Supporting Information

Cooperative palladium/Lewis acid-catalyzed transfer hydrocyanation of alkenes and alkynes using 1-methylcyclohexa-2,5-diene-1-carbonitrile

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1. Instrumentation and chemicals:

All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in heat-gun-dried glassware under an argon atmosphere. THF and Et_2O were freshly distilled from potassium under argon. 1,4-Dioxane (99,8%, extra dry, AcroSeal) was used as received from *Acros Organics*. All other solvents and reagents were purified according to standard procedures or were used as received from *Aldrich, Acros Organics, Alfa Aesar* and *ABCR.*

NMR: ^{1}H, ^{13}C NMR spectra were recorded on a *Bruker* DPX *300*, a *Bruker* AV *300*, a *Bruker* AV 400 at 300 K, or a *Varian* 600 *UNITY* plus spectrometer at 299 K. Chemical shifts (δ (ppm)) are reported relative to TMS ($\delta(^{1}H)$ 0.0 ppm, $\delta(^{13}C)$ 0.0 ppm). The solvents residual proton resonance and the respective carbon resonance ($CHCl_3$, $\delta(^{1}H)$ 7.26 ppm, $\delta(^{13}C)$ 77.16 ppm) were used for calibration.

TLC: *Merck* silica gel 60 F 254 plates; detection with UV light or by dipping into a solution of $KMnO_4$ (1.5 g in 400 mL H_2O, 5 g $NaHCO_3$).

Flash column chromatography (FC): *Merck* or *Fluka* silica gel 60 (40-63 μm) at approximately 0.2 bar.

IR spectra were recorded on a *Digilab* Varian 3100 FT-IR Excalibur Series.

Melting points (**M.P.**) were determined on a *SMP 10 apparatus* (*Stuart Scientific*) and are uncorrected.

HRMS ESI (m/z) spectra were recorded on a *Bruker MicroTof* or an *Orbitrap LTQ XL* (Nanospray) of *Thermo Scientific*. GC/MS (EI, 70 eV) was performed on a combined setup of an *Agilent 6890N* chromatograph equipped with a *HP-5* column using helium (~1bar) as carrier gas and a *Waters-Micromass Quarto Micro Spectrometer*.

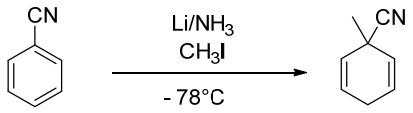
GC-FID was conducted on an *Agilent GC 6890* equipped with a flame ionization detector (FID) and a *Agilent HP-5, Methyl Siloxan, (Model No: 19091Z-413)* column using H_2 as carrier gas with a flow rate of 1.5 mL min^{-1}. The method used starts with the injection temperature T_0, the column is heated to temperature T_1 (ramp) and this temperature is held for an additional time t (T_0 = 50 °C, T_1 = 300 °C, ramp = 10 °C min^{-1}, t = 15 min). (Standard mesitylene peak comes at 5.34 min).

Agilent GC 7890A, Flame Ionization Detection (FID), carrier gas: H_2 Column: *Agilent HP-5*, Phenyl-Methyl Siloxan (Model No: 19091J-413 30m x 320μm, 0,25μm Film). The method used starts with the injection temperature T_0, the column is heated to temperature T_1 (ramp) and this temperature is held for an additional time t (T_0 = 50 °C, T_1 = 300 °C, ramp = 10 °C min^{-1}, t = 15 min), constant flow 1,5mL/min, split mode 15:1. (Standard mesitylene peak comes at 5.01 min)

GC-MS chromatograms were recorded on an Agilent Technologies 7820A GC-system equipped with an *Agilent 5977B MSD(EI)* detector and a *HP-5MS* column with helium as carrier gas; the major signals are quoted as ratio of m/z in Daltons; the method used starts with the injection temperature T_0, after holding this temperature for 3 min, the column is heated to temperature T_1 (ramp) and this temperature is held for an additional time t (T_0 = 50 °C, T_1 = 300 °C, ramp = 10 °C min^{-1} , t = 15 min).

2. Synthesis of donor nitriles

Synthesis of 1-methylcyclohexa-2,5-diene-1-carbonitrile (2a)

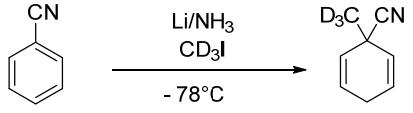


2a

A solution of benzonitrile (10.2 mL, 100 mmol, 1.0 equiv) and *tert*-butyl alcohol (9.6 mL, 100 mmol, 1.0 equiv) in dry Et_2O (60 mL) was added to the liquid ammonia solution (300 mL) at –78 °C. Lithium (1.39 g, 200 mmol) was added to the stirred solution in small pieces until the blue color persisted. After 40 min at this temperature, iodomethane (18.6 mL, 0.30 mol, 3.0 equiv) was added slowly over a period of 5 min and the resulting yellow solution was stirred for 1 h at –78 °C. Ammonia was evaporated overnight, and the residue was dissolved in H_2O (100 mL). The mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification by flash column chromatography (Et_2O/pentane = 5/95) provided 1-methylcyclohexa-2,5-diene-1-carbonitrile **2a** (9.54 g, 80% yield) as a colorless liquid.[1]

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.94 – 5.83 (m, 2H), 5.70 – 5.65 (m, 2H), 2.85 – 2.51 (m, 2H), 1.49 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 126.33, 125.55, 122.31, 32.53, 28.53, 25.38. **HRMS (ESI):** Exact mass calculated for $C_8H_9NNa^+$ [M+Na^+]: 142.0627, mass found: 142.0623. The spectral data are consistent with those reported in the literature.[1]

Synthesis of 1-(methyl-*d*$_3$)cyclohexa-2,5-diene-1-carbonitrile (2a-*d*3)

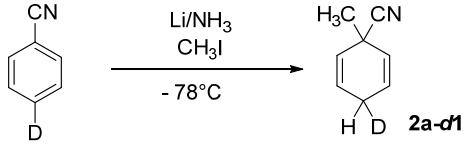


2-*d*3

A solution of benzonitrile (1.0 mL, 10 mmol, 1.0 equiv) and *tert*-butyl alcohol (0.95 mL, 10 mmol, 1.0 equiv) in dry Et_2O (10 mL) was added to the liquid ammonia solution (50 mL) at –78 °C. Lithium (0.14 g, 20 mmol) was added to the stirred solution in small pieces until the blue color persisted. After 40 min at this temperature, iodomethane-d_3 (5.1 g, 35 mmol, 3.5 equiv) was added slowly over a period of 5 min and the resulting yellow solution was stirred for 1 h at –78 °C. Ammonia was evaporated overnight, and the residue was dissolved in H_2O (20 mL). The mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification by flash column chromatography (Et_2O/pentane = 5/95) provided 1-(methyl-*d*3)cyclohexa-2,5-diene-1-carbonitrile **2a-*d*3** (0.95 g, 78% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 – 5.82 (m, 2H), 5.71 – 5.65 (d, 2H), 2.88 – 2.45 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 126.39, 125.53, 122.35, 32.38, 25.40. **HRMS (ESI):** Exact mass calculated for $C_8H_6D_3NNa^+$ [M+Na^+]: 145.0816, mass found: 145.0812.

Synthesis of 1-methylcyclohexa-2,5-diene-1-carbonitrile-4-*d* (2a-*d*1)

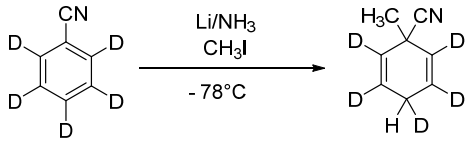


2a-*d*1

A solution of benzonitrile-4-*d* (1.0 g, 10 mmol, 1.0 equiv) and *tert*-butyl alcohol (0.95 mL, 10 mmol, 1.0 equiv) in dry Et_2O (10 mL) was added to the liquid ammonia solution (50 mL) at –78 °C. Lithium (0.14 g, 20 mmol) was added to the stirred solution in small pieces until the blue color persisted. After 40 min at this temperature, iodomethane (2.2 mL, 35 mmol, 3.5 equiv) was added slowly over a period of 5 min and the resulting yellow solution was stirred for 1 h at –78 °C. Ammonia was evaporated overnight, and the residue was dissolved in H_2O (20 mL). The mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification by flash column chromatography (Et_2O/pentane = 5/95) provided 1:1 cis/trans diastereoisomeric mixture of 1-methylcyclohexa-2,5-diene-1-carbonitrile-4-*d* **2a-*d*1** (0.91 g, 75% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 – 5.87 (m, 2H), 5.69 – 5.65 (m, 2H), 2.70 – 2.60 (m, 1H), 1.48 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 126.38, 125.72, 122.43, 32.64, 28.63, 25.12 (t, J = 19.7 Hz). **HRMS (ESI):** Exact mass calculated for $C_8H_8DNNa^+$ [M+Na^+]: 143.0690, mass found: 143.0695.

Synthesis of 1-methylcyclohexa-2,5-diene-1-carbonitrile-2,3,4,5,6-*d*5 (2a-*d*5)

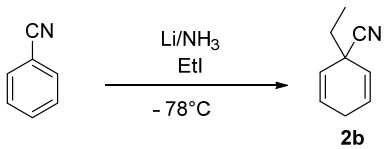


2a-*d*5

A solution of benzonitrile-*d*5 (1.1 g, 10 mmol, 1.0 equiv) and *tert*-butyl alcohol (0.95 mL, 10 mmol, 1.0 equiv) in dry Et_2O (10 mL) was added to the liquid ammonia solution (50 mL) at –78 °C. Lithium (0.14 g, 20 mmol) was added to the stirred solution in small pieces until the blue color persisted. After 40 min at this temperature, iodomethane (2.2 mL, 35 mmol, 3.5 equiv) was added slowly over a period of 5 min and the resulting yellow solution was stirred for 1 h at –78 °C. Ammonia was evaporated overnight, and the residue was dissolved in H_2O (20 mL). The mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification by flash column chromatography (Et_2O/pentane = 5/95) provided 1:1 cis/trans diastereoisomeric mixture of 1-methylcyclohexa-2,5-diene-1-carbonitrile-2,3,4,5,6-*d*5 **2a-*d*5** (1.1 g, 88% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.63 (dt, J_1 = 3.5 Hz, J_2 = 20.2 Hz, 1H), 1.48 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 125.92 (t, J = 24.5 Hz), 125.26 (t, J = 25.3 Hz), 122.44, 32.39, 28.59, 24.82 (t, J = 19.6 Hz). **HRMS (ESI):** Exact mass calculated for $C_8H_4D_5NNa^+$ [M+Na^+]: 147.0941, mass found: 147.0944.

Synthesis of 1-ethylcyclohexa-2,5-diene-1-carbonitrile (2b)



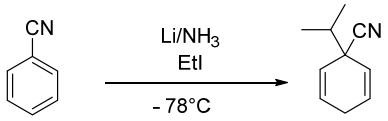
2b

A solution of benzonitrile (1.0 g, 10 mmol, 1.0 equiv) and *tert*-butyl alcohol (0.95 mL, 10 mmol, 1.0 equiv) in dry Et_2O (10 mL) was added to the liquid ammonia solution (50 mL) at –78 °C. Lithium (0.14 g, 20 mmol) was added to the stirred solution in small pieces until the blue color persisted. After 40 min at this temperature, bromoethane (2.6 mL, 35 mmol, 3.5 equiv) was added slowly over a period of 5 min and the resulting yellow solution was stirred for 1 h at –78 °C. Ammonia was evaporated overnight, and the residue was dissolved in H_2O (20 mL). The

mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification by flash column chromatography (Et_2O/pentane = 5/95) provided 1-ethylcyclohexa-2,5-diene-1-carbonitrile **2b** (1.07 g, 81% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.99 – 5.86 (m, 2H), 5.64 – 5.59 (m, 2H), 2.83 – 2.50 (m, 2H), 1.77 (q, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 127.62, 124.14, 121.94, 37.41, 34.05, 25.82, 8.42. **HRMS (ESI):** Exact mass calculated for $C_9H_{11}NNa^+$ [M+Na^+]: 156.0784, mass found: 156.0782.

Synthesis of 1-isopropylcyclohexa-2,5-diene-1-carbonitrile (2c)

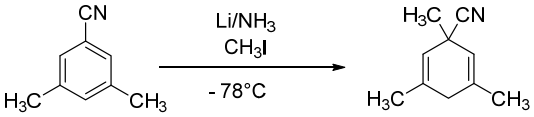


2c

A solution of benzonitrile (1.0 g, 10 mmol, 1.0 equiv) and *tert*-butyl alcohol (0.95 mL, 10 mmol, 1.0 equiv) in dry Et_2O (10 mL) was added to the liquid ammonia solution (50 mL) at −78 °C. Lithium (0.14 g, 20 mmol) was added to the stirred solution in small pieces until the blue color persisted. After 40 min at this temperature, 2-bromopropane (3.3 mL, 35 mmol, 3.5 equiv) was added slowly over a period of 5 min and the resulting yellow solution was stirred for 1 h at −78 °C. Ammonia was evaporated overnight, and the residue was dissolved in H_2O (20 mL). The mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification by flash column chromatography (Et_2O/pentane = 5/95) provided 1-isopropylcyclohexa-2,5-diene-1-carbonitrile **2c** (1.23 g, 84% yield) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.03 – 5.92 (m, 2H), 5.64 – 5.59 (m, 2H), 2.82 – 2.50 (m, 2H), 2.02 – 1.88 (m, 1H), 1.01 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 128.28, 123.03, 121.75, 41.69, 37.20, 26.08, 17.33. **HRMS (ESI):** Exact mass calculated for $C_{10}H_{13}NNa^+$ [M+Na^+]: 170.0940, mass found: 170.0936.

Synthesis of 1,3,5-trimethylcyclohexa-2,5-diene-1-carbonitrile (2d)

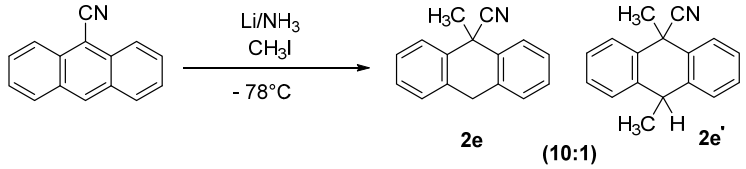


2d

A solution of 3,5-dimethylbenzonitrile (1.3 g, 10 mmol, 1.0 equiv) and *tert*-butyl alcohol (0.95 mL, 10 mmol, 1.0 equiv) in dry Et_2O (10 mL) was added to the liquid ammonia solution (50 mL) at −78 °C. Lithium (0.14 g, 20 mmol) was added to the stirred solution in small pieces until the blue color persisted. After 40 min at this temperature, iodomethane (2.2 mL, 35 mmol, 3.5 equiv) was added slowly over a period of 5 min and the resulting yellow solution was stirred for 1 h at −78 °C. Ammonia was evaporated overnight, and the residue was dissolved in H_2O (20 mL). The mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification by flash column chromatography (Et_2O/pentane = 10/90) provided 1,3,5-trimethylcyclohexa-2,5-diene-1-carbonitrile **2d** (1.0 g, 69% yield) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.37 (s, 2H), 2.64 – 2.35 (m, 2H), 1.75 (s, 6H), 1.43 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 134.19, 123.05, 120.09, 35.30, 35.01, 28.60, 22.55. **HRMS (ESI):** Exact mass calculated for $C_{10}H_{13}NNa^+$ [M+Na^+]: 170.0940, mass found: 170.0931.

Synthesis of 9-methyl-9,10-dihydroanthracene-9-carbonitrile (2e)

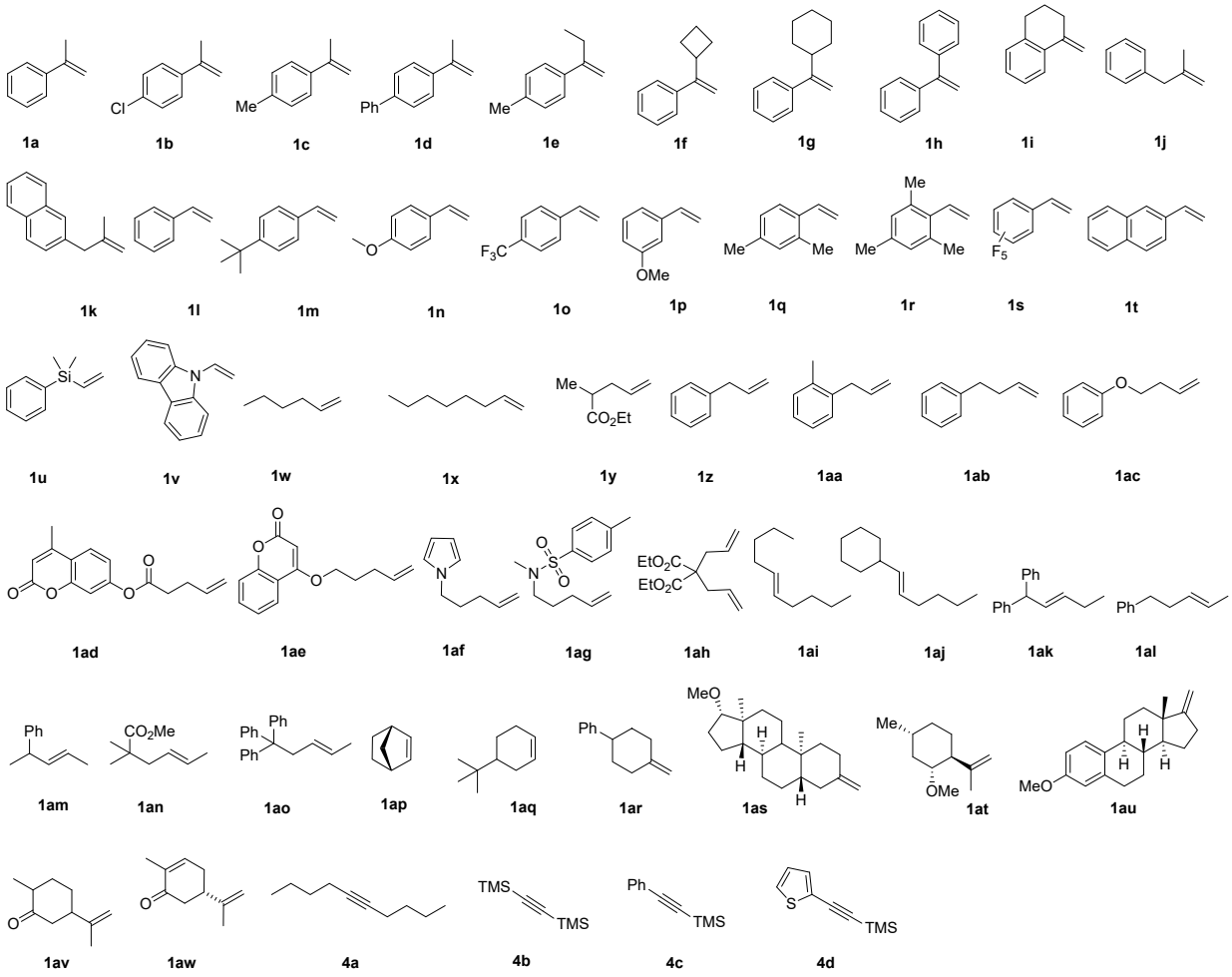


A solution of anthracene-9-carbonitrile (2.0 g, 10 mmol, 1.0 equiv) and *tert*-butyl alcohol (0.95 mL, 10 mmol, 1.0 equiv) in dry Et_2O (10 mL) was added to the liquid ammonia solution (50 mL) at −78 °C. Lithium (0.14 g, 20 mmol) was added to the stirred solution in small pieces until the blue color persisted. After 40 min at this temperature, iodomethane (2.2 mL, 35 mmol, 3.5 equiv) was added slowly over a period of 5 min and the resulting yellow solution was stirred for 1 h at −78 °C. Ammonia was evaporated overnight, and the residue was dissolved in H_2O (20 mL). The mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification by flash column chromatography (Et_2O/pentane = 10/90) provided 9-methyl-9,10-dihydroanthracene-9-carbonitrile **2e** and 9,10,10-trimethyl-9,10-dihydroanthracene-9-carbonitrile **2e'** as inseparable mixture in 10:1 (white solid, 1.8 g, 80% yield).

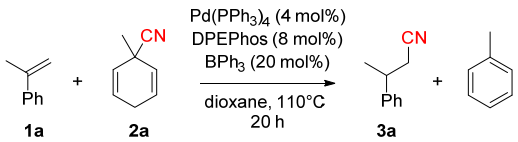
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.52 (m, 2H), 7.34 – 7.12 (m, 6H), 4.02 – 3.82 (m, 2H), 1.65 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 136.05, 133.99, 128.37, 127.96, 127.36, 125.96, 122.81, 43.73, 34.49, 30.93. **HRMS (ESI):** Exact mass calculated for $C_{16}H_{13}NNa^+$ [M+Na^+]: 242.0940, mass found: 242.0947.

Note: Nitriles **2a-e** and **2-d$_3$** are stable compounds and they are stored in the fridge at 4 °C. However, it is observed that after a long period of storage (30-40 days), it decomposes slightly and the efficiency of the transfer hydrocyanation process got affected.

Variations of alkenes and alkynes

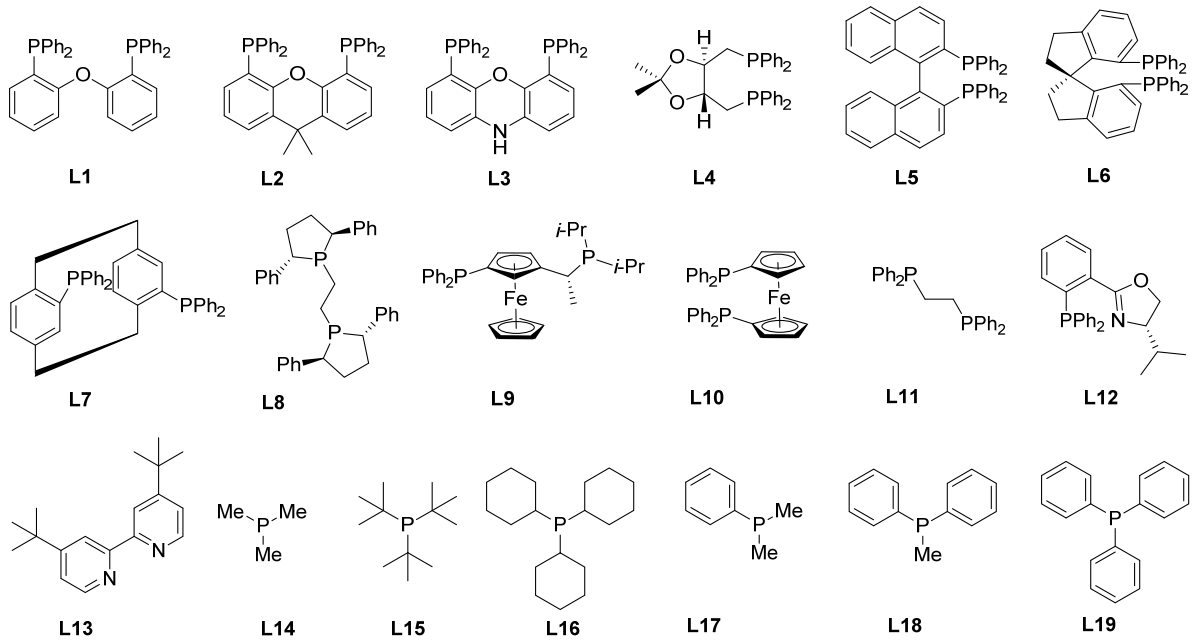


3. Optimization studies



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added BPh_3 (9.7 mg, 40 µmol, 20 mol%) inside a glove-box. To this, $Pd(PPh_3)_4$ (9.3 mg, 8.0 µmol, 4.0 mol%) and DPEphos (8.6 mg, 16 µmol, 8.0 mol%) were added outside the glove-box followed by addition of 1,4-dioxane (1.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 1-methylcyclohexa-2,5-diene-1-carbonitrile **2a** (36 mg, 0.30 mmol, 1.5 equiv) and α-methyl styrene **1a** (26 µL, 0.20 mmol, 1.0 equiv) were added. The resulting mixture was then stirred at 110 °C for 20 h. Subsequently, the reaction was cooled down to room temperature, and mesitylene (28 µL, 0.20 mmol) as internal standard was added to the solution. The yield of **3a** based on α-methylstyrene was measured by GC analysis. [Compound Retention time (min) *mesitylene* 5.34, *nitrile* ***2*** 6.13, *3-phenylbutanenitrile* **3a** 9.42]

Ligand screening



Entry	Catalyst	Ligand	Lewis acid	Solvent	Yield (%)
1	$Pd(PPh_3)_4$	L1	BPh_3	1,4-dioxane	87[a]
2	-	-	BPh_3	1,4-dioxane	0
3	$Pd(PPh_3)_4$	-	BPh_3	1,4-dioxane	0
4	$Pd(PPh_3)_4$	L1	-	1,4-dioxane	5
5	$Pd(PPh_3)_4$	L2	BPh_3	1,4-dioxane	80[a]
6	$Pd(PPh_3)_4$	L3	BPh_3	1,4-dioxane	38[a]
7	$Pd(PPh_3)_4$	L4	BPh_3	1,4-dioxane	<5
8	$Pd(PPh_3)_4$	L5	BPh_3	1,4-dioxane	<5
9	$Pd(PPh_3)_4$	L6	BPh_3	1,4-dioxane	<5
10	$Pd(PPh_3)_4$	L7	BPh_3	1,4-dioxane	12
11	$Pd(PPh_3)_4$	L8	BPh_3	1,4-dioxane	<5
12	$Pd(PPh_3)_4$	L9	BPh_3	1,4-dioxane	8
13	$Pd(PPh_3)_4$	L10	BPh_3	1,4-dioxane	64[a]
14	$Pd(PPh_3)_4$	L11	BPh_3	1,4-dioxane	<5
15	$Pd(PPh_3)_4$	L12	BPh_3	1,4-dioxane	<5
16	$Pd(PPh_3)_4$	L13	BPh_3	1,4-dioxane	<5
17	$Pd(PPh_3)_4$	L14	BPh_3	1,4-dioxane	<5
18	$Pd(PPh_3)_4$	L15	BPh_3	1,4-dioxane	10
19	$Pd(PPh_3)_4$	L16	BPh_3	1,4-dioxane	<5
20	$Pd(PPh_3)_4$	L17	BPh_3	1,4-dioxane	12
21	$Pd(PPh_3)_4$	L18	BPh_3	1,4-dioxane	8
22	$Pd(PPh_3)_4$	L19	BPh_3	1,4-dioxane	<5
23	$Pd(PPh_3)_4$[b]	L1	BPh_3	1,4-dioxane	53[a]
24	$Ni(cod)_2$	L1	$AlMe_2Cl$	toluene	34[a]
25	$Ni(cod)_2$	L1	BPh_3	1,4-dioxane	<5
26	$Pd_2(dba)_3$	L1	BPh_3	1,4-dioxane	10

Solvent screening

1	$Pd(PPh_3)_4$	L1	BPh_3	toluene	70[a]
2	$Pd(PPh_3)_4$	L1	BPh_3	benzene (80°C)	20
3	$Pd(PPh_3)_4$	L1	BPh_3	THF (80°C)	13

Lewis acid screening

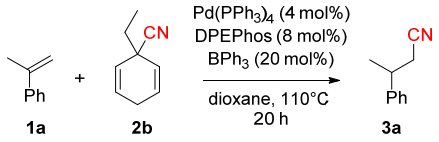
1	$Pd(PPh_3)_4$	L1	$AlCl_3$	1,4-dioxane	0
2	$Pd(PPh_3)_4$	L1	$AlMe_2Cl$	1,4-dioxane	26
3	$Pd(PPh_3)_4$	L1	$AlMe_3$	1,4-dioxane	20
4	$Pd(PPh_3)_4$	L1	$BF_3.OEt$	1,4-dioxane	23
5	$Pd(PPh_3)_4$	L1	$BEt_3.THF$	1,4-dioxane	12
6	$Pd(PPh_3)_4$	L1	$B(C_6F_5)_3$	1,4-dioxane	86[a]
7	$Pd(PPh_3)_4$	L1	BPh_3[c]	1,4-dioxane	47[a]
8	$Pd(PPh_3)_4$	L1	BPh_3[d]	1,4-dioxane	90[a]

[a]Isolated yield (linear:branched ≥ 20:1). [b]2.5 mol% $Pd(PPh_3)_4$ loading. [c]10 mol% BPh_3 loading, [d] 100 mol% BPh_3 loading

Note: BPh_3 and $B(C_6F_5)_3$ are highly hygroscopic. They are stored in a glove-box. The efficiency of the transfer hydrocyanation process is highly dependent on the quality of the Lewis acid.

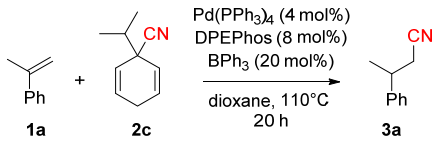
Variation of donor nitriles

Reaction with 1-ethylcyclohexa-2,5-diene-1-carbonitrile (2b)



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added BPh_3 (24 mg, 0.10 mmol, 20 mol%) inside a glove-box. To this, $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), and DPEphos (21 mg, 40 µmol, 8.0 mol%) were added outside the glove-box followed by addition of 1,4-dioxane (3.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 1-ethylcyclohexa-2,5-diene-1-carbonitrile **2b** (0.10 g, 0.75 mmol, 1.5 equiv) and α-methyl styrene **1a** (65 µL, 0.50 mmol, 1.0 equiv) were added. The resulting mixture was then stirred at 110 °C for 20 h. Subsequently, the volatiles were removed under reduced pressure. The residue was purified by flash chromatography to obtain the nitrile **3a** (39 mg, 53%) as a colorless oil.

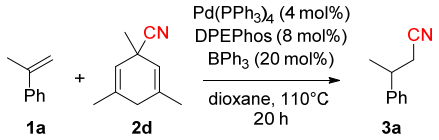
Reaction with 1-isopropylcyclohexa-2,5-diene-1-carbonitrile (2c)



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added BPh_3 (24 mg, 0.10 mmol, 20 mol%) inside a glove-box. To this, $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), and DPEphos (21 mg, 40 µmol, 8.0 mol%) were added outside the glove-box followed by addition of 1,4-dioxane (3.0 mL) under a positive pressure of argon and the resultant reaction

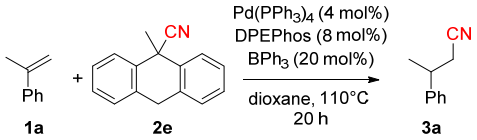
mixture was kept stirring at rt for 10 minutes. To this mixture, 1-isopropylcyclohexa-2,5-diene-1-carbonitrile **2c** (0.11 g, 0.75 mmol, 1.5 equiv) and α-methyl styrene **1a** (65 µL, 0.50 mmol, 1.0 equiv) were added. The resulting mixture was then stirred at 110 °C for 20 h. Subsequently, the volatiles were removed under reduced pressure. The residue was purified by flash chromatography to obtain the nitrile **3a** (29 mg, 39%) as a colorless oil.

Reaction with 1,3,5-trimethylcyclohexa-2,5-diene-1-carbonitrile (2d)



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added BPh_3 (24 mg, 0.10 mmol, 20 mol%) inside a glove-box. To this, $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), and DPEphos (21 mg, 40 µmol, 8.0 mol%) were added outside the glove-box followed by addition of 1,4-dioxane (3.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 1,3,5-trimethylcyclohexa-2,5-diene-1-carbonitrile **2d** (0.11 g, 0.75 mmol, 1.5 equiv) and α-methyl styrene **1a** (65 µL, 0.50 mmol, 1.0 equiv) were added. The resulting mixture was then stirred at 110 °C for 20 h. Subsequently, the volatiles were removed under reduced pressure. The residue was purified by flash chromatography to obtain the nitrile **3a** (16 mg, 22%) as a colorless oil.

Reaction with 9-methyl-9,10-dihydroanthracene-9-carbonitrile (2e)



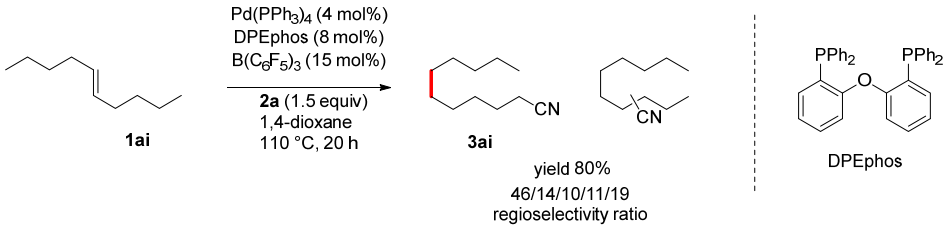
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added BPh_3 (24 mg, 0.10 mmol, 20 mol%) inside a glove-box. To this, $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), and DPEphos (21 mg, 40 µmol, 8.0 mol%) were added outside the glove-box followed by addition of 1,4-dioxane (3.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 9-methyl-9,10-dihydroanthracene-9-carbonitrile **2e** (0.16 g, 0.75 mmol, 1.5 equiv) and α-methyl styrene **1a** (65 µL, 0.50 mmol, 1.0 equiv) were added. The resulting mixture was then stirred at 110 °C for 20 h. Subsequently, the volatiles were removed under reduced pressure. GC analysis shows that the nitrile **2e** was failed to afford the product **3a** (0%).

Reaction with 3-methylbutanenitrile (2f)

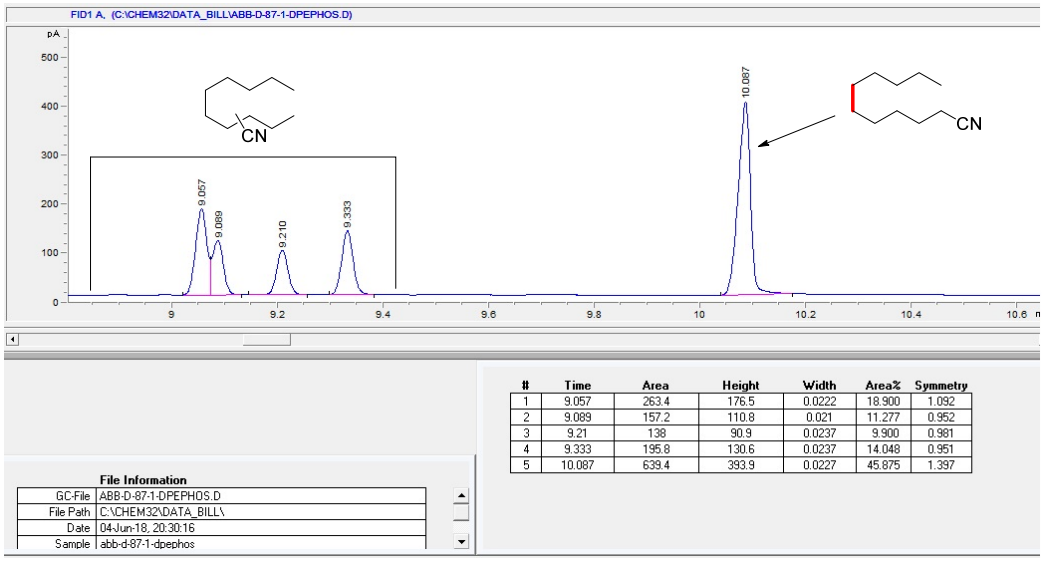
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%) inside a glove-box. To this, $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), and DPEphos (21 mg, 40 µmol, 8.0 mol%) were added outside the glove-box followed by addition of 1,4-dioxane (3.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 3-methylbutanenitrile **2f** (0.26

mL, 2.50 mmol, 5.0 equiv) and α-methyl styrene **1a** (65 µL, 0.50 mmol, 1.0 equiv) were added. The resulting mixture was then stirred at 110 °C for 20 h. Subsequently, the reaction was cooled down to room temperature, and mesitylene (70 µL, 0.50 mmol) was added as internal standard to the solution. GC analysis shows that the nitrile **3e** was formed in 15% yield.

Optimization studies for chain walking hydrocyanation of internal alkenes

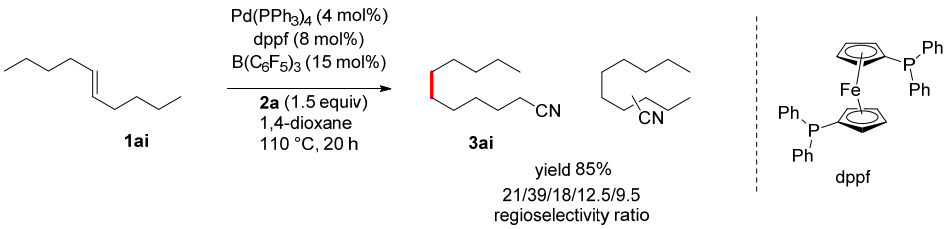


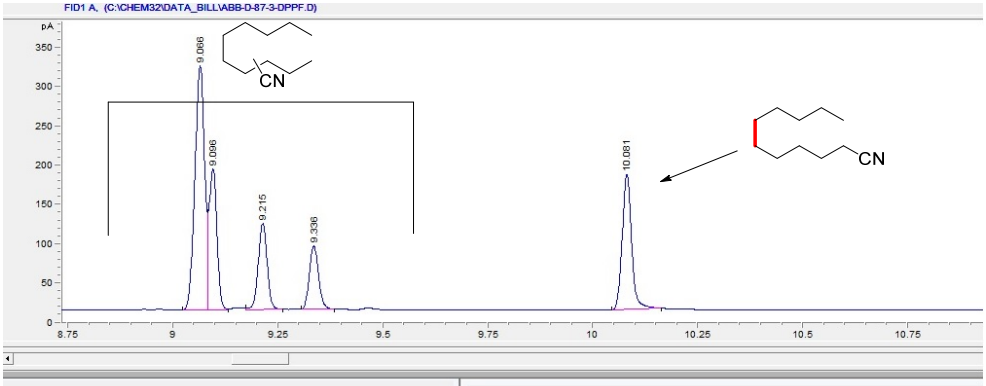
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added $B(C_6F_5)_3$ (16 mg, 30 µmol, 15 mol%) inside a glove-box. To this, $Pd(PPh_3)_4$ (9.3 mg, 8.0 µmol, 4.0 mol%) and DPEphos (8.6 mg, 16 µmol, 8.0 mol%) were added outside the glove-box followed by addition of 1,4-dioxane (1.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 1-methylcyclohexa-2,5-diene-1-carbonitrile **2a** (36 mg, 0.30 mmol, 1.5 equiv) and *trans*-5-decene **1ai** (38 µL, 0.20 mmol, 1.0 equiv) were added. The resulting mixture was then stirred at 110 °C for 20 h. Subsequently, the reaction was cooled down to room temperature, and mesitylene (28 µL, 0.20 mmol) as internal standard was added to the solution. The yield of **3ai** based on *trans*-5-decene **1ai** was measured by GC analysis.



#	Time	Area	Height	Width	Area%	Symmetry
1	9.057	263.4	176.5	0.0222	18.900	1.092
2	9.089	157.2	110.8	0.021	11.277	0.952
3	9.21	138	90.9	0.0237	9.900	0.981
4	9.333	195.8	130.6	0.0237	14.048	0.951
5	10.087	639.4	393.9	0.0227	45.875	1.397

Reaction with dppf in place of DPEphos for 20 h





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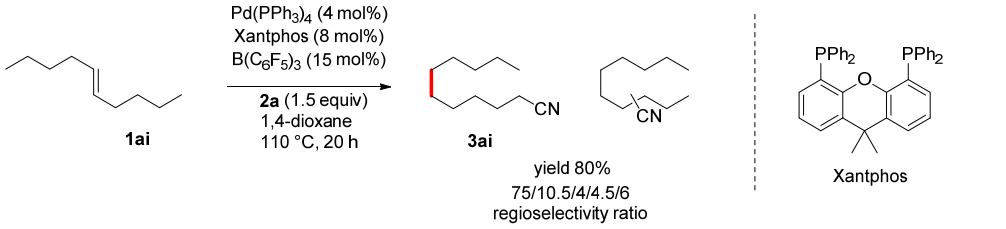
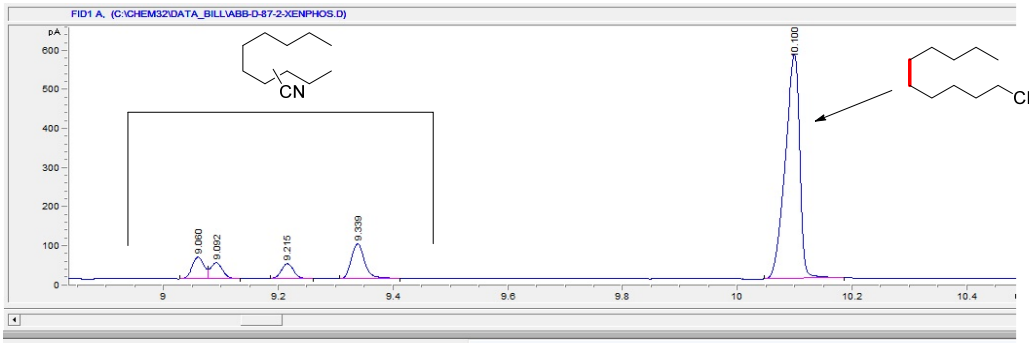
File Path	C:\CHEM32\DATA_BILL\
Date	04-Jun-18, 22:16:19
Sample	abb-d-87-3-dppf
Sample Info	
Barcode	
Operator	gcuser
Method	M4.M

#	Time	Area	Height	Width	Area%	Symmetry
1	9.066	501.5	310.7	0.0236	38.856	1.206
2	9.096	233	179.8	0.0191	18.056	0.944
3	9.215	162.7	109.2	0.0229	12.604	1.011
4	9.336	122.5	80.7	0.0242	9.492	0.885
5	10.081	270.9	172	0.0244	20.993	0.862

Reaction with Xantphos in place of DPEphos for 20 h





File Information	
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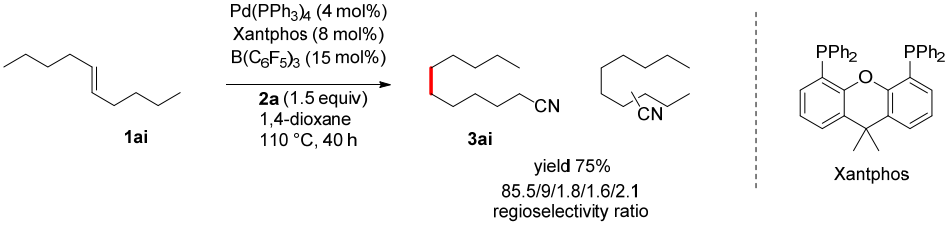
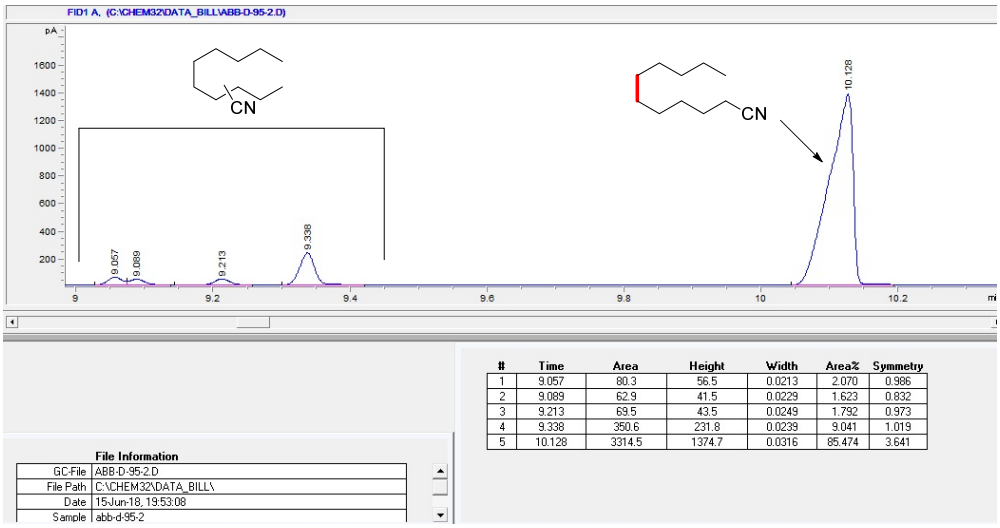
Date	04-Jun-18, 21:23:17
Sample	abb-d-87-2-xenphos

#	Time	Area	Height	Width	Area%	Symmetry
1	9.06	80.4	55.7	0.0216	5.954	0.968
2	9.092	60.3	41.5	0.0227	4.465	0.866
3	9.215	55.7	37.9	0.0229	4.130	0.843
4	9.339	142.3	88.9	0.0239	10.541	0.897
5	10.1	1011.1	573.6	0.0266	74.909	1.686

Reaction with Xantphos in place of DPEphos for 40 h

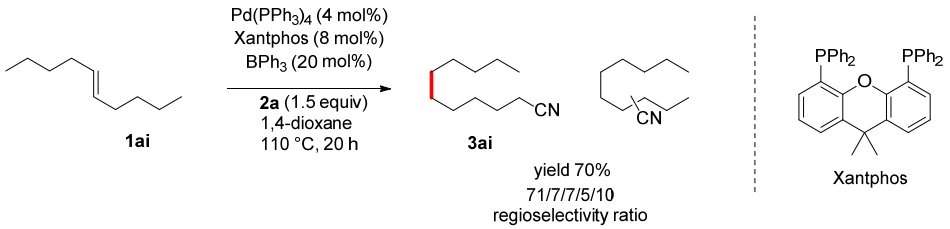




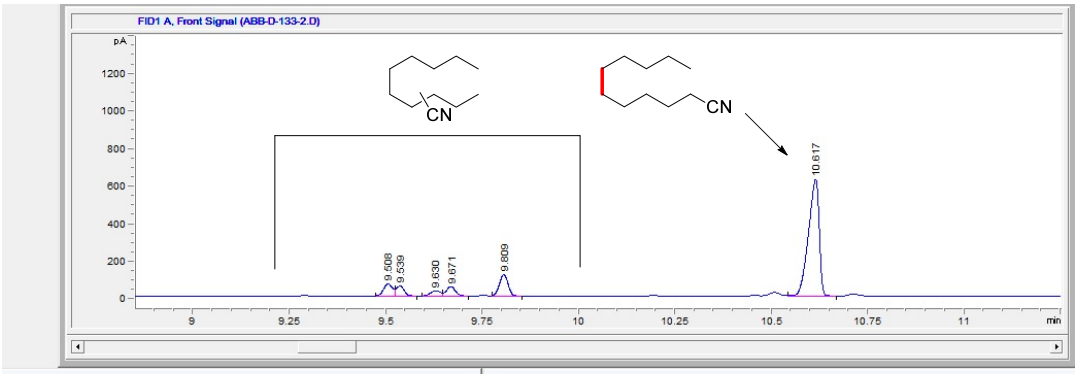
#	Time	Area	Height	Width	Area%	Symmetry
1	9.057	80.3	56.5	0.0213	2.070	0.986
2	9.089	62.9	41.5	0.0229	1.623	0.832
3	9.213	69.5	43.5	0.0249	1.792	0.973
4	9.338	350.6	231.8	0.0239	9.041	1.019
5	10.128	3314.5	1374.7	0.0316	85.474	3.641

File Information	
GC-File	ABB-D-95-2.D
File Path	C:\CHEM32\DATA_BILL\
Date	15-Jun-18, 19:53:08
Sample	abb-d-95-2

Reaction with BPh_3 in place of $B(C_6F_5)_3$



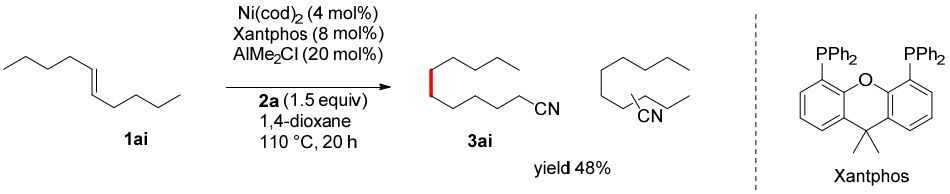
yield 70%
71/7/7/5/10
regioselectivity ratio



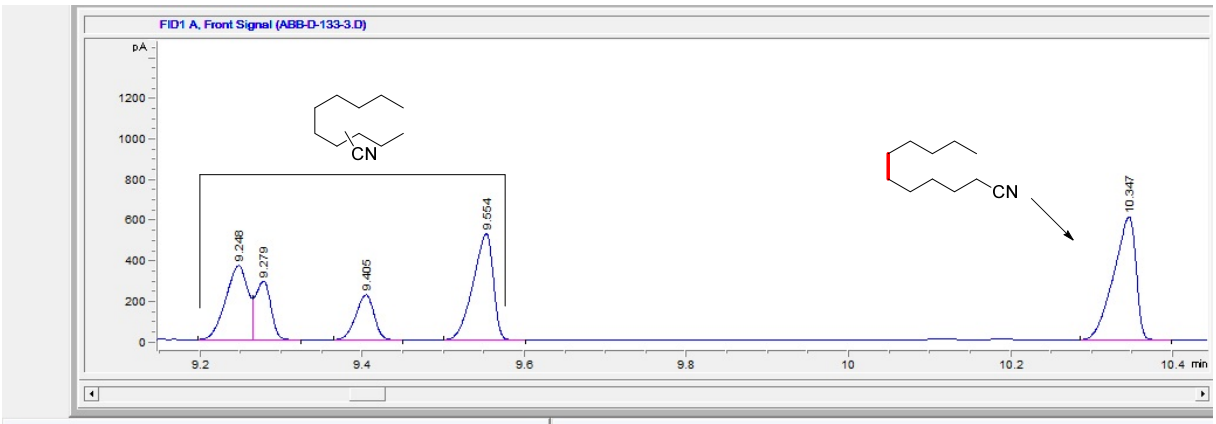
File Information	
GC-File	ABB-D-133-2.D
File Path	C:\CHEM32\1\DATA\
Date	04-Sep-18, 12:34:33
Sample	abb-d-133-2
Sample Info	
Barcode	
Operator	gcuser
Method	M4BILL.M

#	Time	Area	Height	Width	Area%	Symmetry
1	9.508	101.2	65.3	0.0233	6.048	1.043
2	9.539	77.3	52.1	0.0221	4.616	0.889
3	9.63	47.5	26.8	0.0271	2.839	1.026
4	9.671	79.5	49.2	0.0245	4.747	1.109
5	9.809	174.9	112.7	0.0241	10.445	1.034
6	10.617	1193.8	618.4	0.0277	71.305	1.984

Reaction with Ni/Xantphos



yield 48%



File Information	
GC-File	ABB-D-133-3.D
File Path	C:\CHEM32\1\DATA\
Date	20-Sep-18, 22:33:51
Sample	abb-d-133-3
Sample Info	
Barcode	
Operator	gcuser
Method	M4BILL.M

#	Time	Area	Height	Width	Area%	Symmetry
1	9.248	694.2	364.7	0.0286	19.950	1.399
2	9.279	383.1	286.2	0.0204	11.009	1.004
3	9.405	344.1	220.9	0.0242	9.887	1.193
4	9.554	902.1	522	0.0266	25.922	1.838
5	10.347	1156.5	603.3	0.0276	33.232	2.103

Optimization table for chain walking studies

Entry	Catalyst	Ligand	Lewis acis	Yield (%)	l:b
1	$Pd(PPh_3)_4$	DPEphos	$B(C_6F_5)_3$	80	46:54
3	$Pd(PPh_3)_4$	dppf	$B(C_6F_5)_3$	85	21:79
4	$Pd(PPh_3)_4$	Xantphos	$B(C_6F_5)_3$	80	75:25
5[a]	$Pd(PPh_3)_4$	Xantphos	$B(C_6F_5)_3$	75	85.5:14.5
6	$Pd(PPh_3)_4$	Xantphos	BPh_3	70	71:29
7	$Ni(cod)_2$	Xantphos	$B(C_6F_5)_3$	<5	-
8	$Ni(cod)_2$	Xantphos	$AlMe_2Cl$	48	33:77

[a]Reaction time 40 h.

4. General procedure

GP1: Transfer hydrocyanation of α–substituted styrenes and alkynes

To a flame-dried screw-capped test tube equipped with a magnetic stir bar BPh_3 (24.0 mg, 100 µmol, 20 mol%) was added inside a glove-box. To this, $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%) and DPEphos (21 mg, 40 µmol, 8.0 mol%) were added outside the glove-box followed by addition of 1,4-dioxane (3.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 1-methylcyclohexa-2,5-diene-1-carbonitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and styrene **1a–1v** and **4a–ad** (1.0 equiv) were added. The resulting mixture was then stirred at 110 °C for 20 h. Subsequently, the volatiles were removed under reduced pressure. The residue was purified by flash chromatography to obtain the corresponding nitrile derivatives (**3a**–**3v** and **5a–5d)**.

GP2: Transfer hydrocyanation of alkenes

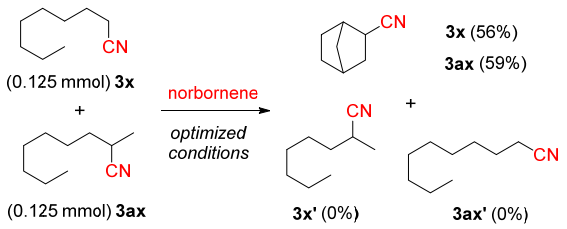
To a flame-dried screw-capped test tube equipped with a magnetic stir bar $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%) was added inside a glove-box. To this, $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%) and DPEphos (21 mg, 40 µmol, 8.0 mol%) were added outside the glove-box followed by addition of 1,4-dioxane (3.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 1-methylcyclohexa-2,5-diene-1-carbonitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and alkenes **1w–1ah** and **1ap–1aw** (1.0 equiv) were added. The resulting mixture was then stirred at 100 °C for 20 h. Subsequently, the volatiles were removed under reduced pressure. The residue was purified by flash chromatography to obtain the corresponding nitrile derivatives (**3w**–**3ah** and **3ap**–**5aw)**.

GP3: Transfer hydrocyanation of internal alkenes

To a flame-dried screw-capped test tube equipped with a magnetic stir bar $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%) was added inside a glove-box. To this, $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%) and Xantphos (23 mg, 40 µmol, 8.0 mol%) were added outside the glove-box followed by addition of 1,4-dioxane (3.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 1-methylcyclohexa-2,5-diene-1-carbonitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and alkenes **1ai–1ao** (1.0 equiv) were added. The resulting mixture was then stirred at 110 °C for 40 h. Subsequently, the volatiles were removed under reduced pressure. The residue was purified by flash chromatography to obtain the corresponding nitrile derivatives (**3ai**–**3ao)**.

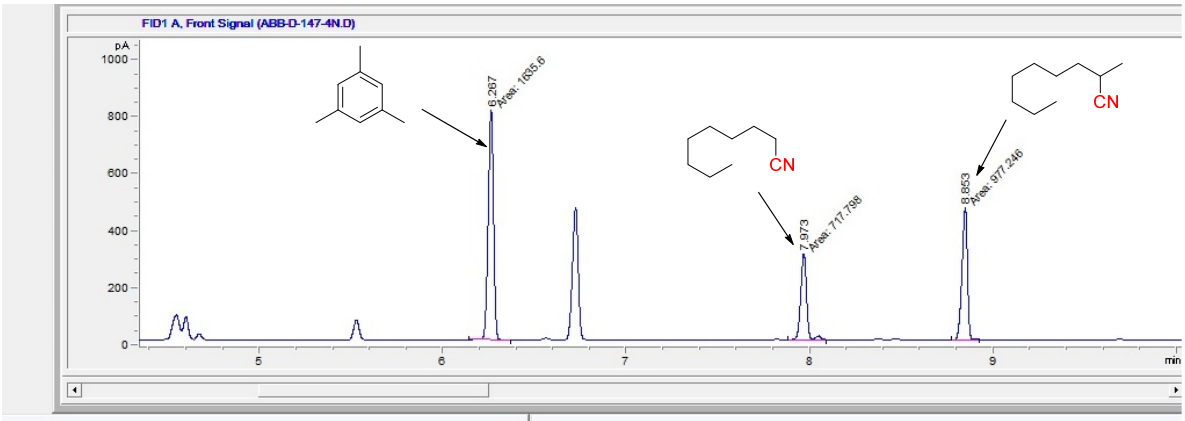
5. Mechanistic experiments

Study for the reversible nature of hydrocyanation



To a flame-dried screw-capped test tube equipped with a magnetic stir bar $B(C_6F_5)_3$ (30 mg, 58 µmol) was added inside a glove-box. To this, $Pd(PPh_3)_4$ (12 mg, 10 µmol) and Xantphos (12 mg, 20 µmol) were added outside the glove-box followed by addition of 1,4-dioxane (2.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, nonanenitrile **3x** (18 mg, 0.125 mmol), 2-methylnonanenitrile **3ax** (19 mg, 0.125 mmol) and norbornene (118 mg, 1.25 mmol) were added. The resulting mixture was then stirred at 110 °C for 20 h. Subsequently, the reaction was cooled down to room temperature, and mesitylene (18 µL, 0.125 mmol) was added as internal standard to the solution. GC analysis shows that branched **3ax** (41%) and linear nitrile **3x** (44%) were consumed in almost equal amounts (manuscript Scheme 3, eq 1).

This result shows that both branched and linear nitriles are active HCN donors. Moreover, in this experiment unreacted nitrile **3x** (8 C atoms) was not converted to its branched isomer **3x'** and accordingly branched **3ax** (9 C atoms) not to its corresponding linear nitrile **3ax'**.



File Information	
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File Path	C:\CHEM32\1\DATA\
Date	14-Sep-18, 11:49:52
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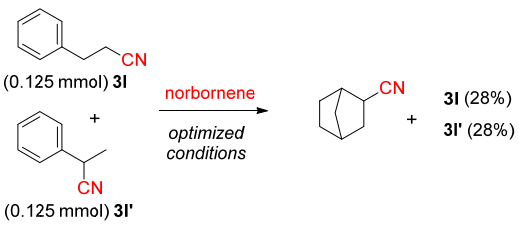
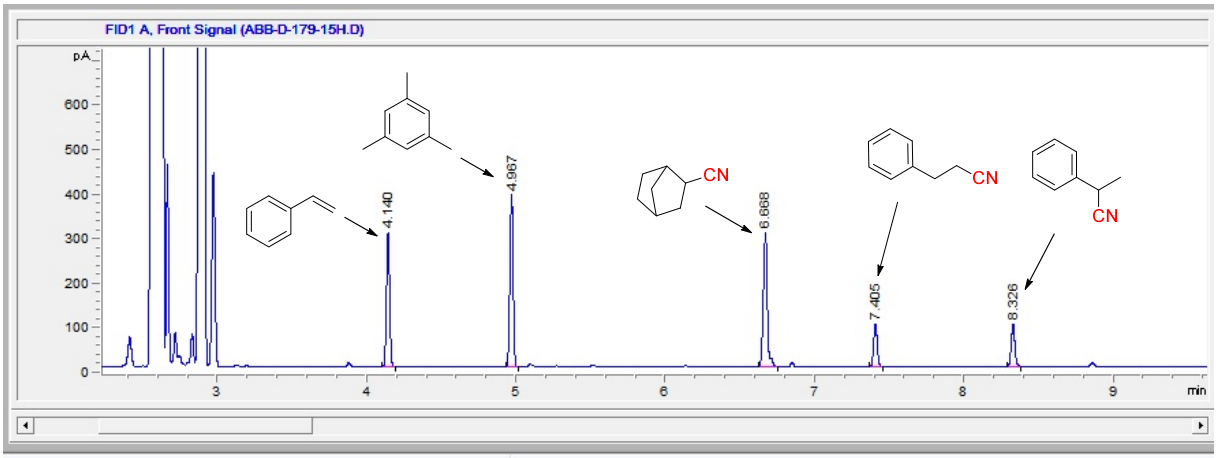
Sample Info	
Barcode	
Operator	gcuser
Method	M4BILL.M

#	Time	Area	Height	Width	Area%	Symmetry
1	6.267	1635.6	807.8	0.0337	49.108	1.11
2	7.973	717.8	304.2	0.0393	21.551	1.053
3	8.853	977.2	467.4	0.0348	29.341	1.466



To a flame-dried screw-capped test tube equipped with a magnetic stir bar $B(C_6F_5)_3$ (30 mg, 58 µmol) was added inside a glove-box. To this, $Pd(PPh_3)_4$ (12 mg, 10 µmol) and Xantphos (12 mg, 20 µmol) were added outside the glove-box followed by addition of 1,4-dioxane (2.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 3-phenylpropanenitrile **3l** (17 µL, 0.125 mmol), 2-phenylpropanenitrile **3l'** (17 µL, 0.125 mmol) and norbornene (118 mg, 1.25 mmol) were added. The resulting mixture was then stirred at 110 °C for 20 h. Subsequently, the reaction was cooled down to room temperature, and mesitylene (18 µL, 0.125 mmol) was added as internal standard to the solution. GC analysis shows that branched **3l'** (72%) and linear nitrile **3l** (72%) were consumed in equal amounts (manuscript Scheme 3, eq 2).

This result shows that both branched and linear nitriles are active HCN donors.



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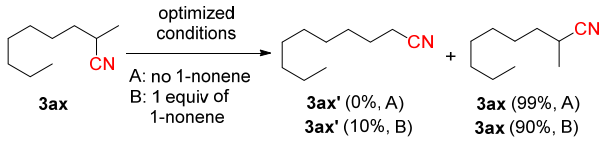
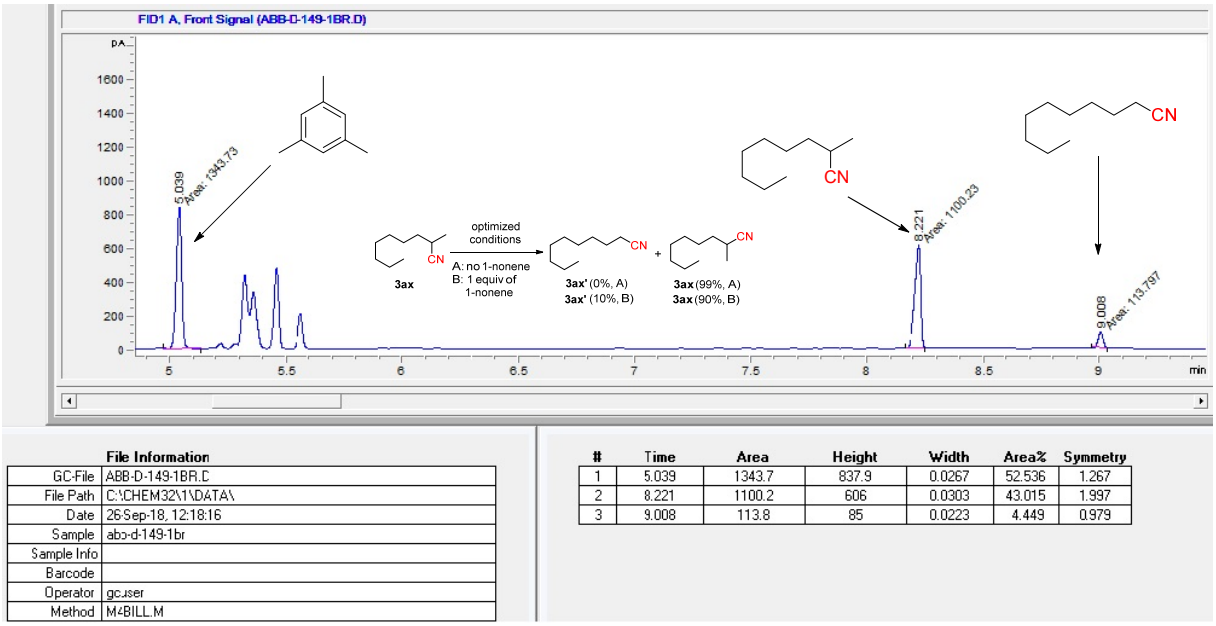
Sample Info	
Barcode	
Operator	gcuser
Method	M4BILL.M

#	Time	Area	Height	Width	Area%	Symmetry
1	4.14	451	300.6	0.0235	23.458	1
2	4.967	588.5	385.7	0.0242	30.610	1.092
3	6.668	561	301.3	0.0289	29.181	1.045
4	7.405	161	95.2	0.0265	8.376	1.044
5	8.326	161	94.6	0.0263	8.375	0.994



To a flame-dried screw-capped test tube equipped with a magnetic stir bar $B(C_6F_5)_3$ (30 mg, 58 µmol) was added inside a glove-box. To this, $Pd(PPh_3)_4$ (12 mg, 10 µmol) and Xantphos (12 mg, 20 µmol) were added outside the glove-box followed by addition of 1,4-dioxane (1.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 2-methylnonanenitrile **3ax** (19 mg, 0.125 mmol) and 1-nonene (22 µL, 1.25 mmol) were added. The resulting mixture was then stirred at 110 °C for 20 h. Subsequently, the reaction was cooled down to room temperature, and mesitylene (18 µL, 0.125 mmol) was added as internal standard to the solution. GC analysis shows that 10% of the isomeric linear nitrile **3ax'** was formed (manuscript Scheme 3, eq 2).

Importantly, in the absence of 1-nonene, the starting nitriles could be recovered without formation of the other regioisomer.



File Information	
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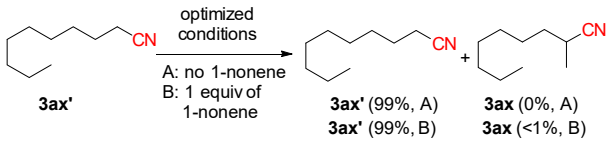
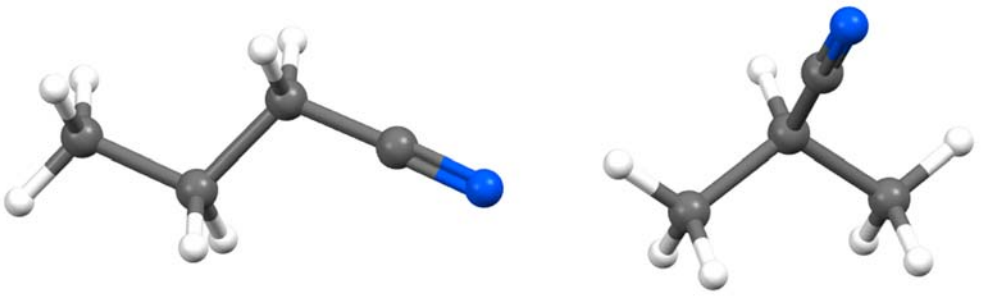
File Path	C:\CHEM32\1\DATA\
Date	26-Sep-18, 12:18:16
Sample	abb-d-149-1br
Sample Info	
Barcode	
Operator	gc.user
Method	M4BILL.M

#	Time	Area	Height	Width	Area%	Symmetry
1	5.039	1343.7	837.9	0.0267	52.536	1.267
2	8.221	1100.2	606	0.0303	43.015	1.997
3	9.008	113.8	85	0.0223	4.449	0.979



To a flame-dried screw-capped test tube equipped with a magnetic stir bar $B(C_6F_5)_3$ (30 mg, 58 µmol) was added inside a glove-box. To this, $Pd(PPh_3)_4$ (12 mg, 10 µmol) and Xantphos (12 mg, 20 µmol) were added outside the glove-box followed by addition of 1,4-dioxane (1.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, nonanenitrile **3x** (18 mg, 0.125 mmol) and 1-nonene (22 µL, 1.25 mmol) were added. The resulting mixture was then stirred at 110 °C for 20 h. Subsequently, the reaction was cooled down to room temperature, and mesitylene (18 µL, 0.125 mmol) was added as internal standard to the solution. GC analysis shows that only unreacted nonanenitrile **3x**.

