Supporting Information

Ligand-enabled ortho-C–H olefination of phenylacetic amides with unactivated alkenes

Ming-Zhu Lu, Xing-Rong Chen, Hui Xu, Hui-Xiong Dai,* Jin-Quan Yu*

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1. General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. The solvents were purchased from commercial suppliers and dried by 4A molecular sieves. $^1$H-NMR and $^{13}$C-NMR spectra were recorded at 25 °C on Agilent AV 400 and Varian Inova 400M NMR spectrometers (CDCl$_3$ as solvent). Chemical shifts for $^1$H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe$_4$ (δ 0.0) and relative to the signal of SiMe$_4$ (δ 0.00 singlet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets) and etc. Coupling constants are reported as a $J$ value in Hz. $^{13}$C NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe$_4$ (δ 0.0) and relative to the signal of chloroform-$d$ (δ 77.00 triplet). High resolution mass spectra were recorded at the Center for Mass Spectrometry (Agilent Technologies 6224 TOF LC/MS), Shanghai Institute of Organic Chemistry. Flash chromatography was performed using 300-400 mesh silica gel with the indicated solvent system.
2. Optimization of Conditions.

Table S1. Intinal screening using a weakly monodentate auxiliary.\textsuperscript{a,b,c}

![Chemical structures and reactions](image)

| Substrate | Product | Yield |
|-----------|---------|-------|
| MeCOH     | Me\(\text{Me}O\) | N.R.  |
| Me\(\text{H}O\) | Me\(\text{H}O\) | N.R.  |
| Me\(\text{H}O\) | Me\(\text{H}O\) | N.R.  |

\textsuperscript{a}Reaction conditions: Substrates (0.1 mmol), 2a (3.0 equiv), Pd(OAc)_2 (10 mol%), ligand (20 mol%), Ag_2CO_3 (2.0 equiv), DCE (2.0 mL), 80 °C, 12 h. \textsuperscript{b}Isolated yield. \textsuperscript{c}The data in parentheses is the ratio of linear and branched isomers which was determined by \textsuperscript{1}H NMR analysis.
Table S2. Screening the Catalysts

| Entry | Catalyst      | Oxidant      | Time (h) | Yield (%) |
|-------|---------------|--------------|----------|-----------|
| 1     | Pd(OAc)$_2$   | Ag$_2$CO$_3$ (2.0) | 12       | 82 (2.8/1) |
| 2     | Pd(OPiv)$_2$  | Ag$_2$CO$_3$ (2.0) | 12       | 82 (2.8/1) |
| 3     | Pd(TFA)$_2$   | Ag$_2$CO$_3$ (2.0) | 12       | 32 (2.5/1) |
| 4     | PdCl$_2$      | Ag$_2$CO$_3$ (2.0) | 12       | 37 (3.0/1) |
| 5     | Pd(PPh$_3$)$_2$Cl$_2$ | Ag$_2$CO$_3$ (2.0) | 12       | 0         |
| 6     | Pd(CH$_3$CN)$_2$(BF$_4$)$_2$ | Ag$_2$CO$_3$ (2.0) | 12       | 29 (2.3/1) |
| 7     | Pd$_2$(dba)$_3$ | Ag$_2$CO$_3$ (2.0) | 12       | 51 (2.6/1) |

*Reaction conditions: 1 (0.1 mmol), 2a (3.0 equiv), catalyst (10 mol%), ligand (20 mol%), Ag$_2$CO$_3$ (2.0 equiv), DCE (2.0 mL), 80 °C, 12 h. *Isolated yield. *The data in parentheses is the ratio of linear and branched isomers which was determined by $^1$H NMR analysis.
Table S3. Screening the Oxidants.$^{a,b,c}$

![Image of reaction scheme](image)

| Entry | Oxidant       | Yield (%) | Entry | Oxidant       | Yield (%) |
|-------|---------------|-----------|-------|---------------|-----------|
| 1     | Ag$_2$CO$_3$ (2.0) | 82 (2.8/1) | 8     | Cu(OAc)$_2$ (2.0) | 83 (3.6/1) |
| 2     | AgOAc (2.0)    | 82 (2.6/1) | 9     | Cu(OPiv)$_2$ (2.0) | 28 (3.0/1) |
| 3     | Ag$_2$O (2.0)  | 37 (2.4/1) | 10    | Cu(OTf)$_2$ (2.0) | trace     |
| 4     | AgNO$_3$ (2.0) | 27 (2.7/1) | 11    | CuCl$_2$ (2.0)  | trace     |
| 5     | AgOTf (2.0)    | 21 (2.2/1) | 12    | BQ (2.0)       | 35 (3.3/1) |
| 6     | AgBF$_4$ (2.0) | trace     | 13    | NMO (2.0)      | 17 (2.9/1) |
| 7     | AgF (2.0)      | 47 (2.8/1) | 14    | K$_2$S$_2$O$_8$ (2.0) | trace     |

$^a$Reaction conditions : 1 (0.1 mmol), 2a (3.0 equiv), Pd(OAc)$_2$ (10 mol%), ligand (20 mol%), oxidant (2.0 equiv), DCE (2.0 mL), 80 °C, 12 h. $^b$Isolated yield. $^c$The data in parentheses is the ratio of linear and branched isomers which was determined by $^1$H NMR analysis.
Table S4. Screening the Solvents\textsuperscript{a,b,c}

\[
\begin{array}{cccc}
\text{Entry} & \text{Solvent} & \text{Yield (%)} & \text{Entry} & \text{Solvent} & \text{Yield (%)} \\
1 & \text{DCE} & 83 (3.6/1) & 8 & \text{DMF} & \text{trace} \\
2 & \text{dioxane} & 31 (2.5/1) & 9 & \text{HFIP} & 25 (0.7/1) \\
3 & \text{THF} & 33 (2.1/1) & 10 & \text{t-AmI/OH} & 37 (1.6/1) \\
4 & \text{DCM} & 73 (3.0/1) & 11 & \text{hexane} & \text{trace} \\
5 & \text{MeCN} & 21 (2.3/1) & 12 & \text{PhCF}_{3} & 67 (2.7/1) \\
6 & \text{acetone} & 41 (1.6/1) & 13 & \text{toluene} & 70 (2.8/1) \\
7 & \text{DME} & \text{trace} & 14 & \text{DMSO} & \text{trace} \\
\end{array}
\]

\textsuperscript{a}Reaction conditions : 1 (0.1 mmol), 2a (3.0 equiv), Pd(OAc)$_2$ (10 mol%), ligand (20 mol%), Cu(OAc)$_2$ (2.0 equiv), solvent (2.0 mL), 80 °C, 12 h. \textsuperscript{b}Isolated yield. \textsuperscript{c}The data in parentheses is the ratio of linear and branched isomers which was determined by $^1$H NMR analysis.
Table S5. Screening the Reaction Time.a,b,c

| Entry | Catalyst     | Oxidant               | Time (h) | Yield (%) |
|-------|--------------|-----------------------|----------|-----------|
| 1     | Pd(OAc)₂     | Cu(OAc)₂ (2.0)        | 3        | 69 (3.6/1)|
| 2     | Pd(OAc)₂     | Cu(OAc)₂ (2.0)        | 6        | 85 (3.8/1)|
| 3     | Pd(OAc)₂     | Cu(OAc)₂ (2.0)        | 12       | 83 (3.6/1)|
| 4     | Pd(OAc)₂     | Cu(OAc)₂ (2.0)        | 18       | 80 (3.5/1)|

*aReaction conditions: 1 (0.1 mmol), 2a (3.0 equiv), Pd(OAc)₂ (10 mol%), ligand (20 mol%), Cu(OAc)₂ (2.0 equiv), DCE (2.0 mL), 80 °C, time. bIsolated yield. cThe data in parentheses is the ratio of linear and branched isomers which was determined by ¹H NMR analysis.
Table S6. Screening the Ligands.$^{a,b,c}$

| Ligand | Value (Ratio) | Ligand | Value (Ratio) | Ligand | Value (Ratio) |
|--------|---------------|--------|---------------|--------|---------------|
| Ni     | 76% (2.4/1)   | NiMe   | 77% (2.1/1)   | trace | 55% (2.6/1)   |
| NiMe   | 64% (2.5/1)   | NiMe   | 58% (2.9/1)   | trace | trace         |
| NiMe   | 62% (2.5/1)   | NiMe   | 81% (1.3/1)   | trace | 83% (2.3/1)   |
| NiMe   | 43% (2.3/1)   | NiMe   | 76% (1.9/1)   | 73% (1.5/1)| 62% (2.0/1) |
| NiMe   | 63% (2.9/1)   | NiMe   | 77% (1.9/1)   | 79% (2.3/1)| 60% (2.7/1) |
| NiMe   | 42% (2.3/1)   | NiMe   | 46% (2.5/1)   | 54% (2.9/1)| 61% (2.5/1) |
| NiMe   | 56% (2.2/1)   | NiMe   | 54% (2.9/1)   | 70% (1.8/1)| 46% (2.1/1) |
| NiMe   | 47% (2.7/1)   | NiMe   | 77% (1.7/1)   | N.R.   | N.R.          |
| NiMe   | 57% (1.5/1)   | N.R.   | 85% (3.8/1)   | 88% (3.7/1)| N.R.          |

$^{a}$Reaction conditions: 1 (0.1 mmol), 2a (3.0 equiv), Pd(OAc)$_2$ (10 mol%), ligand (20 mol%), Cu(OAc)$_2$ (2.0 equiv), DCE (2.0 mL), 80 °C, 6 h. $^{b}$Isolated yield. $^{c}$The data in parentheses is the ratio of linear and branched isomers which was determined by $^1$H NMR analysis.
Table S7. Screening the Amount of Reagents.\textsuperscript{a,b,c}

| Entry | Catalyst (mol\%) | Oxidant (equiv) | Atmosphere | Yield (%) |
|-------|------------------|-----------------|------------|-----------|
| 1     | Pd(OAc)$_2$ (10) | Cu(OAc)$_2$ (2.0) | Air        | 88 (3.7/1) |
| 2     | Pd(OAc)$_2$ (10) | —               | Air        | <10       |
| 3     | Pd(OAc)$_2$ (10) | —               | O$_2$      | 32 (4.1/1) |
| 4$^d$ | Pd(OAc)$_2$ (10) | —               | O$_2$      | 50 (4.0/1) |
| 5$^e$ | Pd(OAc)$_2$ (10) | —               | O$_2$      | 46 (4.0/1) |
| 6     | Pd(OAc)$_2$ (10) | Cu(OAc)$_2$ (0.5) | O$_2$      | 89 (3.7/1) |
| 7     | Pd(OAc)$_2$ (10) | Cu(OAc)$_2$ (0.3) | O$_2$      | 89 (4.0/1) |
| 8     | Pd(OAc)$_2$ (10) | Cu(OAc)$_2$ (0.2) | O$_2$      | 90 (4.2/1) |
| 9$^f$ | Pd(OAc)$_2$ (10) | Cu(OAc)$_2$ (0.2) | O$_2$      | 81 (3.5/1) |
| 10$^g$| Pd(OAc)$_2$ (5)  | Cu(OAc)$_2$ (0.2) | O$_2$      | 87 (4.0/1) |

$^a$Reaction conditions: 1 (0.1 mmol), 2a (3.0 equiv), Pd(OAc)$_2$ (10 mol\%), ligand (20 mol\%), Cu(OAc)$_2$ (2.0 equiv), DCE (2.0 mL), 80 °C, 6 h. $^b$Isolated yield. $^c$The data in parentheses is the ratio of linear and branched isomers which was determined by $^1$H NMR analysis. $^d$12 h. $^e$At 100 °C. $^f$2a (2.0 equiv) was used. $^g$Ligand (10 mol\%) was used.
3. Structures of Substrates

Aliphatic alkenes

- 2a
- 2b
- 2c
- 2d
- 2e
- 2f
- 2g
- 2h
- 2i
- 4a
- 4b
- 4c
- 4d
- 4e
- 4f
- 4g
- 4h
- 4i
- 4j
- 4k
- 4l
- 4m
- 4n
- 4o
- 4p
- 4q
- 4r
- 4s
- 4t
Phenylacetic amides
4. Experimental Section

4.1 Preparation of Phenylacetic Amides

The previous reported procedure was followed. To an oven-dried 50 mL round-bottom flask, 2,3,5,6-tetrafluoro-4-((trifluoromethyl)aniline (3.0 mmol) was dissolved in toluene (15.0 mL). Acid chloride (3.0 mmol), prepared from the corresponding carboxylic acid and oxalyl chloride, was added via syringe. Then, the mixture was heated to reflux under N₂ for 12 h. After cooling to room temperature, the mixture was concentrated in vacuo and the solid was recrystallized from ethyl acetate/hexane to give the pure amide substrates. Phenylacetic amides 6e, 6j, 6o, 6q, 6r, 6t and 8c had been synthesized and characterized. Other phenylacetic amides were synthesized and characterized before according the same procedure.

2-(2-Oxo-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)ethyl)phenyl acetate (6e)

White solid: \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 7.45-7.36 (m, 3H), 7.31 (d, \(J = 7.4\) Hz, 1H), 7.14 (d, \(J = 8.0\) Hz, 1H), 3.73 (s, 2H), 2.38 (s, 3H); \(^13\)C NMR (100 MHz, CDCl₃) \(\delta\) 170.5, 168.0, 149.0, 131.1, 129.7, 127.2, 126.2, 123.0, 38.2, 20.8; HRMS (ESI-TOF) [M+NH₄]⁺ calculated for C₁₇H₁₄F₁₁N₂O₃: 427.0887, found: 427.0881.

