245, 1160, 1106, 1069, 1054, 1027, 862, 790, 773, 734, 706, 686, 584, 544, 518, 503, 452, 415. **HRMS** m/z [M+H]\(^+\) calculated for C\(_{15}\)H\(_{24}\)N\(_2\)O\(_8\)F\(_3\): 417.1485, found: 417.1489.

**Synthesis of compound 23**

\(N,N'-(3,3,3\text{-trifluoropropane-1,2-diyl)bis(N-(4-methoxybenzyl)-O-methylhydroxylamine}}\)

Compound 23 was prepared according to general procedure from \(N\)-(4-methoxybenzyl)-O-methylhydroxylamine (125 mg, 0.75 mmol, 2.5 equiv), sodium carbonate (47.7 mg, 0.45 mmol, 1.5 equiv) and I (140 mg, 0.3 mmol, 1 equiv) to afford a colorless liquid (84.9 mg, 0.198 mmol, 66% yield). **Rf** = 0.44 (hexanes:ethyl acetate= 10:1). **LRMS** (EI, 70 eV): m/z (%): 398(1), 397(6), 365(1), 207(1), 180(3), 122(9), 121(100), 91(3), 78(3), 77(3), 73(2). **\(^1\)H NMR** (250 MHz, Chloroform-\(d\)) \(\delta\) 7.20 (d, \(J\) = 8.6 Hz, 2H), 7.17 (d, \(J\) = 8.6 Hz, 2H), 6.77 (d, \(J\) = 8.5 Hz, 2H), 6.74 (d, \(J\) = 8.6 Hz, 2H), 3.98 (d, \(J\) = 12.8 Hz, 1H), 3.82 (d, \(J\) = 12.8 Hz, 1H), 3.76 – 3.62 (m, 8H), 3.31 (ddt, \(J\) = 16.1, 11.2, 5.7 Hz, 1H), 3.20 (s, 7H), 2.81 (dd, \(J\) = 14.1, 4.9 Hz, 1H). **\(^{19}\)F NMR** (235 MHz, Chloroform-\(d\)) \(\delta\) -71.11. **\(^{13}\)C NMR** (63 MHz, Chloroform-\(d\)) \(\delta\) 159.2 (d, \(J\) = 3.4 Hz), 130.9, 129.1, 129.0, 125.8 (q, \(J\) = 283.0 Hz), 113.8, 62.3, 61.8 (q, \(J\) = 26.5 Hz), 61.1, 61.0, 59.0, 55.3, 51.9. **IR** (ATR, cm\(^{-1}\)) 3104, 3061,

\textbf{Synthesis of compound 24}

3,3,3-trifluoro- \( N^1,N^2 \)-dihexyl- \( N^1,N^2 \)-bis(4-methoxybenzyl)propane-1,2-diamine

Compound 24 was prepared according to general procedure from \( N \)-(4-methoxybenzyl)hexan-1-amine (111 mg, 0.5 mmol, 2.5 equiv), sodium carbonate (31.8 mg, 0.3 mmol, 1.5 equiv) and 1 (93.2 mg, 0.2 mmol, 1 equiv) to afford a colorless oil (80.1 mg, 0.149 mmol, 75% yield). \( R_f = 0.53 \) (hexanes:ethyl acetate= 10:1). \textbf{LRMS} (EI, 70 eV): m/z (%): 236(1), 235(8), 234(46), 232(1), 220(1), 123(1), 122(11), 121(100), 91(2), 90(1), 78(2), 77(2). \textbf{\(^1H\) NMR} (250 MHz, Chloroform-\( d \)) \( \delta \) 7.2 – 7.1 (m, 4H), 6.8 (d, \( J = 3.5 \) Hz, 2H), 6.8 (d, \( J = 3.5 \) Hz, 2H), 3.7 (s, 3H), 3.7 (s, 3H), 3.7 – 3.5 (m, 2H), 3.5 (d, \( J = 13.5 \) Hz, 1H), 3.4 – 3.2 (m, 2H), 2.7 (dd, \( J = 13.7, 7.0 \) Hz, 1H), 2.6 (dd, \( J = 9.2, 5.6 \) Hz, 1H), 2.6 – 2.4 (m, 2H), 2.3 (qt, \( J = 13.0, 7.0 \) Hz, 2H), 1.5 – 1.3 (m, 4H), 1.4 – 1.0 (m, 12H), 0.9 – 0.8 (m, 6H). \textbf{\(^{19}F\) NMR} (235 MHz, Chloroform-\( d \)) \( \delta \) -68.1. \textbf{\(^{13}C\) NMR} (63 MHz, Chloroform-\( d \)) \( \delta \) 158.8, 158.7, 132.0, 131.5, 130.2, 130.0, 127.6 (q, \( J = 290.6 \) Hz), 113.6, 113.6, 58.9 (q, \( J = 23.8 \) Hz), 58.4, 55.3, 54.7, 54.1, 51.7, 50.5, 31.9, 31.9, 28.9, 27.2, 26.8, 22.8, 14.2. \textbf{IR} (ATR, cm\(^{-1}\)) 3061, 3031, 2997, 2955, 2929, 2857, 2836, 1737, 1612, 1510, 1465, 1374, 1300, 1244, 1170, 1153, 1100, 1036, 980, 909, 820, 760, 733, 700, 571, 516. \textbf{HRMS} m/z [M+H]^+ calculated for C_{31}H_{48}N_{2}O_{2}F_{3}^+: 537.3668, found: 537.3671.

\textbf{Synthesis of compound 25}

\( N^1,N^2 \)-dicyclopropyl-3,3,3-trifluoro-\( N^1,N^2 \)-bis(4-methoxybenzyl)propane-1,2-diamine

Compound 25 was prepared according to general procedure from \( N \)-(4-methoxybenzyl)cyclopropanamine (66.5 mg, 0.375 mmol, 2.5 equiv), sodium carbonate (23.8 mg, 0.225 mmol, 1.5 equiv) and 1 (69.9 mg, 0.15 mmol, 1 equiv) to afford a pale yellow oil (56.1 mg, 0.125 mmol, 83% yield). \( R_f = 0.45 \) (hexanes:ethyl acetate= 10:1). \textbf{LRMS} (EI, 70 eV): m/z (%): 447(1), 327(1), 191(2), 190(16), 190(8), 176(2), 122(10), 121(100), 91(3), 78(4), 77(4). \textbf{\(^1H\) NMR} (250 MHz, Chloroform-\( d \)) \( \delta \) 7.26 – 7.14 (m, 4H), 6.96 – 6.81 (m, 4H), 3.93 – 3.57 (m, 9H), 3.76 (d, \( J = 13.6 \) Hz, 1H), 3.63 (d, \( J = 13.6 \) Hz, 1H), 3.03 (dd, \( J = 13.7, 7.1 \) Hz, 1H), 2.92 (dd, \( J = 13.6, 5.4 \) Hz, 1H), 2.39 – 2.24 (m, 1H), 2.26 (s, 0H), 1.81 (p, \( J = 5.5 \) Hz, 1H), 0.57 – 0.20 (m, 8H). \textbf{\(^{19}F\) NMR} (235 MHz, Chloroform-\( d \)) \( \delta \) -67.9. \textbf{\(^{13}C\) NMR} (63 MHz, Chloroform-\( d \)) \( \delta \) 158.85, 158.76, 132.18, 130.81,
130.27, 130.02, 127.43 (q, J = 289.1 Hz), 113.50, 113.43, 60.77 (q, J = 24.2 Hz), 58.68, 55.65, 55.24, 52.27, 37.23, 35.06, 8.46, 7.45, 7.26, 7.15. IR (ATR, cm⁻¹) 3090, 3074, 3006, 2952, 2936, 2910, 2836, 1738, 1611, 1585, 1510, 1458, 1442, 1350, 1300, 1242, 1173, 1144, 1106, 1035, 1021, 907, 821, 761, 733, 598, 516. HRMS m/z [M+H]^+ calculated for C_{25}H_{32}N_{2}O_{2}F_{3}: 449.2416, found: 449.2406.

**Synthesis of compound 26**

2,2′-(((3,3,3-trifluoropropane-1,2-diyl)bis((4-methoxybenzyl)azanediyl))diacetate

Compound 26 was prepared according to general procedure from ethyl (4-methoxybenzyl)glycinate (167 mg, 0.75 mmol, 2.5 equiv), sodium carbonate (47.7 mg, 0.45 mmol, 1.5 equiv) and I (140 mg, 0.3 mmol, 1 equiv) to afford a colorless liquid (128.0 mg, 0.237 mmol, 79% yield). Rf = 0.22 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 376(2), 222(1), 157(3), 156(32), 155(10), 154(100), 140(3), 139(4), 138(6), 125(2), 119(4), 118(6), 113(2), 111(6), 91(2), 77(3), 75(3). \(^1\)H NMR (250 MHz, Chloroform-d) \(\delta\) 7.32 (d, \(J = 8.6\) Hz, 2H), 7.15 (d, \(J = 8.6\) Hz, 2H), 6.84 (d, \(J = 6.4\) Hz, 2H), 6.81 (d, \(J = 6.2\) Hz, 2H), 4.22 – 4.03 (m, 4H), 3.92 (d, \(J = 13.3\) Hz, 1H), 3.84 – 3.62 (m, 9H), 3.68 – 3.24 (m, 5H), 3.11 (dd, \(J = 14.2, 7.9\) Hz, 1H), 2.95 (dd, \(J = 14.0, 4.7\) Hz, 1H), 1.32 – 1.17 (m, 6H). \(^19\)F NMR (235 MHz, Chloroform-d) \(\delta\) -68.56. \(^13\)C NMR (63 MHz, Chloroform-d) \(\delta\) 171.4, 159.1, 159.0, 130.5, 130.3, 130.1, 127.2 (q, \(J = 290.7\) Hz), 113.7, 113.7, 60.6, 60.2, 59.4 (q, \(J = 24.2\) Hz), 57.8, 55.3, 55.2, 53.6, 51.6, 50.4, 14.3, 14.2. IR (ATR, cm⁻¹) 3101, 3073, 3061, 3034, 2980, 2958, 2938, 2908, 2837, 1733, 1612, 1585, 1510, 1463, 1443, 1371, 1302, 1244, 1171, 1144, 1097, 1031, 916, 832, 812, 761, 732, 698, 571, 518. HRMS m/z [M+H]^+ calculated for C_{27}H_{36}N_{2}O_{6}F_{3}: 541.2525, found: 541.2537.

**Synthesis of compound 27**

\(N^1,N^2\)-diallyl-3,3,3-trifluoro- \(N^1,N^2\)-bis(4-methoxybenzyl)propane-1,2-diamine

Compound 27 was prepared according to general procedure from \(N\)-(4-methoxybenzyl)prop-2-en-1-amine A1 (88.6 mg, 0.5 mmol, 2.5 equiv), sodium carbonate (31.8 mg, 0.3 mmol, 1.5 equiv) and I (93.2 mg, 0.2 mmol, 1 equiv) to afford a pale yellow oil (66.9 mg, 0.149 mmol, 75% yield). Rf = 0.47 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 91(100), 210(79), 211(13), 92(8), 65(8), 181(4), 118(2), 89(2), 212(1), 208(1), 73(1), 109(1), 63(1), 207(1), 397(1), 51(1), 182(1), 165(1), 77(1). \(^1\)H NMR (250 MHz, Chloroform-d) \(\delta\) 7.25 – 7.08 (m, 4H), 6.87 – 6.70 (m, 4H), 5.93 – 5.59 (m, 2H), 5.23 – 4.98 (m, 4H), 3.75 (s, 3H), 3.74 (s, 3H), 3.72 – 3.63 (m,
2H), 3.58 (d, $J = 17.8$ Hz, 2H), 3.44 (td, $J = 8.5, 4.3$ Hz, 1H), 3.32 (d, $J = 13.2$ Hz, 1H), 3.19 (dd, $J = 18.9, 6.3$ Hz, 1H), 3.06 (dd, $J = 14.7, 6.0$ Hz, 1H), 2.88 (dd, $J = 6.9, 5.0$ Hz, 1H), 2.80 (dd, $J = 11.4, 5.9$ Hz, 1H), 2.57 (dd, $J = 13.7, 4.3$ Hz, 1H). $^{19}$F NMR (235 MHz, Chloroform-$d$) $\delta$ -68.3. $^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 158.9, 137.0, 135.5, 131.0, 130.3, 130.0, 127.5 (q, $J = 289.8$ Hz), 117.9, 117.5, 113.8, 113.7, 58.0, 57.7 (q, $J = 24.0$ Hz), 56.8, 55.3, 53.7, 53.4, 50.5. IR (ATR, cm$^{-1}$) 3075, 3002, 2953, 2936, 2910, 2836, 1738, 1612, 1510, 1463, 1442, 1368, 1300, 1242, 1170, 1149, 1093, 1035, 993, 879, 808, 760, 703, 564, 515. HRMS m/z [M+H]$^+$ calculated for C$_{25}$H$_{32}$N$_2$F$_3$: 449.2416, found: 449.2421.

Synthesis of compound 28

$N^1,N^2$-diethyl-3,3,3-trifluoro-$N^1,N^2$-di(prop-2-yn-1-yl)propane-1,2-diamine

Compound 28 was prepared according to general procedure from N-ethylprop-2-yn-1-aminium chloride (89.7 mg, 0.75 mmol, 2.5 equiv), sodium carbonate (127 mg, 0.75 mmol, 4.0 equiv) and 1 (140 mg, 0.3 mmol, 1 equiv) to afford a colorless liquid (29.4 mg, 0.113 mmol, 38% yield). $R_f$ = 0.34 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 221(2), 221(1), 164(1), 110(1), 108(1), 97(4), 97(3), 96(100), 69(1), 68(3), 68(3), 66(2), 56(6). $^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 3.72 – 3.40 (m, 5H), 2.97 – 2.77 (m, 2H), 2.71 (dd, $J = 13.9, 4.6$ Hz, 2H), 2.15 (dd, $J = 13.9, 4.6$ Hz, 2H), 2.23 (t, $J = 2.3$ Hz, 1H), 2.18 (t, $J = 2.2$ Hz, 1H), 1.10 (t, $J = 7.0$ Hz, 3H), 1.07 (t, $J = 7.1$ Hz, 3H). $^{19}$F NMR (235 MHz, Chloroform-$d$) $\delta$ -69.41. $^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 127.0 (q, $J = 289.2$ Hz), 80.8, 78.6, 73.1, 72.4, 60.3 (q, $J = 24.7$ Hz), 49.6 (d, $J = 1.6$ Hz), 48.0, 44.3, 41.9, 40.1, 13.9, 12.9 (q, $J = 1.5$ Hz). IR (ATR, cm$^{-1}$) 3308, 2973, 2938, 2849, 1737, 1459, 1435, 1382, 1326, 1296, 1249, 1156, 1097, 1063, 1044, 981, 936, 900, 856, 798, 700, 627, 498. HRMS m/z [M+H]$^+$ calculated for C$_{13}$H$_{20}$N$_2$F$_3$: 261.1579, found: 261.1580.

Synthesis of compound 29

3,3,3-trifluoro-$N^1,N^2$-bis(4-methoxybenzyl)-$N^1,N^2$-di(prop-2-yn-1-yl)propane-1,2-diamine

Compound 29 was prepared according to general procedure from N-(4-methoxybenzyl)prop-2-yn-1-amine (131 mg, 0.75 mmol, 2.5 equiv), sodium carbonate (47.7 mg, 0.45 mmol, 1.5 equiv) and 1 (140 mg, 0.3 mmol, 1 equiv) to afford a colorless liquid (110.2 mg, 0.248 mmol, 82% yield). $R_f$ = 0.37 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 365(1), 323(2), 283(1), 189(3), 188(20), 122(9), 121(100), 91(2), 78(3), 77(2), 77(1). $^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 7.28 – 7.08 (m, 4H), 6.75 (d, $J = 8.3$ Hz, 4H), 3.84 (d, $J = 13.6$ Hz, 1H), 3.76 –
3.43 (m, 10H), 3.37 (dd, J = 5.8, 2.3 Hz, 2H), 3.26 (s, 2H), 2.91 (dd, J = 13.4, 8.9 Hz, 1H), 2.76 (dd, J = 13.6, 4.5 Hz, 1H), 2.22 – 2.09 (m, 2H). 19F NMR (235 MHz, Chloroform-d) δ -68.86. 13C NMR (63 MHz, Chloroform-d) δ 159.1, 130.5, 130.2, 130.0, 127.1 (q, J = 288.9 Hz), 113.9 (d, J = 4.6 Hz), 80.6, 78.2, 73.7, 72.8, 58.7 (q, J = 24.8 Hz), 57.6, 55.3, 53.3, 49.5, 41.3, 39.9. IR (ATR, cm⁻¹) 3292, 3064, 3034, 3000, 2955, 2935, 2908, 2836, 2725, 1612, 1585, 1510, 1463, 1442, 1367, 1302, 1244, 1171, 1146, 1095, 1034, 981, 903, 875, 831, 811, 761, 699, 632, 515, 428. HRMS m/z [M+H]^+: 445.2103, found: 445.2104.

Synthesis of compound 30

3,3,3-trifluoro-N1,N2-diisobutyl-N1,N2-bis(3-phenylprop-2-yn-1-yl)propane-1,2-diamine

Compound 30 was prepared according to general procedure from N-isobutyl-3-phenylprop-2-yn-1-amine (154.8 mg, 0.80 mmol, 2.5 equiv), sodium carbonate (50.9 mg, 0.48 mmol, 1.5 equiv) and 1 (149.1 mg, 0.32 mmol, 1 equiv) to afford a colorless oil (119.4 mg, 0.255 mmol, 80% yield). Rf = 0.68 (hexanes:diisopropyl ether= 10:1). 1H NMR (250 MHz, Chloroform-d) δ 7.46 – 7.33 (m, 4H), 7.31 – 7.16 (m, 6H), 3.80 (d, J = 17.3 Hz, 1H), 3.75 – 3.55 (m, 4H), 2.96 (dd, J = 13.8, 7.5 Hz, 1H), 2.83 (dd, J = 13.7, 4.9 Hz, 1H), 2.66 (dd, J = 12.9, 7.1 Hz, 1H), 2.51 (dd, J = 12.9, 7.6 Hz, 1H), 2.34 (td, J = 12.3, 11.1, 7.3 Hz, 2H), 1.80 (dhept, J = 20.1, 6.7 Hz, 2H), 0.98 – 0.85 (m, 12H). 19F NMR (235 MHz, Chloroform-d) δ -68.95. 13C NMR (63 MHz, Chloroform-d) δ 131.9, 131.7, 128.4, 128.1, 127.2 (q, J = 289.1 Hz), 123.5, 123.4, 86.6, 85.7, 84.5, 84.4, 62.8, 61.4 (q, J = 24.7 Hz), 59.2, 51.4, 42.9, 41.4, 26.7, 26.2, 20.9, 20.7, 20.5. IR (ATR, cm⁻¹) 3081, 3060, 3034, 3022, 2955, 2928, 2905, 2870, 2824, 2746, 2725, 1598, 1489, 1468, 1442, 1385, 1365, 1327, 1251, 1156, 1103, 1044, 1029, 946, 913, 868, 754, 689, 600, 526, 509, 628, 596, 566, 540, 510, 481, 461. HRMS m/z [M+H]^+ calculated for C25H28N2O2F3+: 445.2103, found: 445.2104.
Synthesis of compound 31

Compound 31 was prepared according to general procedure from \( N\)-(3-phenylprop-2-yn-1-yl)cyclohexanamine (160 mg, 0.75 mmol, 2.5 equiv), sodium carbonate (47.7 mg, 0.45 mmol, 1.5 equiv) and 1 (140 mg, 0.3 mmol, 1 equiv) to afford a colorless liquid (143.3 mg, 0.275 mmol, 92% yield). \( R_f = 0.63 \) (hexanes:diisopropyl ether= 10:1). ¹H NMR (250 MHz, Chloroform-\( d \)) \( \delta \) 7.41 – 7.24 (m, 4H), 7.23 – 7.03 (m, 6H), 3.76 (s, 2H), 3.73 – 3.56 (m, 3H), 2.96 (d, \( J = 6.0 \) Hz, 2H), 2.84 – 2.67 (m, 1H), 2.50 (t, \( J = 9.7, 7.8 \) Hz, 1H), 1.86 (q, \( J = 11.2, 10.7 \) Hz, 4H), 1.77 – 1.60 (m, 4H), 1.50 (d, \( J = 11.3 \) Hz, 2H), 1.43 – 0.87 (m, 10H). ¹³C NMR (63 MHz, Chloroform-\( d \)) \( \delta \) 131.7, 128.3, 128.3, 128.0, 127.5 (q, \( J = 290.4 \) Hz), 123.7, 123.6, 88.2, 87.1, 84.9, 83.6, 62.3, 59.4 (q, \( J = 24.5 \) Hz), 58.3, 47.0, 40.0, 36.6, 32.6, 31.3, 30.5, 30.2, 26.3, 26.1, 26.1, 26.0. IR (ATR, cm⁻¹) 3081, 3057, 3033, 3020, 2927, 2853, 2667, 1598, 1489, 1443, 1382, 1346, 1252, 1154, 1107, 1071, 1028, 1001, 947, 913, 892, 873, 846, 753, 689, 604, 526, 510. HRMS m/z [M+H]⁺ calculated for \( C_{33}H_{40}N_{2}F_{3} \): 521.3144, found: 521.3142.

Synthesis of compound 32

Di-tert-butyl 3,3'-((3,3,3-trifluoropropane-1,2-diyl)bis(phenethylazanediyl))bis(azetidine-1-carboxylate)

Compound 32 was prepared according to general procedure from tert-butyl 3-(phenethylamino)azetidine-1-carboxylate (138 mg, 0.5 mmol, 2.5 equiv), sodium carbonate (31.8 mg, 0.3 mmol, 1.5 equiv) and 1 (93.2 mg, 0.2 mmol, 1 equiv) to afford a pale yellow oil (85.9 mg, 0.133 mmol, 66% yield). \( R_f = 0.48 \) (hexanes:ethyl acetate= 7:3). LRMS (EI, 70 eV): m/z (%): 362(24), 361(100), 271(5), 269(10), 257(5), 189(10), 165(12), 163(15), 160(5), 134(6), 106(8), 105(89), 103(6), 91(12), 79(11), 77(9), 56(6). ¹H NMR (250 MHz, Chloroform-\( d \)) \( \delta \) 7.3 – 7.0 (m, 10H), 4.0 – 3.8 (m, 6H), 3.7 – 3.5 (m, 4H), 3.3 – 3.2 (m, 1H), 3.2 – 2.9 (m, 2H), 2.8 – 2.5 (m, 8H), 1.4 (s, 9H), 1.4 (s, 9H). ¹⁹F NMR (235 MHz, Chloroform-\( d \)) \( \delta \) -69.5. ¹³C NMR (63 MHz, Chloroform-\( d \)) \( \delta \) 156.3, 156.1, 139.5, 139.2, 128.8, 128.7, 128.6, 128.5, 126.8 (q, \( J = 290.4 \) Hz), 126.5, 126.4, 79.7, 79.6, 60.7 (q, \( J = 24.0 \) Hz), 55.1, 53.7, 51.8, 49.4, 47.9, 47.0, 36.4, 33.2, 28.4, 28.4. IR (ATR, cm⁻¹) 3087, 3064, 3027, 2976, 2965, 2934, 2884, 2247, 1690, 1477, 1455, 1391, 1365, 1295, 1253, 1157, 1117, 1031, 873, 846, 753, 689, 604, 526, 510.
907, 859, 773, 727, 698, 647, 569, 503. **HRMS m/z [M+H]^+** calculated for C_{35}H_{50}N_{4}O_{4}F_{3}^+: 647.3784, found: 647.3795.

**Synthesis of compound 33**

1,1’-(3,3,3-trifluoropropane-1,2-diyil)bis(3-((tert-butyldimethylsilyl)oxy)azetidine)

Compound 33 was prepared according to general procedure from 3-((tert-butyldimethylsilyl)oxy)azetidine (141 mg, 0.75 mmol, 2.5 equiv), sodium carbonate (47.7 mg, 0.45 mmol, 1.5 equiv) and 1 (140 mg, 0.3 mmol, 1 equiv) to afford a colorless oil (92.8 mg, 0.198 mmol, 66% yield). **Rf** = 0.33 (hexanes:ethyl acetate= 10:1). **LRMS** (EI, 70 eV): m/z (%): 453(2), 453(1), 411(3), 202(9), 201(17), 201(14), 200(100), 200(82), 158(2), 144(2), 128(2), 115(2), 103(6), 102(4), 101(37), 77(2), 75(5), 74(2), 73(16), 60(2), 59(11), 57(1).

**1H NMR** (250 MHz, Chloroform-d) δ 4.4 (dp, J = 12.4, 6.2 Hz, 2H), 3.7 (dt, J = 12.0, 4.9 Hz, 4H), 3.1 (t, J = 6.6 Hz, 1H), 3.0 (t, J = 6.8 Hz, 1H), 2.7 (td, J = 6.4, 3.1 Hz, 2H), 2.7 – 2.3 (m, 3H), 0.8 (s, 18H), -0.0 (s, 12H). **19F NMR** (235 MHz, Chloroform-d) δ -72.1. **13C NMR** (63 MHz, Chloroform-d) δ 125.9 (q, J = 282.8 Hz), 65.5, 65.5 (q, J = 25.7 Hz), 65.0, 62.7, 62.1, 57.0 (d, J = 2.0 Hz), 25.9, 18.1, -4.9. **IR** (ATR, cm⁻¹) 2952, 2846, 2771, 1733, 1480, 1438, 1367, 1306, 1259, 1201, 1153, 1123, 1048, 960, 913, 865, 733, 679, 584, 505. **HRMS m/z [M+H]^+** calculated for C_{21}H_{44}N_{2}O_{2}F_{3}Si_{2}^+: 469.2893, found: 469.2892.

**Synthesis of compound 34**

Dimethyl 1,1’-(3,3,3-trifluoropropane-1,2-diyil)bis(azetidine-3-carboxylate)

Compound 34 was prepared according to the general procedure 3-(methoxycarbonyl)azetidin-1-ium trifluoromethanesulfonate (137 mg, 0.5 mmol, 2.5 equiv), sodium carbonate (84.8 mg, 0.8 mmol, 4.0 equiv) and 1 (93.2 mg, 0.2 mmol, 1 equiv) to afford a pale yellow oil (47.9 mg, 0.148 mmol, 74% yield). **Rf** = 0.28 (hexanes:ethyl acetate= 7:3). **LRMS** (EI, 70 eV): m/z (%): 293(5), 239(3), 196(2), 129(7), 128(100), 110(2), 69(1), 68(5), 59(4), 55(11). **1H NMR** (250 MHz, Chloroform-d) δ 3.76 – 3.59 (m, 8H), 3.63 – 3.49 (m, 3H), 3.47 (t, J = 7.3 Hz, 1H), 3.41 – 3.16 (m, 4H), 2.80 – 2.59 (m, 1H), 2.62 – 2.47 (m, 2H). **19F NMR** (235 MHz, Chloroform-d) δ -72.00. **13C NMR** (63 MHz, Chloroform-d) δ 173.3, 173.1, 125.6 (q, J = 282.9 Hz), 64.5 (q, J = 25.8 Hz), 57.7, 56.9, 56.0 (q, J = 2.1 Hz), 55.3, 52.0, 34.5, 33.7. **IR** (ATR, cm⁻¹) 2955, 2846, 2771, 1733, 1480, 1438, 1367, 1306, 1259, 1201, 1153, 1123, 1048, 960, 913, 865, 733, 679, 584, 505. **HRMS m/z [M+H]^+** calculated for C_{13}H_{20}N_{2}O_{4}F_{3}^+: 325.1375, found: 325.1380.
Synthesis of compound 35

1,1’-(3,3,3-trifluoropropane-1,2-diyl)bis(pyrrolidin-1-ium) 2,2,2-trifluoroacetate

Compound 35 was prepared according to the general procedure from pyrrolidine (63 µL, 0.75 mmol, 2.5 equiv), sodium carbonate (47.7 mg, 0.45 mmol, 1.5 equiv) and 1 (140 mg, 0.3 mmol, 1 equiv) and isolated as the corresponding bisamminium trifluoroacetate salt, which is a pale yellow syrup (71.5 mg, 0.154 mmol, 51% yield). \( R_f = 0.25 \) (hexanes:ethyl acetate= 7:3). \( \text{LRMS (EI, 70 eV): m/z ( %):} \)

\[
\begin{align*}
84(100), 55(9), 85(6), 110(2), 54(2), 56(2), 96(2), 69(1), 83(1), 60(1), 82(1), 70(1), 152(1). \\
\end{align*}
\]

\( \text{1H NMR (250 MHz, Methylenechloride-d}_2) \delta 11.26 \text{ (bs, 2H), 4.10 \text{–} 3.10 \text{ (m, 6H), 2.92 \text{–} 2.17 \text{ (m, 4H), 1.79 \text{ (d, J = 6.4 Hz, 4H).}} \)

\( \text{19F NMR (235 MHz, Methylenechloride-d}_2) \delta -66.21 \text{ (s, 3F), -74.39 \text{ (s, 6F).}} \)

\( \text{13C NMR (63 MHz, Methylenechloride-d}_2) \delta 126.1 \text{ (q, J = 294.0 Hz), 114.3 \text{ (q, J = 291.1 Hz), 58.8 \text{ (q, J = 26.7 Hz), 56.0, 52.5 \text{ (q, J = 2.4 Hz), 48.9, 24.4, 23.5.}} \)

\( \text{IR (ATR, cm}\text{-1}) 2971, 2946, 2927, 2856, 1740, 1672, 1458, 1365, 1139, 1113, 876, 835, 795, 720, 703, 597, 518, 428. \)

\( \text{HRMS m/z [M+H]+ calculated for C}_{11}\text{H}_{20}\text{N}_{2}\text{F}_3+: 237.1579, found: 237.1582.} \)

Synthesis of compound 36

1,1’-(3,3,3-trifluoropropane-1,2-diyl)di-3-piperidine

Compound 36 was prepared according to general procedure from piperidine (103 µL, 0.75 mmol, 2.5 equiv), sodium carbonate (47.7 mg, 0.45 mmol, 1.5 equiv) and 1 (140 mg, 0.3 mmol, 1 equiv) to afford a colorless oil (52.9 mg, 0.200 mmol, 67% yield). \( R_f = 0.33 \) (hexanes:ethyl acetate= 10:1). \( \text{LRMS (EI, 70 eV): m/z ( %):} \)

\[
\begin{align*}
293(5), 239(3), 196(2), 129(7), 128(100), 110(2), 69(1), 68(5), 59(4), 55(11). \\
\end{align*}
\]

\( \text{1H NMR (250 MHz, Chloroform-d) \delta 3.16 \text{ (ddq, J = 12.5, 9.0, 4.5, 3.6 Hz, 1H), 2.90 \text{–} 2.57 \text{ (m, 5H), 2.56 \text{–} 2.32 \text{ (m, 5H), 1.67 \text{–} 1.22 \text{ (m, 12H).}} \)

\( \text{19F NMR (235 MHz, Chloroform-d) \delta -68.79.} \)

\( \text{13C NMR (63 MHz, Chloroform-d) \delta 127.2 \text{ (q, J = 290.6 Hz), 64.3 \text{ (q, J = 23.8 Hz), 55.1 \text{ (q, J = 1.7 Hz), 54.8, 51.0, 27.1, 26.3, 24.8, 24.5.}} \)

\( \text{IR (ATR, cm}\text{-1}) 2932, 2854, 2823, 2813, 2782, 1740, 1469, 1442, 1381, 1356, 1319, 1309, 1292, 1253, 1201, 1151, 1134, 1099, 1078, 1065, 1041, 1018, 995, 963, 906, 868, 844, 784, 764, 710, 699, 630, 593, 457. \)

\( \text{HRMS m/z [M+H]+ calculated for C}_{13}\text{H}_{24}\text{N}_{2}\text{F}_3+: 265.1892, found: 265.1892.} \)
Synthesis of compound 37

1,1′-(3,3,3-trifluoropropan-1,2-diyl)bis(3-((tert-butyldimethylsilyl)oxy)piperidine)

Compound 37 was prepared according to general procedure from 3-((tert-butyldimethylsilyl)oxy)piperidine (162 mg, 0.75 mmol, 2.5 equiv), sodium carbonate (47.7 mg, 0.45 mmol, 1.5 equiv) and 1 (140 mg, 0.3 mmol, 1 equiv) to afford a colorless oil (134 mg, 0.255 mmol, 85% yield). Rf = 0.65 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 467(1), 310(1), 231(1), 230(6), 229(23), 228(100), 226(1), 190(1), 170(1), 142(1), 128(1), 121(1), 112(1), 106(2), 101(1), 96(4), 89(1), 77(1), 75(2), 74(1), 73(11), 59(1). 1H NMR (250 MHz, Chloroform-d) 3.77 – 3.49 (m, 2H), 3.35 – 3.10 (m, 1H), 3.06 – 2.25 (m, 8H), 2.13 – 1.76 (m, 4H), 1.74 – 1.34 (m, 7H), 1.32 – 1.07 (m, 2H), 0.88 (s, 18H), 0.19 – 0.08 (m, 12H). 19F NMR (235 MHz, Chloroform-d) δ -68.97, -69.44, -69.48, -69.52. 13C NMR (63 MHz, Chloroform-d) δ 129.3, 129.3, 129.2, 124.7, 124.6, 69.1, 69.0, 68.9, 68.7, 68.5, 68.5, 64.5, 64.1, 64.1, 63.8, 63.7, 63.7, 63.4, 63.3, 63.0, 62.9, 62.7, 62.1, 62.1, 61.6, 61.3, 58.9, 58.7, 57.6, 56.5, 54.3, 54.1, 54.0, 53.8, 53.7, 53.4, 53.4, 51.3, 50.3, 49.5, 49.4, 34.5, 34.4, 34.1, 34.1, 26.0, 26.0, 18.3, 18.3, 18.3, -4.5, -4.5. IR (ATR, cm⁻¹) 2931, 2888, 2857, 2826, 2802, 2710, 1472, 1388, 1361, 1320, 1253, 1164, 1097, 1039, 987, 939, 832, 773, 702, 668, 466, 394. HRMS m/z [M+H]+ calculated for C₂₅H₅₂N₂O₂F₃Si₂+: 525.3519, found: 525.3508.

Synthesis of compound 38

1,1′-(3,3,3-trifluoropropan-1,2-diyl)bis(3-((tert-butyldimethylsilyl)oxy)methyl)piperidine

Compound 38 was prepared according to general procedure from 3-((tert-butyldimethylsilyl)oxy)methyl)piperidine (172 mg, 0.75 mmol, 2.5 equiv), sodium carbonate (47.7 mg, 0.45 mmol, 1.5 equiv) and 1 (140 mg, 0.3 mmol, 1 equiv) to afford a colorless oil (126 mg, 0.228 mmol, 76% yield). Rf = 0.55 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 1H NMR (250 MHz, Chloroform-d) 3.54 – 3.30 (m, 4H), 3.21 (p, J = 8.4 Hz, 1H), 3.08 – 2.36 (m, 8H), 2.06 (t, J = 10.2 Hz, 1H), 1.95 – 1.35 (m, 9H), 0.89 (s, 20H), 0.03 (s, 12H). 19F NMR (235 MHz, Chloroform-d) δ -68.87, -68.96, -69.00, -69.12. 13C NMR (63 MHz, Chloroform-d) δ 127.2 (q, J = 290.5 Hz), 64.6 (q, J = 23.7, 23.2 Hz), 64.0 (q, J = 24.0 Hz), 57.8, 57.7, 57.4, 55.0, 54.9, 54.8, 54.6, 54.5, 52.8, 51.9, 51.8, 50.3, 50.1, 39.9, 39.8, 39.3, 39.3, 39.1, 39.1, 27.5, 27.2, 27.1, 26.1, 26.0, 25.9, 25.7, 25.2, 25.2, 25.1, 18.5, 18.4, -5.2, -5.3. IR (ATR, cm⁻¹) 2951, 2929, 2904, 2856, 2803, 2788, 2746, 2714, 1470, 1388, 1361, 1253, 1174, 1156, 1097, 1005, 939, 909, 834,
773, 734, 666, 397. **HRMS** m/z [M+H]+ calculated for C_{27}H_{56}N_{2}O_{2}F_{3}Si_{2}+: 553.3832, found: 553.3842.

**Synthesis of compound 39**

1,1’-(3,3,3-trifluoropropane-1,2-diyl)bis(4-benzylpiperidine)

Compound 39 was prepared according to general procedure from 4-benzylpiperidine (88 µL, 0.5 mmol, 2.5 equiv), sodium carbonate (31.8 mg, 0.3 mmol, 1.5 equiv) and 1 (93.2 mg, 0.2 mmol, 1 equiv) to afford a pale yellow oil (79.1 mg, 0.178 mmol, 89% yield). **Rf** = 0.23 (hexanes:ethyl acetate= 10:1). **LRMS** (EI, 70 eV): m/z (%): 256(1), 190(1), 189(15), 188(1), 117(2), 96(2), 92(1), 91(14), 82(1), 70(2), 68(1), 67(1), 55(2). **1H NMR** (250 MHz, Chloroform-d) δ 7.3 – 7.0 (m, 10H), 4.0 – 3.8 (m, 6H), 3.7 – 3.5 (m, 4H), 3.3 – 3.2 (m, 1H), 3.2 – 2.9 (m, 2H), 2.8 – 2.5 (m, 8H), 1.4 (s, 9H), 1.4 (s, 9H). **19F NMR** (235 MHz, Chloroform-d) δ -68.79. **13C NMR** (63 MHz, Chloroform-d) δ 140.8, 140.7, 129.2, 128.3, 128.3, 126.2 (q, J = 291.0 Hz), 126.0, 125.9, 63.7 (q, J = 24.2 Hz), 54.4, 54.1, 51.3, 48.8, 43.3, 43.2, 38.2, 37.8, 33.3, 33.1, 32.2, 32.1. **IR** (ATR, cm⁻¹) 3084, 3063, 3027, 2917, 2846, 2832, 2785, 2751, 2681, 1494, 1468, 1453, 1391, 1347, 1306, 1259, 1158, 1140, 1099, 1056, 1031, 973, 910, 862, 744, 698, 647, 613, 591, 574, 509, 444. **HRMS** m/z [M+H]+ calculated for C_{27}H_{36}N_{2}F_{3}+: 445.2831, found: 445.2832.

**Synthesis of compound 40**

4,4’-(3,3,3-trifluoropropane-1,2-diyl)bis(morpholin-4-iium) trifluoroacetate

Compound 40 was prepared according to general procedure from morpholine (66 µL, 0.75 mmol, 2.5 equiv), sodium carbonate (47.7 mg, 0.45 mmol, 1.5 equiv) and 1 (140 mg, 0.3 mmol, 1 equiv) and isolated as the corresponding bisamminium trifluoroacetate salt, which is a colorless syrup (120 mg, 0.242 mmol, 81% yield). **Rf** = 0.45 (ethyl acetate). **LRMS** (EI, 70 eV): m/z (%): 100(100), 56(18), 101(9), 70(6), 55(5), 54(4), 124(3), 72(3), 74(2), 57(2), 98(2), 123(2), 168(2). **1H NMR** (250 MHz, Methylenechloride-d₂) δ 9.53 (s, 2H), 3.98 (s, 4H), 3.91 – 3.75 (m, 2H), 3.73 – 3.52 (m, 4H), 3.51 – 3.07 (m, 4H), 3.07 – 2.87 (m, 2H), 2.80 – 2.57 (m, 2H). **19F NMR** (235 MHz, Methylenechloride-d₂) -65.33 (s, 3F), -74.44 (s, 6F). **13C NMR** (63 MHz, Methylenechloride-d₂) 161.3 (q, J = 38.1 Hz), 125.7 (q, J = 293.0 Hz), 114.0 (q, J = 289.8, 286.9 Hz), 67.5, 64.1, 62.0 (q, J = 26.2 Hz), 53.3 (q, J = 2.8 Hz), 49.8. **IR** (ATR, cm⁻¹) 3458, 3305, 3020, 2968, 2929, 2863, 2708, 2576, 2473, 1777, 1709, 1672, 1458, 1367, 1304, 1248, 1158.
1139, 1110, 1051, 1018, 984, 950, 923, 909, 869, 854, 835, 797, 753, 720, 706, 639, 518, 482, 447, 428, 387. **HRMS** m/z [M+H]^+ calculated for C_{11}H_{20}N_{2}O_{2}F_{3}^+: 269.1477, found: 269.1482.

**Synthesis of compound 41**

4,4′-(3,3,3-trifluoropropane-1,2-diyl)bis(1-benzylpiperazine)

Compound 41 was prepared according to general procedure from morpholine (132 mg, 0.75 mmol, 2.5 equiv), sodium carbonate (47.7 mg, 0.45 mmol, 1.5 equiv) and 1 (140 mg, 0.3 mmol, 1 equiv) to afford a colorless syrup (61.1 mg, 0.137 mmol, 46% yield). Rf = 0.30 (hexanes:ethyl acetate= 7:3). **LRMS** (EI, 70 eV): m/z (%): 447(1), 446(5), 190(14), 189(100), 187(2), 146(5), 99(2), 98(3), 97(5), 92(4), 91(45), 83(2), 70(8), 65(2), 56(3). **1H NMR** (250 MHz, Chloroform-d) 7.38 – 7.05 (m, 10H), 3.42 (d, J = 6.4 Hz, 4H), 3.13 (td, J = 8.7, 3.3 Hz, 1H), 2.90 – 2.18 (m, 18H). **19F NMR** (235 MHz, Chloroform-d) δ -69.19. **13C NMR** (63 MHz, Chloroform-d) δ 138.1, 138.0, 129.3, 129.3, 128.3, 128.3, 127.2, 127.2, 126.8 (q, J = 289.9 Hz), 131.1, 63.4 (q, J = 24.4 Hz), 63.1, 63.1, 54.0, 53.4, 53.2, 49.5. **IR** (ATR, cm^{-1}) 3108, 3085, 3063, 3029, 3003, 2935, 2877, 2809, 2768, 2695, 2681, 1494, 1455, 1367, 1350, 1314, 1262, 1150, 1130, 1105, 1073, 1029, 1010, 909, 864, 825, 732, 696, 642, 605, 580, 455, 407. **HRMS** m/z [M+H]^+ calculated for C_{25}H_{34}N_{4}F_{3}^+: 447.2736, found: 447.2746.

