

Supporting Information

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

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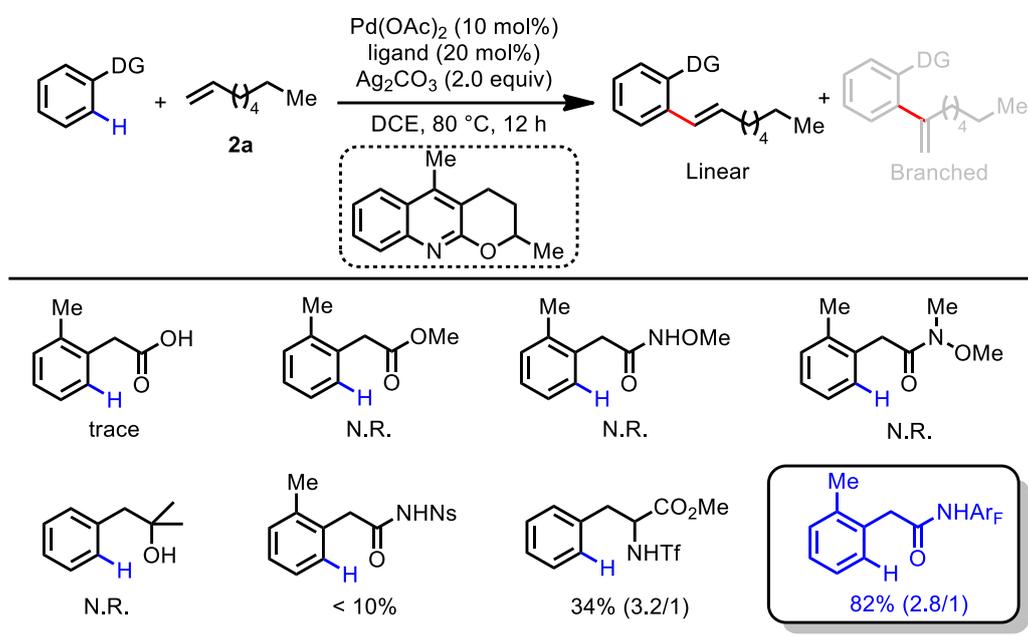
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1. General Information

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. ^1H -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 ^1H 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.

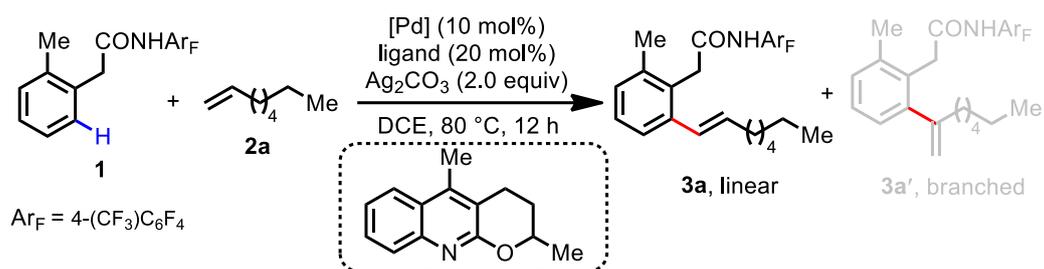
2. Optimization of Conditions.

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



^aReaction conditions : Substrates (0.1 mmol), **2a** (3.0 equiv), Pd(OAc)₂ (10 mol%), ligand (20 mol%), Ag₂CO₃ (2.0 equiv), DCE (2.0 mL), 80 °C, 12 h. ^bIsolated yield. ^cThe data in parentheses is the ratio of linear and branched isomers which was determined by ¹H NMR analysis.

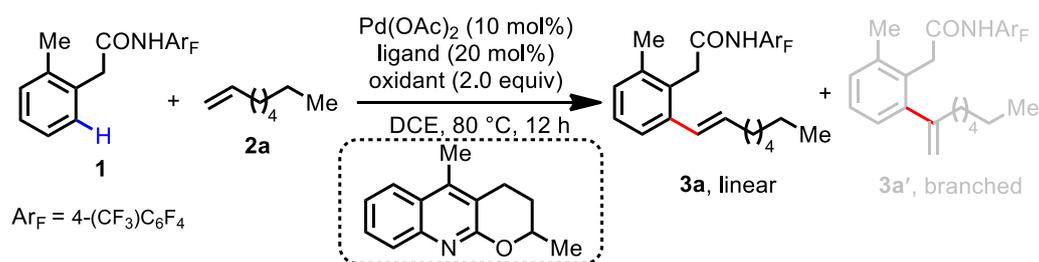
Table S2. Screening the Catalysts.^{a,b,c}



Entry	Catalyst	Oxidant	Time (h)	Yield (%)
1	Pd(OAc)₂	Ag₂CO₃ (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) ₄ (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)

^aReaction conditions : **1** (0.1 mmol), **2a** (3.0 equiv), catalyst (10 mol%), ligand (20 mol%), Ag₂CO₃ (2.0 equiv), DCE (2.0 mL), 80 °C, 12 h. ^bIsolated yield. ^cThe data in parentheses is the ratio of linear and branched isomers which was determined by ¹H NMR analysis.

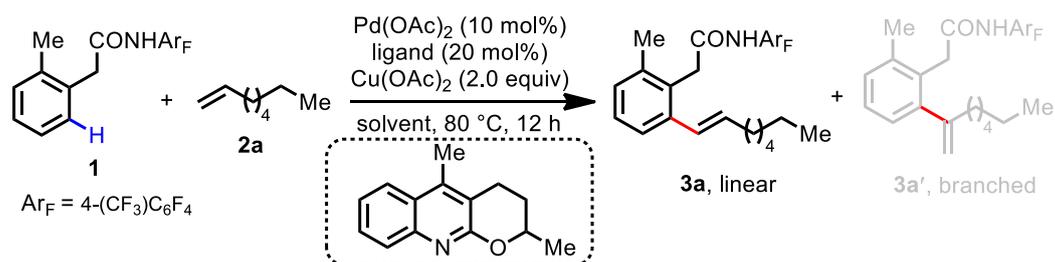
Table S3. Screening the Oxidants.^{a,b,c}



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

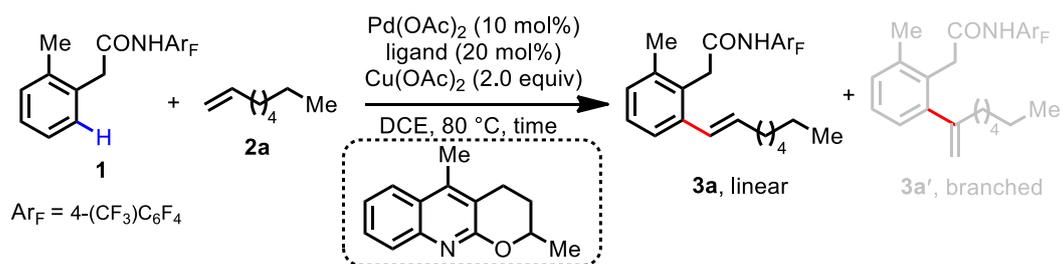
^aReaction conditions : **1** (0.1 mmol), **2a** (3.0 equiv), Pd(OAc)₂ (10 mol%), ligand (20 mol%), oxidant (2.0 equiv), DCE (2.0 mL), 80 °C, 12 h. ^bIsolated yield. ^cThe data in parentheses is the ratio of linear and branched isomers which was determined by ¹H NMR analysis.

Table S4. Screening the Solvents.^{a,b,c}



Entry	Solvent	Yield (%)	Entry	Solvent	Yield (%)
1	DCE	83 (3.6/1)	8	DMF	trace
2	dioxane	31 (2.5/1)	9	HFIP	25 (0.7/1)
3	THF	33 (2.1/1)	10	<i>t</i> -AmylOH	37 (1.6/1)
4	DCM	73 (3.0/1)	11	hexane	trace
5	MeCN	21 (2.3/1)	12	PhCF ₃	67 (2.7/1)
6	acetone	41 (1.6/1)	13	toluene	70 (2.8/1)
7	DME	trace	14	DMSO	trace