2-(4-(Tert-butyl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (6j)
White solid: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J$ = 7.4 Hz, 2H), 7.27 (d, $J$ = 7.6 Hz, 2H), 7.12 (s, 1H), 3.79 (s, 2H), 1.33 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.2, 151.2, 130.2, 129.1, 126.4, 43.0, 34.658, 31.2; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{19}$H$_{20}$F$_7$N$_2$: 425.1458, found: 425.1453.

2-(2,4-Dimethylphenyl)-N-(2,3,5,6-tetrafluoro-(trifluoromethyl)phenyl)acetamide (6o)

White solid: $^1$H NMR (400 MHz, acetone-d$_6$) $\delta$ 9.42 (s, 1H), 7.22 (d, $J$ = 7.6 Hz, 1H), 7.06 (s, 1H), 7.01 (d, $J$ = 7.6 Hz, 1H), 3.89 (s, 2H), 2.35 (s, 3H), 2.31 (s, 3H); $^{13}$C NMR (100 MHz, acetone-d$_6$) $\delta$ 169.4, 137.5, 137.3, 131.6, 131.0, 130.9, 127.2, 40.6, 20.7, 19.3; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{17}$H$_{16}$F$_7$N$_2$: 397.1145, found: 397.1141.

2-(2,4-Dichlorophenyl)-N-(2,3,5,6-tetrafluoro-(trifluoromethyl)phenyl)acetamide (6q)

White solid: $^1$H NMR (400 MHz, acetone-d$_6$) $\delta$ 9.74 (s, 1H), 7.56 (s, 2H), 7.42 (d, $J$ = 8.3 Hz, 1H), 4.11 (s, 2H); $^{13}$C NMR (100 MHz, acetone-d$_6$) $\delta$ 167.9, 135.8, 134.0, 133.9, 132.7, 129.4, 127.9, 40.0; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{15}$H$_{10}$Cl$_2$F$_7$N$_2$: 437.0053, found: 437.0051.
2-(2,3-Dichlorophenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (6r)

![Chemical structure of 6r](image)

White solid: $^1$H NMR (400 MHz, acetone-d$_6$) δ 9.77 (s, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.51 (d, $J = 7.7$ Hz, 1H), 7.38 (t, $J = 7.8$ Hz, 1H), 4.17 (s, 2H); $^{13}$C NMR (100 MHz, acetone-d$_6$) δ 167.9, 136.2, 133.1, 133.0, 131.2, 130.0, 128.438, 41.4; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{15}$H$_{10}$Cl$_2$F$_7$N$_2$: 437.0053, found: 437.0051.

2-Phenyl-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)butanamide (6t)

![Chemical structure of 6t](image)

White solid: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42-7.36 (m, 2H), 7.35-7.26 (m, 3H), 6.96 (s, 1H), 3.55 (t, $J = 7.5$ Hz, 1H), 2.33-2.20 (m, 2H), 1.94-1.82 (m, 1H), 0.94 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.4, 138.4, 129.3, 128.0, 128.0, 55.0, 26.2, 12.0; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{17}$H$_{16}$F$_7$N$_2$O: 397.1145, found: 397.1142.

2-(3-Benzoylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)propanamide (8c)

![Chemical structure of 8c](image)

White solid: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (s, 1H), 7.75 (d, $J = 7.3$ Hz, 2H), 7.70 (d, $J = 7.5$ Hz, 1H), 7.65-7.58 (m, 2H), 7.54-7.44 (m, 3H), 7.40 (s, 1H), 3.95 (q, $J = 7.0$ Hz, 1H), 1.63 (d, $J = 6.9$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.1,
171.6, 140.8, 138.1, 137.1, 132.8, 131.5, 129.9, 129.8, 129.2, 129.1, 128.4, 46.9, 18.6;
HRMS (ESI-TOF) [M+NH4]+ calculated for C23H18F7N2O2: 487.1251, found: 487.1243.

4.2 Preparation of Unactivated Alkenes

Alkenes 2a-2i, 4a-4c, 4j, 4l-4m were purchased from commercial vendors and used without further purification.

2-(But-3-en-1-yl)isoindoline-1,3-dione (4d)

\[
\text{N-(3-but-enyl)phthalimide as a white solid. } ^1\text{H NMR (400 MHz, CDCl}_3\text{) } \delta \text{ 7.84-7.78 (m, 2H), 7.72-7.66 (m, 2H), 5.82-5.72 (m, 1H), 5.07-4.99 (m, 2H), 3.75 (t, } J = 7.1 \text{ Hz, 2H), 2.43 (q, } J = 7.0 \text{ Hz, 2H); } ^{13}\text{C NMR (100 MHz, CDCl}_3\text{) } \delta \text{ 168.0, 134.3, 133.6, 131.9, 122.9, 117.3, 37.1, 32.6.}
\]

Pent-4-en-1-yl 4-methylbenzenesulfonate (4f)

To an oven-dried 100 mL round-bottom flask equipped with a magnetic stir bar, TsCl (1.90 g 10 mmol,) and DMAP (0.12 g, 1 mmol) were added. Dichloromethane (30 mL)
and triethylamine (1.8 mL, 12 mmol) were then added via syringe and the flask was cooled to 0 °C with an ice bath, after which 4-penten-1-ol (1.0 mL 10.0 mmol) was added dropwise via syringe. The mixture was allowed to warm to room temperature and stirring was continued for an additional 2 hours. The reaction mixture was quenched by the slow addition of water (10 mL). After drying of the organic phase over Na₂SO₄ and concentration under reduced pressure, the crude reaction product was purified by column chromatography on silica gel using hexane/EtOAc (10:1) as eluent to afford the product as a colorless oil. 

**1H NMR (400 MHz, CDCl₃)** δ 7.78 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 5.74-5.62 (m, 1H), 4.98-4.92 (m, 2H), 4.03 (td, J = 6.5, 1.6 Hz, 2H), 2.44 (s, 3H), 2.08 (q, J = 7.3 Hz, 2H), 1.79-1.69 (m, 2H); 

**13C NMR (100 MHz, CDCl₃)** δ 144.7, 136.6, 133.1, 129.8, 127.8, 115.8, 69.876, 29.3, 27.9, 21.6.

*Tert*-butyl(pent-4-en-1-yloxy)diphenylsilane (4g)

![4g]

To a stirred solution of 4-penten-1-ol (1) (2.50 mL, 24.2 mmol), imidazole (1.98 g, 29.0 mmol), and a catalytic amount of DMAP in DMF (25 mL) was added TBDPSCl (6.61mL, 25.4mmol) at 0 °C and stirring was continued for 19 h at rt. The reaction mixture was diluted with Et₂O and washed with 10% HCl, saturated aqueous NaHCO₃. The residue upon work up was chromatographed on silicagel with hexane/EtOAc (19:1) as eluant to give silyl ether as a colorless oil. 

**1H NMR (400 MHz, CDCl₃)** δ 7.73-7.65 (m, 4H), 7.46-7.36 (m, 6H), 5.87-5.77 (m, 1H), 5.06-4.91 (m, 2H), 3.72-3.66 (m, 2H), 2.21-2.12 (m, 2H), 1.72-1.64 (m, 2H), 1.07 (s, 9H); 

**13C NMR (100 MHz, CDCl₃)** δ 138.5, 135.6, 134.0, 129.5, 127.6, 63.3, 31.8, 30.1, 26.9, 19.2.

Pent-4-en-1-yl diphenylphosphinate (4i)

![4i]
To a dry, 100 mL round-bottom flask equipped with a magnetic stir bar was added diphenylphosphinic chloride (2.3 mL 12 mmol). Dichloromethane (30 mL) and triethylamine (2.8 mL, 20 mmol) were added via syringe and the flask was cooled to 0 °C with an ice bath, after which 4-penten-1-ol (1.0 mL 10.0 mmol) was added dropwise via syringe. The mixture was allowed to warm to room temperature and stirring was continued for an additional 2 hours. The reaction mixture was quenched by the slow addition of water (10 mL). After drying of the organic phase over Na₂SO₄ and concentration under reduced pressure, the crude reaction product was purified by column chromatography on silica gel using hexane/EtOAc (10:1) as eluent to afford the product as a colorless oil. \( ^1 \text{H NMR (400 MHz, CDCl}_3 \) δ 10.45 (s, 1H), 7.73 (dd, \( J = 12.3, 7.6 \text{ Hz, 4H}), 7.50 \) (t, \( J = 7.4 \text{ Hz, 2H}), 7.45-7.35 \) (m, 4H), 7.24-7.20 (m, 1H), 7.13 (d, \( J = 4.7 \text{ Hz, 2H}), 6.82 \) (d, \( J = 15.5 \text{ Hz, 1H}), 5.87 \) (dt, \( J = 15.0, 7.3 \text{ Hz, 1H}), 4.11-4.07 \) (m, 2H), 4.06 (s, 2H), 2.50 (dd, \( J = 12.0, 7.6 \text{ Hz, 2H}), 2.44 \) (s, 3H), 1.95-1.87 (m, 2H); \( ^{13} \text{C NMR (100 MHz, CDCl}_3 \) δ 137.3, 132.1 (d, \( J_{c-p} = 2.7 \text{ Hz}), 131.5 \) (d, \( J_{c-p} = 136.4 \text{ Hz}), 131.6 \) (d, \( J_{c-p} = 100.3 \text{ Hz}), 128.5 \) (d, \( J_{c-p} = 13.1 \text{ Hz}), 115.3 \) (d, \( J_{c-p} = 6.0 \text{ Hz), 29.7, 29.6; }^{31} \text{P NMR (162 MHz, CDCl}_3 \) δ 31.4.

**But-3-en-1-yl benzo[b]thiophene-2-carboxylate (4n)⁵**

A solution of DCAD (10 mmol) in DCM (15 mL) was slowly added at 22 °C via cannula to a solution of PPh₃ (2.62 g, 10 mmol), but-3-ene-1-ol (0.86 mL, 10 mmol) and benzo[b]thiophene-2-carboxylic acid (1.78 g, 10 mmol) in DCM (10 mL). The resulting cloudy mixture was stirred at the same temperature 12 h. Filtration of the mixture afforded reduced DCAD as a white powder. The filtrate was concentrated in vacuo to afford the crude product. The crude product was purified by column chromatography on silica gel using hexane/EtOAc (10:1) as eluent to afford the product as a colorless oil. \( ^1 \text{H NMR (400 MHz, CDCl}_3 \) δ 8.06 (s, 1H), 7.87 (t, \( J = 6.9 \text{ Hz, 2H}), 7.48-7.38 \) (m, 2H), 5.94-5.82 (m, 1H), 5.20 (d, \( J = 17.2 \text{ Hz, 1H}), 5.13 \) (d, \( J = 
10.2 Hz, 1H), 4.40 (td, \( J = 6.8, 1.0 \) Hz, 2H), 2.54 (q, \( J = 6.6 \) Hz, 2H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 162.7, 142.2, 138.7, 133.7, 133.6, 130.4, 126.9, 125.5, 124.8, 122.71, 117.6, 64.5, 33.1.

**But-3-en-1-yl benzofuran-2-carboxylate (4o)**

![Chemical Structure](image)

A solution of DCAD (10 mmol) in DCM (15 mL) was slowly added at 22 °C via cannula to a solution of PPh\(_3\) (2.62 g, 10 mmol), but-3-ene-1-ol (0.86 mL, 10 mmol) and benzofuran-2-carboxylic acid (1.62 g, 10 mmol) in DCM (10 mL). The resulting cloudy mixture was stirred at the same temperature 12 h. Filtration of the mixture afforded reduced DCAD as a white powder. The filtrate was concentrated in vacuo to afford the crude product. The crude product was purified by column chromatography on silica gel using hexane/EtOAc (10:1) as eluent to afford the product as a colorless oil. \( ^{1} \)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.67 (d, \( J = 7.9 \) Hz, 1H), 7.58 (d, \( J = 8.4 \) Hz, 1H), 7.51 (s, 1H), 7.44 (t, \( J = 7.5 \) Hz, 1H), 7.32-7.26 (m, 1H), 5.92-5.80 (m, 1H), 5.22-5.15 (m, 1H), 5.12 (d, \( J = 10.3 \) Hz, 1H), 4.43 (td, \( J = 6.8, 1.8 \) Hz, 2H), 2.55 (q, \( J = 6.6 \) Hz, 2H); \( ^{13} \)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 159.5, 155.7, 145.5, 133.5, 127.6, 126.9, 123.7, 122.8, 117.6, 113.8, 112.3, 64.4, 33.1.

**2-(But-3-en-1-yl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide (4p)**

![Chemical Structure](image)

To an oven-dried 50 mL round-bottom flask equipped with a magnetic stir bar, saccharin (1.83 g, 10 mmol), dry DMF (10 mL) was added via syringe and the flask was cooled to 0 °C with an ice bath, NaH (1.0 mL 10.0 mmol,) was added in batch. Then the reaction mixture was continued for 1 h at rt. 4-Bromo-1-buten (2.0 mL, 20.0
mmol) was added via syringe and stirred for 12 h at 120 °C. The resulting mixture was cooled to room temperature and poured into water, extracted the mixture by methylene chloride (50 mL). The combined organic layer was washed by water (50 mL), and dried over Na₂SO₄, the crude reaction product was purified by column chromatography on silica gel using hexane/EtOAc (10:1) as eluent to afford the product as a colorless solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.03 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 7.2 Hz, 1H), 7.92-7.78 (m, 2H), 5.87-5.76 (m, 1H), 5.15 (d, J = 17.1 Hz, 1H), 5.08 (d, J = 10.2 Hz, 1H), 3.82 (t, J = 7.5 Hz, 2H), 2.58 (q, J = 6.7 Hz, 2H); **¹³C NMR (100 MHz, CDCl₃)** δ 158.8, 137.6, 134.6, 133.7, 127.3, 125.1, 120.8, 118.0, 38.5, 32.6.

