

Supporting Information

Brønsted Acid-Mediated Selective α -Alkenylation of 3,4-Dihydro-2*H*-pyrans

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1. General methods

All experiments were conducted with a Schlenk tube under an argon atmosphere. Flash column chromatography was performed over silica gel (200-300 mesh). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was accomplished by UV light (254 nm), phosphomolybdic acid or KMnO_4 staining solutions followed by heating, also by Gas Chromatograph-Mass spectrometer analysis (GC-MS). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectrum were recorded at ambient temperature using Bruker AscendTM 400 (400 MHz) spectrometer, Bruker AVANCE III 500M spectrometers or JNM-ECZ500R/S1 (500 MHz) spectrometer. ^1H NMR chemical shifts (in ppm) were referenced to CDCl_3 ($\delta = 7.26$ ppm), Acetone- d_6 ($\delta = 2.05$ ppm) and DMSO- d_6 ($\delta = 2.50$ ppm) as internal standards. ^{13}C NMR spectrum were obtained by using the same NMR spectrometers and were calibrated with CDCl_3 ($\delta = 77.0$ ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd, = double doublet, dt = double triplet, td = triple doublet, m = multiplet. HRMS data were obtained on Thermo Scientific Orbitrap Elite Mass Spectrometer with an ESI source (Ion Trap) or Agilent 7820A GC-MS with EI mode.

2. Optimization of Experimental Conditions

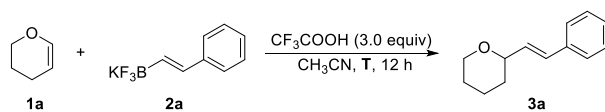


Table S1^[a]

Entry	T /°C	Yield of 3a (%) ^b
1	-30	46
2	-10	50
3	RT	64(63 °)
4	40	50
5	60	60
6	80	61
7	120	32

^[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.5 mmol, 2.5 equiv), CF₃COOH (0.6 mmol, 3.0 equiv),

CH₃CN (2.0 mL). ^[b] Determined by GC analysis by using dodecane as the internal standard. ^[c] Isolated yield.

Table S2^[a]

Entry	Additive (1 equiv)	Yield of 3a (%) ^b
1	Zn(OTf) ₂	53
2	ZnI ₂	56
3	FeCl ₂	73
4	Fe(OAc) ₂	54
5	Fe(OTf) ₂	63
6	NaOTf	55
7	Bromoferrocene	63
8	Ferrocene	58
9	CuI	52
10	Ni(dppf)Cl ₂	50

^[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.5 mmol, 2.5 equiv), CF₃COOH (0.6 mmol, 3.0 equiv),

CH₃CN (2.0 mL). **additive (1.0 equiv)** ^[b] Determined by GC analysis by using dodecane as the internal standard.

Table S3^[a]

Entry	FeCl ₂ (X equiv)	Yield of 4a (%) ^b
1	0.1	60
2	0.2	76
3	0.5	75
4	1.5	73
5	2.0	66

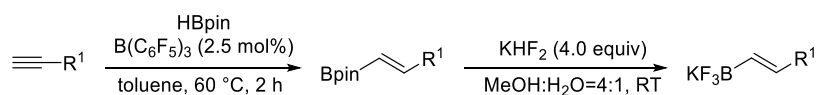
^[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.5 mmol, 2.5 equiv), CF₃COOH (0.6 mmol, 3.0 equiv),

CH₃CN (2.0 mL). **FeCl₂ (X equiv)** ^[b] Determined by GC analysis by using dodecane as the internal standard; ^[c]

Isolated yield.

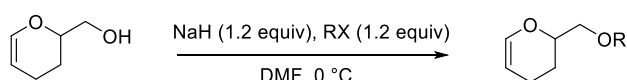
3. General procedures for the preparation of the starting materials

3.1 General procedure A for preparation of potassium alkenyltrifluoroborates (2a-2t)^{1,2}



To a 50 mL Schlenk flask equipped with a magnetic stirring bar, B(C₆F₅)₃ (2.5 mol%) was added and the flask was evacuated and refilled with argon (three times). The alkyne compound (1.0 equiv) was dissolved in toluene and added into the flask. The reaction mixture was stirred and heated at 60 °C for 2 h. After cooling to room temperature, the reaction mixture was evaporated to dryness in vacuo. Then the crude product and MeOH was added to a 100 mL Erlenmeyer flask equipped with a magnetic stirring bar. An aqueous solution of potassium hydrogen fluoride (KHF₂, 4 M in H₂O, 4.0 equiv) was slowly added to the flask. Upon completion of the addition, the flask was stirred overnight. The resulting mixture was transferred to a 250 mL round-bottom flask, and the mixture was diluted with toluene for azeotropic removal water. The biphasic mixture was concentrated under reduced pressure using rotary evaporation (20 mbar/40–50 °C). Subsequently, toluene/MeOH mixture (v/v = 10: 1) were added to the resulting residue and concentrated under reduced pressure. This process was repeated four times. The resulting residue was dissolved in acetone and filtered to remove insoluble salts. The combined filtrate was diluted with toluene and concentrated under reduced pressure. This cycle was repeated two times. The flask was dried overnight under high vacuum on a Schlenk line to give the desired potassium trifluoroborates as white solid.

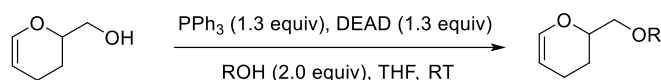
3.2 General procedure B for preparation of 2-substituted 3,4-dihydro-2H-pyrans (4c-l)³



To a 100 mL Schlenk flask equipped with a magnetic stirring bar and evacuated and refilled with argon (three times), 2-hydroxymethyl-3,4-dihydro-2H-pyran in DMF was

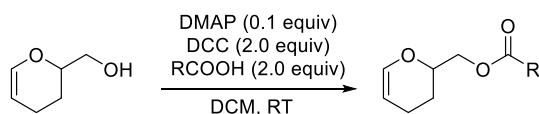
added and cooled to 0 °C. Then NaH (1.2 equiv) was slowly added. The mixture was stirred for 20 min and halide compound (1.2 equiv) was then added dropwise. After the starting material was completely consumed (detected by TLC), the reaction mixture was diluted with ethyl acetate, washed with saturated aqueous NH₄Cl (2 times), brine (2 times), dried over Na₂SO₄ and evaporated under reduced pressure. The crude reaction was purified by column chromatography to afford corresponding product.

3.3 General procedure C for preparation of 2-substituted 3,4-dihydro-2*H*-pyrans (4a-b, 4q)⁴



To a 100 mL Schlenk flask equipped with a magnetic stirring bar, 2-hydroxymethyl-3,4-dihydro-2*H*-pyran and PPh₃ (1.3 equiv) were added and the flask was evacuated and refilled with argon (three times). Dry THF (20 mL) and phenol compound (2.0 equiv) was added at room temperature. Then, diethyl azodicarboxylate (1.3 equiv) was added dropwise. After stirring for 4 h, the reaction mixture was diluted with ethyl acetate, washed with saturated aqueous NH₄Cl (2 times), brine (2 times), dried over Na₂SO₄ and evaporated under reduced pressure. The crude reaction was purified by column chromatography to afford corresponding product.

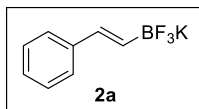
3.4 General procedure D for preparation of 2-substituted 3,4-dihydro-2*H*-pyrans (4m-o, 4r-s)⁵



To a 25 mL round-bottom flask, 2-hydroxymethyl-3,4-dihydro-2*H*-pyran, carboxylic acid (2.0 equiv), DMAP (0.1 equiv), DCM and dicyclohexylcarbodiimide (2.0 equiv) were successively added. The mixture was stirred at room temperature overnight and diluted with ethyl acetate, washed with saturated aqueous NH₄Cl (2 times), brine (2 times), dried over Na₂SO₄ and evaporated under reduced pressure. The crude reaction was purified by column chromatography to afford corresponding product.

5. Characterization of the starting materials

Potassium (E)-trifluoro(styryl)borate (2a)

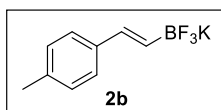


Following the **procedure A** on 10 mmol scale, white solid, yield: 77% (1.52 g).

Spectroscopic data are in agreement with those previously reported⁶.

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.36 – 7.29 (m, 2H), 7.25 (m, 2H), 7.11 (m, 1H), 6.48 (d, *J* = 18.2 Hz, 1H), 6.19 (dq, *J* = 18.2, 3.6 Hz, 1H).

Potassium (E)-trifluoro(4-methylstyryl)borate (2b)

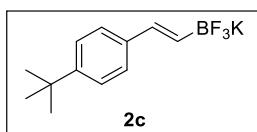


Following the **procedure A** on 5 mmol scale, white solid, yield: 66% (0.74 g).

Spectroscopic data are in agreement with those previously reported⁶.

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.19 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.42 (d, *J* = 18.2 Hz, 1H), 6.10 (dq, *J* = 18.2, 3.6 Hz, 1H), 2.25 (s, 3H).

Potassium (E)-(4-(tert-butyl)styryl)trifluoroborate (2c)

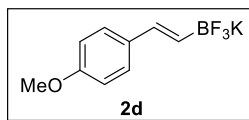


Following the **procedure A** on 5 mmol scale, white solid, yield: 78% (1.04 g).

Spectroscopic data are in agreement with those previously reported⁷.

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.30 – 7.15 (m, 4H), 6.43 (d, *J* = 18.2 Hz, 1H), 6.11 (dd, *J* = 18.2, 3.6 Hz, 1H), 1.26 (s, 9H).

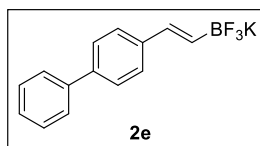
Potassium (E)-trifluoro(4-methoxystyryl)borate (2d)



Following the **procedure A** on 5 mmol scale, white solid, yield: 67% (0.81 g). Spectroscopic data are in agreement with those previously reported⁸.

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.30 – 7.17 (m, 2H), 6.90 – 6.76 (m, 2H), 6.38 (d, J = 18.1 Hz, 1H), 6.05 – 5.92 (m, 1H), 3.72 (s, 3H).

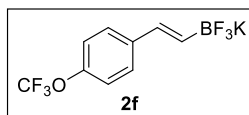
Potassium (E)-2-([1,1'-biphenyl]-4-yl)vinyltrifluoroborate (2e)



Following the **procedure A** on 5 mmol scale, white solid, yield: 53% (0.76 g). Spectroscopic data are in agreement with those previously reported¹¹.

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.67 – 7.62 (m, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.48 – 7.38 (m, 4H), 7.32 (m, 1H), 6.51 (d, J = 18.2 Hz, 1H), 6.25 (m, 1H).

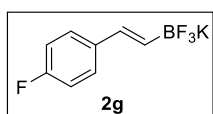
Potassium (E)-trifluoro(4-(trifluoromethoxy)styryl)borate (2f)



Following the **procedure A** on 5 mmol scale, white solid, yield: 53% (0.76 g). Spectroscopic data are in agreement with those previously reported¹².

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.56 – 7.37 (m, 2H), 7.22 (d, J = 8.2 Hz, 2H), 6.49 (d, J = 18.4 Hz, 1H), 6.22 (m, 1H).

Potassium (E)-trifluoro(4-fluorostyryl)borate (2g)

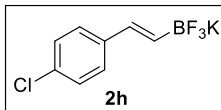


Following the **procedure A** on 5 mmol scale, white solid, yield: 71% (0.81 g).

Spectroscopic data are in agreement with those previously reported⁶.

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.51 – 7.21 (m, 2H), 7.14 – 6.95 (m, 2H), 6.43 (d, J = 18.2 Hz, 1H), 6.10 (m, 1H).

Potassium (E)-(4-chlorostyryl)trifluoroborate (2h)

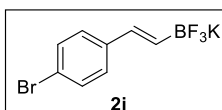


Following the **procedure A** on 5 mmol scale, white solid, yield: 68% (0.83 g).

Spectroscopic data are in agreement with those previously reported⁶.

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.44 – 6.84 (m, 4H), 6.44 (d, J = 18.3 Hz, 1H), 6.32 – 6.06 (m, 1H).

Potassium (E)-(4-bromostyryl)trifluoroborate (2i)

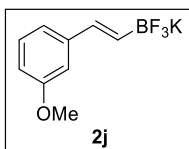


Following the **procedure A** on 5 mmol scale, white solid, yield: 69% (1.00 g).

Spectroscopic data are in agreement with those previously reported⁸.

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.51 – 7.35 (m, 2H), 7.30 – 7.21 (m, 2H), 6.42 (d, J = 18.2 Hz, 1H), 6.36 – 6.11 (m, 1H).

Potassium (E)-trifluoro(3-methoxystyryl)borate (2j)

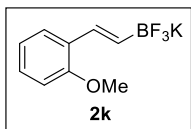


Following the **procedure A** on 5 mmol scale, white solid, yield: 78% (0.94 g).

Spectroscopic data are in agreement with those previously reported⁹.

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.15 (t, J = 7.8 Hz, 1H), 6.93 – 6.80 (m, 2H), 6.68 (dd, J = 8.3, 2.5 Hz, 1H), 6.42 (d, J = 18.2 Hz, 1H), 6.25 – 6.04 (m, 1H), 3.73 (s, 3H).

Potassium (E)-trifluoro(2-methoxystyryl)borate (2k)

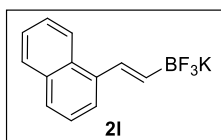


Following the **procedure A** on 5 mmol scale, white solid, yield: 46% (0.55 g).

Spectroscopic data are in agreement with those previously reported¹⁰.

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.39 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.09 (m, 1H), 6.92 – 6.74 (m, 3H), 6.06 (dd, *J* = 18.4, 3.5 Hz, 1H), 3.75 (s, 3H).

Potassium (E)-trifluoro(2-(naphthalen-1-yl)vinyl)borate (2l)

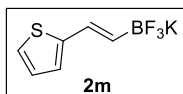


Following the **procedure A** on 5 mmol scale, white solid, yield: 65% (0.85 g).

Spectroscopic data are in agreement with those previously reported⁹.

¹H NMR (500 MHz, DMSO-*d*₆) δ 8.15 (d, *J* = 8.1 Hz, 1H), 7.87 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.53 – 7.41 (m, 3H), 7.24 (d, *J* = 17.9 Hz, 1H), 6.41 – 6.05 (m, 1H).

Potassium (E)-trifluoro(2-(thiophen-2-yl)vinyl)borate (2m)

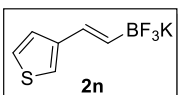


Following the **procedure A** on 5 mmol scale, white solid, yield: 85% (0.92 g).

Spectroscopic data are in agreement with those previously reported⁶.

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.18 (d, *J* = 5.1 Hz, 1H), 6.91 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.80 (d, *J* = 3.5 Hz, 1H), 6.56 (d, *J* = 17.9 Hz, 1H), 5.89 (m, 1H).

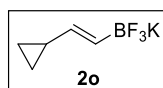
Potassium (E)-trifluoro(2-(thiophen-3-yl)vinyl)borate (2n)



Following the **procedure A** on 5 mmol scale, white solid, yield: 70% (0.76 g). Spectroscopic data are in agreement with those previously reported⁸.

¹H NMR (500 MHz, DMSO-*d*₆) δ 7.37 (dd, *J* = 5.2, 2.8 Hz, 1H), 7.20 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.12 (d, *J* = 2.6 Hz, 1H), 6.46 (d, *J* = 18.2 Hz, 1H), 5.96 (dq, *J* = 18.2, 3.6 Hz, 1H).

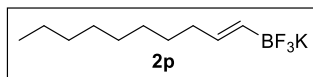
Potassium (E)-(2-cyclopropylvinyl)trifluoroborate (2o)



Following the **procedure A** on 5 mmol scale, white solid, yield: 51% (0.44 g). Spectroscopic data are in agreement with those previously reported⁶.

¹H NMR (500 MHz, DMSO-*d*₆) δ 5.35 – 5.15 (m, 1H), 4.98 (dd, *J* = 17.5, 8.3 Hz, 1H), 1.39 – 1.08 (m, 1H), 0.57 – 0.42 (m, 2H), 0.22 – 0.08 (m, 2H).

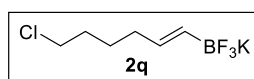
Potassium (E)-dec-1-en-1-yltrifluoroborate (2p)



Following the **procedure A** on 5 mmol scale, white solid, yield: 60% (0.74 g). Spectroscopic data are in agreement with those previously reported¹⁴.

¹H NMR (500 MHz, DMSO-*d*₆) δ 5.45 (dt, *J* = 17.6, 6.3 Hz, 1H), 5.33 – 5.15 (m, 1H), 1.86 (q, *J* = 6.6 Hz, 2H), 1.47 – 1.10 (m, 13H), 0.85 (t, *J* = 6.8 Hz, 3H).

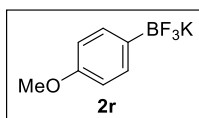
Potassium (E)-(6-chlorohex-1-en-1-yl)trifluoroborate (2q)



Following the **procedure A** on 5 mmol scale, white solid, yield: 58% (0.65 g). Spectroscopic data are in agreement with those previously reported¹⁴.

¹H NMR (500 MHz, DMSO-*d*₆) δ 5.46 (m, 1H), 5.33 – 5.13 (m, 1H), 3.61 (t, *J* = 6.7 Hz, 2H), 1.90 (q, *J* = 7.0 Hz, 2H), 1.68 (m, 2H), 1.48 – 1.07 (m, 2H).

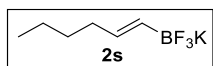
Potassium trifluoro(4-methoxyphenyl)borate (2r)



Following the **procedure A** on 5 mmol scale, white solid, yield: 80% (0.86 g). Spectroscopic data are in agreement with those previously reported¹³.

¹H NMR (500 MHz, Acetone-*d*₆) δ 7.38 (d, *J* = 8.2 Hz, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 3.70 (s, 2H).

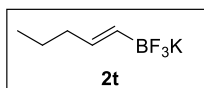
Potassium (E)-trifluoro(hex-1-en-1-yl)borate (2s)



Following the **procedure A** on 5 mmol scale, white solid, yield: 30% (0.29 g). Spectroscopic data are in agreement with those previously reported⁸.

¹H NMR (500 MHz, DMSO-*d*₆) δ 5.56 – 5.36 (m, 1H), 5.25 – 5.14 (m, 1H), 2.01 – 1.78 (m, 2H), 1.30 – 1.21 (m, 4H), 0.93 – 0.78 (m, 3H).

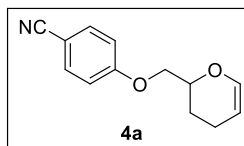
Potassium (E)-trifluoro(pent-1-en-1-yl)borate (2t)



Following the **procedure A** on 5 mmol scale, white solid, yield: 41% (0.36 g). Spectroscopic data are in agreement with those previously reported¹³.

¹H NMR (500 MHz, DMSO-*d*₆) δ 5.51 – 5.41 (m, 1H), 5.20 (m, 1H), 1.92 – 1.76 (m, 2H), 1.28 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H).

4-((3,4-dihydro-2H-pyran-2-yl)methoxy)benzonitrile (4a)



Following the **procedure C** on 5 mmol scale, white solid (m. p. = 70-72 °C), yield: 92% (0.99 g), *R*_f = 0.5 (silica gel, PE: EtOAc = 20:1, v/v), column chromatography (silica

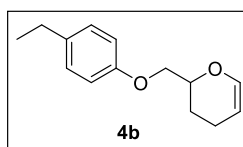
gel, PE: EtOAc = 80:1, v/v).

¹H NMR (500 MHz, CDCl₃) δ 7.55 – 7.48 (m, 2H), 6.96 – 6.88 (m, 2H), 6.34 (dt, J = 6.2, 2.0 Hz, 1H), 4.69 (m, 1H), 4.16 (m, 1H), 4.11 – 3.97 (m, 2H), 2.17 – 2.05 (m, 1H), 2.02 – 1.86 (m, 2H), 1.75 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 161.92 (s), 143.21 (s), 133.92 (s), 119.08 (s), 115.25 (s), 104.19 (s), 100.72 (s), 72.78 (s), 70.31 (s), 24.27 (s), 19.07 (s).

HRMS (EI): [M] Calcd. for C₁₃H₁₃NO₂ 215.0946; Found 215.0939.

2-((4-ethylphenoxy)methyl)-3,4-dihydro-2H-pyran (4b)



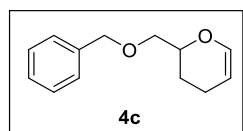
Following the **procedure C** on 5 mmol scale, colorless oil liquid, yield: 95% (1.04 g), R_f = 0.6 (silica gel, PE: EtOAc = 20:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

¹H NMR (500 MHz, CDCl₃) δ 7.23 – 7.16 (m, 2H), 6.98 – 6.91 (m, 2H), 6.51 (dt, J = 6.0, 1.8 Hz, 1H), 4.80 (m, 1H), 4.26 (m, 1H), 4.22 – 3.96 (m, 2H), 2.67 (q, J = 7.6 Hz, 2H), 2.26 – 2.15 (m, 1H), 2.14 – 2.00 (m, 2H), 1.86 (m, 1H), 1.30 (td, J = 7.6, 1.4 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 156.66 (s), 143.32 (s), 136.44 (s), 128.48 (s), 114.31 (s), 100.33 (s), 73.05 (s), 69.98 (s), 27.78 (s), 24.38 (s), 19.03 (s), 15.66 (s).

HRMS (EI): [M] Calcd. for C₁₄H₁₈O₂ 218.1307; Found 218.1299.

2-((benzyloxy)methyl)-3,4-dihydro-2H-pyran (4c)

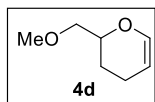


Following the **procedure B** on 5 mmol scale, colorless oil liquid, yield: 85% (0.87 g). Spectroscopic data are in agreement with those previously reported³.

¹H NMR (500 MHz, CDCl₃) δ 7.37 (m, 4H), 7.30 (m, 1H), 6.42 (d, J = 6.2 Hz, 1H),

4.73 – 4.67 (m, 1H), 4.66 – 4.51 (m, 2H), 4.04 (m, 1H), 3.69 – 3.46 (m, 2H), 2.11 (m, 1H), 2.03 – 1.94 (m, 1H), 1.86 (m, 1H), 1.71 (m, 1H).

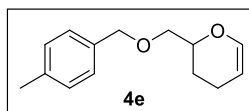
2-(methoxymethyl)-3,4-dihydro-2H-pyran (4d)



Following the **procedure B** on 5 mmol scale, colorless oil liquid, yield: 80% (0.51 g). Spectroscopic data are in agreement with those previously reported³.

¹H NMR (500 MHz, CDCl₃) δ 6.34 (dt, J = 6.2, 1.9 Hz, 1H), 4.63 (m, 1H), 3.94 (m, 1H), 3.52 – 3.39 (m, 2H), 3.36 (s, 3H), 2.06 (m, 1H), 1.97 – 1.88 (m, 1H), 1.81 – 1.74 (m, 1H), 1.63 (m, 1H).

2-(((4-methylbenzyl)oxy)methyl)-3,4-dihydro-2H-pyran (4e)



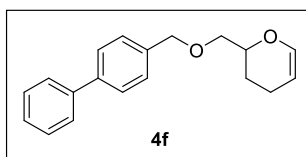
Following the **procedure B** on 5 mmol scale, colorless oil liquid, yield: 57% (0.62 g), R_f = 0.6 (silica gel, PE: EtOAc = 20:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

¹H NMR (500 MHz, CDCl₃) δ 7.27 – 7.22 (m, 2H), 7.16 (d, J = 7.8 Hz, 2H), 6.40 (dt, J = 6.3, 1.9 Hz, 1H), 4.68 (m, 1H), 4.61 – 4.49 (m, 2H), 4.02 (m, 1H), 3.63 – 3.45 (m, 2H), 2.35 (s, 3H), 2.09 (m, 1H), 1.96 (m, 1H), 1.88 – 1.80 (m, 1H), 1.74 – 1.63 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 143.53 (s), 137.24 (s), 134.98 (s), 128.98 (s), 127.78 (s), 100.36 (s), 74.00 (s), 73.19 (s), 72.17 (s), 24.51 (s), 21.07 (s), 19.28 (s).

HRMS (EI): [M] Calcd. for C₁₄H₁₈O₂ 218.1307; Found 218.1305.

2-(((1,1'-biphenyl)-4-ylmethoxy)methyl)-3,4-dihydro-2H-pyran (4f)



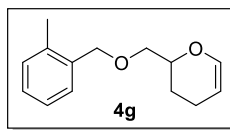
Following the **procedure B** on 5 mmol scale, colorless oil liquid, yield: 48% (0.68 g), $R_f = 0.5$ (silica gel, PE: EtOAc = 20:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.67 – 7.55 (m, 4H), 7.52 – 7.43 (m, 4H), 7.40 – 7.32 (m, 1H), 6.45 (dt, $J = 6.3, 2.0$ Hz, 1H), 4.72 (m, 1H), 4.70 – 4.62 (m, 2H), 4.08 (m, 1H), 3.69 – 3.55 (m, 2H), 2.19 – 2.07 (m, 1H), 2.01 (m, 1H), 1.93 – 1.85 (m, 1H), 1.74 (m, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 143.54 (s), 140.82 (s), 140.54 (s), 137.11 (s), 128.69 (s), 128.13 (s), 127.20 (s), 127.09 (s), 127.01 (s), 100.43 (s), 74.02 (s), 73.07 (s), 72.46 (s), 24.52 (s), 19.31 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{19}\text{H}_{20}\text{O}_2$ 280.1463; Found 280.1470.

2-(((2-methylbenzyl)oxy)methyl)-3,4-dihydro-2H-pyran (4g)



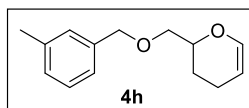
Following the **procedure B** on 5 mmol scale, colorless oil liquid, yield: 72% (0.78 g), $R_f = 0.6$ (silica gel, PE: EtOAc = 20:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.34 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.24 – 7.15 (m, 3H), 6.41 (dt, $J = 6.2, 2.0$ Hz, 1H), 4.70 (m, 1H), 4.65 – 4.55 (m, 2H), 4.04 (m, 1H), 3.65 – 3.50 (m, 2H), 2.36 (s, 3H), 2.16 – 2.06 (m, 1H), 2.04 – 1.94 (m, 1H), 1.91 – 1.81 (m, 1H), 1.71 (m, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 143.56 (s), 136.77 (s), 135.91 (s), 130.20 (s), 128.64 (s), 127.81 (s), 125.67 (s), 100.42 (s), 74.00 (s), 72.48 (s), 71.85 (s), 24.58 (s), 19.31 (s), 18.77 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_2$ 218.1307; Found 218.1314.

2-(((3-methylbenzyl)oxy)methyl)-3,4-dihydro-2H-pyran (**4h**)



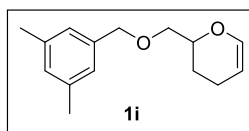
Following the **procedure B** on 5 mmol scale, colorless oil liquid, yield: 76% (0.83 g), $R_f = 0.6$ (silica gel, PE: EtOAc = 20:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.25 (t, $J = 7.5$ Hz, 1H), 7.21 – 7.15 (m, 2H), 7.12 (d, $J = 7.6$ Hz, 1H), 6.42 (dt, $J = 6.3, 1.9$ Hz, 1H), 4.70 (m, 1H), 4.63 – 4.52 (m, 2H), 4.05 (m, 1H), 3.67 – 3.42 (m, 2H), 2.37 (s, 3H), 2.17 – 2.05 (m, 1H), 2.04 – 1.94 (m, 1H), 1.91 – 1.83 (m, 1H), 1.77 – 1.65 (m, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 143.52 (s), 137.95 (s), 137.92 (s), 128.43 (s), 128.31 (s), 128.20 (s), 124.75 (s), 100.37 (s), 73.99 (s), 73.39 (s), 72.39 (s), 24.51 (s), 21.30 (s), 19.28 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_2$ 218.1307; Found 218.1312.

2-(((3,5-dimethylbenzyl)oxy)methyl)-3,4-dihydro-2H-pyran (**4i**)



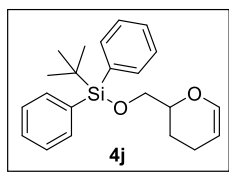
Following the **procedure B** on 5 mmol scale, colorless oil liquid, yield: 66% (0.77 g), $R_f = 0.6$ (silica gel, PE: EtOAc = 20:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.00 (d, $J = 1.7$ Hz, 2H), 6.96 (d, $J = 1.9$ Hz, 1H), 6.44 (dt, $J = 6.2, 2.0$ Hz, 1H), 4.72 (m, 1H), 4.60 – 4.50 (m, 2H), 4.06 (m, 1H), 3.68 – 3.51 (m, 2H), 2.35 (s, 6H), 2.13 (m, 1H), 2.03 – 1.95 (m, 1H), 1.93 – 1.85 (m, 1H), 1.72 (m, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 143.49 (s), 137.83 (s), 137.74 (s), 129.14 (s), 125.50 (s), 100.29 (s), 73.94 (s), 73.39 (s), 72.35 (s), 24.48 (s), 21.12 (s), 19.23 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_2$ 232.1463; Found 232.1470.

tert-butyl((3,4-dihydro-2H-pyran-2-yl)methoxy)diphenylsilane (4j)

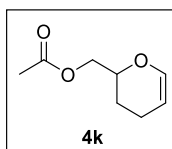


Following the **procedure B** on 5 mmol scale, colorless oil liquid, yield: 70% (1.23 g).

Spectroscopic data are in agreement with those previously reported¹⁵.

¹H NMR (500 MHz, CDCl₃) δ 7.78 (m, 4H), 7.52 – 7.40 (m, 6H), 6.44 (td, *J* = 5.4, 2.9 Hz, 1H). 4.75 – 4.70 (m, 1H), 4.02 (m, 1H), 3.93 – 3.85 (m, 1H), 3.78 (m, 1H), 2.14 (m, 1H), 2.08 – 1.97 (m, 2H), 1.80 (m, 1H), 1.19 – 1.11 (m, 9H).

(3,4-dihydro-2H-pyran-2-yl)methyl acetate (4k)

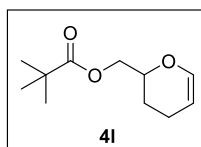


Following the **procedure B** on 5 mmol scale, colorless oil liquid, yield: 85% (0.66 g).

Spectroscopic data are in agreement with those previously reported³.

¹H NMR (500 MHz, CDCl₃) δ 6.38 (dd, *J* = 6.1, 2.1 Hz, 1H), 4.74 – 4.69 (m, 1H), 4.23 – 4.11 (m, 2H), 4.04 (m, 1H), 2.10 (s, 3H), 2.05 – 1.94 (m, 1H), 1.89 – 1.80 (m, 1H), 1.69 (m, 2H).

(3,4-dihydro-2H-pyran-2-yl)methyl pivalate (4l)

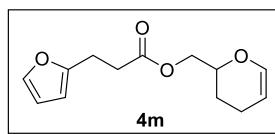


Following the **procedure B** on 5 mmol scale, colorless oil liquid, yield: 86% (0.85 g).

Spectroscopic data are in agreement with those previously reported³.

¹H NMR (500 MHz, CDCl₃) δ 6.34 (d, *J* = 6.0 Hz, 1H), 4.70 – 4.64 (m, 1H), 4.14 (d, *J* = 5.0 Hz, 2H), 4.00 (m, 1H), 2.14 – 2.03 (m, 1H), 2.01 – 1.94 (m, 1H), 1.83 (m, 1H), 1.71 – 1.60 (m, 1H), 1.20 (s, 9H).

(3,4-dihydro-2H-pyran-2-yl)methyl 3-(furan-2-yl)propanoate (4m)



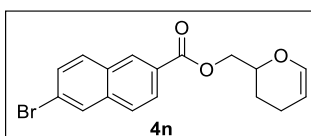
Following the **procedure D** on 5 mmol scale, colorless oil liquid, yield: 86% (1.02 g), $R_f = 0.5$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 50:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.25 (d, $J = 1.9$ Hz, 1H), 6.33 (dt, $J = 6.2, 2.0$ Hz, 1H), 6.22 (dd, $J = 3.2, 1.9$ Hz, 1H), 5.98 (dd, $J = 3.1, 1.1$ Hz, 1H), 4.66 (m, 1H), 4.21 – 4.10 (m, 2H), 3.98 (m, 1H), 2.94 (dd, $J = 8.1, 7.1$ Hz, 2H), 2.67 (dd, $J = 8.3, 6.9$ Hz, 2H), 2.11 – 2.01 (m, 1H), 1.95 (m, 1H), 1.78 (m, 1H), 1.62 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 172.31 (s), 153.91 (s), 143.20 (s), 141.13 (s), 110.08 (s), 105.24 (s), 100.46 (s), 72.55 (s), 66.17 (s), 32.44 (s), 24.05 (s), 23.31 (s), 19.04 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_4$ 236.1049; Found 236.1046.

(3,4-dihydro-2H-pyran-2-yl)methyl 6-bromo-2-naphthoate (4n)



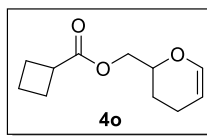
Following the **procedure D** on 5 mmol scale, colorless oil liquid, yield: 93% (1.61 g), $R_f = 0.5$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 50:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 8.50 (d, $J = 1.6$ Hz, 1H), 8.04 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.93 (d, $J = 2.0$ Hz, 1H), 7.69 (dd, $J = 16.3, 8.7$ Hz, 2H), 7.52 (dd, $J = 8.7, 1.9$ Hz, 1H), 6.42 (dt, $J = 6.3, 1.9$ Hz, 1H), 4.75 – 4.69 (m, 1H), 4.51 – 4.41 (m, 2H), 4.20 (m, 1H), 2.14 (m, 1H), 2.06 – 1.98 (m, 1H), 1.94 (m, 1H), 1.79 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 166.13 (s), 143.31 (s), 136.32 (s), 130.93 (s), 130.76 (s), 130.73 (s), 130.04 (s), 129.79 (s), 127.52 (s), 127.12 (s), 126.32 (s), 122.58 (s), 100.51 (s), 72.69 (s), 66.79 (s), 24.27 (s), 19.13 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{17}\text{H}_{15}\text{BrO}_3$ 346.0205; Found 346.0205.

(3,4-dihydro-2H-pyran-2-yl)methyl cyclobutanecarboxylate (4o)



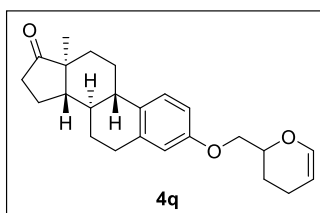
Following the **procedure D** on 5 mmol scale, colorless oil liquid, yield: 75% (0.74 g), $R_f = 0.5$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 50:1, v/v).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.34 (dt, $J = 6.0, 1.9$ Hz, 1H), 4.68 (m, 1H), 4.21 – 4.10 (m, 2H), 4.05 – 3.97 (m, 1H), 3.17 (m, 1H), 2.33 – 2.23 (m, 2H), 2.23 – 2.14 (m, 2H), 2.13 – 2.04 (m, 1H), 2.01 – 1.78 (m, 4H), 1.71 – 1.60 (m, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 175.30 (s), 143.27 (s), 100.39 (s), 72.71 (s), 65.90 (s), 37.88 (s), 25.19 (s), 25.18 (s), 24.14 (s), 19.08 (s), 18.33 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{11}\text{H}_{16}\text{O}_3$ 196.1099; Found 196.1095.

(8R,9S,13S,14S)-3-((3,4-dihydro-2H-pyran-2-yl)methoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4q)



Following the **procedure C** on 5 mmol scale, white solid (m. p. = 104-106 °C), yield: 74% (1.35 g), $R_f = 0.6$ (silica gel, PE: EtOAc = 5:1, v/v), column chromatography (silica gel, PE: EtOAc = 20:1, v/v).

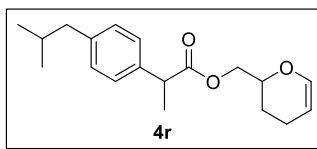
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.55 – 7.48 (m, 2H), 6.96 – 6.88 (m, 2H), 6.34 (dt, $J = 6.2, 2.0$ Hz, 1H), 4.69 (m, 1H), 4.16 (m, 1H), 4.11 – 3.98 (m, 2H), 2.10 (m, 1H), 2.03 – 1.87 (m, 2H), 1.75 (m, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 220.14 (s), 156.37 (s), 143.12 (s), 137.30 (s), 131.92 (s), 125.92 (s), 114.27 (s), 111.77 (s), 100.17 (s), 72.83 (s), 69.65 (s), 49.95 (s), 47.52 (s), 43.53 (s), 37.94 (s), 35.43 (s), 31.21 (s), 29.25 (s), 26.15 (s), 25.54 (s), 24.18 (s), 21.19

(s), 18.86 (s), 13.45 (s).

HRMS (EI): [M] Calcd. for C₂₄H₃₀O₃ 366.2195; Found 366.2186.

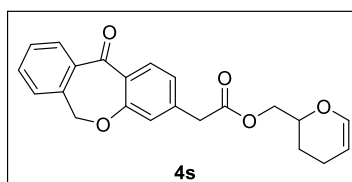
(3,4-dihydro-2H-pyran-2-yl)methyl 2-(4-isobutylphenyl)propanoate (4r)



Following the **procedure D** on 5 mmol scale, colorless oil liquid, yield: 62% (0.94 g), Spectroscopic data are in agreement with those previously reported¹⁶.

¹H NMR (500 MHz, CDCl₃) δ 7.24 – 7.19 (m, 2H), 7.16 – 7.06 (m, 2H), 6.36 – 6.30 (m, 1H), 4.67 (m, 1H), 4.23 – 4.11 (m, 2H), 3.98 (m, 1H), 3.76 (m, 1H), 2.44 (d, J = 7.2 Hz, 2H), 2.03 (m, 1H), 1.94 (m, 1H), 1.84 (dt, J = 13.5, 6.8 Hz, 1H), 1.78 – 1.68 (m, 1H), 1.58 (m, 1H), 1.51 (d, J = 7.2 Hz, 3H), 0.89 (d, J = 6.6 Hz, 6H).

(3,4-dihydro-2H-pyran-2-yl)methyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-3-yl)acetate (4s)



Following the **procedure D** on 5 mmol scale, colorless oil liquid, yield: 93% (1.61 g), R_f = 0.5 (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 50:1, v/v).

¹H NMR (400 MHz, CDCl₃) δ 8.11 (s, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.59 – 7.31 (m, 4H), 7.01 (d, J = 8.4 Hz, 1H), 6.36 (d, J = 6.2 Hz, 1H), 5.16 (s, 2H), 4.70 (m, 1H), 4.21 (m, 2H), 4.10 – 3.96 (m, 1H), 3.69 (s, 2H), 2.16 – 1.89 (m, 2H), 1.81 (m, 1H), 1.72 – 1.57 (m, 1H).

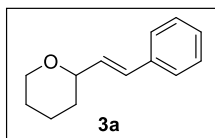
¹³C NMR (101 MHz, CDCl₃) δ 190.68 (s), 171.24 (s), 160.38 (s), 143.19 (s), 140.34 (s), 136.27 (s), 135.45 (s), 132.66 (s), 132.40 (s), 129.36 (s), 129.15 (s), 127.71 (s), 127.54 (s), 125.03 (s), 120.95 (s), 100.47 (s), 73.50 (s), 72.49 (s), 66.53 (s), 39.88 (s), 24.07 (s),

19.04 (s).

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{22}H_{21}O_5^+$ 365.1384; Found 365.1385.

6. Characterization of Products

(E)-2-styryltetrahydro-2H-pyran (**3a**)

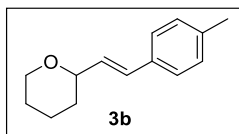


Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 85% (32.0 mg). Spectroscopic data are in agreement with those previously reported¹⁷.

¹H NMR (500 MHz, CDCl₃) δ 7.42 – 7.36 (m, 2H), 7.31 (t, $J = 7.6$ Hz, 2H), 7.23 (m, 1H), 6.60 (d, $J = 16.0$ Hz, 1H), 6.23 (dd, $J = 16.0, 5.8$ Hz, 1H), 4.12 – 4.05 (m, 1H), 3.98 (m, 1H), 3.56 (td, $J = 11.5, 2.3$ Hz, 1H), 1.90 (m, 1H), 1.78 – 1.71 (m, 1H), 1.68 – 1.46 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 136.95 (s), 130.77 (s), 129.67 (s), 128.41 (s), 127.37 (s), 126.35 (s), 77.97 (s), 68.36 (s), 32.17 (s), 25.80 (s), 23.37 (s).

(E)-2-(4-methylstyryl)tetrahydro-2H-pyran (**3b**)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 87% (35.2 mg), $R_f = 0.6$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

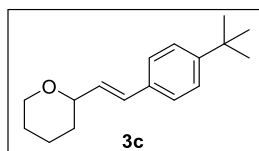
¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, $J = 7.7$ Hz, 2H), 7.12 (d, $J = 7.7$ Hz, 2H), 6.58 (d, $J = 16.0$ Hz, 1H), 6.19 (dd, $J = 16.0, 5.7$ Hz, 1H), 4.12 – 4.06 (m, 1H), 4.01 – 3.94 (m, 1H), 3.56 (t, $J = 11.4$ Hz, 1H), 2.34 (s, 3H), 1.90 (d, $J = 10.0$ Hz, 1H), 1.75 (d, $J =$

12.6 Hz, 1H), 1.69 – 1.46 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 137.07 (s), 134.11 (s), 129.67 (s), 129.61 (s), 129.08 (s), 126.22 (s), 78.03 (s), 68.29 (s), 32.15 (s), 25.78 (s), 23.34 (s), 21.07 (s).

HRMS (EI): [M] Calcd. for C₁₄H₁₈O 202.1358; Found 202.1351.

(E)-2-(4-(tert-butyl)styryl)tetrahydro-2H-pyran (3c)



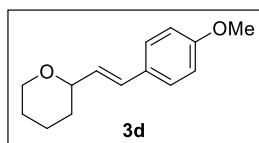
Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 86% (42.0 mg), R_f = 0.6 (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

¹H NMR (500 MHz, CDCl₃) δ 7.35 (s, 4H), 6.59 (dd, J = 16.0, 1.1 Hz, 1H), 6.20 (dd, J = 16.0, 5.8 Hz, 1H), 4.13 – 4.06 (m, 1H), 4.02 – 3.96 (m, 1H), 3.56 (td, J = 11.5, 2.2 Hz, 1H), 1.91 (m, 1H), 1.78 – 1.72 (m, 1H), 1.72 – 1.44 (m, 4H), 1.34 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 150.36 (s), 134.16 (s), 130.02 (s), 129.39 (s), 126.04 (s), 125.32 (s), 78.06 (s), 68.32 (s), 34.45 (s), 32.24 (s), 31.22 (s), 25.80 (s), 23.37 (s).

HRMS (EI): [M] Calcd. for C₁₇H₂₄O 244.1827; Found 244.1823.

(E)-2-(4-methoxystyryl)tetrahydro-2H-pyran (3d)



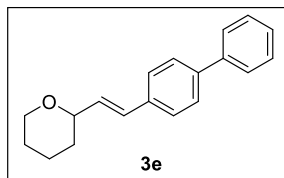
Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 71% (31.0 mg). Spectroscopic data are in agreement with those previously reported¹⁷.

¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.28 (m, 2H), 6.87 – 6.80 (m, 2H), 6.53 (d, J = 15.9 Hz, 1H), 6.08 (dd, J = 16.0, 6.0 Hz, 1H), 4.09 – 4.03 (m, 1H), 3.98 – 3.90 (m, 1H), 3.80 (s, 3H), 3.54 (td, J = 11.5, 2.4 Hz, 1H), 1.89 (m, 1H), 1.73 (m, 1H), 1.67 – 1.45 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 159.05 (s), 129.72 (s), 129.37 (s), 128.61 (s), 127.54 (s),

113.85 (s), 78.21 (s), 68.39 (s), 55.22 (s), 32.26 (s), 25.84 (s), 23.41 (s).

(E)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)tetrahydro-2H-pyran (3e)



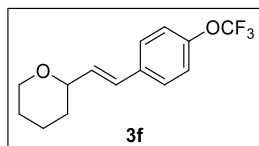
Following the **procedure E** on 0.2 mmol scale, white solid (m. p. = 71 - 72 °C), yield: 53% (28.0 mg), $R_f = 0.5$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.59 (m, 4H), 7.46 (m, 4H), 7.39 – 7.32 (m, 1H), 6.66 (d, $J = 16.0$ Hz, 1H), 6.29 (dd, $J = 16.0, 5.8$ Hz, 1H), 4.11 (m, 1H), 4.05 – 3.98 (m, 1H), 3.58 (td, $J = 11.6, 2.4$ Hz, 1H), 1.92 (m, 1H), 1.82 – 1.75 (m, 1H), 1.73 – 1.44 (m, 4H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 140.66 (s), 140.09 (s), 136.02 (s), 130.90 (s), 129.18 (s), 128.69 (s), 127.17 (s), 127.12 (s), 126.84 (s), 126.78 (s), 77.98 (s), 68.38 (s), 32.20 (s), 25.81 (s), 23.38 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{19}\text{H}_{20}\text{O}$ 264.1514; Found 264.1506.

(E)-2-(4-(trifluoromethoxy)styryl)tetrahydro-2H-pyran (3f)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 91% (49.5 mg), $R_f = 0.6$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

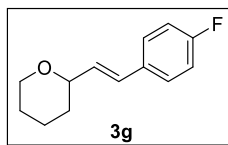
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.41 – 7.35 (m, 2H), 7.14 (d, $J = 8.2$ Hz, 2H), 6.60 – 6.54 (m, 1H), 6.19 (dd, $J = 16.0, 5.6$ Hz, 1H), 4.10 – 4.04 (m, 1H), 3.97 (m, 1H), 3.54 (td, $J = 11.5, 2.3$ Hz, 1H), 1.89 (m, 1H), 1.77 – 1.70 (m, 1H), 1.66 – 1.41 (m, 4H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 148.36 (s), 135.80 (s), 131.90 (s), 128.09 (s), 127.56 (s), 120.96 (s), 77.73 (s), 68.42 (s), 32.16 (s), 25.79 (s), 23.37 (s).

^{19}F NMR (471 MHz, CDCl_3) δ -57.79 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{14}\text{H}_{15}\text{F}_3\text{O}_2$ 272.1024; Found 272.1017.

(E)-2-(4-fluorostyryl)tetrahydro-2H-pyran (3g)



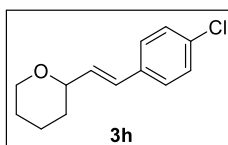
Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 96% (39.6 mg). Spectroscopic data are in agreement with those previously reported¹⁹.

^1H NMR (500 MHz, CDCl_3) δ 7.33 (m, 2H), 7.01 – 6.94 (m, 2H), 6.55 (d, J = 16.0 Hz, 1H), 6.12 (dd, J = 16.0, 5.8 Hz, 1H), 4.09 – 4.03 (m, 1H), 3.99 – 3.91 (m, 1H), 3.53 (td, J = 11.5, 2.3 Hz, 1H), 1.88 (m, 1H), 1.72 (dt, J = 12.7, 2.3 Hz, 1H), 1.67 – 1.43 (m, 4H).

^{13}C NMR (126 MHz, CDCl_3) δ 163.13 (s), 161.17 (s), 133.09 (d, J = 3.3 Hz), 130.50 (s), 128.51 (s), 127.81 (d, J = 7.7 Hz), 115.29 (d, J = 21.6 Hz), 77.84 (s), 68.36 (s), 32.14 (s), 25.77 (s), 23.34 (s).

^{19}F NMR (471 MHz, CDCl_3) δ -114.68 (s).

(E)-2-(4-chlorostyryl)tetrahydro-2H-pyran (3h)

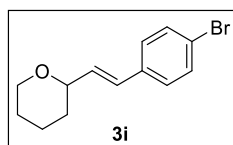


Following the **procedure E** on 0.2 mmol scale, white solid, yield: 81% (36.1 mg). Spectroscopic data are in agreement with those previously reported¹⁷.

^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.21 (m, 4H), 6.56 – 6.49 (m, 1H), 6.17 (dd, J = 16.0, 5.7 Hz, 1H), 4.08 – 4.02 (m, 1H), 3.94 (m, 1H), 3.52 (td, J = 11.5, 2.3 Hz, 1H), 1.87 (m, 1H), 1.71 (m, 1H), 1.68 – 1.37 (m, 4H).

^{13}C NMR (126 MHz, CDCl_3) δ 135.46 (s), 132.92 (s), 131.43 (s), 128.56 (s), 128.35 (s), 127.53 (s), 77.72 (s), 68.37 (s), 32.09 (s), 25.76 (s), 23.33 (s).

(E)-2-(4-bromostyryl)tetrahydro-2H-pyran (3i)

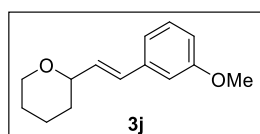


Following the **procedure E** on 0.2 mmol scale, white solid, yield: 67% (35.8 mg). Spectroscopic data are in agreement with those previously reported²⁰.

¹H NMR (500 MHz, CDCl₃) δ 7.41 (m, 2H), 7.26 – 7.20 (m, 2H), 6.55 – 6.48 (m, 1H), 6.19 (dd, *J* = 16.0, 5.7 Hz, 1H), 4.09 – 4.03 (m, 1H), 3.95 (m, 1H), 3.53 (td, *J* = 11.5, 2.2 Hz, 1H), 1.89 (dt, *J* = 9.7, 2.6 Hz, 1H), 1.72 (dt, *J* = 13.0, 2.3 Hz, 1H), 1.68 – 1.36 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 135.91 (s), 131.57 (s), 131.51 (s), 128.39 (s), 127.87 (s), 121.07 (s), 77.71 (s), 68.37 (s), 32.07 (s), 25.76 (s), 23.34 (s).

(E)-2-(3-methoxystyryl)tetrahydro-2H-pyran (3j)

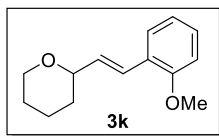


Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 82% (35.8 mg). Spectroscopic data are in agreement with those previously reported²⁰.

¹H NMR (500 MHz, CDCl₃) δ 7.22 (t, *J* = 7.9 Hz, 1H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.95 – 6.91 (m, 1H), 6.78 (dd, *J* = 8.0, 2.2 Hz, 1H), 6.60 – 6.53 (m, 1H), 6.22 (dd, *J* = 16.0, 5.7 Hz, 1H), 4.07 (m, 1H), 4.01 – 3.94 (m, 1H), 3.80 (s, 3H), 3.54 (td, *J* = 11.5, 2.4 Hz, 1H), 1.89 (m, 1H), 1.80 – 1.71 (m, 1H), 1.70 – 1.42 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 159.63 (s), 138.39 (s), 131.07 (s), 129.48 (s), 129.34 (s), 119.01 (s), 113.09 (s), 111.45 (s), 77.83 (s), 68.31 (s), 55.04 (s), 32.12 (s), 25.76 (s), 23.33 (s).

(E)-2-(2-methoxystyryl)tetrahydro-2H-pyran (3k)



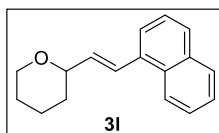
Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 51% (22.2 mg), $R_f = 0.45$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 7.44 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.24 – 7.17 (m, 1H), 6.94 – 6.88 (m, 2H), 6.85 (d, $J = 8.5$ Hz, 1H), 6.23 (dd, $J = 16.2, 6.1$ Hz, 1H), 4.07 (m, 1H), 4.02 – 3.94 (m, 1H), 3.83 (s, 3H), 3.54 (td, $J = 11.5, 2.3$ Hz, 1H), 1.89 (m, 1H), 1.79 – 1.72 (m, 1H), 1.70 – 1.43 (m, 4H).

^{13}C NMR (126 MHz, CDCl_3) δ 156.72 (s), 131.41 (s), 128.44 (s), 126.79 (s), 125.93 (s), 124.80 (s), 120.52 (s), 110.71 (s), 78.58 (s), 68.35 (s), 55.35 (s), 32.22 (s), 25.85 (s), 23.42 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_2$ 218.1307; Found 218.1301.

(E)-2-(2-(naphthalen-1-yl)vinyl)tetrahydro-2H-pyran (3l)



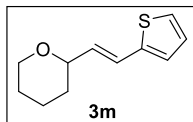
Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 79% (37.6 mg), $R_f = 0.5$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 8.19 (d, $J = 8.1$ Hz, 1H), 7.91 – 7.83 (m, 1H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.64 (d, $J = 7.0$ Hz, 1H), 7.57 – 7.46 (m, 3H), 7.39 (d, $J = 15.7$ Hz, 1H), 6.29 (dd, $J = 15.7, 5.7$ Hz, 1H), 4.19 – 4.07 (m, 2H), 3.62 (td, $J = 11.6, 2.3$ Hz, 1H), 1.99 – 1.89 (m, 1H), 1.88 – 1.78 (m, 1H), 1.74 – 1.54 (m, 4H).

^{13}C NMR (126 MHz, CDCl_3) δ 134.77 (s), 134.05 (s), 133.50 (s), 131.15 (s), 128.37 (s), 127.70 (s), 126.84 (s), 125.80 (s), 125.60 (s), 125.53 (s), 123.88 (s), 123.72 (s), 78.12 (s), 68.37 (s), 32.27 (s), 25.81 (s), 23.38 (s).

HRMS (EI): [M] Calcd. for C₁₇H₁₈O 238.1358; Found 238.1356.

(E)-2-(2-(thiophen-2-yl)vinyl)tetrahydro-2H-pyran (3m)



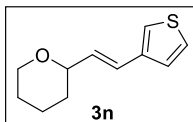
Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 83% (32.2 mg), R_f = 0.6 (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

¹H NMR (500 MHz, CDCl₃) δ 7.16 – 7.10 (m, 1H), 6.94 (m, 2H), 6.71 (d, J = 15.7 Hz, 1H), 6.05 (dd, J = 15.8, 5.7 Hz, 1H), 4.06 (m, 1H), 3.93 (m, 1H), 3.52 (td, J = 11.4, 2.3 Hz, 1H), 1.88 (m, 1H), 1.82 – 1.69 (m, 1H), 1.68 – 1.39 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 142.19 (s), 130.39 (s), 127.22 (s), 125.57 (s), 124.00 (s), 122.92 (s), 77.56 (s), 68.36 (s), 32.09 (s), 25.80 (s), 23.35 (s).

HRMS (EI): [M] Calcd. for C₁₁H₁₄OS 194.0765; Found 194.0763.

(E)-2-(2-(thiophen-3-yl)vinyl)tetrahydro-2H-pyran (3n)



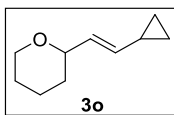
Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 88% (34.2 mg), R_f = 0.6 (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

¹H NMR (500 MHz, CDCl₃) δ 7.24 (dd, J = 5.1, 2.9 Hz, 1H), 7.20 (dd, J = 5.1, 1.1 Hz, 1H), 7.13 (m, 1H), 6.59 (d, J = 16.0 Hz, 1H), 6.07 (dd, J = 16.0, 5.9 Hz, 1H), 4.06 (m, 1H), 3.93 (m, 1H), 3.53 (td, J = 11.5, 2.4 Hz, 1H), 1.88 (m, 1H), 1.76 – 1.61 (m, 1H), 1.66 – 1.40 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 139.57 (s), 130.65 (s), 125.82 (s), 124.94 (s), 123.96 (s), 121.94 (s), 77.84 (s), 68.33 (s), 32.14 (s), 25.80 (s), 23.35 (s).

HRMS (EI): [M] Calcd. for C₁₁H₁₄OS 194.0765; Found 194.0758.

(E)-2-(2-cyclopropylvinyl)tetrahydro-2H-pyran (3o)



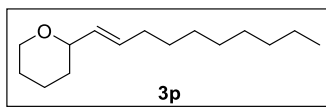
Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 44% (17.3 mg), $R_f = 0.7$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 5.54 (dd, $J = 15.4, 6.3$ Hz, 1H), 5.24 – 5.15 (m, 1H), 4.02 – 3.95 (m, 1H), 3.75 – 3.68 (m, 1H), 3.46 (td, $J = 11.5, 2.2$ Hz, 1H), 1.83 (m, 1H), 1.67 – 1.55 (m, 2H), 1.54 – 1.44 (m, 2H), 1.42 – 1.32 (m, 2H), 0.74 – 0.63 (m, 2H), 0.36 (m, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 135.51 (s), 128.80 (s), 78.08 (s), 68.32 (s), 32.19 (s), 25.84 (s), 23.42 (s), 13.47 (s), 6.65 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{10}\text{H}_{16}\text{O}$ 152.1201; Found 152.1192.

(E)-2-(dec-1-en-1-yl)tetrahydro-2H-pyran (3p)



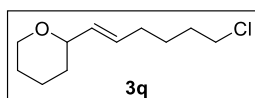
Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 36% (16.2 mg), $R_f = 0.7$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

^1H NMR (500 MHz, CDCl_3) δ 5.66 (m, 1H), 5.45 (m, 1H), 3.99 (m, 1H), 3.76 – 3.69 (m, 1H), 3.46 (td, $J = 11.6, 2.3$ Hz, 1H), 2.05 – 1.94 (m, 2H), 1.86 – 1.79 (m, 1H), 1.64 – 1.44 (m, 4H), 1.43 – 1.31 (m, 3H), 1.26 (m, 10H), 0.87 (t, $J = 7.0$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 131.96 (s), 131.10 (s), 78.28 (s), 68.30 (s), 32.31 (s), 32.18 (s), 31.85 (s), 29.42 (s), 29.23 (s), 29.18 (s), 29.08 (s), 25.85 (s), 23.40 (s), 22.63 (s), 14.06 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{15}\text{H}_{28}\text{O}$ 224.2140; Found 224.2150.

(E)-2-(6-chlorohex-1-en-1-yl)tetrahydro-2H-pyran (3q)



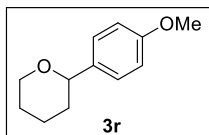
Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 39% (15.8 mg), $R_f = 0.7$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.64 (m, 1H), 5.48 (m, 1H), 3.99 (m, 1H), 3.77 – 3.70 (m, 1H), 3.52 (t, $J = 6.7$ Hz, 2H), 3.46 (td, $J = 11.6, 2.4$ Hz, 1H), 2.05 (q, $J = 7.7$ Hz, 2H), 1.86 – 1.80 (m, 1H), 1.80 – 1.70 (m, 2H), 1.64 – 1.57 (m, 1H), 1.56 – 1.45 (m, 5H), 1.42 – 1.31 (m, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 131.88 (s), 130.74 (s), 78.05 (s), 68.30 (s), 44.91 (s), 32.11 (s), 31.95 (s), 31.43 (s), 26.19 (s), 25.78 (s), 23.33 (s).

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{11}\text{H}_{20}\text{ClO}^+$ 203.1198; Found 203.1199.

2-(4-methoxyphenyl)tetrahydro-2H-pyran (3r)

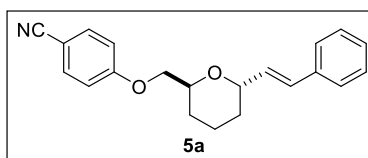


Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 60% (23.0 mg). Spectroscopic data are in agreement with those previously reported²¹.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.31 – 7.24 (m, 1H), 6.87 (d, $J = 9.0$ Hz, 1H), 4.30 – 4.24 (m, 1H), 4.15 – 4.09 (m, 1H), 3.79 (s, 3H), 3.61 (td, $J = 11.7, 2.5$ Hz, 1H), 1.94 (m, 1H), 1.85 – 1.67 (m, 1H), 1.70 – 1.52 (m, 4H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 158.80 (s), 135.57 (s), 127.13 (s), 113.62 (s), 79.77 (s), 69.04 (s), 55.25 (s), 33.83 (s), 25.88 (s), 24.01 (s).

(E)-4-((6-styryltetrahydro-2H-pyran-2-yl)methoxy)benzonitrile (5a)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 47% (30.0 mg), $R_f = 0.6$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

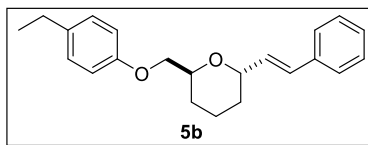
d.r. = 5.56:1

^1H NMR (500 MHz, CDCl_3) δ 7.59 – 7.53 (m, 2H), 7.43 – 7.29 (m, 4H), 7.27 – 7.22 (m, 1H), 7.00 – 6.95 (m, 2H), 6.60 (dd, $J = 16.3, 1.9$ Hz, 1H), 6.32 (dd, $J = 16.3, 4.8$ Hz, 1H), 4.65 (m, 1H), 4.21 – 4.13 (m, 1H), 4.12 – 3.92 (m, 2H), 1.97 – 1.86 (m, 1H), 1.83 – 1.66 (m, 4H), 1.62 – 1.50 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 162.11 (s), 136.71 (s), 133.87 (s), 131.77 (s), 129.14 (s), 128.53 (s), 127.61 (s), 126.28 (s), 119.15 (s), 115.31 (s), 103.97 (s), 72.82 (s), 70.83 (s), 68.95 (s), 28.95 (s), 27.41 (s), 18.52 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{21}\text{H}_{21}\text{NO}_2$ 319.1572.; Found 319.1572.

(E)-2-((4-ethylphenoxy)methyl)-6-styryltetrahydro-2H-pyran (5b)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 63% (30.0 mg), $R_f = 0.6$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

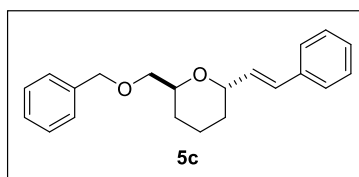
d.r. = 5.00:1

^1H NMR (500 MHz, CDCl_3) δ 7.42 – 7.37 (m, 2H), 7.33 (m, 2H), 7.24 (m, 1H), 7.14 – 7.09 (m, 2H), 6.91 – 6.85 (m, 2H), 6.61 (dd, $J = 16.3, 1.9$ Hz, 1H), 6.35 (dd, $J = 16.2, 4.8$ Hz, 1H), 4.66 (m, 1H), 4.18 (m, 1H), 4.02 (m, 2H), 2.60 (q, $J = 7.6$ Hz, 2H), 1.91 (m, 1H), 1.81 – 1.73 (m, 4H), 1.63 – 1.53 (m, 1H), 1.22 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 156.89 (s), 136.91 (s), 136.49 (s), 131.44 (s), 129.65 (s), 128.61 (s), 128.50 (s), 127.48 (s), 126.34 (s), 114.54 (s), 72.72 (s), 70.42 (s), 69.40 (s), 29.32 (s), 27.92 (s), 27.55 (s), 18.64 (s), 15.82 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{22}\text{H}_{26}\text{O}_2$ 322.1933.; Found 322.1927.

(E)-2-((benzyloxy)methyl)-6-styryltetrahydro-2H-pyran (5c)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 92% (56.7 mg), $R_f = 0.6$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

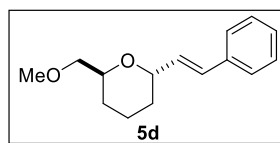
d.r. = 3.67:1

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.51 – 7.19 (m, 10H), 6.60 (dd, $J = 16.2, 1.2$ Hz, 1H), 6.35 (dd, $J = 16.3, 4.9$ Hz, 1H), 4.65 – 4.55 (m, 3H), 4.04 (m, 1H), 3.59 (dd, $J = 10.0, 6.2$ Hz, 1H), 3.48 (dd, $J = 10.0, 4.7$ Hz, 1H), 1.93 – 1.82 (m, 1H), 1.79 – 1.61 (m, 4H), 1.49 (m, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 138.38 (s), 136.95 (s), 131.20 (s), 129.90 (s), 128.47 (s), 128.28 (s), 127.59 (s), 127.47 (s), 127.42 (s), 126.31 (s), 73.22 (s), 72.51 (s), 72.49 (s), 70.19 (s), 29.33 (s), 27.50 (s), 18.67 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_2$ 308.1776.; Found 308.1779.

(E)-2-(methoxymethyl)-6-styryltetrahydro-2H-pyran (5d)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 88% (40.8 mg), $R_f = 0.6$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

d.r. = 4.00:1

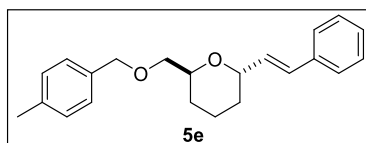
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.42 – 7.37 (m, 2H), 7.31 (m, 2H), 7.28 – 7.20 (m, 1H), 6.58 (dd, $J = 16.2, 1.8$ Hz, 1H), 6.36 (dd, $J = 16.3, 4.8$ Hz, 1H), 4.63 (m, 1H), 3.97 (m, 1H), 3.48 (m, 1H), 3.39 (s, 3H), 3.39 – 3.35 (m, 1H), 1.89 (m, 1H), 1.73 (m, 3H), 1.64 –

1.56 (m, 1H), 1.51 – 1.40 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 136.97 (s), 131.36 (s), 129.80 (s), 128.49 (s), 127.45 (s), 126.33 (s), 75.51 (s), 72.66 (s), 69.84 (s), 59.19 (s), 29.05 (s), 27.47 (s), 18.66 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{15}\text{H}_{20}\text{O}_2$ 232.1463; Found 232.1462.

(E)-2-(((4-methylbenzyl)oxy)methyl)-6-styryltetrahydro-2H-pyran (5e)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 68% (43.9 mg), R_f = 0.6 (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

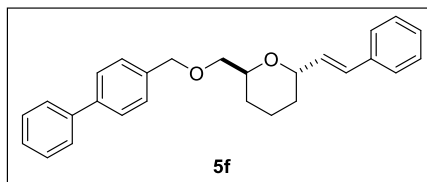
d.r. = 4.81:1

^1H NMR (500 MHz, CDCl_3) δ 7.45 – 7.37 (m, 2H), 7.32 (m, 2H), 7.27 – 7.21 (m, 3H), 7.16 (d, J = 7.7 Hz, 2H), 6.60 (dd, J = 16.3, 1.8 Hz, 1H), 6.35 (dd, J = 16.2, 4.9 Hz, 1H), 4.66 – 4.47 (m, 3H), 4.02 (m, 1H), 3.65 – 3.32 (m, 2H), 2.35 (s, 3H), 1.92 – 1.82 (m, 1H), 1.76 – 1.60 (m, 4H), 1.55 – 1.42 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 137.13 (s), 136.96 (s), 135.28 (s), 131.17 (s), 129.92 (s), 128.96 (s), 128.46 (s), 127.72 (s), 127.41 (s), 126.31 (s), 73.08 (s), 72.49 (s), 72.26 (s), 70.20 (s), 29.32 (s), 27.48 (s), 21.10 (s), 18.65 (s).

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{22}\text{H}_{27}\text{O}_2^+$ 323.2006.; Found 323.2008.

(E)-2-(((1,1'-biphenyl)-4-ylmethoxy)methyl)-6-styryltetrahydro-2H-pyran (5f)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 89% (68.4 mg), R_f = 0.5 (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

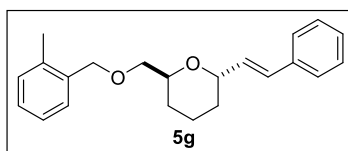
d.r. = 5.07:1

¹H NMR (500 MHz, CDCl₃) δ 7.61 – 7.54 (m, 4H), 7.47 – 7.37 (m, 6H), 7.36 – 7.28 (m, 3H), 7.26 – 7.20 (m, 1H), 6.59 (dd, J = 16.2, 1.9 Hz, 1H), 6.35 (ddd, J = 16.3, 4.9, 1.4 Hz, 1H), 4.61 (m, 3H), 4.03 (m, 1H), 3.70 – 3.45 (m, 2H), 1.86 (m, 1H), 1.78 – 1.62 (m, 4H), 1.50 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 140.92 (s), 140.47 (s), 137.47 (s), 136.99 (s), 131.27 (s), 129.93 (s), 128.73 (s), 128.52 (s), 128.10 (s), 127.47 (s), 127.22 (s), 127.10 (s), 127.07 (s), 126.35 (s), 73.00 (s), 72.59 (s), 70.26 (s), 29.35 (s), 27.55 (s), 18.70 (s).

HRMS (EI): [M] Calcd. for C₂₇H₂₈O₂ 384.2089.; Found 384.2090.

(E)-2-(((2-methylbenzyl)oxy)methyl)-6-styryltetrahydro-2H-pyran (5g)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 83% (52.5 mg), R_f = 0.6 (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

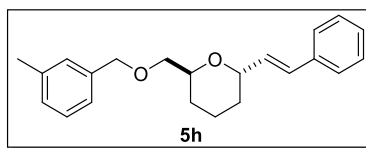
d.r. = 3.36:1

¹H NMR (500 MHz, CDCl₃) δ 7.40 (d, J = 7.6 Hz, 2H), 7.33 (q, J = 7.9, 7.4 Hz, 3H), 7.27 – 7.14 (m, 4H), 6.60 (d, J = 16.2 Hz, 1H), 6.34 (dd, J = 16.3, 4.9 Hz, 1H), 4.59 (m, 3H), 4.04 (m, 1H), 3.56 (m, 2H), 2.35 (s, 3H), 1.92 – 1.83 (m, 1H), 1.78 – 1.62 (m, 4H), 1.50 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 136.97 (s), 136.65 (s), 136.20 (s), 131.20 (s), 130.13 (s), 129.91 (s), 128.51 (s), 128.48 (s), 127.67 (s), 127.43 (s), 126.31 (s), 125.64 (s), 72.57 (s), 72.51 (s), 71.70 (s), 70.22 (s), 29.39 (s), 27.54 (s), 18.81 (s), 18.69 (s).

HRMS (ESI): [M+H]⁺ Calcd. for C₂₂H₂₇O₂⁺ 323.2006.; Found 323.2012.

(E)-2-(((3-methylbenzyl)oxy)methyl)-6-styryltetrahydro-2H-pyran (5h)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 78% (50.3 mg), $R_f = 0.6$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

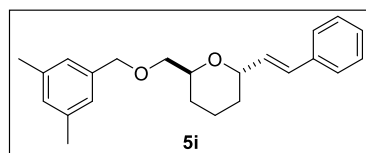
d.r. = 3.93:1

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.44 – 7.38 (m, 2H), 7.36 – 7.29 (m, 2H), 7.27 – 7.22 (m, 2H), 7.21 – 7.14 (m, 2H), 7.11 (d, $J = 7.5$ Hz, 1H), 6.61 (dd, $J = 16.3, 1.8$ Hz, 1H), 6.36 (dd, $J = 16.3, 4.9$ Hz, 1H), 4.63 – 4.52 (m, 3H), 4.05 (m, 1H), 3.63 – 3.45 (m, 2H), 2.36 (s, 3H), 1.88 (m, 1H), 1.80 – 1.61 (m, 4H), 1.55 – 1.43 (m, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 138.25 (s), 137.87 (s), 136.94 (s), 131.16 (s), 129.89 (s), 128.45 (s), 128.34 (s), 128.20 (s), 128.16 (s), 127.39 (s), 126.29 (s), 124.67 (s), 73.25 (s), 72.46 (s), 72.43 (s), 70.18 (s), 29.32 (s), 27.47 (s), 21.32 (s), 18.64 (s).

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{22}\text{H}_{27}\text{O}_2^+$ 323.2006.; Found 323.2009.