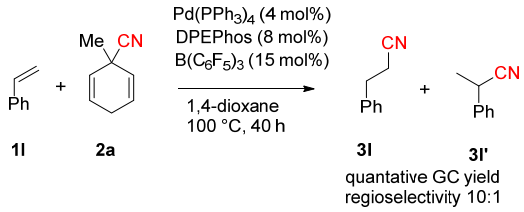


1 **2**

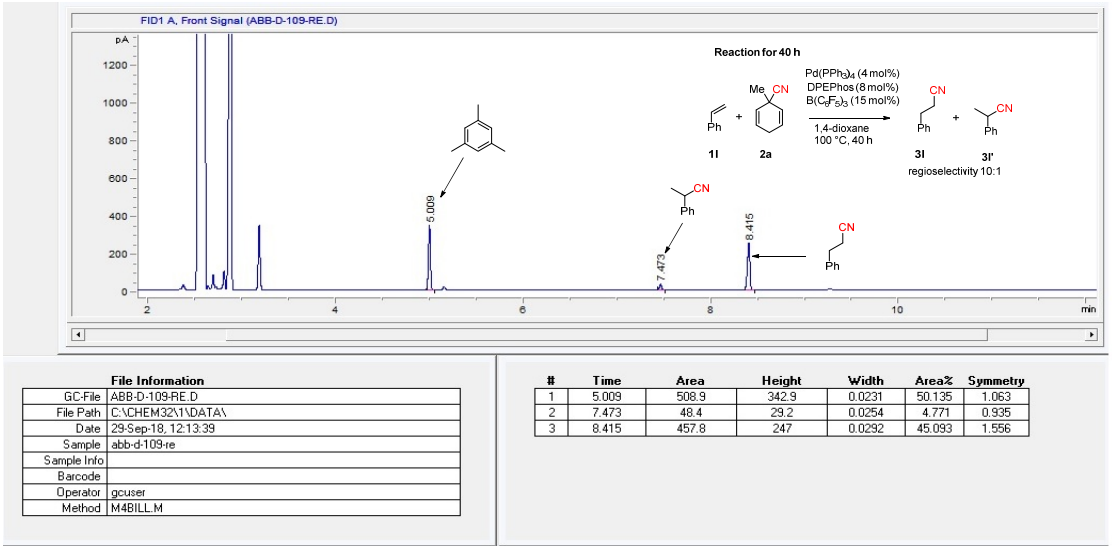
We have calculated the relative gas phase free energy ΔG(298.15K) for 1-propyl nitrile (**1**) and 2-propyl nitrile (**2**) with DFT (PW6B95-D3//TPSS-D3/def2-TZVP). The secondary isomer **2** is more stable by 0.43 kcal/mol in the conformation shown above. This demonstrates that within

the error of the method, there is no significant difference in the thermodynamic stabilities of these two isomers

Time dependent study

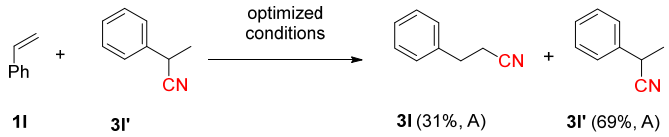


To a flame-dried screw-capped test tube equipped with a magnetic stir bar $B(C_6F_5)_3$ (20 mg, 38 µmol, 15 mol%) was added inside a glove-box. To this, $Pd(PPh_3)_4$ (12 mg, 10 µmol) and DPEphos (11 mg, 20 µmol) were added outside the glove-box followed by addition of 1,4-dioxane (1.5 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 1-methylcyclohexa-2,5-diene-1-carbonitrile **2a** (45 mg, 0.375 mmol) and styrene **1l** (28 µL, 0.25 mmol) were added. The resulting mixture was then stirred at 100 °C for 40 h. Subsequently, the reaction was cooled down to room temperature, and mesitylene (35 µL, 0.25 mmol) as internal standard was added to the solution. The yield and regioselectivity of **3l** based on styrene **1l** was measured by GC analysis.



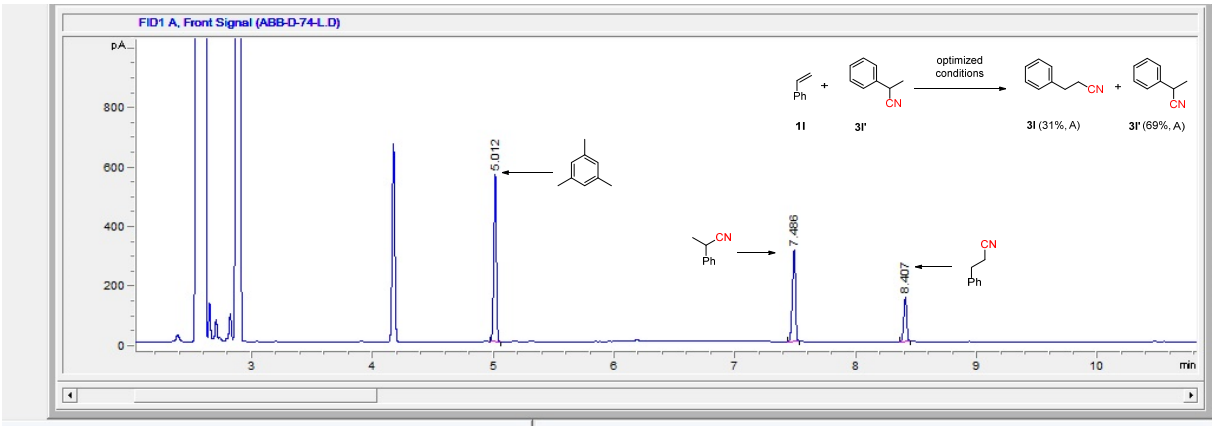
The transfer hydrocyanation of alkene **1l**, where l/b-selectivity was improved from 9:1 (20 h) to 10:1 (40 h). This study shows that, l/b product selectivity can only be improved slightly upon extending reaction time.

Isomerization study of 3l' to 3l



To a flame-dried screw-capped test tube equipped with a magnetic stir bar $B(C_6F_5)_3$ (30 mg, 58 µmol) was added inside a glove-box. To this, $Pd(PPh_3)_4$ (12 mg, 10 µmol) and DPEphos (11 mg, 20 µmol) were added outside the glove-box followed by addition of 1,4-dioxane (1.5 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for

10 minutes. To this mixture, 2-phenylpropanenitrile **3l'** (33 mg, 0. 25 mmol) and styrene **1l** (28 µL, 0.25 mmol) were added. The resulting mixture was then stirred at 110 °C for 20 h. Subsequently, the reaction was cooled down to room temperature, and mesitylene (35 µL, 0.25 mmol) was added as internal standard to the solution. GC analysis shows that 31% of the isomeric linear nitrile **3l** was formed.



File Information	
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File Path	C:\CHEM32\1\DATA\
Date	30-Sep-18, 15:21:49
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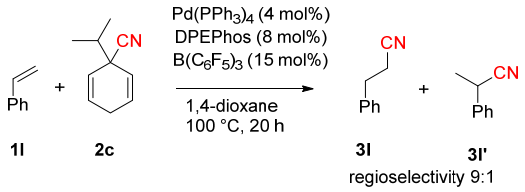
Sample Info	
Barcode	
Operator	gcuser
Method	M4BILL.M

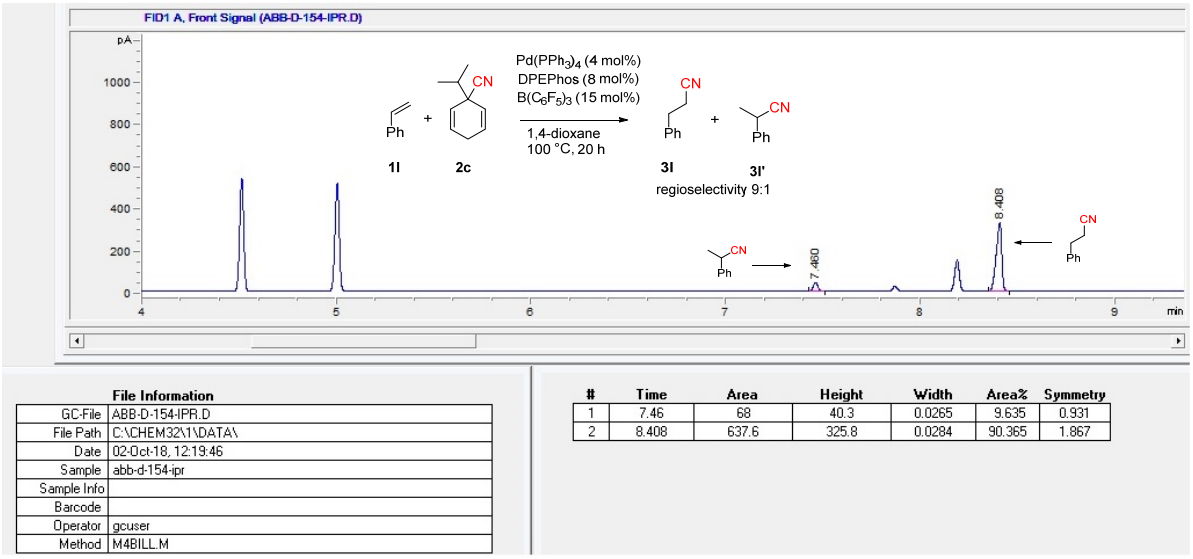
#	Time	Area	Height	Width	Area%	Symmetry
1	5.012	843.1	560	0.023	51.113	1.185
2	7.486	553.6	305.5	0.0279	33.561	1.395
3	8.407	252.8	148.1	0.0267	15.326	1.202

Effect of CHD reagent on catalysis



To a flame-dried screw-capped test tube equipped with a magnetic stir bar $B(C_6F_5)_3$ (20 mg, 38 µmol, 15 mol%) was added inside a glove-box. To this, $Pd(PPh_3)_4$ (12 mg, 10 µmol) and DPEphos (11 mg, 20 µmol) were added outside the glove-box followed by addition of 1,4-dioxane (1.5 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 1-isopropylcyclohexa-2,5-diene-1-carbonitrile **2c** (55 mg, 0.375 mmol) and styrene **1l** (28 µL, 0.25 mmol) were added. The resulting mixture was then stirred at 100 °C for 20 h. Subsequently, the reaction was cooled down to room temperature, and mesitylene (35 µL, 0.25 mmol) as internal standard was added to the solution. The yield and regioselectivity of **3l** based on styrene **1l** was measured by GC analysis.

The reaction with reagent **2c** in combination with styrene **1l** gave **3l** with 9:1 l/b-selectivity and as expected no change in regioselectivity was noted as compared with the result achieved with reagent **2a**. The CHD-reagent do not have any influence on the regiochemistry since it is not involved in the regiodetermining hydropalladation step. The regioselectivity is controlled by the used ligand.



File Information	
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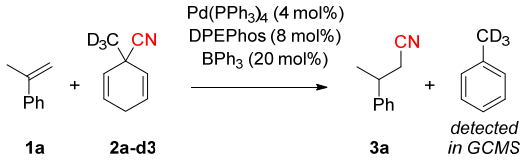
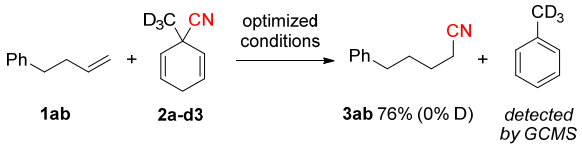
File Path	C:\CHEM32\1\DATA\
Date	02-Oct-18, 12:19:46
Sample	abb-d-154-ipr
Sample Info	
Barcode	
Operator	gcuser
Method	M4BILL.M

#	Time	Area	Height	Width	Area%	Symmetry
1	7.46	68	40.3	0.0265	9.635	0.931
2	8.408	637.6	325.8	0.0284	90.365	1.867

Deuterium labeling experiment

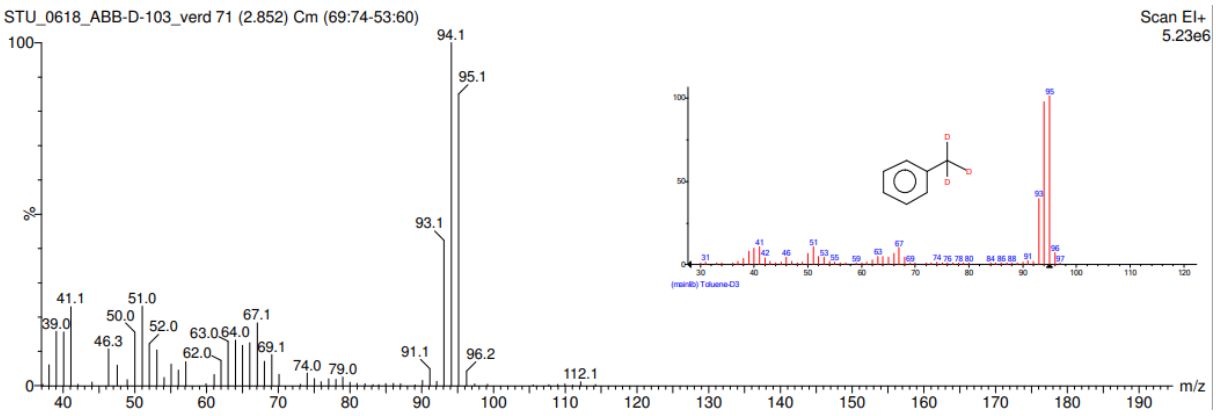


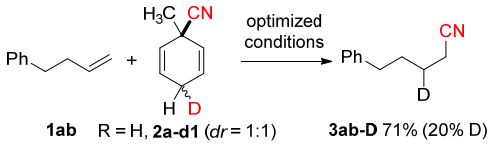
To a flame-dried screw-capped test tube equipped with a magnetic stir bar BPh_3 (24 mg, 0.10 mmol, 20 mol%) was added inside the glove-box. To this, $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%) and DPEphos (21 mg, 40 µmol, 8.0 mol%) were added outside the glove-box followed by addition of 1,4-dioxane (3.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 1-(methyl-*d*3)cyclohexa-2,5-diene-1-carbonitrile **2-*d*3** (92 mg, 0.75 mmol, 1.5 equiv) and α-methyl styrene **1a** (65 µL, 0.50 mmol, 1.0 equiv) were added. The resulting mixture was then stirred at 110 °C for 20 h. Subsequently, the volatiles were removed under reduced pressure. The residue was purified by flash chromatography to obtain nitrile **3a** (61 mg, 84% yield).



To a flame-dried screw-capped test tube equipped with a magnetic stir bar $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), was added inside the glove-box. To this, $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%) and DPEphos (21 mg, 40 µmol, 8.0 mol%) were added outside the glove-box followed by addition of 1,4-dioxane (3.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 1-(methyl-*d*3)cyclohexa-2,5-diene-1-carbonitrile **2-*d*3** (92 mg, 0.75 mmol, 1.5 equiv) and but-3-en-1-ylbenzene **1ab** (75 µL, 0.50 mmol, 1.0 equiv) were added. were added. The resulting mixture was then stirred at 100 °C for 20 h. Subsequently, the volatiles were removed under reduced pressure. The residue was purified by flash chromatography to obtain nitrile **3ab** (61 mg, 76% yield).

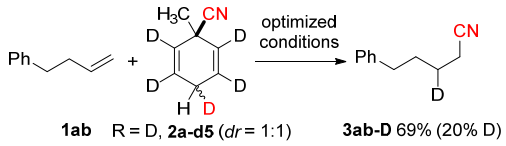
Also a crude GC analysis was performed to detect the *toluene-d3*. This result indicated that the H-atom, which gets transferred to the alkene/alkyne is derived from the methylene group and not from the α-CH_3-group in **2-*d3***.





1ab R = H, **2a-d1** (*dr* = 1:1) **3ab-D** 71% (20% D)

To a flame-dried screw-capped test tube equipped with a magnetic stir bar $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), was added inside the glove-box. To this, $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%) and DPEphos (21 mg, 40 µmol, 8.0 mol%) were added outside the glove-box followed by addition of 1,4-dioxane (3.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 1:1 cis/trans diastereoisomeric mixture of 1-methylcyclohexa-2,5-diene-1-carbonitrile-4-*d* **2a-*d*1** (90 mg, 0.75 mmol, 1.5 equiv) and but-3-en-1-ylbenzene **1ab** (75 µL, 0.50 mmol, 1.0 equiv) were added. The resulting mixture was then stirred at 100 °C for 20 h. Subsequently, the volatiles were removed under reduced pressure. The residue was purified by flash chromatography to obtain nitrile **3ab-d** (57 mg, 71% yield).

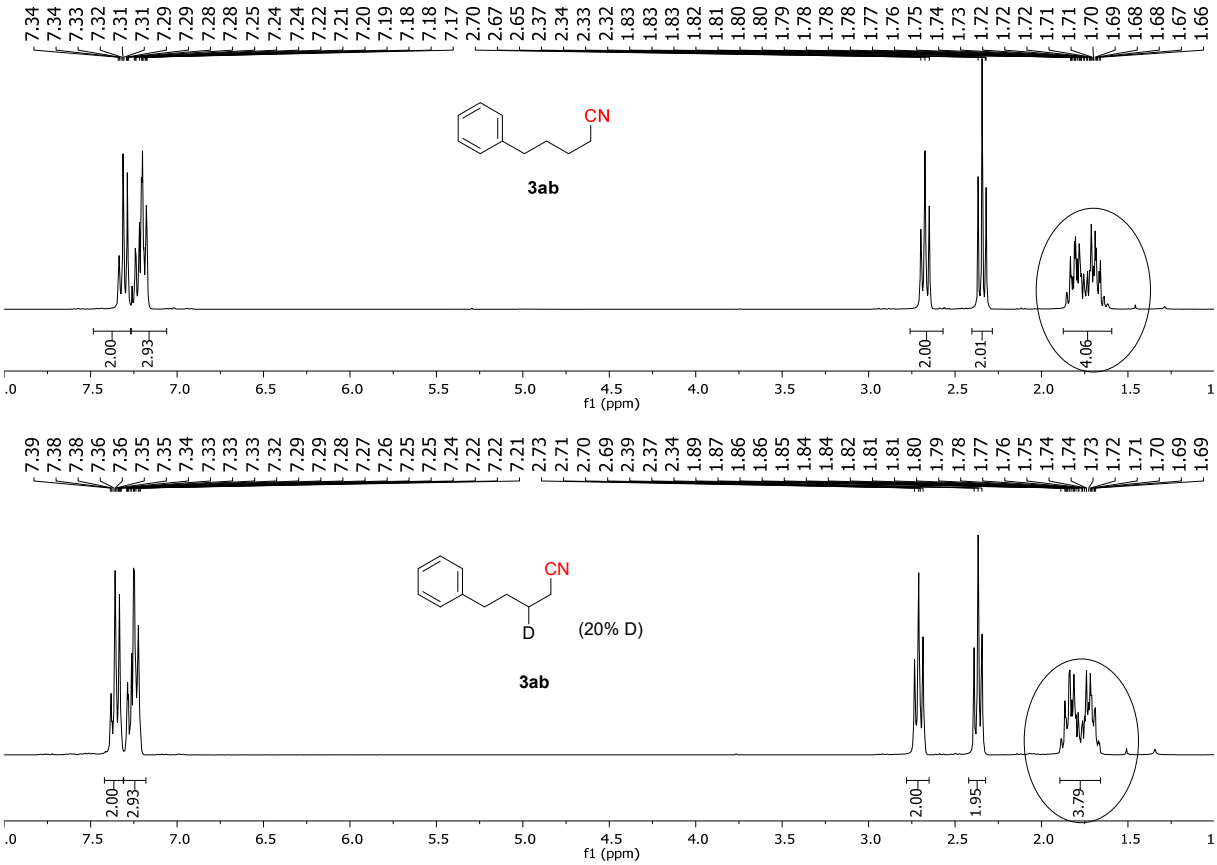


1ab R = D, **2a-d5** (*dr* = 1:1) **3ab-D** 69% (20% D)

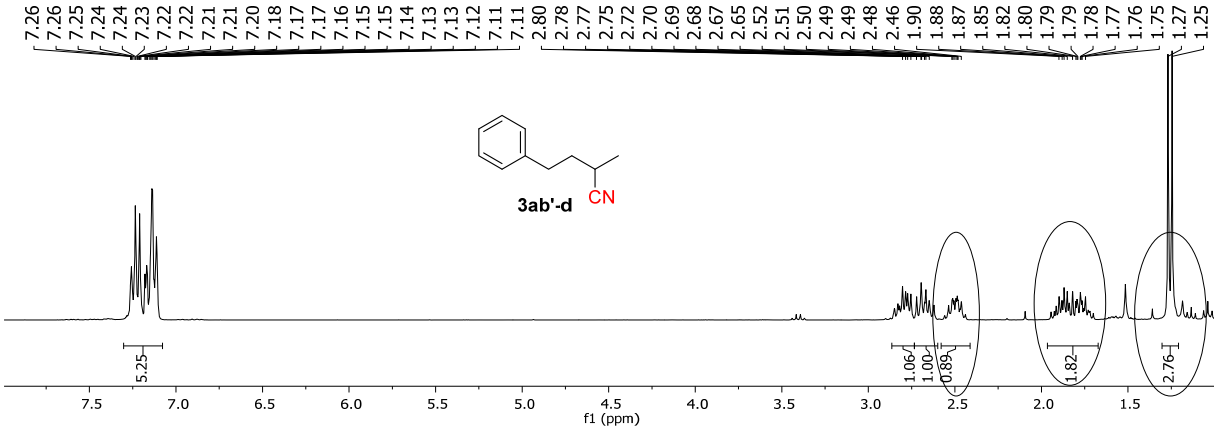
To a flame-dried screw-capped test tube equipped with a magnetic stir bar $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), was added inside the glove-box. To this, $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%) and DPEphos (21 mg, 40 µmol, 8.0 mol%) were added outside the glove-box followed by addition of 1,4-dioxane (3.0 mL) under a positive pressure of argon and the resultant reaction mixture was kept stirring at rt for 10 minutes. To this mixture, 1:1 cis/trans diastereoisomeric mixture of 1-methylcyclohexa-2,5-diene-1-carbonitrile-2,3,4,5,6-*d*5 **2a-*d*5** (93 mg, 0.75 mmol, 1.5 equiv) and but-3-en-1-ylbenzene **1ab** (75 µL, 0.50 mmol, 1.0 equiv) were added. The resulting mixture was then stirred at 100 °C for 20 h. Subsequently, the volatiles were removed under reduced pressure. The residue was purified by flash chromatography to obtain nitrile **3ab-d** (55 mg, 69 % yield) with 8% branched isomer. Also 12% (8.0 mg) deuterium incorporated isomerized alkenes isolated.

^{1}H-NMR analysis of the nitrile **3a** shows that the incorporation of deuterium (20%) at β-position.

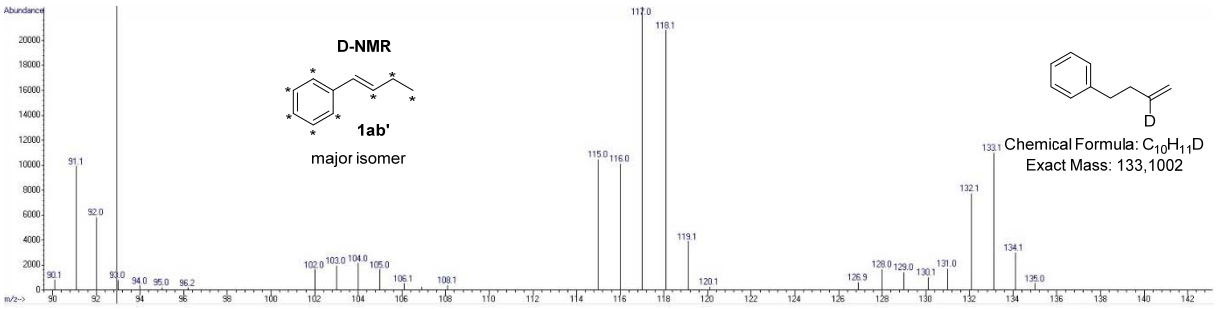
This result indicated that the H-atom, which gets transferred to the alkene/alkyne is derived from the methylene group in **2a-*d1*** or **2a-*d*5**. (Scheme 3, eq. 3 of the manuscript).



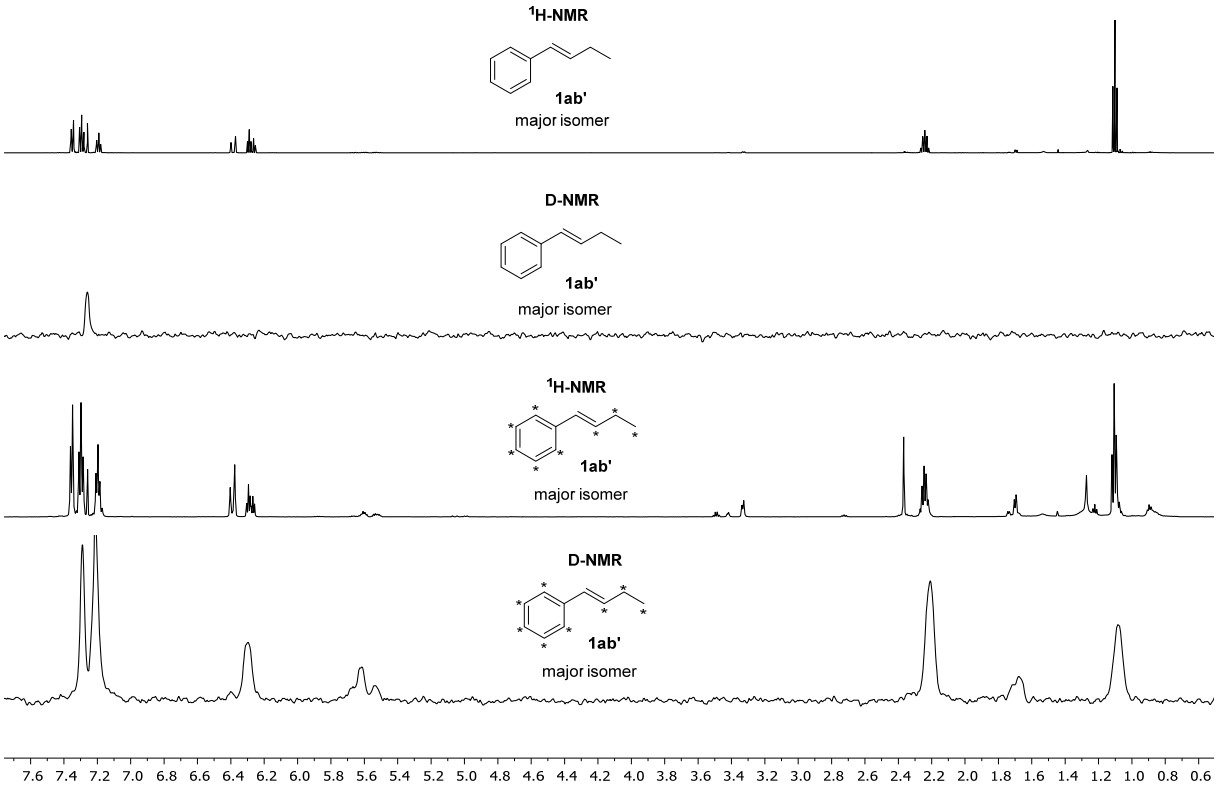
Deuterium incorporated branched isomer (**3ab'-d**)



Also a crude GCMS analysis was performed to detect the *D-alkenes.*

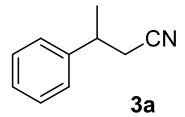


^{1}H-NMR analysis of the remaining alkenes



6. Synthesis and characterization of nitriles

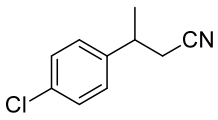
3-Phenylbutanenitrile (3a)



3a

The reaction was performed according to the **GP1** with BPh_3 (24 mg, 0.10 mmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and α-methylstyrene **1a** (65 µL, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 85:15) afforded 3-phenylbutanenitrile **3a** (65 mg, 89%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2H), 7.21 – 7.11 (m, 3H), 3.06 (t x q, $J_1 = J_2 = 7.0$ Hz, 1H), 2.65 – 2.29 (m, 2H), 1.35 (d, $J = 7.0$ Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.24, 128.90, 127.36, 126.60, 118.61, 36.57, 26.34, 20.71. **HRMS (ESI):** Exact mass calculated for $C_{10}H_{11}NNa^+$ [M+Na^+]: 168.0784, mass found: 168.0779. The spectral data are consistent with those reported in the literature.[2]

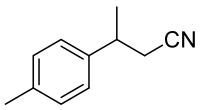
3-(4-Chlorophenyl)butanenitrile (3b)



3b

The reaction was performed according to the **GP1** with BPh_3 (24 mg, 0.10 mmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 1-chloro-4-(prop-1-en-2-yl)benzene **1b** (71 µL, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 85:15) afforded 3-(4-chlorophenyl)butanenitrile **3b** (72 mg, 80%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.21 – 7.15 (m, 2H), 3.15 (t x q, $J_1 = J_2 = 7.0$ Hz, 1H), 2.69 – 2.46 (m, 2H), 1.43 (d, $J = 7.0$ Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.55, 133.14, 129.03, 127.98, 118.19, 36.01, 26.30, 20.60. **HRMS (ESI):** Exact mass calculated for $C_{10}H_{10}ClNNa^+$ [M+Na^+]: 202.0394, mass found: 202.0401. The spectral data are consistent with those reported in the literature.[3]

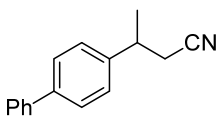
3-(*p*-Tolyl)butanenitrile (3c)



3c

The reaction was performed according to the **GP1** with BPh_3 (24 mg, 0.10 mmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 1-methyl-4-(prop-1-en-2-yl)benzene **1c** (73 µL, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 3-(*p*-tolyl)butanenitrile **3c** (69 mg, 86%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.24 – 7.11 (m, 4H), 3.14 (t x q, $J_1 = J_2 = 7.0$ Hz, 1H), 2.77 – 2.47 (m, 2H), 2.34 (s, 3H), 1.44 (d, $J = 7.0$ Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 140.31, 137.04, 129.62, 126.51, 118.75, 36.27, 26.55, 21.11, 20.85. **HRMS (ESI):** Exact mass calculated for $C_{11}H_{13}NNa^+$ [M+Na^+]: 182.0940, mass found: 182.0932. The spectral data are consistent with those reported in the literature.[3]

3-([1,1'-Biphenyl]-4-yl)butanenitrile (3d)

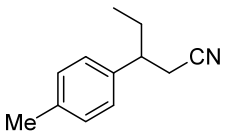


3d

The reaction was performed according to the **GP1** with BPh_3 (24 mg, 0.10 mmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 4-(prop-1-en-2-yl)-1,1'-biphenyl **1d** (97 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 3-([1,1'-biphenyl]-4-yl)butanenitrile **3d** as (102 mg, 92%) a white solid. **MP**: 75 °C **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 4H), 7.52 – 7.42 (m, 2H), 7.42 – 7.30 (m, 3H), 3.23 (t x q, $J_1 = J_2 = 7.0$ Hz, 1H), 2.85 – 2.45 (m, 2H), 1.51 (d, $J = 7.0$ Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 142.27, 140.72, 140.38, 128.89, 127.65, 127.44, 127.13, 127.08, 118.63, 36.30, 26.40, 20.77.

HRMS (ESI): Exact mass calculated for $C_{16}H_{15}NNa^+$ [M+Na$^+$]: 244.1097, mass found: 244.1100.

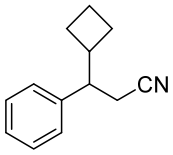
3-(*p*-Tolyl)pentanenitrile (3e)



3e

The reaction was performed according to the **GP1** with BPh_3 (24 mg, 0.10 mmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 1-(but-1-en-2-yl)-4-methylbenzene **1e** (73 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 3-(*p*-tolyl)pentanenitrile **3e** (70 mg, 81%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.25 – 6.96 (m, 4H), 2.88 – 2.78 (m, 1H), 2.68 – 2.49 (m, 2H), 2.36 (s, 3H), 1.96 – 1.64 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.71, 136.91, 129.52, 127.13, 118.75, 43.53, 28.03, 24.84, 21.04, 11.83. **HRMS (ESI):** Exact mass calculated for $C_{12}H_{15}NNa^+$ [M+Na$^+$]: 196.1097, mass found: 196.1097.

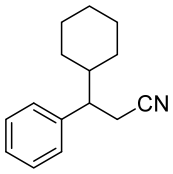
3-Cyclobutyl-3-phenylpropanenitrile (3f)



3f

The reaction was performed according to the **GP1** with BPh_3 (24 mg, 0.10 mmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and (1-cyclobutylvinyl)benzene **1f** (79 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 3-cyclobutyl-3-phenylpropanenitrile **3f** (81 mg, 87%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.28 – 7.09 (m, 5H), 2.83 – 2.75 (m, 1H), 2.69 – 2.53 (m, 1H), 2.54 – 2.33 (m, 2H), 2.26 – 2.04 (m, 1H), 1.89 – 1.63 (m, 4H), 1.58 – 1.44 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 140.39, 128.80, 127.50, 127.41, 118.67, 48.77, 39.94, 27.58, 26.94, 22.42, 17.50. **HRMS (ESI):** Exact mass calculated for $C_{13}H_{15}NNa^+$ [M+Na$^+$]: 208.1097, mass found: 208.1104.

3-Cyclohexyl-3-phenylpropanenitrile (3g)

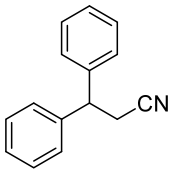


3g

The reaction was performed according to the **GP1** with BPh_3 (24 mg, 0.10 mmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and (1-cyclohexylvinyl)benzene **1g** (93 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 3-cyclohexyl-3-phenylpropanenitrile **3g** (83 mg, 78%) as a colorless oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.29 – 7.24 (m, 1H), 7.22 – 7.18 (m, 2H), 2.74 – 2.62 (m, 3H), 1.92 – 1.88 (m, 1H), 1.81 – 1.76 (m, 1H), 1.74 – 1.67 (m, 1H), 1.67 – 1.58 (m, 2H), 1.49 – 1.44 (m, 1H), 1.39 – 1.24 (m, 1H), 1.23 – 1.05 (m, 2H), 0.98 (tdd, J_1 = 3.7 Hz, J_2 = 11.4 Hz, J_3 = 12.6 Hz, 1H), 0.85 – 0.72 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.39, 128.72, 127.91, 127.29, 119.05, 48.23, 41.47, 31.12, 30.76, 26.25, 26.23, 26.15, 22.05. **HRMS (ESI):** Exact mass calculated for $C_{15}H_{19}NNa^+$ [M+Na$^+$]: 236.1410, mass found: 236.1407.

3,3-Diphenylpropanenitrile (3h)

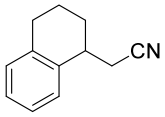
The reaction was performed according to the **GP1** with BPh_3 (24 mg, 0.10 mmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and ethene-1,1-diyldibenzene **1h** (88 µL, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 3,3-diphenylpropanenitrile **3h** (61 mg, 59%) as white solid. **MP**: 76 °C.



3h

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 4H), 7.32 – 7.27 (m, 2H), 7.27 – 7.24 (m, 4H), 4.39 (t, *J* = 7.7 Hz, 1H), 3.04 (d, *J* = 7.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.33, 128.99, 127.64, 127.49, 118.51, 47.24, 24.32. **HRMS (ESI):** Exact mass calculated for $C_{15}H_{13}NNa^+$ [M+Na^+]: 230.0940, mass found: 230.0943. The spectral data are consistent with those reported in the literature.[4]

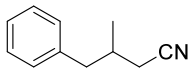
2-(1,2,3,4-Tetrahydronaphthalen-1-yl)acetonitrile (3i)



3i

The reaction was performed according to the **GP1** with BPh_3 (48 mg, 0.20 mmol, 20 mol%), $Pd(PPh_3)_4$ (46 mg, 40 µmol, 4.0 mol%), DPEphos (42 mg, 80 µmol, 8.0 mol%), nitrile **2a** (179 mg, 1.50 mmol, 1.5 equiv) and 1-methylene-1,2,3,4-tetrahydronaphthalene **1i** (144 mg, 1.00 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 2-(1,2,3,4-tetrahydronaphthalen-1-yl)acetonitrile **3i** (127 mg, 74%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.18 – 7.15 (m, 3H), 7.13 – 7.10 m, 1H), 3.26 – 3.18 (m, 1H), 2.95 – 2.47 (m, 4H), 2.13 – 2.03 (m, 1H), 1.98 – 1.73 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 137.26, 136.74, 129.67, 128.10, 126.97, 126.25, 118.98, 34.86, 29.42, 28.22, 24.84, 19.54. **HRMS (ESI):** Exact mass calculated for $C_{12}H_{13}NNa^+$ [M+Na^+]: 194.0940, mass found: 194.0939. The spectral data are consistent with those reported in the literature.[5]

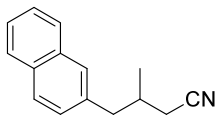
3-Methyl-4-phenylbutanenitrile (3j)



3j

The reaction was performed according to the **GP1** with BPh_3 (24 mg, 0.10 mmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and (2-methylallyl)benzene **1j** (66 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 3-methyl-4-phenylbutanenitrile **3j** (68 mg, 86%) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 2H), 7.17 – 7.10 (m, 1H), 7.10 – 7.05 (m, 2H), 2.56 (d, *J* = 6.9 Hz, 2H), 2.36 – 1.84 (m, 3H), 1.02 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.02, 129.04, 128.61, 126.58, 118.62, 42.07, 32.52, 23.65, 19.44. **HRMS (ESI):** Exact mass calculated for $C_{11}H_{13}NNa^+$ [M+Na^+]: 182.0940, mass found: 182.0944. The spectral data are consistent with those reported in the literature.[6]

3-Methyl-4-(naphthalen-1-yl)butanenitrile (3k)

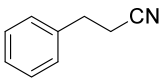


3k

The reaction was performed according to the **GP1** with BPh_3 (24 mg, 0.10 mmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 2-(2-methylallyl)naphthalene **1k** (96 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 3-methyl-4-(naphthalen-1-yl)butanenitrile **3k** (94 mg, 90%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 3H), 7.64 (s, 1H), 7.54 – 7.45 (m, 2H), 7.31 (dd, J_1 = 1.8 Hz, *J* = 8.4 Hz, 1H), 2.84 (d, *J* = 6.8 Hz, 2H), 2.34 – 2.20 (m, 3H), 1.17 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 136.55, 133.58, 132.34, 128.33, 127.70, 127.56, 127.55, 127.29, 126.25, 125.64, 118.65, 42.20, 32.45, 23.71, 19.53. **HRMS (ESI):** Exact mass calculated for $C_{15}H_{15}NNa^+$ [M+Na^+]: 232.1097, mass found: 232.1100.

3-Phenylpropanenitrile (3l)

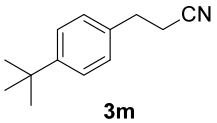
The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89



3l

mg, 0.75 mmol, 1.5 equiv) and styrene **1l** (57 µL, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3l** was determined by GC analysis (l/b: 90/10). Flash column chromatography (pentane:diethyl ether = 85:15) afforded 3-phenylpropanenitrile **3l** (linear product 53 mg, yield 80%; branched product: yield: 10% based on GC) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.21 (d, *J* = 7.0 Hz, 1H), 7.18 – 7.12 (m, 2H), 2.88 (t, *J* = 7.4 Hz, 2H), 2.54 (t, *J* = 7.4 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.10, 128.81, 128.24, 127.16, 119.15, 31.47, 19.21. **HRMS (ESI):** Exact mass calculated for $C_9H_9NNa^+$ [M+Na$^+$]: 154.0627, mass found: 154.0621. The spectral data are consistent with those reported in the literature.[4]
In a complementary Ni-catalyzed transfer hydrocyanation of styrene gave the product in 56% yield with 2:1 linear: branch selectivity.

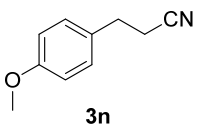
3-(4-(*tert*-Butyl)phenyl)propanenitrile (3m)



3m

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 1-(tert-butyl)-4-vinylbenzene **1m** (92 µL, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 85:15) afforded 3-(4-(*tert*-butyl)phenyl)propanenitrile **3m** (79 mg, 84%) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.10 – 7.07 (m, 2H), 2.85 (t, *J* = 7.4 Hz, 2H), 2.52 (t, *J* = 7.4 Hz, 2H), 1.24 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 150.28, 135.15, 128.05, 125.88, 119.39, 34.59, 31.44, 31.20, 19.42. **HRMS (ESI):** Exact mass calculated for $C_{13}H_{17}NNa^+$ [M+Na$^+$]: 210.1253, mass found: 210.1255. The spectral data are consistent with those reported in the literature.[7]

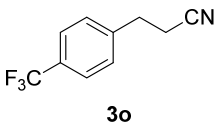
3-(4-Methoxyphenyl)propanenitrile (3n)



3n

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 1-methoxy-4-vinylbenzene **1n** (69 µL, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3n** was determined by GC analysis (l/b: 91/9). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 3-(4-methoxyphenyl)propanenitrile **3n** (linear product 64 mg, yield 79%; branched product: yield: 8% based on GC) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.18 – 7.13 (m, 2H), 6.90 – 6.85 (m, 2H), 3.80 (s, 3H), 2.89 (t, *J* = 7.3 Hz, 2H), 2.57 (t, *J* = 7.3 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 158.87, 130.25, 129.40, 119.31, 114.35, 55.36, 30.84, 19.71. **HRMS (ESI):** Exact mass calculated for $C_{10}H_{11}NONa^+$ [M+Na$^+$]: 184.0733, mass found: 184.0733. The spectral data are consistent with those reported in the literature.[7]

3-(4-(Trifluoromethyl)phenyl)propanenitrile (3o)

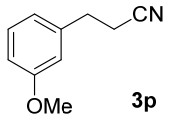


3o

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 1-(trifluoromethyl)-4-vinylbenzene **1o** (74 µL, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3o** was determined by GC analysis (l/b: 90/10). Flash column chromatography (pentane:diethyl ether = 70:30) afforded 3-(4-(trifluoromethyl)phenyl)propanenitrile **3o** (linear product 85 mg, yield 85%; branched product: 9 mg, yield: 9%) as a yellow oil. Linear product: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 3.01 (t, *J* = 7.3 Hz, 2H), 2.66 (d, *J* = 7.3 Hz, 2H). **^{13}C**

NMR (75 MHz, $CDCl_3$) δ 142.08 (q, *J* = 1.5 Hz), 125.90 (q, *J* = 3.7 Hz), 122.37 (q, *J* = 275.9 Hz), 120.45, 118.72, 115.41, 31.31, 19.04. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -62.74. **HRMS (ESI):** Exact mass calculated for $C_{10}H_8F_3NNa^+$ [M+Na^+]: 222.0501, mass found: 222.0500. The spectral data are consistent with those reported in the literature.[7]

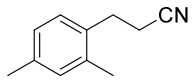
3-(3-Methoxyphenyl)propanenitrile (3p)



3p

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 1-methoxy-3-vinylbenzene **1p** (69 µL, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3p** was determined by GC analysis (l/b: 89/11). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 3-(3-methoxyphenyl)propanenitrile **3p** (linear product 59 mg, yield 73%; branched product: yield: 9% based on GC) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.9 Hz, 1H), 6.87 – 6.73 (m, 3H), 3.81 (s, 3H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.67 – 2.56 (t, *J* = 7.4 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 160.07, 139.72, 130.03, 120.60, 119.21, 114.23, 112.63, 55.33, 31.72, 19.34. **HRMS (ESI):** Exact mass calculated for $C_{10}H_{11}NONa^+$ [M+Na^+]: 184.0733, mass found: 184.0734. The spectral data are consistent with those reported in the literature.[8]

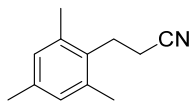
3-(2,4-Dimethylphenyl)propanenitrile (3q)



3q

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 2,4-dimethyl-1-vinylbenzene **1q** (73 µL, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 85:15) afforded 3-(2,4-dimethylphenyl)propanenitrile **3q** (72 mg, 90%) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.14 – 7.06 (m, 1H), 7.04 – 7.01 (m, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 136.86, 135.55, 133.27, 131.40, 128.67, 127.08, 119.28, 28.48, 20.89, 19.04, 18.09. **HRMS (ESI):** Exact mass calculated for $C_{11}H_{13}NNa^+$ [M+Na^+]: 182.0940, mass found: 182.0949.

3-Mesitylpropanenitrile (3r)

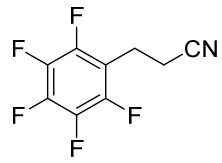


3r

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 1,3,5-trimethyl-2-vinylbenzene **1r** (73 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 85:15) afforded 3-mesitylpropanenitrile **3r** (65 mg, 75%) as yellow solid. **MP**: 87 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.89 (s, 2H), 3.03 (t, *J* = 8.3 Hz, 2H), 2.49 (t, *J* = 8.3 Hz, 2H), 2.34 (s, 6H), 2.28 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 136.65, 136.12, 131.97, 129.45, 119.44, 25.26, 20.88, 19.73, 16.79. **HRMS (ESI):** Exact mass calculated for $C_{12}H_{15}NNa^+$ [M+Na^+]: 196.1097, mass found: 196.1097. The spectral data are consistent with those reported in the literature.[7]

3-(Perfluorophenyl)propanenitrile (3s)

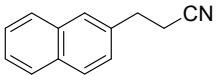
The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 1,2,3,4,5-pentafluoro-6-vinylbenzene **1s** (69 µL, 0.50 mmol, 1.0



3s

equiv). After cooling to room temperature, the regioselectivity of **3s** was determined by GC analysis (l/b: 92/8). Flash column chromatography (pentane:diethyl ether = 60:40) afforded 3-(perfluorophenyl)propanenitrile **3s** (linear product 86 mg, yield 78%; branched product: 9 mg, yield: 7%) as a yellow oil. Linear product: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.09 (m, 2H), 2.68 (t, J = 7.3 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.19 (dm, J = 251.2 Hz), 140.62 (dm, J = 253.7 Hz), 137.59 (dm, J = 253.7 Hz), 117.74, 111.10 (td, J_1 = 4.1 Hz, J_2 = 18.1 Hz), 18.85 (q, J = 1.8 Hz), 17.17 (d, J = 2.0 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$) δ -143.13 – -143.26 (m), -154.37 – -154.52 (m), -161.15 – -161.35 (m). **HRMS (ESI):** Exact mass calculated for $C_9H_4F_5NNa^+$ [M+Na^+]: 244.0156, mass found: 244.0157. The spectral data are consistent with those reported in the literature.[9]

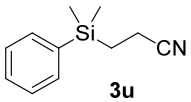
3-(Naphthalen-2-yl)propanenitrile (3t)



3t

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 2-vinylnaphthalene **1t** (77 mg, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3t** was determined by GC analysis (l/b: 90/10). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 3-(naphthalen-2-yl)propanenitrile **3t** (linear product 80 mg, yield 88%; branched product: 7 mg, yield: 7%) as a white solid. **MP**: 100 °C. Linear product: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 3H), 7.69 (s, 1H), 7.54 – 7.47 (m, 2H), 7.34 (dd, J_1 = 1.7 Hz, J_2 = 8.5 Hz, 1H), 3.11 (t, J = 7.4 Hz, 2H), 2.69 (t, J = 7.4 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 135.58, 133.60, 132.61, 128.74, 127.78, 127.73, 126.96, 126.45, 126.41, 126.01, 119.20, 31.79, 19.30. **HRMS (ESI):** Exact mass calculated for $C_{13}H_{11}NNa^+$ [M+Na^+]: 204.0784, mass found: 204.0788. The spectral data are consistent with those reported in the literature.[10]

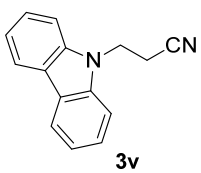
3-(Dimethyl(phenyl)silyl)propanenitrile (3u)



3u

The reaction was performed according to the **GP1** with BPh_3 (24.0 mg, 100 µmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and dimethyl(phenyl)(vinyl)silane **1u** (91 µL, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 3-(dimethyl(phenyl)silyl)propanenitrile **3u** (91 mg, 96%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54 – 7.46 (m, 2H), 7.46 – 7.36 (m, 3H), 2.41 – 2.17 (m, 2H), 1.50 – 0.94 (m, 2H), 0.38 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 136.67, 133.53, 129.61, 128.15, 121.13, 12.19, 11.97, -3.47. **HRMS (ESI):** Exact mass calculated for $C_{11}H_{15}NSiNa^+$ [M+Na^+]: 212.0866, mass found: 212.0864. The spectral data are consistent with those reported in the literature.[11]

3-(9*H*-Carbazol-9-yl)propanenitrile (3v)

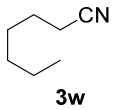


3v

The reaction was performed according to the **GP1** with BPh_3 (24.0 mg, 100 µmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 9-vinyl-9*H*-carbazole **1v** (97 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 3-(9*H*-carbazol-9-yl)propanenitrile **3v** (92 mg, 83%) as a white solid. **MP**: 157 °C **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.08 (d, J = 7.8 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.38 (d, J = 8.1 Hz, 2H),

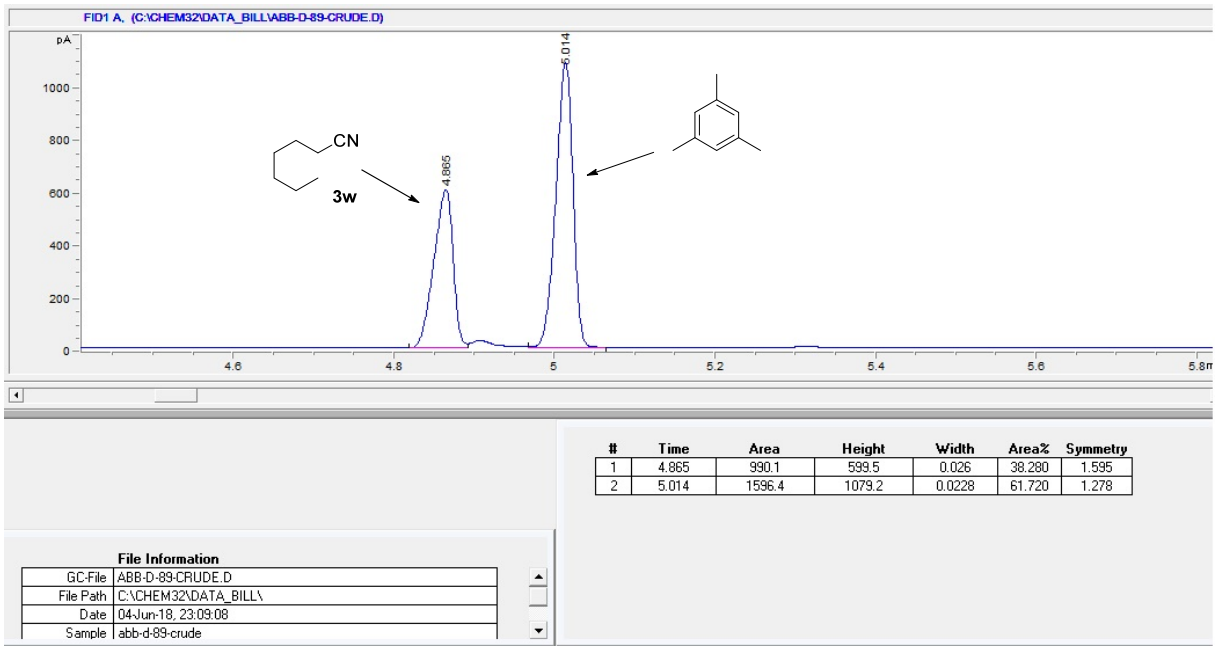
7.29 – 7.23 (m, 2H), 4.62 (t, *J* = 7.2 Hz, 2H), 2.81 (t, *J* = 7.2 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 139.68, 126.34, 123.54, 120.86, 120.12, 117.41, 108.28, 39.08, 17.40. **HRMS (ESI):** Exact mass calculated for $C_{15}H_{12}N_2Na^+$ [M+Na^+]: 243.0893, mass found: 243.0902. The spectral data are consistent with those reported in the literature.[4]

Heptanenitrile (3w)

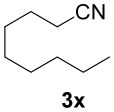


3w

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and hex-1-ene **1w** (63 µL, 0.50 mmol, 1.0 equiv). Subsequently, the reaction was cooled down to room temperature, and mesitylene (70 µL) as internal standard was added to the solution. After cooling to room temperature, the regioselectivity of heptanenitrile **3w** was determined by GC analysis (l/b: >99/1, GC yield 99%).

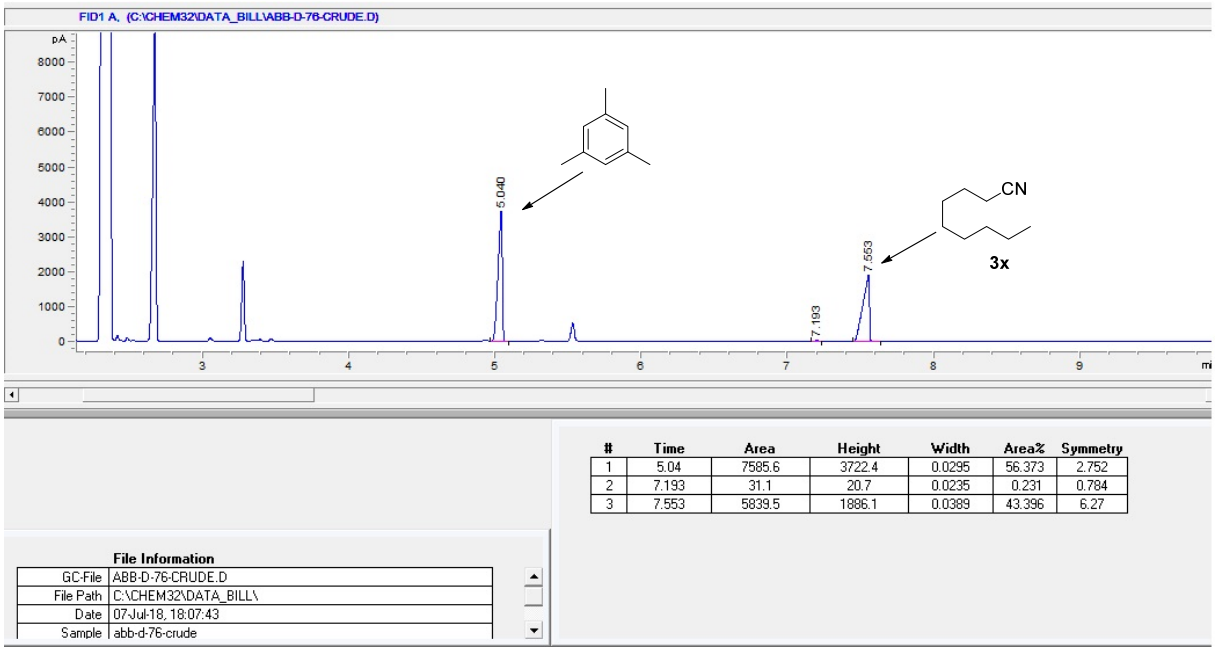


Nonanenitrile (3x)

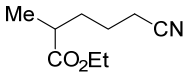


3x

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and oct-1-ene **1x** (78 µL, 0.50 mmol, 1.0 equiv). Subsequently, the reaction was cooled down to room temperature, and mesitylene (70 µL) as internal standard was added to the solution. After cooling to room temperature, the regioselectivity of nonanenitrile **3x** was determined by GC analysis (l/b: >99/1, GC yield 80%).



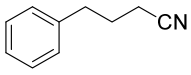
Ethyl 5-cyano-2-methylpentanoate (3y)



3y

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and ethyl 2-methylpent-4-enoate **1y** (82 µL, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3y** was determined by GC analysis (l/b: 85/15). Flash column chromatography (pentane:diethyl ether = 80:20) afforded ethyl 5-cyano-2-methylpentanoate **3y** (linear product 56 mg, yield 66%; branched product: yield: 12% based on GC) as a yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.08 (m, 2H), 2.45 – 2.35 (m, 1H), 2.35 – 2.25 (m, 2H), 1.77 – 1.67 (m, 1H), 1.65 – 1.58 (m, 2H), 1.56 – 1.49 (m, 1H), 1.20 (td, J_1 = 1.8 Hz, J_2 = 7.1 Hz, 3H), 1.12 (dd, J_1 = 1.8 Hz, J = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.77, 119.36, 60.37, 38.81, 32.49, 23.16, 17.07, 17.06, 14.18. **HRMS (ESI):** Exact mass calculated for $C_9H_{15}NO_2Na^+$ [M+Na^+]: 192.0995, mass found: 192.0996.

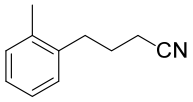
4-Phenylbutanenitrile (3z)



3z

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and allylbenzene **1z** (66 µL, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3z** was determined by GC analysis (l/b: 94/6). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 4-phenylbutanenitrile **3z** (linear product 60 mg, yield 83%; branched product: yield: 5% based on GC) as a yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.31 – 7.21 (m, 3H), 2.82 (t, J = 7.2 Hz, 2H), 2.34 (t, J = 7.2 Hz, 2H), 2.02 (t x t, J_1 = J_2 = 7.2 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.76, 128.65, 128.44, 126.48, 119.48, 34.36, 26.90, 16.34. **HRMS (ESI):** Exact mass calculated for $C_{10}H_{11}NNa^+$ [M+Na^+]: 168.0784, mass found: 168.0783. The spectral data are consistent with those reported in the literature.[13]

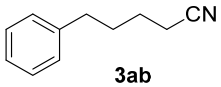
4-(o-Tolyl)butanenitrile (3aa)



3aa

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 1-allyl-2-methylbenzene **1aa** (74 µL, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3aa** was determined by GC analysis (l/b: 90/10). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 4-(o-tolyl)butanenitrile **3aa** (linear product 59 mg, yield 73%; branched product: yield: 8% based on GC) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.22 – 7.12 (m, 4H), 2.82 – 2.77 (m, 2H), 2.40 – 2.35 (m, 5H), 2.01 – 1.91 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.04, 135.96, 130.57, 128.96, 126.67, 126.21, 119.59, 31.90, 25.77, 19.22, 16.76. **HRMS (ESI):** Exact mass calculated for $C_{11}H_{13}NNa^+$ [M+Na^+]: 182.0940, mass found: 182.0923.

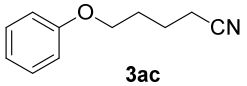
5-Phenylpentanenitrile (3ab)



3ab

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and but-3-en-1-ylbenzene **1ab** (75 µL, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3ab** was determined by GC analysis (l/b: 90/10). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 5-phenylpentanenitrile **3ab** (linear product 61 mg, yield 76%; branched product: yield: 8% based on GC) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.26 – 7.16 (m, 3H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.34 (t, *J* = 7.0 Hz, 2H), 1.89 – 1.59 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 141.30, 128.53, 128.42, 126.14, 119.65, 35.04, 30.30, 24.92, 17.09. **HRMS (ESI):** Exact mass calculated for $C_{11}H_{13}NNa^+$ [M+Na^+]: 182.0940, mass found: 182.0924. The spectral data are consistent with those reported in the literature.[9]

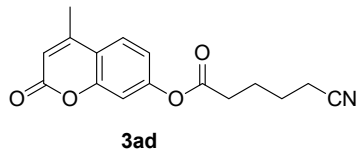
5-Phenoxypentanenitrile (3ac)



3ac

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and (but-3-en-1-yloxy)benzene **1ac** (74 mg, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3ac** was determined by GC analysis (l/b: 90/10). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 5-phenoxypentanenitrile **3ac** (linear product 68 mg, yield 78%; branched product: yield: 7% based on GC) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 2H), 6.91 – 6.84 (m, 1H), 6.84 – 6.78 (m, 2H), 3.93 (t, *J* = 5.6 Hz, 2H), 2.37 (t, *J* = 6.9 Hz, 2H), 2.11 – 1.66 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.84, 129.65, 121.05, 119.60, 114.59, 66.68, 28.36, 22.64, 17.13. **HRMS (ESI):** Exact mass calculated for $C_{11}H_{13}NONa^+$ [M+Na^+]: 198.0889, mass found: 198.0878.

4-Methyl-2-oxo-2*H*-chromen-7-yl 5-cyanopentanoate (3ad)

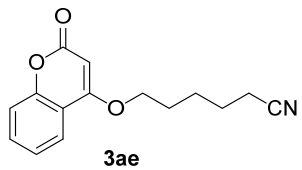


3ad

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 4-methyl-2-oxo-2*H*-chromen-7-yl pent-4-enoate **1ad** (129 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (diethyl ether) afforded 4-methyl-2-oxo-2*H*-chromen-7-yl 5-

cyanopentanoate **3ad** [linear product 122 mg, yield 86%; branched product: 11 mg, yield: 7%, (l/b: 92/8)] as a white solid. **MP**: 110 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.59 (m, 1H), 7.09 – 7.02 (m, 2H), 6.23 (s, 1H), 2.68 – 2.63 (m, 2H), 2.44 – 2.39 (m, 5H), 1.96 – 1.74 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.60, 160.38, 154.17, 152.93, 151.93, 125.47, 119.21, 117.95, 117.90, 114.53, 110.32, 33.32, 24.75, 23.68, 18.67, 17.01. **HRMS (ESI):** Exact mass calculated for $C_{16}H_{15}NO_4Na^+$ [M+Na^+]: 308.0893, mass found: 308.0897.

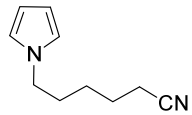
6-((2-Oxo-2*H*-chromen-4-yl)oxy)hexanenitrile (3ae)



3ae

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 4-(pent-4-en-1-yloxy)-2*H*-chromen-2-one **1ae** (115 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (diethyl ether) afforded 6-((2-oxo-2*H*-chromen-4-yl)oxy)hexanenitrile **3ae** [linear product 110 mg, yield 81%; branched product: 12 mg, yield: 9%, (l/b: 90/10)] as a white solid. **MP**: 134 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 – 7.73 (m, 1H), 7.51 – 7.47 (m, 1H), 7.28 – 7.18 (m, 2H), 5.61 (s, 1H), 4.12 – 4.09 (m, 2H), 2.41 – 2.38 (m, 2H), 1.95 – 1.89 (m, 2H), 1.78 – 1.64 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.51, 162.81, 153.24, 132.41, 123.92, 122.93, 119.46, 116.67, 115.59, 90.43, 68.78, 27.77, 25.20, 25.02, 17.09. **HRMS (ESI):** Exact mass calculated for $C_{15}H_{15}NO_3Na^+$ [M+Na^+]: 280.0944, mass found: 280.0951.

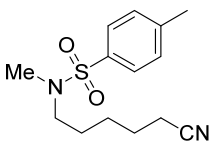
6-(1*H*-Pyrrol-1-yl)hexanenitrile (3af)



3af

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 1-(pent-4-en-1-yl)-1*H*-pyrrole **1af** (68 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 30:70) afforded 6-(1*H*-pyrrol-1-yl)hexanenitrile **3af** [linear product 56 mg, yield 69%; branched product: 6 mg, yield: 8%, (l/b: 90/10)] as yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.65 (t, *J* = 2.1 Hz, 2H), 6.16 (t, *J* = 2.1 Hz, 2H), 3.91 (t, *J* = 7.0 Hz, 2H), 2.33 (t, *J* = 7.1 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.72 – 1.60 (m, 2H), 1.51 – 1.39 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 120.43, 119.48, 108.16, 49.19, 30.81, 25.94, 25.06, 17.08. **HRMS (ESI):** Exact mass calculated for $C_{10}H_{14}N_2Na^+$ [M+Na^+]: 185.1049, mass found: 185.1049.

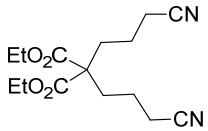
N-(5-Cyanopentyl)-N,4-dimethylbenzenesulfonamide (3ag)



3ag

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and *N*,4-dimethyl-*N*-(pent-4-en-1-yl)benzenesulfonamide **1ag** (127 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (diethyl ether) afforded *N*-(5-cyanopentyl)-*N*,4-dimethylbenzenesulfonamide **3ag** [linear product 109 mg, yield 77%; branched product: 12 mg, yield: 9%, (l/b: 90/10)] as yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 2.95 (t, *J* = 6.6 Hz, 2H), 2.67 (s, 3H), 2.39 (s, 3H), 2.34 – 2.29 (m, 2H), 1.71 – 1.60 (m, 2H), 1.59 – 1.43 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.38, 134.46, 129.70, 127.34, 119.60, 49.57, 34.70, 26.78, 25.50, 24.88, 21.45, 17.05. **HRMS (ESI):** Exact mass calculated for $C_{14}H_{20}N_2O_2SNa^+$ [M+Na^+]: 303.1138, mass found: 303.1141.

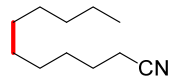
Diethyl 2,2-bis(3-cyanopropyl)malonate (3ah)



3ah

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (119 mg, 1.00 mmol, 2.0 equiv) and diethyl 2,2-diallylmalonate **1ah** (120 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 40:60) afforded diethyl 2,2-bis(3-cyanopropyl)malonate **3ah** (100 mg, yield 68%) as white solid. **MP**: 62 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.22 – 4.07 (m, 4H), 2.34 – 2.29 (m, 4H), 2.04 – 1.86 (m, 4H), 1.68 – 1.45 (m, 4H), 1.23 – 1.18 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.50, 119.03, 61.70, 56.66, 32.02, 20.64, 17.41, 14.04. **HRMS (ESI):** Exact mass calculated for $C_{15}H_{22}N_2O_4Na^+$ [M+Na^+]: 317.1472, mass found: 317.1485.

