Supporting Information

Enantioselective and Regioselective Cu-Catalyzed Borocyanation of 1-Aryl-1,3-Butadienes

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General information

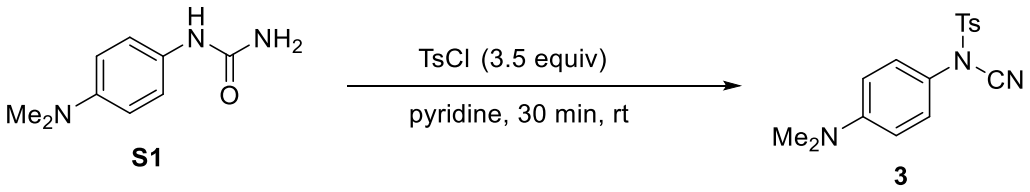
All experiments were performed under an atmosphere of nitrogen, using anhydrous solvents, unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded using 400 and 500 MHz spectrometers, with chemical shift values being reported in ppm relative to residual chloroform (δ_H = 7.27 or δ_C = 77.0) as internal standards. All coupling constants (*J*) are reported in Hertz (Hz). Mass spectra were obtained using positive and negative electrospray (ES±) or gas chromatography (GC) methodology. Infra-red spectra were recorded as evaporated films or neat using a FT/IR spectrometer. Column chromatography was carried out using 35-70 m, 60 Å silica gel. Routine TLC analysis was carried out on aluminum sheets coated with silica gel 60 F254, 0.2 mm thickness and plates were viewed using a 254 nm ultraviolet lamp and dipped in aqueous potassium permanganate. Enantiomeric ratios were determined by HPLC analysis Chiral Technologies Chiralpak® IA (4.6 x 250 mm), Chiralcel® OD-H (4.6 x 250 mm) in comparison with authentic racemic materials. Specific rotations were measured on a Rudolph Research Analytical Autopol I Automatic Polarimeter. Melting points were measured on a Stuart Scientific capillary melting point apparatus and are uncorrected.

Materials

Reagents were either purchased directly from commercial suppliers or prepared according to literature procedures. K_3PO_4, K_2CO_3, diboron pinacol ester, CuTc and Xantphos were purchased from Sigma-Aldrich and used as received.

1a-1z[1] and chiral PHOX ligands[2] were prepared according to the methods previously reported.

The synthesis of compound 3



According to the reported procedure[3], a 250 mL round-bottom flask was charged with **S1** (18 g, 100 mmol, 1 equiv) and pyridine (80 mL). *p*-Toluenesulfonyl chloride (67 g, 350 mmol, 3.5 equiv) was added portion wise over 5 minutes. The reaction mixture was stirred at room temperature for 30 min. The reaction was quenched with 800 mL water and left to stir for an additional 30 min. The precipitate formed was filtered and washed with water. The crude product was recrystallised from ethanol and the pure **3** (22 g, 70 mmol, 70%) was isolated as a pale yellow solid. Melting Point: 81-83 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 2.50 (s, 3H, CH_3), 2.99 (s, 6H, 2 X CH_3), 6.57 (d, *J* = 9.1 Hz, 2H, ArCH), 6.94 (d, *J* = 9.0 Hz, 2H, ArCH), 7.35 (d, *J* = 8.4 Hz, 2H, ArCH), 7.66 (d, *J* = 8.2 Hz, 2H, ArCH).

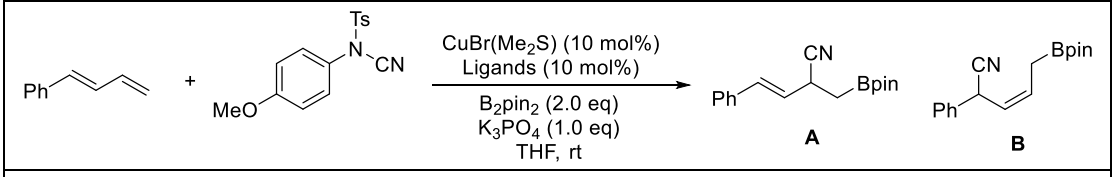
^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 21.8 (CH_3), 40.2 (CH_3), 109.3 (ArC), 112.1 (ArCH), 121.9 (*C*N), 128.1 (ArCH), 128.5 (ArCH), 130.1 (ArCH), 132.6 (ArC), 146.4 (ArC), 151.2 (ArC).

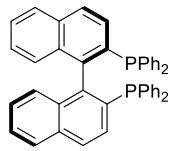
HRMS (m/z, ESI): Calcd. for $C_{16}H_{17}N_3O_2S$ [M+H]: 316.1114, found: 316.1107.

ν_{max} (thin film/cm^{-1}): 2231, 1595, 1516, 1444, 1340, 1367, 1231, 1185, 1171, 1081, 951.

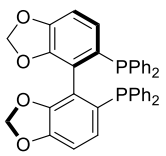
Optimization of the copper-catalyzed enantioselective borocyanation of dienes

Table S1. Screening of chiral ligands[a,b]

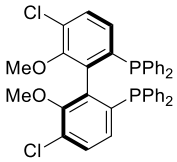




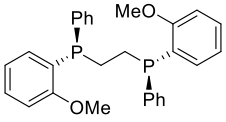
yield[a] (A/B): 33%/30%
ee[b] of A: 45%



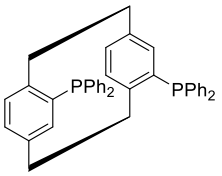
yield (A/B): 32%/32%
ee of A: 39%



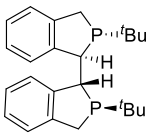
yield (A/B): 40%/40%
ee of A: 44%



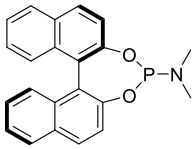
yield (A/B): 11%/-
ee of A: 2%



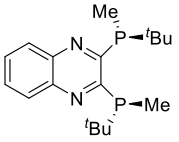
yield (A/B): 31%/22%
ee of A: 39%



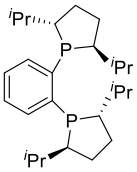
yield (A/B): 31%/-
ee of A: 2%



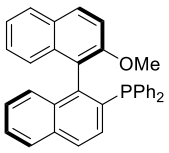
yield (A/B): 36%/22%
ee of A: 15%



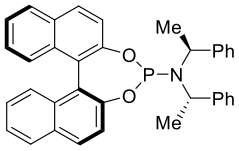
yield (A/B): 28%/-
ee of A: 2%



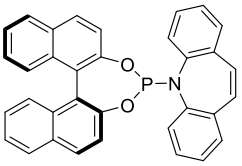
yield (A/B): 7%/8%
ee of A: 53%



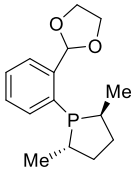
yield (A/B): 12%/1%
ee of A: 16%



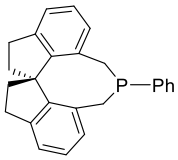
yield (A/B): 8%/1%
ee: n.d.



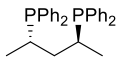
yield (A/B): 6%/1%
ee: n.d.



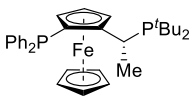
yield (A/B): 55%/3%
ee of A: 2%



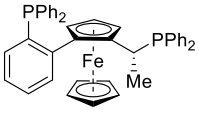
yield (A/B): 45%/3%
ee of A: 7%



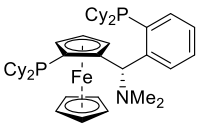
yield (A/B): 50%/2%
ee of A: 40%



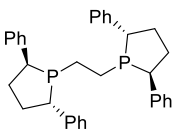
yield (A/B): 14%/9%
ee of A: 31%



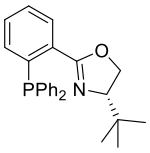
yield (A/B): 45%/12%
ee of A: 2%



yield (A/B): 22%/10%
ee of A: 40%



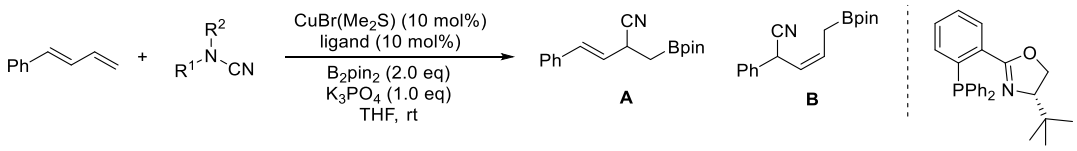
yield (A/B): trace
ee: n.d.

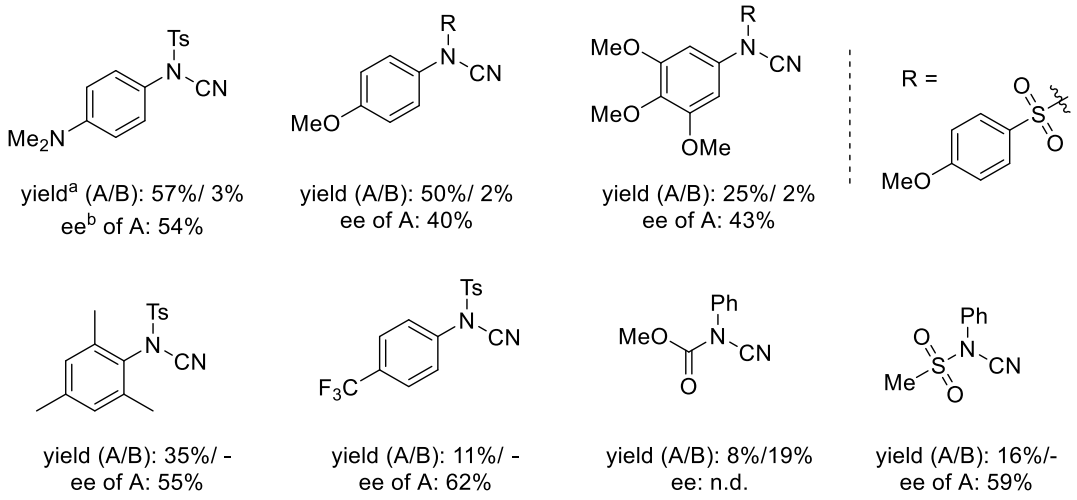


yield (A/B): 57%/3%
ee of A: 54%

[a] Yield and regioselectivity (**A**:**B**) were determined by ^{1}H-NMR analysis of crude reaction mixtures. [b] The ee values were determined by HPLC analysis on a chiral stationary phase.`

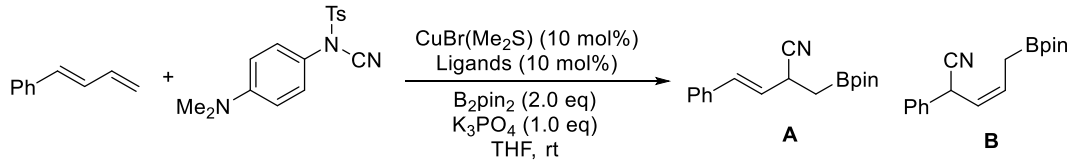
Table S2. Screening of cyanating agents[a,b]

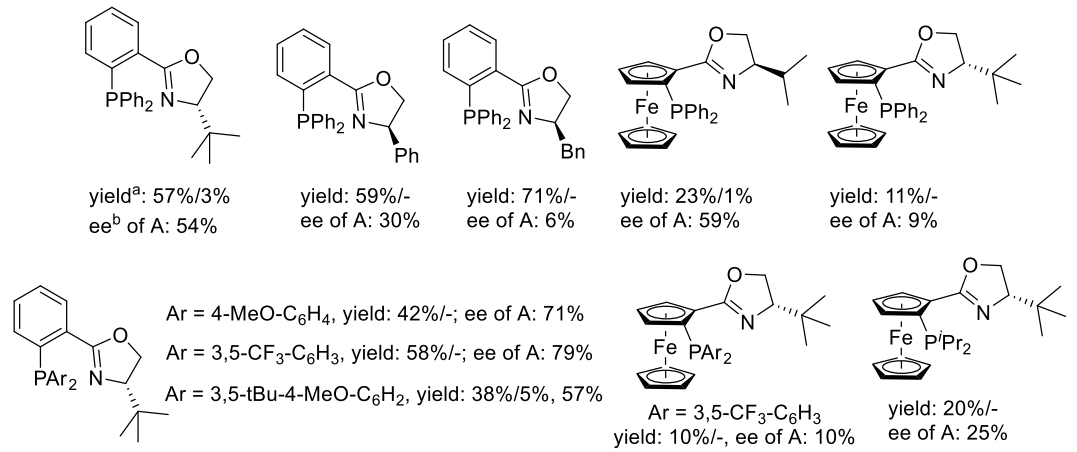




[a] Yield and regioselectivity (**A**:**B**) were determined by ^{1}H-NMR analysis of crude reaction mixtures. [b] The ee values were determined by HPLC analysis on a chiral stationary phase.`

Table S3. Screening of chiral PHOX ligands[a,b]





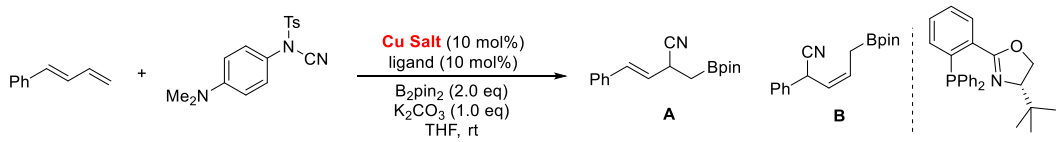
[a] Yield and regioselectivity (**A**:**B**) were determined by ^{1}H-NMR analysis of crude reaction mixtures. [b] The ee values were determined by HPLC analysis on a chiral stationary phase.

Table S4. Screening of bases[a,b]

entry	Base	Yield (A/B)	ee of A
1	KOtBu	32%/-	14%
2	NaOtBu	73%/-	28%
3	LiOtBu	51%/-	4%
4	NaOMe	53%/3%	69%
5	NaOEt	55%/3%	42%
6	NaOtAmyl	44%/-	14%
7	LiOEt	47%/3%	50%
8	KOH	55%/3%	21%
9	Na_2CO_3	2%/-	-
10	K_2CO_3	48%/2%	71%
11	Cs_2CO_3	40%/-	12%
12	CsF	54%/-	48%
13	LiOH	49%/4%	69%
14	$LiNH_2$	31%/-	69%
15	Ag_2CO_3	16%/-	56%
16	NaOH	50%/3%	31%

[a] Yield and regioselectivity (**A**:**B**) were determined by ^{1}H-NMR analysis of crude reaction mixtures. [b] The ee values were determined by HPLC analysis on a chiral stationary phase.

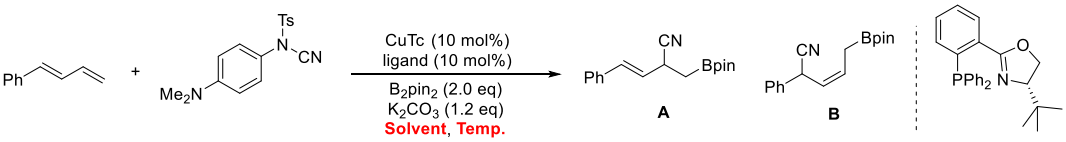
Table S5. Screening of Copper sources[a,b]



entry	Cu	Yield	ee of A
1	CuCl	65%	80%
2	CuI	22%	74%
3	$CuPF_6(MeCN)_4$	60%	62%
4	$CuBF_4(MeCN)_4$	57%	70%
5	CuTc	62%	83%
6	CuOAc	42%	83%
7	CuCN	47%	63%
8	$CuCl_2$	49%	70%
9	$Cu(OAc)_2$	47%	82%
10	$Cu(OTf)_2$	55%	58%

[a] Yield and regioselectivity (**A**:**B**) were determined by ^{1}H-NMR analysis of crude reaction mixtures. [b] The ee values were determined by HPLC analysis on a chiral stationary phase.

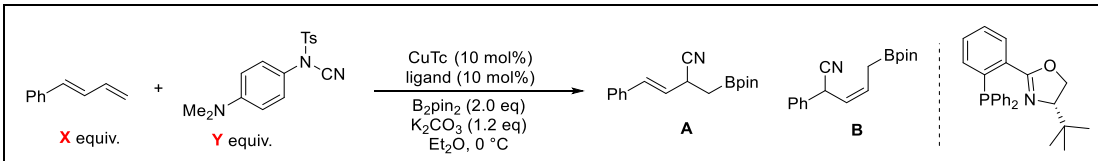
Table S6. Screening of solvents[a,b]



entry	Solvent	Temperature	Yield	ee of A
1	2-Me-THF	25 °C	78%	86%
2	MTBE	25 °C	70%	86%
3	Dioxane	25 °C	78%	82%
4	Et_2O	25 °C	80%	88%
5	toluene	25 °C	46%	87%
6	MeCN	25 °C	24%	20%
7	2-Me-THF	0 °C	51%	88%
8	MTBE	0 °C	56%	88%
9	Dioxane/THF	0 °C	43%	86%
10	Et_2O	0 °C	60%	91%
11	THF	0 °C	65%	87%
12	THF	-10 °C	50%	87%

[a] Yield and regioselectivity (**A**:**B**) were determined by ^{1}H-NMR analysis of crude reaction mixtures. [b] The ee values were determined by HPLC analysis on a chiral stationary phase.

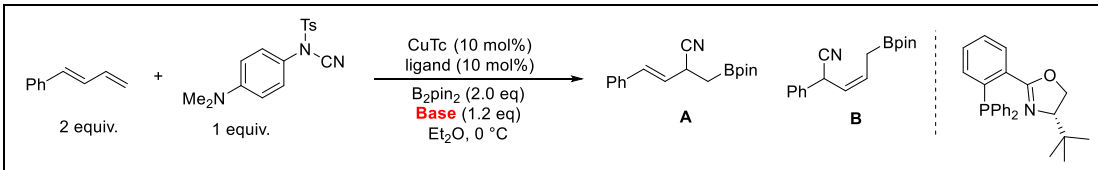
Table S7. Screening the loading of base and cyanating agent[a,b]



entry	X	Y	Yield	ee of A
1	1.0	1.5	63%	91%
2	1.0	2.0	67%	91%
3	1.2	1.0	68%	91%
4	1.5	1.0	70%	91%
5	2.0	1.0	85%	91%

[a] Yield and regioselectivity (**A**:**B**) were determined by ^{1}H-NMR analysis of crude reaction mixtures. [b] The ee values were determined by HPLC analysis on a chiral stationary phase.

Table S8. Screening of bases[a,b]

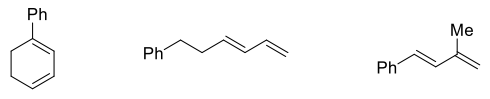


entry	Base	Yield	ee of A
1	Na_3PO_4	48%	90%
2	K_3PO_4	90%	91%
3	LiOtBu	88%	62%
4	KOtBu	60%	84%

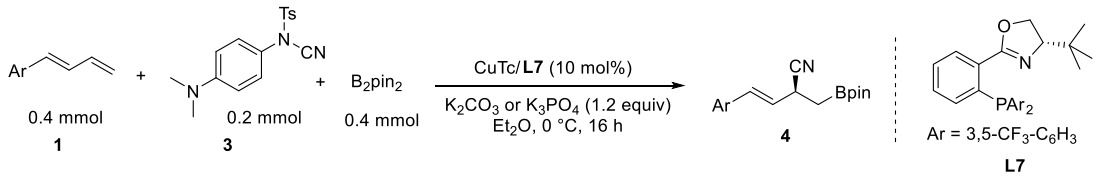
[a] Yield and regioselectivity (**A**:**B**) were determined by ^{1}H-NMR analysis of crude reaction mixtures. [b] The ee values were determined by HPLC analysis on a chiral stationary phase.

Table S9. Unsuccessful substrates

The following substrates were tested under the optimized conditions, however, the desired product was not observed.

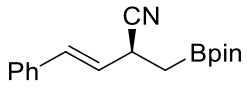


General procedure for the copper-catalyzed enantioselective borocyanation of dienes



To a 10 mL vial, CuTc (4 mg, 0.02 mmol, 10 mol %), chiral ligand **L7** (13 mg, 0.02 mmol, 10 mol%) and 2 mL dry Et_2O were added under a nitrogen atmosphere. The solution was stirred at room temperature for 30 min to generate the copper/**L7** complex. In another 10 mL vial, K_2CO_3 (33 mg, 0.24 mmol, 1.2 equiv) or K_3PO_4 (51 mg, 0.24 mmol, 1.2 equiv), *N*-cyano-*N*-(4-(dimethylamino)phenyl)-4-methylbenzenesulfonamide (63 mg, 0.2 mmol, 1.0 equiv), B_2pin_2 (102 mg, 0.4 mmol, 2.0 equiv), diene (0.4 mmol) and 2 mL dry Et_2O were mixed under a nitrogen atmosphere. This solution was then stirred for 5 min at 0 °C, before the solution of copper/**L7** complex was added by syringe and the new mixture was stirred for 16 h at 0 °C. The product mixture was then filtered through celite, concentrated in *vacuo* and the crude product mixture was purified by chromatography to afford the pure products.

(*S,E*)-4-Phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4a)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 90% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (48 mg, 0.170 mmol, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.26 (s, 12H, 4 x CH_3), 1.30 (dd, *J* = 16.1, 8.2 Hz, 1H, CH_2Bpin), 1.41 (dd, *J* = 16.1, 7.2 Hz, 1H, CH_2Bpin), 3.59 – 3.64 (m, 1H, CHCN), 6.10 (dd, *J* = 15.8, 6.5 Hz, 1H, CH=CH), 6.68 (d, *J* = 15.8 Hz, 1H, CH=CH), 7.25 – 7.28 (m, 1H, ArCH), 7.31 – 7.37 (m, 4H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.9 (CH_3), 29.7 (*C*H-CN), 84.1 (O*C*(CH_3)$_2$), 121.2 (*C*N), 124.9 (ArCH), 126.5 (*C*H=CH), 128.1 (ArCH), 129.0 (*C*H=CH), 132.4 (ArCH), 135.9 (ArC), (*C*H_2B not observed).

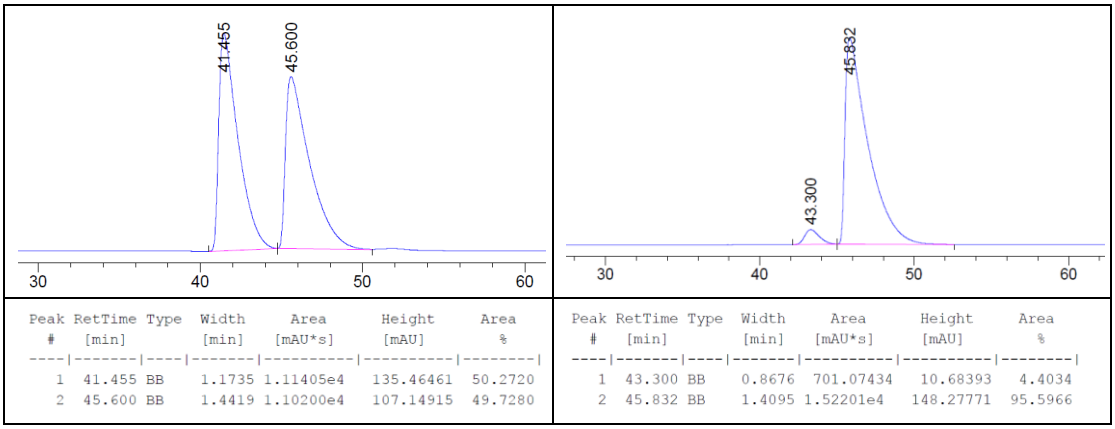
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.8.

HRMS (m/z, ESI): Calcd. for $C_{17}H_{22}BNO_2$ [M+H]: 284.1816, found: 284.1804.

ν_{max} (thin film/cm^{-1}): 2978, 2240, 1449, 1407, 1371, 1331, 1272, 1166, 1140, 964.

Specific rotation: $[\alpha]_D^{27}$+16.3 (c = 0.92, $CHCl_3$).

Enantiomeric purity of **4a** was determined by HPLC analysis in comparison with authentic racemic material (91% e.e. shown; OD-H column, 998:2 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.455	BB	1.1735	1.11405e4	135.46461	50.2720
2	45.600	BB	1.4419	1.10200e4	107.14915	49.7280

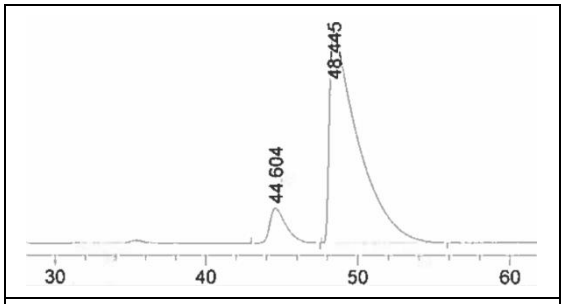
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.300	BB	0.8676	701.07434	10.68393	4.4034
2	45.832	BB	1.4095	1.52201e4	148.27771	95.5966

The gram-scale synthesis of this compound was conducted following a modified version of the General Procedure:

To a 100 mL flask, CuTc (50 mg, 0.25 mmol, 5 mol %), chiral ligand **L7** (163 mg, 0.25 mmol, 5 mol%) and 50 mL dry Et_2O were added under a nitrogen atmosphere. The solution was stirred at room temperature for 30 min to generate the copper/**L7** complex. In another 250 mL flask, K_2CO_3 (828 mg, 6.0 mmol, 1.2 equiv), *N*-cyano-*N*-(4-(dimethylamino)phenyl)-4-methylbenzenesulfonamide (1.6 g, 5.0 mmol, 1.0 equiv), B_2pin_2 (2.5 g, 10.0 mmol, 2.0 equiv), diene (1.3 g, 10.0 mmol) and 50 mL dry Et_2O were mixed under a nitrogen atmosphere. This solution was then stirred for 5 min at 0 °C, before the solution of copper/**L7** complex was added by syringe and the new mixture was stirred for 16 h at 0 °C. The product mixture was then filtered through celite, concentrated in vacuo and the crude product mixture was purified by column

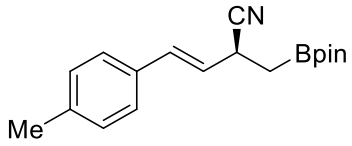
chromatography (Hexane/EtOAc/AcOH = 100/3/1) to afford the title compound as a colorless oil (892 mg, 3.15 mmol, 64%).

Enantiomeric purity of **4a** was determined by HPLC analysis in comparison with authentic racemic material (83% e.e. shown; OD-H column, 998:2 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.604	BB	1.0172	3380.90527	45.17247	8.7323
2	48.445	BB	1.7086	3.53363e4	271.47873	91.2677

(*S,E*)-2-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(p-tolyl)but-3-enenitrile (4b)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 70% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (41 mg, 0.138 mmol, 69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.26 (s, 12H, 4 x CH_3), 1.31 (dd, *J* = 16.1, 8.3 Hz, 1H, CH_2Bpin), 1.41 (dd, *J* = 16.1, 7.2 Hz, 1H, CH_2Bpin), 2.35 (s, 3H, CH_3), 3.58-3.63 (m, 1H, CHCN), 6.05 (dd, *J* = 15.8, 6.6 Hz, 1H, CH=CH), 6.65 (d, *J* = 15.8 Hz, 1H, CH=CH), 7.13 (d, *J* = 8.0 Hz, 2H, ArCH), 7.25 (d, *J* = 8.2 Hz, 2H, ArCH). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 21.2 (CH_3), 24.8 (CH_3), 24.9 (CH_3), 29.7 (*C*H-CN), 84.0 (*C*$(CH_3)_2$), 121.4 (*C*N), 123.9 (CH=CH), 126.4 (ArCH), 129.4 (ArCH), 132.3 (CH=CH), 133.1 (ArC), 138.0 (ArC), (*C*H_2B not observed).

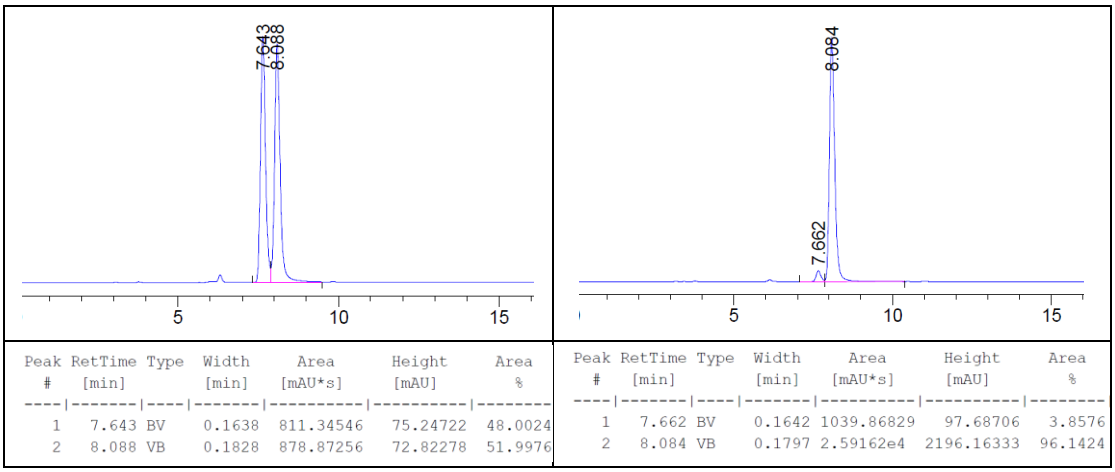
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.4.

HRMS (m/z, ESI): Calcd. for $C_{18}H_{24}BNO_2$ [M+Na]: 320.1792, found: 320.1781.

ν_{max} (thin film/cm^{-1}): 2978, 2924, 2241, 1513, 1407, 1371, 1332, 1279, 1167, 1141, 966.

Specific rotation: $[\alpha]_D^{27}$+15.8 (c = 0.83, $CHCl_3$).

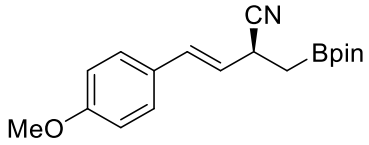
Enantiomeric purity of **4b** was determined by HPLC analysis in comparison with authentic racemic material (92% e.e. shown; OD-H column, 99:1 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.643	BV	0.1638	811.34546	75.24722	48.0024
2	8.088	VB	0.1828	878.87256	72.82278	51.9976

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.662	BV	0.1642	1039.86829	97.68706	3.8576
2	8.084	VB	0.1797	2.59162e4	2196.16333	96.1424

(*S,E*)-4-(4-Methoxyphenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4c)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 52% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (30 mg, 0.096 mmol, 48%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.27 (s, 12H, 4 x CH_3), 1.31 (dd, *J* = 16.1, 8.3 Hz, 1H, CH_2Bpin), 1.45 (dd, *J* = 16.1, 7.2 Hz, 1H, CH_2Bpin), 3.58-3.63 (m, 1H, CHCN), 3.83 (s, 3H, CH_3), 5.97 (dd, *J* = 15.8, 6.6 Hz, 1H, CH=CH), 6.63 (d, *J* = 15.8 Hz, 1H, CH=CH), 6.86-6.89 (m, 2H, ArCH), 7.29-7.32 (m, 2H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.9 (CH_3), 29.7 (*C*H-CN), 55.3 (OCH_3), 84.0 (*C*(CH_3)$_2$), 114.1 (ArCH), 121.4 (*C*N), 122.7 (CH=CH), 127.7 (ArCH), 128.6 (ArC), 131.8 (CH=CH), 159.6 (ArC), (*C*H_2B not observed).

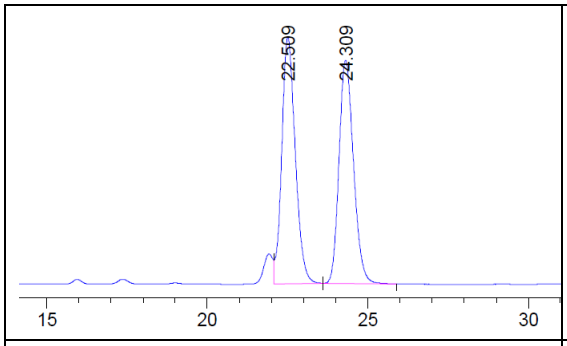
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.7.

HRMS (m/z, ESI): Calcd. for $C_{18}H_{24}BNO_3$ [M+H]: 314.1922, found: 314.1916.

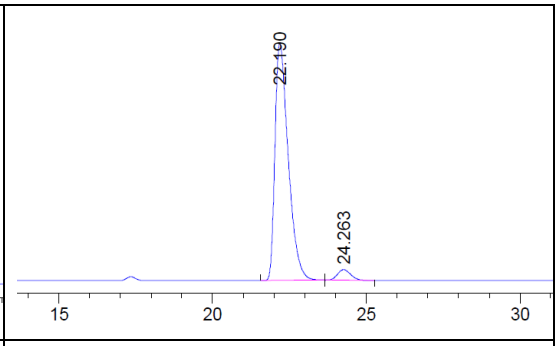
ν_{max} (thin film/cm^{-1}): 2977, 2934, 2240, 1607, 1511, 1372, 1333, 1249, 1175, 1141, 1032, 966.

Specific rotation: $[\alpha]_D^{27}$+12.9 (c = 0.89, $CHCl_3$).

Enantiomeric purity of **4c** was determined by HPLC analysis in comparison with authentic racemic material (91% e.e. shown; OD-H column, 99:1 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).

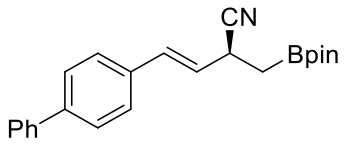


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.509	VB	0.4487	2706.88794	92.69602	50.6479
2	24.309	BB	0.4862	2637.62915	84.02187	49.3521



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.190	BB	0.4558	3.11273e4	1038.19360	95.6423
2	24.263	BB	0.4727	1418.23816	46.64223	4.3577

(*S,E*)-4-([1,1'-Biphenyl]-4-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4d)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 79% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a white solid (55 mg, 0.154 mmol, 77%). Melting Point: 69-71 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.30 (s, 12H, 4 x CH_3), 1.35 (dd, *J* = 16.1, 8.2 Hz, 1H, CH_2Bpin), 1.45 (dd, *J* = 16.1, 7.2 Hz, 1H, CH_2Bpin), 3.64-3.69 (m, 1H, CHCN), 6.17 (dd, *J* = 15.8, 6.5 Hz, 1H, CH=CH), 6.75 (d, *J* = 15.8 Hz, 1H, CH=CH), 7.38 (t, *J* = 7.5 Hz, 1H, ArCH), 7.45-7.48 (m, 4H, ArCH), 7.59-7.63 (m, 4H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.9 (CH_3), 29.8 (*C*H-CN), 84.1 (*C*(CH_3)$_2$), 121.2 (*C*N), 125.0 (CH=CH), 127.0 (ArCH), 127.4 (ArCH), 127.5 (ArCH), 128.8 (ArCH), 132.0 (CH=CH), 134.9 (ArC), 140.5 (ArC), 140.9 (ArC), (*C*H_2B and 1 ArCH not observed).

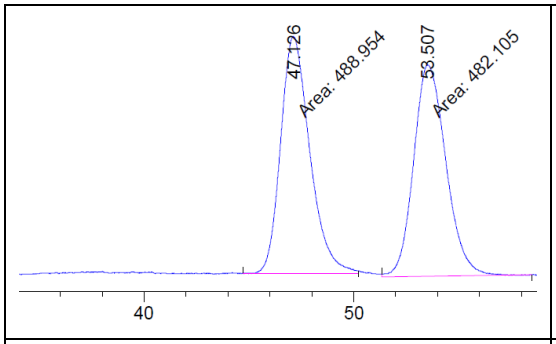
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.9.

HRMS (m/z, ESI): Calcd. for $C_{23}H_{26}BNO_2$ [M+H]: 360.2129, found: 360.2130.

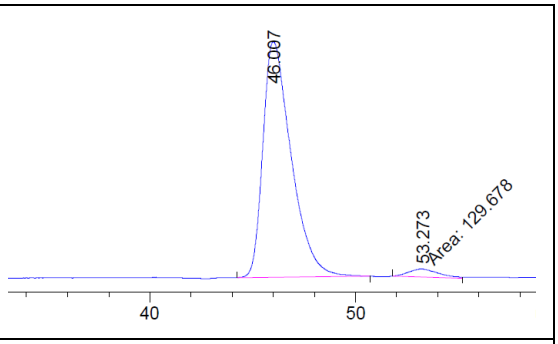
ν_{max} (thin film/cm^{-1}): 3029, 2977, 2932, 2239, 1486, 1407, 1371, 1332, 1271, 1141, 966.

Specific rotation: $[\alpha]_D^{27}$+22.6 (c = 1.45, $CHCl_3$).

Enantiomeric purity of **4d** was determined by HPLC analysis in comparison with authentic racemic material (93% e.e. shown; OD-H column, 99:1 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).

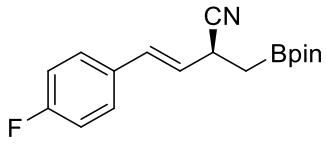


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.126	MM	1.6168	488.95370	5.04030	50.3526
2	53.507	MM	1.7872	482.10529	4.49600	49.6474



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.007	BB	1.3754	3578.96899	37.36859	96.5034
2	53.273	MM	1.7037	129.67827	1.26861	3.4966

(*S*,*E*)-4-(4-Fluorophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4e)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 82% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (50 mg, 0.166 mmol, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.26 (s, 12H, 4 x CH_3), 1.30 (dd, *J* = 16.1, 8.2 Hz, 1H, CH_2Bpin), 1.41 (dd, *J* = 16.1, 7.2 Hz, 1H, CH_2Bpin), 3.58-3.63 (m, 1H, CHCN), 6.02 (dd, *J* = 15.8, 6.5 Hz, 1H, CH=CH), 6.49 (d, *J* = 15.8 Hz, 1H, CH=CH), 7.00-7.04 (m, 2H, ArCH), 7.31-7.35 (m, 2H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.9 (CH_3), 29.6 (*C*H-CN), 84.1 (*C*(CH_3)$_2$), 115.6 (d, *J* = 21.6 Hz, ArCH), 121.1 (*C*N), 124.7 (d, *J* = 1.9 Hz, CH=CH), 128.0 (d, *J* = 31.9 Hz, ArCH), 131.2 (CH=CH), 132.0 (d, *J* = 3.6 Hz, ArC), 161.6 (d, *J* = 246.2 Hz, ArC), (*C*H_2B not observed).