(E)-2-(((3,5-dimethylbenzyl)oxy)methyl)-6-styryltetrahydro-2H-pyran (5i)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 86% (57.9 mg), $R_f = 0.6$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

d.r. = 3.44:1

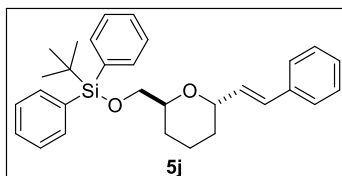
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.43 – 7.38 (m, 2H), 7.36 – 7.29 (m, 2H), 7.27 – 7.20 (m, 1H), 6.98 (m, 2H), 6.93 (s, 1H), 6.61 (dd, $J = 16.2, 1.8$ Hz, 1H), 6.35 (dd, $J = 16.3, 4.9$ Hz, 1H), 4.64 – 4.42 (m, 3H), 4.08 – 4.00 (m, 1H), 3.66 – 3.34 (m, 2H), 2.32 (s, 6H), 1.93 – 1.83 (m, 1H), 1.78 – 1.61 (m, 4H), 1.53 – 1.43 (m, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 138.21 (s), 137.79 (s), 136.97 (s), 131.17 (s), 129.94 (s),

129.11 (s), 128.46 (s), 127.40 (s), 126.31 (s), 125.48 (s), 73.32 (s), 72.47 (s), 72.45 (s), 70.22 (s), 29.37 (s), 27.51 (s), 21.21 (s), 18.66 (s).

HRMS (EI): [M] Calcd. for C₂₃H₂₈O₂ 336.2089.; Found 336.2094.

(E)-tert-butyl-diphenyl((6-styryltetrahydro-2H-pyran-2-yl)methoxy)silane (5j)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 57% (52.1 mg), R_f = 0.6 (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

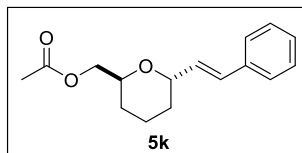
d.r. = 11.11:1

¹H NMR (400 MHz, CDCl₃) δ 7.81 (m, 4H), 7.54 – 7.44 (m, 8H), 7.41 (m, 2H), 7.36 – 7.30 (m, 1H), 6.70 (dd, J = 16.2, 1.8 Hz, 1H), 6.38 (dd, J = 16.2, 4.8 Hz, 1H), 4.61 (m, 1H), 4.09 – 4.00 (m, 1H), 3.92 (m, 1H), 3.77 (m, 1H), 1.91 (m, 1H), 1.86 – 1.71 (m, 4H), 1.56 (m, 1H), 1.20 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 136.99 (s), 135.56 (s), 133.65 (s), 133.57 (s), 130.95 (s), 130.14 (s), 129.52 (s), 128.42 (s), 127.56 (s), 127.33 (s), 126.26 (s), 72.24 (s), 71.75 (s), 66.08 (s), 29.72 (s), 27.25 (s), 26.83 (s), 19.20 (s), 18.62 (s).

HRMS (EI): [M] Calcd. for C₃₀H₃₆O₂Si 456.2485.; Found 456.2488.

(E)-(6-styryltetrahydro-2H-pyran-2-yl)methyl acetate (5k)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 41% (21.3 mg), R_f = 0.6 (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

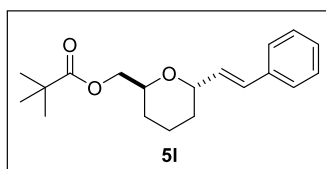
d.r.= 4.60:1

¹H NMR (500 MHz, CDCl₃) δ 7.42 – 7.37 (m, 2H), 7.32 (m, 2H), 7.25 – 7.22 (m, 1H), 6.59 (dd, J = 16.2, 1.8 Hz, 1H), 6.30 (dd, J = 16.2, 4.9 Hz, 1H), 4.61 (m, 1H), 4.24 – 4.06 (m, 2H), 4.02 (m, 1H), 2.11 (s, 3H), 1.93 – 1.82 (m, 1H), 1.80 – 1.68 (m, 3H), 1.68 – 1.59 (m, 1H), 1.50 – 1.39 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 171.13 (s), 136.85 (s), 130.37 (s), 130.12 (s), 128.43 (s), 127.47 (s), 126.44 (s), 78.24 (s), 75.42 (s), 67.40 (s), 31.51 (s), 27.34 (s), 23.01 (s), 20.97 (s).

HRMS (EI): [M] Calcd. for C₁₆H₂₀O₃ 260.1412; Found 264.1410.

(E)-(6-styryltetrahydro-2H-pyran-2-yl)methyl pivalate (5I)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 53% (32.0 mg), R_f = 0.6 (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

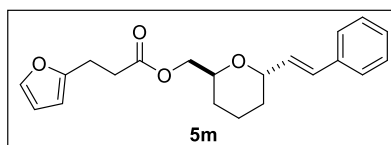
d.r. = 5.21:1

¹H NMR (500 MHz, CDCl₃) δ 7.41 – 7.36 (m, 2H), 7.32 (dd, J = 8.5, 6.9 Hz, 2H), 7.28 – 7.20 (m, 1H), 6.60 (dd, J = 16.2, 1.9 Hz, 1H), 6.26 (dd, J = 16.2, 4.7 Hz, 1H), 4.59 (m, 1H), 4.27 – 4.19 (m, 1H), 4.09 – 3.99 (m, 2H), 1.90 – 1.81 (m, 1H), 1.78 – 1.68 (m, 3H), 1.71 – 1.62 (m, 1H), 1.43 (m, 1H), 1.23 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 178.37 (s), 136.88 (s), 131.37 (s), 129.68 (s), 128.52 (s), 127.50 (s), 126.26 (s), 72.17 (s), 69.09 (s), 65.83 (s), 38.76 (s), 29.33 (s), 27.18 (s), 27.10 (s), 18.62 (s).

HRMS (EI): [M] Calcd. for C₁₉H₂₆O₃ 302.1882; Found 302.1887.

(E)-(6-styryltetrahydro-2H-pyran-2-yl)methyl 3-(furan-2-yl)propanoate (5m)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 78% (53.0 mg), $R_f = 0.6$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

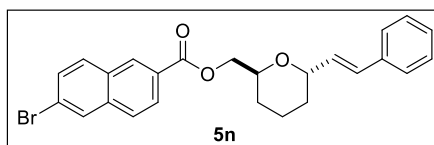
d.r. = 7.14:1

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.41 – 7.37 (m, 2H), 7.31 (m, 2H), 7.27 (d, $J = 1.9$ Hz, 1H), 7.26 – 7.19 (m, 1H), 6.58 (dd, $J = 16.3, 1.8$ Hz, 1H), 6.28 (dd, $J = 16.3, 4.9$ Hz, 1H), 6.24 (m, 1H), 6.01 (d, $J = 3.1$ Hz, 1H), 4.59 (m, 1H), 4.29 – 4.06 (m, 2H), 4.01 (m, 1H), 2.98 (t, $J = 7.6$ Hz, 2H), 2.71 (m, 2H), 1.86 (m, 1H), 1.77 – 1.66 (m, 3H), 1.66 – 1.56 (m, 1H), 1.43 (m, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 172.45 (s), 154.05 (s), 141.15 (s), 136.82 (s), 131.53 (s), 129.47 (s), 128.53 (s), 127.56 (s), 126.32 (s), 110.13 (s), 105.26 (s), 72.42 (s), 69.02 (s), 66.25 (s), 32.57 (s), 29.18 (s), 27.03 (s), 23.40 (s), 18.56 (s).

HRMS (EI): $[M]$ Calcd. for $\text{C}_{21}\text{H}_{24}\text{O}_4$ 340.1675.; Found 340.1680.

(E)-(6-styryltetrahydro-2H-pyran-2-yl)methyl 6-bromo-2-naphthoate (5n)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 64% (57.6 mg), $R_f = 0.5$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

d.r. > 20:1

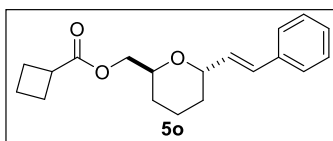
$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.60 (s, 1H), 8.11 (dd, $J = 8.6, 1.7$ Hz, 1H), 8.04 (d, $J = 1.9$ Hz, 1H), 7.79 (dd, $J = 8.7, 5.2$ Hz, 2H), 7.60 (dd, $J = 8.7, 2.0$ Hz, 1H), 7.34 (m, 2H), 7.29 – 7.17 (m, 3H), 6.62 (dd, $J = 16.3, 1.9$ Hz, 1H), 6.30 (dd, $J = 16.2, 4.7$ Hz, 1H), 4.69 – 4.65 (m, 1H), 4.50 (dd, $J = 11.5, 7.1$ Hz, 1H), 4.38 (dd, $J = 11.4, 4.1$ Hz, 1H), 4.22 (m,

1H), 1.95 – 1.88 (m, 1H), 1.76 (m, 4H), 1.56 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 166.29 (s), 136.80 (s), 136.42 (s), 131.63 (s), 131.00 (s), 130.86 (s), 130.12 (s), 129.89 (s), 129.47 (s), 128.53 (s), 127.83 (s), 127.20 (s), 126.46 (s), 126.30 (s), 122.60 (s), 72.44 (s), 69.14 (s), 66.95 (s), 29.30 (s), 27.29 (s), 18.71 (s).

HRMS (ESI): [M+H]⁺ Calcd. for C₂₅H₂₄BrO₃⁺ 451.0904.; Found 451.0909.

(E)-(6-styryltetrahydro-2H-pyran-2-yl)methyl cyclobutanecarboxylate (5o)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 59% (35.4 mg), R_f = 0.6 (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

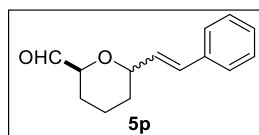
d.r. > 20:1

¹H NMR (500 MHz, CDCl₃) δ 7.40 – 7.35 (m, 2H), 7.34 – 7.27 (m, 2H), 7.26 – 7.19 (m, 1H), 6.57 (dd, J = 16.2, 1.8 Hz, 1H), 6.26 (dd, J = 16.2, 4.8 Hz, 1H), 4.58 (m, 1H), 4.24 – 4.04 (m, 2H), 4.01 (m, 1H), 3.19 (m, 1H), 2.36 – 2.15 (m, 4H), 2.04 – 1.80 (m, 3H), 1.77 – 1.66 (m, 3H), 1.66 – 1.60 (m, 1H), 1.47 – 1.36 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 175.51 (s), 136.90 (s), 131.50 (s), 129.61 (s), 128.55 (s), 127.55 (s), 126.32 (s), 72.37 (s), 69.16 (s), 65.92 (s), 38.03 (s), 29.28 (s), 27.09 (s), 25.31 (s), 25.27 (s), 18.64 (s), 18.41 (s).

HRMS (EI): [M] Calcd. for C₁₉H₂₄O₃ 300.1725.; Found 300.1722.

(E)-6-styryltetrahydro-2H-pyran-2-carbaldehyde (5p)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 33% (14.3 mg), R_f = 0.6 (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

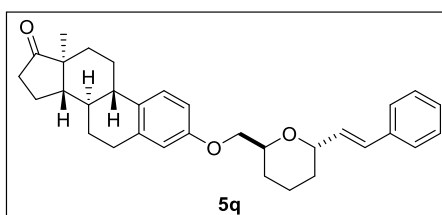
d.r. = 1.67:1

¹H NMR (400 MHz, CDCl₃) mixture: δ 7.26 (m, 5H), 6.62 (dd, J = 78.3, 15.9 Hz, 1H), 6.23 (ddd, J = 74.5, 15.8, 7.3 Hz, 1H), 5.57 (d, J = 21.1 Hz, 1H), 4.58 (m, 1H), 4.22 (m, 1H), 2.13 – 1.75 (m, 2H), 1.75 – 1.42 (m, 5H).

¹³C NMR (101 MHz, CDCl₃) mixture: δ 136.46 (s), 134.10 (s), 131.30 (s), 129.38 (s), 128.59 (s), 128.49 (s), 127.91 (s), 127.69 (s), 126.57 (s), 126.53 (s), 123.40 (s), 102.98 (s), 102.53 (s), 80.29 (s), 79.82 (s), 78.53 (s), 76.28 (s), 30.93 (s), 30.32 (s), 28.44 (s), 25.03 (s), 15.81 (s), 15.74 (s).

HRMS (ESI): [M+H]⁺ Calcd. for C₁₄H₁₇O₂⁺ 217.1224; Found 217.1225.

(8R,9S,13S,14S)-13-methyl-3-(((E)-styryl)tetrahydro-2H-pyran-2-yl)methoxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (5q)



Following the **procedure E** on 0.2 mmol scale, white solid (m. p. = 148 - 150 °C), yield: 73% (68.7 mg), R_f = 0.4 (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

d.r. = 9.09:1

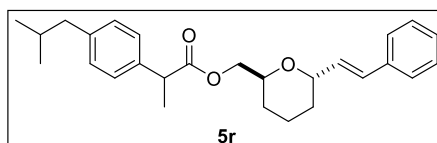
¹H NMR (500 MHz, CDCl₃) δ 7.40 – 7.35 (m, 2H), 7.34 – 7.28 (m, 2H), 7.27 – 7.21 (m, 1H), 7.18 (dd, J = 8.7, 1.0 Hz, 1H), 6.75 (dd, J = 8.6, 2.8 Hz, 1H), 6.68 (d, J = 2.7 Hz, 1H), 6.60 (dd, J = 16.3, 1.8 Hz, 1H), 6.33 (dd, J = 16.3, 4.8 Hz, 1H), 4.63 (d, J = 4.9 Hz, 1H), 4.16 (m, 1H), 4.06 (m, 1H), 3.94 (m, 1H), 2.95 – 2.83 (m, 2H), 2.49 (dd, J = 19.0, 8.6 Hz, 1H), 2.42 – 2.35 (m, 1H), 2.28 – 2.20 (m, 1H), 2.13 (m, 1H), 2.07 – 2.02 (m, 1H), 2.02 – 1.85 (m, 3H), 1.81 – 1.70 (m, 4H), 1.66 – 1.53 (m, 3H), 1.53 – 1.36 (m, 4H), 0.90 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 220.95 (s), 156.84 (s), 137.62 (s), 136.88 (s), 132.10 (s), 131.41 (s), 129.63 (s), 128.47 (s), 127.47 (s), 126.31 (s), 126.21 (s), 114.71 (s), 112.25

(s), 72.70 (s), 70.23 (s), 69.40 (s), 50.33 (s), 47.94 (s), 43.91 (s), 38.28 (s), 35.80 (s), 31.51 (s), 29.56 (s), 29.32 (s), 27.49 (s), 26.48 (s), 25.83 (s), 21.51 (s), 18.60 (s), 13.79 (s).

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{32}H_{39}O_3^+$ 471.2894.; Found 471.2904.

(E)-(6-styryltetrahydro-2H-pyran-2-yl)methyl 2-(4-isobutylphenyl)propanoate (5r)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 53% (43.1 mg), $R_f = 0.6$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

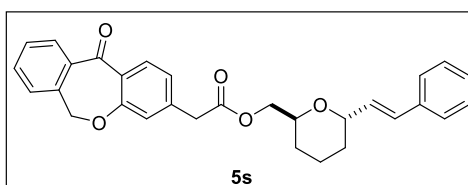
d.r. = 8.53:1

1H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.34 (m, 2H), 7.31 (m, 2H), 7.24 (m, 1H), 7.23 – 7.18 (m, 2H), 7.07 – 7.02 (m, 2H), 6.54 (ddd, $J = 16.4, 12.4, 1.8$ Hz, 1H), 6.22 (ddd, $J = 16.3, 4.9, 3.4$ Hz, 1H), 4.53 (m, 1H), 4.28 – 4.01 (m, 2H), 3.98 (m, 1H), 3.75 (q, $J = 7.2$ Hz, 1H), 2.39 (dd, $J = 7.2, 4.5$ Hz, 2H), 1.86 – 1.74 (m, 2H), 1.66 (m, 3H), 1.54 (m, 1H), 1.49 (d, $J = 7.1$ Hz, 3H), 1.33 (m, 1H), 0.86 (dd, $J = 6.6, 2.8$ Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.70 (s), 140.46 (s), 137.66 (s), 136.90 (s), 131.40 (s), 129.63 (s), 129.26 (s), 128.53 (s), 127.54 (s), 127.20 (s), 126.35 (s), 72.30 (s), 69.07 (s), 66.18 (s), 44.99 (s), 30.13 (s), 29.34 (s), 26.94 (s), 22.34 (s), 18.54 (s).

HRMS (EI): $[M]$ Calcd. for $C_{27}H_{34}O_3$ 406.2508.; Found 406.2503.

(E)-(6-styryltetrahydro-2H-pyran-2-yl)methyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-3-yl)acetate (5s)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 69% (64.7

mg), $R_f = 0.4$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

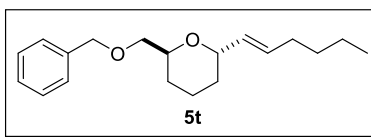
d.r. = 18.53:1

^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, $J = 2.4$ Hz, 1H), 7.87 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.55 (m, 1H), 7.50 – 7.41 (m, 2H), 7.39 – 7.17 (m, 6H), 6.99 (d, $J = 8.5$ Hz, 1H), 6.55 (dd, $J = 16.2, 1.8$ Hz, 1H), 6.26 (dd, $J = 16.2, 4.9$ Hz, 1H), 5.14 (s, 2H), 4.58 (m, 1H), 4.37 – 3.98 (m, 3H), 3.70 (s, 2H), 1.85 (m, 1H), 1.77 – 1.56 (m, 4H), 1.43 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 190.74 (s), 171.38 (s), 160.43 (s), 140.43 (s), 136.83 (s), 136.37 (s), 135.54 (s), 132.69 (s), 132.48 (s), 131.52 (s), 129.52 (s), 129.46 (s), 129.21 (s), 128.53 (s), 127.76 (s), 127.74 (s), 127.54 (s), 126.36 (s), 125.09 (s), 121.01 (s), 73.57 (s), 72.42 (s), 69.01 (s), 66.61 (s), 40.10 (s), 29.22 (s), 27.03 (s), 18.58 (s).

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{30}\text{H}_{29}\text{O}_5^+$ 469.2010.; Found 469.2010.

(E)-2-((benzyloxy)methyl)-6-(hex-1-en-1-yl)tetrahydro-2H-pyran (5t)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 48% (27.6 mg), $R_f = 0.6$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

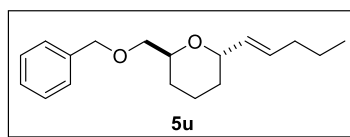
d.r. = 5.88:1

^1H NMR (500 MHz, CDCl_3) δ 7.37 – 7.30 (m, 4H), 7.30 – 7.23 (m, 1H), 5.70 – 5.55 (m, 2H), 4.62 – 4.52 (m, 2H), 4.34 (q, $J = 4.7$ Hz, 1H), 3.95 (m, 1H), 3.59 – 3.33 (m, 2H), 2.11 – 1.99 (m, 2H), 1.79 – 1.72 (m, 2H), 1.70 – 1.52 (m, 3H), 1.47 – 1.41 (m, 1H), 1.41 – 1.28 (m, 4H), 0.90 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 138.57 (s), 133.03 (s), 129.79 (s), 128.41 (s), 127.75 (s), 127.59 (s), 73.34 (s), 72.66 (s), 72.61 (s), 69.99 (s), 32.29 (s), 31.47 (s), 29.45 (s), 27.69 (s), 22.32 (s), 18.66 (s), 14.03 (s).

HRMS (EI): $[\text{M}]$ Calcd. for $\text{C}_{19}\text{H}_{28}\text{O}_2$ 288.2089.; Found 288.2079.

(E)-2-((benzyloxy)methyl)-6-(pent-1-en-1-yl)tetrahydro-2H-pyran (5u)



Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 49% (26.9 mg), $R_f = 0.6$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

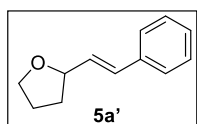
d.r. = 5.90:1

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.36 – 7.30 (m, 4H), 7.28 – 7.23 (m, 1H), 5.68 – 5.54 (m, 2H), 4.61 – 4.51 (m, 2H), 4.33 (q, $J = 4.6, 4.2$ Hz, 1H), 3.94 (m, 1H), 3.59 – 3.33 (m, 2H), 2.02 (m, 2H), 1.79 – 1.70 (m, 2H), 1.69 – 1.52 (m, 3H), 1.46 – 1.35 (m, 3H), 0.89 (t, $J = 7.3$ Hz, 3H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 138.49 (s), 132.70 (s), 129.94 (s), 128.33 (s), 127.67 (s), 127.51 (s), 73.26 (s), 72.57 (s), 72.54 (s), 69.91 (s), 34.61 (s), 29.37 (s), 27.62 (s), 22.36 (s), 18.58 (s), 13.71 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{18}\text{H}_{26}\text{O}_2$ 274.1933.; Found 274.1933.

(E)-2-styryltetrahydrofuran (5a')



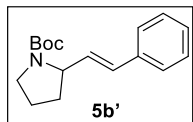
Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 72% (25.1 mg), $R_f = 0.6$ (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.39 (m, 2H), 7.31 (m, 2H), 7.25 – 7.20 (m, 1H), 6.59 (d, $J = 15.9$ Hz, 1H), 6.22 (dd, $J = 15.8, 6.6$ Hz, 1H), 4.48 (q, $J = 6.9$ Hz, 1H), 4.02 – 3.94 (m, 1H), 3.85 (m, 1H), 2.18 – 2.08 (m, 1H), 1.98 – 1.89 (m, 1H), 1.72 (m, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 136.79 (s), 130.45 (s), 130.36 (s), 128.44 (s), 127.42 (s), 126.39 (s), 79.60 (s), 68.11 (s), 32.33 (s), 25.85 (s).

HRMS (EI): [M] Calcd. for C₁₂H₁₄O 174.1045.; Found 174.1038.

tert-butyl (E)-2-styrylpyrrolidine-1-carboxylate (5b')



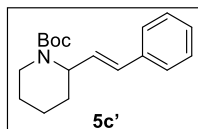
Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 46% (25.2 mg), R_f = 0.6 (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.16 (m, 5H), 6.43 (d, J = 15.6 Hz, 1H), 6.11 (d, J = 14.1 Hz, 1H), 4.48 (m, 1H), 3.85 – 3.10 (m, 2H), 2.11 (m, 1H), 2.01 – 1.73 (m, 3H), 1.45 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 154.60 (s), 136.99 (s), 130.65 (s), 129.35 (s), 128.43 (s), 127.17 (s), 126.20 (s), 79.09 (s), 58.89 (s), 46.21 (s), 32.48 (s), 28.42 (s), 22.99 (s).

HRMS (EI): [M] Calcd. for C₁₇H₂₃NO₂ 273.1729.; Found 273.1736.

tert-butyl (E)-2-styrylpiperidine-1-carboxylate (5c')



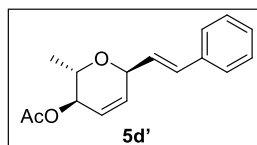
Following the **procedure E** on 0.2 mmol scale, colorless oil liquid, yield: 53% (30.5 mg), R_f = 0.6 (silica gel, PE: EtOAc = 10:1, v/v), column chromatography (silica gel, PE: EtOAc = 80:1, v/v).

¹H NMR (500 MHz, CDCl₃) δ 7.40 – 7.28 (m, 4H), 7.23 (m, 1H), 6.39 (dd, J = 16.1, 1.7 Hz, 1H), 6.18 (dd, J = 16.2, 4.8 Hz, 1H), 4.96 (s, 1H), 4.00 (m, 1H), 2.91 (m, 1H), 1.87 – 1.71 (m, 2H), 1.62 (m, 4H), 1.48 (s, 9H).

¹³C NMR (126 MHz, CDCl₃) δ 155.38 (s), 137.04 (s), 130.71 (s), 128.71 (s), 128.52 (s), 127.34 (s), 126.21 (s), 79.44 (s), 52.20 (s), 39.85 (s), 29.49 (s), 28.46 (s), 25.54 (s), 19.67 (s).

HRMS (ESI): [M+H]⁺ Calcd. for C₁₈H₂₆NO₂⁺ 288.1959.; Found 288.1954.

(2S,3R,6S)-2-methyl-6-((E)-styryl)-3,6-dihydro-2H-pyran-3-yl acetate (5d')



Following the **procedure F** on 0.2 mmol scale, colorless oil liquid, yield: 59% (30.5 mg), $R_f = 0.5$ (silica gel, PE: EtOAc = 5:1, v/v), column chromatography (silica gel, PE: EtOAc = 20:1, v/v).

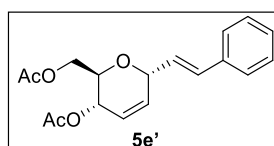
d.r. = 5.37:1

^1H NMR (400 MHz, CDCl_3) δ 7.33 (d, $J = 7.6$ Hz, 2H), 7.25 (t, $J = 7.5$ Hz, 2H), 7.19 (m, 1H), 6.52 (d, $J = 16.0$ Hz, 1H), 6.21 (m, 1H), 5.95 – 5.88 (m, 1H), 5.79 (m, 1H), 4.95 (dt, $J = 6.8, 2.4$ Hz, 1H), 4.79 – 4.74 (m, 1H), 3.81 (t, $J = 6.6$ Hz, 1H), 2.02 (s, 3H), 1.19 (dd, $J = 6.4, 1.7$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 170.67 (s), 136.35 (s), 132.68 (s), 131.38 (s), 128.55 (s), 127.89 (s), 126.85 (s), 126.54 (s), 124.86 (s), 71.89 (s), 70.06 (s), 67.56 (s), 21.17 (s), 17.60 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_3$ 258.1256.; Found 258.1254.

((2R,3S,6R)-3-acetoxy-6-((E)-styryl)-3,6-dihydro-2H-pyran-2-yl)methyl acetate (5e')



Following the **procedure F** on 0.2 mmol scale, colorless oil liquid, yield: 46% (29.1 mg), $R_f = 0.5$ (silica gel, PE: EtOAc = 5:1, v/v), column chromatography (silica gel, PE: EtOAc = 20:1, v/v).

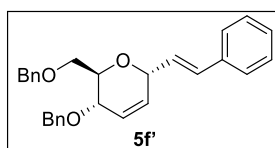
d.r. = 11.50:1

^1H NMR (500 MHz, CDCl_3) δ 7.40 – 7.36 (m, 2H), 7.32 (m, 2H), 7.26 (m, 1H), 6.66 – 6.57 (m, 1H), 6.25 (dd, $J = 16.1, 5.5$ Hz, 1H), 6.00 (m, 1H), 5.88 (m, 1H), 5.27 (m, 1H), 4.92 (m, 1H), 4.30 – 4.13 (m, 2H), 3.94 (m, 1H), 2.09 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 170.80 (s), 170.29 (s), 136.17 (s), 133.06 (s), 130.84 (s), 128.57 (s), 128.01 (s), 126.53 (s), 125.90 (s), 125.25 (s), 72.58 (s), 68.98 (s), 65.04 (s), 63.15 (s), 20.98 (s), 20.78 (s).

HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{18}\text{H}_{21}\text{O}_5^+$ 317.1384.; Found 317.1390.

(2R,3S,6R)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-((E)-styryl)-3,6-dihydro-2H-pyran (5f')



Following the **procedure F** on 0.2 mmol scale, colorless oil liquid, yield: 39% (32.2 mg), $R_f = 0.5$ (silica gel, PE: EtOAc = 5:1, v/v), column chromatography (silica gel, PE: EtOAc = 20:1, v/v).

d.r. = 3.00:1

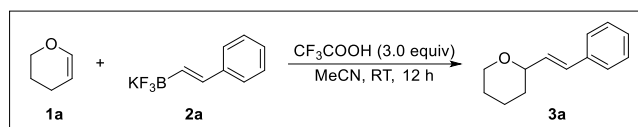
^1H NMR (400 MHz, CDCl_3) δ 7.34 (m, 15H), 6.12 (d, $J = 10.4$ Hz, 1H), 5.83 (dd, $J = 10.2, 2.5$ Hz, 1H), 5.16 (d, $J = 2.6$ Hz, 1H), 4.85 (d, $J = 11.8$ Hz, 1H), 4.69 – 4.60 (m, 3H), 4.51 (m, 2H), 4.23 (d, $J = 9.4$ Hz, 1H), 4.05 (m, 1H), 3.76 (dd, $J = 10.7, 4.1$ Hz, 1H), 3.67 (dd, $J = 10.7, 2.0$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 138.17 (s), 138.05 (s), 138.03 (s), 130.81 (s), 128.35 (s), 128.31 (s), 127.99 (s), 127.92 (s), 127.81 (s), 127.79 (s), 127.76 (s), 127.71 (s), 127.67 (s), 127.57 (s), 126.50 (s), 93.94 (s), 73.35 (s), 71.02 (s), 70.35 (s), 70.01 (s), 69.30 (s), 68.74 (s).

HRMS (EI): $[\text{M}]$ Calcd. for $\text{C}_{28}\text{H}_{28}\text{O}_3$ 412.2038.; Found 412.2033.

7. Scale-up reactions and synthetic applications.

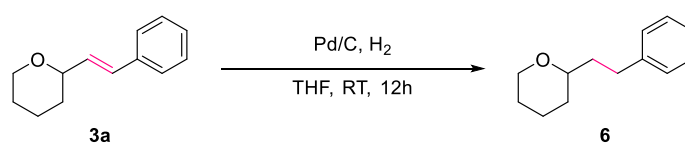
7.1 12 mmol scale reactions.



To a 500mL flame-dried Schlenk flask were added FeCl_2 (20 mol%), **2a** (30 mmol, 2.5 equiv), and the flask was evacuated and refilled with argon (three times). Subsequently, CH_3CN (180 mL), **1a** (12 mmol, 1.0 equiv) and CF_3COOH (36 mmol, 3.0 equiv) were added and the reaction was stirred at room temperature for 12 h. The reaction mixture was diluted with ethyl acetate and the solution washed with saturated aqueous NaHCO_3 , water and brine. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by flash column chromatography to afford the final product **3a** (1.66 g, 74%) as colorless liquid.

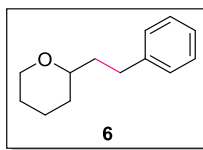
7.2 Synthetic applications.

a.



To the alkene **3a** (0.5 mmol, 1.0 equiv) in THF (5 mL), was added palladium on activated carbon (5 %, 0.1 equiv). The reaction solution was purged with hydrogen balloon for 15 minutes and then went overnight under hydrogen balloon. Then, the reaction was filtered over a short path of Celite, concentrated in vacuo, and the crude mixture was purified by flash column chromatography to afford the final product **6** (88.5 mg, 93%) as colorless liquid.

2-phenethyltetrahydro-2H-pyran (**6**)²²

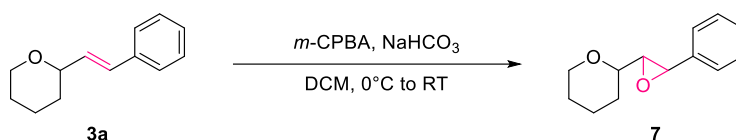


Spectroscopic data are in agreement with those previously reported²³.

¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.17 (m, 5H), 4.03 (m, 1H), 3.44 (td, J = 11.7, 2.4 Hz, 1H), 3.26 (m, 1H), 2.74 (m, 2H), 1.92 – 1.79 (m, 2H), 1.70 (m, 1H), 1.64 – 1.42 (m, 4H), 1.32 (m, 1H).

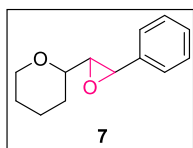
¹³C NMR (126 MHz, CDCl₃) δ 142.36 (s), 128.42 (s), 128.22 (s), 125.59 (s), 76.83 (s), 68.39 (s), 38.26 (s), 31.89 (s), 31.72 (s), 26.14 (s), 23.46 (s).

b.



To a 100 mL dried Schlenk flask was added **3a** (0.5 mmol, 1.0 equiv), NaHCO₃ (0.65 mmol, 1.3 equiv) and DCM (2 mL) under argon atmosphere. Then *m*-CPBA (73%, 1.2 equiv) dissolved in DCM (2 mL) was added dropwise at 0 °C. The reaction was stirred for 1 h and then allowed to warm to room temperature. After completion of the reaction (TLC monitoring), the reaction mixture is quenched with aqueous Na₂S₂O₄, and the aqueous phase is extracted with DCM. The combined organic layers are washed successively with a saturated solution of NaHCO₃ and brine and dried over Na₂SO₄. The filtrate was concentrated under reduced pressure and the crude mixture was purified by flash column chromatography to afford the final product **7** (87.8 mg, 86%, 1.5 :1) as colorless liquid.

2-(3-phenyloxiran-2-yl)tetrahydro-2H-pyran (**7**)²⁴



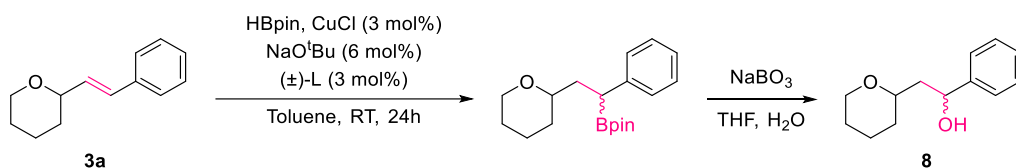
¹H NMR (400 MHz, CDCl₃) major isomer: δ 7.40 – 7.28 (m, 5H), 4.05 (m, 1H), 3.92

(d, $J = 2.0$ Hz, 1H), 3.49 (m, 2H), 3.04 (dd, $J = 4.2, 2.1$ Hz, 1H), 1.94 (m, 1H), 1.84 – 1.74 (m, 1H), 1.66 – 1.43 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3) major isomer: δ 137.23 (s), 128.37 (s), 128.08 (s), 125.70 (s), 76.23 (s), 68.45 (s), 64.07 (s), 56.02 (s), 28.34 (s), 25.87 (s), 22.85 (s).

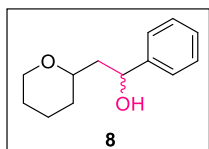
HRMS (EI): [M] Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_2$ 204.1150; Found 204.1142.

c.



A mixture of CuCl (3 mol%), NaO^tBu (6 mol%), and DTBM-segphos (3 mol%) in anhydrous toluene (0.2 mL) was stirred for 10 min in a Schlenk tube under an atmosphere of argon. Pinacolborane (0.6 mmol, 1.2 equiv) was added to the reaction mixture and stirred for 10 min at room temperature. **3a** (0.5 mmol, 1.0 equiv) was dissolved in toluene (0.3 mL) and added. The reaction was monitored by TLC and was filtered through a pad of Celite and concentrated, and it was diluted with THF (1 mL) and water (1.0 mL) and then followed by addition of NaBO₃ (1.0 mmol, 2.0 equiv) and the mixture was allowed to stir for 3h at room temperature. The product was purified by chromatography on silica gel to afford the final product **8** (87.8 mg, 75%, 1 :1) as colorless liquid.

1-phenyl-2-(tetrahydro-2H-pyran-2-yl)ethan-1-ol (8)^{25,22}

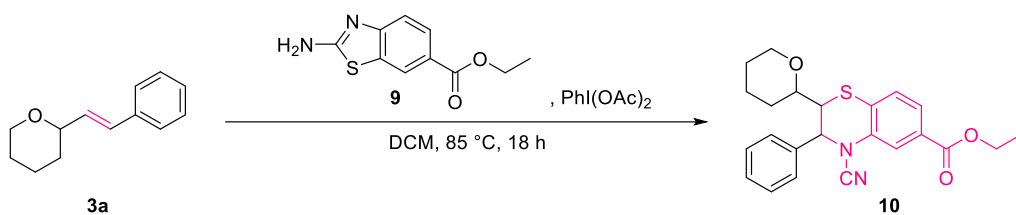


^1H NMR (400 MHz, CDCl_3) mixture: δ 7.33 (m, 8H), 7.23 (m, 2H), 4.97 (m, 1H), 4.91 (dd, $J = 9.9, 3.0$ Hz, 1H), 4.32 (s, 1H), 4.00 (dt, $J = 11.4, 7.1$ Hz, 2H), 3.79 (d, $J = 4.8$ Hz, 1H), 3.60 (t, $J = 10.6$ Hz, 1H), 3.43 (m, 3H), 1.96 – 1.76 (m, 5H), 1.62 – 1.35 (m, 11H).

^{13}C NMR (101 MHz, CDCl_3) mixture: δ 144.83 (s), 144.47 (s), 128.14 (s), 128.11 (s), 127.05 (s), 126.80 (s), 125.60 (s), 125.42 (s), 78.84 (s), 75.24 (s), 74.27 (s), 71.08 (s), 68.28 (s), 68.25 (s), 45.57 (s), 44.29 (s), 32.08 (s), 31.47 (s), 25.74 (s), 25.63 (s), 23.15 (s), 23.02 (s).

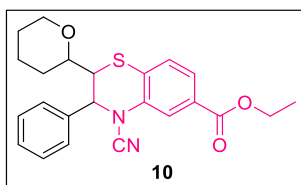
HRMS (ESI): $[\text{M}+\text{H}]^+$ Calcd. for $\text{C}_{13}\text{H}_{19}\text{O}_2^+$ 207.1380; Found 207.1380.

d.



A 10 mL pressure-resistant tube equipped with a magnetic stir bar was charged with the $\text{PhI}(\text{OAc})_2$ (0.2 mmol, 2.0 equiv), 2-benzoaminothiazole **9** (0.1 mmol, 1.0 equiv), then the tube was evacuated and backfilled with argon for three times. Under argon atmosphere, DCM (1 mL) and **3a** (0.3 mmol, 3.0 equiv) were added to the system. The mixture was stirred at 85 °C for 18 hours. After completion of the reaction (monitored by TLC), then cooled to room temperature. Solvent and volatile reagents were removed by rotary evaporation and the residue was purified by flash column chromatography on silica gel to give the final product **10** (28.1 mg, 69%) as colorless liquid.

ethyl 4-cyano-3-phenyl-2-(tetrahydro-2H-pyran-2-yl)-3,4-dihydro-2H-benzo[b][1,4]thiazine-6-carboxylate (10)²⁶



^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.7 Hz, 1H), 7.81 (s, 1H), 7.50 (d, J = 8.6 Hz, 1H), 7.32 (m, 3H), 7.17 (m, 2H), 5.81 (d, J = 3.0 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 4.15 – 4.08 (m, 1H), 3.47 (td, J = 11.5, 3.0 Hz, 1H), 3.23 (t, J = 10.3 Hz, 1H), 3.07 (dd, J = 9.8, 2.9 Hz, 1H), 2.22 (d, J = 13.0 Hz, 1H), 1.88 (d, J = 13.1 Hz, 1H), 1.56 (m, 2H),

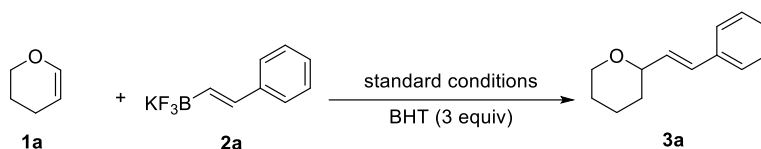
1.38 (m, 4H), 1.24 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.21 (s), 138.40 (s), 136.88 (s), 130.02 (s), 128.67 (s), 128.26 (s), 127.80 (s), 125.79 (s), 125.65 (s), 117.99 (s), 116.51 (s), 112.04 (s), 76.31 (s), 68.98 (s), 61.09 (s), 59.31 (s), 48.77 (s), 29.83 (s), 25.65 (s), 23.10 (s), 14.25 (s).

HRMS (EI): [M] Calcd. for $\text{C}_{23}\text{H}_{24}\text{N}_2\text{O}_3\text{S}$ 408.1508; Found 408.1511.

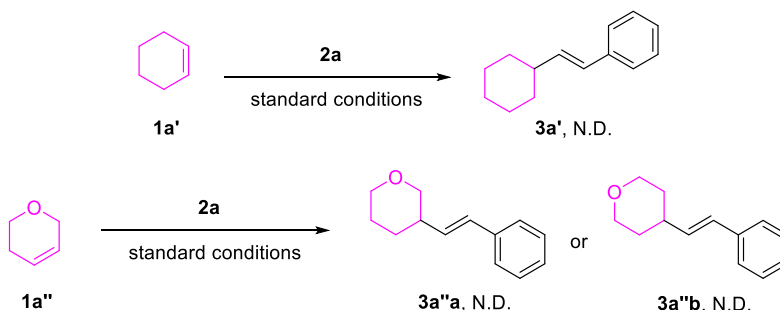
8. Control experiments.

A.



To a flame-dried Schlenk tube were added FeCl_2 (20 mol%), **2a** (0.5 mmol, 2.5 equiv) and additional BHT (0.6 mmol, 3.0 equiv), and the tube was evacuated and refilled with argon (three times). Subsequently, CH_3CN (3 mL), **1a** (0.2 mmol, 1.0 equiv) and CF_3COOH (0.6 mmol, 3.0 equiv) were added and the reaction was stirred at room temperature for 12 h. **3a** yield 73% determined by GC analysis by using dodecane as the internal standard.

B.



To a flame-dried Schlenk tube were added FeCl_2 (20 mol%), **2a** (0.5 mmol, 2.5 equiv) and the tube was evacuated and refilled with argon (three times). Subsequently, CH_3CN (3 mL), **1a'** or **1a''** (0.2 mmol, 1.0 equiv) and CF_3COOH (0.6 mmol, 3.0 equiv) were

added and the reaction was stirred at room temperature for 12 h. None of the corresponding product was detected by GC.

9. General methods for determination of the d.r. ratios and configurations

Taking **5d** as an illustration, we showed the determination details of the d.r. ratios and configurations by means of ^1H NMR and ^1H ^1H NOESY NMR. Upon completion, the reaction was filtered over a short path of celite and then concentrated in vacuo to obtain the ^1H NMR spectrum of the crude product (Figure S1). Then, it was further purified by column chromatography to afford the pure product **5d** and *sub-5d*, and the NMR spectrum of them were obtained respectively (Figure S2-5). By comparing the ^1H NMR spectrum of the crude product with compound **5d** and *sub-5d*, we could confirm the characteristic peak (for example, the hydrogen atom H1 of **5d** is around 4.69 ppm and 3.70 ppm of *sub-5d*). Based on the integration of the H1 signals of compounds **5d** and *sub-5d*, the d.r. ratio is about 4.00:1. As for the configurations, no obvious signals between H1 and H5 have been represented in ^1H ^1H NOESY NMR of **5d**, but *sub-5d* does, so H1 and H5 of **5d** were on the different sides of the six-membered ring. In the same way, the d.r. ratios and configurations of other **5a-u** compounds were also determined.

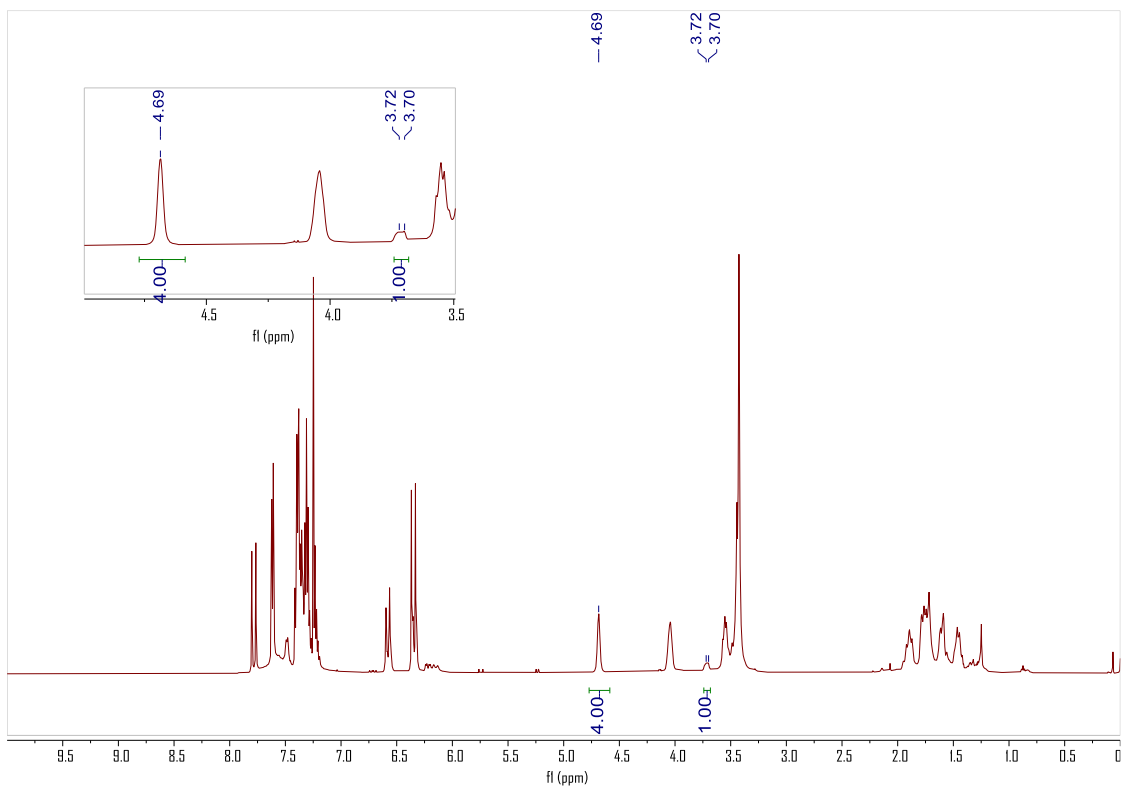


Figure S1: ^1H NMR spectrum of the crude product

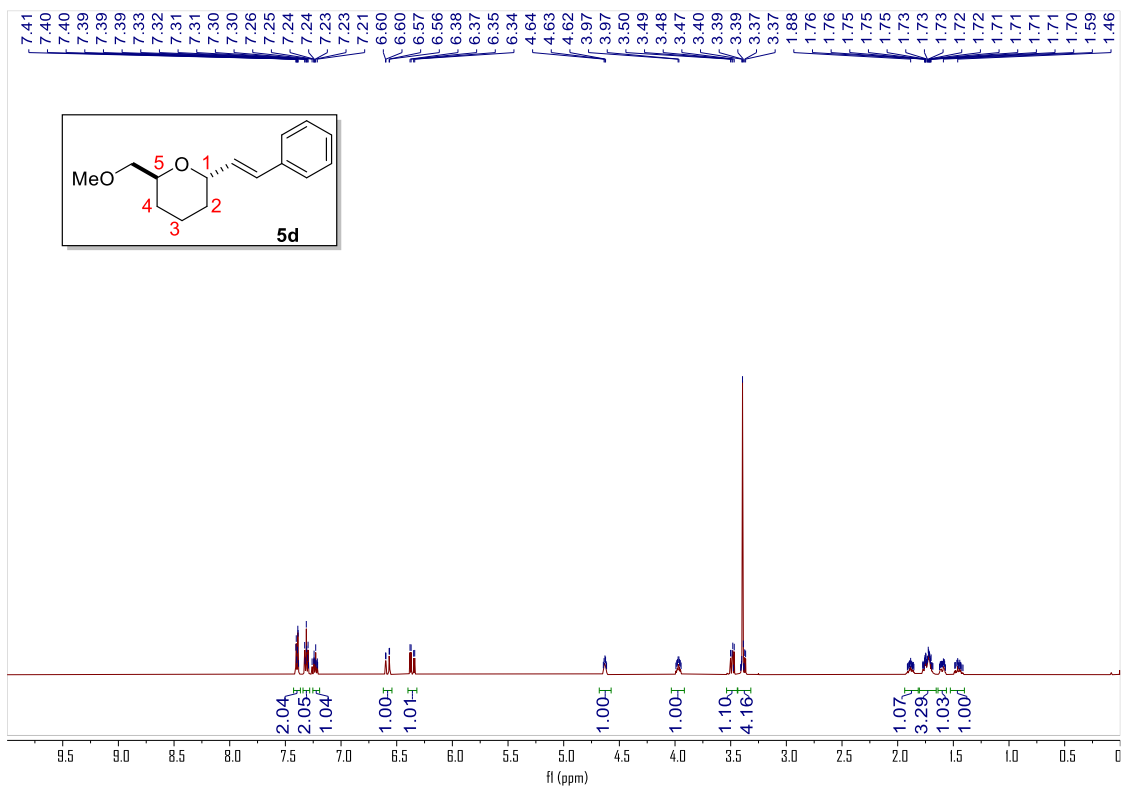


Figure S2: ^1H NMR spectrum of **5d**

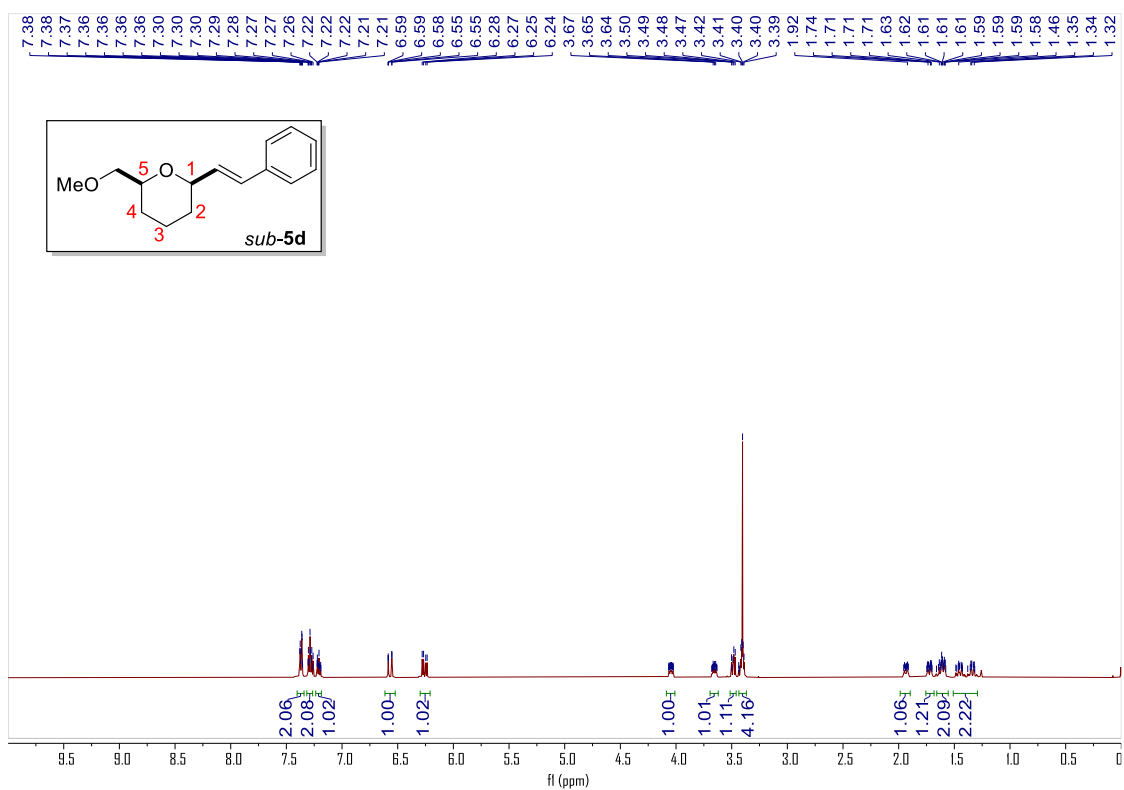


Figure S3: ^1H NMR spectrum of *sub-5d*

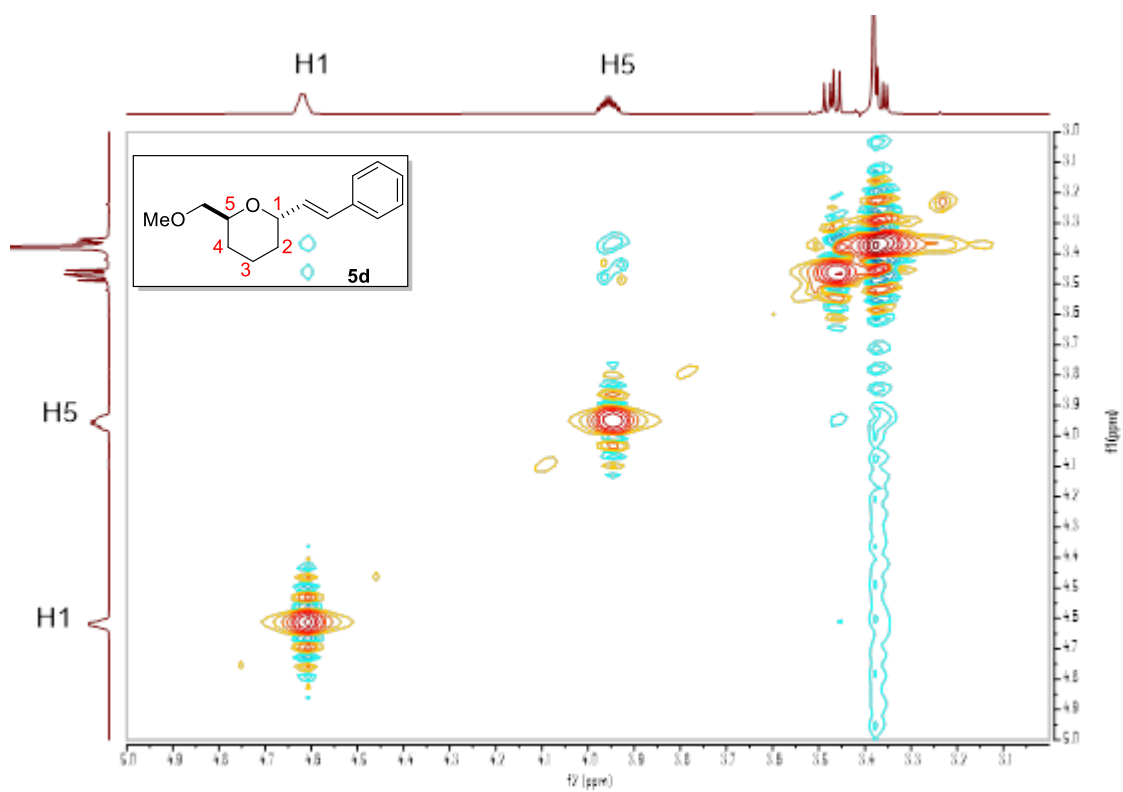


Figure S4: ^1H ^1H NOESY NMR spectrum of *5d*

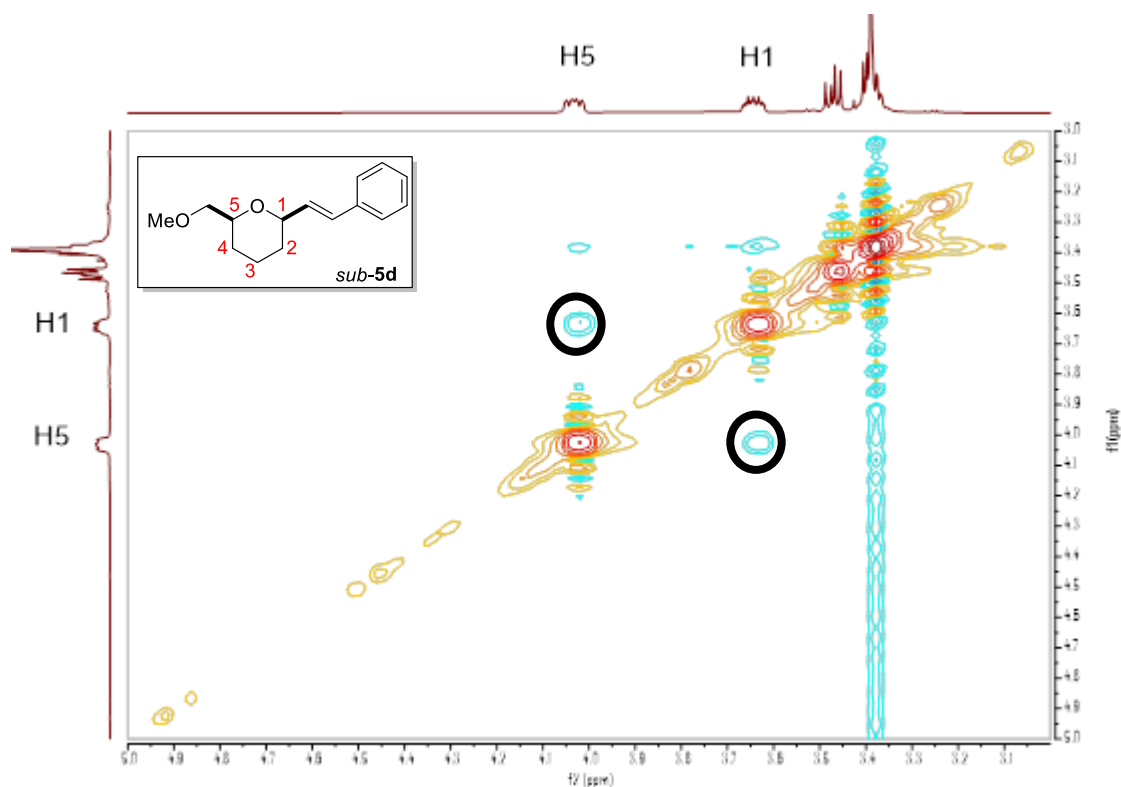
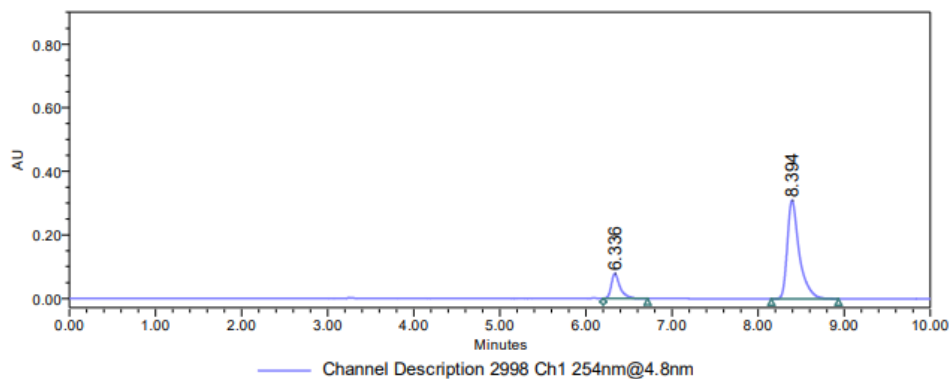


Figure S5: ¹H ¹H NOESY NMR spectrum of *sub-5d*

Taking **5d'** as an illustration, we showed the determination details of the d.r. ratios and configurations by means of HPLC and ¹H ¹H COSY NMR. Upon completion, the reaction was concentrated in vacuo and purified by preparative TLC to give the crude product and then determined by HPLC (Figure S6). Then, it was further purified by column chromatography to afford the pure product **5d'** and *sub-5d'*, and the NMR spectrum and HPLC determination of them were obtained respectively (Figure S7-10). By comparing the peak time and the integration of the signals of compounds **5d'** and *sub-5d'*, the d.r. ratio is about 6.69:1. As for the configurations, no obvious signals between H1 and H5 have been represented in ¹H ¹H COSY NMR of **5d'**, but *sub-5d'* does, so H1 and H5 of **5d'** were on the different sides of the six-membered ring. In the same way, the d.r. ratios and configurations of **5e'**, **5f'** were also determined.

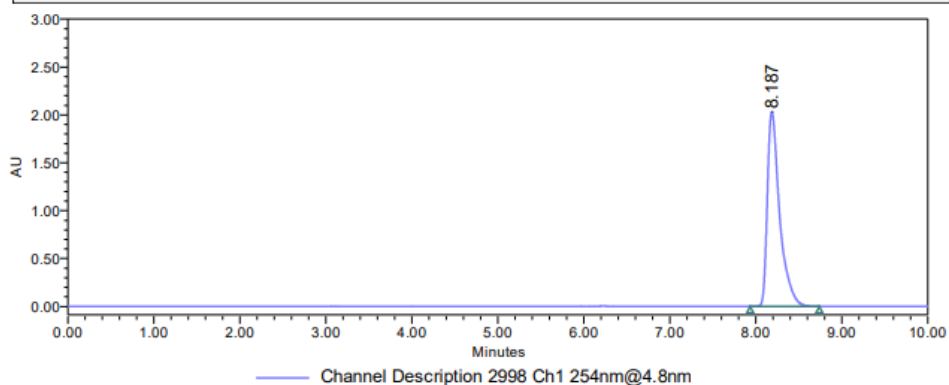
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Sample Type:	Unknown	Sample Set Name:	1
Vial:	1:B,1	Acq. Method Set:	100298
Injection #:	1	Processing Method:	00
Injection Volume:	10.00 ul	Channel Name:	2998 Ch1 254nm@4.8nm
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	2998 Ch1 254nm@4.8nm
Date Acquired:	2/29/2024 5:59:54 AM CST		
Date Processed:	2/29/2024 7:29:50 AM CST		



	Retention Time (min)	Int Type	Width (sec)	Area (μV*sec)	Height (μV)	% Area
1	6.34	VB	31.00	552802	78260	15.69
2	8.39	BB	46.90	2971441	309178	84.31

Figure S6: HPLC determination of the crude product

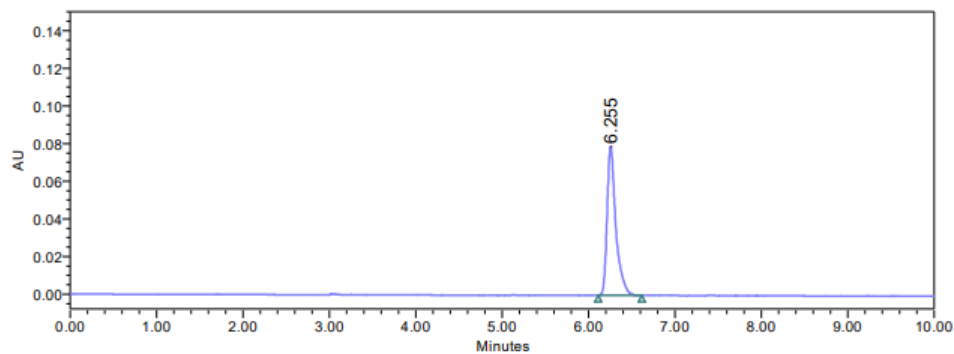
SAMPLE INFORMATION			
Sample Name:	1017-2	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	1
Vial:	1:B,3	Acq. Method Set:	100298
Injection #:	1	Processing Method:	00
Injection Volume:	10.00 ul	Channel Name:	2998 Ch1 254nm@4.8nm
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	2998 Ch1 254nm@4.8nm
Date Acquired:	2/29/2024 6:41:23 AM CST		
Date Processed:	2/29/2024 7:32:53 AM CST		



	Retention Time (min)	Int Type	Width (sec)	Area (μV*sec)	Height (μV)	% Area
1	8.19	bb	48.20	20187432	2032432	100.00

Figure S7: HPLC determination of 5d'

SAMPLE INFORMATION			
Sample Name:	1017-1	Acquired By:	System
Sample Type:	Unknown	Sample Set Name:	1
Vial:	1:B,2	Acq. Method Set:	100298
Injection #:	1	Processing Method:	00
Injection Volume:	10.00 ul	Channel Name:	2998 Ch1 254nm@4.8nm
Run Time:	20.0 Minutes	Proc. Chnl. Descr.:	2998 Ch1 254nm@4.8nm
Date Acquired:	2/29/2024 6:20:38 AM CST		
Date Processed:	2/29/2024 7:31:19 AM CST		



Channel Description 2998 Ch1 254nm@4.8nm

	Retention Time (min)	Int Type	Width (sec)	Area (μV*sec)	Height (μV)	% Area
1	6.26	BB	30.30	555952	79133	100.00

Figure S8: HPLC determination of *sub-5d'*

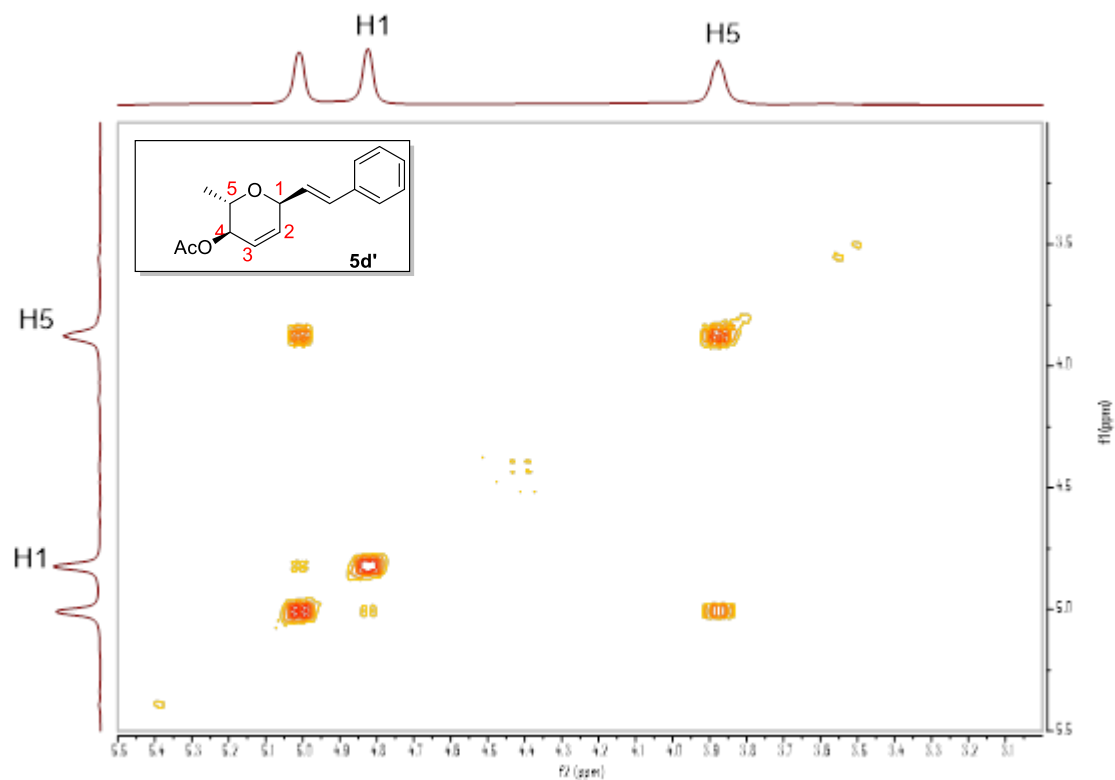


Figure S9: ^1H ^1H COSY NMR spectrum of **5d'**

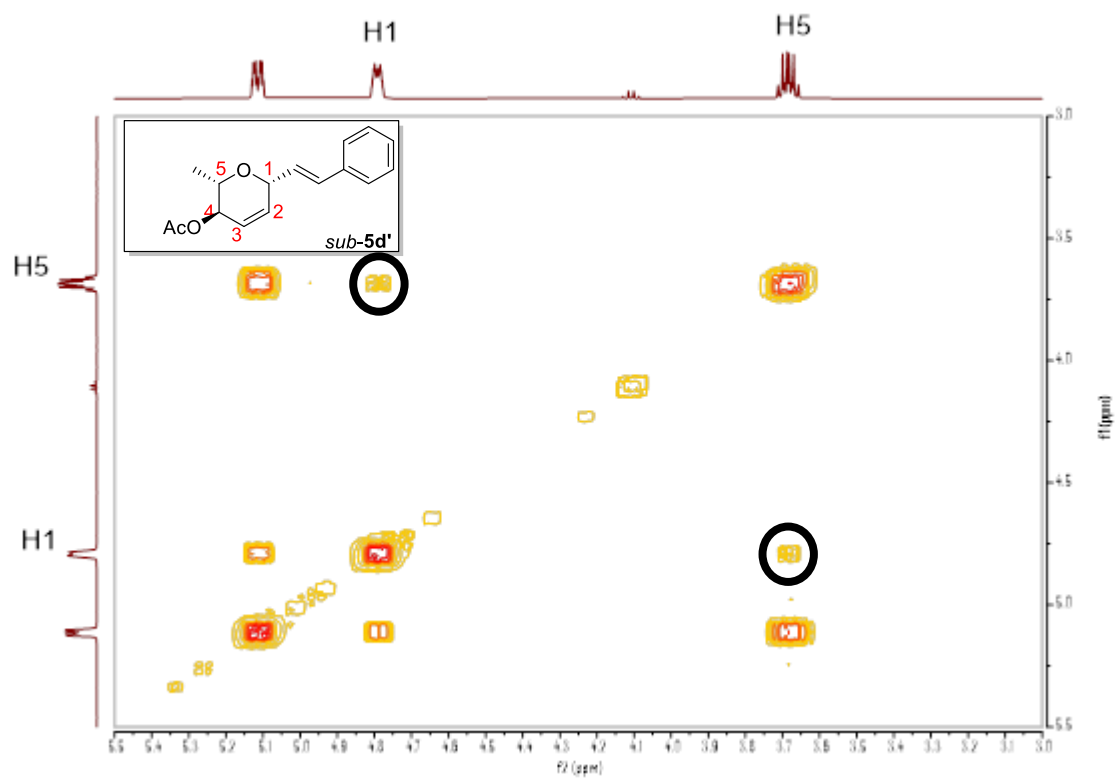
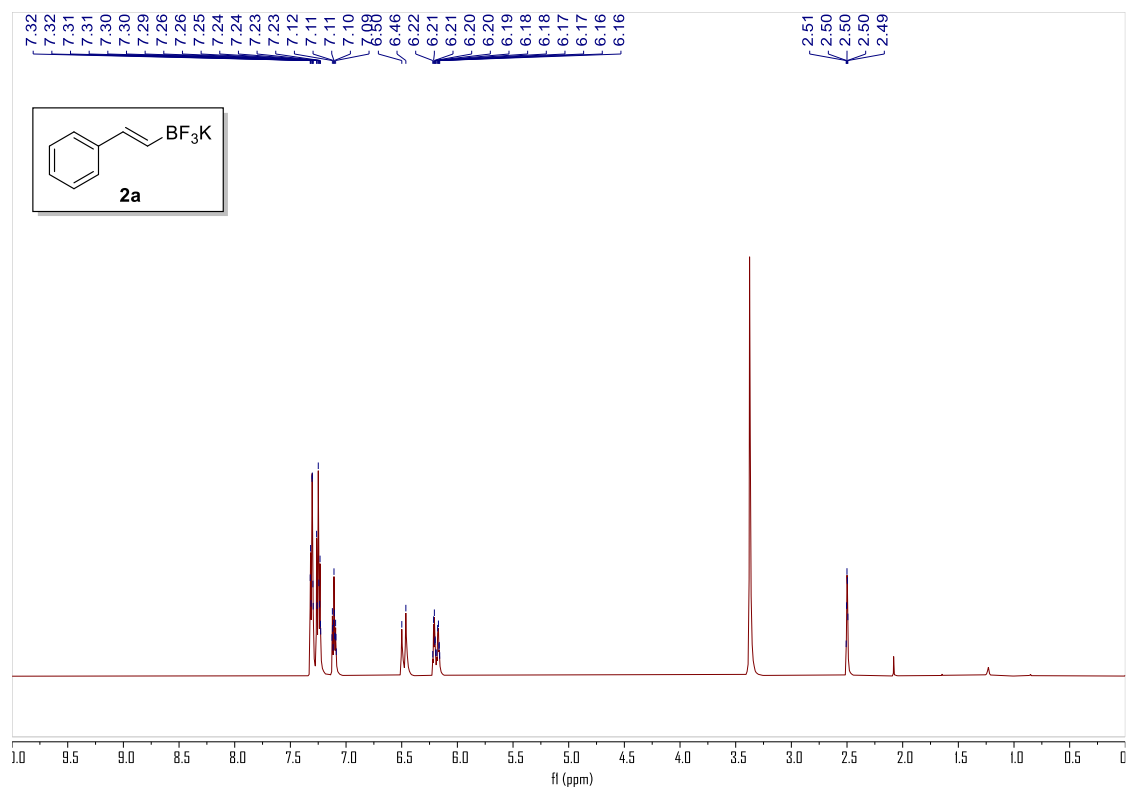


