Engaging Alkenes and Alkynes in Deaminative Alkyl–Alkyl and Alkyl–Vinyl Cross-Couplings of Alkylpyridinium Salts

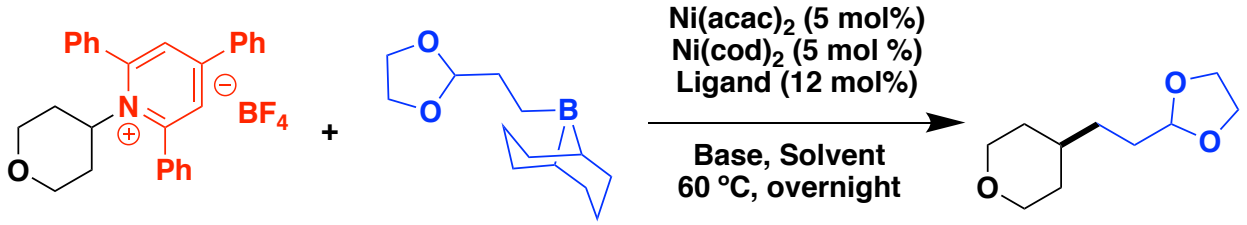
Kristen M. Baker, Diana Lucas Baca, Shane L. Plunkett, Mitchell E. Daneker, Mary P. Watson*
Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716
mpwatson@udel.edu

Supplementary Information

General Information

Reactions were performed in oven-dried Schlenk flasks or in oven-dried, round-bottomed flasks unless otherwise noted. Round-bottomed flasks were fitted with rubber septa, and reactions were conducted under an atmosphere of N_2. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed on silica gel 60 (40-63 μm, 60Å) unless otherwise noted. Commercial reagents, including 2,4,6-triphenylpyrylium tetrafluoroborate, were purchased from Sigma Aldrich, Acros, AstaTech, Fisher, Strem, TCI, Combi Blocks, Alfa Aesar, AK Scientific, Bide Pharmatech, Oakwood, or Cambridge Isotopes Laboratories and used as received with the following exceptions: MeCN and CH_2Cl_2 were dried by passing through drying columns.[1] MeCN was then degassed by sparging with N_2. Oven-dried potassium carbonate was added to $CDCl_3$ to remove trace acid. Potassium fluoride for small scale cross-couplings was dried in the oven overnight at 115 °C, passed through a sieve (U.S. Standard Test Sieve, E-11 Standard, No. 200) to ensure uniformity throughout the powder, and then stored in a desiccator. 4Å Molecular sieves were purchased and heated at 200 °C under vacuum, then crushed and stored in a desiccator. Proton nuclear magnetic resonance (^{1}H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra, and fluorine nuclear magnetic resonance spectra (^{19}F NMR) were recorded on both 400 MHz and 600 MHz spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.16). Chemical shifts for fluorine were externally referenced to $CFCl_3$ in $CDCl_3$ ($CFCl_3$ = δ 0). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, dt = doublet of triplets, dq = doublet of quartets, dp = doublet of pentets, tt = triplet of triplets, td = triplet of doublets, h = heptet), coupling constants in Hertz (Hz), integration. Infrared (IR) spectra were obtained using FTIR spectrophotometers with material loaded onto a KBr plate. The mass spectral data were obtained at the University of Delaware mass spectrometry facility. Melting points were taken on a Thomas-Hoover Uni-Melt Capillary Melting Point Apparatus.

High-Throughput Experimentation (HTE) Studies



Representative Preparation of Alkylborane. According to literature procedure, 2-vinyl-1,3-dioxalane (0.50 mL, 5.0 mmol, 1.0 equiv) and 9-borabicyclo[3.3.1]nonane (9-BBN, 0.5 M in THF, 10 mL, 5.0 mmol, 1.0 equiv) were combined and stirred in a bomb at room temperature under a N_2 atmosphere.[2] The bomb was then sealed with a Teflon stopper, and moved into a N_2-atmosphere glovebox.

General HTE Procedure. In a N_2-atmosphere glovebox, 250-µL vials containing pre-plated ligands (1 µmol of ligand in each, 12 mol %) were charged with a stir bar and placed in a 96-well reaction plate. $Ni(acac)_2$ (92 µg, 0.42 µmol, 5 mol %), $Ni(cod)_2$ (117 µg, 0.42 µmol, 5 mol %), and pyridinium salt **3a** (4.0 mg, 8.3 µmol, 1.0 equiv) were added as stock solutions in MeCN, such that the total amount of MeCN was 40 µL. Base was added to the solution of alkylborane. Then, a solution of alkylborane (0.5 M in THF as described above, 50 µL, 25 µmmol, 3.0 equiv) and base (28 µmol, 3.3 equiv) was added to each vial. The reaction plate was sealed, and the mixtures were stirred at 60 °C in an aluminum heating block overnight in the glovebox. The plate was then removed from the glovebox. A solution of 1,3,5-trimethoxybenzene (internal standard, 460 µg, 2.8 µmol, 0.33 equiv) and MeOH (100 µL) was added to each vial. 30 µL of each reaction mixture was then transferred to a second 96-well plate and diluted with 500 µL of MeOH. Using a centrifuge, any solids were deposited, before GC analysis.

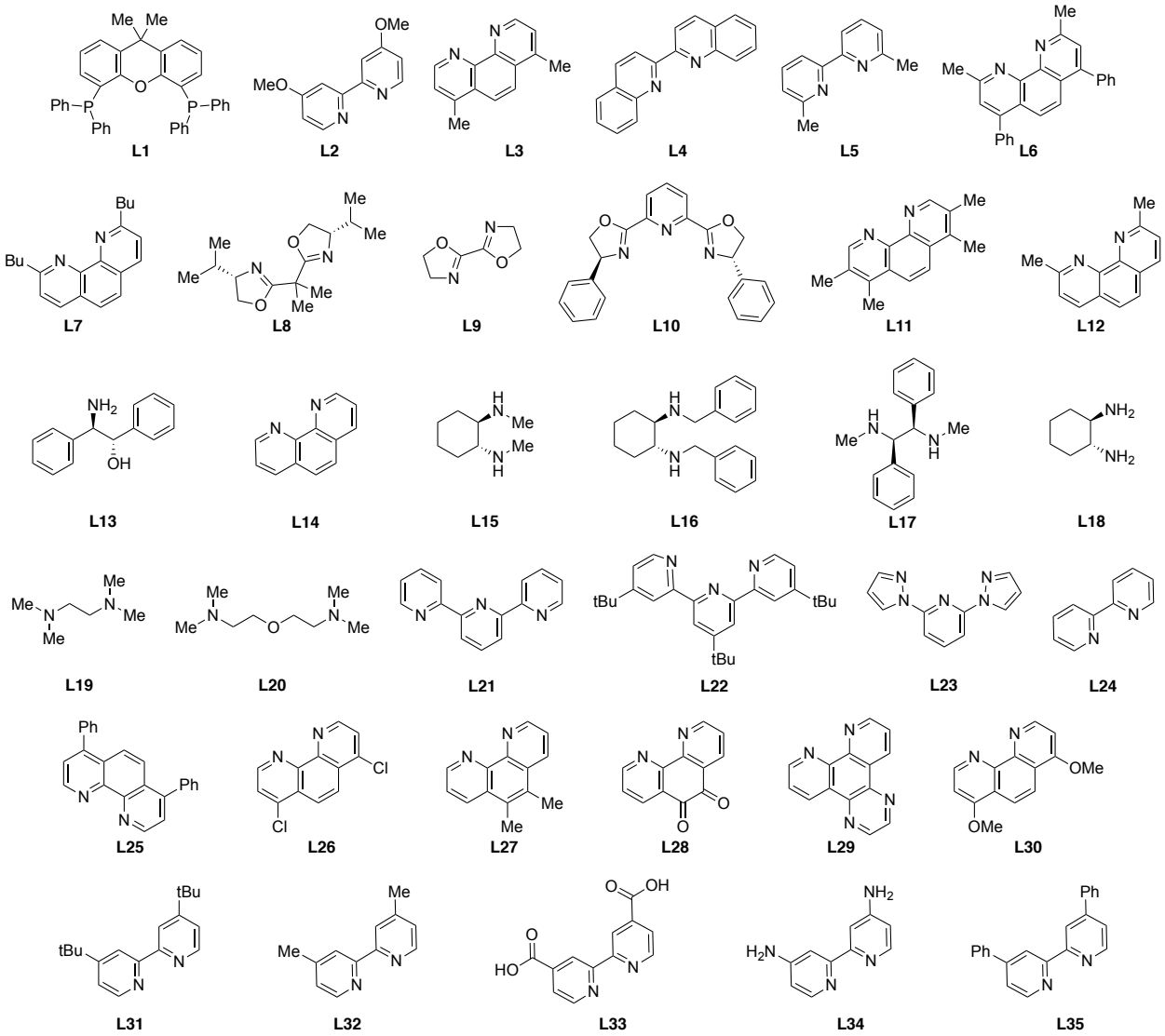


Figure S-1. Ligands used in HTE studies.

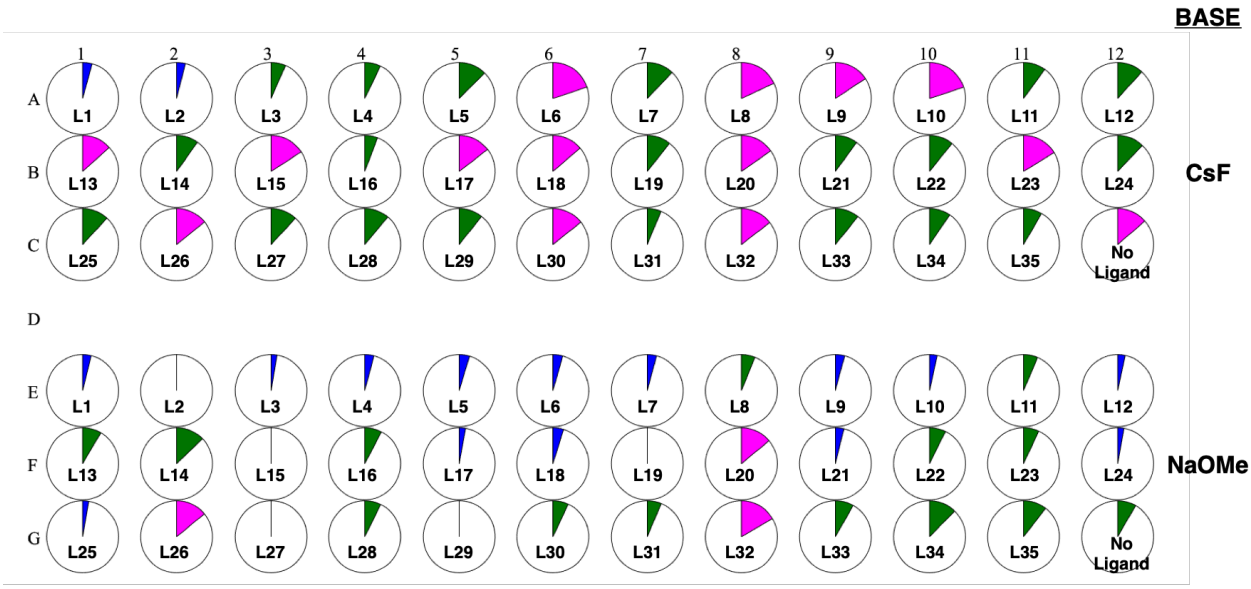


Figure S-2. HTE plate of 36 ligands vs. 2 bases. Ligand number denoted on each pie chart. Yields, as determined by GC analysis using 1,3,5-trimethoxybenzene as internal standard, are shown in pie charts for each reaction. In blue: 0–5% yield. In green: 5–13% yield. In magenta: 13–20% yield.

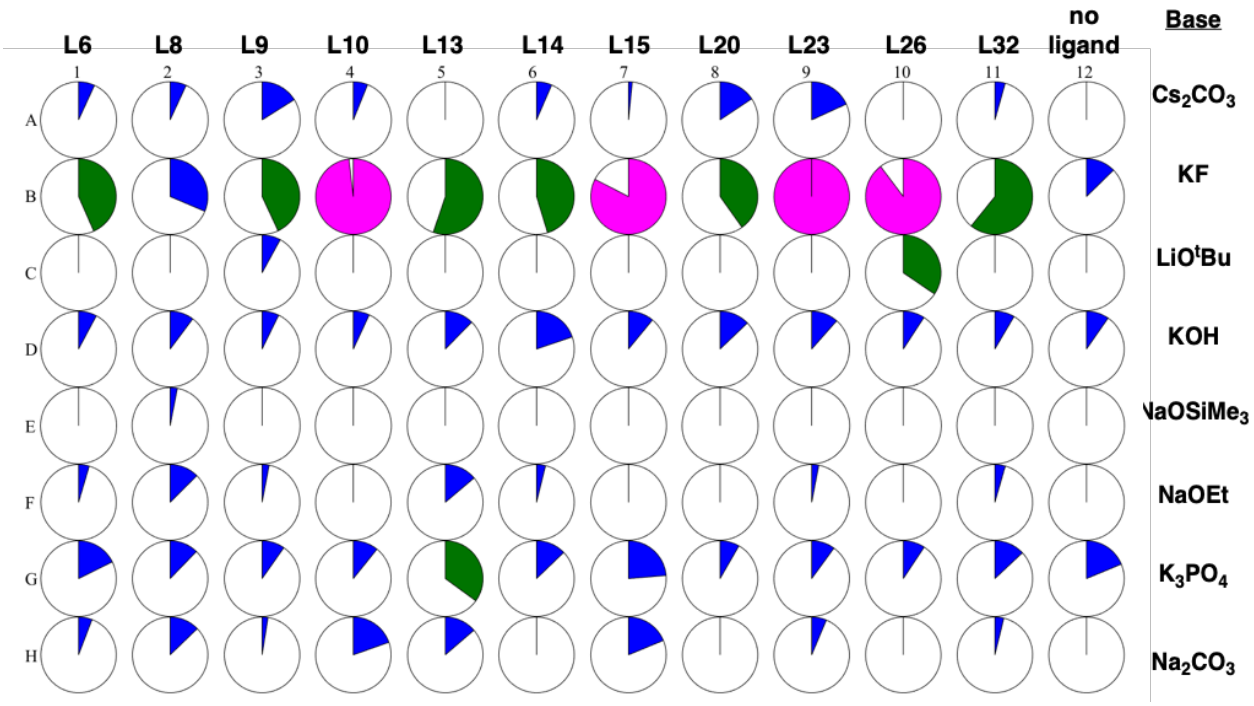
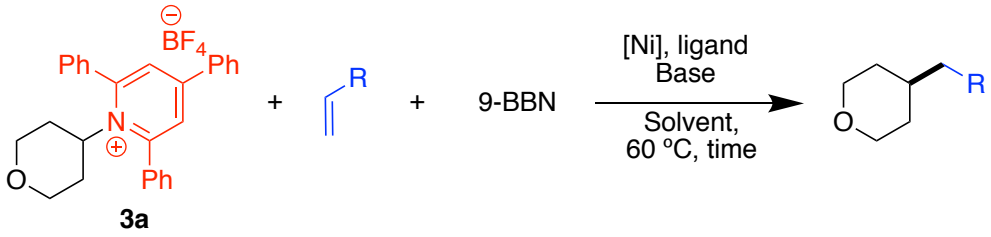


Figure S-3. HTE plate of 12 ligands vs. 8 bases. Yields, as determined by GC analysis using 1,3,5-trimethoxybenzene as internal standard, are shown in pie charts for each reaction. In blue: 0–33% yield. In green: 34–66% yield. In magenta: 67–100% yield.

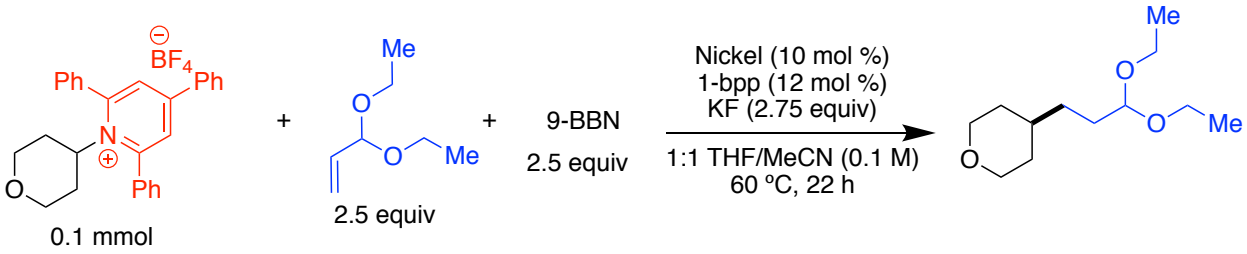
Optimization Studies



General Optimization Procedure. In a N_2-atmosphere glovebox, 9-borabicyclo[3.3.1]nonane (9-BBN, 0.5 M in THF), KF, and alkene were stirred in an oven-dried 1-dram vial equipped with a stirbar at 80 °C in an aluminum heating block for 30 min. Meanwhile, nickel salt, ligand, and solvent were stirred for 15 min. Pyridinium salt **3a** (48.0 mg, 0.10 mmol, 1.0 equiv) was added to the vial containing 9-BBN. The nickel/ligand solution was added afterwards. The vial was capped with a Teflon-lined cap and removed from the glovebox. The

mixture was stirred at 80 °C in an aluminum heating block for 24 h, unless otherwise stated. The mixture was then diluted with Et_2O (3 mL) and filtered through a plug of silica gel, which was rinsed with Et_2O (10 mL). The filtrate was concentrated. 1,3,5-Trimethoxybenzene (internal standard) was added. $CDCl_3$ was added, and the yield was determined by ^1H NMR analysis. Changes to this general procedure are noted in the tables below.

