**Synthesis of Heterocyclic and Carbocyclic Fluoro-olefins by Ring-Closing
Metathesis**

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Brown**

Supporting Information

Index

Page	¹ H NMR of compound number	Page	Experimental procedure & data for compound number
S3	6	S26	7
S4	7	S27	8
S5	8	S28	9
S6	9	S29	10
S7	10	S30	13
S8	12	S31	14
S9	13	S32	15
S10	14	S33	16
S11	15	S34	17
S12	16	S35	18
S13	17	S36	19
S14	18	S37	20
S15	19	S38	21
S16	20	S39	22
S17	21	S40	23
S18	22	S41	25
S19	23	S42	26
S20	25	S43	27
S21	26		
S22	27		
S23	28 crude		
S24	28 after partial purification		
S25	38 partially purified sample after standing overnight		

Compound 6

Compound 7

Compound 8

User Name S Salim
INB Reference ss3524-046-b
h CDC13 u auto 26

Compound 9

User Name S Salim
INB Reference ss3524-007-b
h CDC13 u auto 37

Compound 10

Compound 12

ss3326-060-b □

Compound 13

SS3524 SS3804-1-B

Compound 14

Compound 15

Compound 16

S13

Compound 17

3.2917
3.2745
3.2525
3.2427

4.8328
4.8255
4.7765
4.7691
4.6466
4.6393
4.4824
4.4751
4.7670

5.3571
5.2983
5.2836
5.2493

6.0162
5.9819
5.9599
5.9476
5.9403
5.9256

7.4642
7.4373
7.4079
7.3834
7.3564
7.3344
7.3123

ss3804-006-b

Compound 18

SS3804-007-B

Compound 19

Compound 20

Compound 21

Compound 22

Compound 23

Compound 25

User Name s salim
LNB Reference ss3524-carbocycle (6 membered)
h CDCl3 u auto 59

Compound 26

Compound 27

Compound **28** crude

Compound 28 after partial purification

Compound **29** partially purified sample after standing overnight

7

$C_{13}H_{17}FN_2O_2S$

284.15

colourless oil

To a solution of Boc protected sulfamide **6** (989 mg, 2.57 mmol) in CH_2Cl_2 (50 mL) was added TFA (10 mL), the mixture was stirred for 2 h at r.t. then quenched by the addition of sat. aq. $NaHCO_3$ (50 mL). The mixture was extracted with CH_2Cl_2 (3 x 30 mL), dried ($MgSO_4$) and the solvent removed *in vacuo*. The resulting colourless oil was purified by column chromatography, eluting with Et_2O /hexane (1:9) to furnish compound **7** as a colourless oil (606 mg, 2.13 mmol, 83 %).

1H NMR (400MHz, $CDCl_3$) δ 3.73-3.66 (4H, m, N- CH_2), 4.36 (2H, s, CH_2), 4.55 (1H, dd, $J = 3.5$ Hz, $J_{H-F} = 48.5$ Hz, CH_2), 4.72 (1H, dd, $J = 3.4$ Hz, $J_{H-F} = 16.4$ Hz, CH_2), 5.01 (1H, t, $J = 6.3$ Hz, NH), 5.18 (1H, dd, $J = 17.0$, 1.3 Hz, CH_2), 5.24 (1H, dd, $J = 10.1$, 1.0 Hz, CH_2), 5.83 (1H, ddt, $J = 17.0$, 10.4, 6.8 Hz, CH), 7.33-7.24 (5H, m, CH)

^{13}C NMR (100 MHz, $CDCl_3$) δ 42.3 (d, $J_{C-F} = 33.3$ Hz, CH_2), 49.8 (CH_2), 50.5 (CH_2), 92.6 (d, $J_{C-F} = 17.3$ Hz, CH_2), 119.6 (CH_2), 127.9 (CH), 128.5 (CH), 128.6 (CH), 132.6 (CH), 135.1 (C), 161.3 (d, $J_{C-F} = 256.5$ Hz, CF)

IR ν_{max}/cm^{-1} : 3323, 2941, 1491, 1320 (SO_2), 1146 (SO_2), 854

LRMS (ES^+ , CH_3CN) m/z (relative intensity %) 285 [$M+H$] $^+$ (100)

HRMS (ES^+) Calcd for $C_{13}H_{18}FN_2O_2S$: 285.1073, found 285.1068

8

$\text{C}_{28}\text{H}_{23}\text{FN}_2\text{O}_2\text{S}$

374.01

colourless oil

To a stirring solution of sulfamide **7** (100 mg, 0.35 mmol) in THF (5 mL) was added *t*-BuOK (42.6, 0.35 mmol), 18-crown-6 (92.5, 0.35 mmol) and benzyl bromide (68 μL , 0.35 mmol). The mixture was stirred at r.t. for 10 mins then quenched by the addition of H_2O (5 mL) and extracted with Et_2O (3 x 5 mL). The combined Et_2O layers were washed with brine (10 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The resulting colourless oil was purified by column chromatography, eluting with Et_2O /hexane (1:9) to furnish compound **8** as colourless oil (101 mg, 0.27 mmol, 77 %).

