Identifying the potential of pulsed irradiation in synthesis: copper-photocatalysed C–F functionalisation

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Supplementary Information

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I. General

NMR experiments were performed either on a Bruker Avance III NMR spectrometer operating at 400 MHz (¹H), 100 MHz (¹³C) or 376 MHz (¹⁹F) or on a Bruker Avance III NMR spectrometer operating at 600 MHz (¹H), 150 MHz (¹³C) or 564 MHz (¹⁹F). The deuterated solvent used was CDCl₃. Chemical shifts were recorded in ppm. Spectra were calibrated by assignment of the residual solvent peak to δ₇.26 and δ₇₇.16 for CDCl₃. Coupling constants (J) were recorded in Hz. Infrared spectrometry was performed on a Shimadzu FTIR 8400s spectrometer, with samples analyzed either as thin films on NaCl plates or using an ATR attachment. EIMS analyses were conducted on a Thermo-Scientific LTQ-Orbitrap mass spectrometer. EIMS analyses were performed using a Kratos Analytical Concept ISQ hybrid magnetic sector quadrupole tandem or Shimadzu GCMS-QP2010 mass spectrometers.

TLC was performed using Merck silica gel 60-F₂₅₄ plates. Developed TLC plates were visualized by UV absorbance (254 nm) or through application of heat to a plate stained with cerium molybdate {Ce(NH₄)₂(NO₃)₂, (NH₄)₃Mo₇O₂₄·4H₂O, H₂SO₄, H₂O}. Flash column chromatography was performed with flash grade silica gel (60 µm) and the indicated eluent in accordance with standard techniques.¹ Unless otherwise specified, reactions were conducted with magnetic stirring under N₂. Unless otherwise specified all reagents employed in these studies were used as received from Sigma-Aldrich, AK Scientific, Combi-Blocks, and Oakwood and were used without purification. i-Pr₂NEt (Sigma-Aldrich) was distilled prior to use. [Cu(bcp)(XP)]PF₆ (2) was prepared according to a literature procedure.²

II. Pulsed LED Photoreactor Experimental Set-Up

Circuit. Our in-house constructed circuit featured a series of integrated circuits (IC) (making up the timing circuit) and voltage regulating components that were used to pulse the blue LED photoreactor:

A Goodwill Instrument Co. GPD-5030 dual tracking power supply was used to provide 12 V DC to a voltage regulator (L7805CP), which reduced this output to 5 V DC (Figs. S1A & S1B). This enabled the power supply to drive both the integrated circuits (ICs) and the LED photoreactor. The timing circuit was created by taking the 5 V output of the regulator and connecting the 555-timer chip (NE555) in an astable configuration and feedback from the resistors and capacitor (between the voltage regulator output and common ground) causes a voltage instability in the 555-timer chip that allows it to oscillate between on and off.

Figure S1A. Schematic representation of the circuit used to pulse the LED photoreactor.

Figure S1B. Photograph of the circuit constructed and employed to pulse the LED photoreactor.
The combination of the resistor and capacitor values in the circuit caused an oscillation of approximately 100 kHz with a 75% duty cycle. However, because LEDs operating at these currents with 75% duty cycle would overheat, the output of the 555-timer chip was inverted by a quad NOR flip-flop IC (CD74HCT00E). The NOR flip-flop gate inputs were connected in parallel, meaning that they were either both low or both high. The NOR flip-flop gate inverts the input, so when the input is high, the output was low and vice versa. This created an output that was a square wave voltage operating at 100 kHz and a 25% duty cycle, which was then fed into the base of a MOSFET transistor (FQP27P06). This allowed current to flow from the collector to the emitter, this activation completed the circuit and turned the LEDs back on. The transistor was needed as it allowed the controlled timing and pulsing obtained by the timing circuit and enabled the 12 V power supply to drive the LEDs. As a result the LEDs operated at 100 kHz and a 25% duty cycle.

**Photoreactor.** Our custom photoreactor was constructed using of 2 m of blue LEDs strips (120 LEDs) purchased from Banggood.com (Fig. S2A). Under our above-mentioned pulsed LED conditions this photoreactor operates at 18-W (12 V, 1.5 A) providing 454 nm, ~28,000 lux (measured at the center of the photoreactor using a Trotec BF05 Luxmeter). A photograph of the complete experimental set-up is provided (Fig. S2B). Under conventional (continuous) operation this photoreactor operates at 24-W (12 V, 2 A) providing 453 nm, ~28,000 lux (measured at the center of the photoreactor using a Trotec BF05 Luxmeter).

![Photograph of blue LED photoreactor.](image)
III. Preparation of Materials

Experimental procedures for the preparation of previously unreported compounds are described below. These procedures were not optimized.

1-Decylpyrroldine (4h)

![Image of Pulsed LED Photoreactor Experimental Set-Up](Figure S2B. Photograph of Pulsed LED Photoreactor Experimental Set-Up.)

Pyrrolidine (3.5 mL, 42 mmol) was added to a magnetically stirred solution of 1-iododecane (4.3 mL, 20 mmol) in MeCN (10 mL) maintained at r.t. under N₂ and the ensuing mixture heated at reflux. After 16 h, the mixture was concentrated under reduced pressure to provide a yellow oil. The ensuing oil was then added to a magnetically stirred mixture of KOH (3.0 g, 53 mmol) in MeOH (20 mL) and the bright yellow solution maintained at r.t. under N₂. After 4 h, the mixture was concentrated under reduced pressure. The ensuing residue was then subjected to chromatography (silica plug, contained in a sintered glass funnel: Et₂O elution) to provide title compound 4h (780 mg, 15% yield) as a colorless oil.

\[
\text{H NMR (600 MHz, CDCl}_3\text{)} \delta 2.54–2.48 (m, 4 H), 2.43 (t, J = 8 Hz, 2H), 1.82–1.76 (m, 4H), 1.56–1.50 (m, 2H), 1.35–1.25 (m, 14H), 0.89 (t, J = 7 Hz, 3H) ppm.
\]

\[
\text{C NMR (150 MHz, CDCl}_3\text{)} \delta 56.7, 54.3, 31.9, 29.62, 29.59, 29.58, 29.3, 29.1, 27.8, 23.4, 22.7, 14.1 ppm.
\]

IR (NaCl) 2925, 2784, 2960, 1460, 1378, 1350, 1292, 1149 cm⁻¹.

EIMS (m/z, relative intensity) 211 (M⁺, 2), 84 (100).

N-(Pentafluorophenyl)nonanamide (6a)
Nonanoic acid (0.92 g, 6.00 mmol) was added to a magnetically stirred solution of pentafluoroaniline (1.10 g, 6.00 mmol), EDCI (1.30 g, 8.50 mmol) and DMAP (100 mg, 0.70 mmol) in CH$_2$Cl$_2$ (20 mL) maintained at 0 °C under N$_2$. After 5 min, NEt$_3$ (1.50 mL, 12.0 mmol) was added slowly and the reaction mixture warmed to room temperature. After 16 h, KHSO$_4$ (10 mL of a saturated aqueous solution) was added and the phases separated. The organic layer was then washed with NaHCO$_3$ (10 mL of a saturated aqueous solution) and H$_2$O (10 mL) then dried (MgSO$_4$), filtered, and concentrated under reduced pressure. The ensuing solid was then recrystallized from EtOAc to provide title compound 6a (310 mg, 15% yield) as a colorless solid.

$^1$H NMR (600 MHz, CDCl$_3$) δ 6.85 (s, 1H), 2.37 (s, 1H), 2.28 (t, $J = 6$ Hz, 1H), 1.70–1.62 (m, 1H), 1.60–1.53 (m, 1H), 1.31–1.16 (m, 10H), 0.84–0.80 (m, 3H) ppm.

$^{13}$C NMR (150 MHz, CDCl$_3$) δ 171.8, 143.7, 142.1, 138.6, 136.9, 36.2, 31.8 29.3, 29.1, 29.0, 25.5, 22.7, 14.1 ppm.

$^{19}$F NMR (564 MHz, CDCl$_3$) δ –144.9 (d, $J = 18$ Hz, 2F), –156.6 (s, 1F), –162.4 (s, 2F) ppm.

IR (NaCl) 3250, 2924, 2957, 1682, 1652, 1524, 1490, 1458, 1002, 953 cm$^{-1}$.

EIMS (m/z, relative intensity) 323 (M$^+$, 2), 183 (70), 141 (45), 57 (100).

2-(4-Fluorophenyl)-N-(pentafluorophenyl)acetamide (6c)

DMAP (67 mg, 546 μmol) was added to a magnetically stirred solution of pentafluoroaniline (1.00 g, 5.46 mmol) and 2-(4-fluorophenyl)acetic acid (926 mg, 6.01 mmol) in DMF (20 mL) maintained at 0 °C under N$_2$. After 5 min, EDCI (1.47 g, 7.65 mmol) and NEt$_3$ (1.90 mL, 13.7 mmol) were added and the ensuing mixture was slowly warmed to 25 °C. After 16 h, the reaction mixture was diluted with H$_2$O and EtOAc/hexane (20 mL of a 1:1 v/v solution). The phases were separated and the aqueous layer was further extracted with EtOAc/hexane (2 x 20 mL of a 1:1 v/v solution). The combined organic phase was then washed with KHSO$_4$ (20 mL of a saturated aqueous solution), NaHCO$_3$ (20 mL of a saturated aqueous solution), and H$_2$O (20 mL), successively. The organic phase was then dried (Na$_2$SO$_4$), filtered, and concentrated under reduced pressure. The ensuing residue was then subjected to flash column chromatography (silica gel, 0→30% EtOAc/hexane elution; 1% NEt$_3$ was present in the eluent) to provide title compound 6c (400 mg, 24% yield) as a colorless solid.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.35 (dd, $J = 8.0, 5.5$ Hz, 2H), 7.13 (t, $J = 8.8$ Hz, 2H), 6.64 (bs, 1H), 3.81 (s, 2H) ppm.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ –113.9 (s, 1F), –144.8 (d, $J = 16$ Hz, 2F), –155.9 (t, $J = 21$ Hz, 1F), –162.1 (t, $J = 19$ Hz, 2F) ppm.

$^{13}$C NMR (150 MHz, CDCl$_3$) δ 169.1, 163.3, 161.6, 143.0 (d, $J = 143$ Hz), 137.8 (d, $J = 253$ Hz), 131.1 (d, $J = 8$ Hz), 129.3 (d, $J = 3$ Hz), 116.3 (d, $J = 22$ Hz), 111.5 (t, $J = 19$ Hz), 42.5 ppm.

IR (NaCl) 3153, 2989, 2982, 1671, 1511, 1496, 1227, 1016, 1002, 963, 838 cm$^{-1}$.

EIMS (m/z, relative intensity) 323 (M$^+$, 2), 183 (70), 141 (45), 57 (100).

N-(Pentafluorophenyl)pent-4-enamide (6d)
4-Pentenoic acid (0.50 g, 5.00 mmol) was added to a magnetically stirred solution of pentafluoroaniline (1.10 g, 6.00 mmol), EDCI (1.30 g, 8.50 mmol) and DMAP (100 mg, 0.70 mmol) in CH₂Cl₂ (20 mL) maintained at 0 °C under N₂. After 5 min, NEt₃ (1.50 mL, 12.0 mmol) was added slowly and the reaction mixture was warmed to room temperature. After 16 h, KHSO₄ (10 mL of a saturated aqueous solution) was added and the phases separated. The organic phase was then washed with NaHCO₃ (10 mL of a saturated aqueous solution) and H₂O (10 mL) then dried (MgSO₄), filtered, and concentrated under reduced pressure. The ensuing solid was then recrystallized from EtOAc to provide title compound 6d (220 mg, 20% yield) as a colorless solid.

¹H NMR (600 MHz, CDCl₃) δ 6.71 (s, 1H), 5.87–5.76 (m, 1H), 5.11–5.00 (m, 2H), 2.51–2.40 (m, 4H) ppm.

¹³C NMR (150 MHz, CDCl₃) δ 170.6, 143.9, 142.3, 138.6, 137.0, 116.5, 111.7, 60.4, 35.5 ppm.

¹⁹F NMR (564 MHz, CDCl₃) δ –144.8 (d, J = 12 Hz, 2F), –156.5 (s, 1F), –162.3 (s, 2F) ppm.

IR (NaCl) 3245, 1681, 1648, 1543, 1502, 1490, 1000 cm⁻¹.

EIMS (m/z, relative intensity) 265 (M⁺, 2), 183 (50), 55 (100).