^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.7.

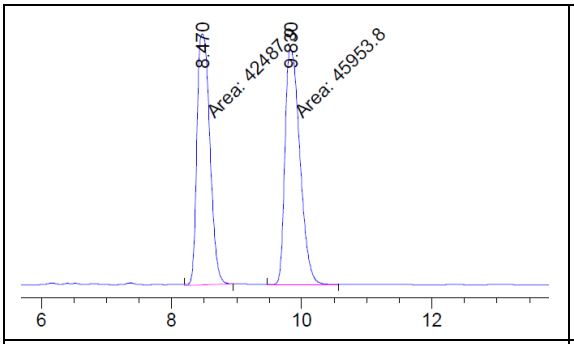
^{19}F NMR (470 MHz, $CDCl_3$) δ ppm -113.6.

HRMS (m/z, ESI): Calcd. for $C_{17}H_{21}BFNO_2$ [M+Na]: 324.1542, found: 324.1529.

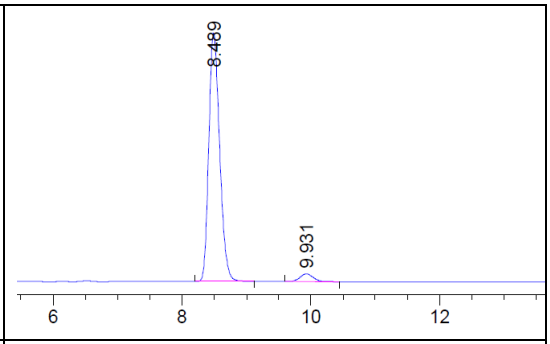
ν_{max} (thin film/cm^{-1}): 2979, 2932, 2360, 2240, 1734, 1602, 1509, 1409, 1372, 1334, 1228, 1141, 966.

Specific rotation: $[\alpha]_D^{27}$+15.8 (c = 1.17, $CHCl_3$).

Enantiomeric purity of **4e** was determined by HPLC analysis in comparison with authentic racemic material (93% e.e. shown; OD-H column, 99:1 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).

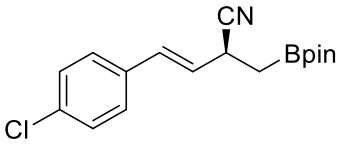


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.470	MM	0.2308	4.24879e4	3067.70020	48.0406
2	9.830	MM	0.2654	4.59538e4	2885.95239	51.9594



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.489	BB	0.1828	2.33501e4	1991.04016	96.3659
2	9.931	BB	0.2221	880.56201	61.85740	3.6341

(*S*,*E*)-4-(4-Chlorophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4f)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 90% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a

white solid (56 mg, 0.178 mmol, 89%). Melting Point: 43-44 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.26 (s, 12H, 4 x CH_3), 1.30 (dd, *J* = 16.1, 8.2 Hz, 1H, CH_2Bpin), 1.41 (dd, *J* = 16.1, 7.1 Hz, 1H, CH_2Bpin), 3.59-3.63 (m, 1H, CHCN), 6.08-6.13 (m, 1H, CH=CH), 6.65 (d, *J* = 15.8 Hz, 1H, CH=CH), 7.26-7.32 (m, 4H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.9 (CH_3), 29.7 (*C*H-CN), 84.1 (*C*(CH_3)$_2$), 121.0 (*C*N), 125.6 (CH=CH), 127.7 (ArCH), 128.9 (ArCH), 131.2 (CH=CH), 133.8 (ArC), 134.4 (ArC), (*C*H_2B not observed).

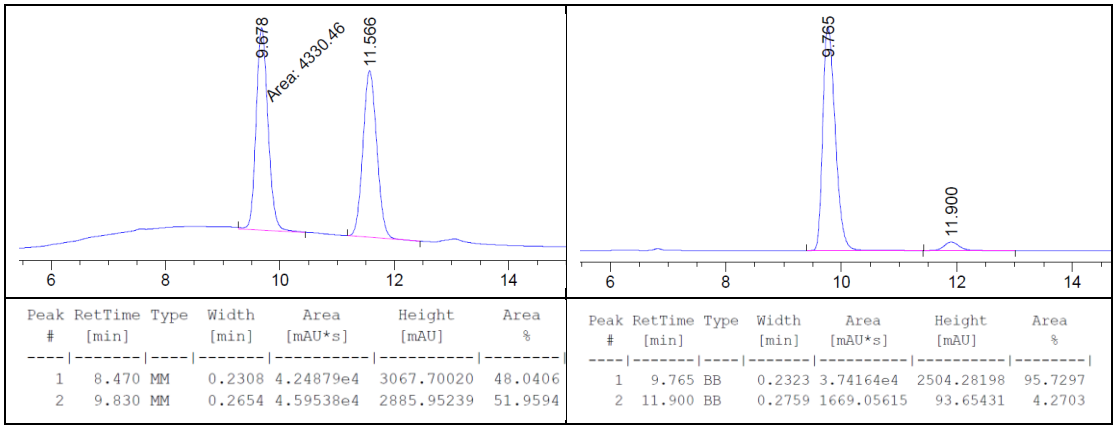
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.7.

HRMS (m/z, ESI): Calcd. for $C_{17}H_{21}ClBNO_2$ [M+H]: 318.1427, found: 318.1420.

ν_{max} (thin film/cm^{-1}): 2978, 2931, 2241, 1738, 1594, 1491, 1372, 1333, 1141, 1091, 966.

Specific rotation: $[\alpha]_D^{27}$+3.8 (c = 0.35, $CHCl_3$).

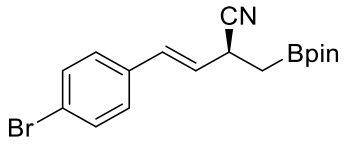
Enantiomeric purity of **4f** was determined by HPLC analysis in comparison with authentic racemic material (91% e.e. shown; OD-H column, 99:1 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.470	MM	0.2308	4.24879e4	3067.70020	48.0406
2	9.830	MM	0.2654	4.59538e4	2885.95239	51.9594

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.765	BB	0.2323	3.74164e4	2504.28198	95.7297
2	11.900	BB	0.2759	1669.05615	93.65431	4.2703

(*S*,*E*)-4-(4-Bromophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4g)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 80% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a

white solid (52 mg, 0.144 mmol, 72%). Melting Point: 42-44 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.28 (s, 12H, 4 x CH_3), 1.32 (dd, *J* = 16.1, 8.2 Hz, 1H, CH_2Bpin), 1.43 (dd, *J* = 16.2, 7.2 Hz, 1H, CH_2Bpin), 3.60-3.64 (m, 1H, CHCN), 6.11 (dd, *J* = 15.8, 6.5 Hz, 1H, CH=CH), 6.65 (dd, *J* = 15.8, 0.6 Hz, 1H, CH=CH), 7.23-7.26 (m, 2H, ArCH), 7.46-7.48 (m, 2H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.9 (CH_3), 29.7 (*C*H-CN), 84.1 (*C*(CH_3)$_2$), 121.0 (*C*N), 122.0 (ArC), 125.7 (CH=CH), 128.0 (ArCH), 131.3 (CH=CH), 131.8 (ArCH), 134.8 (ArC), (*C*H_2B not observed)

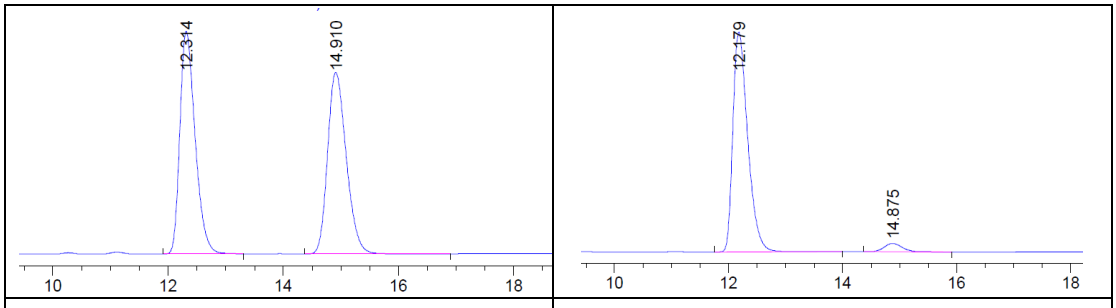
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.7.

HRMS (m/z, ESI): Calcd. for $C_{17}H_{21}BBrNO_2$ [M+H]: 362.0921, found: 362.0917.

ν_{max} (thin film/cm^{-1}): 2978, 2932, 2240, 1588, 1488, 1372, 1333, 1279, 1167, 1141, 1072, 1008, 966.

Specific rotation: $[\alpha]_D^{27}$+19.6 (c = 0.67, $CHCl_3$).

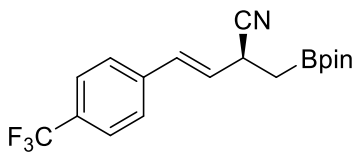
Enantiomeric purity of **4g** was determined by HPLC analysis in comparison with authentic racemic material (91% e.e. shown; OD-H column, 99:1 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.314	BB	0.2827	9016.60156	489.97684	49.9220
2	14.910	BB	0.3499	9044.77344	399.92865	50.0780

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.179	BB	0.2787	2.56971e4	1422.95996	95.5431
2	14.875	BB	0.3406	1198.73083	54.50460	4.4569

(*S,E*)-2-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(4-(trifluoromethyl)phenyl)but-3-enenitrile (4h)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 77%

NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a white solid (41 mg, 0.118 mmol, 59%). Melting Point: 35-37 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.27 (s, 12H, 4 x CH_3), 1.32 (dd, *J* = 16.2, 8.2 Hz, 1H, CH_2Bpin), 1.43 (dd, *J* = 16.2, 7.2 Hz, 1H, CH_2Bpin), 3.62-3.67 (m, 1H, CHCN), 6.21 (dd, *J* = 15.9, 6.4 Hz, 1H, CH=CH), 6.74 (d, *J* = 15.8 Hz, 1H, CH=CH), 7.45 (d, *J* = 8.2 Hz, 2H, ArCH), 7.58 (d, *J* = 8.3 Hz, 2H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 16.5 (*C*H_2Bpin), 24.8 (CH_3), 24.8 (CH_3), 29.7 (*C*H-CN), 84.1 (*C*$(CH_3)_2$), 120.8 (*C*N), 123.0 (q, *J* = 270.2 Hz, CF_3), 125.6 (q, *J* = 3.7 Hz, ArCH), 126.7 (CH=CH), 127.6 (ArCH), 129.6 (q, *J* = 32.1 Hz, ArC), 131.1 (CH=CH), 139.3 (ArC)

^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.4.

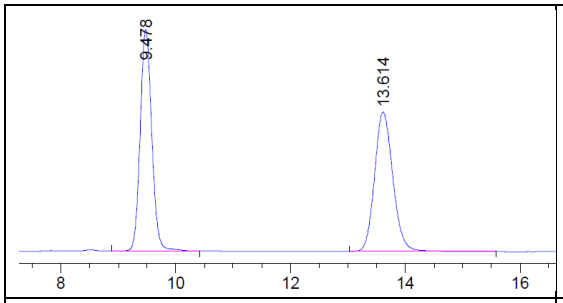
^{19}F NMR (470 MHz, $CDCl_3$) δ ppm -62.6.

HRMS (m/z, ESI): Calcd. for $C_{18}H_{21}BF_3NO_2$ [M+H]: 352.1690, found: 352.1690.

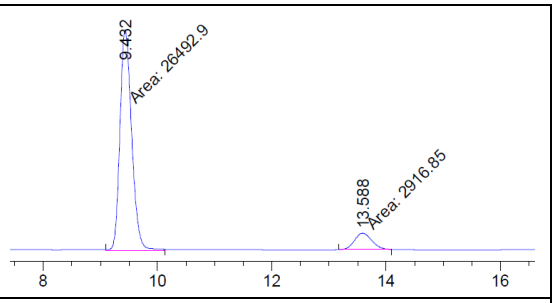
ν_{max} (thin film/cm^{-1}): 2980, 2242, 1616, 1373, 1323, 1268, 1165, 1122, 1067, 1016, 966.

Specific rotation: $[\alpha]_D^{27}$+19.1 (c = 1.31, $CHCl_3$).

Enantiomeric purity of **4h** was determined by HPLC analysis in comparison with authentic racemic material (80% e.e. shown; OD-H column, 99:1 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).

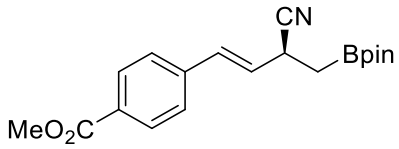


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.478	BB	0.2155	1809.83667	129.14993	50.0463
2	13.614	BB	0.3429	1806.48535	81.41520	49.9537



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.432	MM	0.2373	2.64929e4	1860.98889	90.0820
2	13.588	MM	0.3518	2916.84619	138.18604	9.9180

Methyl (*S,E*)-4-(3-cyano-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)benzoate (4i)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 80% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (39 mg, 0.114 mmol, 57%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.28 (s, 12H, 4 x CH_3), 1.34 (dd, *J* = 16.1, 8.2 Hz, 1H, CH_2Bpin), 1.45 (dd, *J* = 16.1, 7.2 Hz, 1H, CH_2Bpin), 3.64-3.68 (m, 1H, CHCN), 3.94 (s, 3H, CH_3), 6.24 (dd, *J* = 15.8, 6.4 Hz, 1H, CH=CH), 6.75 (d, *J* = 15.8 Hz, 1H, CH=CH), 7.43 (d, *J* = 8.3 Hz, 2H, ArCH), 8.01 (d, *J* = 8.2 Hz, 2H, ArCH). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.8 (CH_3), 29.7 (*C*H-CN), 52.1 (OCH_3), 84.1 (*C*$(CH_3)_2$), 120.8 (*C*N), 126.4 (ArCH), 127.6 (CH=CH), 129.6 (ArC), 130.0 (ArCH), 127.4 (ArCH), 131.5 (CH=CH), 140.3 (ArC), 166.7 (CO), (*C*H_2B not observed).

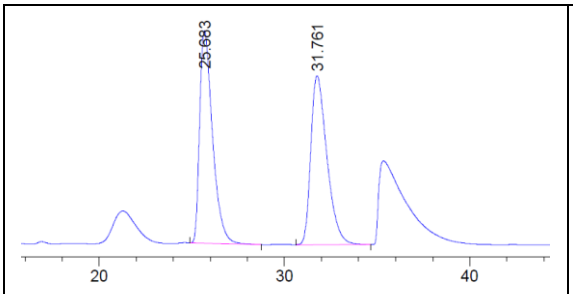
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.8.

HRMS (m/z, ESI): Calcd. for $C_{19}H_{24}BNO_4$ [M+H]: 324.1871, found: 324.1868.

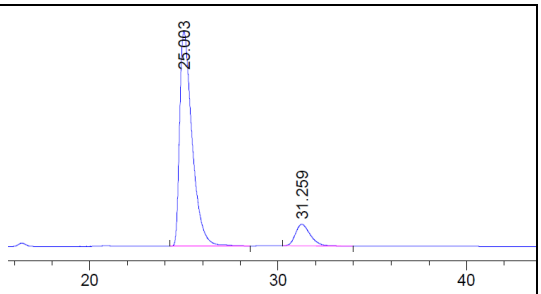
ν_{max} (thin film/cm^{-1}): 2979, 2242, 1720, 1608, 1436, 1372, 1334, 1278, 1178, 1141, 1109, 966.

Specific rotation: $[\alpha]_D^{27}$+2.8 (c = 1.15, $CHCl_3$).

Enantiomeric purity of **4i** was determined by HPLC analysis in comparison with authentic racemic material (79% e.e. shown; OD-H column, 99:1 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).

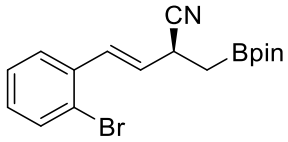


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.683	BB	0.7365	5337.39063	110.69483	50.0024
2	31.761	BB	0.9151	5336.86816	88.05579	49.9976



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.003	BB	0.6904	1.28490e4	280.53479	89.3585
2	31.259	BB	0.8262	1530.15613	28.14935	10.6415

(*S,E*)-4-(2-Bromophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4j)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 74% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (47 mg, 0.130 mmol, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.29 (s, 12H, 4 x CH_3), 1.35 (dd, *J* = 16.1, 8.1 Hz, 1H, CH_2Bpin), 1.45 (dd, *J* = 16.1, 7.3 Hz, 1H, CH_2Bpin), 3.65-3.69 (m, 1H, CHCN), 6.08 (dd, *J* = 15.7, 6.9 Hz, 1H, CH=CH), 6.49 (d, *J* = 15.8 Hz, 1H, CH=CH), 7.14-7.17 (m, 1H, ArCH), 7.30 (t, *J* = 7.5 Hz, 1H, ArCH), 7.47 (d, *J* = 7.8 Hz, 1H, ArCH), 7.57 (d, *J* = 8.0 Hz, 1H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.8 (CH_3), 29.8 (*C*H-CN), 84.1 (*C*(CH_3)$_2$), 121.0 (*C*N), 123.7 (ArC), 127.2 (CH=CH), 127.6 (ArCH), 127.9 (ArCH), 129.4 (ArCH), 131.5 (CH=CH), 133.1 (ArCH), 135.8 (ArC), (*C*H_2B not observed).

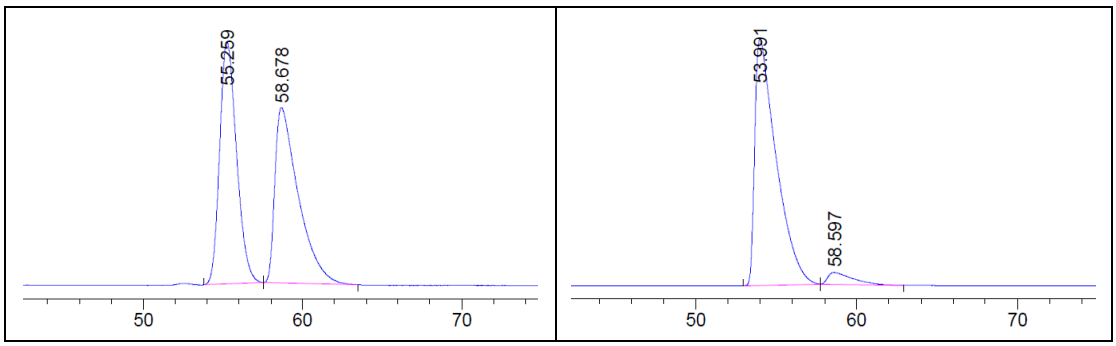
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.6.

HRMS (m/z, ESI): Calcd. for $C_{17}H_{21}BBr NO_2$ [M+H]: 362.0921, found: 362.0918.

ν_{max} (thin film/cm^{-1}): 3063, 2978, 2930, 2242, 1467, 1407, 1373, 1334, 1279, 1141, 966.

Specific rotation: $[\alpha]_D^{27}$+20.7 (c = 0.81, $CHCl_3$).

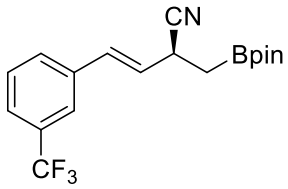
Enantiomeric purity of **4j** was determined by HPLC analysis in comparison with authentic racemic material (90% e.e. shown; OD-H column, 995:5 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	55.259	BB	1.0630	1911.04724	25.89570	49.8986
2	58.678	BB	1.3297	1918.81702	18.75432	50.1014

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	53.991	BB	1.3261	5.94354e4	641.97607	94.7802
2	58.597	BB	1.4677	3273.27563	30.41258	5.2198

(*S,E*)-2-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(3-(trifluoromethyl)phenyl)but-3-enenitrile (4k)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 82% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (51 mg, 0.146 mmol, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.28 (s, 12H, 4 x CH_3), 1.33 (dd, *J* = 16.1, 8.2 Hz, 1H, CH_2Bpin), 1.44 (dd, *J* = 16.1, 7.2 Hz, 1H, CH_2Bpin), 3.63-3.68 (m, 1H, CHCN), 6.21 (dd, *J* = 15.9, 6.4 Hz, 1H, CH=CH), 6.74 (dd, *J* = 15.9 Hz, 1 H, CH=CH), 7.45-7.48 (m, 1H, ArCH), 7.53 (d, *J* = 8.0 Hz, 2H, ArCH), 7.62 (s, 1H, ArCH). ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.7 (CH_3), 24.8 (CH_3), 29.6 (*C*H-CN), 84.2 (*C*$(CH_3)_2$), 120.8 (*C*N), 122.9 (q, *J* = 270.4 Hz, CF_3), 123.0 (q, *J* = 3.8 Hz, ArCH), 124.6 (q, *J* = 3.8 Hz, ArCH), 127.0 (CH=CH), 129.2 (ArCH), 129.7 (ArCH), 130.8 (q, *J* = 32.2 Hz, ArC), 131.0 (CH=CH), 136.7 (ArC), (*C*H_2B not observed)

^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.6.

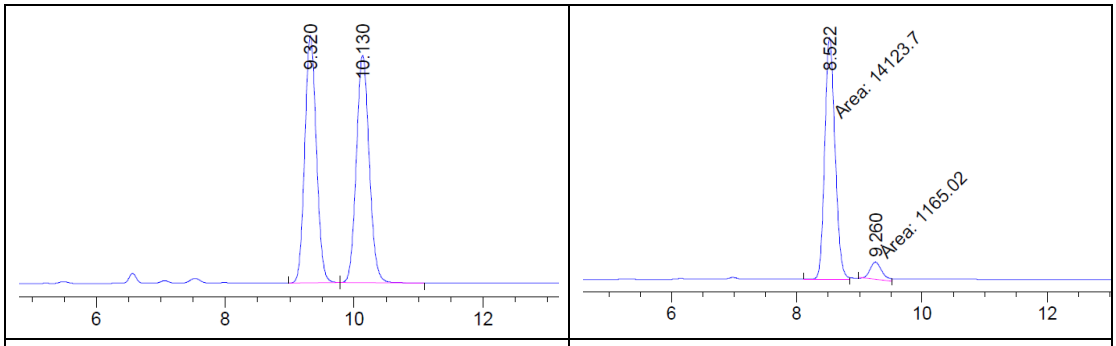
^{19}F NMR (470 MHz, $CDCl_3$) δ ppm -62.9.

HRMS (m/z, ESI): Calcd. for $C_{18}H_{21}BF_3NO_2$ [M+H]: 352.1690, found: 352.1685.

ν_{max} (thin film/cm^{-1}): 2980, 2241, 1409, 1372, 1327, 1164, 1123, 1072, 965.

Specific rotation: $[\alpha]_D^{27}$+12.1 (c = 1.21, $CHCl_3$).

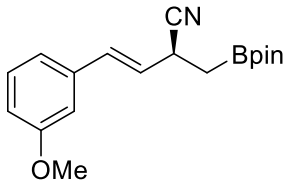
Enantiomeric purity of **4k** was determined by HPLC analysis in comparison with authentic racemic material (85% e.e. shown; OD-H column, 99:1 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.320	BB	0.1958	1307.57422	104.62811	49.4033
2	10.130	BB	0.2140	1339.16125	96.42029	50.5967

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.522	MM	0.1907	1.41237e4	1234.61011	92.3798
2	9.260	MM	0.2205	1165.02490	88.07177	7.6202

(*S*,*E*)-4-(3-Methoxyphenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4l)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 93% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (44 mg, 0.140 mmol, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.28 (s, 12H, 4 x CH_3), 1.32 (dd, *J* = 16.1, 8.2 Hz, 1H, CH_2Bpin), 1.42 (dd, *J* = 16.1, 7.2 Hz, 1H, CH_2Bpin), 3.60-3.65 (m, 1H, CHCN), 3.83 (s, 3H, CH_3), 6.11 (dd, *J* = 15.8, 6.5 Hz, 1H, CH=CH), 6.67 (d, *J* = 15.8 Hz, 1H, CH=CH), 6.83 (dd, *J* = 8.2, 2.3 Hz, 1H, ArCH), 6.90 (s, 1H, ArCH), 6.96 (d, *J* = 7.7 Hz, 1H, ArCH), 7.26 (t, *J* = 7.9 Hz, 1H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.9 (CH_3), 29.7 (*C*H-CN), 55.2 (OCH_3), 84.1 (*C*$(CH_3)_2$), 111.8 (ArCH), 113.8 (ArCH), 119.1 (ArCH), 121.2 (*C*N), 125.2 (CH=CH), 129.7 (ArCH), 132.3 (CH=CH), 137.3 (ArC), 159.8 (ArC), (*C*H_2B not observed)

^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.8.

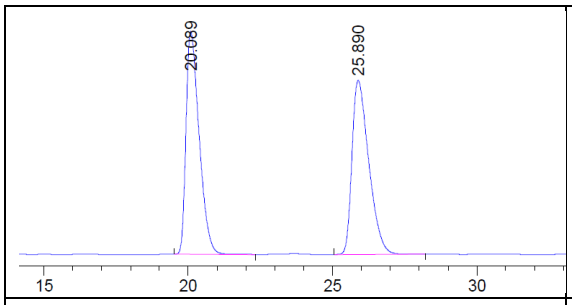
HRMS (m/z, ESI): Calcd. for $C_{18}H_{24}BNO_3$ [M+H]: 314.1922, found: 314.1914.

ν_{max} (thin film/cm^{-1}): 2978, 2241, 1599, 1580, 1372, 1333, 1266, 1141, 1042, 966.

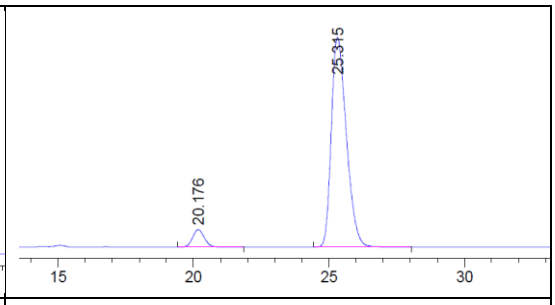
Specific rotation: $[\alpha]_D^{27}$+13.8 (c = 0.50, $CHCl_3$).

Enantiomeric purity of **4l** was determined by HPLC analysis in

comparison with authentic racemic material (88% e.e. shown; OD-H column, 99:1 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).

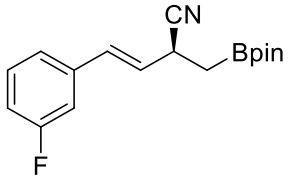


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.320	BB	0.1958	1307.57422	104.62811	49.4033
2	10.130	BB	0.2140	1339.16125	96.42029	50.5967



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.176	BB	0.4641	1150.02661	38.53820	6.0567
2	25.315	BB	0.5960	1.78376e4	462.45102	93.9433

(*S,E*)-4-(3-Fluorophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4m)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 85% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (50 mg, 0.166 mmol, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.28 (s, 12H, 4 x CH_3), 1.32 (dd, *J* = 16.1, 8.2 Hz, 1H, CH_2Bpin), 1.42 (dd, *J* = 16.1, 7.1 Hz, 1H, CH_2Bpin), 3.61-3.66 (m, 1H, CHCN), 6.13 (dd, *J* = 15.8, 6.5 Hz, 1H, CH=CH), 6.49 (d, *J* = 15.8 Hz, 1H, CH=CH), 6.96 (dt, *J* = 8.4, 2.4 Hz, 1H, ArCH), 7.07 (d, *J* = 10.0 Hz, 1H, ArCH), 7.13 (d, *J* = 7.7 Hz, 1H, ArCH), 7.28-7.33 (m, 1H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.8 (CH_3), 29.6 (*C*H-CN), 84.1 (*C*$(CH_3)_2$), 112.9 (d, *J* = 21.1 Hz, ArCH), 114.9 (d, *J* = 21.3 Hz, ArCH), 120.9 (*C*N), 122.5 (d, *J* = 2.3 Hz, ArCH), 126.4 (CH=CH), 130.1 (d, *J* = 8.6 Hz, ArCH), 131.3 (d, *J* = 2.7 Hz, CH=CH), 138.2 (d, *J* = 7.8 Hz, ArC), 162.1 (d, *J* = 244.1 Hz, ArC), (*C*H_2B not observed).

^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.8.

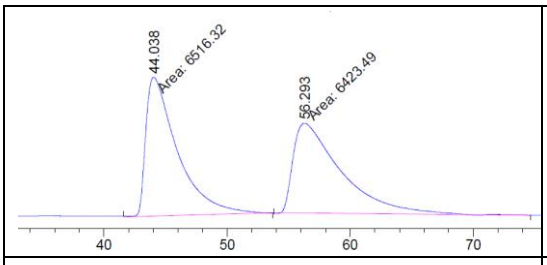
^{19}F NMR (470 MHz, $CDCl_3$) δ ppm -113.2.

HRMS (m/z, ESI): Calcd. for $C_{17}H_{21}BFNO_2$ [M+Na]: 324.1542, found: 325.1538.

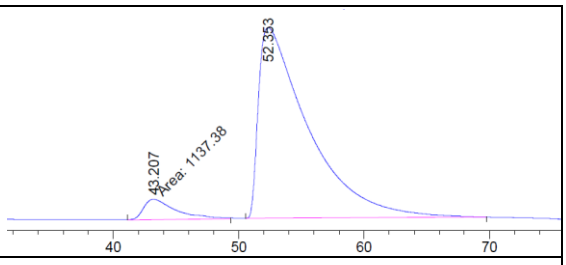
ν_{max} (thin film/cm^{-1}): 2979, 2932, 2241, 1611, 1583, 1487, 1371, 1332, 1267, 1166, 1140, 965.

Specific rotation: $[\alpha]_D^{27}$+13.4 (c = 1.11, $CHCl_3$).

Enantiomeric purity of **4m** was determined by HPLC analysis in comparison with authentic racemic material (87% e.e. shown; IA-H column, 998:2 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).

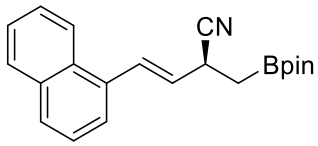


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.038	MM	2.9585	6516.31592	36.70946	50.3587
2	56.293	MM	4.5164	6423.49170	23.70438	49.6413



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.207	MM	2.9613	1137.37891	6.40124	6.4068
2	52.353	BB	3.5251	1.66153e4	59.80850	93.5932

(*S,E*)-4-(Naphthalen-1-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4n)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 76% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (49 mg, 0.148 mmol, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.30 (s, 12H, 4 x CH_3), 1.43 (dd, *J* = 16.2, 8.3 Hz, 1H, CH_2Bpin), 1.52 (dd, *J* = 16.2, 7.0 Hz, 1H, CH_2Bpin), 3.74-3.79 (m, 1H, CHCN), 6.16 (dd, *J* = 15.6, 6.4 Hz, 1H, CH=CH), 7.46-7.57 (m, 5H, ArCH and CH=CH), 7.82 (d, *J* = 8.2 Hz, 1H, ArCH), 7.87-7.89 (m, 1H, ArCH), 8.13 (d, *J* = 8.1 Hz, 1H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.9 (CH_3), 30.0 (*C*H-CN), 84.1 (*C*(CH_3)$_2$), 121.3 (*C*N), 123.8 (CH=CH), 124.1 (ArCH), 125.6 (ArCH), 126.0 (ArCH), 126.3 (ArCH),

128.1 (ArCH), 128.5 (ArCH), 128.6 (ArCH), 129.9 (CH=CH), 131.0 (ArC), 133.6 (ArC), 133.7 (ArC), (*C*H_2B not observed).

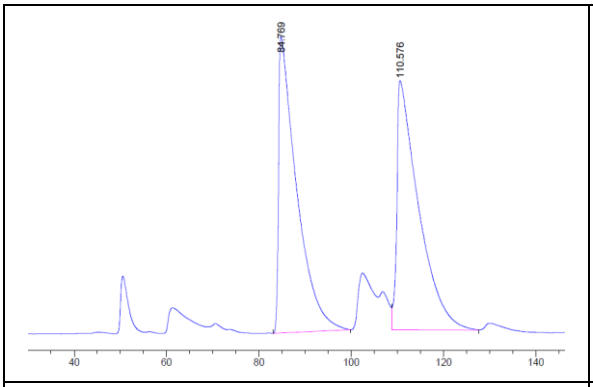
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.8.

HRMS (m/z, ESI): Calcd. for $C_{21}H_{24}BNO_2$ [M+H]:334.1973, found: 334.1918.

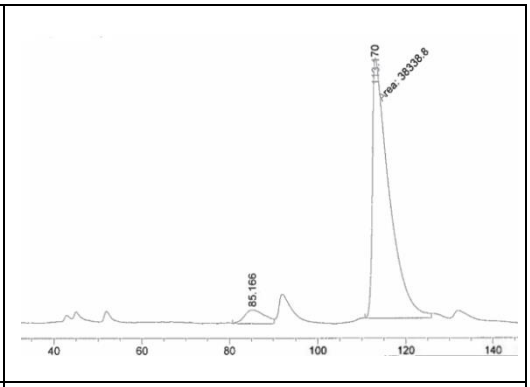
ν_{max} (thin film/cm^{-1}): 3060, 2977, 2932, 2239, 1591, 1508, 1371, 1333, 1272, 1040, 965.

Specific rotation: $[\alpha]_D^{27}$+24.8 (c = 0.55, $CHCl_3$).

Enantiomeric purity of **4n** was determined by HPLC analysis in comparison with authentic racemic material (89% e.e. shown; IB-H column, 998:2 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 210 nm).

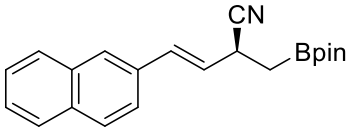


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	84.769	BB	3.3783	1.44640e5	533.77832	49.6861
2	110.576	VB	4.0909	1.46467e5	448.85458	50.3139



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	85.166	VV	3.7872	2417.86694	7.53520	5.4667
2	113.170	MM	4.6622	4.18112e4	149.46782	94.5333

(*S,E*)-4-(Naphthalen-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4o)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 88% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a white solid (57 mg, 0.172 mmol, 86%). Melting Point: 52-53 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.29 (s, 12H, 4 x CH_3), 1.37 (dd, *J* = 16.1, 8.2 Hz, 1H, CH_2Bpin), 1.47 (dd, *J* = 16.1, 7.2 Hz, 1H, CH_2Bpin), 3.67-3.72 (m, 1H, CHCN), 6.24 (dd, *J* = 15.8, 6.6 Hz, 1H, CH=CH), 6.87 (d, *J* = 15.7 Hz, 1H, CH=CH), 7.46-7.53 (m, 2H, ArCH),

7.56 (dd, *J* = 8.6, 1.7 Hz, 1H, ArCH), 7.76 (s, 1H, ArCH), 7.81-7.84 (m, 3H, ArCH).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.9 (CH_3), 29.8 (*C*H-CN), 84.1 (*C*(CH_3)$_2$), 121.3 (*C*N), 123.3 (CH=CH), 125.2 (ArCH), 126.2 (ArCH), 126.4 (ArCH), 126.8 (ArCH), 127.7 (ArCH), 128.0 (ArCH), 128.4 (ArCH), 132.5 (CH=CH), 133.2 (ArC), 133.3 (ArC), 133.5 (ArC), (*C*H_2B not observed).

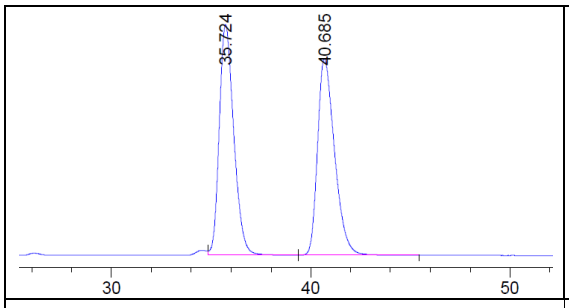
^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 32.5.

HRMS (m/z, ESI): Calcd. for $C_{21}H_{24}BNO_2$ [M+H]: 334.1973, found: 334.1971.

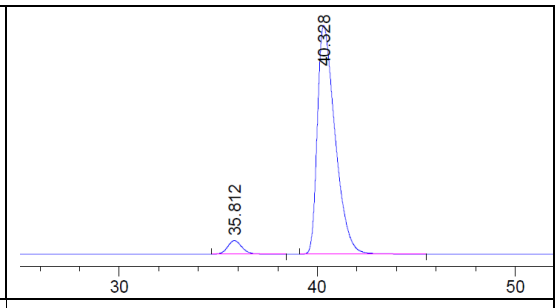
ν_{max} (thin film/cm^{-1}): 2977, 2930, 2240, 1739, 1508, 1407, 1371, 1334, 1271, 1141, 965.

Specific rotation: $[\alpha]_D^{27}$+30.3 (c = 0.78, $CHCl_3$).

Enantiomeric purity of **4o** was determined by HPLC analysis in comparison with authentic racemic material (91% e.e. shown; OD-H column, 99:1 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).

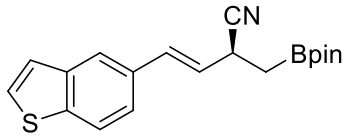


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.724	VB	0.7795	2.13192e4	420.46658	50.0335
2	40.685	BB	0.9095	2.12906e4	358.18857	49.9665



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.812	BB	0.7696	2233.87427	44.65767	4.4972
2	40.328	BB	0.9484	4.74391e4	761.96033	95.5028

(*S,E*)-4-(Benzo[b]thiophen-5-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4p)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 93% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a white solid (61 mg, 0.180 mmol, 90%). Melting Point: 45-47 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.28 (s, 12H, 4 x CH_3), 1.36 (dd, *J* = 16.1, 8.3 Hz, 1H,

CH_2Bpin), 1.46 (dd, *J* = 16.1, 7.1 Hz, 1H, CH_2Bpin), 3.65-3.69 (m, 1H, CHCN), 6.17 (dd, *J* = 15.8, 6.6 Hz, 1H, CH=CH), 6.65 (d, *J* = 15.8 Hz, 1H, CH=CH), 7.33 (d, *J* = 5.4 Hz, 1H, ArCH), 7.40 (d, *J* = 8.5 Hz, 1H, ArCH), 7.46 (d, *J* = 5.4 Hz, 1H, ArCH), 7.79 (s, 1H, ArCH), 7.83 (d, *J* = 8.4 Hz, 1H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.9 (CH_3), 29.8 (*C*H-CN), 84.1 (*C*(CH_3)$_2$), 121.3 (*C*N), 122.1 (ArCH), 122.4 (ArCH), 122.7 (ArCH), 123.9 (ArCH), 124.5 (CH=CH), 127.2 (ArCH), 132.3 (ArC), 132.5 (CH=CH), 139.4 (ArC), 140.0 (ArC), (*C*H_2B not observed)

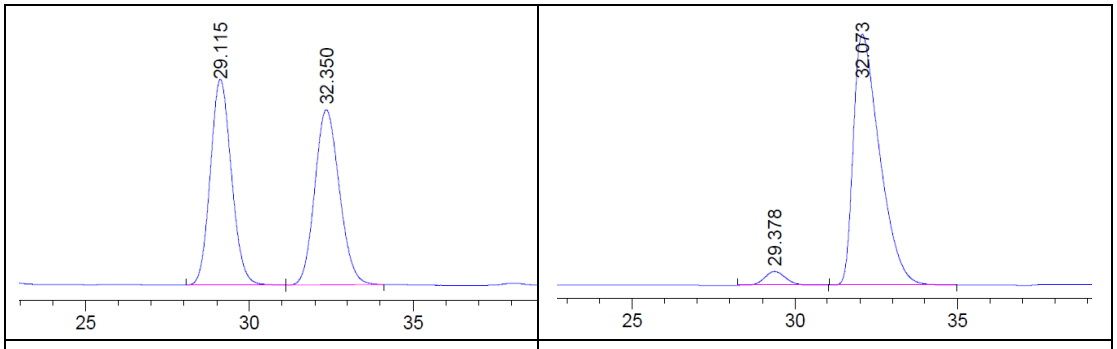
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.8.