^1H NMR (400MHz, CDCl_3) δ 3.72 (2H, d, $J = 6.8$ Hz, CH_2), 3.82 (2H, d, $J_{\text{H-F}} = 16.2$ Hz, CH_2), 4.40 (2H, s, CH_2), 4.46 (2H, s, CH_2), 4.43 (1H, dd, $J = 3.1$ Hz, $J_{\text{H-F}} = 48.0$ Hz, CH_2), 4.75 (1H, dd, $J = 3.1$ Hz, $J_{\text{H-F}} = 16.2$ Hz, CH_2), 5.12 (1H, dd, $J = 1.3, 17.2$ Hz, CH_2), 5.20 (1H, dd, $J = 1.0, 10.1$ Hz, CH_2), 5.83 (1H, ddt, $J = 10.1, 17.0, 6.6$ Hz, CH), 7.23 -7.38 (10H, m, CH)

^{13}C NMR (100 MHz, CDCl_3) δ 47.0 (d, $J_{\text{C-F}} = 29.7$ Hz, CH_2), 50.0 (CH_2), 50.8 (CH_2), 51.4 (CH_2), 94.9 (d, $J_{\text{C-F}} = 17.8$ Hz, CH_2), 119.7 (CH_2), 127.9 (CH), 128.0 (CH), 128.3 (CH), 127.4 (CH), 128.5 (CH x 2), 133.0 (CH), 135.7 (C), 136.4 (C), 161.0 (d, $J_{\text{C-F}} = 261$ Hz, CF)

IR $\nu_{\text{max}} / \text{cm}^{-1}$: 3031, 2921, 1331 (SO_2), 1174 (SO_2)

LRMS (ES^+ , CH_3CN) m/z (relative intensity %) 375 [$\text{M}+\text{H}]^+$ (100)

HRMS (ES^+) Calcd for $\text{C}_{20}\text{H}_{24}\text{FN}_2\text{O}_2\text{S}$: 375.1542, found 375.1516

9

$C_{14}H_{19}N_2O_2SF$

298.38

colourless oil

To a stirring solution of sulfamide **7** (100 mg, 0.33 mmol) in THF (5 mL) was added *t*-BuOK (35 mg, 0.33 mmol), 18-crown 6 (87 mg, 0.33 mmol) and iodomethane (20 μ L, 0.33 mmol), the mixture was stirred for 10 minutes, then quenched with H₂O (5 mL) and extracted with Et₂O (3 x 5 mL), the combined Et₂O layers were washed with brine (10 mL), dried (Na₂SO₄) and concentrated under reduced pressure. The resulting colourless oil purified by column chromatography, eluting with Et₂O/hexane (3:7) to furnish compound **9** as a colourless oil (74 mg, 0.25 mmol, 75 %).

¹H NMR (400MHz, CDCl₃) δ 2.83 (3H, s, CH₃), 3.70 (2H, d, J = 6.8 Hz, CH₂), 3.86 (2H, d, J_{H-F} = 14.4 Hz, CH₂), 4.37 (2H, s, CH₂), 4.58 (1H, dd, J = 3.0 Hz, J_{H-F} = 47.8 Hz, CH₂), 4.79 (1H, dd, J = 3.3 Hz, J_{H-F} = 16.2 Hz, CH₂), 5.15 (1H, dd, J = 1.0, 17.2 Hz, CH₂), 5.22 (1H, dd, J = 1.0, 10.1 Hz, CH₂), 5.84 (1H, tdd, J = 6.8, 10.1, 17.0 Hz, CH), 7.37-7.34 (5H, m, CH)

¹³C NMR (100 MHz, CDCl₃) δ 34.9 (CH₃), 49.7 (CH₂), 50.6 (CH₂), 50.9 (d, J_{C-F} = 31.0 Hz, CH₂), 94.2 (d, J_{C-F} = 17.6 Hz, CH₂), 119.8 (CH₂), 128.0 (CH), 128.8 (CH x 2), 132.7 (CH), 136.2 (C), 161.0 (d, J_{C-F} = 259.1 Hz, CF)

IR ν_{max}/cm^{-1} : 2926, 1351 (SO₂), 1194 (SO₂), 1010, 930

LRMS (ES⁺, CH₃CN) m/z (relative intensity %) 321 [M+Na]⁺ (100)

10

$C_{15}H_{21}FN_2O_2S$

312.13

colourless oil

To a stirring solution of sulfamide **7** (100 mg, 0.35 mmol) in THF (5 mL) was added *t*-BuOK (43 mg, 0.35 mmol), 18-crown-6 (93 mg, 0.35 mmol) and bromoethane (27 μ L, 0.35 mmol), the mixture was stirred at r.t. for 10 minutes then quenched with H₂O (5 mL) and extracted with Et₂O (3 x 5 mL), the combined Et₂O layers were washed with brine (10 mL), dried (Na₂SO₄) and concentrated under reduced pressure. The resulting colourless oil was purified by column chromatography, eluting with Et₂O/hexane (1:9) to furnish compound **16** as a colourless oil (75 mg, 0.24 mmol, 69 %).