N-(Pentafluorophenyl)-3,5-bis(trifluoromethyl)benzamide (6f)

3,5-Bis(trifluoromethyl)benzoic acid (0.65 g, 2.50 mmol) was added to a magnetically stirred solution of pentafluoroaniline (0.50 g, 2.50 mmol), EDCI (0.60 g, 3.50 mmol) and DMAP (60 mg, 0.40 mmol) in CH₂Cl₂ (20 mL) maintained at 0 °C under N₂. After 5 min, NEt₃ (0.90 mL, 7.50 mmol) was added slowly and the reaction mixture warmed to room temperature. After 16 h, KHSO₄ (10 mL of a saturated aqueous solution) was added and the phases separated. The organic phase was then washed with NaHCO₃ (10 mL of a saturated aqueous solution) and H₂O (10 mL) then dried (MgSO₄), filtered, and concentrated under reduced pressure. The ensuing solid was then recrystallized from EtOAc to provide title compound 6f (80 mg, 6% yield) as a colorless solid.

¹H NMR (600 MHz, CDCl₃) δ 8.33 (s, 2 H), 8.05 (s, 1 H), 7.72 (s, 1 H) ppm.

¹³C NMR (150 MHz, CDCl₃) δ 162.8, 143.1, 141.1 (dm, J = 180 Hz), 139.3 (dm, J = 200 Hz), 137.1, 134.5, 132.8 (q, J = 88 Hz), 127.9, 126.3, 122.7 (q, J = 360 Hz) ppm.

¹⁹F NMR (564 MHz, CDCl₃) δ –62.8 (d, J = 18 Hz), –144.4 (m, 1F), –154.8 (m, 1F), –161.5 (m, 1F) ppm.

IR (NaCl) 1680, 1653, 1500, 1278, 1188, 1135, 1005, 940, 910 cm⁻¹.

EIMS (m/z, relative intensity) 423 (M⁺, 4), 241 (100), 213 (60), 163 (15).

Compound S1
DMAP (13.3 mg, 0.109 mmol) was added to a magnetically stirred mixture of pentafluoroaniline (1.00 g, 5.46 mmol), Boc₂O (1431 mg, 6.55 mmol) and Na₂CO₃ (1158 mg, 10.92 mmol) in THF (10 mL) maintained at r.t. under N₂. The ensuing mixture was then heated at 60 ºC. After 16 h, the mixture was cooled to r.t. and H₂O (5 mL) and EtOAc (20 mL) were added and the phases were separated. The ensuing aqueous phase was then extracted with EtOAc (2x 20 mL) and the combined organic fractions were dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The ensuing residue was then subjected to chromatography (silica plug, contained in a sintered glass funnel: ~3 cm height, 5 cm diameter; CH₂Cl₂ elution) to provide title compound S1 (1.15 g, 55% yield) as a colorless solid.

**1H NMR (400 MHz, CDCl₃)** \(\delta = 1.45 \text{ (s, 18H)} \text{ ppm.}\)

**19F NMR (376 MHz, CDCl₃)** \(\delta = 145.9 \text{ (d, } J = 17 \text{ Hz, 2F)}, \text{ } 154.7 \text{ (t, } J = 21 \text{ Hz, 1F)}, \text{ } 163.0 \text{ (t, } J = 19 \text{ Hz, 2F)} \text{ ppm.}\)

**13C NMR (150 MHz, CDCl₃)** \(\delta = 149.2, 143.6 \text{ (d, } J = 251 \text{ Hz)}, \text{ } 141.1 \text{ (d, } J = 256 \text{ Hz)}, \text{ } 137.5 \text{ (d, } J = 252 \text{ Hz)}, \text{ } 115.0 \text{ (td, } J = 15, 5 \text{ Hz)}, \text{ } 84.6, 27.7 \text{ ppm.}\)

**IR (NaCl)** 1810, 1777, 1734, 1519, 1372, 1271, 12448, 1149, 1119, 1099, 1066, 994, 852 cm⁻¹.

**EIMS (m/z, relative intensity)** 227 \{[M–(Boc, t-Bu)]⁺, 7\}, 57 (100).

**tert-Butyl (pentafluorophenyl)carbamate (6g)**

TFA (260 µL, 3.39 mmol) was added to a CH₂Cl₂ solution (10 mL) containing compound S1 (1.30 g, 3.39 mmol) maintained at 0 ºC under N₂. After 3 h, the solution was concentrated under reduced pressure. The resulting residue was subjected to flash column chromatography (silica gel, 0→10% EtOAc/hexane elution; 1% NEt₃ was present in the eluent) to provide title compound 6g (490 mg, 51% yield) as a colorless solid.

**1H NMR (400 MHz, CDCl₃)** \(\delta = 5.98 \text{ (bs, 1H)}, \text{ } 1.53 \text{ (s, 9H)} \text{ ppm.}\)

**19F NMR (376 MHz, CDCl₃)** \(\delta = 146.3 \text{ (d, } J = 16 \text{ Hz, 2F)}, \text{ } 157.8 \text{ (t, } J = 21 \text{ Hz, 1F)}, \text{ } 162.8 \text{ (m, 2F) ppm.}\)

**13C NMR (150 MHz, CDCl₃)** \(\delta = 152.2, 142.9 \text{ (d, } J = 254 \text{ Hz)}, \text{ } 149.7 \text{ (d, } J = 256 \text{ Hz)}, \text{ } 137.8 \text{ (d, } J = 252 \text{ Hz),} \text{ } 112.7, 84.6, 27.8 \text{ ppm.}\)

**IR (NaCl)** 3318, 1710, 1525, 1487, 1451, 1326, 1278, 1251, 1162, 1012, 974 cm⁻¹.

**EIMS (m/z, relative intensity)** 183 \{[M–Boc]⁺, 6\}, 41 (30), 57 (100).

**1,2,3,4,5-pentafluoro-6-(4-methoxyphenoxy)benzene (6i)**

4-Methoxyphenol (1.00 g, 8.05 mmol) was added to a magnetically stirred solution of hexafluorobenzene (1.10 g, 6.00 mmol) and K₂CO₃ in MeCN (20 mL) maintained at r.t. under N₂. The ensuing mixture was then heated at reflux. After 16 h, the reaction mixture was cooled, NaCl (30 mL of a saturated aqueous solution) was added and the phases separated. The aqueous phase was then further extracted with EtOAc (3x 20 mL) and organic fractions were combined, dried (MgSO₄), filtered, and concentrated under reduced pressure. The ensuing residue was subjected to flash column chromatography (silica gel, 10→30% EtOAc/hexane elution) to provide title compound 6i (800 mg, 46% yield) as a colorless solid.

**1H NMR (600 MHz, CDCl₃)** \(\delta = 6.88–6.82 \text{ (m, 2H)}, \text{ } 6.79–6.75 \text{ (m, 2H), } 3.71 \text{ (s, 3H) ppm.}\)
IR (NaCl) 1322, 1700, 1521, 14118.4, 116.9, 52.4, 30.9 ppm.

EIMS (m/z, relative intensity) 290 (M+, 100), 275 (70), 247 (20), 169 (25), 123 (30).

**Methyl 6,7,8,9-tetrafluorodibenzo[b,e][1,4]dioxine-2-carboxylate (6k)**

H₂SO₄ (one drop) was added to a mixture of 3,4-dihydroxybenzoic acid (0.92 g, 6.00 mmol) in MeOH (20 mL) maintained under N₂. The ensuing mixture was then heated at reflux. After 16 h, the mixture was concentrated under reduced pressure and MeCN (20 mL) added. Hexafluorobenzene (1.10 g, 6.00 mmol) and K₂CO₃ were then added to the ensuing mixture and the magnetically stirred mixture was then heated at reflux. After 16 h, the reaction mixture was quenched with NaCl (30 mL of a saturated aqueous solution) and phases separated. The aqueous phase was then further extracted with EtOAc (3x 20 mL) and organic fractions were combined, dried (MgSO₄), filtered, and concentrated under reduced pressure. The ensuing solid was then recrystallized from EtOAc and triturated (Et₂O) to provide title compound 6k (300 mg, 12% yield) as a colorless solid.

**6,7,8,9-Tetrafluorodibenzo[b,e][1,4]dioxin-2-yl)methanol (6l)**

LiAlH₄ (96 mg, 2.53 mmol) was added to a magnetically stirred solution of ester 6k (276 mg, 0.88 mmol) in Et₂O (20 mL) maintained at r.t. under N₂. After 14 h, the reaction mixture was cooled to 0 °C, and H₂O (100 μL), NaOH (100 μL of a 1 M aqueous solution), and H₂O (300 μL), were added successively. The mixture was warmed to r.t. After 0.25 h, MgSO₄ was added. After 0.25 h, the mixture was filtered through Celite® to provide title compound 6l (230 mg, 91% yield) as a colorless solid.
Furan-2-ylmethyl 2,3,4,5,6-pentafluorobenzoate (8i)

![Structural formula](image)

DMAP (52 mg, 429 μmol) was added to a magnetically stirred solution of pentafluorobenzoic acid (1.00 g, 4.72 mmol) and furfuryl alcohol (371 μL, 4.29 mmol) in CH₂Cl₂ (20 mL) at 0 °C under N₂. After 5 min, EDCI (1.15 g, 6.00 mmol) and NEt₃ (1.19 mL, 10.7 mmol) were added and the ensuing mixture was warmed to r.t. After 16 h, the reaction mixture was washed with KH₂SO₄ (20 mL of a saturated aqueous solution), NaHCO₃ (20 mL of a saturated aqueous solution), and H₂O (20 mL) successively. The organic phase was then dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The ensuing residue was then subjected to chromatography (silica plug contained in a sintered glass funnel: ~3 cm height, 5 cm diameter; 10% EtOAc/hexane elution) to provide title compound 8i as a colorless oil (521 mg, 38% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.48 (dd, J = 1.8, 0.6 Hz, 1H), 6.54 (d, J = 3.2 Hz, 1H), 6.42 (dd, J = 3.3, 1.8 Hz, 1H), 5.38 (s, 2H) ppm.

¹⁹F NMR (376 MHz, CDCl₃) δ −137.8 (m, 2F), −148.3 (t, J = 21 Hz, 1F), −160.3 (m, 2F) ppm.

¹³C NMR (150 MHz, CDCl₃) δ 158.7, 148.1, 145.5 (d, J = 256 Hz), 143.8, 143.3 (d, J = 262 Hz), 137.7 (d, J = 253 Hz), 111.7, 110.7, 107.9 (td, J = 16, 3.9 Hz), 60.0 ppm.

IR (NaCl) 1739, 1501, 1391, 1298, 1192, 951 cm⁻¹.

EIMS (m/z, relative intensity) 292 (M⁺, 15), 195 (15), 81 (100).

N-Methyl-N-(pentafluorophenyl)acetamide (8j)

![Structural formula](image)

NaH (149 mg of 60% dispersion in mineral oil, 3.73 mmol) was added to a magnetically stirred solution of N-(pentafluorophenyl)acetamide (500 mg, 2.22 mmol) in DMF (8 mL) maintained at 0 °C under N₂. After 0.5 h, iodomethane (166 μL, 2.66 mmol) was added dropwise and the ensuing mixture was warmed to room temperature. After 16 h, EtOAc/hexane (20 mL of 1:1 v/v solution) and H₂O (10 mL) were added and the phases separated. The aqueous phase was then further extracted with EtOAc/hexane (2x 20 mL of 1:1 v/v solution) and the combined organic fractions were dried (Na₂SO₄), filtered, and concentrated under reduced pressure. The ensuing residue was subjected to flash column chromatography (silica gel, 20% EtOAc/hexane elution) to provide title compound 8j (358 mg, 67% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 3.36 (s, 0.7H), 3.23 (s, 2.3H), 2.33 (s, 0.7H), 1.94 (s, 2.3H) ppm; 4 signals observed (rotamers present).

¹⁹F NMR (376 MHz, CDCl₃) δ −145.16 (d, J = 15.8 Hz, 0.4F), −145.72 (d, J = 15.8 Hz, 1.6F), −153.0 (t, J = 21.3 Hz, 0.8F), −155.4 (t, J = 21.3 Hz, 0.2F), −160.3 (m, 1.6 F), −162.2 (m, 0.4F) ppm; 6 signals observed (rotamers present).

¹³C NMR (150 MHz, CDCl₃) δ 170.6, 170.1, 144.1 (d, J = 250 Hz), 141.4 (d, J = 255 Hz), 140.9 (d, J = 255 Hz), 138.0 (d, J = 257 Hz), 119.0 (td, J = 15Hz, 6 Hz), 117.9 (td, J = 15 Hz, 6 Hz), 38.4, 35.8, 21.4, 21.1 ppm; 12 signals observed (rotamers present).

IR (NaCl) 1685, 1522, 1510, 1374, 1342, 1323, 991 cm⁻¹.


4,5,6,7-Tetrafluoro-3-(pentafluorophenyl)-2-phenylbenzofuran (8l)

S-9
Acetophenone (2.32 mL, 20.0 mmol) was added to a magnetically stirred mixture of hexafluorobenzene (2.30 mL, 20.0 mmol) and NaH (800 mg of 60% dispersion in mineral oil, 20.0 mmol) in DMF (20 mL) maintained under N₂. The ensuing mixture was then heated at 80 °C. After 5 h, the mixture was cooled, and Et₂O (50 mL) and H₂O (50 mL) were added and the phases separated. The aqueous phase was then further extracted with Et₂O (2x 20 mL) and the combined organic fractions were dried (MgSO₄), filtered, and concentrated under reduced pressure. The ensuing residue was subjected to flash column chromatography (silica gel, 10% CH₂Cl₂/hexane, then EtOAc elution) to provide title compound 8l (150 mg, 3% yield) as a colorless solid (after recrystallization from hexane).