**Synthesis of compound 42**

4,4′-(3,3,3-trifluoropropane-1,2-diyl)bis(1-(pyridin-2-yl)piperazine)

Compound 42 was prepared according to general procedure from 1-(pyridin-2-yl)piperazine (57.1 µL, 0.375 mmol, 2.5 equiv), sodium carbonate (23.8 mg, 0.225 mmol, 1.5 equiv) and 1 (70 mg, 0.15 mmol, 1 equiv) to afford a pale yellow oil (55.2 mg, 0.131 mmol, 88% yield). Rf = 0.28 (hexanes:ethyl acetate= 7:3). **LRMS** (EI, 70 eV): m/z (%): 420(3), 177(12), 176(100), 147(21), 133(5), 121(28), 119(7), 107(11), 95(5), 82(5), 79(9), 78(11), 56(6). **1H NMR** (250 MHz, Chloroform-d) 8.17 (dd, J = 4.9, 1.9 Hz, 2H), 7.53 – 7.36 (m, 2H), 6.69 – 6.53 (m, 4H), 3.63 – 3.25 (m, 9H), 3.09 – 2.74 (m, 5H), 2.76 – 2.47 (m, 5H). **19F NMR** (235 MHz, Chloroform-d) δ -69.33. **13C NMR** (63 MHz, Chloroform-d) δ 159.6 (d, J = 7.8 Hz), 148.0 (d, J = 1.6 Hz), 137.6, 126.6 (q, J = 289.1 Hz), 107.2 (d, J = 4.3 Hz), 63.4 (q, J = 24.8 Hz), 54.0 (q, J = 2.0 Hz), 53.3, 49.6, 46.3, 45.4. **IR** (ATR, cm^{-1}) 3097, 3050, 2936, 2888, 2836, 2756, 2690, 1592, 1563, 1479, 1455,
Synthesis of compound 43

3,3’-(3,3,3-trifluoropropane-1,2-diyl)bis(3-azabicyclo[3.2.2]nonane)

Compound 43 was prepared according to general procedure from 3-azabicyclo[3.2.2]nonane (125 mg, 0.4 mmol, 2.5 equiv), sodium carbonate (63.6 mg, 0.6 mmol, 1.5 equiv) and 1 (186 mg, 0.4 mmol, 1 equiv) to afford a white solid (80.5 mg, 0.234 mmol, 58% yield). Rf = 0.75 (hexanes:diisopropyl ether = 10:1).

M.p. = 69-72 °C. LRMS (EI, 70 eV): m/z (%): 186(1), 139(10), 138(100), 112(2), 106(1), 95(1), 95(1), 93(1), 91(1), 81(1), 81(1), 79(3), 77(2), 73(1), 68(1), 67(4), 67(3), 58(14), 55(4). ¹H NMR (250 MHz, Chloroform-d) δ: 3.30 (dd, J = 8.6, 5.5 Hz, 1H), 2.94 (qd, J = 11.4, 3.8 Hz, 7H), 2.62 (dddd, J = 35.2, 23.9, 13.4, 6.3 Hz, 11H), 1.90 (s, 5H), 1.71 (dd, J = 25.8, 5.3 Hz, 14H), 1.62 – 1.54 (m, 17H). ¹⁹F NMR (235 MHz, Chloroform-d) δ: -69.56. ¹³C NMR (63 MHz, Chloroform-d) δ: 127.6 (q, J = 291.2, 290.7 Hz), 63.8 (q, J = 23.9 Hz), 63.3, 59.4, 55.3 (q, J = 1.5 Hz), 31.6, 30.7, 25.9, 25.8, 25.7, 25.7. IR (ATR, cm⁻¹): 2925, 2900, 2857, 2812, 2793, 2758, 2715, 2677, 1451, 1402, 1387, 1364, 1323, 1292, 1263, 1200, 1177, 1150, 1136, 1126, 1095, 1042, 1011, 983, 957, 920, 875, 864, 852, 839, 805, 757, 713, 661, 590, 519, 484, 475. HRMS m/z [M+H]⁺ calculated for C₁₉H₂₈N₆F₃⁺: 345.2525, found: 345.2525.

Supplementary Figure 6: Unsuccessful substrates under conditions of homodiamination procedure.
Optimization of the reaction conditions for heterodiamination

An 8 mL test tube was charged with stirring bar, 1 (23.3 mg, 0.05 mmol), solvent (250 or 500 µL/0.05 mmol) and sodium carbonate (0-7.9 mg, 0-0.075 mmol, 0-1.5 equiv) according to **Supplementary Table 2**. To a stirred mixture, N-methyl-1-(naphthalen-1-yl)methanamine (1.0 equiv, neat or in corresponding solvent at 0.1-0.2 M concentration) was added via syringe in one portion or by syringe pump over the indicated time ($t_1$) and at temperature ($T_1$). After completion of addition, reaction mixture was stirred for indicated time ($t_2$) at the same temperature ($T_1$). Pyrrolidine (1.0-2.5 equiv) was added in one portion and the temperature was maintained at or allowed to reach $T_2$. Aliquots were taken after the indicated time ($t_3$) and analysed by GC-MS.

**Supplementary Figure 7**: Reaction scheme of heterodiamination procedure

**Supplementary Table 2**: Optimization of reaction conditions for heterodiamination

<table>
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<th>#</th>
<th>Scale [mmol]</th>
<th>Na₂CO₃ [x equiv]</th>
<th>Pyrrolidine [y equiv]</th>
<th>Cfinal [mol/L]</th>
<th>Solvent</th>
<th>$T_1$</th>
<th>$T_2$</th>
<th>Medium of amine</th>
<th>Mode of addition</th>
<th>$t_1$ delay [min]</th>
<th>$t_2$ delay [min]</th>
<th>$t_3$ [h; min]</th>
<th>GC-MS conversions [%] (isolated yield)</th>
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<td>CH$_2$Cl$_2$ sol. one portion</td>
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<td>5</td>
<td>30</td>
<td>53</td>
<td>15</td>
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<td>MeCN</td>
<td>25</td>
<td>25</td>
<td>MeCN sol. one portion</td>
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<td>16</td>
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<td>MeCN sol. one portion</td>
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<td>-20</td>
<td>MeCN sol. syringe pump</td>
<td>30</td>
<td>15</td>
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<td>0</td>
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Study of reaction mechanism by $^{19}$F-NMR spectroscopy

A 5 mm O.D. NMR tube was charged with (4-fluorophenyl)(3,3,3-trifluoroprop-1-en-2-yl)iodonium trifluoromethanesulfonate (23.3 mg, 0.05 mmol) acetonitrile-d$_3$ (500 µL) and sealed with a hollow cap. An LDPE tube was filled with five layers of substances in a following sequence: acetonitrile (100 µL), air (100 µL), solution of $N$-methyl-1-(naphthalen-1-yl)methanamine (8.56 mg, 0.05 mmol, 1.00 equiv in 100 µL MeCN), air (100 µL) and acetonitrile (100 µL), then was placed in the NMR tube. These substances were added in one portion to the reaction mixture at t=0 second. Recording of $^{19}$F-NMR spectra (proton decoupled, No. dummy scan= 0, No. scan= 1) was started at t=−60 seconds and 15 seconds time intervals were applied between experiments.

**Supplementary Figure 8:** Reaction scheme and monitoring of homodiamination reaction by $^{19}$F-NMR-spectroscopy, in the presence of one equivalent amine
Study of the first stage of reaction conditions II by $^{19}$F-NMR spectroscopy

An 8 mL test tube was charged with stirring bar, (4-fluorophenyl)(3,3,3-trifluoroprop-1-en-2-yl)iodonium trifluoromethanesulfonate (23.3 mg, 0.05 mmol), acetonitrile-$d_3$ (500 µL) and cooled to -20°C. To the stirred mixture, solution of $N$-methyl-1-(naphthalen-1-yl)methanamine (8.56 mg, 0.05 mmol, 1.00 equiv, in 500 µL acetonitrile-$d_3$) was added via syringe over 30 minutes. After completion of addition, reaction mixture was stirred for 15 minutes at the same temperature, then the complete reaction mixture was transferred to a 0.5 mm O.D. NMR tube at room temperature. $^{19}$F-NMR spectra was recorded within 10 minutes.

**Supplementary Figure 9:** Reaction scheme of the first stage of reaction conditions II and study by $^{19}$F-NMR spectroscopy

![Reaction scheme](image)

$^{19}$F-NMR spectra of (4-fluorophenyl)(3,3,3-trifluoroprop-1-en-2-yl)iodonium trifluoromethanesulfonate

$^{19}$F-NMR spectra of the reaction mixture of homodiamination

-69.58 ppm

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56
Generation of intermediate X by independent route

A 0.5 mm O.D. NMR tube was charged with 1-(naphthalen-1-ylmethyl)-2-(trifluoromethyl)aziridine (6) (18 mg, 0.72 mmol), sodium carbonate (38 mg, 0.358 mmol, 5 equiv) and acetonitrile-$d_3$ (500 µL). The mixture was treated with methyl triflate (20 µL, 0.179 mmol, 2.5 equiv) at room temperature and recording of $^{19}$F-NMR spectra was started immediately. After 2.5 hours, complete consumption of 1-(naphthalen-1-ylmethyl)-2-(trifluoromethyl)aziridine was observed.

Supplementary Figure 10: Generation of intermediate X from trifluoromethyl aziridine 6 and its reaction with excess amine

Addition of N-methyl-1-(naphthalen-1-yl)methanamine (49 mg, 0.286 mmol, 4.0 equiv) led to the formation of corresponding diamine. Also, this result was confirmed by GC-MS spectra of the mixture.
Synthesis of heterofunctionalized diamines

General procedure A
A 30 mL screwed cap vial was charged with rare-earth magnetic stirring bar, 1 (1 equiv) and acetonitrile (10 mL/mmol), then the vial was sealed with Teflon septa and screw cap. The stirred reaction mixture was cooled to -20 °C (bath temp= -23 °C) and solution of first amine (1 equiv, 0.1 M in acetonitrile) was added dropwise (0.3 mmol/h) by syringe pump, then the stirring was continued for 10 mins/0.1 mmol to obtain the solution of aziridinium intermediate. After that second amine or other nucleophile (2.5 equiv) was added in one portion and the mixture was allowed to warm room temperature over 16 hours. Reaction mixture was concentrated onto Celite under reduced pressure and the obtained residue was purified by flash column chromatography. Gradient elution was performed by using either hexanes:ethyl acetate or hexanes:diisopropyl ether or dichloromethane:isopropanol eluent system, according to TLC eluents.

General procedure B
Aziridinium intermediate solution was prepared according to general procedure A. A separate, oven dried vial was charged with stirring bar, appropriate heterocycle (2.6 equiv) and sealed with Teflon septa and screw cap. Vial was evacuated and backfilled with argon (repeated three times), then THF (3.2 mL/mmol heterocycle) was added under argon atmosphere. The stirred mixture was cooled to -78°C and solution of LiHMDS (2.5 equiv, 1 M in THF) was added dropwise. After 1 hour, HMPA (1 equiv) was added in one portion and stirring was continued at -78°C for 10 minutes. To the solution of deprotonated heterocycle, solution of aziridinium intermediate was added at -78°C, then allowed to warm room temperature over 16 hours. Purification was carried out according to general procedure A.

General procedure C
Aziridinium intermediate solution was prepared according to general procedure A. A separate, oven dried vial was charged with stirring bar, appropriate nucleophile (2.5 equiv) and sealed with Teflon septa and screw cap. Vial was evacuated and backfilled with argon (repeated three times), then THF (3.2 mL/mmol nucleophile) was added under argon atmosphere. To the stirred mixture, NaH (2.5 equiv, 60 w% in oil) was added in one portion under argon atmosphere at room temperature and stirring was continued for 1 hour. After that, solution of aziridinium intermediate was added and the mixture was stirred at room temperature for 16 hours. Purification was carried out according to general procedure A.
**General procedure D**

A 30 mL screwed cap vial was charged with rare-earth magnetic stirring bar, 1 (1 equiv) and THF (10 mL/mmol), then the vial was sealed with Teflon septa and screwed cap. The stirred reaction mixture was cooled to -55 °C (bath temp= -58 °C) and solution of N-methyl-1-(naphthalen-1-yl)methanamine (1 equiv, 0.1 M in THF) was added dropwise (0.3 mmol/h) by syringe pump, then the stirring was continued for 10 mins/0.1 mmol to obtain the solution of aziridinium intermediate. A separate, oven dried vial was charged with stirring bar, appropriate heterocycle (1.1 equiv) and sealed with Teflon septa and screw cap. Vial was evacuated and backfilled with argon (repeated three times), then THF (3.2 mL/mmol heterocycle) was added under argon atmosphere. The stirred mixture was cooled to -78°C and solution of sBuLi (1.15 equiv, 1.6 M in hexanes) was added dropwise. After 1 hour, solution of aziridinium intermediate was added at -78°C, then allowed to warm room temperature over 16 hours. Purification was carried out according to *general procedure A*.

**Synthesis of compound 44**

3,3,3-trifluoro-N1-hexyl-N2-methyl-N2-(naphthalen-1-ylmethyl)propane-1,2-diamine

Compound 44 was prepared according to *general procedure A* from 1 (93.2 mg, 0.2 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (34.2 mg, 0.2 mmol, 1 equiv) and hexylamine (66 µL, 0.5 mmol, 2.5 equiv) to afford a pale yellow oil (41.3 mg, 0.113 mmol, 56% yield). **R**r = 0.48 (hexanes:ethyl acetate= 7:3). **LRMS** (EI, 70 eV): m/z (%): 366(1), 253(3), 252(2), 234(8), 233(49), 232(2), 212(4), 202(4), 197(4), 194(4), 190(2), 182(2), 170(2), 168(2), 142(13), 141(100), 140(2), 139(6), 116(2), 115(25), 114(63), 57(2), 56(2), 55(2). **1H NMR** (250 MHz, Chloroform-d) δ 8.19 – 8.06 (m, 1H), 7.94 – 7.69 (m, 2H), 7.61 – 7.44 (m, 2H), 7.50 – 7.35 (m, 2H), 4.36 (d, J = 13.0 Hz, 1H), 4.27 (d, J = 13.2 Hz, 1H), 3.47 (dd, J = 8.6, 3.5 Hz, 1H), 2.87 (dd, J = 12.7, 10.6 Hz, 1H), 2.64 (dd, J = 12.7, 3.4 Hz, 1H), 2.49 (q, J = 2.0 Hz, 3H), 2.46 – 1.88 (m, 3H), 1.39 – 0.92 (m, 8H), 0.87 (t, J = 6.9 Hz, 3H). **19F NMR** (235 MHz, Chloroform-d) δ -66.63. **13C NMR** (63 MHz, Chloroform-d) δ 134.2, 134.0, 132.4, 128.9, 128.7, 127.7 (q, J = 292.0 Hz), 126.2, 125.9, 125.3, 124.4, 60.9 (q, J = 24.4 Hz), 58.4, 49.3, 45.2 (q, J = 2.0 Hz), 35.9, 31.8, 29.8, 27.0, 22.7, 14.2. **IR** (ATR, cm⁻¹) 3047, 2955, 2928, 2856, 2840, 2826, 1510, 1463, 1375, 1255, 1157, 1103, 1052, 1019, 907, 862, 790, 774, 730, 706, 644, 605, 543, 519, 503, 420. **HRMS** m/z [M+H]^+ calculated for C21H30N2F3+: 367.2361, found: 367.2359.
Synthesis of compound 45

1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)-3-(pyrrolidin-1-yl)propan-2-amine

Compound 45 was prepared according to general procedure A from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and pyrrolidine (63 µL, 0.75 mmol, 2.5 equiv) to afford an off white solid (76.9 mg, 0.229 mmol, 76% yield). Rf = 0.60 (hexanes:ethyl acetate = 7:3). M.p. = 45-47 °C.

LRMS (EI, 70 eV): m/z (%): 336(1), 168(1), 142(4), 141(30), 140(1), 139(4), 116(1), 115(14), 84(100), 82(1), 70(1), 56(2), 55(5). $^1$H NMR (300 MHz, Chloroform-d) δ 8.33 (d, J = 7.2 Hz, 1H), 7.86 (dd, J = 7.0, 2.3 Hz, 1H), 7.80 (d, J = 8.2 Hz, 1H), 4.40 (d, J = 13.4 Hz, 1H), 4.31 (d, J = 13.4 Hz, 1H), 3.50 (pd, J = 8.8, 3.9 Hz, 1H), 3.02 (dd, J = 13.1, 9.3 Hz, 1H), 2.65 (dd, J = 13.1, 3.9 Hz, 1H), 2.56 – 2.39 (m, 7H), 1.80 – 1.66 (m, 4H). $^{19}$F NMR (235 MHz, Chloroform-d) δ -67.8. $^{13}$C NMR (75 MHz, Chloroform-d) δ 134.5, 134.0, 132.5, 128.5, 128.2, 127.6, 127.4 (q, J = 291.7 Hz), 125.8, 125.8, 125.3, 124.9, 62.7 (q, J = 24.1 Hz), 58.3, 54.4, 52.3, 36.8, 23.6. IR (ATR, cm$^{-1}$) 3091, 3046, 2955, 2911, 2874, 2816, 2781, 2698, 1597, 1509, 1460, 1391, 1354, 1312, 1252, 1202, 1170, 1149, 1119, 1097, 1071, 1051, 1031, 946, 883, 845, 791, 774, 709, 622, 559, 542, 520, 454, 414. HRMS m/z [M+H]$^+$ calculated for C$_{19}$H$_{24}$N$_2$F$_3$+: 337.1892, found: 337.1895.

Synthesis of compound 46

1,1,1-trifluoro-N-methyl-3-(2-methylpiperidin-1-yl)-N-(naphthalen-1-ylmethyl)propan-2-amine

Compound 46 was prepared according to general procedure A from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and 2-methylpiperidine (88 µL, 0.75 mmol, 2.5 equiv) to afford a pale yellow oil (73.5 mg, 0.201 mmol, 67% yield). Rf = 0.33 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 142(2), 141(18), 139(2), 116(1), 115(5), 115(1), 113(8), 112(100), 110(2), 96(1), 84(1), 83(1), 70(1), 69(1), 56(1), 55(4). $^1$H NMR (250 MHz, Chloroform-d) δ 8.32 (dd, J = 20.1, 7.6 Hz, 1H), 7.85 (dd, J = 16.0, 8.2 Hz, 2H), 7.63 – 7.36 (m, 4H), 4.51 – 4.23 (m, 2H), 3.47 (dq, J = 12.1, 4.9, 3.5 Hz, 1H), 3.13 (dd, J = 13.8, 9.4 Hz, 0H), 2.76 (dt, J = 38.9, 14.3, 5.9 Hz, 3H), 2.55 – 2.45 (m, 3H), 2.41 – 1.99 (m, 2H), 1.57 (d, J = 11.6 Hz, 2H), 1.51 – 1.40 (m, 2H), 1.34 – 1.13 (m, 2H), 1.02 (t, J = 5.9 Hz, 3H). $^{19}$F NMR (235 MHz, Chloroform-d) δ -67.46. $^{13}$C NMR (63 MHz, Chloroform-d) δ 134.6, 134.5, 134.0, 132.6, 128.5, 128.2, 127.7 (q, J = 291.6, 291.1 Hz), 127.5, 125.9, 125.7, 125.3, 125.2, 125.2, 124.9, 62.2 (q, J = 23.4 Hz), 61.0 (q, J = 23.4 Hz), 58.7, 58.4, 56.5, 56.2, 52.8, 52.2, 51.5,
Synthesis of compound 47

3,3,3-trifluoro-N\textsubscript{1},N\textsubscript{1}-diisopropyl-N\textsubscript{2}-methyl-N\textsubscript{2}-(naphthalen-1-ylmethyl)propane-1,2-diamine

Compound 47 was prepared according to general procedure A with 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl) methanamine (51.4 mg, 0.3 mmol, 1 equiv) and diisopropylamine (105 µL, 0.75 mmol, 2.5 equiv) to afford a pale yellow oil (59.3 mg, 0.162 mmol, 54% yield). \( R_f = 0.65 \) (hexanes:ethyl acetate=10:1). M.p. = 43-46 °C. LRMS (EI, 70 eV): m/z (%): 209(1), 170(1), 168(1), 167(1), 153(1), 152(1), 142(4), 141(35), 140(1), 139(3), 138(1), 116(1), 115(21), 114(100), 112(1), 89(1), 84(1), 73(1), 72(13), 71(1), 70(1), 70(1), 56(2).

\( ^1\text{H NMR} \) (250 MHz, Chloroform-\( d \)) \( \delta \) 8.32 (d, \( J = 8.6 \) Hz, 1H), 7.97 – 7.76 (m, 2H), 7.64 – 7.38 (m, 4H), 4.51 – 4.27 (m, 2H), 3.48 – 3.24 (m, 1H), 2.94 (hept, \( J = 6.6 \) Hz, 2H), 2.78 (d, \( J = 5.8 \) Hz, 2H), 2.50 (s, 3H), 0.96 (s, 6H), 0.93 (s, 6H). \( ^{19}\text{F NMR} \) (235 MHz, Chloroform-\( d \)) \( \delta -66.27 \). \( ^{13}\text{C NMR} \) (63 MHz, Chloroform-\( d \)) \( \delta \) 134.7, 134.0, 132.6, 130.5, 128.5, 128.1, 127.4, 125.8, 125.7, 125.3, 125.1, 63.6 (q, \( J = 22.0 \) Hz), 59.1, 48.0, 42.7, 36.4, 20.9, 20.6. \( \text{IR (ATR, cm}^{-1}\text{)} \) 3094, 3050, 2965, 2939, 2927, 2883, 2856, 2817, 2800, 2732, 1598, 1510, 1459, 1390, 1377, 1361, 1309, 1306, 1290, 1249, 1209, 1160, 1127, 1096, 1052, 1042, 1018, 966, 941, 888, 855, 837, 811, 793, 773, 695, 603, 564, 532, 519, 505, 414. HRMS m/z [M+H]\(^+\) calculated for C\textsubscript{21}H\textsubscript{30}N\textsubscript{2}F\textsubscript{3}: 367.2361, found: 367.2355.

Synthesis of compound 48

\( N^1\)-(adamantan-1-yl)-3,3,3-trifluoro-N\textsubscript{2}-methyl-N\textsubscript{2}-(naphthalen-1-ylmethyl)propane-1,2-diamine

Compound 48 was prepared according to general procedure A with 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl) methanamine (51.4 mg, 0.3 mmol, 1 equiv) and 1-adamantylamine (47.6 mg, 0.315 mmol, 1.0 equiv) to afford a pale yellow oil (90.1 mg, 0.216 mmol, 72% yield). \( R_f = 0.60 \) (hexanes:ethyl acetate=7:3). LRMS (EI, 70 eV): m/z (%): 417(1), 416(1), 415(1), 355(1), 287(2), 233(9), 233(5), 165(11), 164(82), 141(39), 141(14), 136(12), 135(100), 115(7), 93(7), 79(12). \( ^1\text{H NMR} \) (250 MHz, Chloroform-\( d \)) \( \delta \) 8.15 (d, \( J = 8.2 \) Hz, 1H), 7.94 – 7.72 (m, 2H), 7.64 – 7.34 (m, 4H), 4.32 (s, 2H), 3.59 (bs, \( J = 9.2 \) Hz, 0H), 3.49 (ddd, \( J = 11.2 \), 8.4, 3.3
Hz, 2H), 2.90 (t, J = 11.4 Hz, 1H), 2.71 (dd, J = 11.9, 3.5 Hz, 1H), 2.45 (s, 3H), 2.02 – 1.89 (m, 3H), 1.66 – 1.41 (m, 6H), 1.34 (d, J = 17.1 Hz, 6H). $^{19}$F NMR (235 MHz, Chloroform-d) δ -66.63. $^{13}$C NMR (63 MHz, Chloroform-d) δ 134.3, 133.8, 132.4, 128.9, 128.7, 128.2, 127.1 (q, J = 292.4 Hz), 126.5, 125.9, 125.3, 124.6, 62.6 (q, J = 24.8 Hz), 58.6, 51.1, 41.8, 36.4, 36.1 – 35.6 (m), 35.1, 29.4.

IR (ATR, cm⁻¹) 3047, 2904, 2849, 2819, 1510, 1482, 1452, 1368, 1357, 1289, 1256, 1236, 1197, 1151, 1119, 1103, 1079, 1052, 1027, 907, 852, 791, 774, 729, 702, 638, 563, 539, 518, 478, 441, 418. HRMS m/z [M+H]$^+$ calculated for C$_{25}$H$_{32}$N$_2$F$_3$: 417.2518, found: 417.2518.

Synthesis of compound 49

N$^1$-ethyl-3,3,3-trifluoro-N$^2$-methyl-N$^3$-(naphthalen-1-ylmethyl)-N$^1$-phenylpropane-1,2-diamine

Compound 49 was prepared according to general procedure A with I (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and N-ethylaniline (96 µL, 0.75 mmol, 2.5 equiv) to afford a pale yellow oil (92.3 mg, 0.239 mmol, 80% yield). $R_f$ = 0.70 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 387(1), 386(6), 142(3), 141(24), 139(3), 135(16), 134(100), 115(11), 107(2), 106(24), 105(2), 104(4), 91(2), 79(4), 78(2), 77(8). $^1$H NMR (250 MHz, Chloroform-d) δ 8.13 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.82 (dd, J = 6.0, 3.3 Hz, 1H), 7.62 – 7.34 (m, 4H), 7.27 – 7.11 (m, 2H), 6.75 (t, J = 7.2 Hz, 1H), 6.57 (d, J = 8.3 Hz, 2H), 4.35 (s, 2H), 3.82 – 3.67 (m, 1H), 3.68 (dd, J = 15.7, 4.2 Hz, 1H), 3.52 (dd, J = 15.3, 8.0 Hz, 1H), 3.48 – 3.11 (m, 2H), 2.60 (s, 3H), 1.07 (t, J = 7.0 Hz, 3H). $^{19}$F NMR (235 MHz, Chloroform-d) δ -66.22. $^{13}$C NMR (63 MHz, Chloroform-d) δ 146.8, 134.0, 133.9, 132.4, 129.4, 128.5 (d, J = 1.3 Hz), 127.8, 127.7 (q, J = 293.6 Hz), 126.0, 125.7, 125.1, 124.9, 116.2, 112.1, 60.5 (q, J = 22.9 Hz), 59.6, 47.7, 46.0, 35.9, 11.5. IR (ATR, cm⁻¹) 3095, 3060, 3043, 2971, 2932, 2897, 2861, 2810, 1598, 1504, 1463, 1374, 1353, 1242, 1211, 1192, 1153, 1126, 1100, 1061, 1039, 1022, 973, 907, 854, 790, 774, 744, 691, 649, 574, 547, 506, 445, 431, 417. HRMS m/z [M+H]$^+$ calculated for C$_{25}$H$_{26}$N$_2$F$_3$: 387.2048, found: 387.2049.
Synthesis of compound 50
3,3,3-trifluoro-N\(^1\),N\(^2\)-dimethyl-N\(^3\)-(naphthalen-1-ylmethyl)-N\(^4\)-(2-(trifluoromethyl)phenyl)propane-1,2-diamine

Compound 50 was prepared according to general procedure A with 1 (93.2 mg, 0.2 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (34.2 mg, 0.2 mmol, 1 equiv), 2-trifluoromethyl-N-methylaniline (91.2 mg, 0.5 mmol, 2.5 equiv) and 2,6-di-tert-butylpyridine (116 µL, 0.5 mmol, 2.5 equiv) to afford a colorless oil (39.3 mg, 0.089 mmol, 45% yield). \(R_f=0.65\) (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 189(10), 188(100), 173(2), 172(3), 168(1), 159(1), 154(1), 145(2), 142(3), 141(20), 140(1), 139(3), 128(1), 127(4), 126(1), 118(1), 116(1), 115(8), 109(1), 91(2), 77(1). \(^1\)H NMR (250 MHz, Chloroform-\(d\)) 8.14 (d, \(J=7.2\) Hz, 1H), 7.84 – 7.68 (m, 2H), 7.56 (d, \(J=7.8\) Hz, 1H), 7.52 – 7.28 (m, 5H), 7.14 (dd, \(J=14.2, 7.3\) Hz, 2H), 4.27 (s, 2H), 3.51 (ddq, \(J=12.7, 8.4, 4.3\) Hz, 1H), 3.29 (dd, \(J=13.6, 8.1\) Hz, 1H), 3.16 (dd, \(J=13.6, 4.2\) Hz, 1H), 2.54 (s, 3H), 2.34 (s, 3H). \(^{19}\)F NMR (235 MHz, Chloroform-\(d\)) \(\delta\) -59.64 (s, 3F), -67.66 (s, 3F). \(^{13}\)C NMR (63 MHz, Chloroform-\(d\)) \(\delta\) 153.1, 134.0, 133.0, 132.4, 129.6, 128.6, 128.3, 127.7 (d, \(J=5.5\) Hz), 127.5, 127.5, 127.1, 126.5 (d, \(J=20.7\) Hz), 126.1, 125.8, 125.4, 124.7, 124.7, 124.6, 122.0, 62.7 (q, \(J=24.0\) Hz), 58.2, 53.8, 45.5, 36.4. IR (ATR, cm\(^{-1}\)) 3067, 3048, 2959, 2901, 2861, 2810, 1602, 1584, 1510, 1496, 1453, 1431, 1392, 1314, 1252, 1105, 1052, 1035, 980, 934, 854, 791, 763, 734, 703, 647, 600, 564, 417. HRMS m/z [M+H]+ calculated for C\(_{21}\)H\(_{20}\)N\(_2\)F\(_6\)+: 441.1760, found: 441.1775.

Synthesis of compound 51
N-(4-methoxybenzyl)-N-(3,3,3-trifluoro-2-(methyl(naphthalen-1-ylmethyl)amino)propyl)-L-leucinate

Compound 51 was prepared according to general procedure A with 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and methyl (4-methoxybenzyl)-L-leucinate (199 mg, 0.75 mmol, 2.5 equiv) to afford a pale yellow oil (118 mg, 0.223 mmol, 74% yield). \(R_f=0.35\) (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 471(2), 279(9), 278(48), 142(3), 141(25), 122(11), 121(100), 115(4), 91(2), 77(2). \(^1\)H NMR (250 MHz, Chloroform-\(d\)) 8.32 – 8.08 (m, 1H), 7.99 – 7.72 (m, 2H), 7.64 – 7.36 (m, 4H), 7.08 (d, \(J=8.1\) Hz, 1H), 7.04 (d, \(J=8.3\) Hz, 1H), 6.79 (d, \(J=8.4\) Hz, 1H), 6.74 (d, \(J=8.4\) Hz, 1H), 4.44 – 4.19 (m, 2H), 3.86 – 3.61 (m, 7H), 3.55 – 3.27 (m, 3H), 3.23 – 3.06 (m, 1H), 3.03 – 2.68 (m, 1H), 2.54 – 2.33 (m, 3H), 1.75 – 1.41 (m, 3H), 0.91 – 0.60 (m, 6H). \(^{19}\)F
NMR (235 MHz, Chloroform-\(d\)) \(\delta\) -66.1, -66.6 (d. r.= 50:50). \(^{13}\)C NMR (63 MHz, Chloroform-\(d\)) \(\delta\) 173.8, 173.7, 158.8, 134.3, 134.1, 134.0, 132.4, 132.3, 131.0, 130.8, 130.3, 130.2, 128.6, 128.6, 128.2, 128.1, 127.3, 126.0, 125.9, 125.7, 125.3, 124.6, 124.3, 113.6, 63.8, 63.5, 63.3, 62.9, 62.5, 60.6, 60.5, 58.2, 58.1, 56.0, 55.8, 55.2, 55.2, 51.1, 48.5, 48.1, 39.3, 38.6, 36.9, 36.3, 30.9, 24.7, 24.6, 22.8, 22.7, 22.3, 22.2. IR (ATR, cm\(^{-1}\)) 3039, 2996, 2955, 2929, 2908, 2868, 2837, 1731, 1612, 1585, 1510, 1463, 1367, 1302, 1245, 1156, 1103, 1054, 1035, 984, 909, 824, 791, 774, 732, 706, 519, 417. HRMS m/z [M+H]\(^+\) calculated for C\(_{30}\)H\(_{38}\)N\(_2\)O\(_3\)F\(_3\): 531.2835, found: 531.2838.

Synthesis of compound 52
3-(4-bromo-1\(H\)-pyrazol-1-yl)-1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine

Compound 52 was prepared according to general procedure A with 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and 4-bromopyrazole (112 mg, 0.75 mmol, 2.5 equiv) and sodium hydride (30 mg, 60 w% in oil, 0.75 mmol, 2.5 equiv) to afford a white solid (94.2 mg, 0.229 mmol, 76% yield). \(R_f\) = 0.35 (hexanes:ethyl acetate= 10:1). M.p. = 131-133 °C. LRMS (EI, 70 eV): m/z (%): 270(1), 252(5), 234(2), 196(2), 171(14), 170(100), 168(4), 142(23), 141(97), 141(87), 139(10), 115(31). \(^1\)H NMR (250 MHz, Chloroform-\(d\)) 7.75 – 7.59 (m, 2H), 7.44 (d, \(J = 8.2\) Hz, 1H), 7.39 – 7.16 (m, 4H), 7.11 (d, \(J = 7.1\) Hz, 1H), 7.03 (s, 1H), 4.24 – 3.98 (m, 4H), 3.80 (ddp, \(J = 12.9, 8.6, 4.6\) Hz, 1H), 2.53 – 2.17 (m, 3H). \(^19\)F NMR (235 MHz, Chloroform-\(d\)) \(\delta\) -67.00. \(^{13}\)C NMR (63 MHz, Chloroform-\(d\)) \(\delta\) 140.4, 133.9, 133.1, 132.1, 130.6, 128.7, 128.4, 127.7, 126.6 (q, \(J = 292.7\) Hz), 126.3, 125.8, 125.1, 123.9, 93.2, 63.1 (q, \(J = 25.0\) Hz), 58.7, 48.7 (q, \(J = 2.2\) Hz), 35.2. IR (ATR, cm\(^{-1}\)) 3138, 3094, 3066, 3033, 2997, 2963, 2929, 2880, 2861, 2806, 1507, 1473, 1449, 1382, 1295, 1252, 1224, 1192, 1164, 1156, 1106, 1068, 1019, 950, 866, 846, 791, 734, 720, 692, 645, 610, 580, 448, 420. HRMS m/z [M+H]\(^+\) calculated for C\(_{18}\)H\(_{18}\)N\(_3\)F\(_3\)Br\(^+\): 412.0636, found: 412.0640.
**Synthesis of compound 53**

2-(3,3,3-trifluoro-2-(methyl(naphthalen-1-ylmethyl)amino)propyl)isoindoline-1,3-dione

Compound 53 was prepared according to general procedure A with 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and potassium phthalimide (139 mg, 0.75 mmol, 2.5 equiv) to afford a white solid (97.0 mg, 0.235 mmol, 78% yield). \( R_f = 0.70 \) (hexanes:ethyl acetate= 7:3). M.p.= 112-114 °C. LRMS (EI, 70 eV): \( m/z \) (%): 412(1), 271(3), 252(9), 171(3), 170(21), 160(4), 160(2), 154(2), 142(13), 141(100), 139(4), 115(14), 104(2), 77(3), 76(2). \(^1\)H NMR (250 MHz, Chloroform-\( d_2 \)) 7.59 – 7.32 (m, 7H), 7.22 – 7.06 (m, 2H), 6.76 (t, \( J = 7.5 \) Hz, 1H), 6.52 (t, \( J = 7.6 \) Hz, 1H), 4.17 – 3.85 (m, 3H), 3.60 (dqd, \( J = 11.4, 8.2, 3.3 \) Hz, 1H), 3.33 (dd, \( J = 13.9, 3.4 \) Hz, 1H), 2.57 (s, 3H). \(^{19}\)F NMR (235 MHz, Chloroform-\( d_2 \)) \( \delta \) -66.58. \(^{13}\)C NMR (63 MHz, Chloroform-\( d_2 \)) \( \delta \) 167.3, 133.7, 133.5, 133.2, 131.9, 131.8, 128.1, 126.8 (q, \( J = 293.3 \) Hz), 132.2, 128.7, 128.4, 128.1, 126.8 (q, \( J = 24.5 \) Hz), 36.1, 33.9 (q, \( J = 2.6 \) Hz). IR (ATR, cm\(^{-1}\)) 3048, 3005, 2951, 2895, 2860, 2826, 2746, 1771, 1707, 1616, 1598, 1510, 1466, 1428, 1405, 1377, 1334, 1252, 1226, 1192, 1161, 1103, 1055, 1018, 970, 953, 875, 801, 786, 770, 726, 713, 702, 614, 529, 509, 449, 432. HRMS m/z [M+H]+ calculated for \( C_{23}H_{20}N_2O_2F_3 \): 413.1477, found: 413.1469.

**Synthesis of compound 54**

1,1,1-trifluoro-3-(1H-indol-1-yl)-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine

Compound 54 was prepared according to general procedure B from 1 (140 mg, 0.3 mmol), indole (91.4 mg, 0.78 mmol, 2.6 equiv), solution of LiHMDS (750 μL, 1 M in THF, 0.75 mmol, 2.5 equiv) and HMPA (132 μL, 0.75 mmol, 2.5 equiv) to afford a pale yellow oil (86.7 mg, 0.227 mmol, 76% yield). \( R_f = 0.60 \) (hexanes:ethyl acetate= 1:1). LRMS (EI, 70 eV): \( m/z \) (%): 383(3), 382(12), 252(11), 142(12), 141(100), 139(4), 131(4), 130(30), 116(3), 115(14), 103(5), 89(3), 77(5). \(^1\)H NMR (300 MHz, Chloroform-\( d_2 \)) 7.89 (d, \( J = 8.2 \) Hz, 1H), 7.81 (d, \( J = 8.3 \) Hz, 1H), 7.80 – 7.74 (m, 1H), 7.72 (d, \( J = 7.9 \) Hz, 1H), 7.52 (t, \( J = 7.5 \) Hz, 1H), 7.37 – 7.29 (m, 2H), 7.25 – 7.20 (m, 2H), 7.18 (d, \( J = 7.2 \) Hz, 1H), 7.14 – 7.05 (m, 1H), 7.01 (d, \( J = 3.2 \) Hz, 1H), 6.53 (d, \( J = 3.2 \) Hz, 1H), 4.49 (dd, \( J = 15.0, 4.5 \) Hz, 1H), 4.38 (dd, \( J = 15.0, 8.6 \) Hz, 1H), 4.29 (d, \( J = 13.5 \) Hz, 1H), 4.23 (d, \( J = 13.3 \) Hz, 1H), 3.85 (pd, \( J = 8.4, 4.5 \) Hz, 1H), 2.68 (s, 3H). \(^{19}\)F NMR (282 MHz, Chloroform-\( d_2 \)) \( \delta \) -66.82 (d, \( J = 8.4 \) Hz). \(^{13}\)C NMR (75 MHz, Chloroform-\( d_2 \)) \( \delta \) 135.8, 133.8, 133.1, 132.1, 129.0, 128.9, 128.7, 128.4,
128.4, 127.6, 126.1, 125.7, 125.1, 124.1, 121.9, 121.3, 119.7, 108.9, 101.8, 62.4 (q, \( J = 24.4 \) Hz), 58.8, 43.5 (q, \( J = 2.4 \) Hz), 35.7. \( \text{IR (ATR, cm}^{-1}\) 3050, 2983, 2944, 2860, 2810, 1511, 1479, 1463, 1377, 1314, 1248, 1174, 1158, 1069, 1052, 1014, 964, 907, 864, 791, 776, 763, 730, 696, 648, 584, 424. \( \text{HRMS m/z [M+H]}^+ \) calculated for \( \text{C}_{23}\text{H}_{22}\text{N}_{2}\text{F}_{3}^+ \): 383.1730, found: 383.1734.

**Synthesis of compound 55**

1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)-3-(1H-pyrrolo[2,3-b]pyridin-1-yl)propan-2-amine

Compound 55 was prepared according to general procedure B from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv), 7-azaindole (92.1 mg, 0.78 mmol, 2.6 equiv), solution of LiHMDS (750 \( \mu \)L, 1 M in THF, 0.75 mmol, 2.5 equiv) and HMPA (132 \( \mu \)L, 0.75 mmol, 2.5 equiv) to afford a pale yellow solid (55.7 mg, 0.145 mmol, 48% yield). \( R_f = 0.54 \) (hexanes:ethyl acetate= 1:1). M.p. = 75-78 °C. LRMS (EI, 70 eV): m/z (%): 383(4), 265(3), 242(11), 222(11), 170(29), 142(12), 141(100), 139(6), 131(23), 119(11), 118(24), 115(20), 104(4), 104(3), 78(3), 77(4). \( ^1H \text{NMR (300 MHz, Chloroform-}d\) 8.27 (d, \( J = 4.7 \) Hz, 1H), 7.94 – 7.86 (m, 1H), 7.76 (d, \( J = 8.3 \) Hz, 1H), 7.69 (d, \( J = 8.3 \) Hz, 1H), 7.48 (d, \( J = 8.6 \) Hz, 1H), 7.38 (t, \( J = 7.6 \) Hz, 1H), 7.31 – 7.22 (m, 1H), 7.17 – 7.03 (m, 3H), 6.96 (d, \( J = 3.5 \) Hz, 1H), 6.33 (d, \( J = 3.5 \) Hz, 1H), 4.58 (d, \( J = 7.0 \) Hz, 2H), 4.22 (d, \( J = 13.5 \) Hz, 1H), 4.19 – 4.07 (m, 2H), 2.61 (s, 3H). \( ^19\text{F NMR (282 MHz, Chloroform-}d\) \( \delta =-66.97 \) (d, \( J = 8.0 \) Hz). \( ^{13}\text{C NMR (75 MHz, Chloroform-}d\) \( \delta =147.3, 142.6, 133.7, 133.4, 132.1, 129.0, 128.6, 128.3, 128.2, 127.4, 127.0 \) (q, \( J = 293.4 \) Hz), 125.8, 125.5, 125.0, 123.9, 120.9, 115.9, 100.1, 62.4 (q, \( J = 24.3 \) Hz), 58.5, 41.2, 35.7. \( \text{IR (ATR, cm}^{-1}\) 3053, 2988, 2952, 2884, 2864, 2812, 2249, 1595, 1572, 1510, 1432, 1310, 1249, 1208, 1175, 1157, 1110, 1073, 1054, 1017, 906, 866, 793, 773, 726, 699, 648, 597, 479, 415. \( \text{HRMS m/z [M+H]}^+ \) calculated for \( \text{C}_{22}\text{H}_{21}\text{N}_{2}\text{F}_{3}^+ \): 384.1682, found: 384.1686.
Synthesis of compound 56
3-(1H-benzo[d]imidazol-1-yl)-1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine

Compound 56 was prepared according to general procedure B from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv), benzimidazole (92.1 mg, 0.78 mmol, 2.6 equiv), solution of LiHMDS (750 μL, 1 M in THF, 0.75 mmol, 2.5 equiv) and HMPA (132 μL, 0.75 mmol, 2.5 equiv) to afford an off-white solid (54.1 mg, 0.141 mmol, 47% yield). Rf = 0.25 (hexanes:ethyl acetate= 1:1). M.p.= 73-76 °C. LRMS (EI, 70 eV): m/z (%): 383(3), 253(3), 252(16), 221(1), 141(100), 142(13), 141(10), 139(3), 131(9), 115(12), 77(5).