¹H NMR (400MHz, CDCl₃) δ 1.22 (3H, t, J = 7.1 Hz, CH₃), 3.33 (2H, q, J = 7.1 Hz, CH₂), 3.70 (2H, d, J = 6.8 Hz, CH₂), 3.93 (2H, d, J_{H-F} = 14.7 Hz, CH₂), 4.37 (2H, s, CH₂), 4.57 (1H, tdd, J = 0.8, 3.3 Hz, J_{H-F} = 48.0 Hz, CH), 4.78 (1H, dd, J = 3.3 Hz, J_{H-F} = 16.4 Hz, CH), 5.13 (1H, dd, J = 1.5, 17.0 Hz, CH₂), 5.22 (1H, dd, J = 1.5, 10.1 Hz, CH₂), 5.84 (1H, tdd, J = 6.6, 10.0, 17.0 Hz, CH), 7.32-7.37 (5H, m, CH)

¹³C NMR (100 MHz, CDCl₃) δ 12.8 (CH₃), 42.5 (CH₂), 47.0 (d, J_{C-F} = 30.7 Hz, CH₂), 49.5 (CH₂), 50.4 (CH₂), 94.5 (d, J_{C-F} = 17.8 Hz, CH₂), 119.4 (CH₂), 127.7 (CH), 128.5 (CH), 128.6 (CH), 132.8 (CH), 136.1 (C), 161.1 (d, J_{C-F} = 259.0 Hz, CF)

IR ν_{max} / cm⁻¹: 2976, 2928, 1326 (SO₂), 1148 (SO₂), 1028

LRMS (ES⁺, CH₃CN) m/z (relative intensity %) 313 [M+H]⁺ (100)

HRMS (ES⁺) Calcd for C₁₅H₂₂FN₂O₂S: 313.1386, found 313.1376

13 $\text{C}_{11}\text{H}_{13}\text{FN}_2\text{O}_2\text{S}$

256.01

white solid

To a stirring solution of fluoro-olefin **7** (40 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) was added ruthenium complex **11** (7.1 mg, 8.4 μmol), the mixture was heated at reflux for 6 h, then concentrated under reduced pressure. The resulting brown oil was purified by column chromatography, eluting with Et_2O /hexane (2:8) to furnish compound **13** as a white solid (28 mg, 0.11 mmol, 79 %).

^1H NMR (400MHz, CDCl_3) δ 3.70 (2H, dd, $J = 6.0$ Hz, $J_{\text{H-F}} = 3.8$ Hz CH_2), 3.95 (2H, dd, $J = 7.0$ Hz, $J_{\text{H-F}} = 8.5$ Hz, CH_2), 4.32 (2H, s, CH_2), 4.76 (1H, t, $J = 6.6$ Hz, NH), 5.34 (1H, td, $J = 5.9$ Hz, $J_{\text{H-F}} = 19.3$ Hz), 7.33-7.40 (5H, m, CH)

^{13}C NMR (100 MHz, CDCl_3) δ 40.4 (d, $J_{\text{C-F}} = 10.6$ Hz, CH_2), 42.6 (d, $J_{\text{C-F}} = 39.5$ Hz, CH_2), 103.5 (d, $J_{\text{C-F}} = 19.0$ Hz, CH_2), 128.3 (CH), 128.6 (CH), 128.9 (CH), 135.3 (C), 161.0 (d, $J_{\text{C-F}} = 267.5$ Hz, CF)

IR $\nu_{\text{max}} / \text{cm}^{-1}$: 3276 (NH), 3030, 1672, 1341 (SO_2), 1152 (SO_2), 727

LRMS (ES^+ , CH_3CN) m/z (relative intensity %) 297 $[\text{M} + \text{CH}_3\text{CN}]^+$ (100)

Mpt (CH_2Cl_2) = 118-120 $^\circ\text{C}$

14

$C_{18}H_{19}FN_2O_2S$

346.42

colourless oil

To a stirring solution of fluoro-olefin **8** (50 mg, 0.15 mmol) in CH_2Cl_2 (2.5 mL) was added ruthenium complex **11** (7.6 mg, 9.0 μ mol). The mixture was heated in a sealed vial for 10 h at 100 °C then concentrated under reduced pressure. The resulting brown oil was purified by column chromatography, eluting with Et_2O /hexane (2:8) to furnish compound **14** as a colourless oil (36 mg, 0.10 mmol, 78 %).

1H NMR (400MHz, $CDCl_3$) δ 3.72 (2H, dd, $J = 6.1$ Hz, $J_{H-F} = 3.6$, CH_2), 3.90 (2H, d, $J_{H-F} = 10.6$ Hz, CH_2), 4.50 (2H, s, CH_2), 4.40 (2H, s, CH_2), 5.54 (1H, td, $J = 6.1$ Hz, $J_{H-F} = 18.0$ Hz, CH), 7.38 -7.42 (10H, m, CH)

^{13}C NMR (100 MHz, $CDCl_3$) δ 40.4 (CH_2), 45.7 (CH_2), 46.0 (CH_2), 52.4 (d, $J_{C-F} = 52.4$ Hz, CH_2), 105.9 (d, $J_{C-F} = 18.5$ Hz, CH_2), 128.0 (CH), 128.5 (CH), 129.0 (CH), 135.3 (C), 135.9 (C), 160.0 (d, $J_{C-F} = 269.6$ Hz, CF)

IR ν_{max}/cm^{-1} : 3044, 3030, 2887, 1495, 1369 (SO_2), 1156 (SO_2)

LRMS (ES^+ , CH_3CN) m/z (relative intensity %) 347 $[M+H]^+$ (100)

HRMS (ES^+) Calcd for $C_{18}H_{20}FN_2O_2S$: 347.1229, found 347.1207

15 $\text{C}_{12}\text{H}_{15}\text{FN}_2\text{O}_2\text{S}$

270.32

colourless oil

To a stirring solution of fluoro-olefin **9** (30 mg, 0.10 mmol) in CH_2Cl_2 (2.5 mL) was added ruthenium complex **11** (5.0 mg, 6.4 μmol). The mixture was heated in a sealed vial for 10 h at 100 °C, then concentrated under reduced pressure. The resulting brown oil was purified by column chromatography, eluting with Et_2O /hexane (2:8) to furnish compound **15** as a colourless oil (21 mg, 0.078 mmol, 77 %).

