Supporting Information

Carbonyl *anti*-(*α*-Amino)allylation *via* Ruthenium Catalyzed Hydrogen Auto-Transfer: Use of an Acetylenic Pyrrole as an Allylmetal Pronucleophile

Wandi Zhang,[‡] Weijie Chen,[‡] Hongde Xiao, Michael J. Krische*

Department of Chemistry, University of Texas at Austin,
Austin, TX 78712, USA

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I. General Information:

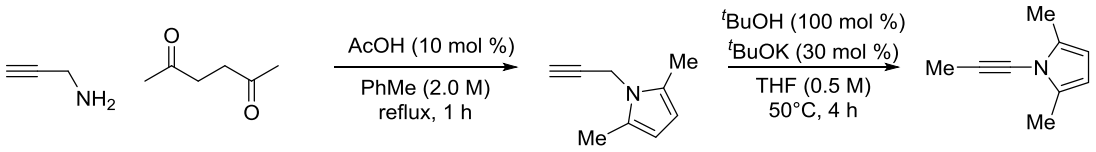
All reactions were run under an atmosphere of argon, unless otherwise indicated. Resealable pressure tubes (13x100 mm) were dried in the oven prior to use. Dioxane was dried over sodium-benzophenone and was distilled immediately prior to use. $HClRu(CO)(PPh_3)_3$ was prepared according to literature procedure.[1] All ligands were used as received from Strem Chemicals Inc. Alcohols were used as received from commercial sources. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates. Visualization was accomplished with UV light followed by dipping in Seebach's stain solution then heating. Purification of reactions was carried out by flash chromatography using Silicycle silica gel (40–63 μm).

II. Spectroscopy, Spectrometry, and Data Collection:

Infrared spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion (M+H, M+Na), or a suitable fragment ion. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian Gemini (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for deuteriochloroform. Data reported as multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Integration and coupling constants were reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with a Varian Gemini (100 MHz) spectrometer and were routinely run with broadband decoupling. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.16 ppm for deuteriochloroform. Fluorine-19 nuclear magnetic resonance (^{19}F NMR) spectra were recorded with a Varian Gemini 400 (100 MHz) spectrometer.

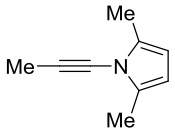
III. Experimental Details and Spectral Data

A. Preparation of Acetylenic Pyrrole 1



To a solution of propargyl amine (2.75 g, 50 mmol, 100 mol %) and 2,5-hexanedione (7.1 g, 50 mmol, 100 mol %) in toluene (25 mL, 2.0 M) was added acetic acid (0.29 mL, 5 mmol, 10 mol %) dropwise. The reaction mixture was allowed to reflux for 1 hour and then cooled to room temperature. The reaction mixture was washed with saturated aqueous NH_4Cl, $NaHCO_3$, and brine. The solvent was removed *in vacuo* and afforded crude product as a brown solid.[2] To the crude product dissolved in THF (100 mL, 0.5 M) under argon was added *tert*-BuOH (4.74 mL, 50 mmol, 100 mol %) and *tert*-BuOK (1.68 g, 15 mmol, 30 mol %). The reaction was stirred at 50°C for 4 hours until complete consumption of starting material as monitored by TLC. The reaction mixture was filtered through a short pad of celite and then washed with EtOAc. The filtrate was then washed with H_2O. The solvent was removed *in vacuo* and the residue was subjected to column chromatography (SiO_2; hexanes). The title compound was obtained in 41% yield (2.73 g, 20 mmol) as a colorless liquid.

2,5-dimethyl-1-(prop-1-yn-1-yl)-1H-pyrrole (1).



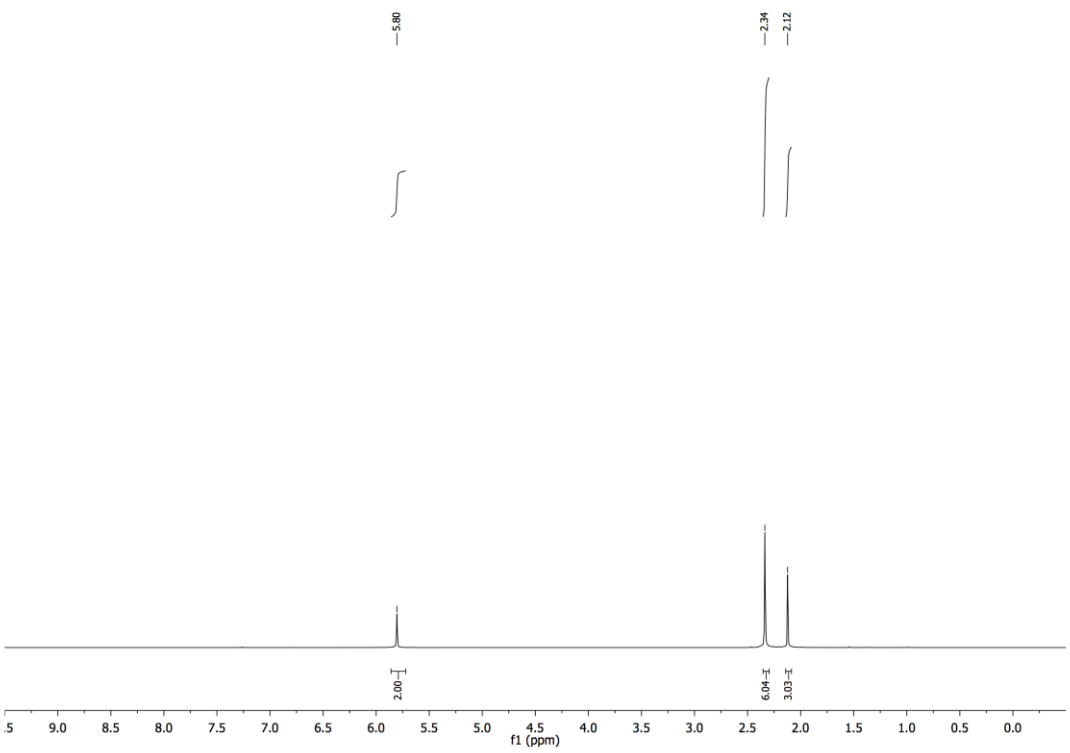
Rf=0.4 (100% Hexanes).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80 (s, 2H), 2.34 (s, 6H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 131.0, 106.0, 70.5, 67.4, 12.5, 3.2.

HRMS (ESI) Calcd. for $C_9H_{12}N$ $[M+H]^+$: 134.0964, Found: 134.0962.

FTIR (neat): 2919, 2265, 1537, 1412, 1372, 1325, 1210, 1023, 980, 954, 759 cm^{-1}.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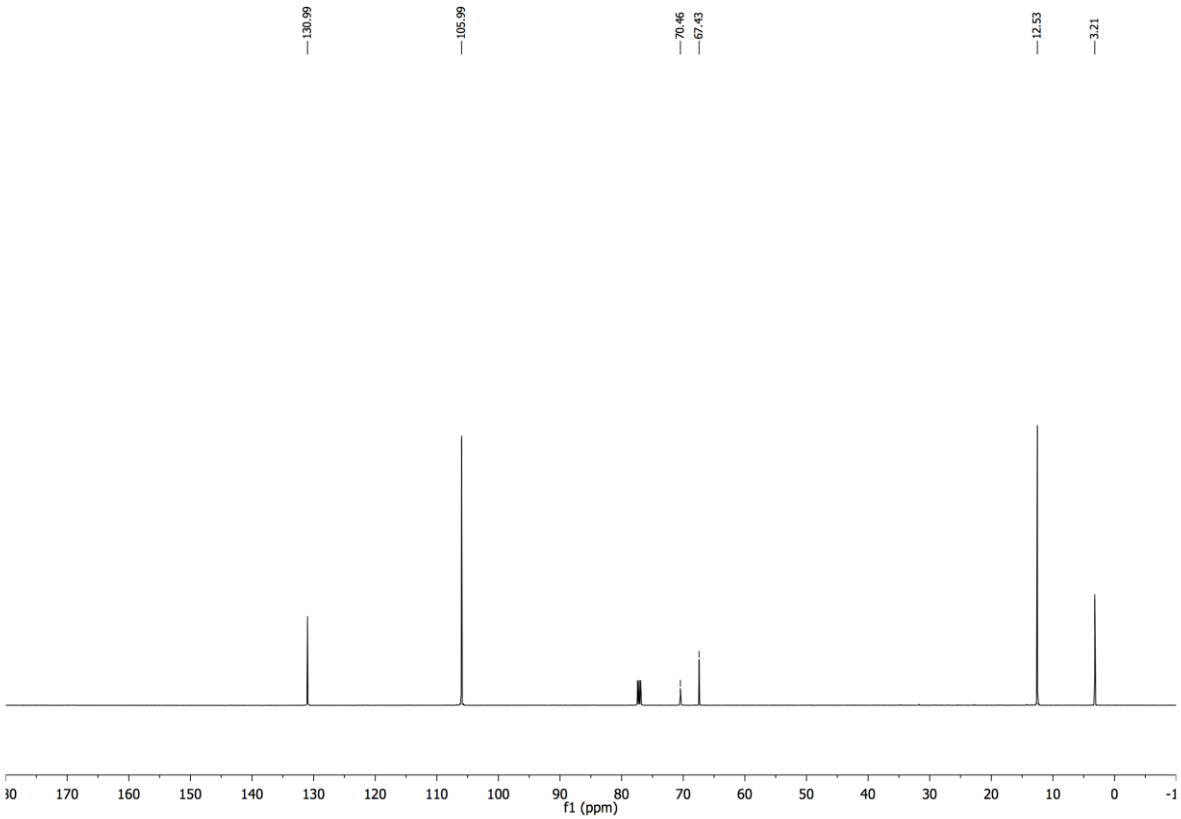
2.34
2.12
2.00
6.04
3.03
f1 (ppm)


130.99
105.99
70.46
67.43
12.53
3.21
f1 (ppm)

B. General Procedure for the Couplings of Alcohols 2a-2u and 1

To a resealable pressure tube (13x100) were added $HClRu(CO)(PPh_3)_3$ (9.5 mg, 0.010 mmol, 5 mol %) and dippf (4.2 mg, 0.010 mmol, 5 mol %). At this stage the solid alcohol coupling partners (0.20 mmol, 100 mol %) were added. The tube was sealed with a rubber septum and purged with argon. Dioxane (0.40 mL, 0.5 M) was added to the reaction vessel. At this stage, the liquid alcohol coupling partners (0.20 mmol, 100 mol %) were added. Acetylenic pyrrole **1** (0.60 mmol, 300 mol %) was added to the reaction vessel and the rubber septum was quickly replaced with a screw cap. The mixture was allowed to stir at the indicated temperature for the indicated time. The reaction mixture was then allowed to cool to room temperature. The solvents were removed *in vacuo* and the residue was subjected to column chromatography (SiO_2).

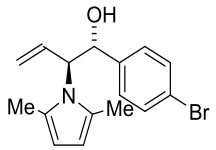
1 mmol Scale Procedure

To a resealable pressure tube were added $HClRu(CO)(PPh_3)_3$ (47.6 mg, 0.050 mmol, 5 mol %) and dippf (20.9 mg, 0.050 mmol, 5 mol %). At this stage the solid alcohol coupling partners (1.0 mmol, 100 mol %) were added. The tube was sealed with a rubber septum and purged with argon. Dioxane (2.0 mL, 0.5 M) was added to the reaction vessel. At this stage, the liquid alcohol coupling partners (1.0 mmol, 100 mol %) were added. Acetylenic pyrrole **1** (3.0 mmol, 300 mol %) was added to the reaction vessel and the rubber septum was quickly replaced with a screw cap. The mixture was allowed to stir at the indicated temperature for the indicated time. The reaction mixture was then allowed to cool to room temperature. The solvents were removed *in vacuo* and the residue was subjected to column chromatography (SiO_2).

From Aldehyde Oxidation Level

To a resealable pressure tube (13x100) were added $RuBr(CO)_3(\eta^3\text{-}C_3H_5)$ (3.1 mg, 0.010 mmol, 5 mol %) and dippf (4.2 mg, 0.010 mmol, 5 mol %). At this stage the coupling partner aldehyde (0.2 mmol, 100 mol %) was added. The tube was sealed with a rubber septum and purged with argon. Dioxane (0.4 mL, 0.5 M) was added to the reaction vessel. Acetylenic pyrrole **1** (0.6 mmol, 300 mol %) was added to the reaction vessel followed by 2-propanol (0.6 mmol, 300 mol %) and the rubber septum was quickly replaced with a screw cap. The mixture was allowed to stir at the indicated temperature for the indicated time. The reaction mixture was then allowed to cool to room temperature. The solvents were removed *in vacuo* and the residue was subjected to column chromatography (SiO_2).

1-(4-bromophenyl)-2-(2,5-dimethyl-1*H*-pyrrol-1-yl)but-3-en-1-ol (3a).



In accordance with the general procedure at 125°C for 24 hours, the title compound was obtained in 83% yield (53.2 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 10% EtOAc/hexanes). Comparable yield and equivalent diastereoselectivity was observed when the reaction was conducted on 1 mmol scale (74% yield, dr = > 20:1) and from aldehyde oxidation level (70% yield, dr = > 20:1).

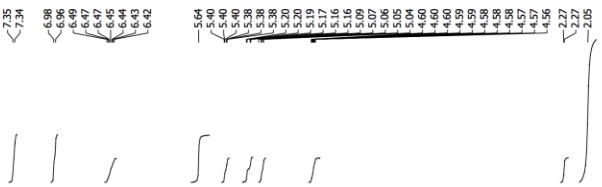
R_f =0.6 (20% EtOAc/Hexanes).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.32 (m, 2H), 7.00 – 6.94 (m, 2H), 6.45 (ddd, *J* = 16.9, 10.5, 6.2 Hz, 1H), 5.64 (s, 2H), 5.39 (dt, *J* = 10.5, 1.5 Hz, 1H), 5.18 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.05 (dd, *J* = 9.5, 2.5 Hz, 1H), 4.58 (ddt, *J* = 9.6, 6.3, 1.7 Hz, 1H), 2.27 (d, *J* = 2.8 Hz, 1H), 2.05 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.19, 134.43, 131.38, 127.92, 127.75, 122.03, 119.91, 106.88, 73.51, 64.18, 14.36.

HRMS (ESI) Calcd. for $C_{16}H_{19}BrNO$ $[M+H]^+$: 320.0645, Found: 320.0643.

FTIR (neat): 3462, 2921, 2360, 1486, 1395, 1292, 1072, 1010, 929, 816, 757 cm^{-1}.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5.07
5.06
5.05
5.04
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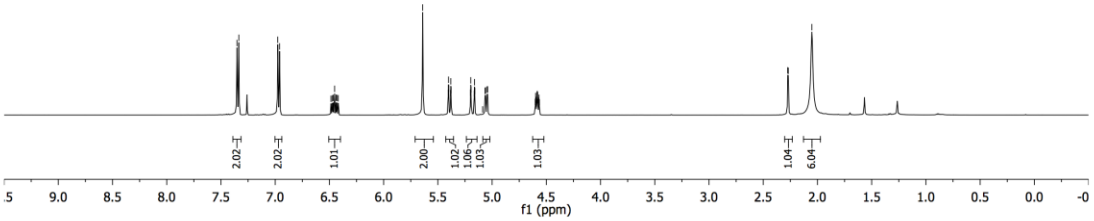
2.05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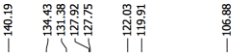
f1 (ppm)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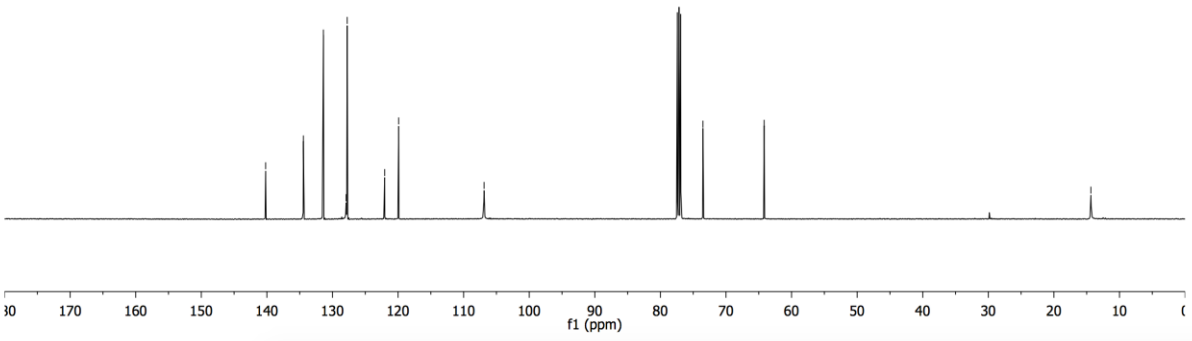
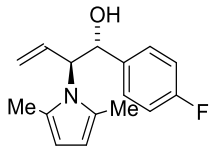
64.18
14.36


f1 (ppm)

2-(2,5-dimethyl-1*H*-pyrrol-1-yl)- 1-(4-fluorophenyl)but-3-en-1-ol (3b).



In accordance with the general procedure at 125°C for 24 hours, the title compound was obtained in 75% yield (38.9 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 10% EtOAc/hexanes).

R_f=0.41 (20% EtOAc/Hexanes)

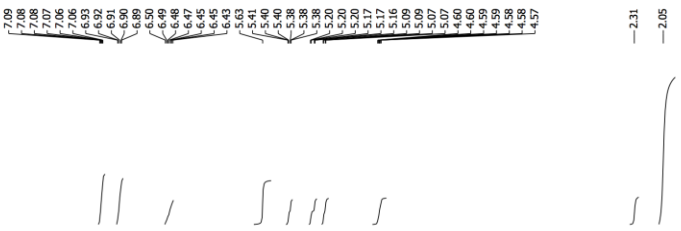
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.03 (m, 2H), 6.91 (t, *J* = 8.7 Hz, 2H), 6.47 (ddd, *J* = 16.9, 10.4, 6.1 Hz, 1H), 5.63 (s, 2H), 5.39 (dd, *J* = 10.4, 1.5 Hz, 1H), 5.18 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.08 (dd, *J* = 9.5, 2.1 Hz, 1H), 4.62 – 4.54 (m, 1H), 2.31 (d, *J* = 2.7 Hz, 1H), 2.05 (s, 6H).

^{19}F NMR (100 MHz, $CDCl_3$) δ -114.2.

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, $J_{C\text{-}F}$ = 246.2 Hz), 136.9 (d, $J_{C\text{-}F}$ = 3.2 Hz), 134.6, 127.9, 127.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 119.7, 115.2 (d, $J_{C\text{-}F}$ = 21.4 Hz), 106.8, 73.5, 64.4, 14.3.

HRMS (ESI) Calcd. for $C_{16}H_{19}FNO^+$ $[M+H]^+$: 260.1451, Found: 260.1445.

FTIR (neat): 3439, 2970, 2929, 1739, 1604, 1509, 1395, 1292, 1221, 1043, 854, 834, 752 cm^{-1}.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6.48
6.47
6.45
6.45
6.43
5.63
5.41
5.40
5.40
5.38
5.38
5.20
5.20
5.17
5.17
5.16
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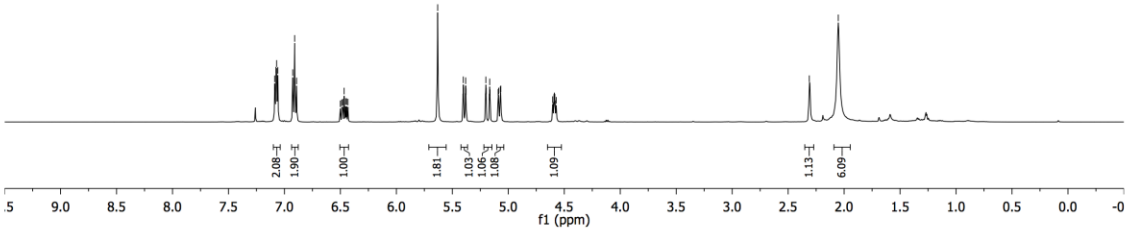
2.05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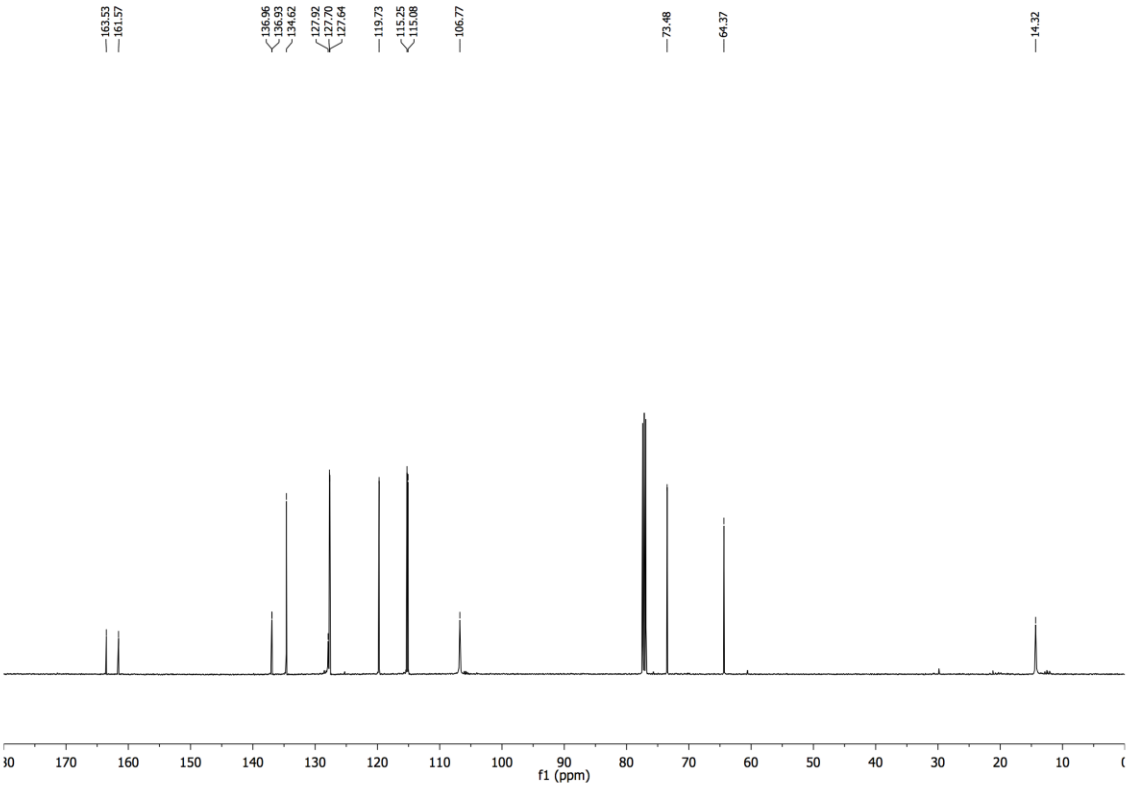
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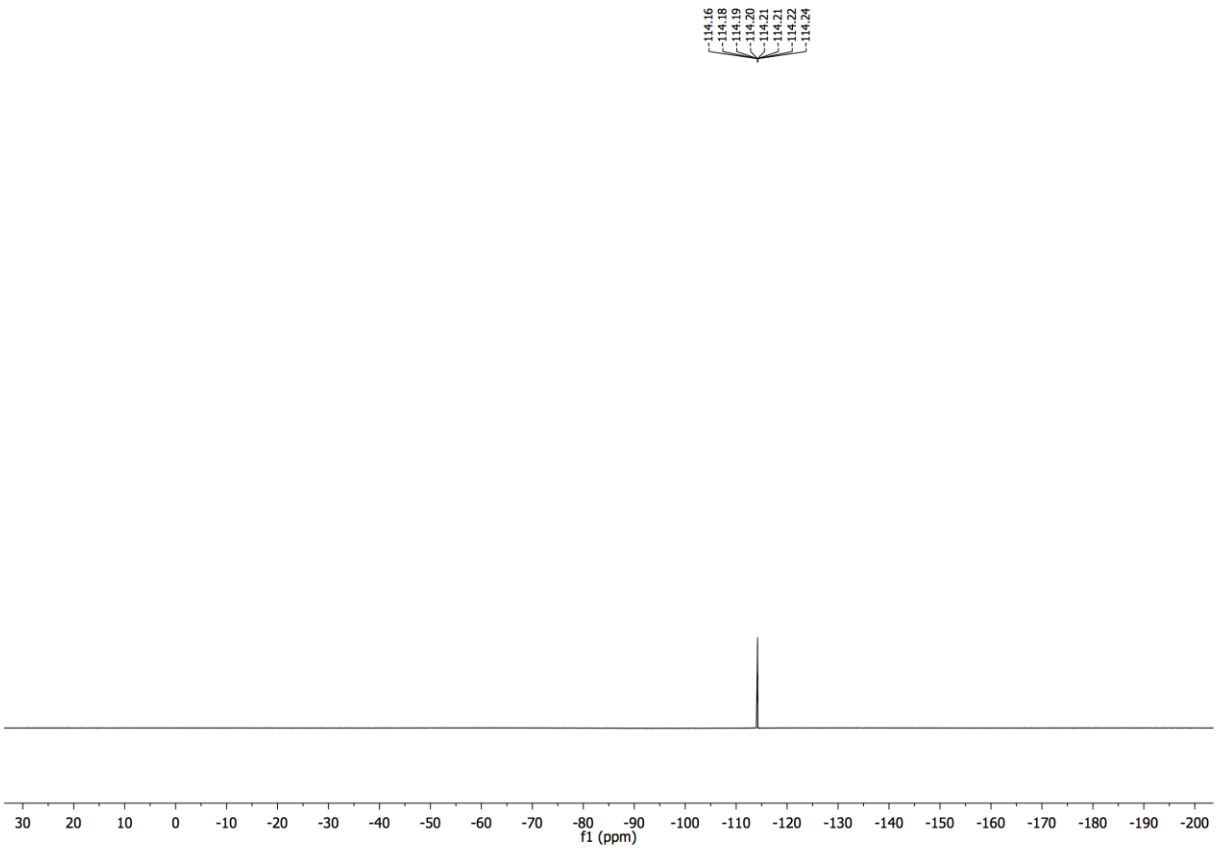
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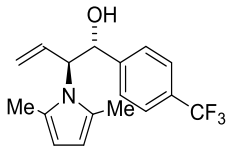
f1 (ppm)

2-(2,5-dimethyl-1H-pyrrol-1-yl)-1-(4-(trifluoromethyl)phenyl)but-3-en-1-ol (3c).



In accordance with the general procedure at 125°C for 24 hours, the title compound was obtained in 96% yield (59.4 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 10% EtOAc/hexanes).

R_f=0.40 (20% EtOAc/Hexanes)

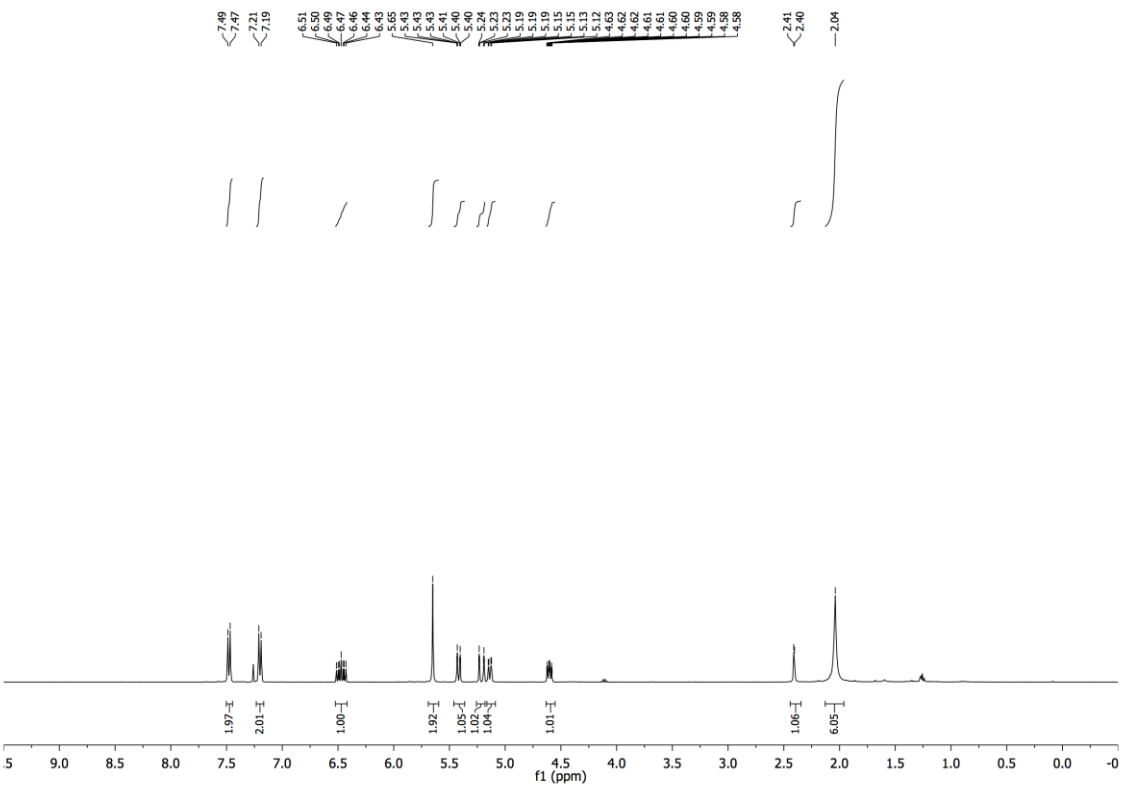
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.47 (ddd, *J* = 17.0, 10.4, 6.3 Hz, 1H), 5.65 (s, 2H), 5.42 (dt, *J* = 10.5, 1.4 Hz, 1H), 5.21 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.14 (dd, *J* = 9.5, 2.3 Hz, 1H), 4.64 – 4.57 (m, 1H), 2.41 (d, *J* = 2.8 Hz, 1H), 2.04 (s, 6H).

^{19}F NMR (100 MHz, $CDCl_3$) δ -62.5.

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 134.2, 130.2 (q, J_{C-F} = 32.4 Hz), 128.0, 126.4, 125.2 (q, J_{C-F} = 3.8 Hz), 124.2 (q, J_{C-F} = 272.0 Hz), 120.2, 107.0, 73.5, 64.2, 14.3.

HRMS (ESI) Calcd. for $C_{17}H_{19}F_3NO^+$ $[M+H]^+$: 310.1419, Found: 310.1415.