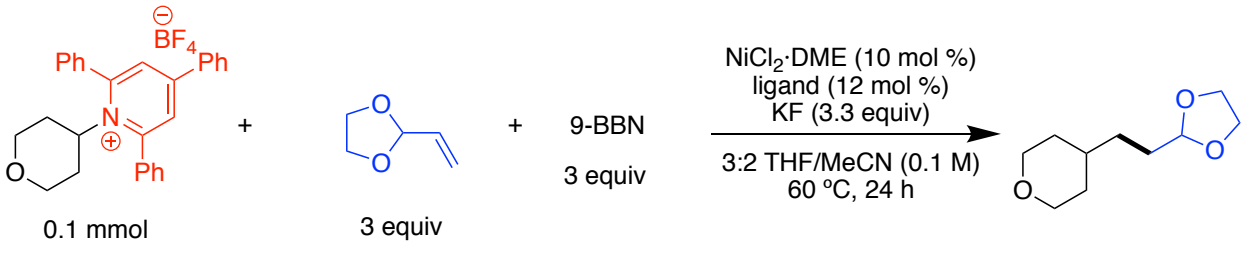
Effect of Nickel Precursor

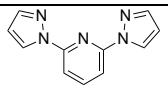
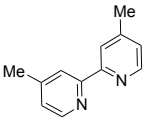
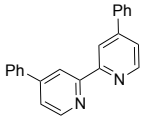
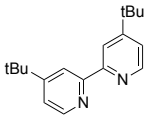
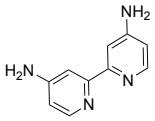
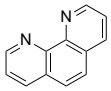
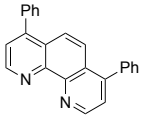
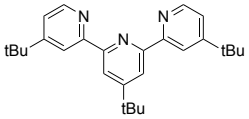


entry	Nickel	yield[a]
1	$NiCl_2 \cdot DME$	65
2	$NiBr_2 \cdot DME$	44
3	NiI_2	76
4	$Ni(acac)_2$	100
5	$NiCl_2 \cdot 4H_2O$	95
6	$Ni(OAc)_2$	28
7	$Ni(OTf)_2$	68

[a] Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

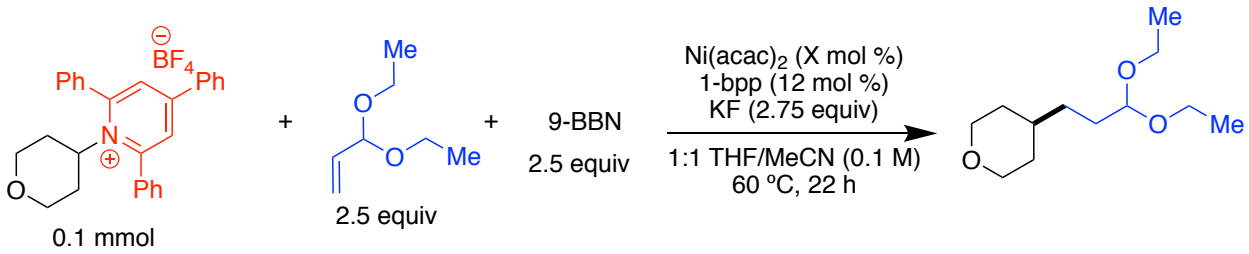
Effect of Ligand



entry	ligand	yield[a]
1	 1-bpp	55
2	 dmbpy	14
3	 diphenbpy	14
4	 di^{t}bubpy	27
5	 diaminobpy	6
6	 phen	15
7	 bphen	21
8	 ttb-terpy	62

[a] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

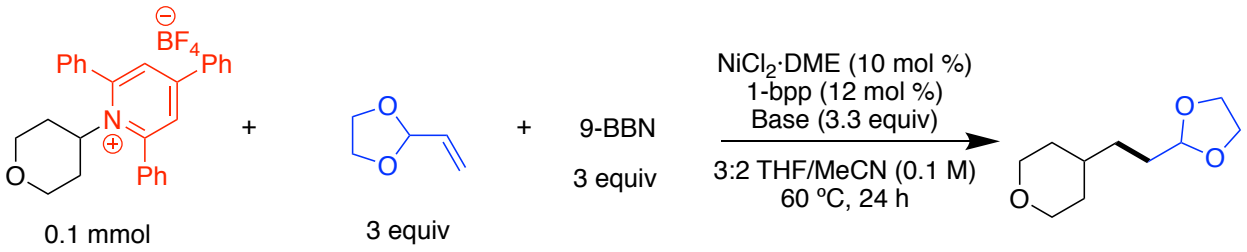
Effect of Catalyst Loading



entry	mol (%)	yield[a]
1	2	50
2	5	57
3	10	80
4	15	95
5	20	99

[a] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

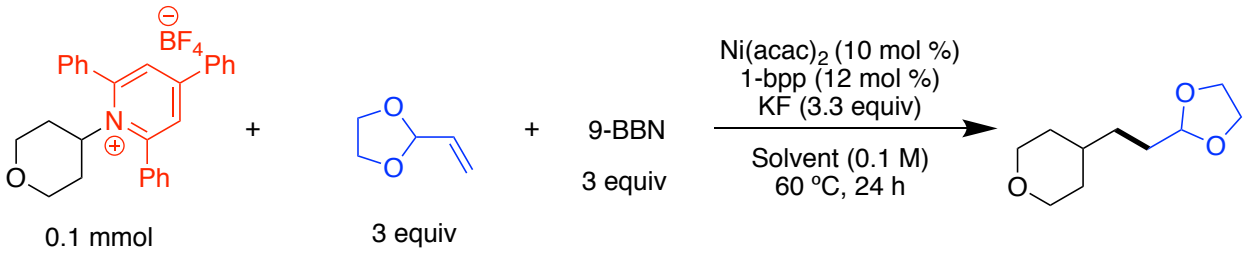
Effect of Base



entry	base	yield[a]
1	KF (spray dried)	75
2	KF (oven dried)	68
3	KF	18
4	CsF	60
5	KBr	0
6	NaI	4
7	AgF	0
8	NaCl	0
9	LiF	0

[a] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Effect of Solvent



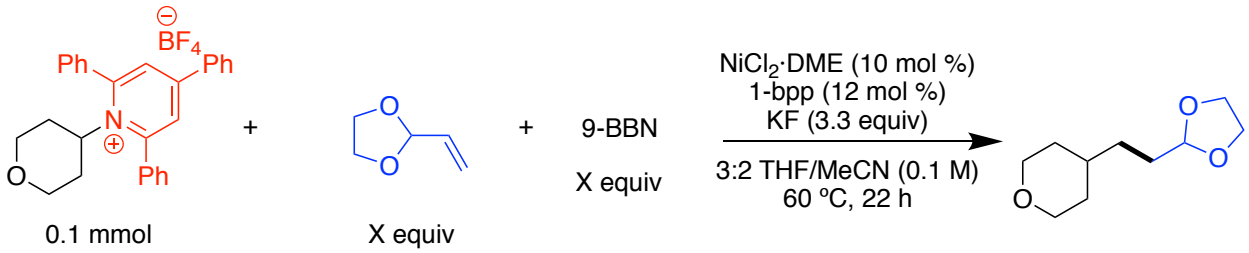
0.1 mmol

3 equiv

entry	solvent	yield[a]
1	MeCN	93
2	DMA	21
3	DMF	21
4	NMP	31
5	Dioxane	20

[a] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Effect of Organoborane Stoichiometry



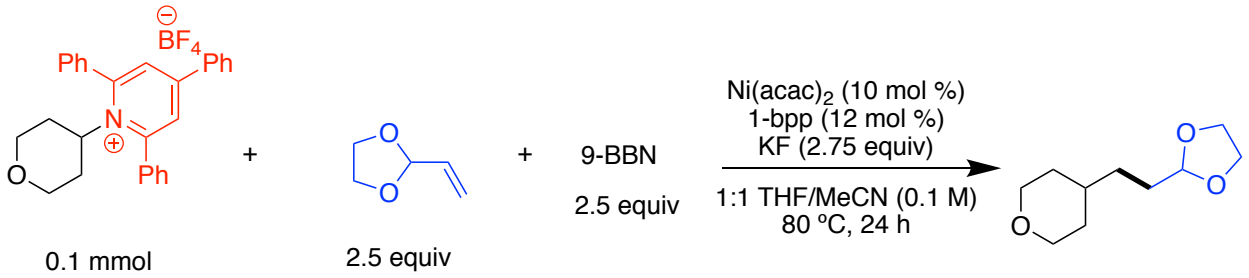
0.1 mmol X equiv

entry	equiv of organoborane (X)	yield[a]
1	2.5	49
2	2.6	48
3	2.7	47
4	2.8	42
5	2.9	46
6	3.0	26
7	3.1	15
8	3.2	15
9	3.3	28
10	3.4	41
11	3.5	15

[a] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Effect of Stirring KF with Solution of 9-BBN and Alkene

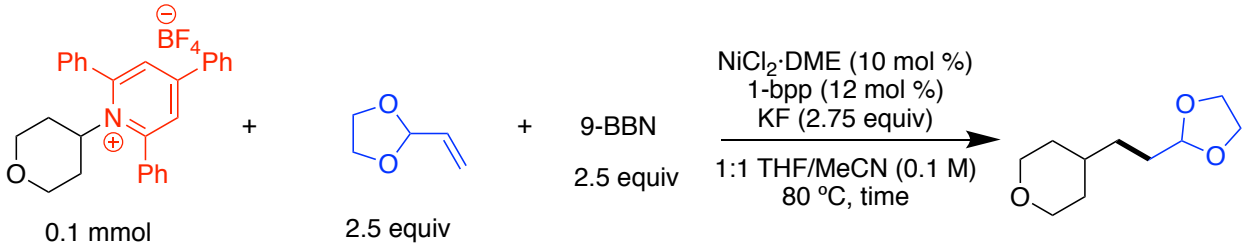
In these experiments, KF was stirred with the solution of 9-BBN and alkene at 80 °C for the times indicated in the table below.



entry	stirring time (min)	yield[a]
1	15	78
2	30	93
3	45	93
4	60	83

[a] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Effect of Reaction Time

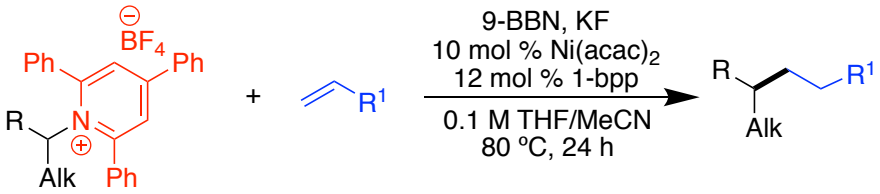


entry	reaction time (h)	yield[a]
1	1	6
2	2	10
3	4	15
4	18	86
5	20	80
6	22	100
7	24	98

[a] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

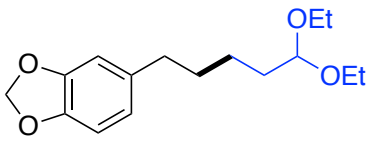
Cross-Couplings of Pyridinium Salts and Alkenes and Alkynes via Organoboranes

General Procedure A: Alkylation of Alkyl Pyridinium Salts with Alkenes

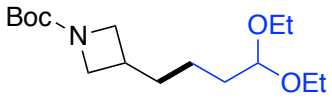


An oven-dried, 25-mL Schlenk flask equipped with a mechanical stirbar was charged with KF (160 mg, 2.75 mmol, 2.75 equiv) and alkene (2.5 mmol, 2.5 equiv), if solid. The flask was fitted with a rubber septum, sealed with parafilm, and evacuated and backfilled with nitrogen five times. 9-BBN (0.5 M solution in THF, 2.5 mmol, 2.5 equiv, 0.50 mL) and alkene, if liquid, were added via syringe. The mixture was stirred and heated at 80 °C in an oil bath for 30 min. A second oven-dried, 10-mL Schlenk flask equipped with a mechanical stirbar was charged with $Ni(acac)_2$

(2.5 mg, 0.10 mmol, 0.10 equiv), 1-bpp (2.6 mg, 0.12 mmol, 0.12 equiv), and pyridinium salt (1.0 mmol, 1.0 equiv). The flask was fitted with a rubber septum, and evacuated and backfilled with nitrogen five times. Acetonitrile (3 mL) was added, and the mixture was stirred for 15 min at room temperature. The catalyst solution was then transferred to the 25-mL Schlenk flask via syringe, rinsing with acetonitrile (2 mL), and then the mixture was stirred at 80 °C in an oil bath for 24 h. The mixture was allowed to cool to room temperature. For nonpolar products that might co-elute with organoborane species, H_2O_2 (0.4 mL) was added, and the mixture was vigorously stirred for 5 min to oxidize the boron species. For polar products, this oxidation step was skipped. The aqueous layer was washed with EtOAc (3 x 20 mL), dried ($MgSO_4$), filtered through a short pad of silica gel, and concentrated. The cross-coupled product was then purified via silica gel chromatography.

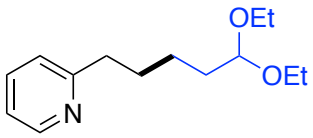


5-(5,5-Diethoxypentyl)-2H-1,3-benzodioxole (7). Prepared via General Procedure A using pyridinium salt **3b**. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (2% → 20% Et_2O/hexanes) to give **7** (run 1: 149 mg, 52%; run 2: 164 mg, 58%) as an orange oil: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.71 (d, *J* = 7.9 Hz, 1H), 6.66 (d, *J* = 1.7 Hz, 1H), 6.63 – 6.59 (m, 1H), 5.90 (s, 2H), 4.47 (t, *J* = 5.7 Hz, 1H), 3.63 (dq, *J* = 9.4, 7.1 Hz, 2H), 3.48 (dq, *J* = 9.4, 7.0 Hz, 2H), 2.58 – 2.46 (m, 2H), 1.68 – 1.52 (m, 4H), 1.43 – 1.34 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.6, 145.5, 136.6, 121.2, 109.0, 108.2, 103.0, 100.8, 61.1, 35.7, 33.6, 31.8, 24.4, 15.5; FTIR (neat) 2930, 1723, 1489, 1245, 1039, 809 cm^{-1}; HRMS (LIFDI+) $[M]^+$ calculated for $C_{16}H_{24}O_4$: 280.1675, found 280.1665.

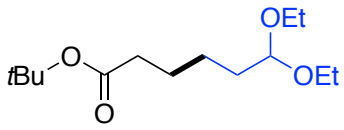


***Tert*-butyl 3-(4,4-diethoxybutyl)azetidine-1-carboxylate (8).** Prepared via General Procedure A using pyridinium salt **3c**. During work-up, the oxidation step with H_2O_2 was not used. The crude mixture was purified by silica gel chromatography (10% → 25% → 50% Et_2O/hexanes) to give **8** (run 1: 198 mg, 66%; run 2: 187 mg, 62%) as a yellow oil: ^{1}H NMR (400 MHz,

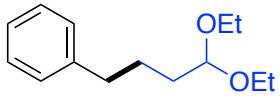
Chloroform-*d*) δ 4.46 (t, *J* = 5.7 Hz, 1H), 3.98 (t, *J* = 8.3 Hz, 2H), 3.63 (dq, *J* = 9.4, 7.1 Hz, 2H), 3.56 – 3.41 (m, 4H), 2.46 (tt, *J* = 7.9, 5.5 Hz, 1H), 1.62 – 1.54 (m, 4H), 1.43 (s, 9H), 1.34 – 1.25 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.6, 102.8, 79.3, 61.1, 34.4, 33.5, 31.1, 29.0, 28.6, 22.3, 15.5; FTIR (neat) 2974, 2876, 2361, 1700, 1399, 1132 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{16}H_{32}NO_4$: 302.2331, found 302.2326.



