Supplementary Information

Lewis Acid-Controlled Pd-Catalyzed Chemodivergent Hydrocyanation of Cyclopropenes

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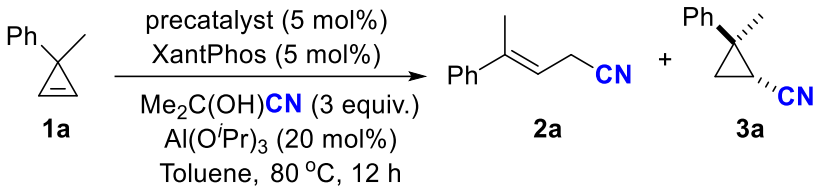
1. General information

All air and moisture sensitive manipulations were carried out with standard Schlenk technique or in a nitrogen-filled glove box (Vigor). Dried and oxygen free solvents were obtained from solvent purification system (Vigor YJC-7) and used thereafter. Column chromatography was performed using 200-300 mesh silica gels. The NMR spectra were recorded on a Bruker-400 MHz or 500 MHz instrument and chemical shifts are reported in ppm relative to the residual deuterated solvents. Chemical shifts (δ) are given in ppm and calibrated using the signal of residual undeuterated solvent as internal reference (δ_H = 7.26 ppm or 0.00 ppm, and δ_C = 77.16 ppm. Coupling constants (*J*) are reported in Hz and apparent splitting patterns are designated using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). High-resolution mass spectra (HRMS) were performed with electrospray spectrometer Waters Micromass Q-TOF Premier Mass Spectrometer. Shimadzu Nexis GC-2030 determined GC yields. $Pd(dba)_2$ was purchased from bidepharm (https://www.bidepharm.com/). The substrates and reagents for catalytic reactions were degassed and stored in the glovebox.

2. Optimization reaction conditions

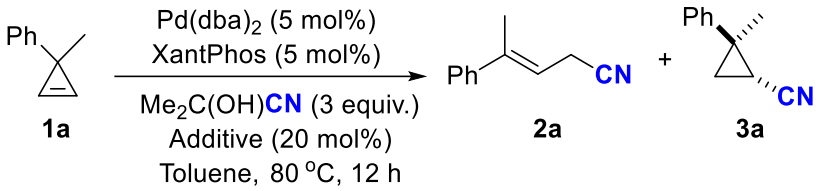
Table S1: Screening of precatalyst



Entry	Precatalyst	Additive	**2a** Yield/%[b]	**3a** Yield/%[b]
1	$Ni(cod)_2$	-	75	ND
2	$Ni(acac)_2$	-	61	ND
3	$Ni(OAc)_2$	-	20	ND
4	$[RhCl(cod)]_2$[c]	-	ND	ND
5	$Pd(OAc)_2$	-	67	ND
6	$PdCl_2$	-	28	ND
7	$Pd(PPh_3)_4$	-	52	ND
8	$Pd(acac)_2$	-	45	ND
9	$Ni(cod)_2$	$Al(O^iPr)_3$	67	ND
10	$Ni(acac)_2$	$Al(O^iPr)_3$	40	ND
11	$Ni(OAc)_2$	$Al(O^iPr)_3$	20	ND
12	$[RhCl(cod)]_2$[c]	$Al(O^iPr)_3$	ND	ND
13	$Pd(OAc)_2$	$Al(O^iPr)_3$	13	44
14	$PdCl_2$	$Al(O^iPr)_3$	20	21
15	$Pd(PPh_3)_4$	$Al(O^iPr)_3$	12	47
16	$Pd(acac)_2$	$Al(O^iPr)_3$	21	54

[a] All reactions were carried with **1a** (0.2 mmol), $Me_2C(OH)CN$ (0.6 mmol), catalyst (5 mol%), XantPhos (5 mol%), additive (20 mol%), Toluene (0.3 mL), 80 °C, 12 h. [b] Yield was determined via gas chromatography analysis using *n*-dodecane as an internal standard. ND = No detected. [c] 2.5 mol% catalyst was used.

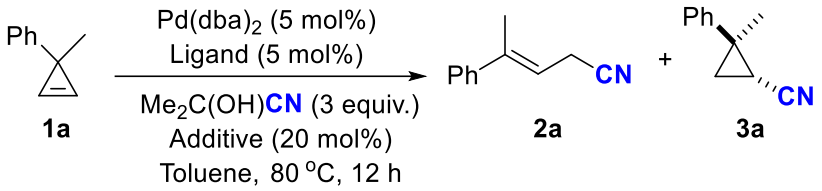
Table S2: Screening of additive



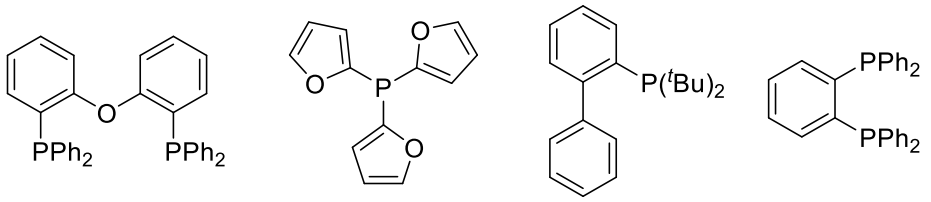
Entry	Additive	**2a** Yield/%[b]	**3a** Yield/%[b]
1	LiBr	10	6
2	Li_2SO_4	58	12
3	$TiCl_4$	23	ND
4	$ZnCl_2$	52	ND
5	$CuSO_4$	32	ND
6	I_2	13	ND
7	$AlCl_3$	43	10
8	Al_2O_3	81	ND
9	$Al(OAc)_2(OH)$	65	ND
10	$Al(OAc)_3$	55	7
10	$Al(O^sBu)_3$	32	35
11	$Al(O^tBu)_3$	21	45

[a] All reactions were carried with **1a** (0.2 mmol), $Me_2C(OH)CN$ (0.6 mmol), $Pd(dba)_2$ (5 mol%), XantPhos (5 mol%), additive (20 mol%), Toluene (0.3 mL), 80 °C, 12 h. [b] Yield was determined via gas chromatography analysis using *n*-dodecane as an internal standard. ND = No detected.

Table S3: Screening of ligand



Entry	Ligand	Additive	**2a** Yield/%[b]	**3a** Yield/%[b]
1	**L1**	-	81	ND
2	**L2**	-	14	ND
3	**L3**	-	43	ND
4	**L4**	-	58	ND
5	**L5**	-	72	ND
6	**L1**	$Al(O^iPr)_3$	15	57
7	**L2**	$Al(O^iPr)_3$	80	ND
8	**L3**	$Al(O^iPr)_3$	14	trace
9	**L4**	$Al(O^iPr)_3$	38	ND
10	**L5**	$Al(O^iPr)_3$	46	ND
11	**L6**	$Al(O^iPr)_3$	42	ND
12	**L7**	$Al(O^iPr)_3$	32	16[c]
13	**L8**	$Al(O^iPr)_3$	54	ND



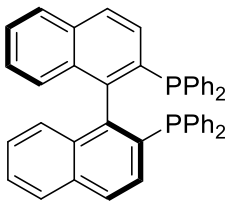
L1

L2

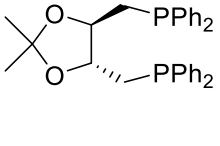
L3

L4

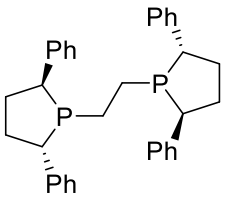
L5



L6



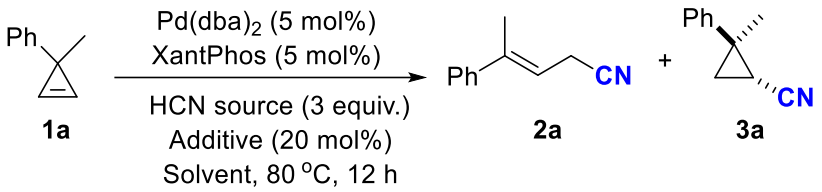
L7



L8

[a] All reactions were carried with **1a** (0.2 mmol), $Me_2C(OH)CN$ (0.6 mmol), $Pd(dba)_2$ (5 mol%), bidentate ligand (5 mol%) or monodentate ligand (10 mol%), additive (20 mol%), Toluene (0.3 mL), 80 °C, 12 h. [b] Yield was determined via gas chromatography analysis using *n*-dodecane as an internal standard. ND = No detected. [c] When L7 was used as the ligand, compound **3a** was obtained with 0% *ee*. The enantiomeric excess (*ee*) values were determined using chiral HPLC under the following conditions: Daicel Chiralpak OD-H column, hexane/^{i}PrOH = 95:5, 0.8 mL/min flow rate, detection at 214 nm. The retention times were tR1 = 8.40 min and tR2 = 9.39 min

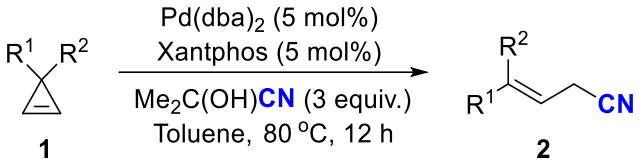
Table S4: Screening of HCN source



Entry	HCN source	Solvent	Additive	**2a** Yield/%[b]	**3a** Yield/%[b]
1	TMSCN	Toluene	-	ND	ND
2	TMSCN	MeOH	-	23	ND
3	$Zn(CN)_2$	Toluene	-	ND	ND
4	$Zn(CN)_2$	MeOH	-	ND	ND
5	CuCN	Toluene	-	ND	ND
6	CuCN	MeOH	-	ND	ND
7	TMSCN	Toluene	$Al(O^iPr)_3$	ND	ND
8	TMSCN	MeOH	$Al(O^iPr)_3$	20	ND
9	$Zn(CN)_2$	Toluene	$Al(O^iPr)_3$	ND	ND
10	$Zn(CN)_2$	MeOH	$Al(O^iPr)_3$	ND	ND
11	CuCN	Toluene	$Al(O^iPr)_3$	ND	ND
12	CuCN	MeOH	$Al(O^iPr)_3$	ND	ND

[a] All reactions were carried with **1a** (0.2 mmol), HCN source (0.6 mmol), $Pd(dba)_2$ (5 mol%), XantPhos (5 mol%), additive (20 mol%), Solvent (0.3 mL), 80 °C, 12 h. [b] Yield was determined via gas chromatography analysis using *n*-dodecane as an internal standard. ND = No detected.

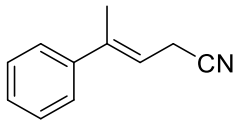
3. General procedure for the ring-opening hydrocyanation and the data for products



1 2

General procedure A: In a N_2-filled glovebox, Xantphos (5.8 mg, 0.01 mmol) and $Pd(dba)_2$ (5.8 mg, 0.01 mmol) and toluene (0.3 mL) were added to an oven-dried 4 mL screw-cap vial. The resulting mixture was stirred for 10 min and then cyclopropene **1** (0.2 mmol) and acetone cyanohydrin (0.6 mmol) were added. The vial was taken out of the glovebox and heated at 80 °C for 12 hours. Subsequently, the reaction was cooled down to room temperature and the reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel to afford the desired product **2**.

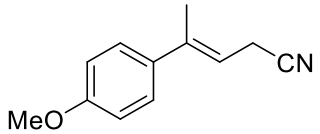
(*E*)-4-phenylpent-3-enenitrile (2a)



2a

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **2a** as a colorless oil (26.7 mg, yield: 85%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5H), 5.73-5.69 (m, 1H), 3.25 (d, J = 6.8 Hz, 2H), 2.10 (d, J = 1.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.10, 141.54, 128.57, 127.95, 125.96, 118.20, 114.67, 17.09, 16.49; **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{11}H_{11}N^+$, 157.0886; found 157.0883. The above data matched the reported data.[1]

(*E*)-4-(4-methoxyphenyl)pent-3-enenitrile (2b)

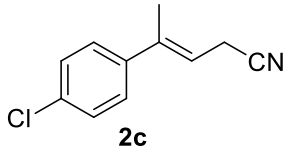


2b

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford **2b** as a colorless oil (30.7 mg, yield: 82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 2H),

6.91-6.85 (m, 2H), 5.66-5.62 (m, 1H), 3.82 (s, 3H), 3.23 (d, J = 6.8 Hz, 2H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.49, 140.80, 134.53, 127.07, 118.37, 113.90, 113.03, 55.45, 17.07, 16.44; **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_{13}NO^+$, 187.0992; found 187.0990. The above data matched the reported data.[1]

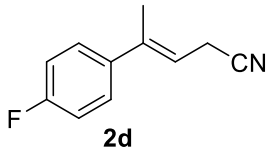
(*E*)-4-(4-chlorophenyl)pent-3-enenitrile (2c)



2c

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **2c** as a colorless oil (32.9 mg, yield: 86%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 4H), 5.72-5.68 (m, 1H), 3.25 (d, J = 6.8 Hz, 2H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.47, 133.83, 128.72, 127.27, 117.98, 115.23, 17.09, 16.44; **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{11}H_9NCl^+$, 190.0418; found 190.0417. The above data matched the reported data.[1]

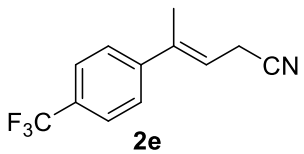
(*E*)-4-(4-fluorophenyl)pent-3-enenitrile (2d)



2d

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **2d** as a colorless oil (30.8 mg, yield: 88%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 2H), 7.05-7.00 (m, 2H), 5.68-5.64 (m, 1H), 3.24 (d, J = 6.8 Hz, 2H), 2.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.60 (d, J = 247.2 Hz), 140.57, 138.16 (d, J = 3.3 Hz), 127.60 (d, J = 8.0 Hz), 118.09, 115.42 (d, J = 21.5 Hz), 114.67, 17.08, 16.62; **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{11}H_{10}NF^+$, 175.0792; found 175.0786.

(*E*)-4-(4-(trifluoromethyl)phenyl)pent-3-enenitrile (2e)

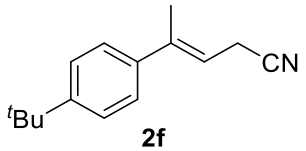


2e

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **2e** as a colorless oil (32.0 mg, yield: 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz,

2H), 7.46 (d, *J* = 8.4 Hz, 2H), 5.80-5.75 (m, 1H), 3.28 (dd, *J* = 6.8, 1.2 Hz, 2H), 2.12 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.56, 140.57, 129.98 (q, *J* = 32.6 Hz), 126.33, 125.57 (q, *J* = 3.8 Hz), 122.86, 117.78, 116.76, 17.13, 16.46; **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_{10}NF_3^+$, 225.0760; found 225.0751. The above data matched the reported data.[4]

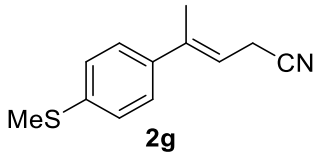
(*E*)-4-(4-(tert-butyl)phenyl)pent-3-enenitrile (2f)



2f

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **2f** as a colorless oil (34.5 mg, yield: 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.33-7.29 (m, 2H), 5.72-5.68 (m, 1H), 3.25 (d, *J* = 6.8 Hz, 2H), 2.08 (s, 3H), 1.33 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.05, 141.17, 139.10, 125.62, 125.48, 118.33, 113.93, 34.66, 31.41, 17.09, 16.38. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{14}H_{16}N^+$, 198.1277; found 198.1277.

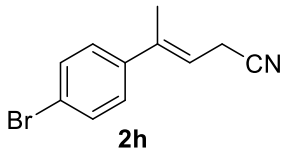
(*E*)-4-(4-(methylthio)phenyl)pent-3-enenitrile (2g)



2g

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford **2g** as a colorless oil (25.6 mg, yield: 63%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2H), 7.24-7.20 (m, 2H), 5.72-5.67 (m, 1H), 3.25 (d, *J* = 6.8 Hz, 2H), 2.49 (s, 3H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.81, 138.75, 138.39, 126.53, 126.35, 118.20, 114.17, 17.11, 16.35, 15.88. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_{13}NS^+$, 203.0763; found 203.0763.

(*E*)-4-(4-bromophenyl)pent-3-enenitrile (2h)

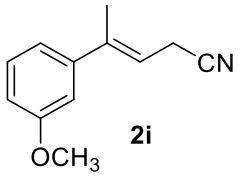


2h

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **2h** as a

colorless oil (37.6 mg, yield: 80%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.44 (m, 2H), 7.24-7.21 (m, 2H), 5.73-5.68 (m, 1H), 3.24 (d, *J* = 6.8 Hz, 2H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.91, 140.48, 131.64, 127.58, 121.93, 117.93, 115.28, 17.08, 16.35; **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{11}H_9NBr^+$, 233.9913; found 233.9913. The above data matched the reported data.[4]

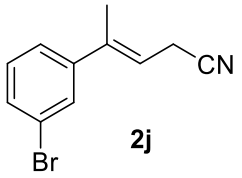
(*E*)-4-(3-methoxyphenyl)pent-3-enenitrile (2i)



2i

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford **2i** as a colorless oil (27.7 mg, yield: 74%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 1H), 6.96-6.94 (m, 1H), 6.89-6.88 (m, 1H), 6.86-6.84 (m, 1H), 5.74-5.70 (m, 1H), 3.83 (s, 3H), 3.24 (d, *J* = 6.8 Hz, 2H), 2.08 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.75, 143.64, 141.42, 129.55, 118.46, 118.16, 114.86, 113.17, 111.97, 55.40, 17.04, 16.54. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_{13}NO^+$, 187.0992; found 187.0991.

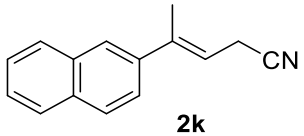
(*E*)-4-(3-bromophenyl)pent-3-enenitrile (2j)



2j

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **2j** as a colorless oil (24.3 mg, yield: 52%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (t, *J* = 2.0 Hz, 1H), 7.44-7.41 (m, 1H), 7.30-7.26 (m, 1H), 7.23-7.19 (m, 1H), 5.74-5.69 (m, 1H), 3.25 (d, *J* = 6.8 Hz, 2H), 2.07 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.17, 140.37, 130.91, 130.11, 129.15, 124.61, 122.75, 117.88, 115.96, 17.08, 16.45. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{11}H_9BrN^+$, 233.9913; found 233.9913.

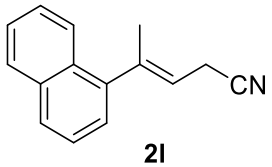
(*E*)-4-(naphthalen-2-yl)pent-3-enenitrile (2k)



2k

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **2k** as a colorless oil (26.5 mg, yield: 64%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86-7.80 (m, 4H), 7.54-7.47 (m, 3H), 5.89-5.84 (m, 1H), 3.31 (d, *J* = 6.8 Hz, 2H), 2.20 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.33, 139.22, 133.38, 133.00, 128.30, 128.17, 127.68, 126.50, 126.26, 124.88, 124.07, 118.22, 115.16, 17.19, 16.49. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{15}H_{13}N^+$, 207.1043; found 207.1036. The above data matched the reported data.[1]

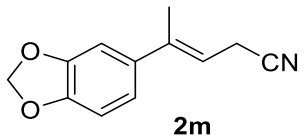
(*E*)-4-(naphthalen-1-yl)pent-3-enenitrile (2l)



2l

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **2l** as a colorless oil (29.4 mg, yield: 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91-7.86 (m, 2H), 7.82-7.80 (m, 1H), 7.53-7.49 (m, 2H), 7.46 (dd, *J* = 8.4, 6.8 Hz, 1H), 7.28-7.26 (m, 1H), 5.61-5.56 (m, 1H), 3.37 (d, *J* = 6.8 Hz, 2H), 2.20 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.28, 141.71, 133.83, 130.82, 128.60, 127.91, 126.28, 126.00, 125.49, 125.36, 125.01, 118.18, 117.56, 19.47, 16.86. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{15}H_{13}N^+$, 207.1043; found 207.1038.

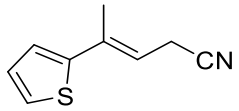
(*E*)-4-(benzo[d][1,3]dioxol-5-yl)pent-3-enenitrile (2m)



2m

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 8/1) to afford **2m** as a yellow oil (30.6 mg, yield: 76%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.86-6.83 (m, 2H), 6.78-6.75 (m, 1H), 5.96 (s, 2H), 5.63-5.59 (m, 1H), 3.22 (dq, *J* = 7.2, 0.8 Hz, 2H), 2.04 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.88, 147.41, 140.96, 136.38, 119.56, 118.22, 113.64, 108.20, 106.48, 101.29, 17.04, 16.65. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_{11}NO_2^+$, 201.0784; found 201.0783.

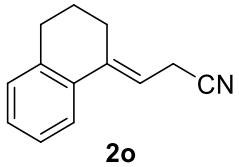
(*E*)-4-(thiophen-2-yl)pent-3-enenitrile (2n)



2n

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **2n** as a colorless oil (27.4 mg, yield: 84%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.06 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.99 (dd, *J* = 5.2, 3.6 Hz, 1H), 5.88-5.83 (m, 1H), 3.25 (d, *J* = 6.8 Hz, 2H), 2.11 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.41, 134.94, 127.58, 124.81, 124.02, 117.90, 112.88, 16.85, 16.31. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_9H_9NS^+$, 163.0450; found 163.0447. he above data matched the reported data.[4]

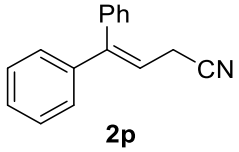
(*E*)-3-(3,4-dihydronaphthalen-1(2H)-ylidene)propanenitrile (2o)



2o

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **2o** as a colorless oil (23.1 mg, yield: 63%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57-7.52 (m, 1H), 7.22-7.16 (m, 2H), 7.14-7.11 (m, 1H), 5.97-5.92 (m, 1H), 3.25 (d, *J* = 7.0 Hz, 2H), 2.79 (t, *J* = 6.2 Hz, 2H), 2.51 (t, *J* = 5.4 Hz, 2H), 1.90-1.84 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.33, 138.06, 134.42, 129.08, 128.00, 126.44, 124.06, 118.33, 110.50, 30.32, 26.81, 22.74, 16.53. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{13}H_{13}N^+$, 183.1043; found 183.1040.

4,4-diphenylbut-3-enenitrile (2p)

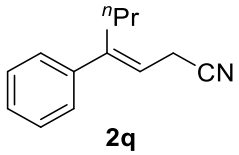


2p

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford **2p** as a white solid (21.5 mg, yield: 49%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.36 (m, 3H), 7.32-7.28 (m, 3H), 7.24-7.21 (m, 2H), 7.19-7.16 (m, 2H), 6.04 (t, *J* = 7.6 Hz, 1H), 3.15 (d, *J* = 7.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.69, 140.82, 138.11, 129.51,

128.93, 128.49, 128.33, 128.27, 127.57, 118.27, 115.58, 18.51. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{16}H_{13}N^+$, 219.1043; found 219.1036. The above data matched the reported data.[5]

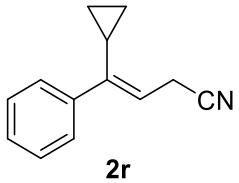
(*E*)-4-phenylhept-3-enenitrile (2q)



2q

According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **2q** as a colorless oil (25.5 mg, yield: 69%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 5H), 5.60 (t, *J* = 7.2 Hz, 1H), 3.26 (d, *J* = 7.2 Hz, 2H), 2.48 (t, *J* = 7.2 Hz, 2H), 1.44-1.34 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.66, 141.46, 128.56, 127.84, 126.61, 118.39, 115.14, 32.26, 21.40, 16.94, 13.95. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{13}H_{15}N^+$, 185.1199; found 185.1200.

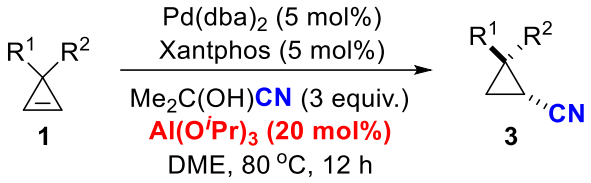
(*E*)-4-cyclopropyl-4-phenylbut-3-enenitrile (2r)



2r

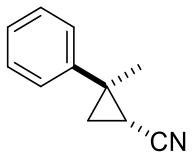
According to the general procedure A, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **2r** as a colorless oil (18.3 mg, yield: 50%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 5H), 5.68-5.64 (m, 1H), 3.44 (d, *J* = 6.8 Hz, 2H), 1.75-1.67 (m, 1H), 0.93-0.88 (m, 2H), 0.40-0.36 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.96, 140.55, 128.14, 127.58, 127.40, 118.46, 117.71, 16.94, 11.69, 6.79. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{13}H_{13}N^+$, 183.1043; found 183.1036.

4. General procedure for the ring-retentive hydrocyanation and the data for products



General procedure B: In a N_2-filled glovebox, Xantphos (5.8 mg, 0.01 mmol) and $Pd(dba)_2$ (5.8 mg, 0.01 mmol) and dimethoxyethane (DME) (0.3 mL) were added to an oven-dried 4 mL screw-cap vial. The resulting mixture was stirred for 10 min and then cyclopropene **1** (0.2 mmol), acetone cyanohydrin (0.6 mmol) and $Al(O^iPr)_3$ (8.2 mg, 0.04 mmol) were added. The vial was taken out of the glovebox and heated at 80 °C for 12 hours. Subsequently, the reaction was cooled down to room temperature and the reaction mixture was concentrated under reduced pressure and the residue purified by flash column chromatography on silica gel to afford the desired product **3**.

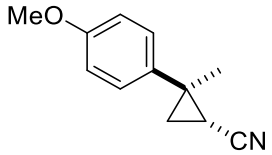
2-methyl-2-phenylcyclopropane-1-carbonitrile (3a)



3a

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3a** as a colorless oil (24.5 mg, yield: 78%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.23 (m, 5H), 1.69-1.66 (m, 4H), 1.57 (dd, J = 9.2, 4.8 Hz, 1H), 1.33-1.30 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.83, 128.90, 127.52, 127.47, 120.40, 28.84, 23.60, 21.41, 11.40. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{11}H_{11}N^+$, 157.0886; found 157.0886. The above data matched the reported data.[2]

2-(4-methoxyphenyl)-2-methylcyclopropane-1-carbonitrile (3b)

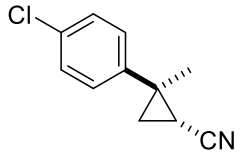


3b

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford **3b** as a colorless oil (26.6 mg, yield: 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21-7.17 (m, 2H),

6.87-6.82 (m, 2H), 3.79 (s, 3H), 1.63-1.60 (m, 4H), 1.52 (dd, J = 9.2, 4.8 Hz, 1H), 1.28 (t, J = 5.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.79, 134.90, 128.61, 120.50, 114.13, 55.39, 28.24, 23.78, 21.40, 11.30. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_{13}NO^+$, 187.0992; found 187.0988.

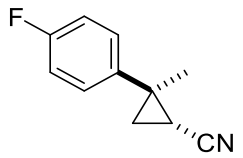
2-(4-chlorophenyl)-2-methylcyclopropane-1-carbonitrile (3c)



3c

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3c** as a colorless oil (30.6 mg, yield: 80%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 2H), 7.24-7.21 (m, 2H), 1.69-1.65 (m, 4H), 1.56 (dd, J = 9.2, 4.8 Hz, 1H), 1.36-1.33 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.27, 133.28, 129.01, 128.93, 120.02, 28.26, 23.47, 21.33, 11.46. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{11}H_9NCl^+$, 190.0418; found 190.0416. The above data matched the reported data.[6]

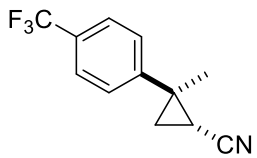
2-(4-fluorophenyl)-2-methylcyclopropane-1-carbonitrile (3d)



3d

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3d** as a colorless oil (28.7 mg, yield: 82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.22 (m, 2H), 7.03-6.98 (m, 2H), 1.66-1.63 (m, 4H), 1.54 (dd, J = 9.2, 4.8 Hz, 1H), 1.36-1.33 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.94 (d, J = 246.5 Hz), 138.63 (d, J = 3.3 Hz), 129.27 (d, J = 8.3 Hz), 120.17, 115.72 (d, J = 21.4 Hz), 28.31, 23.78, 21.36, 11.38. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{11}H_{10}NF^+$, 175.0792; found 175.0787.

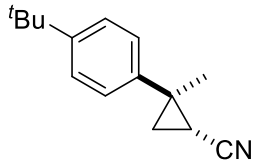
2-methyl-2-(4-(trifluoromethyl)phenyl)cyclopropane-1-carbonitrile (3e)



3e

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3e** as a colorless oil (27.5 mg, yield: 61%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 1.71 (dd, *J* = 9.2, 5.6 Hz, 1H), 1.68 (s, 3H), 1.59 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.40-1.37 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.68, 129.80 (q, *J* = 32.6 Hz), 127.96, 125.93 (q, *J* = 3.8 Hz), 125.39, 122.68, 119.80, 28.51, 23.27, 21.36, 11.60. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_{10}NF_3^+$, 225.0760; found 225.0752.

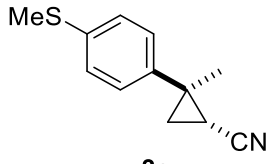
2-(4-(tert-butyl)phenyl)-2-methylcyclopropane-1-carbonitrile (3f)



3f

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3f** as a colorless oil (32.0 mg, yield: 75%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.33 (m, 2H), 7.21-7.18 (m, 2H), 1.68-1.64 (m, 4H), 1.57-1.54 (m, 1H), 1.31-1.29 (m, 10H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.46, 139.74, 127.10, 125.77, 120.56, 34.62, 31.42, 28.36, 23.52, 21.49, 11.42. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{14}H_{16}N^+$, 198.1277; found 198.1277.

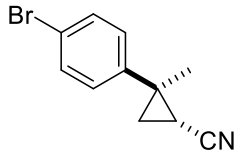
2-methyl-2-(4-(methylthio)phenyl)cyclopropane-1-carbonitrile (3g)



3g

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford **3g** as a colorless oil (20.3 mg, yield: 50%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22-7.16 (m, 4H), 2.47 (s, 3H), 1.65-1.62 (m, 4H), 1.53 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.31-1.28 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.58, 137.81, 127.97, 126.92, 120.29, 28.37, 23.50, 21.37, 15.92, 11.41. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_{13}NS^+$, 203.0763; found 203.0761.

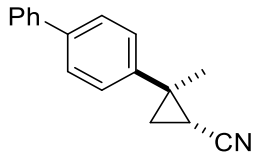
2-(4-bromophenyl)-2-methylcyclopropane-1-carbonitrile (3h)



3h

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3h** as a colorless oil (29.6 mg, yield: 63%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.16-7.12 (m, 2H), 1.66-1.62 (m, 4H), 1.53 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.33-1.29 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.75, 131.93, 129.24, 121.28, 119.95, 28.26, 23.36, 21.26, 11.39. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{11}H_9NBr^+$, 233.9913; found 233.9909. The above data matched the reported data.[6]

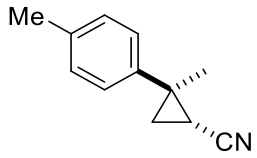
2-([1,1'-biphenyl]-4-yl)-2-methylcyclopropane-1-carbonitrile (3i)



3i

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3i** as a white solid (34.5 mg, yield: 74%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62-7.58 (m, 4H), 7.50-7.46 (m, 2H), 7.41-7.36 (m, 3H), 1.76-1.72 (m, 4H), 1.64 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.40-1.37 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.74, 140.49, 140.41, 128.92, 127.83, 127.57, 127.53, 127.11, 120.29, 28.41, 23.43, 21.48, 11.52. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{17}H_{15}N^+$, 233.1199; found 233.1199.

2-methyl-2-(p-tolyl)cyclopropane-1-carbonitrile (3j)

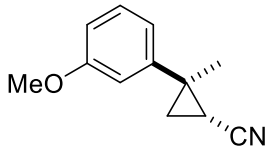


3j

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3j** as a white solid (24.6 mg, yield: 72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21-7.15 (m, 4H), 2.36 (s, 3H), 1.69-1.64 (m, 4H), 1.57 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.33-1.30 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.84, 137.17, 129.48, 127.34, 120.48, 28.48, 23.62, 21.39,

21.10, 11.33. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_{13}N^+$, 171.1043; found 171.1039. The above data matched the reported data.[6]

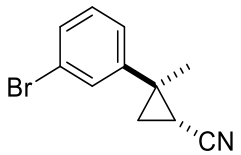
2-(3-methoxyphenyl)-2-methylcyclopropane-1-carbonitrile (3k)



3k

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford **3k** as a colorless oil (24.7 mg, yield: 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 1H), 6.88-6.80 (m, 3H), 3.83 (s, 3H), 1.72-1.66 (m, 4H), 1.58 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.33-1.30 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.88, 144.35, 129.90, 120.29, 119.63, 113.57, 112.51, 55.35, 28.72, 23.43, 21.42, 11.40. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_{13}NO^+$, 187.0992; found 187.0990.

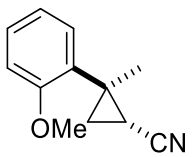
2-(3-bromophenyl)-2-methylcyclopropane-1-carbonitrile (3l)



3l

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3l** as a colorless oil (20.2 mg, yield: 43%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.36 (m, 2H), 7.21-7.17 (m, 2H), 1.69-1.64 (m, 4H), 1.55 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.33-1.30 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.01, 130.75, 130.64, 130.47, 126.19, 122.79, 119.87, 28.41, 23.37, 21.27, 11.47. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{11}H_9NBr^+$, 233.9913; found 233.9916.

2-(2-methoxyphenyl)-2-methylcyclopropane-1-carbonitrile (3m)

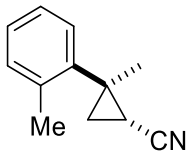


3m

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to afford **3m** as a

colorless oil (16.8 mg, yield: 45%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.22 (m, 1H), 7.16 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.90-6.85 (m, 2H), 3.88 (s, 3H), 1.59-1.55 (m, 4H), 1.42 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.28-1.24 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.18, 131.00, 129.48, 128.90, 121.01, 120.48, 110.75, 55.42, 25.94, 22.13, 21.28, 10.75. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_{13}NO^+$, 187.0992; found 187.0991.

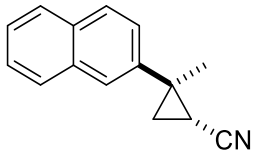
2-methyl-2-(o-tolyl)cyclopropane-1-carbonitrile (3n)



3n

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3n** as a colorless oil (10.9 mg, yield: 32%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22-7.12 (m, 4H), 2.42 (s, 3H), 1.67 (dd, *J* = 9.2, 5.6 Hz, 1H), 1.57 (s, 3H), 1.46 (dd, *J* = 9.2, 5.6 Hz, 1H), 1.38-1.33 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.94, 137.09, 130.96, 129.18, 127.72, 126.41, 120.55, 28.59, 22.72, 21.88, 19.22, 11.18. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_{13}N^+$, 171.1043; found 171.1039.

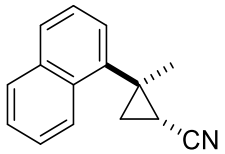
2-methyl-2-(naphthalen-2-yl)cyclopropane-1-carbonitrile (3o)



3o

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3o** as a colorless oil (30.6 mg, yield: 74%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86-7.76 (m, 3H), 7.68 (s, 1H), 7.51-7.43 (m, 2H), 7.39-7.35 (m, 1H), 1.76-1.72 (m, 4H), 1.67-1.62 (m, 1H), 1.39-1.34 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.05, 133.28, 132.54, 128.72, 127.75, 127.70, 126.59, 126.25, 126.08, 125.51, 120.33, 28.96, 23.46, 21.37, 11.33. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{15}H_{13}N^+$, 207.1043; found 207.1035.

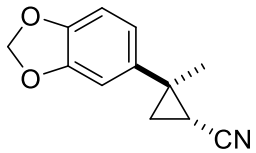
2-methyl-2-(naphthalen-1-yl)cyclopropane-1-carbonitrile (3p)



3p

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3p** as a colorless oil (21.1 mg, yield: 51%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.93-7.87 (m, 1H), 7.79 (dd, *J* = 6.8, 2.8 Hz, 1H), 7.61 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.46-7.38 (m, 2H), 1.82 (dd, *J* = 9.2, 5.6 Hz, 1H), 1.78 (s, 3H), 1.62 (dd, *J* = 9.2, 5.0 Hz, 1H), 1.53 (t, *J* = 5.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.04, 134.08, 131.35, 129.18, 128.51, 126.73, 126.42, 126.09, 125.47, 123.98, 120.58, 28.04, 23.56, 21.73, 11.23. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{15}H_{13}N^+$, 207.1043; found 207.1036.

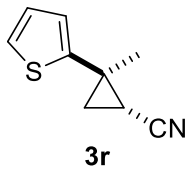
2-(benzo[d][1,3]dioxol-5-yl)-2-methylcyclopropane-1-carbonitrile (3q)



3q

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 8/1) to afford **3q** as a colorless oil (29.7 mg, yield: 74%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.75-6.72 (m, 3H), 5.93 (s, 2H), 1.63-1.59 (m, 4H), 1.49 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.27-1.24 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.86, 146.79, 136.74, 120.69, 120.28, 108.32, 108.21, 101.25, 28.75, 23.86, 21.45, 11.34. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_{11}NO_2^+$, 201.0784; found 201.0783. The above data matched the reported data.[6]

2-methyl-2-(thiophen-2-yl)cyclopropane-1-carbonitrile (3r)

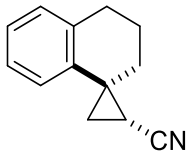


3r

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3r** as a colorless oil (18.9 mg, yield: 58%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16-7.14 (m, 1H),

6.92-6.89 (m, 1H), 6.85-6.83 (m, 1H), 1.77-1.73 (m, 4H), 1.65 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.42-1.38 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.29, 127.08, 124.14, 124.03, 119.57, 24.39, 23.61, 22.91, 14.21. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_9H_9NS^+$, 163.0450; found 163.0445. The above data matched the reported data.[6]

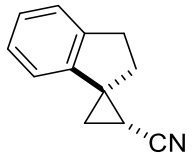
3',4'-dihydro-2'H-spiro[cyclopropane-1,1'-naphthalene]-2-carbonitrile (3s)



3s

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3s** as a colorless oil (21.6 mg, yield: 59%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18-7.10 (m, 3H), 6.62-6.60 (m, 1H), 2.93 (t, *J* = 6.0 Hz, 2H), 2.06-1.96 (m, 4H), 1.77 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.66 (dd, *J* = 9.2, 5.2 Hz, 1H), 1.38 (t, *J* = 6.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.21, 136.40, 129.49, 126.69, 126.56, 121.29, 119.67, 31.53, 30.16, 26.59, 23.00, 21.75, 15.60. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{13}H_{13}N^+$, 183.1043; found 183.1040.

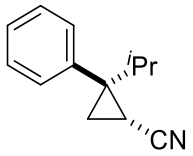
2',3'-dihydrospiro[cyclopropane-1,1'-indene]-2-carbonitrile (3t)



3t

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3t** as a colorless oil (16.2 mg, yield: 48%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.13 (m, 3H), 6.65 (d, *J* = 8.4 Hz, 1H), 3.21-3.05 (m, 2H), 2.51-2.44 (m, 1H), 2.36-2.28 (m, 1H), 1.66-1.61 (m, 2H), 1.52-1.46 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.50, 142.82, 127.65, 126.96, 124.95, 119.96, 118.49, 34.75, 31.30, 30.46, 21.17, 13.36. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_{10}N^+$, 168.0808; found 168.0810.

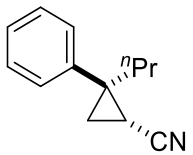
2-isopropyl-2-phenylcyclopropane-1-carbonitrile (3u)



3u

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3u** as a colorless oil (18.1 mg, yield: 49%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.22 (m, 5H), 1.74-1.60 (m, 2H), 1.43 (dd, *J* = 8.8, 4.8 Hz, 1H), 1.28 (t, *J* = 5.2 Hz, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.28, 131.16, 128.07, 127.67, 120.71, 39.17, 35.27, 21.22, 20.00, 19.46, 10.64. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{13}H_{15}N^+$, 185.1199; found 185.1200.

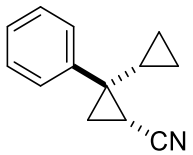
2-phenyl-2-propylcyclopropane-1-carbonitrile (3v)



3v

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3v** as a colorless oil (28.9 mg, yield: 78%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.24 (m, 5H), 1.90-1.82 (m, 1H), 1.60-1.53 (m, 2H), 1.36-1.19 (m, 4H), 0.82 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.58, 129.70, 128.66, 127.76, 120.16, 42.70, 34.74, 20.01, 19.79, 13.91, 10.32. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{13}H_{15}N^+$, 185.1199; found 185.1200.

1-phenyl-[1,1'-bi(cyclopropane)]-2-carbonitrile (3w)

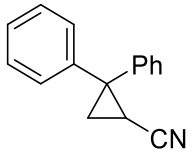


3w

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3w** as a colorless oil (19.0 mg, yield: 52%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.23 (m, 5H), 1.76 (dd, *J* = 9.2, 5.4 Hz, 1H), 1.38-1.24 (m, 3H), 0.70-0.57 (m, 2H), 0.36-0.19 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.55, 128.72, 128.62, 127.55, 120.12, 34.51, 17.54,

15.80, 10.99, 3.71, 3.32. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{13}H_{13}N^+$, 183.1043; found 183.1037.