Figure S10: ^1H ^1H COSY NMR spectrum of *sub-5d'*

10. NMR Spectroscopic Data

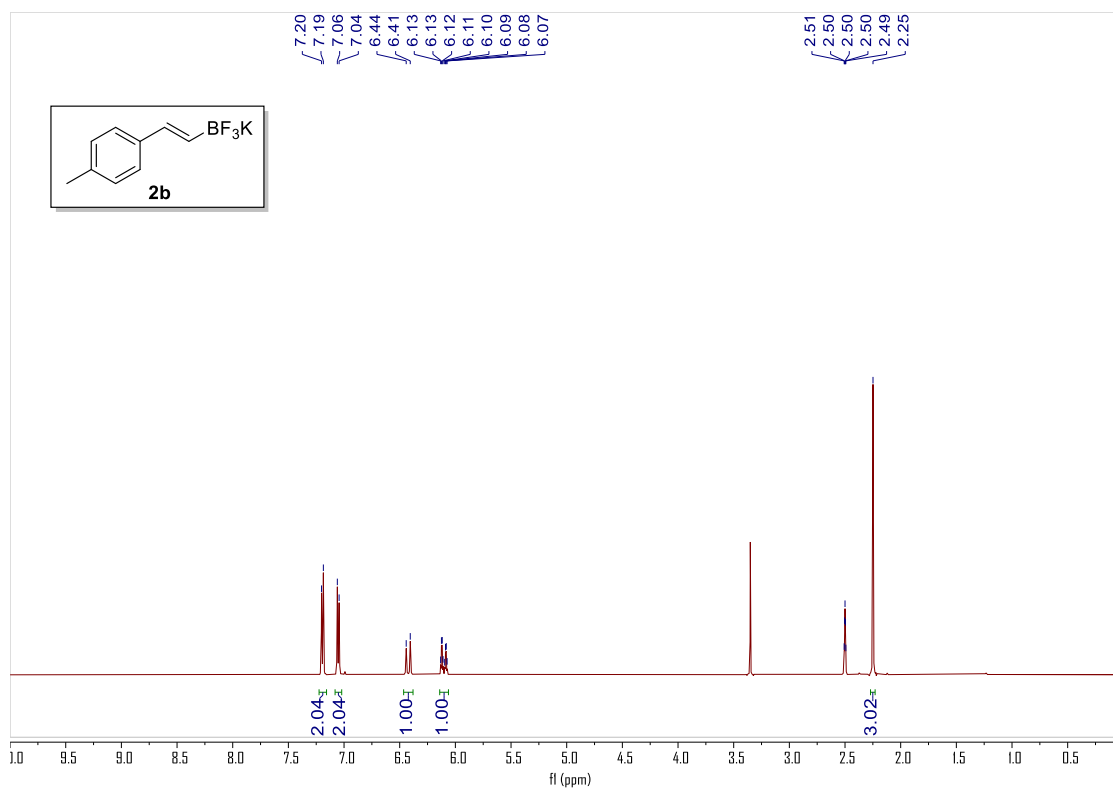
Potassium (E)-trifluoro(styryl)borate (2a)

^1H spectrum (500 MHz, DMSO- d_6)



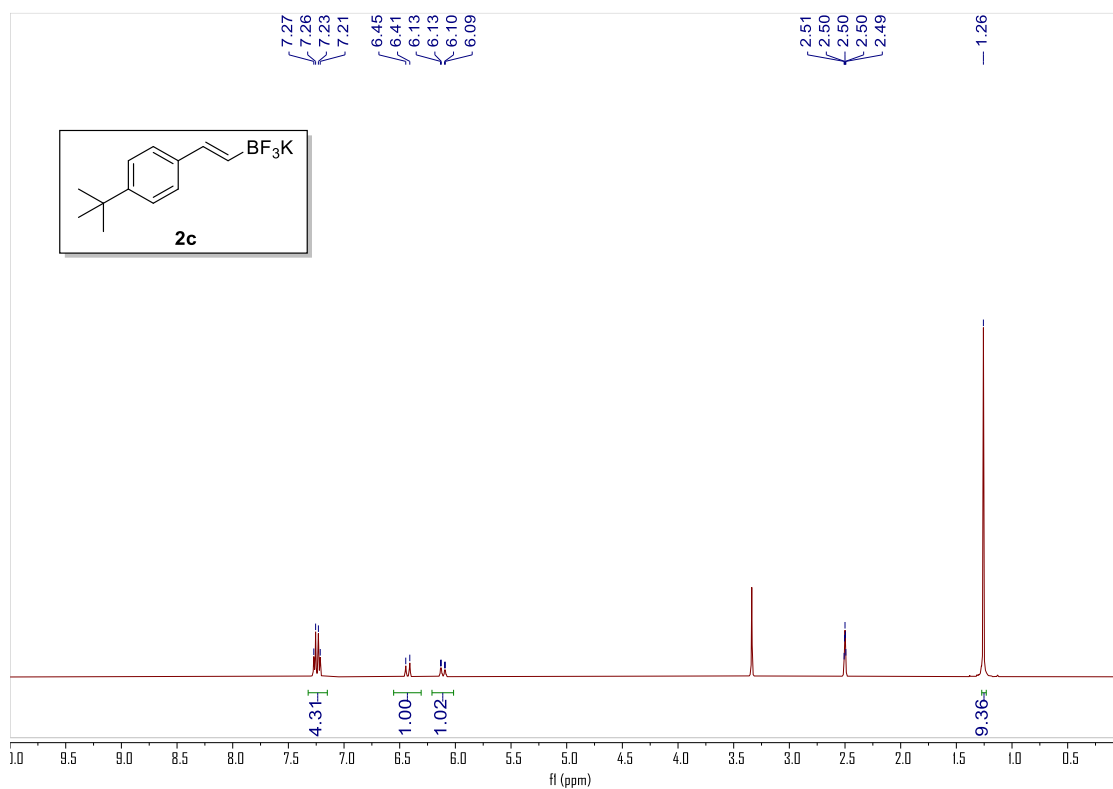
Potassium (E)-trifluoro(4-methylstyryl)borate (2b)

¹H spectrum (500 MHz, DMSO-d6)



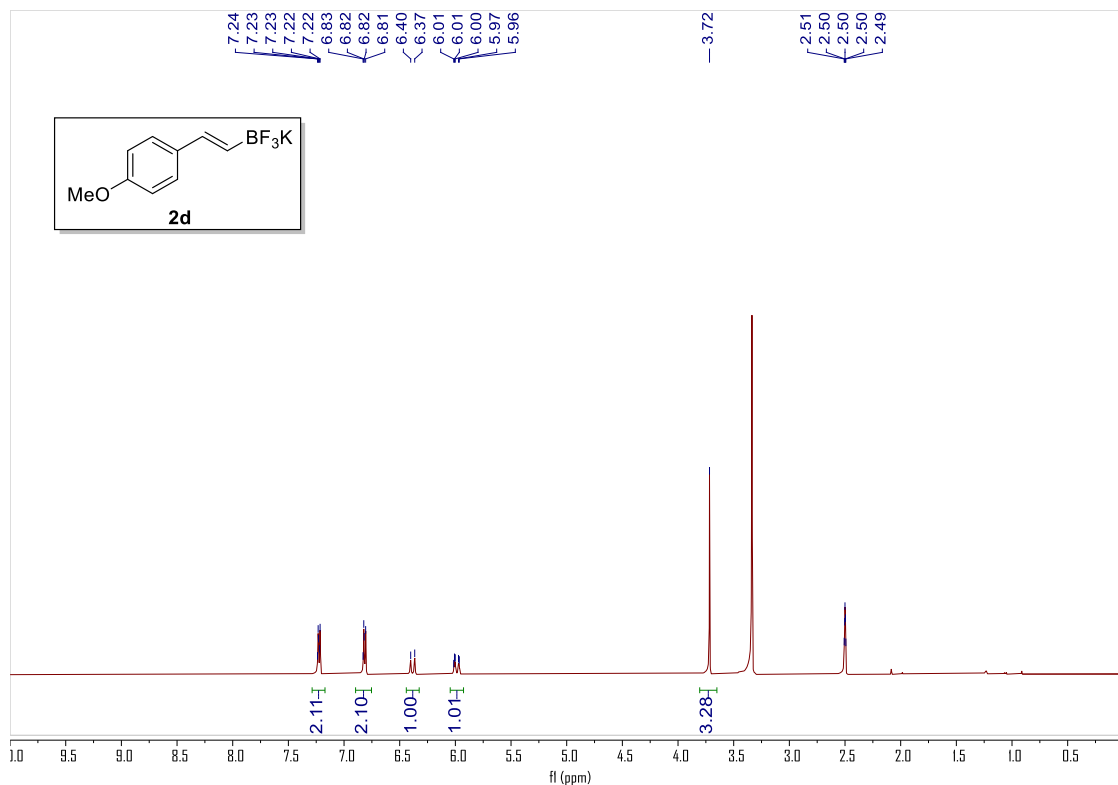
Potassium (E)-(4-(tert-butyl)styryl)trifluoroborate (2c)

¹H spectrum (500 MHz, DMSO-d6)



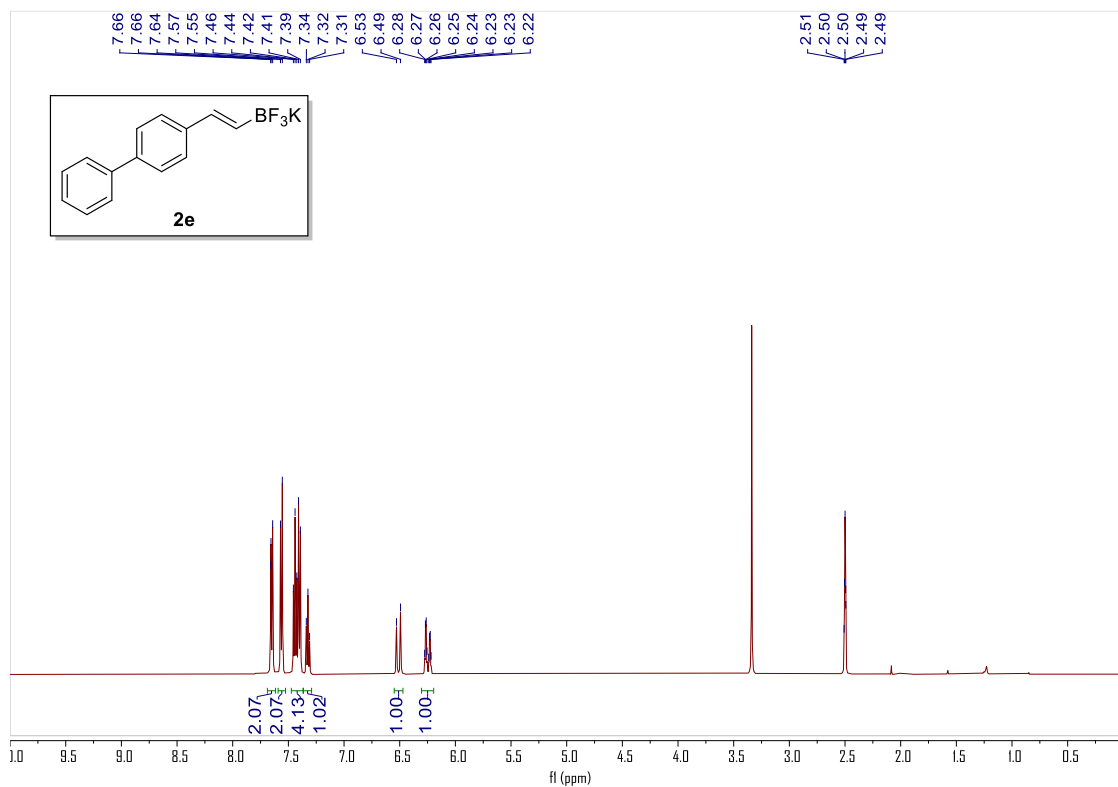
Potassium (E)-trifluoro(4-methoxystyryl)borate (2d)

¹H spectrum (500 MHz, DMSO-d₆)



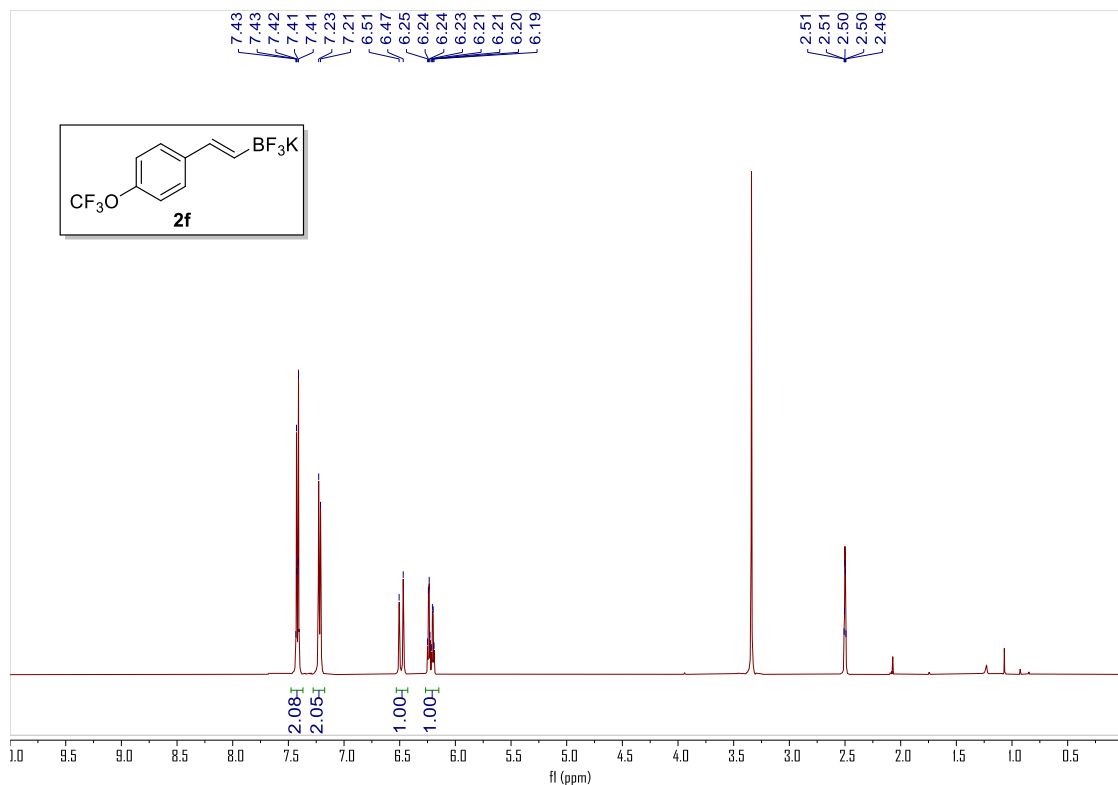
Potassium (E)-(2-([1,1'-biphenyl]-4-yl)vinyl)trifluoroborate (2e)

¹H spectrum (500 MHz, DMSO-d₆)



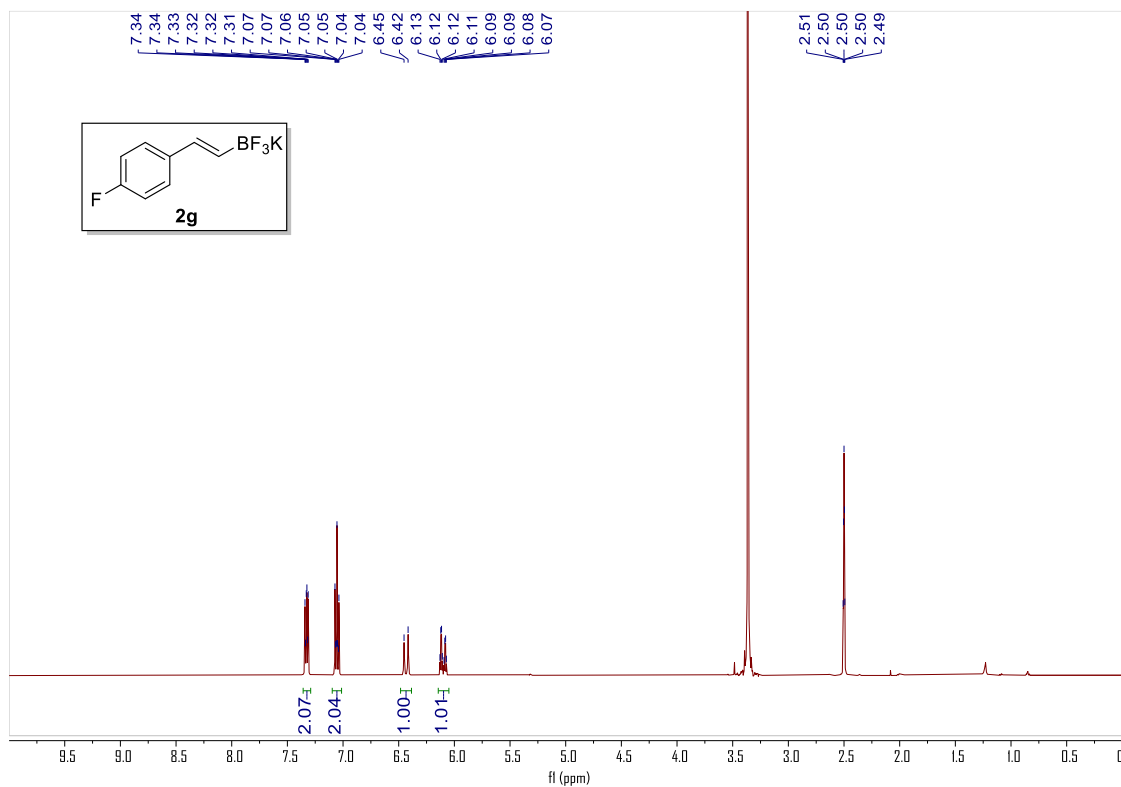
Potassium (E)-trifluoro(4-(trifluoromethoxy)styryl)borate (2f)

¹H spectrum (500 MHz, DMSO-d₆)



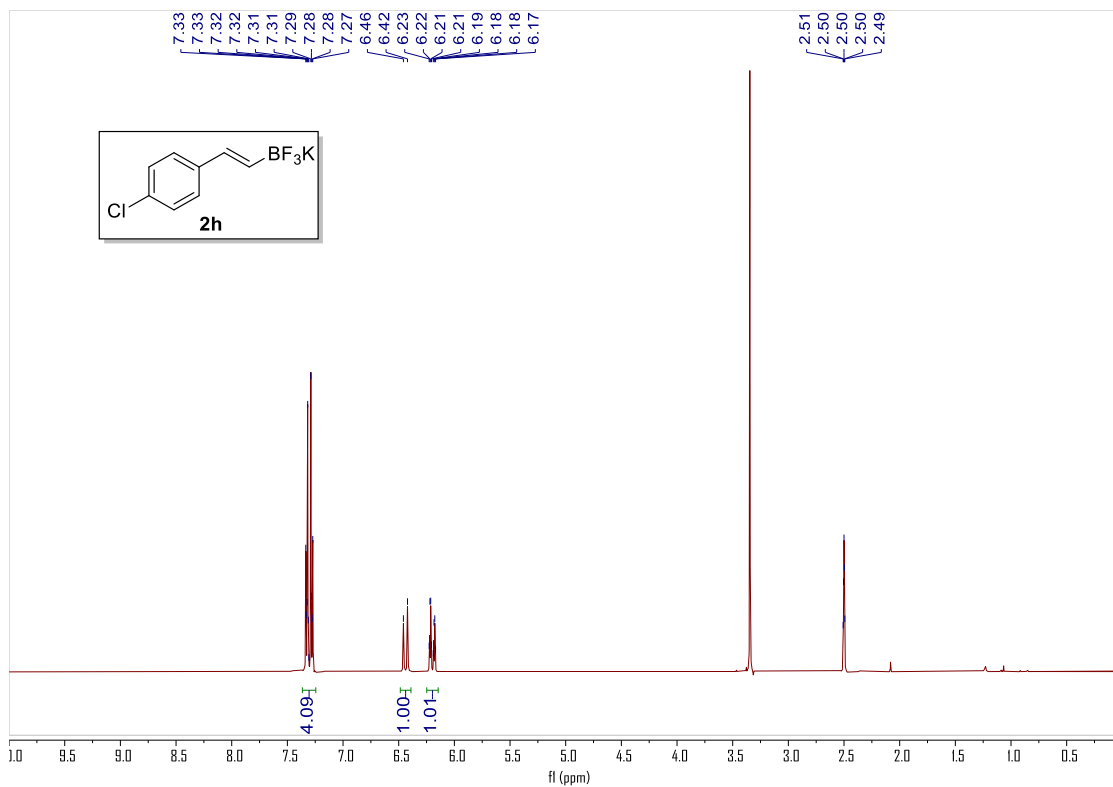
Potassium (E)-trifluoro(4-fluorostyryl)borate (2g)

¹H spectrum (500 MHz, DMSO-d₆)



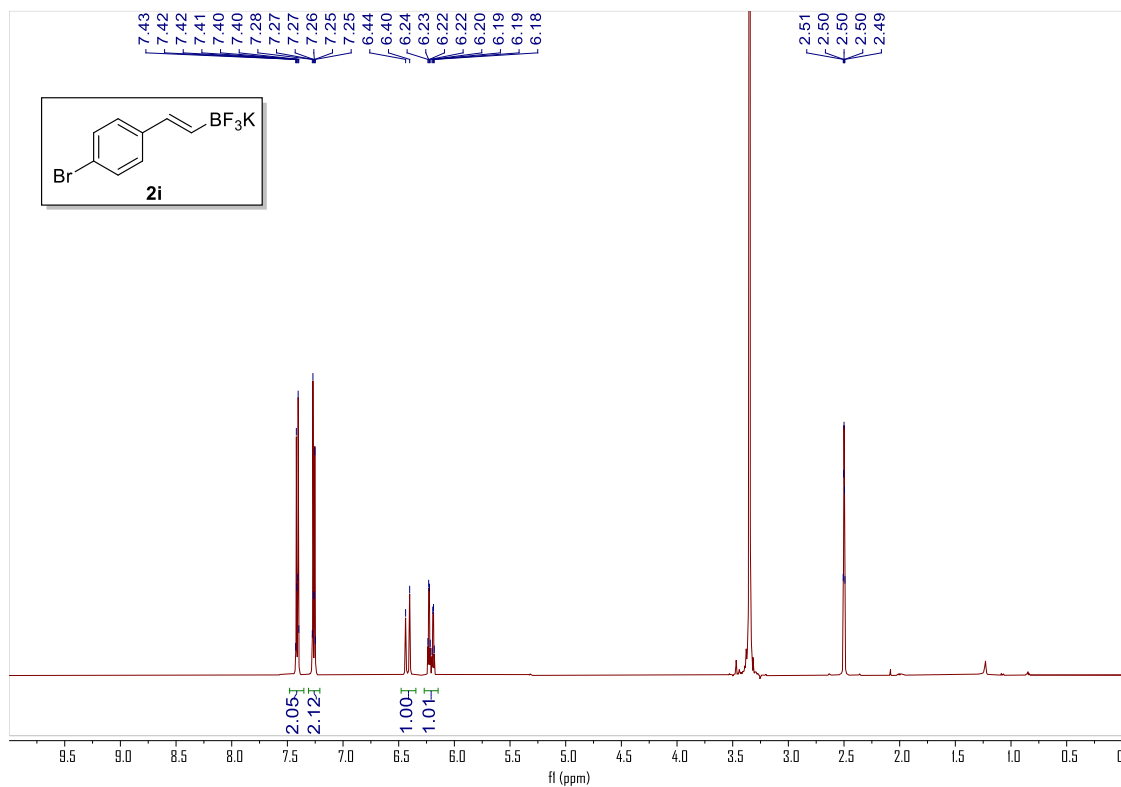
Potassium (E)-(4-chlorostyryl)trifluoroborate (2h)

¹H spectrum (500 MHz, DMSO-d6)



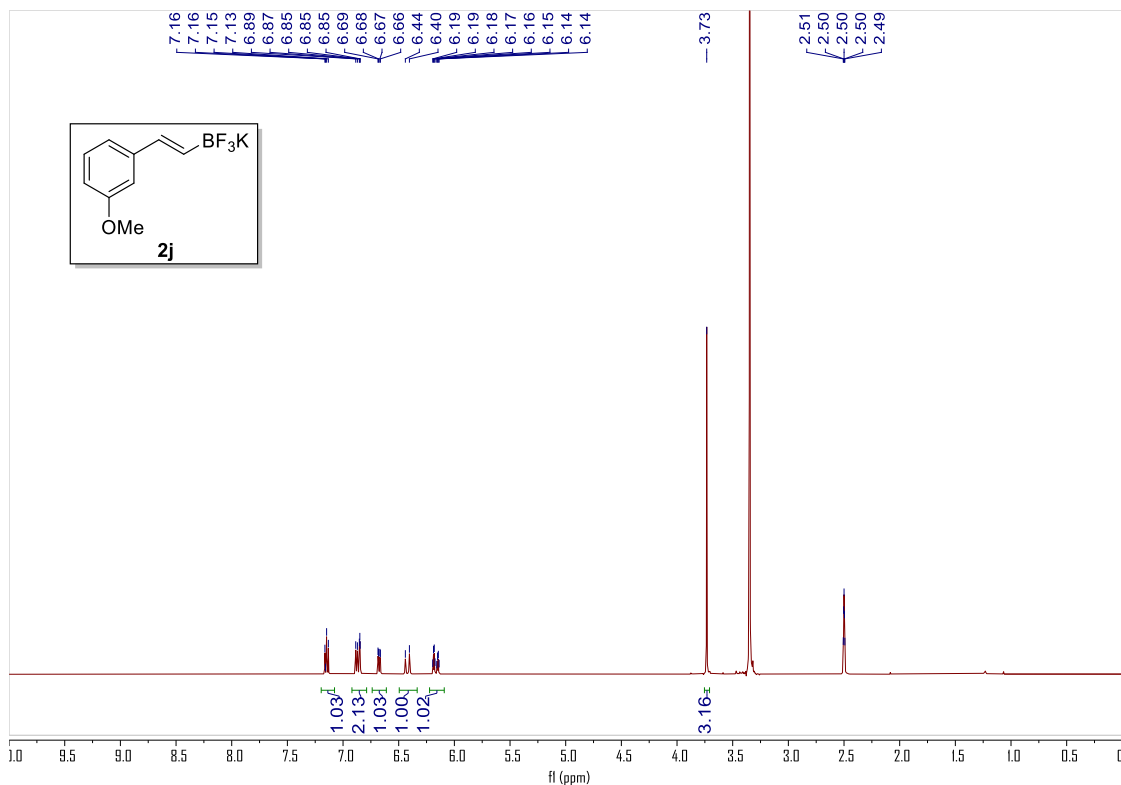
Potassium (E)-(4-bromostyryl)trifluoroborate (2i)

¹H spectrum (500 MHz, DMSO-d6)



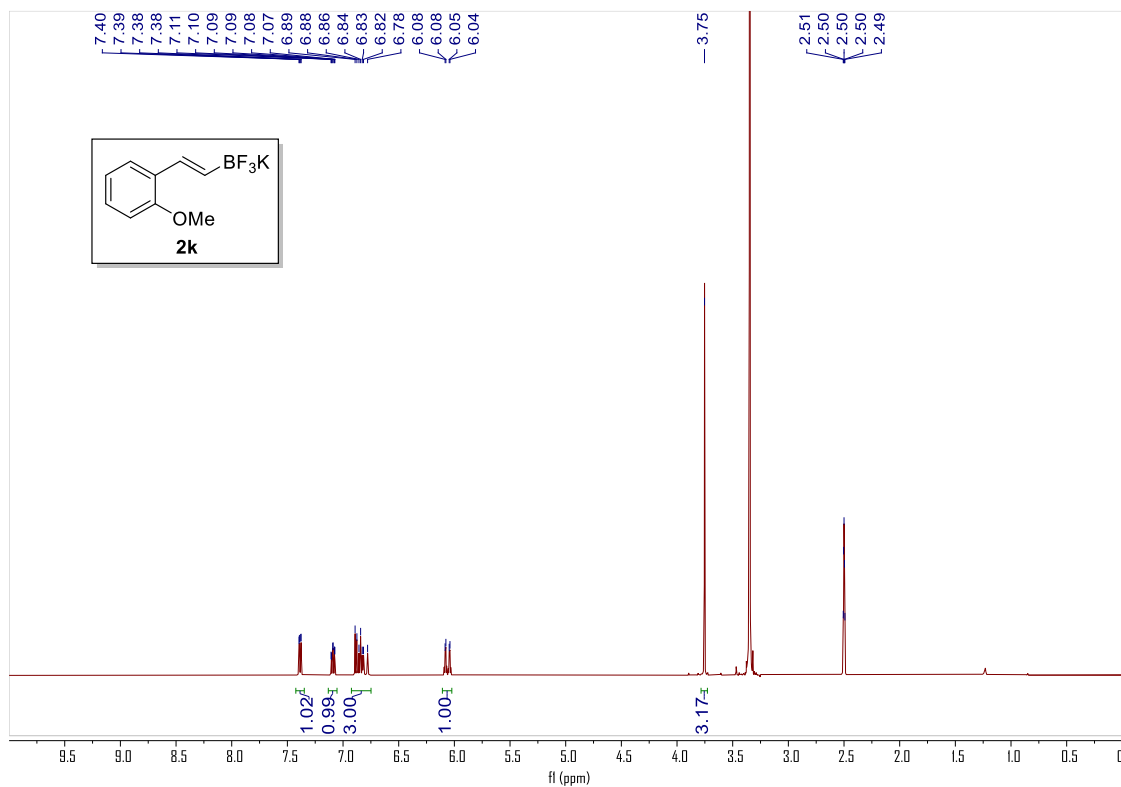
Potassium (E)-trifluoro(3-methoxystyryl)borate (2j)

¹H spectrum (500 MHz, DMSO-d₆)



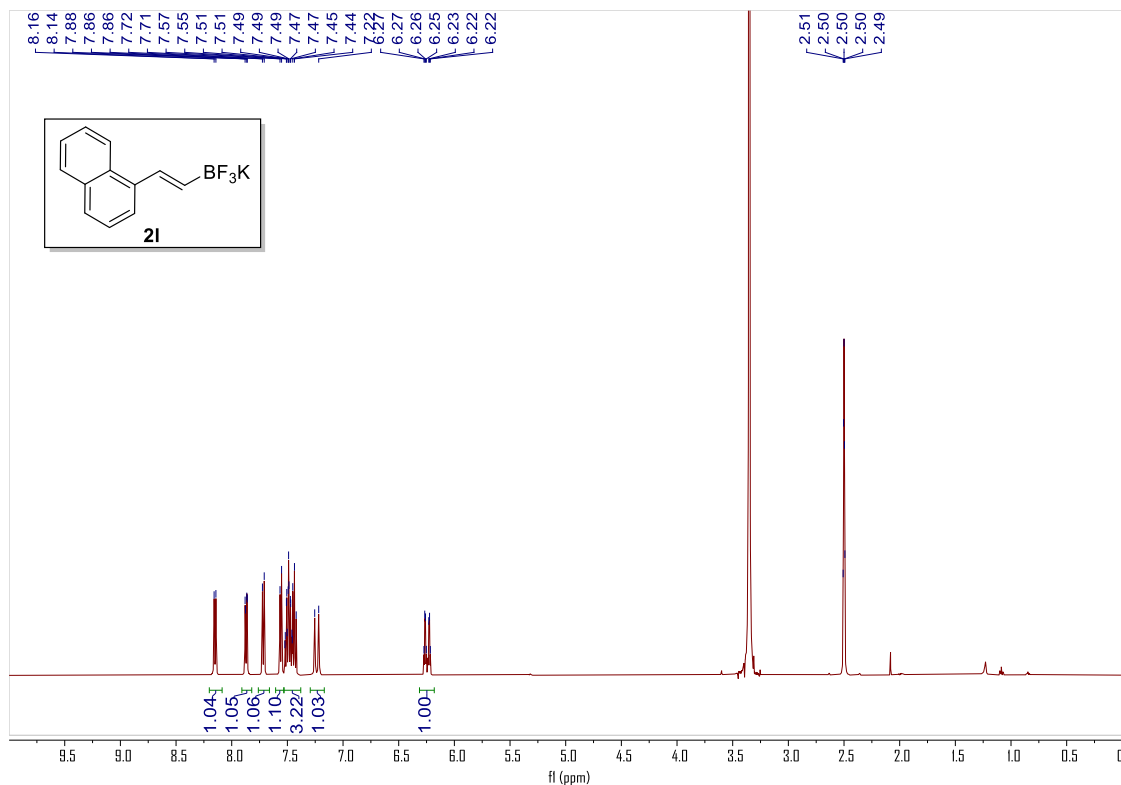
Potassium (E)-trifluoro(2-methoxystyryl)borate (2k)

¹H spectrum (500 MHz, DMSO-d₆)



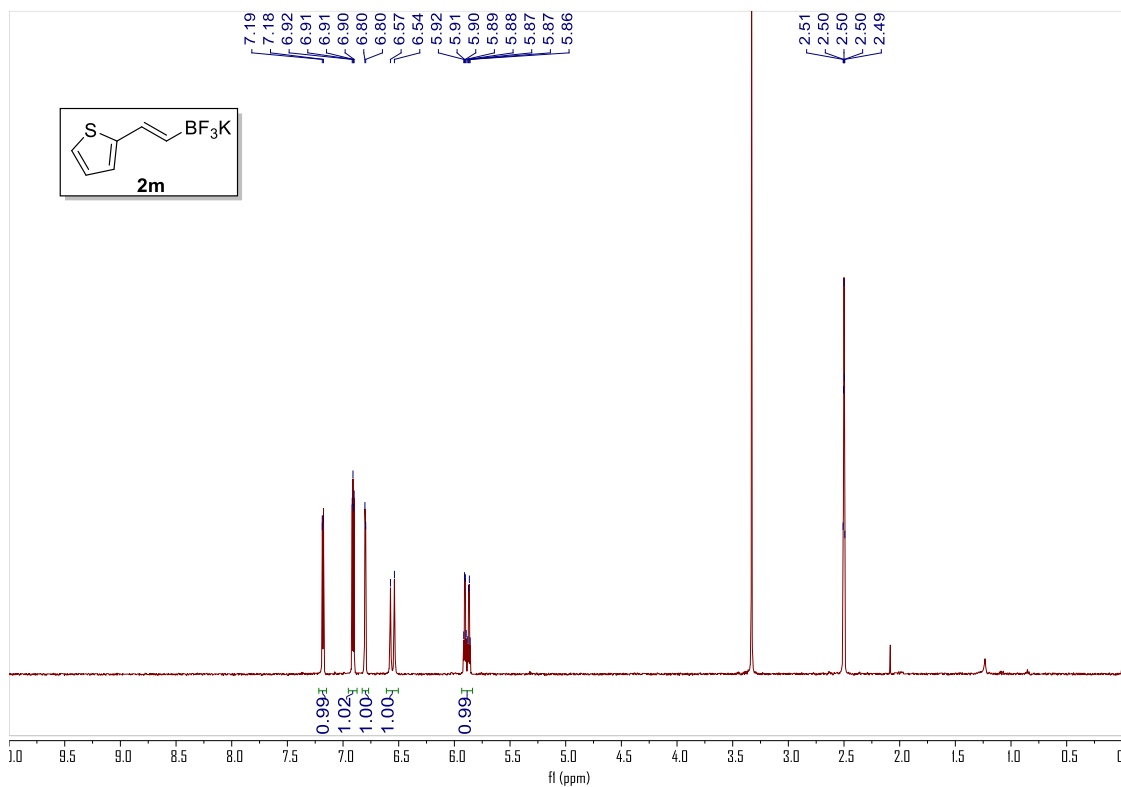
Potassium (E)-trifluoro(2-(naphthalen-1-yl)vinyl)borate (2l)

¹H spectrum (500 MHz, DMSO-d6)



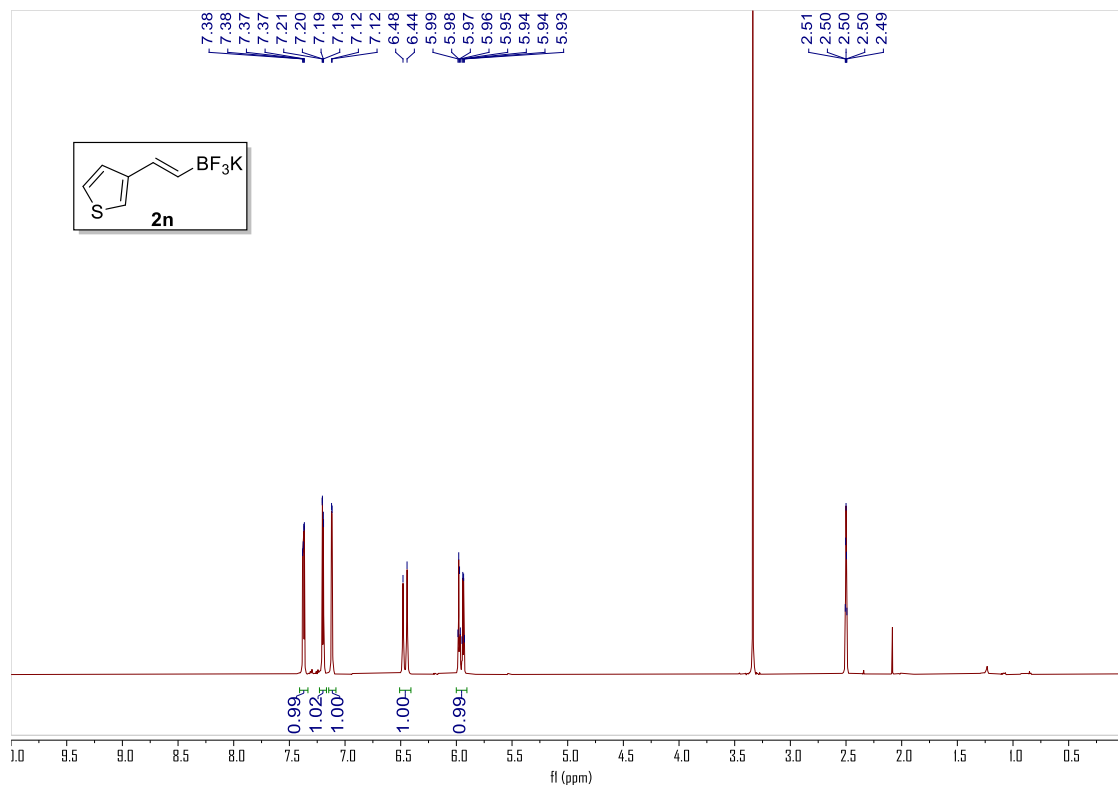
Potassium (E)-trifluoro(2-(thiophen-2-yl)vinyl)borate (2m)

¹H spectrum (500 MHz, DMSO-d6)



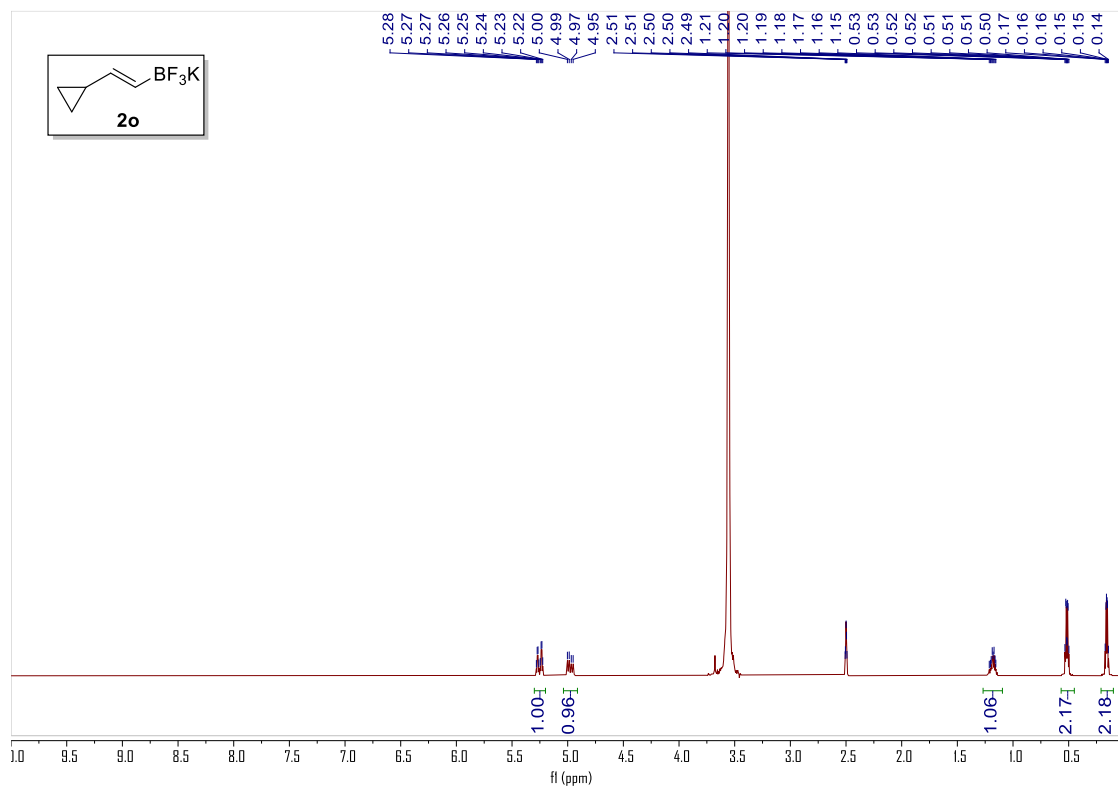
Potassium (E)-trifluoro(2-(thiophen-3-yl)vinyl)borate (2n)

¹H spectrum (500 MHz, DMSO-d₆)



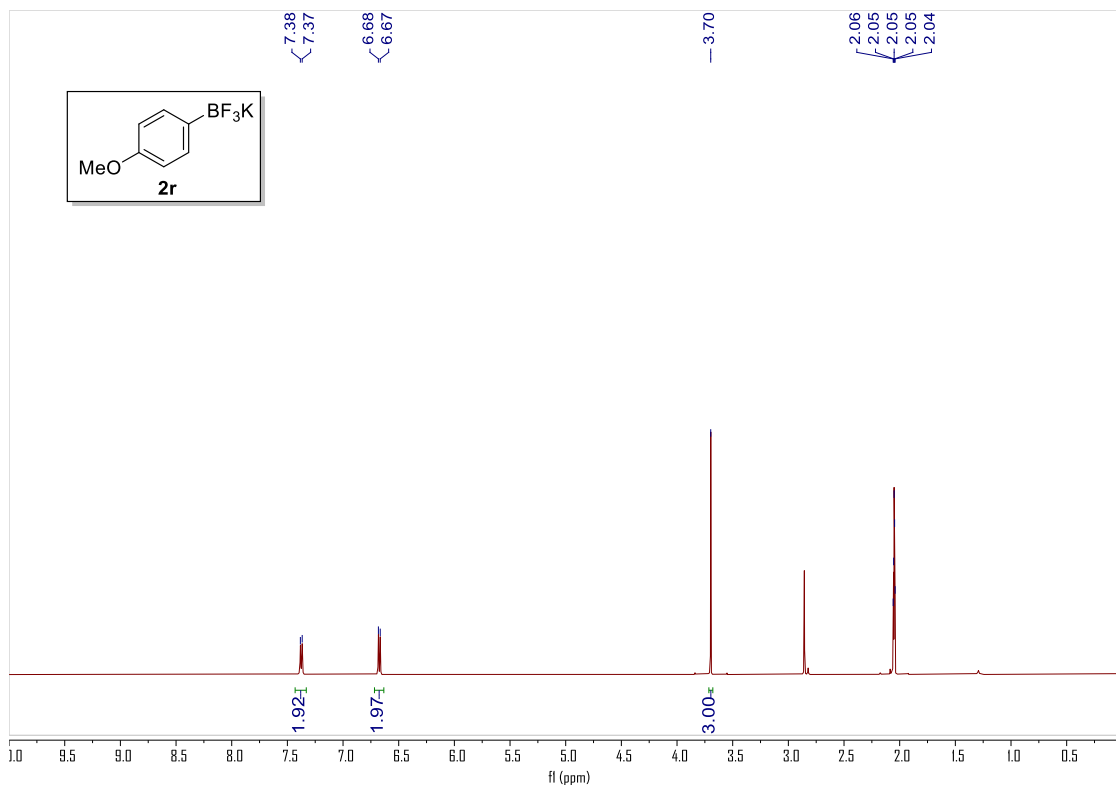
Potassium (E)-(2-cyclopropylvinyl)trifluoroborate (2o)

¹H spectrum (500 MHz, DMSO-d₆)



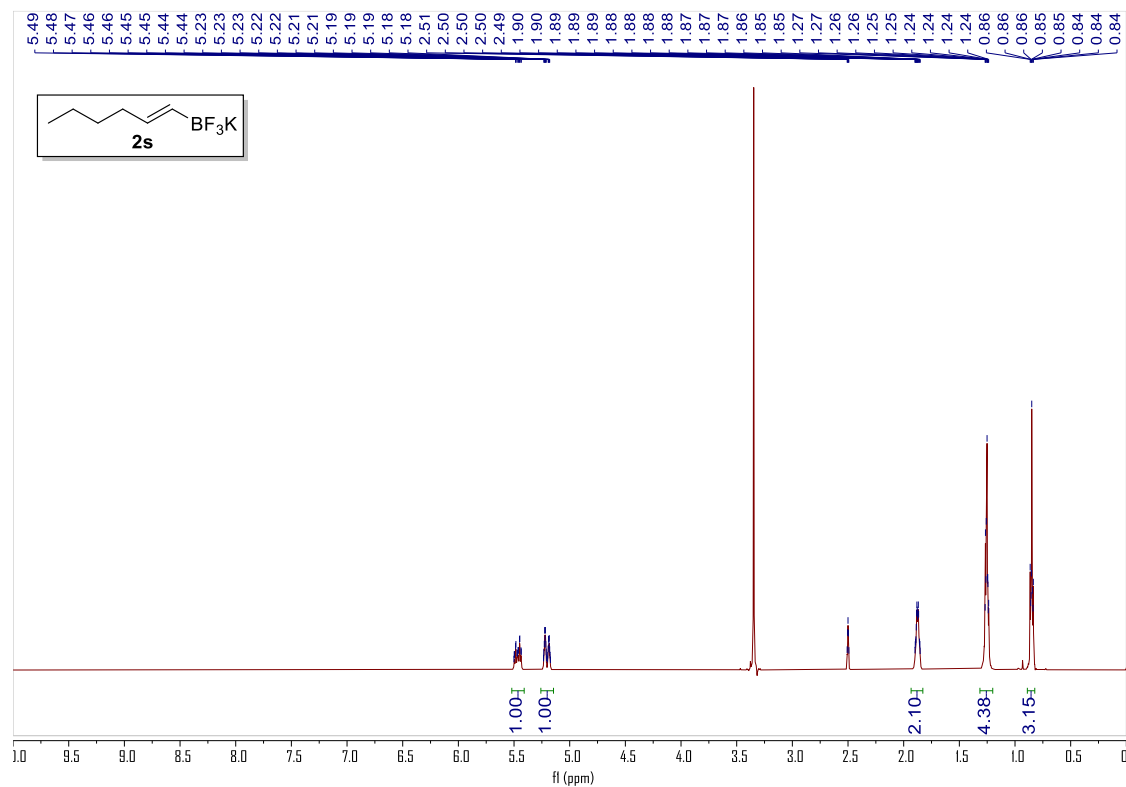
Potassium trifluoro(4-methoxyphenyl)borate (2r)

^1H spectrum (500 MHz, Acetone- d_6)

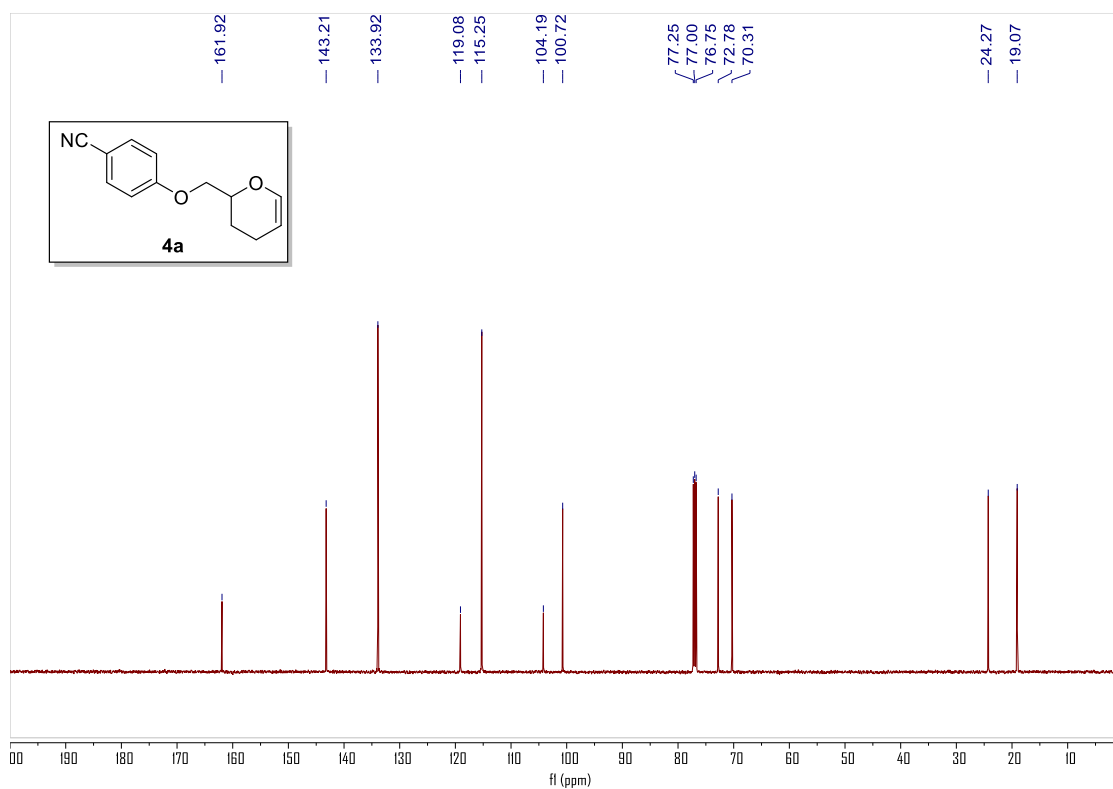


Potassium (E)-trifluoro(hex-1-en-1-yl)borate (2s)

^1H spectrum (500 MHz, DMSO- d_6)

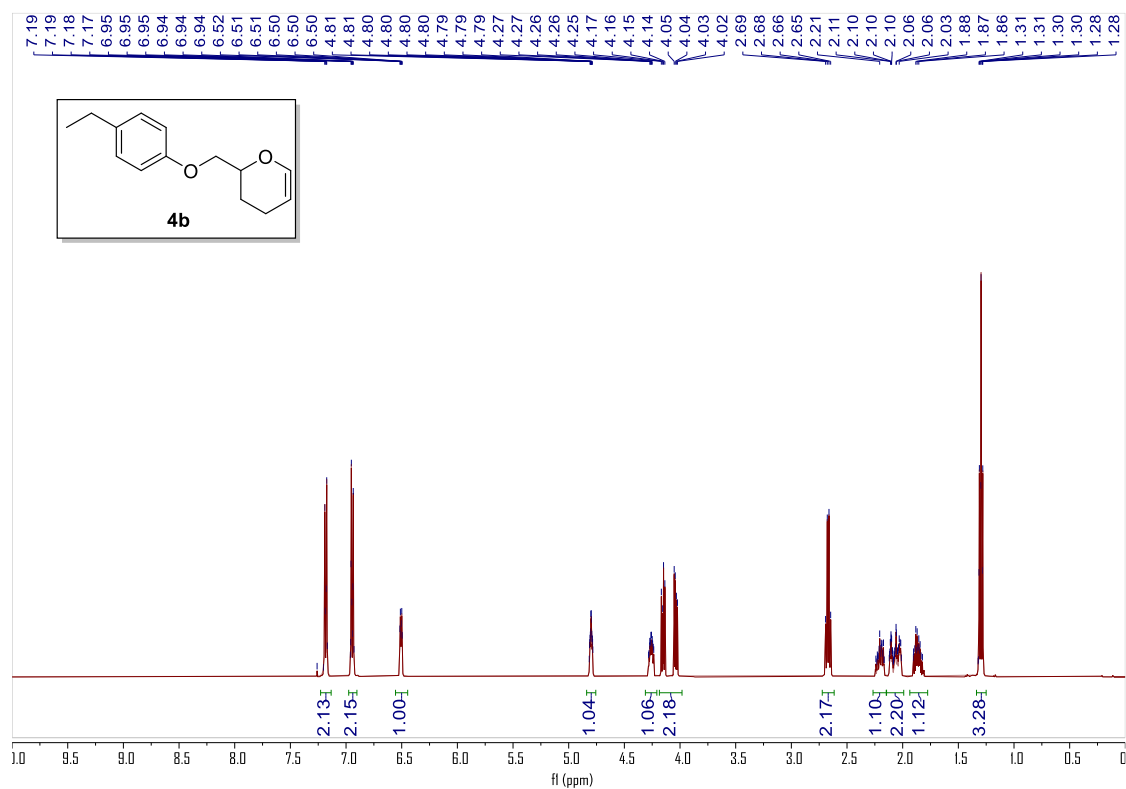


¹³C spectrum (126 MHz, CDCl₃)

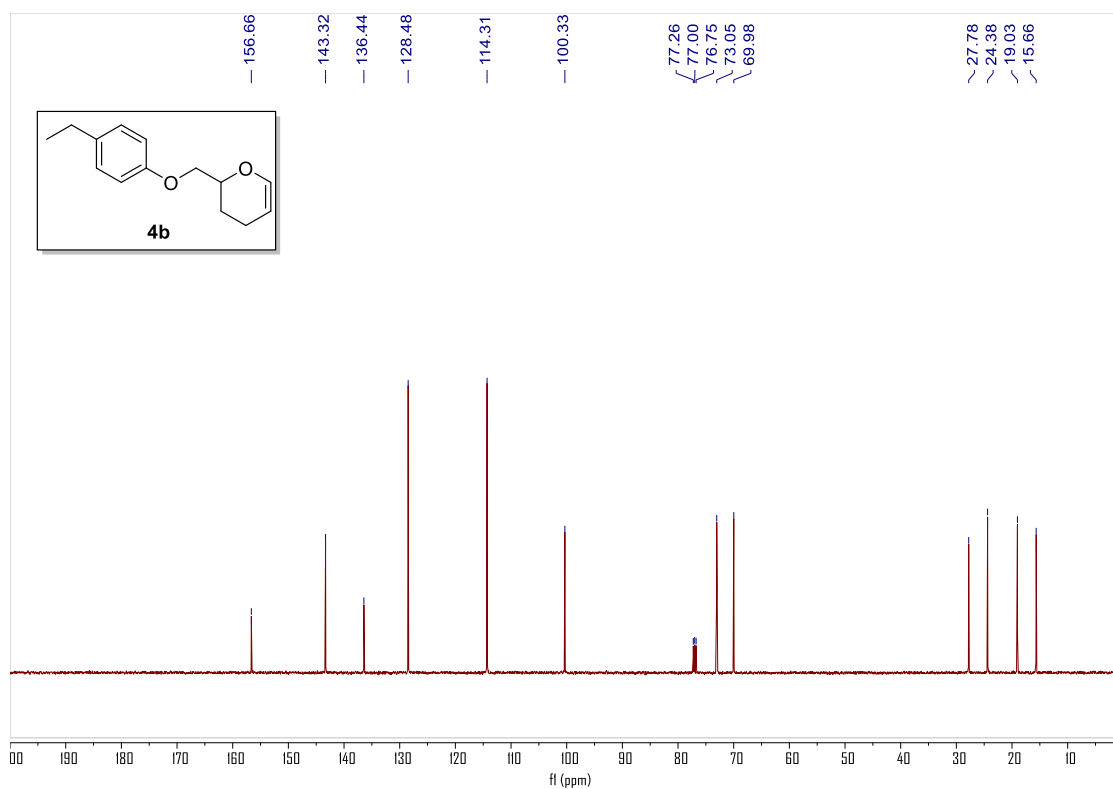


2-((4-ethylphenoxy)methyl)-3,4-dihydro-2H-pyran (**4b**)

¹H spectrum (500 MHz, CDCl₃)

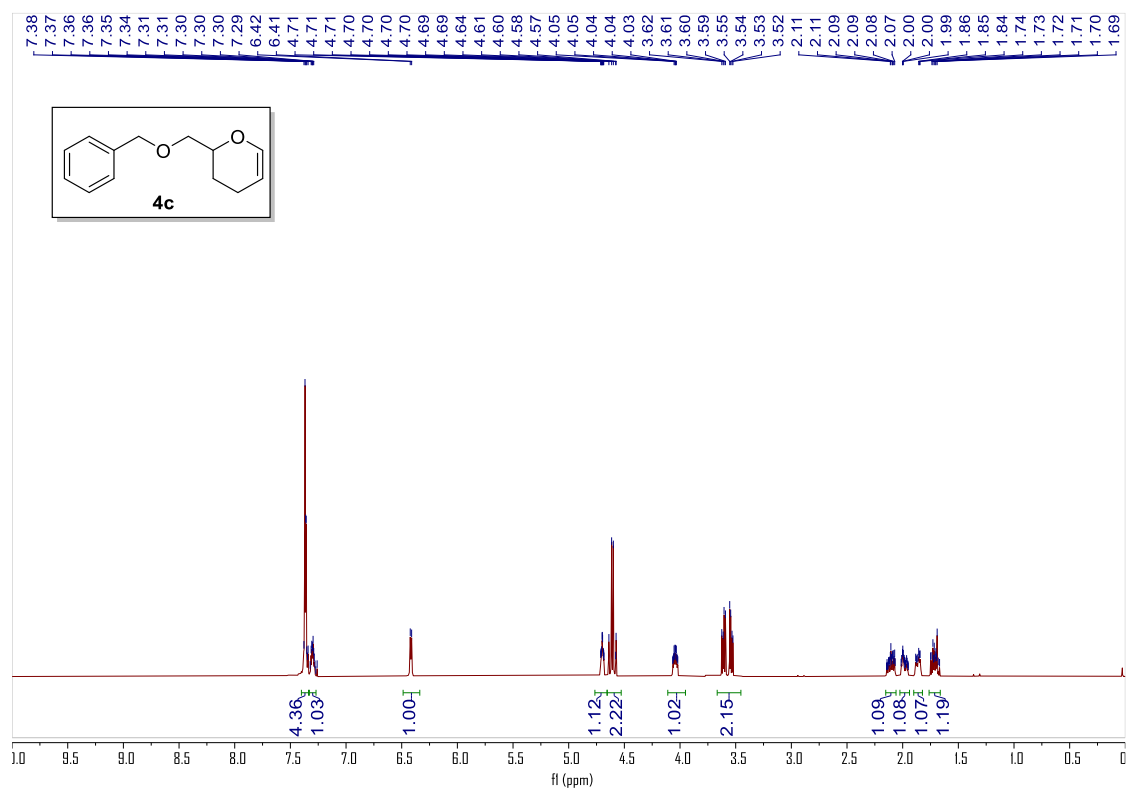


¹³C spectrum (126 MHz, CDCl₃)



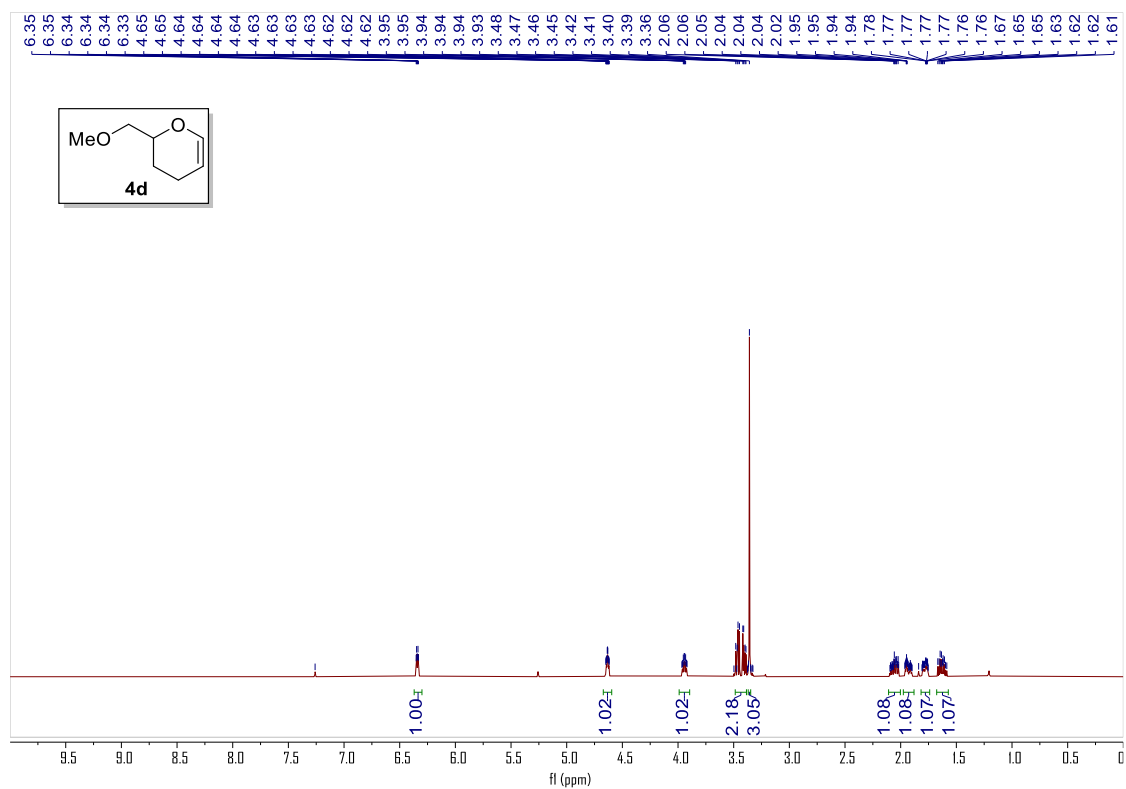
2-((benzyloxy)methyl)-3,4-dihydro-2H-pyran (**4c**)

¹H spectrum (500 MHz, CDCl₃)



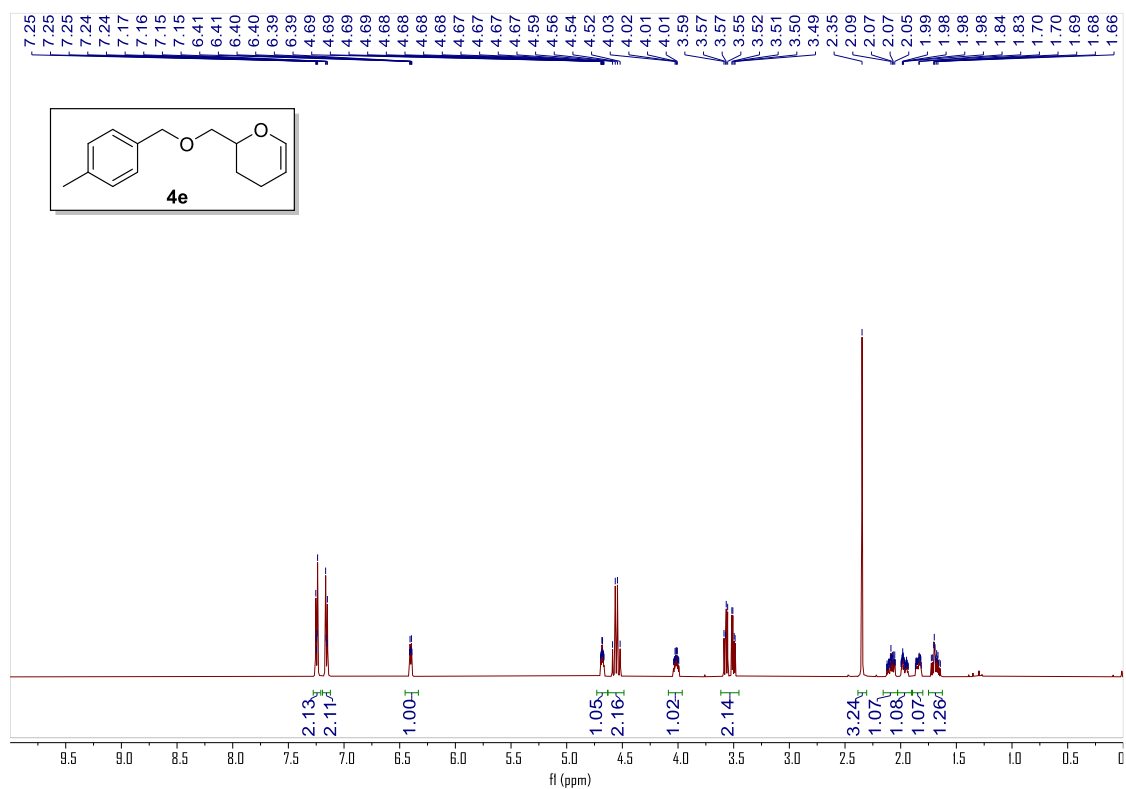
2-(methoxymethyl)-3,4-dihydro-2H-pyran (4d)

^1H spectrum (500 MHz, CDCl_3)

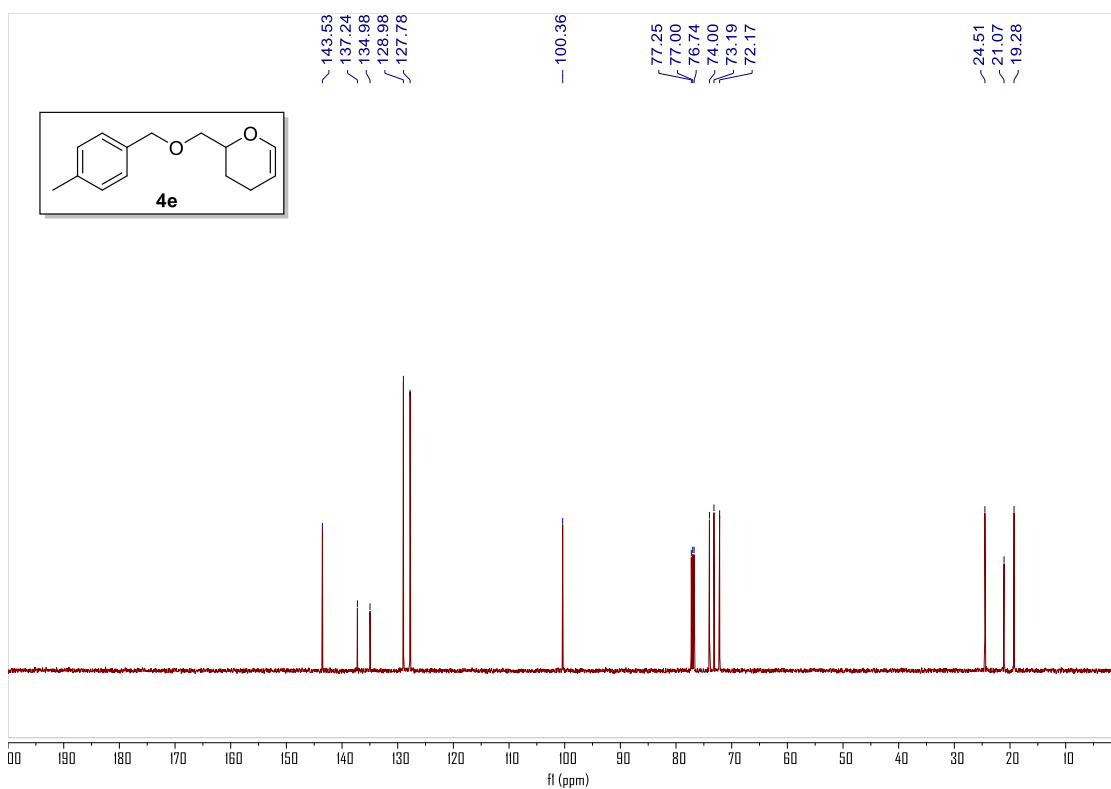


2-(((4-methylbenzyl)oxy)methyl)-3,4-dihydro-2H-pyran (4e)

^1H spectrum (500 MHz, CDCl_3)

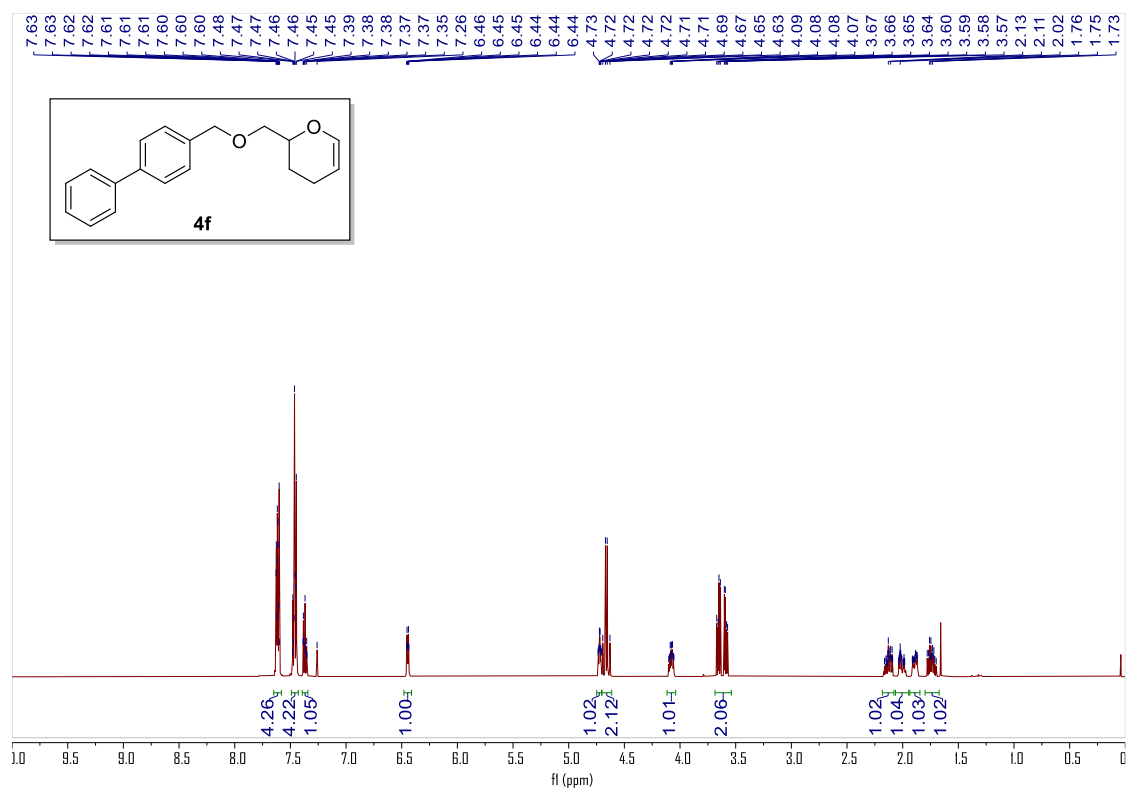


¹³C spectrum (126 MHz, CDCl₃)