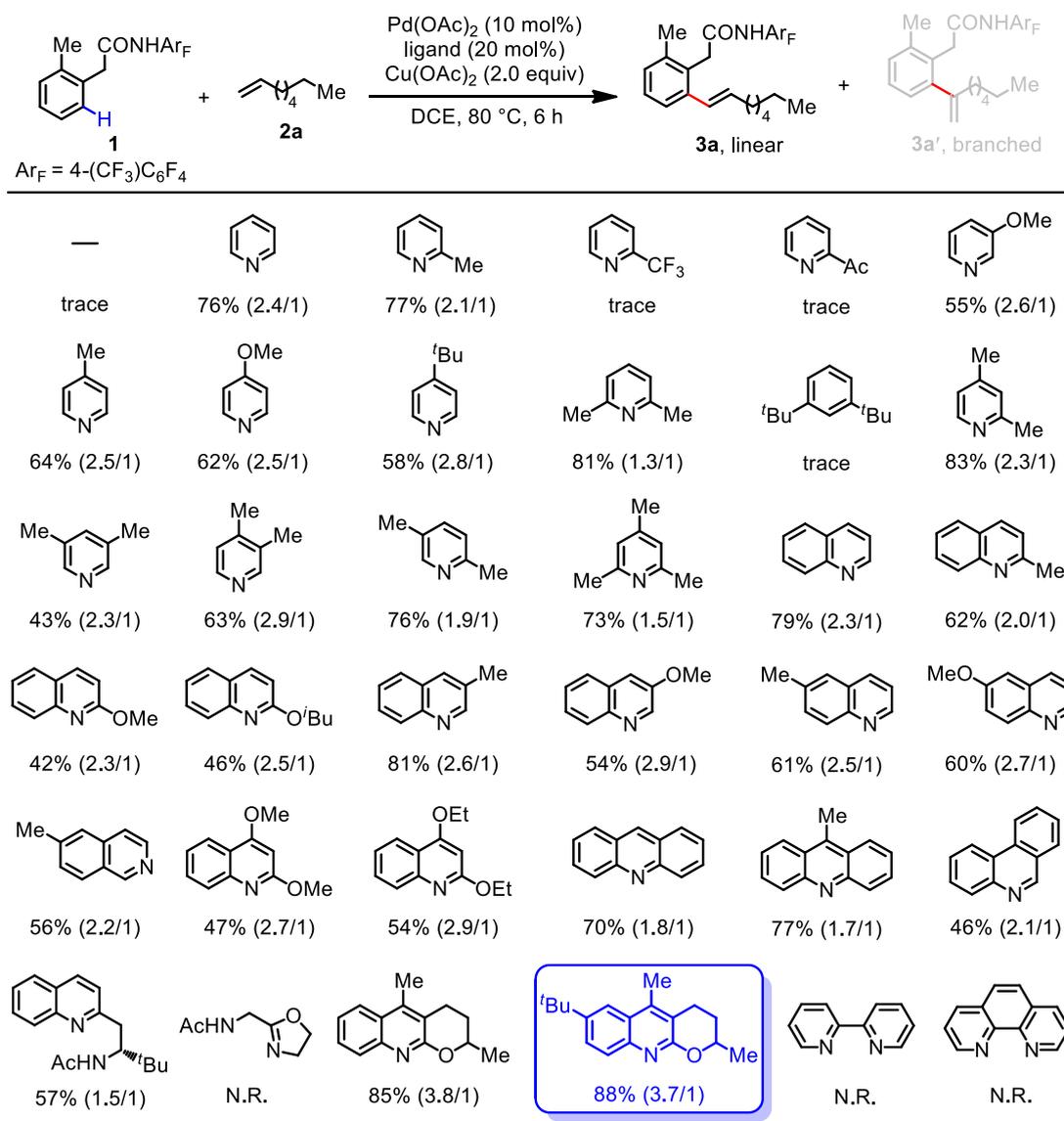
^aReaction conditions : **1** (0.1 mmol), **2a** (3.0 equiv), Pd(OAc)₂ (10 mol%), ligand (20 mol%), Cu(OAc)₂ (2.0 equiv), solvent (2.0 mL), 80 °C, 12 h. ^bIsolated yield. ^cThe data in parentheses is the ratio of linear and branched isomers which was determined by ¹H NMR analysis.

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)

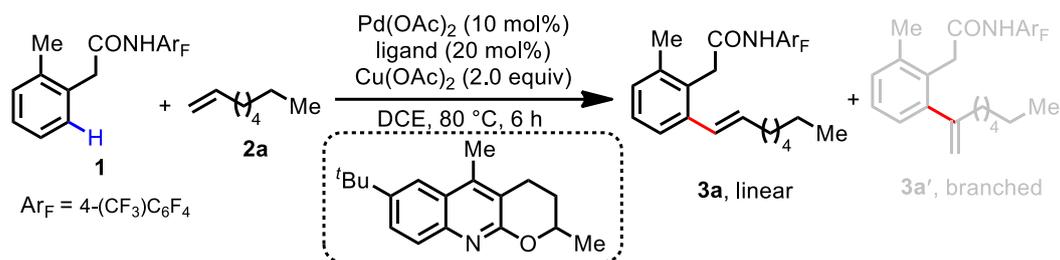
^aReaction conditions : **1** (0.1 mmol), **2a** (3.0 equiv), Pd(OAc)₂ (10 mol%), ligand (20 mol%), Cu(OAc)₂ (2.0 equiv), DCE (2.0 mL), 80 °C, time. ^bIsolated yield. ^cThe data in parentheses is the ratio of linear and branched isomers which was determined by ¹H NMR analysis.

Table S6. Screening the Ligands.^{a,b,c}



^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, 6 h. ^bIsolated yield. ^cThe data in parentheses is the ratio of linear and branched isomers which was determined by ¹H NMR analysis.

Table S7. Screening the Amount of Reagents.^{a,b,c}

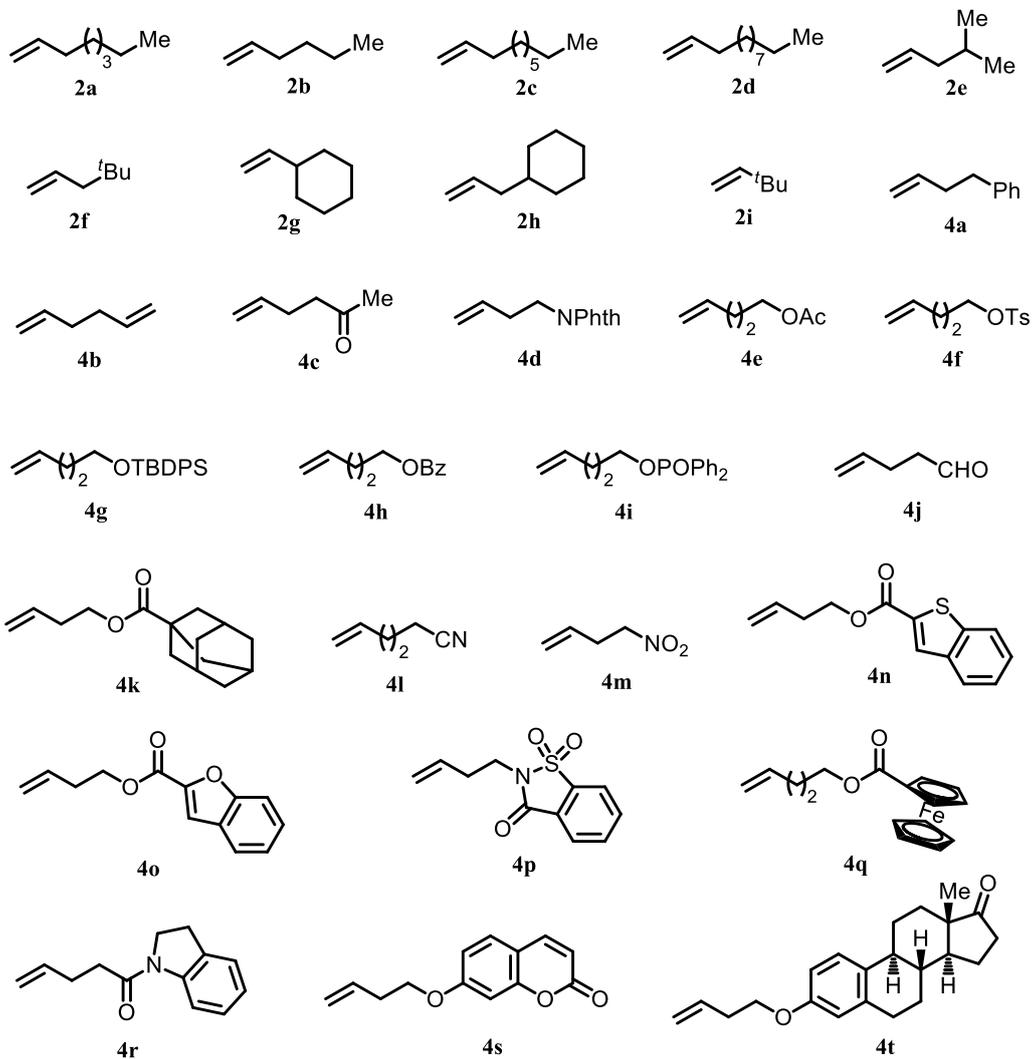


Entry	Catalyst (mol%)	Oxidant (equiv)	Atmosphere	Yield (%)
1	Pd(OAc) ₂ (10)	Cu(OAc) ₂ (2.0)	Air	88 (3.7/1)
2	Pd(OAc) ₂ (10)	—	Air	<10
3	Pd(OAc) ₂ (10)	—	O ₂	32 (4.1/1)
4 ^d	Pd(OAc) ₂ (10)	—	O ₂	50 (4.0/1)
5 ^e	Pd(OAc) ₂ (10)	—	O ₂	46 (4.0/1)
6	Pd(OAc) ₂ (10)	Cu(OAc) ₂ (0.5)	O ₂	89 (3.7/1)
7	Pd(OAc) ₂ (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)	O₂	87 (4.0/1)