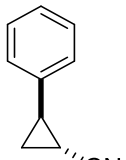
2,2-diphenylcyclopropane-1-carbonitrile (3x)



3x

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3x** as a white solid (27.6 mg, yield: 63%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.8 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.32-7.16 (m, 6H), 2.19 (dd, *J* = 9.2, 5.6 Hz, 1H), 1.99 (t, *J* = 5.4 Hz, 1H), 1.76 (dd, *J* = 9.2, 5.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.36, 139.01, 129.45, 128.91, 128.85, 127.98, 127.85, 127.45, 119.57, 38.33, 21.07, 12.27. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{16}H_{13}N^+$, 219.1043; found 219.1035. The above data matched the reported data.[6]

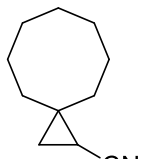
2-phenylcyclopropane-1-carbonitrile (3y)



3y

According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3y** as a colorless oil (19.2 mg, yield: 67%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.22 (m, 3H), 7.13-7.08 (m, 2H), 2.67-2.59 (m, 1H), 1.65-1.52 (m, 2H), 1.49-1.42 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.69, 128.89, 127.54, 126.45, 121.17, 25.03, 15.35, 6.73. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{10}H_9N^+$, 143.0730; found 143.0728. The above data matched the reported data.[2]

spiro[2.7]decane-1-carbonitrile (3z)

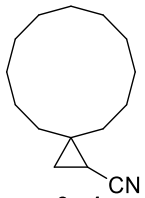


3z

According to the general procedure B, the residue was purified by flash column

chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3z** as a colorless oil (17.9 mg, yield: 55%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.83-1.49 (m, 13H), 1.34 (dd, *J* = 16.8, 11.6 Hz, 1H), 1.17 (d, *J* = 8.8 Hz, 1H), 1.03-0.89 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 120.96, 35.73, 32.54, 28.56, 26.84, 26.52, 25.13, 25.07, 24.44, 22.77, 11.70. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{11}H_{16}N^+$, 162.1277; found 162.1280.

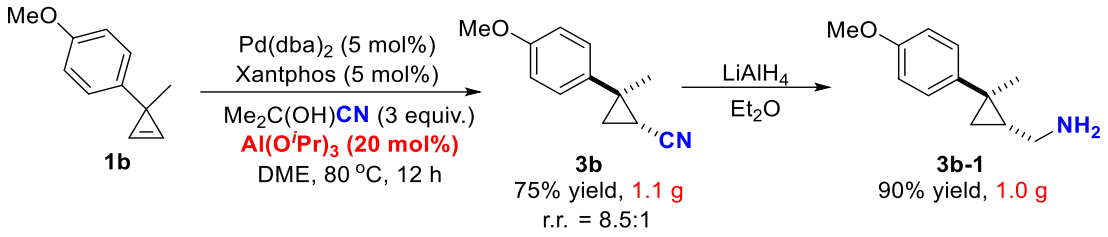
spiro[2.11]tetradecane-1-carbonitrile (3a-1)



3a-1

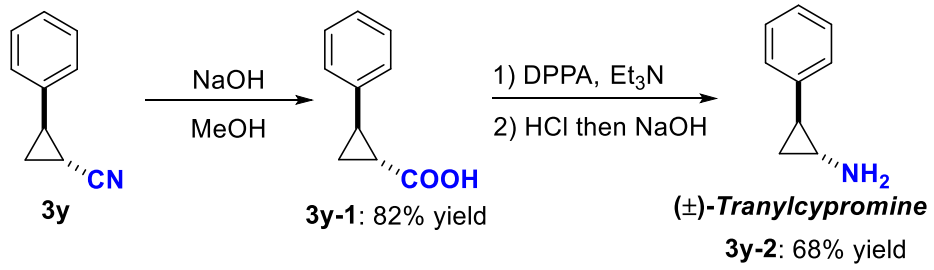
According to the general procedure B, the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3a-1** as a colorless oil (21.5 mg, yield: 49%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.71-1.59 (m, 1H), 1.55-1.19 (m, 21H), 1.14 (d, *J* = 5.4 Hz, 1H), 0.97-0.86 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 121.23, 31.90, 29.03, 28.39, 26.07, 26.01, 25.95, 22.39, 22.38, 22.21, 22.18, 21.28, 20.92, 20.70, 9.08. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{15}H_{24}N^+$, 218.1903; found 218.1905.

5. Gram-scale and product transformations



In a N_2-filled glovebox, Xantphos (231 mg, 0.4 mmol) and $Pd(dba)_2$ (230 mg, 0.4 mmol) and DME (12 mL) were added to an oven-dried 50 mL Schlenk tube. The resulting mixture was stirred for 10 min and then cyclopropene **1b** (1.25 g, 7.8 mmol), acetone cyanohydrin (2.0 g, 23.4 mmol) and $Al(O^iPr)_3$ (326 mg, 1.6 mmol) were added. The vial was taken out of the glovebox and heated at 80 °C for 12 hours. Subsequently, the reaction was cooled down to room temperature and the reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **3b** as a colorless oil (1.1 g, yield: 75%).

Synthesis of **3b-1**: $LiAlH_4$ (448 mg, 11.8 mmol) was added in one portion to a solution of **3b** (1.1 g, 5.9 mmol) in 100 mL Et_2O at -20 °C. After stirring for 1 hours at room temperature, the reaction mixture was cooled to 0 °C and quenched by slow addition of 1 M NaOH. The resulting white precipitate was filtered through a pad of celite and washed with Et_2O. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 3/1) to afford **3b-1** as a colorless oil (1.0 g, yield: 90%). **^{1}H NMR** (400 Hz, $CDCl_3$): δ 7.18 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 3.77 (s, 3H), 2.88 (dd, J = 13.2, 6.6 Hz, 1H), 2.78 (dd, J = 13.2, 8.0 Hz, 1H), 1.38 (s, 3H), 1.23-1.14 (m, 1H), 1.01 (dd, J = 8.8, 4.6 Hz, 1H), 0.48-0.41 (m, 1H). **^{13}C NMR** (100 Hz, $CDCl_3$): δ 157.65, 140.43, 128.38, 113.69, 55.31, 42.89, 28.98, 24.00, 20.81, 19.17. **HRMS-EI** (m/z): $[M]^+$ calcd for $C_{12}H_{17}NO^+$, 191.1305; found 191.1306.



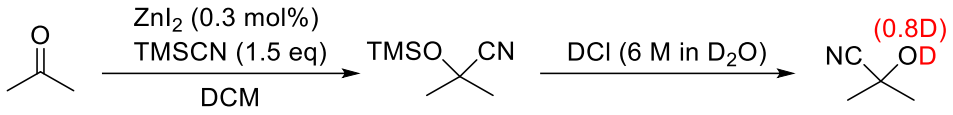
Synthesis of 3y-1: Compound **3y** (28.6 mg, 0.2 mmol) was dissolved in MeOH (2 mL) and NaOH (30 wt%, 2 mL) was added. The reaction mixture was stirred for 12 h at 50

°C. Subsequently, the reaction was cooled down to room temperature, and concd HCl was added until the pH 2. Then, the reaction mixture was extracted with DCM three times. The organic layers were combined and concentrated in vacuo. The crude product was purified by flash column chromatography (DCM/Methanol = 20/1) to afford **3y-1** as a white solid (26.6 mg, yield: 82%). **^{1}H NMR** (400 Hz, $CDCl_3$): δ 10.12 (br, 1H), 7.34-7.22 (m, 3H), 7.16-7.14 (m, 2H), 2.66-2.62 (m, 1H), 1.96-1.91 (m, 1H), 1.73-1.68 (m, 1H), 1.48-1.42 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 179.9, 139.6, 128.7, 126.8, 126.4, 27.3, 24.1, 17.7. **HRMS-ESI (m/z)**: $[M+Na]^+$ calcd for $C_{10}H_{10}NaO_2$, 185.0573; found 185.0574. The above data matched the reported data.[7]

Synthesis of 3y-2: A mixture of **3y-1** (26.0 mg, 0.16 mmol) in dry ^{t}BuOH (1.3 mL), diphenylphosporazidate (55 mg, 0.2 mmol), and triethylamine (20.2 mg, 0.2 mmol) was stirred at 90 °C under nitrogen atmosphere for 48 h. The solution was concentrated and poured into 10% aqueous Na_2CO_3 (3 mL) and extracted with Et_2O three times. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated. The resulting *t*-butyl carbamate was dissolved in MeOH (1 mL), and 1 M aqueous HCl (2 mL) was added. The solution was maintained at reflux overnight. Then the mixture was cooled and concentrated. The solution was washed with Et_2O three times, and the aqueous phase was alkalinized with 10% aqueous NaOH until pH 10. The mixture was extracted with EtOAc three times. The combined organic phases were dried over K_2CO_3, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (DCM/Methanol = 10/1) to afford **3y-2** as a white solid (14.6 mg, yield: 68%). **^{1}H NMR** (400 Hz, $CDCl_3$): δ 7.30-7.24 (m, 2H), 7.20-7.14 (m, 1H), 7.06-7.03 (m, 2H), 2.61-2.54 (m, 1H), 1.91-1.87 (m, 1H), 1.11-1.04 (m, 1H), 1.04-0.96 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.5, 128.4, 125.7, 125.5, 35.5, 26.5, 18.6. **HRMS-ESI** (m/z): $[M+H]^+$ calcd for $C_9H_{11}N$, 134.0964; found 134.0966. The above data matched the reported data.[7]

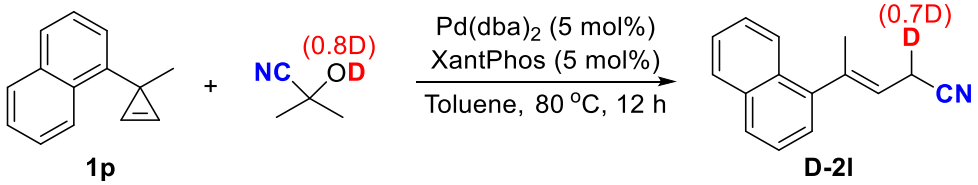
6. Deuterium experiment

Synthesis of $(CH_3)_2C(OD)CN$



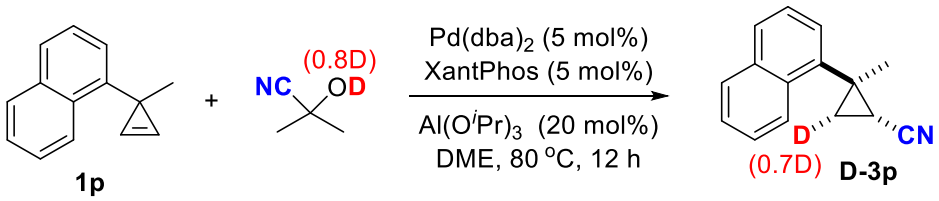
The synthesis of $(CH_3)_2C(OD)CN$ was modified based on Naka's method.[8] ***Caution! HCN is produced. The experiment should be conducted in a well-ventilated fume hood. A KOH base trap for HCN should be attached to the outlet of an evaporator before concentration under reduced pressure.*** Acetone (591.6 mg, 10.2 mmol), anhydrous dichloromethane (5 mL) and trimethylsilyl cyanide (2 mL, 15 mmol) were added to a 30-mL round-bottom flask at 0°C under argon. The mixture was stirred at 0 ºC for 10 min and then ZnI_2 (10 mg, 0.03 mmol) was added. The mixture was then stirred at rt (25 °C) for 4 h. ^{1}H NMR monitoring of the reaction mixture indicated the complete consumption of acetone. After that, DCl (6 M in D_2O, 10 mL) and diethyl ether (10 mL) were added to split the silyl ether, and the reaction mixture was stirred at rt for 16 h. This step was monitored by GC-MS. The cyanohydrin was extracted 3 times with diethyl ether (in total, 30 mL). The ether phase was dried over $MgSO_4$, and concentrated under reduced pressure to provide $(CH_3)_2C(OD)CN$ as a colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.69-3.58 (m, 0.14H), 1.61 (s, 6H).

Deuterium ring-opening hydrocyanation



In a N_2-filled glovebox, Xantphos (5.8 mg, 0.01 mmol) and $Pd(dba)_2$ (5.8 mg, 0.01 mmol) and toluene (0.3 mL) were added to an oven-dried 4 mL screw-cap vial. The resulting mixture was stirred for 10 min and then **1p** (0.2 mmol) and deuterium acetone cyanohydrin (0.6 mmol) were added. The vial was taken out of the glovebox and heated at 80 ºC for 12 hours. Subsequently, the reaction was cooled down to room temperature and the reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **D-2l** as a colorless oil (27.0 mg, yield: 65%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.83 (m, 2H), 7.78 (d, J = 8.0 Hz, 1H), 7.50-7.46 (m, 2H), 7.42 (dd, J = 8.0, 7.6 Hz, 1H), 7.25-7.23 (m, 1H), 5.57-5.53 (m, 1H), 3.33-3.30 (m, 1.3H), 2.16 (s, 3H).

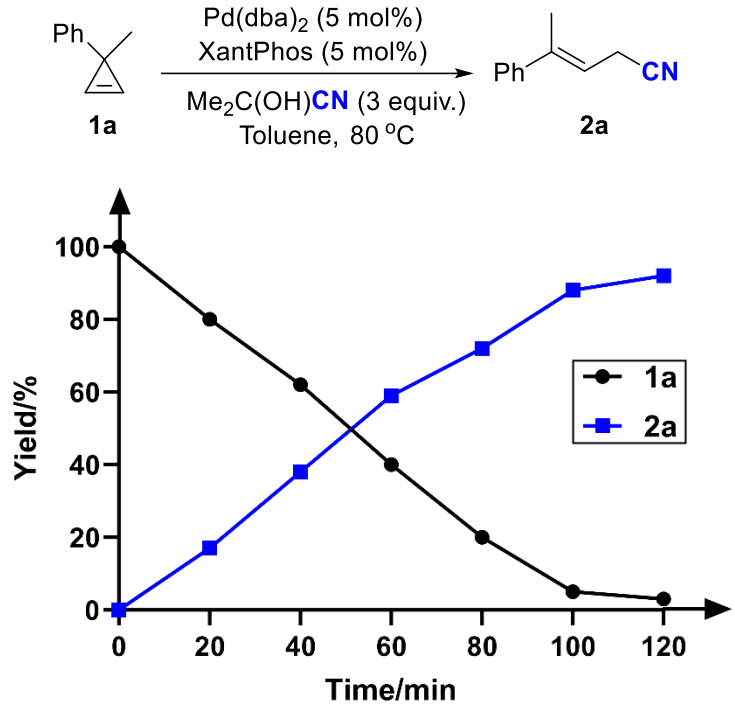
Deuterium ring-retentive hydrocyanation



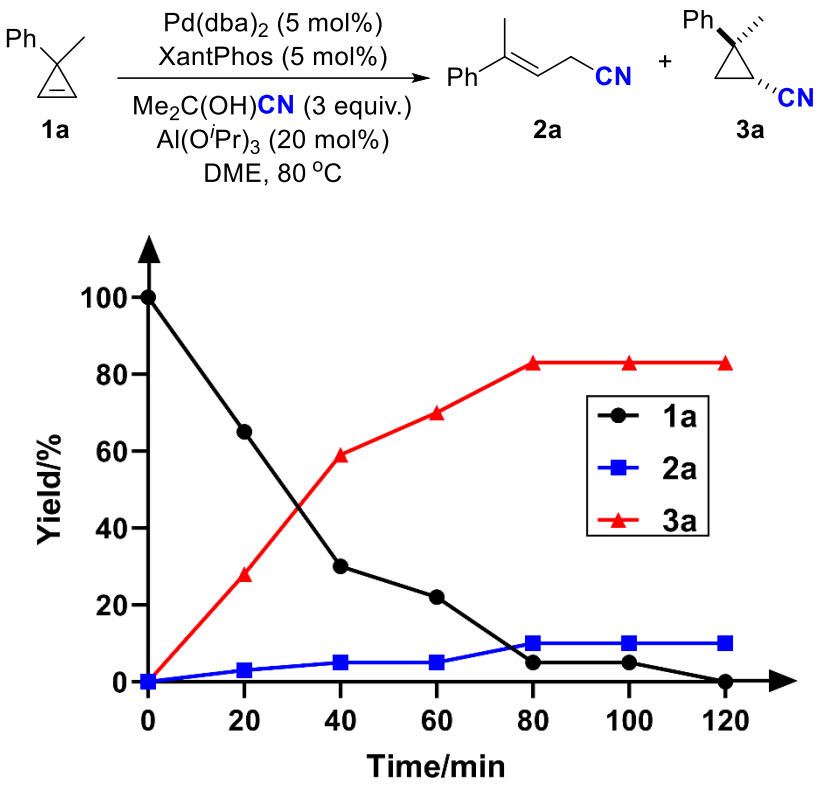
1p D-3p

In a N_2-filled glovebox, Xantphos (5.8 mg, 0.01 mmol) and $Pd(dba)_2$ (5.8 mg, 0.01 mmol) and dimethoxyethane (DME) (0.3 mL) were added to an oven-dried 4 mL screw-cap vial. The resulting mixture was stirred for 10 min and then **1p** (0.2 mmol), deuterium acetone cyanohydrin (0.6 mmol) and $Al(O^iPr)_3$ (8.2 mg, 0.04 mmol) were added. The vial was taken out of the glovebox and heated at 80 °C for 12 hours. Subsequently, the reaction was cooled down to room temperature and the reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to afford **D-3p** as a colorless oil (9.9 mg, yield: 24%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (dd, J = 8.4, 1.2 Hz, 1H), 7.93-7.87 (m, 1H), 7.79 (dd, J = 6.8, 2.8 Hz, 1H), 7.61 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.53 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.46-7.38 (m, 2H), 1.81 (d, J = 9.2 Hz, 1H), 1.77 (s, 3H), 1.61 (d, J = 8.8 Hz, 1H), 1.54-1.51 (m, 0.3 H).

7. Tracking time course study



Reaction conditions: In a N_2-filled glovebox, XantPhos (58.0 mg, 0.1 mmol) and $Pd(dba)_2$ (58.0 mg, 0.1 mmol) and toluene (3.0 mL) were added to an oven-dried 25 mL Schlenk tube. The resulting mixture was stirred for 10 min and then cyclopropene **1a** (260 mg, 2.0 mmol), acetone cyanohydrin (510 mg, 6.0 mmol) and *n*-dodecane (0.2 mL) were added sequentially. The Schlenk tube was taken out of the glovebox and heated at 80 °C. Take out 0.01 mL of reaction solution at each detection time point, then dilute with 1.0 mL ethyl acetate and detect the content of each component by using gas chromatography.



Reaction conditions: In a N_2-filled glovebox, XantPhos (58.0 mg, 0.1 mmol) and $Pd(dba)_2$ (58.0 mg, 0.1 mmol) and DME (3.0 mL) were added to an oven-dried 25 mL Schlenk tube. The resulting mixture was stirred for 10 min and then cyclopropene **1a** (260 mg, 2.0 mmol), acetone cyanohydrin (510 mg, 6.0 mmol), $Al(O^iPr)_3$ (81.6 mg, 0.4 mmol) and *n*-dodecane (0.2 mL) were added sequentially. The Schlenk tube was taken out of the glovebox and heated at 80 °C. Take out 0.01 mL of reaction solution at each detection time point, then dilute with 1.0 mL ethyl acetate and detect the content of each component by using gas chromatography.

8. References

(1) H.-J. Zhang, A. W. Schuppe, S.-T. Pan, J.-X. Chen, B.-R. Wang, T. R. Newhouse and L. Yin, Copper-catalyzed vinylogous aerobic oxidation of unsaturated compounds with air, *J. Am. Chem. Soc.,* 2018, **140**, 5300–5310.

(2) A. L. Chandgude and R. Fasan, Highly diastereo- and enantioselective synthesis of nitrile-substituted cyclopropanes by Myoglobin-mediated carbene transfer catalysis, *Angew. Chem. Int. Ed.,* 2018, **57**, 15852–15856.

(3) H. Xie, F. Li, Y. Xu, C. Wang, Y. Xu, J. Wu, Z. Li, Z. Wang and L. Wang, *Vitreoscilla* hemoglobin: a natural carbene transfer catalyst for diastereo- and enantioselective synthesis of nitrile-substituted cyclopropanes, *Green Chem.,* 2023, **25**, 6853–6858.

(4) Y. Liang, H. Huang, N. Huang, L. Liao and X. Zhao, Catalytic enantioselective construction of chiral γ-azido nitrilesthrough nitrile group-promoted electrophilic reaction of alkenes, *Org. Lett.,* 2023, **25**, 6757−6762.

(5) M. Ahmad and A. Ahmad, Cu-catalyzed cyanomethylation of imines and α,β-alkenes with acetonitrile and its derivatives, *RSC Adv.,* 2021, **11**, 5427−5431.

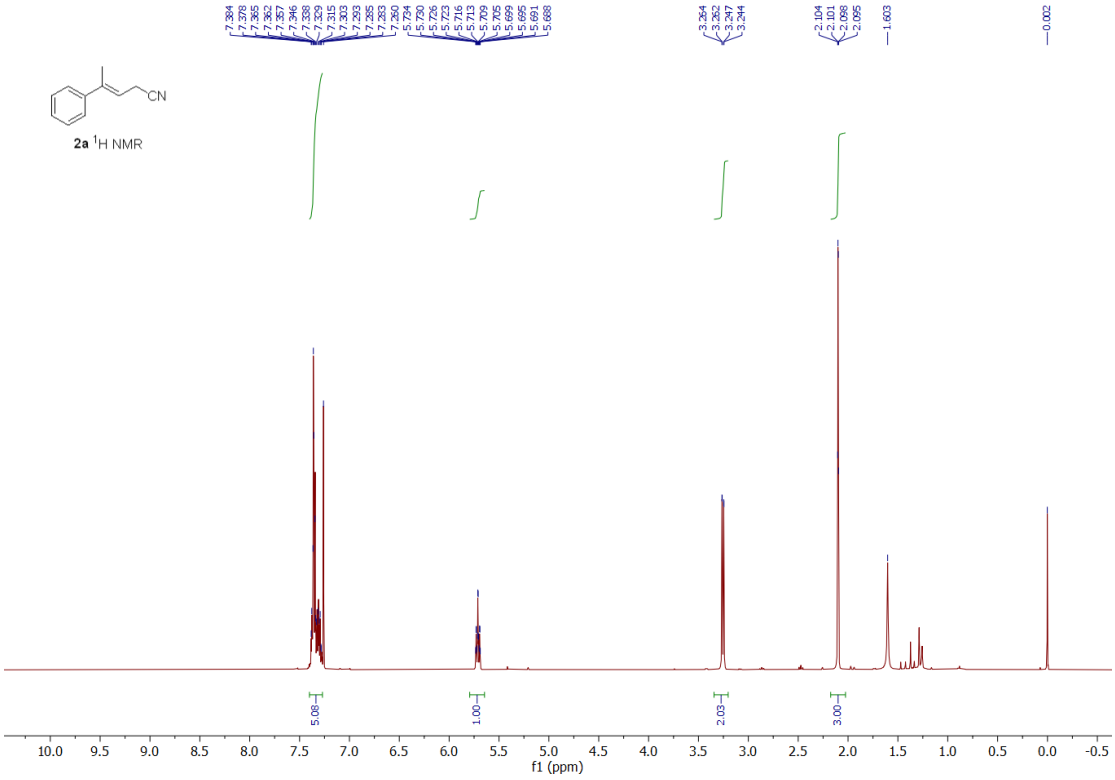
(6) K. Hock, R. Spitzner and R. Koenigs, Towards nitrile-substituted cyclopropanes – a slow-release protocol for safe and scalable applications of diazo acetonitrile, *Green Chem.,* 2017, **19**, 2118–2122.

(7) R. Yu, S.-Z. Cai, C. Li and X. Fang, Nickel-catalyzed asymmetric hydroaryloxy- and hydroalkoxycarbonylation of cyclopropenes, *Angew. Chem. Int. Ed.,* 2022, **61**, e202200733.

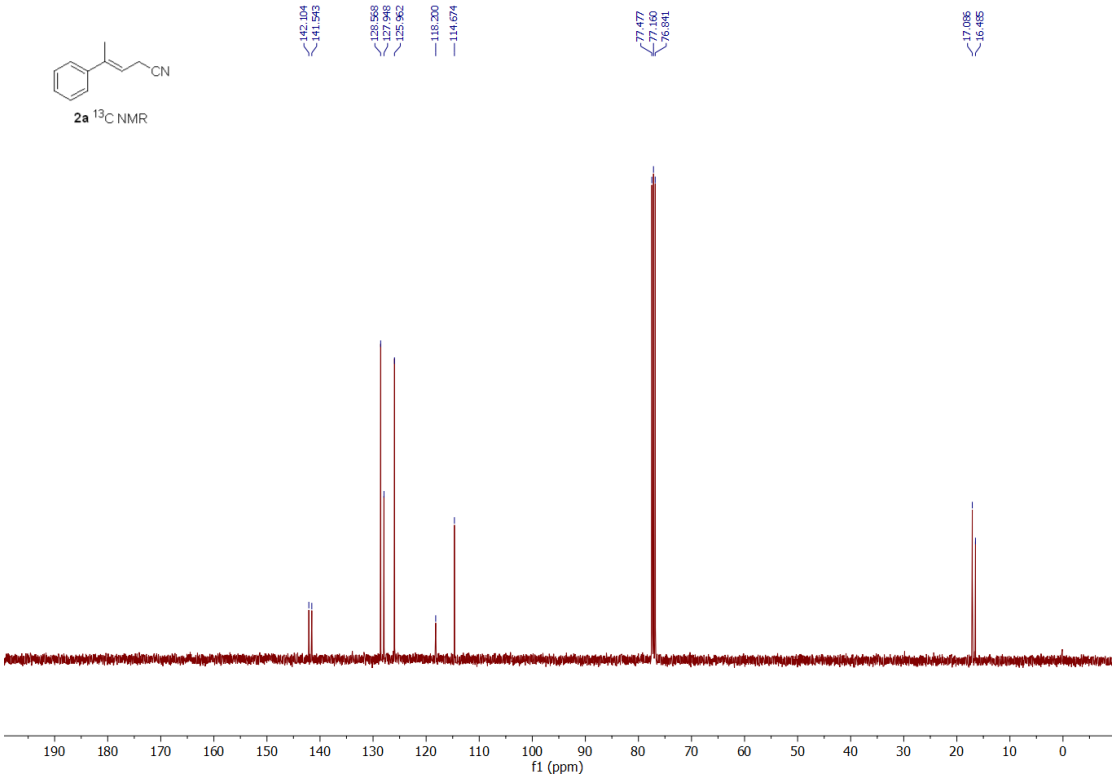
(8) T. Kanda, A. Naraoka, H. Naka, Catalytic transfer hydration of cyanohydrins to α-hydroxyamides, *J. Am. Chem. Soc.,* 2019, **141**, 825–830.

9. NMR Spectra

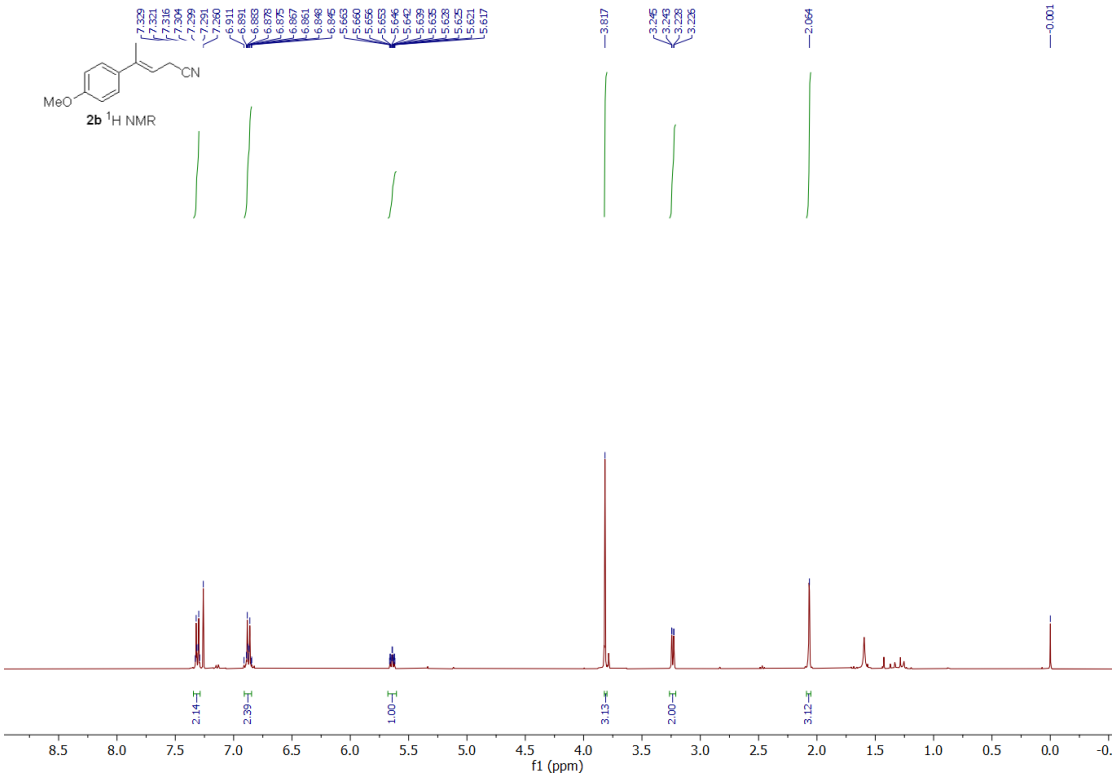
^{1}H NMR Spectra of 2a (400 MHz, Chloroform-*d*)



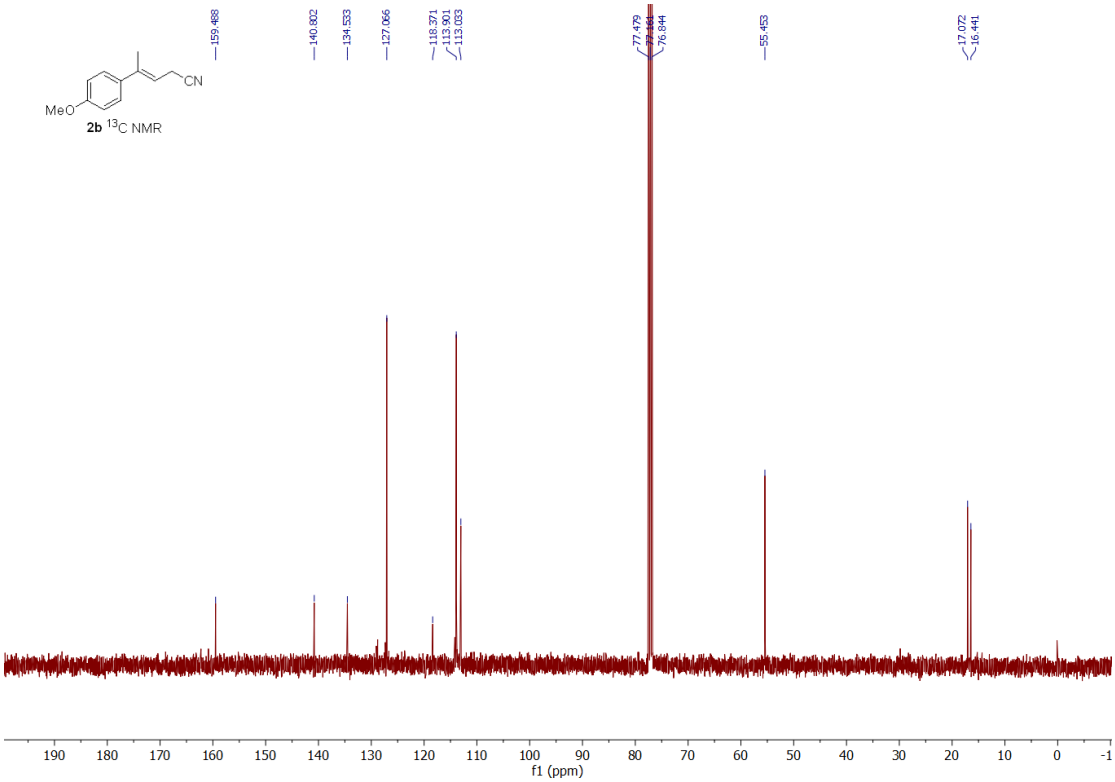
^{13}C NMR Spectra of 2a (100 MHz, Chloroform-*d*)



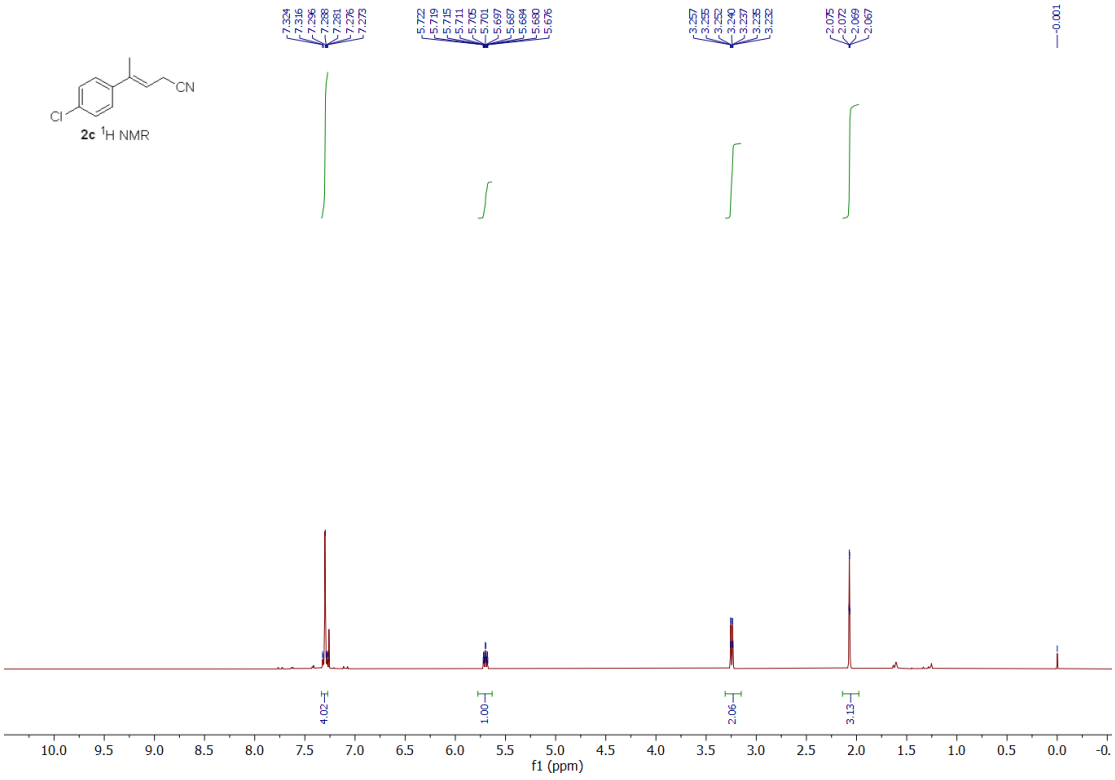
^{1}H NMR Spectra of 2b (400 MHz, Chloroform-*d*)



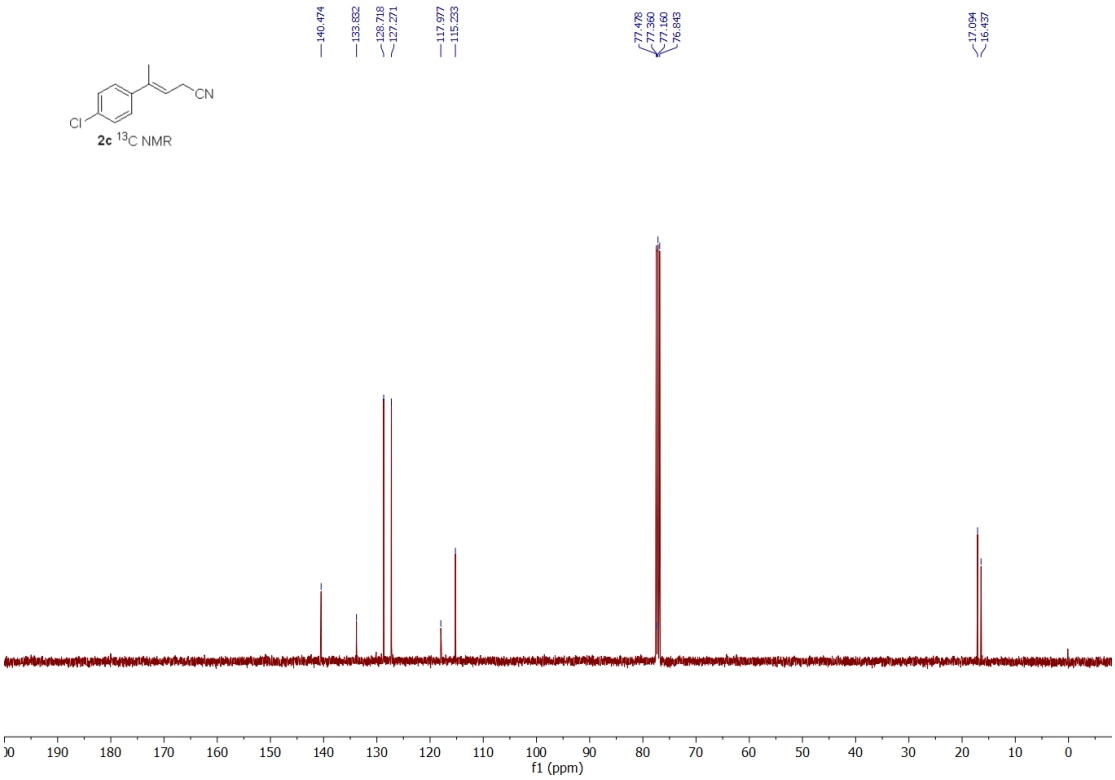
^{13}C NMR Spectra of 2b (100 MHz, Chloroform-*d*)



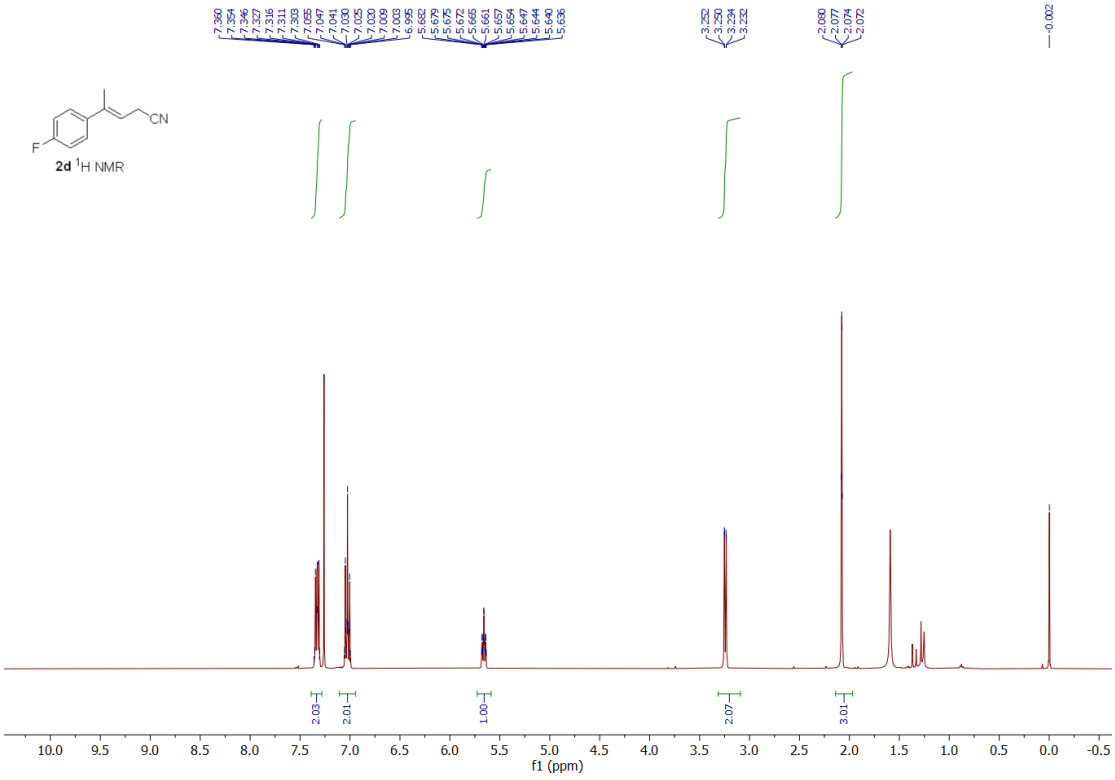
^{1}H NMR Spectra of 2c (400 MHz, Chloroform-*d*)



^{13}C NMR Spectra of 2c (100 MHz, Chloroform-*d*)



^{1}H NMR Spectra of 2d (400 MHz, Chloroform-*d*)



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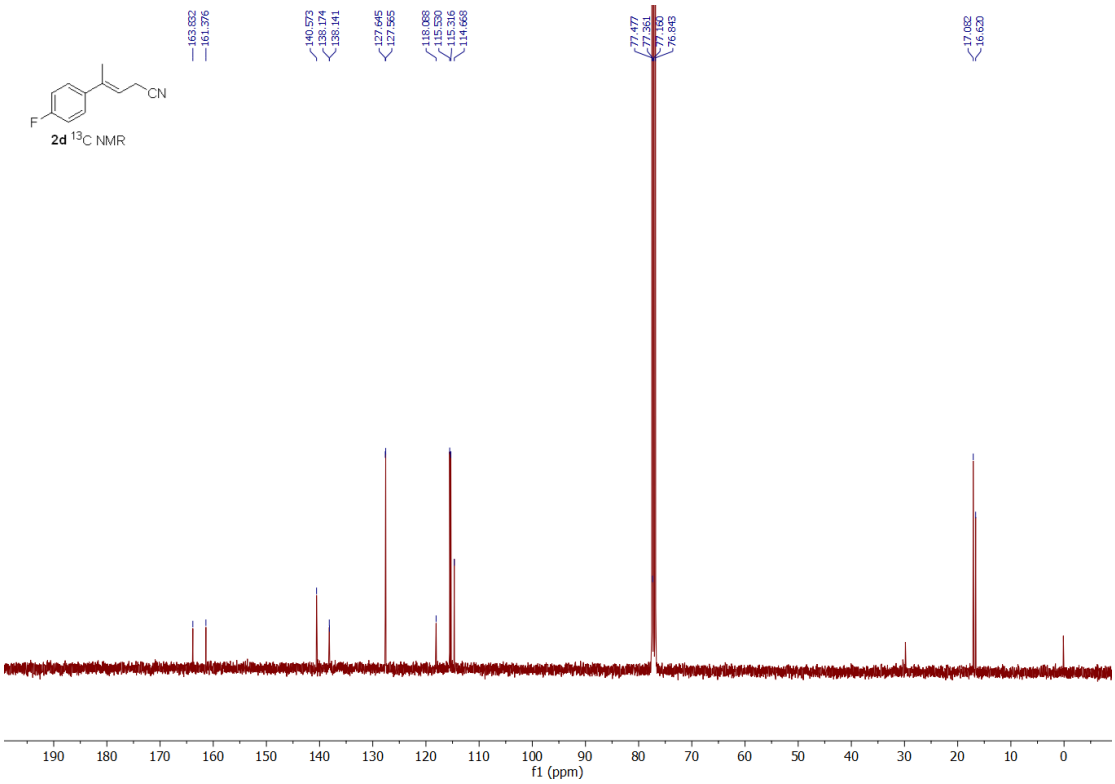