**H NMR** (600 MHz, CDCl₃) δ 7.58 (d, J = 7.2 Hz, 2H), 7.52–7.40 (complex m, 3H) ppm.

**19F NMR** (564 MHz, CDCl₃) δ –137.5 (d, J = 21 Hz, 2F), –151.7 (t, J = 21 Hz, 1F), –152.4 (m, 1F), –159.5 (t, J = 20 Hz, 1F), –160.5 (td, J = 21, 7 Hz, 2F), –160.9 (t, J = 19 Hz, 2F), –162.4 (t, J = 20 Hz, 1F) ppm.

**13C NMR** (150 MHz, CDCl₃) δ 156.3, 145.0 (d, J = 250 Hz), 142.0 (d, J = 254 Hz), 139.3 (d, J = 250 Hz), 137.9 (d, J = 250 Hz), 134.2 (d, J = 252 Hz), 130.6, 129.2, 128.0, 126.5, 114.9 (d, J = 16 Hz), 106.1 (td, J = 19, 4 Hz), 99.4 ppm.

**IR (NaCl)** 1538, 1489, 1451, 1440, 1157, 1092, 1047, 1031, 1010, 990, 767, 690 cm⁻¹.

**EIMS (m/z, relative intensity)** 432 (M⁺, 100), 412 (40), 206 (15).

**N-(4-Bromo-2,3,5,6-tetrafluorophenyl)acetamide** (12)

2,3,5,6-Tetrafluoroaniline (0.50 g, 2.80 mmol) was added to a magnetically stirred mixture of NaHCO₃ (0.33g, 3.9 mmol) and Br₂ (0.2 mL, 3.6 mmol) in MeOH (30 mL) maintained under N₂. After 48 h, the solution was quenched with Na₂S₂O₃ (20 mL of a saturated aqueous solution) and extracted with Et₂O (3x 50 mL). The combined organic phases were dried (MgSO₄), filtered, and concentrated under reduced pressure, to provide an off-white solid. The ensuing solid was then added to a magnetically stirred mixture of Ac₂O (0.2 mL, 2.3 mmol) and H₂SO₄ (0.05 mL) in PhMe (20 mL), which was then heated at 80 °C. After 48 h, the mixture was concentrated under reduced pressure to provide a crude solid, which was recrystallized from hot PhMe to provide title compound 12 (180 mg, 20% yield) as a colorless solid.

**H NMR** (600 MHz, CDCl₃) δ 7.16 (s, 1H), 2.32 (s, 3H) ppm.

**19F NMR** (564 MHz, CDCl₃) δ –145.4 (d, J = 16 Hz, 2F), –161.5 (s, 2F) ppm.

IR (NaCl) 3256, 3224, 3178, 1695, 1524, 1519, 1497 1020, 987 cm⁻¹.


### IV. Visible Light-Mediated Copper-Photocatalysed Reactions

**General Procedure 1: Dual α-Amino C–H/ C–F Functionalization Reactions**
In a nitrogen-filled glovebox, [Cu(bcp)(XP)]PF₆ (2) (8.6 mg, 7.5 μmol) was added to a 20-mL screw-top vial (PTFE tape-lined thread) containing the perfluorinated substrate (500 μmol), tertiary amine (1.00 mmol), Gd(OTf)₃ (121 mg, 200 μmol), MeCN (3.85 mL), and a stir bar. The vial was then capped, the joint was wrapped with PARAFILM®, and removed from the glovebox and placed in a water bath (suspended with Cu wire) maintained at 45 °C that was contained within a 18 W blue LED photoreactor (switched off) and magnetically stirred (Figure S2). The vial was then irradiated (25% duty cycle at 100 kHz). After 24 h, the reaction mixture was quenched by exposure to air and analyzed by ¹⁹F NMR spectroscopy (after the addition of 1-bromo-4-fluorobenzene as an internal standard) or concentrated under reduced pressure and the ensuing residue was purified by flash column chromatography on silica gel.

**General Procedure 2: Hydrodefluorination Reactions**

In a nitrogen-filled glovebox, [Cu(bcp)(XP)]PF₆ (2) (8.6 mg, 7.5 μmol) was added to a 20-mL screw-top vial (PTFE tape-lined thread) containing the perfluorinated substrate (500 μmol), i-Pr₂NEt (4a) (129 mg, 1.00 mmol), MeCN (7.70 mL), and a stir bar. The vial was then capped, the joint was wrapped with PARAFILM®, and removed from the glovebox and placed in a water bath (suspended with Cu wire) maintained at 45 °C that was contained within a 18 W blue LED photoreactor (switched off) and magnetically stirred (Figure S2). The vial was then irradiated (25% duty cycle at 100 kHz). After 24 h, the reaction mixture was quenched by exposure to air and analyzed by ¹⁹F NMR spectroscopy (after the addition of 1-bromo-4-fluorobenzene as an internal standard) or concentrated under reduced pressure and the ensuing residue was purified by flash column chromatography on silica gel.

**N-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)acetamide (5a)**

![Image of N-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)acetamide (5a)]

Reaction between N-(pentafluorophenyl)acetamide (3a) (500 μmol) and i-Pr₂NEt (4a) following General Procedure 1. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/hexane elution; 1% NEt₃ was also present in the eluent) and then was recrystallized to provide title compound 5a as a colorless solid (145 mg, 87% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.04 (bs, 1H), 4.66 (q, J = 7.3 Hz, 2H), 3.37 (sept, J = 6.6 Hz, 6H), 0.94 (d, J = 6.8 Hz, 6H) ppm.

¹³C NMR (150 MHz, CDCl₃) δ 168.3, 144.8 (d, J = 242 Hz), 142.3 (d, J = 249 Hz), 124.5, 113.7, 46.0, 45.7, 22.7, 22.4, 19.7 ppm.

IR (ATR) 2965, 1673, 1529, 1501, 1275, 1215, 1148, 1083, 1005, 985, 940, 726 cm⁻¹.


**N-(4-((dicyclohexylamino)methyl)-2,3,5,6-tetrafluorophenyl)acetamide (5b)**

![Image of N-(4-((dicyclohexylamino)methyl)-2,3,5,6-tetrafluorophenyl)acetamide (5b)]

Reaction between N-(pentafluorophenyl)acetamide (3a) (500 μmol) and Cy₂NMe (4b) following General Procedure 1. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/hexane elution; 1% NEt₃ was also present in the eluent) to provide title compound 5b as a colorless solid (115 mg, 57% yield).
1H NMR (600 MHz, CDCl₃) δ 7.11 (bs, 1H), 3.85 (s, 2H), 2.46 (t, J = 11.8 Hz, 2H), 2.25 (s, 3H), 1.76 (complex m, 8H), 1.61 (d, J = 12.9 Hz, 2H), 1.36 (m, 4H), 1.22 (m, 4H), 1.08 (m, 2H) ppm.

19F NMR (564 MHz, CDCl₃) δ −144.3 (s, 2F), −147.0 (s, 2F) ppm.

13C NMR (150 MHz, CDCl₃) δ 168.3, 145.6 (d, J = 249 Hz), 141.9 (d, J = 249 Hz), 118.8, 114.4, 57.7, 37.8, 31.8, 26.6, 26.2 ppm.

IR (NaCl) 2929, 2853, 2362, 2339, 1684, 1499, 1477, 1296, 1272, 1033, 891, 668 cm⁻¹.


N-(4-(1-(Dicyclohexylamino)propyl)-2,3,5,6-tetrafluorophenyl)acetamide (5c)

Reaction between N-(pentafluorophenyl)acetamide (3a) (395 μmol) and Cy₂NPr (4c) following General Procedure 1. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/ hexane elution; 1% NEt₃ was present in the eluent) to provide title compound 5c as a colorless solid (32 mg, 19% yield).

1H NMR (600 MHz, CDCl₃) δ 7.07 (bs, 1H), 4.33 (dd, J = 9.2, 6.2, 1H), 2.86 (t, J = 11.5 Hz, 2H), 2.24 (s, 3H), 2.01 (m, 1H), 1.86 (m, 1H), 1.78 (d, J = 11.1 Hz, 2H), 1.68 (t, J = 14.4 Hz, 4H), 1.59 (d, J = 12.2 Hz, 2H), 1.46 (qd, J = 12.2, 3.1 Hz, 4H), 1.37–1.17 (complex m, 8H), 1.05 (qt, J = 12.8, 3.5 Hz, 2H), 0.81 (t, J = 7.3 Hz, 3H) ppm.

19F NMR (564 MHz, CDCl₃) δ −140.9 (s, 2F), −146.4 (s, 2F) ppm.

13C NMR (150 MHz, CDCl₃) δ 168.2, 145.1 (d, J = 245 Hz), 142.2 (d, J = 249 Hz), 123.3, 113.7, 55.5, 53.7, 34.1, 33.6, 26.9, 26.8, 26.3, 26.0, 11.8 ppm.

IR (NaCl) 3251, 2929, 2853, 1683, 1646, 1520, 1476, 1453, 1371, 1272, 1182, 1134, 1117, 1098, 986, 892, 735 cm⁻¹.

EIMS (m/z, relative intensity) 428 (M⁺, 1), 181 (8), 138 (100), 56 (50).

N-(4-(1-(Diethylamino)propyl)-2,3,5,6-tetrafluorophenyl)acetamide (5d)

Reaction between N-(perfluorophenyl)acetamide (3a) (500 μmol) and triethylamine (4d) following General Procedure 1 {Gd(OTf)₃ not added}. Title compound 5d was formed in 66% yield (average of two experiments) as determined via 19F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→50% EtOAc/ hexane elution; 1% NEt₃ was present in the eluent) to provide a sample of product 5d as a colorless solid.

1H NMR (400 MHz, CDCl₃) δ 7.25 (bs, 1H), 4.43 (q, J = 7.1 Hz, 1H), 2.72 (sextet, J = 7.2 Hz, 2H), 2.38 (sextet, J = 6.5 Hz, 2H), 2.25 (s, 3H), 1.55 (d, J = 7.3 Hz, 3H), 1.06 (t, J = 6.7 Hz, 6H) ppm.

19F NMR (376 MHz, CDCl₃) δ −140.3 (s, 2F), −146.0 (s, 2F) ppm.

13C NMR (150 MHz, CDCl₃) δ 168.2, 145.4 (d, J = 246 Hz), 142.3 (d, J = 251 Hz), 118.9, 114.9, 51.4, 43.4, 29.7, 23.0, 17.2, 12.5 ppm.

IR (NaCl) 3254, 2975, 2938, 1684, 1646, 1496, 1472, 1373, 1275, 1102, 982, 944 cm⁻¹.


N-(2,3,5,6-tetrafluoro-4-((hexadecyl(methyl)amino)methyl)phenyl)acetamide (5e)
Reaction between \( N \)-\((\text{pentafluorophenyl})\)acetamide (3a) (500 \( \mu \)mol) and \( N, N \)-dimethylhexadecan-1-amine (4e) following General Procedure 1. Title compound 5e was formed in 21\% yield (average of two experiments) as determined via \(^{19}\text{F} \) NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0\( \to \)30\% EtOAc/ hexane elution; 1\% NEt\(_3\) was present in the eluent) to provide a sample of product 5e (+ co-eluting starting material 3a) as a colorless solid.

\(^1\text{H} \) NMR (600 MHz, CDCl\(_3\)) \( \delta 7.17 \) (bs, 1H), 3.72 (s, 2H), 2.42 (t, \( J = 7.5 \) Hz, 2H), 2.25 (s, 6H), 1.53 (t, \( J = 6.6 \) Hz, 2H), 1.28 (s, 24H), 0.90 (t, \( J = 7.1 \) Hz, 3H) ppm.

\(^{19}\text{F} \) NMR (564 MHz, CDCl\(_3\)) \( \delta -139.5, -142.3, -145.7, -146.1 \) ppm; 4 signals observed (rotamers present).

\(^{13}\text{C} \) NMR (150 MHz, CDCl\(_3\)) \( \delta 168.3, 145.5, 119.3, 115.5, 60.4, 57.3 \) ppm.

IR (NaCl) 3257, 2975, 2792, 1684, 1525, 1501, 1478, 1373, 1277, 1034, 1002, 985, 937 cm\(^{-1}\).

EIMS (\( m/z \), relative intensity) 290 (M\(^+\)), 84 (100).