HRMS (m/z, ESI): Calcd. for $C_{19}H_{22}BSNO_2$ [M+H]: 340.1537, found: 340.1535.

ν_{max} (thin film/cm^{-1}): 2977, 2930, 2239, 1468, 1406, 1371, 1331, 1270, 1166, 1141, 1050, 965.

Specific rotation: $[\alpha]_D^{27}$+21.4 (c = 1.20, $CHCl_3$).

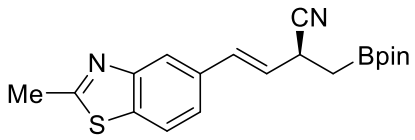
Enantiomeric purity of **4p** was determined by HPLC analysis in comparison with authentic racemic material (92% e.e. shown; OD-H column, 90:10 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.115	BB	0.6975	2665.99634	59.40943	50.2262
2	32.350	BB	0.8061	2641.98560	50.52069	49.7738

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.378	BB	0.6914	2488.99438	55.68920	4.1879
2	32.073	BB	0.8432	5.69438e4	1014.00031	95.8121

(*S,E*)-4-(2-Methylbenzo[d]thiazol-5-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4q)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 81%

NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/10/1) afforded the title compound as a colorless oil (55 mg, 0.156 mmol, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.28 (s, 12H, 4 x CH_3), 1.35 (dd, *J* = 16.0, 8.3 Hz, 1H, CH_2Bpin), 1.45 (dd, *J* = 16.1, 6.9 Hz, 1H, CH_2Bpin), 2.85 (s, 3H, CH_3), 3.65-3.69 (m, 1H, CHCN), 6.19 (dd, *J* = 15.8, 6.5 Hz, 1H, CH=CH), 6.82 (d, *J* = 15.8 Hz, 1H, CH=CH), 7.39 (d, *J* = 8.3 Hz, 1H, ArCH), 7.77 (d, *J* = 8.3 Hz, 1H, ArCH), 7.91 (s, 1H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 20.2 (CH_3), 24.8 (CH_3), 24.9 (CH_3), 29.7 (*C*H-CN), 84.1 (*C*$(CH_3)_2$), 120.3 (ArCH), 121.2 (*C*N), 121.5 (ArCH), 123.1 (CH=CH), 125.3 (ArCH), 132.2 (CH=CH), 134.2 (ArC), 135.3 (ArC), 153.9 (ArC), 167.9 (ArC), (*C*H_2B not observed).

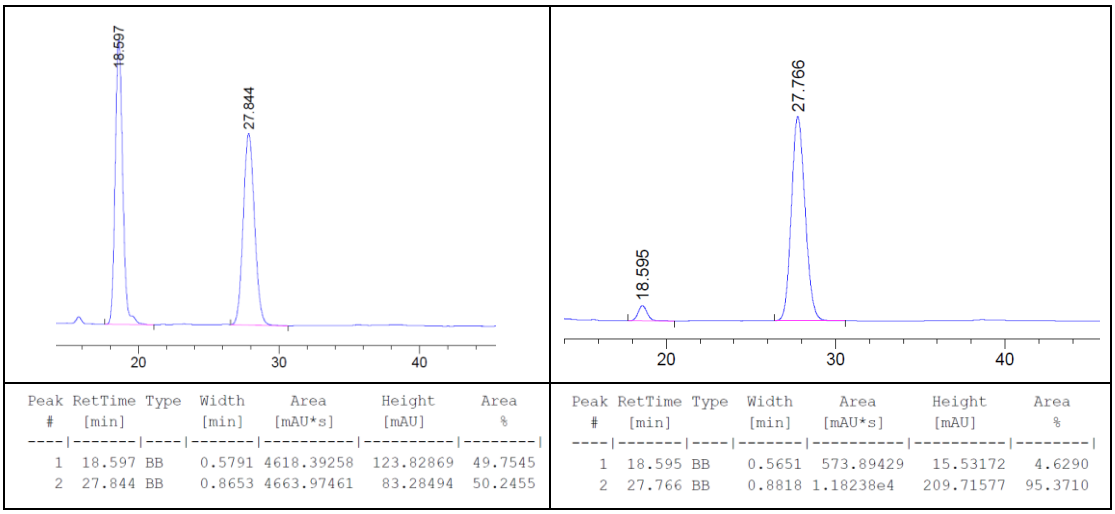
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 31.9.

HRMS (m/z, ESI): Calcd. for $C_{19}H_{23}BSN_2O_2$ [M+H]: 355.1646, found: 355.1641.

ν_{max} (thin film/cm^{-1}): 2978, 2239, 1610, 1517, 1446, 1372, 1332, 1157, 1091.

Specific rotation: $[\alpha]_D^{27}$+11.4 (c = 2.30, $CHCl_3$).

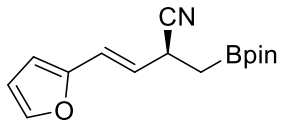
Enantiomeric purity of **4q** was determined by HPLC analysis in comparison with authentic racemic material (91% e.e. shown; OD-H column, 90:10 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.597	BB	0.5791	4618.39258	123.82869	49.7545
2	27.844	BB	0.8653	4663.97461	83.28494	50.2455

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.595	BB	0.5651	573.89429	15.53172	4.6290
2	27.766	BB	0.8818	1.18238e4	209.71577	95.3710

(*S*,*E*)-4-(Furan-2-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4r)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 88% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (42 mg, 0.154 mmol, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.27 (s, 12H, 4 x CH_3), 1.28 (dd, *J* = 16.1, 8.1 Hz, 1H, CH_2Bpin), 1.40 (dd, *J* = 16.1, 7.4 Hz, 1H, CH_2Bpin), 3.58-3.62 (m, 1H, CHCN), 6.06 (dd, *J* = 15.8, 6.4 Hz, 1H, CH=CH), 6.28 (d, *J* = 3.3 Hz, 1H, ArCH), 6.38-6.39 (m, ArCH), 6.51 (d, *J* = 15.8 Hz, 1H, CH=CH), 7.36 (d, *J* = 0.8 Hz, 1H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.8 (CH_3), 29.5 (*C*H-CN), 84.1 (*C*(CH_3)$_2$), 109.0 (ArCH), 111.4 (ArCH), 119.4 (ArCH), 121.0 (*C*N), 123.4 (CH=CH), 142.4 (CH=CH), 151.4 (ArC), (*C*H_2B not observed).

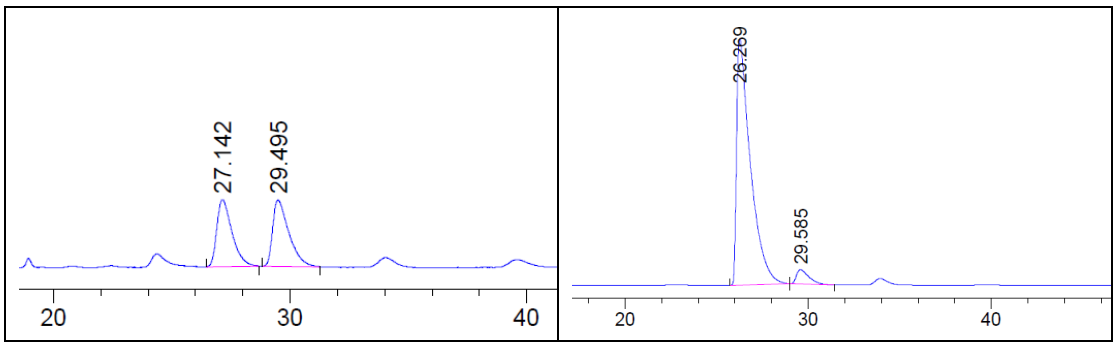
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.5.

HRMS (m/z, ESI): Calcd. for $C_{15}H_{20}BNO_3$ [M+Na]: 296.1428, found: 296.1418.

ν_{max} (thin film/cm^{-1}): 2979, 2932, 2243, 1788, 1682, 1372, 1333, 1271, 1167, 1140, 966.

Specific rotation: $[\alpha]_D^{27}$+12.8 (c = 0.70, $CHCl_3$).

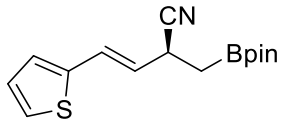
Enantiomeric purity of **4r** was determined by HPLC analysis in comparison with authentic racemic material (90% e.e. shown; OD-H column, 998:2 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.145	BB	0.6784	1916.31323	42.63267	49.7029
2	29.498	BB	0.7106	1939.22229	40.35392	50.2971

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.269	BB	0.7458	3.29915e4	629.08618	94.9950
2	29.585	BB	0.6991	1738.23340	36.79716	5.0050

(*S,E*)-2-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-4-(thiophen-2-yl)but-3-enenitrile (4s)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 80% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (45 mg, 0.156 mmol, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.27 (s, 12H, 4 x CH_3), 1.29 (dd, *J* = 16.1, 8.4 Hz, 1H, CH_2Bpin), 1.41 (dd, *J* = 16.1, 7.1 Hz, 1H, CH_2Bpin), 3.56-3.61 (m, 1H, CHCN), 5.95 (dd, *J* = 15.7, 6.4 Hz, 1H, CH=CH), 6.82 (d, *J* = 15.7 Hz, 1H, CH=CH), 6.97-6.98 (m, 2H, ArCH), 7.18-19 (m, 1H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.7 (CH_3), 24.9 (CH_3), 29.5 (*C*H-CN), 84.1 (*C*(CH_3)$_2$), 121.0 (*C*N), 124.3 (ArCH), 124.9 (CH=CH), 125.5 (ArCH), 126.5 (ArCH), 127.5 (CH=CH), 140.7 (ArC), (*C*H_2B not observed).

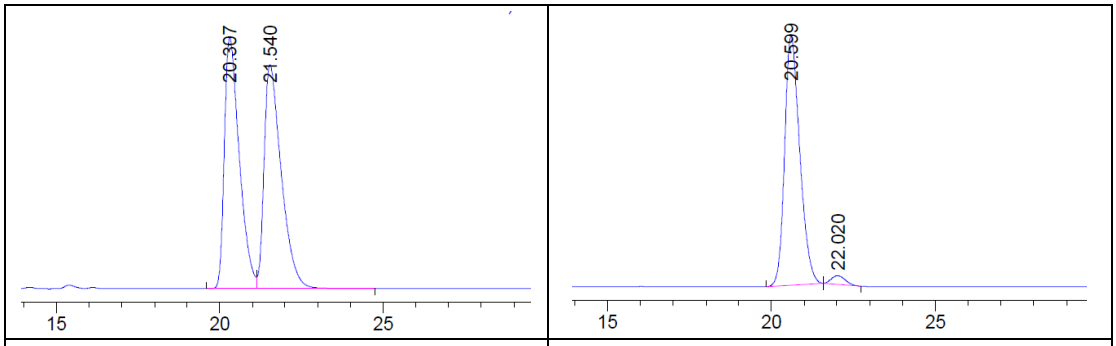
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.5.

HRMS (m/z, ESI): Calcd. for $C_{15}H_{20}BSNO_2$ [M+H]: 290.1381, found: 290.1377.

ν_{max} (thin film/cm^{-1}): 2978, 2932, 2241, 1647, 1470, 1407, 1372, 1333, 1271, 1167, 1141, 965.

Specific rotation: $[\alpha]_D^{27}$+10.7 (c = 0.71, $CHCl_3$).

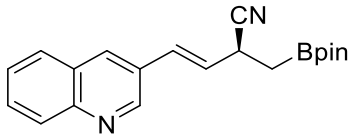
Enantiomeric purity of **4s** was determined by HPLC analysis in comparison with authentic racemic material (94% e.e. shown; OD-H column, 998:2 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.307	BV	0.4800	1.12030e4	353.23157	49.2117
2	21.540	VB	0.5517	1.15618e4	315.37286	50.7883

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.599	BB	0.4901	2865.95703	89.37000	96.8824
2	22.020	BB	0.4353	92.22459	3.13436	3.1176

(*S*,*E*)-4-(Quinolin-3-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4t)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 76% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (using deactivated silica, Hexane/EtOAc/CH_2Cl_2 = 10/1/1) afforded the title compound as a colorless oil (48 mg, 0.144 mmol, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.29 (s, 12H, 4 x CH_3), 1.39 (dd, *J* = 16.2, 8.4 Hz, 1H, CH_2Bpin), 1.49 (dd, *J* = 16.2, 7.0 Hz, 1H, CH_2Bpin), 3.70-3.75 (m, 1H, CHCN), 6.38 (dd, *J* = 16.0, 6.3 Hz, 1H, CH=CH), 6.89 (d, *J* = 15.7 Hz, 1H, CH=CH), 7.58 (t, *J* = 7.3 Hz, 1H, ArCH), 7.70-7.74 (m, 1H, ArCH), 7.82 (d, *J* = 8.2 Hz, 1H, ArCH), 8.07-8.11 (m, 2H, ArCH), 9.00 (d, *J* = 2.2 Hz, 1H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.9 (CH_3), 29.9 (*C*H-CN), 84.2 (*C*(CH_3)$_2$), 120.8 (*C*N), 127.2 (CH=CH), 127.3 (ArCH), 127.9 (ArC), 127.9 (ArCH), 128.8 (ArC), 129.3 (ArCH), 129.3 (ArCH), 129.6 (ArCH), 133.1 (CH=CH), 147.7 (ArC), 148.9 (ArCH), (*C*H_2B not observed)

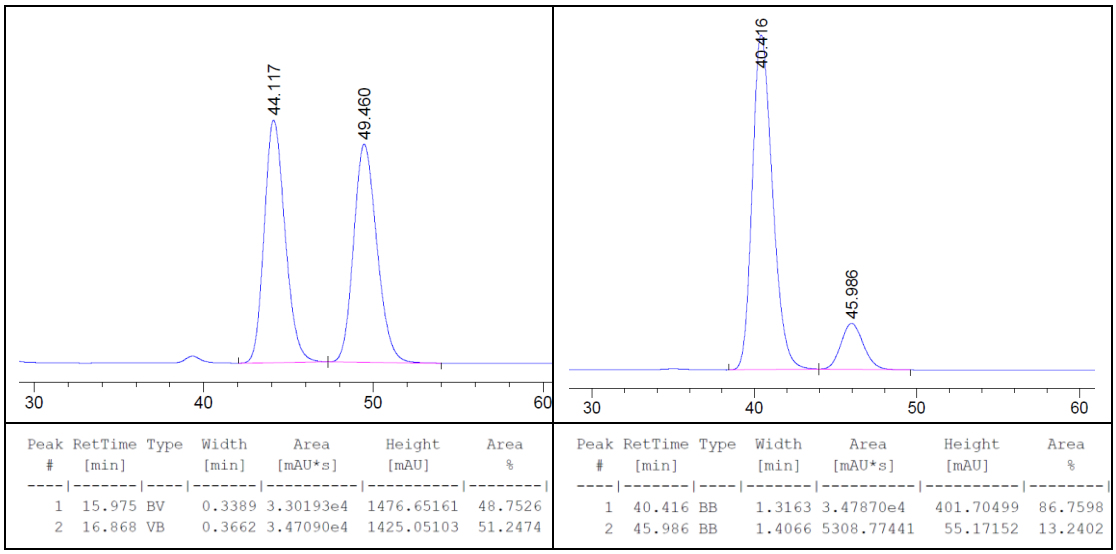
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 33.2.

HRMS (m/z, ESI): Calcd. for $C_{20}H_{23}BN_2O_2$ [M+H]: 335.1925, found: 335.1915.

ν_{max} (thin film/cm^{-1}): 2977, 2241, 1611, 1518, 1371, 1333, 1158, 1141, 1092, 965.

Specific rotation: $[\alpha]_D^{27}$+9.1 (c = 2.70, $CHCl_3$).

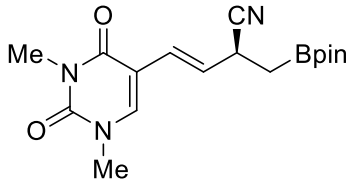
Enantiomeric purity of **4t** was determined by HPLC analysis in comparison with authentic racemic material (74% e.e. shown; OD-H column, 90:10 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.975	BV	0.3389	3.30193e4	1476.65161	48.7526
2	16.868	VB	0.3662	3.47090e4	1425.05103	51.2474

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.416	BB	1.3163	3.47870e4	401.70499	86.7598
2	45.986	BB	1.4066	5308.77441	55.17152	13.2402

(*S,E*)-4-(1,3-Dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-5-yl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4u)



Prepared according to the General Procedure on a 0.2 mmol scale (=7:1 *rs* and 54% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (using deactivated silica, Hexane/EtOAc/CH_2Cl_2 = 10/1/1) afforded the title compound as a white solid (34 mg, 0.098 mmol, 49%). Melting Point: 72-74 ^oC.

^1H NMR (500 MHz, $CDCl_3$) δ ppm 1.24-1.30 (m, 13H, 4 x CH_3 and 1H from CH_2Bpin), 1.35 (dd, *J* = 16.1, 7.9 Hz, 1H, CH_2Bpin), 3.37 (s, 3H, CH_3), 3.45 (s, 3H, CH_3), 3.55-3.60 (m, 1H, CHCN), 6.32 (d, *J* = 15.5 Hz, 1H, CH=CH), 6.64 (dd, *J* = 15.7, 6.2 Hz, 1H, CH=CH), 7.22 (s, 1H, CH=C).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.8 (CH_3), 28.1 (*C*H-CN), 30.2 (CH_3), 37.2 (CH_3), 84.1 (*C*(CH_3)$_2$), 109.8 (*C*=CH), 120.1 (*C*N), 123.7 (CH=CH), 126.6 (*C*H=C), 140.9 (CH=CH), 151.0 (C=O), 161.8 (C=O), (*C*H_2B not observed)

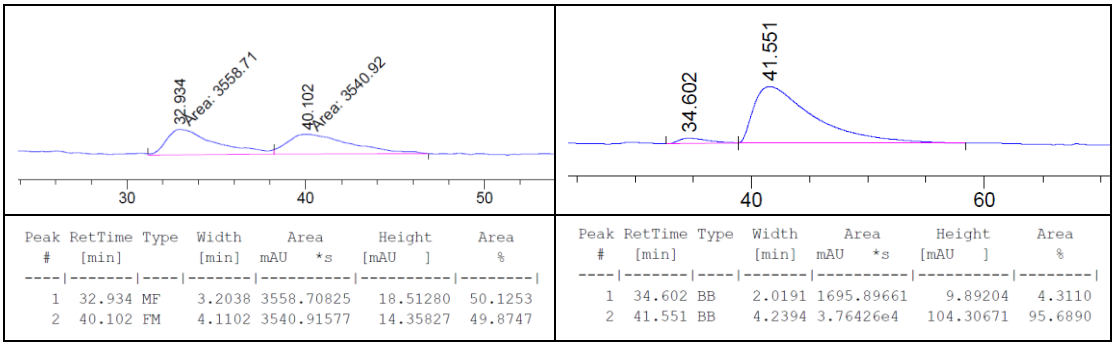
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.2.

HRMS (m/z, ESI): Calcd. for $C_{17}H_{24}BN_3O_4$ [M+Na]: 368.1752, found: 368.1750.

ν_{max} (thin film/cm^{-1}): 2978, 2240, 1705, 1611, 1455, 1371, 1143, 1091, 967.

Specific rotation: $[\alpha]_D^{27}$-25.2 (c = 0.30, $CHCl_3$).

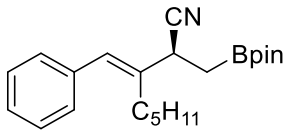
Enantiomeric purity of **4u** was determined by HPLC analysis in comparison with authentic racemic material (90% e.e. shown; AD-H column, 90:10 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 210 nm).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.934	MF	3.2038	3558.70825	18.51280	50.1253
2	40.102	FM	4.1102	3540.91577	14.35827	49.8747

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.602	BB	2.0191	1695.89661	9.89204	4.3110
2	41.551	BB	4.2394	3.76426e4	104.30671	95.6890

(*S*,*E*)-3-Benzylidene-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)octanenitrile (4v)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 55% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (36 mg, 0.102 mmol, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.87 (t, *J* = 6.8 Hz, 3H, CH_3), 1.28-1.31 (m, 16H, 4 x CH_3 and 2 x CH_2), 1.45 (d, *J* = 8.0 Hz, 2H, CH_2Bpin), 1.50-1.56 (m, 2H, CH_2), 2.26-2.32 (m, 1H, CH_2), 2.35-2.41 (m, 1H, CH_2), 3.56 (t, *J* = 8.0 Hz, 1H, CHCN), 6.62 (s, 1H, CH=C), 7.22-7.28 (m, 3H, ArCH), 7.34-7.37 (m, 2H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 14.0 (CH_3), 22.3 (CH_2), 24.8 (CH_3), 24.9 (CH_3), 28.1 (CH_2), 29.9 (CH_2), 31.8 (CH_2), 33.2 (*C*H-CN), 84.0 (*C*(CH_3)$_2$), 121.9 (*C*N), 126.9 (CH=C), 128.1 (ArCH), 128.3 (ArCH), 128.5 (ArCH), 137.0 (*C*=CH), 138.6 (ArC), (*C*H_2B not observed)

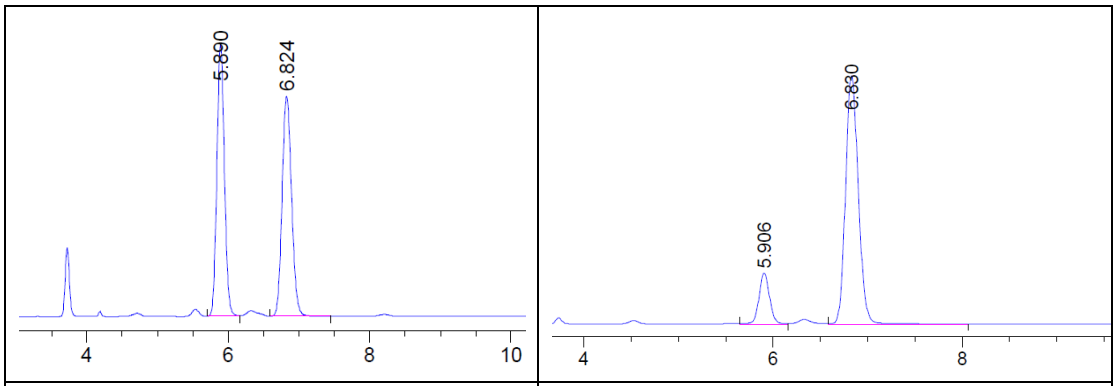
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.6.

HRMS (m/z, ESI): Calcd. for $C_{22}H_{32}BNO_2$ [M+Na]: 376.2418, found: 376.2407.

ν_{max} (thin film/cm^{-1}): 2956, 2930, 2858, 2236, 1465, 1369, 1332, 1280, 1166, 1141, 1009, 966.

Specific rotation: $[\alpha]_D^{27}$-6.9 (c = 0.45, $CHCl_3$).

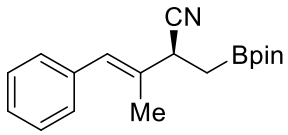
Enantiomeric purity of **4v** was determined by HPLC analysis in comparison with authentic racemic material (71% e.e. shown; OD-H column, 99:1 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.890	BV	0.1145	9790.96582	1320.70654	49.8372
2	6.824	VB	0.1441	9854.94043	1064.02686	50.1628

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.906	VV	0.1197	2565.62573	333.73590	14.3943
2	6.830	VB	0.1447	1.52583e4	1637.64307	85.6057

(*S,E*)-3-Methyl-4-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4w)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 63% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a

colorless oil (34 mg, 0.114 mmol, 57%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.27 (s, 6H, 2 x CH_3), 1.28 (s, 6H, 2 x CH_3), 1.38 (dd, *J* = 15.9, 7.9 Hz, 1H, CH_2Bpin), 1.42 (dd, *J* = 15.9, 8.1 Hz, 1H, CH_2Bpin), 1.98 (s, 3H, CH_3), 3.57 (t, *J* = 8.0 Hz, 1H, CHCN), 6.57 (s, 1H, CH=C), 7.24-7.28 (m, 3H, ArCH), 7.35-7.38 (m, 2H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 15.3 (CH_3), 24.8 (CH_3), 24.8 (CH_3), 36.3 (*C*H-CN), 84.0 (*C*(CH_3)$_2$), 121.5 (*C*N), 126.9 (*C*H=C), 128.2 (ArCH), 128.3 (ArCH), 128.9 (ArCH), 133.5 (*C*=CH), 136.8 (ArC), (*C*H_2B not observed).

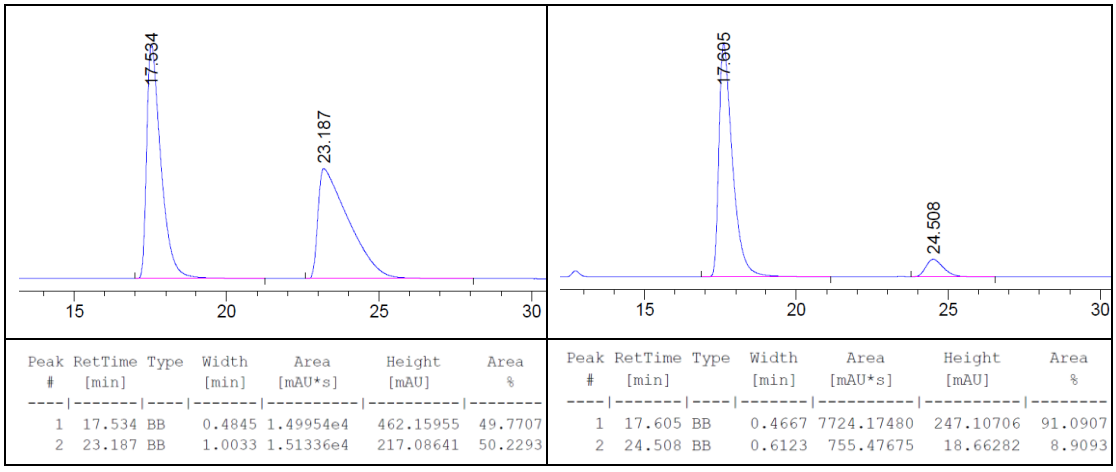
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.9.

HRMS (m/z, ESI): Calcd. for $C_{18}H_{24}BNO_2$ [M+Na]: 320.1792, found: 320.1789.

ν_{max} (thin film/cm^{-1}): 2978, 2932, 2235, 1600, 1448, 1405, 1333, 1263, 1167, 1141, 966.

Specific rotation: $[\alpha]_D^{27}$+22.3 (c = 1.01, $CHCl_3$).

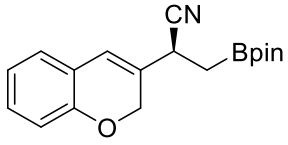
Enantiomeric purity of **4w** was determined by HPLC analysis in comparison with authentic racemic material (82% e.e. shown; OD-H column, 99:1 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.534	BB	0.4845	1.49954e4	462.15955	49.7707
2	23.187	BB	1.0033	1.51336e4	217.08641	50.2293

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.605	BB	0.4667	7724.17480	247.10706	91.0907
2	24.508	BB	0.6123	755.47675	18.66282	8.9093

(*S*)-2-(2H-Chromen-3-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanenitrile (4x)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 63% NMR yield of crude material using $MeNO_2$ as internal standard). Column

chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (34 mg, 0.114 mmol, 57%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.27 (s, 12H, 4 x CH_3), 1.36-1.47 (m, 2H, CH_2Bpin), 3.52 (t, *J* = 7.8 Hz, 1H, CHCN), 4.80 (s, 2H, CH_2), 6.51 (s, 1H, CH=C), 6.82 (d, *J* = 8.1 Hz, 1H, ArCH), 6.89 (t, *J* = 7.5 Hz, 1H, ArCH), 7.01 (d, *J* = 7.4 Hz, 1H, ArCH), 7.15 (t, *J* = 6.7 Hz, 1H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.7 (CH_3), 24.8 (CH_3), 30.3 (d, *J* = 2.2 Hz, *C*H-CN), 66.1 (CH_2), 84.3 (*C*(CH_3)$_2$), 115.6 (ArCH), 119.9 (*C*N), 121.7 (ArC), 121.7 (ArCH), 122.0 (d, *J* = 2.9 Hz, *C*H=C), 126.9 (ArCH), 128.8 (*C*=CH), 129.6 (ArCH), 153.1 (ArC), (CH_2B not observed).

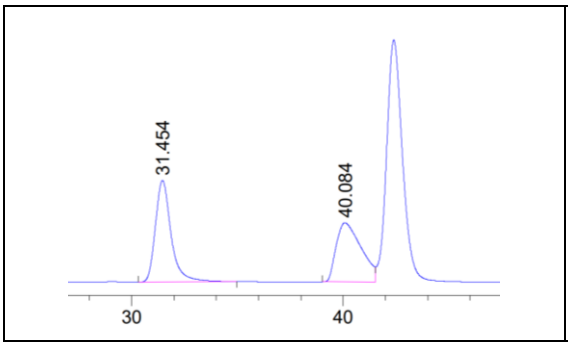
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.2.

HRMS (m/z, ESI): Calcd. for $C_{18}H_{22}BNO_3$ [M+H]: 312.1766, found: 312.1762.

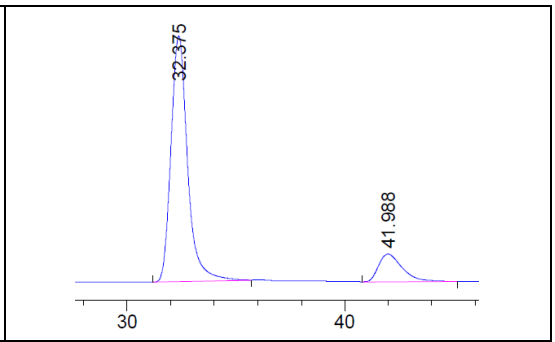
ν_{max} (thin film/cm^{-1}): 2978, 2932, 2242, 1714, 1607, 1579, 1488, 1460, 1372, 1336, 1280, 1167, 1141, 1038.

Specific rotation: $[\alpha]_D^{27}$-0.6 (c = 1.9, $CHCl_3$).

Enantiomeric purity of **4x** was determined by HPLC analysis in comparison with authentic racemic material (72% e.e. shown; IA-H column, 99:1 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).

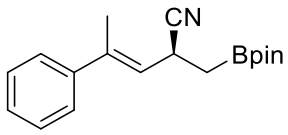


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.454	BB	0.7858	2545.08472	49.17488	52.1765
2	40.084	BV	1.1673	2332.75586	28.60899	47.8235



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.375	BB	0.8093	4499.84326	84.77016	86.1012
2	41.988	BB	0.9477	726.38440	9.56828	13.8988

(*S*,*E*)-4-Phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pent-3-enenitrile (4y)



Prepared according to the General Procedure on a 0.2 mmol scale (13:1 *rs* and 35% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (13 mg, 0.044 mmol, 22%). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.26 (s, 6H, 2 x CH_3), 1.27 (s, 6H, 2 x CH_3), 1.31 (dd, *J* = 16.0, 8.3 Hz, 1H, CH_2Bpin), 1.43 (dd, *J* = 16.0, 6.8 Hz, 1H, CH_2Bpin), 2.15 (s, 3H, CH_3), 3.73-3.79 (m, 1H, CHCN), 5.63 (dd, *J* = 9.2, 0.9 Hz, 1H, CH=C), 7.30-7.39 (m, 5H, ArCH).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 16.6 (CH_3), 24.8 (CH_3), 25.8 (*C*H-CN), 84.0 (*C*(CH_3)$_2$), 121.8 (*C*N), 123.5 (*C*H=C), 125.9 (ArCH), 127.6 (ArCH), 128.4 (ArCH), 139.2 (*C*=CH), 142.4 (ArC), (*C*H_2B not observed).

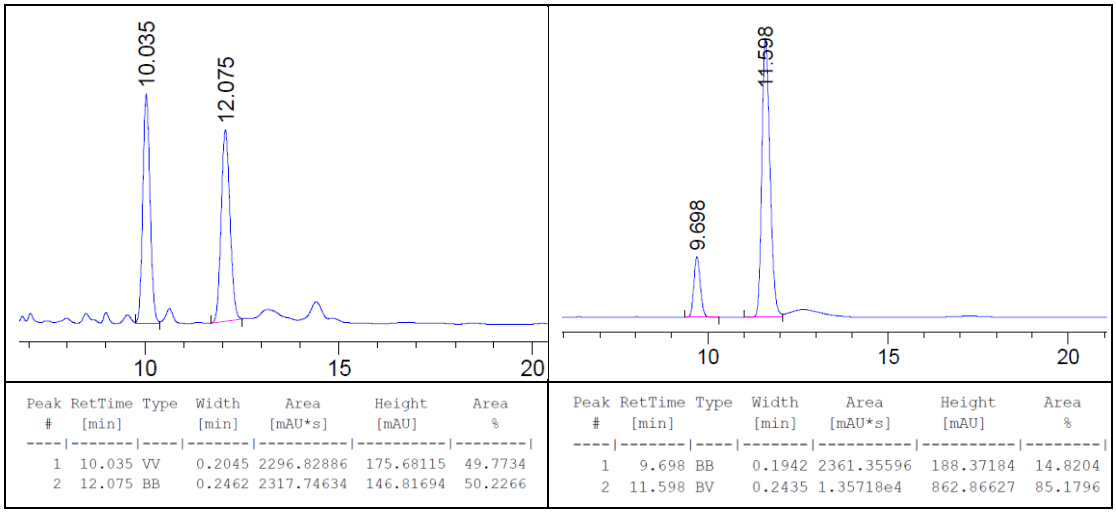
^{11}B NMR (128 MHz, $CDCl_3$) δ ppm 32.7.

HRMS (m/z, ESI): Calcd. for $C_{18}H_{24}BNO_2$ [M+Na]: 320.1792, found: 320.1787.

ν_{max} (thin film/cm^{-1}): 2978, 2930, 2236, 1494, 1446, 1372, 1333, 1273, 1166, 1142, 966.

Specific rotation: $[\alpha]_D^{27}$+25.3 (c = 0.42, $CHCl_3$).

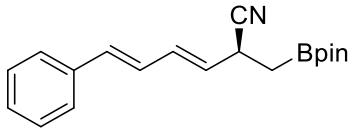
Enantiomeric purity of **4y** was determined by HPLC analysis in comparison with authentic racemic material (70% e.e. shown; OD-H column, 99:1 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.035	VV	0.2045	2296.82886	175.68115	49.7734
2	12.075	BB	0.2462	2317.74634	146.81694	50.2266

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.698	BB	0.1942	2361.35596	188.37184	14.8204
2	11.598	BV	0.2435	1.35718e4	862.86627	85.1796

(*S,3E,5E*)-6-Phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)hexa-3,5-dienenitrile (4z)



Prepared according to the General Procedure on a 0.2 mmol scale (>20:1 *rs* and 63% NMR yield of crude material using $MeNO_2$ as internal standard). Column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (25 mg, 0.082 mmol, 41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.28-1.33 (m, 13H, 4 x CH_3 and 1H from CH_2Bpin), 1.39 (dd, *J* = 16.1, 7.1 Hz, 1H, CH_2Bpin), 3.54-3.58 (m, 1H, CHCN), 5.72 (dd, *J* = 15.2, 6.6 Hz, 1H, CH=CH), 6.49 (dd, *J* = 15.2, 10.8 Hz, 1H, CH=CH), 6.60 (d, *J* = 15.7 Hz, 1H, CH=CH), 6.72 (dd, *J* = 15.6, 10.3 Hz, 1H, CH=CH), 7.25-7.28 (m, 1H, ArCH), 7.34 (t, *J* = 7.4 Hz, 2H, ArCH), 7.41 (d, *J* = 7.5 Hz, 2H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.8 (CH_3), 29.5 (*C*H-CN), 84.0 (*C*$(CH_3)_2$), 121.1 (*C*N), 126.5 (ArCH), 127.2 (CH=CH), 127.9 (CH=CH), 128.4 (CH=CH), 128.7 (ArCH), 132.8 (CH=CH), 133.8 (ArCH), 136.8 (ArC), (*C*H_2B not observed).

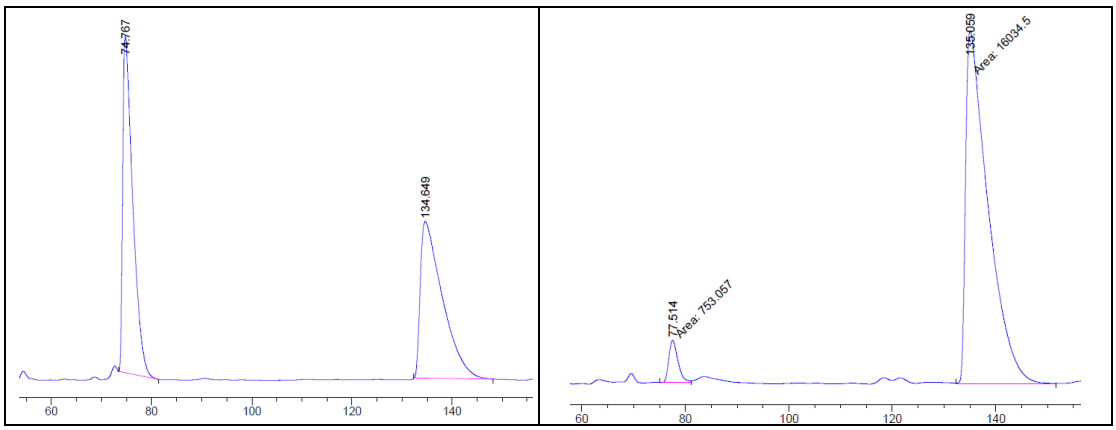
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.4.