1H NMR (250 MHz, Chloroform-d) 7.68 (dt, J = 16.3, 7.0 Hz, 4H), 7.46 (d, J = 8.6 Hz, 1H), 7.37 (ddd, J = 8.2, 6.8, 1.4 Hz, 1H), 7.31 – 7.13 (m, 3H), 7.14 – 6.98 (m, 2H), 6.82 (d, J = 8.1 Hz, 1H), 4.26 (d, J = 7.7 Hz, 1H), 4.23 (d, J = 13.8 Hz, 1H), 4.12 (d, J = 13.0 Hz, 1H), 3.66 (pd, J = 8.3, 5.8 Hz, 1H), 2.66 – 2.56 (m, 4H).

19F NMR (235 MHz, Chloroform-d) δ -66.56.

13C NMR (75 MHz, Chloroform-d) δ 143.5, 143.4, 133.7, 133.1, 132.4, 131.8, 128.7, 128.4, 127.8, 126.7 (q, J = 293.2 Hz), 126.3, 125.9, 124.9, 123.4, 123.1, 122.3, 120.6, 108.7, 60.8 (q, J = 24.7 Hz), 58.5, 41.9 (d, J = 2.2 Hz), 35.8.

IR (ATR, cm⁻¹) 3210, 3056, 2927, 2900, 2867, 2812, 1727, 1616, 1598, 1502, 1459, 1371, 1287, 1251, 1229, 1175, 1153, 1103, 1082, 1038, 1025, 954, 865, 776, 733, 698, 588, 451, 425.


Synthesis of compound 57
1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)-3-(1H-pyrrolo[2,3-b]pyridin-1-yl)propan-2-amine

Compound 57 was prepared according to general procedure A with 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and indazole (89.5 mg, 0.75 mmol, 2.5 equiv) to afford a white solid (69.3 mg, 0.181 mmol, 60% yield). Rf = 0.43 (hexanes:ethyl acetate= 1:1). M.p.= 130-132 ºC.

LRMS (EI, 70 eV): m/z (%): 383(1), 327(1), 265(3), 171(5), 170(64), 168(12), 142(13), 141(100), 124(5), 119(9), 118(43), 115(36), 103(5), 89(5), 77(6), 77(4).

1H NMR (300 MHz, Chloroform-d) 7.78 – 7.65 (m, 4H), 7.58 (d, J = 8.4 Hz, 1H), 7.38 (dd, J = 8.8, 6.6 Hz, 1H), 7.31 – 7.23 (m, 1H), 7.22 – 7.18 (m, 2H), 7.15 (d, J = 8.1 Hz, 2H), 6.48 (t, J = 7.7 Hz, 1H), 4.69 (dd, J = 13.9, 3.5 Hz, 1H), 4.57 (dd, J = 13.9, 10.2 Hz, 1H), 4.42 – 4.26 (m, 1H), 4.22 (s, 2H), 2.51 (s, 3H). 19F NMR (282 MHz, Chloroform-d) δ -66.87 (d, J = 8.3 Hz).

13C NMR (75 MHz, Chloroform-d) δ 149.1, 133.6, 133.1, 131.9, 128.5, 128.0, 127.7, 126.4, 125.7,
125.6, 124.8, 124.7, 124.0 (q, $J = 289.9$ Hz), 123.7, 121.8, 120.5, 117.4, 64.0 (q, $J = 25.2$ Hz), 59.2, 49.6 (d, $J = 2.7$ Hz), 34.6. IR (ATR, cm$^{-1}$) 3119, 3053, 3009, 3000, 2975, 2952, 2841, 2807, 1628, 1595, 1516, 1509, 1443, 1382, 1365, 1302, 1289, 1259, 1244, 1174, 1127, 1096, 1072, 1052, 1031, 871, 829, 790. HRMS m/z [M+H]$^+$ calculated for C$_{22}$H$_{21}$N$_3$F$_3$: 384.1682, found: 384.1686.

Synthesis of compound 58

3-(1H-benzo[d][1,2,3]triazol-1-yl)-1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine

Compound 58 was prepared according to general procedure A with 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and 1H-benzotriazole (89.3 mg, 0.75 mmol, 2.5 equiv) to afford a pale yellow oil (68.5 mg, 0.178 mmol, 59% yield). $R_f$ = 0.30 (hexanes:ethyl acetate = 1:1). M.p. = 77-82 °C. LRMS (EI, 70 eV): m/z (%): 384(1), 252(1), 171(3), 170(29), 142(12), 141(100), 139(7), 115(12), 115(7), 77(8), 77(5), 51(3). $^1$H NMR (300 MHz, Chloroform-d) 7.98 – 7.89 (m, 1H), 7.68 – 7.59 (m, 2H), 7.24 (ddt, $J = 15.1, 12.7, 5.0$ Hz, 5H), 7.03 (d, $J = 6.9$ Hz, 1H), 7.00 – 6.92 (m, 2H), 4.90 (dd, $J = 14.7, 10.3$ Hz, 1H), 4.66 (dd, $J = 14.7, 3.9$ Hz, 1H), 4.17 (d, $J = 12.9$ Hz, 1H), 4.11 (d, $J = 13.3$ Hz, 1H), 4.04 – 3.89 (m, 1H), 2.71 (q, $J = 2.0$ Hz, 3H). $^{19}$F NMR (282 MHz, Chloroform-d) $\delta$ -66.98 (d, $J = 8.0$ Hz). $^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 145.7, 133.5, 132.9, 132.4, 131.7, 128.6, 128.2, 127.7, 127.4, 126.5 (q, $J = 292.6$ Hz), 125.9, 125.6, 124.7, 123.7, 123.3, 120.1, 108.4, 60.8 (q, $J = 25.2$ Hz), 58.3, 44.3, 35.8. IR (ATR, cm$^{-1}$) 3064, 3046, 3002, 2976, 2955, 2900, 2854, 2816, 1510, 1449, 1367, 1313, 1251, 1234, 1157, 1100, 1082, 1054, 1015, 953, 790, 776, 746, 720, 698, 567, 431. HRMS m/z [M+H]$^+$ calculated for C$_{21}$H$_{19}$N$_4$F$_3$: 385.1635, found: 385.1636.
Synthesis of compound 59

1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)-3-(5-phenyl-2H-tetrazol-2-yl)propan-2-amine

Compound 59 was prepared according to general procedure A with 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and 5-phenyl-1H-tetrazole (110 mg, 0.75 mmol, 2.5 equiv) to afford a colorless oil (77.6 mg, 0.189 mmol, 63% yield). \( R_f = 0.49 \) (hexanes:ethyl acetate= 1:1). LRMS (EI, 70 eV): m/z (%): 384(5), 383(23), 382(6), 142(13), 141(100), 139(5), 131(10), 115(17), 77(11). \( ^1H \) NMR (300 MHz, Chloroform-\( d \)) 7.98 – 7.85 (m, 2H), 7.65 (d, \( J = 8.2 \) Hz, 1H), 7.48 (qd, \( J = 9.5, 8.6, 5.1 \) Hz, 4H), 7.30 (t, \( J = 7.6 \) Hz, 1H), 7.21 (d, \( J = 6.9 \) Hz, 1H), 7.09 (dt, \( J = 6.4, 3.4 \) Hz, 2H), 5.03 (dd, \( J = 14.0, 11.0 \) Hz, 1H), 4.59 (dd, \( J = 14.0, 3.5 \) Hz, 1H), 4.20 (dd, \( J = 13.2, 8.7 \) Hz, 2H), 4.09 (dd, \( J = 16.1, 8.1, 4.2 \) Hz, 1H), 2.67 (q, \( J = 2.0 \) Hz, 3H). \( ^19F \) NMR (282 MHz, Chloroform-\( d \)) \( \delta = -66.99 \) (d, \( J = 7.9 \) Hz). \( ^13C \) NMR (75 MHz, Chloroform-\( d \)) \( \delta = 165.0, 133.7, 132.4, 132.0, 130.3, 128.9, 128.7, 128.2, 127.9, 127.2, 126.9, 126.2, 125.7, 124.9, 124.1 (q, \( J = 293.0 \) Hz), 61.1 (q, \( J = 25.9 \) Hz), 58.2, 48.8, 35.7. IR (ATR, cm\(^{-1}\)) 3685, 3661, 2988, 2971, 2901, 2847, 2253, 1530, 1510, 1466, 1451, 1375, 1312, 1255, 1171, 1140, 1109, 1073, 1052, 1044, 873, 788, 774, 732, 703, 693, 588, 447, 431, 418. HRMS m/z [M+H]\(^+\) calculated for C\(_{22}\)H\(_{21}\)N\(_4\)F\(_3\): 412.1744, found: 412.1749.

Synthesis of compound 60

1,1,1-trifluoro-3-(4-methoxy-7H-pyrrolo[2,3-d]pyrimidin-7-yl)-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine

Compound 60 was prepared according to general procedure B from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv), 4-methoxy-7H-pyrrolo[2,3-d]pyrimidine (116 mg, 0.78 mmol, 2.6 equiv), solution of LiHMDS (750 μL, 1 M in THF, 0.75 mmol, 2.5 equiv) and HMPA (132 µL, 0.75 mmol, 2.5 equiv) to afford an beige solid (63.8 mg, 0.154 mmol, 51% yield). \( R_f = 0.35 \) (hexanes:ethyl acetate= 1:1). M.p. = 78-80 °C. LRMS (EI, 70 eV): m/z (%): 414(1), 273(4), 273(3), 253(7), 170(27), 163(3), 162(5), 162(5), 150(10), 149(24), 142(7), 142(5), 141(100), 116(3), 115(26), 93(6), 92(3), 78(3). \( ^1H \) NMR (500 MHz, Chloroform-\( d \)) 8.22 (s, 1H), 7.68 (d, \( J = 8.1 \) Hz, 1H), 7.65 (d, \( J = 8.2 \) Hz, 1H), 7.34 (d, \( J = 8.5 \) Hz, 1H), 7.31 (ddd, \( J = 8.0, 6.9, 1.2 \) Hz, 1H), 7.24 (dd, \( J = 8.3, 6.9 \) Hz, 1H), 7.10 (dd, \( J = 6.9, 1.2 \) Hz, 1H), 7.07 (ddd, \( J = 8.3, 6.9, 1.3 \) Hz, 1H), 6.64 (d, \( J = 3.5 \) Hz, 1H), 6.22 (dd, \( J = 3.5, 0.7 \) Hz, 1H), 4.37 (dd, \( J = 14.5, 10.1 \) Hz, 1H), 4.32 (dd, \( J = 14.4, 4.4 \) Hz, 1H), 4.17 (d, \( J = 12.8 \) Hz, 1H), 4.14
(s, 3H), 4.09 (d, J = 13.1 Hz, 1H), 4.01 – 3.90 (m, 1H), 2.63 (q, J = 2.0 Hz, 3H). \(^{19}\)F NMR (282 MHz, Chloroform-\(d\)) \(\delta\) -66.78 (d, J = 8.2 Hz). \(^{13}\)C NMR (75 MHz, Chloroform-\(d\)) \(\delta\) 162.6, 151.5, 150.4, 133.6, 133.0, 132.0, 128.4, 128.1, 127.8, 126.9 (q, J = 293.1 Hz), 126.1, 125.7, 125.4, 124.9, 123.8, 105.5, 98.5, 60.7 (q, J = 24.5 Hz), 58.3, 53.8, 41.4 (q, J = 1.8 Hz), 35.9.

IR (ATR, cm\(^{-1}\)) 3119, 3036, 3002, 2952, 2897, 2856, 2819, 2253, 1595, 1561, 1509, 1475, 1414, 1388, 1357, 1323, 1265, 1248, 1164, 1124, 1103, 1066, 1052, 983, 793, 777, 764, 717, 702, 639, 607, 586, 542, 442, 417. HRMS m/z [M+H]\(^+\) calculated for C\(_{22}\)H\(_{22}\)N\(_4\)F\(_3\): 415.1740, found: 415.1739.

**Synthesis of compound 61**

1,3-dimethyl-7-(3,3,3-trifluoro-2-(methyl(naphthalen-1-ylmethyl)amino)propyl)-3,7-dihydro-1H-purine-2,6-dione

Compound 61 was prepared according to general procedure B from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv), methyl theophylline (141 mg, 0.78 mmol, 2.6 equiv), solution of LiHMDS (750 \(\mu\)L, 1 M in THF, 0.75 mmol, 2.5 equiv) and HMPA (132 \(\mu\)L, 0.75 mmol, 2.5 equiv) to afford a white solid (81.0 mg, 0.182 mmol, 60\% yield). \(R_f\) = 0.49 (dichloromethane:isopropanol= 1:1). M.p. = 215-218 °C. LRMS (EI, 70 eV): m/z (%): 355(1), 304(9), 193(4), 170(23), 170(9), 142(11), 141(100), 115(19), 109(4).

\(^1\)H NMR (300 MHz, Chloroform-\(d\)) 7.66 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 7.4 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.37 – 7.28 (m, 2H), 7.28 – 7.23 (m, 1H), 7.22 (s, 1H), 7.21 – 7.14 (m, 1H), 4.22 (d, J = 11.5 Hz, 2H), 4.07 (d, J = 13.1 Hz, 1H), 4.03 (s, 1H), 4.02 – 3.95 (m, 1H), 3.34 (s, 3H), 3.05 (s, 3H), 2.78 (q, J = 2.3 Hz, 3H). \(^{19}\)F NMR (282 MHz, Chloroform-\(d\)) \(\delta\) -66.36 (d, J = 6.3 Hz). \(^{13}\)C NMR (75 MHz, Chloroform-\(d\)) \(\delta\) 153.9, 151.0, 148.1, 141.3, 133.5, 132.4, 132.0, 129.1, 128.4, 127.9, 126.7 (d, J = 293.4 Hz), 125.8, 125.2, 125.0, 123.5, 105.9, 57.9, 57.9 (q, J = 24.8 Hz), 43.2, 36.5, 29.6, 27.6. IR (ATR, cm\(^{-1}\)) 3112, 3075, 2951, 2927, 2901, 2860, 2819, 2798, 1697, 1642, 1599, 1548, 1473, 1407, 1378, 1292, 1248, 1231, 1180, 1141, 1109, 1088, 1072, 1028, 970, 871, 784, 770, 759, 749, 702, 621, 590, 492, 417, 397. HRMS m/z [M+H]\(^+\) calculated for C\(_{22}\)H\(_{22}\)N\(_4\)O\(_2\)F\(_3\): 446.1797, found: 446.1797.
Synthesis of compound 62

**Nα-(tert-butoxycarbonyl)-1-(3,3,3-trifluoro-2-(methyl(naphthalen-1-ylmethyl)amino)propyl)-L-tryptophanate**

Compound 62 was prepared according to **general procedure B** from 1 (140 mg, 0.3 mmol), *N*-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv), methyl *N*-(((tert-butoxycarbonyl)-L-tryptophanate (115 mg, 0.78 mmol, 2.6 equiv), solution of LiHMDS (750 μL, 1 M in THF, 0.75 mmol, 2.5 equiv) and HMPA (132 μL, 0.75 mmol, 2.5 equiv) to afford a colorless oil (56.8 mg, 0.0973 mmol, 32% yield).

**Rf** = 0.29 (hexanes:ethyl acetate= 1:1). **LRMS** (El, 70 eV): m/z (%): 489(1), 430(3), 207(5), 193(3), 171(2), 170(27), 170(10), 168(2), 168(2), 165(2), 142(8), 142(5), 141(100), 115(9), 73(2). **1H NMR** (500 MHz, Chloroform-d) - δ 7.78 (dt, *J* = 8.5, 1.6 Hz, 1H), 7.70 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.62 (dd, *J* = 8.7, 3.9 Hz, 1H), 7.50 (td, *J* = 7.8, 7.3, 1.5 Hz, 1H), 7.41 (dddd, *J* = 8.1, 6.8, 2.3, 1.2 Hz, 1H), 7.24 – 7.15 (m, 2H), 7.13 – 7.03 (m, 3H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 6.6 Hz, 1H), 4.98 (d, *J* = 8.3 Hz, 1H), 4.62 – 4.53 (m, 1H), 4.35 – 4.24 (m, 2H), 4.20 (d, *J* = 13.4 Hz, 1H), 4.17 – 4.13 (m, 1H), 3.70 (pt, *J* = 12.1, 7.0, 6.0 Hz, 1H), 3.62 (d, *J* = 6.1 Hz, 3H), 3.24 – 3.08 (m, 2H), 2.63 (dt, *J* = 3.6, 1.9 Hz, 3H), 1.42 (s, 9H). **19F NMR** (282 MHz, Chloroform-d) - δ -66.72 (d, *J* = 8.1 Hz). **13C NMR** (75 MHz, Chloroform-d) - δ 172.8, 155.3, 136.0, 133.9, 132.6, 132.0, 127.9, 126.8 (q, *J* = 292.2 Hz), 126.0, 125.7, 125.1, 123.9, 122.2, 119.6, 108.9, 79.9, 61.6 (d, *J* = 24.3 Hz), 58.6, 58.5, 54.3, 54.1, 52.3, 43.5, 36.2, 28.4. **IR** (ATR, cm⁻¹) - 3431, 3379, 3051, 2976, 2951, 2931, 2861, 1741, 1710, 1614, 1497, 1468, 1439, 1367, 1251, 1161, 1102, 1054, 1017, 861, 793, 776, 739, 428. **HRMS** m/z [M+H]+ calculated for C₃₂H₃₇N₃O₄F₃+: 584.2731, found: 584.2730.

Synthesis of compound 63

1-(3,3,3-trifluoro-2-(methyl(naphthalen-1-ylmethyl)amino)propyl)pyridine-2(1H)-thione

Compound 63 was prepared according to **general procedure B** from 1 (140 mg, 0.3 mmol), *N*-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv), 2-mercaptopyridine (86.7 mg, 0.78 mmol, 2.6 equiv), solution of LiHMDS (750 μL, 1 M in THF, 0.75 mmol, 2.5 equiv) and HMPA (132 μL, 0.75 mmol, 2.5 equiv) to afford a yellow oil (78.5 mg, 0.209 mmol, 69% yield). **Rf** = 0.59 (hexanes:ethyl acetate= 1:1). **LRMS** (El, 70 eV): m/z (%): 265(8), 235(6), 196(5), 169(6), 168(22), 142(12), 141(100), 139(6), 115(23), 112(7), 111(6), 78(6). **1H NMR** (300 MHz,
Chloroform-\textit{d})  8.36 (dd, \(J = 5.1, 1.9\) Hz, 1H), 8.26 – 8.19 (m, 1H), 7.83 (dt, \(J = 8.3, 3.0\) Hz, 1H), 7.76 (d, \(J = 8.3\) Hz, 1H), 7.53 – 7.46 (m, 3H), 7.45 – 7.34 (m, 2H), 7.06 (d, \(J = 8.1\) Hz, 1H), 6.95 (dd, \(J = 7.4, 4.9\) Hz, 1H), 4.40 (d, \(J = 13.7\) Hz, 1H), 4.34 (d, \(J = 13.7\) Hz, 1H), 3.84 – 3.66 (m, 2H), 3.45 (dd, \(J = 14.6, 11.3\) Hz, 1H), 2.52 (d, \(J = 2.2\) Hz, 3H).

\begin{align*}
\text{\textbf{19F NMR (282 MHz, Chloroform-\textit{d}) \(\delta = 67.71\) (d, \(J = 7.7\) Hz).}} \\
\text{\textbf{13C NMR (75 MHz, Chloroform-\textit{d}) \(\delta = 158.2, 149.3, 132.3, 128.4, 128.2, 127.5, 127.2\) (q, \(J = 292.4\) Hz), 125.8, 125.7, 125.2, 124.9, 122.2, 62.5 (q, \(J = 25.2\) Hz), 58.4, 36.1, 27.2.}} \\
\text{\textbf{IR (ATR, cm}^{-1}\text{) 3047, 2988, 2942, 2863, 2810, 2253, 1578, 1557, 1510, 1455, 1415, 1374, 1327, 1252, 1166, 1123, 1103, 1072, 1010, 985, 916, 852, 793, 781, 757, 733, 722, 689, 479, 415.}} \\
\text{\textbf{HRMS m/z [M+H]^+ calculated for C}_{20}H_{20}N_{2}S_{3}F^+: 377.1294, found: 377.1298.}} \\
\end{align*}

\textbf{Synthesis of compound 64}

1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)-3-(10H-phenothiazin-10-yl)propan-2-amine

Compound 64 was prepared according to \textit{general procedure B} from 1 (140 mg, 0.3 mmol), \(N\)-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv), phenothiazine (1.59 mg, 0.78 mmol, 2.6 equiv), solution of LiHMDS (750 \(\mu\)L, 1 M in THF, 0.75 mmol, 2.5 equiv) and HMPA (132 \(\mu\)L, 0.75 mmol, 2.5 equiv) to afford a yellow oil (88.2 mg, 0.190 mmol, 63% yield).

\(R_f = 0.63\) (hexanes:ethyl acetate= 1:1). \textbf{LRMS (EI, 70 eV): m/z (%): 465(5), 464(15), 213(14), 212(100), 212(19), 181(7), 180(49), 179(9), 141(34), 115(12).} \textbf{1H NMR (300 MHz, Chloroform-\textit{d}) 8.24 – 8.11 (m, 1H), 7.93 – 7.82 (m, 1H), 7.76 (d, \(J = 8.2\) Hz, 1H), 7.53 (tt, \(J = 7.1, 3.7\) Hz, 2H), 7.36 – 7.23 (m, 3H), 7.22 (t, \(J = 7.5\) Hz, 1H), 7.19 (t, \(J = 7.8\) Hz, 1H), 7.10 – 6.99 (m, 3H), 6.92 (s, 1H), 6.89 (s, 1H), 4.40 (dd, \(J = 12.0\) Hz, 2H), 4.27 (d, \(J = 13.5\) Hz, 1H), 4.24 (dd, \(J = 14.1, 3.9\) Hz, 1H), 3.99 (ddq, \(J = 14.3, 8.9, 5.3, 4.6\) Hz, 1H), 2.51 (s, 3H).} \textbf{19F NMR (282 MHz, Chloroform-\textit{d}) \(\delta = 69.80\) (d, \(J = 8.4\) Hz).} \textbf{13C NMR (75 MHz, Chloroform-\textit{d}) \(\delta = 144.8, 134.0, 133.9, 132.3, 128.4, 128.1, 127.7, 127.4, 126.7\) (q, \(J = 287.8\) Hz), 126.4, 125.8, 125.6, 125.2, 124.6, 123.3, 115.4, 59.0, 58.9 (q, \(J = 25.6\) Hz), 43.1, 36.9.} \textbf{IR (ATR, cm}^{-1}\text{) 3063, 2988, 2952, 2884, 2864, 2807, 2252, 1592, 1571, 1456, 1337, 1279, 1251, 1231, 1207, 1158, 1099, 1049, 1028, 900, 856, 791, 774, 749, 604, 508, 445, 427.} \textbf{HRMS m/z [M+H]^+ calculated for C}_{27}H_{24}N_{2}S_{3}F^+: 465.1607, found: 465.1610.
Synthesis of compound 65

$N^2$-cyclopropyl-3,3,3-trifluoro-$N^2$-(4-methoxybenzyl)-$N^1$-methyl-$N^1$-(naphthalen-1-ylmethyl)propane-1,2-diamine

Compound 65 was prepared according to general procedure A from 1 (140 mg, 0.3 mmol), $N$-(4-methoxybenzyl)cyclopropanamine (53.2 mg, 0.3 mmol, 1 equiv) and $N$-methyl-1-(naphthalen-1-yl)methanamine (122 µL, 0.75 mmol, 2.5 equiv) to afford a white solid (68.9 mg, 0.156 mmol, 52% yield). $R_f$ = 0.38 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 321(1), 301(4), 265(1), 212(2), 185(11), 184(78), 176(4), 142(20), 141(100), 141(66), 139(4), 122(5), 121(51), 115(13), 91(4), 78(4), 77(5).

$^1$H NMR (250 MHz, Chloroform-d) $\delta$ 8.43 – 8.29 (m, 1H), 7.95 – 7.75 (m, 2H), 7.60 – 7.37 (m, 4H), 7.04 (d, $J = 8.2$ Hz, 2H), 6.75 (d, $J = 8.5$ Hz, 2H), 4.10 (d, $J = 12.9$ Hz, 1H), 3.86 – 3.73 (m, 4H), 3.66 (s, 2H), 3.55 (ddt, $J = 15.6$, 6.7, 4.0 Hz, 1H), 3.13 (dd, $J = 13.2$, 9.4 Hz, 1H), 2.57 (dd, $J = 13.2$, 3.8 Hz, 1H), 2.27 (s, 3H), 2.24 – 2.15 (m, 1H), 0.33 – 0.07 (m, 4H).

$^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -69.20.

$^{13}$C NMR (63 MHz, Chloroform-d) $\delta$ 158.6, 134.5, 134.0, 132.7, 132.2, 128.5, 128.3, 127.7, 127.1 (q, $J = 287.8$ Hz), 125.8, 125.3, 125.2, 113.4, 61.8, 60.9 (q, $J = 24.8$ Hz), 55.4, 55.3, 54.5, 42.6, 35.0, 7.8, 7.7. IR (ATR, cm$^{-1}$) 3048, 3005, 2951, 2895, 2860, 2826, 2746, 1771, 1707, 1616, 1598, 1510, 1466, 1428, 1405, 1377, 1334, 1252, 1226, 1192, 1161, 1103, 1055, 1018, 970, 953, 875, 801, 786, 770, 726, 713, 702, 614, 529, 509, 449, 432. HRMS m/z [M+H]$^+$ calculated for C$_{26}$H$_{30}$N$_2$O$_2$F$_3$: 443.2310, found: 443.2313.

Synthesis of compound 66

$N^2$-allyl-3,3,3-trifluoro-$N^2$-(4-methoxybenzyl)-$N^1$-methyl-$N^1$-(naphthalen-1-ylmethyl)propane-1,2-diamine

Compound 66 was prepared according to general procedure A from 1 (93.2 mg, 0.2 mmol), A1 (35.5 mg, 0.2 mmol, 1 equiv) and $N$-methyl-1-(naphthalen-1-yl)methanamine (81.5 µL, 0.5 mmol, 2.5 equiv) to afford a colorless oil (64.6 mg, 0.146 mmol, 73% yield). $R_f$ = 0.50 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 321(2), 185(8), 184(54), 142(12), 141(100), 139(2), 122(2), 121(24), 115(8), 78(2), 77(2). $^1$H NMR (250 MHz, Chloroform-d) 8.44 – 8.31 (m, 1H), 7.99 – 7.77 (m, 2H), 7.62 – 7.48 (m, 2H), 7.52 – 7.38 (m, 2H), 7.13 (d, $J = 8.3$ Hz, 2H), 6.81 (d, $J = 8.5$ Hz, 2H), 5.69 (ddt, $J = 16.6$, 10.1, 6.4 Hz, 1H), 5.20 – 5.02 (m, 2H), 4.12 (d, $J = 12.9$ Hz, 1H), 3.79 (s, 4H), 3.64 – 3.44 (m, 3H), 3.09 (dt, $J = 27.5$, 7.6 Hz, 3H), 2.60 (dd, $J = 13.3$, 3.8 Hz, 1H), 2.29 (s, 3H). $^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -69.11. $^{13}$C
NMR (63 MHz, Chloroform-d) 158.8, 137.0, 134.5, 134.1, 132.7, 129.9, 128.5, 128.3, 127.8, 127.3 (q, J = 288.5 Hz), 125.9, 125.8, 125.3, 117.4, 113.7, 61.7, 57.3 (q, J = 24.6 Hz), 55.3, 54.2, 53.5, 53.4, 42.7. IR (ATR, cm⁻¹) 3067, 3047, 3031, 3002, 2952, 2836, 2815, 2789, 1642, 1612, 1585, 1463, 1365, 1302, 1246, 1207, 1170, 1149, 1126, 1096, 1036, 1010, 994, 909, 885, 831, 776, 732, 703, 649, 603, 554, 519, 414, 432. HRMS m/z [M+H]+ calculated for C₂₆H₃₀N₂OF₃+: 443.2310, found: 443.2309.

Synthesis of compound 67

3,3,3-trifluoro-N²-(4-methoxybenzyl)-N¹-methyl-N¹-(naphthalen-1-ylmethyl)-N²-(prop-2-yn-1-yl)propane-1,2-diamine

Compound 67 was prepared according to general procedure A from 1 (140 mg, 0.3 mmol), N-(4-methoxybenzyl)prop-2-yn-1-amine (52.6 mg, 0.3 mmol, 1 equiv) and N-methyl-1-(naphthalen-1-yl)methanamine (122 µL, 0.75 mmol, 2.5 equiv) to afford a white solid (57.0 mg, 0.129 mmol, 43% yield). Rf = 0.43 (hexanes:diisopropyl ether= 10:1). LRMS (EI, 70 eV): m/z (%): 355(1), 299(1), 185(13), 184(88), 142(13), 142(8), 141(100), 139(5), 121(37), 115(16), 77(4). ¹H NMR (250 MHz, Chloroform-d) 8.40 – 8.29 (m, 1H), 7.96 – 7.78 (m, 2H), 7.58 – 7.49 (m, 1H), 7.48 (t, J = 7.8 Hz, 3H), 7.10 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.5 Hz, 2H), 4.16 (d, J = 12.9 Hz, 1H), 3.87 (t, J = 10.6 Hz, 2H), 3.79 (s, 3H), 3.55 (dd, J = 17.8, 13.5 Hz, 2H), 3.47 (d, J = 17.3 Hz, 1H), 3.29 (d, J = 17.1 Hz, 1H), 3.11 (dd, J = 13.1, 9.3 Hz, 1H), 2.67 (dd, J = 13.3, 3.3 Hz, 1H), 2.37 (s, 3H), 2.21 (d, J = 9.0 Hz, 1H). ¹⁹F NMR (235 MHz, Chloroform-d) δ -69.40. ¹³C NMR (63 MHz, Chloroform-d) δ 158.9, 134.4, 134.0, 132.6, 130.5, 129.9, 128.6, 128.4, 127.9, 126.9 (q, J = 288.1, 287.6, 287.6 Hz), 126.0, 125.8, 125.3, 125.2, 113.8, 80.9, 72.6, 61.5, 58.1 (q, J = 25.2 Hz), 55.3, 53.8, 53.1, 42.6, 40.0. HRMS m/z [M+H]+ calculated for C₂₆H₂₈N₂OF₃+: 441.2154, found: 441.2148.
Synthesis of compound 68
3,3,3-trifluoro-N\textsuperscript{2}-isobutyl-N\textsuperscript{1}-methyl-N\textsuperscript{1}-(naphthalen-1-ylmethyl)-N\textsuperscript{2}-(3-phenylprop-2-yn-1-yl)propane-1,2-diamine

Compound 68 was prepared according to general procedure A from 1 (140 mg, 0.3 mmol), N-isobutyl-3-phenylprop-2-yn-1-amine (56.2 mg, 0.3 mmol, 1 equiv) and N-methyl-1-(naphthalen-1-yl)methanamine (122 µL, 0.75 mmol, 2.5 equiv) to afford a white solid (49.7 mg, 0.11 mmol, 37% yield). \(R_f\) = 0.60 (hexanes:diisopropyl ether= 10:1). LRMS (EI, 70 eV): m/z (%): 311(2), 200(2), 185(13), 184(92), 142(6), 141(100), 140(3), 139(4), 116(3), 116(2), 115(53), 89(2), 73(2). ¹H NMR (250 MHz, Chloroform-\(d\)) 8.25 – 8.12 (m, 1H), 7.82 – 7.59 (m, 2H), 7.30 (ddd, \(J\) = 21.7, 10.0, 5.6 Hz, 6H), 7.15 (s, 3H), 3.97 (d, \(J\) = 13.0 Hz, 1H), 3.78 (d, \(J\) = 13.0 Hz, 1H), 3.70 – 3.36 (m, 3H), 2.90 (dd, \(J\) = 13.2, 8.2 Hz, 1H), 2.58 (dd, \(J\) = 13.3, 3.8 Hz, 1H), 2.24 (s, 5H), 1.59 (dp, \(J\) = 13.6, 7.2 Hz, 1H), 0.76 (d, \(J\) = 6.4 Hz, 3H), 0.67 (d, \(J\) = 6.4 Hz, 3H). ¹³C NMR (63 MHz, Chloroform-\(d\)) \(\delta\) 134.5, 134.0, 132.6, 131.7, 128.5, 128.4, 128.1, 127.6, 127.0 (q, \(J\) = 288.4, 287.7 Hz), 125.9, 125.8, 125.3, 125.0, 123.4, 86.7, 84.4, 61.4, 60.5 (q, \(J\) = 25.0 Hz), 58.5, 54.4, 42.6, 41.7, 26.6, 20.6, 20.4. IR (ATR, cm\(^{-1}\)) 3054, 2955, 2945, 2928, 2915, 2908, 2868, 2849, 2820, 1716, 1598, 1510, 1490, 1465, 1443, 1365, 1255, 1160, 1097, 1054, 1010, 907, 885, 861, 841, 793, 776, 756, 732, 691, 649, 645, 621, 605, 554, 526, 430, 415. HRMS m/z [M+H]\(^+\) calculated for C\(_{28}\)H\(_{32}\)N\(_2\)F\(_3\): 453.2518, found: 453.2516.

Synthesis of compound 69
2-(3-(\((\text{tert}-\text{butyldimethylsilyl})\)oxy)azetidin-1-yl)-3,3,3-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-1-amine

Compound 69 was prepared according to general procedure A from 1 (140 mg, 0.3 mmol), 3-\((\text{tert}-\text{butyldimethylsilyl})\)oxyazetidine (56.2 mg, 0.3 mmol, 1 equiv) and N-methyl-1-(naphthalen-1-yl)methanamine (122 µL, 0.75 mmol, 2.5 equiv) to afford a white solid (71.5 mg, 0.158 mmol, 53% yield). \(R_f\) = 0.48 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 268(1), 185(10), 184(69), 168(1), 142(12), 141(100), 140(2), 115(4), 115(3), 110(2), 101(3), 101(2), 75(2), 73(5), 59(4). ¹H NMR (250 MHz, Chloroform-\(d\)) 8.26 (d, \(J\) = 7.7 Hz, 1H), 7.94 – 7.72 (m, 2H), 7.61 – 7.35 (m, 4H), 4.31 (p, \(J\) = 6.2 Hz, 1H), 4.09 (d, \(J\) = 12.9 Hz, 1H), 3.76 (d, \(J\) = 13.0 Hz, 1H), 3.71 – 3.60 (m, 1H), 3.30 (td, \(J\) = 6.5, 2.6 Hz, 1H), 3.15 (t, \(J\) = 6.7 Hz, 1H), 3.06 – 2.89 (m, 2H), 2.65 (qd, \(J\) = 13.6, 4.8 Hz, 2H), 2.32 (s, 3H), 0.88 (s, 9H), -0.00
(s, 6H). $^{19}$F NMR (235 MHz, Chloroform-$d$) $\delta$ -72.80. $^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 134.0, 134.0, 132.6, 128.6, 128.4, 127.9, 126.0, 125.8, 124.8, 123.8 (q, $J = 283.1$, 282.7, 282.1 Hz), 65.1, 64.9 (q, $J = 25.2$ Hz), 62.8, 62.5, 61.5, 55.7 (q, $J = 2.2$, 1.7 Hz), 43.2, 25.9, 18.1, -4.9, -5.0. IR (ATR, cm$^{-1}$) 3094, 3047, 2953, 2929, 2887, 2854, 2789, 2773, 2712, 1510, 1463, 1377, 1304, 1259, 1218, 1134, 1079, 1007, 939, 883, 835, 791, 774, 733, 698, 674, 414, 397. HRMS m/z [M+H]$^+$ calculated for C$_{24}$H$_{36}$N$_2$O$_2$F$_3$: 453.2549, found: 453.2548.

**Synthesis of compound 70**

3,3,3-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)-2-(pyrrolidin-1-yl)propan-1-amine

Compound 70 was prepared according to general procedure A from I (93.2 mg, 0.2 mmol), pyrrolidine (14.2 mg, 0.2 mmol, 1 equiv) and N-methyl-1-(naphthalen-1-yl) methanamine (81.5 µL, 0.5 mmol, 2.5 equiv) to afford a colorless oil (45.9 mg, 0.136 mmol, 68% yield). $R_f = 0.43$ (hexanes:ethyl acetate= 10:1). M.p. = 51–54 °C. LRMS (EI, 70 eV): m/z (%): 296(1), 210(1), 185(10), 184(66), 142(13), 141(100), 140(2), 139(2), 115(9), 91(2), 75(2), 73(8). $^1$H NMR (250 MHz, Chloroform-$d$) 8.41 – 8.27 (m, 1H), 7.99 – 7.73 (m, 2H), 7.61 – 7.37 (m, 4H), 4.09 (d, $J = 12.8$ Hz, 1H), 3.87 (d, $J = 12.8$ Hz, 1H), 3.58 (pd, $J = 8.7$, 3.6 Hz, 1H), 2.99 (dd, $J = 13.3$, 9.0 Hz, 1H), 2.88 – 2.71 (m, 4H), 2.63 (dd, $J = 13.3$, 3.5 Hz, 1H), 2.31 (s, 3H), 1.75 – 1.54 (m, 4H). $^{19}$F NMR (235 MHz, Chloroform-$d$) $\delta$ -69.81. $^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 134.6, 134.0, 132.7, 128.5, 128.2, 127.7, 124.8 (q, $J = 289.1$ Hz), 61.3, 59.6 (q, $J = 24.7$ Hz), 54.3 – 53.6 (m), 48.7, 42.7, 24.1. IR (ATR, cm$^{-1}$) 3094, 3044, 2953, 2929, 2887, 2854, 2789, 2773, 2712, 1510, 1463, 1377, 1304, 1259, 1218, 1134, 1079, 1007, 939, 883, 835, 791, 774, 733, 698, 674, 414, 397. HRMS m/z [M+H]$^+$ calculated for C$_{19}$H$_{24}$N$_2$F$_3$: 337.1892, found: 337.1885.

**Synthesis of compound 71**

3,3,3-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)-2-(2-methylpiperidin-1-yl)-N-(naphthalen-1-ylmethyl)propan-1-amine

Compound 71 was prepared according to general procedure A from I (93.2 mg, 0.2 mmol), 2-methylpiperidine (19.8 mg, 0.2 mmol, 1 equiv) and N-methyl-1-(naphthalen-1-yl) methanamine (81.5 µL, 0.5 mmol, 2.5 equiv) to afford a colorless oil (61.7 mg, 0.169 mmol, 85% yield). $R_f = 0.68$ (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 185(7), 184(47), 180(3), 142(13), 141(100), 140(2), 139(3), 115(11), 112(3), 110(2), 55(6). $^1$H NMR (250 MHz, Chloroform-$d$) 8.55 – 8.27 (m, 1H), 7.97 – 7.74 (m, 2H), 7.62 – 7.36 (m, 4H), 4.24 – 3.77 (m,
2H), 3.77 – 3.58 (m, 1H), 3.22 – 2.80 (m, 2H), 2.78 – 2.42 (m, 2H), 2.43 – 2.19 (m, 3H), 2.02 (td, J = 10.9, 4.6 Hz, 1H), 1.82 – 1.22 (m, 6H), 1.17 (d, J = 6.3 Hz, 1H), 1.04 (d, J = 6.1 Hz, 1H), 0.89 (dtd, J = 24.7, 12.4, 6.3 Hz, 1H). \(^{19}\text{F NMR}\) (235 MHz, Chloroform-\(d\)) \(\delta\) -66.66, -70.84 (d, r. = 46:54). \(^{13}\text{C NMR}\) (63 MHz, Chloroform-\(d\)) \(\delta\) 134.5, 134.0, 134.0, 132.7, 132.7, 128.5, 128.4, 128.3, 128.1, 127.8, 127.4, 126.6 (q, J = 284.8, 283.8, 283.5 Hz), 125.8, 125.7, 125.4, 125.2, 125.1, 61.9, 61.3, 57.5 (q, J = 22.8 Hz), 57.0 (q, J = 25.4 Hz), 55.6, 54.6, 52.4, 46.5 (q, J = 1.8 Hz), 46.4, 42.9, 42.7, 36.5, 36.3, 26.8, 26.5, 25.2, 24.4, 21.0, 20.3. \(^{1}\text{H NMR}\) (250 MHz, Methanol-\(d_4\) & Acetone-\(d_6\)) \(\delta\) 8.35 (d, J = 7.9 Hz, 1H), 7.92 – 7.70 (m, 2H), 7.45 (dt, J = 17.3, 7.4 Hz, 4H), 4.09 (d, J = 12.8 Hz, 1H), 3.85 (d, J = 12.7 Hz, 1H), 3.50 – 3.24 (m, 2H), 3.04 – 2.80 (m, 2H), 2.68 – 2.39 (m, 3H), 2.33 (s, 4H), 1.65 – 1.23 (m, 4H), 0.88 (s, 9H), 0.03 (s, 6H). \(^{19}\text{F NMR}\) (235 MHz, Methanol-\(d_4\) & Acetone-\(d_6\)) \(\delta\) -69.95. \(^{13}\text{C NMR}\) (63 MHz, Methanol-\(d_4\) & Acetone-\(d_6\)) \(\delta\) 135.4, 133.9, 129.4, 129.3, 128.9, 128.3 (q, J = 290.5, 289.9 Hz), 126.8, 126.3, 126.1, 69.9, 64.6 (q, J = 24.1 Hz), 62.1, 54.0, 47.6, 43.1, 36.9, 36.7, 26.4, 18.9, -4.4. \(^{1}\text{H NMR}\) (ATR, cm\(^{-1}\)) 3044, 2966, 2931, 2847, 2813, 2813, 1510, 1453, 1377, 1343, 1309, 1256, 1231, 1146, 1127, 1099, 1061, 1010, 967, 907, 889, 858, 829, 791, 774, 733, 698, 649, 624, 557, 520, 457, 414, 655, 613, 553, 520, 466, 411. \(^{1}\text{HRMS}\) m/z [M+H]\(^+\) calculated for C\(_{21}\)H\(_{28}\)N\(_2\)F\(_3\)Si\(^+\): 365.2205, found: 365.2205.