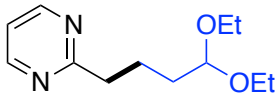
2-(5,5-Diethoxypentyl)pyridine (9). Prepared via General Procedure A using pyridinium salt **3d.** During work-up, the oxidation step with H_2O_2 was not used. The crude mixture was purified by silica gel chromatography (10% → 20% EtOAc/hexanes) to give **9** (run 1: 154 mg, 64%; run 2: 169 mg, 71%) as a yellow oil: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.56 (s, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.14 (m, 2H), 4.47 (t, *J* = 5.7 Hz, 1H), 3.62 (dq, *J* = 9.4, 7.0 Hz, 2H), 3.47 (dq, *J* = 9.4, 7.1 Hz, 2H), 2.79 (t, *J* = 7.7 Hz, 2H), 1.76 (h, *J* = 7.6 Hz, 2H), 1.71 – 1.60 (m, 2H), 1.52 – 1.40 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.3, 149.2, 136.5, 122.9, 121.1, 102.9, 61.0, 38.4, 33.6, 29.9, 24.7, 15.9; FTIR (neat) 2974, 2929, 2864, 1434, 1128, 994, 749 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{14}H_{24}NO_2$: 238.1807, found 238.1791.



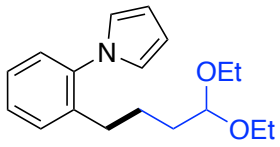
***Tert*-butyl 6,6-diethoxyhexanoate (10).** Prepared via General Procedure A using pyridinium salt **3e**. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (10% → 25% Et_2O/hexanes) to give **10** (run 1: 138 mg, 53%; run 2: 159 mg, 61%) as a light yellow oil: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.47 (t, *J* = 5.7 Hz, 1H), 3.63 (dq, *J* = 9.3, 7.1 Hz, 2H), 3.48 (dq, *J* = 9.4, 7.0 Hz, 2H), 2.21 (t, *J* = 7.5 Hz, 2H), 1.66 – 1.56 (m, 4H), 1.43 (s, 9H), 1.41 – 1.30 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.2, 102.8, 80.2, 61.0, 35.6, 33.4, 28.2, 25.1, 24.4, 15.5; FTIR (neat) 2975, 2931, 1733, 1652, 1151 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{14}H_{29}O_4$: 261.2066, found 261.2187.



(4,4-Diethoxybutyl)benzene (11). Prepared via General Procedure A using pyridinium salt **3f.** During work-up, the oxiation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (5% → 40% Et_2O/hexanes) to give **11** (run 1: 211 mg, 78%; run 2: 222 mg, 85%) as a light yellow oil: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 2H), 7.24 (s, 3H), 4.56 (t, *J* = 5.2 Hz, 1H), 3.79 – 3.65 (m, 2H), 3.54 (tt, *J* = 8.6, 6.5 Hz, 2H), 2.70 (t, *J* = 7.0 Hz, 2H), 1.88 – 1.64 (m, 4H), 1.26 (td, *J* = 7.1, 1.3 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.5, 128.7, 128.4, 125.9, 103.0, 61.1, 35.9, 33.4, 26.8, 15.5; FTIR (neat) 2977, 2928, 1373, 1129, 1063, 699 cm^{-1}; HRMS (CI) $[M–OEt]^+$ calculated for $C_{12}H_{17}O$: 177.1279, found 177.1280.

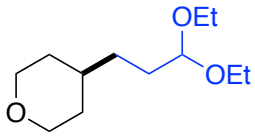


2-(4,4-Diethoxybutyl)pyrimidine (12). Prepared via General Procedure A using pyridinium salt **3g**. During work-up, the oxdation step with H_2O_2 was not used. The crude mixture was purified by silica gel chromatography (10% → 50% EtOAc/hexanes) to give **12** (run 1: 142 mg, 63%; run 2: 153 mg, 67%) as a yellow oil: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 4.9 Hz, 2H), 7.12 (t, *J* = 4.9 Hz, 1H), 4.53 (t, *J* = 5.8 Hz, 1H), 3.63 (dq, *J* = 9.4, 7.1 Hz, 2H), 3.48 (dq, *J* = 9.4, 7.0 Hz, 2H), 2.99 (t, *J* = 7.7 Hz, 2H), 1.96 – 1.84 (m, 2H), 1.74 – 1.65 (m, 2H), 1.19 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.3, 157.1, 118.6, 102.8, 61.0, 39.3, 33.3, 24.1, 15.5; FTIR (neat) 2973, 2875, 1560, 1425, 1129, 1061 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{12}H_{21}N_2O_2$: 225.1603, found 225.1596.

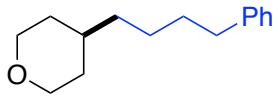


1-[2-(4,4-Diethoxybutyl)phenyl]-1H-pyrrole (13). Prepared via General Procedure A using pyridinium salt **3h**. During work-up, the oxidation step with H_2O_2 was not used. The crude mixture was purified by silica gel chromatography (25% EtOAc/hexanes) to give **13** (run 1: 211 mg, 74%; run 2: 208 mg, 73%) as a dark red oil: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (dd, *J* = 4.1, 2.0 Hz, 2H), 7.26 – 7.22 (m, 2H), 6.76 (t, *J* = 2.1 Hz, 2H), 6.29 (t, *J* = 2.1 Hz, 2H), 4.42 – 4.35 (m, 1H), 3.57 (dq, *J* = 9.3, 7.0 Hz, 2H), 3.42 (dq, *J* = 9.3, 7.0 Hz, 2H), 2.54 – 2.48 (m, 2H), 1.56 – 1.48 (m, 4H), 1.17 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.4, 138.5, 130.1, 127.9,

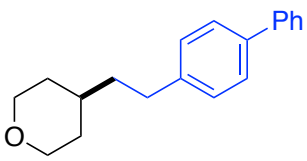
127.3, 126.7, 122.5, 108.8, 102.7, 61.0, 33.9, 30.9, 26.0, 15.5; FTIR (neat) 2973, 2928, 1717, 1502, 1065, 726 cm^{-1}; HRMS (ESI-) $[M-H-Et-OEt]^-$ calculated for $C_{14}H_{14}NO$: 212.1076, found 212.1070.



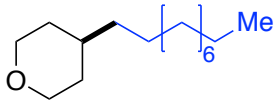
4-(3,3-Diethoxypropyl)oxane (6). Prepared via General Procedure A using pyridinium salt **3a**. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (1% MeOH, 5% Et_2O/toluene) to give **6** (run 1: 203 mg, 93%; run 2: 198 mg, 91%) as a light yellow oil: ^1H NMR (400 MHz, Chloroform-*d*) δ 4.46 (t, *J* = 5.7 Hz, 1H), 4.00 – 3.89 (m, 2H), 3.64 (dq, *J* = 9.4, 7.1 Hz, 2H), 3.49 (dq, *J* = 9.4, 7.0 Hz, 2H), 3.36 (td, *J* = 11.9, 2.1 Hz, 2H), 1.66 – 1.58 (m, 4H), 1.46 (dddt, *J* = 14.5, 10.4, 6.9, 3.7 Hz, 1H), 1.34 – 1.24 (m, 4H), 1.20 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 103.2, 68.3, 61.1, 35.0, 33.7, 32.0, 30.7, 15.5. FTIR (neat) 2361, 2336, 1062, 667cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{12}H_{25}O_3$: 217.1804, found 217.1377.



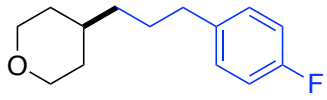
4-(4-Phenylbutyl)oxane (14). Prepared via General Procedure A using pyridinium salt **3a**. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (5%→ 10% Et_2O/hexanes) to give **14** (run 1: 220 mg, 47%; run 2: 218 mg, 46%) as a yellow oil: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 1H), 7.21 – 7.14 (m, 4H), 4.00 – 3.86 (m, 2H), 3.35 (td, *J* = 11.8, 2.1 Hz, 2H), 2.65 – 2.56 (m, 2H), 1.61 (d, *J* = 7.5 Hz, 4H), 1.52 – 1.39 (m, 1H), 1.34 (ddd, *J* = 10.9, 8.1, 5.8 Hz, 2H), 1.30 – 1.18 (m, 4H);^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.5, 128.2, 128.1, 125.4, 68.0, 36.6, 35.8, 34.7, 33.0, 31.5, 25.8; FTIR (neat) 2926, 2852, 1094, 698 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{15}H_{23}O$: 219.1747, found 219.1736.



4-(2-{[1,1'-Biphenyl]-4-yl}ethyl)oxane (15). Prepared via General Procedure A using pyridinium salt **3a**. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (10% → 50% Et_2O/hexanes) to give **15** (run 1: 135 mg, 51%; run 2: 142 mg, 54%) as a yellow oil: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.60 – 7.56 (m, 2H), 7.54 – 7.50 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.33 (td, *J* = 7.2, 1.3 Hz, 1H), 7.25 (s, 2H), 3.97 (ddd, *J* = 12.4, 4.9, 1.7 Hz, 2H), 3.38 (td, *J* = 11.8, 2.0 Hz, 2H), 2.71 – 2.65 (m, 2H), 1.68 (dt, *J* = 13.2, 2.3 Hz, 2H), 1.65 – 1.59 (m, 2H), 1.40 – 1.29 (m, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.8, 141.2, 138.8, 128.75, 128.73, 127.10, 127.03, 127.0, 68.2, 38.9, 34.7, 33.2, 32.4; FTIR (neat) 2917, 2837, 1094, 767 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{19}H_{23}O$: 267.1749, found 267.1735.

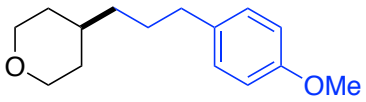


4-Decyloxane (16). Prepared via General Procedure A using pyridinium salt **3a**. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (100% toluene) to give **16** (run 1: 96 mg, 43%; run 2: 112 mg, 50%) as a light yellow oil: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 3.94 (dtd, *J* = 11.6, 2.4, 1.1 Hz, 2H), 3.36 (td, *J* = 11.8, 2.1 Hz, 2H), 1.61 – 1.54 (m, 2H), 1.44 (m, 1H), 1.31 – 1.21 (m, 20H), 0.88 (t, *J* = 7.0 Hz, 3H);^{13}C NMR (101 MHz, Chloroform-*d*) δ 68.4, 37.1, 35.1, 33.4, 32.1, 31.1, 30.0, 29.82, 29.79 29.5, 26.5, 22.8, 14.3; FTIR (neat) 2954, 2923, 2852, 1465 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{15}H_{31}O$: 227.2375, found 227.2368.

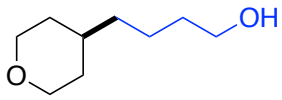


4-[3-(4-Fluorophenyl)propyl]oxane (17). Prepared via General Procedure A using pyridinium salt **3a**. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (5% → 10% Et_2O/hexanes) to give **17** (run 1: 123 mg, 56%; run 2: 112 mg, 52%) as a light yellow oil: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 7.09 (m, 2H), 7.03 – 6.91 (m, 2H), 3.94 (dd, *J* = 11.5, 4.5 Hz, 2H), 3.35 (td, *J* = 11.8, 2.1 Hz, 2H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.64 – 1.58 (m, 3H), 1.47 (ddt, *J* = 10.9, 7.6, 3.7 Hz, 1H), 1.31 – 1.23 (m, 5H); ^{13}C

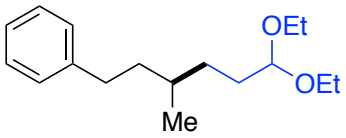
NMR (101 MHz, Chloroform-*d*) δ161.3 (d, J_{C-F} = 243.4 Hz) 138.3 (d, J_{C-F} = 3.0 Hz), 129.8 (d, J_{C-F} = 8.1 Hz), 115.12 (d, J_{C-F} = 21.2 Hz), 68.3, 36.6, 35.4, 35.0, 33.3, 28.6; ^{19}F NMR (376 MHz, Chloroform-*d*) δ –118.03; FTIR (neat) 2926, 2854, 1265, 737 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{14}H_{20}FO$: 223.1498, found 223.1400.



4-[3-(4-Methoxyphenyl)propyl]oxane (18). Prepared via General Procedure A using pyridinium salt **3a**. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (2% → 7% → 15% Et_2O/hexanes) to give **18** (run 1: 185 mg, 79%; run 2: 187 mg, 77%) as a light yellow oil: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 7.03 (m, 2H), 6.88 – 6.77 (m, 2H), 3.94 (ddt, *J* = 11.4, 4.4, 1.1 Hz, 2H), 3.79 (s, 3H), 3.36 (td, *J* = 11.8, 2.1 Hz, 2H), 2.54 (t, *J* = 7.7 Hz, 2H), 1.66 – 1.55 (m, 4H), 1.55 – 1.43 (m, 1H), 1.33 – 1.20 (m, 4H);^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.8, 134.8, 129.3, 113.8, 68.3, 55.4, 36.7, 35.3, 35.1, 33.3, 28.7; FTIR (neat) 2927, 2837, 1512, 1245, 1036 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{15}H_{23}O_2$: 235.1698, found 235.1685.

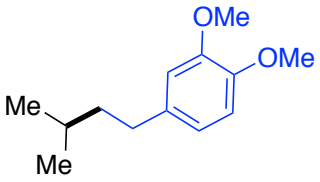


4-(Tetrahydro-2H-pyran-4-yl)-1-butanol (19). Prepared via General Procedure A using pyridinium salt **3a**. During work-up, the oxidation step with H_2O_2 was not used. The crude mixture was purified by silica gel chromatography (5% → 50% Et_2O/hexanes) to give **19** (run 1: 158 mg, 68%; run 2: 159 mg, 69%) as a yellow oil: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 3.97 – 3.91 (m, 2H), 3.65 (t, *J* = 6.6 Hz, 2H), 3.36 (td, *J* = 11.8, 2.1 Hz, 2H), 1.62 – 1.58 (m, 2H), 1.57 – 1.53 (m, 2H), 1.47 (dtd, *J* = 14.4, 7.5, 6.9, 3.6 Hz, 1H), 1.41 – 1.35 (m, 2H), 1.30 – 1.24 (m, 4H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 68.3, 63.1, 36.9, 35.1, 33.3, 33.0, 22.7; FTIR (neat) 3344, 2922, 2849, 1095, 736 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_9H_{19}O_2$: 159.1385, found 159.1374.

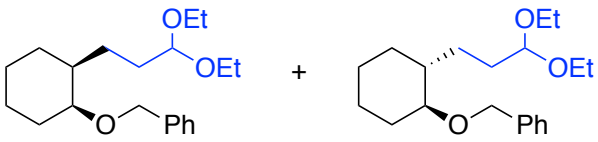


(6,6-Diethoxy-3-methylhexyl)benzene (20). Prepared via General Procedure A using pyridinium salt **3i**. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified

by silica gel chromatography (1% → 5% Et_2O/hexanes) to give **20** (run 1: 175 mg, 65%; run 2: 188 mg, 70%) as a yellow oil: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.27 (m, 2H), 7.18 (m, 3H), 4.46 (t, *J* = 5.7 Hz, 1H), 3.64 (dq, *J* = 9.4, 7.1 Hz, 2H), 3.49 (dq, *J* = 9.4, 7.1 Hz, 2H), 2.74 – 2.49 (m, 2H), 1.73 – 1.36 (m, 7H), 1.21 (t, *J* = 7.0 Hz, 6H), 0.94 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.1, 128.5, 128.4, 125.7, 103.3, 62.0, 60.9, 39.0, 33.6, 32.5, 31.7, 31.1, 19.7, 15.5; FTIR (neat) 2973, 2928, 1456, 1127, 1063, 698 cm^{-1}; HRMS (ESI+) $[M–OEt]^+$ calculated for $C_{15}H_{23}O$: 219.1749, found 219.1743.



1,2-Dimethoxy-4-(3-methylbutyl)benzene (21). Prepared via General Procedure A using pyridinium salt **3j**. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (2% → 10% EtOAc/hexanes) to give **21** (run 1: 107 mg, 51%; run 2: 107 mg, 51%) as a light yellow oil: ^1H NMR (400 MHz, Chloroform-*d*) δ 6.81 – 6.77 (m, 1H), 6.72 (d, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 2.61 – 2.51 (m, 2H), 1.62 – 1.55 (m, 1H), 1.50 – 1.41 (m, 2H), 0.93 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.8, 147.0, 135.9, 120.2, 111.7, 111.2, 56.0, 55.9, 41.2, 33.6, 27.9, 22.7; FTIR (neat) 2952, 1515, 1261, 1030 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{13}H_{21}O_2$: 209.1542, found 209.1530.