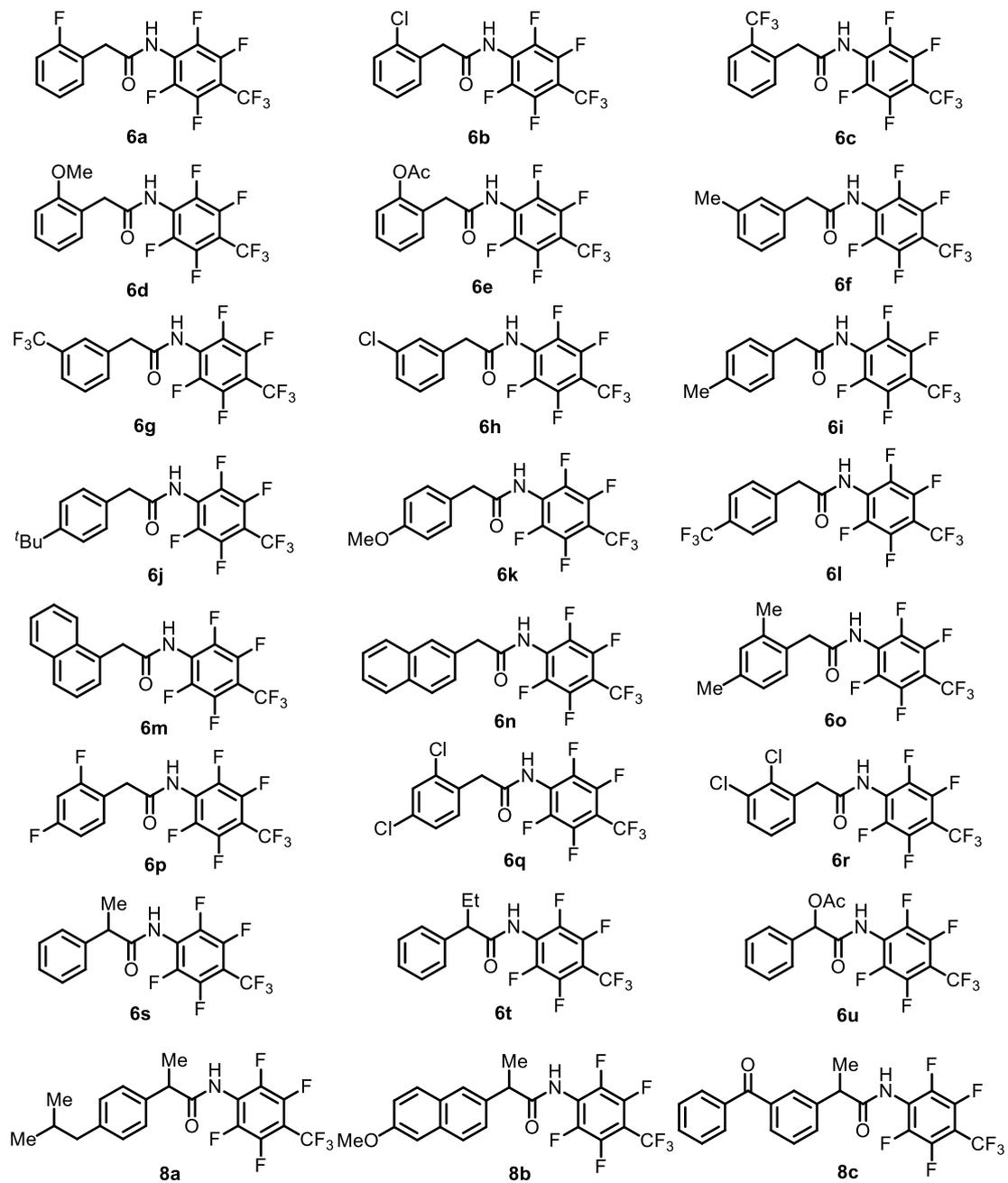
^aReaction conditions : **1** (0.1 mmol), **2a** (3.0 equiv), Pd(OAc)₂ (10 mol%), ligand (20 mol%), Cu(OAc)₂ (2.0 equiv), DCE (2.0 mL), 80 °C, 6 h. ^bIsolated yield. ^cThe data in parentheses is the ratio of linear and branched isomers which was determined by ¹H NMR analysis. ^d12 h. ^eAt 100 °C. ^f**2a** (2.0 equiv) was used. ^gligand (10 mol%) was used.

3. Structures of Substrates

Aliphatic alkenes

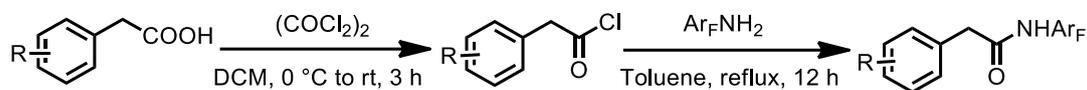


Phenylacetic amides



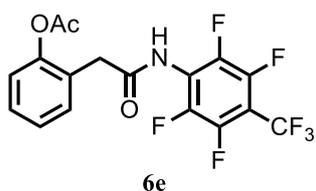
4. Experimental Section

4.1 Preparation of Phenylacetic Amides



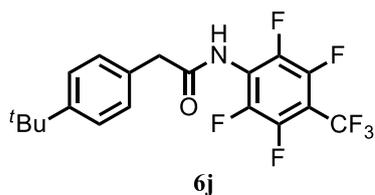
The previous reported procedure was followed.¹ To an oven-dried 50 mL round-bottom flask, 2,3,5,6-tetrafluoro-4-(trifluoromethyl)aniline (3.0 mmol) was dissolved in toluene (15.0 mL). Acid chloride (3.0 mmol), prepared from the corresponding carboxylic acid and oxalyl chloride, was added *via* syringe. 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.¹

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



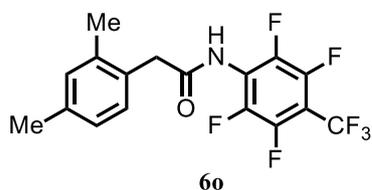
White solid: ¹H NMR (400 MHz, CDCl₃) δ 7.45-7.36 (m, 3H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 3.73 (s, 2H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.5, 168.0, 149.0, 131.1, 129.7, 127.2, 126.2, 123.0, 38.2, 20.8; HRMS (ESI-TOF) [M+NH₄]⁺ calculated for C₁₇H₁₄F₇N₂O₃: 427.0887, found: 427.0881.

2-(4-(*Tert*-butyl)phenyl)-*N*-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (**6j**)



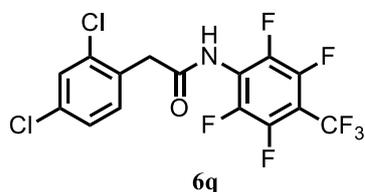
White solid: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 (d, $J = 7.4$ Hz, 2H), 7.27 (d, $J = 7.6$ Hz, 2H), 7.12 (s, 1H), 3.79 (s, 2H), 1.33 (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.2, 151.2, 130.2, 129.1, 126.4, 43.0, 34.658, 31.2; **HRMS (ESI-TOF)** $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{19}\text{H}_{20}\text{F}_7\text{N}_2\text{O}$: 425.1458, found: 425.1453.

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



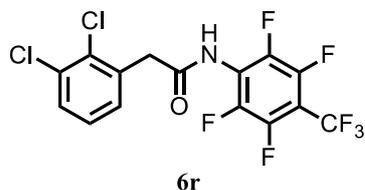
White solid: $^1\text{H NMR}$ (400 MHz, acetone-d_6) δ 9.42 (s, 1H) 7.22 (d, $J = 7.6$ Hz, 1H), 7.06 (s, 1H), 7.01 (d, $J = 7.6$ Hz, 1H), 3.89 (s, 2H), 2.35 (s, 3H), 2.31 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, acetone-d_6) δ 169.4, 137.5, 137.3, 131.6, 131.0, 130.9, 127.2, 40.6, 20.7, 19.3; **HRMS (ESI-TOF)** $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{17}\text{H}_{16}\text{F}_7\text{N}_2\text{O}$: 397.1145, found: 397.1141.

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



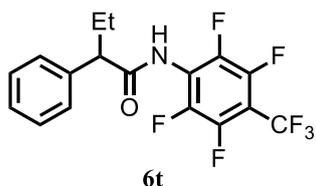
White solid: $^1\text{H NMR}$ (400 MHz, acetone-d_6) δ 9.74 (s, 1H), 7.56 (s, 2H), 7.42 (d, $J = 8.3$ Hz, 1H), 4.11 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, acetone-d_6) δ 167.9, 135.8, 134.0, 133.9, 132.7, 129.4, 127.9, 40.0; **HRMS (ESI-TOF)** $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{F}_7\text{N}_2\text{O}$: 437.0053, found: 437.0051.

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



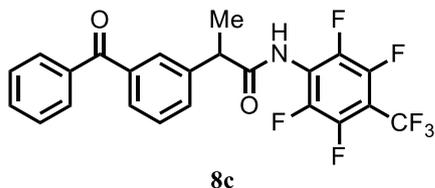
White solid: $^1\text{H NMR}$ (400 MHz, acetone- d_6) δ 9.77 (s, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.51 (d, $J = 7.7$ Hz, 1H), 7.38 (t, $J = 7.8$ Hz, 1H), 4.17 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, acetone- d_6) δ 167.9, 136.2, 133.1, 133.0, 131.2, 130.0, 128.438, 41.4; **HRMS** (ESI-TOF) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{F}_7\text{N}_2\text{O}$: 437.0053, found: 437.0051.

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



White solid: $^1\text{H NMR}$ (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, 1H), 1.94-1.82 (m, 1H), 0.94 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.4, 138.4, 129.3, 128.0, 128.0, 55.0, 26.2, 12.0; **HRMS** (ESI-TOF) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{17}\text{H}_{16}\text{F}_7\text{N}_2\text{O}$: 397.1145, found: 397.1142.

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



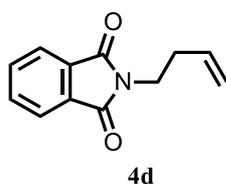
White solid: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 (s, 1H), 7.75 (d, $J = 7.3$ Hz, 2H), 7.70 (d, $J = 7.5$ Hz, 1H), 7.65-7.58 (m, 2H), 7.54-7.44 (m, 3H), 7.40 (s, 1H), 3.95 (q, $J = 7.0$ Hz, 1H), 1.63 (d, $J = 6.9$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 197.1,

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

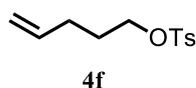
Alkenes **2a-2i**, **4a-4c**, **4j**, **4l-4m** were purchased from commercial vendors and used without further purification.

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



To an oven-dried 50 mL round-bottom flask equipped with a magnetic stir bar, potassium phthalimid (2.94 g, 15.8 mmol), 4-bromo-1-buten (1.70 g, 12.6 mmol), TBAB (0.2 g, 0.62 mmol) were added in MeCN (30 ml). The mixture was then heated to reflux for 5 h. After cooling to ambient temperature, the mixture was filtered to remove the excess of phthalimid and the filtrate was then evaporated under reduced pressure. After dissolved in DCM (100 ml), The residue was washed with brine twice. The organic phase was dried over Na₂SO₄ and the crude mixture was purified by column chromatography on silica gel using hexane/EtOAc (10:1) as eluent to afford *N*-(3-butenyl)phthalimide as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 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 Hz, 2H), 2.43 (q, *J* = 7.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 168.0, 134.3, 133.6, 131.9, 122.9, 117.3, 37.1, 32.6.