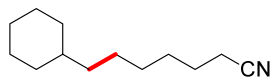
Undecanenitrile (3ai)



3ai

The reaction was performed according to the **GP3** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), Xantphos (23 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and *trans*-5-decene **1ai** (95 µL, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3ai** was determined by GC analysis (l/b: 86/14). Flash column chromatography (pentane:diethyl ether = 85:15) afforded undecanenitrile **3ai** (linear product 56 mg, yield 67%; branched products: yield: 8% based on GC) as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.31 (t, *J* = 7.1 Hz, 2H), 1.74 – 1.54 (m, 2H), 1.50 – 1.36 (m, 2H), 1.32 – 1.19 (m, 12H), 0.94 – 0.79 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 119.76, 31.83, 29.43, 29.28, 29.22, 28.73, 28.64, 25.38, 22.62, 17.07, 14.03. **HRMS (ESI):** Exact mass calculated for $C_{11}H_{21}NNa^+$ [M+Na^+]: 190.1566, mass found: 190.1569. The spectral data are consistent with those reported in the literature.[14]

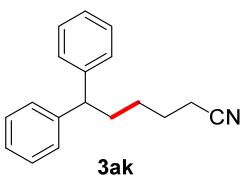
7-Cyclohexylheptanenitrile (3aj)



3aj

The reaction was performed according to the **GP3** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), Xantphos (23 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and *(E)*-hex-1-en-1-ylcyclohexane **1aj** (83 mg, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3aj** was determined by GC analysis (l/b: 78/22). Flash column chromatography (pentane:diethyl ether = 80:20) afforded 7-cyclohexylheptanenitrile **3aj** (linear product 56 mg, yield 58%; branched products 17 mg, yield: 15%) as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.32 (t, *J* = 7.1 Hz, 2H), 1.81 – 1.56 (m, 7H), 1.50 – 1.38 (m, 2H), 1.33 – 1.08 (m, 10H), 0.98 – 0.75 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 119.80, 37.62, 37.32, 33.42, 29.07, 28.68, 26.73, 26.51, 26.42, 25.39, 17.11. **HRMS (ESI):** Exact mass calculated for $C_{13}H_{23}NNa^+$ [M+Na^+]: 216.1723, mass found: 216.1731.

6,6-Diphenylhexanenitrile (3ak)

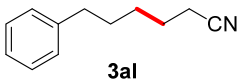


3ak

The reaction was performed according to the **GP3** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), Xantphos (23 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and *(E)*-pent-2-ene-1,1-diyldibenzene **1ak** (111 mg, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3ak** was determined by GC analysis (l/b: 82/18). Flash column chromatography (pentane:diethyl ether = 60:40) afforded 6,6-diphenylhexanenitrile **3ak** (linear product 79 mg, yield 63%; branched

products 17 mg, yield: 14%) as colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 6.70 (m, 10H), 3.96 (t, *J* = 7.8 Hz, 1H), 2.30 (t, *J* = 7.2 Hz, 2H), 2.13 (d x t, $J_1 = J_2$ = 7.9 Hz, 2H), 1.72 (p, *J* = 7.4 Hz, 2H), 1.50 – 1.44 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.66, 128.58, 127.78, 126.33, 119.71, 51.17, 34.90, 27.26, 25.46, 17.04. **HRMS (ESI):** Exact mass calculated for $C_{18}H_{19}NNa^+$ [M+Na^+]: 272.1410, mass found: 272.1414.

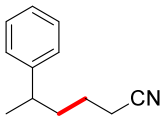
6-Phenylhexanenitrile (3al)



3al

The reaction was performed according to the **GP3** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), Xantphos (23 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and *(E)*-pent-3-en-1-ylbenzene **1al** (73 mg, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3al** was determined by GC analysis (l/b: 84/16). Flash column chromatography (pentane:diethyl ether = 70:30) afforded 6-phenylhexanenitrile **3al** (linear product 49 mg, yield 57%; branched products 9 mg, yield: 10%) as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37 – 7.21 (m, 5H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.36 (t, *J* = 7.1 Hz, 2H), 1.77 – 1.66 (m, 4H), 1.59 – 1.48 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 142.06, 128.43, 128.41, 125.92, 119.75, 35.63, 30.63, 28.32, 25.36, 17.11. **HRMS (ESI):** Exact mass calculated for $C_{12}H_{15}NNa^+$ [M+Na^+]: 196.1097, mass found: 196.1100. The spectral data are consistent with those reported in the literature.[15]

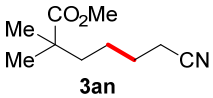
5-Phenylhexanenitrile (3am)



3am

The reaction was performed according to the **GP3** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), Xantphos (23 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and *(E)*- pent-3-en-2-ylbenzene **1am** (73 mg, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3am** was determined by GC analysis (l/b: 80/20). Flash column chromatography (pentane:diethyl ether = 70:30) afforded 5-phenylhexanenitrile **3am** (linear product 49 mg, yield 56%; branched products 12 mg, yield: 14%) as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.24 – 7.07 (m, 5H), 2.86 – 2.57 (m, 1H), 2.20 – 2.12 (m, 2H), 1.68 – 1.57 (m, 2H), 1.56 – 1.35 (m, 2H), 1.19 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 146.32, 128.61, 126.93, 126.33, 119.67, 39.49, 37.17, 23.65, 22.40, 17.20. **HRMS (ESI):** Exact mass calculated for $C_{12}H_{15}NNa^+$ [M+Na^+]: 196.1097, mass found: 196.1098. The spectral data are consistent with those reported in the literature.[15]

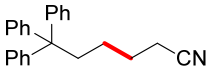
Methyl 6-cyano-2,2-dimethylhexanoate (3an)



3an

The reaction was performed according to the **GP3** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), Xantphos (23 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and methyl *(E)*-2,2-dimethylhex-4-enoate **1an** (78 mg, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3an** was determined by GC analysis (l/b: 85/15). Flash column chromatography (pentane:diethyl ether = 60:40) afforded methyl 6-cyano-2,2-dimethylhexanoate **3an** (linear product 53 mg, yield 58%; branched products 9 mg, yield: 10%) as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.64 (s, 3H), 2.32 (t, *J* = 7.1 Hz, 2H), 1.69 – 1.49 (m, 4H), 1.43 – 1.29 (m, 2H), 1.15 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 178.13, 119.60, 51.82, 42.21, 39.72, 25.81, 25.21, 24.23, 17.04. **HRMS (ESI):** Exact mass calculated for $C_{10}H_{17}NO_2Na^+$ [M+Na^+]: 206.1151, mass found: 206.1174.

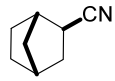
6,6,6-Triphenylhexanenitrile (3ao)



3ao

The reaction was performed according to the **GP3** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), Xantphos (23 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and *(E)*- pent-3-ene-1,1,1-triyltribenzene **1ao** (149 mg, 0.50 mmol, 1.0 equiv). After cooling to room temperature, the regioselectivity of **3ao** was determined by GC analysis (l/b: 90/10). Flash column chromatography (pentane:diethyl ether = 60:40) afforded 6,6,6-triphenylhexanenitrile **3ao** (linear product 116 mg, yield 71%; branched products 13 mg, yield: 8%) as white solid. **MP**: 90 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 12H), 7.11 – 7.05 (m, 3H), 2.52 – 2.47 (m, 2H), 2.09 (t, *J* = 7.3 Hz, 2H), 1.53 (p, *J* = 7.4 Hz, 2H), 1.19 – 1.09 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 147.14, 129.17, 128.00, 126.08, 119.61, 56.62, 39.77, 26.26, 25.22, 17.11. **HRMS (ESI):** Exact mass calculated for $C_{24}H_{23}NNa^+$ [M+Na^+]: 348.1723, mass found: 348.1722.

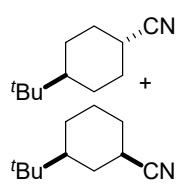
Bicyclo[2.2.1]heptane-2-carbonitrile (3ap)



3ap

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and norbornene **1ap** (47 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 90:10) afforded bicyclo[2.2.1]heptane-2-carbonitrile **3ap** (38 mg, 63%, *dr* > 20:1) as a colorless oil. The *dr* was determined by ^{1}H NMR analysis. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 2.58 (bs, 1H), 2.45 – 2.27 (m, 2H), 1.83 – 1.75 (m, 1H), 1.72 – 1.67 (m, 1H), 1.64 – 1.49 (m, 3H), 1.39 – 1.33 (m, 1H), 1.25 – 1.13 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 123.60, 41.89, 37.25, 36.18, 36.11, 31.16, 28.58, 28.46. **HRMS (ESI):** Exact mass calculated for $C_8H_{11}NNa^+$ [M+Na^+]: 144.0784, mass found: 144.0781. The spectral data are consistent with those reported in the literature.[4]

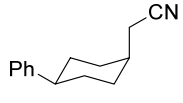
4-(*tert*-Butyl)cyclohexane-1-carbonitrile (3aq) & 3-(*tert*-butyl)cyclohexane-1-carbonitrile (3aq')



3aq

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 4-(*tert*-butyl)cyclohex-1-ene **1aq** (69 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 90:10) afforded 4-(*tert*-butyl)cyclohexane-1-carbonitrile **3aq** & 3-(*tert*-Butyl)cyclohexane-1-carbonitrile **3aq'** (inseparable 2:1 regioisomeric mixture based on ^{1}H NMR, 75 mg, 91%) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.42 – 2.23 (m, 1H), 2.16 – 1.98 (m, 2H), 1.92 – 1.64 (m, 2H), 1.58 – 1.31 (m, 2H), 1.27 – 1.10 (m, 1H), 1.07 – 0.86 (m, 2H), 0.83 – 0.80 (m, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 122.95, 122.88, 47.05, 46.76, 32.53, 32.37, 31.25, 30.45, 29.89, 28.93, 28.33, 27.31, 27.30, 26.21, 26.07, 25.49. **HRMS (ESI):** Exact mass calculated for $C_{11}H_{19}NNa^+$ [M+Na^+]: 188.1410, mass found: 188.1416. The spectral data are consistent with those reported in the literature.[12]

2-(4-Phenylcyclohexyl)acetonitrile (3ar)

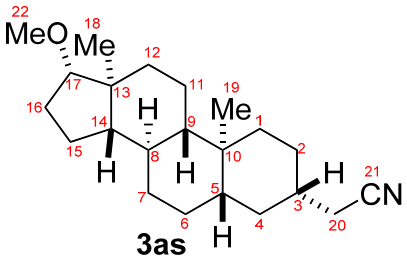


3ar

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and (4-methylenecyclohexyl)benzene **1ar** (86 mg, 0.50 mmol, 1.0 equiv). Flash

column chromatography (pentane:diethyl ether = 70:30) afforded 2-(4-phenylcyclohexyl)acetonitrile **3ar** (84 mg, 84%, *dr* > 20:1) as white solid. **MP**: 67 °C. The assignment of the isomers is based on NOESY NMR experiments (see spectral data). The *dr* was determined by ^{1}H NMR analysis. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.25 – 7.20 (m, 3H), 2.51 (tt, J_1 = 3.3 Hz, J_2 = 12.2 Hz, 1H), 2.32 (d, J = 6.5 Hz, 2H), 2.10 – 1.93 (m, 4H), 1.80 – 1.74 (m, 1H), 1.61 – 1.47 (m, 2H), 1.42 – 1.22 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 146.65, 128.42, 126.77, 126.15, 118.79, 43.64, 34.46, 33.49, 32.62, 24.64. **HRMS (ESI):** Exact mass calculated for $C_{14}H_{17}NNa^+$ [M+Na^+]: 222.1253, mass found: 222.1258.

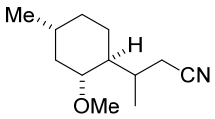
2-((5S,8R,10S,13S,14S,17S)-17-Methoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)acetonitrile (3as)



3as

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and (5S,8R,9S,10S,13S,14S,17S)-17-methoxy-10,13-dimethyl-3-methylenehexadecahydro-1*H*-cyclopenta[*a*]phenanthrene **1as** (151 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 60:40) afforded compound **2**-((5S,8R,10S,13S,14S,17S)-17-methoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)acetonitrile **3as** (148 mg, 90%, *dr* > 20:1) as white solid. **MP**: 169 °C. The *dr* was determined by ^{1}H NMR analysis. The assignment of the isomers is based on NMR experiments (see spectral data). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.31 (s, 3H), 3.20 – 3.17 (m, 1H), 2.29 – 2.21 (m, 2H), 2.00 – 1.93 (m, 1H), 1.91 – 1.85 (m, 1H), 1.72 (dt, J_1 = 3.3 Hz, J_2 = 13.1 Hz, 1H), 1.65 – 1.62 (m, 3H), 1.58 – 1.48 (m, 2H), 1.40 – 1.32 (m, 3H), 1.31 – 1.04 (m, 8H), 0.97 – 0.91 (m, 2H), 0.87 – 0.80 (m, 1H), 0.75 (s, 3H), 0.71 (s, 3H), 0.66 – 0.61 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 119.01 (CN), 90.94 (C17), 57.94 (C22), 54.61 (C9), 51.41 (C14), 46.36 (C5), 43.06 (C13), 38.18 (C12), 38.11 (C1), 35.88 (C10), 35.40 (C8), 35.23 (C3), 34.78 (C4), 31.64 (C7), 28.64 (C6), 28.17 (C2), 27.79 (C16), 24.69 (C20), 23.40 (C15), 20.82 (C11), 12.37 (C19), 11.75 (18). **HRMS (ESI):** Exact mass calculated for $C_{22}H_{35}NONa^+$ [M+Na^+]: 222.1253, mass found: 222.1258.

3-((1S,2R,4R)-2-Methoxy-4-methylcyclohexyl)butanenitrile (3at)

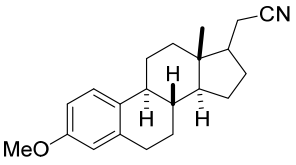


3at

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and (1S,2R,4R)-2-methoxy-4-methyl-1-(prop-1-en-2-yl)cyclohexane **1at** (84 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 70:30) afforded 3-((1S,2R,4R)-2-methoxy-4-methylcyclohexyl)butanenitrile **3at** (major isomer 57 mg, yield 58% and minor isomer 19 mg, yield 20%; *dr* = 3:1) as colorless liquid. The *dr* was determined by ^{1}H NMR analysis. **Major isomer**: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.30 (s, 3H), 2.97 (td, J_1 = 4.1 Hz, J_2 = 10.5, 1H), 2.44 (dd, J_1 = 6.1 Hz, J_2 = 16.5 Hz, 1H), 2.36 – 2.08 (m, 3H), 1.69 – 1.57 (m, 2H), 1.45 – 1.25 (m, 2H), 1.19 – 1.01 (m, 4H), 1.00 – 0.86 (m, 4H), 0.84 – 0.72 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 120.29, 80.05, 55.39, 46.64, 39.13, 34.42, 32.02, 31.13, 27.10, 22.16, 22.13, 16.31. **Minor isomer**: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.30 (s, 3H), 2.91 (td, J_1 = 4.2 Hz, J_2 = 10.6 Hz, 1H), 2.46 – 2.40 (m, 1H), 2.30 – 2.21 (m, 2H), 2.15 – 2.11 (m, 1H), 1.67 – 1.63 (m, 1H), 1.55 – 1.51 (m, 1H), 1.40 – 1.31 (m, 2H), 1.02 (qd, J_1 =

3.6 Hz, J_2 = 12.9 Hz, 1H), 0.95 – 0.89 (m, 6H), 0.88 – 0.78 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 119.58, 80.14, 55.84, 46.34, 39.33, 34.24, 31.28, 29.58, 23.95, 23.27, 22.23, 14.28. **HRMS (ESI):** Exact mass calculated for $C_{12}H_{21}NONa^+$ [M+Na^+]: 218.1515, mass found: 218.1524.

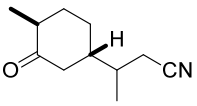
2-((8S,9S,13R,14S)-3-Methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)acetonitrile (3au)



3au

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and (8S,9S,13S,14S)-3-methoxy-13-methyl-17-methylene-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthrene **1au** (141 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 60:40) afforded 2-((8S,9S,13R,14S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-17-yl)acetonitrile **3au** (113 mg, 73%, *dr* = 5:1, inseparable mixture) as white solid. **MP**: 143 °C. The *dr* was determined by ^{1}H NMR analysis. **^{1}H NMR** (300 MHz, $CDCl_3$) both isomers δ: 7.20 (d, J = 8.6 Hz, 1H), 6.72 (dd, J_1 = 2.8 Hz, J_2 = 8.6 Hz, 1H), 6.64 (d, J = 2.8 Hz, 1H), 3.78 (s, 3H), 3.02 – 2.63 (m, 2H), 2.60 – 1.72 (m, 9H), 1.65 – 1.08 (m, 7H), 0.87 (s, 0.5H), 0.68 (s, 2.5H). **^{13}C NMR** (75 MHz, $CDCl_3$) major isomer δ: 157.63, 137.97, 132.54, 126.35, 119.82, 113.95, 111.59, 55.29, 46.88, 43.94, 43.69, 42.72, 38.94, 37.50, 29.87, 28.40, 27.81, 26.38, 24.07, 20.54, 12.35. **^{13}C NMR** (75 MHz, $CDCl_3$) minor isomer δ: 157.65, 132.40, 126.37, 120.31, 113.93, 111.63, 54.53, 49.54, 45.03, 43.57, 39.18, 33.95, 29.94, 28.67, 28.26, 26.44, 25.32, 20.62, 17.71. **HRMS (ESI):** Exact mass calculated for $C_{21}H_{27}NONa^+$ [M+Na^+]: 332.1985, mass found: 332.1966.

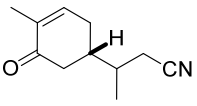
3-((1S,4S)-4-Methyl-3-oxocyclohexyl)butanenitrile (3av)



3av

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and (2S,5S)-2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-one **1av** (76 mg, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 60:40) afforded 3-((1S,4S)-4-methyl-3-oxocyclohexyl)butanenitrile **3av** (59 mg, 66%, *dr* = 1:1, inseparable mixture) as colorless liquid. The starting material (+)-dihydrocarvone was a 10:1 isomeric mixture and the major isomer is *trans.* In the transfer hydrocyantion we observed four inseperable isomeric nitrile with ratio of 10:10:1:1. The *dr* was determined by ^{1}H NMR analysis. **^{1}H NMR** (500 MHz, $CDCl_3$) both isomers δ 2.46 – 2.18 (m, 4H), 2.16 – 1.94 (m, 2H), 1.91 – 1.61 (m, 3H), 1.52 – 1.35 (m, 1H), 1.35 – 1.22 (m, 1H), 1.07 – 1.03 (m, 3H), 1.02 – 0.96 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) both isomers δ 211.56, 211.39, 118.62, 77.59, 77.16, 76.74, 45.53, 44.77, 44.71, 44.22, 43.78, 43.75, 35.30, 35.22, 34.39, 34.36, 29.37, 27.75, 22.30, 22.20, 16.30, 16.27, 14.24. **HRMS (ESI):** Exact mass calculated for $C_{11}H_{17}NONa^+$ [M+Na^+]: 202.1202, mass found: 202.1205.

3-((S)-4-Methyl-5-oxocyclohex-3-en-1-yl)butanenitrile (3aw)

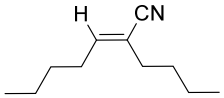


3aw

The reaction was performed according to the **GP2** with $B(C_6F_5)_3$ (39 mg, 75 µmol, 15 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and (S)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-one **1aw** (75 mg, 0.50 mmol, 1.0

equiv). Flash column chromatography (pentane:diethyl ether = 60:40) afforded 3-((S)-4-methyl-5-oxocyclohex-3-en-1-yl)butanenitrile **3aw** (67 mg, 75%, *dr* = 1:1, inseparable mixture) as colorless liquid. The *dr* was determined by ^{1}H NMR analysis. **^{1}H NMR** (400 MHz, $CDCl_3$) both isomers δ 6.69 – 6.66 (m, 1H), 2.48 – 2.21 (m, 4H), 2.17 – 1.94 (m, 3H), 1.87 – 1.75 (m, 1H), 1.70 – 1.68 m, 3H), 1.06 – 1.02 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) both isomers δ 198.77, 198.65, 144.13, 144.02, 135.60, 135.55, 118.43, 118.40, 42.02, 40.82, 39.30, 39.21, 34.35, 34.28, 29.99, 28.67, 22.14, 22.10, 16.46, 16.36, 15.55, 15.54. **HRMS (ESI):** Exact mass calculated for $C_{11}H_{15}NONa^+$ [M+Na^+]: 200.1046, mass found: 200.1056.

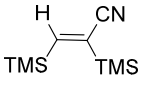
(*E*)-2-Butylhept-2-enenitrile (5a)



5a

The reaction was performed according to the **GP1** with BPh_3 (24 mg, 0.10 mmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 5-decyne **4a** (90 µL, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 50:1) afforded (*E*)-2-butylhept-2-enenitrile **5a** (72 mg, 87%, 96:4 *E/Z* inseparable mixture) as colorless liquid. The *E/Z* was determined by ^{1}H NMR analysis. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.53 – 6.14 (m, 1H), 2.16 (dt, J_1 = 7.3 Hz, J_2 = 11.5 Hz, 4H), 1.63 – 1.23 (m, 8H), 0.90 (td, J_1 = 5.4 Hz, J_2 = 7.2 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 148.14, 120.30, 115.04, 30.66, 30.22, 28.27, 28.23, 22.35, 22.09, 13.85, 13.83. **HRMS (ESI):** Exact mass calculated for $C_{11}H_{19}NNa^+$ [M+Na^+]: 188.1410, mass found: 188.1412.

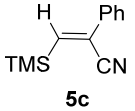
(*Z*)-2,3-Bis(trimethylsilyl)acrylonitrile (5b)



5b

The reaction was performed according to the **GP1** with BPh_3 (24 mg, 0.10 mmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and 1,2-bis(trimethylsilyl)ethyne **4b** (113 µL, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 50:1) afforded (*Z*)-2,3-bis(trimethylsilyl)acrylonitrile **5b** (33 mg, 33%) as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.58 (s, 1H), 0.31 (s, 9H), 0.21 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 170.57, 133.19, 121.77, 0.09, -0.07. **HRMS (ESI):** Exact mass calculated for $C_9H_{19}NSi_2Na^+$ [M+Na^+]: 220.0948, mass found: 220.0965.

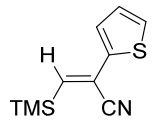
(*Z*)-2-Phenyl-3-(trimethylsilyl)acrylonitrile (5c)



5c

The reaction was performed according to the **GP1** with BPh_3 (24 mg, 0.10 mmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and trimethyl(phenylethynyl)silane **4c** (98 µL, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 50:1) afforded major regiosiomer (*Z*)-2-phenyl-3-(trimethylsilyl)acrylonitrile **5c** (62 mg, 62%) as colorless liquid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 5H), 6.88 (s, 1H), 0.02 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 152.83, 136.03, 130.02, 129.65, 129.11, 128.85, 119.97, 0.00. Also minor regioisomer (*E*)-3-phenyl-2-(trimethylsilyl)acrylonitrile isolated in 15% yiled (15 mg) **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.69 – 7.56 (m, 2H), 7.46 – 7.36 (m, 3H), 7.10 (s, 1H), 0.34 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 147.71, 135.12, 129.69, 129.00, 127.97, 125.76, 118.06, -1.27. The spectral data are consistent with those reported in the literature.[4] **HRMS (ESI):** Exact mass calculated for $C_{12}H_{15}NSiNa^+$ [M+Na^+]: 224.0866, mass found: 224.0869.

(*Z*)-2-(Thiophen-2-yl)-3-(trimethylsilyl)acrylonitrile (5d)



5d

The reaction was performed according to the **GP1** with BPh_3 (24 mg, 0.10 mmol, 20 mol%), $Pd(PPh_3)_4$ (23 mg, 20 µmol, 4.0 mol%), DPEphos (21 mg, 40 µmol, 8.0 mol%), nitrile **2a** (89 mg, 0.75 mmol, 1.5 equiv) and trimethyl(thiophen-2-ylethynyl)silane **4d** (83 µL, 0.50 mmol, 1.0 equiv). Flash column chromatography (pentane:diethyl ether = 50:1) afforded compound (*Z*)-2-(thiophen-2-yl)-3-(trimethylsilyl)acrylonitrile **5d** (75 mg, 72%) as colorless liquid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.03 (dd, J_1 = 3.7 Hz, J_2 = 5.1 Hz, 1H), 6.81 (s, 1H), 0.32 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.99, 141.21, 128.17, 127.19, 127.18, 121.72, 116.93, -1.22. **HRMS (ESI):** Exact mass calculated for $C_{10}H_{13}NSSiNa^+$ [$M+Na^+$]: 230.0430, mass found: 230.0440.

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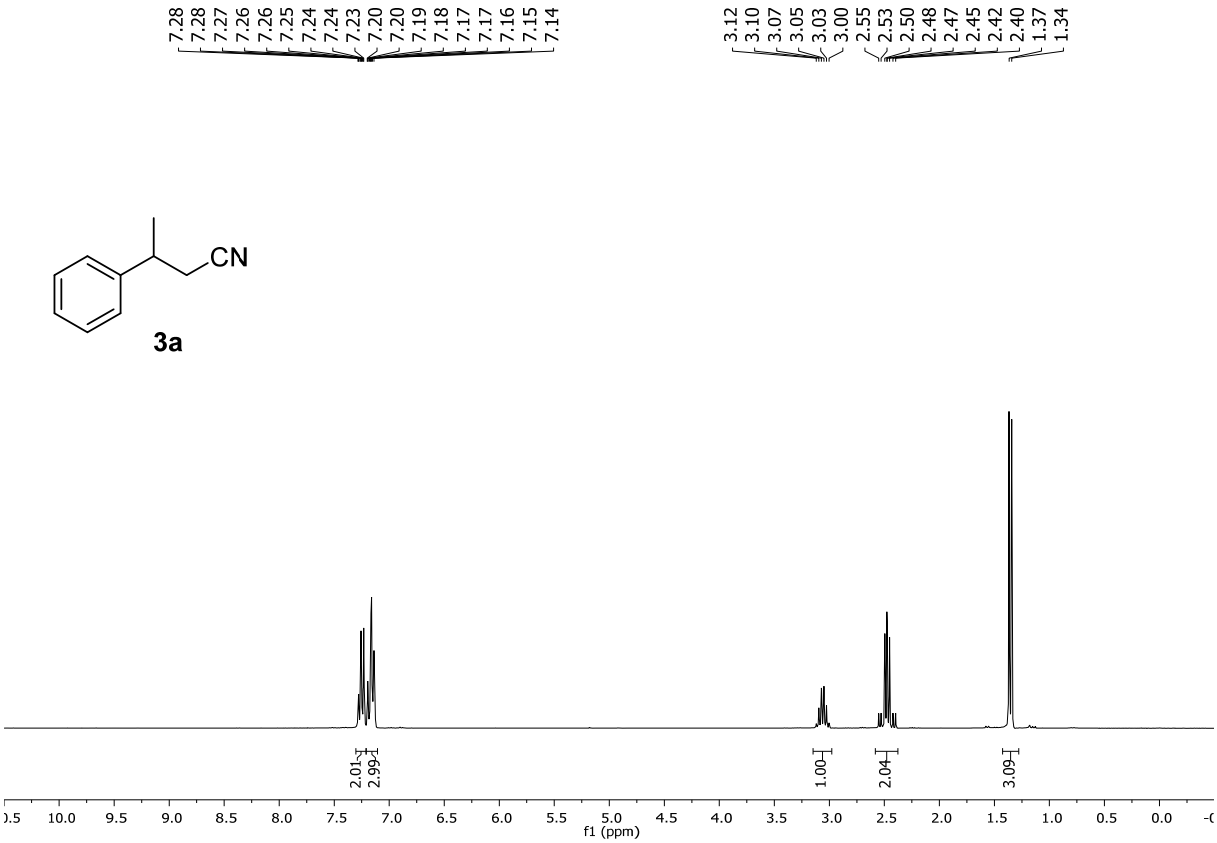
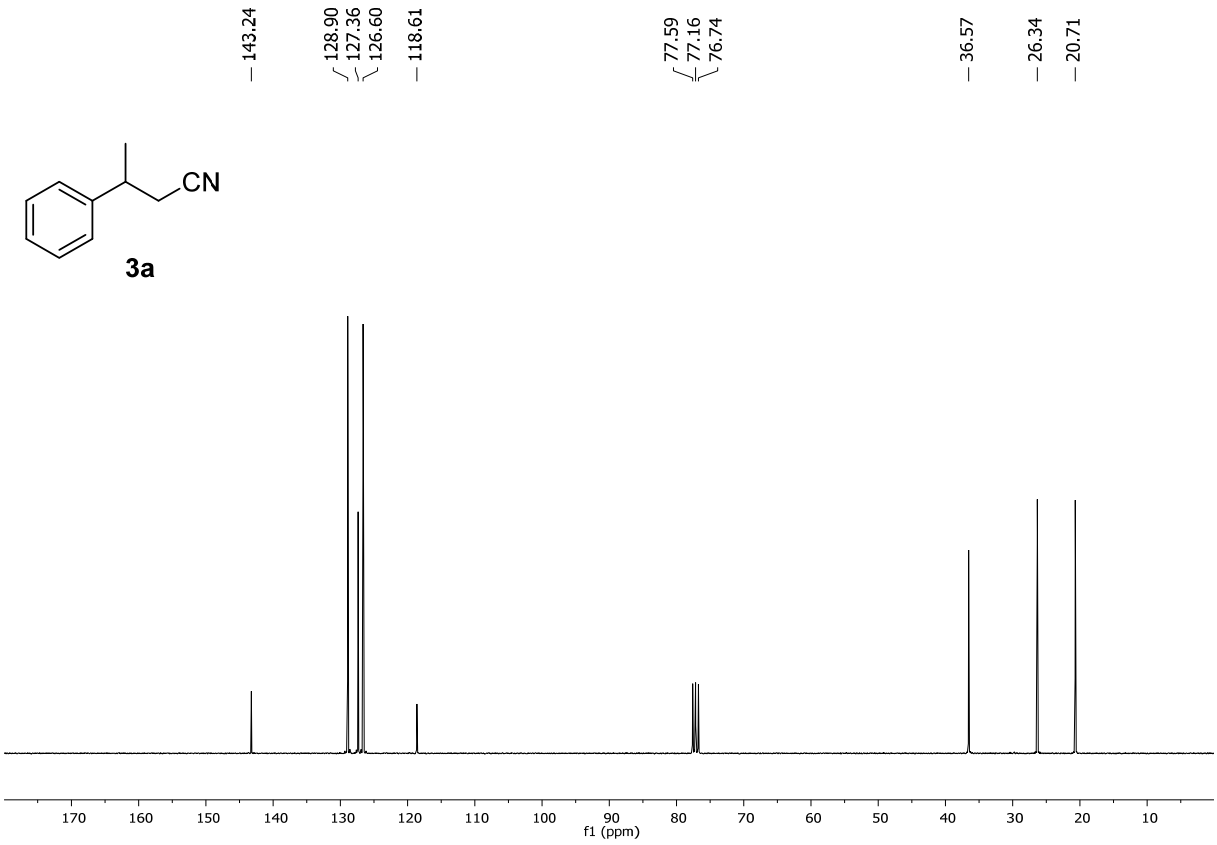
NMR spectra of all unknown compounds
3-Phenylbutanenitrile (3a)

^{1}H-NMR

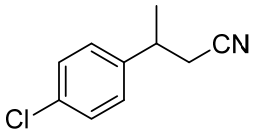


^{13}C-NMR

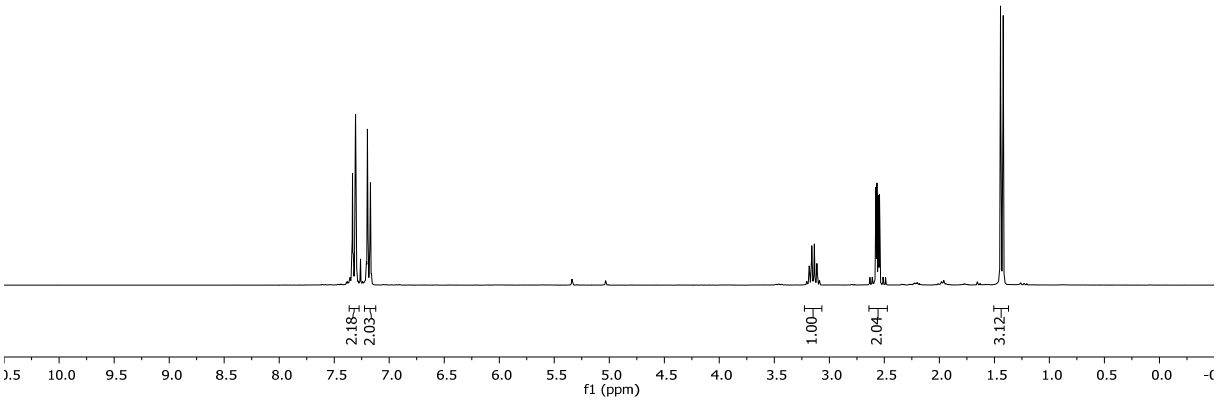


3-(4-Chlorophenyl)butanenitrile (3b)

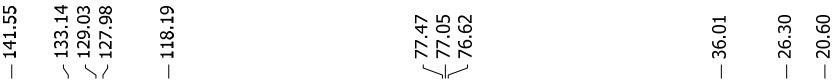
^{1}H-NMR

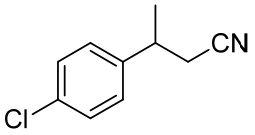


3b

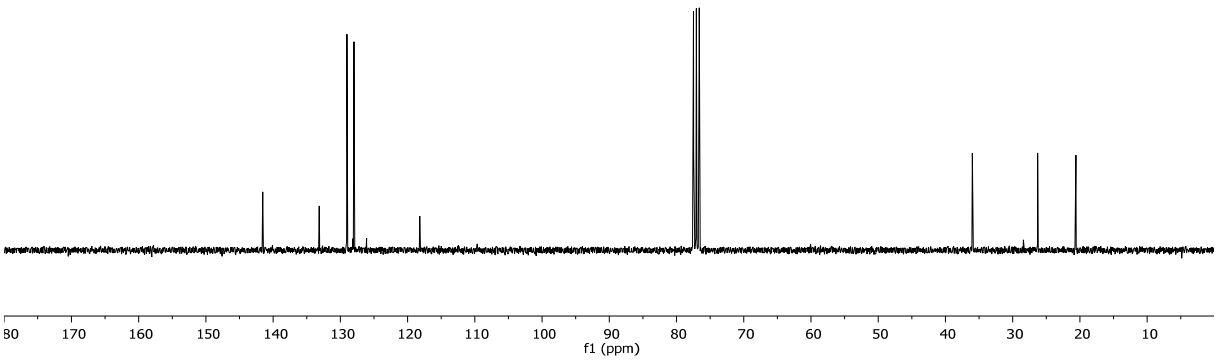


^{13}C-NMR



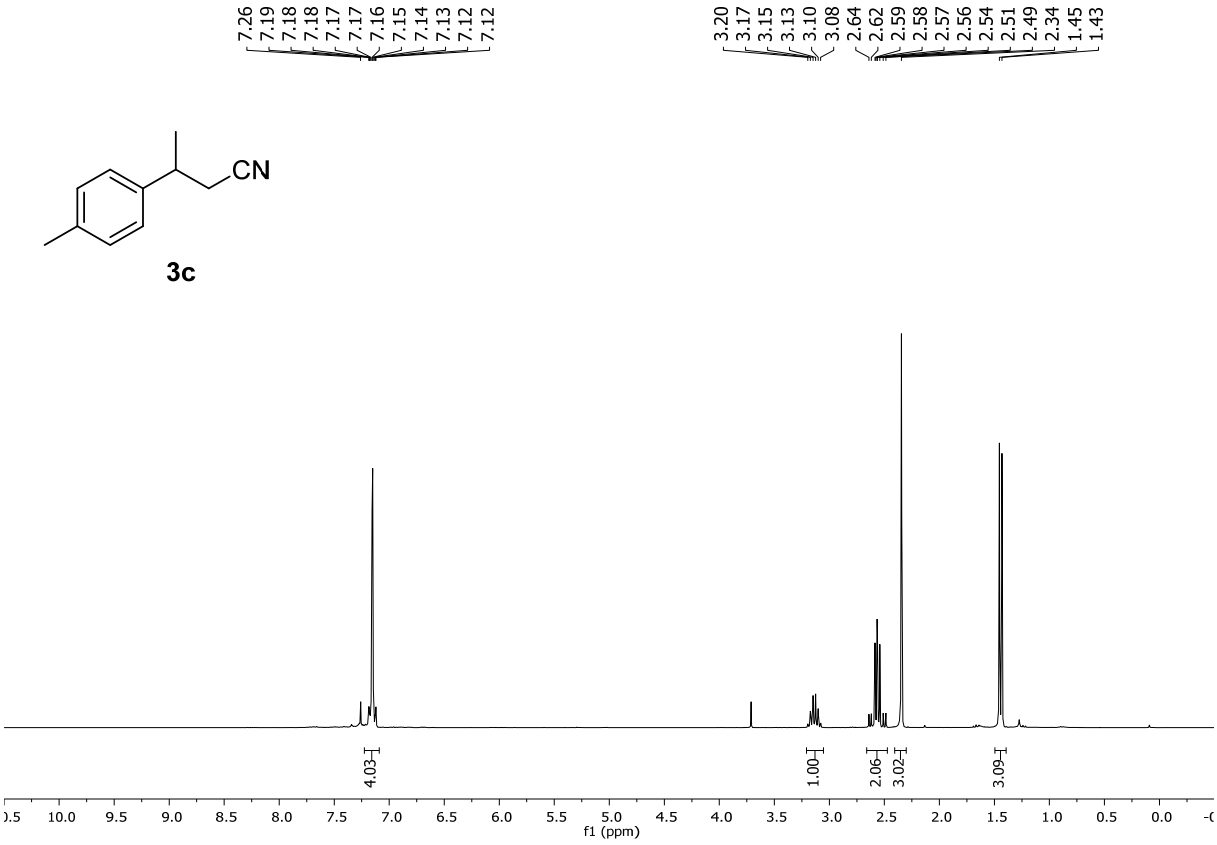


3b

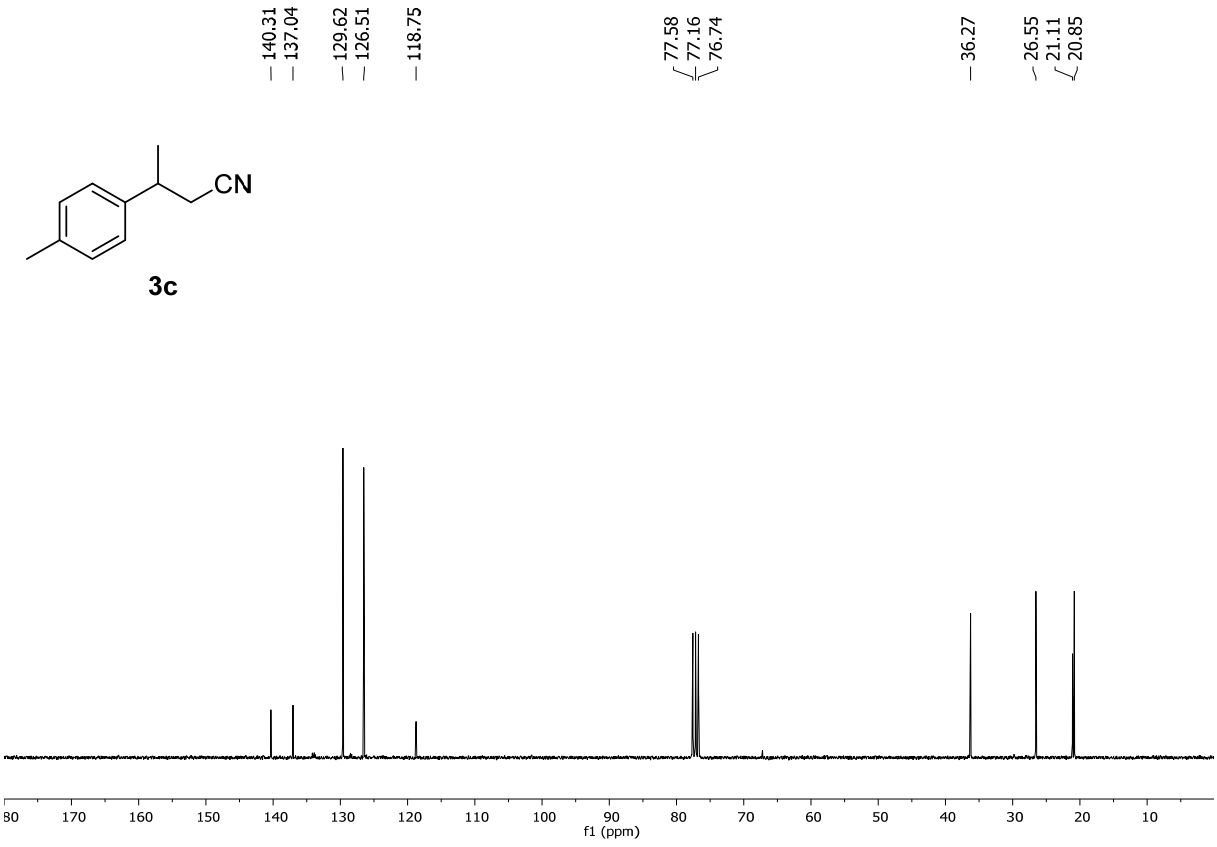


3-(*p*-Tolyl)butanenitrile (3c)

^{1}H-NMR

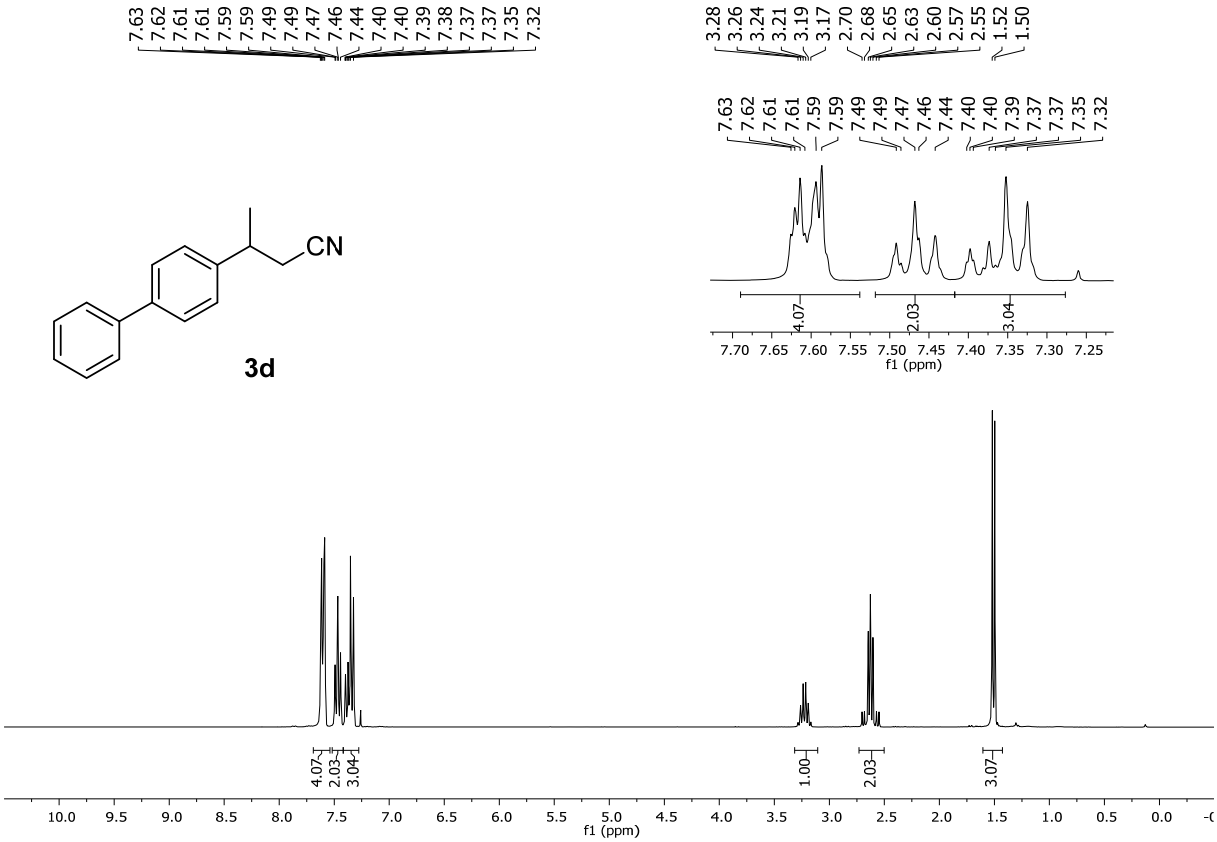


^{13}C-NMR

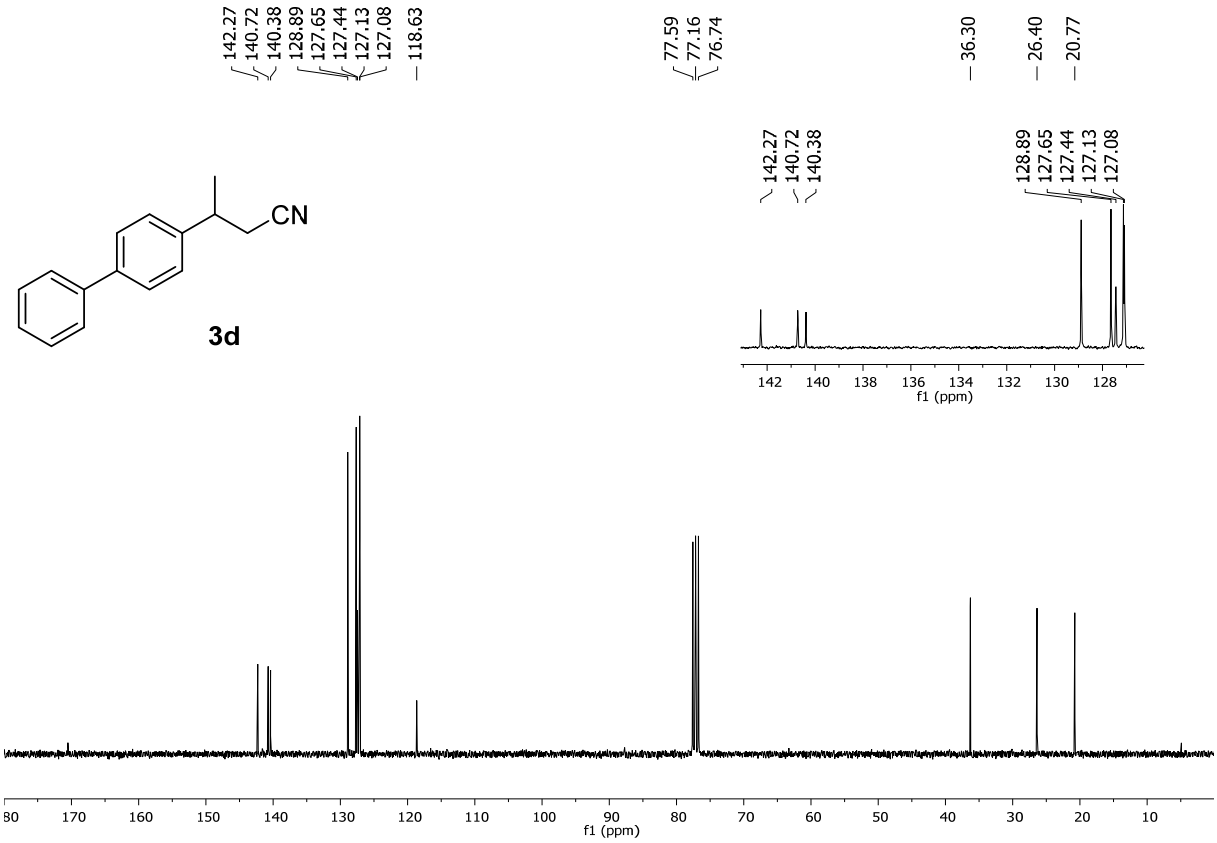


3-([1,1'-Biphenyl]-4-yl)butanenitrile (3d)

^{1}H-NMR

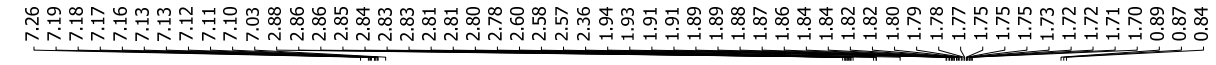


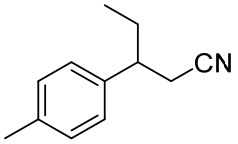
^{13}C-NMR



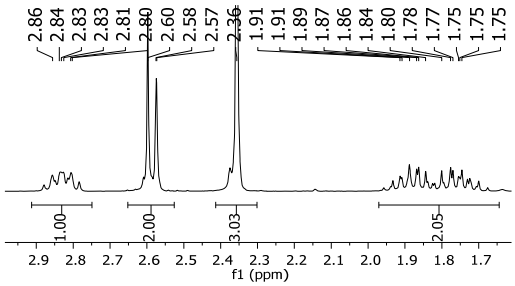
3-(*p*-Tolyl)pentanenitrile (3e)

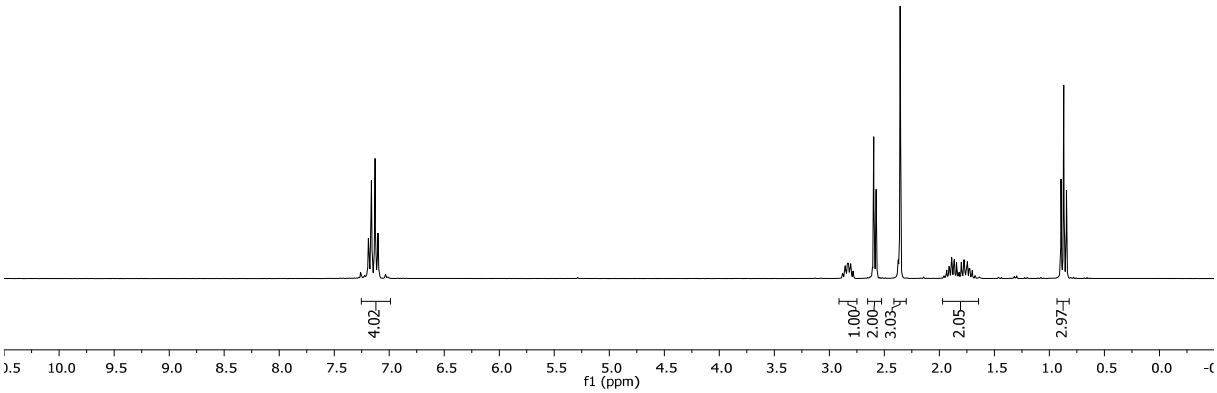
^{1}H-NMR



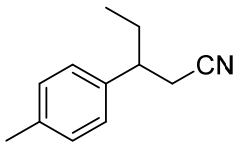


3e

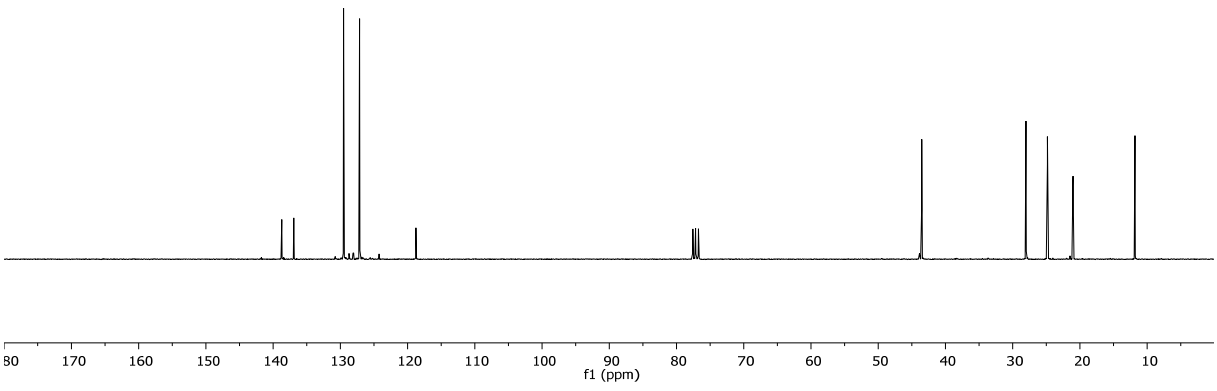




^{13}C-NMR

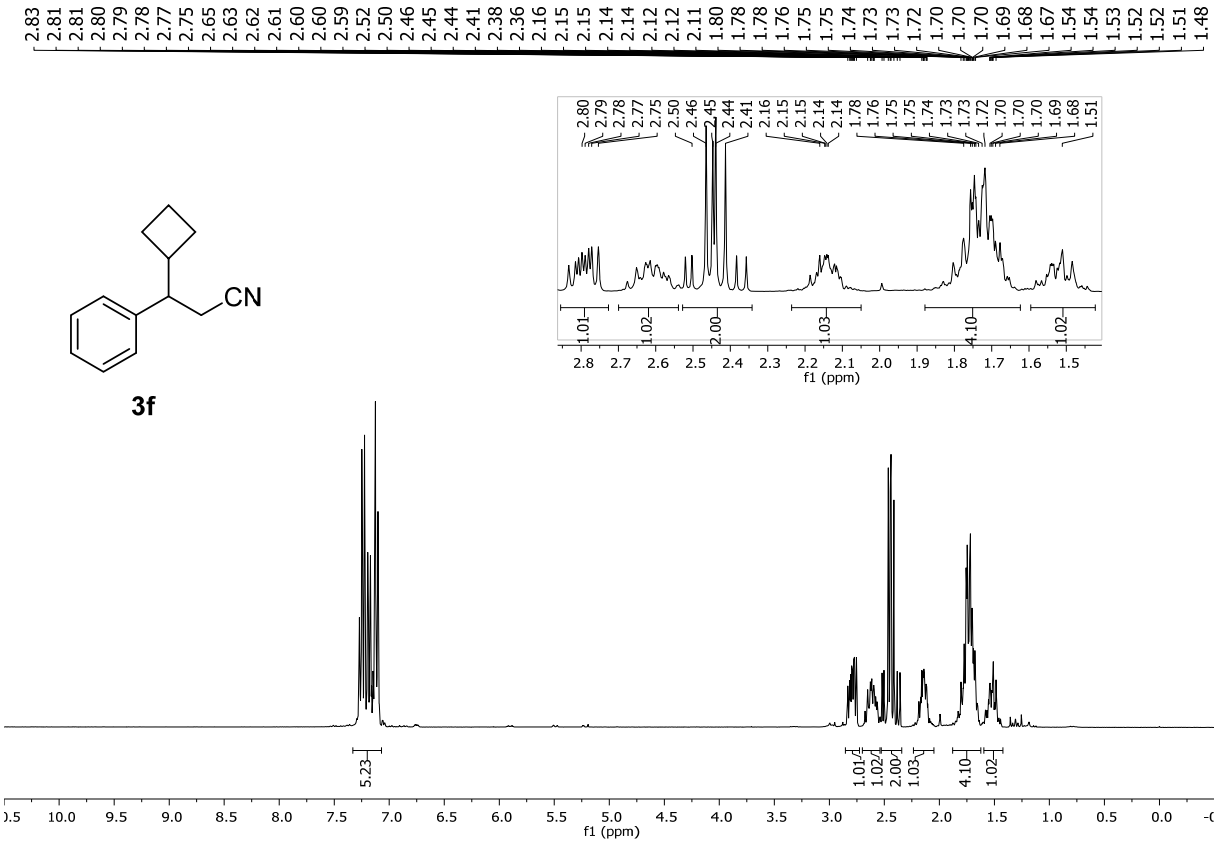


3e

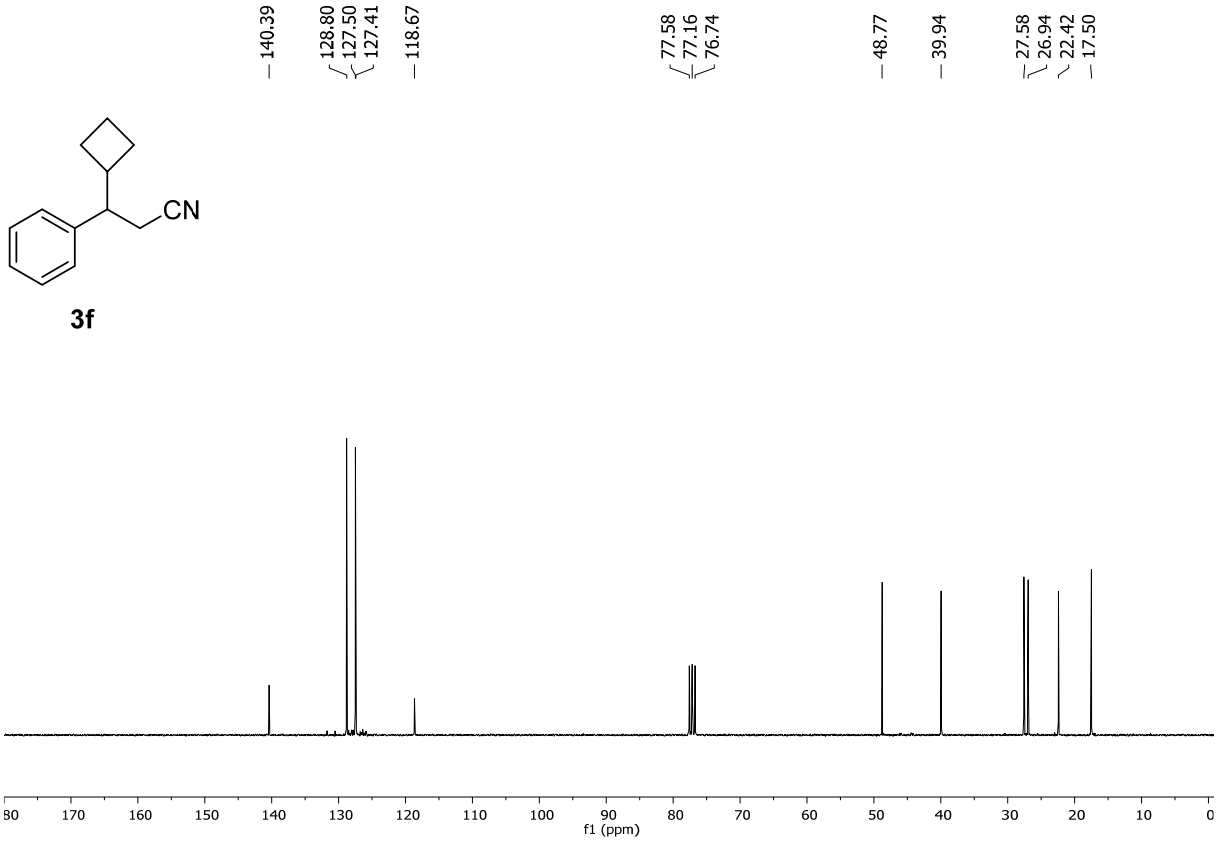


3-Cyclobutyl-3-phenylpropanenitrile (3f)

^{1}H-NMR

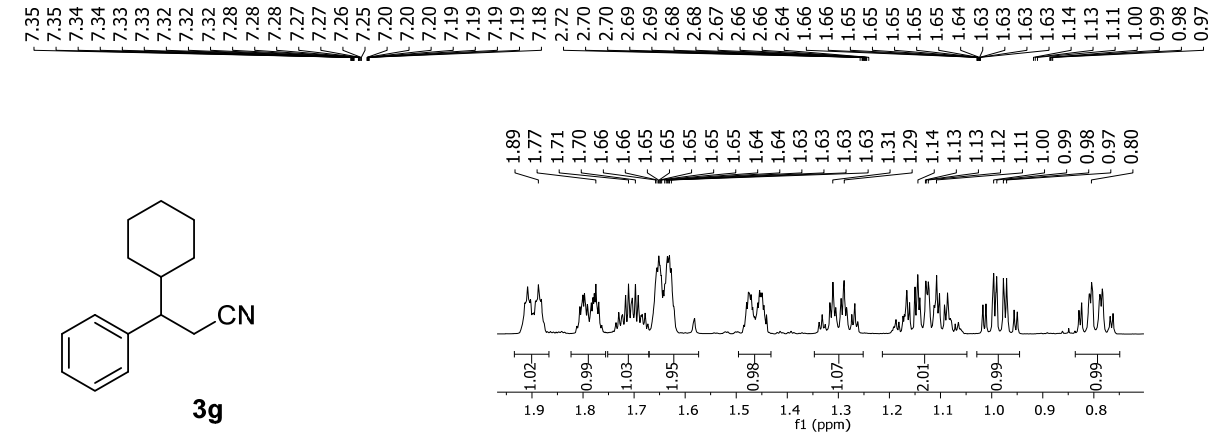


^{13}C-NMR

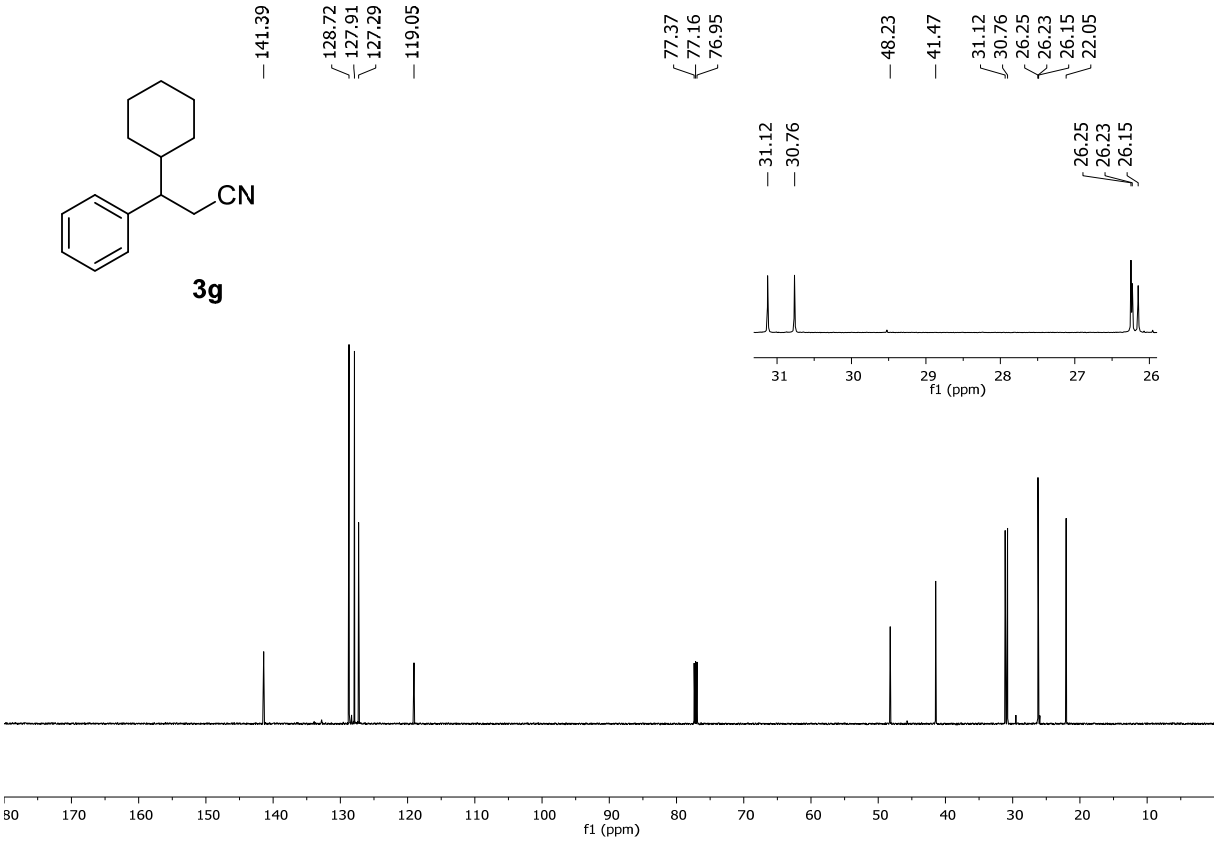


3-Cyclohexyl-3-phenylpropanenitrile (3g)

^{1}H-NMR

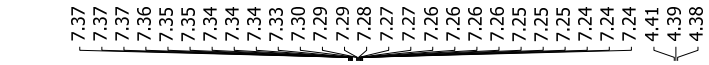


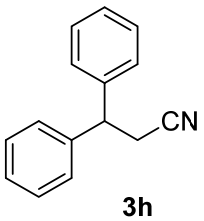
^{13}C-NMR



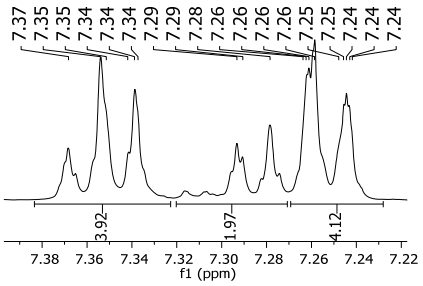
3,3-Diphenylpropanenitrile (3h)