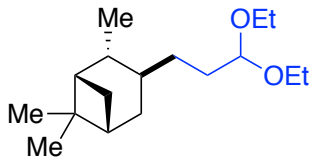


22a **22b**

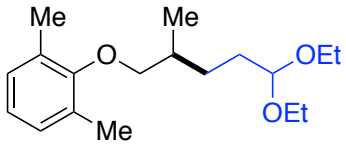
({[(1S)-2-(3,3-Diethoxypropyl)cyclohexyl]oxy}methyl)benzene (22). Prepared via General Procedure A using pyridinium salt **3k**. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (10% Et_2O/hexanes) to give **22a** (run 1: 100 mg, 32%; run 2: 111 mg, 35%) and **22b** (run 1: 100 mg, 32%; run 2: 111 mg, 35%), both as light yellow oils. The combined yield was 66% (run 1: 200 mg, 63%; run 2: 222 mg, 69%) as a 1:1 mixture of diastereomers.

22a: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.33 – 7.18 (m, 5H), 4.52 (d, *J* = 11.9 Hz, 1H), 4.37 (t, *J* = 5.6 Hz, 1H), 4.31 (d, *J* = 11.9 Hz, 1H), 3.54 (ddq, *J* = 9.3, 8.4, 7.0 Hz, 2H), 3.47 (dt, *J* = 5.1, 2.4 Hz, 1H), 3.44 – 3.33 (m, 2H), 1.89 (dt, *J* = 14.5, 4.5 Hz, 1H), 1.59 – 1.42 (m, 6H), 1.37 – 1.17 (m, 6H), 1.12 (q, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.5, 128.2, 127.4, 127.2, 103.3, 70.1, 60.9, 60.7, 40.8, 31.3, 31.0, 28.5, 27.5, 25.0, 21.1, 15.4; FTIR (neat) 2928, 1443, 1061, 696 cm^{-1}; HRMS (LIFDI+) $[M–H]^+$ calculated for $C_{20}H_{31}O_3$: 319.2273, found 319.2281.

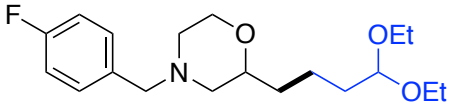
22b: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.27 (m, 5H), 4.63 (d, *J* = 11.5 Hz, 1H), 4.46 (t, *J* = 5.8 Hz, 1H), 4.42 (d, *J* = 11.5 Hz, 1H), 3.62 (dqd, *J* = 9.3, 7.1, 2.2 Hz, 2H), 3.47 (dq, *J* = 9.3, 7.0 Hz, 2H), 3.01 (td, *J* = 9.5, 4.3 Hz, 1H), 2.19 – 2.10 (m, 1H), 1.91 – 1.78 (m, 2H), 1.78 – 1.73 (m, 1H), 1.73 – 1.49 (m, 5H), 1.45 – 1.35 (m, 1H), 1.19 (m, 8H), 1.01 – 0.91 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.1, 128.3, 127.8, 127.4, 103.4, 81.7, 70.6, 60.8, 60.7, 42.9, 31.1, 30.6, 30.3, 27.2, 25.4, 24.7, 15.4, 15.4; FTIR (neat) 2972, 2926, 2855, 1453, 1069, 697 cm^{-1}; HRMS (ESI+) $[M–Et+H]^+$ calculated for $C_{18}H_{27}O_3$: 291.1960, found 291.1946.



1R,3S,5R)-2-(3,3-Diethoxypropyl)-3,6,6-trimethylbicyclo[3.1.1]heptane (23). Prepared via General Procedure A using pyridinium salt **3l**. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (100% toluene) to give **23** (run 1: 275 mg, 54%; run 2: 269 mg, 50%) as a single diastereomer and a light yellow oil: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 4.48 (t, *J* = 5.6 Hz, 1H), 3.65 (dqd, *J* = 9.2, 7.0, 2.0 Hz, 2H), 3.58 – 3.46 (m, 2H), 2.27 (dtt, *J* = 12.1, 8.0, 3.9 Hz, 1H), 2.13 (dddd, *J* = 11.3, 9.4, 4.3, 2.4 Hz, 1H), 1.89 (tt, *J* = 6.0, 3.0 Hz, 1H), 1.77 – 1.67 (m, 2H), 1.67 – 1.51 (m, 5H), 1.46 – 1.38 (m, 1H), 1.21 (t, *J* = 7.0 Hz, 6H), 1.18 (s, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.99 (s, 3H), 0.75 (d, *J* = 9.5 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 103.3, 61.0, 60.8, 48.3, 43.9, 42.1, 38.9, 36.4, 36.1, 34.8, 34.2, 31.9, 28.2, 23.1, 21.9, 15.5, 14.3. FTIR (neat) 2923, 2855, 1727, 1067, 697 cm^{-1}; HRMS (ESI+) $[M–OEt]^+$ calculated for $C_{15}H_{27}O$: 223.2062, found 223.2049.

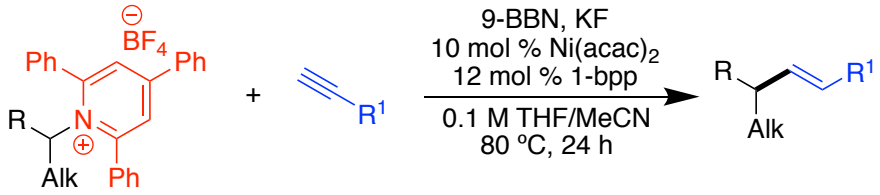


2-[(5,5-Diethoxy-2-methylpentyl)oxy]-1,3-dimethylbenzene (24). Prepared via General Procedure A using pyridinium salt **3m**. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (5% → 30% Et_2O/hexanes) to give **24** (run 1: 122 mg, 41%; run 2: 128 mg, 43%) as a yellow oil: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.00 (d, *J* = 7.4 Hz, 2H), 6.90 (m, 6.8 Hz, 1H), 4.51 (t, *J* = 5.6 Hz, 1H), 3.71 – 3.58 (m, 3H), 3.52 (m, 3H), 2.27 (s, 6H), 1.96 (dp, *J* = 13.0, 6.4 Hz, 1H), 1.82 – 1.58 (m, 3H), 1.39 – 1.27 (m, 1H), 1.21 (d, *J* = 7.0, Hz, 6H), 1.10 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.0, 131.1, 128.9, 123.8, 103.3, 61.8, 61.1, 34.4, 31.4, 28.6, 17.2, 16.5, 15.5; FTIR (neat) 2973, 2927, 1473, 1203, 1062, 769 cm^{-1}; HRMS (LIFDI) [M] calculated for $C_{18}H_{30}O_3$: 294.2195, found 294.2181.

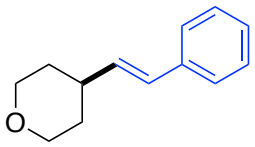


2-(4,4-Diethoxybutyl)-4-[(4-fluorophenyl)methyl]morpholine (25). Prepared via General Procedure A using pyridinium salt **3n**. During work-up, the oxidation step with H_2O_2 was not used. The crude mixture was purified by silica gel chromatography (20% → 80% Et_2O/hexanes) to give **25** (run 1: 239 mg, 69%; run 2: 225 mg, 64%) as a yellow oil: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.26 (m, 2H), 7.04 – 6.96 (m, 2H), 4.46 (t, *J* = 5.7 Hz, 1H), 3.83 (ddd, *J* = 11.4, 3.4, 1.5 Hz, 1H), 3.62 (dddd, *J* = 14.2, 12.3, 5.9, 3.6 Hz, 3H), 3.51 – 3.41 (m, 5H), 2.73 – 2.58 (m, 2H), 2.12 (td, *J* = 11.4, 3.4 Hz, 1H), 1.82 (t, *J* = 10.6 Hz, 1H), 1.63 – 1.56 (m, 2H), 1.54 – 1.33 (m, 4H), 1.19 (td, *J* = 7.1, 1.2 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.2 (d, $J_{C\text{-}F}$ = 246.4 Hz), 133.6 (d, $J_{C\text{-}F}$ = 3.0 Hz), 130.8 (d, $J_{C\text{-}F}$ = 8.9 Hz), 128.5 (d, $J_{C\text{-}F}$ = 11.1 Hz), 115.2 (d, $J_{C\text{-}F}$ = 21.2 Hz), 102.9, 75.7, 66.9, 62.6, 61.2, 61.0, 58.7, 53.2, 33.7, 33.6, 20.8, 15.5; ^{19}F NMR (565 MHz, Chloroform-*d*) δ –115.85; FTIR (neat) 2973, 2929, 2869, 1113, 1062, 850 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{19}H_{31}FNO_3$: 340.2288, found 340.2271.

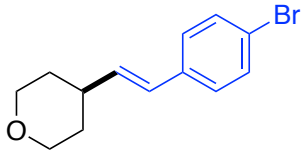
General Procedure B: Vinylation of Alkyl Pyridinium Salts with Alkynes



Vinylation of alkyl pyridinium salts was accomplished using a very similar procedure to General Procedure A, except that the alkene (General Procedure A) was replaced by an alkyne.

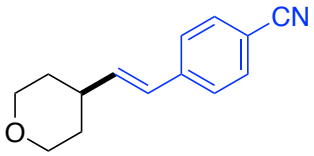


(*E*)-4-Styryltetrahydro-2*H*-pyran (26). Prepared via General Procedure B using pyridinium salt **3a**. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (10% Et_2O/hexanes) to give **26** (run 1:113 mg, 60%, run 2:118 mg, 63%) as a light yellow oil: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.16 (dd, *J* = 16.0, 6.8 Hz, 1H), 4.01 (ddd, *J* = 11.3, 4.8, 1.8 Hz, 2H), 3.47 (td, *J* = 11.6, 2.2 Hz, 2H), 2.38 (ddd, *J* = 11.2, 8.9, 5.0 Hz, 1H), 1.74 – 1.67 (m, 2H), 1.63 – 1.51 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.6, 134.7, 128.7, 128.4, 127.2, 126.2, 67.9, 38.5, 32.8. The spectral data matches that previously reported in the literature.[3]

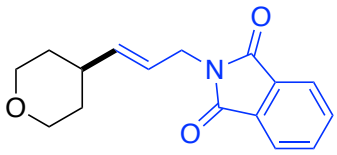


(*E*)-4-(4-Bromostyryl)tetrahydro-2*H*-pyran (27). Prepared via General Procedure B using pyridinium salt **3a**, except that KF, 9-BBN, and alkyne were stirred at 80 °C for 1 h instead of 30 min prior to addition of the other reagents. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (5% → 10% Et_2O/hexanes) to give **27** (127 mg, 48%) as a yellow solid (mp 56–63 °C): ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45 – 7.38 (m, 2H), 7.24 – 7.19 (m, 2H), 6.35 – 6.29 (m, 1H), 6.15 (dd, *J* = 16.0, 6.8 Hz, 1H), 4.01 (ddd, *J* = 11.7, 4.6, 1.9 Hz, 2H), 3.46 (td, *J* = 11.8, 2.2 Hz, 2H), 2.37 (ddt, *J* = 10.9, 6.9, 3.3 Hz, 1H), 1.72 – 1.64 (m, 2H), 1.61 – 1.53 (m, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 136.7,

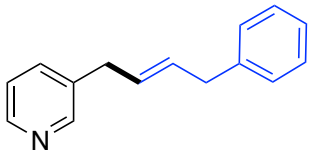
135.6, 131.75, 127.8, 127.4, 120.9, 67.8, 38.5, 32.7. The spectral data matches that previously reported in the literature.[4]



(*E*)-4-(2-(Tetrahydro-2*H*-pyran-4-yl)vinyl)benzonitrile (30). Prepared via General Procedure B using pyridinium salt **3a**. During work-up, the oxidation step with H_2O_2 was not used. The crude mixture was purified by silica gel chromatography (10% → 15% Et_2O/hexanes) to give 30 (164 mg, 71%) as a light yellow oil: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.54 (m, 2H), 7.49 – 7.37 (m, 2H), 6.39 (d, *J* = 16.1 Hz, 1H), 6.30 (dd, *J* = 16.0, 6.5 Hz, 1H), 4.02 (ddd, *J* = 11.6, 4.5, 1.9 Hz, 2H), 3.47 (td, *J* = 11.7, 2.2 Hz, 2H), 2.42 (dtt, *J* = 10.8, 7.0, 3.7 Hz, 1H), 1.71 (ddd, *J* = 13.2, 4.1, 2.1 Hz, 2H), 1.57 (dtd, *J* = 13.5, 11.6, 4.4 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.2, 138.8, 132.5, 127.1, 126.7, 119.2, 110.4, 67.7, 38.6, 32.4; FTIR (neat) 2871, 2361, 667^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{14}H_{16}NO$: 214.1232, found 214.1222.



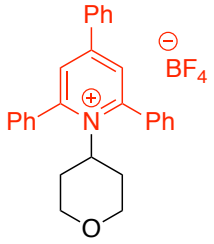
(*E*)-2-(3-(Tetrahydro-2*H*-pyran-4-yl)allyl)isoindoline-1,3-dione (29). Prepared via General Procedure B using pyridinium salt **3a**, except that KF, 9-BBN, and alkyne were stirred at 80 °C for 1 h instead of 30 min prior to addition of the other reagents. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (10% Et_2O/hexanes) to give 29 (106 mg, 53%) as a light yellow solid (mp 60–65 °C): ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.85 (dt, *J* = 6.4, 3.2 Hz, 2H), 7.75 – 7.67 (m, 2H), 5.70 (ddt, *J* = 15.5, 6.3, 1.4 Hz, 1H), 5.51 (dtd, *J* = 15.4, 6.2, 1.4 Hz, 1H), 4.25 (dt, *J* = 6.2, 1.1 Hz, 2H), 3.93 (ddd, *J* = 11.8, 4.5, 2.0 Hz, 2H), 3.37 (td, *J* = 11.7, 2.2 Hz, 2H), 2.23 – 2.13 (m, 1H), 1.59 (ddd, *J* = 13.3, 4.1, 2.0 Hz, 2H), 1.43 (dtd, *J* = 13.4, 11.6, 4.4 Hz, 2H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.1, 138.9, 134.1, 132.3, 123.4, 121.9, 67.8, 39.7, 37.6, 32.4; FTIR (neat) 2929, 2842, 1771, 1713, 1393, 720 cm^{-1}; HRMS (ESI+) $[M+H]^+$ calculated for $C_{16}H_{18}NO_3$: 272.1287, found 272.1275.



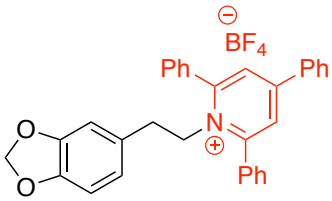
(*E*)-3-(4-Phenylbut-2-en-1-yl)pyridine (30). Prepared via General Procedure B using pyridinium salt **3o**, except that KF, 9-BBN, and alkyne were stirred at 80 °C for 1 h instead of 30 min prior to addition of the other reagents. During work-up, the oxidation step with H_2O_2 was used. The crude mixture was purified by silica gel chromatography (5% → 10% Et_2O/hexanes) to give **30** (124 mg, 59%) as a light yellow oil: ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.48 – 8.43 (m, 2H), 7.51 (dt, *J* = 7.9, 1.8 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.25 – 7.20 (m, 2H), 7.20 – 7.16 (m, 2H), 5.76 – 5.60 (m, 2H), 3.38 (t, *J* = 5.5 Hz, 4H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.1, 147.6, 140.5, 136.3, 136.1, 131.8, 129.2, 128.64, 128.60, 126.2, 123.5, 39.1, 36.2. The spectral data matches that previously reported in the literature.[5]

Preparation of Pyridinium Salts

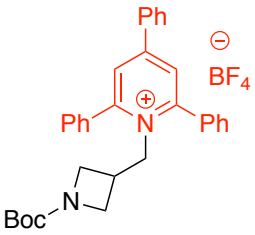
If previously reported, the pyridinium salts were prepared as previously described: **3a**, **3c**, **3i**, **3k**, **3n**;[6] **3e**, **3j**;[7] **3f–3h** and **3o**;[8] **3b** and **3n**;[9] **3l**.[10]