**1-(Indolin-1-yl)pent-4-en-1-one (4r)**

\[
\text{\includegraphics[width=0.2\textwidth]{image}}
\]

An oven-dried 250 mL 2-neck flask under argon was charged with pent-4-enoic acid (1.02 mL, 10 mmol), EDCI (2.11 g, 11 mmol), HOBt (1.48 g, 11 mmol), indoline (1.12 mL, 10 mmol), DIPEA (5.0 mL, 30 mmol). DCM (30 mL) was added via syringe. After stirring for an additional 20 h at room temperature, the reaction mixture was quenched with H₂O (30 mL). The organic solution was separated and the aqueous layer was extracted with DCM (2×30 mL). The combined organic layer was washed with brine (30 mL), and dried over Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography on silica gel using hexane/EtOAc (5:1) as eluent to afford the product as a colorless solid. **¹H NMR (400 MHz, CDCl₃)** δ 8.24 (d, J = 7.9 Hz, 1H), 7.22-7.15 (m, 2H), 7.00 (t, J = 7.4 Hz, 1H), 5.98-5.86 (m, 1H), 5.10 (d, J = 17.1 Hz, 1H), 5.02 (d, J = 10.2 Hz, 1H), 4.03 (t, J = 8.4 Hz, 2H), 3.18 (t, J = 8.4 Hz, 2H), 2.50 (s, 4H); **¹³C NMR (100 MHz, CDCl₃)** δ 170.4, 143.0, 137.3, 130.9, 127.5, 124.4, 123.5, 116.9, 115.3, 47.9, 35.1, 28.5, 28.0.

**7-(But-3-en-1-yloxy)-2H-chromen-2-one (4s)**

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To a solution of 7-hydroxy-2H-chromen-2-one (1.62 g, 10 mmol) and K$_2$CO$_3$ (5.50 g, 40 mmol) in CH$_3$CN (40 mL) was added 4-bromo-but-1-ene (1.60 mL, 15 mmol), and the mixture was heated to reflux for 12 h. It was then cooled to room temperature and the solvent was removed in vacuo. The residue was partitioned between HCl and water and the aqueous layer was extracted with CH$_2$Cl$_2$ (2x10 mL). The combined organic extracts were washed with water (2 x 10 mL), dried over Na$_2$SO$_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using hexane/EtOAc (5:1) as eluent to afford the product as a colorless solid. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58 (d, $J = 9.5$ Hz, 1H), 7.31 (d, $J = 8.6$ Hz, 1H), 6.78 (d, $J = 8.6$ Hz, 1H), 6.72 (s, 1H), 6.18 (dd, $J = 9.5$, 1.2 Hz, 1H), 5.91-5.79 (m, 1H), 5.14 (d, $J = 17.2$ Hz, 1H), 5.08 (d, $J = 10.2$ Hz, 1H), 4.01 (t, $J = 6.6$ Hz, 2H), 2.56-2.48 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.9, 161.0, 155.6, 143.3, 133.6, 128.6, 117.3, 112.8, 112.7, 112.3, 101.2, 67.6, 33.1.

(8R,9S,13S,14S)-3-(but-3-en-1-yloxy)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (4t)$^5$

To a solution of estrone (1.40 g, 5 mmol) and K$_2$CO$_3$ (2.76 g, 20 mmol) in CH$_3$CN (20 mL) was added 4-bromo-but-1-ene (1.0 mL, 10 mmol), and the mixture was heated to reflux for 12 h. It was then cooled to room temperature and the solvent was removed in vacuo. The residue was partitioned between HCl and water and the aqueous layer was extracted with CH$_2$Cl$_2$ (2x10 mL). The combined organic extracts were washed with water (2 x 10 mL), dried over Na$_2$SO$_4$ and concentrated in vacuo.
The crude product was purified by column chromatography on silica gel using hexane/EtOAc (4:1) as eluent to afford the product as a colorless solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.20 (d, \(J = 8.5\) Hz, 1H), 6.72 (d, \(J = 8.5\) Hz, 1H), 6.66 (s, 1H), 5.96-5.85 (m, 1H), 5.17 (d, \(J = 17.2\) Hz, 1H), 5.10 (d, \(J = 10.3\) Hz, 1H), 3.99 (t, \(J = 6.7\) Hz, 2H), 2.89 (d, \(J = 8.7\) Hz, 2H), 2.56-2.46 (m, 3H), 2.40 (d, \(J = 9.8\) Hz, 1H), 2.26 (d, \(J = 9.9\) Hz, 1H), 2.17-1.92 (m, 4H), 1.69-1.40 (m, 6H), 0.91 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 220.9, 156.9, 137.7, 134.5, 132.0, 126.2, 116.8, 114.6, 112.2, 67.1, 50.4, 48.0, 43.9, 38.3, 35.8, 33.7, 31.6, 29.6, 26.5, 25.9, 21.6, 13.8.

4.3 General Procedure for ortho-C(sp\(^2\))–H Olefination of Phenylacetic Amide 1 with Aliphatic Alkenes.

Phenylacetic amide 1 (0.10 mmol, 36.5 mg), Pd(OAc)\(_2\) (0.005 mmol, 5 mol%), L22 (0.01 mmol, 2.7 mg) and Cu(OAc)\(_2\) (0.02 mmol, 3.6 mg) were weighed in air and placed in an oven-dried sealed tube (35 mL) with a magnetic stir bar. The tube was evacuated and refilled with O\(_2\) three times. DCE (2.0 mL) was added via syringe and the reaction mixture was stirred for 5 min. Then, aliphatic alkenes 2 (0.30 mmol) was added via syringe and the mixture was heated to 80 °C for 6 hours under vigorous stirring. After cooling to ambient temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was purified by flash chromatography on silica gel using an eluent of hexane/EtOAc (19/1 to 9/1) to give the desired olefination products.

4.4 General Procedure for ortho-C(sp\(^2\))–H Olefination of Phenylacetic Amides with Unactivated Alkenes 2e.

Phenylacetic amides 6 (0.10 mmol), Pd(OAc)\(_2\) (0.005 mmol, 5 mol%), L22 (0.01 mmol, 2.7 mg) and Cu(OAc)\(_2\) (0.02 mmol, 3.6 mg) were weighed in air and placed in an oven-dried sealed tube (35 mL) with a magnetic stir bar. The tube was evacuated and refilled with O\(_2\) three times. DCE (2.0 mL) was added via syringe and the reaction mixture was stirred for 5 min. Then, aliphatic alkenes 2e (0.30 mmol, 38 µL) was added via syringe and the mixture was heated to 80 °C for 6 hours under vigorous
stirring. After cooling to ambient temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was purified by flash chromatography on silica gel using an eluent of hexane/EtOAc (19/1 to 9/1) to give the desired olefination products.

4.5 General Procedure for Late-Stage Diversification of Drug Molecules.

The starting material 8 (0.10 mmol), Pd(OAc)$_2$ (0.01 mmol, 2.2 mg), L22 (0.02 mmol, 5.4 mg) and Cu(OAc)$_2$ (0.10 mmol, 18.2 mg) were weighed in air and placed in an oven-dried sealed tube (35 mL) with a magnetic stir bar. The tube was evacuated and refilled with O$_2$ three times. DCE (2.0 mL) was added via syringe and the reaction mixture was stirred for five minutes. Then, 1-octene 2a (0.30 mmol, 47 µL) was added via syringe and the mixture was heated to 100 °C for 12 hours under vigorous stirring. After cooling to ambient temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was purified by flash chromatography on silica gel using an eluent of hexane/EtOAc (19/1 to 9/1) to give the desired olefination products.

4.6 General Procedure for Large Scale Synthesis.

Phenylacetic amide 1 (3.0 mmol, 1.09 g), Pd(OAc)$_2$ (0.15 mmol, 5 mol%), L21 (0.30 mmol, 64.0 mg) and Cu(OAc)$_2$ (3.0 mmol, 0.54 g) were weighed in air and placed in an oven-dried sealed tube (100 mL) with a magnetic stir bar. The tube was evacuated and refilled with O$_2$ three times. DCE (60 mL) was added via syringe and the reaction mixture was stirred for 10 min. Then, 1-octene 2a (9.0 mmol, 1.41 mL) was added via syringe and the mixture was heated to 80 °C for 12 hours under vigorous stirring. After cooling to ambient temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was purified by flash chromatography on silica gel using an eluent of hexane/EtOAc (19/1 to 9/1) to give the desired olefination products.

4.6 General Procedure for Hydrogenation.
To two paralleled oven-dried round-bottom flask (50 mL) was added Pd/C (10 wt. % loading on carbon, 5.0 mg), amide 3a (33.3 mg, 0.07 mmol) and EtOAc (2 mL). The reaction flask was evacuated and refilled with H₂ (3 times, balloon). After stirring at room temperature for 24 hours, the reaction mixture was filtered through a small pad of Celite. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel using an eluent of hexane/EtOAc (9/1) to give the desired product as colorless oil (66.4 mg, 99%).

4.7 General Procedure for Deprotection.

To a solution of 3i (35.8 mg, 0.08 mmol) in MeOH (4 mL), BF₃•Et₂O (68.1 mg, 0.48 mmol) by was added via syringe. The reaction mixture was heated to 110 °C for 24 hours. After cooling to room temperature, triethylamine (101.0 mg, 1.0 mmol) was added via syringe. the reaction mixture was filtered through a small pad of Celite and the solvent was removed under vacuum. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel using an eluent of hexane/EtOAc (19/1) to give the desired product as colorless oil (20.4 mg, 83%).
5. Experimental Data

(E)-2-(2-methyl-6-(oct-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (3a)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (41.4 mg, 87% yield), linear/branched ratio = 4.0/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J = 7.7$ Hz, 1H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.17 (d, $J = 7.4$ Hz, 1H), 6.81 (s, 1H), 6.61 (d, $J = 15.5$ Hz, 1H), 6.15 (dt, $J = 15.4$, 6.9 Hz, 1H), 3.93 (s, 2H), 2.39 (s, 3H), 2.24 (dd, $J = 14.5$, 7.2 Hz, 2H), 1.50-1.41 (m, 2H), 1.38-1.28 (m, 6H), 0.89 (t, $J = 6.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.5, 138.8, 137.7, 136.4, 129.8, 128.9, 128.5, 126.7, 125.5, 37.5, 33.3, 31.7, 29.2, 28.9, 22.6, 20.2, 14.0; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{24}$H$_{28}$F$_7$N$_2$O: 493.2084, found: 493.2081.

2-(2-Methyl-6-(oct-1-en-2-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (3a')

White solid: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.23 (d, $J = 7.4$ Hz, 1H), 7.21 (t, $J = 6.8$ Hz, 1H), 7.06 (d, $J = 7.3$ Hz, 1H), 6.87 (s, 1H), 5.27 (d, $J = 1.2$ Hz, 1H), 4.93 (s, 1H), 3.87 (s, 2H), 2.39 (s, 3H), 2.35-2.27 (m, 2H), 1.45-1.39 (m, 2H), 1.33-1.26 (m, 6H), 0.87 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.9, 149.8, 144.9, 138.0, 129.8, 128.9, 127.9, 127.2, 114.7, 38.6, 38.4, 31.7, 29.0, 27.6, 22.6, 20.0, 14.0; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{24}$H$_{28}$F$_7$N$_2$O: 493.2084, found: 493.2078.
(E)-2-(2-(hex-1-en-1-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (3b)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (41.5 mg, 92% yield). Linear/branched ratio = 4.6/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J = 7.6$ Hz, 1H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.17 (d, $J = 7.2$ Hz, 1H), 6.78 (s, 1H), 6.61 (d, $J = 15.4$ Hz, 1H), 6.14 (dt, $J = 15.4$, 6.9 Hz, 1H), 3.93 (s, 2H), 2.39 (s, 3H), 2.25 (dd, $J = 14.2$, 7.4 Hz, 2H), 1.44 (dd, $J = 15.0$, 7.6 Hz, 2H), 1.36 (dd, $J = 14.5$, 7.1 Hz, 2H), 0.92 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.5, 138.8, 137.7, 136.5, 129.8, 128.9, 128.5, 126.7, 125.5, 37.6, 33.0, 31.4, 22.2, 20.2, 13.9; HRMS (ESI-TOF) [M+NH$_4]^+$ calculated for C$_{22}$H$_{24}$F$_7$N$_2$O: 465.1771, found: 465.1767.

2-(2-(Hex-1-en-2-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (3b')

White solid: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 (d, $J = 7.3$ Hz, 1H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.06 (d, $J = 7.6$ Hz, 1H), 6.82 (s, 1H), 5.27 (s, 1H), 4.93 (s, 1H), 3.87 (s, 2H), 2.39 (s, 3H), 2.35-2.28 (m, 2H), 1.45-1.32 (m, 4H), 0.89 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.9, 149.8, 144.9, 138.0, 129.8, 129.0, 128.0, 127.2, 114.7, 38.5, 38.3, 29.8, 22.4, 20.0, 13.9; HRMS (ESI-TOF) [M+NH$_4]^+$ calculated for C$_{22}$H$_{24}$F$_7$N$_2$O: 465.1771, found: 465.1769.