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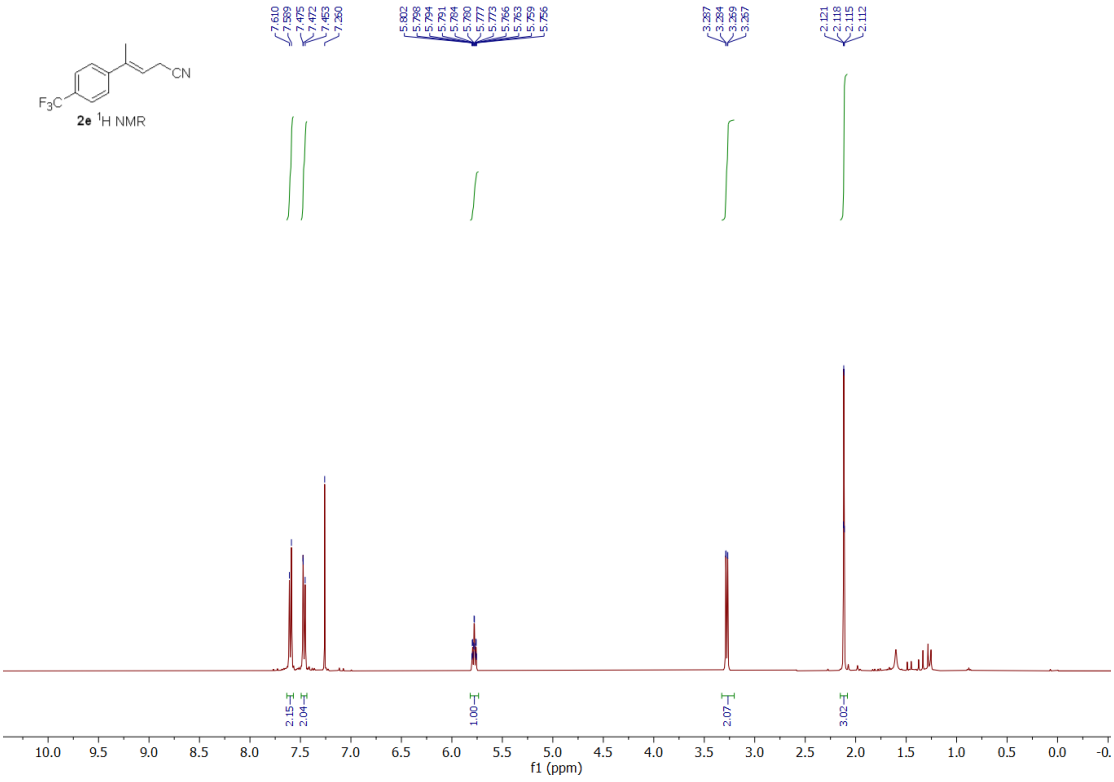

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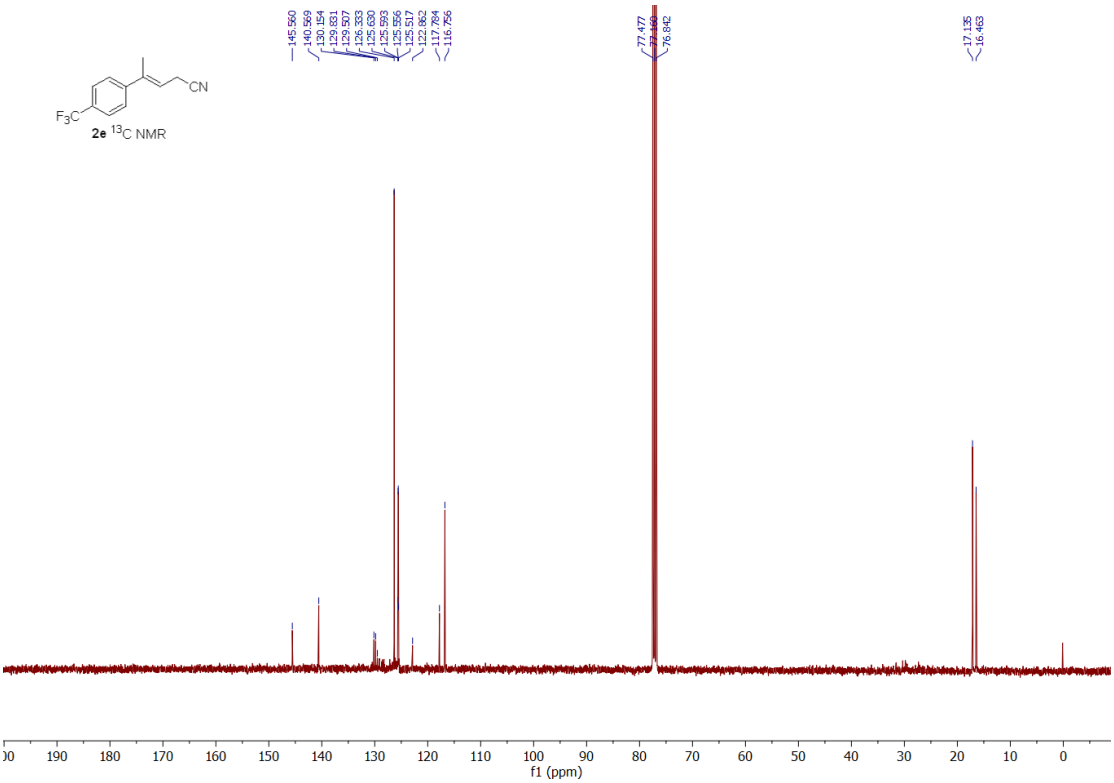
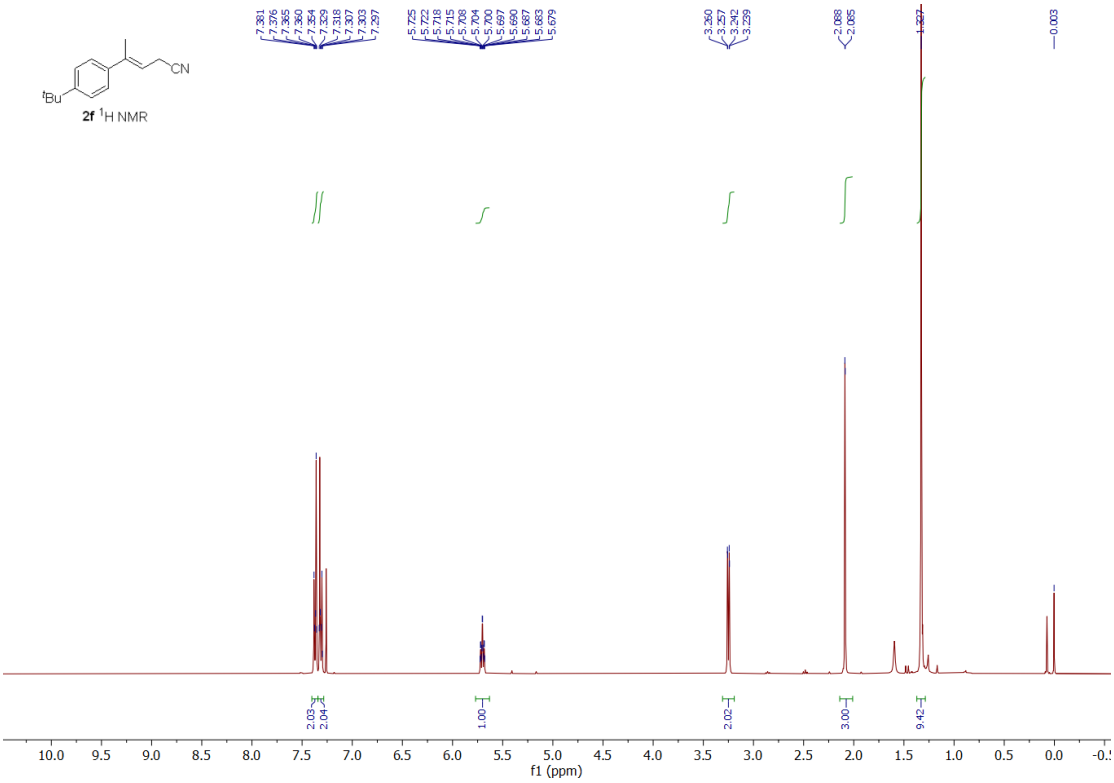
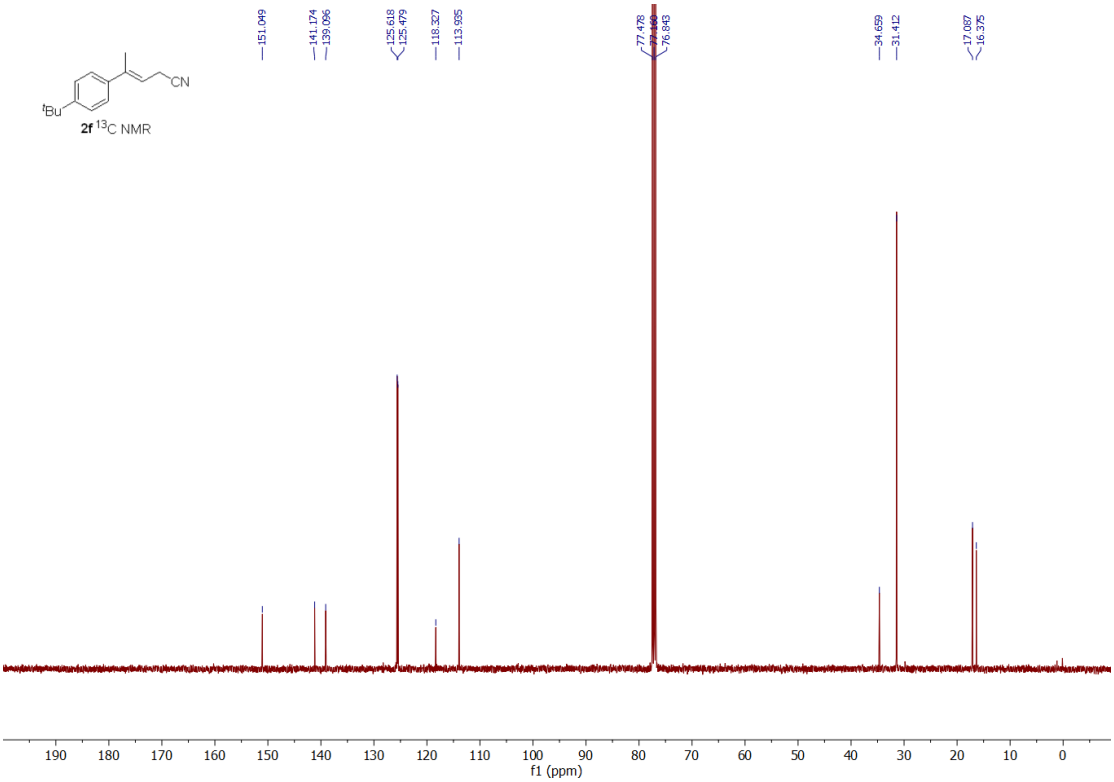


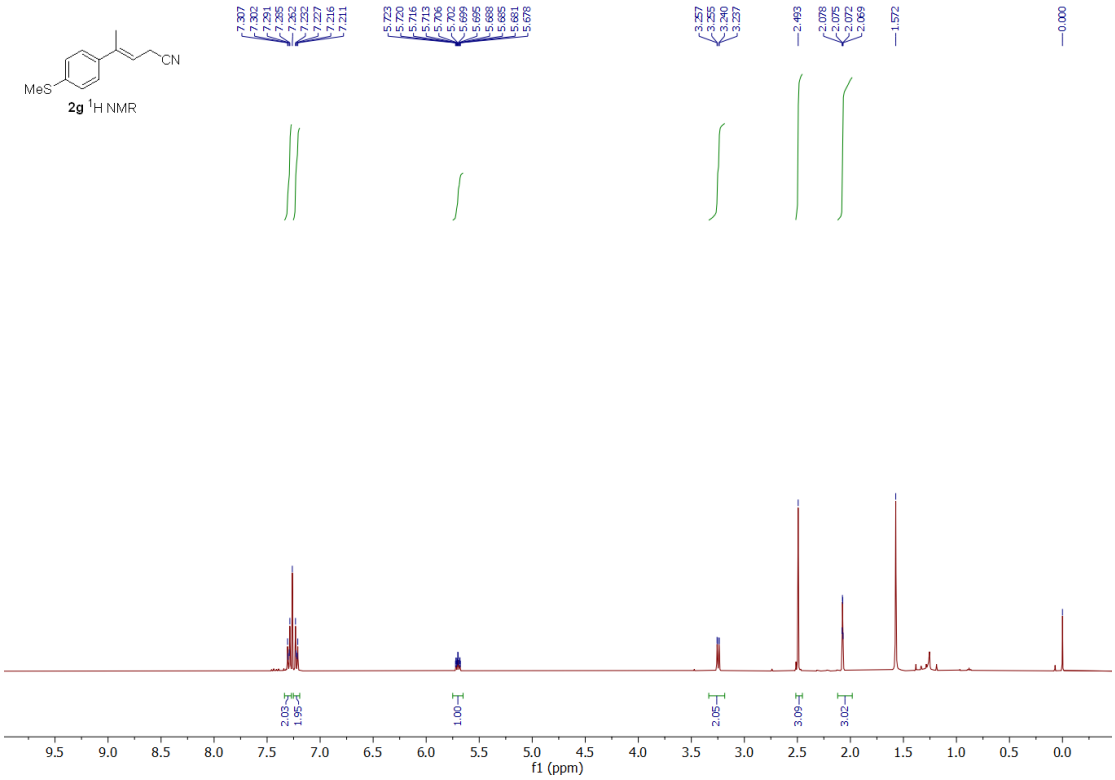
^{1}H NMR Spectra of 2f (400 MHz, Chloroform-*d*)



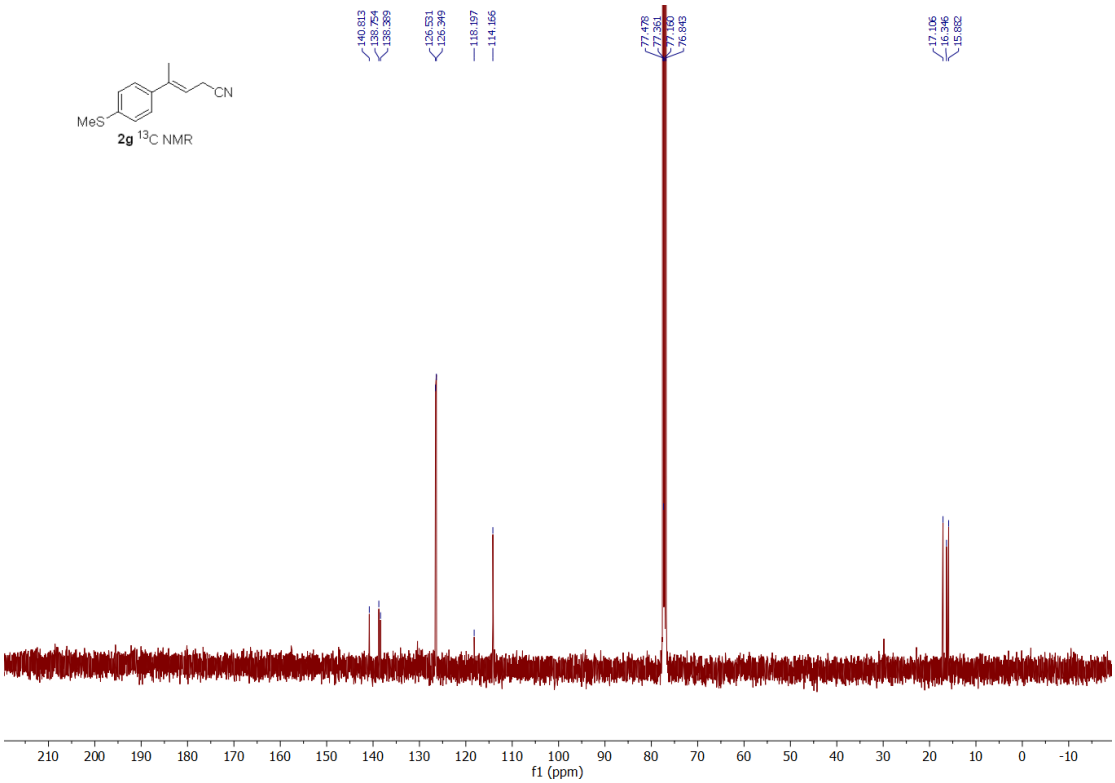
^{13}C NMR Spectra of 2f (100 MHz, Chloroform-*d*)



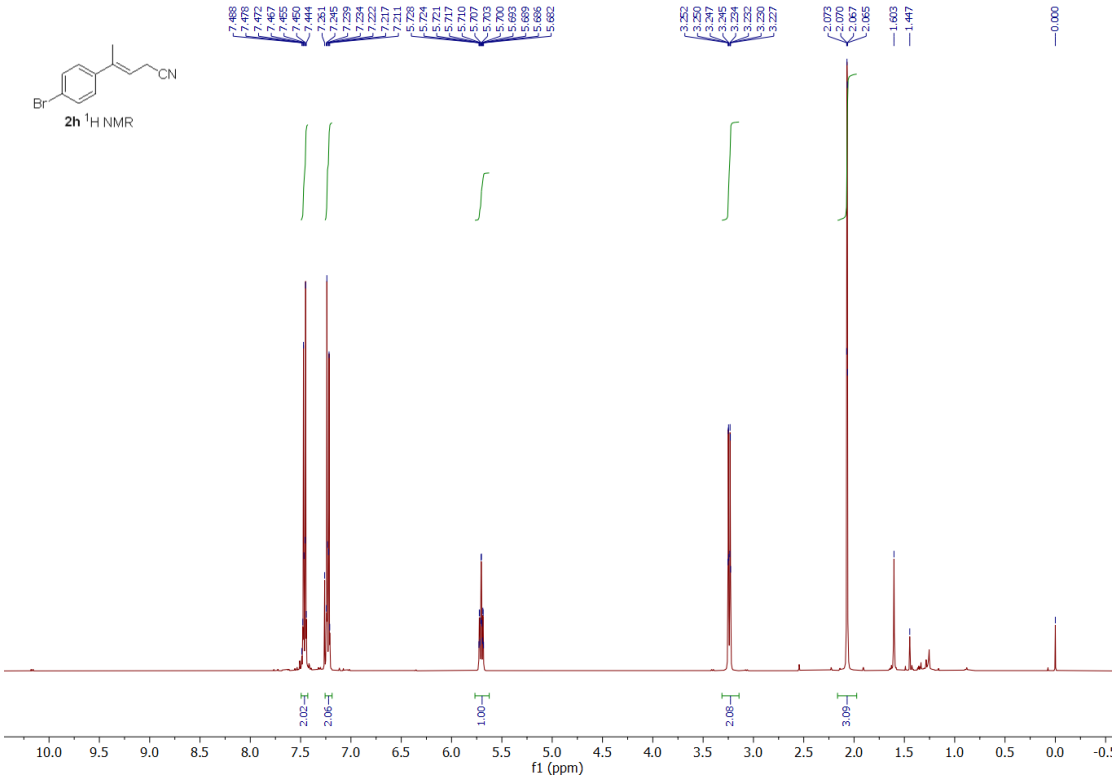
^{1}H NMR Spectra of 2g (400 MHz, Chloroform-*d*)



^{13}C NMR Spectra of 2g (100 MHz, Chloroform-*d*)



^{1}H NMR Spectra of 2h (400 MHz, Chloroform-*d*)



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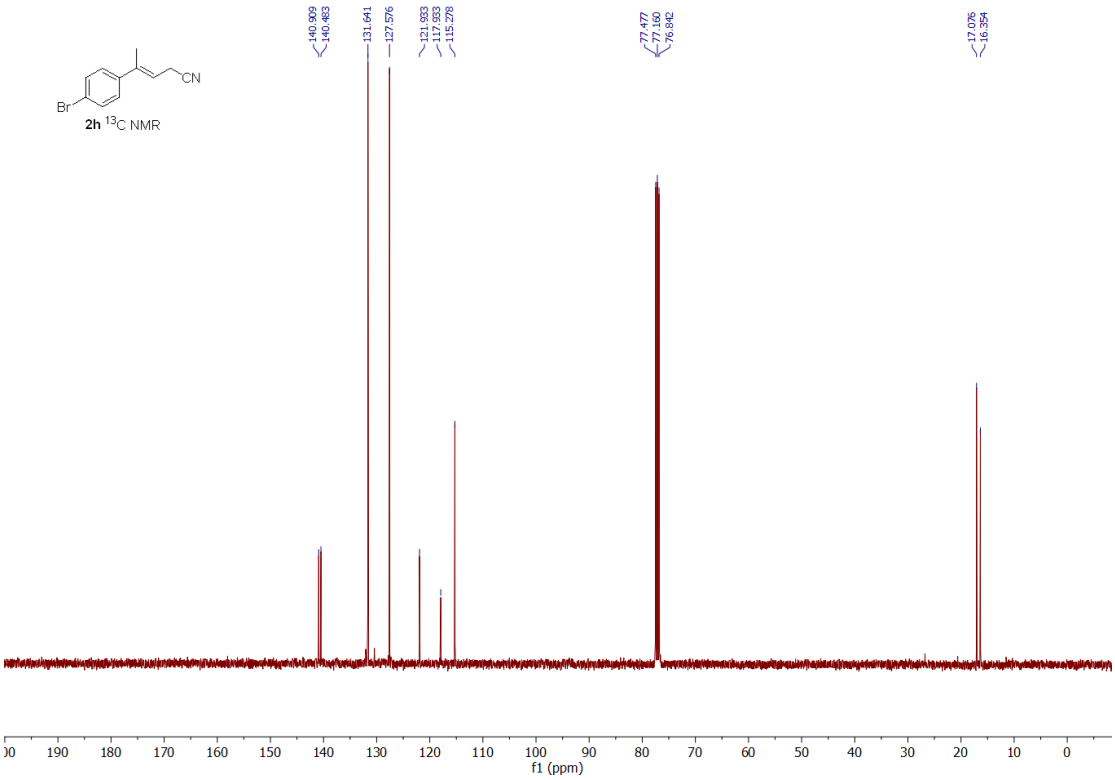
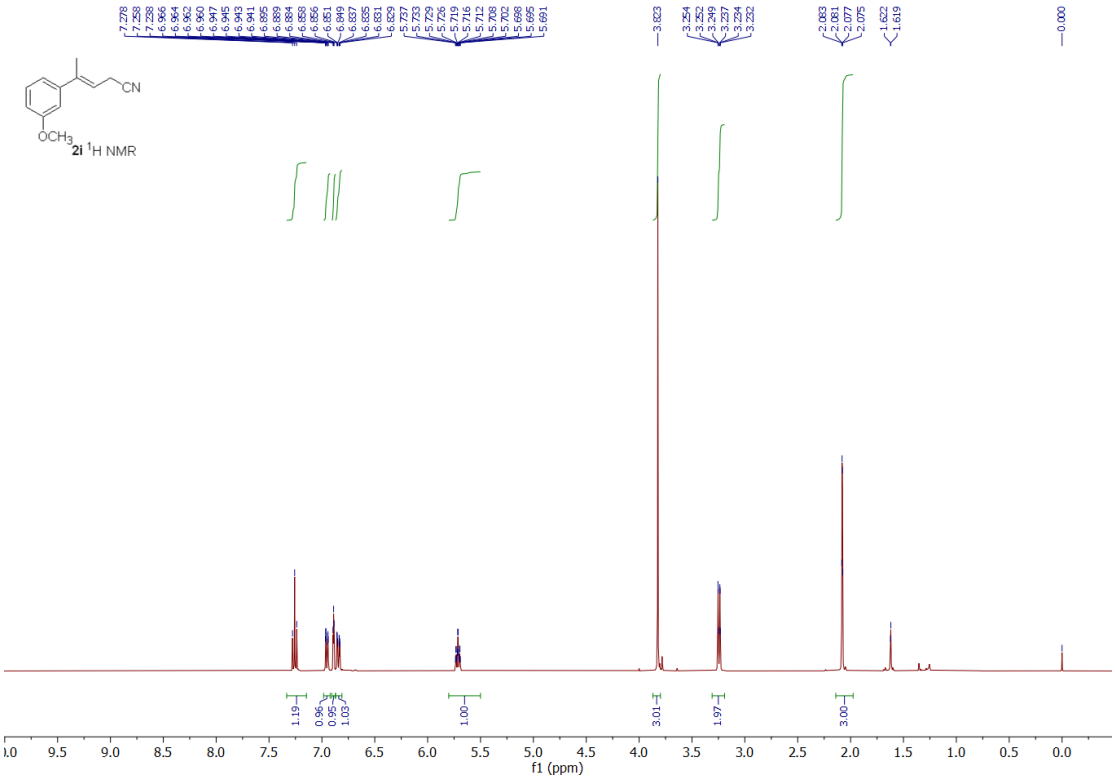
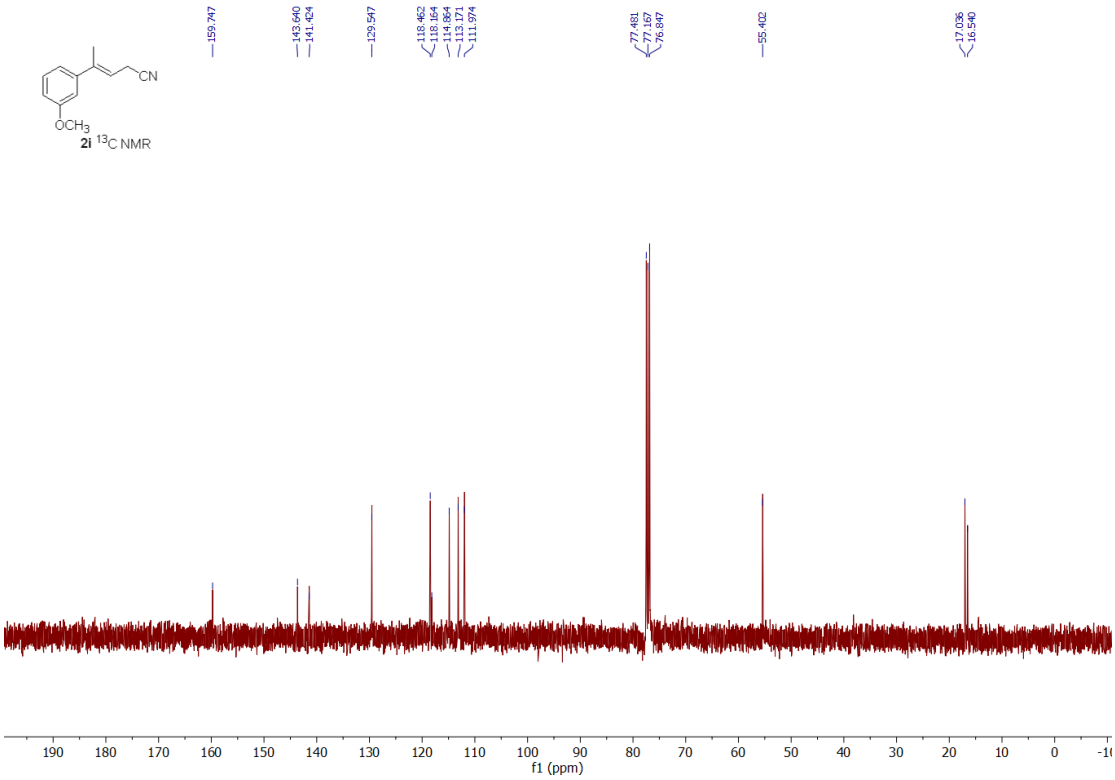


^{1}H NMR Spectra of 2i (400 MHz, Chloroform-*d*)



^{13}C NMR Spectra of 2i (100 MHz, Chloroform-*d*)



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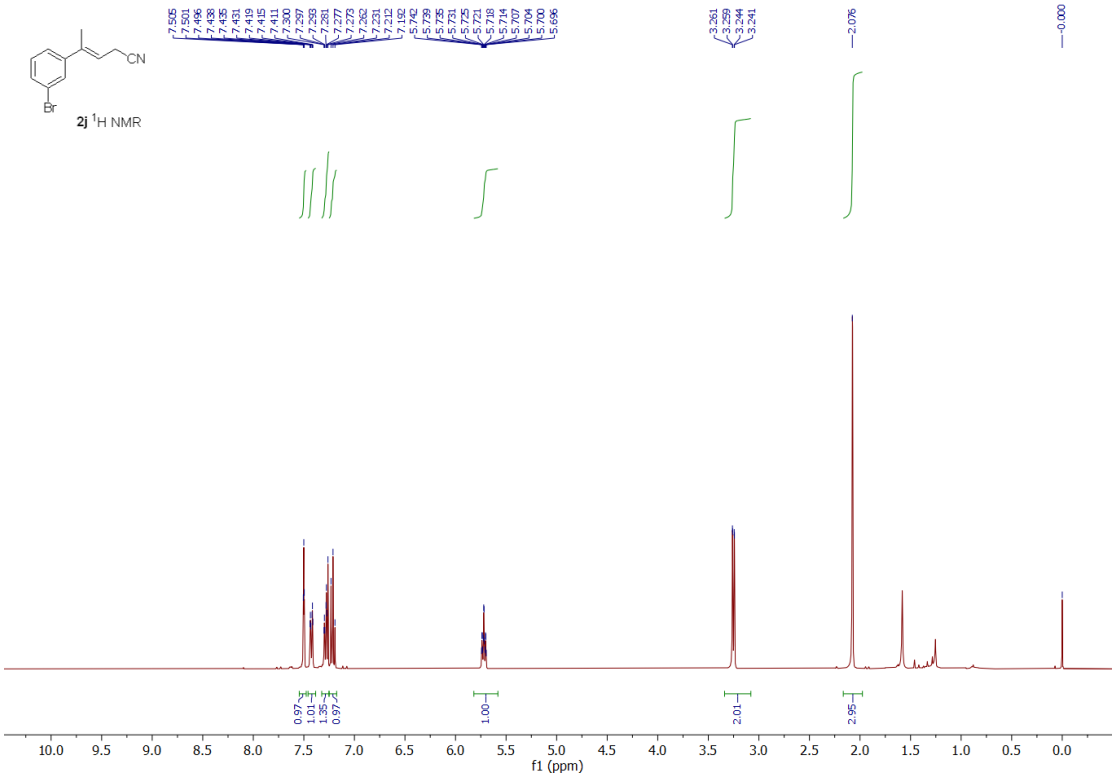

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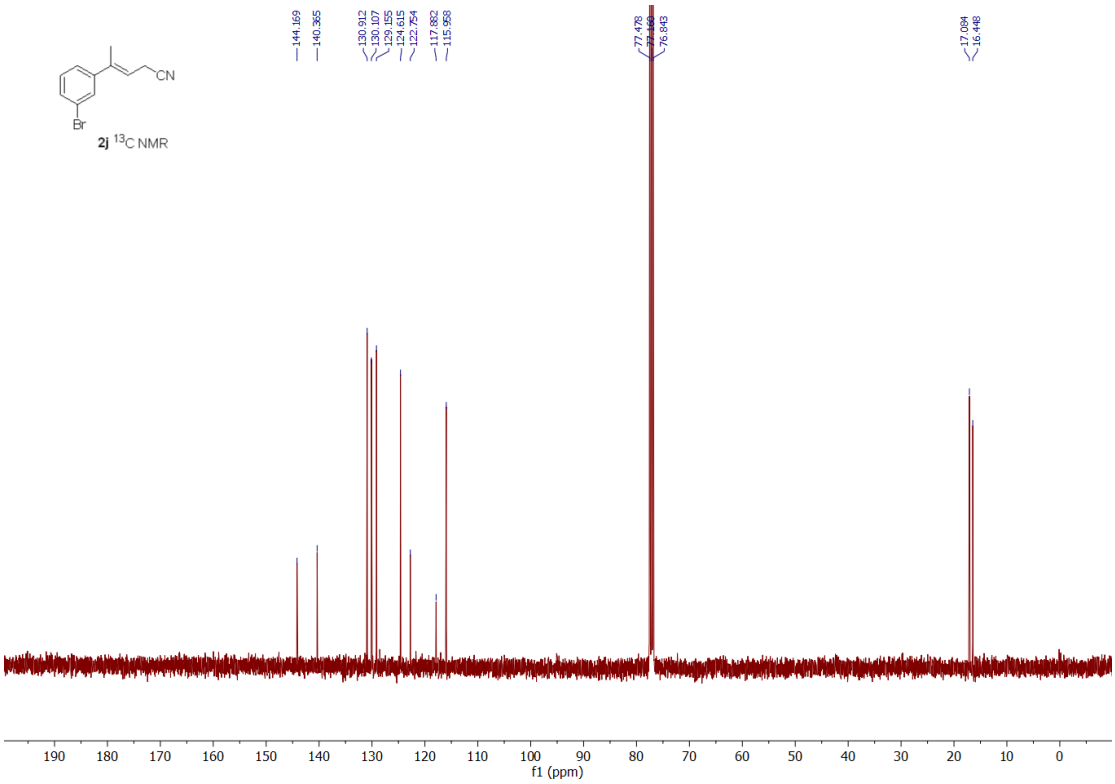
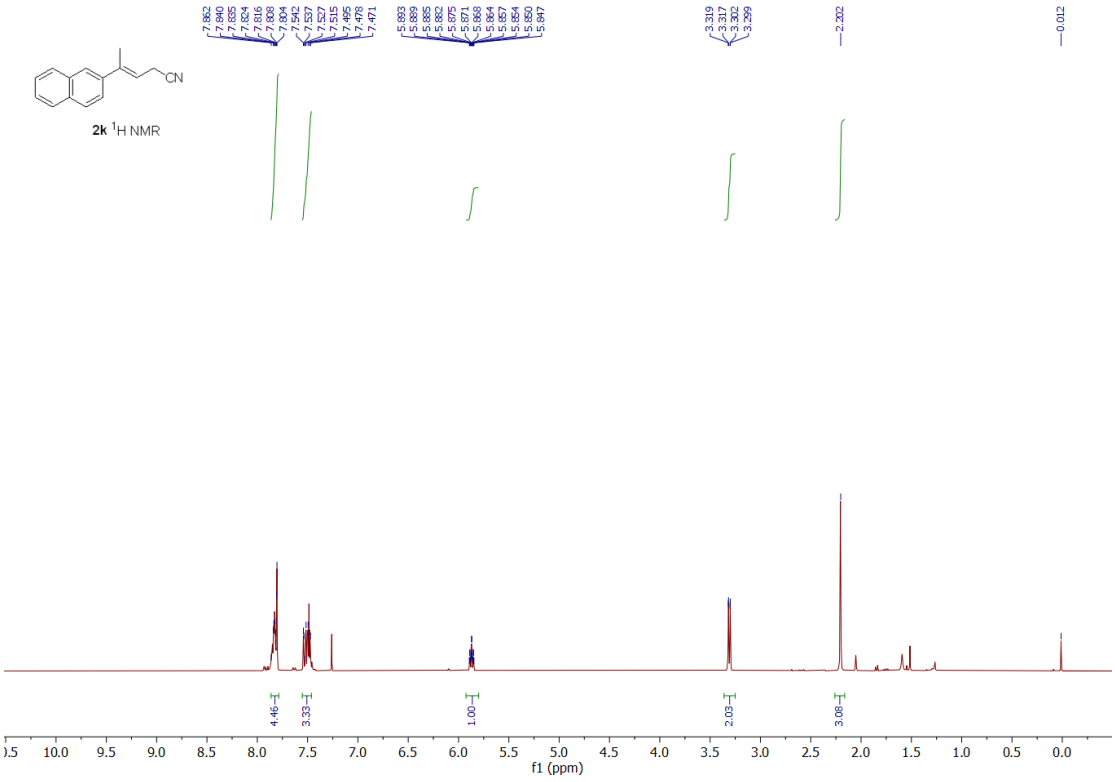


^{1}H NMR Spectra of 2k (400 MHz, Chloroform-*d*)



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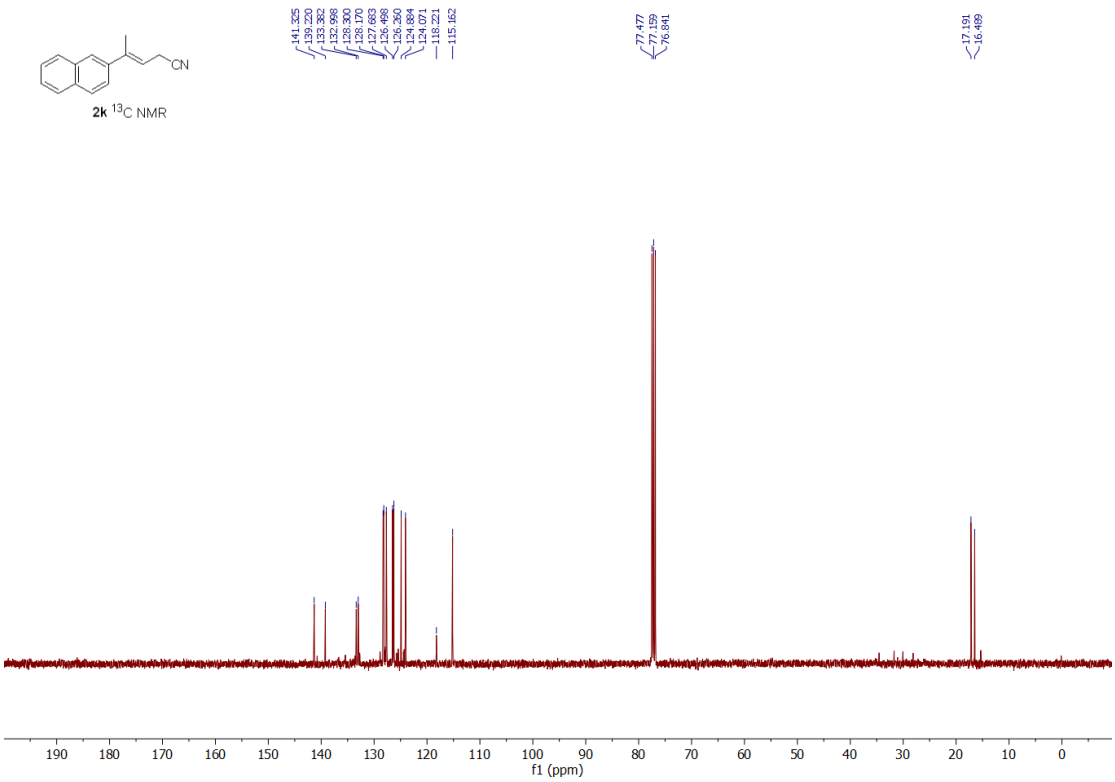
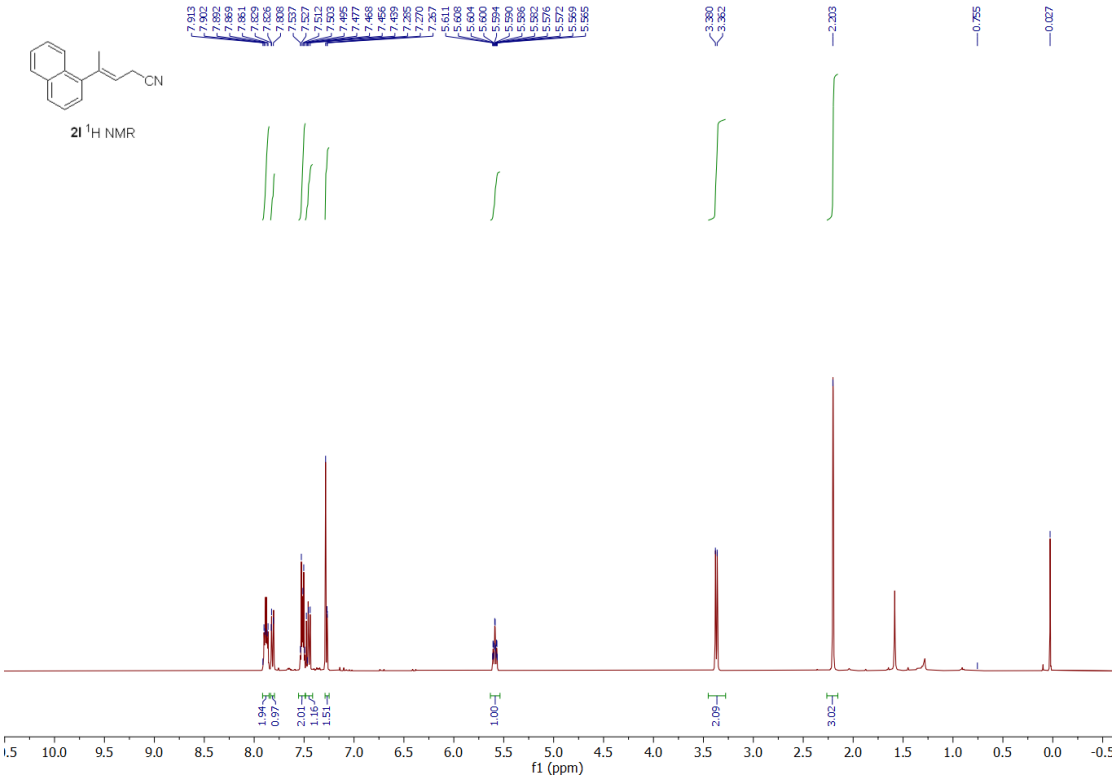