**Synthesis of compound 72**

2-(3-((tert-butyldimethylsilyl)oxy)piperidin-1-yl)-3,3,3-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-1-amine

Compound 72 was prepared according to general procedure A from 1 (93.2 mg, 0.2 mmol), 3-((tert-butyldimethylsilyl)oxy)piperidine (43.1 mg, 0.2 mmol, 1 equiv) and N-methyl-1-(naphthalen-1-yl)methanamine (81.5 µL, 0.5 mmol, 2.5 equiv) to afford a colorless oil (55.6 mg, 0.116 mmol, 58% yield). \(R_f = 0.38\) (hexanes:ethyl acetate= 10:1). **M.p.** = 64–67 °C. LRMS (EI, 70 eV): m/z (%): 296(1), 210(1), 185(10), 184(66), 144(1), 142(13), 141(100), 140(2), 139(2), 118(1), 115(9), 91(2), 77(1), 75(2), 73(8), 68(1), 57(1). \(^{1}\text{H NMR}\) (250 MHz, Methanol-\(d_4\) & Acetone-\(d_6\)) \(\delta\) 8.35 (d, J = 7.9 Hz, 1H), 7.92 – 7.70 (m, 2H), 7.45 (dt, J = 17.3, 7.4 Hz, 4H), 4.09 (d, J = 12.8 Hz, 1H), 3.85 (d, J = 12.7 Hz, 1H), 3.50 – 3.24 (m, 2H), 3.04 – 2.80 (m, 2H), 2.68 – 2.39 (m, 3H), 2.33 (s, 4H), 1.65 – 1.23 (m, 4H), 0.88 (s, 9H), 0.03 (s, 6H). \(^{19}\text{F NMR}\) (235 MHz, Methanol-\(d_4\) & Acetone-\(d_6\)) \(\delta\) -69.95. \(^{13}\text{C NMR}\) (63 MHz, Methanol-\(d_4\) & Acetone-\(d_6\)) \(\delta\) 135.4, 133.9, 129.4, 129.3, 128.9, 128.3 (q, J = 290.5, 289.9 Hz), 126.8, 126.3, 126.1, 69.9, 64.6 (q, J = 24.1 Hz), 62.1, 54.0, 47.6, 43.1, 36.9, 36.7, 26.4, 18.9, -4.4. \(^{1}\text{IR}\) (ATR, cm\(^{-1}\)) 3044, 2966, 2931, 2847, 2813, 2813, 1510, 1453, 1377, 1343, 1309, 1256, 1231, 1146, 1127, 1099, 1061, 1010, 967, 907, 889, 858, 829, 791, 774, 733, 698, 649, 624, 557, 520, 457, 414, 655, 613, 553, 520, 466, 411. \(^{1}\text{HRMS}\) m/z [M+H]\(^+\) calculated for C\(_{26}\)H\(_{40}\)N\(_2\)OF\(_3\)Si\(^+\): 481.2857, found: 481.2859.
Synthesis of compound 73
2-(4-benzylpiperazin-1-yl)-3,3,3-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-1-amine

Compound 73 was prepared according to general procedure A from 1 (93.2 mg, 0.2 mmol), N-benzylpiperazine (35.3 mg, 0.2 mmol, 1 equiv) and N-methyl-1-(naphthalen-1-yl)methanamine (81.5 µL, 0.5 mmol, 2.5 equiv) to afford a colorless oil (63.9 mg, 0.145 mmol, 72% yield). Rf = 0.58 (hexanes:ethyl acetate = 7:3). LRMS (EI, 70 eV): m/z (%): 257(1), 185(7), 184(51), 177(2), 146(1), 142(12), 141(100), 140(1), 139(2), 115(7), 92(2), 91(24), 65(2), 56(1). ¹H NMR (250 MHz, Chloroform-d) δ 8.48 – 8.34 (m, 1H), 7.97 – 7.77 (m, 2H), 7.47 – 7.22 (m, 5H), 4.12 – 3.92 (m, 2H), 3.52 (s, 2H), 3.29 (pd, J = 8.8, 3.3 Hz, 1H), 2.93 (dd, J = 13.7, 9.1 Hz, 1H), 2.85 (d, J = 4.7 Hz, 2H), 2.73 (q, J = 7.3, 5.9 Hz, 2H), 2.62 (dd, J = 13.4, 3.4 Hz, 1H), 2.41 (dq, J = 13.1, 5.7, 4.3 Hz, 4H), 2.33 (s, 3H). ¹⁹F NMR (235 MHz, Chloroform-d) δ -68.1. ¹³C NMR (63 MHz, Chloroform-d) δ 137.9, 134.7, 134.0, 132.6, 129.3, 128.5, 128.4, 128.2, 127.5, 127.3, 127.0 (d, J = 290.7 Hz), 125.9, 125.8, 125.2 (d, J = 1.6 Hz), 64.0 (q, J = 23.9 Hz), 63.1, 61.4, 53.8, 53.5 (d, J = 2.0 Hz), 49.2, 42.8. IR (ATR, cm⁻¹) 3061, 2969, 2956, 2941, 2901, 2844, 2810, 2769, 1509, 1494, 1455, 1394, 1367, 1351, 1295, 1255, 1217, 1156, 1124, 1102, 1076, 1052, 1028, 1010, 940, 907, 879, 858, 835, 793, 776, 732, 698, 638, 607, 519, 457, 414. HRMS m/z [M+H]+ calculated for C₂₆H₃₁N₃F₃+: 442.2470, found: 442.2474.

Synthesis of compound 74
3,3,3-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)-2-(4-(pyridin-2-yl)piperazin-1-yl)propan-1-amine

Compound 74 was prepared according to general procedure A from 1 (93.2 mg, 0.2 mmol), N-benzylpiperazine (35.3 mg, 0.2 mmol, 1 equiv) and N-methyl-1-(naphthalen-1-yl)methanamine (81.5 µL, 0.5 mmol, 2.5 equiv) to afford a colorless oil (69.7 mg, 0.163 mmol, 81% yield). M.p. = 92-95 °C. LRMS (EI, 70 eV): m/z (%): 185(7), 184(47), 142(12), 141(100), 139(2), 133(2), 121(3), 119(3), 115(8), 107(4), 79(5), 78(4). ¹H NMR (250 MHz, Chloroform-d) δ 8.4 – 8.3 (m, 1H), 8.2 (dd, J = 5.0, 2.0 Hz, 1H), 7.8 (t, J = 9.3 Hz, 2H), 7.4 (dt, J = 7.8, 4.9 Hz, 5H), 6.6 (d, J = 7.0 Hz, 1H), 6.6 (d, J = 9.0 Hz, 1H), 4.1 (d, J = 12.9 Hz, 1H), 4.0 (d, J = 12.9 Hz, 1H), 3.6 – 3.2 (m, 5H), 3.0 (dd, J = 13.6, 9.3 Hz, 1H), 2.8 (t, J = 5.2 Hz, 2H), 2.8 (q, J = 6.7, 5.8
Hz, 2H), 2.6 (dd, \( J = 13.5, 3.5 \) Hz, 1H), 2.3 (s, 3H). **19F NMR** (235 MHz, Chloroform-\( d \)) \( \delta \) -68.3. **13C NMR** (63 MHz, Chloroform-\( d \)) \( \delta \) 159.4, 147.9, 137.6, 134.4, 134.0, 132.5, 128.5, 128.3, 127.6, 126.9 (q, \( J = 290.8 \) Hz), 125.9, 125.8, 125.2, 125.0, 113.2, 107.2, 64.1 (q, \( J = 24.1 \) Hz), 61.4, 53.4 (q, \( J = 2.0 \) Hz), 49.2, 46.1, 42.9. **IR** (ATR, cm\(^{-1}\)) 3058, 3036, 3005, 2978, 2959, 2949, 2918, 2887, 2854, 2834, 2782, 1737, 1594, 1563, 1509, 1479, 1435, 1380, 1363, 1336, 1310, 1258, 1239, 1150, 1126, 1100, 1025, 1014, 978, 951, 916, 878, 837, 771, 729, 712, 614, 550, 445, 403. **HRMS** m/z [M+H]\(^+\) calculated for C\(_{24}\)H\(_{28}\)N\(_4\)F\(_3\): 429.2266, found: 429.2264.

**Synthesis of compound 75**

2-(3,4-dihydroisoquinolin-2(1H)-yl)-3,3,3-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-1-amine

Compound 75 was prepared according to **general procedure A** from 1 (93.2 mg, 0.2 mmol), 1,2,3,4-tetrahydroisoquinoline (37.6 \( \mu \)L, 0.2 mmol, 1 equiv) and N-methyl-1-(naphthalen-1-yl)methanamine (81.5 \( \mu \)L, 0.5 mmol, 2.5 equiv) to afford a colorless oil (84.6 mg, 0.212 mmol, 71% yield). \( R_f = 0.40 \) (hexanes:ethyl acetate= 10:1). **LRMS** (EI, 70 eV): m/z (%): 257(1), 214(3), 185(4), 185(3), 184(47), 142(13), 141(100), 139(3), 117(5), 115(16), 105(3). **1H NMR** (300 MHz, Chloroform-\( d \)) \( \delta \) 8.35 (d, \( J = 8.6 \) Hz, 1H), 7.84 (d, \( J = 8.5 \) Hz, 1H), 7.80 (d, \( J = 8.5 \) Hz, 1H), 7.51 – 7.34 (m, 3H), 7.24 – 7.10 (m, 4H), 7.04 – 6.95 (m, 1H), 4.12 (d, \( J = 12.8 \) Hz, 1H), 4.11 (d, \( J = 14.5 \) Hz, 1H), 3.97 (d, \( J = 14.8 \) Hz, 1H), 3.96 (d, \( J = 12.8 \) Hz, 1H), 3.64 – 3.47 (m, 1H), 3.20 – 2.93 (m, 3H), 2.92 – 2.81 (m, 2H), 2.75 (dd, \( J = 13.5, 3.6 \) Hz, 1H), 2.34 (s, 3H). **19F NMR** (282 MHz, Chloroform-\( d \)) \( \delta \) -67.90 (d, \( J = 8.5 \) Hz). **13C NMR** (75 MHz, Chloroform-\( d \)) \( \delta \) 135.2, 134.6, 133.9, 132.5, 128.3, 128.2, 127.6, 127.2 (q, \( J = 291.4 \) Hz), 126.4, 126.0, 125.8, 125.7, 125.6, 125.1, 63.7 (q, \( J = 23.9 \) Hz), 61.2, 53.8, 51.6, 47.3, 42.8, 30.4. **IR** (ATR, cm\(^{-1}\)) 3047, 3023, 2921, 2819, 1597, 1509, 1499, 1465, 1453, 1392, 1253, 1147, 1100, 1051, 1038, 1018, 933, 883, 859, 829, 793, 776, 739, 716, 702, 550, 520, 431, 414. **HRMS** m/z [M+H]\(^+\) calculated for C\(_{24}\)H\(_{26}\)N\(_2\)F\(_3\): 399.2043, found: 399.2044.
Synthesis of compound 76

2-(3-azabicyclo[3.2.2]nonan-3-yl)-3,3,3-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-1-amine

Compound 76 was prepared according to general procedure A from 1 (140 mg, 0.3 mmol), 3-azabicyclo[3.2.2]nonane (37.6 mg, 0.3 mmol, 1 equiv) and N-methyl-1-(naphthalen-1-yl)methanimine (122 µL, 0.75 mmol, 2.5 equiv) to afford a white solid (64.0 mg, 0.164 mmol, 55% yield). Rf = 0.70 (hexanes:ethyl acetate = 10:1). M.p. = 114-117 °C. LRMS (EI, 70 eV): m/z (%): 206(1), 185(9), 184(62), 142(13), 139(3), 126(2), 115(9), 112(5), 67(4), 55(2). 1H NMR (250 MHz, Chloroform-d) δ 8.40 – 8.29 (m, 1H), 7.93 – 7.73 (m, 2H), 7.60 – 7.37 (m, 4H), 4.05 (d, J = 12.9 Hz, 1H), 3.94 (d, J = 12.9 Hz, 1H), 3.36 (tt, J = 11.3, 5.7 Hz, 1H), 2.97 (dd, J = 13.1, 8.7 Hz, 1H), 2.81 (qd, J = 11.7, 4.2 Hz, 4H), 2.59 (dd, J = 13.2, 3.6 Hz, 1H), 2.33 (s, 3H), 1.81 (s, 2H), 1.67 (d, J = 9.1 Hz, 4H), 1.63 – 1.44 (m, 4H). 19F NMR (235 MHz, Chloroform-d) δ -68.81. 13C NMR (63 MHz, Chloroform-d) δ 134.6, 134.0, 132.7, 129.8 (q, J = 292.0, 291.5 Hz), 128.5, 128.3, 127.7, 125.8, 125.2, 125.1, 64.0 (q, J = 24.2 Hz), 61.8, 59.0, 54.6, 42.3, 31.4, 25.6, 25.5. IR (ATR, cm⁻¹) 3064, 3037, 2996, 2921, 2857, 2827, 2802, 2765, 1509, 1458, 1449, 1402, 1382, 1358, 1344, 1300, 1256, 1173, 1151, 1134, 1102, 1089, 1051, 1011, 964, 882, 869, 859, 839, 793, 774, 708, 681, 614, 583, 552, 522, 464, 415. HRMS m/z [M+H]+ calculated for C23H30N2F3+: 391.2361, found: 391.2363.

Synthesis of compound 77

N,N-diethyl-1,1,1-trifluoro-3-(10H-phenothiazin-10-yl)propan-2-amine

Compound 77 was prepared according to general procedure B from 1 (140 mg, 0.3 mmol), diethylamine (31 µL, 0.3 mmol, 1 equiv), phenothiazine (159 mg, 0.78 mmol, 2.6 equiv), solution of LiHMDS (750 µL, 1 M in THF, 0.75 mmol, 2.5 equiv) and HMPA (132 µL, 0.75 mmol, 2.5 equiv) to afford a white solid (68.9 mg, 0.188 mmol, 62% yield). Rf = 0.67 (hexanes:ethyl acetate = 3:1). M.p. = 65-69 °C. LRMS (EI, 70 eV): m/z (%): 366(7), 293(2), 224(1), 213(15), 212(100), 198(9), 180(41), 179(7), 126(3), 98(3), 77(1), 56(1). 1H NMR (250 MHz, Methanol-d₄) δ 7.23 – 7.03 (m, 4H), 7.00 – 6.84 (m, 4H), 4.21 (dd, J = 14.6, 9.2 Hz, 1H), 4.12 (dd, J = 14.4, 4.4 Hz, 1H), 3.76 (pd, J = 8.8, 4.2 Hz, 1H), 2.61 (qd, J = 6.9, 2.8 Hz, 4H), 0.77 (t, J = 7.1 Hz, 6H). 19F NMR (235 MHz, Methanol-d₄) δ -71.60. 13C NMR (63 MHz, Methanol-d₄) δ 145.1, 127.6, 127.5, 127.4 (q, J = 289.0 Hz), 126.4, 123.0, 58.0 (q, J = 24.9 Hz), 44.6, 43.5 (q, J = 1.8 Hz).

Synthesis of compound 78
1,1,1,3-tetrafluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine

Compound 78 was prepared according to general procedure A from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and cesium fluoride (114 mg, 0.75 mmol, 2.5 equiv) to afford a colorless oil (55.6 mg, 0.195 mmol, 65% yield). R_f = 0.63 (hexanes:ethyl acetate = 10:1). LRMS (EI, 70 eV): m/z (%): 286(2), 285(14), 284(2), 252(2), 216(2), 168(2), 158(4), 142(17), 141(100), 140(2), 139(7), 127(2), 126(2), 116(2), 115(18), 89(2). ¹H NMR (250 MHz, Chloroform-d) 8.31 – 8.18 (m, 1H), 7.97 – 7.79 (m, 2H), 7.64 – 7.46 (m, 3H), 7.52 – 7.39 (m, 1H), 4.92 – 4.73 (m, 1H), 4.74 – 4.54 (m, 1H), 4.35 (s, 2H), 3.61 (dqdd, J = 17.3, 8.6, 6.8, 4.9 Hz, 1H), 2.57 (s, 3H). ¹⁹F NMR (235 MHz, Chloroform-d) δ = -67.89 (t, J = 7.7 Hz, 3F), -229.51 (tdq, J = 46.1, 17.8, 6.5 Hz, 1F). ¹³C NMR (63 MHz, Chloroform-d) δ 134.1, 133.6, 132.4, 128.7, 127.7, 126.1, 126.1 (qd, J = 289.2, 10.0 Hz), 125.9, 125.3, 124.5, 79.5 (qd, J = 174.7, 2.3 Hz), 62.5 (qd, J = 26.0, 20.8 Hz), 58.9, 37.5. IR (ATR, cm⁻¹) 3048, 2962, 2897, 2864, 2817, 1598, 1510, 1463, 1397, 1374, 1316, 1272, 1249, 1160, 1112, 1054, 1018, 852, 791, 774, 734, 708, 614, 586, 564, 544, 532, 519, 444, 415. HRMS m/z [M+H]^+ calculated for C₁₅H₁₆NF₄+: 286.1219, found: 286.1219.

Synthesis of compound 79
3-chloro-1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine

Compound 79 was prepared according to general procedure A from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and tetrabutylammonium chloride (215 mg, 0.75 mmol, 2.5 equiv) to afford a colorless oil (72.3 mg, 0.239 mmol, 80% yield). R_f = 0.68 (hexanes:ethyl acetate = 10:1). LRMS (EI, 70 eV): m/z (%): 303(3), 301(10), 252(4), 232(3), 142(16), 141(100), 139(7), 115(17). ¹H NMR (250 MHz, Chloroform-d) 8.28 (dd, J = 7.2, 1.8 Hz, 1H), 7.92 (dt, J = 6.4, 2.5 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.58 (qd, J = 4.3, 1.9 Hz, 2H), 7.52 (d, J = 5.5 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H), 4.42 (dd, J = 13.5, 2.8 Hz, 2H), 3.91 – 3.70 (m, 2H), 3.63 (pd, J = 8.1, 4.6 Hz, 1H), 2.53 (s, 3H). ¹⁹F NMR (235 MHz, Chloroform-d) δ = -68.17. ¹³C NMR (63 MHz, Chloroform-d) δ 134.0, 133.7, 132.3, 128.6, 128.5, 127.6, 126.0, 125.9, 125.4 (d,
\[ J = 290.8 \text{ Hz}, \ 125.3, \ 124.6, \ 65.2 \ (q, \ J = 25.9 \text{ Hz}), \ 58.6, \ 39.2 \ (d, \ J = 2.0 \text{ Hz}), \ 36.1. \ \textbf{IR} \ (\text{ATR}, \ \text{cm}^{-1}) \ 3048, \ 2945, \ 2863, \ 2816, \ 1598, \ 1510, \ 1448, \ 1374, \ 1337, \ 1256, \ 1171, \ 1137, \ 1105, \ 1083, \ 1017, \ 970, \ 940, \ 784, \ 770, \ 733, \ 688, \ 649, \ 576, \ 542, \ 519, \ 415. \ \textbf{IR} \ (\text{ATR}, \ \text{cm}^{-1}) \ 3048, \ 2945, \ 2863, \ 2816, \ 1598, \ 1510, \ 1477, \ 1448, \ 1374, \ 1337, \ 1256, \ 1171, \ 1137, \ 1105, \ 1083, \ 1017, \ 970, \ 940, \ 784, \ 770, \ 733, \ 688, \ 649, \ 576, \ 542, \ 519, \ 415. \ \textbf{HRMS} \ m/z \ [\text{M+H}]^{+} \ \text{calculated} \ \text{for} \ C_{15}H_{16}N^{37}\text{ClF}_{3}^{+} : 304.0894, \ \text{found}: 304.0893.

\textit{Synthesis of compound 80}

3-bromo-1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine

Compound 80 was prepared according to \textit{general procedure A} from 1 (140 mg, 0.3 mmol), \( N \)-methyl-1-(naphthalen-1-yl) methanamine (51.4 mg, 0.3 mmol, 1 equiv) and tetrabutylammonium bromide (244 mg, 0.75 mmol, 2.5 equiv) to afford a colorless oil (74.1 mg, 0.214 mmol, 71% yield). \( R_f = 0.75 \) (hexanes:ethyl acetate= 10:1). \textbf{LRMS} (EI, 70 eV): \( m/z \ (%) : \ 347(4), \ 345(4), \ 278(4), \ 276(4), \ 252(3), \ 218(1), \ 168(2), \ 142(16), \ 141(100), \ 139(8), \ 127(2), \ 126(2), \ 116(2), \ 115(17), \ 89(1), \ 63(1). \ \textbf{1H NMR} \ (250 MHz, \text{Chloroform-}d) \ 8.35 – 8.21 \ (m, 1H), \ 7.97 – 7.79 \ (m, 2H), \ 7.69 – 7.30 \ (m, 4H), \ 4.42 \ (dd, \ J = 13.5, 3.9 \text{ Hz, 2H}), \ 3.79 – 3.61 \ (m, 1H), \ 3.67 – 3.54 \ (m, 2H), \ 2.55 – 2.47 \ (m, 3H). \ \textbf{19F NMR} \ (235 MHz, \text{Chloroform-}d) \ \delta -67.98. \ \textbf{13C NMR} \ (63 MHz, \text{Chloroform-}d) \ \delta 134.0, \ 133.6, \ 132.3, \ 128.6, \ 128.5, \ 127.6, \ 126.0, \ 125.9, \ 125.4 \ (d, \ J = 291.7 \text{ Hz}), \ 125.3, \ 124.7, \ 65.2 \ (q, \ J = 25.8 \text{ Hz}), \ 58.3, \ 35.9, \ 25.9 \ (q, \ J = 1.7 \text{ Hz}). \ \textbf{IR} \ (\text{ATR}, \ \text{cm}^{-1}) \ 3048, \ 2979, \ 2944, \ 2860, \ 2813, \ 1598, \ 1510, \ 1453, \ 1373, \ 1326, \ 1249, \ 1167, \ 1102, \ 1075, \ 1008, \ 968, \ 913, \ 858, \ 844, \ 791, \ 780, \ 771, \ 732, \ 658, \ 641, \ 573, \ 539, \ 518, \ 415. \ \textbf{HRMS} \ m/z \ [\text{M+H}]^{+} \ \text{calculated} \ \text{for} \ C_{15}H_{16}N^{81}\text{BrF}_{3}^{+} : 348.0398, \ \text{found}: 348.0401.

\textit{Synthesis of compound 81}

1,1,1-trifluoro-3-iodo-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine

Compound 81 was prepared according to \textit{general procedure A} from 1 (140 mg, 0.3 mmol), \( N \)-methyl-1-(naphthalen-1-yl) methanamine (51.4 mg, 0.3 mmol, 1 equiv) and sodium iodide (114 mg, 0.75 mmol, 2.5 equiv) to afford a colorless oil (91.8 mg, 0.234 mmol, 78% yield). \( R_f = 0.77 \) (hexanes:ethyl acetate= 10:1). \textbf{LRMS} (EI, 70 eV): \( m/z \ (%) : \ 393(5), \ 324(11), \ 252(5), \ 223(1), \ 196(1), \ 168(4), \ 142(14), \ 141(100), \ 139(8), \ 115(19), \ 98(2), \ 77(1). \ \textbf{1H NMR} \ (250 MHz, \text{Acetone-}d_{6}) \ 8.36 – 8.25 \ (m, 1H), \ 7.98 – 7.80 \ (m, 2H), \ 7.64 \ (d, \ J = 7.0 \text{ Hz, 1H}), \ 7.61 – 7.40 \ (m, 3H), \ 4.45 \ (s, 2H), \ 3.81 \ (td, \ J = 8.1, \ 6.1 \text{ Hz, 1H}), \ 3.65 – 3.45 \ (m, 2H), \ 2.43 \ (t, \ J = 1.8 \text{ Hz, 3H}). \ \textbf{19F NMR} \ (235 MHz, \text{Acetone-}d_{6}) \ \delta -68.19. \ \textbf{13C NMR} \ (63 MHz, \text{Acetone-}d_{6}) \ \delta 134.9, \ 134.8, \ 133.1, \ 129.2, \ 129.0, \ 128.1, \ 126.6, \ 126.5, \ 126.1 \ (q, \ J = 292.6 \text{ Hz}), \ 126.0, \ 125.8, \ 66.3 \ (q, \ J = 25.4 \text{ Hz}), \ 58.3 \ (d, \ J = 1.4 \text{ Hz}), 82
35.6, -2.8. **IR** (ATR, cm$^{-1}$) 3047, 2979, 2841, 2810, 1598, 1510, 1463, 1452, 1373, 1319, 1246, 1160, 1102, 1018, 1000, 888, 855, 837, 791, 777, 732, 710, 621, 605, 570, 537, 518, 414. **HRMS** m/z [M+H]$^+$ calculated for C$_{15}$H$_{16}$NIF$_3$: 394.0280, found: 394.0280.

**Synthesis of compound 82**
3-azido-1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine

Compound 82 was prepared according to **general procedure A** from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl) methanamine (51.4 mg, 0.3 mmol, 1 equiv) and sodium azide (48.8 mg, 0.75 mmol, 2.5 equiv) to afford a white crystalline solid (73.7 mg, 0.239 mmol, 80% yield). **Rf** = 0.65 (hexanes:ethyl acetate= 10:1). **M.p.** = 79-80 °C. **LRMS** (EI, 70 eV): m/z (%): 308(1), 280(1), 253(3), 252(17), 169(2), 168(4), 142(13), 141(100), 139(7), 116(2), 115(17). **$^1$H NMR** (250 MHz, Chloroform-d) δ 8.26 (d, $J$ = 8.0 Hz, 1H), 7.91 (dd, $J$ = 7.5, 1.9 Hz, 1H), 7.86 (dd, $J$ = 13.2 Hz, 1H), 4.43 (d, $J$ = 13.2 Hz, 1H), 3.61 (dd, $J$ = 12.6, 9.6 Hz, 1H), 3.31 (dd, $J$ = 12.6, 3.6 Hz, 1H), 2.55 (s, 3H).

**19F NMR** (235 MHz, Chloroform-d) δ -67.45. **$^{13}$C NMR** (63 MHz, Chloroform-d) δ 134.4, 133.6, 132.7, 129.0, 128.9, 128.2, 126.4, 126.3, 126.0 (q, $J$ = 290.4 Hz), 125.6, 124.7, 62.8 (q, $J$ = 25.1 Hz), 59.0, 47.4 (q, $J$ = 2.1 Hz), 36.3. **IR** (ATR, cm$^{-1}$) 3061, 3037, 3000, 2975, 2942, 2917, 2877, 2856, 2806, 2169, 2106, 1597, 1509, 1479, 1455, 1394, 1377, 1320, 1290, 1248, 1198, 1177, 1157, 1112, 1071, 1051, 1031, 973, 951, 915, 845, 810, 793, 776, 722, 712, 649, 583, 542, 440, 421. **HRMS** m/z [M+H]$^+$ calculated for C$_{15}$H$_{16}$N$_4$F$_3$: 309.1327, found: 309.1326.

**Synthesis of compound 83**
4,4,4-trifluoro-3-(methyl(naphthalen-1-ylmethyl)amino)butanenitrile

Compound 83 was prepared according to **general procedure A** from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl) methanamine (51.4 mg, 0.3 mmol, 1 equiv) and potassium cyanide (48.8 mg, 0.75 mmol, 2.5 equiv) to afford an off white solid (71.9 mg, 0.248 mmol, 83% yield). **Rf** = 0.23 (hexanes:ethyl acetate= 10:1). **M.p.** = 50-54 °C. **LRMS** (EI, 70 eV): m/z (%): 293(5), 292(26), 291(2), 252(3), 223(1), 168(2), 142(21), 141(100), 139(8), 115(21), 54(3). **$^1$H NMR** (250 MHz, Chloroform-d) δ 8.3 – 8.1 (m, 1H), 8.0 – 7.8 (m, 2H), 7.7 – 7.4 (m, 4H), 4.4 (d, $J$ = 2.9 Hz, 2H), 3.7 (dq, $J$ = 10.1, 7.7, 4.9 Hz, 1H), 2.8 (dd, $J$ = 17.1, 10.1 Hz, 1H), 2.6 (dd, $J$ = 17.1, 4.9 Hz, 1H), 2.5 (q, $J$ = 1.8 Hz, 3H). **$^{19}$F NMR** (235 MHz, Chloroform-d) δ -69.2. **$^{13}$C NMR** (63 MHz, Chloroform-d) δ 134.0, 132.7, 132.2, 128.8, 128.6, 127.7, 126.3, 126.1, 125.9 (q, $J$ = 290.9 Hz), 83
125.3, 124.4, 116.4, 59.6 (q, \( J = 27.3 \) Hz), 58.2 (d, \( J = 1.5 \) Hz), 36.0 (d, \( J = 1.4 \) Hz), 16.1 (q, \( J = 2.3 \) Hz). \( \text{IR} \) (ATR, \( \text{cm}^{-1} \)) 3088, 3054, 3002, 2968, 2941, 2915, 2893, 2851, 2810, 2254, 1598, 1510, 1465, 1438, 1419, 1390, 1368, 1356, 1303, 1285, 1259, 1241, 1191, 1171, 1150, 1110, 1065, 1051, 1012, 968, 946, 844, 804, 783, 774, 737, 720, 703, 608, 546, 421. \( \text{HRMS} \) m/z [M+H]^+ calculated for \( \text{C}_{16}\text{H}_{14}\text{N}_{2}\text{F}_{3}^+ \): 291.1109, found: 291.1110.

**Synthesis of compound 84**

\( \text{N-}(4\text{-methoxybenzyl})-\text{N-}(1,1,1,3\text{-tetrafluoropropan-2-yl})\text{prop-2-en-1-amine} \)

Compound 84 was prepared according to \textit{general procedure A} from \( \mathbf{1} \) (140 mg, 0.3 mmol), \( \text{N-}(4\text{-methoxybenzyl})\text{prop-2-en-1-amine} \) (53.2 mg, 0.3 mmol, 1 equiv) and cesium fluoride (114 g, 0.75 mmol, 2.5 equiv) to afford a colorless oil (64.1 mg, 0.220 mmol, 73% yield). \( \mathbf{R_f} = 0.60 \) (hexanes:ethyl acetate= 10:1). \( \text{LRMS} \) (EI, 70 eV): m/z (%): 291(2), 222(1), 183(1), 170(1), 148(7), 122(17), 121(100), 121(68), 110(4), 91(8), 90(3), 89(5), 78(12), 77(12), 65(3), 52(2), 51(3). \( \text{HRMS m/z [M+H]^+ calculated for C}_{16}\text{H}_{14}\text{N}_{2}\text{F}_{3}^+ \): 292.1325, found: 292.1319.

**Synthesis of compound 85**

\( \text{1-}(\text{pyridin-2-yl})-4-(1,1,1,3\text{-tetrafluoropropan-2-yl})\text{piperazine} \)

Compound 85 was prepared according to \textit{general procedure A} from with \( \mathbf{1} \) (140 mg, 0.3 mmol), \( \text{N-benzylpiperazine} \) (49.0 mg, 0.3 mmol, 1 equiv) and cesium fluoride (114 g, 0.75 mmol, 2.5 equiv) to afford a white solid (53.2 mg, 0.192 mmol, 64% yield). \( \mathbf{R_f} = 0.60 \) (hexanes:ethyl acetate= 7:3). \( \text{M.p.}= 44\text{--}47 \degree \text{C} \). \( \text{LRMS} \) (EI, 70 eV): m/z (%): 277(10), 208(1), 133(13), 121(6), 120(7), 119(13), 110(6), 108(7), 107(100), 79(22), 78(17), 74(5), 56(6), 52(4), 51(6). \( \text{HRMS m/z [M+H]^+ calculated for C}_{14}\text{H}_{18}\text{NOF}_{4}^+ \): 292.1325, found: 292.1319.
1H), 2.9 (p, J = 6.3, 5.3 Hz, 4H). $^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -68.3 (d, J = 6.8 Hz, 3F), -228.8 (q, J = 6.8 Hz, 1F). $^{13}$C NMR (63 MHz, Chloroform-d) $\delta$ 159.43, 147.97, 137.66, 125.51 (qd, J = 288.1, 9.7 Hz), 113.54, 107.23, 80.53 (qd, J = 175.1, 2.3 Hz), 65.40 (qd, J = 26.2, 20.6 Hz), 50.08, 46.07. IR (ATR, cm$^{-1}$) 3097, 3060, 2999, 2961, 2917, 2895, 2843, 2768, 2710, 2649, 1598, 1560, 1483, 1439, 1385, 1364, 1340, 1316, 1302, 1282, 1245, 1231, 1205, 1154, 1112, 1097, 1015, 997, 980, 963, 940, 924, 851, 771, 717, 702, 622, 605, 569, 520, 495, 458. HRMS m/z [M+H]$^+$ calculated for C$_{12}$H$_{16}$N$_3$F$_4$: 278.1280, found: 278.1281.

Synthesis of compound 86

3-(benzyloxy)-1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine

Compound 86 was prepared according to general procedure C from 1 (93.2 mg, 0.2 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (34.2 mg, 0.2 mmol, 1 equiv), benzyl alcohol (52 µL, 0.5 mmol, 2.5 equiv) and sodium hydride (20 mg, 60 w% in oil, 0.5 mmol, 2.5 equiv) to afford a colorless oil (37.2 mg, 0.0996 mmol, 50% yield). $R_f$ = 0.50 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 267(4), 252(2), 232(1), 171(7), 170(3), 156(3), 142(15), 141(100), 139(3), 126(5), 115(11), 91(13), 65(2). $^1$H NMR (250 MHz, Chloroform-d) 8.28 (dd, J = 6.4, 2.7 Hz, 1H), 7.97 – 7.75 (m, 2H), 7.62 – 7.28 (m, 9H), 4.55 (s, 2H), 4.37 (s, 2H), 3.79 (dd, J = 10.3, 4.3 Hz, 1H), 3.64 (ddq, J = 12.6, 8.5, 4.2 Hz, 1H), 2.51 (s, 3H). $^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -68.13. $^{13}$C NMR (63 MHz, Chloroform-d) $\delta$ 137.9, 134.3, 134.1, 132.5, 128.6, 128.3, 127.9, 127.7, 127.6, 126.7 (q, J = 289.1, 288.7 Hz), 126.0, 125.8, 125.3, 124.7, 73.5, 66.1 (q, J = 1.8 Hz), 63.2 (q, J = 25.4 Hz), 58.9, 37.3. IR (ATR, cm$^{-1}$) 3064, 3036, 2942, 2863, 2809, 1714, 1598, 1510, 1455, 1367, 1313, 1249, 1209, 1160, 1105, 1072, 1029, 907, 849, 791, 774, 730, 696, 649, 625, 587, 544, 461, 417. HRMS m/z [M+H]$^+$ calculated for C$_{22}$H$_{28}$NO$_3$F$_3$: 374.1732, found: 374.1732.
Synthesis of compound 87
3-(4-bromophenoxy)-1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine

Compound 87 was prepared according to general procedure C from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv), 4-bromo-phenol (130 mg, 0.75 mmol, 2.5 equiv) and sodium hydride (30 mg, 60 w% in oil, 0.75 mmol, 2.5 equiv) to afford a colorless oil (114 mg, 0.261 mmol, 87% yield). Rf = 0.68 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 440(1), 439(3), 437(2), 253(3), 252(20), 207(1), 185(1), 168(2), 155(3), 142(13), 142(6), 141(100), 139(5), 115(10), 115(5), 63(1). 1H NMR (250 MHz, Chloroform-d) 8.31 (dd, J = 6.0, 3.4 Hz, 1H), 8.00 – 7.81 (m, 2H), 7.67 – 7.43 (m, 4H), 7.40 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 8.7 Hz, 2H), 4.42 (d, J = 3.0 Hz, 2H), 4.54 – 4.08 (m, 2H), 3.92 – 3.66 (m, 1H), 2.61 (s, 3H).

19F NMR (235 MHz, Chloroform-d) δ -67.62. 13C NMR (63 MHz, Chloroform-d) δ 157.2, 134.1, 133.8, 132.4, 128.6, 127.8, 126.5 (q, J = 289.7, 286.6, 288.5 Hz), 126.0, 125.9, 125.3, 124.7, 116.4, 113.7, 64.1 (q, J = 1.6 Hz), 61.9 (q, J = 25.7 Hz), 59.0, 37.1. IR (ATR, cm⁻¹) 3061, 3048, 3007, 2948, 2917, 2891, 2867, 2813, 2793, 1592, 1578, 1489, 1469, 1446, 1395, 1382, 1374, 1272, 1235, 1215, 1166, 1126, 1100, 1071, 1054, 1036, 1024, 1001, 892, 821, 803, 790, 776, 739, 710, 654, 641, 625, 607, 518, 503, 476, 442, 428.

HRMS m/z [M+H]+ calculated for C₂₁H₂₀NOBrF₃+: 438.0680, found: 438.0680.

Synthesis of compound 88
3,3,3-trifluoro-2-(methyl(naphthalen-1-ylmethyl)amino)propyl benzoate

Compound 88 was prepared according to general procedure A from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and sodium benzoate (108 mg, 0.75 mmol, 2.5 equiv) to afford a white solid (91.7 mg, 0.237 mmol, 79% yield). Rf = 0.49 (hexanes:ethyl acetate= 10:1). M.p. = 94-96 °C. LRMS (EI, 70 eV): m/z (%): 440(1), 439(3), 437(2), 253(3), 252(20), 207(1), 185(1), 168(2), 155(3), 142(13), 142(6), 141(100), 139(5), 115(10), 115(5), 63(1). 1H NMR (250 MHz, Chloroform-d) 8.16 (d, J = 8.4 Hz, 1H), 8.00 – 7.89 (m, 2H), 7.84 (t, J = 8.3 Hz, 2H), 7.61 (t, J = 7.3 Hz, 1H), 7.54 – 7.37 (m, 5H), 7.31 (t, J = 7.6 Hz, 1H), 4.74 (dd, J = 11.7, 8.6 Hz, 1H), 4.53 (dd, J = 11.8, 4.5 Hz, 1H), 4.38 (s, 2H), 3.80 (ddq, J = 13.1, 8.5, 4.8, 4.2 Hz, 1H), 2.62 (s, 3H). 19F NMR (235 MHz, Chloroform-d) δ -67.16. 13C NMR (63 MHz, Chloroform-d) δ 166.1, 134.0, 133.6, 133.2, 132.4, 129.8, 129.7, 128.5, 128.5, 127.7, 126.1, 125.8, 125.2, 124.3, 124.3 (q, J = 291.0, 290.5 Hz), 61.7 (q, J = 25.5 Hz), 59.8 (d, J
Synthesis of compound 89
3-(cyclohexylthio)-1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine
Compound 89 was prepared according to general procedure A from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv), cyclohexanethiol (92 µL, 0.75 mmol, 2.5 equiv) to afford a colorless oil (89.3 mg, 0.234 mmol, 78% yield). Rf = 0.63 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 381(1), 267(2), 253(2), 252(11), 171(3), 170(16), 168(2), 142(16), 141(100), 139(3), 115(11), 83(2), 55(4), 55(2). 1H NMR (250 MHz, Chloroform-d) δ 8.31 (d, J = 7.9 Hz, 1H), 7.95 – 7.77 (m, 2H), 7.65 – 7.40 (m, 4H), 4.43 (d, J = 13.8 Hz, 1H), 4.36 (d, J = 13.7 Hz, 1H), 3.50 (ddh, J = 16.3, 8.2, 4.2 Hz, 1H), 2.98 (dd, J = 13.5, 10.3 Hz, 1H), 2.82 (dd, J = 13.5, 4.0 Hz, 1H), 2.82 (dd, J = 13.5, 4.0 Hz, 1H), 2.82 (dd, J = 13.5, 4.0 Hz, 1H), 2.82 (dd, J = 13.5, 4.0 Hz, 1H), 2.82 (dd, J = 13.5, 4.0 Hz, 1H), 2.82 (dd, J = 13.5, 4.0 Hz, 1H), 2.82 (dd, J = 13.5, 4.0 Hz, 1H), 2.82 (dd, J = 13.5, 4.0 Hz, 1H), 2.82 (dd, J = 13.5, 4.0 Hz, 1H), 2.82 (dd, J = 13.5, 4.0 Hz, 1H), 2.82 (dd, J = 13.5, 4.0 Hz, 1H). 19F NMR (235 MHz, Chloroform-d) δ -68.07. 13C NMR (63 MHz, Chloroform-d) δ 134.1, 134.0, 132.5, 128.5, 128.3, 127.6, 125.9, 125.8, 125.3, 124.9, 124.9 (q, J = 292.2 Hz), 63.9 (q, J = 24.8 Hz), 58.4, 43.9, 36.0, 33.4, 33.4, 27.0, 26.1, 26.0, 25.9. IR (ATR, cm⁻¹) 3047, 2928, 2853, 2832, 2810, 1598, 1510, 1448, 1373, 1327, 1252, 1163, 1102, 1080, 1001, 968, 907, 886, 856, 791, 773, 732, 689, 649, 574, 540, 519, 415. HRMS m/z [M+H]+ calculated for C22H21N2O2F3+: 388.1524, found: 388.1527.