(E)-2-(2-(dec-1-en-1-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethy
Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (43.7 mg, 87% yield). Linear/branched ratio = 4.3/1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.36 (d, \(J = 7.7 \) Hz, 1H), 7.24 (t, \(J = 7.6 \) Hz, 1H), 7.17 (d, \(J = 7.1 \) Hz, 1H), 6.79 (s, 1H), 6.60 (d, \(J = 15.5 \) Hz, 1H), 6.15 (dt, \(J = 15.4, 6.9 \) Hz, 1H), 3.93 (s, 2H), 2.38 (s, 3H), 2.27-2.21 (m, 2H), 1.48-1.42 (m, 2H), 1.31-1.26 (m, 10H), 0.88 (t, \(J = 6.9 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 168.5, 138.8, 137.7, 136.5, 129.8, 128.9, 128.5, 126.7, 125.5, 37.5, 33.3, 31.9, 29.5, 29.2, 29.2, 22.7, 20.2, 14.1; HRMS (ESI-TOF) [M+NH\(_4\)]\(^+\) calculated for C\(_{26}\)H\(_{32}\)F\(_7\)N\(_2\)O: 521.2397, found: 521.2394.

2-(2-(Dec-1-en-2-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (3c’)

White solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta \) 7.25 (d, \(J = 6.9 \) Hz, 1H), 7.21 (t, \(J = 6.8 \) Hz, 1H), 7.06 (d, \(J = 7.2 \) Hz, 1H), 6.82 (s, 1H), 5.27 (s, 1H), 4.93 (s, 1H), 3.87 (s, 2H), 2.39 (s, 3H), 2.33-2.28 (m, 2H), 1.45-1.40 (m, 2H), 1.31-1.24 (m, 11H), 0.87 (t, \(J = 6.7 \) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta \) 168.9, 149.9, 144.9, 138.0, 129.8, 128.9, 128.0, 127.2, 114.7, 38.6, 38.5, 31.8, 29.4, 29.3, 29.2, 27.7, 22.6, 20.0, 14.1; HRMS (ESI-TOF) [M+NH\(_4\)]\(^+\) calculated for C\(_{26}\)H\(_{32}\)F\(_7\)N\(_2\)O: 521.2397, found: 521.2394.

(\(E\))-2-(2-(dodec-1-en-1-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (3d)
Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (44.2 mg, 83% yield). Linear/branched ratio = 3.9/1; \( ^{1}H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.36 (d, \( J = 7.7 \) Hz, 1H), 7.24 (t, \( J = 7.6 \) Hz, 1H), 7.17 (d, \( J = 7.1 \) Hz, 1H), 6.80 (s, 1H), 6.61 (d, \( J = 15.1 \) Hz, 1H), 6.15 (dt, \( J = 15.5, 6.9 \) Hz, 1H), 3.93 (s, 2H), 2.39 (s, 3H), 2.24 (dd, \( J = 14.5, 7.1 \) Hz, 2H), 1.50-1.42 (m, 2H), 0.88 (t, \( J = 6.6 \) Hz, 3H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 168.5, 138.8, 137.7, 136.5, 129.8, 128.9, 128.5, 126.7, 125.5, 37.5, 33.3, 31.9, 29.6, 29.6, 29.5, 29.3, 29.3, 29.2, 22.7, 20.2, 14.1; HRMS (ESI-TOF) [M+NH\(_4\)]\(^{+}\) calculated for C\(_{28}\)H\(_{36}\)F\(_{7}\)N\(_2\)O: 549.2710, found: 549.2706.

2-(2-(Dodec-1-en-2-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (3d)

White solid; \( ^{1}H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.23 (d, \( J = 7.3 \) Hz, 1H), 7.20 (t, \( J = 8.1 \) Hz, 1H), 7.06 (d, \( J = 7.8 \) Hz, 1H), 6.81 (s, 1H), 5.27 (s, 1H), 4.93 (s, 1H), 3.87 (s, 2H), 2.39 (s, 3H), 2.33-2.28 (m, 2H), 1.43-1.40 (m, 2H), 1.33-1.20 (m, 14H), 0.88 (t, \( J = 6.5 \) Hz, 3H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 168.8, 149.9, 144.9, 138.0, 129.8, 128.9, 128.0, 127.1, 114.8, 38.6, 38.5, 31.9, 29.6, 29.5, 29.4, 29.3, 27.7, 22.7, 20.0, 14.1; HRMS (ESI-TOF) [M+NH\(_4\)]\(^{+}\) calculated for C\(_{28}\)H\(_{36}\)F\(_{7}\)N\(_2\)O: 549.2710, found: 549.2706.

\((E)-2-(2-methyl-6-(4-methylpent-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluo
Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (33.6 mg, 75% yield). Linear/branched ratio = 4.0/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (d, $J = 7.3$ Hz, 1H), 7.25 (t, $J = 7.6$ Hz, 1H), 7.18 (d, $J = 7.5$ Hz, 1H), 6.78 (s, 1H), 6.60 (d, $J = 15.5$ Hz, 1H), 6.18 (dt, $J = 15.3$, 7.7 Hz, 1H), 3.93 (s, 2H), 2.38 (s, 3H), 2.14 (td, $J = 7.1$, 1.2 Hz, 1H), 1.73 (td, $J = 13.3$, 6.6 Hz, 1H), 0.94 (d, $J = 6.6$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.5, 138.8, 137.7, 135.1, 129.8, 128.9, 128.5, 127.8, 125.9, 42.6, 37.6, 28.5, 22.3, 20.2; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{22}$H$_{24}$F$_7$N$_2$O: 465.1771, found: 465.1767.

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (30.1 mg, 65% yield). Linear/branched ratio = 7.2/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 (d, $J = 7.3$ Hz, 1H), 7.25 (t, $J = 7.6$ Hz, 1H), 7.19 (d, $J = 7.3$ Hz, 1H), 6.78 (s, 1H), 6.59 (d, $J = 15.4$ Hz, 1H), 6.18 (dt, $J = 15.3$, 7.7 Hz, 1H), 3.94 (s, 2H), 2.39 (s, 3H), 2.13 (d, $J = 7.6$ Hz, 1H), 0.94 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.5, 138.8, 137.7, 133.5, 129.9, 128.9, 128.5, 125.6, 47.8, 37.6, 31.3, 29.3, 20.2; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{23}$H$_{26}$F$_7$N$_2$O: 479.1928, found: 479.1925.
(E)-2-(2-(3-cyclohexylprop-1-en-1-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (3g)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (37.3 mg, 77% yield). Linear/branched ratio = 6.2/1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37 (d, $J = 7.7$ Hz, 1H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.17 (d, $J = 7.3$ Hz, 1H), 6.78 (s, 1H), 6.58 (d, $J = 15.4$ Hz, 1H), 6.14 (dt, $J = 15.0$, 7.3 Hz, 1H), 3.93 (s, 2H), 2.38 (s, 3H), 2.14 (t, $J = 7.0$ Hz, 2H), 1.74-1.63 (m, 4H), 1.43-1.36 (m, 1H), 1.29-1.15 (m, 4H), 1.00-0.89 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.5, 138.9, 137.7, 135.0, 129.8, 128.9, 128.5, 127.7, 125.6, 41.3, 38.0, 37.6, 33.1, 26.5, 26.3, 20.2; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{25}$H$_{28}$F$_7$N$_2$O: 505.2804, found: 505.2802.

(3g)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (34.2 mg, 72% yield). Linear/branched ratio = 9.2/1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 (d, $J = 7.5$ Hz, 1H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.15 (d, $J = 7.3$ Hz, 1H), 6.77 (s, 1H), 6.55 (d, $J = 15.6$ Hz, 1H), 6.07 (dd, $J = 15.7$, 6.9 Hz, 1H), 3.91 (s, 2H), 2.37 (s, 3H), 2.23-2.05 (m, 1H), 1.79-1.73 (m, 4H), 1.32-1.13 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.6, 142.1, 138.9, 137.6, 129.7, 129.0, 128.4, 125.5, 124.3, 41.4, 37.6,
32.8, 26.0, 25.9, 20.2; **HRMS (ESI-TOF) [M+NH₄]⁺** calculated for C₂₄H₂₃F₇N₂O: 491.1928, found: 491.1925.

(E)-2-(2-(3,3-dimethylbut-1-en-1-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(tri fluoromethyl)phenyl)acetamide (3i)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (26.2 mg, 58% yield). Single isomer was obtained; **¹H NMR (400 MHz, CDCl₃)** δ 7.35 (d, J = 7.5 Hz, 1H), 7.25 (t, J = 7.8 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 6.76 (s, 1H), 6.52 (d, J = 15.8 Hz, 1H); **¹³C NMR (100 MHz, CDCl₃)** δ 168.6, 147.1, 138.9, 137.6, 129.7, 129.1, 128.4, 125.6, 121.7, 37.6, 33.8, 29.4, 20.2; **HRMS (ESI-TOF) [M+NH₄]⁺** calculated for C₂₂H₂₄F₇N₂O: 465.1771, found: 465.1766.

(E)-2-(2-methyl-6-(4-phenylbut-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(triflu oromethyl)phenyl)acetamide (5a)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (31.7 mg, 64% yield). Linear/branched ratio = 5.0/1; **¹H NMR (400 MHz, CDCl₃)** δ 7.34-7.27 (m, 2H), 7.27-7.26 (m, 1H), 7.23-7.20 (m, 3H), 7.17 (d, J = 7.2 Hz, 1H), 6.70 (s, 1H), 6.60 (d, J = 15.5 Hz, 1H), 6.14 (dt, J = 15.5, 6.9 Hz, 1H), 3.84 (s, 2H), 2.81 (t, J = 7.5 Hz, 1H), 2.59 (q, J = 7.0 Hz, 2H), 2.37 (s, 3H); **¹³C NMR (100 MHz, CDCl₃)** δ 168.4, 141.3, 138.6, 137.7, 134.9, 129.9, 129.1, 128.5, 128.4, 128.4, 127.7, 125.9, 125.6, 37.5, 35.5, 34.8, 20.2; **HRMS (ESI-TOF) [M+NH₄]⁺** calculated for C₂₆H₂₄F₇N₂O: 513.1771, found: 513.1767.
2-(2-Methyl-6-(4-phenylbut-1-en-2-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoro methyl)phenyl)acetamide (5a′)

![Chemical structure of 5a′](image)

White solid: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.28-7.21 (m, 4H), 7.20-7.14 (m, 3H), 7.09 (d, \(J = 6.4\) Hz, 1H), 6.76 (s, 1H), 5.35 (d, \(J = 1.3\) Hz, 1H), 4.99 (s, 1H), 3.81 (s, 2H), 2.78 (t, \(J = 7.6\) Hz, 2H), 2.68-2.64 (m, 2H), 2.39 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.8, 148.8, 144.4, 141.2, 138.1, 129.9, 129.1, 128.4, 128.3, 128.0, 127.1, 126.0, 115.4, 39.9, 38.4, 33.8, 20.0; HRMS (ESI-TOF) [M+NH\(_4\)]\(^+\) calculated for C\(_{26}\)H\(_{24}\)F\(_7\)N\(_2\)O: 513.1771, found: 513.1766.

\((E)\)-2-(2-(hexa-1,5-dien-1-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoro methyl)phenyl)acetamide (5b)

![Chemical structure of 5b](image)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (24.9 mg, 56% yield). Linear/branched ratio = 4.2/1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.35 (d, \(J = 7.7\) Hz, 1H), 7.24 (t, \(J = 7.6\) Hz, 1H), 7.18 (d, \(J = 7.9\) Hz, 1H), 6.77 (s, 1H), 6.63 (d, \(J = 15.5\) Hz, 1H), 6.14 (dt, \(J = 15.4, 6.7\) Hz, 1H), 5.89-5.79 (m, 1H), 5.09-4.96 (m, 2H), 3.92 (s, 2H), 2.38 (s, 3H), 2.38-2.33 (m, 2H), 2.27-2.21 (m, 2H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.2, 138.6, 137.72, 137.71, 135.3, 129.9, 129.0, 128.5, 127.3, 125.6, 115.2, 37.6, 33.3, 32.5, 20.2; HRMS (ESI-TOF) [M+NH\(_4\)]\(^+\) calculated for C\(_{22}\)H\(_{22}\)F\(_7\)N\(_2\): 463.1615, found: 463.1612.

\((E)\)-2-(2-methyl-6-(5-oxohex-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoro methyl)phenyl)acetamide (5c)
Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 4/1). The desired product was obtained as a white solid (32.1 mg, 70% yield). Linear/branched ratio = 4.7/1; "H NMR (400 MHz, CDCl3) δ 7.29 (d, J = 7.6 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.17 (d, J = 6.8 Hz, 1H), 7.09 (s, 1H), 6.65 (d, J = 15.5 Hz, 1H), 6.08 (dt, J = 15.5, 6.7 Hz, 1H), 3.89 (s, 2H), 2.65 (t, J = 7.0 Hz, 2H), 2.52 (q, J = 7.2 Hz, 2H), 2.41 (s, 3H), 2.16 (s, 3H); "C NMR (100 MHz, CDCl3) δ 208.3, 168.5, 138.3, 137.8, 133.7, 130.0, 129.3, 128.3, 128.2, 125.5, 42.6, 37.4, 29.9, 27.1, 20.2; HRMS (ESI-TOF) [M+NH4]+ calculated for C22H22F7N2O2: 479.1564, found: 479.1556.

