Aryl-Nickel-Catalyzed Benzylic Dehydrogenation of Electron-Deficient Heteroarenes

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General Experimental

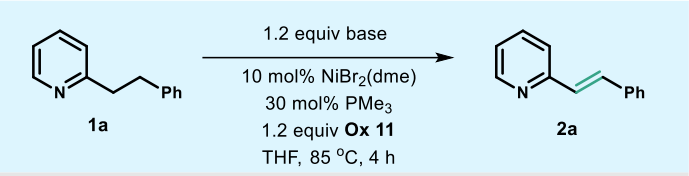
General Experimental Procedures: All reactions were carried out under an inert nitrogen atmosphere with dry solvents under anhydrous conditions unless otherwise stated. All reactions were capped with a rubber septum, or Teflon-coated silicon microwave cap unless otherwise stated. Stainless steel cannula or syringe was used to transfer solvent, and air- and moisture sensitive liquid reagents. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light as the visualizing agent and potassium permanganate, an acidic solution of *p*-anisaldehyde, phosphomolybdic acid, or I_2 on SiO_2 as developing agents. Flash column chromatography employed SiliaFlash® P60 (40-60 μm, 230-400 mesh) silica gel purchased from SiliCycle, Inc.

Materials: All reaction solvents were purified using a Seca solvent purification system by Glass contour. TMEDA, Et_3N were distilled over CaH_2. $Zn(TMP)_2$ (0.5 M in toluene), PMe_3 (1.0 M in THF), TBAI and *n*-BuLi (2.5 M in hexanes) were purchased from Sigma-Aldrich. $NiBr_2$(dme) was purchased from Strem. All other reagents were used as received without further purification, unless otherwise stated.

Instrumentation: All new compounds were characterized by means of ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR, FT-IR (thin film), and HR-MS. Copies of the ^{1}H- and ^{13}C-NMR spectra can be found at the end of each experimental procedure. NMR spectra were recorded using a Varian 400 MHz NMR spectrometer, Varian 500 MHz NMR spectrometer, or a Varian 600 MHz NMR spectrometer. All ^{1}H-NMR data are reported in δ units, parts per million (ppm), and were calibrated relative to the signals for residual chloroform (7.26 ppm) in deuterochloroform ($CDCl_3$) or Acetone-d_6 (2.05 ppm). All ^{13}C-NMR data are reported in ppm relative to $CDCl_3$ (77.16 ppm) or Acetone-d_6 (206.26 ppm) and were obtained with ^{1}H decoupling unless otherwise stated. The following abbreviations or combinations thereof were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, abq = ab quartet, br = broad, m = multiplet, and a = apparent. All IR spectra were taken on an FT-IR/Raman Thermo Nicolet 6700. High resolution mass spectra (HR-MS) were recorded on a Waters Xevo Qtof mass spectrometer using ESI-TOF (electrospray ionization-time of flight). Gas chromatography mass spectra (GC-MS) were recorded on an Agilent Technologies 6890N Network Gas Chromatograph System with an Agilent Technologies 5973N Mass Selective Detector. Optical rotation data was obtained using a Perkin-Elmer 341 polarimeter.

Additional Optimization Studies

Figure SI-1. Optimization of base

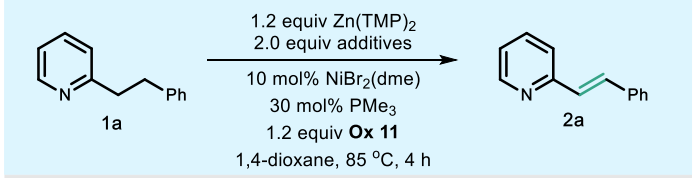


Entry	base	Yield (%)[a]
1	LiHMDS	0 (3)
2	LiCyan + $ZnCl_2$	12 (22)
3	LDA + $ZnCl_2$	28 (46)
4	LiTMP + $ZnCl_2$	18 (35)
5	$Zn(TMP)_2$	51 (62)
6	MgTMPCl•LiCl	8 (19)
7	$LiZn(TMP)Et_2$	4 (4)
8	$Zn(TMP)_2$[b]	70 (100)

[a] ^{1}H NMR yield was determined using 1,3,5-trimethoxybenzene as an internal standard. Conversion shown in parentheses. [b] 1,4-dioxane was used as solvent.

For entries 2–4, substrate **1a** was treated with base at –40 °C for 30 minutes. Then a solution of $ZnCl_2$ in THF (1.0 M, 2.0 equiv) was added and stirred at room temperature for 30 minutes.

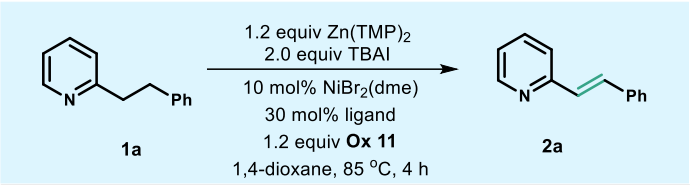
Figure SI-2. Optimization of additive



Entry	additives	Yield (%)[a]
1	none	70 (100)
2	$ZnCl_2$	17 (35)
3	ZnI_2	19 (46)
4	NaI	45 (64)
5	TBAC	36 (56)
6	TBAB	54 (74)
7	TBAI	94 (100)

[a] ^{1}H NMR yield was determined using 1,3,5-trimethoxybenzene as an internal standard. Conversion shown in parentheses.

Figure SI-3. Optimization of ligand and catalyst



1a 2a

Entry	Deviation from Standard	Yield (%)[a]
1	no ligand	45 (47)
2	PMe_3	94 (100)
3	PMe_3[b]	70 (100)
4	$P(n\text{-}Bu)_3$	25 (32)
5	$P(t\text{-}Bu)_3$	28 (28)
6	PCy_3	33 (44)
7	PPh_2Me	42 (59)
8	PPh_3	52 (55)
9	$P(4\text{-}OMe\text{-}Ph)_3$	42 (55)
10	$P(OMe)_3$	54 (55)
11	XPhos	39 (45)
12	Box[c]	37 (59)
13	Bipy	13 (55)
14	Et_3N	47 (65)
15	TMEDA	34 (46)
16	$[Pd(allyl)Cl]_2$ (5 mol%)	50 (79)
17	$Pd(OAc)_2$	62 (70)
18	$Pd(dba)_2$	59 (91)
19	$PdCl_2(PhCN)_2$	69 (91)

[a] ^1H NMR yield was determined using 1,3,5-trimethoxybenzene as an internal standard. Conversion shown in parentheses. [b] No TBAI was used. [c] Box = 2,2-methylenebis((4R,5S)-4,5-diphenyl-2-oxazoline.

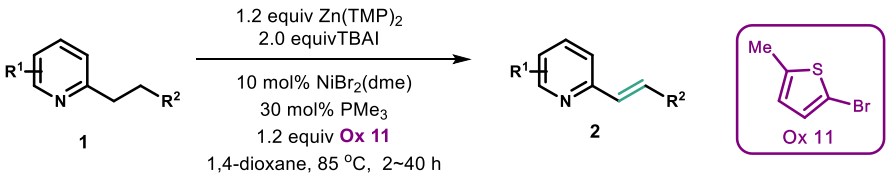
General Experimental Procedure

1. Preparation of $NiBr_2$(dme)/PMe_3 and 2-bromo-5-methylthiophene stock solution (1.00 mmol scale)

To a flame-dried microwave vial equipped with a magnetic stir bar was added $NiBr_2$(dme) (30.8 mg, 0.10 mmol, 10 mol%). The reaction vessel was evacuated and backfilled with N_2 (this process was repeated three times). To the reaction vessel was added anhydrous 1,4-dioxane (2.1 mL, 0.4 M), PMe_3 (0.30 mL, 1.0 M in THF, 0.3 mmol, 30 mol%), and 2-bromo-5-methylthiophene (137 μL, 1.2 mmol, 1.2 equiv), and the mixture was stirred for 2 minutes at ambient temperature to give a homogeneous dark blue solution.

For a 0.20 mmol scale reaction, 0.5 mL of this stock solution containing $NiBr_2$(dme) (6.2 mg, 0.02 mmol, 10 mol%), PMe_3 (0.06 mL, 0.06 mmol, 30 mol%), and 2-bromo-5-methylthiophene (27.4 μL, 0.24 mmol, 1.2 equiv) was used.

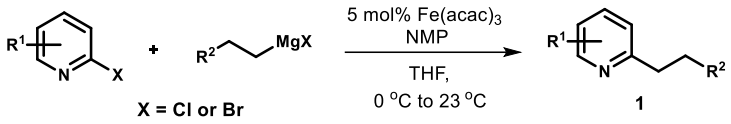
2. General Experimental **Procedure A** for Benzylic Dehydrogenation



To a flame-dried microwave vial equipped with a magnetic stir bar was added starting material **1** (0.20 mmol, 1.0 equiv) and TBAI (148 mg, 0.40 mmol, 2.0 equiv). The reaction vessel was sealed, evacuated and backfilled with N_2 (this process was repeated three times). To the reaction vessel was added anhydrous 1,4-dioxane (1.5 mL) and commercial $Zn(TMP)_2$ (0.48 mL, 0.5 M in toluene, 0.24 mmol, 1.2 equiv) at room temperature. Then to this mixture was added 0.5 mL of a stock solution containing $NiBr_2$(dme) (6.2 mg, 0.02 mmol, 10 mol %), PMe_3 (0.06 mL, 0.06 mmol, 30 mol%), and 2-bromo-5-methylthiophene (27.4 μL, 0.24 mmol, 1.2 equiv) in 1,4-dioxane. The reaction vessel was placed into a pre-heated 85 ºC oil bath, and stirred until complete consumption of starting material as determined by TLC analysis. (Note: more reproducible results can be obtained using the sequential addition procedure.)

The reaction mixture was cooled to ambient temperature and quenched by the addition of sat. aq. NH_4Cl (5 mL). The reaction mixture was diluted with EtOAc (5 mL) and the organic phase was separated. The aqueous phase was extracted with EtOAc (3 × 5 mL) and the combined organic extracts were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation. The crude mixture was purified by flash column chromatography on silica gel.

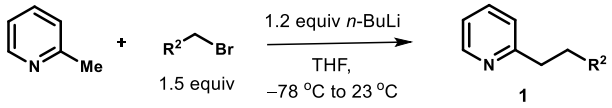
3. General Experimental **Procedure B** for substrate preparation through an Fe-catalyzed cross-coupling reaction[1]



To a flame-dried microwave vial equipped with a magnetic stir bar was added magnesium (264 mg, 11 mol, 1.1 equiv), a catalytic amount of I_2 (5 mg), and THF (5 mL, 2.0 M). The resulting mixture was heated to 80 °C, then removed the oil bath and alkyl bromide (10 mol, 1.0 equiv) was added via syringe dropwise over 10 minutes to maintain a gentle reflux. The reaction vessel was then stirred for 30 minutes at room temperature.

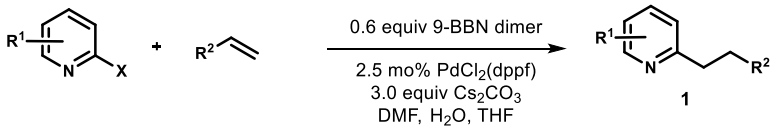
A flame-dried flask under N_2 was charged with aryl halide (5.0 mmol, 1.0 equiv), $Fe(acac)_3$ (88 mg, 0.25 mmol 5 mol%), N-methylpyrrolidone (3.0 mL), and THF (30 mL, 0.15 M). A solution of alkyl magnesium bromide/chloride (3.0 mL, 2.0 M in THF, 6.00 mmol, 1.2 equiv) is added via syringe to the resulting red solution at 0 °C, causing an immediate color change to dark brown or black. The resulting mixture was stirred at room temperature for 30 minutes, and the reaction was diluted with Et_2O and is carefully quenched by the slow addition of aq. 1.0 M HCl (10 mL). The reaction mixture was diluted with water (20 mL) and EtOAc (20 mL) and the organic phase was separated. The aqueous phase was extracted with EtOAc (3 × 25 mL) and the combined organic extracts were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation. The crude mixture was purified by flash column chromatography on silica gel.

4. General Experimental **Procedure C** for substrate preparation through an S_N2 reaction



A flame-dried flask under N_2 was charged with 2-methylpyridine (3 mmol, 1.0 equiv) and THF (10 mL, 0.3 M). A solution of *n*-BuLi (1.5 mL, 2.5 M in hexanes, 3.6 mmol, 1.2 equiv) was added dropwise via syringe at –78 °C. The resulting red solution was stirred at –78 °C for 30 minutes before the addition of alkyl bromide (4.5 mmol, 1.5 equiv). The resulting mixture was slowly warmed to room temperature and stirred for 1 hour. The reaction was quenched upon the addition of sat. aq. NH_4Cl (10 mL) and then diluted with Et_2O (10 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL) and the combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation. The crude mixture was purified by flash column chromatography on silica gel.

5. General Experimental **Procedure D** for substrate preparation through a hydroboration-Suzuki coupling reaction[2]

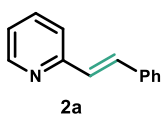


A flame-dried vial equipped with a magnetic stir bar was charged with 9-borabicyclo[3.3.1]nonane dimer (300 mg, 1.2 mmol, 0.6 equiv), capped with a rubber septum, and evacuated and backfilled with N_2 three times. The vial was cooled to 0 °C and anhydrous THF (3.0 mL, 0.50 M) was added to the vial in a single portion. To the reaction mixture was added alkene (1.6 mmol, 0.8 equiv) and the mixture was stirred for 10 minutes at 0 °C. Following this, the reaction mixture was slowly warmed to room temperature by removing the ice-water bath. After stirring for 1 hour, the reaction mixture was cooled back down to 0 °C. To the reaction mixture was added degassed deionized water (1.8 mL, 100.0 mmol, 50.0 equiv) dropwise over 1 minute. At this time, the biphasic reaction mixture became a cloudy white color. The reaction mixture containing alkylborane was stirred for 10 minutes before use in the Suzuki coupling

To a flame-dried, 20 mL vial equipped with a magnetic stir bar was added with aryl halide (2 mmol, 1.0 equiv), $PdCl_2$(dppf) (40 mg, 0.05 mmol, 2.5 mol%) and Cs_2CO_3 (2.0 g, 6.0 mmol, 3.0 equiv). The reaction vessel was capped, and evacuated and backfilled with N_2 three times. Anhydrous DMF (10 ml, 0.2 M) was added to the vial and the prepared solution of alkylborane (3 mL, 0.5 M) was added to the reaction mixture in a single portion. The resulting reaction mixture was placed in a preheated 60 °C oil bath and stirred for 16 hours. The reaction mixture was cooled to room temperature and diluted with Et_2O (20 ml), and then filtered through a pad of Celite. The resulting filtrate was washed with sat. aq. $NaHCO_3$ (20 ml). The aqueous phase was extracted with EtOAc (3 × 10 mL) and the combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation. The crude mixture was purified by flash column chromatography on silica gel.

Characterization Data for Benzylic Dehydrogenation Products

(*E*)-2-styrylpyridine (2a)

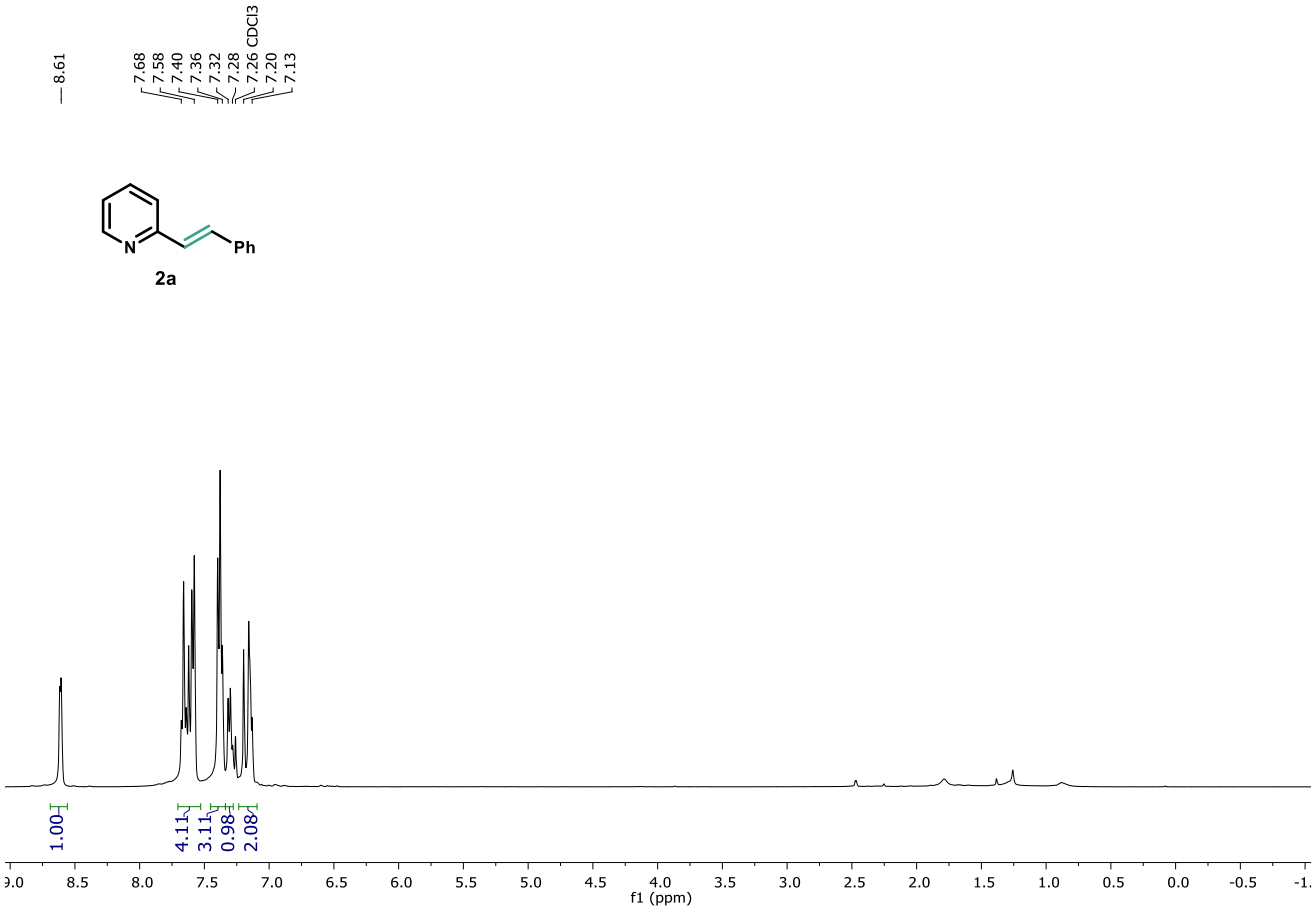


2a

Compound **2a** was prepared from known compound **1a** (36.6 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (4 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 20:1 to 10:1) afforded **2a** (33.3 mg, 92%) as a yellow solid. The characterization data match those previously reported in the literature.[3]

For a gram scale reaction with 2 mol% $NiBr_2$(dme)/ 6 mol% PMe_3:
To a flame-dried 250 mL flask equipped with a magnetic stir bar was added starting material **1a** (1.0 g, 5.5 mmol, 1.0 equiv) and TBAI (4.1 g, 0.40 mmol, 2.0 equiv). The flask was evacuated and backfilled with N_2 (this process was repeated three times). To the flask was added 1,4-dioxane (55 mL) and commercial $Zn(TMP)_2$ (13.2 mL, 0.5 M in toluene, 6.6 mmol, 1.2 equiv) at room temperature. Then to this mixture was added 2 mL of a stock solution containing $NiBr_2$(dme) (33.7 mg, 0.11 mmol, 2 mol %), PMe_3 (0.34 mL, 0.33 mmol, 6 mol%), and 2-bromo-5-methylthiophene (0.75 mL, 6.6 mmol, 1.2 equiv) in 1,4-dioxane. The flask was sealed with parafilm, placed into a pre-heated 85 ºC oil bath, and stirred for 4 hours. The reaction was quenched following general dehydrogenation **procedure A**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 20:1 to 10:1) afforded **2a** (758 mg, 77%) as a yellow solid.

R_f: 0.42 (hexanes/EtOAc = 4:1)
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* = 3.9 Hz, 1H), 7.68–7.58 (m, 4H), 7.40–7.36 (m, 3H), 7.32–7.28 (m, 1H), 7.20–7.13 (m, 2H)
^{13}C NMR (101 MHz, $CDCl_3$): δ 155.8, 149.8, 136.8, 136.7, 132.9, 128.9, 128.5, 128.1, 127.2, 122.2, 122.2
IR (cm^{-1}): 3055, 1597, 1583, 1467, 1449, 1427, 1148, 967, 774, 734, 689, 550, 531
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{13}H_{12}N^+$: 182.0964; found: 182.0970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3.11
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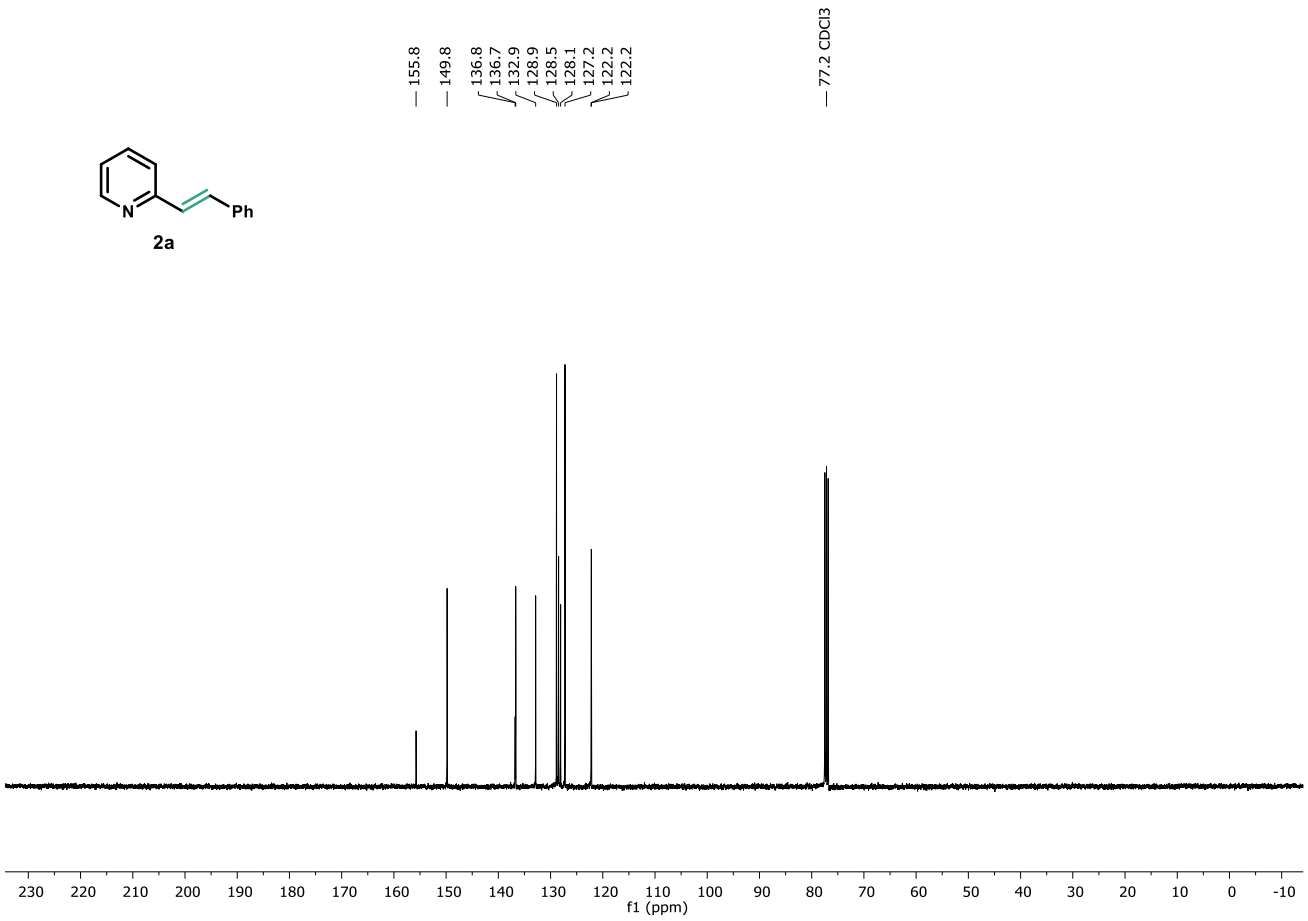
f1 (ppm)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128.5
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127.2
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122.2
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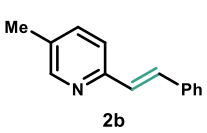
Ph
2a
f1 (ppm)

(*E*)-5-methyl-2-styrylpyridine (2b)



2b

Compound **2b** was prepared from **1b** (39.4 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (12 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 10:1) afforded **2a** (32.1 mg, 82%) as a yellow oil.

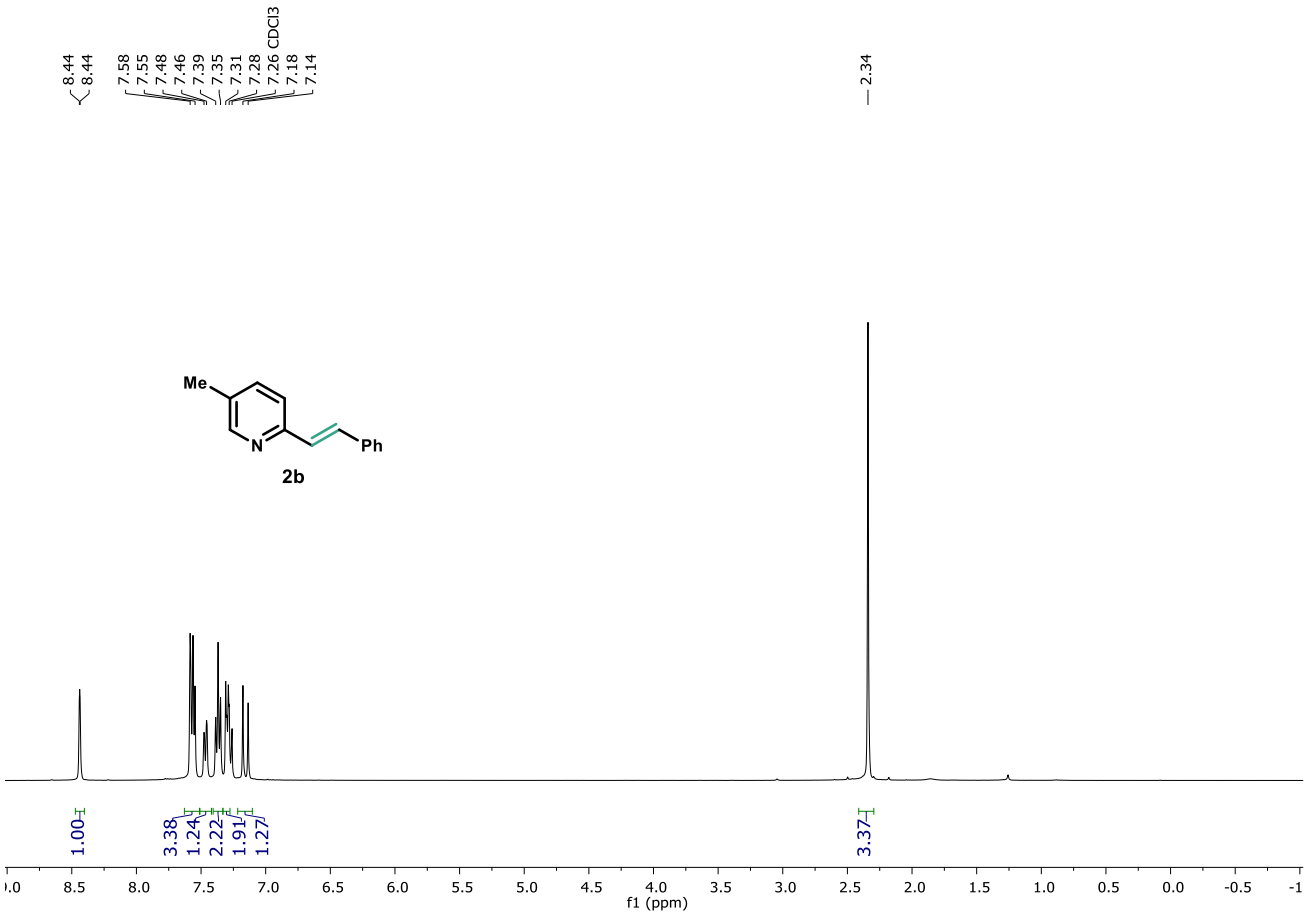
R$_f$: 0.66 (hexanes/EtOAc = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, *J* = 2.3 Hz, 1H), 7.58–7.55 (m, 3H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.39–7.35 (m, 2H), 7.31–7.28 (m, 2H), 7.16 (d, *J* = 16.2 Hz, 1H), 2.34 (s, 3H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.1, 150.3, 137.2, 137.0, 131.8, 131.8, 128.8, 128.2, 128.1, 127.1, 121.7, 18.4

IR (cm^{-1}): 3023, 2919, 1594, 1478, 1379, 1195, 1026, 975, 822, 762, 734, 690, 532, 507

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{14}H_{14}N^+$: 196.1121 found: 196.1126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Ph
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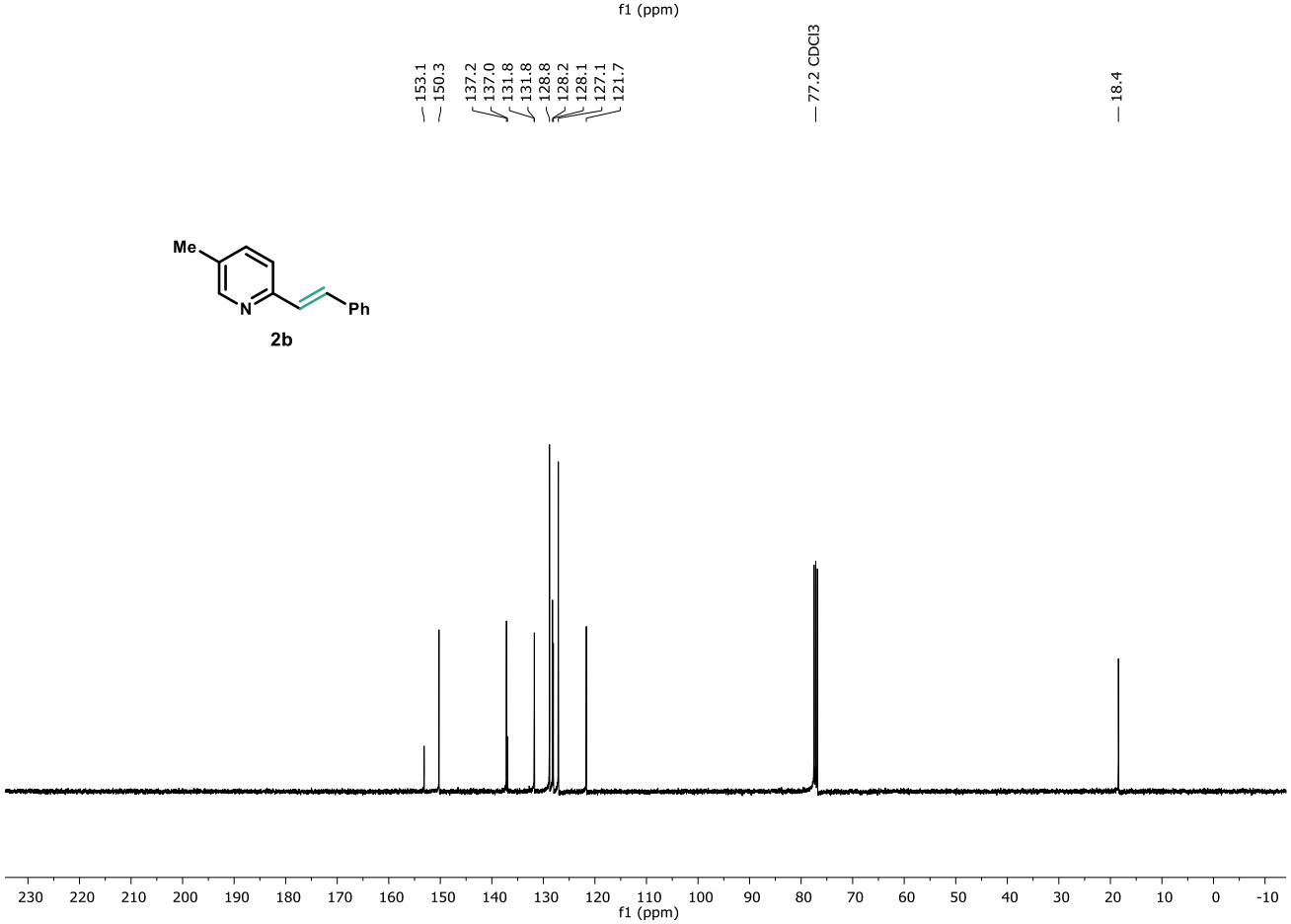
f1 (ppm)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137.0
131.8
131.8
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128.2
128.1
127.1
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Me
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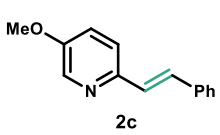
Ph
2b
f1 (ppm)

(*E*)-5-methoxy-2-styrylpyridine (2c)



2c

Compound **2c** was prepared from **1c** (42.6 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (12 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 10:1) afforded **2c** (30.4 mg, 72%) as a yellow oil.

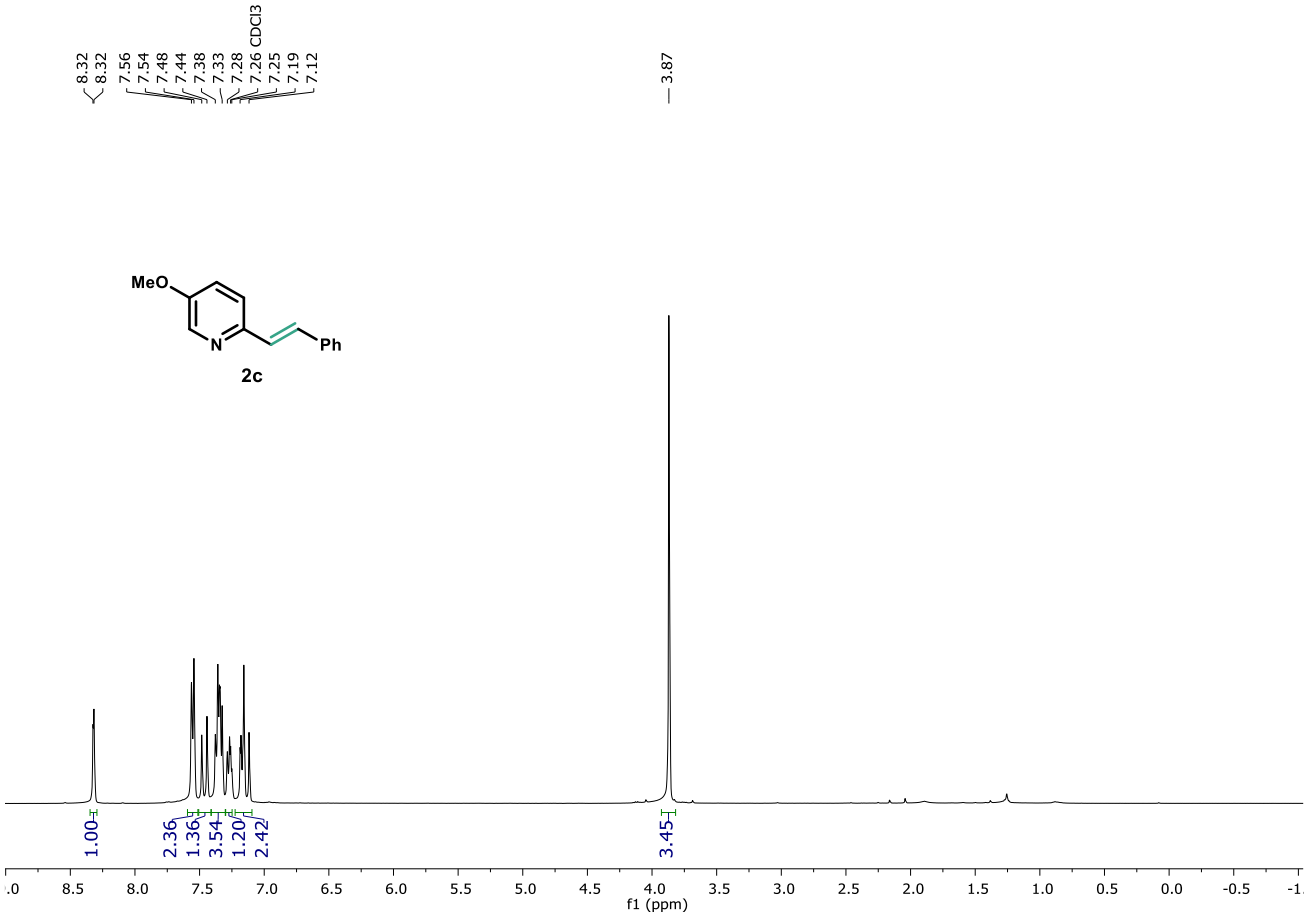
R$_f$: 0.40 (hexanes/EtOAc = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 3.1 Hz, 1H), 7.56–7.54 (m, 2H), 7.48–7.44 (m, 1H), 7.38–7.33 (m, 3H), 7.28–7.26 (m, 1H), 7.19–7.12 (m, 2H), 3.87 (s, 3H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.8, 148.6, 137.6, 137.1, 130.6, 128.8, 128.0, 127.6, 126.9, 122.5, 120.9, 55.8

IR (cm^{-1}): 3026, 2938, 2839, 1565, 1477, 1266, 1242, 1219, 1027, 968, 821, 761, 691, 543

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{14}H_{14}NO^+$: 212.1070; found: 212.1075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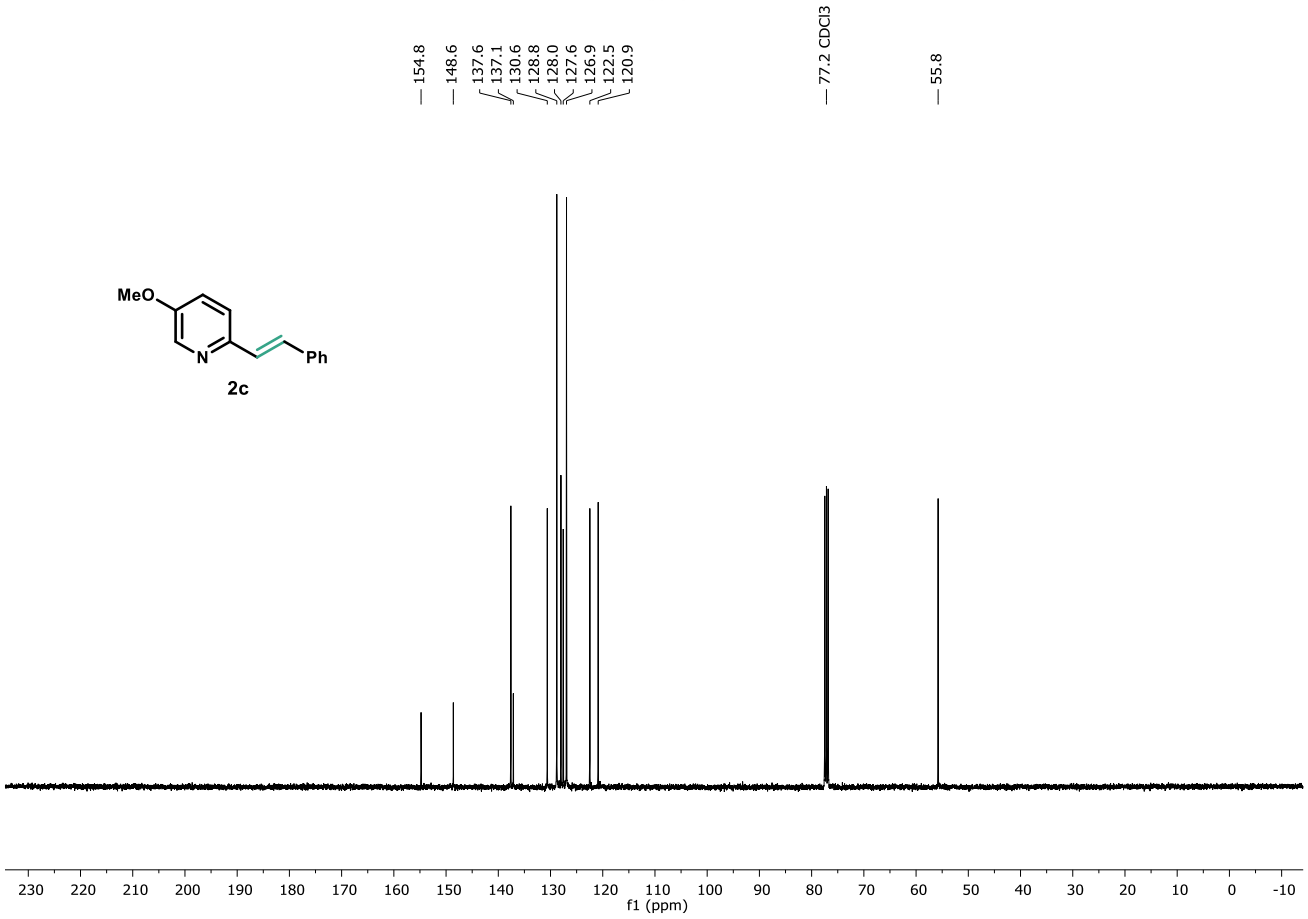
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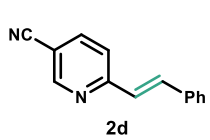
Ph
2c
f1 (ppm)

(*E*)-6-styrylnicotinonitrile (2d)



2d

Compound **2d** was prepared from **1d** (41.6 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (12 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 10:1) afforded **2d** (14.9 mg, 36%) as a white solid.

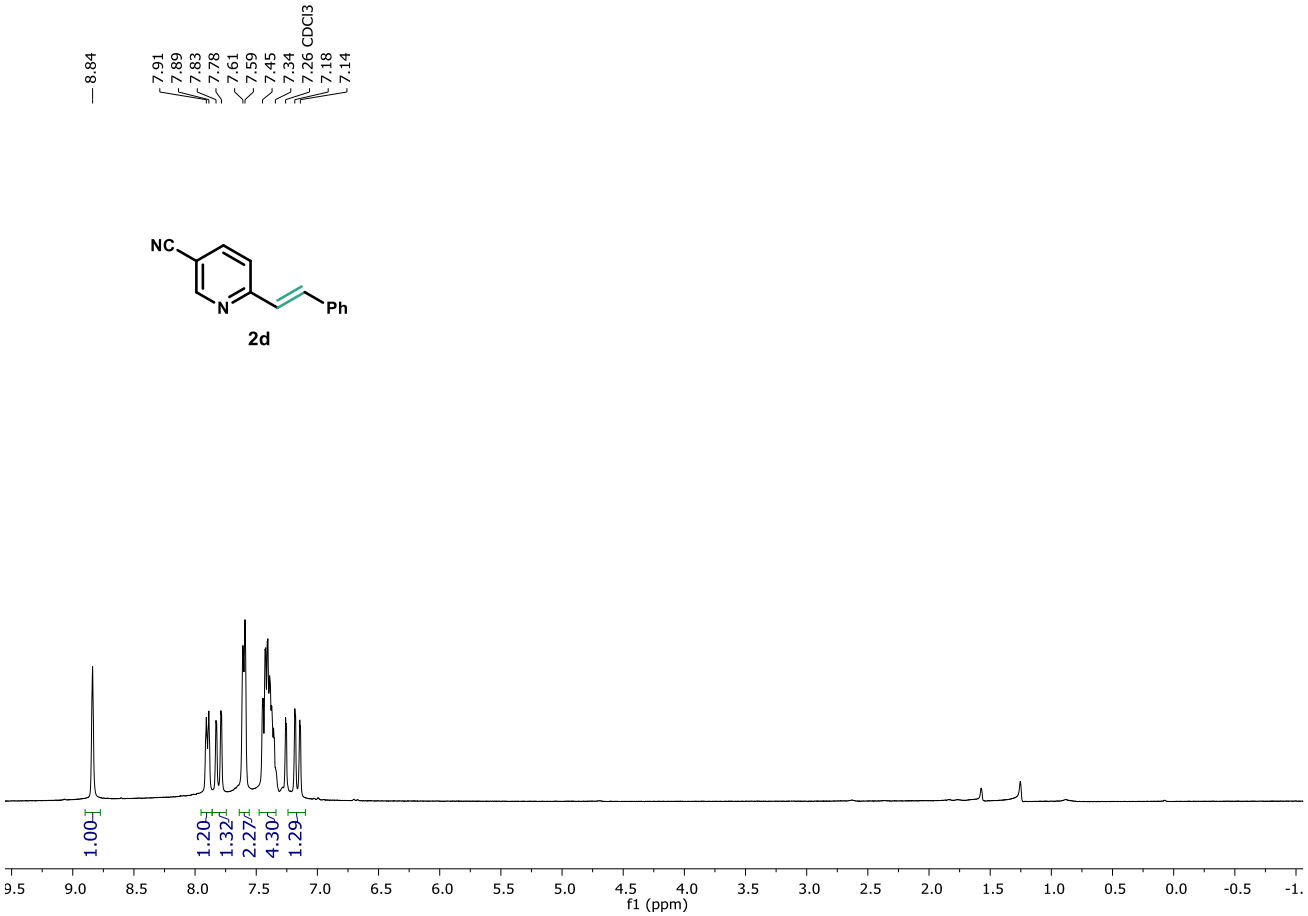
R$_f$: 0.50 (hexanes/EtOAc = 4:1)

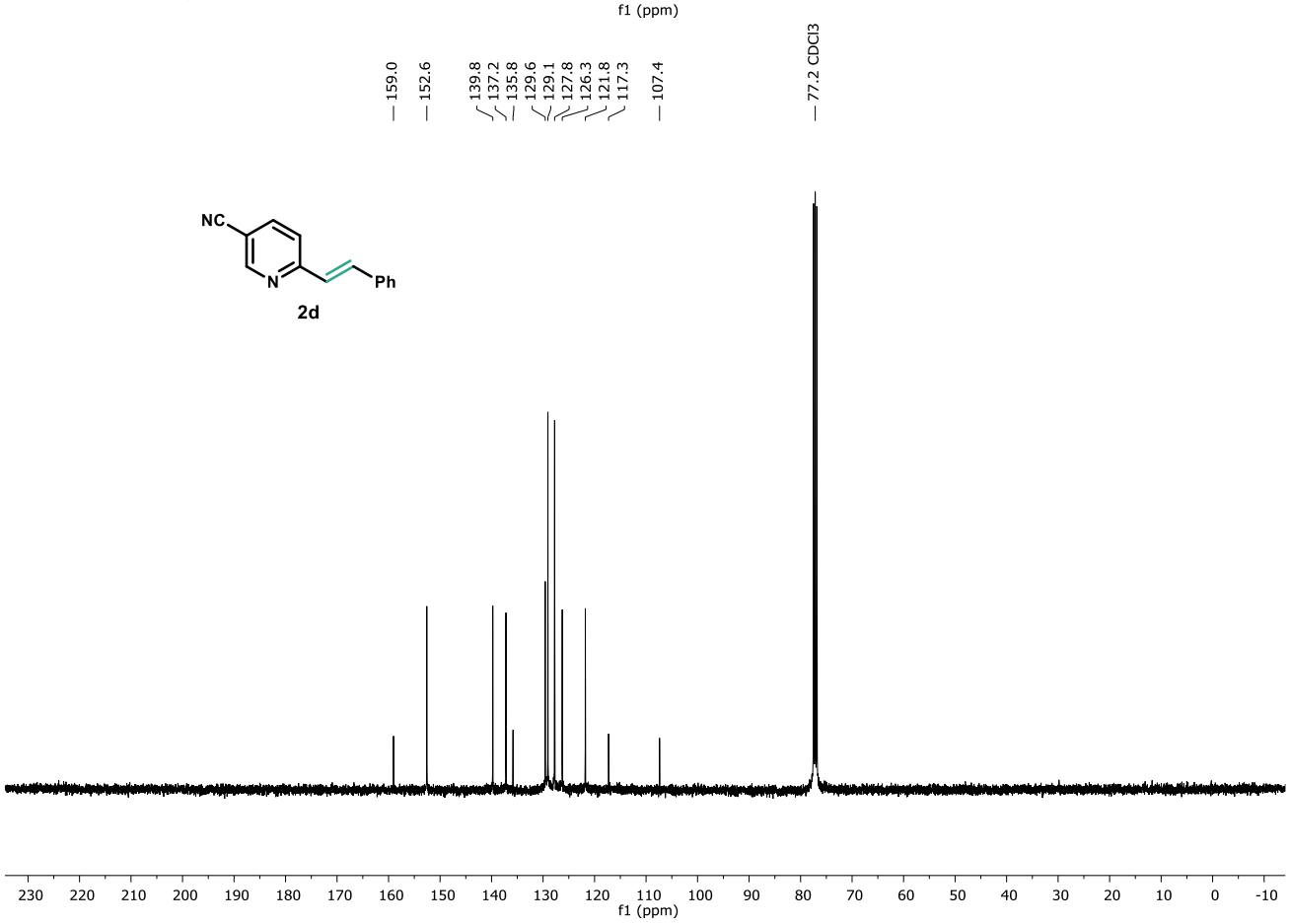
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (s, 1H), 7.91–7.89 (m, 1H), 7.81 (d, *J* = 16.0 Hz, 1H), 7.61 (s, 1H), 7.59 (s, 1H), 7.45–7.34 (m, 4H), 7.16 (d, *J* = 16.0 Hz, 1H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.0, 152.6, 139.8, 137.2, 135.8, 129.6, 129.1, 127.8, 126.3, 121.8, 117.3, 107.4

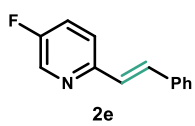
IR (cm^{-1}): 3059, 2228, 1585, 1475, 1380, 1194, 971, 823, 766, 692, 556

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{14}H_{11}N_2^+$: 207.0917; found: 207.0922


8.84
7.91
7.89
7.83
7.78
7.61
7.59
7.45
7.34
7.26 CDCl3
7.18
7.14
NC
N
Ph
2d
1.00
1.20
1.32
2.27
4.30
1.29
f1 (ppm)


159.0
152.6
139.8
137.2
135.8
129.6
129.1
127.8
126.3
121.8
117.3
107.4
77.2 CDCl3
NC
N
Ph
2d
f1 (ppm)

(*E*)-5-fluoro-2-styrylpyridine (2e)



2e

Compound **2e** was prepared from **1e** (40.2 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (6 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 20:1 to 10:1) afforded **2e** (26.3 mg, 66%) as a yellow oil.

R$_f$: 0.25 (hexanes/EtOAc = 10:1)

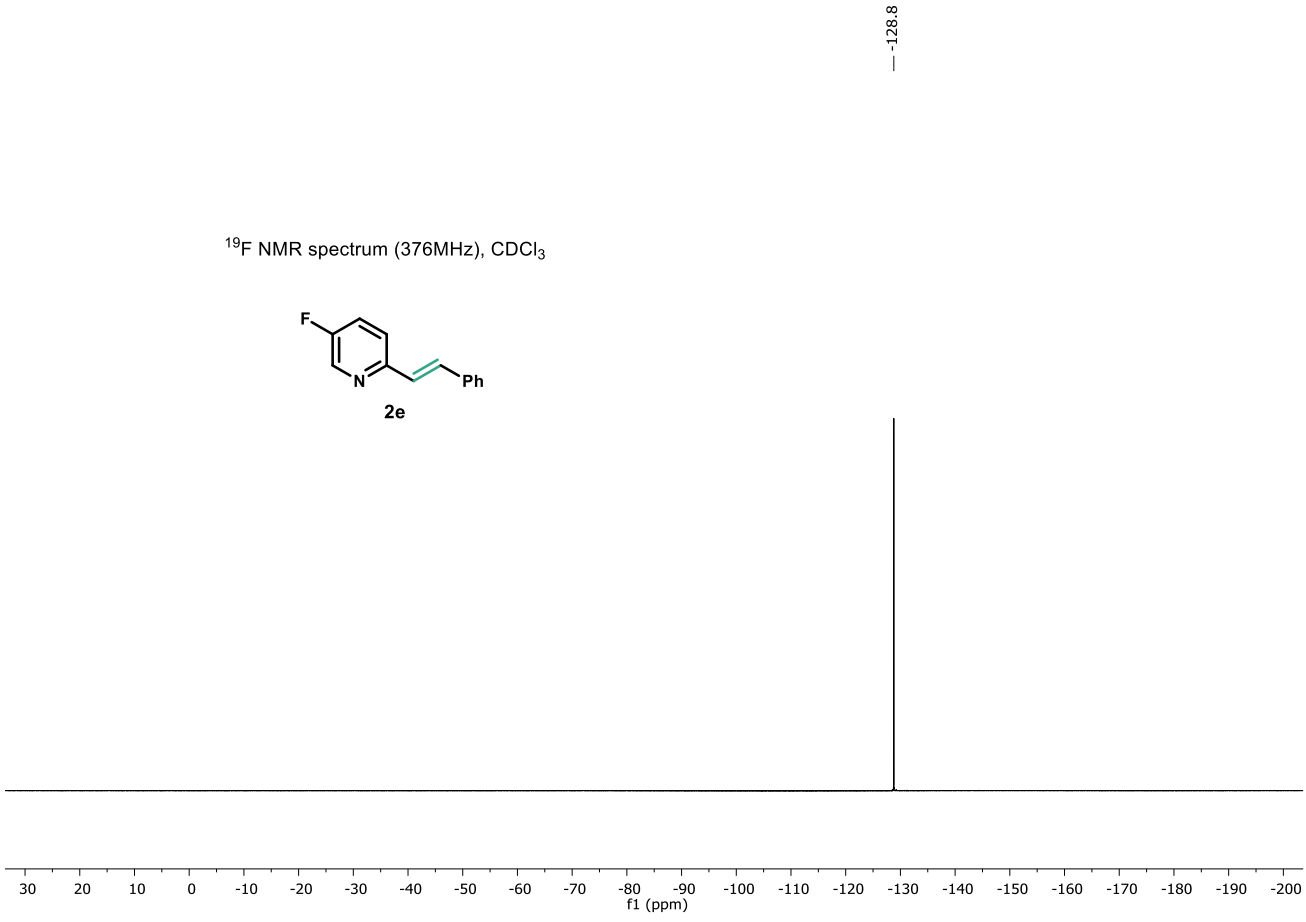
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 7.58–7.52 (m, 3H), 7.40–7.37 (m, 4H), 7.32–7.28 (m, 1H), 7.15 (d, J = 16.1 Hz, 1H)

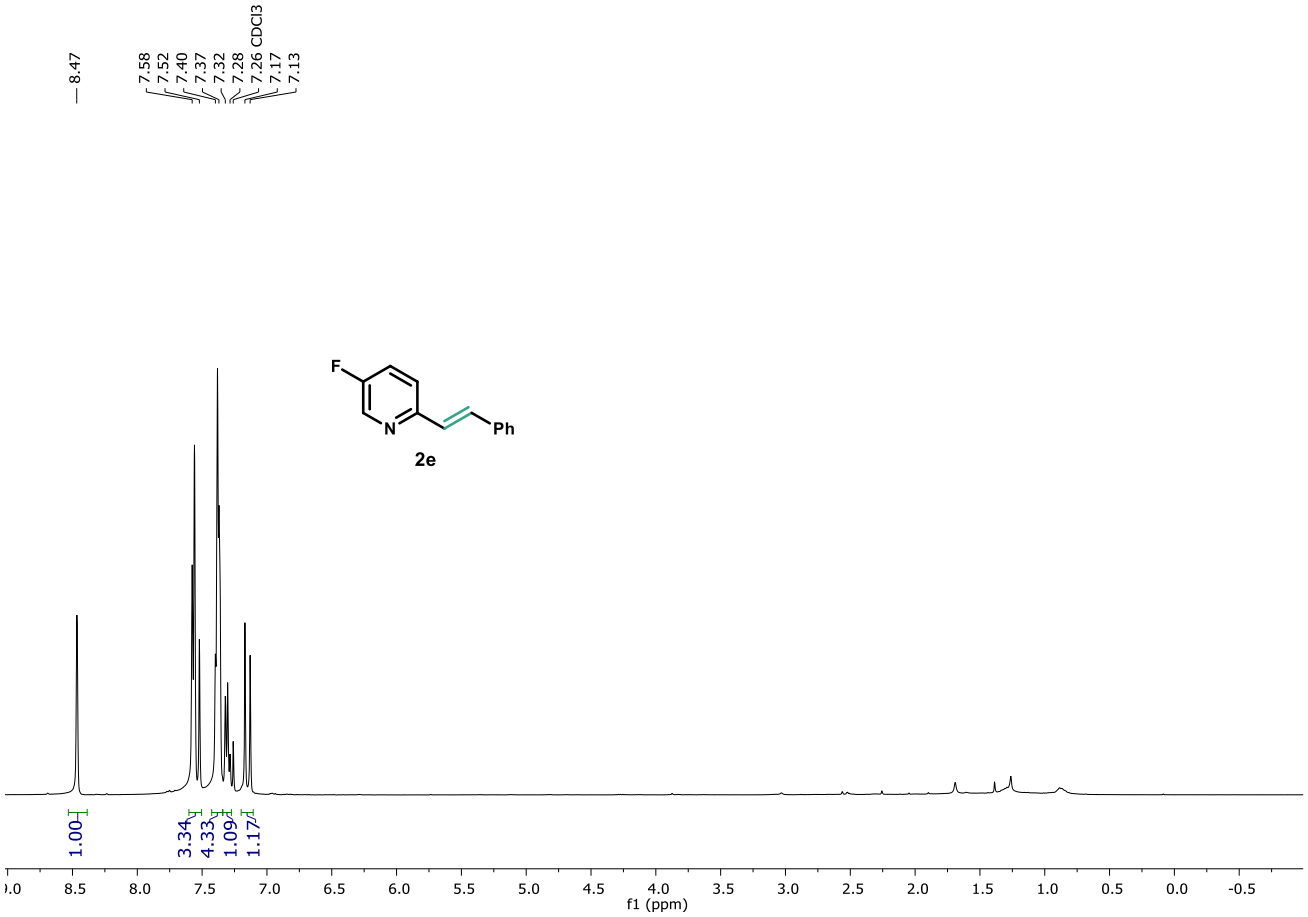
^{13}C NMR (101 MHz, $CDCl_3$): δ 158.5 (d, J = 256.4 Hz), 152.2 (d, $J_{C\text{-}F}$ = 4.2 Hz), 138.0 (d, $J_{C\text{-}F}$ = 23.8 Hz), 136.6, 132.8 (d, $J_{C\text{-}F}$ = 2.5 Hz), 128.9, 128.5, 127.2, 126.8, 123.4 (d, $J_{C\text{-}F}$ = 18.6 Hz), 122.8 (d, $J_{C\text{-}F}$ = 4.2 Hz)

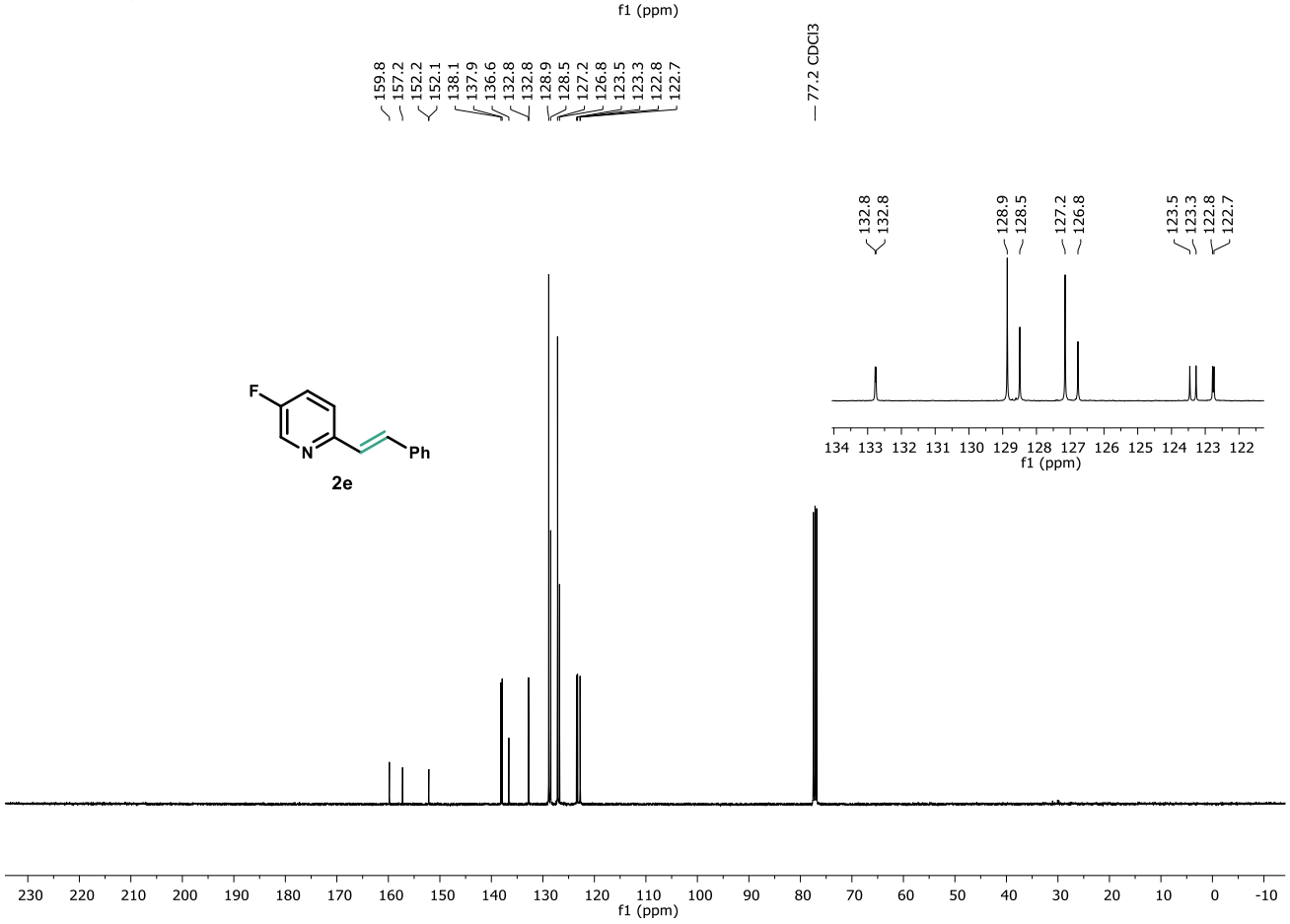
^{19}F NMR (376 MHz, $CDCl_3$): δ –128.8 (t, J = 6.2 Hz)

IR (cm^{-1}): 3030, 2924, 1637, 1576, 1475, 1384, 1223, 970, 909, 822, 759, 730, 688, 531, 506

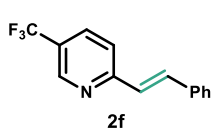
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{13}H_{11}FN^+$: 200.0870; found: 200.0876




8.47
7.58
7.52
7.40
7.37
7.32
7.28
7.26 CDCl3
7.17
7.13
F
N
Ph
2e
1.00
3.34
4.33
1.09
1.17
f1 (ppm)


159.8
157.2
152.2
152.1
138.1
137.9
136.6
132.8
132.8
128.9
128.5
127.2
126.8
123.5
123.3
122.8
122.7
77.2 CDCl3
132.8
132.8
128.9
128.5
127.2
126.8
123.5
123.3
122.8
122.7
F
N
Ph
2e
f1 (ppm)

(*E*)-2-styryl-5-(trifluoromethyl)pyridine (2f)



2f

Compound **2f** was prepared from **1f** (50.2 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (1 hour). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 20:1 to 10:1) afforded **2f** (27.8 mg, 56%) as a white solid. The characterization data match those previously reported in the literature.[4]

R$_f$: 0.50 (hexanes/EtOAc = 7:1)

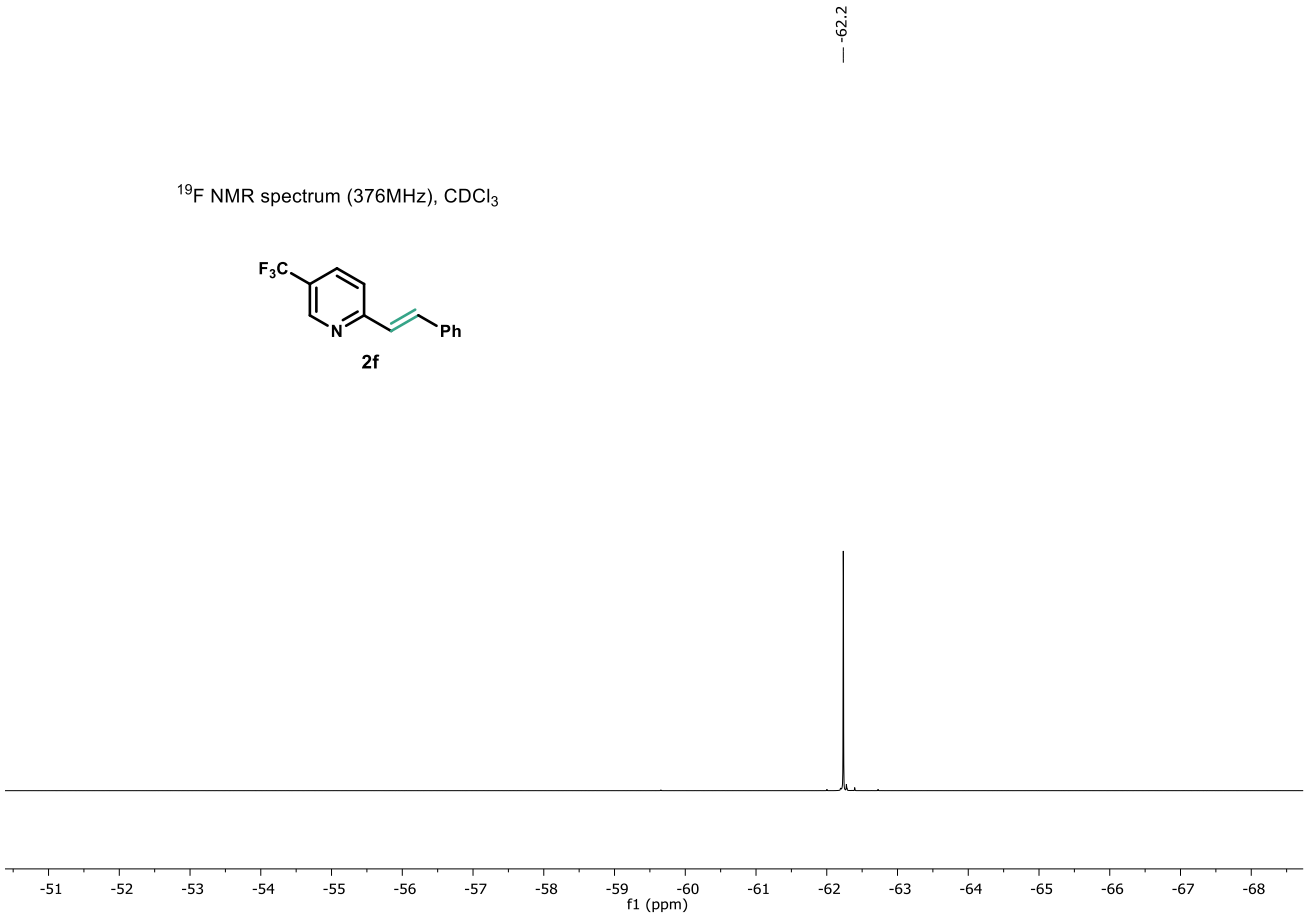
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 16.1 Hz, 1H), 7.61 (s, 1H), 7.59 (s, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.42–7.32 (m, 3H), 7.20 (d, *J* = 16.0 Hz, 1H)

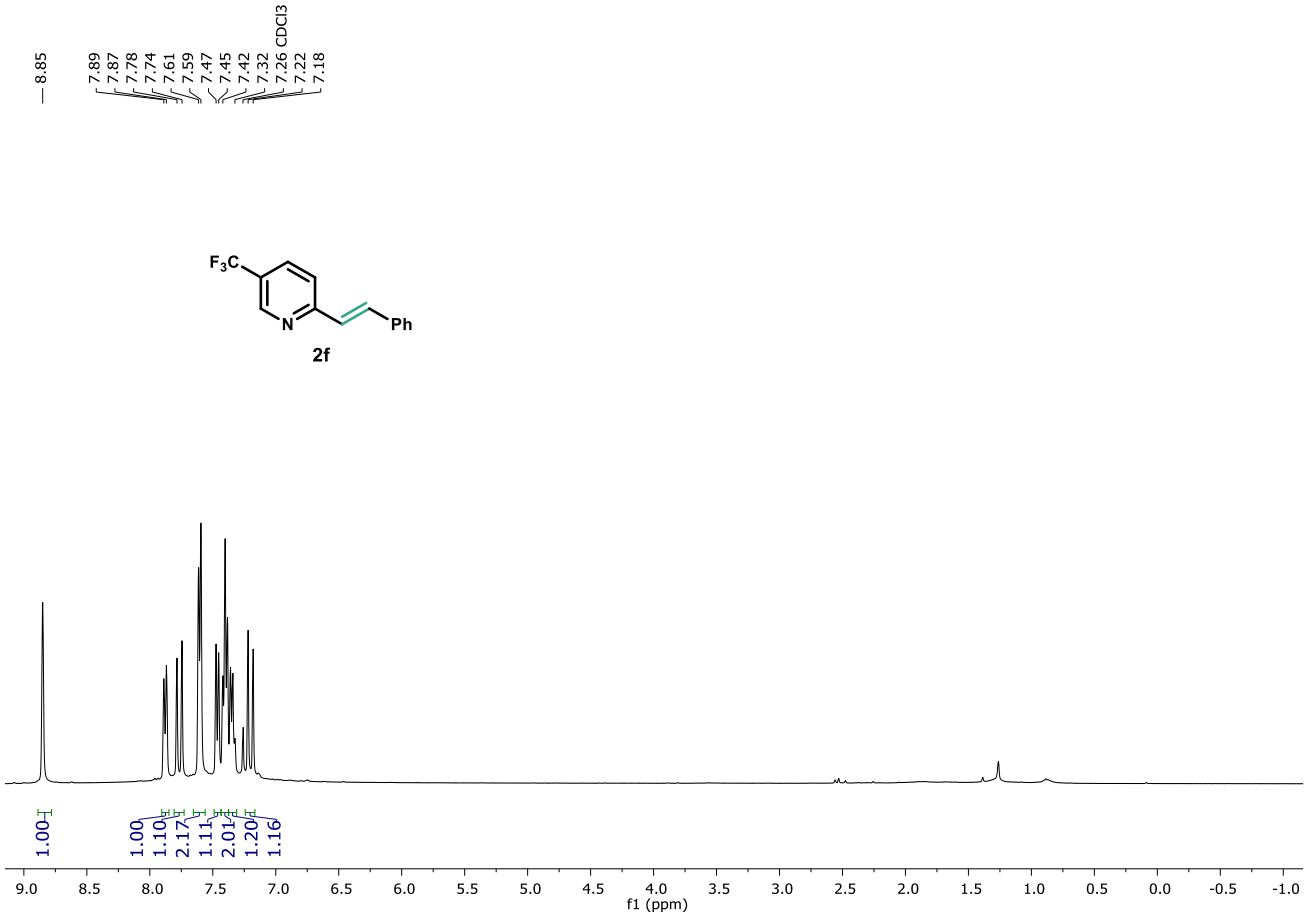
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.1, 146.7 (q, J_{C-F} = 4.1 Hz), 136.2, 135.8, 133.8 (q, J_{C-F} = 3.3 Hz), 129.2, 129.0, 127.6, 126.6, 124.6 (q, J_{C-F} = 32.9 Hz), 123.9 (q, J_{C-F} = 272.7 Hz), 121.5