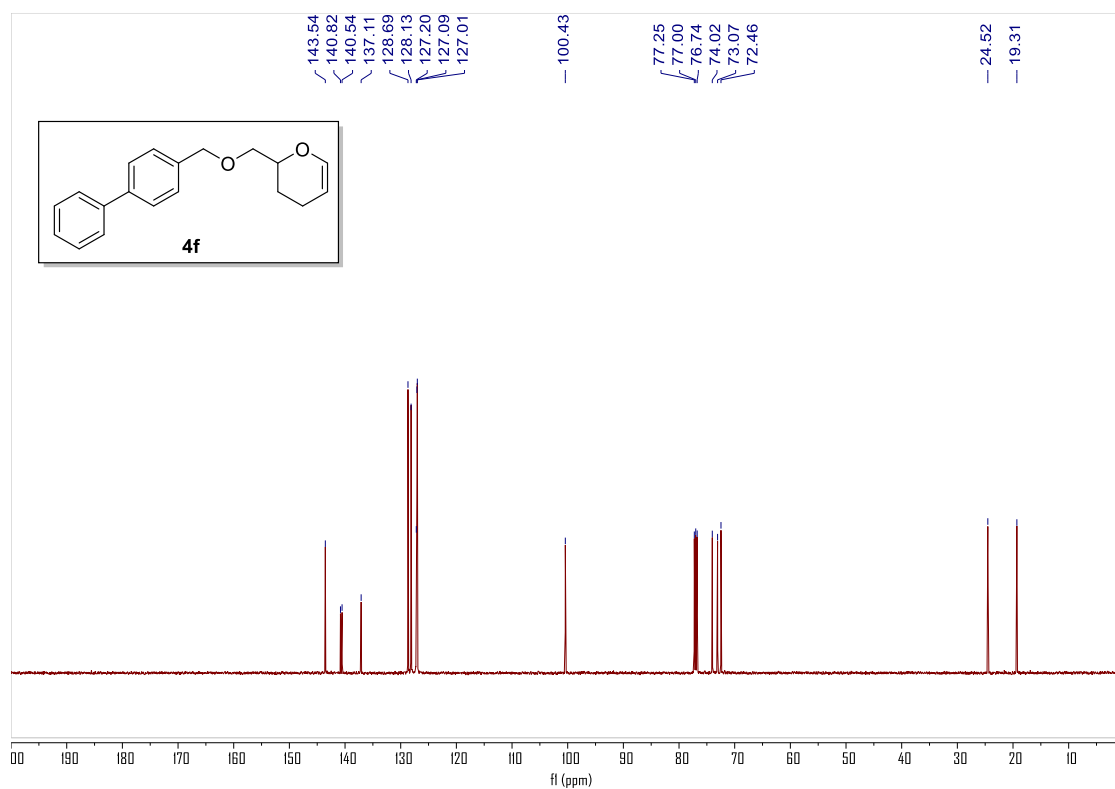


2-((([1,1'-biphenyl]-4-ylmethoxy)methyl)-3,4-dihydro-2H-pyran (**4f**)

¹H spectrum (500 MHz, CDCl₃)

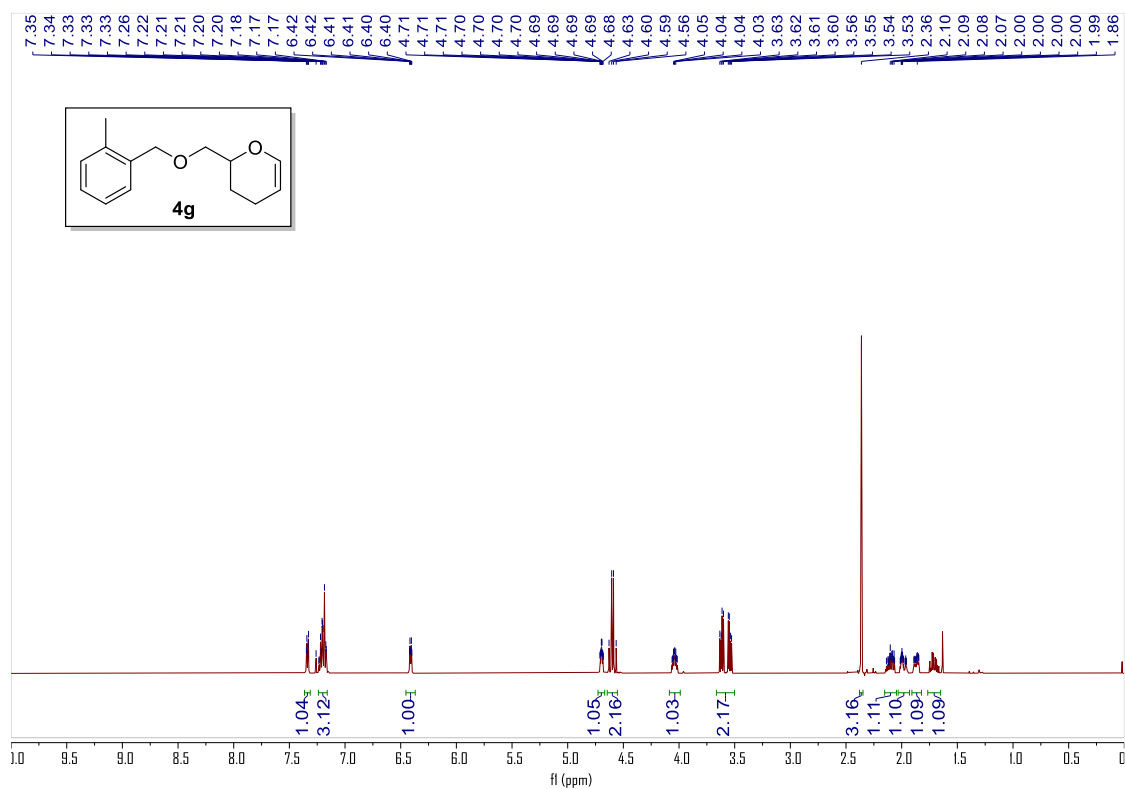


^{13}C spectrum (126 MHz, CDCl_3)

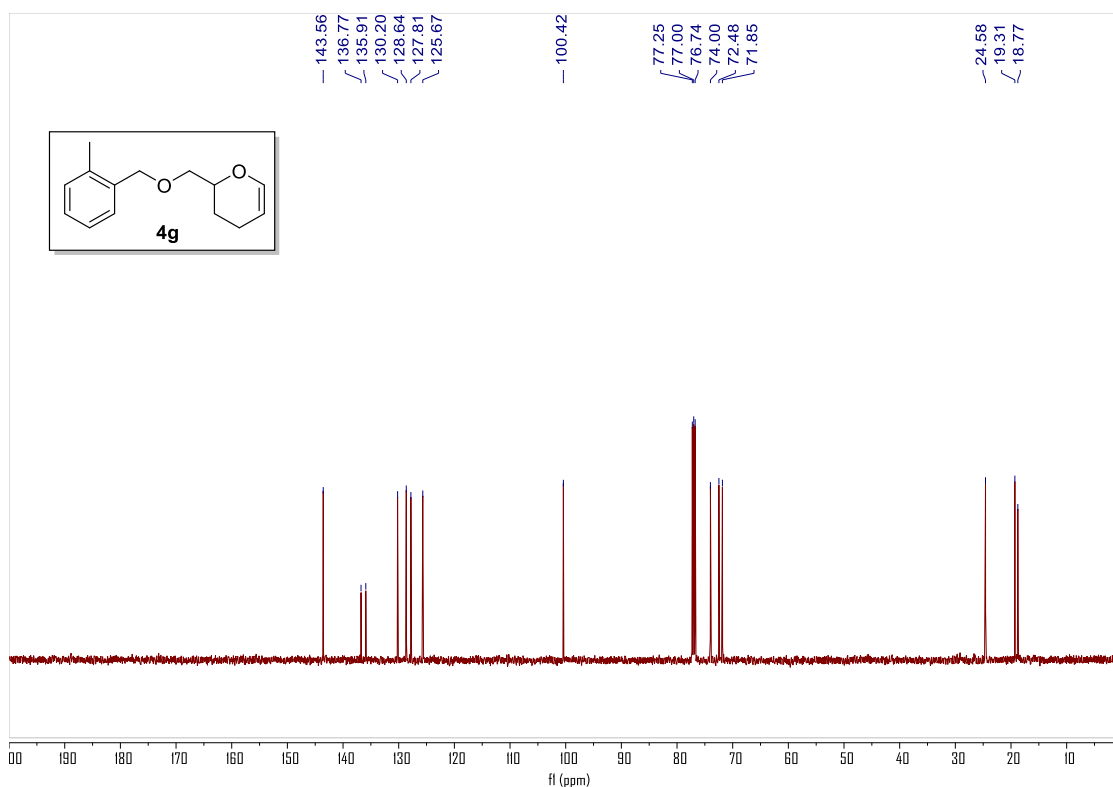


2-(((2-methylbenzyl)oxy)methyl)-3,4-dihydro-2H-pyran (**4g**)

^1H spectrum (500 MHz, CDCl_3)

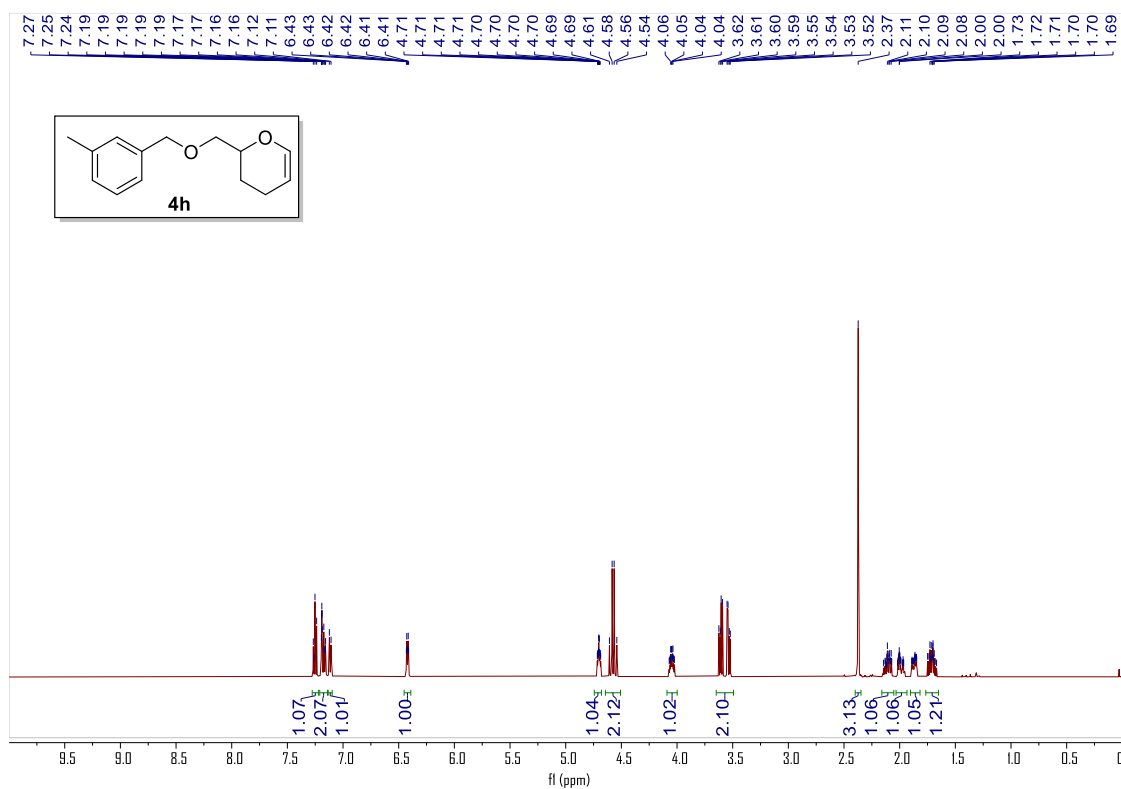


¹³C spectrum (126 MHz, CDCl₃)

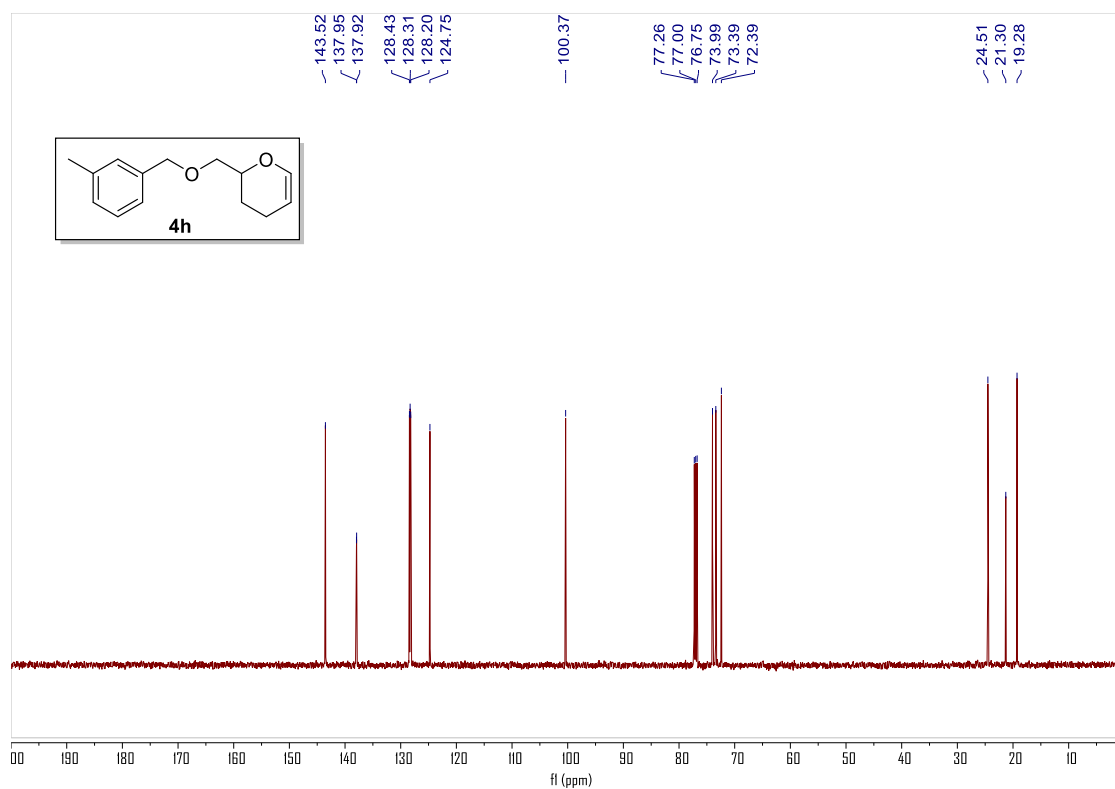


2-(((3-methylbenzyl)oxy)methyl)-3,4-dihydro-2H-pyran (**4h**)

¹H spectrum (500 MHz, CDCl₃)

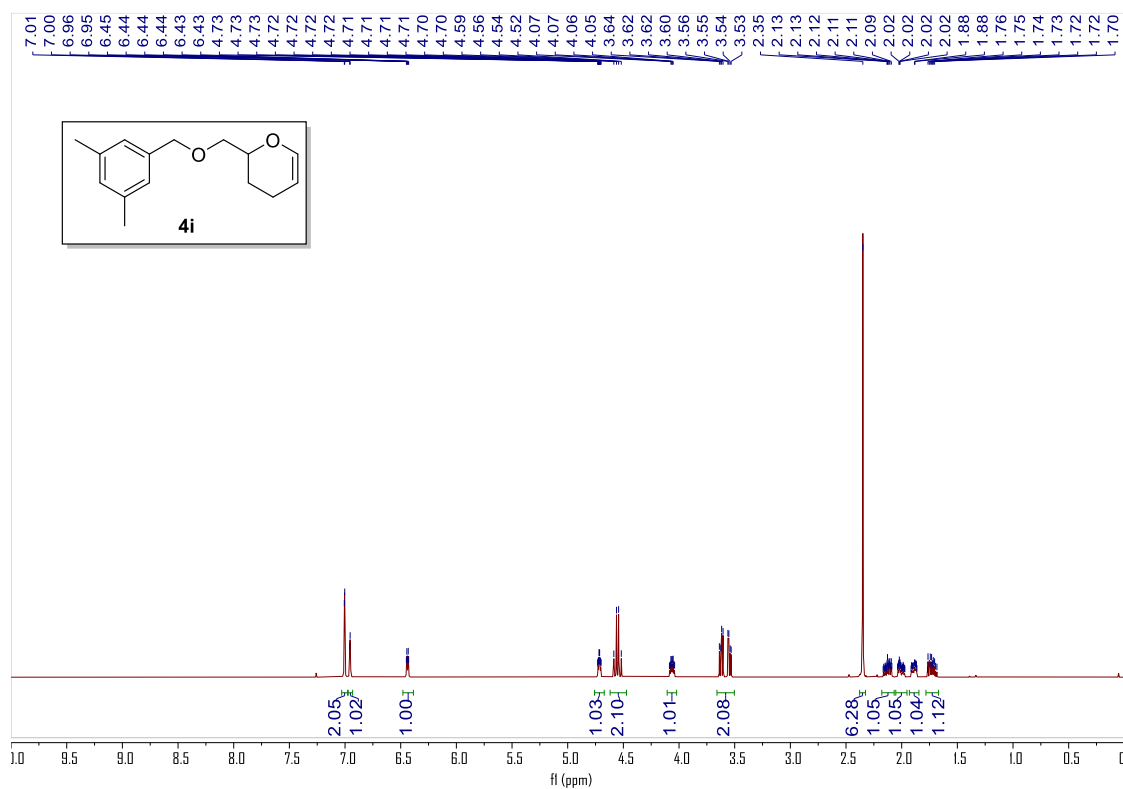


¹³C spectrum (126 MHz, CDCl₃)

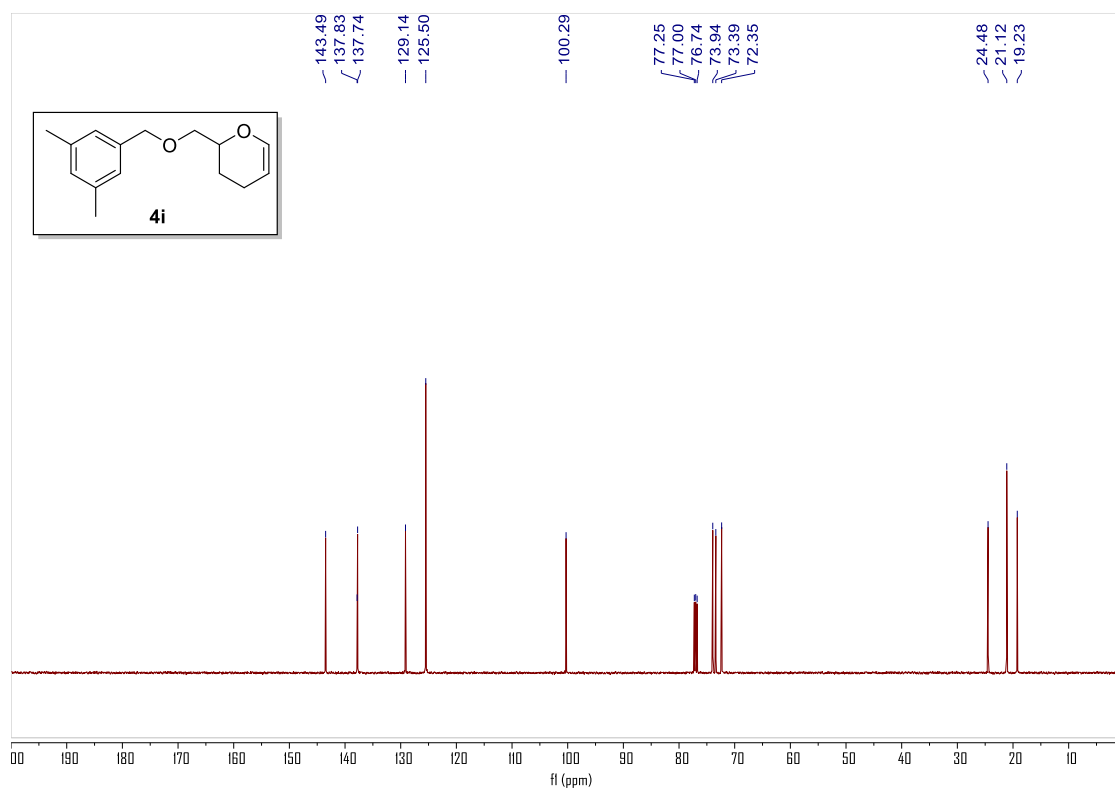


2-(((3,5-dimethylbenzyl)oxy)methyl)-3,4-dihydro-2H-pyran (**4i**)

¹H spectrum (500 MHz, CDCl₃)

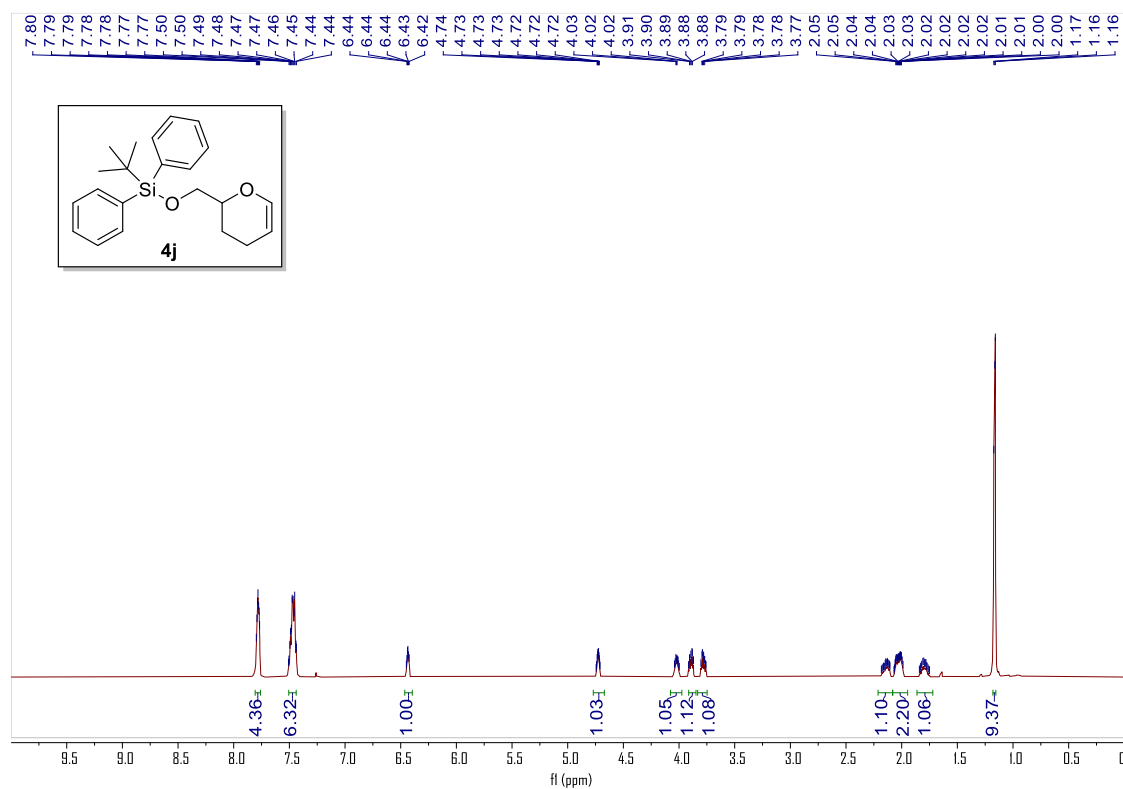


^{13}C spectrum (126 MHz, CDCl_3)



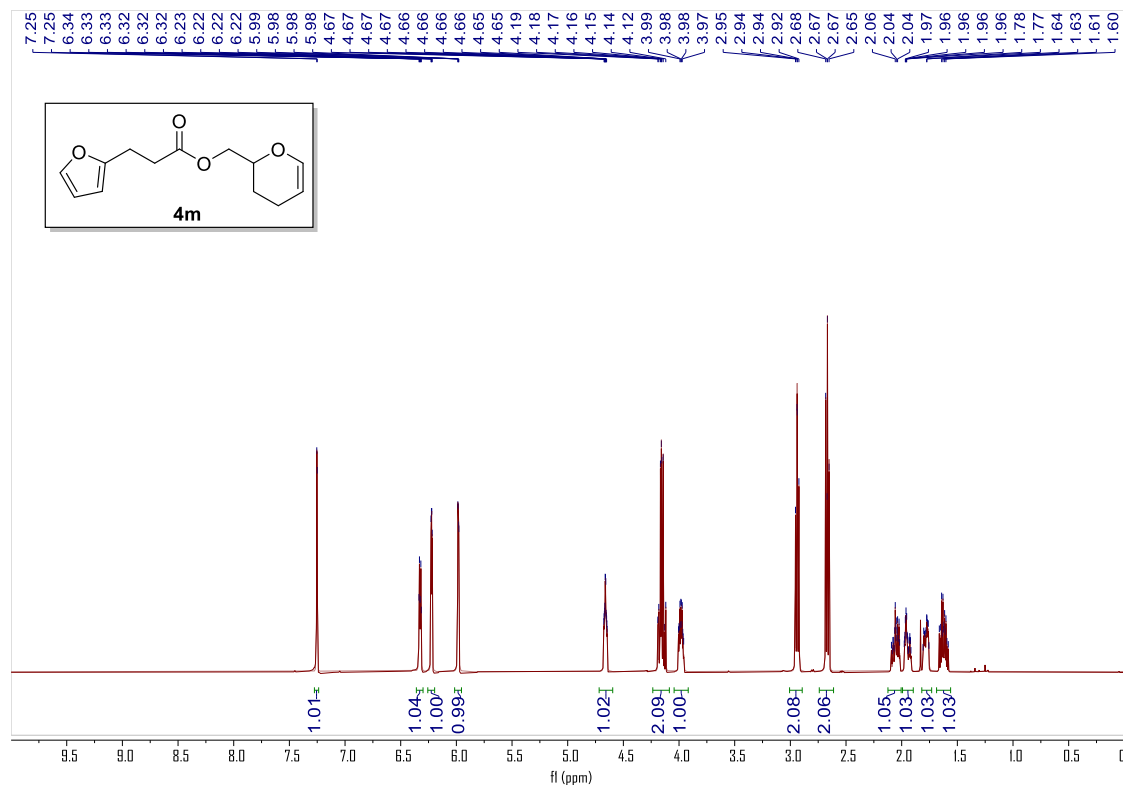
tert-butyl((3,4-dihydro-2H-pyran-2-yl)methoxy)diphenylsilane (**4j**)

^1H spectrum (500 MHz, CDCl_3)

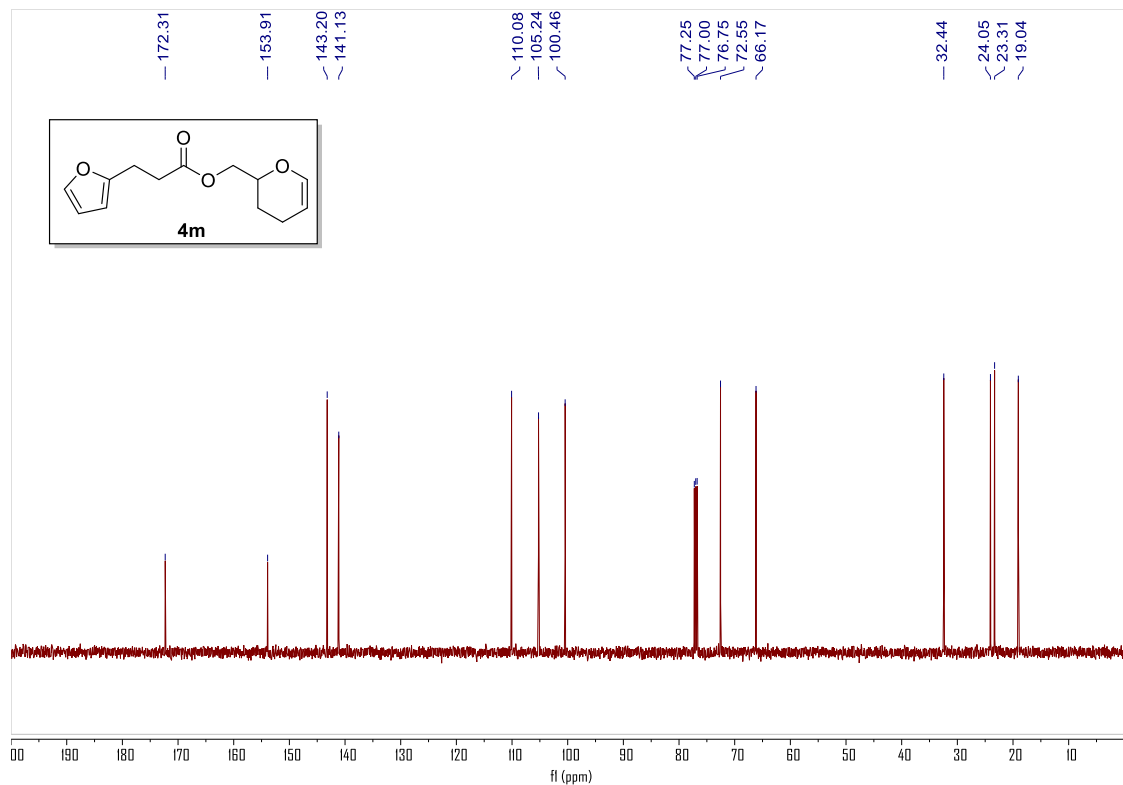


(3,4-dihydro-2H-pyran-2-yl)methyl 3-(furan-2-yl)propanoate (4m)

^1H spectrum (500 MHz, CDCl_3)

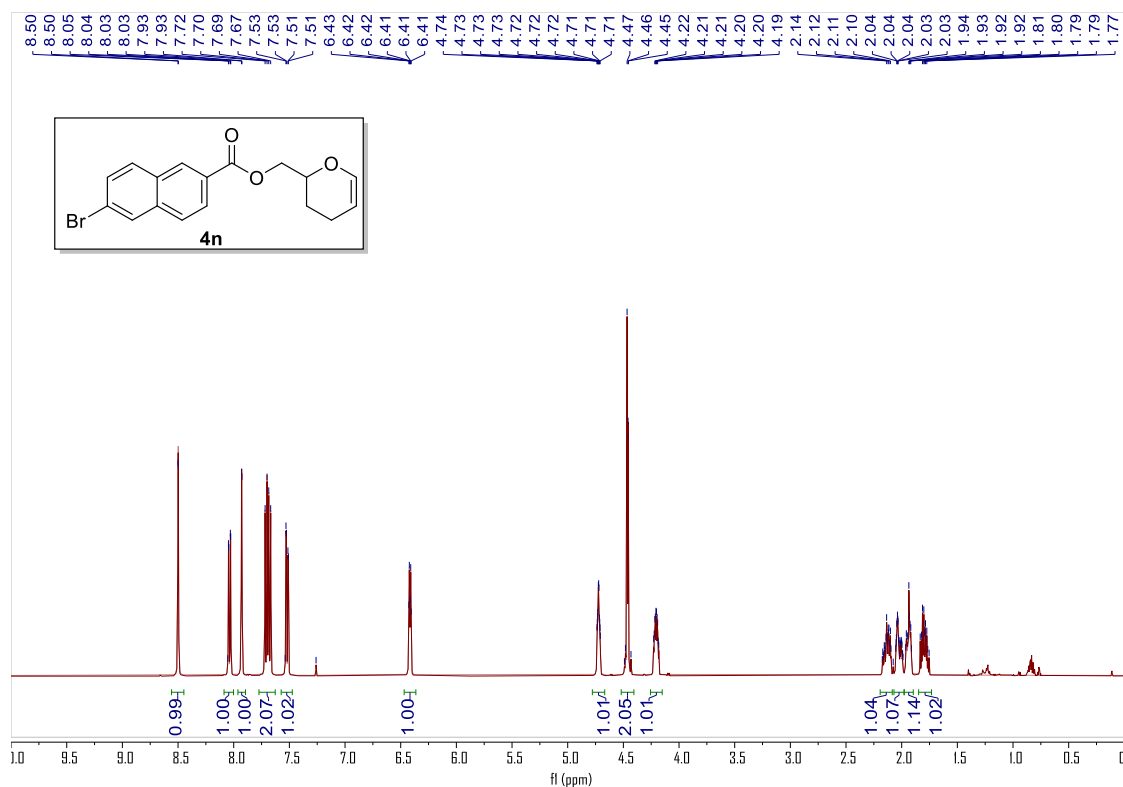


^{13}C spectrum (126 MHz, CDCl_3)

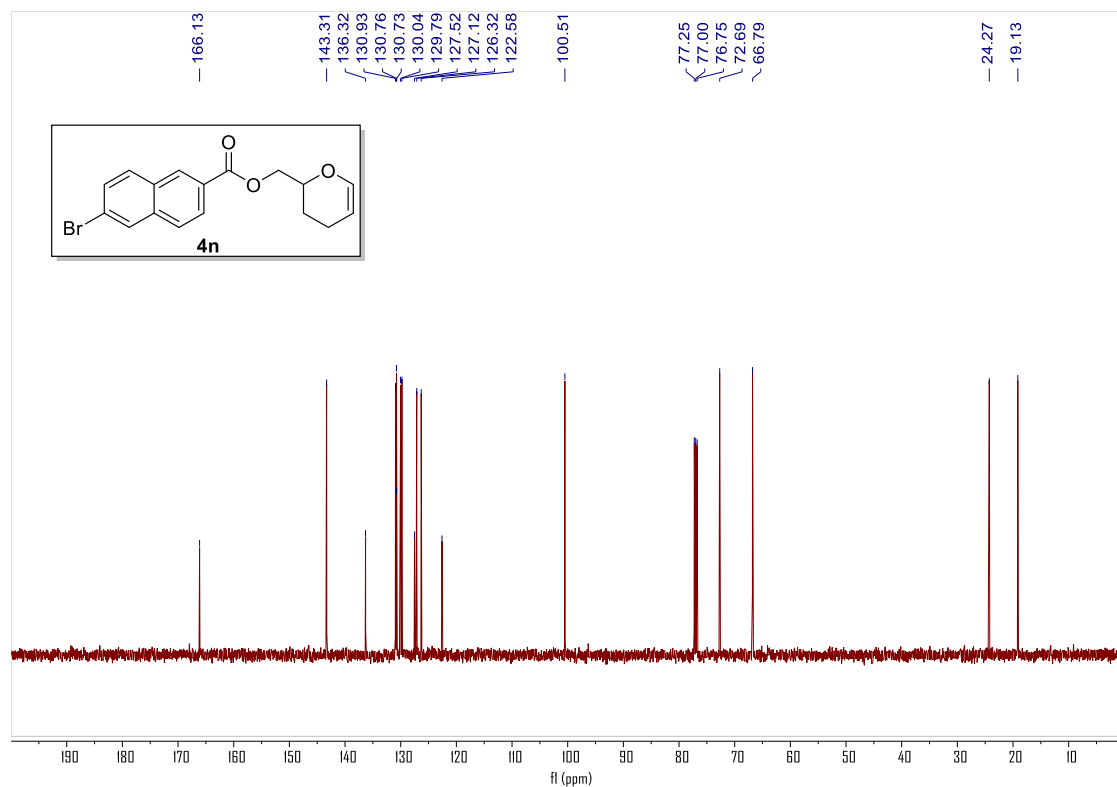


(3,4-dihydro-2H-pyran-2-yl)methyl 6-bromo-2-naphthoate (4n)

^1H spectrum (500 MHz, CDCl_3)

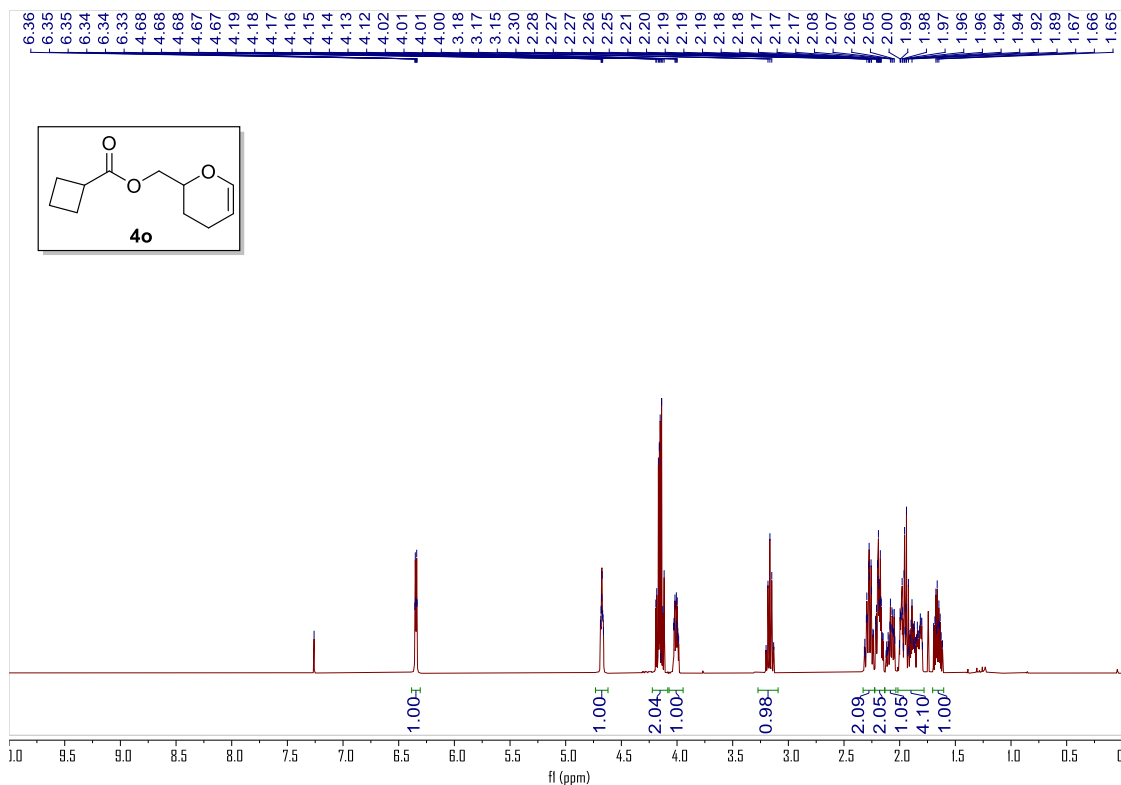


^{13}C spectrum (126 MHz, CDCl_3)

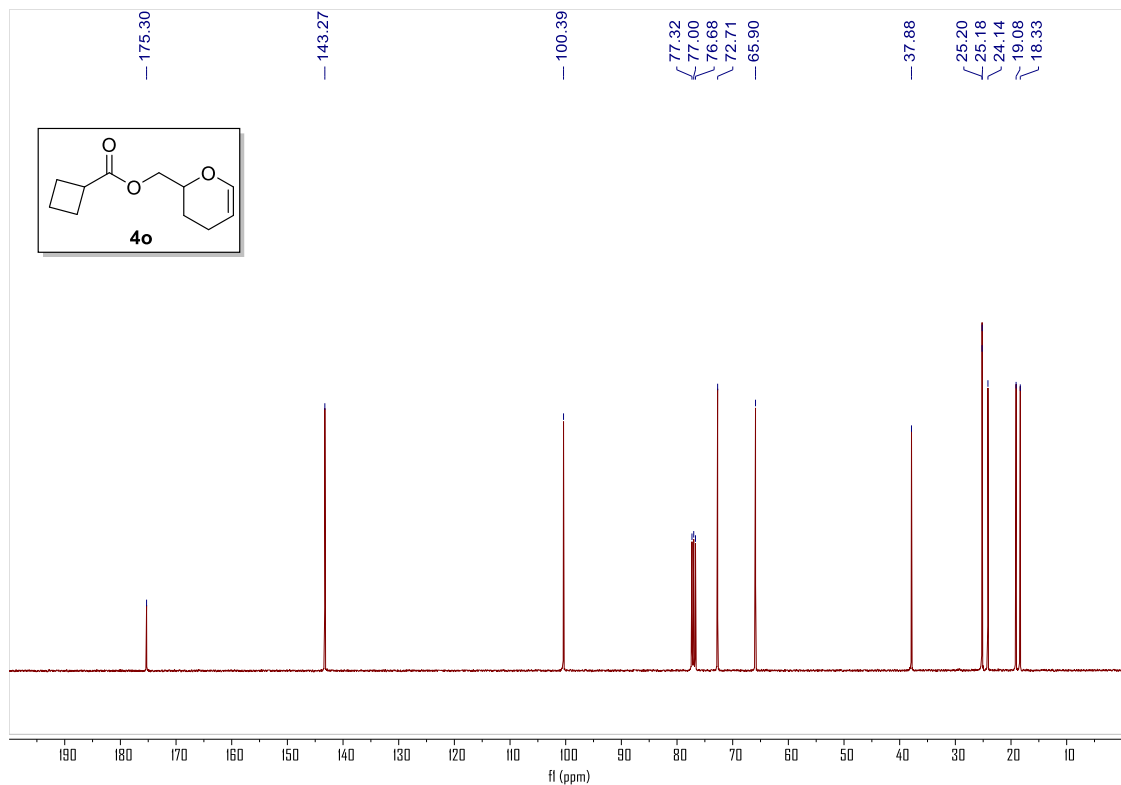


(3,4-dihydro-2H-pyran-2-yl)methyl cyclobutanecarboxylate (4o)

¹H spectrum (500 MHz, CDCl₃)

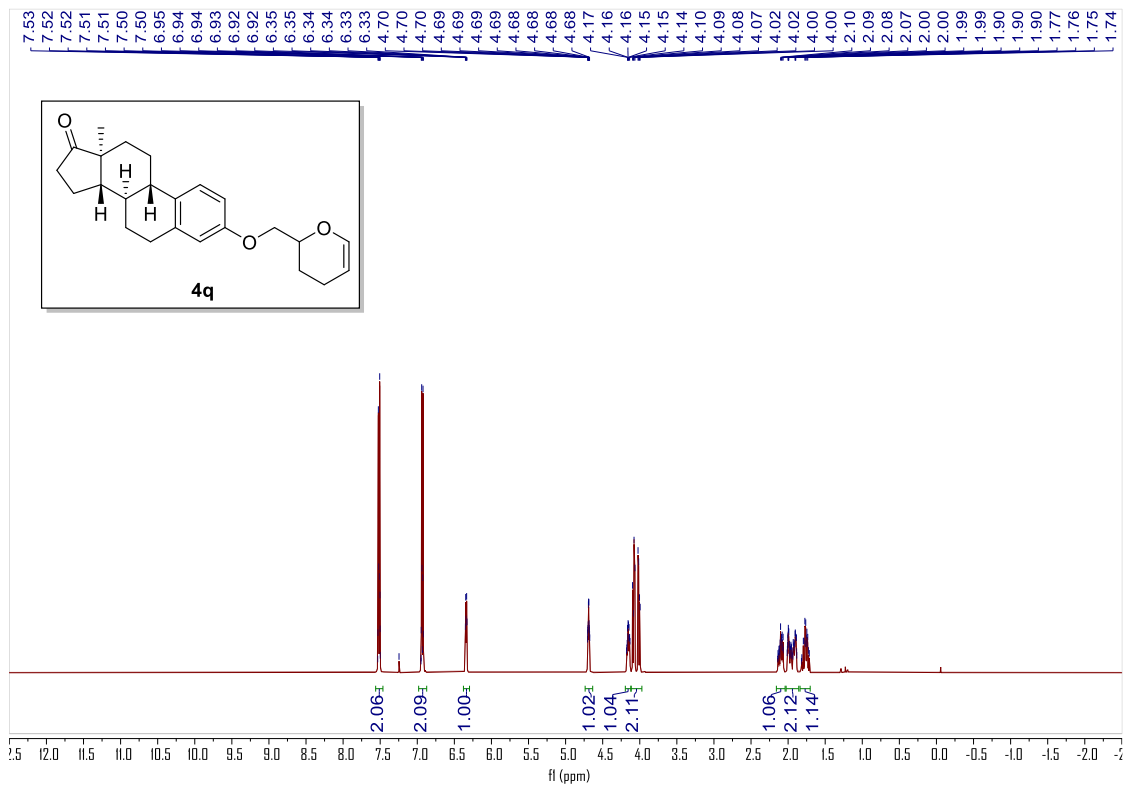


¹³C spectrum (126 MHz, CDCl₃)

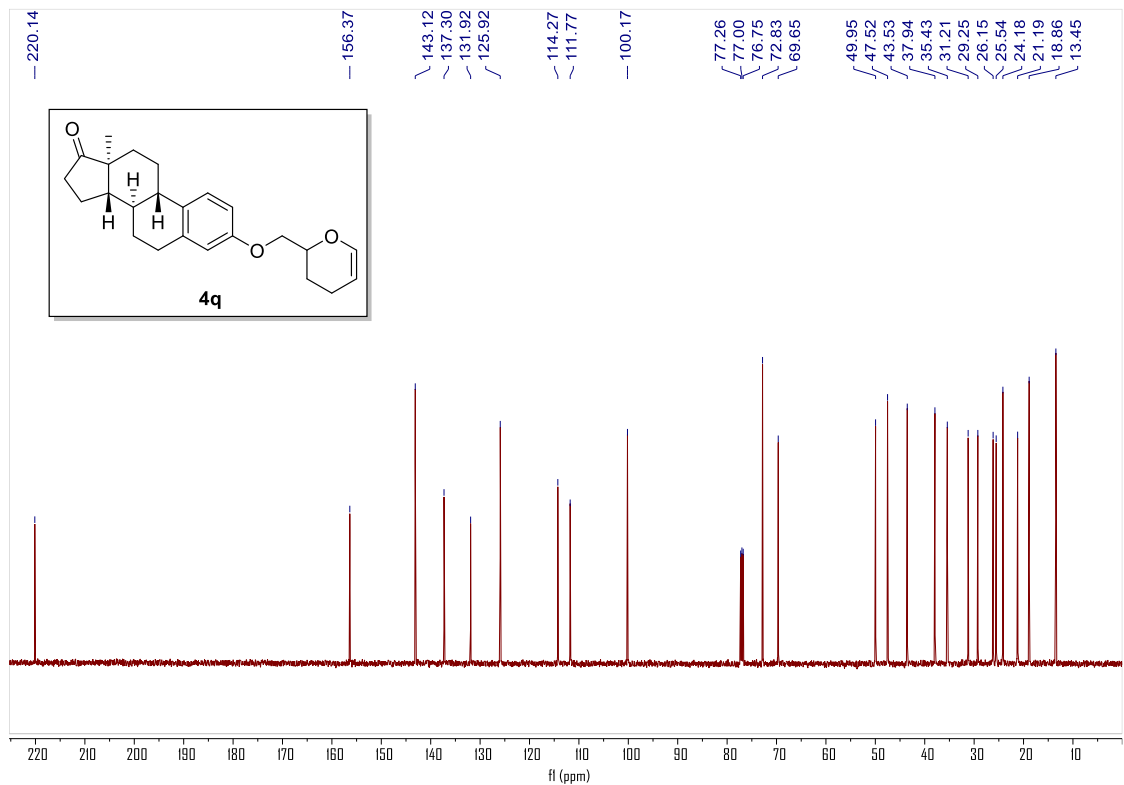


(8R,9S,13S,14S)-3-((3,4-dihydro-2H-pyran-2-yl)methoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (4q)

^1H spectrum (500 MHz, CDCl_3)

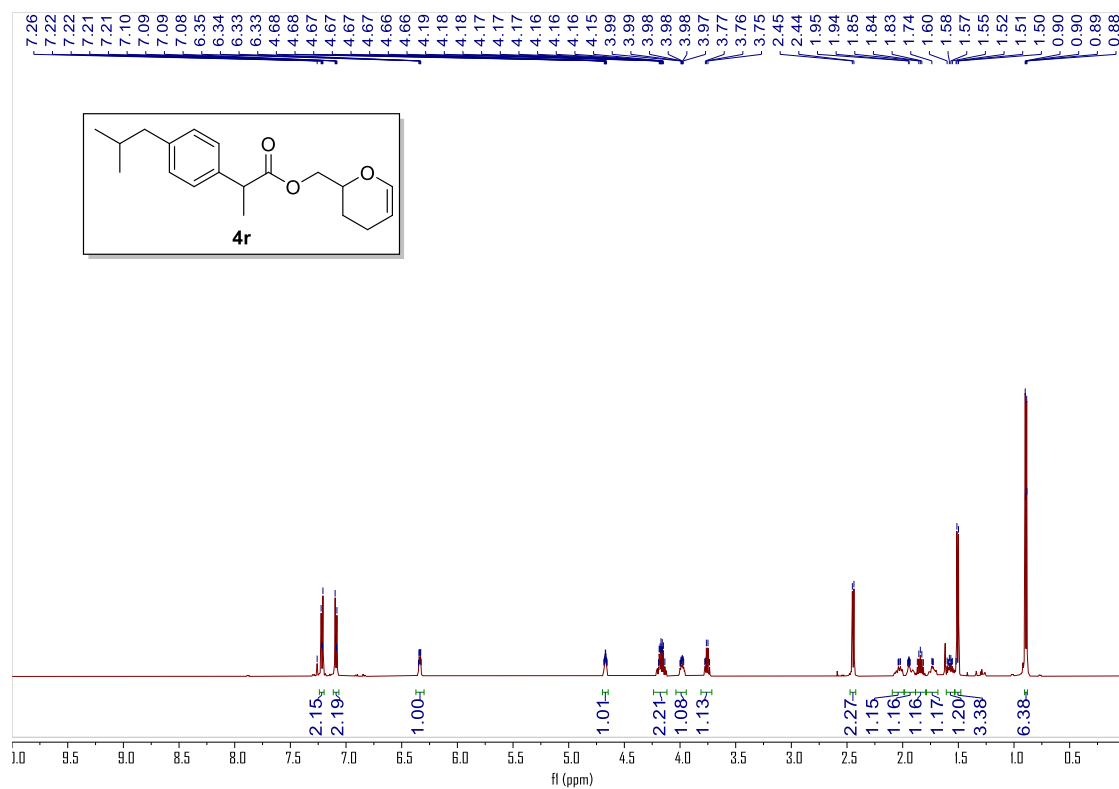


^{13}C spectrum (126 MHz, CDCl_3)



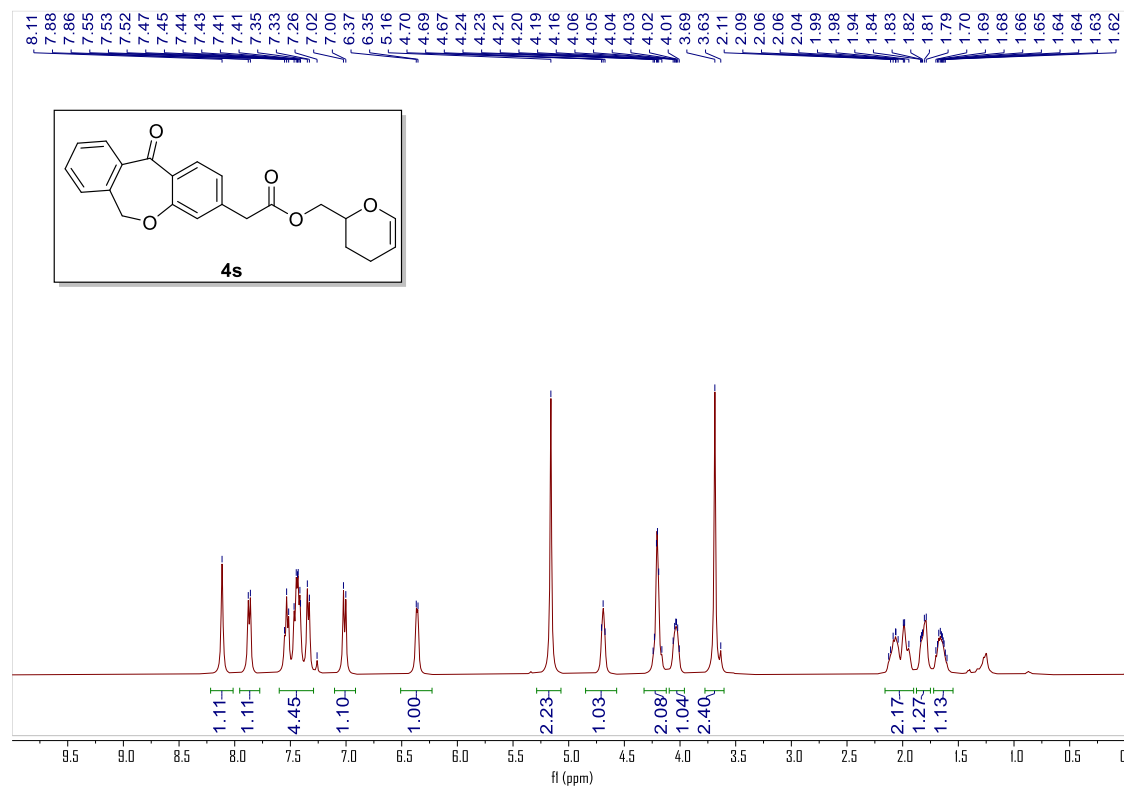
(3,4-dihydro-2H-pyran-2-yl)methyl 2-(4-isobutylphenyl)propanoate (4r)

^1H spectrum (500 MHz, CDCl_3)

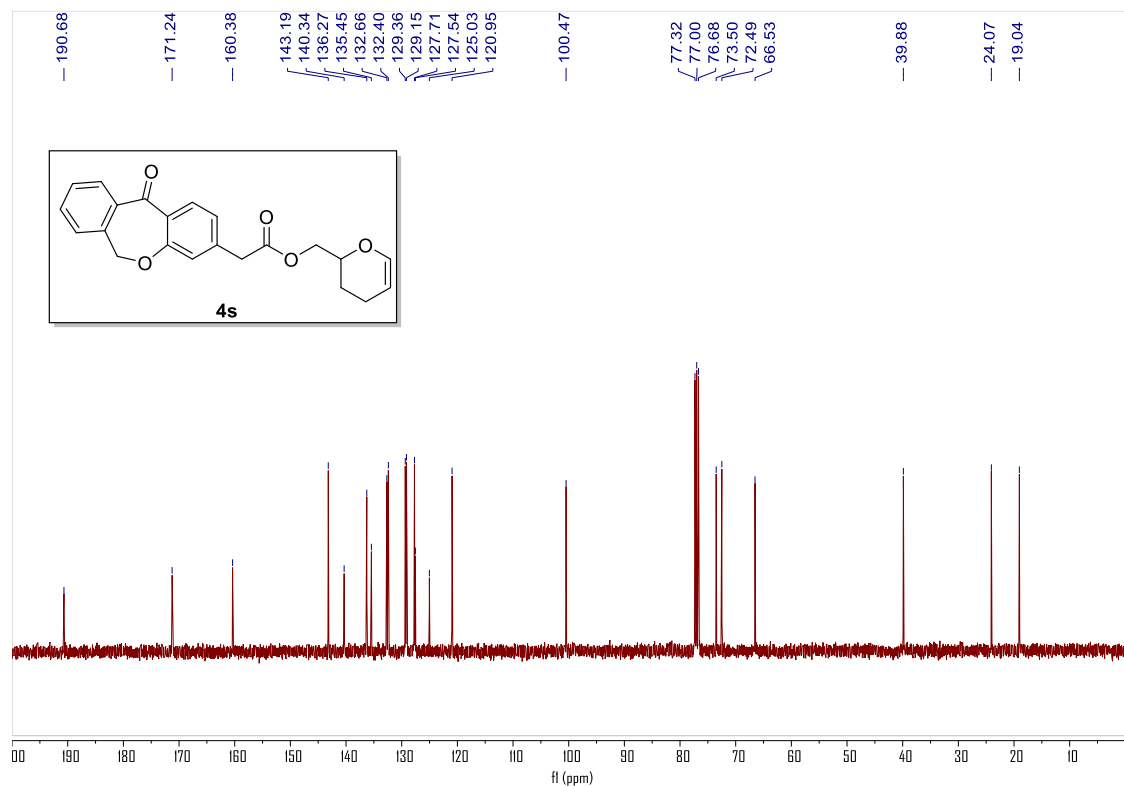


(3,4-dihydro-2H-pyran-2-yl)methyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-3-yl)acetate (4s)

¹H spectrum (400 MHz, CDCl₃)

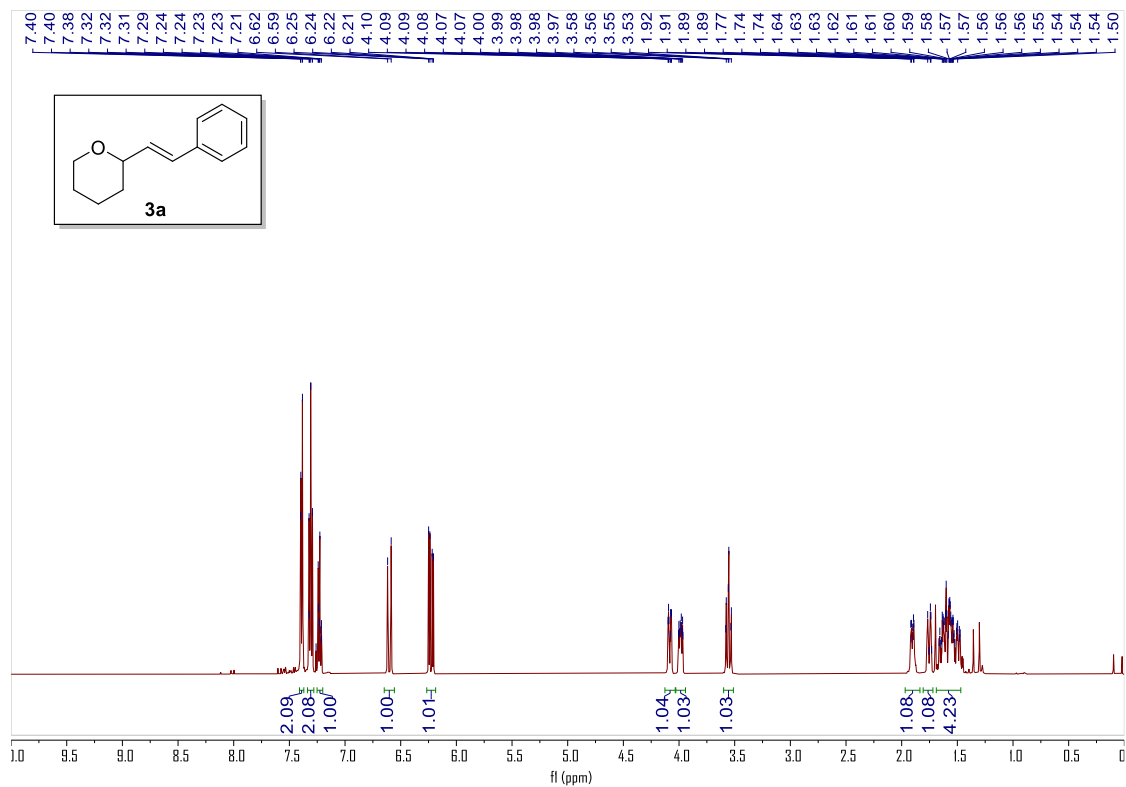


¹³C spectrum (101 MHz, CDCl₃)

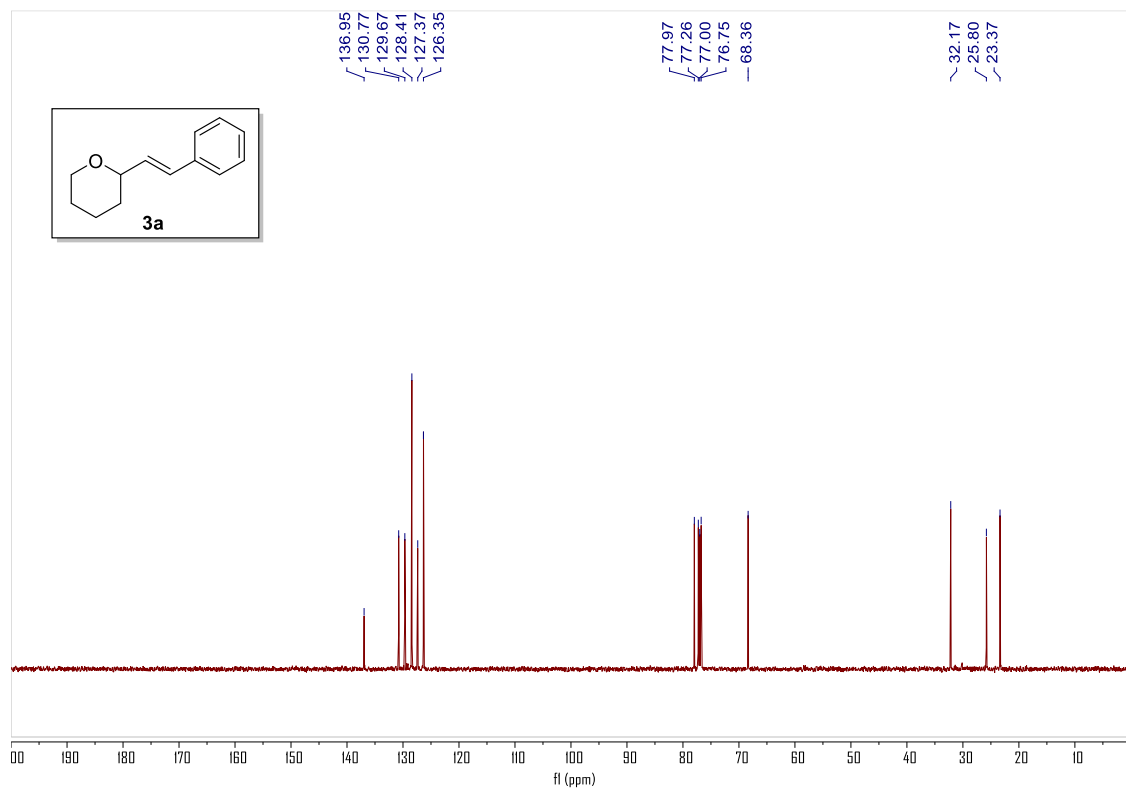


(E)-2-styryltetrahydro-2H-pyran (3a)

^1H spectrum (500 MHz, CDCl_3)

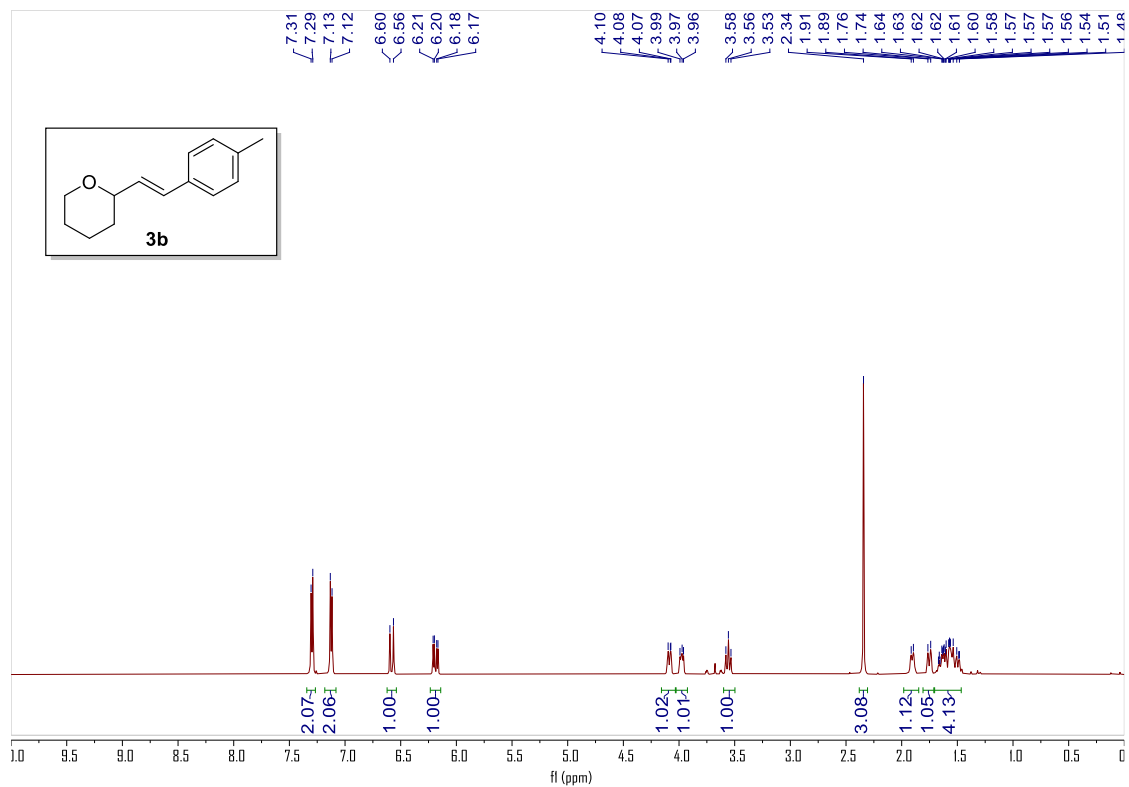


^{13}C spectrum (126 MHz, CDCl_3)

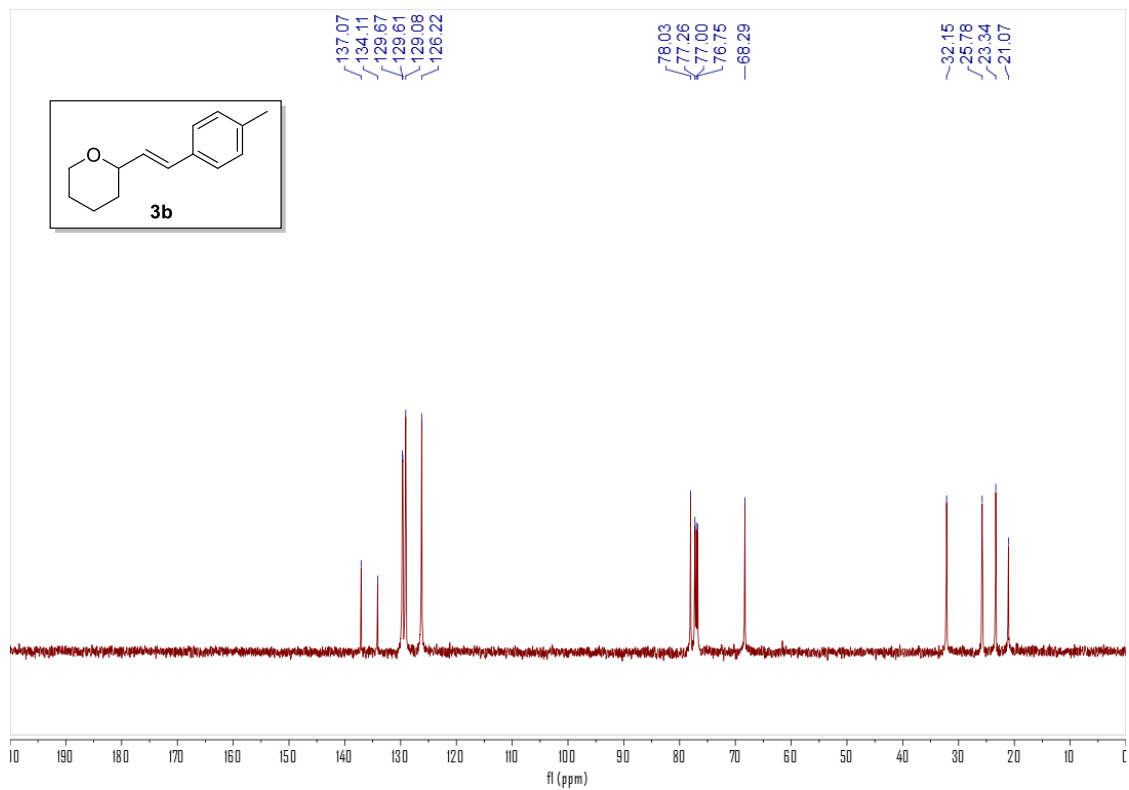


(E)-2-(4-methylstyryl)tetrahydro-2H-pyran (**3b**)

^1H spectrum (500MHz, CDCl_3)

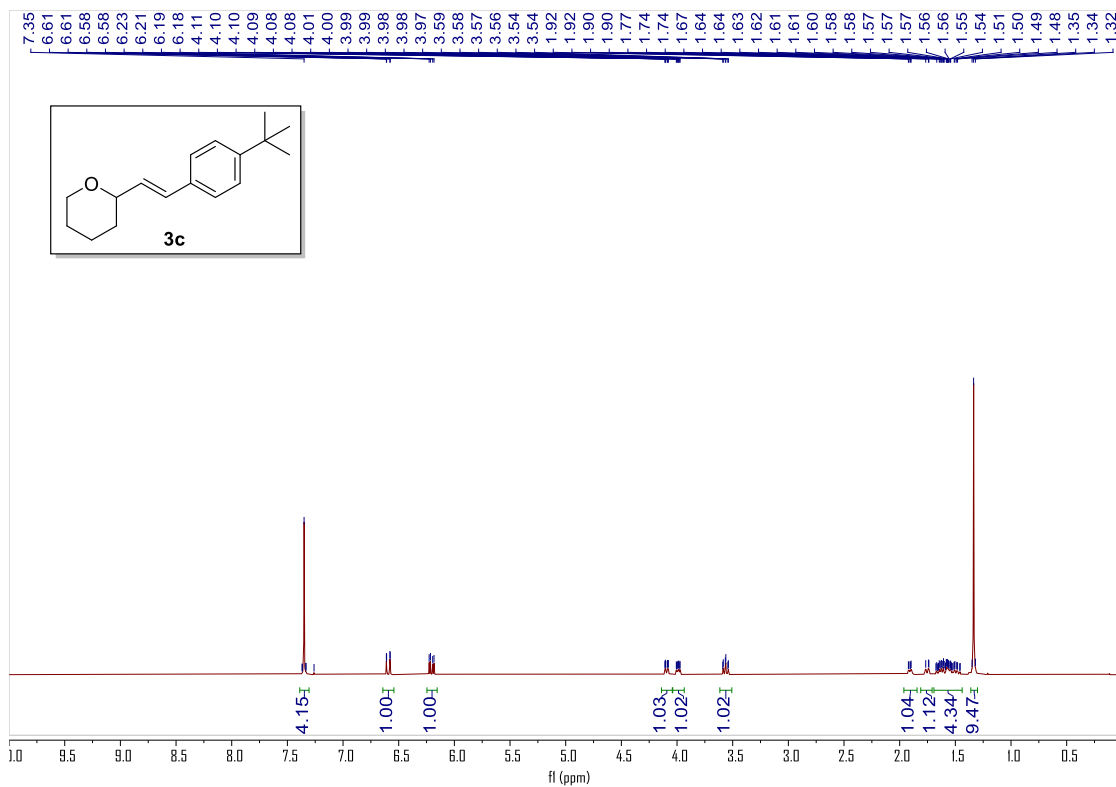


^{13}C spectrum (126 MHz, CDCl_3)