FTIR (neat): 3462, 2970, 1739, 1395, 1324, 1164, 1123, 1068, 928, 836, 759 cm^{-1}.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1.04
1.01
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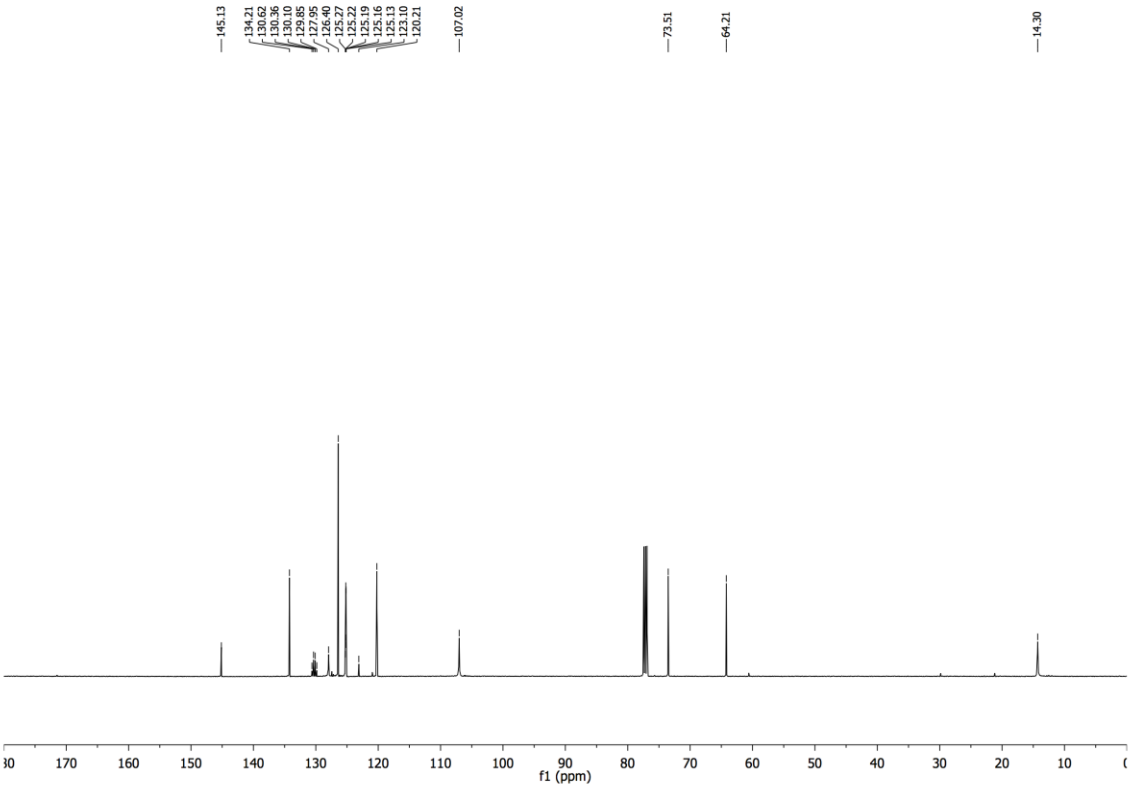
f1 (ppm)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73.51
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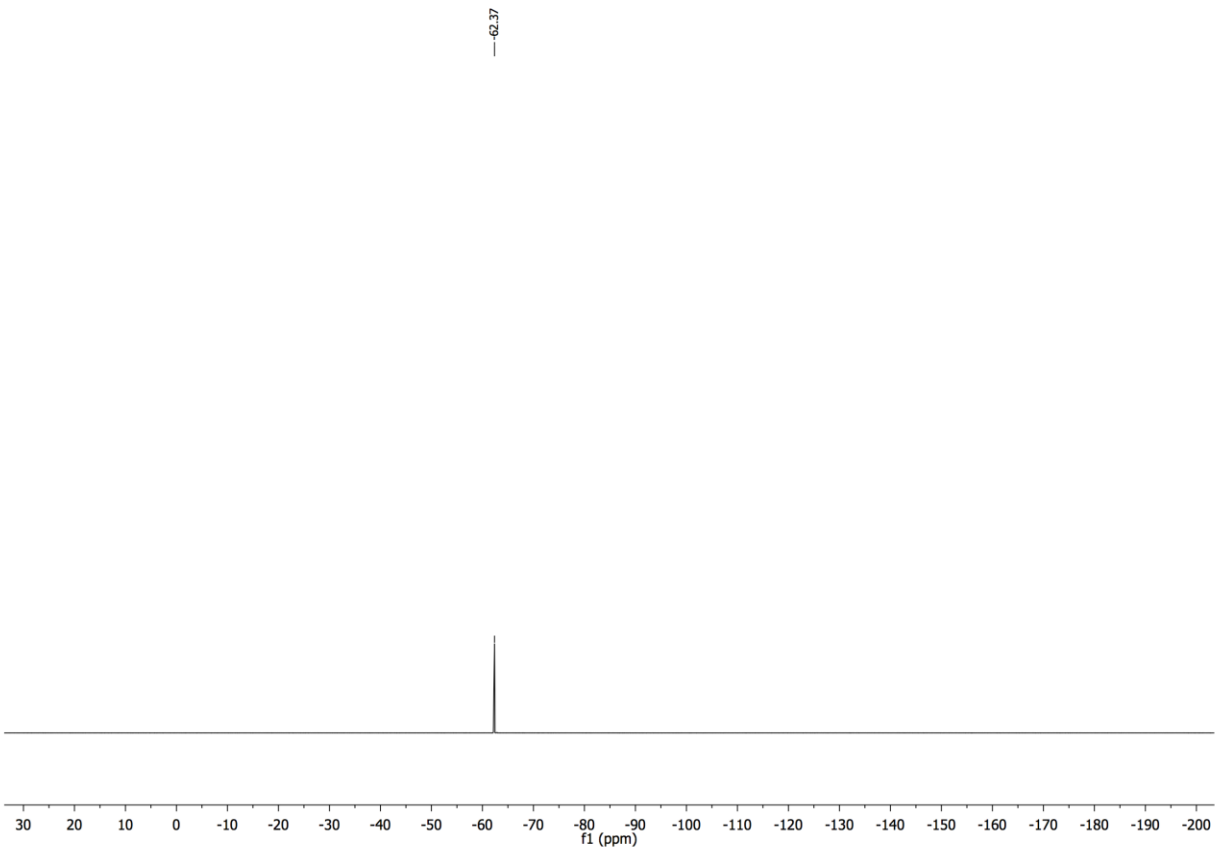
14.30
f1 (ppm)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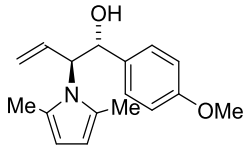
f1 (ppm)

2-(2,5-dimethyl-1H-pyrrol-1-yl)-1-(4-methoxyphenyl)but-3-en-1-ol (3d).



In accordance with the general procedure at 125°C for 24 hours, the title compound was obtained in 50% yield (27.1 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 10% EtOAc/hexanes).

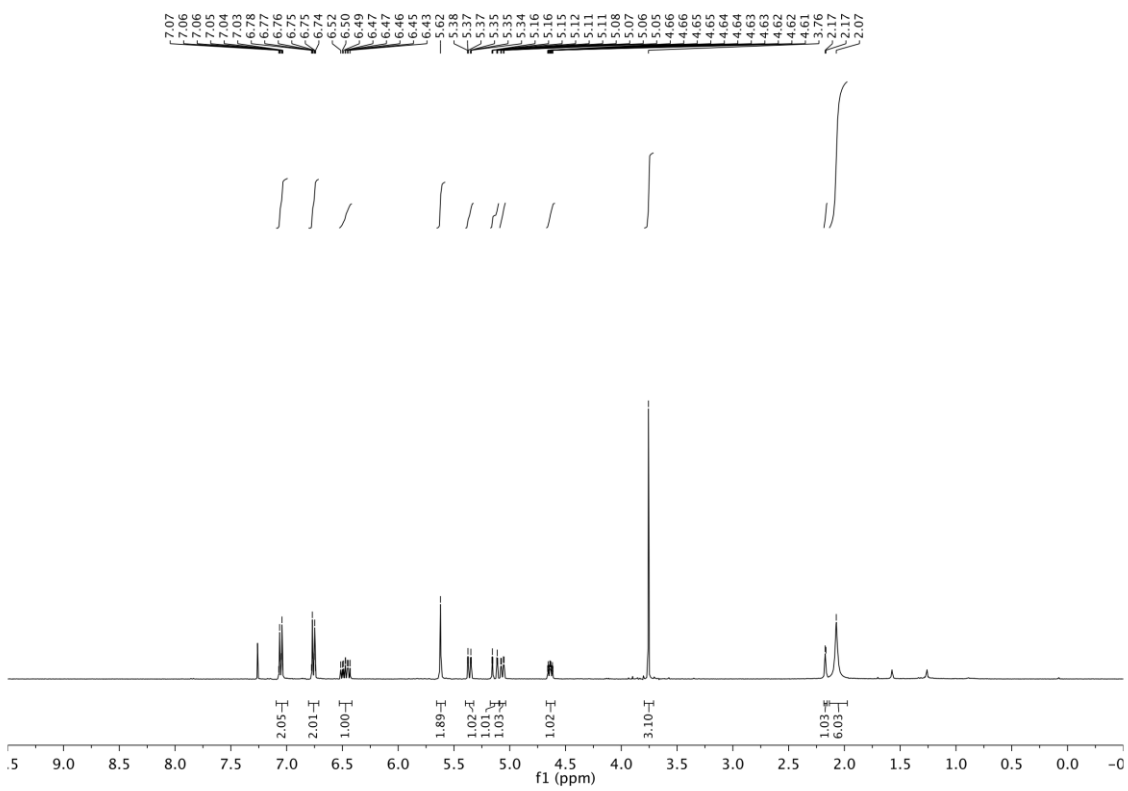
R_f=0.29 (20% EtOAc/Hexanes)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 7.02 (m, 2H), 6.79 – 6.73 (m, 2H), 6.47 (ddd, *J* = 17.2, 10.4, 6.0 Hz, 1H), 5.62 (s, 2H), 5.36 (dt, *J* = 10.4, 1.5 Hz, 1H), 5.13 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.07 (dd, *J* = 9.4, 2.2 Hz, 1H), 4.64 (ddt, *J* = 9.4, 5.9, 1.7 Hz, 1H), 3.76 (s, 3H), 2.17 (d, *J* = 2.6 Hz, 1H), 2.07 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 135.0, 133.4, 128.0, 127.2, 119.2, 113.7, 106.5, 73.9, 64.3, 55.3, 14.4.

HRMS (ESI) Calcd. for $C_{17}H_{21}NO_2Na^+$ $[M+Na]^+$: 294.1470, Found: 294.1452.

FTIR (neat): 3458, 2970, 1738, 1612, 1512, 1396, 1373, 1243, 1036, 925, 828, 750 cm^{-1}.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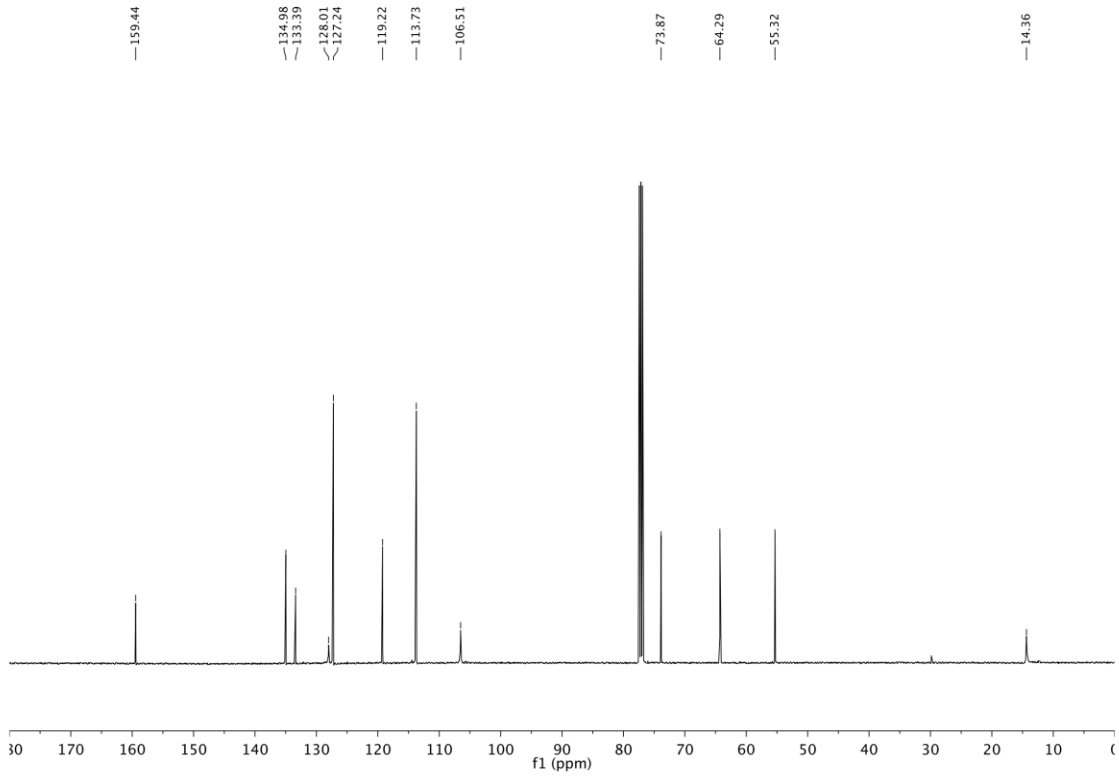
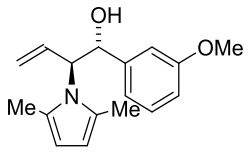
1.03
6.03
f1 (ppm)


159.44
134.98
133.39
128.01
127.24
119.22
113.73
106.51
73.87
64.29
55.32
14.36
f1 (ppm)

2-(2,5-dimethyl-1H-pyrrol-1-yl)-1-(3-methoxyphenyl)but-3-en-1-ol (3e).



In accordance with the general procedure at 125°C for 24 hours, the title compound was obtained in 71% yield (38.5 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 7.5-10% EtOAc/hexanes).

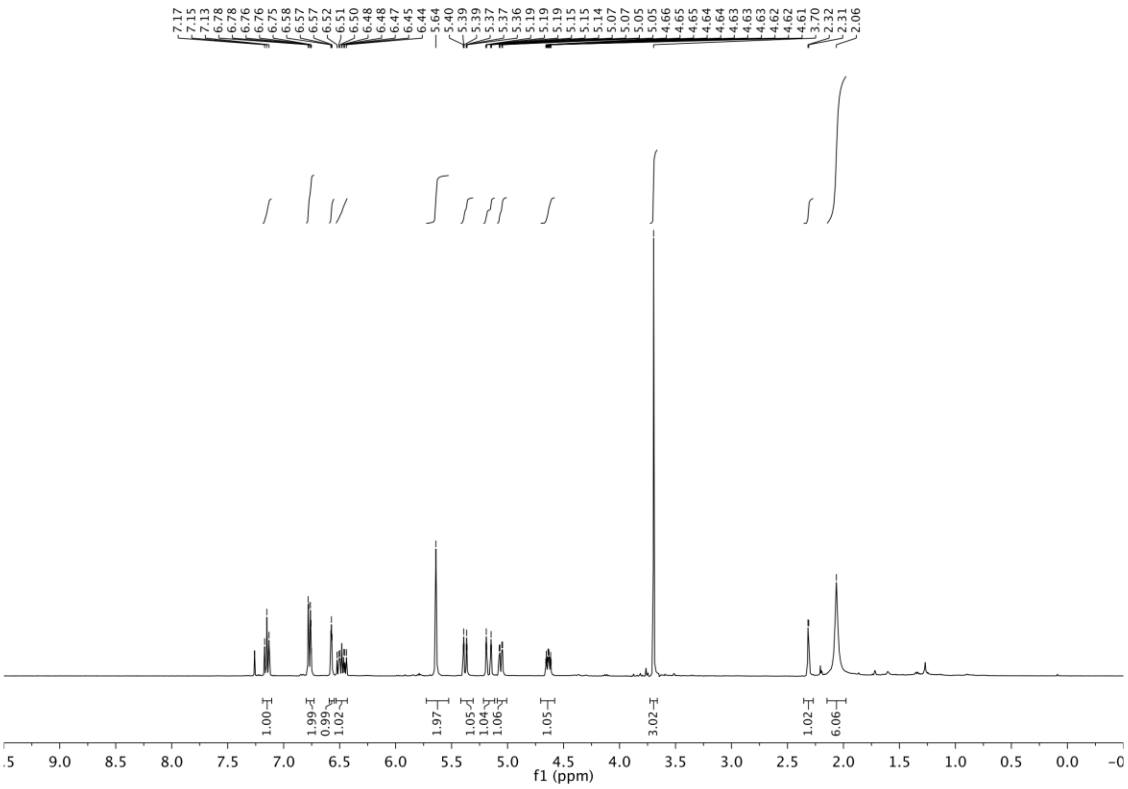
R_f =0.37 (20% EtOAc/Hexanes)

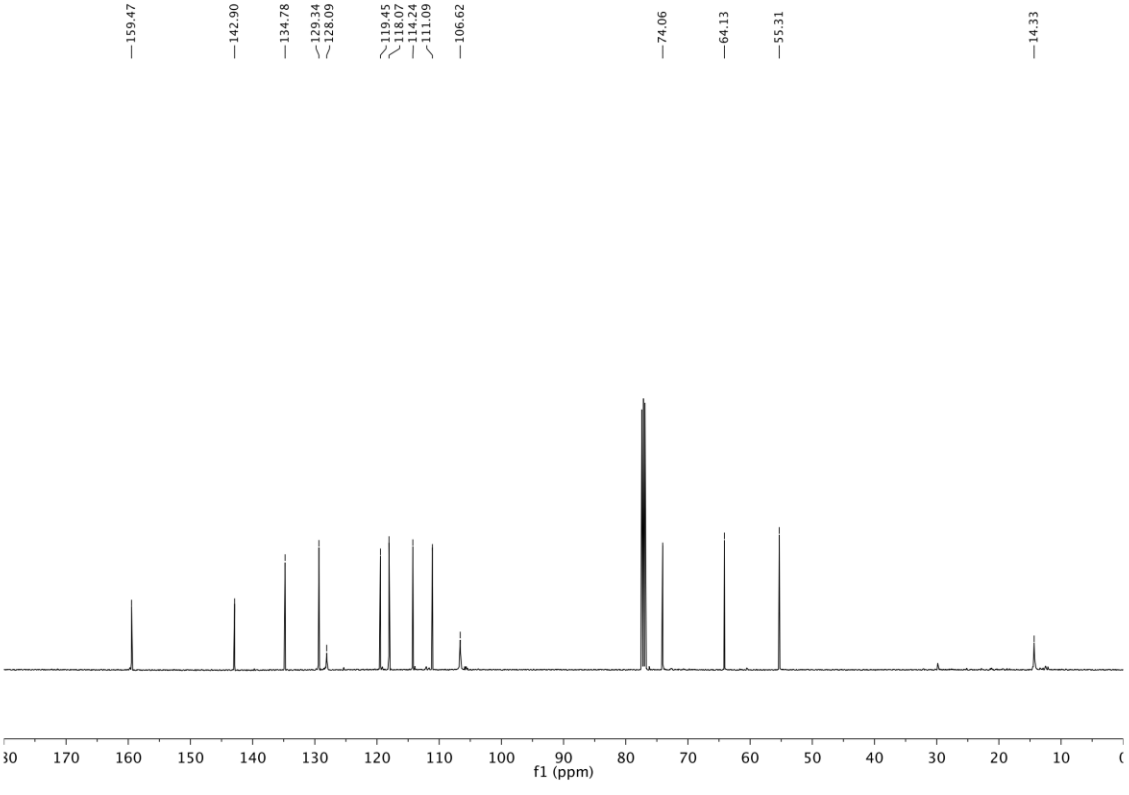
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.9 Hz, 1H), 6.77 (dd, *J* = 8.0, 2,2 Hz, 2H), 6.57 (t, *J* = 2.1 Hz, 1H), 6.48 (ddd, *J* = 17.3, 10.5, 6.0 Hz, 1H), 5.64 (s, 2H), 5.38 (dt, *J* = 10.5, 1.5 Hz, 1H), 5.17 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.06 (dd, *J* = 9.4, 2.5 Hz, 1H), 4.63 (ddt, *J* = 9.4, 6.1, 1.7 Hz, 1H), 3.70 (s, 3H), 2.31 (d, *J* = 2.8 Hz, 1H), 2.06 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 142.9, 134.8, 129.3, 128.1, 119.5, 118.1, 114.2, 111.1, 106.6, 74.1, 64.1, 55.3, 14.3.

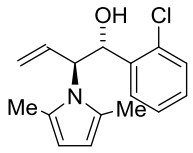
HRMS (ESI) Calcd. for $C_{17}H_{21}NO_2Na^+$ $[M+Na]^+$: 294.1470, Found: 294.1457.

FTIR (neat): 3464, 2934, 1739, 1602, 1455, 1395, 1290, 1256, 1156, 1038, 925, 750, 698 cm^{-1}.


7.17
7.15
7.13
6.78
6.78
6.76
6.76
6.75
6.58
6.57
6.52
6.51
6.50
6.48
6.48
6.47
6.45
6.44
5.64
5.40
5.39
5.39
5.37
5.37
5.36
5.19
5.19
5.19
5.15
5.15
5.14
5.07
5.07
5.05
5.05
4.66
4.65
4.65
4.64
4.64
4.63
4.63
4.62
4.62
4.61
3.70
2.32
2.31
2.06
1.00
1.99
0.99
1.02
1.97
1.05
1.04
1.06
1.05
3.02
1.02
6.06
f1 (ppm)


159.47
142.90
134.78
129.34
128.09
119.45
118.07
114.24
111.09
106.62
74.06
64.13
55.31
14.33
f1 (ppm)

1-(2-chlorophenyl)-2-(2,5-dimethyl-1H-pyrrol-1-yl)but-3-en-1-ol (3f).



In accordance with the general procedure at 125°C for 24 hours, the title compound was obtained in 86% yield (47.4 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 8% EtOAc/hexanes).

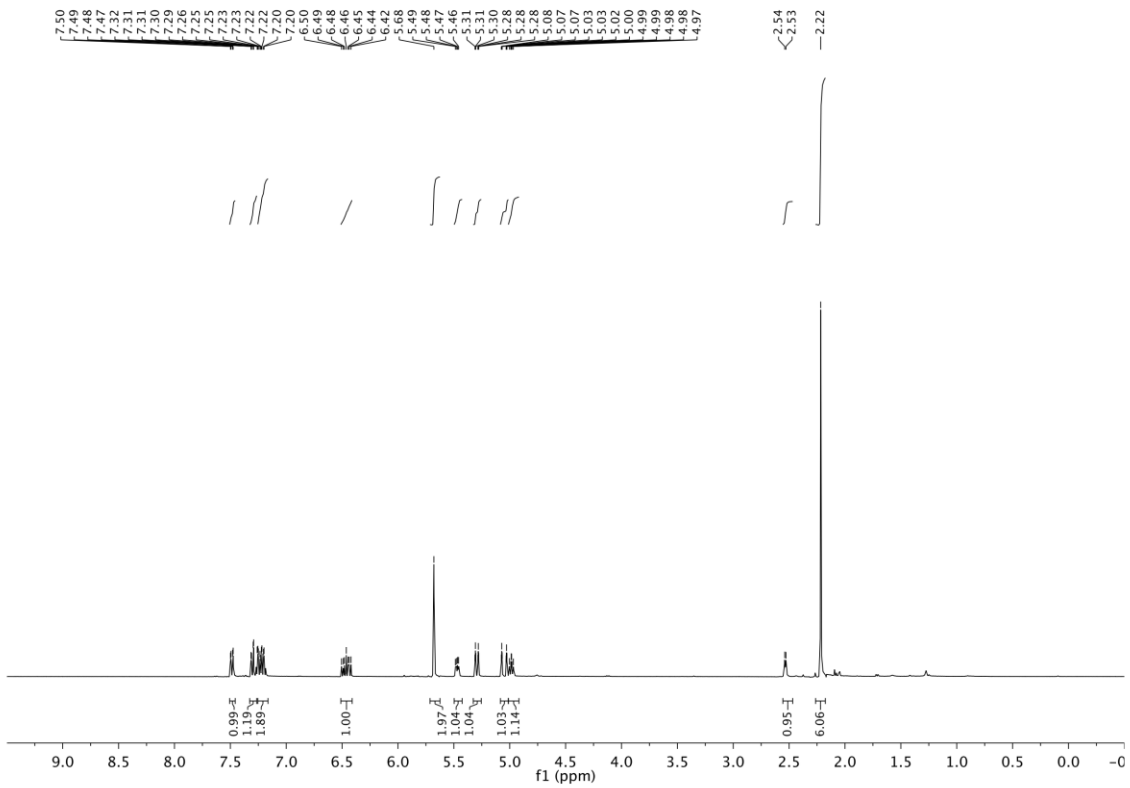
R_f=0.43 (20% EtOAc/Hexanes)

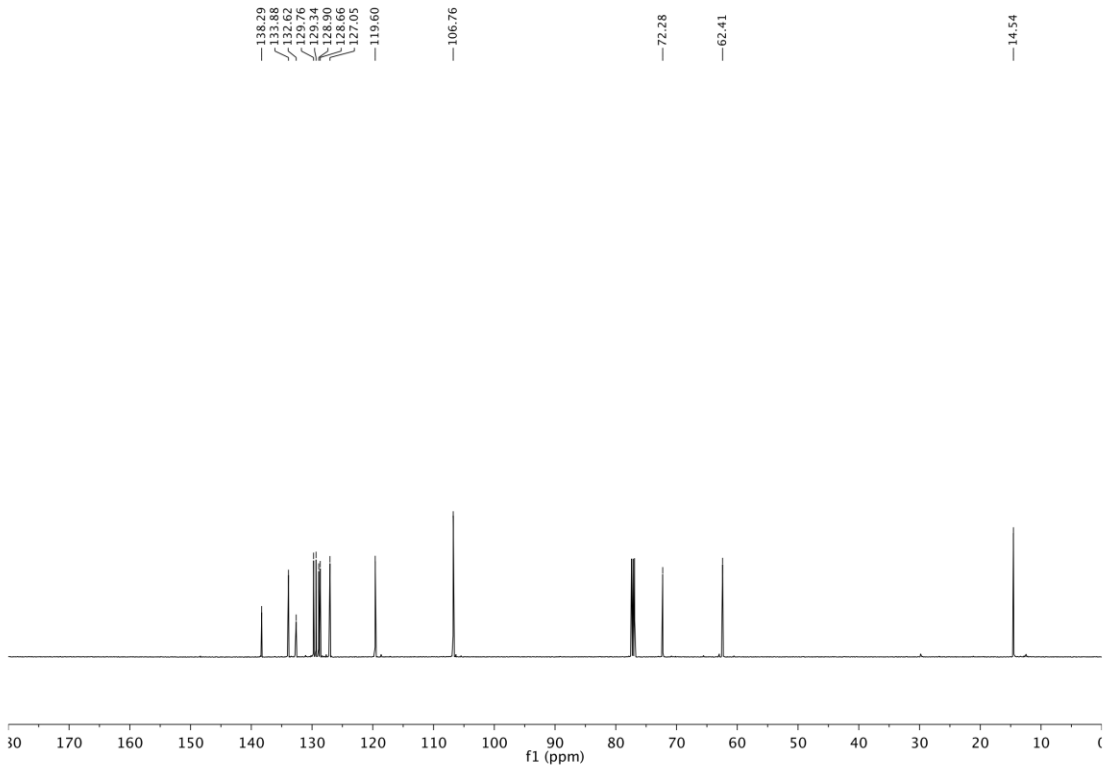
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.30 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.33 – 7.17 (m, 2H), 6.46 (ddd, *J* = 17.0, 10.4, 6.5 Hz, 1H), 5.67 (s, 2H), 5.47 (dd, *J* = 7.9, 3.7 Hz, 1H), 5.29 (dt, *J* = 10.4, 1.4 Hz, 1H), 5.05 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.01 – 4.94 (m, 1H), 2.53 (d, *J* = 4.2 Hz, 1H), 2.22 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 133.9, 132.6, 129.8, 129.3, 128.9, 128.7, 127.1, 119.6, 106.8, 72.3, 62.4, 14.5.

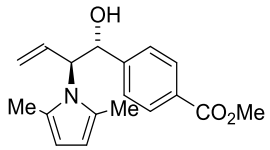
HRMS (ESI) Calcd. for $C_{16}H_{19}ClNO^+$ $[M+H]^+$: 276.1155, Found: 276.1147.

FTIR (neat): 3446, 2970, 1739, 1439, 1393, 1287, 1239, 1034, 927, 751 cm^{-1}.


7.50
7.49
7.48
7.47
7.32
7.31
7.31
7.30
7.29
7.26
7.25
7.25
7.23
7.23
7.22
7.22
7.20
7.20
6.50
6.49
6.48
6.46
6.45
6.44
6.42
5.68
5.49
5.48
5.47
5.46
5.31
5.31
5.30
5.28
5.28
5.28
5.08
5.07
5.07
5.03
5.02
5.00
4.99
4.99
4.98
4.98
4.97
2.54
2.53
2.22
0.99
1.19
1.89
1.00
1.97
1.04
1.04
1.03
1.14
0.95
6.06
f1 (ppm)


138.29
133.88
132.62
129.76
129.34
128.90
128.66
127.05
119.60
106.76
72.28
62.41
14.54
f1 (ppm)

methyl 4-(2-(2,5-dimethyl-1H-pyrrol-1-yl)-1-hydroxybut-3-en-1-yl)benzoate (3g)



In accordance with the general procedure at 125°C for 24 hours, the title compound was obtained in 73% yield (43.7 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 7.5%-15% EtOAc/hexanes).