HRMS (m/z, ESI): Calcd. for $C_{19}H_{24}BNO_2$ [M+Na]: 332.1792, found: 332.1796.

ν_{max} (thin film/cm^{-1}): 2978, 2242, 1738, 1449, 1373, 1338, 1271, 1216, 1142, 968.

Specific rotation: $[\alpha]_D^{27}$+6.9 (c = 1.04, $CHCl_3$).

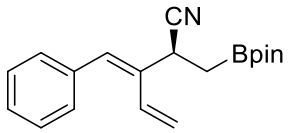
Enantiomeric purity of **4z** was determined by HPLC analysis in comparison with authentic racemic material (91% e.e. shown; OD-H column, 998:2 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	74.767	BB	1.9244	1.29900e4	93.04284	49.5096
2	134.649	BB	3.6360	1.32474e4	43.32114	50.4904

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	77.514	MM	2.0036	753.05670	6.26435	4.4858
2	135.059	MM	5.0359	1.60345e4	53.06752	95.5142

(*S,E*)-3-Benzylidene-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)pent-4-enenitrile (9)



Prepared according to the General Procedure, on a 0.2 mmol scale (>20:1 *rs* and 72% NMR yield of crude material using $MeNO_2$ as internal standard), column chromatography (Hexane/EtOAc/AcOH = 100/3/1) afforded the title compound as a colorless oil (42 mg, 0.136 mmol, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.28 (s, 6H, 2 x CH_3), 1.29 (s, 6H, 2 x CH_3), 1.49-1.57 (m, 2H, CH_2Bpin), 3.91 (t, *J* = 7.8 Hz, 1H, CHCN), 5.32 (dd, *J* = 11.4, 1.4 Hz, 1H, C*H*$_2$=CH), 5.49 (d, *J* = 17.9 Hz, 1H, C*H*$_2$=CH), 6.69 (dd, *J* = 17.9, 11.4 Hz, 1H, CH_2=CH), 6.86 (s, 1H, CH=C), 7.28-7.31 (m, 3H, ArCH), 7.35-7.38 (m, 2H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 24.9 (CH_3), 30.0 (*C*H-CN), 84.0 (*C*(CH_3)$_2$), 116.5 (*C*H_2=CH), 121.8 (*C*N), 127.6 (ArCH), 128.2 (ArCH), 129.5 (ArCH), 131.1 (*C*H=C), 131.6 (*C*H_2=CH), 134.6 (*C*H=C), 136.0 (ArC), (*C*H_2B not observed)

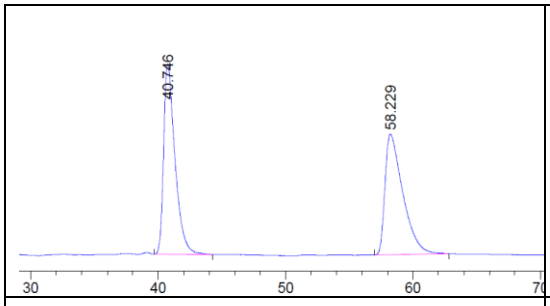
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.6.

HRMS (m/z, ESI): Calcd. for $C_{19}H_{24}BNO_2$ [M+H]: 310.1973, found: 310.1959.

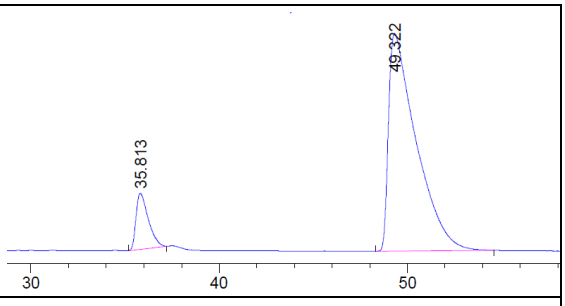
ν_{max} (thin film/cm^{-1}): 2978, 2932, 2238, 1674, 1450, 1372, 1333, 1271, 1167, 1141, 966.

Specific rotation: $[\alpha]_D^{27}$+3.3 (c = 2.38, $CHCl_3$).

Enantiomeric purity of **9** was determined by HPLC analysis in comparison with authentic racemic material (80% e.e. shown; OD-H column, 998:2 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.746	BB	0.9203	3659.89551	59.11248	50.0733
2	58.229	BB	1.3544	3649.17749	37.53061	49.9267

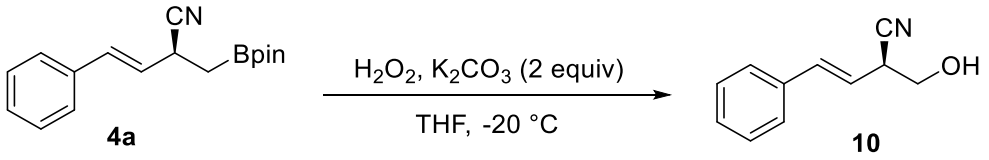


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.813	BB	0.6608	710.21967	15.66783	10.2463
2	49.322	BB	1.3711	6221.23682	61.04088	89.7537

Compound **9** was transformed into the corresponding ester **S2** after Bpin oxidation and esterification of the resulting alcohol. The absolute configuration of the corresponding ester **S2** was determined by X-ray crystallography after recrystallization.

Manipulations of chiral Borocyanation products

(*S,E*)-2-(Hydroxymethyl)-4-phenylbut-3-enenitrile (10)



To a 10 mL vial was added **4a** (57 mg, 0.2 mmol), K_2CO_3 (55mg, 0.4 mmol) and 2 mL THF. The solution was stirred at -20 °C for 5 min before H_2O_2 (0.1mL, 30% wt. in H_2O) was added drop-wise. The reaction mixture was monitored by TLC and quenched by addition of saturated aqueous $Na_2S_2O_3$ (2 mL). The mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with water and brine, dried by anhydrous Na_2SO_4 and concentrated in *vacuo*. The crude product was purified by column chromatography (silica gel, eluting with 10:1 to 4:1 hexane/ethyl acetate) to afford the pure alcohol **10** (31 mg, 0.180 mmol, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 2.45 (t, *J* = 5.2 Hz, 1H, OH), 3.63-3.66 (m, 1H, CHCN), 3.89 (t, *J* = 6.1 Hz, 2H, CH_2), 6.04 (dd, *J* = 15.9, 6.5 Hz, 1H, CH=CH), 6.80 (d, *J* = 15.9 Hz, 1H, CH=CH), 7.28-7.40 (m, 5H, ArCH).

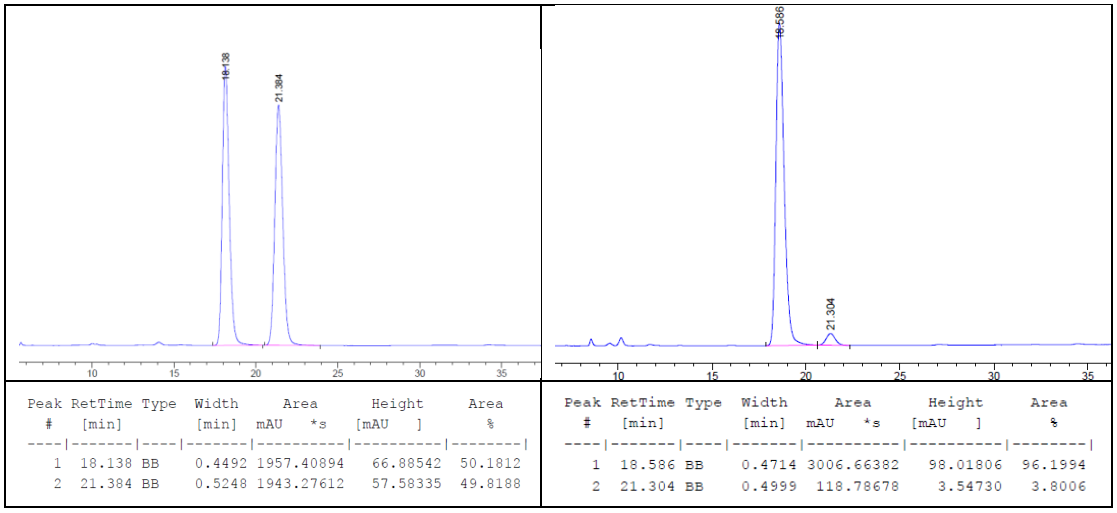
^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 38.1 (CHCN), 63.4 (CH_2), 118.7 (*C*N), 119.1 (ArCH), 126.7 (ArCH), 128.6 (CH=CH), 128.8 (ArCH), 135.3 (ArC), 135.6 (CH=CH).

HRMS (m/z, ESI): Calcd. for $C_{11}H_{11}NO$ [M+H]: 174.0913, found: 174.0906.

ν_{max} (thin film/cm^{-1}): 3422, 3027, 2946, 2885, 2246, 1495, 1449, 1374, 1208, 1057, 965.

Specific rotation: $[\alpha]_D^{27}$+12.2 (c = 1.16, $CHCl_3$).

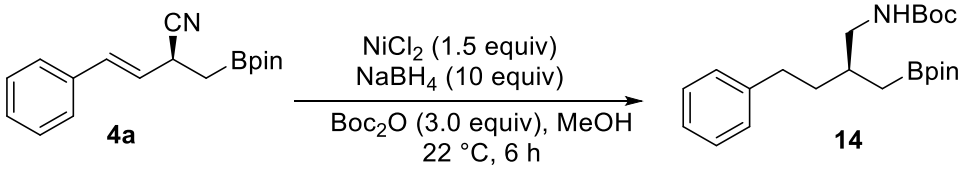
Enantiomeric purity of **10** was determined by HPLC analysis in comparison with authentic racemic material (92% e.e. shown; OD-H column, 90:10 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.138	BB	0.4492	1957.40894	66.88542	50.1812
2	21.384	BB	0.5248	1943.27612	57.58335	49.8188

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.586	BB	0.4714	3006.66382	98.01806	96.1994
2	21.304	BB	0.4999	118.78678	3.54730	3.8006

tert-Butyl (_S_)-(4-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)butyl)carbamate[4] (14)



To a solution of compound **4a** (28 mg, 0.1 mmol), $NiCl_2$ (19 mg, 0.15 mmol) and Boc_2O (65 mg, 0.3 mmol) in MeOH at 0 °C was added $NaBH_4$ (38 mg, 1 mmol). The mixture was allowed to stir for 4 h at 0 °C. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl and diluted with Et_2O. The layers were separated and the aqueous layer was washed with Et_2O. The combined organic layers were washed with brine, dried with Na_2SO_4, and evaporated at reduced pressure. The crude product was purified by column chromatography (silica gel, eluting with 10:1 hexane/ethyl acetate) to afford compound **14** (22 mg, 0.056 mmol, 56%).

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 0.81-0.93 (m, 2H, CH_2Bpin), 1.27 (s, 6H, 2 x CH_3), 1.28 (s, 6H, 2 x CH_3), 1.46 (s, 9H, 3 x CH_3), 1.53-1.58 (m, 1H, CH_2), 1.62-1.70 (m, 1H, CH_2), 1.82-1.87 (m, 1H, CH), 2.66 (t, *J* = 8.4 Hz, 2H, CH_2), 3.03-3.08 (m, 1H, CH_2N), 3.21-3.26 (m, 1H, CH_2N), 4.95 (s, 1H, NH), 7.17-7.20 (m, 3H, ArCH), 7.27-7.30 (m, 2H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (2 x CH_3), 24.9 (2 x CH_3), 28.5 (3 x CH_3), 33.3 (CH_2), 34.6 (CH), 36.8 (CH_2), 46.2 (CH_2), 77.2 ($C(CH_3)_3$), 83.3 ($C(CH_3)_2$), 125.6 (ArCH), 128.3 (ArCH), 128.3 (ArCH),142.7 (ArC), 156.1 (C=O).

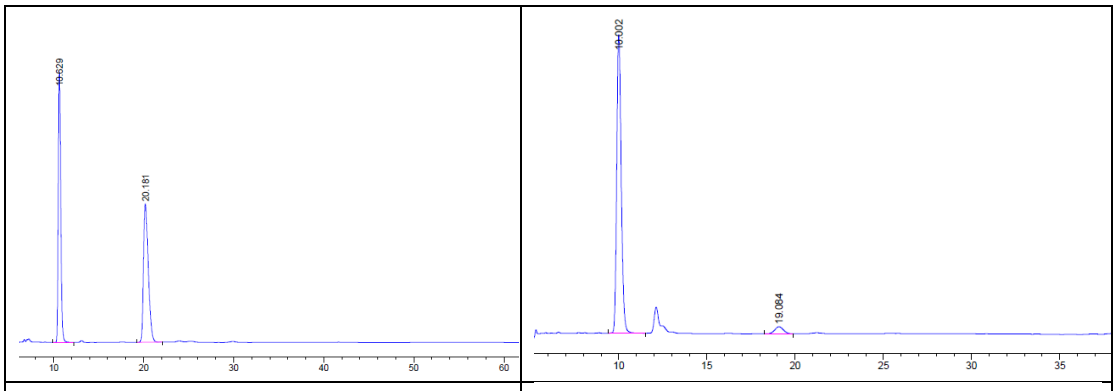
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 34.0.

HRMS (m/z, ESI): Calcd. for $C_{22}H_{36}BNO_4$ [M+Na]: 412.2630, found: 412.2626.

ν_{max} (thin film/cm^{-1}): 3370, 3026, 2977, 2928, 1715, 1509, 1454, 1366, 1320, 1248, 1167, 1144, 968.

Specific rotation: $[\alpha]_D^{27}$+2.0 (c = 2.24, $CHCl_3$).

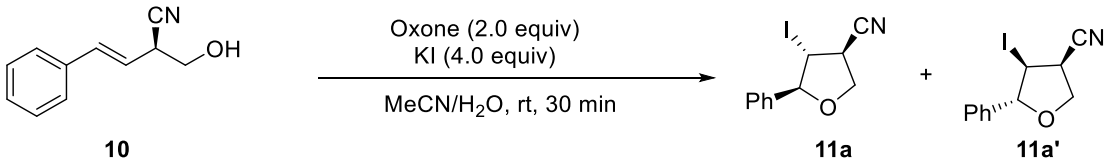
Enantiomeric purity of **14** was determined by HPLC analysis in comparison with authentic racemic material (91% e.e. shown; OD-H column, 90:10 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 210 nm).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.629	BB	0.2901	1.78139e4	943.61786	49.8744
2	20.181	BB	0.5682	1.79037e4	482.56931	50.1256

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.002	BB	0.2744	7400.95898	416.29977	95.7686
2	19.084	BB	0.5286	327.00281	9.73924	4.2314

(*3S,4R,5S*)-4-Iodo-5-phenyltetrahydrofuran-3-carbonitrile (11a) and (3S,4S,5R)-4-iodo-5-phenyltetrahydrofuran-3-carbonitrile[5] (11a')



10 **11a** **11a'**

To a stirred solution of Oxone® (123 mg, 0.4 mmol) in 2.5 mL of a 4:1 H_2O-CH_3CN mixture, was added KI (133 mg, 0.8 mmol). After 10 min, to the deep purple solution was added **10** (35 mg, 0.2 mmol) in 1 mL of CH_3CN. The reaction was followed by TLC. After 30 min, the reaction mixture was diluted with H_2O (10 mL), washed with a saturated solution of $Na_2S_2O_3$ and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried and evaporated at reduced pressure. The crude product was then purified by column chromatography (silica gel, eluting with 10:1 hexane/ethyl acetate) to afford **11a** and **11a'** (major **11a**, 26 mg, 0.088 mmol, 44%; minor **11a'**, 17

mg, 0.058 mmol, 29%).

HRMS (m/z, ESI): Calcd. for $C_{11}H_{10}INO$ [M+H]: 299.9880, found: 299.9866.

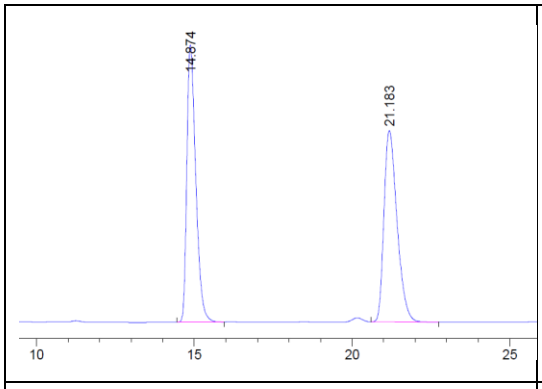
ν_{max} (thin film/cm^{-1}): 3031, 2969, 2888, 2245, 1738, 1493, 1455, 1365, 1216, 1042, 1025, 976.

Major **11a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 3.50 (q, *J* = 7.1 Hz, 1H, CH-CN), 4.13 (t, *J* = 7.4 Hz, 1H, CH-I), 4.28 (dd, *J* = 9.0, 6.4 Hz, 1H, CH_2), 4.49 (dd, *J* = 9.0, 7.4 Hz, 1H, CH_2), 5.25 (d, *J* = 7.3 Hz, 1H, CH), 7.38-7.42 (m, 5H, ArCH).

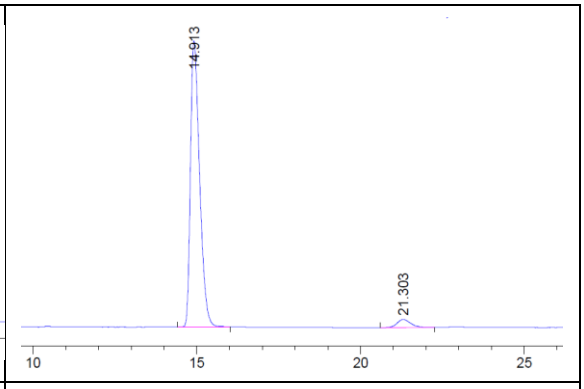
^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 25.4 (*C*H-I), 38.2 (*C*H-CN), 69.8 (CH_2), 89.3 (*C*H-Ph), 118.3 (CN), 126.1 (ArCH), 128.8 (ArCH), 129.0 (ArCH), 137.3 (ArC).

Specific rotation: $[\alpha]_D^{27}$+75.1 (c = 0.88, $CHCl_3$).

Enantiomeric purity of **11a** was determined by HPLC analysis in comparison with authentic racemic material (92% e.e. shown; OD-H column, 90:10 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.874	BB	0.3052	2953.17871	149.00768	49.8319
2	21.183	BB	0.4449	2973.09741	102.95809	50.1681



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.913	BB	0.2978	3248.47290	166.39165	95.9403
2	21.303	BB	0.4291	137.45786	4.72882	4.0597

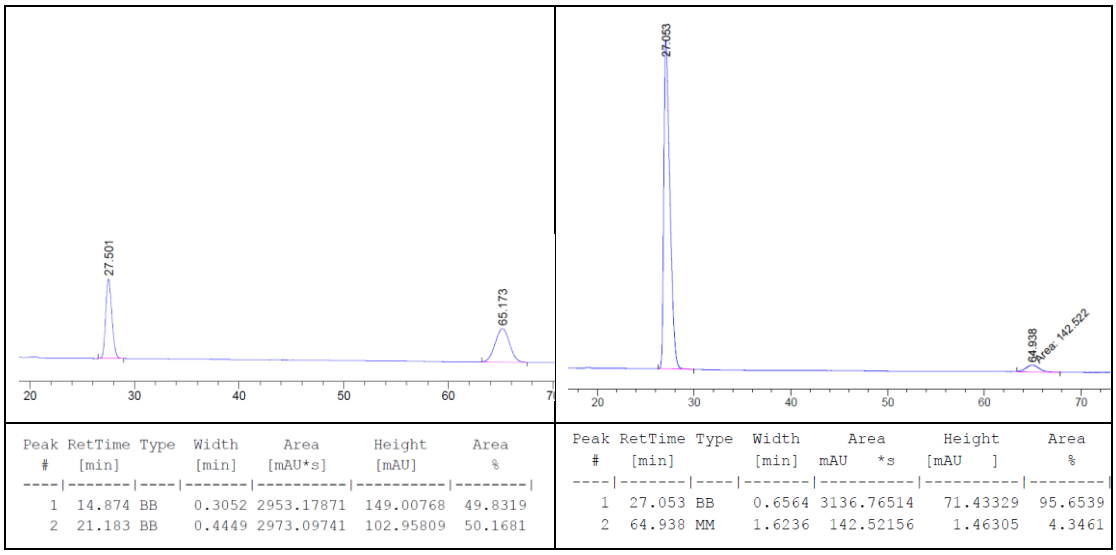
Minor **11a'**: ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 3.49-3.54 (m, 1H, CH-CN), 4.07 (t, *J* = 8.1 Hz, 1H, CH-I), 4.26-4.29 (m, 1H, CH_2), 4.36-4.39 (m, 1H, CH_2), 5.02 (d, *J* = 8.7 Hz, 1H, CH), 7.40-7.44 (m, 3H, ArCH), 7.46-7.48 (m, 2H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.9 (*C*H-I), 41.8 (*C*H-CN), 69.8 (CH_2), 90.3 (*C*H-Ph), 118.1 (CN), 126.5 (ArCH), 128.9 (ArCH), 129.2 (ArCH), 136.0 (ArC).

Specific rotation: $[\alpha]_D^{27}$+73.2 (c = 0.73, $CHCl_3$).

Enantiomeric purity of **11a'** was determined by HPLC analysis in

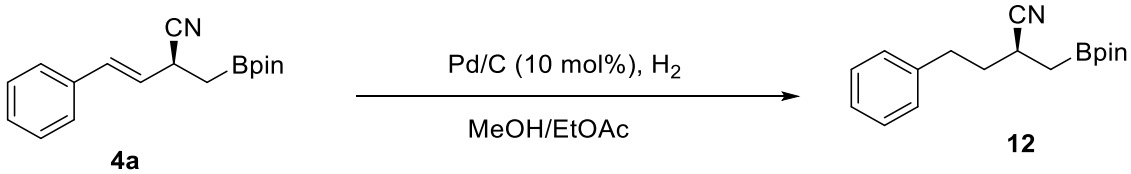
comparison with authentic racemic material (91% e.e. shown; OD-H column, 90:10 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 254 nm).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.874	BB	0.3052	2953.17871	149.00768	49.8319
2	21.183	BB	0.4449	2973.09741	102.95809	50.1681

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.053	BB	0.6564	3136.76514	71.43329	95.6539
2	64.938	MM	1.6236	142.52156	1.46305	4.3461

(*S*)-4-Phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)butanenitrile (12)



4a **12**

Compound **4a** (57 mg, 0.2 mmol) was dissolved in MeOH (6mL) and EtOAc (3 mL) and Pd/C (10 wt. %, 21 mg, 0.02 mmol) was added. The reaction mixture was stirred under a hydrogen atmosphere for 12 h at room temperature. The reaction was filtered through celite, and the cake was washed with CH_2Cl_2 (2 × 5 mL). The organic layers were combined and concentrated in *vacuo.* The crude product was purified by column chromatography (Hexane/EtOAc = 30:1) to afford **12** as a colorless oil (56 mg, 0.196 mmol, 98%).

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 1.15-1.24 (m, 2H, CH_2Bpin), 1.27 (s, 12H, 4 x CH_3), 1.87-2.01 (m, 2H, CH_2), 2.71-2.78 (m, 2H, CHCN and CH_2), 2.88-2.94 (m, 1H, CH_2), 7.22-7.25 (m, 3H, ArCH), 7.31-7.34 (m, 2H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 26.4 (*C*H-CN), 33.4 (CH_2), 36.0 (CH_2), 83.9

($C(CH_3)_2$), 123.0 (*C*N), 126.3 (ArCH), 128.4 (ArCH), 128.5 (ArCH), 140.4 (ArC), (CH_2B not observed)

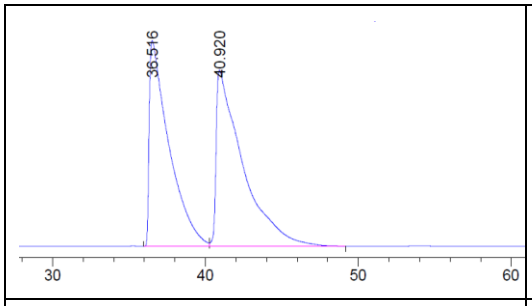
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 32.8.

HRMS (m/z, ESI): Calcd. for $C_{17}H_{24}BNO_2$ [M+Na]: 308.1792, found: 308.1788.

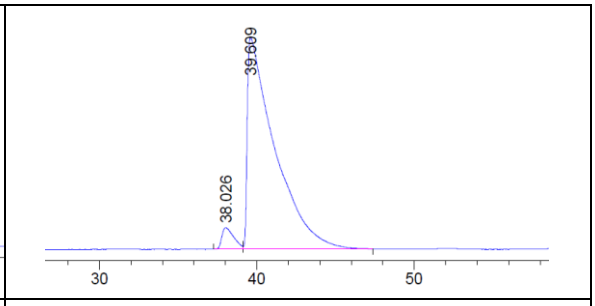
ν_{max} (thin film/cm^{-1}): 3027, 2978, 2931, 2236, 1455, 1373, 1329, 1166, 1142, 967.

Specific rotation: $[\alpha]_D^{27}$+21.8 (c = 0.80, $CHCl_3$).

Enantiomeric purity of **12** was determined by HPLC analysis in comparison with authentic racemic material (91% e.e. shown; OD-H column, 998:2 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 210 nm).

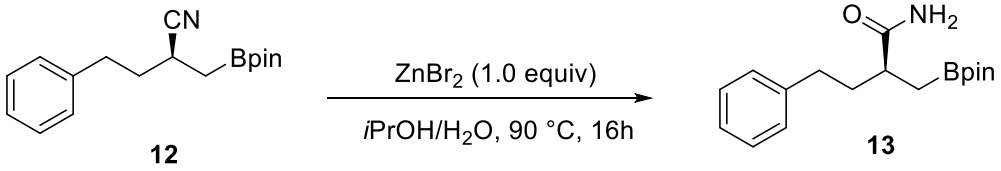


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.516	BV	1.1731	1.88474e4	210.00568	46.4282
2	40.920	VB	1.5426	2.17474e4	180.11722	53.5718



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.026	BV	0.7575	1527.51111	28.85828	4.2551
2	39.609	VB	1.5640	3.43711e4	282.78067	95.7449

(*S*)-4-Phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)butanamide[6] (13)



12 **13**

An oven-dried vial was charged with **12** (29 mg, 0.1 mmol), $ZnBr_2$ (22 mg, 0.1 mmol), water (0.50 mL) and isopropanol (0.3 mL). The vial was sealed and heated at 90 °C for 16 h. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (2 x 5 mL). The combined organic layers were concentrated in *vacuo* and the crude product purified by column chromatography (silica gel, eluting with 3:1 to 1:1 hexane/ethyl acetate) to afford amide **13** (17 mg, 0.055 mmol, 55%).

^1H NMR (500 MHz, $CDCl_3$) δ ppm 1.03 (dd, *J* = 16.3, 6.0 Hz, 1H, CH_2Bpin), 1.13 (dd, *J* = 16.2, 8.5 Hz, 1H, CH_2Bpin), 1.26 (s, 12H, 4 x CH_3), 1.17-1.80 (m, 1H, CH_2), 2.01-2.09 (m,

1H, CH_2), 2.42-2.48 (m, 1H, CH), 2.59-2.65 (m, 1H, CH_2), 2.68-2.74 (m, 1H, CH_2), 5.39 (br, 1H, NH_2), 5.75 (br, 1H, NH_2), 7.18-7.21 (m, 3H, ArCH), 7.27-7.30 (m, 2H, ArCH).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 24.8 (CH_3), 33.6 (CH_2), 36.1 (CH_2), 41.3 (CH), 83.4 ($C(CH_3)_2$), 125.8 (ArCH), 128.4 (ArCH), 128.4 (ArCH), 141.9 (ArC), 178.7 (CO), (CH_2B not observed).

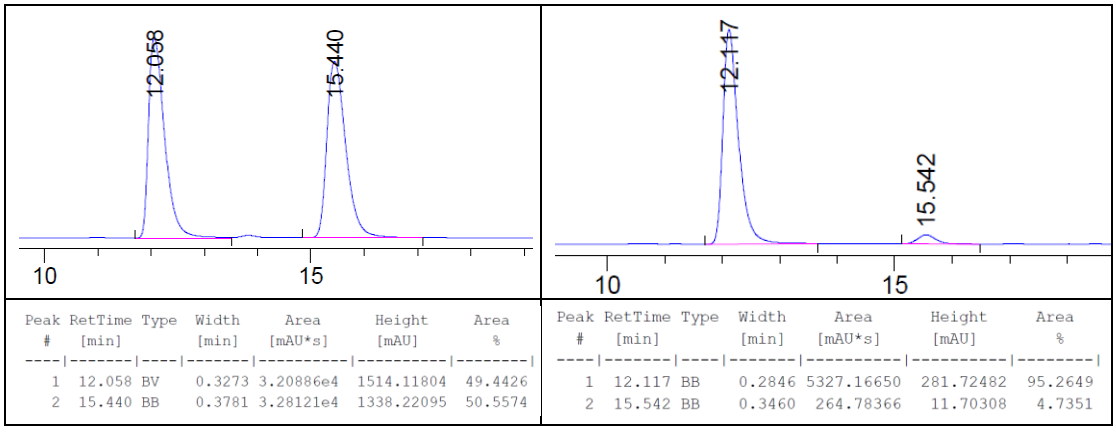
^{11}B NMR (160 MHz, $CDCl_3$) δ ppm 33.6.

HRMS (m/z, ESI): Calcd. for $C_{17}H_{26}BNO_3$ [M+H]: 304.2079, found: 304.2065.

ν_{max} (thin film/cm^{-1}): 2976, 2924, 2854, 1648, 1586, 1455, 1372, 1327, 1167, 1142, 1108, 967.

Specific rotation: $[\alpha]_D^{27}$+3.2 (c = 1.19, $CHCl_3$).

Enantiomeric purity of **13** was determined by HPLC analysis in comparison with authentic racemic material (91% e.e. shown; IA-H column, 90:10 hexanes:*i*-PrOH, 1.0 mL/min, 20 °C, 210 nm).



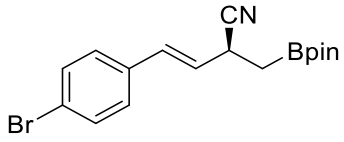
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.058	BV	0.3273	3.20886e4	1514.11804	49.4426
2	15.440	BB	0.3781	3.28121e4	1338.22095	50.5574

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.117	BB	0.2846	5327.16650	281.72482	95.2649
2	15.542	BB	0.3460	264.78366	11.70308	4.7351

X-ray crystal structures

(*S*,*E*)-4-(4-Bromophenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)but-3-enenitrile (4g)

CCDC 1904527



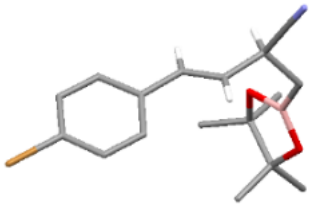


Table S10 Crystal data and structure refinement for 1904527.

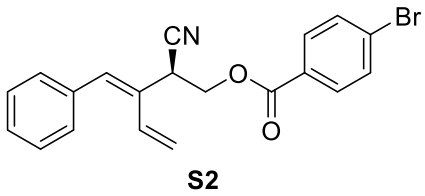
Identification code	1904527
Empirical formula	$C_{17}H_{21}BBrNO_2$
Formula weight	362.07
Temperature/K	100.03(15)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.3502(4)
b/Å	7.4500(2)
c/Å	20.6376(6)
α/°	90
β/°	91.376(3)
γ/°	90
Volume/Å^3	1744.59(9)
Z	4
ρ_{calc}g/cm^3	1.378
μ/mm^{-1}	2.362
F(000)	744.0
Crystal size/mm^3	0.452 × 0.266 × 0.07
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.59 to 60.818
Index ranges	-15 ≤ h ≤ 15, -10 ≤ k ≤ 10, -29 ≤ l ≤ 27
Reflections collected	29396
Independent reflections	8734 [R_{int} = 0.0547, R_{sigma} = 0.0597]
Data/restraints/parameters	8734/1/405
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0407, wR_2 = 0.0861
Final R indexes [all data]	R_1 = 0.0536, wR_2 = 0.0894

Largest diff. peak/hole / e $Å^{-3}$	0.79/-0.45
Flack parameter	0.002(6)

(S,E)-3-benzylidene-2-cyanopent-4-en-1-yl 4-bromobenzoate (S2 – a derivative of 9)

Compound **9** was transformed into the corresponding ester **S2** after Bpin oxidation and esterification of the resulting alcohol. The absolute configuration of the corresponding ester **S2** was determined by X-ray crystallography after recrystallization.

CCDC 1905065



S2

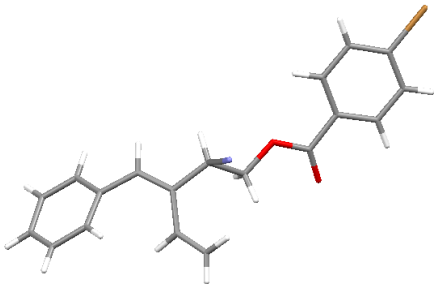


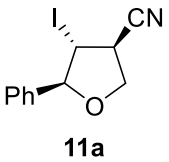
Table S11 Crystal data and structure refinement for 1095065.

Identification code	1095065
Empirical formula	$C_{20}H_{16}BrNO_2$
Formula weight	382.25
Temperature/K	100.0(3)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	14.62776(18)
b/Å	8.05742(10)
c/Å	15.00218(18)
α/°	90
β/°	97.0979(12)
γ/°	90
Volume/Å^3	1754.64(4)
Z	4
ρ_{calc}g/cm^3	1.447
μ/mm^{-1}	3.280
F(000)	776.0
Crystal size/mm^3	0.2 × 0.15 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.936 to 130.164
Index ranges	-17 ≤ h ≤ 16, -9 ≤ k ≤ 9, -17 ≤ l ≤ 17
Reflections collected	16624
Independent reflections	5680 [R_{int} = 0.0396, R_{sigma} = 0.0296]
Data/restraints/parameters	5680/1/433
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0322, wR_2 = 0.0875

Final R indexes [all data]	R_1 = 0.0359, wR_2 = 0.0942
Largest diff. peak/hole / e Å^{-3}	0.29/-0.38
Flack parameter	0.016(13)

(3S,4R,5S)-4-iodo-5-phenyltetrahydrofuran-3-carbonitrile (11a)

CCDC 1914139



11a

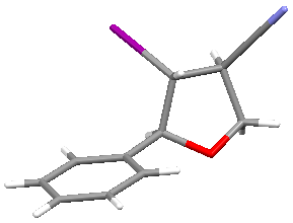


Table S12 Crystal data and structure refinement for 1914139.

Identification code	1914139
Empirical formula	$C_{11}H_{10}I_{0.96}NO$
Formula weight	294.02
Temperature/K	99.95(17)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.8268(5)
b/Å	5.6439(3)
c/Å	9.8652(5)
α/°	90
β/°	99.353(5)
γ/°	90
Volume/Å^3	539.86(5)
Z	2
ρ_{calc}g/cm^3	1.809
μ/mm^{-1}	2.818
F(000)	284.0
Crystal size/mm^3	0.249 × 0.017 × 0.015
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.184 to 60.436
Index ranges	$-12 \le h \le 13$, $-7 \le k \le 7$, $-12 \le l \le 13$
Reflections collected	3833
Independent reflections	3833 [R_{int} = 0.0447, R_{sigma} = 0.0525]
Data/restraints/parameters	3833/1/130
Goodness-of-fit on F^2	1.228
Final R indexes [I>=2σ (I)]	R_1 = 0.0590, wR_2 = 0.2182
Final R indexes [all data]	R_1 = 0.0714, wR_2 = 0.2365
Largest diff. peak/hole / e Å^{-3}	2.56/-2.48
Flack parameter	-0.02(7)

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1. a) Nguyen, V. T.; Hang, D.; Pham, H. H.; Nguyen, V. D.; Carsten, F. H.; Arman, H. D.; Larionov, O. V. *J. Am. Chem. Soc.*, **2018**, *140*, 8434. b) Yasukawa, N.; Yokoyama, H.; Masuda, M.; Monguchi, Y.; Sajiki, H.; Sawama, Y. *Green Chem.*, **2018**, *20*, 1213. c) Kormann, C.; Heinemannb, F. W.; Gmeinera, P. *Tetrahedron* **2006**, *62*, 6899. d) Adamson, N. J.; Hull, E.; Malcolmson, S. J. *J. Am. Chem. Soc. 2017*, **139**, *21*, 7180.

2. a) Adamson, N. J.; Wilbur, K. C. E.; Malcolmson, S. J. *J. Am. Chem. Soc.* **2018**, *140*, 2761. b) Tani, K.; Behenna, D. C.; McFadden, R. M.; Stoltz, B. M. *Org. Lett.* **2007**, *9*, 2529. c) Krout, M. R.; Mohr, J. T.; Stoltz, B. M. *Org. Synth.* **2009**, *86*, 181.