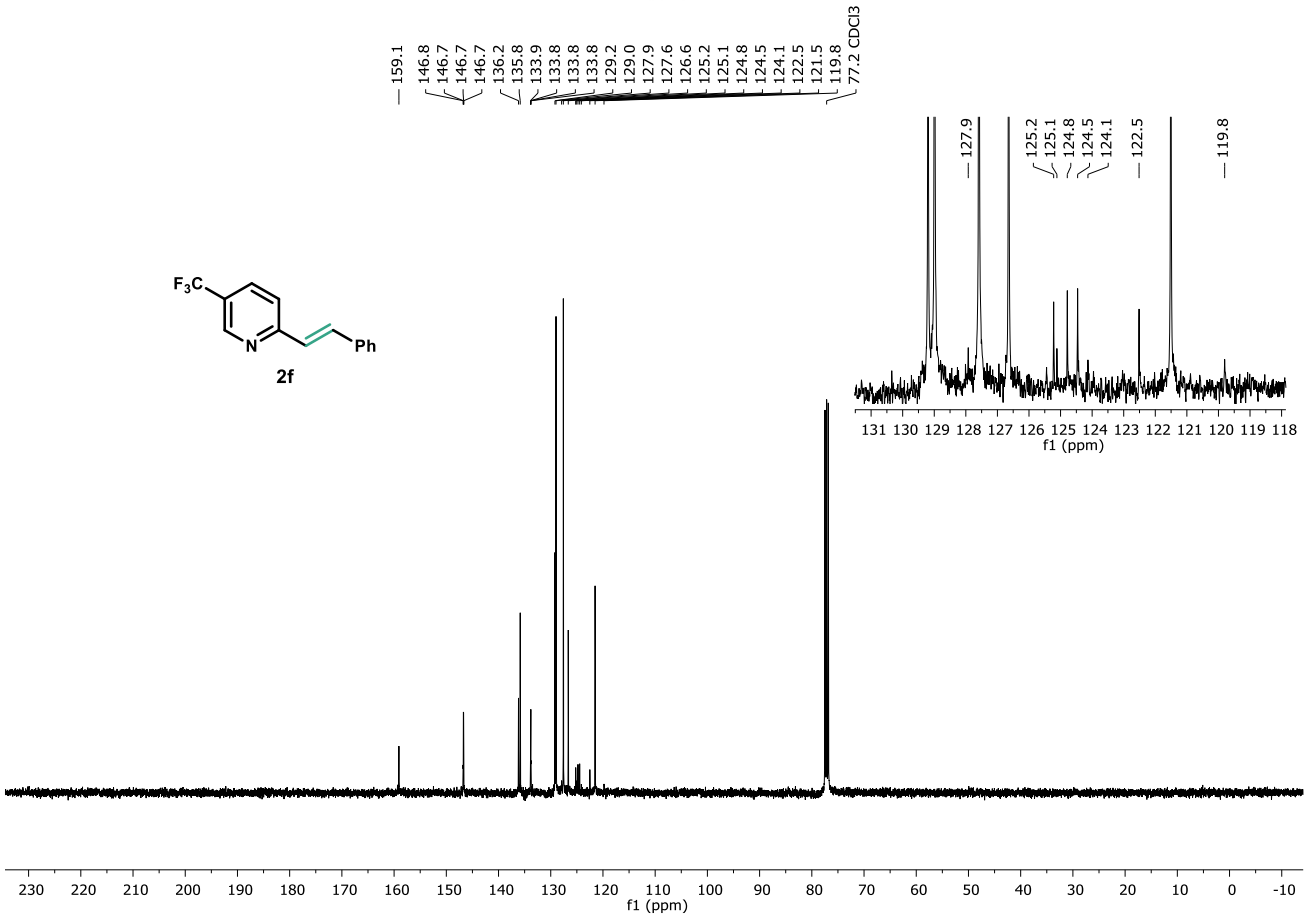
^{19}F NMR (376 MHz, $CDCl_3$): δ –62.2 (s)

IR (cm^{-1}): 3030, 1600, 1328, 1130, 1114, 1081, 1015, 740, 691, 525

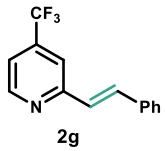
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{14}H_{11}F_3N^+$: 250.0838; found: 250.0844




8.85
7.89
7.87
7.78
7.74
7.61
7.59
7.47
7.45
7.42
7.32
7.26 CDCl3
7.22
7.18
F3C
N
Ph
2f
1.00
1.00
1.10
2.17
1.11
2.01
1.20
1.16
f1 (ppm)


159.1
146.8
146.7
146.7
146.7
136.2
135.8
133.9
133.8
133.8
133.8
129.2
129.0
127.9
127.6
126.6
125.2
125.1
124.8
124.5
124.1
122.5
121.5
119.8
77.2 CDCl3
127.9
125.2
125.1
124.8
124.5
124.1
122.5
119.8
F3C
N
Ph
2f
f1 (ppm)
f1 (ppm)

(*E*)-2-styryl-4-(trifluoromethyl)pyridine (2g)



Compound **2g** was prepared from **1g** (50.2 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (2 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 10:1) afforded **2g** (34.7 mg, 70%) as a white solid. The characterization data match those previously reported in the literature.[5]

R_f: 0.50 (hexanes/EtOAc = 4:1)

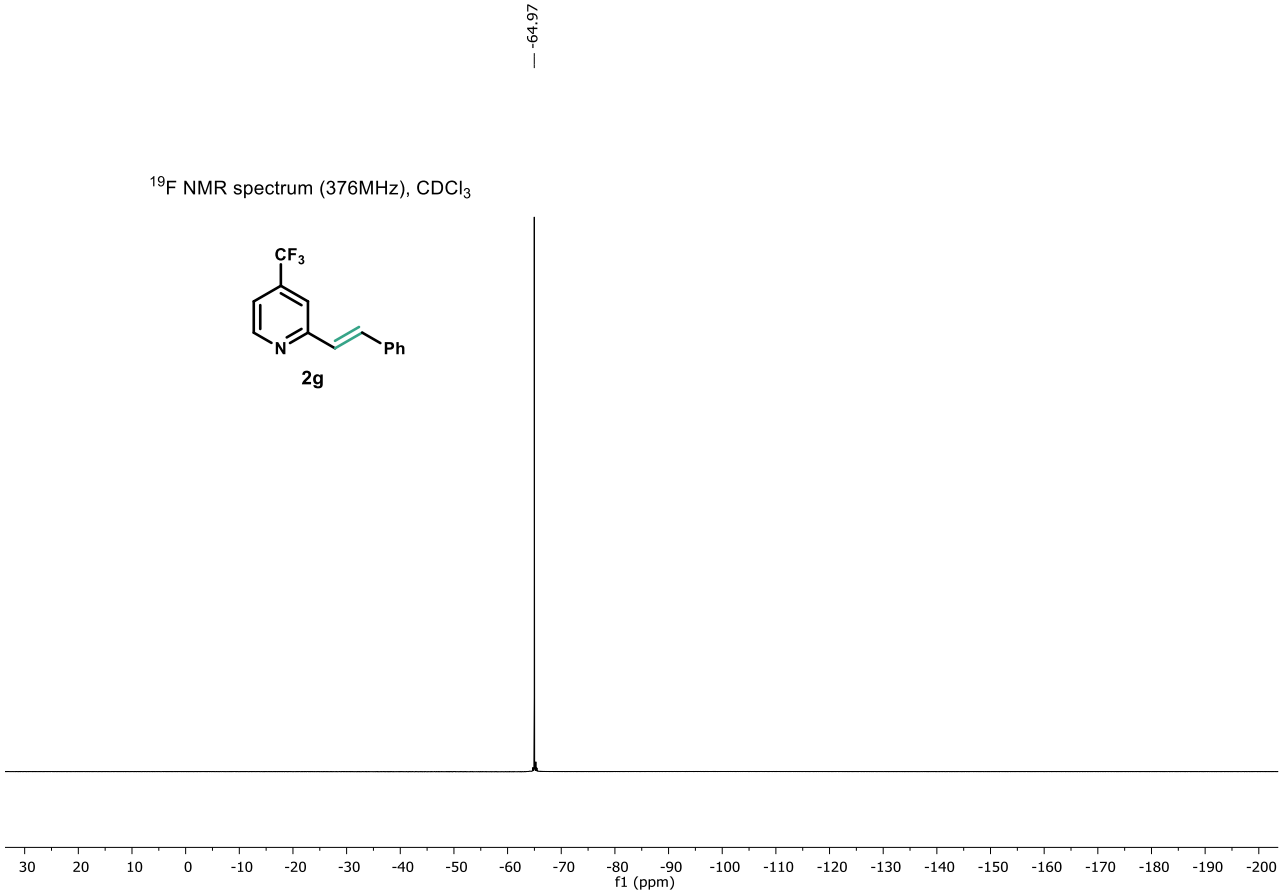
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (d, *J* = 5.0 Hz, 1H), 7.73 (d, *J* = 16.1 Hz, 1H), 7.61–7.58 (m, 3H), 7.42–7.32 (m, 4H), 7.21 (d, *J* = 16.1 Hz, 1H)

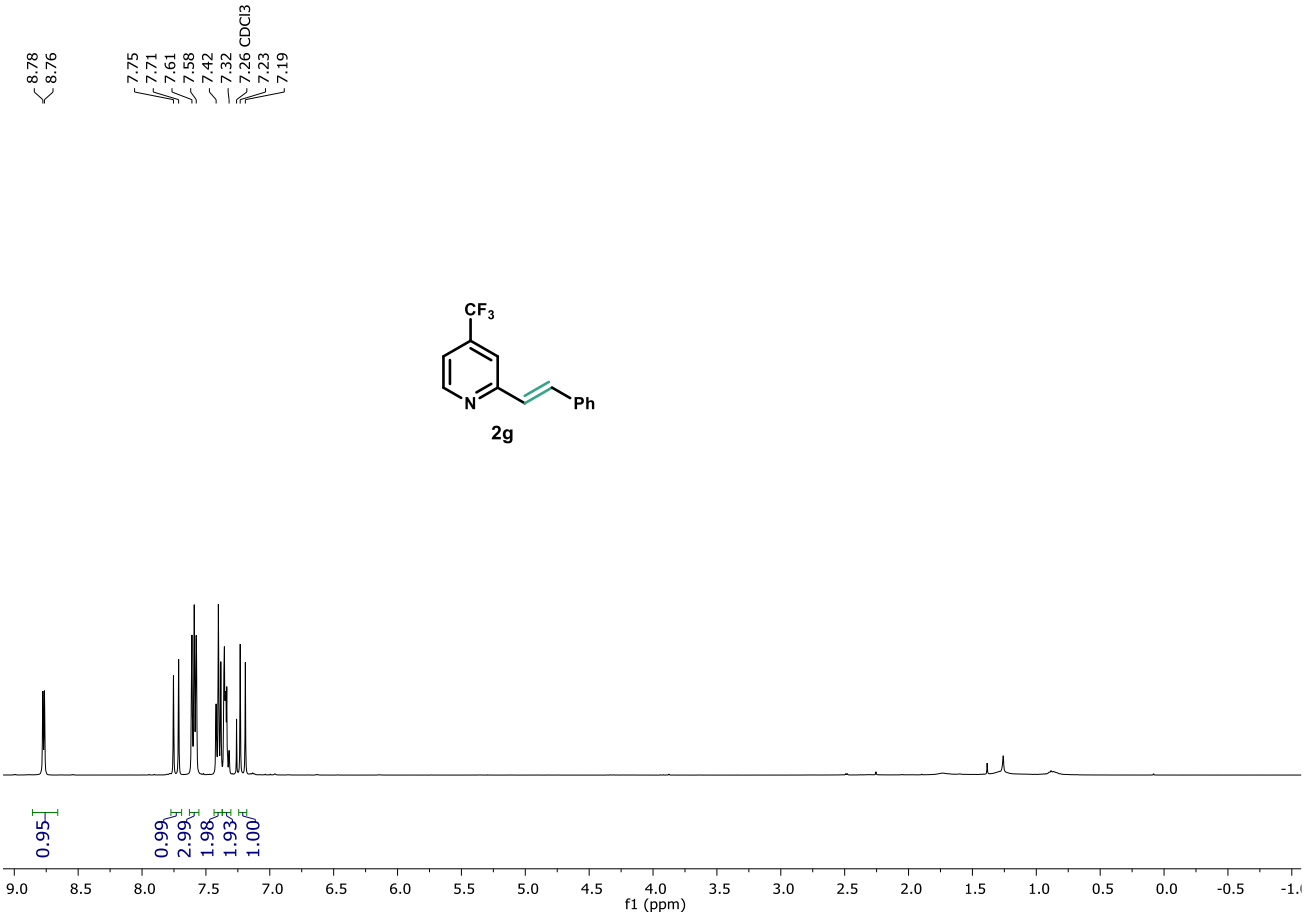
^{13}C NMR (101 MHz, $CDCl_3$): δ 157.2, 150.7, 139.0 (q, J_{C-F} = 33.8 Hz), 136.2, 134.9, 129.1, 129.0, 127.5, 126.8, 123.0 (q, J_{C-F}= 273.1 Hz), 117.5 (q, J_{C-F} = 3.6 Hz), 117.4 (q, J_{C-F} = 3.6 Hz)

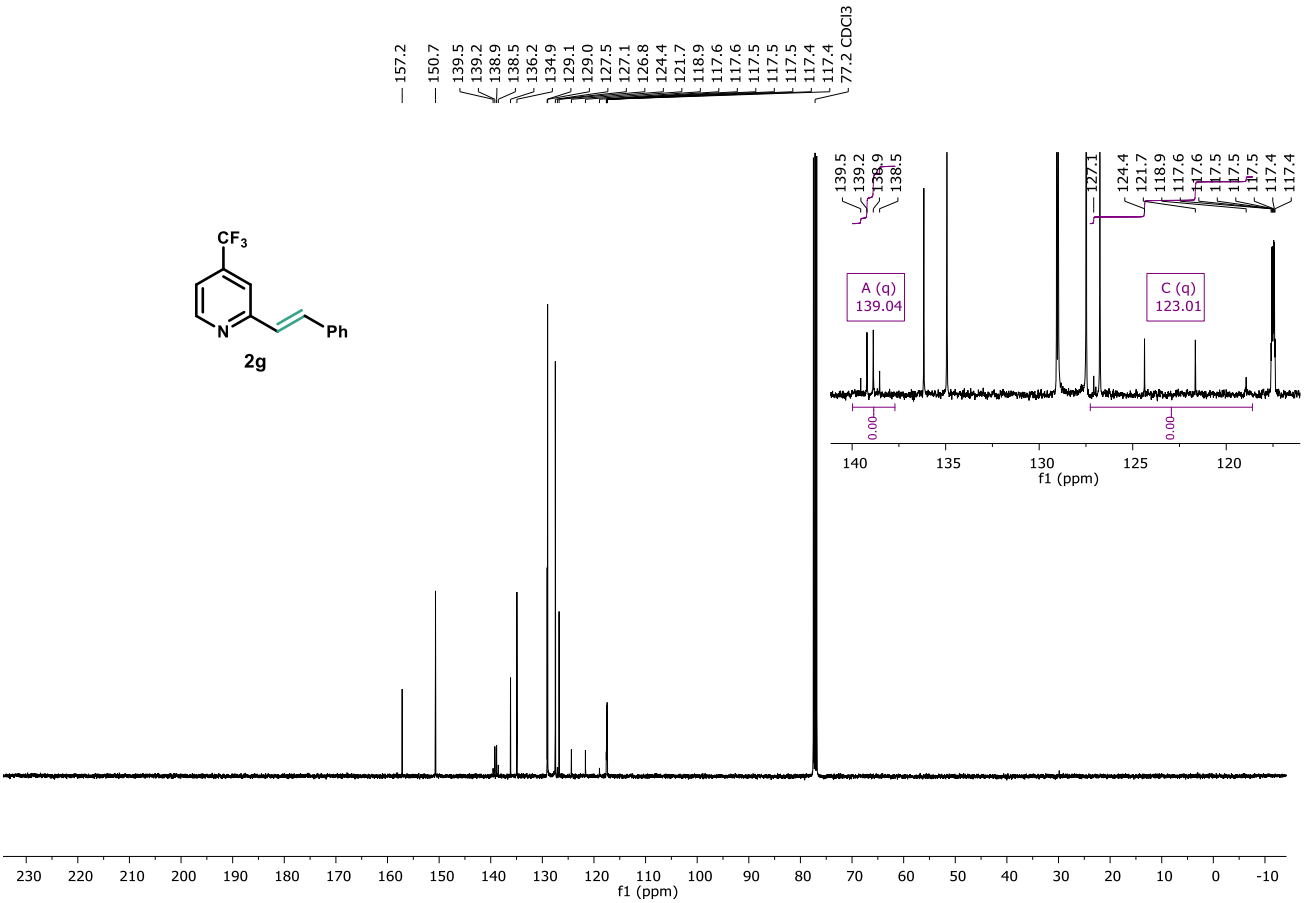
^{19}F NMR (376 MHz, $CDCl_3$) δ –65.0 (s)

IR (cm^{-1}): 3028, 1638, 1565, 1404, 1335, 1168, 1132, 1085, 967, 897, 835, 735, 691, 667, 552

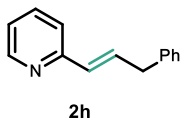
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{14}H_{11}F_3N^+$: 250.0838; found: 250.0844




8.78
8.76
7.75
7.71
7.61
7.58
7.42
7.32
7.26 CDCl3
7.23
7.19
CF3
N
Ph
2g
0.95
0.99
2.99
1.98
1.93
1.00
f1 (ppm)


157.2
150.7
139.5
139.2
138.9
138.5
136.2
134.9
129.1
129.0
127.5
127.1
126.8
124.4
121.7
118.9
117.6
117.6
117.5
117.5
117.4
117.4
77.2 CDCl3
CF3
N
Ph
2g
A (q)
139.04
C (q)
123.01
0.00
0.00
f1 (ppm)

(*E*)-2-(3-phenylprop-1-en-1-yl)pyridine (2h)



2h

Compound **2h** was prepared from known compound **1h**[16] (39.4 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (4.5 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 10:1) afforded **2h** (30.5 mg, 78%) as a yellow oil.

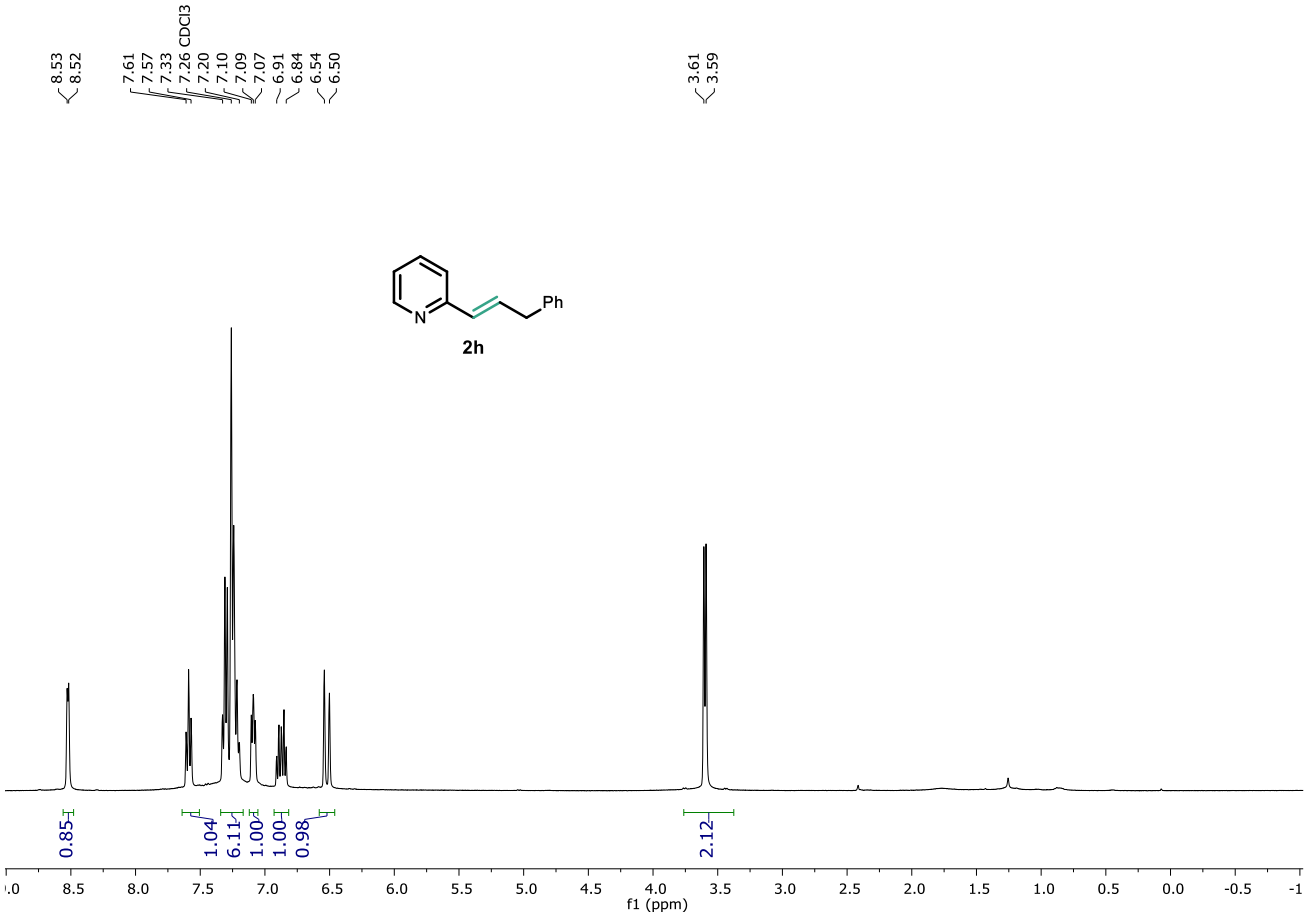
R$_f$: 0.42 (hexanes/EtOAc = 4:1)

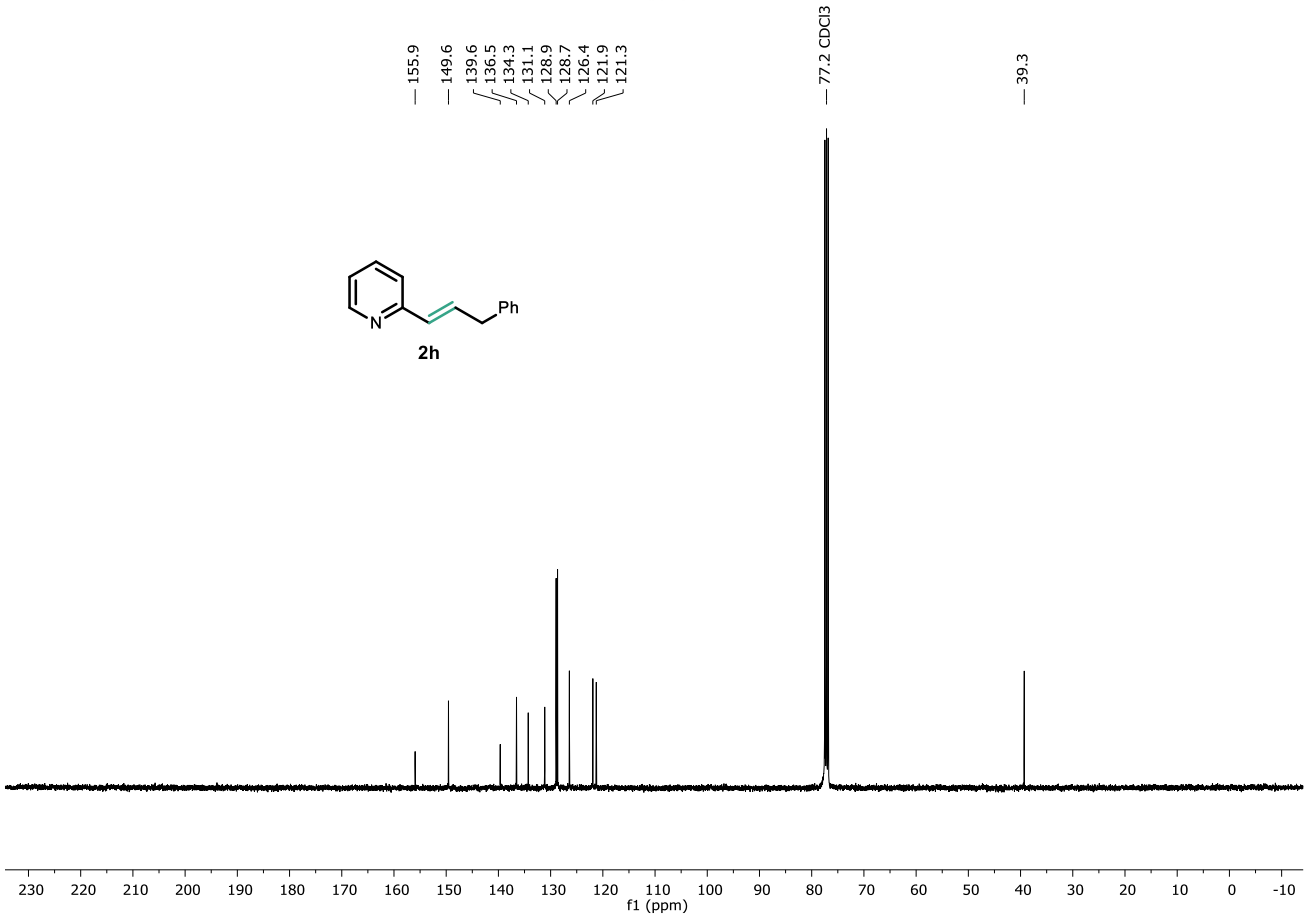
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 4.8 Hz, 1H), 7.61–7.57 (m, 1H), 7.33–7.10 (m, 6H), 7.09 (t, *J* = 6.1 Hz, 1H), 6.91–6.84 (m, 1H), 6.52 (d, *J* = 15.6 Hz, 1H), 3.60 (d, *J* = 6.9 Hz, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.9, 149.6, 139.6, 136.5, 134.3, 131.1, 128.9, 128.7, 126.4, 121.9, 121.3, 39.3

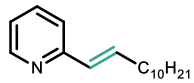
IR (cm^{-1}): 3058, 2923, 1685, 1586, 1470, 1434, 1217, 972, 750, 698, 619

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{14}H_{14}N^+$: 196.1121; found: 196.1121


8.53
8.52
7.61
7.57
7.33
7.26 CDCl3
7.20
7.10
7.09
7.07
6.91
6.84
6.54
6.50
3.61
3.59
Ph
N
2h
0.85
1.04
6.11
1.00
1.00
0.98
2.12
f1 (ppm)


155.9
149.6
139.6
136.5
134.3
131.1
128.9
128.7
126.4
121.9
121.3
77.2 CDCl3
39.3
Ph
N
2h
f1 (ppm)

(*E*)-2-(dodec-1-en-1-yl)pyridine (2i)



2i

Compound **2i** was prepared from **1i** (49.4 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (4.5 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 10:1) afforded **2i** (44.7 mg, 91%) as a colorless oil.

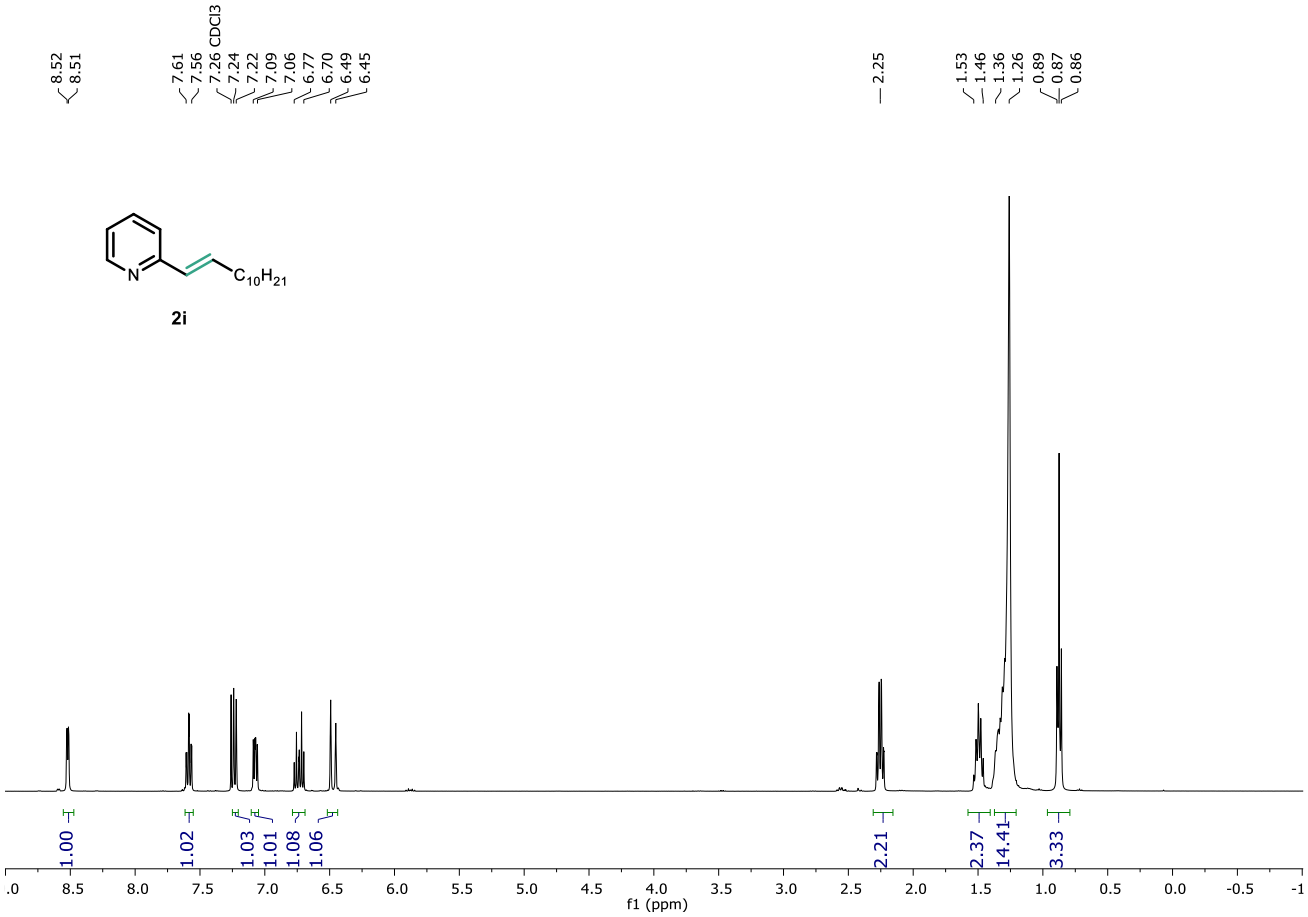
R$_f$: 0.58 (hexanes/EtOAc = 4:1)

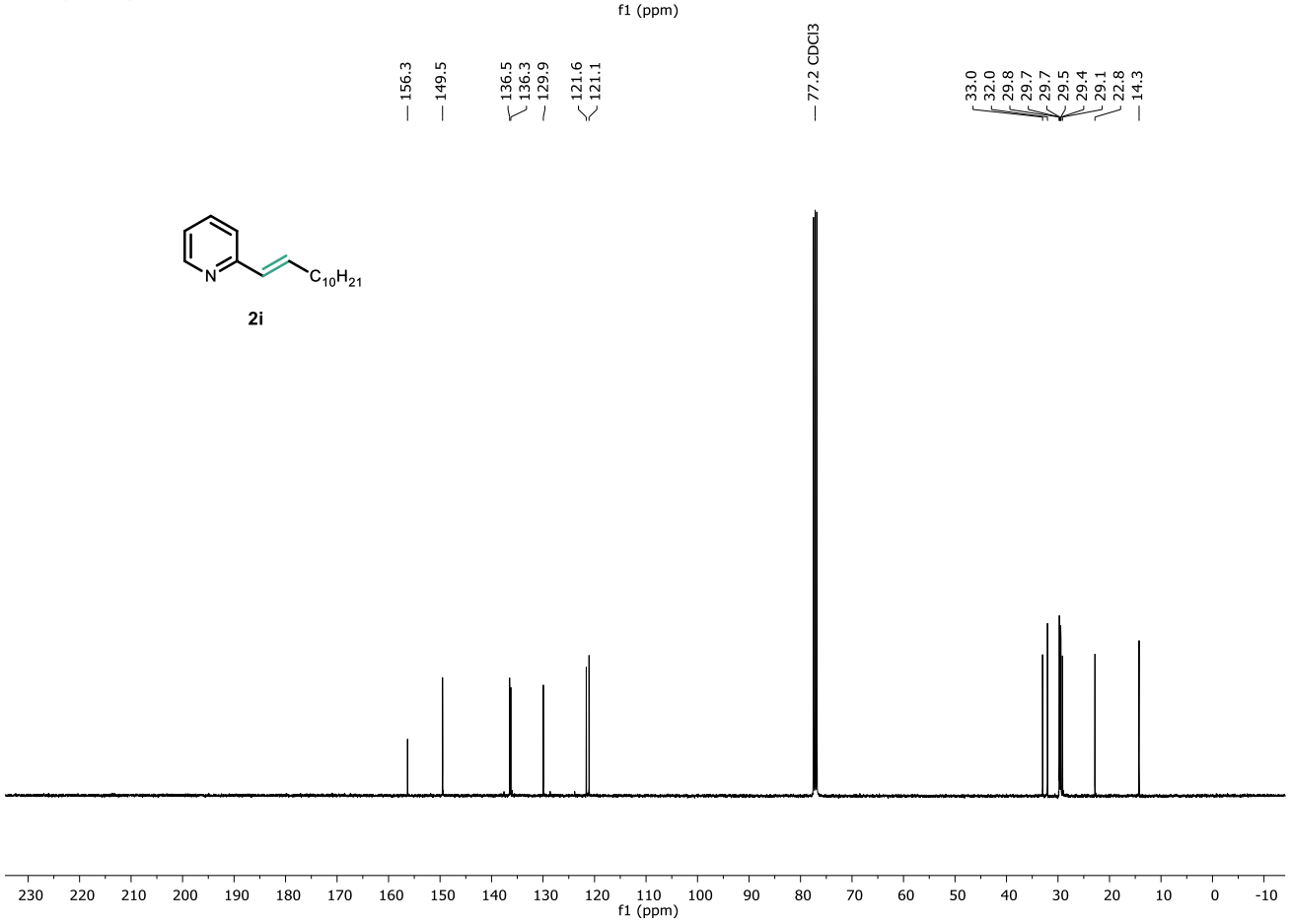
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 4.1 Hz, 1H), 7.61–7.56 (m, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.09–7.06 (m, 1H), 6.77–6.70 (m, 1H), 6.47 (d, *J* = 15.7 Hz, 1H), 2.25 (dq, *J* = 7.2, 1.5 Hz, 2H), 1.53–1.46 (m, 2H), 1.36–1.26 (m, 14H), 0.87 (t, *J* = 6.8 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.3, 149.5, 136.5, 136.3, 129.9, 121.6, 121.1, 33.0, 32.0, 29.8, 29.7, 29.7, 29.5, 29.4, 29.1, 22.8, 14.3

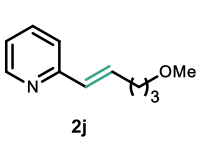
IR (cm^{-1}): 2922, 2852, 1585, 1468, 1430, 969, 742

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{17}H_{28}N^+$: 246.2216; found: 246.2222


8.52
8.51
7.61
7.56
7.26 CDCl3
7.24
7.22
7.09
7.06
6.77
6.70
6.49
6.45
2.25
1.53
1.46
1.36
1.26
0.89
0.87
0.86
2i
1.00
1.02
1.03
1.01
1.08
1.06
2.21
2.37
14.41
3.33
f1 (ppm)


156.3
149.5
136.5
136.3
129.9
121.6
121.1
77.2 CDCl3
33.0
32.0
29.8
29.7
29.7
29.5
29.4
29.1
22.8
14.3
2i
f1 (ppm)

(*E*)-2-(5-methoxypent-1-en-1-yl)pyridine (2j)



2j

Compound **2j** was prepared from **1j** (35.8 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (12 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 5:1 to 3:1) afforded **2j** (24.0 mg, 68%) as a colorless oil.

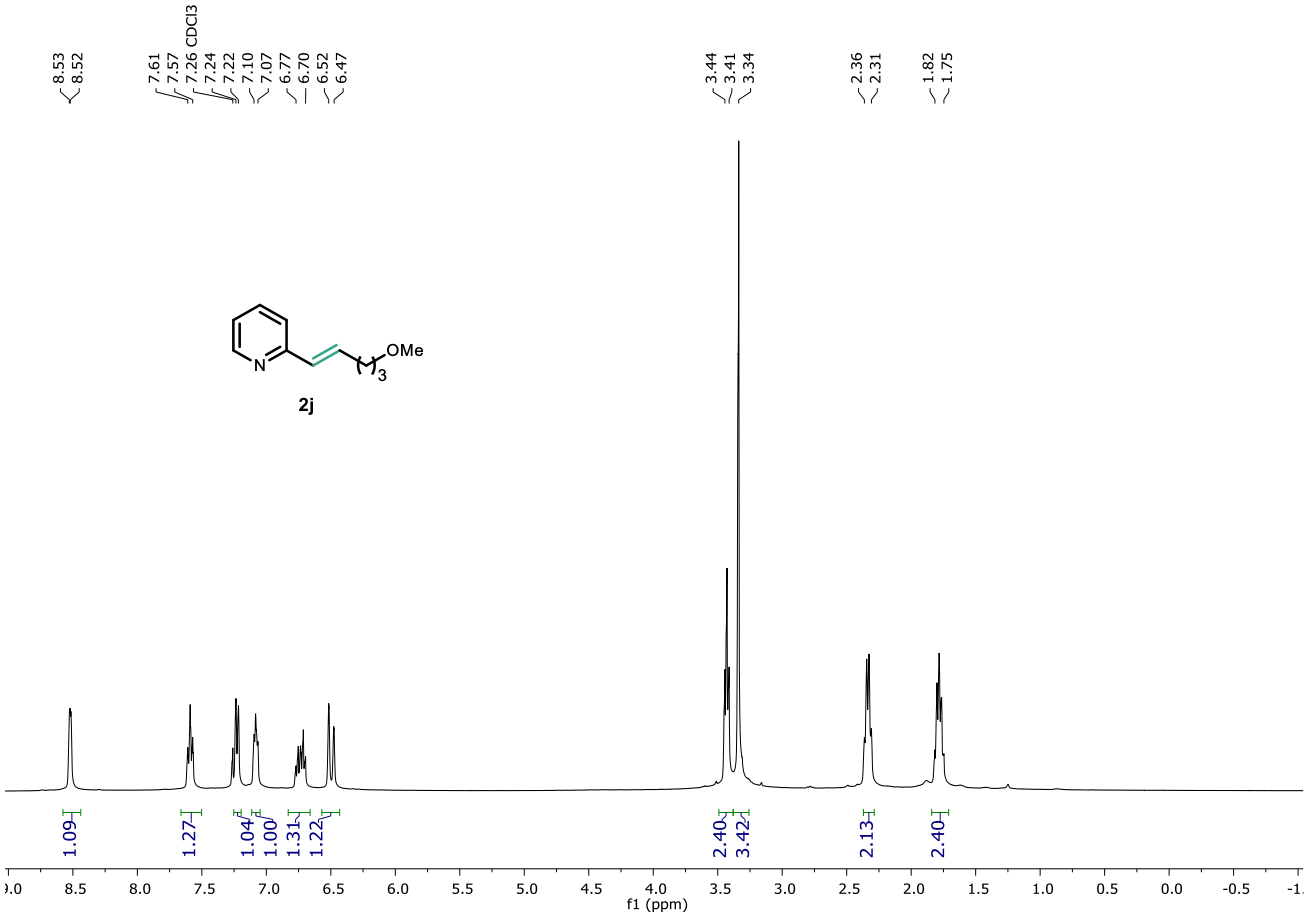
R$_f$: 0.39 (hexanes/EtOAc = 1:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 3.0 Hz, 1H), 7.61–7.57 (m, 1H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.10–7.07 (m, 1H), 6.77–6.70 (m, 1H), 6.50 (d, *J* = 15.6, 1H), 3.44–3.41 (m, 2H), 3.34 (s, 3H), 2.36–2.31 (m, 2H), 1.82–1.75 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.1, 149.5, 136.5, 135.2, 130.4, 121.7, 121.2, 72.2, 58.7, 29.5, 29.1

IR (cm^{-1}): 2925, 2867, 1585, 1469, 1430, 1116, 970, 746

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{11}H_{16}NO^+$: 178.1226; found: 178.1232


8.53
8.52
7.61
7.57
7.26 CDCl3
7.24
7.22
7.10
7.07
6.77
6.70
6.52
6.47
3.44
3.41
3.34
2.36
2.31
1.82
1.75
OMe
3
2j
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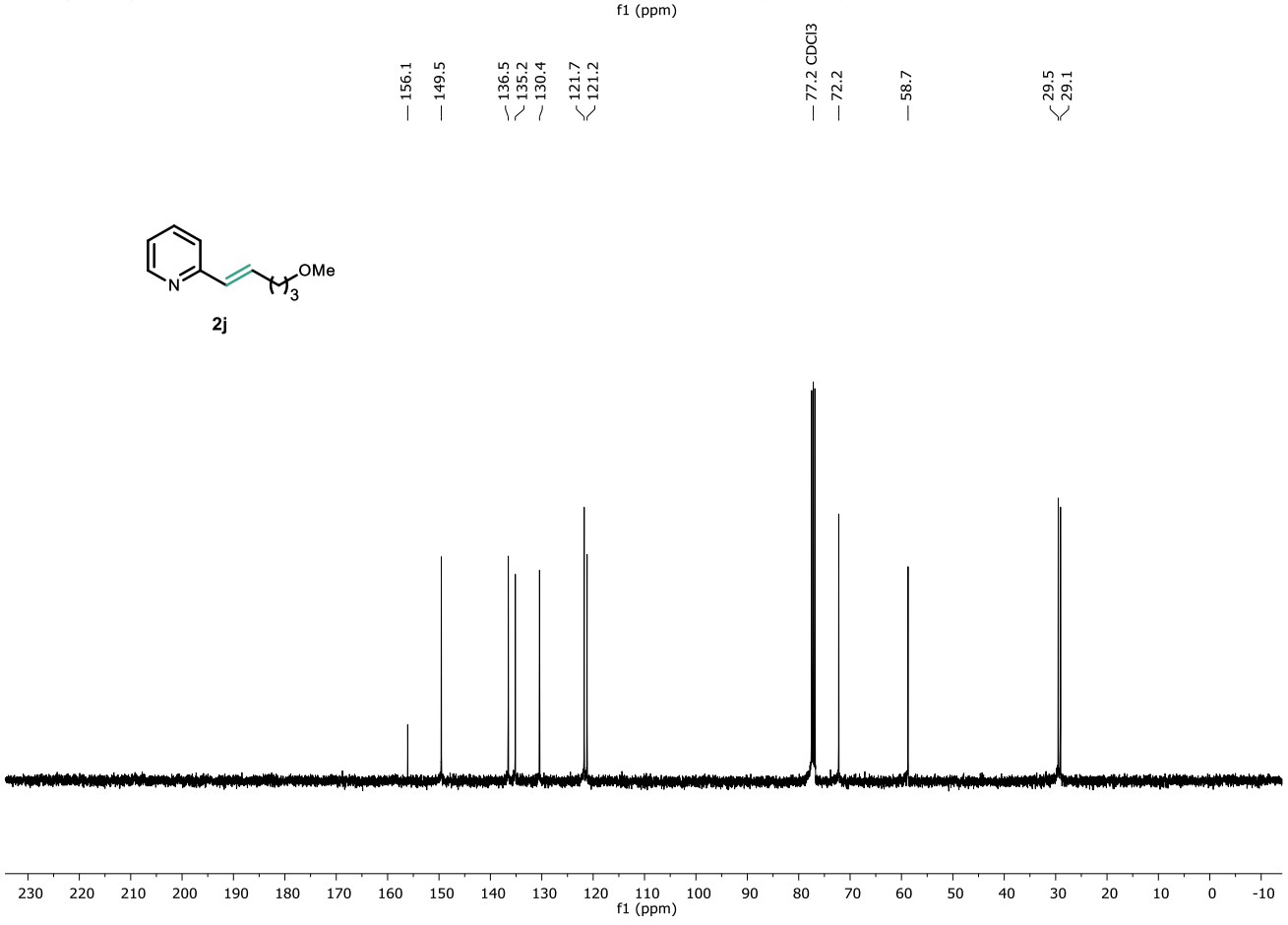
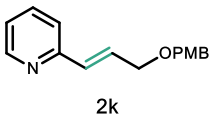
1.04
1.00
1.31
1.22
2.40
3.42
2.13
2.40
f1 (ppm)


156.1
149.5
136.5
135.2
130.4
121.7
121.2
77.2 CDCl3
72.2
58.7
29.5
29.1
OMe
3
2j
f1 (ppm)

(*E*)-2-(3-((4-methoxybenzyl)oxy)prop-1-en-1-yl)pyridine (2k)



2k

Compound **2k** was prepared from **1k** (51.4 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (12 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 10:1) afforded **2k** (21.2 mg, 42%) as a yellow oil.

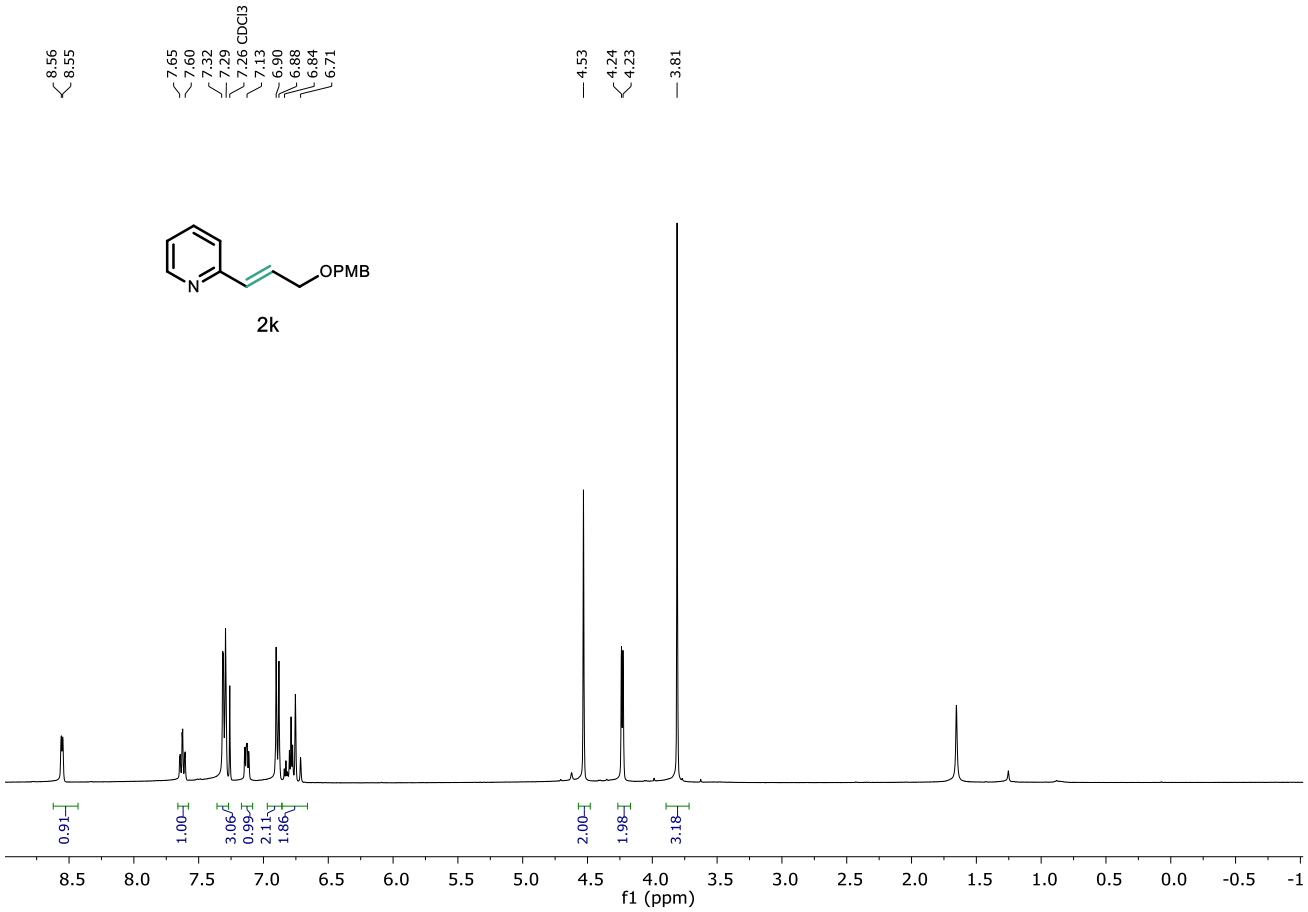
R$_f$: 0.42 (hexanes/EtOAc = 2:1)

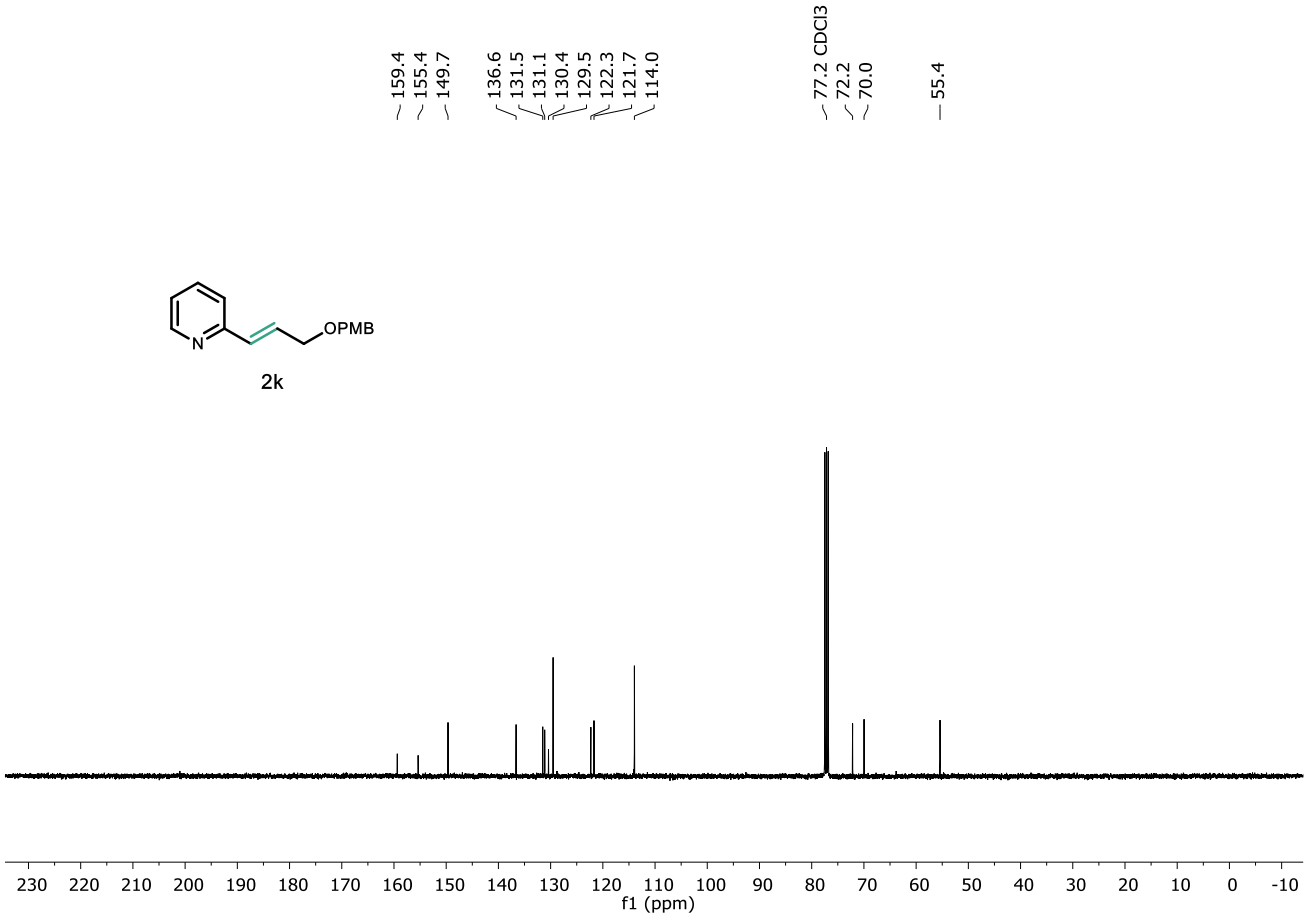
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 3.9 Hz, 1H), 7.65–7.60 (m, 1H), 7.32–7.29 (m, 3H), 7.13 (dd, *J* = 7.4, 4.9 Hz, 1H), 6.89 (d, *J* = 8.6 Hz, 2H), 6.84–6.71 (m, 2H), 4.53 (s, 2H), 4.23 (d, *J* = 4.7 Hz, 2H), 3.81 (s, 3H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.4, 155.4, 149.7, 136.6, 131.5, 131.1, 130.4, 129.5, 122.3, 121.7, 114.0, 72.2, 70.0, 55.4

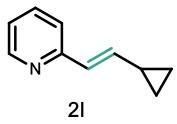
IR (cm^{-1}): 3002, 2836, 1612, 1585, 1512, 1245, 1173, 1033, 972, 820, 754, 542

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{16}H_{18}NO_2^+$: 256.1332; found: 256.1338


8.56
8.55
7.65
7.60
7.32
7.29
7.26 CDCl3
7.13
6.90
6.88
6.84
6.71
4.53
4.24
4.23
3.81
OPMB
2k
0.91
1.00
3.06
0.99
2.11
1.86
2.00
1.98
3.18
f1 (ppm)


159.4
155.4
149.7
136.6
131.5
131.1
130.4
129.5
122.3
121.7
114.0
77.2 CDCl3
72.2
70.0
55.4
OPMB
2k
f1 (ppm)

(*E*)-2-(2-cyclopropylvinyl)pyridine (2l)



2l

Compound **2l** was prepared from **1l** (29.4 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (12 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 10:1) afforded **2l** (24.6 mg, 85%) as a yellow oil.

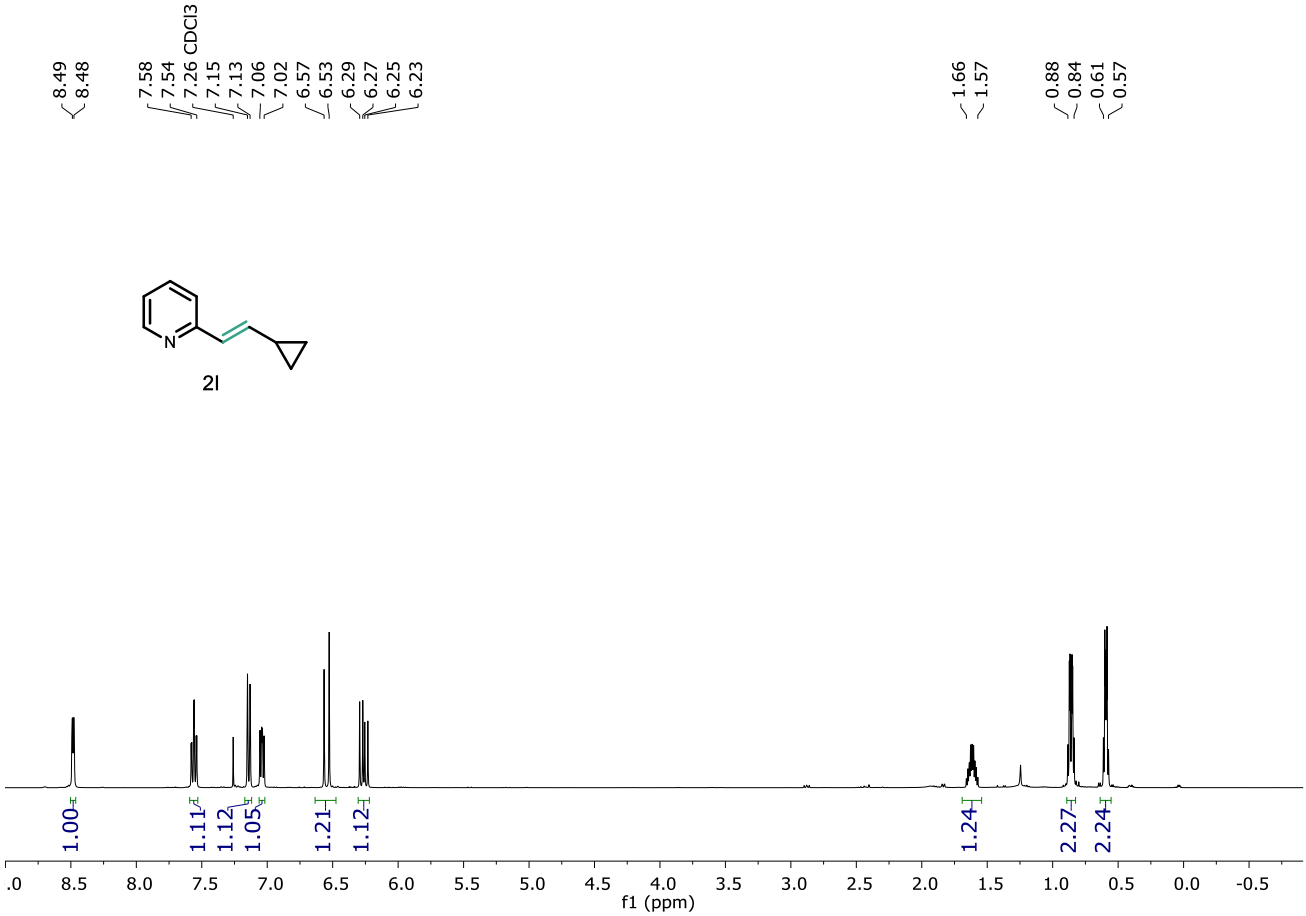
R$_f$: 0.48 (hexanes/EtOAc = 2:1)

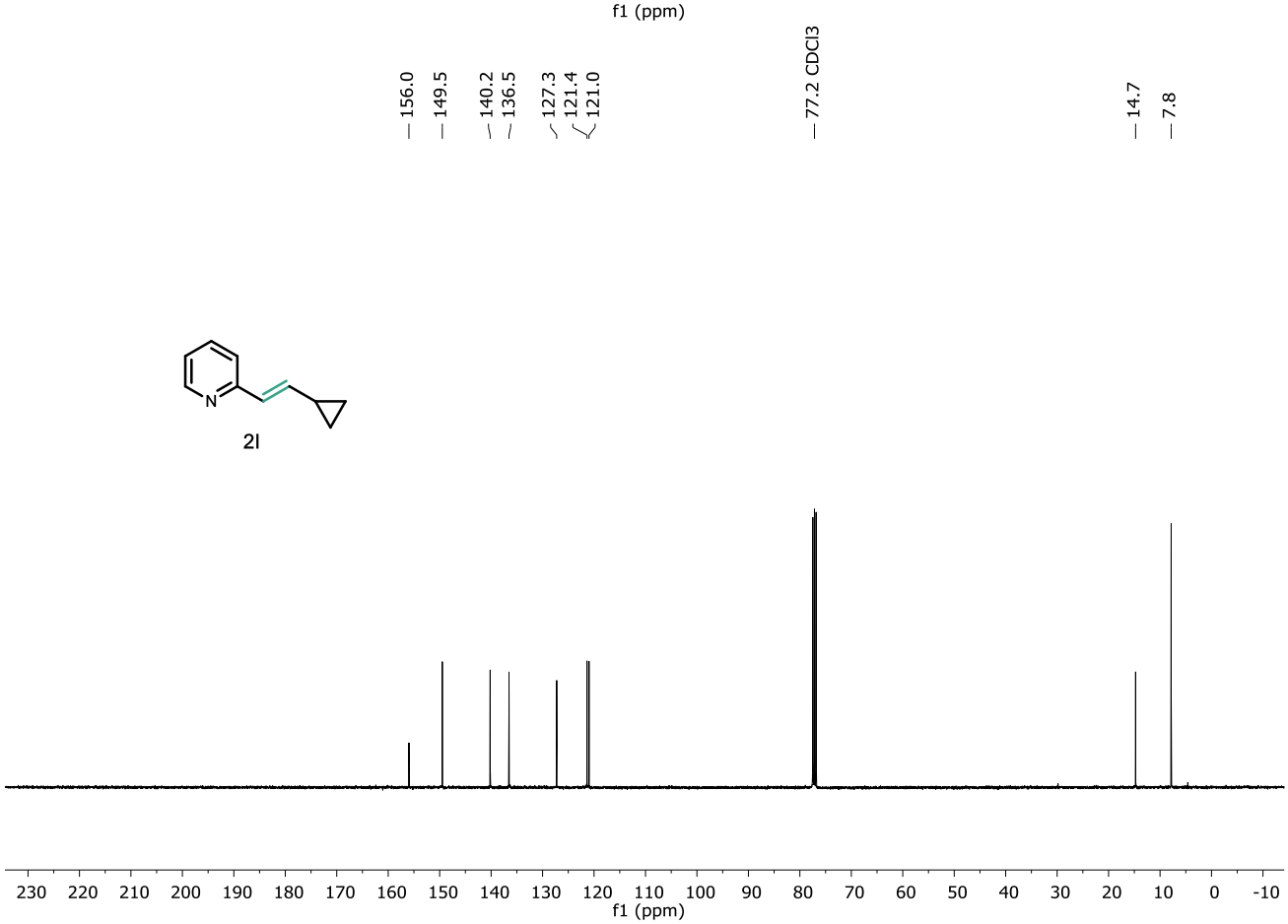
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 4.8 Hz, 1H), 7.58–7.54 (m, 1H), 7.14 (d, *J* = 7.9 Hz, 1H), 7.06–7.02 (m, 1H), 6.55 (d, *J* = 15.5 Hz, 1H), 6.26 (dd, *J* = 15.5, 9.5 Hz, 1H), 1.66–1.57 (m, 1H), 0.88–0.84 (m, 2H), 0.61–0.57 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.0, 149.5, 140.2, 136.5, 127.3, 121.4, 121.0, 14.7, 7.8

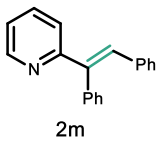
IR (cm^{-1}): 2923, 2851, 1734, 1464, 1377, 743

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{10}H_{12}N^+$: 146.0964; found:146.0970


8.49
8.48
7.58
7.54
7.26 CDCl3
7.15
7.13
7.06
7.02
6.57
6.53
6.29
6.27
6.25
6.23
1.66
1.57
0.88
0.84
0.61
0.57
2l
1.00
1.11
1.12
1.05
1.21
1.12
1.24
2.27
2.24
f1 (ppm)


156.0
149.5
140.2
136.5
127.3
121.4
121.0
77.2 CDCl3
14.7
7.8
2l
f1 (ppm)

2-(1,2-diphenylvinyl)pyridine (2m)



2m

Compound **2m** was prepared from known compound **1m**[10] (51.8 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** with 2.1 equiv $Zn(TMP)_2$ (52 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 10:1) afforded **2m-*E*** (33.4 mg, 65%) as a colorless oil and **2m-*Z*** (7.6 mg, 15%) as a yellow oil. (*E*/*Z* = 4:1 as shown in ^{1}H NMR) The characterization data match those previously reported in the literature.[6] (Note: Batches of laboratory prepared $Zn(TMP)_2$[17] gave a slightly different *E*/*Z* ratio.)