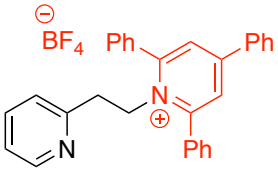
3a



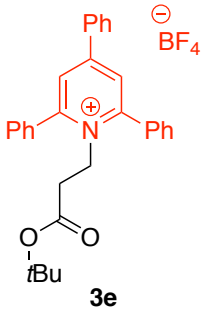
3b



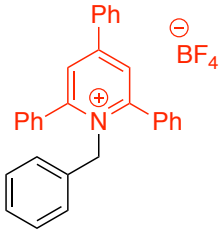
3c



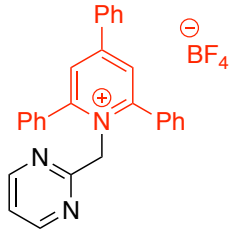
3d



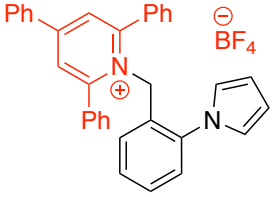
3e



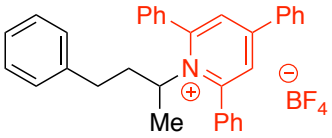
3f



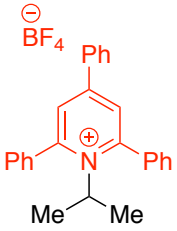
3g



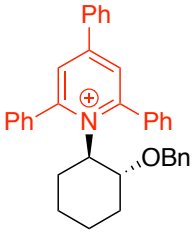
3h



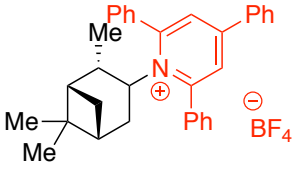
3i



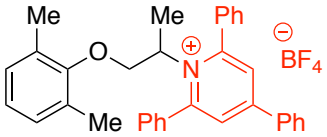
3j



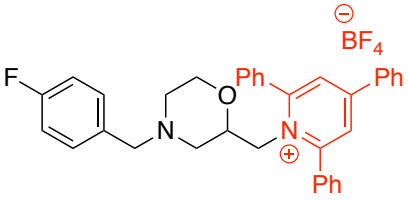
3k



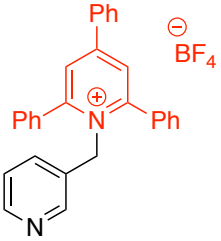
3l



3m

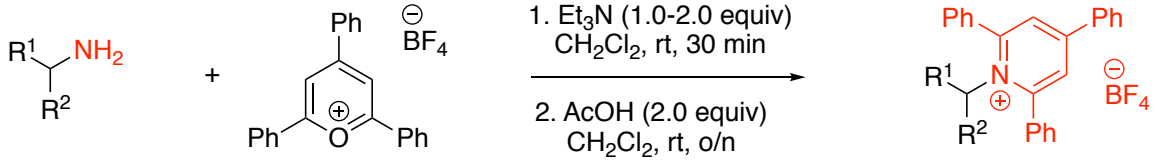


3n

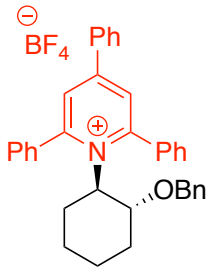


3o

General Procedure C: Synthesis of Pyridinium Salts



Under air, 2,4,6-triphenylpyrylium tetrafluoroborate (1.0 equiv), powdered activated 4Å molecular sieves (500 mg/mmol), and CH_2Cl_2 were added to a round-bottomed flask was a stirbar. The alkyl amine (1.0 equiv) was added, and the flask was fitted with a septum. With a vent needle, Et_3N (1.0 equiv for free-base amines; 2.0 equiv for amine hydrochloride salts) was added via syringe. The vent needle was removed, and the mixture was stirred for 30 min at room temperature. The vent needle was re-inserted, and acetic acid (2.0 equiv) was added via syringe. The vent needle was removed, and the mixture was stirred overnight at room temperature. The mixture was filtered through a short Celite plug using CH_2Cl_2. The filtrate was then washed with aq. HCl (1.0 M, 2 x 30 mL), sat. aq. $NaHCO_3$ (2 x 30 mL), and sat. NaCl (2 x 30 mL), dried ($MgSO_4$), filtered, and concentrated. Et_2O was added to the residue to precipitate the pyridinium salt. The solid pyridinium salt was then filtered and washed with Et_2O.

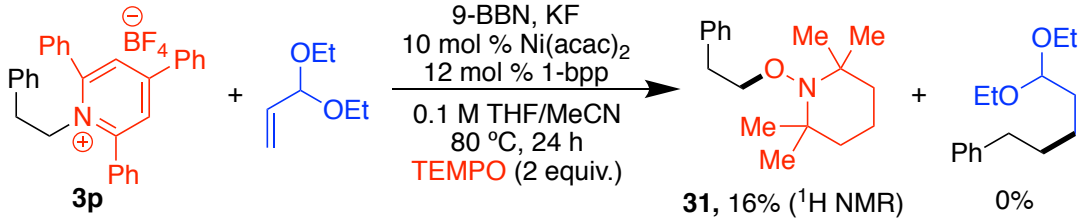


1-((*Trans*)-2-(benzyloxy)cyclohexyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (3k). Prepared via General Procedure B from (*1S,2S*)-2-(benzyloxy)cyclohexan-1-amine HCl (2.42 g, 10.0 mmol, 1.0 equiv) and 2,4,6-triphenylpyrillium tetrafluoroborate (3.96 g, 10.0 mmol, 1.0 equiv) to give **3k** (5.06 g, 91%) as an orange solid (mp 145 – 148 °C): ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 6.1 Hz, 1H), 8.09 – 8.04 (m, 1H), 7.92 (d, *J* = 2.4 Hz, 1H), 7.81 – 7.78 (m, 2H), 7.71 (d, *J* = 2.4 Hz, 1H), 7.65 – 7.51 (m, 9H), 7.49 – 7.34 (m, 4H), 7.04 – 7.00 (m, 2H), 6.94 (d, *J* = 7.7 Hz, 1H), 4.78 (ddd, *J* = 13.1, 10.3, 3.1 Hz, 1H), 4.57 (d, *J* = 12.1 Hz, 1H), 4.21 (d, *J* = 12.1 Hz, 1H), 3.40 – 3.30 (m, 1H), 2.62 (d, *J* = 12.7 Hz, 1H), 2.13 (d, *J* = 9.5 Hz, 1H), 1.59 (t, *J* = 9.4 Hz, 3H), 0.74 – 0.67 (m, 3H). ; ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 156.8, 154.9, 138.0, 134.3, 134.0, 133.5, 132.0, 131.9, 131.0, 130.7, 129.7, 129.6, 129.4, 129.0, 128.7, 128.5,

128.2, 128.0, 127.9, 126.9, 126.4, 77.5, 74.7, 68.9, 32.4, 31.6, 25.7, 23.3, 15.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -153.42, -153.37; FTIR: 2940, 1618, 1561, 1102, 975, 702 cm^{-1}; HRMS (ESI^+) $[M\text{-}BF_4]^+$ calculated for $C_{36}H_{34}NO$: 496.2635, found 496.2640.

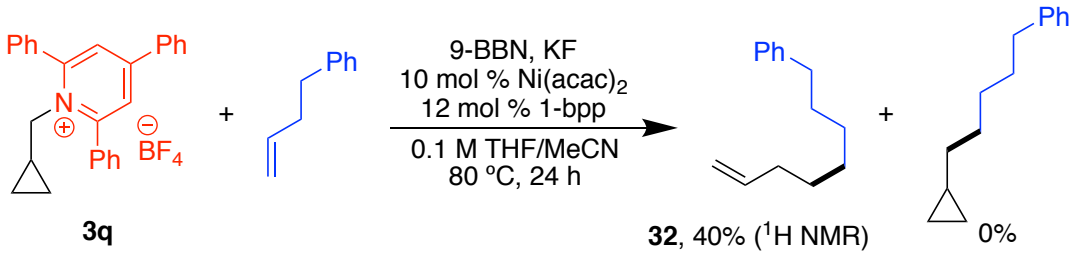
Mechanistic Experiments

Radical Trap Experiment



In a N_2-atmosphere glovebox, 9-BBN (0.5 M in THF, 0.5 mL, 0.25 mmol, 2.5 equiv), KF (16 mg, 0.275 mmol, 2.75 equiv), and alkene (38 µL, 0.25 mmol, 2.5 equiv) were stirred in an oven-dried 1-dram vial fitted with a stir bar at 80 °C in an aluminum heating block for 30 minutes. Meanwhile, $Ni(acac)_2$ (2.6 mg, 0.010 mmol, 10 mol %) and 1-bpp (2.5 mg, 0.012, 12 mol %) were stirred in MeCN (0.5 mL) at room temperature for 15 minutes. Then pyridinium salt **3p** (50 mg, 0.10 mmol, 1.0 equiv) and TEMPO (31 mg, 0.20 mmol, 2.0 equiv) were added to the vial containing 9-BBN, alkene, and KF. The nickel/ligand solution was added, the vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at 80 °C in an aluminum heating block for 24 h. The mixture was then diluted with Et_2O (3 mL) and filtered through a plug of silica gel, which was rinsed with Et_2O (10 mL). The filtrate was concentrated. 1,3,5-Trimethoxybenzene (internal standard) was added. The yield of the known TEMPO adduct product **31**[11] was determined to be 16% by ^{1}H NMR analysis. No cross-coupled product was observed.

Radical Clock Experiment



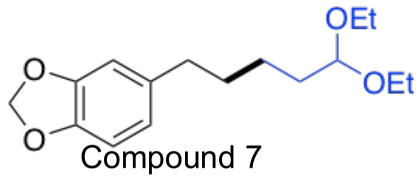
In a N_2-atmosphere glovebox, 9-BBN (0.5 M in THF, 0.5 mL, 0.25 mmol, 2.5equiv), KF (16 mg, 0.275 mmol, 2.75 equiv), and alkene (38 μL, 0.25 mmol, 2.5 equiv) were stired in an oven-dried 1-dram vial fitted with a stir bar at 80 °C in an aluminum heating block for 30 minutes. Meanwhile, $Ni(acac)_2$ (2.6 mg, 0.010 mmol, 10 mol %) and 1-bpp (2.5 mg, 0.012, 12 mol %) were stirred in MeCN (0.5 mL) at room temperature for 15 minutes. Then pyridinium salt **3q** (45 mg, 0.10 mmol, 1.0 equiv) was added to the vial containing 9-BBN, alkene, and KF. The nickel/ligand solution was added, the vial was capped with a Teflon-lined cap and removed from the glovebox. The mixture was stirred at 80 °C in an aluminum heating block for 24 h. The mixture was then diluted with Et_2O (3 mL) and filtered through a plug of silica gel, which was rinsed with Et_2O (10 mL). The filtrate was concentrated. 1,3,5-Trimethoxybenzene (internal standard) was added. The yield of the known ring-opened product **32**[12] was determined to be 40% by ^{1}H NMR analysis. No cyclopropyl product was observed.

References

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J., Safe and convenient procedure for solvent purification. *Organometallics* **1996,** *15* (5), 1518-1520.
2. Brown, H. C.; Chen, J., Hydroboration. 57. Hydroboration with 9-borabicyclo[3.3.1]nonane of alkenes containing representative functional groups. *The Journal of Organic Chemistry* **1981,** *46* (20), 3978-3988.
3. Chen, H.; Sun, S.; Liao, X., Nickel-Catalyzed Decarboxylative Alkenylation of Anhydrides with Vinyl Triflates or Halides. *Organic Letters* **2019,** *21* (10), 3625-3630.
4. Zhou, Q.-Q.; Düsel, S. J. S.; Lu, L.-Q.; König, B.; Xiao, W.-J., Alkenylation of unactivated alkyl bromides through visible light photocatalysis. *Chemical Communications* **2019,** *55* (1), 107-110.
5. Silvia Roscales, I. G. S., Aurelio G. Csaky, Regioselective 1,6-Conjudate Addition of Boronic Acids and Grignard Reagents to Dienylpyridines. *Synlett* **2011,** *15*, 2234-2236.
6. Plunkett, S.; Basch, C. H.; Santana, S. O.; Watson, M. P., Harnessing Alkyl Pyridinium Salts as Electrophiles in De-aminative Alkyl-Alkyl Cross-Couplings. *J. Am. Chem. Soc.* **2019,** *141* (6), 2257-2262.
7. Liao, J.; Basch, C. H.; Hoerrner, M. E.; Talley, M. R.; Boscoe, B. P.; Tucker, J. W.; Garnsey, M. R.; Watson, M. P., Deaminative Reductive Cross-Electrophile Couplings of Alkylpyridinium Salts and Aryl Bromides. *Org. Lett.* **2019,** *21* (8), 2941-2946.
8. Liao, J.; Guan, W.; Boscoe, B. P.; Tucker, J. W.; Tomlin, J. W.; Garnsey, M. R.; Watson, M. P., Transforming Benzylic Amines into Diarylmethanes: Cross-Couplings of Benzylic Pyridinium Salts via C–N Bond Activation. *Org. Lett.* **2018,** *20* (10), 3030-3033.

9. Basch, C. H.; Liao, J.; Xu, J.; Piane, J. J.; Watson, M. P., Harnessing Alkyl Amines as Electrophiles for Nickel-Catalyzed Cross Couplings via C–N Bond Activation. *J. Am. Chem. Soc.* **2017,** *139* (15), 5313-5316.
10. Wu, J.; He, L.; Noble, A.; Aggarwal, V. K., Photoinduced Deaminative Borylation of Alkylamines. *J. Am. Chem. Soc.* **2018,** *140* (34), 10700-10704.
11. Patel, V. F.; Pattenden, G., Free radical reactions in synthesis. Homolysis of alkylcobalt complexes in the presence of radical-trapping agents. *Journal of the Chemical Society, Perkin Transactions 1* **1990,** (10), 2703-2708.
12. Uemura, M.; Yorimitsu, H.; Oshima, K., Synthesis of Cp*CH2PPh2 and its use as a ligand for the nickel-catalysed cross-coupling reaction of alkyl halides with aryl Grignard reagents. *Chemical Communications* **2006,** (45), 4726-4728.

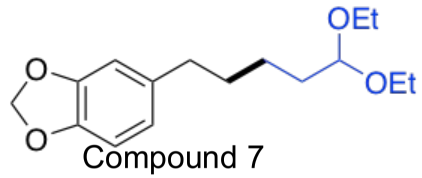
KMB-2-067..1.fid
PROTON8 CDCl3 /opt/nmrdata bakekr 23



Compound 7
^{1}H NMR (600 MHz, $CDCl_3$)

KMB-2-067_pdt.2.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 59

147.57
145.54
136.60
121.17
108.98
108.17
102.97
100.82
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.05
35.72
33.57
31.76
24.44
15.49

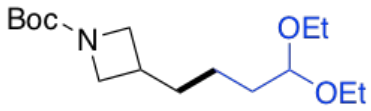


Compound 7
^{13}C NMR (101 MHz, $CDCl_3$)

S33

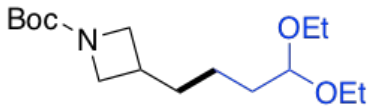
f1 (ppm)

KMB-2-123_pdt.1.fid
PROTON_16 CDCl3 /opt/topspin bakekr 32



Compound 8
^{1}H NMR (400 MHz, $CDCl_3$)

KMB-2-123_pdt.2.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 32



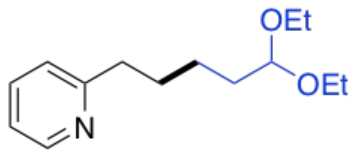
Compound 8
^{13}C NMR (101 MHz. $CDCl_3$)

156.56
102.79
79.27
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.14
34.40
33.51
31.12
28.96
28.55
22.33
15.49

S35

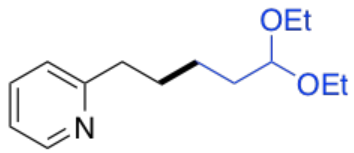
f1 (ppm)

KMB-2-066....1.fid
PROTON8 CDCl3 /opt/nmrdata bakeb 13



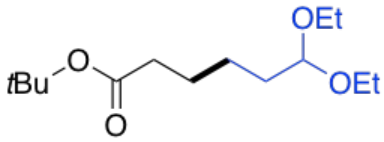
Compound 9
^{1}H NMR (600 MHz, $CDCl_3$)

KMB-2-066_pdt.2.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 40



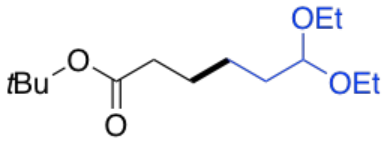
Compound 9
^{13}C NMR (101 MHz. $CDCl_3$)

KMB-2-151_pdt.1.fid
PROTON_16 CDCl3 /opt/topspin bakeb 20



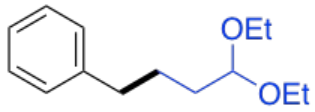
Compound 10
^{1}H NMR (400 MHz, $CDCl_3$)

KMB-2-151_pdt.2.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 20



Compound 10
^{13}C NMR (101 MHz. $CDCl_3$)

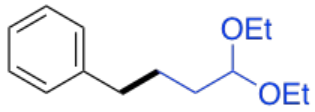
KMB-2-295_PDT___.1.fid



Compound 11

^{1}H NMR (400 MHz. $CDCl_3$)

KMB-2-295_PDT___.2.fid
HMBCGP

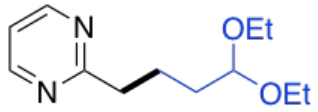


Compound 11
^{13}C NMR (101 MHz. $CDCl_3$)