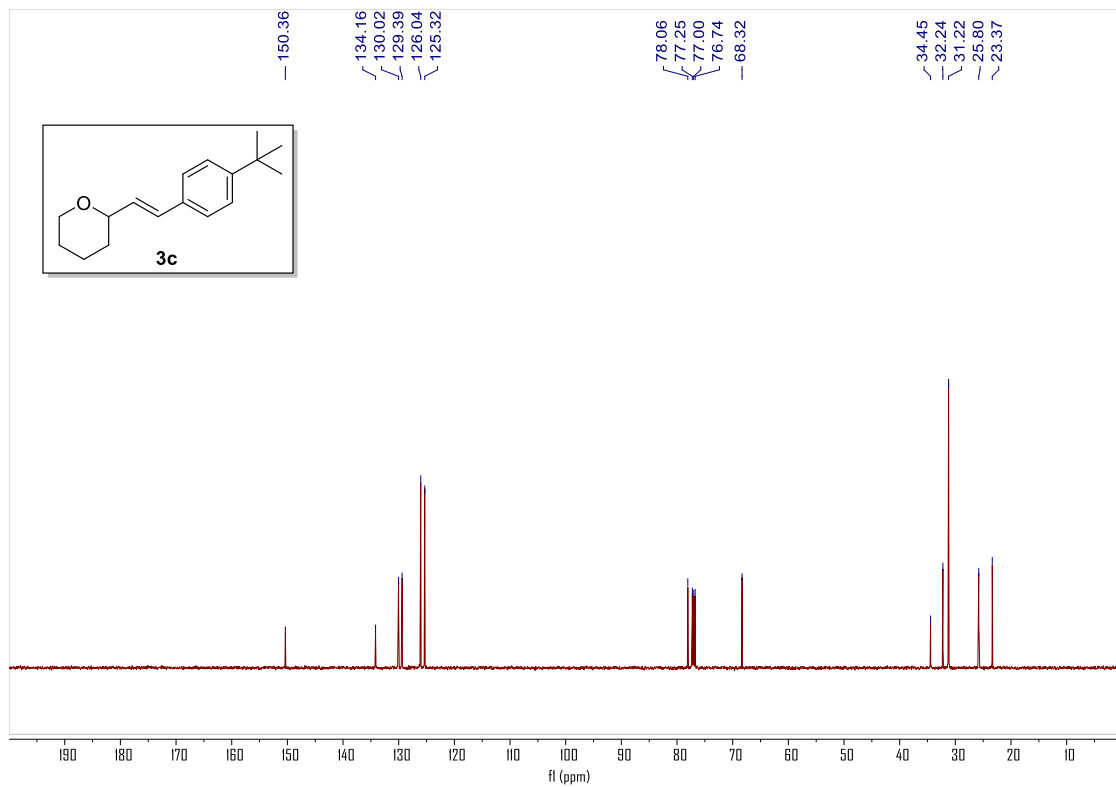


(E)-2-(4-(tert-butyl)styryl)tetrahydro-2H-pyran (**3c**)

¹H spectrum (500 MHz, CDCl₃)

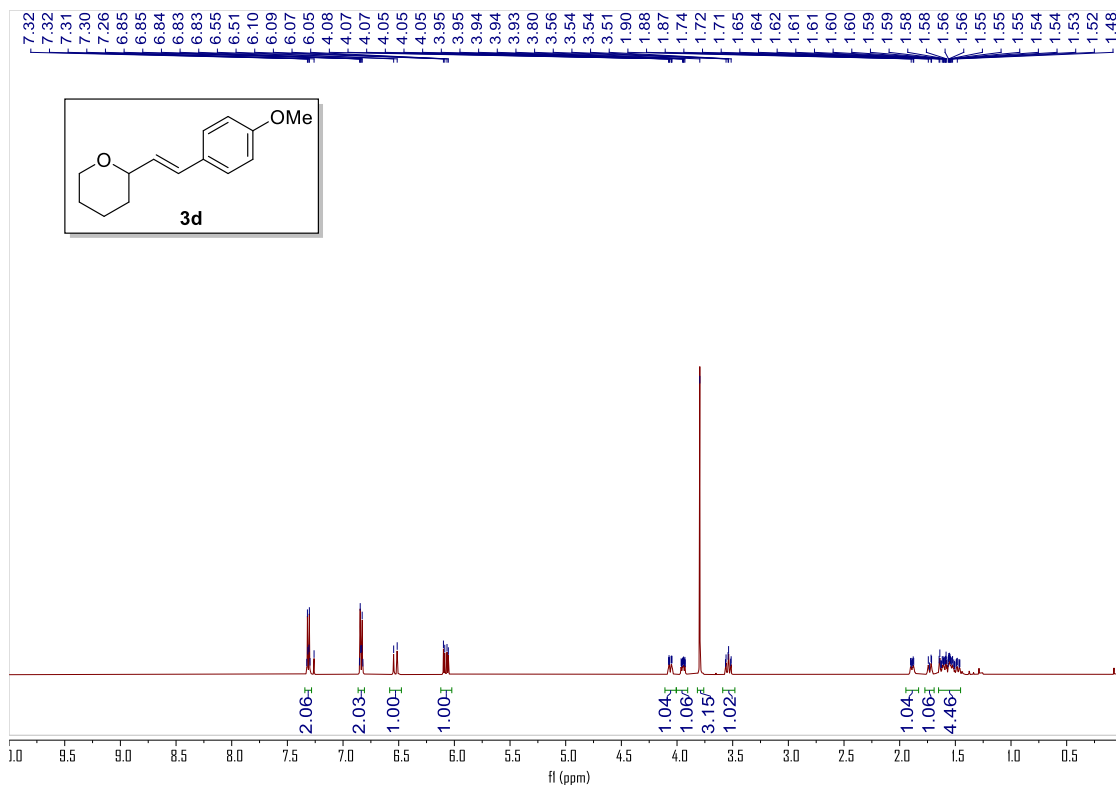


¹³C spectrum (126 MHz, CDCl₃)

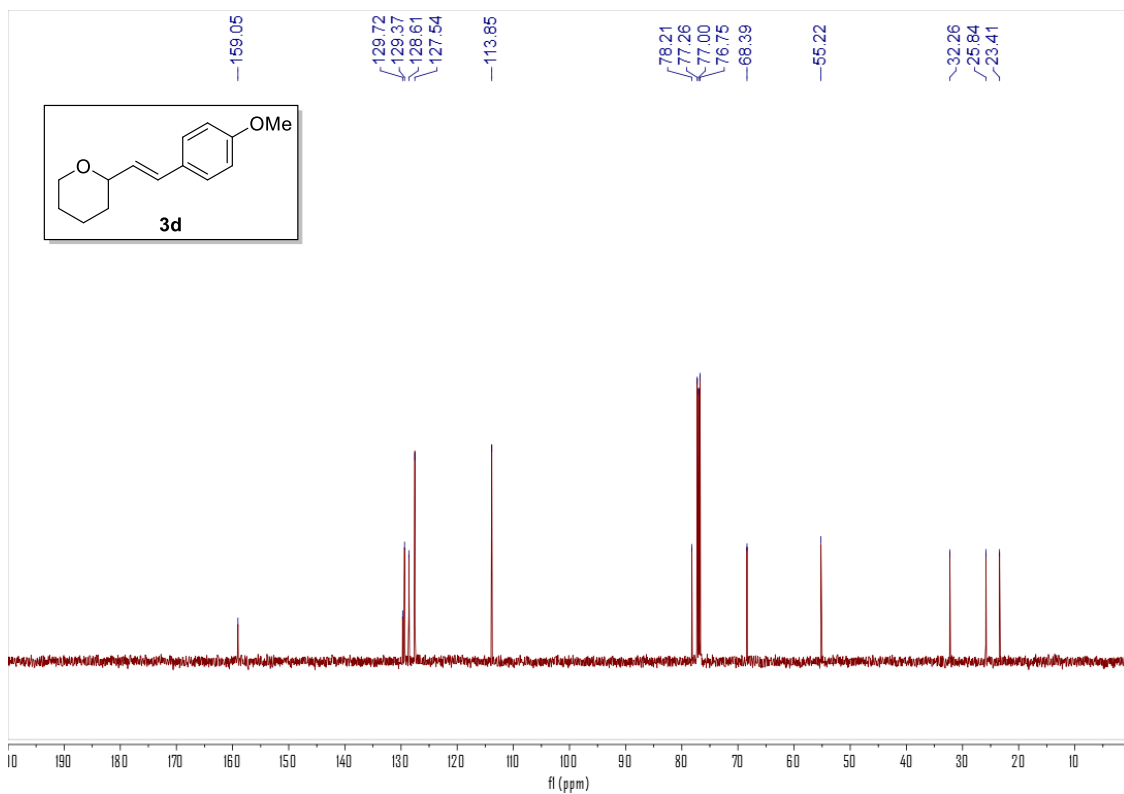


(E)-2-(4-methoxystyryl)tetrahydro-2H-pyran (3d)

¹H spectrum (500 MHz, CDCl₃)

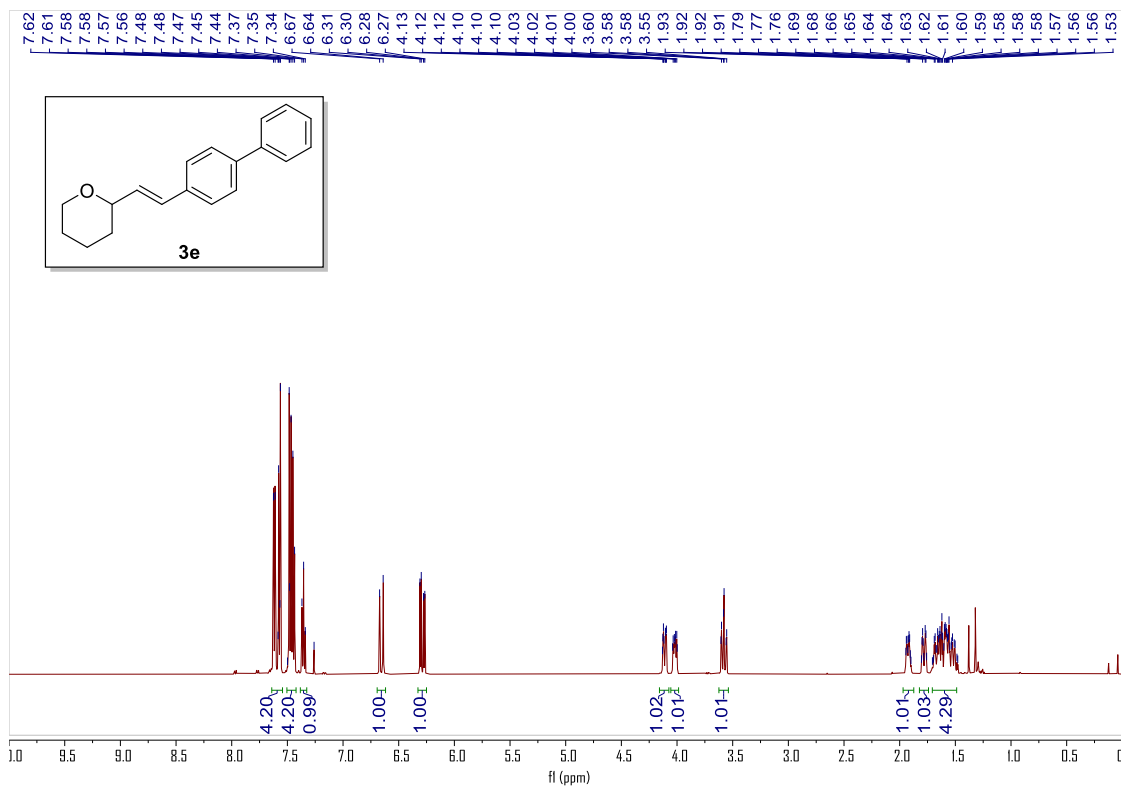


¹³C spectrum (126 MHz, CDCl₃)

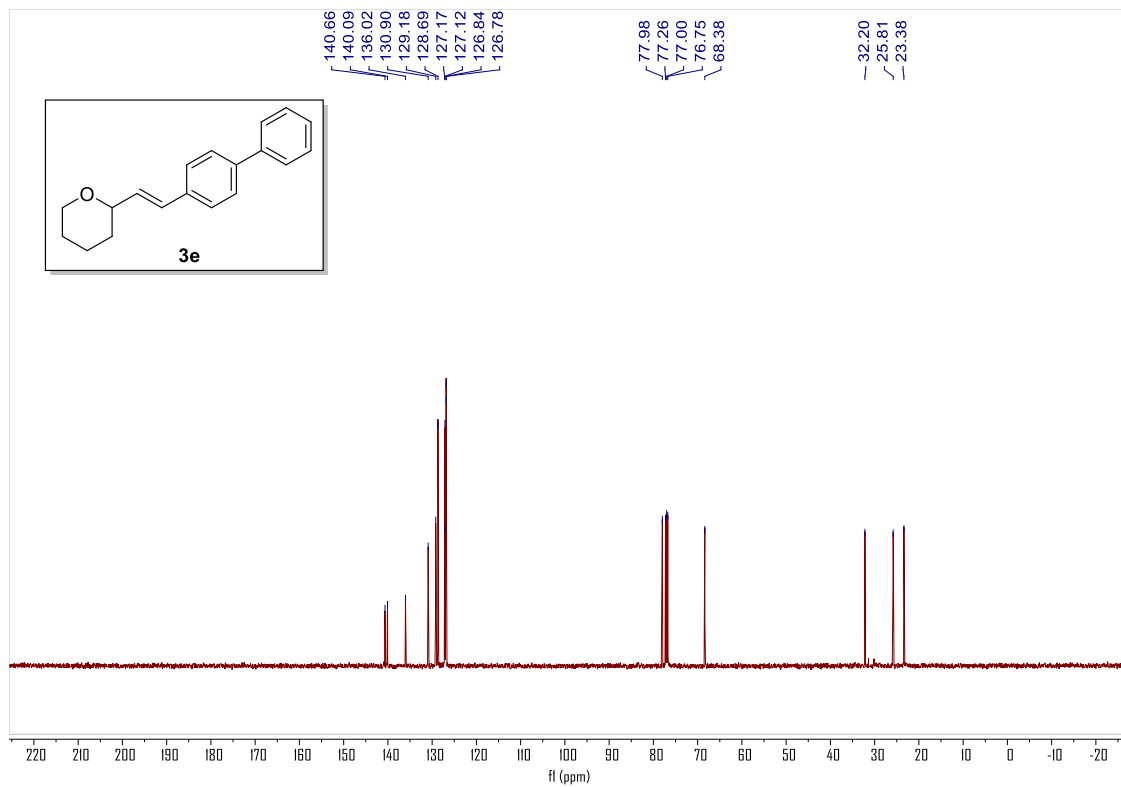


(E)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)tetrahydro-2H-pyran (3e)

¹H spectrum (500 MHz, CDCl₃)

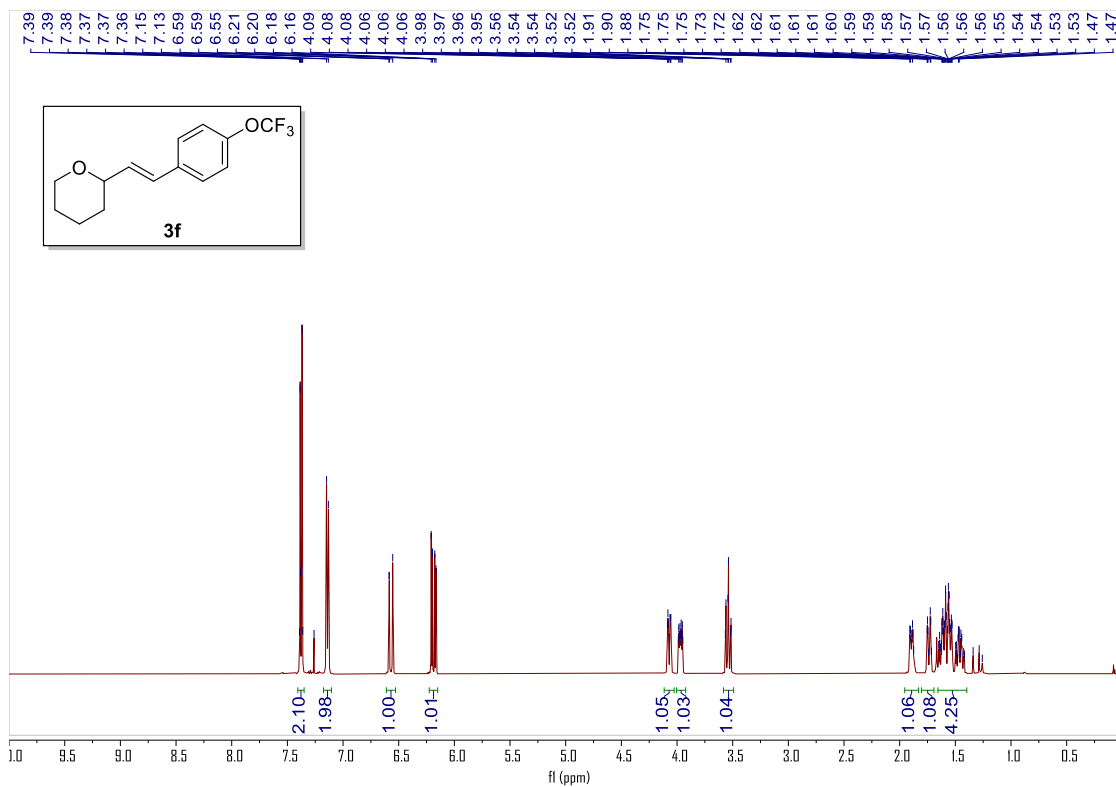


¹³C spectrum (126 MHz, CDCl₃)

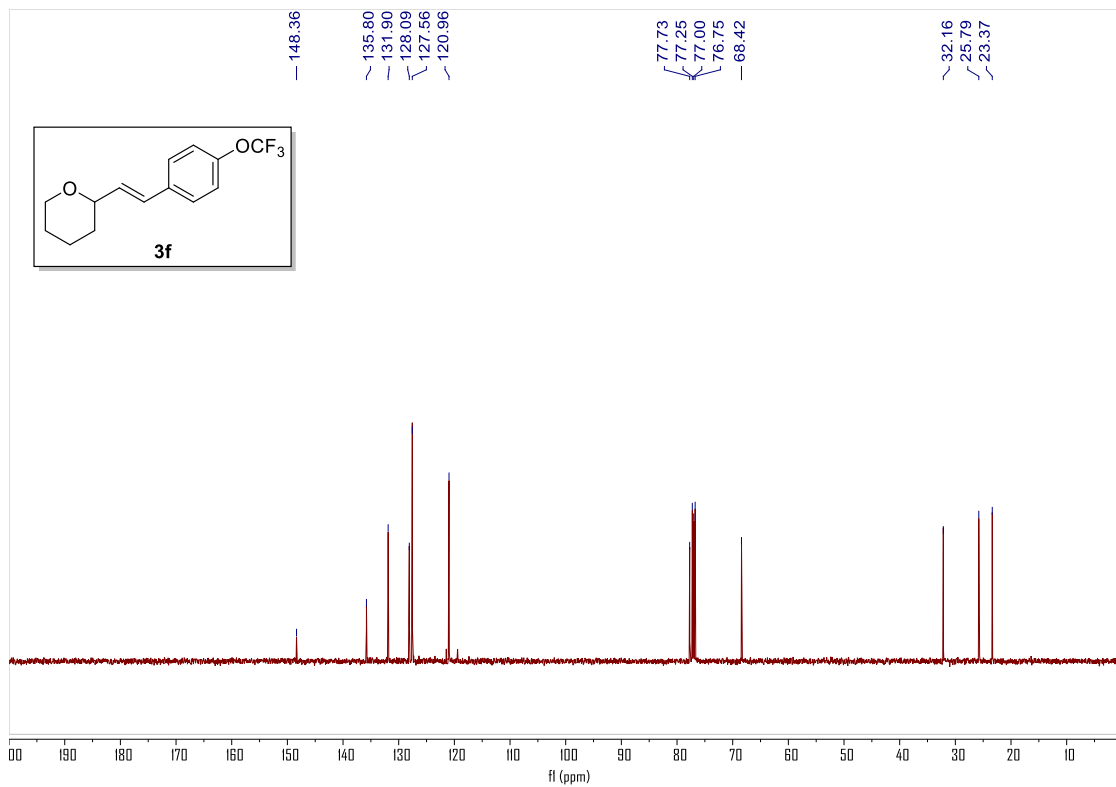


(E)-2-(4-(trifluoromethoxy)styryl)tetrahydro-2H-pyran (3f)

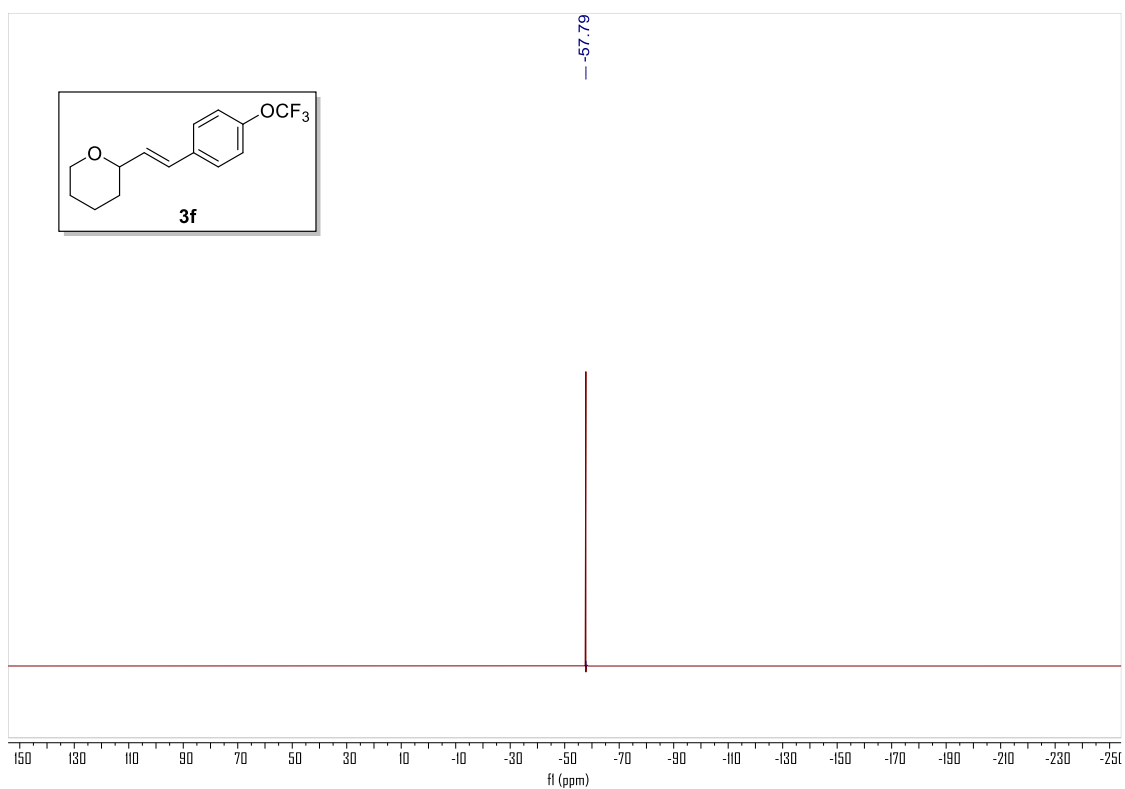
¹H spectrum (500 MHz, CDCl₃)



¹³C spectrum (126 MHz, CDCl₃)

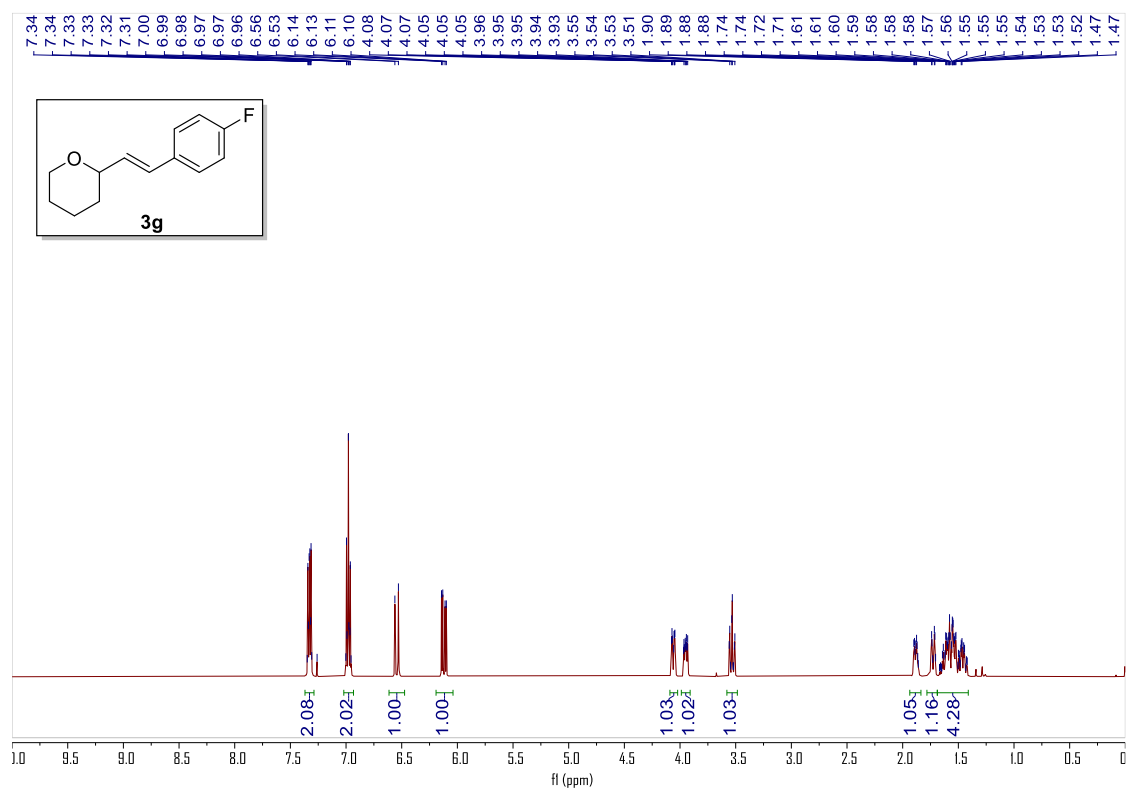


^{19}F spectrum (471 MHz, CDCl_3)

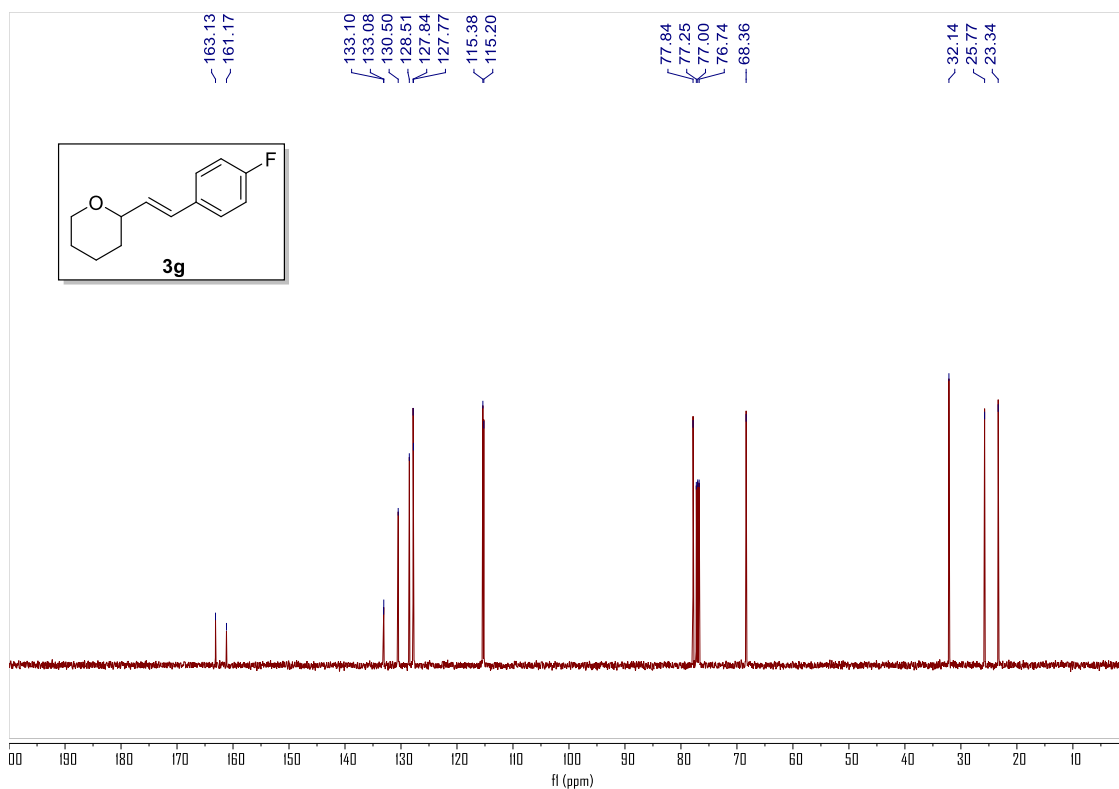


(E)-2-(4-fluorostyryl)tetrahydro-2H-pyran (**3g**)

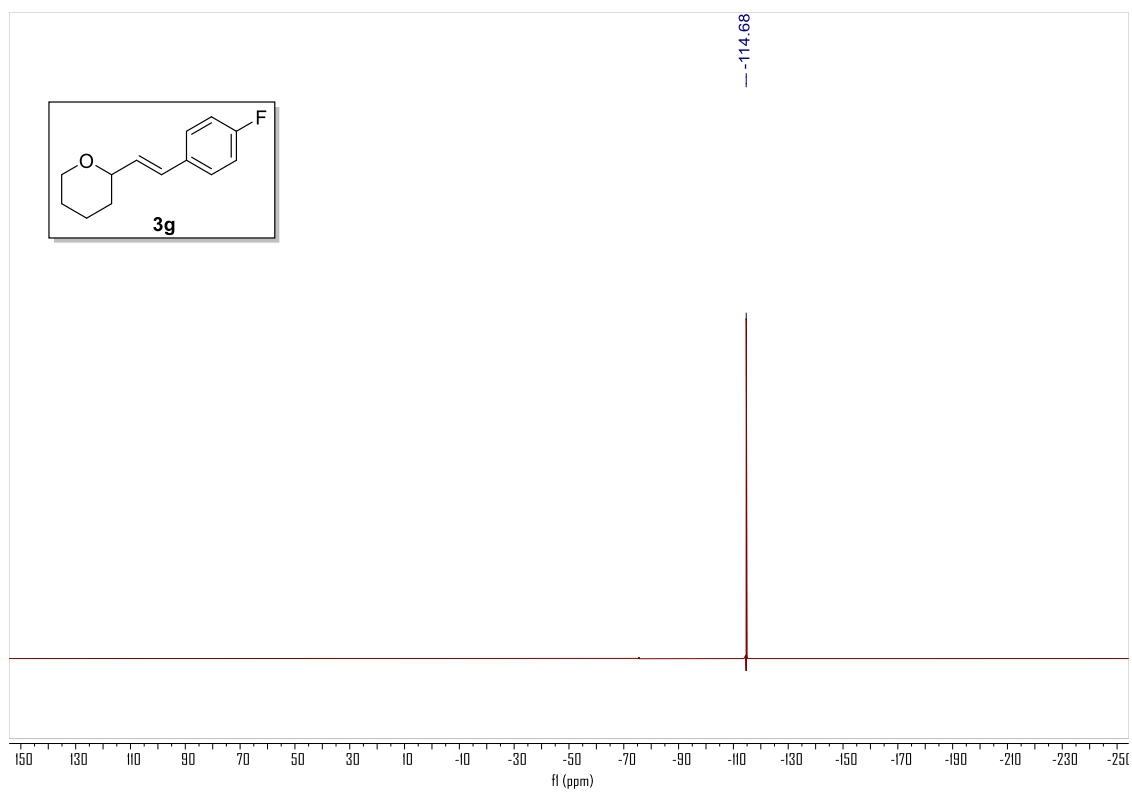
^1H spectrum (500 MHz, CDCl_3)



^{13}C spectrum (126 MHz, CDCl_3)

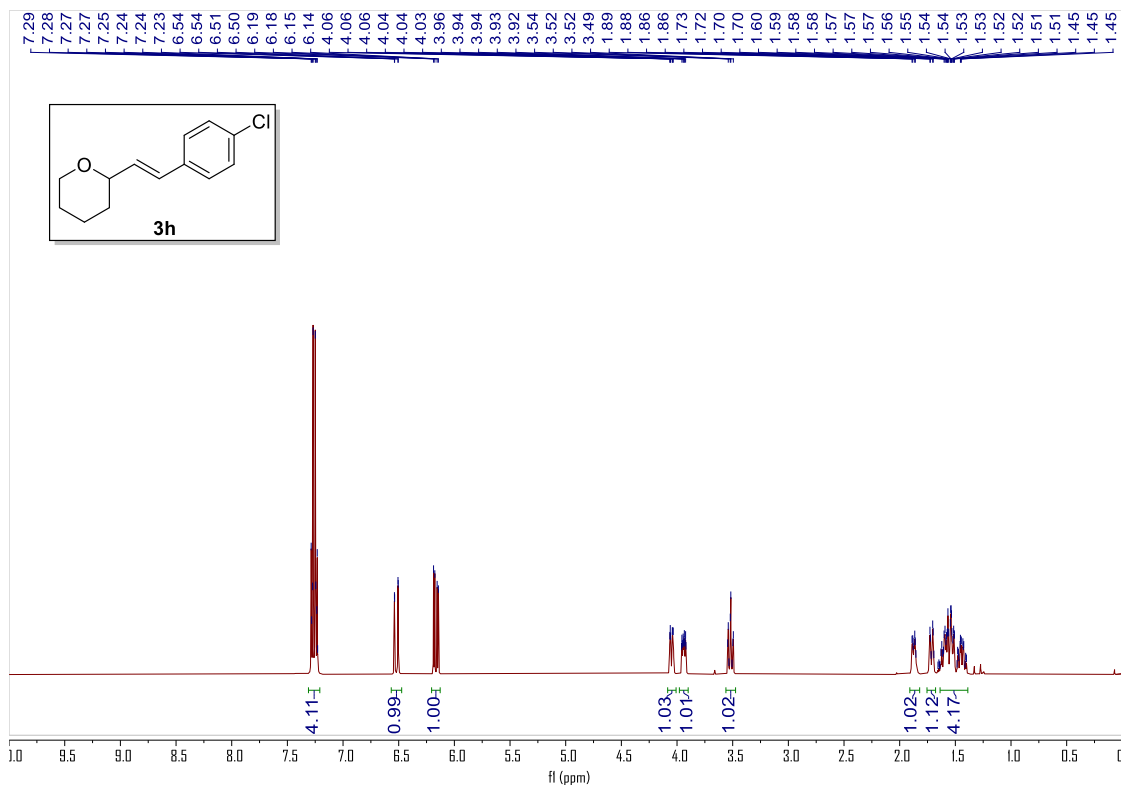


^{19}F spectrum (471 MHz, CDCl_3)

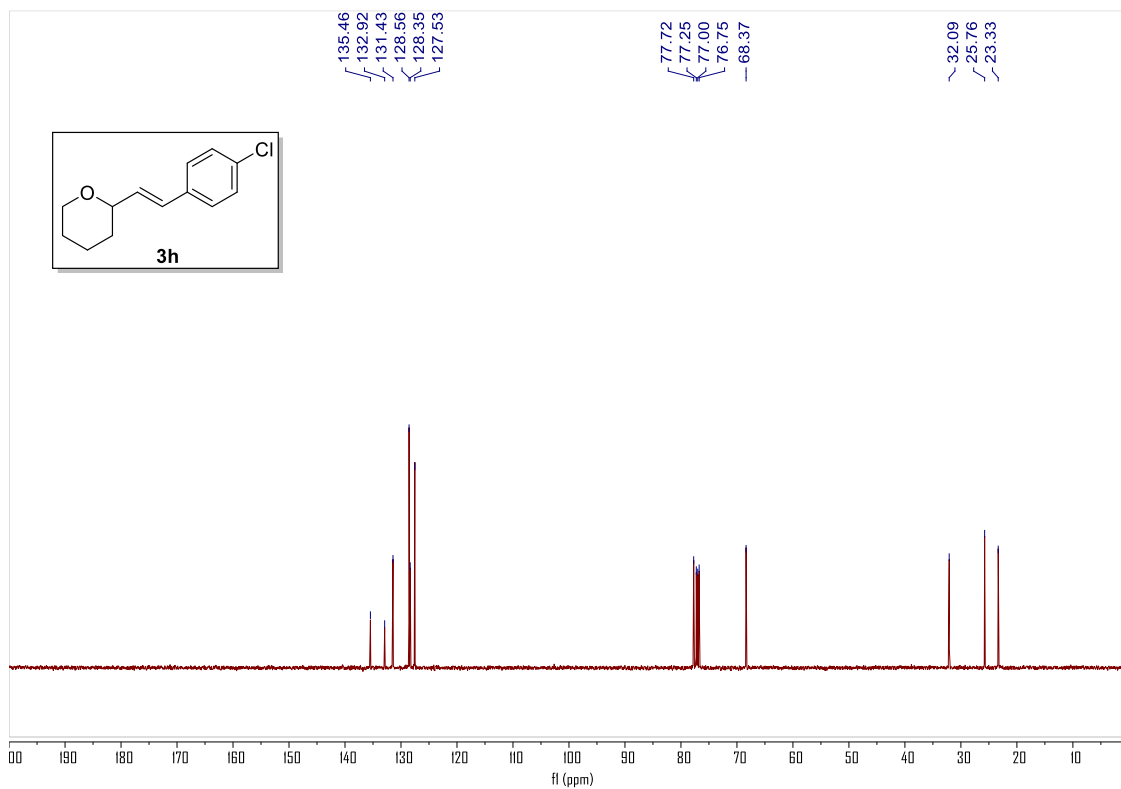


(E)-2-(4-chlorostyryl)tetrahydro-2H-pyran (**3h**)

¹H spectrum (500 MHz, CDCl₃)

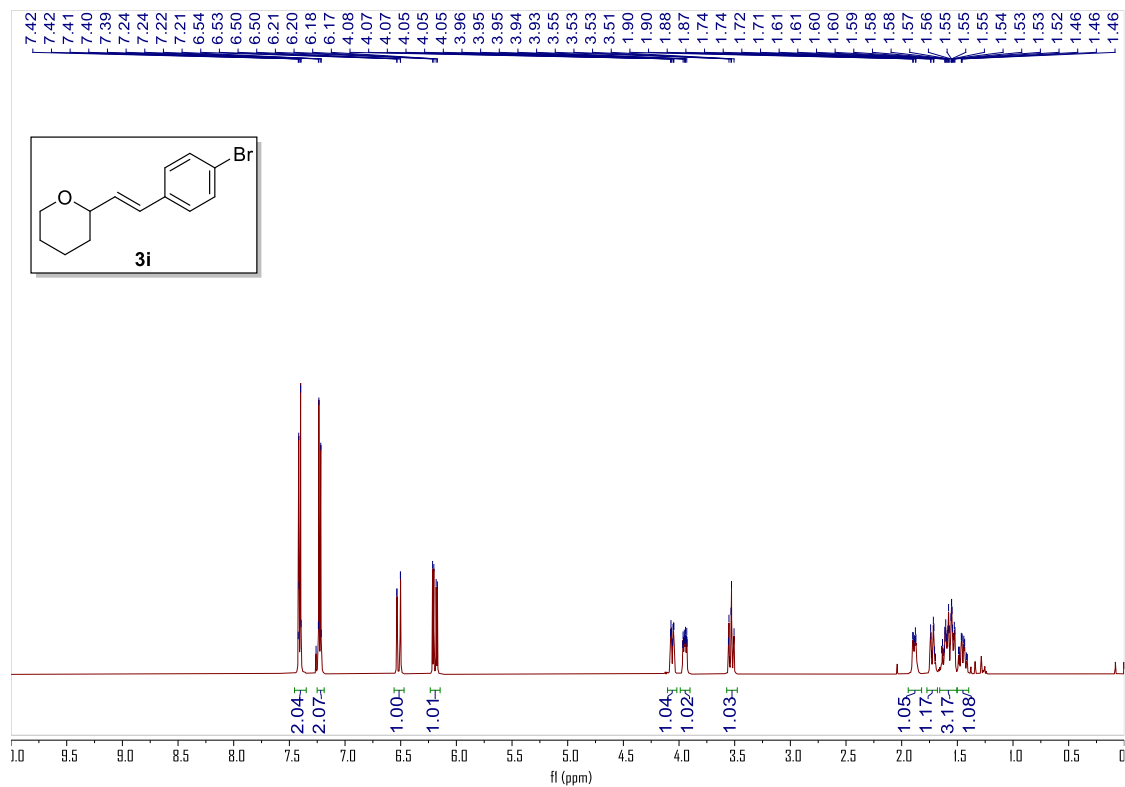


¹³C spectrum (126 MHz, CDCl₃)

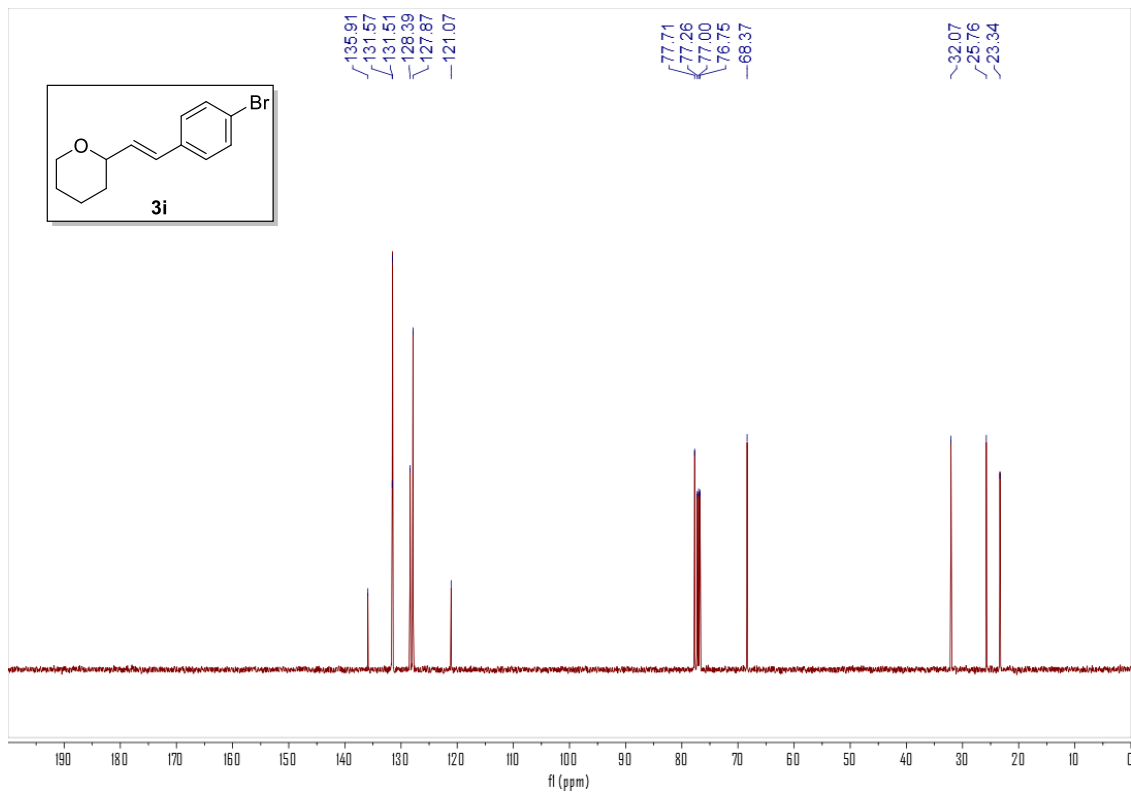


(E)-2-(4-bromostyryl)tetrahydro-2H-pyran (**3i**)

¹H spectrum (500 MHz, CDCl₃)

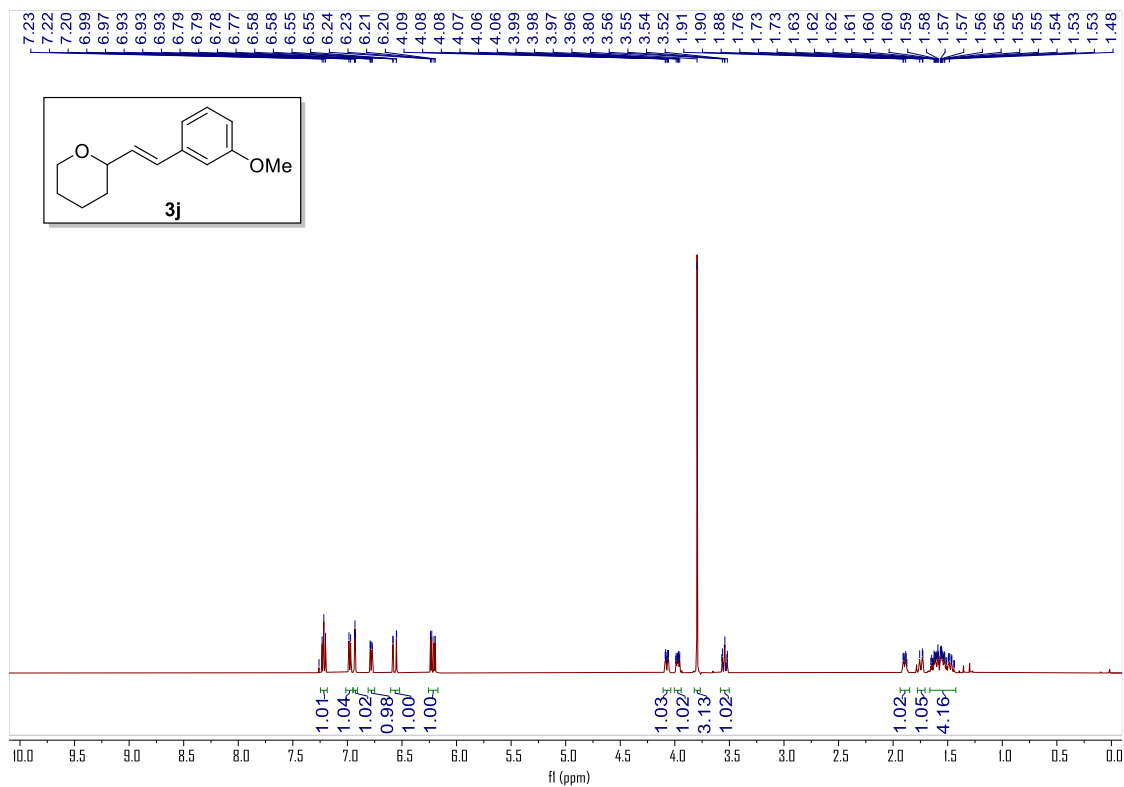


¹³C spectrum (126 MHz, CDCl₃)

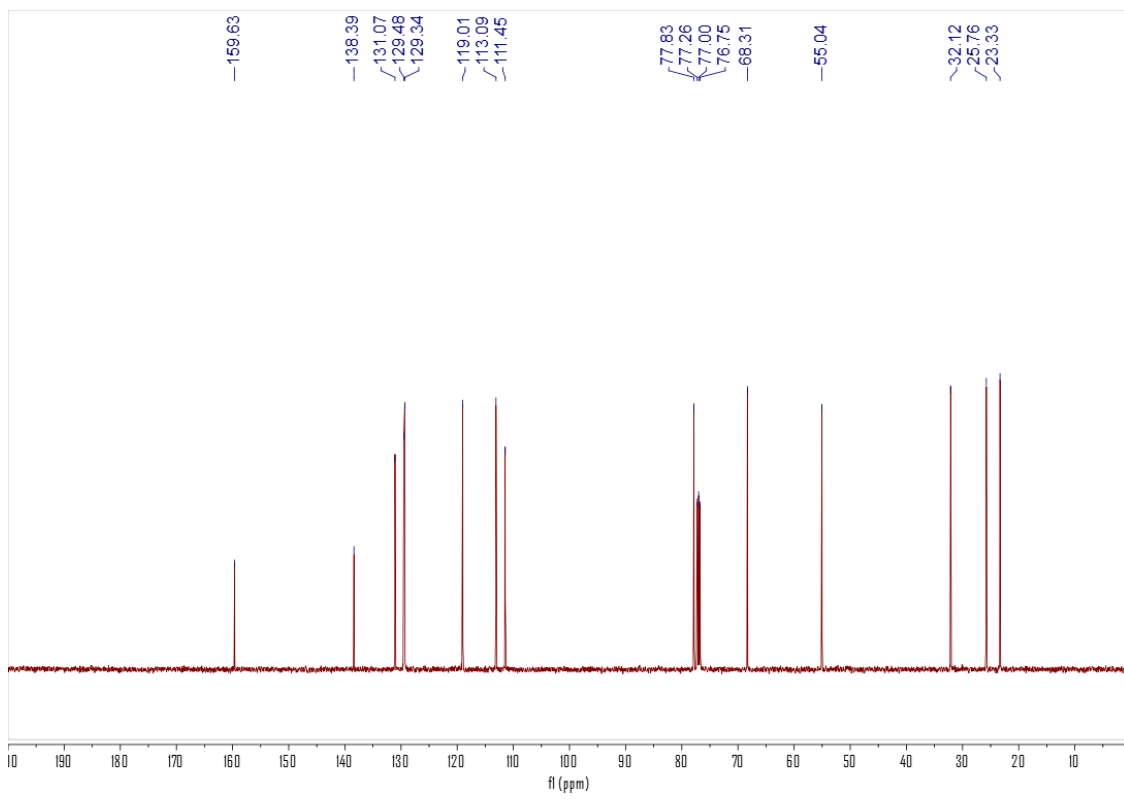


(E)-2-(3-methoxystyryl)tetrahydro-2H-pyran (3j)

¹H spectrum (400 MHz, CDCl₃)

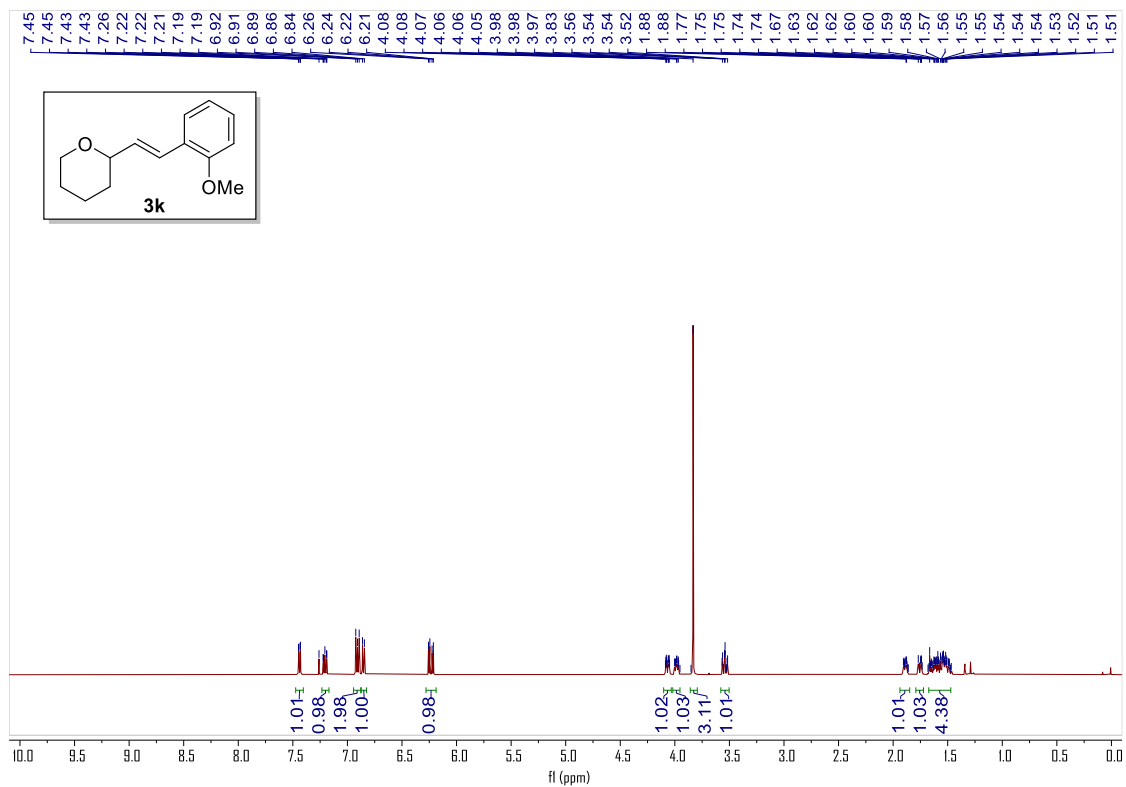


¹³C spectrum (126 MHz, CDCl₃)

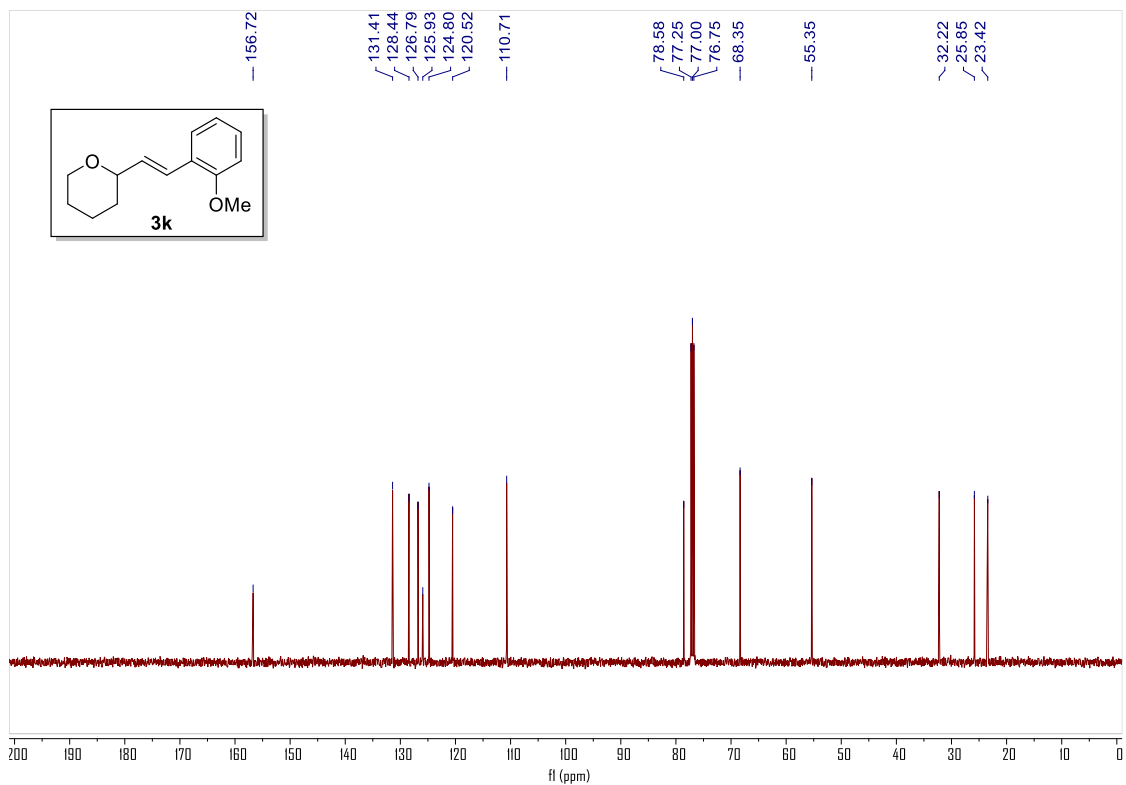


(E)-2-(2-methoxystyryl)tetrahydro-2H-pyran (3k)

¹H spectrum (500 MHz, CDCl₃)

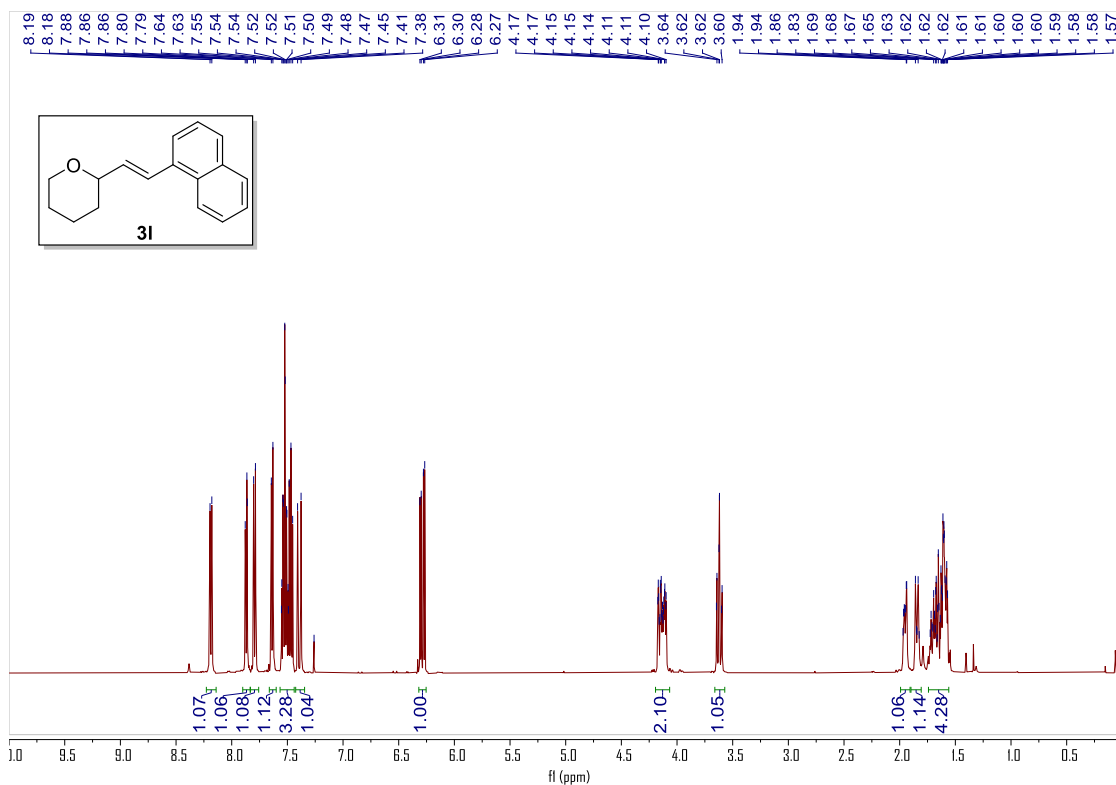


¹³C spectrum (126 MHz, CDCl₃)

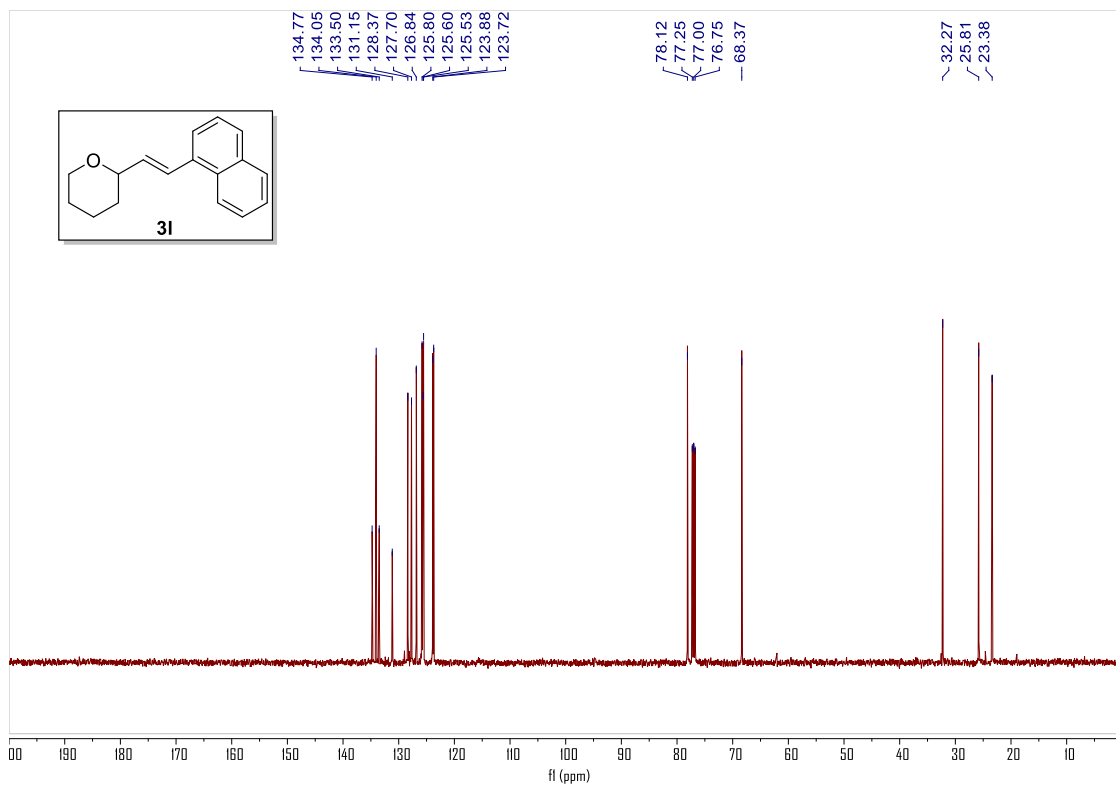


(E)-2-(2-(naphthalen-1-yl)vinyl)tetrahydro-2H-pyran (3I)

^1H spectrum (500 MHz, CDCl_3)

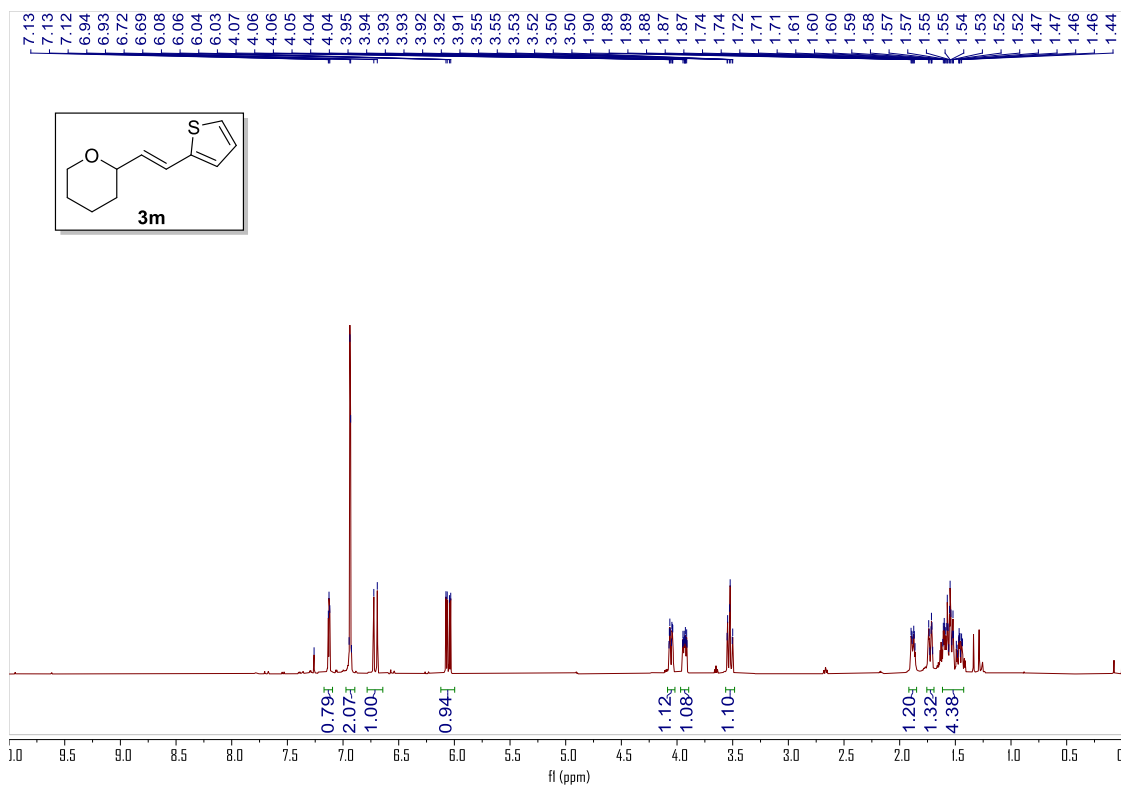


^{13}C spectrum (126 MHz, CDCl_3)

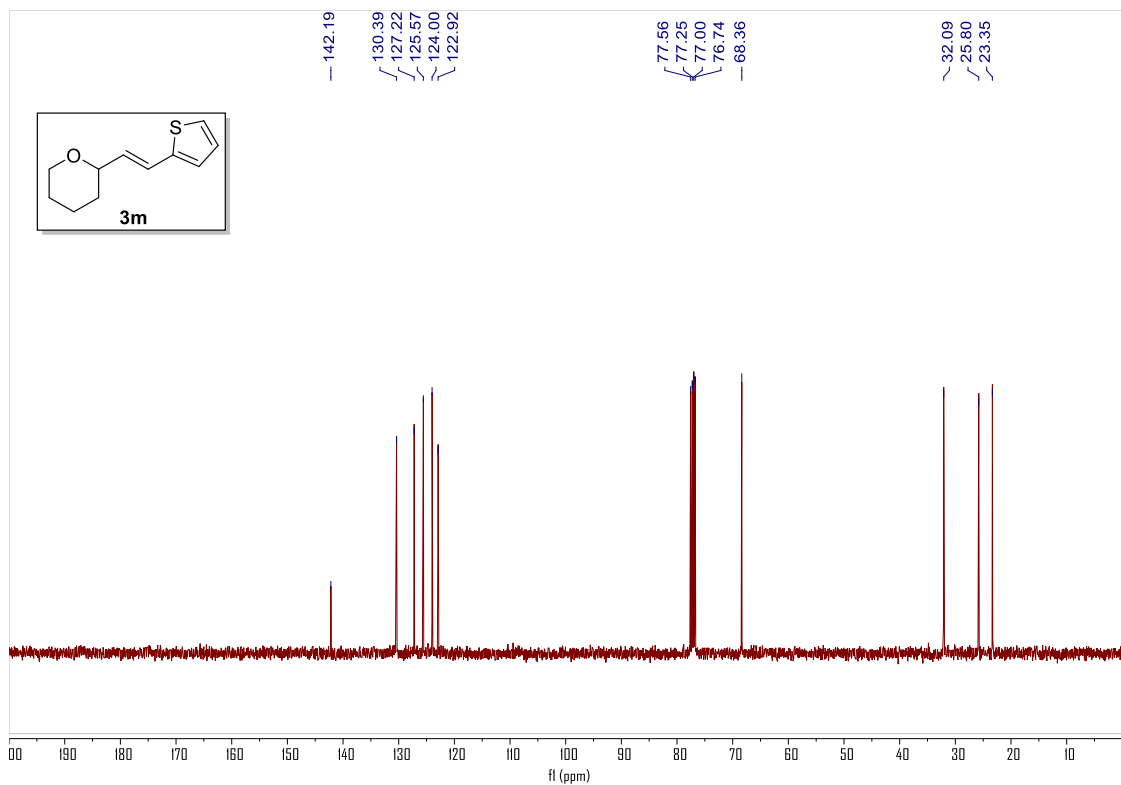


(E)-2-(2-(thiophen-2-yl)vinyl)tetrahydro-2H-pyran (3m)

¹H spectrum (500 MHz, CDCl₃)

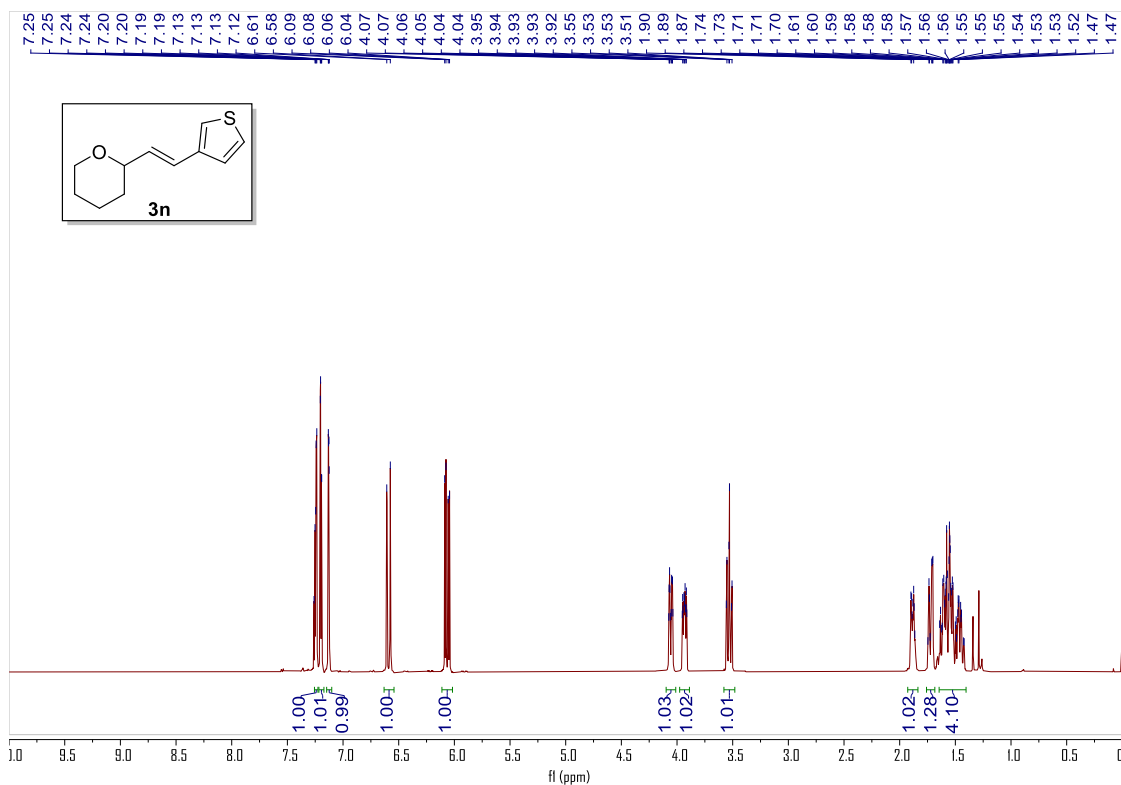


¹³C spectrum (126 MHz, CDCl₃)