3. Cai, Y.; Qian, X.; Rérat, A.; Auffrant, A.; Gosmini, C. *Adv. Synth. Catal.* **2015**, *357*, 3419.

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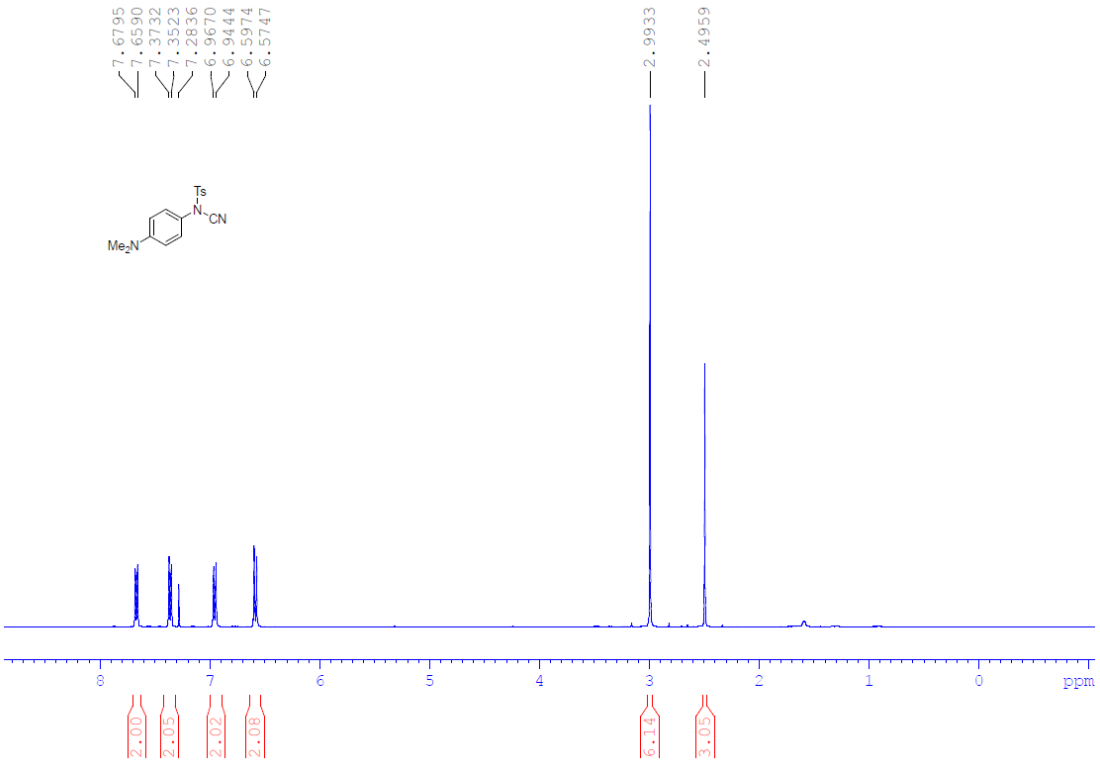
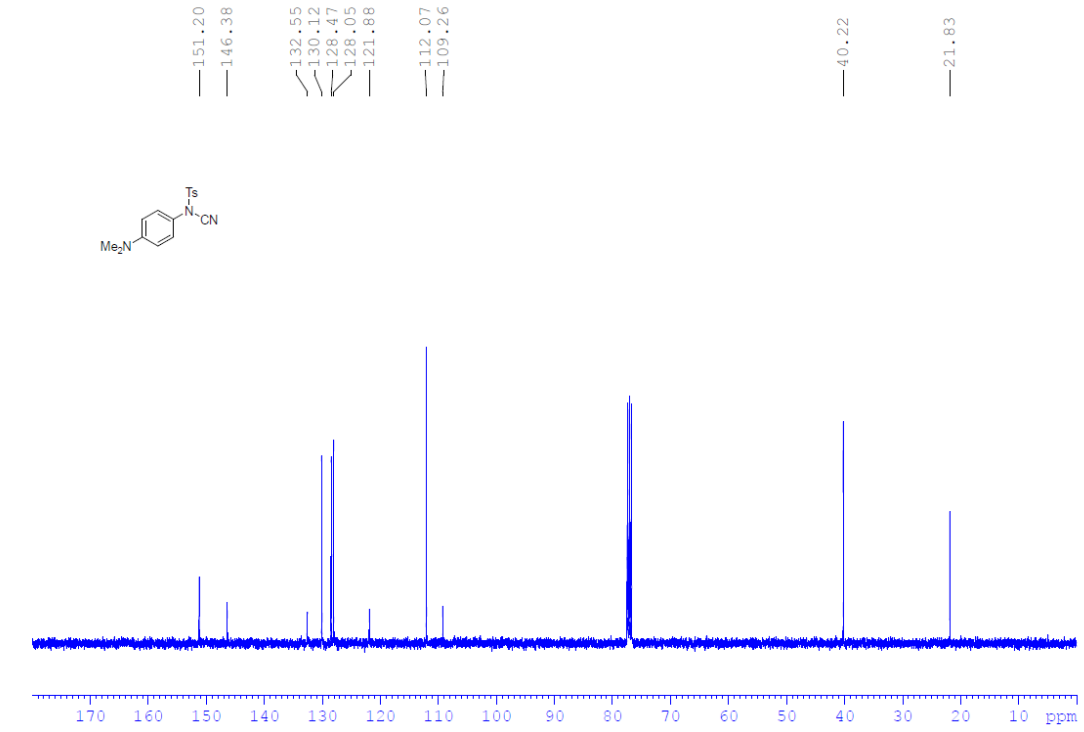
5. Curini, M.; Epifano, F.; Marcotullio, M. C.; Montanari, F. *Synlett* **2004**, 368.

NMR spectra of compounds

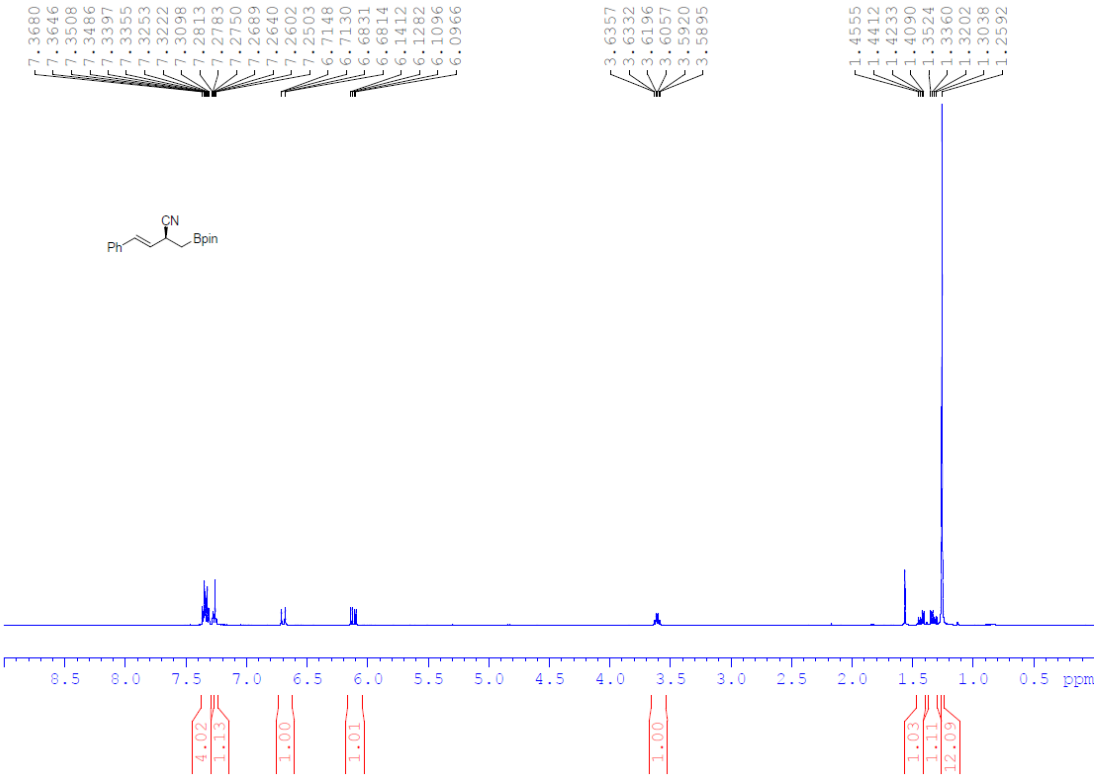
^{1}H NMR of compound **3** (400 MHz, $CDCl_3$)



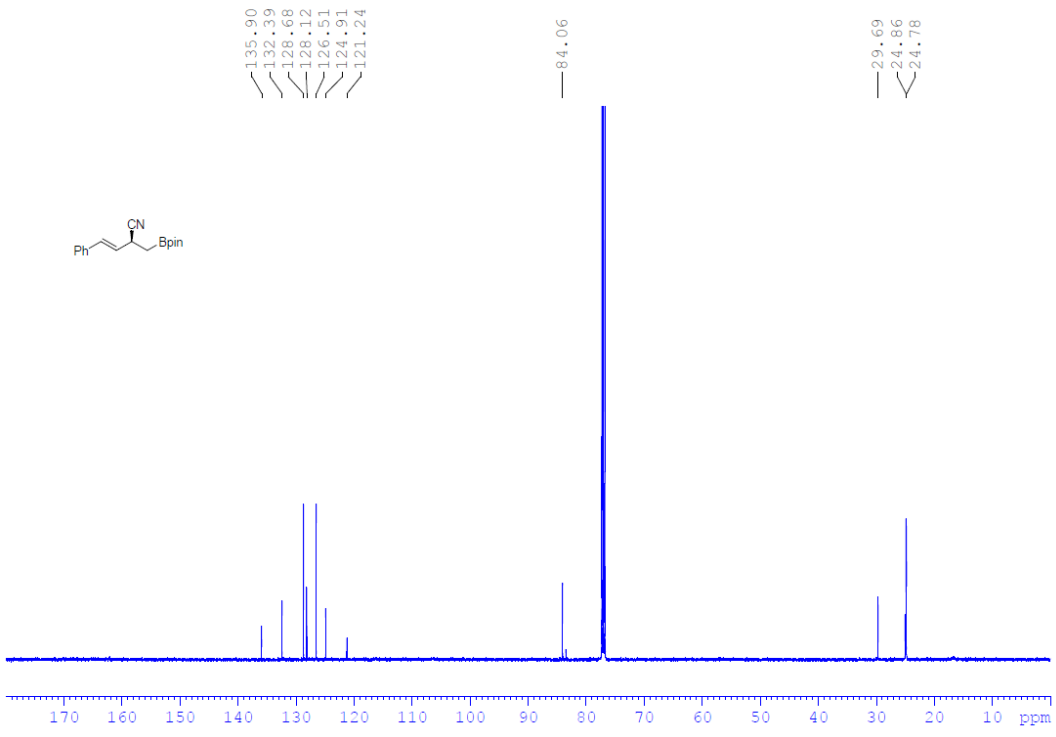
^{13}C NMR of compound **3** (100 MHz, $CDCl_3$)



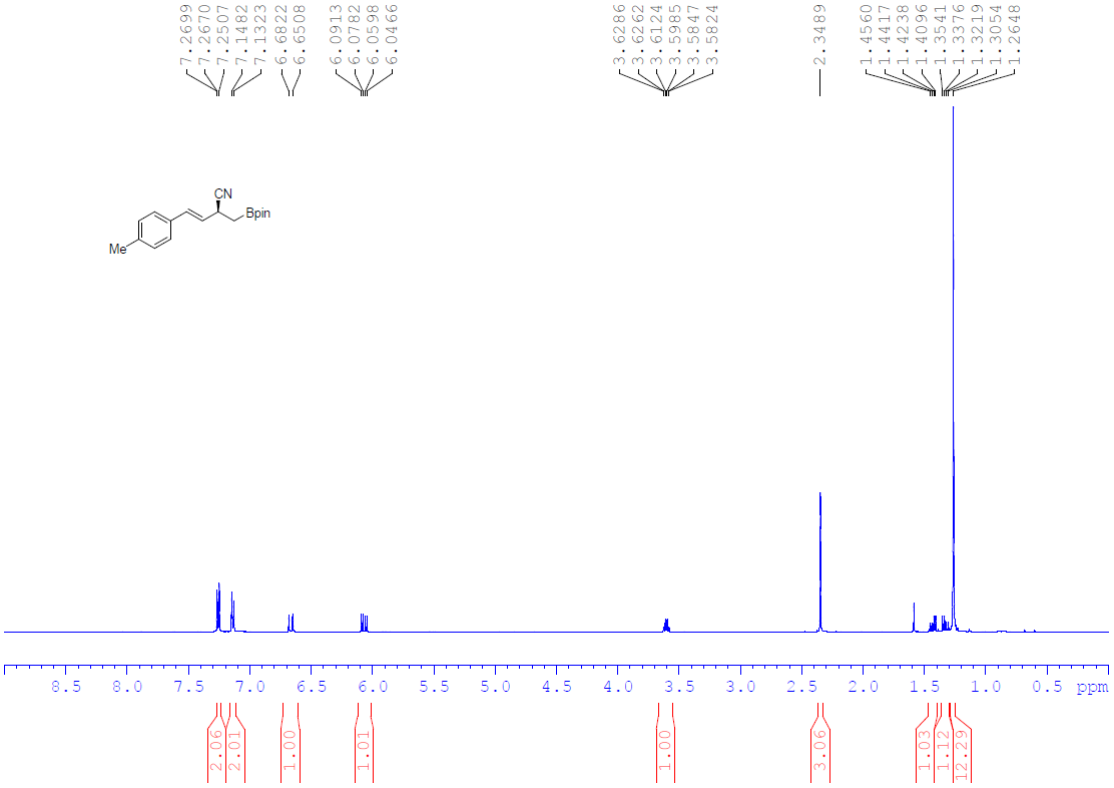
^{1}H NMR of compound **4a** (500 MHz, $CDCl_3$)



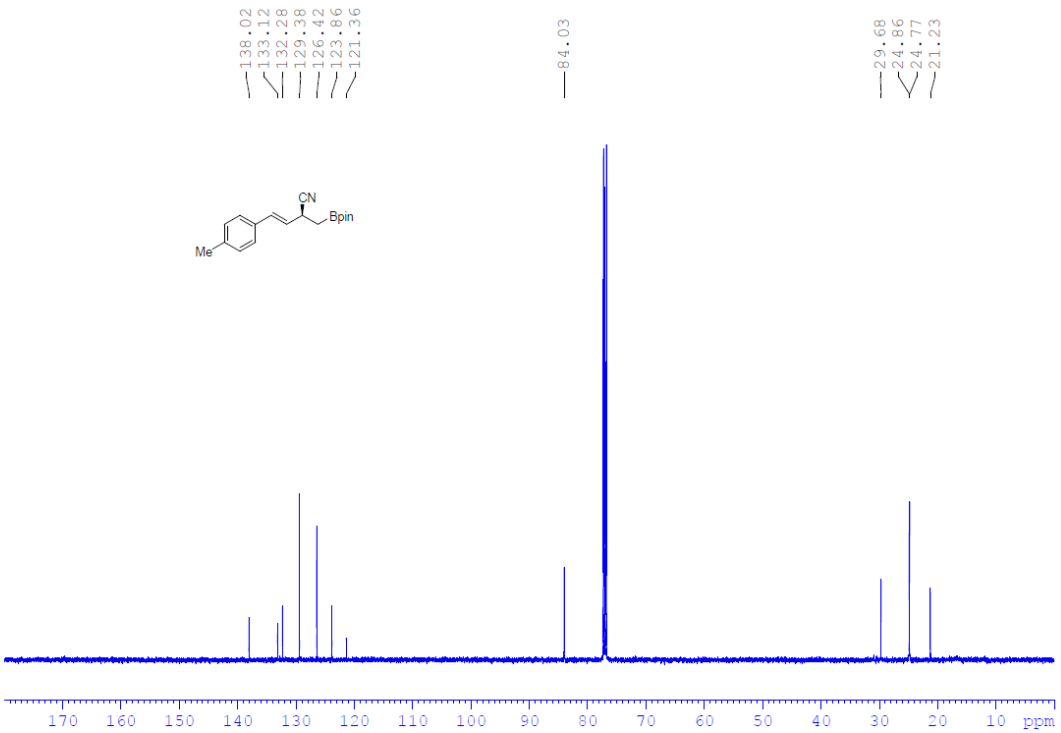
^{13}C NMR of compound **4a** (125 MHz, $CDCl_3$)



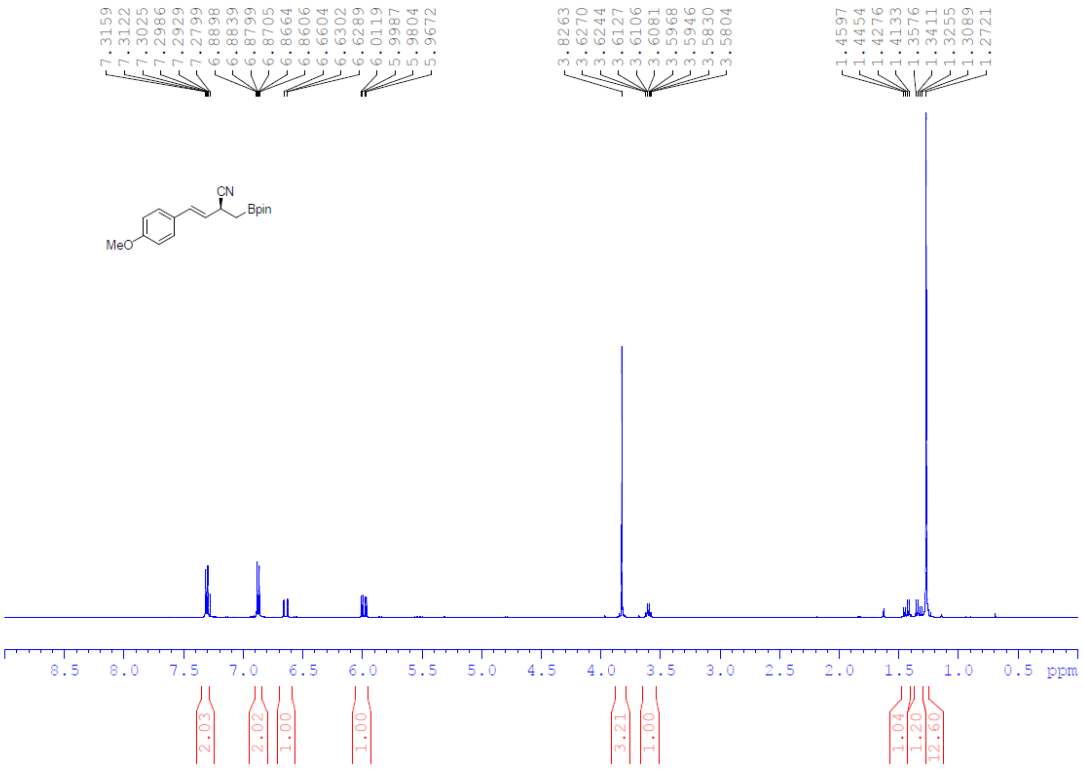
^{1}H NMR of compound **4b** (500 MHz, $CDCl_3$)



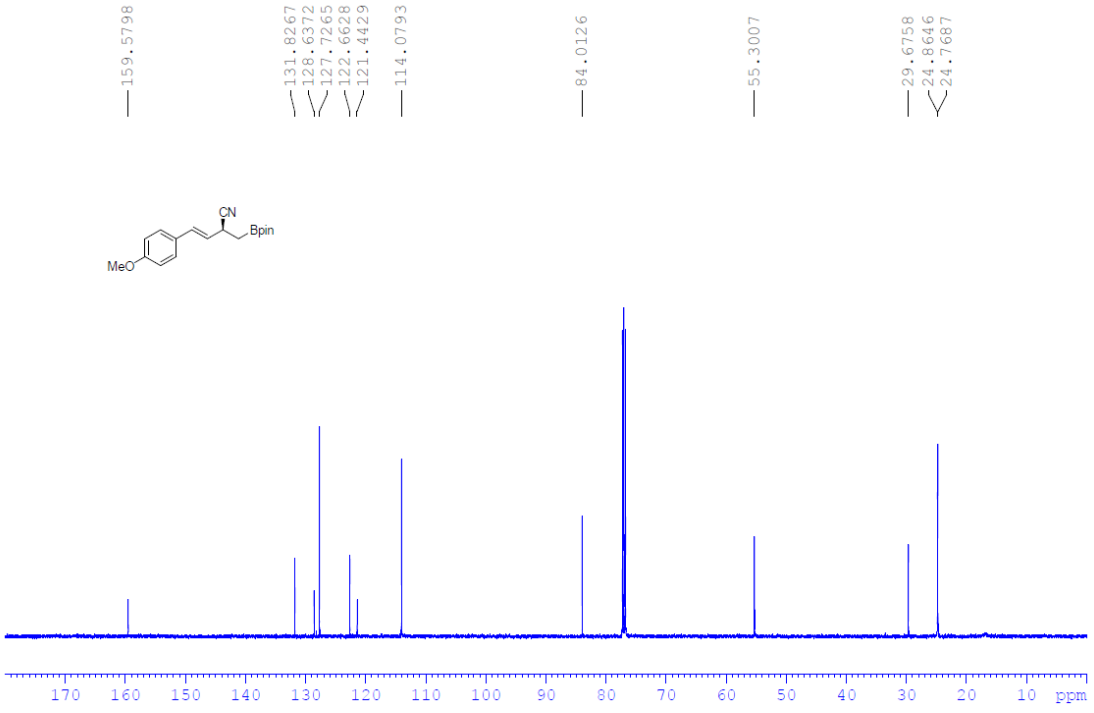
^{13}C NMR of compound **4b** (125 MHz, $CDCl_3$)



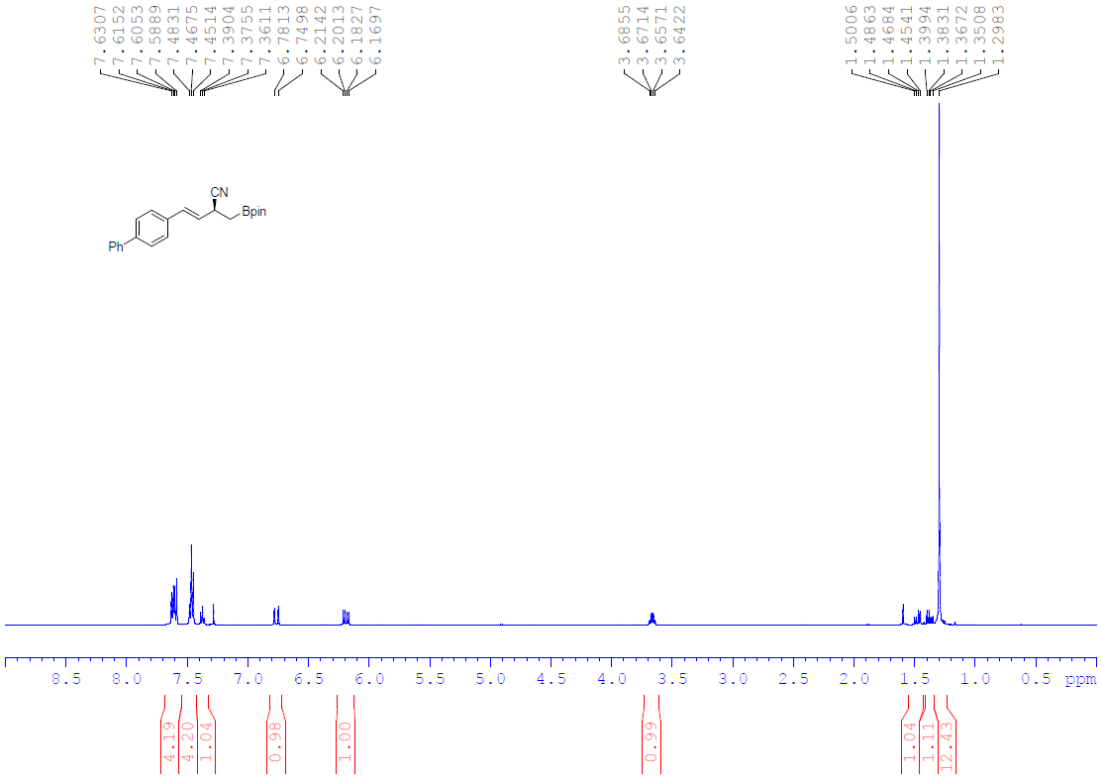
^{1}H NMR of compound **4c** (500 MHz, $CDCl_3$)



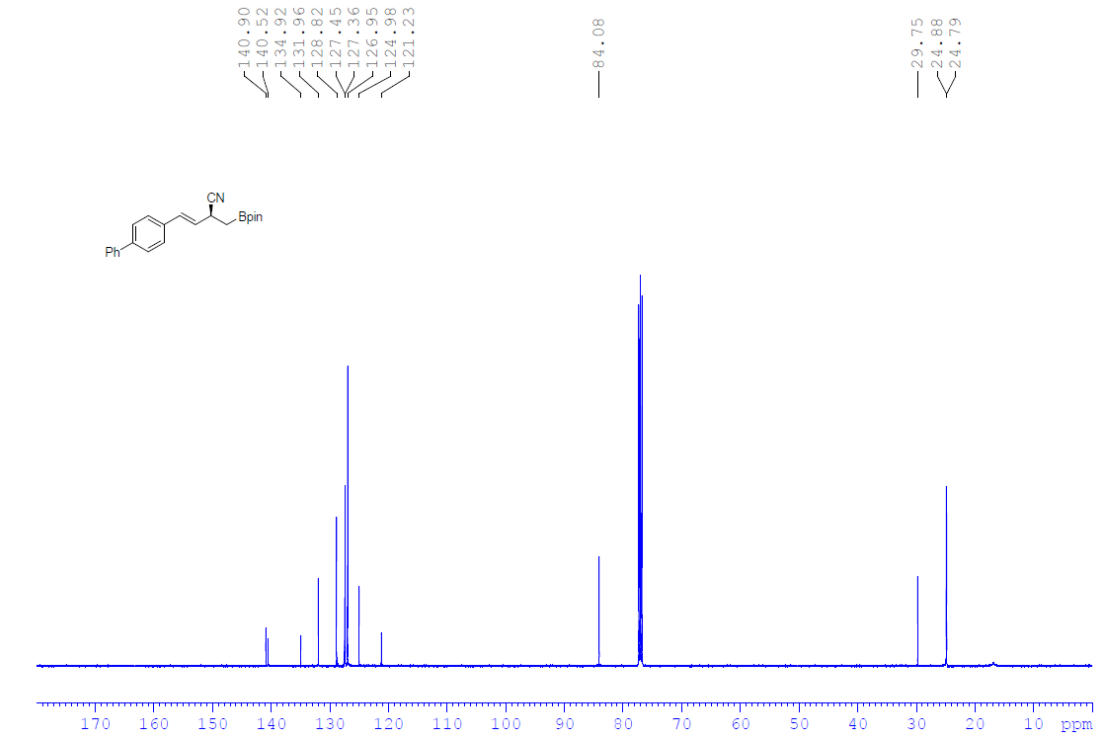
^{13}C NMR of compound **4c** (125 MHz, $CDCl_3$)



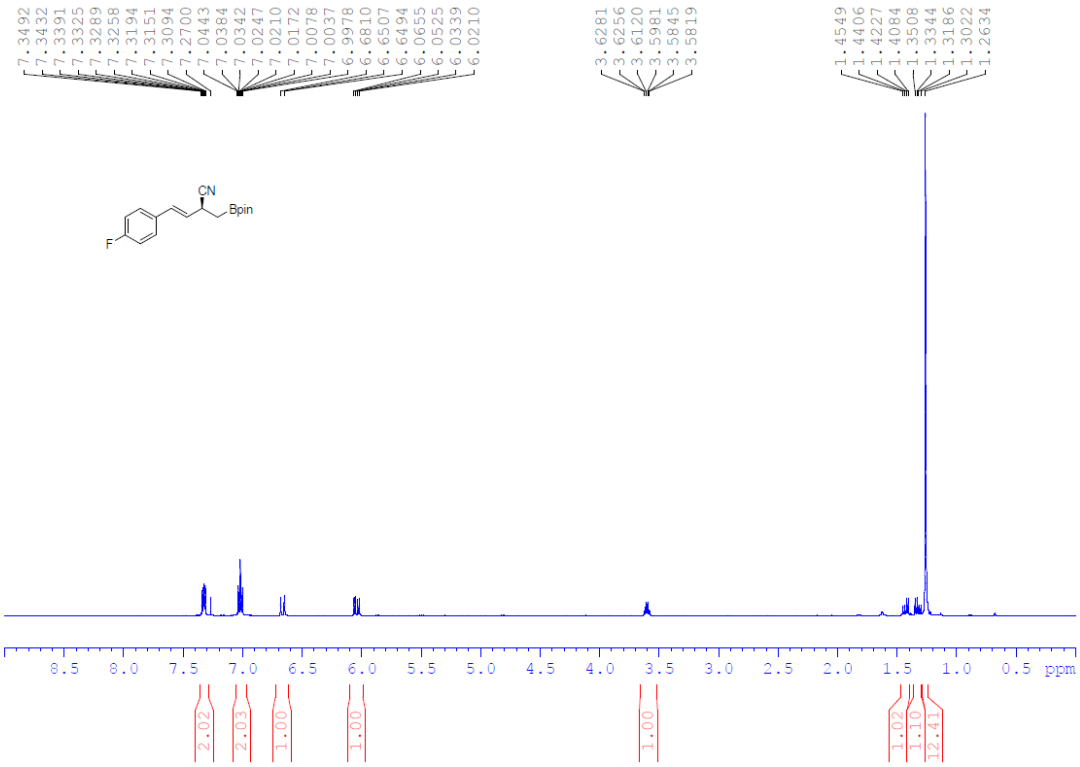
^{1}H NMR of compound **4d** (500 MHz, $CDCl_3$)



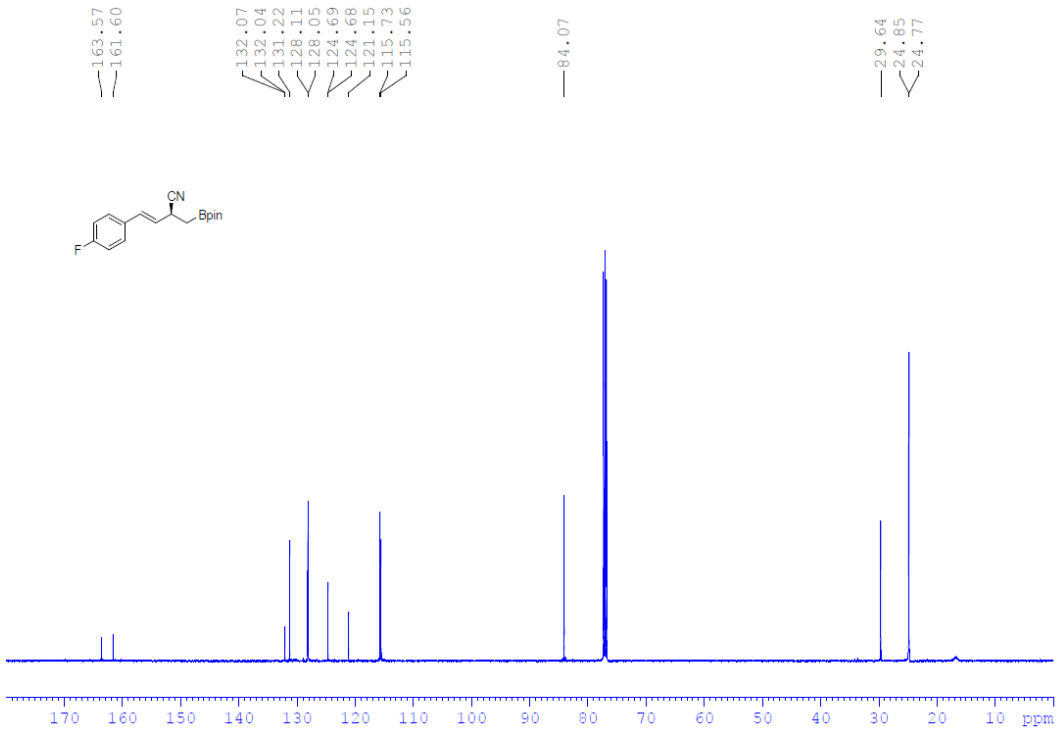
^{13}C NMR of compound **4d** (125 MHz, $CDCl_3$)



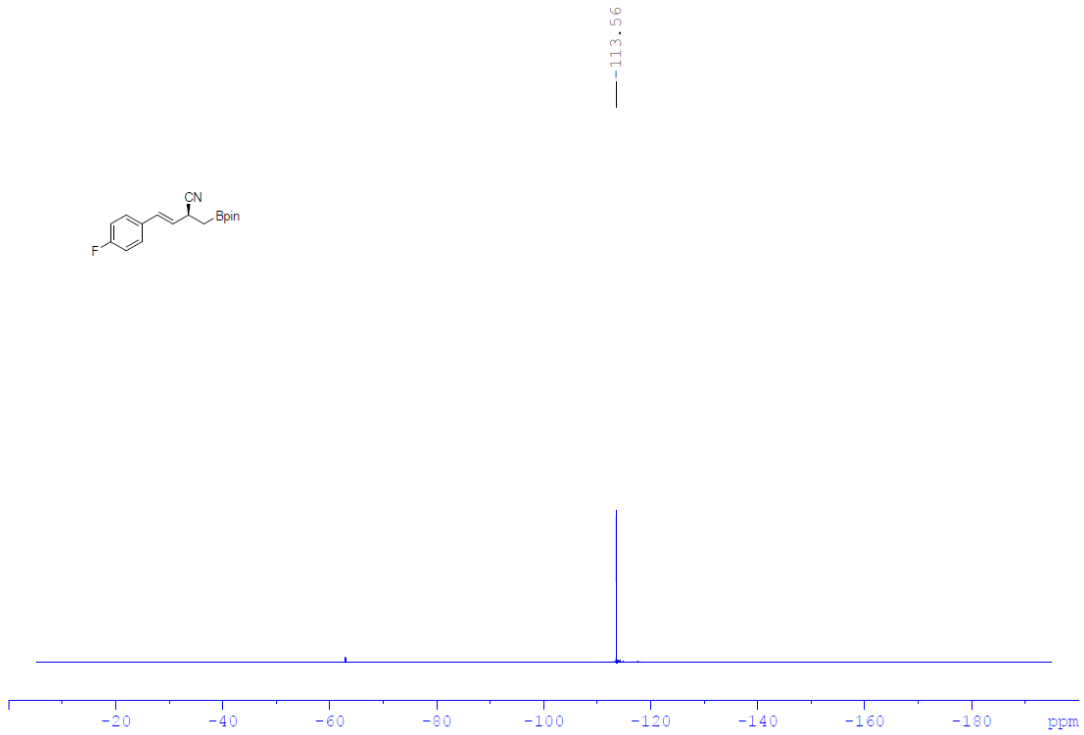
^{1}H NMR of compound **4e** (500 MHz, $CDCl_3$)



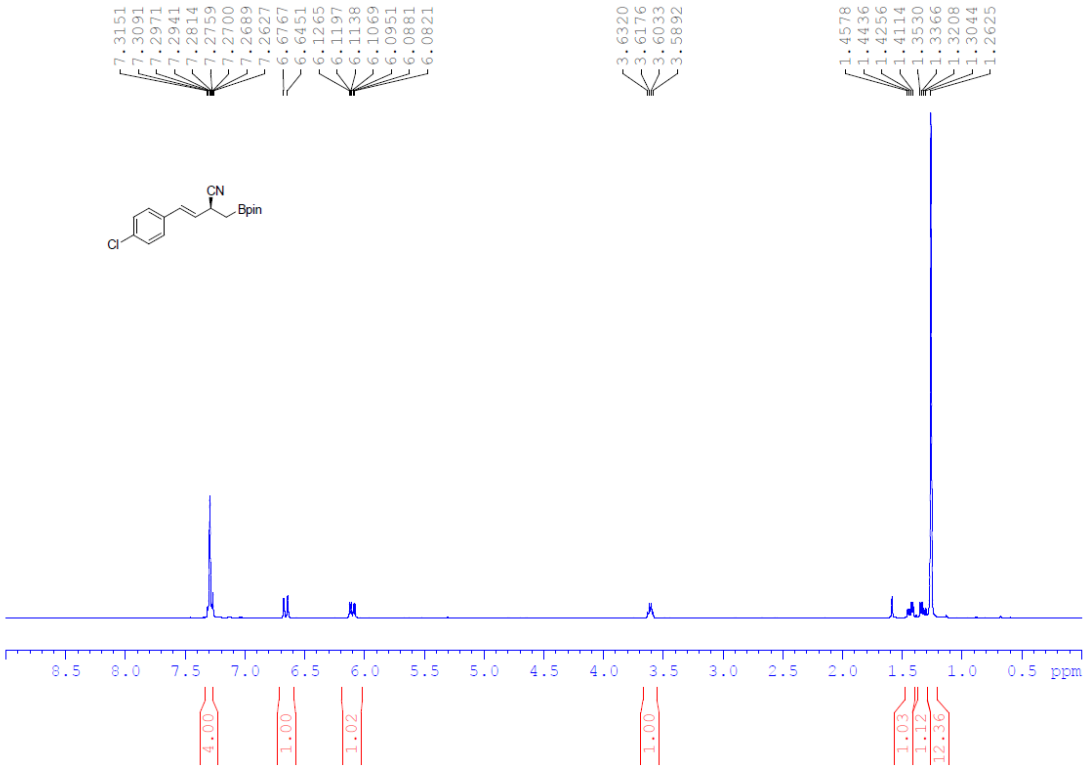
^{13}C NMR of compound **4e** (125 MHz, $CDCl_3$)



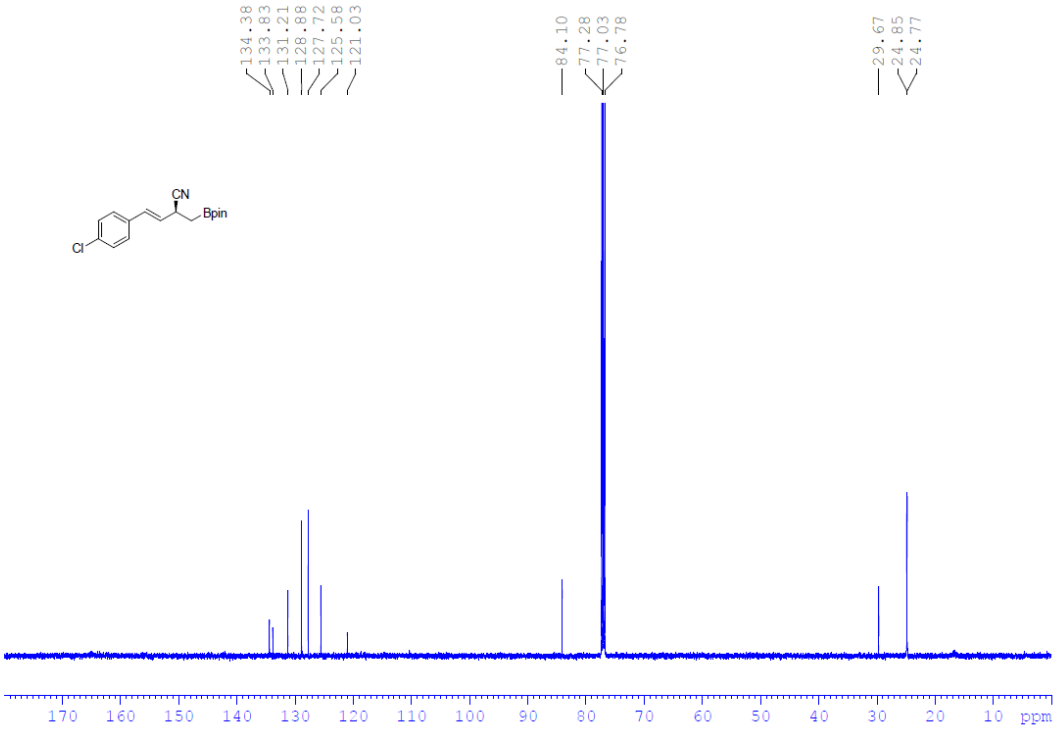
^{19}F NMR of compound **4e** (470 MHz, $CDCl_3$)