^{1}H NMR Spectra of 2l (400 MHz, Chloroform-*d*)



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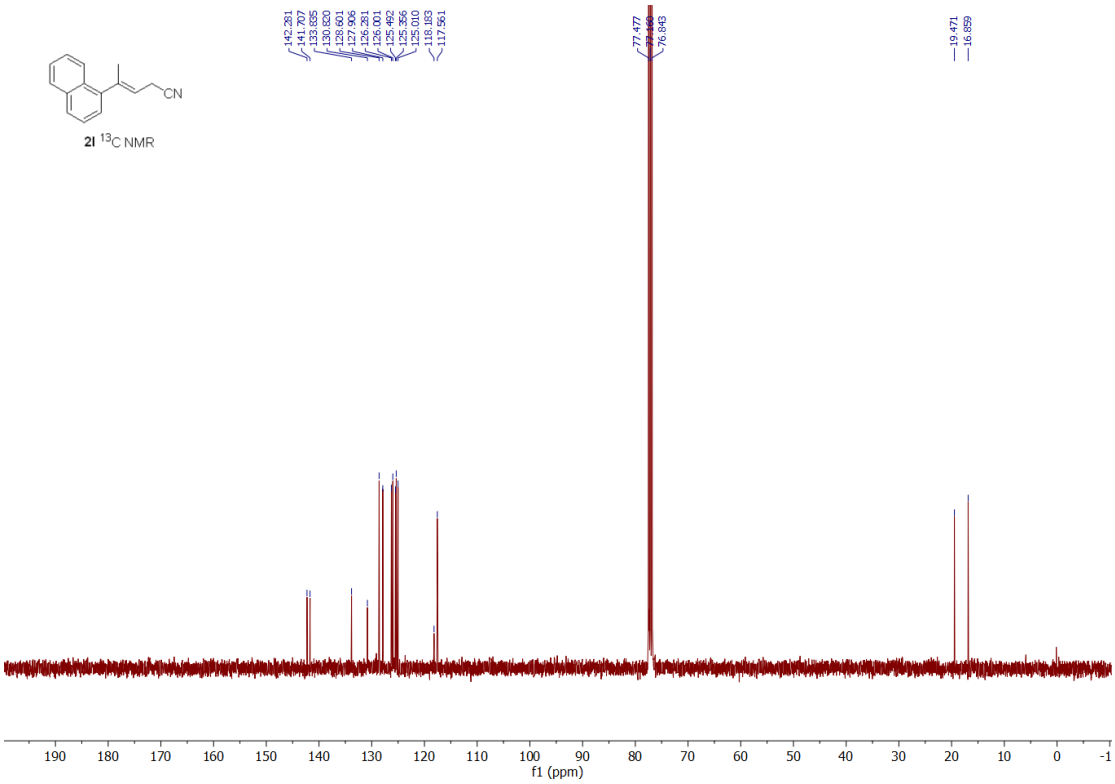
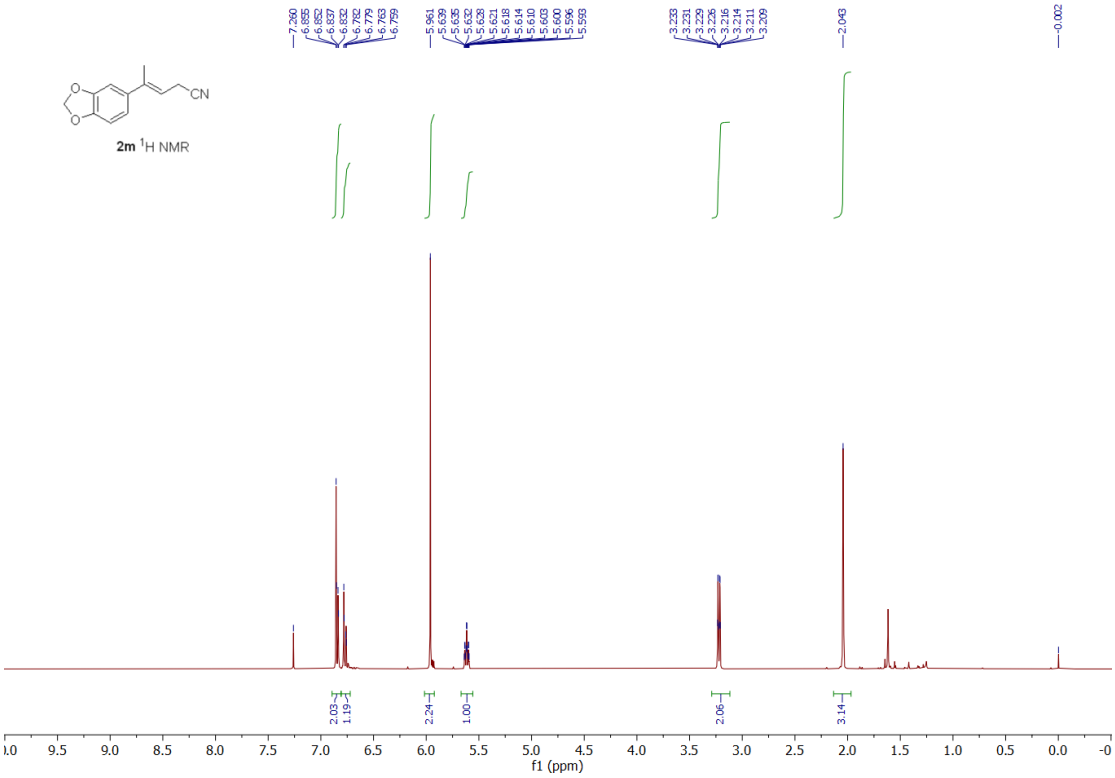
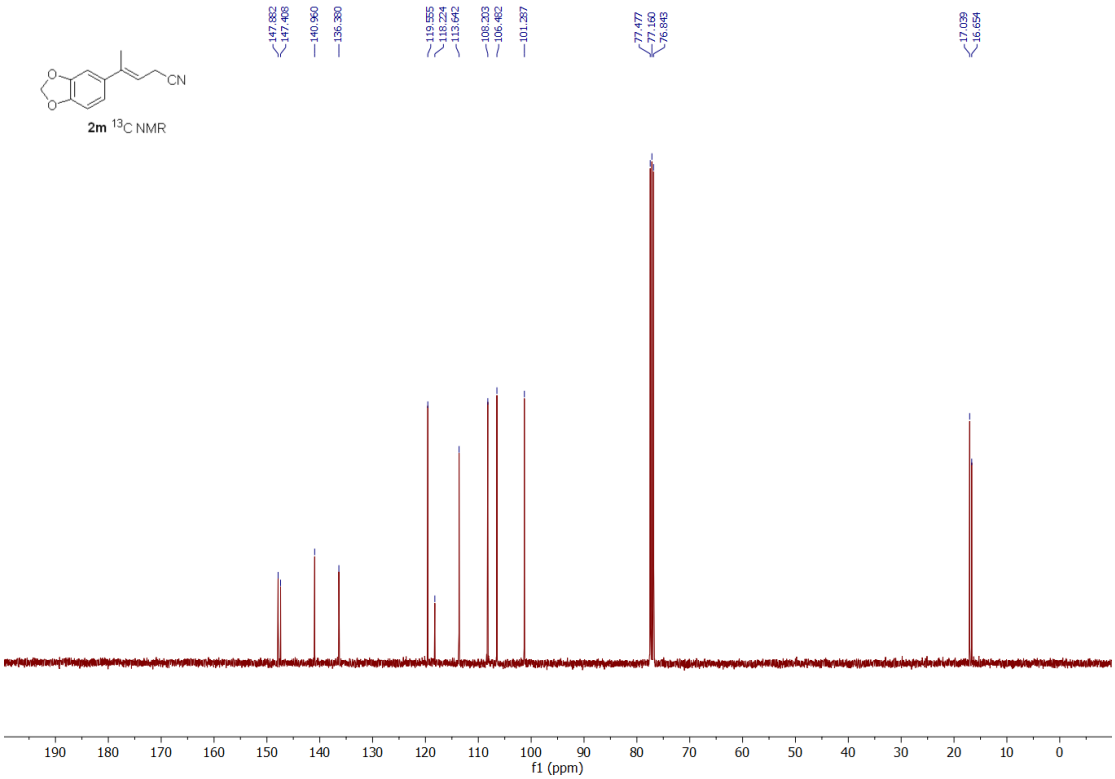


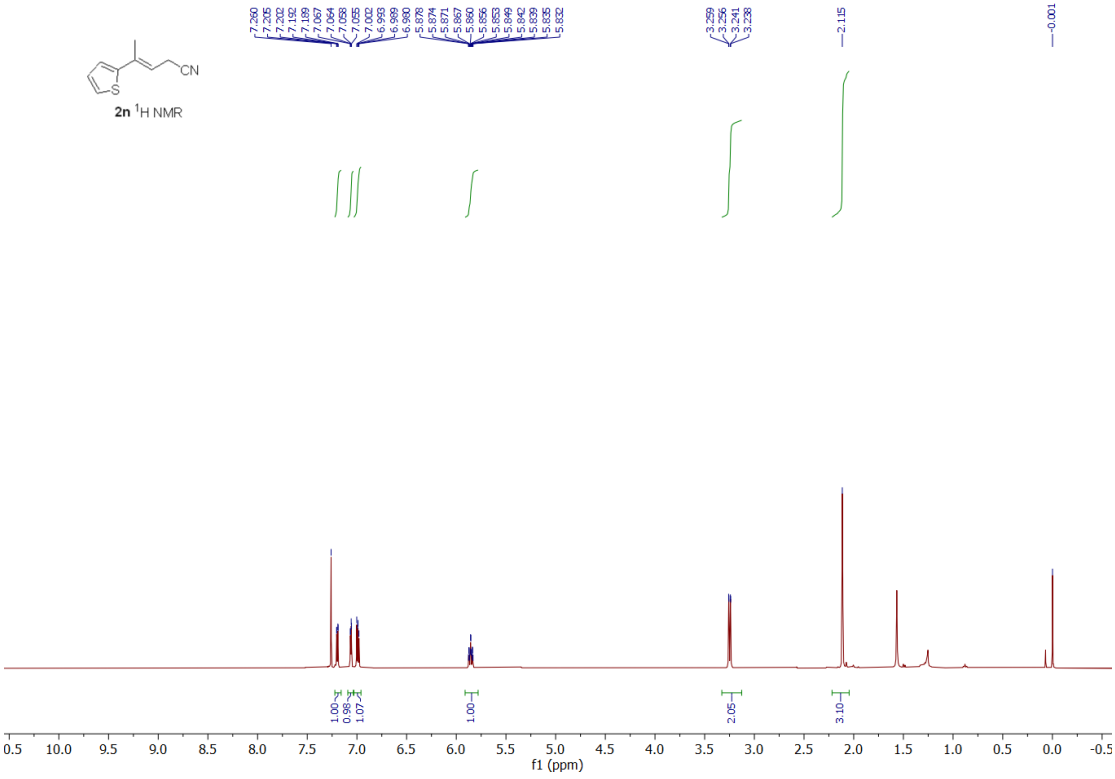
^{1}H NMR Spectra of 2m (400 MHz, Chloroform-*d*)



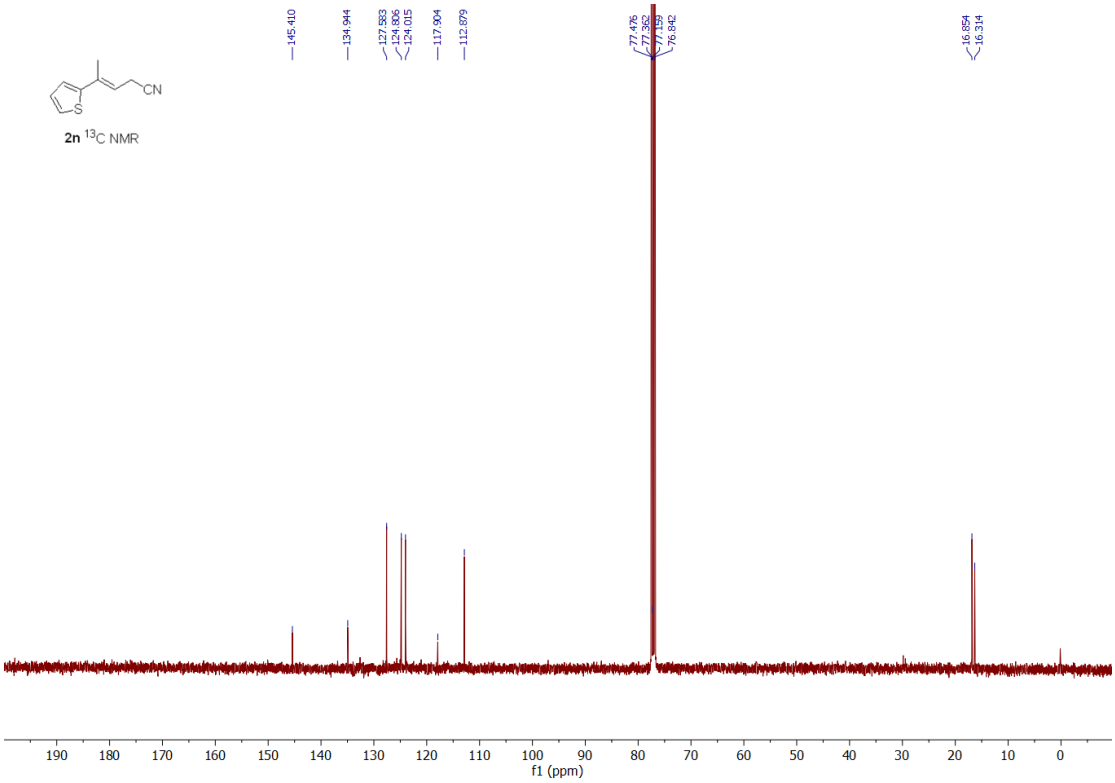
^{13}C NMR Spectra of 2m (100 MHz, Chloroform-*d*)



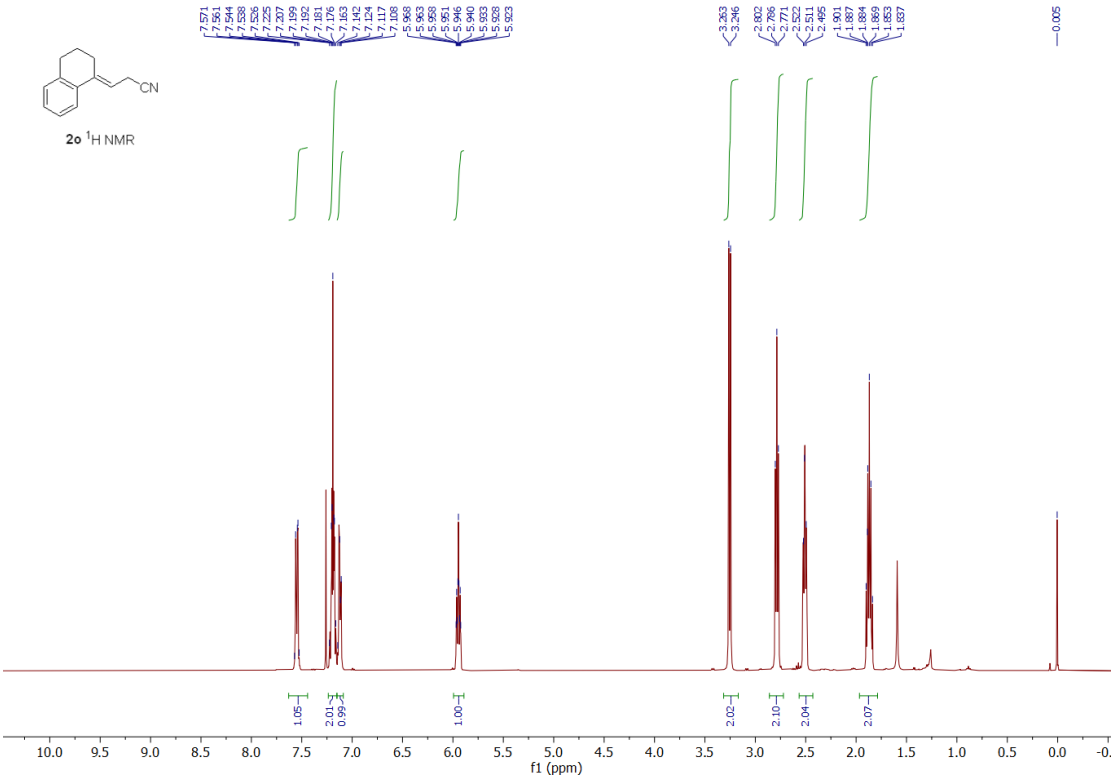
^{1}H NMR Spectra of 2n (400 MHz, Chloroform-*d*)



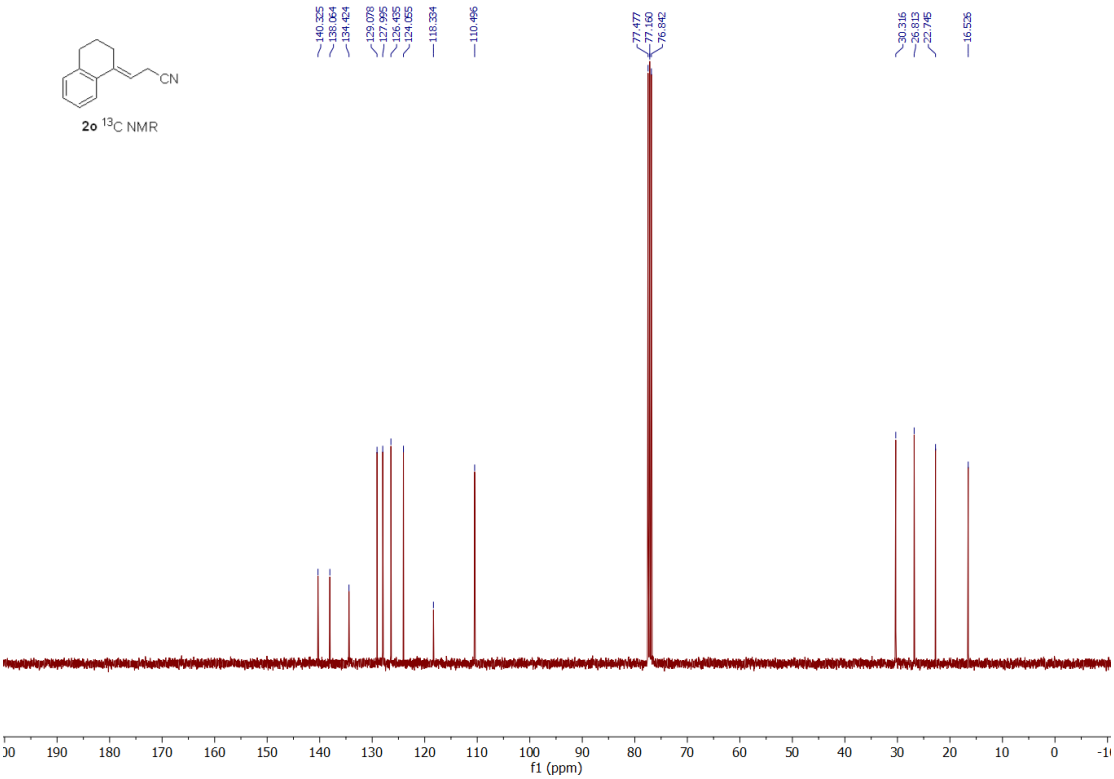
^{13}C NMR Spectra of 2n (100 MHz, Chloroform-*d*)



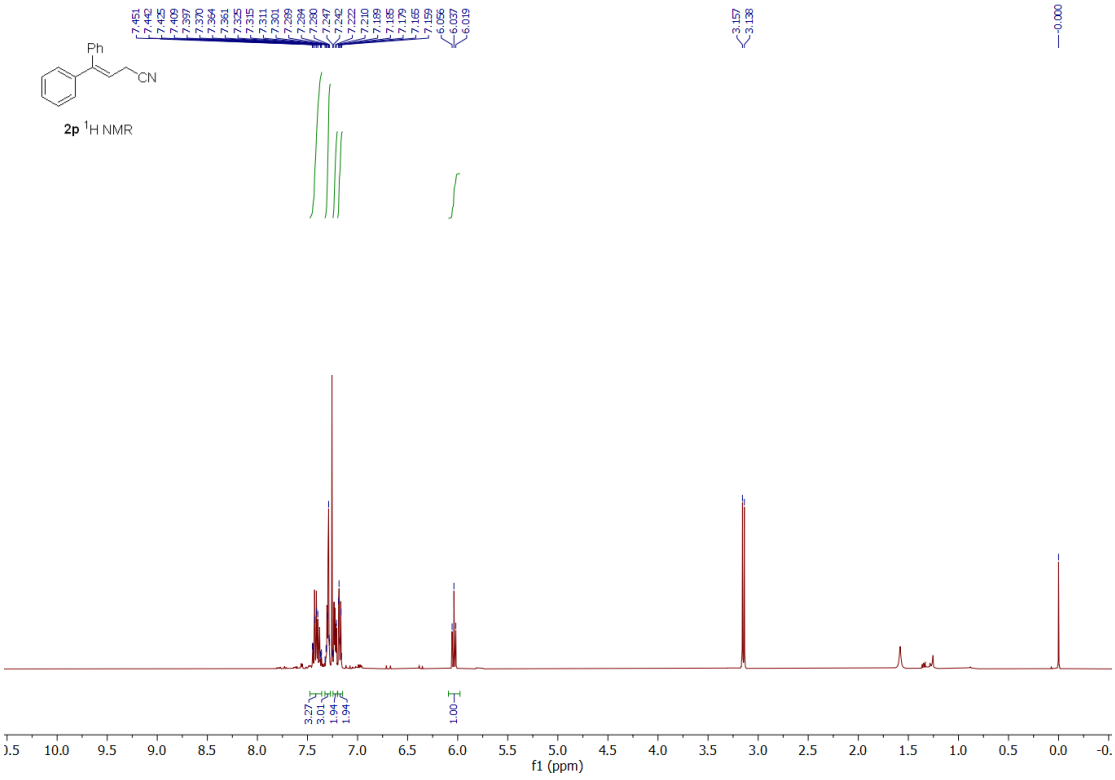
^{1}H NMR Spectra of 2o (400 MHz, Chloroform-*d*)



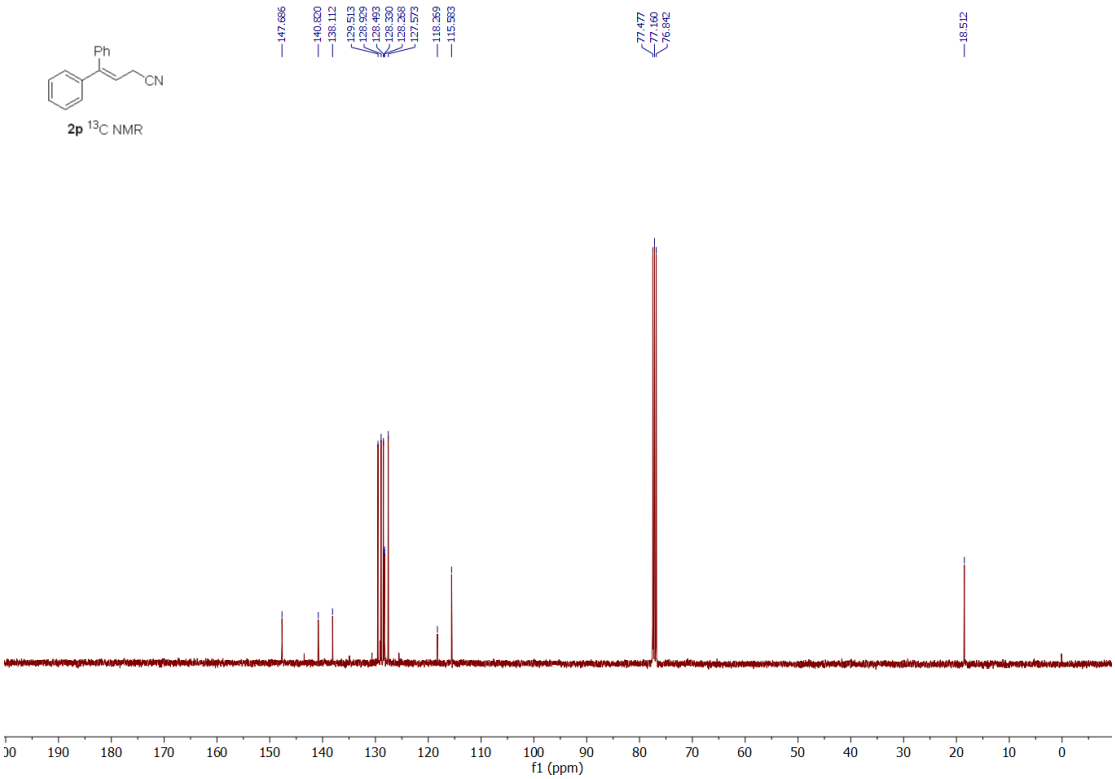
^{13}C NMR Spectra of 2o (100 MHz, Chloroform-*d*)



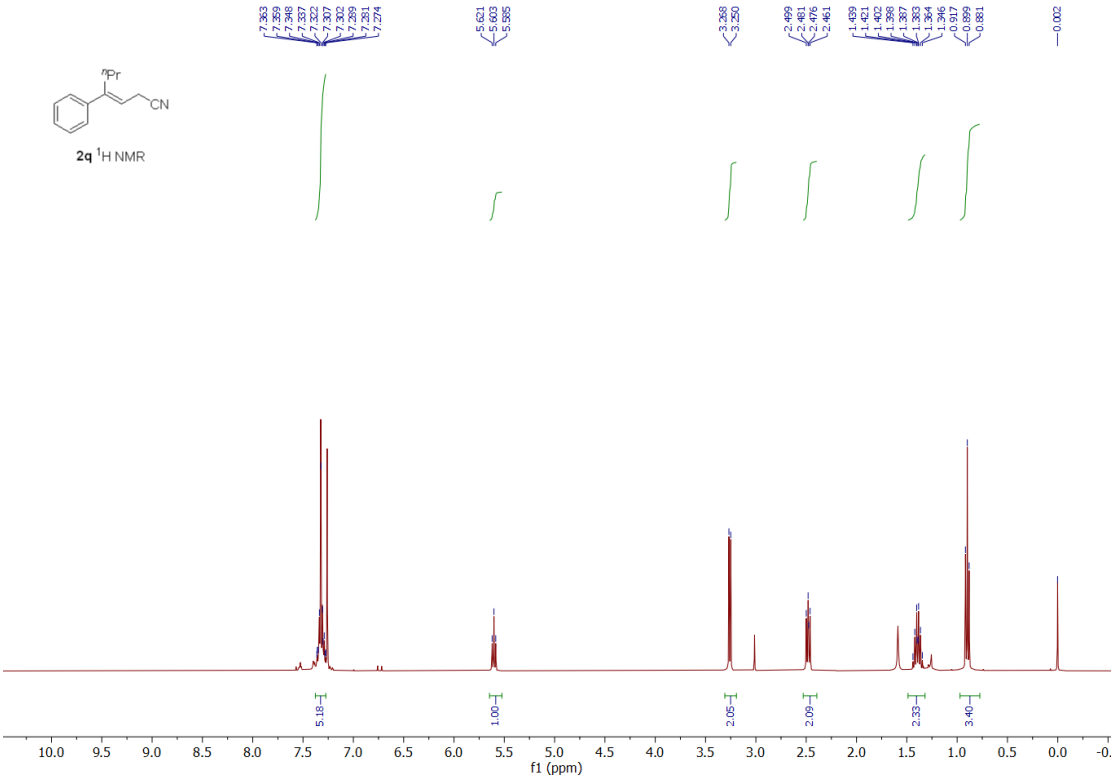
^{1}H NMR Spectra of 2p (400 MHz, Chloroform-*d*)



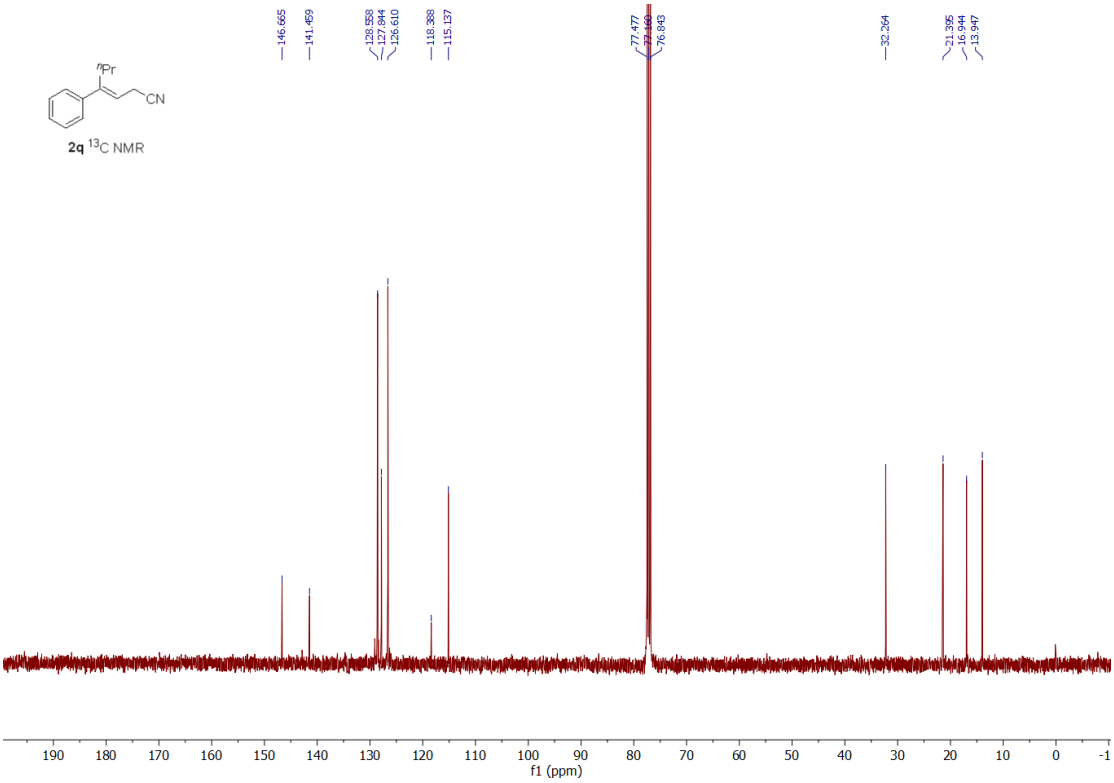
^{13}C NMR Spectra of 2p (100 MHz, Chloroform-*d*)



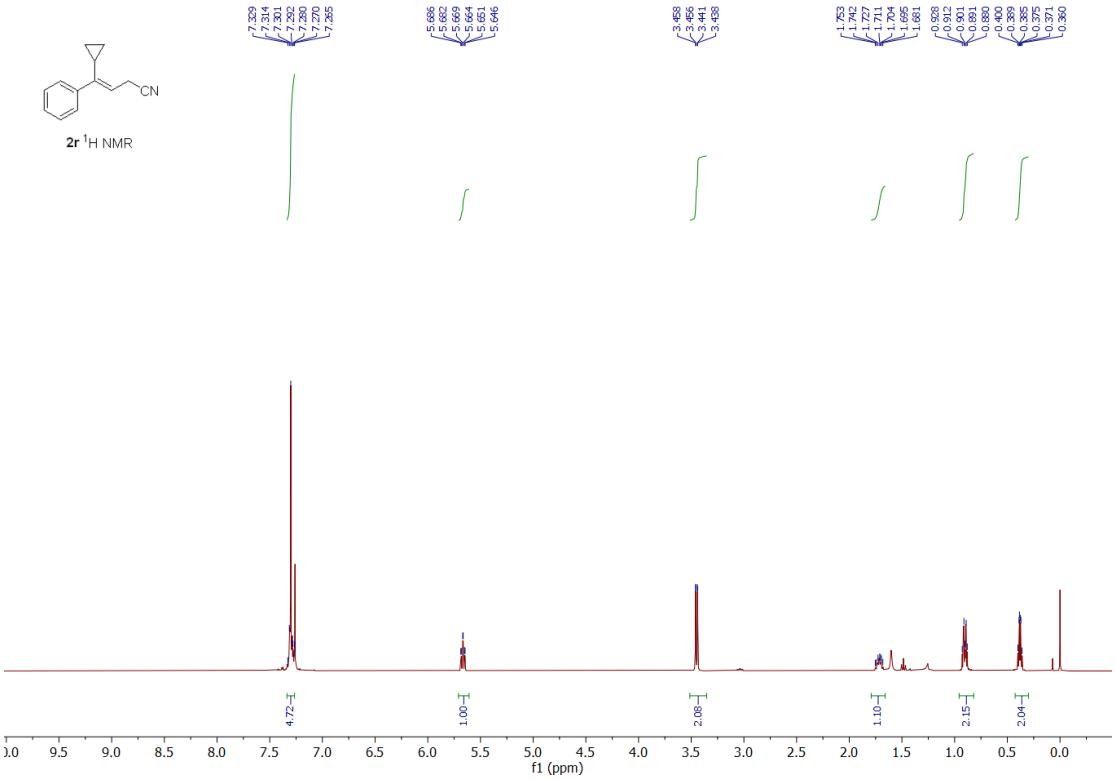
^{1}H NMR Spectra of 2q (400 MHz, Chloroform-*d*)



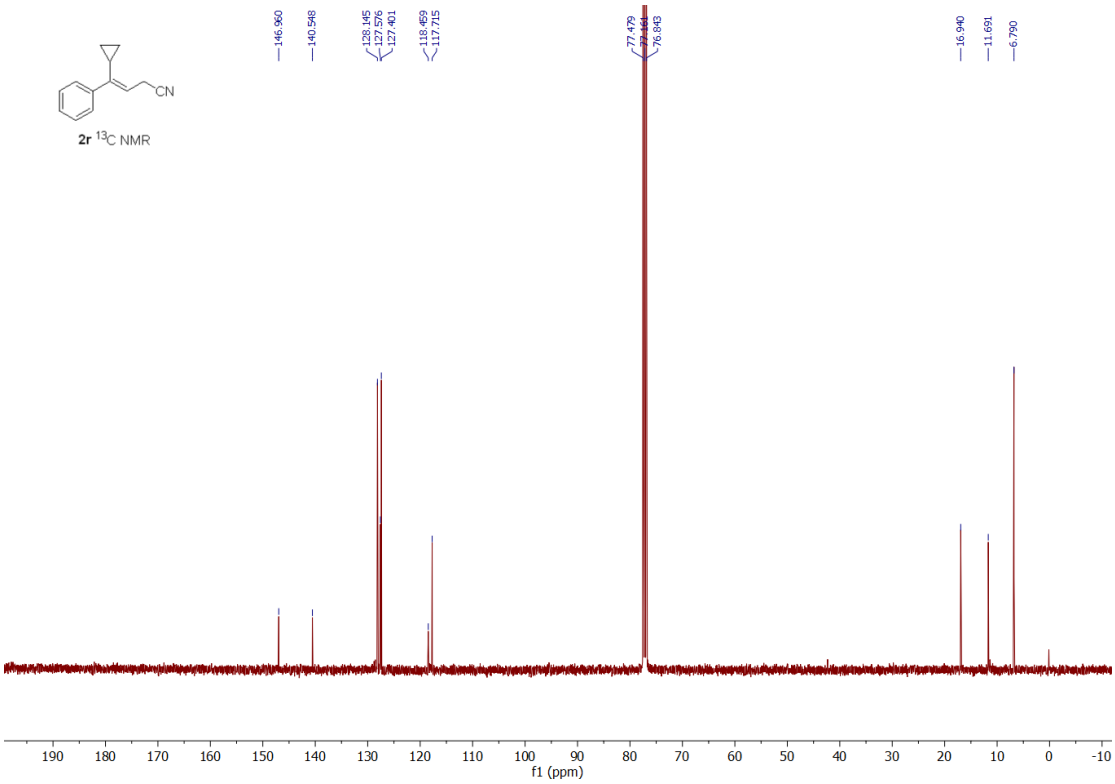
^{13}C NMR Spectra of 2q (100 MHz, Chloroform-*d*)



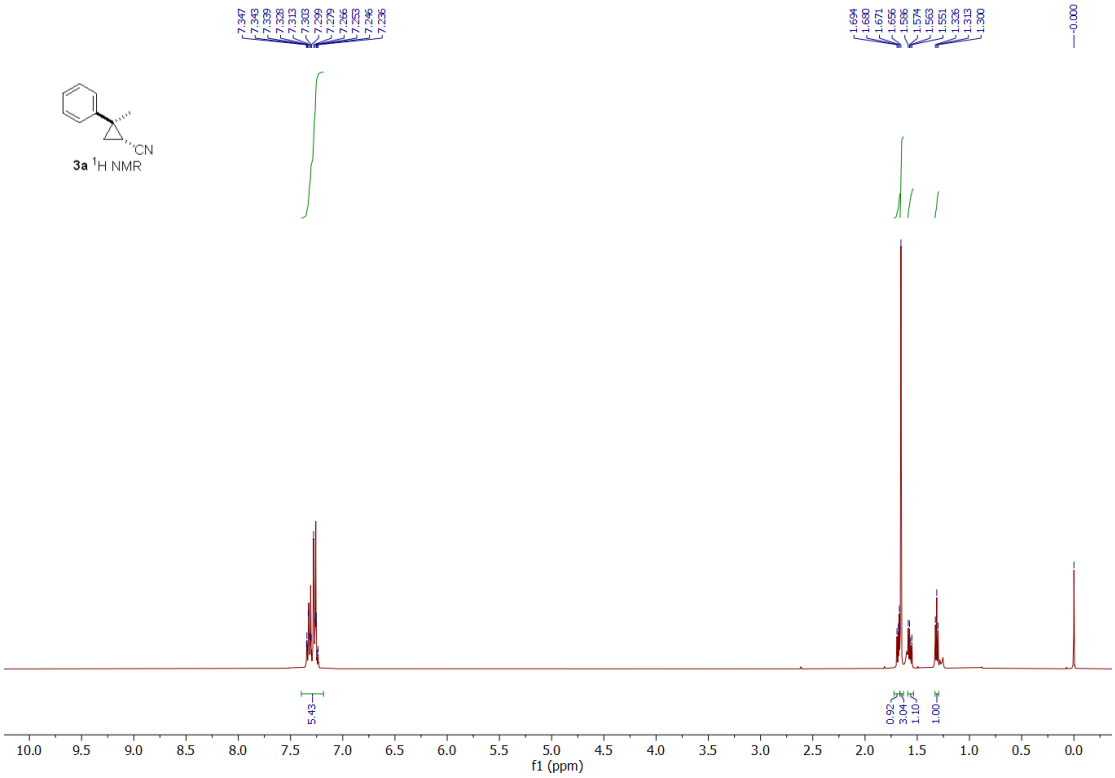
^{1}H NMR Spectra of 2r (400 MHz, Chloroform-*d*)



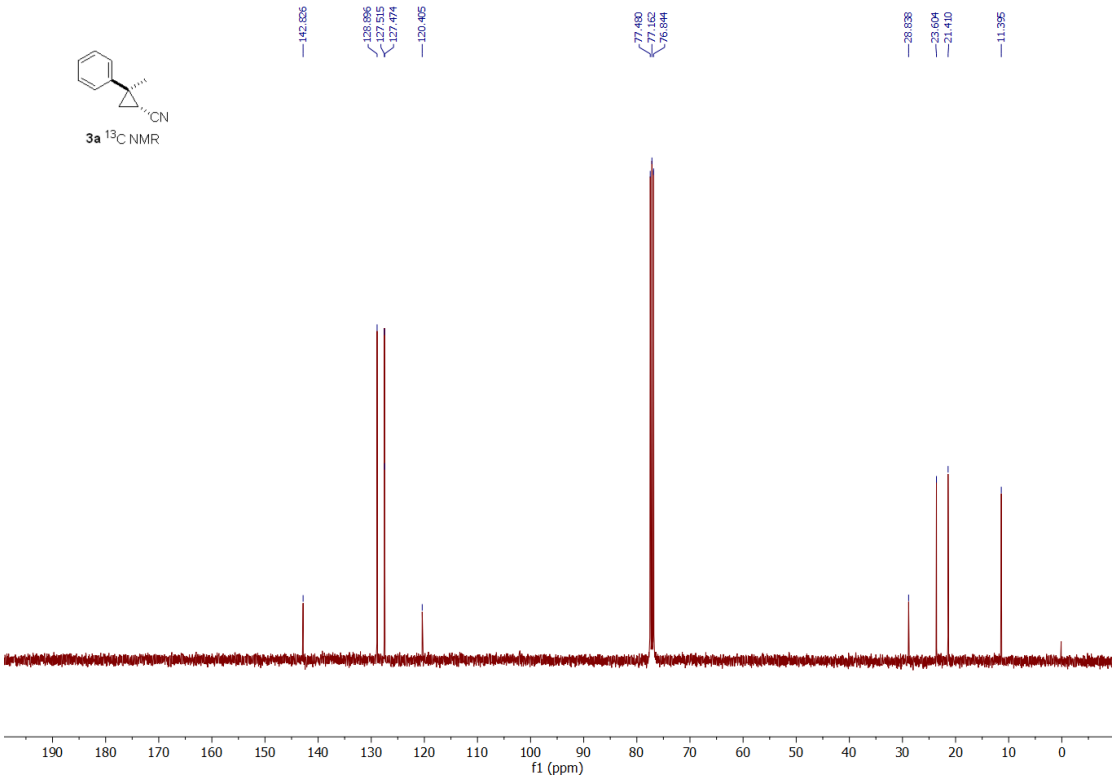
^{13}C NMR Spectra of 2r (100 MHz, Chloroform-*d*)