\( N \)-\((2,3,5,6\text{-Tetrafluoro-4-(1-methylpyrrolidin-2-yl)}\)phenyl)acetamide (5f)

\( N \)-\((4\text{-}(1\text{-Ethylpyrrolidin-2-yl})\)-2,3,5,6-tetrafluorophenyl)acetamide (5g)
Reaction between $N$-(pentafluorophenyl)acetamide (3a) (500 μmol) and $N$-ethylpyrrolidine (4g) following General Procedure 1. Title compound 5g was formed in 34% yield (average of two experiments) as determined via $^{19}$F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→60% EtOAc/ hexane elution; 1% NEt$_3$ was present in the eluent) to provide a sample of product 5g (+ co-eluting starting material 3a) as a colorless solid.

$^{1}$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.67 (bs, 1H), 3.81 (t, $J$ = 7.6 Hz, 1H), 3.29 (t, $J$ = 7.6 Hz, 1H), 2.60 (m, 1H), 2.31-2.13 (complex m, 6H), 2.07 (m, 2H), 1.87 (m, 1H), 1.02 (t, $J$ = 7.3 Hz, 3H) ppm.

$^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ $-$143.3 (s, 2F), $-$146.7 (s, 2F) ppm.

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 169.0, 145.4 (d, $J$ = 247 Hz), 142.2 (d, $J$ = 250 Hz), 120.3, 114.6 (t, $J$ = 14 Hz), 58.9, 53.5, 48.6, 30.6, 23.4, 13.4 ppm.

IR (NaCl) 3254, 3218, 1684, 1652, 1540, 1506, 1471, 1370, 1276, 1149, 1090, 1000, 984, 923 cm$^{-1}$.

EIMS ($m/z$, relative intensity) 304 (M$^+$, 15), 289 (100), 218 (55), 178 (35), 98 (60).

$N$-(4-(1-Decylpyrrolidin-2-yl)-2,3,5,6-tetrafluorophenyl)acetamide (5h)

Reaction between $N$-(pentafluorophenyl)acetamide (3a) (500 μmol) and $N$-decylpyrrolidine (4h) following General Procedure 1. Title compound 5h was formed in 50% yield (average of two experiments) as determined via $^{19}$F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 10→60% EtOAc/ hexane elution; 1% NEt$_3$ was present in the eluent) to provide a sample of product 5h as a colorless solid.

$^{1}$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.01 (bs, 1H), 3.70 (t, $J$ = 7.6 Hz, 1H), 3.20 (t, $J$ = 8.2 Hz, 1H), 2.39 (m, 1H), 2.21-2.04 (complex m, 6H), 1.97 (m, 2H), 1.77 (d, $J$ = 9.1 Hz, 1H), 1.31 (quin, $J$ = 6.7 Hz, 2H), 1.23-1.07 (complex m, 14H), 0.80 (t, $J$ = 7.5 Hz, 3H) ppm.

$^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ $-$143.2 (s, 2F), $-$146.8 (s, 2F) ppm.

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 168.3, 145.4 (d, $J$ = 249 Hz), 142.2 (d, $J$ = 250 Hz), 120.6, 114.5, 59.2, 54.9, 53.9, 31.9, 30.7, 29.57, 29.56, 29.4, 29.3, 28.6, 27.4, 23.5, 22.7, 14.1 ppm.

IR (NaCl) 3225, 2927, 2855, 2793, 1683, 1652, 1531, 1475, 1456, 1277, 1147, 1093, 997, 983 cm$^{-1}$.

EIMS ($m/z$, relative intensity) 416 (M$^+$, 2), 289 (100), 218 (24), 178 (14).

$N$-(2,3,5,6-Tetrafluoro-4-(1-isopropylpyrrolidin-2-yl)phenyl)acetamide (5i)

Reaction between $N$-(pentafluorophenyl)acetamide (3a) (400 μmol) and $N$-isopropylpyrrolidine (4i) following General Procedure 1. Title compound 5i was formed in 17% yield (average of two experiments) as determined via $^{19}$F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 30→60% EtOAc/ hexane elution; 1% NEt$_3$ was present in the eluent) to provide a sample of product 5i (+ co-eluting starting material 3a) as a colorless solid.
$^1$H NMR (600 MHz, CDCl$_3$) δ 7.73 (bs, 1H), 4.20 (t, $J = 6.9$ Hz, 1H), 3.10 (t, $J = 8.3$ Hz, 1H), 2.79 (quin, $J = 6.5$ Hz, 1H), 2.60 (q, $J = 7.9$ Hz, 1H), 2.25-2.13 (complex m, 4H), 2.02 (m, 2H), 1.82 (m, 1H), 1.02 (d, $J = 6.6$ Hz, 3H), 0.96 (d, $J = 6.3$ Hz, 3H) ppm.

$^{19}$F NMR (564 MHz, CDCl$_3$) δ –143.6 (s, 2F), –146.8 (s, 2F) ppm.

$^{13}$C NMR (150 MHz, CDCl$_3$) δ 169.0, 145.3 (d, $J = 247$ Hz), 142.3 (d, $J = 250$ Hz), 121.6, 114.5 (t, $J = 14$ Hz), 54.5, 50.0, 47.4, 31.6, 23.8, 21.5, 16.0 ppm.

IR (NaCl) 3242, 2970, 2937, 1684, 1521, 1501, 1476, 1456, 1277, 992, cm$^{-1}$.

EIMS (m/z, relative intensity) 318 (M$^+$, 10), 303 (100), 218 (70), 178 (20).

N-4-(((2-(Dimethylamino)ethyl)(methyl)amino)methyl)-2,3,5,6-tetrafluorophenylacetamide (5j)

\[
\begin{array}{c}
\text{NHAc} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{H} \\
\text{NMe} \\
\text{NMe}_2 \\
\end{array}
\]

Reaction between N-(pentafluorophenyl)acetamide (3a) (500 μmol) and TMEDA (4j) following General Procedure 1 {Gd(OTf)$_3$ not added}. Title compound 5j was formed in 67% yield (average of two experiments) as determined via $^{19}$F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was dissolved in CH$_2$Cl$_2$ (10 mL) and HCl (10 mL of a 2 M aqueous solution) was added. The aqueous phase was washed with CH$_2$Cl$_2$ (3x 10 mL) then treated with K$_2$CO$_3$ (saturated aqueous solution) until pH >7. The aqueous phase was then extracted with CH$_2$Cl$_2$ (3x 10 mL) to provide a sample of product 5j as a pale yellow solid.

$^1$H NMR (600 MHz, CDCl$_3$) δ 8.39 (bs, 1H), 3.65 (s, 2H), 2.49 (t, $J = 7.0$ Hz, 2H), 2.42 (t, $J = 6.3$ Hz, 2H), 2.21 (s, 6H), 2.16 (s, 3H), 2.12 (s, 3H) ppm.

$^{19}$F NMR (564 MHz, CDCl$_3$) δ –142.7 (s, 2F), –145.9 (s, 2F) ppm.

$^{13}$C NMR (150 MHz, CDCl$_3$) δ 169.1, 145.4 (d, $J = 245$ Hz), 142.2 (d, $J = 250$ Hz), 115.9 (t, $J = 14$ Hz), 113.8 (t, $J = 18$ Hz), 57.0, 54.5, 48.4, 45.5, 41.5, 22.7 ppm.

IR (NaCl) 3200, 2951, 2826, 1700, 1481, 1371, 1295, 1276, 1136, 1124, 1026, 910 cm$^{-1}$.

EIMS (m/z, relative intensity) 321 (M$^+$, 1), 263 (11), 178 (20), 58 (100).

N-4-(((3-(Dimethylamino)propyl)(methyl)amino)methyl)-2,3,5,6-tetrafluorophenylacetamide  (p-5k)

\[
\begin{array}{c}
\text{NHAc} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{H} \\
\text{NMe} \\
\text{NMe}_2 \\
\end{array} + \begin{array}{c}
\text{NHAc} \\
\text{MeN} \\
\text{NMe}_2 \\
\end{array}
\]

Reaction between N-(pentafluorophenyl)acetamide (3a) (500 μmol) and $N,N,N',N'$-tetramethylpropane-1,3-diamine (4k) following General Procedure 1 {Gd(OTf)$_3$ not added}. Compound p-5k was formed in 60% yield (average of two experiments) and compound o-5k was formed in 6% yield (average of two experiments) as determined via $^{19}$F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was dissolved in CH$_2$Cl$_2$ (10 mL) and HCl (10 mL of a 2 M aqueous solution) was added. The aqueous phase was washed with CH$_2$Cl$_2$ (3x 10 mL) then treated with K$_2$CO$_3$ (saturated aqueous solution) until pH >7. The aqueous phase was then extracted with CH$_2$Cl$_2$ (3x 10 mL) to provide a sample of product p-5k (which contained traces of compound o-5k) as a pale yellow solid.
$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.50 (bs, 1H), 3.66 (s, 1.5H), 3.60 (s, 0.5H) 2.41 (t, $J = 7.3$ Hz, 2H), 2.31 (t, $J = 7.7$ Hz, 2H), 2.22 (s, 6H), 2.19 (s, 6H), 1.67 (t, $J = 7.4$ Hz, 2H) ppm; 8 signals observed (rotamers present).

$^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ –142.9 (s, 1.5F), –143.3 (s, 0.5F) –146.1 (s, 1.5F), –146.3 (s, 0.5F) ppm; 4 signals observed (rotamers present).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 169.0, 145.4 (d, $J = 246$ Hz), 142.2 (d, $J = 251$ Hz), 115.8 (t, $J = 14$ Hz), 114.3 (t, $J = 17$ Hz), 57.6, 55.1, 48.0, 45.3, 41.5, 25.4, 22.7 ppm.

IR (NaCl) 3205, 2450, 2793, 1688, 1527, 1483, 1371, 1295, 1277, 1124, 1029, 910 cm$^{-1}$.

EIMS (m/z, relative intensity) 335 (M$^+$, 1), 263 (5), 178 (25), 115 (30), 58 (100).

$N$-((2-(Dimethylamino)butyl)(methyl)amino)methyl)-2,3,5,6-tetrafluorophenylacetamide (5l)

![Diagram of N-(2-(Dimethylamino)butyl)(methyl)amino)methyl)-2,3,5,6-tetrafluorophenylacetamide (5l)](image)

Reaction between $N$-(pentafluorophenyl)acetamide (3a) (500 $\mu$mol) and $N,N,N’,N’$-tetramethylbutane-1,4-diamine (4l) following General Procedure 1 {Gd(OTf)$_3$ not added}. Compound p-5l was formed in 45% yield (average of two experiments) and compound o-5l was formed in 3% yield (average of two experiments) as determined via $^{19}$F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was dissolved in CH$_2$Cl$_2$ (10 mL) and HCl (10 mL of a 2 M aqueous solution) was added. The aqueous phase was washed with CH$_2$Cl$_2$ (3x 10 mL) then treated with K$_2$CO$_3$ (saturated aqueous solution) until pH >7. The aqueous phase was then extracted with CH$_2$Cl$_2$ (3x 10 mL) to provide a sample of product p-5l (which contained traces of compound o-5l) as a pale yellow solid.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.25 (bs, 1H), 3.67 (s, 2H), 2.40 (t, $J = 6.5$ Hz, 2H), 2.31 (m, 2H), 2.24 (s, 3H), 2.21 (s, 6H), 2.19 (s, 3H), 1.50 (m, 4H) ppm.

$^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ –139.8 (s, 0.7H), –142.8 (s, 1.3F), –145.6 (s, 0.7F), –146.1 (s, 1.4F) ppm; 4 signals observed (rotamers present).

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 168.8, 145.5 (d, $J = 247$ Hz), 142.2 (d, $J = 250$ Hz), 115.6, 114.5, 60.8, 59.5, 59.4, 56.8, 48.1, 45.3, 45.1, 41.8, 41.5, 28.8, 25.2, 25.0, 22.8 ppm.

IR (NaCl) 3199, 2947, 2865, 1680, 1516, 1501, 1371, 1275, 1126, 1029, 909 cm$^{-1}$.

EIMS (m/z, relative intensity) 349 (M$^+$, 1), 284 (6), 221 (10), 71 (100).

$N$-((2-(Dimethylamino)hexyl)(methyl)amino)methyl)-2,3,5,6-tetrafluorophenylacetamide (5m)

![Diagram of N-(2-(Dimethylamino)hexyl)(methyl)amino)methyl)-2,3,5,6-tetrafluorophenylacetamide (5m)](image)

Reaction between $N$-(pentafluorophenyl)acetamide (3a) (500 $\mu$mol) and $N,N,N’,N’$-tetramethylhexane-1,6-diamine (4m) following General Procedure 1 {Gd(OTf)$_3$ not added}. Compound p-5m was formed in 65% yield (average of two experiments) and compound o-5m was formed in 7% yield (average of two experiments) as determined via $^{19}$F NMR spectroscopy with the aid of a calibrated internal standard. The
ensuing residue obtained from the reaction mixture was dissolved in CH$_2$Cl$_2$ (10 mL) and HCl (10 mL of a 2 M aqueous solution) was added. The aqueous phase was washed with CH$_2$Cl$_2$ (3x 10 mL) then treated with K$_2$CO$_3$ (saturated aqueous solution) until pH >7. The aqueous phase was then extracted with CH$_2$Cl$_2$ (3x 10 mL) to provide a sample of product _p-5m_ (which contained traces of compound _o-5m_) as a pale yellow solid.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.15 (bs, 1H), 3.68 (s, 2H), 2.39 (t, $J=7.4$ Hz, 2H), 2.29 (m, 2H), 2.27 (s, 6H), 2.24 (s, 3H), 2.23 (s, 3H), 1.46 (m, 4H), 1.29 (m, 4H) ppm.