^1H NMR (400MHz, CDCl_3) δ 3.00 (3H, s, CH_3), 3.64 (2H, dd, $J = 6.2$ Hz, $J_{\text{H-F}} = 3.5$ Hz, CH_2), 4.05 (2H, d, $J_{\text{H-F}} = 10.8$ Hz, CH_2), 4.40 (2H, s, CH_2), 5.54 (1H, dt, $J = 6.3$ Hz, $J_{\text{H-F}} = 17.9$ Hz, CH), 7.35-7.38 (5H, m, CH)

^{13}C NMR (100 MHz, CDCl_3) δ 36.5 (CH_3), 40.1 (d, $J = 10.8$ Hz, CH_2), 50.0 (d, $J_{\text{C-F}} = 36.0$ Hz, CH_2), 52.4 (CH_2), 104.5 (d, $J_{\text{C-F}} = 18.0$ Hz, CH_2), 128.0 (CH), 128.2 (CH), 128.7 (CH), 135.8 (C), 160.0 (d, $J_{\text{C-F}} = 267.0$ Hz, CF)

IR ν_{max} / cm^{-1} : 2969, 1367 (SO_2), 1454, 1188 (SO_2), 982

LRMS (ES^+ , CH_3CN) m/z (relative intensity %) 271 $[\text{M}+\text{H}]^+$ (100)

16 $\text{C}_{13}\text{H}_{17}\text{FN}_2\text{O}_2\text{S}$

284.35

colourless oil

To a stirring solution of fluoro-olefin **10** (30 mg, 0.107 mmol) in CH_2Cl_2 (2.5 mL) was added ruthenium complex **11** (5.5 mg, 6.4 μmol). The mixture was heated in a sealed vial for 10 h at 100 $^\circ\text{C}$, then concentrated under reduced pressure. The resulting brown oil was purified by column chromatography, eluting with Et_2O /hexane (1:9) to furnish compound **16** as a colourless oil (23.1 mg, 0.081 mmol, 85 %).

^1H NMR (400MHz, CDCl_3) δ 1.23 (3H, t, $J = 7.1$ Hz, CH_3), 3.41 (2H, q, $J = 7.1$ Hz, CH_2), 3.63 (2H, dd, $J = 6.1$ Hz, $J_{\text{H-F}} = 3.5$ Hz, CH_2), 4.06 (2H, d, $J_{\text{H-F}} = 10.6$ Hz, CH_2), 4.40 (2H, s, CH_2), 5.47 (1H, td, $J = 6.1$ Hz, $J_{\text{H-F}} = 18.0$ Hz, CH), 7.31-7.39 (5H, m, CH)

^{13}C NMR (100 MHz, CDCl_3) δ 13.6 (CH_3), 40.1 (d, $J_{\text{C-F}} = 10.7$, CH_2), 43.6 (CH_2), 45.8 (d, $J_{\text{C-F}} = 36.3$ Hz, CH_2), 52.0 (CH_2), 104.4 (d, $J_{\text{C-F}} = 18.0$ Hz, CH_2), 128.0 (CH), 128.2 (CH), 128.7 (CH), 135.8 (C), 160.3 (d, $J_{\text{C-F}} = 257.0$ Hz, CF)

IR ν_{max} / cm^{-1} : 2982, 2928, 1454, 1366 (SO_2), 1152 (SO_2), 1003

LRMS (ES^+ , CH_3CN) m/z (relative intensity %) 285 $[\text{M}+\text{H}]^+$ (100)

HRMS (ES^+) Calcd for $\text{C}_{13}\text{H}_{18}\text{FN}_2\text{O}_2\text{S}$: 285.1073, found 285.1061

17

$C_{13}H_{16}FN$

205.16

colourless oil

To a stirring solution of *N*-allyl-*N*-benzylamine (400 mg, 2.72 mmol) in DMF (7 mL) was added 1M NaHMDS (270 μ L, 2.72 mmol), 3-chloro-2-fluoro-propene (246 μ L, 2.72 mmol) and NaI (17.0 mg, 0.11mmol). The mixture was stirred at r.t. for 10 h. then quenched with H₂O (10 mL) and extracted with EtOAc (3 x 10 mL), the combined EtOAc layers were washed with H₂O (10 mL x 3), brine (3 x 10 mL) dried (Na₂SO₄) and concentrated under reduced pressure. The resulting brown oil was purified by column chromatography, eluting with Et₂O/hexane (2:8) to furnish compound **17** as colourless oil (403 mg, 1.10 mmol, 71 %).