2m-*E* (major) **R$_f$**: 0.55 (hexanes/EtOAc = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, *J* = 4.4 Hz, 1H), 7.85 (s, 1H), 7.57–7.53 (m, 1H), 7.44–7.36 (m, 3H), 7.28–7.24 (m, 2H), 7.18–7.11 (m, 4H), 7.08–7.05 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 1H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 159.0, 149.3, 140.5, 139.3, 136.9, 136.5, 131.1, 130.4, 130.2, 129.2, 128.1, 127.8, 127.4, 122.6, 122.1

IR (cm^{-1}): 3056, 1582, 1463, 1444, 1428, 1152, 1072, 1029, 954, 784, 742, 589, 517

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{19}H_{16}N^+$: 258.1277; found: 258.1283

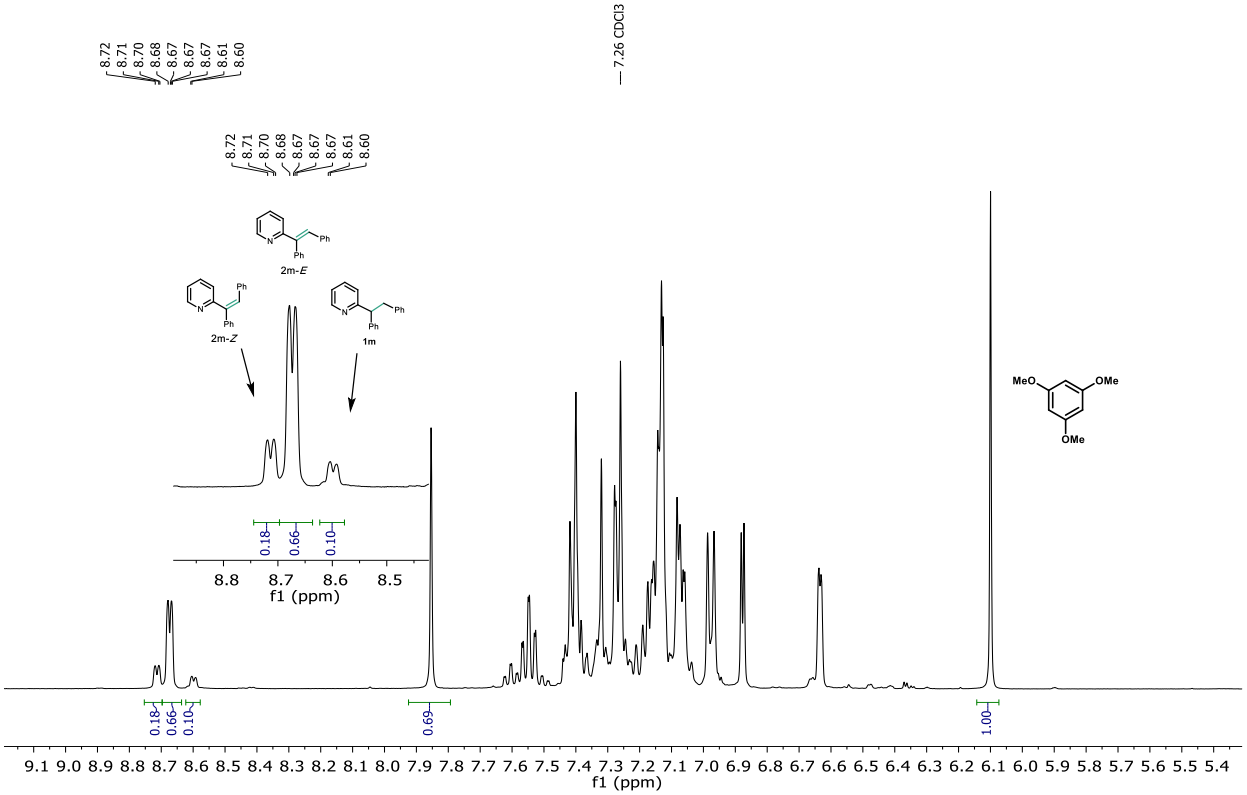
2m-*Z* (minor) **R$_f$**: 0.50 (hexanes/EtOAc = 4:1)

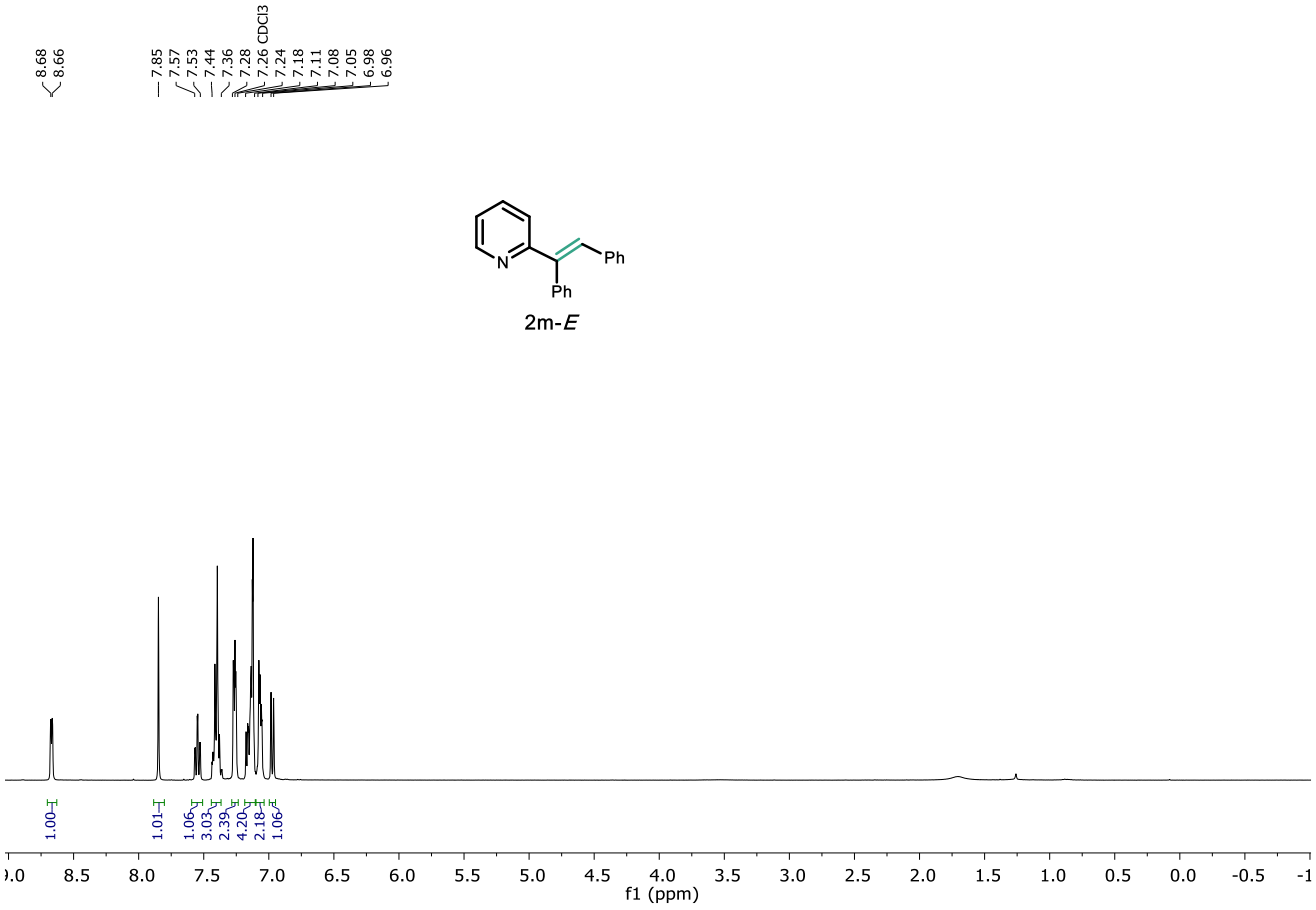
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.8 Hz, 1H), 7.60 (td, *J* = 7.7, 1.7 Hz, 1H), 7.35–7.27 (m, 5H), 7.25–7.18 (m, 2H), 7.16–7.11 (m, 4H), 6.97 (dd, *J* = 6.6, 2.8 Hz, 2H)

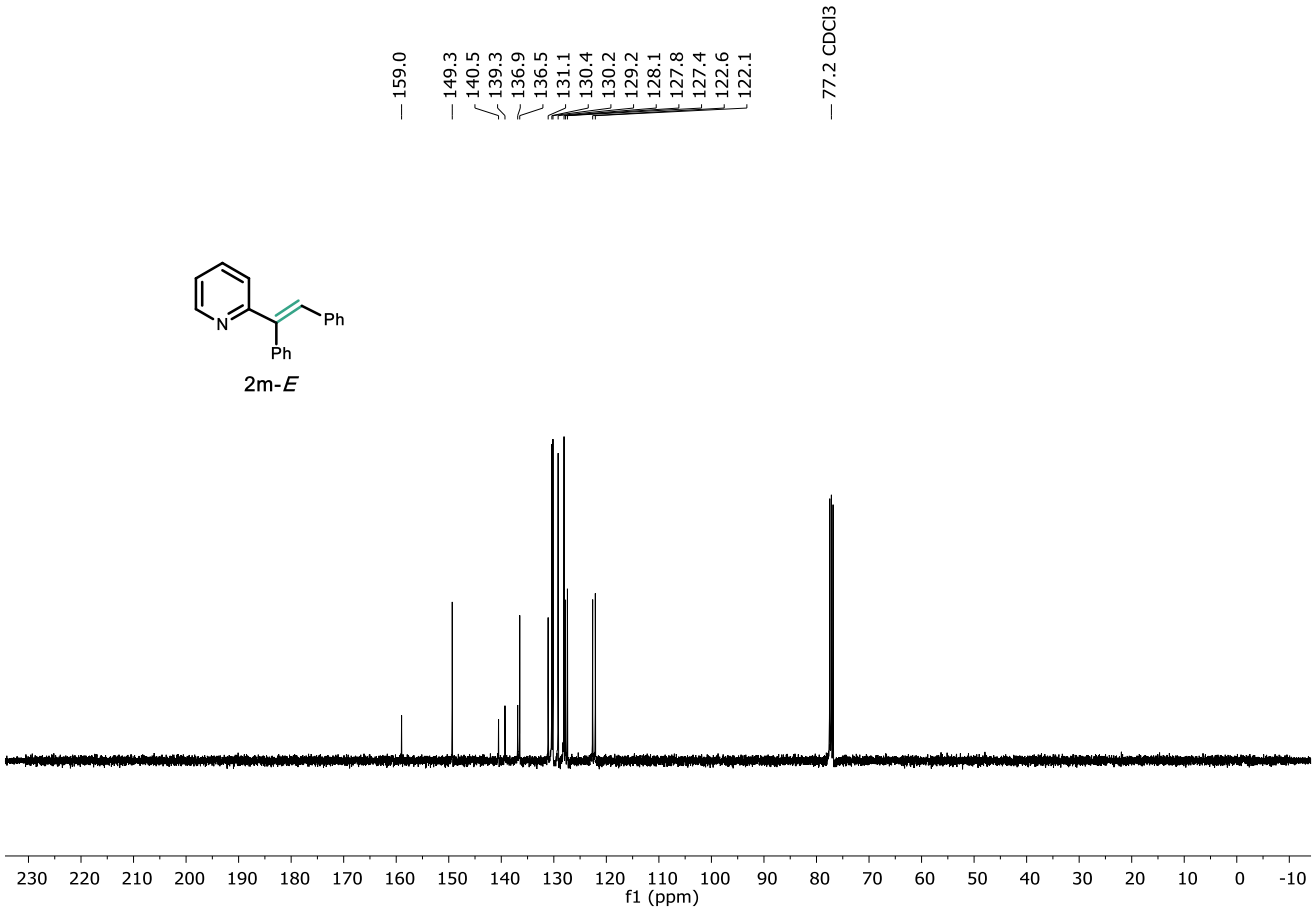
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.6, 150.3, 142.2, 142.0, 137.1, 136.6, 130.1, 129.6, 128.5, 128.2, 127.9, 127.6, 127.3, 126.1, 122.4

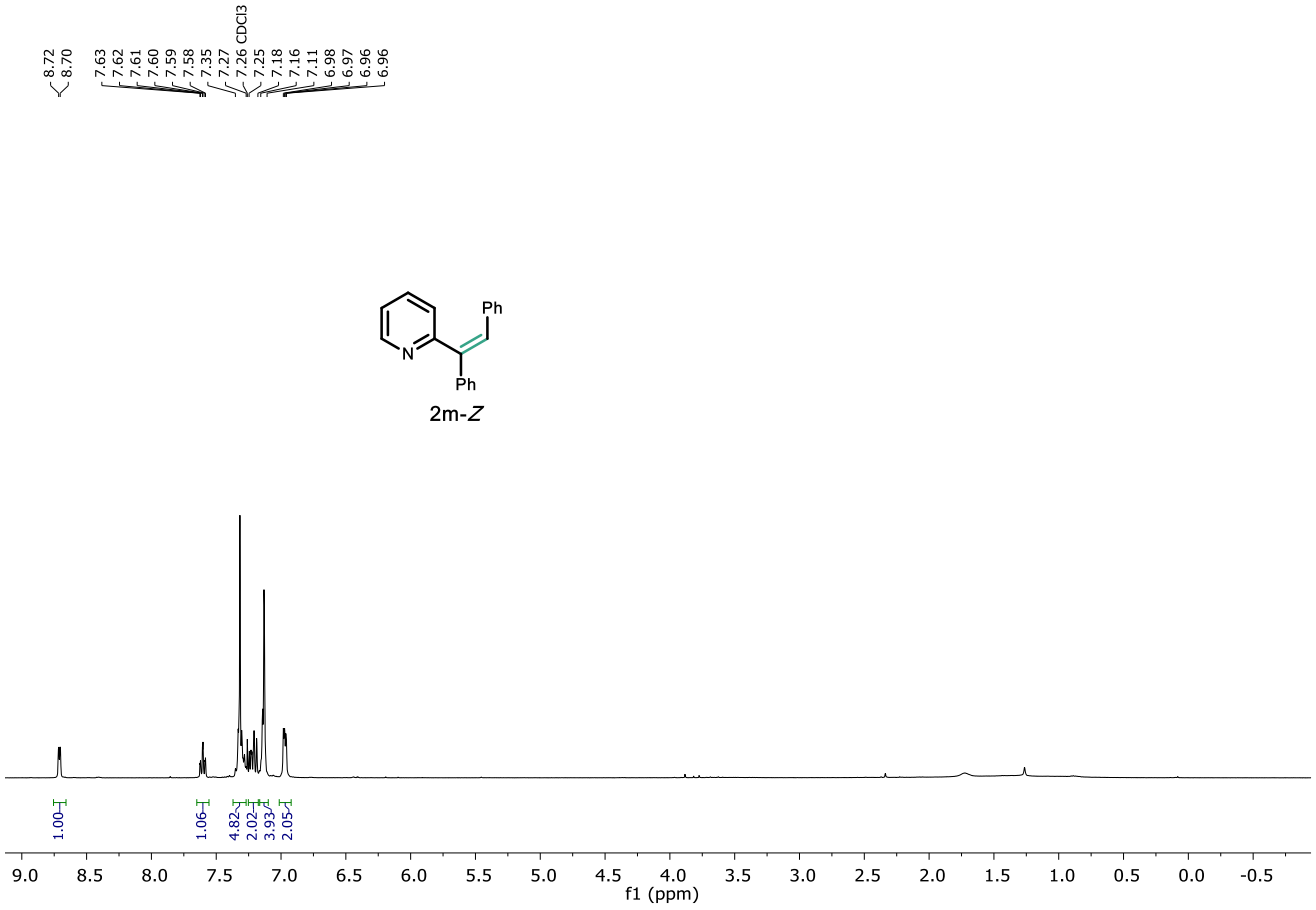
IR (cm^{-1}): 3055, 3022, 2922, 1582, 1492, 1446, 1428, 1147, 1076, 992, 795, 761, 694, 592

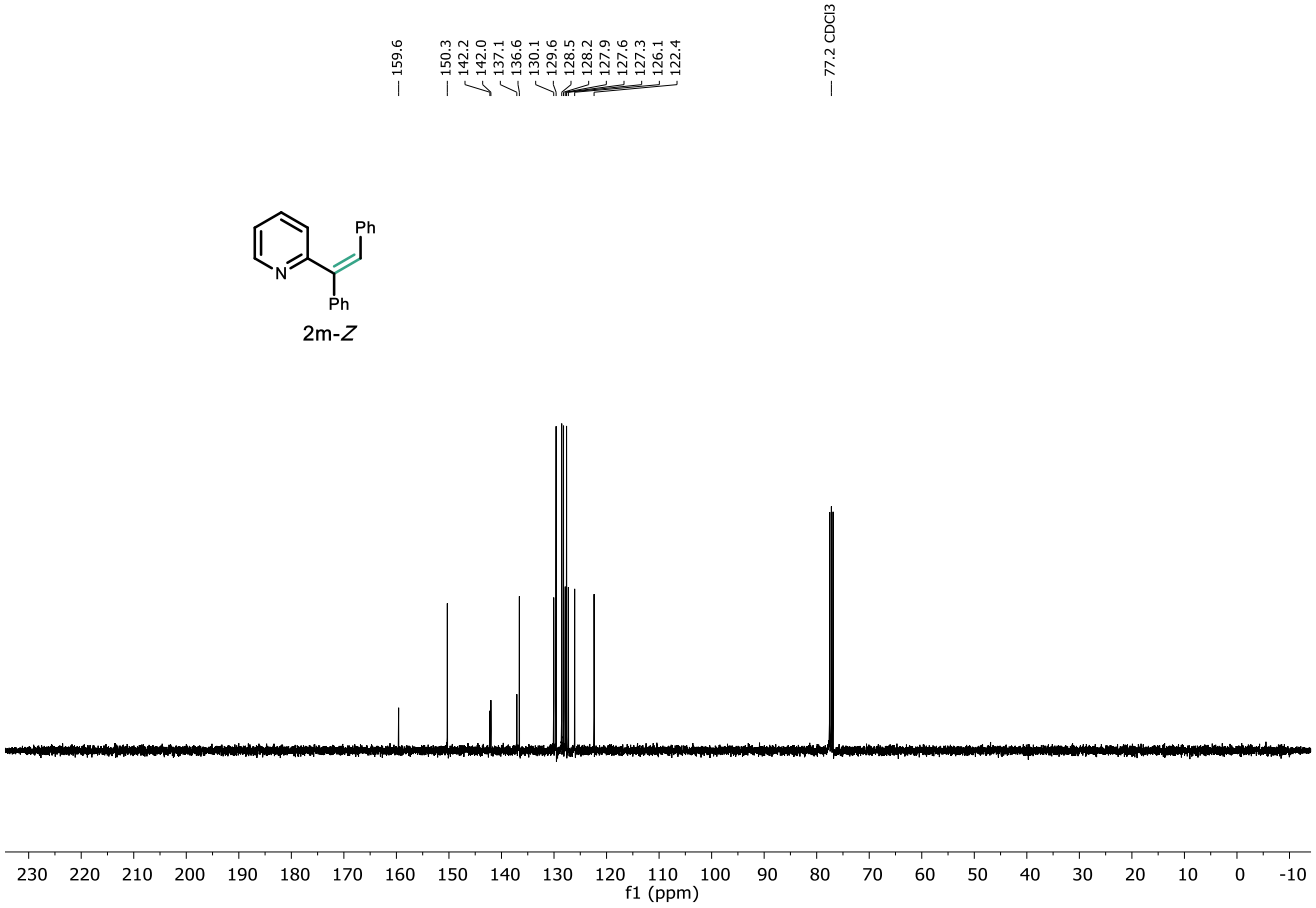
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{19}H_{16}N^+$: 258.1277; found: 258.1283



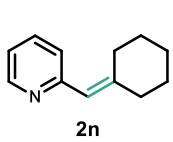

8.68
8.66
7.85
7.57
7.53
7.44
7.36
7.28
7.26 CDCl3
7.24
7.18
7.11
7.08
7.05
6.98
6.96
N
Ph
Ph
2m-E
1.00
1.01
1.06
3.03
2.39
4.20
2.18
1.06
f1 (ppm)


159.0
149.3
140.5
139.3
136.9
136.5
131.1
130.4
130.2
129.2
128.1
127.8
127.4
122.6
122.1
77.2 CDCl3
N
Ph
Ph
2m-E
f1 (ppm)


8.72
8.70
7.63
7.62
7.61
7.60
7.59
7.58
7.35
7.27
7.26 CDCl3
7.25
7.18
7.16
7.11
6.98
6.97
6.96
6.96
Ph
N
Ph
2m-Z
1.00
1.06
4.82
2.02
3.93
2.05
f1 (ppm)


159.6
150.3
142.2
142.0
137.1
136.6
130.1
129.6
128.5
128.2
127.9
127.6
127.3
126.1
122.4
77.2 CDCl3
Ph
N
Ph
2m-Z
f1 (ppm)

2-(cyclohexylidenemethyl)pyridine (2n)



2n

Compound **2n** was prepared from **1n** (35.0 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (12 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 10:1) afforded **2n** (29.8 mg, 86%) as a yellow oil.

R$_f$: 0.45 (hexanes/EtOAc = 4:1)

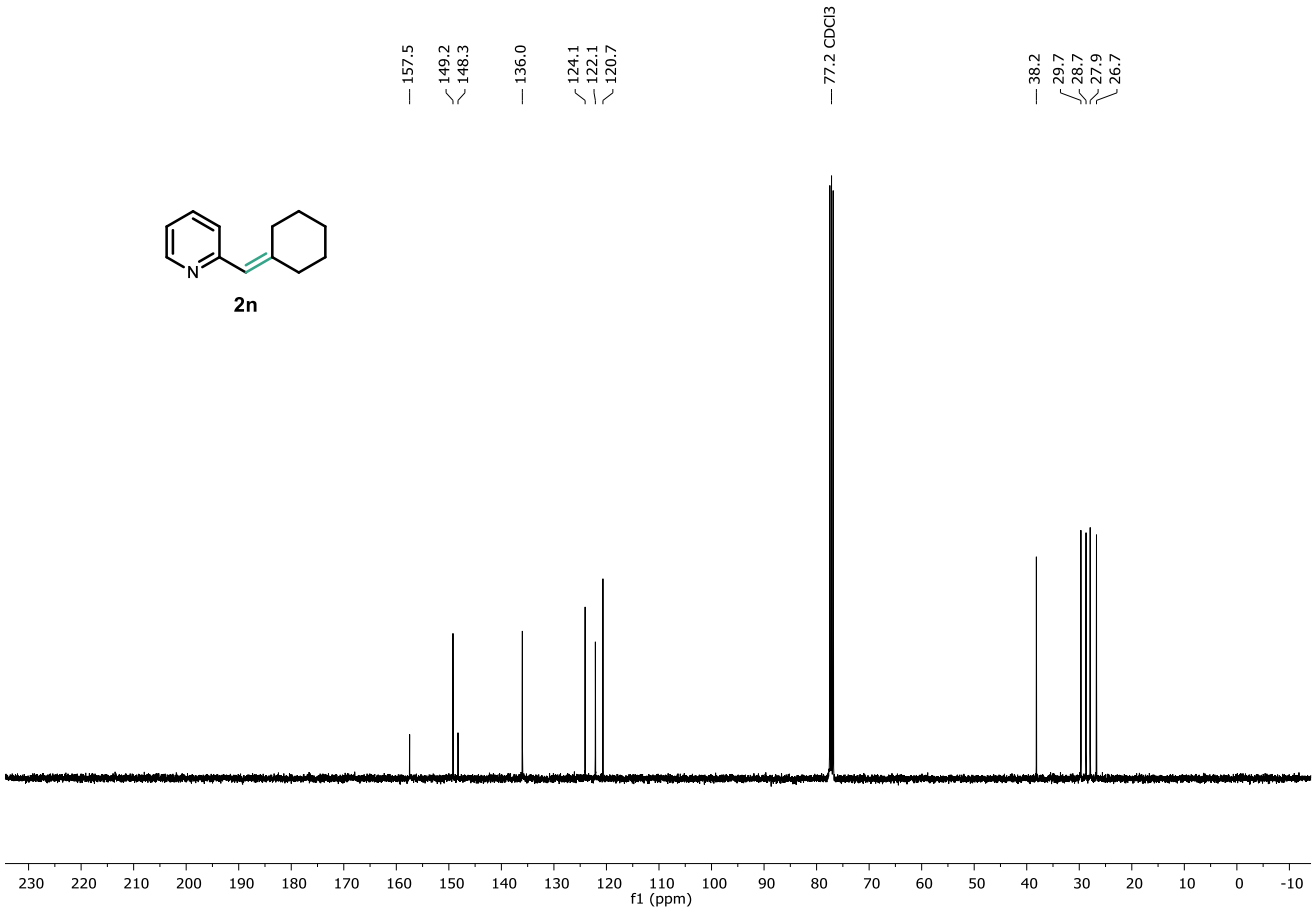
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 3.0 Hz, 1H), 7.62–7.57 (m, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.05 (dd, *J* = 7.5, 4.9 Hz, 1H), 6.28 (s, 1H), 2.66–2.63 (m, 2H), 2.29 (t, *J* = 5.9 Hz, 2H), 1.71–1.56 (m, 6H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.5, 149.2, 148.3, 136.0, 124.1, 122.1, 120.7, 38.2, 29.7, 28.7, 27.9, 26.7

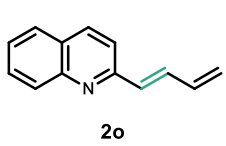
IR (cm^{-1}): 2923, 2852, 1648, 1584, 1560, 1472, 1446, 1427, 1148, 933, 848, 751, 741, 662, 530

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{12}H_{16}N^+$: 174.1277; found: 174.1283


8.56
8.56
7.62
7.57
7.26 CDCl3
7.17
7.15
7.05
6.28
2.66
2.63
2.31
2.29
2.28
1.71
1.56
2n
1.00
0.97
1.00
1.03
1.08
2.11
2.08
6.14
f1 (ppm)


157.5
149.2
148.3
136.0
124.1
122.1
120.7
77.2 CDCl3
38.2
29.7
28.7
27.9
26.7
2n
f1 (ppm)

(*E*)-2-(buta-1,3-dien-1-yl)quinoline (2o)



2o

Compound **2o** was prepared from **1o** (50.8 mg, 0.28 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (16 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 10:1) afforded **2o** (42.6 mg, 85%) as a yellow oil. The characterization data match those previously reported in the literature.[9]

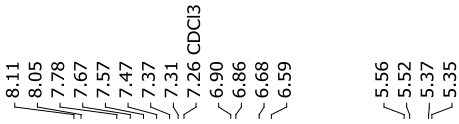
R$_f$: 0.61 (hexanes/EtOAc = 4:1)

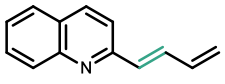
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11–8.05 (m, 2H), 7.78–7.67 (m, 2H), 7.57–7.47 (m, 2H), 7.37–7.31 (m, 1H), 6.86 (d, *J* = 15.8 Hz, 1H), 6.68–6.59 (m, 1H), 5.54 (d, *J* = 17.1 Hz, 1H), 5.36 (d, *J* = 10.1 Hz, 1H)

^{13}C NMR (151 MHz, $CDCl_3$): 156.0, 148.4, 136.8, 136.4, 135.2, 133.3, 129.8, 129.4, 127.6, 127.4, 126.3, 121.0, 119.4

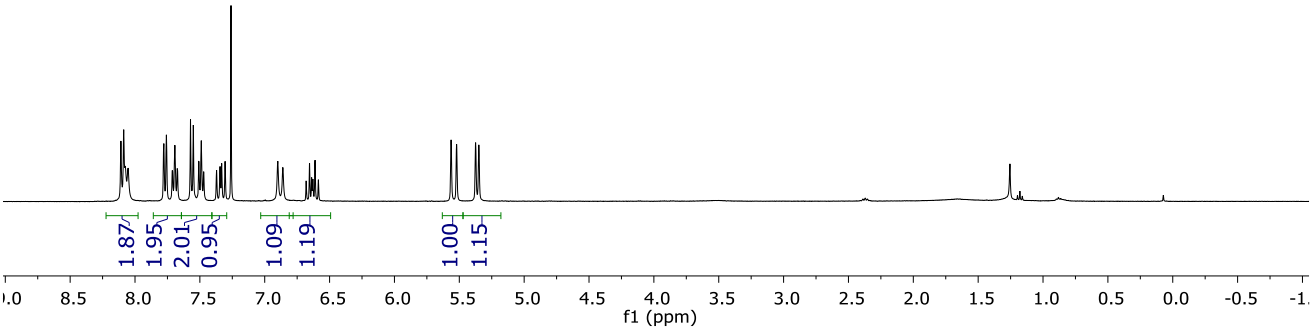
IR (cm^{-1}): 2924, 2854, 1598, 1503, 1428, 1118, 1005, 823, 754, 621

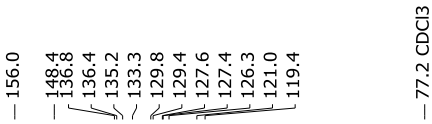
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{13}H_{12}N^+$: 182.0964; found: 182.0970

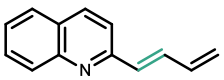

8.11
8.05
7.78
7.67
7.57
7.47
7.37
7.31
7.26 CDCl3
6.90
6.86
6.68
6.59
5.56
5.52
5.37
5.35



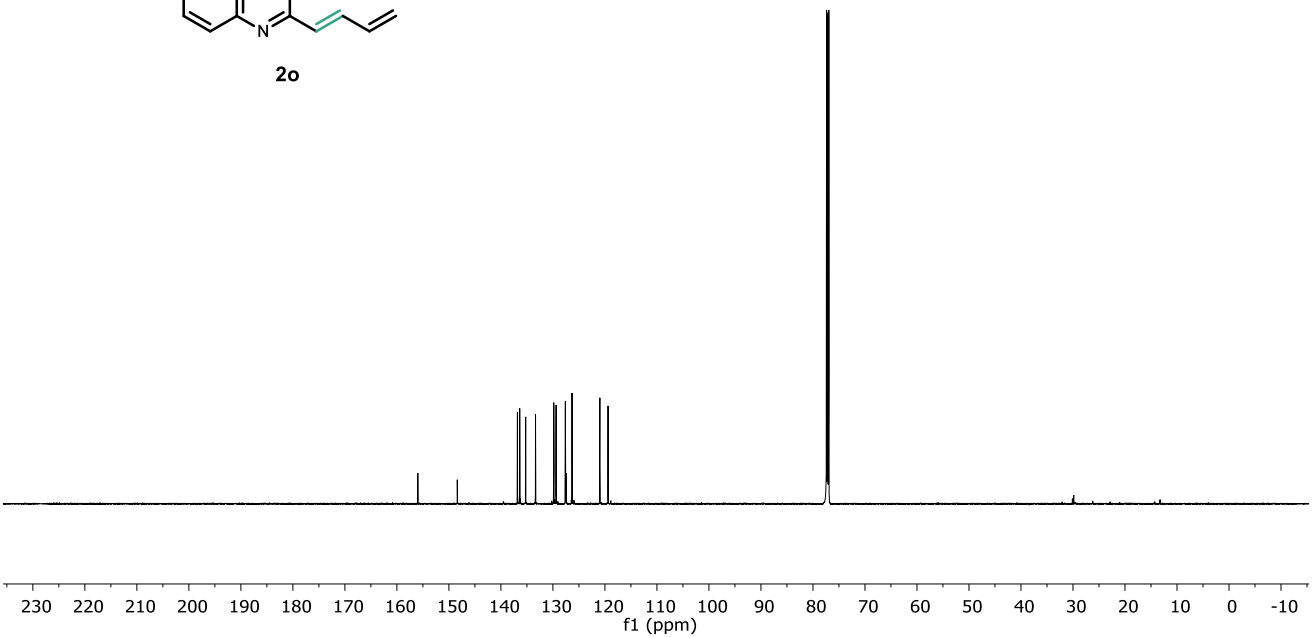
2o


1.87
1.95
2.01
0.95
1.09
1.19
1.00
1.15
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
-0.5
f1 (ppm)

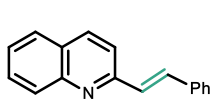

156.0
148.4
136.8
136.4
135.2
133.3
129.8
129.4
127.6
127.4
126.3
121.0
119.4
77.2 CDCl3



2o


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

(*E*)-2-styrylquinoline (2p)



2p

Compound **2p** was prepared from known compound **1p**[11] (46.6 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (4.5 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 20:1 to 15:1) afforded **2p** (44.2 mg, 90%) as a white solid. The characterization data match those previously reported in the literature.[3]

R$_f$: 0.57 (hexanes/EtOAc = 4:1)

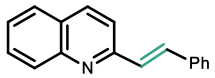
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14–8.07 (m, 2H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.73–7.64 (m, 5H), 7.53–7.46 (m, 1H), 7.46–7.39 (m, 3H), 7.35–7.31 (m, 1H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.1, 148.4, 136.6, 136.5, 134.5, 129.9, 129.3, 129.1, 128.9, 128.8, 127.6, 127.5, 127.4, 126.3, 119.4

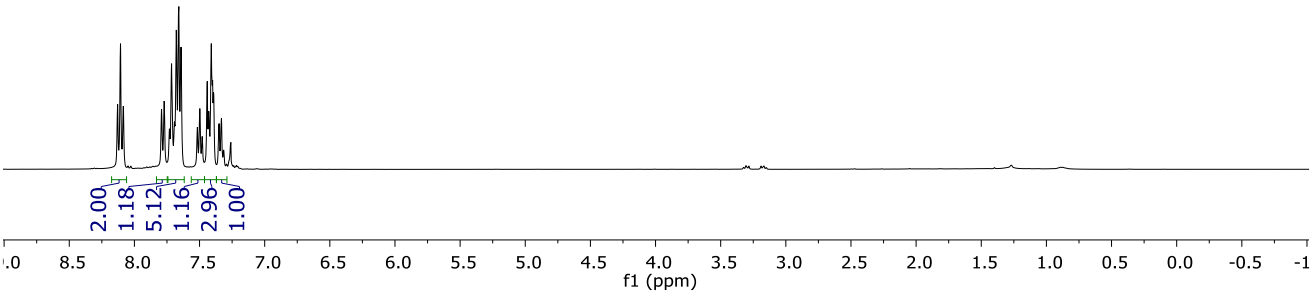
IR (cm^{-1}): 3057, 1594, 1503, 1264, 965, 819, 736, 692, 480

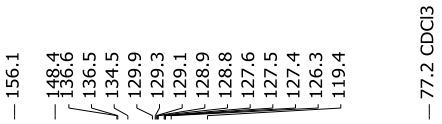
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{17}H_{14}N^+$: 232.1121; found: 232.1126

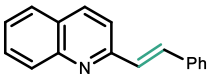

8.14
8.07
7.79
7.77
7.73
7.64
7.53
7.46
7.39
7.35
7.31
7.26 CDCl3


N
Ph

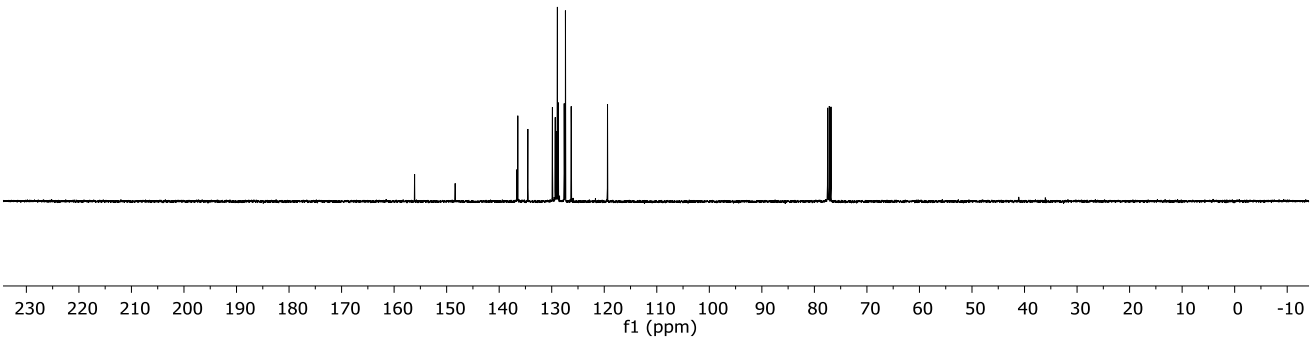
2p


2.00
1.18
5.12
1.16
2.96
1.00
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
-0.5
f1 (ppm)

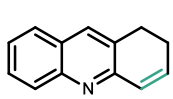

156.1
148.4
136.6
136.5
134.5
129.9
129.3
129.1
128.9
128.8
127.6
127.5
127.4
126.3
119.4
77.2 CDCl3


N
Ph

2p


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

(*E*)-2-styrylquinoline (2q)



2q

Compound **2q** was prepared from known compound **1q**[13] (36.6 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (1.5 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 20:1 to 15:1) afforded **2q** (28.8 mg, 79%) as a white solid.

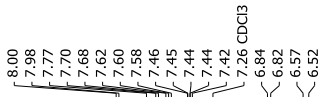
R_f: 0.26 (hexanes/EtOAc = 4:1)

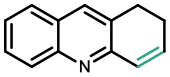
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.5 Hz, 1H), 7.77 (s, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.62–7.58 (m, 1H), 7.46–7.42 (m, 1H), 6.83 (d, *J* = 9.9 Hz, 1H), 6.57–6.52 (m, 1H), 3.03 (t, *J* = 7.7 Hz, 2H), 2.49–2.44 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.3, 147.4, 137.1, 133.0, 130.2, 129.8, 128.9, 128.7, 127.9, 127.0, 126.0, 27.6, 23.5

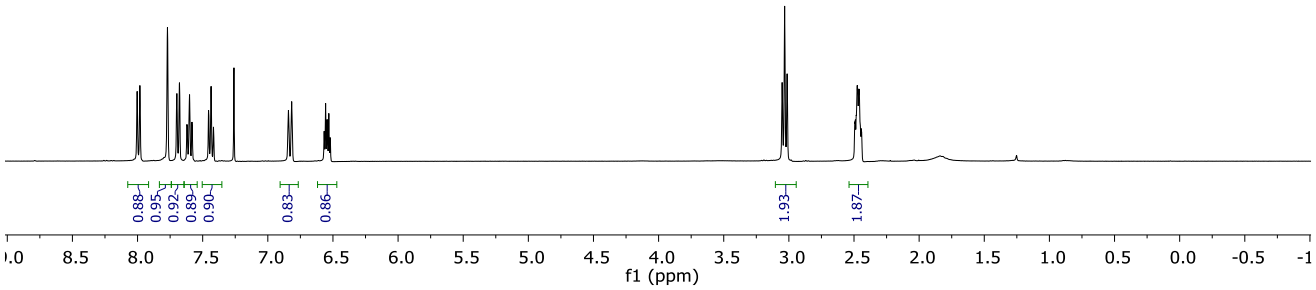
IR (cm^{-1}): 3040, 2932, 1620, 1494, 1419, 1235, 1007, 815, 753, 613, 481

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{13}H_{12}N^+$: 182.0964; found: 182.0970

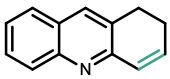

8.00
7.98
7.77
7.70
7.68
7.62
7.60
7.58
7.46
7.45
7.44
7.44
7.42
7.26 CDCl3
6.84
6.82
6.57
6.52
3.05
3.03
3.01
2.49
2.44



2q


0.88
0.95
0.92
0.89
0.90
0.83
0.86
1.93
1.87
f1 (ppm)

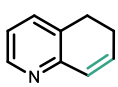

154.3
147.4
137.1
133.0
130.2
129.8
128.9
128.7
127.9
127.0
126.0
77.2 CDCl3
27.6
23.5



2q

f1 (ppm)

(*E*)-2-styrylquinoline (2r)



2r

Compound **2r** was prepared from commercially available compound **1r** (36.6 mg, 0.27 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (2 hour). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 8:1) afforded **2r** (30.4 mg, 84%) as a yellow oil.

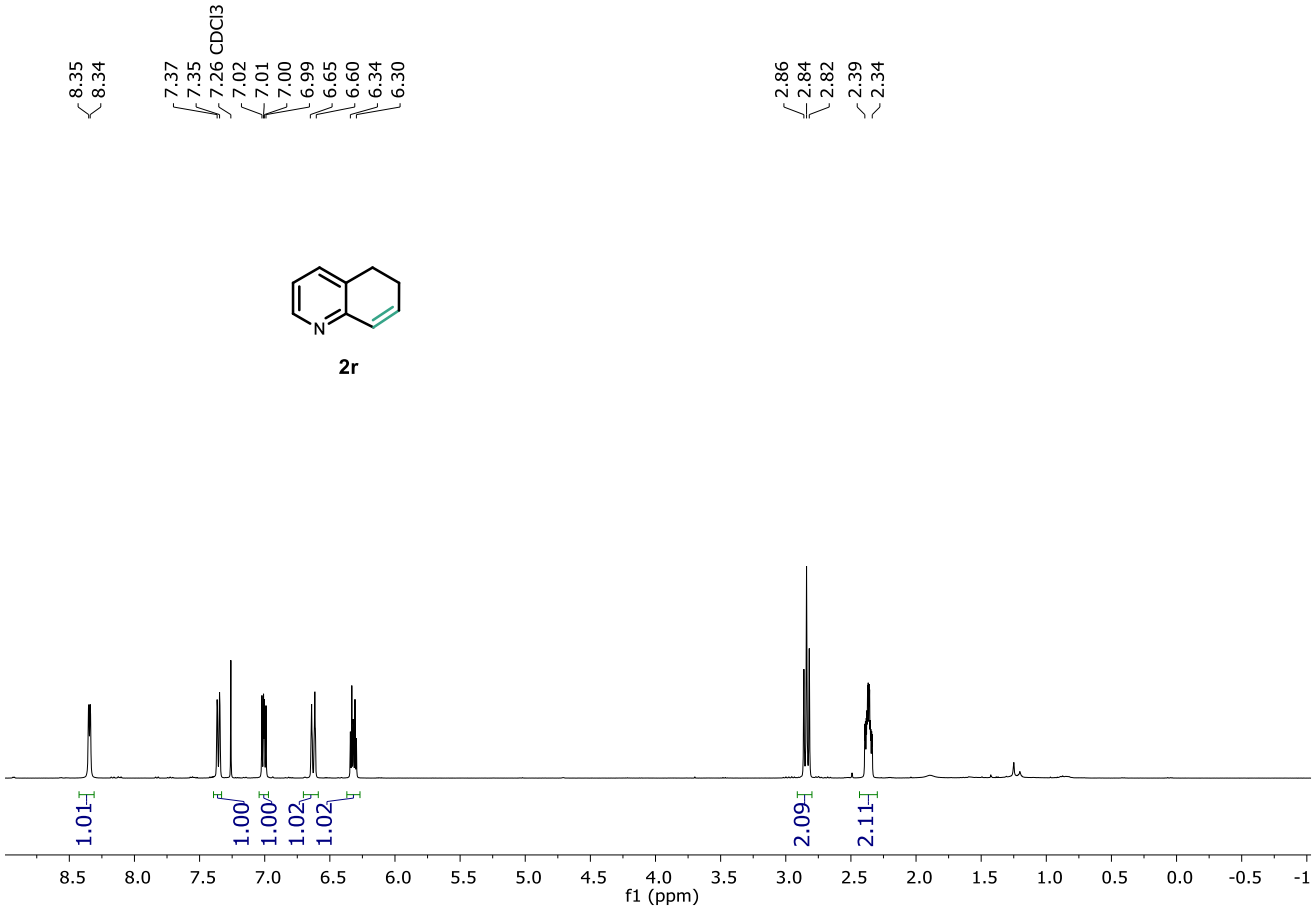
R$_f$: 0.27 (hexanes/EtOAc = 5:1)

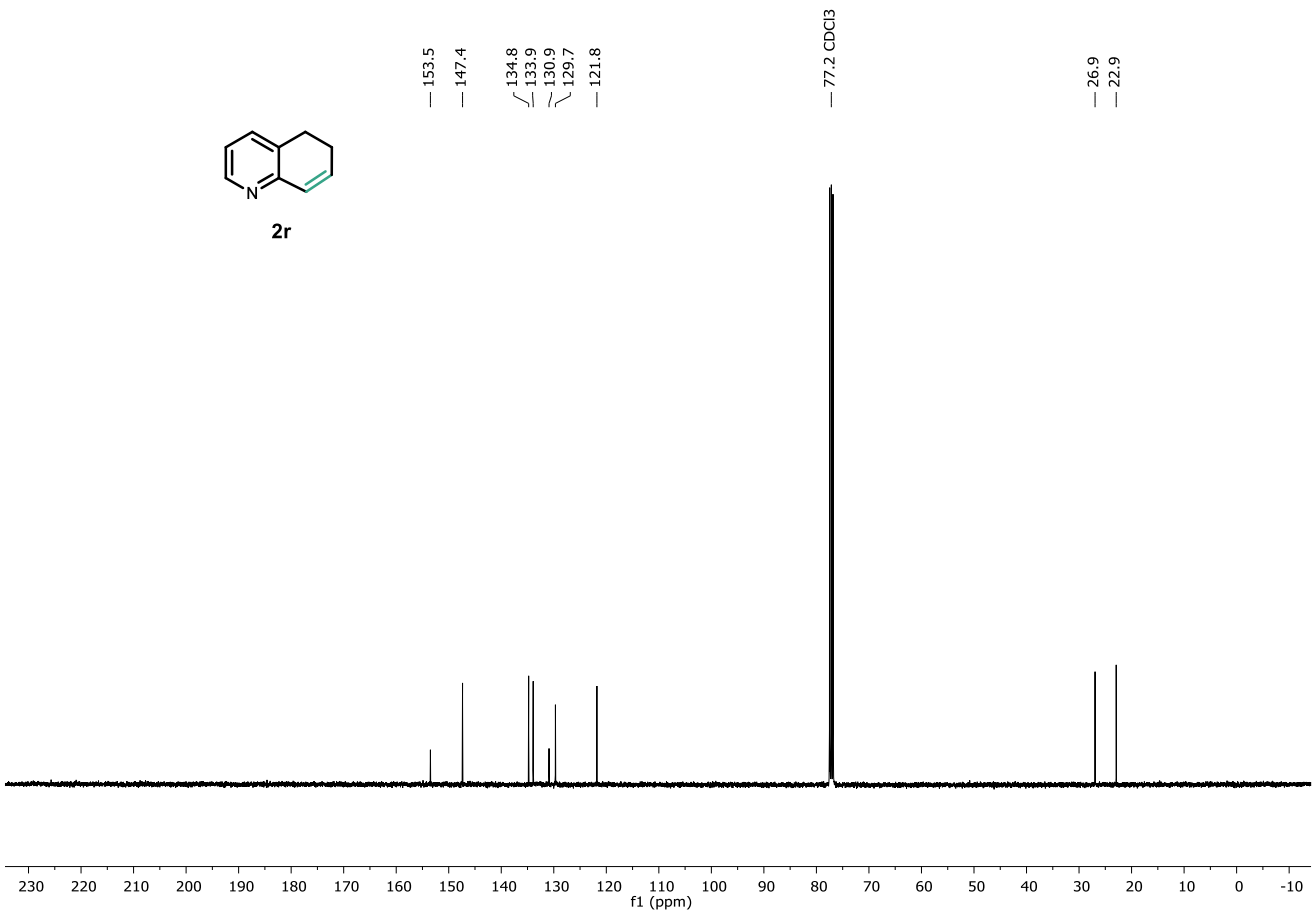
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 4.6 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.01 (dd, *J* = 7.5, 5.0 Hz, 1H), 6.65–6.60 (m, 1H), 6.38–6.27 (m, 1H), 2.84 (t, *J* = 8.3 Hz, 2H), 2.39–2.34 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.5, 147.4, 134.8, 133.9, 130.9, 129.7, 121.8, 26.9, 22.9

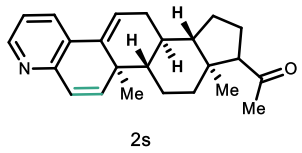
IR (cm^{-1}): 2932, 2833, 1584, 1566, 1438, 1182, 1112, 1010, 884, 805, 704, 554

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_9H_{10}N^+$: 132.0808; found: 132.0813


8.35
8.34
7.37
7.35
7.26 CDCl3
7.02
7.01
7.00
6.99
6.65
6.60
6.34
6.30
2.86
2.84
2.82
2.39
2.34
2r
1.01
1.00
1.00
1.02
1.02
2.09
2.11
f1 (ppm)


153.5
147.4
134.8
133.9
130.9
129.7
121.8
77.2 CDCl3
26.9
22.9
2r
f1 (ppm)

1-((6aS,8aR)-6a,8a-dimethyl-6a,6b,8,8a,9,10,11,11a,11b,12-decahydro-7H-cyclopenta[5,6]-naphtho[2,1-f]quinolin-9-yl)ethan-1-one (2s)



2s

Compound **2s** was prepared from known compound **1s**[7] (34.9 mg, 0.1 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** with 2.1 equiv $Zn(TMP)_2$ (2 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 5:1 to 2:1) afforded **2s** (23.2 mg, 67%) as a white solid. (Note: The use of 1.2 equivalents of base led to lower yields and conversions, suggesting that deprotonation of the ketone occurs. No dehydrogenation of the ketone is observed as kinetic enolate formation by $Zn(TMP)_2$ will first enolize the methyl ketone, which cannot undergo β-hydride elimination.)

R_f: 0.48 (hexanes/EtOAc = 1:1)

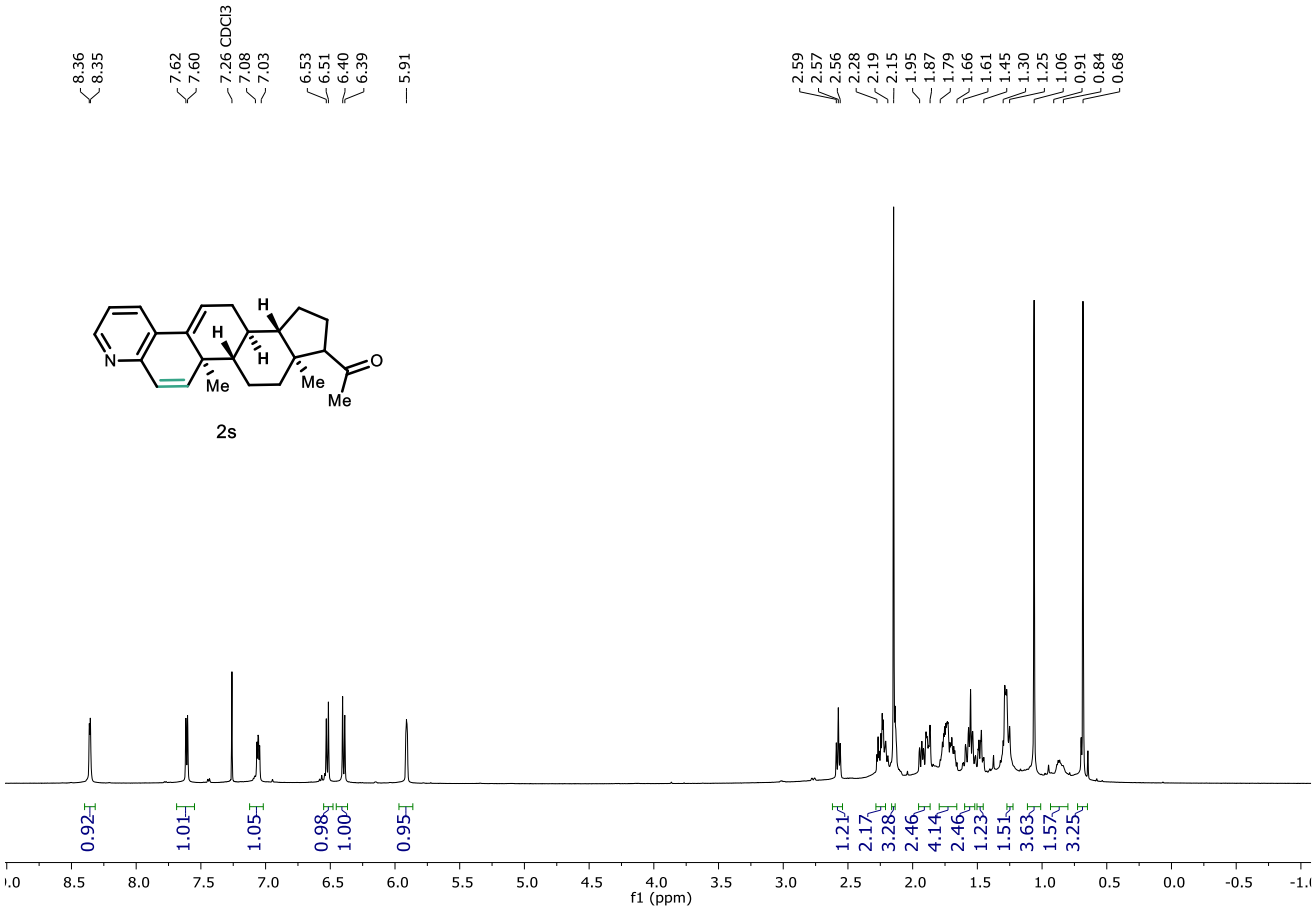
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{20.0}}$: –126.5° (*c* 1.0, $CHCl_3$)

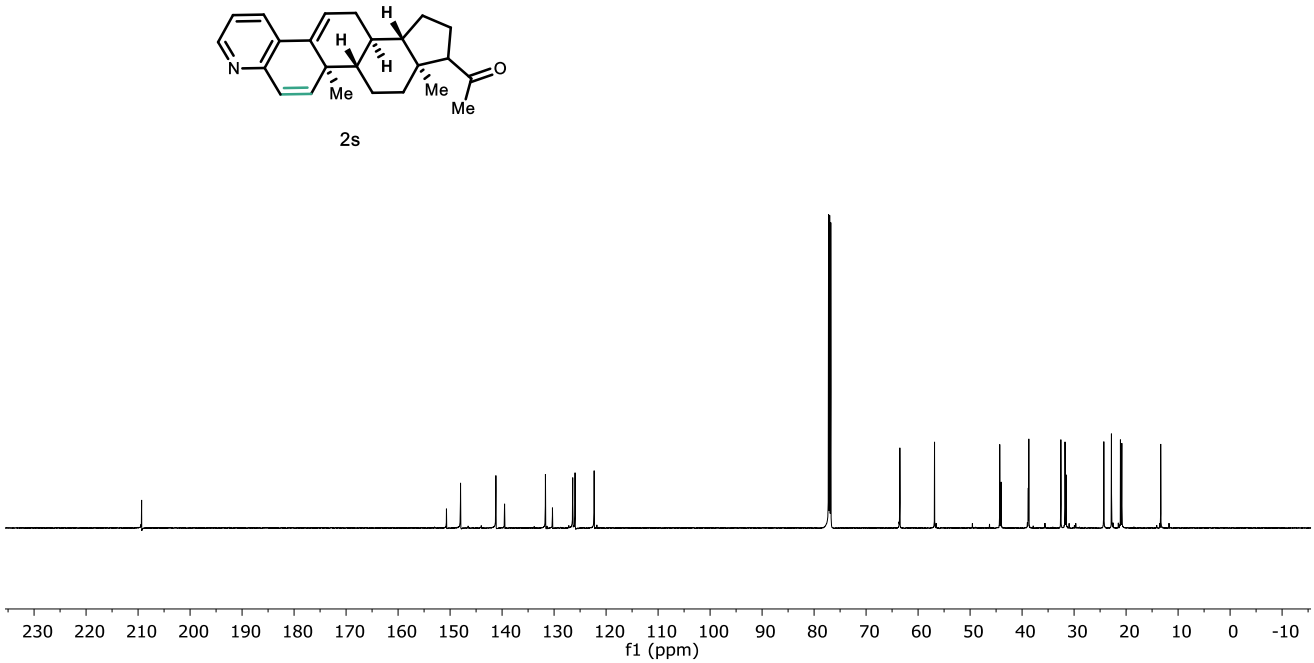
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 5.4 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.08–7.03 (m, 1H), 6.46 (dd, *J* = 76.1, 9.8 Hz, 2H), 5.91 (s, 1H), 2.57 (t, *J* = 9.0 Hz, 1H), 2.28–2.15 (m, 2H), 2.15 (s, 3H), 1.95–1.87 (m, 2H), 1.79–1.66 (m, 4H), 1.61–1.45 (m, 3H), 1.30–1.25 (m, 1H), 1.06 (s, 3H), 0.91–0.84 (m, 1H), 0.68 (s, 3H)

^{13}C NMR (151 MHz, $CDCl_3$): δ 209.3, 150.7, 148.0, 141.2, 139.5, 131.7, 130.3, 126.4, 126.0, 122.3, 63.5, 56.8, 44.3, 44.0, 38.8, 38.7, 32.5, 31.7, 31.5, 24.3, 22.8, 21.1, 20.8, 13.3

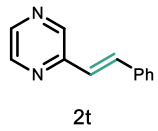
IR (cm^{-1}): 2927, 2885, 1699, 1433, 1357, 1265, 1225, 1184, 1161, 968, 797, 737, 592

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{24}H_{30}NO^+$: 348.2322; found: 348.2327


8.36
8.35
7.62
7.60
7.26 CDCl3
7.08
7.03
6.53
6.51
6.40
6.39
5.91
2.59
2.57
2.56
2.28
2.19
2.15
1.95
1.87
1.79
1.66
1.61
1.45
1.30
1.25
1.06
0.91
0.84
0.68
2s
0.92
1.01
1.05
0.98
1.00
0.95
1.21
2.17
3.28
2.46
4.14
2.46
1.23
1.51
3.63
1.57
3.25
f1 (ppm)


209.3
150.7
148.0
141.2
139.5
131.7
130.3
126.4
126.0
122.3
63.5
56.8
44.3
44.0
38.8
38.7
32.5
31.7
31.5
24.3
22.8
21.1
20.8
13.3
2s
f1 (ppm)

(*E*)-2-styrylpyrazine (2t)



2t

Compound **2t** was prepared from compound **1t** (36.8 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (6 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 10:1 to 5:1) afforded **2t** (30.3 mg, 83%) as a white solid.

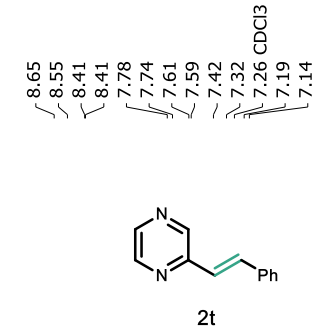
R_f: 0.54 (hexanes/EtOAc = 2:1)

^{1}H NMR (400 MHz, $CDCl_3$): 8.65 (s, 1H), 8.55 (s, 1H), 8.41 (d, *J* = 2.5 Hz, 1H), 7.76 (d, *J* = 16.1 Hz, 1H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.42–7.32 (m, 3H), 7.16 (d, *J* = 16.1 Hz, 1H)

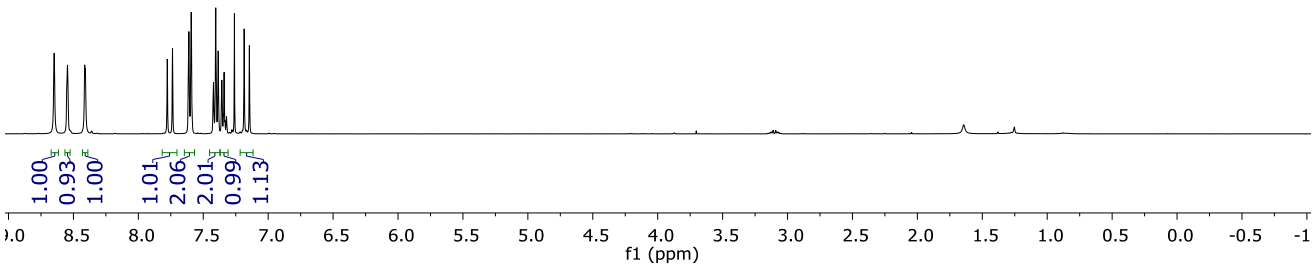
^{13}C NMR (101 MHz, $CDCl_3$): δ 151.4, 144.5, 143.9, 142.9, 136.2, 135.3, 129.1, 129.0, 127.5, 124.2

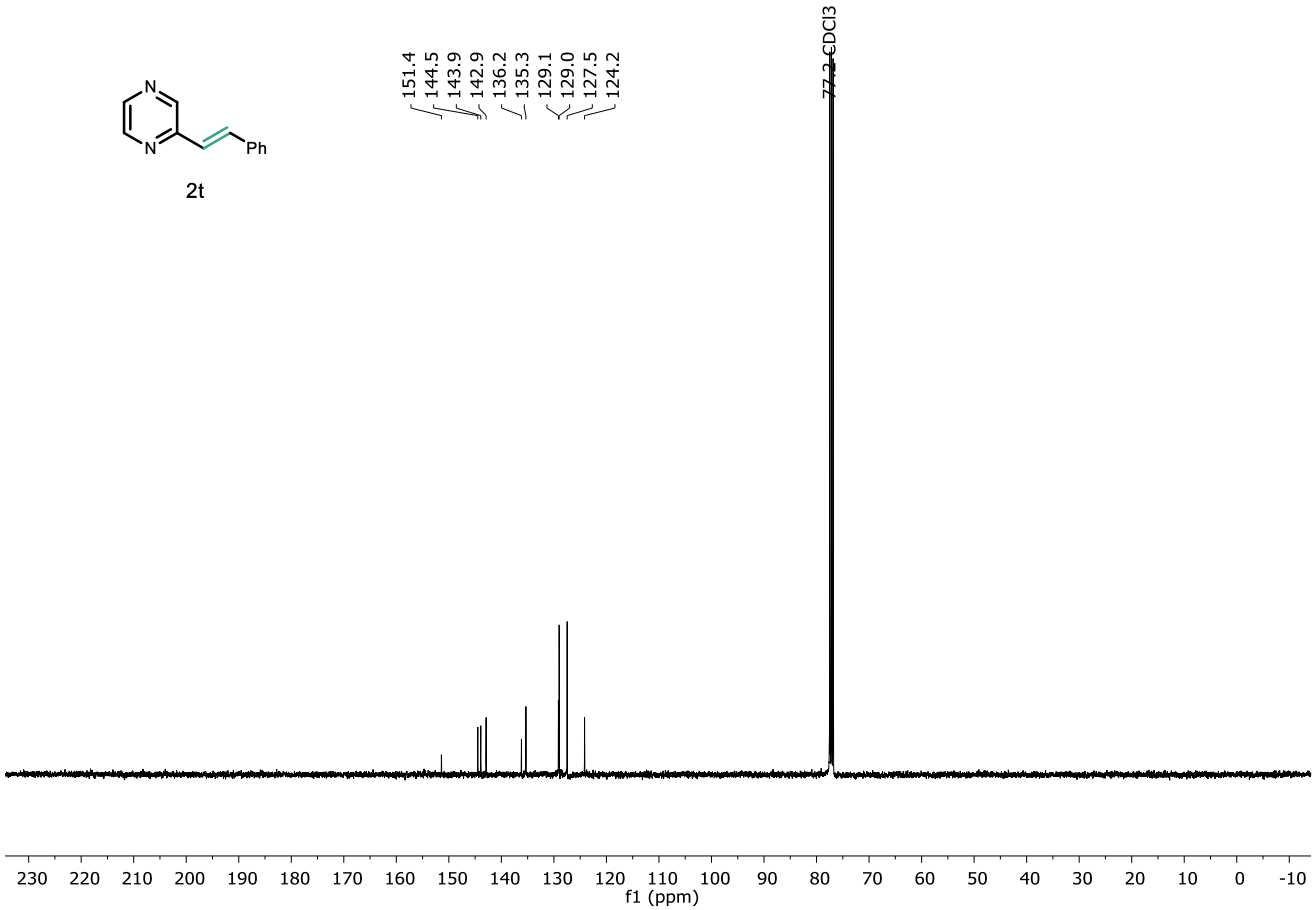
IR (cm^{-1}): 3060, 3029, 2929, 1635, 1493, 1475, 1398, 1137, 1016, 963, 741, 690

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{12}H_{11}N_2^+$:183.0917; found: 183.0922


8.65
8.55
8.41
8.41
7.78
7.74
7.61
7.59
7.42
7.32
7.26 CDCl3
7.19
7.14
N
N
Ph

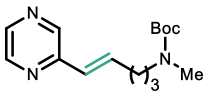
2t


1.00
0.93
1.00
1.01
2.06
2.01
0.99
1.13
f1 (ppm)


151.4
144.5
143.9
142.9
136.2
135.3
129.1
129.0
127.5
124.2
77.2 CDCl3
N
N
Ph
f1 (ppm)

2t

tert-butyl (E)-methyl(5-(pyrazin-2-yl)pent-4-en-1-yl)carbamate (2u)



2u

Compound **2u** was prepared from compound **1u** (55.4 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (3 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 10:1 to 5:1) afforded **2u** (23.8 mg, 43%) as a yellow oil.

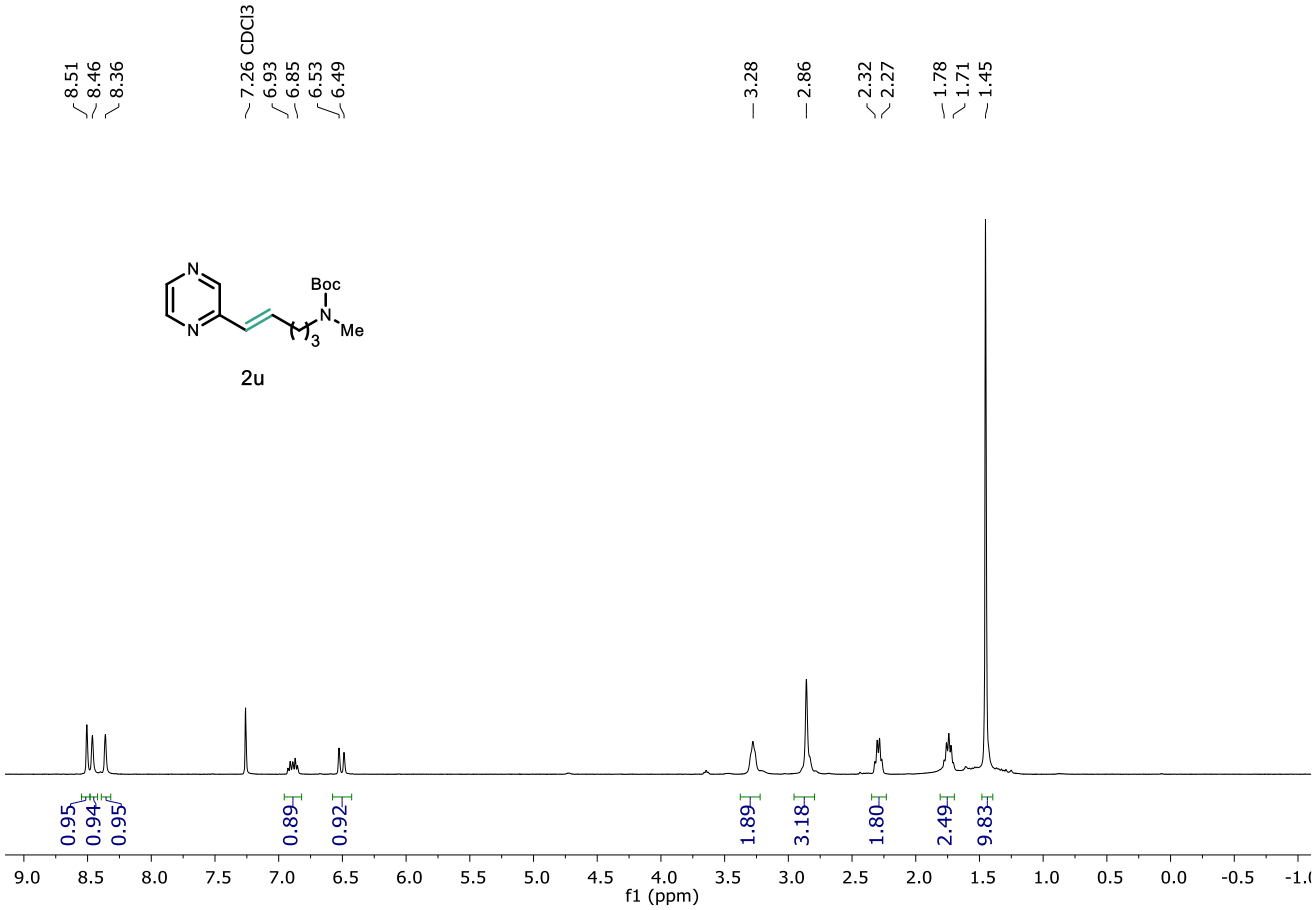
R_f: 0.50 (hexanes/EtOAc = 2:1)

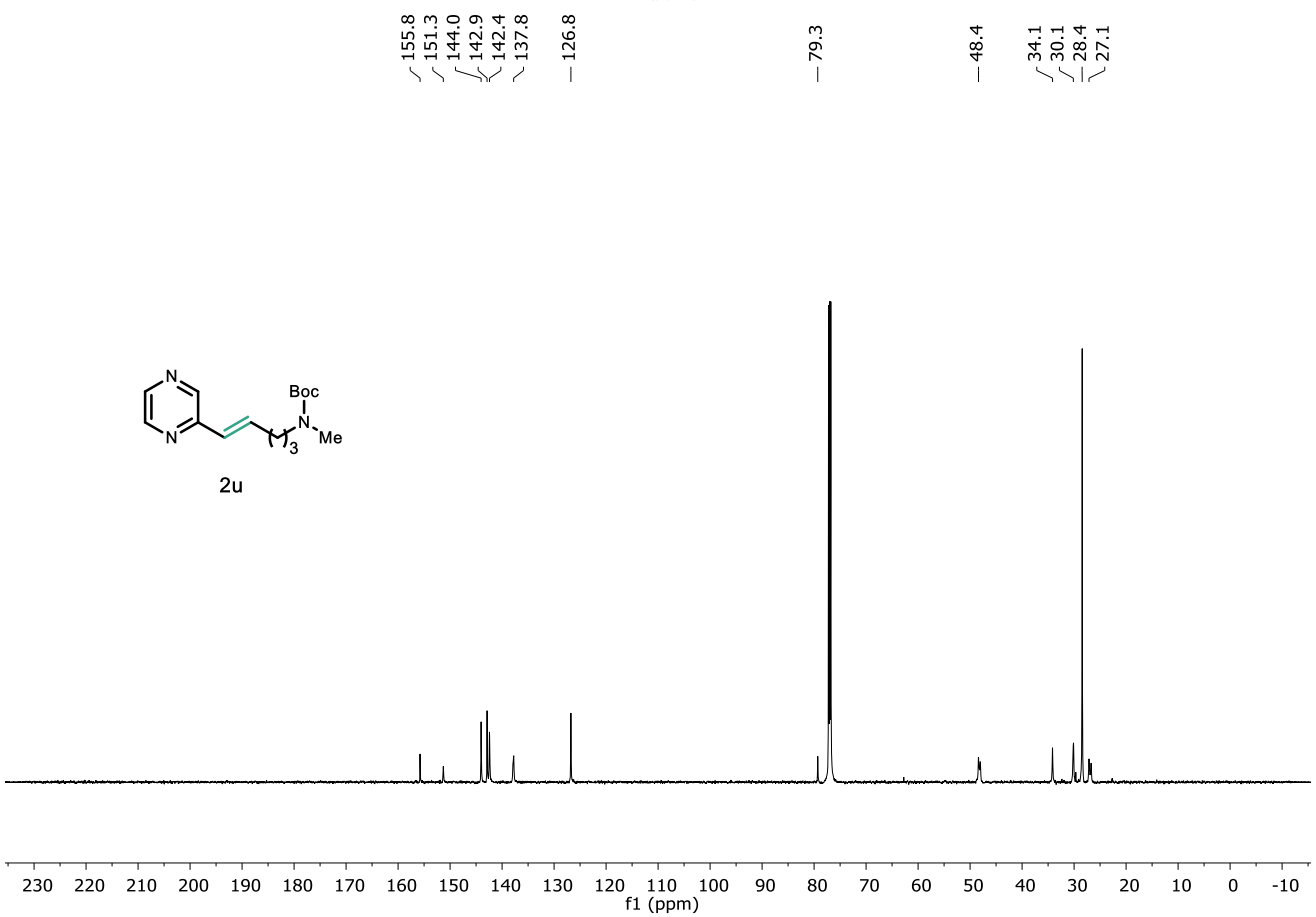
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H), 8.46 (s, 1H), 8.36 (s, 1H), 6.93–6.85 (m, 1H), 6.51 (d, *J* = 15.6 Hz, 1H), 3.28 (brs, 2H), 2.86 (s, 3H), 2.32–2.27 (m, 2H), 1.78–1.71 (m, 2H), 1.45 (s, 9H)

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.8, 151.3, 144.0, 142.9, 142.4, 137.8, 126.8, 79.3, 48.4, 34.1, 30.1, 28.4, 27.1

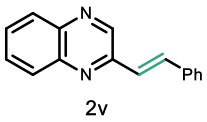
IR (cm^{-1}): 2974, 2930, 1690, 1478, 1396, 1365, 1167, 1058, 973, 874, 772

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{15}H_{24}N_3O_2^+$: 278.1863; found: 278.1869


8.51
8.46
8.36
7.26 CDCl3
6.93
6.85
6.53
6.49
3.28
2.86
2.32
2.27
1.78
1.71
1.45
Boc
N
Me
3
2u
0.95
0.94
0.95
0.89
0.92
1.89
3.18
1.80
2.49
9.83
f1 (ppm)


155.8
151.3
144.0
142.9
142.4
137.8
126.8
79.3
48.4
34.1
30.1
28.4
27.1
Boc
N
Me
3
2u
f1 (ppm)

(*E*)-2-styrylquinoxaline (2v)



2v

Compound **2v** was prepared from known compound **1v**[11] (46.8 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (16 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 10:1 to 5:1) afforded **2v** (28.2 mg, 60%) as a yellow solid. The characterization data match those previously reported in the literature.[3]

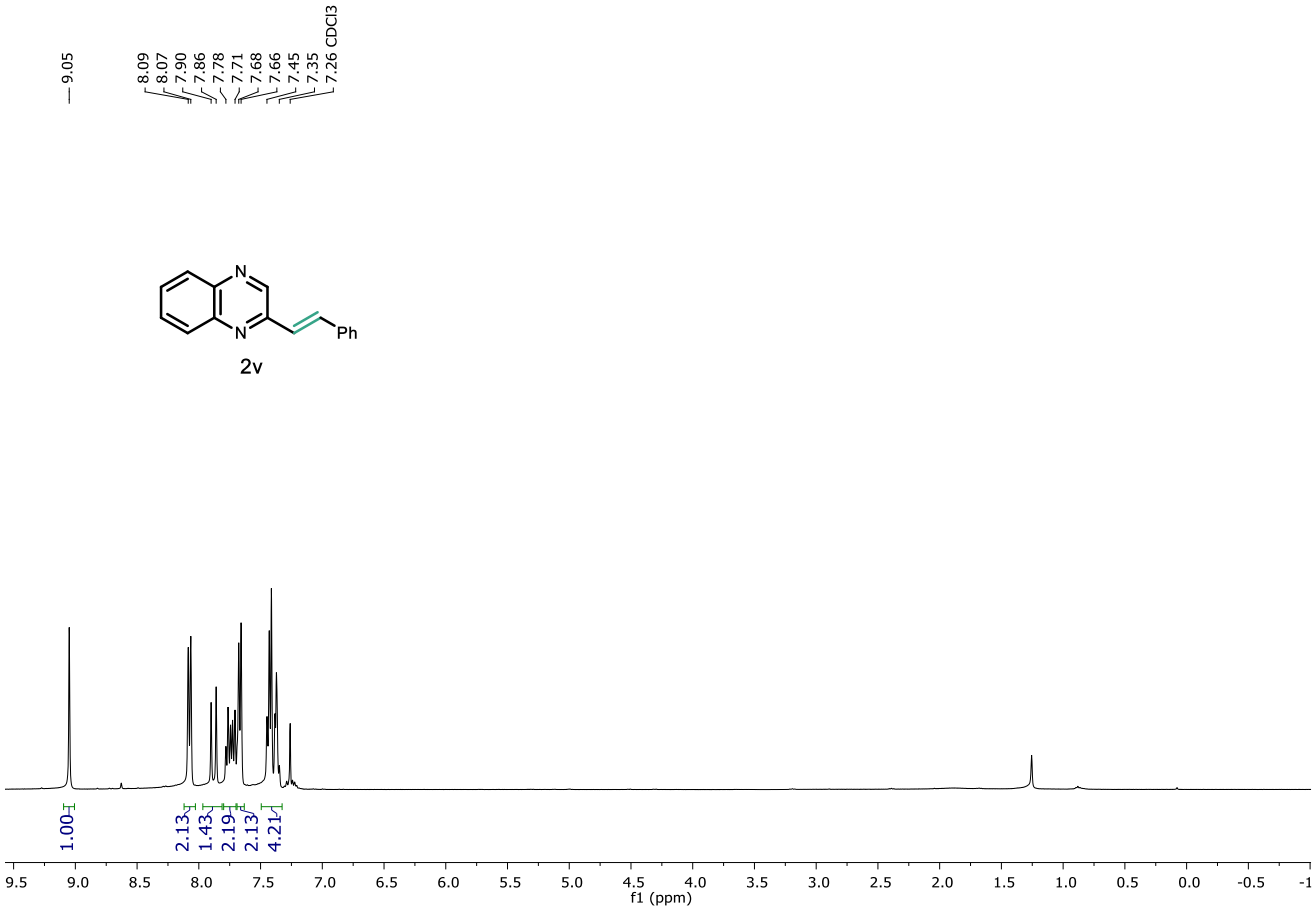
R$_f$: 0.65 (hexanes/EtOAc = 2:1)

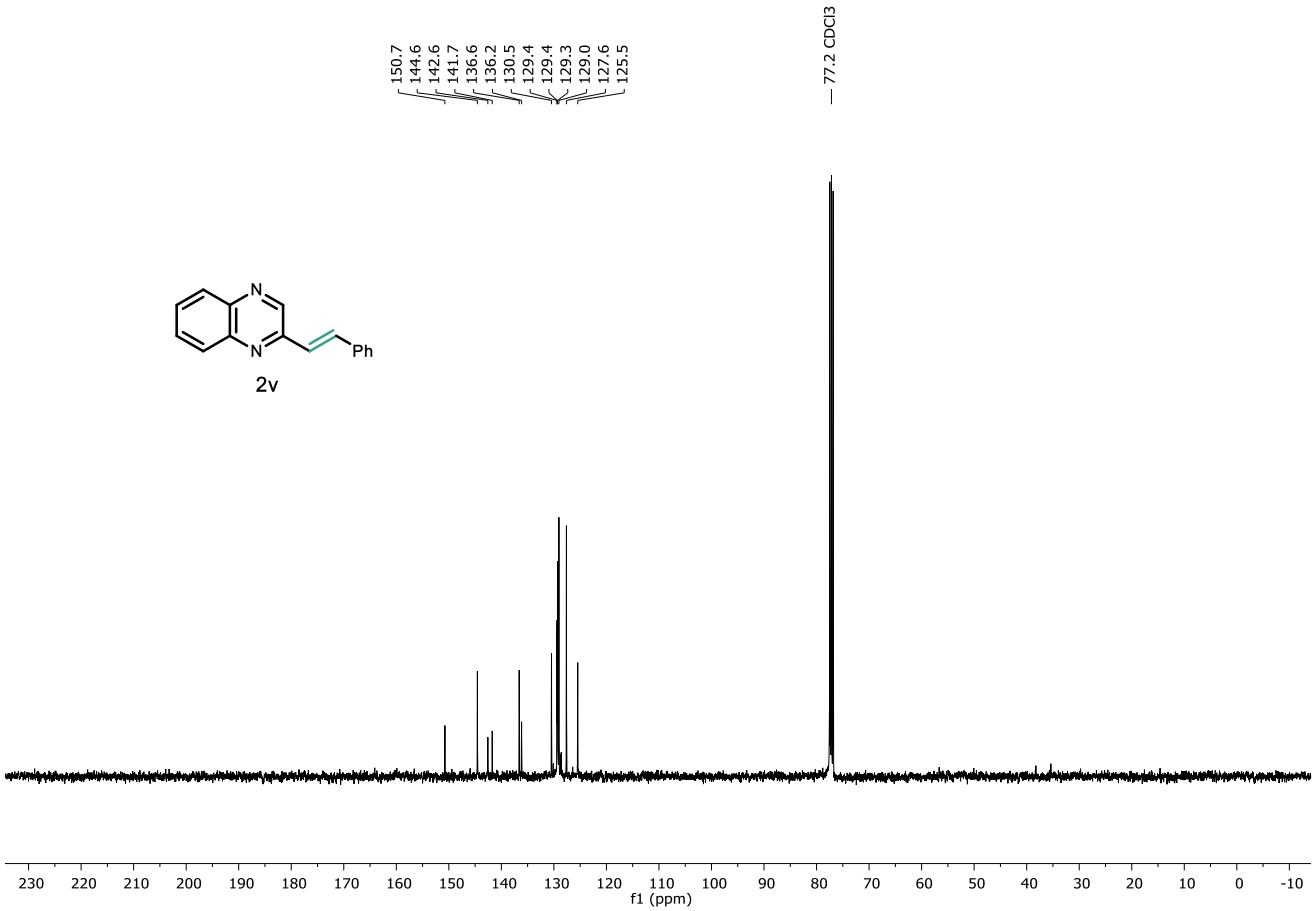
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.05 (s, 1H), 8.08 (d, *J* = 8.2 Hz, 2H), 7.88 (d, *J* = 16.3 Hz, 1H), 7.78–7.71 (m, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.45–7.35 (m, 4H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.7, 144.6, 142.6, 141.7, 136.6, 136.2, 130.5, 129.4, 129.4, 129.3, 129.0, 127.6, 125.5

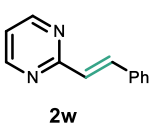
IR (cm^{-1}): 3058, 2924, 1633, 1541, 1492, 1448, 1122, 969, 750, 691

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{16}H_{13}N_2^+$: 233.1073; found: 233.1079


9.05
8.09
8.07
7.90
7.86
7.78
7.71
7.68
7.66
7.45
7.35
7.26 CDCl3
N
N
Ph
2v
1.00
2.13
1.43
2.19
2.13
4.21
9.5 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 -0.5 -1
f1 (ppm)


150.7
144.6
142.6
141.7
136.6
136.2
130.5
129.4
129.4
129.3
129.0
127.6
125.5
77.2 CDCl3
N
N
Ph
2v
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

(*E*)-2-styrylpyrimidine (2w)



2w

Compound **2w** was prepared from compound **1w** (36.8 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (4 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 8:1 to 4:1) afforded **2w** (26.0 mg, 71%) as a yellow solid. The characterization data match those previously reported in the literature.[5]

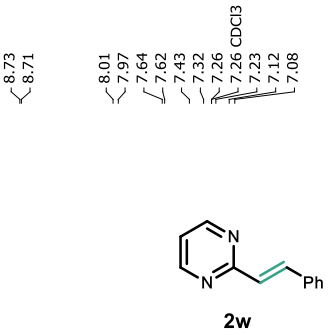
R$_f$: 0.48 (hexanes/EtOAc = 2:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (d, *J* = 4.8 Hz, 2H), 7.99 (d, *J* = 16.0 Hz, 1H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.43–7.32 (m, 3H), 7.25 (d, *J* = 15.9 Hz, 1H), 7.12–7.08 (m, 1H)

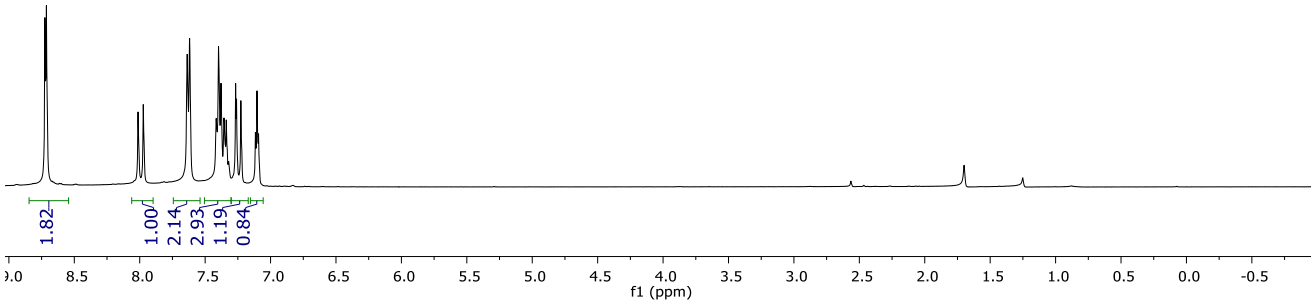
^{13}C NMR (101 MHz, $CDCl_3$): δ 165.0, 157.2, 138.3, 136.1, 129.3, 128.9, 127.8, 127.5, 118.7

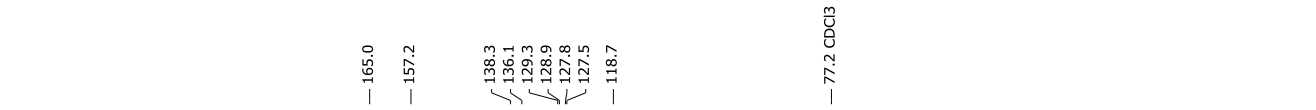
IR (cm^{-1}): 3029, 2960, 1637, 1566, 1552, 1412, 1219, 976, 793, 690, 532

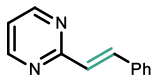
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{12}H_{11}N_2^+$: 183.0917; found: 183.0922


8.73
8.71
8.01
7.97
7.64
7.62
7.43
7.32
7.26
7.26 CDCl3
7.23
7.12
7.08
N
N
Ph

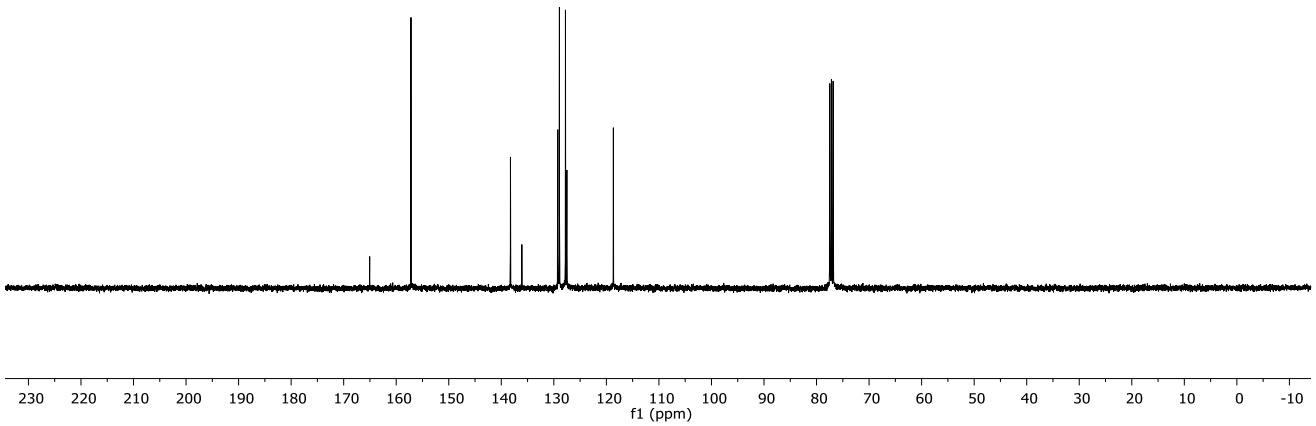
2w


1.82
1.00
2.14
2.93
1.19
0.84
f1 (ppm)

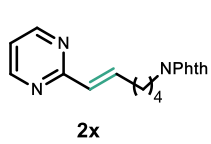

165.0
157.2
138.3
136.1
129.3
128.9
127.8
127.5
118.7
77.2 CDCl3


N
N
Ph

2w


f1 (ppm)

(*E*)-2-(6-(pyrimidin-2-yl)hex-5-en-1-yl)isoindoline-1,3-dione (2x)



2x

Compound **2x** was prepared from compound **1x** (31.0 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (2 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 3:1 to 1:1) afforded **2x** (21.2 mg, 69%) as a yellow solid.