142.47
128.56
128.42
125.86
102.96
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.09
35.86
33.38
26.76
15.50

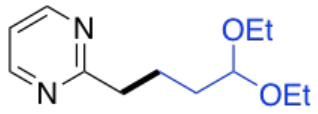
f1 (ppm)

KMB-2-166_pdt.1.fid
PROTON_16 CDCl3 /opt/topspin bakekr 53



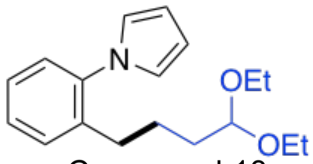
Compound 12
^{1}H NMR (400 MHz, $CDCl_3$)

KMB-2-166_pdt.2.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 53



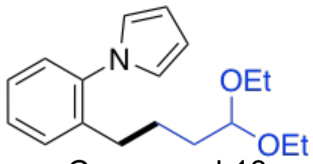
Compound 12
^{13}C NMR (101 MHz. $CDCl_3$)

KMB-2-096_pdt.1.fid
PROTON_16 CDCl3 /opt/topspin/bakekr 50



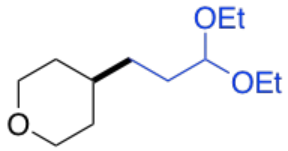
Compound 13
^{1}H NMR (400 MHz, $CDCl_3$)

KMB-2-096_pdt.2.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 50



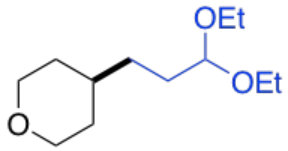
Compound 13
^{13}C NMR (101 MHz. $CDCl_3$)

KMB-3-5-2-C.1.fid
PROTON_16 CDCl3 /opt/topspin bakekr 45



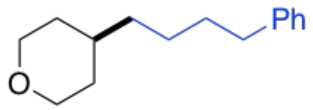
Compound 6
^{1}H NMR (400 MHz, $CDCl_3$)

KMB-3-024C_pdt.2.fid
C13CPD256 CDCl3 /opt/topspin bakekr 45



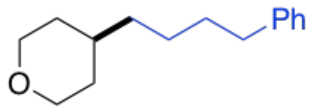
Compound 6
^{13}C NMR (101 MHz. $CDCl_3$)

KMB_229_2_B_PDT.1.fid
PROTON_16 CDCl3 /opt/topspin bakekr 15



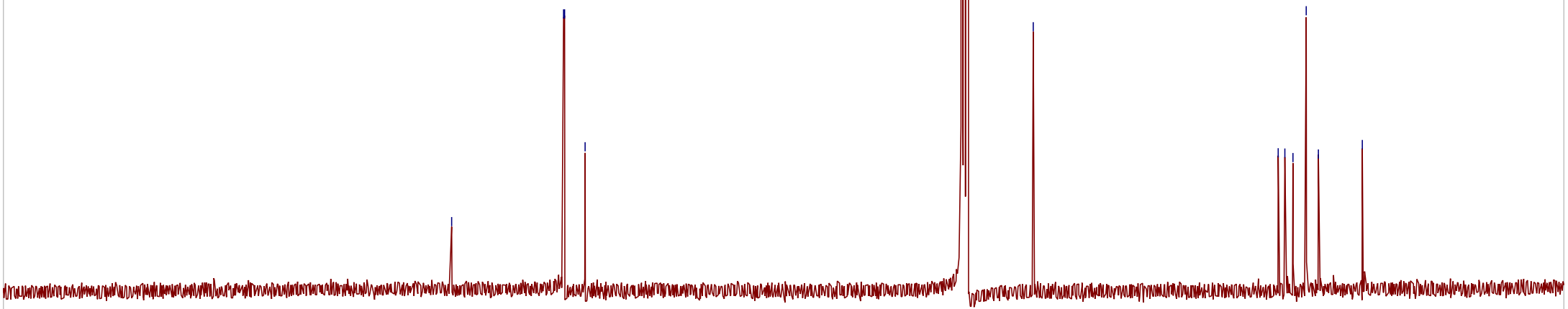
Compound 14
^{1}H NMR (400 MHz, $CDCl_3$)

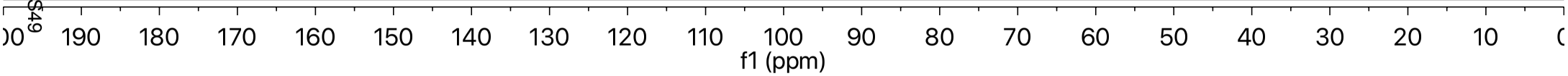
KMB_229_2_B_PDT.2.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 15

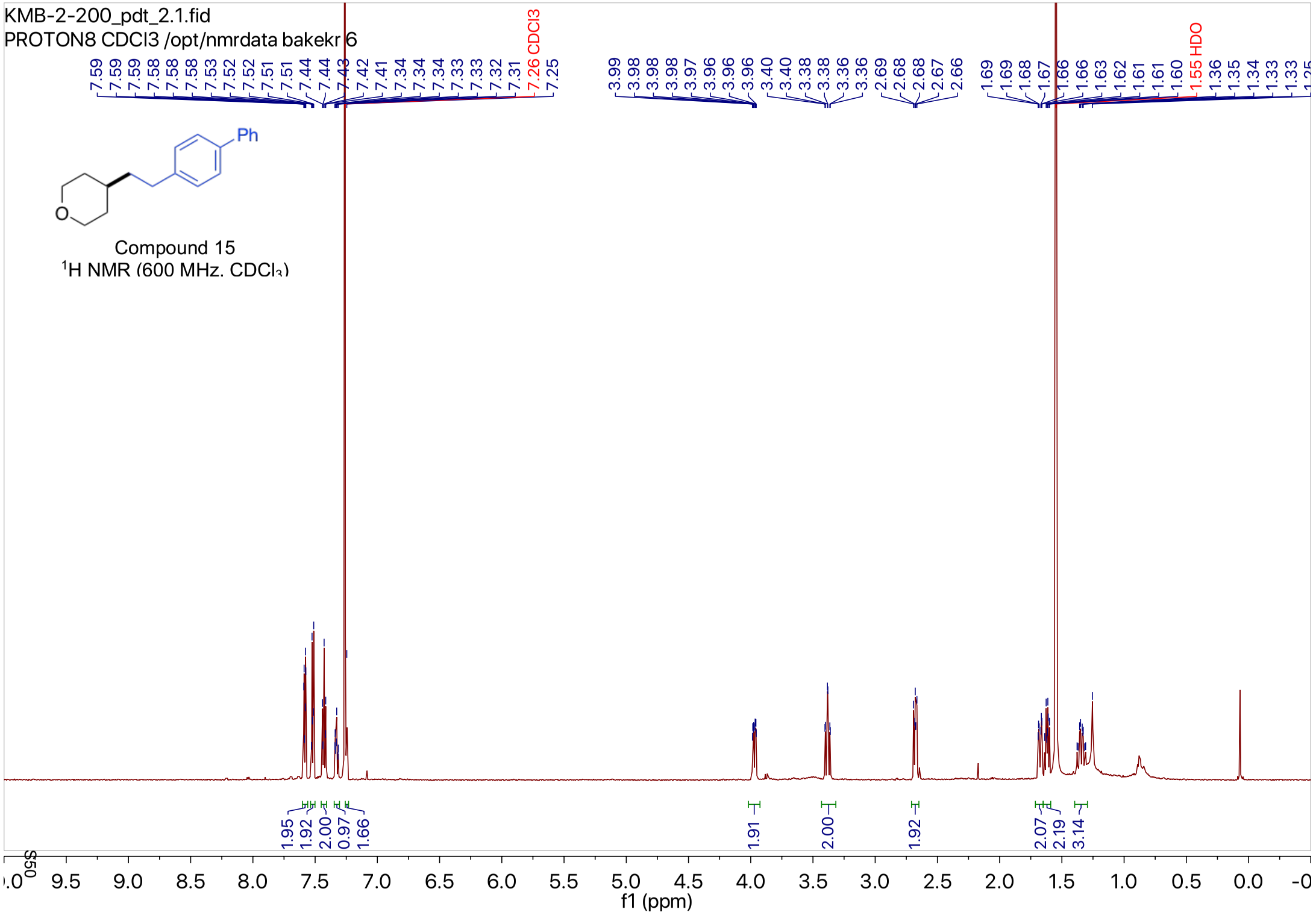


Compound 14
^{13}C NMR (101 MHz. $CDCl_3$)

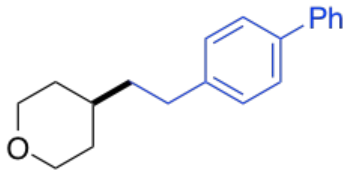
142.54
128.20
128.07
125.44
77.16 CDCl3
76.84 CDCl3
76.53 CDCl3
68.01
36.62
35.76
34.73
33.03
31.47
25.84






KMB-2-200_pdt_2.1.fid
PROTON8 CDCl3 /opt/nmrdata bakekr 6
7.59 7.59 7.59 7.58 7.58 7.58 7.53 7.52 7.52 7.51 7.51 7.44 7.44 7.43 7.42 7.41 7.34 7.34 7.34 7.33 7.33 7.32 7.31 7.26 CDCl3 7.25
3.99 3.98 3.98 3.98 3.97 3.96 3.96 3.96 3.40 3.40 3.38 3.38 3.36 3.36 2.69 2.68 2.68 2.67 2.66
1.69 1.69 1.68 1.67 1.66 1.66 1.63 1.62 1.61 1.61 1.60 1.55 HDO 1.36 1.35 1.34 1.33 1.33
Ph
O
Compound 15
1H NMR (600 MHz. CDCl3)
1.95 1.92 2.00 0.97 1.66
1.91 2.00 1.92 2.07 2.19 3.14
f1 (ppm)

KMB-2-200_pdt.4.fid



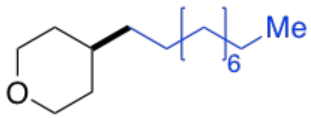
Compound 15

^{13}C NMR (101 MHz. $CDCl_3$)

141.68
141.05
138.69
128.75
128.73
127.10
127.03
126.99
77.35 CDCl3
77.03 CDCl3
76.72 CDCl3
68.10
38.74
34.54
33.10
32.31
31.00

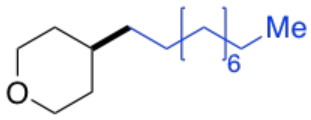
f1 (ppm)

KMB-2-204_pdt.2.fid
PROTON8 CDCl3 /opt/nmrdata bakekr 13

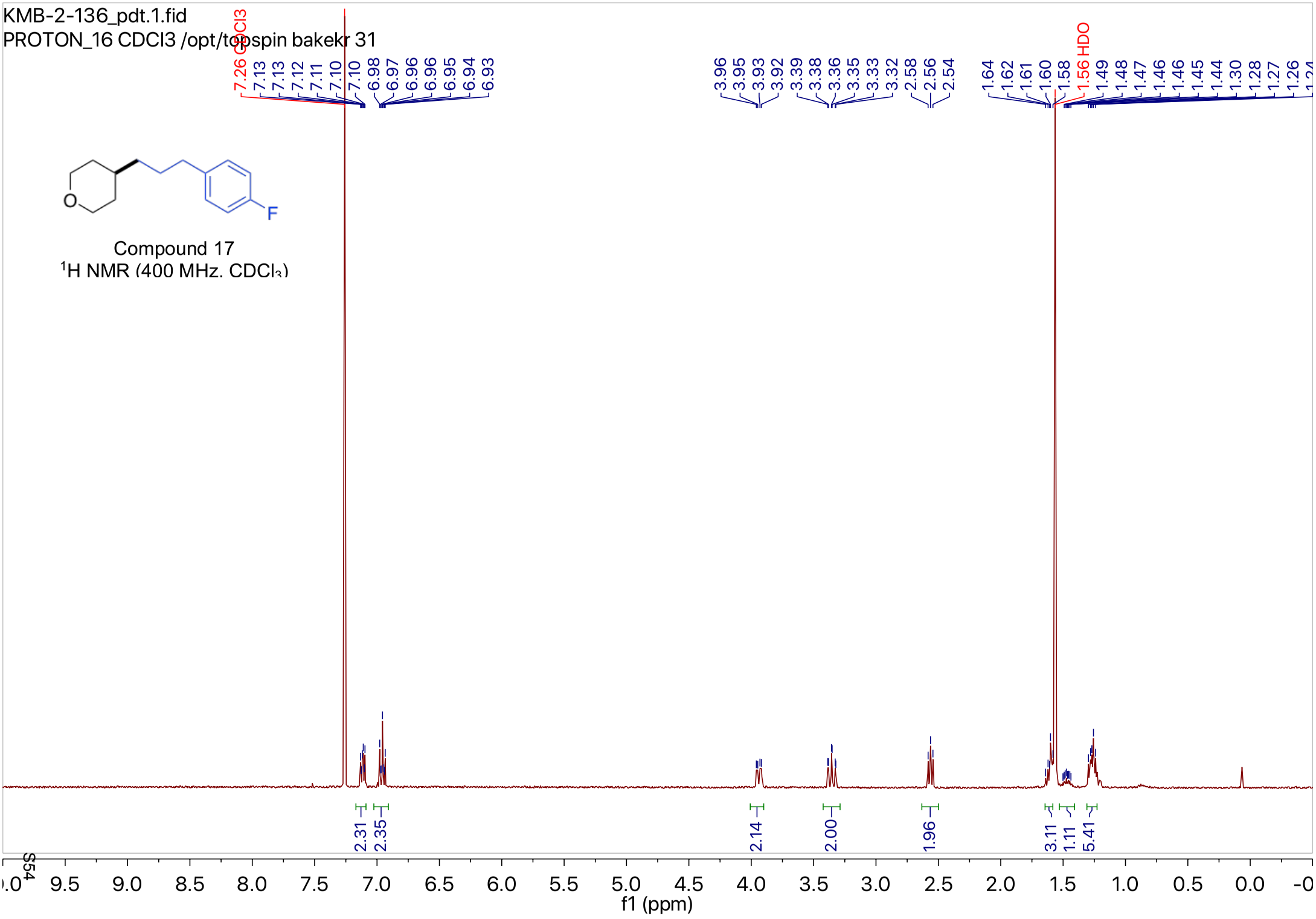


Compound 16
^{1}H NMR (600 MHz, $CDCl_3$)

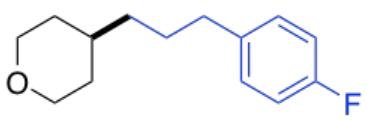
KMB-2-204_pdt.4.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 10



Compound 16
^{13}C NMR (101 MHz. $CDCl_3$)

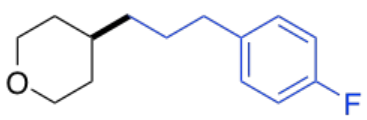

KMB-2-136_pdt.1.fid
PROTON_16 CDCl3 /opt/topspin bakekr 31
7.26 CDCl3
7.13
7.13
7.12
7.11
7.10
7.10
6.98
6.97
6.96
6.96
6.95
6.94
6.93
3.96
3.95
3.93
3.92
3.39
3.38
3.36
3.35
3.33
3.32
2.58
2.56
2.54
1.64
1.62
1.61
1.60
1.58
1.56 HDO
1.49
1.48
1.47
1.46
1.46
1.45
1.44
1.30
1.28
1.27
1.26
O
F
Compound 17
1H NMR (400 MHz. CDCl3)
2.31
2.35
2.14
2.00
1.96
3.11
1.11
5.41
f1 (ppm)

KMB-2-136_pdt.2.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 31



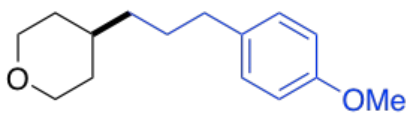
Compound 17
^{13}C NMR (101 MHz. $CDCl_3$)