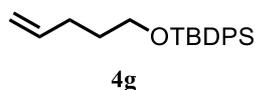
Pent-4-en-1-yl 4-methylbenzenesulfonate (**4f**)³



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)

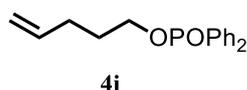
and triethylamine (1.8 mL, 12 mmol) were then added *via* syringe and the flask was cooled to 0 °C with an ice bath, after which 4-penten-1-ol (1.0 mL 10.0 mmol) was added dropwise *via* syringe. The mixture was allowed to warm to room temperature and stirring was continued for an additional 2 hours. 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)⁴**



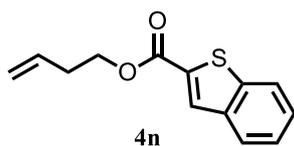
To a stirred solution of 4-penten-1-ol (1) (2.50 mL, 24.2 mmol), imidazole (1.98 g, 29.0 mmol), and a catalytic amount of DMAP in DMF (25 mL) was added TBDPSCl (6.61 mL, 25.4 mmol) at 0 °C and stirring was continued for 19 h at rt. The reaction mixture was diluted with Et₂O and washed with 10% HCl, saturated 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)



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. **¹H NMR (400 MHz, CDCl₃)** δ 10.45 (s, 1H), 7.73 (dd, *J* = 12.3, 7.6 Hz, 4H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.45-7.35 (m, 4H), 7.24-7.20 (m, 1H), 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), 4.11-4.07 (m, 2H), 4.06 (s, 2H), 2.50 (dd, *J* = 12.0, 7.6 Hz, 2H), 2.44 (s, 3H), 1.95-1.87 (m, 2H); **¹³C NMR (100 MHz, CDCl₃)** δ 137.3, 132.1 (d, *J*_{c-p} = 2.7 Hz), 131.5 (d, *J*_{c-p} = 136.4 Hz), 131.6 (d, *J*_{c-p} = 100.3 Hz), 128.5 (d, *J*_{c-p} = 13.1 Hz), 115.3, 62.3 (d, *J*_{c-p} = 6.0 Hz), 29.7, 29.6; **³¹P NMR (162 MHz, CDCl₃)** δ 31.4.

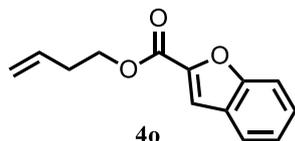
But-3-en-1-yl benzo[b]thiophene-2-carboxylate (4n)⁵



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. **¹H NMR (400 MHz, CDCl₃)** δ 8.06 (s, 1H), 7.87 (t, *J* = 6.9 Hz, 2H), 7.48-7.38 (m, 2H), 5.94-5.82 (m, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.13 (d, *J* =

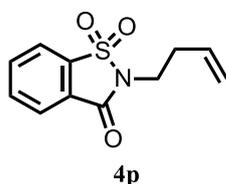
10.2 Hz, 1H), 4.40 (td, $J = 6.8, 1.0$ Hz, 2H), 2.54 (q, $J = 6.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.7, 142.2, 138.7, 133.7, 133.6, 130.4, 126.9, 125.5, 124.8, 122.71, 117.6, 64.5, 33.1.

But-3-en-1-yl benzofuran-2-carboxylate (4o)⁷



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. ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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.

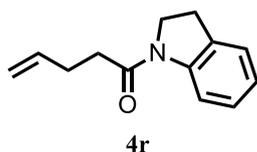
2-(But-3-en-1-yl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide (4p)⁶



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

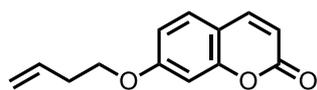
mmol) was added *via* syringe and stirred for 12 h at 120 °C. The resulting mixture was cooled to room temperature and poured into water, extracted the mixture by methylene chloride (50 mL). The combined organic layer was washed by water (50 mL), and dried over Na₂SO₄, the crude reaction product was 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, 134.2, 133.7, 127.3, 125.1, 120.8, 118.0, 38.5, 32.6.

1-(Indolin-1-yl)pent-4-en-1-one (4r)⁷



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.

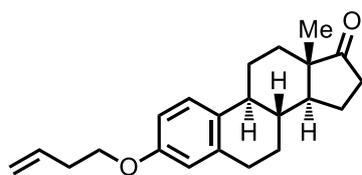
7-(But-3-en-1-yloxy)-2H-chromen-2-one (4s)⁵



4s

To a solution of 7-hydroxy-2H-chromen-2-one (1.62 g, 10 mmol) and K_2CO_3 (5.50 g, 40 mmol) in CH_3CN (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_2Cl_2 (2x10 mL). The combined organic extracts were washed with water (2 x 10 mL), dried over Na_2SO_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. 1H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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



4t

To a solution of estrone (1.40 g, 5 mmol) and K_2CO_3 (2.76 g, 20 mmol) in CH_3CN (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_2Cl_2 (2x10 mL). The combined organic extracts were washed with water (2 x 10 mL), dried over Na_2SO_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. **¹H NMR (400 MHz, CDCl₃)** δ 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); **¹³C NMR (100 MHz, CDCl₃)** δ 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(sp²)-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 O₂ 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(sp²)-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 O₂ 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 O₂ 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 O₂ 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.

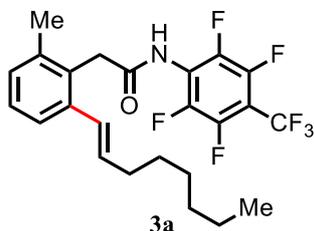
To two paralleled oven-dried round-bottom flask (50 mL) was added Pd/C (10 wt. % loading on carbon, 5.0 mg), amide **3a** (33.3 mg, 0.07 mmol) and EtOAc (2 mL). The reaction flask was evacuated and refilled with H₂ (3 times, balloon). After stirring at room temperature for 24 hours, the reaction mixture 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%,)

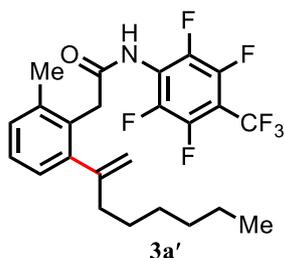
5. Experimental Data

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



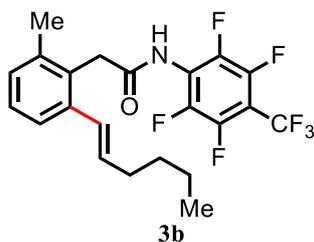
Substrate **1** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (41.4 mg, 87% yield), linear/branched ratio = 4.0/1; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.36 (d, $J = 7.7$ Hz, 1H), 7.24 (t, $J = 7.6$ 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); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 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) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{24}\text{H}_{28}\text{F}_7\text{N}_2\text{O}$: 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')



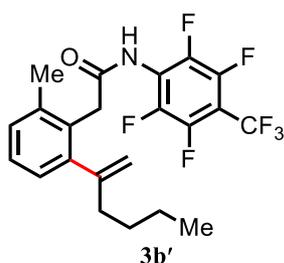
White solid: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.23 (d, $J = 7.4$ Hz, 1H), 7.21 (t, $J = 6.8$ Hz, 1H), 7.06 (d, $J = 7.3$ Hz, 1H), 6.87 (s, 1H), 5.27 (d, $J = 1.2$ Hz, 1H), 4.93 (s, 1H), 3.87 (s, 2H), 2.39 (s, 3H), 2.35-2.27 (m, 2H), 1.45-1.39 (m, 2H), 1.33-1.26 (m, 6H), 0.87 (t, $J = 6.8$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 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) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{24}\text{H}_{28}\text{F}_7\text{N}_2\text{O}$: 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; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 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); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 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)** $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{22}\text{H}_{24}\text{F}_7\text{N}_2\text{O}$: 465.1771, found: 465.1767.

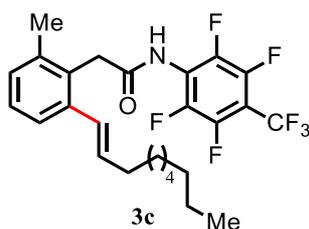
2-(2-(Hex-1-en-2-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (3b')



White solid: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 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); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 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)** $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{22}\text{H}_{24}\text{F}_7\text{N}_2\text{O}$: 465.1771, found: 465.1769.

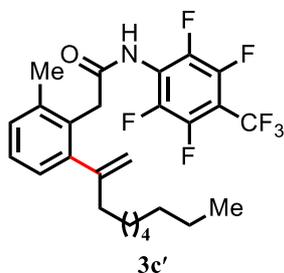
(E)-2-(2-(dec-1-en-1-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (3b)

1)phenyl)acetamide (3c)



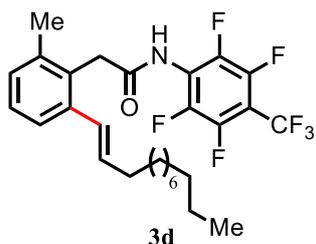
Substrate **1** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (43.7 mg, 87% yield). Linear/branched ratio = 4.3/1; **¹H NMR (400 MHz, CDCl₃)** δ 7.36 (d, *J* = 7.7 Hz, 1H), 7.24 (t, *J* = 7.6 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); **¹³C NMR (100 MHz, CDCl₃)** δ 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+NH₄]⁺** calculated for C₂₆H₃₂F₇N₂O: 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')



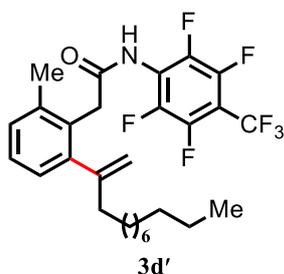
White solid: **¹H NMR (400 MHz, CDCl₃)** δ 7.25 (d, *J* = 6.9 Hz, 1H), 7.21 (t, *J* = 6.8 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.82 (s, 1H), 5.27 (s, 1H), 4.93 (s, 1H), 3.87 (s, 2H), 2.39 (s, 3H), 2.33-2.28 (m, 2H), 1.45-1.40 (m, 2H), 1.31-1.24 (m, 11H), 0.87 (t, *J* = 6.7 Hz, 3H); **¹³C NMR (100 MHz, CDCl₃)** δ 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+NH₄]⁺** calculated for C₂₆H₃₂F₇N₂O: 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; **¹H NMR (400 MHz, CDCl₃)** δ 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), 1.35-1.20 (m, 14H), 0.88 (t, *J* = 6.6 Hz, 3H); **¹³C NMR (100 MHz, CDCl₃)** δ 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+NH₄]⁺** calculated for C₂₈H₃₆F₇N₂O: 549.2710, found: 549.2706.