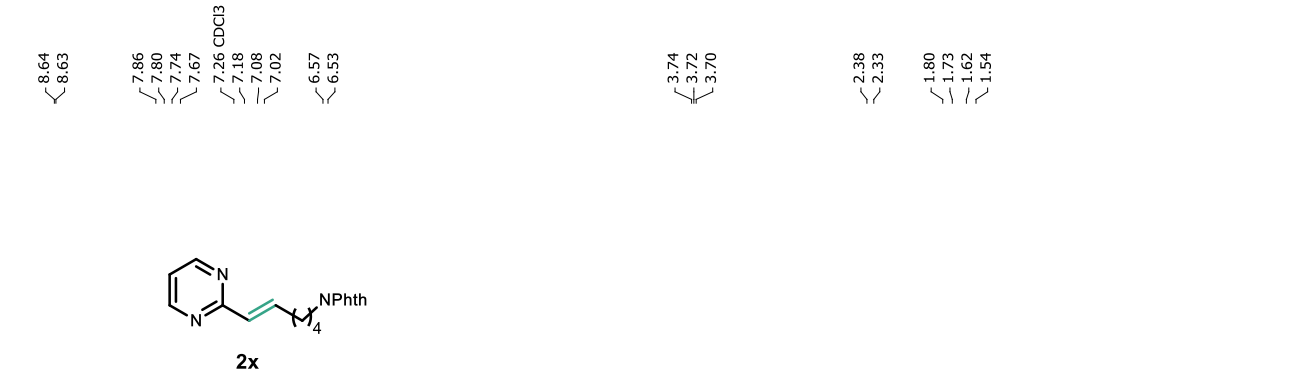
R_f: 0.26 (hexanes/EtOAc = 1:1)

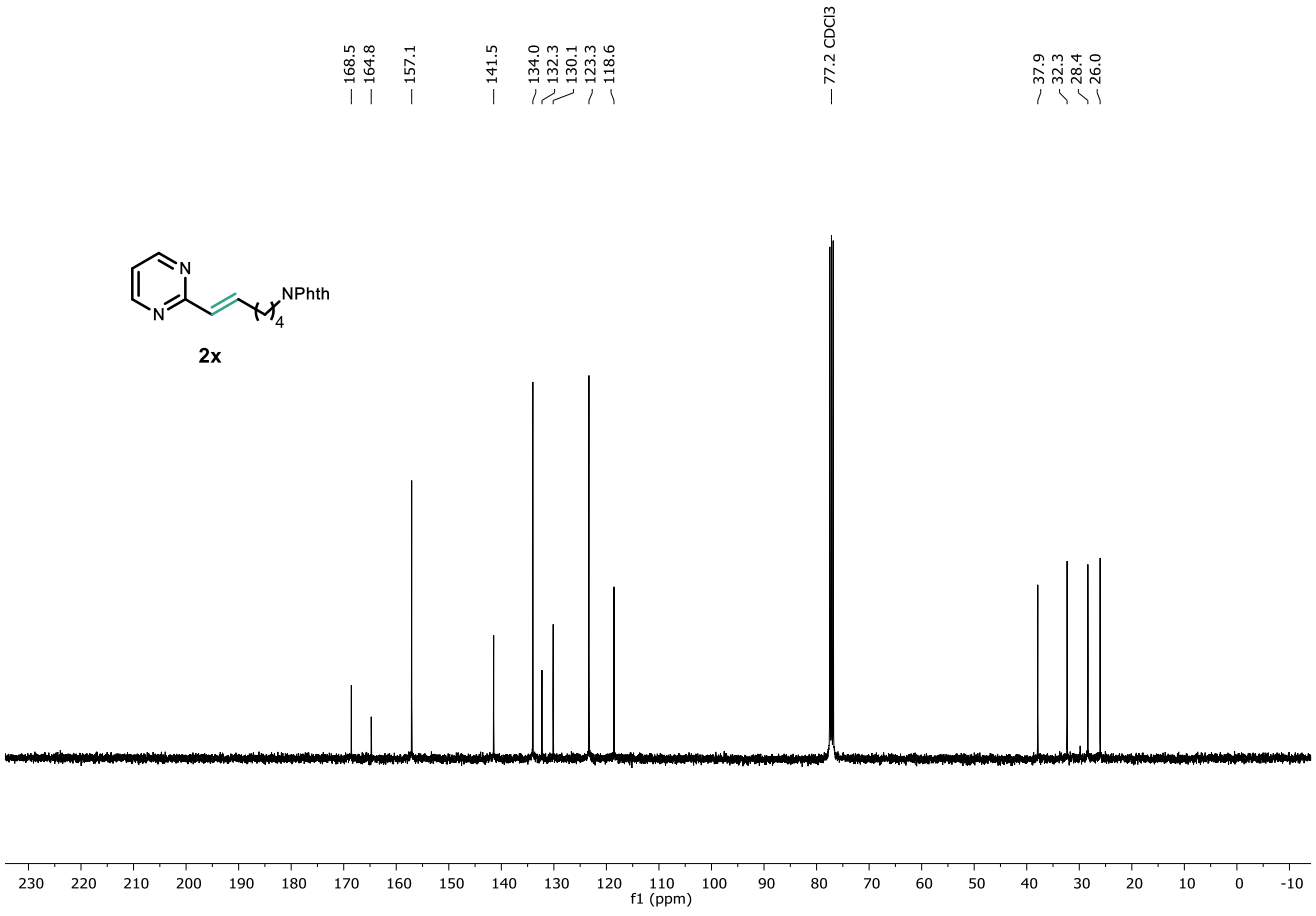
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, *J* = 4.8 Hz, 2H), 7.86–7.80 (m, 2H), 7.74–7.67 (m, 2H), 7.18–7.08 (m, 1H), 7.08–7.02 (m, 1H), 6.55 (d, *J* = 15.6 Hz, 1H), 3.72 (t, *J* = 7.1 Hz, 2H), 2.38–2.33 (m, 2H), 1.80–1.73 (m, 2H), 1.62–1.54 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.5, 164.8, 157.1, 141.5, 134.0, 132.3, 130.1, 123.3, 118.6, 37.9, 32.3, 28.4, 26.0

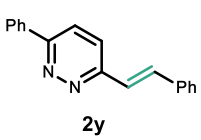
IR (cm^{-1}): 2929, 1770, 1704, 1553, 1418, 1395, 1370, 1039, 978, 719, 530

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{18}H_{18}N_3O_2^+$: 308.1394; found: 308.1399


8.64
8.63
7.86
7.80
7.74
7.67
7.26 CDCl3
7.18
7.08
7.02
6.57
6.53
3.74
3.72
3.70
2.38
2.33
1.80
1.73
1.62
1.54
N
N
NPhth
4
2x
1.84
1.86
2.06
1.00
0.89
1.13
2.49
2.21
2.23
2.23
f1 (ppm)


168.5
164.8
157.1
141.5
134.0
132.3
130.1
123.3
118.6
77.2 CDCl3
37.9
32.3
28.4
26.0
N
N
NPhth
4
2x
f1 (ppm)

***(E)*-3-phenyl-6-styrylpyridazine (2y)**



2y

Compound **2y** was prepared from compound **1y** (52.0 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (4 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 10:1 to 6:1) afforded **2y** (23.0 mg, 45%) as a white solid. It should be noted that **2y** was obtained in 86% NMR yield, but only a modest 45% isolated yield could be achieved due to the compound's instability to chromatography.

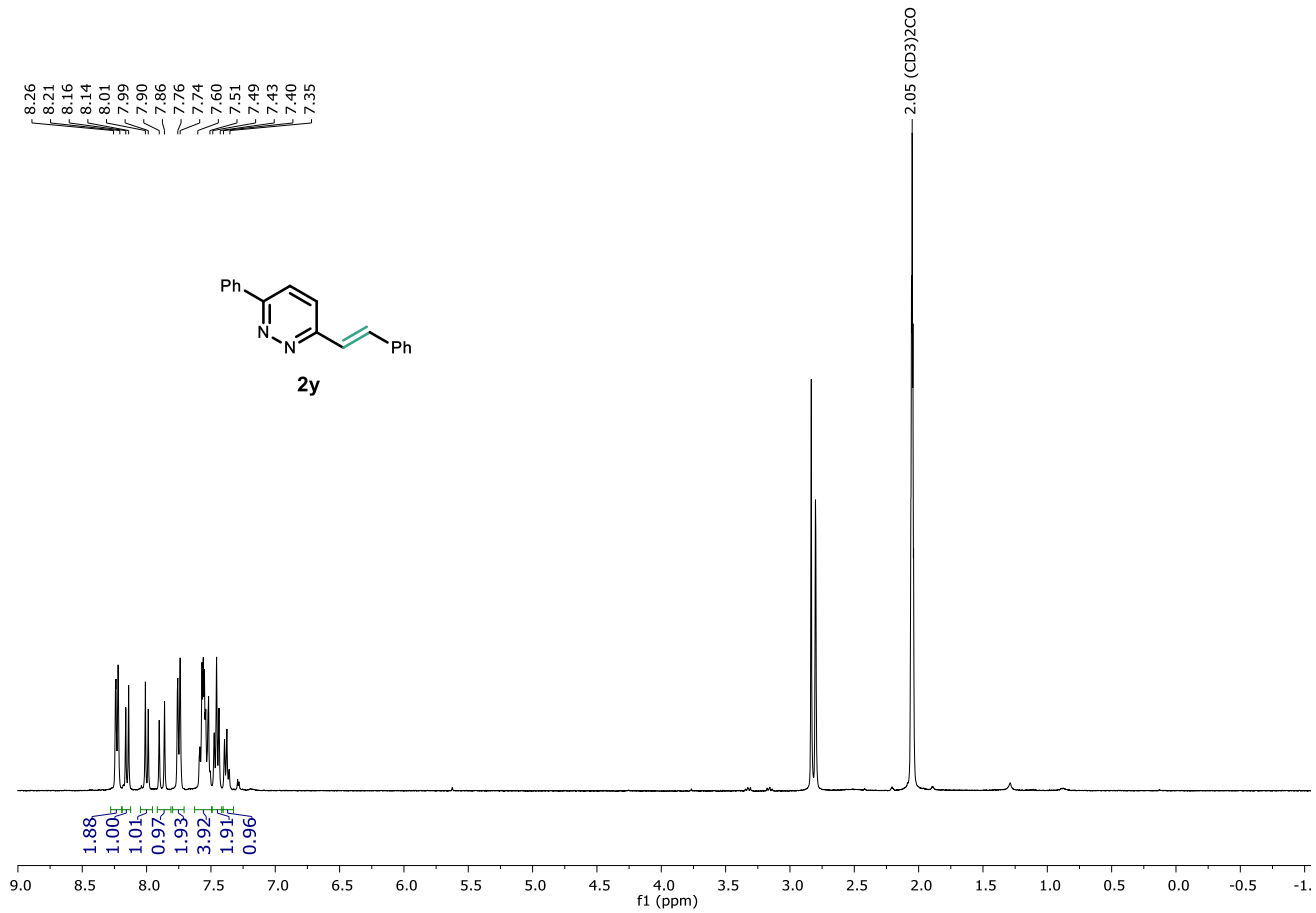
R_f: 0.29 (hexanes/EtOAc = 4:1)

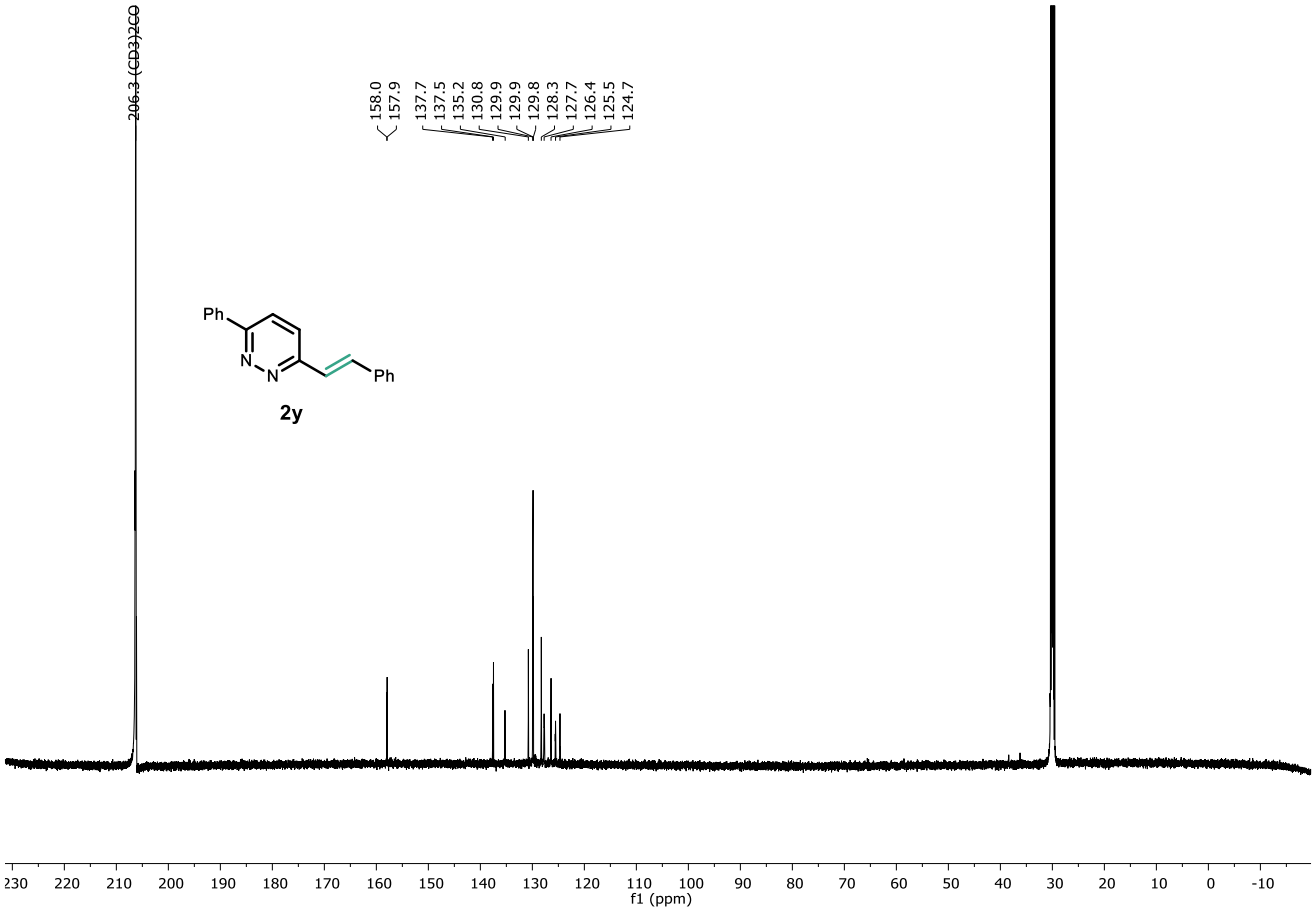
^{1}H NMR (400 MHz, Acetone-d_6): δ 8.26–8.21 (m, 2H), 8.15 (d, J = 8.9 Hz, 1H), 8.00 (d, J = 8.9 Hz, 1H), 7.88 (d, J = 16.5 Hz, 1H), 7.75 (d, J = 6.8 Hz, 2H), 7.60–7.51 (m, 4H), 7.49–7.43 (m, 2H), 7.40–7.35 (m, 1H)

^{13}C NMR (151 MHz, Acetone-d_6): δ 158.0, 157.9, 137.7, 137.5, 135.2, 130.8, 129.9, 129.9, 129.8, 128.3, 127.7, 126.4, 125.5, 124.7

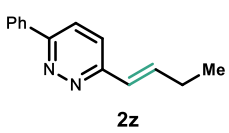
IR (cm^{-1}): 3055, 3033, 1450, 1415, 963, 738, 691

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{18}H_{15}N_2^+$: 259.1230; found: 259.1235


8.26
8.21
8.16
8.14
8.01
7.99
7.90
7.86
7.76
7.74
7.60
7.51
7.49
7.43
7.40
7.35
2.05 (CD3)2CO
Ph
N
N
Ph
2y
1.88
1.00
1.01
0.97
1.93
3.92
1.91
0.96
f1 (ppm)


206.3 (CD3)2CO
158.0
157.9
137.7
137.5
135.2
130.8
129.9
129.9
129.8
128.3
127.7
126.4
125.5
124.7
Ph
N
N
Ph
2y
f1 (ppm)

***(E)*-3-(but-1-en-1-yl)-6-phenylpyridazine (2z)**



2z

Compound **2z** was prepared from compound **1z** (46.0 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (2 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 10:1 to 6:1) afforded **2z** (35.6 mg, 77%) as a white solid.

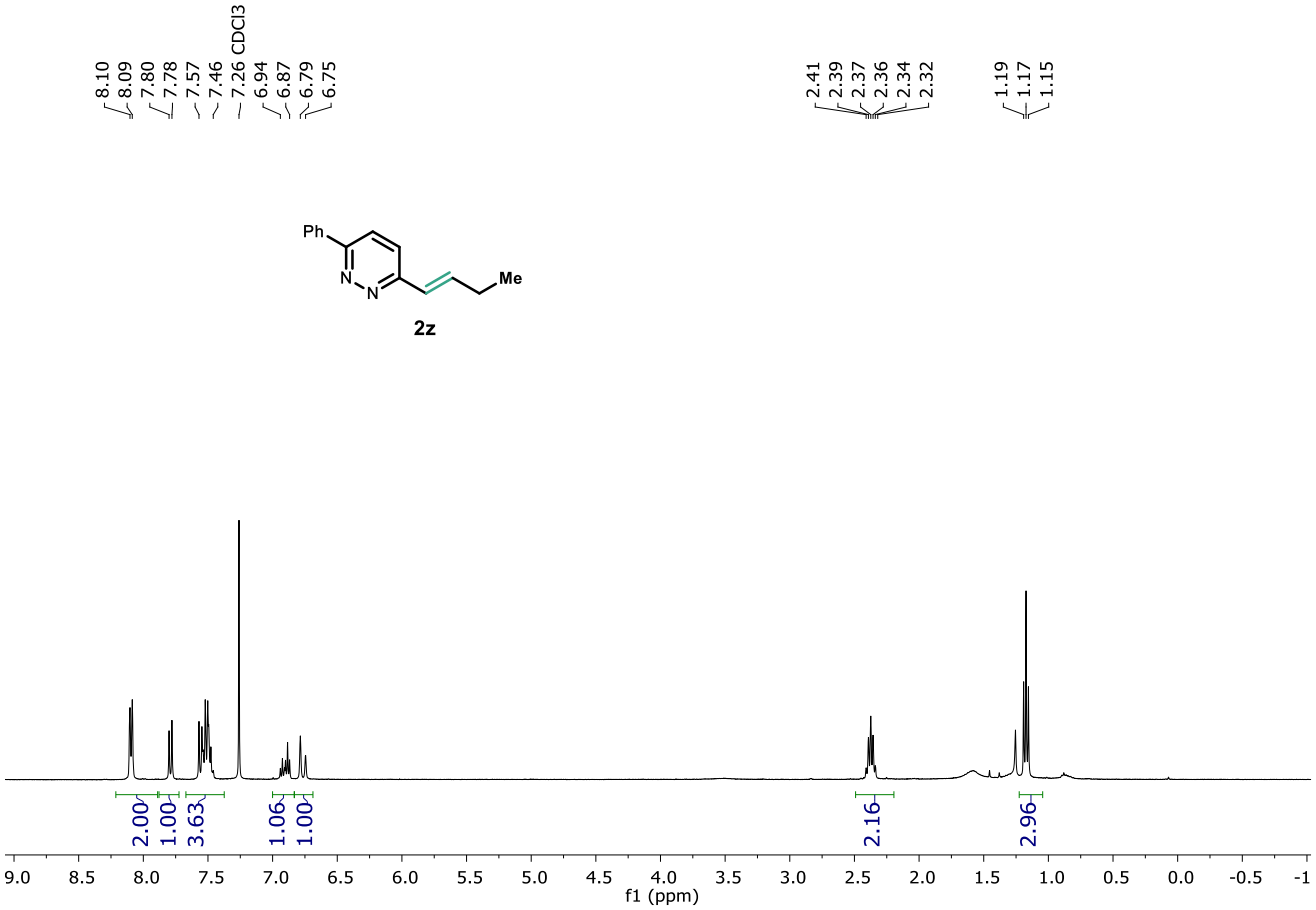
R_f: 0.31 (hexanes/EtOAc = 4:1)

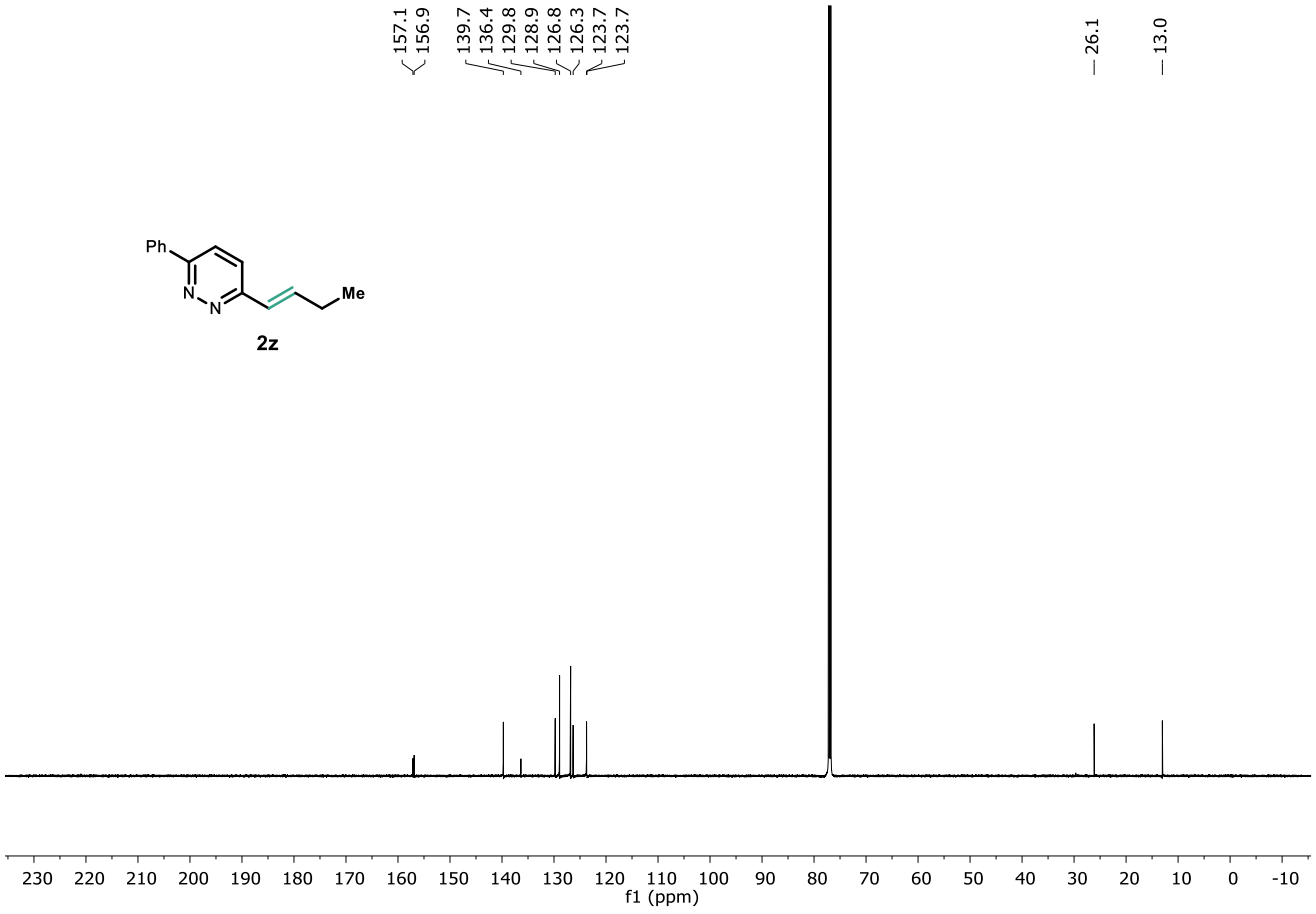
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.0 Hz, 2H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.57–7.46 (m, 4H), 6.94–6.87 (m, 1H), 6.77 (d, *J* = 16.2 Hz, 1H), 2.37 (p, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.4 Hz, 3H)

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.1, 156.9, 139.7, 136.4, 129.8, 128.9, 126.8, 126.3, 123.7, 123.7, 26.1, 13.0

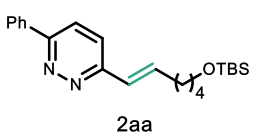
IR (cm^{-1}): 3055, 2965, 2925, 1652, 1585, 1450, 1415, 1123, 969, 869, 754, 697, 572

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{14}H_{15}N_2^+$: 211.1230; found: 211.1235


8.10
8.09
7.80
7.78
7.57
7.46
7.26 CDCl3
6.94
6.87
6.79
6.75
2.41
2.39
2.37
2.36
2.34
2.32
1.19
1.17
1.15
Ph
N
N
Me
2z
2.00
1.00
3.63
1.06
1.00
2.16
2.96
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
-0.5
-1
f1 (ppm)


157.1
156.9
139.7
136.4
129.8
128.9
126.8
126.3
123.7
123.7
26.1
13.0
Ph
N
N
Me
2z
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

(E)-3-(6-((tert-butyldimethylsilyl)oxy)hex-1-en-1-yl)-6-phenylpyridazine (2aa)



2aa

Compound **2aa** was prepared from compound **1aa** (74.0 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (16 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 10:1) afforded **2aa** (61.4 mg, 83%) as a yellow solid.

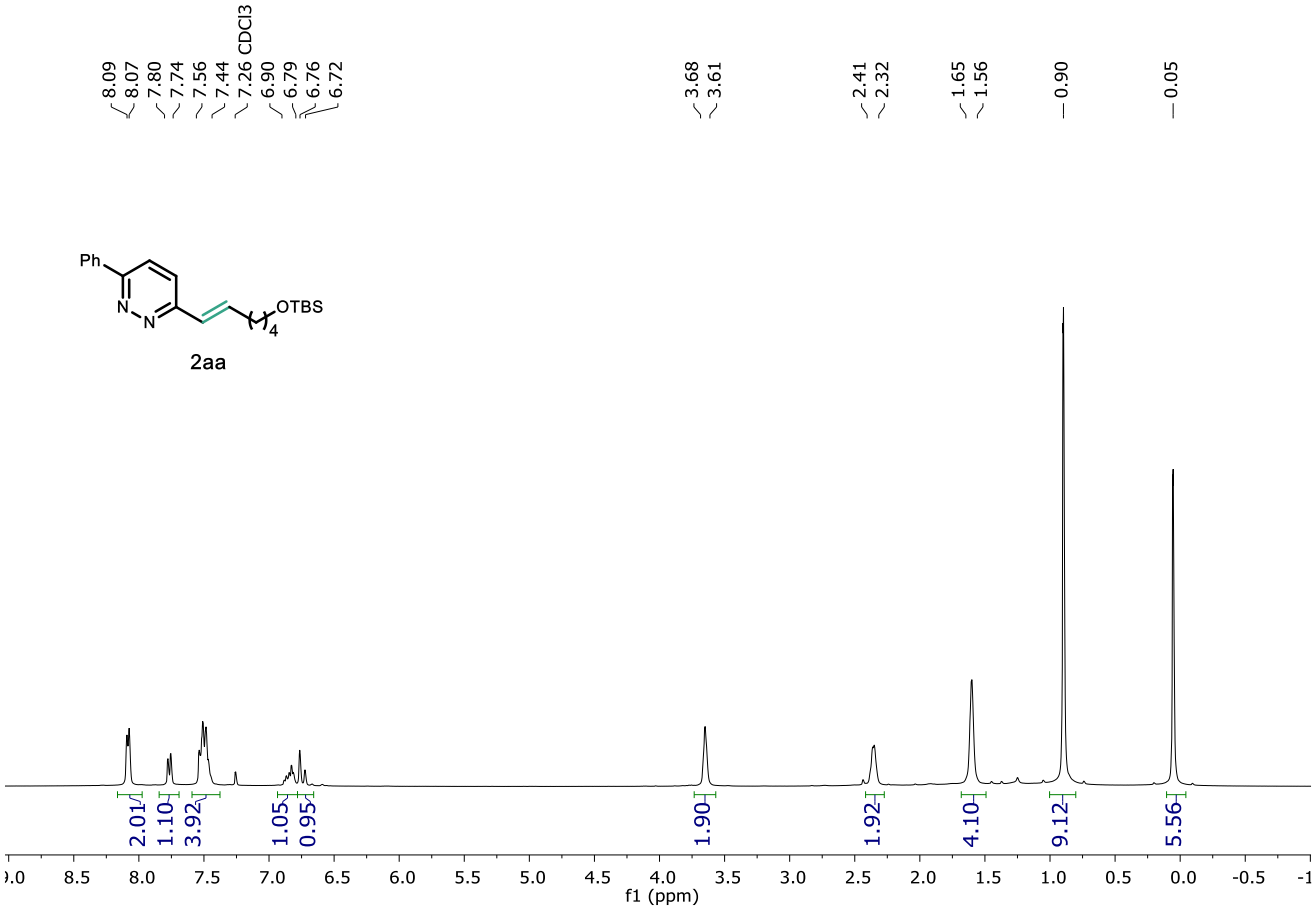
R$_f$: 0.58 (hexanes/EtOAc = 4:1)

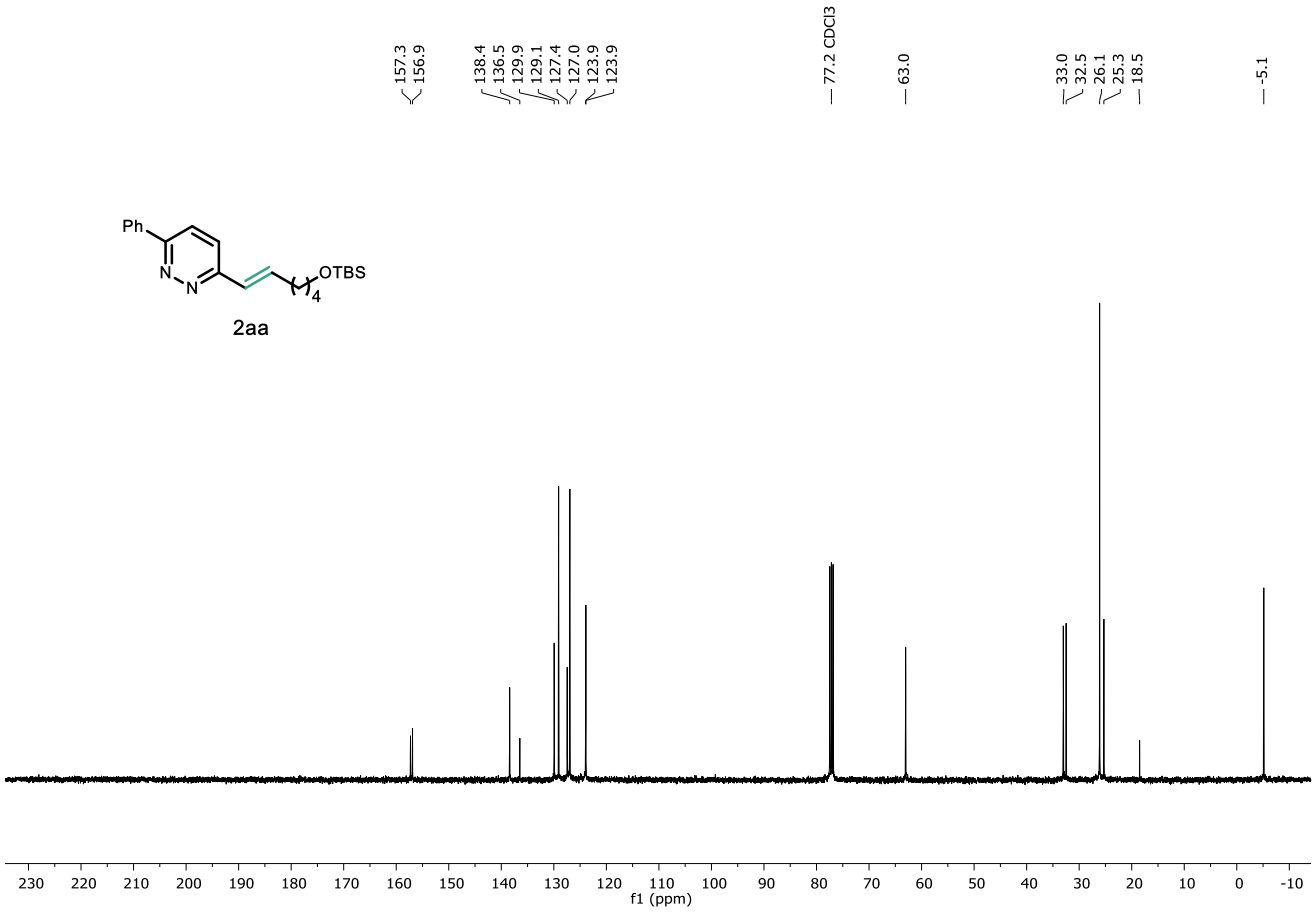
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 6.4 Hz, 2H), 7.77 (d, *J* = 26.4 Hz, 1H), 7.56–7.44 (m, 4H), 6.90–6.79 (m, 1H), 6.74 (d, *J* = 17.1 Hz, 1H), 3.68–3.61 (m, 2H), 2.41–2.32 (m, 2H), 1.65–1.56 (m, 4H), 0.90 (s, 9H), 0.05 (s, 6H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.3, 156.9, 138.4, 136.5, 129.9, 129.1, 127.4, 127.0, 123.9, 123.9, 63.0, 33.0, 32.5, 26.1, 25.3, 18.5, –5.1

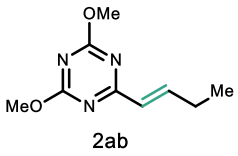
IR (cm^{-1}): 2928, 2856, 1652, 1416, 1255, 1099, 836, 776, 694

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{22}H_{33}N_2OSi^+$: 369.2357; found: 369.2362


8.09
8.07
7.80
7.74
7.56
7.44
7.26 CDCl3
6.90
6.79
6.76
6.72
3.68
3.61
2.41
2.32
1.65
1.56
0.90
0.05
Ph
N
N
OTBS
4
2aa
2.01
1.10
3.92
1.05
0.95
1.90
1.92
4.10
9.12
5.56
f1 (ppm)


157.3
156.9
138.4
136.5
129.9
129.1
127.4
127.0
123.9
123.9
77.2 CDCl3
63.0
33.0
32.5
26.1
25.3
18.5
-5.1
Ph
N
N
OTBS
4
2aa
f1 (ppm)

***(E)*-2-(but-1-en-1-yl)-4,6-dimethoxy-1,3,5-triazine (2ab)**



2ab

Compound **2ab** was prepared from compound **1ab** (39.4 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (3 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 10:1) afforded **2ab** (12.2 mg, 30%) as a yellow oil.

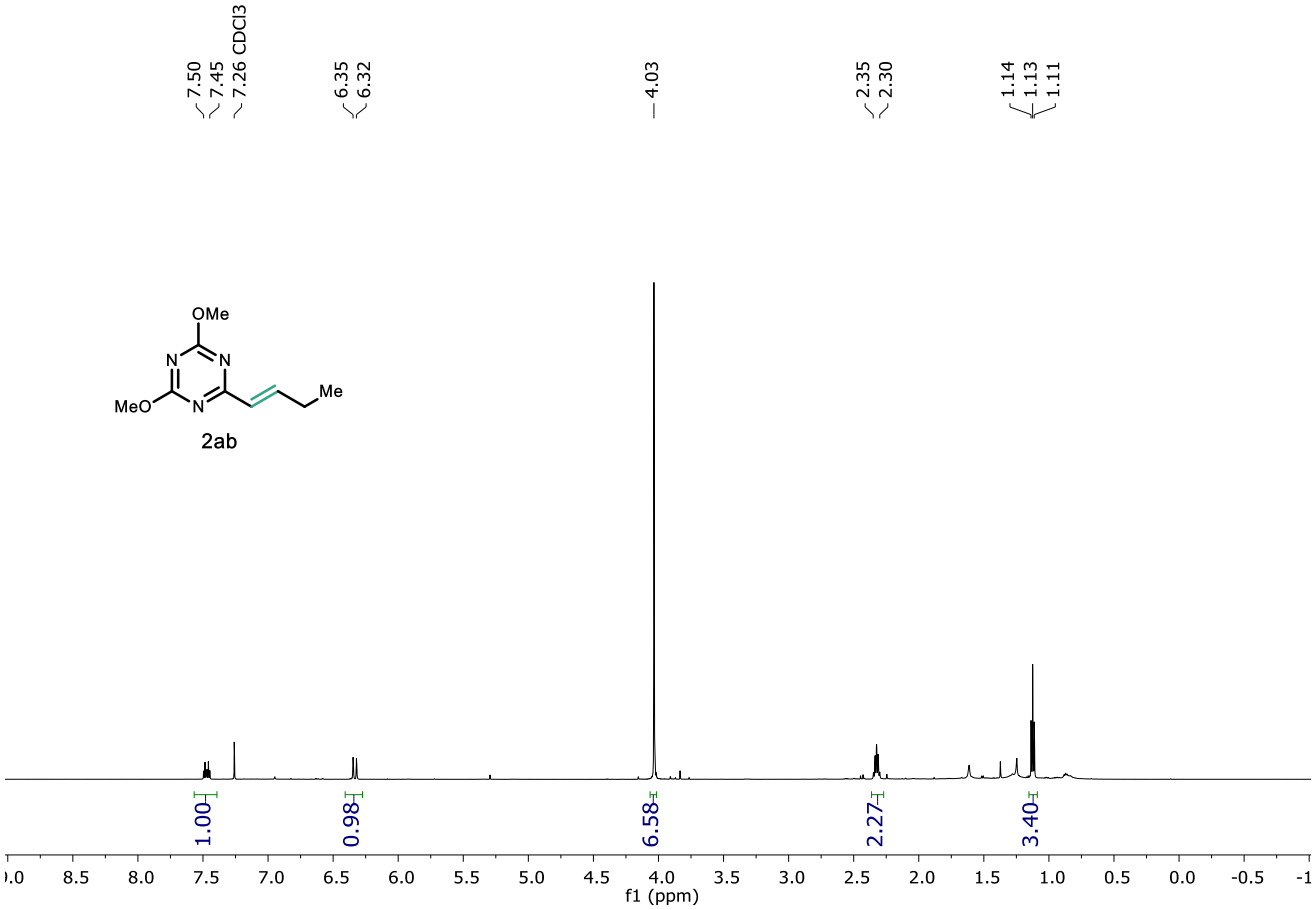
R_f: 0.45 (hexanes/EtOAc = 4:1)

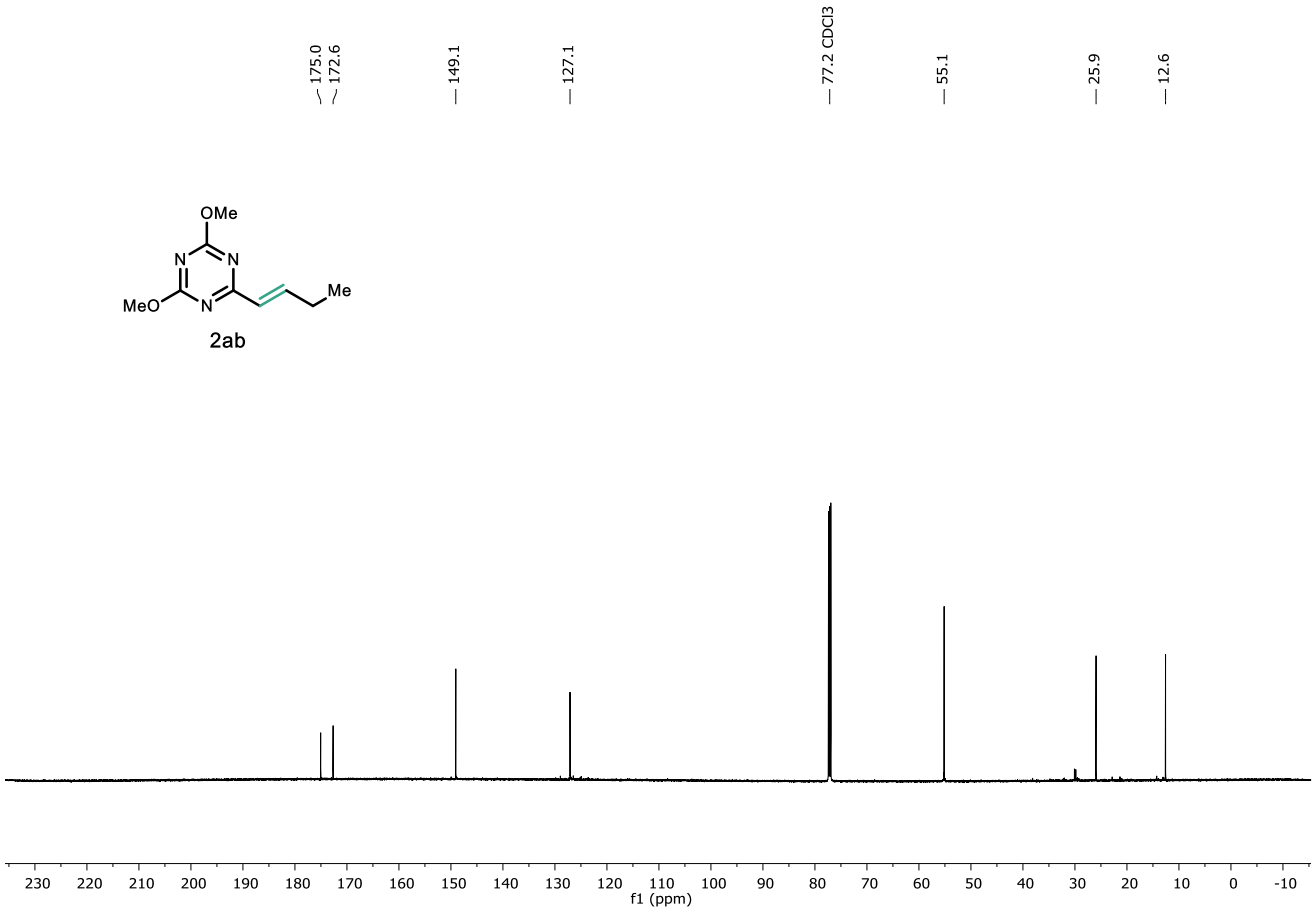
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50–7.45 (m, 1H), 6.33 (d, *J* = 15.6 Hz, 1H), 4.03 (s, 6H), 2.35–2.30 (m, 2H), 1.13 (t, *J* = 7.5 Hz, 3H)

^{13}C NMR (151 MHz, $CDCl_3$): δ 175.0, 172.6, 149.1, 127.1, 55.1, 25.9, 12.6

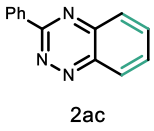
IR (cm^{-1}): 2932, 1543, 1500, 1459, 1353, 1111, 1083, 820

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_9H_{14}N_3O_2^+$: 196.1081; found: 196.1086


7.50
7.45
7.26 CDCl3
6.35
6.32
4.03
2.35
2.30
1.14
1.13
1.11
OMe
N
N
MeO
N
Me
2ab
1.00
0.98
6.58
2.27
3.40
f1 (ppm)


175.0
172.6
149.1
127.1
77.2 CDCl3
55.1
25.9
12.6
OMe
N
N
MeO
N
Me
2ab
f1 (ppm)

***(E)*- 3-phenylbenzo[e][1,2,4]triazine (2ac)**



2ac

Compound **2ac** was prepared from compound **1ac** (21.0 mg, 0.10 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (3 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 8:1 to 5:1) afforded **2ac** (12.1 mg, 58%) as a white solid.

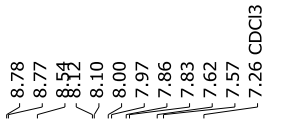
R_f: 0.64 (hexanes/EtOAc = 2:1)

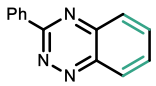
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.77 (d, *J* = 8.1 Hz, 2H), 8.55 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 8.00–7.97 (m, 1H), 7.86–7.83 (m, 1H), 7.62–7.57 (m, 3H)

^{13}C NMR (151 MHz, $CDCl_3$): δ 160.0, 146.6, 141.3, 135.8, 135.7, 131.6, 130.3, 129.8, 129.3, 129.1, 128.9

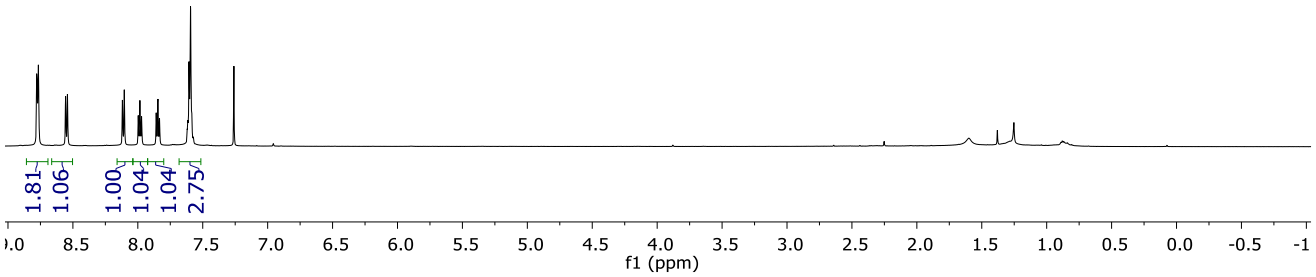
IR (cm^{-1}): 3063, 2924, 2854, 1510, 1331, 1018, 772, 703, 552

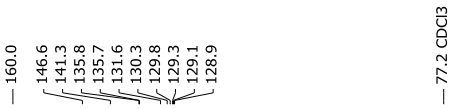
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{13}H_{10}N_3^+$: 208.0869; found: 208.0875

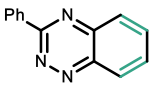

8.78
8.77
8.54
8.12
8.10
8.00
7.97
7.86
7.83
7.62
7.57
7.26 CDCl3


Ph
N
N
N

2ac


1.81
1.06
1.00
1.04
1.04
2.75
f1 (ppm)


160.0
146.6
141.3
135.8
135.7
131.6
130.3
129.8
129.3
129.1
128.9
77.2 CDCl3


Ph
N
N
N

2ac

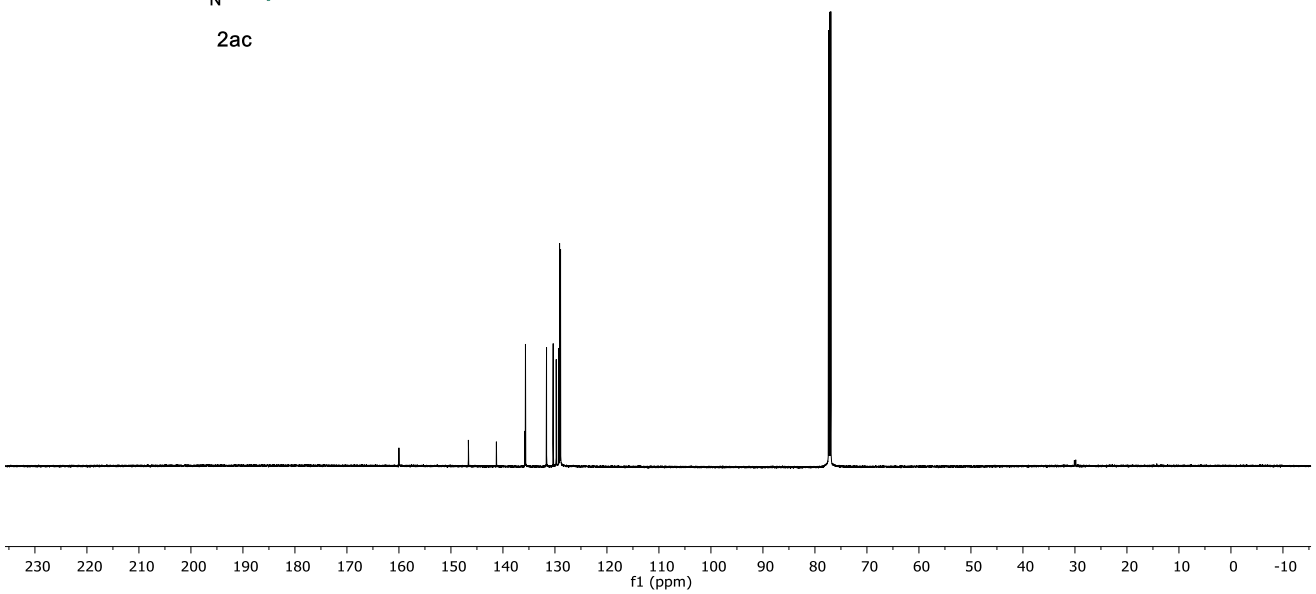
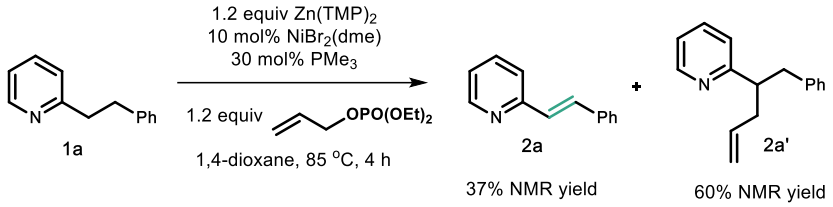

f1 (ppm)

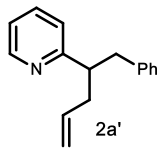
Figure SI-4. Characterization of allylation byproduct



To a flame-dried microwave vial equipped with a magnetic stir bar was added starting material **1a** (36.6 mg, 0.20 mmol, 1.0 equiv). The reaction vessel was evacuated and backfilled with N_2 (this process was repeated three times). To the reaction vessel was added 1,4-dioxane (1.5 mL) and commercial $Zn(TMP)_2$ (0.48 mL, 0.5 M in toluene, 0.24 mmol, 1.2 equiv) at room temperature. Then to this mixture was added a stock solution of $NiBr_2$(dme) (6.2 mg, 0.02 mmol, 10 mol %), PMe_3 (0.06 mL, 1.0 M in THF, 0.06 mmol, 30 mol%), and allyl diethyl phosphate (42 μL, 0.24 mmol, 1.2 equiv) in 1,4-dioxane (0.5 mL, 0.5 M). The reaction vessel was sealed with parafilm, placed into a pre-heated 85 ºC oil bath, and stirred until complete consumption of starting material was observed as determined by TLC analysis.

The reaction mixture was cooled to ambient temperature and quenched by the addition of sat. aq. NH_4Cl (5 mL). The reaction mixture was diluted with EtOAc (5 mL) and the organic phase was separated. The aqueous phase was extracted with EtOAc (3 × 5 mL) and the combined organic extracts were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation. ^{1}H-NMR yield was determined using 1,3,5-trimethoxybenzene as an internal standard.

2-(1-phenylpent-4-en-2-yl)pyridine (2a')



2a' was isolated by preparatory thin layer chromatography (hexanes/EtOAc = 5:1) as a colorless oil.

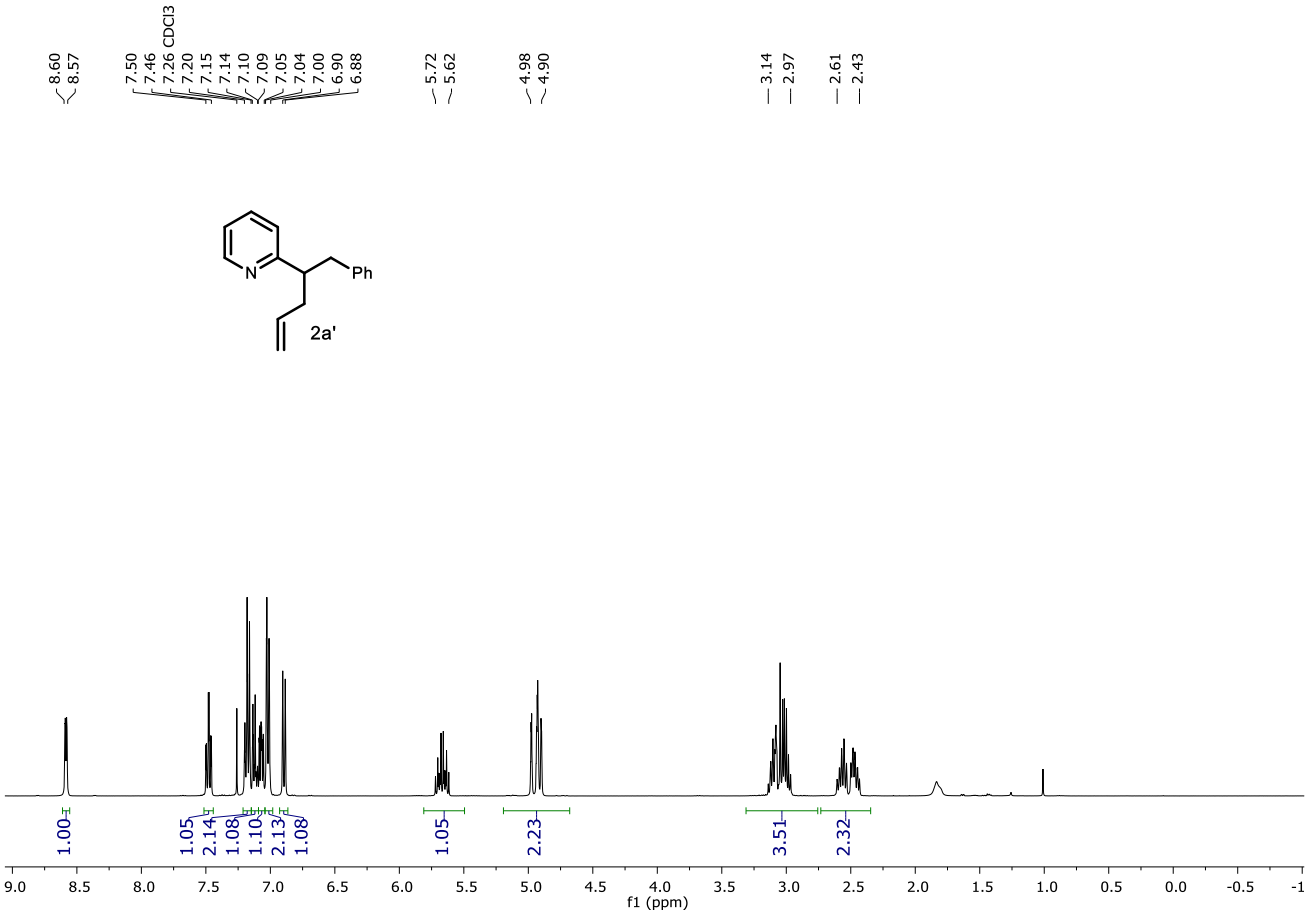
R$_f$: 0.48 (hexanes/EtOAc = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60–8.57 (m, 1H), 7.50–7.46 (m, 1H), 7.20–7.15 (m, 2H), 7.14–7.05 (m, 2H), 7.04–7.00 (m, 2H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.72–5.62 (m, 1H), 4.98–4.90 (m, 2H), 3.14–2.97 (m, 3H), 2.61–2.43 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 163.5, 149.5, 140.5, 136.7, 136.0, 129.2, 128.2, 125.9, 123.5, 121.4, 116.4, 49.7, 41.4, 39.1

IR (cm^{-1}): 3062, 3026, 2920, 1640, 1589, 1569, 1472, 1454, 1434, 994, 911, 744, 698

GC-MS (m/z): [M] calc'd for $C_{16}H_{17}N$: 223.1; found: 223.2


8.60
8.57
7.50
7.46
7.26 CDCl3
7.20
7.15
7.14
7.10
7.09
7.05
7.04
7.00
6.90
6.88
5.72
5.62
4.98
4.90
3.14
2.97
2.61
2.43
N
Ph
2a'
1.00
1.05
2.14
1.08
1.10
2.13
1.08
1.05
2.23
3.51
2.32
f1 (ppm)

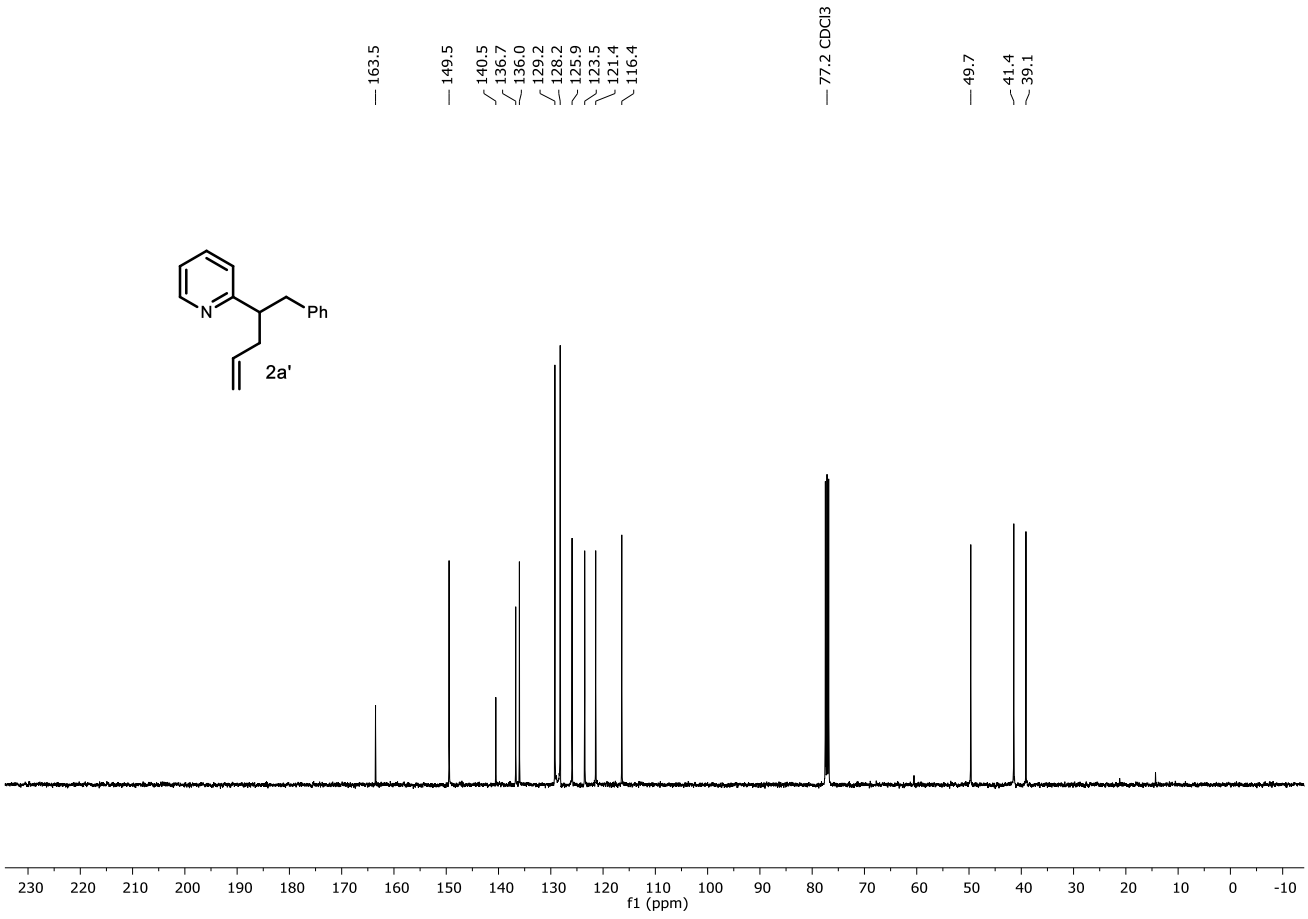
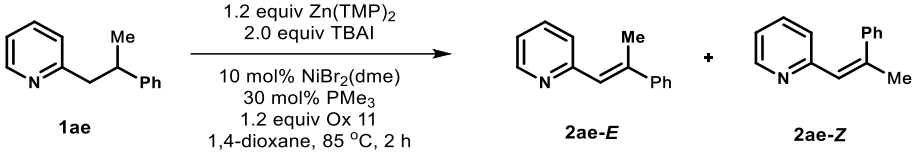

163.5
149.5
140.5
136.7
136.0
129.2
128.2
125.9
123.5
121.4
116.4
77.2 CDCl3
49.7
41.4
39.1
N
Ph
2a'
f1 (ppm)

Figure SI-5. Dehydrogenation of *β,β*–disubstituted substrate **1ae**



Compound **2ae** was prepared from compound **1ae** (39.4 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (12 hours). ^{1}H NMR yield was determined using 1,3,5-trimethoxybenzene as an internal standard. NMR yield: **2ae-*E*** 25%, **2ae-*Z*** 27%, and the conversion is 53%. **2ae-*E*** was isolated by preparatory thin layer chromatography (hexanes/EtOAc = 5:1) as a colorless oil, but **2ae-*Z*** is copolar with **1ae**. The characterizatioin data match those previously reported in the literature.[18]

(E)-2-(2-phenylprop-1-en-1-yl)pyridine (2ae-*E*)

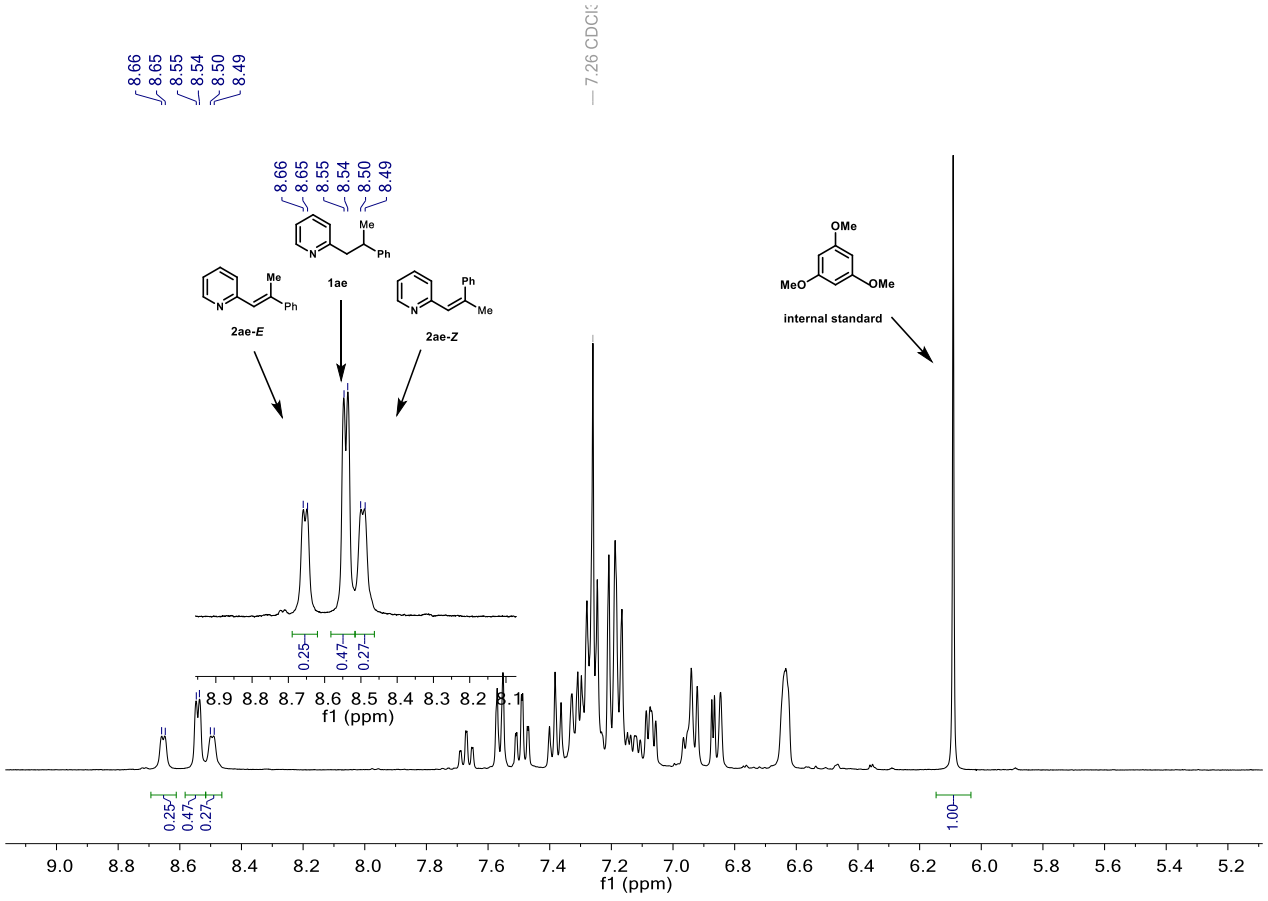
R$_f$: 0.48 (hexanes/EtOAc = 4:1)

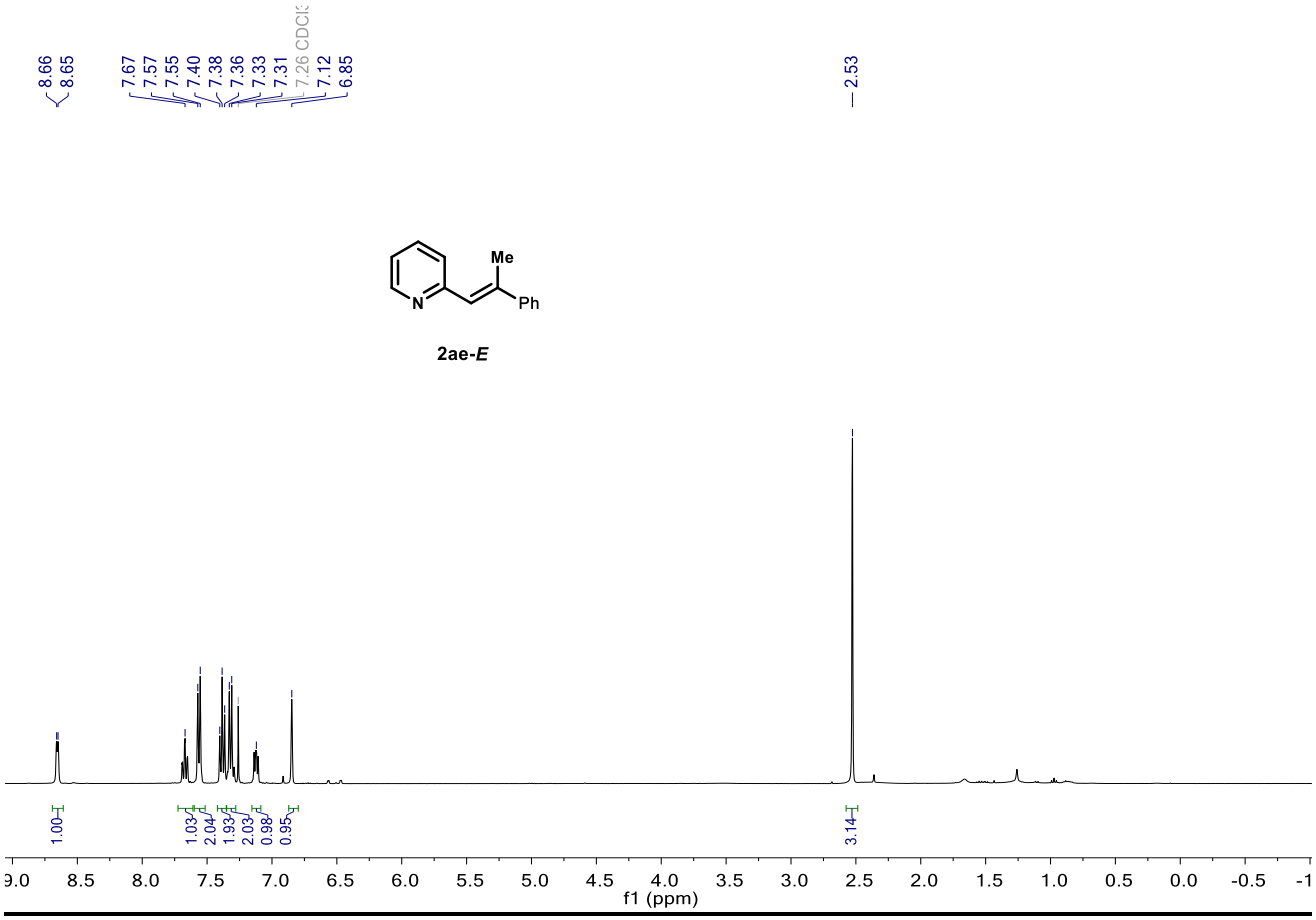
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, *J* = 4.3 Hz, 1H), 7.67 (td, *J* = 7.7, 1.8 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.12 (dd, *J* = 7.1, 5.2 Hz, 1H), 6.85 (s, 1H), 2.53 (s, 3H)

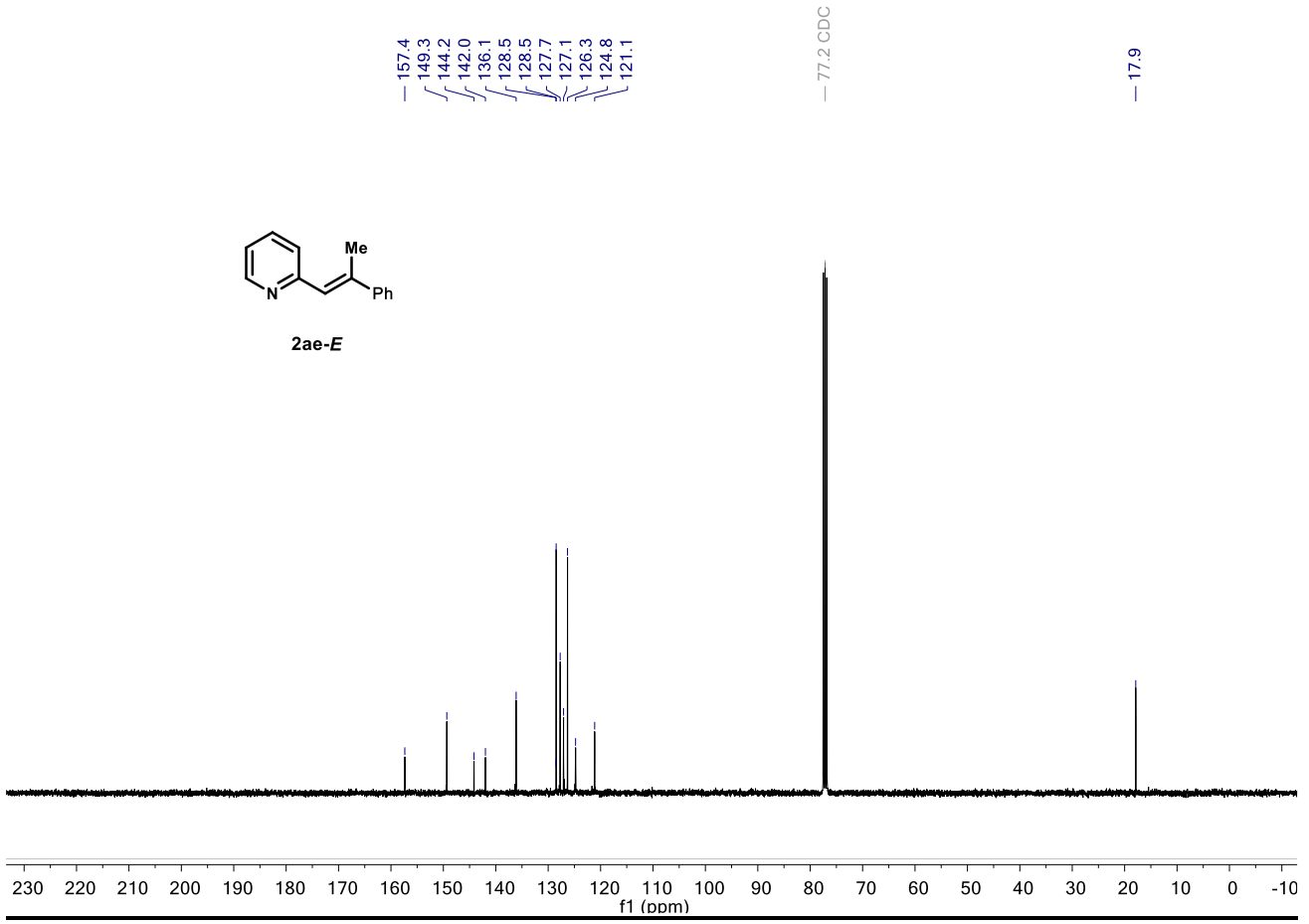
^{13}C NMR (101 MHz, $CDCl_3$): δ 157.4, 149.3, 144.2, 142.0, 136.1, 128.5, 128.5, 127.7, 127.1, 126.3, 124.8, 121.1, 17.9

IR (cm^{-1}): 3058, 2920, 1628, 1583, 1558, 1470, 1445, 1424, 1149, 1069, 892, 870, 757, 694

GC-MS (m/z): [M] calc'd for $C_{14}H_{13}N$: 195.1; found: 195.1

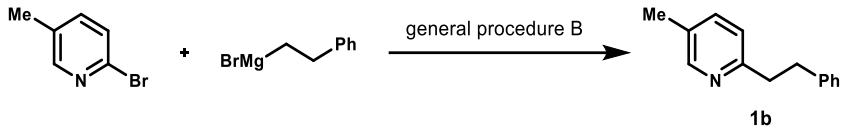



8.66
8.65
7.67
7.57
7.55
7.40
7.38
7.36
7.33
7.31
7.26 CDCl3
7.12
6.85
2.53
Me
N
Ph
2ae-E
1.00
1.03
2.04
1.93
2.03
0.98
0.95
3.14
f1 (ppm)


157.4
149.3
144.2
142.0
136.1
128.5
128.5
127.7
127.1
126.3
124.8
121.1
77.2 CDC
17.9
Me
N
Ph
2ae-E
f1 (ppm)

Characterization Data for Substrates

5-methyl-2-phenethylpyridine (1b)



1b

Compound **1b** was prepared from 2-bromo-5-methylpyridine (344 mg, 2.0 mmol, 1.0 equiv) according to **general procedure B**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 20:1 to 10:1) afforded **1b** (315 mg, 80%) as a colorless oil.