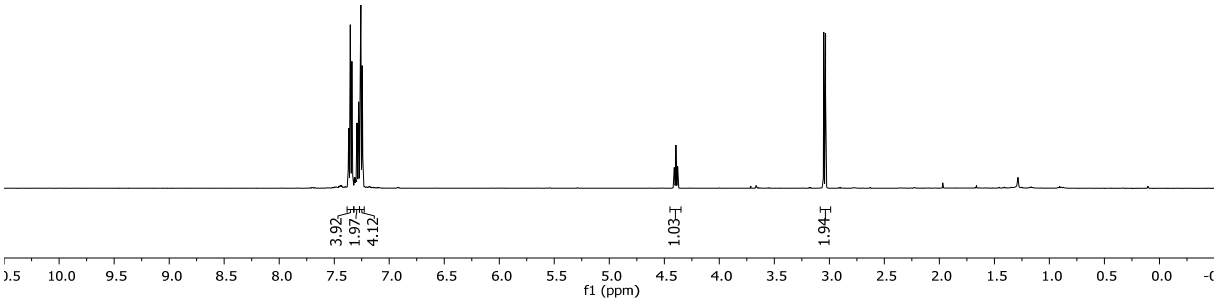
^{1}H-NMR





3h





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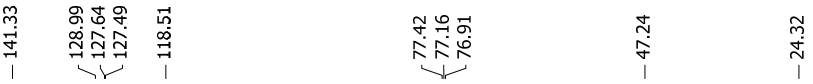
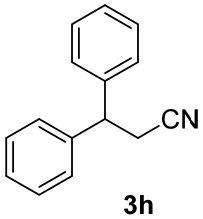
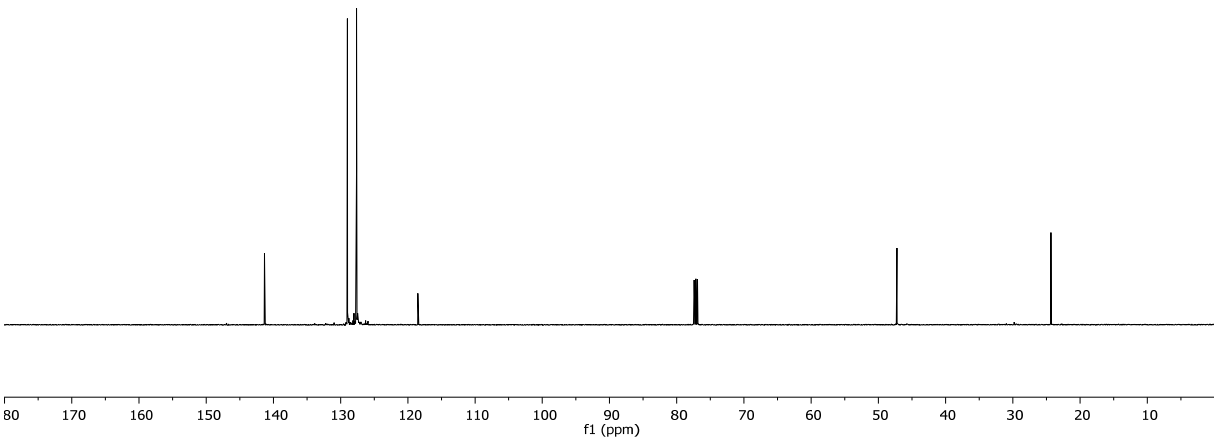


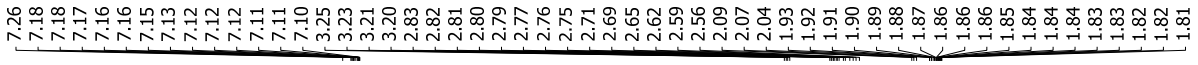


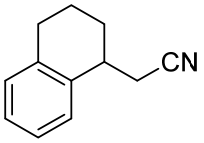
3h



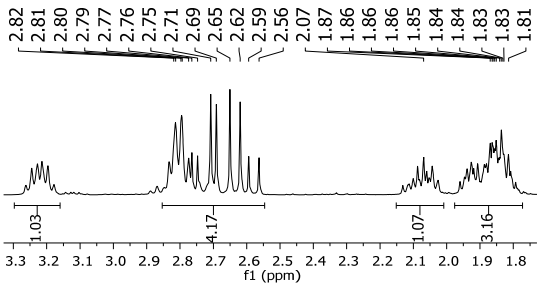
2-(1,2,3,4-Tetrahydronaphthalen-1-yl)acetonitrile (3i)

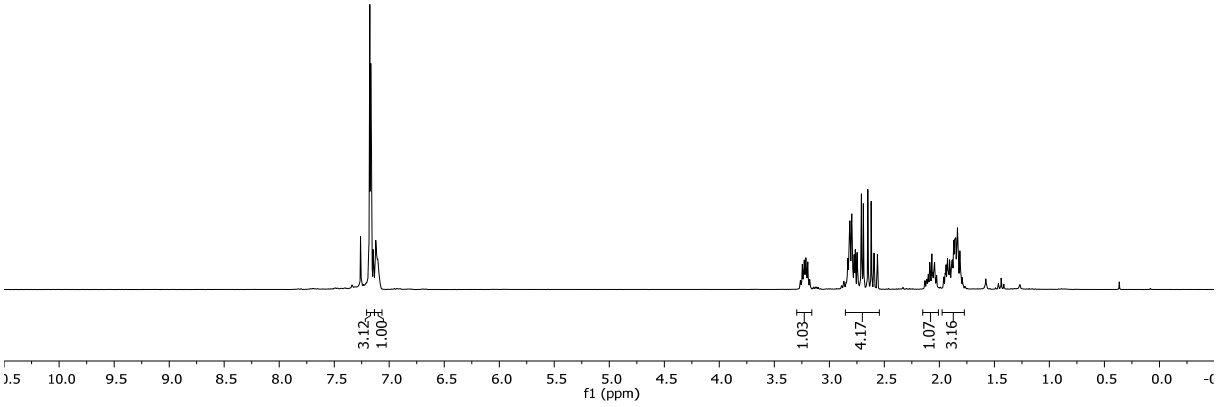
^{1}H-NMR



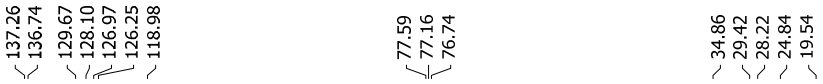


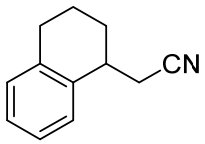
3i



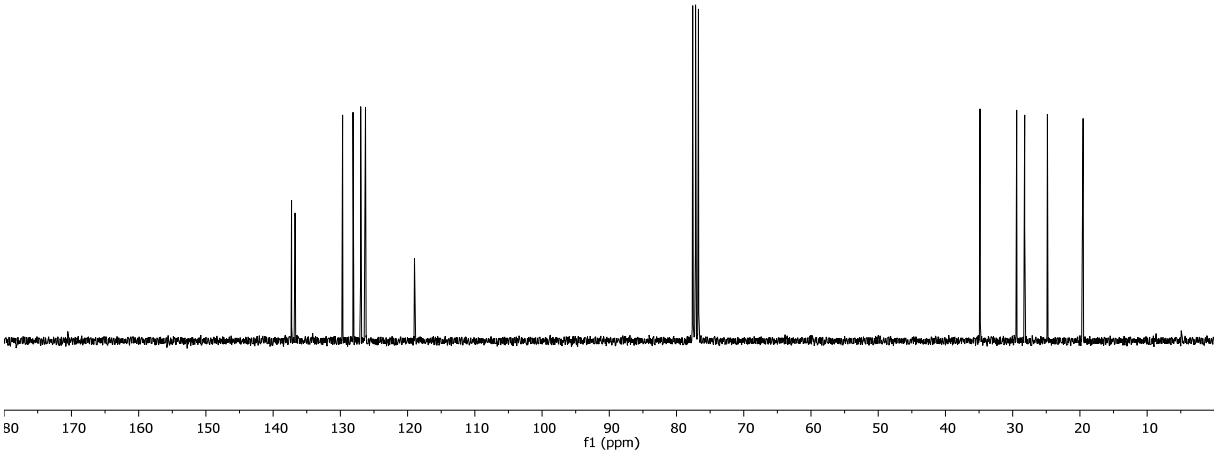


^{13}C-NMR



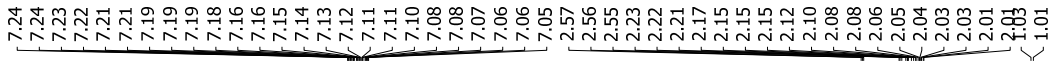


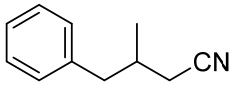
3i



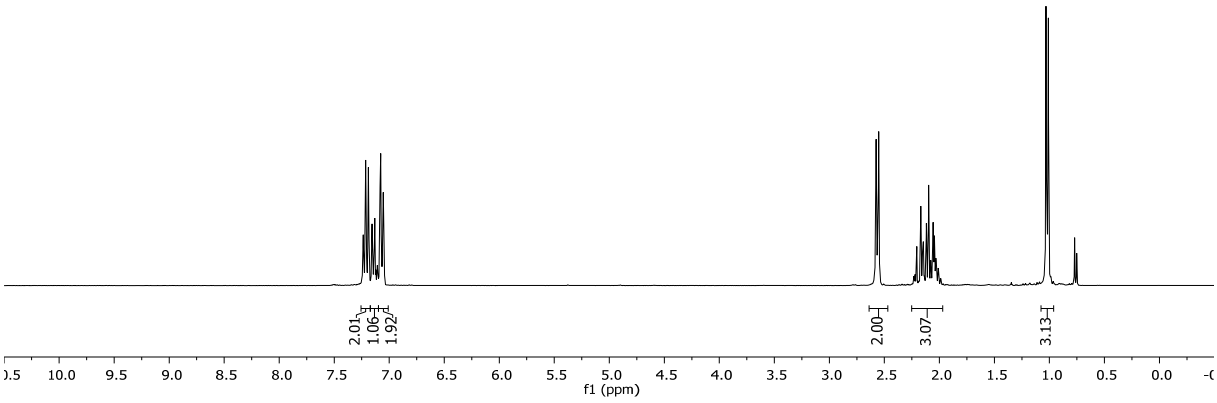
3-Methyl-4-phenylbutanenitrile (3j)

^{1}H-NMR

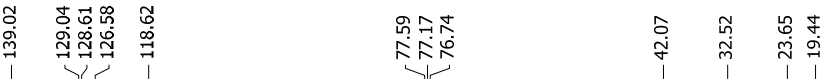


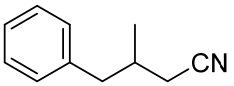


3j

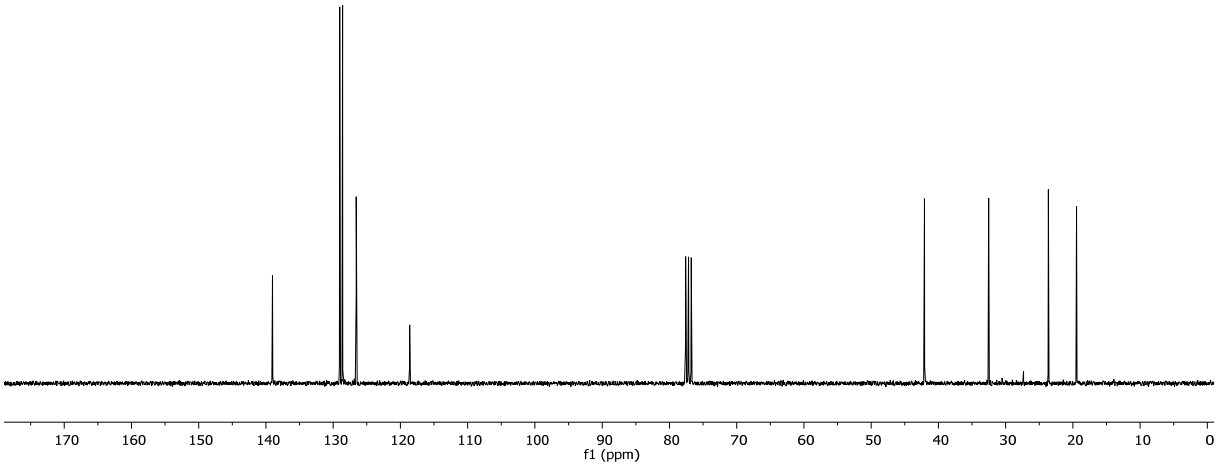


^{13}C-NMR



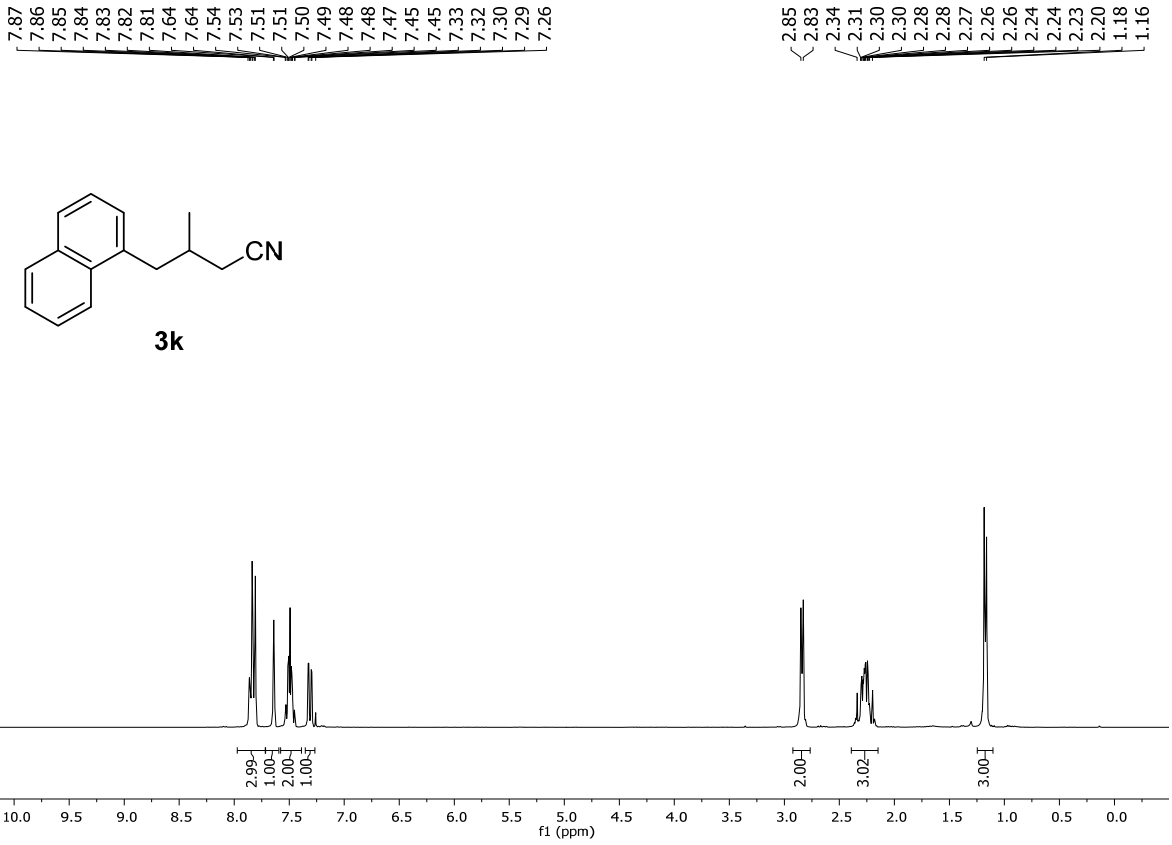


3j

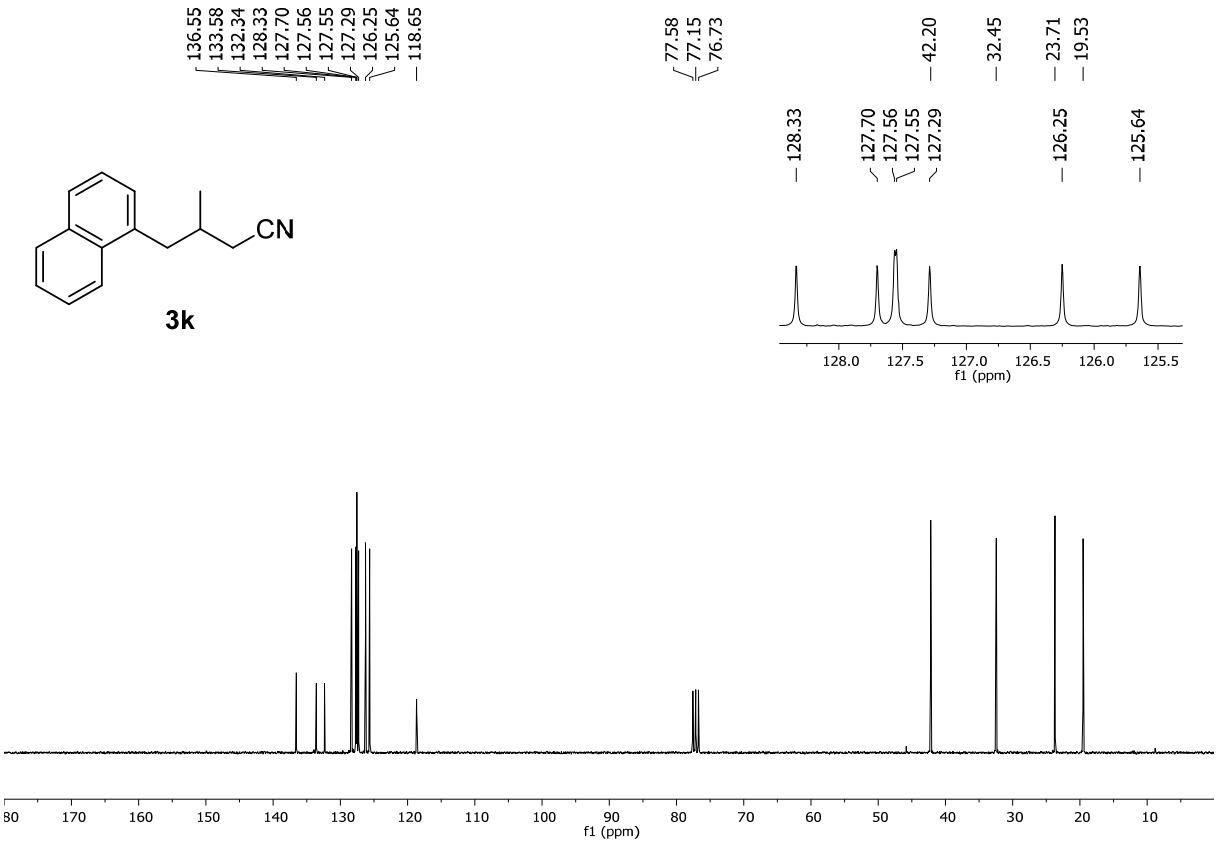


3-Methyl-4-(naphthalen-1-yl)butanenitrile (3k)

^{1}H-NMR

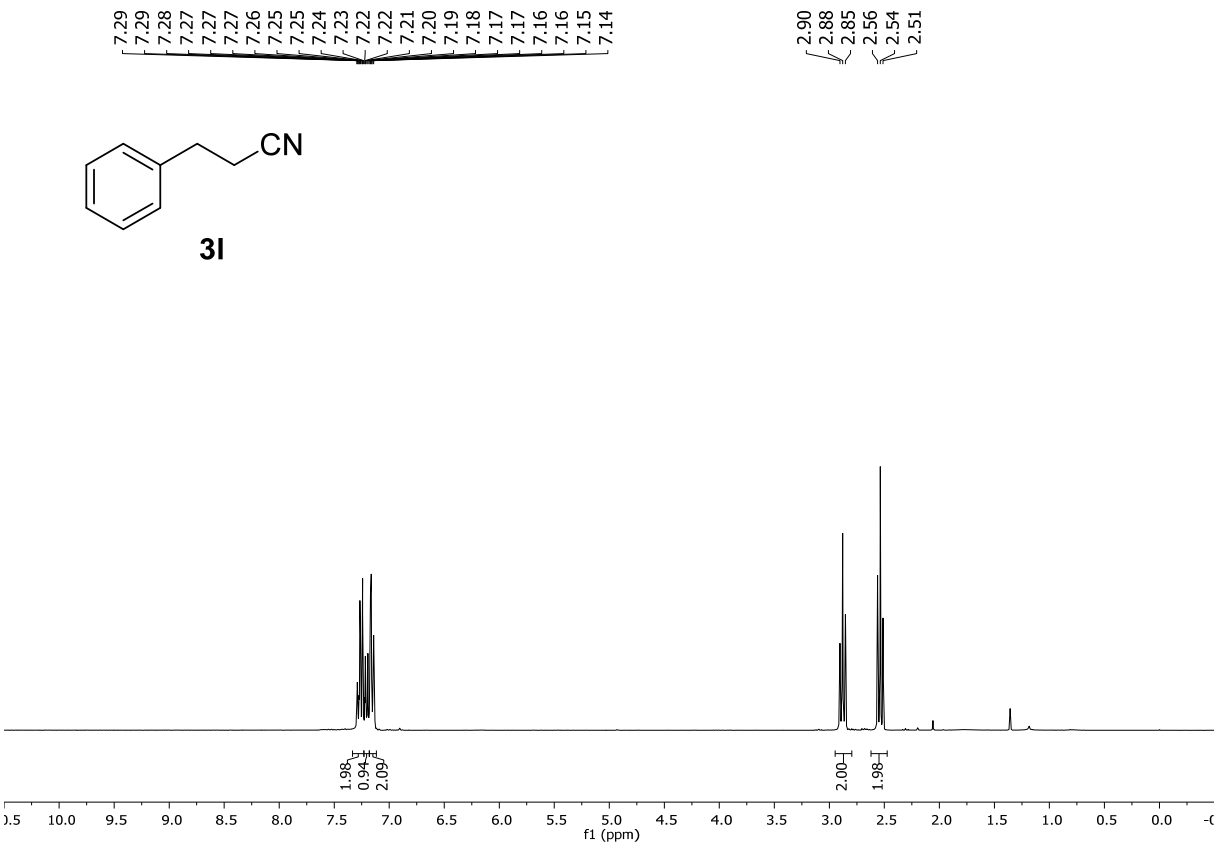


^{13}C-NMR

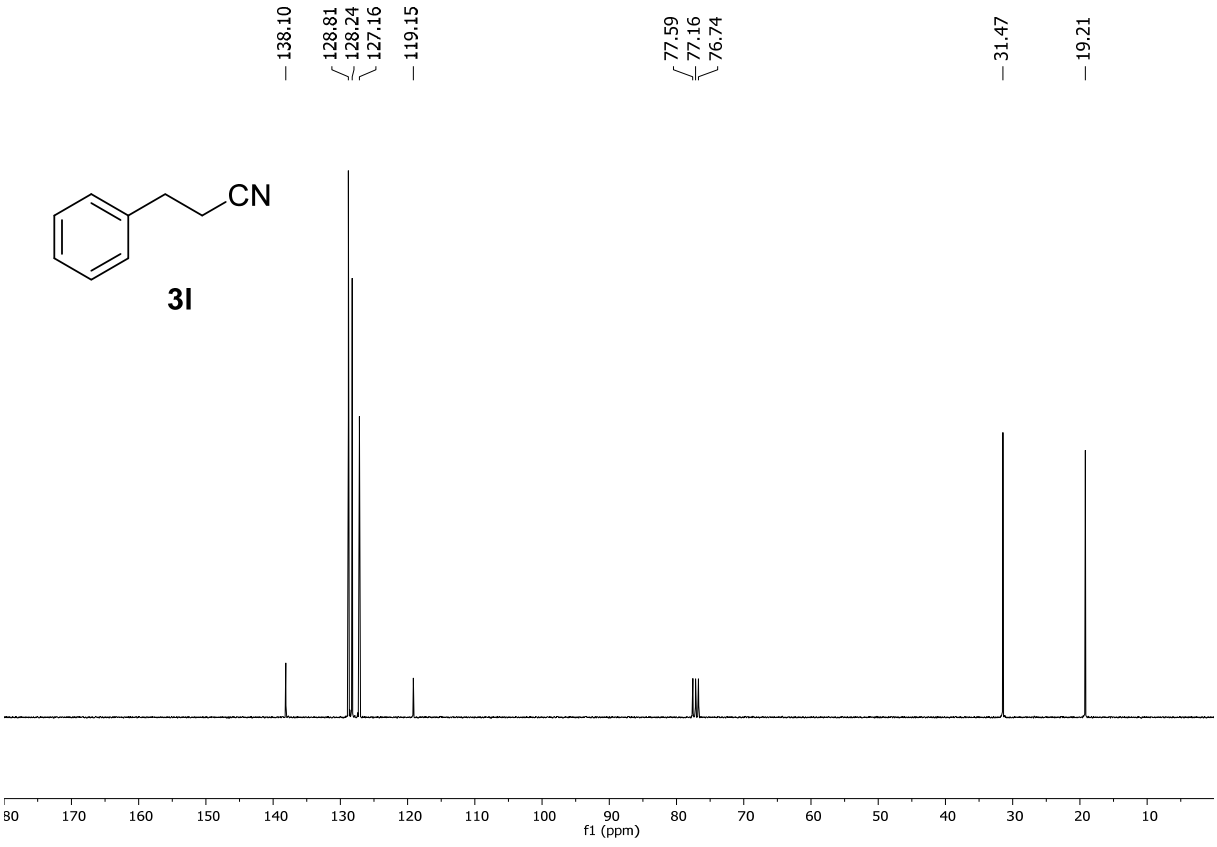


3-Phenylpropanenitrile (3l)

^{1}H-NMR

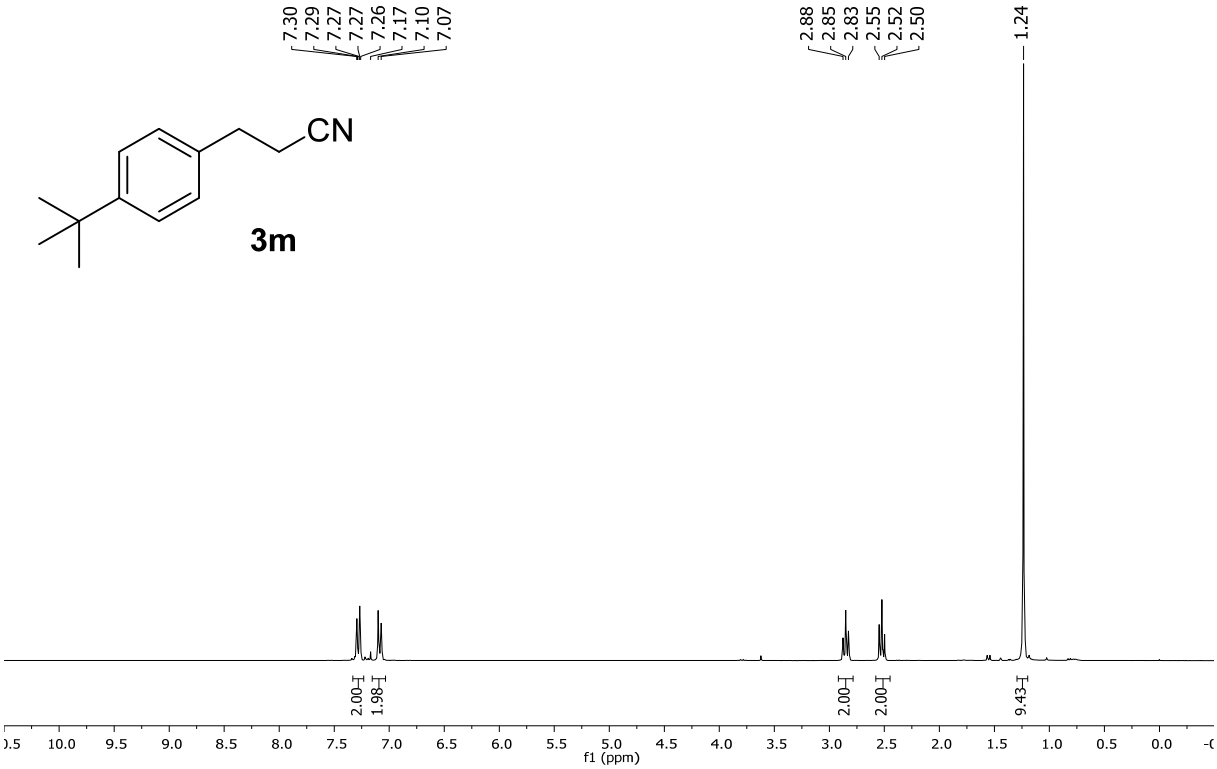


^{13}C-NMR

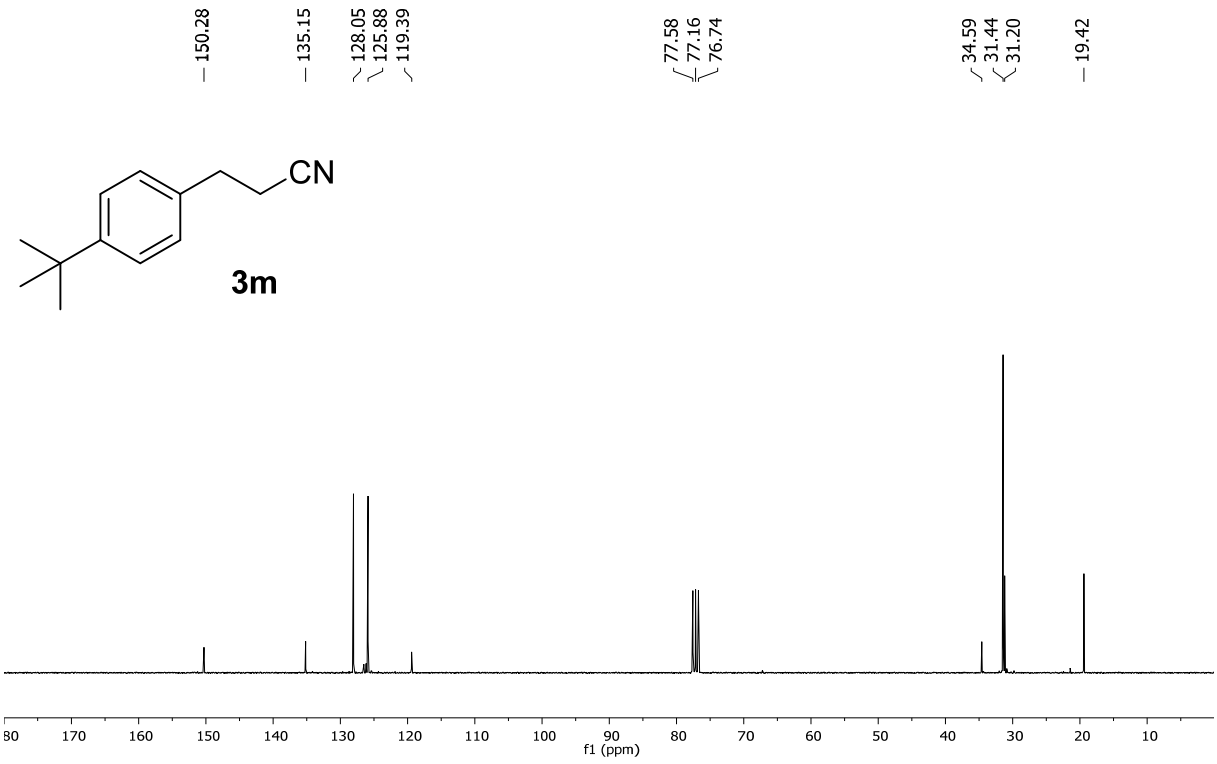


3-(4-(*tert*-Butyl)phenyl)propanenitrile (3m)

^{1}H-NMR

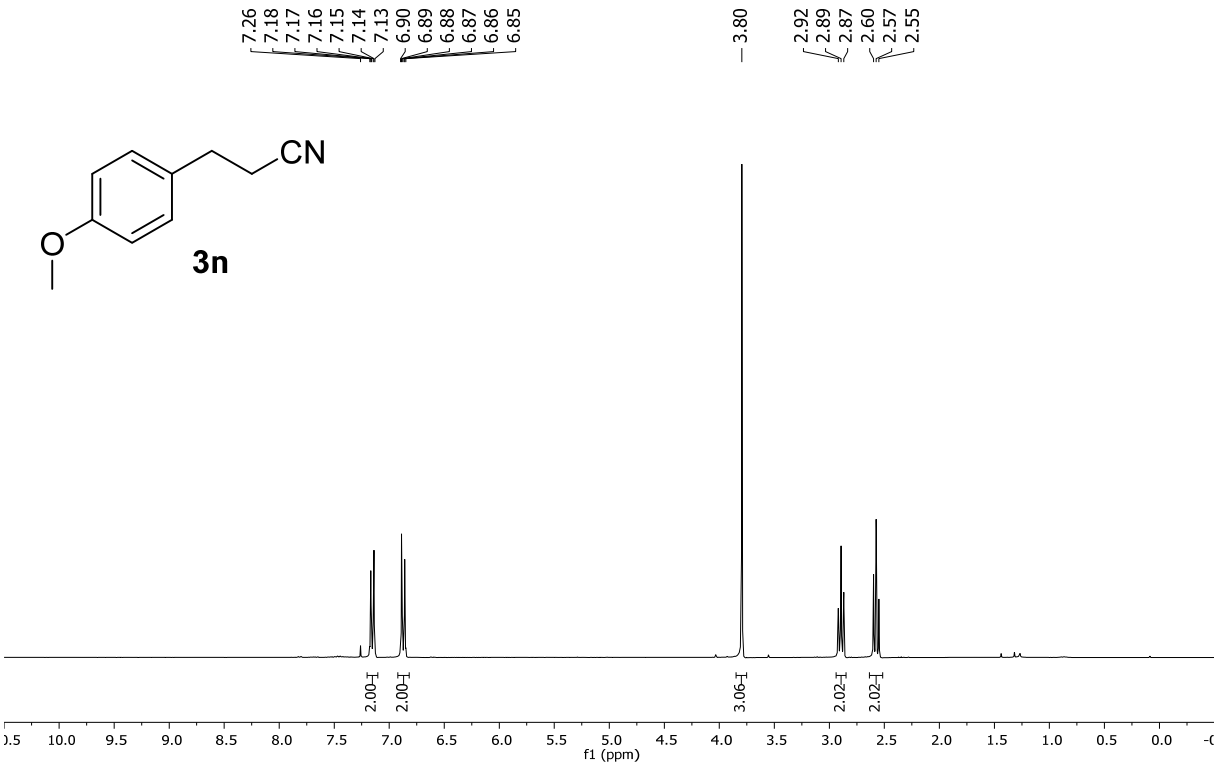


^{13}C-NMR

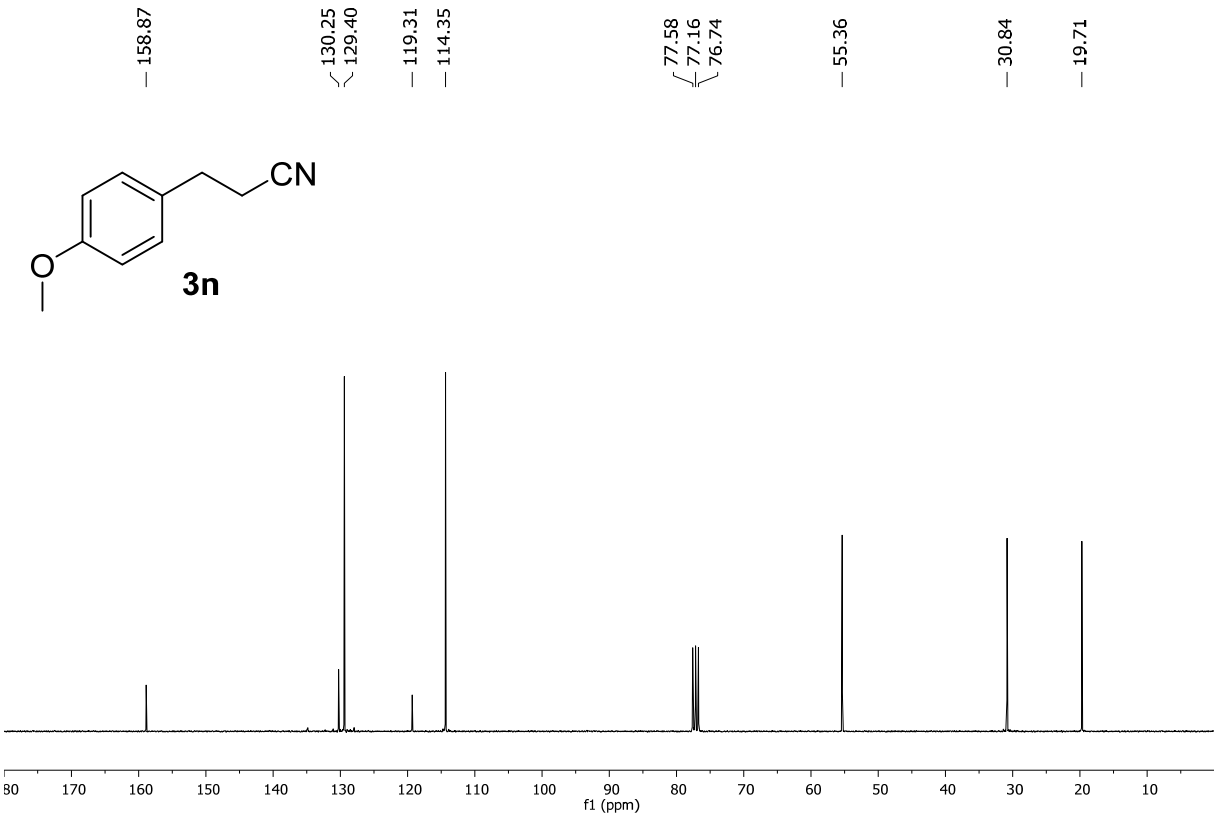


3-(4-Methoxyphenyl)propanenitrile (3n)

^{1}H-NMR

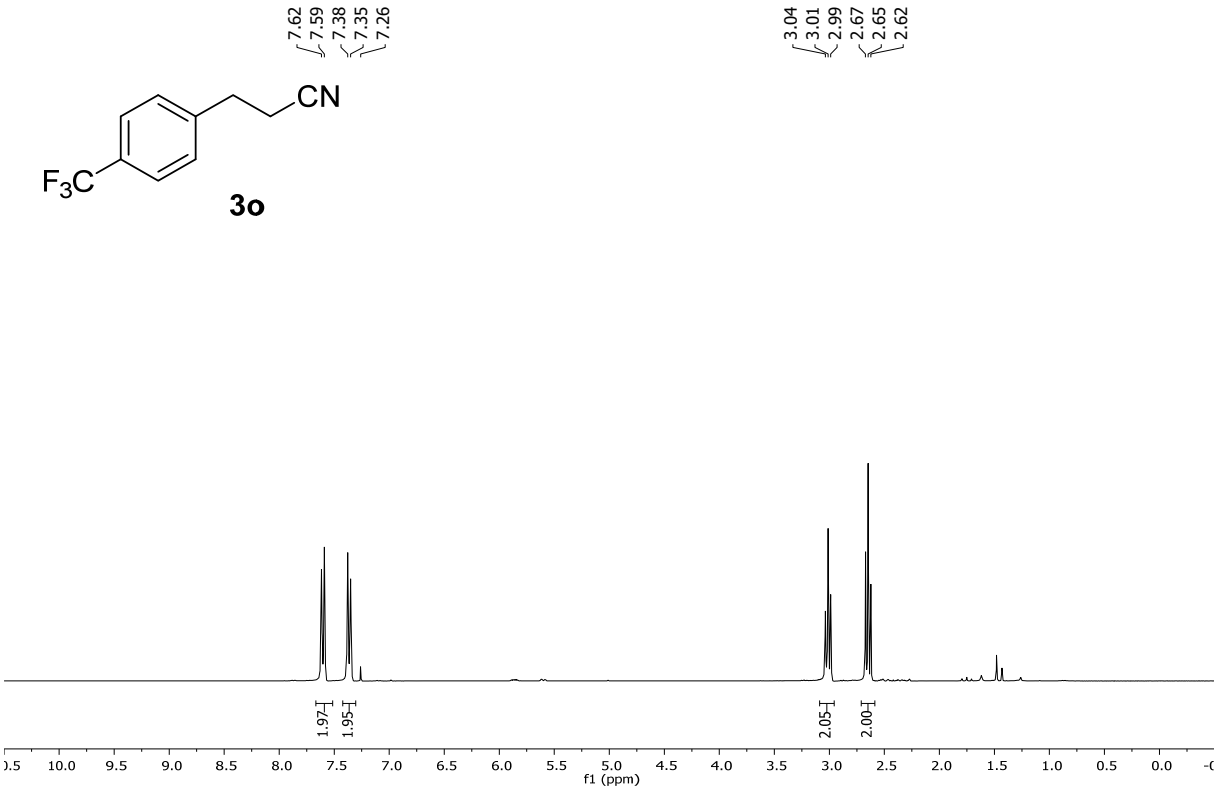


^{13}C-NMR

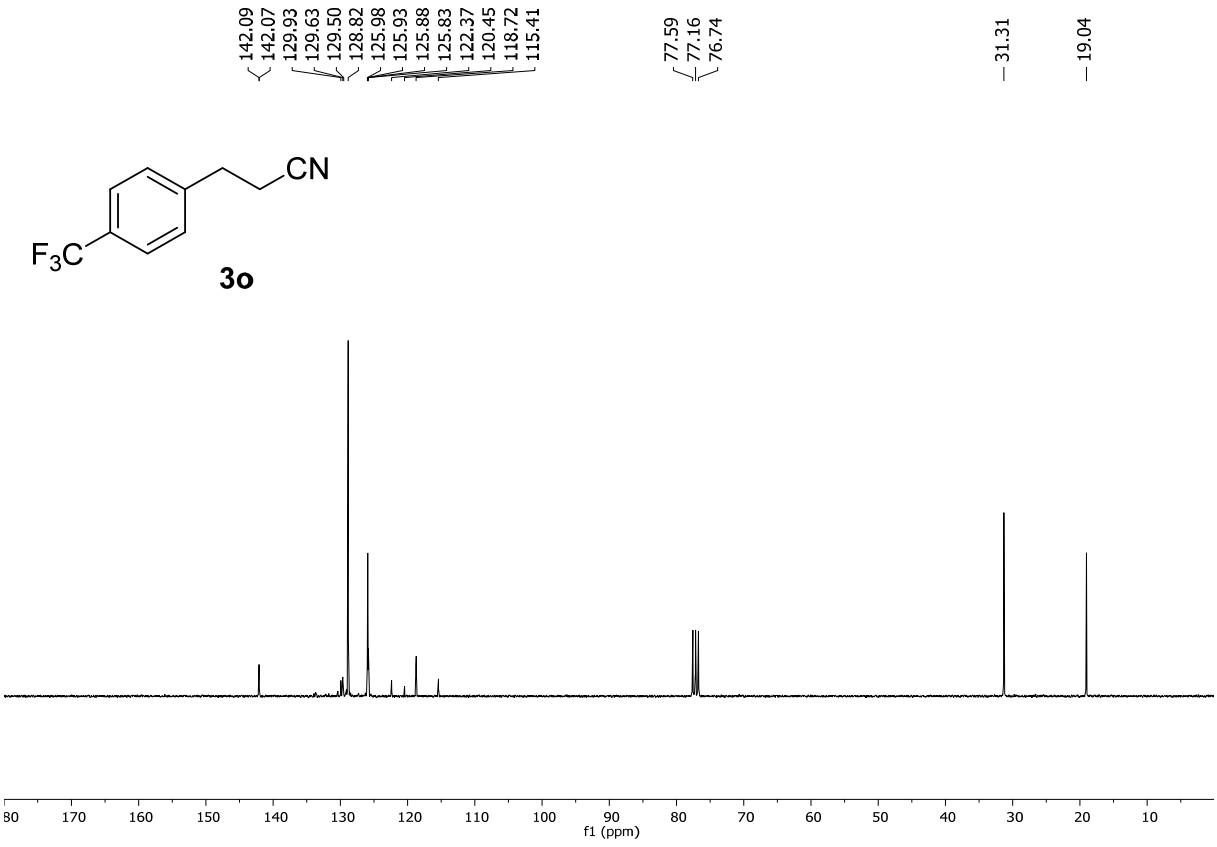


3-(4-(Trifluoromethyl)phenyl)propanenitrile (3o)

^{1}H-NMR

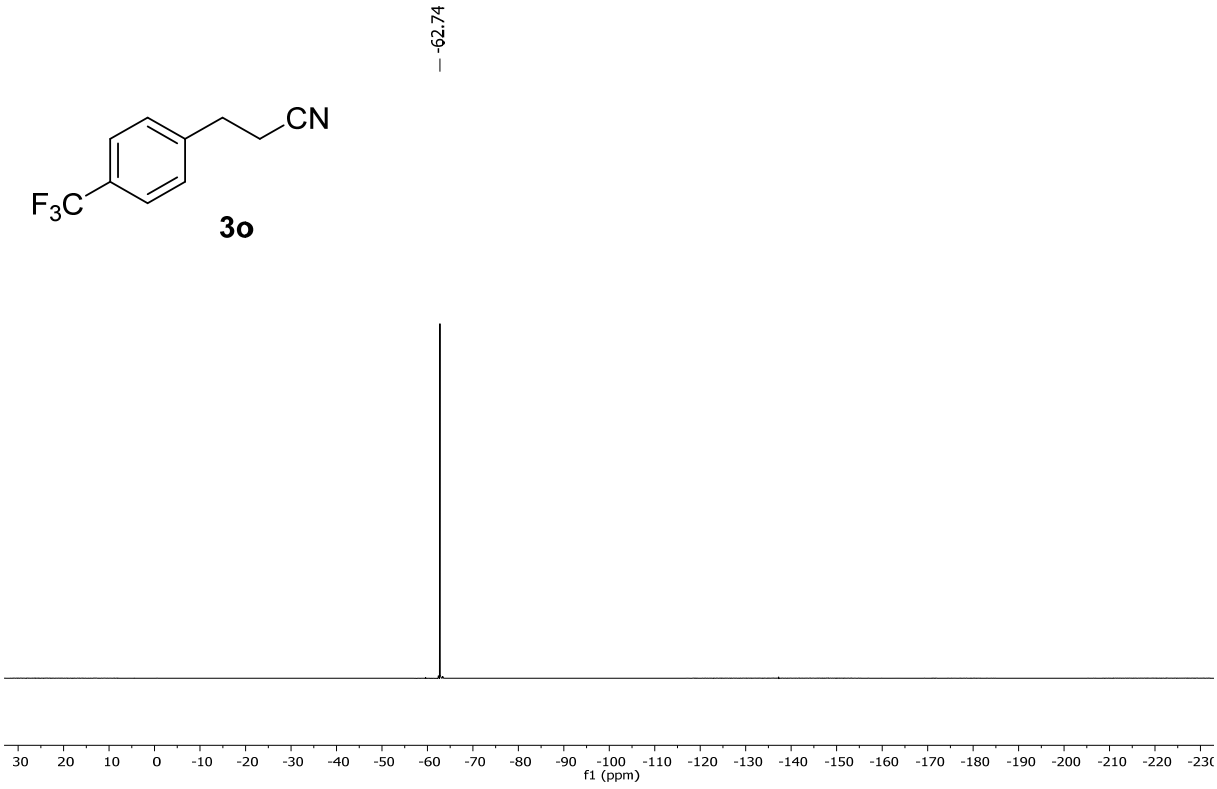


^{13}C-NMR



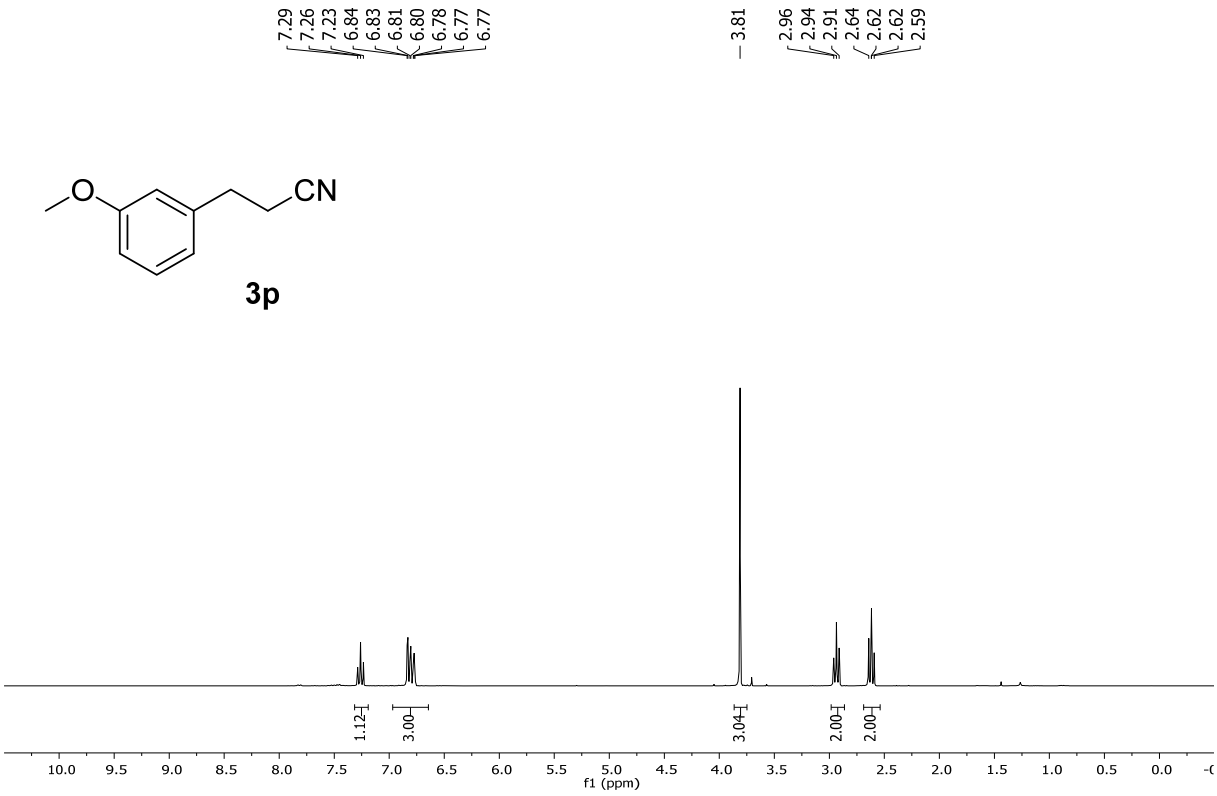
3-(4-(Trifluoromethyl)phenyl)propanenitrile (3o)

^{19}F-NMR

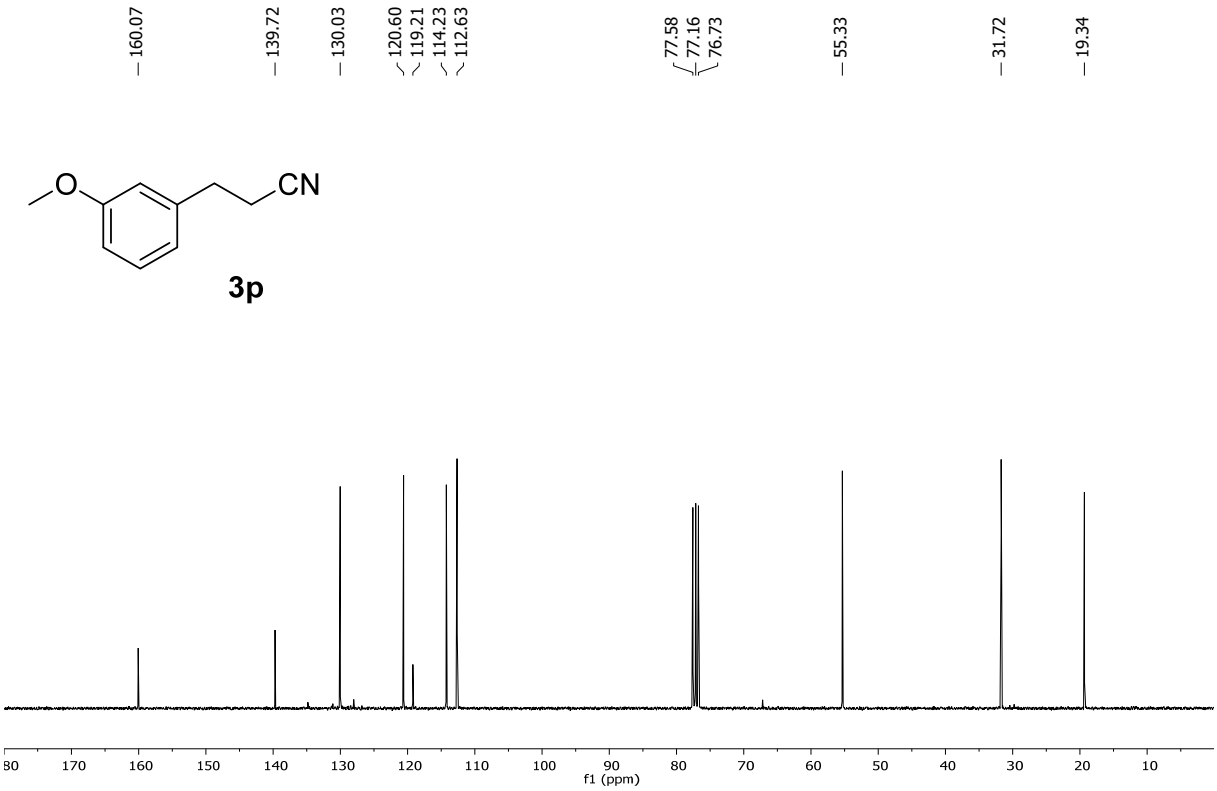


3-(3-Methoxyphenyl)propanenitrile (3p)

^{1}H-NMR

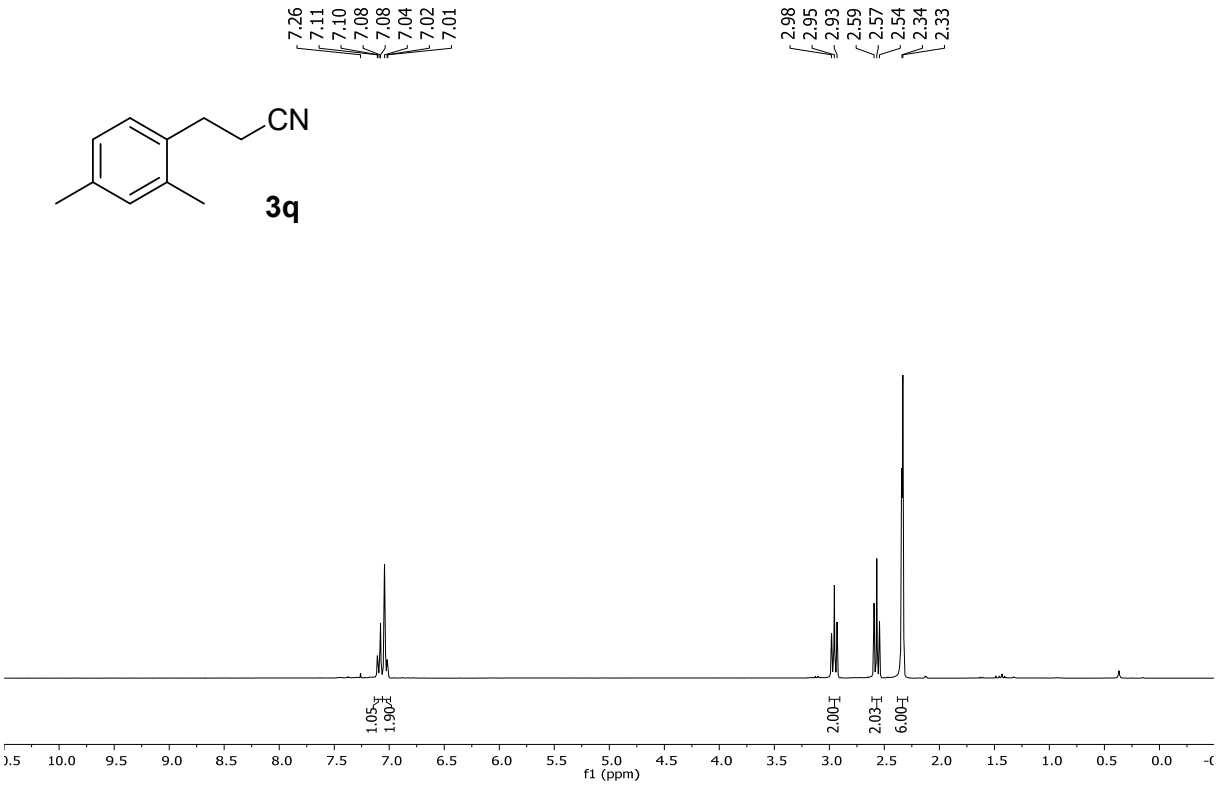


^{13}C-NMR

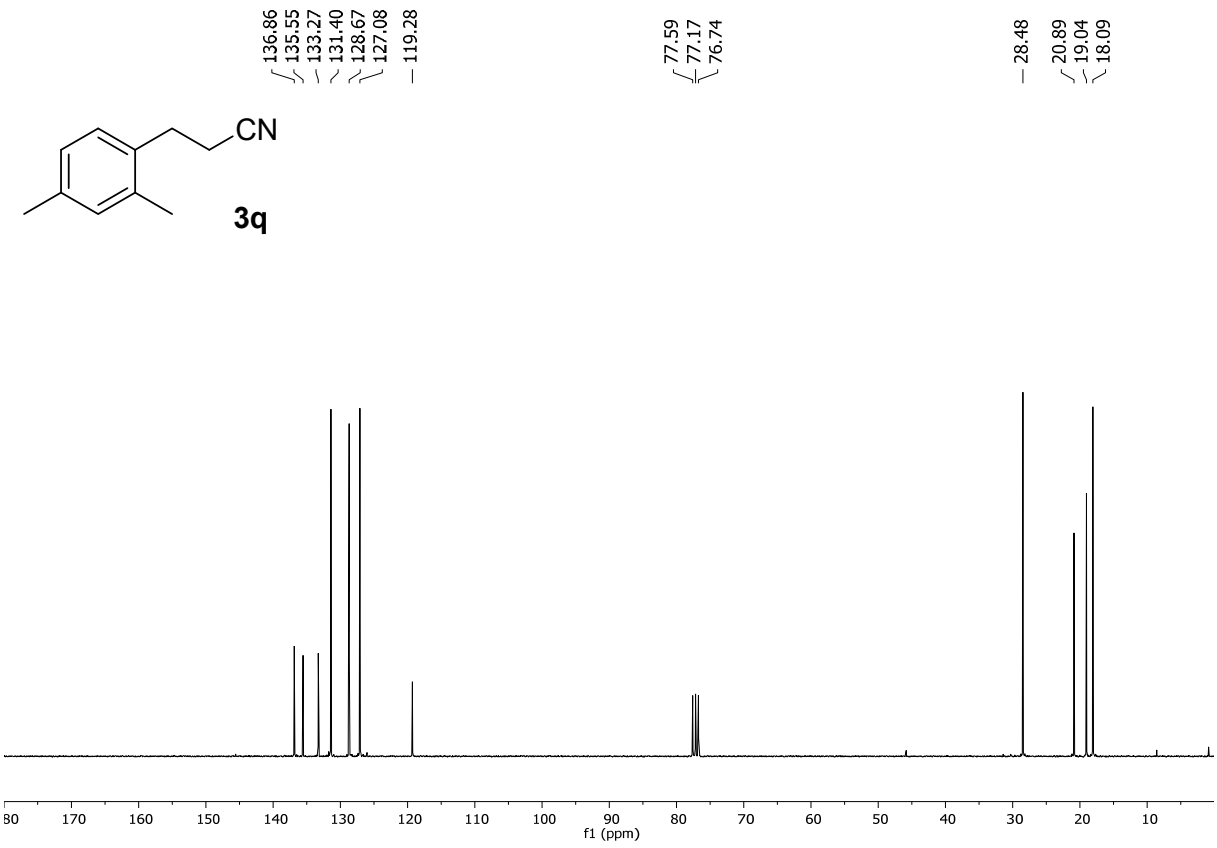


3-(2,4-Dimethylphenyl)propanenitrile (3q)

^{1}H-NMR

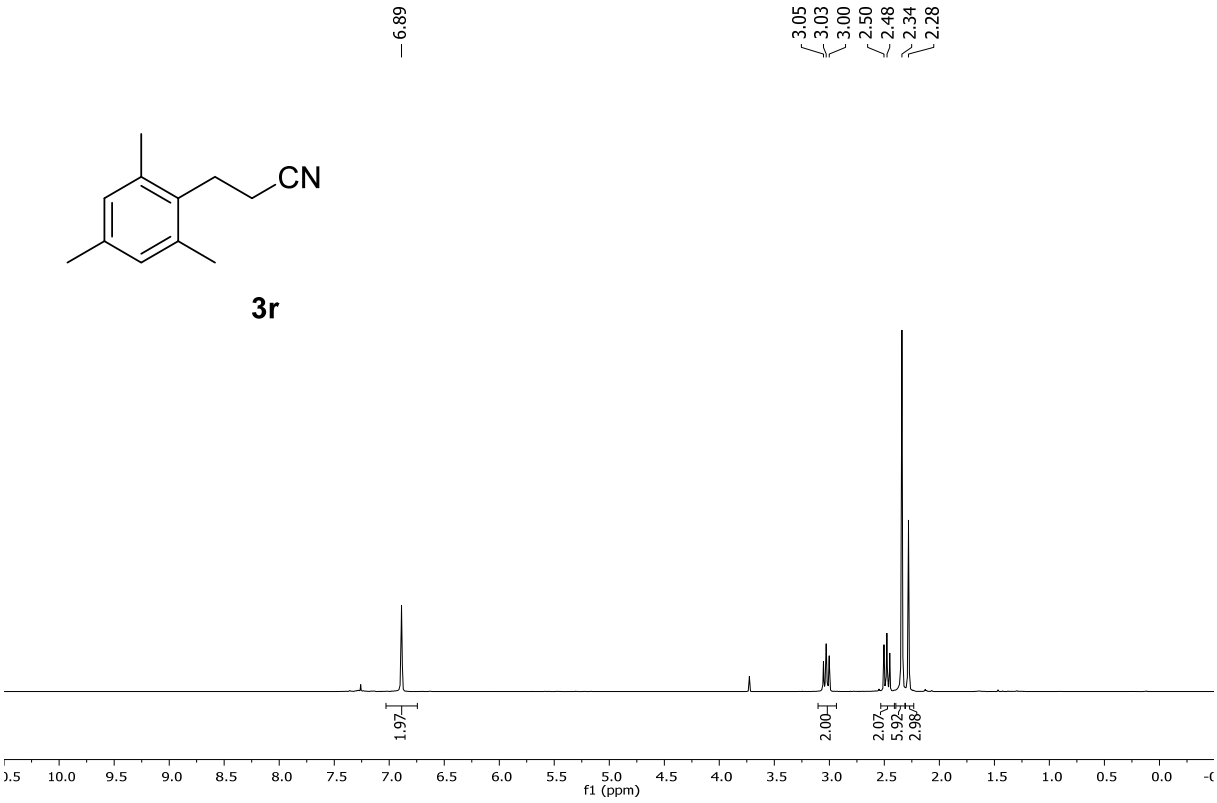


^{13}C-NMR



3-Mesitylpropanenitrile (3r)