Synthesis of compound 90
3-([(4-chlorophenyl)thio]-1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine
Compound 90 was prepared according to general procedure A from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv), 4-chlorotioiphenol (108 mg, 0.75 mmol, 2.5 equiv) to afford a white solid (83.0 mg, 0.203 mmol, 68% yield). Rf = 0.68 (hexanes:ethyl acetate= 10:1). M.p. = 71-73 °C. LRMS (EI, 70 eV): m/z (%): 141(100), 252(26), 142(15), 115(14), 253(4), 139(4), 409(2), 168(2), 108(2), 170(2), 157(2). 1H NMR (250 MHz, Chloroform-d) δ 8.28 (d, J = 7.5 Hz, 1H), 8.00 – 7.80 (m, 2H), 7.68 – 7.40 (m, 5H), 7.20 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 4.39 (td, J = 13.5, 6.5 Hz, 2H), 3.52 (tt, J = 12.9, 6.4 Hz, 1H), 3.27 (dd, J = 13.6, 9.6 Hz, 1H), 3.17 (dd, J = 13.5, 7.3 Hz, 1H), 2.56 (s, 3H). 19F NMR (235 MHz, Chloroform-d) δ -67.35. 13C NMR (63 MHz,
Chloroform-$d$ $\delta$ 134.2, 134.0, 133.5, 132.5, 132.4, 130.8, 129.2, 128.6, 128.4, 127.7, 126.0, 125.8, 125.3, 124.8, 124.7 (q, $J = 292.8, 292.3$ Hz), 62.0 (q, $J = 25.1$ Hz), 58.2, 36.1, 31.8 (q, $J = 1.0$ Hz).

IR (ATR, cm$^{-1}$) 3068, 3047, 3010, 3000, 2959, 2935, 2919, 2870, 2856, 2805, 1509, 1473, 1387, 1364, 1327, 1296, 1255, 1226, 1171, 1154, 1123, 1102, 1090, 1073, 1012, 966, 864, 852, 827, 817, 804, 787, 771, 742, 716, 691, 587, 540, 496, 420. HRMS m/z [M+H]$^+$ calculated for C$_{21}$H$_{20}$NF$_3$SCl$^+$: 410.0957, found: 410.0964.

**Synthesis of compound 91**

3-(benzo[d]thiazol-2-ylthio)-1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine

Compound 91 was prepared according to general general procedure A from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and 2-mercaptobenzthiazole (125 mg, 0.75 mmol, 2.5 equiv) to afford a pale yellow solid (106 mg, 0.245 mmol, 82% yield). $R_f$ = 0.55 (hexanes:ethyl acetate= 10:1). $\text{M.p.}= 82$–85 °C. LRMS (EI, 70 eV): m/z (%): 432(2), 291(4), 284(4), 266(3), 265(17), 264(8), 196(8), 170(3), 169(9), 168(33), 167(7), 154(2), 149(4), 142(12), 141(100), 139(4), 136(4), 116(2), 115(15), 108(2).

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 8.27–8.16 (m, 1H), 7.92–7.68 (m, 4H), 7.63–7.38 (m, 4H), 7.44–7.22 (m, 2H), 4.42 (d, $J = 13.2$ Hz, 1H), 4.36 (d, $J = 13.6$ Hz, 1H), 4.03–3.80 (m, 2H), 3.64 (dd, $J = 13.8, 11.1$ Hz, 1H), 2.57 (t, $J = 2.0$ Hz, 3H). $^{19}$F NMR (235 MHz, Chloroform-$d$) $\delta$ -67.14. $^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 166.0, 153.1 (d, $J = 292.9$ Hz), 135.3, 133.9, 133.4, 132.3, 128.5, 128.4, 127.6, 127.0 (q, $J = 292.9$ Hz), 126.0, 125.9, 125.8, 125.1, 124.7, 124.3, 121.6, 121.0, 61.7 (q, $J = 25.5$ Hz), 58.2, 35.9, 30.6 (q, $J = 1.8$ Hz).

IR (ATR, cm$^{-1}$) 3091, 3051, 3040, 2997, 2968, 2932, 2912, 2857, 2810, 1509, 1458, 1428, 1388, 1363, 1351, 1330, 1309, 1302, 1251, 1164, 1122, 1103, 1069, 1049, 1018, 995, 907, 864, 851, 804, 784, 773, 757, 729, 703, 691, 672, 649, 603, 586, 540, 428, 420. HRMS m/z [M+H]$^+$ calculated for C$_{22}$H$_{20}$N$_2$F$_3$S$_2$+: 433.1020, found: 433.1016.
Synthesis of compound 92
1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)-3-(phenylsulfonyl)propan-2-amine

Compound 92 was prepared according to general procedure A from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and sodium benzenesulfinate (126 mg, 0.75 mmol, 2.5 equiv) to afford a colorless oil (70.7 mg, 0.174 mmol, 58% yield). Rf = 0.65 (ethyl acetate). 1H NMR (250 MHz, Chloroform-d) δ 8.28 – 8.10 (m, 1H), 7.94 – 7.77 (m, 2H), 7.73 – 7.36 (m, 9H), 4.42 – 4.18 (m, 3H), 3.90 – 3.74 (m, 1H), 3.73 – 3.42 (m, 1H), 2.56 – 2.29 (m, 3H). 19F NMR (235 MHz, Chloroform-d) δ -67.74, -67.79. 13C NMR (63 MHz, Chloroform-d) δ 144.1, 143.9, 143.0, 133.7, 133.6, 132.5, 132.4, 132.3, 129.2, 129.2, 128.6, 128.5, 127.6, 127.6, 126.0, 126.0, 125.9, 125.8, 125.4, 125.3, 124.6, 124.6, 123.7 (q, J = 290.0, 289.5 Hz), 63.3 (q, J = 26.5, 26.0 Hz), 62.2 (q, J = 26.3, 26.2, 25.8 Hz), 58.7, 36.8, 36.4. IR (ATR, cm⁻¹) 3058, 2952, 2888, 2863, 2815, 1714, 1477, 1462, 1445, 1371, 1312, 1297, 1249, 1157, 1109, 1052, 1034, 968, 855, 791, 776, 753, 732, 689, 611, 587, 559, 440. HRMS m/z [M+H]+ calculated for C21H21NO2F3S+: 408.1245, found: 408.1241.

Synthesis of compound 93
3-(diphenylphosphanyl)-1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine

Compound 93 was prepared according to general procedure A from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and diphenylphosphane (53.3 uL, 0.75 mmol, 2.5 equiv), under argon atmosphere to afford a colorless oil (77.7 mg, 0.172 mmol, 57% yield). Rf = 0.53 (hexanes:ethyl acetate= 10:1). LRMS (EI, 70 eV): m/z (%): 452(1), 451(5), 408(1), 382(1), 312(12), 310(6), 281(3), 264(1), 236(3), 199(9), 187(9), 186(100), 185(6), 183(21), 171(8), 170(53), 168(8), 142(7), 141(37), 141(36), 121(24), 115(21), 109(6), 108(43), 91(5). 1H NMR (250 MHz, Chloroform-d) δ 8.22 (d, J = 7.9 Hz, 1H), 7.86 (dd, J = 23.7, 7.9 Hz, 2H), 7.65 – 7.48 (m, 3H), 7.39 (dt, J = 22.4, 7.9 Hz, 11H), 4.37 (q, J = 13.8 Hz, 2H), 3.42 (td, J = 14.3, 12.7, 5.3 Hz, 1H), 2.73 – 2.53 (m, 2H), 2.50 (s, 3H). 19F NMR (235 MHz, Chloroform-d) δ -67.93 (d, J = 5.8 Hz). 31P NMR (101 MHz, Chloroform-d) δ -22.55 (q, J = 5.8 Hz). 13C NMR (63 MHz, Chloroform-d) δ 138.9 (d, J = 13.8 Hz), 137.0 (d, J = 15.1 Hz), 134.0, 133.4, 133.4, 133.0, 132.6, 132.3, 129.9 (qd, J = 293.8, 9.5 Hz), 129.2, 128.8, 128.7, 128.6, 128.6, 128.5, 128.2, 127.5 (d, J = 1.6 Hz), 126.1, 125.7, 125.3, 124.5 (d, J = 2.3 Hz), 61.3 (qd, J = 25.6, 14.9 Hz), 57.8, 36.2, 26.6 (d, J = 14.4 Hz). IR (ATR, cm⁻¹...
1) 3068, 3053, 3014, 3000, 2953, 2924, 2854, 2807, 1952, 1884, 1812, 1738, 1726, 1597, 1587, 1510, 1480, 1434, 1374, 1256, 1226, 1157, 1100, 1069, 1025, 998, 907, 889, 845, 793, 780, 734, 693, 580, 540, 503, 476, 415. **HRMS** m/z [M+H]⁺ calculated for C_{27}H_{26}NF_{3}P⁺: 452.1755, found: 452.1757.

**Synthesis of compound 94**

Di(adamantan-1-yl)(3,3,3-trifluoro-2-(methyl(naphthalen-1-ylmethyl)amino)propyl)phosphonium trifluoromethanesulfonate

Compound 94 was prepared according to **general procedure A** from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) and di(adamantan-1-yl)phosphane (90.7 mg, 0.75 mmol, 2.5 equiv), under argon atmosphere to afford a white solid (140 mg, 0.195 mmol, 65% yield). **Rf** = 0.73 (hexanes:diisopropyl ether= 10:1). **M.p.** = 210-214 °C. **¹H NMR** (250 MHz, Methylene Chloride-d$_2$) δ 8.30 – 7.84 (m, 3H), 7.85 – 7.24 (m, 4H), 4.75 (bs, 1H), 4.64 – 4.32 (m, 1H), 4.32 – 3.89 (m, 1H), 3.37 (d, J = 26.2 Hz, 2H), 2.88 (s, 1H), 2.76 (s, 3H), 2.41 – 1.33 (m, 24H), 1.09 (s, 6H). **¹³C NMR** (63 MHz, Methylene Chloride-d$_2$) δ 134.8, 128.6 (qd, J = 292.4, 14.7 Hz), 118.8 (q, J = 321.2 Hz), 65.9, 57.7, 56.2 (qd, J = 26.9, 5.2 Hz), 37.8 (d, J = 40.9 Hz), 37.4 (h, J = 17.0, 17.0, 15.9, 15.7, 14.9 Hz), 35.3 (d, J = 19.6 Hz), 27.7 (d, J = 18.8 Hz), 27.5 (d, J = 18.4 Hz), 22.9, 15.4, 11.0, 10.2. **IR** (ATR, cm⁻¹) 3067, 3050, 3040, 3007, 2913, 2856, 2817, 2413, 1745, 1716, 1452, 1347, 1304, 1269, 1249, 1221, 1166, 1140, 1107, 1046, 1027, 1002, 966, 943, 878, 844, 811, 803, 793, 781, 751, 634, 571, 516, 482, 448, 418. **HRMS** m/z [M+H]⁺ calculated for C_{35}H_{46}NOF_{3}P⁺: 568.3320, found: 568.3309.

**Synthesis of compound 95**

Diethyl 2-(3,3,3-trifluoro-2-(methyl(naphthalen-1-ylmethyl)amino)propyl)malonate

Compound 95 was prepared according to **general procedure A** with 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv), diethyl malonate (114 uL, 0.75 mmol, 2.5 equiv) and sodium hydride (30 mg, 60 w% in oil, 0.75 mmol, 2.5 equiv) to afford a colorless oil (82.1 mg, 0.193 mmol, 64% yield). **Rf** = 0.33 (hexanes:ethyl acetate= 10:1). **LRMS** (EI, 70 eV): m/z (%): 425(1), 380(1), 357(3), 356(12), 284(2), 192(3), 173(2), 171(5), 170(34), 168(2), 142(14), 141(100), 139(4), 115(11). **¹H NMR** (250
MHz, Chloroform-\(d\) \(\delta\) 8.08 (d, \(J = 8.0\) Hz, 1H), 7.93 – 7.71 (m, 2H), 7.63 – 7.37 (m, 4H), 4.36 (d, \(J = 13.3\) Hz, 1H), 4.24 (d, \(J = 13.5\) Hz, 1H), 4.15 (q, \(J = 7.1\) Hz, 2H), 4.01 (dq, \(J = 10.8\), 7.1 Hz, 1H), 3.83 (dq, \(J = 10.8\), 7.1 Hz, 1H), 3.52 (dd, \(J = 9.1\), 5.1 Hz, 1H), 3.50 – 3.29 (m, 1H), 2.53 – 2.43 (m, 3H), 2.20 (dt, \(J = 9.9\), 4.5 Hz, 2H), 1.23 (t, \(J = 7.1\) Hz, 3H), 1.14 (t, \(J = 7.1\) Hz, 3H).

\(^{19}\)F NMR (235 MHz, Chloroform-\(d\)) \(\delta\) -67.43. \(^{13}\)C NMR (63 MHz, Chloroform-\(d\)) \(\delta\) 169.5, 168.6, 134.1, 133.6, 132.3, 128.7, 128.4 (q, \(J = 293.1\) Hz), 128.4, 127.9, 126.2, 125.8, 125.3, 124.2, 61.6, 61.3, 59.9 (q, \(J = 25.1\) Hz), 57.9, 47.8, 35.9, 127.9, 126.2, 125.8, 125.3, 124.2, 61.6, 61.3, 59.9 (q, \(J = 25.1\) Hz), 57.9, 47.8, 35.9, 25.6 (d, \(J = 1.9\) Hz), 14.1, 13.9. IR (ATR, cm\(^{-1}\)) 3050, 2983, 2941, 2905, 2871, 2810, 1730, 1510, 1466, 1448, 1371, 139, 1279, 1258, 1253, 1242, 1207, 1161, 1141, 1110, 1068, 1029, 849, 791, 776, 734, 705, 581, 518, 417. HRMS m/z [M+H]\(^+\) calculated for C\(_{22}\)H\(_{27}\)NO\(_4\)F\(_3\)\(^+\): 426.1892, found: 426.1895.

**Synthesis of compound 96**

1,1,1-trifluoro-\(4\)-(isoquinolin-1-yl)-N-methyl-N-(napthalen-1-yl)methybutan-2-amine

Compound 96 was prepared according to general procedure D from I (140 mg, 0.3 mmol), N-methyl-1-(napthalen-1-ylmethyl)methanamine (51.4 mg, 0.3 mmol, 1 equiv), 1-methylisoquinoline \(4.4\) \(\mu\)L, 0.33 mmol, 1.1 equiv) and \(^n\)BuLi solution (216 \(\mu\)L, 1.6 M in hexanes, 0.345 mmol, 1.15 equiv) to afford a white solid (66.3 mg, 0.162 mmol, 54% yield). \(R_f = 0.50\) (hexanes:ethyl acetate= 5:1). M.p. = 133-135 °C. LRMS (EI, 70 eV): m/z (%): 355(1), 281(2), 207(2), 185(3), 185(3), 184(28), 184(12), 142(12), 141(100), 140(2), 139(3), 115(14), 73(2). \(\text{\(1\)}\)H NMR (300 MHz, Chloroform-\(d\)) \(\delta\) 8.35 (d, \(J = 8.6\) Hz, 1H), 7.84 (d, \(J = 8.5\) Hz, 1H), 7.80 (d, \(J = 8.5\) Hz, 1H), 7.51 – 7.34 (m, 3H), 7.24 – 7.10 (m, 4H), 7.04 – 6.95 (m, 1H), 4.12 (d, \(J = 12.8\) Hz, 1H), 4.11 (d, \(J = 14.5\) Hz, 1H), 3.97 (d, \(J = 14.8\) Hz, 1H), 3.96 (d, \(J = 12.8\) Hz, 1H), 3.64 – 3.47 (m, 1H), 3.20 – 2.93 (m, 3H), 2.92 – 2.81 (m, 2H), 2.75 (dd, \(J = 13.5\), 3.6 Hz, 1H), 2.34 (s, 3H). \(\text{\(19\)}\)F NMR (282 MHz, Chloroform-\(d\)) \(\delta\) -67.33 (d, \(J = 8.2\) Hz). \(\text{\(13\)}\)C NMR (75 MHz, Chloroform-\(d\)) \(\delta\) 160.5, 141.5, 136.0, 134.3, 134.1, 132.5, 129.9, 128.7, 128.4, 127.9, 127.4, 127.1, 126.9, 126.2 (q, \(J = 293.4\) Hz), 125.9, 125.7, 125.3, 125.0, 124.7, 119.4, 61.4 (q, \(J = 24.5\) Hz), 58.3, 36.1, 30.9, 24.4. IR (ATR, cm\(^{-1}\)) 3050, 3006, 2986, 2959, 2931, 2854, 2805, 1624, 1588, 1565, 1506, 1392, 1373, 1304, 1252, 1245, 1156, 1124, 1105, 1063, 844, 821, 803, 783, 777, 730, 698, 571, 536, 505, 461. HRMS m/z [M+H]\(^+\) calculated for C\(_{25}\)H\(_{24}\)N\(_2\)F\(_3\)\(^+\): 409.1886, found: 409.1889.
Synthesis of compound 97
1,1,1-trifluoro-N-methyl-N-(naphthalen-1-ylmethyl)-3-(5,6,7,8-tetrahydroquinolin-8-yl)propan-2-amine

Compound 97 was prepared according to general procedure D from 1 (140 mg, 0.3 mmol), N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv), 5,6,7,8-tetrahydroquinoline (43 µL, 0.33 mmol, 1.1 equiv) and nBuLi solution (216 µL, 1.6 M in hexanes, 0.345 mmol, 1.15 equiv) to afford a white solid (29.2 mg, 0.0733 mmol, 24% yield). Rf = 0.23 (hexanes:ethyl acetate= 10:1). M.p.= 102-105 °C. LRMS (EI, 70 eV): m/z (%): 398(1), 378(2), 355(1), 257(17), 237(23), 228(4), 171(4), 170(28), 146(19), 142(9), 141(61), 139(7), 134(10), 133(100), 132(59), 130(13), 118(9), 117(13), 115(26). 1H NMR (300 MHz, Chloroform-d) δ 8.42 (d, J = 4.7 Hz, 1H), 8.26 – 8.15 (m, 1H), 7.93 – 7.78 (m, 2H), 7.64 – 7.38 (m, 4H), 7.36 – 7.25 (m, 1H), 7.03 (dd, J = 7.6, 4.8 Hz, 1H), 4.48 (d, J = 13.3 Hz, 1H), 4.32 (d, J = 13.2 Hz, 1H), 3.31 (ddt, J = 16.4, 11.5, 5.8 Hz, 1H), 2.92 (tt, J = 11.2, 4.6 Hz, 1H), 2.79 – 2.72 (m, 4H), 2.59 (q, J = 6.1 Hz, 2H), 1.53 – 1.33 (m, 2H), 1.25 – 1.05 (m, 1H), 1.02 – 0.76 (m, 2H). (major diastereomer). 19F NMR (282 MHz, Chloroform-d) δ -66.30 (d, J = 8.3 Hz) minor diastereomer, -66.94 (d, J = 8.2 Hz), major diastereomer. 13C NMR (75 MHz, Chloroform-d) δ 159.8, 146.5, 137.2, 134.5, 134.1, 132.7, 129.0, 128.6, 128.4, 128.3, 128.1, 126.6, 126.0, 125.8, 125.3, 124.9, 123.7, 121.0, 58.6, 58.2, 57.9 (d, J = 24.2 Hz), 36.2, 35.7, 31.1, 29.1, 26.5, 19.8, (major diastereomer). IR (ATR, cm⁻¹) 3066, 3044, 3007, 2972, 2941, 2912, 2897, 2857, 2803, 1571, 1509, 1442, 1425, 1388, 1371, 1258, 1239, 1150, 1129, 1110, 1086, 1065, 1017, 1005, 966, 862, 845, 807, 793, 776, 726, 695, 580, 544, 418. HRMS m/z [M+H]⁺ calculated for C₂₄H₂₆N₂F₃+: 399.2043, found: 399.2046.

Synthesis of compound 98
1,1,1-trifluoro-3-(1H-indol-3-yl)-N-methyl-N-(naphthalen-1-ylmethyl)propan-2-amine

Aziridinium intermediate solution was prepared according to general procedure A from 1 (140 mg, 0.3 mmol) and N-methyl-1-(naphthalen-1-yl)methanamine (51.4 mg, 0.3 mmol, 1 equiv) in acetonitrile. A separate, oven dried vial was charged with stirring bar, indole (42.6 mg, 0.36 mmol, 1.2 equiv) and sealed with Teflon septa and screw cap. Vial was evacuated and backfilled with argon (repeated three times), then toluene (2.5 mL) was added under argon atmosphere. To the stirred mixture, solution of Et₂Zn (1 M in toluene, 360 uL, 0.36 mmol, 1.2 equiv) was added dropwise under argon atmosphere at room temperature and stirring was continued for 1 hour. After
that, solution of aziridinium intermediate was added and the mixture was stirred at room
temperature for 16 hours. Purification was carried out according to general procedure A to afford
a colorless oil (79.9 mg, 0.209 mmol, 70% yield). $R_f = 0.43$ (hexanes:ethyl acetate= 5:1). $M_p =$
73-76 °C. LRMS (EI, 70 eV): m/z (%): 382(6), 252(11), 142(13), 141(100), 139(4), 131(5),
130(41), 115(13), 103(3), 77(4). $^1H$ NMR (250 MHz, Chloroform-d) $\delta$ 7.78 (d, $J = 8.2$ Hz, 1H),
7.70 (d, $J = 8.0$ Hz, 1H), 7.67 – 7.58 (m, 1H), 7.48 – 7.17 (m, 6H), 7.11 (d, $J = 7.0$ Hz, 1H), 7.05
(d, $J = 7.4$ Hz, 1H), 6.74 (d, $J = 2.4$ Hz, 1H), 4.24 (d, $J = 13.6$ Hz, 1H), 4.16 (d, $J = 13.4$ Hz, 1H),
3.80 – 3.52 (m, 1H), 3.15 (s, 1H), 3.12 (s, 1H), 2.57 – 2.43 (m, 3H). $^{19}F$ NMR (235 MHz,
Chloroform-d) $\delta$ -67.64. $^{13}C$ NMR (75 MHz, Chloroform-d) $\delta$ 136.2, 134.1, 133.8, 132.2, 129.1
(d, $J = 292.8$ Hz), 128.2, 128.1, 127.5, 127.3, 125.4, 125.4, 125.0, 124.5, 123.1, 122.0, 119.5, 118.4,
111.8, 111.2, 63.8 (q, $J = 24.0$ Hz), 58.6 (d, $J = 1.4$ Hz), 35.6, 22.5 (q, $J = 1.9$ Hz). IR (ATR, cm$^{-1}$
) 3421, 3278, 3054, 2939, 2857, 2833, 1704, 1619, 1597, 1509, 1456, 1354, 1336, 1251, 1164,
1137, 1102, 1065, 1011, 859, 791, 774, 739, 692, 586, 458, 423. HRMS m/z [M+H]$^+$ calculated
for C$_{23}$H$_{22}$N$_2$F$_3$+: 383.1730, found: 383.1730.

**Supplementary Figure 11:** Unsuccessful substrates under conditions of aziridinium ion
intermediate generation

Following product was observed by GC-MS:
Supplementary Figure 12: Ethylene diamine and trifluoroethylamine moieties in natural products and drugs

1) Natural products with diamine structure

- L-tupinic acid
- L-mimosine
- L-willardine
- L-quisqualic acid

2) Drug molecules with ethylene diamine motif

- Aslimadoline: e-opioid receptor agonist
- Thonzylamine (X= OMe, Y= N)
- Mepyramine (X= OMe, Y= CH)
- Chloropyramine (X= Cl, Y= CH)
- Triprorenamine (X= H, Y= CH)
- Antihistamines
- Encorafenib: oncology

3) Current drug candidate containing trifluoromethyl amine scaffold

- Selatralisib: autoimmune diseases
NMR & IR spectra
Supplementary Figure 13: $^1$H-NMR for compound 1

$^1$H NMR (250 MHz, Acetonitrile$_d_3$) δ 8.20 (dd, $J = 7.8, 4.2$ Hz, 2H), 7.51 – 7.22 (m, 4H).
Supplementary Figure 14: $^{19}$F NMR for compound 1

$^{19}$F NMR (235 MHz, Acetonitrile$_d_3$) δ -64.53, -79.40, -105.44.
Supplementary Figure 15: $^{13}$C NMR for compound 1

$^{13}$C NMR (63 MHz, Acetonitrile-$d_3$) $\delta$ 166.4 (d, $J = 254.6$ Hz), 145.1 (q, $J = 4.7$ Hz), 139.9 (d, $J = 9.5$ Hz), 121.9 (q, $J = 321.0$ Hz), 121.2 (q, $J = 273.8$ Hz), 111.8 (q, $J = 39.8$ Hz), 108.3 (d, $J = 3.2$ Hz).
Supplementary Figure 16: IR for compound 1
Supplementary Figure 17: $^1$H-NMR for compound A1

$^1$H NMR (250 MHz, Chloroform-$d$) δ 7.15 (d, $J = 8.5$ Hz, 2H), 6.77 (d, $J = 8.6$ Hz, 2H), 5.84 (dtt, $J = 6.9, 5.9$ Hz, 1H), 5.11 (dd, $J = 17.2, 1.7$ Hz, 1H), 5.02 (dd, $J = 10.3, 1.2$ Hz, 1H), 3.69 (s, 3H), 3.63 (s, 2H), 3.17 (bs, 2H), 1.52 (bs, 1H).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{hnmr_spectrum}
\caption{Supplementary Figure 17: $^1$H-NMR spectrum for compound A1.}
\end{figure}
Supplementary Figure 18: $^{13}C$ NMR for compound A1

$^{13}C$ NMR (63 MHz, CDCl₃) δ 158.6, 136.8, 132.3, 129.3, 115.9, 113.7, 55.1, 52.6, 51.6.
Supplementary Figure 19: $^1$H-NMR for compound A2

$^1$H NMR (250 MHz, Chloroform-d) δ 7.2 (d, $J = 8.6$ Hz, 2H), 6.8 (d, $J = 8.7$ Hz, 2H), 3.7 (s, 3H), 3.6 (s, 3H), 3.5 (d, $J = 12.7$ Hz, 1H), 3.2 (t, $J = 7.2$ Hz, 1H), 1.8 – 1.6 (m, 2H), 1.4 (dd$J = 7.5$, 6.5 Hz, 2H), 0.8 (d, $J = 6.6$ Hz, 3H), 0.8 (d, $J = 6.6$ Hz, 3H).
Supplementary Figure 20: $^{13}\text{C} NMR$ for compound A2

$^{13}\text{C} NMR$ (63 MHz, CDC$_3$) δ 176.5, 158.7, 132.0, 129.5, 113.7, 59.1, 55.2, 51.6, 42.8, 24.9, 22.8, 22.2.
Supplementary Figure 21: $^1$H-NMR for compound A3

$^1$H NMR (250 MHz, Chloroform-d) $\delta$ 7.25 – 7.08 (m, 7H), 6.78 (d, $J = 8.7$ Hz, 2H), 4.06 (q, $J = 7.1$ Hz, 2H), 3.72 (d, $J = 12.7$ Hz, 1H), 3.71 (s, 3H), 3.55 (d, $J = 12.9$ Hz, 1H), 3.49 (t, $J = 7.0$ Hz, 1H), 2.92 (d, $J = 7.0$ Hz, 2H), 1.89 (s, 1H), 1.11 (q, $J = 7.1$ Hz, 3H).
Supplementary Figure 22: $^{13}$C NMR for compound A3

$^{13}$C NMR (63 MHz, CDC$_3$) δ 174.4, 158.6, 137.3, 131.6, 129.2, 129.2, 128.5, 128.5, 113.6, 61.8, 60.4, 55.0, 51.3, 39.7, 14.1.
Supplementary Figure 23: $^1$H-NMR for compound A4

1H NMR (250 MHz, Chloroform-d) δ 7.25 (d, J = 8.3 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 3.79 (d, J = 0.9 Hz, 3H), 3.70 (s, 2H), 2.14 – 2.04 (m, 3H), 1.76 – 1.56 (m, 12H), 1.16 (s, 1H).
Supplementary Figure 24: $^{13}$C NMR for compound A4

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 158.5, 133.9, 129.5, 113.9, 77.7, 77.2, 76.7, 55.3, 50.9, 44.6, 43.0, 36.9, 29.8.
Supplementary Figure 25: $^1$H-NMR for compound A5

$^1$H NMR (250 MHz, Chloroformd) δ 7.14 (d, $J = 8.6$ Hz, 2H), 6.77 (d, $J = 8.6$ Hz, 2H), 3.68 (s, 2H), 3.67 (s, 3H), 2.05 (tt, $J = 6.3, 3.8$ Hz, 1H), 1.80 (s, 1H), 0.45 – 0.23 (m, 4H).
Supplementary Figure 26: $^{13}$C NMR for compound A5

$^{13}$C NMR (63 MHz, CDC) δ 158.3, 132.6, 129.1, 113.5, 54.9, 52.9, 29.8, 6.2.
Supplementary Figure 27: $^1$H-NMR for compound A6

$^1$H NMR (250 MHz, Chloroform-d) $\delta$ 7.4 – 7.1 (m, 7H), 6.9 (d, $J = 8.9$ Hz, 2H), 3.9 – 3.7 (m, 4H), 3.7 – 3.5 (m, 2H), 1.6 (s, 1H), 1.4 (d, $J = 6.6$ Hz, 3H).
Supplementary Figure 28: $^{13}$C NMR for compound A6

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 158.6, 145.7, 132.8, 129.3, 128.5, 126.9, 126.7, 113.8, 57.4, 55.2, 51.0, 24.5.
Supplementary Figure 29: $^1\text{H}-\text{NMR}$ for compound A7

$^1\text{H}$ NMR (250 MHz, Chloroform-$d$) $\delta$ 7.20 (d, $J = 8.5$ Hz, 2H), 6.82 (d, $J = 8.5$ Hz, 2H), 4.14 ($q$, $J = 7.1$ Hz, 2H), 3.74 (s, 3H), 3.69 (s, 2H), 3.34 (s, 2H), 2.18 (s, 1H), 1.22 ($d$, $J = 7.1$ Hz, 3H).
Supplementary Figure 30: $^{13}$C NMR for compound A7

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 172.3, 158.8, 131.5, 129.4, 113.8, 60.6, 55.1, 52.6, 49.9, 14.1.
Supplementary Figure 31: $^1$H-NMR for compound A8

$^1$H NMR (250 MHz, Chloroform-$d$) \( \delta \) 7.14 (d, \( J = 8.5 \) Hz, 2H), 6.76 (d, \( J = 8.6 \) Hz, 2H), 3.69 (s, 3H), 3.63 (s, 2H), 2.52 (t, \( J = 7.2 \) Hz, 2H), 1.60 (s, 1H), 1.40 (q, \( J = 7.0, 6.4 \) Hz, 2H), 1.29 - 1.07 (m, 6H), 0.79 (t, \( J = 6.4 \) Hz, 3H).
Supplementary Figure 32: $^{13}$C NMR for compound A8

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 158.6, 132.7, 129.3, 113.8, 55.2, 53.5, 49.4, 31.8, 30.1, 27.1, 22.7, 14.1.
Supplementary Figure 33: $^1$H-NMR for compound A9

$^1$H NMR (250 MHz, Chloroform-d) δ 7.16 (d, J = 8.5 Hz, 2H), 6.77 (d, J = 8.6 Hz, 2H), 3.70 (s, 3H), 3.61 (q, J = 12.8 Hz, 2H), 2.56 (dq, J = 12.2, 7.4, 6.5 Hz, 1H), 1.39 (s, 2H), 1.33 – 1.10 (m, 7H), 0.99 (d, J = 6.3 Hz, 3H), 0.81 (t, J = 6.6 Hz, 3H).
Supplementary Figure 34: $^{13}$C NMR for compound A9

$^{13}$C NMR (63 MHz, CDCl₃) δ 158.6, 133.0, 129.3, 113.8, 55.2, 52.5, 50.8, 37.1, 32.1, 25.7, 22.7, 20.3, 14.1.
Supplementary Figure 35: $^1$H-NMR for compound A10

$^1$H NMR (250 MHz, Chloroform) δ 7.14 (d, $J = 8.5$ Hz, 2H), 6.76 (d, $J = 8.5$ Hz, 2H), 3.68 (s, 3H), 3.62 (s, 2H), 2.51 (t, $J = 7.2$ Hz, 2H), 1.67 (s, 1H), 1.49 – 1.32 (m, 2H), 1.18 (s, 10H), 0.79 (t, $J = 6.1$ Hz, 3H).
Supplementary Figure 36: $^{13}$C NMR for compound A10

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 158.6, 132.6, 129.3, 113.7, 55.2, 53.5, 49.4, 31.9, 30.1, 29.6, 29.3, 27.4, 22.7, 14.1.
Supplementary Figure 37: $^1$H-NMR for compound A11

$^1$H NMR (250 MHz, Chloroform-d) $\delta$ 7.29 (d, $J = 8.5$ Hz, 2H), 7.19 (t, $J = 7.9$ Hz, 2H), 6.89 (d, $J = 8.6$ Hz, 2H), 6.74 (t, $J = 7.3$ Hz, 1H), 6.64 (d, $J = 7.7$ Hz, 2H), 4.24 (s, 2H), 3.93 (s, 1H), 3.79 (s, 3H).

![NMR spectrum](image)
Supplementary Figure 38: $^{13}$C NMR for compound A11

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 158.9, 148.2, 131.4, 129.3, 128.9, 117.6, 114.1, 113.0, 55.3, 47.8.
Supplementary Figure 39: $^1$H-NMR for compound A12

$^1$H NMR (250 MHz, Chloroform-d) $\delta$ 7.51 - 7.39 (m, 1H), 7.35 (t, $J = 2.1$ Hz, 1H), 7.27 - 7.11 (m, 3H), 6.83 (dd, $J = 6.4$, 2.1 Hz, 3H), 4.44 (d, $J = 26.7$ Hz, 1H), 4.22 (s, 2H), 3.75 (s, 3H).
Supplementary Figure 40: $^{13}$C NMR for compound A12

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 159.2, 149.4, 148.8, 130.0, 129.8, 128.9, 118.9, 114.3, 112.1, 106.6, 55.3, 47.6.
Supplementary Figure 41: $^1$H-NMR for compound 3-phenylprop-2-yn-1-ol

$^1$H NMR (250 MHz, Chloroform-d) $\delta$ 7.38 (dd, $J = 6.8, 2.8$ Hz, 2H), 7.23 (dd, $J = 5.1, 1.8$ Hz, 3H), 4.44 (s, 2H), 2.77 (s, 1H).
Supplementary Figure 42: $^{13}C$ NMR for 3-phenylprop-2-yn-1-ol

$^{13}C$ NMR (63 MHz, CDCl$_3$) δ 131.7, 128.5, 128.3, 122.6, 87.4, 85.6, 51.4.
Supplementary Figure 43: $^1H$-NMR for compound 3-phenylprop-2-yn-1-yl 4-methylbenzenesulfonate

$^1H$ NMR (250 MHz, Chloroform-d) δ 7.77 (d, $J = 8.4$ Hz, 2H), 7.31 – 7.09 (m, 7H), 4.87 (s, 2H), 2.30 (s, 3H).
Supplementary Figure 44: $^{13}$C NMR for 3-phenylprop-2-yn-1-yl 4-methylbenzenesulfonate

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 145.1, 133.5, 131.8, 129.9, 129.1, 128.3, 128.2, 121.5, 89.0, 80.7, 58.7, 21.6.
Supplementary Figure 45: $^1$H-NMR for compound A13

$^1$H NMR (250 MHz, Methylene Chloride) $\delta$ 7.3 – 7.2 (m, 2H), 7.2 – 7.1 (m, 3H), 3.4 (s, 2H), 2.4 (d, $J = 6.7$ Hz, 2H), 1.6 (d, $J = 13.3$, 6.7 Hz, 1H), 1.2 (s, 1H), 0.8 (s, 3H), 0.8 (s, 3H).
Supplementary Figure 46: $^{13}$C NMR for compound A13

$^{13}$C NMR (63 MHz, CDCl3) δ 132.0, 128.7, 128.4, 124.0, 89.0, 83.3, 57.5, 54.7, 54.3, 53.8, 53.4, 53.0, 39.6, 28.9, 21.0.
Supplementary Figure 47: $^1$H-NMR for compound A14

$^1$H NMR (250 MHz, Methylene Chloride) $\delta$ 7.4 (dq, $J = 8.3$, 3.4, 2.6 Hz, 2H), 7.4 – 7.3 (m, 3H), 3.7 (s, 2H), 2.7 (tt, $J = 10.0$, 3.8 Hz, 1H), 2.0 – 1.6 (m, 5H), 1.5 – 1.0 (m, 6H).
Supplementary Figure 48: $^{13}$C NMR for compound A14

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 132.0, 128.7, 128.3, 124.0, 89.1, 83.0, 55.7, 54.7, 54.3, 53.8, 53.4, 53.0, 36.4, 33.6, 36.7, 25.3.
Supplementary Figure 49: \( ^1H \)-NMR for compound A15

\( ^1H \) NMR (250 MHz, Chloroform-d) \( \delta \) 7.42 – 7.30 (m, 2H), 7.26 – 7.15 (m, 3H), 2.73 (d, \( J = 6.8 \) Hz, 2H), 1.87 (d, \( J = 11.9 \) Hz, 2H), 1.70 – 1.51 (m, 5H), 1.52 – 0.92 (m, 12H), 0.92 – 0.70 (m, 3H).
Supplementary Figure 50: $^{13}$C NMR for compound A15

$^{13}$C NMR (63 MHz, CDCl$_3$) $\delta$ 131.6, 128.2, 127.7, 123.8, 93.6, 84.5, 55.1, 43.3, 38.3, 31.8, 30.7, 27.2, 26.0, 23.1, 22.7, 14.1.
Supplementary Figure 51: $^1$H-NMR for compound A16

$^1$H NMR (250 MHz, Chloroform-d) δ 7.18 (d, $J = 8.4$ Hz, 2H), 6.78 (d, $J = 8.5$ Hz, 2H), 3.73 (s, 2H), 3.70 (s, 3H), 3.32 (d, $J = 2.3$ Hz, 2H), 2.19 (t, $J = 2.0$ Hz, 1H), 1.43 (s, 1H).
Supplementary Figure 52: $^{13}$C NMR for compound A16

$^{13}$C NMR (63 MHz, CDCl$_3$): $^{13}$C NMR (63 MHz, CDCl$_3$) 158.8, 131.5, 129.6, 113.8, 82.2, 71.5, 55.2, 51.6, 37.2.
Supplementary Figure 53: $^1$H-NMR for compound A17

$^1$H NMR (250 MHz, Methanol-d$_4$) δ 7.23 (ddt, J = 14.8, 10.4, 7.0 Hz, 5H), 4.04 (dd, J = 8.8, 7.0 Hz, 2H), 3.78 – 3.47 (m, 3H), 2.74 (d, J = 2.9 Hz, 4H), 1.43 (s, 9H).
Supplementary Figure 54: $^{13}$C NMR for compound A17

$^{13}$C NMR (63 MHz, MeOD) δ 158.1, 140.9, 129.6, 127.3, 80.8, 49.5, 48.6, 37.0, 28.7.
Supplementary Figure 55: IR for compound A17
Supplementary Figure 56: $^1$H-NMR for compound A18

$^1$H NMR (250 MHz, Chloroform-d) δ 4.45 (s, 1H), 3.89 – 2.80 (m, 4H), 2.53 (bs, 1H), 0.83 (s, 9H), -0.01 (s, 6H).
Supplementary Figure 57: $^{13}$C NMR for compound A18

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 71.4, 58.1, 25.9, 18.1, -4.9.
Supplementary Figure 58: $^1$H-NMR for compound A19

$^1$H NMR (250 MHz, Acetonitrile-$d_3$) $\delta$ 7.32 (bs, 2H), 4.34 – 4.18 (m, 1H), 3.70 (dd, $J = 16.6$, 8.7 Hz, 1H), 3.70 (s, 3H).
Supplementary Figure 59: $^{19}$F NMR for compound A19

$^{19}$F NMR (235 MHz, Acetonitrile) δ -79.28.
Supplementary Figure 60: $^{13}$C NMR for compound A19

$^{13}$C NMR (63 MHz, Acetonitrile-$d_3$) $\delta$ 172.1, 121.5 ($q, J = 318.7$ Hz), 53.3, 50.0, 35.4.
Supplementary Figure 61: $^1$H-NMR for compound A20

$^1$H NMR (250 MHz, Chloroform-$d$) δ 3.52 (dt, $J = 7.3, 3.7$ Hz, 1H), 2.83 (dd, $J = 12.2$ Hz, 1H), 2.75 – 2.62 (m, 1H), 2.60 – 2.34 (m, 2H), 2.20 (bs, 1H), 1.81 – 1.54 (m, 2H), 1.33 (m, 12.0 Hz, 2H), 0.88 – 0.68 (m, 9H), 0.01 – 0.13 (m, 6H).
Supplementary Figure 62: $^{13}C$ NMR for compound A20

$^{13}C$ NMR (63 MHz, CDCl$_3$) $\delta$ 67.9, 54.0, 46.1, 33.8, 25.8, 24.4, 18.1, -4.7, -4.8.
Supplementary Figure 63: $^1$H-NMR for compound A21

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 3.47 – 3.21 (m, 2H), 3.06 ($d,J=11.5$ Hz, 1H), 2.93 ($d,J=12.1$ Hz, 1H), 2.46 ($dtdJ=11.8, 2.7$ Hz, 1H), 2.34 – 2.13 (m, 1H), 1.91 (s, 1H), 1.76 – 1.48 (m, 3H), 1.48 – 1.24 (m, 1H), 1.01 ($q,J=11.9$, 3.9 Hz, 1H), 0.82 (s, 9H), -0.03 ($d,J=3.7$ Hz, 6H).
Supplementary Figure 64: $^{13}\text{C\ NMR for compound A21}$

$^{13}\text{C\ NMR (63 MHz, CDCl}_3) \delta$ 66.6, 50.2, 47.2, 40.0, 27.8, 26.3, 26.0, 18.3, -5.4, -5.4.
Supplementary Figure 65: $^1$H-NMR for compound 6

$^1$H NMR (250 MHz, Acetonitrile-d$_3$) $\delta$ 8.29 – 8.07 (m, 1H), 8.03 – 7.76 (m, 2H), 7.67 – 7.32 (m, 4H), 3.97 (s, 2H), 2.49 (pdd $\text{J}_1 = 5.6$, $\text{J}_2 = 3.0$ Hz, 1H), 2.12 (d $\text{J}_1 = 3.1$ Hz, 1H), 1.87 (d $\text{J}_1 = 6.4$ Hz, 1H).
Supplementary Figure 66: $^{19}$F NMR for compound 6

$^{19}$F NMR (235 MHz, Acetonitrile) δ -71.67.
Supplementary Figure 67: $^{13}$C NMR for compound 6