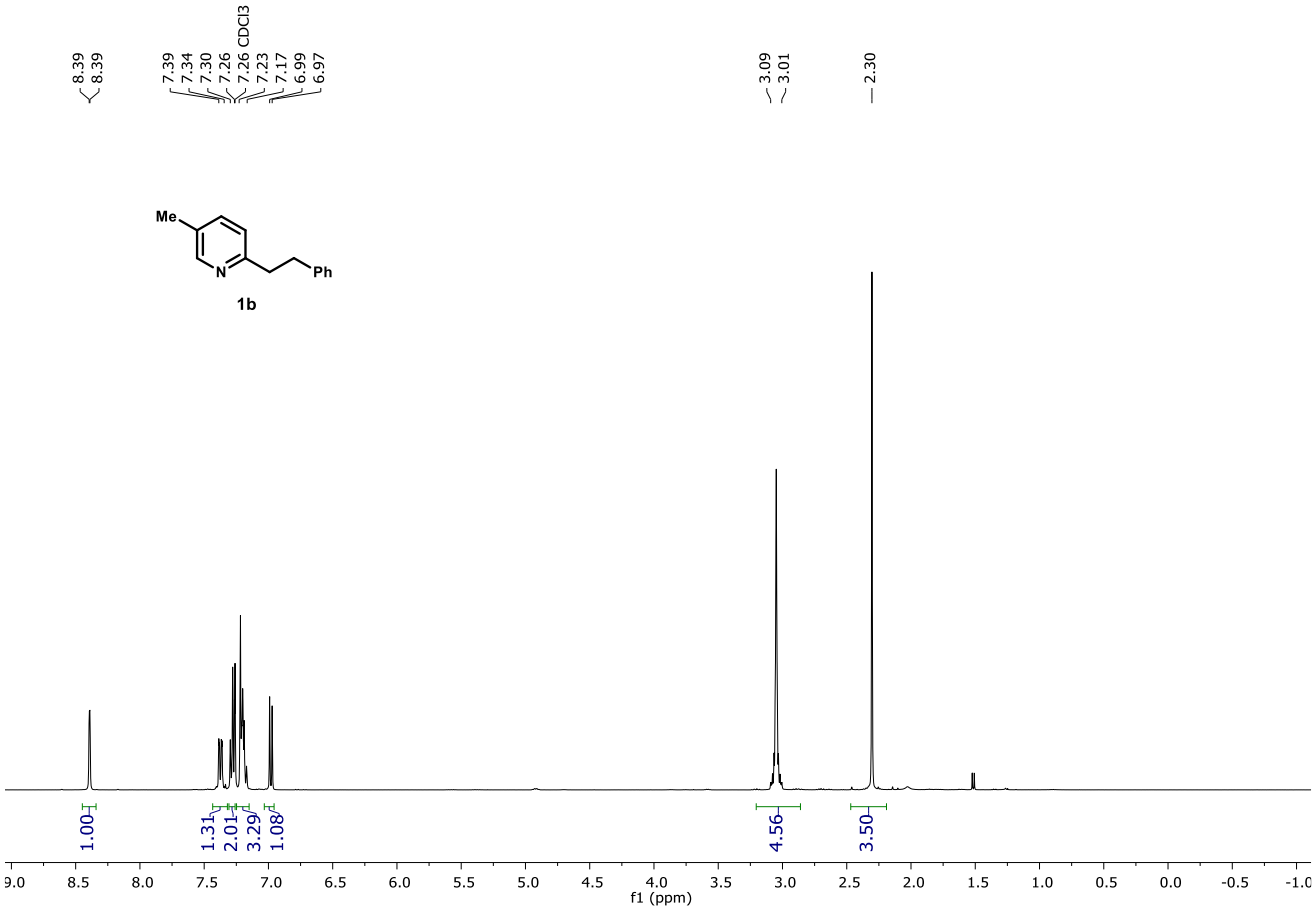
R_f: 0.30 (hexanes/EtOAc = 4:1)

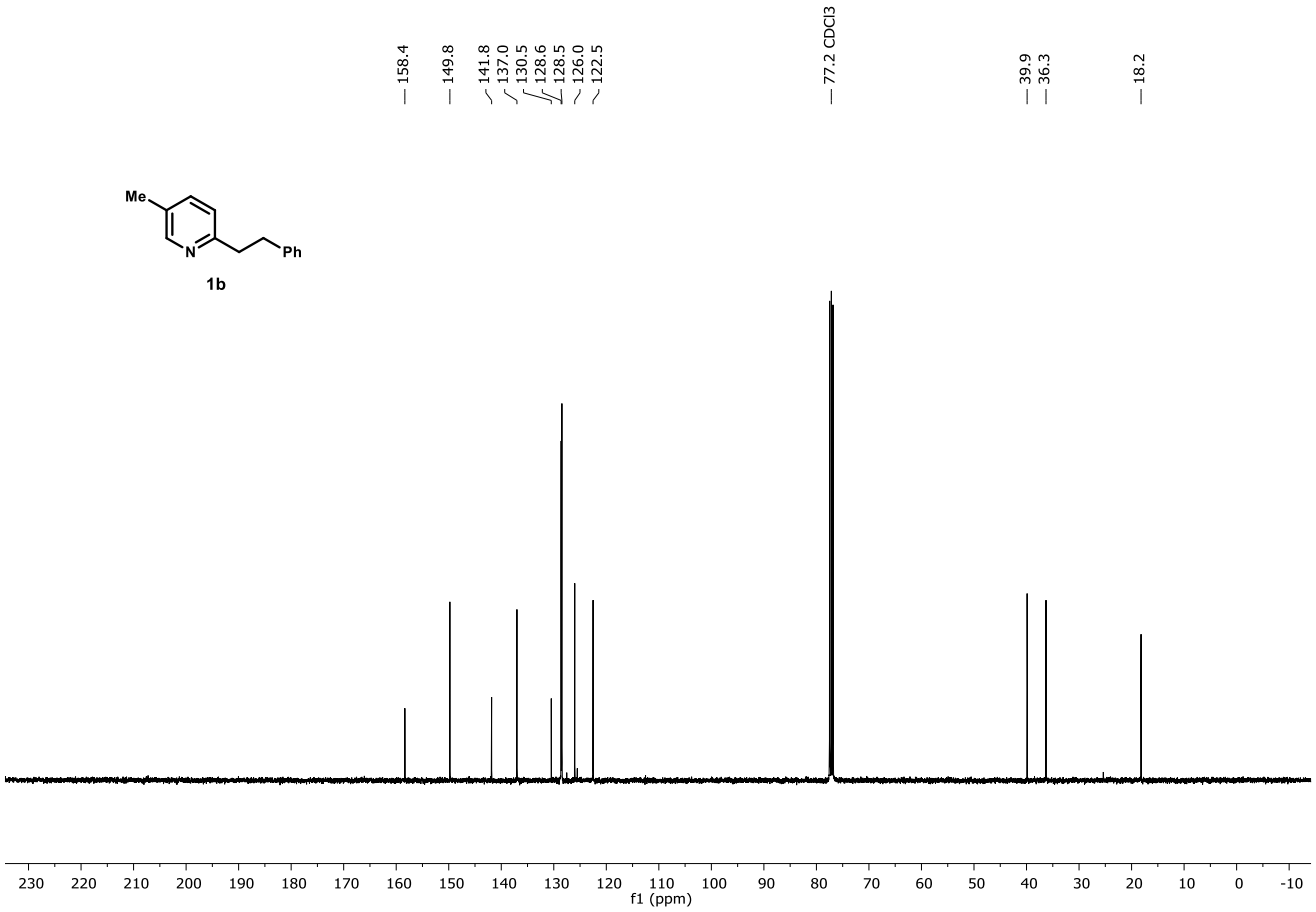
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 2.3 Hz, 1H), 7.39–7. 34 (m, 1H), 7.30–7.26 (m, 2H), 7.23–7.17 (m, 3H), 6.98 (d, *J* = 7.9 Hz, 1H), 3.09–3.01 (m, 4H), 2.30 (s, 3H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 158.4, 149.8, 141.8, 137.0, 130.5, 128.6, 128.5, 126.0, 122.5, 39.9, 36.3, 18.2

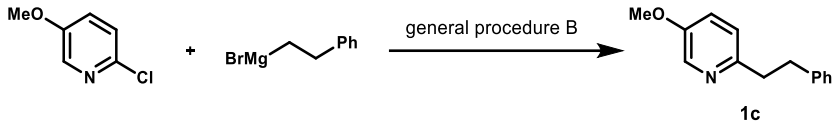
IR (cm^{-1}): 3026, 2924, 1602, 1570, 1487, 1453, 1382, 1030, 819, 697, 524

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{14}H_{16}N^+$: 198.1277; found: 198.1283


8.39
8.39
7.39
7.34
7.30
7.26
7.26 CDCl3
7.23
7.17
6.99
6.97
3.09
3.01
2.30
Me
N
Ph
1b
1.00
1.31
2.01
3.29
1.08
4.56
3.50
f1 (ppm)


158.4
149.8
141.8
137.0
130.5
128.6
128.5
126.0
122.5
77.2 CDCl3
39.9
36.3
18.2
Me
N
Ph
1b
f1 (ppm)

5-methoxy-2-phenethylpyridine (1c)



1c

Compound **1c** was prepared from 2-chloro-5-methoxypyridine (359 mg, 2.5 mmol, 1.0 equiv) according to **general procedure B**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 10:1 to 7:1) afforded **1c** (445 mg, 84%) as a colorless oil.

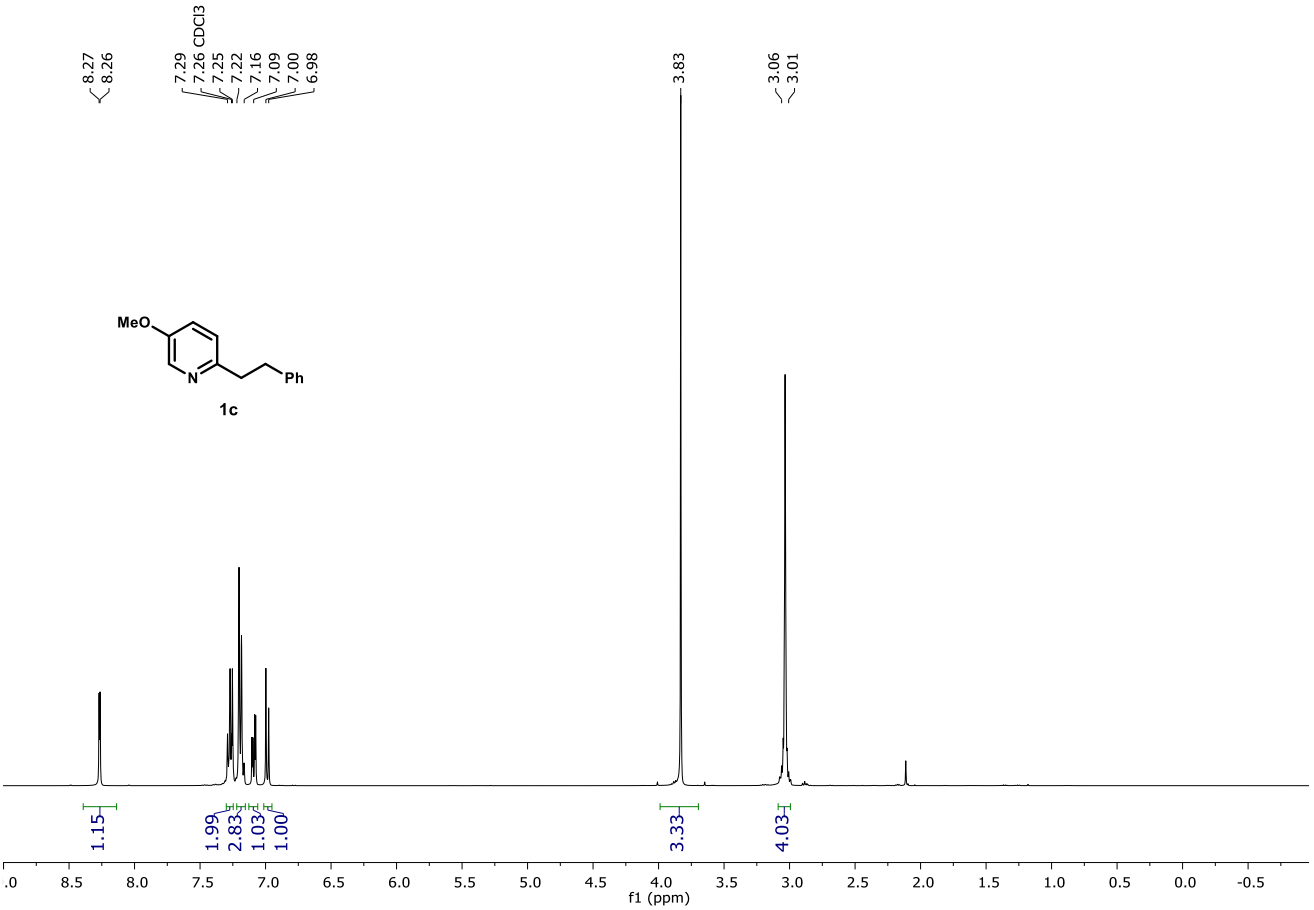
R_f: 0.29 (hexanes/EtOAc = 4:1)

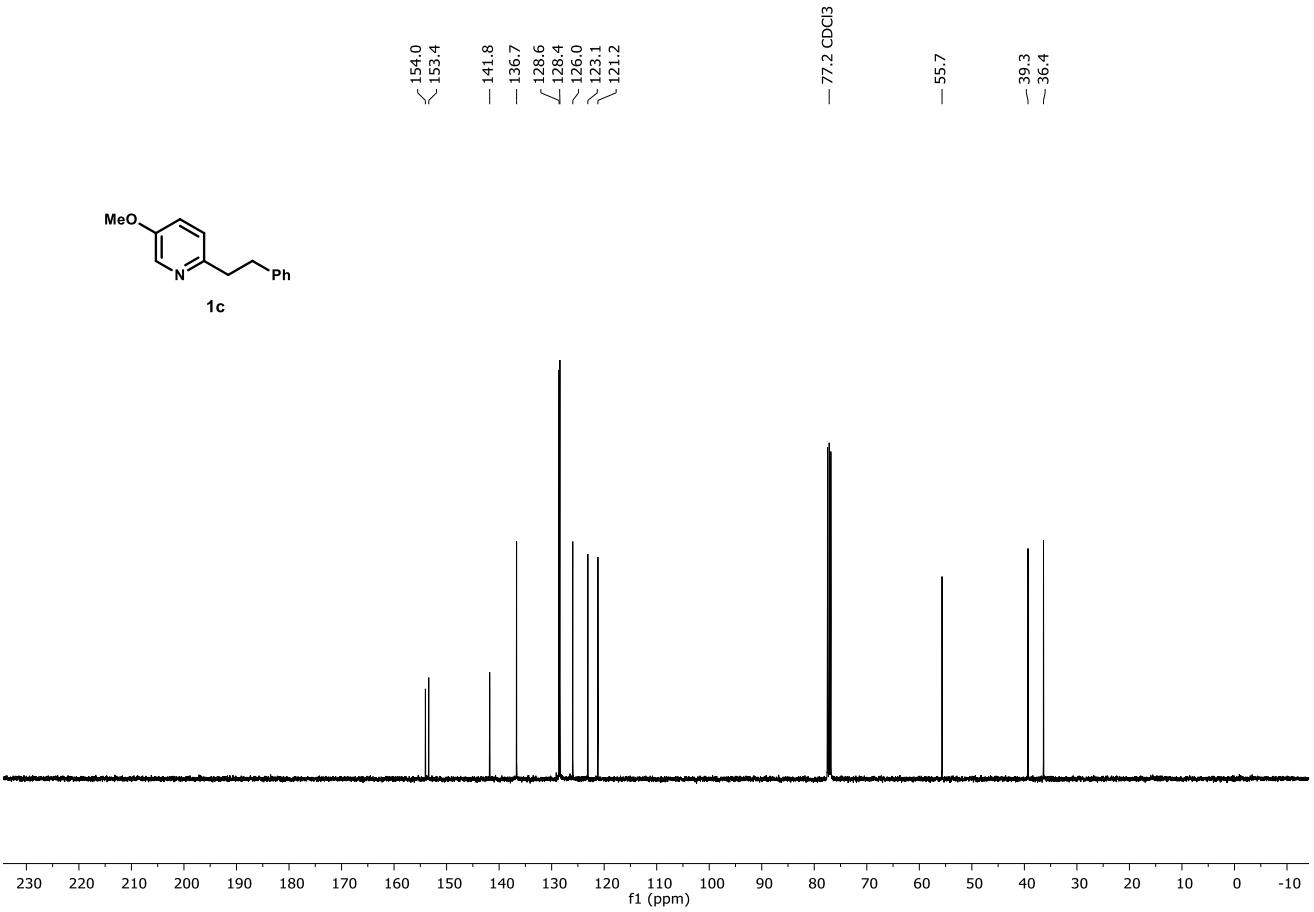
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 3.0 Hz, 1H), 7.29–7.25 (m, 2H), 7.22–7.16 (m, 3H), 7.09 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 3.83 (s, 3H), 3.06–3.01 (m, 4H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.0, 153.4, 141.8, 136.7, 128.6, 128.4, 126.0, 123.1, 121.2, 55.7, 39.3, 36.4

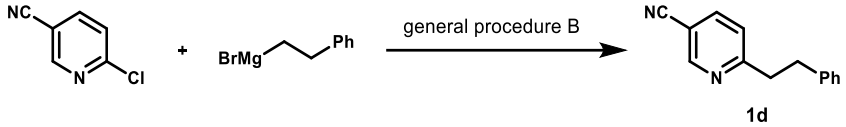
IR (cm^{-1}): 3025, 2938, 2838, 1572, 1483, 1264, 1235, 1031, 826, 750, 697, 535

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{14}H_{16}NO^+$: 214.1226; found: 214.1232


8.27
8.26
7.29
7.26 CDCl3
7.25
7.22
7.16
7.09
7.00
6.98
3.83
3.06
3.01
MeO
N
Ph
1c
1.15
1.99
2.83
1.03
1.00
3.33
4.03
f1 (ppm)


154.0
153.4
141.8
136.7
128.6
128.4
126.0
123.1
121.2
77.2 CDCl3
55.7
39.3
36.4
MeO
N
Ph
1c
f1 (ppm)

6-phenethylnicotinonitrile (1d)



1d

Compound **1d** was prepared from 6-chloronicotinonitrile (277 mg, 2.0 mmol, 1.0 equiv) according to **general procedure B**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 10:1 to 7:1) afforded **1d** (240 mg, 58%) as a white solid.

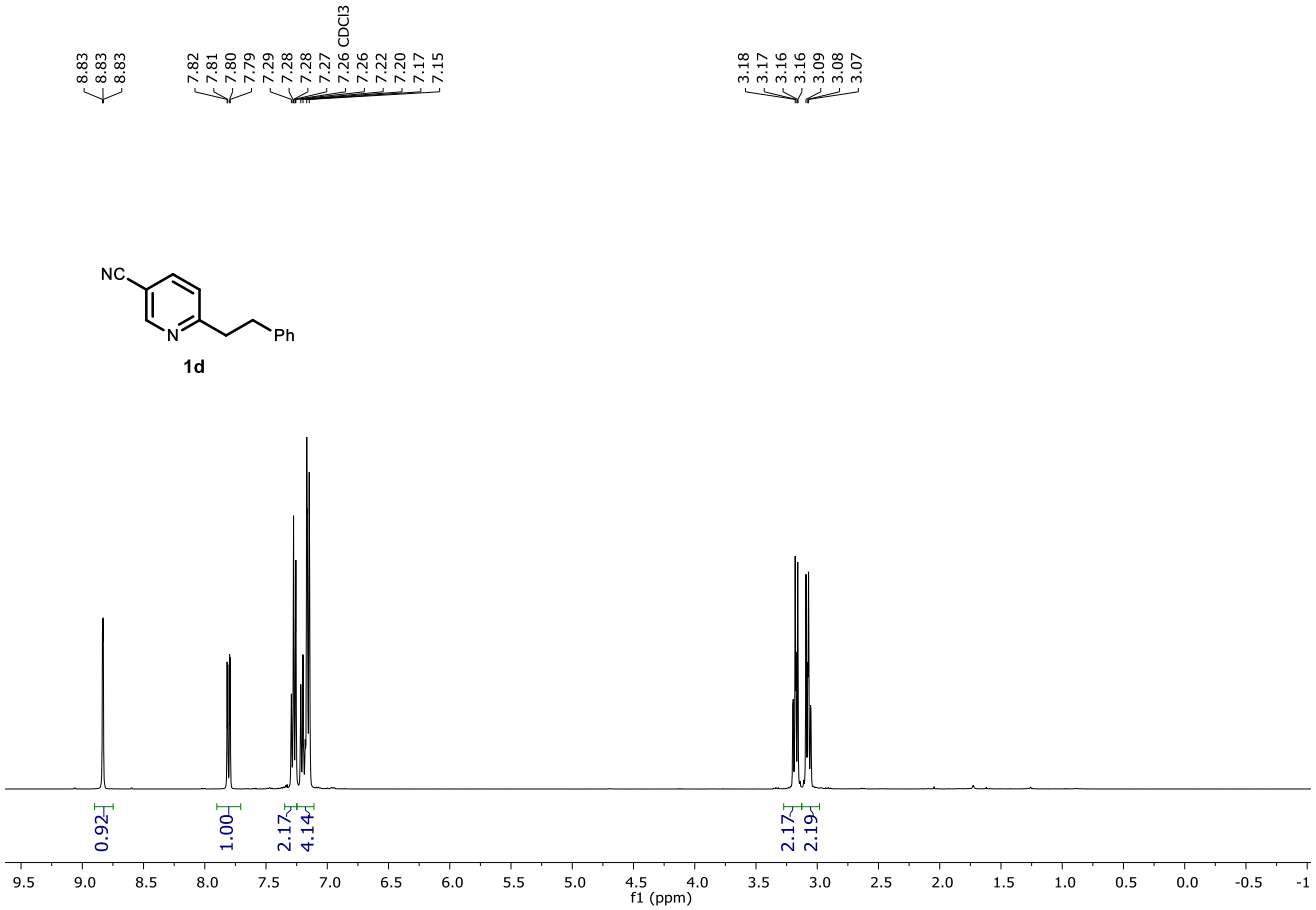
R_f: 0.38 (hexanes/EtOAc = 4:1)

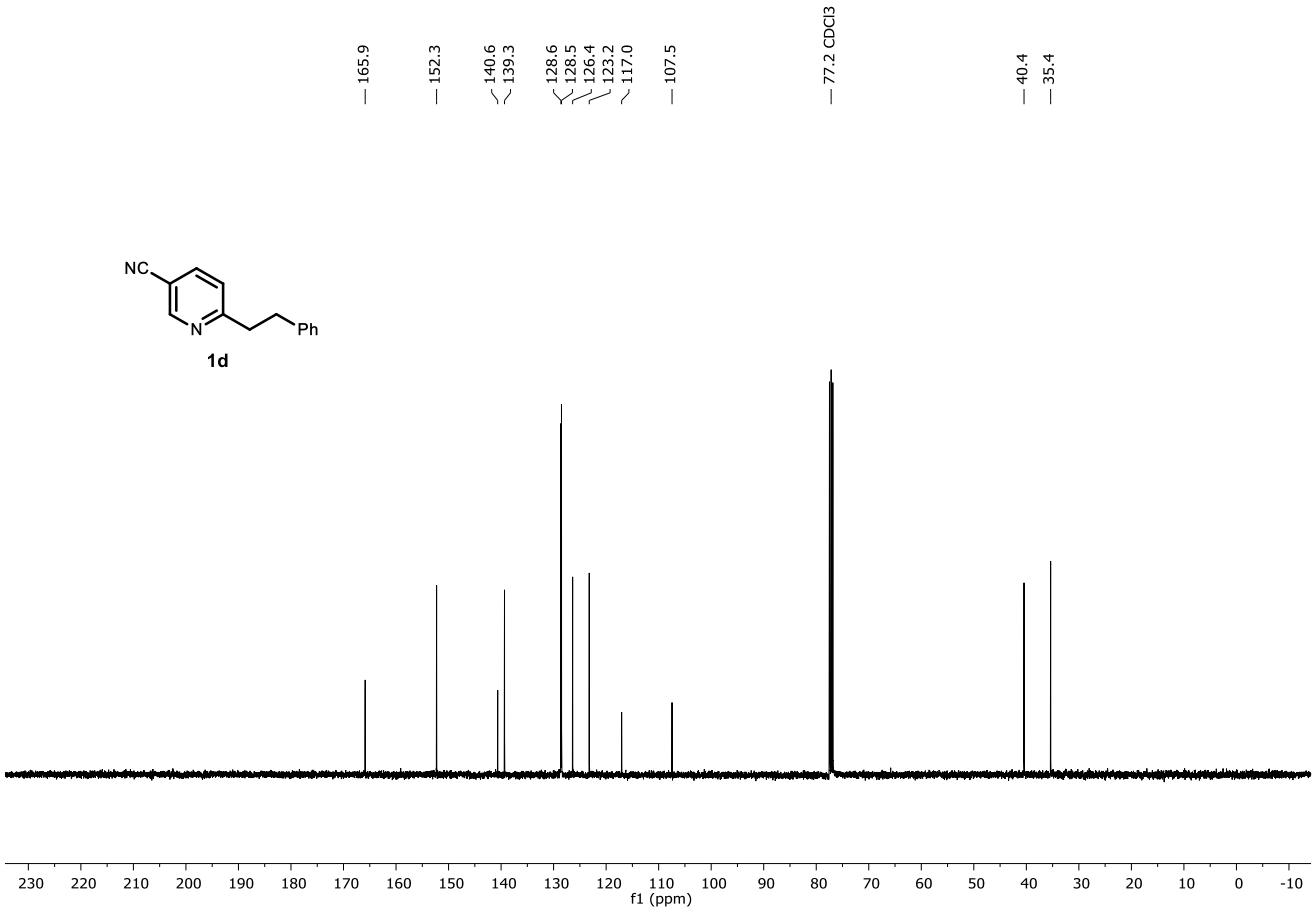
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96–8.73 (m, 1H), 7.80 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.27 (dd, *J* = 8.0, 6.5 Hz, 2H), 7.26–7.15 (m, 4H), 3.32–3.11 (m, 2H), 3.11–2.99 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.9, 152.3, 140.6, 139.3, 128.6, 128.5, 126.4, 123.2, 117.0, 107.5, 40.4, 35.4

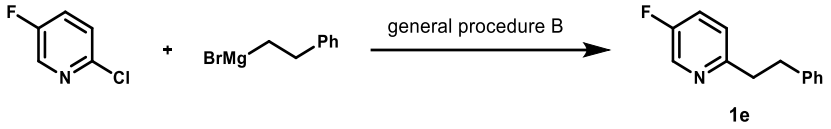
IR (cm^{-1}): 3028, 2232, 1593, 1481, 1454, 1380, 1026, 697, 554, 507

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{14}H_{13}N_2^+$: 209.1073; found: 209.1079


8.83
8.83
8.83
7.82
7.81
7.80
7.79
7.29
7.28
7.28
7.27
7.26 CDCl3
7.26
7.22
7.20
7.17
7.15
3.18
3.17
3.16
3.16
3.09
3.08
3.07
NC
N
Ph
1d
0.92
1.00
2.17
4.14
2.17
2.19
f1 (ppm)


165.9
152.3
140.6
139.3
128.6
128.5
126.4
123.2
117.0
107.5
77.2 CDCl3
40.4
35.4
NC
N
Ph
1d
f1 (ppm)

5-fluoro-2-phenethylpyridine (1e)



1e

Compound **1e** was prepared from 2-chloro-5-fluoropyridine (395 mg, 3.0 mmol, 1.0 equiv) according to **general procedure B**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 10:1 to 7:1) afforded **1e** (465 mg, 77%) as a white solid.

R_f: 0.25 (hexanes/EtOAc = 10:1)

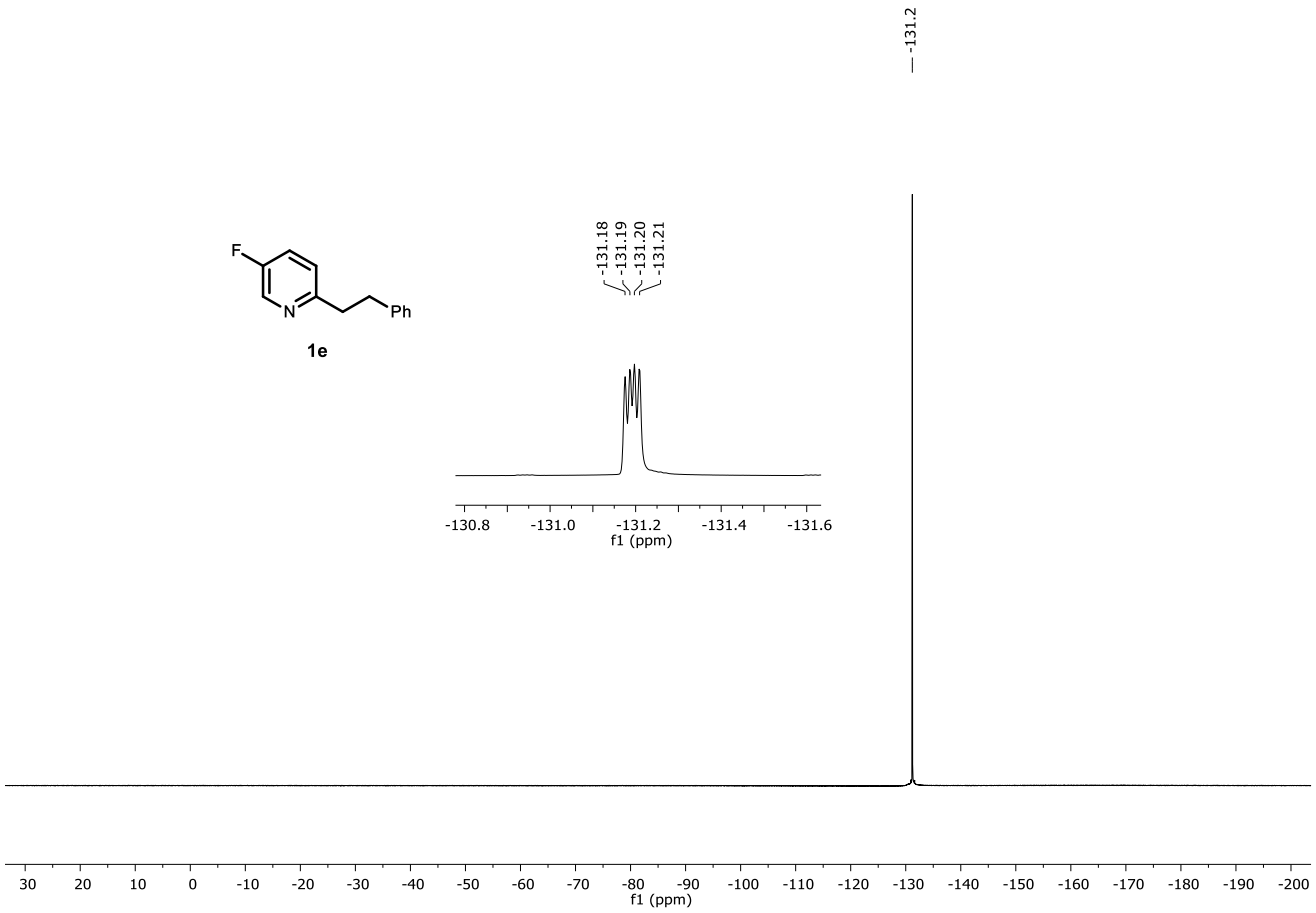
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 3.0 Hz, 1H), 7.31–7.25 (m, 3H), 7.22–7.15 (m, 3H), 7.05 (dd, *J* = 8.6, 4.4 Hz, 1H), 3.13–3.03 (m, 4H)

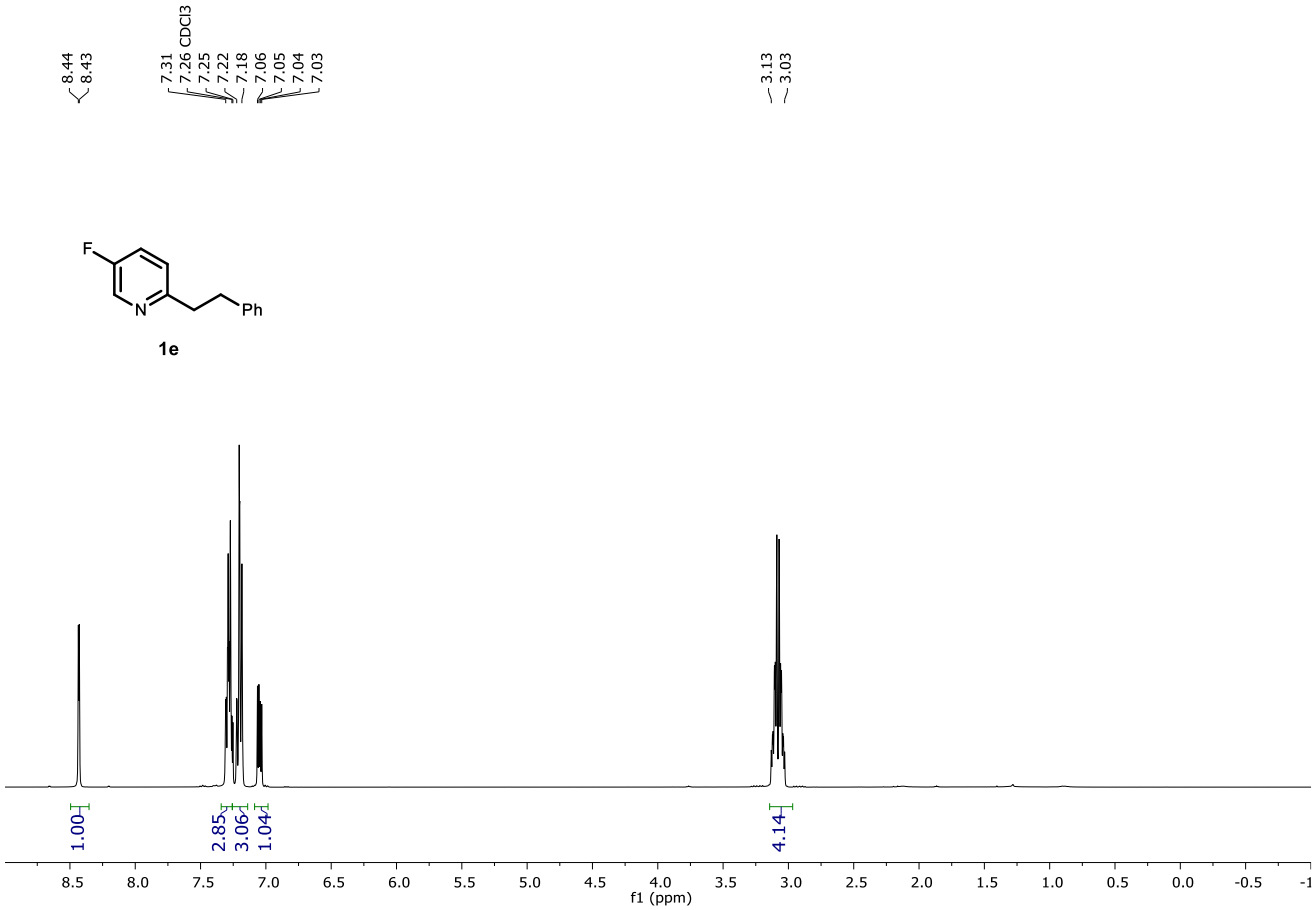
^{13}C NMR (101 MHz, $CDCl_3$): δ 158.2 (d, $J_{C\text{-}F}$ = 253.4 Hz), 157.2 (d, $J_{C\text{-}F}$ = 3.9 Hz), 141.4, 137.4 (d, $J_{C\text{-}F}$ = 23.1 Hz), 128.6, 128.5, 126.1, 123.7 (d, $J_{C\text{-}F}$ = 3.9 Hz), 123.1 (d, $J_{C\text{-}F}$ = 18.1 Hz), 39.4, 36.1

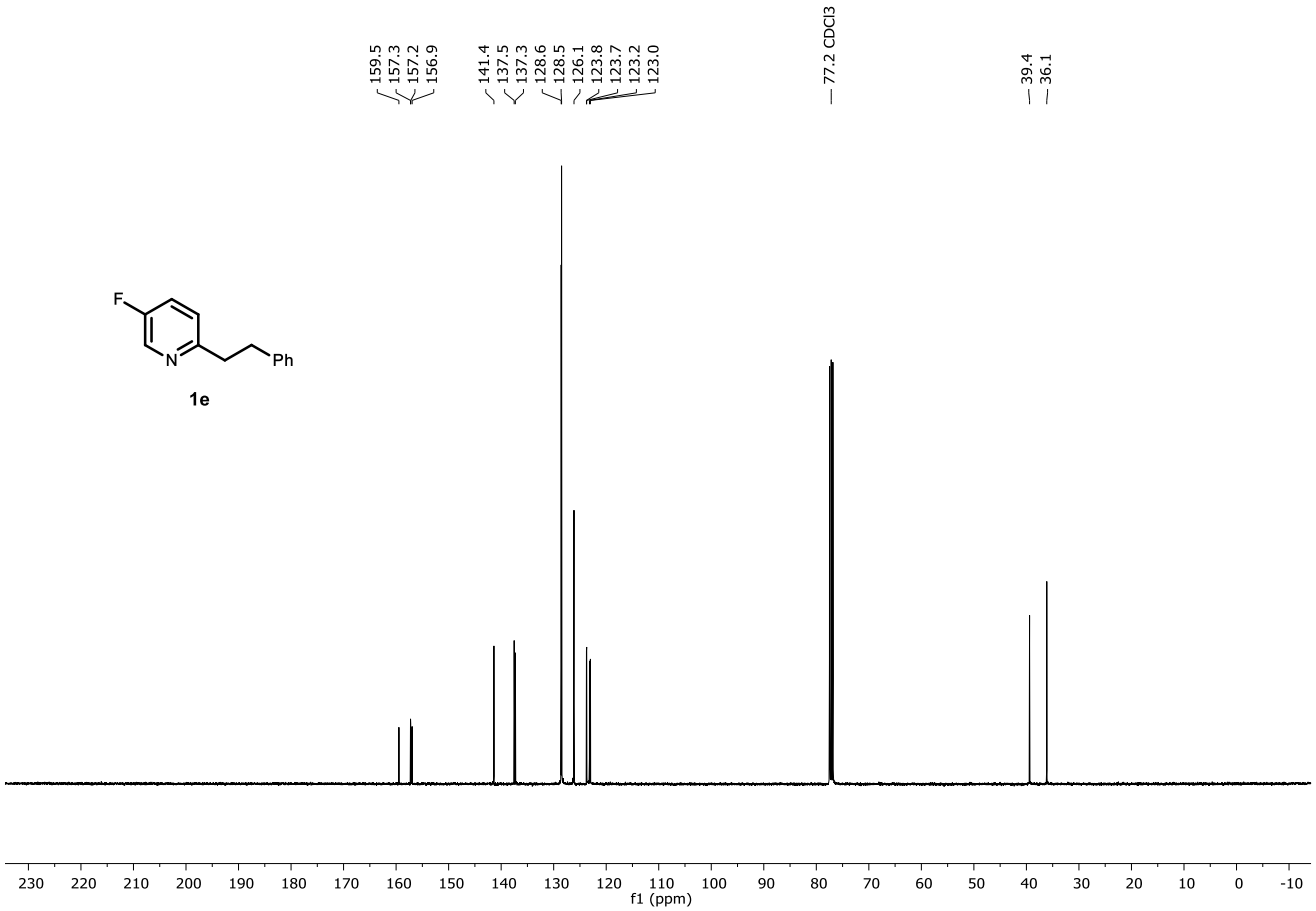
^{19}F NMR (376 MHz, $CDCl_3$): δ –131.2 (q, *J* = 3.8 Hz)

IR (cm^{-1}): 3026, 2924, 1585, 1482, 1222, 824, 750, 697, 496, 420

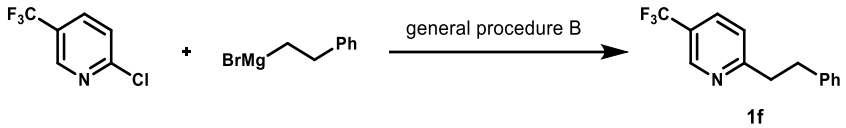
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{13}H_{13}FN^+$: 202.1027; found: 202.1032




8.44
8.43
7.31
7.26 CDCl3
7.25
7.22
7.18
7.06
7.05
7.04
7.03
3.13
3.03
F
N
Ph
1e
1.00
2.85
3.06
1.04
4.14
f1 (ppm)


159.5
157.3
157.2
156.9
141.4
137.5
137.3
128.6
128.5
126.1
123.8
123.7
123.2
123.0
77.2 CDCl3
39.4
36.1
F
N
Ph
1e
f1 (ppm)

2-phenethyl-5-(trifluoromethyl)pyridine (1f)



1f

Compound **1f** was prepared from 2-chloro-5-(trifluoromethyl)pyridine (908 mg, 5.0 mmol, 1.0 equiv) according to **general procedure B**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 20:1 to 15:1) afforded **1f** (950 mg, 76%) as a white solid. The characterization data match those previously reported in the literature.[8]

R$_f$: 0.42 (hexanes/EtOAc = 7:1)

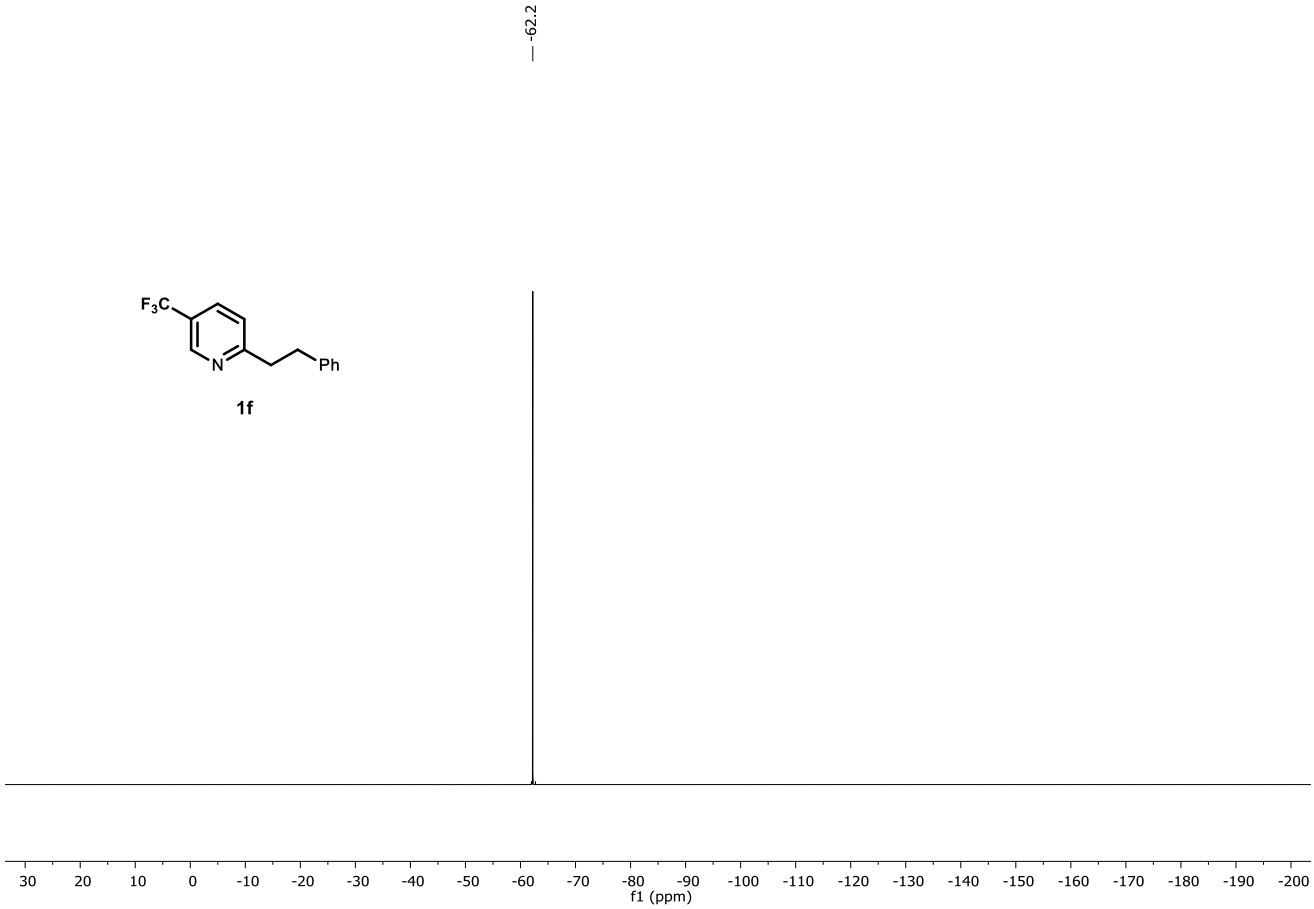
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (s, 1H), 7.79 (dd, J = 8.2, 2.4 Hz, 1H), 7.32–7.27 (m, 2H), 7.24–7.16 (m, 4H), 3.21–3.16 (m, 2H), 3.13–3.07 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 165.4, 146.4 (q, $J_{C\text{-}F}$ = 4.1 Hz), 141.0, 133.40 (q, $J_{C\text{-}F}$ = 3.5 Hz), 128.6, 128.5, 126.6, 124.4 (q, $J_{C\text{-}F}$ = 33.0 Hz), 123.9 (q, $J_{C\text{-}F}$ = 272.1 Hz), 122.8, 40.2, 35.7

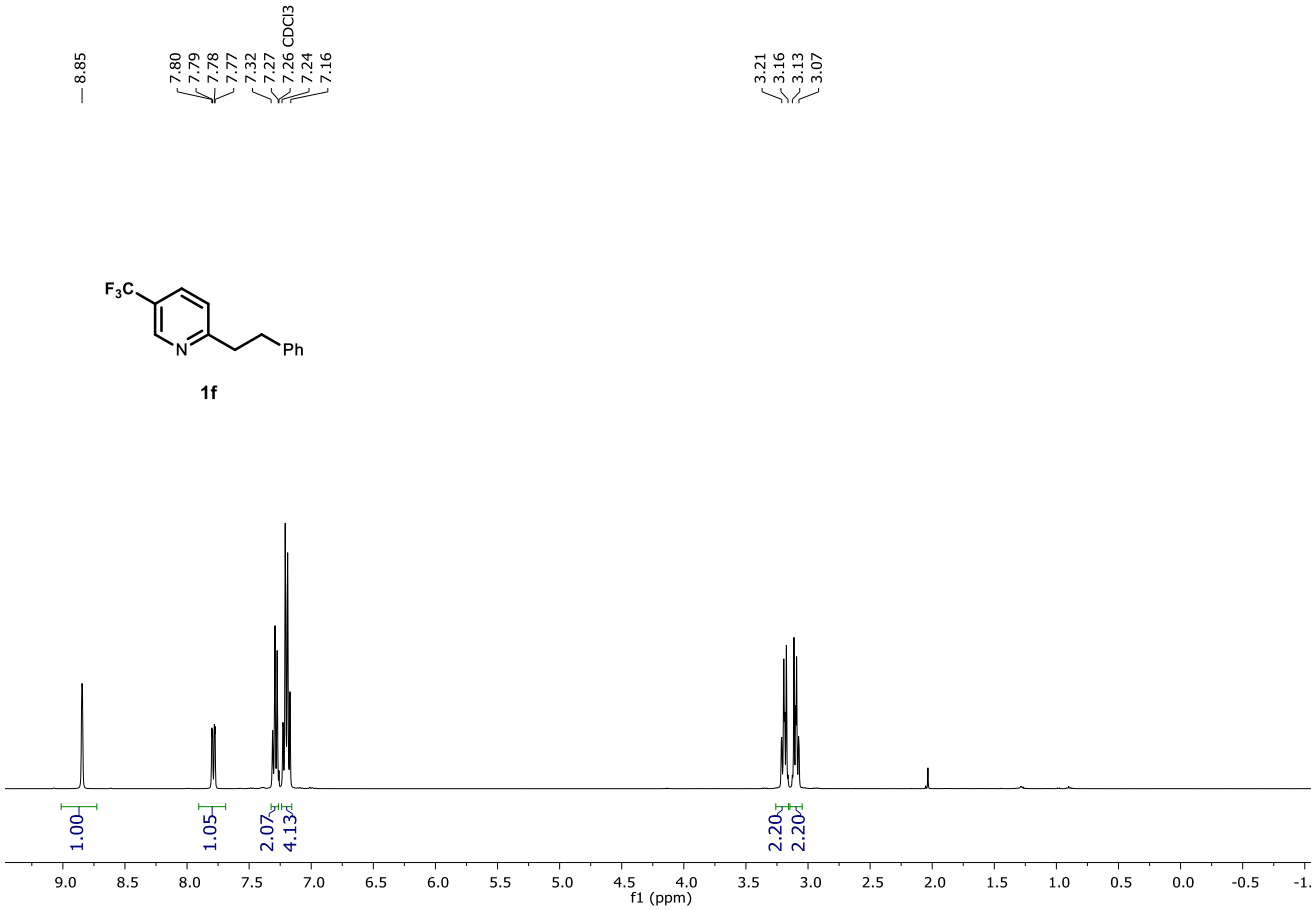
^{19}F NMR (376 MHz, $CDCl_3$): δ –62.2 (s)

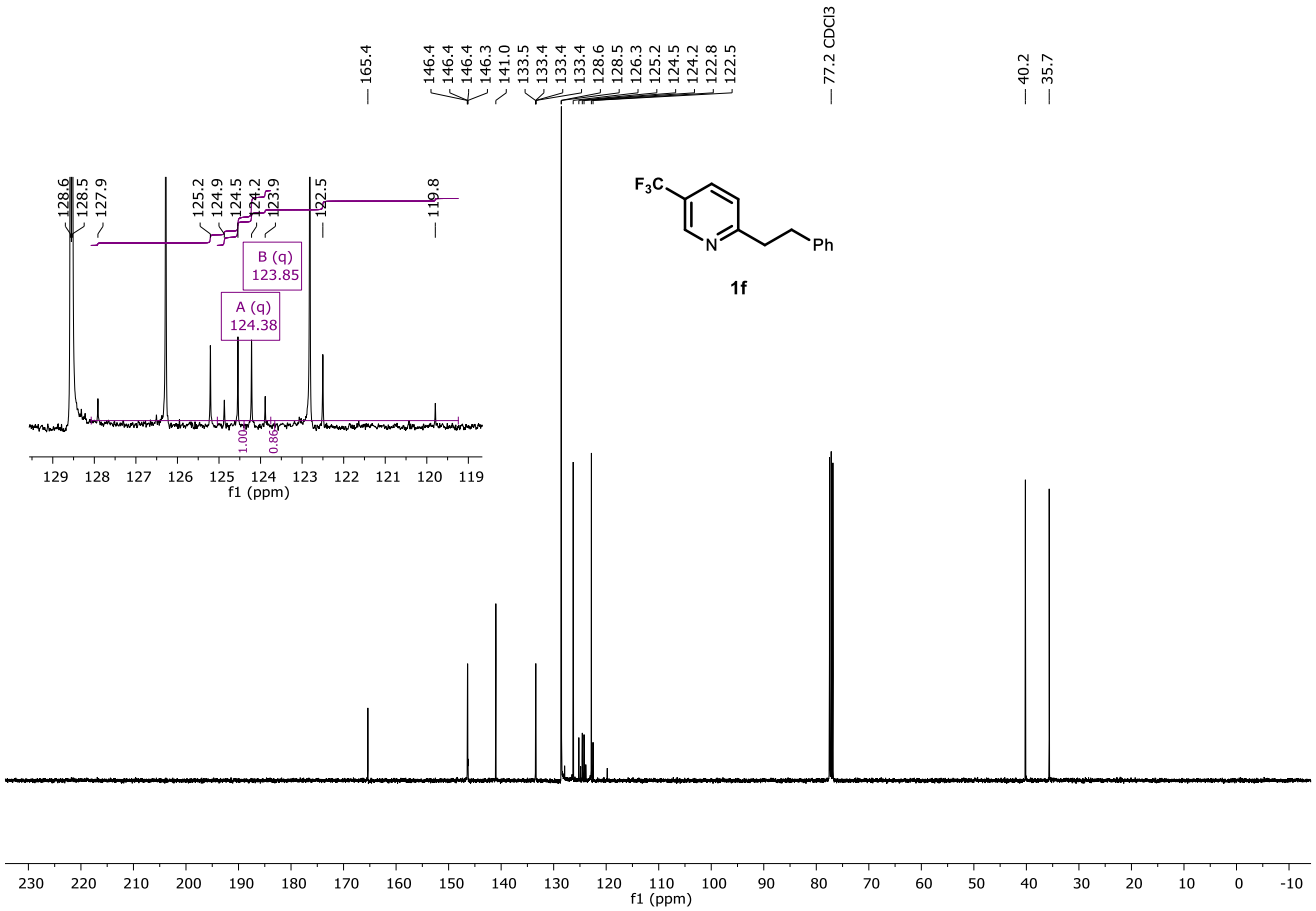
IR (cm^{-1}): 3028, 2926, 1605, 1324, 1120, 1078, 1016, 836, 698, 519, 418

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{14}H_{13}F_3N^+$: 252.0995; found: 252.1000

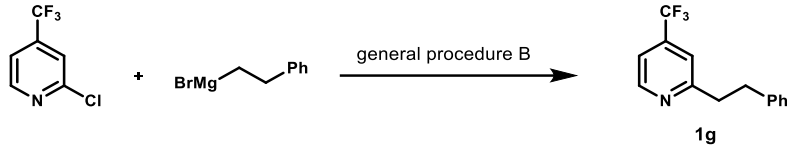


1f


8.85
7.80
7.79
7.78
7.77
7.32
7.27
7.26 CDCl3
7.24
7.16
3.21
3.16
3.13
3.07
F3C
N
Ph
1f
1.00
1.05
2.07
4.13
2.20
2.20
f1 (ppm)


165.4
146.4
146.4
146.4
146.3
141.0
133.5
133.4
133.4
133.4
128.6
128.5
126.3
125.2
124.5
124.2
122.8
122.5
77.2 CDCl3
40.2
35.7
128.6
128.5
127.9
125.2
124.9
124.5
124.2
123.9
122.5
119.8
B (q)
123.85
A (q)
124.38
F3C
N
Ph
1f
f1 (ppm)
f1 (ppm)

2-phenethyl-4-(trifluoromethyl)pyridine (1g)



1g

Compound **1g** was prepared from 2-chloro-4-(trifluoromethyl)pyridine (390 mg, 2.2 mmol, 1.0 equiv) according to **general procedure B**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 20:1 to 10:1) afforded **1g** (470 mg, 86%) as a white solid.

R_f: 0.64 (hexanes/EtOAc = 4:1)

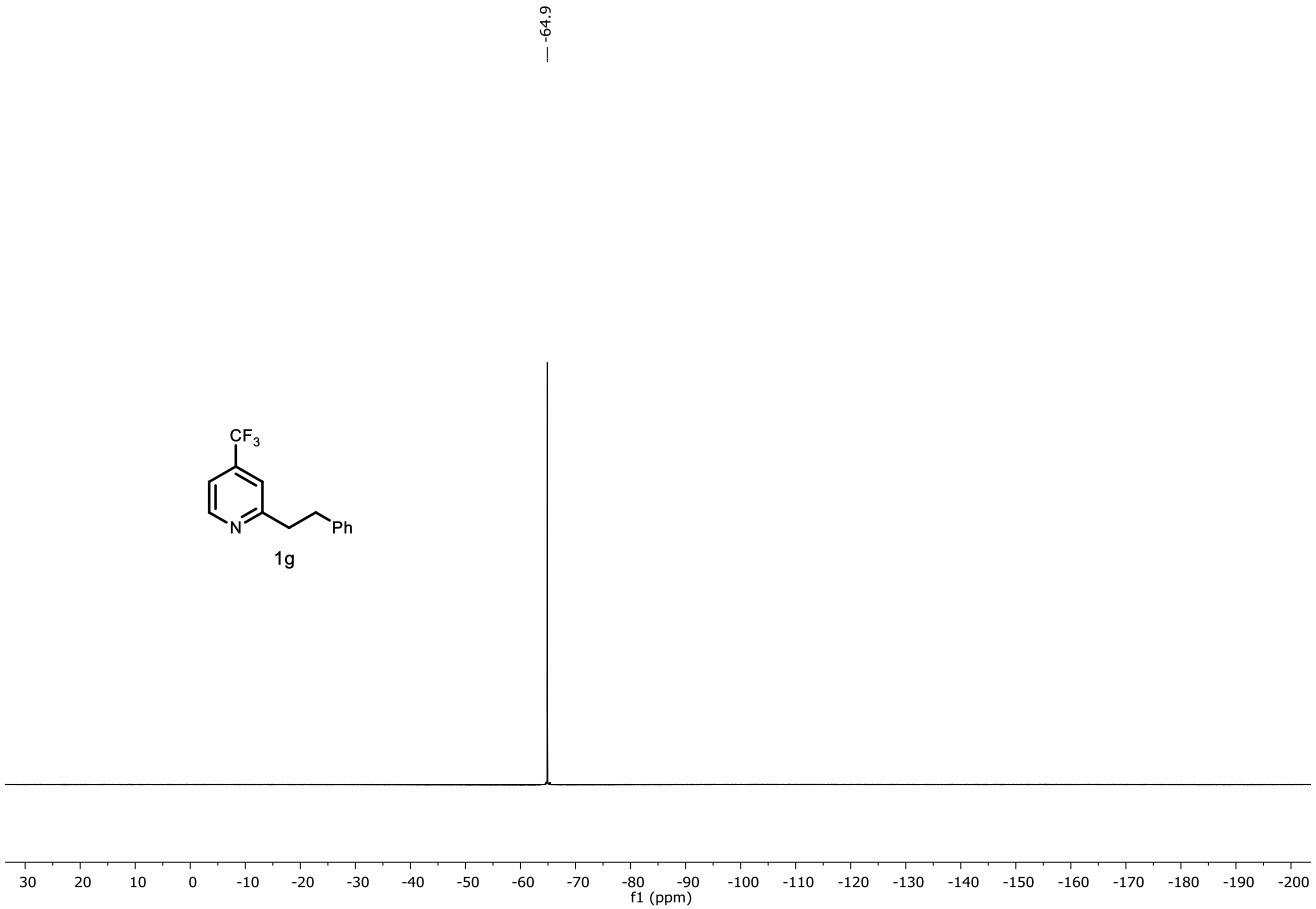
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 5.1 Hz, 1H), 7.35 (d, *J* = 4.9 Hz, 1H), 7.30–7.26 (m, 3H), 7.23–7.17 (m, 3H), 3.21–3.17 (m, 2H), 3.12 – 3.06 (m, 2H)

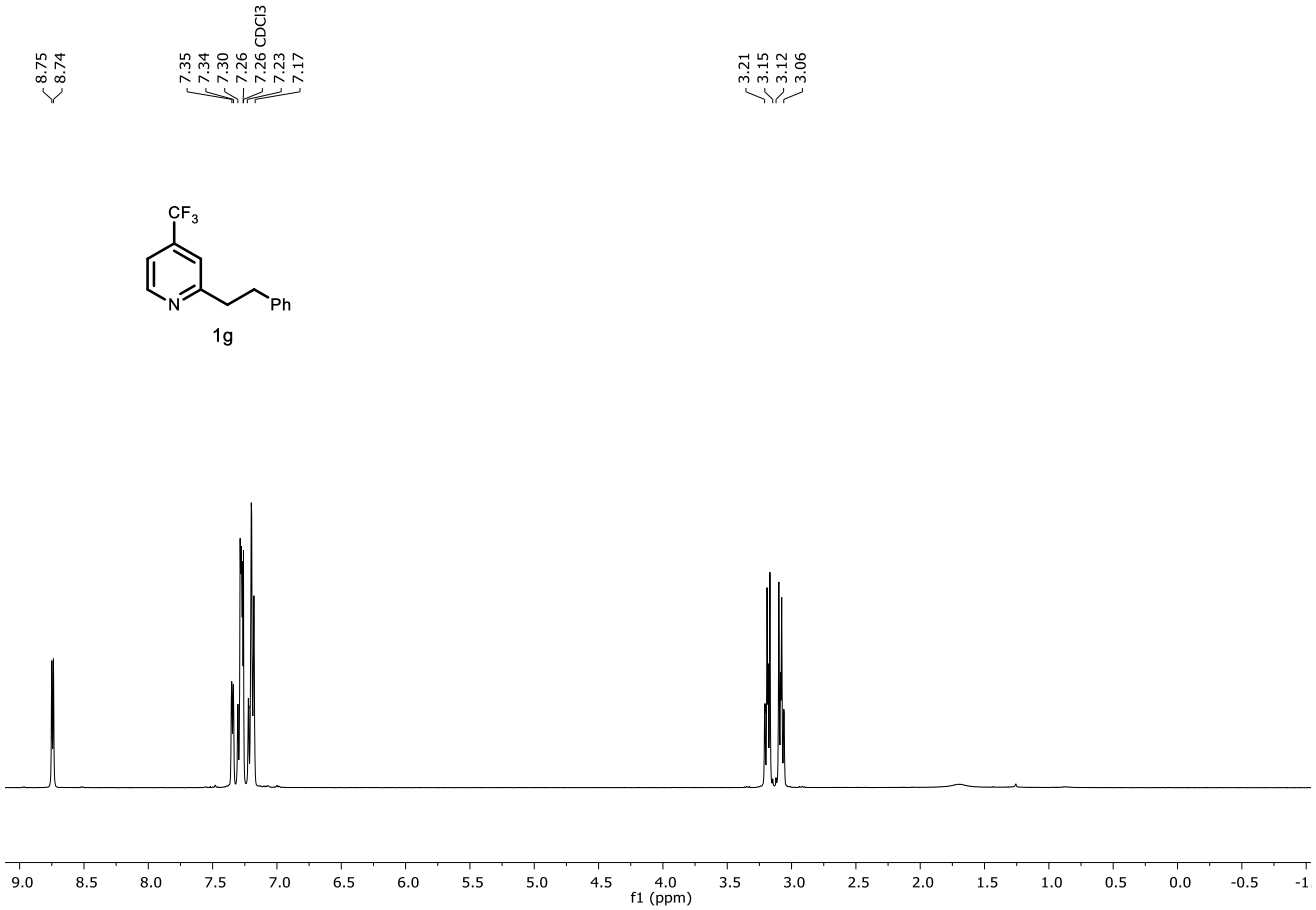
^{13}C NMR (101 MHz, $CDCl_3$): δ 163.0, 150.4, 141.0, 138.7 (q, J_{C-F} = 33.7 Hz), 128.6, 128.6, 126.3, 123.0 (q, J_{C-F} = 274.7 Hz), 118.8 (q, J_{C-F} = 3.6 Hz), 117.0 (q, J_{C-F} = 3.5 Hz), 40.4, 35.9

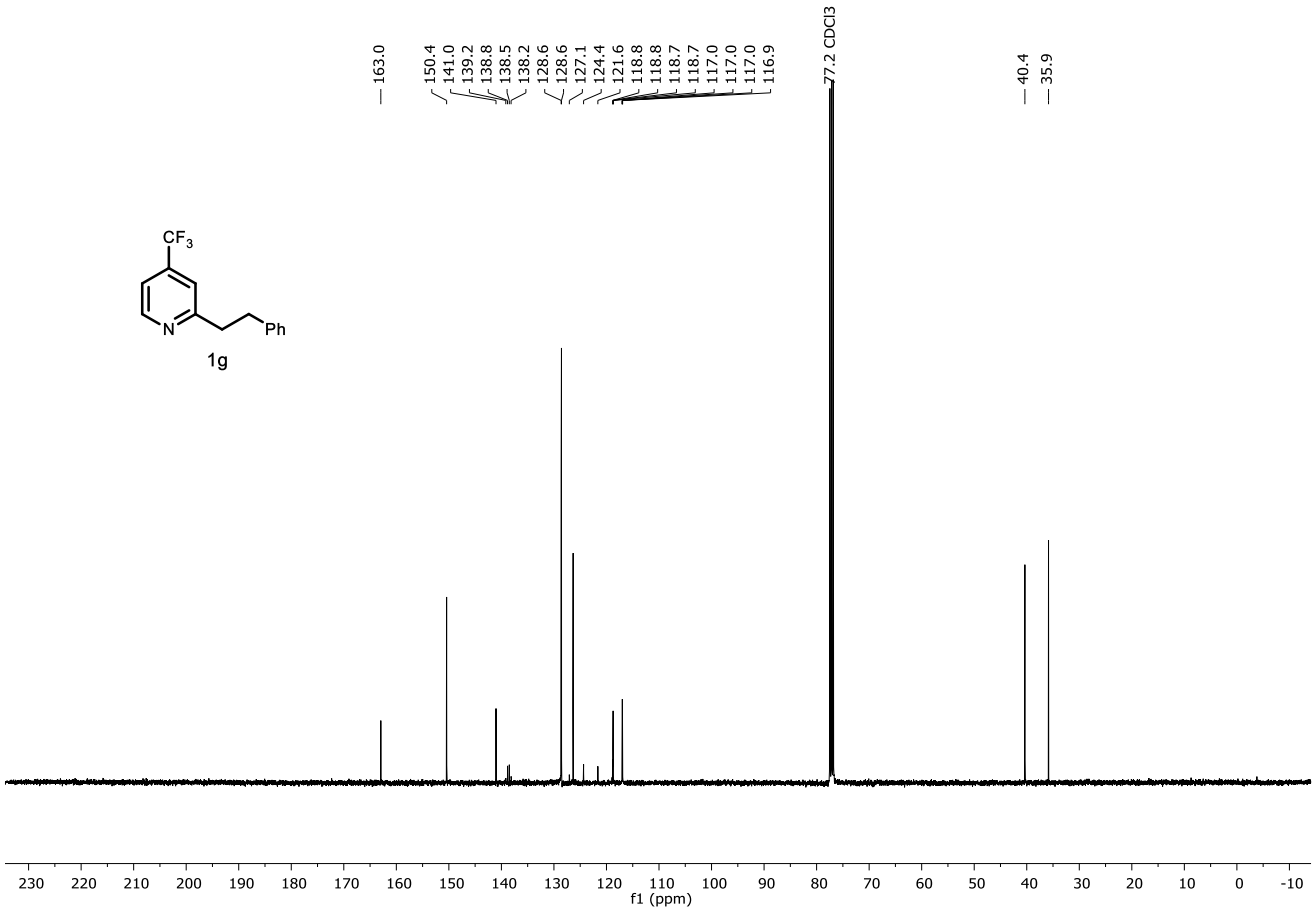
^{19}F NMR (376 MHz, $CDCl_3$): δ –64.9 (s)

IR (cm^{-1}): 3030, 1410, 1329, 1265, 1171, 1136, 1088, 843, 734, 699, 667

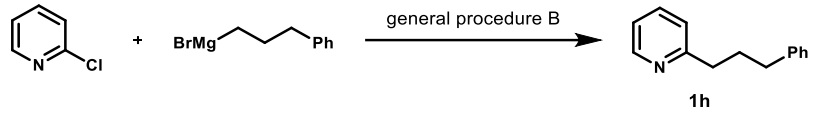
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{14}H_{13}F_3N^+$: 252.0995; found: 252.1000




8.75
8.74
7.35
7.34
7.30
7.26
7.26 CDCl3
7.23
7.17
3.21
3.15
3.12
3.06
CF3
N
Ph
1g
f1 (ppm)


163.0
150.4
141.0
139.2
138.8
138.5
138.2
128.6
128.6
127.1
124.4
121.6
118.8
118.8
118.7
118.7
117.0
117.0
117.0
116.9
77.2 CDCl3
40.4
35.9
CF3
N
Ph
1g
f1 (ppm)

2-(3-phenylpropyl)pyridine (1h)



1h

Compound **1h** was prepared from 2-chloropyridine (565 mg, 5.0 mmol, 1.0 equiv) according to **general procedure B**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 6:1) afforded **1h** (807 mg, 82%) as a yellow oil. The characterization data match those previously reported in the literature[16].