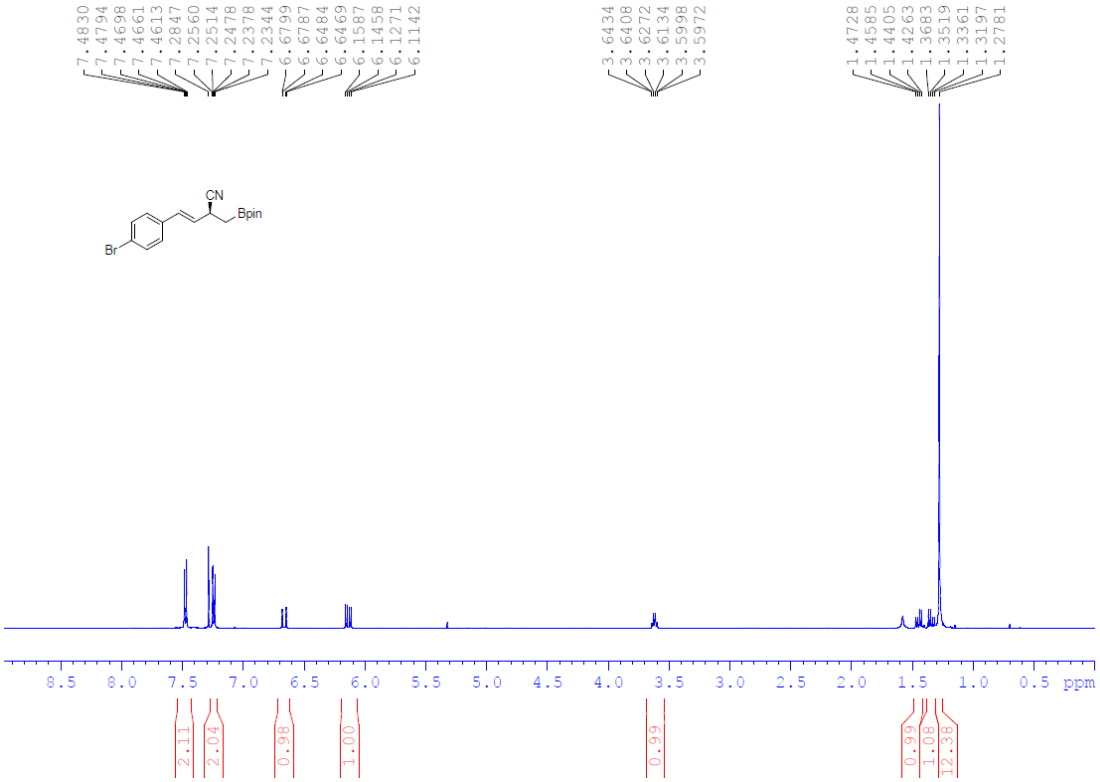
^{1}H NMR of compound **4f** (500 MHz, $CDCl_3$)



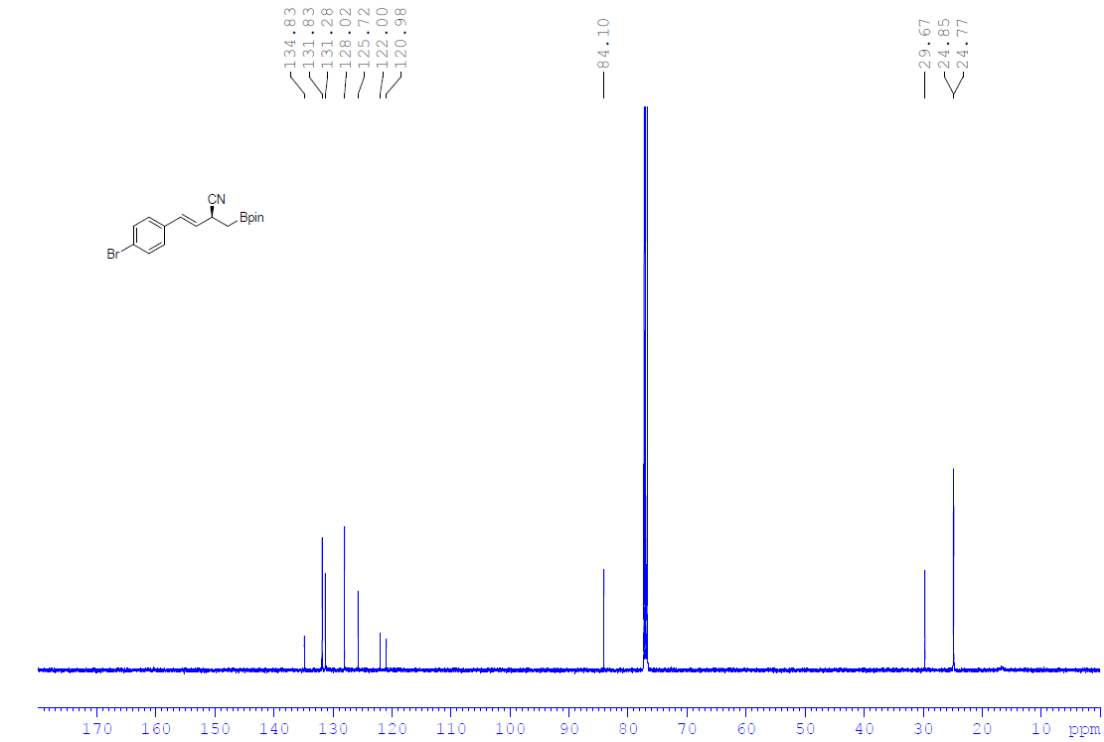
^{13}C NMR of compound **4f** (125 MHz, $CDCl_3$)



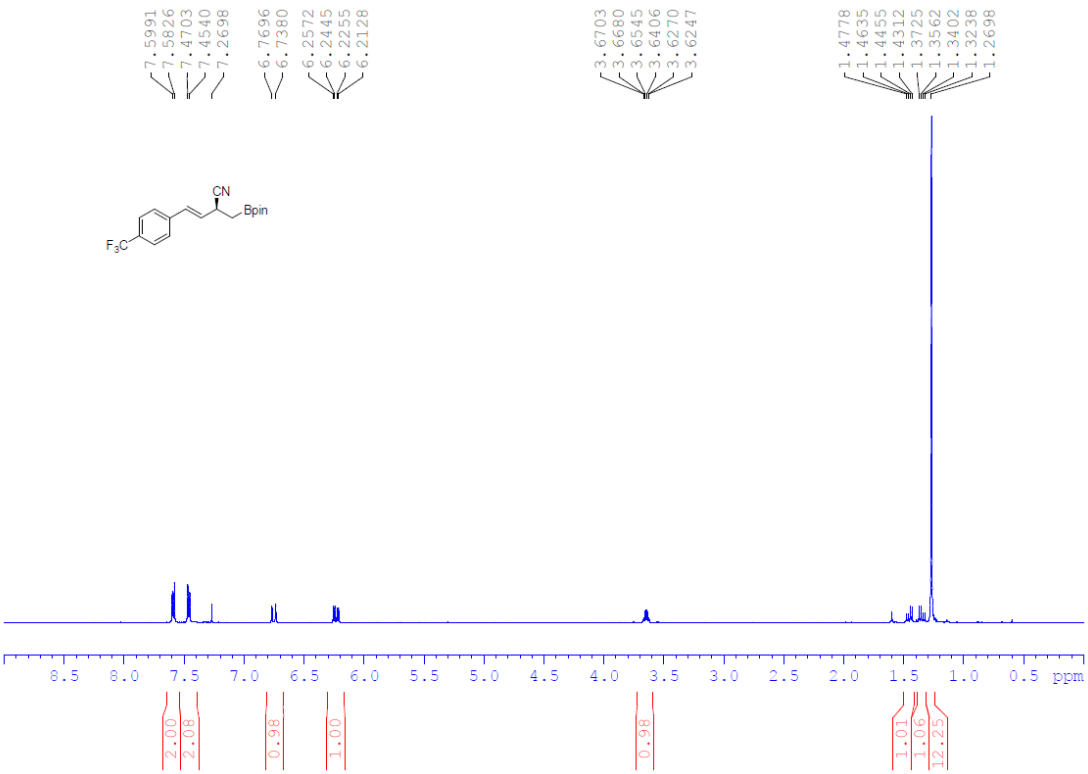
^{1}H NMR of compound **4g** (500 MHz, $CDCl_3$)



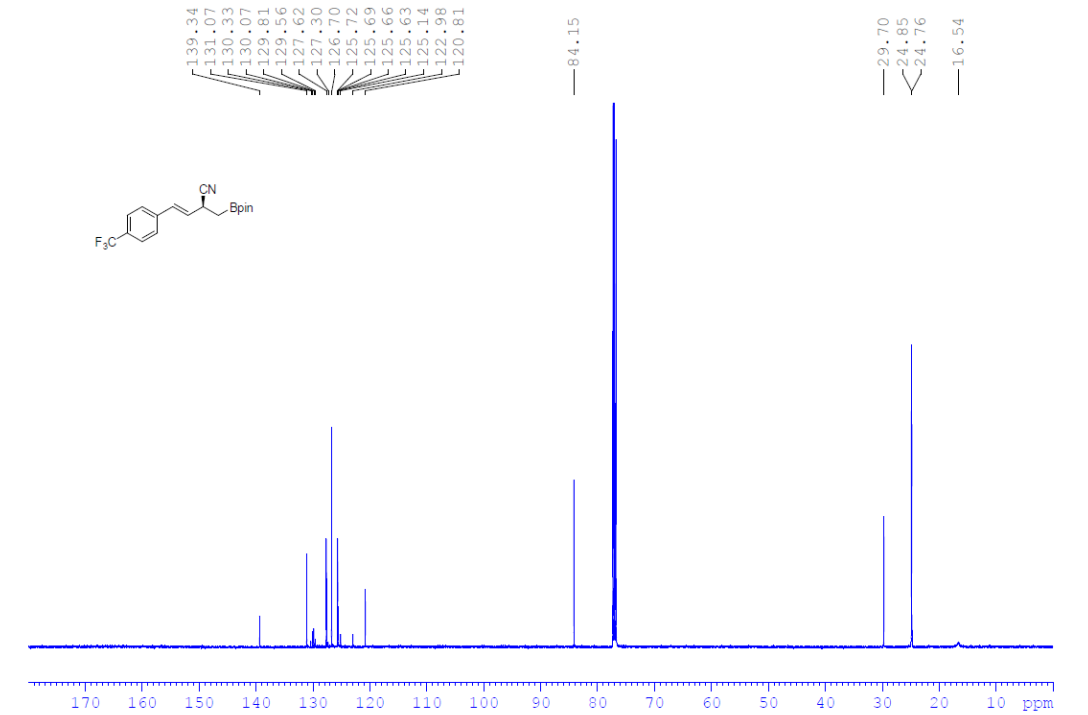
^{13}C NMR of compound **4g** (125 MHz, $CDCl_3$)



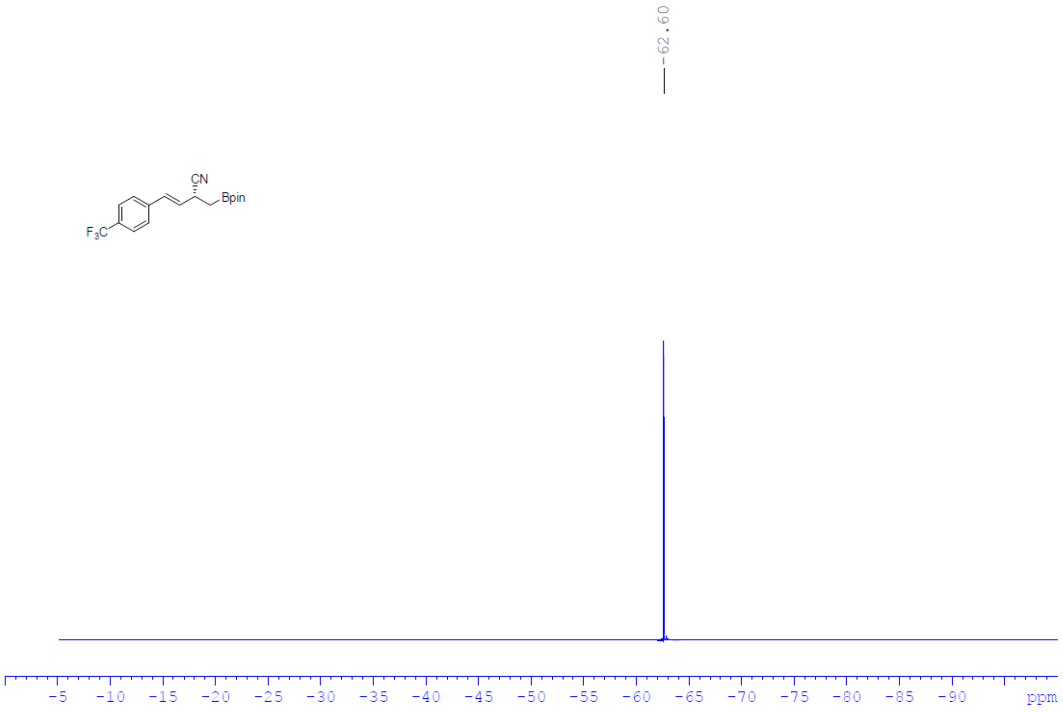
^{1}H NMR of compound **4h** (500 MHz, $CDCl_3$)



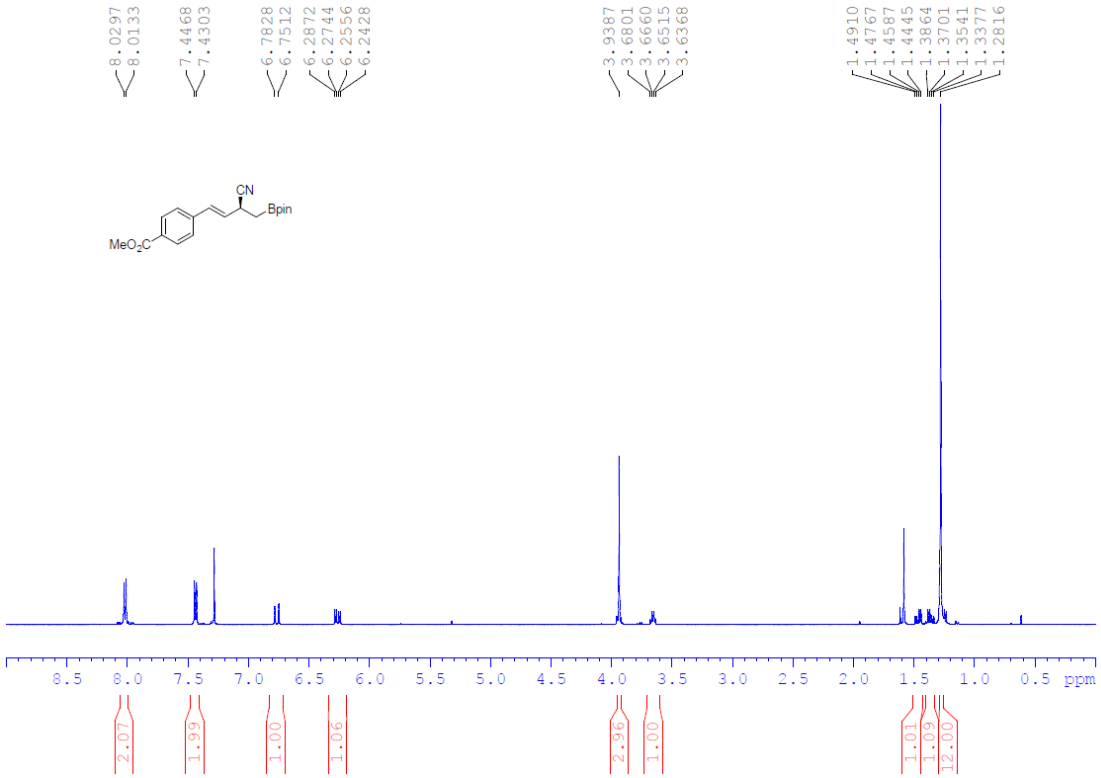
^{13}C NMR of compound **4h** (125 MHz, $CDCl_3$)



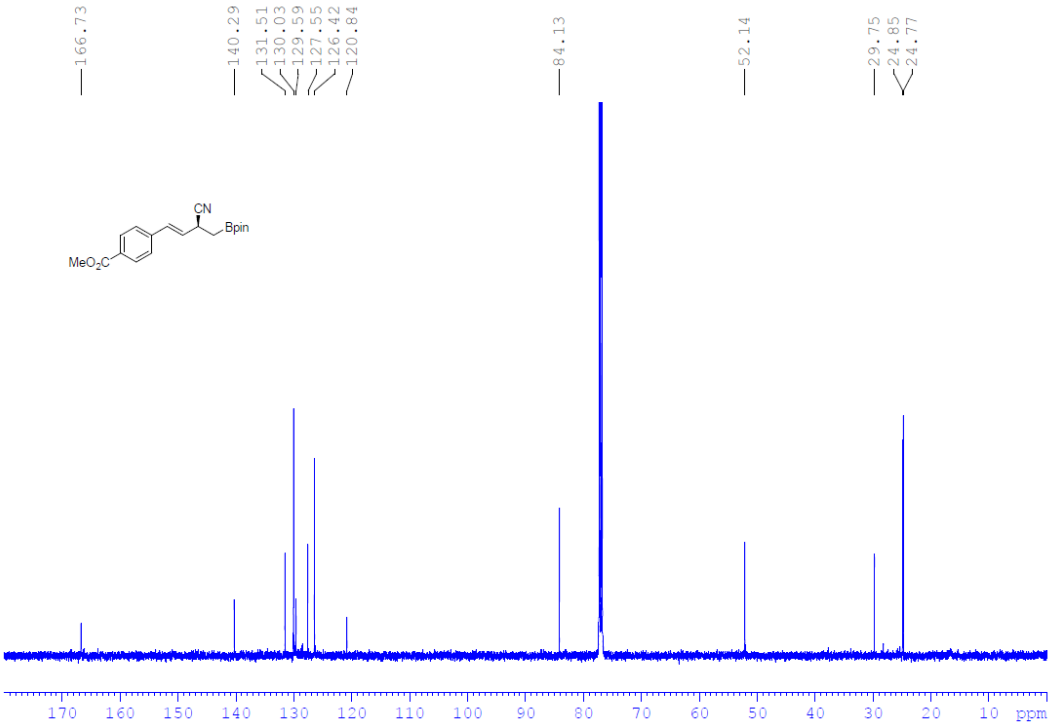
^{19}F NMR of compound **4h** (470 MHz, $CDCl_3$)



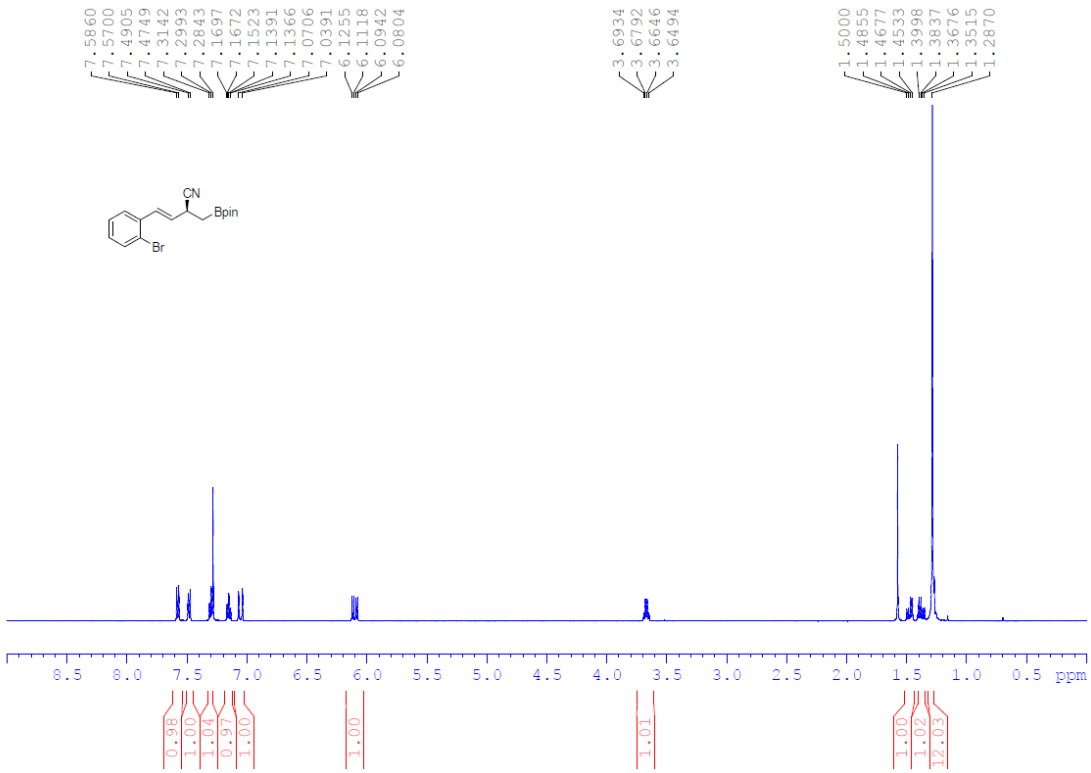
^{1}H NMR of compound **4i** (500 MHz, $CDCl_3$)



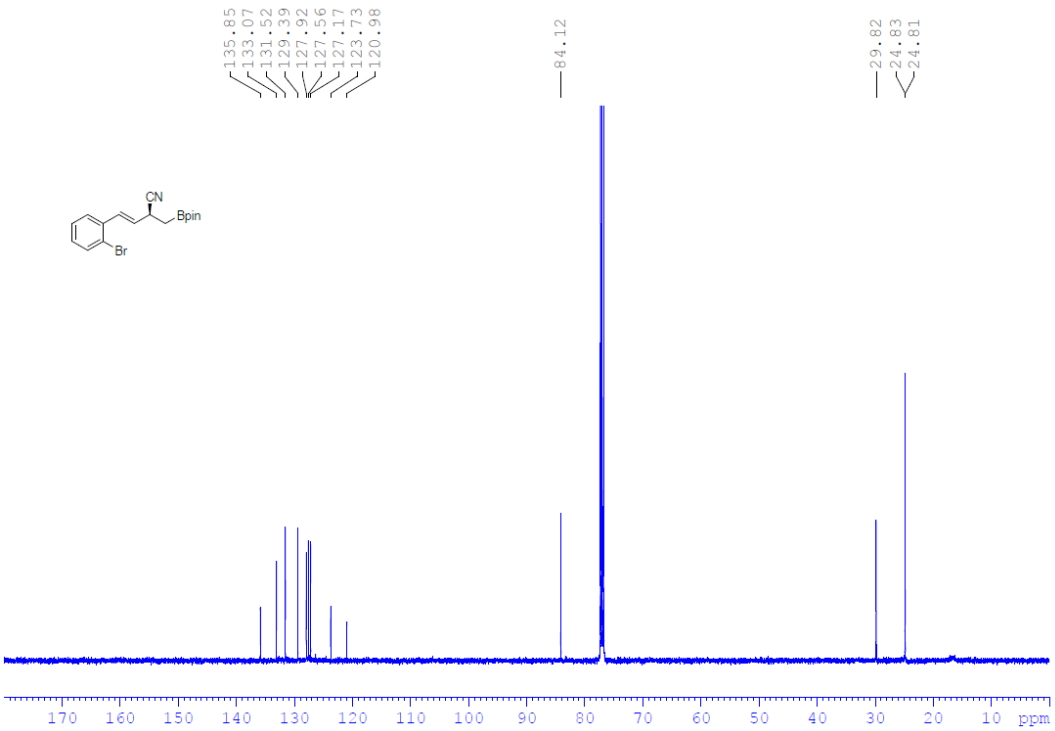
^{13}C NMR of compound **4i** (125 MHz, $CDCl_3$)



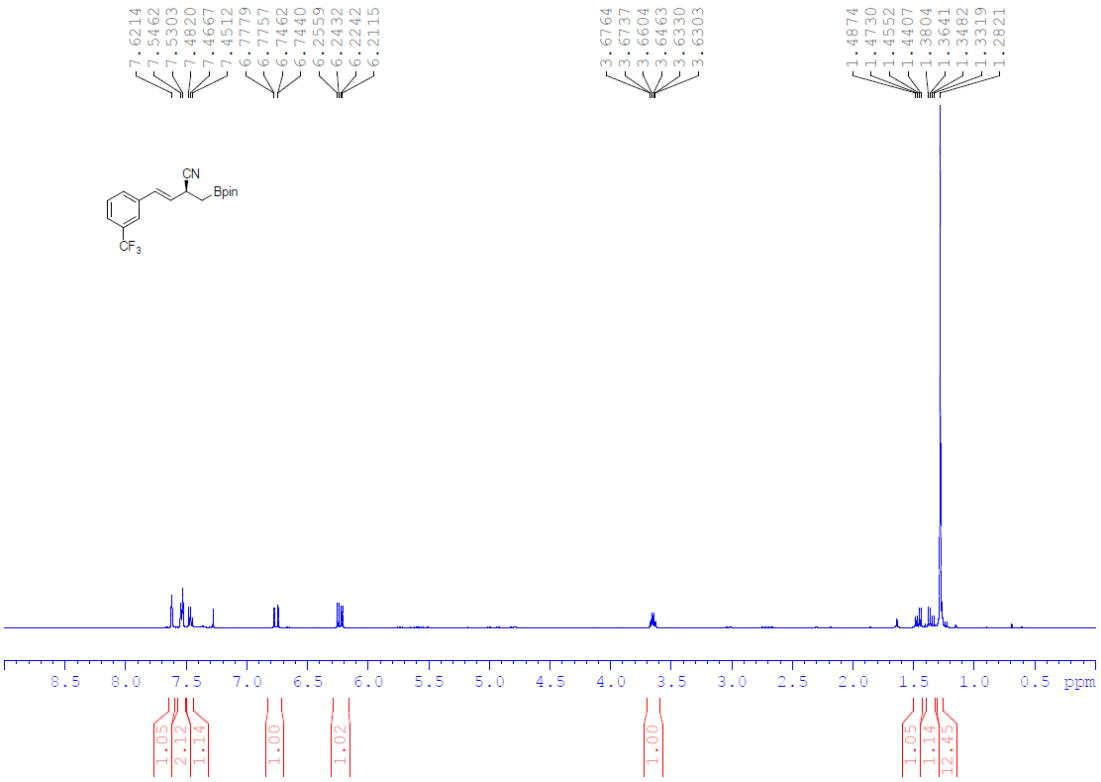
^{1}H NMR of compound **4j** (500 MHz, $CDCl_3$)



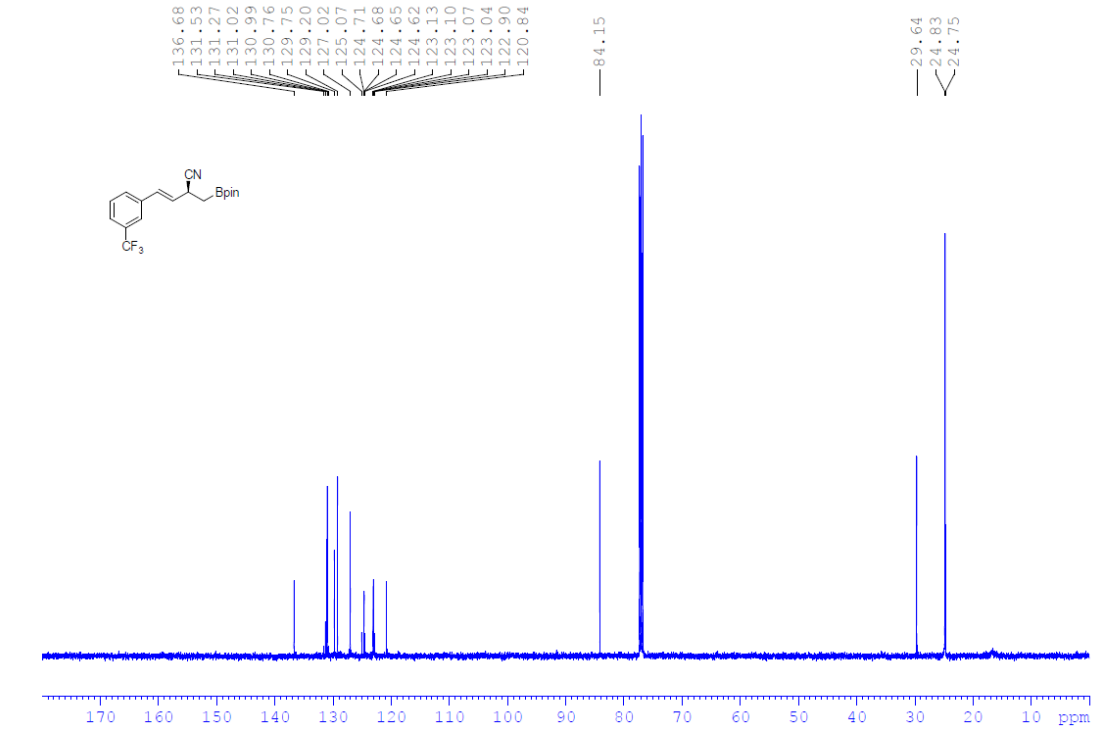
^{13}C NMR of compound **4j** (125 MHz, $CDCl_3$)



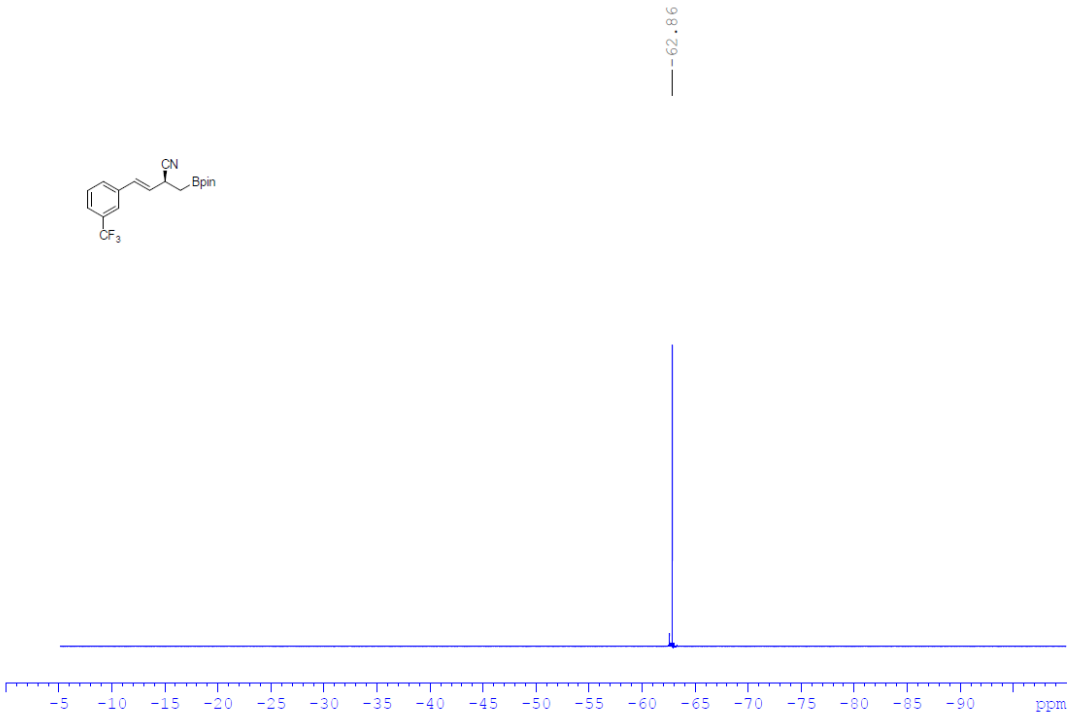
^{1}H NMR of compound **4k** (500 MHz, $CDCl_3$)



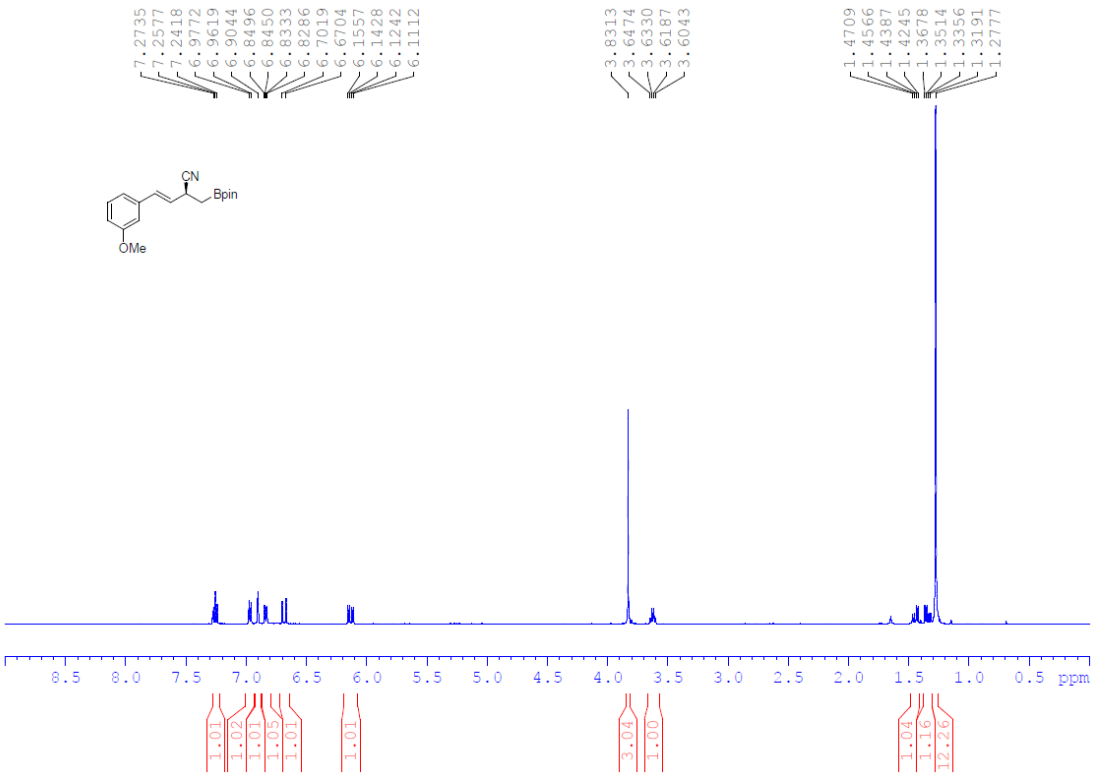
^{13}C NMR of compound **4k** (125 MHz, $CDCl_3$)



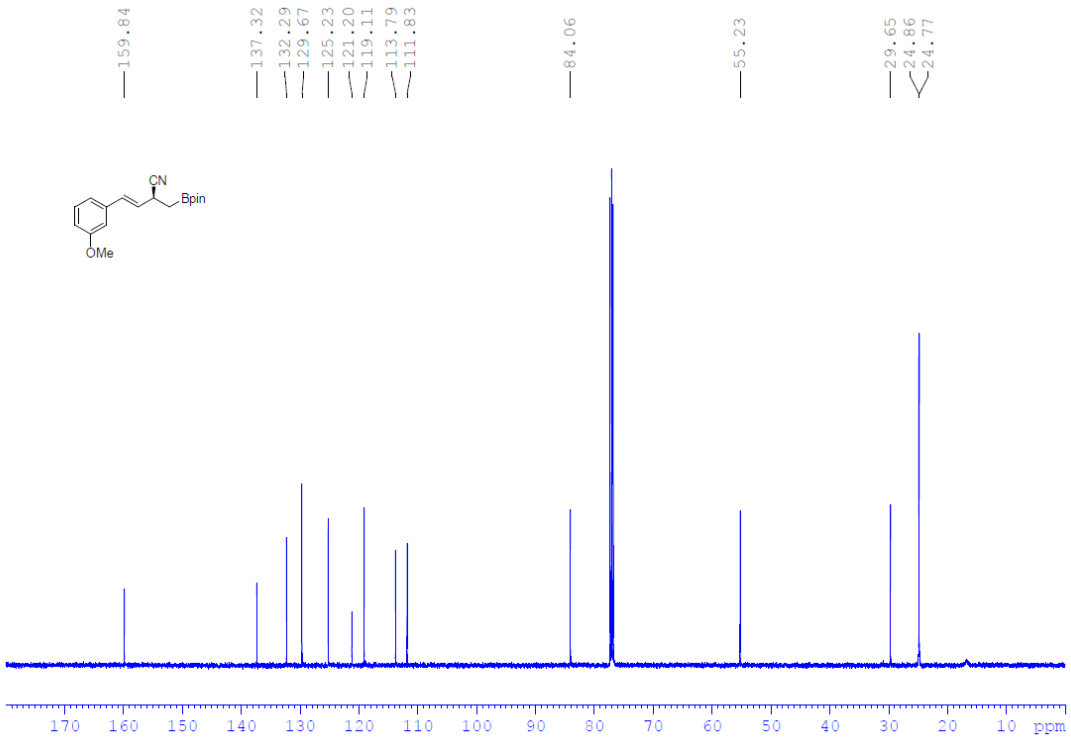
^{19}F NMR of compound **4k** (500 MHz, $CDCl_3$)