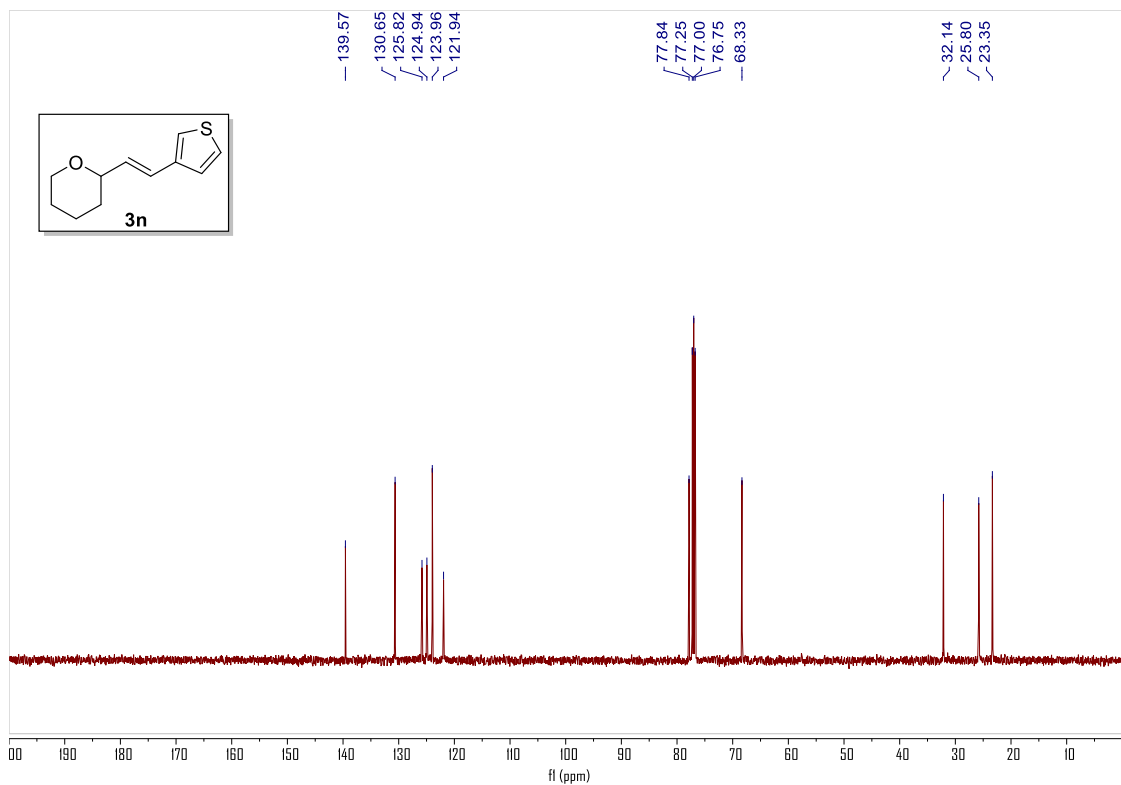


(E)-2-(2-(thiophen-3-yl)vinyl)tetrahydro-2H-pyran (3n)

¹H spectrum (500 MHz, CDCl₃)

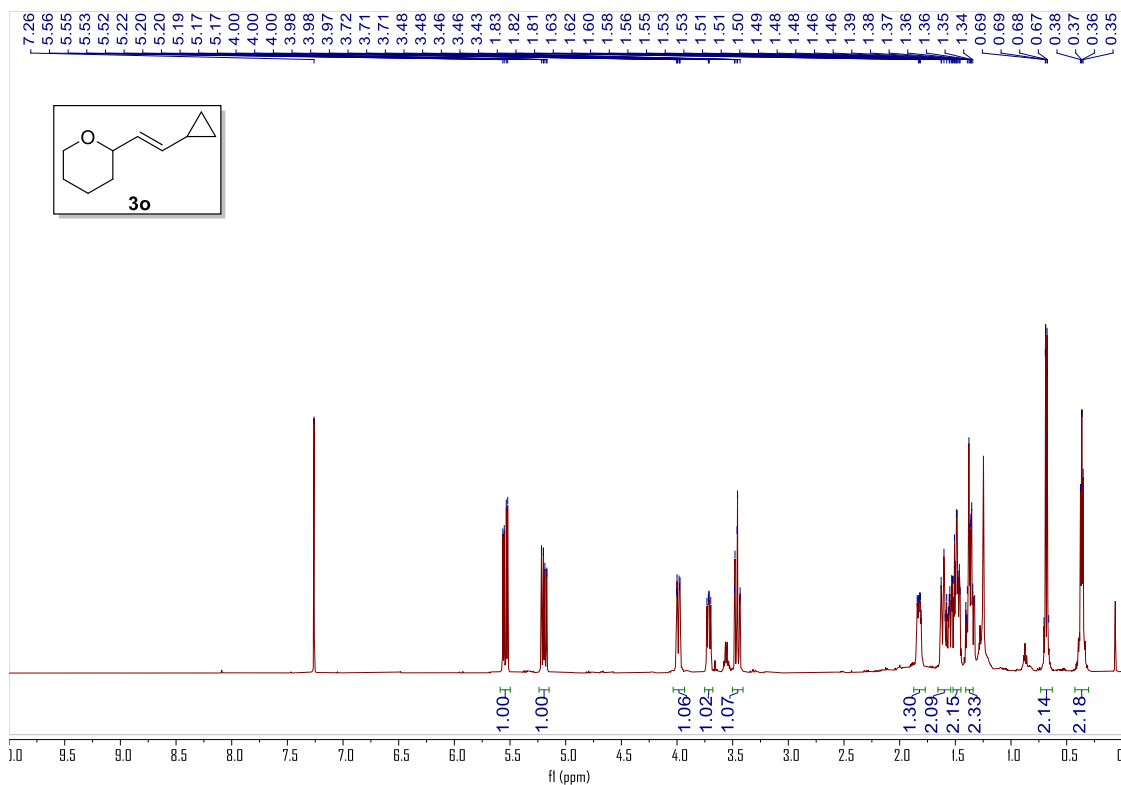


¹³C spectrum (126 MHz, CDCl₃)

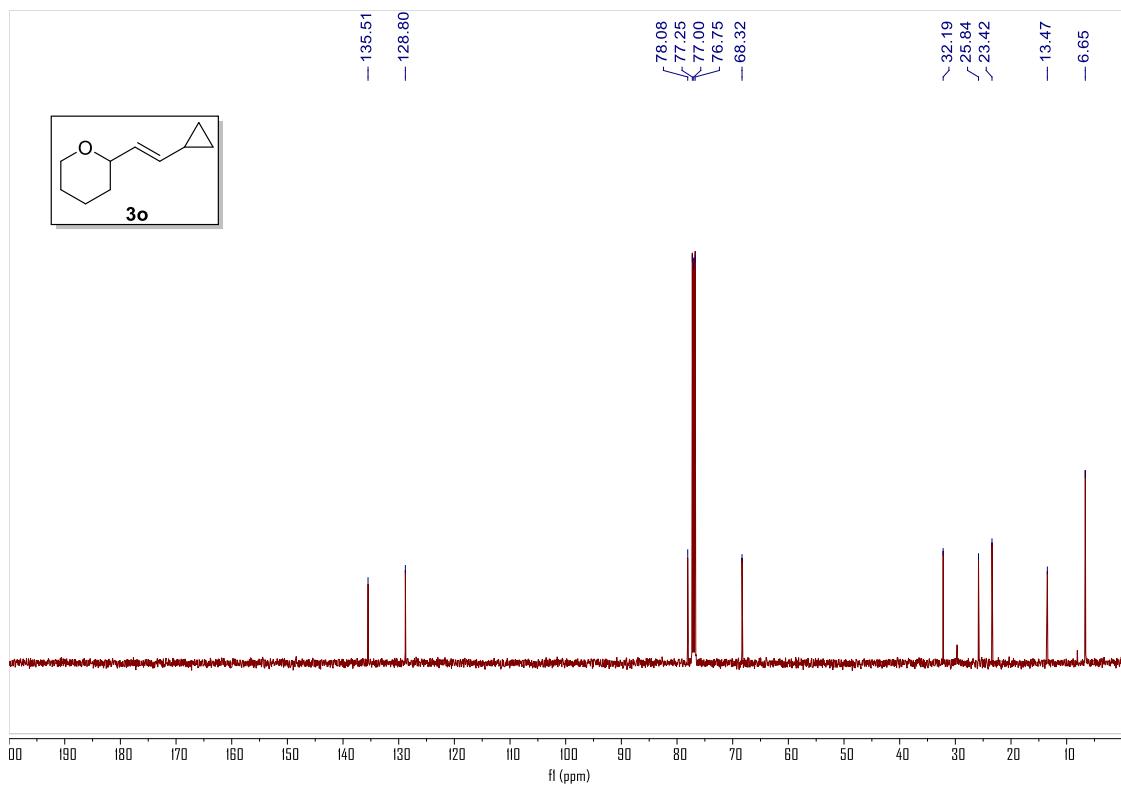


(E)-2-(2-cyclopropylvinyl)tetrahydro-2H-pyran (3o)

¹H spectrum (500 MHz, CDCl₃)

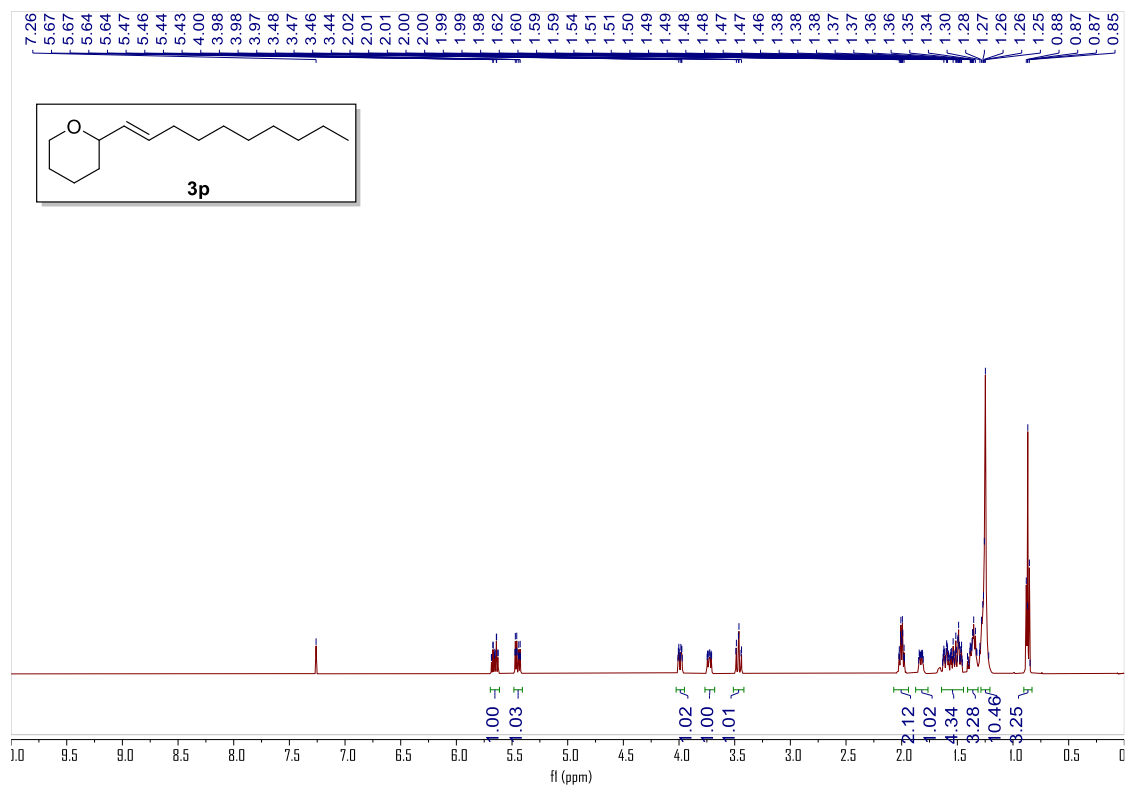


¹³C spectrum (126 MHz, CDCl₃)

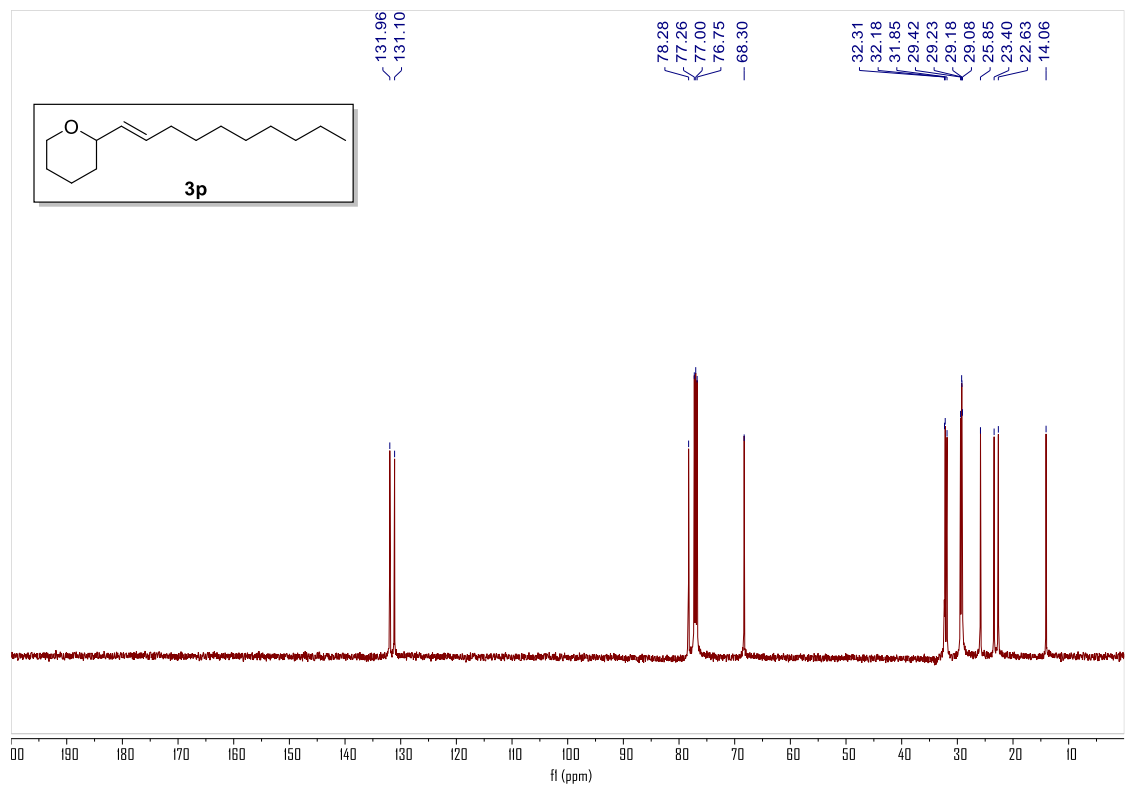


(E)-2-(dec-1-en-1-yl)tetrahydro-2H-pyran (3p)

^1H spectrum (500 MHz, CDCl_3)

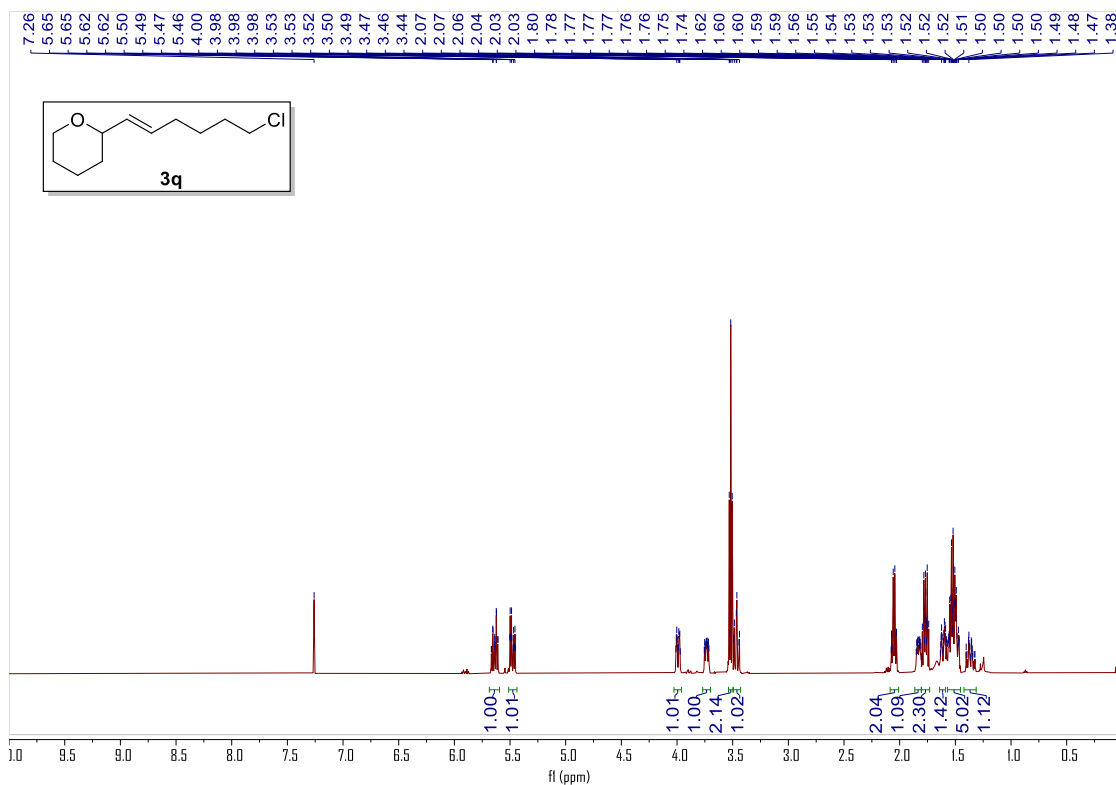


^{13}C spectrum (126 MHz, CDCl_3)

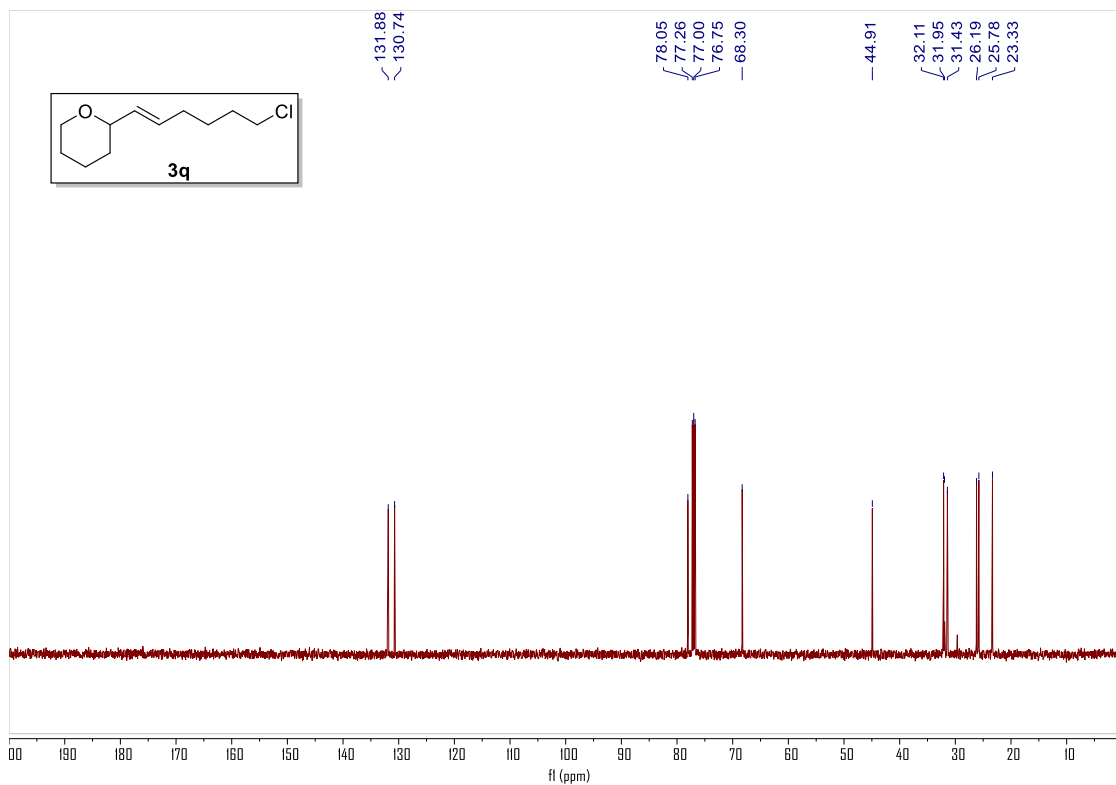


(E)-2-(6-chlorohex-1-en-1-yl)tetrahydro-2H-pyran (3q)

¹H spectrum (500 MHz, CDCl₃)

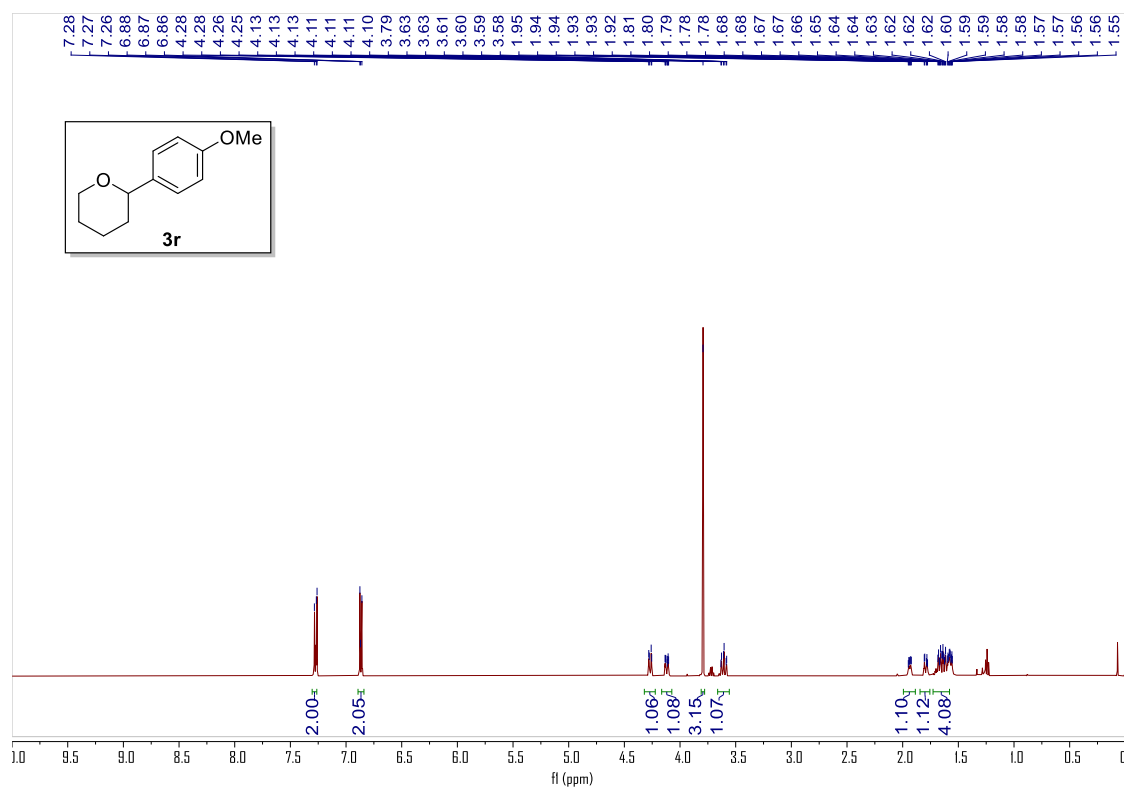


¹³C spectrum (126 MHz, CDCl₃)

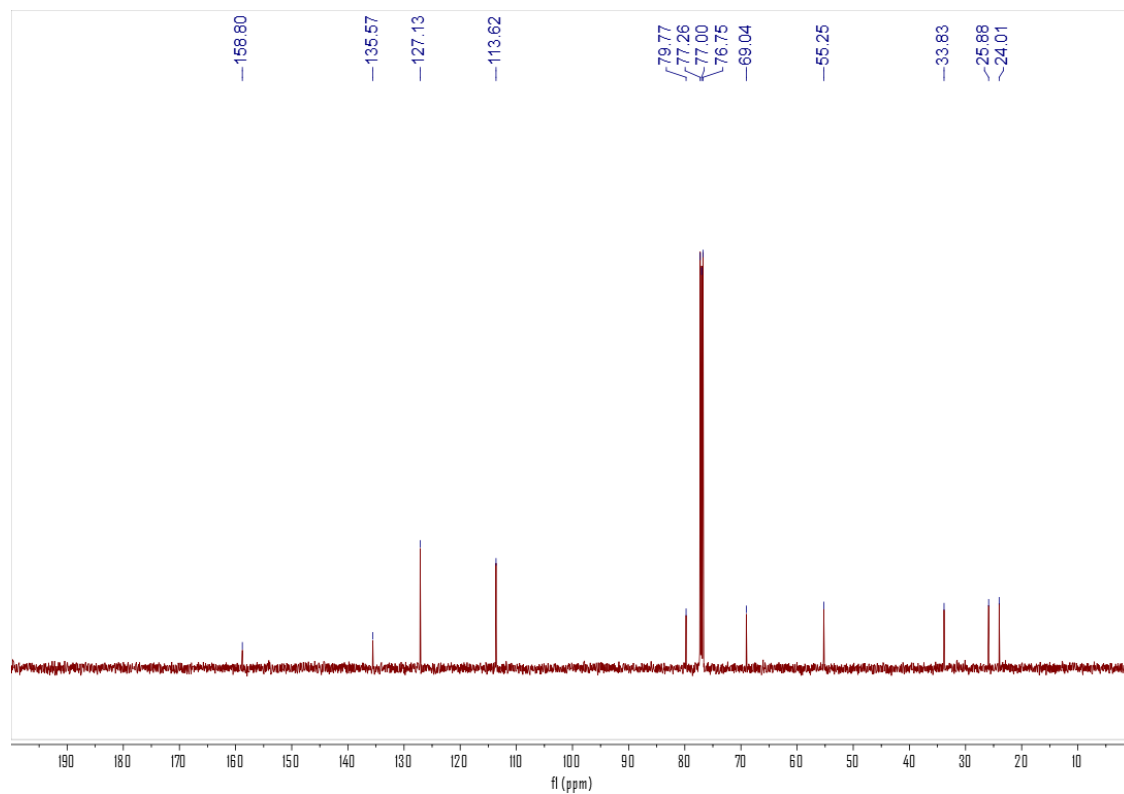


2-(4-methoxyphenyl)tetrahydro-2H-pyran (3r)

^1H spectrum (500 MHz, CDCl_3)

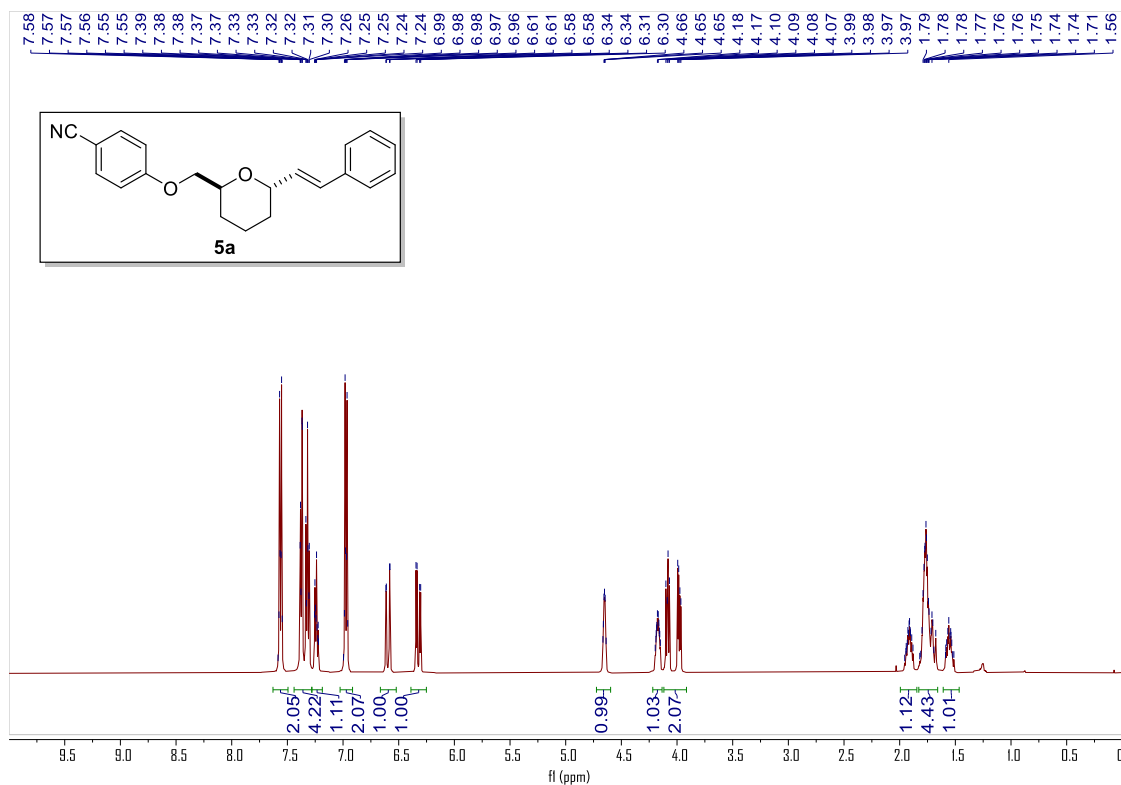


^{13}C spectrum (126 MHz, CDCl_3)

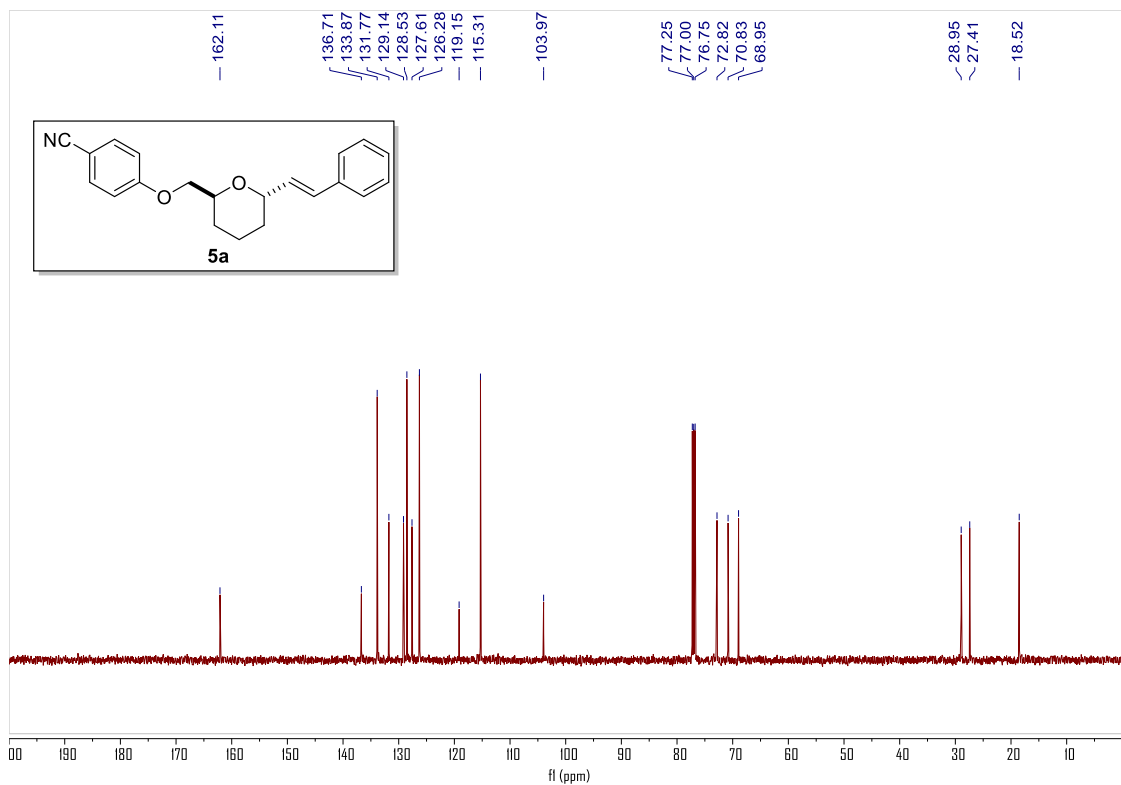


(E)-4-((6-styryltetrahydro-2H-pyran-2-yl)methoxy)benzonitrile (5a)

¹H spectrum (500 MHz, CDCl₃)

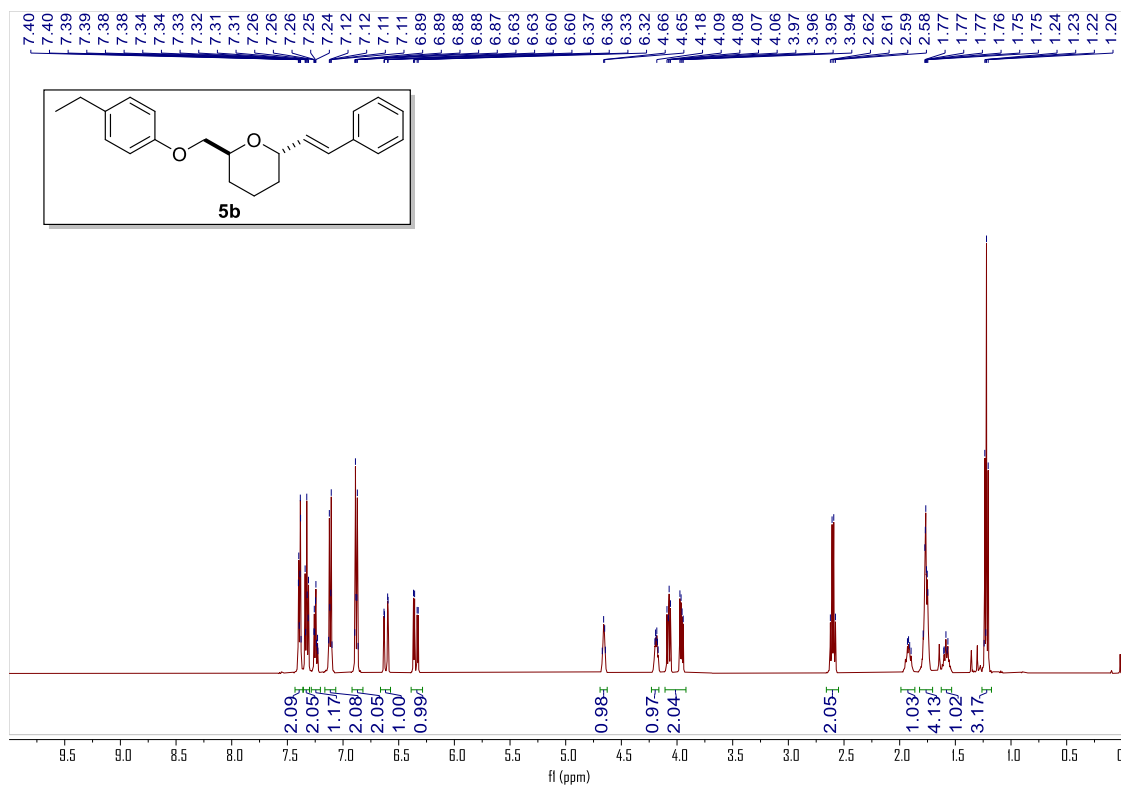


¹³C spectrum (126 MHz, CDCl₃)

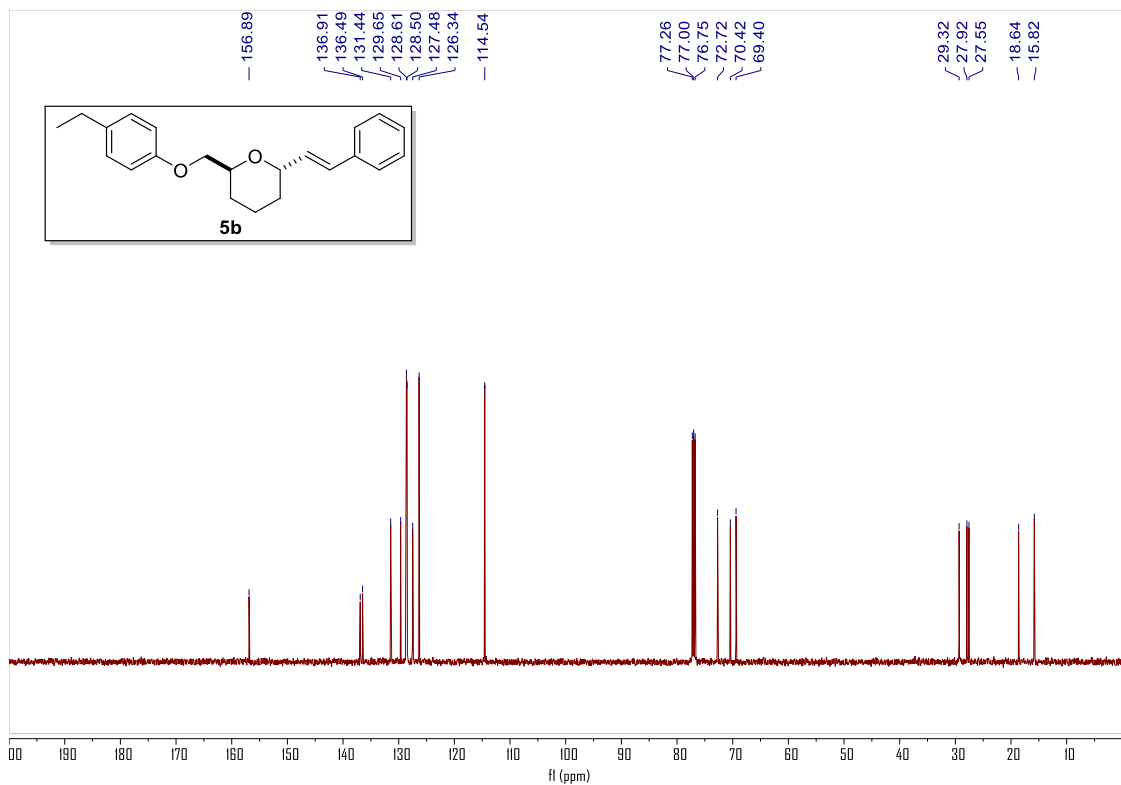


(E)-2-((4-ethylphenoxy)methyl)-6-styryltetrahydro-2H-pyran (**5b**)

^1H spectrum (500 MHz, CDCl_3)

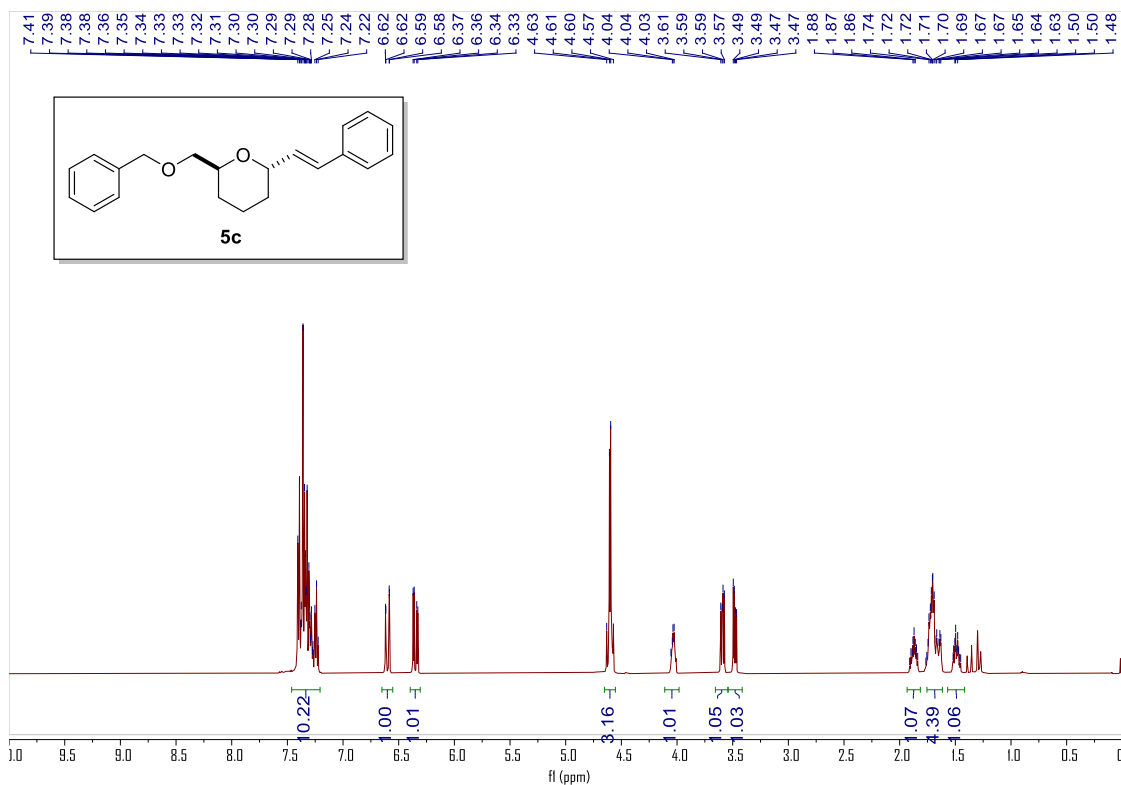


^{13}C spectrum (126 MHz, CDCl_3)

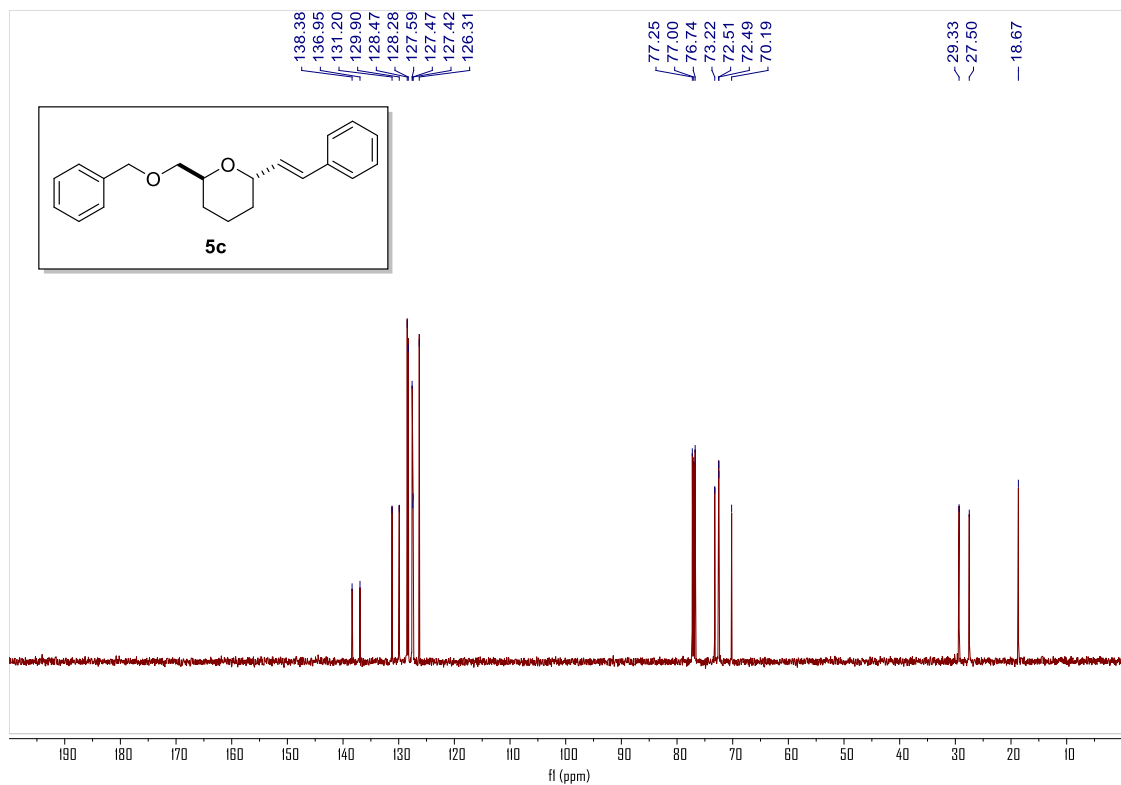


(E)-2-((benzyloxy)methyl)-6-styryltetrahydro-2H-pyran (**5c**)

^1H spectrum (500 MHz, CDCl_3)

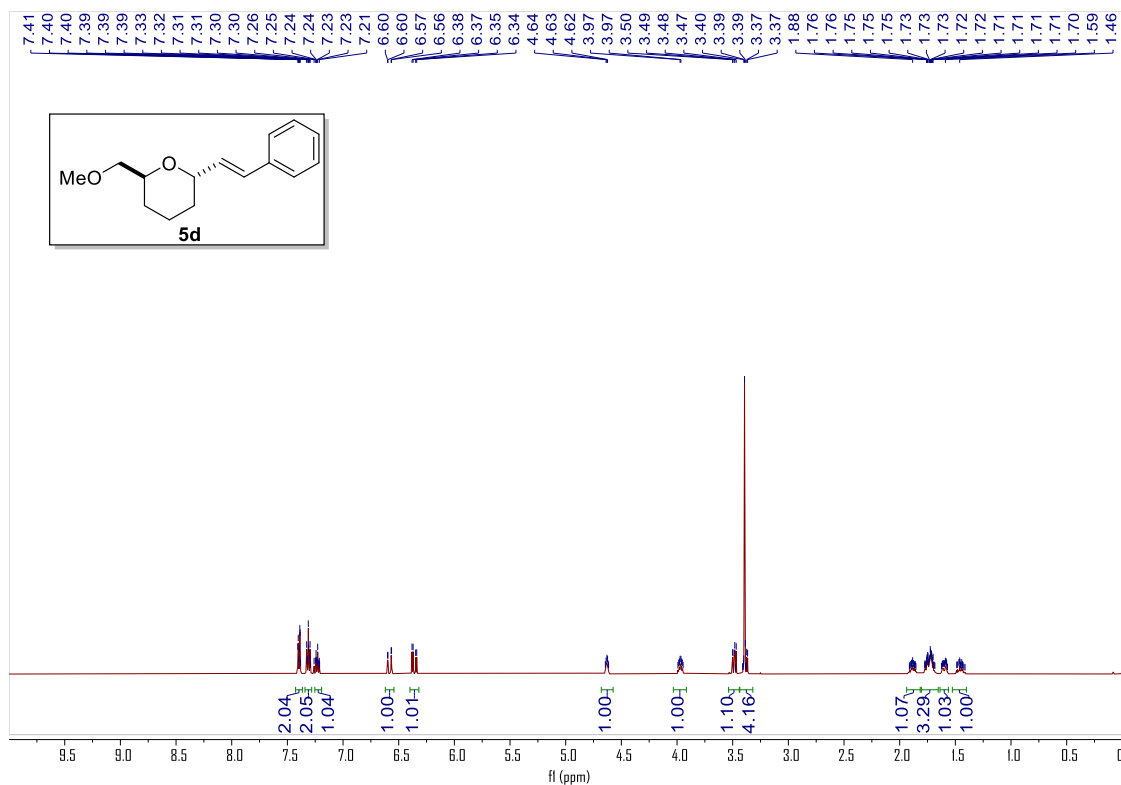


^{13}C spectrum (126 MHz, CDCl_3)

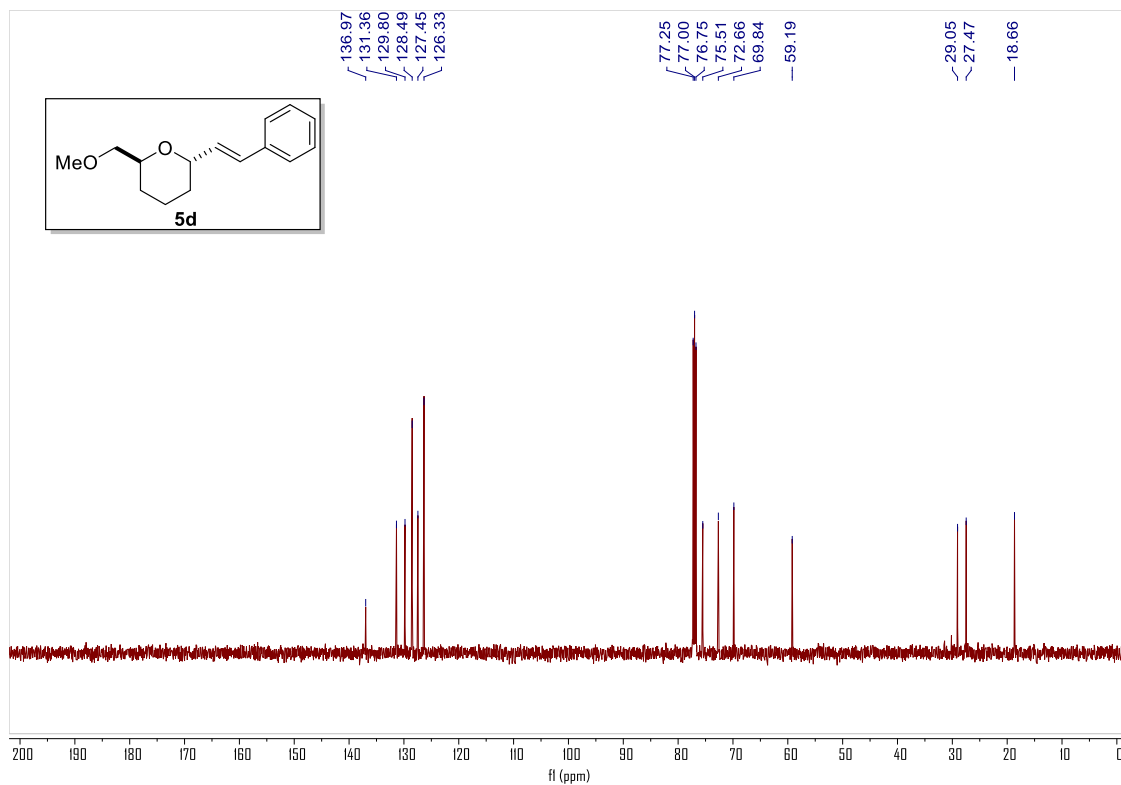


(E)-2-(methoxymethyl)-6-styryltetrahydro-2H-pyran (5d)

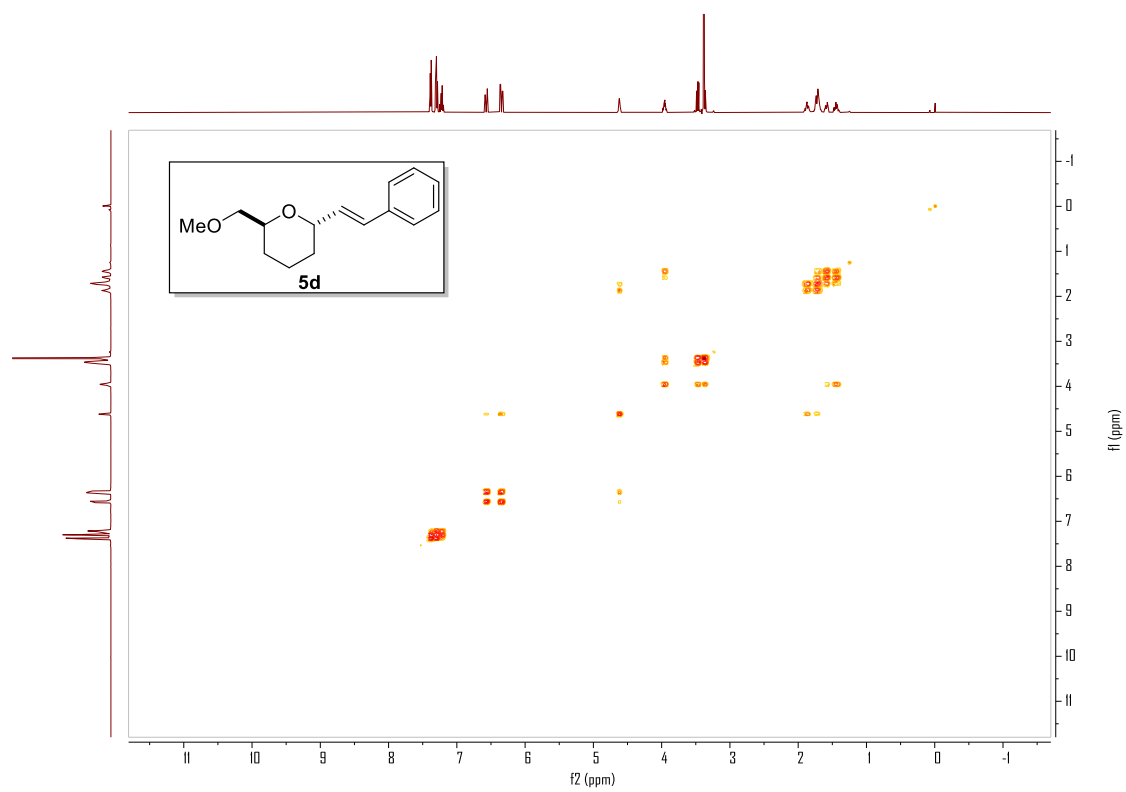
^1H spectrum (500 MHz, CDCl_3)



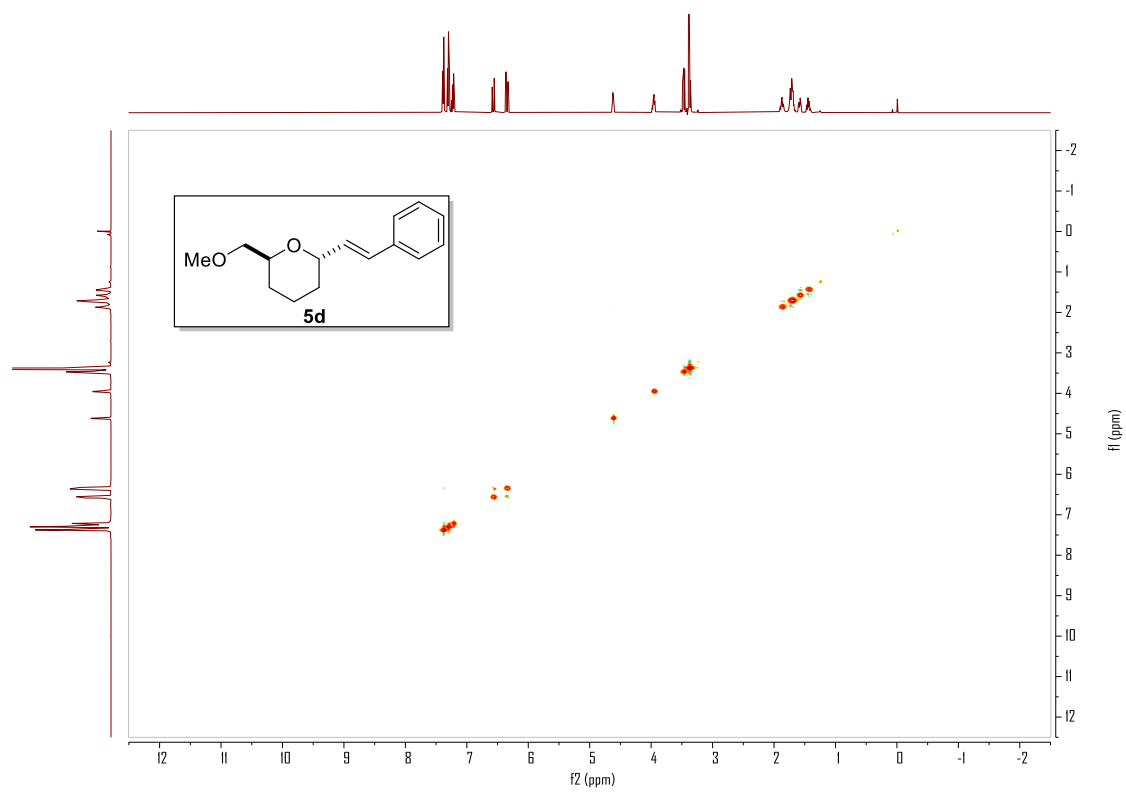
^{13}C spectrum (126 MHz, CDCl_3)



$^1\text{H } ^1\text{H COSY NMR}$

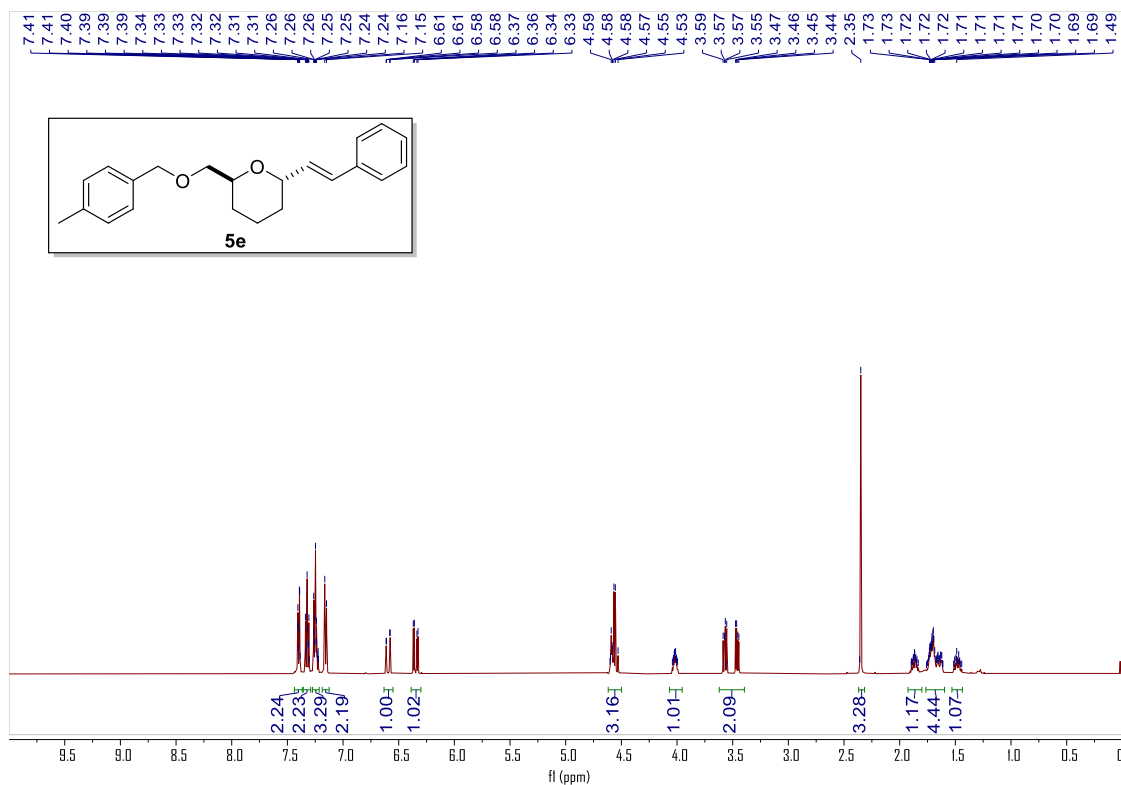


$^1\text{H } ^1\text{H NOESY NMR}$

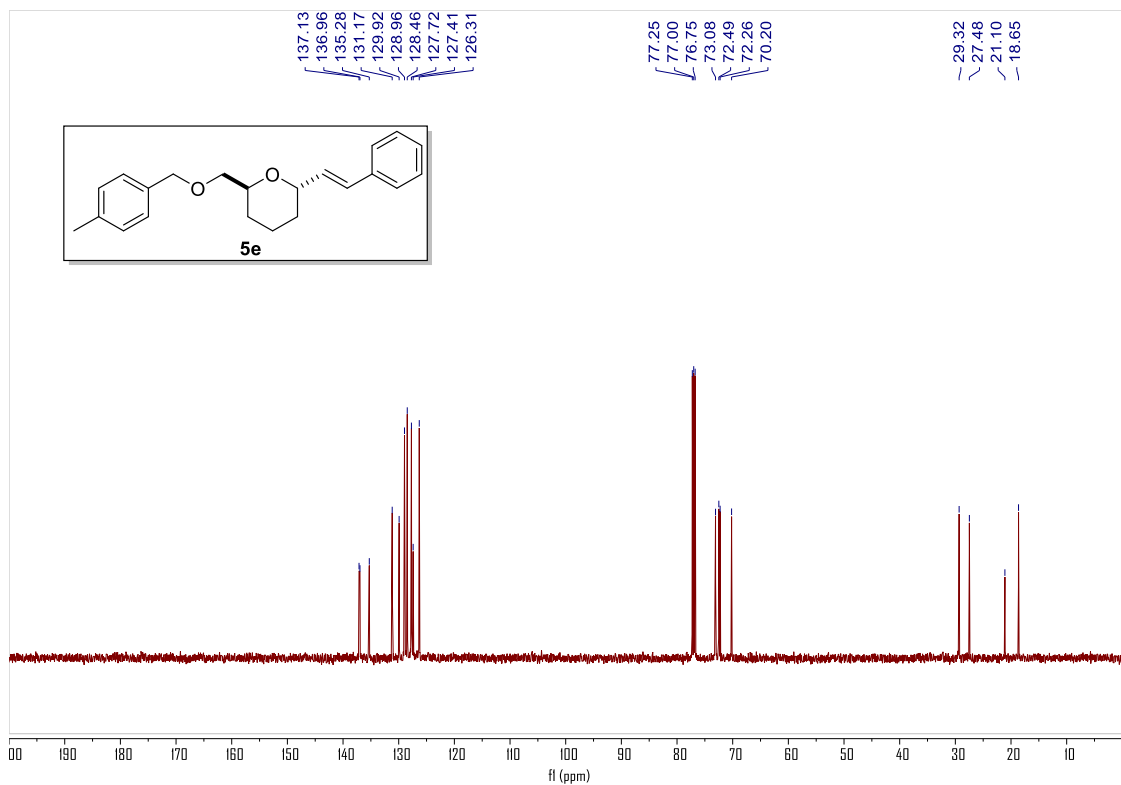


(E)-2-(((4-methylbenzyl)oxy)methyl)-6-styryltetrahydro-2H-pyran (**5e**)

^1H spectrum (500 MHz, CDCl_3)

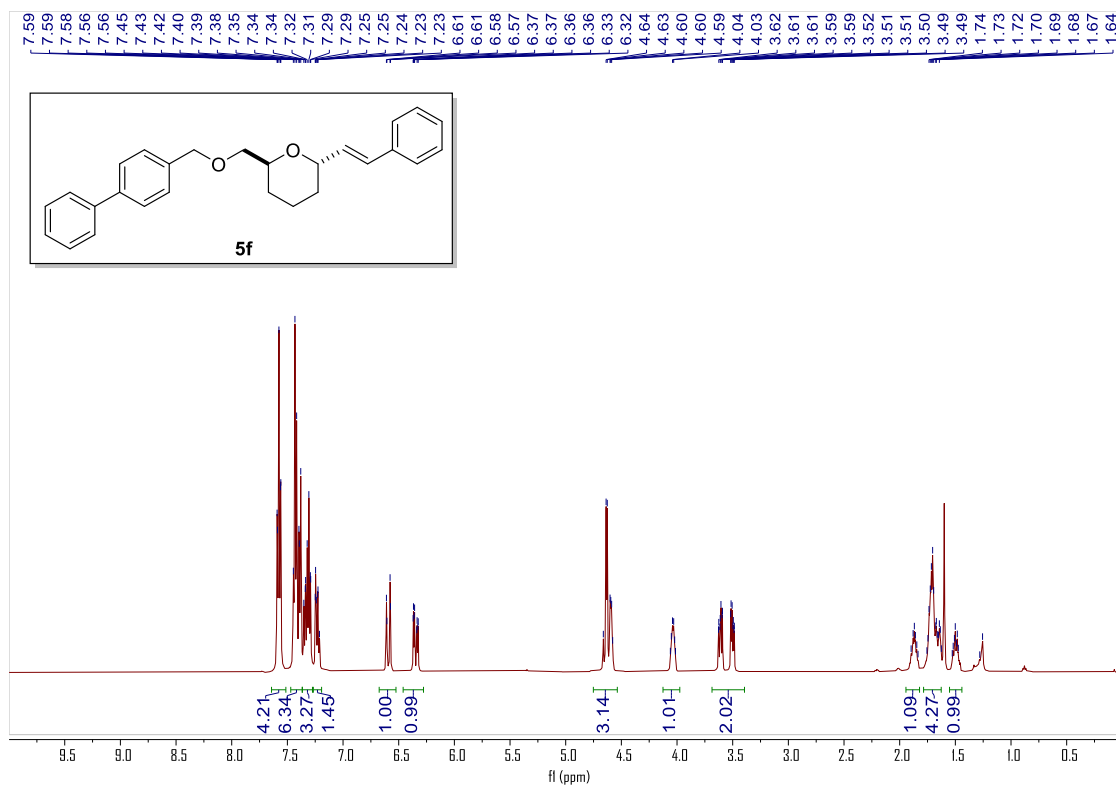


^{13}C spectrum (126 MHz, CDCl_3)

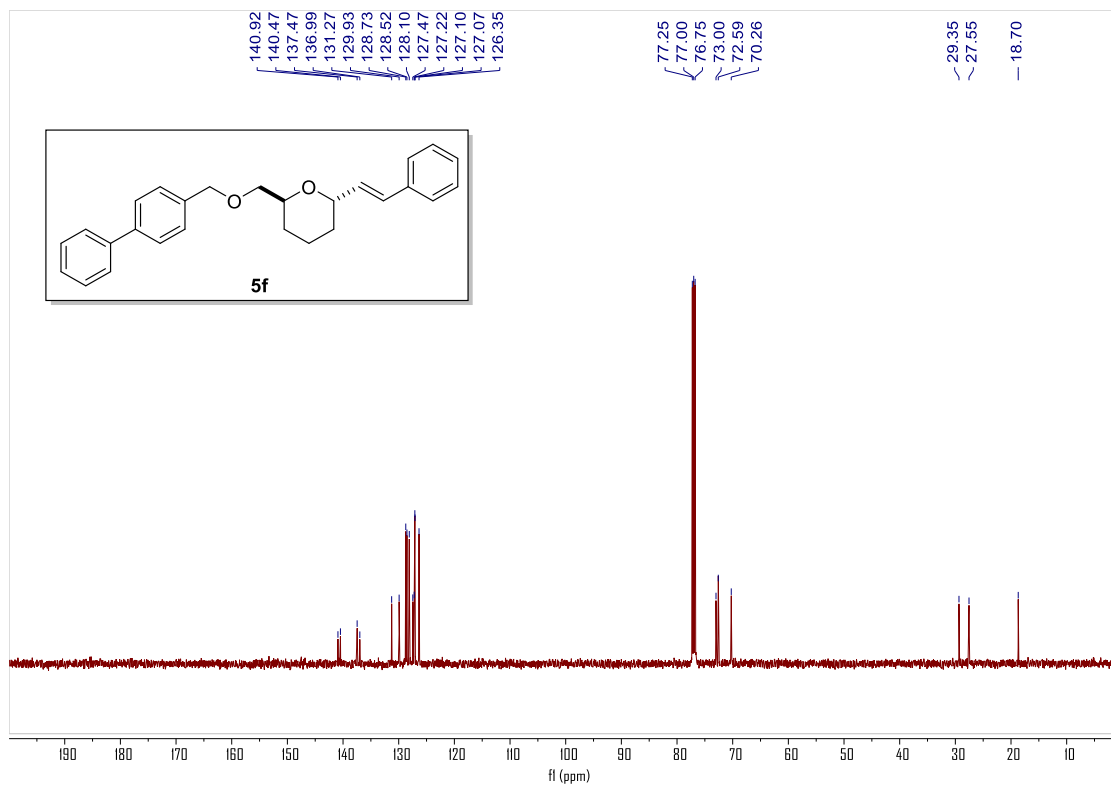


(E)-2-(((1,1'-biphenyl]-4-ylmethoxy)methyl)-6-styryltetrahydro-2H-pyran (5f)

^1H spectrum (500 MHz, CDCl_3)

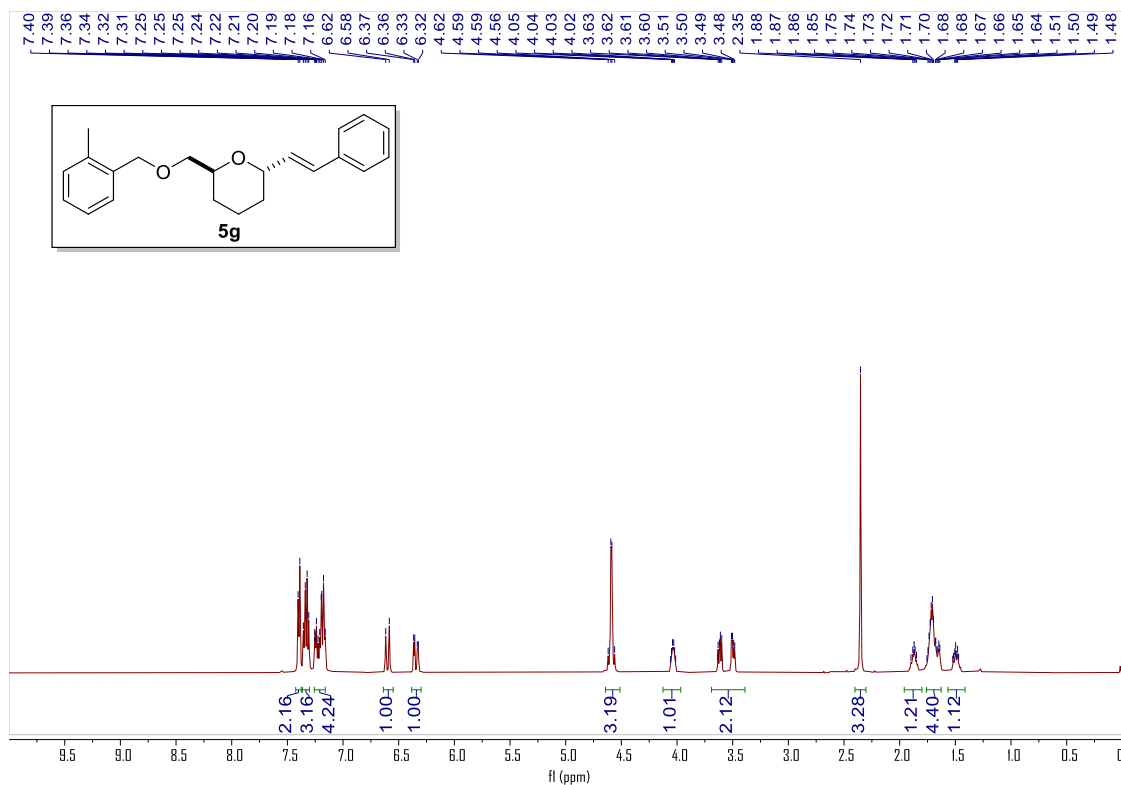


^{13}C spectrum (126 MHz, CDCl_3)