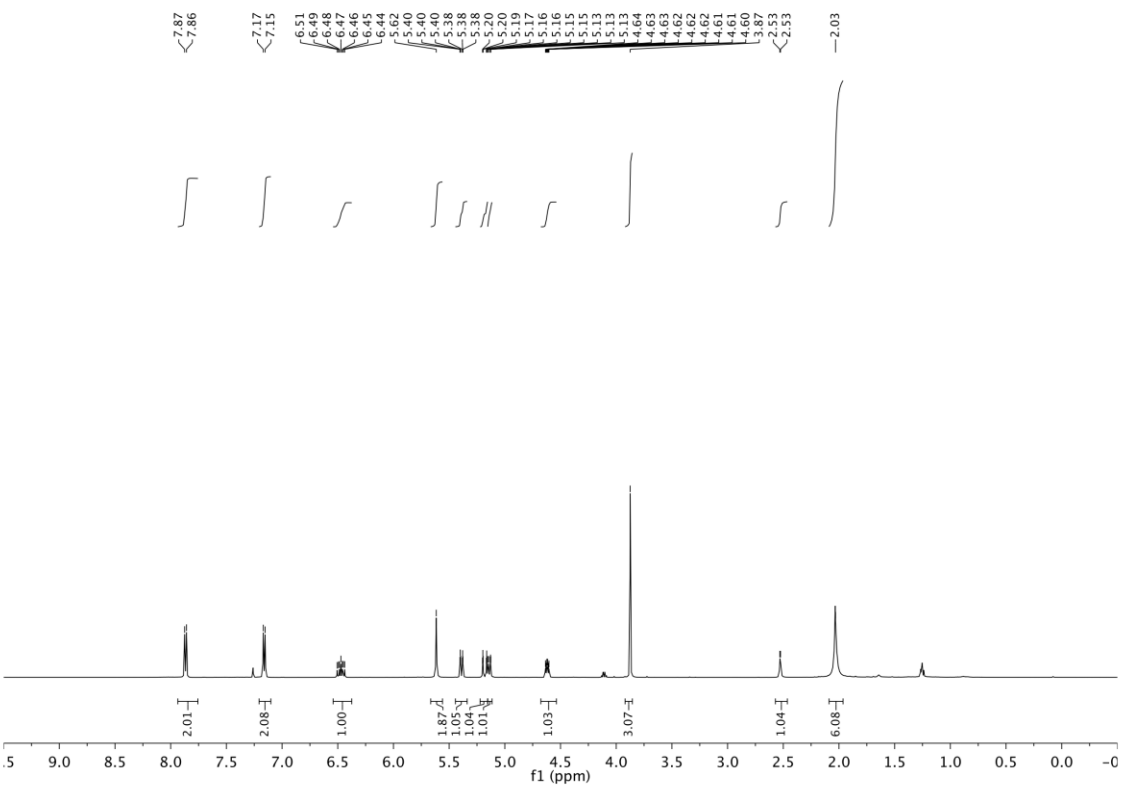
R_f=0.22 (20% EtOAc/Hexanes)

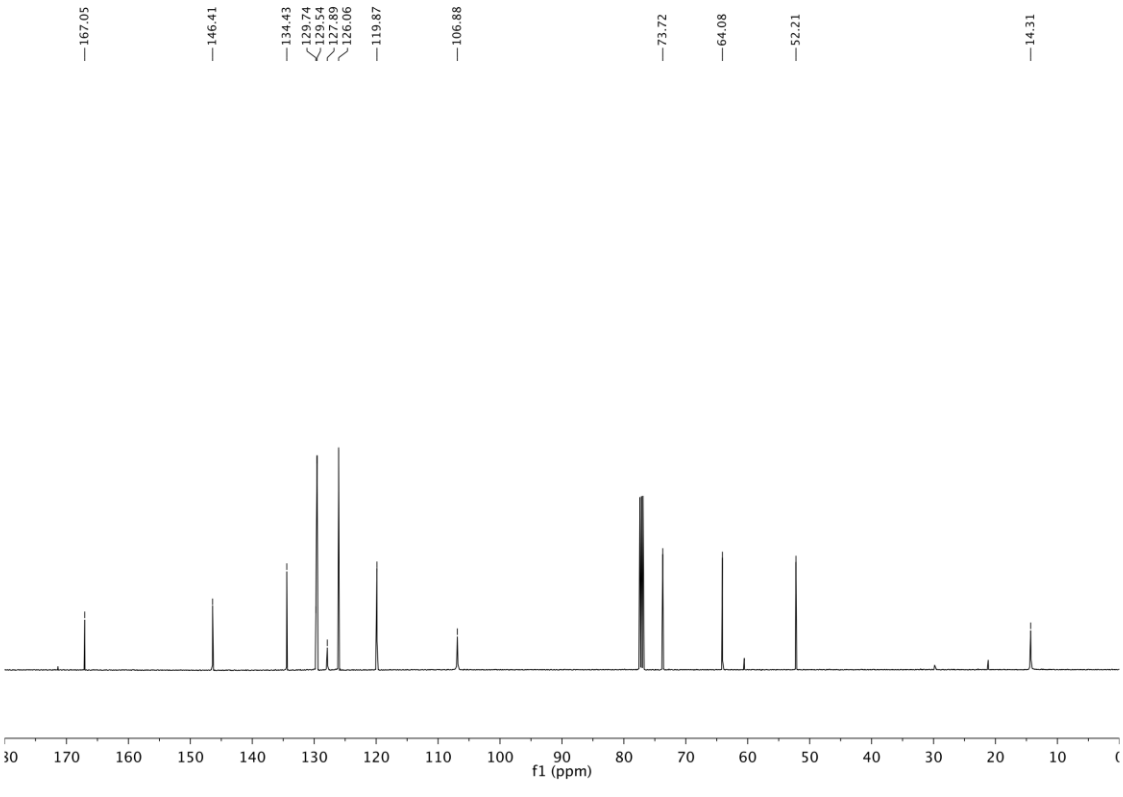
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.19 – 7.13 (m, 2H), 6.47 (ddd, *J* = 16.9, 10.5, 6.1 Hz, 1H), 5.62 (s, 2H), 5.39 (dt, *J* = 10.5, 1.4 Hz, 1H), 5.18 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.14 (dd, *J* = 9.3, 2.1 Hz, 1H), 4.62 (ddt, *J* = 9.4, 6.2, 1.7 Hz, 1H), 3.87 (s, 3H), 2.53 (d, *J* = 2.9 Hz, 1H), 2.03 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 146.4, 134.4, 129.7, 129.5, 127.9, 126.1, 119.9, 106.9, 73.7, 64.1, 52.2, 14.3.

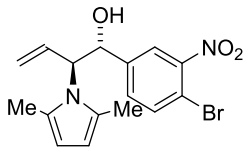
HRMS (ESI) Calcd. for $C_{18}H_{21}NO_3Na^+$ $[M+Na]^+$: 322.1419, Found: 322.1414.

FTIR (neat): 3461, 2952, 2359, 1738, 1707, 1697, 1395, 1281, 1111, 1040, 920, 760, 704 cm^{-1}.


7.87
7.86
7.17
7.15
6.51
6.49
6.48
6.47
6.46
6.45
6.44
5.62
5.40
5.40
5.40
5.38
5.38
5.38
5.20
5.20
5.19
5.17
5.16
5.16
5.15
5.15
5.13
5.13
5.13
4.64
4.63
4.63
4.62
4.62
4.62
4.61
4.61
4.60
3.87
2.53
2.53
2.03
2.01
2.08
1.00
1.87
1.05
1.04
1.01
1.03
3.07
1.04
6.08
f1 (ppm)


167.05
146.41
134.43
129.74
129.54
127.89
126.06
119.87
106.88
73.72
64.08
52.21
14.31
f1 (ppm)

1-(4-bromo-3-nitrophenyl)-2-(2,5-dimethyl-1H-pyrrol-1-yl)but-3-en-1-ol (3h).



In accordance with the general procedure at 125°C for 24 hours, the title compound was obtained in 73% yield (53.3 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 7.5%-12.5% EtOAc/hexanes).

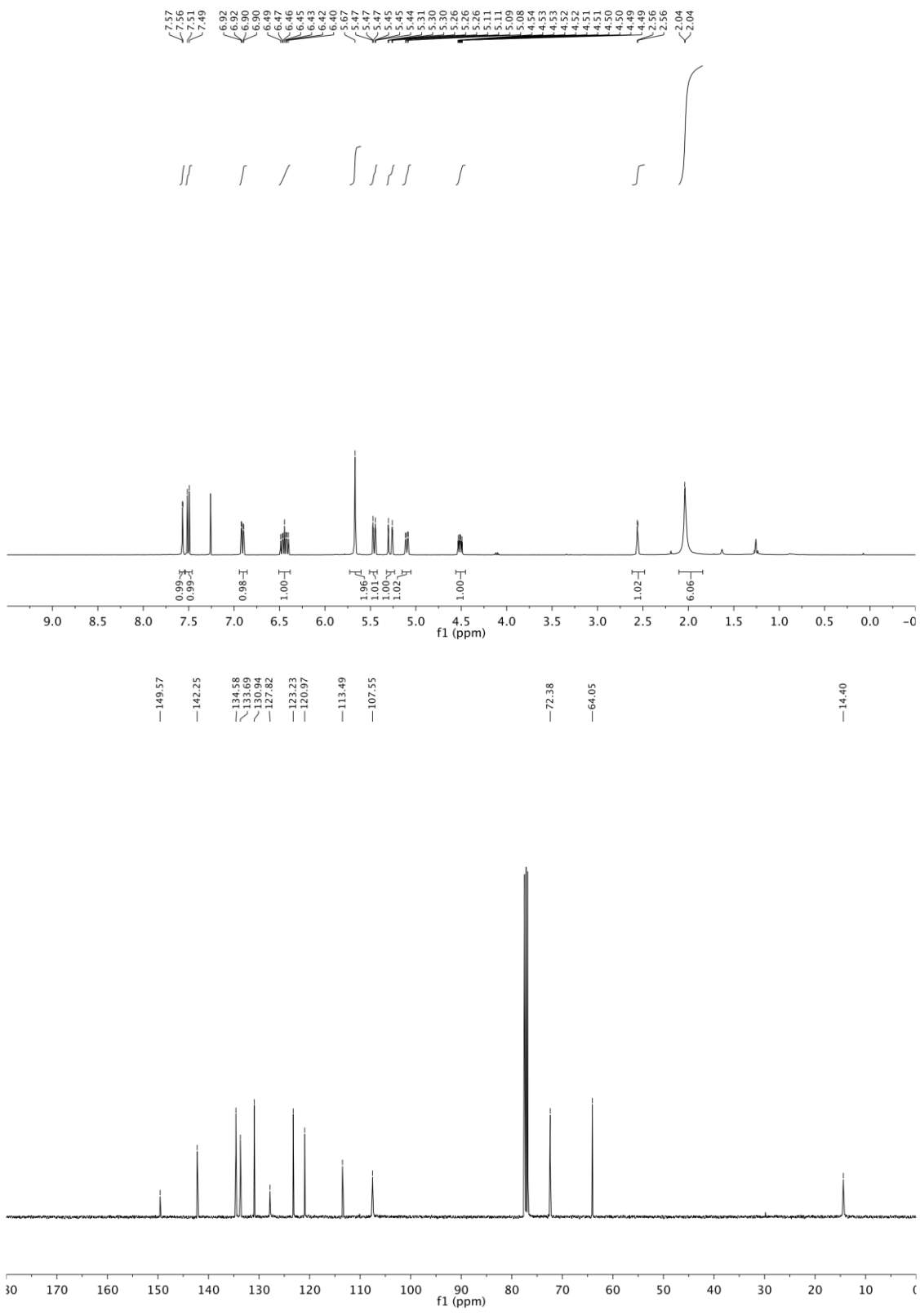
R_f =0.28 (20% EtOAc/Hexanes)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.1 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 6.91 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.45 (ddd, *J* = 17.1, 10.4, 6.5 Hz, 1H), 5.67 (s, 2H), 5.46 (dt, *J* = 10.4, 1.3 Hz, 1H), 5.28 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.10 (dd, *J* = 9.7, 2.4 Hz, 1H), 4.51 (ddt, *J* = 9.6, 6.5, 1.6 Hz, 1H), 2.56 (d, *J* = 2.8 Hz, 1H), 2.04 (s, 6H).

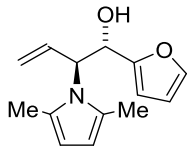
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 142.3, 134.6, 133.7, 130.9, 127.8, 123.2, 121.0, 113.5, 107.6, 72.4, 64.1, 14.4.

HRMS (ESI) Calcd. for $C_{16}H_{17}BrN_2O_3Na^+$ $[M+Na]^+$: 387.0320, Found: 387.0304.

FTIR (neat): 3458, 2978, 2928, 1736, 1707, 1536, 1393, 1373, 1357, 1291, 1243, 1044, 1031, 930, 823, 752 cm^{-1}.


7.57
7.56
7.51
7.49
6.92
6.92
6.90
6.90
6.49
6.47
6.46
6.45
6.43
6.42
6.40
5.67
5.47
5.47
5.47
5.45
5.45
5.44
5.31
5.30
5.30
5.26
5.26
5.16
5.11
5.11
5.09
5.08
4.54
4.53
4.53
4.52
4.52
4.51
4.51
4.50
4.50
4.49
4.49
2.56
2.56
2.04
2.04
0.99
0.99
0.98
1.00
1.96
1.01
1.00
1.02
1.00
1.02
6.06
f1 (ppm)
149.57
142.25
134.58
133.69
130.94
127.82
123.23
120.97
113.49
107.55
72.38
64.05
14.40
f1 (ppm)

2-(2,5-dimethyl-1H-pyrrol-1-yl)-1-(furan-2-yl)but-3-en-1-ol (3i).



In accordance with the general procedure at 125°C for 24 hours with 2-PrOH (200 mol%), the title compound was obtained in 71% yield (32.8 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 10% EtOAc/hexanes).

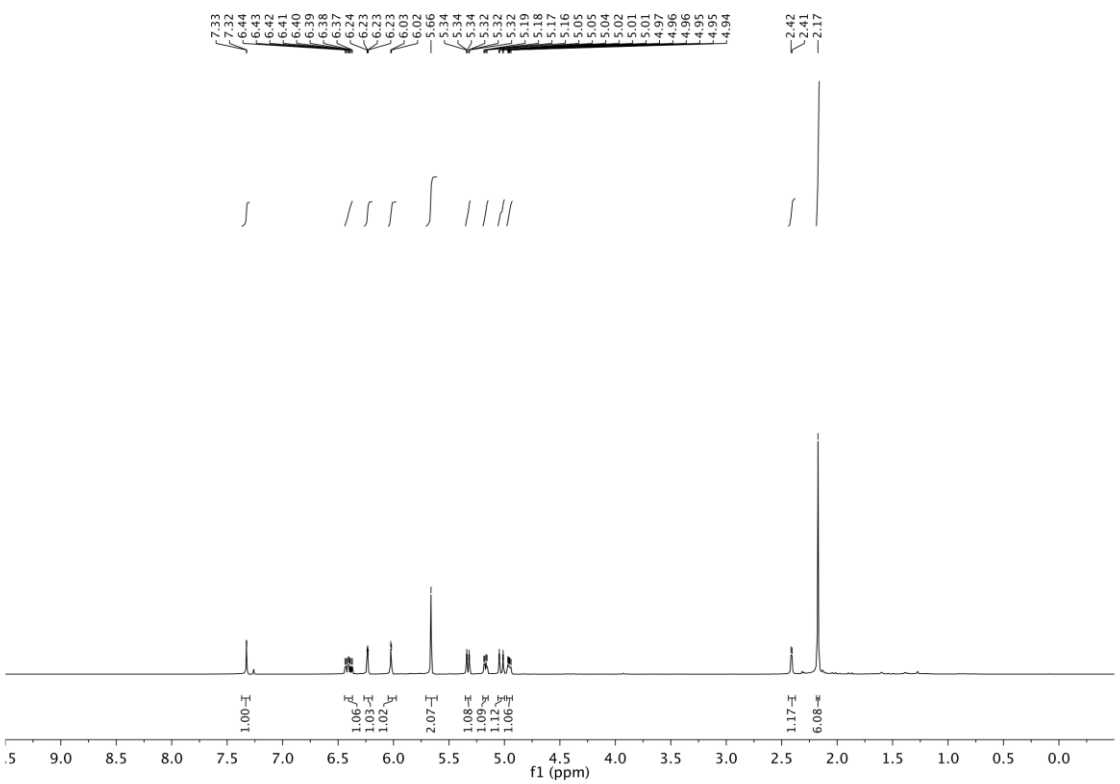
R_f = 0.4 (20% EtOAc/Hexanes).

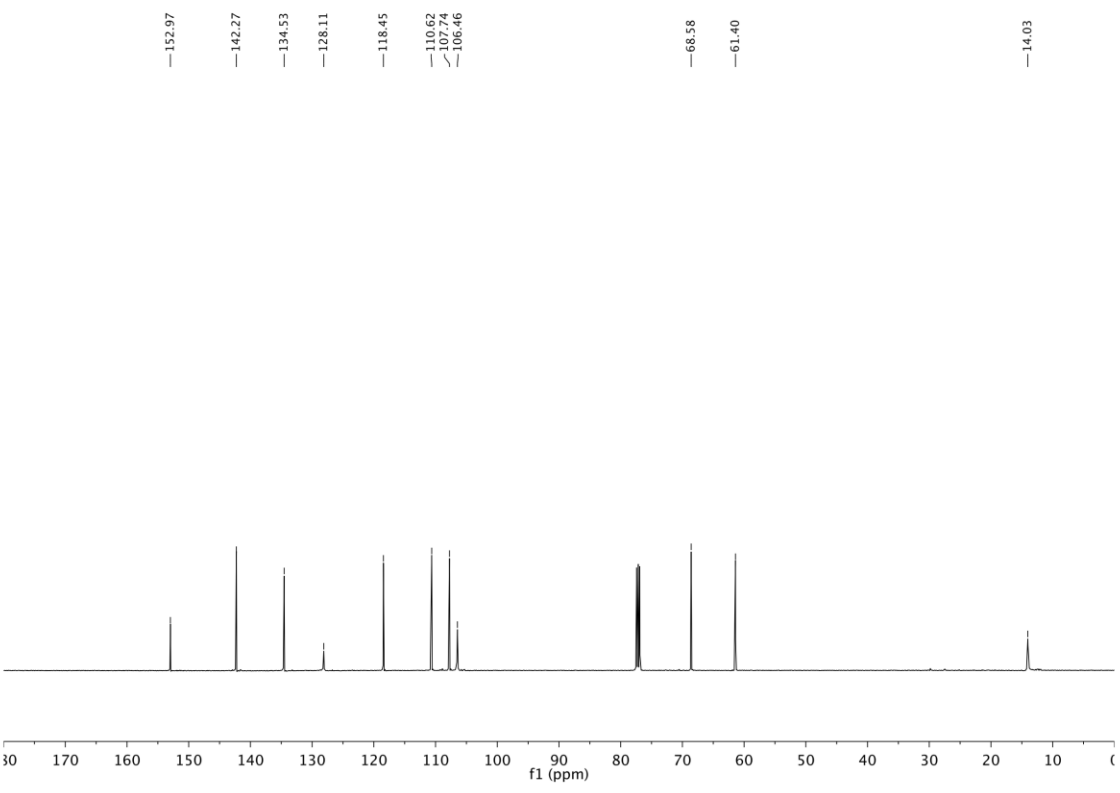
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 1.8 Hz, 1H), 6.40 (ddd, *J* = 17.3, 10.5, 5.0 Hz, 1H), 6.23 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.02 (d, *J* = 3.3 Hz, 1H), 5.66 (s, 2H), 5.33 (dt, *J* = 10.5, 1.6 Hz, 1H), 5.17 (dd, *J* = 9.7, 4.5 Hz, 1H), 5.03 (dt, *J* = 17.2, 1.6 Hz, 1H), 4.95 (ddt, *J* = 9.4, 4.7, 2.0 Hz, 1H), 2.41 (d, *J* = 4.7 Hz, 1H), 2.17 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 142.3, 134.5, 128.1, 118.4, 110.6, 107.7, 106.5, 68.6, 61.4, 14.0.

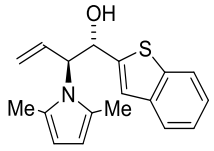
HRMS (ESI) Calcd. for $C_{14}H_{17}NaNO_2$ $[M+Na]^+$: 254.1151, Found: 254.1151.

FTIR (neat): 3429, 2926, 2360, 2342, 1934, 1397, 1292, 1150, 1011, 923, 822, 738 cm^{-1}.


7.33
7.32
6.44
6.43
6.42
6.41
6.40
6.39
6.38
6.37
6.24
6.23
6.23
6.23
6.03
6.02
5.66
5.34
5.34
5.34
5.32
5.32
5.32
5.19
5.18
5.17
5.16
5.05
5.04
5.02
5.01
5.01
4.97
4.96
4.96
4.95
4.95
4.94
2.42
2.41
2.17
1.00
1.06
1.03
1.02
2.07
1.08
1.09
1.12
1.06
1.17
6.08
f1 (ppm)


152.97
142.27
134.53
128.11
118.45
110.62
107.74
106.46
68.58
61.40
14.03
f1 (ppm)

1-(benzo[b]thiophen-2-yl)-2-(2,5-dimethyl-1H-pyrrol-1-yl)but-3-en-1-ol (3j).



In accordance with the general procedure at 125°C for 24 hours, the title compound was obtained in 87% yield (51.8 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 5%-10% EtOAc/hexanes).

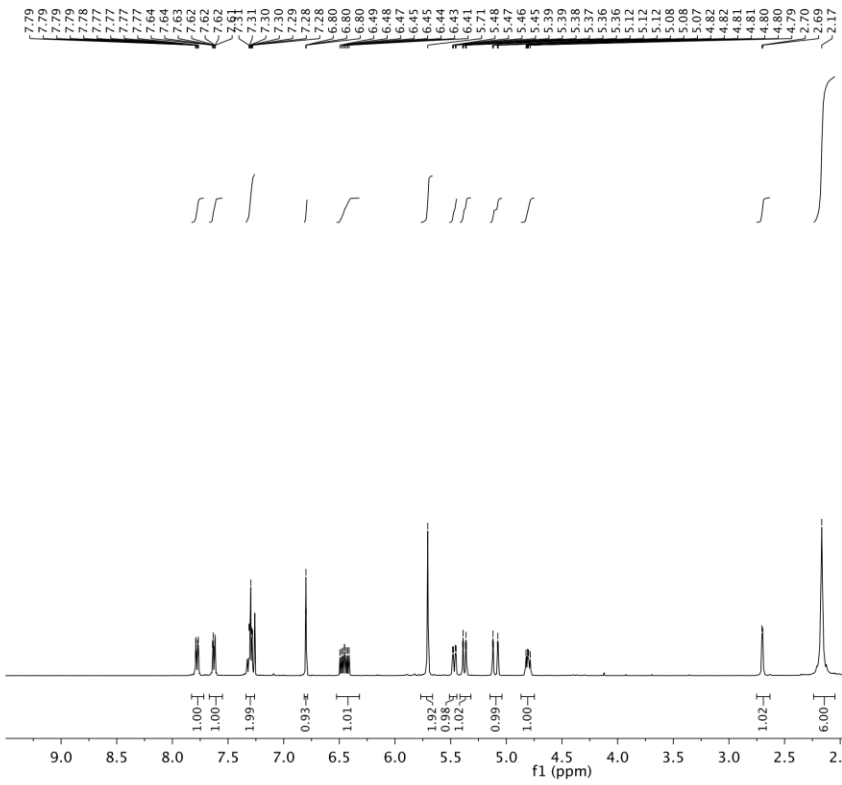
R_f =0.38 (20% EtOAc/Hexanes)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 1H), 7.67 – 7.59 (m, 1H), 7.34 – 7.25 (m, 2H), 6.80 (d, *J* = 0.9 Hz, 1H), 6.45 (ddd, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.71 (s, 2H), 5.47 (dd, *J* = 9.4, 3.1 Hz, 1H), 5.38 (dt, *J* = 10.5, 1.5 Hz, 1H), 5.10 (dt, *J* = 17.2, 1.5 Hz, 1H), 4.80 (ddt, *J* = 9.3, 5.6, 1.8 Hz, 1H), 2.70 (d, *J* = 3.4 Hz, 1H), 2.17 (s, 6H).

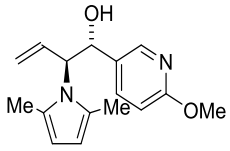
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 139.6, 139.3, 134.2, 128.3, 124.3, 123.7, 122.5, 121.3, 119.4, 106.9, 71.2, 63.7, 14.4.

HRMS (ESI) Calcd. for $C_{18}H_{20}NOS^+$ $[M+H]^+$: 298.1266, Found: 298.1255.

FTIR (neat): 3446, 2970, 1739, 1458, 1395, 1374, 1236, 1042, 928, 822, 745 cm^{-1}.


7.79 7.79 7.79 7.79 7.78 7.77 7.77 7.77 7.77 7.64 7.64 7.63 7.62 7.62 7.62 7.62 7.61 7.31 7.30 7.30 7.29 7.28 7.28 6.80 6.80 6.80 6.49 6.48 6.47 6.45 6.45 6.44 6.43 6.41 5.71 5.48 5.47 5.46 5.45 5.39 5.39 5.38 5.37 5.36 5.36 5.12 5.12 5.12 5.08 5.08 5.07 4.82 4.82 4.81 4.81 4.80 4.80 4.79 2.70 2.69 2.17
1.00 1.00 1.99 0.93 1.01 1.92 0.98 1.02 0.99 1.00 1.02 6.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
145.18 139.64 139.32 134.22 128.26 124.28 123.66 122.48 121.26 119.40 106.85 71.21 63.72 14.36
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

2-(2,5-dimethyl-1H-pyrrol-1-yl)-1-(6-methoxypyridin-3-yl)but-3-en-1-ol (3k).



In accordance with the general procedure at 125°C for 48 hours, the title compound was obtained in 70% yield (38.1 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 20% EtOAc/hexanes).

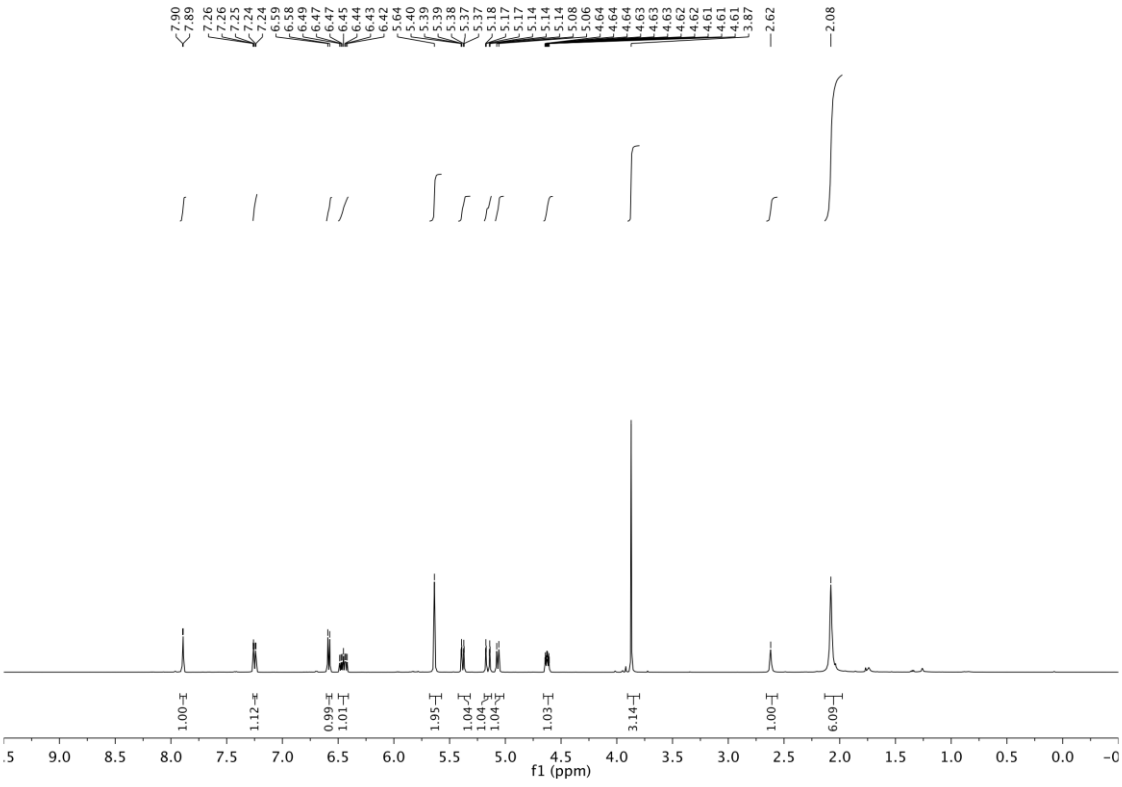
R_f = 0.13 (20% EtOAc/Hexanes).

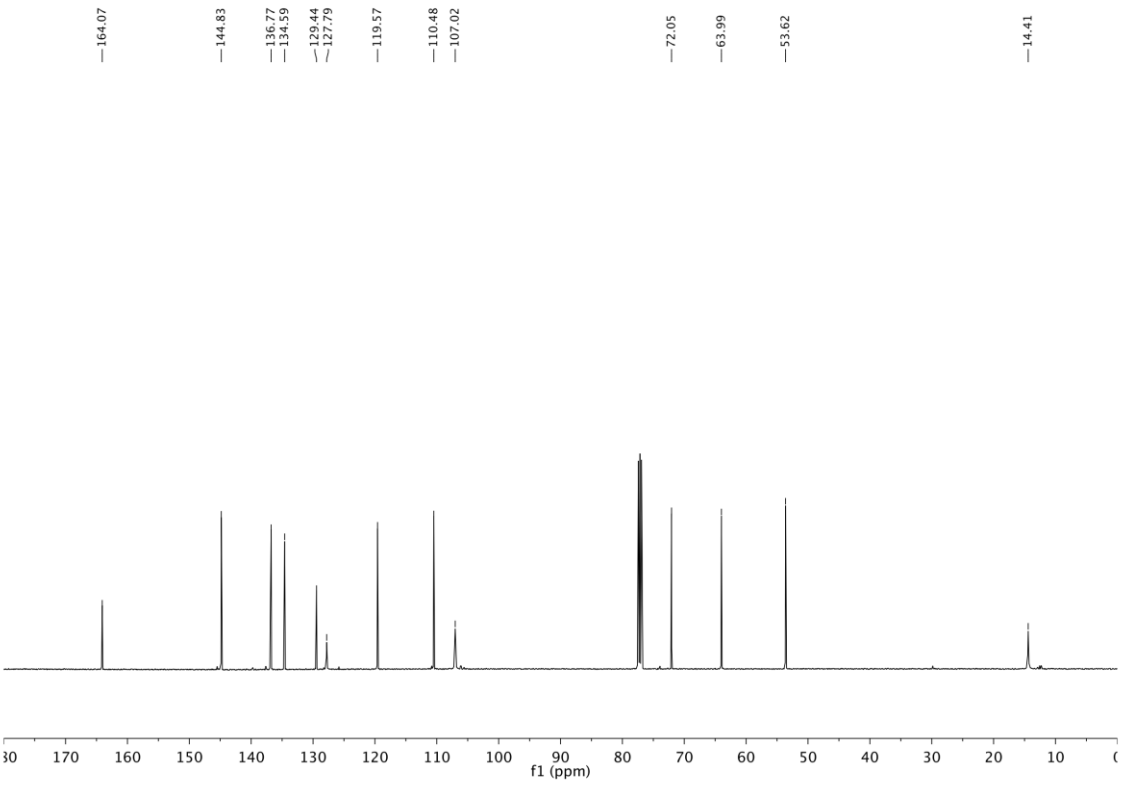
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 2.4 Hz, 1H), 7.25 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.58 (d, *J* = 8.6 Hz, 1H), 6.45 (ddd, *J* = 16.7, 10.5, 5.9 Hz, 1H), 5.64 (s, 2H), 5.38 (dt, *J* = 10.5, 1.5 Hz, 1H), 5.16 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.07 (d, *J* = 9.5 Hz, 1H), 4.63 (ddt, *J* = 9.5, 5.9, 1.7 Hz, 1H), 3.87 (s, 3H), 2.62 (s, 1H), 2.08 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 144.8, 136.8, 134.6, 129.4, 127.8, 119.6, 110.5, 107.0, 72.0, 64.0, 53.6, 14.4.