KMB-2-136_F.1.fid
F19DEC_16 CDCl3 /opt/topspin bakekr 37

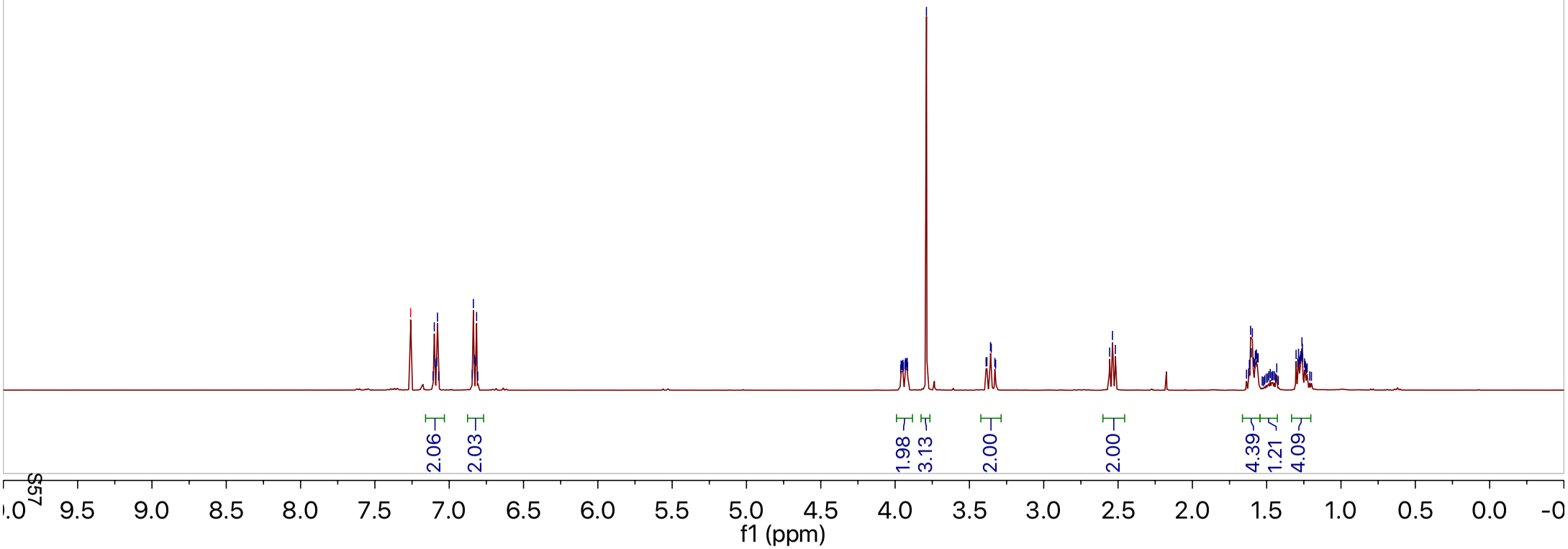


Compound 17
^{19}F NMR (376 MHz, $CDCl_3$)

KMB-2-197_pdt.1.fid
PROTON_16 CDCl3 /opt/topspin bakekr 33

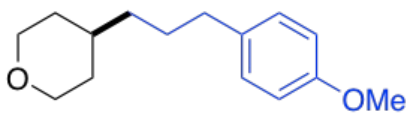


Compound 18
^{1}H NMR (400 MHz, $CDCl_3$)

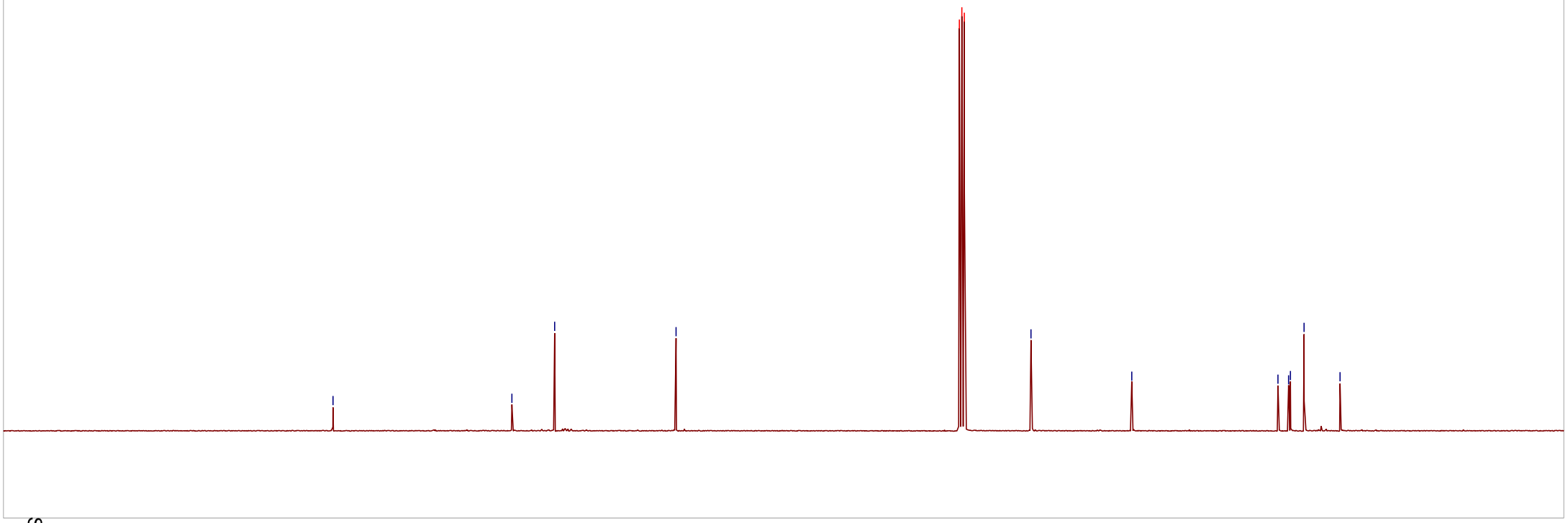


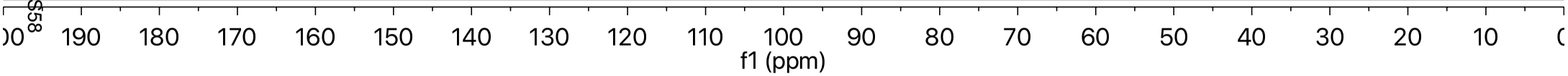
KMB-2-197_pdt.2.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 33

157.75
134.82
129.34
113.79
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
68.30
55.38
36.65
35.29
35.05
33.30
28.69

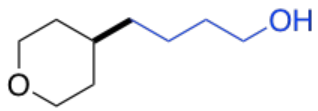


Compound 18
^{13}C NMR (101 MHz. $CDCl_3$)



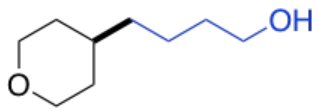


KMB-2-202 B.2.fid
PROTON8 CDCl3 /opt/nmrdata bakekr 24



Compound 19
^{1}H NMR (600 MHz, $CDCl_3$)

KMB-2-202_pdt.2.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 47

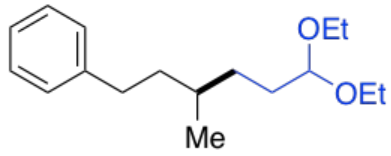


Compound 19
^{13}C NMR (101 MHz. $CDCl_3$)

77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
68.30
63.10
36.85
35.09
33.29
33.03
22.69

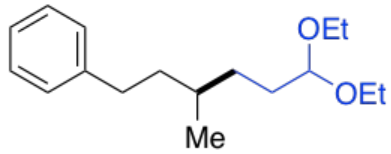
f1 (ppm)

KMB-2-068_pdt.1.fid
PROTON_16 CDCl3 /opt/topspin bakekr 49



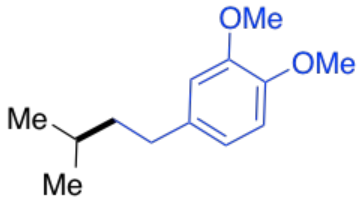
Compound 20
^{1}H NMR (400 MHz, $CDCl_3$)

KMB-2-068_pdt.2.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 49



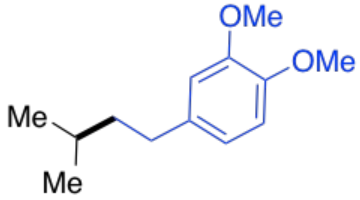
Compound 20
^{13}C NMR (101 MHz. $CDCl_3$)

KMB-2-222_pdt.1.fid
PROTON_16 CDCl3 /opt/topspin bakeb 54



Compound 21
^{1}H NMR (400 MHz, $CDCl_3$)

KMB-2-222_pdt.2.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 54



Compound 21
^{13}C NMR (101 MHz, $CDCl_3$)

148.81
147.01
135.89
120.12
111.72
111.18
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.04
55.91
41.20
33.55
27.85
22.71

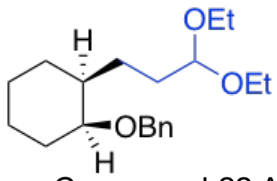
S64

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

f1 (ppm)

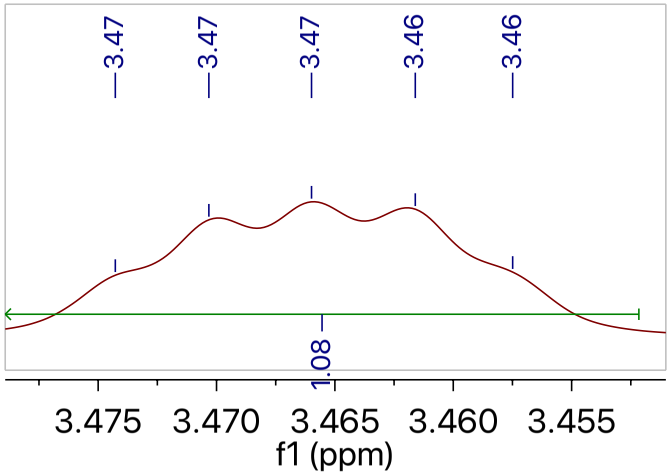
KMB-2-217 2 1.2.fid

PROTON8 CDCl3 /opt/nmrdata bakekr 3

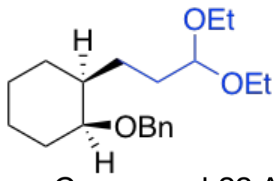


Compound 22 A

^{1}H NMR (600 MHz. $CDCl_3$)

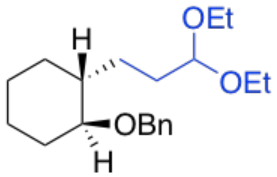


KMB-2-243-A.2.fid
C13CPD256 CDCl3 /opt/topspin bakekr 23

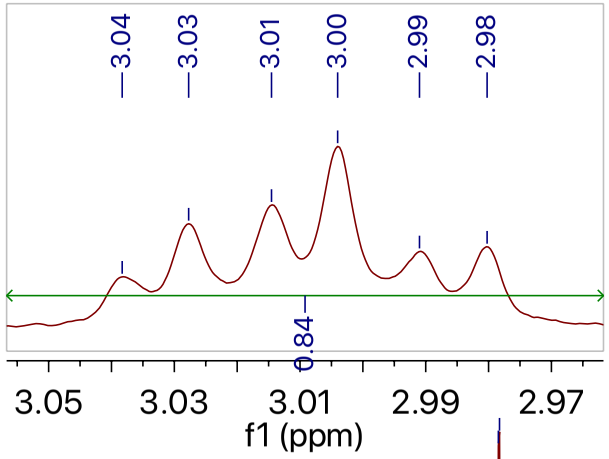


Compound 22 A
^{13}C NMR (101 MHz. $CDCl_3$)

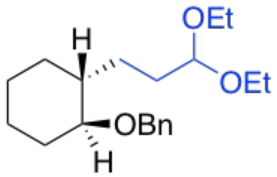
KMB-2-217.2.3.1.fid
PROTON_16 CDCl3 /opt/topspin bakekr 58



Compound 22 B
^{1}H NMR (400 MHz. $CDCl_3$)



KMB-2-217.2.3.2.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 58



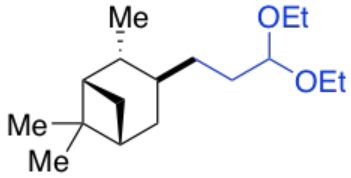
Compound 22 B
^{13}C NMR (101 MHz. $CDCl_3$)

139.13
128.27
127.76
127.37
103.39
81.70
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
70.60
60.83
60.70
42.89
31.08
30.62
30.33
27.20
25.42
24.71
15.39
15.37

S68

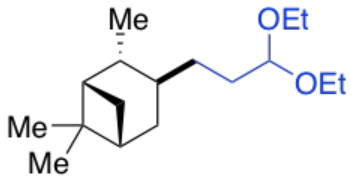
f1 (ppm)

KMB-2-246 B.1.fid
PROTON8 CDCl3 /opt/nmrdata bakekr 24



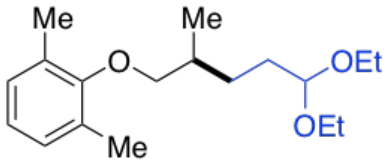
Compound 23
^{1}H NMR (600 MHz, $CDCl_3$)

KMB-2-246_pdtt.2.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 55



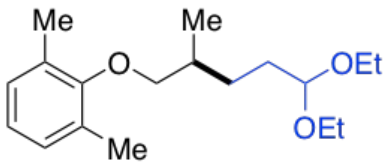
Compound 23
^{13}C NMR (101 MHz. $CDCl_3$)

KMB-2-162_pdt.1.fid
PROTON 16 CDCl3 /opt/topspin.bakekr 40



Compound 24
^{1}H NMR (400 MHz, $CDCl_3$)

KMB-2-162_pdt.3.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 40



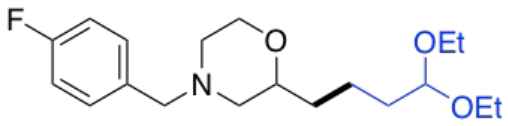
Compound 24
^{13}C NMR (101 MHz. $CDCl_3$)

155.96
131.08
128.92
123.75
103.30
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.17
61.09
34.36
31.39
28.63
17.21
16.45
15.51

S72

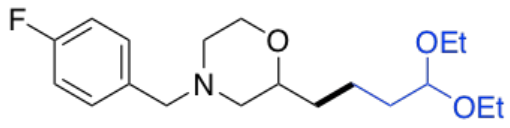
f1 (ppm)

KMB-2-119_pdt.1.fid
PROTON_16 CDCl3 /opt/topspin bakekr 19



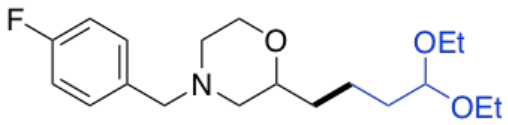
Compound 25
^{1}H NMR (400 MHz, $CDCl_3$)

KMB-2-119_pdt.4.fid
C13CPD1024 CDCl3 /opt/topspin bakekr 57



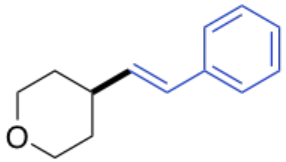
Compound 25
^{13}C NMR (101 MHz. $CDCl_3$)

KMB-2-119 9-28.2.fid
F19CPD16 CDCl3 /opt/nmrdata bakekr 3



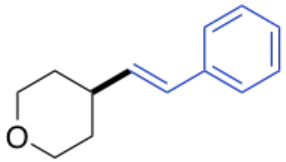
Compound 25
^{19}F NMR (565 MHz, $CDCl_3$)

DLB-1-031.40-60.1.fid
PROTON_16 CDCl3 /opt/topspin dlucasb 48



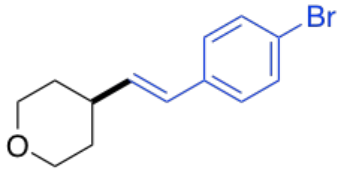
Compound 26
^{1}H NMR (400 MHz, $CDCl_3$)

DLB-1-102_pdt.2.fid
C13CPD256 CDCl3 /opt/topspin bakekr 13



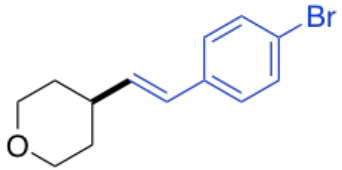
Compound 26
^{13}C NMR (100 MHz. $CDCl_3$)

DLB-1-111PDT1.fid
PROTON8 CDCl3 /opt/nmrdata dlucasb 27



Compound 27
^{1}H NMR (600 MHz, $CDCl_3$)