^{1}H-NMR



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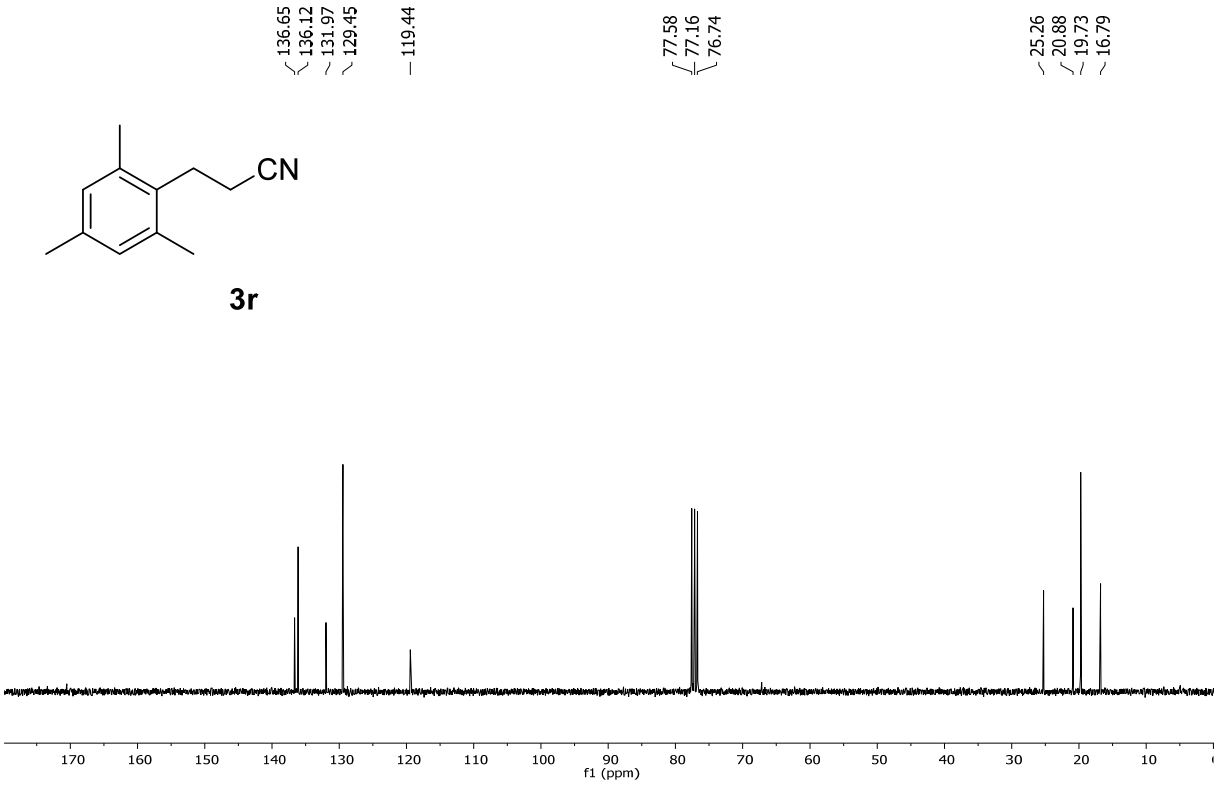
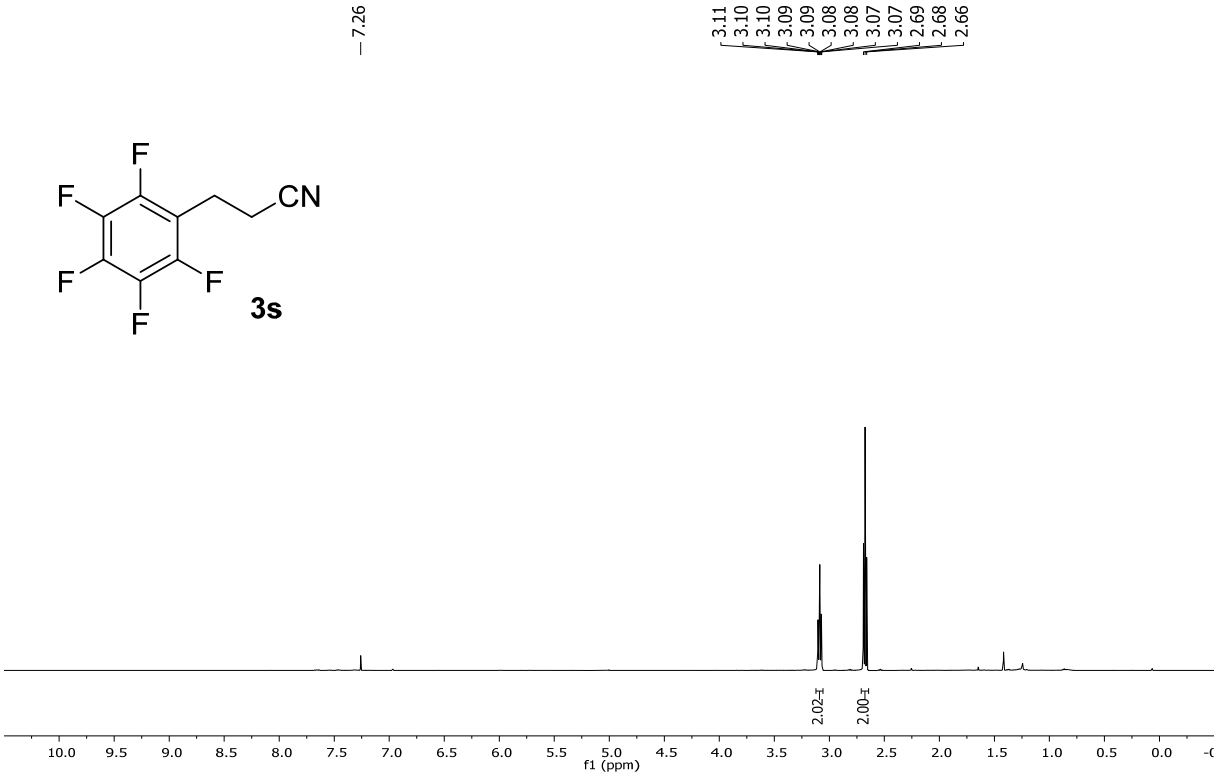
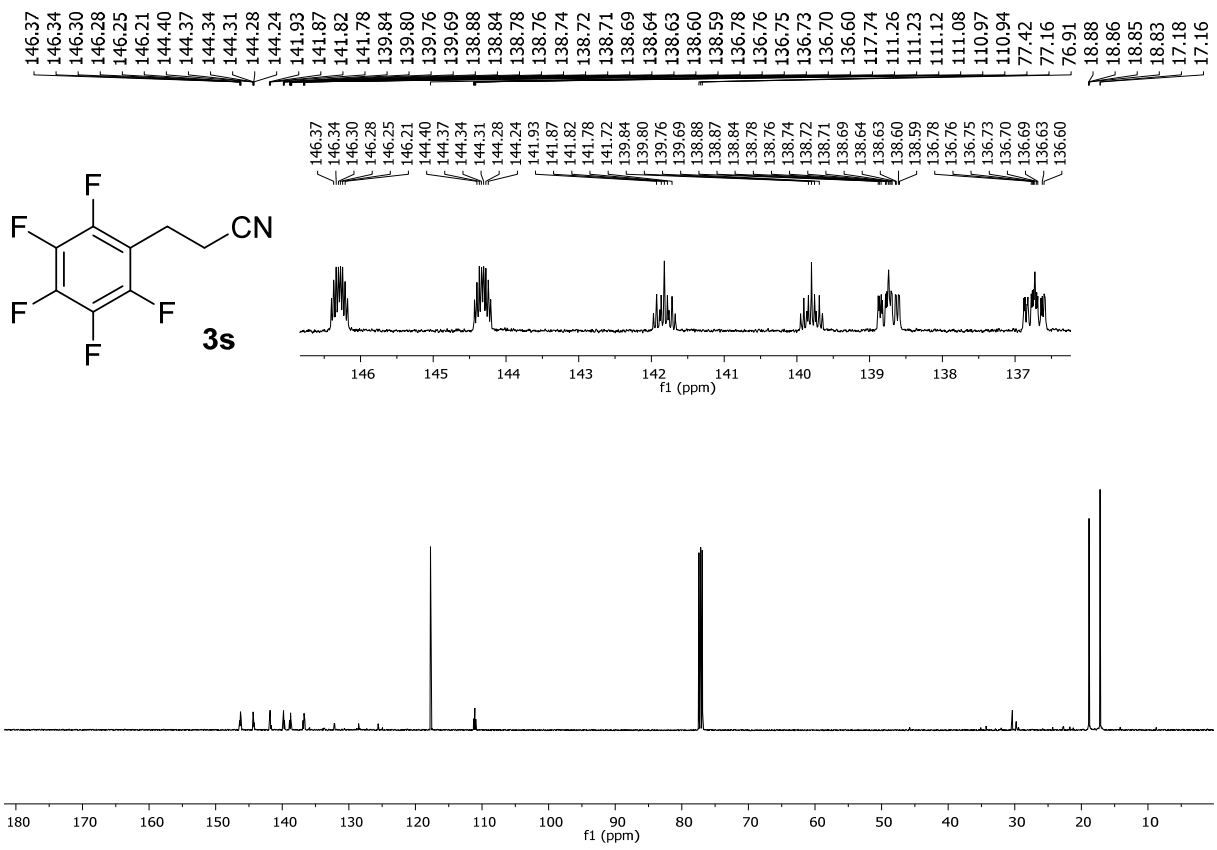


3-(Perfluorophenyl)propanenitrile (3s)

^{1}H-NMR

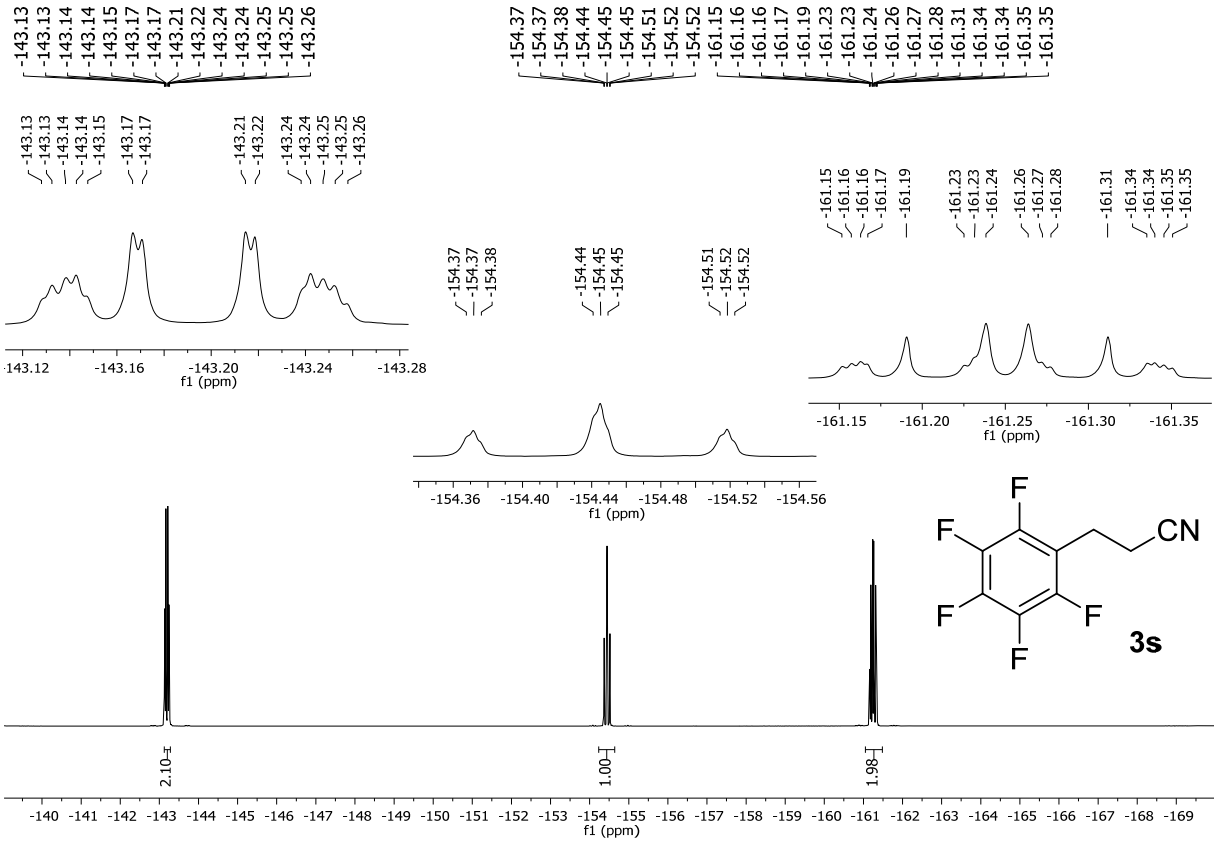


^{13}C-NMR



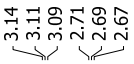
3-(Perfluorophenyl)propanenitrile (3s)

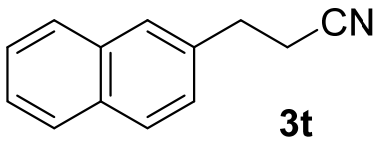
^{19}F-NMR



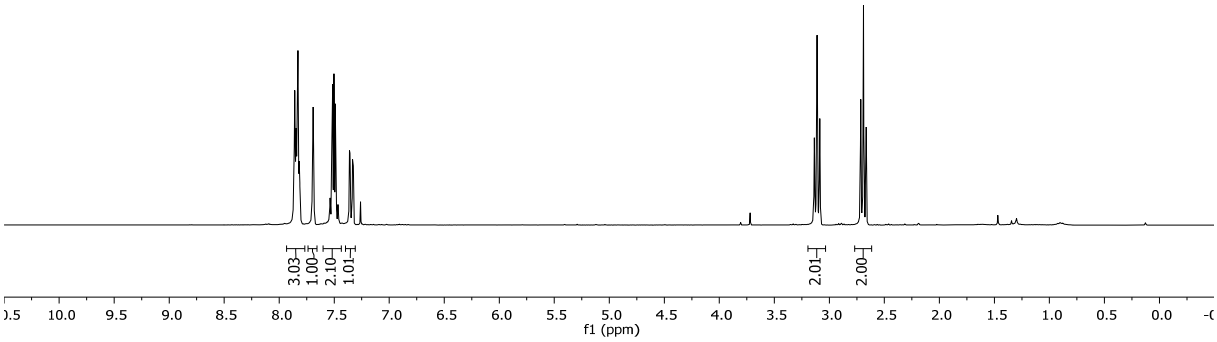
3-(Naphthalen-2-yl)propanenitrile (3t)

^{1}H-NMR

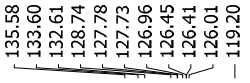


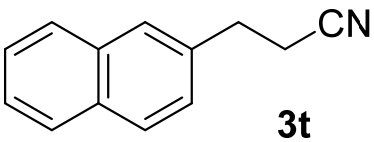


3t



^{13}C-NMR





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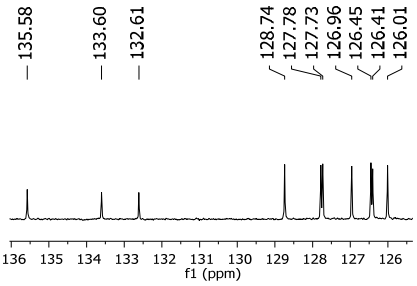
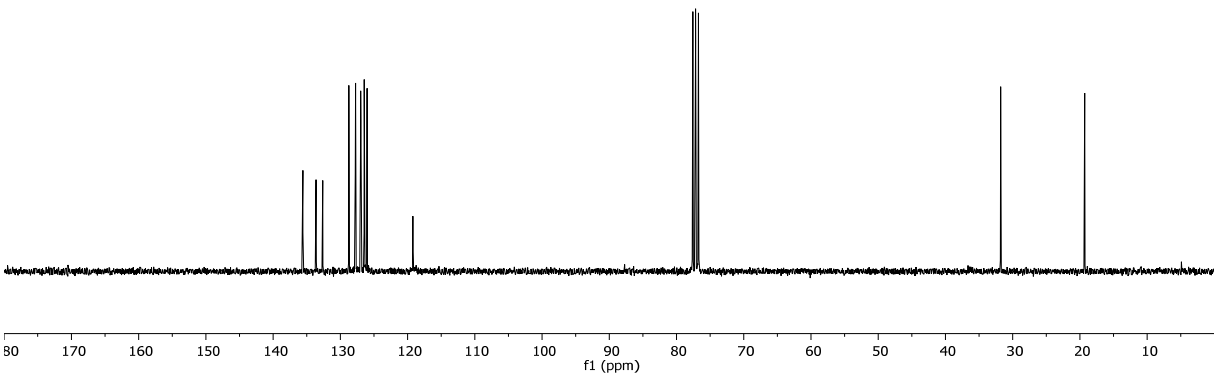
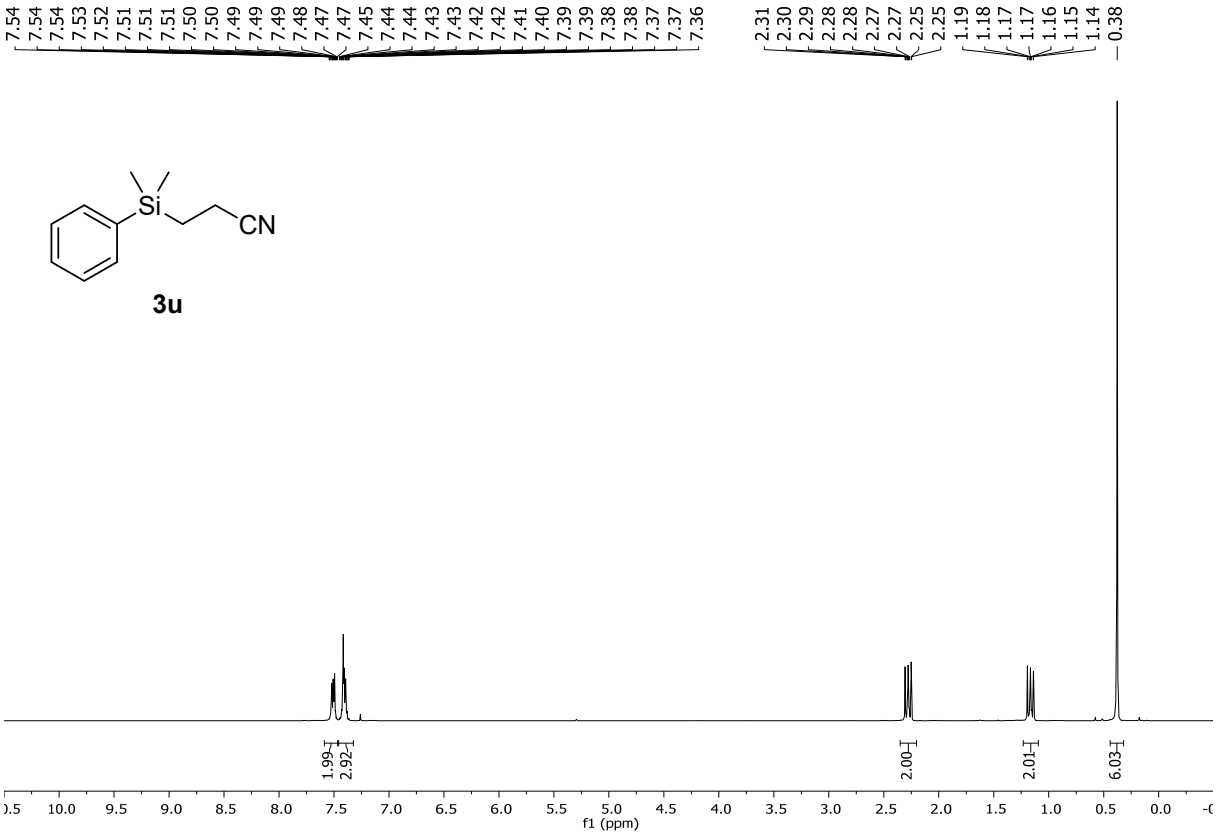




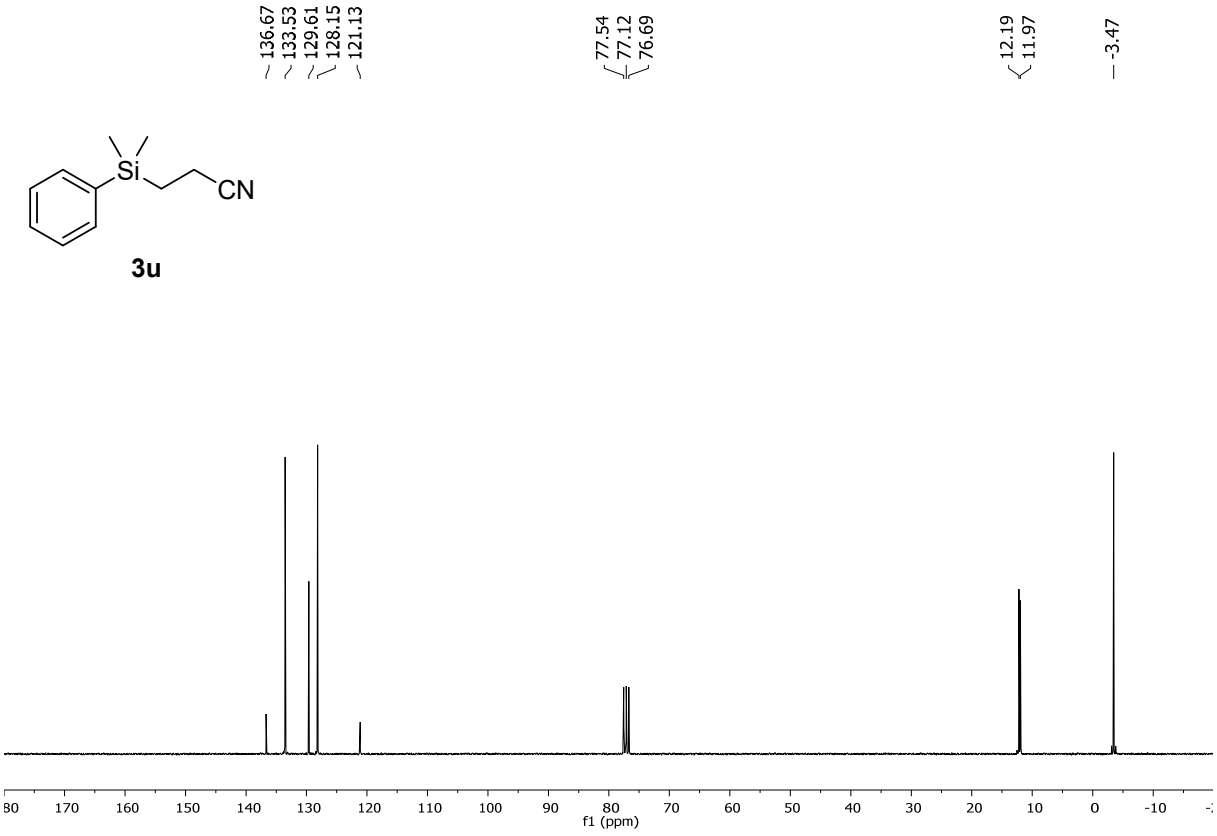
3-(Dimethyl(phenyl)silyl)propanenitrile (3u)

^{1}H-NMR



3u

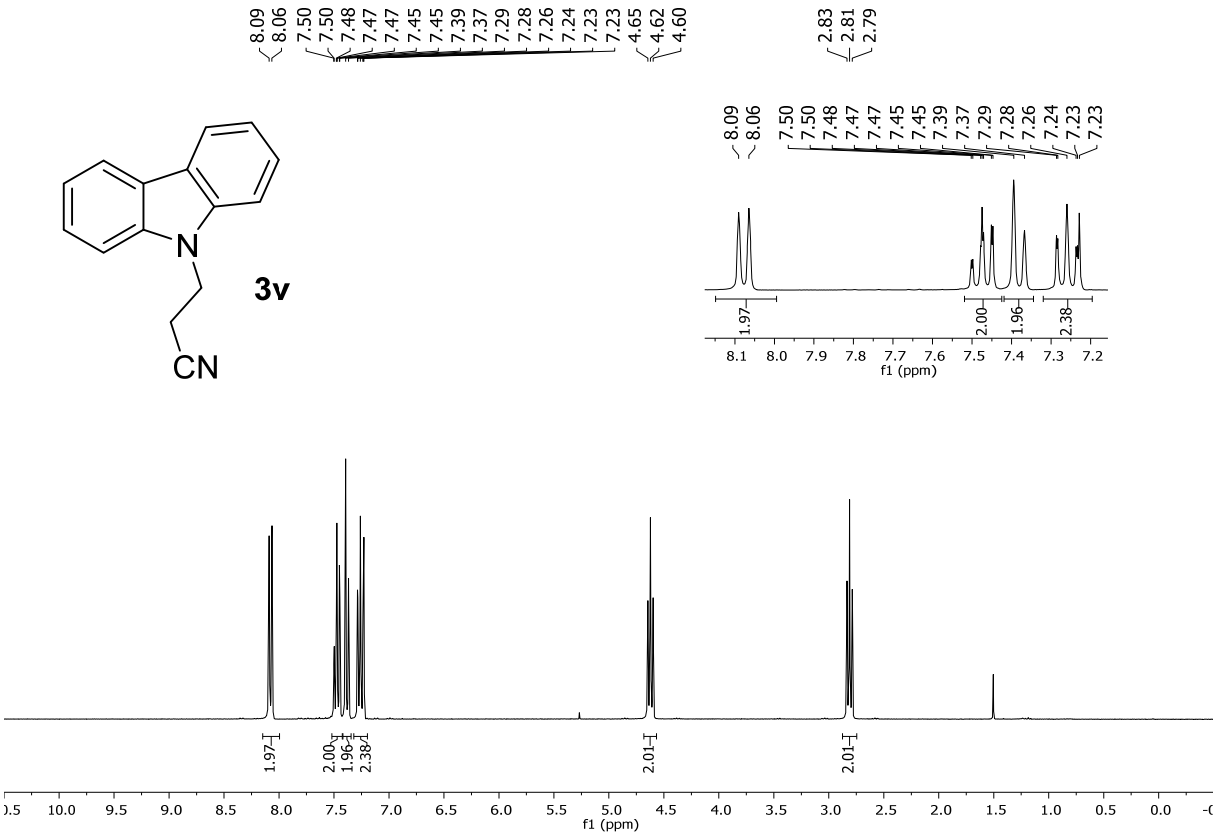
^{13}C-NMR



3u

3-(9*H*-Carbazol-9-yl)propanenitrilen (3v)

^{1}H-NMR



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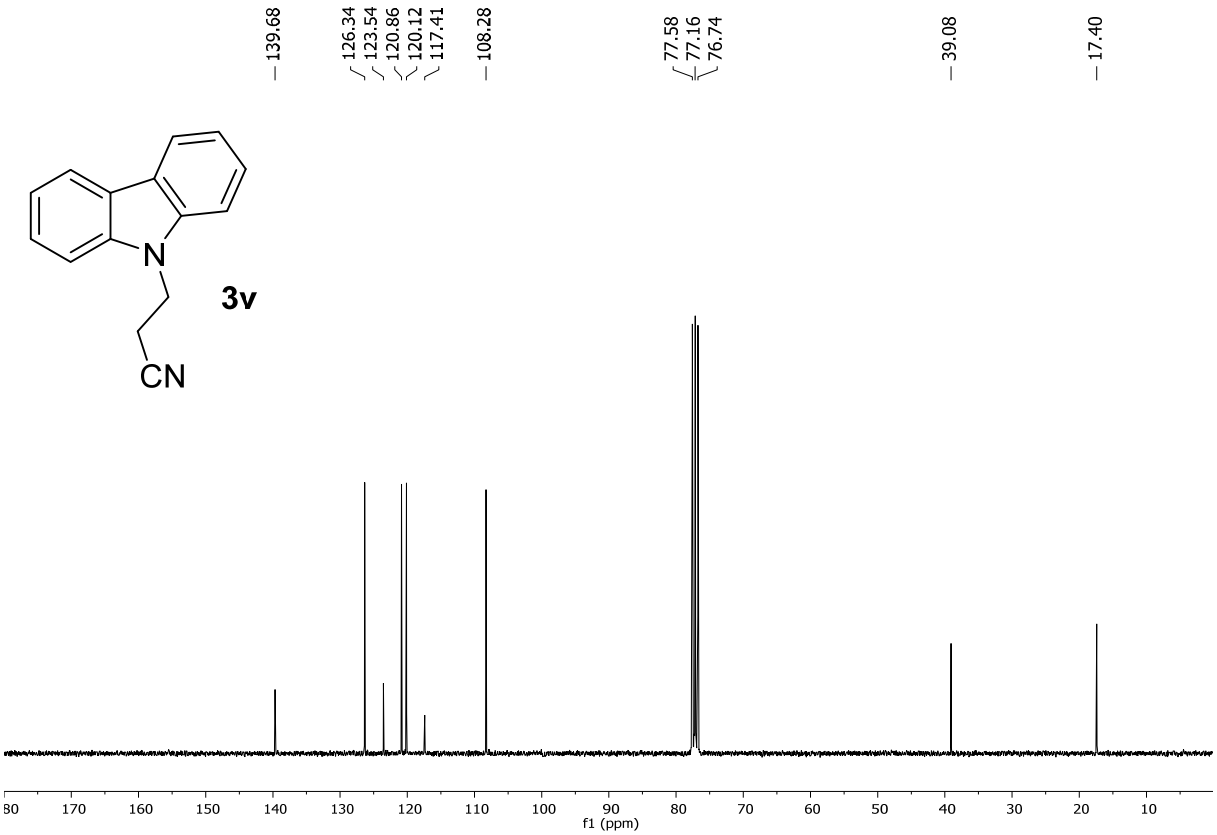
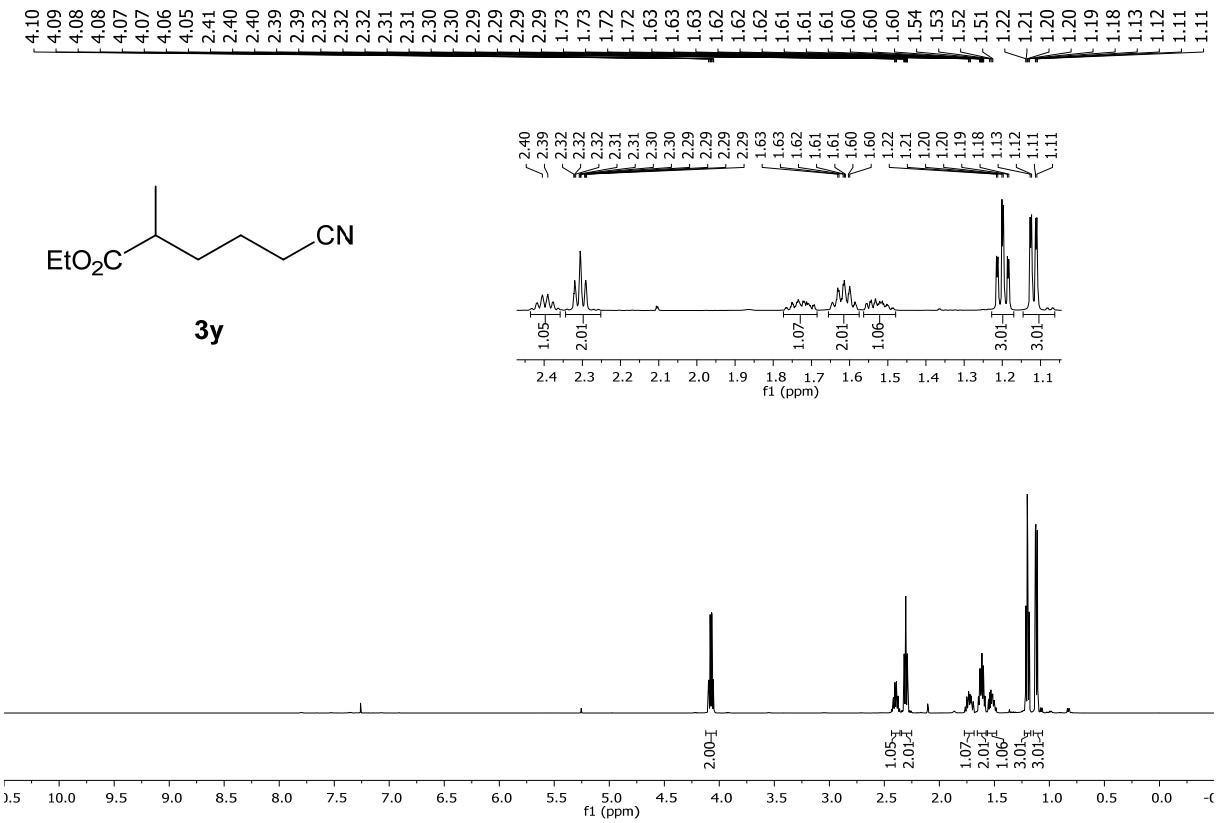
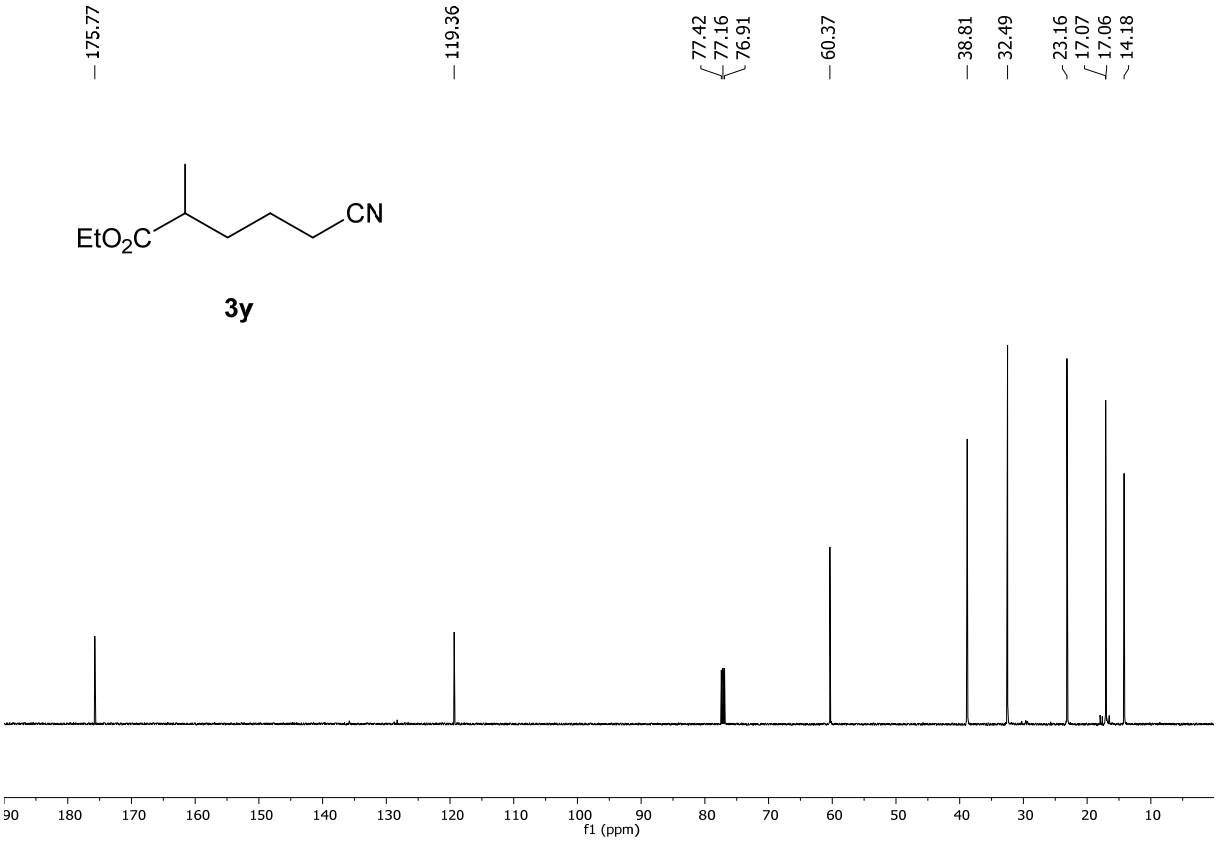


Ethyl 5-cyano-2-methylpentanoate (3y)

^{1}H-NMR

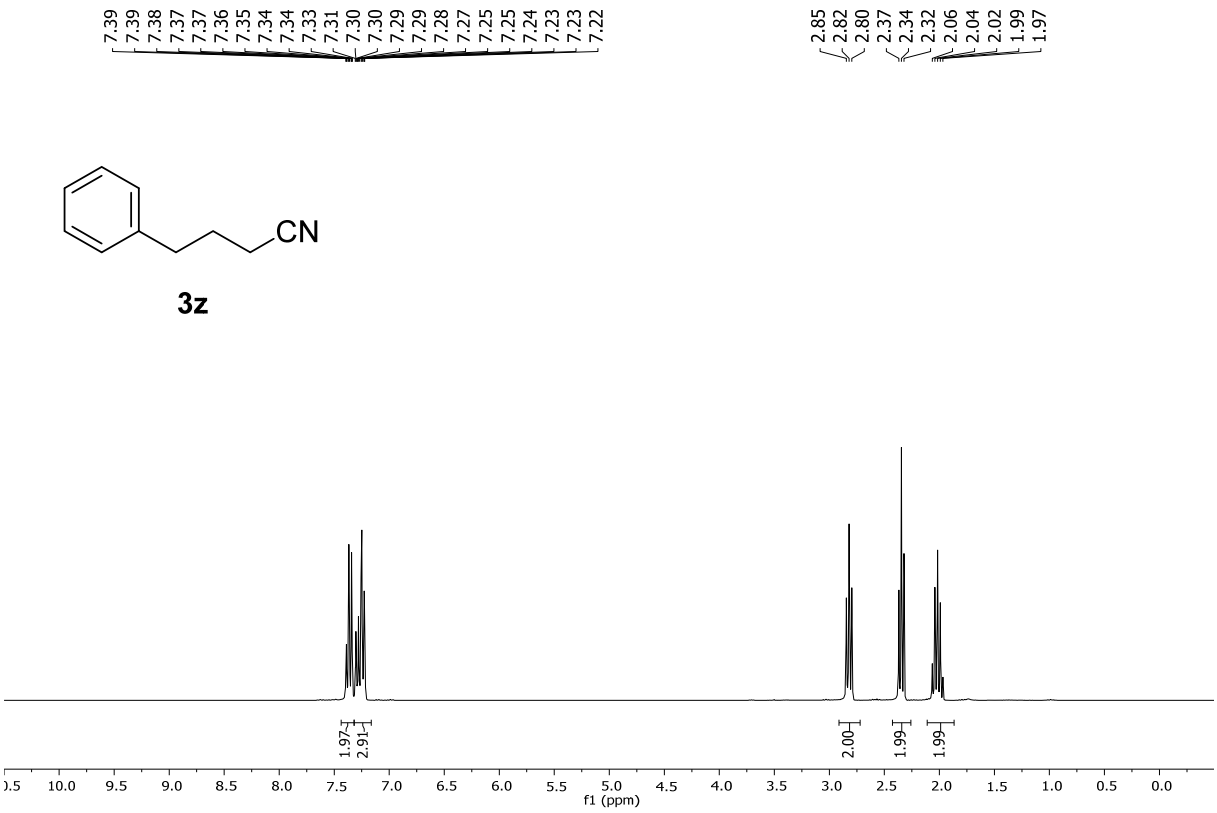


^{13}C-NMR

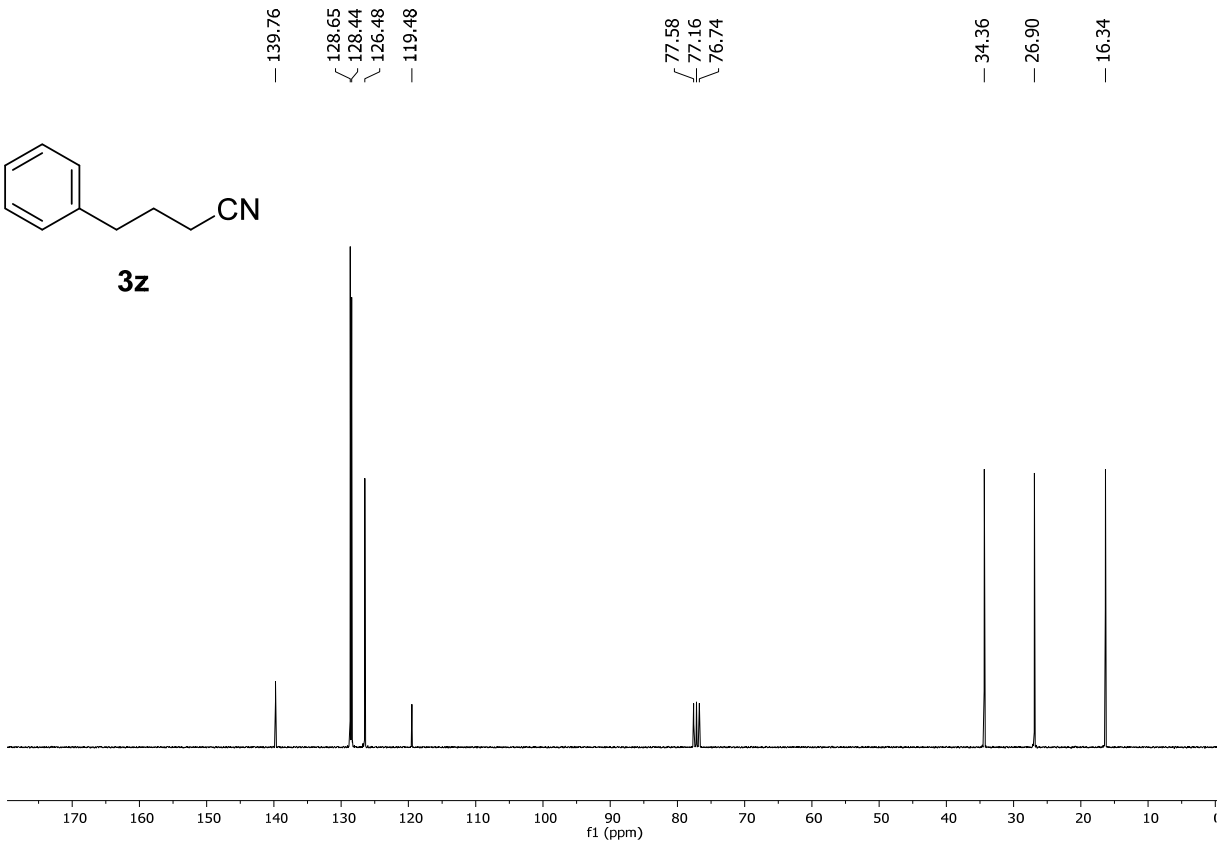


4-Phenylbutanenitrile (3z)

^{1}H-NMR

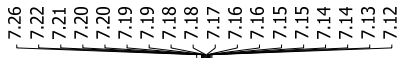


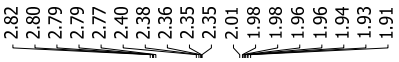
^{13}C-NMR

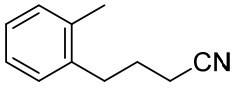


4-(o-Tolyl)butanenitrile (3aa)

^{1}H-NMR







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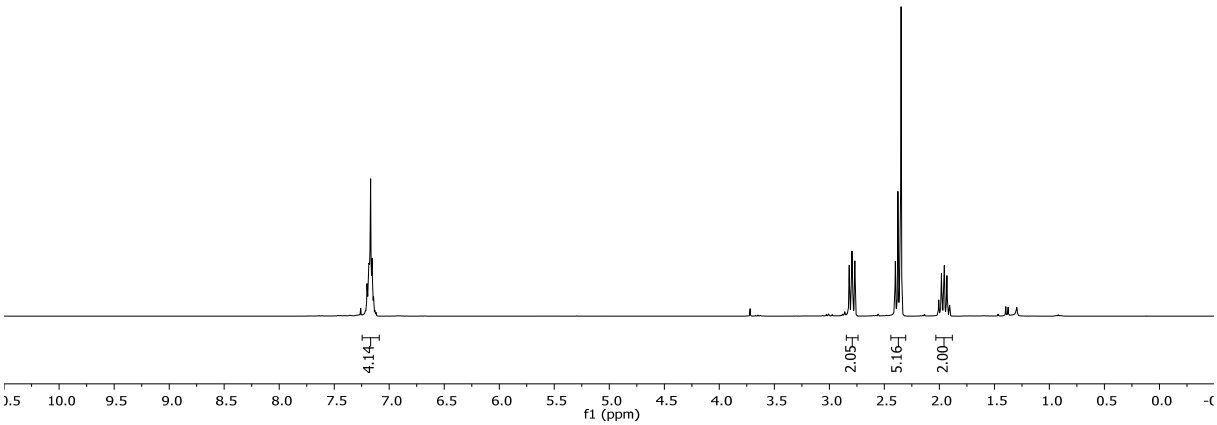

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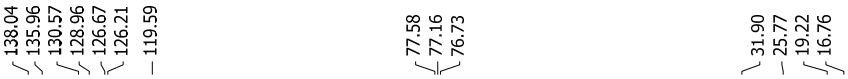

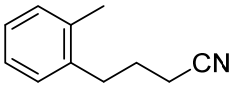

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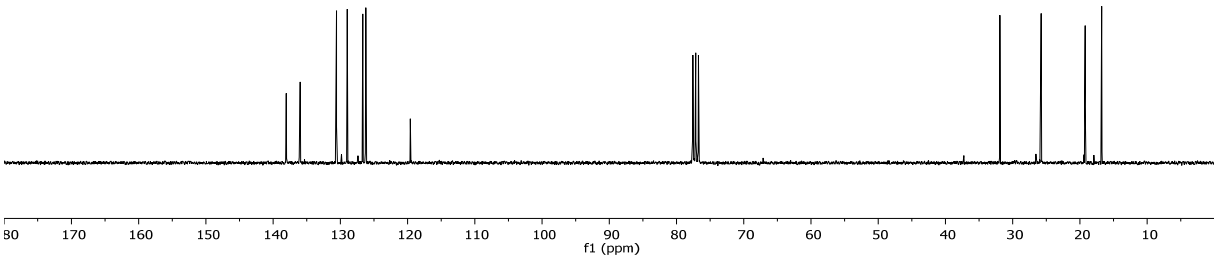
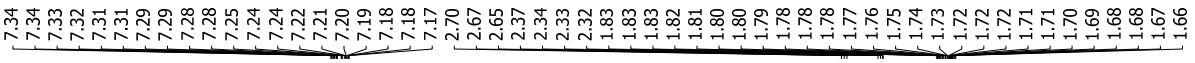
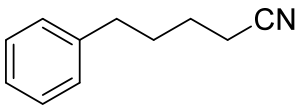


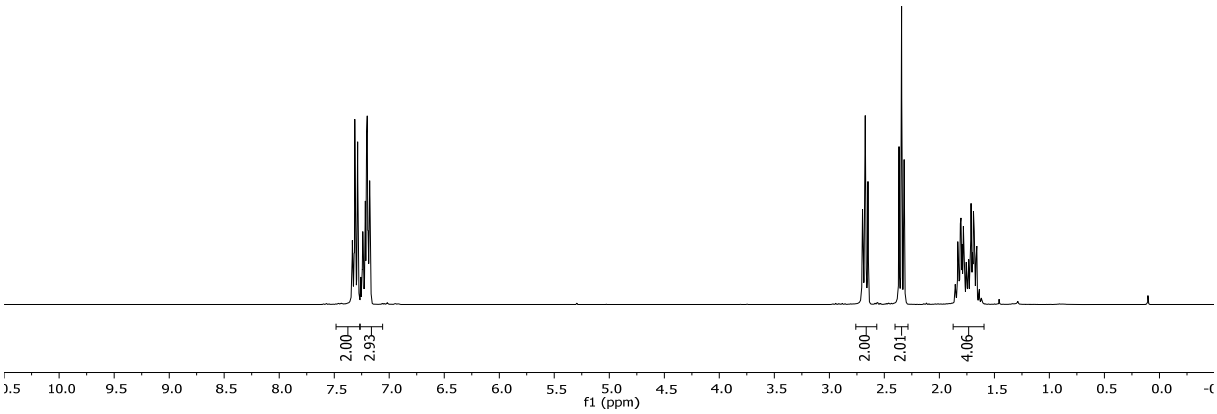
5-Phenylpentanenitrile (3ab)

^{1}H-NMR





3ab



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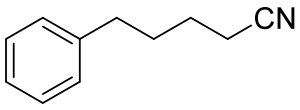

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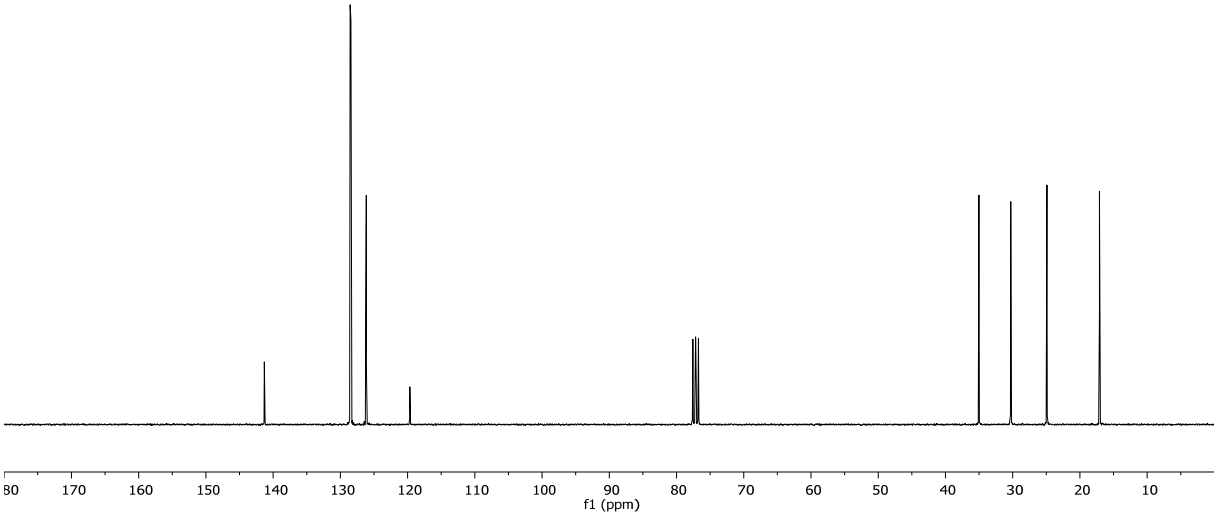
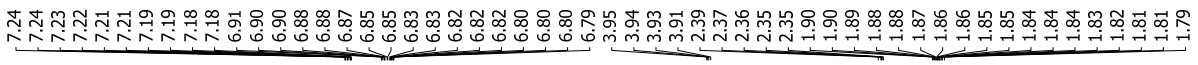
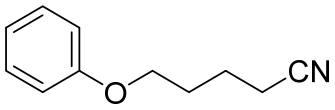


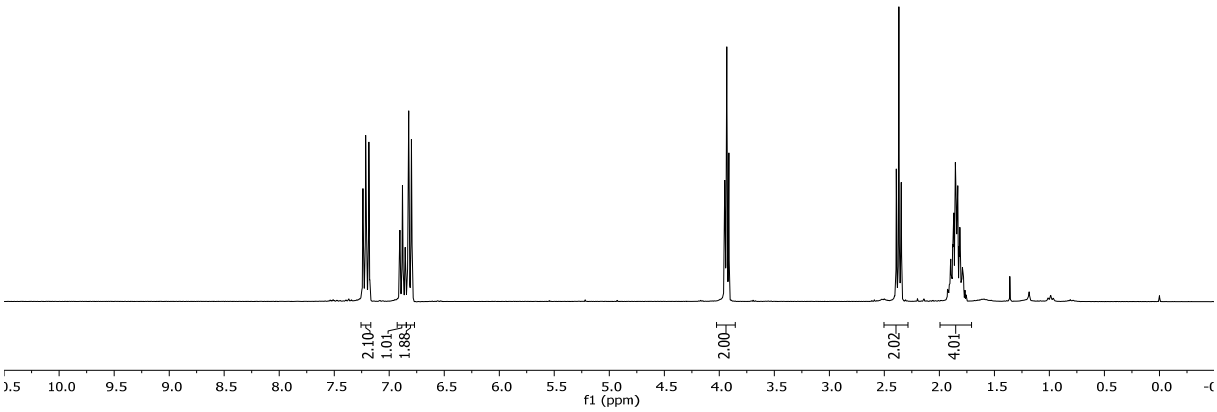
5-Phenoxypentanenitrile (3ac)

^{1}H-NMR

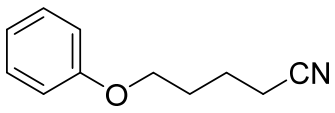




3ac



^{13}C-NMR



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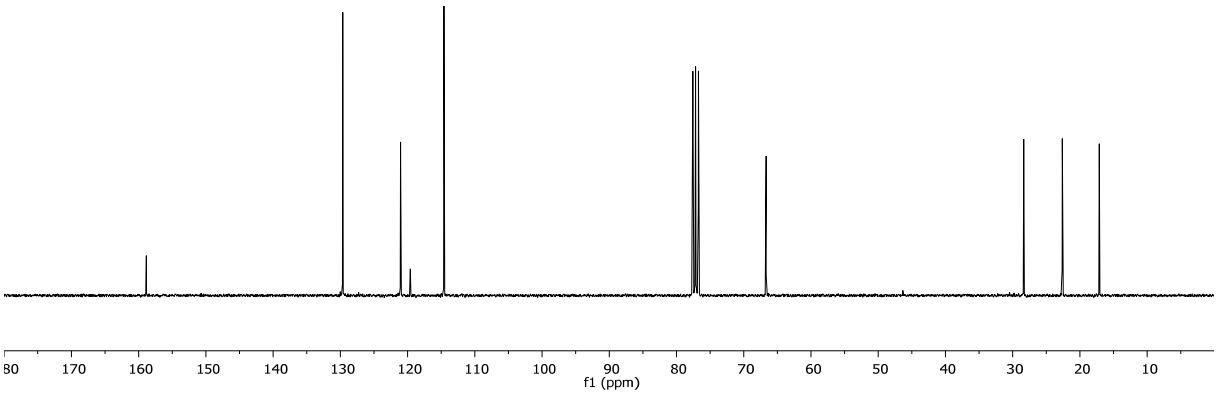
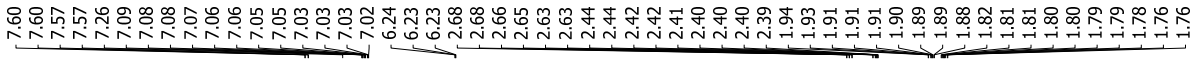
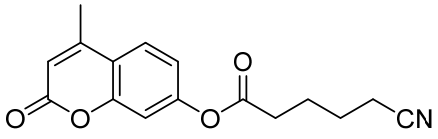


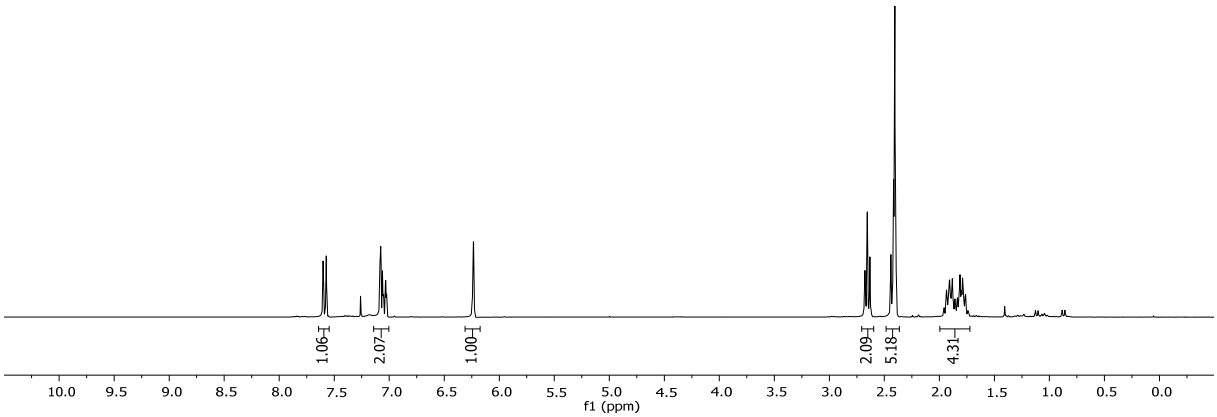
4-Methyl-2-oxo-2*H*-chromen-7-yl 5-cyanopentanoate (3ad)

^{1}H-NMR

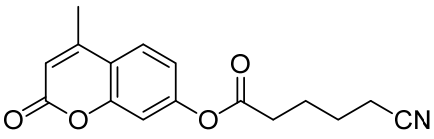




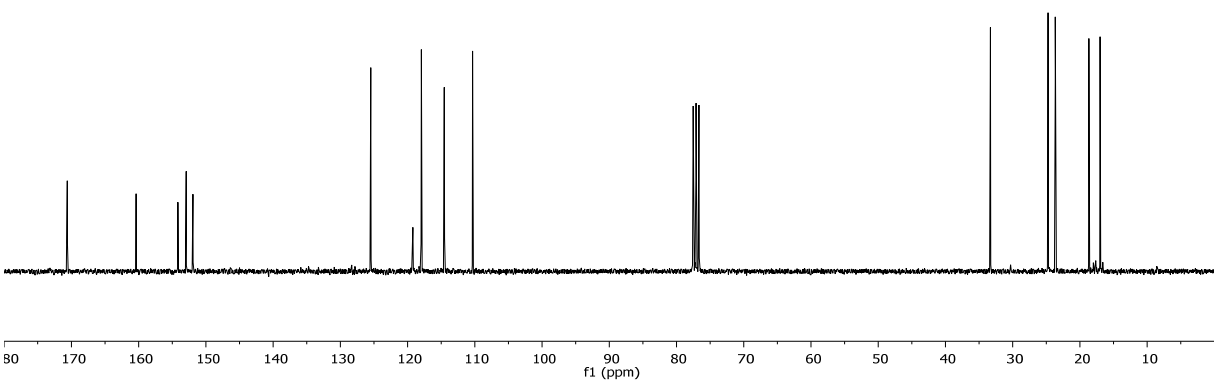
3ad



^{13}C-NMR

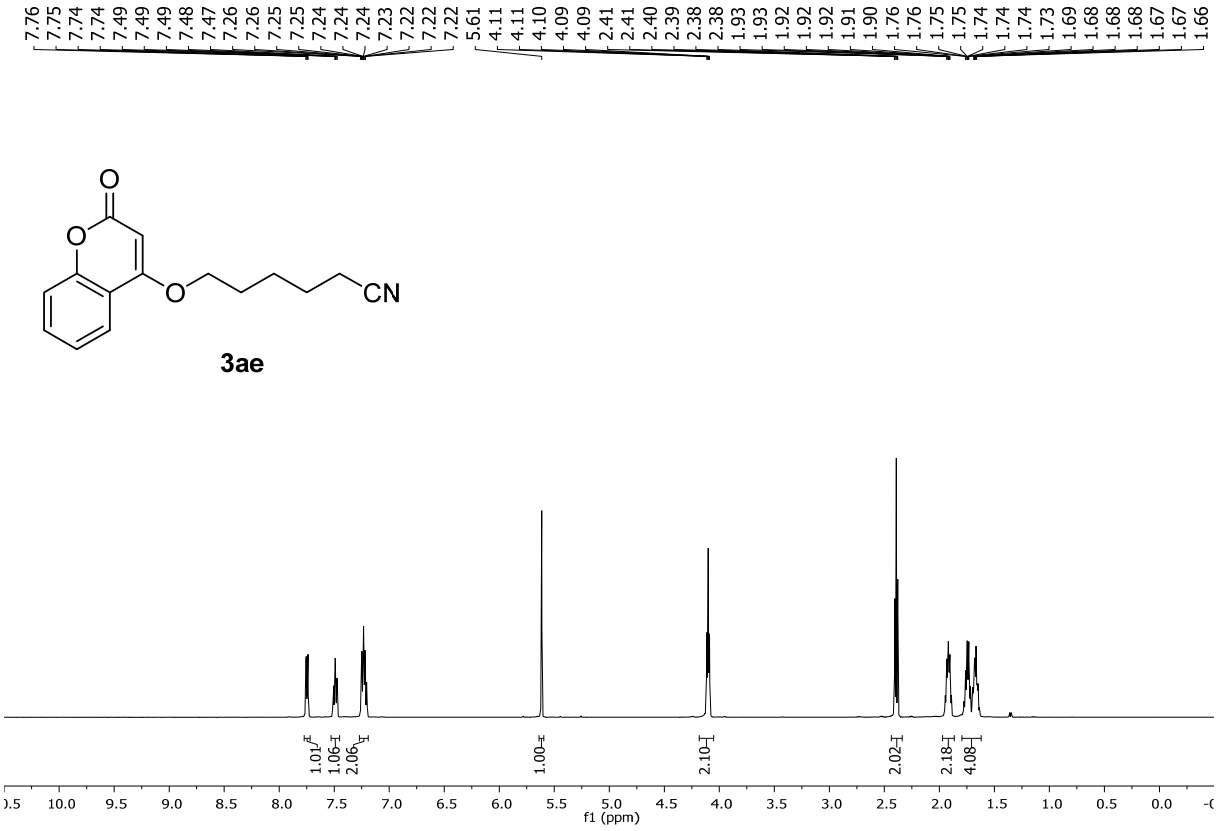


3ad

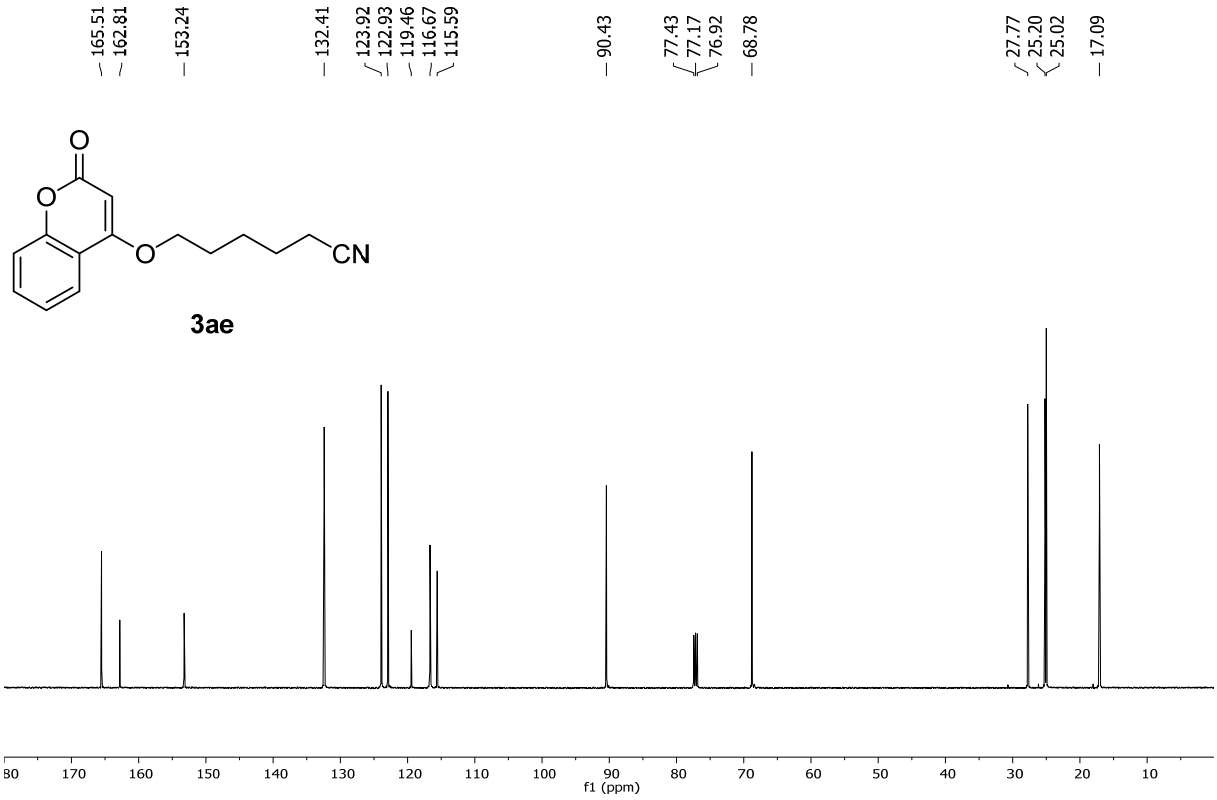


6-((2-Oxo-2*H*-chromen-4-yl)oxy)hexanenitrile (3ae)

^{1}H-NMR

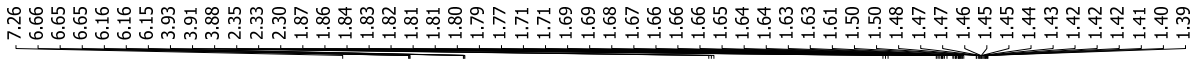


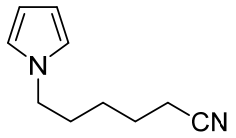
^{13}C-NMR



6-(1*H*-Pyrrol-1-yl)hexanenitrile (3af)

^{1}H-NMR





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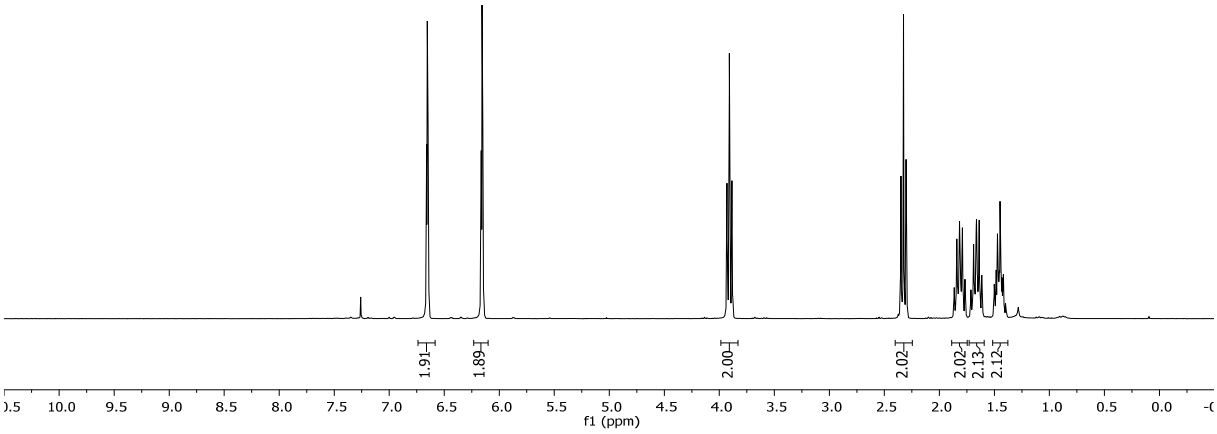
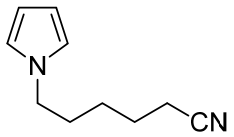