$^{13}$C NMR (63 MHz, Acetonitrile $d_x$) $\delta$ 135.1, 134.6, 132.5, 129.4, 129.0, 127.0, 127.0, 126.8, 126.4, 125.7 (d, $J = 271.3$ Hz), 125.0, 37.9 (q, $J = 39.0$ Hz), 30.8 (q, $J = 1.9$ Hz).
Supplementary Figure 68: $^1$H-NMR for compound 7

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 7.2 (t, $J = 8.6$, 7.5 Hz, 2H), 7.1 (t, $J = 8.6$, 7.4 Hz, 2H), 6.8 – 6.6 (m, 6H), 4.5 (p(d$t = 8.4$, 4.0 Hz, 1H), 3.9 (d,$J = 15.4$, 4.0 Hz, 1H), 3.7 (dd,$J = 15.4$, 8.5 Hz, 1H), 2.9 (s, 6H).
Supplementary Figure 69: $^{19}$F NMR for compound 7

$^{19}$F NMR (235 MHz, CDCl$_3$) δ -70.01.
Supplementary Figure 70: $^{13}$C NMR for compound 7

$^{13}$C NMR (63 MHz, Chloroform-$d$) δ 149.9, 148.2, 129.7, 129.3, 126.0 (q, $J = 288.8$ Hz), 119.0, 117.5, 114.5, 112.6, 59.2 (q, $J = 26.3$ Hz), 49.4 (d, $J = 0.9$ Hz), 39.5, 32.3 (d, $J = 1.6$ Hz).
Supplementary Figure 71: IR for compound 7
Supplementary Figure 72: $^1$H-NMR for compound 8

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 7.22 – 7.02 (m, 4H), 6.78 – 6.54 (m, 6H), 4.36 (td, $J = 7.9, 4.6$ Hz, 1H), 3.77 – 3.53 (m, 2H), 3.42 – 3.16 (m, 4H), 1.08 (q, $J = 6.9$ Hz, 3H), 1.01 (t, $J = 7.1$ Hz, 3H).
Supplementary Figure 73: $^{19}\text{F NMR for compound 8}$

$^{19}\text{F NMR (235 MHz, Chloroform)}\delta -69.86.$
Supplementary Figure 74: $^{13}$C NMR for compound 8

$^{13}$C NMR (63 MHz, Chloroform-d) $\delta$ 147.9, 129.7, 129.2, 126.4 (q, $J = 288.3$ Hz), 119.4, 117.7, 116.6, 113.6, 60.6 (q, $J = 25.5$ Hz), 48.6, 46.5, 39.1, 13.1, 12.1.
Supplementary Figure 75: IR for compound 8
Supplementary Figure 76: $^1$H-NMR for compound 9

$^1$H NMR (250 MHz, Methanol-$d_4$) $\delta$ 7.15 – 6.92 (m, 4H), 6.74 – 6.41 (m, 4H), 4.57 (ddt, $J = 16.7$, 8.5, 4.2 Hz, 1H), 3.78 (dd$J = 14.0$, 9.5 Hz, 2H), 3.61 (q$J = 8.7$ Hz, 1H), 3.48 – 3.32 (m, 2H), 3.26 (q$J = 8.9$ Hz, 1H), 2.99 (t$J = 8.7$ Hz, 2H), 2.89 – 2.65 (m, 2H).
Supplementary Figure 77: $^{19}$F NMR for compound 9

$^{19}$F NMR (235 MHz, Methanol-d$_4$) $\delta$ -72.00.
Supplementary Figure 78: $^{13}$C NMR for compound 9

$^{13}$C NMR (63 MHz, Methanol-d$_4$) δ 152.8, 151.7, 131.0, 129.8, 128.3, 128.2, 127.5 (q, $J = 287.1$ Hz), 125.6, 125.5, 119.2, 118.9, 107.5, 106.9, 56.6 (q, $J = 27.0$ Hz), 54.5, 48.1, 46.3 (q, $J = 1.9$ Hz), 29.3, 29.1.
Supplementary Figure 79: IR for compound 9
Supplementary Figure 80: $^1$H-NMR for compound 10

$^1$H NMR (250 MHz, Chloroform-d) $\delta$ 7.14 (t, $J = 7.8$ Hz, 1H), 7.07 – 6.90 (m, 3H), 6.76 – 6.57 (m, 3H), 6.52 (d, $J = 8.3$ Hz, 1H), 4.76 (tt, $J = 12.9$, 6.3 Hz, 1H), 3.88 (dd, $J = 15.3$, 4.4 Hz, 1H), 3.71 (dd, $J = 15.3$, 7.6 Hz, 1H), 3.39 (dt, $J = 16.3$, 5.5 Hz, 4H), 2.84 (h, $J = 9.8$ Hz, 2H), 2.72 (t, $J = 6.4$ Hz, 2H), 2.14 – 1.74 (m, 4H).
Supplementary Figure 81: $^{19}$F NMR for compound 10

$^{19}$F NMR (235 MHz, Chloroform) $\delta$ -69.3.
Supplementary Figure 82: $^{13}$C NMR for compound 10

$^{13}$C NMR (63 MHz, Chloroform-$d_2$) $\delta$ 144.8, 144.2, 129.9, 129.6, 127.5, 127.2, 124.8 (q, $J = 289.1$ Hz), 123.7, 123.2, 117.7, 116.6, 112.0, 110.0, 56.3 (q, $J = 25.2$ Hz), 50.8, 48.3, 43.6, 28.2, 28.1, 22.2, 22.1.
Supplementary Figure 83: IR for compound 10
Supplementary Figure 84: $^1H$-NMR for compound II

$^1H$ NMR (250 MHz, Chloroform$_d$) $\delta$ 7.04 – 6.72 (m, 8H), 4.60 ($hJ = 8.5$ Hz, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 3.66 (s, 1H), 3.63 (s, 1H), 2.87 (s, 6H).
Supplementary Figure 85: $^{19}$F NMR for compound 11

$^{19}$F NMR (235 MHz, Chloroform$\delta$) $\delta$ -68.26.
Supplementary Figure 86: $^{13}C$ NMR for compound 11

$^{13}C$ NMR (63 MHz, Chloroform-d) δ 152.7, 151.5, 140.5, 129.3 (q, $J = 290.6$ Hz), 122.5, 122.1, 121.1, 121.0, 120.4, 111.8, 111.7, 60.1 (q, $J = 25.3$ Hz), 55.4 (d, $J = 2.4$ Hz), 51.1, 41.1, 34.0 (d, $J = 1.1$ Hz).
Supplementary Figure 87: IR for compound 11
Supplementary Figure 88: $^1$H-NMR for compound 12

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 7.14 – 7.01 (m, 1H), 6.96 (t, $J = 7.8$ Hz, 1H), 6.56 – 6.49 (m, 2H), 6.47 – 6.36 (m, 3H), 6.31 – 6.27 (m, 1H), 4.47 (p, $J = 8.4$, 4.1 Hz, 1H), 3.82 (dd, $J = 15.4$, 4.1 Hz, 1H), 3.59 (dd, $J = 15.4$, 8.4 Hz, 1H), 2.83 (s, 6H), 2.20 (s, 3H), 2.10 (s, 3H).
Supplementary Figure 89: $^{19}$F NMR for compound 12

$^{19}$F NMR (235 MHz, Chloroform) δ -69.99.
Supplementary Figure 90: $^{13}$C NMR for compound 12

$^{13}$C NMR (63 MHz, Chloroform-d) $\delta$ 150.0, 148.1, 139.4, 139.0, 129.5, 129.1, 126.0 (q, $J = 288.8$ Hz), 119.9, 118.4, 115.4, 113.5, 111.6, 109.9, 58.9 (q, $J = 26.2$ Hz), 49.4, 39.8, 32.3 (q, $J = 1.6$ Hz), 22.0, 21.8.
Supplementary Figure 91: IR for compound 12
Supplementary Figure 92: $^1$H-NMR for compound 13

$^1$H NMR (250 MHz, Chloroform-$d$) δ 7.21 (dd, $J = 8.2$, 7.1 Hz, 1H), 7.09 (dd, $J = 8.2$, 7.6 Hz, 1H), 6.56 – 6.27 (m, 6H), 4.51 (pdd, $J = 8.3$, 4.0 Hz, 1H), 3.90 (dd, $J = 15.5$, 3.9 Hz, 1H), 3.71 (dd, $J = 15.5$, 8.6 Hz, 1H), 2.93 (s, 3H), 2.92 (s, 3H).
Supplementary Figure 93: $^{19}F$ NMR for compound 13

$^{19}F$ NMR (235 MHz, Chloroform) δ -70.20 (s, 3F), -111.62 (s, 1F), -111.91 (s, 1F).
Supplementary Figure 94: $^{13}$C NMR for compound 13

$^{13}$C NMR (63 MHz, Chloroform-$d$) δ 164.5 (d, $J = 243.1$ Hz), 164.0 (d, $J = 243.6$ Hz), 151.5 (d, $J = 10.2$ Hz), 149.8 (d, $J = 10.5$ Hz), 130.8 (d, $J = 10.3$ Hz), 130.4 (d, $J = 10.1$ Hz), 125.7 (q, $J = 288.2$ Hz), 109.8 (d, $J = 2.5$ Hz), 107.9 (d, $J = 2.4$ Hz), 105.7 (d, $J = 21.4$ Hz), 104.1 (d, $J = 21.6$ Hz), 101.6 (d, $J = 26.0$ Hz), 99.7 (d, $J = 26.2$ Hz), 58.9 (q, $J = 26.9$ Hz), 49.2, 39.6, 32.5 (q, $J = 1.7$ Hz).
Supplementary Figure 95: IR for compound 13
Supplementary Figure 96: $^1$H-NMR for compound 14

$^1$H NMR (250 MHz, Chloroform-d) δ 7.18 (t, J = 8.1 Hz, 1H), 7.07 (t, J = 8.1 Hz, 1H), 6.77 (dt, J = 7.9, 2.2 Hz, 2H), 6.70 – 6.52 (m, 3H), 6.48 (dd, J = 8.4, 2.6 Hz, 1H), 4.47 (qd, J = 8.3, 4.0 Hz, 1H), 3.88 (dd, J = 15.5, 4.0 Hz, 1H), 3.71 (dd, J = 15.5, 8.6 Hz, 1H), 2.91 (s, 6H).
Supplementary Figure 97: $^{19}$F NMR for compound 14

$^{19}$F NMR (235 MHz, Chloroform) $\delta$ -70.13.
Supplementary Figure 98: $^{13}$C NMR for compound 14

$^{13}$C NMR (63 MHz, Chloroform-d) δ 150.8, 148.9, 135.7, 135.3, 130.7, 125.6 (q, $J = 288.2$ Hz), 119.2, 117.9, 114.5, 112.9, 112.5, 110.8, 58.8 (q, $J = 26.9$ Hz), 49.4, 39.8, 32.5.
Supplementary Figure 99: IR for compound 14
Supplementary Figure 100: $^1$H-NMR for compound 15

$^1$H NMR (250 MHz, Chloroform) $\delta$ 7.13 (d, $J = 8.5$ Hz, 2H), 7.03 (d, $J = 8.5$ Hz, 2H), 6.69 (d, $J = 8.5$ Hz, 2H), 6.62 (d, $J = 8.6$ Hz, 2H), 4.54 (p, $J = 8.4$, 4.0 Hz, 1H), 3.91 (dd, $J = 15.3$, 4.0 Hz, 1H), 3.72 (dd, $J = 15.3$, 8.6 Hz, 1H), 3.04 – 2.86 (m, 6H), 2.34 (s, 3H), 2.28 (s, 3H).
Supplementary Figure 101: $^{19}$F NMR for compound 15

$^{19}$F NMR (235 MHz, Chloroform) $\delta$ -69.96.
**Supplementary Figure 102: $^{13}$C NMR for compound 15**

$^{13}$C NMR (63 MHz, Chloroform-$d$) δ 147.8, 146.1, 130.2, 129.8, 128.2, 126.7, 126.1 (q, $J = 289.4$ Hz), 114.8, 112.9, 59.5 (q, $J = 25.9$ Hz), 49.6, 39.7, 32.3 (q, $J = 1.4$ Hz), 20.4.

![Carbon-13 NMR spectrum](image-url)
Supplementary Figure 103: IR for compound 15
Supplementary Figure 104: $^1$H-NMR for compound 16

$^1$H NMR (250 MHz, Chloroform-$d$) δ 7.27 – 7.17 (m, 2H), 7.17 – 7.07 (m, 2H), 6.61 (d, $J = 9.1$ Hz, 2H), 6.55 (d, $J = 9.1$ Hz, 2H), 4.44 (ddq, $J = 12.1$, 8.3, 4.2 Hz, 1H), 3.88 (dd, $J = 15.5$, 3.8 Hz, 1H), 3.70 (dd, $J = 15.5$, 8.7 Hz, 1H), 2.91 (s, 6H).
Supplementary Figure 105: $^{19}\text{F NMR for compound 16}$

$^{19}\text{F NMR (235 MHz, Chloroform)} \delta -70.13$. 
**Supplementary Figure 106: $^{13}$C NMR for compound 16**

$^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 148.4, 146.6, 129.5, 129.2, 125.7 (q, $J = 288.4$ Hz), 124.1, 122.7, 115.6, 113.8, 59.1 (q, $J = 26.6$ Hz), 49.3, 39.7, 32.4 (q, $J = 1.4$ Hz).
Supplementary Figure 107: IR for compound 16
Supplementary Figure 108: $^1$H-NMR for compound 17

$^1$H NMR (250 MHz, Chloroform-d) δ 7.25 (d, $J = 8.8$ Hz, 2H), 7.16 (d, $J = 8.7$ Hz, 2H), 6.46 (d, $J = 8.9$ Hz, 2H), 6.40 (d, $J = 8.9$ Hz, 2H), 4.34 (d, $J = 8.2$, 3.7 Hz, 1H), 3.78 (d, $J = 15.4$, 3.7 Hz, 1H), 3.60 (d, $J = 15.5$, 8.7 Hz, 1H), 2.80 (s, 6H).
Supplementary Figure 109: $^{19}\text{F NMR for compound 17}$

$^{19}\text{F NMR (235 MHz, Chloroform$\delta$) } \delta -70.16$. 
Supplementary Figure 110: $^{13}$C NMR for compound 17

$^1$H NMR (63 MHz, Chloroform-$d$) δ 148.8, 146.8, 132.4, 132.1, 123.3 (q, $J = 289.3, 288.6$ Hz), 116.0, 114.2, 111.4, 109.9, 58.9 (q, $J = 26.7$ Hz), 49.3, 39.7, 32.4.
Supplementary Figure 111: IR for compound 17
Supplementary Figure 112: $^1H$-NMR for compound 18

$^1H$ NMR (250 MHz, Chloroform-$d$) δ 6.89 (d, $J = 8.8$ Hz, 2H), 6.78 (d, $J = 9.1$ Hz, 2H), 6.73 (d, $J = 8.4$ Hz, 2H), 6.65 (d, $J = 8.9$ Hz, 2H), 4.39 (td, $J = 8.2$, 3.7 Hz, 1H), 3.80 (s, 3H), 3.78 – 3.60 (m, 5H), 2.91 (bs, 6H).
Supplementary Figure 113: $^{19}$F NMR for compound 18

$^{19}$F NMR (235 MHz, Chloroform) $\delta$ -69.95.
Supplementary Figure 114: $^{13}C$ NMR for compound 18

$^{13}C$ NMR (63 MHz, Chloroform-$d$) δ 153.1, 152.5, 144.5, 142.9, 126.2 (q, $J = 289.4$ Hz), 116.6, 115.2, 114.9, 114.8, 60.5 (q, $J = 25.7$ Hz), 55.8, 55.7, 50.2, 40.2, 32.6 (q, $J = 1.1$ Hz).
Supplementary Figure 115: IR for compound 18
Supplementary Figure 116: $^1$H-NMR for compound 19

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 8.04 – 7.88 (m, 1H), 7.79 (d, $J = 7.7$ Hz, 1H), 7.54 – 7.29 (m, 4H), 7.18 – 6.85 (m, 8H), 3.81 (s, 2H), 3.64 (d, $J = 13.0$ Hz, 1H), 3.41 (d, $J = 12.9$ Hz, 1H), 3.20 – 2.98 (m, 1H), 2.76 – 2.55 (m, 1H), 2.25 (dd, $J = 13.6, 3.1$ Hz, 1H), 1.85 (s, 3H), 1.79 (s, 3H).
Supplementary Figure 117: $^{19}$F NMR for compound 19

$^{19}$F NMR (235 MHz, Chloroform-d) δ -67.95.
Supplementary Figure 118: $^{13}$C NMR for compound 19

$^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 134.5, 134.0, 134.0, 132.6, 132.4, 128.5, 128.4, 128.2, 128.1, 127.6, 127.4 ($q, J = 290.4$ Hz), 127.2, 125.8, 125.8, 125.7, 125.3, 125.2, 125.1, 124.7, 61.7 ($q, J = 24.3$ Hz), 61.5, 58.0, 53.6, 42.5, 36.5.
Supplementary Figure 119: IR for compound 19
Supplementary Figure 120: $^1$H-NMR for compound 20

$^1$H NMR (250 MHz, Chloroform-d) δ 3.16 (qt, $J = 8.9$, 5.2 Hz, 1H), 2.74 – 2.48 (m, 2H), 2.46 – 2.21 (m, 4H), 2.06 (h$^f = 7.9$, 6.9 Hz, 4H), 1.69 (tp$^f = 13.3$, 6.6 Hz, 4H), 1.06 – 0.68 (m, 24H).
Supplementary Figure 121: $^{19}$F NMR for compound 20

$^{19}$F NMR (235 MHz, Chloroformd) $\delta$ -68.12.
Supplementary Figure 122: $^{13}C$ NMR for compound 20

$^{13}C$ NMR (63 MHz, Chloroform-$d$) δ 127.7 (q, $J = 289.1$ Hz), 64.6, 60.8, 60.8 (q, $J = 23.8$ Hz), 53.9, 27.3, 26.5, 21.2, 21.1, 20.8, 20.7.
Supplementary Figure 123: IR for compound 20
Supplementary Figure 124: $^1$H-NMR for compound 21

$^1$H NMR (250 MHz, Chloroform-d) δ 7.76 – 6.93 (m, 20H), 3.87 – 3.62 (m, 6H), 3.54 (tt, $J = 12.8, 6.4$ Hz, 1H), 3.35 (dd, $J = 13.5$ Hz, 2H), 3.03 (dd, $J = 13.6, 7.2$ Hz, 1H), 2.74 (dd, $J = 13.6, 4.2$ Hz, 1H).
Supplementary Figure 125: $^{19}$F NMR for compound 21

$^{19}$F NMR (235 MHz, Chloroform) $\delta$ -67.32.
Supplementary Figure 126: $^{13}$C NMR for compound 21

$^{13}$C NMR (63 MHz, Chloroform-d) $\delta$ 139.2, 138.7, 129.3, 129.1, 128.4, 128.4, 127.6 (d, $J = 290.1$ Hz), 127.3, 127.2, 58.7, 57.5 (q, $J = 24.5$ Hz), 54.5, 51.6.
Supplementary Figure 127: IR for compound 21
Supplementary Figure 128: $^1$H-NMR for compound 22

$^1$H NMR (250 MHz, Chloroform) $\delta$ 3.64 (s, 21H), 3.11 (dd, $J$ = 14.3, 8.1 Hz, 1H), 2.97 (dd, $J$ = 14.3, 4.2 Hz, 1H).
Supplementary Figure 129: $^{19}$F NMR for compound 22

$^{19}$F NMR (235 MHz, Chloroform) δ -70.72.
Supplementary Figure 130: $^{13}$C NMR for compound 22

$^{13}$C NMR (63 MHz, Chloroform-<i>d</i>) $\delta$ 171.8, 171.5, 126.5 (q, $J = 290.2$, 289.6, 289.1 Hz), 63.1 (q, $J = 25.3$ Hz), 55.1, 52.6, 51.7, 51.5, 50.7.
Supplementary Figure 131: IR for compound 22
Supplementary Figure 132: $^1H$-NMR for compound 23

$^1H$ NMR (250 MHz, Chloroform-$d$) $\delta$ 7.20 (d, $J = 8.6$ Hz, 2H), 7.17 (d, $J = 8.6$ Hz, 2H), 6.77 (d, $J = 8.5$ Hz, 2H), 6.74 (d, $J = 8.6$ Hz, 2H), 3.98 (d, $J = 12.8$ Hz, 1H), 3.82 (d, $J = 12.8$ Hz, 1H), 3.76 – 3.62 (m, 8H), 3.31 (dd, $J = 16.1$, 11.2, 5.7 Hz, 1H), 3.20 (s, 7H), 2.81 (dd, $J = 14.1$, 4.9 Hz, 1H).
Supplementary Figure 133: $^{19}$F NMR for compound 23

$^{19}$F NMR (235 MHz, Chloroform) $\delta$ -71.11.
Supplementary Figure 134: $^{13}$C NMR for compound 23

$^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 159.2 (d, $J = 3.4$ Hz), 130.9, 129.1, 129.0, 125.8 (q, $J = 283.0$ Hz), 113.8, 62.3, 61.8 (q, $J = 26.5$ Hz), 61.1, 61.0, 59.0, 55.3, 51.9.
Supplementary Figure 135: IR for compound 23
Supplementary Figure 136: $^1$H-NMR for compound 24

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 7.2 – 7.1 (m, 4H), 6.8 (d, $J = 3.5$ Hz, 2H), 6.8 (d, $J = 3.5$ Hz, 2H), 3.7 (s, 3H), 3.7 (s, 3H), 3.7 – 3.5 (m, 2H), 3.5 ($\delta$ = 13.5 Hz, 1H), 3.4 – 3.2 (m, 2H), 2.7 (dd, $J = 13.7$, 7.0 Hz, 1H), 2.6 (dd, $J = 9.2$, 5.6 Hz, 1H), 2.6 – 2.4 (m, 2H), 2.3 (q, $J = 13.0$, 7.0 Hz, 2H), 1.5 – 1.3 (m, 4H), 1.4 – 1.0 (m, 12H), 0.9 – 0.8 (m, 6H).
Supplementary Figure 137: $^{19}$F NMR for compound 24

$^{19}$F NMR (235 MHz, Chloroform$_d$) $\delta$ -68.1.
$^{13}$C NMR for compound 24

$^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 158.8, 158.7, 132.0, 131.5, 130.2, 130.0, 127.6 (q, $J = 290.6$ Hz), 113.6, 113.6, 58.9 (q, $J = 23.8$ Hz), 58.4, 55.3, 54.7, 54.1, 51.7, 50.5, 31.9, 31.9, 28.9, 27.2, 26.8, 22.8, 14.2.
Supplementary Figure 139: IR for compound 24
Supplementary Figure 140: $^1$H-NMR for compound 25

$^1$H NMR (250 MHz, Chloroform-d) δ 7.26 – 7.14 (m, 4H), 6.96 – 6.81 (m, 4H), 3.93 – 3.57 (m, 9H), 3.76 (d, $J = 13.6$ Hz, 1H), 3.63 (d, $J = 13.6$ Hz, 1H), 3.03 (dd, $J = 13.7$, 7.1 Hz, 1H), 2.92 (dd, $J = 13.6$, 5.4 Hz, 1H), 2.39 – 2.24 (m, 1H), 2.26 (s, 0H), 1.81 (p, $J = 5.5$ Hz, 1H), 0.57 – 0.20 (m, 8H).
Supplementary Figure 141: $^{19}$F NMR for compound 25

$^{19}$F NMR (235 MHz, Chloroform) δ -67.9.
Supplementary Figure 142: $^{13}C$ NMR for compound 25

$^{13}C$ NMR (63 MHz, Chloroform-<s>δ</s>) δ 158.9, 158.8, 132.2, 130.8, 130.3, 130.0, 127.4 (q, $J = 289.1$ Hz), 113.5, 113.4, 60.8 (q, $J = 24.2$ Hz), 58.7, 55.7, 55.2, 52.3, 37.2, 35.1, 8.5, 7.5, 7.3, 7.1.
Supplementary Figure 143: IR for compound 25
Supplementary Figure 144: $^1$H-NMR for compound 26

$^1$H NMR (250 MHz, Chloroform-δ) δ 7.32 (d, $J = 8.6$ Hz, 2H), 7.15 (d, $J = 8.6$ Hz, 2H), 6.84 (d, $J = 6.4$ Hz, 2H), 6.81 (d, $J = 6.2$ Hz, 2H), 4.22 – 4.03 (m, 4H), 3.92 (d, $J = 13.3$ Hz, 1H), 3.84 – 3.62 (m, 9H), 3.68 – 3.24 (m, 5H), 3.11 (dd, $J = 14.2$, 7.9 Hz, 1H), 2.95 (dd, $J = 14.0$, 4.7 Hz, 1H), 1.32 – 1.17 (m, 6H).
**Supplementary Figure 145: $^{19}$F NMR for compound 26**

$^{19}$F NMR (235 MHz, Chloroform) δ -68.56.
Supplementary Figure 146: $^{13}$C NMR for compound 26

$^{13}$C NMR (63 MHz, Chloroform-d) δ 171.4, 159.1, 159.0, 130.5, 130.5, 130.3, 130.1, 127.2 (q, $J = 290.7$ Hz), 113.7, 113.7, 60.6, 60.2, 59.4 (q, $J = 24.2$ Hz), 57.8, 55.3, 55.2, 53.6, 51.6, 50.4, 14.3, 14.2.
Supplementary Figure 147: IR for compound 26
Supplementary Figure 148: $^1$H-NMR for compound 27

$^1$H NMR (250 MHz, Chloroform-$d$) δ 7.25 – 7.08 (m, 4H), 6.87 – 6.70 (m, 4H), 5.93 – 5.59 (m, 2H), 5.23 – 4.98 (m, 4H), 3.75 (s, 3H), 3.72 – 3.63 (m, 2H), 3.58 (d, $J = 17.8$ Hz, 2H), 3.44 (dt, $J = 8.5$, 4.3 Hz, 1H), 3.32 (d, $J = 13.2$ Hz, 1H), 3.19 (dd, $J = 18.9$, 6.3 Hz, 1H), 3.06 (dd, $J = 14.7$, 6.0 Hz, 1H), 2.88 (dd, $J = 6.9$, 5.0 Hz, 1H), 2.80 (dd, $J = 11.4$, 5.9 Hz, 1H), 2.57 (dd, $J = 13.7$, 4.3 Hz, 1H).
Supplementary Figure 149: $^{19}F$ NMR for compound 27

$^{19}F$ NMR (235 MHz, Chloroform) $\delta$ -68.3.
Supplementary Figure 150: $^{13}$C NMR for compound 27

$^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 158.9, 137.0, 135.5, 131.6, 131.0, 130.3, 130.0, 127.5 (q, $J = 289.8$ Hz), 117.9, 117.5, 113.8, 113.7, 58.0, 57.7 (q, $J = 24.0$ Hz), 56.8, 55.3, 53.7, 53.4, 50.5.
Supplementary Figure 151: $IR$ for compound 27
Supplementary Figure 152: $^1$H-NMR for compound 28

$^1$H NMR (250 MHz, Chloroform-d) δ 3.72 – 3.40 (m, 5H), 2.97 – 2.77 (m, 2H), 2.71 (dd, $J = 13.9, 4.6$ Hz, 2H), 2.61 (q, $J = 7.2$ Hz, 2H), 2.23 (t, $J = 2.3$ Hz, 1H), 2.18 (t, $J = 2.2$ Hz, 1H), 1.10 (t, $J = 7.0$ Hz, 3H), 1.07 (t, $J = 7.1$ Hz, 3H).
Supplementary Figure 153: $^{19}$F NMR for compound 28

$^{19}$F NMR (235 MHz, Chloroform-$d$) $\delta$ -69.41.
Supplementary Figure 154: $^{13}$C NMR for compound 28

$^{13}$C NMR (63 MHz, Chloroform-δ) δ 127.0 (q, $J = 289.2$ Hz), 80.8, 78.6, 73.1, 72.4, 60.3 (q, $J = 24.7$ Hz), 49.6 (d, $J = 1.6$ Hz), 48.0, 44.3, 41.9, 40.1, 13.9, 12.9 (q, $J = 1.5$ Hz).
Supplementary Figure 155: IR for compound 28
Supplementary Figure 156: $^1$H-NMR for compound 29

$^1$H NMR (250 MHz, Chloroform-d) δ 7.28 – 7.08 (m, 4H), 6.75 (d, $J = 8.3$ Hz, 4H), 3.84 (d, $J = 13.6$ Hz, 1H), 3.76 – 3.43 (m, 10H), 3.37 (dd, $J = 5.8$, 2.3 Hz, 2H), 3.26 (s, 2H), 2.91 (dd, $J = 13.4$, 8.9 Hz, 1H), 2.76 (dd, $J = 13.6$, 4.5 Hz, 1H), 2.22 – 2.09 (m, 2H).
Supplementary Figure 157: $^{19}$F NMR for compound 29

$^{19}$F NMR (235 MHz, Chloroform) δ -68.86.
Supplementary Figure 158: $^{13}$C NMR for compound 29

$^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 159.1, 130.5, 130.2, 130.0, 127.1 (q, $J = 288.9$ Hz), 113.9 (d, $J = 4.6$ Hz), 80.6, 78.2, 73.7, 72.8, 58.7 (q, $J = 24.8$ Hz), 57.6, 55.3, 53.3, 49.5, 41.3, 39.9.
Supplementary Figure 159: IR for compound 29
Supplementary Figure 160: $^1$H-NMR for compound 30

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 7.53 – 7.40 (m, 4H), 7.38 – 7.23 (m, 6H), 3.87 (d, $J = 17.3$ Hz, 1H), 3.82 – 3.62 (m, 4H), 3.03 (dd, $J = 13.8$, 7.5 Hz, 1H), 2.90 (dd, $J = 13.7$, 4.9 Hz, 1H), 2.73 (dd, $J = 12.9$, 7.1 Hz, 1H), 2.58 (dd, $J = 12.9$, 7.6 Hz, 1H), 2.41 (dd, $J = 12.3$, 11.1, 7.3 Hz, 2H), 1.87 (d, $J = 20.1$, 6.7 Hz, 2H), 1.05 – 0.92 (m, 12H).
Supplementary Figure 161: $^{19}$F NMR for compound 30

$^{19}$F NMR (235 MHz, Chloroform) $\delta$ -68.95.
Supplementary Figure 162: $^{13}C$ NMR for compound 30

$^{13}C$ NMR (63 MHz, Chloroform-d) δ 131.9, 131.7, 128.4, 128.1, 127.2 (q, $J = 289.1$ Hz), 123.5, 123.4, 86.6, 85.7, 84.5, 84.4, 62.8, 61.4 (q, $J = 24.7$ Hz), 59.2, 51.4, 42.9, 41.4, 26.7, 26.2, 20.9, 20.7, 20.5.
Supplementary Figure 163: IR for compound 30
Supplementary Figure 164: $^1$H-NMR for compound 31

$^1$H NMR (250 MHz, Chloroform-d) δ 7.41 – 7.24 (m, 4H), 7.23 – 7.03 (m, 6H), 3.76 (s, 2H), 3.73 – 3.56 (m, 3H), 2.96 (dJ = 6.0 Hz, 2H), 2.84 – 2.67 (m, 1H), 2.50 (t, J = 9.7, 7.8 Hz, 1H), 1.86 (qJ = 11.2, 10.7 Hz, 4H), 1.77 – 1.60 (m, 4H), 1.50 (d, J = 11.3 Hz, 2H), 1.43 – 0.87 (m, 10H).
Supplementary Figure 165: $^{19}$F NMR for compound 31

$^{19}$F NMR (235 MHz, Chloroform-$d$) $\delta$ -69.58.
Supplementary Figure 166: $^{13}$C NMR for compound 31

$^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 131.7, 128.3, 128.3, 128.0, 127.5 (q, $J = 290.4$ Hz), 123.7, 123.6, 88.2, 87.1, 84.9, 83.6, 62.3, 59.4 (q, $J = 24.5$ Hz), 58.3, 47.0, 40.0, 36.6, 32.6, 31.3, 30.5, 30.2, 26.3, 26.1, 26.1, 26.0.
Supplementary Figure 167: IR for compound 31
Supplementary Figure 168: $^1$H-NMR for compound 32

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 7.3 – 7.0 (m, 10H), 4.0 – 3.8 (m, 6H), 3.7 – 3.5 (m, 4H), 3.3 – 3.2 (m, 1H), 3.2 – 2.9 (m, 2H), 2.8 – 2.5 (m, 8H), 1.4 (s, 9H), 1.4 (s, 9H).
Supplementary Figure 169: $^{19}\text{F NMR for compound 32}$

$^{19}\text{F NMR (235 MHz, Chloroform$\delta$) $\delta$ -69.5.}$
Supplementary Figure 170: $^{13}$C NMR for compound 32

$^{13}$C NMR (63 MHz, Chloroform-$d$) δ 156.3, 156.1, 139.5, 139.2, 128.8, 128.7, 128.6, 128.5, 126.8 (q, $J = 290.4$ Hz), 126.5, 126.4, 79.7, 79.6, 60.7 (q, $J = 24.0$ Hz), 55.1, 53.7, 51.8, 49.4, 47.9, 47.0, 36.4, 33.2, 28.4, 28.4.
Supplementary Figure 171: IR for compound 32
Supplementary Figure 172: $^1$H-NMR for compound 33

$^1$H NMR (250 MHz, Chloroform$d_6$) δ 4.4 (dp, $J = 12.4$, 6.2 Hz, 2H), 3.7 (dt, $J = 12.0$, 4.9 Hz, 4H), 3.1 (t, $J = 6.6$ Hz, 1H), 3.0 (t, $J = 6.8$ Hz, 1H), 2.7 (td, $J = 6.4$, 3.1 Hz, 2H), 2.7 – 2.3 (m, 3H), 0.8 (s, 18H), -0.0 (s, 12H).
Supplementary Figure 173: $^{19}$F NMR for compound 33

$^{19}$F NMR (235 MHz, Chloroform) $\delta$ -72.1.
Supplementary Figure 174: $^{13}$C NMR for compound 33

$^{13}$C NMR (63 MHz, Chloroform-d) δ 125.9 (q, $J = 282.8$ Hz), 65.5, 65.5 (q, $J = 25.7$ Hz), 65.0, 62.7, 62.1, 57.0 (d, $J = 2.0$ Hz), 25.9, 18.1, -4.9.
Supplementary Figure 175: IR for compound 33
Supplementary Figure 176: $^1$H-NMR for compound 34

$^1$H NMR (250 MHz, Chloroform-d) δ 3.76 – 3.59 (m, 8H), 3.63 – 3.49 (m, 3H), 3.47 (t, $J = 7.3$ Hz, 1H), 3.41 – 3.16 (m, 4H), 2.80 – 2.59 (m, 1H), 2.62 – 2.47 (m, 2H).
Supplementary Figure 177: $^{19}$F NMR for compound 34

$^{19}$F NMR (235 MHz, Chloroform) $\delta$ -72.00.
Supplementary Figure 178: $^{13}$C NMR for compound 34

$^{13}$C NMR (63 MHz, Chloroform-$d$) δ 173.3, 173.1, 125.6 (q, $J = 282.9$ Hz), 64.5 (q, $J = 25.8$ Hz), 57.7, 56.9, 56.0 (q, $J = 2.1$ Hz), 55.3, 52.0, 34.5, 33.7.
Supplementary Figure 179: IR for compound 34
Supplementary Figure 180: $^1$H-NMR for compound 35

$^1$H NMR (250 MHz, Methylenechloride) $\delta$ 11.26 (bs, 2H), 4.10 – 3.10 (m, 6H), 2.92 (d, $J = 38.7$, 7.0 Hz, 4H), 2.23 – 1.97 (m, 4H), 1.79 (d, $J = 6.4$ Hz, 4H).
Supplementary Figure 181: $^{19}F$ NMR for compound 35

$^{19}F$ NMR (235 MHz, Methylenechloride$\text{d}_2$) $\delta$ -66.21 (s, 3F), -74.39 (s, 6F).
Supplementary Figure 182: $^{13}\text{C NMR for compound 35}$

$^{13}\text{C NMR (63 MHz, Methylenechloride-d2)}$ δ 126.1 (q, $J = 294.0$ Hz), 114.3 (q, $J = 291.1$ Hz), 58.8 (q, $J = 26.7$ Hz), 56.0, 52.5 (q, $J = 2.4$ Hz), 48.9, 24.4, 23.5.
Supplementary Figure 183: *IR for compound 35*
Supplementary Figure 184: $^1$H-NMR for compound 36

$^1$H NMR (250 MHz, Chloroform-$d$) δ 3.16 (ddq, $J = 12.5, 9.0, 4.5, 3.6$ Hz, 1H), 2.90 – 2.57 (m, 5H), 2.56 – 2.32 (m, 5H), 1.67 – 1.22 (m, 12H).
Supplementary Figure 185: $^{19}$F NMR for compound 36

$^{19}$F NMR (235 MHz, Chloroform) $\delta$ -68.90.
Supplementary Figure 186: $^{13}$C NMR for compound 36

$^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 127.2 (q, $J = 290.6$ Hz), 64.3 (q, $J = 23.8$ Hz), 55.1 (q, $J = 1.7$ Hz), 54.8, 51.0, 27.1, 26.3, 24.8, 24.5.
Supplementary Figure 187: IR for compound 36
Supplementary Figure 188: $^1$H-NMR for compound 37

$^1$H NMR (250 MHz, Chloroform-$d$) δ 3.77 – 3.49 (m, 2H), 3.35 – 3.10 (m, 1H), 3.06 – 2.25 (m, 8H), 2.13 – 1.76 (m, 4H), 1.74 – 1.34 (m, 4H), 1.32 – 1.07 (m, 2H), 0.88 (s, 18H), 0.19 – 0.08 (m, 12H).
Supplementary Figure 189: $^{19}$F NMR for compound 37

$^{19}$F NMR (235 MHz, CDCl$_3$) $\delta$ -68.97, -69.44, -69.48, -69.52
Supplementary Figure 190: $^{13}$C NMR for compound 37

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 129.3, 129.3, 129.2, 124.7, 124.7, 124.6, 69.1, 69.0, 68.9, 68.7, 68.5, 68.5, 64.5, 64.1, 63.8, 63.7, 63.7, 63.4, 63.3, 63.0, 62.9, 62.7, 62.1, 62.1, 61.6, 61.3, 58.9, 58.7, 57.6, 56.5, 54.1, 54.0, 53.8, 53.7, 53.4, 51.3, 50.3, 49.5, 49.4, 34.5, 34.4, 34.1, 26.0, 26.0, 18.3, 18.3, -4.5, -4.5.
Supplementary Figure 191: IR for compound 37
Supplementary Figure 192: $^1$H-NMR for compound 38

$^1$H NMR (250 MHz, Chloroform-d) δ 3.54 – 3.30 (m, 4H), 3.21 (p, J = 8.4 Hz, 1H), 3.08 – 2.36 (m, 8H), 2.06 (t, J = 10.2 Hz, 1H), 1.95 – 1.35 (m, 9H), 0.89 (s, 20H), 0.03 (s, 12H).
Supplementary Figure 193: $^{19}$F NMR for compound 38

$^{19}$F NMR (235 MHz, CDCl$_3$) δ -68.87, -68.96, -69.00, -69.12.
Supplementary Figure 194: $^{13}$C NMR for compound 38

$^{13}$C NMR (63 MHz, Chloroform-$d$): $\delta$ 127.2 ($q, J = 290.5$ Hz), 64.6 ($q, J = 23.7, 23.2$ Hz), 64.0 ($q, J = 24.0$ Hz), 57.8, 57.7, 57.4, 55.0, 54.9, 54.8, 54.6, 54.5, 52.8, 51.9, 51.8, 50.3, 50.1, 39.9, 39.8, 39.3, 39.3, 39.1, 27.5, 27.2, 27.1, 26.1, 26.0, 25.9, 25.7, 25.2, 25.2, 25.1, 18.5, 18.4, -5.2, -5.3.
Supplementary Figure 195: IR for compound 38
Supplementary Figure 196: $^1$H-NMR for compound 39

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 7.27 – 7.03 (m, 10H), 3.35 – 3.21 (m, 1H), 3.01 (d, $J = 11.2$ Hz, 1H), 2.85 (t, $J = 11.3$ Hz, 3H), 2.64 (dd, $J = 13.1$, 9.2 Hz, 2H), 2.56 – 2.38 (m, 6H), 2.02 (q, $J = 11.0$ Hz, 2H), 1.54 (q, $J = 16.5$, 14.8 Hz, 7H), 1.40 – 1.05 (m, 3H).
Supplementary Figure 197: $^{19}$F NMR for compound 39

$^{19}$F NMR (235 MHz, Chloroform) $\delta$ -68.79.
Supplementary Figure 198: $^{13}$C NMR for compound 39

$^{13}$C NMR (63 MHz, Chloroform) δ 140.8, 140.7, 129.2, 128.3, 128.3, 126.2 (q, $J = 291.0$ Hz), 126.0, 125.9, 63.7 (q, $J = 24.2$ Hz), 54.4, 54.1, 51.3, 48.8, 43.3, 43.2, 38.2, 37.8, 33.3, 33.1, 32.2, 32.1.
Supplementary Figure 199: IR for compound 39
Supplementary Figure 200: $^1$H-NMR for compound 40

$^1$H NMR (250 MHz, Methylenechlorid$\delta$) $\delta$ 9.53 (s, 2H), 3.98 (s, 4H), 3.91 – 3.75 (m, 2H), 3.73 – 3.52 (m, 4H), 3.51 – 3.07 (m, 4H), 3.07 – 2.87 (m, 2H), 2.80 – 2.57 (m, 2H).
Supplementary Figure 201: $^{19}$F NMR for compound 40
Supplementary Figure 202: $^{13}C$ NMR for compound 40

$^{13}C$ NMR (63 MHz, Methylenechloride-d$_2$) δ 161.3 (q, J = 38.1 Hz), 125.7 (q, J = 293.0 Hz), 114.0 (q, J = 289.8, 286.9 Hz), 67.5, 64.1, 62.0 (q, J = 26.2 Hz), 53.3 (q, J = 2.8 Hz), 49.8.
Supplementary Figure 203: IR for compound 40
Supplementary Figure 204: \(^1\text{H-NMR for compound 41}\)