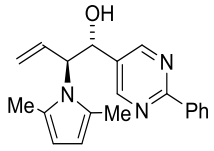
HRMS (ESI) Calcd. for $C_{16}H_{21}N_2O_2$ $[M+H]^+$: 273.1598, Found: 273.1603.

FTIR (neat): 3389, 2927, 2358, 1607, 1493, 1395, 1289, 1.24, 928, 829, 757 cm^{-1}.


7.90
7.89
7.26
7.26
7.25
7.24
7.24
6.59
6.58
6.49
6.47
6.47
6.45
6.44
6.43
6.42
5.40
5.39
5.39
5.38
5.37
5.37
5.18
5.17
5.17
5.14
5.14
5.08
5.06
4.64
4.64
4.64
4.63
4.63
4.62
4.62
4.61
4.61
4.61
3.87
2.62
2.08
1.00
1.12
0.99
1.01
1.95
1.04
1.04
1.04
1.03
3.14
1.00
6.09
f1 (ppm)


164.07
144.83
136.77
134.59
129.44
127.79
119.57
110.48
107.02
72.05
63.99
53.62
14.41
f1 (ppm)

2-(2,5-dimethyl-1H-pyrrol-1-yl)-1-(2-phenylpyrimidin-5-yl)but-3-en-1-ol (3l).



In accordance with the general procedure at 125°C for 24 hours, the title compound was obtained in 94% yield (60.0 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 20% EtOAc/hexanes).

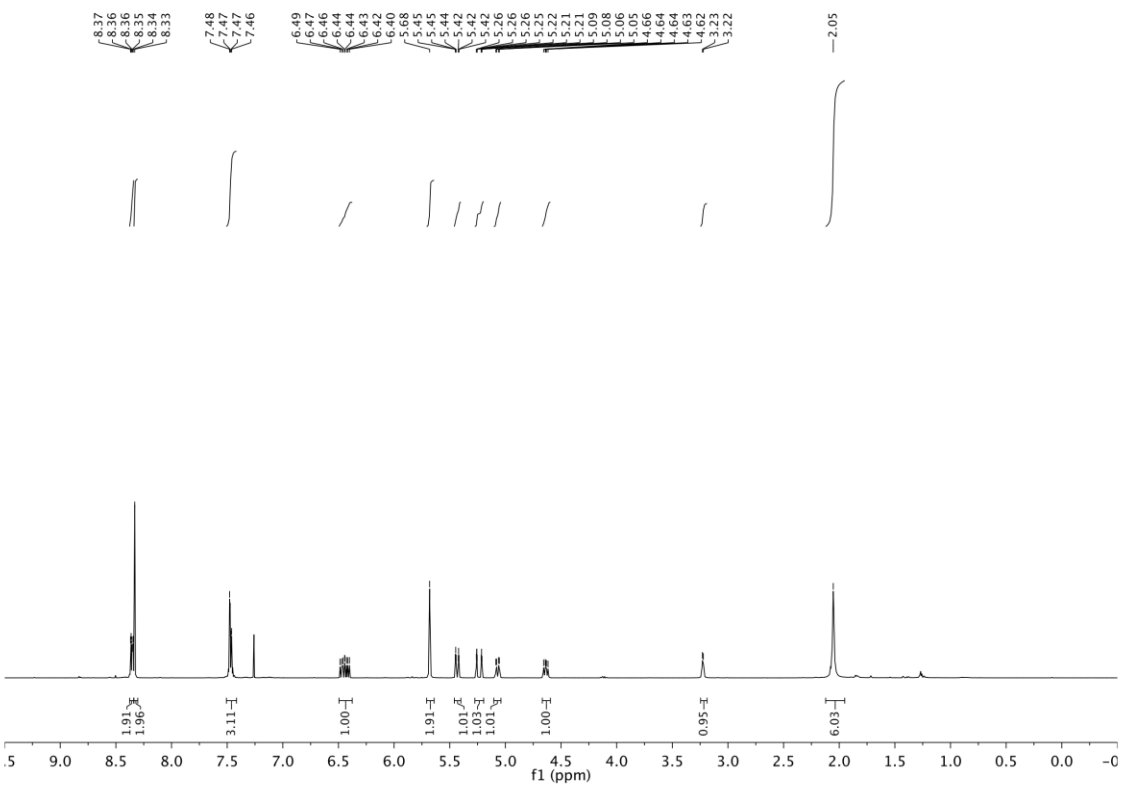
R_f = 0.14 (20% EtOAc/Hexanes).

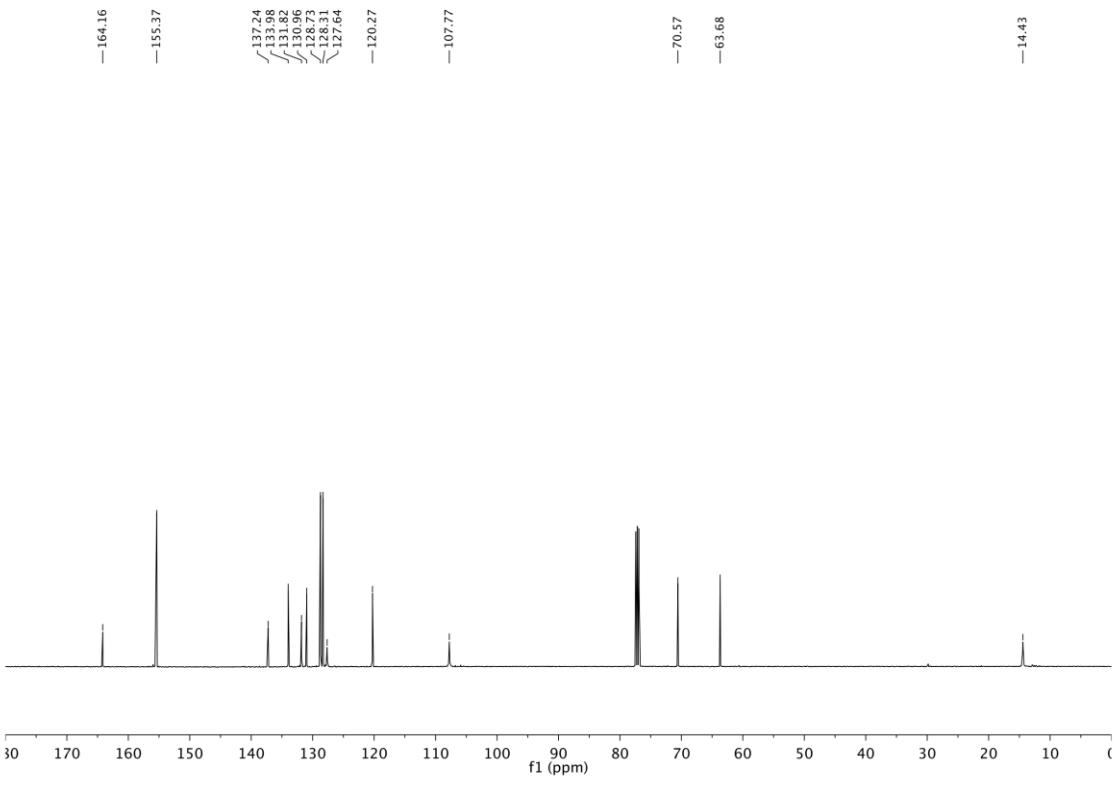
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 – 8.34 (m, 2H), 8.33 (s, 2H), 7.51 – 7.42 (m, 3H), 6.44 (ddd, *J* = 17.2, 10.5, 5.9 Hz, 1H), 5.68 (s, 2H), 5.43 (dt, *J* = 10.5, 1.4 Hz, 1H), 5.27 – 5.19 (m, 1H), 5.07 (dd, *J* = 9.8, 2.6 Hz, 1H), 4.64 (ddt, *J* = 9.6, 5.9, 1.7 Hz, 1H), 3.23 (d, *J* = 3.3 Hz, 1H), 2.05 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 155.4, 137.2, 134.0, 131.8, 131.0, 128.7, 128.3, 127.6, 120.3, 107.8, 70.6, 63.7, 14.4.

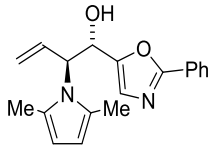
HRMS (ESI) Calcd. for $C_{20}H_{22}N_3O$ $[M+H]^+$: 320.1757, Found: 320.1757.

FTIR (neat): 3260, 2924, 1584, 1545, 1430, 1394, 1291, 1023, 929, 749, 694 cm^{-1}.


8.37
8.36
8.36
8.35
8.34
8.33
7.48
7.47
7.47
7.46
6.49
6.47
6.46
6.44
6.44
6.43
6.42
6.40
5.68
5.45
5.45
5.44
5.42
5.42
5.42
5.26
5.26
5.26
5.25
5.22
5.21
5.21
5.09
5.08
5.06
5.05
4.66
4.64
4.64
4.63
4.62
3.23
3.22
2.05
1.91
1.96
3.11
1.00
1.91
1.01
1.03
1.01
1.00
0.95
6.03
f1 (ppm)


164.16
155.37
137.24
133.98
131.82
130.96
128.73
128.31
127.64
120.27
107.77
70.57
63.68
14.43
f1 (ppm)

2-(2,5-dimethyl-1H-pyrrol-1-yl)-1-(2-phenyloxazol-5-yl)but-3-en-1-ol (3m).



In accordance with the general procedure at 125°C for 24 hours, the title compound was obtained in 77% yield (47.5 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 20% EtOAc/hexanes).

R_f = 0.4 (50% EtOAc/Hexanes).

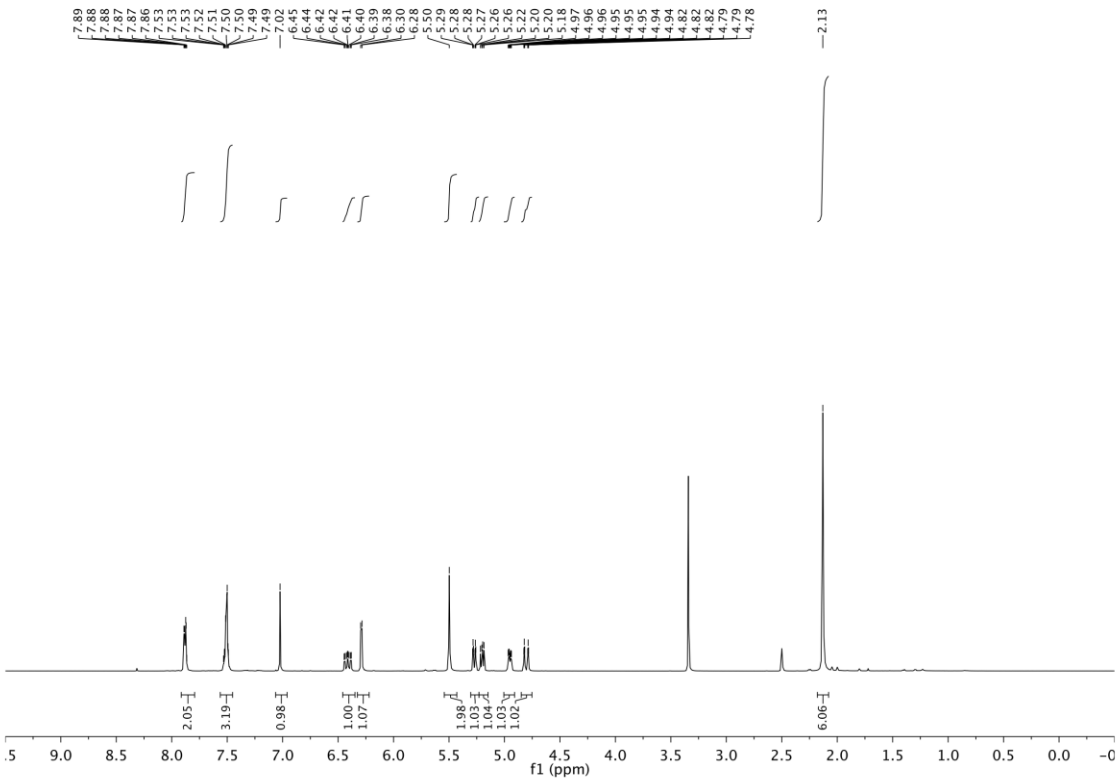
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.91 – 7.79 (m, 2H), 7.56 – 7.45 (m, 3H), 7.02 (s, 1H), 6.41 (ddd, *J* = 17.3, 10.5, 4.2 Hz, 1H), 6.29 (d, *J* = 6.0 Hz, 1H), 5.50 (s, 2H), 5..27 (dt, *J* = 10.6, 1.9 Hz, 1H), 5.20 (dd, *J* = 10.0, 5.9 Hz, 1H), 4.95 (ddt, *J* = 10.1, 4.3, 2.1 Hz, 1H), 4.80 (dt, *J* = 17.3, 1.8 Hz, 1H), 2.13 (s, 6H).

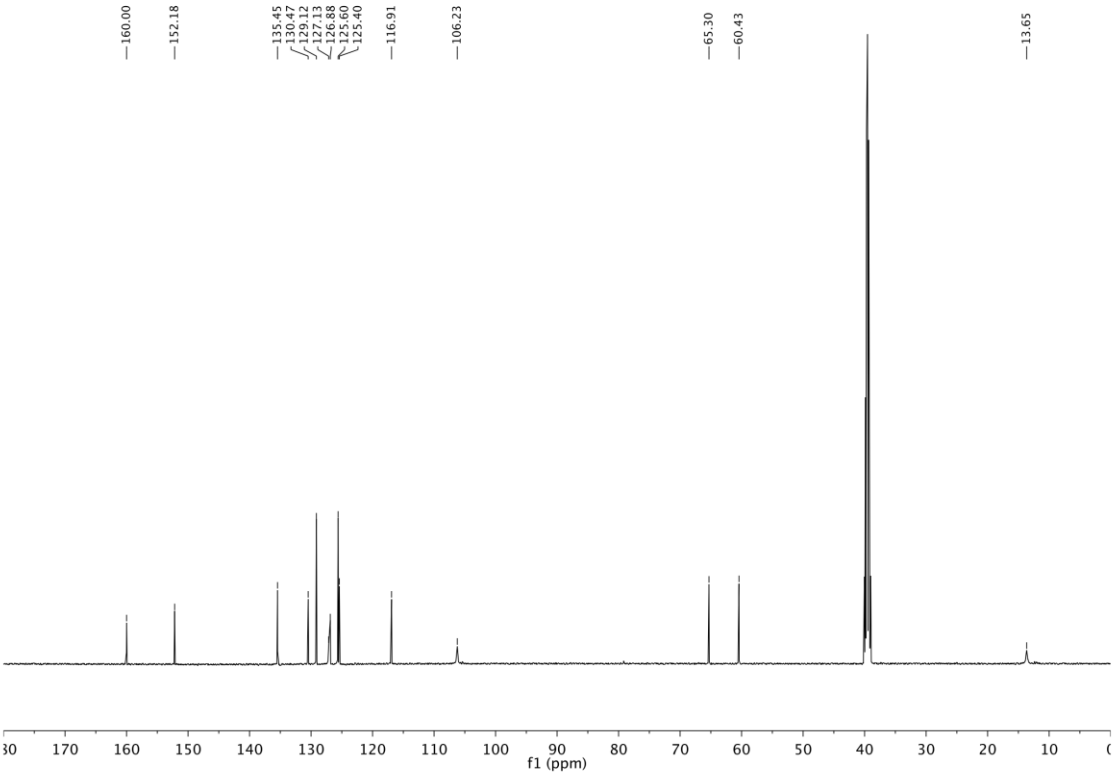
^{13}C NMR (100 MHz, DMSO-d_6): δ 160.0, 152.2, 135.4, 130.5, 129.1, 127.1, 126.9, 125.6, 125.4, 116.9, 106.2, 65.3, 60.4, 13.6.

HRMS (ESI) Calcd. for $C_{19}H_{21}N_2O_2$ $[M+H]^+$: 309.1598, Found: 309.1603.

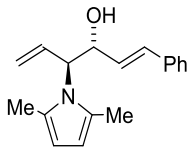
FTIR (neat): 3204, 3099, 2931, 1547, 1396, 1300, 1134, 1041, 977, 920, 824, 754, 713, 684 cm^{-1}.

MP: 183℃ (decomp.)


7.89
7.88
7.88
7.87
7.87
7.86
7.53
7.53
7.52
7.51
7.50
7.50
7.49
7.49
7.02
6.45
6.44
6.42
6.42
6.41
6.40
6.39
6.38
6.30
6.28
5.30
5.29
5.28
5.28
5.27
5.26
5.22
5.20
5.20
5.18
4.97
4.96
4.96
4.95
4.95
4.95
4.94
4.94
4.82
4.82
4.82
4.79
4.79
4.78
2.13
2.05
3.19
0.98
1.00
1.07
1.98
1.03
1.04
1.03
1.02
6.06
f1 (ppm)


160.00
152.18
135.45
130.47
129.12
127.13
126.88
125.60
125.40
116.91
106.23
65.30
60.43
13.65
f1 (ppm)

(E)-4-(2,5-dimethyl-1H-pyrrol-1-yl)-1-phenylhexa-1,5-dien-3-ol (3n).



In accordance with the general procedure at 125°C for 24 hours with 2-PrOH (200 mol%), the title compound was obtained in 72% yield (38.5 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 10% EtOAc/hexanes).

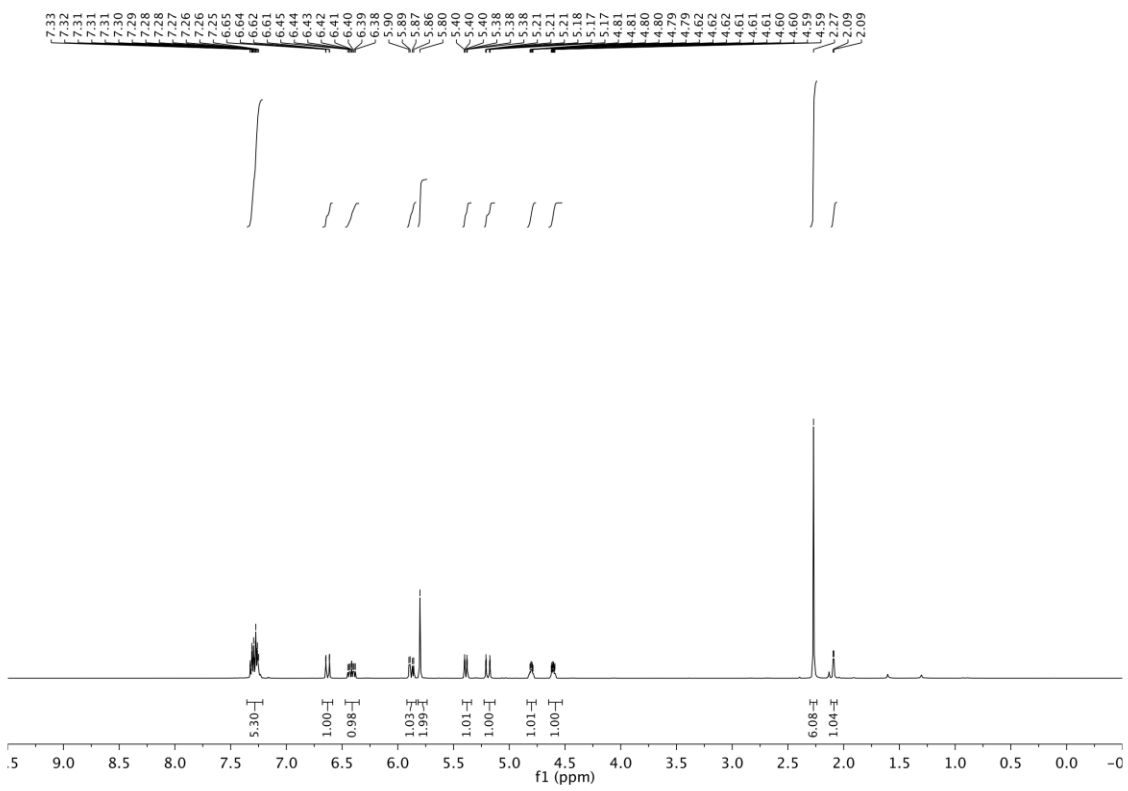
R_f = 0.38 (20% EtOAc/Hexanes).

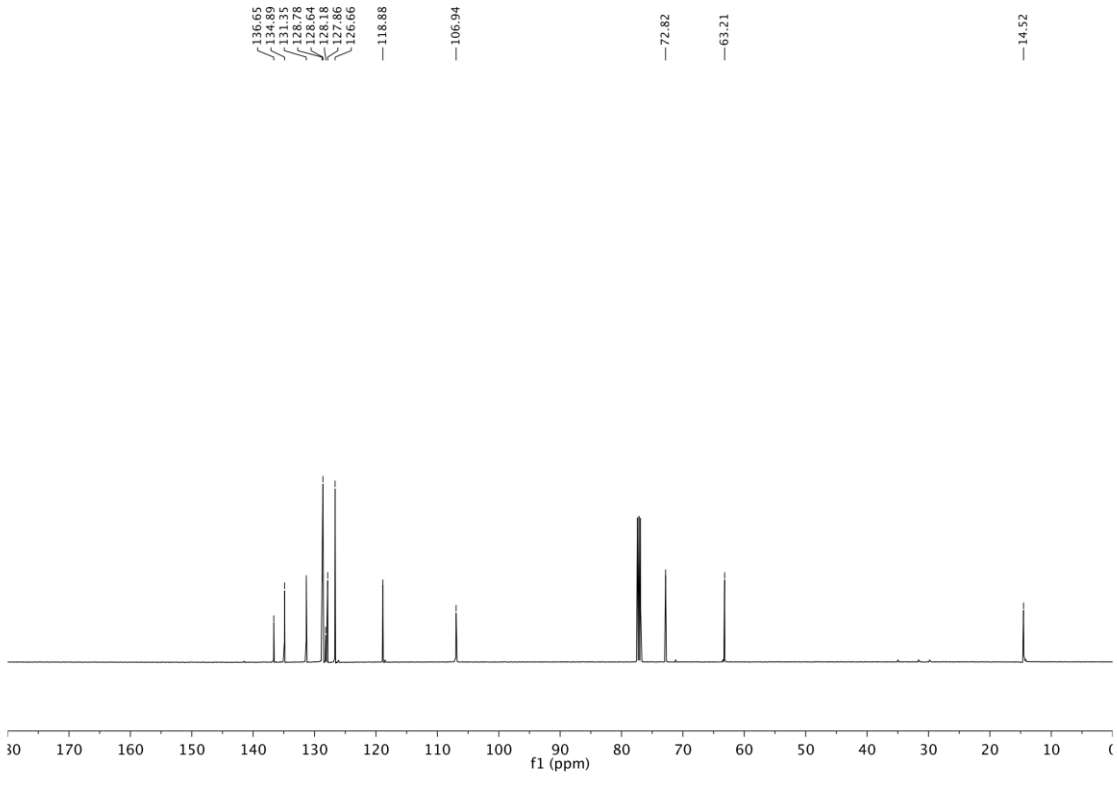
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.21 (m, 5H), 6.63 (dd, *J* = 16.0, 1.4 Hz, 1H), 6.41 (ddd, *J* = 17.3, 10.5, 5.6 Hz, 1H), 5.88 (dd, *J* = 16.0, 5.6 Hz, 1H), 5.80 (s, 2H), 5.39 (dt, *J* = 10.5, 1.5 Hz, 1H), 5.19 (dt, *J* = 17.2, 1.5 Hz, 1H), 4.84 – 4.76 (m, 1H), 4.61 (ddt, *J* = 7.2, 5.2, 2.6 Hz, 1H), 2.27 (s, 6H), 2.09 (d, *J* = 3.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6, 134.9, 131.4, 128.8, 128.6, 128.2, 127.9, 126.7, 118.9, 106.9, 72.8, 63.2, 14.5.

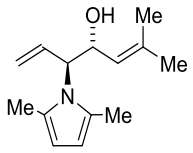
HRMS (ESI) Calcd. for $C_{18}H_{22}NO$ $[M+H]^+$: 268.1696, Found: 268.1700.

FTIR (neat): 3430, 2924, 1519, 1494, 1448, 1395, 1291, 1113, 1022, 973, 928, 747, 693 cm^{-1}.


7.33 7.32 7.31 7.31 7.31 7.30 7.29 7.28 7.28 7.27 7.26 7.26 7.25 6.65 6.64 6.62 6.61 6.45 6.44 6.43 6.42 6.41 6.40 6.39 6.38 5.90 5.89 5.87 5.86 5.80 5.40 5.40 5.40 5.38 5.38 5.38 5.21 5.21 5.21 5.18 5.17 5.17 4.81 4.81 4.80 4.80 4.79 4.79 4.62 4.62 4.62 4.61 4.61 4.61 4.60 4.60 4.59 4.59 2.27 2.09 2.09
5.30 1.00 0.98 1.03 1.99 1.01 1.00 1.01 1.00 6.08 1.04
f1 (ppm)


136.65 134.89 131.35 128.78 128.64 128.18 127.86 126.66 118.88 106.94 72.82 63.21 14.52
f1 (ppm)

3-(2,5-dimethyl-1H-pyrrol-1-yl)-6-methylhepta-1,5-dien-4-ol (3o).



In accordance with the general procedure at 125°C for 24 hours, the title compound was obtained in 73% yield (32.0 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 7.5%-10% EtOAc/hexanes).

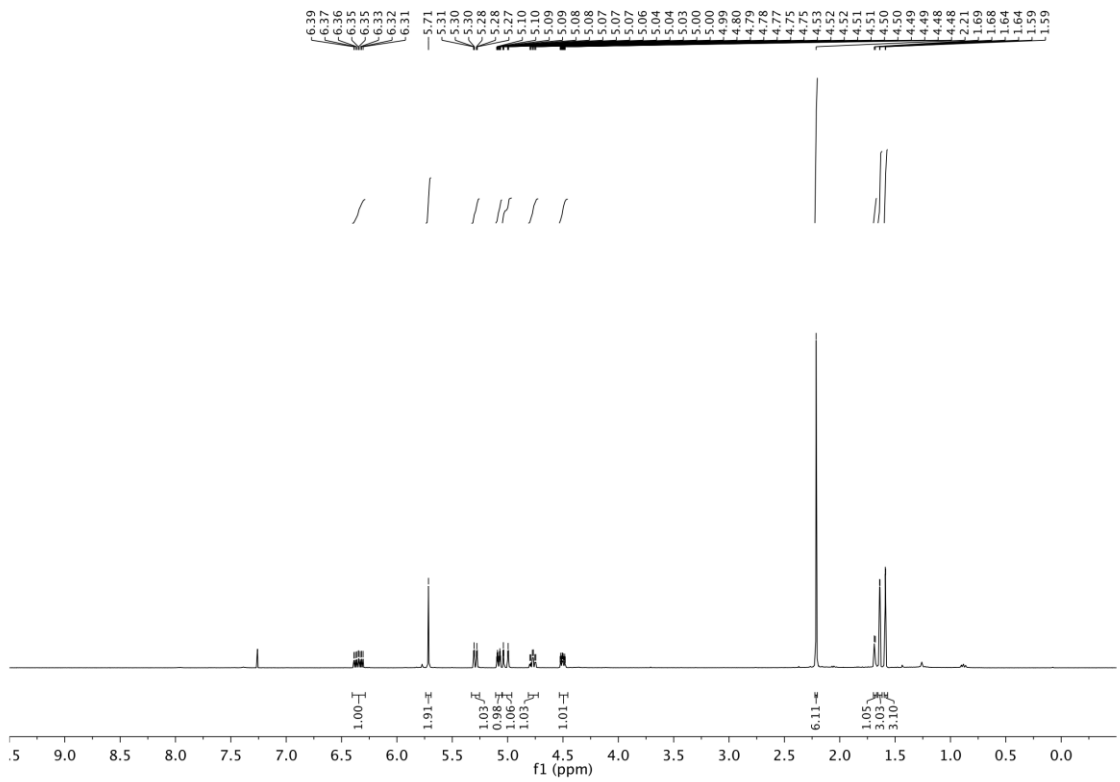
R_f =0.40 (20% EtOAc/Hexanes)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (ddd, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.71 (s, 2H), 5.29 (dt, *J* = 10.5, 1.6 Hz, 1H), 5.08 (ddq, *J* = 8.7, 2.8, 1.4 Hz, 1H), 5.02 (dt, *J* = 17.3, 1.6 Hz, 1H), 4.77 (td, *J* = 8.9, 3.5 Hz, 1H), 4.50 (ddt, *J* = 9.1, 5.6, 1.8 Hz, 1H), 2.21 (s, 6H), 1.68 (d, *J* = 3.6 Hz, 1H), 1.64 (d, *J* = 1.4 Hz, 3H), 1.59 (d, *J* = 1.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 135.0, 128.3, 124.3, 118.4, 106.4, 69.4, 62.9, 26.1, 18.3, 14.4.

HRMS (ESI) Calcd. for $C_{14}H_{22}NO^+$ $[M+H]^+$: 220.1701, Found: 220.1693.

FTIR (neat): 3439, 2970, 2929, 1741, 1444, 1397, 1292, 1216, 1021, 992, 924, 827, 749 cm^{-1}.