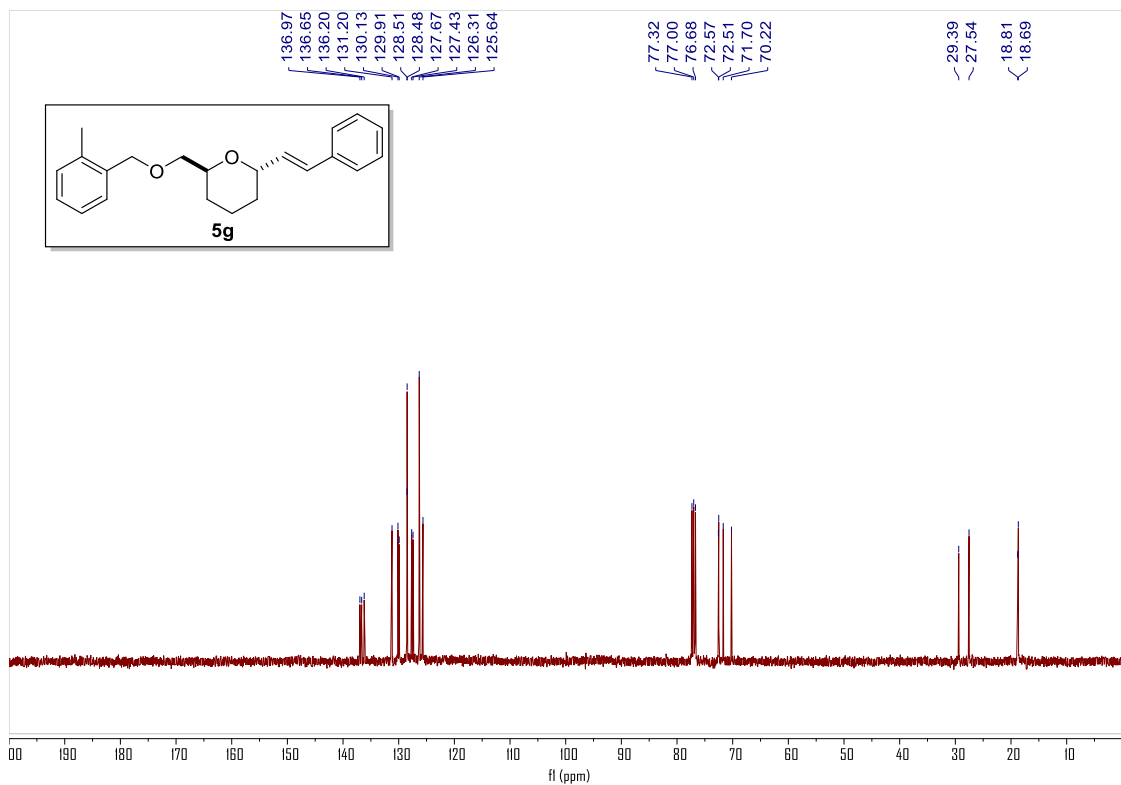


(E)-2-(((2-methylbenzyl)oxy)methyl)-6-styryltetrahydro-2H-pyran (**5g**)

^1H spectrum (500 MHz, CDCl_3)

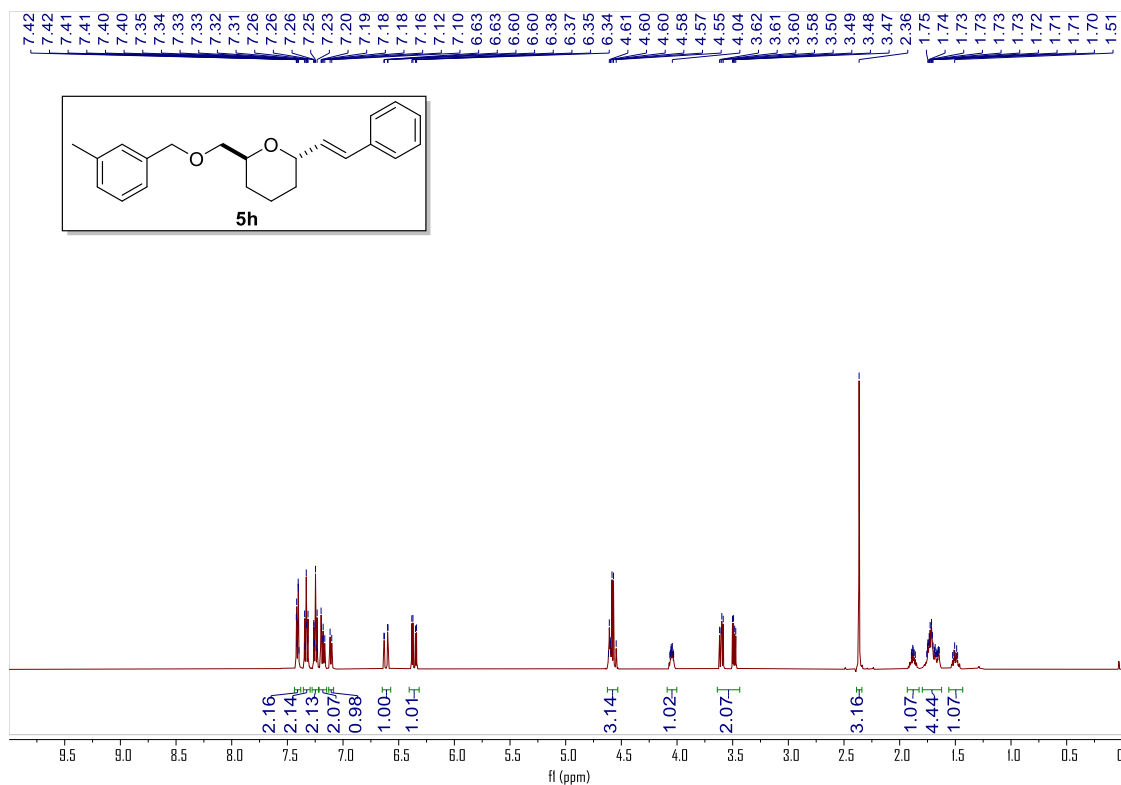


^{13}C spectrum (126 MHz, CDCl_3)

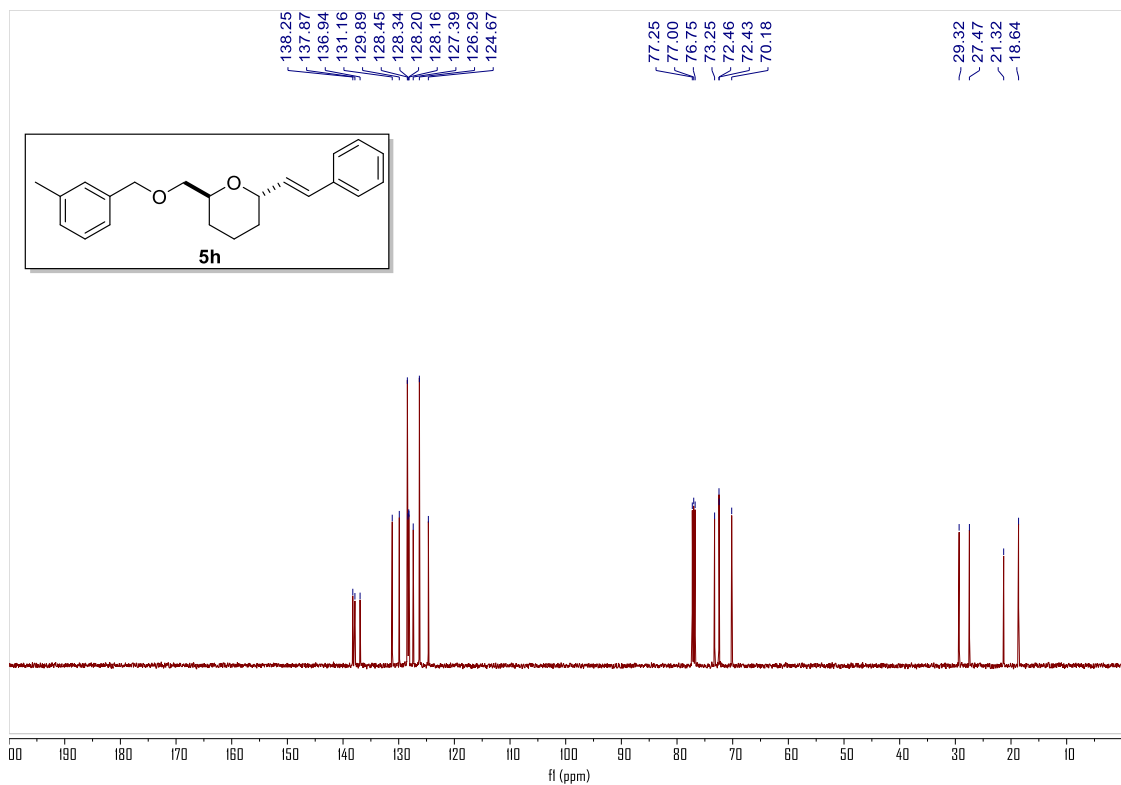


(E)-2-(((3-methylbenzyl)oxy)methyl)-6-styryltetrahydro-2H-pyran (**5h**)

^1H spectrum (500 MHz, CDCl_3)

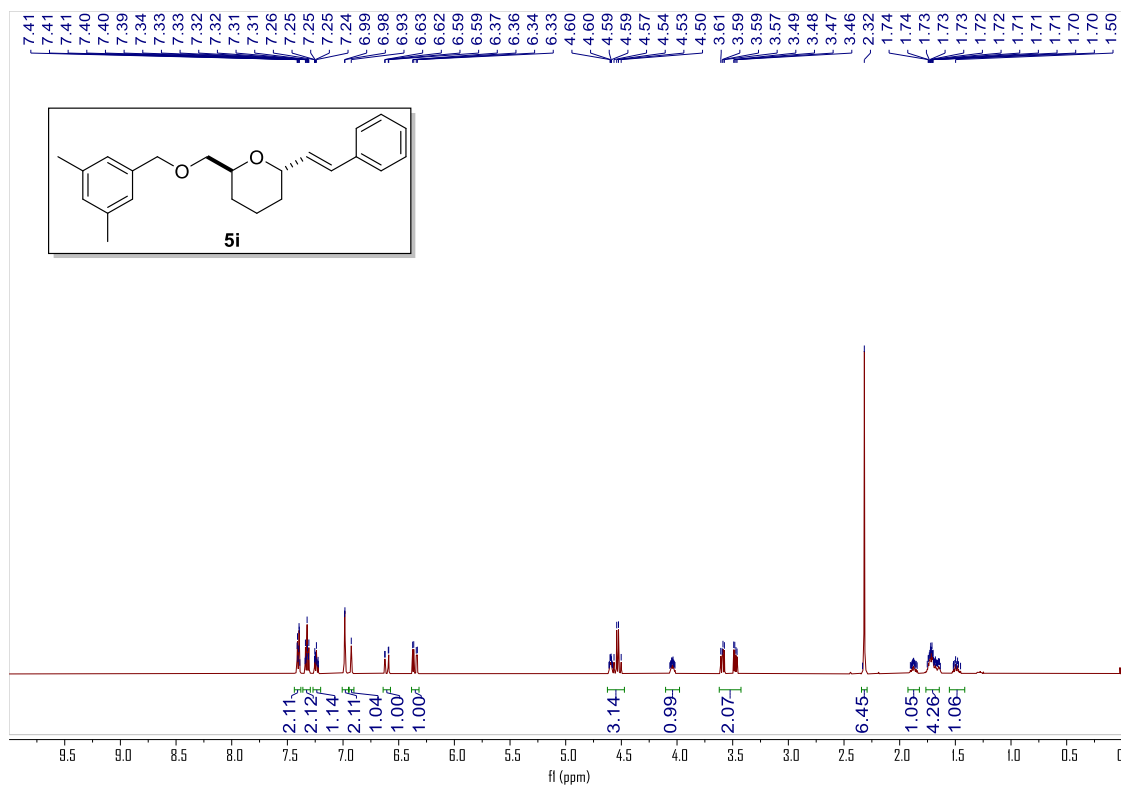


^{13}C spectrum (126 MHz, CDCl_3)

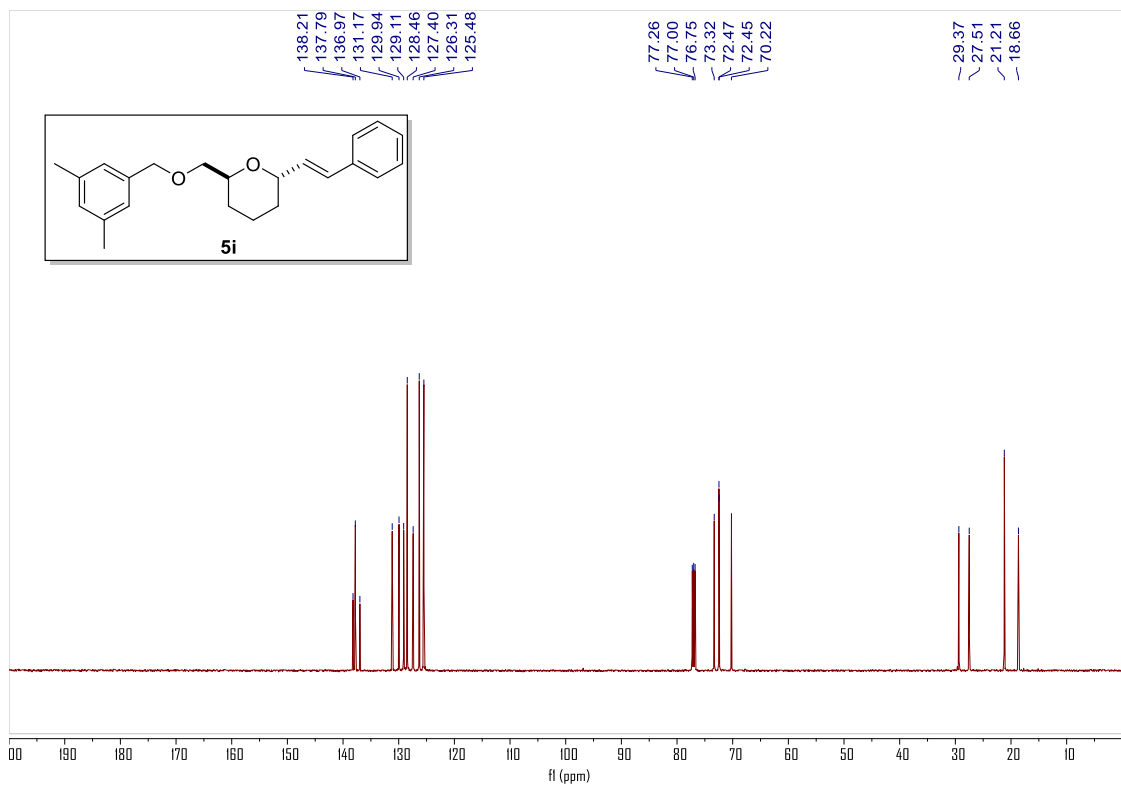


(E)-2-(((3,5-dimethylbenzyl)oxy)methyl)-6-styryltetrahydro-2H-pyran (5i)

¹H spectrum (500 MHz, CDCl₃)

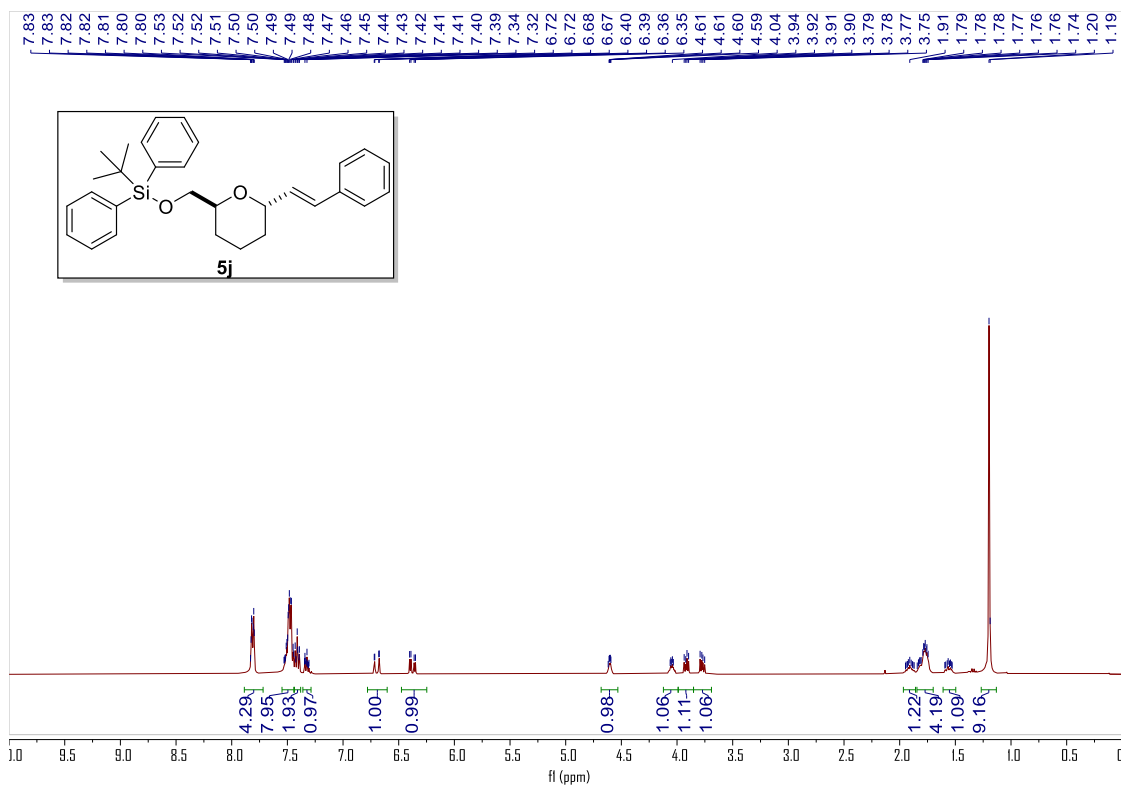


¹³C spectrum (126 MHz, CDCl₃)

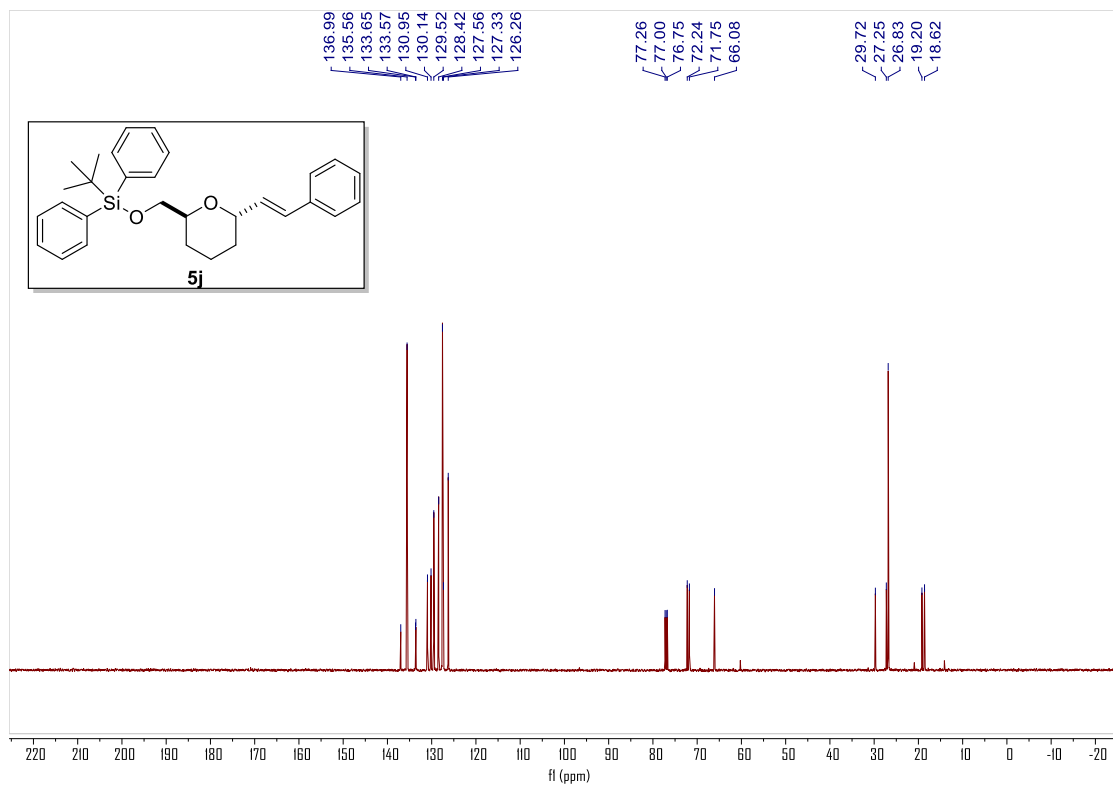


(E)-tert-butyl diphenyl((6-styryltetrahydro-2H-pyran-2-yl)methoxy)silane (5j)

¹H spectrum (500 MHz, CDCl₃)

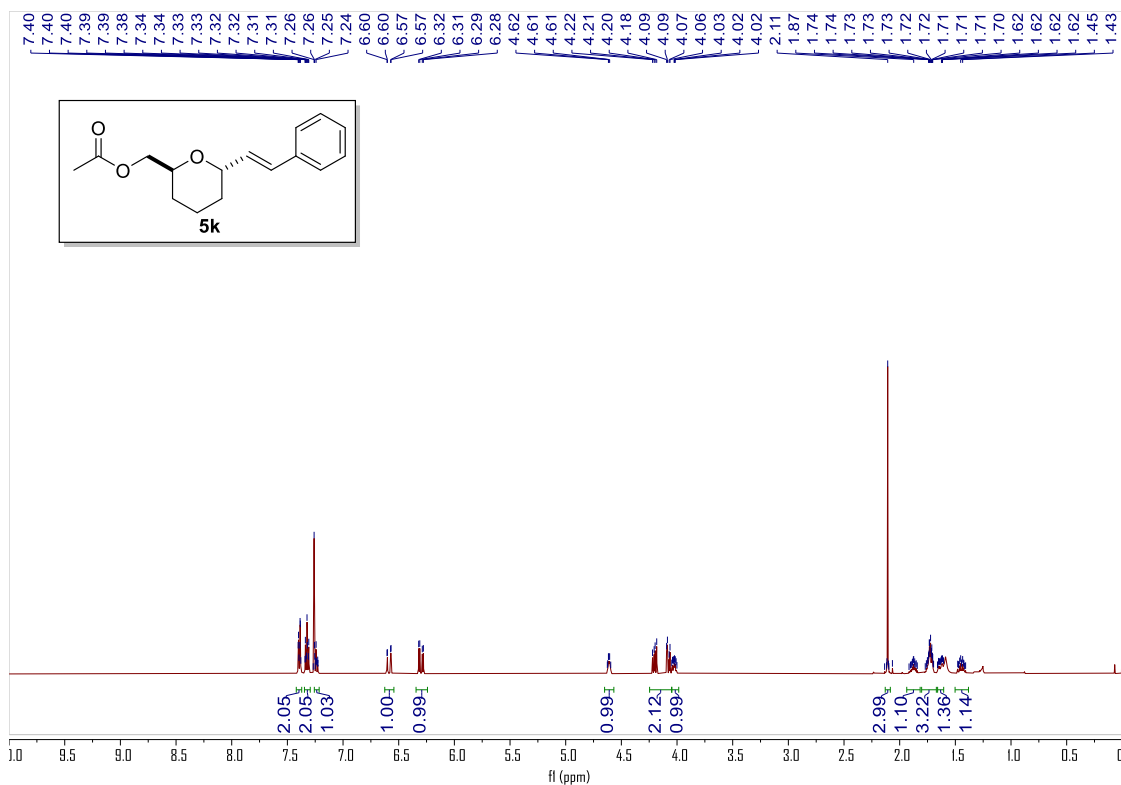


¹³C spectrum (126 MHz, CDCl₃)

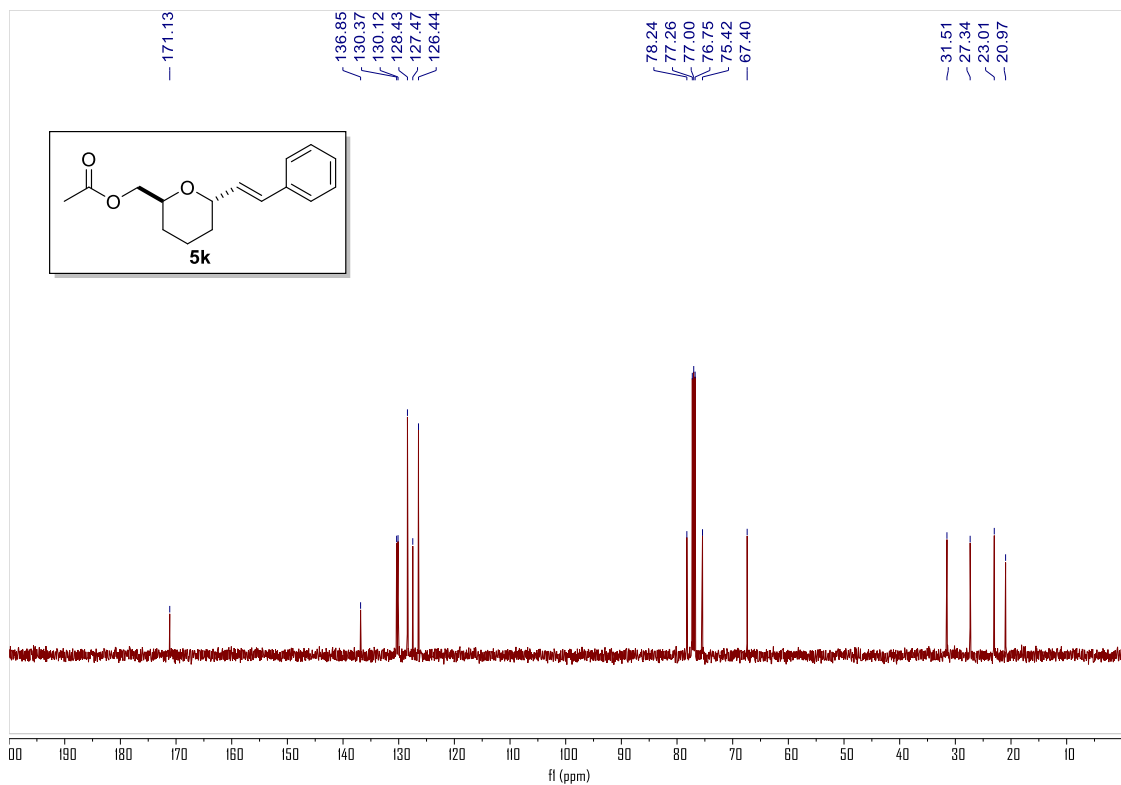


(E)-(6-styryltetrahydro-2H-pyran-2-yl)methyl acetate (5k)

¹H spectrum (500 MHz, CDCl₃)

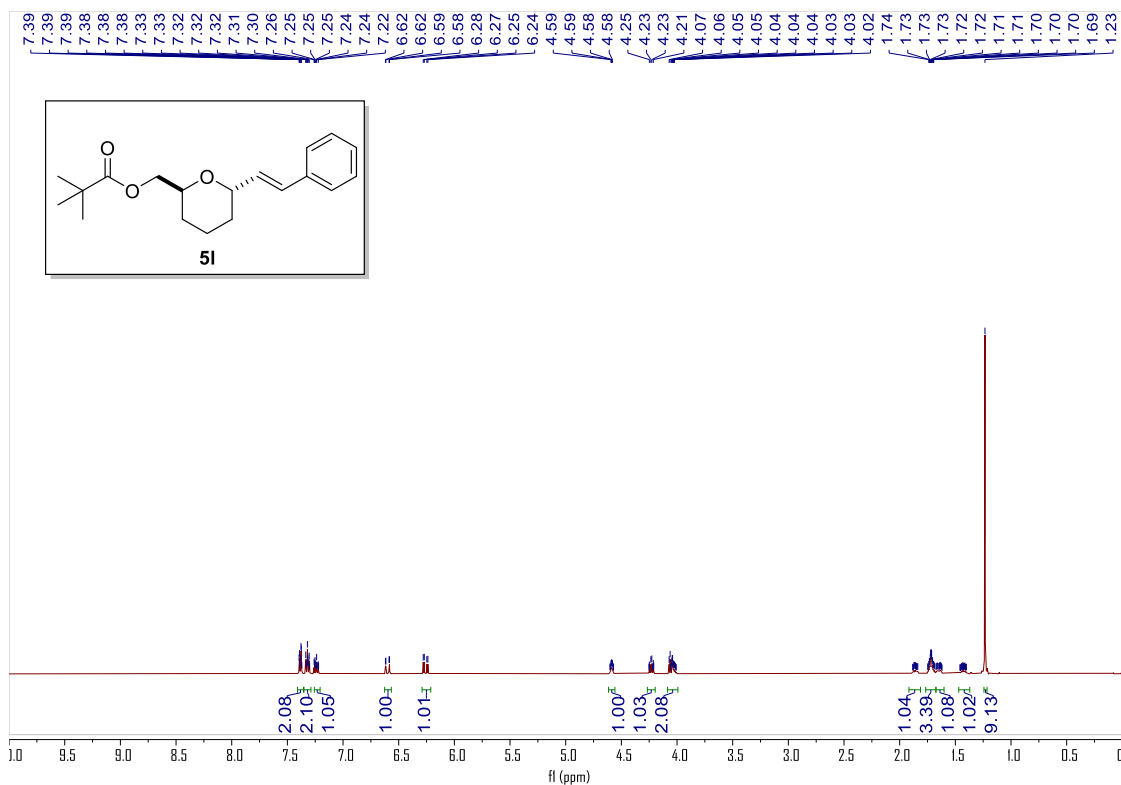


¹³C spectrum (126 MHz, CDCl₃)

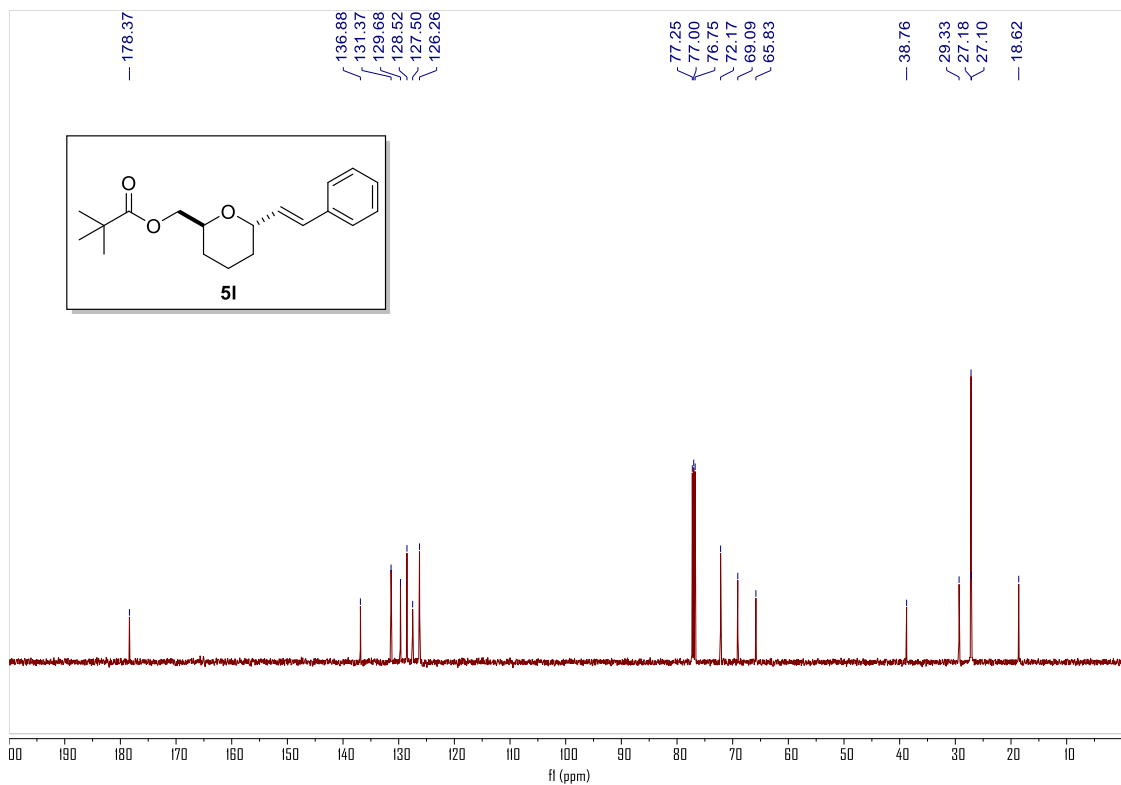


(E)-(6-styryltetrahydro-2H-pyran-2-yl)methyl pivalate (5I)

¹H spectrum (500 MHz, CDCl₃)

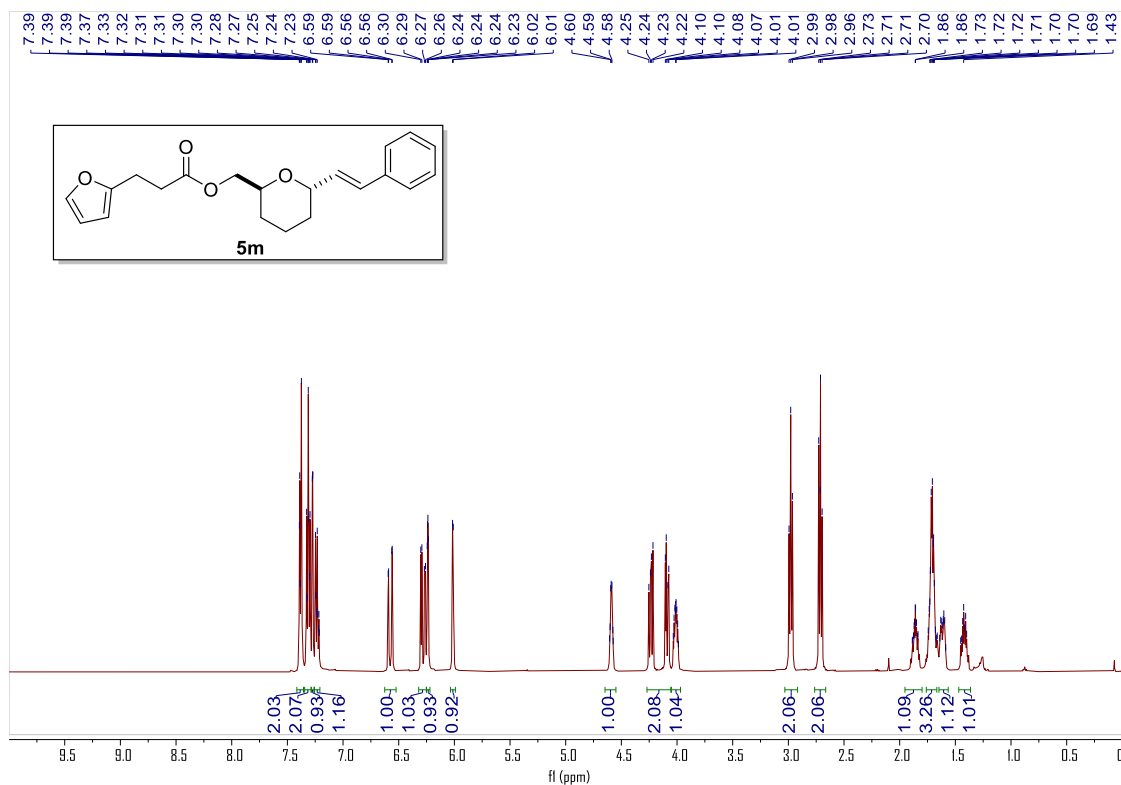


¹³C spectrum (126 MHz, CDCl₃)

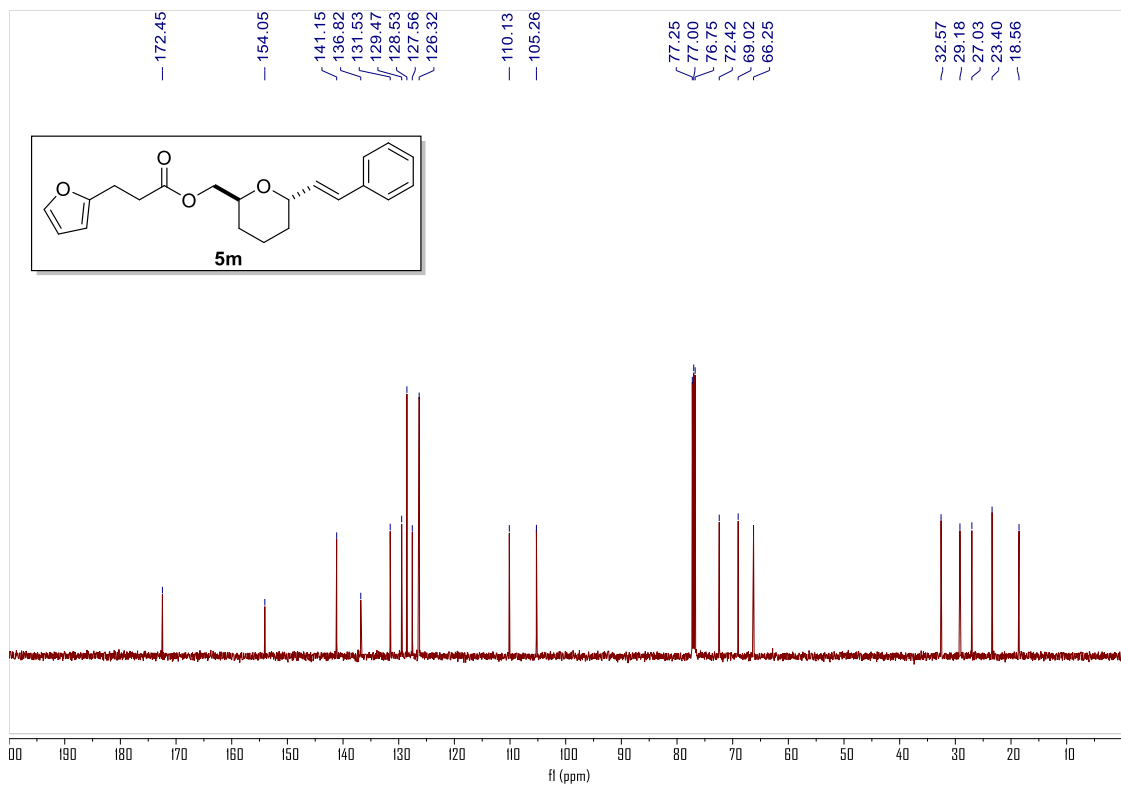


(E)-(6-styryltetrahydro-2H-pyran-2-yl)methyl 3-(furan-2-yl)propanoate (5m)

¹H spectrum (500 MHz, CDCl₃)

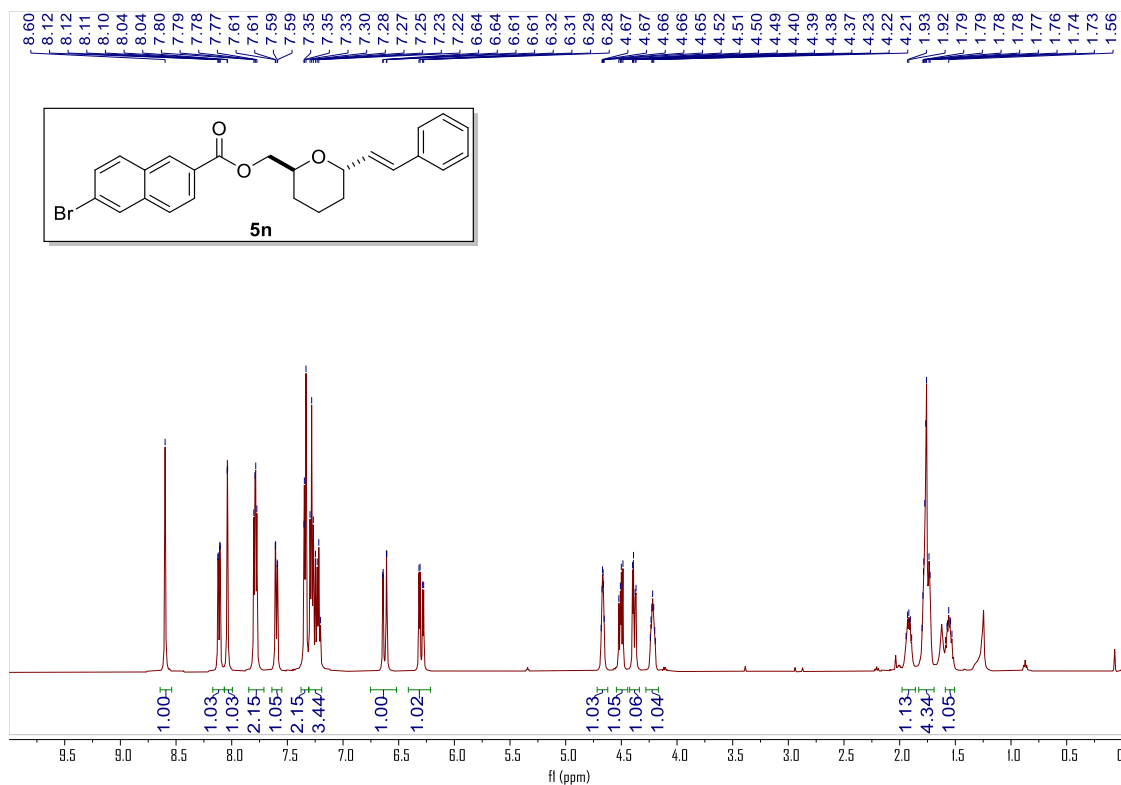


¹³C spectrum (126 MHz, CDCl₃)

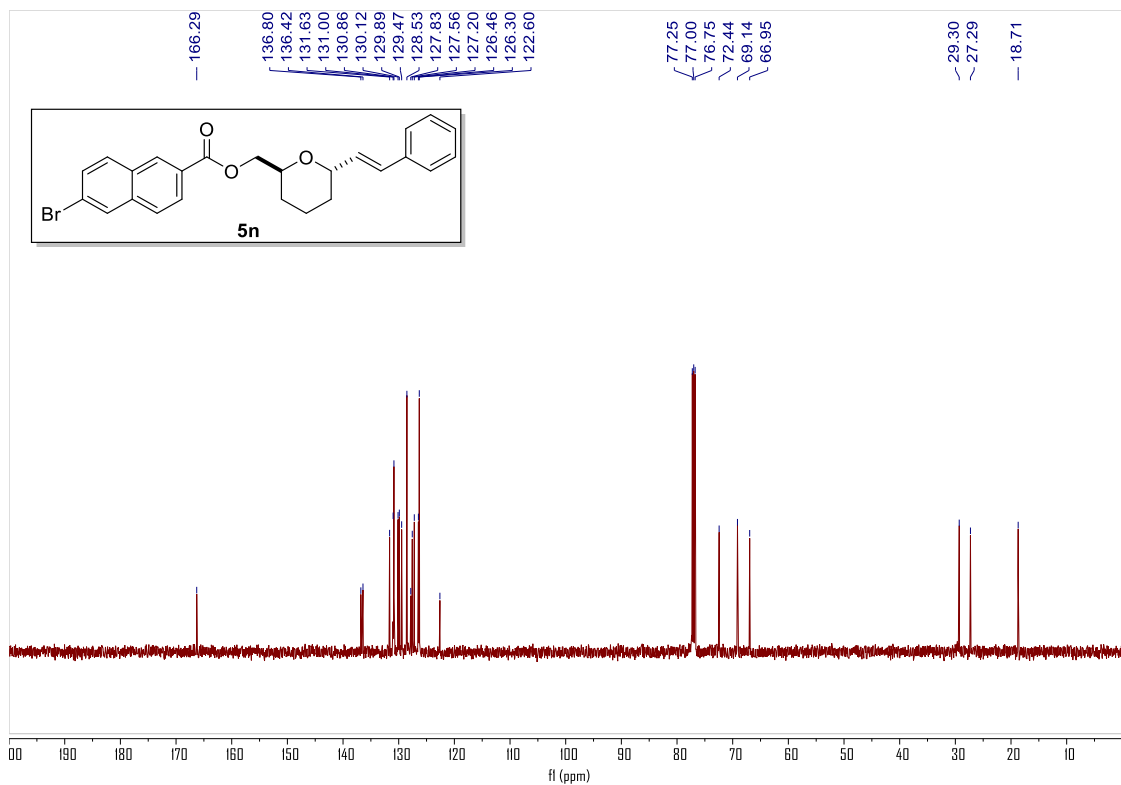


(E)-(6-styryltetrahydro-2H-pyran-2-yl)methyl 6-bromo-2-naphthoate (5n)

^1H spectrum (500 MHz, CDCl_3)

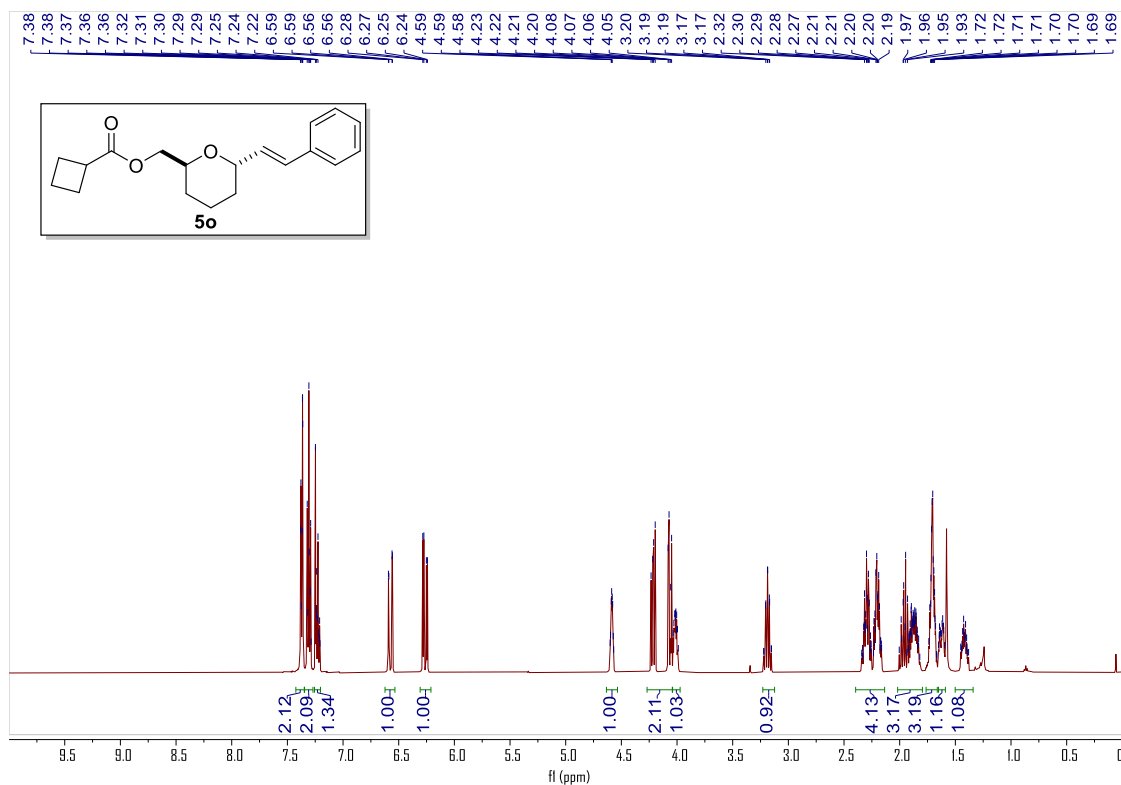


^{13}C spectrum (126 MHz, CDCl_3)

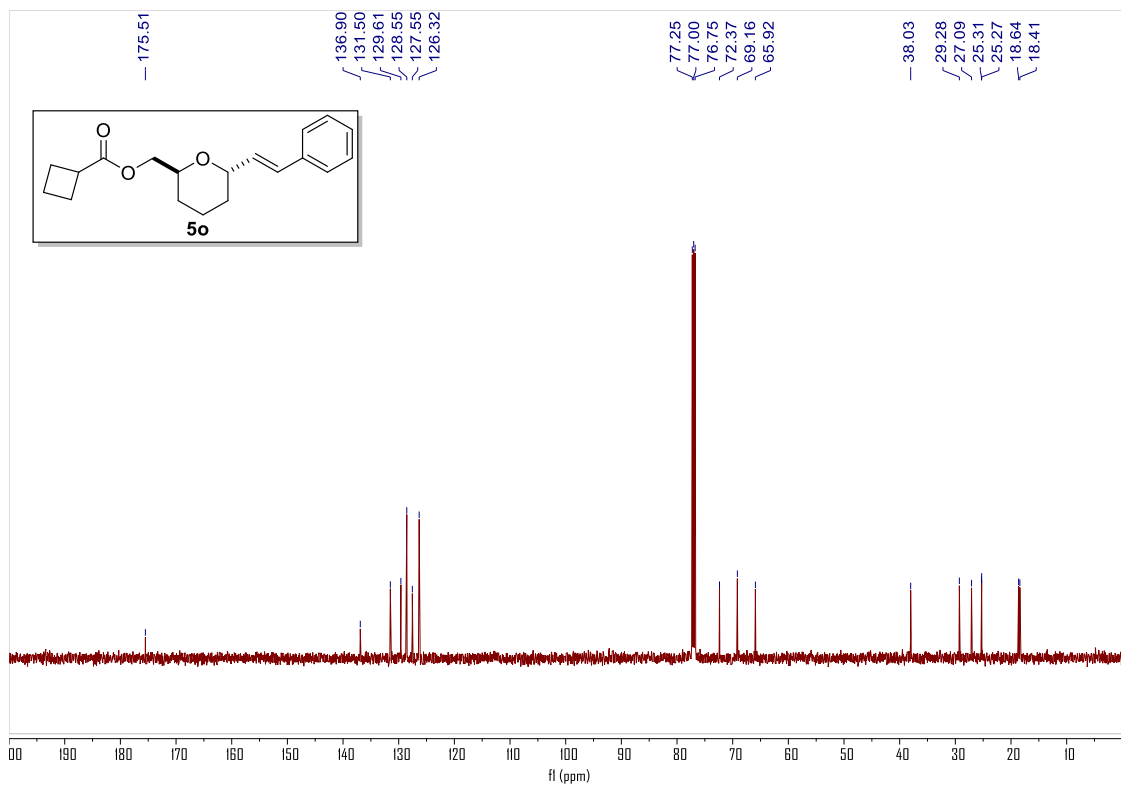


(E)-(6-styryltetrahydro-2H-pyran-2-yl)methyl cyclobutanecarboxylate (**5o**)

^1H spectrum (500 MHz, CDCl_3)

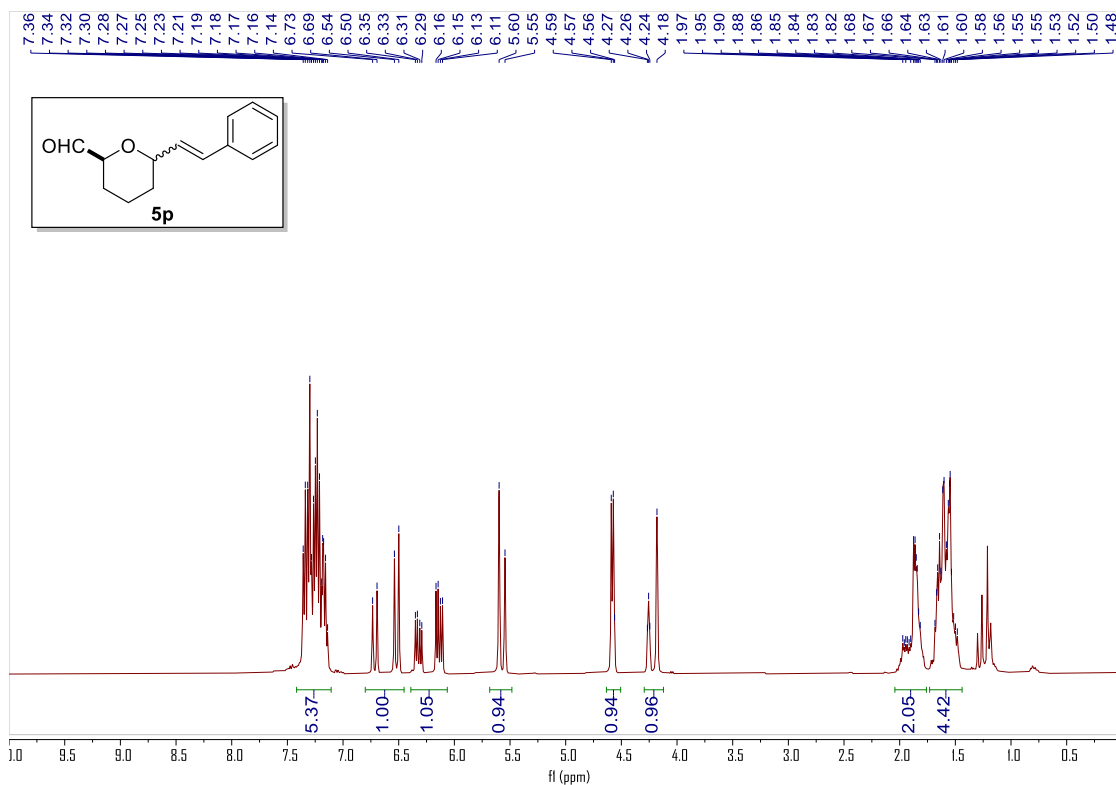


^{13}C spectrum (126 MHz, CDCl_3)

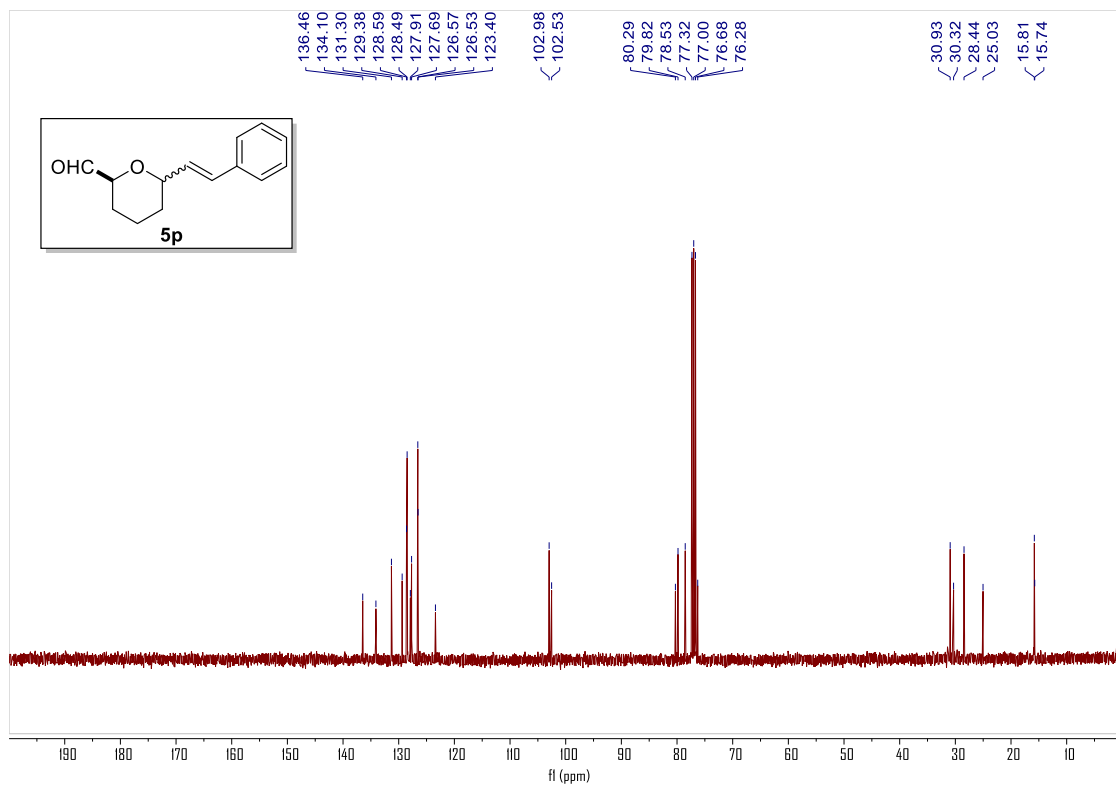


(E)-6-styryltetrahydro-2H-pyran-2-carbaldehyde (5p)

¹H spectrum (400 MHz, CDCl₃)

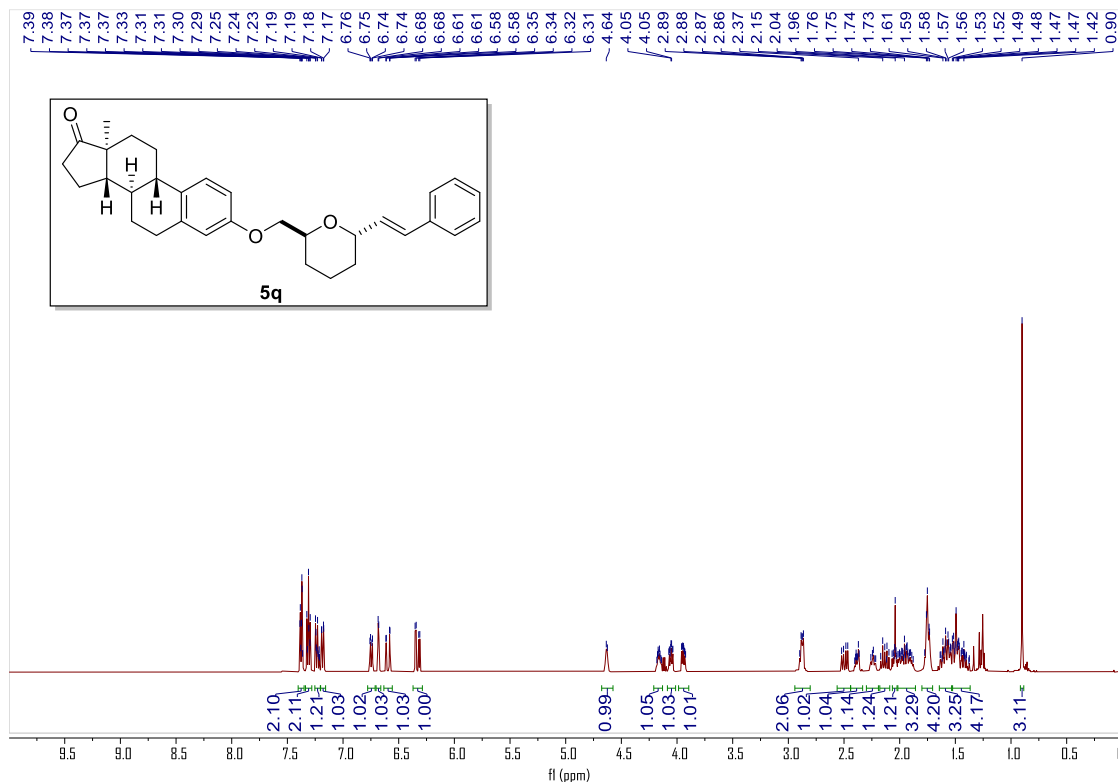


¹³C spectrum (101 MHz, CDCl₃)

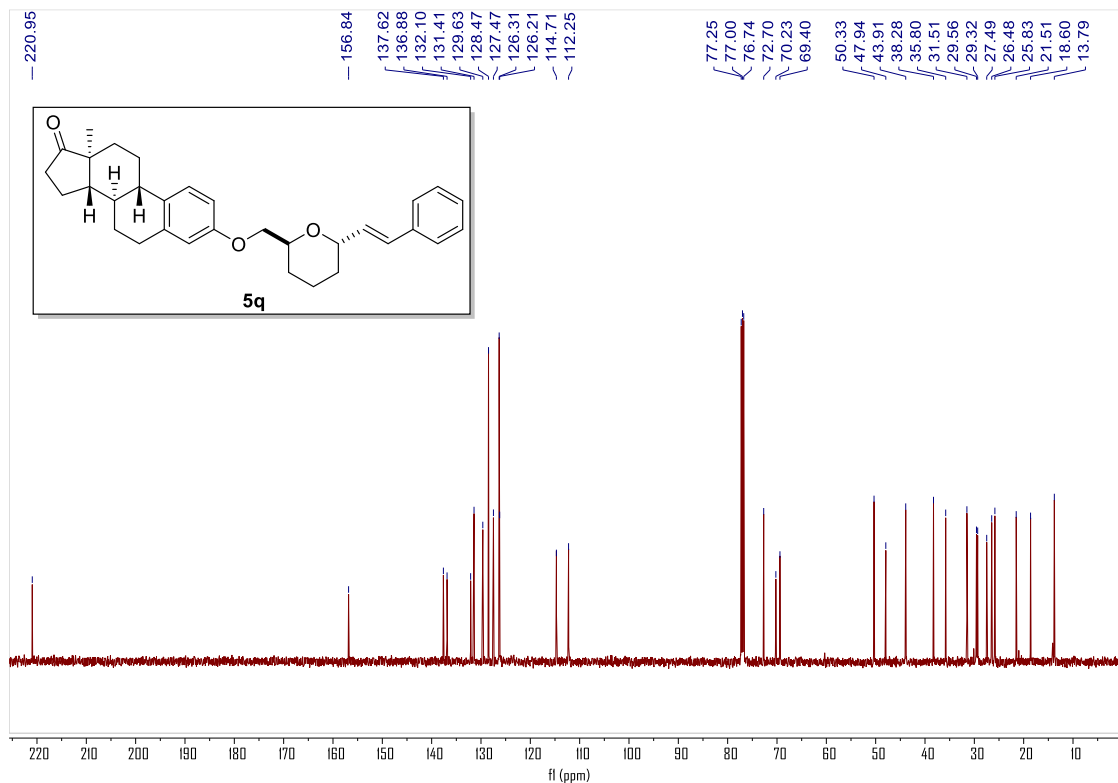


(8R,9S,13S,14S)-13-methyl-3-(((E)-styryl)tetrahydro-2H-pyran-2-yl)methoxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (5q)

^1H spectrum (500 MHz, CDCl_3)



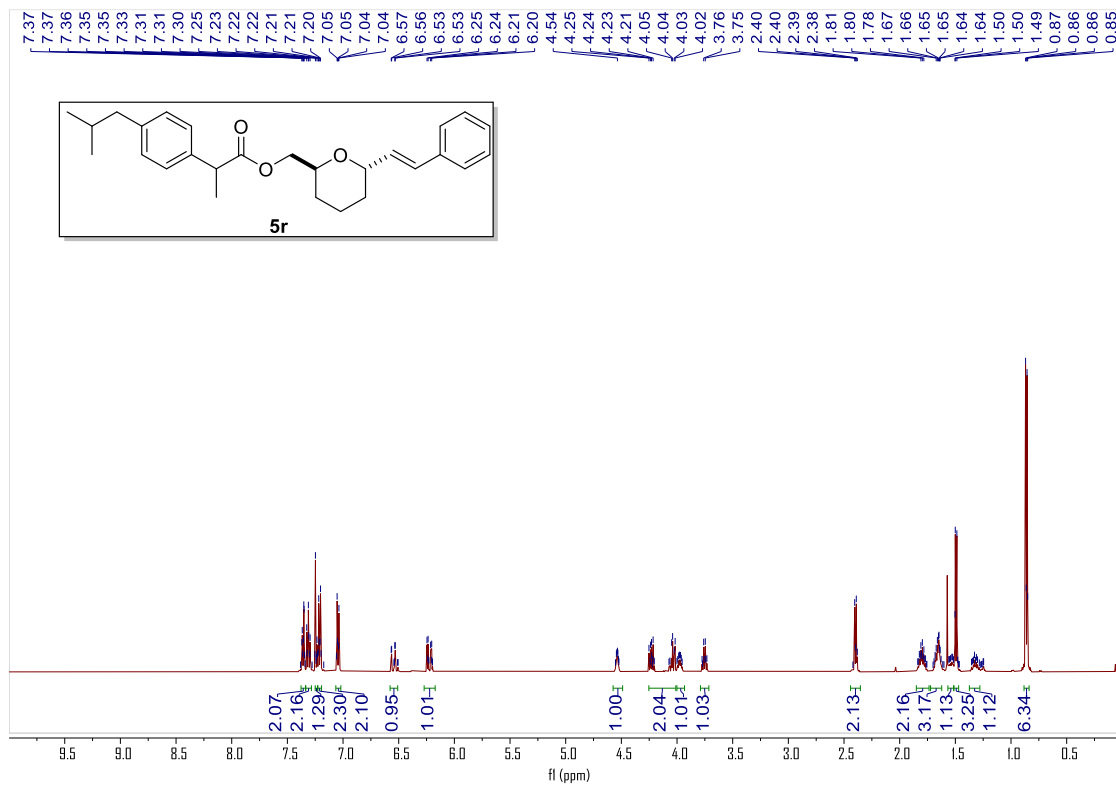
^{13}C spectrum (126 MHz, CDCl_3)



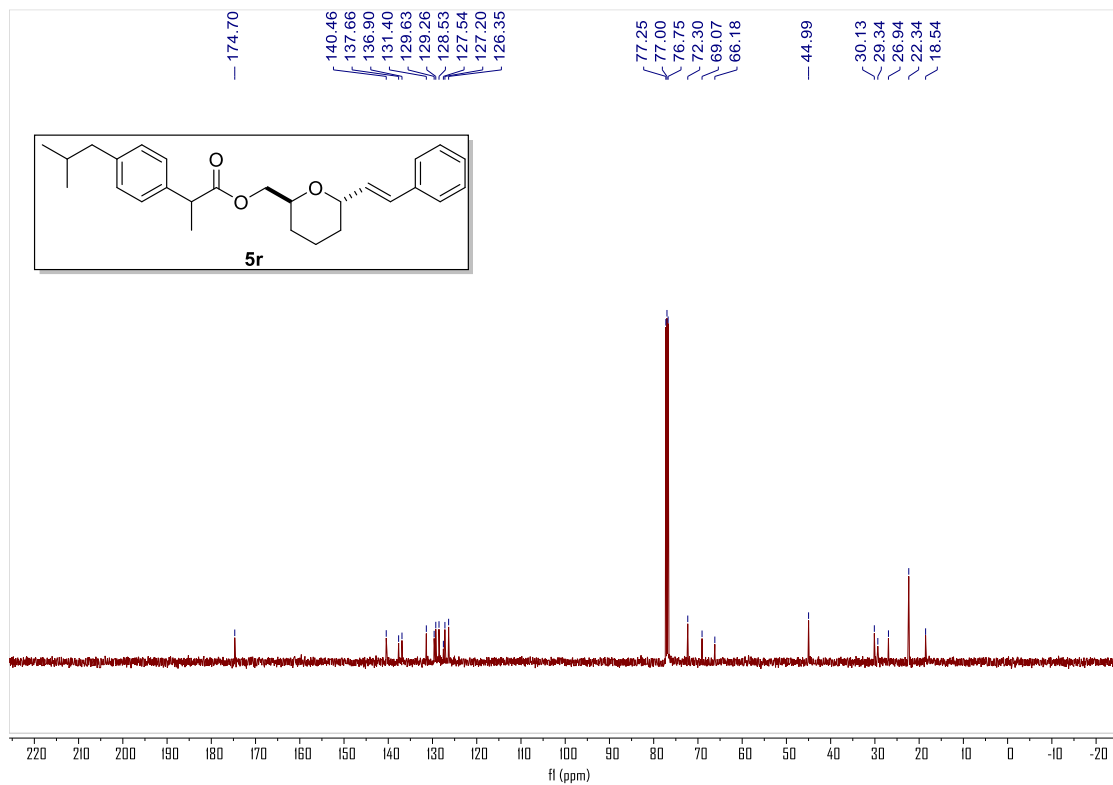
(E)-(6-styryltetrahydro-2H-pyran-2-yl)methyl 2-(4-isobutylphenyl)propanoate

(5r)

¹H spectrum (500 MHz, CDCl₃)

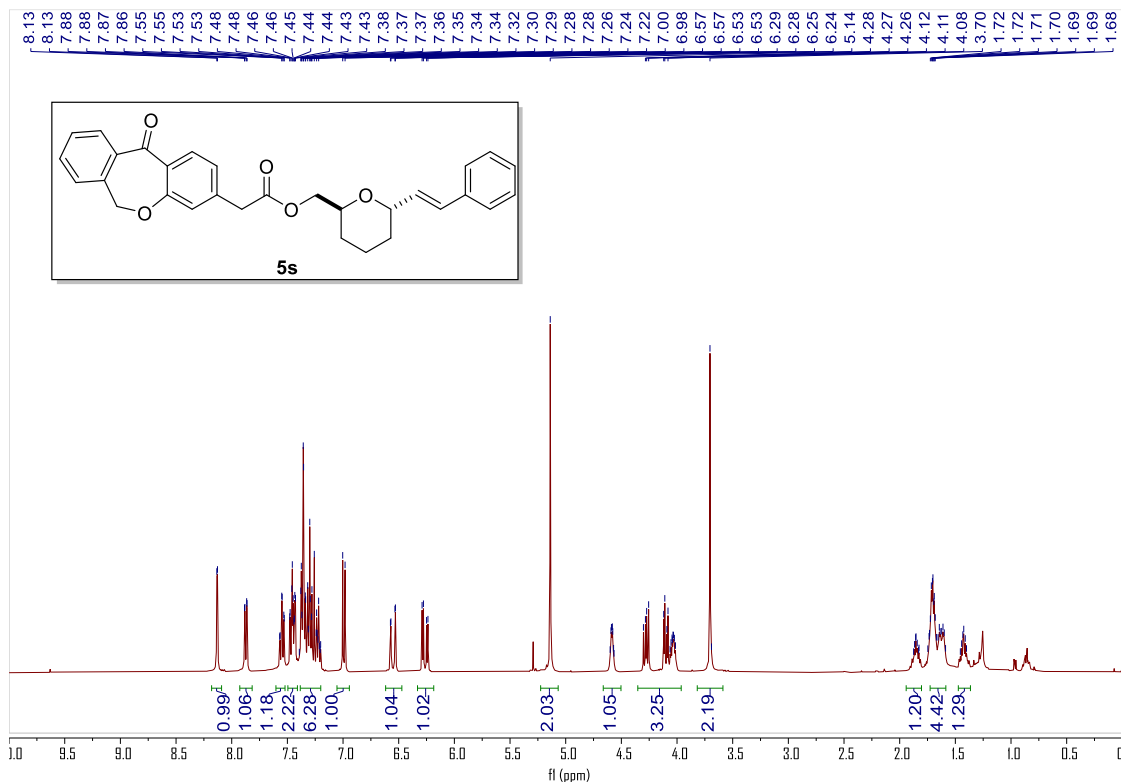


¹³C spectrum (126 MHz, CDCl₃)

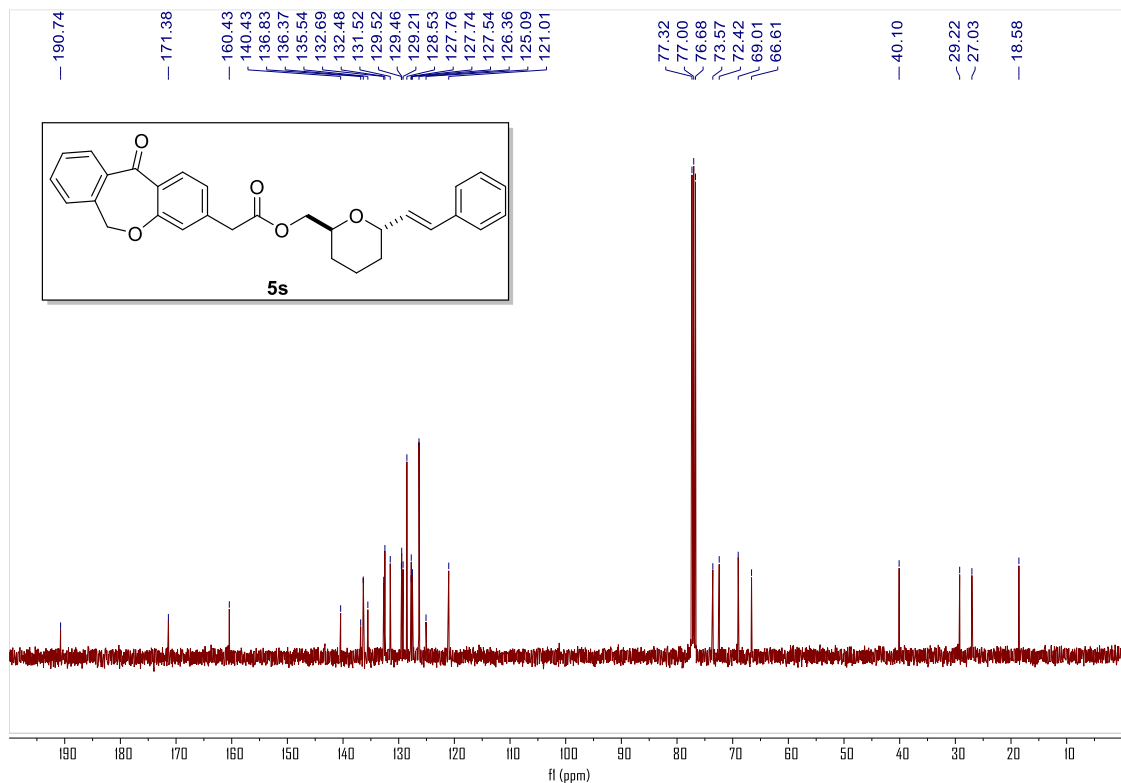


(E)-(6-styryltetrahydro-2H-pyran-2-yl)methyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-3-yl)acetate (5s)