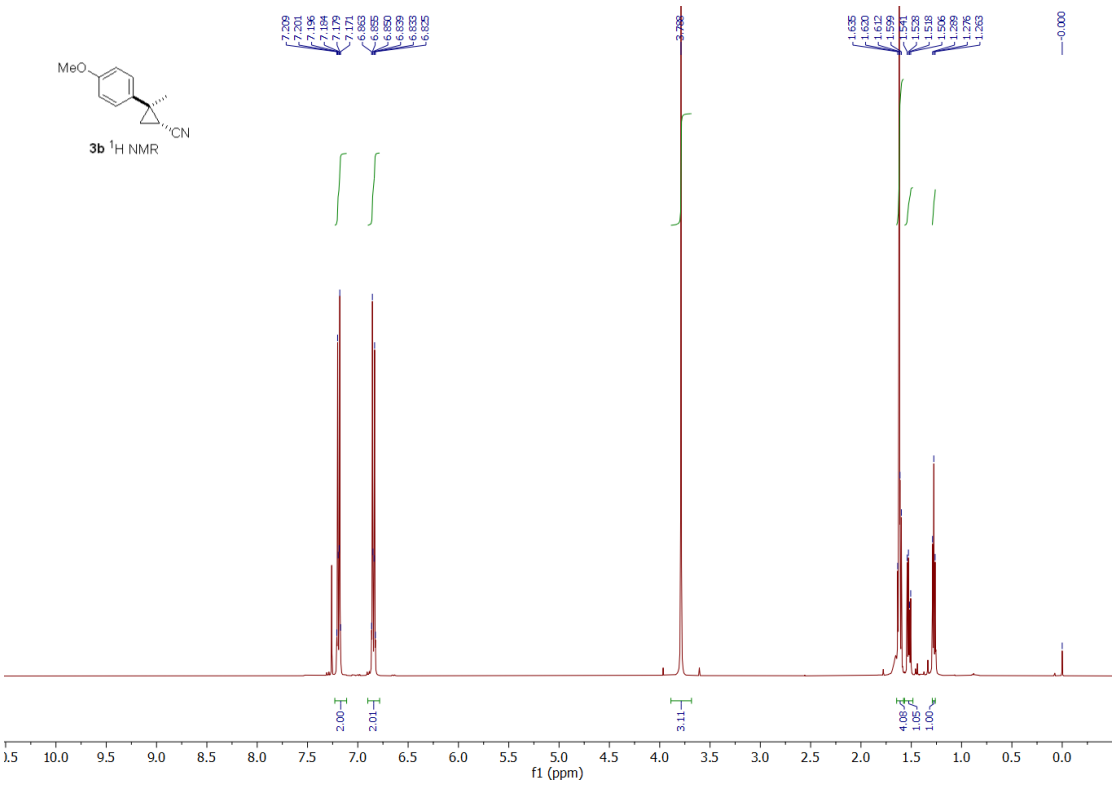
^{1}H NMR Spectra of 3a (400 MHz, Chloroform-*d*)



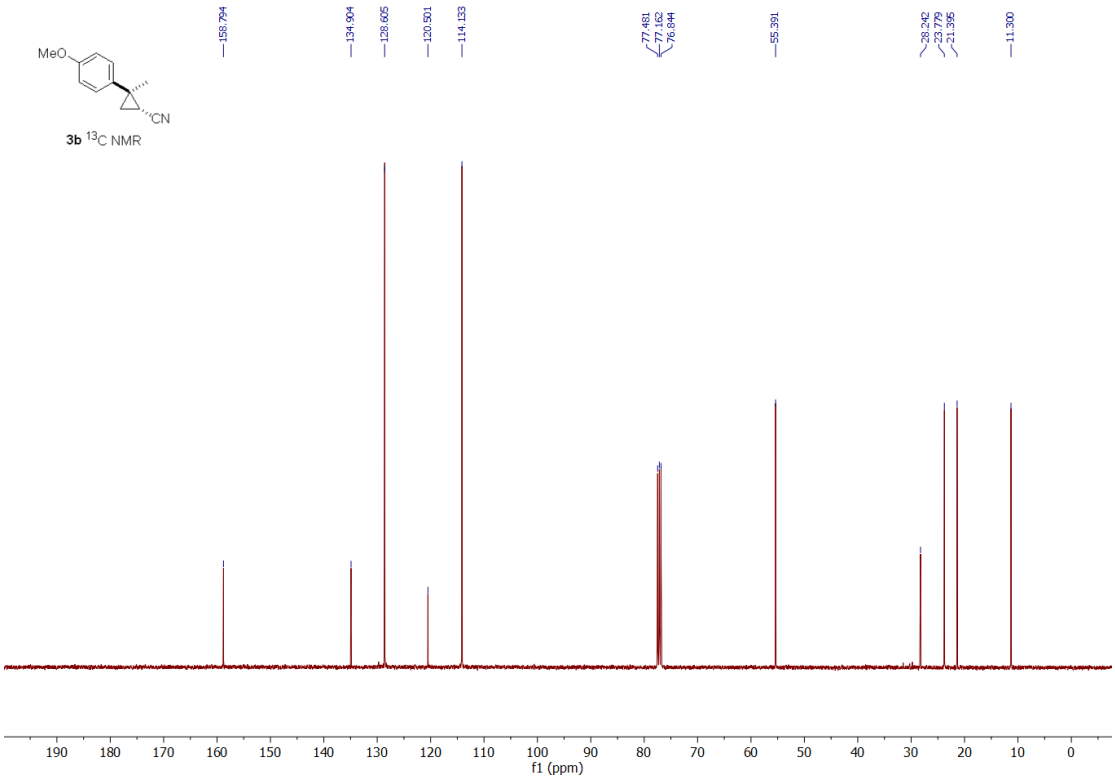
^{13}C NMR Spectra of 3a (100 MHz, Chloroform-*d*)



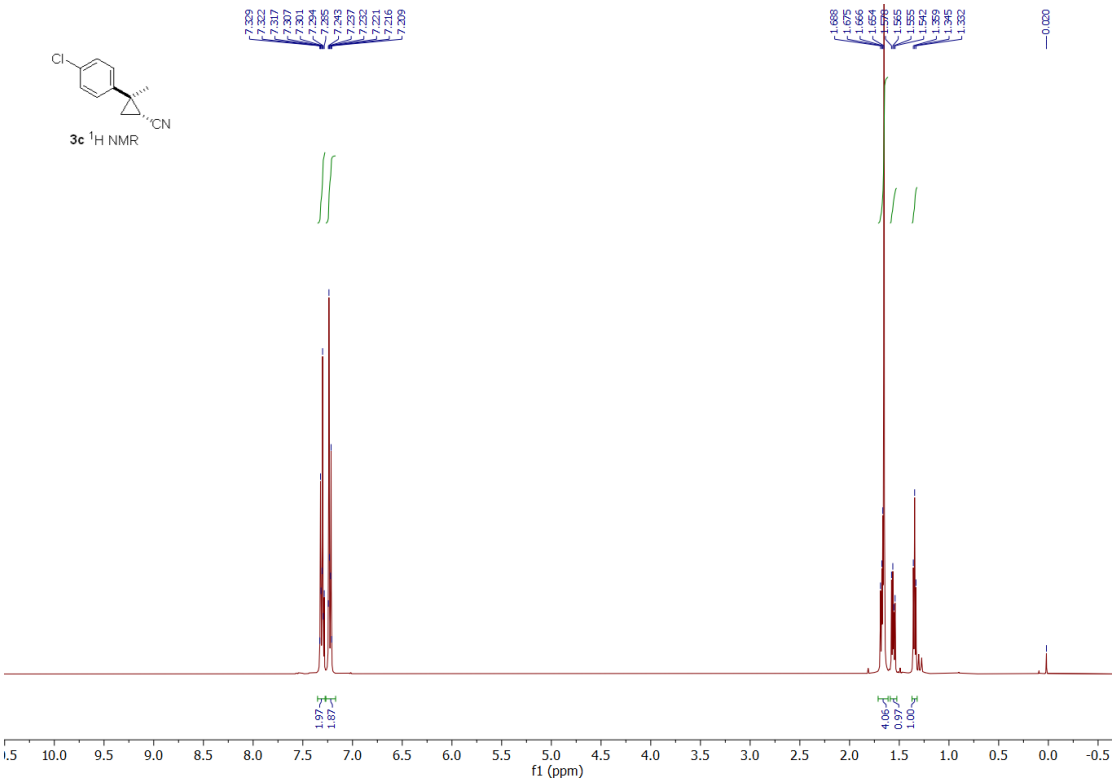
^{1}H NMR Spectra of 3b (400 MHz, Chloroform-*d*)



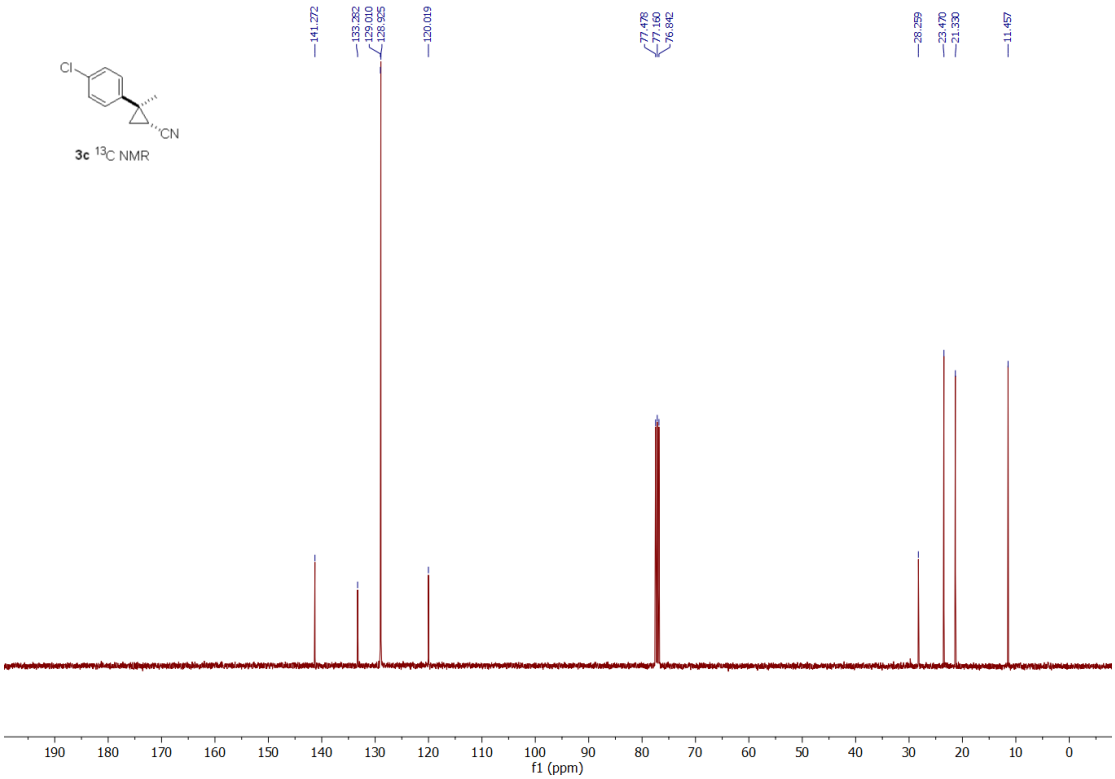
^{13}C NMR Spectra of 3b (100 MHz, Chloroform-*d*)



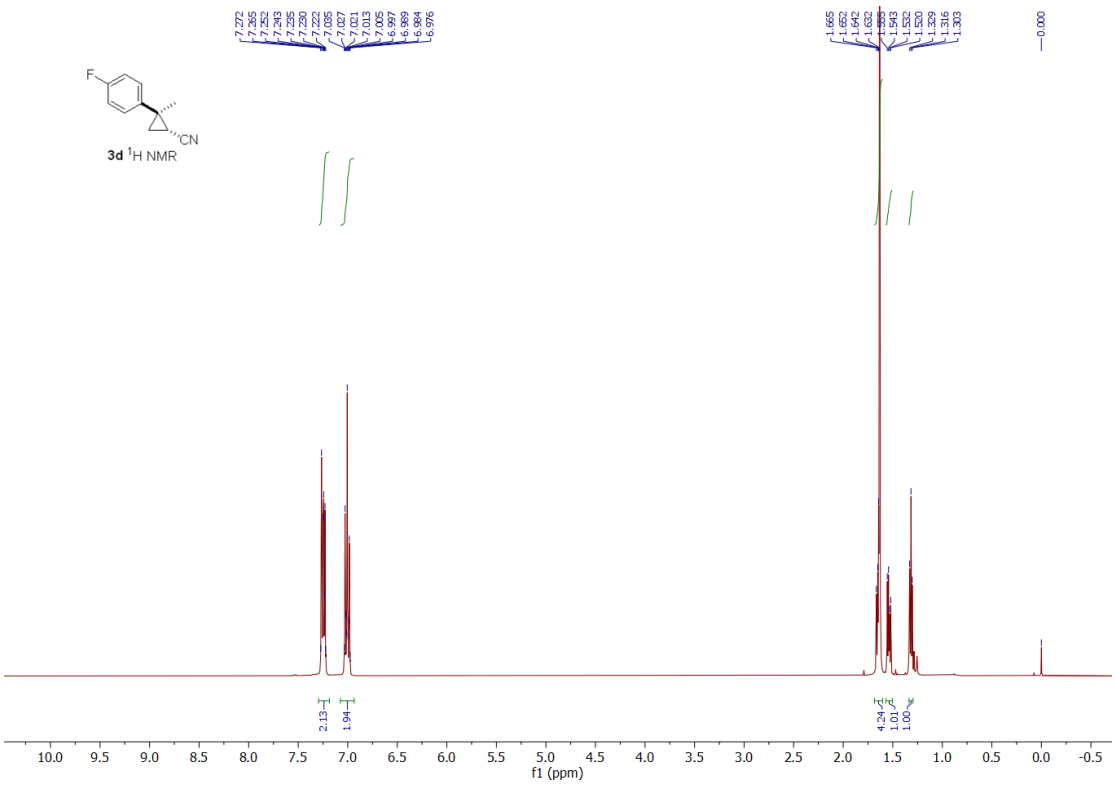
^{1}H NMR Spectra of 3c (400 MHz, Chloroform-*d*)



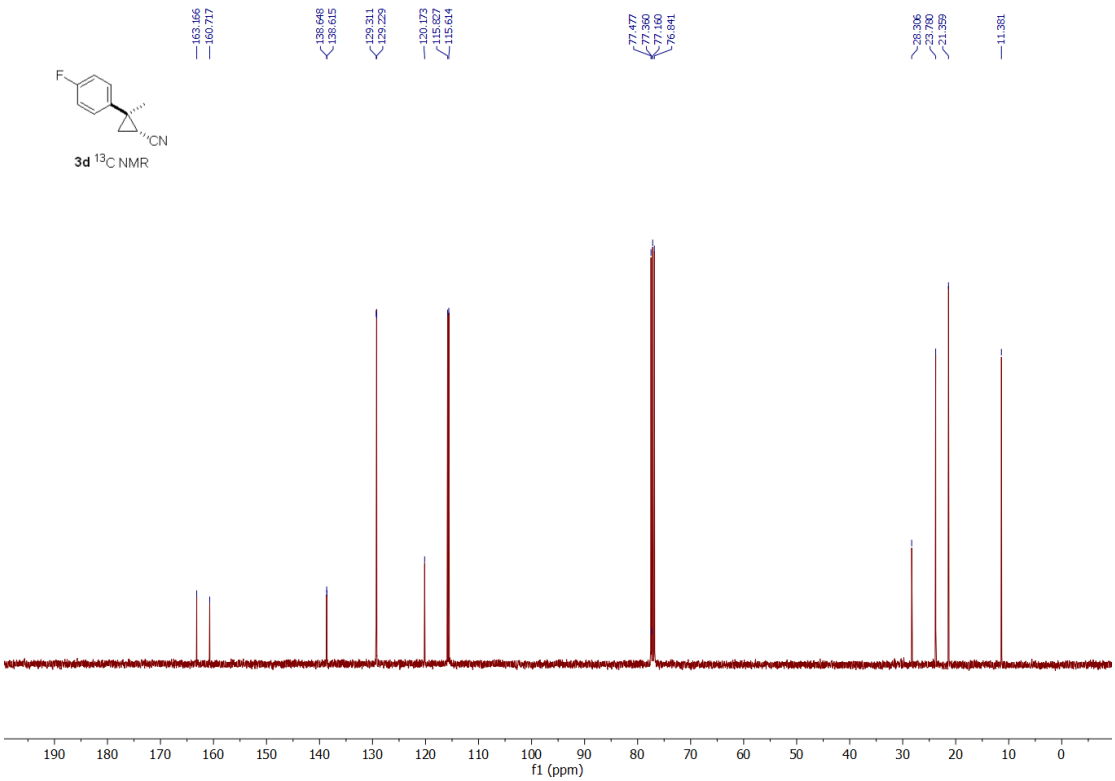
^{13}C NMR Spectra of 3c (100 MHz, Chloroform-*d*)



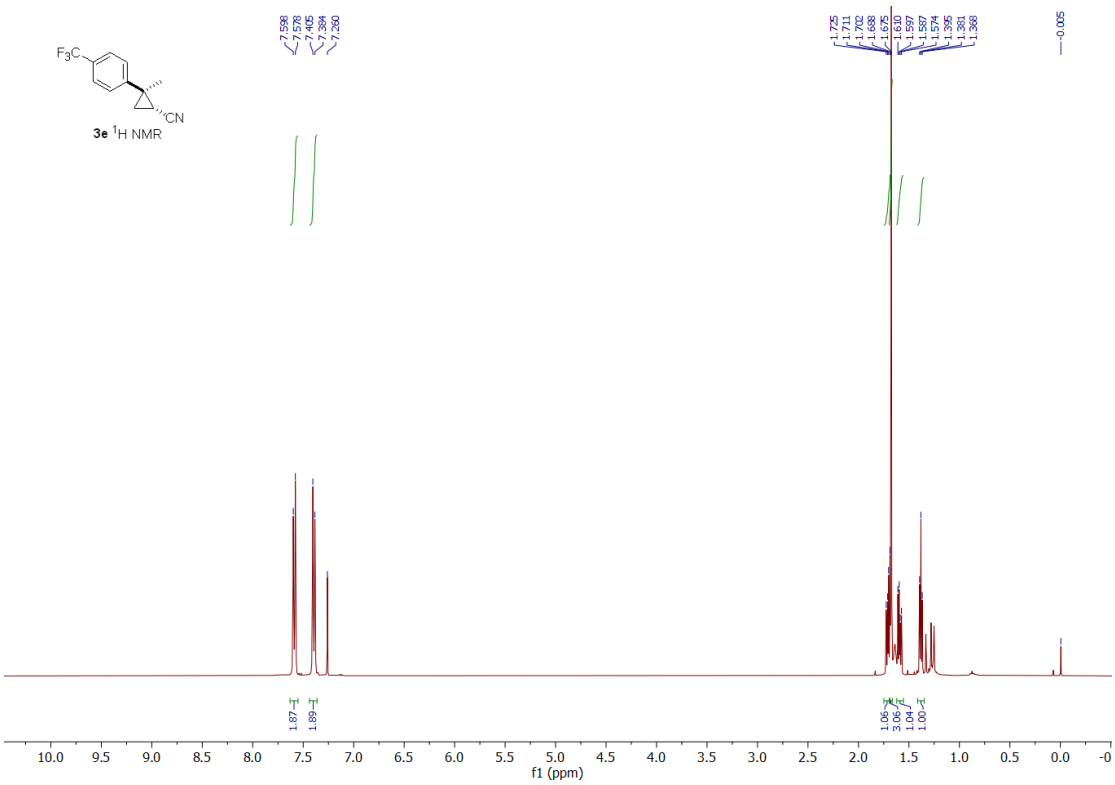
^{1}H NMR Spectra of 3d (400 MHz, Chloroform-*d*)



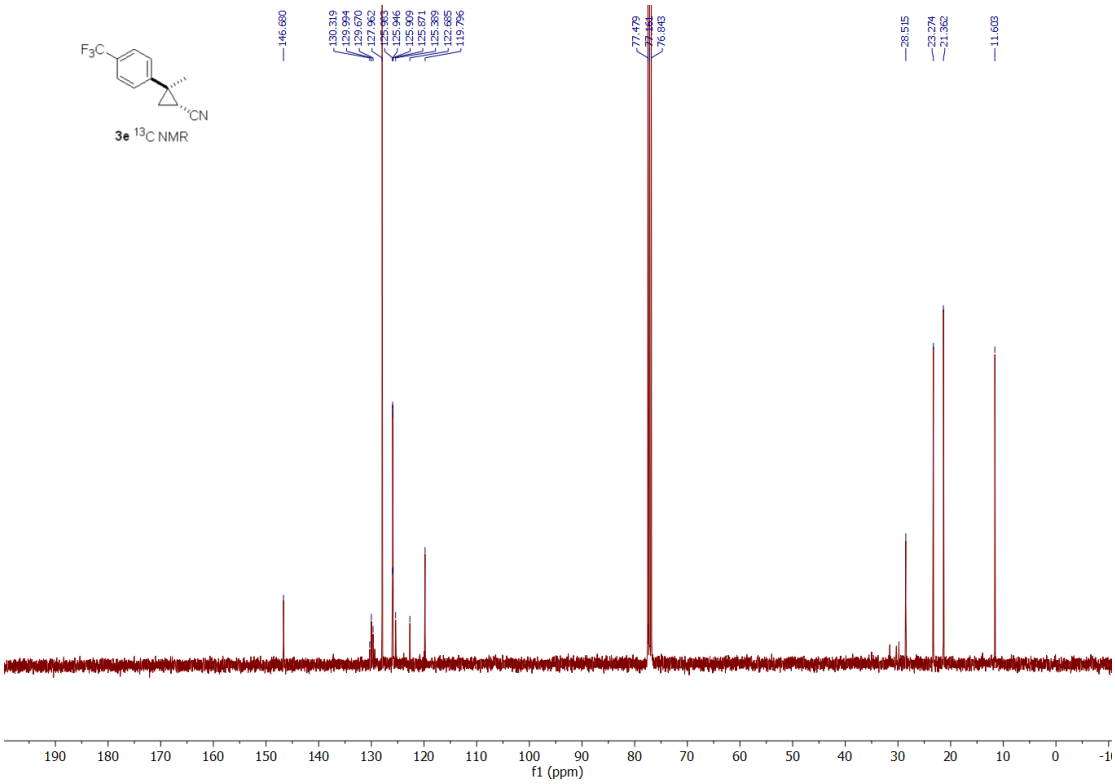
^{13}C NMR Spectra of 3d (100 MHz, Chloroform-*d*)



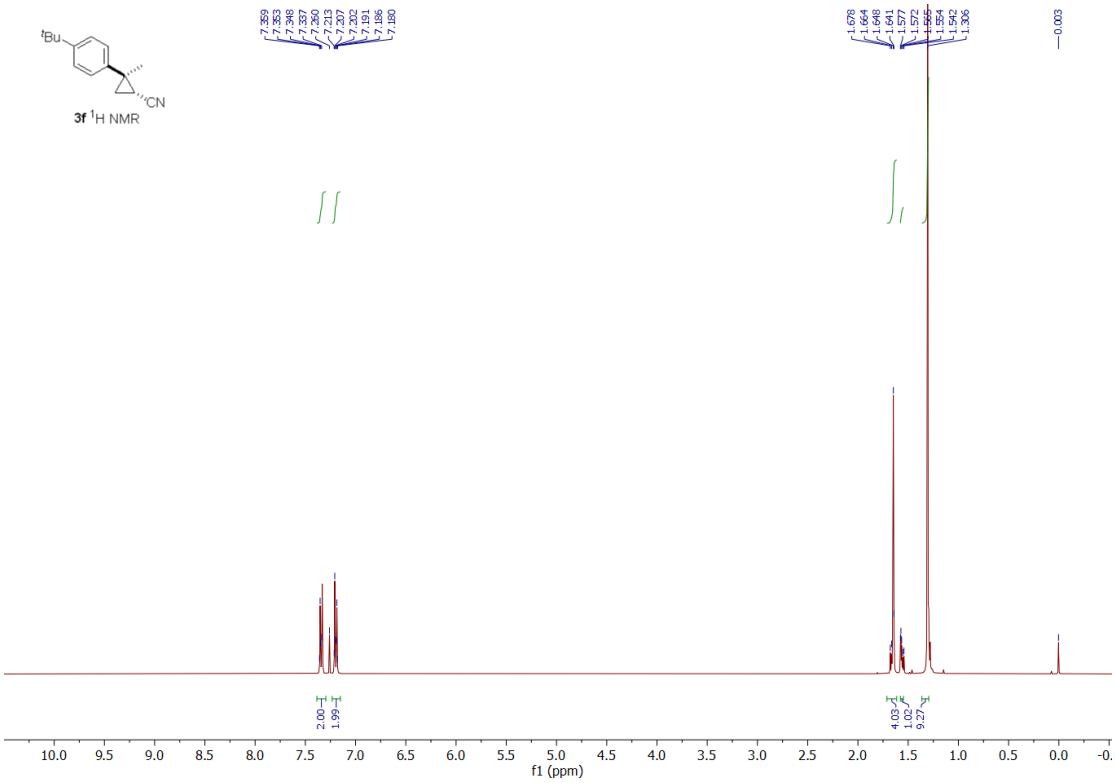
^{1}H NMR Spectra of 3e (400 MHz, Chloroform-*d*)



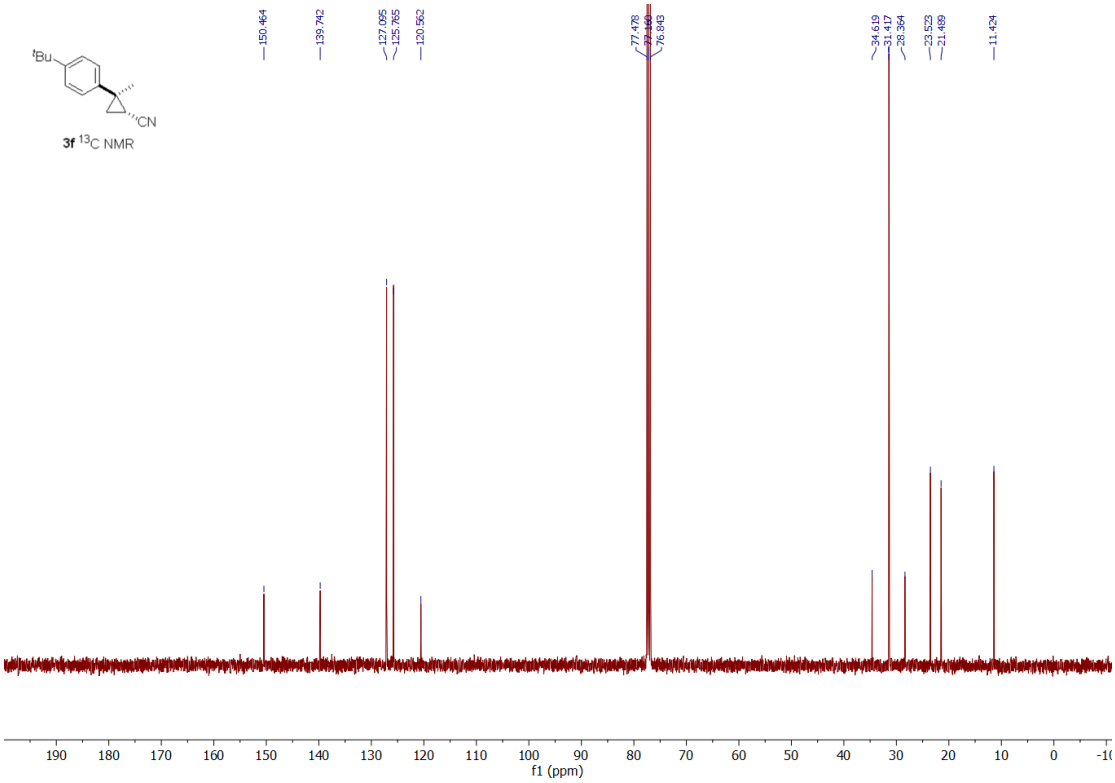
^{13}C NMR Spectra of 3e (100 MHz, Chloroform-*d*)



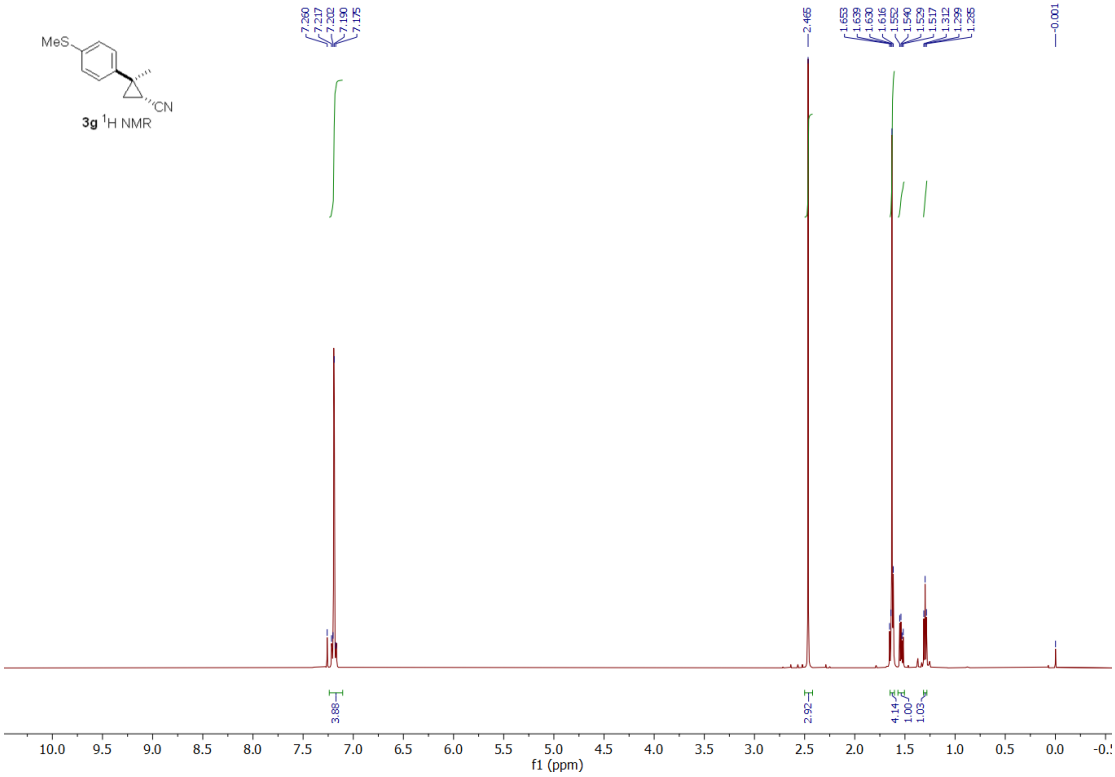
^{1}H NMR Spectra of 3f (400 MHz, Chloroform-*d*)



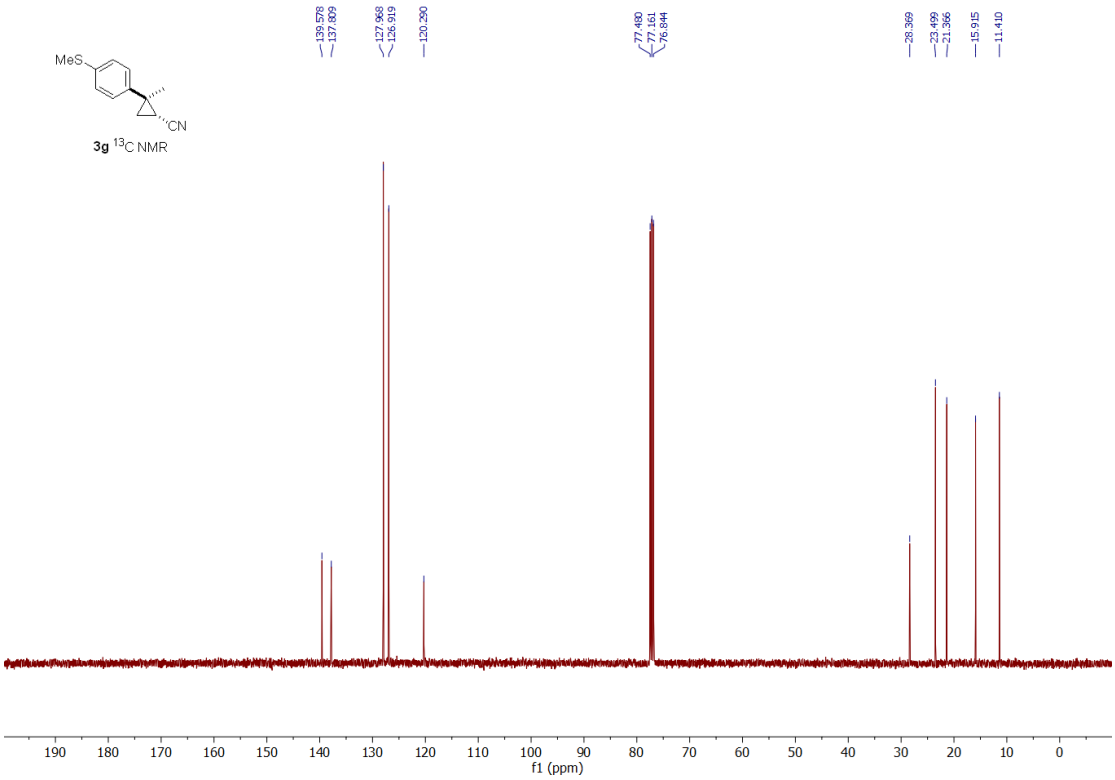
^{13}C NMR Spectra of 3f (100 MHz, Chloroform-*d*)



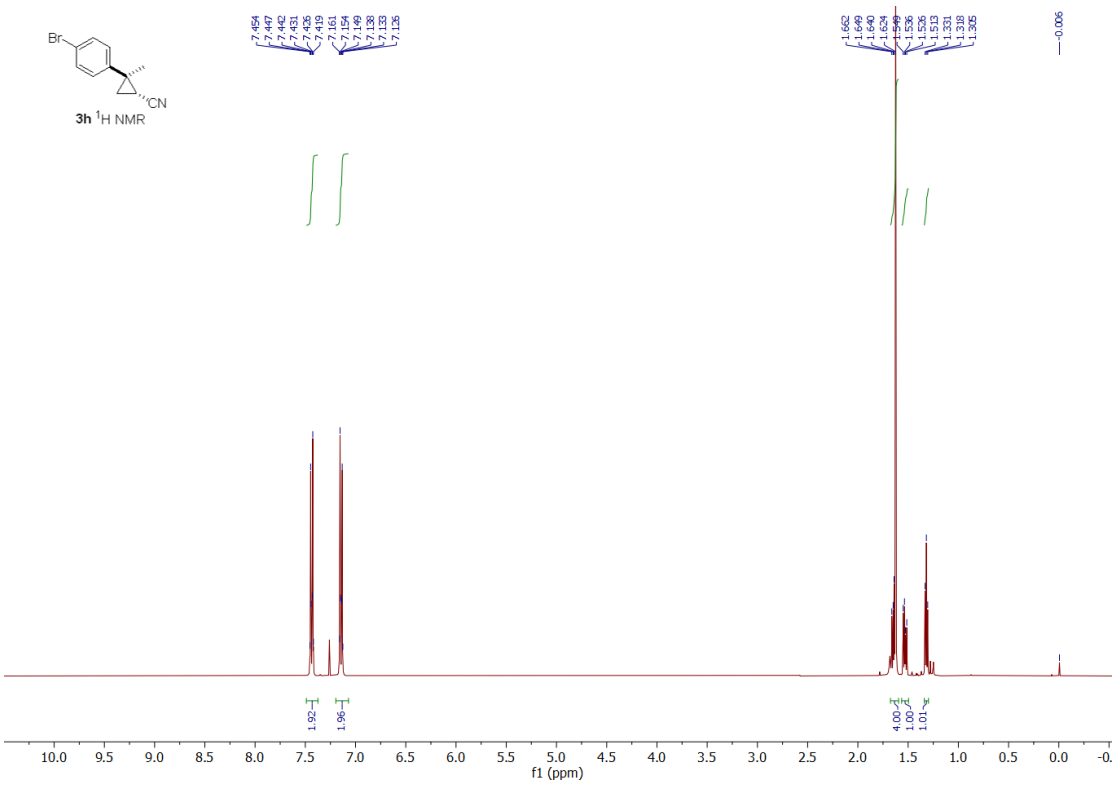
^{1}H NMR Spectra of 3g (400 MHz, Chloroform-*d*)



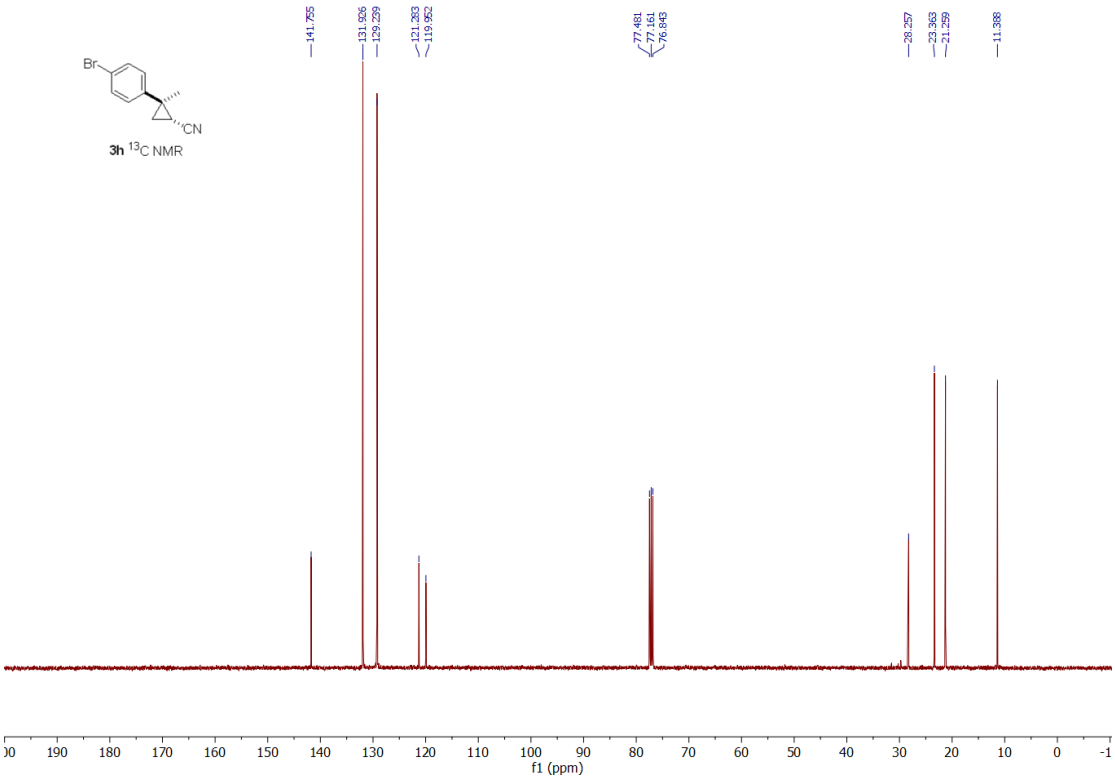
^{13}C NMR Spectra of 3g (100 MHz, Chloroform-*d*)



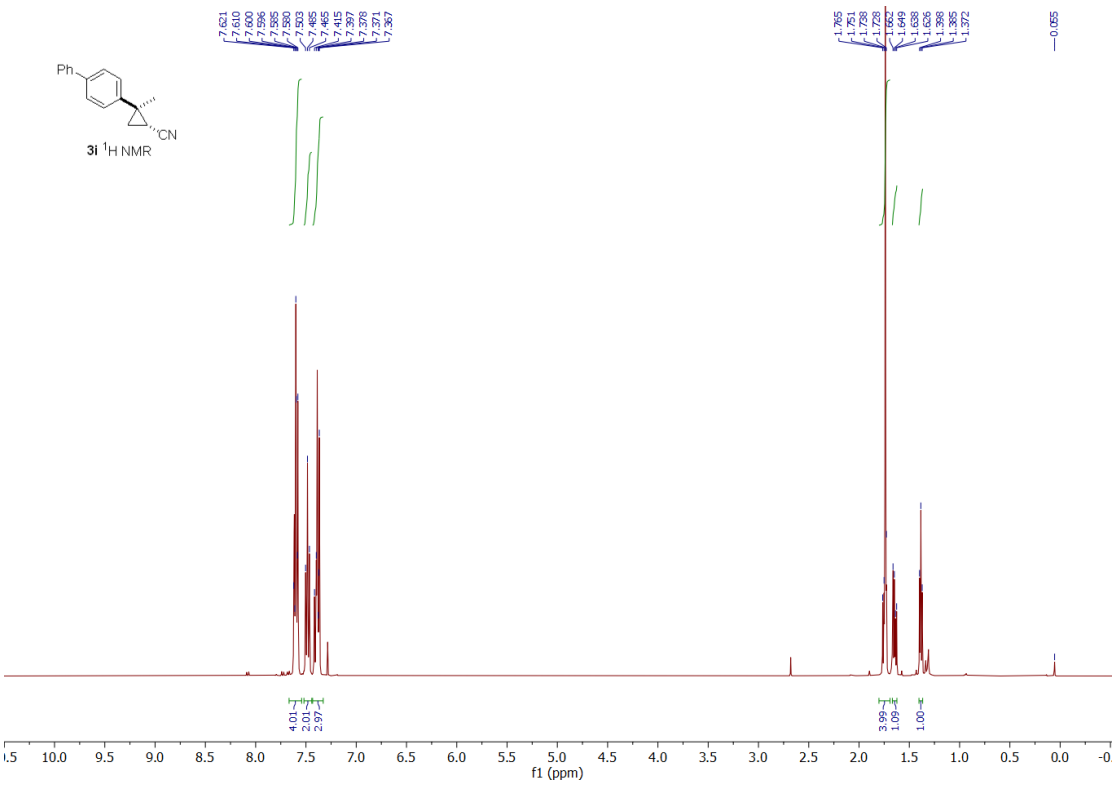
^{1}H NMR Spectra of 3h (400 MHz, Chloroform-*d*)