6.39
6.37
6.36
6.35
6.35
6.33
6.32
6.31
5.71
5.31
5.30
5.30
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5.28
5.27
5.10
5.10
5.09
5.09
5.08
5.08
5.07
5.07
5.07
5.06
5.04
5.04
5.03
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5.00
4.99
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4.78
4.77
4.75
4.75
4.53
4.52
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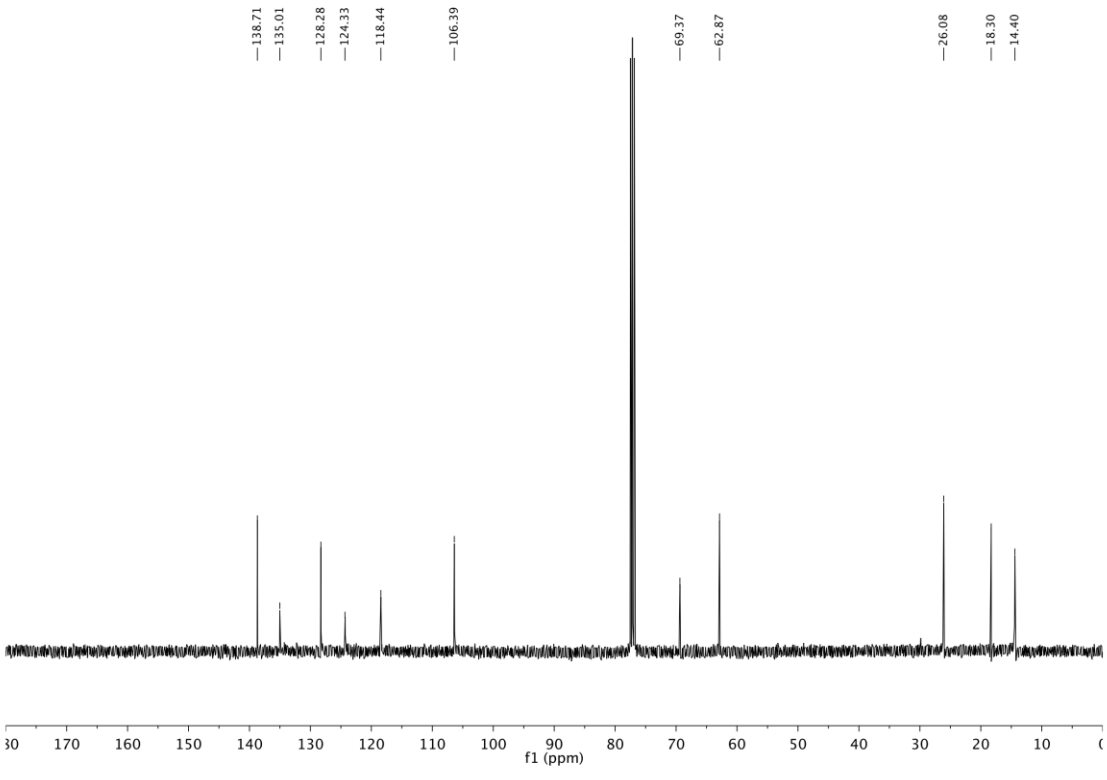
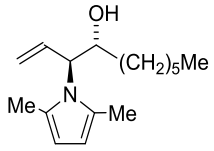
4.51
4.51
4.50
4.50
4.49
4.49
4.48
4.48
2.21
1.69
1.68
1.64
1.64
1.59
1.59
1.00
1.91
1.03
0.98
1.06
1.03
1.01
6.11
1.05
3.03
3.10
f1 (ppm)


138.71
135.01
128.28
124.33
118.44
106.39
69.37
62.87
26.08
18.30
14.40
f1 (ppm)

3-(2,5-dimethyl-1H-pyrrol-1-yl)dec-1-en-4-ol (3p).



In accordance with the general procedure at 125°C for 48 hours, the title compound was obtained in 62% yield (30.9 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 5% EtOAc/hexanes).

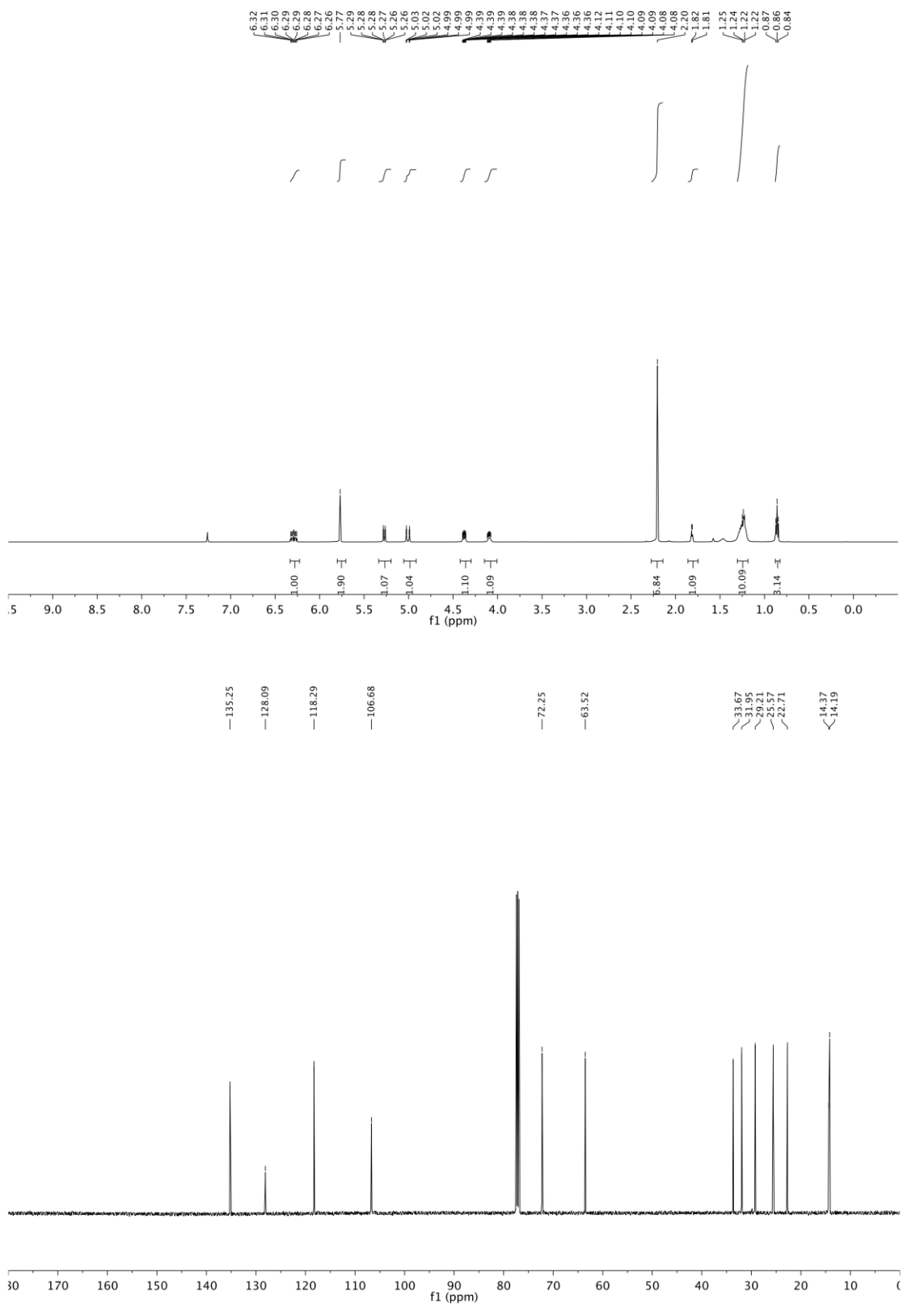
R_f = 0.55 (20% EtOAc/Hexanes).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29 (ddd, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.77 (s, 2H), 5.27 (dt, *J* = 10.5, 1.5 Hz, 1H), 5.01 (dt, *J* = 17.2, 1.5 Hz, 1H), 4.38 (ddt, *J* = 9.2, 5.8, 1.7 Hz, 1H), 4.10 (tq, *J* = 9.5, 6.3, 4.9 Hz, 1H), 2.20 (s, 6H), 1.82 (d, *J* = 4.5 Hz, 1H), 1.31 – 1.18 (m, 10H), 0.86 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.2, 128.1, 118.3, 106.7, 72.2, 63.5, 33.7, 31.9, 29.2, 25.6, 22.7, 14.4, 14.2.

HRMS (ESI) Calcd. for $C_{16}H_{27}NaNO$ $[M+Na]^+$: 272.1985, Found: 272.1989.

FTIR (neat): 3402, 2926, 2857, 1519, 1456, 1397, 1292, 1022, 925, 821, 753 cm^{-1}.


6.32
6.31
6.30
6.29
6.29
6.28
6.27
6.26
5.77
5.29
5.28
5.28
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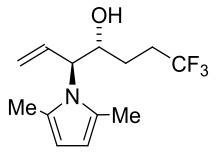
5.26
5.26
5.03
5.02
4.99
4.99
4.99
4.39
4.39
4.39
4.38
4.38
4.38
4.37
4.37
4.36
4.36
4.36
4.12
4.11
4.10
4.10
4.09
4.09
4.08
4.08
2.20
1.82
1.81
1.25
1.24
1.22
1.22
0.87
0.86
0.84
1.00
1.90
1.07
1.04
1.10
1.09
6.84
1.09
10.09
3.14
f1 (ppm)
135.25
128.09
118.29
106.68
72.25
63.52
33.67
31.95
29.21
25.57
22.71
14.37
14.19
f1 (ppm)

3-(2,5-dimethyl-1H-pyrrol-1-yl)-7,7,7-trifluorohept-1-en-4-ol (3q).



In accordance with the general procedure at 125°C for 24 hours, the title compound was obtained in 73% yield (38.1 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 7.5%-10% EtOAc/hexanes).

R_f =0.41 (20% EtOAc/Hexanes)

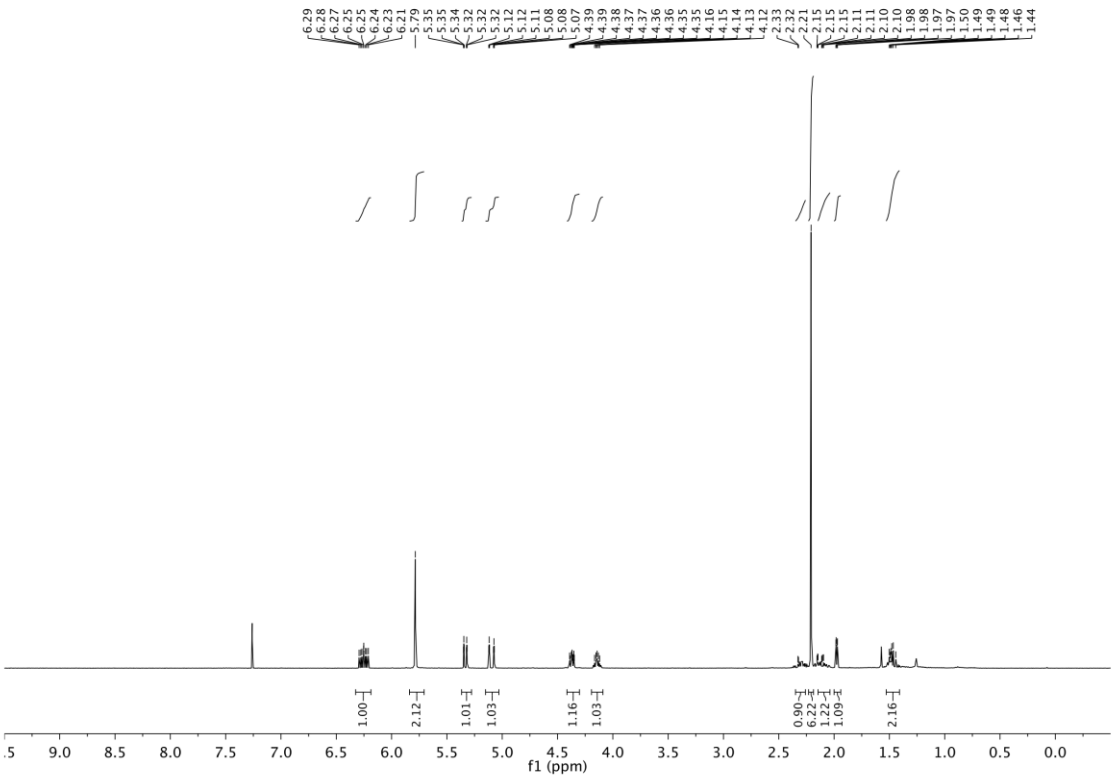
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.25 (ddd, *J* = 16.8, 10.4, 6.2 Hz, 1H), 5.79 (s, 2H), 5.33 (dt, *J* = 10.4, 1.4 Hz, 1H), 5.10 (dt, *J* = 17.1, 1.4 Hz, 1H), 4.37 (ddt, *J* = 9.4, 6.2, 1.6 Hz, 1H), 4.14 (tt, *J* = 9.0, 4.0 Hz, 1H), 2.30 (dddd, *J* = 20.4, 9.3, 4.5, 2.8 Hz, 1H), 2.21 (s, 6H), 2.17 – 2.02 (m, 1H), 1.97 (d, *J* = 4.6 Hz, 1H), 1.55 – 1.40 (m, 2H).

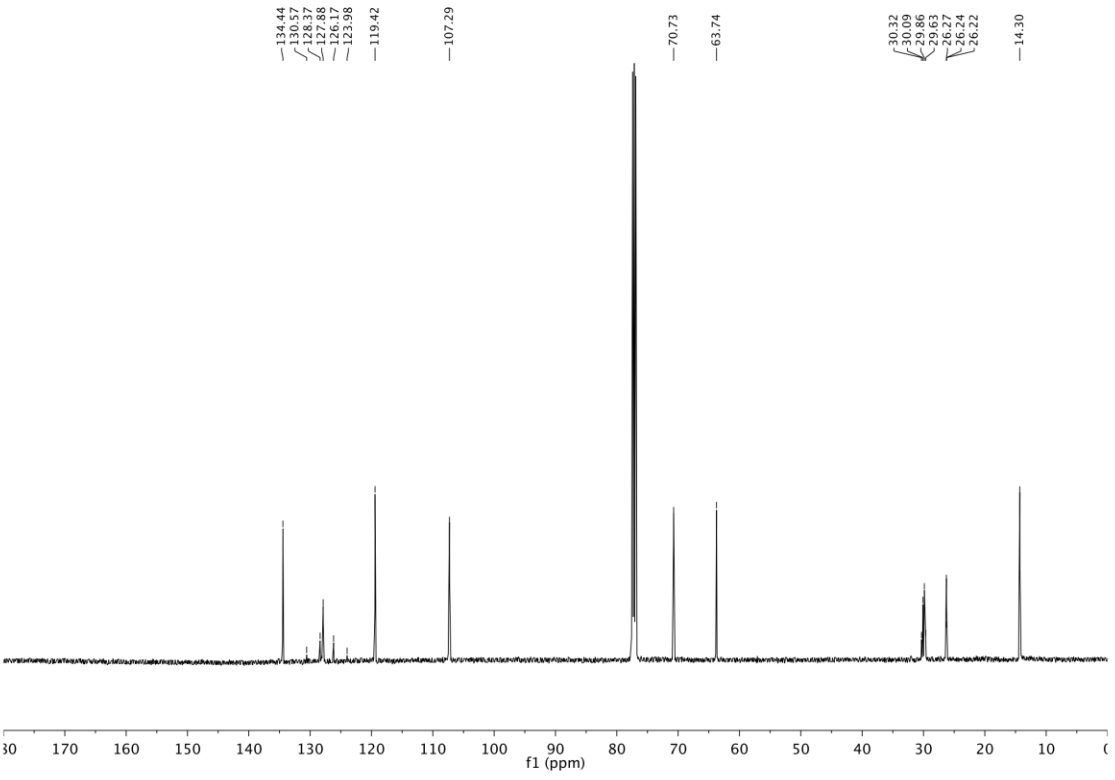
^{19}F NMR (100 MHz, $CDCl_3$) δ -66.0.

^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 127.9, 127.3 (q, J_{C-F} = 276.4 Hz), 119.4, 107.3, 70.7, 63.7, 30.0 (q, J_{C-F} = 29.0 Hz), 26.3 (q, J_{C-F} = 3.3 Hz), 14.3.

HRMS (ESI) Calcd. for $C_{13}H_{19}F_3NO^+$ $[M+H]^+$: 262.1419, Found: 262.1416.

FTIR (neat): 3460, 2934, 1934, 1740, 1520, 1452, 1395, 1290, 1254, 1138, 1042, 928, 820, 755 cm^{-1}.


6.29
6.28
6.27
6.25
6.25
6.24
6.23
6.21
5.79
5.35
5.35
5.34
5.32
5.32
5.32
5.12
5.12
5.11
5.08
5.08
5.07
4.39
4.39
4.38
4.37
4.37
4.36
4.36
4.35
4.35
4.16
4.15
4.14
4.13
4.12
2.33
2.32
2.21
2.15
2.15
2.15
2.11
2.11
2.10
2.10
1.98
1.98
1.97
1.97
1.50
1.49
1.49
1.48
1.46
1.44
1.00
2.12
1.01
1.03
1.16
1.03
0.90
6.22
1.22
1.09
2.16
f1 (ppm)


134.44
130.57
128.37
127.88
126.17
123.98
119.42
107.29
70.73
63.74
30.32
30.09
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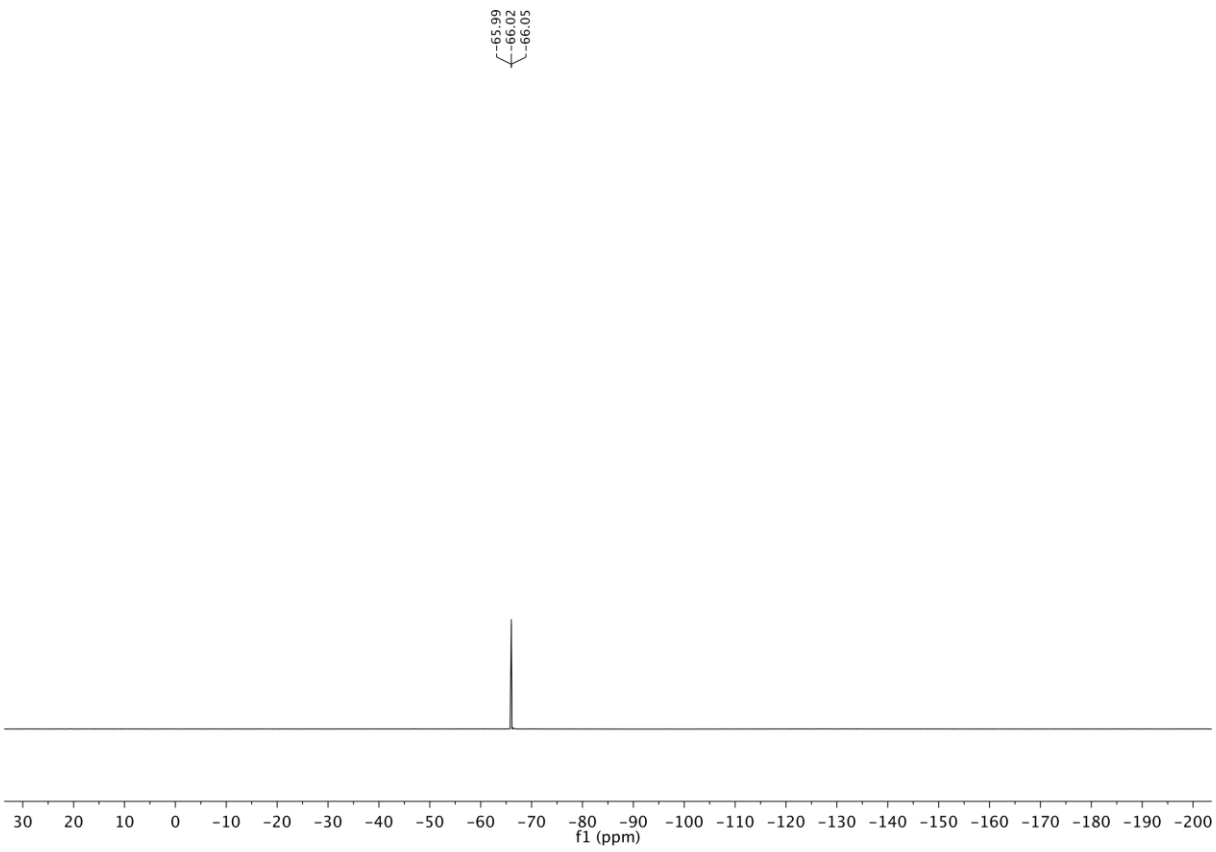
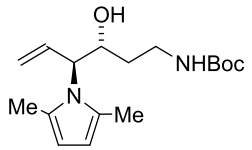
29.63
26.27
26.24
26.22
14.30
f1 (ppm)


-65.99
-66.02
-66.05
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

tert-butyl (4-(2,5-dimethyl-1H-pyrrol-1-yl)-3-hydroxyhex-5-en-1-yl)carbamate (3r).



In accordance with the general procedure at 125°C for 24 hours, the title compound was obtained in 63% yield (38.9 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 20% EtOAc/hexanes).

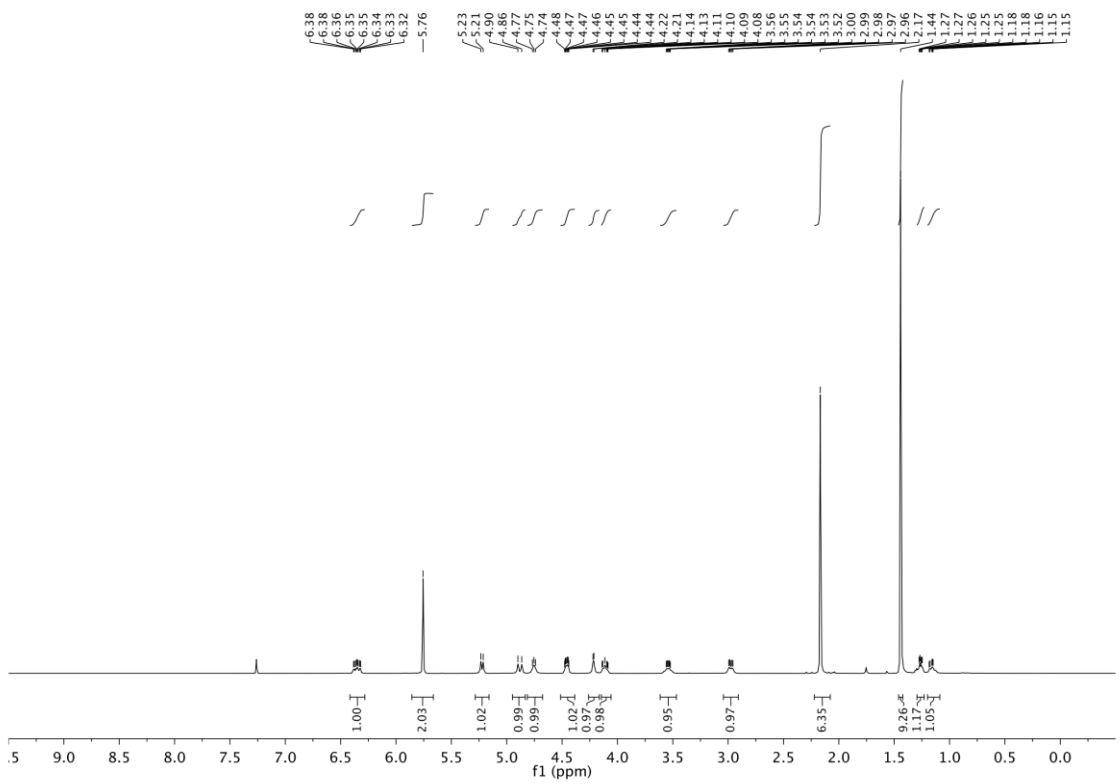
R_f = 0.17 (20% EtOAc/Hexanes).

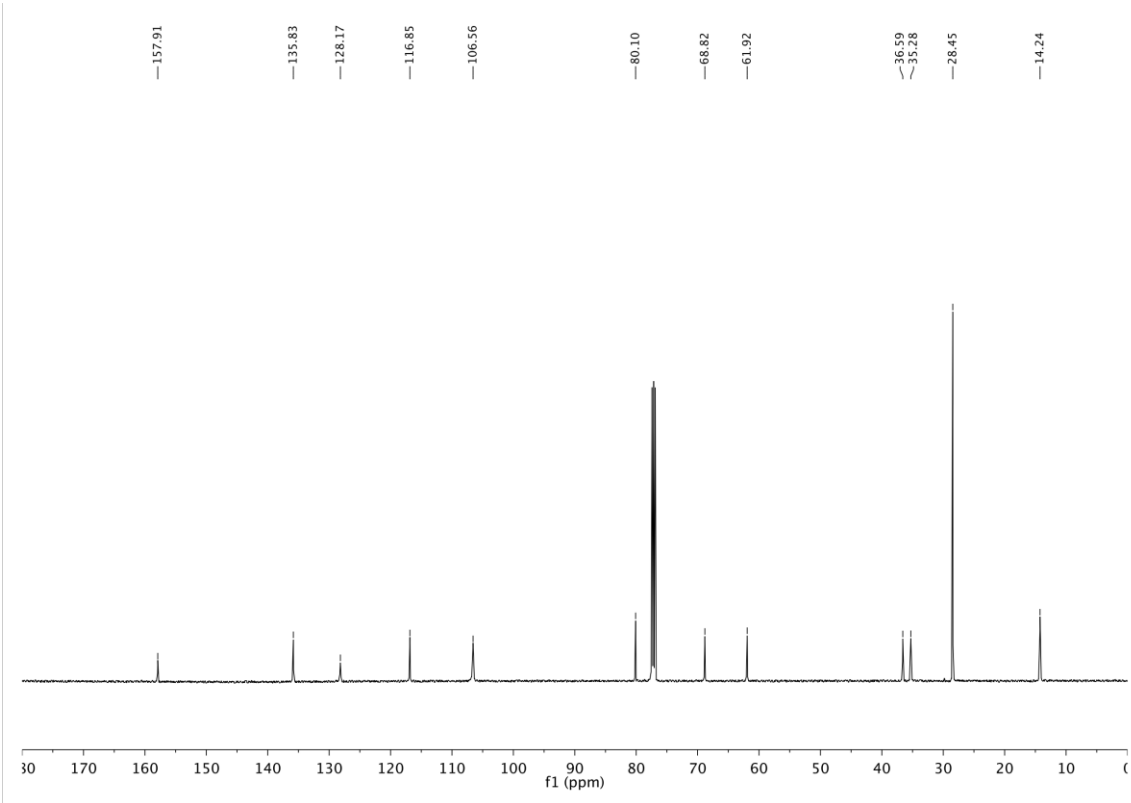
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.35 (ddd, *J* = 17.4, 10.6, 4.2 Hz, 1H), 5.76 (s, 2H), 5.22 (d, *J* = 10.5 Hz, 1H), 4.88 (d, *J* = 17.3 Hz, 1H), 4.75 (d, *J* = 6.7 Hz, 1H), 4.51 – 4.39 (m, 1H), 4.22 (d, *J* = 4.2 Hz, 1H), 4.15 – 4.06 (m, 1H), 3.61 – 3.47 (m, 1H), 2.98 (dq, *J* = 14.6, 4.6 Hz, 1H), 2.17 (s, 6H), 1.44 (s, 9H), 1.26 (dq, *J* = 7.9, 5.3, 3.8 Hz, 1H), 1.16 (td, *J* = 12.1, 11.7, 6.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 135.8, 128.2, 116.8, 106.6, 80.1, 68.8, 61.9, 36.6, 35.3, 28.4, 14.2.

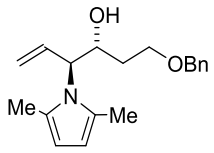
HRMS (ESI) Calcd. for $C_{17}H_{29}N_2O_3$ $[M+H]^+$: 309.2173, Found: 309.2171.

FTIR (neat): 3368, 2977, 2932, 2361, 1687, 1518, 1448, 1397, 1367, 1290, 1252, 1169, 1006, 923, 753 cm^{-1}.


6.38
6.38
6.36
6.35
6.35
6.34
6.33
6.32
5.76
5.23
5.21
4.90
4.86
4.77
4.75
4.74
4.48
4.47
4.47
4.46
4.45
4.44
4.44
4.22
4.21
4.14
4.13
4.11
4.10
4.09
4.08
3.56
3.55
3.54
3.54
3.53
3.52
3.00
2.99
2.98
2.97
2.96
2.17
1.44
1.27
1.27
1.26
1.25
1.25
1.18
1.18
1.16
1.15
1.15
1.00
2.03
1.02
0.99
0.99
1.02
0.97
0.98
0.95
0.97
6.35
9.26
1.17
1.05
f1 (ppm)


157.91
135.83
128.17
116.85
106.56
80.10
68.82
61.92
36.59
35.28
28.45
14.24
f1 (ppm)

1-(benzyloxy)-4-(2,5-dimethyl-1H-pyrrol-1-yl)hex-5-en-3-ol (3s).



In accordance with the general procedure at 125°C for 48 hours, the title compound was obtained in 61% yield (36.5 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 5%-10% EtOAc/hexanes).