\(^1\text{H NMR (250 MHz, Chloroform)}\delta 7.38 – 7.05 (m, 10H), 3.42 (d, \(J = 6.4\) Hz, 4H), 3.13 (td, \(J = 8.7, 3.3\) Hz, 1H), 2.90 – 2.18 (m, 18H).
Supplementary Figure 205: $^{19}$F NMR for compound 41

$^{19}$F NMR (235 MHz, Chloroform) $\delta$ -69.19.
Supplementary Figure 206: $^{13}$C NMR for compound 41

$^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 138.1, 138.0, 129.3, 129.3, 128.3, 128.3, 127.2, 127.2, 126.8 (q, $J = 289.9$ Hz), 63.4 (q, $J = 24.4$ Hz), 63.1, 63.1, 54.0, 53.4, 53.2, 49.5.
Supplementary Figure 207: IR for compound 41
Supplementary Figure 208: $^1$H-NMR for compound 42

$^1$H NMR (250 MHz, Chloroform-δ) δ 8.17 (dd, $J = 4.9$, 1.9 Hz, 2H), 7.53 – 7.36 (m, 2H), 6.69 – 6.53 (m, 4H), 3.63 – 3.25 (m, 9H), 3.09 – 2.74 (m, 5H), 2.76 – 2.47 (m, 5H).
Supplementary Figure 209: $^{19}F$ NMR for compound 42

$^{19}F$ NMR (235 MHz, Chloroform-$d$) $\delta$ -69.33.
Supplementary Figure 210: $^{13}$C NMR for compound 42

$^{13}$C NMR (63 MHz, Chloroform-d$_3$) δ 159.6 (d, $J = 7.8$ Hz), 148.0 (d, $J = 1.6$ Hz), 137.6, 126.6 (q, $J = 289.1$ Hz), 107.2 (d, $J = 4.3$ Hz), 63.4 (q, $J = 24.8$ Hz), 54.0 (q, $J = 2.0$ Hz), 53.3, 49.6, 46.3, 45.4.
Supplementary Figure 211: IR for compound 42
Supplementary Figure 212: $^1$H-NMR for compound 43

$^1$H NMR (250 MHz, Chloroform-d) $\delta$ 3.30 (dd, $J = 8.6$, 5.5 Hz, 1H), 2.94 (qd, $J = 11.4$, 3.8 Hz, 7H), 2.62 (dddd, $J = 35.2$, 23.9, 13.4, 6.3 Hz, 11H), 1.90 (s, 5H), 1.71 (dd, $J = 25.8$, 5.3 Hz, 14H), 1.62 – 1.54 (m, 17H).
Supplementary Figure 213: $^{19}$F NMR for compound 43

$^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -69.56.
Supplementary Figure 214: $^{13}$C NMR for compound 43

$^{13}$C NMR (63 MHz, Chloroform-d$_6$) δ 127.6 (q, $J = 291.2\text{ Hz}$), 63.8 (q, $J = 23.9\text{ Hz}$), 63.3, 59.4, 55.3 (q, $J = 1.5\text{ Hz}$), 31.6, 30.7, 25.9, 25.8, 25.7, 25.7.
Supplementary Figure 215: IR for compound 43
1H NMR (250 MHz, Chloroform-d) δ 8.19 – 8.06 (m, 1H), 7.94 – 7.69 (m, 2H), 7.61 – 7.44 (m, 2H), 7.50 – 7.35 (m, 2H), 4.36 (d, J = 13.0 Hz, 1H), 4.27 (d, J = 13.2 Hz, 1H), 3.47 (dd, J = 8.6, 3.5 Hz, 1H), 2.87 (dd, J = 12.7, 10.6 Hz, 1H), 2.64 (dd, J = 12.7, 3.4 Hz, 1H), 2.49 (q, J = 2.0 Hz, 3H), 2.46 – 1.88 (m, 3H), 1.39 – 0.92 (m, 8H), 0.87 (t, J = 6.9 Hz, 3H).
Supplementary Figure 217: $^{19}$F NMR for compound 44

$^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -66.63.
Supplementary Figure 218: $^{13}$C NMR for compound 44

$^{13}$C NMR (63 MHz, Chloroform-d) δ 134.2, 134.0, 132.4, 128.9, 128.7, 127.7 (q, J = 292.0 Hz), 126.2, 125.9, 125.3, 124.4, 60.9 (q, J = 24.4 Hz), 58.4, 49.3, 45.2 (q, J = 2.0 Hz), 35.9, 31.8, 29.8, 27.0, 22.7, 14.2.
Supplementary Figure 219: IR for compound 44
Supplementary Figure 220: $^1$H-NMR for compound 45

$^1$H NMR (300 MHz, Chloroform-d) δ 8.33 (d, $J = 7.2$ Hz, 1H), 7.86 (dd, $J = 7.0$, 2.3 Hz, 1H), 7.80 (d, $J = 8.2$ Hz, 1H), 7.57 – 7.40 (m, 4H), 4.40 (d, $J = 13.4$ Hz, 1H), 4.31 (d, $J = 13.4$ Hz, 1H), 3.50 (pd, $J = 8.8$, 3.9 Hz, 1H), 3.02 (dd, $J = 13.1$, 9.3 Hz, 1H), 2.65 (dd, $J = 13.1$, 3.9 Hz, 1H), 2.56 – 2.39 (m, 7H), 1.80 – 1.66 (m, 4H).
Supplementary Figure 221: COSY NMR for compound 45
Supplementary Figure 222: $^{19}F$ NMR for compound 45

$^{19}F$ NMR (235 MHz, Chloroform-$d$) $\delta$ -67.8.
Supplementary Figure 223: $^{13}$C NMR for compound 45

$^{13}$C NMR (75 MHz, Chloroform-d$_6$) δ 134.5, 134.0, 132.5, 128.5, 128.2, 127.6, 127.4 (q, $J = 291.7$ Hz), 125.8, 125.8, 125.3, 124.9, 62.7 (q, $J = 24.1$ Hz), 58.3, 54.4, 52.3, 36.8, 23.6.
Supplementary Figure 224: HSQC NMR for compound 45
Supplementary Figure 225: HMBC NMR for compound 45
GC-MS TIC for compound 45

Chemical Formula: C_{10}H_{13}N^+
Exact Mass: 84.08

Chemical Formula: C_{11}H_{14}^+
Exact Mass: 141.07

Chemical Formula: C_{19}H_{23}F_{3}N_{2}^2+
Exact Mass: 336.18
Supplementary Figure 226: IR for compound 45
Supplementary Figure 227: \(^1\)H-NMR for compound 46

\(^1\)H NMR (250 MHz, Chloroform-\(d\)) \(\delta\) 8.32 (dd, \(J = 20.1, 7.6\) Hz, 1H), 7.85 (dd, \(J = 16.0, 8.2\) Hz, 2H), 7.63 – 7.36 (m, 4H), 4.51 – 4.23 (m, 2H), 3.47 (dq, \(J = 12.1, 4.9, 3.5\) Hz, 1H), 3.13 (dd, \(J = 13.8, 9.4\) Hz, 1H), 2.76 (dd, \(J = 16.7, 14.3\) Hz, 3H), 2.55 – 2.45 (m, 3H), 2.41 – 1.99 (m, 2H), 1.57 (d, \(J = 11.6\) Hz, 2H), 1.51 – 1.40 (m, 2H), 1.34 – 1.13 (m, 2H), 1.02 (t, \(J = 5.9\) Hz, 3H).
Supplementary Figure 228: $^{19}$F NMR for compound 46

$^{19}$F NMR (235 MHz, Chloroform-$d$) δ -67.46.
Supplementary Figure 229: $^{13}$C NMR for compound 46

$^{13}$C NMR (63 MHz, Chloroform-d$_3$) 8 134.6, 134.5, 134.0, 132.6, 128.5, 128.5, 128.2, 127.7 (q, J = 291.6, 291.1 Hz), 127.5, 125.9, 125.7, 125.3, 125.2, 124.9, 62.2 (q, J = 23.4 Hz), 61.0 (q, J = 23.4 Hz), 58.7, 58.4, 56.5, 56.2, 52.8, 52.2, 51.5, 50.2, 36.8, 36.6, 34.8, 34.3, 26.1, 23.8, 23.0, 19.0, 17.8.
Supplementary Figure 230: IR for compound 46
Supplementary Figure 231: $^1$H-NMR for compound 47

$^1$H NMR (250 MHz, Chloroform-d) δ 8.32 (d, $J = 8.6$ Hz, 1H), 7.97 – 7.76 (m, 2H), 7.64 – 7.38 (m, 4H), 4.51 – 4.27 (m, 2H), 3.48 – 3.24 (m, 1H), 2.94 (hept, $J = 6.6$ Hz, 2H), 2.78 (d, $J = 5.8$ Hz, 2H), 2.50 (s, 3H), 0.96 (s, 6H), 0.93 (s, 6H).
Supplementary Figure 232: $^{19}\text{F} \text{NMR for compound 47}$

$^{19}\text{F} \text{NMR (235 MHz, Chloroform-d)} \delta -66.27.$
Supplementary Figure 233: $^{13}$C NMR for compound 47

$^{13}$C NMR (63 MHz, Chloroform-d) δ 134.7, 134.0, 132.6, 130.5, 128.5, 128.1, 127.4, 125.8, 125.7, 125.3, 125.1, 63.6 (q, $J = 22.0$ Hz), 59.1, 48.0, 42.7, 36.4, 20.9, 20.6.
Supplementary Figure 234: IR for compound 47
Supplementary Figure 235: \(^1\)H-NMR for compound 48

\(^1\)H NMR (250 MHz, Chloroform-\(d\)) \(\delta\) 8.15 (d, \(J = 8.2\) Hz, 1H), 7.94 – 7.72 (m, 2H), 7.64 – 7.34 (m, 4H), 4.32 (s, 2H), 3.59 (bs, \(J = 9.2\) Hz, 6H), 3.49 (ddd, \(J = 11.2, 8.4, 3.3\) Hz, 2H), 2.90 (t, \(J = 11.4\) Hz, 1H), 2.71 (dd, \(J = 11.9, 3.5\) Hz, 1H), 2.45 (s, 3H), 2.02 – 1.89 (m, 3H), 1.66 – 1.41 (m, 6H), 1.34 (d, \(J = 17.1\) Hz, 6H).
Supplementary Figure 236: $^{19}$F NMR for compound 48

$^{19}$F NMR (235 MHz, Chloroform-$d$) δ -66.63.
Supplementary Figure 237: $^{13}$C NMR for compound 48

$^{13}$C NMR (63 MHz, Chloroform-d): δ 134.3, 133.8, 132.4, 128.9, 128.7, 128.2, 127.1 (q, $J = 292.4$ Hz), 126.5, 125.9, 125.3, 124.6, 62.6 (q, $J = 24.8$ Hz), 58.6, 51.1, 41.8, 36.4, 36.1 – 35.6 (m), 35.1, 29.4.
Supplementary Figure 238: IR for compound 48
Supplementary Figure 239: $^1$H-NMR for compound 49
Supplementary Figure 240: $^{19}$F NMR for compound 49

$^{19}$F NMR (235 MHz, Chloroform-$d$) δ -66.22.
Supplementary Figure 241: $^{13}C$ NMR for compound 49

$^{13}C$ NMR (63 MHz, Chloroform-d) $\delta$ 146.8, 134.0, 133.9, 132.4, 129.4, 128.5 (d, $J = 1.3$ Hz), 127.8, 127.7 (q, $J = 293.6$ Hz), 126.0, 125.7, 125.1, 124.9, 116.2, 112.1, 60.5 (q, $J = 22.9$ Hz), 59.6, 47.7, 46.0, 35.9, 11.5.
Supplementary Figure 242: IR for compound 49
Supplementary Figure 243: $^1$H-NMR for compound 50

$^1$H NMR (250 MHz, Chloroform-d) δ 8.14 (d, J = 7.2 Hz, 1H), 7.84 – 7.68 (m, 2H), 7.56 (d, J = 7.8 Hz, 1H), 7.52 – 7.28 (m, 5H), 7.14 (dd, J = 14.2, 7.3 Hz, 2H), 4.27 (s, 2H), 3.51 (ddq, J = 12.7, 8.4, 4.3 Hz, 1H), 3.29 (dd, J = 13.6, 8.1 Hz, 1H), 3.16 (dd, J = 13.6, 4.2 Hz, 1H), 2.54 (s, 3H), 2.34 (s, 3H).
Supplementary Figure 244: $^{19}$F NMR for compound 50

$^{19}$F NMR (235 MHz, Chloroform-d): $\delta$ -59.64 (s, 3F), -67.66 (s, 3F).
Supplementary Figure 245: $^{13}$C NMR for compound 50

$^{13}$C NMR (65 MHz, Chloroform-d) δ 153.1, 134.0, 133.0, 132.4, 129.6, 128.6, 128.3, 127.7 (d, $J = 5.5$ Hz), 127.5, 127.5, 127.1, 126.5 (d, $J = 20.7$ Hz), 126.1, 125.8, 125.4, 124.7, 124.7, 124.6, 122.0, 62.7 (q, $J = 24.0$ Hz), 58.2, 53.8, 45.5, 36.4.
Supplementary Figure 246: IR for compound 50
Supplementary Figure 247: $^1$H-NMR for compound 51

$^1$H NMR (250 MHz, Chloroform-d) $\delta$ 8.32 – 8.08 (m, 1H), 7.99 – 7.72 (m, 2H), 7.64 – 7.36 (m, 4H), 7.08 (d, $J = 8.1$ Hz, 1H), 7.04 (d, $J = 8.3$ Hz, 1H), 6.79 (d, $J = 8.4$ Hz, 1H), 6.74 (d, $J = 8.4$ Hz, 1H), 4.44 – 4.19 (m, 2H), 3.86 – 3.61 (m, 7H), 3.55 – 3.27 (m, 3H), 3.23 – 3.06 (m, 1H), 3.03 – 2.68 (m, 1H), 2.54 – 2.33 (m, 3H), 1.75 – 1.41 (m, 3H), 0.91 – 0.60 (m, 6H).
Supplementary Figure 248: $^{19}$F NMR for compound 51

$^{19}$F NMR (235 MHz, Chloroform-$d$) δ -66.1, -66.6.
Supplementary Figure 249: $^{13}$C NMR for compound 51

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 173.8, 173.7, 158.8, 134.3, 134.1, 134.0, 132.4, 132.3, 131.0, 130.8, 130.3, 130.2, 128.6, 128.6, 128.2, 128.1, 127.3, 126.0, 125.9, 125.7, 125.3, 124.6, 124.3, 113.6, 63.8, 63.5, 63.3, 62.9, 62.5, 60.6, 60.5, 58.2, 58.1, 56.0, 55.8, 55.2, 55.2, 51.1, 51.1, 48.5, 48.1, 39.3, 38.6, 36.9, 36.3, 30.9, 24.7, 24.6, 22.8, 22.7, 22.3, 22.2.
Supplementary Figure 250: IR for compound 51
Supplementary Figure 251: \(^1\)H-NMR for compound 52

\(^1\)H NMR (250 MHz, Chloroform-\(d\)) \(\delta\) 7.75 – 7.59 (m, 2H), 7.44 (d, \(J = 8.2\) Hz, 1H), 7.39 – 7.16 (m, 4H), 7.11 (d, \(J = 7.1\) Hz, 1H), 7.03 (s, 1H), 4.24 – 3.98 (m, 4H), 3.80 (ddp, \(J = 12.9, 8.6, 4.6\) Hz, 1H), 2.53 – 2.17 (m, 3H).
Supplementary Figure 252: $^{19}$F NMR for compound 52

$^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -67.00.
Supplementary Figure 253: $^{13}$C NMR for compound 52

$^{13}$C NMR (65 MHz, Chloroform-d) δ 140.4, 133.9, 133.1, 132.1, 130.6, 128.7, 128.4, 127.7, 126.6 (q, J = 292.7 Hz), 126.3, 125.8, 125.1, 123.9, 93.2, 63.1 (q, J = 25.0 Hz), 58.7, 48.7 (q, J = 2.2 Hz), 35.2.
Supplementary Figure 254: IR for compound 52
Supplementary Figure 255: $^1$H-NMR for compound 53

$^1$H NMR (250 MHz, Chloroform-d) $\delta$ 7.59 – 7.32 (m, 7H), 7.22 – 7.06 (m, 2H), 6.76 (t, $J = 7.5$ Hz, 1H), 6.52 (t, $J = 7.6$ Hz, 1H), 4.17 – 3.85 (m, 3H), 3.60 (d, $J = 11.4$, 8.2, 3.3 Hz, 1H), 3.33 (dd, $J = 13.9$, 3.4 Hz, 1H), 2.57 (s, 3H).
Supplementary Figure 256: $^{19}$F NMR for compound 53

$^{19}$F NMR (235 MHz, Chloroform-$d$) δ -66.58.
Supplementary Figure 257: $^{13}C$ NMR for compound 53

$^{13}C$ NMR (65 MHz, Chloroform-$d$) δ 167.3, 133.7, 133.5, 133.2, 131.9, 131.8, 128.1, 126.8 (q, $J = 293.3$ Hz), 123.7, 123.1, 58.4, 57.6 (q, $J = 24.5$ Hz), 36.1, 33.9 (q, $J = 2.6$ Hz).
Supplementary Figure 258: IR for compound 53
**Supplementary Figure 259: $^1$H-NMR for compound 54**

$^1$H NMR (300 MHz, Chloroform-d) 6.789 (d, $J = 8.2$ Hz, 1H), 7.81 (d, $J = 8.3$ Hz, 1H), 7.80 - 7.74 (m, 1H), 7.72 (d, $J = 7.9$ Hz, 1H), 7.52 (d, $J = 7.5$ Hz, 1H), 7.37 - 7.29 (m, 2H), 7.25 - 7.20 (m, 2H), 7.18 (d, $J = 7.2$ Hz, 1H), 7.14 - 7.05 (m, 1H), 7.01 (d, $J = 3.2$ Hz, 1H), 6.53 (d, $J = 3.2$ Hz, 1H), 4.49 (dd, $J = 15.0$, 4.5 Hz, 1H), 4.38 (dd, $J = 15.0$, 8.6 Hz, 1H), 4.29 (d, $J = 13.5$ Hz, 1H), 4.23 (d, $J = 13.3$ Hz, 1H), 3.85 (pdd, $J = 8.4$, 4.5 Hz, 1H), 2.68 (s, 3H).
Supplementary Figure 260: COSY NMR for compound 54
Supplementary Figure 261: $^{19}F$ NMR for compound 54

$^{19}F$ NMR (282 MHz, Chloroform$\delta$) δ -66.82 (d, $J = 8.4$ Hz).
Supplementary Figure 262: $^{13}$C NMR for compound 54

$^{13}$C NMR (75 MHz, Chloroform-$d$) δ 135.8, 133.8, 133.1, 132.1, 129.0, 128.9, 128.7, 128.4, 127.6, 126.1, 125.7, 125.1, 124.1, 121.9, 121.3, 119.7, 108.9, 101.8, 62.4 (q, $J = 24.4$ Hz), 58.8, 43.5 (q, $J = 2.4$ Hz), 35.7.
Supplementary Figure 263: HSQC NMR for compound 54
Supplementary Figure 264: *HMBC NMR for compound 54*
Supplementary Figure 265: IR for compound 54
Supplementary Figure 266: $^1$H-NMR for compound 55

$^1$H NMR (300 MHz, Chloroform-d): 8.27 (d, $J = 4.7$ Hz, 1H), 7.94 – 7.86 (m, 1H), 7.76 (d, $J = 8.3$ Hz, 1H), 7.69 (d, $J = 8.3$ Hz, 1H), 7.48 (d, $J = 8.6$ Hz, 1H), 7.38 (d, $J = 7.6$ Hz, 1H), 7.31 – 7.22 (m, 1H), 7.17 – 7.03 (m, 3H), 6.96 (d, $J = 3.5$ Hz, 1H), 6.33 (d, $J = 3.5$ Hz, 1H), 4.58 (d, $J = 7.0$ Hz, 2H), 4.22 (d, $J = 13.5$ Hz, 1H), 4.19 – 4.07 (m, 2H), 2.61 (s, 3H).
Supplementary Figure 267: $^{19}\text{F} \text{NMR for compound 55}$

$^{19}\text{F} \text{NMR (282 MHz, Chloroform)} \delta \ -66.97 \ (d, J = 8.0 \text{ Hz})$. 
Supplementary Figure 268: $^{13}$C NMR for compound 55

$^{13}$C NMR (75 MHz, Chloroform-d) δ 147.3, 142.6, 133.7, 133.4, 132.1, 129.0, 128.6, 128.3, 128.2, 127.4, 127.0 ($q, J = 293.4$ Hz), 125.8, 125.5, 125.0, 123.9, 120.9, 115.9, 100.1, 62.4 ($q, J = 24.3$ Hz), 58.5, 41.2, 35.7.
Supplementary Figure 269: IR for compound 55
Supplementary Figure 270: $^1$H-NMR for compound 56

$^1$H NMR (250 MHz, Chloroform-d) δ 7.68 (dt, $J = 16.3$, 7.0 Hz, 4H), 7.46 (d, $J = 8.6$ Hz, 1H), 7.37 (ddd, $J = 8.2$, 6.8, 1.4 Hz, 1H), 7.31 – 7.13 (m, 3H), 7.14 – 6.98 (m, 2H), 6.82 (d, $J = 8.1$ Hz, 1H), 4.26 (d, $J = 7.7$ Hz, 1H), 4.23 (d, $J = 13.8$ Hz, 1H), 4.12 (d, $J = 13.0$ Hz, 1H), 3.66 (p, $J = 8.3$, 5.8 Hz, 1H), 2.66 – 2.56 (m, 4H).
Supplementary Figure 271: $^{19}$F NMR for compound 56

$^{19}$F NMR (235 MHz, Chloroform-d) δ -66.56.
Supplementary Figure 272: $^{13}C$ NMR for compound 56

$^{13}C$ NMR (65 MHz, Chloroform-$d$) δ 143.5, 143.4, 133.7, 133.1, 132.4, 131.8, 128.7, 128.4, 127.8, 126.7 (q, $J = 293.2$ Hz), 126.3, 125.9, 124.9, 123.4, 123.1, 122.3, 120.6, 108.7, 68.8 (q, $J = 26.7$ Hz), 58.5, 41.9 (d, $J = 2.2$ Hz), 35.8.
Supplementary Figure 273: IR for compound 56
Supplementary Figure 274: $^1$H-NMR for compound 57

$^1$H NMR (300 MHz, Chloroform-d) δ 7.78 – 7.65 (m, 4H), 7.58 (dd, $J = 8.4$ Hz, 1H), 7.38 (dd, $J = 8.8, 6.6$ Hz, 1H), 7.31 – 7.23 (m, 1H), 7.22 – 7.18 (m, 2H), 7.15 (d, $J = 8.1$ Hz, 2H), 6.48 (t, $J = 7.7$ Hz, 1H), 4.69 (dd, $J = 13.9, 3.5$ Hz, 1H), 4.57 (dd, $J = 13.9, 10.2$ Hz, 1H), 4.42 – 4.26 (m, 1H), 4.22 (s, 2H), 2.51 (s, 3H).
Supplementary Figure 275: $^{19}$F NMR for compound 57

$^{19}$F NMR (282 MHz, Chloroform) $\delta$ -66.87 (d, $J = 8.3$ Hz).
Supplementary Figure 276: $^{13}$C NMR for compound 57

$^{13}$C NMR (75 MHz, Chloroform-$d$) δ 149.1, 133.6, 133.1, 131.9, 128.5, 128.0, 127.7, 126.4, 125.7, 125.6, 124.8, 124.7, 124.0 (q, $J = 289.9$ Hz), 123.7, 121.8, 120.5, 117.4, 64.0 (q, $J = 25.2$ Hz), 59.2, 49.6 (d, $J = 2.7$ Hz), 34.6.
Supplementary Figure 277: IR for compound 57
Supplementary Figure 278: $^1$H-NMR for compound 58

$^1$H NMR (300 MHz, Chloroform-d) δ 7.98 – 7.89 (m, 1H), 7.68 – 7.59 (m, 2H), 7.24 (dd, $J = 15.1, 12.7, 5.0$ Hz, 5H), 7.03 (d, $J = 6.9$ Hz, 1H), 7.00 – 6.92 (m, 2H), 4.90 (dd, $J = 14.7, 10.3$ Hz, 1H), 4.66 (dd, $J = 14.7, 3.9$ Hz, 1H), 4.17 (d, $J = 12.9$ Hz, 1H), 4.11 (d, $J = 13.3$ Hz, 1H), 4.04 – 3.89 (m, 1H), 2.71 (q, $J = 2.0$ Hz, 3H).
Supplementary Figure 279: $^{19}$F NMR for compound 58

$^{19}$F NMR (282 MHz, Benzene-$d_6$) $\delta$ -66.98 (d, $J = 8.0$ Hz.)
Supplementary Figure 280: $^{13}$C NMR for compound 58

$^{13}$C NMR (75 MHz, Chloroform-d$_6$) δ 145.7, 133.5, 132.9, 132.4, 131.7, 128.6, 128.2, 127.7, 127.4, 126.5 (q, J = 292.6 Hz), 125.9, 125.6, 124.7, 123.7, 123.3, 120.1, 108.4, 60.8 (q, J = 25.2 Hz), 58.3, 44.3, 35.8.
Supplementary Figure 281: IR for compound 58
Supplementary Figure 282: $^1$H-NMR for compound 59

$^1$H NMR (300 MHz, Chloroform-d) 8 7.98 – 7.85 (m, 2H), 7.65 (d, $J = 8.2$ Hz, 1H), 7.48 (qd, $J = 9.5, 8.6, 5.1$ Hz, 4H), 7.30 (t, $J = 7.6$ Hz, 1H), 7.21 (d, $J = 6.9$ Hz, 1H), 7.09 (dt, $J = 6.4, 3.4$ Hz, 2H), 5.05 (dd, $J = 14.0, 11.0$ Hz, 1H), 4.59 (dd, $J = 14.0, 3.5$ Hz, 1H), 4.20 (dd, $J = 13.2, 8.7$ Hz, 2H), 4.09 (ddd, $J = 16.1, 8.1, 4.2$ Hz, 1H), 2.67 (q, $J = 2.0$ Hz, 3H).
Supplementary Figure 283: COSY NMR for compound 59
Supplementary Figure 284: $^{19}\text{F} \text{NMR for compound 59}$

$^{19}\text{F} \text{NMR (282 MHz, Chloroform-}d\text{)} \delta -66.99 \text{ (d, } J = 7.9 \text{ Hz).}
Supplementary Figure 285: $^{13}$C NMR for compound 59

$^{13}$C NMR (75 MHz, Chloroform-$d$) δ 165.0, 133.7, 132.4, 132.0, 130.3, 128.9, 128.7, 128.2, 127.9, 127.2, 126.9, 126.2, 125.7, 124.9, 124.1 (q, $J = 293.0$ Hz), 61.1 (q, $J = 25.9$ Hz), 58.2, 48.8, 35.7.
Supplementary Figure 286: HSQC NMR for compound 59
Supplementary Figure 287: HMBC NMR for compound 59
Supplementary Figure 288: NOESY NMR for compound 59
Supplementary Figure 289: NOESY NMR for compound 59
Supplementary Figure 290: $^1$H-NMR for compound 60

$^1$H NMR (500 MHz, Chloroform-d) δ 8.22 (s, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.34 (d, J = 8.5 Hz, 1H), 7.31 (ddd, J = 8.0, 6.9, 1.2 Hz, 1H), 7.24 (ddd, J = 8.3, 6.9 Hz, 1H), 7.10 (dd, J = 6.9, 1.2 Hz, 1H), 7.07 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 6.64 (d, J = 5.5 Hz, 1H), 6.22 (dd, J = 3.5, 0.7 Hz, 1H), 4.37 (dd, J = 14.5, 10.1 Hz, 1H), 4.32 (dd, J = 14.4, 4.4 Hz, 1H), 4.17 (d, J = 12.8 Hz, 1H), 4.14 (s, 3H), 4.09 (d, J = 13.1 Hz, 1H), 4.01 – 3.90 (m, 1H), 2.63 (q, J = 2.0 Hz, 3H).
Supplementary Figure 291: COSY NMR for compound 60
Supplementary Figure 292: $^{19}$F NMR for compound 60

$^{19}$F NMR (282 MHz, Chloroform) δ -66.78 (d, $J=8.2$ Hz).
Supplementary Figure 293: $^{13}$C NMR for compound 60

$^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 162.6, 151.5, 150.4, 133.6, 133.0, 132.0, 128.4, 128.1, 127.8, 126.9 (q, $J = 293.1$ Hz), 126.1, 125.7, 125.4, 124.9, 123.8, 105.5, 98.5, 60.7 (q, $J = 24.5$ Hz), 58.3, 53.8, 41.4 (q, $J = 1.8$ Hz), 35.9.
Supplementary Figure 294: HSQC NMR for compound 60
Supplementary Figure 295: *HMBC NMR for compound 60*
Supplementary Figure 296: IR for compound 60
Supplementary Figure 297: $^1$H-NMR for compound 61

$^1$H NMR (300 MHz, Chloroform-d) δ 7.66 (d, $J = 7.6$ Hz, 1H), 7.62 (d, $J = 7.4$ Hz, 1H), 7.40 (d, $J = 8.4$ Hz, 1H), 7.37 – 7.28 (m, 2H), 7.28 – 7.23 (m, 1H), 7.22 (s, 1H), 7.21 – 7.14 (m, 1H), 4.22 (d, $J = 11.5$ Hz, 2H), 4.07 (d, $J = 13.1$ Hz, 1H), 4.03 (s, 1H), 4.02 – 3.95 (m, 1H), 3.34 (s, 3H), 3.05 (s, 3H), 2.78 (q, $J = 2.3$ Hz, 3H).
Supplementary Figure 298: COSY NMR for compound 61
Supplementary Figure 299: $^{19}$F NMR for compound 61

$^{19}$F NMR (282 MHz, Chloroform-$d$) $\delta$ -66.36 (d, $J = 6.3$ Hz).
Supplementary Figure 300: $^{13}C$ NMR for compound 61

$^{13}C$ NMR (75 MHz, Chloroform-d) δ 153.9, 151.0, 148.1, 141.3, 133.5, 132.4, 132.0, 129.1, 128.4, 127.9, 126.7 (d, $J = 293.4$ Hz), 125.8, 125.2, 125.0, 123.5, 105.9, 57.9, 57.9 (q, $J = 24.8$ Hz), 43.2, 36.5, 29.6, 27.6.
Supplementary Figure 301: HSQC NMR for compound 61
Supplementary Figure 302: HMBC NMR for compound 61
Supplementary Figure 303: NOESY NMR for compound 61
Supplementary Figure 304: IR for compound 61
Supplementary Figure 305: $^1$H-NMR for compound 62

$^1$H NMR (500 MHz, Chloroform-d) $^\delta$ 7.78 (dt, $J = 8.5, 1.6$ Hz, 1H), 7.70 (dd, $J = 8.4, 2.5$ Hz, 1H), 7.62 (dd, $J = 8.7, 3.9$ Hz, 1H), 7.50 (dt, $J = 7.8, 7.3, 1.5$ Hz, 1H), 7.41 (dddd, $J = 8.1, 6.8, 2.3, 1.2$ Hz, 1H), 7.24 – 7.15 (m, 2H), 7.13 – 7.03 (m, 3H), 6.84 (d, $J = 8.0$ Hz, 1H), 6.68 (d, $J = 6.6$ Hz, 1H), 4.98 (d, $J = 8.3$ Hz, 1H), 4.62 – 4.53 (m, 1H), 4.35 – 4.24 (m, 2H), 4.20 (d, $J = 13.4$ Hz, 1H), 4.17 – 4.13 (m, 1H), 3.70 (pt, $J = 12.1, 7.0, 6.0$ Hz, 1H), 3.62 (d, $J = 6.1$ Hz, 3H), 3.24 – 3.08 (m, 2H), 2.63 (dt, $J = 3.6, 1.9$ Hz, 3H), 1.42 (s, 9H).
Supplementary Figure 306: COSY NMR for compound 62
Supplementary Figure 307: $^{19}$F NMR for compound 62

$^{19}$F NMR (282 MHz, Chloroform-d) δ -66.72 (d, J = 8.1 Hz).
Supplementary Figure 308: $^{13}C$ NMR for compound 62

$^{13}C$ NMR (75 MHz, Chloroform) δ 172.77, 155.31, 136.00, 133.85, 132.63, 132.02, 128.73, 127.90, 125.99, 125.74, 125.11, 123.86, 122.16, 119.55, 108.89, 79.88, 79.47, 61.42, 58.46, 58.48, 54.31, 54.06, 52.26, 43.47, 36.16, 28.41.

f1 (ppm)

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 10
Supplementary Figure 309: HSQC NMR for compound 62
Supplementary Figure 310: HMBC NMR for compound 62
Supplementary Figure 311: IR for compound 62
Supplementary Figure 312: \(^1H\)-NMR for compound 63

\(^1H\) NMR (300 MHz, Chloroform-d) \(8.86 \ (dd, J = 5.1, 1.9 \text{ Hz}, 1H), 8.26 - 8.19 \ (m, 1H), 7.83 \ (dt, J = 8.3, 3.0 \text{ Hz}, 1H), 7.76 \ (d, J = 8.3 \text{ Hz}, 1H), 7.53 - 7.46 \ (m, 3H), 7.45 - 7.34 \ (m, 2H), 7.06 \ (d, J = 8.1 \text{ Hz}, 1H), 6.95 \ (dd, J = 7.4, 4.9 \text{ Hz}, 1H), 4.40 \ (d, J = 13.7 \text{ Hz}, 1H), 4.34 \ (d, J = 13.7 \text{ Hz}, 1H), 3.84 - 3.66 \ (m, 2H), 3.45 \ (dd, J = 14.6, 11.3 \text{ Hz}, 1H), 2.52 \ (d, J = 2.2 \text{ Hz}, 3H). \)
Supplementary Figure 313: $^{19}$F NMR for compound 63

$^{19}$F NMR (282 MHz, Chloroform) δ -67.71 (d, J = 7.7 Hz).
Supplementary Figure 314: $^{13}$C NMR for compound 63

$^{13}$C NMR (75 MHz, Chloroform-d) δ 158.2, 149.3, 132.3, 128.4, 128.2, 127.5, 127.2 (q, $J = 292.4$ Hz), 125.8, 125.7, 125.2, 124.9, 122.2, 62.5 (q, $J = 25.2$ Hz), 58.4, 36.1, 27.2.
Supplementary Figure 315: IR for compound 63
Supplementary Figure 316: $^1$H-NMR for compound 64

$^1$H NMR (300 MHz, Chloroform-d) $\delta$ 8.24 – 8.11 (m, 1H), 7.93 – 7.82 (m, 1H), 7.76 (d, $J$ = 8.2 Hz, 1H), 7.53 (t, $J$ = 7.1, 3.7 Hz, 2H), 7.36 – 7.23 (m, 3H), 7.22 (t, $J$ = 7.5 Hz, 1H), 7.19 (t, $J$ = 7.8 Hz, 1H), 7.10 – 6.99 (m, 3H), 6.92 (s, 1H), 6.89 (s, 1H), 4.40 (dd, $J$ = 12.0 Hz, 2H), 4.27 (d, $J$ = 13.5 Hz, 1H), 4.24 (dd, $J$ = 14.1, 3.9 Hz, 1H), 3.99 (ddq, $J$ = 14.3, 8.9, 5.3, 4.6 Hz, 1H), 2.51 (s, 3H).
Supplementary Figure 317: $^{19}$F NMR for compound 64

$^{19}$F NMR (282 MHz, Chloroform$\delta$) $\delta$ -69.80 (d, J = 8.4 Hz).
Supplementary Figure 318: $^{13}C$ NMR for compound 64

$^{13}C$ NMR (75 MHz, Chloroform-d$_2$) $\delta$ 144.8, 134.0, 133.9, 132.3, 128.4, 128.1, 127.7, 127.4, 126.7 (q, $J = 287.8$ Hz), 126.4, 125.8, 125.6, 125.2, 124.6, 123.3, 115.4, 59.0, 58.9 (q, $J = 25.6$ Hz), 43.1, 36.9.
Supplementary Figure 319: IR for compound 64
Supplementary Figure 320: $^1$H-NMR for compound 65
Supplementary Figure 321: $^{19}$F NMR for compound 65

$^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -69.20.
Supplementary Figure 322: $^{13}$C NMR for compound 65

$^{13}$C NMR (63 MHz, Chloroform-d) $\delta$ 158.6, 134.5, 134.0, 132.7, 132.2, 130.2, 128.5, 128.3, 127.7, 127.1 (q, $J = 287.8$ Hz), 125.8, 125.3, 125.2, 113.4, 61.8, 60.9 (q, $J = 24.8$ Hz), 55.4, 55.3, 54.5, 42.6, 35.0, 7.8, 7.7.
Supplementary Figure 323: IR for compound 65
Supplementary Figure 324: $^1$H-NMR for compound 66

$^1$H NMR (250 MHz, Chloroform-d) δ 8.44 – 8.31 (m, 1H), 7.99 – 7.77 (m, 2H), 7.62 – 7.48 (m, 2H), 7.52 – 7.38 (m, 2H), 7.13 (d, $J = 8.3$ Hz, 2H), 6.81 (d, $J = 8.5$ Hz, 2H), 5.69 (ddt, $J = 16.6, 10.1, 6.4$ Hz, 1H), 5.20 – 5.02 (m, 2H), 4.12 (d, $J = 12.9$ Hz, 1H), 3.79 (s, 4H), 3.64 – 3.44 (m, 3H), 3.09 (dt, $J = 27.5, 7.6$ Hz, 3H), 2.60 (dd, $J = 13.3, 3.8$ Hz, 1H), 2.29 (s, 3H).
Supplementary Figure 325: $^{19}$F NMR for compound 66

$^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -69.11.
Supplementary Figure 326: $^{13}\text{C} \text{NMR for compound 66}$

$^{13}\text{C} \text{NMR (63 MHz, Chloroform-}d\text{)} \delta 158.8, 137.0, 134.5, 134.1, 132.7, 131.6, 129.9, 128.5, 128.3, 127.8, 127.3 (q, J = 288.5 Hz), 125.9, 125.8, 125.3, 117.4, 113.7, 61.7, 57.3 (q, J = 24.6 Hz), 55.3, 54.2, 53.5, 53.4, 42.7.
Supplementary Figure 327: IR for compound 66
Supplementary Figure 328: $^1$H-NMR for compound 67

$^1$H NMR (250 MHz, Chloroform-d) δ 8.40 – 8.29 (m, 1H), 7.96 – 7.78 (m, 2H), 7.58 – 7.49 (m, 1H), 7.48 (t, $J = 7.8$ Hz, 3H), 7.10 (d, $J = 8.4$ Hz, 2H), 6.80 (d, $J = 8.5$ Hz, 2H), 4.16 (d, $J = 12.9$ Hz, 1H), 3.87 (t, $J = 10.6$ Hz, 2H), 3.79 (s, 3H), 3.55 (dd, $J = 17.8$, 13.5 Hz, 2H), 3.47 (d, $J = 17.3$ Hz, 1H), 3.29 (d, $J = 17.1$ Hz, 1H), 3.11 (dd, $J = 13.1$, 9.3 Hz, 1H), 2.67 (dd, $J = 13.3$, 3.3 Hz, 1H), 2.37 (s, 3H), 2.21 (d, $J = 9.0$ Hz, 1H).
Supplementary Figure 329: $^{19}$F NMR for compound 67

$^{19}$F NMR (235 MHz, Chloroform-d) δ -69.40.
Supplementary Figure 330: $^{13}$C NMR for compound 67

$^{13}$C NMR (63 MHz, Chloroform-d) $\delta$ 158.9, 134.4, 134.0, 132.6, 130.5, 129.9, 128.6, 128.4, 127.9, 126.9 (q, $J = 288.1, 287.6, 287.6$ Hz), 126.0, 125.8, 125.3, 125.2, 113.8, 80.9, 72.6, 61.5, 59.1 (q, $J = 25.2$ Hz), 55.3, 53.8, 53.1, 42.6, 40.0.
Supplementary Figure 331: IR for compound 67
Supplementary Figure 332: ^1^H-NMR for compound 68

^1^H NMR (250 MHz, Chloroform-d) δ 8.25 – 8.12 (m, 1H), 7.82 – 7.59 (m, 2H), 7.30 (ddd, J = 21.7, 10.0, 5.6 Hz, 6H), 7.15 (s, 3H), 3.97 (d, J = 13.0 Hz, 1H), 3.78 (d, J = 13.0 Hz, 1H), 3.70 – 3.36 (m, 3H), 2.90 (dd, J = 13.2, 8.2 Hz, 1H), 2.58 (dd, J = 13.3, 3.8 Hz, 1H), 2.24 (s, 5H), 1.59 (dp, J = 13.6, 7.2 Hz, 1H), 0.76 (d, J = 6.4 Hz, 3H), 0.67 (d, J = 6.4 Hz, 3H).
Supplementary Figure 333: $^{19}$F NMR for compound 68

$^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -69.38.
Supplementary Figure 334: $^{13}$C NMR for compound 68

$^{13}$C NMR (63 MHz, Chloroform) δ 134.48, 134.01, 132.57, 131.67, 128.52, 128.35, 128.09, 127.61, 127.01 (q, $J = 288.4$, 287.7 Hz), 125.87, 125.77, 125.28, 124.97, 123.39, 86.74, 84.39, 61.43, 60.54 (q,J = 25.0 Hz), 58.50, 54.40, 42.64, 41.66, 26.57, 20.56, 20.41.
Supplementary Figure 335: IR for compound 68
Supplementary Figure 336: $^1$H-NMR for compound 69

$^1$H NMR (250 MHz, Chloroform-δ) δ 8.26 (d, $J = 7.7$ Hz, 1H), 7.94 – 7.72 (m, 2H), 7.61 – 7.35 (m, 4H), 4.31 (p, $J = 6.2$ Hz, 1H), 4.09 (d, $J = 12.9$ Hz, 1H), 3.76 (d, $J = 13.0$ Hz, 1H), 3.71 – 3.60 (m, 1H), 3.30 (td, $J = 6.5$, 2.6 Hz, 1H), 3.15 (t, $J = 6.7$ Hz, 1H), 3.06 – 2.89 (m, 2H), 2.65 (qd, $J = 13.6$, 4.8 Hz, 2H), 2.52 (s, 3H), 0.88 (s, 9H), -0.00 (s, 6H).
Supplementary Figure 337: $^{19}$F NMR for compound 69