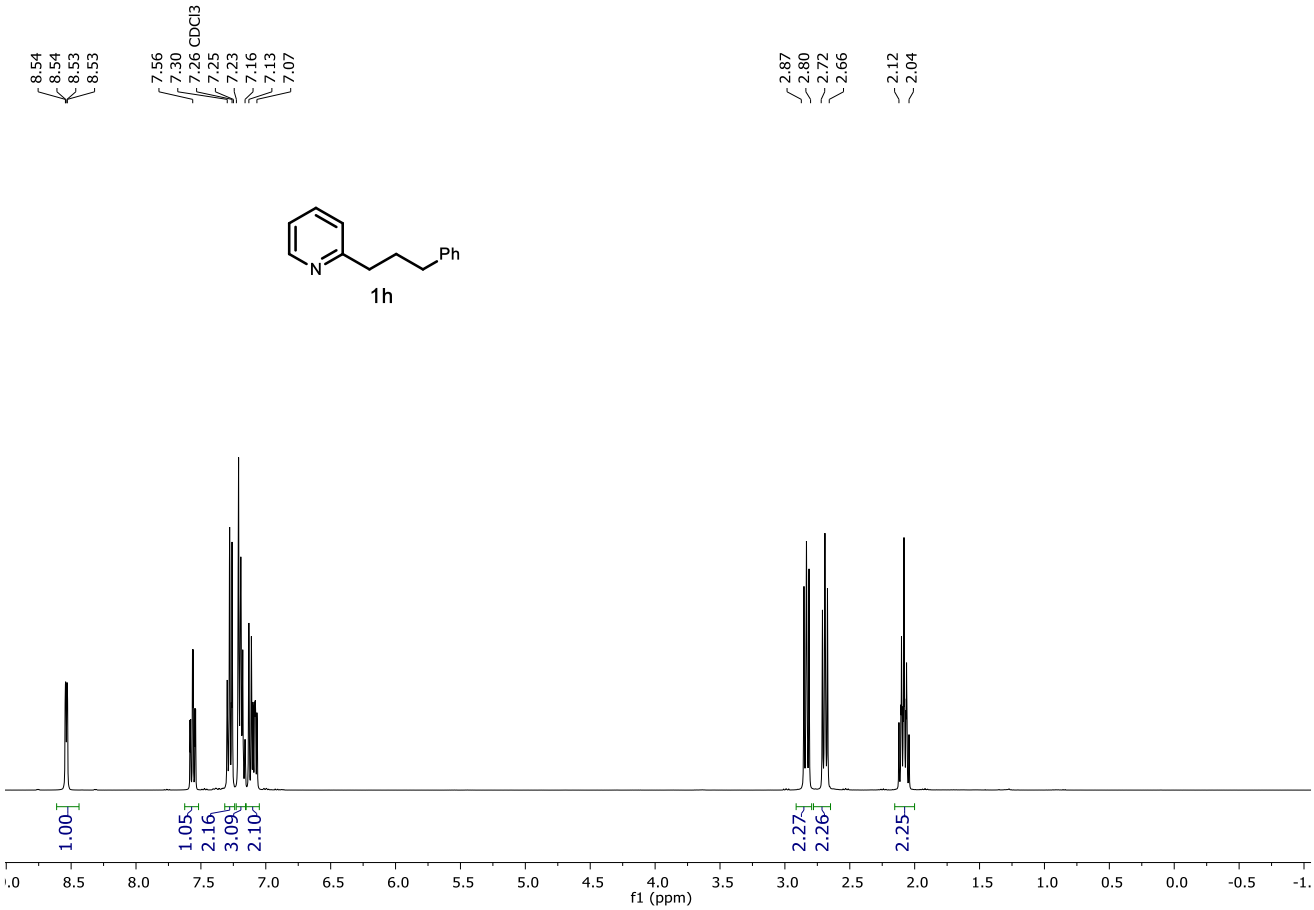
R_f: 0.33 (hexanes/EtOAc = 4:1)

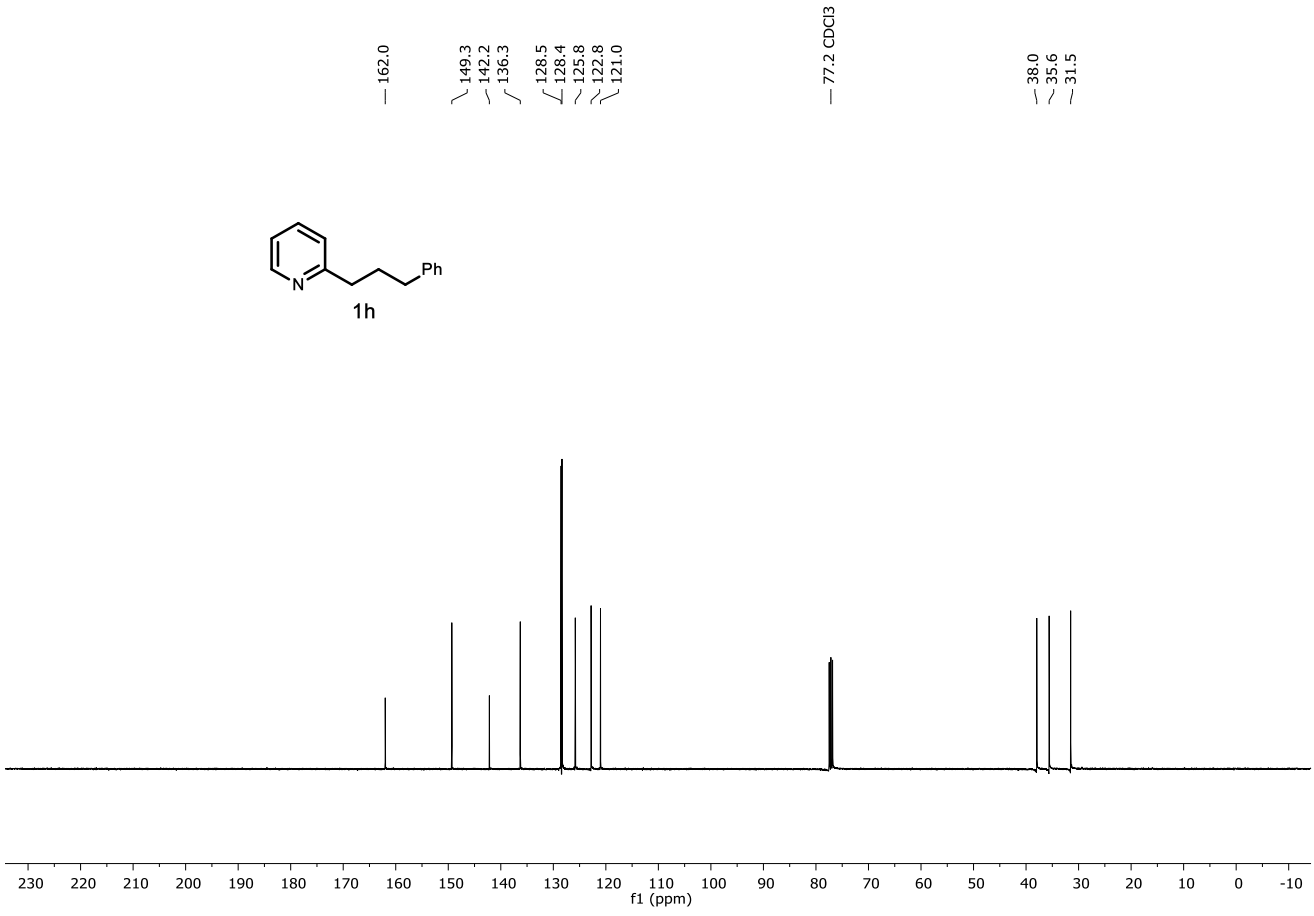
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54–8.53 (m, 1H), 7.56 (atd, *J* = 7.7, 1.9 Hz, 1H), 7.30–7.25 (m, 2H), 7.23–7.16 (m, 3H), 7.13–7.07 (m, 2H), 2.87–2.80 (m, 2H), 2.72–2.66 (m, 2H), 2.12–2.04 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.0, 149.3, 142.2, 136.3, 128.5, 128.4, 125.8, 122.8, 121.0, 38.0, 35.6, 31.5

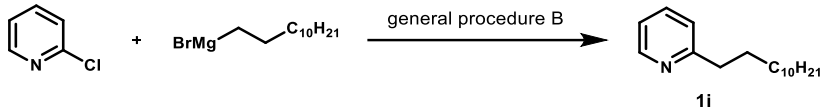
IR (cm^{-1}): 3025, 2930, 2857, 1589, 1473, 1433, 745, 697, 489

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{14}H_{16}N^+$: 198.1277; found: 198.1283


8.54
8.54
8.53
8.53
7.56
7.30
7.26 CDCl3
7.25
7.23
7.16
7.13
7.07
2.87
2.80
2.72
2.66
2.12
2.04
Ph
N
1h
1.00
1.05
2.16
3.09
2.10
2.27
2.26
2.25
f1 (ppm)


162.0
149.3
142.2
136.3
128.5
128.4
125.8
122.8
121.0
77.2 CDCl3
38.0
35.6
31.5
Ph
N
1h
f1 (ppm)

2-dodecylpyridine (1i)



1i

Compound **1i** was prepared from 2-chloropyridine (568 mg, 5.0 mmol, 1.0 equiv) according to **general procedure B**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 8:1) afforded **1i** (261 mg, 21%) as a yellow oil.

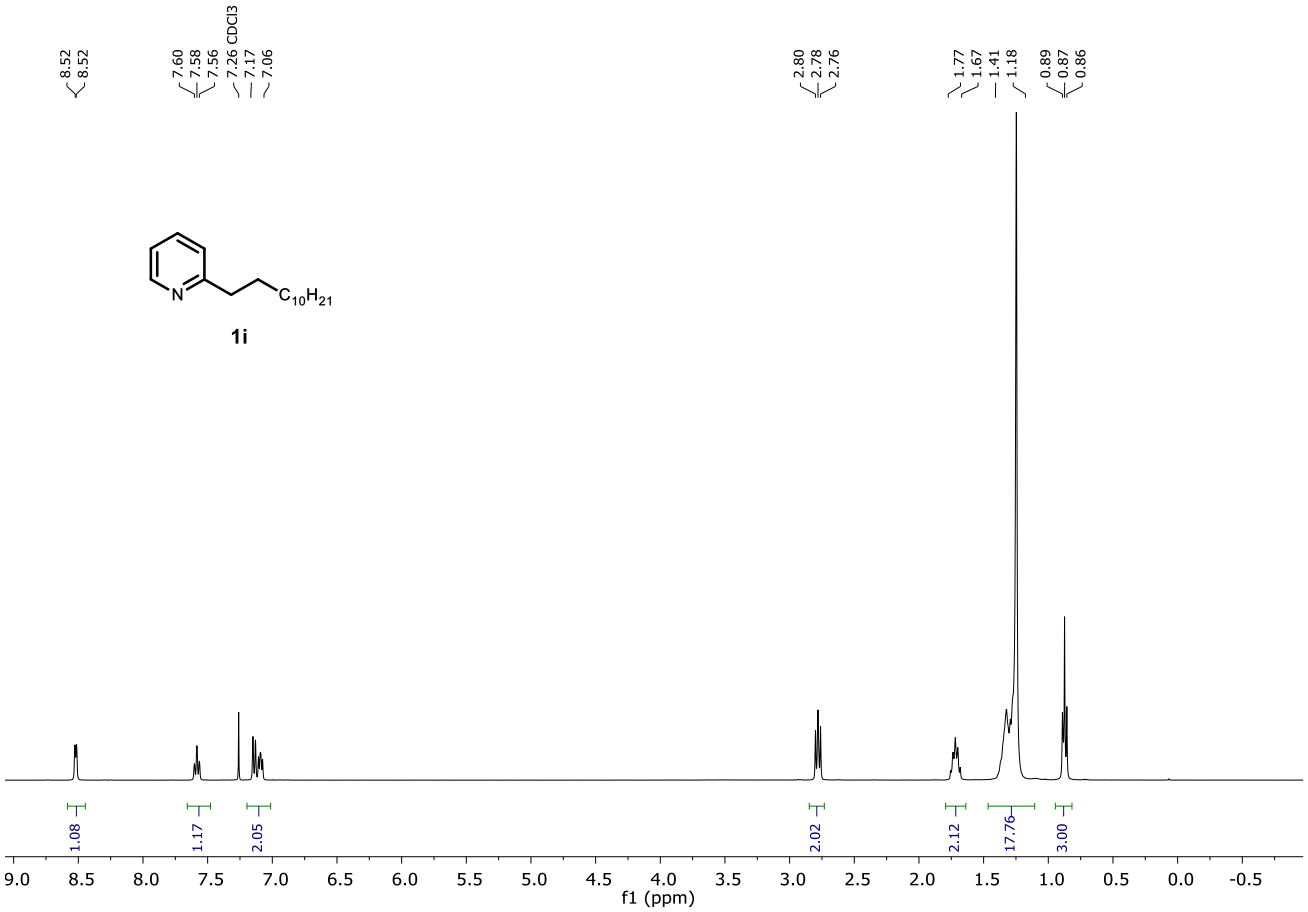
R_f: 0.47 (hexanes/EtOAc = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 4.4 Hz, 1H), 7.58 (at, *J* = 7.6 Hz, 1H), 7.17–7. 06 (m, 2H), 2.78 (t, *J* = 7.6 Hz, 2H), 1.77–1.67 (m, 2H), 1.41–1.18 (m, 18H), 0.87 (t, *J* = 6.8 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.6, 149.2, 136.5, 122.9, 121.0, 38.5, 32.1, 30.1, 29.8, 29.8, 29.7, 29.6, 29.6, 29.5, 22.8, 14.3

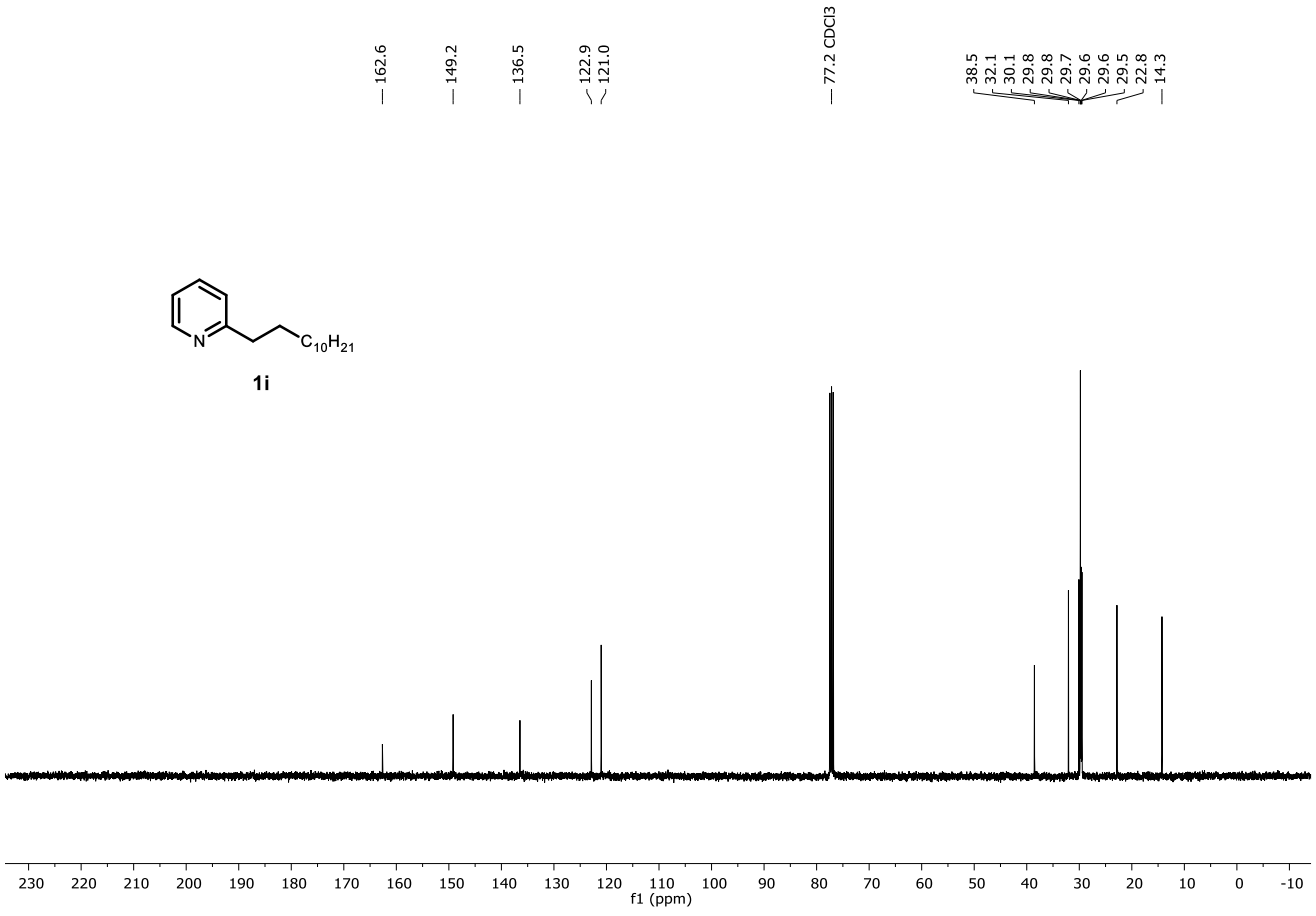
IR (cm^{-1}): 2929, 2852, 1590, 1570, 1468, 1434, 747

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{17}H_{30}N^+$: 248.2373; found: 248.2378


8.52
8.52
7.60
7.58
7.56
7.26 CDCl3
7.17
7.06
2.80
2.78
2.76
1.77
1.67
1.41
1.18
0.89
0.87
0.86
1.08
1.17
2.05
2.02
2.12
17.76
3.00
f1 (ppm)

N
C10H21

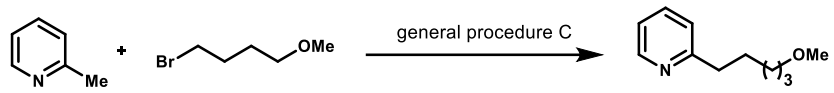
1i


162.6
149.2
136.5
122.9
121.0
77.2 CDCl3
38.5
32.1
30.1
29.8
29.8
29.7
29.6
29.6
29.5
22.8
14.3
f1 (ppm)

N
C10H21

1i

2-(5-methoxypentyl)pyridine (1j)



1j

Compound **1j** was prepared from 2-methylpyridine (280 mg, 3.0 mmol, 1.0 equiv) and 1-bromo-4-methoxybutane (0.47 mL, 3.6 mmol, 1.2 equiv) according to **general procedure C**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 6:1 to 3:1) afforded **1j** (499 mg, 93%) as a yellow oil.

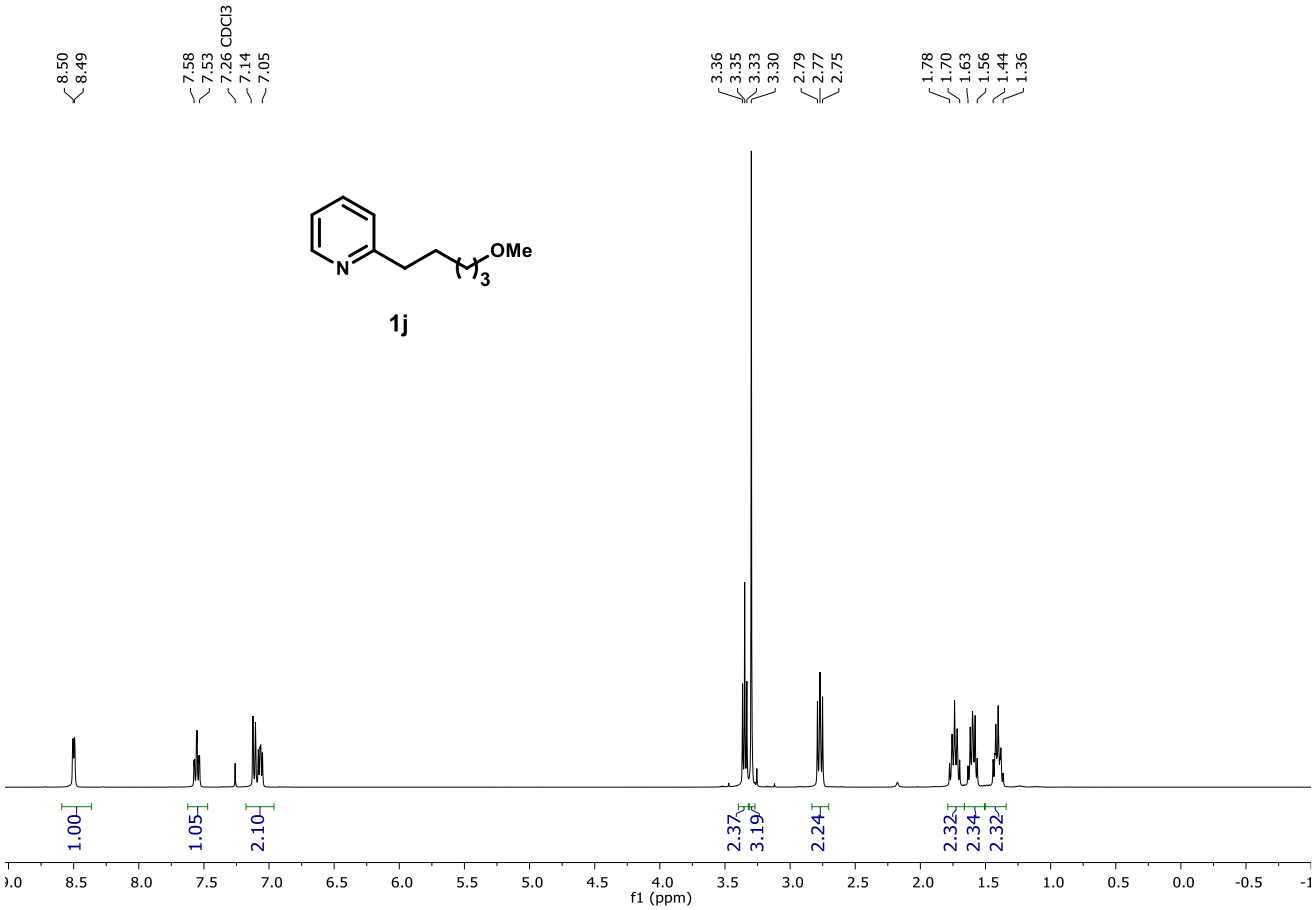
R$_f$: 0.29 (hexanes/EtOAc = 2:1)

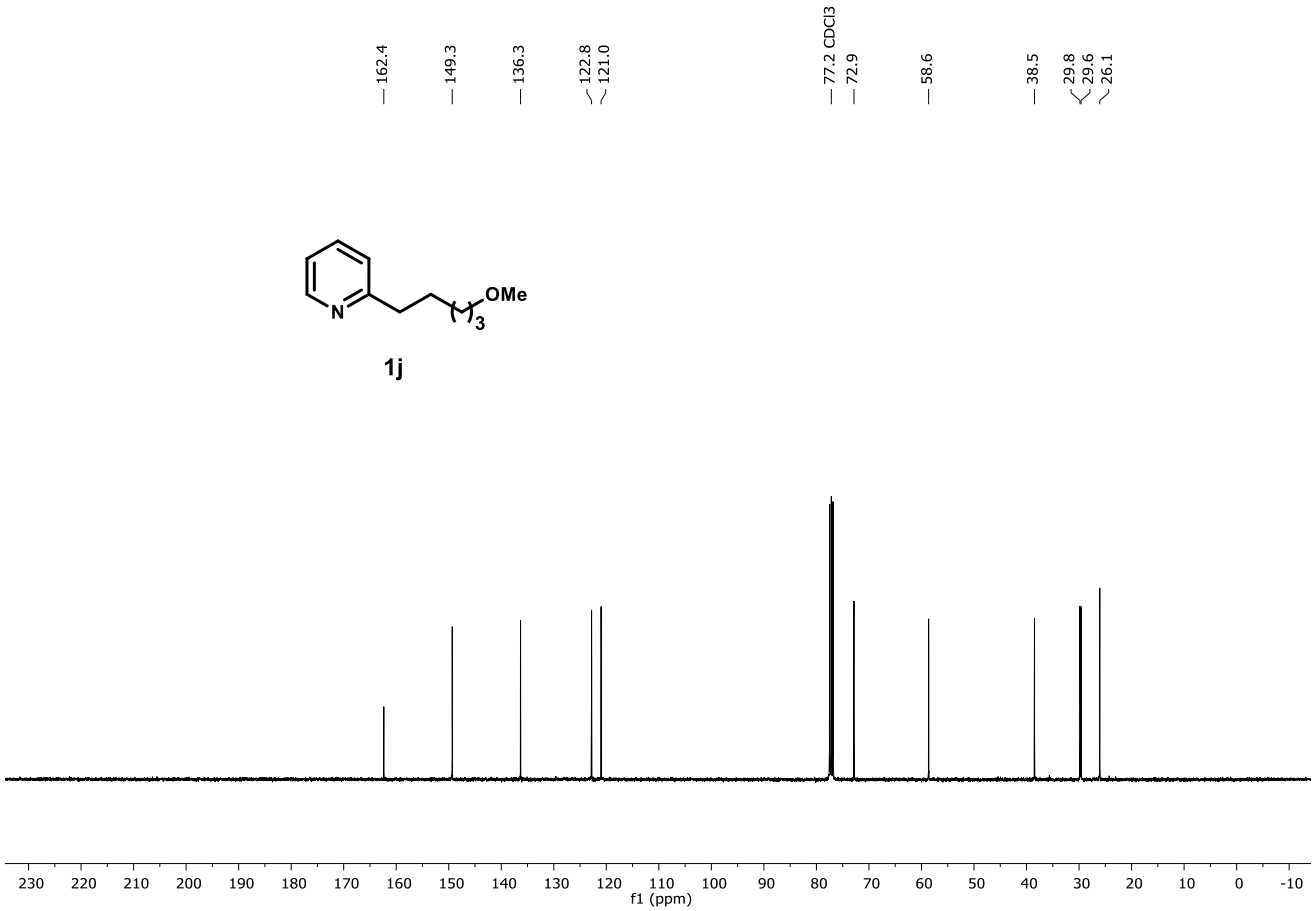
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 4.0 Hz, 1H), 7.58–7.53 (m, 1H), 7.14–7.05 (m, 2H), 3.35 (t, *J* = 6.6 Hz, 2H), 3.30 (s, 3H), 2.88–2.73 (m, 2H), 1.78–1.70 (m, 2H), 1.63–1.56 (m, 2H), 1.44–1.36 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.4, 149.3, 136.3, 122.8, 121.0, 72.9, 58.6, 38.5, 29.8, 29.6, 26.1

IR (cm^{-1}): 2931, 2858, 1590, 1434, 1117, 749

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{11}H_{18}NO^+$: 180.1383; found: 180.1388


8.50
8.49
7.58
7.53
7.26 CDCl3
7.14
7.05
3.36
3.35
3.33
3.30
2.79
2.77
2.75
1.78
1.70
1.63
1.56
1.44
1.36
OMe
3
1j
1.00
1.05
2.10
2.37
3.19
2.24
2.32
2.34
2.32
f1 (ppm)


162.4
149.3
136.3
122.8
121.0
77.2 CDCl3
72.9
58.6
38.5
29.8
29.6
26.1
OMe
3
1j
f1 (ppm)

2-(3-((4-methoxybenzyl)oxy)propyl)pyridine (1k)

1k

To a solution of 3-(pyridin-2-yl)propan-1-ol (0.26 mL, 2.0 mmol, 1.0 equiv) in DMF (5 mL, 0.4 M) was added NaH (91 mg, 60 % dispersion in mineral oil, 2.4 mmol, 1.2 equiv) at 0 °C. The mixture was stirred at this temperature for 30 minutes before the addition of PMBCl (0.24 mL, 2.4 mmol, 1.2 equiv). The resulting mixture was stirred for 4 hours and slowly warmed to room temperature before the reaction is diluted with Et_2O and quenched by the slow addition of sat. aq. NH_4Cl (10 mL). The aqueous phase was extracted with Et_2O (3 × 10 mL) and the combined organic extracts were washed with water (3 × 10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation. The crude mixture was purified by flash column chromatography on silica gel (hexanes/EtOAc = 6:1 to 3:1) to afford **1k** (306 mg, 60%) as a yellow oil.

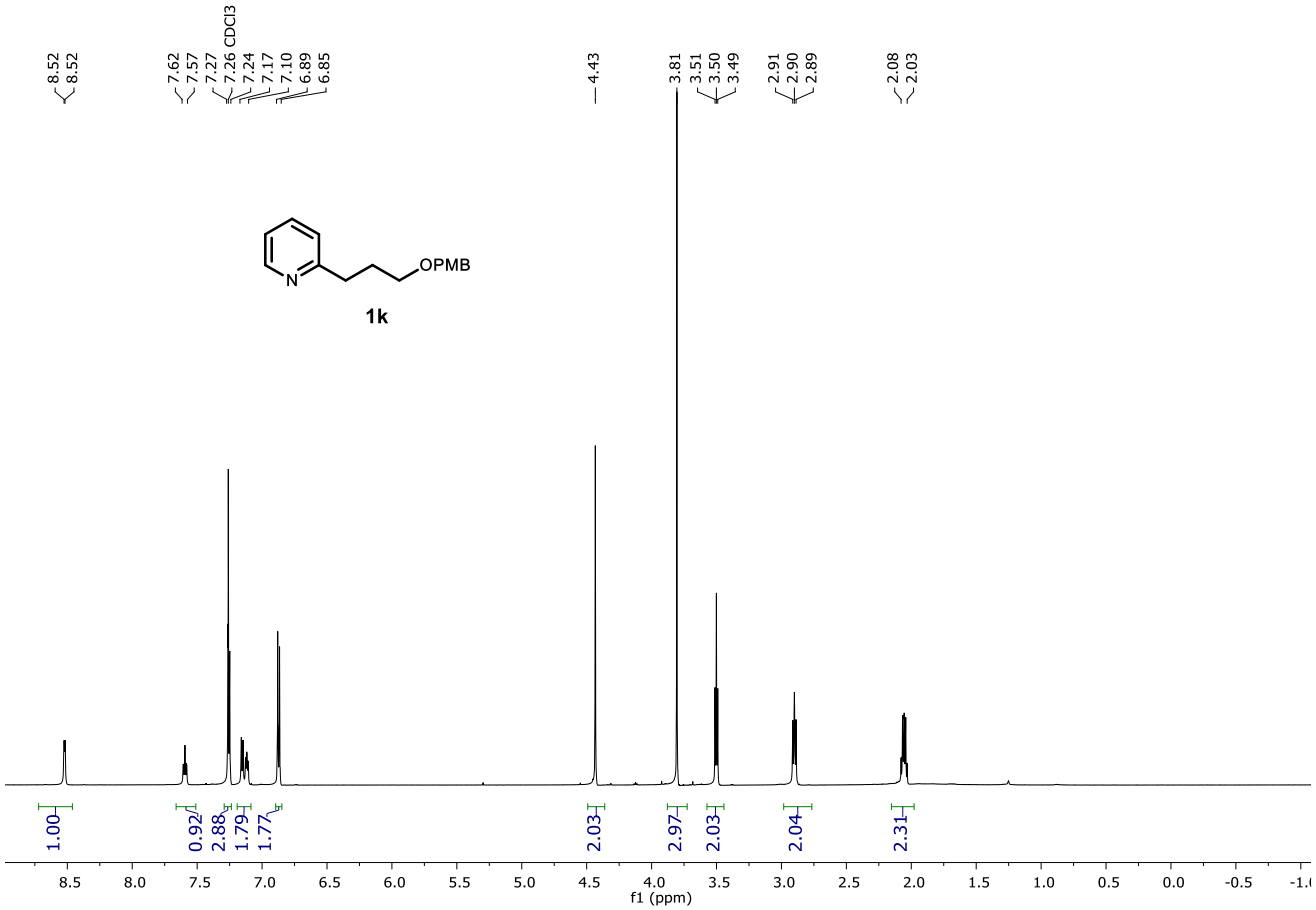
R_f: 0.33 (hexanes/EtOAc = 2:1)

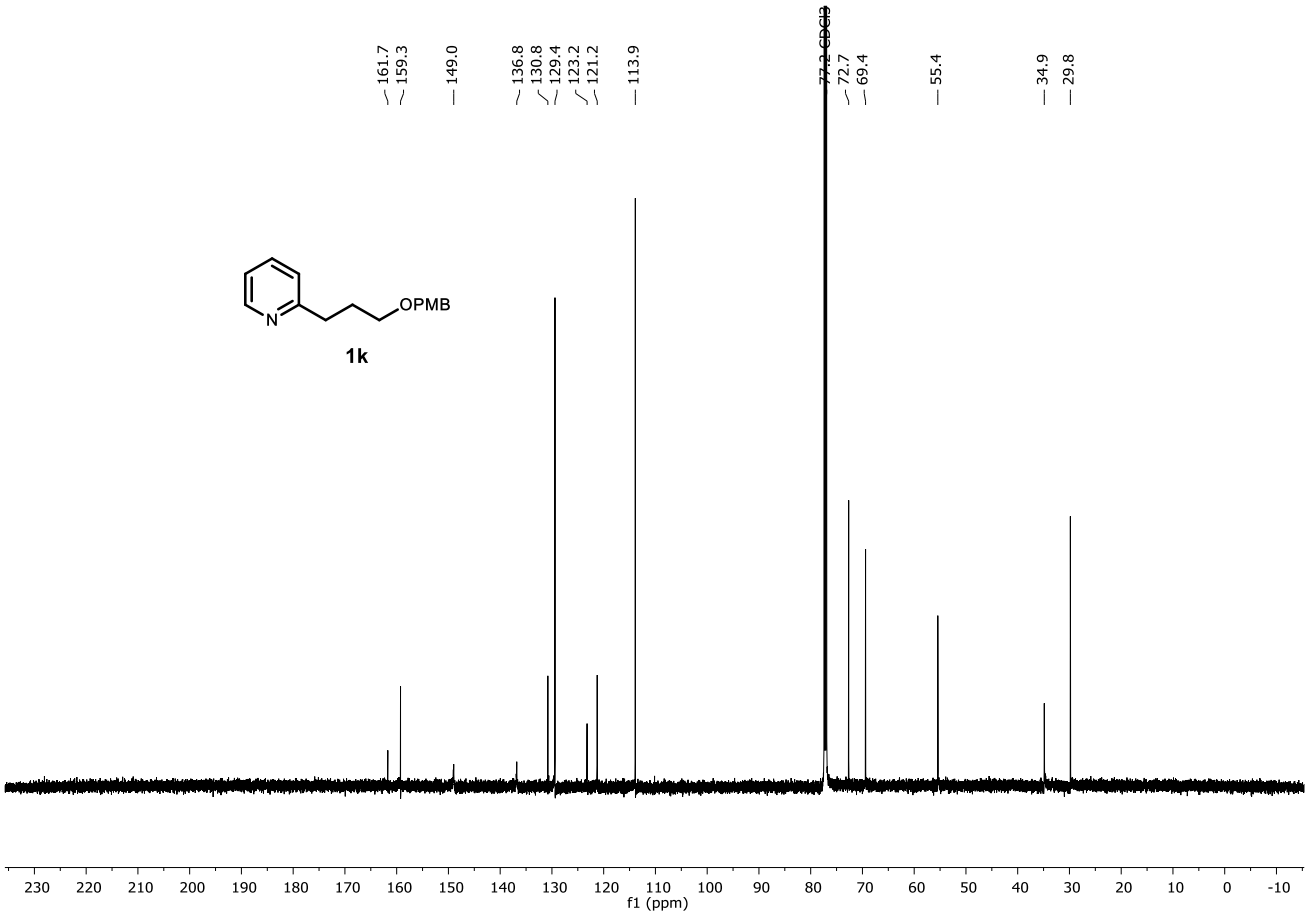
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.52 (d, *J* = 4.3 Hz, 1H), 7.62–7.57 (m, 1H), 7.27–7.24 (m, 2H), 7.17–7.10 (m, 2H), 6.89–6.85 (m, 2H), 4.43 (s, 2H), 3.81 (s, 3H), 3.50 (t, *J* = 6.3 Hz, 2H), 3.21–2.78 (m, 2H), 2.08–2.03 (m, 2H)

^{13}C NMR (151 MHz, $CDCl_3$): δ 161.7, 159.3, 149.0, 136.8, 130.8, 129.4, 123.2, 121.2, 113.9, 72.7, 69.4, 55.4, 34.9, 29.8

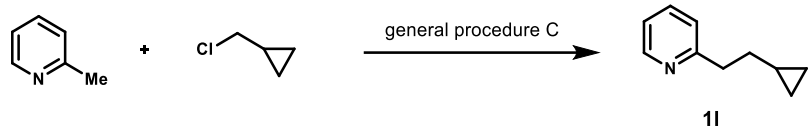
IR (cm^{-1}): 2933, 2855, 1588, 1512, 1244, 1094, 1033, 817, 749, 508

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{16}H_{20}NO_2^+$: 258.1489; found: 258.1494


8.52
8.52
7.62
7.57
7.27
7.26 CDCl3
7.24
7.17
7.10
6.89
6.85
4.43
3.81
3.51
3.50
3.49
2.91
2.90
2.89
2.08
2.03
OPMB
1k
1.00
0.92
2.88
1.79
1.77
2.03
2.97
2.03
2.04
2.31
f1 (ppm)


161.7
159.3
149.0
136.8
130.8
129.4
123.2
121.2
113.9
77.2 CDCl3
72.7
69.4
55.4
34.9
29.8
OPMB
1k
f1 (ppm)

2-(2-cyclopropylethyl)pyridine (1l)



1l

Compound **1l** was prepared from 2-methylpyridine (0.30 mL, 3.0 mmol, 1.0 equiv) and (chloromethyl)cyclopropane (0.34 mL, 3.6 mmol, 1.2 equiv) according to **general procedure C**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 8:1 to 4:1) afforded **1l** (254 mg, 58%) as a yellow oil.

R$_f$: 0.42 (hexanes/EtOAc = 2:1)

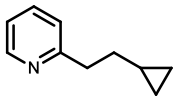
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78–8.32 (m, 1H), 7.56–7.53 (m, 1H), 7.14–7.04 (m, 2H), 2.88–2.84 (m, 2H), 1.64–1.58 (m, 2H), 0.71–0.68 (m, 1H), 0.41–0.38 (m, 2H), 0.03–0.02 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.4, 149.3, 136.2, 122.9, 120.9, 38.6, 35.1, 10.8, 4.6

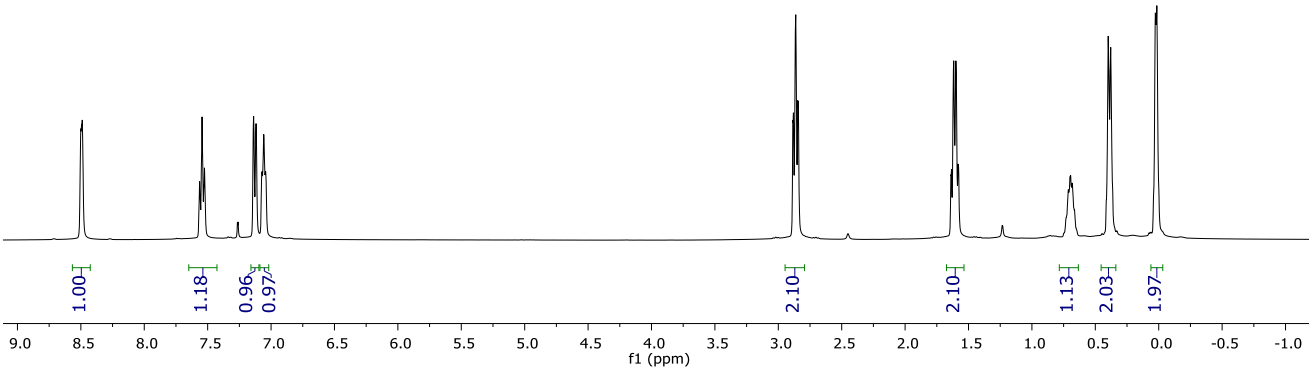
IR (cm^{-1}): 3075, 3000, 2918, 2852, 1593, 1474, 1433, 1015, 747, 514

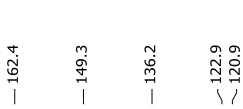
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{10}H_{14}N^+$: 148.1121; found: 148.1126

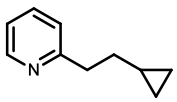

8.50
8.49
8.49
7.56
7.54
7.53
7.26 CDCl3
7.14
7.12
7.07
7.06
7.04
2.88
2.88
2.86
2.85
2.84
1.64
1.63
1.62
1.60
1.58
1.58
0.71
0.70
0.70
0.68
0.41
0.40
0.38
0.03
0.02
0.02



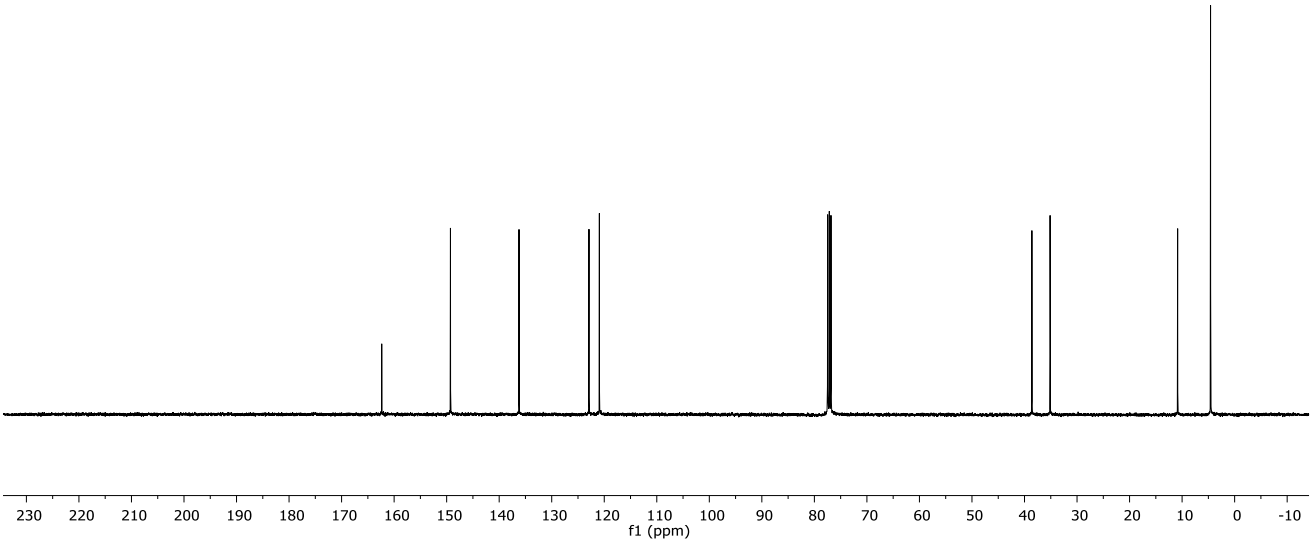
1l


1.00
1.18
0.96
0.97
2.10
2.10
1.13
2.03
1.97
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
-0.5
-1.0
f1 (ppm)

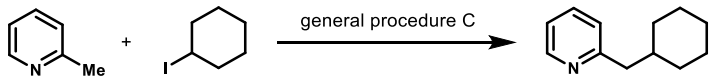

162.4
149.3
136.2
122.9
120.9
77.2 CDCl3
38.6
35.1
10.8
4.6



1l


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

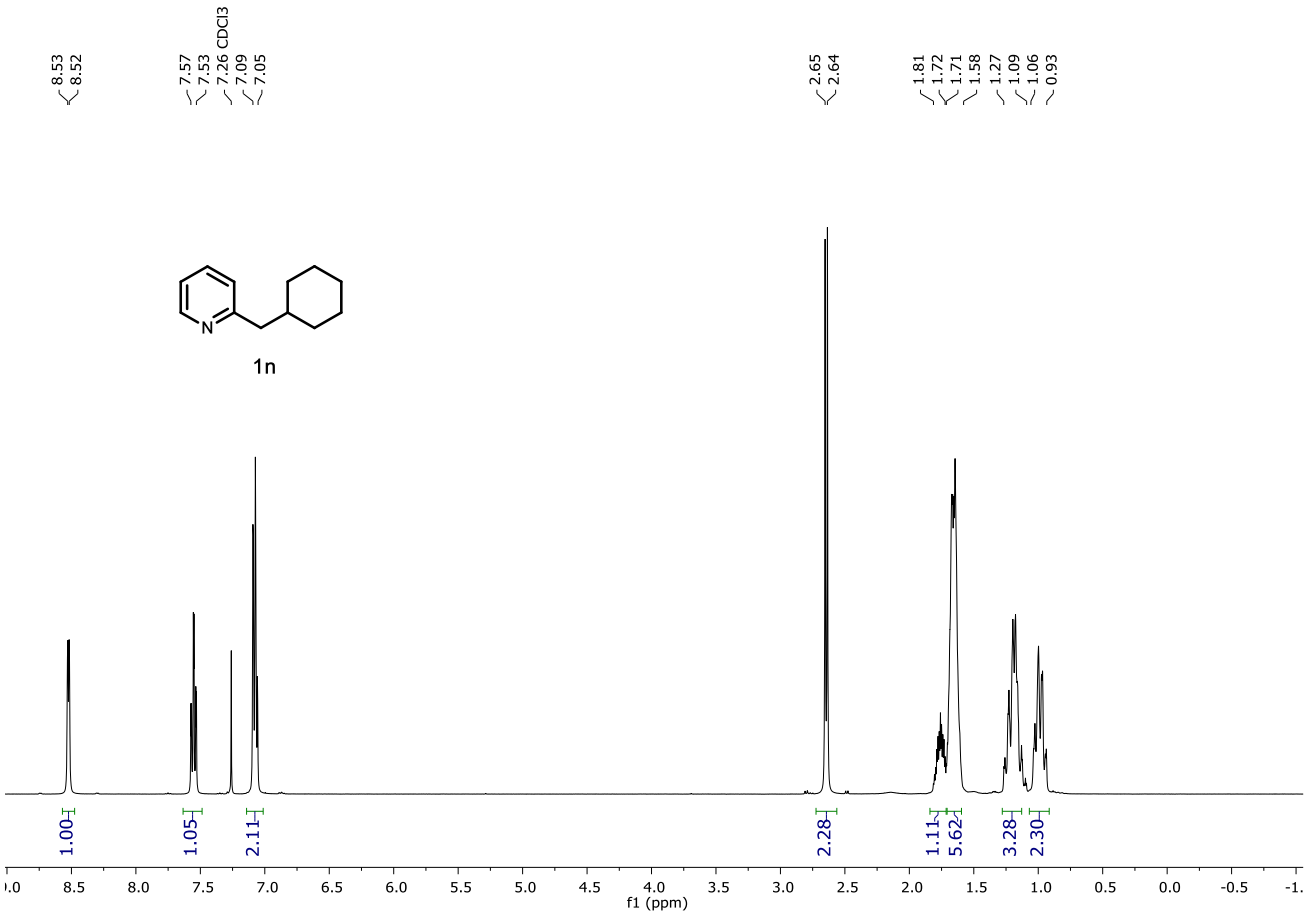
2-(cyclohexylmethyl)pyridine (1n)

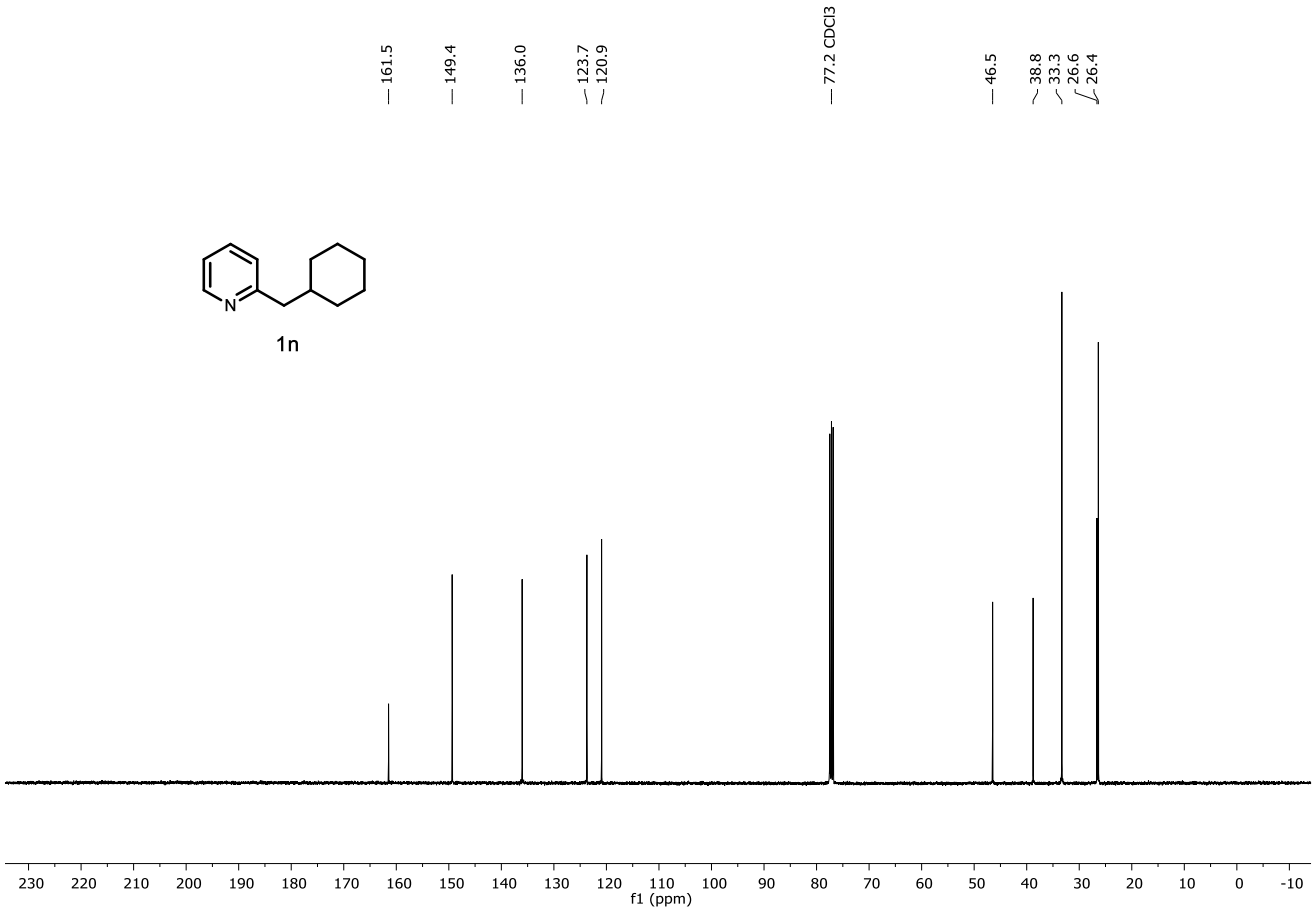


1n

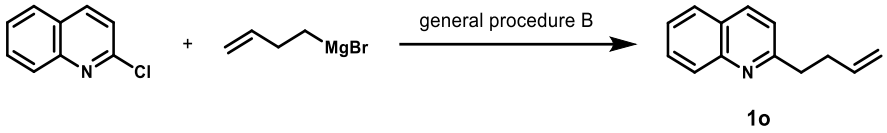
Compound **1n** was prepared from 2-methylpyridine (0.30 mL, 3.0 mmol, 1.0 equiv) and iodocyclohexane (0.54 mL, 4.5 mmol, 1.5 equiv) according to **general procedure C**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 8:1) afforded **1n** (433 mg, 82%) as a yellow oil.

R_f: 0.37 (hexanes/EtOAc = 4:1)
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (d, *J* = 4.8 Hz, 1H), 7.57–7.53 (m, 1H), 7.09–7.05 (m, 2H), 2.64 (d, *J* = 7.1 Hz, 2H), 1.81–1.72 (m, 1H), 1.71–1.58 (m, 5H), 1.27–1.09 (m, 3H), 1.06–0.93 (m, 2H)
^{13}C NMR (101 MHz, $CDCl_3$): δ 161.5, 149.4, 136.0, 123.7, 120.9, 46.5, 38.8, 33.3, 26.6, 26.4
IR (cm^{-1}): 2920, 1588, 1569, 1472, 1433, 750
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{12}H_{18}N^+$: 176.1434; found: 176.1439


8.53
8.52
7.57
7.53
7.26 CDCl3
7.09
7.05
2.65
2.64
1.81
1.72
1.71
1.58
1.27
1.09
1.06
0.93
1n
1.00
1.05
2.11
2.28
1.11
5.62
3.28
2.30
f1 (ppm)


161.5
149.4
136.0
123.7
120.9
77.2 CDCl3
46.5
38.8
33.3
26.6
26.4
1n
f1 (ppm)

2-(but-3-en-1-yl)quinoline (1o)



1o

Compound **1o** was prepared from 2-chloroquinoline (489 mg, 3.0 mmol, 1.0 equiv) according to **general procedure B**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 8:1) afforded **1o** (384 mg, 70%) as a yellow oil.

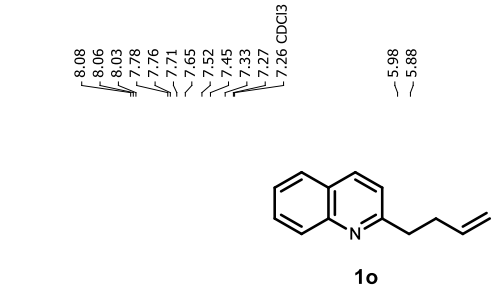
R_f: 0.53 (hexanes/EtOAc = 4:1)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (at, *J* = 8.3 Hz, 2H), 7.78–7.65 (m, 2H), 7.52–7.45 (m, 1H), 7.33–7.27 (m, 1H), 5.98–5.88 (m, 1H), 5.11–4.98 (m, 2H), 3.10–3.06 (m, 2H), 2.62–2.57 (m, 2H)

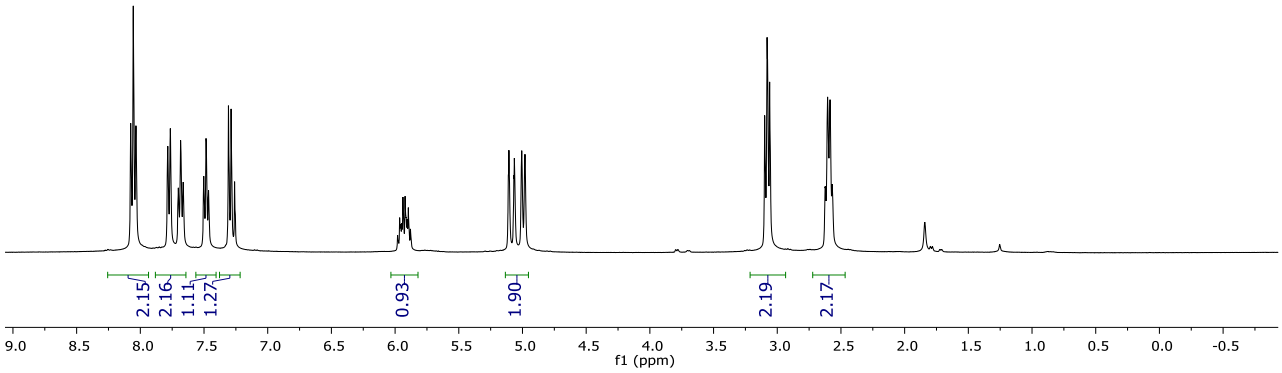
^{13}C NMR (101 MHz, $CDCl_3$): δ 162.2, 148.1, 137.8, 136.3, 129.5, 129.0, 127.6, 126.9, 125.9, 121.6, 115.4, 38.7, 33.9

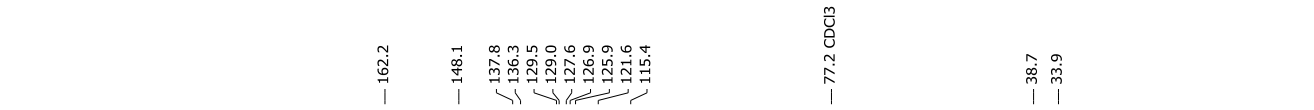
IR (cm^{-1}): 3059, 2925, 1600, 1503, 1426, 1311, 910, 824, 750, 617, 476

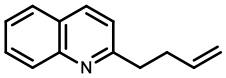
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{13}H_{14}N^+$: 184.1121; found: 184.1126


8.08
8.06
8.03
7.78
7.76
7.71
7.65
7.52
7.45
7.33
7.27
7.26 CDCl3
5.98
5.88
5.11
4.98
3.10
3.06
2.62
2.57

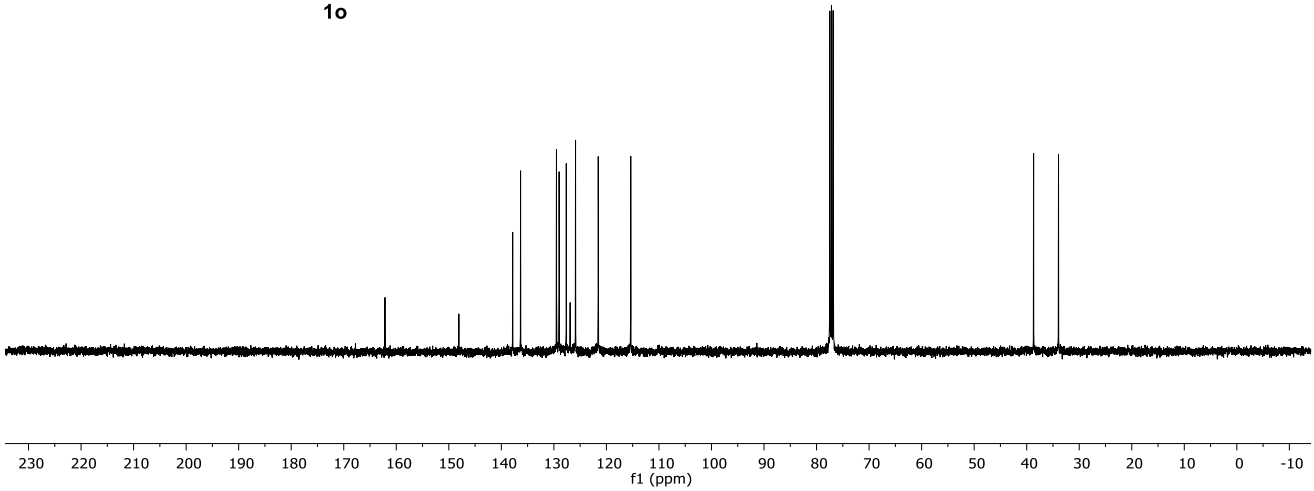
1o


2.15
2.16
1.11
1.27
0.93
1.90
2.19
2.17
f1 (ppm)

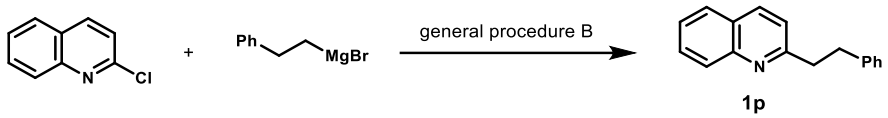

162.2
148.1
137.8
136.3
129.5
129.0
127.6
126.9
125.9
121.6
115.4
77.2 CDCl3
38.7
33.9



1o


f1 (ppm)

2-phenethylquinoline (1p)



1p

Compound **1p** was prepared from 2-chloroquinoline (300 mg, 1.8 mmol, 1.0 equiv) according to **general procedure B**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 8:1) afforded **1p** (348 mg, 83%) as a yellow oil. The characterization data match those previously reported in the literature.[11]

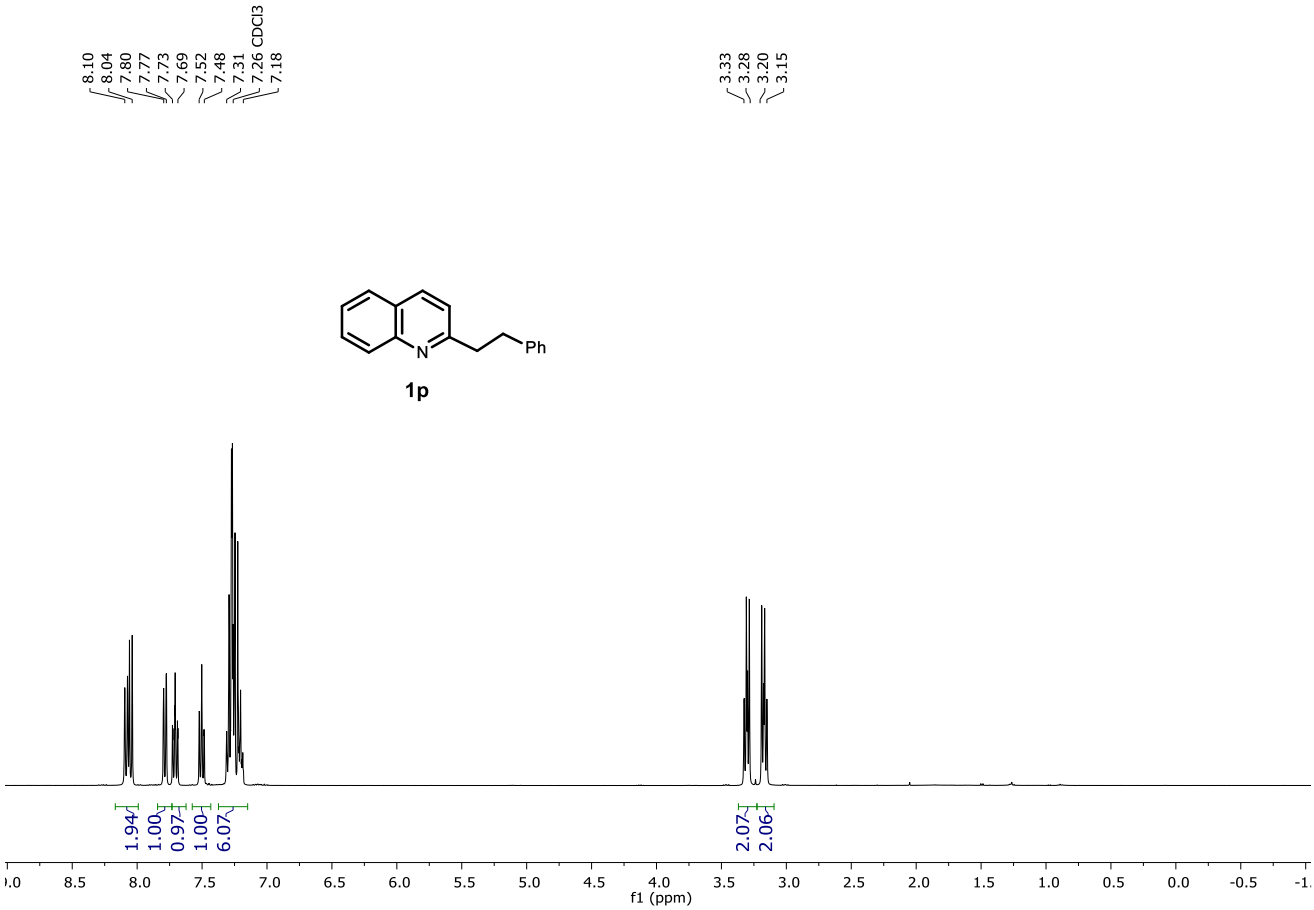
R_f: 0.52 (hexanes/EtOAc = 4:1)

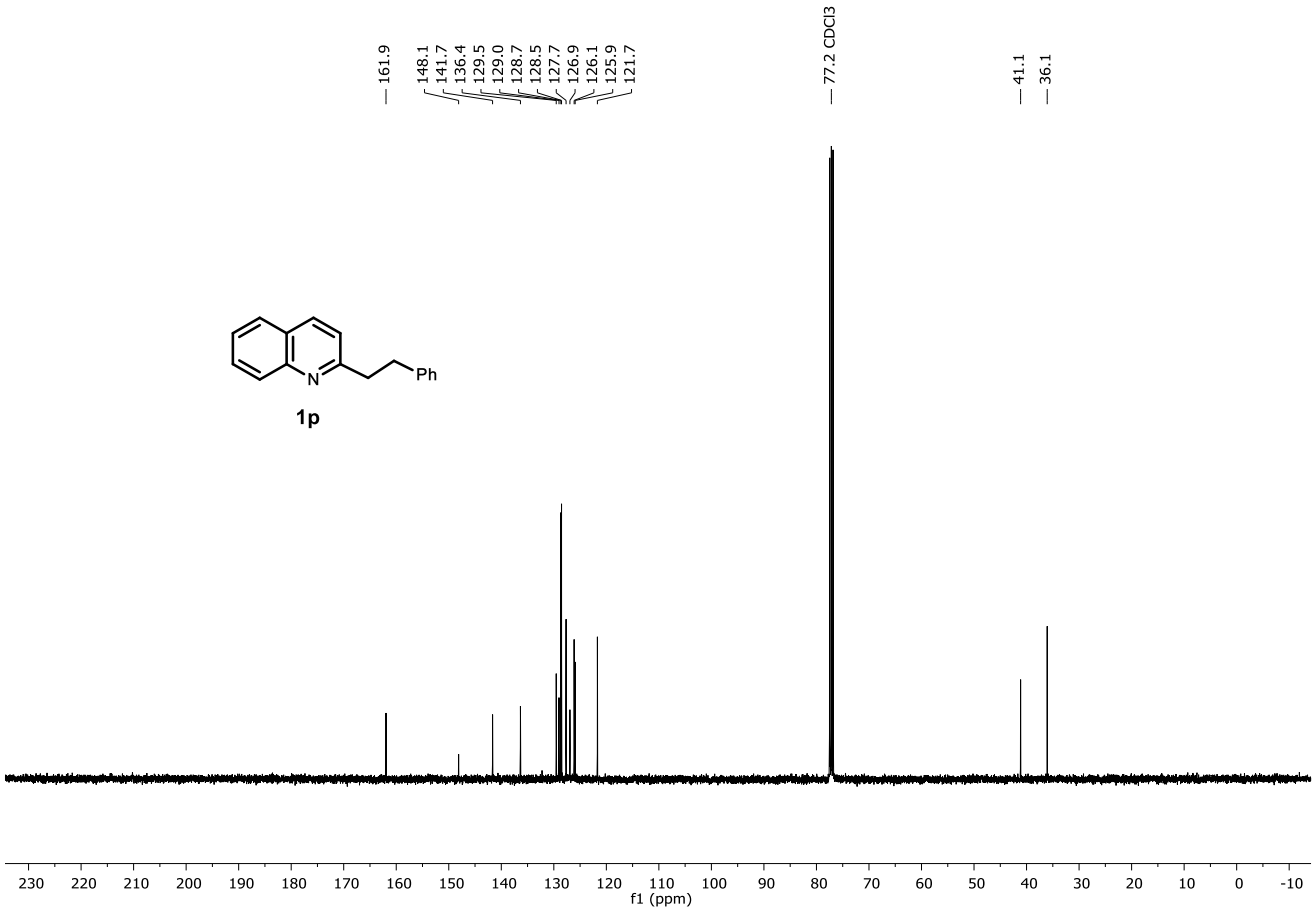
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–8.04 (m, 2H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.73–7.69 (m, 1H), 7.52–7.48 (m, 1H), 7.31–7.18 (m, 6H), 3.33–3.28 (m, 2H), 3.20–3.15 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.9, 148.1, 141.7, 136.4, 129.5, 129.0, 128.7, 128.5, 127.7, 126.9, 126.1, 125.9, 121.7, 41.1, 36.1

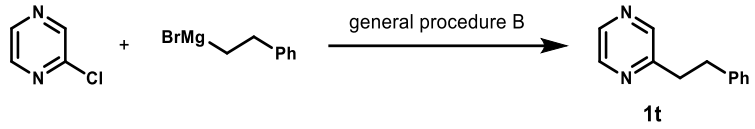
IR (cm^{-1}): 3059, 2929, 1600, 1503, 820, 750, 698

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{17}H_{16}N^+$: 234.1277; found: 234.1283


8.10
8.04
7.80
7.77
7.73
7.69
7.52
7.48
7.31
7.26 CDCl3
7.18
3.33
3.28
3.20
3.15
Ph
1p
1.94
1.00
0.97
1.00
6.07
2.07
2.06
f1 (ppm)


161.9
148.1
141.7
136.4
129.5
129.0
128.7
128.5
127.7
126.9
126.1
125.9
121.7
77.2 CDCl3
41.1
36.1
Ph
1p
f1 (ppm)

2-phenethylpyrazine (1t)



1t

Compound **1t** was prepared from 2-chloropyrazine (0.45 mL, 5.0 mmol, 1.0 equiv) according to **general procedure B**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 8:1) afforded **1t** (886 mg, 96%) as a yellow oil. The characterization data match those previously reported in the literature.[11]

R$_f$: 0.25 (hexanes/EtOAc = 2:1)

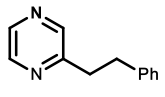
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 8.40 (d, *J* = 2.5 Hz, 1H), 8.36 (d, *J* = 1.5 Hz, 1H), 7.30–7.24 (m, 2H), 7.21–7.17 (m, 3H), 3.15–3.05 (m, 4H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.9, 144.8, 144.2, 142.5, 140.9, 128.6, 128.5, 126.4, 37.3, 35.5

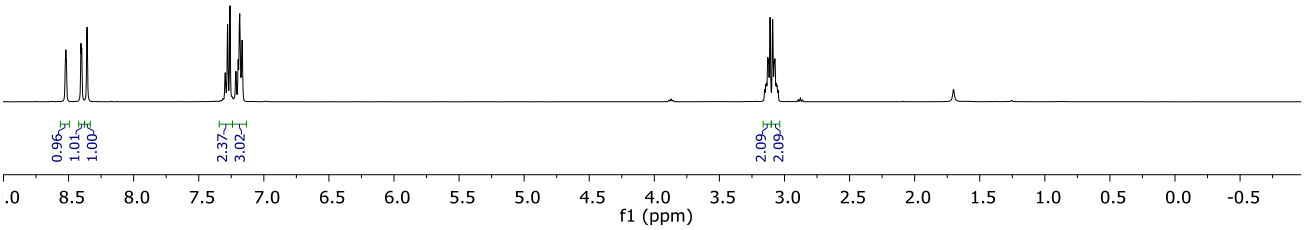
IR (cm^{-1}): 3027, 2926, 1453, 1403, 1124, 1018, 834, 746, 698

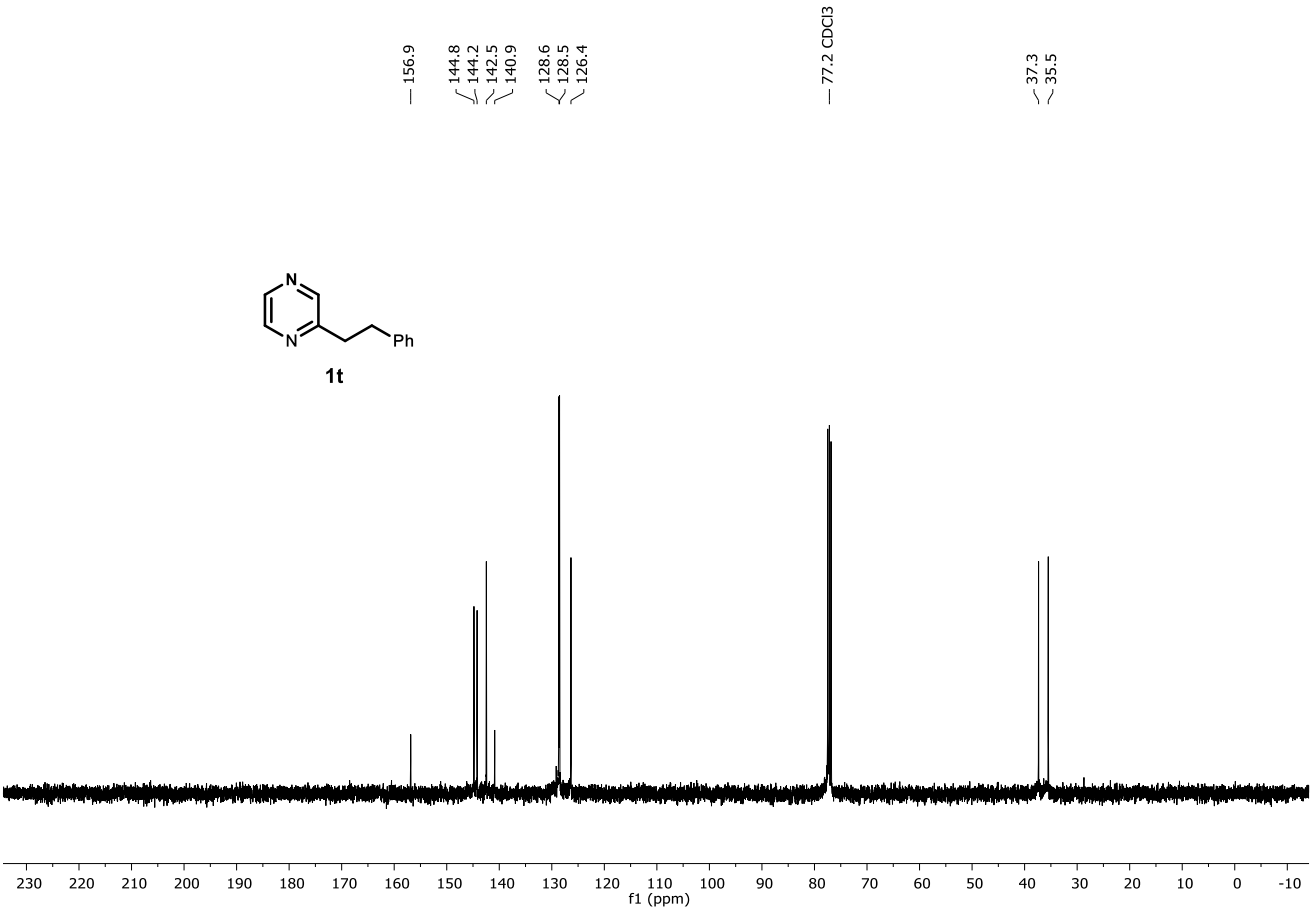
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{12}H_{13}N^+$: 185.1073; found: 185.1079


8.52
8.40
8.40
8.36
8.36
7.30
7.26 CDCl3
7.24
7.21
7.17
3.15
3.14
3.14
3.13
3.12
3.11
3.09
3.08
3.07
3.06
3.06
3.05


N
N
Ph

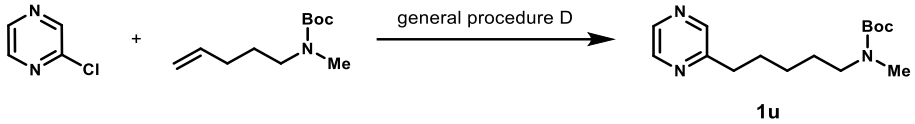
1t


0.96
1.01
1.00
2.37
3.02
2.09
2.09
.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
-0.5
f1 (ppm)


156.9
144.8
144.2
142.5
140.9
128.6
128.5
126.4
77.2 CDCl3
37.3
35.5
N
N
Ph
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

1t

tert-butyl methyl(5-(pyrazin-2-yl)pentyl)carbamate (1u)



1u

Compound **1u** was prepared from 2-chloropyrazine (46.0 mg, 0.40 mmol, 0.8 equiv) and tert-butyl methyl(pent-4-en-1-yl)carbamate[14] (100 mg, 0.5 mmol, 1.0 equiv) according to **general procedure D**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 5:1 to 3:1) afforded **1u** (105 mg, 76%) as a yellow oil.