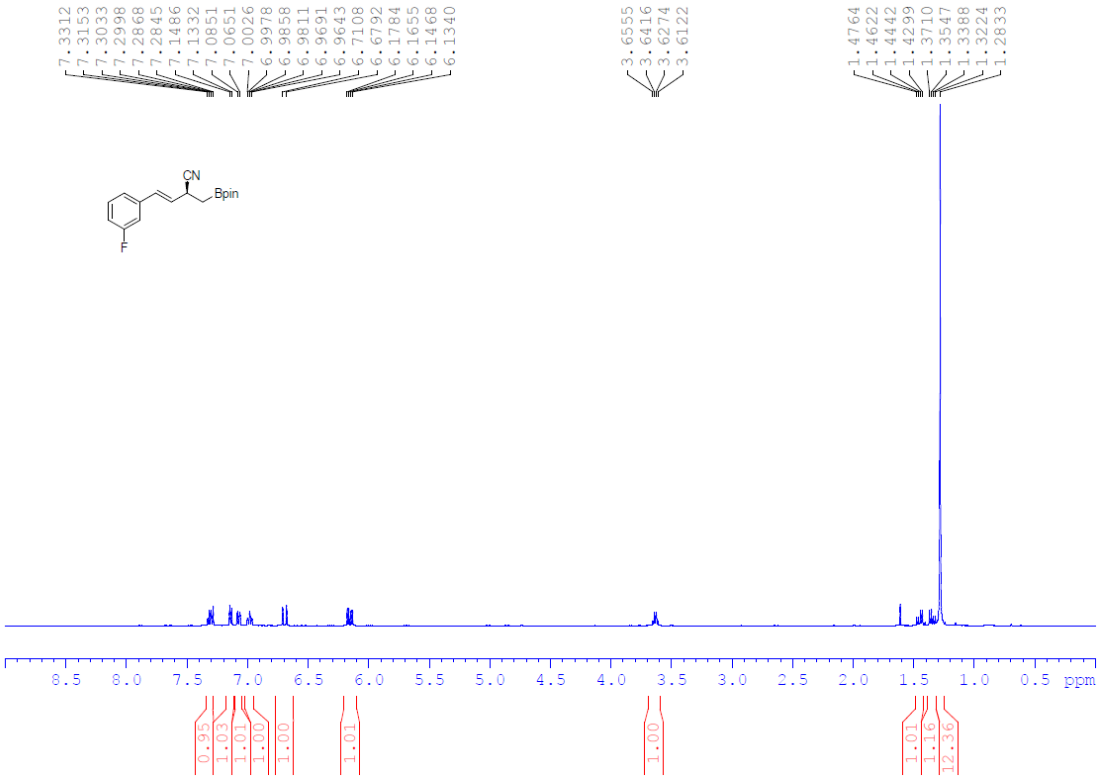
^{1}H NMR of compound **4l** (500 MHz, $CDCl_3$)



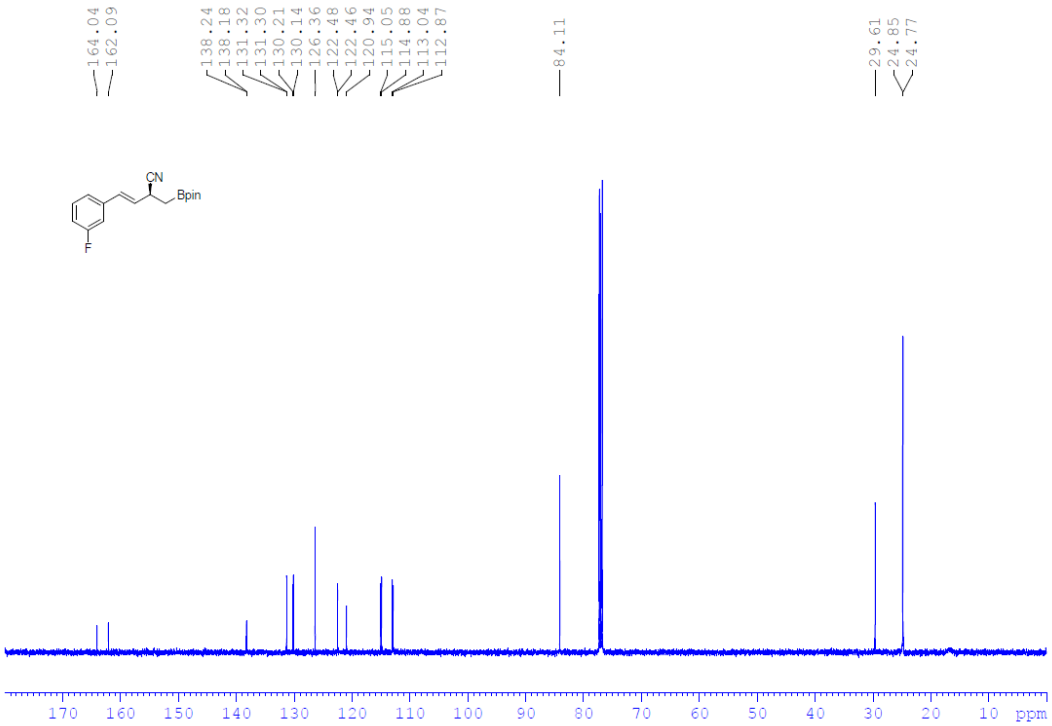
^{13}C NMR of compound **4l** (125 MHz, $CDCl_3$)



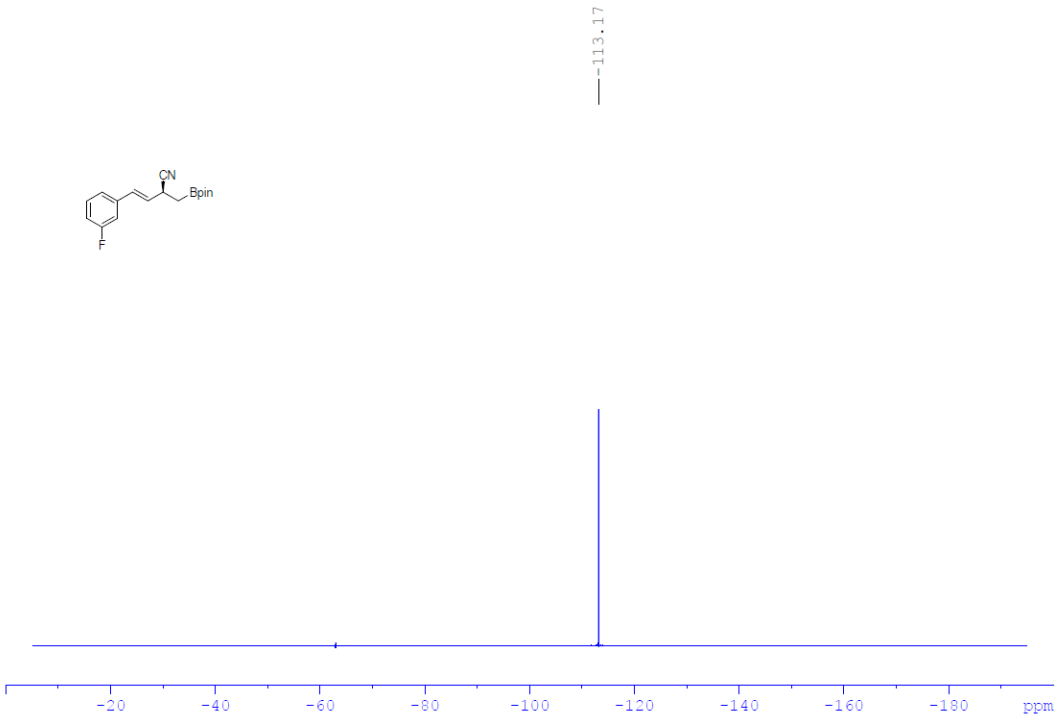
^{1}H NMR of compound **4m** (500 MHz, $CDCl_3$)



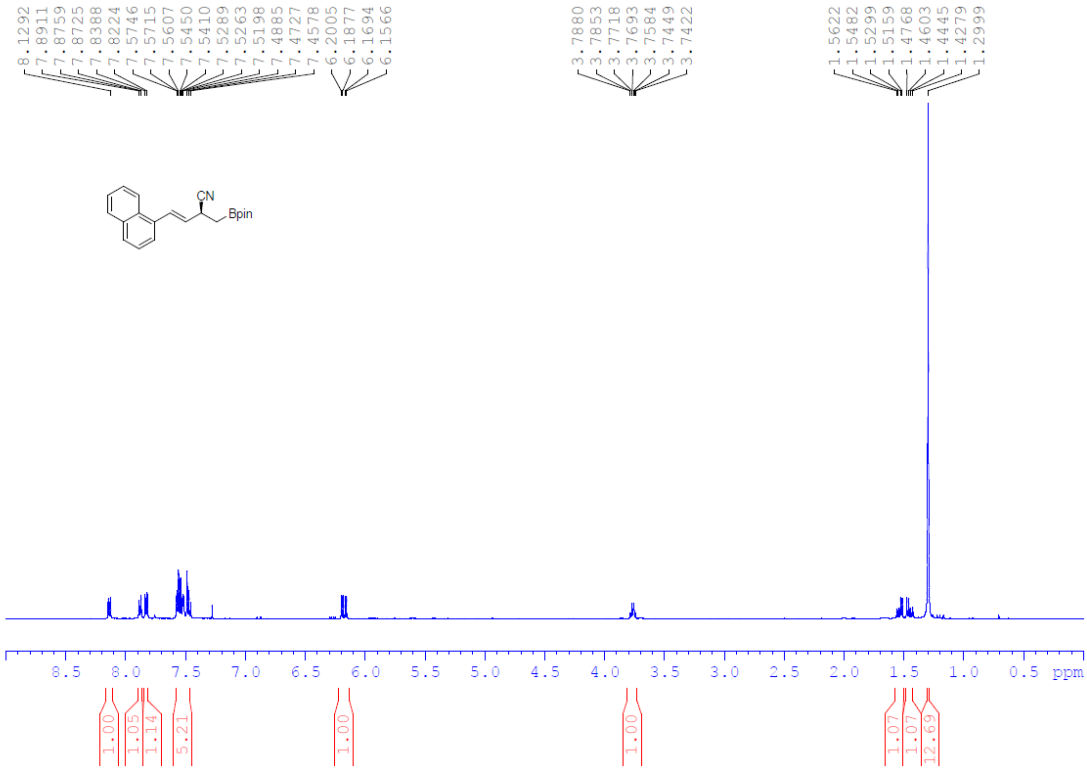
^{13}C NMR of compound **4m** (125 MHz, $CDCl_3$)



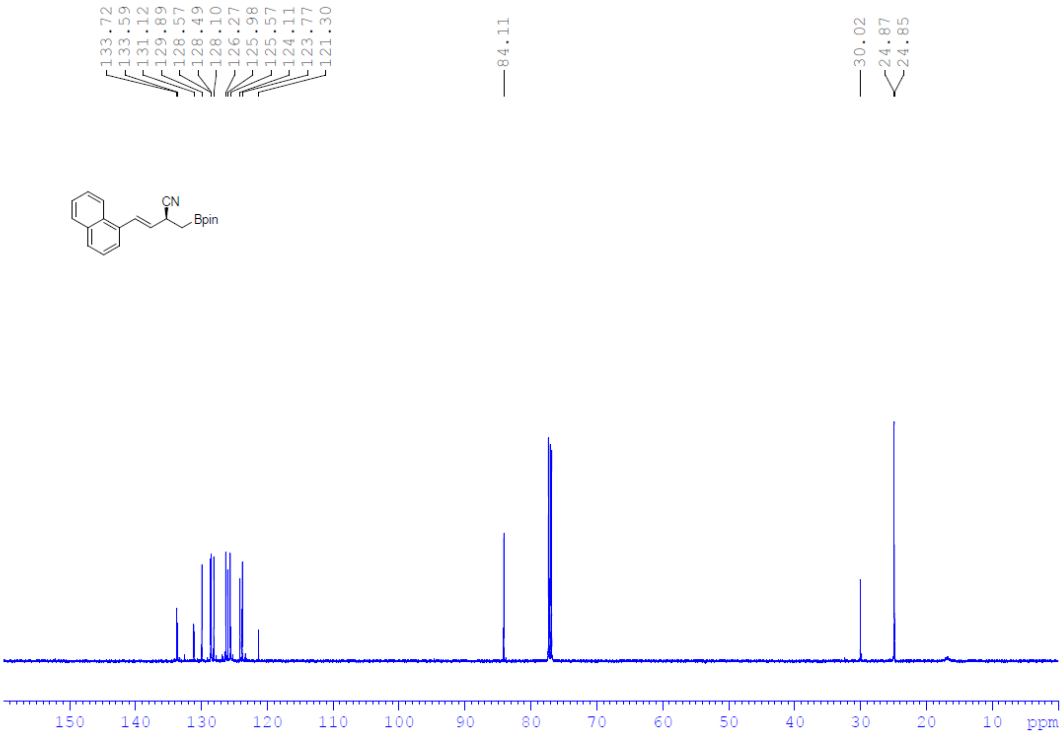
^{19}F NMR of compound **4m** (470 MHz, $CDCl_3$)



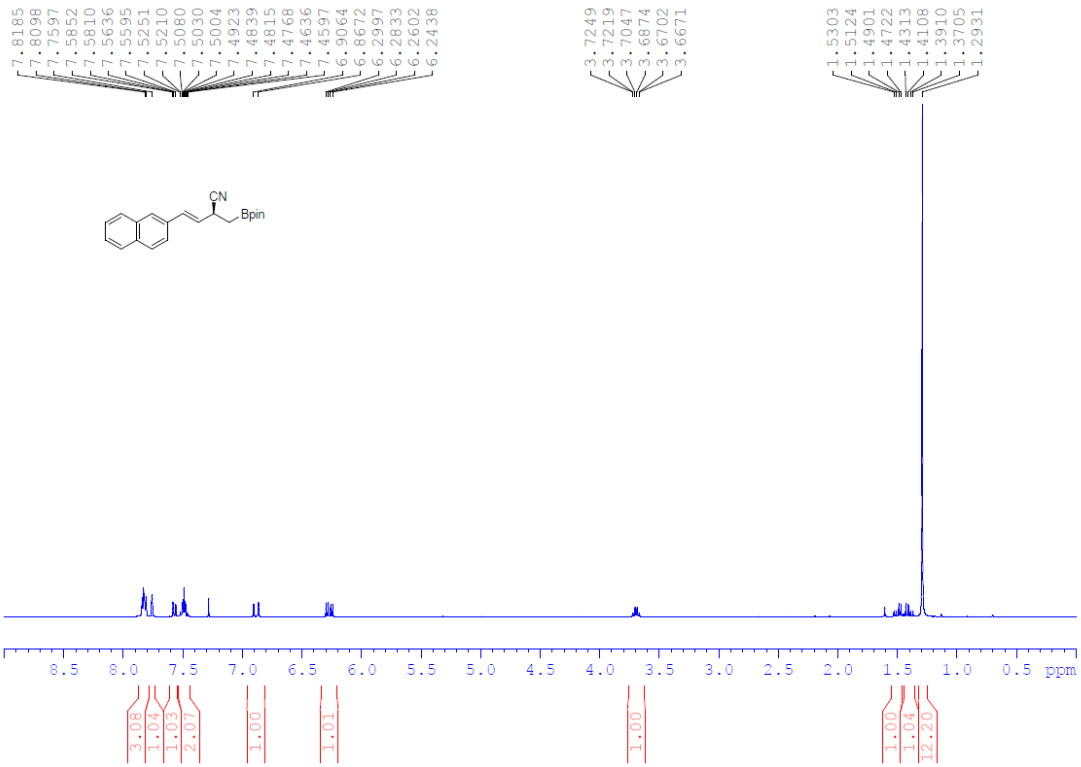
^{1}H NMR of compound **4n** (500 MHz, $CDCl_3$)



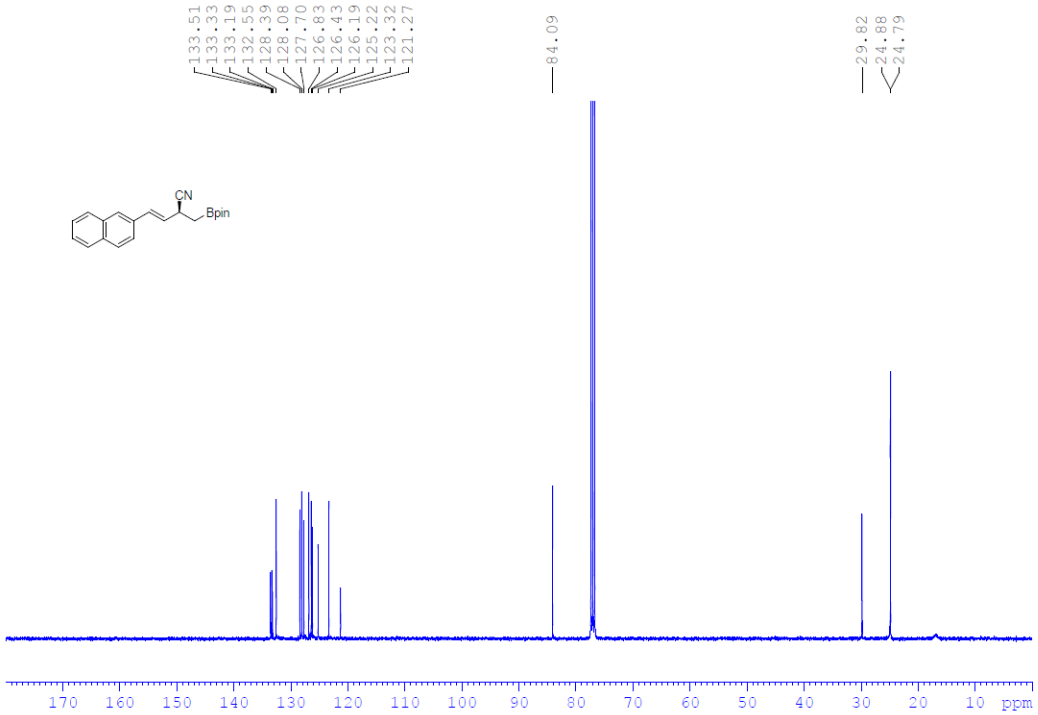
^{13}C NMR of compound **4n** (125 MHz, $CDCl_3$)



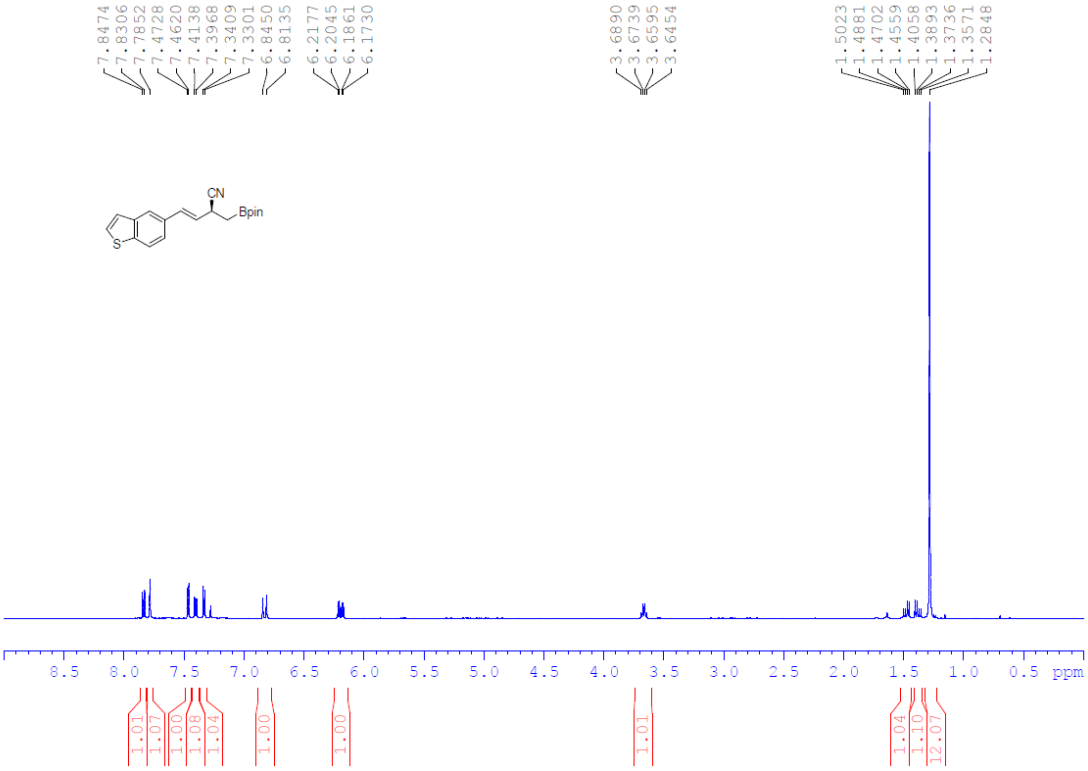
^{1}H NMR of compound **4o** (400 MHz, $CDCl_3$)



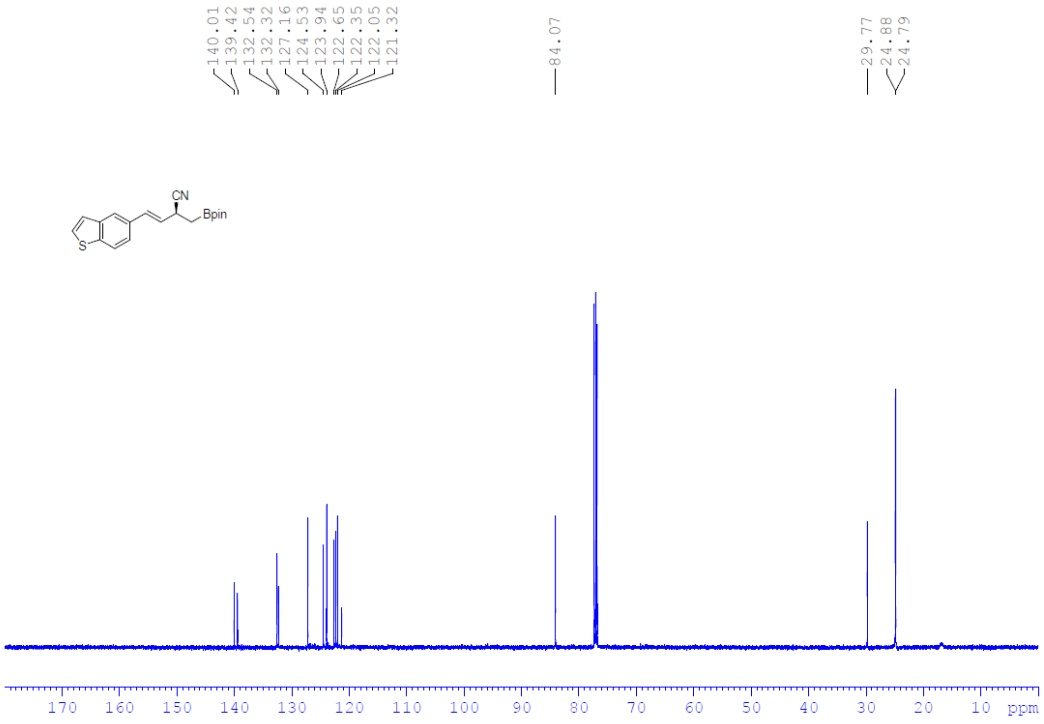
^{13}C NMR of compound **4o** (100 MHz, $CDCl_3$)



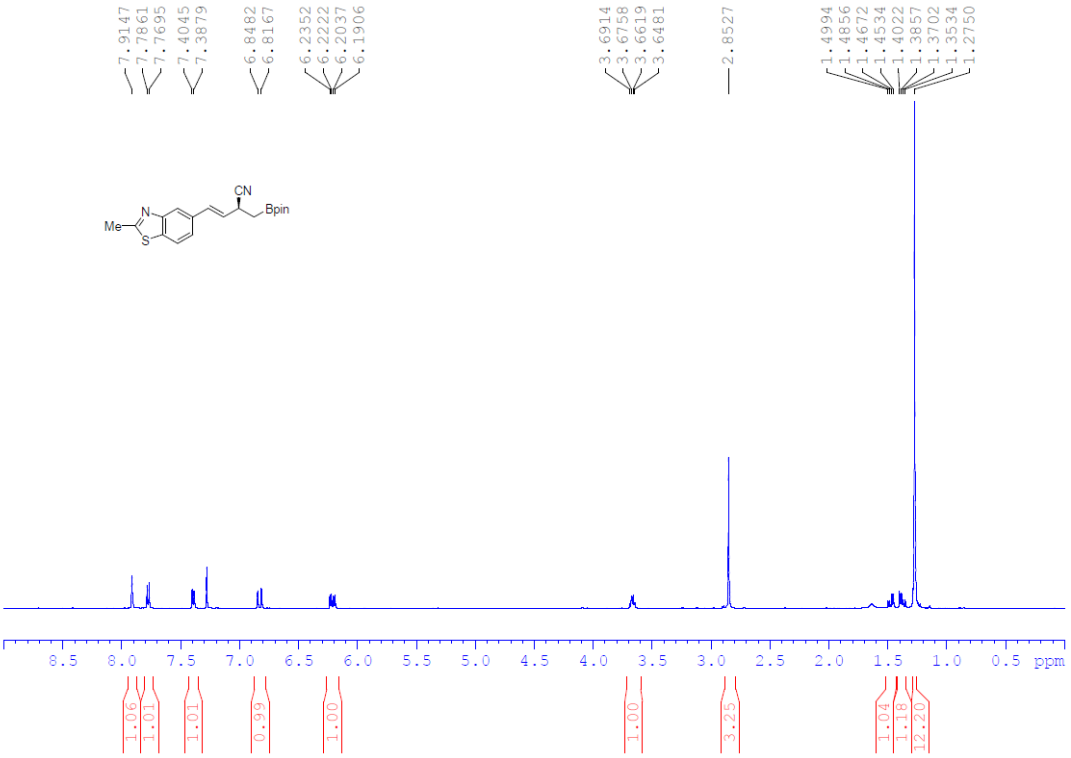
^{1}H NMR of compound **4p** (500 MHz, $CDCl_3$)



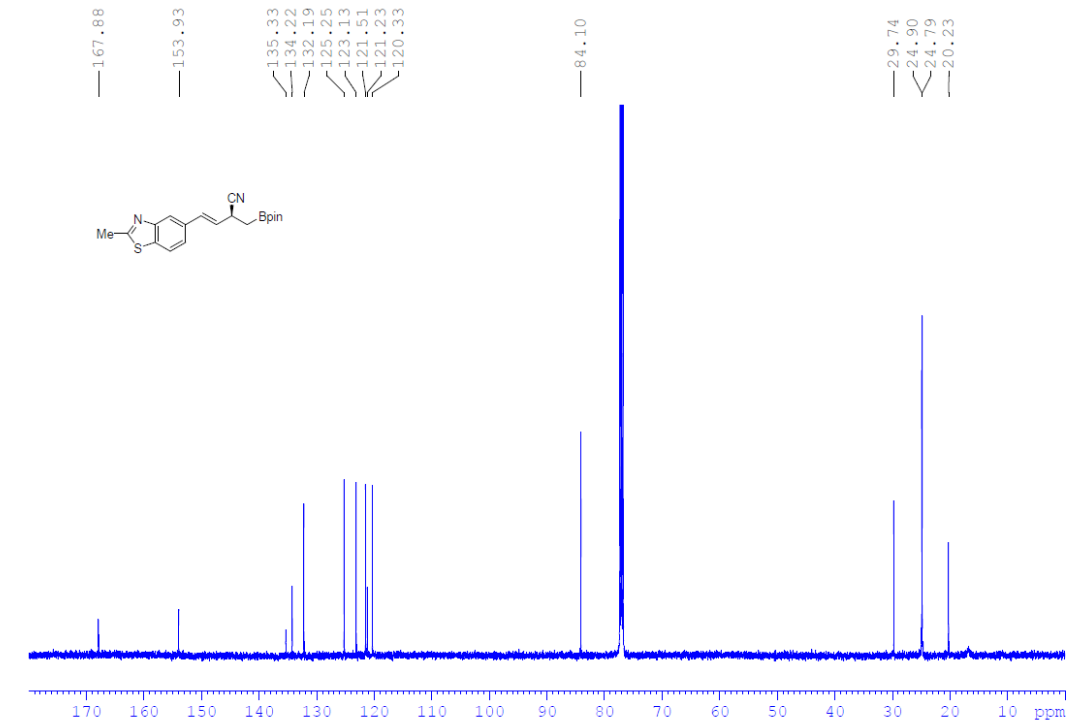
^{13}C NMR of compound **4p** (125 MHz, $CDCl_3$)



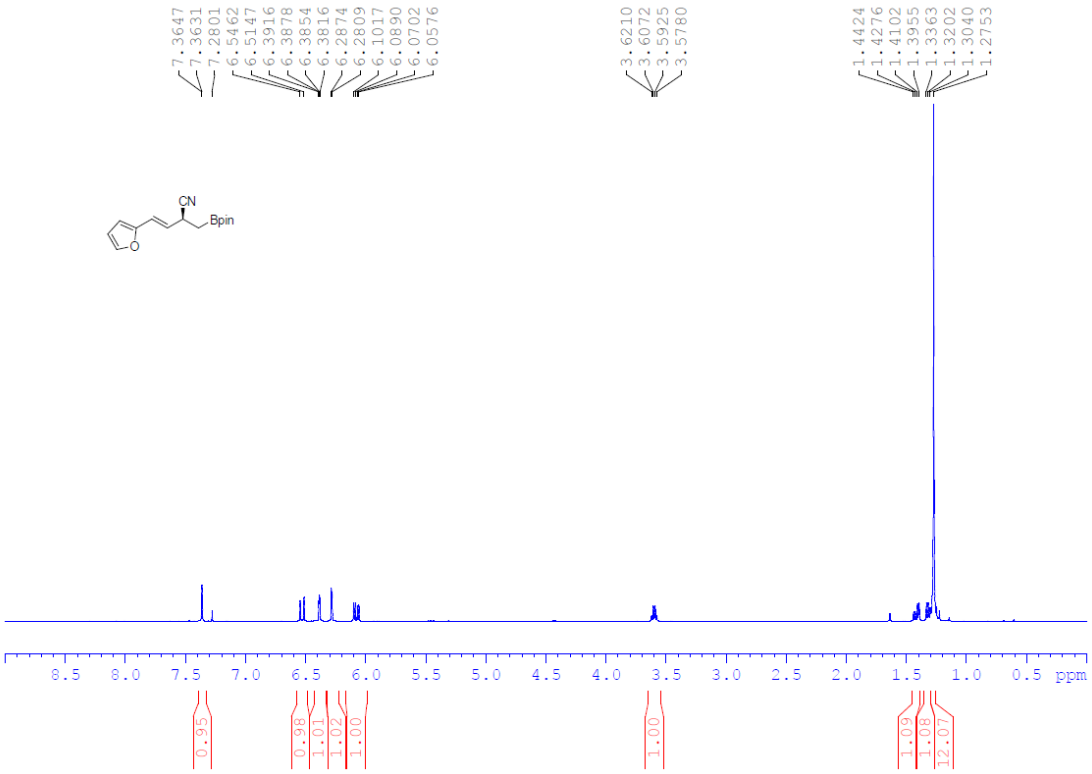
^{1}H NMR of compound **4q** (500 MHz, $CDCl_3$)



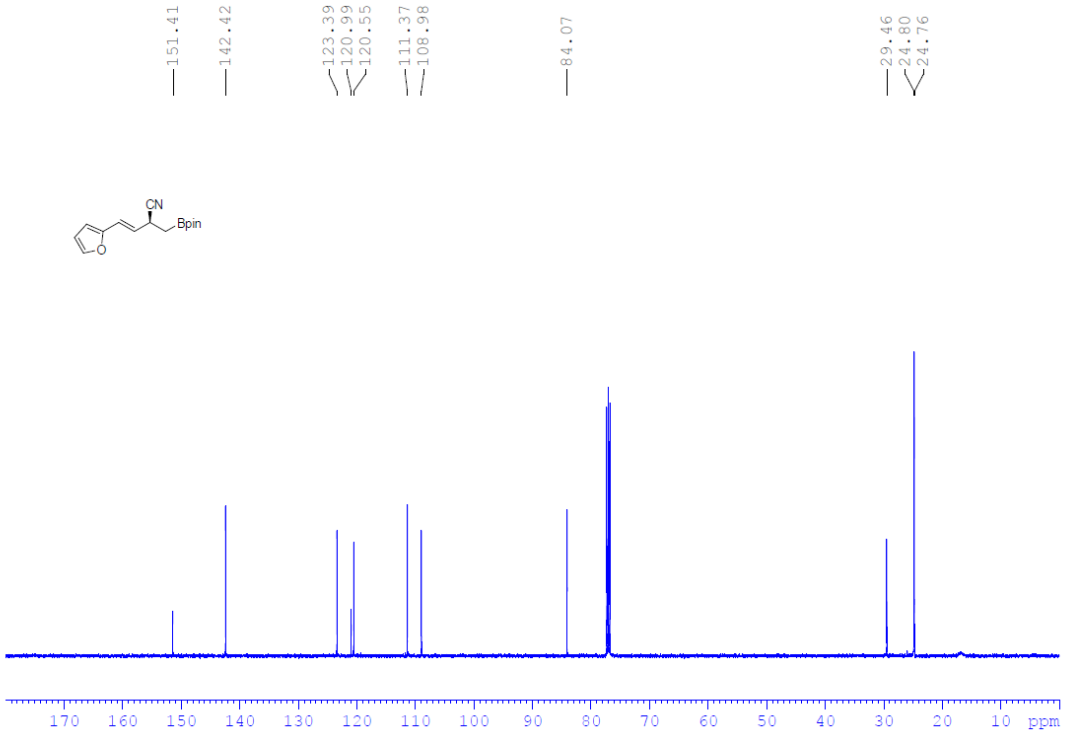
^{13}C NMR of compound **4q** (125 MHz, $CDCl_3$)



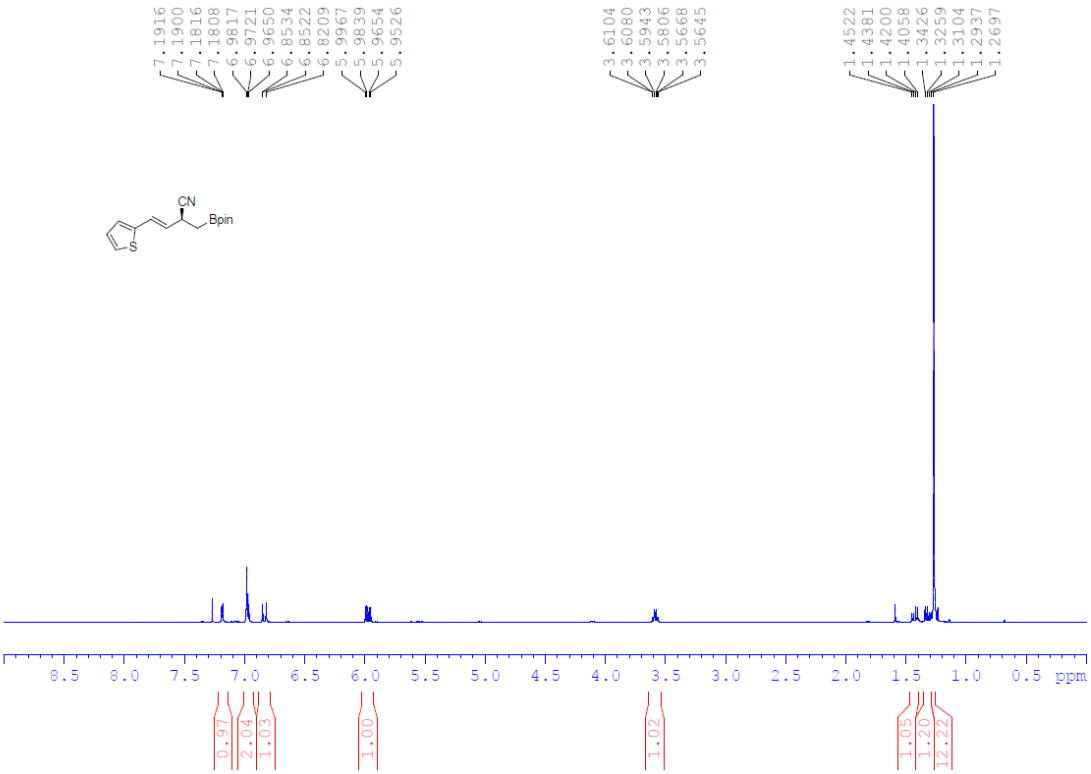
^{1}H NMR of compound **4r** (500 MHz, $CDCl_3$)



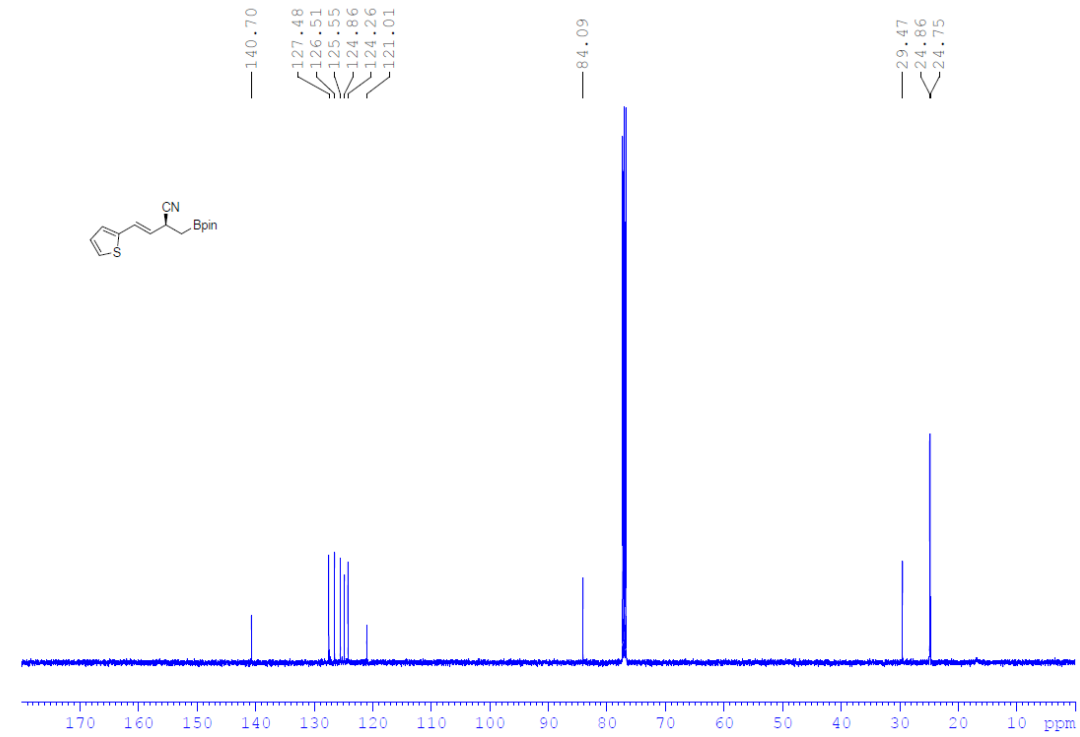
^{13}C NMR of compound **4r** (125 MHz, $CDCl_3$)