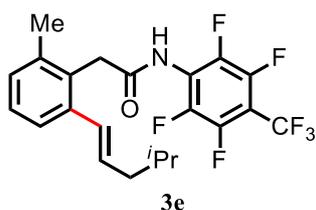
2-(2-(Dodec-1-en-2-yl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (3d')



White solid: **¹H NMR (400 MHz, CDCl₃)** δ 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); **¹³C NMR (100 MHz, CDCl₃)** δ 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, 29.3, 27.7, 22.7, 20.0, 14.1; **HRMS (ESI-TOF) [M+NH₄]⁺** calculated for C₂₈H₃₆F₇N₂O: 549.2710, found: 549.2706.

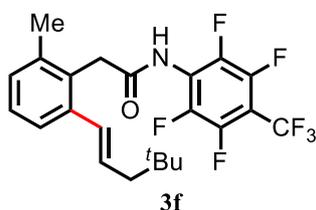
(E)-2-(2-methyl-6-(4-methylpent-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifl

uoromethyl)phenyl)acetamide (3e)



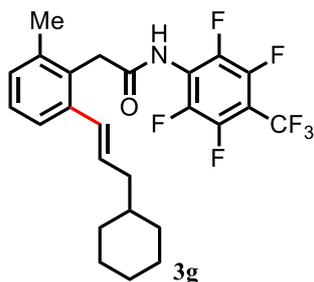
Substrate **1** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (33.6 mg, 75% yield). Linear/branched ratio = 4.0/1; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37 (d, $J = 7.3$ Hz, 1H), 7.25 (t, $J = 7.6$ 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); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.5, 138.8, 137.7, 135.1, 129.8, 128.9, 128.5, 127.8, 125.6, 42.6, 37.6, 28.5, 22.3, 20.2; **HRMS (ESI-TOF)** $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{22}\text{H}_{24}\text{F}_7\text{N}_2\text{O}$: 465.1771, found: 465.1767.

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



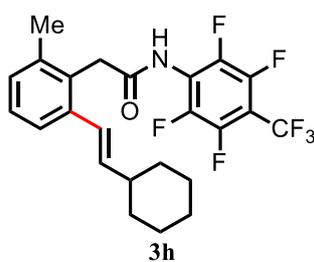
Substrate **1** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (30.1 mg, 65% yield). Linear/branched ratio = 7.2/1; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.38 (d, $J = 7.3$ Hz, 1H), 7.25 (t, $J = 7.6$ 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); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 168.5, 138.8, 137.7, 133.5, 129.9, 128.9, 128.9, 128.5, 125.6, 47.8, 37.6, 31.3, 29.3, 20.2; **HRMS (ESI-TOF)** $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{23}\text{H}_{26}\text{F}_7\text{N}_2\text{O}$: 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; **¹H NMR (400 MHz, CDCl₃)** 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); **¹³C NMR (100 MHz, CDCl₃)** δ 168.5, 138.8, 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+NH₄]⁺** calculated for C₂₅H₂₈F₇N₂O: 505.2804, found: 505.2802.

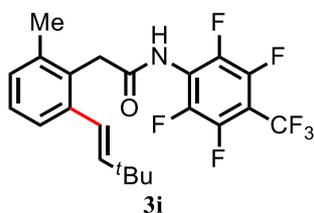
(E)-2-(2-(2-cyclohexylvinyl)-6-methylphenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (3h)



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; **¹H NMR (400 MHz, CDCl₃)** 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); **¹³C NMR (100 MHz, CDCl₃)** δ 168.6, 142.1, 138.9, 137.6, 129.7, 129.0, 128.4, 125.5, 124.3, 41.4, 37.6,

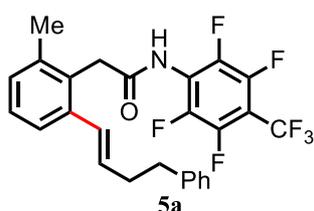
32.8, 26.0, 25.9, 20.2; **HRMS (ESI-TOF)** $[M+NH_4]^+$ calculated for $C_{24}H_{23}F_7N_2O$: 491.1928, found: 491.1925.

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



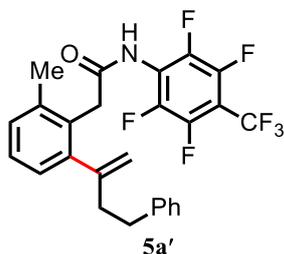
Substrate **1** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (26.2 mg, 58% yield). Single isomer was obtained; 1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, $J = 7.5$ Hz, 1H), 7.25 (t, $J = 7.8$ Hz, 1H), 7.18 (d, $J = 7.6$ Hz, 1H), 6.76 (s, 1H), 6.52 (d, $J = 15.8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) 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)** $[M+NH_4]^+$ calculated for $C_{22}H_{24}F_7N_2O$: 465.1771, found: 465.1766.

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



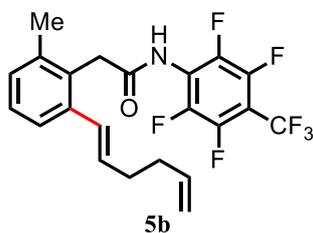
Substrate **1** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (31.7 mg, 64% yield). Linear/branched ratio = 5.0/1; 1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2H), 7.27-7.26 (m, 1H), 7.23-7.20 (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); ^{13}C NMR (100 MHz, $CDCl_3$) 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)** $[M+NH_4]^+$ calculated for $C_{26}H_{24}F_7N_2O$: 513.1771, found: 513.1767.

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



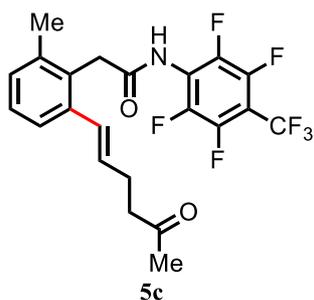
White solid: ¹H NMR (400 MHz, CDCl₃) δ 7.28-7.21 (m, 4H), 7.20-7.14 (m, 3H), 7.09 (d, *J* = 6.4 Hz, 1H), 6.76 (s, 1H), 5.35 (d, *J* = 1.3 Hz, 1H), 4.99 (s, 1H), 3.81 (s, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 2.68-2.64 (m, 2H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.8, 148.8, 144.4, 141.2, 138.1, 129.9, 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+NH₄]⁺ calculated for C₂₆H₂₄F₇N₂O: 513.1771, found: 513.1766.

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



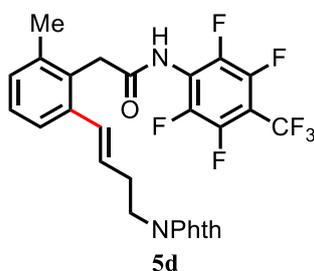
Substrate **1** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (24.9 mg, 56% yield). Linear/branched ratio = 4.2/1; ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 7.7 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 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); ¹³C NMR (100 MHz, CDCl₃) δ 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+NH₄]⁺ calculated for C₂₂H₂₂F₇N₂O: 463.1615, found: 463.1612.

(E)-2-(2-methyl-6-(5-oxohex-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)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; **¹H 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); **¹³C 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.

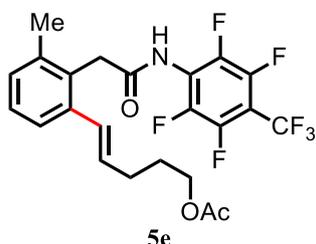
(*E*)-2-(2-(4-(1,3-dioxoisindolin-2-yl)but-1-en-1-yl)-6-methylphenyl)-*N*-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (5d)



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; **¹H 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); **¹³C 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;

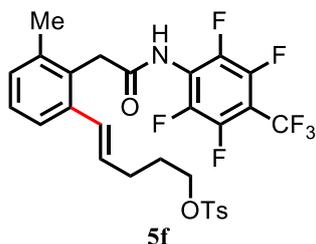
HRMS (ESI-TOF) [M+NH₄]⁺ calculated for C₂₈H₂₃F₇N₃O₃: 582.1622, found: 582.1617.

(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; **¹H 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); **¹³C 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.

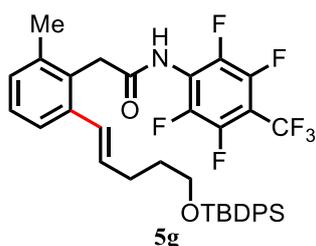
(E)-5-(3-methyl-2-(2-oxo-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)ethyl)phenyl)pent-4-en-1-yl 4-methylbenzenesulfonate (5f)



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; **¹H 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,

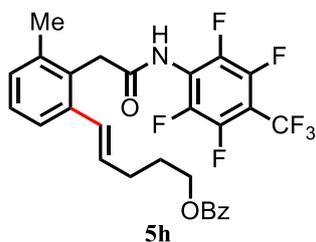
$J = 15.5, 7.1$ Hz, 1H), 4.10 (t, $J = 6.1$ Hz, 2H), 3.92 (s, 2H), 2.44 (s, 3H), 2.39 (s, 3H), 2.33 (dd, $J = 14.1, 7.1$ Hz, 2H), 1.83 (dd, $J = 13.2, 6.5$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.6, 144.9, 138.1, 137.7, 132.9, 132.7, 129.9, 129.9, 129.3, 129.0, 128.2, 127.8, 125.3, 69.5, 37.2, 28.9, 28.1, 21.6, 20.2; HRMS (ESI-TOF) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{28}\text{H}_{28}\text{F}_7\text{N}_2\text{O}_4\text{S}$: 621.1653, found: 621.1645.

(*E*)-2-(2-(5-((*tert*-butyldiphenylsilyloxy)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; ^1H NMR (400 MHz, CDCl_3) δ 7.69-7.61 (m, 4H), 7.44-7.34 (m, 6H), 7.31 (d, $J = 7.5$ Hz, 1H), 7.22 (d, $J = 7.5$ Hz, 1H), 7.18 (d, $J = 7.6$ Hz, 1H), 6.75 (s, 1H), 6.61 (d, $J = 15.3$ Hz, 1H), 6.17-6.09 (m, 1H), 3.89 (s, 2H), 3.72 (t, $J = 6.2$ 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) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{37}\text{H}_{40}\text{F}_7\text{N}_2\text{O}_2\text{Si}$: 705.2742, found: 705.2733.