(E)-2-(2-(4-(1,3-dioxoisoindolin-2-yl)but-1-en-1-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (5d)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 4/1). The desired product was obtained as a white solid (48.5 mg, 86% yield). Linear/branched ratio = 7.0/1; "H NMR (400 MHz, CDCl3) δ 7.81 (dd, J = 5.4, 3.1 Hz, 2H), 7.68 (dd, J = 5.5, 3.0 Hz, 2H), 7.26 (d, J = 7.4 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 6.8 Hz, 1H), 6.95 (s, 1H), 6.65 (d, J = 15.5 Hz, 1H), 6.06 (dt, J = 15.2, 7.0 Hz, 1H), 3.87 (t, J = 6.7 Hz, 2H), 3.83 (s, 2H), 2.64 (q, J = 6.6 Hz, 2H), 2.34 (s, 3H); "C NMR (100 MHz, CDCl3) δ 168.4, 168.3, 138.0, 137.8, 134.0, 131.9, 131.4, 130.1, 129.6, 129.2, 128.4, 125.8, 123.3, 37.4, 37.3, 32.3, 20.2;
HRMS (ESI-TOF) [M+NH₄]⁺ calculated for C₂₈H₂₃F₇N₃O₃: 582.1622, found: 582.1617.

\((E)\)-5-(3-methyl-2-(2-oxo-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)ethyl)phenyl)pent-4-en-1-yl acetate (5e)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (33.4 mg, 68% yield). Linear/branched ratio = 5.1/1;\(^{1}H\) NMR (400 MHz, CDCl₃) δ 7.33 (d, \(J = 7.4\) Hz, 1H), 7.24 (t, \(J = 7.6\) Hz, 1H), 7.18 (d, \(J = 7.0\) Hz, 1H), 7.03 (s, 1H), 6.65 (d, \(J = 15.5\) Hz, 1H), 6.09 (dt, \(J = 15.4, 6.9\) Hz, 1H), 4.14 (t, \(J = 6.6\) Hz, 2H), 3.94 (s, 2H), 3.94 (s, 2H), 2.40 (s, 3H), 2.32 (q, \(J = 7.1\) Hz, 2H), 2.07 (s, 3H), 1.86-1.78 (m, 2H); \(^{13}C\) NMR (100 MHz, CDCl₃) δ 171.4, 168.5, 138.4, 137.8, 134.1, 130.0, 129.1, 128.4, 128.1, 125.4, 63.5, 37.4, 29.4, 28.1, 21.0, 20.2; HRMS (ESI-TOF) [M+NH₄]⁺ calculated for C₂₃H₂₄F₇N₂O₃: 509.1670, found: 509.1660.

\((E)\)-5-(3-methyl-2-(2-oxo-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)ethyl)phenyl)pent-4-en-1-yl 4-methylbenzenesulfonate (5f)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 4/1). The desired product was obtained as a white solid (34.7 mg, 58% yield). Linear/branched ratio = 6.2/1;\(^{1}H\) NMR (400 MHz, CDCl₃) δ 7.78 (d, \(J = 8.3\) Hz, 2H), 7.34 (d, \(J = 8.0\) Hz, 2H), 7.28 (d, \(J = 7.4\) Hz, 1H), 7.22 (t, \(J = 7.5\) Hz, 1H), 7.18 (d, \(J = 6.5\) Hz, 1H), 7.09 (s, 1H), 6.63 (d, \(J = 15.5\) Hz, 1H), 5.99 (dt,
$J = 15.5, 7.1 \text{ Hz, 1H}$, 4.10 (t, $J = 6.1 \text{ Hz, 2H}$), 3.92 (s, 2H), 2.44 (s, 3H), 2.39 (s, 3H), 2.33 (dd, $J = 14.1, 7.1 \text{ Hz, 2H}$), 1.83 (dd, $J = 13.2, 6.5 \text{ Hz, 2H}$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.6, 144.9, 138.1, 137.7, 132.9, 132.7, 129.9, 129.3, 129.0, 128.2, 127.8, 125.3, 69.5, 37.2, 28.9, 28.1, 21.6, 20.2; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{28}$H$_{28}$F$_7$N$_2$O$_4$S: 621.1653, found: 621.1645.

(E)-2-(2-(5-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)oxy)pent-1-en-1-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (5g)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (55.7 mg, 83% yield). Linear/branched ratio = 4.8/1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.69-7.61 (m, 4H), 7.44-7.34 (m, 6H), 7.31 (d, $J = 7.5 \text{ Hz, 1H}$), 7.22 (d, $J = 7.5 \text{ Hz, 1H}$), 7.18 (d, $J = 7.6 \text{ Hz, 1H}$), 6.75 (s, 1H), 6.61 (d, $J = 15.3 \text{ Hz, 1H}$), 6.17-6.09 (m, 1H), 3.89 (s, 2H), 3.72 (t, $J = 6.2 \text{ Hz, 2H}$), 2.38 (s, 3H), 2.37-2.32 (m, 2H), 1.78-1.69 (m, 2H), 1.05 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.5, 138.6, 137.7, 135.8, 135.5, 133.9, 129.8, 129.5, 128.9, 128.4, 127.6, 127.0, 125.6, 63.2, 37.5, 32.1, 29.7, 26.8, 20.2, 19.2; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{37}$H$_{40}$F$_7$N$_2$O$_2$Si: 705.2742, found: 705.2733.

(E)-5-(3-methyl-2-(2-oxo-2-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)ethyl)phenyl)pent-4-en-1-yl benzoate (5h)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (49.8 mg, 90% yield). Linear/branched ratio = 5.0/1; $^1$H NMR (400 MHz, CDCl$_3$) δ
8.01 (d, J = 7.4 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.23 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 7.0 Hz, 1H), 7.04 (s, 1H), 6.68 (d, J = 15.7 Hz, 1H), 6.15 (dt, J = 14.9, 7.0 Hz, 1H), 4.40 (t, J = 6.4 Hz, 2H), 3.93 (s, 2H), 2.42 (q, J = 7.2 Hz, 2H), 2.39 (s, 3H), 1.98 (dd, J = 13.5, 6.7 Hz, 2H); \(^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta 168.5, 166.8, 138.3, 137.8, 134.2, 133.0, 130.1, 129.9, 129.4, 129.1, 128.4, 128.3, 128.1, 125.4, 64.1, 37.4, 29.7, 28.1, 20.2; \text{HRMS (ESI-TOF)} \quad [\text{M}+\text{NH}_4]^+ \quad \text{calculated for C}_{28}\text{H}_{36}\text{F}_7\text{N}_2\text{O}_3: 571.1826, \text{found: 571.1818.}

\((E)-5-(3\text{-methyl-2-(2-oxo-2-((2,3,5,6\text{-tetrafluoromethyl)phenyl)amino})ethyl)phenyl)pent-4-en-1-yl diphenylphosphinate (5i)\)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 4/1). The desired product was obtained as a white solid (34.1 mg, 53% yield). Single isomer was obtained; \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta 10.45\) (s, 1H), 7.76-7.71 (m, 4H), 7.50 (t, J = 7.4 Hz, 2H), 7.43-7.49 (m, 4H), 7.22 (t, J = 4.7 Hz, 2H), 7.13 (d, J = 4.7 Hz, 2H), 6.82 (d, J = 15.5 Hz, 1H), 5.87 (dt, J = 15.0, 7.3 Hz, 1H), 4.09 (q, J = 6.4 Hz, 2H), 4.06 (s, 2H), 2.50 (q, J = 6.2 Hz, 2H), 2.44 (s, 3H), 1.95-1.87 (m, 2H); \(^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta 169.4, 138.2, 138.1, 132.5\) (d, J\(_{c,p} = 2.7\) Hz), 131.4, 131.3, 130.8, 130.4 (d, J\(_{c,p} = 137.3\) Hz), 129.5, 128.6, 128.5, 127.3, 124.6, 62.4 (d, J\(_{c,p} = 6.0\) Hz), 36.6, 28.7 (d, J\(_{c,p} = 7.8\) Hz), 28.3, 20.5; \(^{31}\text{P NMR (CDCl}_3, 162\text{ MHz) \(\delta 32.6; \text{HRMS (ESI-TOF)} \quad [\text{M}+\text{H}]^+ \quad \text{calculated for C}_{33}\text{H}_{28}\text{F}_7\text{NO}_3\text{P: 650.1690, found: 650.1677.}

\((E)-2-(2\text{-methyl-6-(5-oxopent-1-en-1-yl)phenyl})-\text{N-}(2,3,5,6\text{-tetrafluoro-4-(trifluoromethyl)phenyl})acetamide (5j)\)
Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 4/1). The desired product was obtained as a white solid (23.2 mg, 52% yield). Linear/branched ratio = 6.7/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.81 (s, 1H), 7.31 (d, $J = 7.5$ Hz, 1H), 7.23 (t, $J = 7.7$ Hz, 1H), 7.19 (d, $J = 7.1$ Hz, 1H), 6.91 (s, 1H), 6.67 (d, $J = 15.4$ Hz, 1H), 6.10 (dt, $J = 15.5, 6.5$ Hz, 1H), 3.90 (s, 2H), 2.67 (t, $J = 6.8$ Hz, 2H), 2.59 (q, $J = 6.9$ Hz, 2H) 2.40 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.6, 168.4, 138.1, 137.8, 133.2, 130.2, 129.2, 128.5, 128.4, 125.5, 43.0, 37.5, 25.6, 20.2; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{21}$H$_{20}$F$_7$N$_2$O$_2$: 465.1408, found: 465.1404.

(E)-4-(3-methyl-2-(2-oxo-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)ethyl)phenyl)but-3-en-1-yl adamantane-1-carboxylate (5k)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (43.8 mg, 74% yield). Linear/branched ratio = 13.2/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33 (d, $J = 7.7$ Hz, 1H), 7.25 (t, $J = 7.6$ Hz, 1H), 7.20 (d, $J = 7.4$ Hz, 1H), 6.92 (s, 1H), 6.70 (d, $J = 15.7$ Hz, 1H), 6.07 (dt, $J = 15.4, 6.9$ Hz, 1H), 4.21 (t, $J = 6.5$ Hz, 2H), 3.91 (s, 2H), 2.57 (q, $J = 6.4$ Hz, 2H), 2.40 (s, 3H), 1.99 (s, 3H), 1.88 (d, $J = 2.4$ Hz, 6H), 1.70 (q, $J = 12.3$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 177.7, 168.3, 138.3, 137.8, 131.2, 130.2, 129.4, 129.2, 128.5, 125.7, 62.9, 40.7, 38.8, 37.5, 36.5, 32.8, 27.9,
20.2; HRMS (ESI-TOF) [M+NH₄]⁺ calculated for C₃₁H₃₄F₇N₂O₃: 615.2452, found: 615.2443.

(E)-2-(2-(5-cyanopent-1-en-1-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (5I)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 2/1). The desired product was obtained as a white solid (21.7 mg, 45% yield). Linear/branched ratio = 8.0/1; ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, J = 7.4 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H), 6.90 (s, 1H), 6.71 (d, J = 15.6 Hz, 1H), 6.06 (dt, J = 14.9, 7.0 Hz, 1H), 3.92 (s, 2H), 2.46-2.40 (m, 4H), 2.40 (s, 3H), 1.86 (p, J = 7.1 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 168.4, 138.0, 137.8, 132.5, 130.2, 129.3, 129.2, 128.5, 125.4, 119.5, 37.4, 32.0, 24.6, 20.2, 16.5; HRMS (ESI-TOF) [M+NH₄]⁺ calculated for C₂₂H₂₁F₇N₃O: 476.1567, found: 476.1559.

(E)-2-(2-methyl-6-(4-nitrobut-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (5m)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 2/1). The desired product was obtained as a white solid (20.0 mg, 43% yield). Linear/branched ratio > 20/1; ¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, J = 7.4 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.5 Hz, 1H), 6.79 (s, 1H), 6.77 (d, J = 15.7 Hz, 1H), 6.03 (dt, J = 15.5, 7.0 Hz, 1H), 4.53 (t, J = 6.6 Hz, 2H), 3.89 (s, 2H), 2.94 (qd, J = 6.9, 1.4 Hz, 2H), 2.40 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.2, 137.8, 137.5, 131.5, 130.6, 129.3, 128.5, 128.0, 125.6, 74.9, 37.4,
Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 4/1). The desired product was obtained as a white solid (30.6 mg, 51% yield). Single isomer was obtained; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03 (s, 1H), 7.86 (dd, \(J = 7.3, 1.1\) Hz, 1H), 7.83 (dd, \(J = 8.1, 0.7\) Hz, 1H), 7.46-7.36 (m, 3H), 7.25 (d, \(J = 7.6\) Hz, 1H), 7.19 (d, \(J = 7.3\) Hz, 1H), 6.88-6.77 (m, 2H), 6.17 (dt, \(J = 15.6, 7.0\) Hz, 1H), 4.50 (t, \(J = 6.3\) Hz, 2H), 3.93 (s, 2H), 2.75 (q, \(J = 6.3\) Hz, 2H), 2.38 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.3, 162.8, 142.1, 138.6, 138.2, 137.8, 133.2, 130.7, 130.6, 130.2, 129.9, 129.2, 128.5, 127.0, 125.7, 125.5, 124.9, 122.7, 64.3, 37.5, 32.7, 20.2; HRMS (ESI-TOF) [M+NH\(_4\)]\(^+\) calculated for C\(_{29}\)H\(_{24}\)F\(_7\)N\(_2\)O\(_3\)S: 613.1390, found: 613.1387.