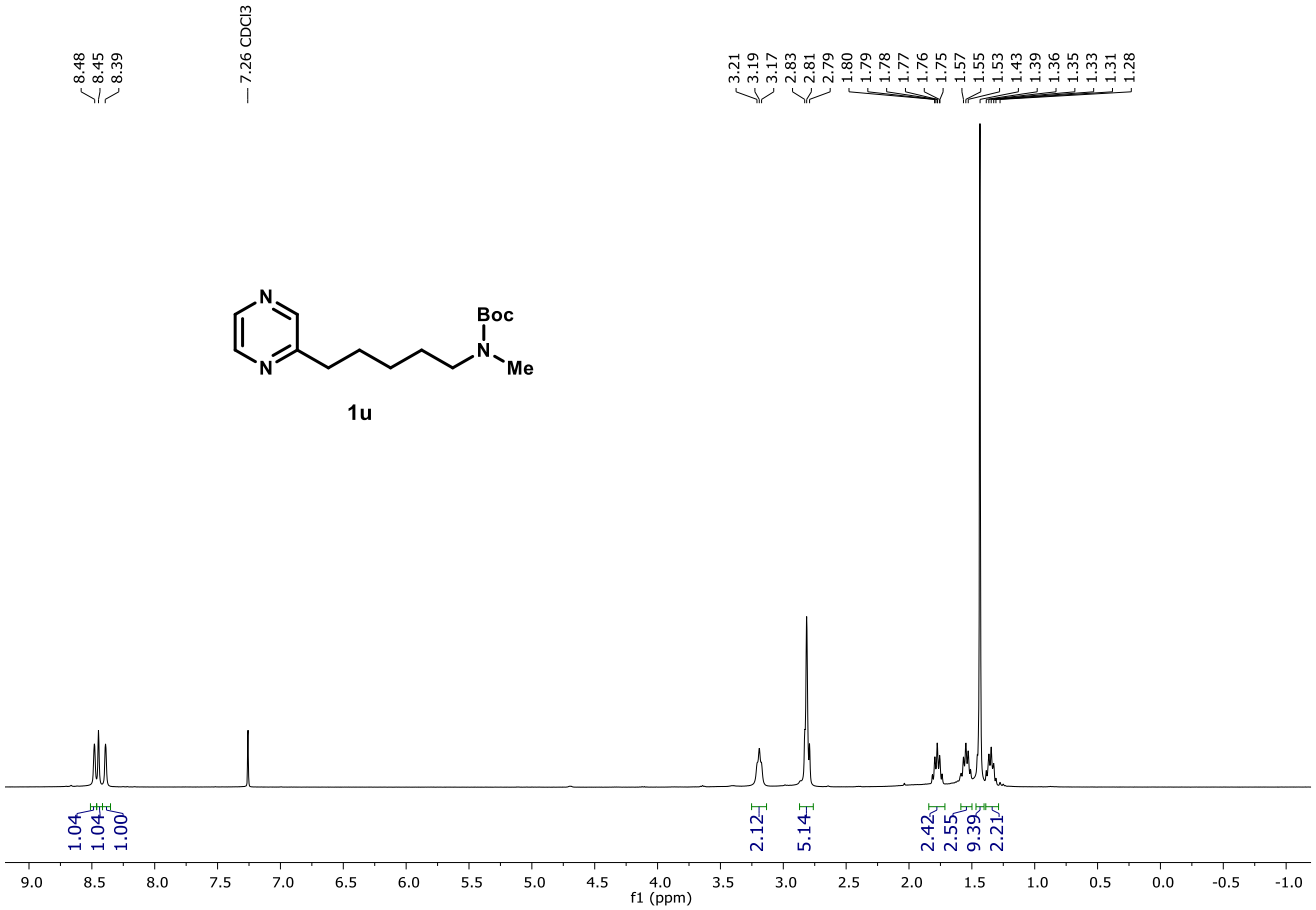
R$_f$: 0.50 (hexanes/EtOAc = 2:1)

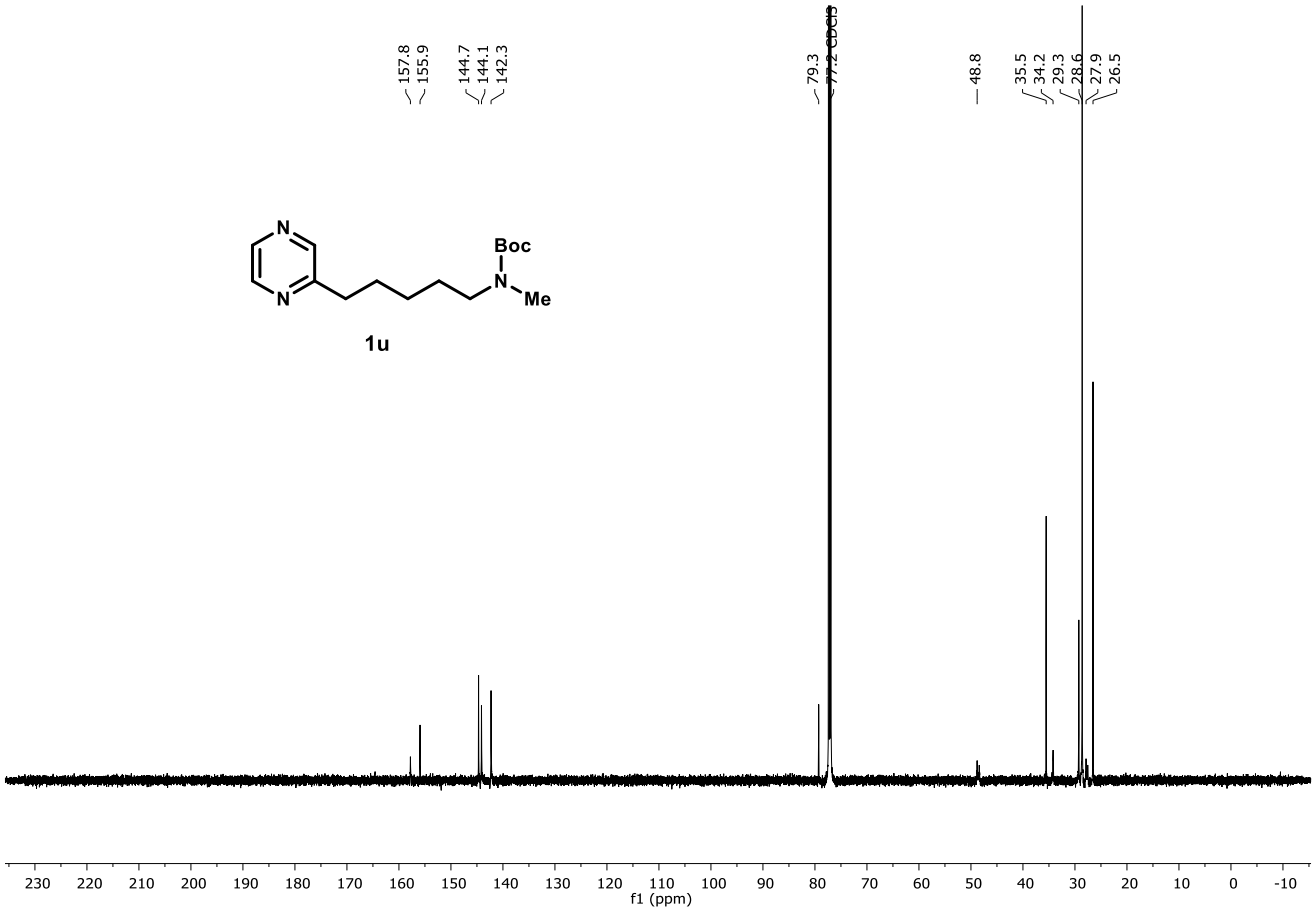
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.45 (s, 1H), 8.39 (s, 1H), 3.19 (t, *J* = 7.3 Hz, 2H), 2.89–2.76 (m, 5H), 1.83–1.71 (m, 2H), 1.62–1.51 (m, 2H), 1.43 (s, 9H), 1.39–1.28 (m, 2H)

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.8, 155.9, 144.7, 144.1, 142.3, 79.3, 48.8, 35.5, 34.2, 29.3, 28.6, 27.9, 26.5

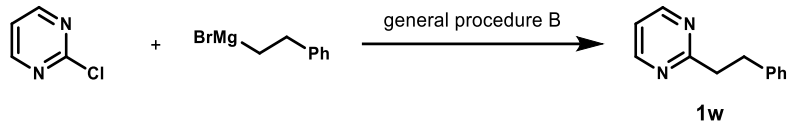
IR (cm^{-1}): 2930, 2860, 1688, 1398, 1159, 1017, 879, 770

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{15}H_{26}N_3O_2^+$: 280.2020; found: 280.2025


8.48
8.45
8.39
7.26 CDCl3
3.21
3.19
3.17
2.83
2.81
2.79
1.80
1.79
1.78
1.77
1.76
1.75
1.57
1.55
1.53
1.43
1.39
1.36
1.35
1.33
1.31
1.28
Boc
N
Me
1u
1.04
1.04
1.00
2.12
5.14
2.42
2.55
9.39
2.21
f1 (ppm)


157.8
155.9
144.7
144.1
142.3
79.3
77.2 CDCl3
48.8
35.5
34.2
29.3
28.6
27.9
26.5
Boc
N
Me
1u
f1 (ppm)

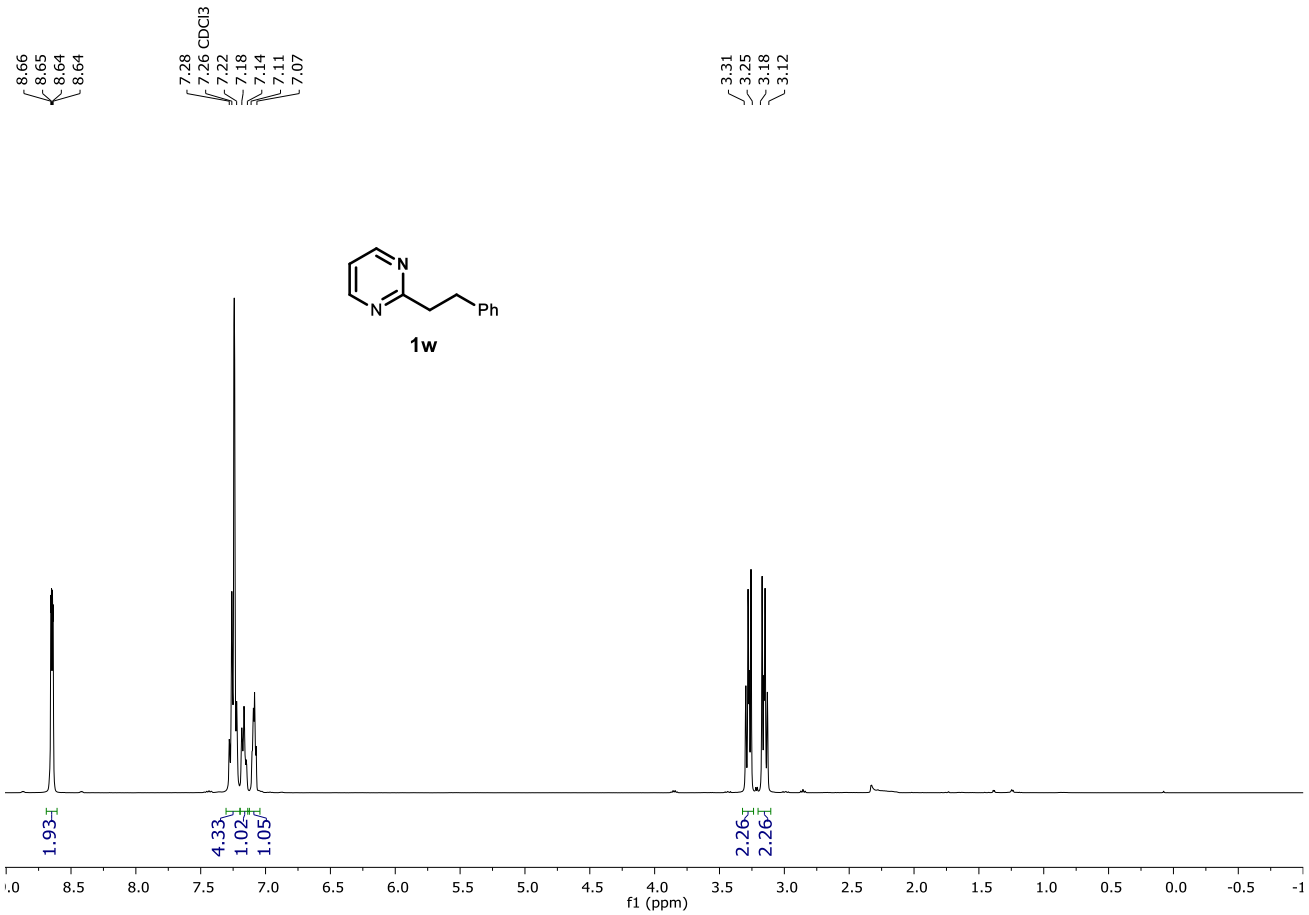
2-phenethylpyrimidine (1w)

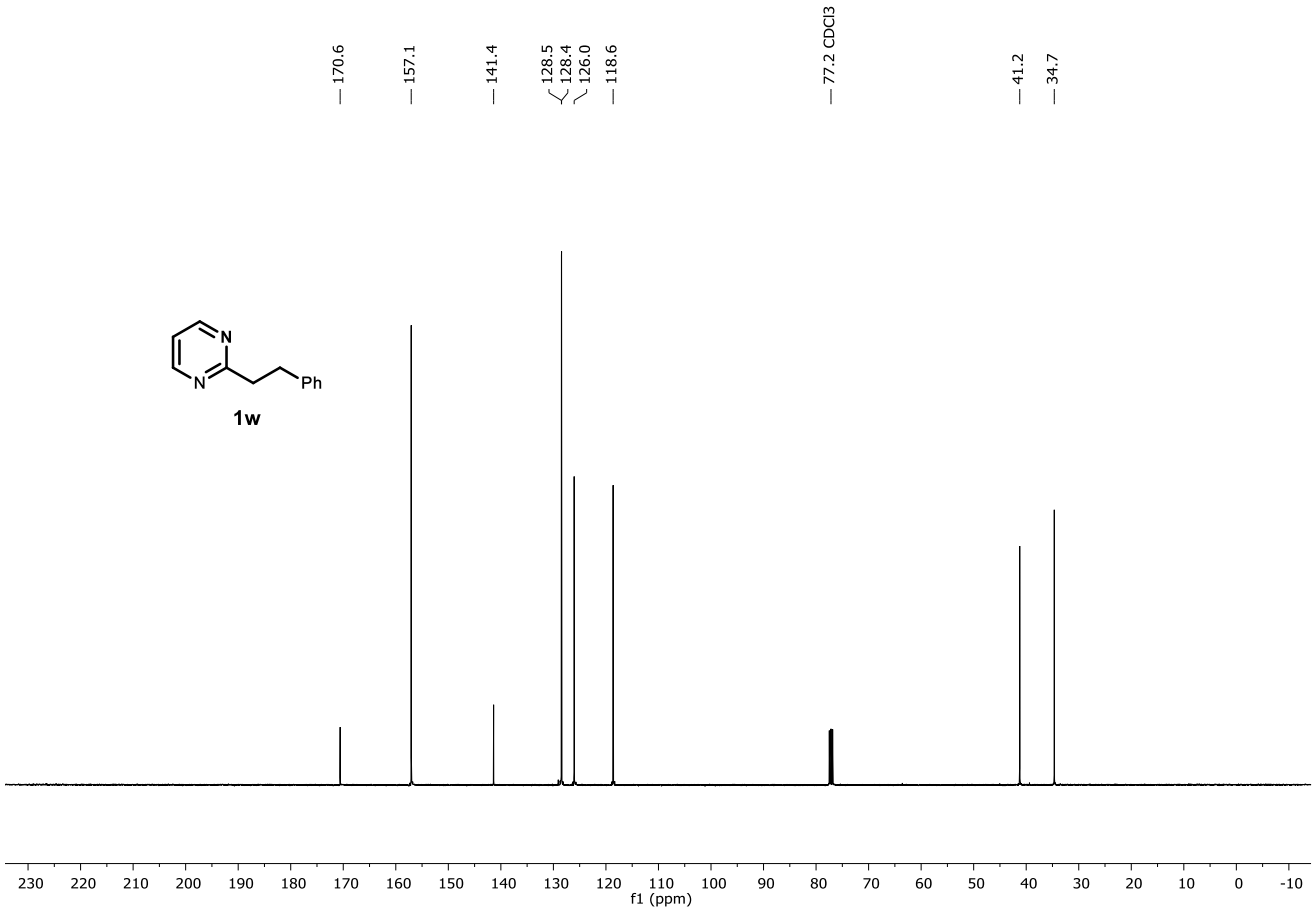


1w

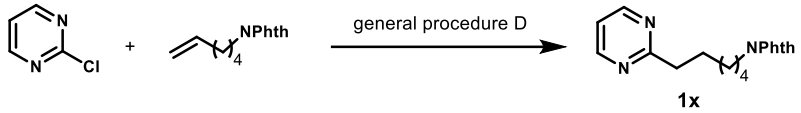
Compound **1w** was prepared from 2-chloropyrimidine (687 mg, 6.0 mmol, 1.0 equiv) according to **general procedure B**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 10:1 to 8:1) afforded **1w** (831 mg, 75%) as a yellow oil. The characterization data match those previously reported in the literature.[12]

R_f: 0.23 (hexanes/EtOAc = 5:1)
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (dd, *J* = 5.0, 2.1 Hz, 2H), 7.28–7.22 (m, 4H), 7.18–7.14 (m, 1H), 7.11–7.07 (m, 1H), 3.31–3.25 (m, 2H), 3.18–3.12 (m, 2H)
^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 157.1, 141.4, 128.5, 128.4, 126.0, 118.6, 41.2, 34.7
IR (cm^{-1}): 3027, 2929, 1559, 1422, 786, 746, 697, 635, 521
ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{12}H_{13}N^+$: 185.1073; found: 185.1079


8.66
8.65
8.64
8.64
7.28
7.26 CDCl3
7.22
7.18
7.14
7.11
7.07
3.31
3.25
3.18
3.12
N
N
Ph
1w
1.93
4.33
1.02
1.05
2.26
2.26
f1 (ppm)


170.6
157.1
141.4
128.5
128.4
126.0
118.6
77.2 CDCl3
41.2
34.7
N
N
Ph
1w
f1 (ppm)

2-(6-(pyrimidin-2-yl)hexyl)isoindoline-1,3-dione (1x)



1x

Compound **1x** was prepared from 2-chloropyrimidine (183 mg, 1.6 mmol, 0.8 equiv) and 2-(hex-5-en-1-yl)isoindoline-1,3-dione[2] (458 mg, 2 mmol, 1.0 equiv) according to **general procedure D**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 3:1 to 1:1) afforded **1x** (210 mg, 43%) as a yellow solid.

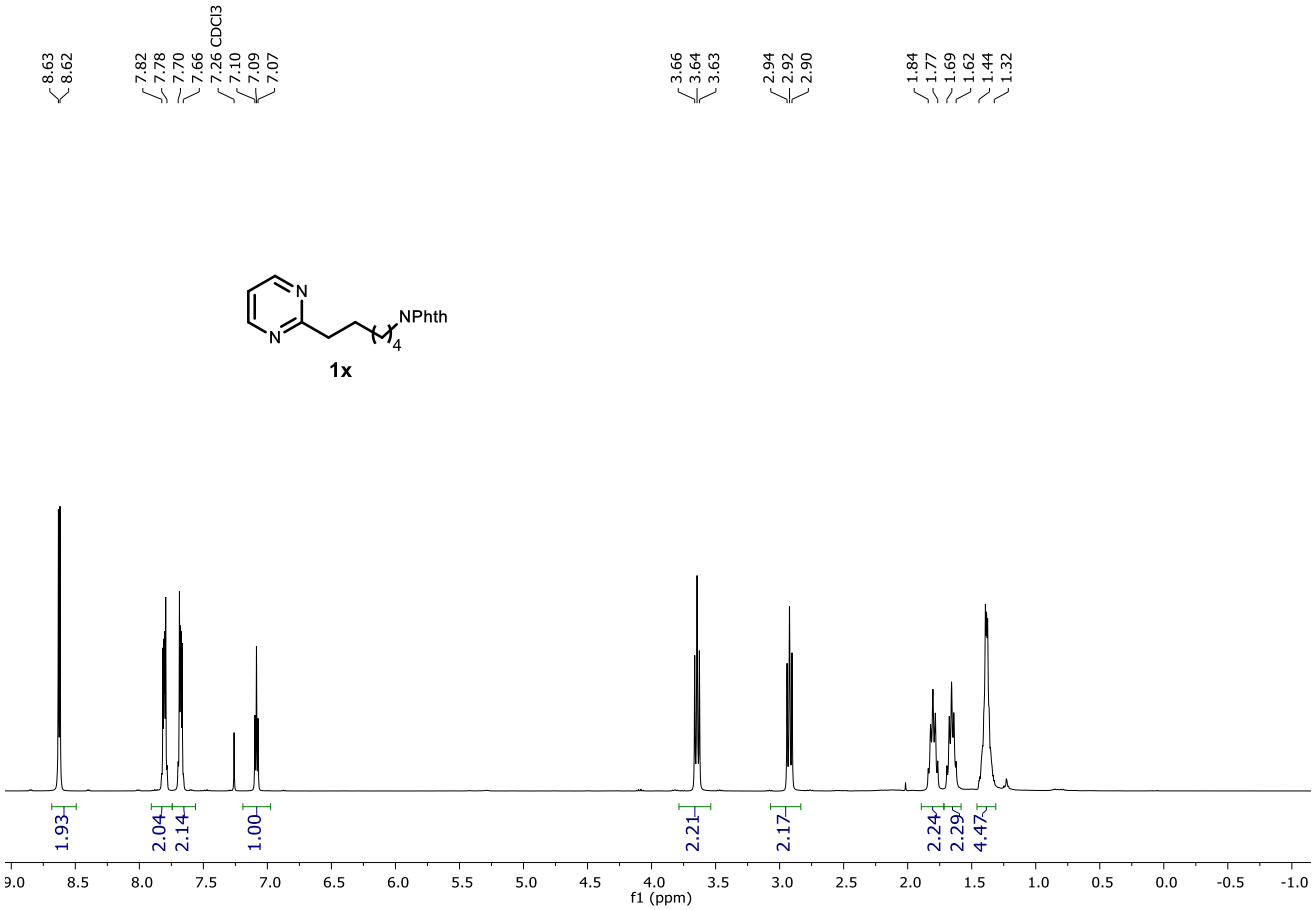
R_f: 0.17 (hexanes/EtOAc = 1:1)

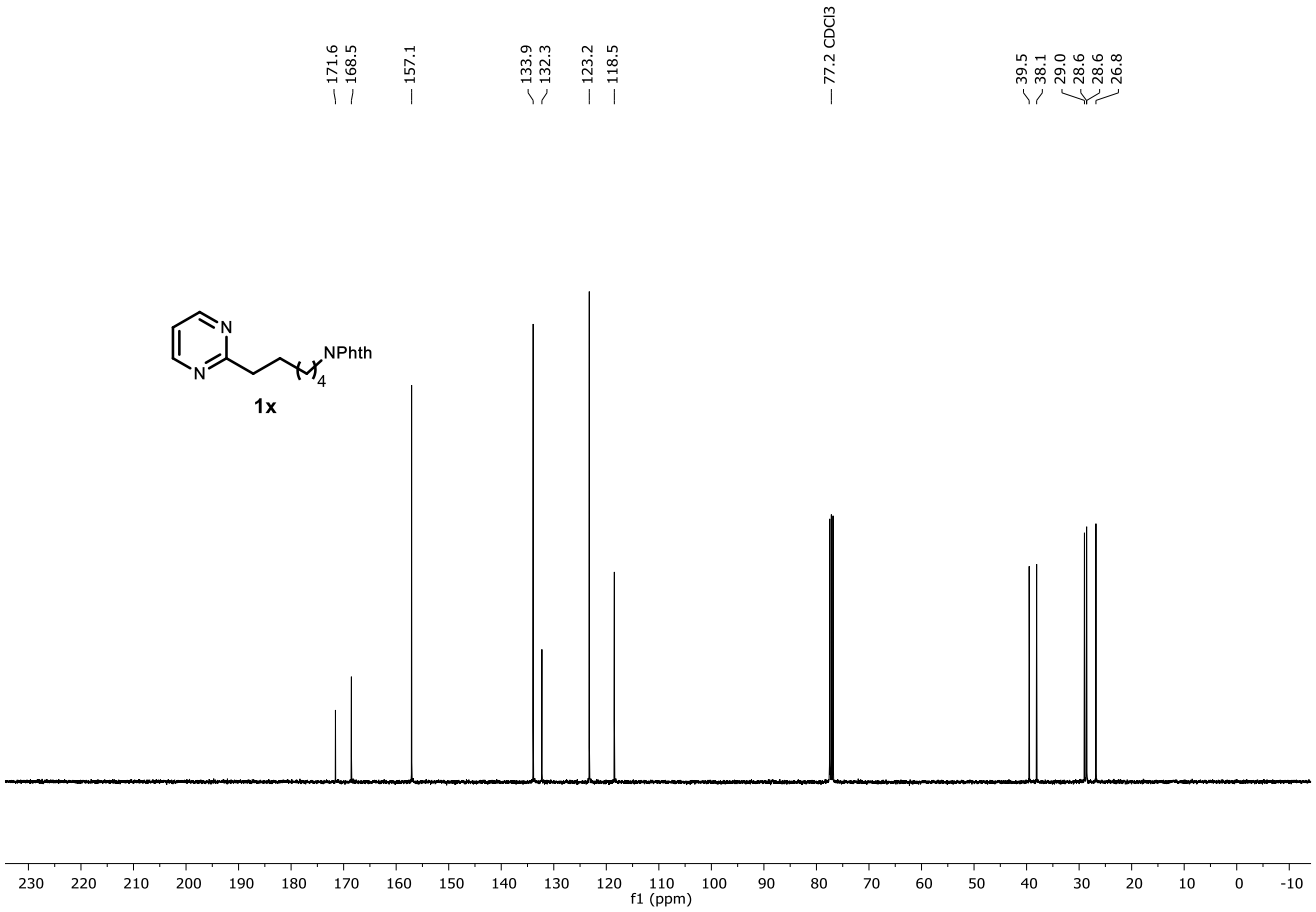
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (d, *J* = 4.9 Hz, 2H), 7.82–7.78 (m, 2H), 7.70–7.66 (m, 2H), 7.09 (at, *J* = 4.9 Hz, 1H), 3.64 (t, *J* = 7.3 Hz, 2H), 3.19–2.71 (m, 2H), 1.84–1.77 (m, 2H), 1.69–1.62 (m, 2H), 1.44–1.32 (m, 4H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 171.6, 168.5, 157.1, 133.9, 132.3, 123.2, 118.5, 39.5, 38.1, 29.0, 28.6, 28.6, 26.8

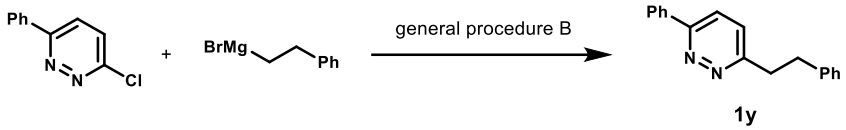
IR (cm^{-1}): 2937, 2858, 1704, 1559, 1395, 1367, 1046, 717, 635, 529

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{18}H_{20}N_3O_2^+$: 310.1550; found: 310.1555


8.63
8.62
7.82
7.78
7.70
7.66
7.26 CDCl3
7.10
7.09
7.07
3.66
3.64
3.63
2.94
2.92
2.90
1.84
1.77
1.69
1.62
1.44
1.32
N
N
NPhth
4
1x
1.93
2.04
2.14
1.00
2.21
2.17
2.24
2.29
4.47
f1 (ppm)


171.6
168.5
157.1
133.9
132.3
123.2
118.5
77.2 CDCl3
39.5
38.1
29.0
28.6
28.6
26.8
N
N
NPhth
4
1x
f1 (ppm)

3-phenethyl-6-phenylpyridazine (1y)



1y

Compound **1y** was prepared from 3-chloro-6-phenylpyridazine (381 mg, 2.0 mmol, 1.0 equiv) according to **general procedure B**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 8:1 to 5:1) afforded **1y** (442 mg, 85%) as a white solid.

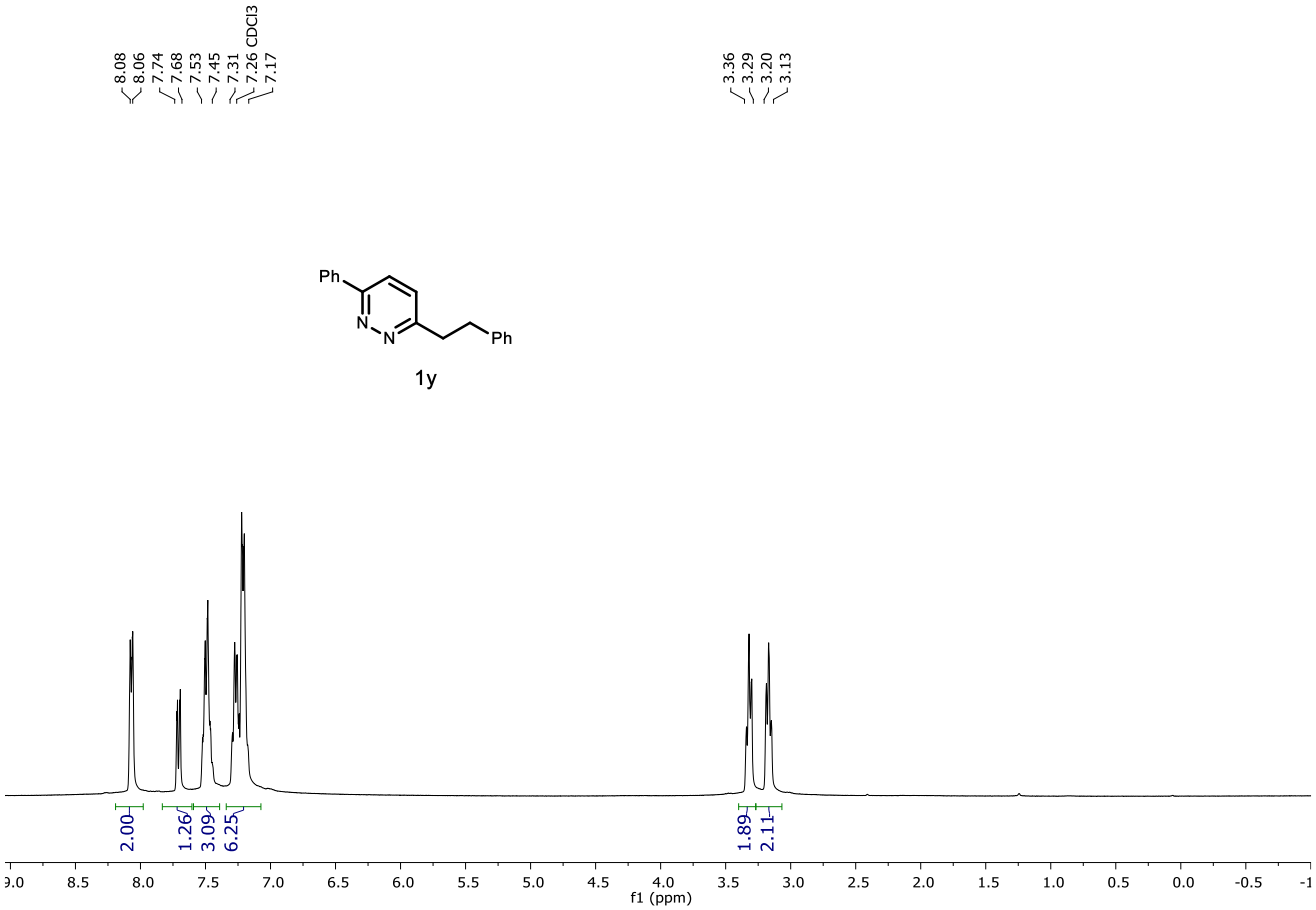
R$_f$: 0.23 (hexanes/EtOAc = 4:1)

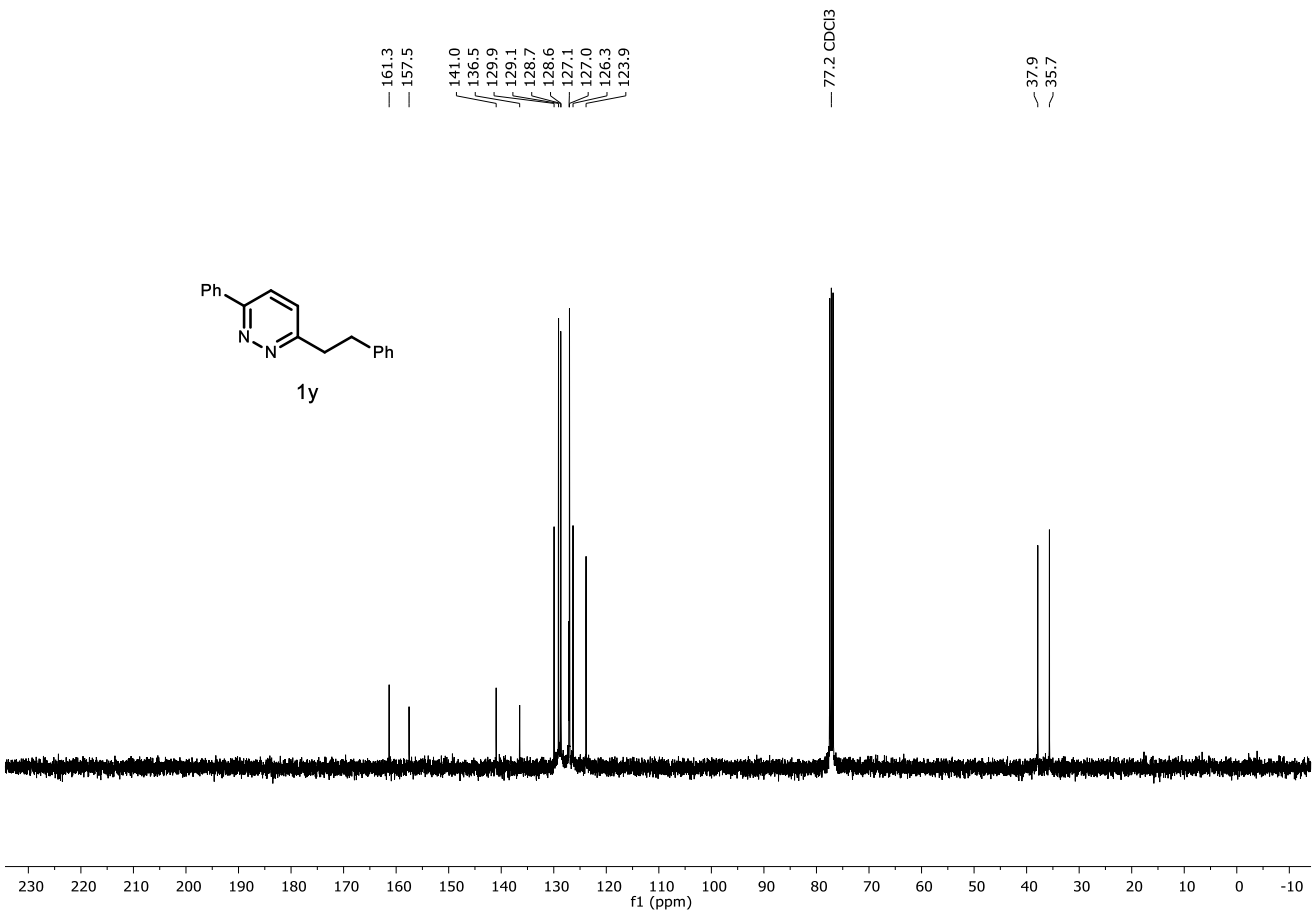
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27–7.99 (m, 2H), 7.74–7.68 (m, 1H), 7.53–7.45 (m, 3H), 7.31–7.17 (m, 6H), 3.36–3.29 (m, 2H), 3.20–3.13 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 161.3, 157.5, 141.0, 136.5, 129.9, 129.1, 128.7, 128.6, 127.1, 127.0, 126.3, 123.9, 37.9, 35.7

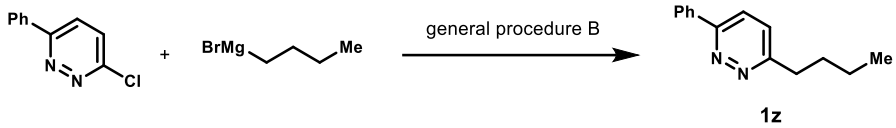
IR (cm^{-1}): 3024, 2930, 1451, 1426, 1006, 872, 745, 690, 511

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{18}H_{17}N_2^+$: 261.1386; found: 261.1392


8.08
8.06
7.74
7.68
7.53
7.45
7.31
7.26 CDCl3
7.17
3.36
3.29
3.20
3.13
Ph
N
N
Ph
1y
2.00
1.26
3.09
6.25
1.89
2.11
f1 (ppm)


161.3
157.5
141.0
136.5
129.9
129.1
128.7
128.6
127.1
127.0
126.3
123.9
77.2 CDCl3
37.9
35.7
Ph
N
N
Ph
1y
f1 (ppm)

3-butyl-6-phenylpyridazine (1z)



Compound **1z** was prepared from 3-chloro-6-phenylpyridazine (285 mg, 1.5 mmol, 1.0 equiv) according to **general procedure B**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 8:1 to 4:1) afforded **1z** (273 mg, 70%) as a white solid.

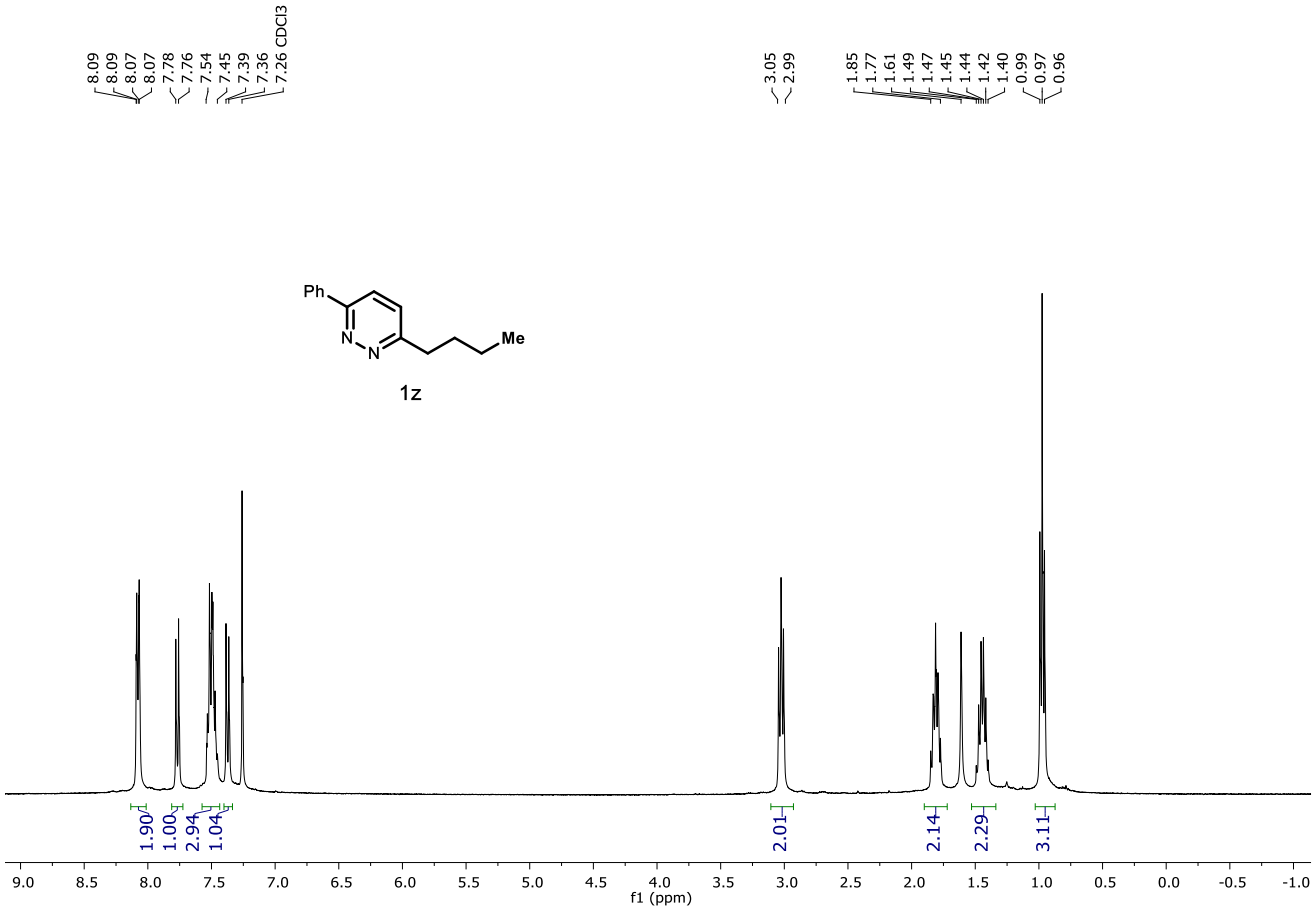
R_f: 0.43 (hexanes/EtOAc = 2:1)

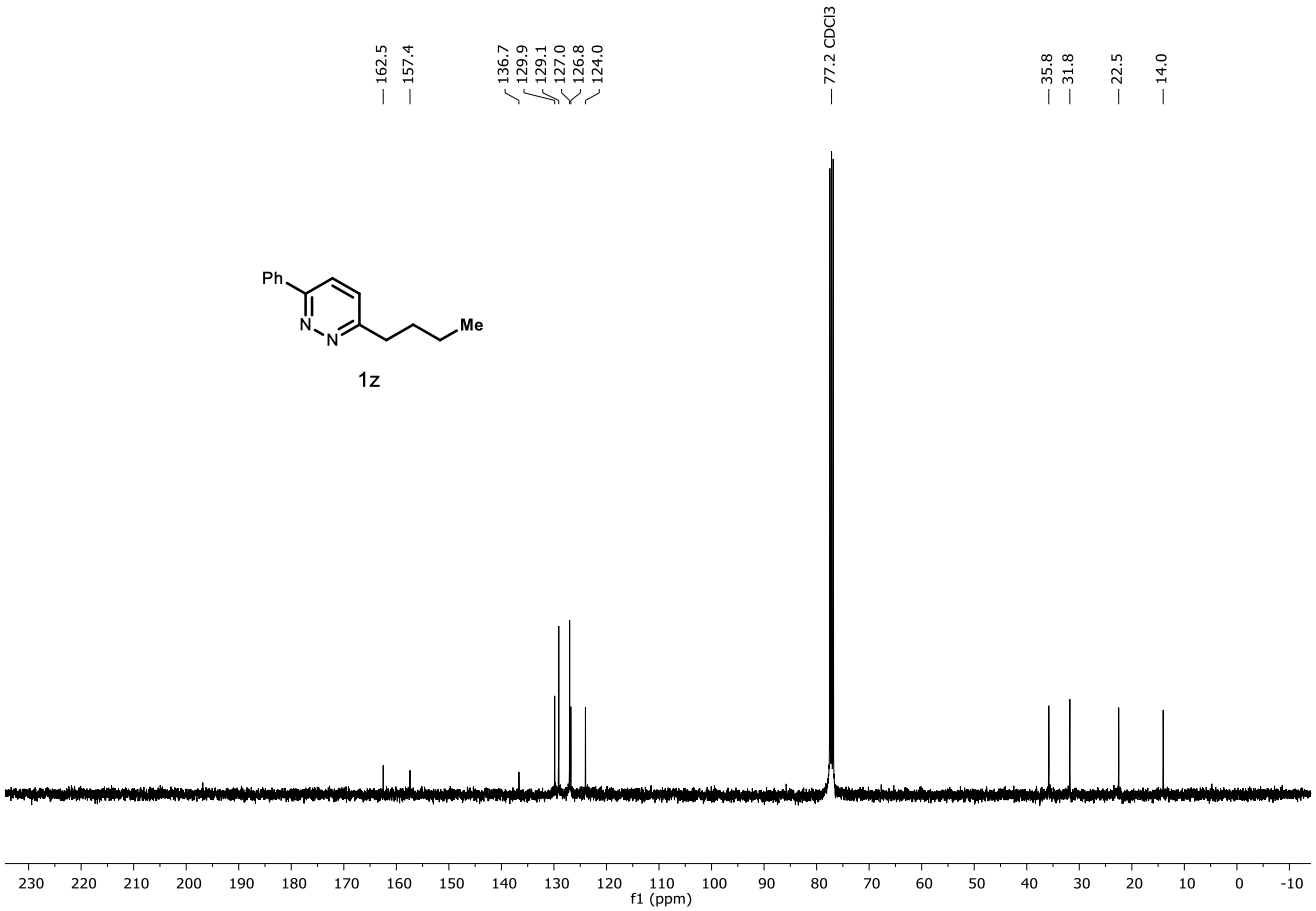
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15–7.95 (m, 2H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.54–7.45 (m, 3H), 7.38 (d, *J* = 8.7 Hz, 1H), 3.05–2.99 (m, 2H), 1.85–1.77 (m, 2H), 1.45 (h, *J* = 7.3 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.5, 157.4, 136.7, 129.9, 129.1, 127.0, 126.8, 124.0, 35.8, 31.8, 22.5, 14.0

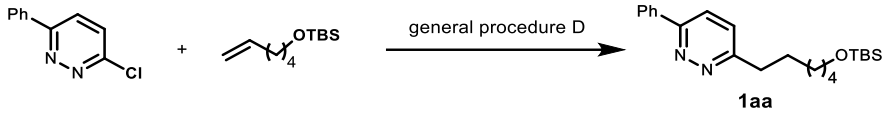
IR (cm^{-1}): 3057, 2955, 2928, 2859, 1422, 1112, 1012, 849, 752, 694

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{14}H_{17}N_2^+$: 213.1386; found: 213.1392


8.09
8.09
8.07
8.07
7.78
7.76
7.54
7.45
7.39
7.36
7.26 CDCl3
3.05
2.99
1.85
1.77
1.61
1.49
1.47
1.45
1.44
1.42
1.40
0.99
0.97
0.96
Ph
N
N
Me
1z
1.90
1.00
2.94
1.04
2.01
2.14
2.29
3.11
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 -0.5 -1.0
f1 (ppm)


162.5
157.4
136.7
129.9
129.1
127.0
126.8
124.0
77.2 CDCl3
35.8
31.8
22.5
14.0
Ph
N
N
Me
1z
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3-(6-((tert-butyldimethylsilyl)oxy)hexyl)-6-phenylpyridazine (1aa)



1aa

Compound **1aa** was prepared from 3-chloro-6-phenylpyridazine (305 mg, 1.6 mmol, 0.8 equiv) and tert-butyl(hex-5-en-1-yloxy)dimethylsilane[2] (284 mg, 2.0 mmol, 1.0 equiv) according to **general procedure D**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 15:1 to 10:1) afforded **1aa** (314 mg, 56%) as a yellow oil.

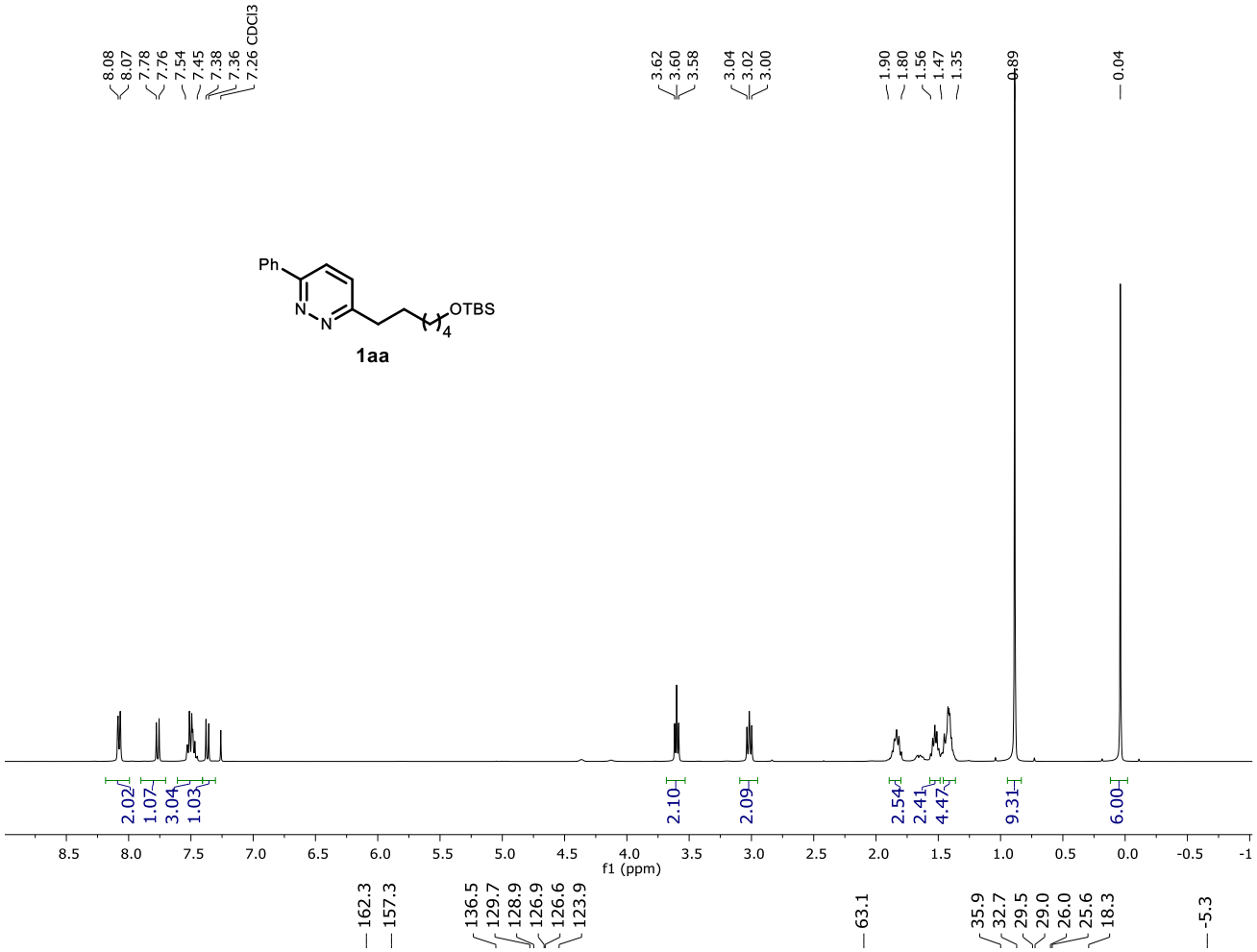
R_f: 0.45 (hexanes/EtOAc = 4:1)

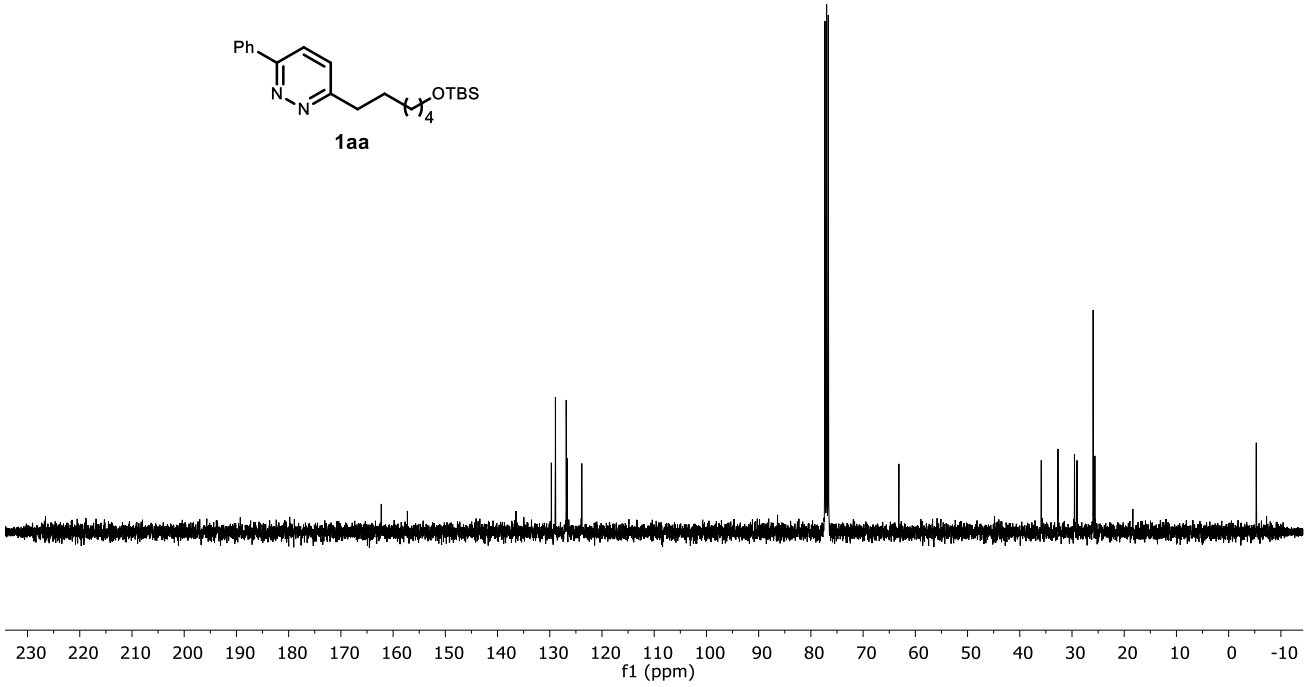
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 6.7 Hz, 2H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.54–7.45 (m, 3H), 7.37 (d, *J* = 8.7 Hz, 1H), 3.60 (t, *J* = 6.4 Hz, 2H), 3.02 (t, *J* = 6.4 Hz, 2H), 1.90–1.80 (m, 2H), 1.56–1.47 (m, 2H), 1.47–1.35 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.3, 157.3, 136.5, 129.7, 128.9, 126.9, 126.6, 123.9, 63.1, 35.9, 32.7, 29.5, 29.0, 26.0, 25.6, 18.3, –5.3

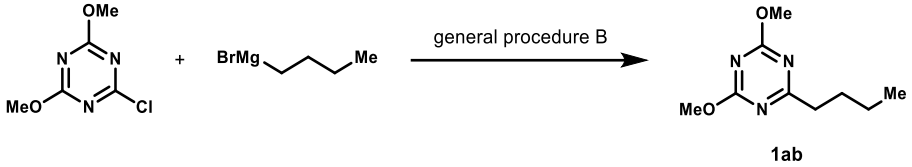
IR (cm^{-1}): 2927, 2856, 1423, 1254, 1096, 1008, 833, 774, 693

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{22}H_{35}N_2OSi^+$: 371.2513; found: 371.2519


8.08
8.07
7.78
7.76
7.54
7.45
7.38
7.36
7.26 CDCl3
3.62
3.60
3.58
3.04
3.02
3.00
1.90
1.80
1.56
1.47
1.35
0.89
0.04
Ph
N
N
OTBS
4
1aa
2.02
1.07
3.04
1.03
2.10
2.09
2.54
2.41
4.47
9.31
6.00
f1 (ppm)


162.3
157.3
136.5
129.7
128.9
126.9
126.6
123.9
63.1
35.9
32.7
29.5
29.0
26.0
25.6
18.3
-5.3
Ph
N
N
OTBS
4
1aa
f1 (ppm)

2-butyl-4,6-dimethoxy-1,3,5-triazine (1ab)



1ab

Compound **1ab** was prepared from 2-chloro-4,6-dimethoxy-1,3,5-triazine (1.05 g, 6.0 mmol, 1.0 equiv) according to **general procedure B**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 8:1 to 4:1) afforded **1ab** (860 mg, 73%) as a colorless oil.

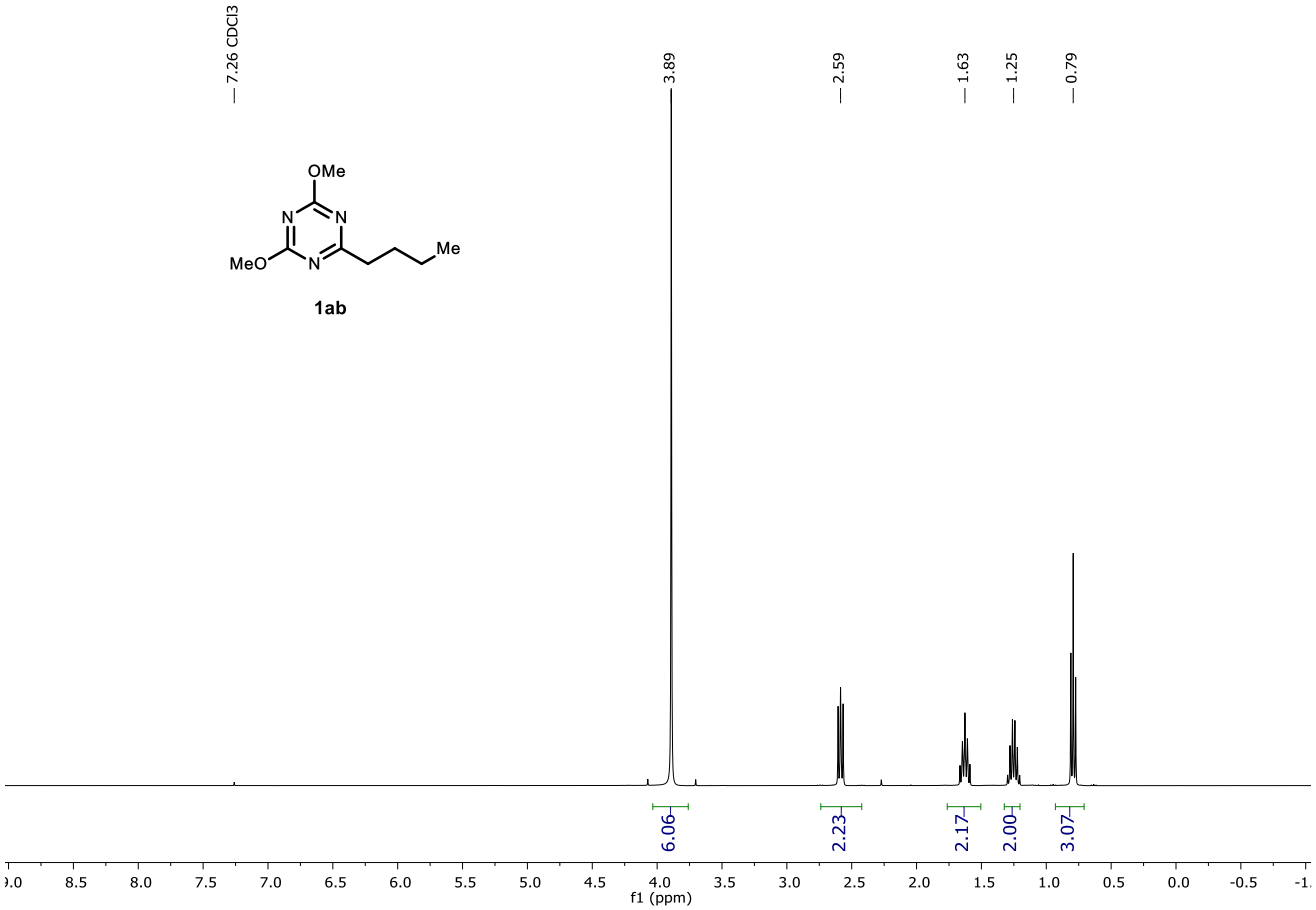
R_f: 0.45 (hexanes/EtOAc = 4:1)

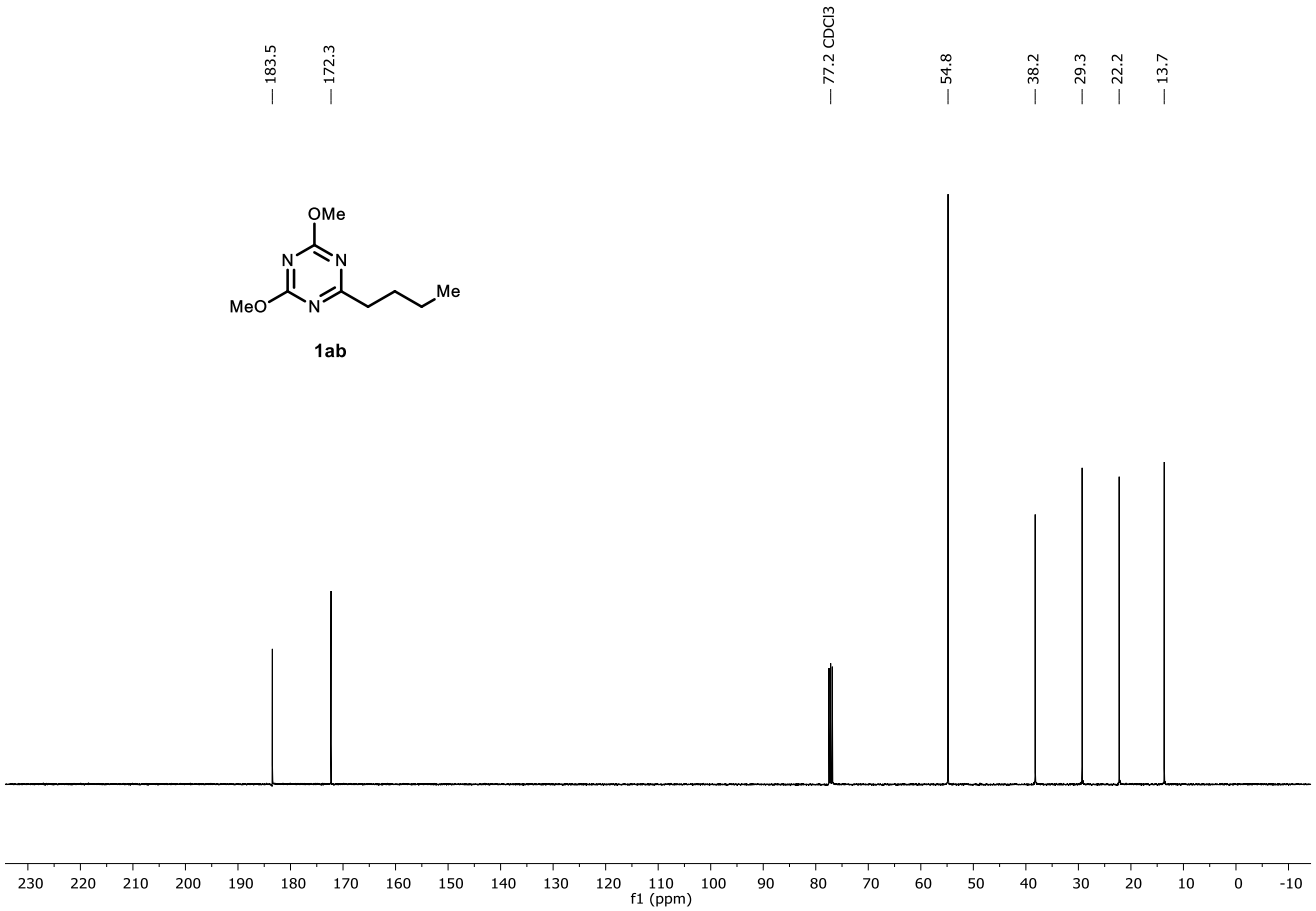
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.89 (s, 6H), 2.59 (t, *J* = 7.4 Hz, 2H), 1.63 (p, *J* = 7.6 Hz, 2H), 1.25 (h, *J* = 7.4 Hz, 2H), 0.79 (t, *J* = 7.4 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 183.5, 172.3, 54.8, 38.2, 29.3, 22.2, 13.7

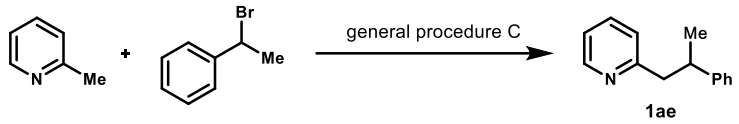
IR (cm^{-1}): 2957, 2872, 1543, 1499, 1458, 1345, 1201, 1088, 939, 826, 464

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_9H_{16}N_3O_2^+$: 198.1237; found: 198.1243


7.26 CDCl3
3.89
2.59
1.63
1.25
0.79
OMe
N
N
MeO
N
Me
1ab
6.06
2.23
2.17
2.00
3.07
f1 (ppm)


183.5
172.3
77.2 CDCl3
54.8
38.2
29.3
22.2
13.7
OMe
N
N
MeO
N
Me
1ab
f1 (ppm)

2-(2-phenylpropyl)pyridine (1ae)



Compound **1ae** was prepared from 2-methylpyridine (372 mg, 4.0 mmol, 1.0 equiv) with (1-bromoethyl)benzene (0.65 mL, 4.8 mmol, 1,2 equiv) according to **general procedure C**. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 10:1 to 4:1) afforded **1ae** (559 mg, 71%) as a colorless oil.