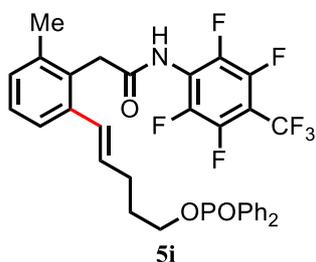
(*E*)-5-(3-methyl-2-(2-oxo-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)ethyl)phenyl)pent-4-en-1-yl benzoate (5h)



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; ^1H NMR (400 MHz, CDCl_3) δ

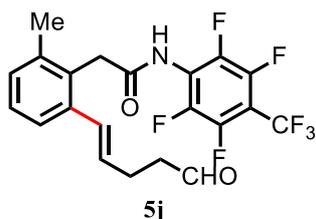
8.01 (d, $J = 7.4$ Hz, 2H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.41 (t, $J = 7.7$ Hz, 2H), 7.23 (t, $J = 7.6$ Hz, 1H), 7.18 (d, $J = 7.0$ Hz, 1H), 7.04 (s, 1H), 6.68 (d, $J = 15.7$ Hz, 1H), 6.15 (dt, $J = 14.9, 7.0$ Hz, 1H), 4.40 (t, $J = 6.4$ Hz, 2H), 3.93 (s, 2H), 2.42 (q, $J = 7.2$ Hz, 2H), 2.39 (s, 3H), 1.98 (dd, $J = 13.5, 6.7$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 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; HRMS (ESI-TOF) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{28}\text{H}_{26}\text{F}_7\text{N}_2\text{O}_3$: 571.1826, found: 571.1818.

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



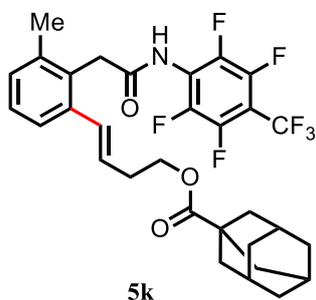
Substrate **1** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 4/1). The desired product was obtained as a white solid (34.1 mg, 53% yield). Single isomer was obtained; ^1H NMR (400 MHz, CDCl_3) δ 10.45 (s, 1H), 7.76-7.71 (m, 4H), 7.50 (t, $J = 7.4$ 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}C NMR (100 MHz, CDCl_3) δ 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}P NMR (CDCl_3 , 162 MHz) δ 32.6; HRMS (ESI-TOF) $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{28}\text{F}_7\text{NO}_3\text{P}$: 650.1690, found: 650.1677.

(*E*)-2-(2-methyl-6-(5-oxopent-1-en-1-yl)phenyl)-*N*-(2,3,5,6-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; **¹H NMR (400 MHz, CDCl₃)** δ 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); **¹³C NMR (100 MHz, CDCl₃)** δ 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+NH₄]⁺** calculated for C₂₁H₂₀F₇N₂O₂: 465.1408, found: 465.1404.

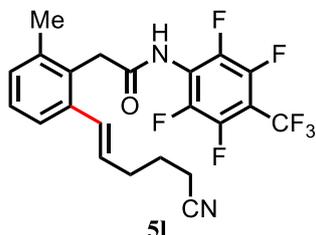
(E)-4-(3-methyl-2-(2-oxo-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)ethyl)phenyl)but-3-en-1-yl adamantane-1-carboxylate (5k)



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; **¹H NMR (400 MHz, CDCl₃)** δ 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); **¹³C NMR (100 MHz, CDCl₃)** δ 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,

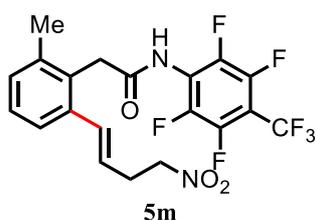
20.2; **HRMS (ESI-TOF)** $[M+NH_4]^+$ calculated for $C_{31}H_{34}F_7N_2O_3$: 615.2452, found: 615.2443.

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



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, $CDCl_3$)** 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); **^{13}C NMR (100 MHz, $CDCl_3$)** 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)** $[M+NH_4]^+$ calculated for $C_{22}H_{21}F_7N_3O$: 476.1567, found: 476.1559.

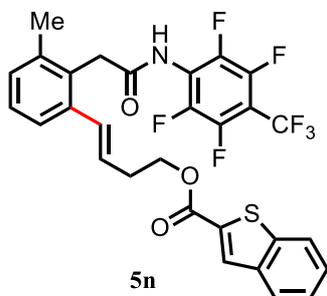
(E)-2-(2-methyl-6-(4-nitrobut-1-en-1-yl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (5m)



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, $CDCl_3$)** 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); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 168.2, 137.8, 137.5, 131.5, 130.6, 129.3, 128.5, 128.0, 125.6, 74.9, 37.4,

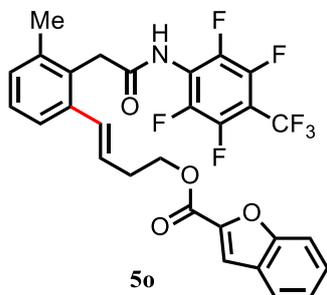
30.9, 20.2; **HRMS (ESI-TOF) [M+NH₄]⁺** calculated for C₂₀H₁₉F₇N₃O₃: 482.1309, found: 482.1303.

(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 (30.6 mg, 51% yield). Single isomer was obtained; **¹H NMR (400 MHz, CDCl₃)** δ 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); **¹³C NMR (100 MHz, CDCl₃)** δ 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+NH₄]⁺** calculated for C₂₉H₂₄F₇N₂O₃S: 613.1390, found: 613.1387.

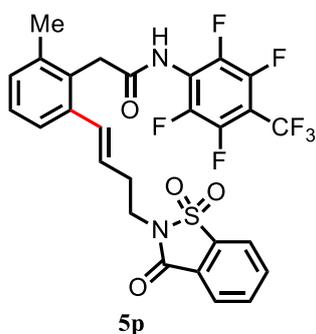
(E)-4-(3-methyl-2-(2-oxo-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)ethyl)phenyl)but-3-en-1-yl benzofuran-2-carboxylate (5o)



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; **¹H NMR (400 MHz, CDCl₃)** δ

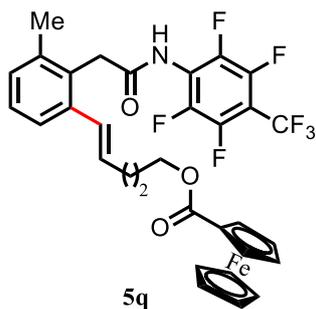
7.66 (d, $J = 7.5$ Hz, 1H), 7.58 (dd, $J = 8.4, 0.8$ Hz, 1H), 7.52 (d, $J = 0.9$ Hz, 1H), 7.44 (dt, $J = 8.4, 1.3$ Hz, 1H), 7.36 (d, $J = 7.5$ Hz, 1H), 7.30 (d, $J = 7.6$ Hz, 1H), 7.27 (d, $J = 7.5$ Hz, 1H), 7.24 (d, $J = 7.6$ Hz, 1H), 6.86 (s, 1H), 6.80 (d, $J = 15.5$ Hz, 1H), 6.16 (dt, $J = 15.5, 6.9$ 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); ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 159.5, 155.7, 145.2, 138.1, 137.8, 130.5, 130.3, 130.0, 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) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{29}\text{H}_{24}\text{F}_7\text{N}_2\text{O}_4$: 597.1619, found: 597.1613.

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



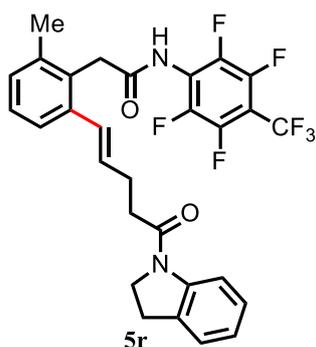
Substrate **1** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 3/1). The desired product was obtained as a white solid (33.5 mg, 56% yield). Linear/branched ratio = 8.7/1; ^1H NMR (400 MHz, CDCl_3) δ 8.06-8.01 (m, 1H), 7.91-7.80 (m, 3H), 7.34 (d, $J = 8.0$ 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); ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 159.0, 137.9, 137.8, 137.5, 134.8, 134.4, 130.5, 130.4, 130.2, 129.3, 128.4, 127.2, 125.7, 125.2, 120.9, 38.8, 37.4, 32.2, 20.2; HRMS (ESI-TOF) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{27}\text{H}_{23}\text{F}_7\text{N}_3\text{O}_4\text{S}$: 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; **¹H NMR (400 MHz, CDCl₃)** 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); **¹³C NMR (100 MHz, CDCl₃)** 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+NH₄]⁺** calculated for C₃₂H₃₀F₇FeN₂O₃: 679.1489, found: 679.1485.

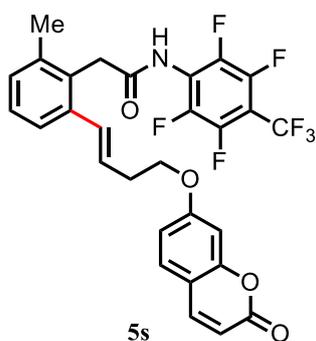
(*E*)-2-(2-(5-(indolin-1-yl)-5-oxopent-1-en-1-yl)-6-methylphenyl)-*N*-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (5r**)**



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; **¹H NMR (400 MHz, CDCl₃)** 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); **¹³C NMR**

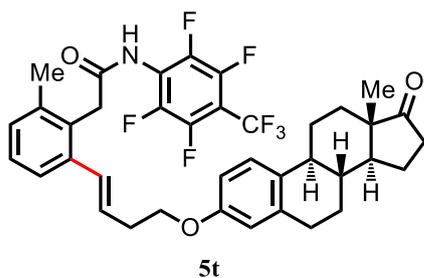
(100 MHz, CDCl₃) δ 171.2, 168.8, 142.1, 138.4, 138.1, 133.8, 130.8, 130.2, 130.2, 130.0, 127.7, 127.1, 125.8, 124.7, 124.0, 116.3, 47.7, 37.3, 34.3, 27.8, 27.7, 20.5; **HRMS (ESI-TOF) [M+1]⁺** calculated for C₂₉H₂₄F₇N₂O₂: 565.1721, found: 565.1713.