\((E)\)-4-(3-methyl-2-(2-oxo-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)ethyl)phenyl)but-3-en-1-yl benzo[b]thiophene-2-carboxylate (5n)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 4/1). The desired product was obtained as a white solid (30.5 mg, 53% yield). Linear/branched ratio > 20/1; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)
7.66 (d, J = 7.5 Hz, 1H), 7.58 (dd, J = 8.4, 0.8 Hz, 1H), 7.52 (d, J = 0.9 Hz, 1H), 7.44 (dt, J = 8.4, 1.3 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.30 (d, J = 7.6 Hz, 1H), 7.27 (d, J = 7.5 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 6.86 (s, 1H), 6.80 (d, J = 15.5 Hz, 1H), 6.16 (dt, J = 15.5, 6.9 Hz, 1H), 4.53 (t, J = 6.4 Hz, 2H), 3.93 (s, 2H), 2.76 (q, J = 6.4 Hz, 2H), 2.38 (s, 3H); 1^3C NMR (100 MHz, CDCl3) δ 168.3, 159.5, 155.7, 145.2, 138.1, 137.8, 130.5, 130.3, 129.2, 128.5, 127.7, 126.8, 125.7, 123.8, 122.8, 114.1, 112.3, 64.2, 37.5, 32.769, 20.2; HRMS (ESI-TOF) [M+NH4]^+ calculated for C29H24F7N2O4: 597.1613, found: 597.1613.

(E)-2-(2-(4-(1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)but-1-en-1-yl)-6-methyl phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (5p)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 3/1). The desired product was obtained as a white solid (33.5 mg, 56% yield). Linear/branched ratio = 8.7/1; 1^1H NMR (400 MHz, CDCl3) δ 8.06-8.01 (m, 1H), 7.91-7.80 (m, 3H), 7.34 (d, J = 8.0 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.1 Hz, 1H), 6.92 (s, 1H), 6.77 (d, J = 15.6 Hz, 1H), 6.12 (dt, J = 15.4, 7.1 Hz, 1H), 3.97 (t, J = 6.8 Hz, 2H), 3.86 (s, 2H), 2.81 (qd, J = 7.0, 1.4 Hz, 2H), 2.36 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 168.3, 159.0, 137.9, 137.8, 137.5, 134.8, 134.4, 130.5, 130.4, 129.3, 128.4, 127.2, 125.7, 125.2, 120.9, 38.8, 37.4, 32.2, 20.2; HRMS (ESI-TOF) [M+NH4]^+ calculated for C27H23F7N3O4S: 618.1292, found: 618.1288.

(E)-5-(3-methyl-2-(2-oxo-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)ethyl)phenyl)pent-4-en-1-yl ferrocene benzoate (5q)
Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 4/1). The desired product was obtained as a yellow solid (26.5 mg, 41% yield). Linear/branched ratio = 5.6/1; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.35 (d, J = 7.5 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 7.3 Hz, 1H), 7.12 (s, 1H), 6.70 (d, J = 15.5 Hz, 1H), 6.14 (dt, J = 15.4, 6.9 Hz, 1H), 4.78 (t, J = 1.9 Hz, 2H), 4.39 (t, J = 1.9 Hz, 2H), 4.30 (t, J = 6.5 Hz, 2H), 4.19 (s, 5H), 3.95 (s, 2H), 2.44-2.37 (m, 2H), 2.40 (s, 3H), 1.96-1.88 (m, 2H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 172.1, 168.5, 138.4, 137.8, 134.2, 129.9, 129.2, 128.3, 128.2, 125.5, 71.4, 71.1, 70.0, 69.7, 63.2, 37.4, 29.5, 28.3, 20.2; HRMS (ESI-TOF) [M+NH\textsubscript{4}]\textsuperscript{+} calculated for C\textsubscript{32}H\textsubscript{30}F\textsubscript{7}FeN\textsubscript{2}O\textsubscript{3}: 679.1489, found: 679.1485.

\textbf{(E)-2-(2-(5-(indolin-1-yl)-5-oxopent-1-en-1-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (5r)}

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\text{Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 2/1). The desired product was obtained as a white solid (20.6 mg, 37% yield). Linear/branched ratio = 9.6/1; } \textsuperscript{1}H \text{ NMR (400 MHz, CDCl}_3) \text{ δ 7.97 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.21 (d, J = 6.8 Hz, 1H), 7.18-7.10 (m, 3H), 7.03 (t, J = 7.7 Hz, 1H), 6.98-6.90 (m, 2H), 6.10-6.00 (m, 1H), 4.02 (t, J = 8.3 Hz, 2H), 3.91 (s, 2H), 3.16 (t, J = 8.3 Hz, 2H), 2.74-2.63 (m, 4H), 2.50 (s, 3H); } \textsuperscript{13}C \text{ NMR}
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(100 MHz, CDCl₃) δ 171.2, 168.8, 142.1, 138.4, 138.1, 133.8, 130.8, 130.2, 130.0, 127.7, 127.1, 125.8, 124.7, 116.3, 47.7, 37.3, 34.3, 27.8, 27.7, 20.5;
HRMS (ESI-TOF) [M+1]^+ calculated for C₂⁹H₂₄F₇N₂O₂: 565.1721, found: 565.1713.

(E)-2-(2-methyl-6-(4-((2-oxo-2H-chromen-7-yl)oxy)but-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (5s)

Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 4/1). The desired product was obtained as a white solid (27.0 mg, 47% yield). Single isomer was obtained; ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, J = 9.6 Hz, 1H), 7.35 (d, J = 7.4 Hz, 1H), 7.29 (d, J = 9.2 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 7.3 Hz, 1H), 6.85 (s, 1H), 6.82-6.71 (m, 3H), 7.23 (d, J = 9.9 Hz, 1H), 6.17 (dd, J = 15.4, 7.6 Hz, 1H), 4.12 (t, J = 6.0 Hz, 2H), 3.93 (s, 2H), 2.75 (dd, J = 12.2, 6.0 Hz, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.3, 161.9, 161.1, 155.8, 143.3, 138.2, 137.8, 131.1, 130.3, 130.2, 129.2, 128.6, 128.5, 125.8, 113.2, 112.8, 112.5, 101.2, 67.6, 37.6, 32.9, 20.2; HRMS (ESI-TOF) [M+NH₄]^+ calculated for C₂⁹H₂₄F₇N₂O₄: 597.1619, found: 597.1615.

2-(2-methyl-6-((E)-4-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)but-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (5t)
Substrate 1 was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 3/1). The desired product was obtained as a white solid (31.8 mg, 56% yield). Linear/branched ratio = 8.5/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 (d, $J = 7.3$ Hz, 1H), 7.24 (s, 1H), 7.21 (d, $J = 7.5$ Hz, 1H), 7.18 (d, $J = 7.1$ Hz, 1H), 7.09 (d, $J = 8.5$ Hz, 1H), 6.87 (d, $J = 15.5$ Hz, 1H), 6.60 (dd, $J = 8.6, 2.7$ Hz, 1H), 6.54 (d, $J = 2.6$ Hz, 1H), 6.24-6.16 (m, 1H), 4.04 (t, $J = 5.9$ Hz, 2H), 3.93 (s, 2H), 2.85-2.79 (m, 2H), 2.72 (dd, $J = 12.1, 6.0$ Hz, 2H), 2.54 (s, 1H), 2.34 (d, $J = 4.5$ Hz, 1H), 2.16 (t, $J = 8.9$ Hz, 2H), 2.12-1.91 (m, 4H), 1.68-1.57 (m, 2H), 1.56-1.35 (m, 6H), 0.90 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 221.0, 168.3, 156.5, 138.3, 137.9, 137.8, 132.5, 132.4, 130.6, 130.2, 129.4, 128.2, 126.2, 125.9, 114.5, 111.6, 66.8, 50.4, 48.0, 43.9, 38.2, 37.6, 35.9, 33.4, 31.5, 29.5, 26.4, 25.7, 21.6, 20.3, 13.7; HRMS (ESI-TOF) [M+NH$_4^+$] calculated for C$_{38}$H$_{40}$F$_7$N$_2$O$_5$: 705.2922, found: 705.2912.

(\textit{E})-2-(2-fluoro-6-(4-methylpent-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7a)

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\begin{array}{c}
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\text{CF}_3 \\
\text{Me} \\
\text{Me} \\
7a
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Substrate 6a was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (32.5 mg, 72% yield). Linear/branched ratio = 6.0/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 (d, $J = 8.0$ Hz, 1H), 7.30 (d, $J = 7.2$ Hz, 1H), 7.05 (t, $J = 8.8$ Hz, 1H), 6.93 (s, 1H), 6.56 (d, $J = 15.6$ Hz, 1H), 6.22 (dt, $J = 15.3, 7.7$ Hz, 1H), 3.94 (s, 2H), 2.15 (d, $J = 7.1$ Hz, 2H), 1.73 (dt, $J = 20.7, 7.1$ Hz, 1H), 0.94 (d, $J = 6.7$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.5, 161.2 (d, $J = 243.6$ Hz), 140.4 (d, $J = 11.2$ Hz), 135.9, 129.6 (d, $J = 9.4$ Hz), 126.2 (d, $J = 30.8$ Hz), 122.6 (d, $J = 29.4$ Hz), 117.6 (d, $J = 15.0$ Hz), 113.9 (d, $J = 22.7$ Hz), 42.5, 33.3 (d, $J = 5.1$ Hz), 28.4, 22.3; HRMS (ESI-TOF) [M+NH$_4^+$] calculated for C$_{21}$H$_{21}$F$_8$N$_2$O: 469.1521, found: 469.1521.

(\textit{E})-2-(2-chloro-6-(4-methylpent-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7a)
Substrate 6b was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (34.8 mg, 74% yield). Linear/branched ratio = 5.5/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (dd, $J = 7.7, 1.0$ Hz, 1H), 7.37 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.27 (t, $J = 7.6$ Hz, 1H), 6.92 (s, 1H), 6.61 (d, $J = 15.5$ Hz, 1H), 6.16 (dt, $J = 15.3, 7.7$ Hz, 1H), 4.09 (s, 2H), 2.14 (td, $J = 7.1, 1.4$ Hz, 2H), 1.73 (dt, $J = 13.5, 6.8$ Hz, 1H), 0.94 (d, $J = 6.7$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.3, 140.9, 136.1, 135.2, 129.4, 128.4, 128.4, 127.2, 126.0, 42.5, 38.1, 28.4, 22.3; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{21}$H$_{21}$ClF$_7$N$_2$O: 485.1225, found: 485.1225.

Substrate 6c was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (34.7 mg, 69% yield). Linear/branched ratio = 6.3/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J = 8.1$ Hz, 1H), 7.64 (d, $J = 7.7$ Hz, 1H), 7.44 (t, $J = 7.9$ Hz, 1H), 6.72 (s, 1H), 6.59 (d, $J = 15.7$ Hz, 1H), 6.20 (dt, $J = 14.9, 7.3$ Hz, 1H), 4.07 (s, 2H), 2.15 (t, $J = 6.8$ Hz, 2H), 1.74 (dt, $J = 13.1, 6.5$ Hz, 1H), 0.94 (d, $J = 6.6$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.3, 141.2, 140.8, 136.8, 131.1, 128.5, 128.1, 126.5, 125.1 (q, $J =$
Substrate 6d was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 5/1). The desired product was obtained as a white solid (30.6 mg, 66% yield). Linear/branched ratio = 5.8/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66 (s, 1H), 7.27 (t, $J = 7.8$ Hz, 1H), 7.14 (d, $J = 7.8$ Hz, 1H), 6.87 (d, $J = 8.2$ Hz, 1H), 6.69 (d, $J = 15.4$ Hz, 1H), 6.14 (dt, $J = 15.2, 7.8$ Hz, 1H), 3.94 (s, 3H), 3.91 (s, 2H), 2.14 (t, $J = 7.1$ Hz, 2H), 1.73 (dt, $J = 13.1, 6.5$ Hz, 1H), 0.94 (d, $J = 6.6$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.9, 156.9, 139.9, 134.8, 131.1, 128.8, 127.5, 119.8, 119.2, 109.0, 55.8, 42.5, 34.6, 28.5, 22.3; HRMS (ESI-TOF) [M+1]$^+$ calculated for C$_{22}$H$_{21}$F$_7$N$_2$O: 464.1455, found: 464.1453.

Substrate 6e was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 5/1). The desired product was obtained as a white solid (28.1 mg, 57% yield). Linear/branched ratio = 4.6/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 (d, $J = 7.7$ Hz, 1H), 7.37 (s, 1H), 7.35 (t, $J = 7.9$ Hz, 1H), 7.00 (d, $J = 8.0$ Hz, 1H), 6.55 (d, $J = 15.4$, 1H), 6.22 (dt, $J = 15.2, 7.7$ Hz, 1H), 3.80 (s, 2H), 2.40 (s, 2H),
2.15 (td, \( J = 7.3, 1.2 \) Hz, 2H), 1.74 (dt, \( J = 13.2, 6.7 \) Hz, 1H), 0.94 (d, \( J = 6.7 \) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 171.0, 168.2, 149.4, 140.5, 135.7, 129.3, 126.4, 124.8, 123.1, 121.1, 42.5, 35.1, 28.4, 22.2, 20.8; \( \text{HRMS (ESI-TOF)} \) [M+NH\(_4\)]\(^+\) calculated for C\(_{23}\)H\(_{24}\)F\(_7\)N\(_2\)O\(_3\): 509.1670, found: 509.1663.