^{13}C-NMR



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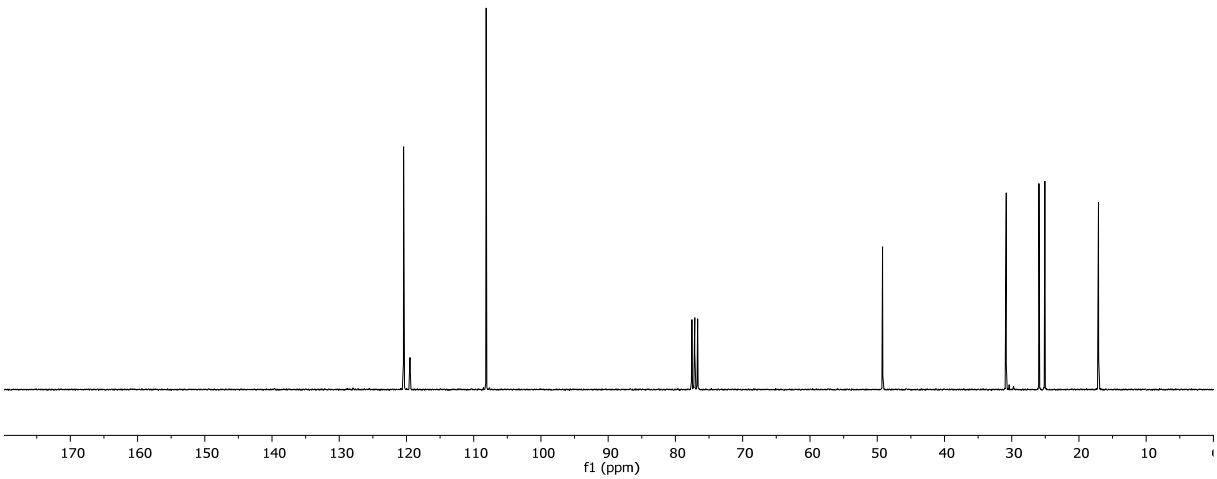
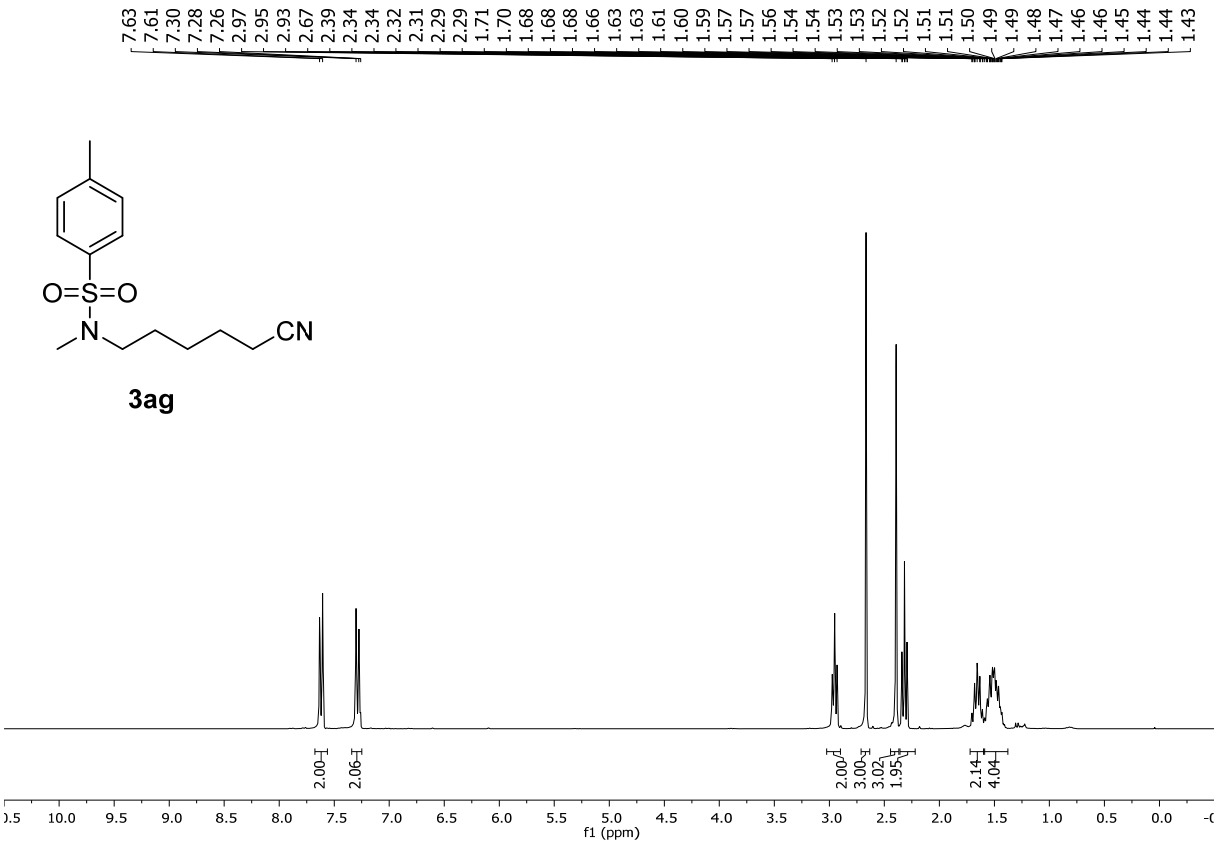
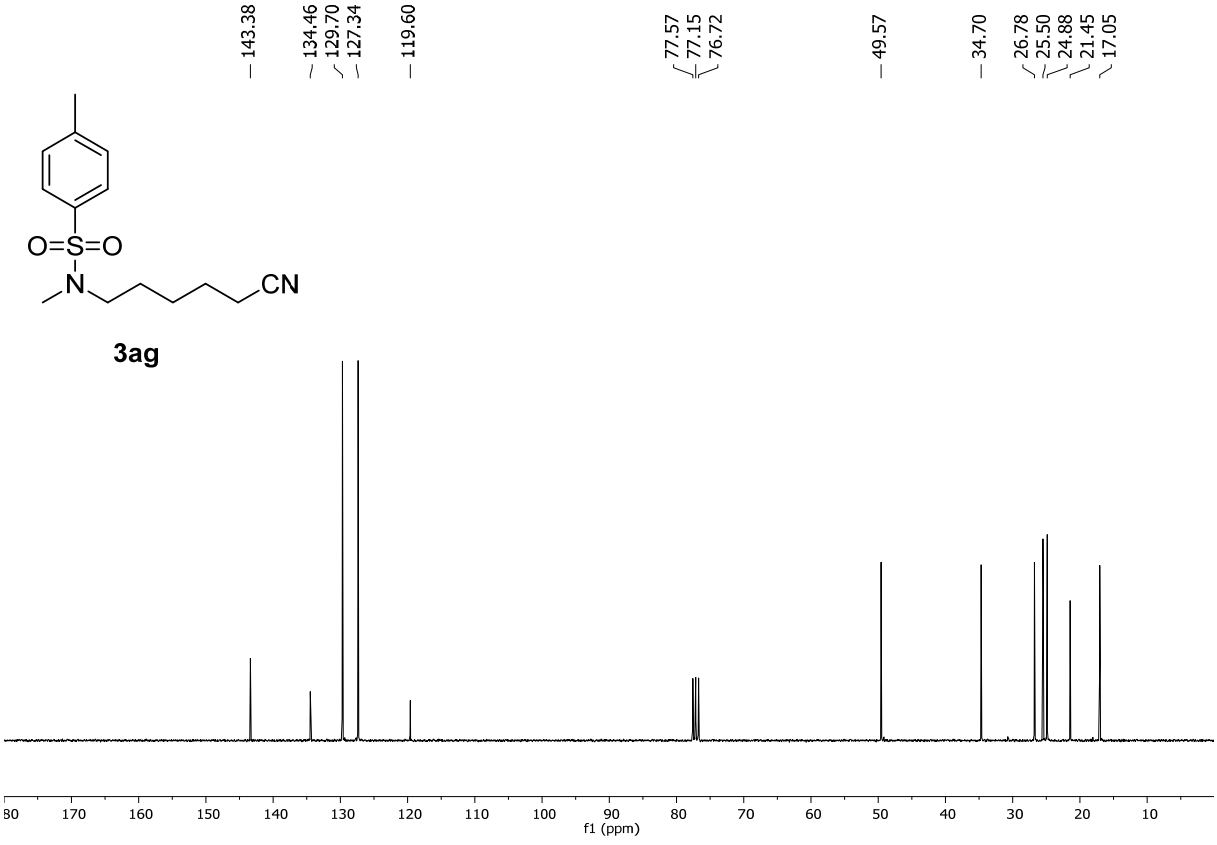


N-(5-Cyanopentyl)-N,4-dimethylbenzenesulfonamide (3ag)

^{1}H-NMR

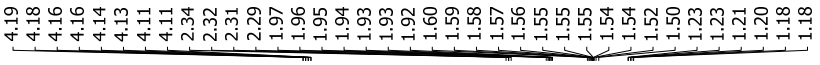


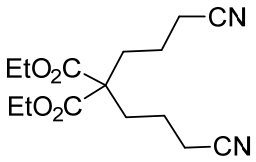
^{13}C-NMR



Diethyl 2,2-bis(3-cyanopropyl)malonate (3ah)

^{1}H-NMR





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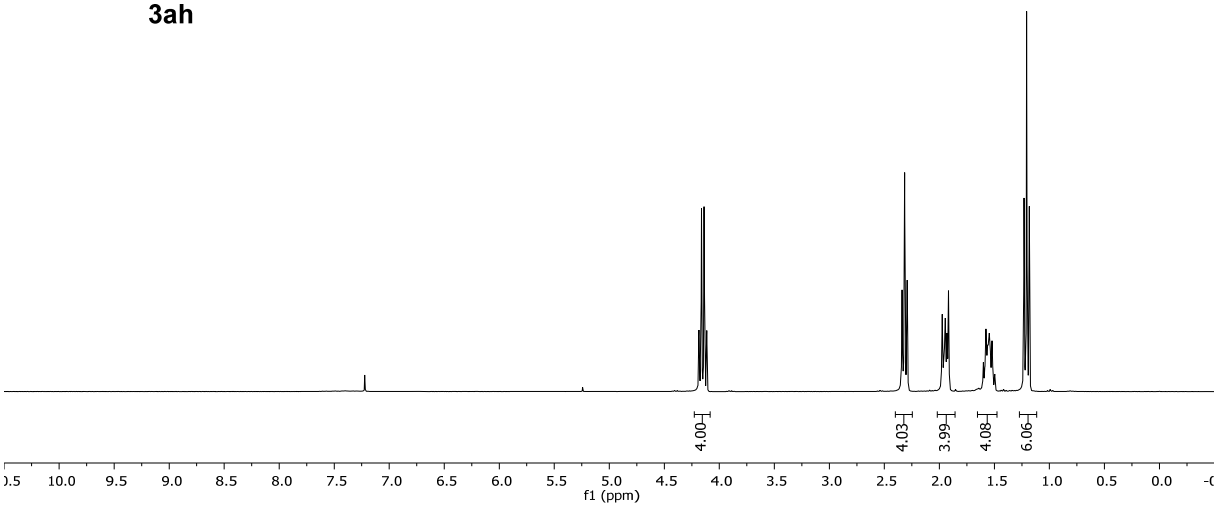
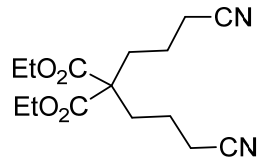


^{13}C-NMR



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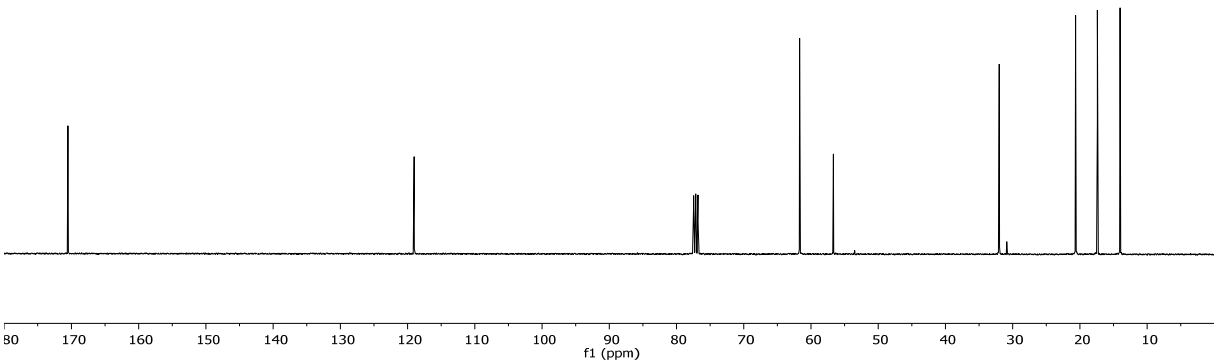
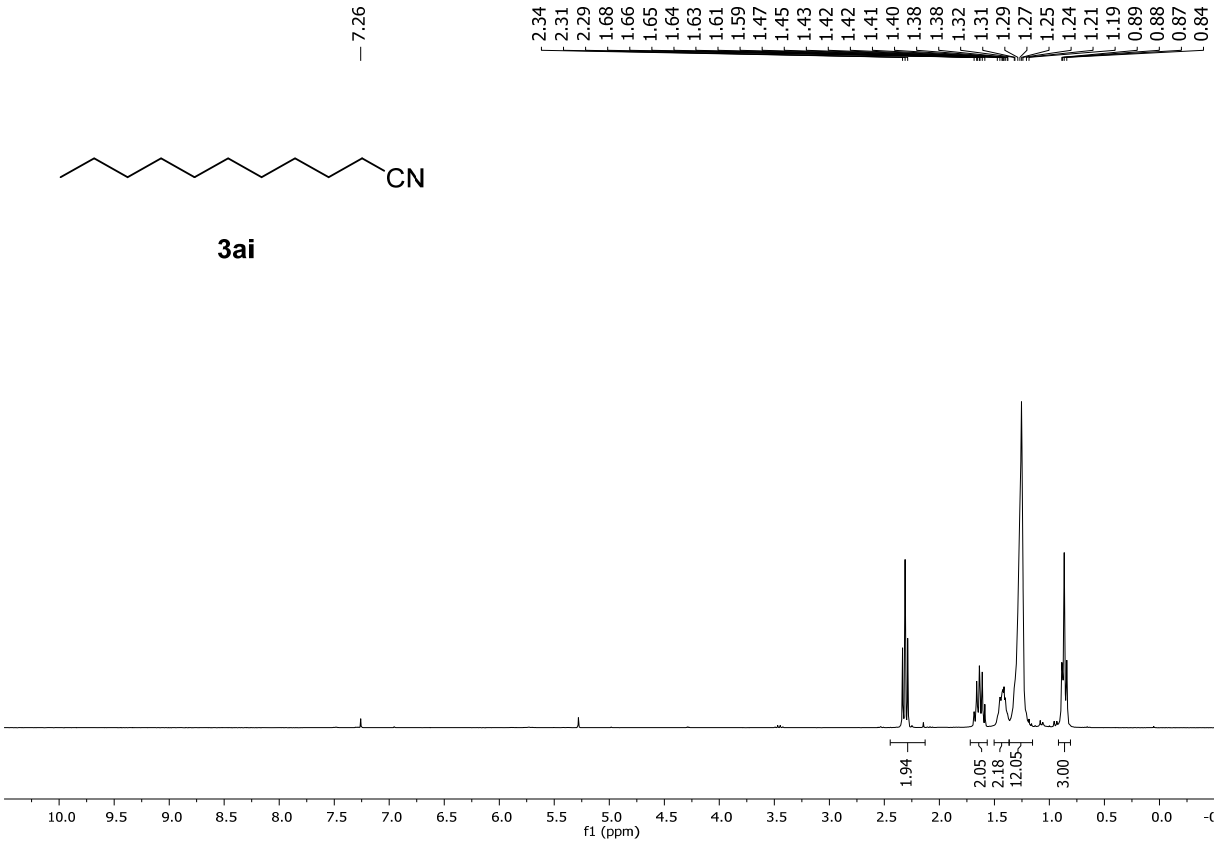


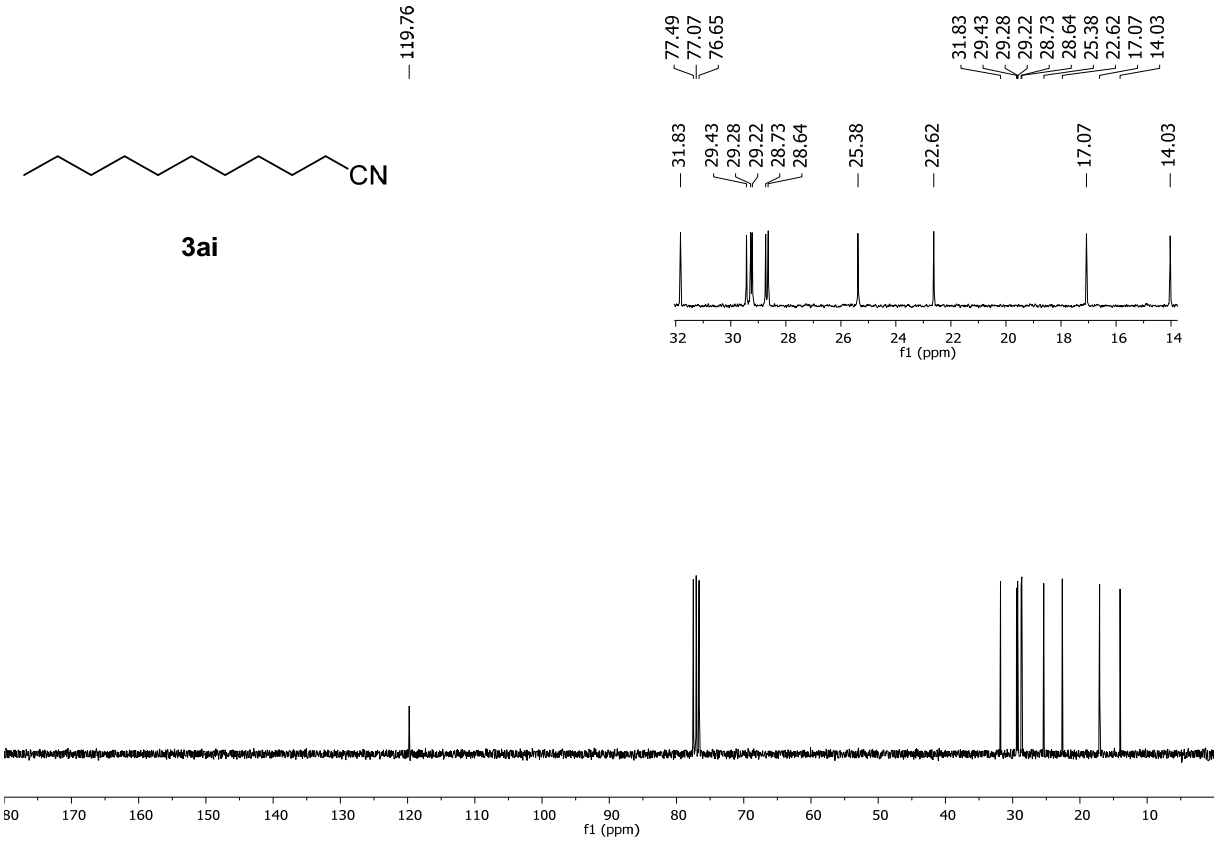
Undecanenitrile (3ai)

^{1}H-NMR



3ai

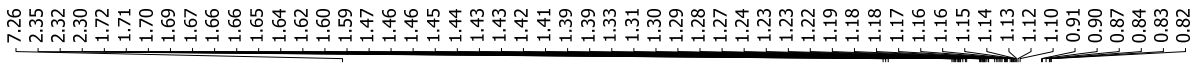
^{13}C-NMR

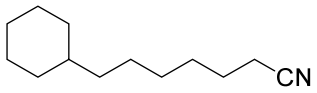


3ai

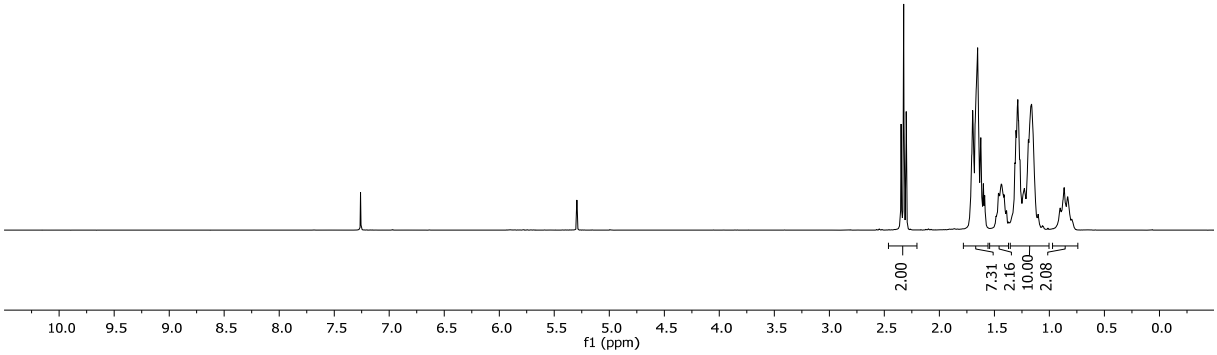
7-Cyclohexylheptanenitrile (3aj)

^{1}H-NMR

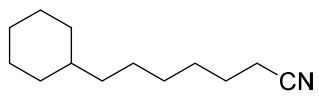




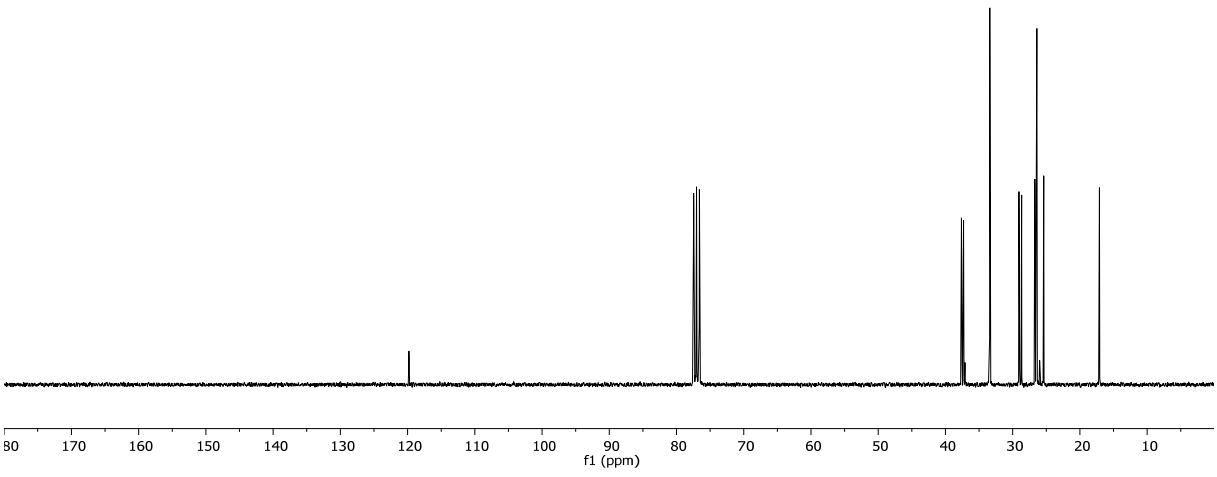
3aj



^{13}C-NMR

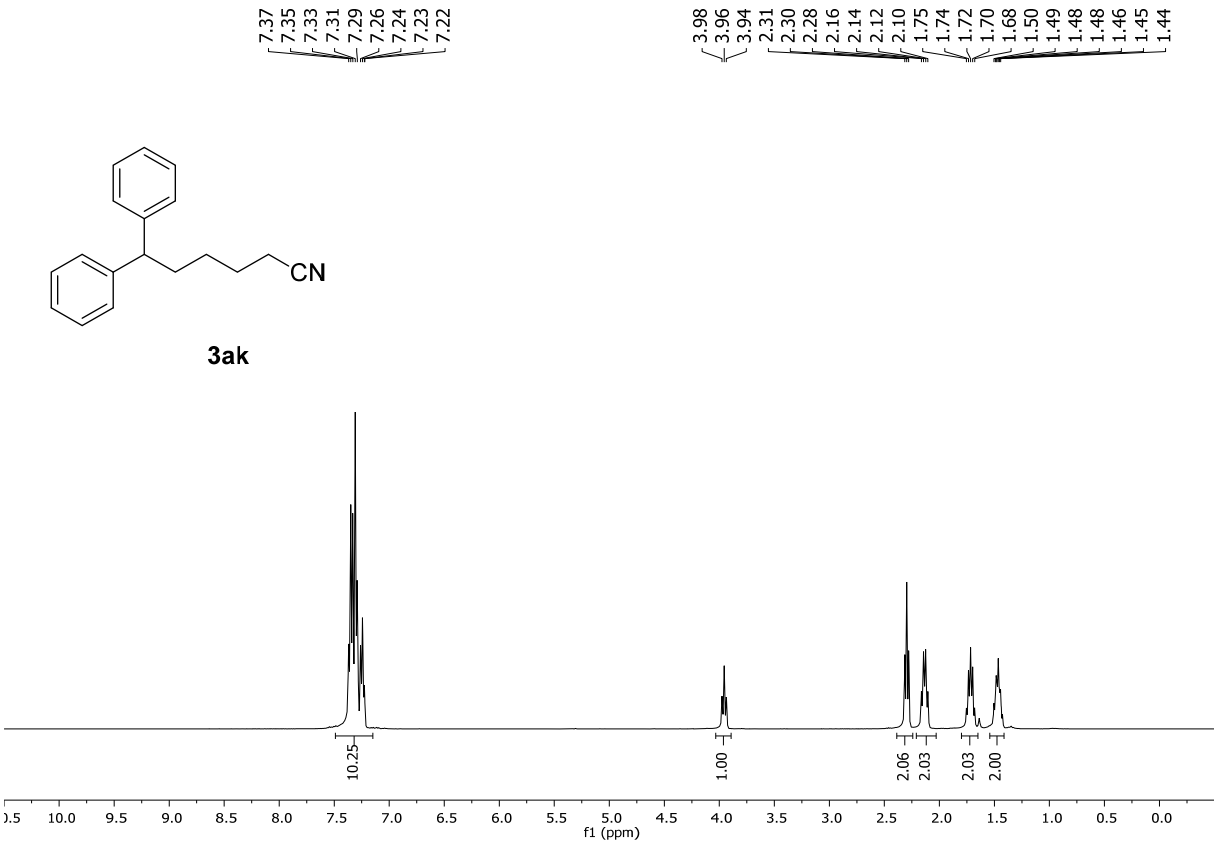


3aj

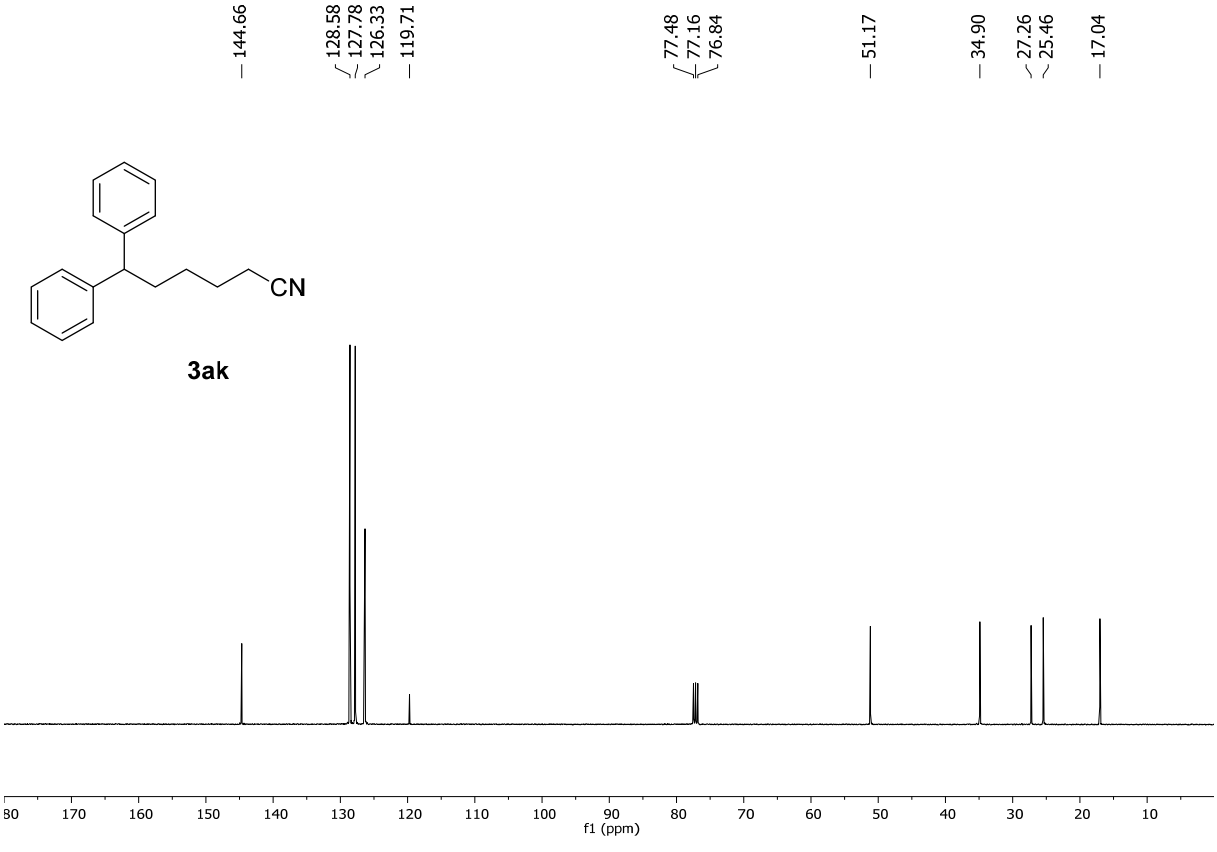


6,6-Diphenylhexanenitrile (3ak)

^{1}H NMR

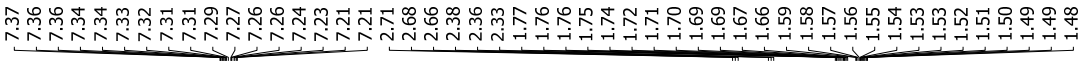


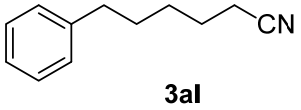
^{13}C NMR



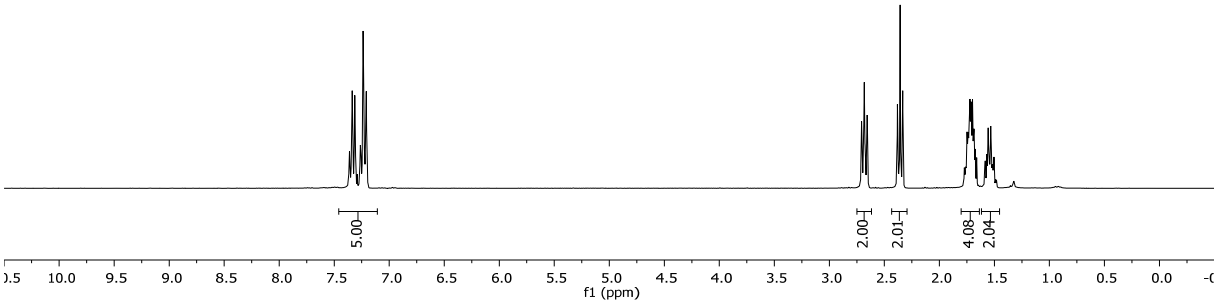
6-Phenylhexanenitrile (3al)

^{1}H-NMR

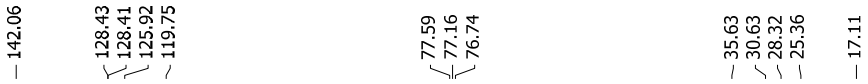


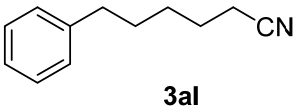


3al

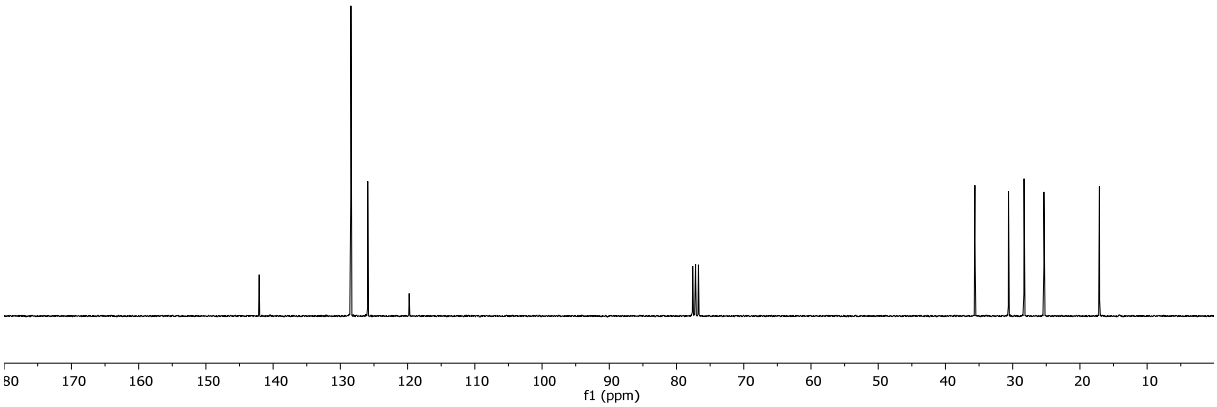


^{13}C-NMR



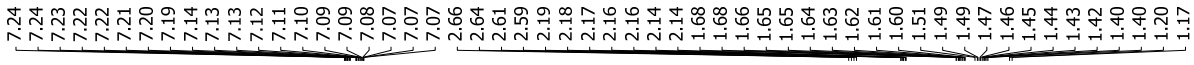


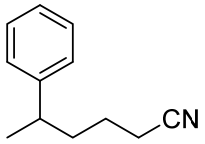
3al



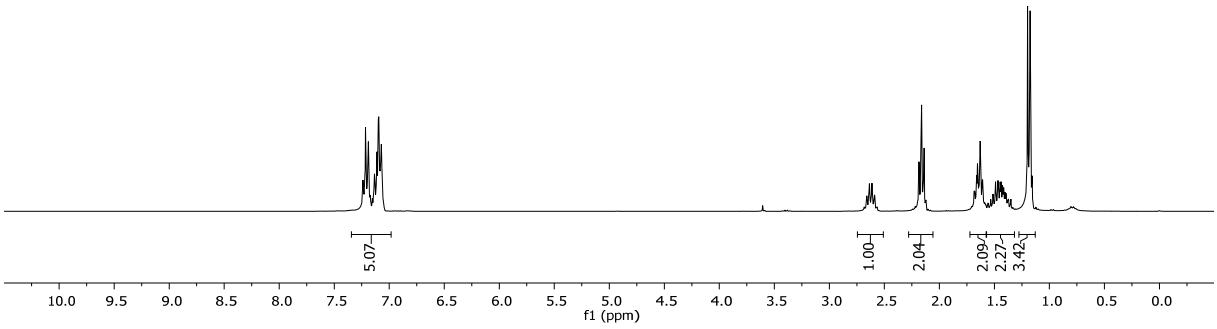
5-Phenylhexanenitrile (3am)

^{1}H-NMR

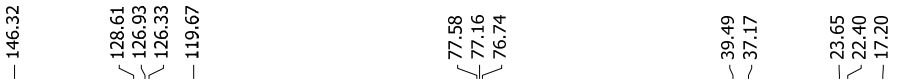


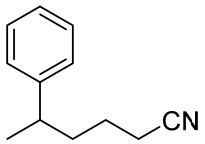


3am

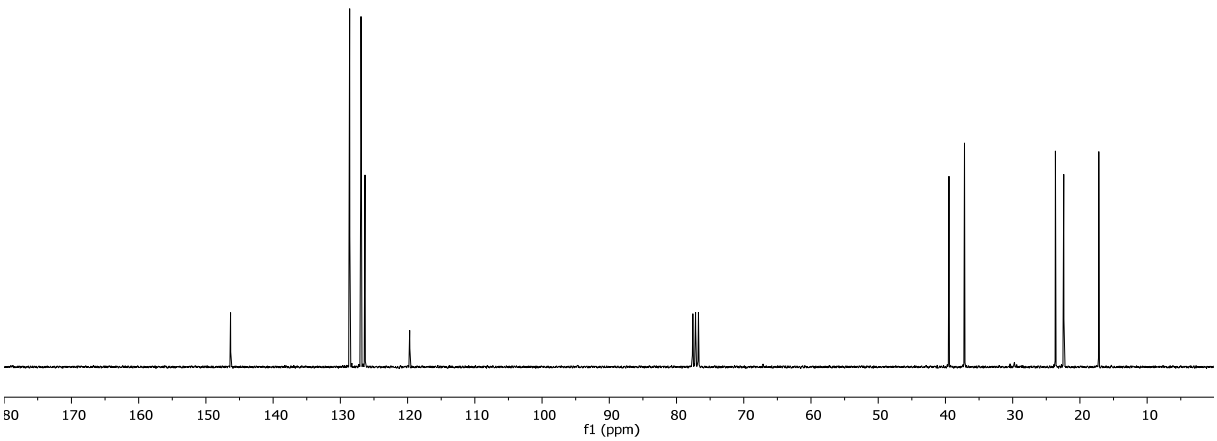


^{13}C-NMR



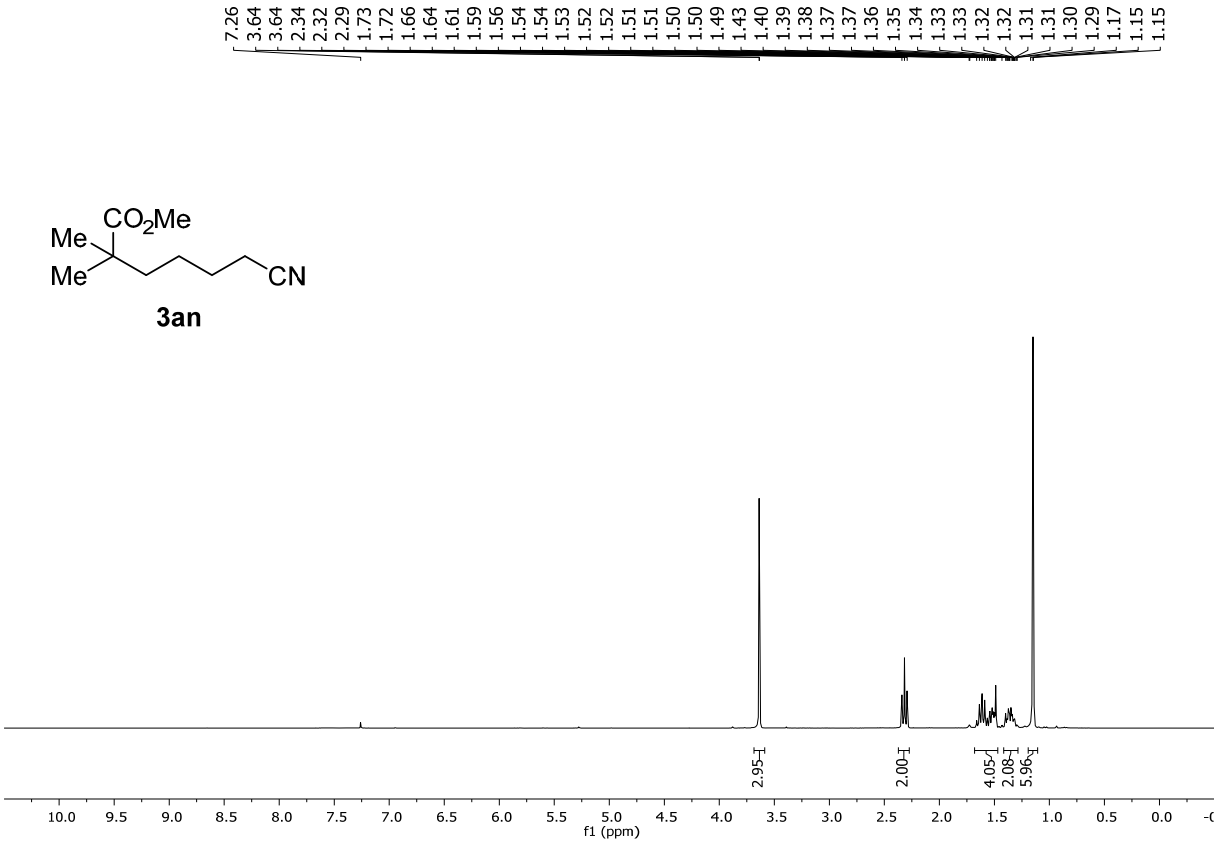


3am

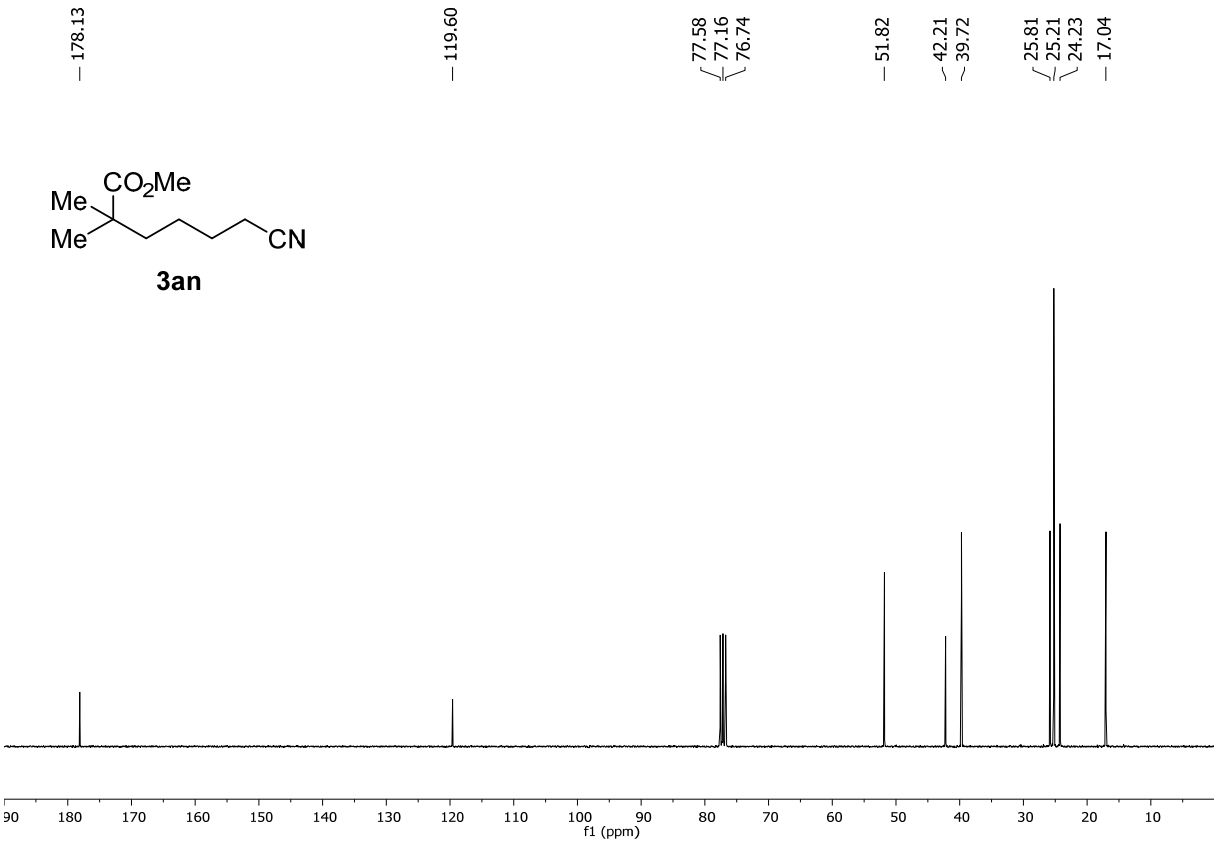


Methyl 6-cyano-2,2-dimethylhexanoate (3an)

^{1}H-NMR

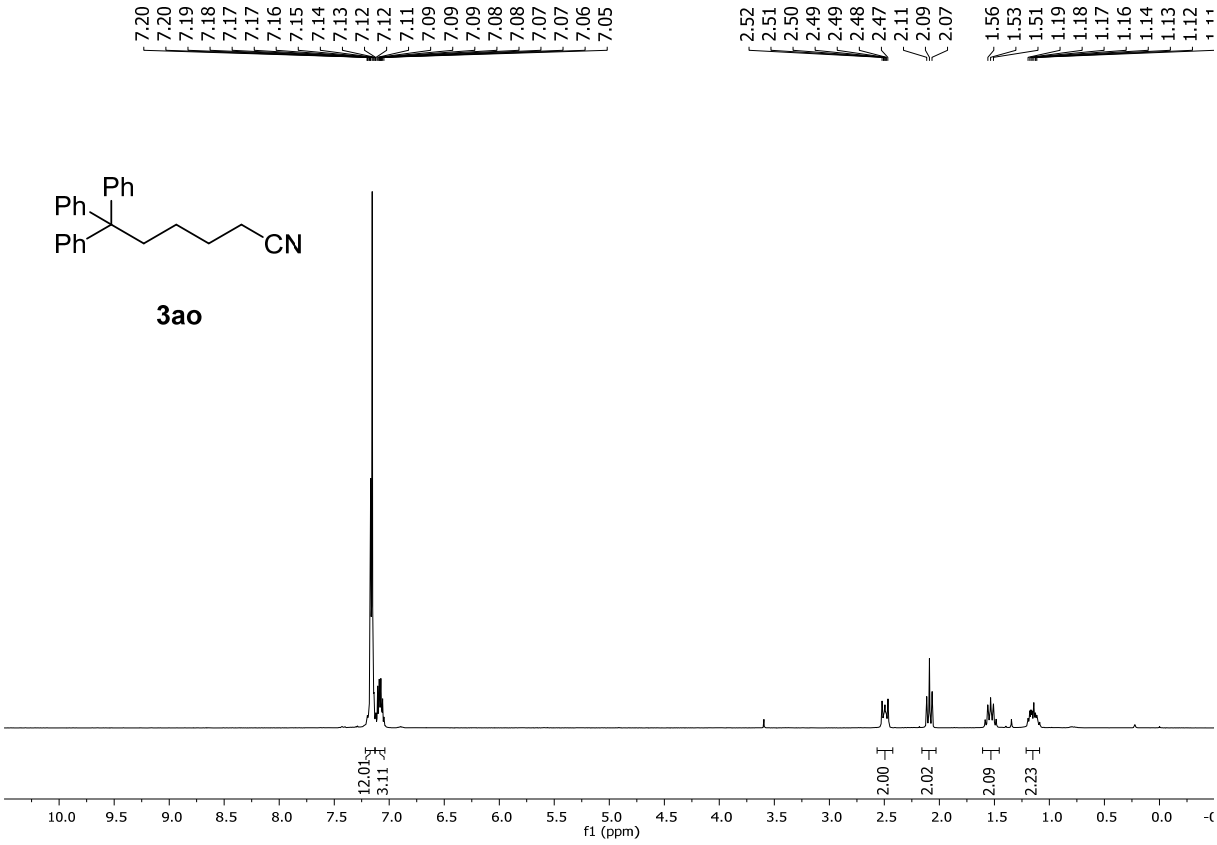


^{13}C-NMR

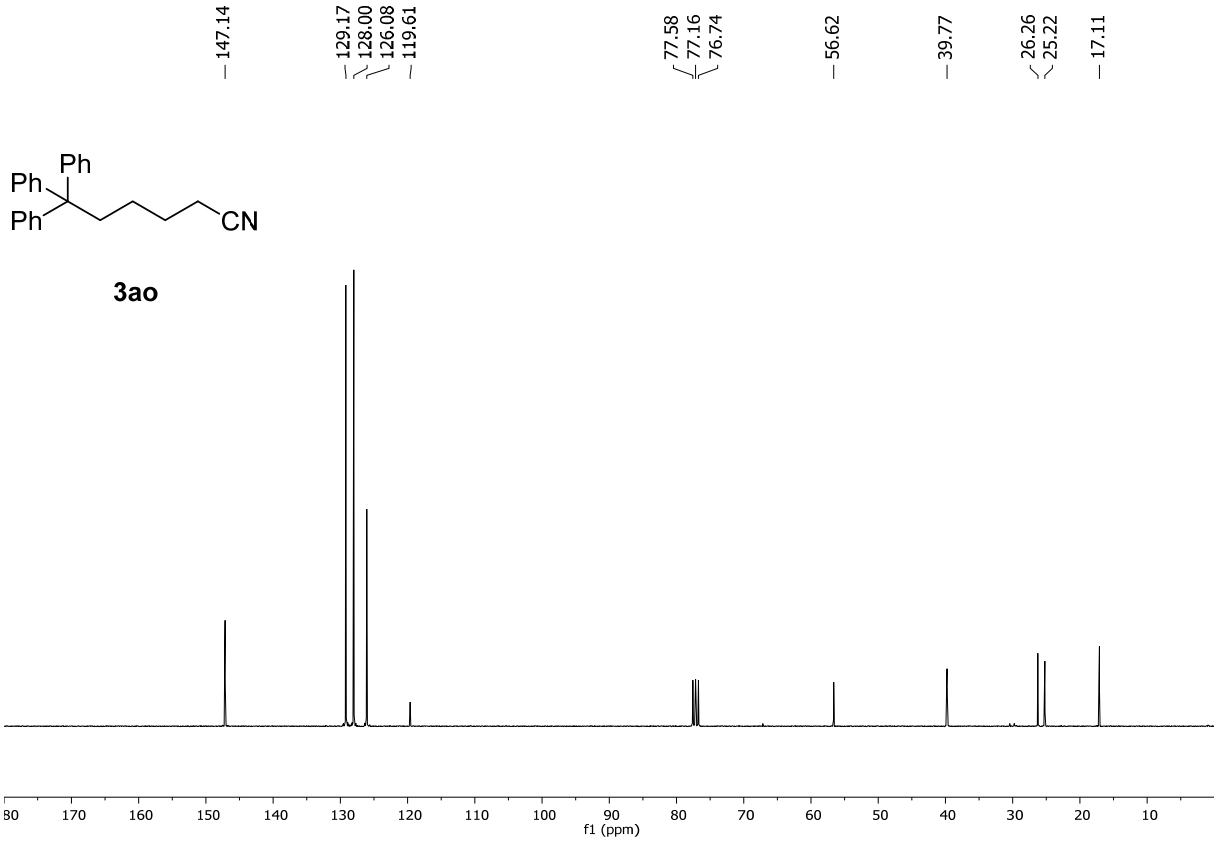


6,6,6-Triphenylhexanenitrile (3ao)

^{1}H-NMR

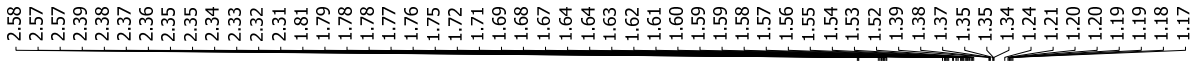


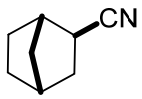
^{13}C-NMR



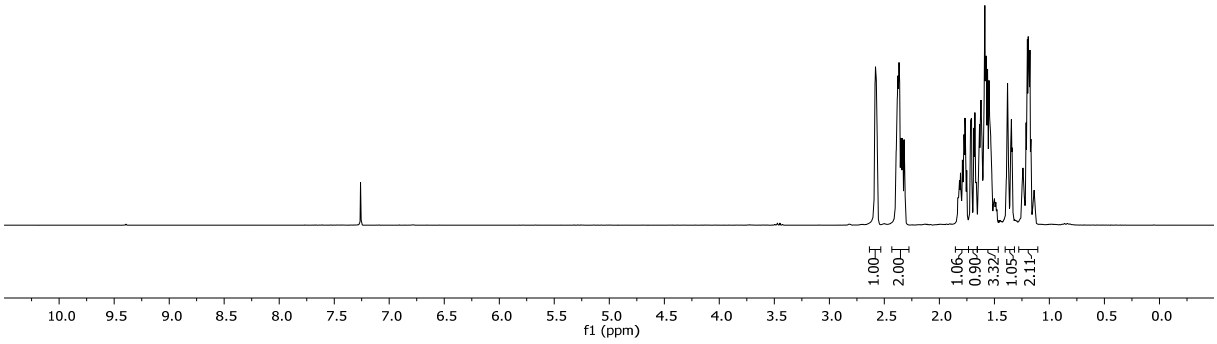
Bicyclo[2.2.1]heptane-2-carbonitrile (3ap)

^{1}H-NMR

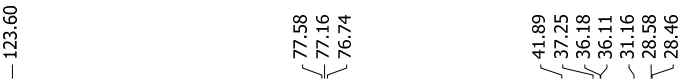


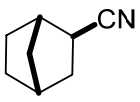


3ap

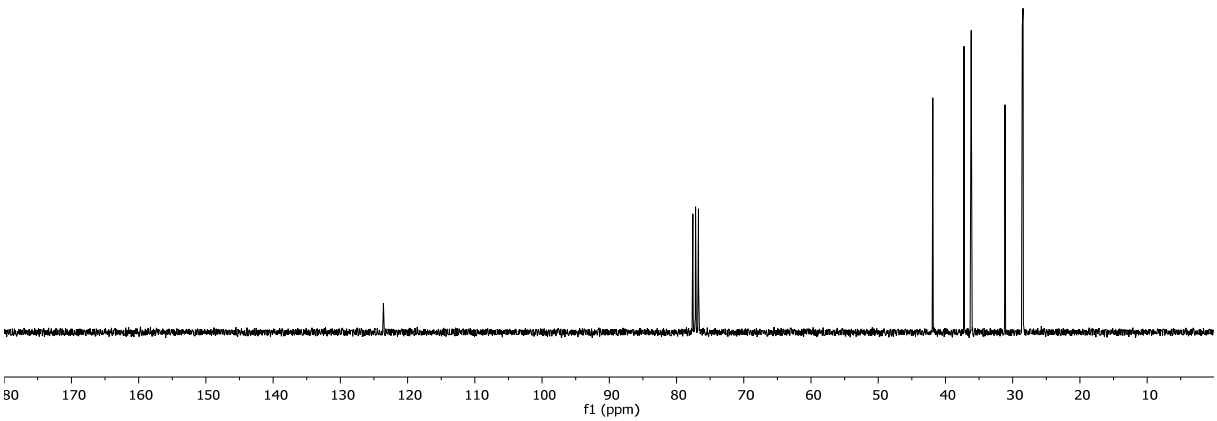


^{13}C-NMR



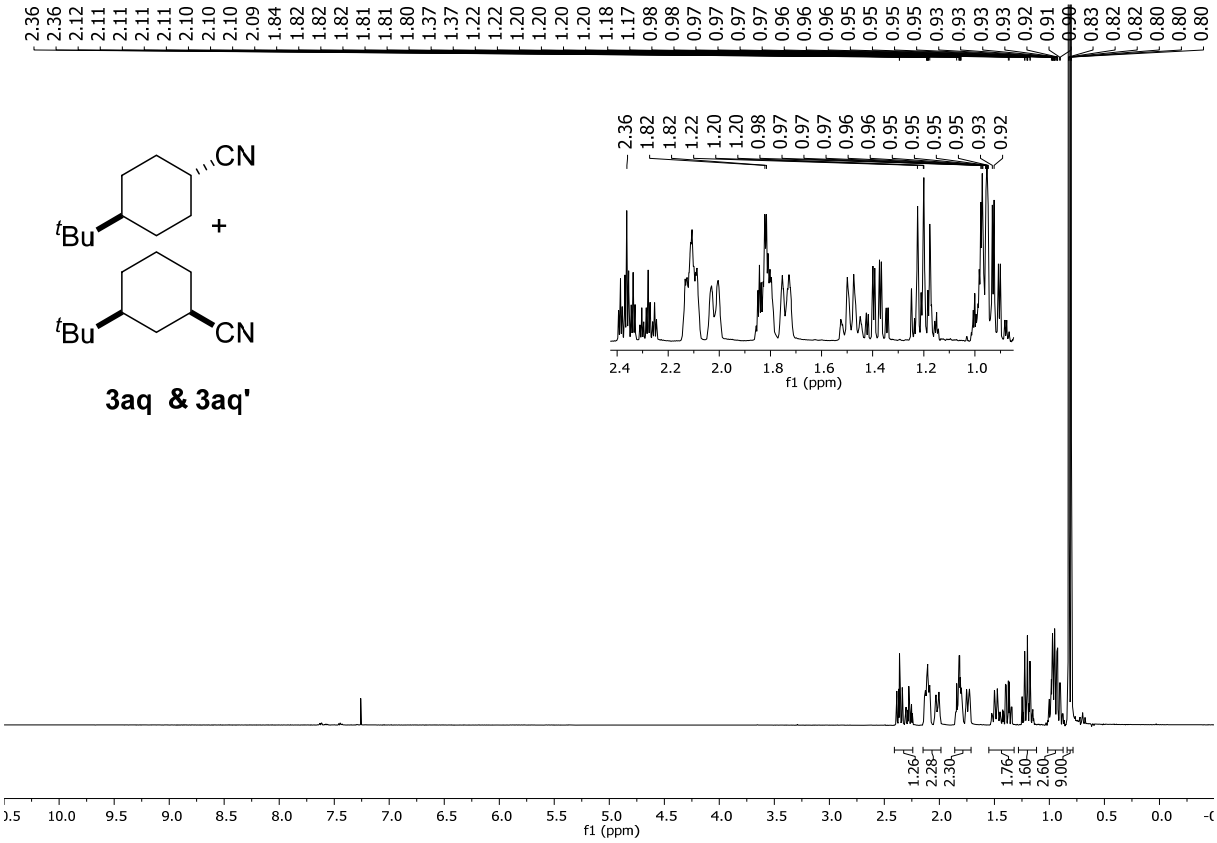


3ap

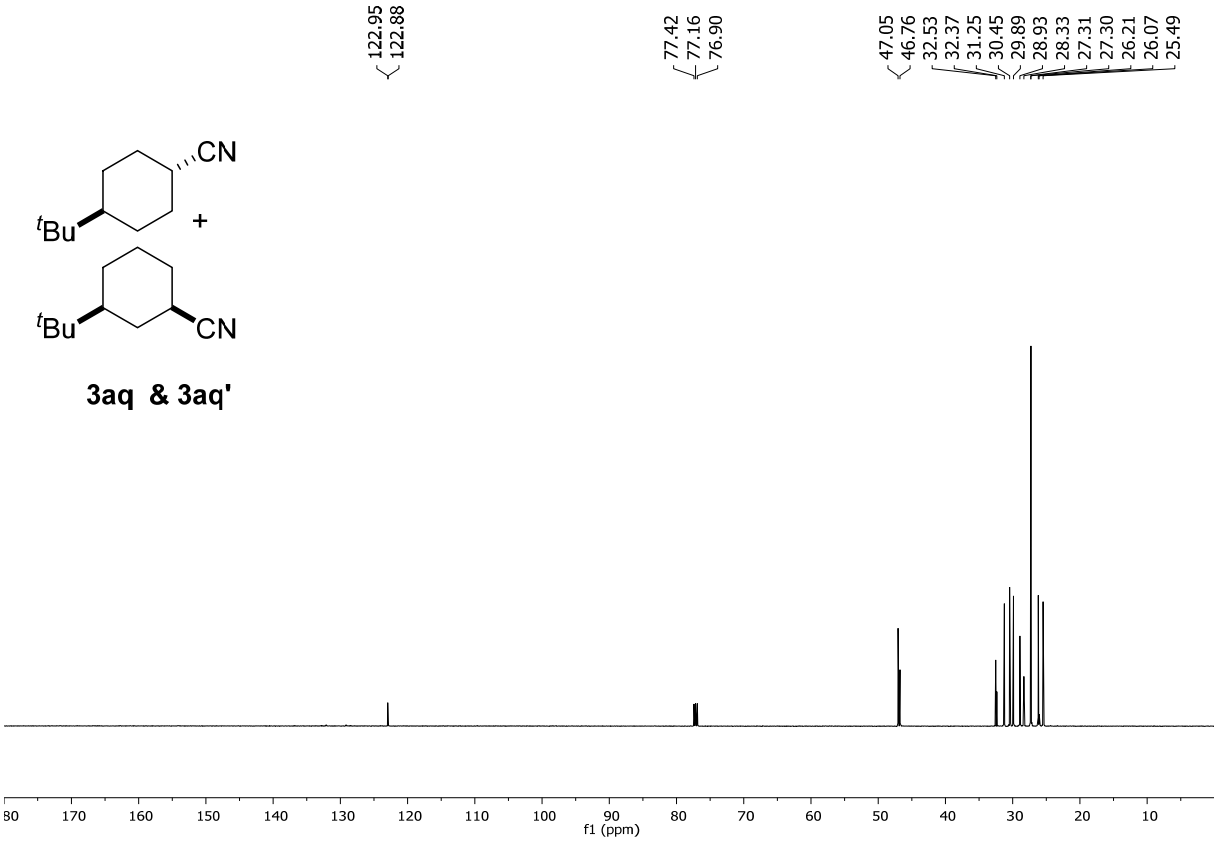


4-(*tert*-Butyl)cyclohexane-1-carbonitrile (3aq) & 3-(*tert*-Butyl)cyclohexane-1-carbonitrile (3aq')

^{1}H-NMR

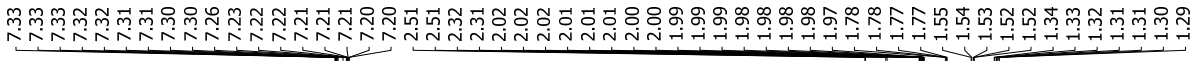


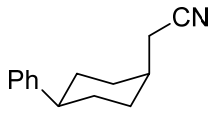
^{13}C-NMR



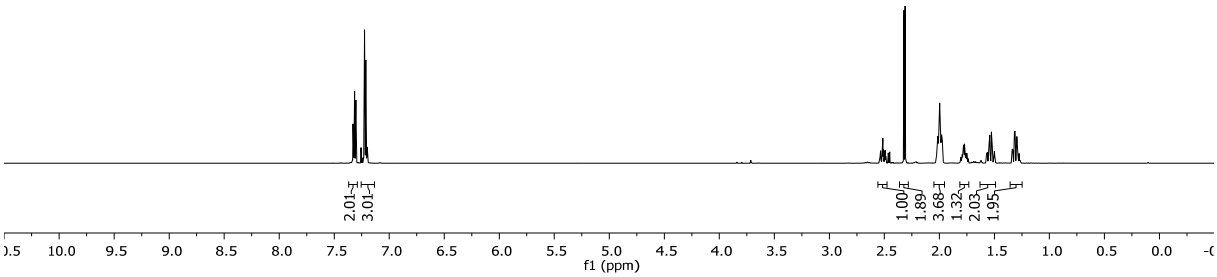
2-(4-Phenylcyclohexyl)acetonitrile (3ar)