(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)



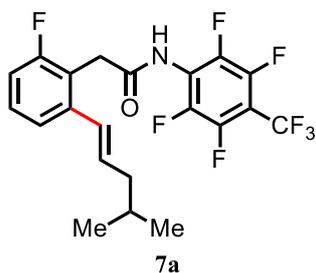
Substrate **1** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 9/1 to 4/1). The desired product was obtained as a white solid (27.0 mg, 47% yield). Single isomer was obtained; ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, *J* = 9.6 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 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; **¹H NMR (400 MHz, CDCl₃)** δ 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); **¹³C NMR (100 MHz, CDCl₃)** δ 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+NH₄]⁺** calculated for C₃₈H₄₀F₇N₂O₃: 705.2922, found: 705.2912.

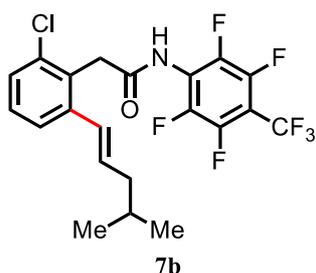
(*E*)-2-(2-fluoro-6-(4-methylpent-1-en-1-yl)phenyl)-*N*-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7a)



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; **¹H NMR (400 MHz, CDCl₃)** δ 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); **¹³C NMR (100 MHz, CDCl₃)** δ 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+NH₄]⁺** calculated for C₂₁H₂₁F₈N₂O: 469.1521, found: 469.1521.

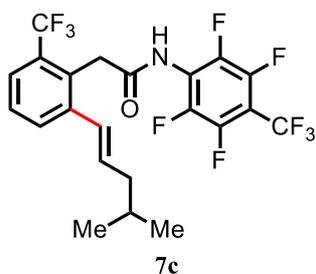
(*E*)-2-(2-chloro-6-(4-methylpent-1-en-1-yl)phenyl)-*N*-(2,3,5,6-tetrafluoro-4-(triflu

oromethyl)phenyl)acetamide (7b)



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; **¹H NMR (400 MHz, CDCl₃)** δ 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); **¹³C NMR (100 MHz, CDCl₃)** δ 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+NH₄]⁺** calculated for C₂₁H₂₁ClF₇N₂O: 485.1225, found: 485.1225.

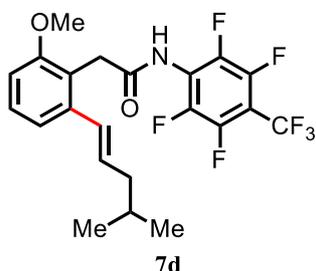
(E)-2-(2-(4-methylpent-1-en-1-yl)-6-(trifluoromethyl)phenyl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7c)



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; **¹H NMR (400 MHz, CDCl₃)** δ 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); **¹³C NMR (100 MHz, CDCl₃)** δ 167.3, 141.2, 140.8, 136.8, 131.1, 128.5, 128.1, 126.5, 125.1 (q, $J =$

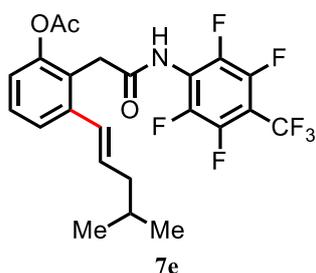
5.8 Hz), 124.4 (d, $J = 235.9$ Hz), 42.5, 37.1, 28.4, 22.3; **HRMS (ESI-TOF)** $[M+NH_4]^+$ calculated for $C_{22}H_{21}F_{10}N_2O$: 519.1489, found: 519.1487.

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



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; **1H NMR (400 MHz, $CDCl_3$)** δ 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, $CDCl_3$)** δ 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 $C_{22}H_{21}F_7NO_2$: 464.1455, found: 464.1453.

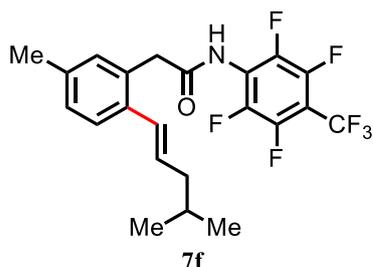
(E)-3-(4-methylpent-1-en-1-yl)-2-(2-oxo-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)ethyl)phenyl acetate (7e)



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; **1H NMR (400 MHz, $CDCl_3$)** δ 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),

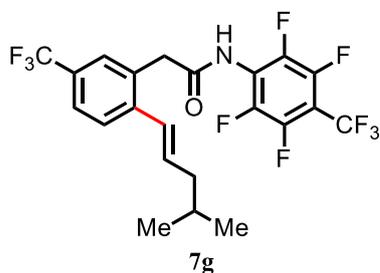
2.15 (td, $J = 7.3, 1.2$ Hz, 2H), 1.74 (dt, $J = 13.2, 6.7$ Hz, 1H), 0.94 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.0, 168.2, 149.4, 140.5, 135.7, 129.3, 126.4, 124.8, 123.1, 121.1, 42.5, 35.1, 28.4, 22.2, 20.8; HRMS (ESI-TOF) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{23}\text{H}_{24}\text{F}_7\text{N}_2\text{O}_3$: 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; ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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; HRMS (ESI-TOF) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{22}\text{H}_{24}\text{F}_7\text{N}_2\text{O}$: 465.1771, found: 465.1770.

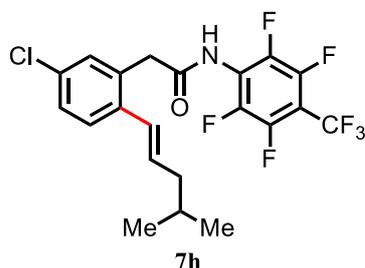
(*E*)-2-(2-(4-methylpent-1-en-1-yl)-5-(trifluoromethyl)phenyl)-*N*-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7g)



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; ^1H NMR (400 MHz, CDCl_3) δ

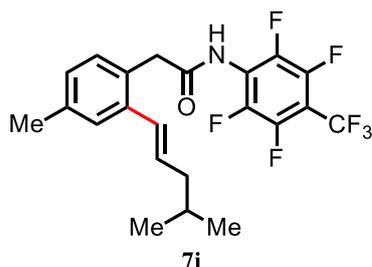
7.65 (d, $J = 8.2$ Hz, 1H), 7.58 (d, $J = 8.2$ Hz, 1H), 7.55 (s, 1H), 6.80 (s, 1H), 6.55 (d, $J = 15.4$ Hz, 1H), 6.31 (dt, $J = 15.5, 7.8$ Hz, 1H), 3.94 (s, 2H), 2.16 (s, 3H), 2.16 (td, $J = 7.2, 1.1$ Hz, 2H), 1.74 (dt, $J = 13.3, 6.6$ Hz, 1H), 0.94 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) 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) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{22}\text{H}_{21}\text{F}_{10}\text{N}_2\text{O}$: 519.1489, found: 519.1488.

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



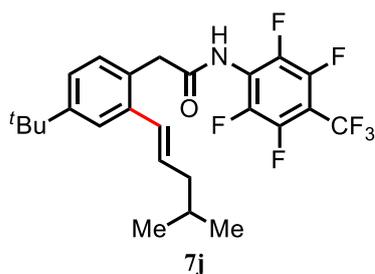
Substrate **6h** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired product was obtained as a white solid (29.9 mg, 64% yield). Linear/branched ratio = 4.9/1; ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.2$ Hz, 1H), 7.31 (dd, $J = 11.2, 2.1$ 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_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) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{21}\text{H}_{21}\text{ClF}_7\text{N}_2\text{O}$: 485.1225, found: 485.1225.

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



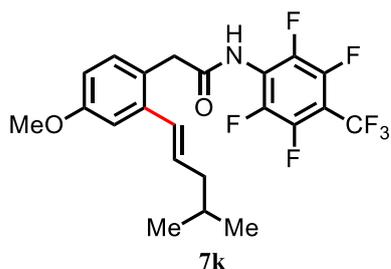
Substrate **6i** was olefinated by two paralleled runs following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a white solid. (54.1 mg, 74% yield). Mono/di = 2.9/1, for mono: linear/branched ratio = 3.0/1. The spectra of diolefinated product is very messy and is not given; **¹H 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); **¹³C 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 C₂₂H₂₄F₇N₂O: 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)



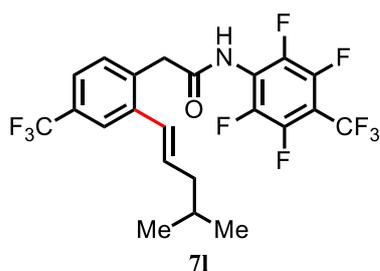
Substrate **6j** was olefinated by two paralleled runs following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a white solid (61.6 mg, 71% yield). Mono/di = 2.7/1, for mono: linear/branched ratio = 4.6/1. The spectra of diolefinated product is very messy and is not given; **¹H 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); **¹³C 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 C₂₅H₃₀F₇N₂O: 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 5/1). 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; **¹H NMR (400 MHz, CDCl₃)** δ 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); **¹³C NMR (100 MHz, CDCl₃)** δ 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+NH₄]⁺** calculated for C₂₂H₂₄F₇N₂O₂: 481.1721, found: 481.1716.

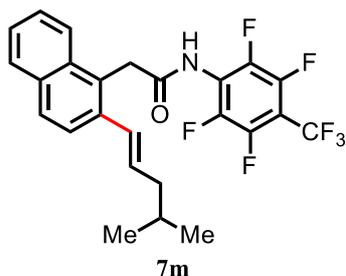
(*E*)-2-(2-(4-methylpent-1-en-1-yl)-4-(trifluoromethyl)phenyl)-*N*-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7l)



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; **¹H NMR (400 MHz, CDCl₃)** δ 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

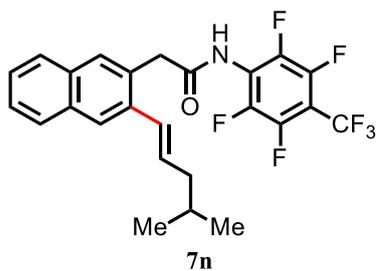
(d, $J = 6.7$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.5, 138.8, 136.6, 133.8, 131.3, 131.2, 130.9, 125.9, 124.3 (q, $J = 3.7$ Hz), 123.9 (q, $J = 3.8$ Hz), 42.6, 41.4, 28.4, 22.3; HRMS (ESI-TOF) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{22}\text{H}_{21}\text{F}_{10}\text{N}_2\text{O}$: 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; ^1H 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) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{25}\text{H}_{24}\text{F}_7\text{N}_2\text{O}$: 501.1771, found: 501.1769.