¹H NMR (400MHz, CDCl₃) δ 3.26 (2H, d, J = 6.3 Hz, CH₂), 3.27 (2H, d, J_{H-F} = 15.0 Hz, CH₂), 3.76 (2H, s, CH₂), 4.47 (1H, dd, J = 2.6 Hz, J_{H-F} = 49.5 Hz, CH₂), 4.80 (1H, dd, J = 2.6 Hz, J_{H-F} = 17.1 Hz, CH₂), 5.26 (1H, dd, J = 10.3, 1.8, Hz, CH₂), 5.33(1H, dd, J = 17.0, 1.8 Hz, CH₂), 5.97 (1H, ddt, J = 17.0, 10.1, 6.3, Hz, CH), 7.12-7.29 (5H, m, CH)

¹³C NMR (100 MHz, CDCl₃) δ 51.9 (d, J_{C-F} = 28.1 Hz, CH₂), 55.4 (CH₂), 56.5 (CH₂), 91.6 (d, J_{C-F} = 18.5 Hz, CH₂), 116.7 (CH₂), 125.9 (CH), 126.2 (CH), 127.7 (CH), 134.0 (CH), 137.1 (C), 162.3 (d, J_{C-F} = 261 Hz, CF)

IR ν_{max} / cm⁻¹: 3085, 3030, 1494, 1452, 1272, 1102

LRMS (ES⁺, CH₃CN) m/z (relative intensity %) 206 [M+H]⁺ (100)

18 $\text{C}_{10}\text{H}_{12}\text{FN}$

165.10

pale yellow oil

To a stirring solution of **17** (50 mg, 0.24 mmol) in CH_2Cl_2 (3 mL) was added TFA (18 μL , 0.24) and ruthenium complex **11** (24 mg, 28.0 μmol). The mixture was heated in a sealed vial for 10 h at 100 $^\circ\text{C}$, then quenched by the addition of saturated aqueous NaHCO_3 (3 mL). The mixture was extracted with CH_2Cl_2 (3 x 3 mL), dried (MgSO_4) and the solvent removed *in vacuo*. The resulting brown oil was purified by column chromatography, eluting with Et_2O /hexane (1:9) to furnish compound **18** as a pale yellow oil (30 mg, 0.18 mmol, 75 %).

^1H NMR (400MHz, CDCl_3) δ 1.63 (1H, brs, NH), 3.36 (2H, d, $J_{\text{H-F}} = 14.2$ Hz, CH_2), 3.90 (2H, s, CH_2), 4.50 (1H, dd, $J = 2.8$ Hz, $J_{\text{H-F}} = 49.6$ Hz, CH_2), 4.73 (1H, dd, $J = 2.8$ Hz, $J_{\text{H-F}} = 17.1$ Hz, CH_2), 7.12-7.29 (5H, m, CH)

^{13}C NMR (100 MHz, CDCl_3) δ 48.9 (d, $J_{\text{C-F}} = 30.2$ Hz, CH_2), 52.6 (CH_2), 91.6 (d, $J_{\text{C-F}} = 18.2$ Hz, CH_2), 127.3 (CH), 128.4 (CH), 128.6 (CH), 139.8 (C), 164.2 (d, $J_{\text{C-F}} = 257$ Hz, CF)

IR $\nu_{\text{max}} / \text{cm}^{-1}$: 3352, 3087, 3050, 2921, 1687, 1488, 1445, 1195

LRMS (ES^+ , CH_3CN) m/z (relative intensity %) 166 $[\text{M}+\text{H}]^+$ (100)

19

$C_{14}H_{18}FN$

219.14

colourless oil

To a stirring solution of *N*-benzyl-*N*-(3-butenyl)amine (200 mg, 1.24 mmol) in DMF (7 mL) was added a solution of 1M NaHMDS (190 μ L, 1.9 mmol), 3-chloro-2-fluoropropene (148 μ L, 1.9 mmol) and NaI (9.3 mg, 0.06 mmol), the mixture was stirred at r.t. for 10 h then quenched with H_2O (10 mL) and extracted with EtOAc (3 x 10 mL), the combined EtOAc layers were washed with H_2O (10 mL x 3), brine (3 x 10 mL) dried (Na_2SO_4) and concentrated under reduced pressure. The resulting brown oil was purified by column chromatography, eluting with Et₂O/hexane (2:8) to furnish compound **19** as a colourless oil (241 mg, 1.10 mmol, 89 %).

1H NMR (400MHz, $CDCl_3$) δ 2.26 (2H, dt, $J = 7.4, 6.8$ Hz, CH_2), 2.62 (2H, t, $J = 7.4$ Hz, CH_2), 3.18 (2H, d, $J_{H-F} = 15.2$ Hz, CH_2), 3.67 (2H, s, CH_2), 4.46 (1H, dd, $J = 2.6$ Hz, $J_{H-F} = 49.5$ Hz, CH), 4.67 (1H, dd, $J = 2.5$ Hz, $J_{H-F} = 17.2$ Hz, CH), 4.97 (1H, ddt, $J = 10.1, 2.3, 1.0$, Hz, CH), 5.03 (1H, dd, $J = 17.1, 3.5$, Hz, CH_2), 5.79 (1H, ddt, $J = 16.9, 10.7, 6.8$, Hz, CH), 7.22-7.32 (5H, m, CH)