^{1}H-NMR

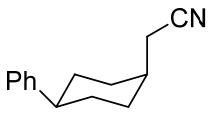




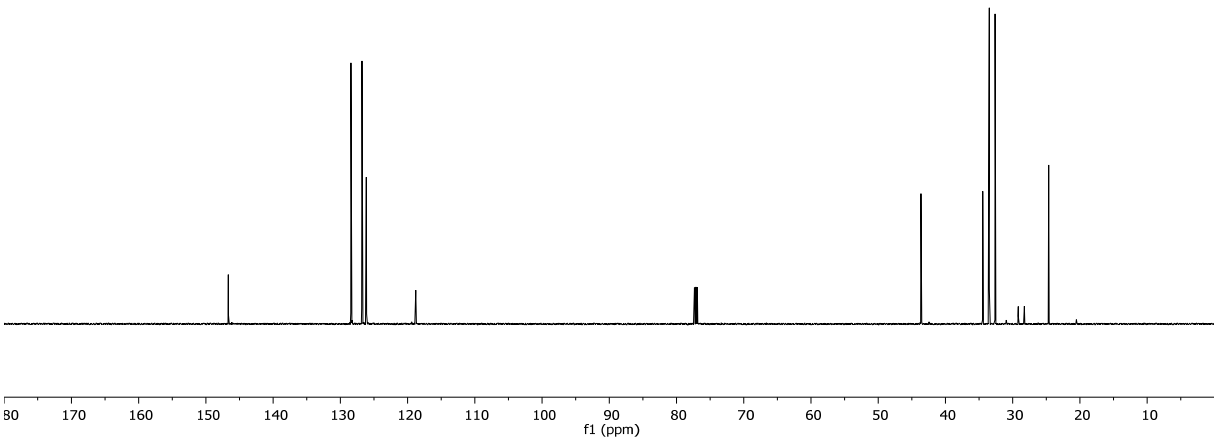
3ar

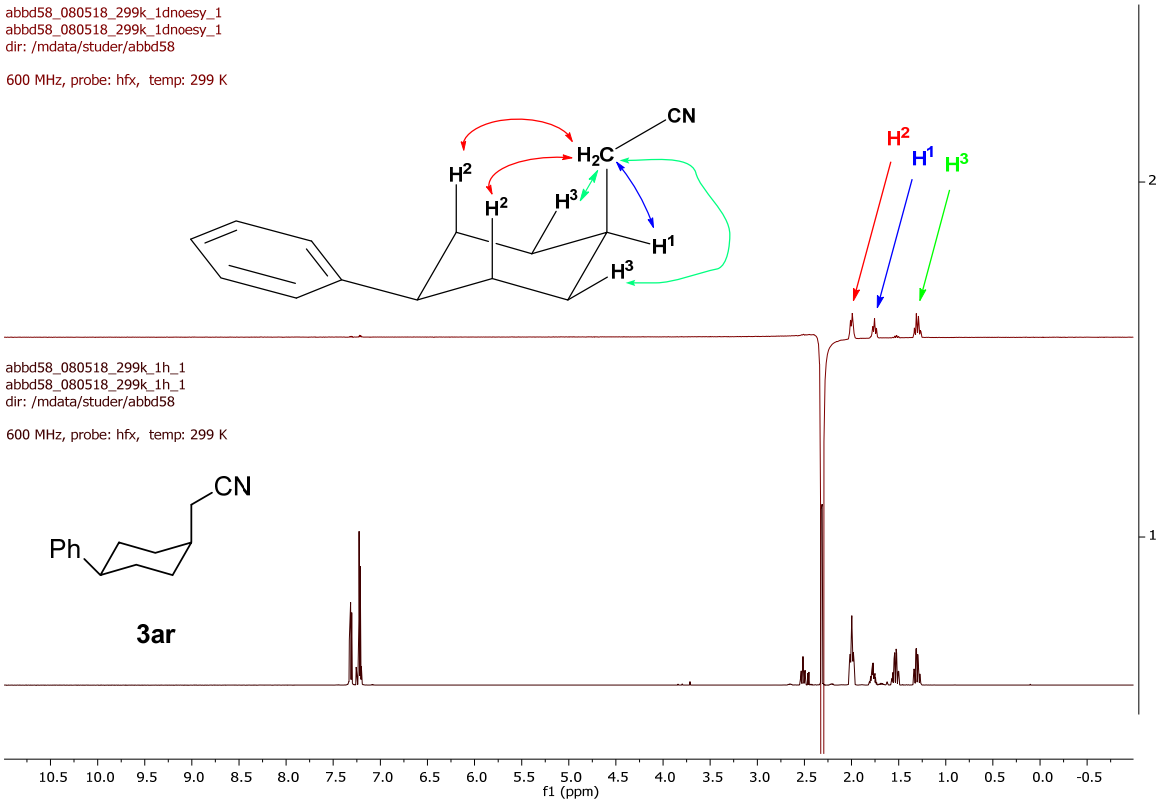


^{13}C-NMR



3ar

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abbd58_080518_299k_1dnoesy_1
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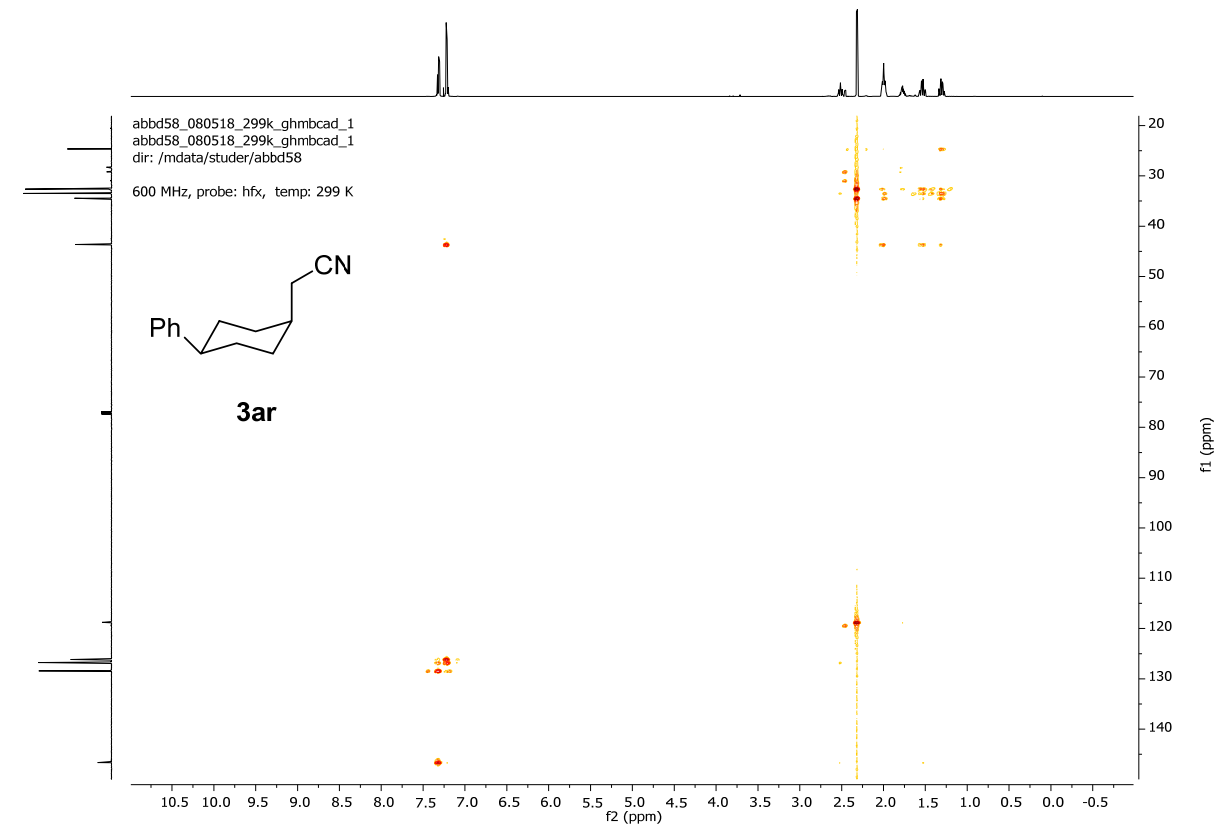
600 MHz, probe: hfx, temp: 299 K
CN
H2C
H2
H2
H3
H3
H1
H3
H2
H1
H3
2
abbd58_080518_299k_1h_1
abbd58_080518_299k_1h_1
dir: /mdata/studer/abbd58
600 MHz, probe: hfx, temp: 299 K
CN
Ph
3ar
1
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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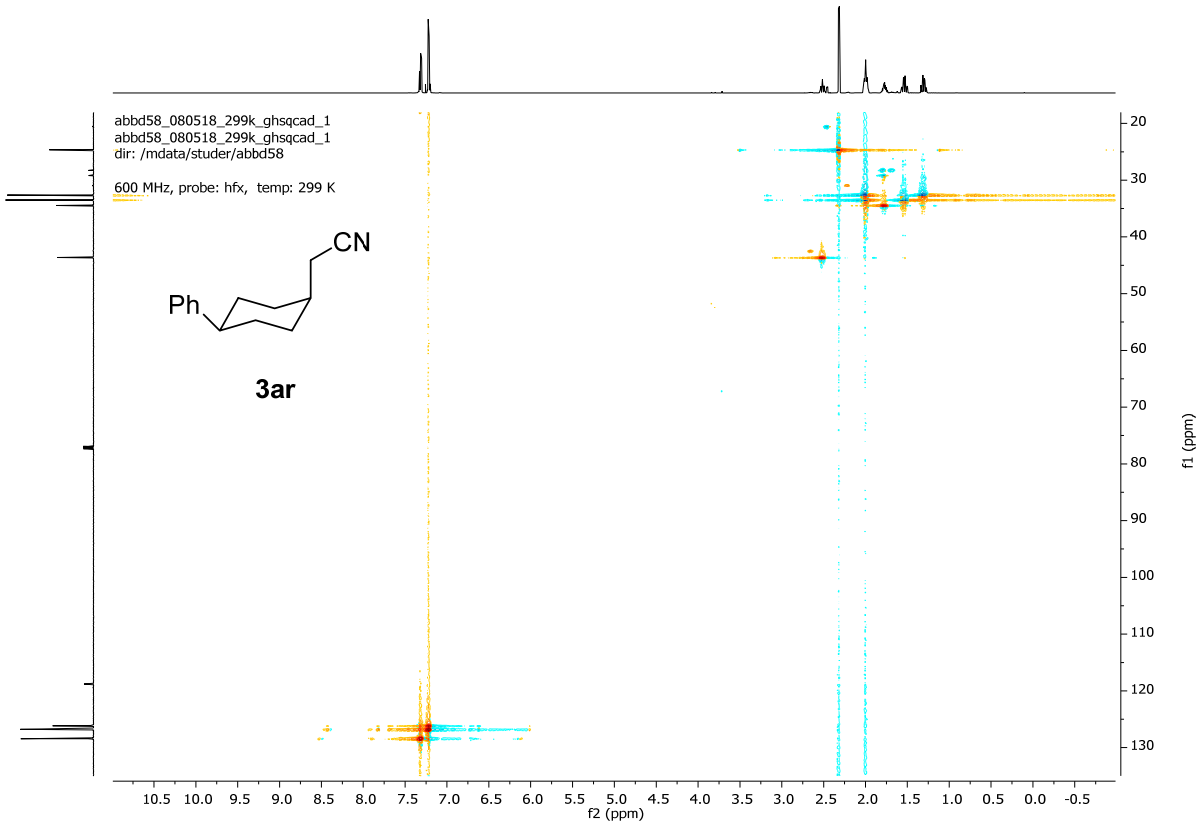
abbd58_080518_299k_ghmbcad_1
dir: /mdata/studer/abbd58
600 MHz, probe: hfx, temp: 299 K
CN
Ph
3ar
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f2 (ppm)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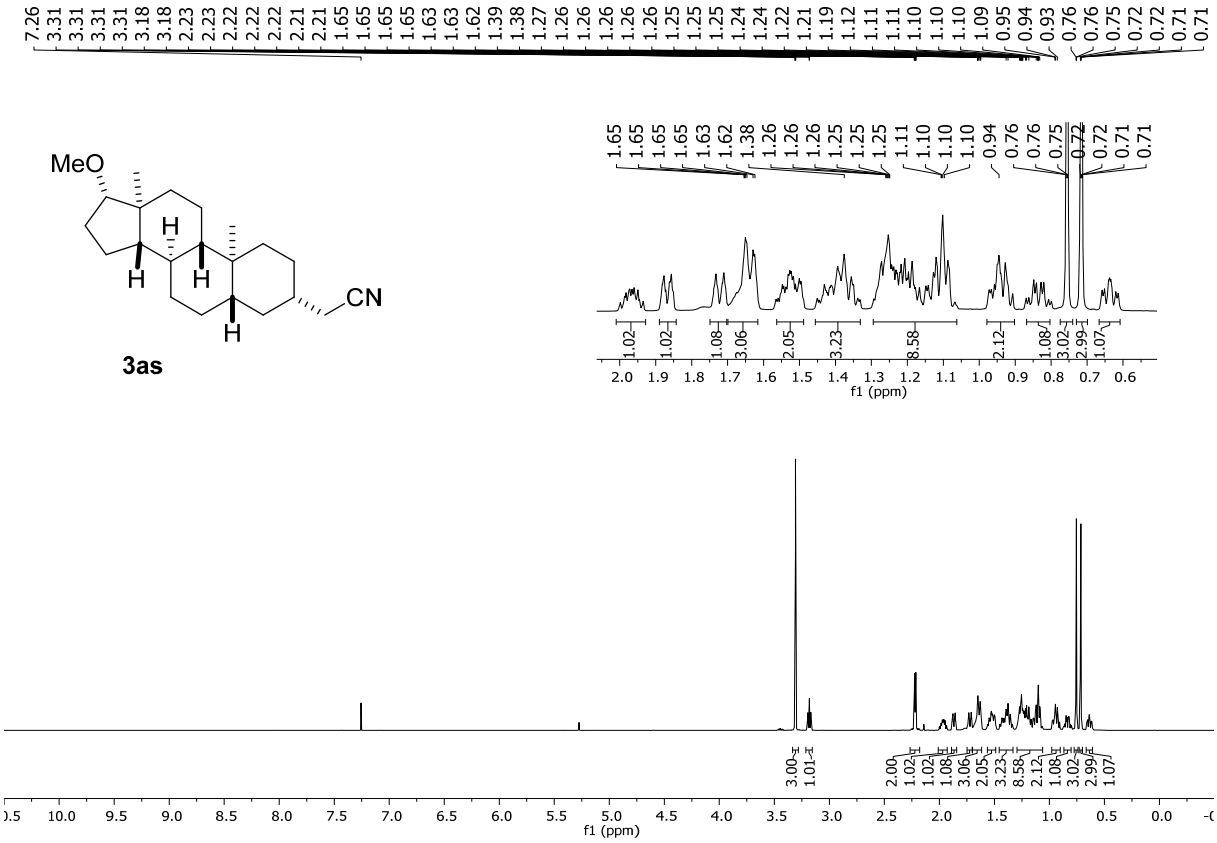
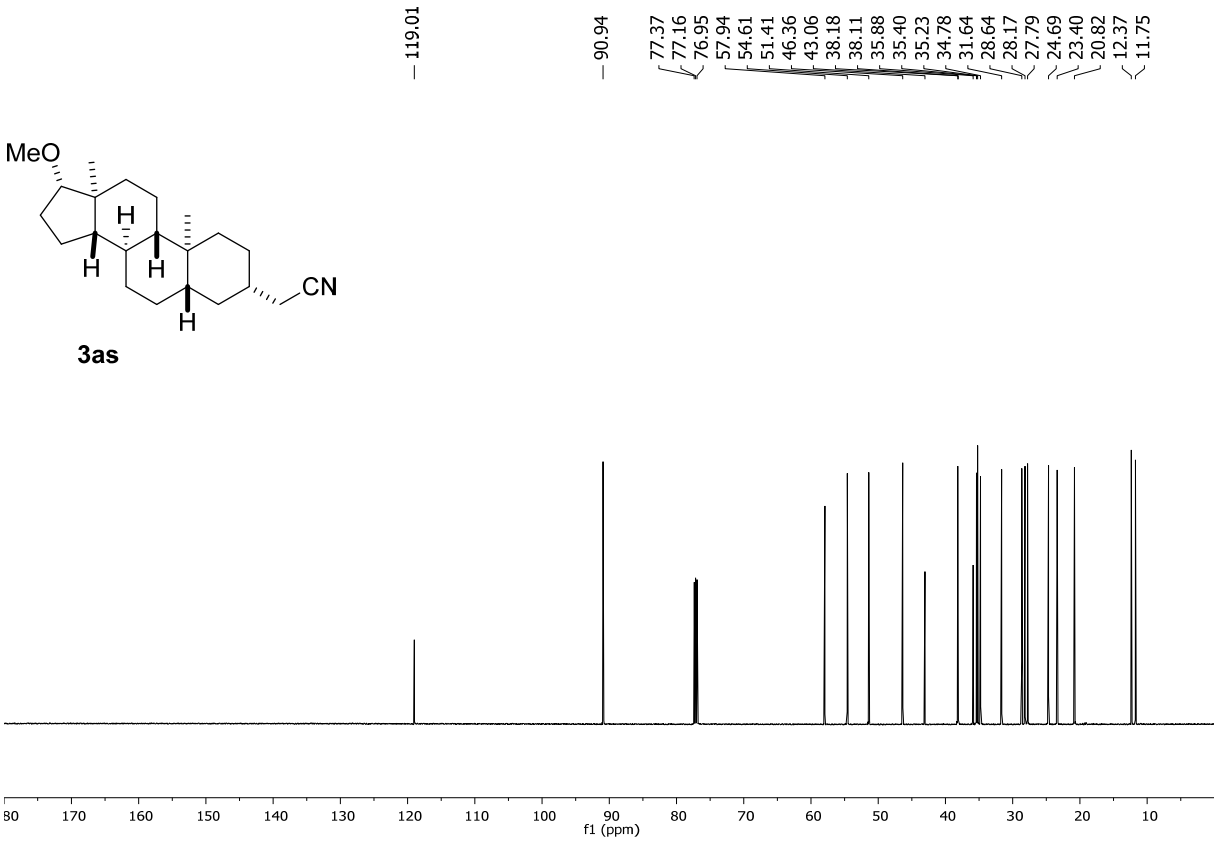
600 MHz, probe: hfx, temp: 299 K
CN
Ph
3ar
f2 (ppm)
f1 (ppm)

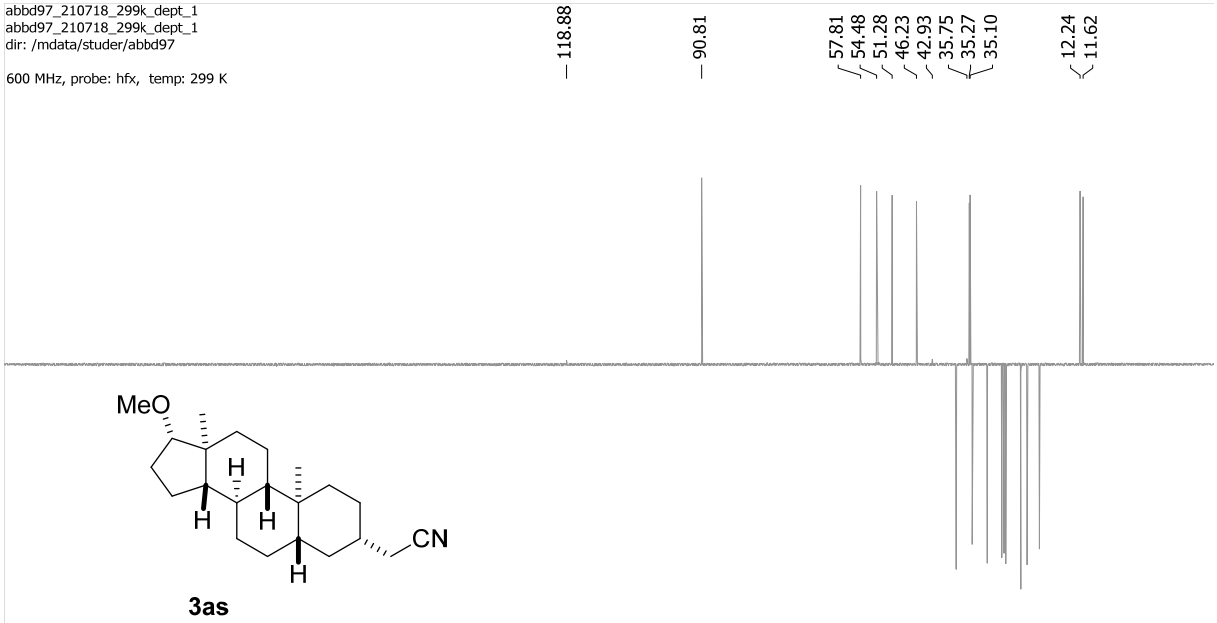
2-((5S,8R,10S,13S,14S,17S)-17-methoxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)acetonitrile (3as)

^{1}H-NMR



^{13}C-NMR

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600 MHz, probe: hfx, temp: 299 K
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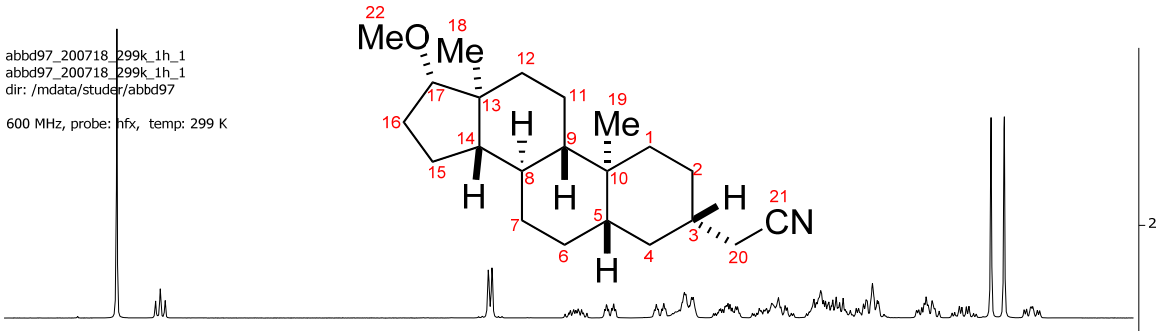
90.81
57.81
54.48
51.28
46.23
42.93
35.75
35.27
35.10
12.24
11.62
MeO
H
H
H
H
CN
3as
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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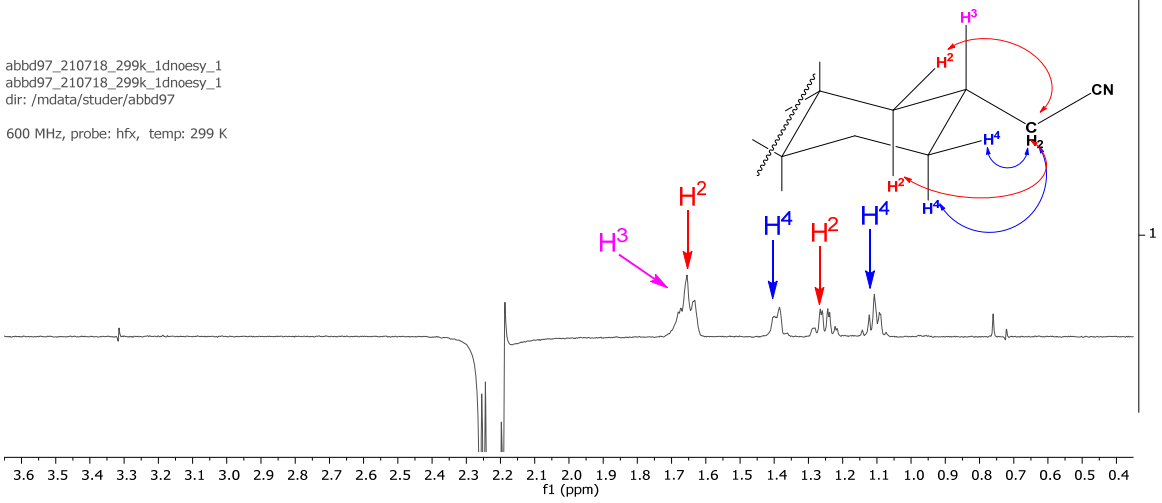
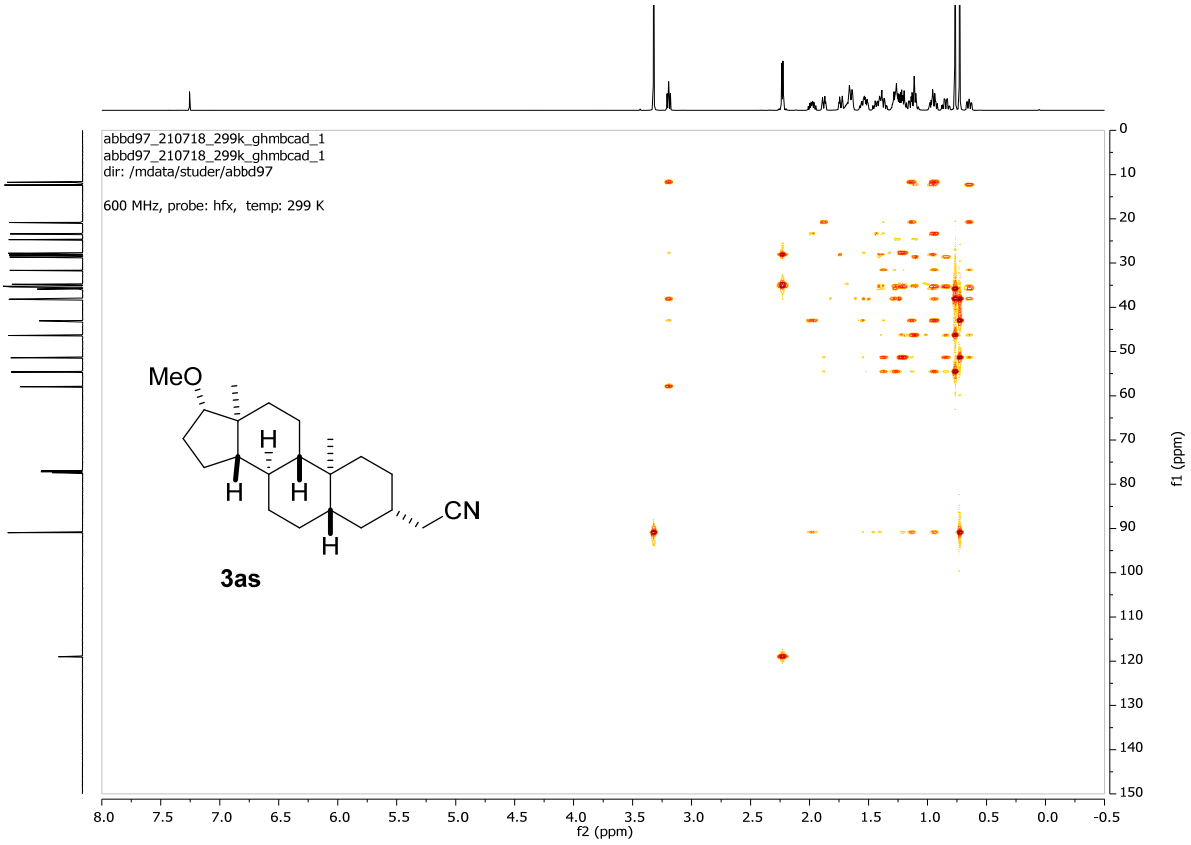
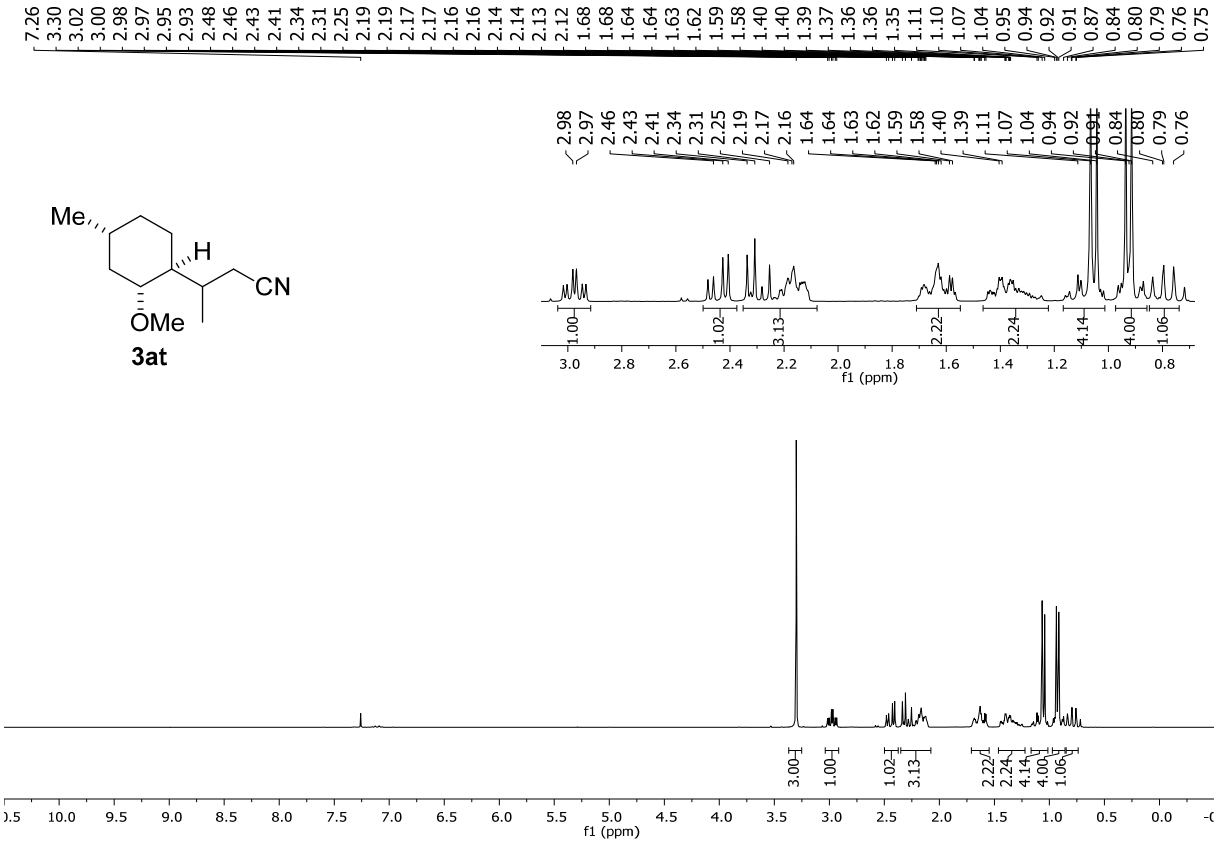
600 MHz, probe: hfx, temp: 299 K
22
MeO
18
Me
12
17
13
11
19
16
H
Me
1
14
9
2
15
8
10
H
H
H
21
5
7
3
CN
6
4
20
H
2


abbd97_210718_299k_1dnoesy_1
abbd97_210718_299k_1dnoesy_1
dir: /mdata/studer/abbd97
600 MHz, probe: hfx, temp: 299 K
H3
H2
CN
C
H2
H4
H2
H4
H3
H2
H4
H2
H4
1
3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4
f1 (ppm)

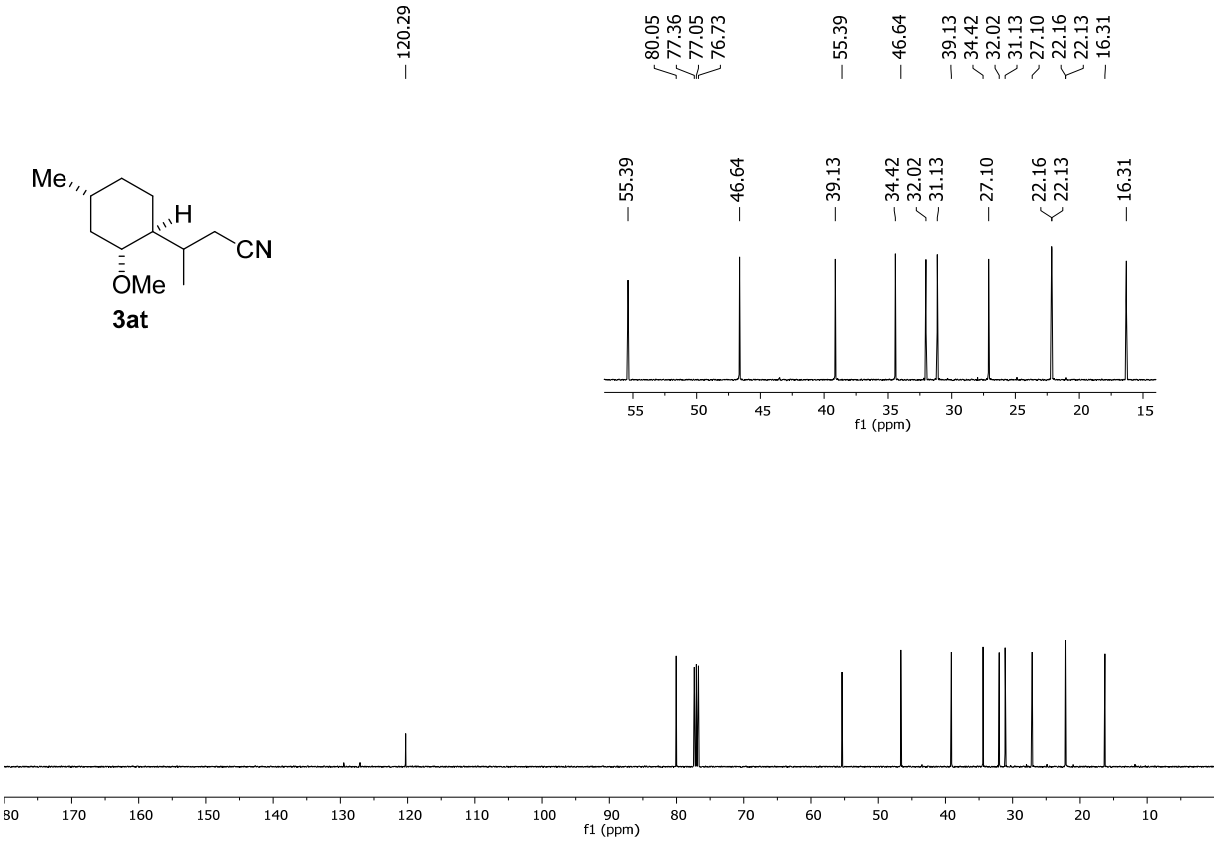

abbd97_210718_299k_ghmbcad_1
abbd97_210718_299k_ghmbcad_1
dir: /mdata/studer/abbd97
600 MHz, probe: hfx, temp: 299 K
MeO
H
H
H
H
CN
3as
f2 (ppm)
f1 (ppm)

3-((1S,2R,4R)-2-Methoxy-4-methylcyclohexyl)butanenitrile (3at)

^{1}H-NMR

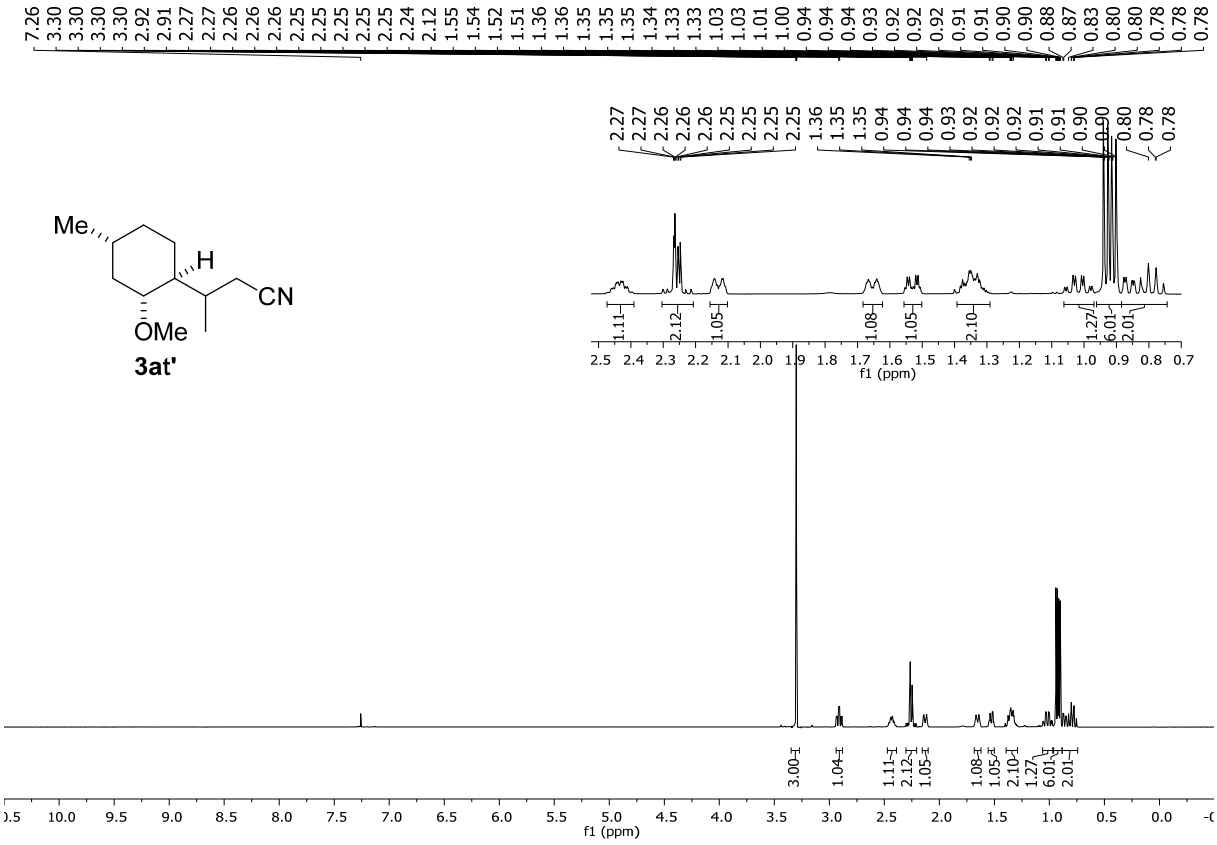


^{13}C-NMR

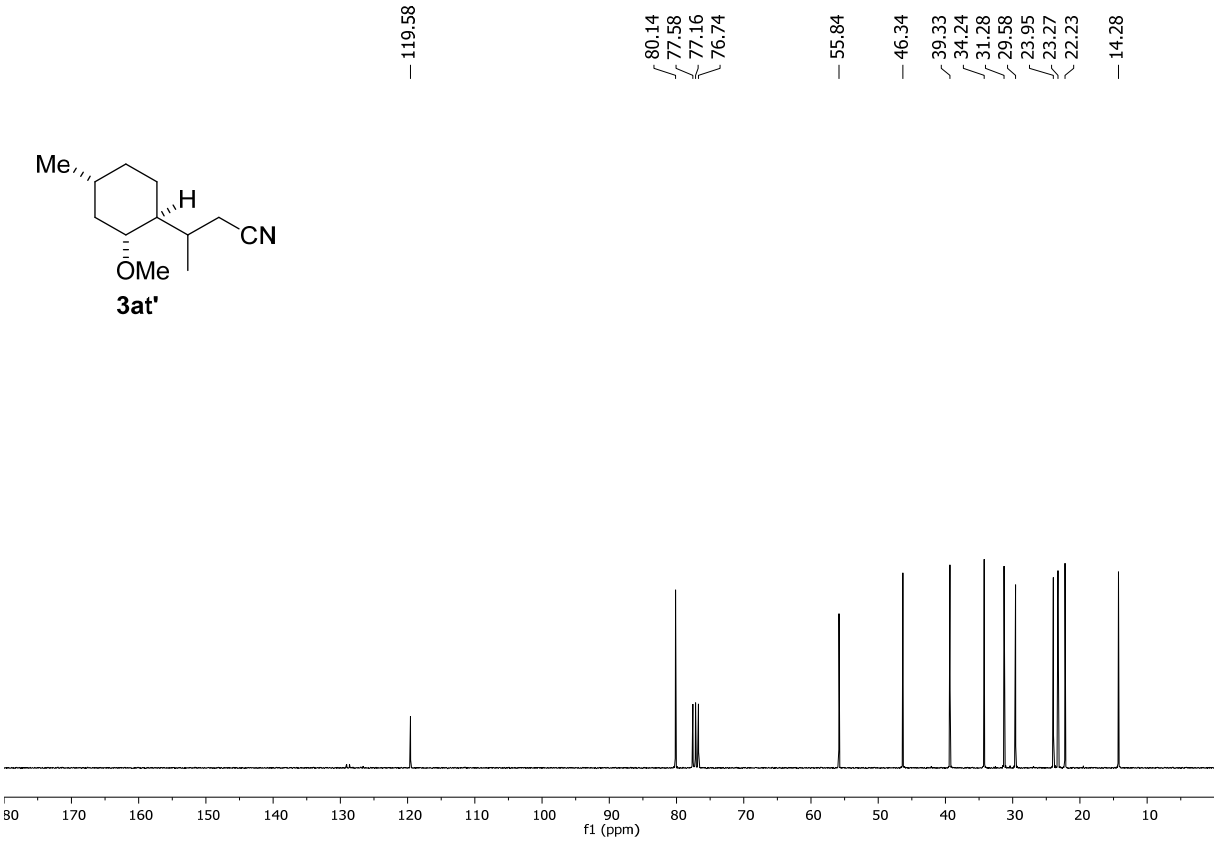


3-((1S,2R,4R)-2-Methoxy-4-methylcyclohexyl)butanenitrile (3at')

^{1}H-NMR

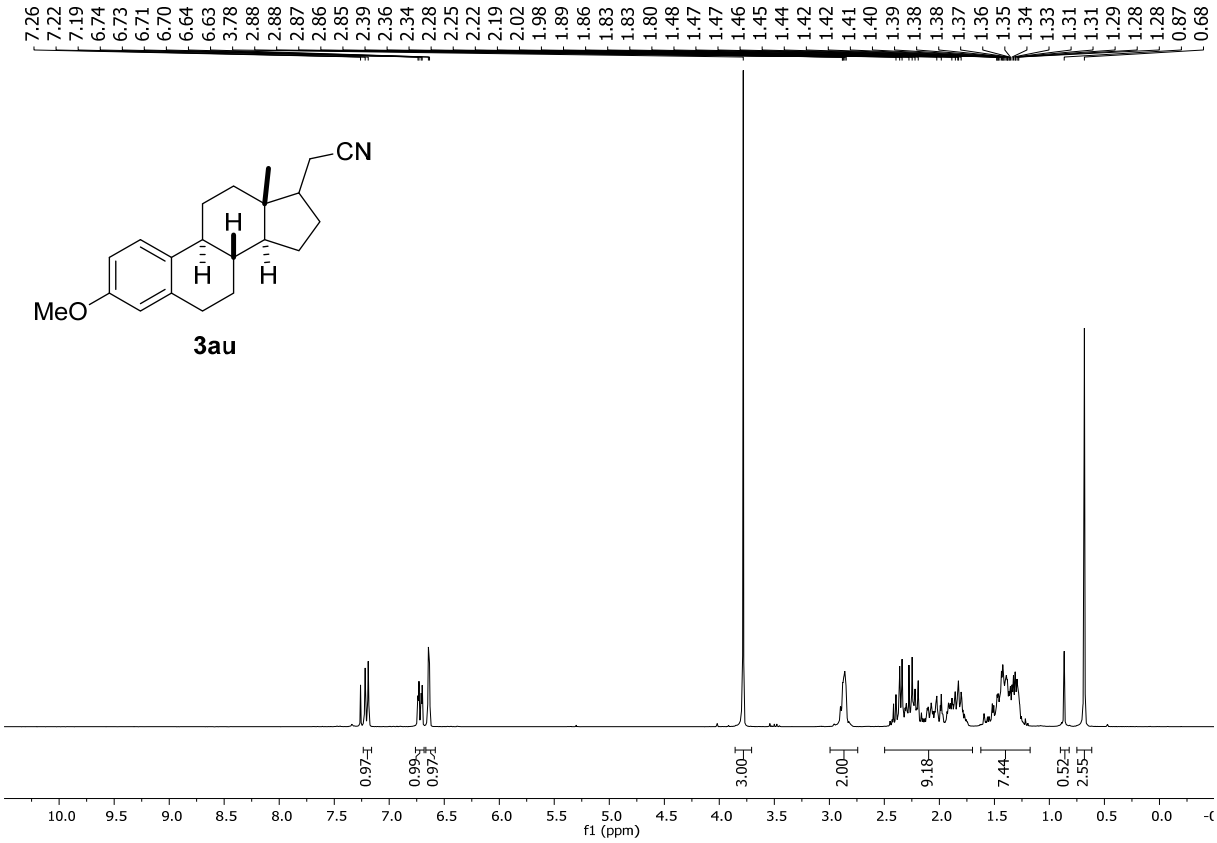


^{13}C-NMR

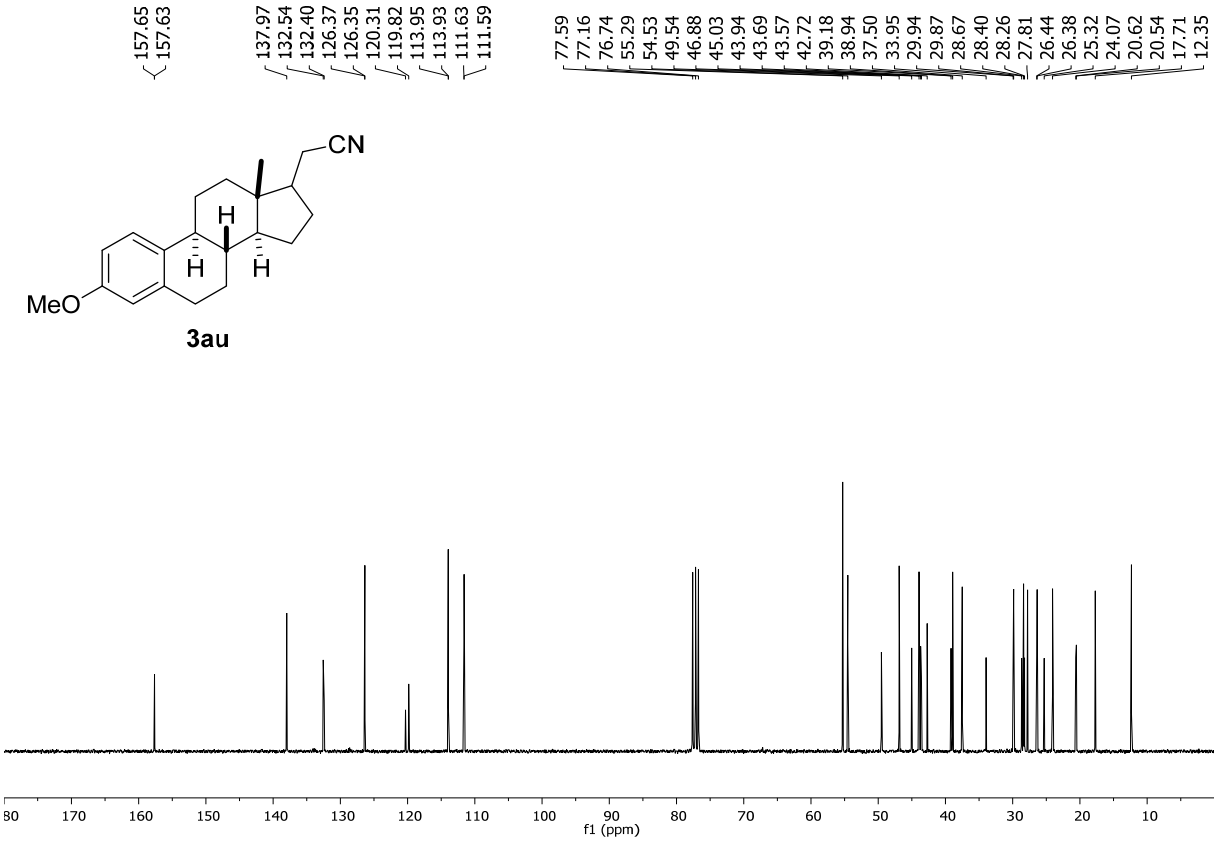


2-((8S,9S,13R,14S)-3-Methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)acetonitrile (3au)

^{1}H-NMR

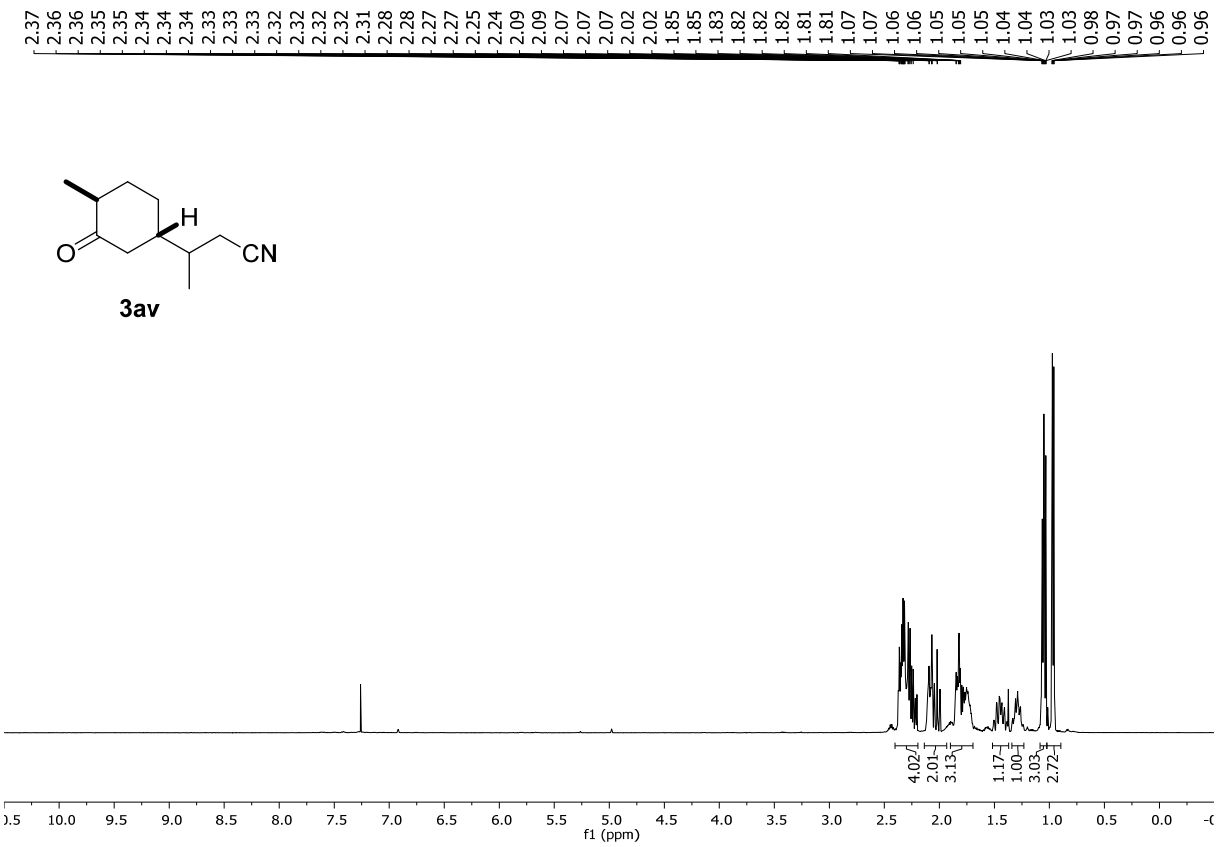


^{13}C-NMR

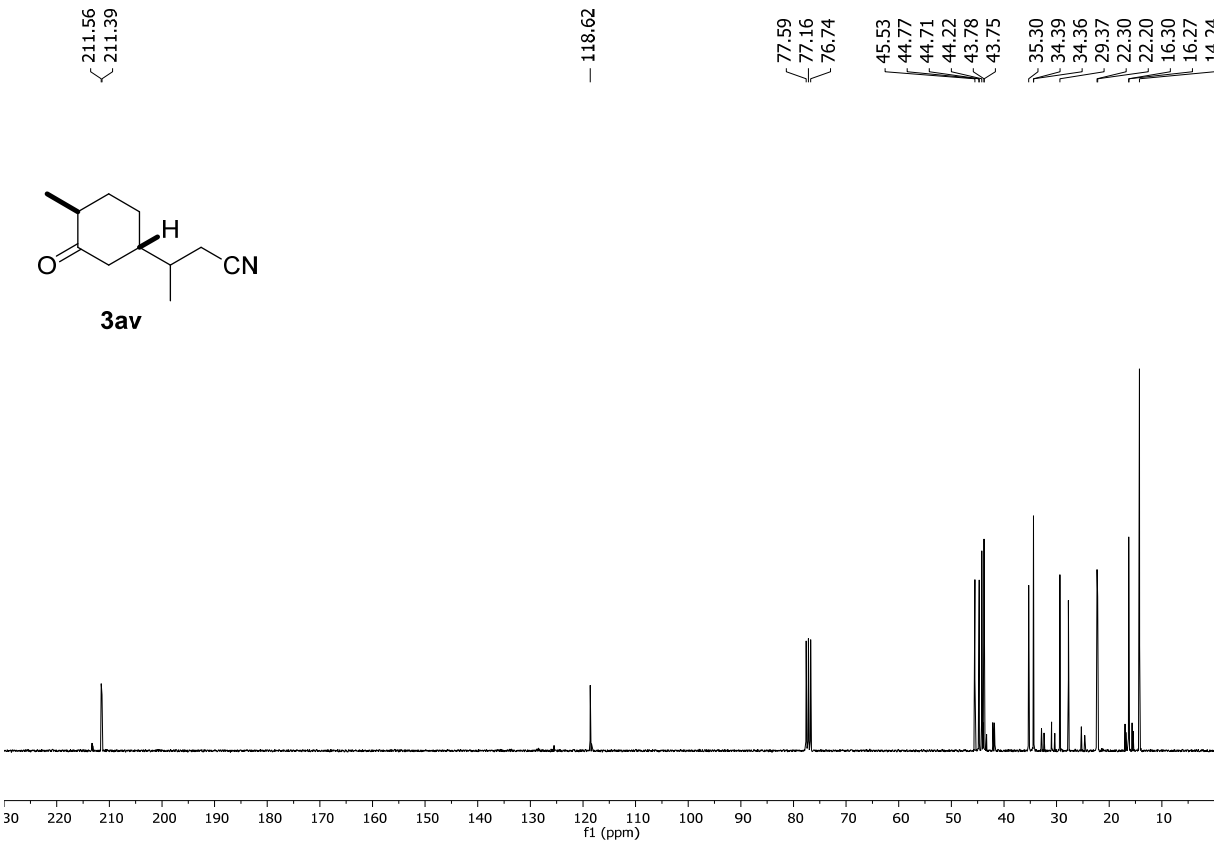


3-((1S,4S)-4-Methyl-3-oxocyclohexyl)butanenitrile (3av)

^{1}H NMR

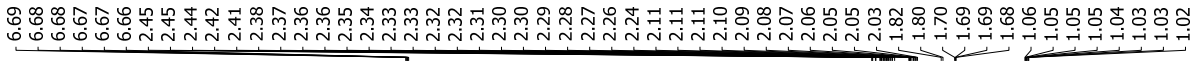


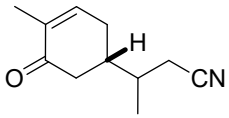
^{13}C NMR



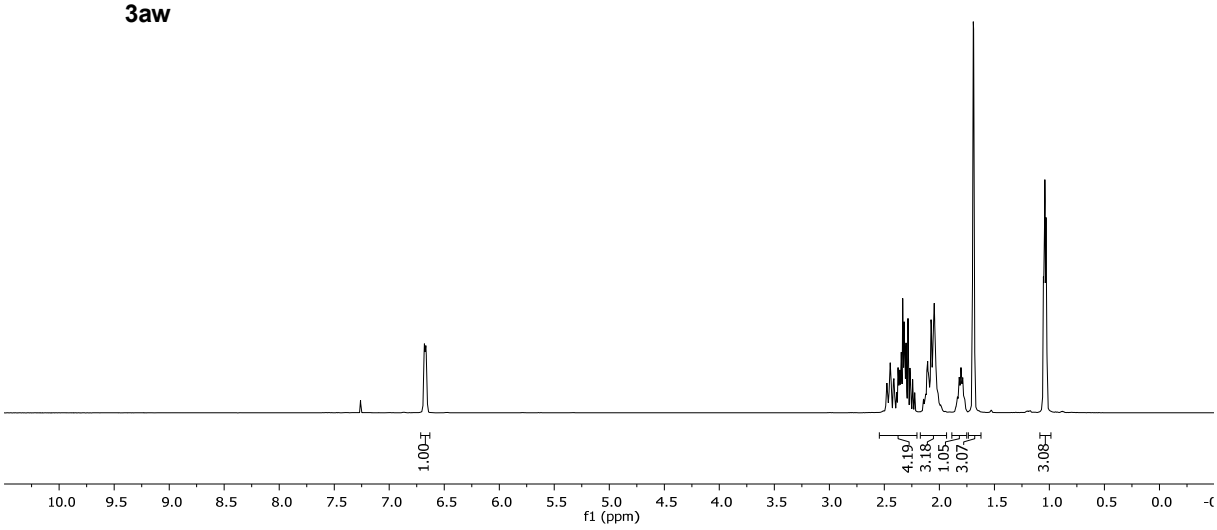
3-((S)-4-Methyl-5-oxocyclohex-3-en-1-yl)butanenitrile (3aw)

^{1}H-NMR

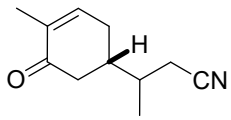




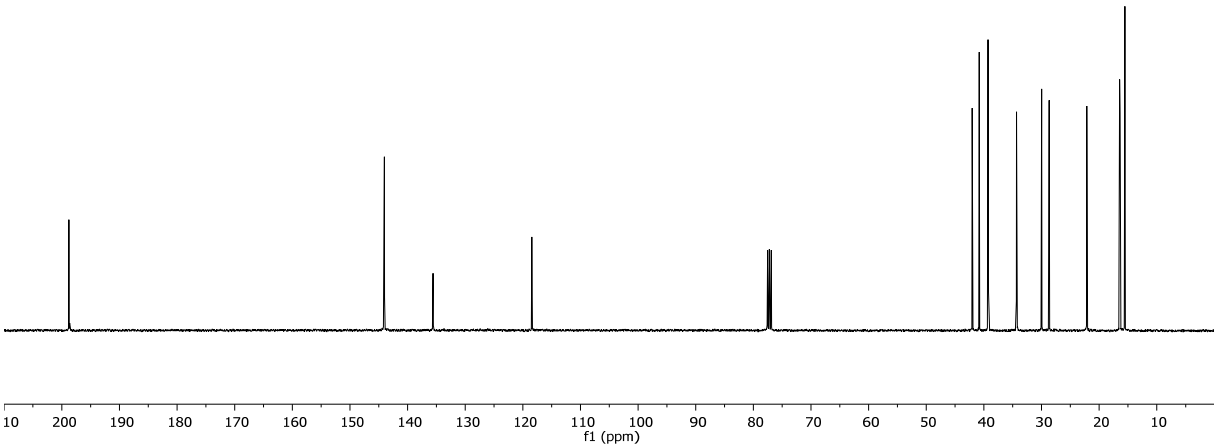
3aw



^{13}C-NMR

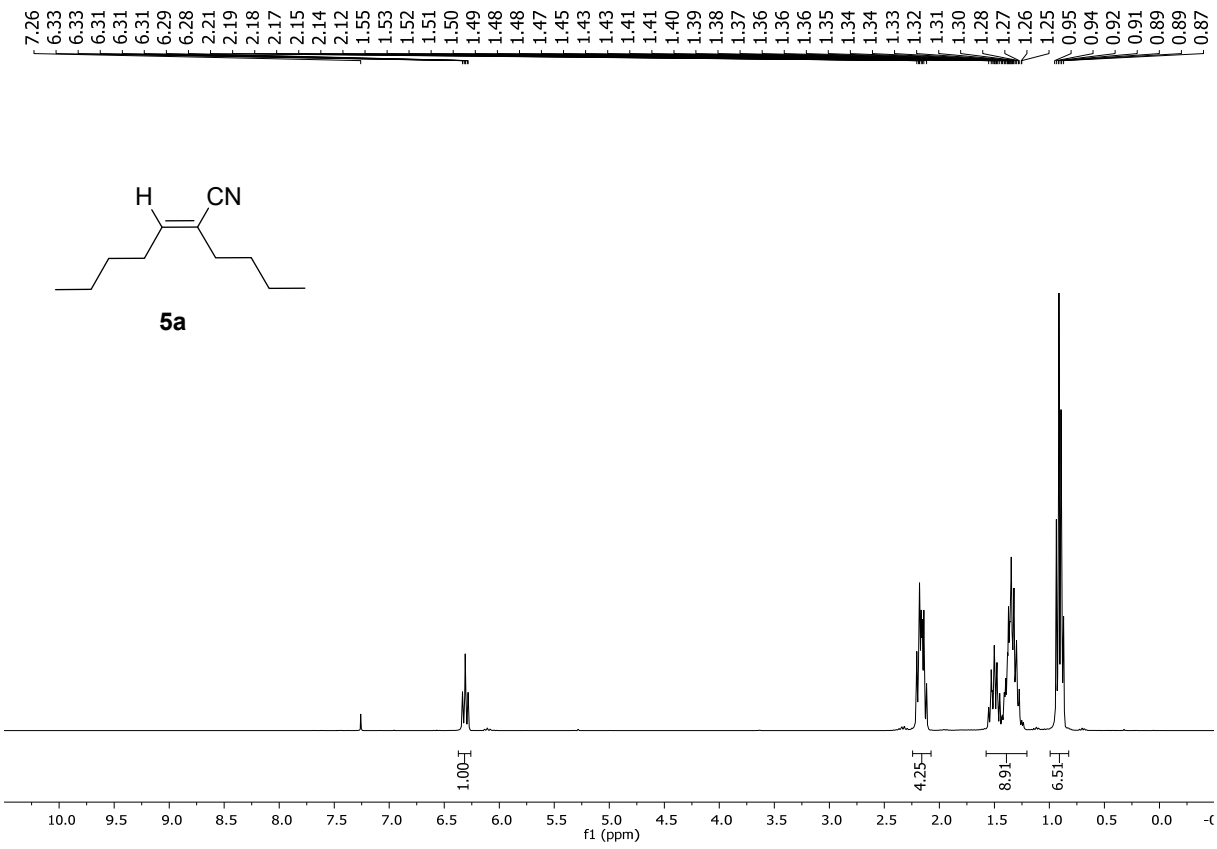


3aw

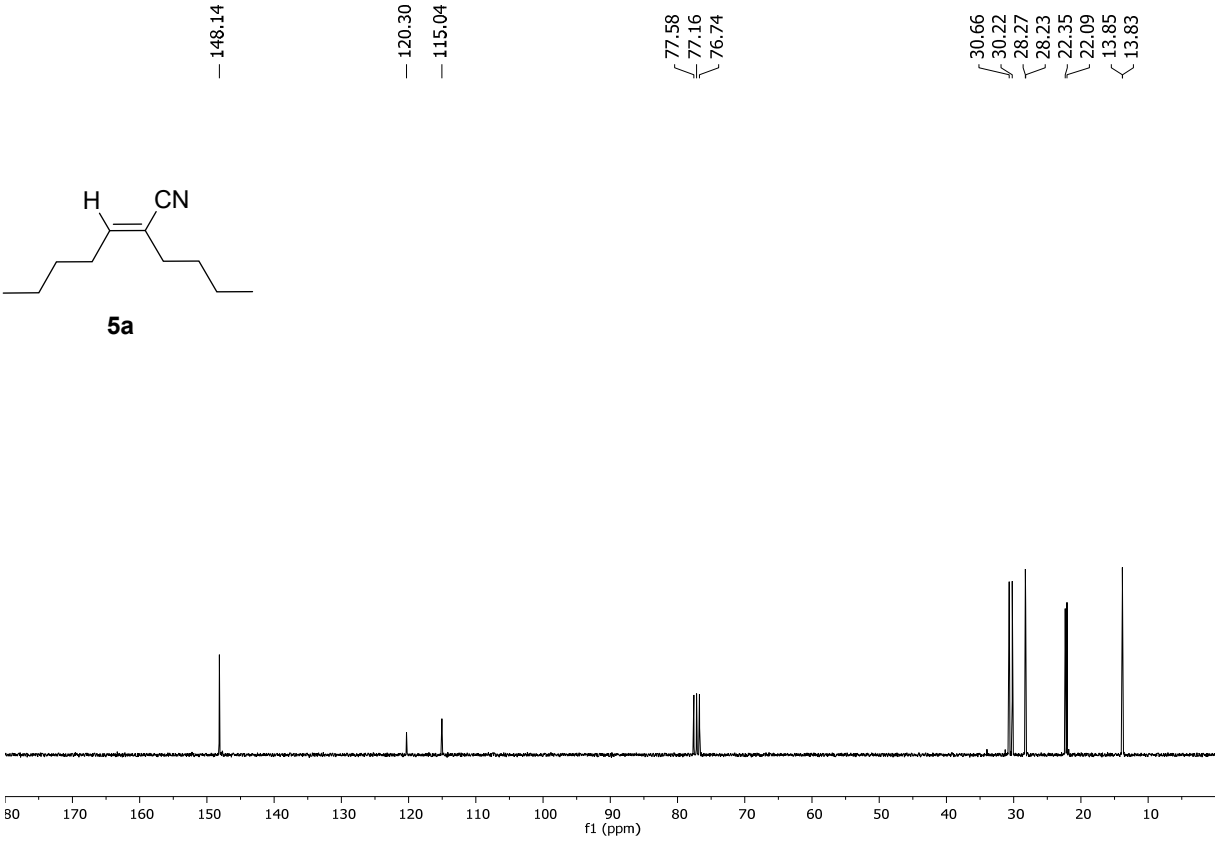


(*E*)-2-Butylhept-2-enenitrile (5a)

^{1}H NMR

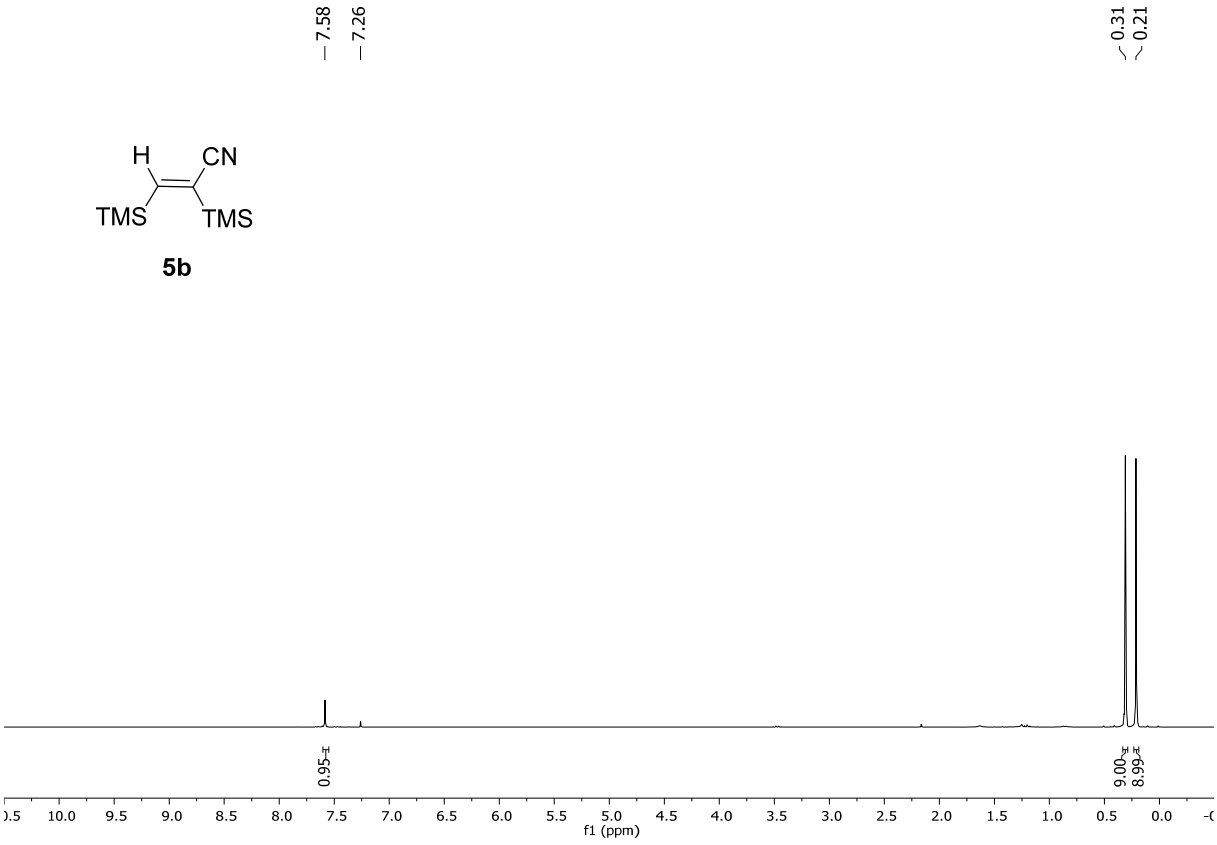


^{13}C NMR

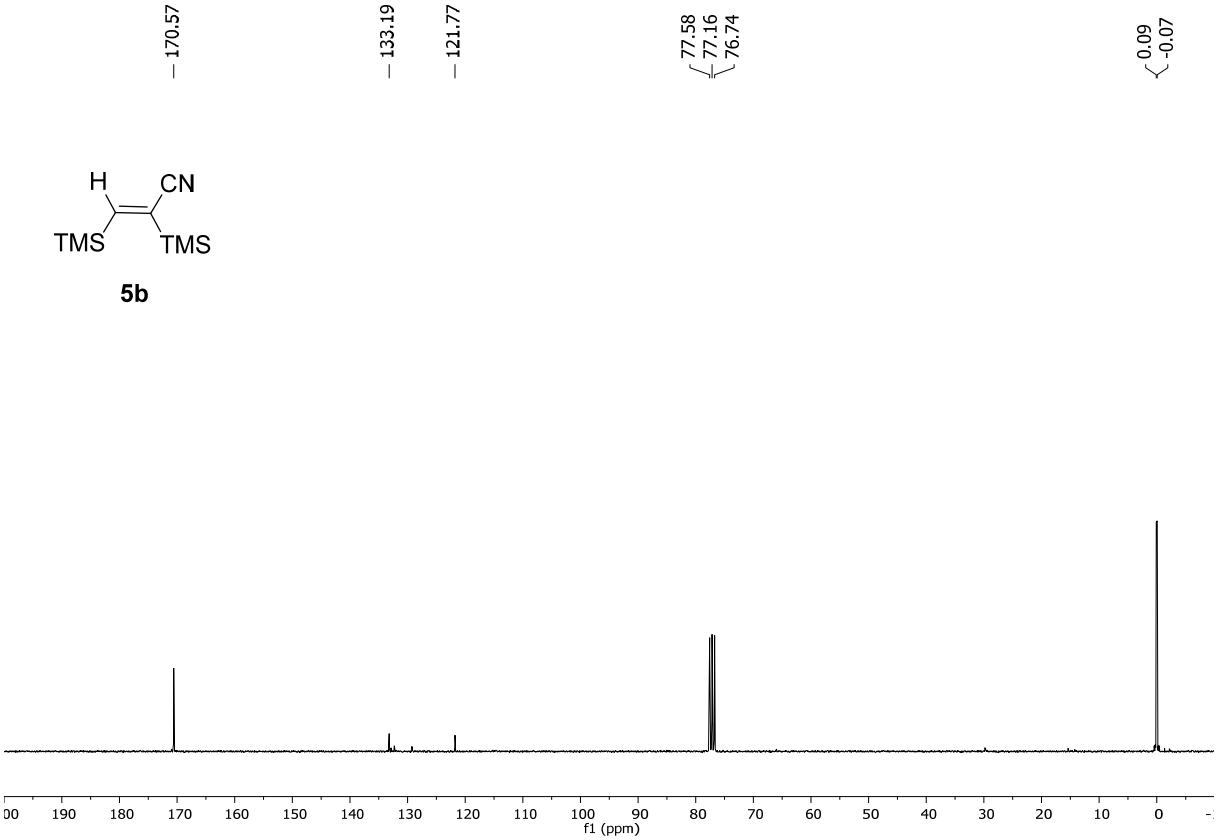


(*Z*)-2,3-Bis(trimethylsilyl)acrylonitrile (5b)