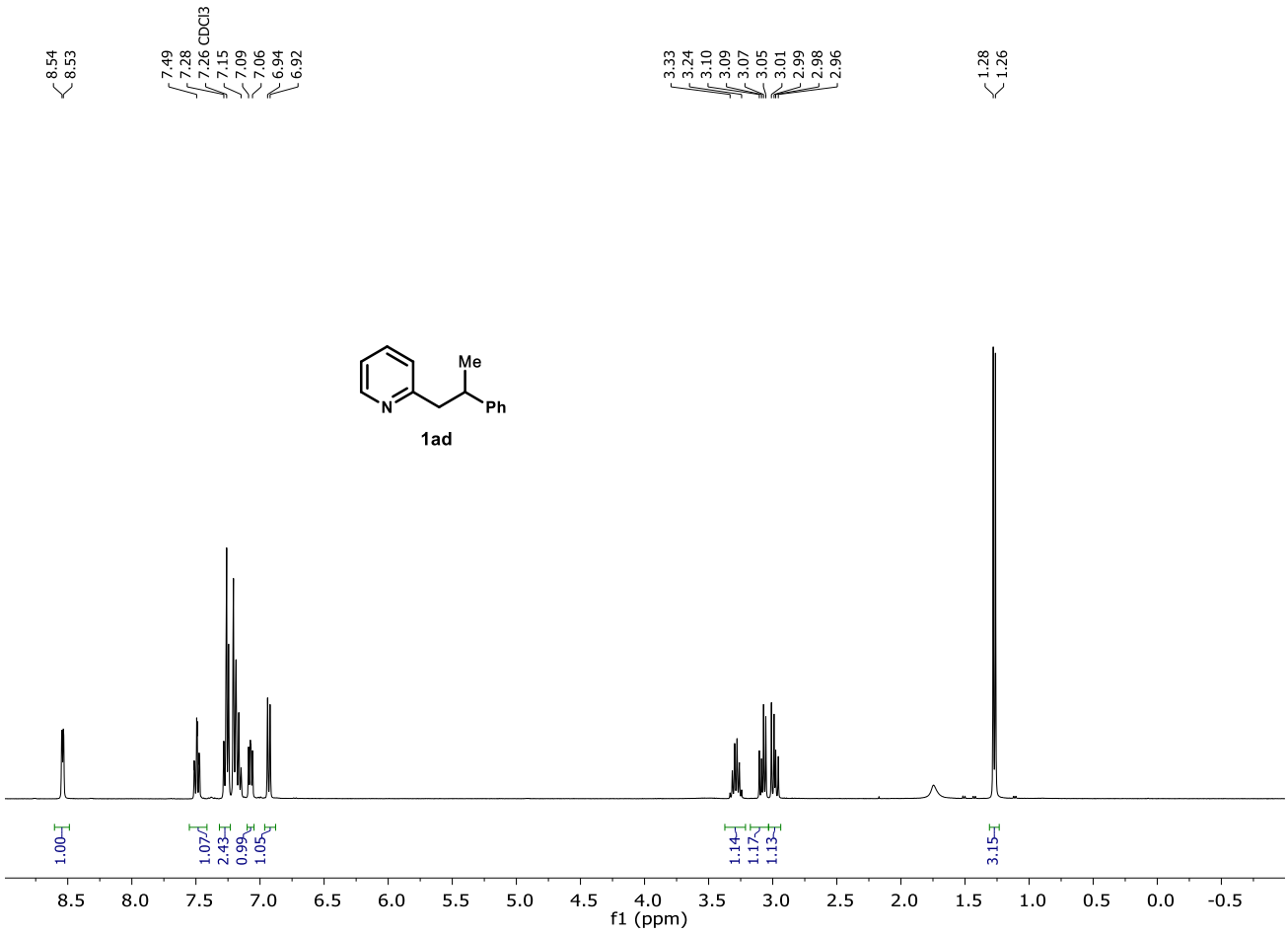
R$_f$: 0.54 (hexanes/EtOAc = 4:1)

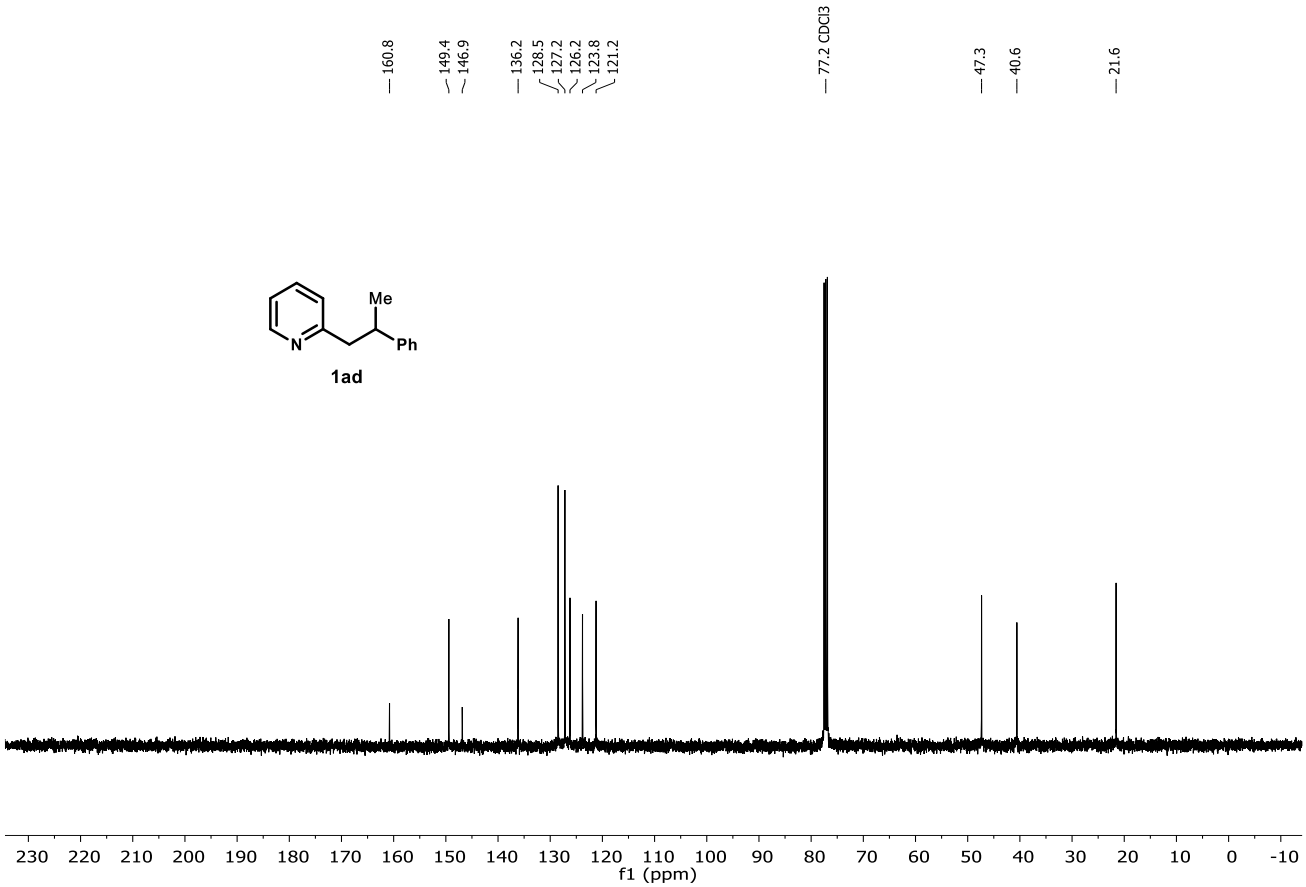
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, *J* = 4.2 Hz, 1H), 7.49 (td, *J* = 7.6, 1.8 Hz, 1H), 7.28–7.15 (m, 5H), 7.09 – 7.06 (m, 1H), 6.93 (d, *J* = 7.8 Hz, 1H),3.33–3.24 (m, 1H), 3.08 (dd, *J* = 13.3, 7.0 Hz, 1H), 2.98 (dd, *J* = 13.3, 8.2 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 3H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 160.8, 149.4, 146.9, 136.2, 128.5, 127.2, 126.2, 123.8, 121.2, 47.3, 40.6, 21.6

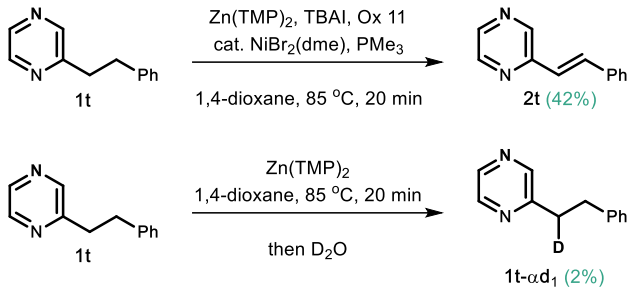
IR (cm^{-1}): 2960, 2925, 1589, 1568, 1473, 1451, 1147, 1013, 760, 748, 698, 558

GC-MS (m/z): [M] calc'd for $C_{14}H_{15}N$: 197.1; found: 197.1

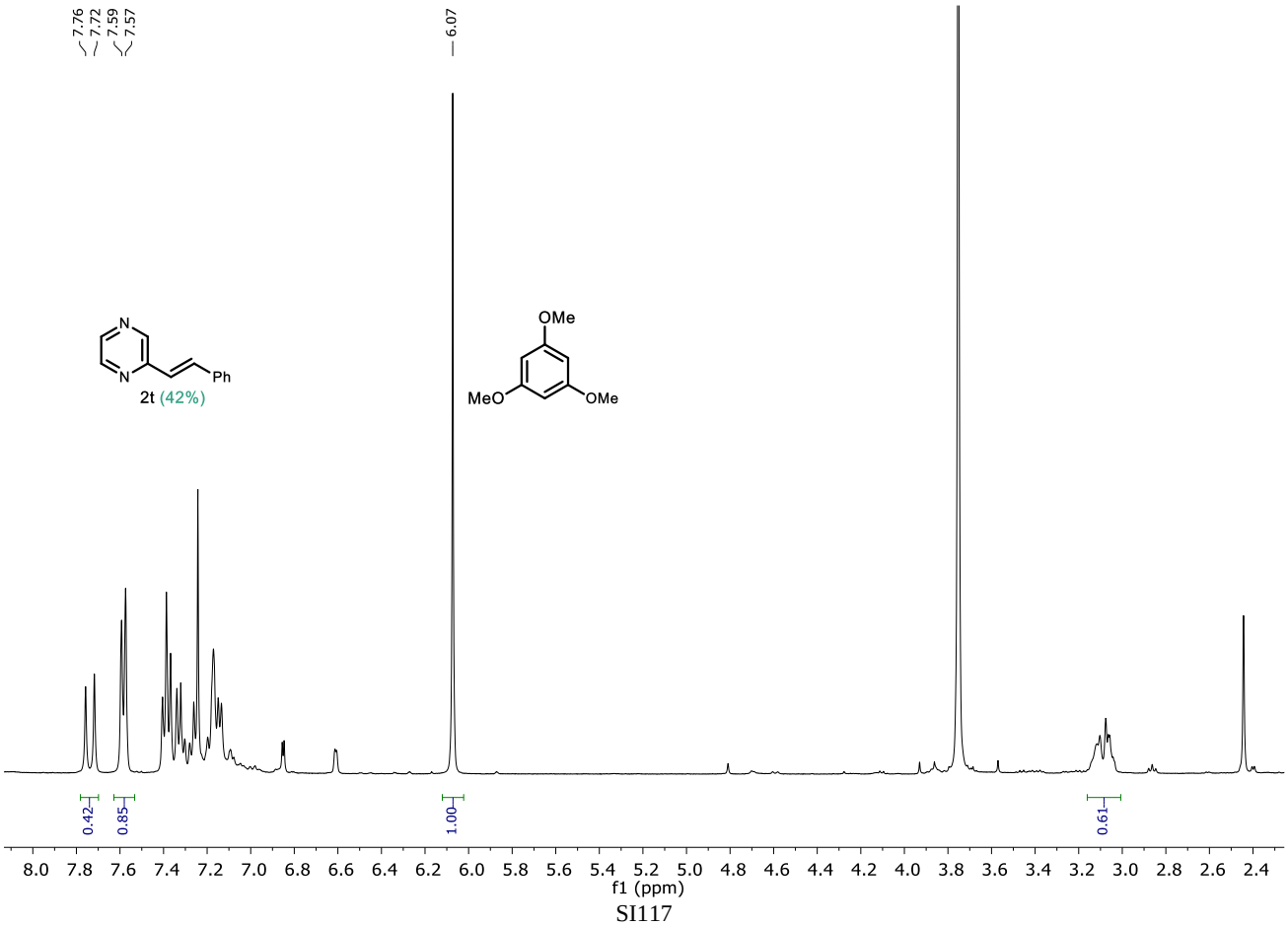

8.54
8.53
7.49
7.28
7.26 CDCl3
7.15
7.09
7.06
6.94
6.92
3.33
3.24
3.10
3.09
3.07
3.05
3.01
2.99
2.98
2.96
1.28
1.26
Me
Ph
N
1ad
1.00
1.07
2.43
0.99
1.05
1.14
1.17
1.13
3.15
f1 (ppm)


160.8
149.4
146.9
136.2
128.5
127.2
126.2
123.8
121.2
77.2 CDCl3
47.3
40.6
21.6
Me
Ph
N
1ad
f1 (ppm)

Experimental Procedures and Characterization Data for Mechanistic Studies

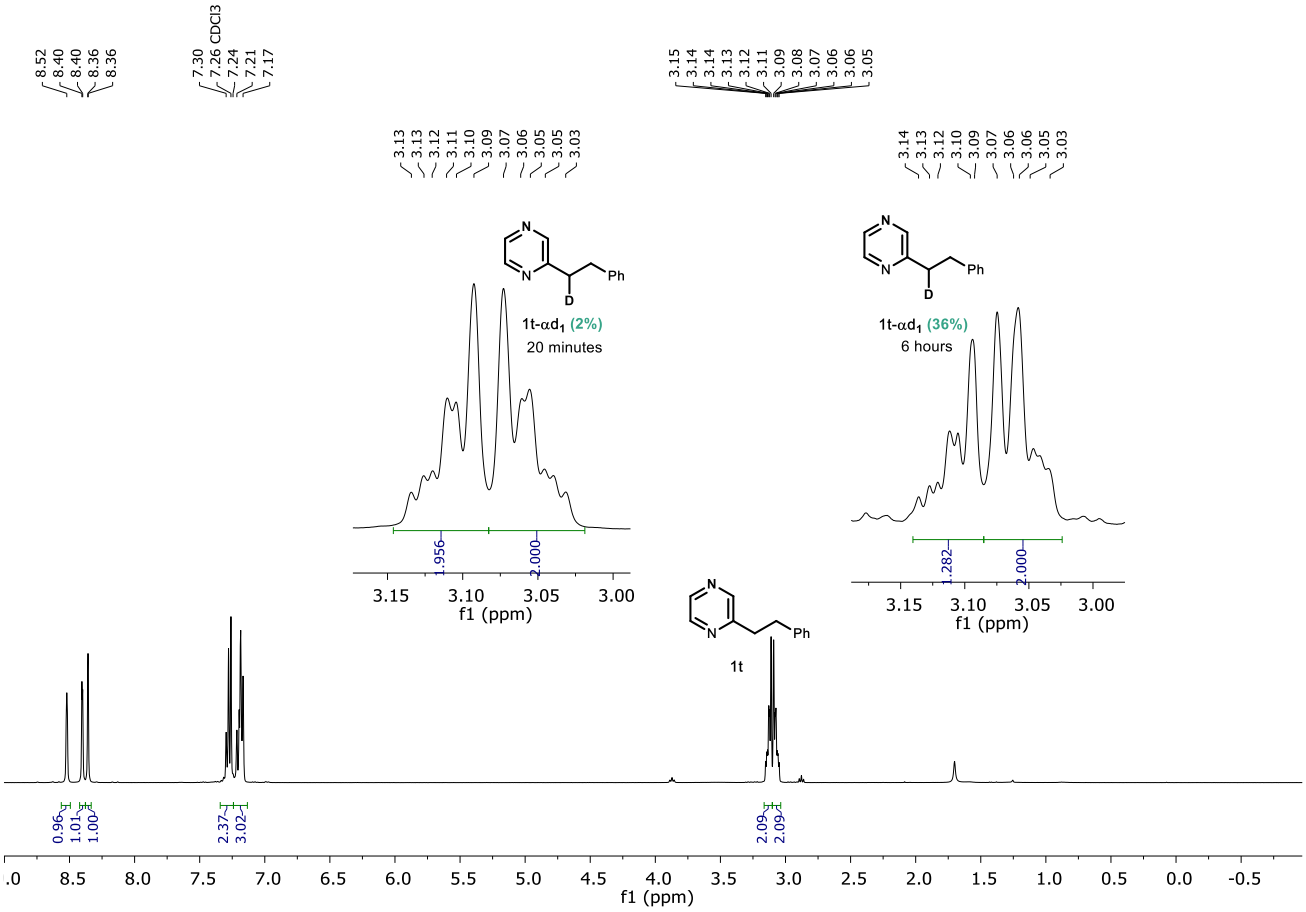


To a flame-dried microwave vial equipped with a magnetic stir bar was added **1t** (18.4 mg, 0.10 mmol, 1.0 equiv) and TBAI (74 mg, 0.20 mmol, 2.0 equiv). The reaction vessel was sealed, evacuated and backfilled with N_2 (this process was repeated three times). To the reaction vessel was added anhydrous 1,4-dioxane (1.0 mL) and commercial $Zn(TMP)_2$ (0.24 mL, 0.5 M in toluene, 0.12 mmol, 1.2 equiv) at room temperature. To this mixture was added 0.25 mL of a stock solution containing $NiBr_2$(dme) (3.1 mg, 0.01 mmol, 10 mol %), PMe_3 (0.03 mL, 0.03 mmol, 30 mol%), and 2-bromo-5-methylthiophene (13.7 μL, 0.12 mmol, 1.2 equiv) in 1,4-dioxane. The reaction vessel was placed into a pre-heated 85 ºC oil bath. The reaction was quenched with sat. aq. NH_4Cl (2 mL) after 20 minutes and diluted with EtOAc (2 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL) and the combined organic extracts were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation. ^{1}H-NMR yield of **2t** was determined to be 42% by using 1,3,5-trimethoxybenzene as an internal standard.



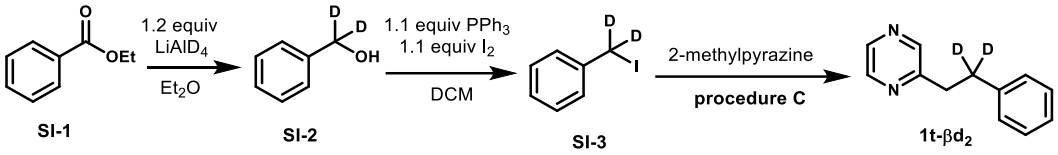
To a flame-dried microwave vial equipped with a magnetic stir bar was added **1t** (18.4 mg, 0.10 mmol, 1.0 equiv). The reaction vessel was sealed, evacuated and backfilled with N_2 (this process was repeated three times). To the reaction vessel was added anhydrous 1,4-dioxane (1.5 mL) and commercial $Zn(TMP)_2$ (0.24 mL, 0.5 M in toluene, 0.12 mmol, 1.2 equiv) at room temperature. The reaction vessel was placed into a pre-heated 85 °C oil bath. The reaction was quenched with D_2O (2 mL) after 20 minutes and diluted with EtOAc (2 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL) and the combined organic extracts were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation. The amount of deuterium incorporation (**1t-αd₁**) was determined to be 2% based on ^{1}H NMR.

Another parallel reaction was quenched with D_2O (2 mL) after 6 hours, and the amount of deuterium incorporation (**1t-αd₁**) was determined to be 36% based on ^{1}H NMR.



^{1}H-NMR yield of **1t-αd₁** after 20 minutes and 6 hours quenched with D_2O

2-(2-phenylethyl-2,2-d2)pyrazine (1t-βd$_2$):



A flame-dried flask was charged with ethyl benzoate **SI-1** (1.5 g, 10 mmol, 1.0 equiv) and Et_2O (30 mL, 0.33 M) and cooled to 0 °C. Then $LiAlD_4$ (504 mg, 12 mmol, 1.2 equiv) was added slowly at 0 °C. The resulting mixture was slowly warmed to room temperature and stirred for 2 hours. The reaction mixture was diluted with Et_2O (20 mL) and quenched upon the dropwise addition of aq. 2.0 M NaOH (6 mL) at 0 °C, filtered through a pad of silica and washed with Et_2O (2 × 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure by rotary evaporation at 10 °C. The crude product **SI-2** was used directly without further purification.

A flame-dried flask was charged with PPh_3 (2.88 g, 11 mmol, 1.1 equiv), I_2 (2.79 g, 11 mmol, 1.1 equiv) and DCM (30 mL, 0.33 M). The resulting mixture was stirred 10 minutes at 0 °C before the addition of a solution of crude **SI-2** in DCM (10 mL). The resulting mixture was slowly warmed to room temperature and stirred for 12 h. The reaction was quenched upon the addition of sat. aq. $Na_2S_2O_3$ (20 mL) and diluted with DCM (10 mL). The aqueous phase was extracted with DCM (3 × 10 mL) and the combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation at 10 °C. Then the resulting mixture was filtered through a pad of silica, washed with pentane (100 mL), and concentrated under reduced pressure by rotary evaporation at 10 °C to afford crude **SI-3** (white crystal at 10 °C), which was used for the next step without further purification.

A flame-dried flask under N_2 was charged with 2-methylpyrazine (470 mg, 5.0 mmol, 1.0 equiv) and THF (10 mL, 0.3 M). A solution of *n*-BuLi (2.4 mL, 2.5 M in hexanes, 6.0 mmol, 1.2 equiv) was added via syringe at –78 °C. The resulting red solution was stirred at –78 °C for 30 minutes before the addition of the solution of **SI-3** (~1.8 equiv). The resulting mixture was slowly warmed to room temperature and stirred for 1 hour. The reaction was quenched upon the addition of sat. aq. NH_4Cl (10 mL) and then diluted with Et_2O (10 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL) and the combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 10:1 to 5:1) afforded **1t-βd$_2$** (167 mg, 18%) as a yellow oil.

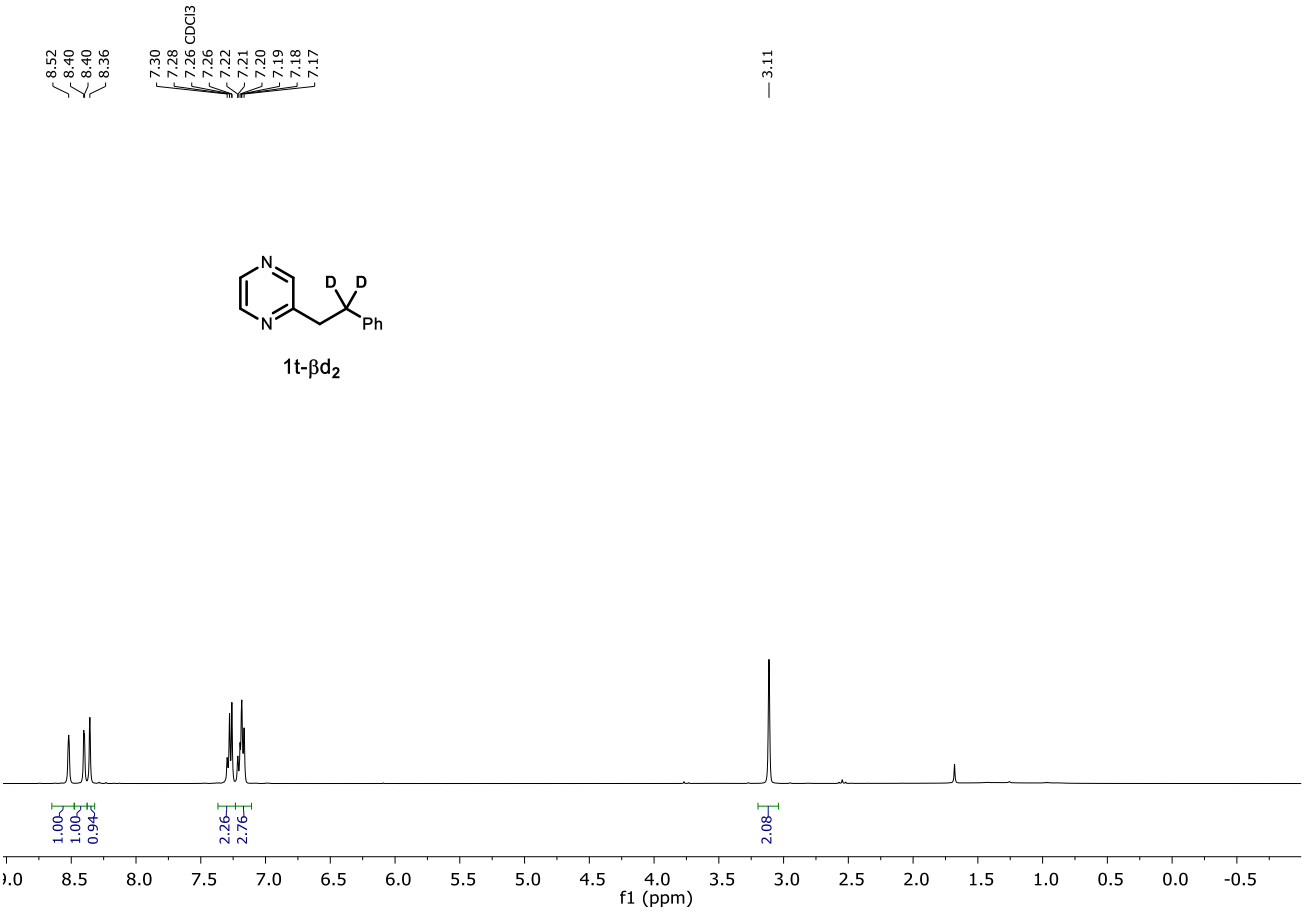
R$_f$: 0.25 (hexanes/EtOAc = 2:1)

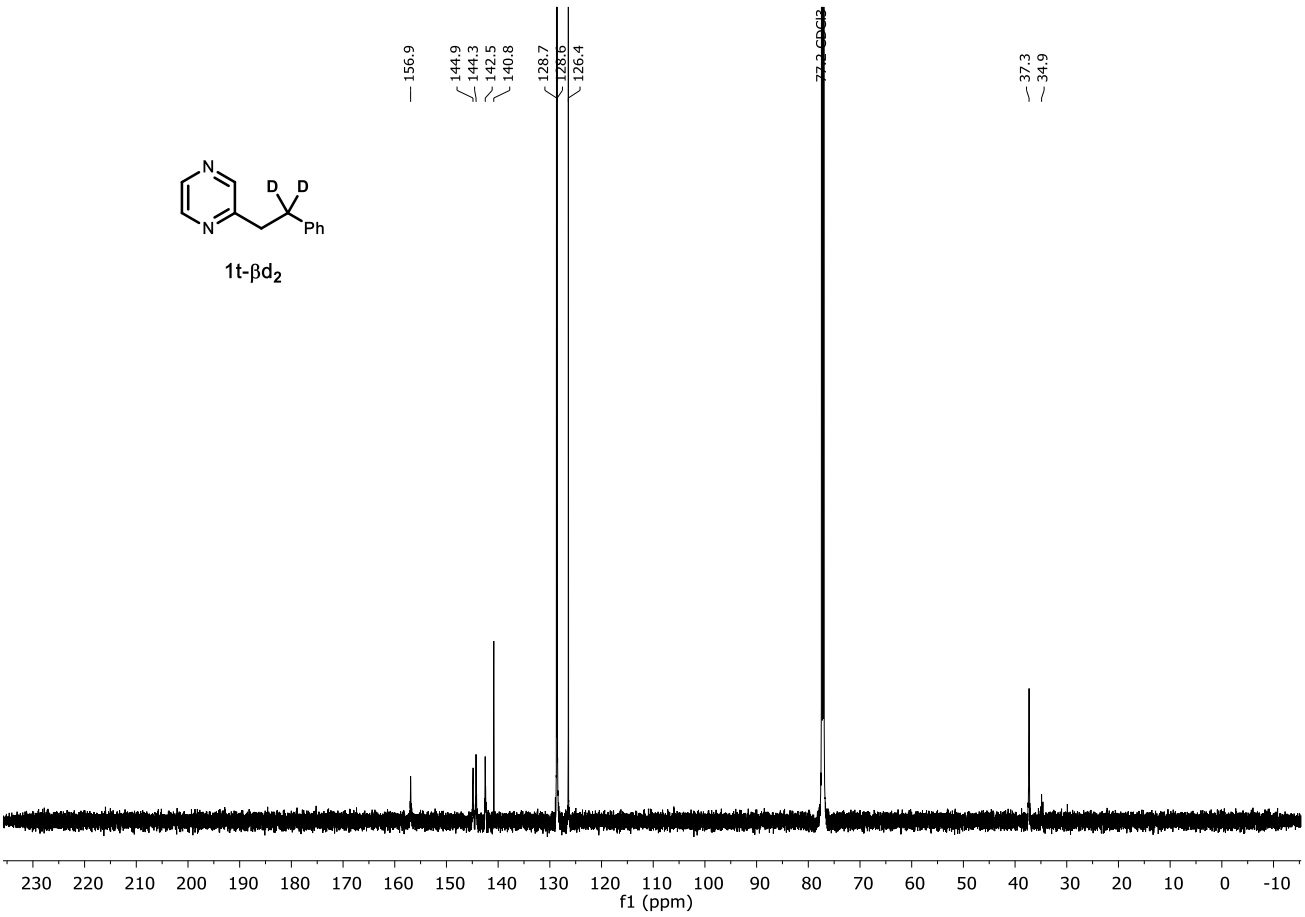
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 8.40 (d, *J* = 2.6 Hz, 1H), 8.36 (s, 1H), 7.30–7.17 (m, 5H), 3.11 (s, 2H)

^{13}C NMR (151 MHz, $CDCl_3$): δ 156.9, 144.9, 144.3, 142.5, 140.8, 128.7, 128.6, 126.4, 37.3, 34.9 (m)

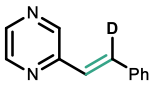
IR (cm^{-1}): 3057, 3024, 2926,1495, 1447, 1402, 1139, 1019, 831, 725, 698

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{12}H_{11}D_2N_2^+$: 187.1199; found: 187.1193


8.52
8.40
8.40
8.36
7.30
7.28
7.26 CDCl3
7.26
7.22
7.21
7.20
7.19
7.18
7.17
3.11
N
N
D
D
Ph
1t-βd2
1.00
1.00
0.94
2.26
2.76
2.08
f1 (ppm)


156.9
144.9
144.3
142.5
140.8
128.7
128.6
126.4
77.2 CDCl3
37.3
34.9
N
N
D
D
Ph
1t-βd2
f1 (ppm)

(E)-2-(2-phenylvinyl-2-d)pyrazine (2t-βd$_1$)



2t-βd$_1$

Compound **2t-βd$_1$** was prepared from compound **1t-βd$_2$** (37.2 mg, 0.20 mmol, 1.0 equiv) according to general dehydrogenation **procedure A** (6 hours). Purification by flash column chromatography on silica gel (hexanes/EtOAc = 10:1 to 5:1) afforded **2t-βd$_1$** (29.3 mg, 80%) as a white solid.

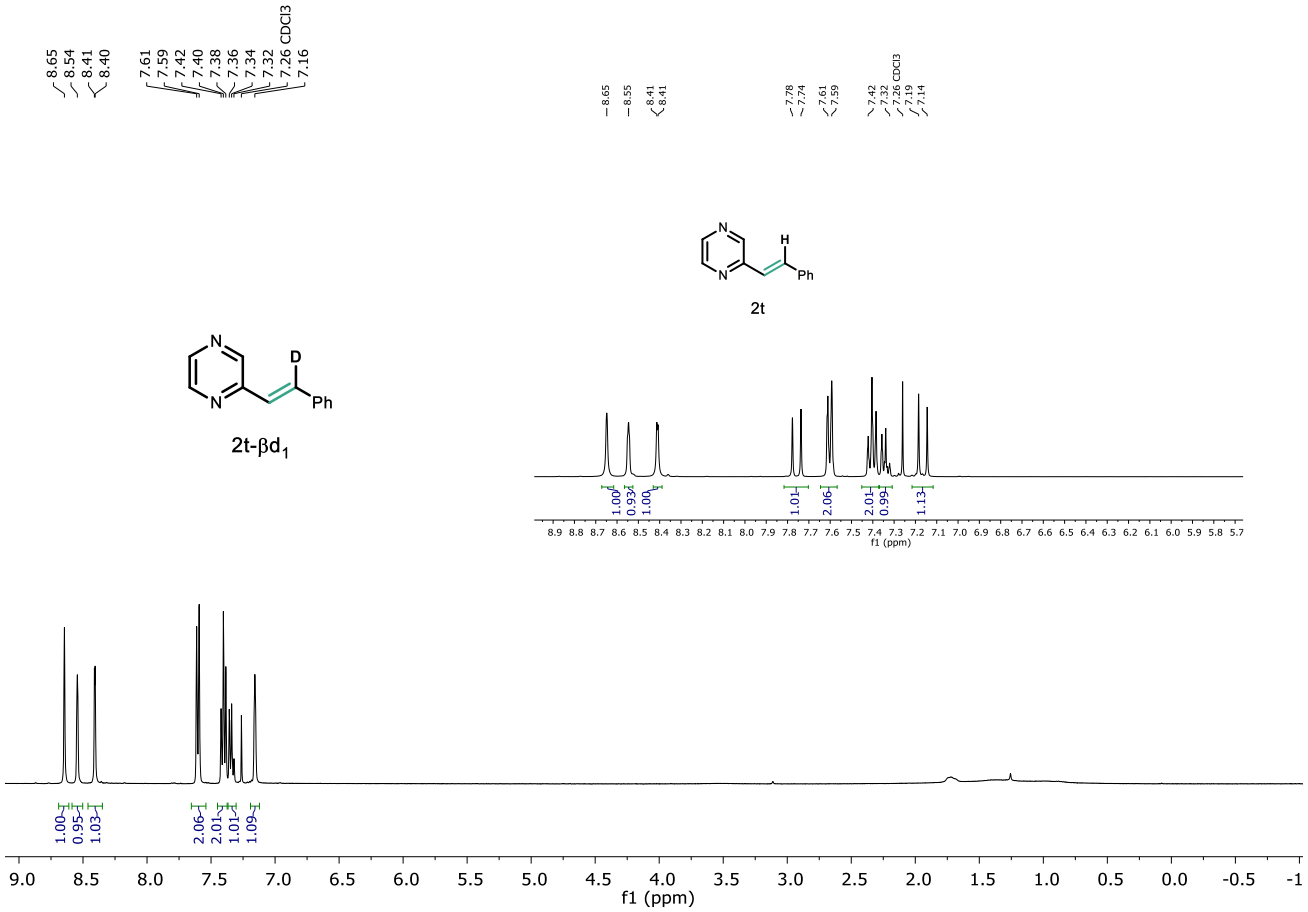
R$_f$: 0.54 (hexanes/EtOAc = 2:1)

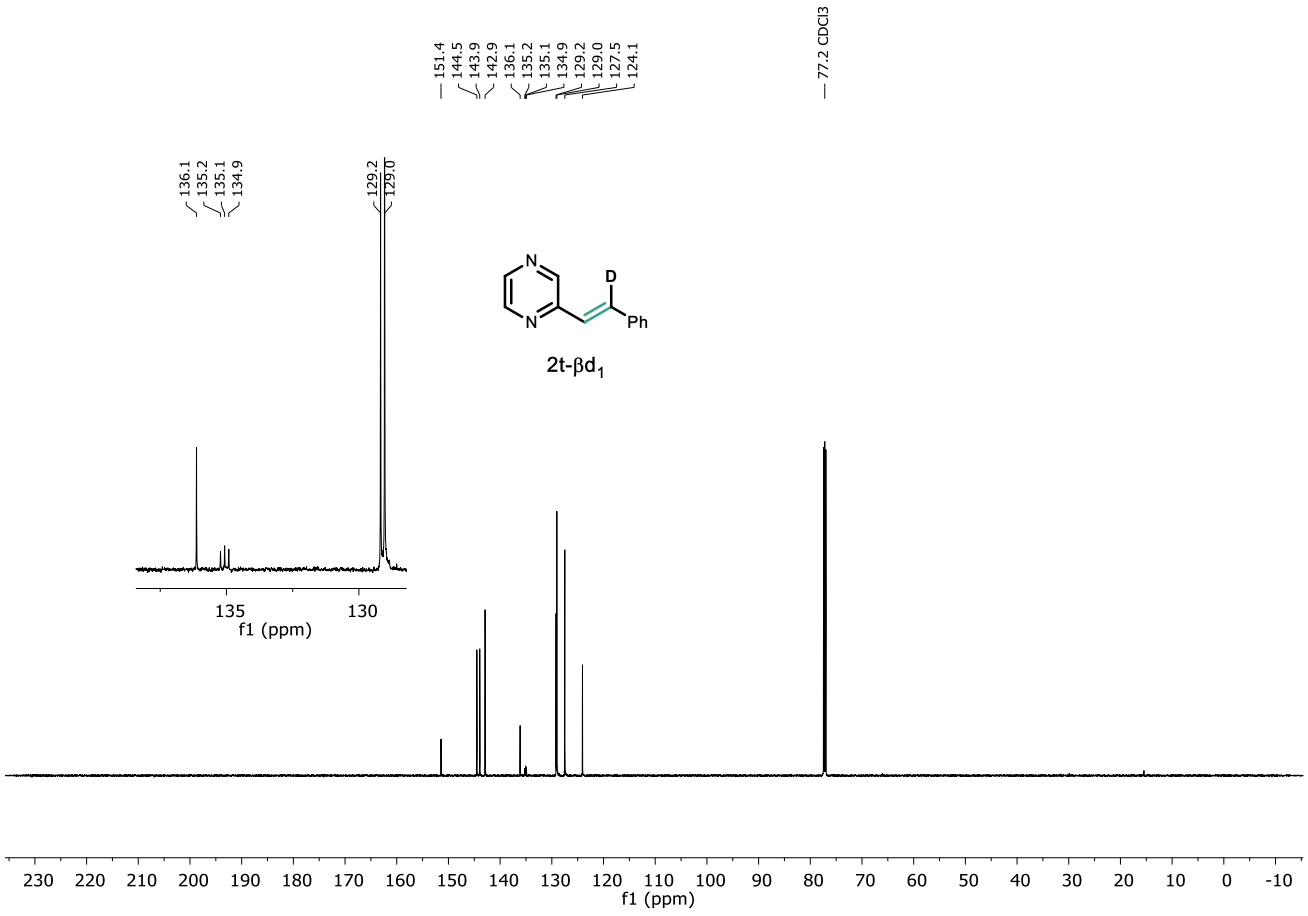
^{1}H NMR (400 MHz, $CDCl_3$): 8.65 (s, 1H), 8.54 (s, 1H), 8.41 (d, *J* = 2.4 Hz, 1H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.42–7.32 (m, 3H), 7.16 (s, 1H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 151.4, 144.5, 143.9, 142.9, 136.1, 135.1 (t), 129.2, 129.0, 127.5, 124.1

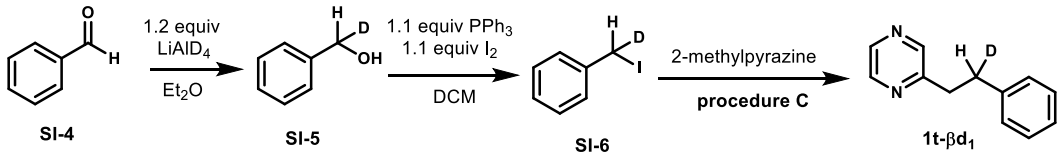
IR (cm^{-1}): 3058, 3024, 2922, 1623, 1492, 1474, 1397, 1142, 1033, 889, 781, 690

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{12}H_{10}DN_2^+$:184.0980; found: 184.0979


8.65
8.54
8.41
8.40
7.61
7.59
7.42
7.40
7.38
7.36
7.34
7.32
7.26 CDCl3
7.16
2t
2t-βd1
1.00
0.95
1.03
2.06
2.01
1.01
1.09
f1 (ppm)


151.4
144.5
143.9
142.9
136.1
135.2
135.1
134.9
129.2
129.0
127.5
124.1
77.2 CDCl3
2t-βd1
135
130
f1 (ppm)

2-(2-phenylethyl-2,2-d2)pyrazine (1t-βd$_1$):



A flame-dried flask was charged with benzaldehyde **SI-4** (0.76 g, 5 mmol, 1.0 equiv) and Et_2O (20 mL, 0.25 M) and cooled to 0 °C. Then $LiAlD_4$ (250 mg, 6 mmol, 1.2 equiv) was added slowly at 0 °C. The resulting mixture was slowly warmed to room temperature and stirred for 2 hours. The reaction was diluted with Et_2O (10 mL), quenched upon the dropwise addition of aq. 2.0 M NaOH (3 mL) at 0 °C, filtered through a pad of silica and washed with Et_2O (3 ×10 mL). The combined organic solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure by rotary evaporation at 10 °C. The crude product **SI-5** was used for the next step without further purification.

A flame-dried flask was charged with PPh_3 (1.44 g, 5.5 mmol, 1.1 equiv), I_2 (1.40 g, 5.5 mmol, 1.1 equiv) and DCM (20 mL, 0.25 M). The resulting mixture was stirred for 10 minutes at 0 °C before the addition of a solution of crude **SI-5** in DCM (5 mL). The resulting mixture was slowly warmed to room temperature and stirred for 12 h. The reaction was quenched upon the addition of sat. aq. $Na_2S_2O_3$ (20 mL) and then diluted with DCM. The aqueous phase was extracted with DCM (3 × 10 mL) and the combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation at 10 °C. The resulting mixture was filtered through a pad of silica, washed with pentane (100 mL), and concentrated under reduced pressure by rotary evaporation at 10 °C to give crude **SI-6**, which was used for the next step without further purification.

Following **procedure C**: A flame-dried flask under N_2 was charged with 2-methylpyrazine (282 mg, 3.0 mmol, 1.0 equiv) and THF (10 mL, 0.3 M). A solution of *n*-BuLi (1.4 mL, 2.5 M in hexanes, 3.6 mmol, 1.2 equiv) was added via syringe at –78 °C. The resulting red solution was stirred at –78 °C for 30 minutes before the addition of the solution of **SI-6** (~1.5 equiv) in THF (5 mL). The resulting mixture was slowly warmed to room temperature and stirred for 1 h. The reaction was quenched upon the addition of sat. aq. NH_4Cl (10 mL) and then diluted with Et_2O (20 mL). The aqueous phase was extracted with EtOAc (3 × 10 mL) and the combined organic extracts were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation. Purification by flash column chromatography on silica gel (hexanes/EtOAc = 10:1 to 5:1) afforded **1t-βd$_1$** (180 mg, 32%) as a yellow oil.

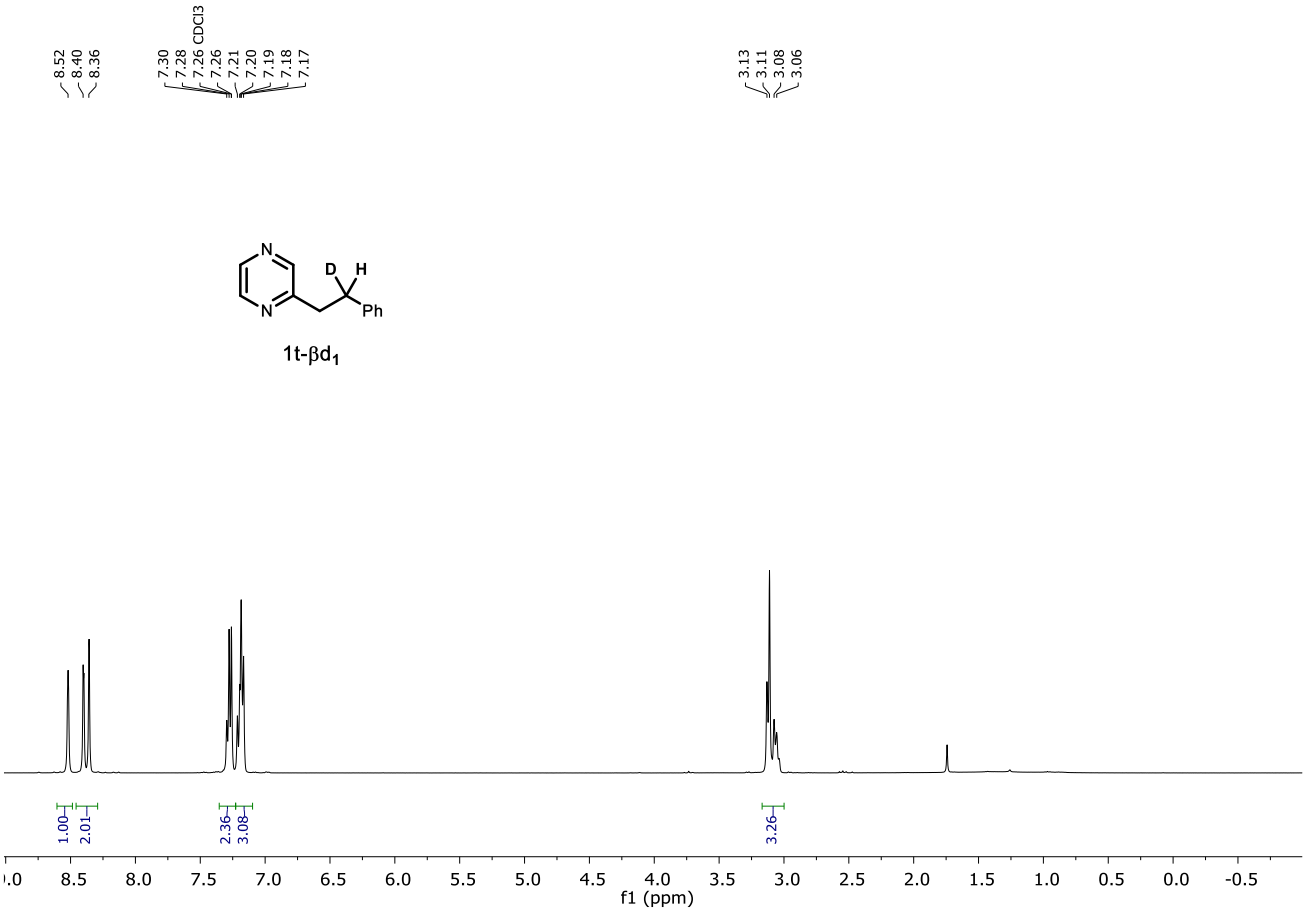
R$_f$: 0.25 (hexanes/EtOAc = 2:1)

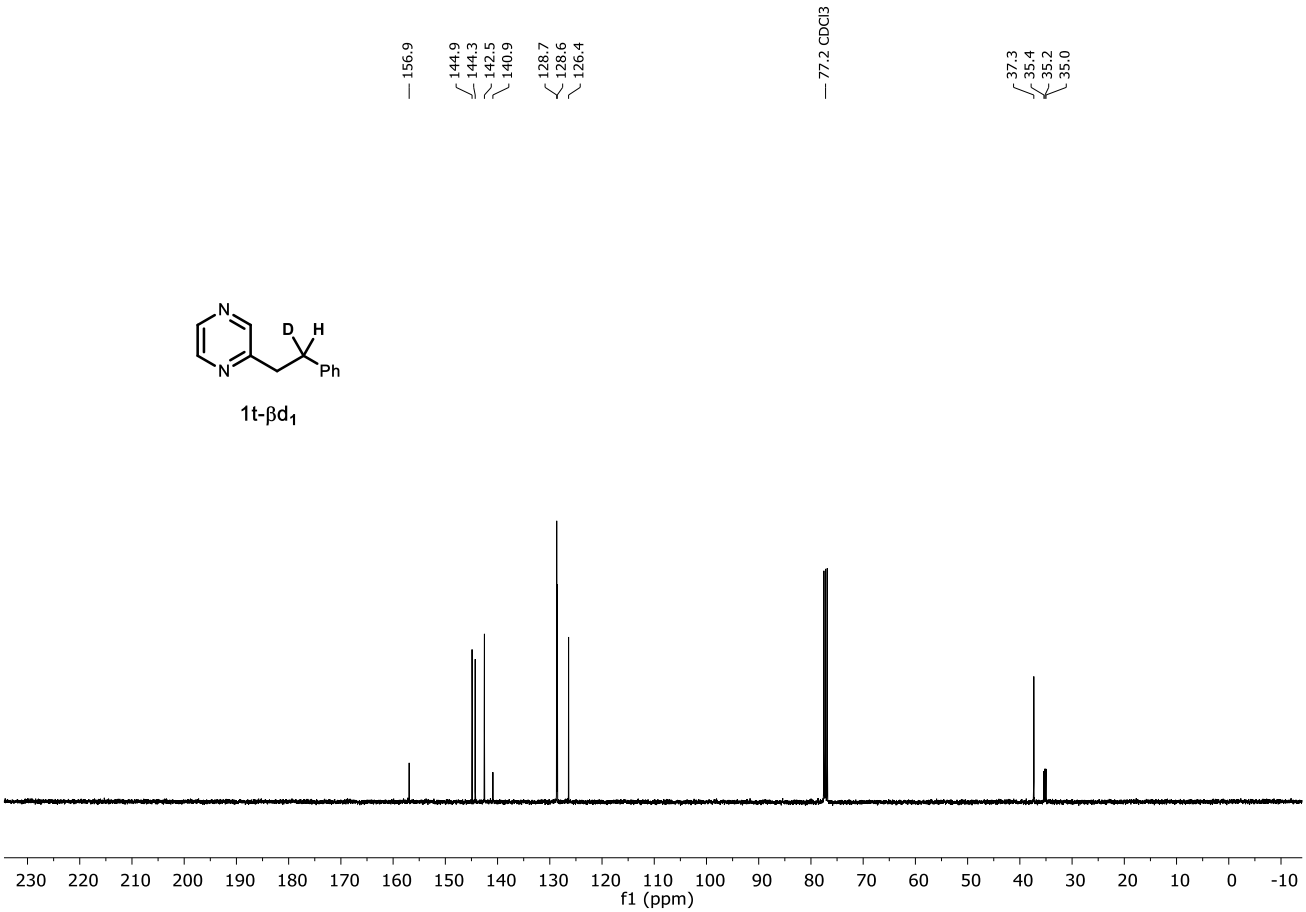
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.52 (s, 1H), 8.40 (s, 1H), 8.36 (s, 1H), 7.30–7.17 (m, 5H), 3.13–3.06 (m, 3H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.9, 144.9, 144.3, 142.5, 140.9, 128.7, 128.6, 126.4, 37.3, 35.3 (t)

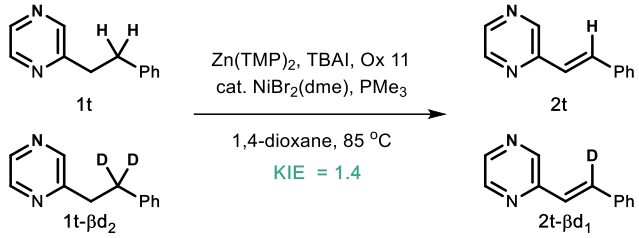
IR (cm^{-1}): 3026, 2923, 1495, 1402, 1135, 1016, 831, 741, 698

ESI-HRMS (m/z): $[M+H]^+$ calc'd for $C_{12}H_{12}DN_2^+$:186.1136; found: 186.1136


8.52
8.40
8.36
7.30
7.28
7.26 CDCl3
7.26
7.21
7.20
7.19
7.18
7.17
3.13
3.11
3.08
3.06
N
N
D
H
Ph
1t-βd1
1.00
2.01
2.36
3.08
3.26
f1 (ppm)


156.9
144.9
144.3
142.5
140.9
128.7
128.6
126.4
77.2 CDCl3
37.3
35.4
35.2
35.0
N
N
D
H
Ph
1t-βd1
f1 (ppm)

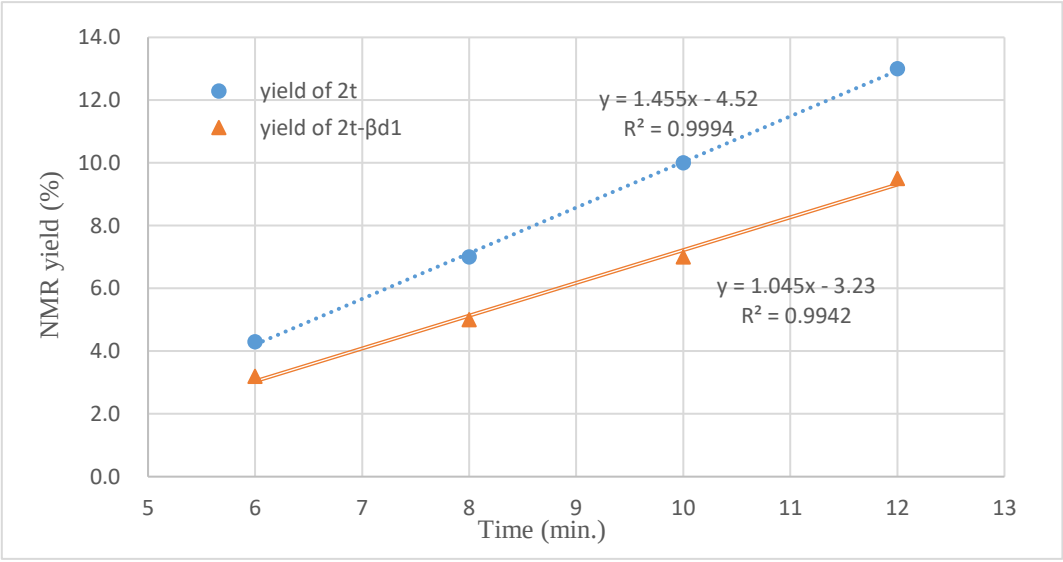
Intermolecular Competition Experiment:



To a flame-dried microwave vial equipped with a magnetic stir bar was added **1t** (18.4 mg, 0.10 mmol, 0.5 equiv), **1t-βd$_2$** (18.6 mg, 0.10 mmol, 0.5 equiv) and TBAI (148 mg, 0.40 mmol, 2.0 equiv). The reaction vessel was sealed, evacuated and backfilled with N_2 (this process was repeated three times). To the reaction vessel was added anhydrous 1,4-dioxane (2.0 mL) and commercial $Zn(TMP)_2$ (0.48 mL, 0.5 M in toluene, 0.24 mmol, 1.2 equiv) at room temperature. To this mixture was added 0.5 mL of a stock solution containing $NiBr_2$(dme) (6.2 mg, 0.02 mmol, 10 mol %), PMe_3 (0.06 mL, 0.06 mmol, 30 mol%), and 2-bromo-5-methylthiophene (27.4 μL, 0.24 mmol, 1.2 equiv) in 1,4-dioxane. The reaction vessel was placed into a pre-heated 85 ºC oil bath. A 0.6 mL aliquot was removed at 6, 8, 10 and 12 minutes, which were separately quenched with sat. aq. NH_4Cl (2 mL) and diluted with EtOAc (2 mL). The aqueous phase was extracted with EtOAc (3 × 2 mL) and the combined organic extracts were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation. ^{1}H-NMR yield was determined using 1,3,5-trimethoxybenzene as an internal standard (shown in the table).

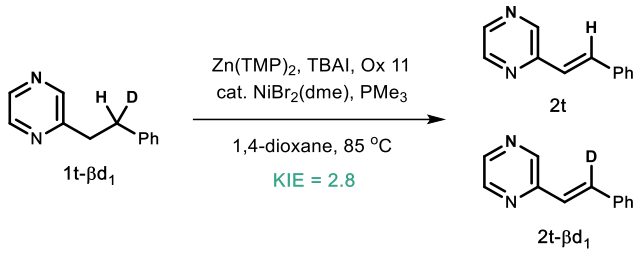
Time (min)	Total NMR yield (%)	**2t** (%)	**2t-βd$_1$** (%)
6	7.5	4.3	3.2
8	12.0	7.0	5.0
10	17.0	10.0	7.0
12	22.5	13.0	9.5

Intermolecular Competition Experiment with **1t** and **1t-βd$_2$**



Kinetic Isotope Effect (KIE) = 1.455/1.045 = 1.4

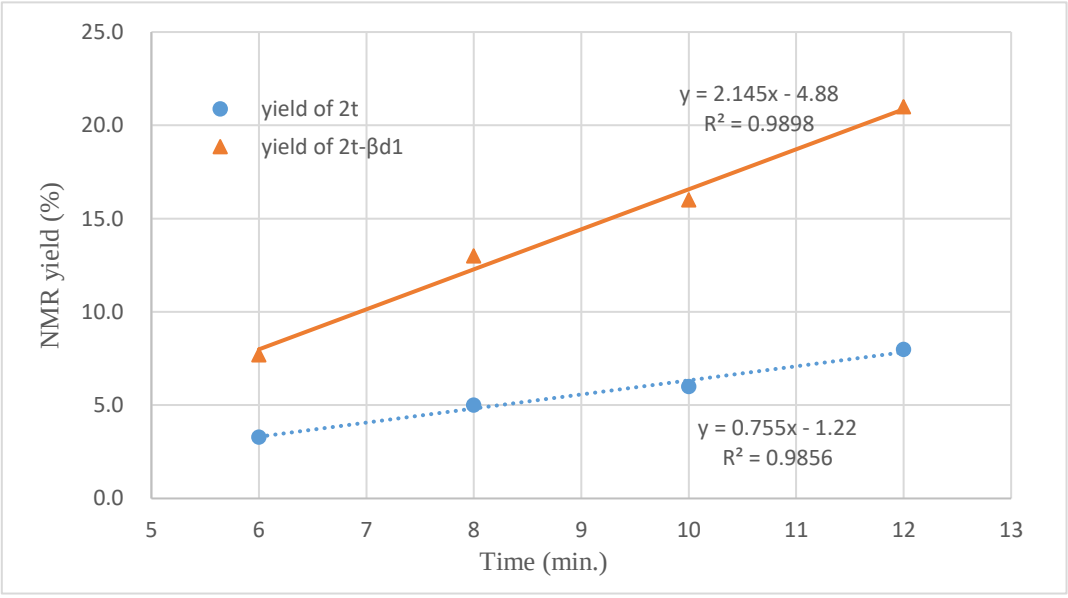
Intramolecular Competition Experiment:



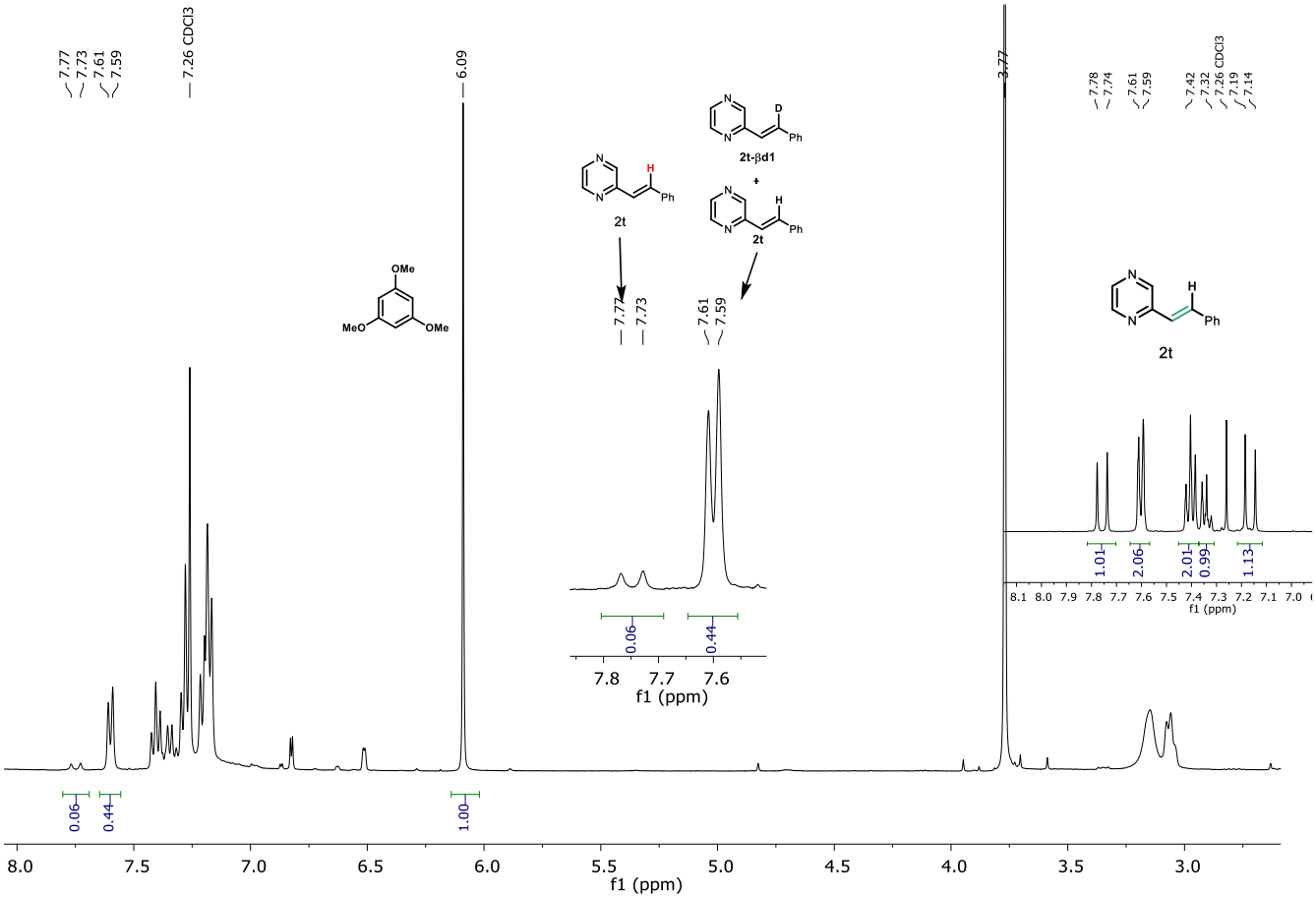
To a flame-dried microwave vial equipped with a magnetic stir bar was added **1t-βd1** (37.0 mg, 0.20 mmol, 1 equiv) and TBAI (148 mg, 0.40 mmol, 2.0 equiv). The reaction vessel was sealed, evacuated and backfilled with N_2 (this process was repeated three times). To the reaction vessel was added anhydrous 1,4-dioxane (2.0 mL) and commercial $Zn(TMP)_2$ (0.48 mL, 0.5 M in toluene, 0.24 mmol, 1.2 equiv) at room temperature. Then to this mixture was added 0.5 mL of a stock solution containing $NiBr_2$(dme) (6.2 mg, 0.02 mmol, 10 mol %), PMe_3 (0.06 mL, 0.06 mmol, 30 mol%), and 2-bromo-5-methylthiophene (27.4 μL, 0.24 mmol, 1.2 equiv) in 1,4-dioxane. The reaction vessel was placed into a pre-heated 85 ºC oil bath. A 0.6 mL aliquot was removed at 6, 8, 10 and 12 minutes, which were separately quenched with sat. aq. NH_4Cl (2 mL) and diluted with EtOAc (2 mL). The aqueous phase was extracted with EtOAc (3 × 2 mL) and the combined organic extracts were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation. ^{1}H-NMR yield was determined using 1,3,5-trimethoxybenzene as an internal standard (shown in the table).

Time (min)	Total NMR yield (%)	**2t** (%)	**2t-βd1** (%)
6	11.0	3.3	7.7
8	18.0	5.0	13.0
10	22.0	6.0	16.0
12	29.0	8.0	21.0

Intramolecular Competition Experiment with **1t-βd1**

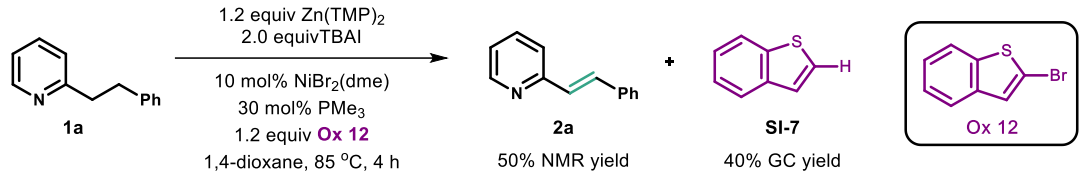


Kinetic Isotope Effect (KIE) = 2.145/0.755 = 2.8

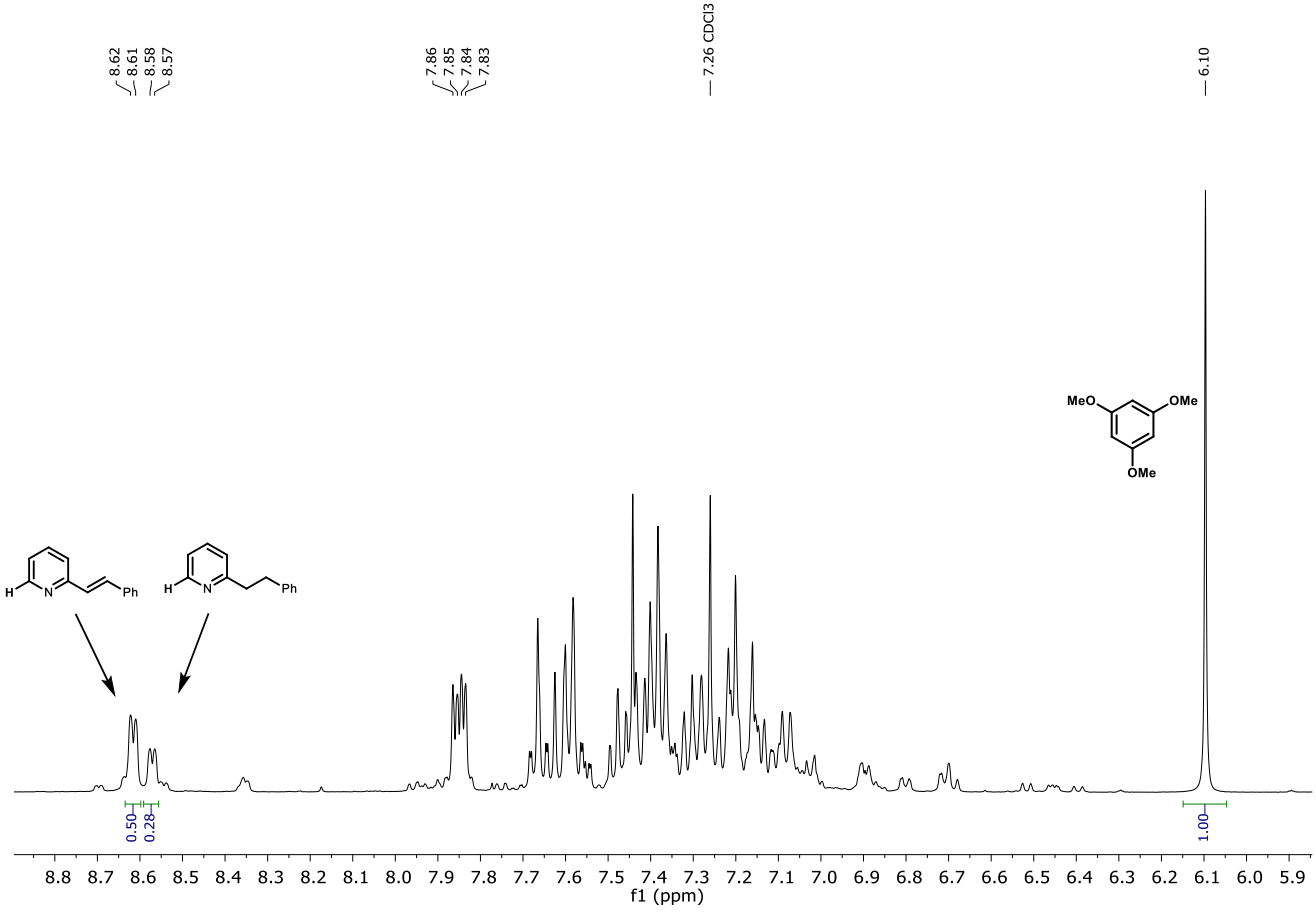


^{1}H-NMR yield after 10 minutes.

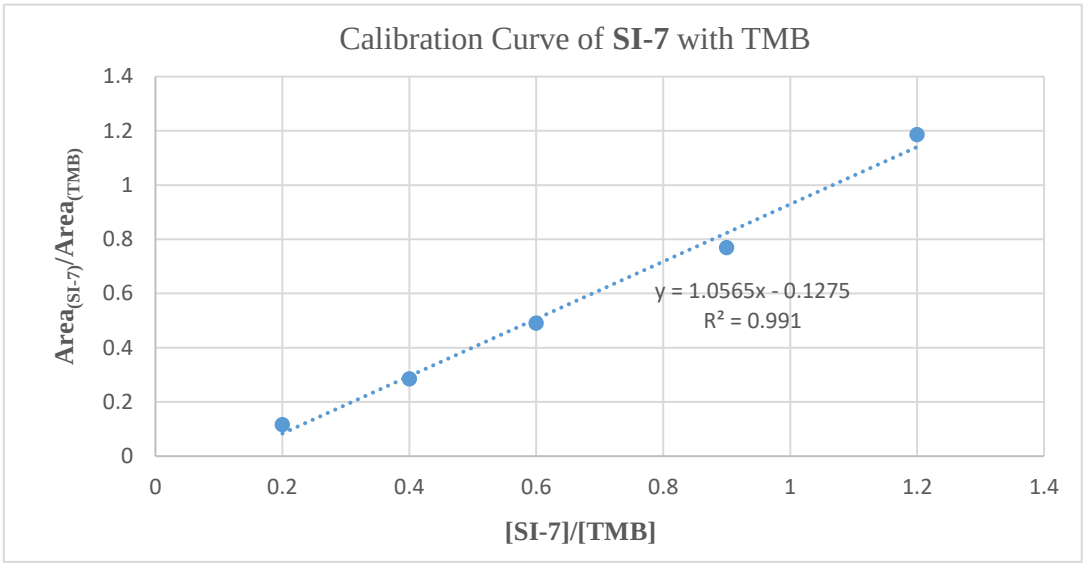
Dehydrogenation of 1a with 2-bromobenzo[*b*]thiophene (Ox12):



Compound **1a** (18.3 mg, 0.10 mmol, 1.0 equiv) was subjected to general dehydrogenation **procedure A** using 2-bromobenzo[*b*]thiophene (**Ox 12**) as oxidant. After 4 hours, the reaction was quenched with sat. aq. NH_4Cl (2 mL) and diluted with EtOAc (2 mL). The aqueous phase was extracted with EtOAc (3 × 2 mL) and the combined organic extracts were washed with brine (5 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure by rotary evaporation. ^{1}H-NMR yield of **2a** was determined using 1,3,5-trimethoxybenzene (TMB) as an internal standard.

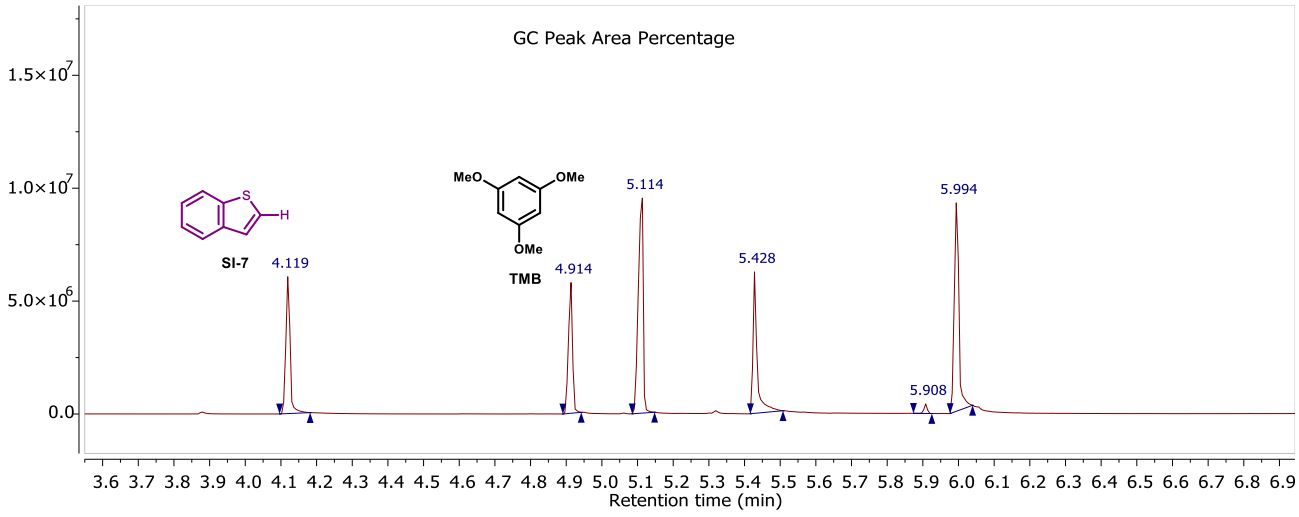


Benzothiophene (**SI-7**) is volatile and the NMR yield could not be obtained accurately.
The GC yield of **SI-7** was calculated to be 40% based on its Calibration Curve, which is close to the NMR yield of **2a** (50%).



TMB = 1,3,5-trimethoxybenzene (internal standard)

[**SI-7**]/[TMB]	$Area_{(SI-7)}/Area_{(TMB)}$
0.2	0.1168
0.4	0.2855
0.6	0.4912
0.9	0.7696
1.2	1.186



peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	4.119	263	270	292	BB	5659781	52256790	53.38%	13.805%
2	4.914	404	408	425	BB	5201957	47918705	47.00%	12.155%
3	5.114	438	443	459	PB	9549583	93960024	94.85%	24.528%
4	5.428	495	498	535	BB	5265123	57813940	58.36%	15.092%
5	5.910	578	582	587	BB	381550	2602217	2.63%	0.679%
6	5.994	593	598	637	BB	8807537	99062490	100.00%	25.860%

The GC peak area ratio (**y**) of **SI-7** (1.0 equiv) to TMB (0.333 equiv) is 53.38%/47.00% = 1.136. The molar ratio (**x**) is calculated to be 1.196. Therefore, the GC yield of **SI-7** is 1.196 x 0.333 = 40%

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Ethynylbenzenes: Convenient Approach to Mono-, Bis-, and Tris-Chalcogenophene-Annulated Benzenes. *Org. Lett*. **2009**, *11*, 2473-2475.

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