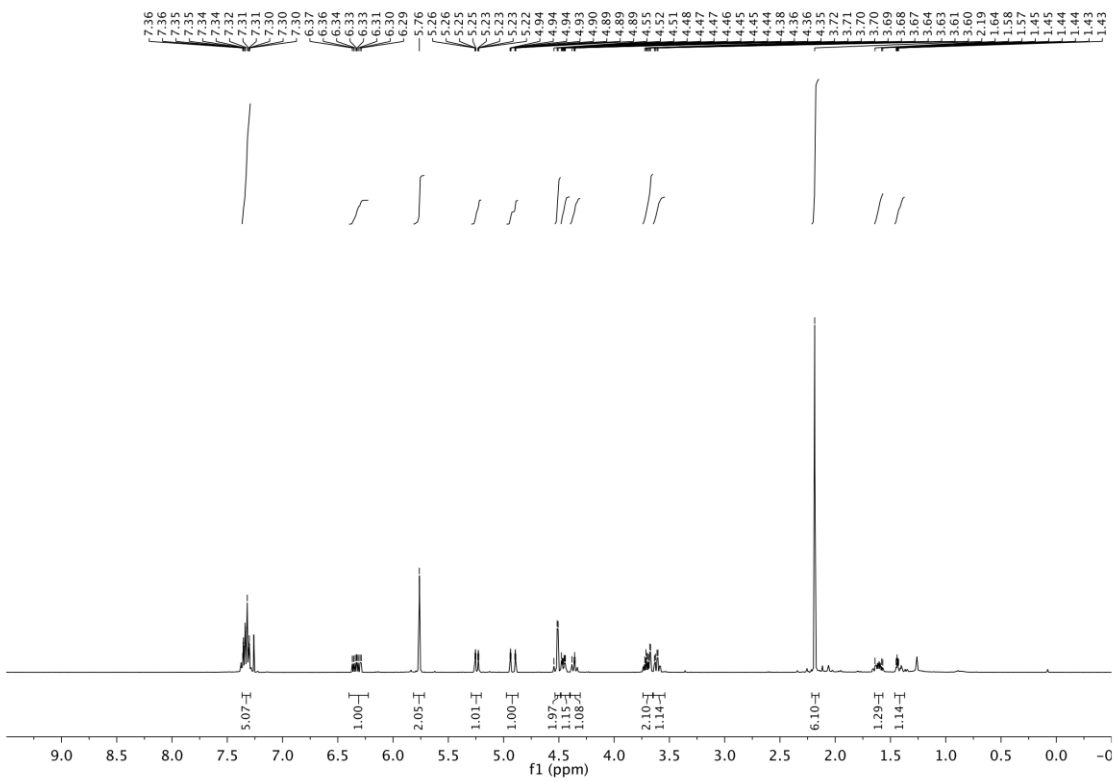
R_f =0.38 (20% EtOAc/Hexanes)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 6.33 (ddd, *J* = 17.2, 10.5, 4.5 Hz, 1H), 5.76 (s, 2H), 5.24 (dt, *J* = 10.5, 1.7 Hz, 1H), 4.92 (dt, *J* = 17.3, 1.7 Hz, 1H), 4.51 (d, *J* = 5.2 Hz, 2H), 4.46 (ddt, *J* = 11.8, 4.4, 2.2 Hz, 1H), 4.36 (tt, *J* = 9.8, 2.1 Hz, 1H), 3.71 (ddd, *J* = 9.5, 5.4, 4.0 Hz, 1H), 3.66 – 3.57 (m, 2H), 2.19 (s, 6H), 1.61 (dtd, *J* = 14.9, 9.3, 4.0 Hz, 1H), 1.43 (dddd, *J* = 14.8, 5.5, 3.4, 2.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 135.3, 128.7, 128.2, 128.0, 127.8, 117.3, 106.7, 73.6, 72.6, 69.6, 62.5, 32.9, 14.3.

HRMS (ESI) Calcd. for $C_{19}H_{26}NO_2^+$ $[M+H]^+$: 300.1964, Found: 300.1960.

FTIR (neat): 3472, 2928, 2863, 1739, 1454, 1397, 1291, 1241, 1092, 923, 820, 747, 698 cm^{-1}.


7.36
7.36
7.35
7.35
7.34
7.34
7.32
7.31
7.31
7.30
7.30
7.30
6.37
6.36
6.34
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6.33
6.31
6.30
6.29
5.76
5.26
5.26
5.25
5.25
5.23
5.23
5.23
5.22
4.94
4.94
4.94
4.93
4.90
4.89
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4.47
4.46
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4.44
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3.69
3.68
3.67
3.64
3.63
3.61
3.60
2.19
1.64
1.58
1.57
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1.44
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1.43
1.43
5.07
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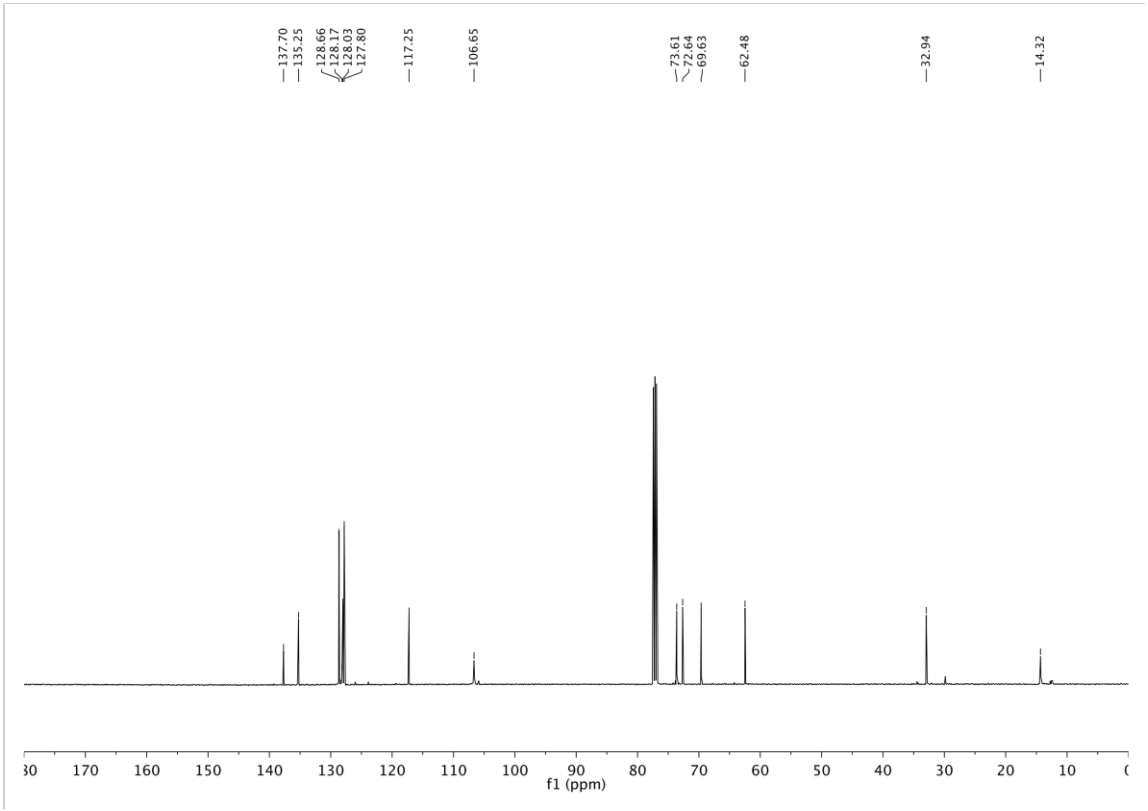
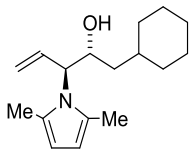
1.08
2.10
1.14
6.10
1.29
1.14
f1 (ppm)


137.70
135.25
128.66
128.17
128.03
127.80
117.25
106.65
73.61
72.64
69.63
62.48
32.94
14.32
f1 (ppm)

1-cyclohexyl-3-(2,5-dimethyl-1H-pyrrol-1-yl)pent-4-en-2-ol (3t).



In accordance with the general procedure at 125°C for 48 hours, the title compound was obtained in 75% yield (39.2 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 3%-5% EtOAc/hexanes).

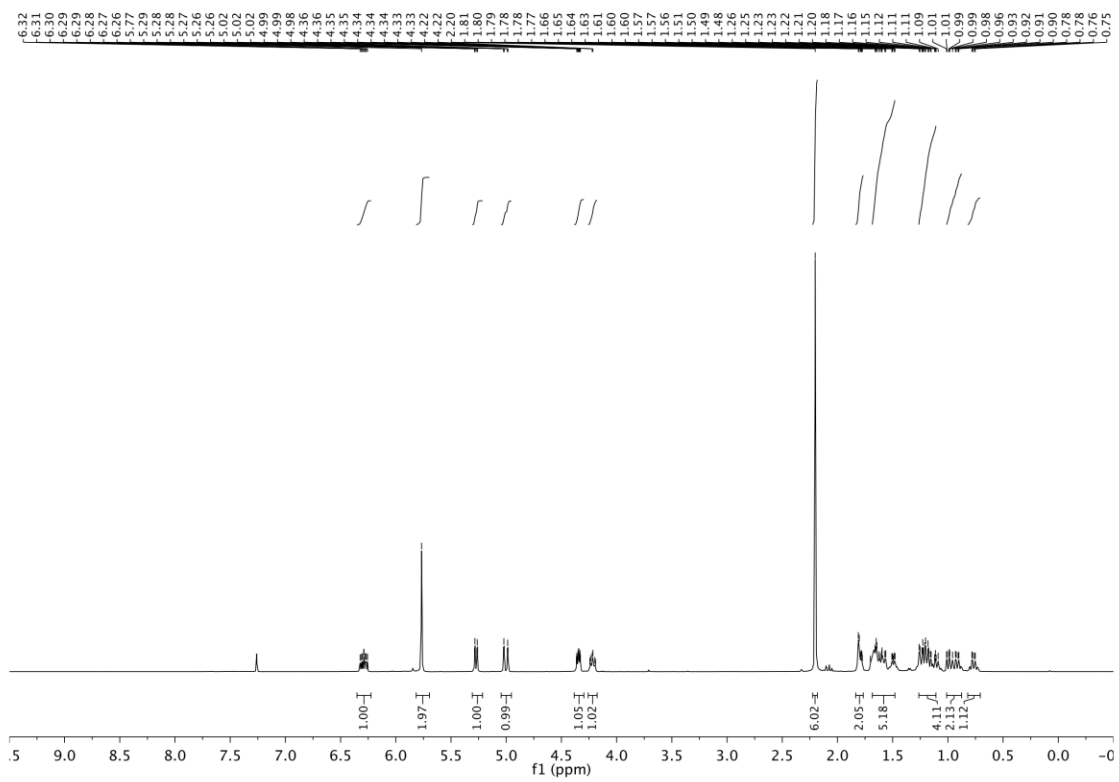
R_f =0.38 (10% EtOAc/Hexanes)

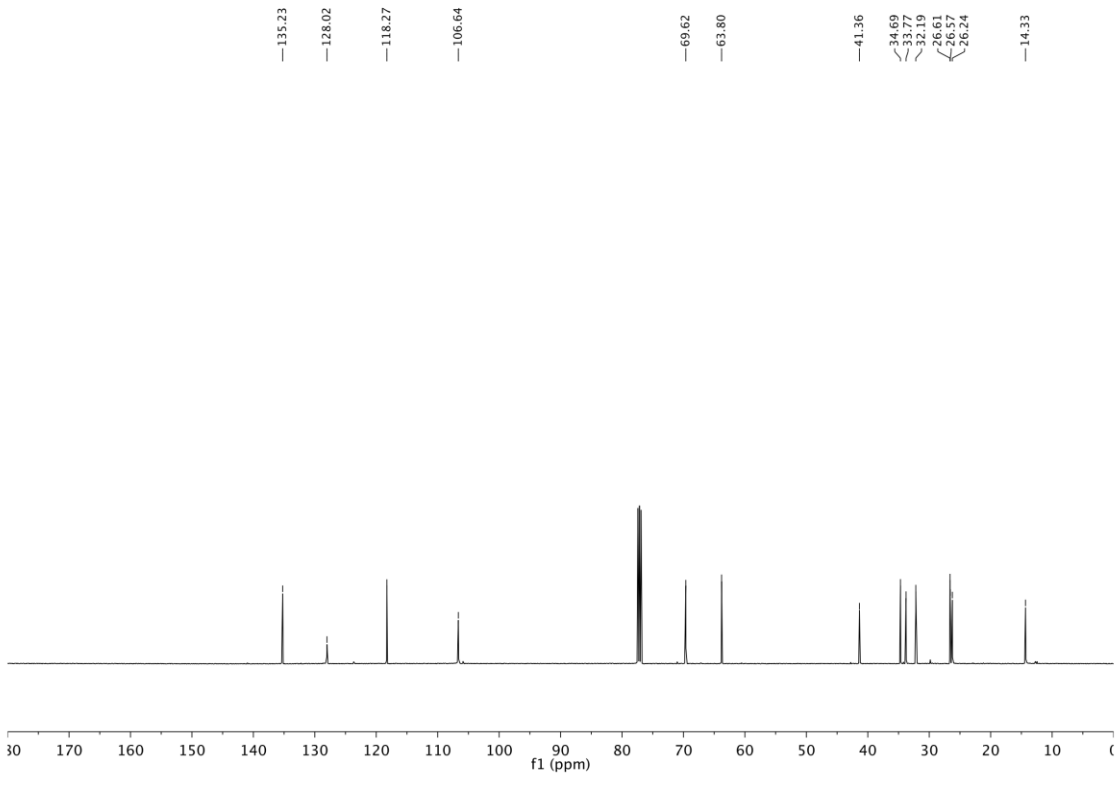
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.29 (ddd, *J* = 17.3, 10.5, 5.7 Hz, 1H), 5.77 (s, 2H), 5.27 (dt, *J* = 10.4, 1.6 Hz, 1H), 5.00 (dt, *J* = 17.2, 1.5 Hz, 1H), 4.35 (ddt, *J* = 9.3, 5.8, 1.7 Hz, 1H), 4.26 – 4.17 (m, 1H), 2.20 (s, 6H), 1.79 (dd, *J* = 12.9, 3.2 Hz, 2H), 1.73 – 1.44 (m, 4H), 1.31 – 1.04 (m, 4H), 1.04 – 0.85 (m, 3H), 0.77 (qd, *J* = 12.4, 3.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 128.0, 118.3, 106.6, 69.6, 63.8, 41.4, 34.7, 33.8, 32.2, 26.6(1), 26.5(7), 26.2, 14.3.

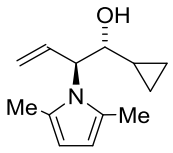
HRMS (ESI) Calcd. for $C_{17}H_{27}NONa^+$ $[M+Na]^+$: 284.1990, Found: 284.1985.

FTIR (neat): 3464, 2922, 2851, 1741, 1724, 1447, 1397, 1241, 1044, 988, 922, 751, 733 cm^{-1}.


f1 (ppm)


f1 (ppm)

1-cyclopropyl-2-(2,5-dimethyl-1H-pyrrol-1-yl)but-3-en-1-ol (3u).



In accordance with the general procedure at 125°C for 48 hours in dioxane (1.0 M), the title compound was obtained in 63% yield (25.9 mg, *dr* = >20:1) as a yellow liquid after column chromatography (SiO_2; 10% EtOAc/hexanes).

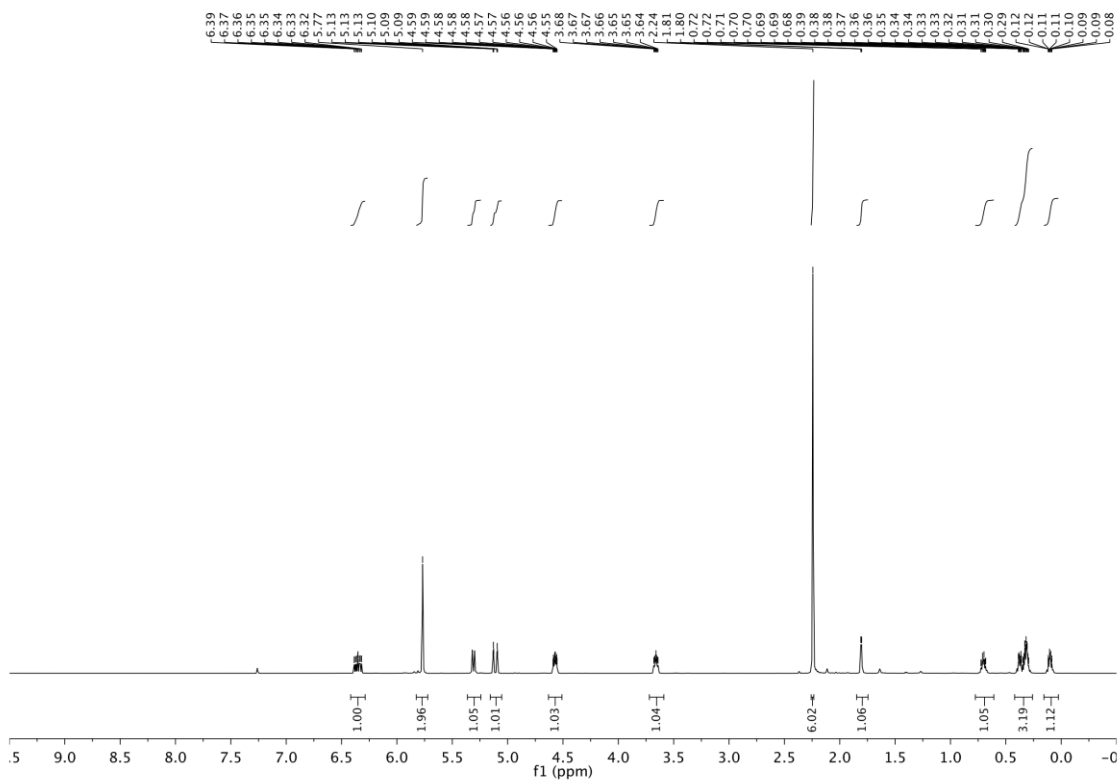
R_f = 0.42 (20% EtOAc/Hexanes).

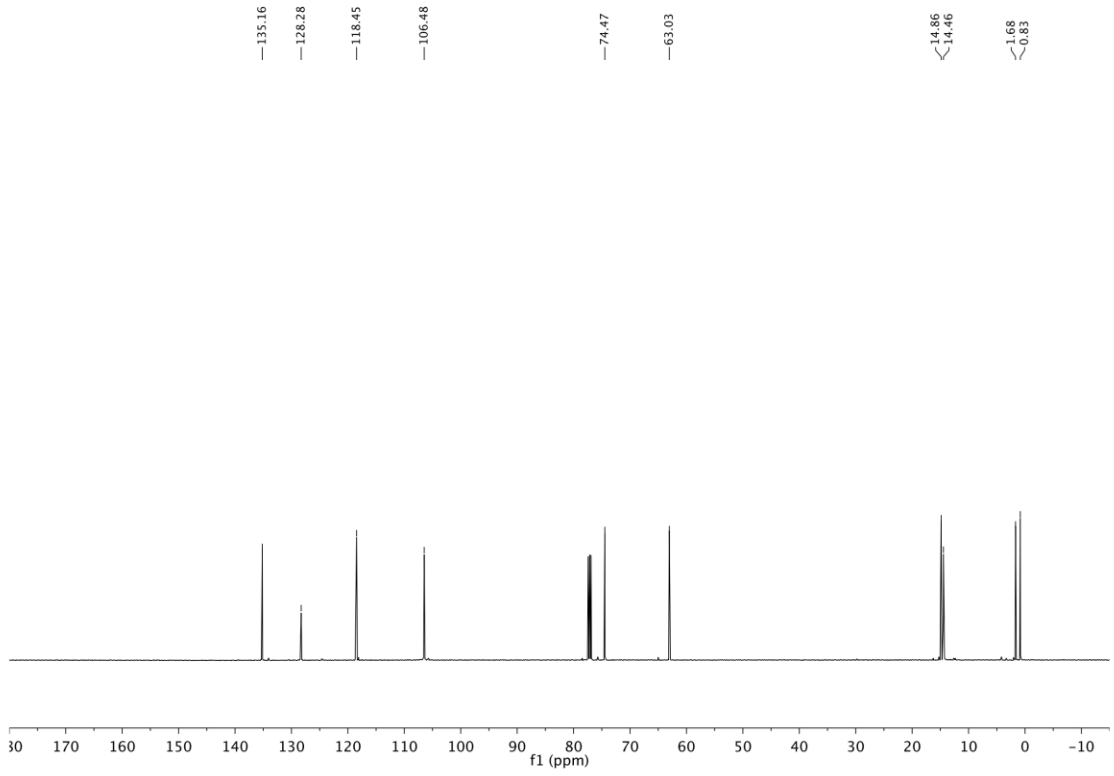
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.35 (ddd, *J* = 17.4, 10.5, 5.6 Hz, 1H), 5.77 (s, 2H), 5.31 (dt, *J* = 10.6, 1.6 Hz, 1H), 5.11 (dt, *J* = 17.3, 1.6 Hz, 1H), 4.57 (ddt, *J* = 9.2, 5.8, 1.8 Hz, 1H), 3.66 (ddd, *J* = 9.3, 6.5, 3.4 Hz, 1H), 2.24 (s, 6H), 1.81 (d, *J* = 3.6 Hz, 1H), 0.78 – 0.61 (m, 1H), 0.42 – 0.26 (m, 3H), 0.16 – 0.02 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.2, 128.3, 118.4, 106.5, 74.5, 63.0, 14.9, 14.5, 1.7, 0.8.

HRMS (ESI) Calcd. for $C_{13}H_{20}NO$ $[M+H]^+$: 206.1539, Found: 206.1539.

FTIR (neat): 3444, 3084, 2930, 1519, 1398, 1293, 1138, 1021, 926, 828, 753 cm^{-1}.

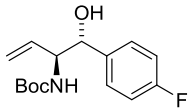

f1 (ppm)


f1 (ppm)

C. General Procedure and Preparation of 4b, 4n, 4q

To a solution of adduct **3** (0.2 mmol, 100 mol %) in EtOH (4 mL) was added hydroxylamine hydrochloride (139 mg, 2 mmol, 1000 mol %) followed by H_2O (2 mL). The mixture was allowed to stir at 100 °C for 24 hours. After cooled to room temperature, the reaction mixture was washed with 2N aqueous NaOH and extracted three times with Et_2O.The combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* and the crude amine was dissolved in THF (1 mL, 0.2 M). $(Boc)_2O$ (65.5 mg, 0.3 mmol, 150 mol %) was subsequently added and the reaction mixture was allowed to stir at room temperature overnight. Saturated aqueous NH_4Cl was added to the reaction mixture. The mixture was extracted three times with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was then removed *in vacuo*, and the residue was purified by flash chromatography (SiO_2: 20% EtOAc/Hexanes) to furnish the title compound.

tert-butyl (1-(4-fluorophenyl)-1-hydroxybut-3-en-2-yl)carbamate (4b).



In accordance with the general procedure, the title compound was obtained in 69% yield as a yellow solid after column chromatography (SiO_2; 20% EtOAc/hexanes).

R_f = 0.22 (20% EtOAc/Hexanes).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (dd, J = 8.5, 5.5 Hz, 2H), 7.02 (t, J = 8.7 Hz, 2H), 5.68 (ddd, J = 16.8, 10.5, 5.9 Hz, 1H), 5.23 – 5.06 (m, 2H), 4.93 – 4.79 (m, 2H), 4.43 (s, 1H), 3.14 (s, 1H), 1.44 (s, 9H).

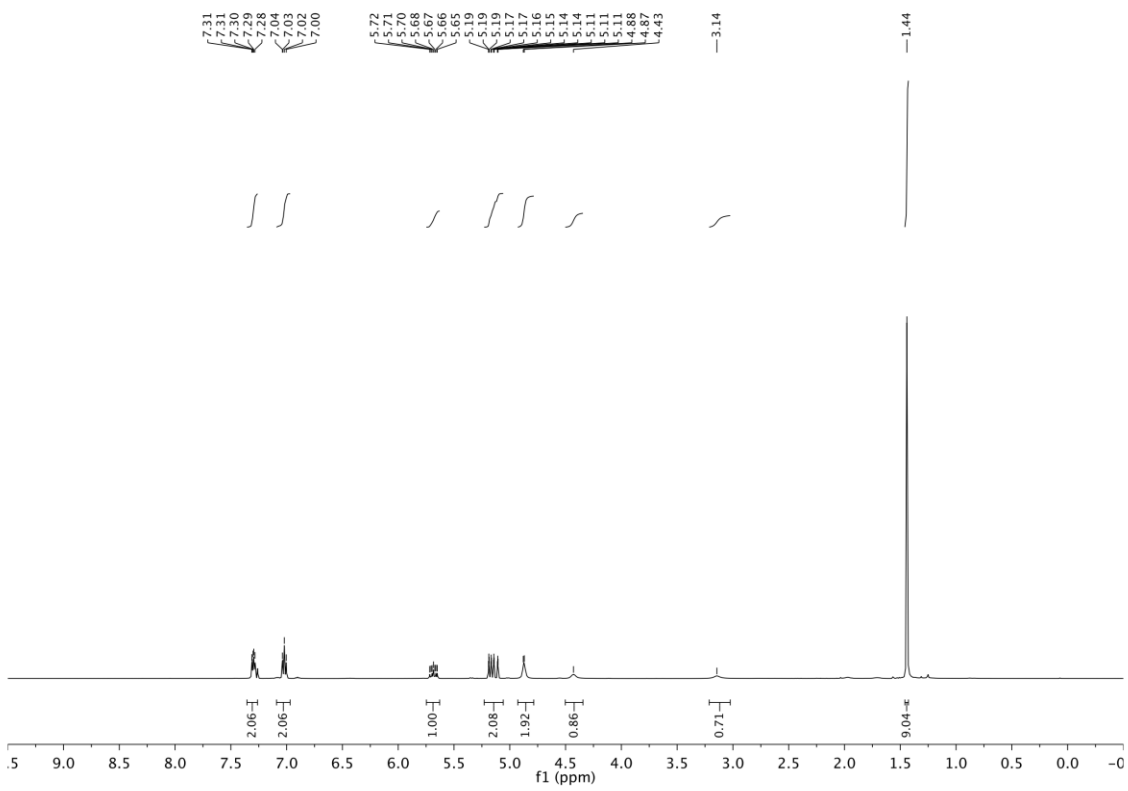
^{19}F NMR (100 MHz, $CDCl_3$): δ -115.06

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4(d, J_{C-F} = 245.7 Hz), 156.2, 136.2(d, J_{C-F} = 3.1 Hz), 133.2, 128.1(d, J_{C-F} = 8.0 Hz), 117.8, 115.2(d, J_{C-F} = 21.3 Hz), 80.2, 75.8, 58.9, 28.5.

HRMS (ESI) Calcd. for $C_{15}H_{20}FNNaO_3$ $[M+Na]^+$: 304.1319, Found: 304.1328.

FTIR (neat): 3329, 2978, 2925, 1687, 1590, 1550, 1508, 1430, 1222, 1160, 1024, 837, 749, 694 cm^{-1}.

MP: 121-123℃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7.31
7.30
7.29
7.28
7.04
7.03
7.02
7.00
5.72
5.71
5.70
5.68
5.67
5.66
5.65
5.19
5.19
5.19
5.17
5.17
5.16
5.15
5.14
5.14
5.11
5.11
5.11
4.88
4.87
4.43
3.14
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2.06
2.06
1.00
2.08
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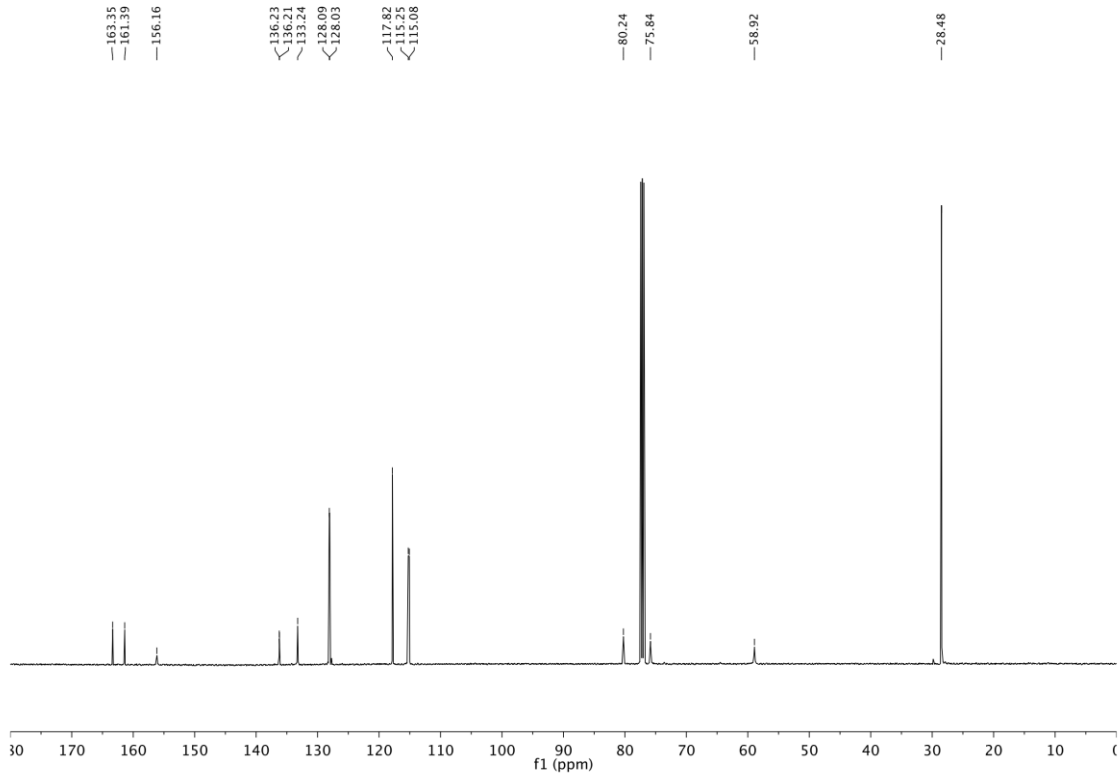
0.86
0.71
9.04
f1 (ppm)


163.35
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136.23
136.21
133.24
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128.03
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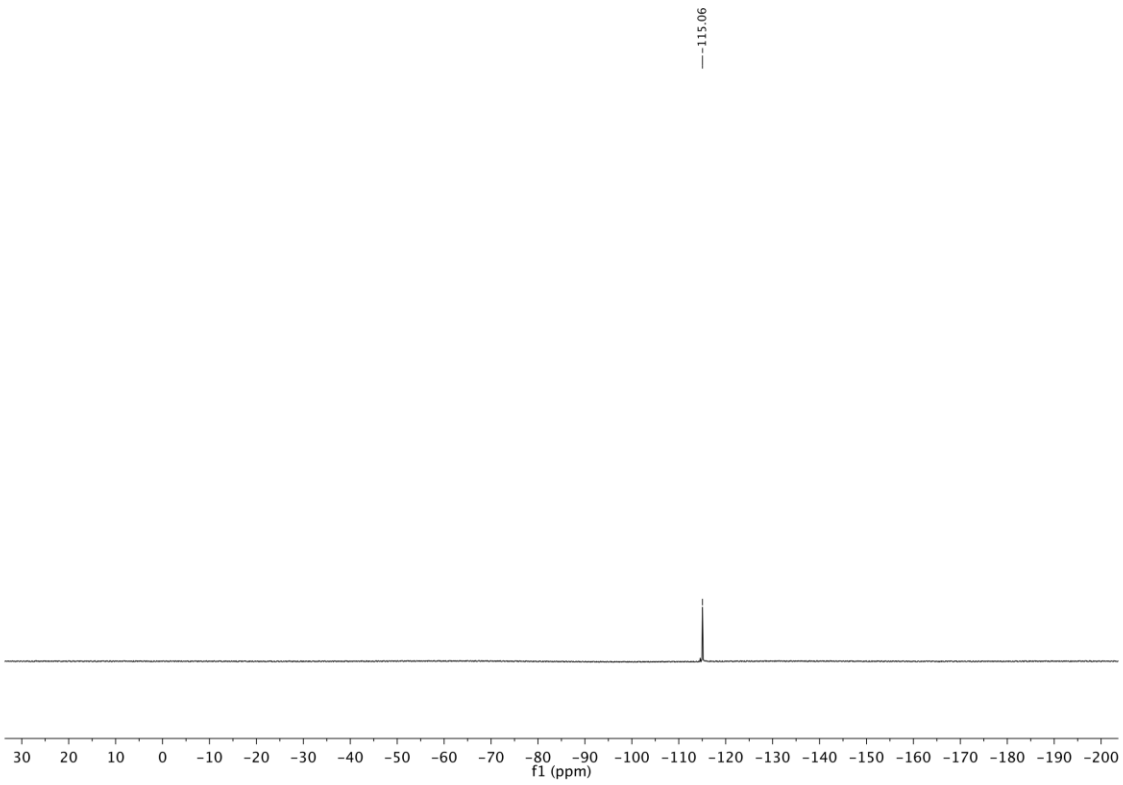
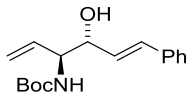
115.25
115.08
80.24
75.84
58.92
28.48
f1 (ppm)


-115.06
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

tert-butyl (E)-(4-hydroxy-6-phenylhexa-1,5-dien-3-yl)carbamate (4n).