\( (E)\)-2-(5-methyl-2-(4-methylpent-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7f)

Substrate 6f was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (28.7 mg, 64% yield). Linear/branched ratio = 4.8/1; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.45 (d, \( J = 7.9 \) Hz, 1H), 7.15 (d, \( J = 8.4 \) Hz, 1H), 7.10 (s, 1H), 6.81 (s, 1H), 6.49 (d, \( J = 15.5 \) Hz, 1H), 6.16 (dt, \( J = 15.4, 7.8 \) Hz, 1H), 3.85 (s, 2H), 2.36 (s, 3H), 2.11 (td, \( J = 7.2, 1.3 \) Hz, 2H), 1.71 (dt, \( J = 13.4, 6.7 \) Hz, 1H), 0.92 (d, \( J = 6.7 \) Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 168.7, 137.8, 135.1, 133.7, 131.6, 129.9, 129.6, 127.0, 126.6, 42.5, 41.7, 28.5, 22.3, 21.0; \( \text{HRMS (ESI-TOF)} \) [M+NH\(_4\)]\(^+\) calculated for C\(_{22}\)H\(_{24}\)F\(_7\)N\(_2\)O: 465.1771, found: 465.1770.

\( (E)\)-2-(2-(4-methylpent-1-en-1-yl)-5-(trifluoromethyl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7g)

Substrate 6g was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (24.1 mg, 48% yield). Linear/branched ratio = 4.7/1; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \)
7.65 (d, J = 8.2 Hz, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.55 (s, 1H), 6.80 (s, 1H), 6.55 (d, J = 15.4 Hz, 1H), 6.31 (dt, J = 15.5, 7.8 Hz, 1H), 3.94 (s, 2H), 2.16 (s, 3H), 2.16 (td, J = 7.2, 1.1 Hz, 2H), 1.74 (dt, J = 13.3, 6.6 Hz, 1H), 0.94 (d, J = 6.6 Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) δ 167.6, 143.1, 141.6, 137.1, 130.6, 129.8, 127.6 (q, J = 4.2 Hz), 127.4, 126.0, 125.5 (q, J = 3.7 Hz), 42.6, 41.5, 28.4, 22.3; HRMS (ESI-TOF) [M+NH\textsubscript{4}]\textsuperscript{+} calculated for C\textsubscript{22}H\textsubscript{21}F\textsubscript{10}N\textsubscript{2}O: 519.1489, found: 519.1488.

\((E)-2-(5\text{-}chloro\text{-}2\text{-}(4\text{-}methylpent\text{-}1\text{-}en\text{-}1\text{-}yl)phenyl)\text{-}N\text{-}(2,3,5,6\text{-}tetrafluoro\text{-}4\text{-}(trifluoromethyl)phenyl)acetamide\) (7h)

Substrate 6h was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (29.9 mg, 64% yield). Linear/branched ratio = 4.9/1; \(^{1}\)H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.48 (d, J = 8.2 Hz, 1H), 7.31 (dd, J = 11.2, 2.1 Hz, 1H), 7.30 (s, 1H), 6.77 (s, 1H), 6.47 (d, J = 15.5 Hz, 1H), 6.20 (dt, J = 15.5, 8.0 Hz, 1H), 3.85 (s, 2H), 2.12 (td, J = 7.2, 1.3 Hz, 2H), 1.72 (dt, J = 13.3, 6.7 Hz, 1H), 0.93 (d, J = 6.7 Hz, 6H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}) δ 167.7, 136.6, 135.3, 133.3, 131.7, 130.7, 128.9, 128.4, 125.9, 42.5, 41.4, 28.4, 22.3; HRMS (ESI-TOF) [M+NH\textsubscript{4}]\textsuperscript{+} calculated for C\textsubscript{21}H\textsubscript{21}ClF\textsubscript{7}N\textsubscript{2}O: 485.1225, found: 485.1225.

\((E)-2-(4\text{-}methyl\text{-}2\text{-}(4\text{-}methylpent\text{-}1\text{-}en\text{-}1\text{-}yl)phenyl)\text{-}N\text{-}(2,3,5,6\text{-}tetrafluoro\text{-}4\text{-}(trifluoromethyl)phenyl)acetamide\) (7i)
Substrate 6i was olefinated by two paralleled runs following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a white solid (54.1 mg, 74% yield). Mono/di = 2.9/1, for mono: linear/branched ratio = 3.0/1. The spectra of diolefinated product is very messy and is not given; $^1$H NMR (400 MHz, CDCl₃) δ 7.36 (s, 1H), 7.18 (d, $J$ = 7.7 Hz, 1H), 7.10 (d, $J$ = 7.7 Hz, 1H), 6.80 (s, 1H), 6.51 (d, $J$ = 15.5 Hz, 1H), 6.19 (dt, $J$ = 15.5, 7.8 Hz, 1H), 3.85 (s, 2H), 2.12 (td, $J$ = 7.2, 1.3 Hz, 2H), 1.72 (dt, $J$ = 12.9, 6.4 Hz, 1H), 0.93 (d, $J$ = 6.6 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl₃) δ 168.9, 138.6, 137.8, 134.3, 130.9, 128.7, 127.7, 127.2, 126.9, 42.6, 41.3, 28.5, 22.3, 21.2; HRMS (ESI-TOF) [M+NH₄]$^+$ calculated for C₂₂H₂₅F₇N₂O: 465.1771, found: 465.1768.

(E)-2-(4-(tert-butyl)-2-(4-methylpent-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7j)

Substrate 6j was olefinated by two paralleled runs following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a white solid (61.6 mg, 71% yield). Mono/di = 2.7/1, for mono: linear/branched ratio = 4.6/1. The spectra of diolefinated product is very messy and is not given; $^1$H NMR (400 MHz, CDCl₃) δ 7.53 (s, 1H), 7.31 (d, $J$ = 8.0 Hz, 1H), 7.21 (d, $J$ = 7.9 Hz, 1H), 6.79 (s, 1H), 6.53 (d, $J$ = 15.4 Hz, 1H), 6.17 (dt, $J$ = 15.5, 7.9 Hz, 1H), 3.85 (s, 2H), 2.13 (t, $J$ = 7.0 Hz, 2H), 1.73 (dt, $J$ = 13.4, 6.8 Hz, 1H), 1.34 (s, 9H), 0.93 (d, $J$ = 6.6 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl₃) δ 168.9, 151.8, 137.5, 134.1, 130.7, 127.5, 127.2, 125.1, 124.0, 42.6, 41.3, 34.7, 31.3, 28.5, 22.3; HRMS (ESI-TOF) [M+NH₄]$^+$ calculated for C₂₃H₂₆F₈N₂O: 507.2241, found: 507.2232.

(E)-2-(4-methoxy-2-(4-methylpent-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7k)
Substrate 6k was olefinated by two paralleled runs following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a white solid (63.9 mg, 67% yield). Mono/di = 3.2/1, for mono: linear/branched ratio = 4.0/1. The spectra of diolefinated product is very messy and is not given; $^1$H NMR (400 MHz, CDC$_3$) $\delta$ 7.21 (d, $J = 8.4$ Hz, 1H), 7.07 (d, $J = 2.5$ Hz, 1H), 6.84 (dd, $J = 8.4$, 2.6 Hz, 1H), 6.79 (s, 1H), 6.49 (d, $J = 15.6$ Hz, 1H), 6.20 (dt, $J = 15.5$, 8.4 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 2H), 2.12 (td, $J = 7.1$, 1.3 Hz, 2H), 1.72 (dt, $J = 13.3$, 6.6 Hz, 1H), 1.34 (s, 9H), 0.93 (d, $J = 6.6$ Hz, 6H); $^{13}$C NMR (100 MHz, CDC$_3$) $\delta$ 169.1, 159.8, 139.3, 134.7, 132.1, 126.9, 122.4, 113.3, 112.4, 55.3, 42.5, 40.9, 28.4, 22.3; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{22}$H$_{24}$F$_7$N$_2$O$_2$: 481.1721, found: 481.1716.

(E)-2-(2-(4-methylpent-1-en-1-yl)-4-(trifluoromethyl)phenyl)N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7l)

Substrate 6l was olefinated by two paralleled runs following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a white solid (64.1 mg, 62% yield). Mono/di = 5.2/1, for mono: linear/branched ratio = 5.2/1. The spectra of diolefinated product is very messy and is not given; $^1$H NMR (400 MHz, CDC$_3$) $\delta$ 7.77 (s, 1H), 7.53 (d, $J = 7.9$ Hz, 1H), 7.42 (d, $J = 8.0$ Hz, 1H), 6.74 (s, 1H), 6.56 (d, $J = 15.5$ Hz, 1H), 6.28 (dt, $J = 15.5$, 8.4 Hz, 1H), 3.94 (s, 2H), 2.16 (td, $J = 7.1$, 0.9 Hz, 2H), 1.76 (dt, $J = 13.6$, 6.7 Hz, 1H), 0.95
(d, J = 6.7 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.5, 138.8, 136.6, 133.8, 131.3, 131.2, 130.9, 125.9, 124.3 (q, J = 3.7 Hz), 123.9 (q, J = 3.8 Hz), 42.6, 41.4, 28.4, 22.3; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{22}$H$_{21}$F$_{10}$N$_2$O: 519.1489, found: 519.1488.

$(E)$-2-(2-(4-methylpent-1-en-1-yl)naphthalen-1-yl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7m)

Substrate 6m was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a white solid (32.7 mg, 68% yield). Linear/branched ratio = 5.9/1; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (s, 1H), 7.89-7.82 (m, 2H), 7.67 (d, J = 8.6 Hz, 1H), 7.60 (t, J = 8.4 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 15.4 Hz, 1H), 6.77 (s, 1H), 6.33 (dt, J = 15.4, 7.3 Hz, 1H), 4.37 (s, 2H), 2.23 (td, J = 7.2, 1.3 Hz, 2H), 1.80 (dt, J = 13.2, 6.6 Hz, 1H), 0.98 (d, J = 6.7 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.7, 136.1, 136.0, 133.0, 132.3, 129.1, 128.8, 127.7, 127.6, 126.1, 125.1, 124.9, 123.3, 42.8, 36.7, 28.5, 22.3; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{25}$H$_{24}$F$_7$N$_2$O: 501.1771, found: 501.1769.

$(E)$-2-(3-(4-methylpent-1-en-1-yl)naphthalen-2-yl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7n)

Substrate 6n was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a
white solid (28.0 mg, 58% yield). Linear/branched ratio = 4.9/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (s, 1H), 7.86-7.81 (m, 3H), 7.79 (s, 1H), 7.53-7.48 (m, 2H), 6.83 (s, 1H), 6.63 (d, $J$ = 15.4 Hz, 1H), 6.32 (dt, $J$ = 15.0, 7.3 Hz, 1H), 4.04 (s, 2H), 2.17 (td, $J$ = 7.2, 1.2 Hz, 2H), 1.77 (dt, $J$ = 13.4, 6.8 Hz, 1H), 0.96 (d, $J$ = 6.7 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.6, 135.9, 135.1, 133.4, 132.6, 130.0, 129.1, 127.7, 127.3, 127.0, 126.8, 126.4, 126.0, 42.6, 42.2, 28.5, 22.3; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{25}$H$_{24}$F$_7$N$_2$O: 501.1771, found: 501.1768.

(E)-2-(2,4-dimethyl-6-(4-methylpent-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7o)

Substrate 6o was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a white solid (33.8 mg, 73% yield). Linear/branched ratio = 4.1/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.18 (s, 1H), 7.00 (s, 1H), 6.79 (s, 1H), 7.56 (d, $J$ = 15.4 Hz, 1H), 6.12 (dt, $J$ = 15.4, 7.6 Hz, 1H), 3.88 (s, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 2.13 (td, $J$ = 7.2, 1.3 Hz, 2H), 1.73 (dt, $J$ = 13.4, 6.7 Hz, 1H), 0.94 (d, $J$ = 6.6 Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 168.8, 138.6, 138.2, 137.5, 134.7, 130.7, 127.9, 126.1, 126.0, 42.6, 37.2, 28.5, 22.3, 21.1, 20.1; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{23}$H$_{26}$F$_7$N$_2$O: 479.1928, found: 479.1924.