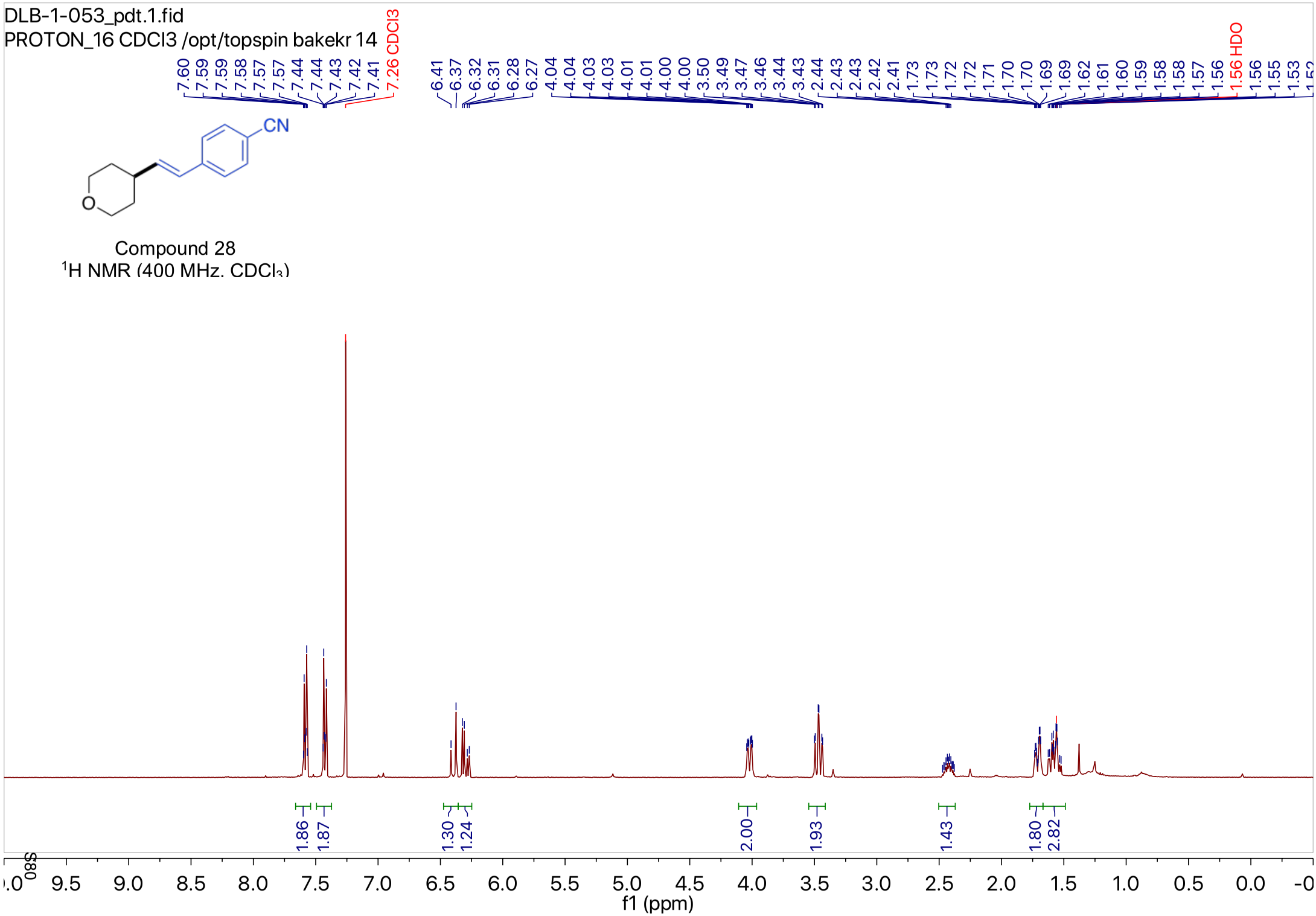
DLB-1-111.38-51.2.fid
C13CPD1024 CDCl3 /opt/nmrdata dlucasb 8



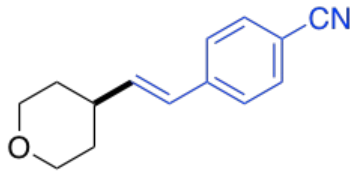
Compound 27
^{13}C NMR (151 MHz, $CDCl_3$)

136.69
135.60
131.75
127.75
127.38
120.90
77.37 CDCl3
77.16 CDCl3
76.95 CDCl3
67.83
38.53
32.69

f1 (ppm)


DLB-1-053_pdt.1.fid
PROTON_16 CDCl3 /opt/topspin bakekr 14
7.60 7.59 7.59 7.58 7.57 7.57 7.44 7.44 7.43 7.42 7.41 7.26 CDCl3
6.41 6.37 6.32 6.31 6.28 6.27 4.04 4.04 4.03 4.03 4.01 4.01 4.00 4.00 3.50 3.49 3.47 3.46 3.44 3.43 2.44 2.43 2.43 2.42 2.41 1.73 1.73 1.72 1.72 1.71 1.70 1.70 1.69 1.69 1.62 1.61 1.60 1.59 1.58 1.58 1.57 1.56 1.56 HDO 1.56 1.55 1.53
CN
O
Compound 28
1H NMR (400 MHz. CDCl3)
1.86 1.87 1.30 1.24 2.00 1.93 1.43 1.80 2.82
f1 (ppm)

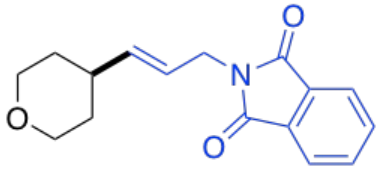
DLB-1-053_pdt.2.fid
C13CPD256 CDCl3 /opt/topspin bakekr 14



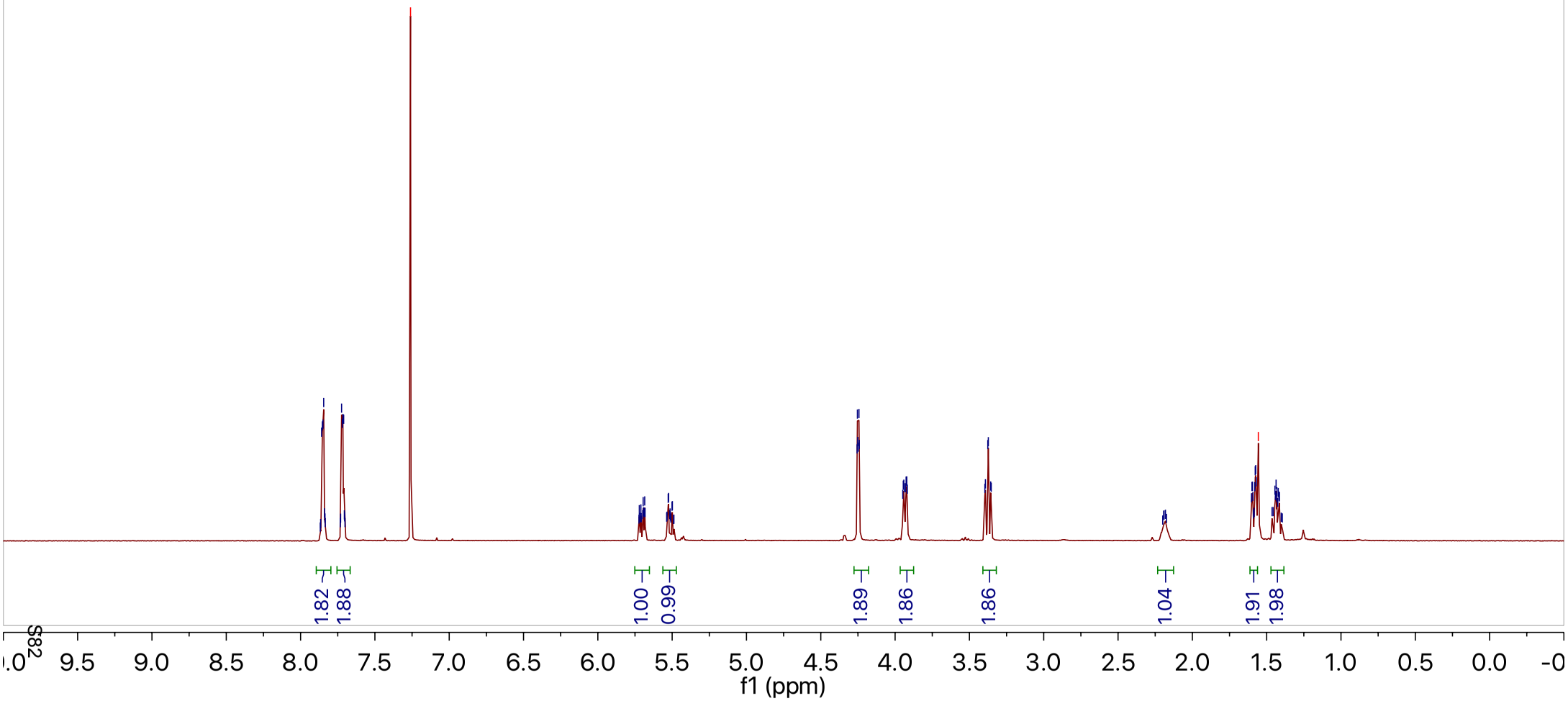
Compound 28
^{13}C NMR (101 MHz. $CDCl_3$)

142.18
138.80
132.52
127.11
126.67
119.23
110.41
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.73
38.64
32.41

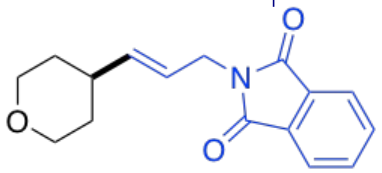
DLB-1-052PDT.1.fid
PROTON8 CDCl3 /opt/nmrdata dlucasb 28



Compound 29
^{1}H NMR (600 MHz, $CDCl_3$)

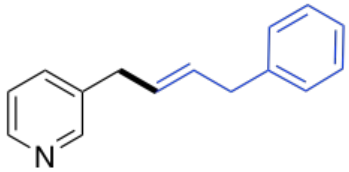


DLB-1-052Pdt.1.fid
C13CPD256 CDCl3 /opt/nmrdata dlucasb 7

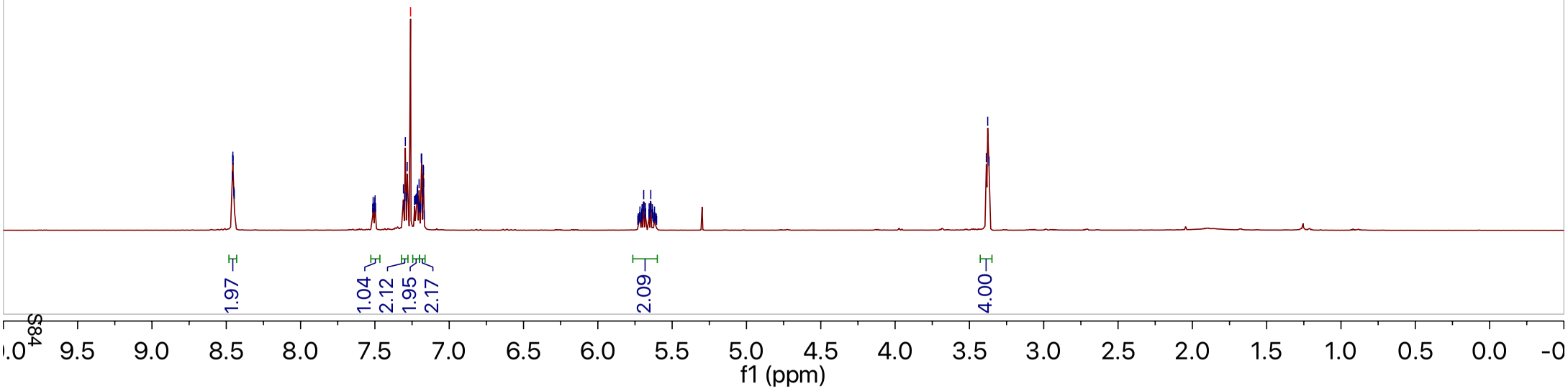


Compound 29
^{13}C NMR (151 MHz, $CDCl_3$)

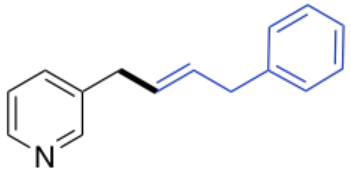
DLB-1-118Pdt.4.fid
PROTON8 CDCl3 /opt/nmrdata dlucasb 5



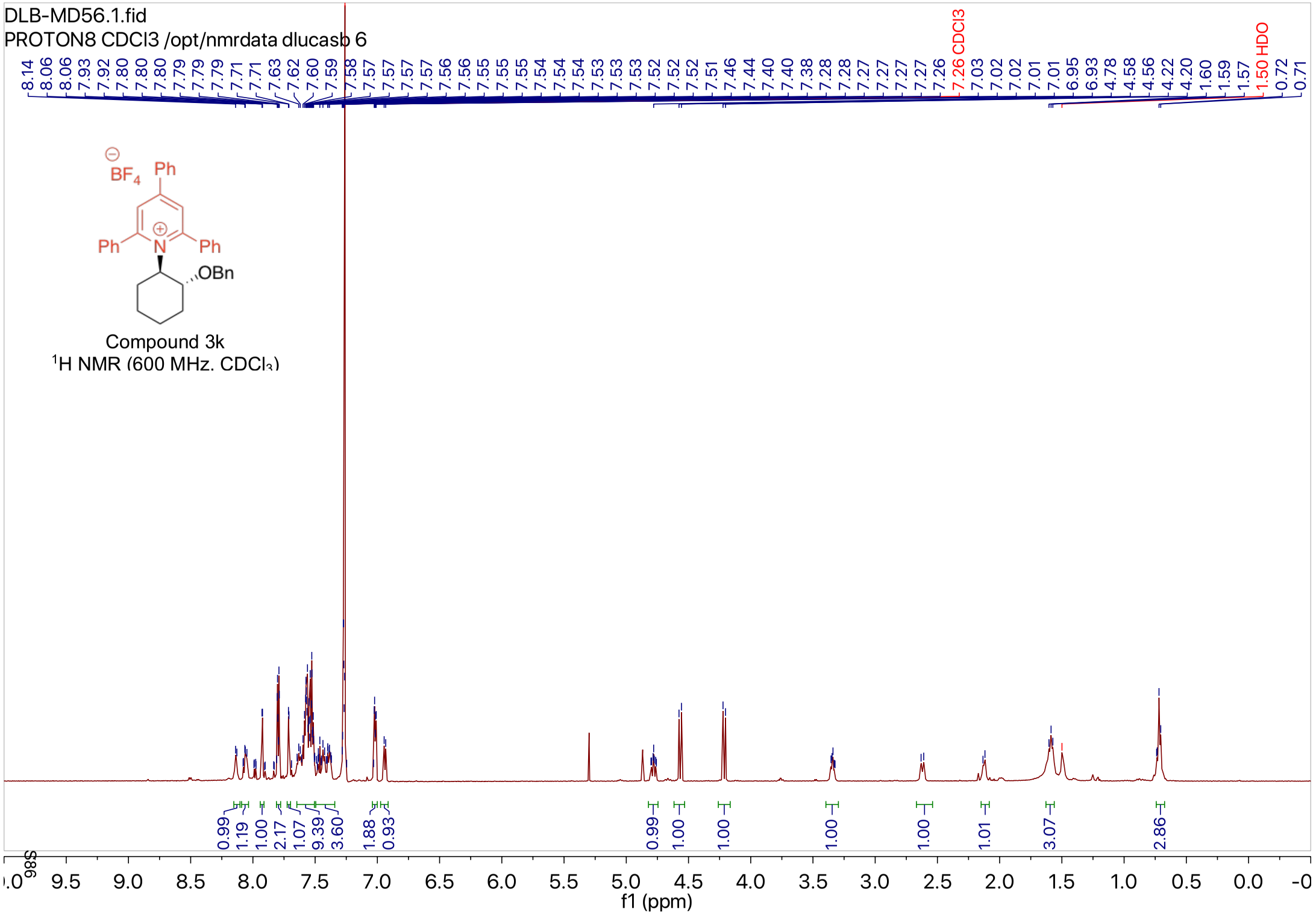
Compound 30
^{1}H NMR (600 MHz, $CDCl_3$)

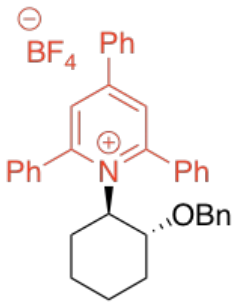


DLB-1-118Pdt.3.fid
C13CPD1024 CDCl3 /opt/nmrdata dlucasb 3



Compound 30
^{13}C NMR (101 MHz, $CDCl_3$)


DLB-MD56.1.fid
PROTON8 CDCl3 /opt/nmrdata dlucasb 6
7.26 CDCl3
1.50 HDO
Ph
Ph
Ph
OBn
Compound 3k
f1 (ppm)



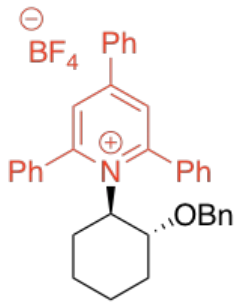
Compound 3k

^{13}C NMR (151 MHz. $CDCl_3$)

159.23
156.78
154.94
138.00
134.28
133.96
133.52
132.03
131.91
130.99
130.72
129.66
129.59
129.35
128.71
128.46
128.20
127.95
127.91
126.85
126.42

77.53
74.71
68.86

32.37
31.64
25.67
23.34



Compound 3k

^{19}F NMR (376 MHz, $CDCl_3$)

-153.37
-153.42

S88

10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210