In accordance with the general procedure, the title compound was obtained in 62% over two steps (35.9 mg) as a yellow oil after column chromatography (SiO_2; 15%-20% EtOAc/hexanes).

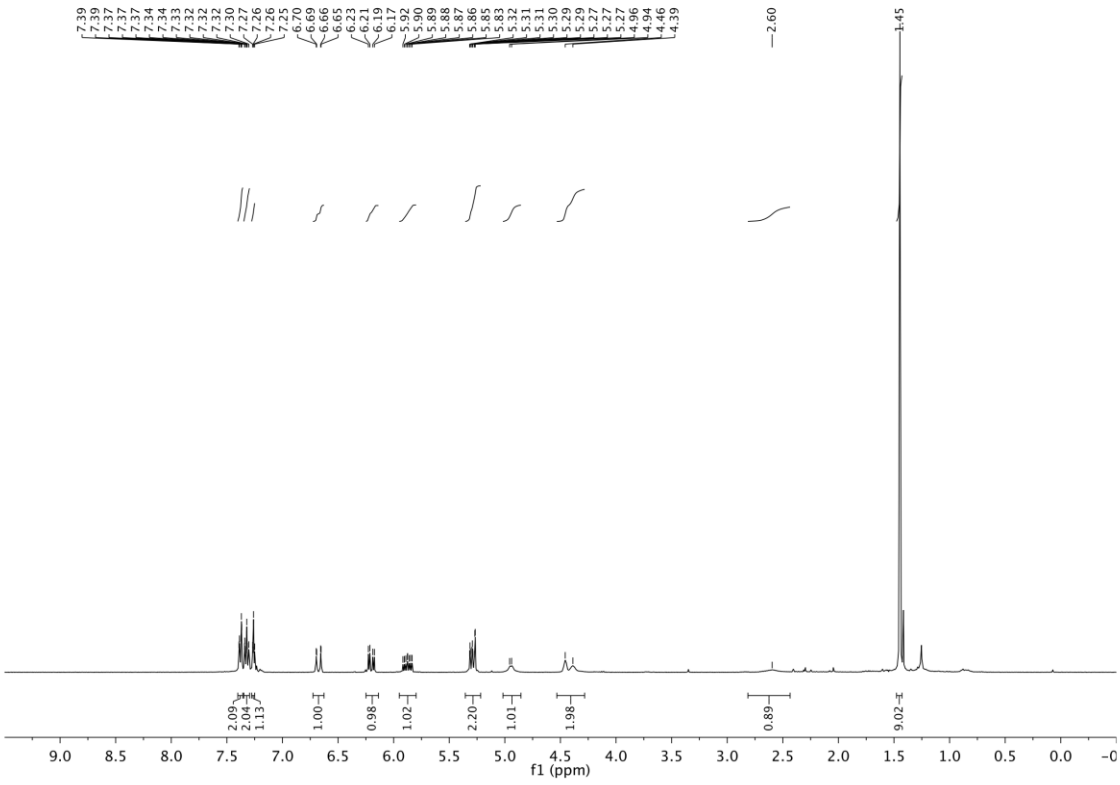
R_f=0.18 (20% EtOAc/Hexanes)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.1 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.22 (m, 1H), 6.72 – 6.63 (m, 1H), 6.20 (dd, *J* = 16.0, 5.7 Hz, 1H), 5.88 (ddd, *J* = 16.7, 10.5, 5.6 Hz, 1H), 5.35 – 5.22 (m, 2H), 4.94 (d, *J* = 8.2 Hz, 1H), 4.51 – 4.27 (m, 2H), 2.64 (br s, 1H), 1.45 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 136.6, 134.0, 132.1, 128.7, 128.0, 126.8, 126.7, 117.7, 80.1, 74.8, 57.9, 28.5.

HRMS (ESI) Calcd. for $C_{17}H_{23}NO_3Na^+$ $[M+Na]^+$: 312.1576, Found: 312.1576.

FTIR (neat): 3350, 2982, 2927, 1740, 1682, 1524, 1447, 1367, 1250, 1166, 1000, 967, 922, 750 cm^{-1}.


7.39
7.39
7.37
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7.37
7.34
7.33
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7.30
7.27
7.26
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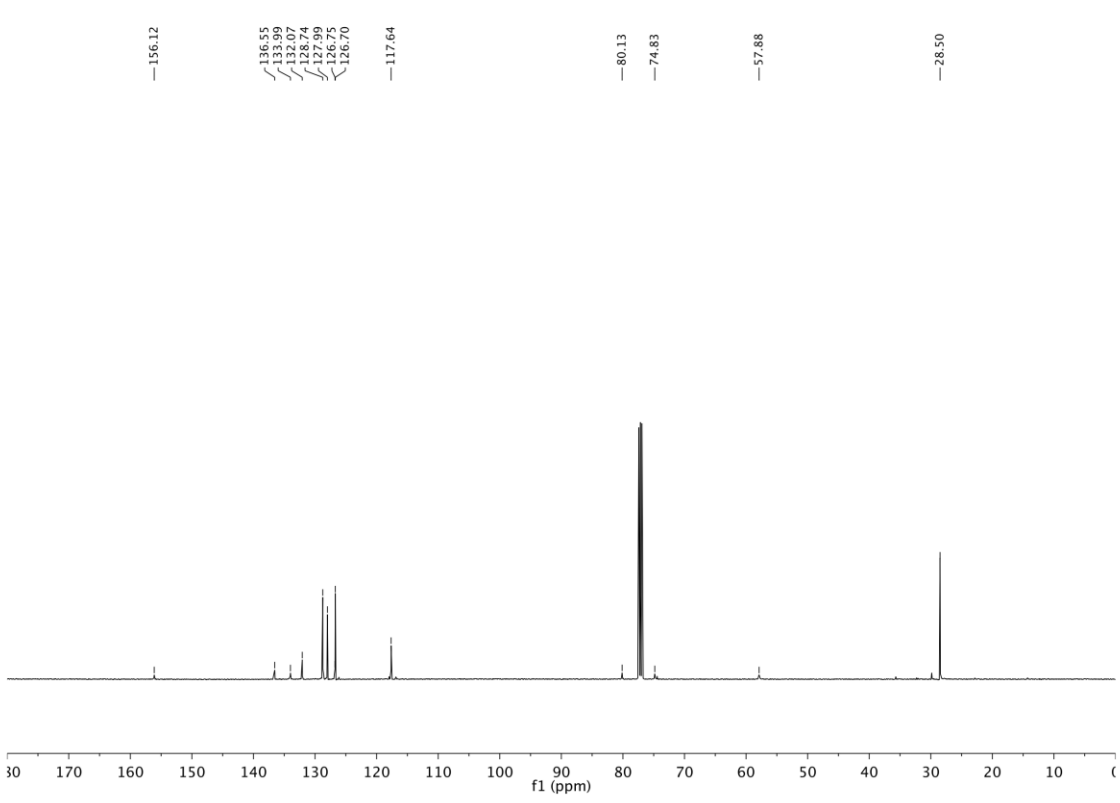
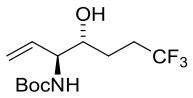
5.27
5.27
4.96
4.94
4.46
4.39
2.60
1.45
2.09
2.04
1.13
1.00
0.98
1.02
2.20
1.01
1.98
0.89
9.02
f1 (ppm)


156.12
136.55
133.99
132.07
128.74
127.99
126.75
126.70
117.64
80.13
74.83
57.88
28.50
f1 (ppm)

tert-butyl (7,7,7-trifluoro-4-hydroxyhept-1-en-3-yl)carbamate (4q).



In accordance with the general procedure, the title compound was obtained in 68% over two steps as a yellow oil (38.5 mg) after column chromatography (SiO_2; 20%-25% EtOAc/hexanes).

R_f =0.20 (20% EtOAc/Hexanes)

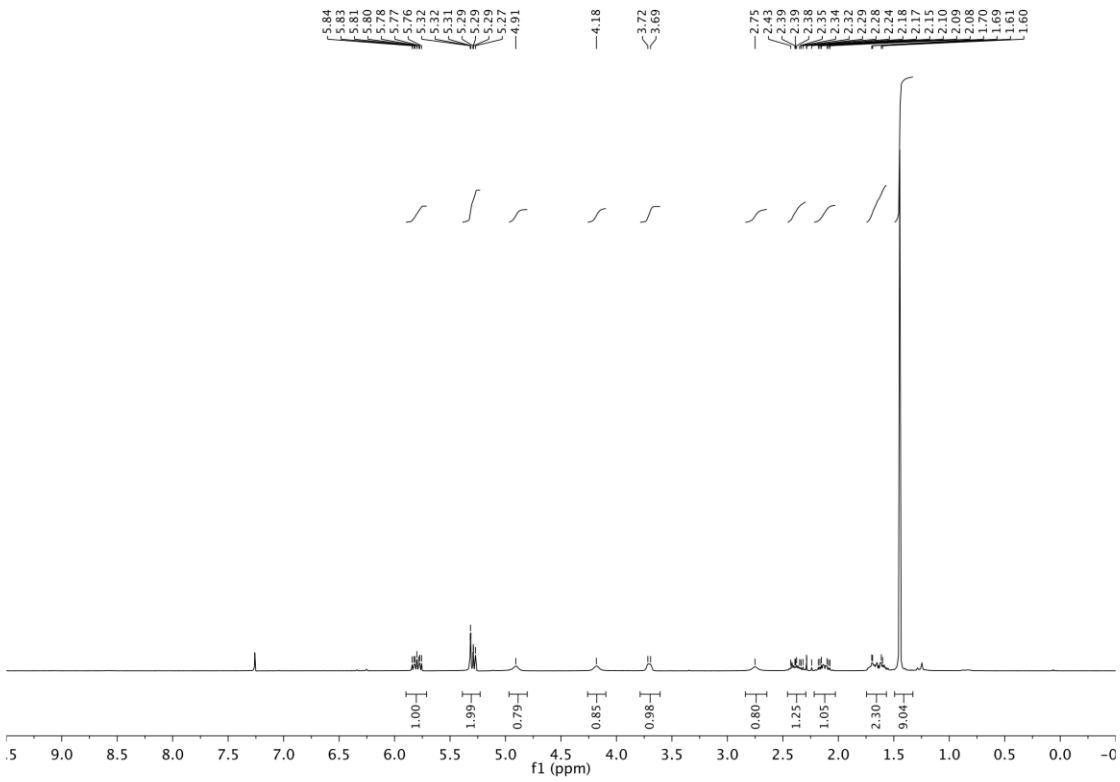
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddd, *J* = 17.1, 10.7, 6.5 Hz, 1H), 5.37 – 5.22 (m, 2H), 4.90 (br s, 1H), 4.18 (br s, 1H), 3.70 (dd, *J* = 9.9, 4.4 Hz, 1H), 2.73 (br s, 1H), 2.47 – 2.30 (m, 1H), 2.20 – 2.06 (m, 1H), 1.75 – 1.54 (m, 2H), 1.45 (s, 9H).

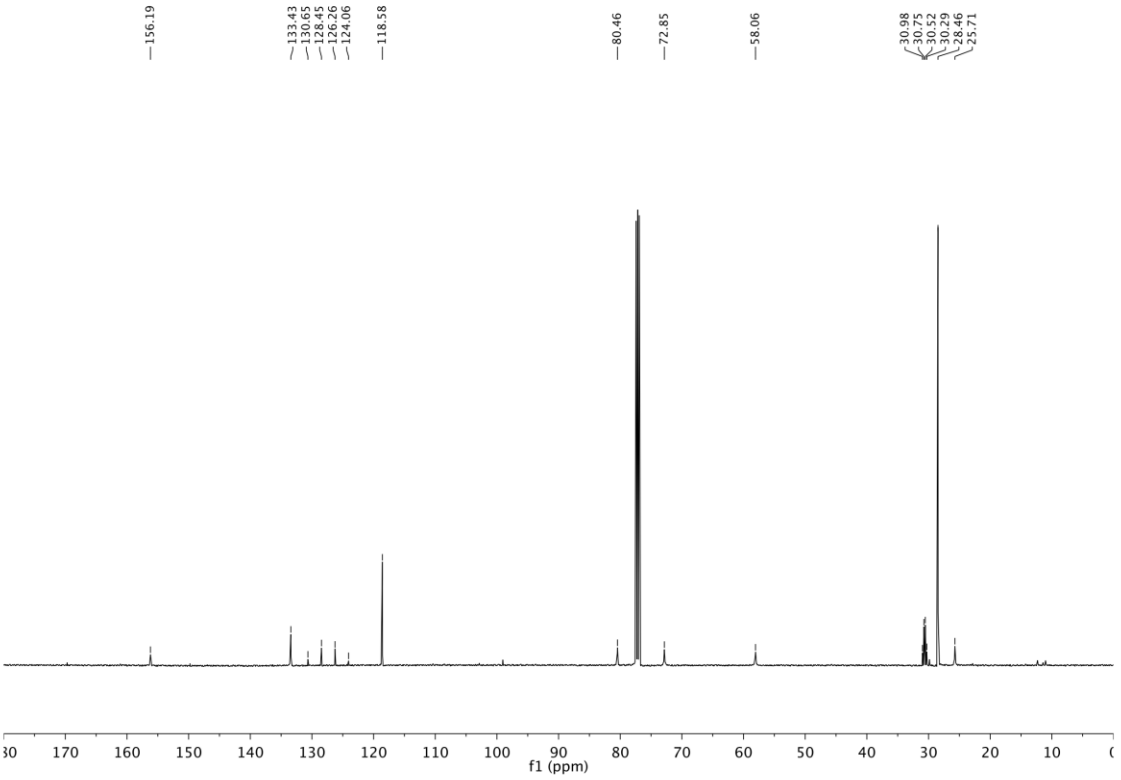
^{19}F NMR (100 MHz, $CDCl_3$) δ -66.4.

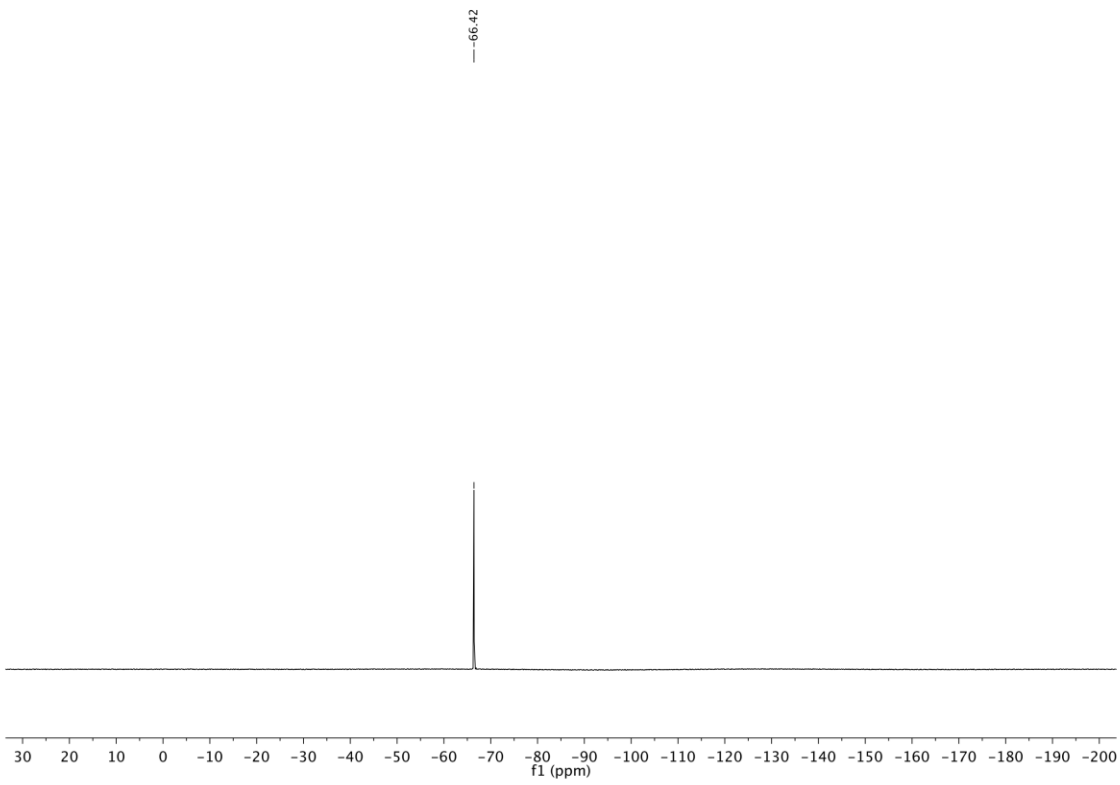
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 133.4, 127.4 (q, J_{C-F} = 276.0), 118.6, 80.5, 72.9, 58.1, 30.6 (q, J_{C-F} = 29.0), 28.5, 25.7.

HRMS (ESI) Calcd. for $C_{12}H_{20}F_3NO_3Na^+$ $[M+Na]^+$: 306.1293, Found: 306.1292.

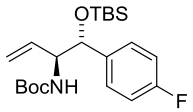
FTIR (neat): 3347, 2987, 2944, 1740, 1676, 1529, 1449, 1368, 1305, 1246, 1224, 1161, 1131, 1008, 935, 859, 769 cm^{-1}.


5.84
5.83
5.81
5.80
5.78
5.77
5.76
5.32
5.32
5.31
5.29
5.29
5.29
5.27
4.91
4.18
3.72
3.69
2.75
2.43
2.39
2.39
2.38
2.35
2.34
2.32
2.29
2.28
2.24
2.18
2.17
2.15
2.10
2.09
2.08
1.70
1.69
1.61
1.60
1.00
1.99
0.79
0.85
0.98
0.80
1.25
1.05
2.30
9.04
f1 (ppm)


156.19
133.43
130.65
128.45
126.26
124.06
118.58
80.46
72.85
58.06
30.98
30.75
30.52
30.29
28.46
25.71
f1 (ppm)


-66.42
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

D. Procedure and Preparation of S1



To a stirred solution of compound **4b** (0.2 mmol, 100 mol %) in anhydrous DMF (1 mL, 0.2 M) were added imidazole (0.6 mmol, 300 mol %) and TBSCl (0.3 mmol, 150 mol %). The mixture was allowed to stir at 60 °C for 15 hours. H_2O was then added after the mixture cooled to room temperature. The mixture was extracted three times with EtOAc, and the combined organic layers was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed in *vacuo* and the residue was subjected to column chromatography (SiO_2; 3%-5% EtOAc/Hexanes). The title compound was obtained as a colorless oil in 90% yield (71.3 mg).

R_f = 0.64 (20% EtOAc/Hexanes).

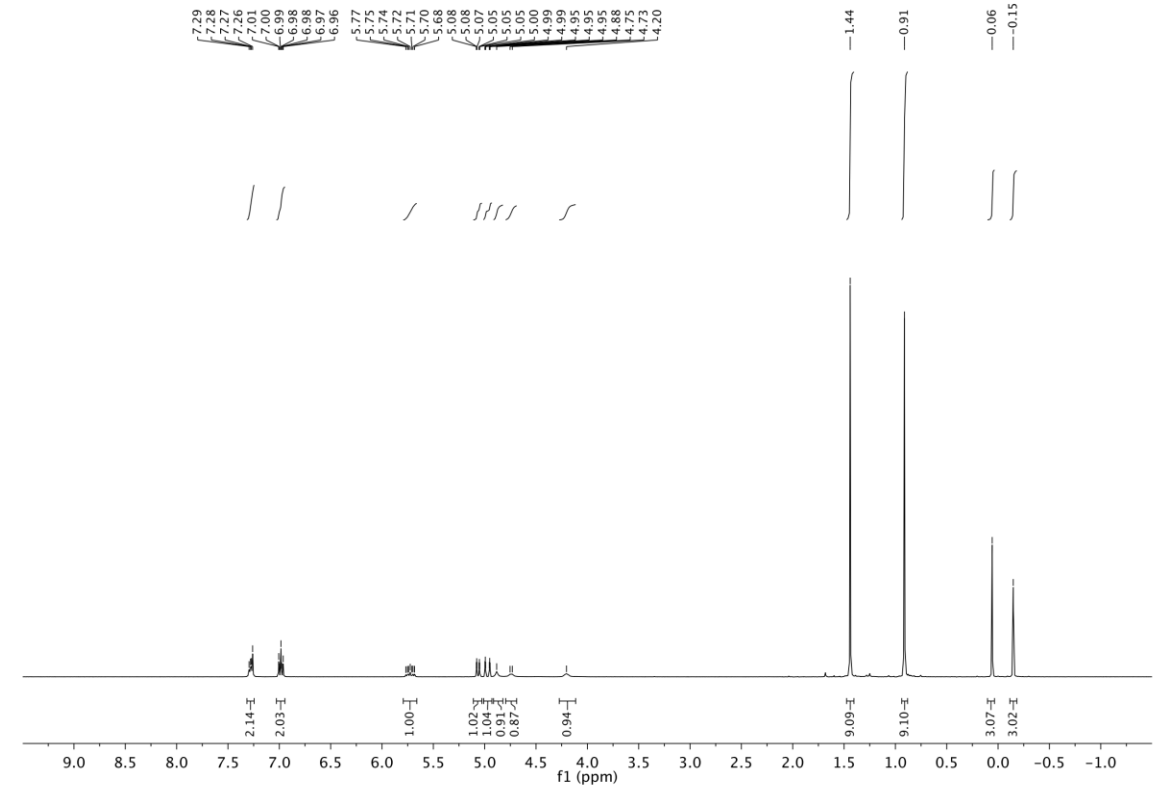
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.03 – 6.95 (m, 2H), 5.72 (ddd, *J* = 17.0, 10.5, 6.3 Hz, 1H), 5.06 (dt, *J* = 10.6, 1.3 Hz, 1H), 4.97 (dt, *J* = 17.3, 1.4 Hz, 1H), 4.88 (s, 1H), 4.74 (d, *J* = 8.6 Hz, 1H), 4.20 (s, 1H), 1.44 (s, 9H), 0.91 (s, 9H), 0.06 (s, 3H), -0.15 (s, 3H).

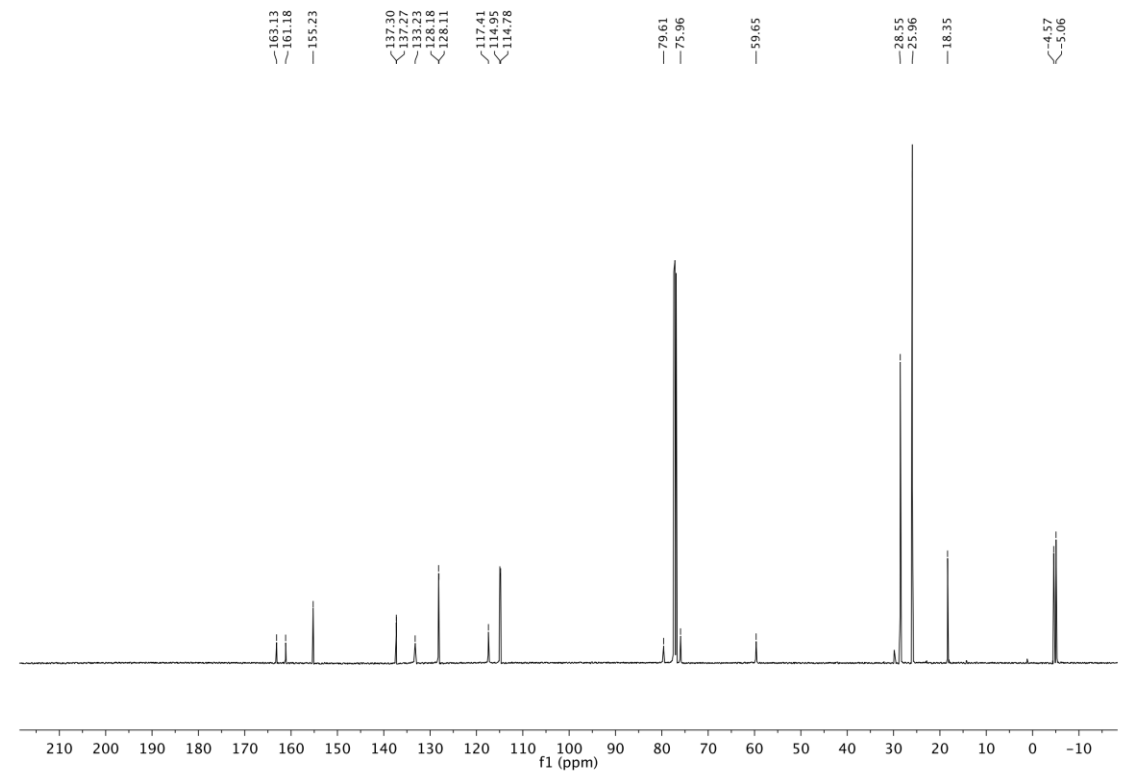
^{19}F HMR (100 MHz, $CDCl_3$) δ -115.6.

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 (d, J_{C-F} = 244.8 Hz), 155.2, 137.3 (d, J_{C-F} = 3.1 Hz),, 133.23, 128.1 (d, J_{C-F} = 8.0 Hz),, 117.41, 114.9 (d, J_{C-F} = 21.3 Hz)., 79.61, 75.96, 59.65, 28.55, 25.96, 18.35, -4.57, -5.06.

HRMS (ESI) Calcd. for $C_{21}H_{34}FNaNO_3Si$ $[M+Na]^+$: 418.2192, Found: 418.2184.

FTIR (neat): 2956, 2930, 2858, 1707, 1509, 1366, 1253, 1223, 1169, 1088, 992, 864, 837, 776, 669 cm^{-1}.


7.29
7.28
7.27
7.26
7.01
7.00
6.99
6.98
6.98
6.97
6.96
5.77
5.75
5.74
5.72
5.71
5.70
5.68
5.08
5.08
5.07
5.05
5.05
5.00
4.99
4.99
4.95
4.95
4.95
4.88
4.75
4.73
4.20
1.44
0.91
0.06
-0.15
2.14
2.03
1.00
1.02
1.04
0.91
0.87
0.94
9.09
9.10
3.07
3.02
f1 (ppm)


163.13
161.18
155.23
137.30
137.27
133.23
128.18
128.11
117.41
114.95
114.78
79.61
75.96
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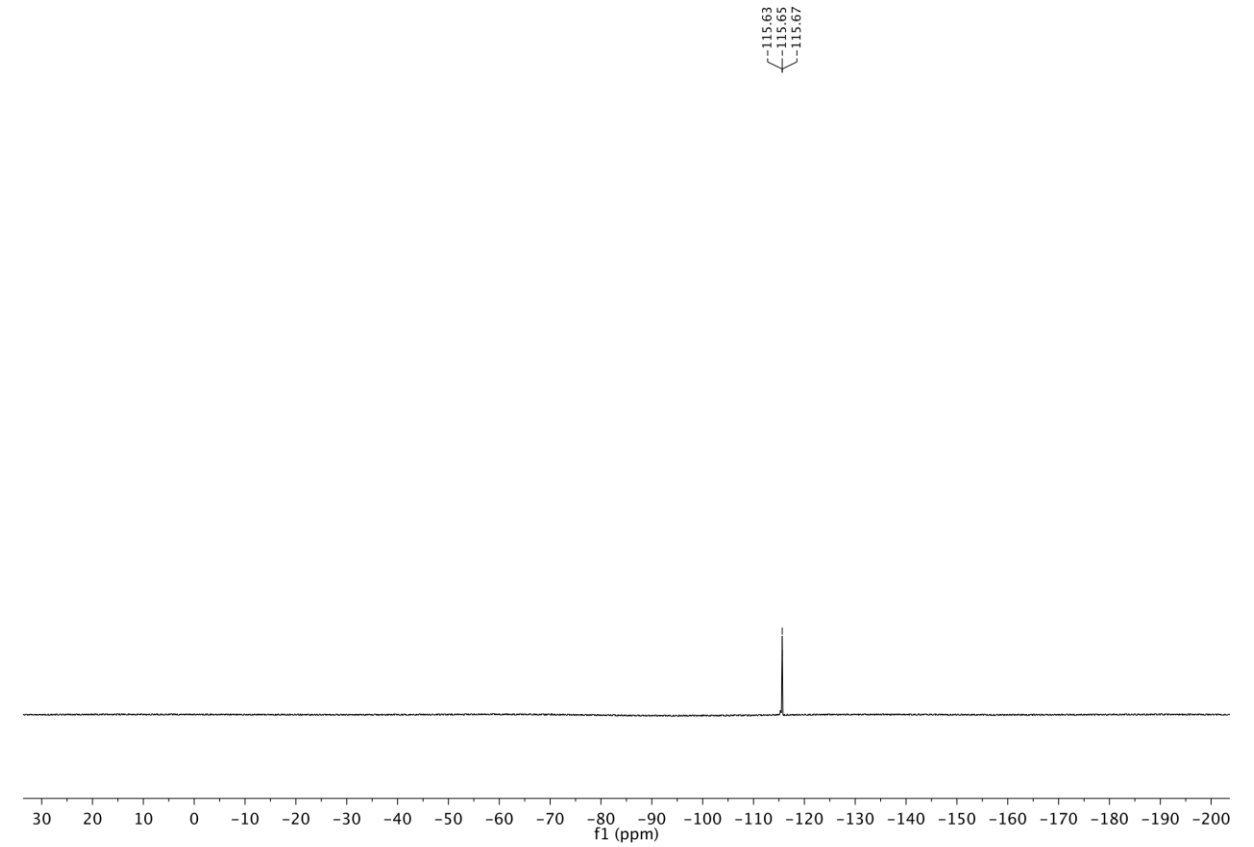
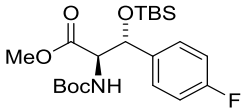
28.55
25.96
18.35
-4.57
-5.06
f1 (ppm)


-115.63
-115.65
-115.67
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

E. General Procedure and Preparation of 5b



To a stirred solution of compound **S1** (0.15 mmol, 100 mol%) in MeCN:CCl_4:H_2O (1.5 mL, 1:1:1.5, 0.1 M) were added $NaIO_4$ (0.75 mmol, 500 mol %) and $RuCl_3 \cdot xH_2O$ (0.0075 mmol, 5 mol %). The mixture was allowed to stir at room temperature for 12 hours until the complete consumption of the starting material as monitored by TLC. The mixture was diluted with DCM, filtered through a short pad of celite and washed with DCM. The filtrate was washed with H_2O and the aqueous phase was extracted three times with DCM. The combined organic layers was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed in *vacuo* and the residue was dissolved in $CHCl_3$:MeOH (1.5 mL, 2:1, 0.1 M). $TMSCH_2N_2$ in hexanes (0.15 mL, 0.3 mmol, 200 mol %) was then added dropwise. The mixture was allowed to stir at room temperature for 2 hours. The solvent was then removed in *vacuo* and the residue was subjected to column chromatography (SiO_2; 3%-5% EtOAc/Hexanes). The title compound was obtained as a colorless oil in 65% yield over two steps (41.7 mg).