^{13}C NMR (100 MHz, $CDCl_3$) δ 31.8 (CH_2), 43.0 (CH_2), 53.4 (d, $J_{C-F} = 28.4$ Hz, CH_2), 57.9 (CH_2), 92.5 (d, $J_{C-F} = 17.9$ Hz, CH_2), 115.6 (CH_2), 126.9 (CH), 128.2 (CH), 128.7 (CH), 132.6 (CH), 139.2 (C), 163.9 (d, $J_{C-F} = 260$ Hz, CF)

IR ν_{max} / cm^{-1} : 3085, 3030, 2948, 1494, 1453, 911

LRMS (ES^+ , CH_3CN) m/z (relative intensity %) 220 [$M+H$] $^+$ (100)

HRMS (ES^+) Calcd for $C_{14}H_{19}FN$: 220.1501, found 220.1490

20

$C_{12}H_{14}FN$

191.11

pale yellow oil

To a stirring solution of **19** (40 mg, 0.18 mmol) in CH_2Cl_2 (3 mL) was added ruthenium complex **11** (18.0 mg, 21.6 μ mol). The mixture was heated in a sealed vial for 10 h at 100 $^{\circ}C$, then concentrated under reduced pressure. The resulting brown oil was purified by column chromatography, eluting with Et_2O /hexane (2:8) to furnish compound **20** as a pale yellow oil (29 mg, 0.15 mmol, 83 %).

1H NMR (400MHz, $CDCl_3$) δ 2.16-2.19 (2H, m, CH_2), 2.54 (2H, tt, $J = 5.6, 1.3$ Hz, CH_2), 3.02 (2H, dd, $J = 1.5, 2.5$, CH_2), 3.63 (2H, s, CH_2), 5.25 (1H, dtd, $J = 1.5, 1.3, 4.0$ Hz, $J_{H-F} = 15.7$ Hz, CH), 7.26-7.36 (5H, m, CH)

^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0 (CH_2), 49.4 (CH_2), 51.6 (d, $J_{C-F} = 32.5$ Hz, CH_2), 62.3 (CH_2), 100.0 (d, $J_{C-F} = 12.4$ Hz, CH), 127.5 (CH), 128.5 (CH), 129.2 (CH), 138.0 (C), 157.1 (d, $J_{C-F} = 253$ Hz, CF)

IR ν_{max}/cm^{-1} : 2933, 1496, 1554, 1168, 1148, 906

LRMS (ES^+ , CH_3CN) m/z (relative intensity %) 192 $[M+H]^+$ (100)

HRMS (ES^+) Calcd for $C_{12}H_{14}FN$: 192.1188, found 192.1206

21

$C_{13}H_{19}FO_4$

258.13

colourless oil

To a stirring solution of diethyl 2-(2-fluoroallyl)malonate (50 mg, 0.24 mmol) in DMF (5 mL) was added a 1M solution of NaHMDS (240 μ L, 0.24 mmol), the mixture was stirred for 10 mins, allyl bromide (40 μ L, 0.24 mmol) was added the reaction was stirred at 60 $^{\circ}$ C for 12 h. The mixture was quenched with H₂O (5 mL) and extracted with EtOAc (3 x 10 mL). The combined EtOAc layers were washed with brine (10 mL), dried (Na₂SO₄) and concentrated under reduced pressure. The resulting colourless oil purified by column chromatography, eluting with Et₂O/hexane (1:10) to furnish compound **21** as colourless oil (50 mg, 0.19 mmol, 80 %).

¹H NMR (400MHz, CDCl₃) δ 1.63 (6H, t, J = 7.1 Hz, CH₃), 2.67 (2H, d, J = 7.0 Hz, CH₂), 2.78 (2H, d, J_{H-F} = 21.0 Hz, CH₂), 4.13 (4H, q, J = 7.1 Hz, CH₂), 5.25 (1H, dd, J = 2.8 Hz, J_{H-F} = 49.3 Hz, CH₂), 5.60 (1H, dd, J = 2.8 Hz, J_{H-F} = 17.0 Hz, CH₂), 5.09-5.04 (2H, m, CH₂), 5.56 (1H, ddt, J = 17.9, 10.3, 7.0 Hz, CH)

¹³C NMR (100 MHz, CDCl₃) δ 14.0 (CH₃), 35.0 (d, J_{C-F} = 26.5 Hz, CH₂), 36.3 (CH₂), 55.8 (d, J_{C-F} = 3.2 Hz, C), 61.5 (CH₂), 94.3 (d, J = 19.3 Hz, CH₂) 119.6 (CH₂), 132.0 (CH), 162. (d, J_{C-F} = 258.0 Hz, CF), 170.1 (CO)

IR ν_{max} / cm⁻¹: 3398, 1734(C=O), 1286, 1207, 1184

LRMS (ES⁺, CH₃CN) m/z (relative intensity %) 259 [M+H]⁺ (100)

HRMS (ES⁺) Calcd for C₁₃H₂₀FO₄: 259.1345, found 259.1355

22 $C_{14}H_{21}FO_4$

272.14

colourless oil

To a stirring solution of diethyl 2-(2-fluoroallyl)malonate (100 mg, 0.48 mmol) in DMF (5 mL) was added a 1M solution of NaHMDS (480 μ L, 0.48 mmol), the mixture was stirred for 10 mins, 4-bromo-1-butene (88 μ L, 0.48 mmol) was added and the reaction was stirred at 60 $^{\circ}$ C for 12 h. The mixture was quenched with H₂O (10 mL) and extracted with EtOAc (3 x 10 mL), the combined EtOAc layers were washed with brine (10 mL), dried (Na₂SO₄) and concentrated under reduced pressure. The resulting colourless oil purified by column chromatography, eluting with Et₂O/hexane (3:7) to furnish compound **22** as colourless oil (116.7 mg, 0.43 mmol, 90 %).