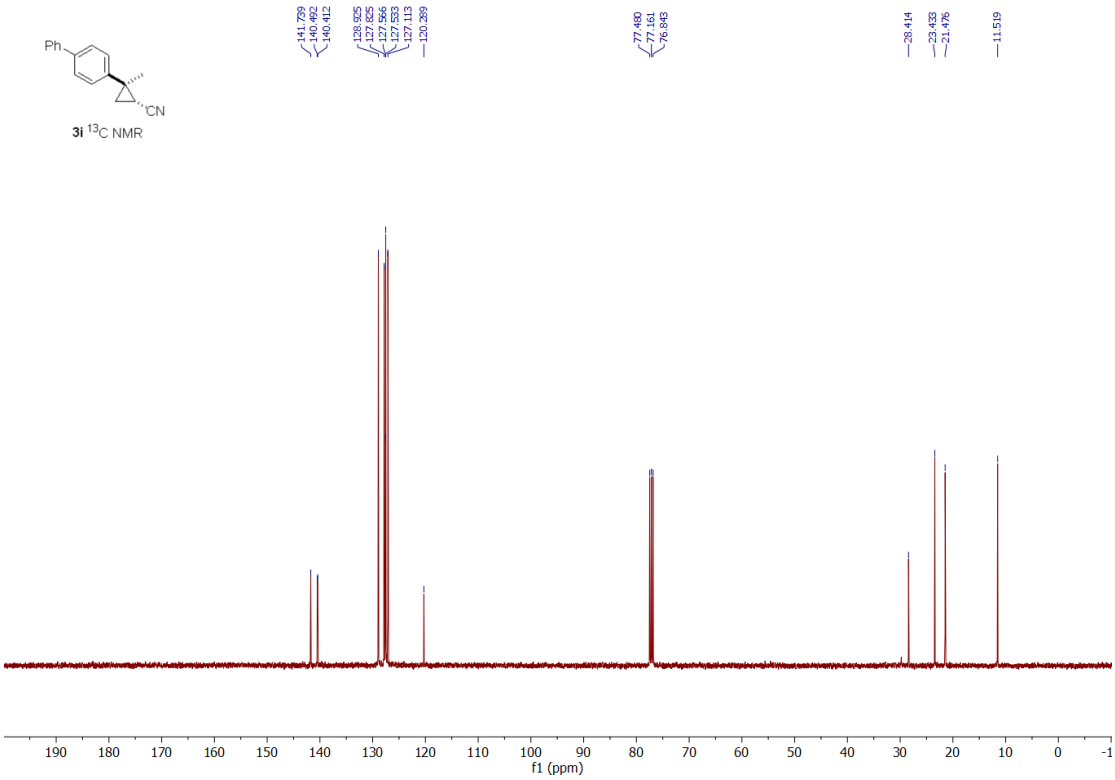
^{13}C NMR Spectra of 3h (100 MHz, Chloroform-*d*)



^{1}H NMR Spectra of 3i (400 MHz, Chloroform-*d*)



^{13}C NMR Spectra of 3i (100 MHz, Chloroform-*d*)



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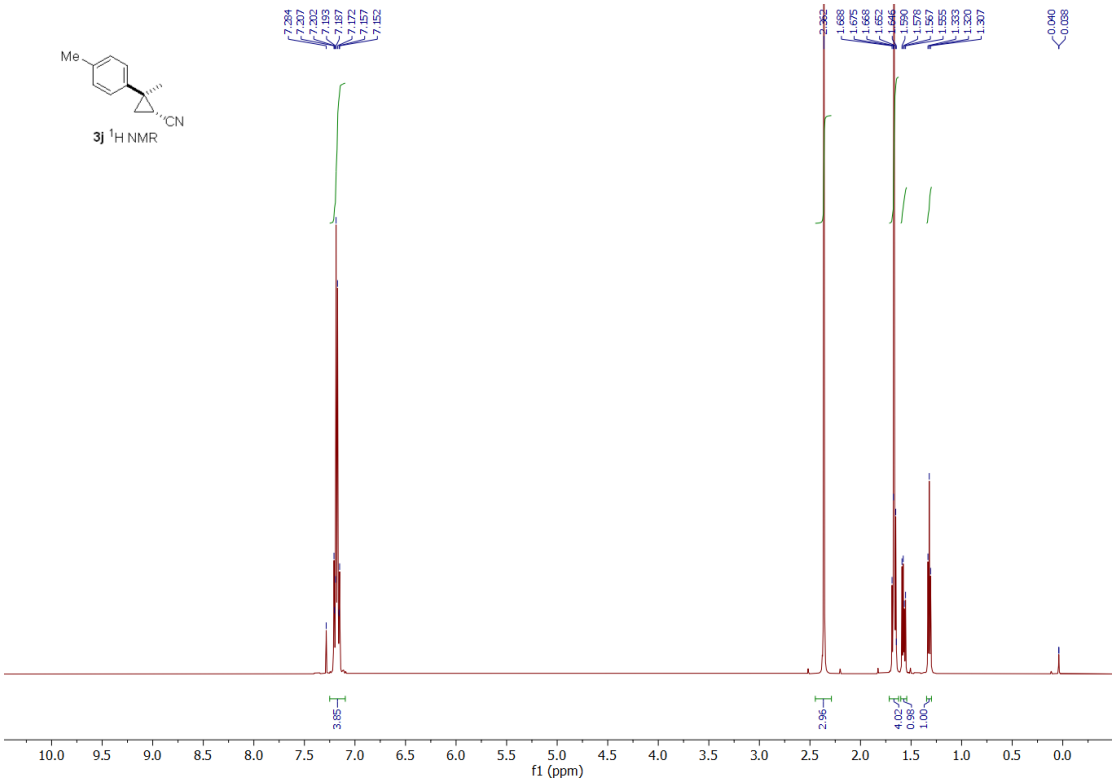
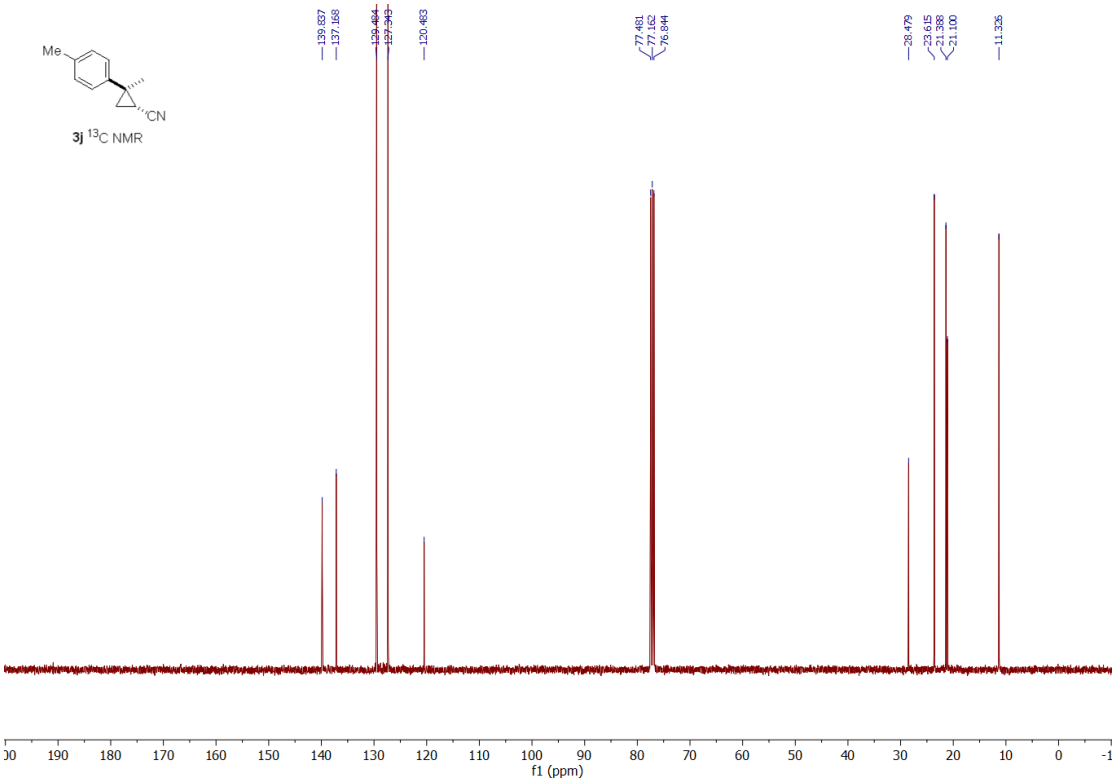
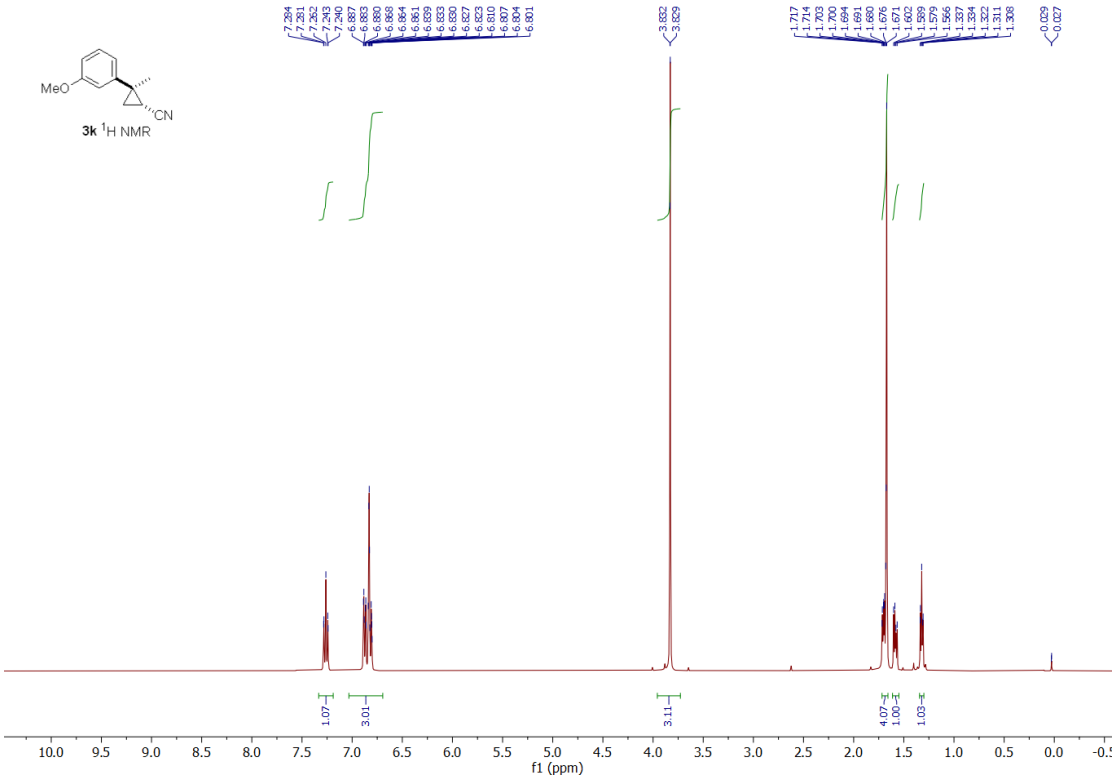


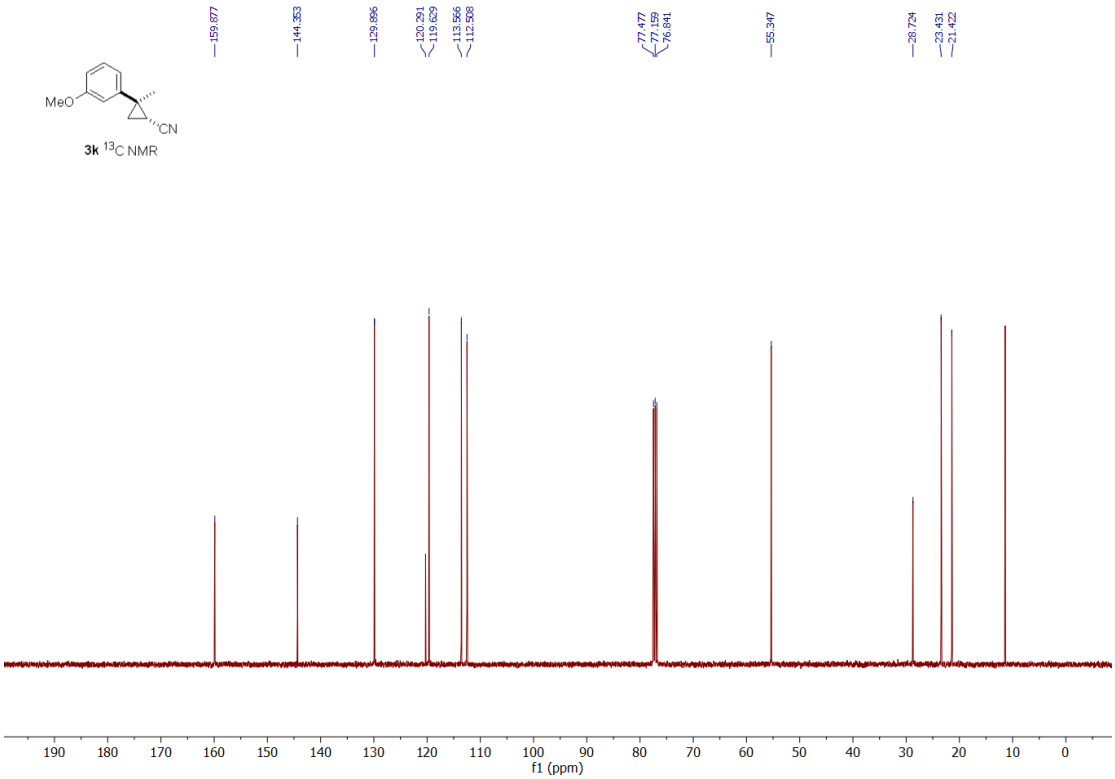
^{13}C NMR Spectra of 3j (100 MHz, Chloroform-*d*)



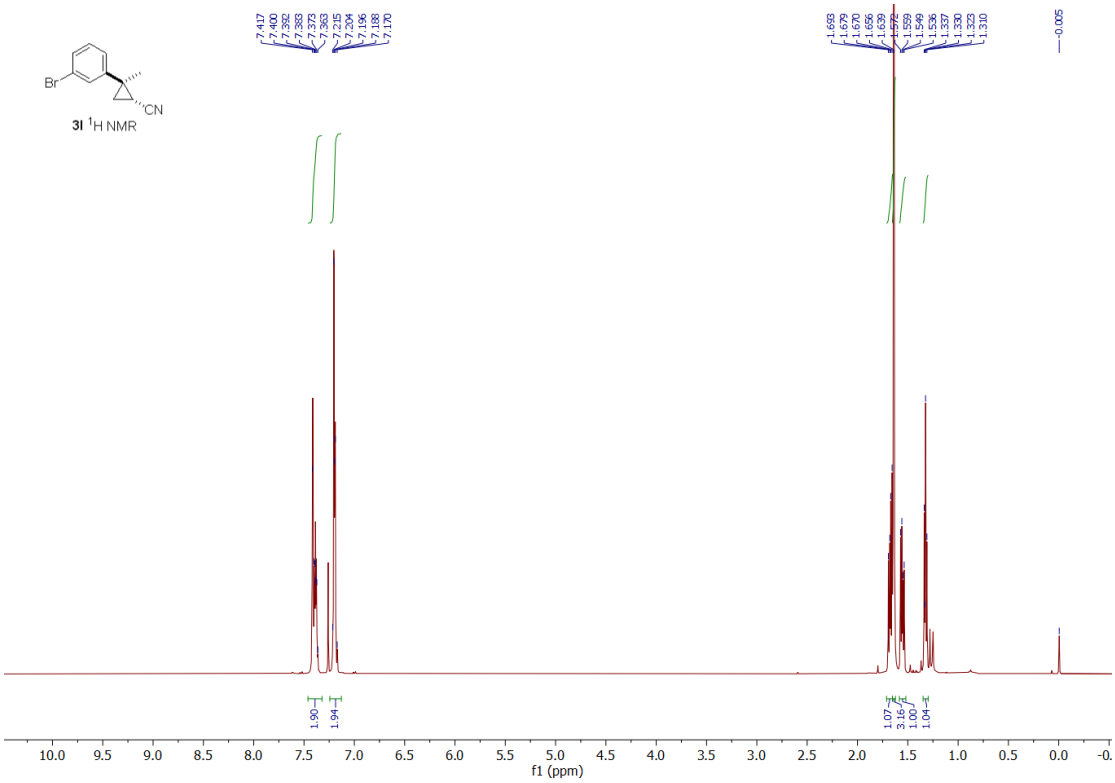
^{1}H NMR Spectra of 3k (400 MHz, Chloroform-*d*)



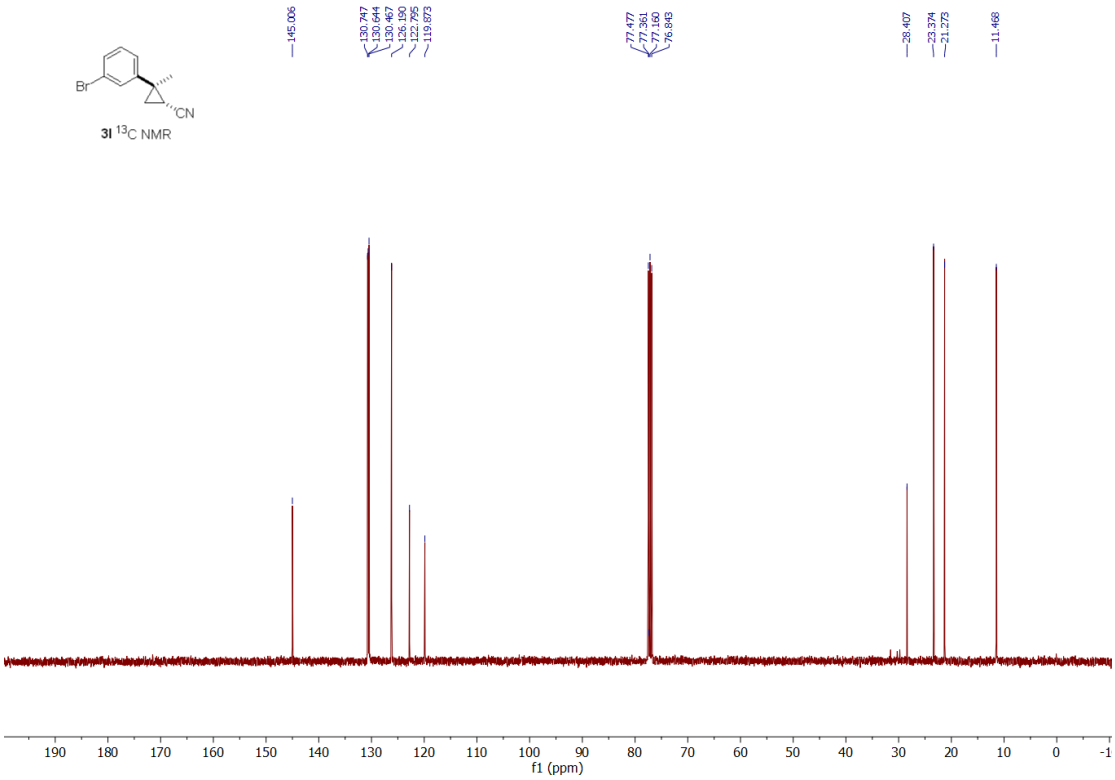
^{13}C NMR Spectra of 3k (100 MHz, Chloroform-*d*)



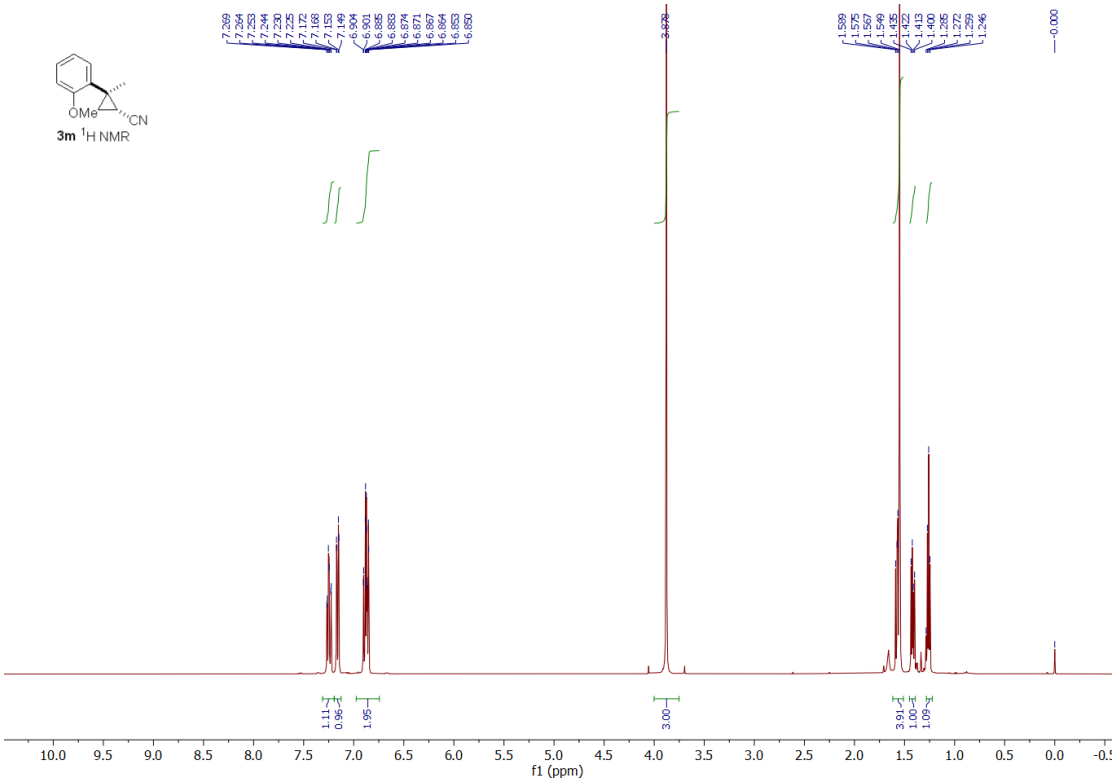
^{1}H NMR Spectra of 3l (400 MHz, Chloroform-*d*)



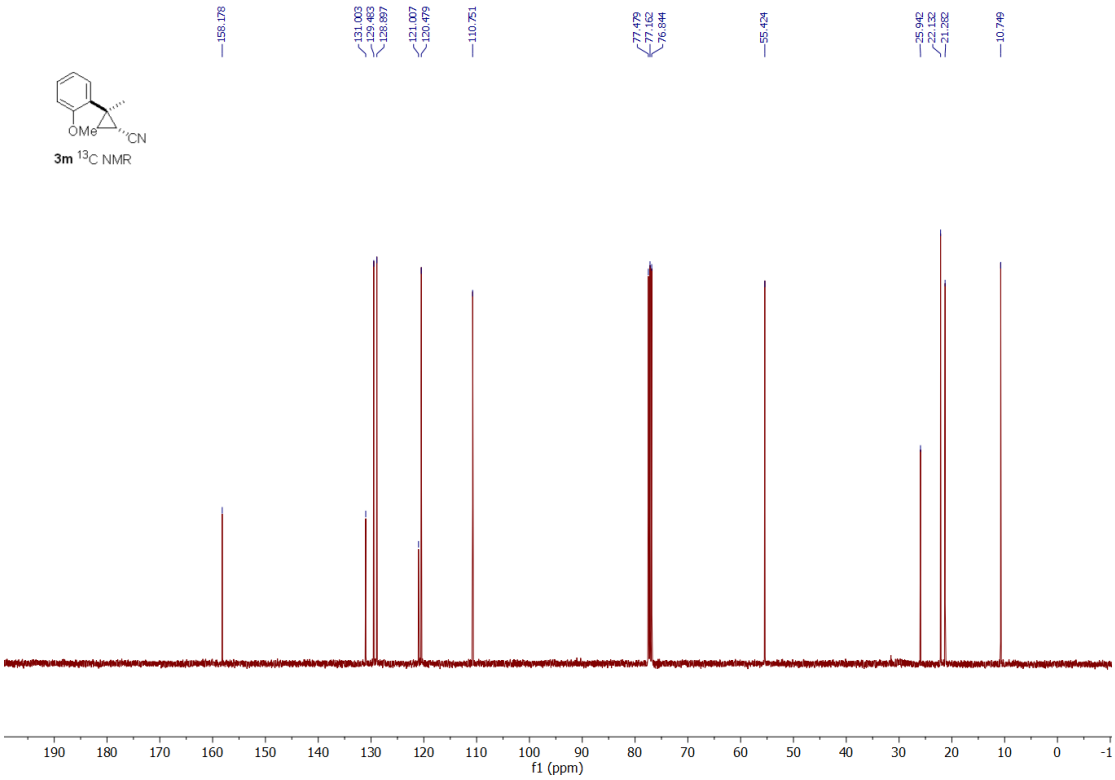
^{13}C NMR Spectra of 3l (100 MHz, Chloroform-*d*)



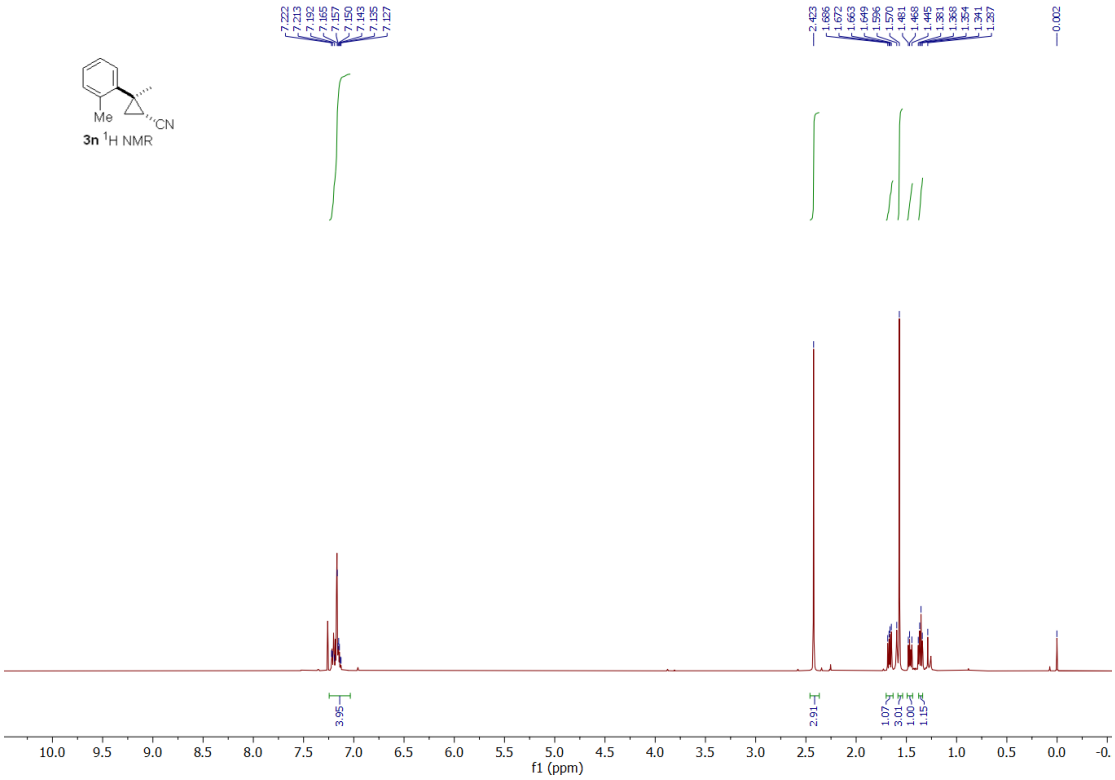
^{1}H NMR Spectra of 3m (400 MHz, Chloroform-*d*)



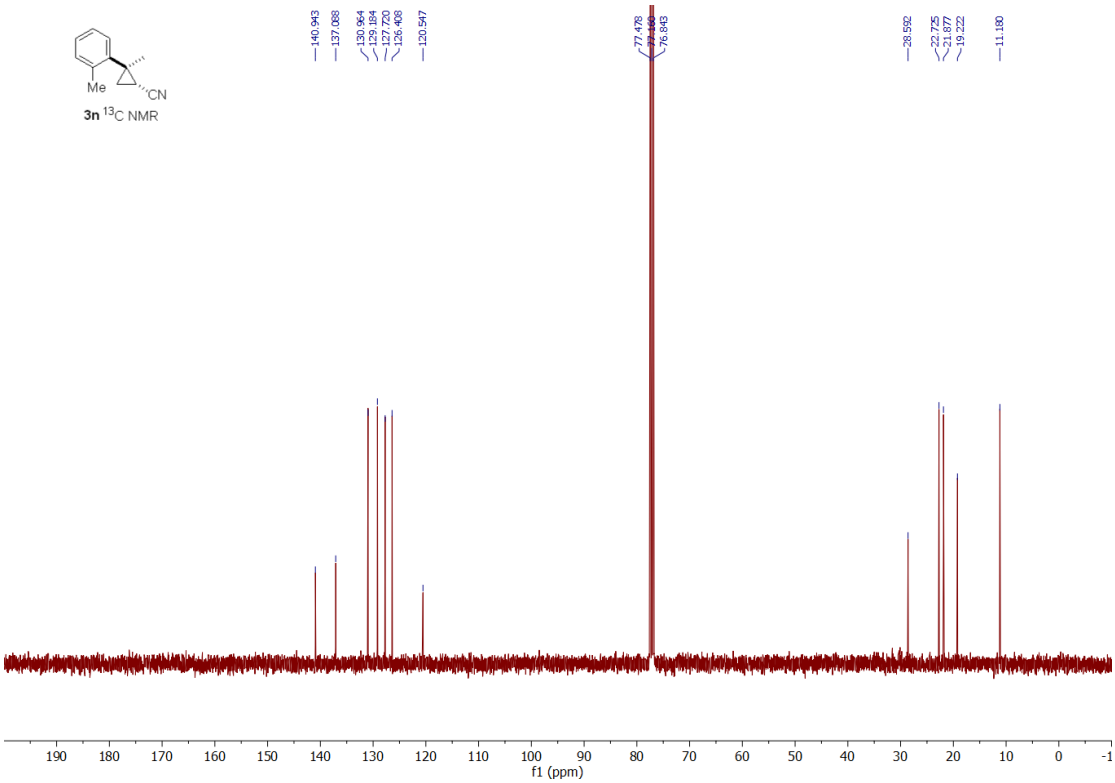
^{13}C NMR Spectra of 3m (100 MHz, Chloroform-*d*)



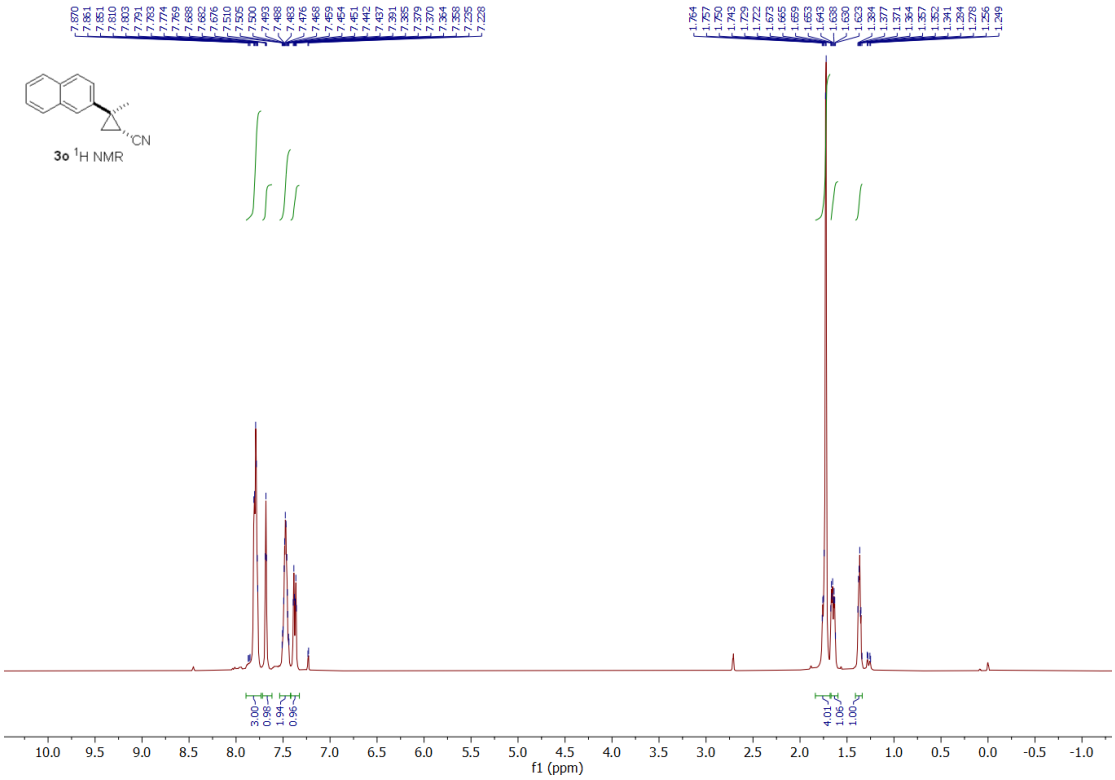
^{1}H NMR Spectra of 3n (400 MHz, Chloroform-*d*)



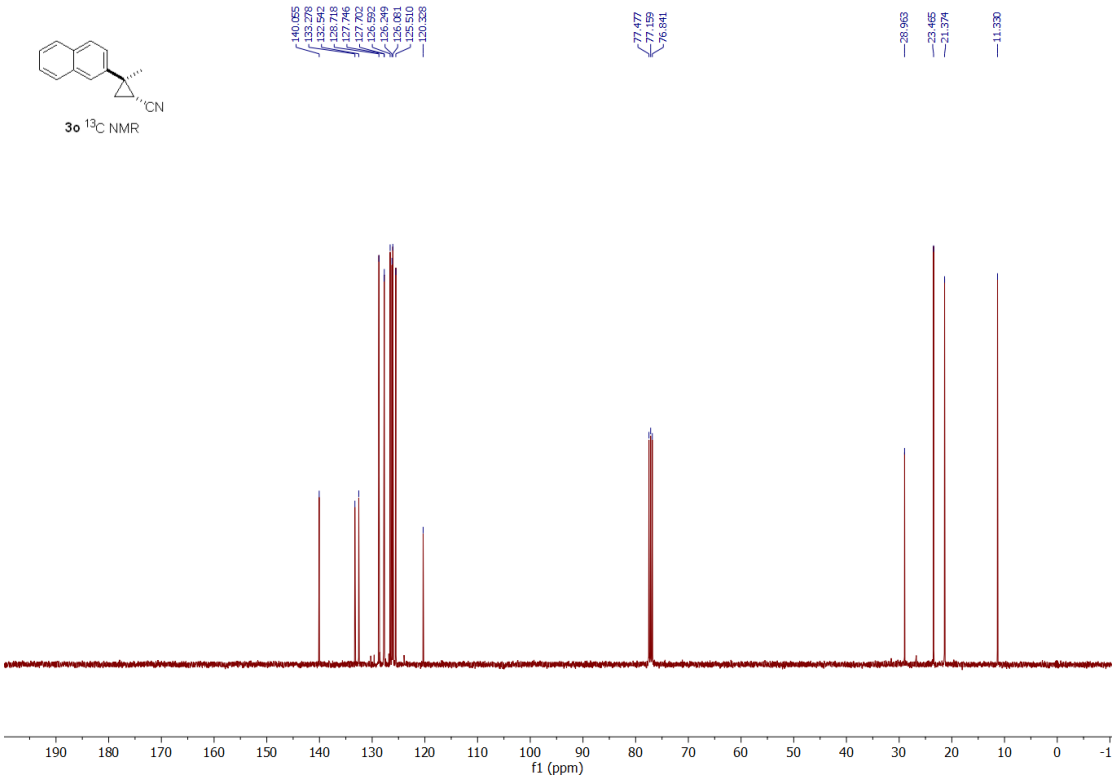
^{13}C NMR Spectra of 3n (100 MHz, Chloroform-*d*)



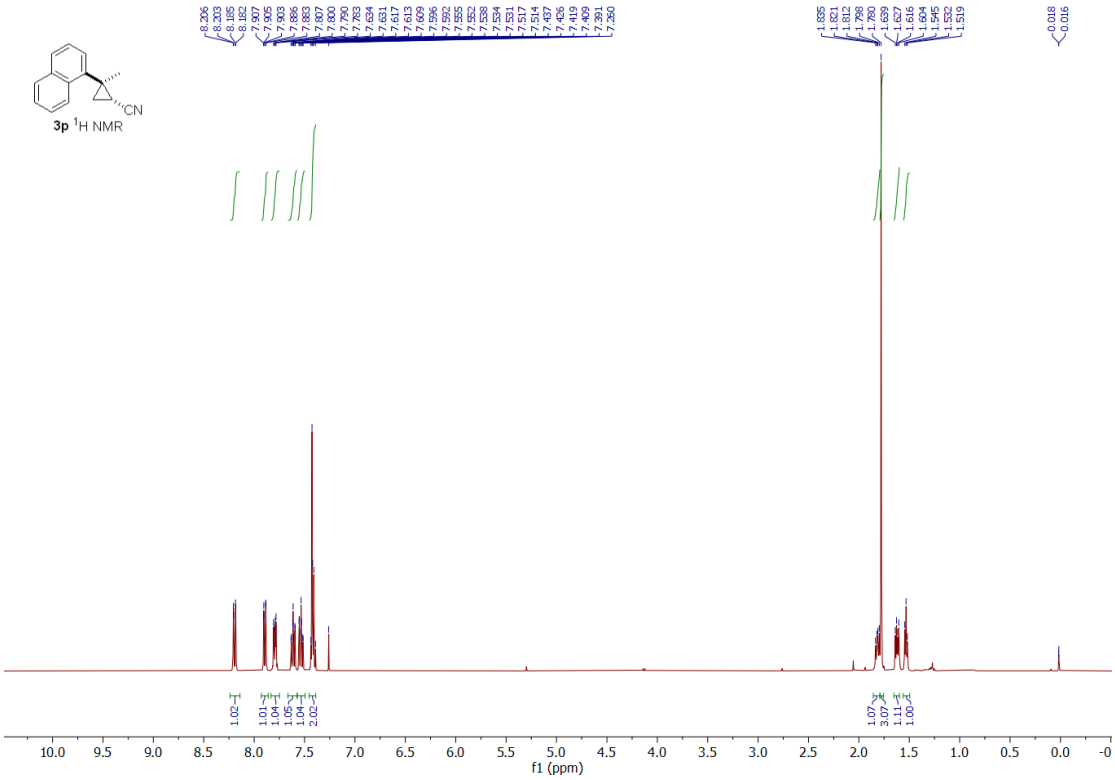
^{1}H NMR Spectra of 3o (400 MHz, Chloroform-*d*)



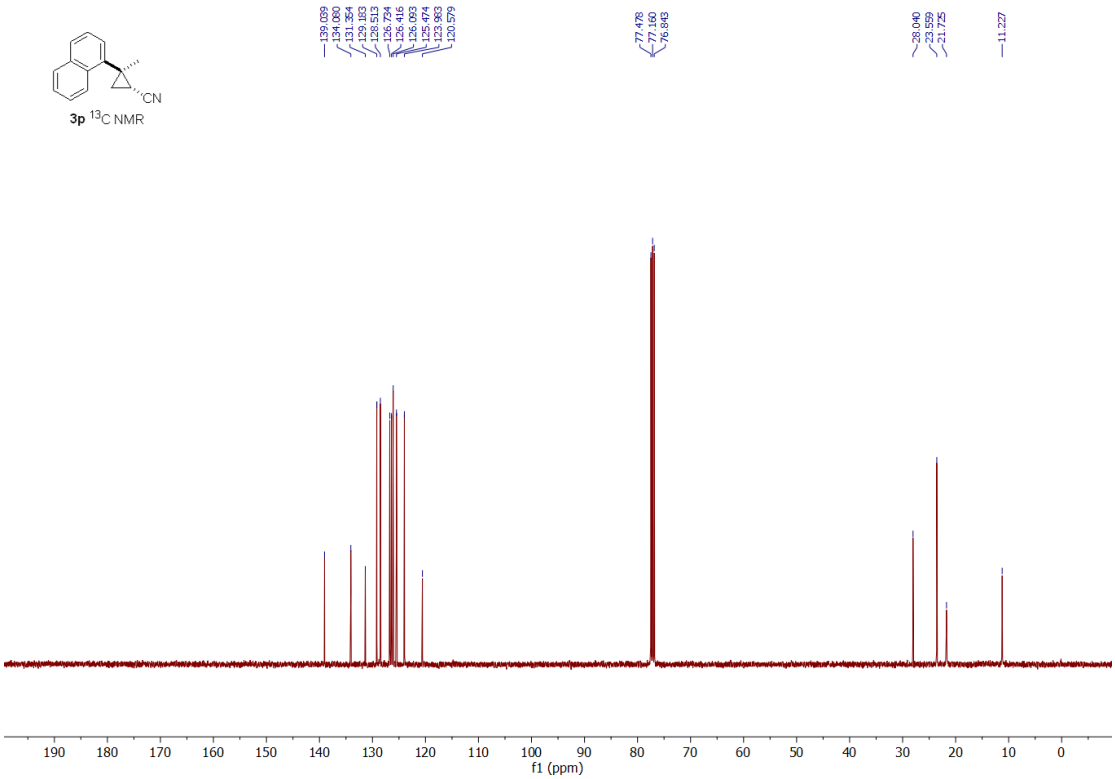
^{13}C NMR Spectra of 3o (100 MHz, Chloroform-*d*)