$^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ −142.8 (s, 2F), −146.2 (s, 2F) ppm.

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 168.7, 145.5 (d, $J=247$ Hz), 142.3 (d, $J=250$ Hz), 115.7 (t, $J=16$ Hz), 114.8 (t, $J=17$ Hz), 59.6, 56.7, 48.3, 45.1, 41.9, 27.33, 27.29, 27.2, 27.1 ppm.

IR (NaCl) 3209, 2939, 2859, 1679, 1525, 1476, 1448, 1274, 1030 cm$^{-1}$.

EIMS ($m/z$, relative intensity) 377 (M$^+$, 1), 178 (26), 157 (12), 126 (19), 112 (38) 58 (100).

_N-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)nonanamide (7a)_

Reaction between _N-(pentafluorophenyl)nonanamide (6a) (500 µmol) and _i-Pr$_2$NEt (4a) following General Procedure 1. Title compound 7a was formed in 63% yield (average of two experiments) as determined via $^{19}$F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/ hexane elution; 1% NEt$_3$ was present in the eluent) to provide a sample of product 7a (+ co-eluting starting material 6a) as a colorless solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.12 (bs, 1H), 4.65 (q, $J=7.2$ Hz, 1H), 3.36 (sept, $J=6.7$ Hz, 2H), 2.43 (t, $J=7.2$ Hz, 2H), 1.73 (quin, $J=7.4$ Hz, 3H), 1.51 (d, $J=7.1$ Hz, 3H), 1.30 (complex m, 15 H), 1.12 (d, $J=6.6$ Hz, 6H), 0.94 (d, $J=6.6$ Hz, 6H), 0.90 (t, $J=6.6$ Hz, 5H) ppm; 44 protons observed (starting material present).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −142.3 (d, $J=12$ Hz, 2F), −146.6 (d, $J=22$ Hz, 2F) ppm.

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 171.9, 145.0 (d, $J=241$ Hz), 142.3 (d, $J=253$ Hz), 124.5, 113.8 (t, $J=14$ Hz), 46.1, 45.8, 31.9, 29.4, 29.3, 29.2, 25.6, 22.81, 22.76, 22.6, 19.8, 14.2 ppm.

HRESIMS Found: [M + H]$^+$, 433.2840. C$_{23}$H$_{23}$F$_3$N$_2$O requires [M + H]$^+$, 433.2837.

_N-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)-2-phenylacetamide (p-7b) & _N-(2-(1-(Diisopropylamino)ethyl)-3,4,5,6-tetrafluorophenyl)-2-phenylacetamide (o-7b)_

Reaction between _N-(pentafluorophenyl)-2-phenylacetamide (6b) (500 µmol) and _i-Pr$_2$NEt (4a) following General Procedure 1. Compound _p-7b_ was formed in 80% yield (average of two experiments) and compound _o-7b_ was formed in 5% yield (average of two experiments) as determined via $^{19}$F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/ hexane elution; 1%
NET₃ was present in the eluent) to provide compound p-7b as a colorless solid (which contained traces of compound o-7b).

¹H NMR (600 MHz, CDCl₃) δ 7.31–7.21 (complex m, 5H), 6.94 (bs, 1H), 4.54 (q, J = 7.1 Hz, 1H), 3.69 (s, 2H), 3.25 (sept, J = 6.7 Hz, 2H), 1.39 (d, J = 7.5 Hz, 3H), 1.01 (d, J = 7.0 Hz, 6H), 0.82 (d, J = 7.0 Hz, 6H) ppm.

¹⁹F NMR (564 MHz, CDCl₃) δ −124.8 (s, 0.13F), −135.9 (d, J = 22 Hz, 0.13F), −141.0 (d, J = 20 Hz, 0.13F), −142.2 (d, J = 13 Hz, 2F), −146.5 (d, J = 24 Hz, 2F), −164.3 (td, J = 21, 4.8 Hz, 0.12F) ppm.

¹³C NMR (150 MHz, CDCl₃) δ 169.5, 144.8 (d, J = 245 Hz), 142.2 (d, J = 250 Hz), 134.0, 129.4, 129.2, 127.8, 124.6 (t, J = 17 Hz), 113.6 (t, J = 15 Hz), 45.9, 45.6, 43.4, 22.7, 22.4, 19.6 ppm.

IR (NaCl) 2927, 2854, 1733, 1514, 1450, 1357, 1287, 1163, 1092, 996 cm⁻¹.

EIMS (m/z, relative intensity) 428 (M⁺, 3), 413 (20), 192 (83), 109 (50), 86 (100).

N-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)-2-(4-fluorophenyl)acetamide (7c)

Reaction between 2-(4-fluorophenyl)-N-(pentafluorophenyl)acetamide (6c) (500 μmol) and i-Pr₂NEt (4a) following General Procedure 1. Title compound 7c was formed in 86% yield (average of two experiments) as determined via ¹⁹F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→20% EtOAc/ hexane elution; 1% NEt₃ was present in the eluent) to provide a sample of product 7c as a colorless solid.

¹H NMR (600 MHz, CDCl₃) δ 7.34 (t, J = 5.7 Hz, 2H), 7.09 (t, J = 8.8 Hz, 2H), 6.92 (bs, 1H), 4.65 (q, J = 8.0 Hz, 1H), 3.78 (s, 2H), 3.35 (sept, J = 7.0 Hz, 2H), 1.50 (d, J = 6.8 Hz, 3H), 1.11 (d, J = 6.8 Hz, 6H), 0.92 (d, J = 6.8 Hz, 6H) ppm.

¹⁹F NMR (564 MHz, CDCl₃) δ −114.4 (s, 1F), −142.1 (s, 2F), −146.5 (d, J = 13 Hz, 2F) ppm.

¹³C NMR (150 MHz, CDCl₃) δ 169.2, 163.2, 161.5, 144.8 (d, J = 245 Hz), 142.3 (d, J = 250 Hz), 131.1 (d, J = 8 Hz), 129.7 (d, J = 3 Hz), 124.8 (t, J = 16 Hz), 116.1 (d, J = 21 Hz), 113.4 (t, J = 15 Hz), 46.0, 45.7, 42.5, 22.7, 22.4, 19.6 ppm.

IR (NaCl) 3245, 2971, 2936, 1675, 1648, 1514, 1450, 1357, 1287, 1163, 1092, 996 cm⁻¹.

EIMS (m/z, relative intensity) 428 (M⁺, 3), 413 (20), 192 (83), 109 (50), 86 (100).

N-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)pent-4-enamide (7d)

Reaction between N-(pentafluorophenyl)pent-4-enamide (6d) (500 μmol) and i-Pr₂NEt (4a) following General Procedure 1. Title compound 7d was formed in 64% yield (average of two experiments) as determined via ¹⁹F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/ hexane elution; 1% NEt₃ was present in the eluent) to provide a sample of product 7d as a colorless solid.
\( ^1H \text{NMR} (600 \text{ MHz}, \text{CDCl}_3) \delta \ 7.04 \text{ (bs, 1H)}, 5.82 \text{ (m, 1H)}, 5.07 \text{ (d, } J = 17 \text{ Hz, 1H)}, 5.01 \text{ (d, } J = 9.8 \text{ Hz, 1H)}, 4.56 \text{ (q, } J = 7.3 \text{ Hz, 1H)}, 3.28 \text{ (sept, } J = 6.7 \text{ Hz, 2H)}, 2.51–2.40 \text{ (complex m, 4H)}, 1.42 \text{ (d, } J = 7.4 \text{ Hz, 3H)}, 1.03 \text{ (d, } J = 6.8 \text{ Hz, 6H)}, 0.86 \text{ (d, } J = 6.8 \text{ Hz, 6H)} \text{ ppm.}

\( ^19F \text{NMR} (564 \text{ MHz}, \text{CDCl}_3) \delta \ -142.2 \text{ (bs, 2F)}, -146.5 \text{ (d, } J = 24 \text{Hz, 2F)} \text{ ppm.}

\( ^{13}C \text{NMR} (150 \text{ MHz}, \text{CDCl}_3) \delta \ 170.5, 144.8 \text{ (d, } J = 245 \text{ Hz)}, 142.1 \text{ (d, } J = 250 \text{ Hz)}, 136.4, 124.5 \text{ (t, } J = 16 \text{ Hz)}, 116.3, 113.6 \text{ (t, } J = 14 \text{ Hz)}, 46.0, 45.7, 35.5, 29.3, 22.7, 22.4, 19.7 \text{ ppm.}

IR (ATR) 2971, 1671, 1524, 1476, 1399, 1363, 1290, 1212, 1152, 1084, 1004, 944, 914 \text{ cm}^{-1}. \text{HRESIMS Found: } [\text{M + H}]^+, 375.2055. \text{C}_{19}\text{H}_{27}\text{F}_4\text{N}_2\text{O requires } [\text{M + H}]^+, 375.2054.

\( N-(4-(1-(\text{Diisopropylamino})ethyl)-2,3,5,6-\text{tetrafluorophenyl})\text{benzamide (7e) } \)

\begin{center}
\includegraphics[width=0.3\textwidth]{image}
\end{center}

Reaction between \( N-(\text{pentafluorophenyl})\text{benzamide (6e)} \) and \( i-\text{Pr}_2\text{NEt (4a)} \) following General Procedure 1. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→10% EtOAc/hexane elution; 1% \( \text{NEt}_3 \) was also present in the eluent) to provide title compound \( 7e \) as a colorless solid (102 mg, 46% yield).

\( ^1H \text{NMR} (600 \text{ MHz}, \text{CDCl}_3) \delta \ 7.81 \text{ (d, } J = 7.7 \text{ Hz, 2H)}, 7.62 \text{ (bs, 1H)}, 7.49 \text{ (t, } J = 7.3 \text{ Hz, 1H)}, 7.39 \text{ (t, } J = 7.7 \text{ Hz, 2H)}, 4.78 \text{ (q, } J = 6.4 \text{ Hz, 1H)}, 3.28 \text{ (sept, } J = 6.7 \text{ Hz, 2H)}, 1.43 \text{ (d, } J = 7.3 \text{ Hz, 3H)}, 1.03 \text{ (d, } J = 6.6 \text{ Hz, 6H)}, 0.86 \text{ (d, } J = 6.6 \text{ Hz, 6H)} \text{ ppm.}

\( ^19F \text{NMR} (564 \text{ MHz}, \text{CDCl}_3) \delta \ -142.1 \text{ (d, } J = 21 \text{Hz, 2F)}, -146.3 \text{ (d, } J = 21 \text{ Hz, 2F)} \text{ ppm.}

\( ^{13}C \text{NMR} (150 \text{ MHz}, \text{CDCl}_3) \delta \ 165.7, 144.9 \text{ (d, } J = 245 \text{ Hz)}, 142.3 \text{ (d, } J = 251 \text{ Hz)}, 132.8, 132.6, 128.8, 127.7, 124.4 \text{ (t, } J = 17 \text{ Hz)}, 114.0 \text{ (t, } J = 15 \text{ Hz)}, 16.0, 45.7, 22.7, 19.7 \text{ ppm.}

IR (ATR) 3299, 2968, 1672, 1466, 972 \text{ cm}^{-1}. \text{HRESIMS Found: } [\text{M + H}]^+, 397.1900. \text{C}_{21}\text{H}_{25}\text{F}_4\text{N}_2\text{O requires } [\text{M + H}]^+, 397.1898.

\( N-(4-(1-(\text{Diisopropylamino})ethyl)-2,3,5,6-\text{tetrafluorophenyl)-3,5-bis(trifluoromethyl)benzamide (7f) } \)

\begin{center}
\includegraphics[width=0.3\textwidth]{image}
\end{center}

Reaction with \( N-(\text{pentafluorophenyl)-3,5-bis(trifluoromethyl)benzamide (6f)} \) (40 \( \mu \text{mol}), following the General Procedure 1. Title compound \( 7f \) was formed in 25% yield (average of two experiments) as determined via \( ^{19}F \text{NMR spectroscopy with the aid of a calibrated internal standard.} \)

\( ^{19}F \text{NMR (564 MHz, CDCl}_3) \delta \ -63.5 \text{ (s, 6F)}, -140.1 \text{ (quin, } J = 11 \text{ Hz, 2F)}, -145.8 \text{ (m, 2F)} \text{ ppm.}

EIMS (\text{m/z, relative intensity}) 532 (M\textsuperscript{*}, 3), 517 (27), 432 (19), 241 (68), 213 (14), 86 (100).