¹H NMR (400MHz, CDCl₃) δ 1.10 (6H, t, J = 7.1 Hz, CH₃), 1.76-1.80 (2H, m, CH₂), 1.87-1.92 (2H, m, CH₂), 2.73 (2H, d, J_{H-F} = 21.0 Hz, CH₂), 4.03 (4H, q, J = 7.1 Hz, CH₂), 4.15 (1H, dd, J = 3.1 Hz, J_{H-F} = 49.7 Hz, CH₂), 4.48 (1H, dd, J = 2.8 Hz, J_{H-F} = 17.2 Hz, CH₂), 4.80 (1H, dd, J = 1.3, 10.1 Hz, CH), 4.86 (1H, dd, J = 1.3, 17.0 Hz, CH₂), 5.61 (1H, ddt, J = 1.5, 17.0, 6.3 Hz, CH)

¹³C NMR (100 MHz, CDCl₃) δ 13.9 (CH₃), 28.3 (CH₂), 31.0 (CH₂), 35.1 (d, J_{C-F} = 25.8 Hz, CH₂), 55.8 (d, J_{C-F} = 2.9 Hz, CH), 61.4 (d, J_{C-F} 11.0 Hz, CH₂), 93.9 (d, J = 19.7 Hz, CH₂) 115.1 (CH₂), 137.3 (CH), 162. (d, J_{C-F} = 261.0 Hz, CF), 170.5 (CO)

IR ν_{max} / cm⁻¹: 1732 (C=O), 1463, 1207, 1178

LRMS (ES⁺, CH₃CN) m/z (relative intensity %) 273 [M+H]⁺ (100)

HRMS (ES⁺) Calcd for C₁₄H₂₁FO₄: 273.1502, found 273.1497

23 $C_{15}H_{23}FO_4$

286.17

colourless oil

To a stirring solution of diethyl 2-(2-fluoroallyl)malonate (100 mg, 0.48 mmol) in DMF (5 mL) was added a 1M solution of NaHMDS (480 μ L, 0.48 mmol), the mixture was stirred for 10 mins, 5-bromo-1-pentane (56 μ L, 0.48 mmol) was added the reaction was stirred at 60 °C for 12 h. The mixture was quenched with H₂O (10 mL) and extracted with EtOAc (3 x 10 mL), the combined EtOAc layers were washed with brine (10 mL), dried (Na₂SO₄) and concentrated under reduced pressure. The resulting colourless oil was purified by column chromatography, eluting with Et₂O/hexane (3:7) to furnish compound **23** as colourless oil (118.2 mg, 0.41 mmol, 85 %).

¹H NMR (400MHz, CDCl₃) δ 1.24 (6H, t, J = 7.0 Hz, CH₃), 1.33-1.20 (2H, m, CH₂), 1.97-1.98 (2H, m, CH₂), 2.07 (2H, q, J = 7.0 Hz, CH₂), 2.88 (2H, d, J_{H-F} = 21.5 Hz, CH₂), 4.19 (4H, q, J = 7.0 Hz, CH₂), 4.31 (1H, dd, J = 2.5 Hz, J_{H-F} = 49.2 Hz, CH₂), 4.63 (1H, dd, J = 2.5 Hz, J_{H-F} = 17.0 Hz, CH), 4.96 (1H, dd, J = 1.0, 10.1 Hz, CH₂), 5.01 (1H, dd, J = 1.5, 17.1 Hz, CH), 5.77 (1H, ddt, J = 17.1, 10.5, 6.2 Hz, CH)

¹³C NMR (100 MHz, CDCl₃) δ 14.2 (CH₃), 23.5 (CH₂), 31.4 (CH₂), 33.9 (CH₂), 35.3 (d, J_{C-F} = 26.0 Hz, CH₂), 56.3 (C), 61.7 (CH₂), 94.2 (d, J = 20.3 Hz, CH₂), 115.2 (CH₂), 138.2 (CH), 162.7 (d, J_{C-F} = 257.7 Hz, CF), 170.9 (CO)

IR ν_{max} / cm⁻¹: 2982, 1732 (C=O), 1180, 1043, 913, 858

LRMS (ES⁺, CH₃CN) m/z (relative intensity %) 350 [M+Na+CH₃CN]⁺ (100)

HRMS (ES⁺) Calcd for C₁₅H₂₃FO₄Na: 309.1472, found 309.1472

25 $\text{C}_{12}\text{H}_{17}\text{FO}_4$

244.11

colourless oil

To a stirring solution of **22** (30 mg, 0.12 mmol) in CH_2Cl_2 (2.5 mL) was added ruthenium complex **11** (10.5 mg, 12 μmol). The mixture was heated in a sealed vial for 10 h at 100 $^\circ\text{C}$, concentrated under reduced pressure. The resulting brown oil was purified by column chromatography, eluting with Et_2O /hexane (2:8) to furnish compound **25** as a colourless oil (22.0 mg, 0.09 mmol, 73 %).