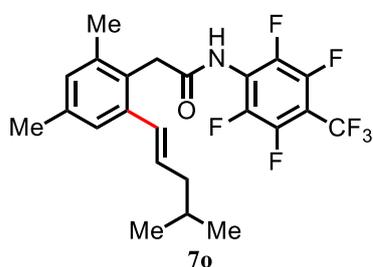
(E)-2-(3-(4-methylpent-1-en-1-yl)naphthalen-2-yl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)acetamide (7n)



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

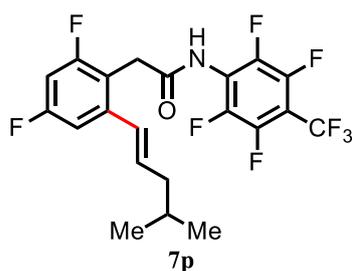
white solid (28.0 mg, 58% yield). Linear/branched ratio = 4.9/1; **¹H NMR (400 MHz, CDCl₃)** δ 7.98 (s, 1H), 7.86-7.81 (m, 3H), 7.79 (s, 1H), 7.53-7.48 (m, 2H), 6.83 (s, 1H), 6.63 (d, *J* = 15.4 Hz, 1H), 6.32 (dt, *J* = 15.0, 7.3 Hz, 1H), 4.04 (s, 2H), 2.17 (td, *J* = 7.2, 1.2 Hz, 2H), 1.77 (dt, *J* = 13.4, 6.8 Hz, 1H), 0.96 (d, *J* = 6.7 Hz, 6H); **¹³C NMR (100 MHz, CDCl₃)** δ 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+NH₄]⁺** calculated for C₂₅H₂₄F₇N₂O: 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)



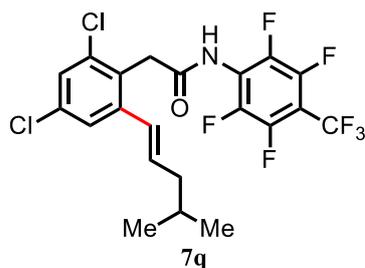
Substrate **6o** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a white solid (33.8 mg, 73% yield). Linear/branched ratio = 4.1/1; **¹H NMR (400 MHz, CDCl₃)** δ 7.18 (s, 1H), 7.00 (s, 1H), 6.79 (s, 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); **¹³C NMR (100 MHz, CDCl₃)** δ 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+NH₄]⁺** calculated for C₂₃H₂₆F₇N₂O: 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)



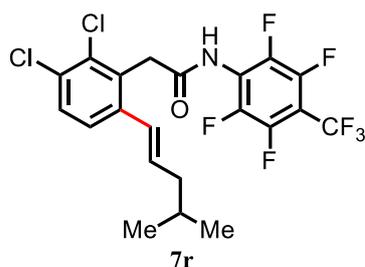
Substrate **6p** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a white solid (27.8 mg, 59% yield). Linear/branched ratio = 3.8/1; **¹H NMR (400 MHz, CDCl₃)** δ 7.08-7.04 (m, 1H), 6.92 (s, 1H), 6.82-6.76 (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); **¹³C NMR (100 MHz, CDCl₃)** 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+NH₄**]⁺ calculated for C₂₁H₂₀F₉N₂O: 487.1426, found: 487.1421.

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



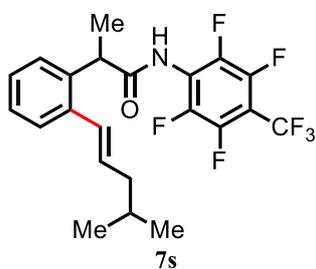
Substrate **6q** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 5/1). The desired olefination product was obtained as a white solid (34.2 mg, 68% yield). Linear/branched ratio = 5.3/1; **¹H NMR (400 MHz, CDCl₃)** δ 7.40 (d, *J* = 2.1 Hz, 1H), 7.38 (d, *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); **¹³C NMR (100 MHz, CDCl₃)** 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+NH₄**]⁺ calculated for C₂₁H₂₀Cl₂F₇N₂O: 519.0835, found: 519.0834.

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



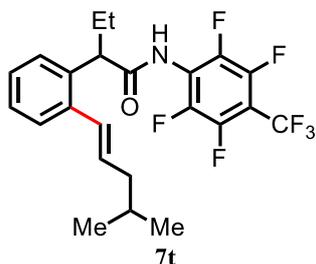
Substrate **6r** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 5/1). The desired olefination product was obtained as a white solid (41.8 mg, 83% yield). Linear/branched ratio = 4.6/1; **¹H NMR (400 MHz, CDCl₃)** δ 7.43 (d, *J* = 8.5 Hz, 1H), 7.36 (d, *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); **¹³C NMR (100 MHz, CDCl₃)** δ 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+NH₄]⁺** calculated for C₂₁H₂₀Cl₂F₇N₂O: 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)



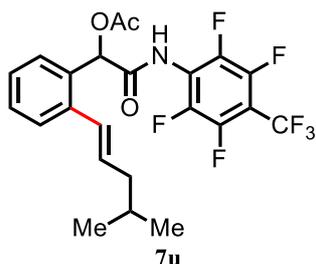
Substrate **6s** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 9/1). The desired olefination product was obtained as a white solid (28.2 mg, 63% yield). Linear/branched ratio = 4.9/1; **¹H NMR (400 MHz, CDCl₃)** δ 7.52-7.47 (m, 1H), 7.34-7.28 (m, 3H), 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); **¹³C NMR (100 MHz, CDCl₃)** δ 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+NH₄]⁺** calculated for C₂₁H₂₄F₇N₂O: 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; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 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); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 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)** $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{23}\text{H}_{26}\text{F}_7\text{N}_2\text{O}$: 479.1928, found: 479.1925.

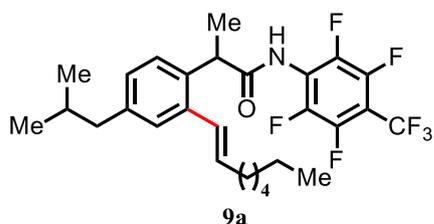
(E)-1-(2-(4-methylpent-1-en-1-yl)phenyl)-2-oxo-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)ethyl acetate (7u)



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; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 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); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 169.4,

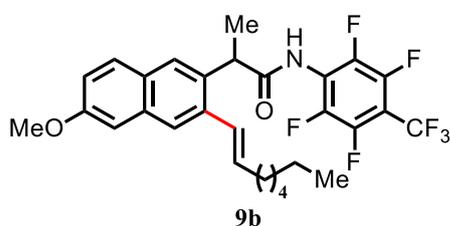
166.4, 138.1, 135.5, 130.7, 129.9, 128.3, 127.6, 127.6, 127.0, 72.7, 42.5, 29.7, 28.5, 22.3, 22.3, 20.8; **HRMS (ESI-TOF) [M+NH₄]⁺** calculated for C₂₃H₂₄F₇N₂O₃: 509.1670, found: 509.1663.

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



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.

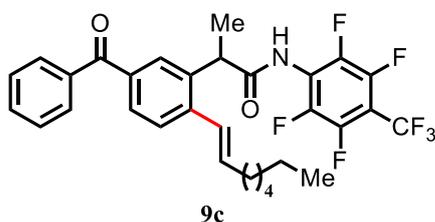
(E)-2-(6-methoxy-3-(oct-1-en-1-yl)naphthalen-2-yl)-N-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)propanamide (9b)



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),

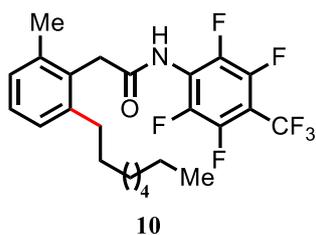
7.13 (s, 1H), 6.77 (s, 1H), 6.70 (d, $J = 15.3$ Hz, 1H), 6.26 (dt, $J = 15.4, 7.8$ Hz, 1H), 4.19 (q, $J = 7.2$ Hz, 1H), 3.93 (s, 3H), 2.27 (q, $J = 7.0$ Hz, 2H), 1.73 (d, $J = 7.1$ Hz, 3H), 1.49-1.45 (m, 2H), 1.39-1.25 (m, 6H), 0.88 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.4, 158.3, 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) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{29}\text{H}_{32}\text{F}_7\text{N}_2\text{O}_2$: 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)



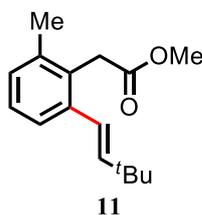
Substrate **8c** was olefinated following the general olefination procedure (eluent: hexane/ethyl acetate = 19/1 to 5/1). The desired olefination product was obtained as a white solid (32.4 mg, 56% yield). Linear/branched ratio = 3.8/1; ^1H NMR (400 MHz, CDCl_3) δ 7.82 (s, 1H), 7.78 (d, $J = 7.1$ Hz, 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}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) $[\text{M}+\text{NH}_4]^+$ calculated for $\text{C}_{31}\text{H}_{32}\text{F}_7\text{N}_2\text{O}_2$: 597.2347, found: 597.2343.

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%.); **¹H NMR (400 MHz, CDCl₃)** δ 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); **¹³C NMR (100 MHz, CDCl₃)** δ 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+NH₄]⁺** calculated for C₂₄H₃₀F₇N₂O: 495.2241, found: 495.2238.

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



To a solution of **3i** (35.8 mg, 0.08 mmol) in MeOH (4 mL), BF₃•Et₂O (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%.); **¹H NMR (400 MHz, CDCl₃)** δ 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); **¹³C NMR (100 MHz, CDCl₃)** δ 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. ¹H and ¹³C NMR Spectra of Products