HREIMS Found: M\textsuperscript{*}, 532.1580. C_{22}H_{22}F_{10}N_2O requires M\textsuperscript{*}, 532.1572.

\( \text{tert-Butyl (4-(1-(\text{diisopropylamino})ethyl)-2,3,5,6-\text{tetrafluorophenyl)carbamate (7g) } \)

S-19
Reaction between tert-butyl (pentafluorophenyl)carbamate (6g) (326 µmol) and i-Pr₂NEt (4a) following General Procedure 1. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→15% EtOAc/hexane elution; 1% NEt₃ was present in the eluent) to provide title compound 7g as a colorless solid (110 mg, 86% yield).

'H NMR (600 MHz, CDCl₃) δ 6.00 (bs, 1H), 4.65 (q, J = 7.2 Hz, 2H), 3.43 (sept, J = 6.6 Hz, 2H), 1.53 (s, 9H), 1.15 (d, J = 6.5 Hz, 6H), 0.95 (d, J = 6.9 Hz, 6H) ppm.

'F NMR (564 MHz, CDCl₃) δ −142.5 (dd, J = 22.4, 9.1 Hz, 2F), −148.1 (dd, J = 22.4, 9.6 Hz, 2F) ppm.

'C NMR (150 MHz, CDCl₃) δ 152.3, 144.8 (d, J = 6.9 Hz), 123.6 (d, J = 18 Hz), 114.5 (t, J = 16 Hz), 81.9, 49.5, 45.6, 28.1, 22.6, 22.5, 19.7 ppm.

IR (ATR) 3272, 2972, 1711, 1524, 1475, 1298, 1154, 960, 951 cm⁻¹.


4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenylamine (p-7h)
& 2-(1-(Diisopropylamino)ethyl)-3,4,5,6-tetrafluorophenylamine (o-7h)

Reaction between pentafluoroaniline (6h) (500 µmol) and i-Pr₂NEt (4a) following General Procedure 1. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→15% EtOAc/hexane elution; 1% NEt₃ was present in the eluent) to provide title compounds 7h as a colorless oil (90 mg, 1.4:1 mixture of p-7h : o-7h, 62% yield).

'H NMR (600 MHz, CDCl₃) δ 4.46 (q, J = 7.3 Hz, 1H), 3.75 (bs, 2H), 3.25 (sept, J = 6.6 Hz, 2H), 1.39 (d, J = 7.2 Hz, 3H), 1.02 (d, J = 6.7 Hz, 6H), 0.85 (d, J = 6.8 Hz, 6H) ppm.

'F NMR (564 MHz, CDCl₃) δ −144.1 (d, J = 22 Hz, 2F), −162.4 (d, J = 23 Hz, 2F) ppm.


N-Isopropyl-N-(1-(2,3,5,6-tetrafluoro-4-(methoxyphenoxy)phenyl)ethyl)propan-2-amine (7i)

Reaction between 1,2,3,4,5-pentafluoro-6-(4-methoxyphenoxy)benzene (6i) (400 µmol) and i-Pr₂NEt (4a) following General Procedure 1. Title compound 7i was formed in 28% yield (average of two experiments) as determined via ¹⁹F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/hexane elution; 1% NEt₃ was present in the eluent) to provide a sample of product 7i (+ co-eluting starting material 6i) as a colorless solid.
The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0–15% EtOAc/ hexane elution; 1% NEt₃ was present in the eluent) to provide a sample of compound *p-7j* (which contained traces of compound *m-7j*) as a colorless solid.

**N-Isopropyl-N-(1-(1,3,4-trifluorodibenzo[b,e][1,4]dioxin-2-yl)ethyl)propan-2-amine (p-7j)** & **N-Isopropyl-N-(1-(2,3,4-trifluorodibenzo[b,e][1,4]dioxin-1-yl)ethyl)propan-2-amine (m-7j)**

Reaction between 1,2,3,4-tetrafluorodibenzo[b,e][1,4]dioxide (6j) (400 µmol) and i-Pr₂NEt (4a) following General Procedure 1. Compound *p-7j* was formed in 48% yield (average of two experiments) and compound *m-7j* was formed in 9% yield (average of two experiments) as determined via ¹⁹F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0–15% EtOAc/ hexane elution; 1% NEt₃ was present in the eluent) to provide a sample of compound *p-7j* (which contained traces of compound *m-7j*) as a colorless solid.

**Methyl 8-(1-(diisopropylamino)ethyl)-6,7,9-trifluorodibenzo[b,e][1,4]dioxide-2-carboxylate (7k)**

Reaction between methyl 6,7,9-tetrafluorodibenzo[b,e][1,4]dioxide-2-carboxylate (6k) (500 µmol) and i-Pr₂NEt (4a) following General Procedure 1. Title compound 7k was formed in 71% yield (average of two experiments) as determined via ¹⁹F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0–10% EtOAc/ hexane elution; 1% NEt₃ was present in the eluent) to provide a sample of title compound 7k as a colorless solid.
\( ^{19}\text{F NMR (564 MHz, CDCl}_3) \delta -141.3 \text{ (d, } J = 29 \text{ Hz, 1F),} -144.3 \text{ (dd, } J = 223, 22 \text{ Hz, 1F),} -164.4 \text{ (t, } J = 26 \text{ Hz, 1F) ppm.} \\
^{13}\text{C NMR (150 MHz, CDCl}_3) \delta 165.4, 145.0 \text{ (d, } J = 244 \text{ Hz),} 144.4, 143.9 \text{ (d, } J = 244 \text{ Hz),} 140.5, 136.3 \text{ (d, } J = 249 \text{ Hz),} 130.3 \text{ (dt, } J = 12.7, 4.8 \text{ Hz),} 127.1, 126.8, 119.8 \text{ (td, } J = 17, 2.5 \text{ Hz),} 118.3, 117.1 \text{ (dd, } J = 233, 16 \text{ Hz),} 116.7, 52.3, 45.7, 45.6, 22.7, 22.5, 19.9 \text{ ppm.} \\
\text{HRESIMS Found: } [M + H]^+, 424.1729. \text{ C}_{22}\text{H}_{25}\text{F}_2\text{NO}_4 \text{ requires } [M + H]^+, 424.1730. \\
\text{(8-1-(Diisopropylamino)ethyl)-6,7,9-trifluorodibenzo[b,e][1,4]dioxin-2-yl)methanol (p-7l) (9-1-(Diisopropylamino)ethyl)-6,7,8-trifluorodibenzo[b,e][1,4]dioxin-2-yl)methanol (m-7l) \\

\begin{align*}
\text{Reaction between (6,7,8,9-tetrafluorodibenzo[b,e][1,4]dioxin-2-yl)methanol (6l) (500 } \mu \text{mol) and } i-\text{PrN}_2 \text{Et (4a) following General Procedure 1. Compound p-7l was formed in 53\% yield (average of two experiments) and compound m-7l was formed in 9\% yield (average of two experiments) as determined via } ^{19}\text{F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30\% EtOAc/hexane elution; 1\% NEt}_3 \text{ was present in the eluent) to provide a sample of compound p-7l (which contained traces of compound m-7l) as a colorless solid.} \\
^{1}\text{H NMR (600 MHz, CDCl}_3) \delta 7.01–6.86 \text{ (complex m, 3H),} 4.62–4.55 \text{ (complex m, 3H),} 3.36 \text{ (sept, } J = 6.4 \text{ Hz, 2H),} 2.15 \text{ (bs, 1H),} 1.50 \text{ (d, } J = 7.0 \text{ Hz, 3H),} 1.12 \text{ (d, } J = 6.7 \text{ Hz, 6H),} 0.97 \text{ (d, } J = 6.7 \text{ Hz, 6H) ppm.} \\
^{19}\text{F NMR (564 MHz, CDCl}_3) \delta -141.1 \text{ (dd, } J = 31, 9 \text{ Hz, 1F),} -144.1 \text{ (dd, } J = 23, 11 \text{ Hz, 1F),} -163.8 \text{ (qd, } J = 21, 9 \text{ Hz, 1F) ppm.} \\
^{13}\text{C NMR (150 MHz, CDCl}_3) \delta 144.7 \text{ (d, } J = 242 \text{ Hz),} 144.0 \text{ (d, } J = 243 \text{ Hz),} 140.7, 140.2, 140.0, 139.6, 138.1, 137.9, 136.3, \text{ (d, } J = 247 \text{ Hz),} 130.8 \text{ (m),} 128.1 \text{ (dt, } J = 18, 4 \text{ Hz),} 123.0 \text{ (d, } J = 36 \text{ Hz),} 119.3 \text{ (t, } J = 17 \text{ Hz),} 116.1 \text{ (dd, } J = 209, 10 \text{ Hz),} 64.2, 45.63, 45.61, 22.7, 22.5, 20.0 \text{ ppm.} \\
\text{IR (NaCl) 3326, 2970, 2873, 1700, 1654, 1596, 1481, 1279, 1214, 1150, 1114, 1005, 988 cm}^{-1}. \\
\text{EIMS } (m/z, \text{ relative intensity}) 395 \text{ (M}^+, 6), 380 \text{ (28),} 295 \text{ (65),} 86 \text{ (100).} \\
\text{1,2,3,4,5-Pentafluorobenzene (9a) } \\
\begin{align*}
\text{Reaction with 1,2,3,4,5,6-hexafluorobenzene (8a) (500 } \mu \text{mol) following General Procedure 2. Title compound 9a was formed in 85\% yield (average of two experiments) as determined via } ^{19}\text{F NMR spectroscopy with the aid of a calibrated internal standard.} \\
^{19}\text{F NMR (564 MHz, CDCl}_3) \delta -139.6 \text{ (quin, } J = 11 \text{ Hz, 2F),} -155.1 \text{ (t, } J = 20 \text{ Hz, 1F),} -163.2 \text{ (m, } 2\text{H) ppm.} \\
\text{EIMS } (m/z, \text{ relative intensity}) 168 \text{ (M}^+, 13), 154 \text{ (14),} 114 \text{ (63),} 86 \text{ (100).} \\
\text{HREIMS Found: } M^+, 168.0002. \text{ C}_{9}\text{H}_{9}\text{F}_{6} \text{ requires } M^+, 167.9998. \\
\text{1,2,4,5-Tetrafluoro-3-(trifluoromethyl)benzene (9b) } \\
3. \text{Senaweera, S. M.; Singh, A.; Weaver, J. D. J. Am. Chem. Soc. } \text{2014, 136, 3002.} \)
Reaction with 1,2,3,4,5-pentafluoro-6-(trifluoromethyl)benzene (8b) (500 μmol) following General Procedure 2. Title compound 9b was formed in 65% yield (average of two experiments) as determined via $^{19}$F NMR spectroscopy with the aid of a calibrated internal standard. $^{19}$F NMR (564 MHz, CDCl$_3$) δ −57.0 (t, $J = 23$ Hz, 3F), −137.5 (m, 2H), −141.8 (m, 2H) ppm.
EIMS (m/z, relative intensity) 218 (M$^+$, 14), 189 (14), 114 (54), 86 (100).

1-(2,3,5,6-Tetrafluorophenyl)ethenone (9c)

Reaction with 1-(pentafluorophenyl)ethanone (8c) (500 μmol) following General Procedure 2. Title compound 9c was formed in 60% yield (average of two experiments) as determined via $^{19}$F NMR spectroscopy with the aid of a calibrated internal standard. $^{19}$F NMR (564 MHz, CDCl$_3$) δ −138.8 (quin, $J = 10$ Hz, 2F), −143.2 (m, 2F) ppm.
EIMS (m/z, relative intensity) 192 (M$^+$, 41), 177 (100), 149 (59), 99 (43), 43 (86).

Methyl 2,3,5,6-tetrafluorobenzoate (9d)

Reaction with methyl 2,3,4,5,6-pentafluorobenzoate (8d) (500 μmol) following General Procedure 2. Title compound 9d was formed in 83% yield (average of two experiments) as determined via $^{19}$F NMR spectroscopy with the aid of a calibrated internal standard. $^{19}$F NMR (564 MHz, CDCl$_3$) δ −138.7 (m, 2F), −140.9 (m, 2F) ppm.
EIMS (m/z, relative intensity) 208 (M$^+$, 24), 177 (100), 149 (54), 99 (32).
HREIMS Found: M$^+$, 208.0142. C$_8$H$_5$F$_4$O$_2$ requires M$^+$, 208.0147.