^1H spectrum (500 MHz, CDCl_3)

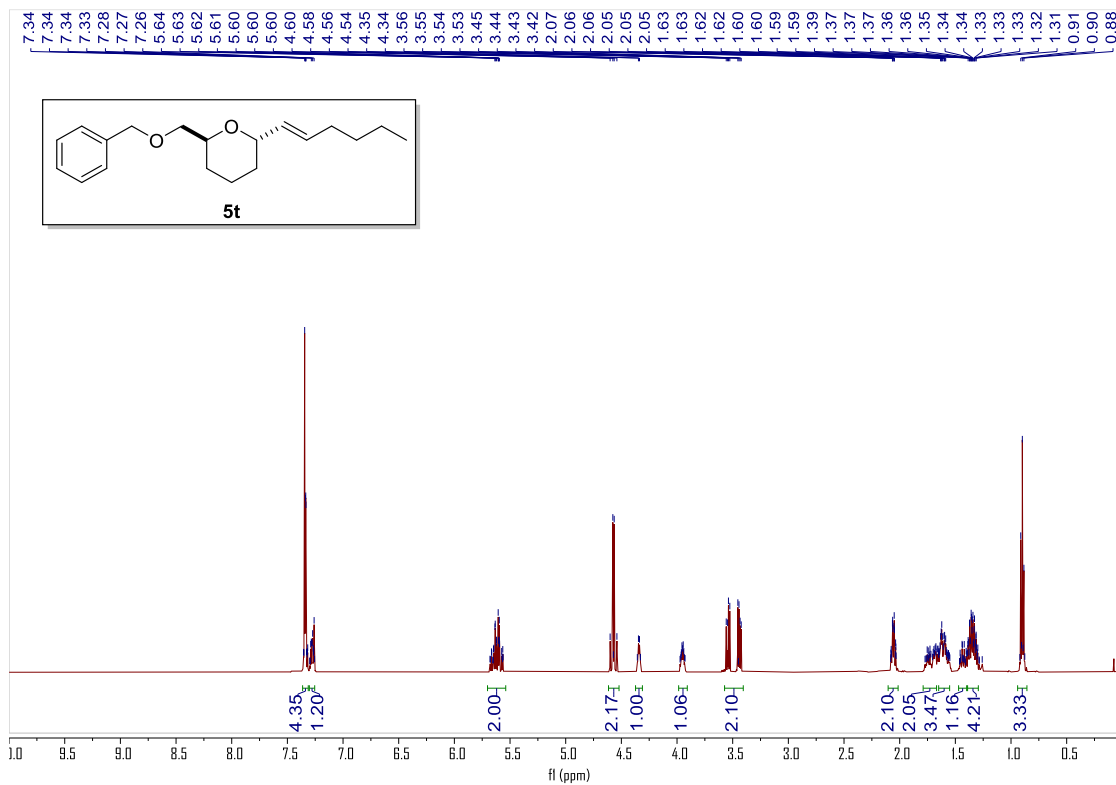


^{13}C spectrum (126 MHz, CDCl_3)

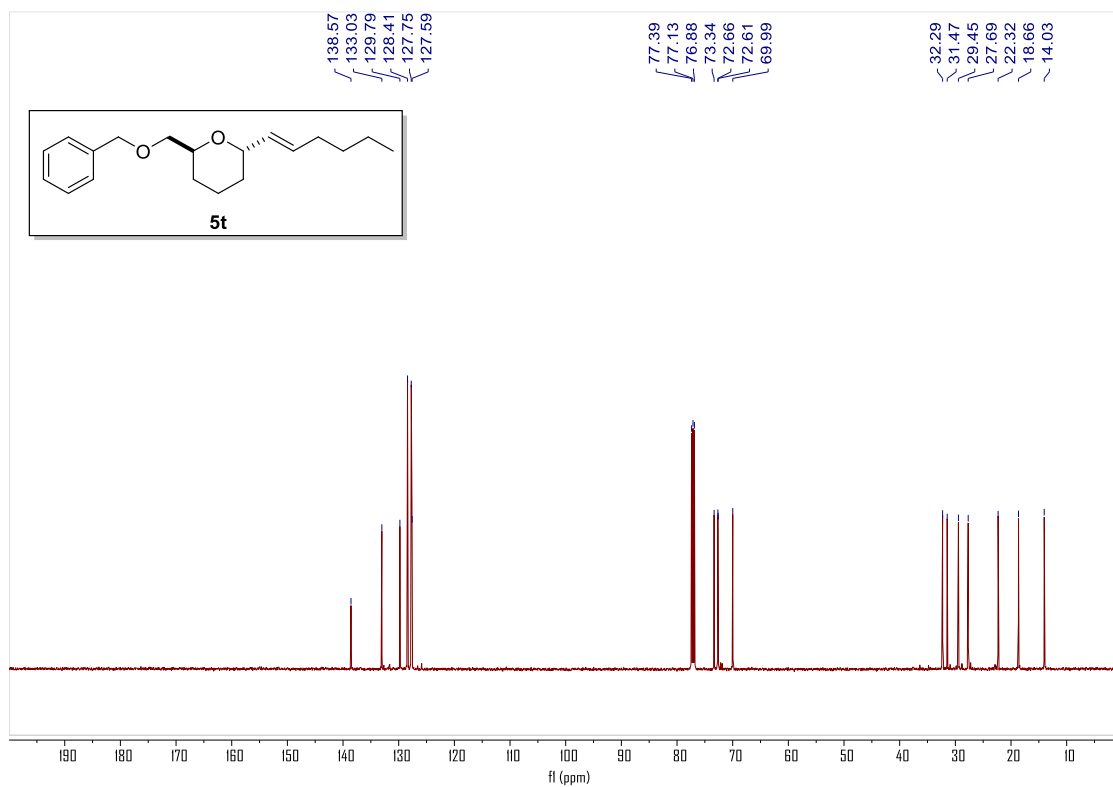


(E)-2-((benzyloxy)methyl)-6-(hex-1-en-1-yl)tetrahydro-2H-pyran (5t)

¹H spectrum (500 MHz, CDCl₃)

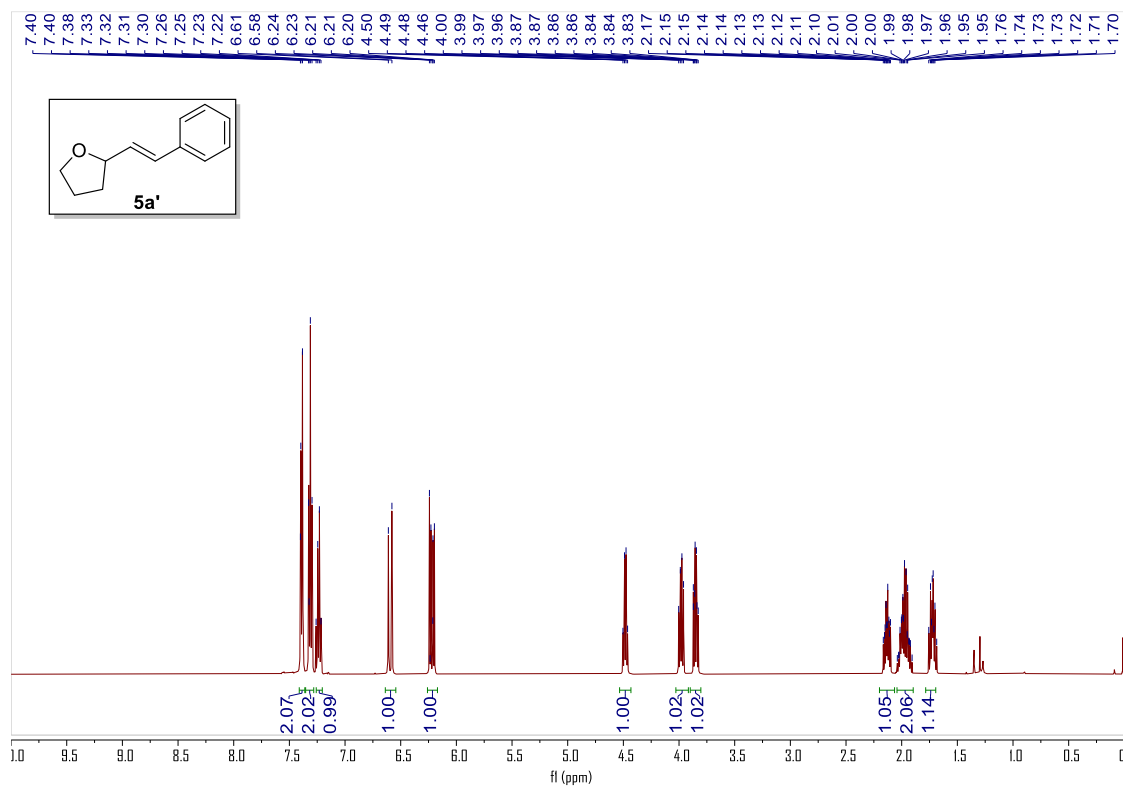


¹³C spectrum (126 MHz, CDCl₃)

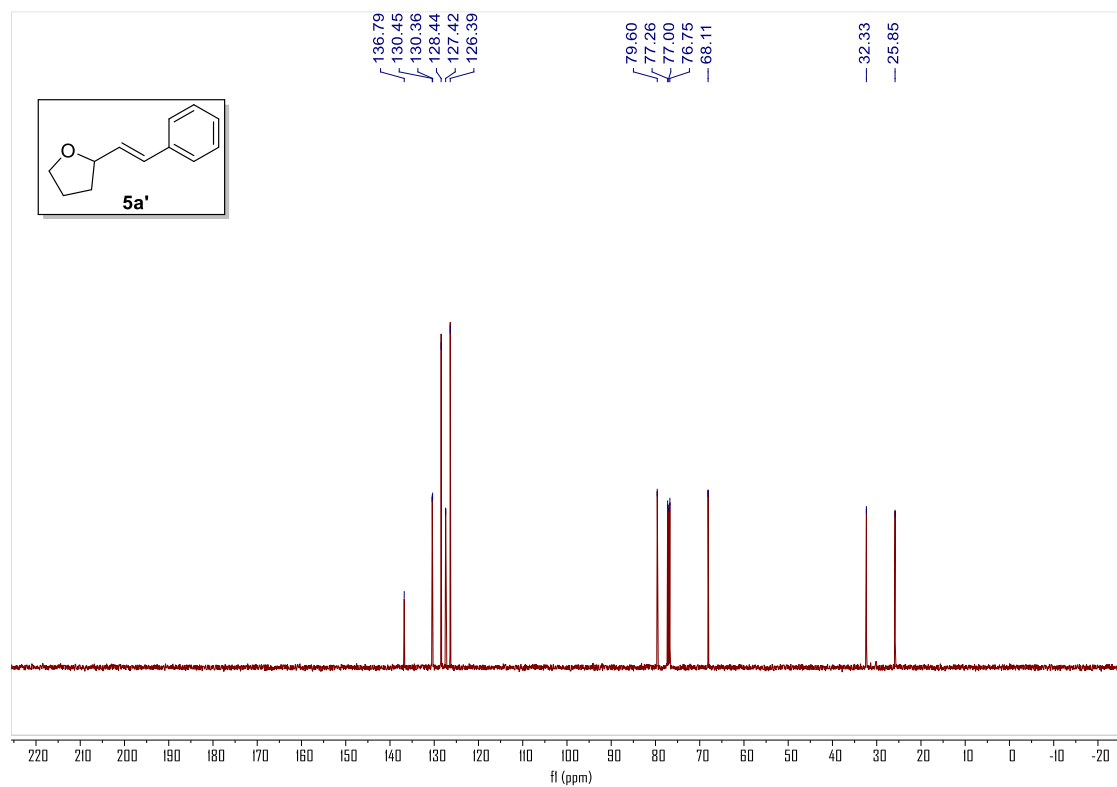


(E)-2-styryltetrahydrofuran (5a')

¹H spectrum (500 MHz, CDCl₃)

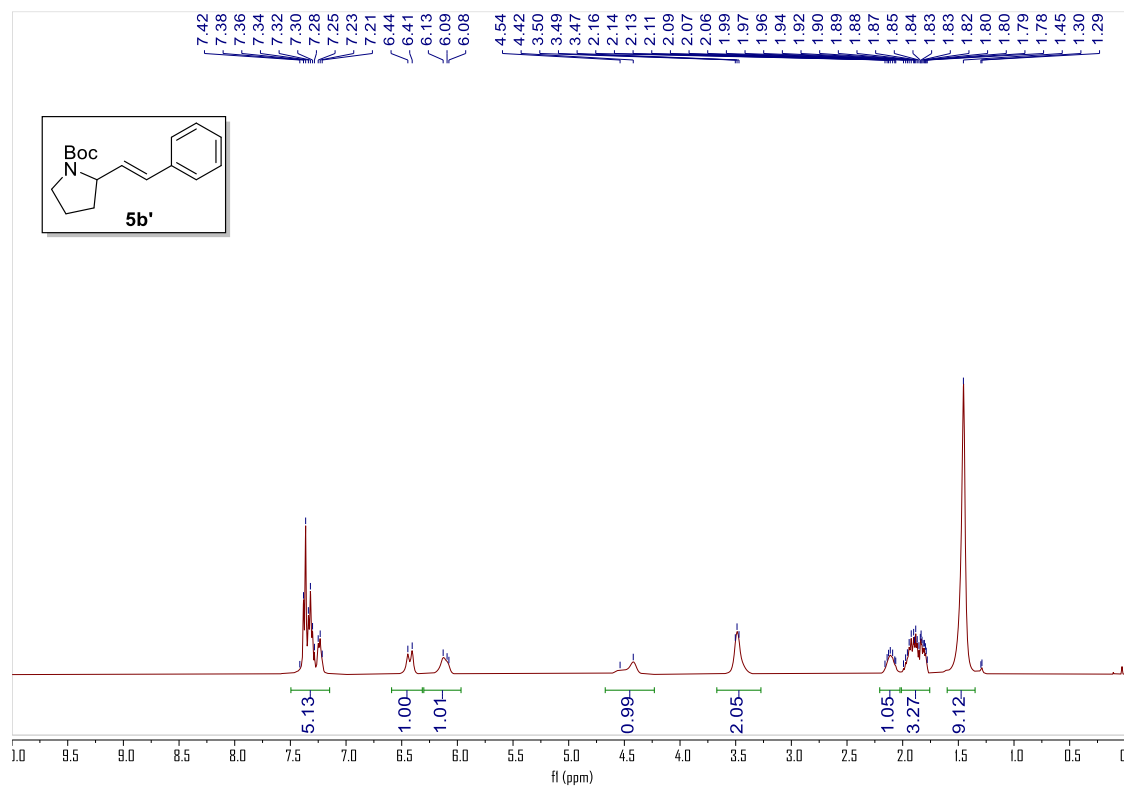


¹³C spectrum (126 MHz, CDCl₃)

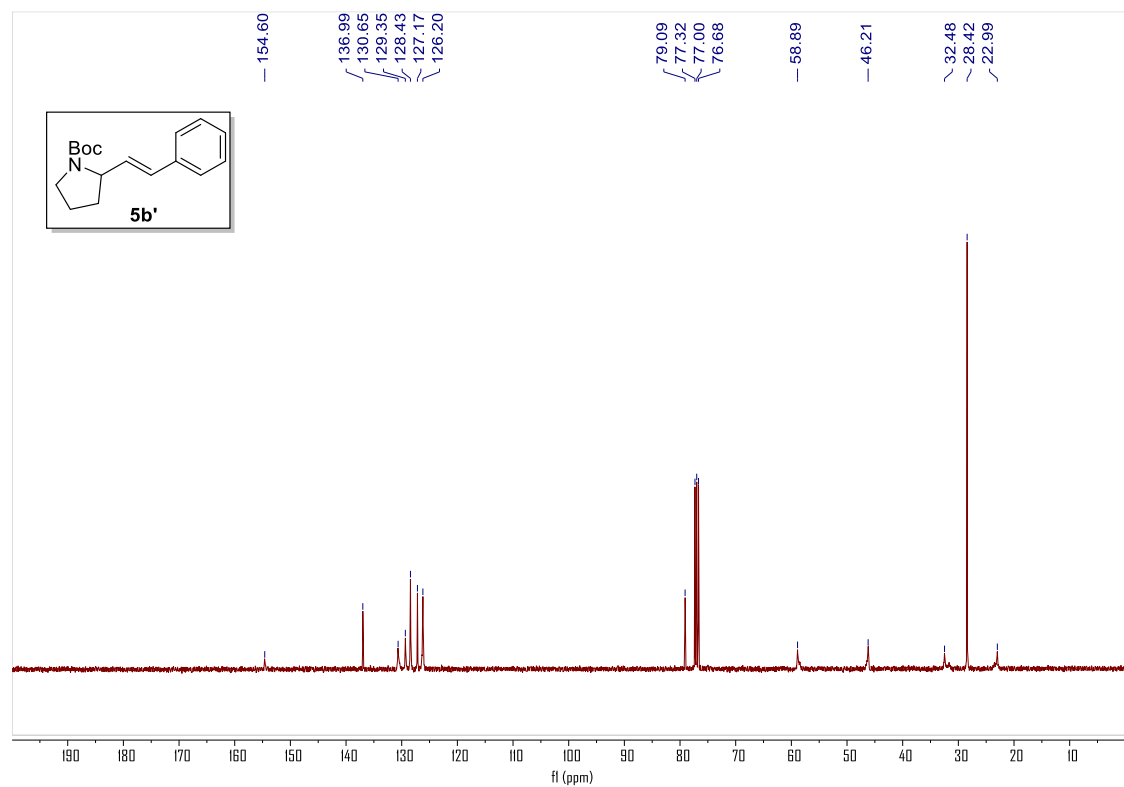


tert-butyl (E)-2-styrylpyrrolidine-1-carboxylate (**5b'**)

^1H spectrum (400 MHz, CDCl_3)

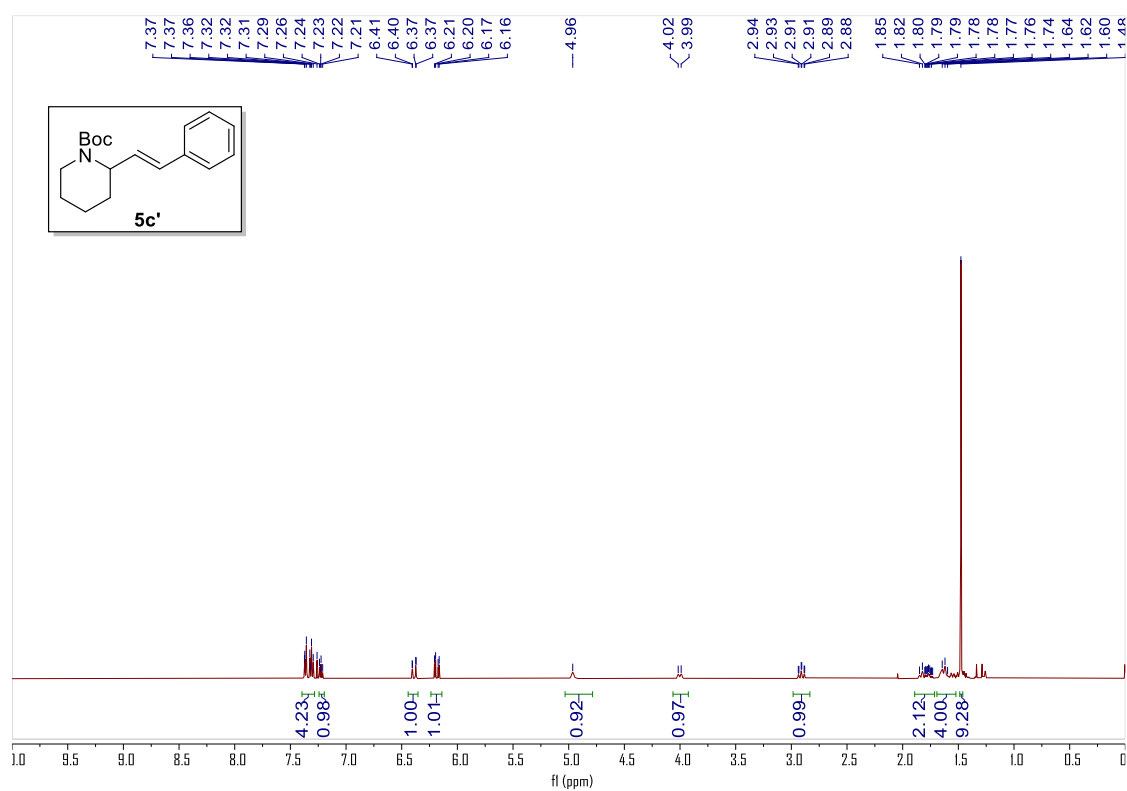


^{13}C spectrum (101 MHz, CDCl_3)

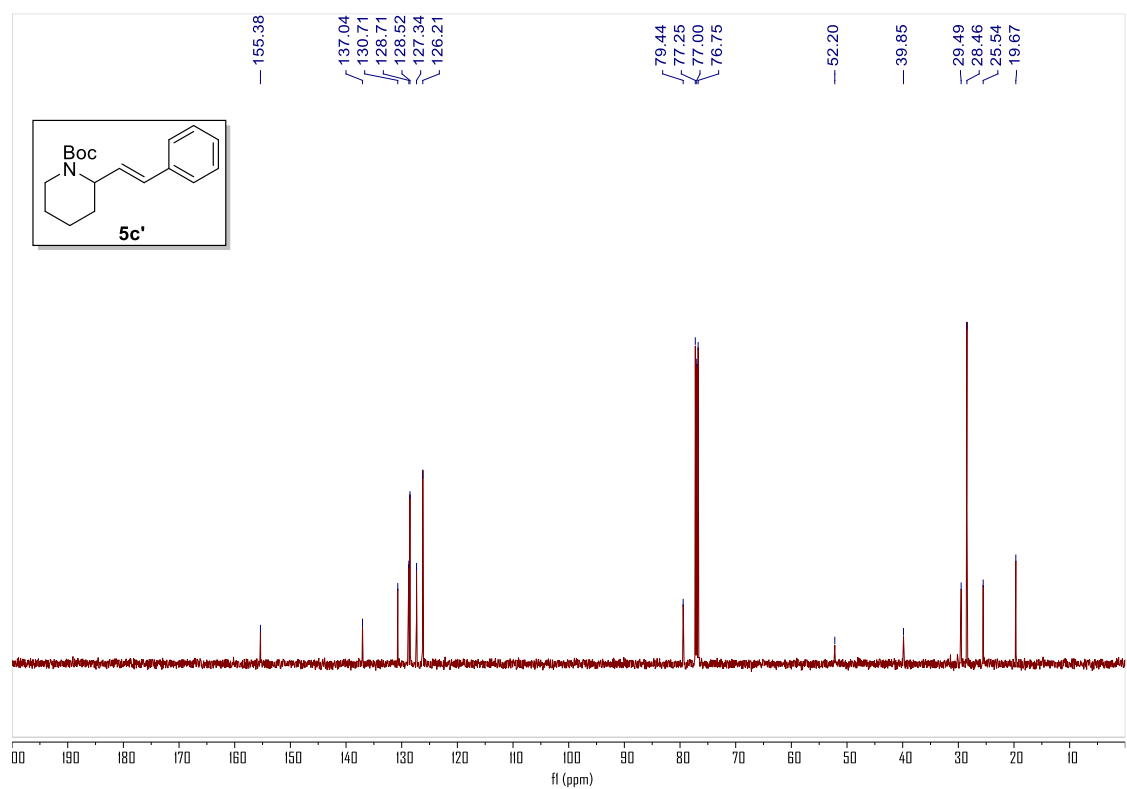


tert-butyl (E)-2-styrylpiperidine-1-carboxylate (5c')

¹H spectrum (500 MHz, CDCl₃)

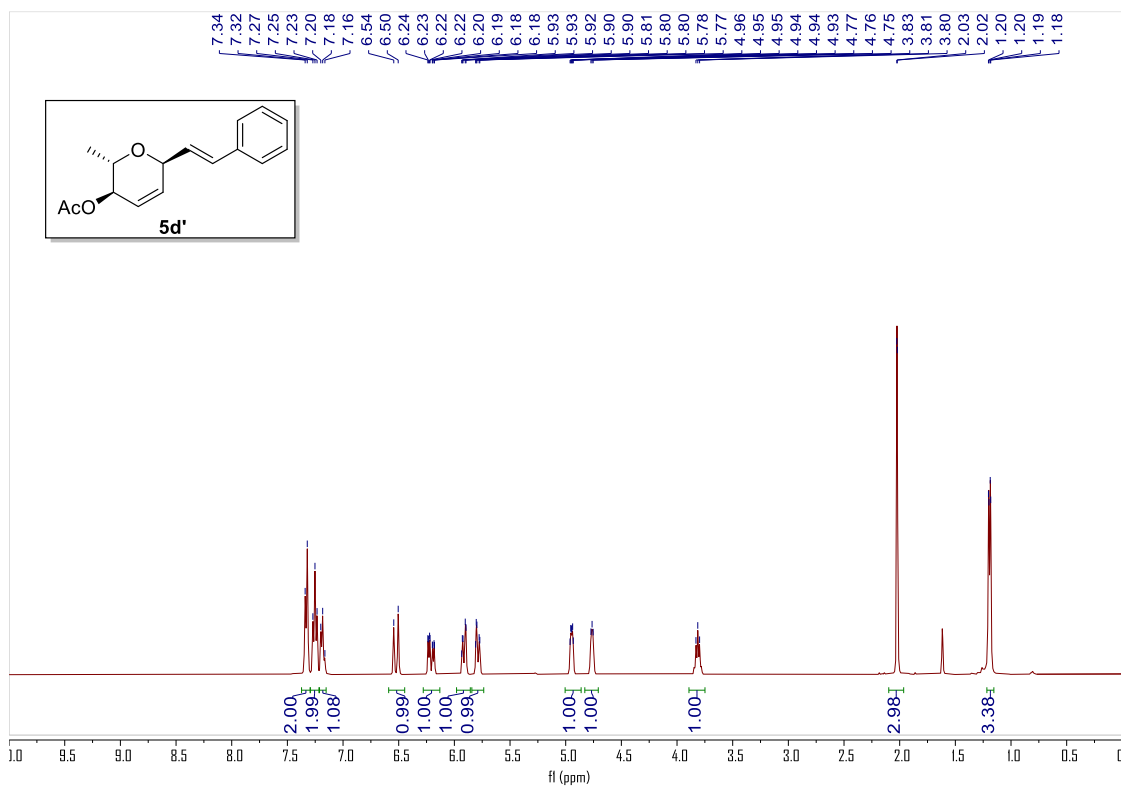


¹³C spectrum (126 MHz, CDCl₃)

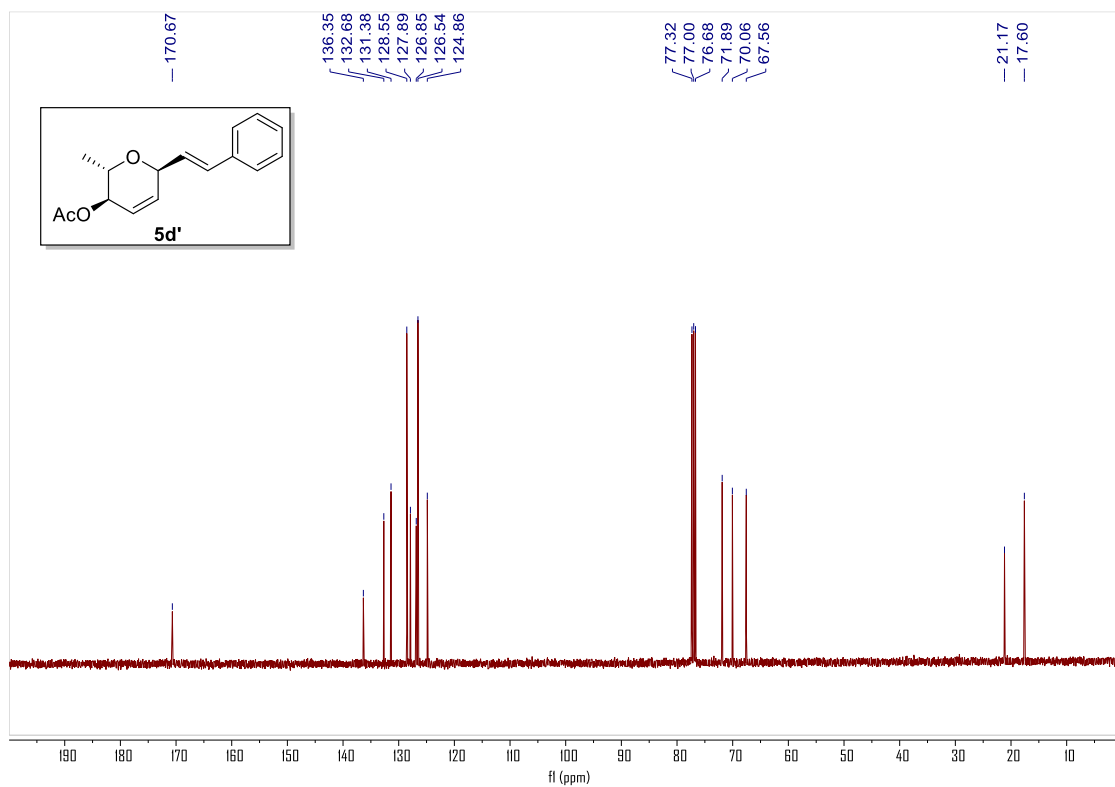


(2S,3R,6S)-2-methyl-6-((E)-styryl)-3,6-dihydro-2H-pyran-3-yl acetate (5d')

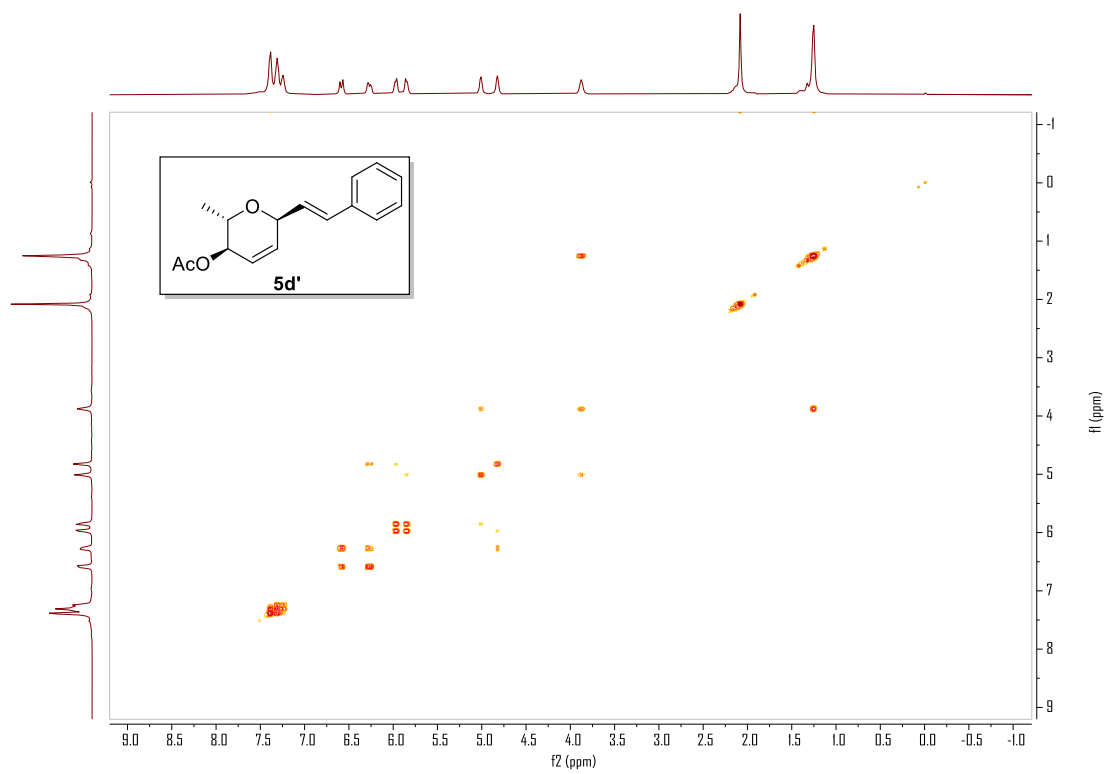
¹H spectrum (400 MHz, CDCl₃)



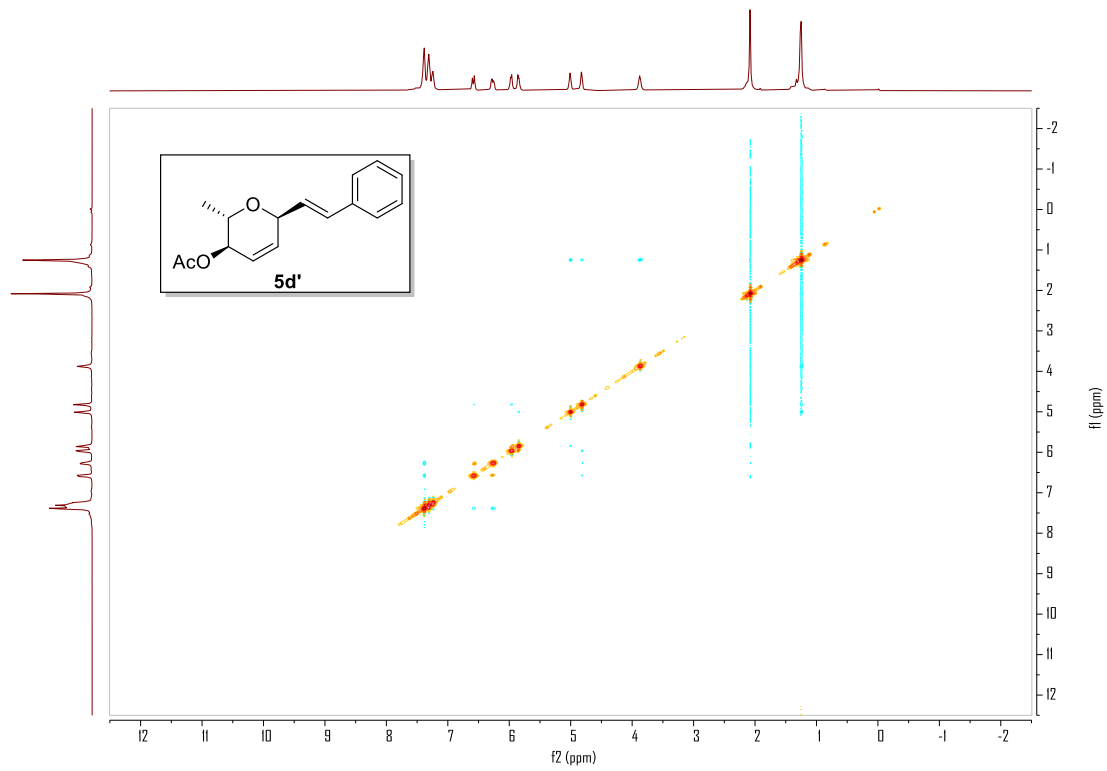
¹³C spectrum (101 MHz, CDCl₃)



^1H ^1H COSY NMR

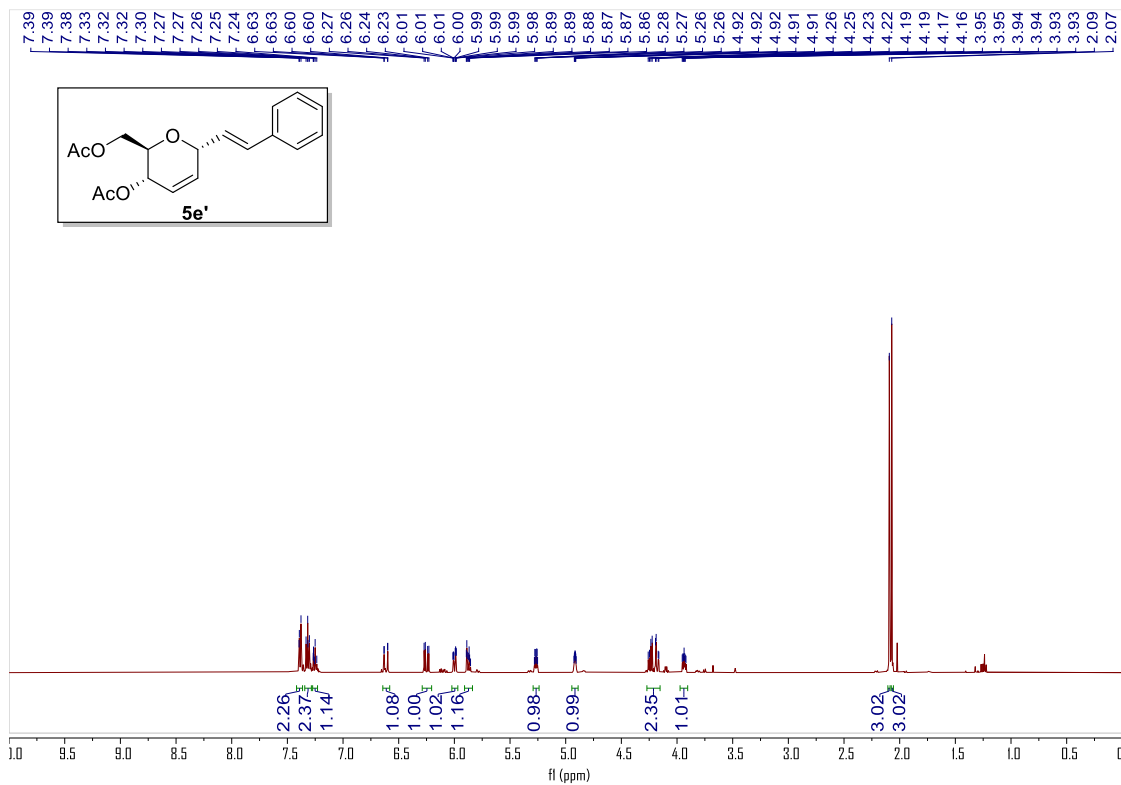


^1H ^1H NOESY NMR

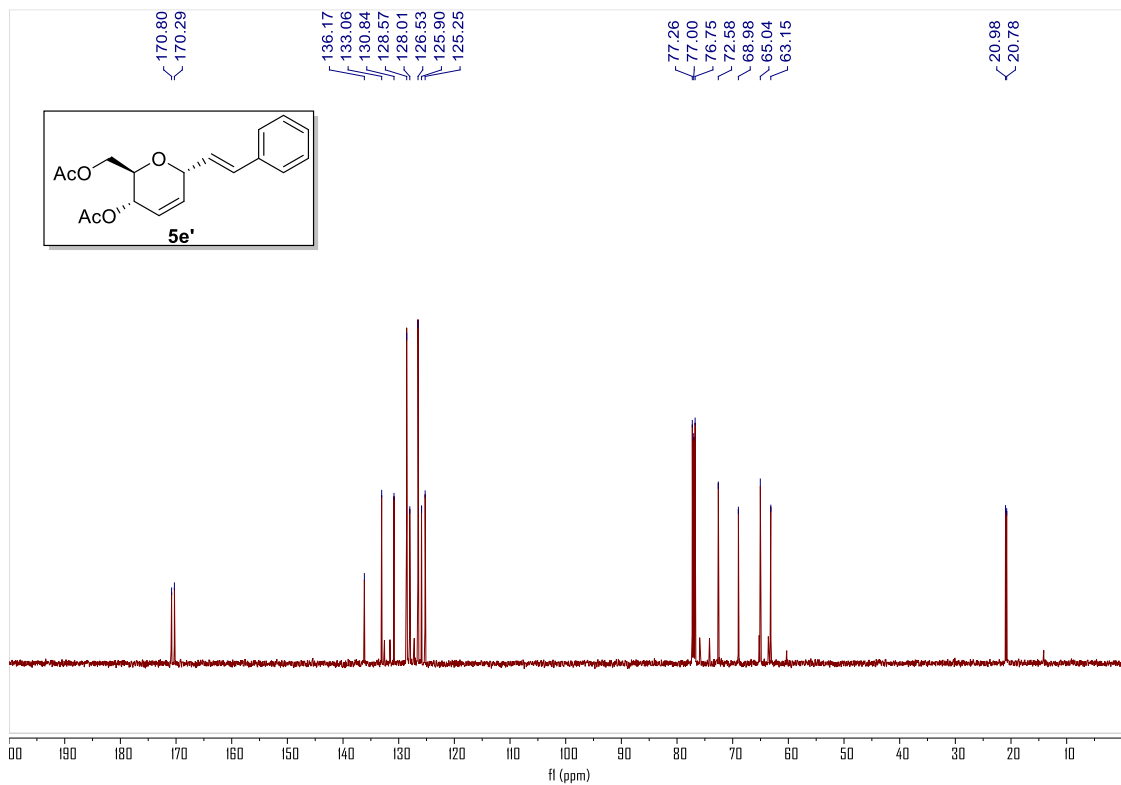


((2R,3S,6R)-3-acetoxy-6-((E)-styryl)-3,6-dihydro-2H-pyran-2-yl)methyl acetate
(5e')

¹H spectrum (500 MHz, CDCl₃)

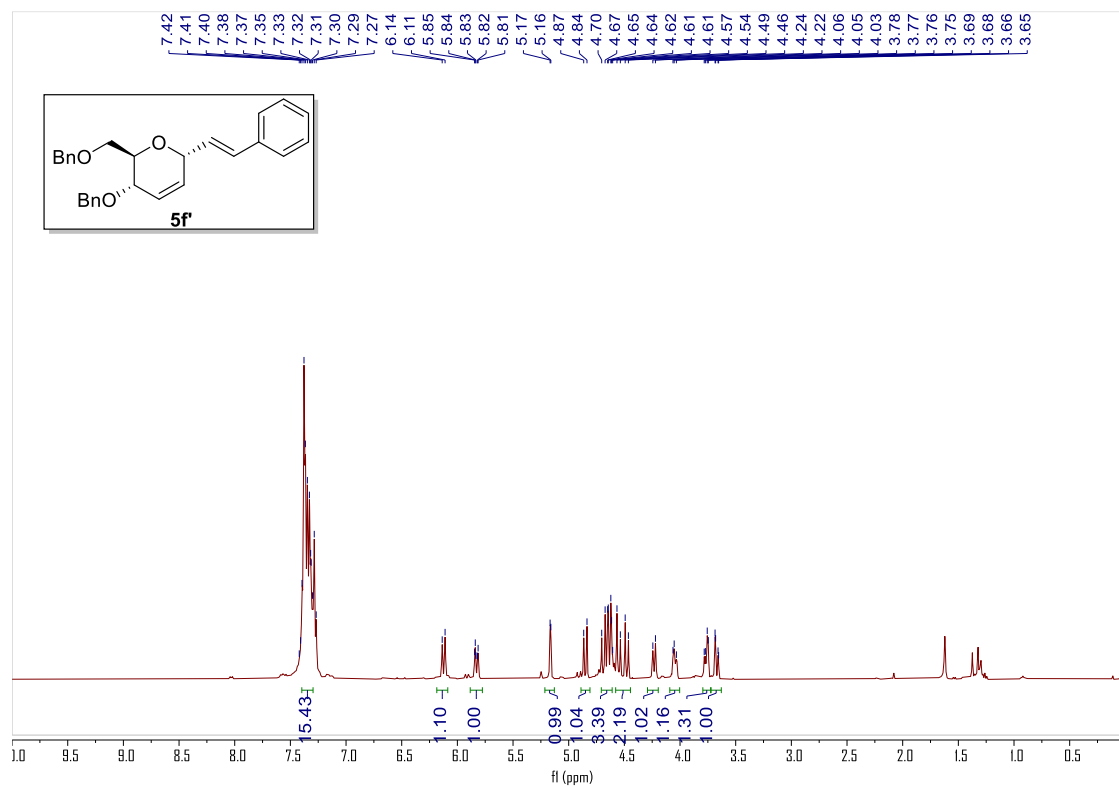


¹³C spectrum (126 MHz, CDCl₃)

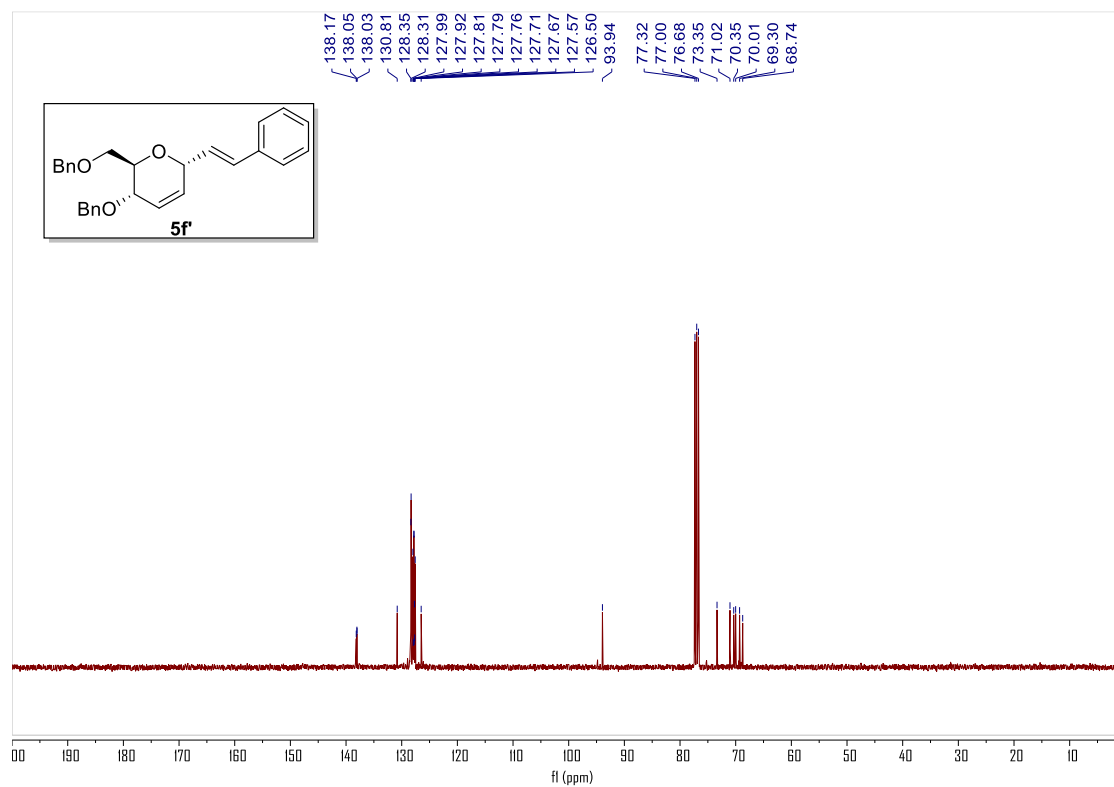


(2R,3S,6R)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-((E)-styryl)-3,6-dihydro-2H-pyran (5f')

¹H spectrum (400 MHz, CDCl₃)

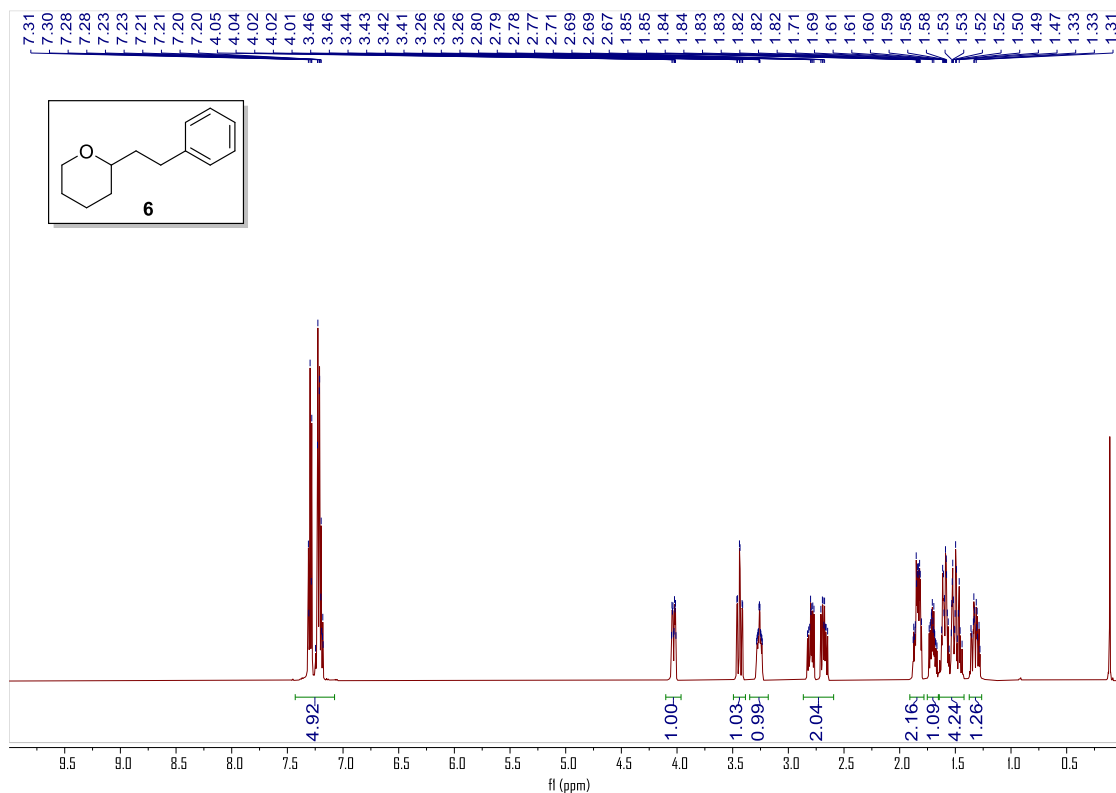


¹³C spectrum (101 MHz, CDCl₃)

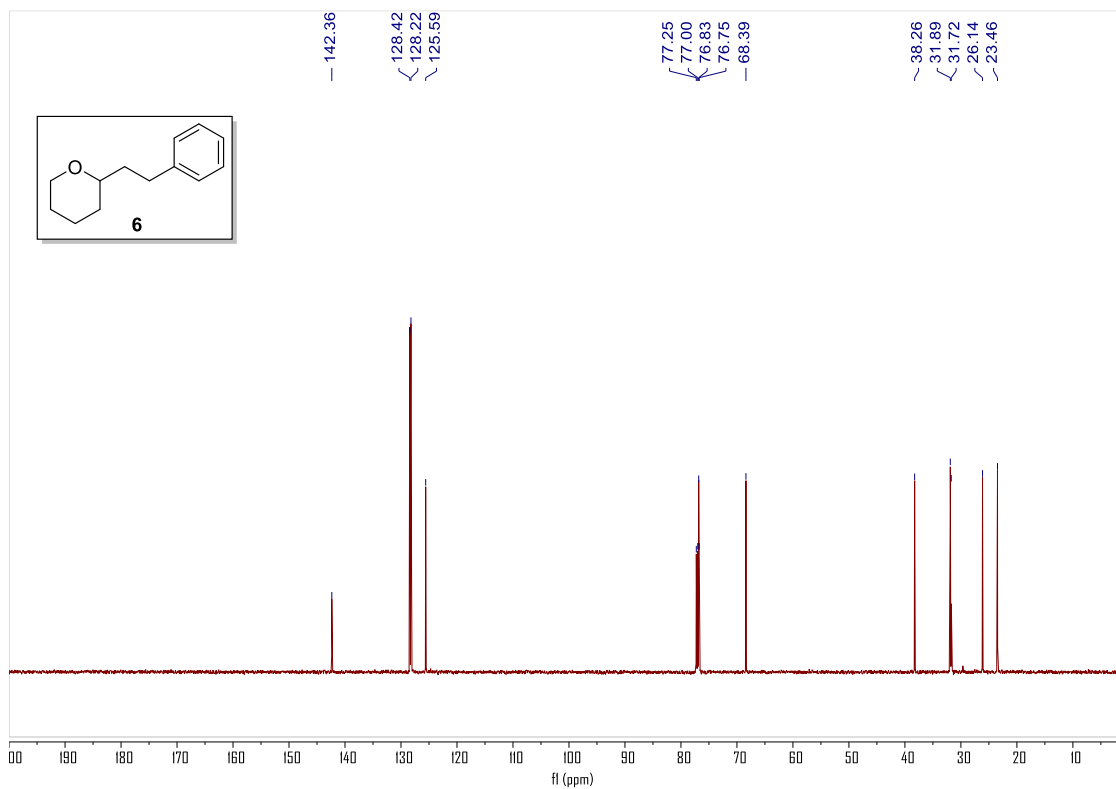


2-phenethyltetrahydro-2H-pyran (6)

^1H spectrum (500 MHz, CDCl_3)

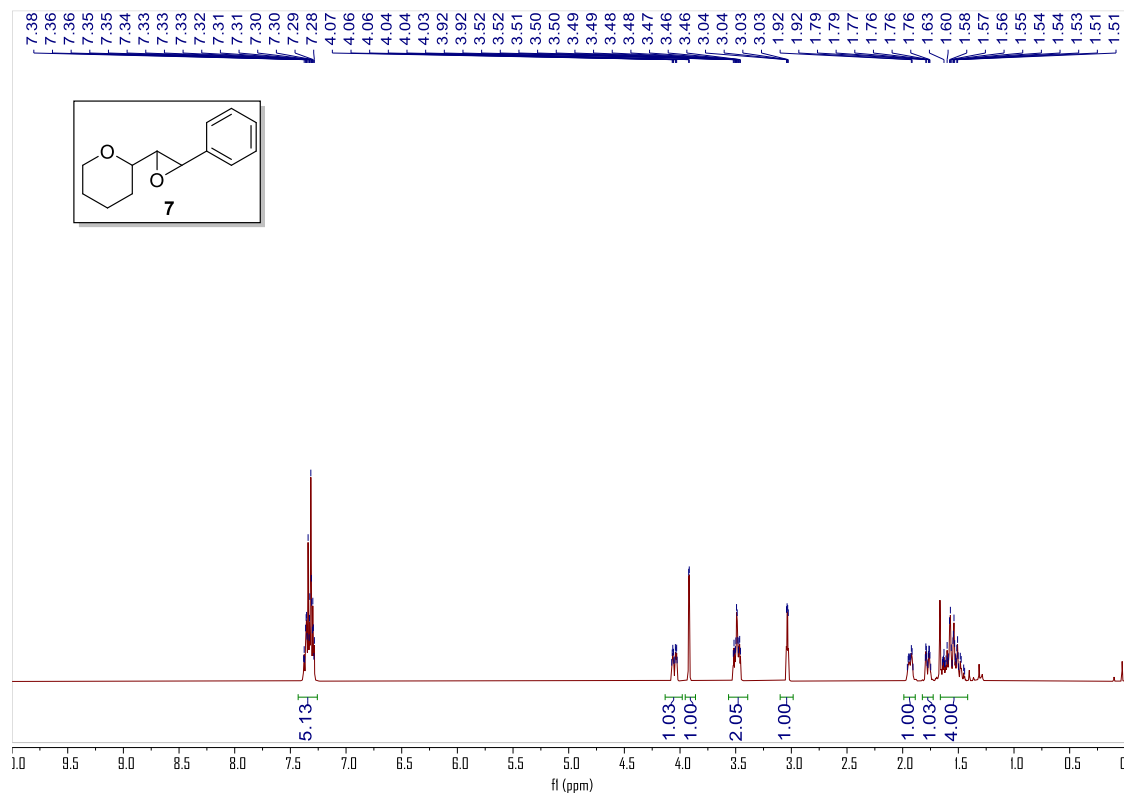


^{13}C spectrum (126 MHz, CDCl_3)

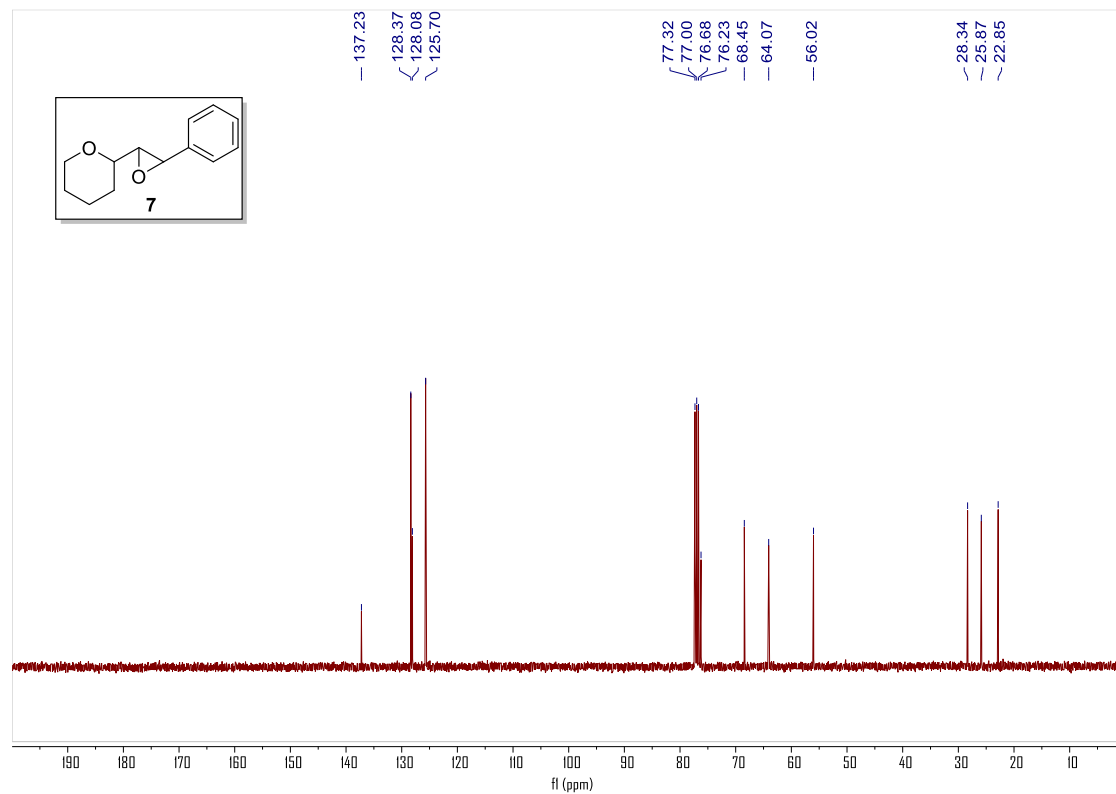


2-(3-phenyloxiran-2-yl)tetrahydro-2H-pyran (7)

^1H spectrum (400 MHz, CDCl_3)

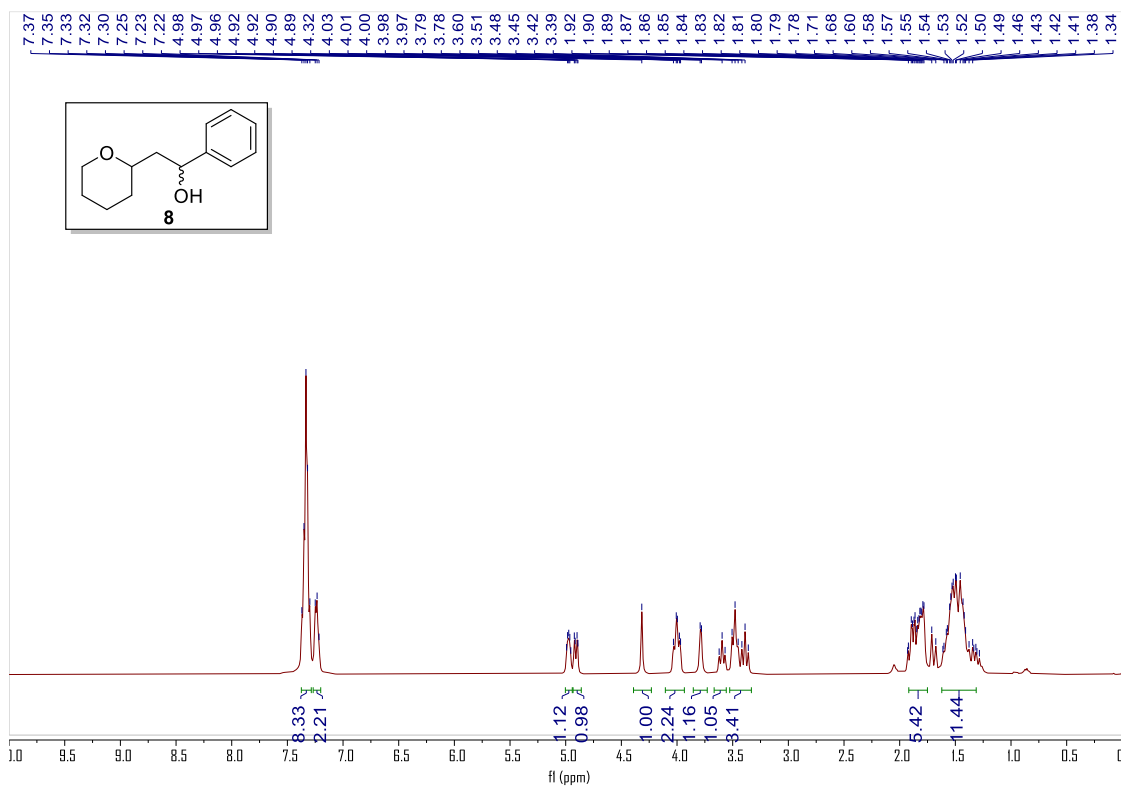


^{13}C spectrum (101 MHz, CDCl_3)

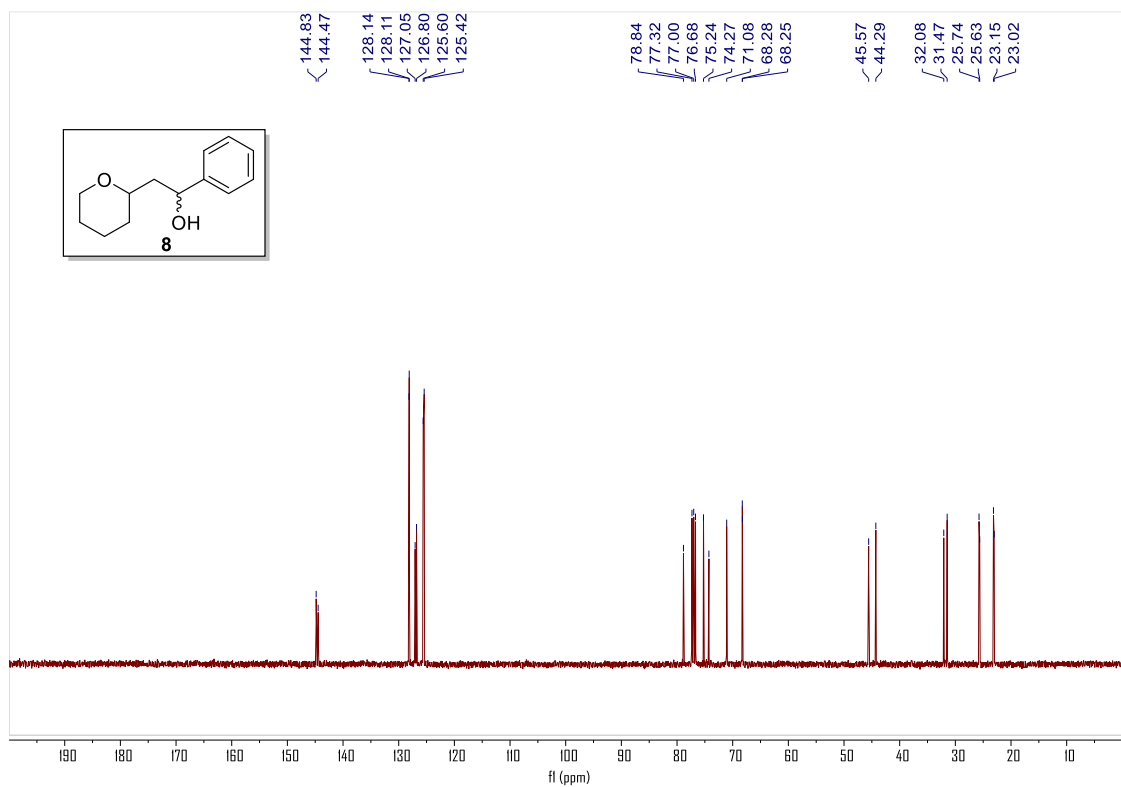


1-phenyl-2-(tetrahydro-2H-pyran-2-yl)ethan-1-ol (8)

^1H spectrum (400 MHz, CDCl_3)

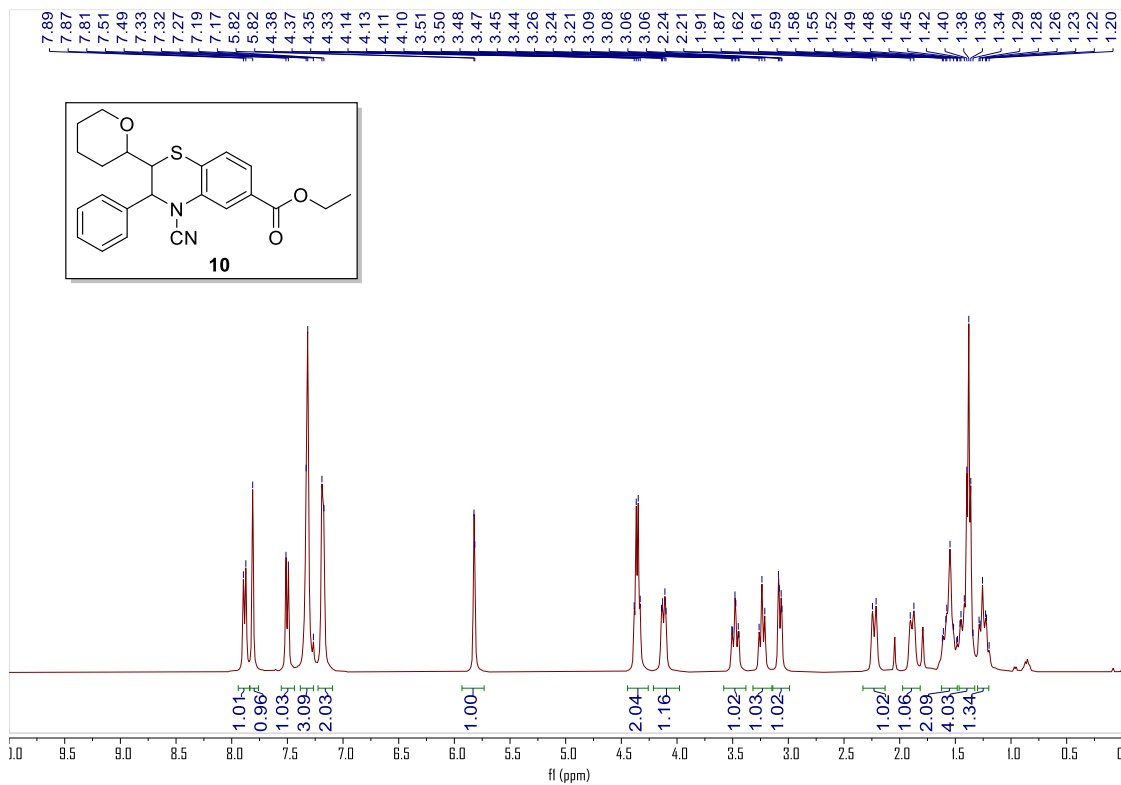


^{13}C spectrum (126 MHz, CDCl_3)

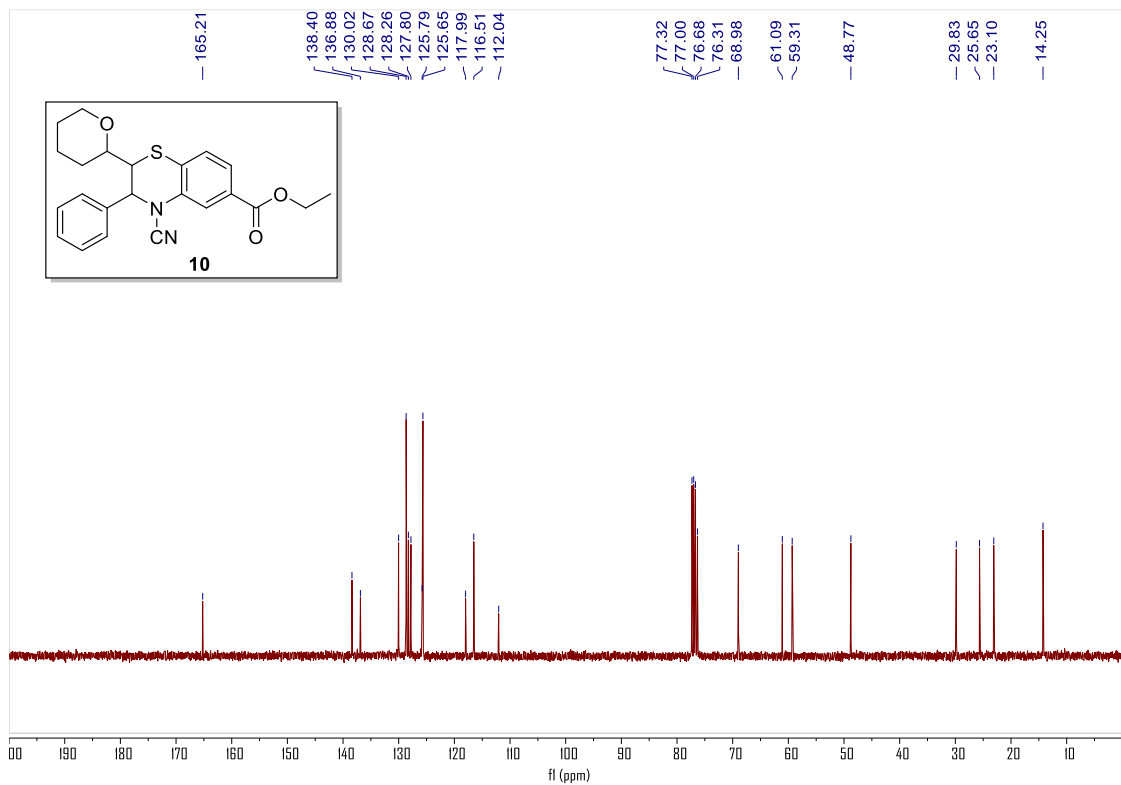


ethyl 4-cyano-3-phenyl-2-(tetrahydro-2H-pyran-2-yl)-3,4-dihydro-2H-benzo[b][1,4]thiazine-6-carboxylate (10)

¹H spectrum (400 MHz, CDCl₃)



¹³C spectrum (101 MHz, CDCl₃)



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