(E)-2-(2,4-difluoro-6-(4-methylpent-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7p)
Substrate 6p was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a white solid (27.8 mg, 59% yield). Linear/branched ratio = 3.8/1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.08-7.04 (m, 1H), 6.92 (s, 1H), 6.82-6.76 (m, 1H), 6.54 (dd, $J = 15.5$, 1.2 Hz, 1H), 6.23 (dt, $J = 15.4$, 7.2 Hz, 1H), 3.88 (d, $J = 1.7$ Hz, 2H), 2.14 (td, $J = 7.1$, 1.4 Hz, 2H), 1.80-1.68 (m, 1H), 0.94 (d, $J = 6.7$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.3, 162.5 (dd, $J = 247.4$, 13.9 Hz), 161.3 (dd, $J = 245.3$, 13.0 Hz), 141.6 (dd, $J = 10.3$, 5.7 Hz), 136.9, 125.6, 113.7 (dd, $J = 15.2$, 3.7 Hz), 109.4 (dd, $J = 21.8$, 3.2 Hz), 102.4 (t, $J = 26.5$ Hz), 42.4, 32.8 (d, $J = 4.0$ Hz), 28.3, 22.3; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{21}$H$_{20}$F$_6$N$_2$O: 487.1426, found: 487.1421.

\[(E)-2-(2,4\text{-dichloro}-6-(4\text{-methylpent-1-en-1-yl})\text{phenyl})-N-(2,3,5,6\text{-tetrafluoro}-4-(\text{ trifluoromethyl})\text{phenyl})\text{acetamide (7q)}\]

Substrate 6q was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 5/1). The desired olefination product was obtained as a white solid (34.2 mg, 68% yield). Linear/branched ratio = 5.3/1; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, $J = 2.1$ Hz, 1H), 7.38 (d, $J = 2.1$ Hz, 1H), 6.92 (s, 1H), 6.56 (d, $J = 15.5$ Hz, 1H), 6.18 (dt, $J = 15.3$, 7.4 Hz, 1H), 4.03 (s, 2H), 2.14 (td, $J = 7.1$, 1.4 Hz, 2H), 1.75 (dt, $J = 13.5$, 6.7 Hz, 1H), 0.94 (d, $J = 6.7$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.9, 142.0, 137.4, 135.8, 134.6, 127.9, 127.0, 126.3, 126.0, 42.5, 37.6, 28.4, 22.3; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{21}$H$_{20}$Cl$_3$F$_7$N$_2$O: 519.0835, found: 519.0834.

\[(E)-2-(2,3\text{-dichloro}-6-(4\text{-methylpent-1-en-1-yl})\text{phenyl})-N-(2,3,5,6\text{-tetrafluoro}-4-(\text{ trifluoromethyl})\text{phenyl})\text{acetamide (7r)}\]
Substrate 6r was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 5/1). The desired olefination product was obtained as a white solid (41.8 mg, 83% yield). Linear/branched ratio = 4.6/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 (d, $J = 8.5$ Hz, 1H), 7.36 (d, $J = 8.5$ Hz, 1H), 6.92 (s, 1H), 6.56 (d, $J = 15.4$ Hz, 1H), 6.15 (dt, $J = 15.4$, 7.6 Hz, 1H), 4.12 (s, 2H), 2.14 (td, $J = 7.2$, 1.2 Hz, 2H), 1.73 (dt, $J = 13.6$, 6.6 Hz, 1H), 0.94 (d, $J = 6.7$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.8, 139.1, 136.6, 133.4, 132.0, 130.4, 130.0, 126.7, 126.3, 42.5, 38.9, 28.438, 22.3; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{21}$H$_{20}$Cl$_2$F$_7$N$_2$O: 519.0835, found: 519.0832.

(E)-2-(2-(4-methylpent-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)propanamide (7s)

Substrate 6s was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a white solid (28.2 mg, 63% yield). Linear/branched ratio = 4.9/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52-7.47 (m, 1H), 7.34-7.28 (m, 3H), 6.73 (s, 1H), 6.63 (d, $J = 15.5$ Hz, 1H), 6.15 (dt, $J = 15.4$, 7.6 Hz, 1H), 4.13 (q, $J = 7.1$ Hz, 1H), 2.14 (t, $J = 7.0$ Hz, 2H), 1.74 (dt, $J = 13.3$, 6.7 Hz, 1H), 1.62 (d, $J = 7.1$ Hz, 3H), 0.95 (d, $J = 6.6$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.2, 137.5, 136.3, 134.8, 128.2, 128.1, 127.5, 127.3, 127.3, 43.6, 42.6, 28.5, 22.3, 22.3, 17.4; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{21}$H$_{24}$F$_{7}$N$_2$O: 465.1771, found: 465.1770.
(E)-2-(2-(4-methylpent-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)butanamide (7t)

Substrate 6t was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a white solid (25.8 mg, 56% yield). Linear/branched ratio = 5.3/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50-7.47 (m, 1H), 7.32-7.28 (m, 3H), 6.75 (s, 1H), 6.65 (d, $J = 15.6$ Hz, 1H), 6.13 (dt, $J = 15.4$, 7.6 Hz, 1H), 3.89 (dd, $J = 7.9$, 6.8 Hz, 1H), 2.33 (dt, $J = 14.1$, 7.2 Hz, 1H), 2.15 (d, $J = 7.0$ Hz, 2H), 1.97-1.86 (m, 1H), 1.74 (dt, $J = 13.4$, 6.7 Hz, 1H), 0.950 (t, $J = 7.4$ Hz, 3H), 0.949 (d, $J = 6.6$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.5, 137.9, 135.0, 134.8, 128.1, 128.0, 127.6, 127.6, 127.5, 50.7, 42.6, 28.5, 25.1, 22.4, 22.3, 12.2; HRMS (ESI-TOF) [M+NH$_4$]$^+$ calculated for C$_{23}$H$_{28}$F$_7$N$_2$O: 479.1928, found: 479.1925.

(7u)

$(E)$-1-(2-(4-methylpent-1-en-1-yl)phenyl)-2-oxo-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)ethyl acetate (7u)

Substrate 6u was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 5/1). The desired olefination product was obtained as a white solid (30.5 mg, 62% yield). Linear/branched ratio = 5.2/1; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.50 (d, $J = 6.6$ Hz, 1H), 7.46 (dd, $J = 7.6$, 1.4 Hz, 1H), 7.41-7.35 (m, 1H), 7.33-7.28 (m, 1H), 6.75 (d, $J = 15.5$ Hz, 1H), 6.58 (s, 1H), 6.18 (dt, $J = 15.4$, 7.8 Hz, 1H), 2.23 (s, 3H), 2.15 (td, $J = 7.1$, 1.4 Hz, 2H), 1.74 (dt, $J = 13.3$, 6.7 Hz, 1H), 0.95 (d, $J = 6.7$ Hz, 3H), 0.94 (d, $J = 6.7$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.4,
166.4, 138.1, 135.5, 130.7, 129.9, 128.3, 127.6, 127.6, 127.0, 72.7, 42.5, 29.7, 28.5, 22.3, 22.3, 20.8; **HRMS (ESI-TOF)** [M+NH₄]⁺ calculated for C₂₃H₂₄F₇N₂O₃: 509.1670, found: 509.1663.

**(E)-2-(4-isobutyl-2-(oct-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)propanamide (9a)**

![Diagram of 9a](image)

Substrate **8a** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a white solid (37.2 mg, 70% yield). Linear/branched ratio = 2.5/1; **¹H NMR (400 MHz, CDCl₃)** δ 7.26 (s, 1H), 7.22 (d, J = 7.9 Hz, 1H), 7.08 (d, J = 7.9 Hz, 1H), 6.76 (s, 1H), 6.61 (d, J = 15.4 Hz, 1H), 6.14 (dt, J = 15.4, 7.8 Hz, 1H), 4.09 (q, J = 6.9 Hz, 1H), 2.48 (d, J = 7.2 Hz, 2H), 2.23 (dd, J = 14.6, 7.2 Hz, 2H), 1.88 (dt, J = 13.6, 6.7 Hz, 1H), 1.61 (d, J = 7.1 Hz, 3H), 1.49-1.42 (m, 2H), 1.35-1.27 (m, 6H), 0.92 (d, J = 6.7 Hz, 6H), 0.88 (t, J = 6.8 Hz, 3H); **¹³C NMR (100 MHz, CDCl₃)** δ 172.4, 141.8, 137.2, 135.7, 133.6, 128.9, 128.1, 127.0, 126.4, 43.0, 43.4, 33.4, 31.7, 30.1, 29.3, 28.9, 22.6, 22.4, 17.3, 14.0; **HRMS (ESI-TOF)** [M+NH₄]⁺ calculated for C₂₈H₃₆F₇N₂O: 549.2710, found: 549.2707.

**(E)-2-(6-methoxy-3-(oct-1-en-1-yl)naphthalen-2-yl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)propanamide (9b)**

![Diagram of 9b](image)

Substrate **8b** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 5/1). The desired olefination product was obtained as a white solid (35.1 mg, 63% yield). Linear/branched ratio = 2.9/1; **¹H NMR (400 MHz, CDCl₃)** δ 7.83 (s, 1H), 7.72 (s, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H),
7.13 (s, 1H), 6.77 (s, 1H), 6.70 (d, J = 15.3 Hz, 1H), 6.26 (dt, J = 15.4, 7.8 Hz, 1H), 4.19 (q, J = 7.2 Hz, 1H), 3.93 (s, 3H), 2.27 (q, J = 7.0 Hz, 2H), 1.73 (d, J = 7.1 Hz, 3H), 1.49-1.45 (m, 2H), 1.39-1.25 (m, 6H), 0.88 (t, J = 6.4 Hz, 3H); \(^{13}\text{C NMR (100 MHz, CDCl}_3\)) δ 172.4, 158.3, 136.4, 136.4, 134.3, 132.6, 129.1, 128.3, 126.6, 126.4, 125.3, 119.2, 105.4, 55.4, 44.3, 33.4, 31.7, 29.3, 29.0, 22.6, 17.6, 14.1; HRMS (ESI-TOF) [M+NH\(_4\)]\(^+\) calculated for C\(_{29}\)H\(_{32}\)F\(_7\)N\(_2\)O\(_2\): 573.2347, found: 573.2342.

\((E)\)-2-(5-benzoyl-2-(oct-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)propanamide (9c)

Substrate 8c was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 5/1). The desired olefination product was obtained as a white solid (32.4 mg, 56% yield). Linear/branched ratio = 3.8/1; \(^1\text{H NMR (400 MHz, CDCl}_3\)) δ 7.82 (s, 1H), 7.78 (d, J = 7.1 Hz, 2H), 7.72 (dd, J = 8.1, 1.5 Hz, 1H), 7.63-7.58 (m, 2H), 7.49 (t, J = 7.6 Hz, 2H), 6.83 (s, 1H), 6.68 (d, J = 15.4 Hz, 1H), 6.33 (dt, J = 15.4, 7.7 Hz, 1H), 4.17 (q, J = 7.3 Hz, 1H), 2.28 (q, J = 7.1 Hz, 2H), 1.66 (d, J = 7.1 Hz, 3H), 1.50-1.43 (m, 2H), 1.37-1.29 (m, 6H), 0.89 (t, J = 6.6 Hz, 3H); \(^{13}\text{C NMR (100 MHz, CDCl}_3\)) δ 195.8, 171.5, 141.7, 138.5, 137.4, 136.8, 136.4, 132.6, 120.0, 129.9, 129.4, 128.4, 127.2, 125.6, 44.1, 33.5, 31.7, 29.1, 28.9, 22.6, 17.4, 14.0; HRMS (ESI-TOF) [M+NH\(_4\)]\(^+\) calculated for C\(_{31}\)H\(_{32}\)F\(_7\)N\(_2\)O\(_2\): 597.2347, found: 597.2343.

2-(2-Methyl-6-octylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (10)

![Diagram of 2-(2-Methyl-6-octylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (10)]
To two paralleled oven-dried round-bottom flask (50 mL) was added Pd/C (10 wt. % loading on carbon, 5.0 mg), amide 3a (33.3 mg, 0.07 mmol) and EtOAc (2 mL). The reaction flask was evacuated and refilled with H₂ (3 times, balloon). After stirring at room temperature for 24 hours, the reaction mixture was filtered through a small pad of Celite. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel using an eluent of hexane/EtOAc (9/1) to give the desired product as colorless oil (66.4 mg, 99%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.22 (d, \(J = 7.5\) Hz, 1H), 7.18-7.12 (m, 2H), 6.74 (s, 1H), 3.89 (s, 2H), 2.65 (t, \(J = 7.8\) Hz, 1H), 2.38 (s, 3H), 1.63-1.56 (m, 2H), 1.39-1.35 (m, 2H), 1.32-1.22 (m, 8H), 0.88 (t, \(J = 6.7\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.9, 142.3, 137.8, 129.9, 129.0, 128.4, 128.2, 37.2, 33.8, 31.8, 31.2, 29.7, 29.4, 29.2, 22.6, 20.2, 14.1; HRMS (ESI-TOF) [M+NH\(_4\)]\(^+\) calculated for C\(_{24}\)H\(_{30}\)F\(_7\)N\(_2\)O: 495.2241, found: 495.2238.

\((E)\)-methyl 2-(2-(3,3-dimethylbut-1-en-1-yl)-6-methylphenyl)acetate (11)

![Chemical Structure](image)

To a solution of 3i (35.8 mg, 0.08 mmol) in MeOH (4 mL), BF\(_3\)•Et\(_2\)O (68.1 mg, 0.48 mmol) was added via syringe. The mixture was heated to 110 °C for 24 hours. After cooling to room temperature, triethylamine (101.0 mg, 1.0 mmol) was added via syringe. The reaction mixture was filtered through a small pad of Celite. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel using an eluent of hexane/EtOAc (19/1) to give the desired product as colorless oil (20.4 mg, 83%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.25 (d, \(J = 7.1\) Hz, 1H), 7.13 (t, \(J = 7.6\) Hz, 1H), 7.07 (d, \(J = 7.5\) Hz, 1H), 6.54 (d, \(J = 15.8\) Hz, 1H), 6.03 (d, \(J = 15.9\) Hz, 1H), 3.73 (s, 2H), 3.67 (s, 3H), 2.34 (s, 3H), 1.12 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 171.9, 145.2, 138.8, 137.1, 130.2, 128.9, 127.2,
124.5, 122.8, 51.9, 35.2, 33.6, 29.6, 20.3; **HRMS (ESI-TOF) [M+NH₄]⁺** calculated for C₁₆H₂₆NO₂: 264.1958, found: 264.1955.

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6. $^1$H and $^{13}$C NMR Spectra of Products
OTBDPS

4g
$\text{OPOPh}_2$

4i

\begin{figure}
\centering
\includegraphics[width=\textwidth]{spectrum.png}
\caption{NMR spectrum of compound 4i.}
\end{figure}
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