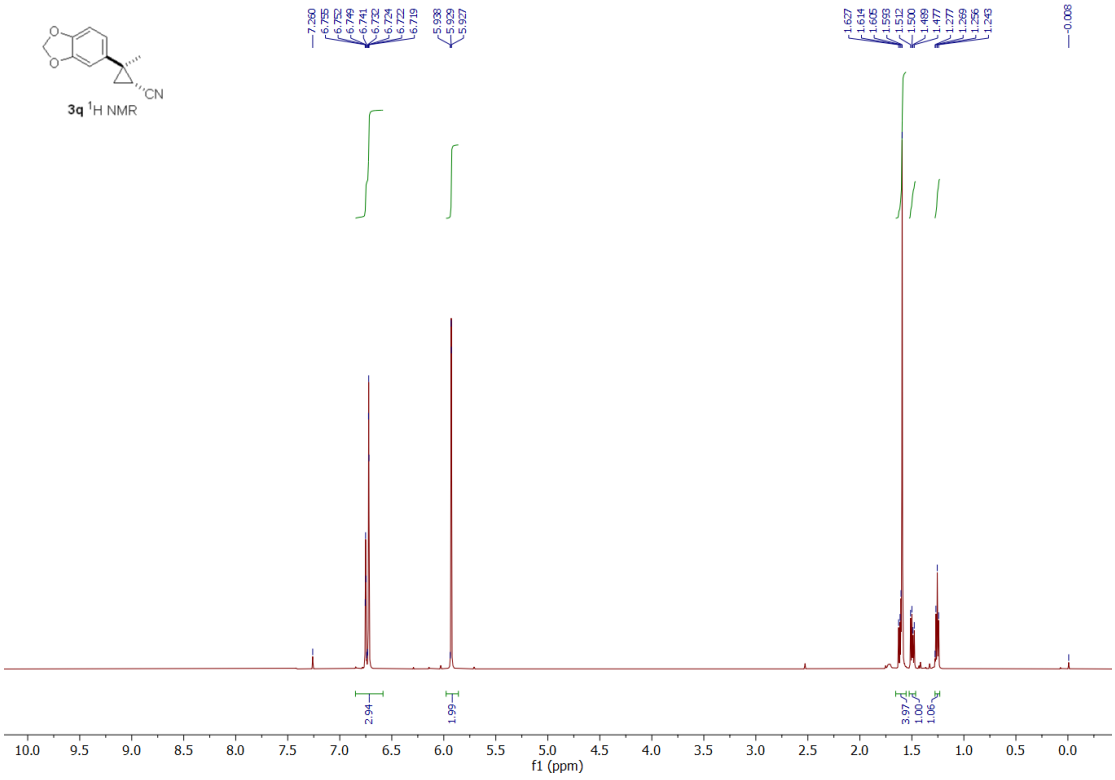
^{1}H NMR Spectra of 3p (400 MHz, Chloroform-*d*)



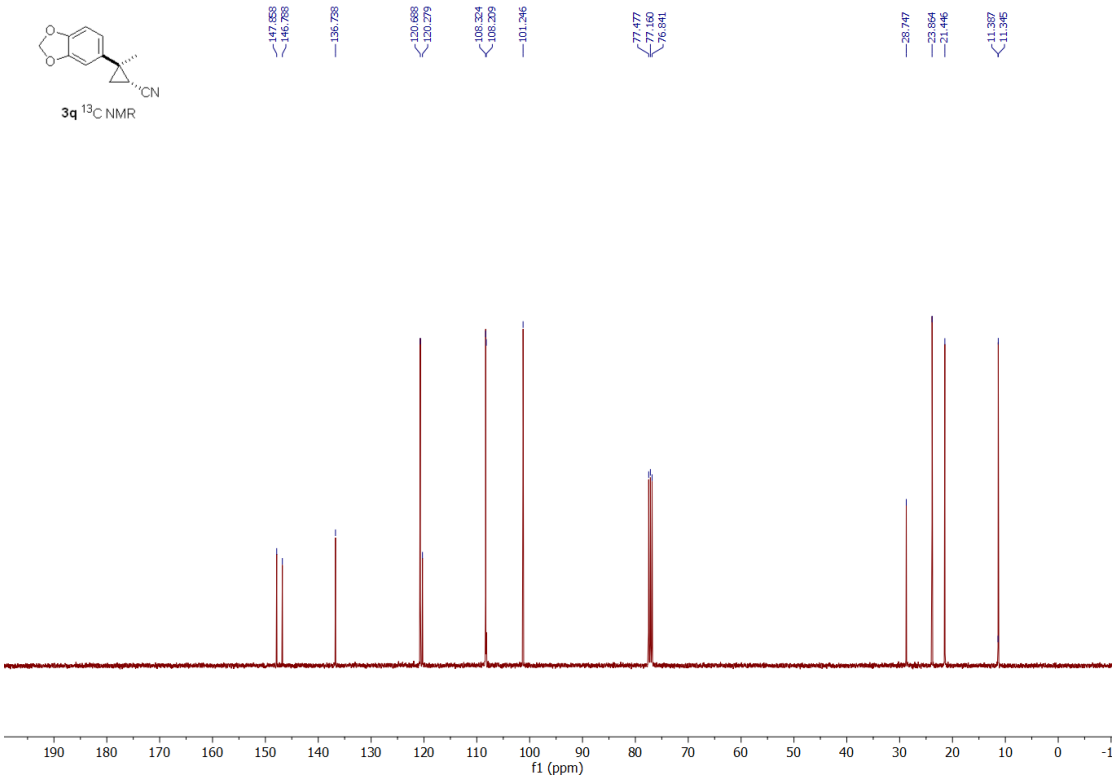
^{13}C NMR Spectra of 3p (100 MHz, Chloroform-*d*)



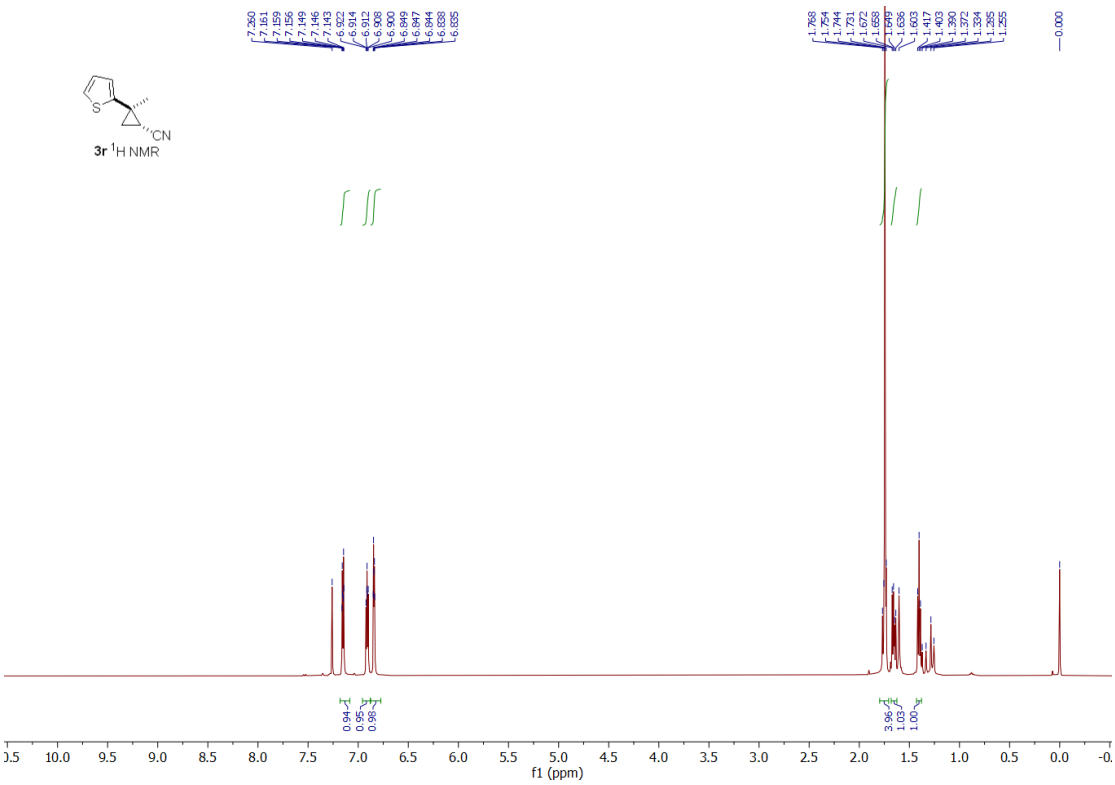
^{1}H NMR Spectra of 3q (400 MHz, Chloroform-*d*)



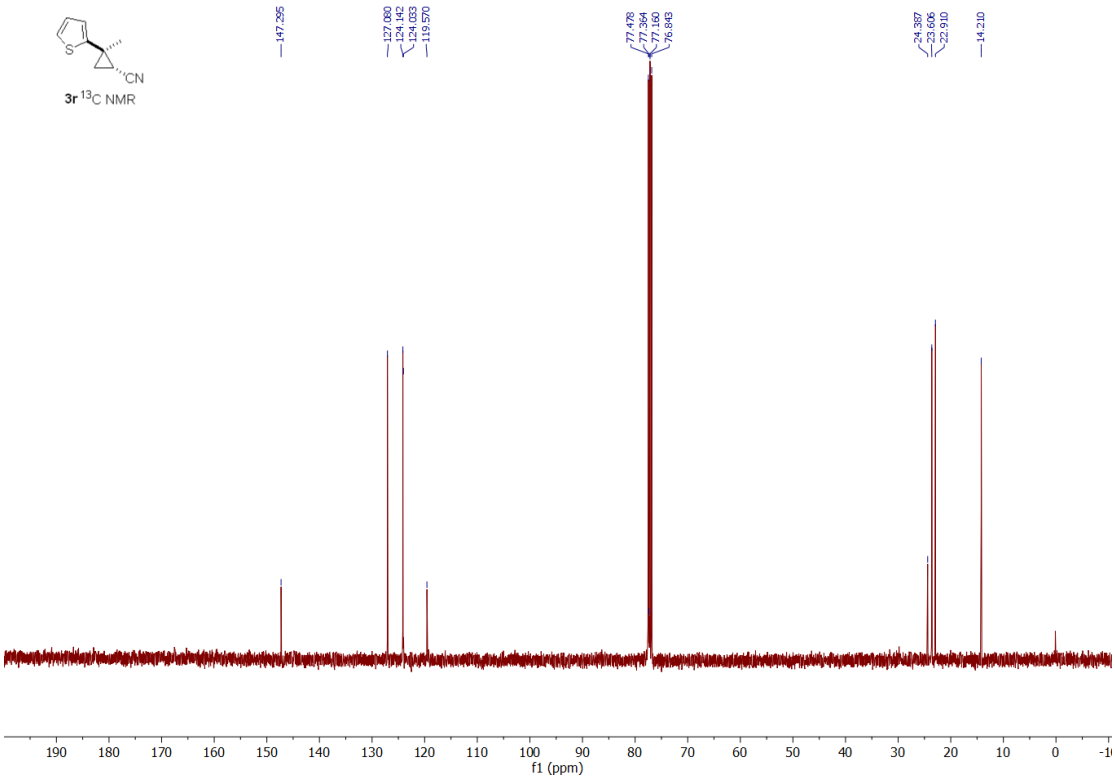
^{13}C NMR Spectra of 3q (100 MHz, Chloroform-*d*)



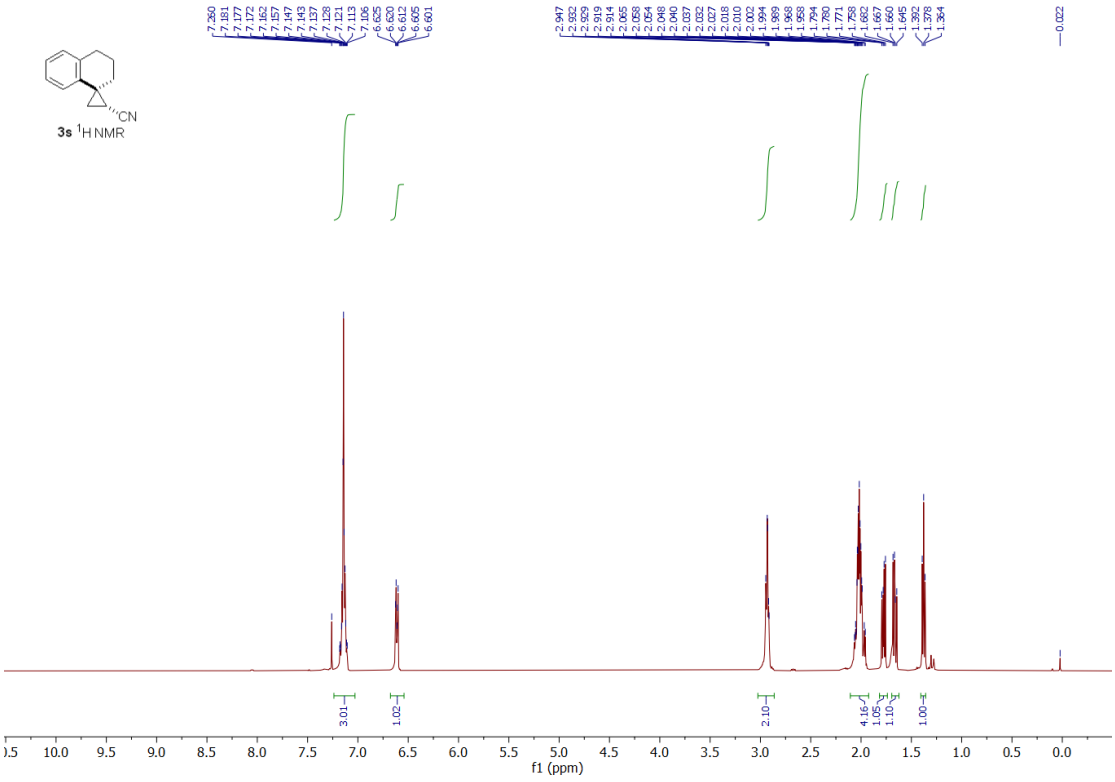
^{1}H NMR Spectra of 3r (400 MHz, Chloroform-*d*)



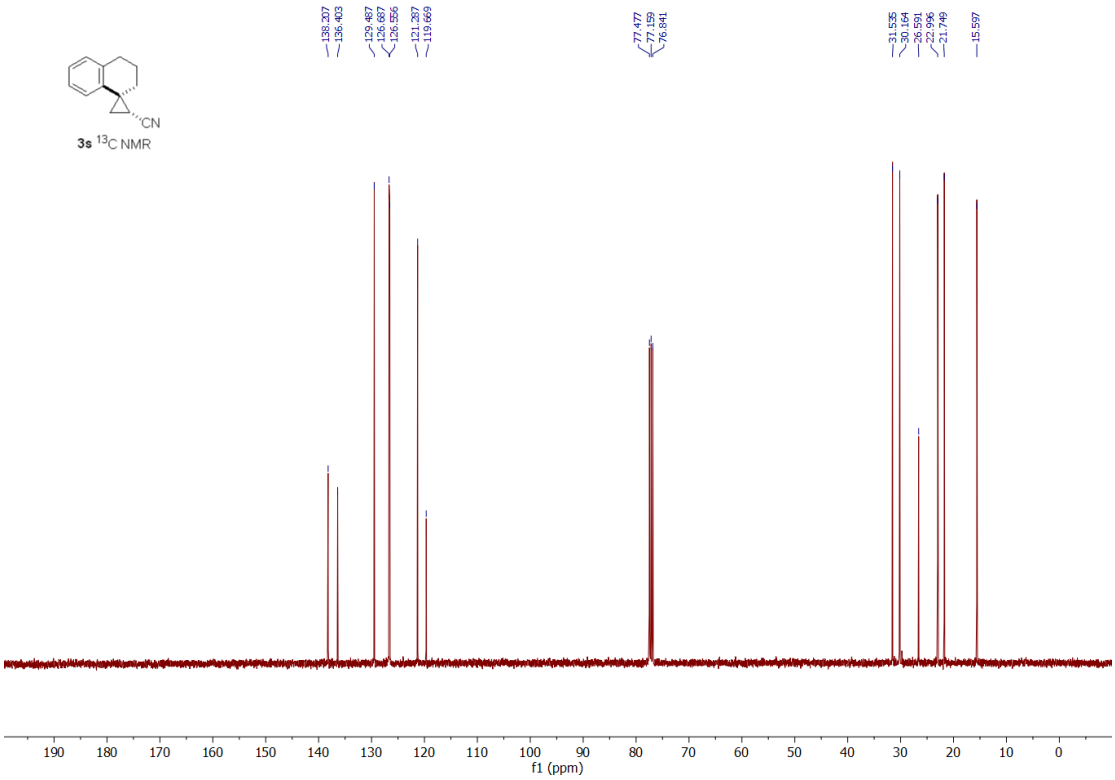
^{13}C NMR Spectra of 3r (100 MHz, Chloroform-*d*)



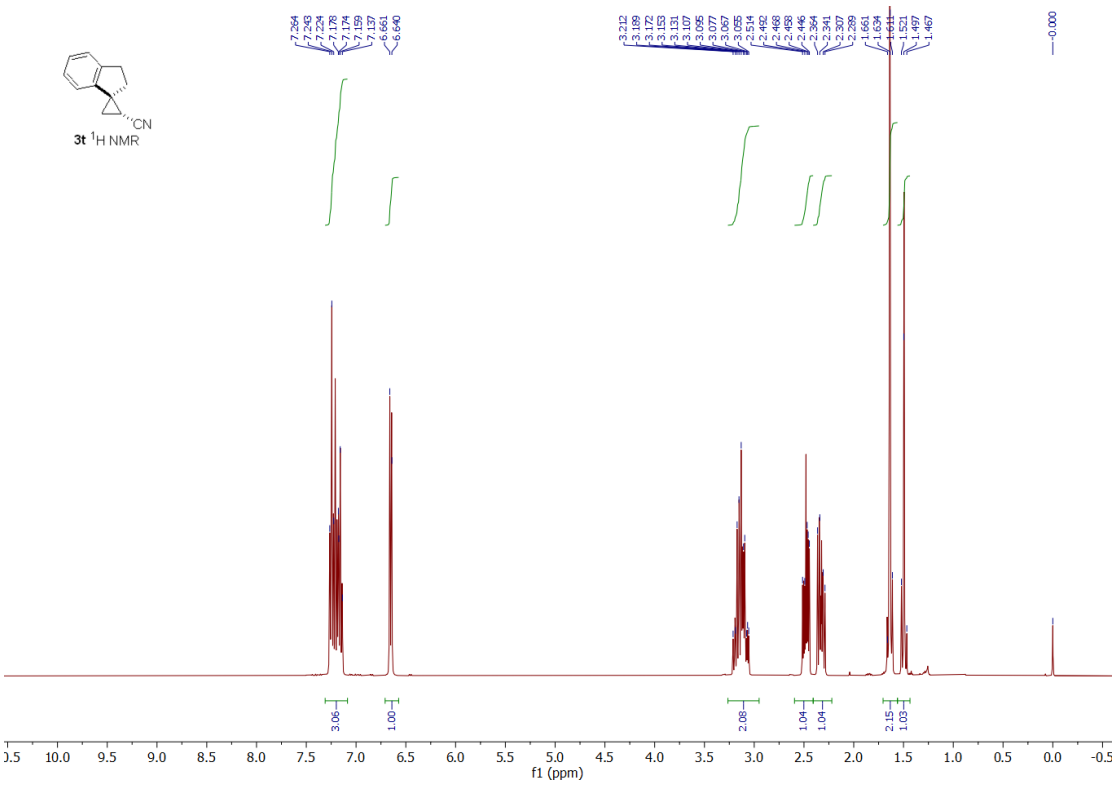
^{1}H NMR Spectra of 3s (400 MHz, Chloroform-*d*)



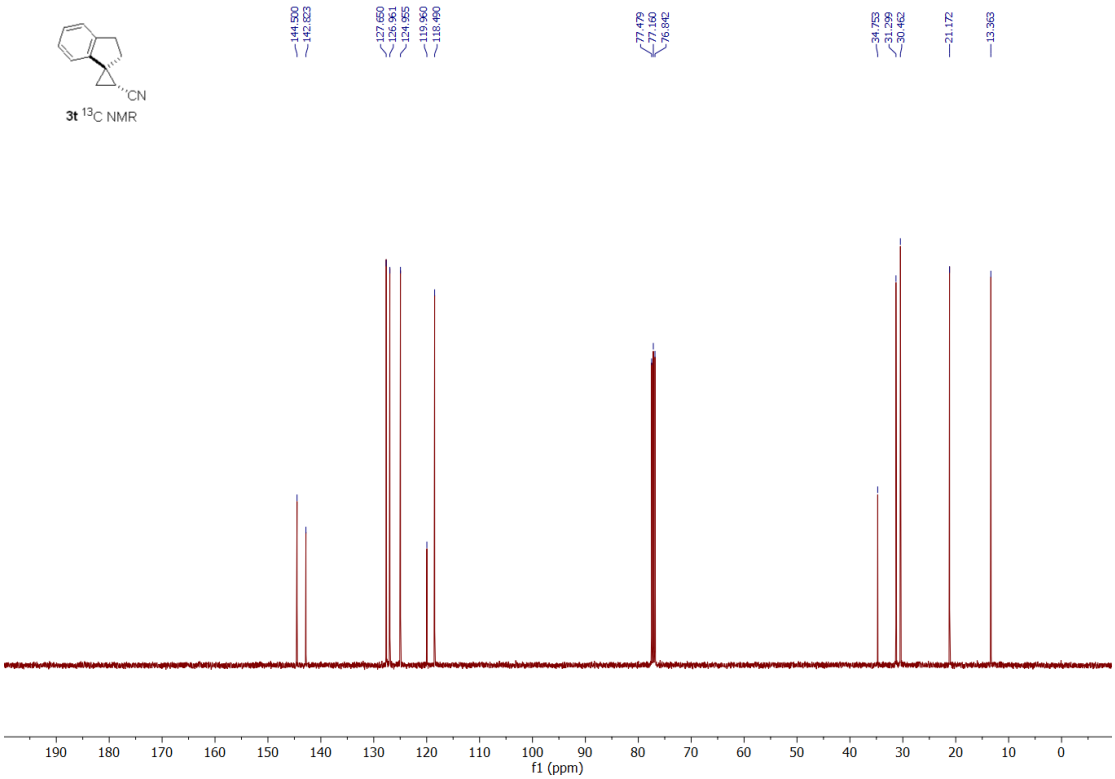
^{13}C NMR Spectra of 3s (100 MHz, Chloroform-*d*)



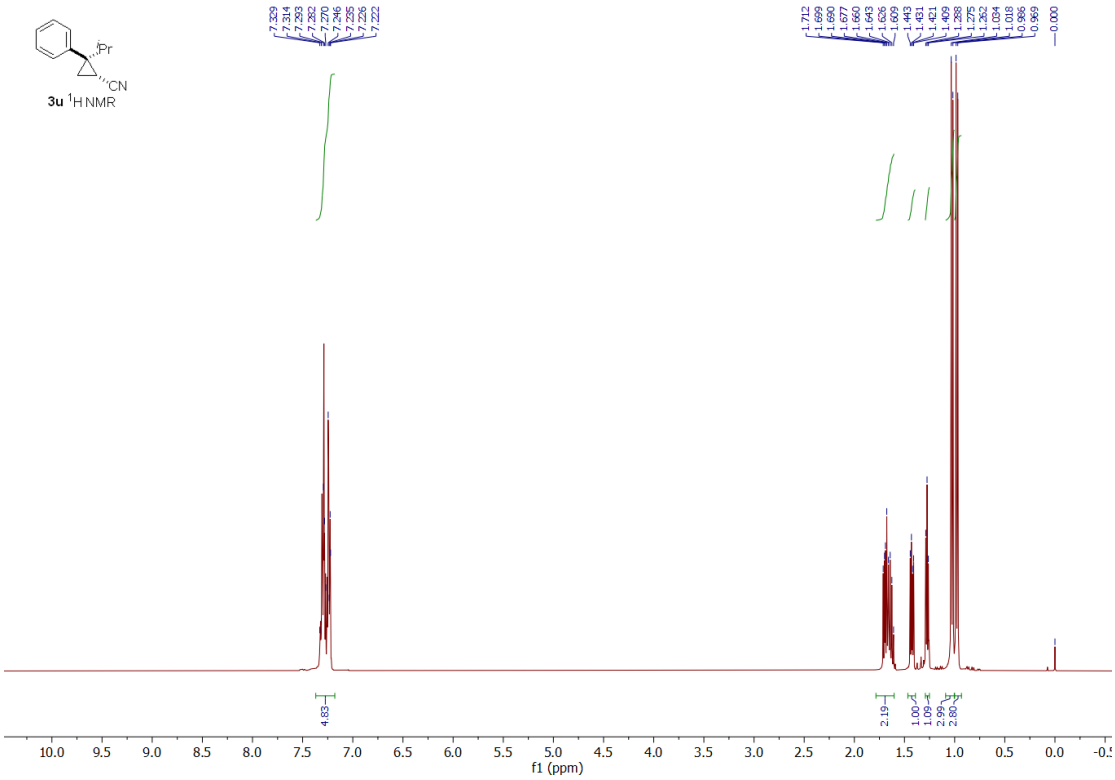
^{1}H NMR Spectra of 3t (400 MHz, Chloroform-*d*)



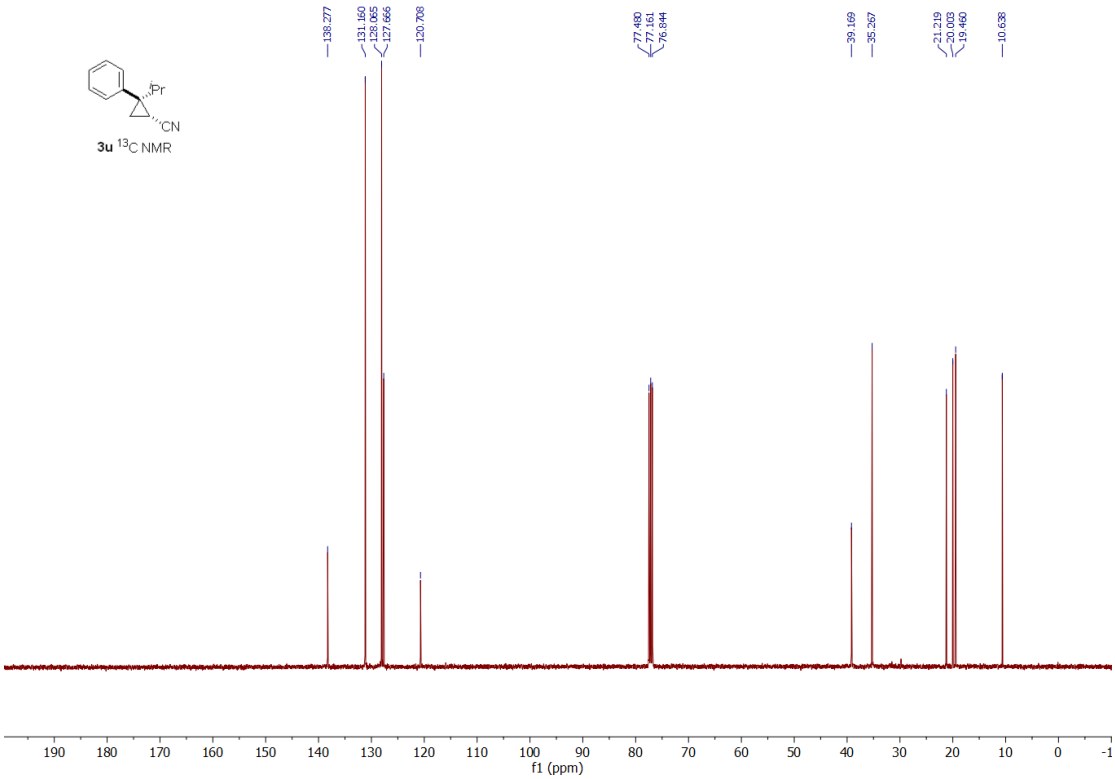
^{13}C NMR Spectra of 3t (100 MHz, Chloroform-*d*)



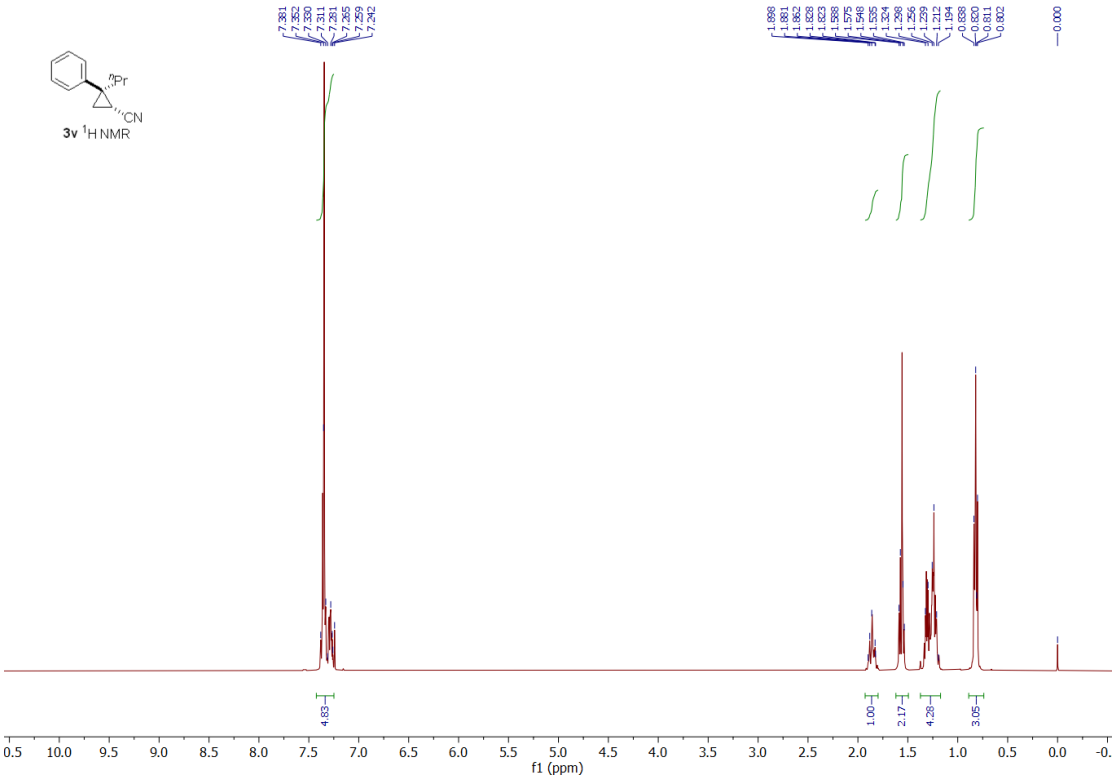
^{1}H NMR Spectra of 3u (400 MHz, Chloroform-*d*)



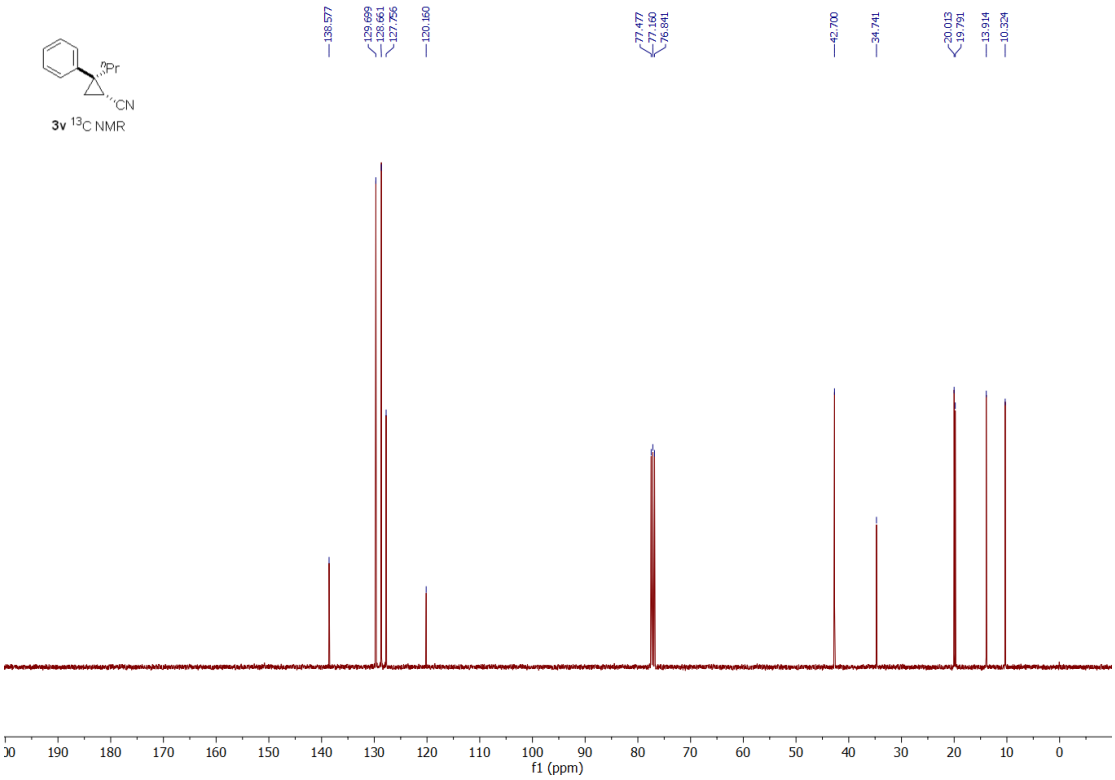
^{13}C NMR Spectra of 3u (100 MHz, Chloroform-*d*)



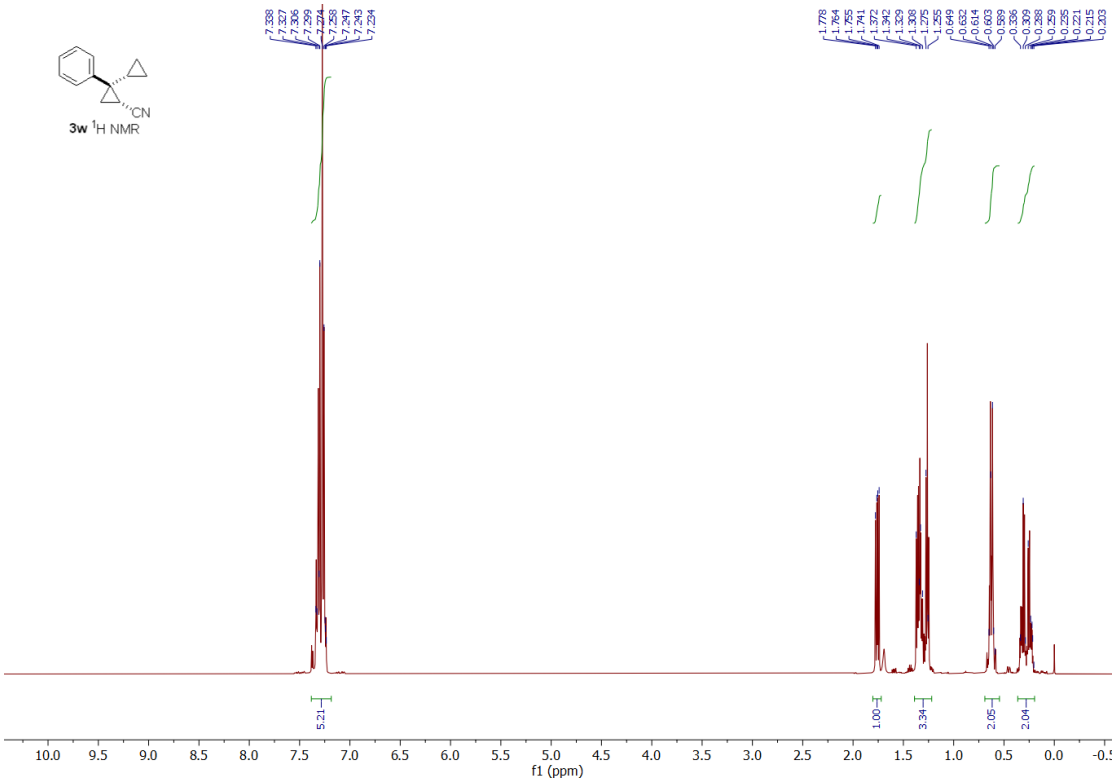
^{1}H NMR Spectra of 3v (400 MHz, Chloroform-*d*)



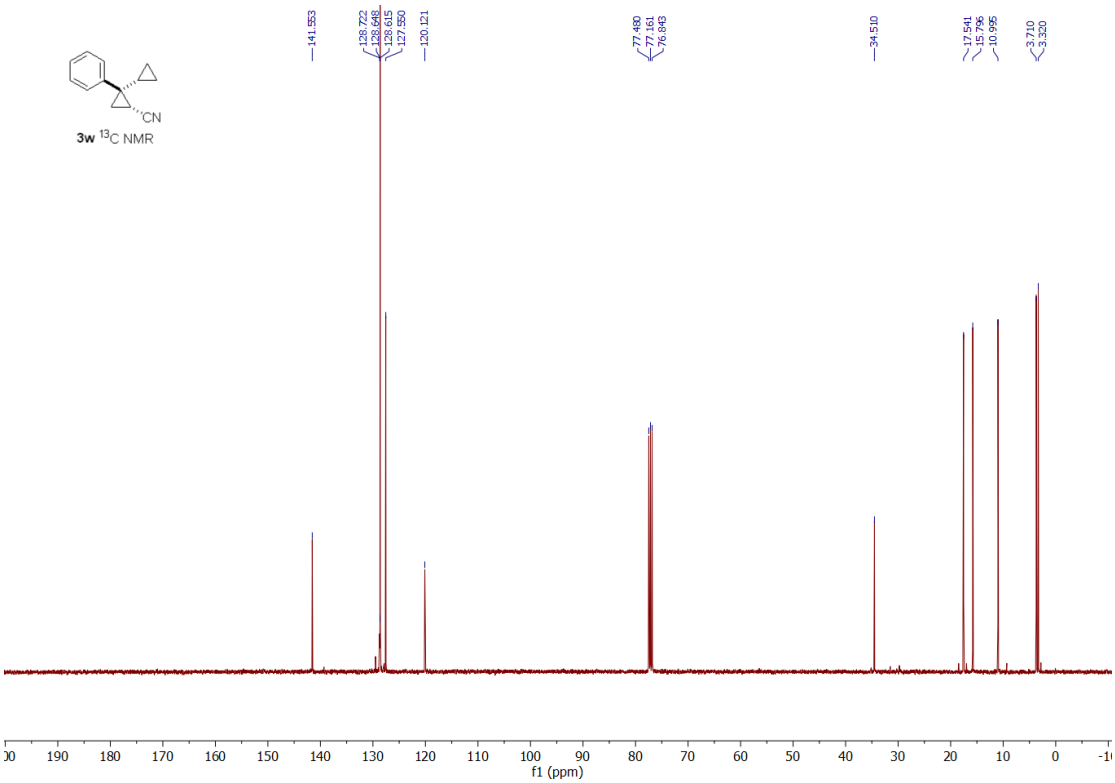
^{13}C NMR Spectra of 3v (100 MHz, Chloroform-*d*)



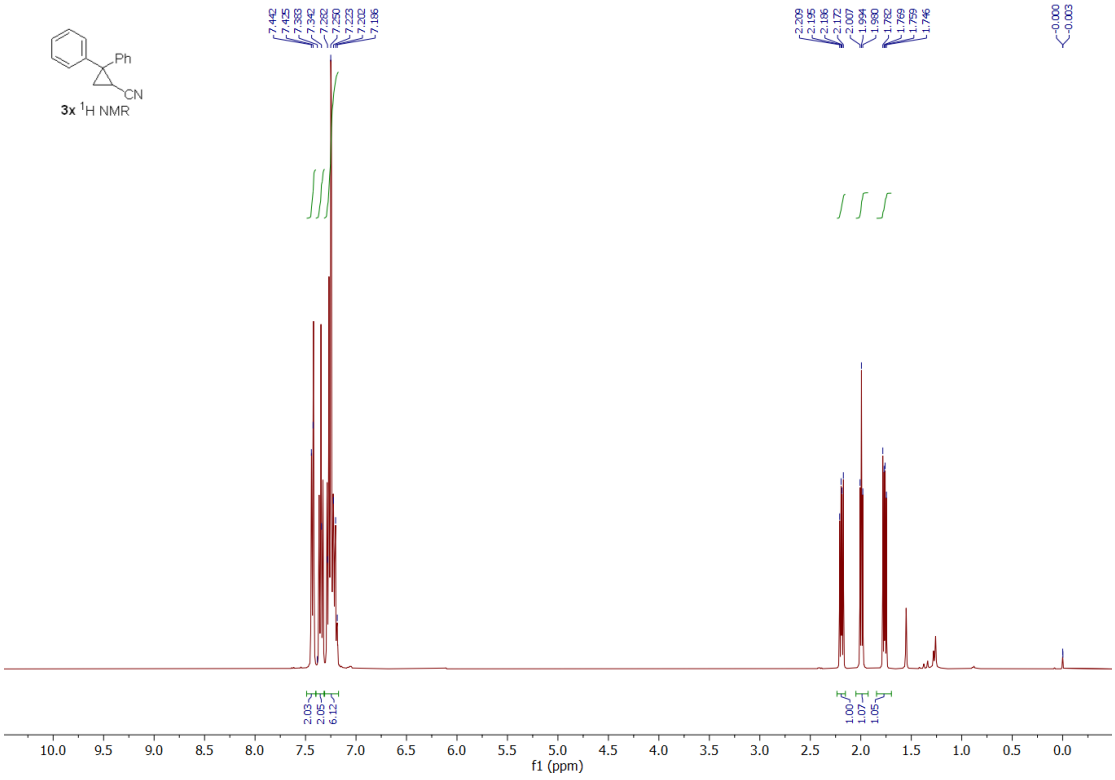
^{1}H NMR Spectra of 3w (400 MHz, Chloroform-*d*)