2,3,5,6-Tetrafluoro-N-methylbenzamide (9e)

Reaction with 2,3,4,5,6-pentafluoro-N-methoxy-N-methylbenzamide (8e) (500 μmol) following General Procedure 2. Title compound 9e was formed in 27% yield (average of two experiments) as determined via $^{19}$F NMR spectroscopy with the aid of a calibrated internal standard. $^{19}$F NMR (564 MHz, CDCl$_3$) δ −139.2 (quin, $J = 10$ Hz, 2F), −143.2 (m, 2F) ppm.
EIMS (m/z, relative intensity) 207 (M$^+$, 32), 188 (46), 177 (100), 149 (65), 99 (46), 58 (35).
HREIMS Found: M$^+$, 207.0301. C$_8$H$_5$F$_4$N$_2$O$_1$ requires M$^+$, 207.0307.
Phenyl 2,3,5,6-tetrafluorobenzoate (9f)

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\begin{array}{c}
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\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{O} \\
\text{Bn}
\end{array}
\]

Reaction with phenyl 2,3,4,5,6-pentafluorobenzoate (8f) (500 μmol) following General Procedure 2. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→10% EtOAc/hexane elution) to provide title compound 9f (70 mg, 49% yield) as a colorless solid.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) δ 7.47 (m, 2H), 7.44–7.37 (complex m, 3H), 7.22 (quin, \(J = 8.3\) Hz, 1H), 5.45 (s, 2H) ppm.

\(^{19}\)F NMR (564 MHz, CDCl\(_3\)) δ –137.4 (m, 2F), –139.2 (m, 2F) ppm.

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) δ 159.5, 145.8 (d, \(J = 250\) Hz), 144.6 (d, \(J = 257\) Hz), 134.6, 128.72, 128.70, 128.4, 113.6 (t, \(J = 16\) Hz), 108.8 (t, \(J = 22\) Hz), 68.4 ppm.

IR (NaCl) 1739, 1501, 1456, 1391, 1297, 1192, 951 cm\(^{-1}\).

EIMS (\(m/z\), relative intensity) 284 (M\(^+\), 30), 177 (40), 149 (13), 91 (100).

(Pentafluorophenyl)methyl 2,3,5,6-tetrafluorobenzoate (9g)

\[
\begin{array}{c}
\text{O} \\
\text{F} \\
\text{F} \\
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\text{F}
\end{array}
\]

Reaction with (pentafluorophenyl)methyl 2,3,4,5,6-pentafluorobenzoate (8g) (500 μmol) following General Procedure 2. Title compound 9g was formed in 35% yield (average of two experiments) as determined via \(^{19}\)F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→10% EtOAc/hexane elution) to provide a sample of title compound 9g as a colorless oil.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) δ 7.16 (quin, \(J = 8.0\) Hz, 1H), 5.43 (s, 2H) ppm.

\(^{19}\)F NMR (564 MHz, CDCl\(_3\)) δ –137.0 (m, 2F), –138.8 (m, 2F), –141.4 (dd, \(J = 21, 7\) Hz, 2F), –151.3 (t, \(J = 20\) Hz, 1F), –161.1 (m, 2F) ppm.

\(^{13}\)C NMR (150 MHz, CDCl\(_3\)) δ 160.0, 145.9 (d, \(J = 250\) Hz), 145.8 (d, \(J = 252\) Hz), 144.5 (dt, \(J = 258, 4\) Hz), 142.3 (d, \(J = 257\) Hz), 137.5 (d, \(J = 253\) Hz), 112.5 (t, \(J = 16\) Hz), 109.3 (t, \(J = 23\) Hz), 108.3 (td, \(J = 17, 4\) Hz), 55.0 ppm.

IR (NaCl) 1748, 1525, 1506, 1313, 1295, 1190, 1133, 1059, 969, 939, 712 cm\(^{-1}\).

EIMS (\(m/z\), relative intensity) 374 (M\(^+\), 22), 181 (100), 149 (22), 99 (27).

HREIMS Found: M\(^+\), 374.0000. C\(_{14}\)H\(_3\)F\(_9\)O\(_2\) requires M\(^+\), 373.9989.

Prop-2-yn-1-yl 2,3,5,6-tetrafluorobenzoate (9h)

\[
\begin{array}{c}
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\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{O} \\
\text{F}
\end{array}
\]

Reaction with prop-2-yn-1-yl 2,3,4,5,6-pentafluorobenzoate (8h) (500 μmol) following General Procedure 2. Title compound 9h was formed in 43% yield (average of two experiments) as determined via \(^{19}\)F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→10% EtOAc/
hex NMR (600 MHz, CDCl₃) δ 7.25 (quin, J = 8.0 Hz, 1H), 4.98 (d, J = 2.74, 2H), 2.59 (t, J = 2.5 Hz, 1H) ppm.

19F NMR (564 MHz, CDCl₃) δ −137.3 (m, 2F), −139.2 (m, 2F) ppm.

13C NMR (150 MHz, CDCl₃) δ 158.9, 145.9 (d, J = 251 Hz), 144.7 (d, J = 259 Hz), 112.7 (t, J = 16 Hz), 109.2 (t, J = 22 Hz), 76.1, 76.0, 53.8 ppm.

EIMS (m/z, relative intensity) 232 (M⁺, 10), 177 (100), 149 (30), 99 (25).

**Furan-2-ylmethyl 2,3,5,6-tetrafluorobenzoate (9i)**

![Furan-2-ylmethyl 2,3,5,6-tetrafluorobenzoate (9i)](image)

Reaction with furan-2-ylmethyl 2,3,4,5,6-pentafluorobenzoate (8i) (500 μmol) following General Procedure 2. Title compound 9i was formed in 48% yield (average of two experiments) as determined via 19F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→10% EtOAc/hexane elution) to provide a sample of title compound 9i (+ co-eluting starting material 8i) as a colorless solid.

1H NMR (600 MHz, CDCl₃) δ 7.48 (d, J = 1.8 Hz, 1H), 7.21 (quin, J = 8.1 Hz, 1H), 6.54 (t, J = 2.2 Hz, 1H), 6.42 (dd, J = 3.2, 1.9 Hz, 1H), 5.38 (s, 2H) ppm.

19F NMR (564 MHz, CDCl₃) δ −137.4 (m, 2F), −139.2 (m, 2F) ppm.

13C NMR (150 MHz, CDCl₃) δ 159.3, 145.9 (d, J = 251 Hz), 144.7 (d, J = 259 Hz), 143.8, 113.3 (t, J = 16 Hz), 111.6, 110.7, 108.8 (t, J = 22 Hz), 59.9 ppm.

EIMS (m/z, relative intensity) 274 (M⁺, 20), 177 (15), 81 (100).

**N-Methyl-N-(2,3,5,6-tetrafluorophenyl)acetamide (9j)**

& **N-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)-N-methylacetamide (p-9j*) & N-(2-(1-(diisopropylamino)ethyl)-3,4,5,6-tetrafluorophenyl)-N-methylacetamide (o-9j*)**

![N-Methyl-N-(2,3,5,6-tetrafluorophenyl)acetamide (9j) & N-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)-N-methylacetamide (p-9j*) & N-(2-(1-(diisopropylamino)ethyl)-3,4,5,6-tetrafluorophenyl)-N-methylacetamide (o-9j*)](image)

Reaction with N-methyl-N-(pentafluorophenyl)acetamide (8j) (500 μmol) following General Procedure 2. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→20% EtOAc/hexane elution; 1% NEt₃ was present in the eluent) to provide hydrodefluorination product 9j as a colorless solid (49 mg, 44% yield) and a colorless solid (17 mg, 10% yield; 3.7:1 mixture of p-9j* and o-9j*).

**N-Methyl-N-(2,3,5,6-tetrafluorophenyl)acetamide (9j)**

1H NMR (600 MHz, CDCl₃) δ 7.07 (quin, J = 8.8 Hz, 0.8H), 6.98 (quin, J = 8.8 Hz, 0.2H), 3.29 (s, 0.5H), 3.16 (s, 2.5H), 2.25 (s, 0.5H), 1.86 (s, 2.5H) ppm; 6 signals observed (rotamers present).

19F NMR (564 MHz, CDCl₃) δ −137.3 (quin, J = 10 Hz, 1.7F), −139.0 (quin, J = 10 Hz, 0.3F), −145.5 (m, 0.3F), −146.2 (m, 1.7F) ppm; 4 signals observed (rotamers present).

13C NMR (150 MHz, CDCl₃) δ 170.5, 170.1, 146.1 (d, J = 248 Hz), 143.3 (d, J = 250 Hz), 124.0 (t, J = 15 Hz), 116.0 (t, J = 22 Hz), 105.0 (t, J = 22 Hz), 38.4, 35.7, 21.5, 21.1 ppm; 11 signals observed (rotamers present).

N-(4-(1-(Diisopropylamino)ethyl)-2,3,5,6-tetrafluorophenyl)-N-methylacetamide (p-9j*) & N-(2-(1-(diisopropylamino)ethyl)-3,4,5,6-tetrafluorophenyl)-N-methylacetamide (o-9j*)

HRESIMS Found: [M + H]+, 349.1898. C_{17}H_{25}F_{4}N_{2}O requires [M + H]+, 349.1898.

1,2,4,5-Tetrafluoro-3-vinylbenzene (9k)

Reaction with 1,2,3,4,5-pentafluoro-6-vinylbenzene (8k) (500 μmol) following General Procedure 2. Title compound 9k was formed in 14% yield (average of two experiments) as determined via 19F NMR spectroscopy with the aid of a calibrated internal standard.

19F NMR (564 MHz, CDCl3) δ –141.4 (quin., J = 11 Hz, 2F), –146.2 (m, 2F) ppm.

EIMS (m/z, relative intensity) 176 (M+, 3), 132 (14), 90 (100), 43 (19).

HREIMS Found: M+ H+ 176.0244. C_{8}H_{4}F_{4} requires M+ H+ 176.0249.

4,5,7-Trifluoro-3-(pentafluorophenyl)-2-phenylbenzofuran (9l)

Reaction with 4,5,6,7-tetrafluoro-3-(pentafluorophenyl)-2-phenylbenzofuran (8l) (100 μmol) following General Procedure 2 (this reaction was performed in a 2:1 MeCN/DMF solution). Title compound 9l was formed in 24% yield (average of two experiments) as determined via 19F NMR spectroscopy with the aid of a calibrated internal standard.

19F NMR (564 MHz, CDCl3) δ –137.7 (m, 2F), –138.3 (m, 2F), –152.1 (m, 1F), –159.8 (t, J = 20 Hz, 1F), –161.2 (t, J = 19 Hz, 1F), –162.7 (t, J = 20 Hz, 1F) ppm.

EIMS (m/z, relative intensity) 414 (M+, 100), 394 (50), 197 (20).

Figure 3B: tert-Butyl (2,3,5,6-tetrafluoro-4-(1-methylpyrrolidin-2-yl)phenyl)carbamate (10)

Reaction between tert-butyl (pentafluorophenyl)carbamate (6g) (1 mmol) and N-methylpyrrolidine (4i) following General Procedure 1. Title compound 10 was formed in 31% yield (average of two experiments) as determined via 19F NMR spectroscopy with the aid of a calibrated internal standard. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0→30% EtOAc/ hexane elution; 1% NEt_{3} was present in the eluent) to provide a sample of compound 10 as a colorless solid.

1H NMR (600 MHz, CDCl3) δ 6.42 (bs, 1H), 3.66 (dd, J = 9.0, 7.3 Hz, 1H), 3.26 (t, J = 7.6 Hz, 1H), 2.32–2.26 (complex m, 4H), 2.19 (m, 1H), 2.12 (m, 2H), 1.88 (dd, J = 15.7, 9.8 Hz, 1H), 1.52 (s, 9H) ppm.

19F NMR (564 MHz, CDCl3) δ –144.0 (dd, J = 21, 9 Hz, 2F), –147.9 (dd, J = 22, 11 Hz, 2F) ppm.
$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 152.3, 145.5 (d, $J = 247$ Hz), 142.2 (d, $J = 249$ Hz), 118.5 (t, $J = 14$ Hz), 115.8 (t, $J = 14$ Hz), 82.0, 60.3, 57.3, 40.9, 30.7, 28.1, 23.7 ppm.

IR (NaCl) 3279, 2979, 2734, 1713, 1653, 1520, 1501, 1481, 1381, 1368, 1303, 1248, 1159, 974 cm$^{-1}$.

EIMS ($m/z$, relative intensity) 348 (M$^+$, 15), 291 (8), 247 (7), 57 (100).

**Figure 3C**

In a nitrogen-filled glovebox, MeCN (150 μL) was added to [Cu(MeCN)$_4$]PF$_6$ (2.8 mg, 7.5 μmol) and Xantphos (4.3 mg, 7.5 μmol) and the ensuing solution was magnetically stirred. After 2 h, a MeCN solution (40 μL) of bathocuproine (2.7 mg, 7.5 μmol) was added. After 1 h, this solution was added to a 20-mL screw-top vial (PTFE tape-lined thread) containing $N$-(pentafluorophenyl)acetamide (3a) (113 mg, 500 μmol), i-Pr$_2$NEt (4a) (129 mg, 1.00 mmol), and Gd(OTf)$_3$ (121 mg, 200 μmol) in MeCN (3.66 mL), and a stir bar. The vial was then capped, the joint was wrapped with PARAFILM®, and removed from the glovebox and placed in a water bath (suspended with Cu wire) maintained at 45 °C that was contained within a 18 W blue LED photoreactor (switched off) and magnetically stirred (Figure S2). The vial was then irradiated (25% duty cycle at 100 kHz). After 24 h, the reaction mixture was quenched by exposure to air. Compound 5a was present in the eluent) to provide a sample of compound 13 and starting material as a colorless solid.