R_f = 0.23 (10% EtOAc/Hexanes).

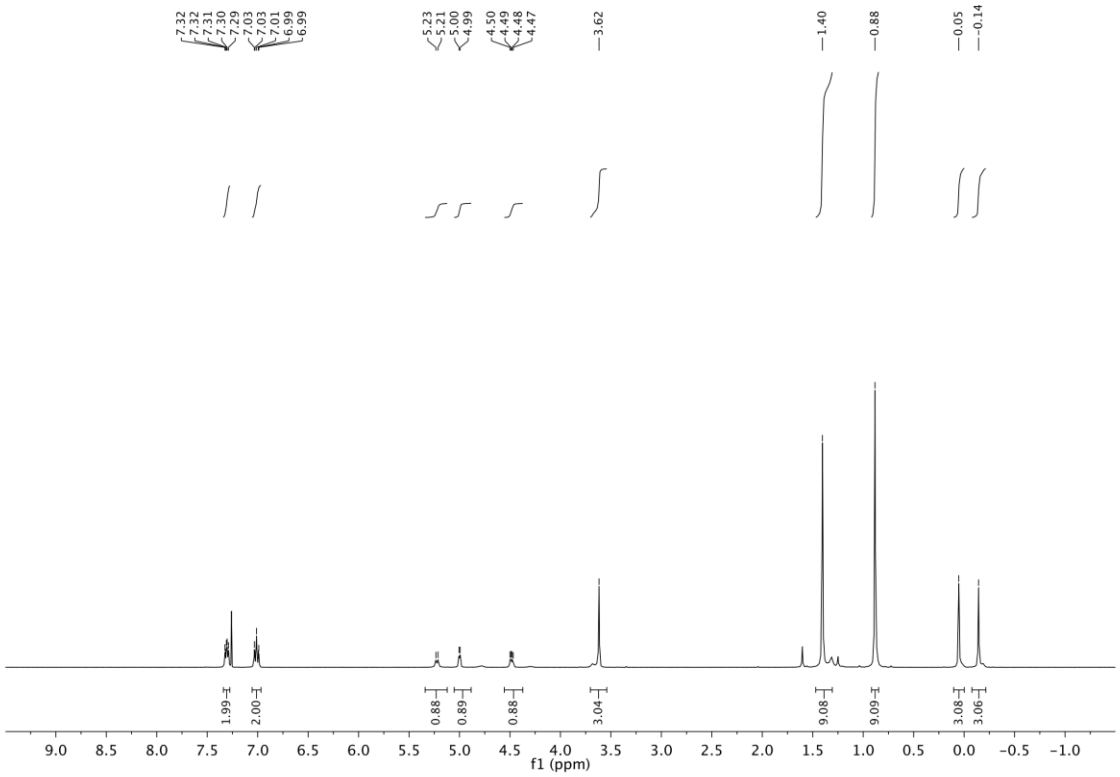
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 5.22 (d, *J* = 8.4 Hz, 1H), 5.00 (d, *J* = 4.3 Hz, 1H), 4.49 (dd, *J* = 8.6, 4.4 Hz, 1H), 3.62 (s, 3H), 1.40 (s, 9H), 0.88 (s, 9H), 0.05 (s, 3H), -0.14 (s, 3H).

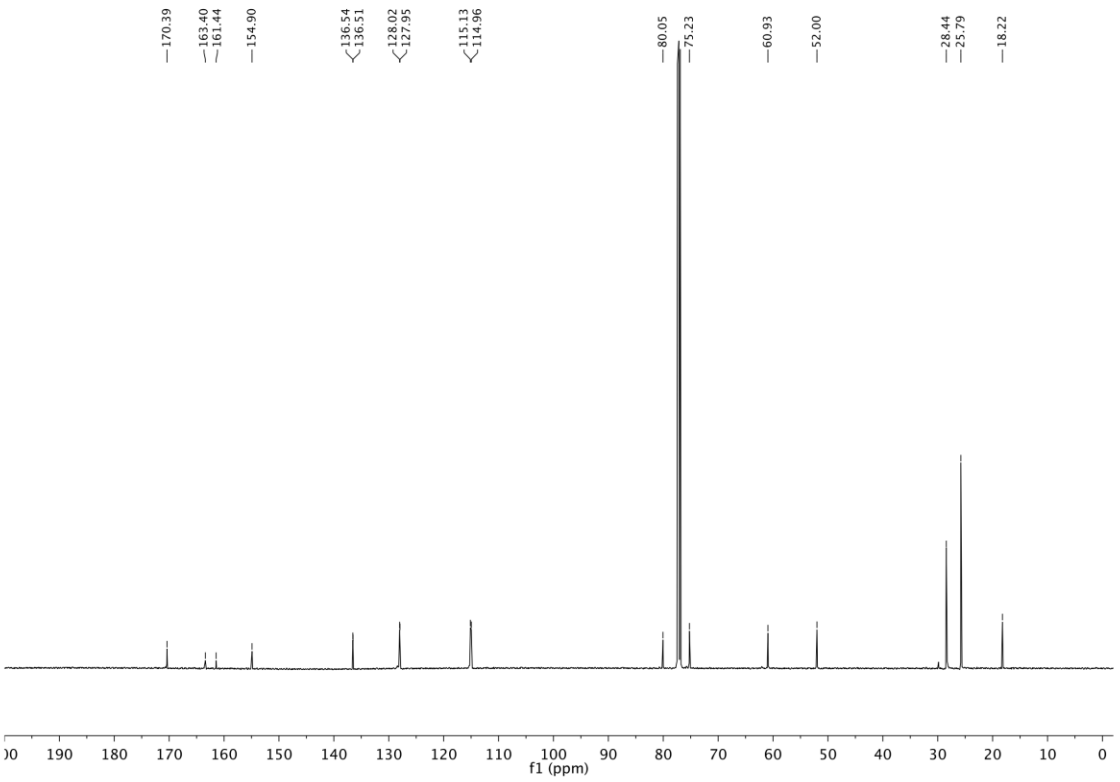
^{19}F NMR (125 MHz, $CDCl_3$) δ -115.0.

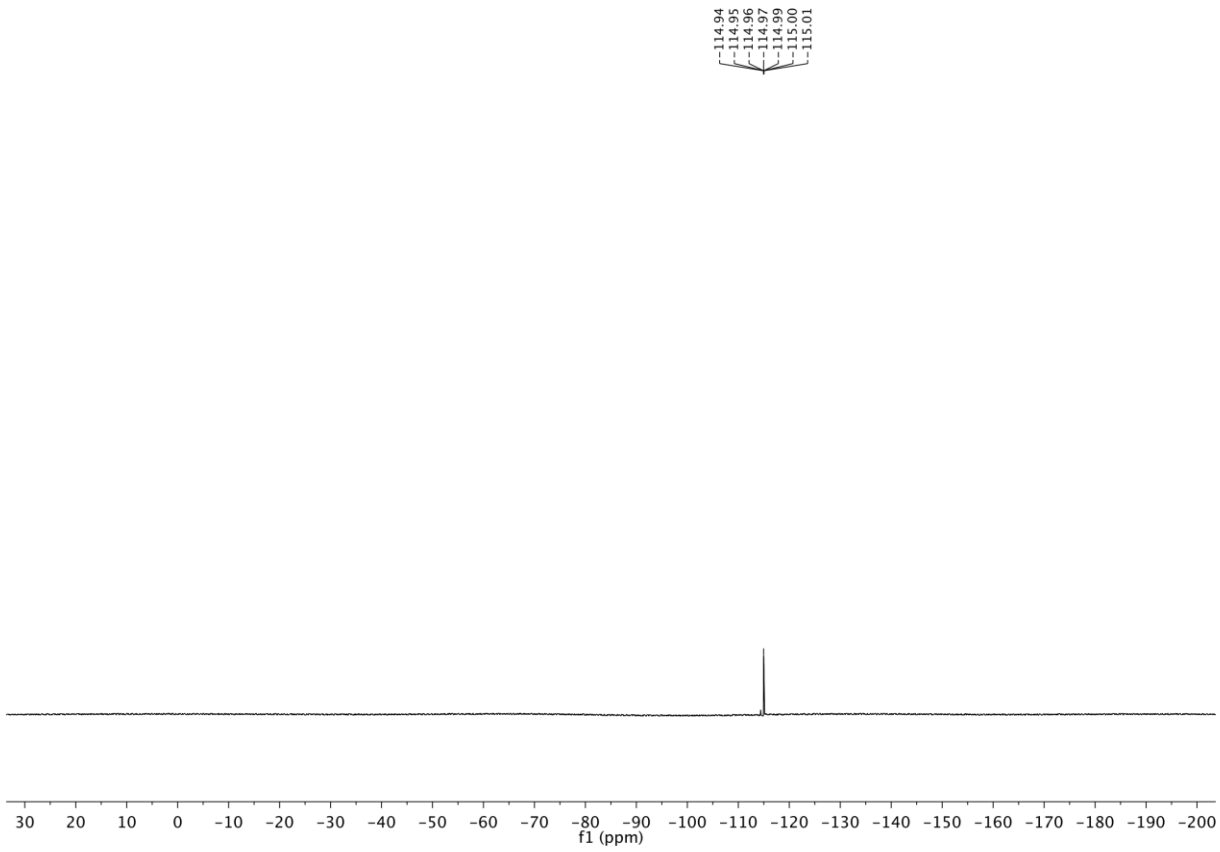
^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 162.4 (d, $J_{C\text{-}F}$ = 245.7 Hz), 154.9, 136.5 (d, $J_{C\text{-}F}$ = 3.1 Hz), 128.0 (d, $J_{C\text{-}F}$ = 8.1 Hz), 115.0 (d, $J_{C\text{-}F}$ = 21.7 Hz), 80.1, 75.2, 60.9, 52.0, 28.4, 25.8, 18.2, -4.7, -5.2.

HRMS (ESI) Calcd. for $C_{21}H_{34}FNO_5SiNa^+$ $[M+Na]^+$: 450.2088, Found: 450.2089.

FTIR (neat): 2954, 2928, 2852, 1712, 1606, 1509, 1365, 1253, 1222, 1156, 1088, 1015, 854, 837, 777,757, 699 cm^{-1}.


7.32
7.32
7.31
7.30
7.29
7.03
7.03
7.01
6.99
6.99
5.23
5.21
5.00
4.99
4.50
4.49
4.48
4.47
3.62
1.40
0.88
0.05
-0.14
1.99
2.00
0.88
0.89
0.88
3.04
9.08
9.09
3.08
3.06
f1 (ppm)


170.39
163.40
161.44
154.90
136.54
136.51
128.02
127.95
115.13
114.96
80.05
75.23
60.93
52.00
28.44
25.79
18.22
f1 (ppm)


-114.94
-114.95
-114.96
-114.97
-114.99
-115.00
-115.01
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

F. Crystallographic Material for 4b

X-ray Experimental for $C_{15}H_{20}FNO_3$ (4b)

X-ray Experimental for complex $C_{15}H_{20}NO_3F$: Crystals grew as long, very thin colorless needles by vapor diffusion of pentane into diethyl ether. The data crystal was cut from a longer crystal and had approximate dimensions; 0.32 x 0.03 x 0.02 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus Cu Kα radiation source (λ = 1.5418Å) with collimating mirror monochromators. A total of 364 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 53 seconds per frame with a detector offset of +/- 42.4° and 120 seconds per frame with a detector offset of +/- 109.8°. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.38.43f.[3] The structure was solved by direct methods using SHELXT[4] and refined by full-matrix least-squares on F2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.[5] Structure analysis was aided by use of the programs PLATON[6] and WinGX.[7] The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms bound to N1 atoms was located in a ΔF map and refined with an isotropic displacement parameter.

The function, $\Sigma w(|Fo|^2 - |Fc|^2)^2$, was minimized, where $w = 1/[(\sigma(Fo))^2 + (0.0829*P)^2 + (1.279*P)]$ and $P = (|Fo|^2 + 2|Fc|^2)/3$. $Rw(F^2)$ refined to 0.226, with R(F) equal to 0.0859 and a goodness of fit, S, = 1.12. Definitions used for calculating R(F), $Rw(F^2)$ and the goodness of fit, S, are given below.[8] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[9] All figures were generated using SHELXTL/PC.[10] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found elsewhere.

.

Table 1. Crystal data and structure refinement for **4b**.

Empirical formula	C15 H20 F N O3	
Formula weight	281.32	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.0624(7) Å	α= 90°.
	b = 10.961(3) Å	β= 90°.
	c = 26.361(4) Å	γ = 90°.
Volume	1462.8(5) $Å^3$	
Z	4	
Density (calculated)	1.277 Mg/m^3	
Absorption coefficient	0.805 mm^{-1}	
F(000)	600	
Crystal size	0.320 x 0.030 x 0.020 mm^3	
Theta range for data collection	3.353 to 75.126°.	
Index ranges	-6<=h<=5, -13<=k<=13, -16<=l<=32	
Reflections collected	3095	
Independent reflections	2260 [R(int) = 0.0495]	
Completeness to theta = 67.684°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.602	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2260 / 120 / 189	
Goodness-of-fit on F^2	1.115	
Final R indices [I>2sigma(I)]	R1 = 0.0859, wR2 = 0.2060	
R indices (all data)	R1 = 0.1075, wR2 = 0.2259	
Absolute structure parameter	-0.1(5)	
Largest diff. peak and hole	0.410 and -0.349 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	7659(13)	4793(7)	4370(2)	29(1)
C2	8520(15)	5686(6)	4041(3)	32(2)
C3	7279(15)	6825(7)	4013(3)	38(2)
C4	5107(16)	7028(7)	4318(3)	40(2)
C5	4209(16)	6184(6)	4659(3)	36(2)
C6	5483(14)	5045(6)	4680(3)	31(2)
C7	8945(13)	3552(6)	4378(2)	29(1)
C8	7725(14)	2666(6)	3980(2)	29(1)
C9	9128(15)	1463(6)	3979(2)	31(2)
C10	8127(18)	409(7)	4112(3)	42(2)
C11	5661(13)	3694(6)	3247(2)	27(1)
C12	4442(13)	4878(7)	2485(3)	32(2)
C13	2766(15)	3897(7)	2236(3)	34(2)
C14	6199(16)	5491(9)	2093(3)	44(2)
C15	2845(15)	5817(7)	2768(3)	36(2)
N9	7818(11)	3209(6)	3479(2)	28(1)
O1	8915(9)	2984(5)	4867(2)	30(1)
O2	3408(8)	3610(5)	3397(2)	31(1)
O3	6425(9)	4295(5)	2824(2)	33(1)
F1	3859(11)	8130(4)	4290(2)	54(1)

Table 3. Bond lengths [Å] and angles [°] for **4b**.

C1-C2	1.379(10)	C10-H10A	0.95
C1-C6	1.399(10)	C10-H10B	0.95
C1-C7	1.508(10)	C11-O2	1.210(8)
C2-C3	1.399(10)	C11-O3	1.354(8)
C2-H2	0.95	C11-N9	1.359(9)
C3-C4	1.380(11)	C12-O3	1.487(8)
C3-H3	0.95	C12-C15	1.507(11)
C4-F1	1.365(8)	C12-C13	1.518(10)
C4-C5	1.366(11)	C12-C14	1.522(10)
C5-C6	1.406(10)	C13-H13A	0.98
C5-H5	0.95	C13-H13B	0.98
C6-H6	0.95	C13-H13C	0.98
C7-O1	1.433(8)	C14-H14A	0.98
C7-C8	1.557(9)	C14-H14B	0.98
C7-H7	1.0000	C14-H14C	0.98
C8-N9	1.450(9)	C15-H15A	0.98
C8-C9	1.497(9)	C15-H15B	0.98
C8-H8	1.00	C15-H15C	0.98
C9-C10	1.309(10)	N9-H9N	0.83(7)
C9-H9	0.95	O1-H1O	0.84

C2-C1-C6	118.4(7)	C4-C5-C6	118.4(7)
C2-C1-C7	120.8(6)	C4-C5-H5	120.8
C6-C1-C7	120.7(6)	C6-C5-H5	120.8
C1-C2-C3	121.7(7)	C5-C6-C1	120.9(7)
C1-C2-H2	119.2	C5-C6-H6	119.6
C3-C2-H2	119.2	C1-C6-H6	119.6
C4-C3-C2	118.1(7)	O1-C7-C1	113.6(6)
C4-C3-H3	121.0	O1-C7-C8	109.3(6)
C2-C3-H3	121.0	C1-C7-C8	112.5(5)
F1-C4-C5	118.8(7)	O1-C7-H7	107.0
F1-C4-C3	118.7(7)	C1-C7-H7	107.0
C5-C4-C3	122.5(7)	C8-C7-H7	107.0

N9-C8-C9	110.2(6)	C12-C13-H13B	109.5
N9-C8-C7	110.1(6)	H13A-C13-H13B	109.5
C9-C8-C7	111.2(5)	C12-C13-H13C	109.5
N9-C8-H8	108.4	H13A-C13-H13C	109.5
C9-C8-H8	108.4	H13B-C13-H13C	109.5
C7-C8-H8	108.4	C12-C14-H14A	109.5
C10-C9-C8	126.4(7)	C12-C14-H14B	109.5
C10-C9-H9	116.8	H14A-C14-H14B	109.5
C8-C9-H9	116.8	C12-C14-H14C	109.5
C9-C10-H10A	120.0	H14A-C14-H14C	109.5
C9-C10-H10B	120.0	H14B-C14-H14C	109.5
H10A-C10-H10B	120.0	C12-C15-H15A	109.5
O2-C11-O3	125.2(6)	C12-C15-H15B	109.5
O2-C11-N9	125.5(6)	H15A-C15-H15B	109.5
O3-C11-N9	109.4(6)	C12-C15-H15C	109.5
O3-C12-C15	111.0(6)	H15A-C15-H15C	109.5
O3-C12-C13	109.5(6)	H15B-C15-H15C	109.5
C15-C12-C13	113.5(6)	C11-N9-C8	123.0(6)
O3-C12-C14	101.7(5)	C11-N9-H9N	128(4)
C15-C12-C14	110.4(7)	C8-N9-H9N	108(4)
C13-C12-C14	110.2(6)	C7-O1-H1O	109.5
C12-C13-H13A	109.5	C11-O3-C12	120.7(5)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	25(3)	33(3)	29(3)	-2(3)	-6(3)	-3(3)
C2	30(3)	31(3)	35(3)	1(3)	-2(3)	-5(3)
C3	31(3)	34(4)	49(4)	7(3)	-3(3)	-7(3)
C4	40(4)	25(3)	53(4)	-4(3)	-5(3)	-3(3)
C5	36(4)	28(3)	43(4)	-8(3)	0(3)	2(3)
C6	24(3)	31(3)	37(3)	-1(3)	4(3)	-4(3)
C7	21(3)	33(3)	33(3)	2(3)	-1(3)	1(3)
C8	24(3)	31(3)	33(3)	4(3)	0(3)	1(3)
C9	36(4)	24(3)	33(3)	-4(3)	-7(3)	5(3)
C10	53(5)	31(4)	41(4)	2(3)	-2(4)	1(4)
C11	19(3)	25(3)	35(3)	-3(3)	-7(3)	1(3)
C12	16(3)	40(4)	40(3)	8(3)	-1(3)	0(3)
C13	29(4)	37(4)	37(3)	-1(3)	-7(3)	8(3)
C14	31(4)	61(5)	40(4)	20(4)	1(3)	0(4)
C15	31(4)	31(4)	45(4)	6(3)	-5(3)	-4(3)
N9	11(2)	36(3)	36(3)	0(2)	-3(2)	1(2)
O1	21(2)	39(3)	31(2)	3(2)	2(2)	3(2)
O2	13(2)	36(3)	43(3)	4(2)	1(2)	-1(2)
O3	18(2)	45(3)	34(2)	13(2)	0(2)	0(2)
F1	56(3)	23(2)	82(3)	3(2)	-2(3)	5(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4b**.

	x	y	z	U(eq)
H2	9992	5525	3828	38
H3	7913	7440	3791	45
H5	2759	6362	4875	43
H6	4858	4440	4908	37
H7	10839	3671	4283	35
H8	5834	2521	4072	35
H9	10919	1466	3872	37
H10A	6344	359	4222	50
H10B	9185	-306	4098	50
H13A	3920	3285	2080	52
H13B	1649	4268	1975	52
H13C	1649	3506	2492	52
H14A	7310	6104	2259	66
H14B	5096	5887	1835	66
H14C	7324	4877	1930	66
H15A	1414	5412	2954	54
H15B	2094	6402	2527	54
H15C	3989	6249	3008	54
H1O	7348	2834	4952	46
H9N	9390(140)	3320(60)	3400(20)	8(14)

Table 6. Torsion angles [°] for **4b**.

C6-C1-C2-C3	0.2(10)
C7-C1-C2-C3	177.2(6)
C1-C2-C3-C4	-1.4(11)
C2-C3-C4-F1	-179.2(7)
C2-C3-C4-C5	2.9(11)
F1-C4-C5-C6	179.1(7)
C3-C4-C5-C6	-2.9(11)
C4-C5-C6-C1	1.6(11)
C2-C1-C6-C5	-0.2(10)
C7-C1-C6-C5	-177.3(6)
C2-C1-C7-O1	148.9(6)
C6-C1-C7-O1	-34.2(8)
C2-C1-C7-C8	-86.3(7)
C6-C1-C7-C8	90.7(7)
O1-C7-C8-N9	-178.1(5)
C1-C7-C8-N9	54.7(7)
O1-C7-C8-C9	-55.6(7)
C1-C7-C8-C9	177.2(6)
N9-C8-C9-C10	-123.2(8)
C7-C8-C9-C10	114.3(8)
O2-C11-N9-C8	-8.9(11)
O3-C11-N9-C8	170.6(6)
C9-C8-N9-C11	132.9(7)
C7-C8-N9-C11	-104.0(7)
O2-C11-O3-C12	-2.8(11)
N9-C11-O3-C12	177.7(6)
C15-C12-O3-C11	59.1(8)
C13-C12-O3-C11	-66.9(8)
C14-C12-O3-C11	176.5(6)

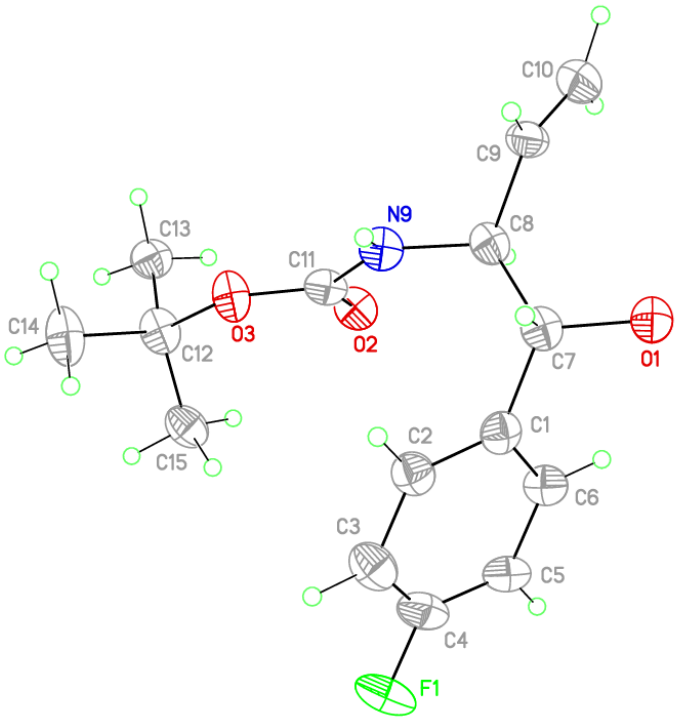
Table 7. Hydrogen bonds for **4b** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C13-H13C...O2	0.98	2.55	3.094(9)	115.1
O1-H1O...O1#1	0.84	2.01	2.832(4)	164.8
N9-H9N...O2#2	0.83(7)	2.06(7)	2.872(7)	167(6)

Symmetry transformations used to generate equivalent atoms:

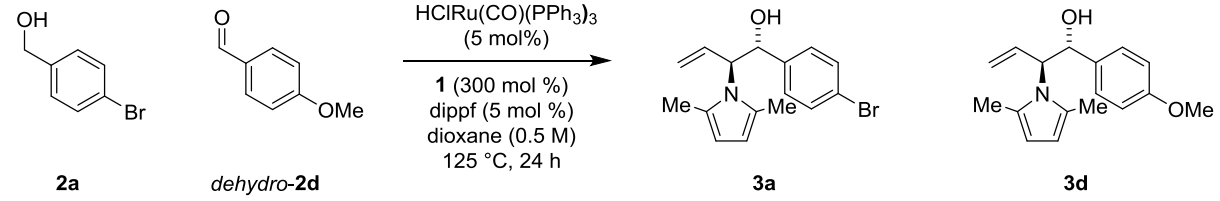
#1 x-1/2,-y+1/2,-z+1 #2 x+1,y,z

Figure 1. View of **4b** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.



G. Competition Experiment Establishing Rapid Redox Equilibrium

Reaction between Alcohol 2a and Aldehyde *dehydro*-2d

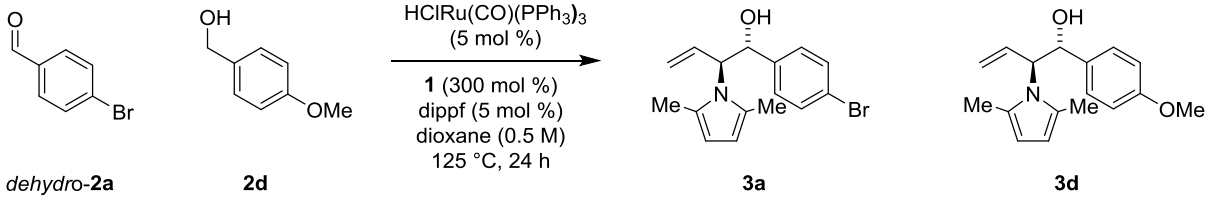


2a *dehydro*-**2d** **3a** **3d**

3a : 3d = 3.3 :1
73% yield
(combined yield based on 100 mol % of alcohol as the limiting reagent)

To a resealable pressure tube (13x100) were added $HClRu(CO)(PPh_3)_3$ (9.5 mg, 0.010 mmol, 5 mol %), dippf (4.2 mg, 0.010 mmol, 5 mol %) and alcohol **2a** (37.4 mg, 0.2 mmol, 100 mol %). The tube was sealed with a rubber septum and purged with argon for 20 minutes. Dioxane (0.40 mL, 0.5 M) was added to the reaction vessel. Aldehyde *dehydro*-**2d** (24.3 μL, 0.2 mmol, 100 mol %) and acetylenic pyrrole **1** (0.60 mmol, 300 mol %) were subsequently added to the reaction vessel and the rubber septum was quickly replaced with a screw cap. The mixture was allowed to stir at 125 °C for 24 hours. The mixture was then allowed to cool to room temperature and the solvent was removed *in vacuo*. The residue was subjected to column chromatography (SiO_2; 7.5%-10% EtOAc/Hexanes) and a 3.3:1 mixture of **3a** (35.9 mg, 56% yield) and **3d** (9.3 mg, 17% yield).

Reaction between Alcohol 2d and Aldehyde *dehydro*-2a



dehydro-**2a** **2d** **3a** **3d**

3a : 3d = 2.9 :1
73% yield
(combined yield based on 100 mol % of alcohol as the limiting reagent)

To a resealable pressure tube (13x100) were added $HClRu(CO)(PPh_3)_3$ (9.5 mg, 0.010 mmol, 5 mol %), dippf (4.2 mg, 0.010 mmol, 5 mol %) and aldehyde *dehydro*-**2a** (37.0 mg, 0.2 mmol, 100 mol %). The tube was sealed with a rubber septum and purged with argon for 20 minutes. Dioxane (0.40 mL, 0.5 M) was added to the reaction vessel. Alcohol **2d** (24.8 μL, 0.2 mmol, 100 mol %) and acetylenic pyrrole 1 (0.60 mmol, 300 mol %) were subsequently added to the reaction vessel and the rubber septum was quickly replaced with a screw cap. The mixture was allowed to stir at 125 °C for 24 hours. The mixture was then allowed to cool to room temperature and the solvent was removed *in vacuo*. The residue was subjected to column chromatography (SiO_2; 7.5%-10% EtOAc/Hexanes) and a 2.9:1 mixture of **3a** (34.5 mg, 54% yield) and **3d** (10.2 mg, 19% yield).

IV. References

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8. Rw(F2) = {Σw(|Fo|2 - |Fc|2)2/Σw(|Fo|)4}1/2 where w is the weight given each reflection.
   R(F) = Σ|Fo| - |Fc|)/Σ|Fo|} for reflections with Fo > 4(σ (Fo)).
   S = [Σw(|Fo|2 - |Fc|2)2/(n - p)]1/2, where n is the number of reflections and p is the number of refined parameters..
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