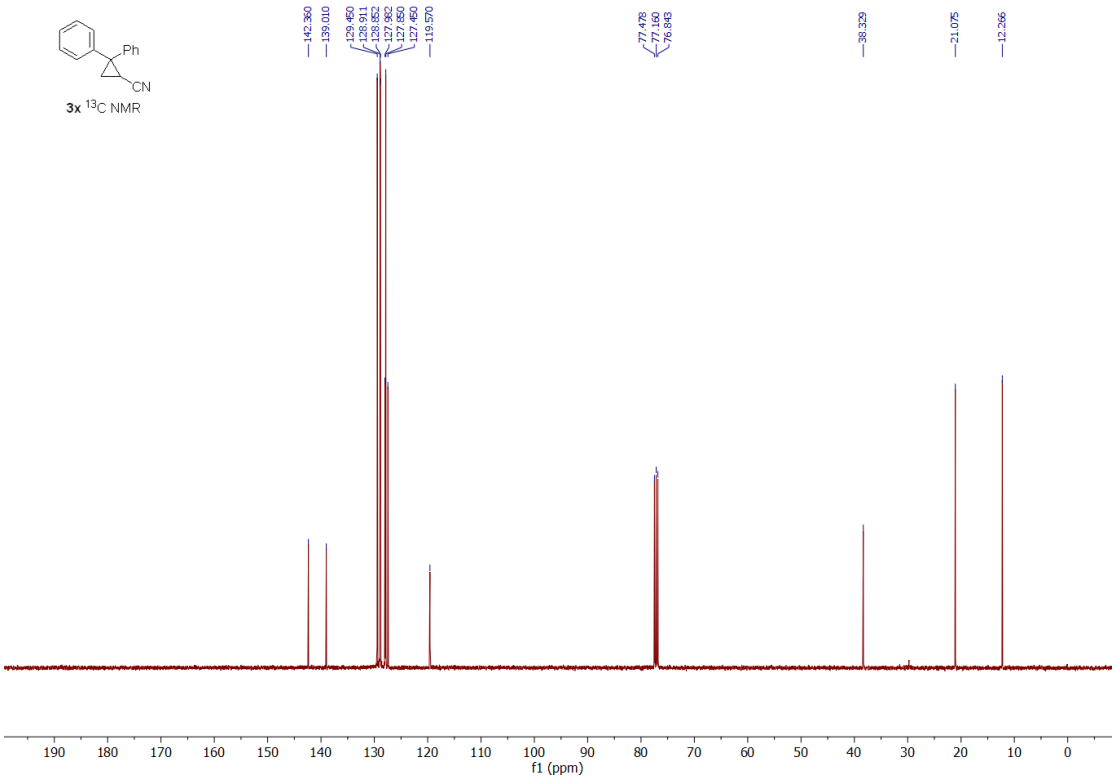
^{13}C NMR Spectra of 3w (100 MHz, Chloroform-*d*)



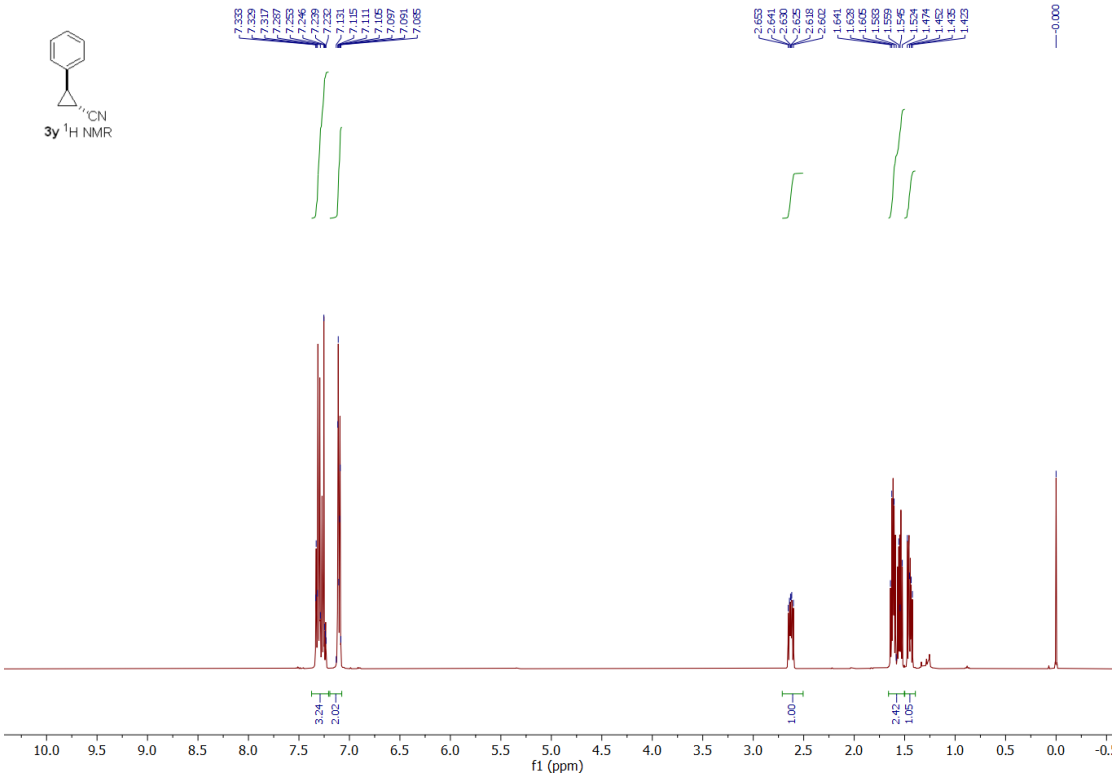
^{1}H NMR Spectra of 3x (400 MHz, Chloroform-*d*)



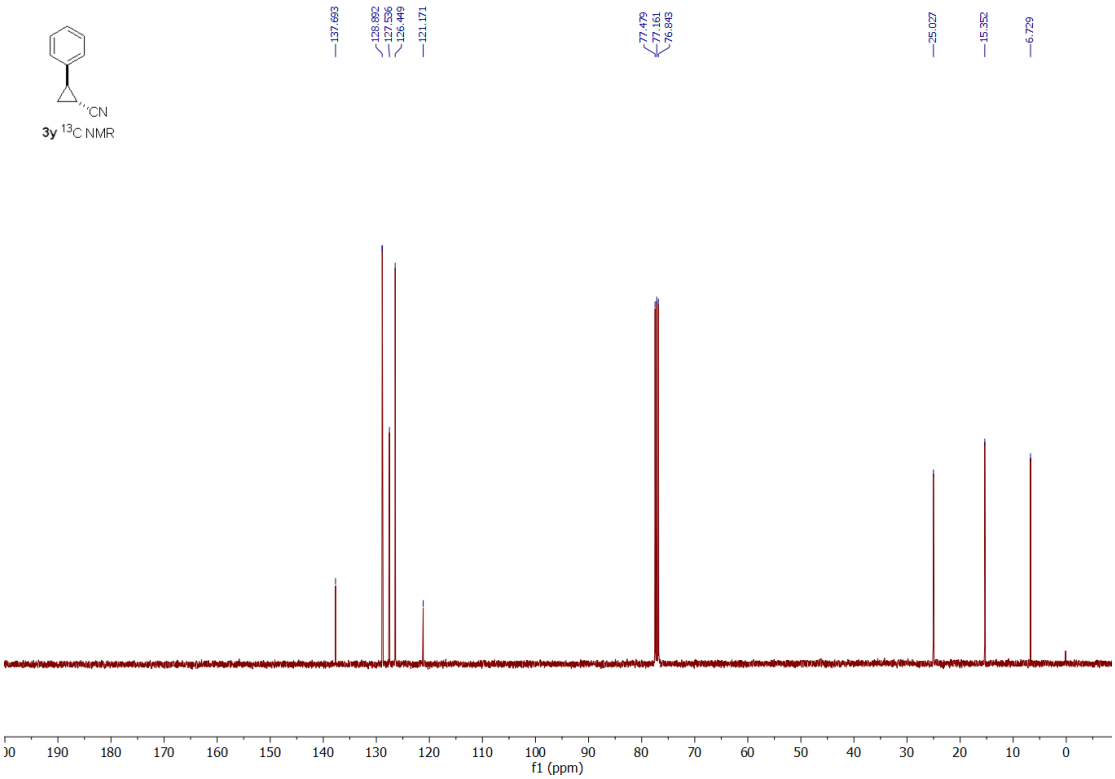
^{13}C NMR Spectra of 3x (100 MHz, Chloroform-*d*)



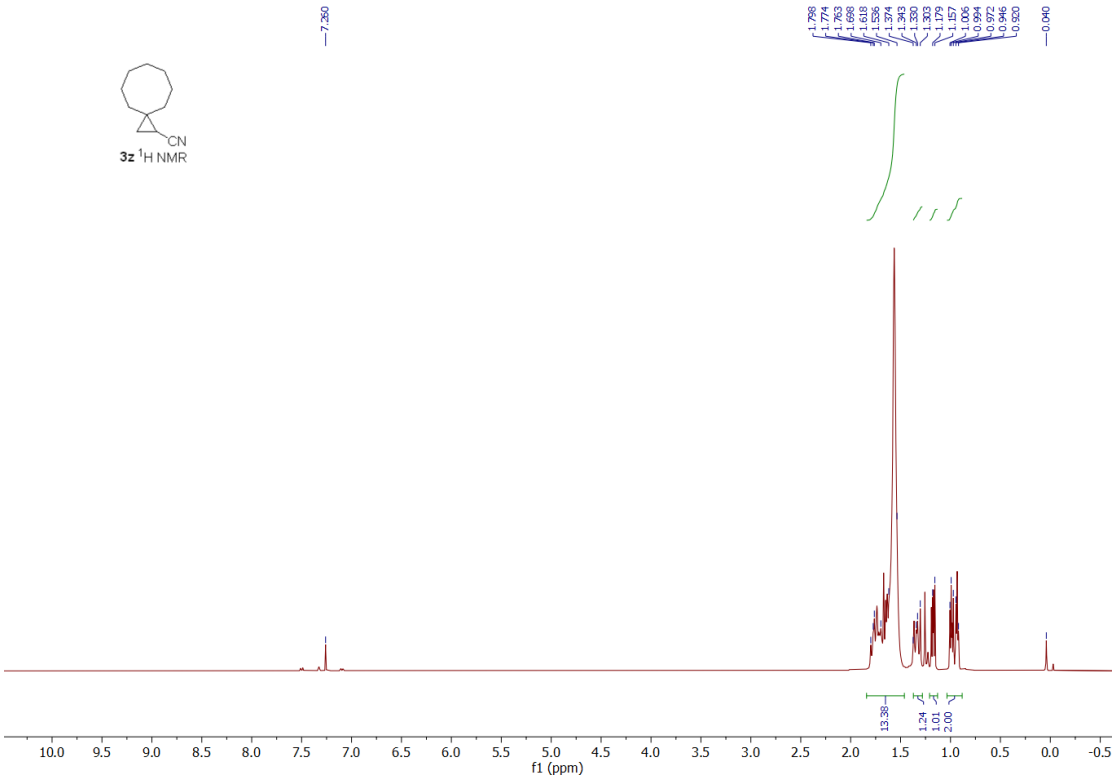
^{1}H NMR Spectra of 3y (400 MHz, Chloroform-*d*)



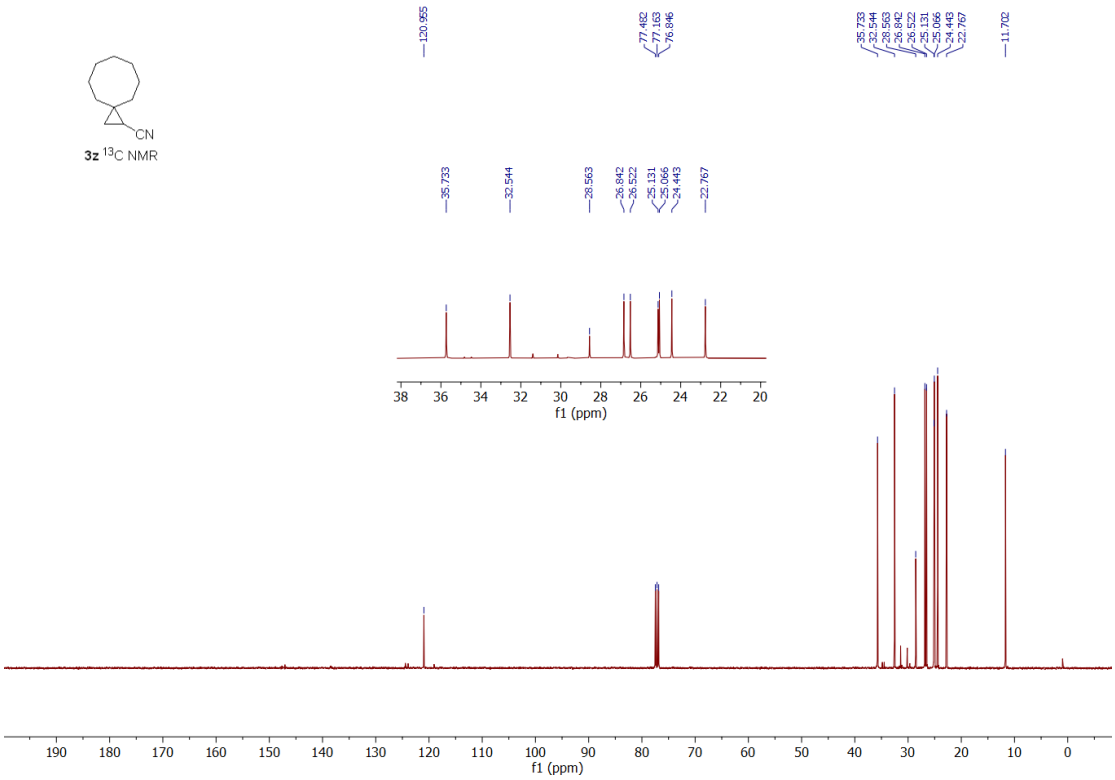
^{13}C NMR Spectra of 3y (100 MHz, Chloroform-*d*)



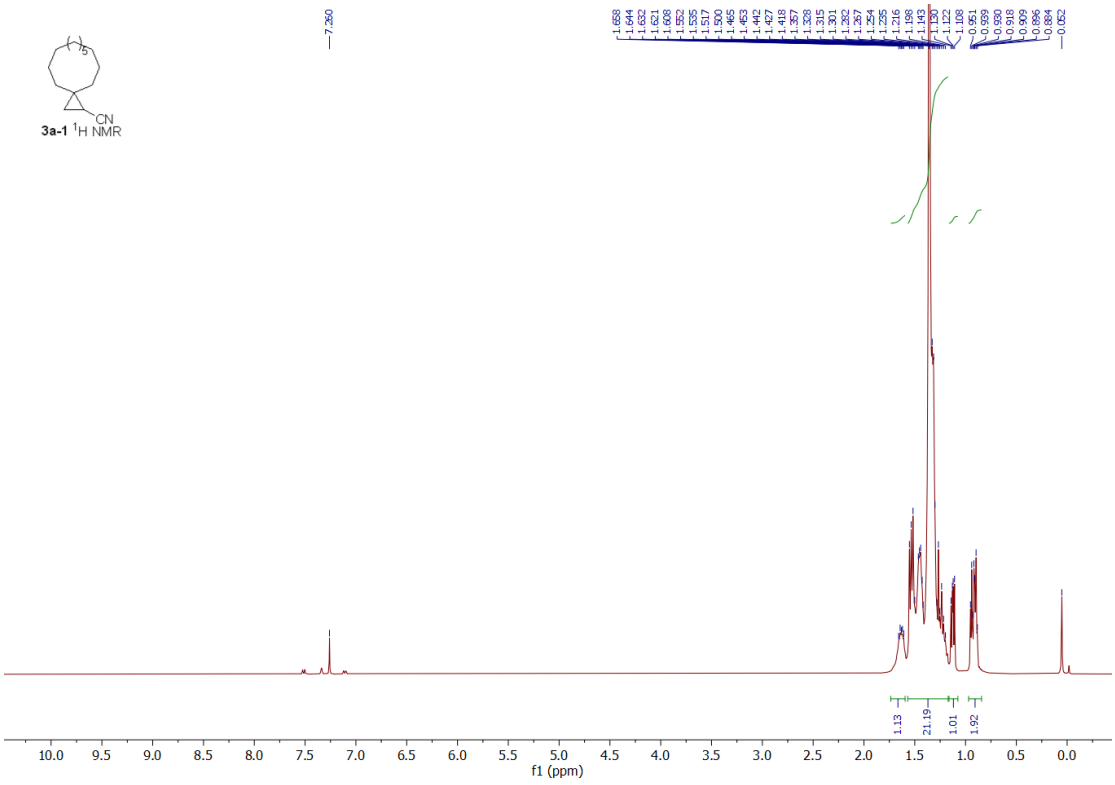
^{1}H NMR Spectra of 3z (400 MHz, Chloroform-*d*)



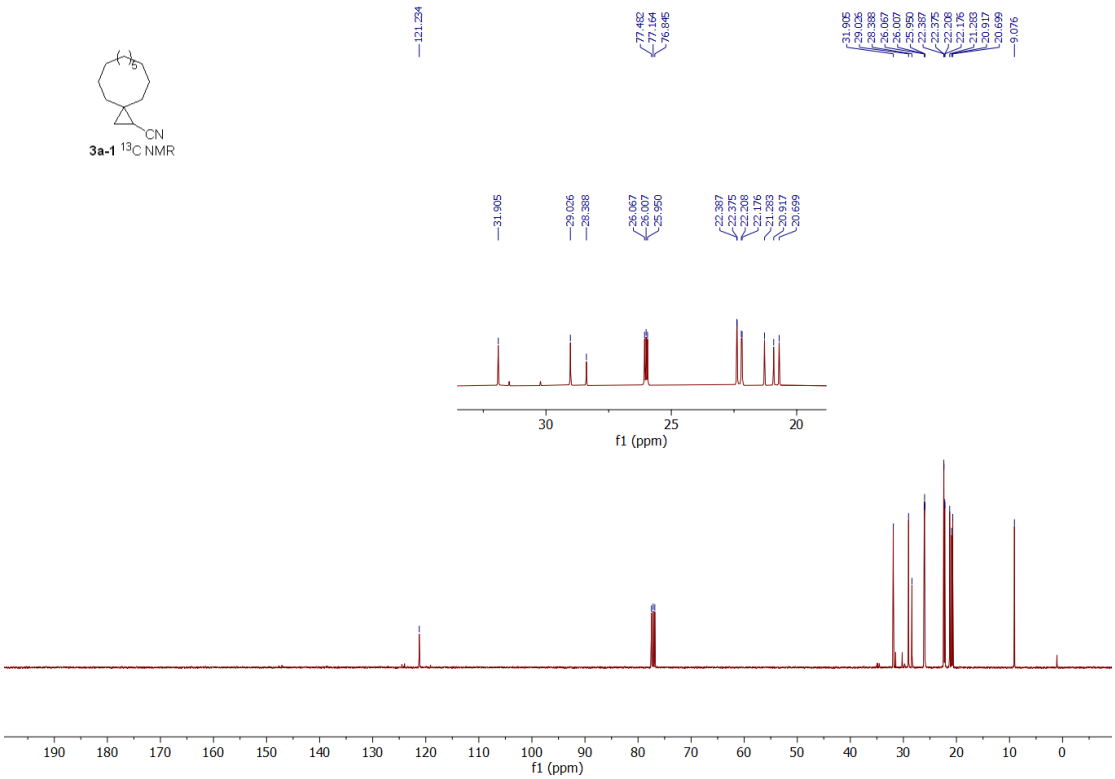
^{13}C NMR Spectra of 3z (100 MHz, Chloroform-*d*)



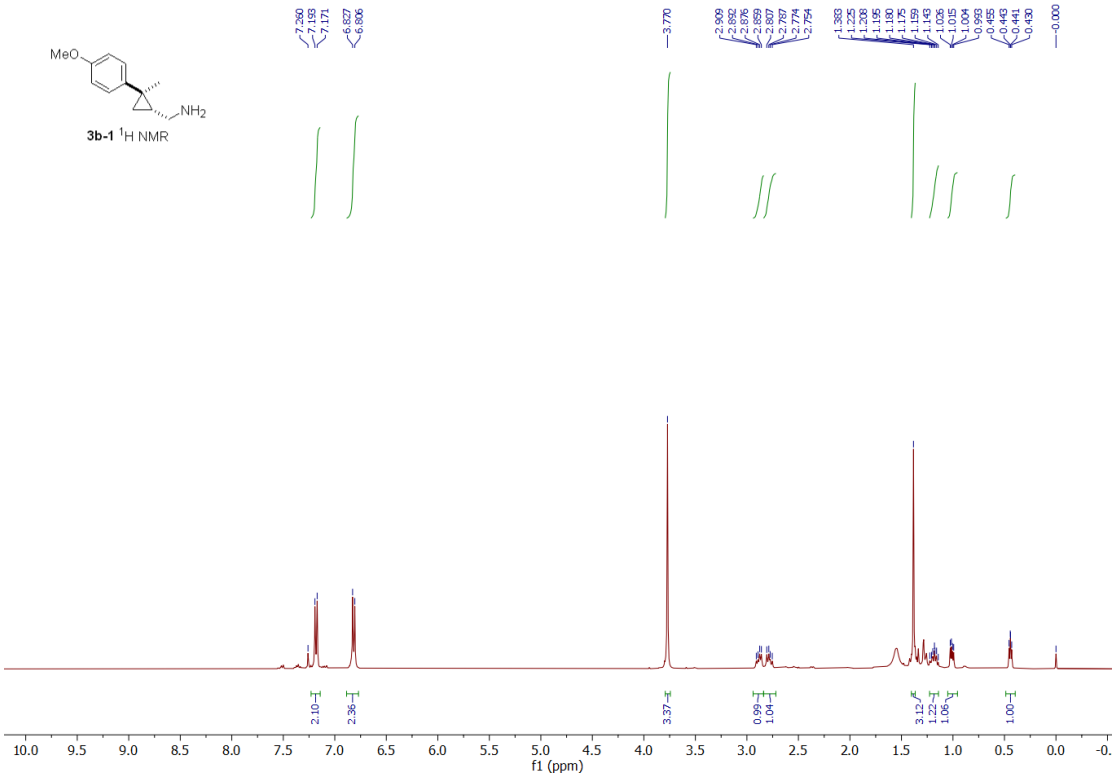
^{1}H NMR Spectra of 3a-1 (400 MHz, Chloroform-*d*)



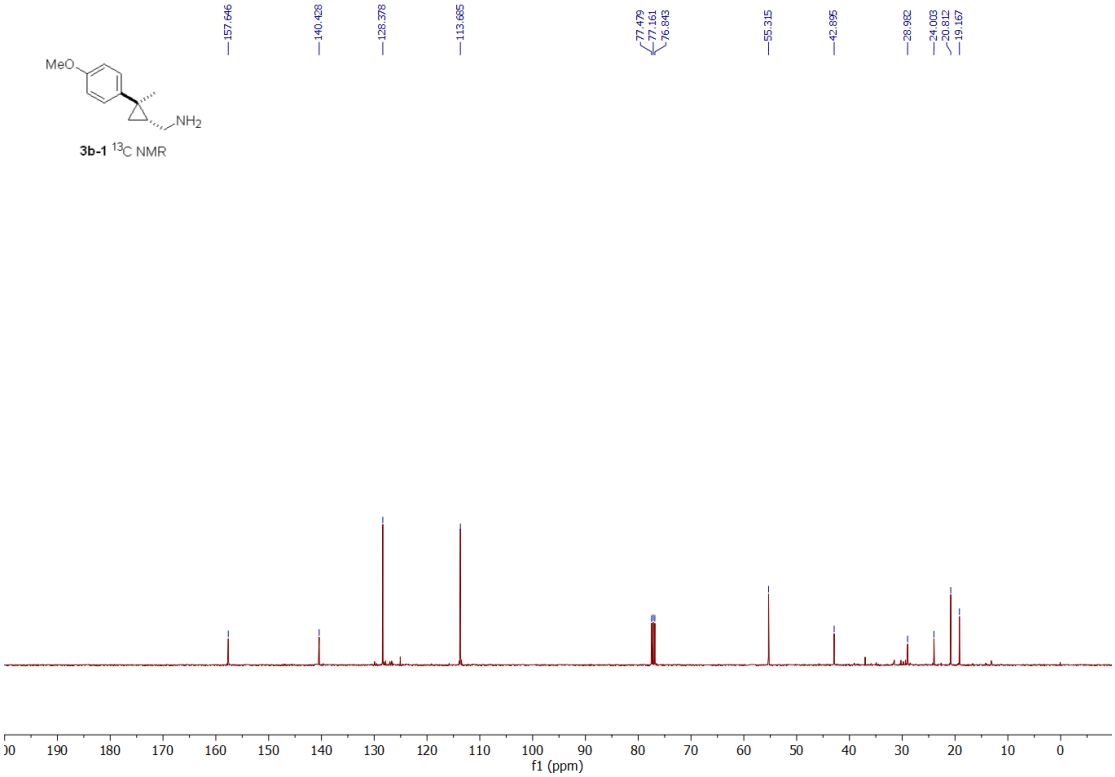
^{13}C NMR Spectra of 3a-1 (100 MHz, Chloroform-*d*)



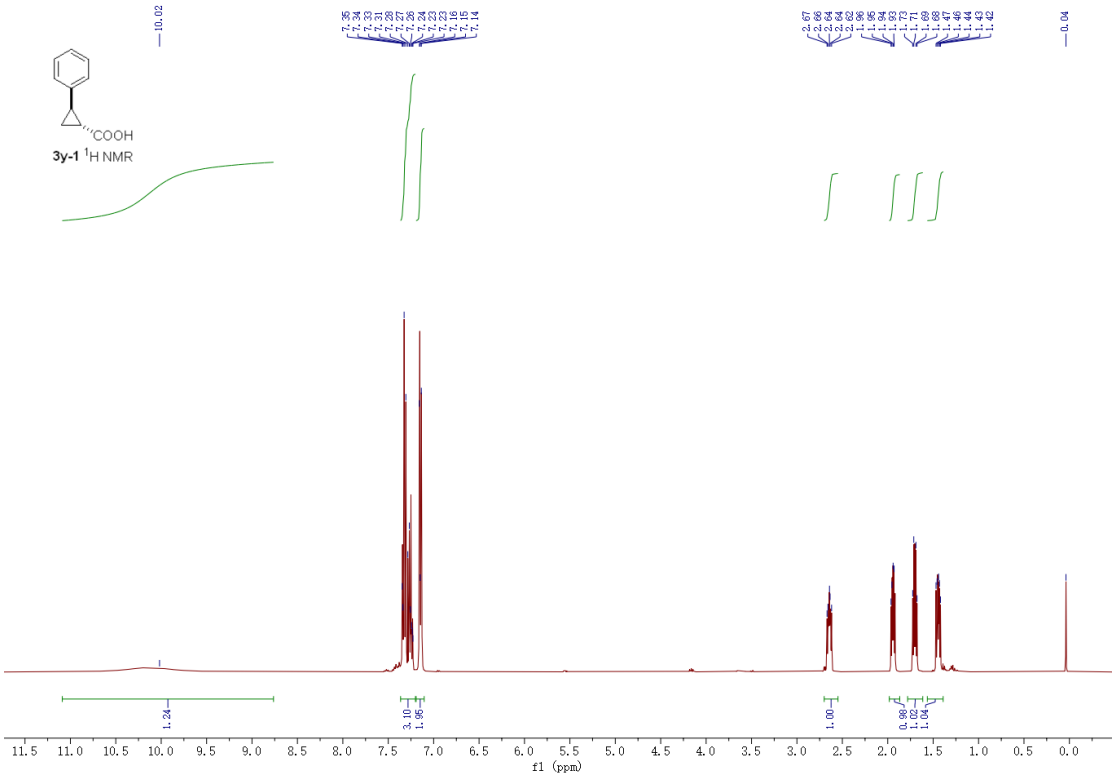
^{1}H NMR Spectra of 3b-1 (400 MHz, Chloroform-*d*)



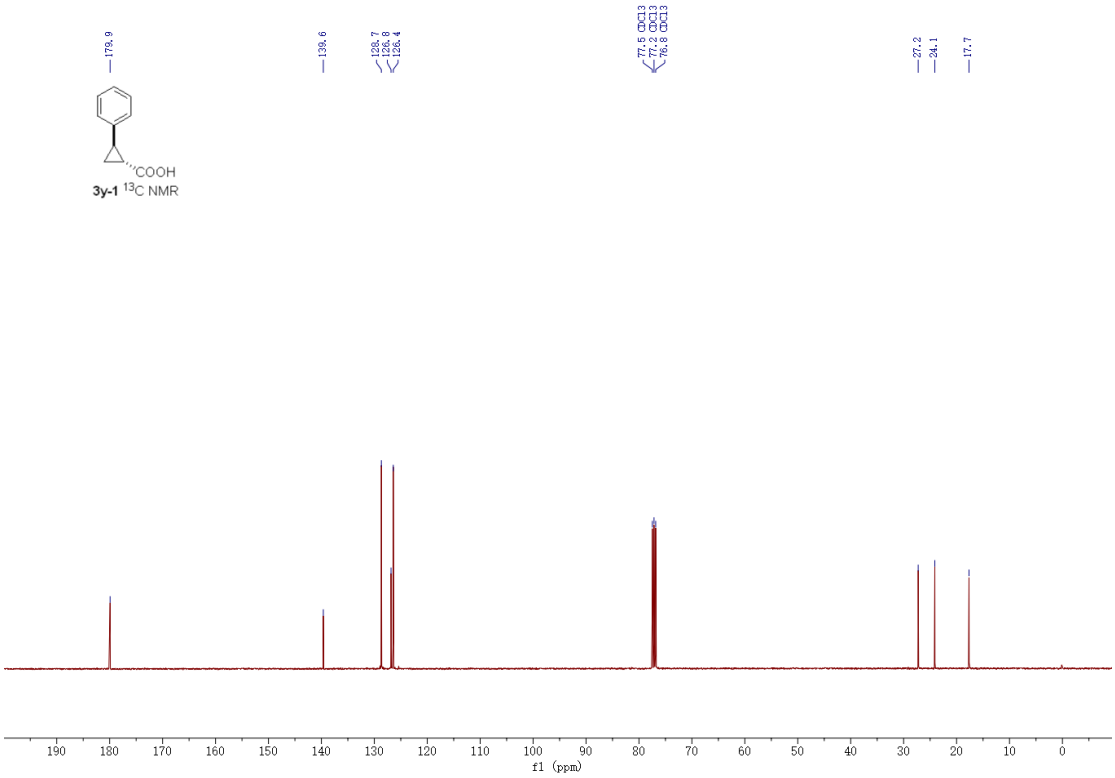
^{13}C NMR Spectra of 3b-1 (100 MHz, Chloroform-*d*)



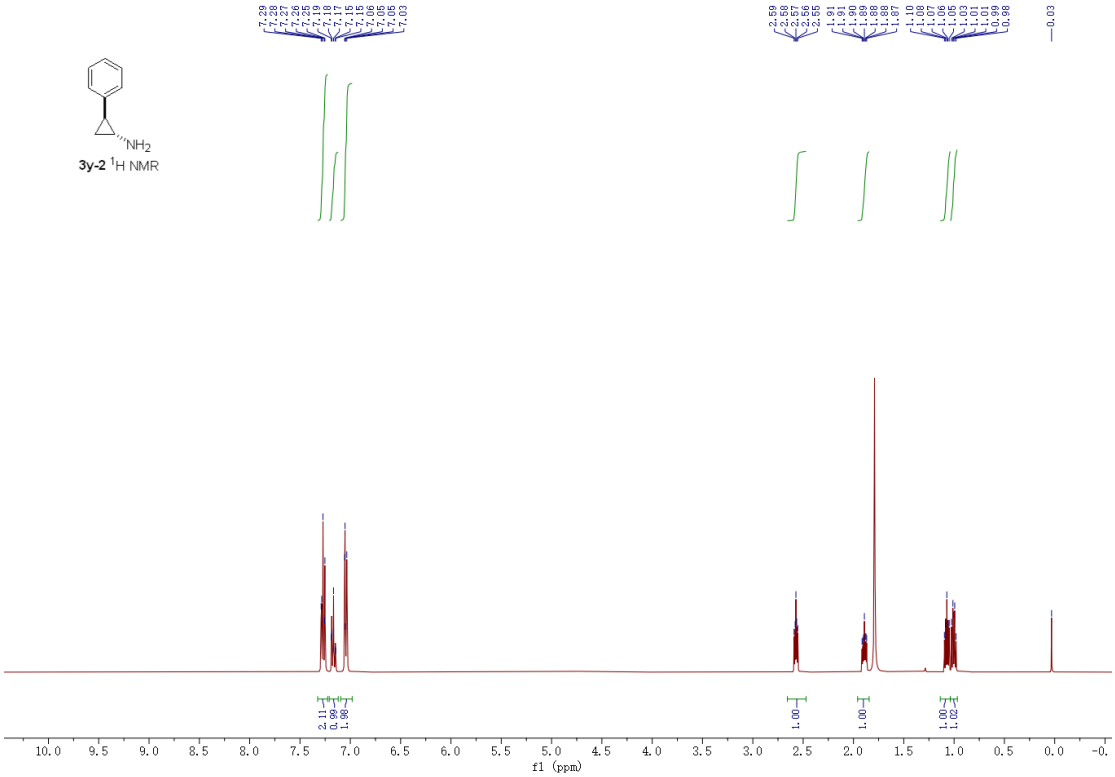
^{1}H NMR Spectra of 3y-1 (400 MHz, Chloroform-*d*)



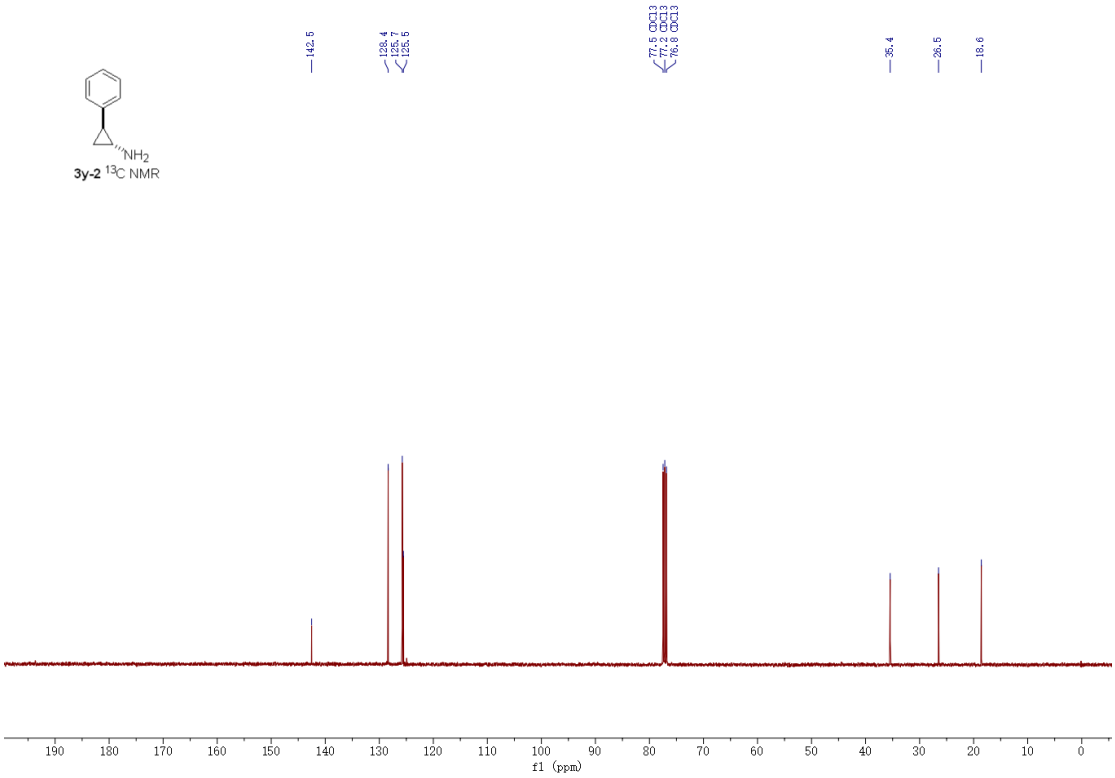
^{13}C NMR Spectra of 3y-1 (100 MHz, Chloroform-*d*)



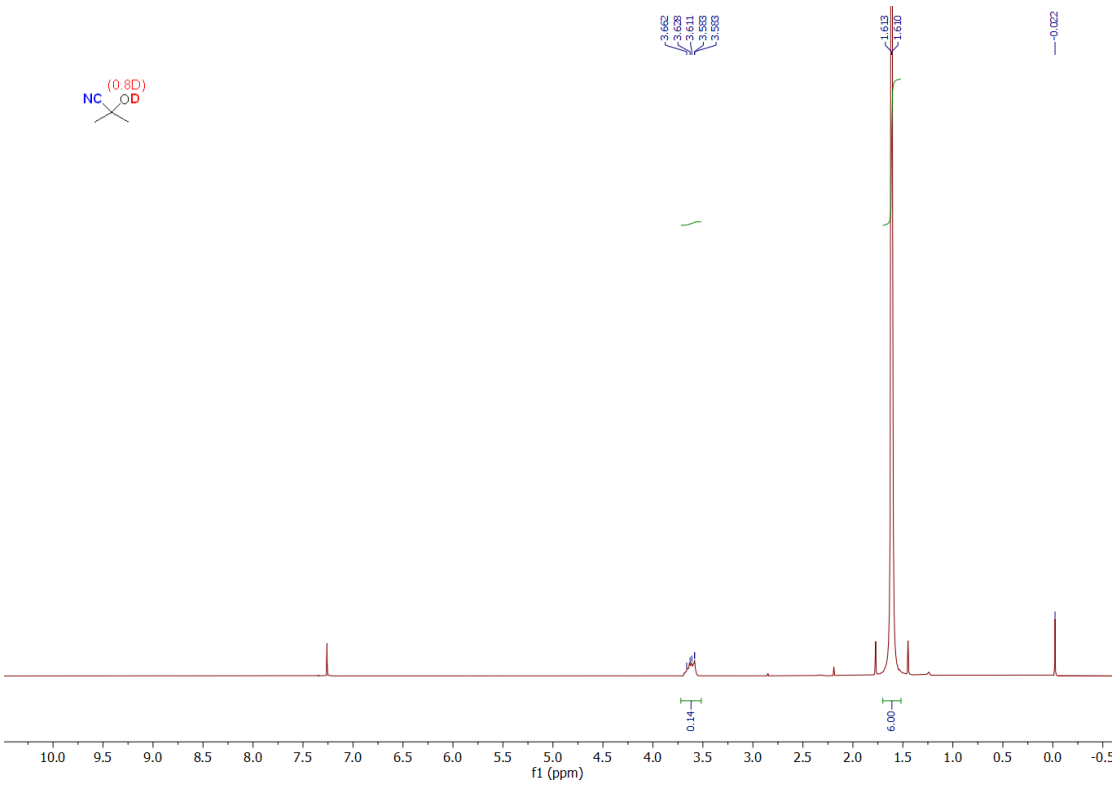
^{1}H NMR Spectra of 3y-2 (400 MHz, Chloroform-*d*)



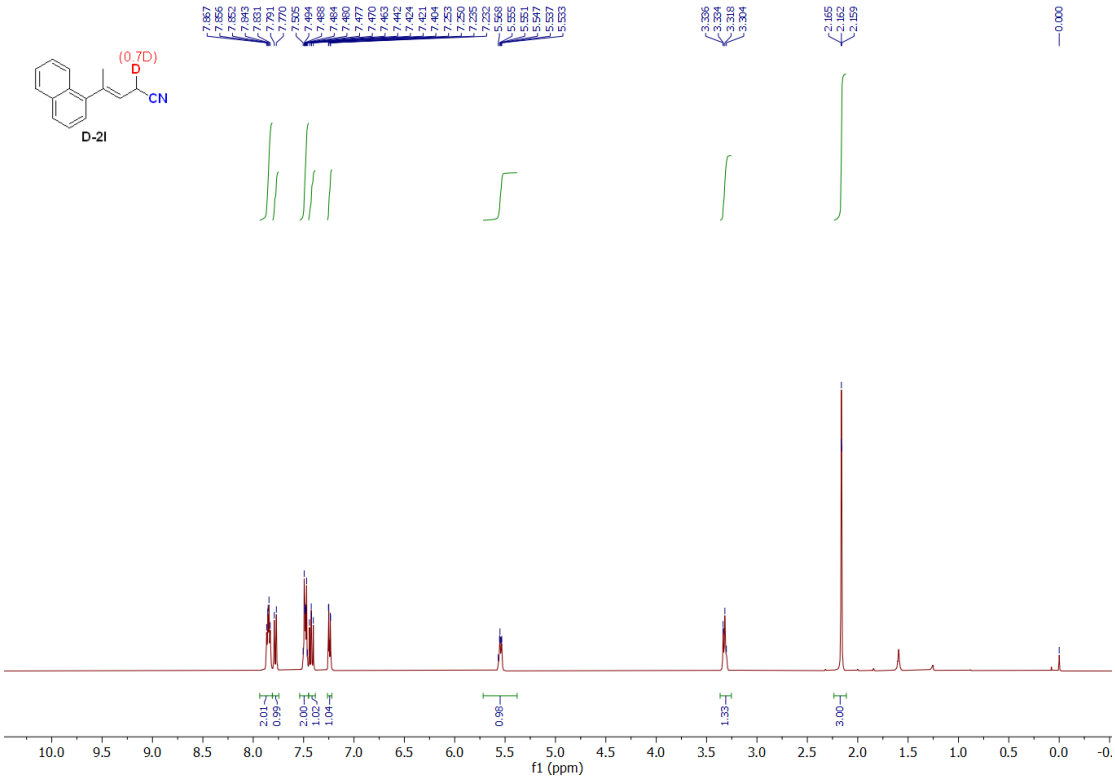
^{13}C NMR Spectra of 3y-2 (100 MHz, Chloroform-*d*)



^{1}H NMR Spectra of $(CH_3)_2C(OD)CN$ (400 MHz, Chloroform-*d*)



^{1}H NMR Spectra of D-2l (400 MHz, Chloroform-*d*)



^{1}H NMR Spectra of D-3p (400 MHz, Chloroform-*d*)