Figure 3D: $N$-(2,3,5,6-Tetrafluorophenyl)acetamide (13)

Reaction between $N$-(4-bromo-2,3,5,6-tetrafluorophenyl)acetamide (12) (472 μmol) and i-Pr$_2$NEt (4a) following General Procedure 1. Compound 13 was formed in 54% yield (average of two experiments) as determined via $^{19}$F NMR spectroscopy with the aid of a calibrated internal standard.$^4$ The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica gel, 0–30% EtOAc/ hexane elution; 1% NEt$_3$ was present in the eluent) to provide a sample of compound 13 and starting material as a colorless solid.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.68 (bs, 1H), 7.00 (quin, $J = 8.3$ Hz, 1H), 2.23 (s, 3H) ppm.

$^{19}$F NMR (564 MHz, CDCl$_3$) $\delta$ –139.2 (s, 2F), –145.5 (s, 2F) ppm.

$^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 168.9, 145.9 (d, $J = 247$ Hz), 142.2 (d, $J = 248$ Hz), 116.8 (t, $J = 13$ Hz), 103.9 (t, $J = 23$ Hz), 22.8 ppm.

EIMS ($m/z$, relative intensity) 207 (M$^+$, 2), 165 (100), 137 (12).

**V. Additional Experiments & Tables**

**Alternative Synthesis of Compound 7g from Substrate S1**

Reaction between compound S1 (400 μmol) and i-Pr$_2$NEt (4a) following General Procedure 1. The ensuing residue obtained from the reaction mixture was subjected to flash column chromatography (silica

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gel, 0→10% EtOAc/hexane elution; 1% NEt₃ was present in the eluent) to provide title compound 7g as a colorless solid (102 mg, 61% yield).

**TEMPO Experiment (50% TEMPO)**
Reaction between N-(pentfluorophenyl)acetamide (3a) (400 μmol), i-Pr₂NEt (4a), and TEMPO (200 μmol) following General Procedure 1. Compound 5a was formed in 8% yield and substrate 3a was present in 85% yield (average of two experiments) as determined via ¹⁹F NMR spectroscopy with the aid of a calibrated internal standard.

**Table S1.** Summary of product yields in reactions shown in Figure 3: comparison of product yields employing pulsed irradiation and conventional irradiation.

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield Employing Pulsed Blue LED Irradiation (%)</th>
<th>Yield Employing Conventional Blue LED Irradiation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>87</td>
<td>54&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>5b</td>
<td>57</td>
<td>34&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>5d</td>
<td>66&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>70&lt;sup&gt;a,b&lt;/sup&gt;</td>
</tr>
<tr>
<td>5e</td>
<td>21&lt;sup&gt;a&lt;/sup&gt;</td>
<td>16&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>5f</td>
<td>26&lt;sup&gt;a&lt;/sup&gt;</td>
<td>13&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>5g</td>
<td>34&lt;sup&gt;a&lt;/sup&gt;</td>
<td>15&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>5h</td>
<td>50&lt;sup&gt;a&lt;/sup&gt;</td>
<td>32&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>5j</td>
<td>67&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>30&lt;sup&gt;a,b&lt;/sup&gt;</td>
</tr>
<tr>
<td>5k</td>
<td>60&lt;sup&gt;a,b&lt;/sup&gt; (p-5k); 6&lt;sup&gt;a,b&lt;/sup&gt; (o-5k)</td>
<td>31&lt;sup&gt;a,b&lt;/sup&gt; (p-5k); 2&lt;sup&gt;a,b&lt;/sup&gt; (o-5k)</td>
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<tr>
<td>5l</td>
<td>45&lt;sup&gt;a,b&lt;/sup&gt; (p-5l); 3&lt;sup&gt;a,b&lt;/sup&gt; (o-5l)</td>
<td>43&lt;sup&gt;a,b&lt;/sup&gt; (p-5l); 4&lt;sup&gt;a,b&lt;/sup&gt; (o-5l)</td>
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<tr>
<td>5m</td>
<td>65&lt;sup&gt;a,b&lt;/sup&gt; (p-5m); 7&lt;sup&gt;a&lt;/sup&gt; (o-5m)</td>
<td>63&lt;sup&gt;a,b&lt;/sup&gt; (p-5m); 6&lt;sup&gt;a,b&lt;/sup&gt; (o-5m)</td>
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<tr>
<td>7a</td>
<td>63&lt;sup&gt;a&lt;/sup&gt;</td>
<td>35&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>7b</td>
<td>80&lt;sup&gt;a&lt;/sup&gt; (p-7b); 5&lt;sup&gt;a&lt;/sup&gt; (o-7b)</td>
<td>43&lt;sup&gt;a&lt;/sup&gt; (p-7b); &lt;2&lt;sup&gt;a&lt;/sup&gt; (o-7b)</td>
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<tr>
<td>7c</td>
<td>86&lt;sup&gt;a&lt;/sup&gt;</td>
<td>44&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>7d</td>
<td>64&lt;sup&gt;a&lt;/sup&gt;</td>
<td>41&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>7g</td>
<td>86&lt;sup&gt;a&lt;/sup&gt;</td>
<td>50&lt;sup&gt;a&lt;/sup&gt;</td>
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<td>7h</td>
<td>62 (1:4:1 p-7h:o-7h)</td>
<td>6&lt;sup&gt;a&lt;/sup&gt; (p-7h); 4&lt;sup&gt;a&lt;/sup&gt; (o-7h)</td>
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<tr>
<td>7i</td>
<td>28&lt;sup&gt;a&lt;/sup&gt;</td>
<td>24&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>7j</td>
<td>48&lt;sup&gt;a&lt;/sup&gt; (p-7j); 9&lt;sup&gt;a&lt;/sup&gt; (m-7j)</td>
<td>39&lt;sup&gt;a&lt;/sup&gt; (p-7j); 2&lt;sup&gt;a&lt;/sup&gt; (m-7j)</td>
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<tr>
<td>7k</td>
<td>71&lt;sup&gt;a&lt;/sup&gt;</td>
<td>36&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>7l</td>
<td>53&lt;sup&gt;a&lt;/sup&gt; (p-7l); 9&lt;sup&gt;a&lt;/sup&gt; (m-7l)</td>
<td>31&lt;sup&gt;a&lt;/sup&gt; (p-7l); 4&lt;sup&gt;a&lt;/sup&gt; (m-7l)</td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined by ¹⁹F NMR spectroscopy with the aid of a calibrated internal standard (average of 2 experiments).

<sup>b</sup>Reaction performed in the absence of Gd(OTf)₃.
VI. $^1$H & $^{19}$F NMR Spectra
19F NMR spectrum
$^1$H NMR spectrum

S-31
The $^{19}F$ NMR spectrum of the compound is shown. The spectrum exhibits peaks at -144.31 and -147.02 ppm. The chemical structure includes fluorine atoms and a NHAc group. The peaks at 2.00 and 2.05 ppm are also highlighted.
$^1$H NMR spectrum

NHAc

F
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NEt$_2$
Et$_3$Sn
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$^{19}F$ NMR spectrum

NHAc

F

F

NEt

Et

5d

-110 -120 -130 -140 -150 -160 -170 -180 -190 ppm
$^{19}$F NMR spectrum of reaction mixture

- $\text{NHAc}$
- $\text{F}$
- $\text{NEt}_2$
- $\text{Et}$
- $5d$
- $S$
$^{19}$F NMR spectrum of reaction mixture

(!) 5e

-145.66
H NMR spectrum

NHAc

F

F

F

NMe

S

1H NMR spectrum
$^{19}$F NMR spectrum
$\text{\textsuperscript{19}F NMR spectrum of reaction mixture}$

$\text{\textsuperscript{19}F NMR spectrum of reaction mixture}$
$^{1}H$ NMR spectrum

NHAc
$^{19}$F NMR spectrum of reaction mixture

![NMR Spectrum Image]
$^{1}H$ NMR spectrum

NHAc
$^{19}$F NMR spectrum

$\text{NHAc}$

$\text{F}$

$\text{F}$

$\text{F}$

$\text{Me}$
1H NMR spectrum
$^{19}$F NMR spectrum of reaction mixture

$\text{NHAc}$
\[ ^{19}\text{F NMR spectrum} \]

\[ \text{NHAc} \]

\[ \text{F} \]

\[ \text{F} \]

\[ \text{F} \]

\[ \text{F} \]

\[ \text{Me}^2 \]

\[ \text{Me} \]

\[ \text{H} \]

\[ -142.69 \]

\[ -145.92 \]
19F NMR spectrum of reaction mixture
19F NMR spectrum of reaction mixture
$^1$H NMR spectrum

![NMR Spectrum Image](image)

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$^{19}F$ NMR spectrum of reaction mixture

![Diagram showing $^{19}F$ NMR spectrum with peaks and chemical structures labeled with resonances.](image)
H NMR spectrum

NMe

NMe

( )

F

F

F

NHAc

5m
$^{19}$F NMR spectrum

$\delta = 125.07$

$\delta = 125.08$

$\delta = 137.21$

$\delta = 137.25$

$\delta = 138.49$

$\delta = 138.52$

$\delta = 142.80$

$\delta = 146.20$

$\delta = 164.12$

$\delta = 164.13$

$\delta = 164.16$

$\delta = 164.17$

$\delta = 164.19$

$\delta = 0.07$

$\delta = 0.06$

$\delta = 0.06$

$\delta = 2.00$

$\delta = 2.11$

$\delta = 0.07$

$^{19}$F NMR spectrum
$^{19}F$ NMR spectrum of reaction mixture

![NMR Spectrum Diagram]
\[^{19}F\text{NMR spectrum}\]
19F NMR spectrum of reaction mixture
$^1$H NMR spectrum
$^1$H NMR spectrum
H NMR spectrum

1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

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1H NMR spectrum
$^{19}$F NMR spectrum
19F NMR spectrum of reaction mixture

-143.54
-147.15
-147.17
\[ ^1H \text{ NMR spectrum} \]

Chemical shifts are indicated at various ppm values.
$^{19}$F NMR spectrum of reaction mixture
H NMR spectrum

1.67
2.36
1.00
3.08
2.01
3.68
6.36
6.66

6.86
6.85
6.78
6.76
4.60
4.59
4.58
4.56
4.56
4.55
4.54
4.52
3.71
3.32
3.31
3.30
3.29
3.28
3.27
3.26
3.25
1.46
1.44
1.43
1.42
1.05
1.04
1.02
1.01
0.88
0.87
0.86
0.85
0.84
$^{19}F$ NMR spectrum of reaction mixture
$^1$H NMR spectrum
$^{19}$F NMR spectrum
$^{19}F$ NMR spectrum of reaction mixture

![Chemical structures and spectra](image)
$^{1}$H NMR spectrum

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$^{19}$F NMR spectrum
$^1$H NMR spectrum of reaction mixture
$^{19}$F NMR spectrum
$^{19}$F NMR spectrum of reaction mixture

\[ \text{Diagram of molecular structures} \]
\[ \text{\textsuperscript{19}F NMR spectrum of reaction mixture} \]
$^{19}$F NMR spectrum of reaction mixture
$^{19}$F NMR spectrum of reaction mixture

-143.22
-139.24
-139.26
-139.28
-139.29
-139.30
-143.51
-143.52
-143.53
-143.55
-143.56
-143.57
-143.59

$^{19}$F NMR spectrum of reaction mixture

-116.51
-116.52
-116.53
-116.54
-116.55
-116.56

19
$^{19}F$ NMR spectrum of reaction mixture

[Diagram of NMR spectrum with peaks and labels]
$^{19}$F NMR spectrum of reaction mixture
$^1\text{H NMR spectrum}$
19F NMR spectrum
19F NMR spectrum of reaction mixture

![NMR spectrum of reaction mixture with chemical structures and ppm scale]
$^1{\text{H}}$ NMR spectrum of reaction mixture
$^1$H NMR spectrum
$^{19}$F NMR spectrum
$^{19}$F NMR spectrum of reaction mixture

S-110
$^{19}F$ NMR spectrum
H NMR spectrum

S-113
$^{19}$F NMR spectrum of reaction mixture
$^1^9$F NMR spectrum of reaction mixture
19F NMR spectrum
19 F NMR spectrum of reaction mixture

13F NMR spectrum of reaction mixture
$^1$H NMR spectrum

Chemical shifts (ppm):
- 7.68
- 7.03
- 7.02
- 7.02
- 7.00
- 6.99
- 6.99
- 6.98

$^{13}$C NMR spectrum

Chemical shifts (ppm):
- 2.23

Structural formula:

- Acetyl groups at positions 1 and 4.
* F NMR spectrum

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19F NMR spectrum of reaction mixture