^{1}H NMR

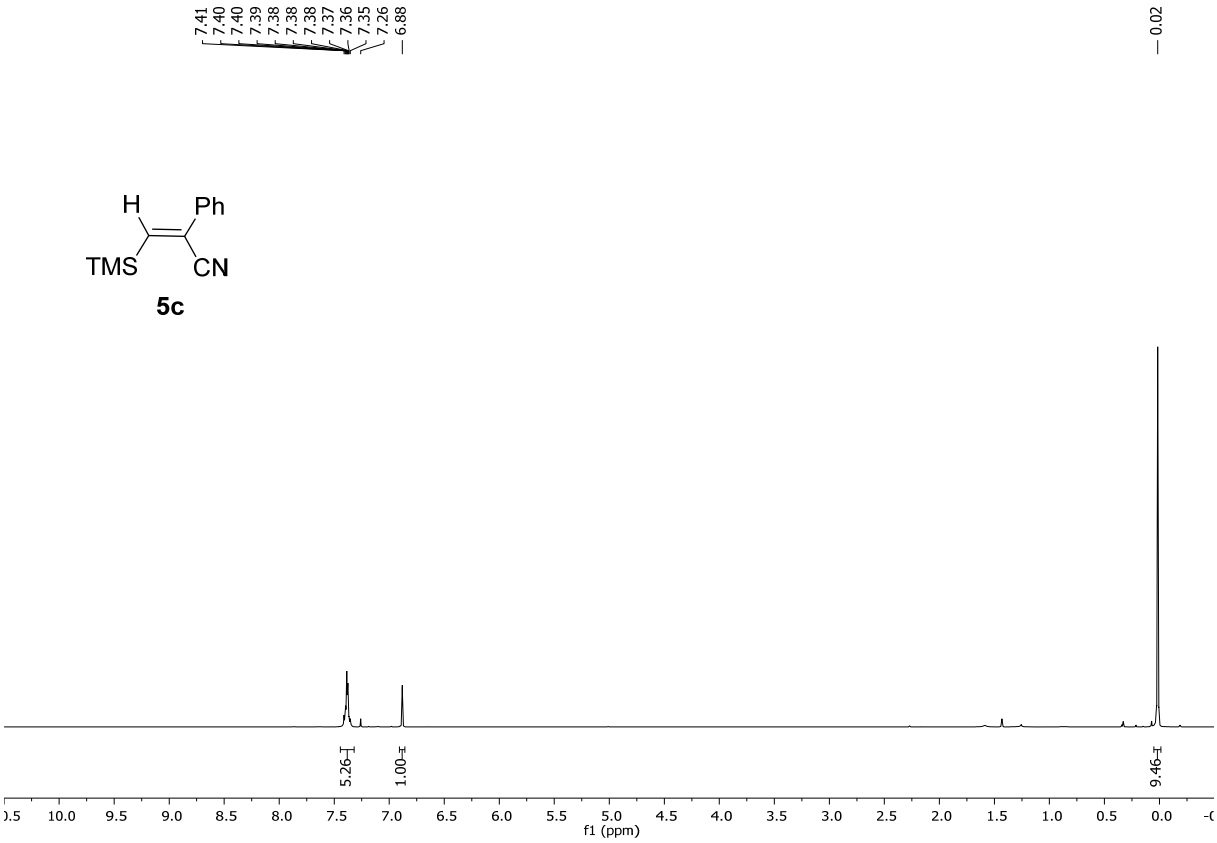


^{13}C NMR

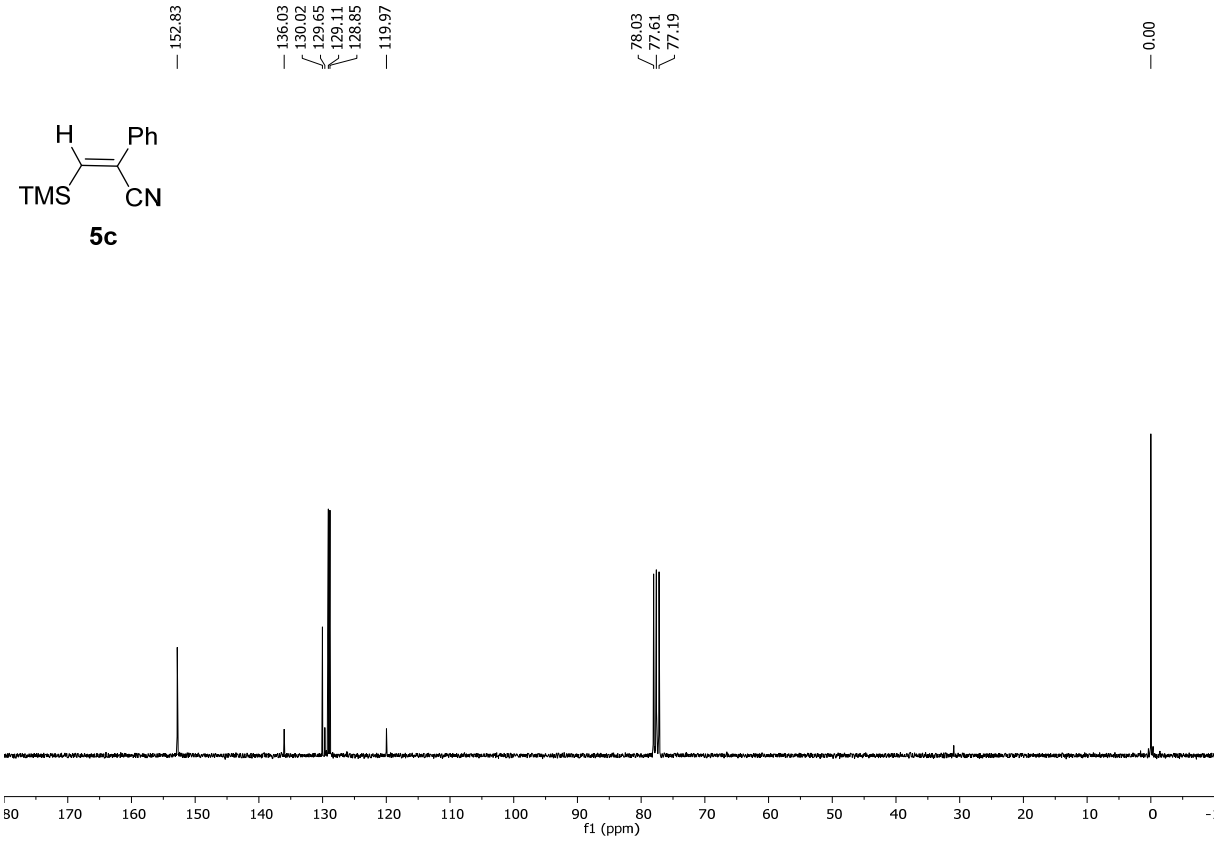


(*Z*)-2-Phenyl-3-(trimethylsilyl)acrylonitrile (5c)

^{1}H NMR

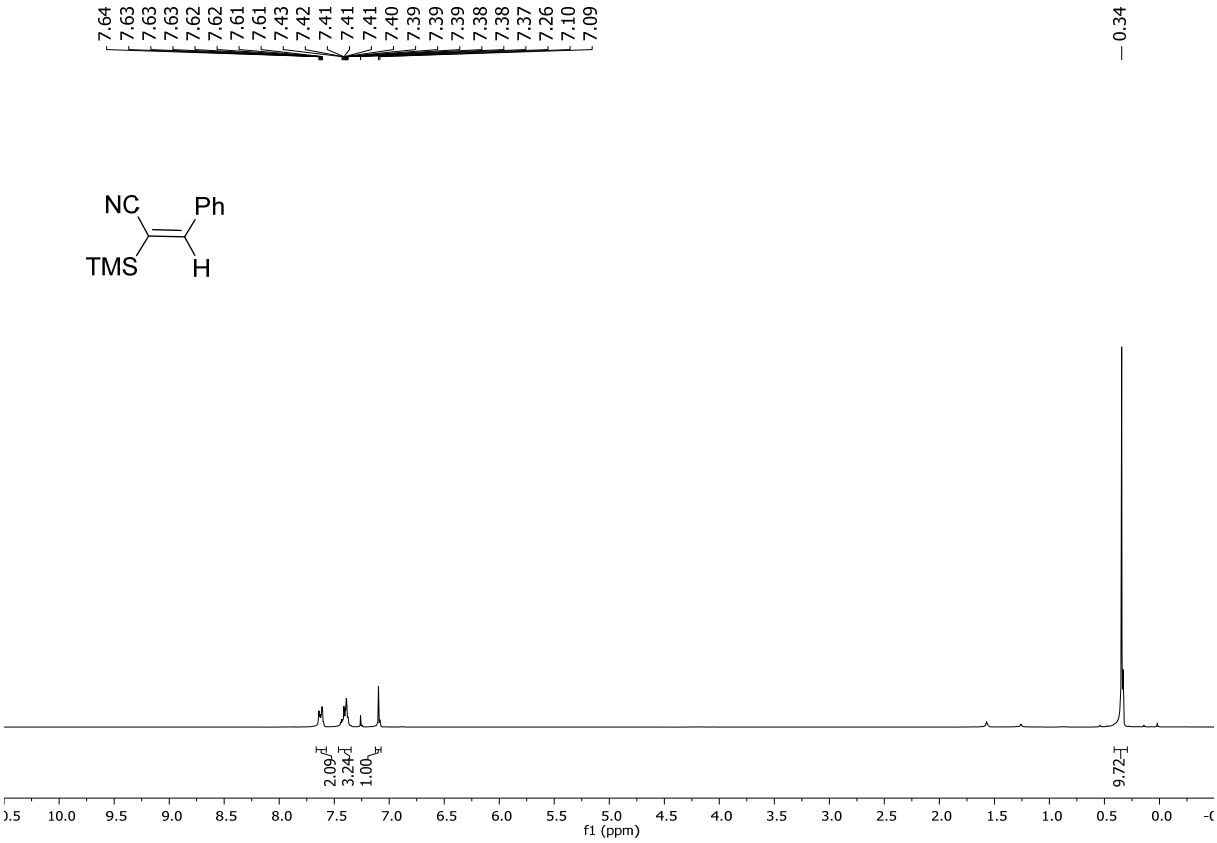


^{13}C NMR

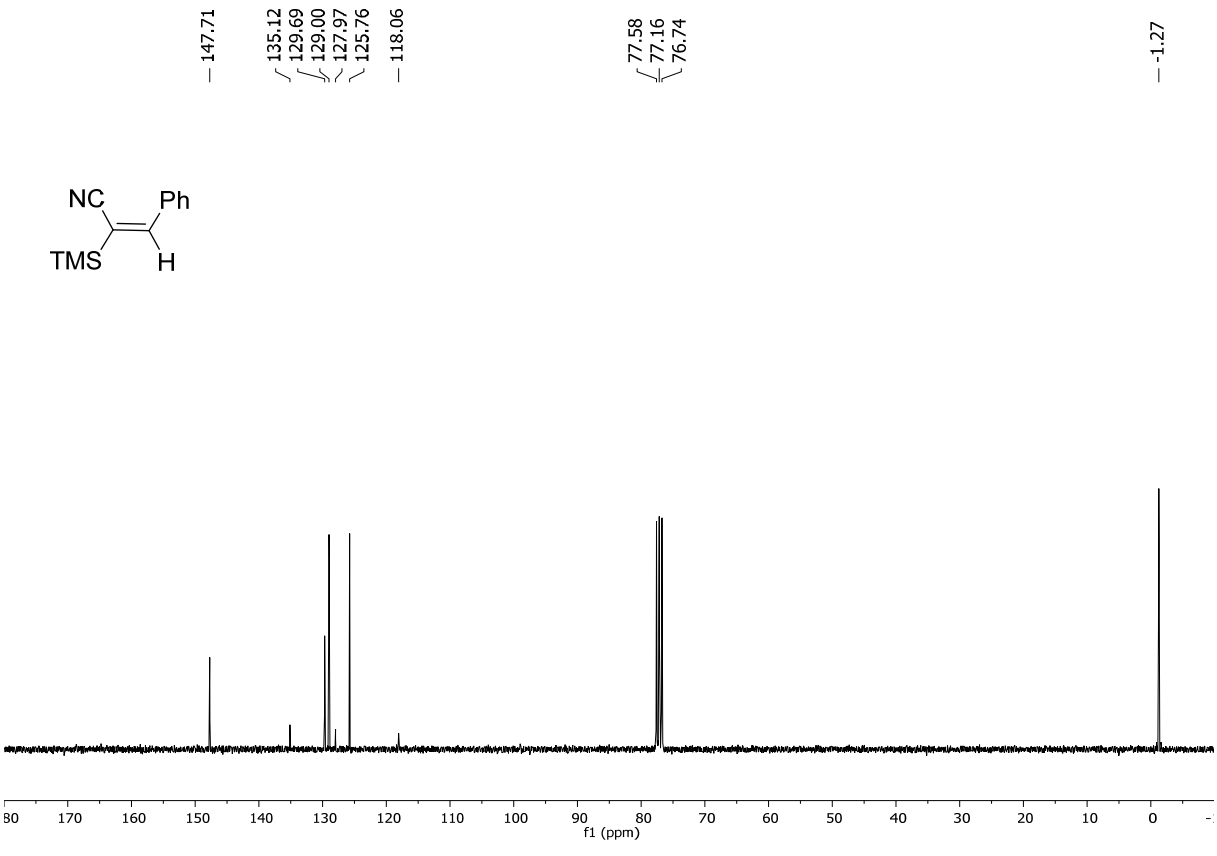


(*E*)-3-Phenyl-2-(trimethylsilyl)acrylonitrile

^{1}H NMR

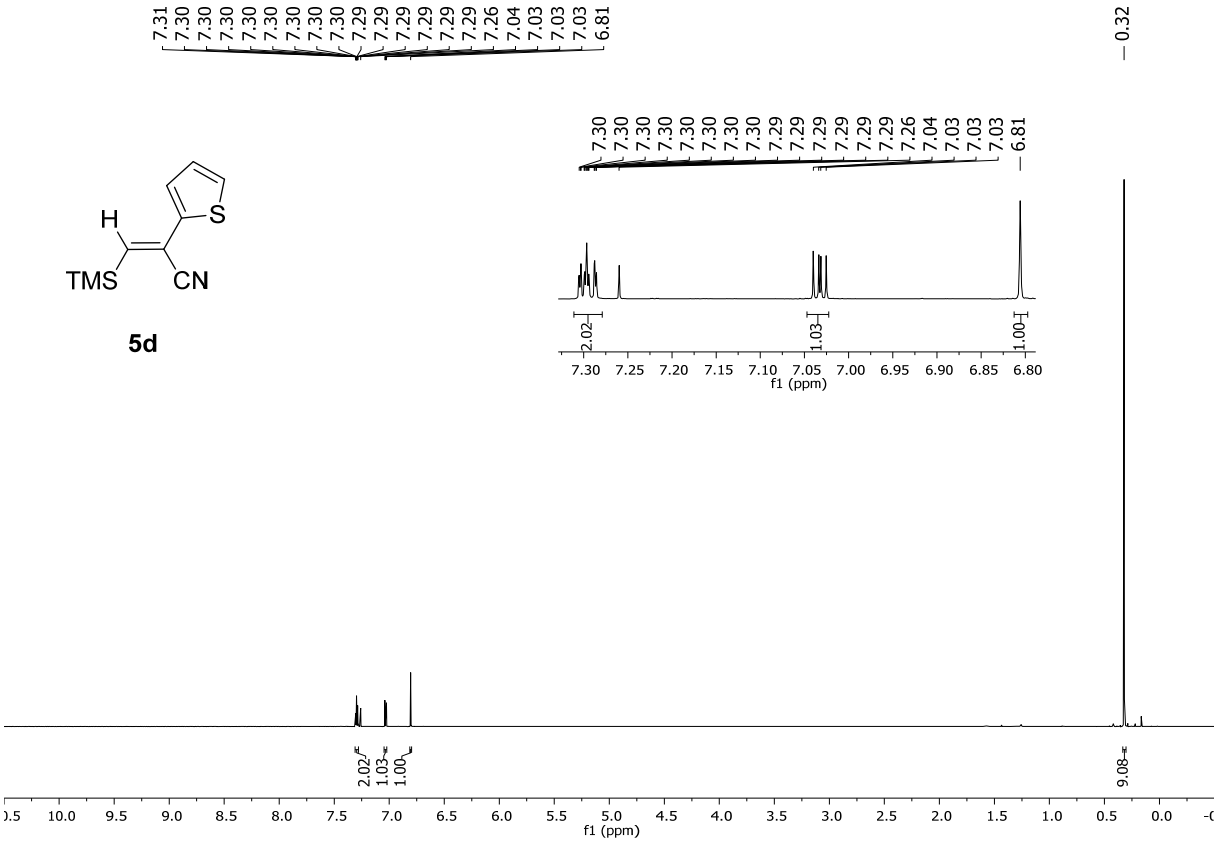


^{13}C NMR

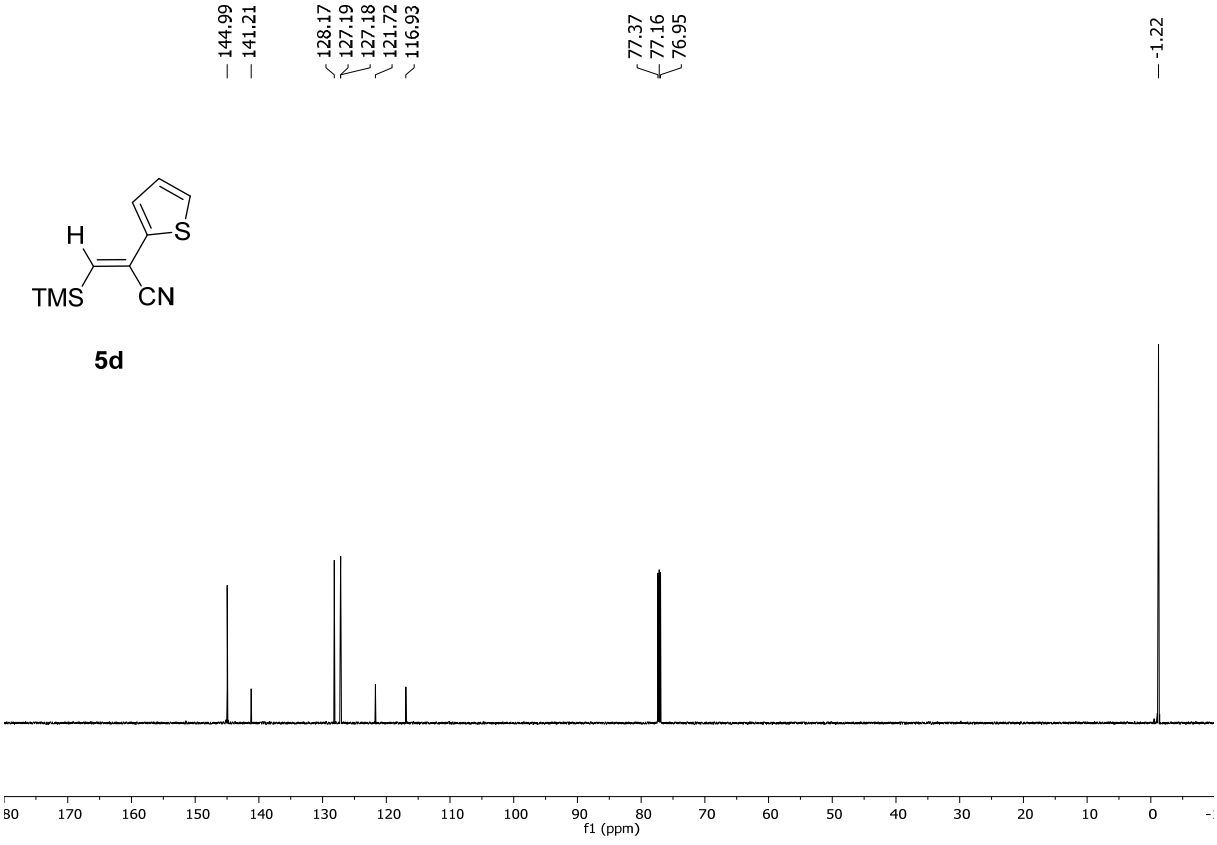


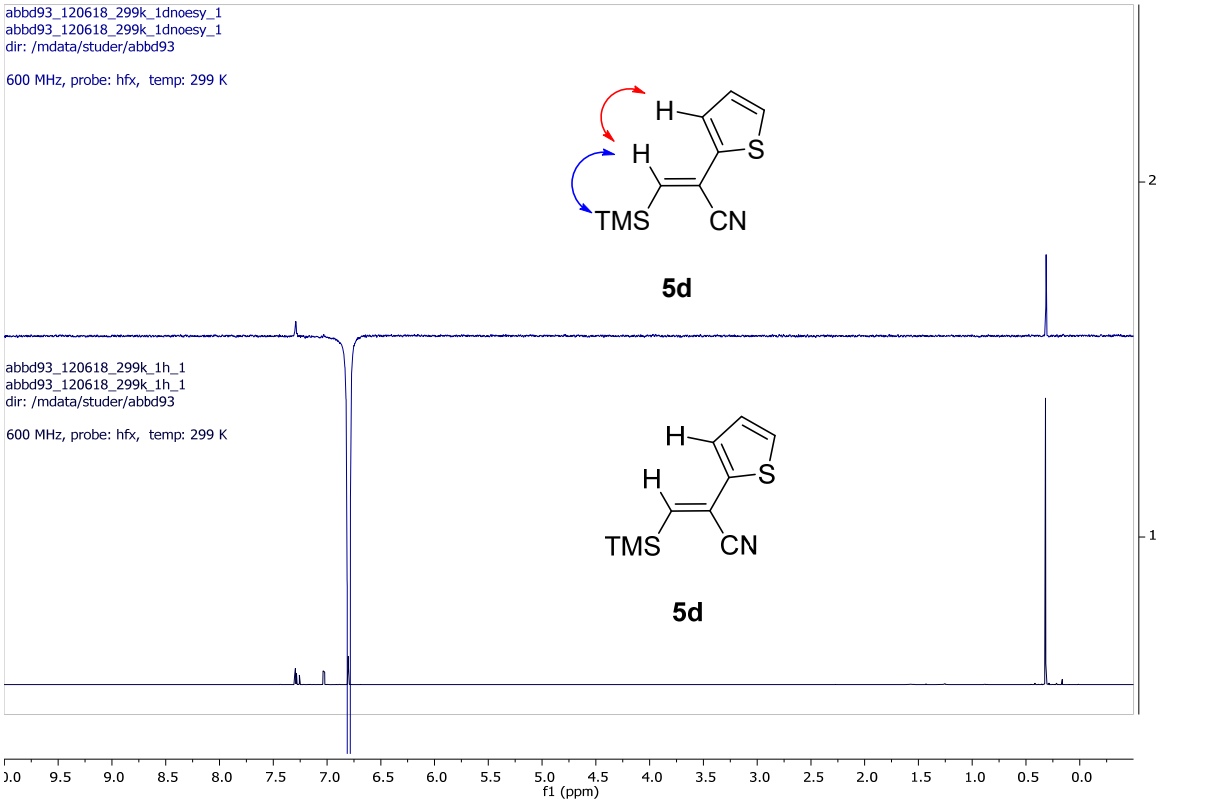
(*Z*)-2-(Thiophen-2-yl)-3-(trimethylsilyl)acrylonitrile (5d)

^{1}H NMR



^{13}C NMR

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abbd93_120618_299k_1dnoesy_1
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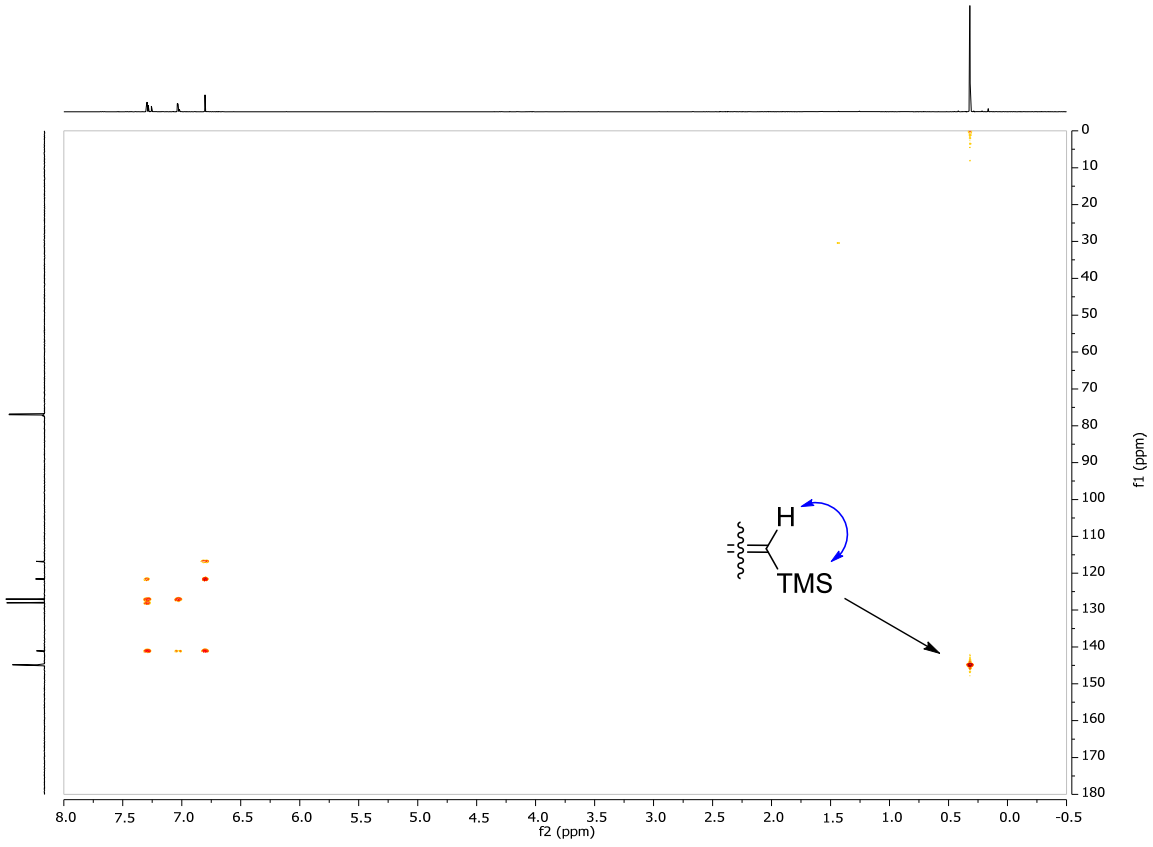
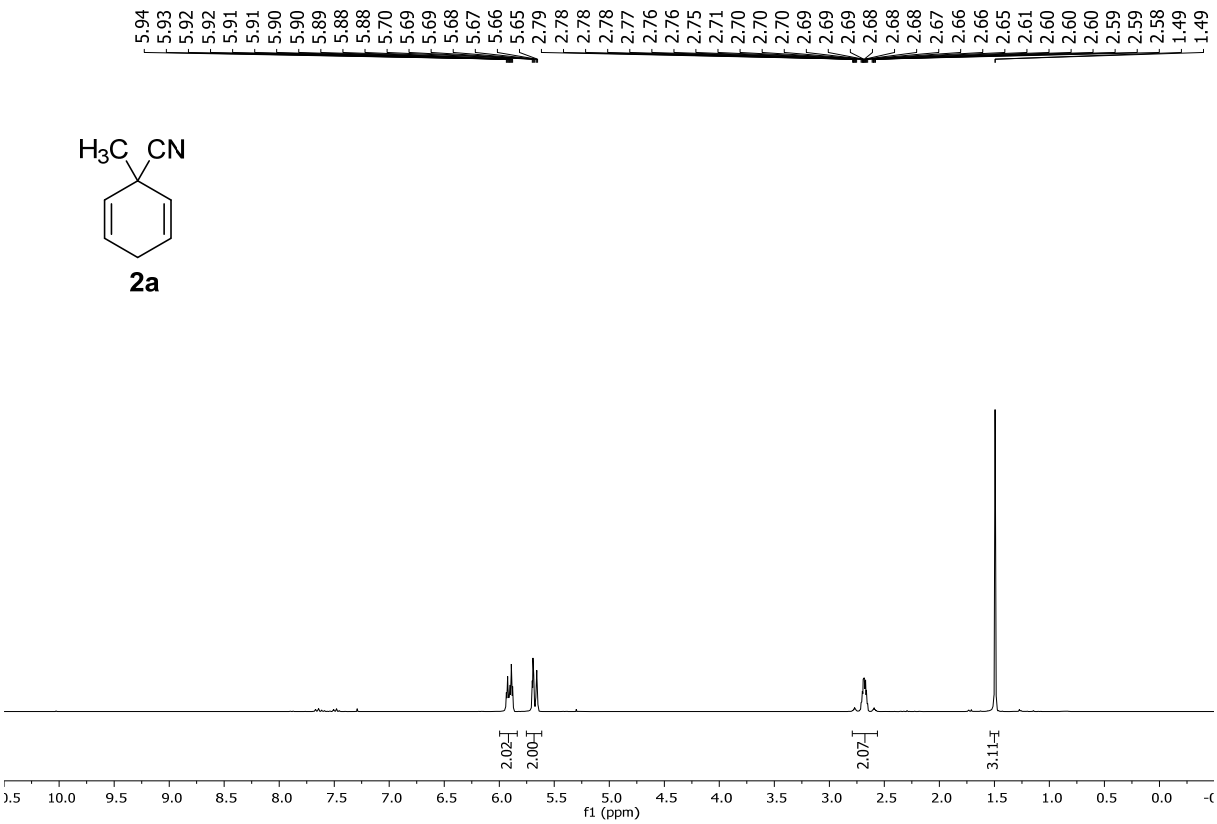
600 MHz, probe: hfx, temp: 299 K
H
H
S
TMS
CN
5d
abbd93_120618_299k_1h_1
abbd93_120618_299k_1h_1
dir: /mdata/studer/abbd93
600 MHz, probe: hfx, temp: 299 K
H
H
S
TMS
CN
5d
f1 (ppm)


H
TMS
f2 (ppm)
f1 (ppm)

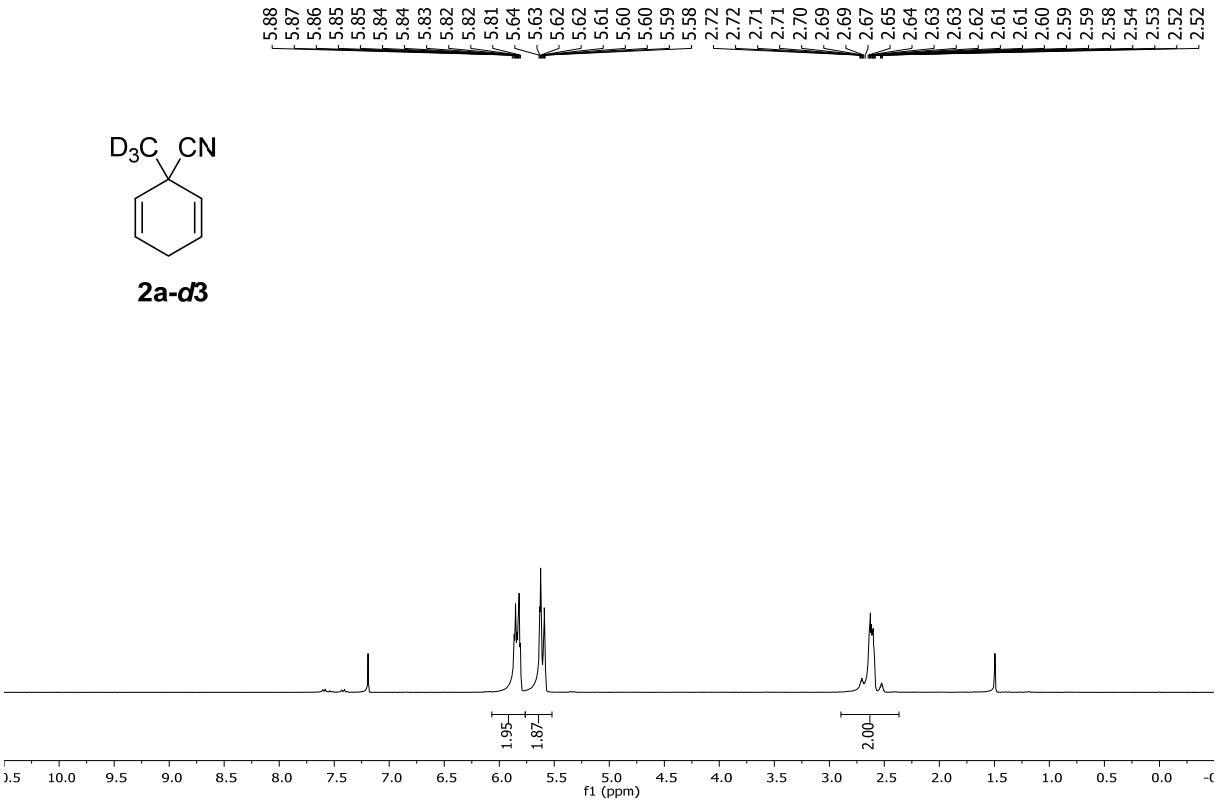
1-Methylcyclohexa-2,5-diene-1-carbonitrile (2a)

^{1}H-NMR



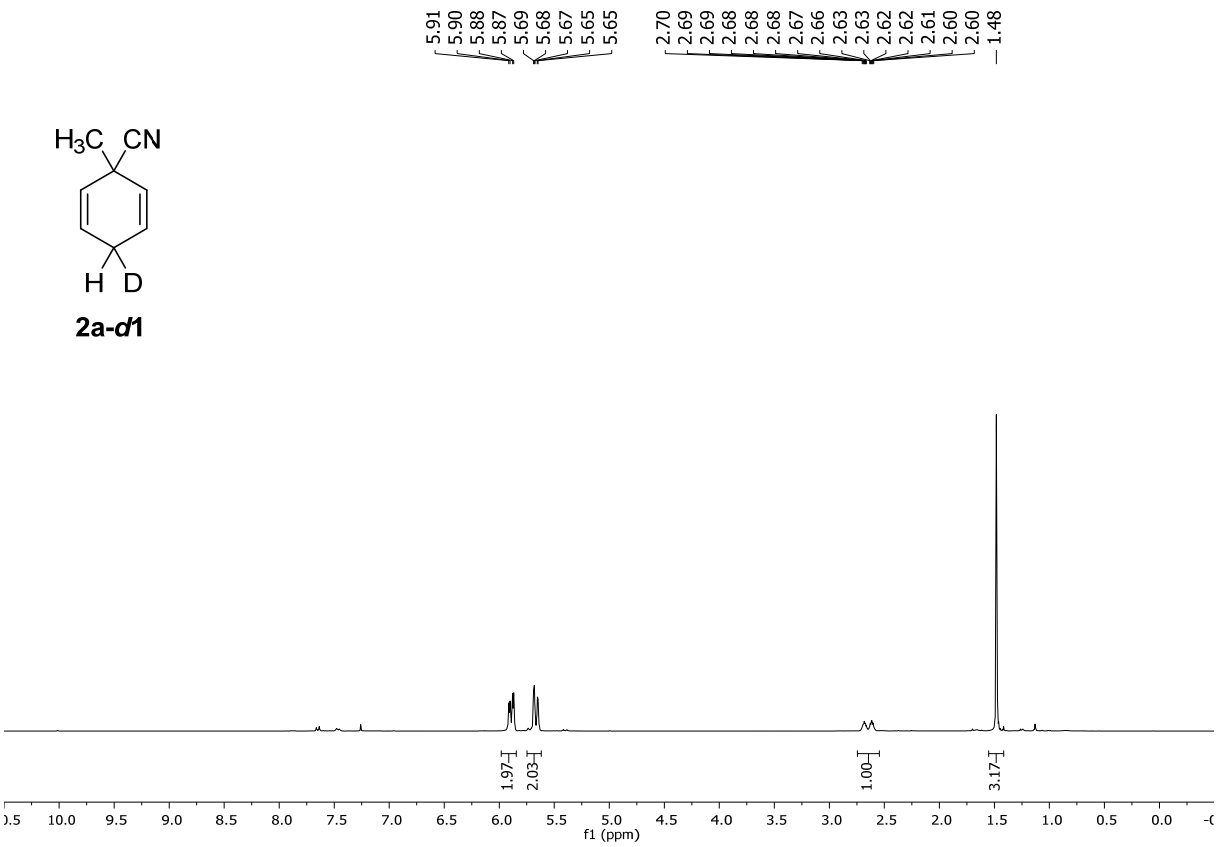
1-(Methyl-d_3)cyclohexa-2,5-diene-1-carbonitrile (2a-*d*3)

^{1}H-NMR

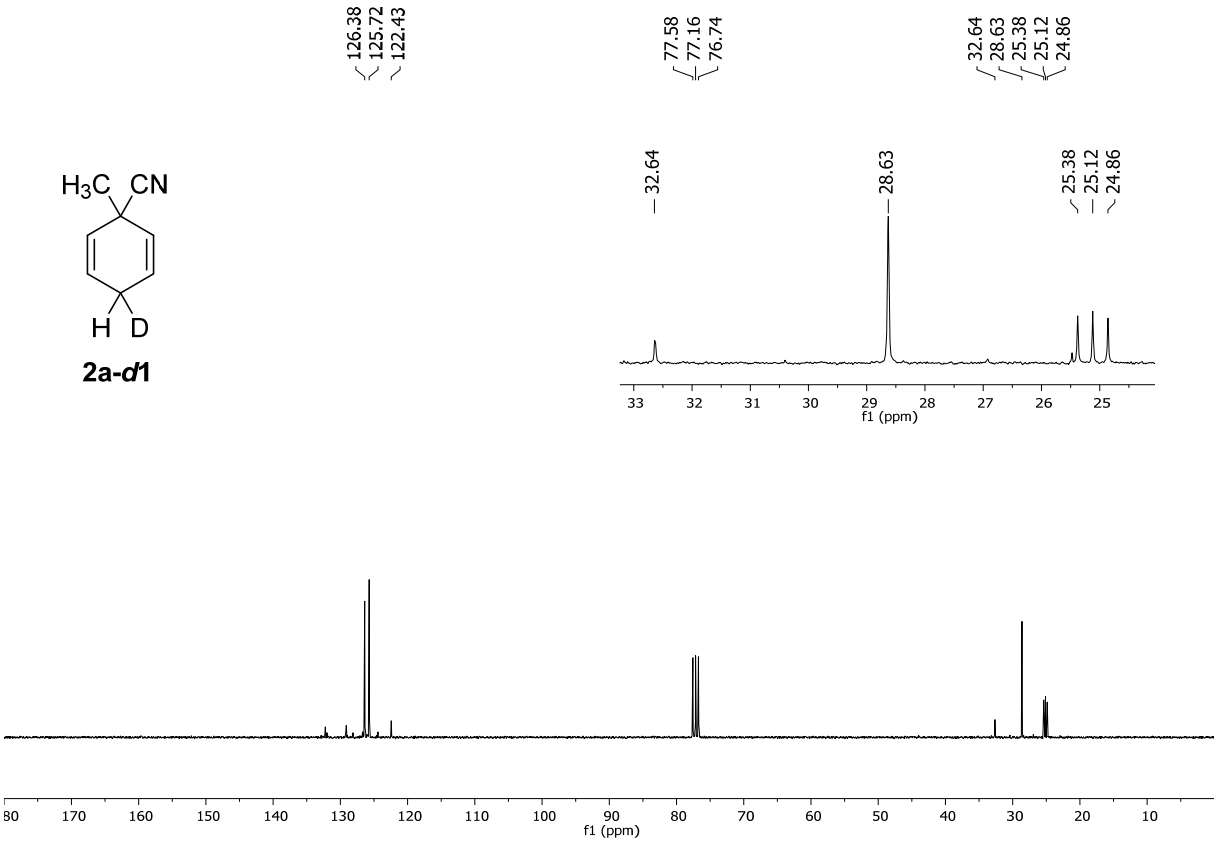


1-Methylcyclohexa-2,5-diene-1-carbonitrile-4-*d* (2a-*d*1)

^{1}H-NMR

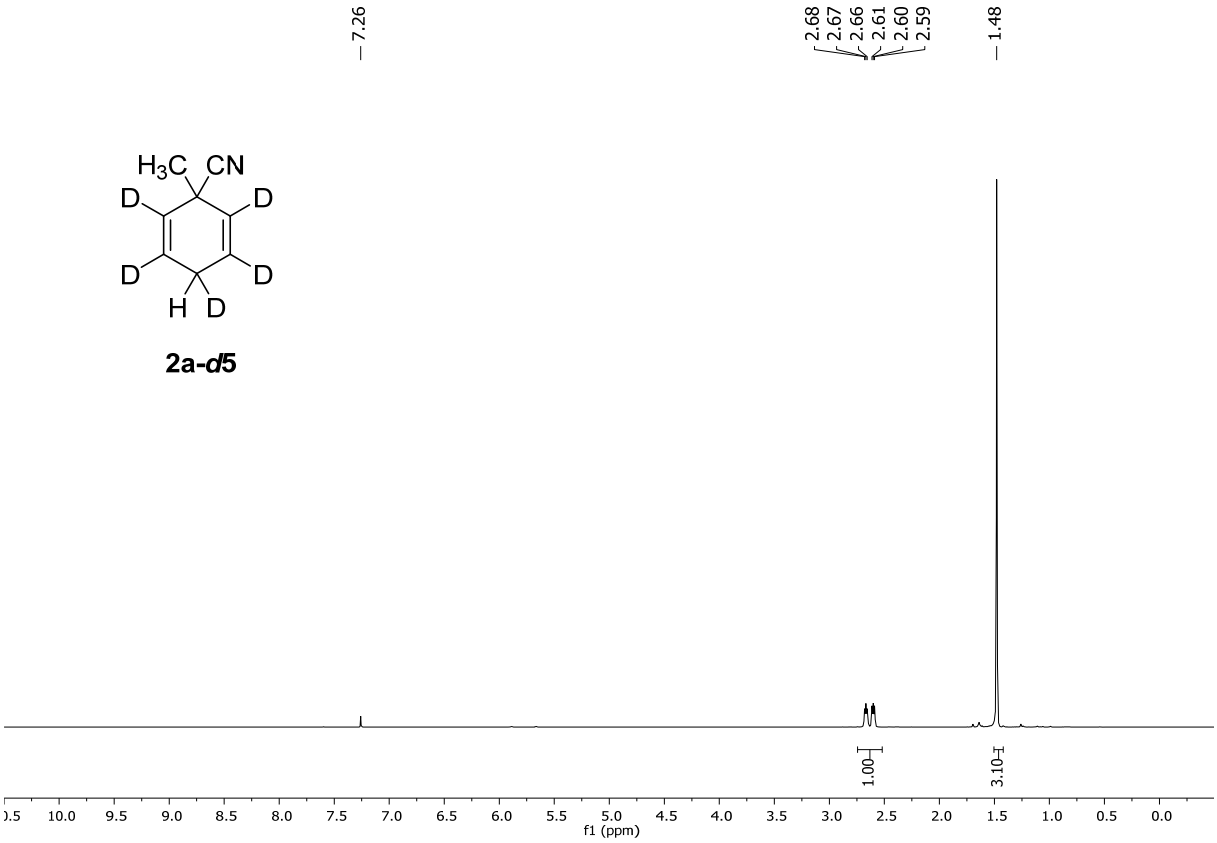


^{13}C-NMR

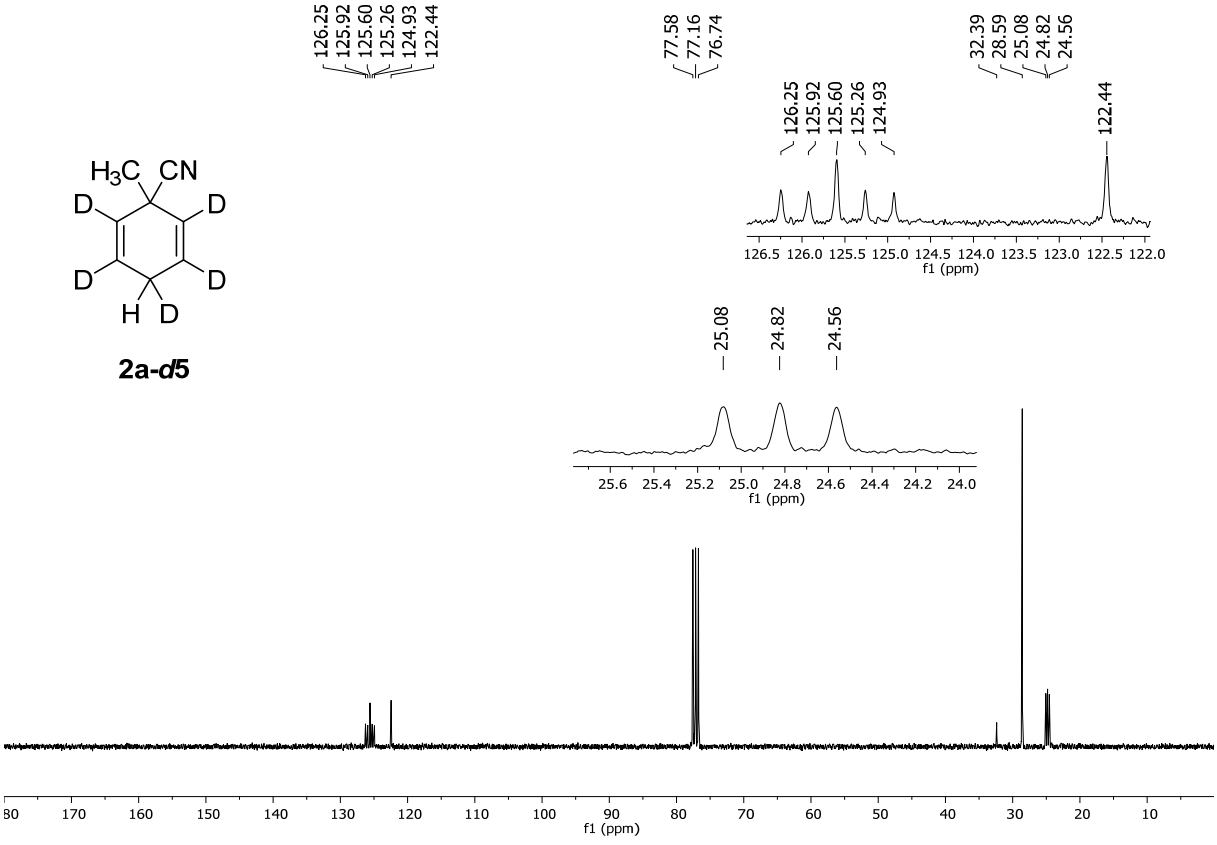


1-Methylcyclohexa-2,5-diene-1-carbonitrile-2,3,4,5,6-*d*5 (2a-*d*5)

^{1}H-NMR

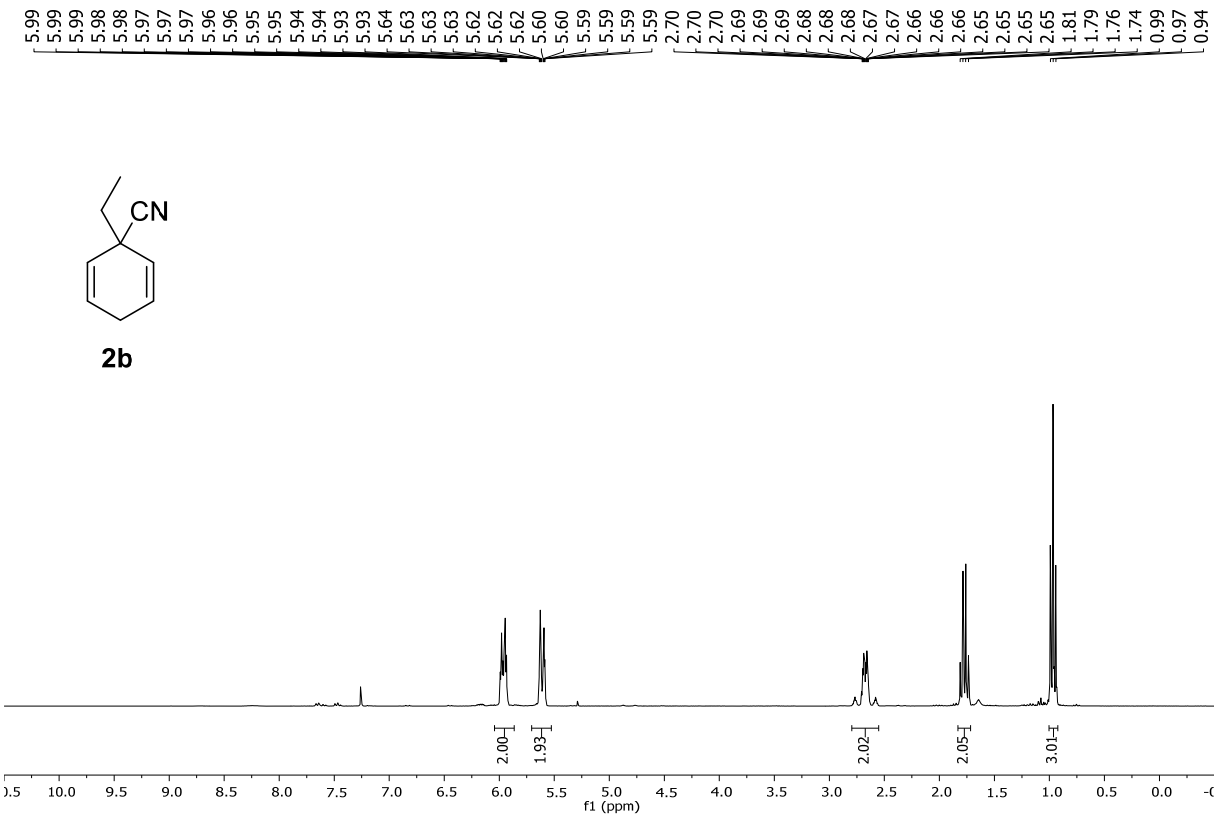


^{13}C-NMR

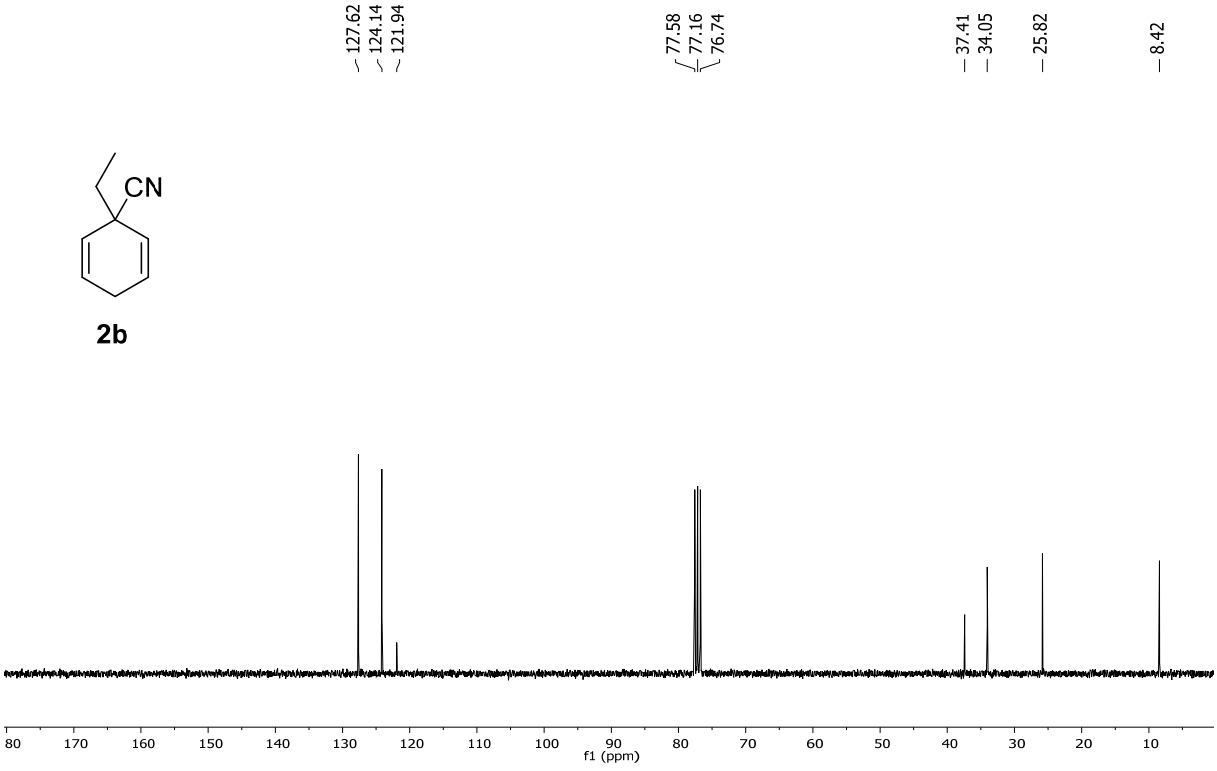


1-Ethylcyclohexa-2,5-diene-1-carbonitrile (2b)

^{1}H-NMR

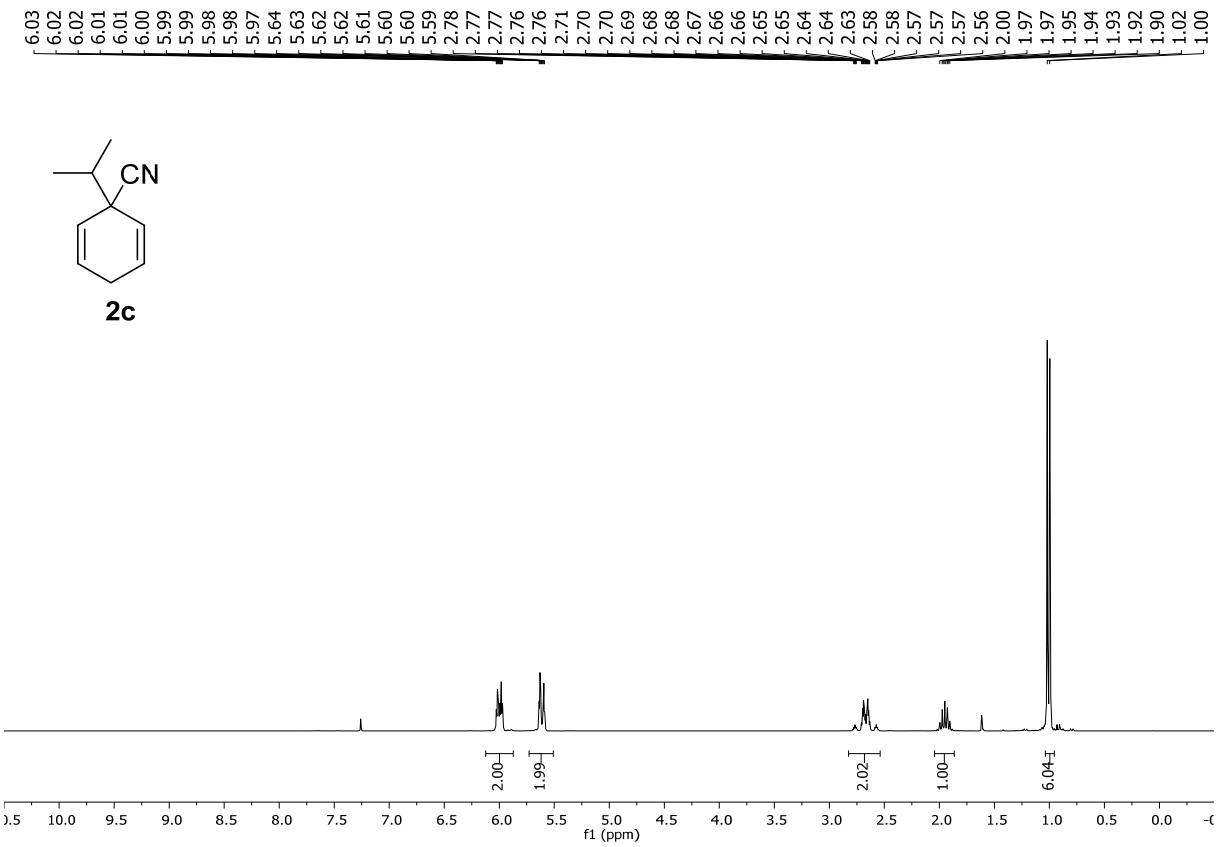


^{13}C-NMR

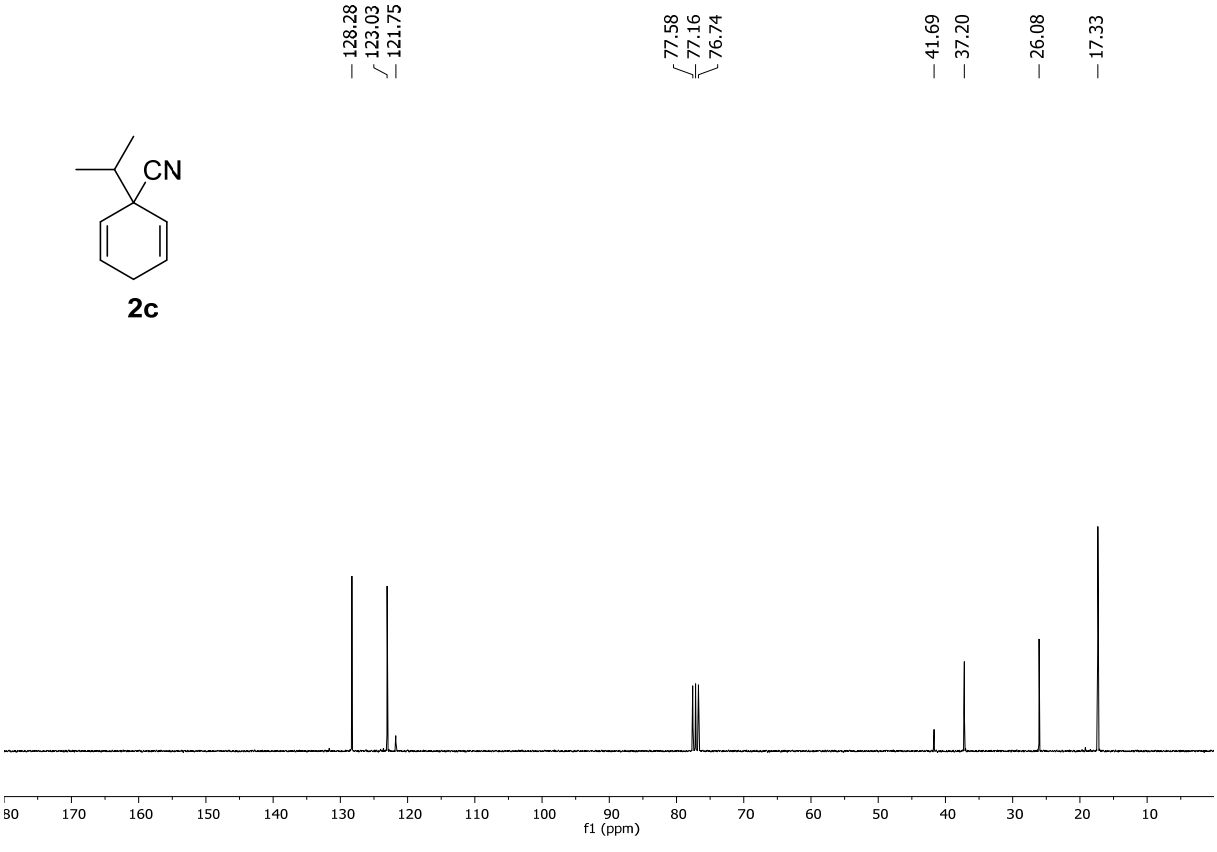


1-Isopropylcyclohexa-2,5-diene-1-carbonitrile (2c)

^{1}H-NMR

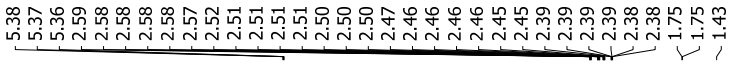


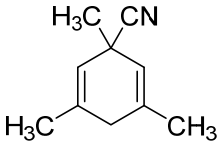
^{13}C-NMR



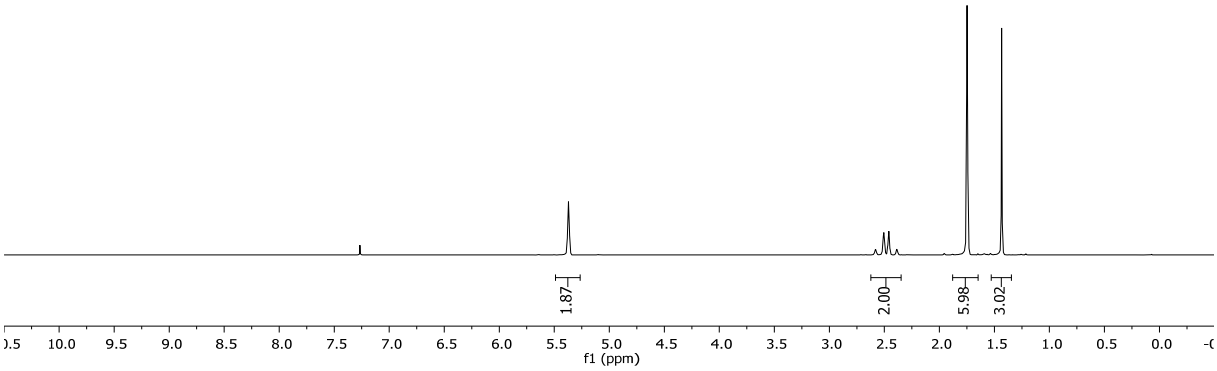
1,3,5-Trimethylcyclohexa-2,5-diene-1-carbonitrile (2d)

^{1}H-NMR

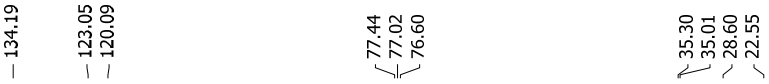


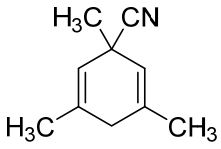


2d

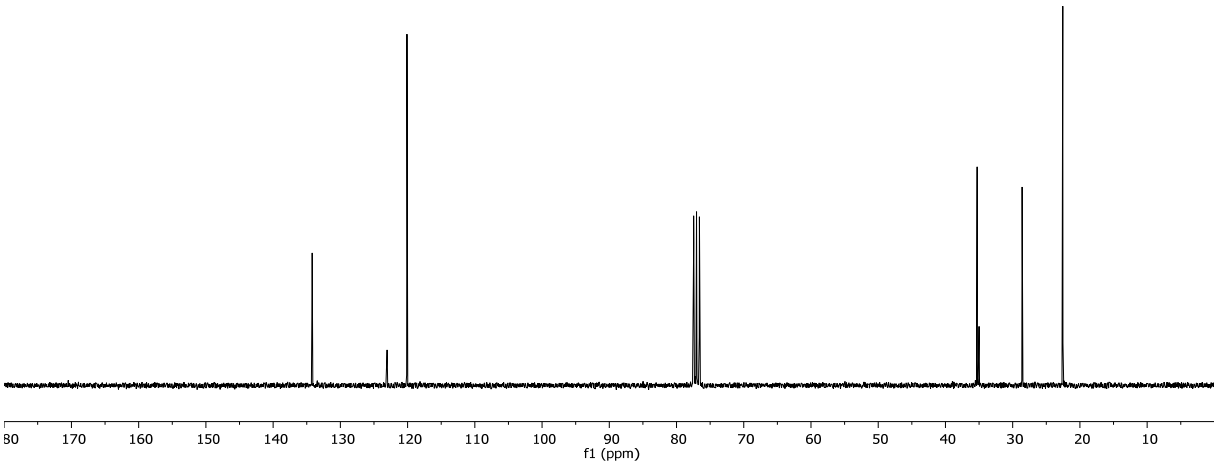


^{13}C-NMR



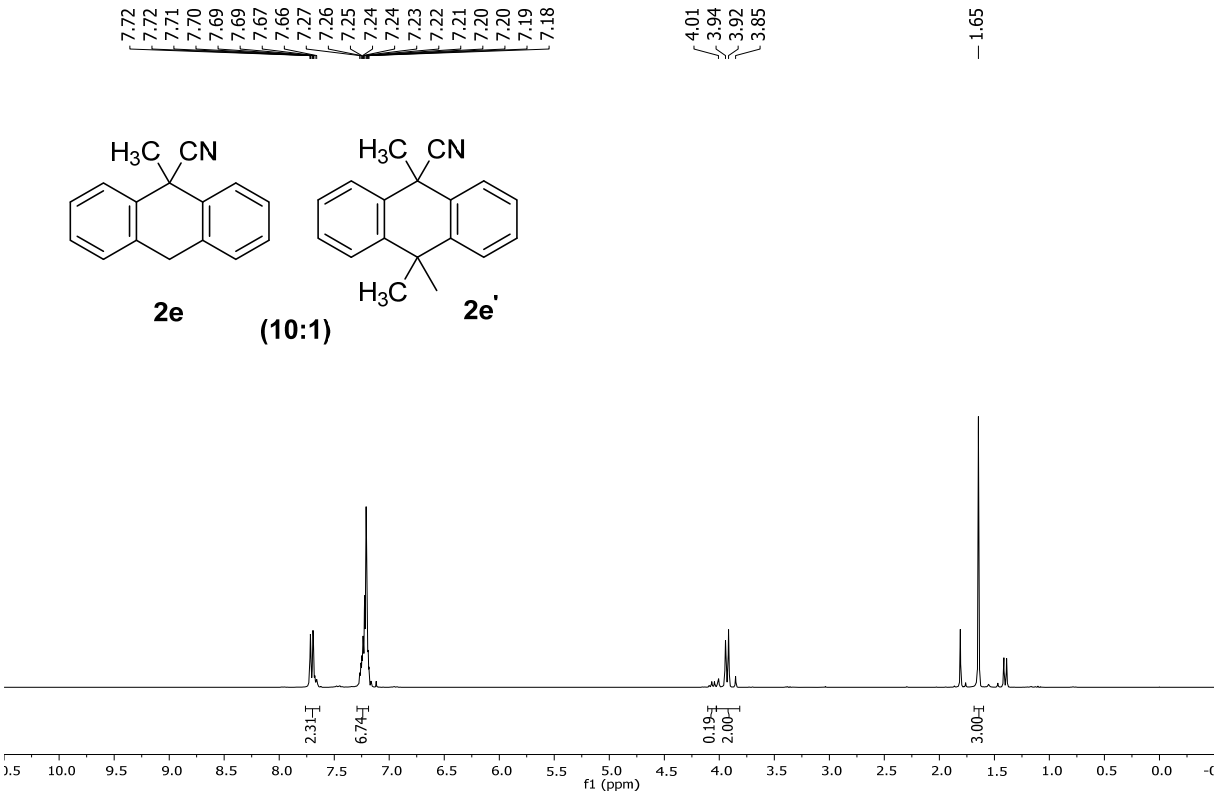


2d



9-Methyl-9,10-dihydroanthracene-9-carbonitrile (2e)

^{1}H-NMR



^{13}C-NMR