$^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -72.80.
Supplementary Figure 338: $^{13}$C NMR for compound 69

$^{13}$C NMR (63 MHz, Chloroform-d) δ 134.0, 134.0, 132.6, 128.6, 128.4, 127.9, 126.0, 125.8, 125.2, 124.8, 123.8 (q, J = 283.1, 282.7, 282.1 Hz), 65.1, 64.9 (q, J = 25.2 Hz), 62.8, 62.5, 61.5, 55.7 (q, J = 2.2, 1.7 Hz), 43.0, 25.9, 18.1, -4.9, -5.0.
Supplementary Figure 340: $^1$H-NMR for compound 70

$^1$H NMR (250 MHz, Chloroform-d) $\delta$ 8.41 – 8.27 (m, 1H), 7.99 – 7.73 (m, 2H), 7.61 – 7.37 (m, 4H), 4.09 (d, $J = 12.8$ Hz, 1H), 3.87 (d, $J = 12.8$ Hz, 1H), 3.58 (pd, $J = 8.7$, 3.6 Hz, 1H), 2.99 (dd, $J = 13.3$, 9.0 Hz, 1H), 2.88 – 2.71 (m, 4H), 2.63 (dd, $J = 13.3$, 3.5 Hz, 1H), 2.31 (s, 3H), 1.75 – 1.54 (m, 4H).
Supplementary Figure 341: Supplementary Figure 342: COSY NMR for compound 70
Supplementary Figure 343: $^{19}$F NMR for compound 70

$^{19}$F NMR (235 MHz, Chloroform-d) δ -69.81.
Supplementary Figure 344: $^{13}$C NMR for compound 70

$^{13}$C NMR (63 MHz, Chloroform-d) δ 134.6, 134.0, 132.7, 128.5, 128.2, 127.7, 124.8 (q, J = 289.1 Hz), 61.3, 59.6 (q, J = 24.7 Hz), 54.3 – 53.6 (m), 48.7, 42.7, 24.1.
Supplementary Figure 345: HSQC NMR for compound 70
Supplementary Figure 346: HMBC NMR for compound 70
GC-MS TIC for compound 70
Supplementary Figure 347: IR for compound 70
Supplementary Figure 348: $^1$H-NMR for compound 71

$^1$H NMR (250 MHz, Chloroform-d) δ 8.55 – 8.27 (m, 1H), 7.97 – 7.74 (m, 2H), 7.62 – 7.36 (m, 4H), 4.24 – 3.77 (m, 2H), 3.77 – 3.58 (m, 1H), 3.22 – 2.80 (m, 2H), 2.78 – 2.42 (m, 2H), 2.43 – 2.19 (m, 3H), 2.02 (td, J = 10.9, 4.6 Hz, 1H), 1.82 – 1.22 (m, 6H), 1.17 (d, J = 6.3 Hz, 1H), 1.04 (d, J = 6.1 Hz, 1H), 0.89 (dt, J = 24.7, 12.4, 6.3 Hz, 1H).
Supplementary Figure 349: $^{19}$F NMR for compound 71

$^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -66.66, -70.84.
Supplementary Figure 350: $^{13}$C NMR for compound 71

$^{13}$C NMR (63 MHz, Chloroform-d) δ 134.5, 134.0, 134.0, 132.7, 132.7, 128.5, 128.4, 128.3, 128.1, 127.8, 127.4, 126.6 (q, $J = 284.8, 283.8, 283.5$ Hz), 125.8, 125.7, 125.4, 125.2, 125.1, 61.9, 61.3, 57.5 (q, $J = 22.8$ Hz), 57.0 (q, $J = 25.4$ Hz), 55.6, 54.6, 52.4, 46.5 (q, $J = 1.8$ Hz), 46.4, 42.9, 42.7, 36.5, 36.3, 26.8, 26.5, 25.2, 24.4, 21.0, 20.3.
Supplementary Figure 351: IR for compound 71
Supplementary Figure 352: $^1$H-NMR for compound 72

$^1$H NMR (250 MHz, Methanol-$d_4$) δ 8.35 (d, $J$ = 7.9 Hz, 1H), 7.92 – 7.70 (m, 2H), 7.45 (d, $J$ = 17.3, 7.4 Hz, 4H), 4.09 (d, $J$ = 12.8 Hz, 1H), 3.85 (d, $J$ = 12.7 Hz, 1H), 3.50 – 3.24 (m, 2H), 3.04 – 2.80 (m, 2H), 2.68 – 2.39 (m, 3H), 2.33 (s, 4H), 1.65 – 1.23 (m, 4H), 0.88 (s, 9H), 0.03 (s, 6H).
Supplementary Figure 353: $^{19}$F NMR for compound 72

$^{19}$F NMR (235 MHz, Methanol-$d_4$) δ -69.95.
Supplementary Figure 354: $^{13}$C NMR for compound 72

$^{13}$C NMR (63 MHz, Methanol-d$_4$) $\delta$ 135.4, 133.9, 129.4, 129.3, 128.9, 128.3 (q, $J = 290.5$, 289.9 Hz), 126.8, 126.3, 126.1, 69.9, 64.6 (q, $J = 24.1$ Hz), 62.1, 54.0, 47.6, 43.1, 36.9, 36.7, 26.4, 18.9, -4.4.
Supplementary Figure 355: IR for compound 72
Supplementary Figure 356: $^1$H-NMR for compound 73
Supplementary Figure 357: $^{19}$F NMR for compound 73

$^{19}$F NMR (235 MHz, Chloroform-$d$) $\delta$ -68.1.
Supplementary Figure 358: $^{13}$C NMR for compound 73

$^{13}$C NMR (63 MHz, Chloroform-$d$) $\delta$ 137.9, 134.7, 134.0, 132.6, 129.3, 128.5, 128.4, 128.2, 127.5, 127.3, 127.0 (d, $J = 290.7$ Hz), 125.9, 125.8, 125.2 (d, $J = 1.6$ Hz), 64.0 (q, $J = 23.9$ Hz), 63.1, 61.4, 53.8, 53.5 (d, $J = 2.0$ Hz), 49.2, 42.8.
Supplementary Figure 359: IR for compound 73
Supplementary Figure 360: $^1$H-NMR for compound 74

$^1$H NMR (250 MHz, Chloroform-d) δ 8.4 – 8.3 (m, 1H), 8.2 (dd, $J = 5.0$, 2.0 Hz, 1H), 7.8 (t, $J = 9.3$ Hz, 2H), 7.4 (dt, $J = 7.8$, 4.9 Hz, 5H), 6.6 (d, $J = 7.0$ Hz, 1H), 6.6 (d, $J = 9.0$ Hz, 1H), 4.1 (d, $J = 12.9$ Hz, 1H), 4.0 (d, $J = 12.9$ Hz, 1H), 3.6 – 3.2 (m, 5H), 3.0 (dd, $J = 13.6$, 9.3 Hz, 1H), 2.8 (t, $J = 5.2$ Hz, 2H), 2.8 (q, $J = 6.7$, 5.8 Hz, 2H), 2.6 (dd, $J = 13.5$, 3.5 Hz, 1H), 2.3 (s, 3H).
Supplementary Figure 361: $^{19}F$ NMR for compound 74

$^{19}F$ NMR (235 MHz, Chloroform-d) $\delta$ -68.3.
Supplementary Figure 362: $^{13}\text{C NMR for compound 74}$

$^{13}\text{C NMR (63 MHz, Chloroform-$d_6$) } \delta 159.4, 147.9, 137.6, 134.4, 134.0, 132.5, 128.5, 128.3,$
$127.6, 126.9 (q, $J = 290.8$ Hz), 125.9, 125.8, 125.2, 125.0, 113.2, 107.2, 64.1 (q, $J = 24.1$ Hz), 61.4, 53.4 (q, $J = 2.0$ Hz), 49.2, 46.1, 42.9.
Supplementary Figure 363: IR for compound 74
Supplementary Figure 364: $^1$H-NMR for compound 75

$^1$H NMR (300 MHz, Chloroform-d) $\delta$ 8.35 (d, $J = 8.6$ Hz, 1H), 7.84 (d, $J = 8.5$ Hz, 1H), 7.80 (d, $J = 8.5$ Hz, 1H), 7.51 – 7.34 (m, 3H), 7.24 – 7.10 (m, 4H), 7.04 – 6.95 (m, 1H), 4.12 (d, $J = 12.8$ Hz, 1H), 4.11 (d, $J = 14.5$ Hz, 1H), 3.97 (d, $J = 14.8$ Hz, 1H), 3.96 (d, $J = 12.8$ Hz, 1H), 3.64 – 3.47 (m, 1H), 3.20 – 2.93 (m, 3H), 2.92 – 2.81 (m, 2H), 2.75 (dd, $J = 13.5$, 3.6 Hz, 1H), 2.34 (s, 3H).
Supplementary Figure 365: $^{19}$F NMR for compound 75

$^{19}$F NMR (282 MHz, Chloroform) $\delta$ -67.90 (d, $J = 8.5$ Hz).
Supplementary Figure 366: $^{13}$C NMR for compound 75

$^{13}$C NMR (75 MHz, Chloroform-d) $\delta$ 135.2, 134.6, 133.9, 132.5, 128.3, 128.2, 127.6, 127.2 (q/$\nu$ = 291.4 Hz), 126.4, 126.0, 125.8, 125.7, 125.6, 125.1, 63.7 (q/$\nu$ = 23.9 Hz), 61.2, 53.8, 51.6, 47.3, 42.8, 30.4.
Supplementary Figure 367: IR for compound 75
Supplementary Figure 368: $^1$H-NMR for compound 76

$^1$H NMR (250 MHz, Chloroform-$d$) δ 8.40 – 8.29 (m, 1H), 7.93 – 7.73 (m, 2H), 7.60 – 7.37 (m, 4H), 4.05 (d, $J = 12.9$ Hz, 1H), 3.94 (d, $J = 12.9$ Hz, 1H), 3.56 (tt, $J = 11.3$, 5.7 Hz, 1H), 2.97 (dd, $J = 13.1$, 8.7 Hz, 1H), 2.81 (qd, $J = 11.7$, 4.2 Hz, 4H), 2.59 (dd, $J = 13.2$, 3.6 Hz, 1H), 2.33 (s, 3H), 1.81 (s, 2H), 1.67 (d, $J = 9.1$ Hz, 4H), 1.63 – 1.44 (m, 4H).
Supplementary Figure 369: $^{19}\text{F NMR for compound 76}$

$^{19}\text{F NMR (235 MHz, Chloroform-d)} \delta -68.81.$
Supplementary Figure 370: $^{13}$C NMR for compound 76

$^{13}$C NMR (63 MHz, Chloroform-d) δ 134.6, 134.0, 132.7, 129.8 (q, $J = 292.0$, 291.5 Hz), 128.5, 128.3, 127.7, 125.8, 125.2, 125.1, 64.0 (q, $J = 24.2$ Hz), 61.8, 59.0, 54.6, 42.3, 31.4, 25.6, 25.5.
Supplementary Figure 371: IR for compound 76
Supplementary Figure 372: $^1$H-NMR for compound 77

$^1$H NMR (250 MHz, Methanol-$d_4$) δ 7.23 – 7.03 (m, 4H), 7.00 – 6.84 (m, 4H), 4.21 (dd, $J = 14.6, 9.2$ Hz, 1H), 4.12 (dd, $J = 14.4, 4.4$ Hz, 1H), 3.76 (pd, $J = 8.8, 4.2$ Hz, 1H), 2.61 (qd, $J = 6.9, 2.8$ Hz, 4H), 0.77 (t, $J = 7.1$ Hz, 6H).
Supplementary Figure 373: $^{19}$F NMR for compound 77

$^{19}$F NMR (235 MHz, Methanol-d$_4$) $\delta$ -71.60.
Supplementary Figure 374: $^{13}$C NMR for compound 77

$^{13}$C NMR (63 MHz, Methanol-$d_4$) $\delta$ 145.1, 127.6, 127.5, 127.4 (q, $J = 289.0$ Hz), 126.4, 123.0, 58.0 (q, $J = 24.9$ Hz), 44.6, 43.5 (q, $J = 1.8$ Hz), 13.8.
Supplementary Figure 375: IR for compound 77
Supplementary Figure 376: $^1$H-NMR for compound 78

$^1$H NMR (250 MHz, Chloroform-d) $\delta$ 8.31 – 8.18 (m, 1H), 7.97 – 7.79 (m, 2H), 7.64 – 7.46 (m, 3H), 7.52 – 7.39 (m, 1H), 4.92 – 4.73 (m, 1H), 4.74 – 4.54 (m, 1H), 4.35 (s, 2H), 3.61 (d, $J = 17.3$, 8.6, 6.8, 4.9 Hz, 1H), 2.57 (s, 3H).
Supplementary Figure 377: $^{19}$F NMR for compound 78

$^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -67.89 (t, $J = 7.7$ Hz), -229.51 (dq, $J = 46.1, 17.8, 6.5$ Hz).
Supplementary Figure 378: $^{13}$C NMR for compound 78

$^{13}$C NMR (63 MHz, Chloroform-d) δ 134.1, 133.6, 132.4, 128.7, 127.7, 126.1, 126.1 (qd, $J =$ 289.2, 10.0 Hz), 125.9, 125.3, 124.5, 79.5 (qd, $J =$ 174.7, 2.3 Hz), 62.5 (qd, $J =$ 26.0, 20.8 Hz), 58.9, 37.5.
Supplementary Figure 379: IR for compound 78
Supplementary Figure 380: $^1$H-NMR for compound 79

$^1$H NMR (250 MHz, Chloroform-d) $\delta$ 8.28 (dd, $J = 7.2$, 1.8 Hz, 1H), 7.92 (dt, $J = 6.4$, 2.5 Hz, 1H), 7.85 (d, $J = 8.2$ Hz, 1H), 7.58 (qd, $J = 4.3$, 1.9 Hz, 2H), 7.52 (d, $J = 5.5$ Hz, 1H), 7.46 (d, $J = 7.2$ Hz, 1H), 4.42 (dd, $J = 13.5$, 2.8 Hz, 2H), 3.91 – 3.70 (m, 2H), 3.63 (pd, $J = 8.1$, 4.6 Hz, 1H), 2.53 (s, 3H).
Supplementary Figure 381: $^{19}$F NMR for compound 79

$^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -68.17.
Supplementary Figure 382: $^{13}$C NMR for compound 79

$^{13}$C NMR (63 MHz, Chloroform-d) δ 134.0, 133.7, 132.3, 128.6, 128.5, 127.6, 126.0, 125.9, 125.4 (d, $J = 290.8$ Hz), 125.3, 124.6, 65.2 (q, $J = 25.9$ Hz), 58.6, 39.2 (d, $J = 2.0$ Hz), 36.1.
Supplementary Figure 383: IR for compound 79
Supplementary Figure 384: $^1$H-NMR for compound 80

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 8.35 – 8.21 (m, 1H), 7.97 – 7.79 (m, 2H), 7.69 – 7.30 (m, 4H), 4.42 (dd, $J = 13.5, 3.9$ Hz, 2H), 3.79 – 3.61 (m, 1H), 3.67 – 3.54 (m, 2H), 2.55 – 2.47 (m, 3H).
Supplementary Figure 385: $^{19}$F NMR for compound 80

$^{19}$F NMR (235 MHz, Chloroform-d) δ -67.98.
Supplementary Figure 386: $^{13}$C NMR for compound 80

$^{13}$C NMR (63 MHz, Chloroform-d) δ 134.0, 133.6, 132.3, 128.6, 128.5, 127.6, 126.0, 125.9, 125.4 (d, $J = 291.7$ Hz), 125.3, 124.7, 65.2 (q, $J = 25.8$ Hz), 58.3, 35.9, 25.9 (q, $J = 1.7$ Hz).
Supplementary Figure 387: IR for compound 80
Supplementary Figure 388: $^1$H-NMR for compound 81

$^1$H NMR (250 MHz, Acetone-$d_6$) $\delta$ 8.36 – 8.25 (m, 1H), 7.98 – 7.80 (m, 2H), 7.64 (d, $J = 7.0$ Hz, 1H), 7.61 – 7.40 (m, 3H), 4.45 (s, 2H), 3.81 (td, $J = 8.1, 6.1$ Hz, 1H), 3.65 – 3.45 (m, 2H), 2.43 (t, $J = 1.8$ Hz, 3H).
Supplementary Figure 389: $^{19}\text{F NMR for compound 81}$

$^{19}\text{F NMR (235 MHz, Acetone$_d_6$)} \delta \approx -68.19$. 

![NMR Spectrum](image)

F (ppm)
Supplementary Figure 390: $^{13}$C NMR for compound 81

$^{13}$C NMR (63 MHz, Acetone $d_6$) δ 134.9, 134.8, 133.1, 129.2, 129.0, 128.1, 126.6, 126.5, 126.1 (q, $J = 292.6$ Hz), 126.0, 125.8, 66.3 (q, $J = 25.4$ Hz), 58.3 (d, $J = 1.4$ Hz), 35.6, -2.8.
Supplementary Figure 391: IR for compound 81
Supplementary Figure 392: $^1$H-NMR for compound 82

$^1$H NMR (250 MHz, Chloroform-$d$) δ 8.26 (d, $J = 8.0$ Hz, 1H), 7.91 (dd, $J = 7.5$, 1.9 Hz, 1H), 7.86 (dd, $J = 7.7$, 1.7 Hz, 1H), 7.67 – 7.41 (m, 4H), 4.43 (d, $J = 13.2$ Hz, 1H), 3.35 (dd, $J = 13.2$ Hz, 1H), 3.61 (dd, $J = 12.6$, 9.6 Hz, 1H), 3.56 – 3.34 (m, 1H), 3.31 (dd, $J = 12.6$, 3.6 Hz, 1H), 2.55 (s, 3H).
Supplementary Figure 393: $^{19}$F NMR for compound 82

$^{19}$F NMR (235 MHz, Chloroform-d) δ -67.45.
Supplementary Figure 394: $^{13}$C NMR for compound 82

$^{13}$C NMR (63 MHz, Chloroform-d) δ 134.4, 133.6, 132.7, 129.0, 128.9, 128.2, 126.4, 126.3, 126.0 (q, J = 290.4 Hz), 125.6, 124.7, 62.8 (q, J = 25.1 Hz), 59.0, 47.4 (q, J = 2.1 Hz), 36.3.
Supplementary Figure 395: IR for compound 82
Supplementary Figure 396: $^1$H-NMR for compound 83

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 8.3 – 8.1 (m, 1H), 8.0 – 7.8 (m, 2H), 7.7 – 7.4 (m, 4H), 4.4 (d, $J = 2.9$ Hz, 2H), 3.7 (dtd, $J = 10.1, 7.7, 4.9$ Hz, 1H), 2.8 (dd, $J = 17.1, 10.1$ Hz, 1H), 2.6 (dd, $J = 17.1, 4.9$ Hz, 1H), 2.5 (q, $J = 1.8$ Hz, 3H).
Supplementary Figure 397: $^{19}$F NMR for compound 83

$^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -69.2.
Supplementary Figure 398: $^{13}$C NMR for compound 83

$^{13}$C NMR (63 MHz, Chloroform-d) δ 134.0, 132.7, 132.2, 128.8, 128.6, 127.7, 126.3, 126.1, 125.9 (q, $J = 290.9$ Hz), 125.3, 124.4, 116.4, 59.6 (q, $J = 27.3$ Hz), 58.2 (d, $J = 1.5$ Hz), 36.0 (d, $J = 1.4$ Hz), 16.1 (q, $J = 2.3$ Hz).
Supplementary Figure 399: IR for compound 83
Supplementary Figure 400: $^1$H-NMR for compound 84

$^1$H NMR (250 MHz, Chloroform-d) $\delta$ 7.17 (d, $J = 8.5$ Hz, 2H), 6.78 (d, $J = 8.6$ Hz, 2H), 5.70 (ddt, $J = 16.5$, 10.1, 6.3 Hz, 1H), 5.14 (d, $J = 21.4$ Hz, 1H), 5.08 (d, $J = 15.4$ Hz, 1H), 4.67 (dt, $J = 6.5$, 3.8 Hz, 1H), 4.56 – 4.42 (m, 1H), 3.74 (s, 2H), 3.71 (s, 3H), 3.68 – 3.38 (m, 1H), 3.25 (d, $J = 6.3$ Hz, 2H).
Supplementary Figure 401: $^{19}\text{F} \text{NMR for compound 84}$

$^{19}\text{F} \text{NMR (235 MHz, Chloroform-d)}$ 8 -68.3 (d, $J = 6.6 \text{ Hz}$), -229.1 (q, $J = 6.6 \text{ Hz}$).
Supplementary Figure 402: $^{13}$C NMR for compound 84

$^{13}$C NMR (63 MHz, Chloroform-$d$) δ 159.1, 136.0, 130.8, 129.8, 126.1 (qd, $J = 288.0$, 8.9 Hz), 118.2, 114.0, 80.6 (qd, $J = 174.9$, 1.8 Hz), 59.5 (qd, $J = 26.4$, 20.8 Hz), 55.4, 54.2, 54.0.
Supplementary Figure 403: IR for compound 84
Supplementary Figure 404: \textsuperscript{1}H-NMR for compound 85

\textsuperscript{1}H NMR (250 MHz, Chloroform-d) \delta 8.3 – 8.0 (m, 1H), 7.5 (dd, J = 7.9, 7.1, 2.0 Hz, 1H), 6.6 (dd, J = 7.7, 4.7 Hz, 2H), 4.8 (q, J = 5.6 Hz, 1H), 4.7 – 4.4 (m, 1H), 3.5 (t, J = 5.0 Hz, 4H), 3.5 – 3.3 (m, 1H), 2.9 (p, J = 6.3, 5.3 Hz, 4H).
Supplementary Figure 405: $^{19}\text{F} \text{NMR for compound 85}$

$^{19}\text{F} \text{NMR (235 MHz, Chloroform-d)} \delta -68.3 \text{ (d, } J = 6.8 \text{ Hz), -228.8 \text{ (q, } J = 6.8 \text{ Hz).}$
Supplementary Figure 406: $^{19}$F NMR for compound 85

$\text{^1H NMR (63 MHz, Chloroform-\textit{d}) $\delta$ 159.4, 148.0, 137.7, 125.5 (qd, $J = 288.1, 9.7$ Hz), 113.5, 107.2, 80.5 (qd, $J = 175.1, 2.3$ Hz), 65.4 (qd, $J = 26.2, 20.6$ Hz), 50.1, 46.1.}$
Supplementary Figure 407: IR for compound 85
Supplementary Figure 408: $^1$H-NMR for compound 86

$^1$H NMR (250 MHz, Chloroform-d) δ 8.28 (dd, $J = 6.4$, 2.7 Hz, 1H), 7.97 – 7.75 (m, 2H), 7.62 – 7.28 (m, 9H), 4.55 (s, 2H), 4.37 (s, 2H), 3.97 – 3.84 (m, 1H), 3.79 (dd, $J = 10.3$, 4.3 Hz, 1H), 3.64 (dd, $J = 12.6$, 8.5, 4.2 Hz, 1H), 2.51 (s, 3H).

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Supplementary Figure 409: $^{19}$F NMR for compound 86

$^{19}$F NMR (235 MHz, Chloroform-d) δ -68.13.
Supplementary Figure 410: $^{13}$C NMR for compound 86

$^{13}$C NMR (63 MHz, Chloroform-d) δ 137.9, 134.3, 134.1, 132.5, 128.6, 128.3, 127.9, 127.7, 127.6, 126.7 (q, J = 289.1, 288.7 Hz), 126.0, 125.8, 125.3, 124.7, 73.5, 66.1 (q, J = 1.8 Hz), 63.2 (q, J = 25.4 Hz), 58.9, 37.3.
Supplementary Figure 411: IR for compound 86
Supplementary Figure 412: $^1$H-NMR for compound 87

$^1$H NMR (250 MHz, Chloroform-d): $\delta$ 8.31 (dd, $J = 6.0$, 3.4 Hz, 1H), 8.00 – 7.81 (m, 2H), 7.67 – 7.43 (m, 4H), 7.40 (d, $J = 8.7$ Hz, 2H), 6.73 (d, $J = 8.7$ Hz, 2H), 4.42 (d, $J = 3.0$ Hz, 2H), 4.54 – 4.08 (m, 2H), 3.92 – 3.66 (m, 1H), 2.61 (s, 3H).
Supplementary Figure 413: $^{19}$F NMR for compound 87

$^{19}$F NMR (235 MHz, Chloroform-d) δ -67.62.
Supplementary Figure 414: $^{13}\text{C}$ NMR for compound 87

$^{13}\text{C}$ NMR (63 MHz, Chloroform-$d$) δ 157.2, 134.1, 133.8, 132.4, 128.6, 127.8, 126.3 (q, $J = 289.7, 289.6, 288.5$ Hz), 126.0, 125.9, 125.3, 124.7, 116.4, 113.7, 64.1 (q, $J = 1.6$ Hz), 61.9 (q, $J = 25.7$ Hz), 59.0, 57.1.
Supplementary Figure 415: IR for compound 87
Supplementary Figure 416: $^1H$-NMR for compound 88

$^1H$ NMR (250 MHz, Chloroform-d) $\delta$ 8.16 (d, $J = 8.4$ Hz, 1H), 8.00 – 7.89 (m, 2H), 7.84 (t, $J = 8.3$ Hz, 2H), 7.61 (t, $J = 7.3$ Hz, 1H), 7.54 – 7.37 (m, 5H), 7.31 (t, $J = 7.6$ Hz, 1H), 4.74 (dd, $J = 11.7, 8.6$ Hz, 1H), 4.53 (dd, $J = 11.8, 4.5$ Hz, 1H), 4.38 (s, 2H), 3.80 (ddq, $J = 13.1, 8.5, 4.8, 4.2$ Hz, 1H), 2.62 (s, 3H).
Supplementary Figure 417: $^{19}$F NMR for compound 88

$^{19}$F NMR (235 MHz, Chloroform-d) δ -67.46.
Supplementary Figure 418: $^{13}C$ NMR for compound 88

$^{13}C$ NMR (63 MHz, Chloroform-d) δ 166.1, 134.0, 133.6, 133.2, 132.4, 129.8, 129.7, 128.5, 127.7, 126.1, 125.8, 125.2, 124.3, 124.3 (q, $J = 291.0, 290.5$ Hz), 61.7 (q, $J = 25.5$ Hz), 59.8 (d, $J = 2.1$ Hz), 58.7, 36.7.
Supplementary Figure 419: IR for compound 88
Supplementary Figure 420: $^1$H-NMR for compound 89

$^1$H NMR (250 MHz, Chloroform-d) δ 8.31 (d, J = 7.9 Hz, 1H), 7.95 – 7.77 (m, 2H), 7.65 – 7.40 (m, 4H), 4.43 (d, J = 13.8 Hz, 1H), 4.36 (d, J = 13.7 Hz, 1H), 3.50 (ddh, J = 16.3, 8.2, 4.2 Hz, 1H), 2.98 (dd, J = 13.5, 10.3 Hz, 1H), 2.82 (dd, J = 13.5, 4.0 Hz, 1H), 2.50 (s, 4H), 2.00 – 1.53 (m, 5H), 1.43 – 1.12 (m, 5H).
Supplementary Figure 421: $^{19}$F NMR for compound 89

$^{19}$F NMR (235 MHz, Chloroform-d) δ -68.07.
**Supplementary Figure 422: $^{13}C$ NMR for compound 89**

$^{13}C$ NMR (63 MHz, Chloroform-\(d_2\)) \(\delta\) 134.1, 134.0, 132.5, 128.5, 128.3, 127.6, 125.9, 125.8, 125.3, 124.9, 124.9 (q, \(J = 292.2\) Hz), 63.9 (q, \(J = 24.8\) Hz), 58.4, 43.9, 36.0, 33.4, 33.4, 27.0, 26.1, 26.0, 25.9.
Supplementary Figure 423: IR for compound 89
Supplementary Figure 424: $^1$H-NMR for compound 90

$^1$H NMR (250 MHz, Chloroform-δ) δ 8.28 (d, $J = 7.5$ Hz, 1H), 8.00 – 7.80 (m, 2H), 7.68 – 7.40 (m, 5H), 7.20 (d, $J = 8.5$ Hz, 2H), 7.10 (d, $J = 8.6$ Hz, 2H), 4.39 (dd, $J = 13.5$, 6.5 Hz, 2H), 3.52 (tt, $J = 12.9$, 6.4 Hz, 1H), 3.27 (dd, $J = 13.6$, 9.6 Hz, 1H), 3.17 (dd, $J = 13.5$, 7.3 Hz, 1H), 2.56 (s, 3H).
Supplementary Figure 425: $^{19}$F NMR for compound 90

$^{19}$F NMR (235 MHz, Chloroform) δ -67.35.
Supplementary Figure 426: $^{13}$C NMR for compound 90

$^{13}$C NMR (63 MHz, Chloroform-d) 8 134.2, 134.0, 133.5, 132.5, 132.4, 130.8, 129.2, 128.6, 128.4, 127.7, 126.0, 125.8, 125.3, 124.8, 124.7 (q, $J = 292.8$, 292.3 Hz), 62.0 (q, $J = 25.1$ Hz), 58.2, 36.1, 31.8 (q, $J = 1.0$ Hz).
Supplementary Figure 427: IR for compound 90
Supplementary Figure 428: $^1$H-NMR for compound 91

$^1$H NMR (250 MHz, Chloroform-d) δ 8.27 – 8.16 (m, 1H), 7.92 – 7.68 (m, 4H), 7.63 – 7.38 (m, 4H), 7.44 – 7.22 (m, 2H), 4.42 (d, $J$ = 13.2 Hz, 1H), 4.36 (d, $J$ = 13.6 Hz, 1H), 4.03 – 3.80 (m, 2H), 3.64 (dd, $J$ = 13.8, 11.1 Hz, 1H), 2.57 (t, $J$ = 2.0 Hz, 3H).
Supplementary Figure 429: $^{19}$F NMR for compound 91

$^{19}$F NMR (235 MHz, Chloroform-d) δ -67.14.
Supplementary Figure 430: $^{13}$C NMR for compound 91

$^{13}$C NMR (63 MHz, Chloroform-$d$) δ 166.0, 153.1 (d, $J = 292.9$ Hz), 135.3, 133.9, 133.4, 132.3, 128.5, 128.4, 127.6, 127.0 (q, $J = 292.9$ Hz), 126.0, 125.9, 125.8, 125.1, 124.7, 124.3, 121.6, 121.0, 61.7 (q, $J = 25.5$ Hz), 58.2, 35.9, 30.6 (q, $J = 1.8$ Hz).
Supplementary Figure 431: IR for compound 91
Supplementary Figure 432: $^1$H-NMR for compound 92

$^1$H NMR (250 MHz, Chloroform-d) δ 8.28 – 8.10 (m, 1H), 7.94 – 7.77 (m, 2H), 7.73 – 7.36 (m, 9H), 4.42 – 4.18 (m, 3H), 3.90 – 3.74 (m, 1H), 3.73 – 3.42 (m, 1H), 2.56 – 2.29 (m, 3H).
Supplementary Figure 433: $^{19}$F NMR for compound 92

$^{19}$F NMR (235 MHz, Chloroform-d) δ -67.74, -67.79.
Supplementary Figure 434: $^{13}$C NMR for compound 92

$^{13}$C NMR (63 MHz, Chloroform-$d$) 8 144.1, 143.9, 134.0, 133.7, 133.6, 152.5, 132.4, 132.3, 129.2, 129.2, 128.6, 128.5, 127.6, 127.6, 126.0, 126.0, 125.9, 125.8, 125.4, 125.3, 124.6, 124.6, 123.7 (q, $J = 290.0$, 289.5 Hz), 63.3 (q, $J = 26.5$, 26.0 Hz), 62.2 (q, $J = 26.3$, 26.2, 25.8 Hz), 58.7, 36.8, 36.4.
Supplementary Figure 435: IR for compound 92
Supplementary Figure 436: $^1H$-NMR for compound 93

$^1H$ NMR (250 MHz, Chloroform-d) $\delta$ 8.22 (d, $J = 7.9$ Hz, 1H), 7.86 (dd, $J = 23.7$, 7.9 Hz, 2H), 7.65 – 7.48 (m, 3H), 7.39 (dt, $J = 22.4$, 7.9 Hz, 1H), 3.97 (q, $J = 13.8$ Hz, 2H), 3.42 (td, $J = 14.3$, 12.7, 5.3 Hz, 1H), 2.73 – 2.53 (m, 2H), 2.50 (s, 3H).
Supplementary Figure 437: $^{19}$F NMR for compound 93

$^{19}$F NMR (235 MHz, Chloroform-d) $\delta$ -67.93 (d, $J = 5.8$ Hz).
Supplementary Figure 438: $^{31}P$ NMR for compound 93

$^{31}P$ NMR (101 MHz, Chloroform-d) $\delta$ -22.55 (q, $J = 5.8$ Hz).
Supplementary Figure 439: $^{13}$C NMR for compound 93

$^{13}$C NMR (63 MHz, Chloroform-d) $\delta$ 138.9 (d, $J = 13.8$ Hz), 137.0 (d, $J = 15.1$ Hz), 134.0, 133.4, 133.4, 133.0, 132.6, 132.3, 132.3, 129.9 (dq, $J = 293.8, 9.5$ Hz), 129.2, 128.8, 128.7, 128.6, 128.6, 128.5, 128.2, 127.5 (d, $J = 1.6$ Hz), 126.1, 125.7, 125.3, 124.5 (d, $J = 2.3$ Hz), 61.3 (qd, $J = 25.6, 14.9$ Hz), 57.8, 36.2, 26.6 (d, $J = 14.4$ Hz).
Supplementary Figure 440: IR for compound 93
Supplementary Figure 441: $^1H$-NMR for compound 94

$^1H$ NMR (250 MHz, Methylene Chloride-$d_2$): $8$ 8.30 – 7.84 (m, 3H), 7.85 – 7.24 (m, 4H), 4.75 (bs, 1H), 4.64–4.32 (m, 1H), 4.32–3.89 (m, 1H), 3.37 (d, $J = 26.2$ Hz, 2H), 2.88 (s, 1H), 2.76 (s, 3H), 2.41–1.33 (m, 24H), 1.09 (s, 6H).
Supplementary Figure 442: $^{19}\text{F NMR for compound 94}$

$^{19}\text{F NMR (235 MHz, Methylene Chloride-}$d$_2$) δ -65.25, -76.93.
Supplementary Figure 443: $^{31}P$ NMR for compound 94

$^{31}P$ NMR (101 MHz, Methylene Chloride-$d_2$) $\delta$ 30.67.
Supplementary Figure 444: $^{13}$C NMR for compound 94

$^{13}$C NMR (63 MHz, Methylene Chloride-d$_2$) $\delta$ 134.8, 128.6 (qd, $J = 292.4, 14.7$ Hz), 118.8 (q, $J = 321.2$ Hz), 65.9, 57.7, 56.2 (qd, $J = 26.9, 5.2$ Hz), 37.8 (d, $J = 40.9$ Hz), 37.4 (b, $J = 17.0, 17.0, 15.9, 15.7, 14.9$ Hz), 35.3 (d, $J = 19.6$ Hz), 27.7 (d, $J = 18.8$ Hz), 27.5 (d, $J = 18.4$ Hz), 22.9, 15.4, 11.0, 10.2.
Supplementary Figure 445: IR for compound 94
Supplementary Figure 446: $^1$H-NMR for compound 95

$^1$H NMR (250 MHz, Chloroform-d) δ 8.08 (d, $J = 8.0$ Hz, 1H), 7.93 – 7.71 (m, 2H), 7.63 – 7.37 (m, 4H), 4.36 (d, $J = 13.3$ Hz, 1H), 4.24 (d, $J = 13.5$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 4.01 (dq, $J = 10.8, 7.1$ Hz, 1H), 3.83 (dq, $J = 10.8, 7.1$ Hz, 1H), 3.52 (dd, $J = 9.1, 5.1$ Hz, 1H), 3.50 – 3.29 (m, 1H), 2.53 – 2.43 (m, 3H), 2.20 (dt, $J = 9.9, 4.5$ Hz, 2H), 1.23 (t, $J = 7.1$ Hz, 3H), 1.14 (t, $J = 7.1$ Hz, 3H).
Supplementary Figure 447: $^{19}\text{F NMR for compound 95}$

$^{19}\text{F NMR (235 MHz, Chloroform-d)}$ δ -67.43.
Supplementary Figure 448: $^{13}$C NMR for compound 95

$^{13}$C NMR (63 MHz, Chloroform-d) $\delta$ 169.5, 168.6, 134.1, 133.6, 132.3, 128.7, 128.4 (q, $J = 293.1$ Hz), 128.4, 127.9, 126.2, 125.8, 125.3, 124.2, 61.6, 61.3, 59.9 (q, $J = 25.1$ Hz), 57.9, 47.8, 35.9, 25.6 (d, $J = 1.9$ Hz), 14.1, 13.9.
Supplementary Figure 449: IR for compound 95
Supplementary Figure 450: $^1$H-NMR for compound 96

$^1$H NMR (300 MHz, Chloroform-d) 8.37 (d, $J = 5.7$ Hz, 1H), 8.16 (d, $J = 8.0$ Hz, 1H), 7.88 – 7.79 (m, 1H), 7.78 (dd, $J = 8.2$, 4.2 Hz, 2H), 7.68 (d, $J = 8.1$ Hz, 2H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.43 (dq, $J = 14.9$, 7.8, 7.2 Hz, 7H), 4.42 (d, $J = 13.3$ Hz, 1H), 4.32 (d, $J = 13.3$ Hz, 1H), 3.49 (dd, $J = 8.5$, 6.0 Hz, 1H), 3.46 – 3.30 (m, 1H), 2.86 (dt, $J = 16.0$, 8.1 Hz, 1H), 2.62 (s, 3H), 2.29 – 2.19 (m, 2H).
Supplementary Figure 451: COSY NMR for compound 96
Supplementary Figure 452: $^{19}$F NMR for compound 96

$^{19}$F NMR (282 MHz, Chloroform$\delta$) $\delta$ -67.33 (d, $J = 8.2$ Hz).
Supplementary Figure 453: $^{13}C$ NMR for compound 96

$^{13}C$ NMR (75 MHz, Chloroform-$d$) $\delta$ 160.5, 141.5, 136.0, 134.3, 134.1, 132.5, 129.9, 128.7, 128.4, 127.9, 127.4, 127.1, 126.9, 126.2 (q, $J = 293.4$ Hz), 125.9, 125.7, 125.3, 125.0, 124.7, 124.3, 119.4, 61.4 (q, $J = 24.5$ Hz), 58.3, 36.1, 30.9, 24.4.
Supplementary Figure 454: HSQC NMR for compound 96
Supplementary Figure 455: *HMBC NMR for compound 96*
Supplementary Figure 456: IR for compound 96
Supplementary Figure 457: $^1$H-NMR for compound 97

$^1$H NMR (300 MHz, Chloroform-d) $\delta$ 8.42 (d, $J = 4.7$ Hz, 1H), 8.26 – 8.15 (m, 1H), 7.93 – 7.78 (m, 2H), 7.64 – 7.38 (m, 4H), 7.36 – 7.25 (m, 1H), 7.03 (dd, $J = 7.6$, 4.8 Hz, 1H), 4.48 (d, $J = 13.3$ Hz, 1H), 4.32 (d, $J = 13.2$ Hz, 1H), 3.31 (ddt, $J = 16.4$, 11.5, 5.8 Hz, 1H), 2.92 (tt, $J = 11.2$, 4.6 Hz, 1H), 2.79 – 2.72 (m, 4H), 2.59 (q, $J = 6.1$ Hz, 2H), 1.53 – 1.33 (m, 2H), 1.25 – 1.05 (m, 1H), 1.02 – 0.76 (m, 2H).
Supplementary Figure 458: COSY NMR for compound 97
Supplementary Figure 459: TOCSY NMR for compound 97
Supplementary Figure 460: $^{19}$F NMR for compound 97

$^{19}$F NMR (282 MHz, Chloroform-d) $\delta$ -66.30 (d, J = 8.3 Hz), -66.94 (d, J = 8.2 Hz).
Supplementary Figure 461: $^{13}$C NMR for compound 97

$^{13}$C NMR (75 MHz, Chloroform-d) δ 159.8, 146.5, 137.2, 134.4, 134.1, 132.7, 129.0, 128.6, 128.4, 128.3, 128.1, 126.6, 126.0, 125.8, 125.3, 124.9, 123.7, 121.0, 58.6, 58.2, 57.9 (d, $J = 24.2$ Hz), 36.2, 35.7, 31.1, 29.1, 26.5, 19.8.
Supplementary Figure 462: HSQC NMR for compound 97
Supplementary Figure 463: HMBC NMR for compound 97
Supplementary Figure 464: IR for compound 97
Supplementary Figure 465: $^1$H-NMR for compound 98

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 7.78 (d, $J = 8.2$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.67 – 7.58 (m, 1H), 7.48 – 7.17 (m, 6H), 7.11 (d, $J = 7.0$ Hz, 1H), 7.05 (d, $J = 7.4$ Hz, 1H), 6.74 (d, $J = 2.4$ Hz, 1H), 4.24 (d, $J = 13.6$ Hz, 1H), 4.16 (d, $J = 13.4$ Hz, 1H), 3.80 – 3.52 (m, 1H), 3.15 (s, 1H), 3.12 (s, 1H), 2.57 – 2.43 (m, 3H).
Supplementary Figure 466: COSY NMR for compound 98
Supplementary Figure 467: TOCSY NMR for compound 98
Supplementary Figure 468: $^{19}$F NMR for compound 98

$^{19}$F NMR (235 MHz, Chloroform-d) δ -67.64.
Supplementary Figure 469: $^{13}$C NMR for compound 98

$^{13}$C NMR (126 MHz, Chloroform-d) δ 136.2, 134.1, 133.8, 132.2, 129.1 (d, $J = 292.8$ Hz), 128.2, 128.1, 127.5, 127.3, 125.4, 125.4, 125.0, 124.5, 123.1, 122.0, 119.5, 118.4, 111.8, 111.2, 63.8 (q, $J = 24.0$ Hz), 58.6 (d, $J = 1.4$ Hz), 35.6, 22.5 (q, $J = 1.9$ Hz).
Supplementary Figure 470: HSQC NMR for compound 98
Supplementary Figure 471: HMBC NMR for compound 98
Supplementary Figure 472: IR for compound 98
Supplementary References