^1H NMR (400 MHz, CDCl_3) δ 1.23 (6H, t, $J = 7.1$ Hz, CH_3), 2.13-2.07 (2H, m, CH_2), 2.73 (2H, t, $J = 2.5$ Hz, CH_2), 4.21 (4H, q, $J = 7.1$ Hz, CH_2), 5.18 (1H, td, $J = 2.5$ Hz, $J_{\text{H-F}} = 17.0$ Hz, CH)

^{13}C NMR (100 MHz, CDCl_3) δ 14.0 (CH_3), 19.7 (d, $J_{\text{C-F}} = 8.0$ Hz, CH_2), 21.14 (CH_2), 30.6 (d, $J_{\text{C-F}} = 29.0$ Hz, CH), 54.0 (CH_2), 61.7 (CH_2), 101.0 (d, $J_{\text{C-F}} = 15.3$ Hz, CH_2), 156.5 (d, $J_{\text{C-F}} = 253.0$ Hz, CF), 170.5 (CO)

IR $\nu_{\text{max}}/\text{cm}^{-1}$: 1735 (C=O), 1448, 1251, 1045, 913

LRMS (ES^+ , CH_3CN) m/z (relative intensity %) 245 $[\text{M}+\text{H}]^+$ (100)

26 $C_{13}H_{19}FO_4$

258.29

colourless oil

To a stirring solution of **23** (30 mg, 0.10 mmol) in CH_2Cl_2 (2.5 mL) was added ruthenium complex **11** (8.5 mg, 10 μ mol). The mixture was heated in a sealed vial for 4 h at 100 $^{\circ}C$, concentrated under reduced pressure. The resulting brown oil was purified by column chromatography, eluting with Et_2O /hexane (2:8) to furnish compound **26** as a colourless oil (20.0 mg, 0.08 mmol, 77 %).

1H NMR (400MHz, $CDCl_3$) δ 1.25 (6H, t, $J = 7.2$ Hz, CH_3), 1.69-1.62 (2H, m, CH_2), 2.10-2.02 (2H, m, CH_2), 2.25-2.21 (2H, m, CH_2), 2.90 (2H, d, $J_{H-F} = 6.0$ Hz, CH_2), 4.20 (4H, m, CH_2), 5.36 (1H, dt, $J = 6.5$ Hz, $J_{H-F} = 19.0$ Hz, CH)

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2 (CH_3), 22.9 (CH_2), 23.2 (d, $J_{C-F} = 8.0$ Hz, CH_2), 35.8 (d, $J_{C-F} = 25.0$ Hz, CH_2), 35.5 (CH_2), 54.5 (C), 61.7 (CH_2), 106.9 (d, $J_{C-F} = 21.48$ Hz, CH_2), 160.1 (d, $J_{C-F} = 285.9$ Hz, CF), 170.9 (CO)

IR ν_{max}/cm^{-1} : 2979, 1733 (C=O), 1254, 1224, 1186, 1163

LRMS (ES^+ , CH_3CN) m/z (relative intensity %) 281 $[M+Na]^+$ (100)

27

$\text{C}_{13}\text{H}_{12}\text{FO}$

192.23

colourless oil

To a stirring solution of 2-allylphenol (389 μL , 2.98 mmol) in DMF (5 mL) was added a solution of NaHMDS in THF (2.98 mL, 1M, 2.98 mmol), the mixture was stirred for 30 minutes. 3-chloro-2-fluoropropene (280 mg, 2.98 mmol) was added and the mixture stirred at r.t. for 12 h. The reaction mixture was quenched with water (10 mL), extracted with Et₂O (3x10 mL). The combined ether layers were washed with brine (10 mL), dried (MgSO₄) and concentrated *in vacuo*. The resulting colourless oil was purified by column chromatography, eluting with EtOAc/hexane (2:98) to furnish compound **27** as colourless oil (570 mg, 2.98 mmol, 99 %).

¹H NMR (400MHz, CDCl₃) δ 3.46 (2H, d, J = 6.7 Hz, CH₂), 4.57 (2H, d, J = 9.1 Hz, CH₂), 4.73 (1H, ddq, J = 3.3, 48.6, 1.0 Hz, CH₂), 4.87 (1H, dd, J = 3.3, 16.7 Hz, CH₂), 5.14-5.05 (2H, m, CH₂), 6.03 (1H, ddt, J = 16.7, 10.0, 6.7 Hz, CH), 6.87 (1H, d, J = 8.0 Hz, CH), 6.98 (1H, t, J = 7.5 Hz, CH), 6.84-7.04 (2H, m, CH)

¹³C NMR (75 MHz, CDCl₃) δ 34.5 (CH₂), 47.0 (d, $J_{\text{C-F}}$ = 37.3 Hz, CH₂), 92.9 (d, $J_{\text{C-F}}$ = 15.8 Hz, CH₂), 111.9 (CH), 115.7 (CH₂), 121.7 (CH), 127.5 (CH), 129.4 (C), 130.3 (CH), 136.9 (CH), 155.8 (C), 161.5 (d, $J_{\text{C-F}}$ = 257.7 Hz, CH₂)

IR ν_{max} / cm⁻¹: 1685, 1491, 1452, 1238, 1217, 854, 750.

LRMS (ES⁺, CH₃CN) m/z (relative intensity %) 215 [M+Na]⁺ (100)