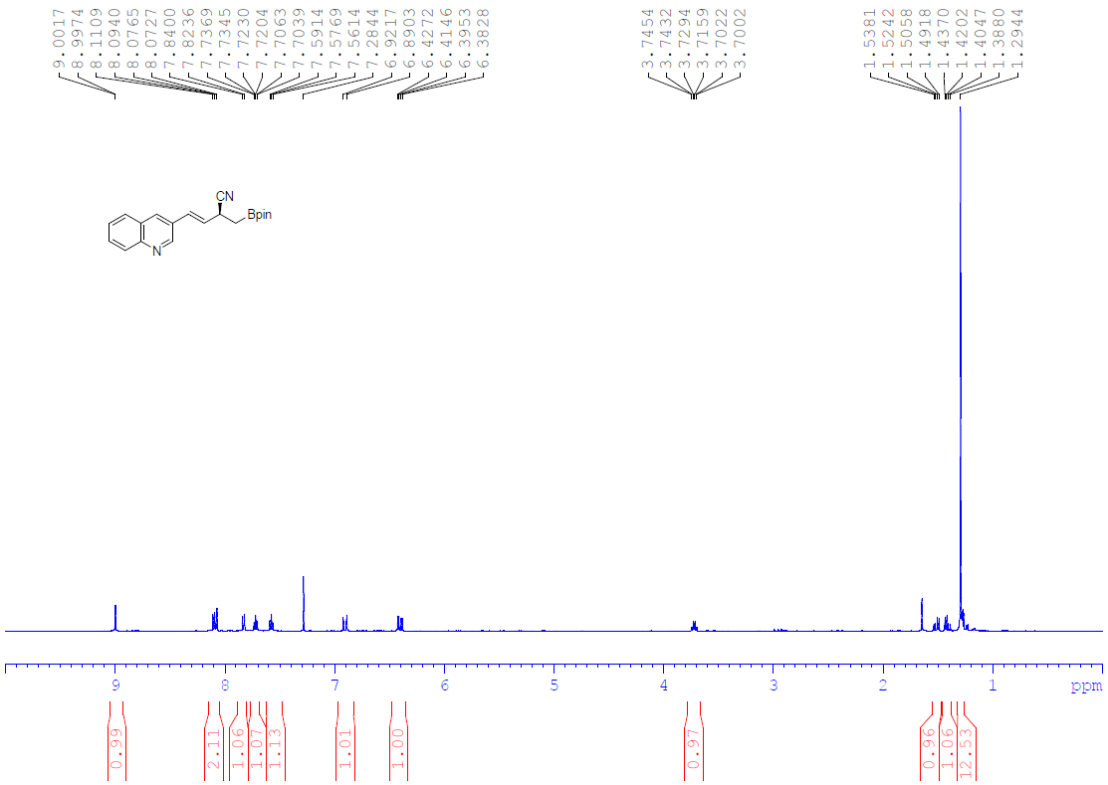
^{1}H NMR of compound **4s** (500 MHz, $CDCl_3$)



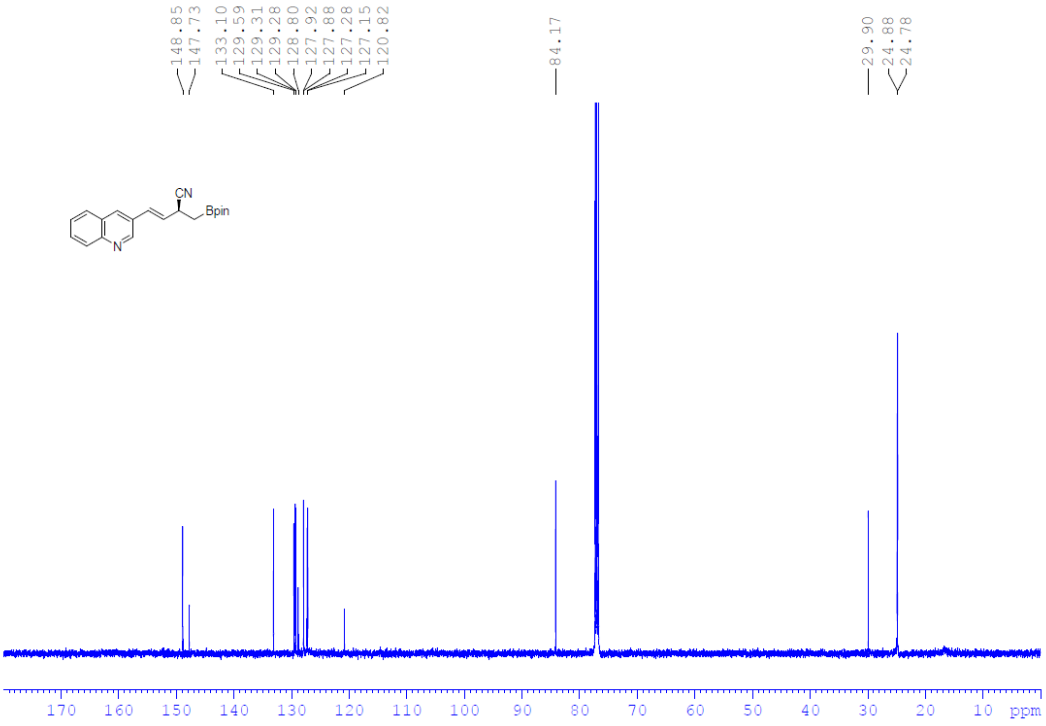
^{13}C NMR of compound **4s** (125 MHz, $CDCl_3$)



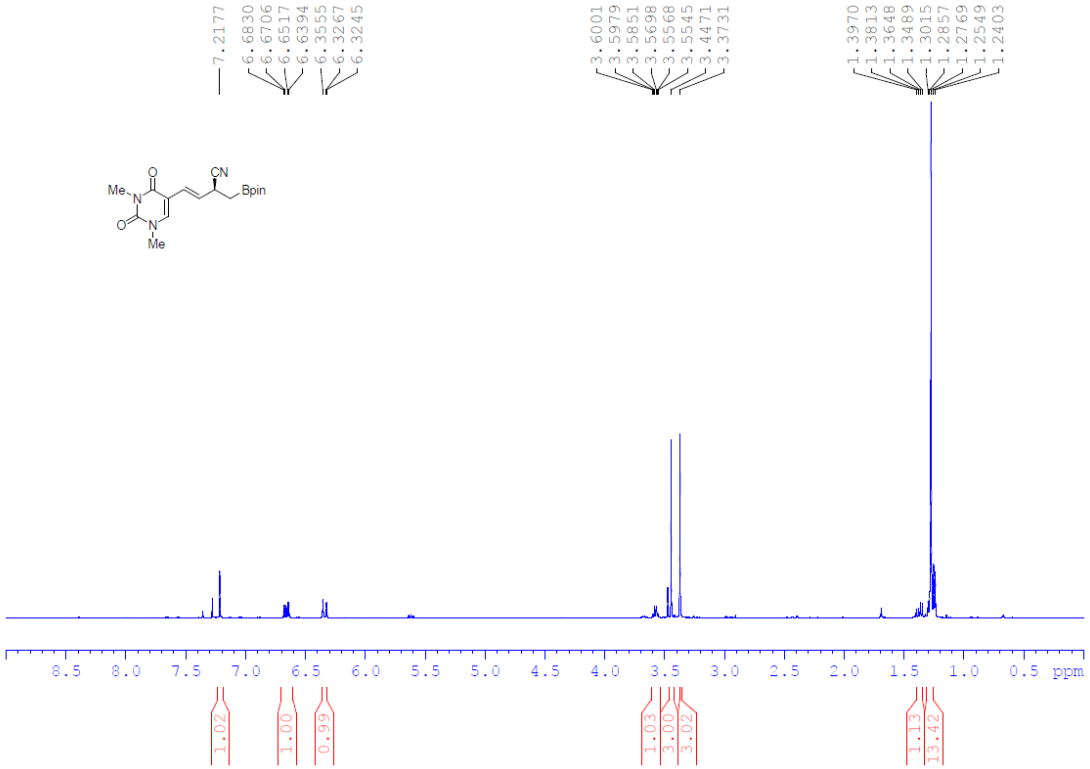
^{1}H NMR of compound **4t** (500 MHz, $CDCl_3$)



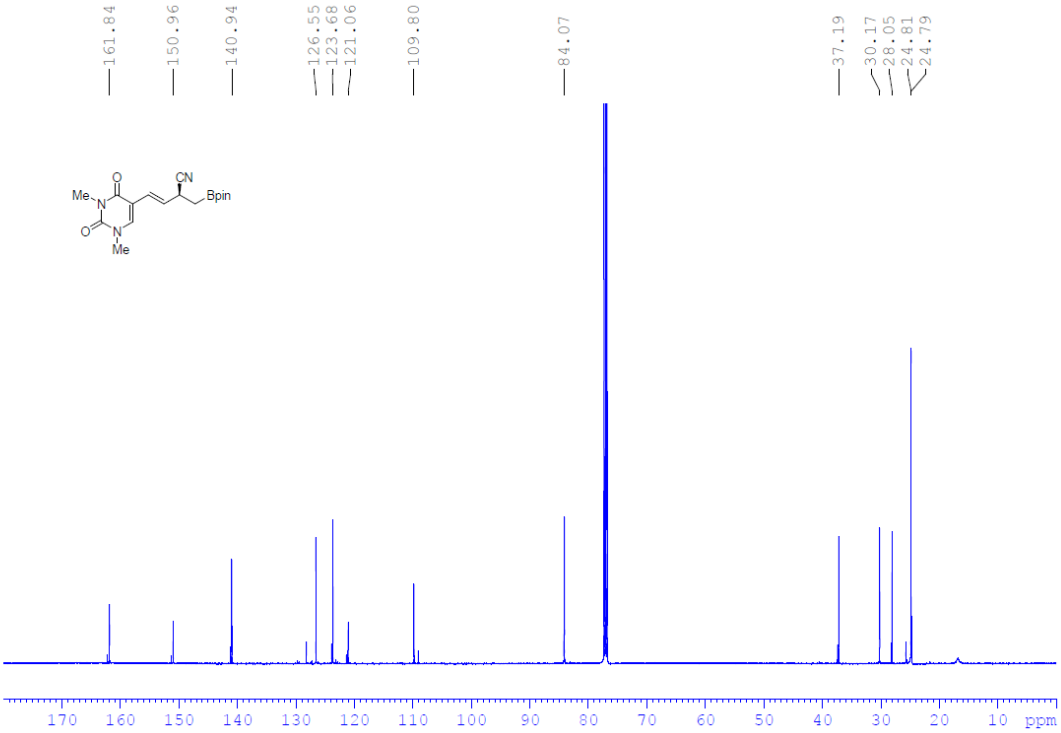
^{13}C NMR of compound **4t** (125 MHz, $CDCl_3$)



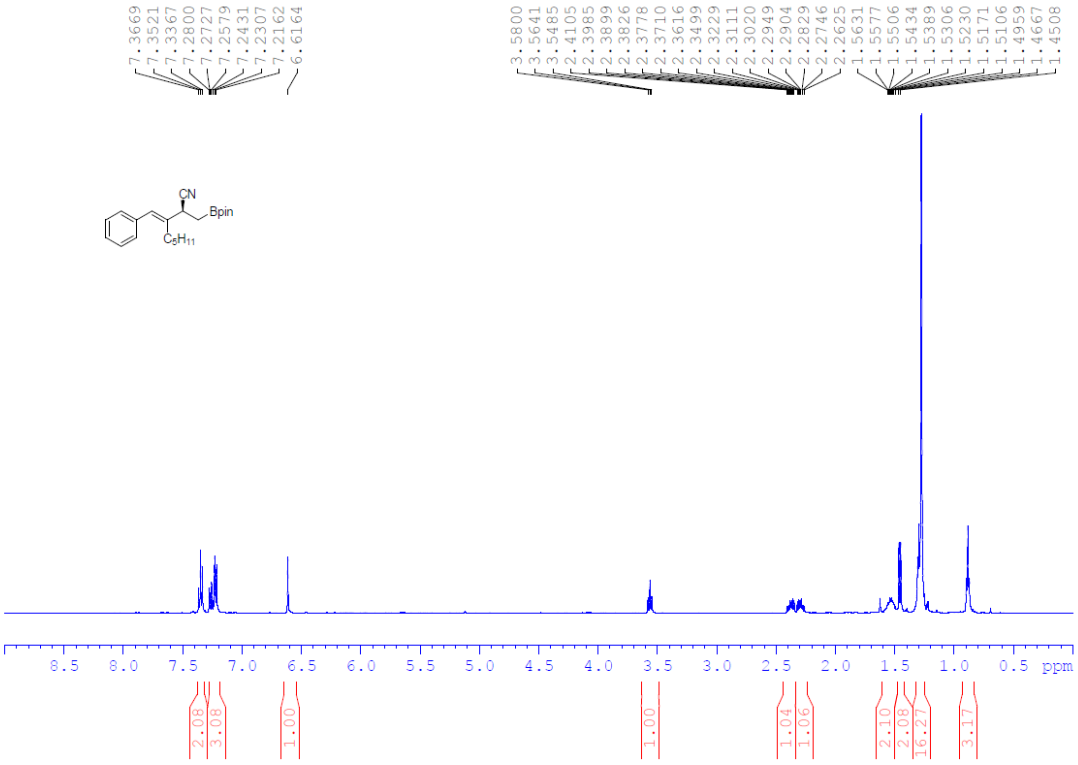
^{1}H NMR of compound **4u** (500 MHz, $CDCl_3$)



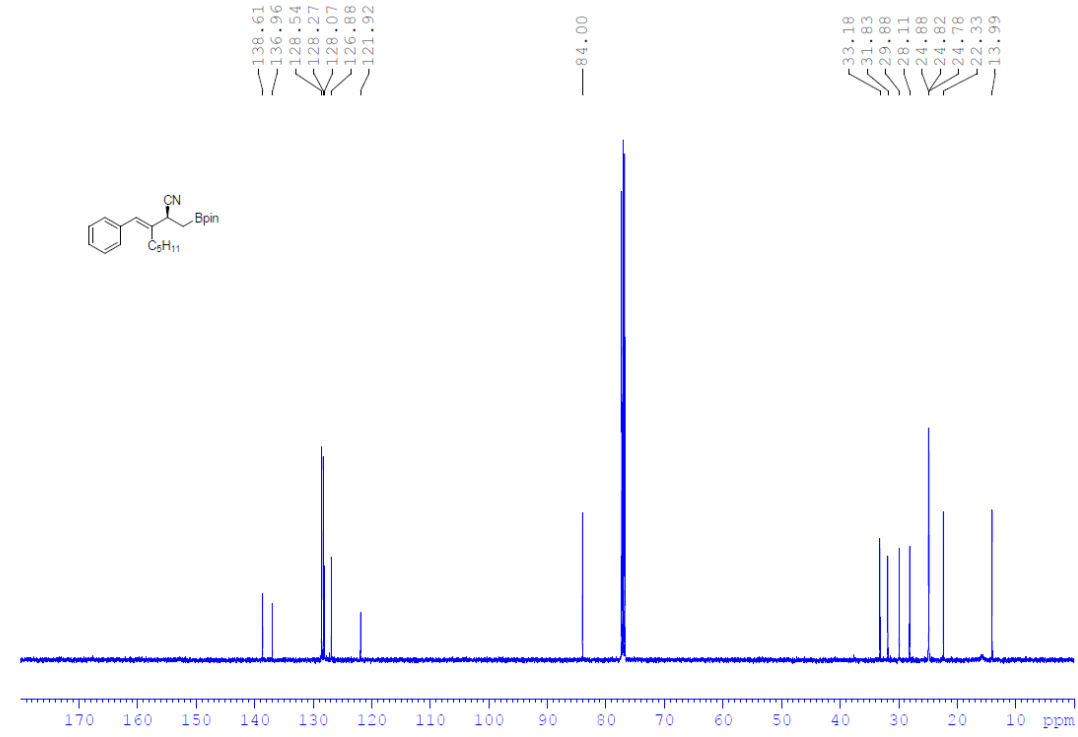
^{13}C NMR of compound **4u** (125 MHz, $CDCl_3$)



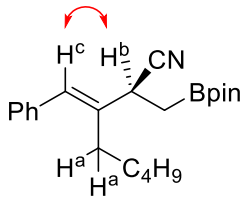
^{1}H NMR of compound **4v** (500 MHz, $CDCl_3$)

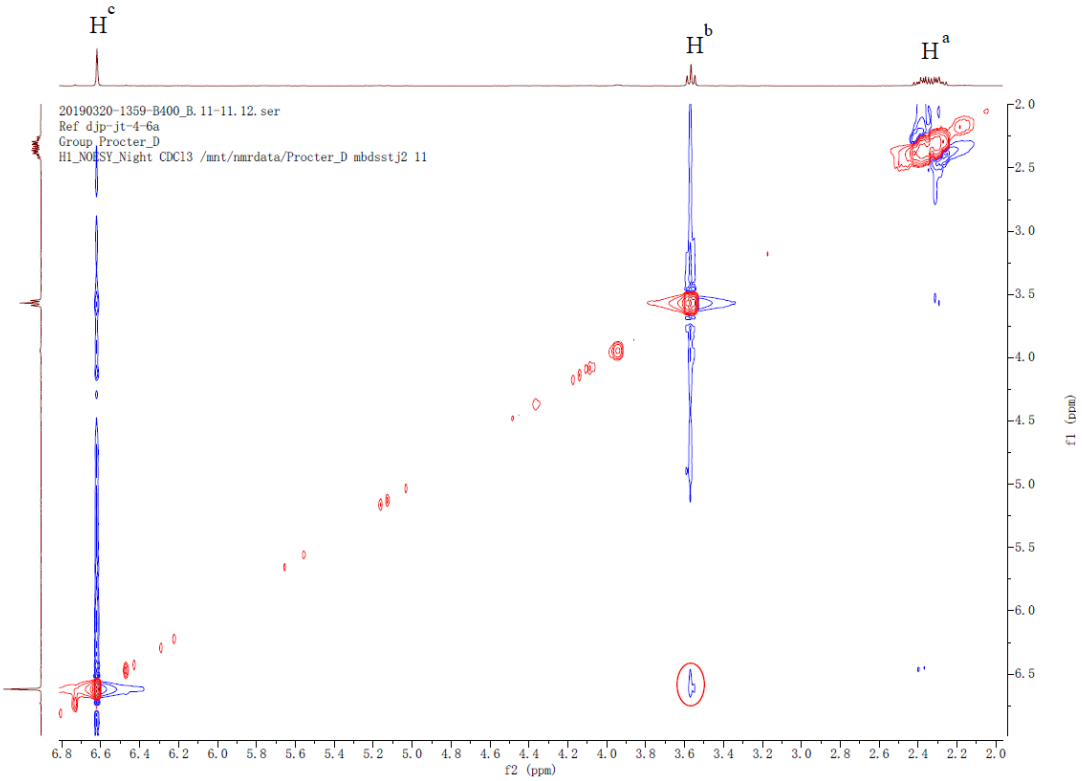


^{13}C NMR of compound **4v** (125 MHz, $CDCl_3$)

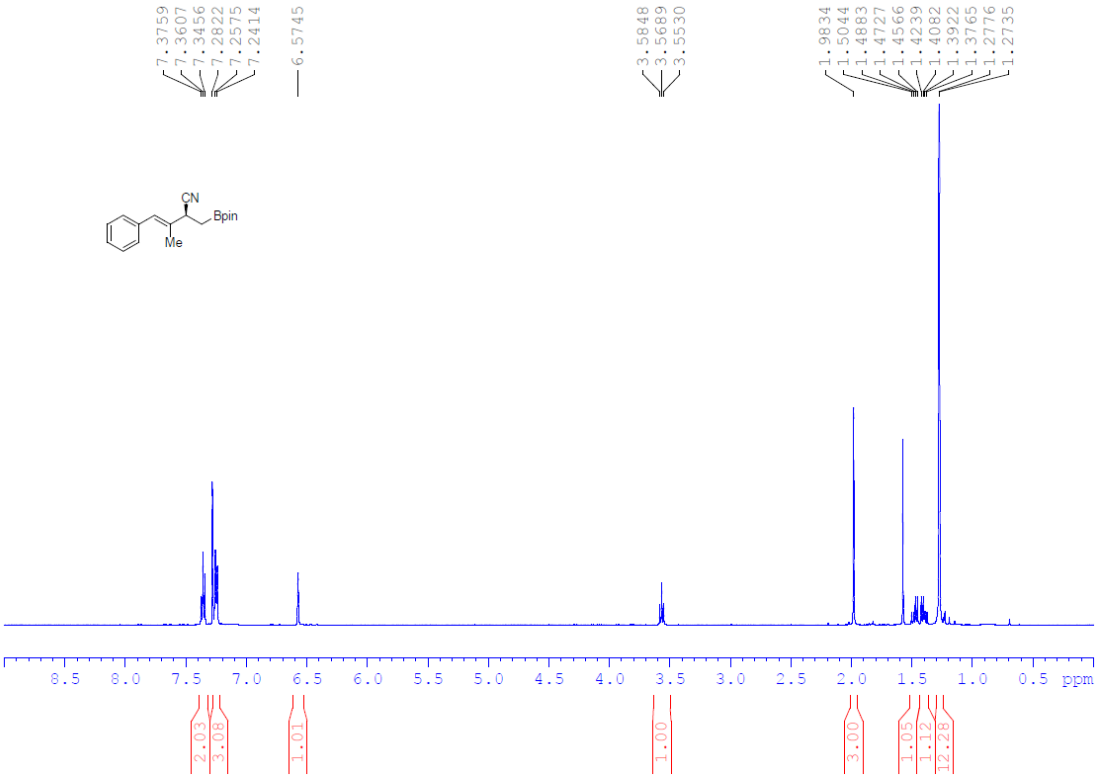


^{1}H NOESY of compound **4v** (400 MHz, $CDCl_3$)

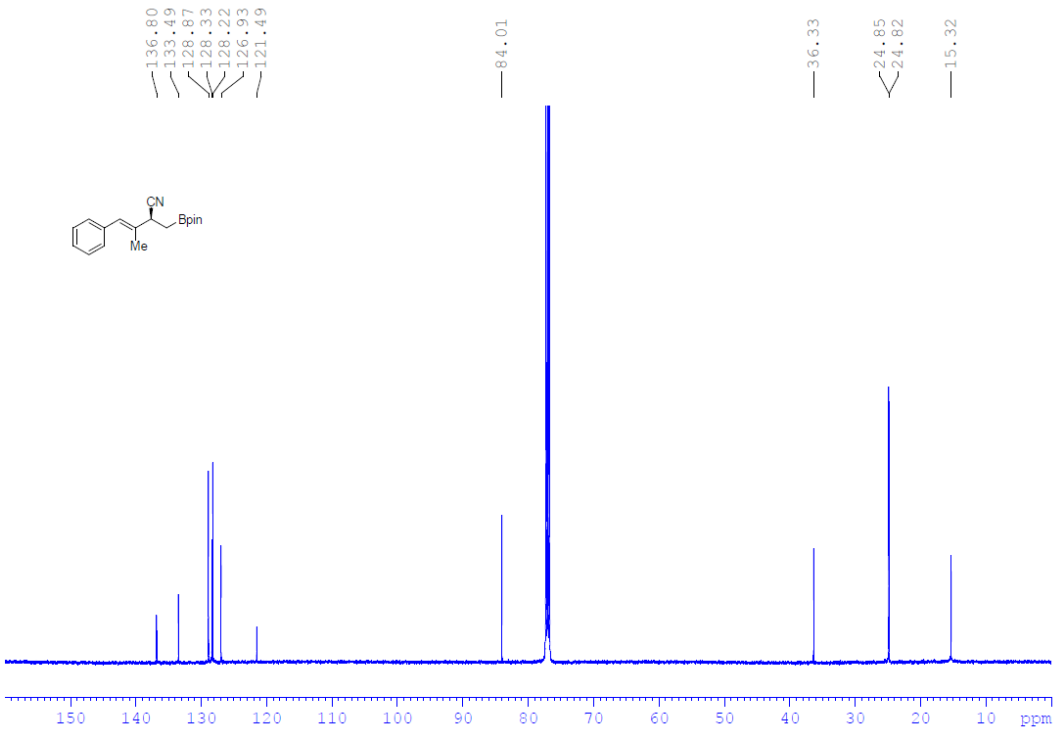




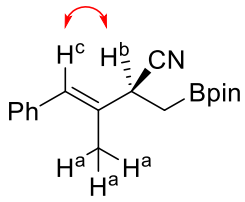
^{1}H NMR of compound **4w** (500 MHz, $CDCl_3$)

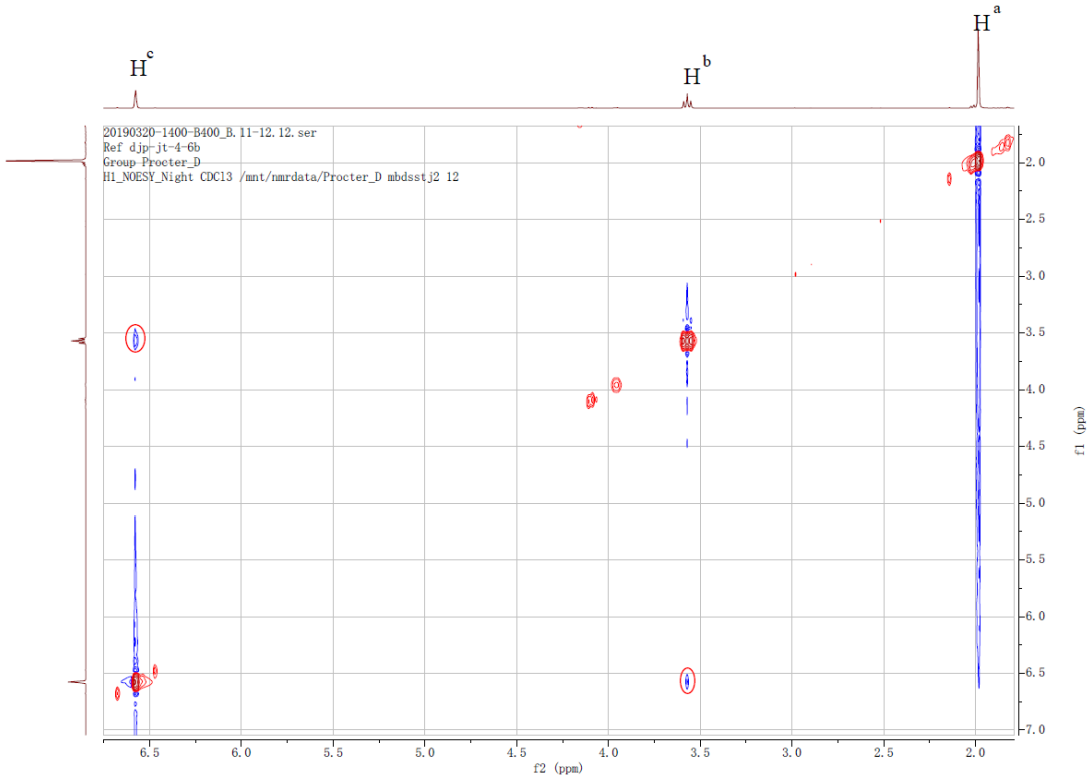


^{13}C NMR of compound **4w** (125 MHz, $CDCl_3$)

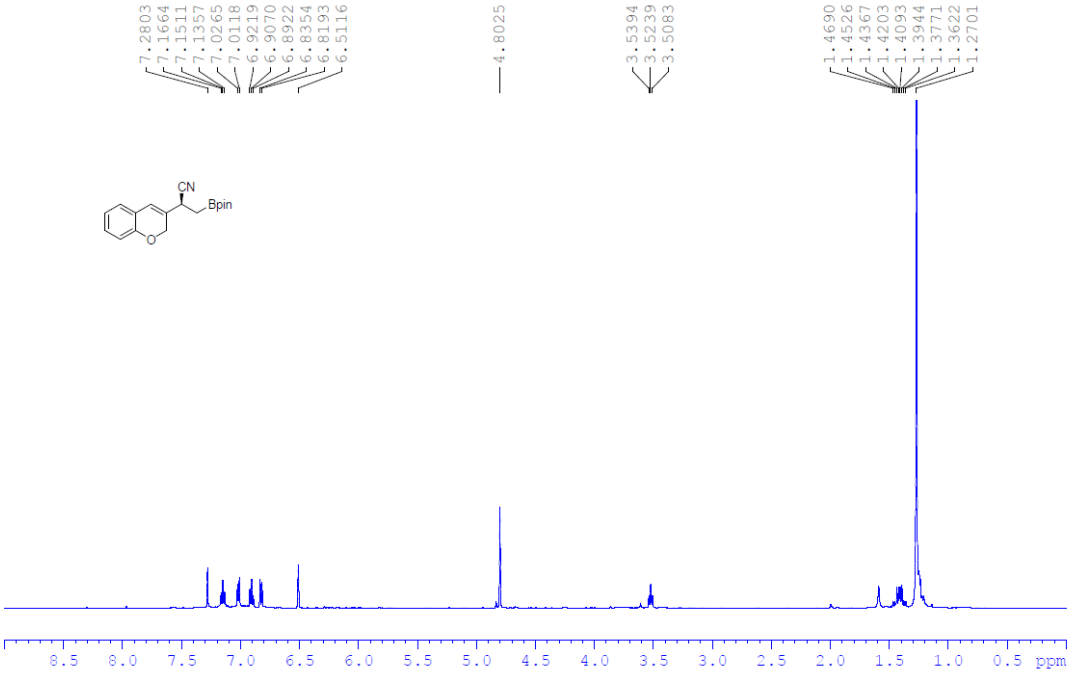


^{1}H NOESY of compound **4w** (400 MHz, $CDCl_3$)

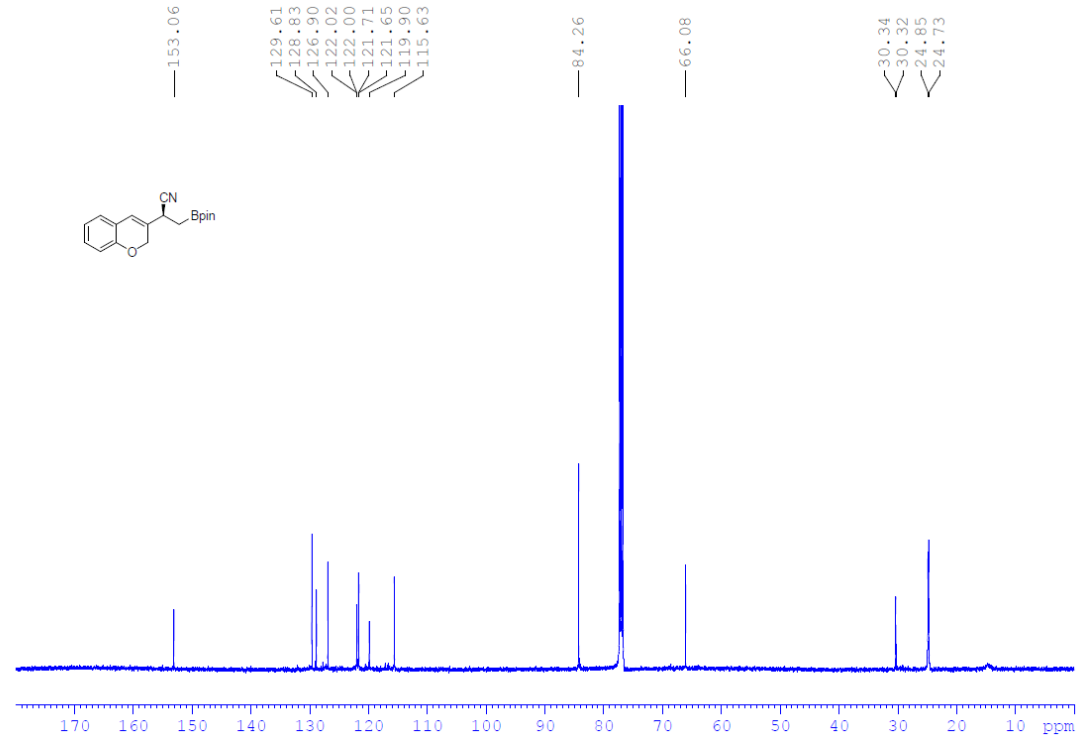




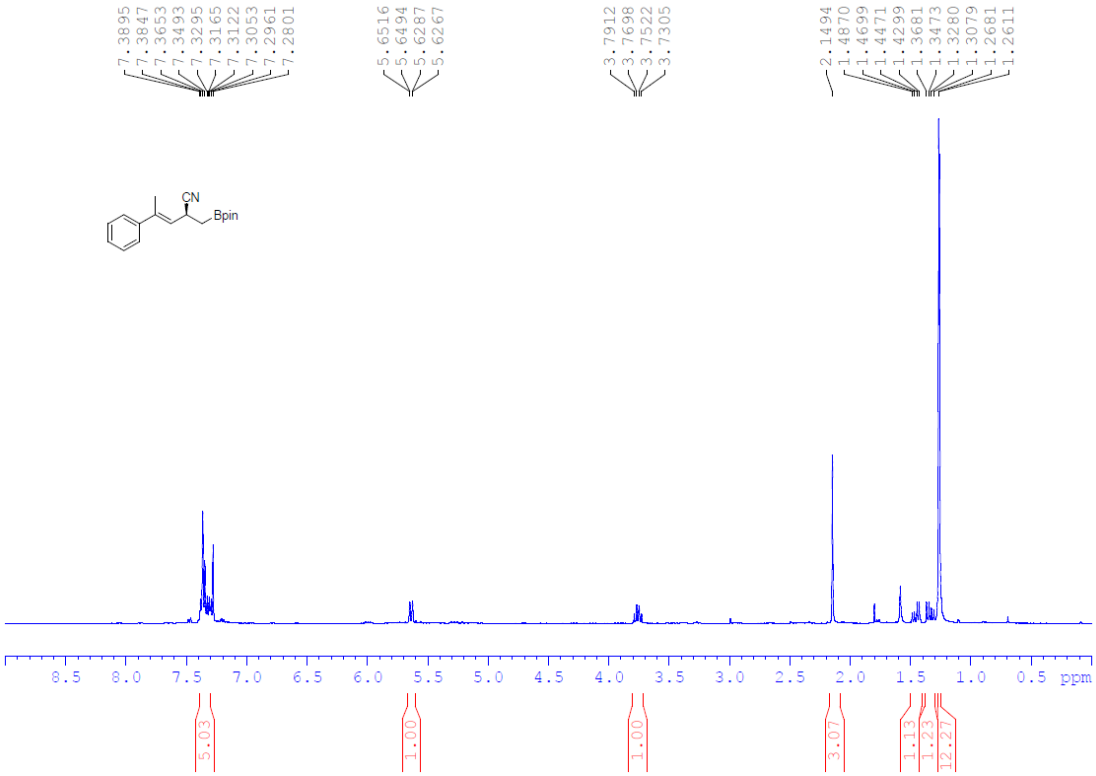
^{1}H NMR of compound **4x** (500 MHz, $CDCl_3$)



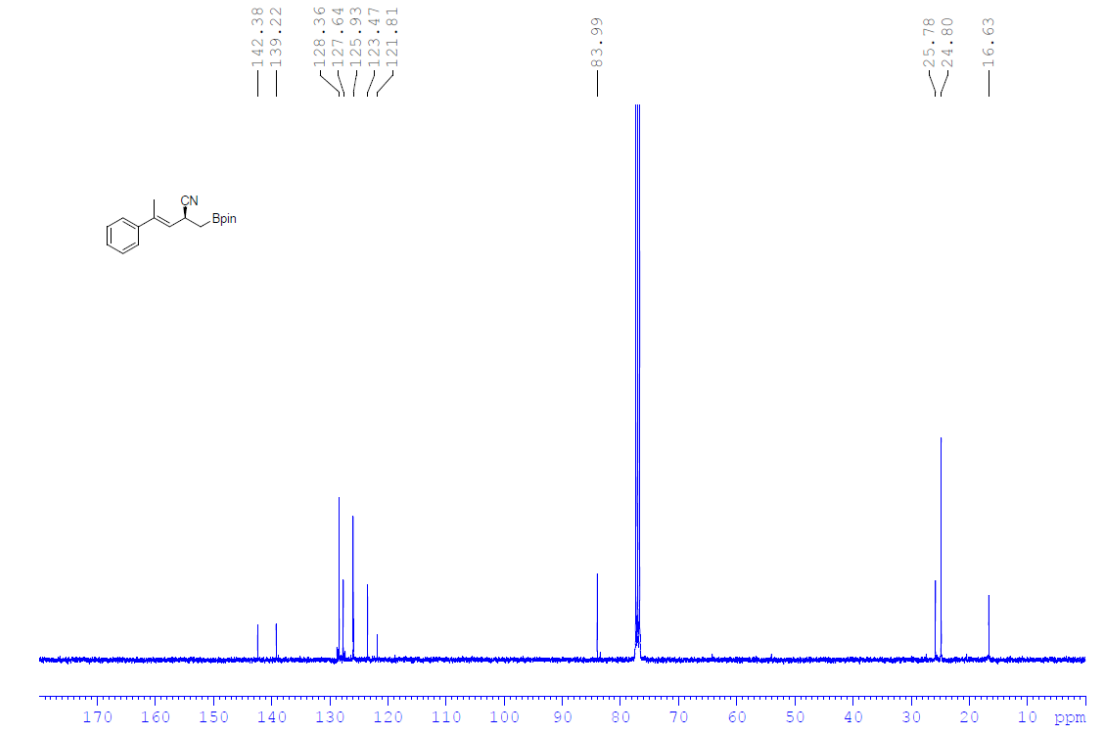
^{13}C NMR of compound **4x** (125 MHz, $CDCl_3$)



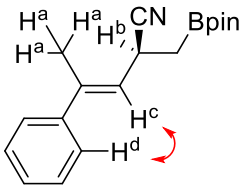
^{1}H NMR of compound **4y** (400 MHz, $CDCl_3$)

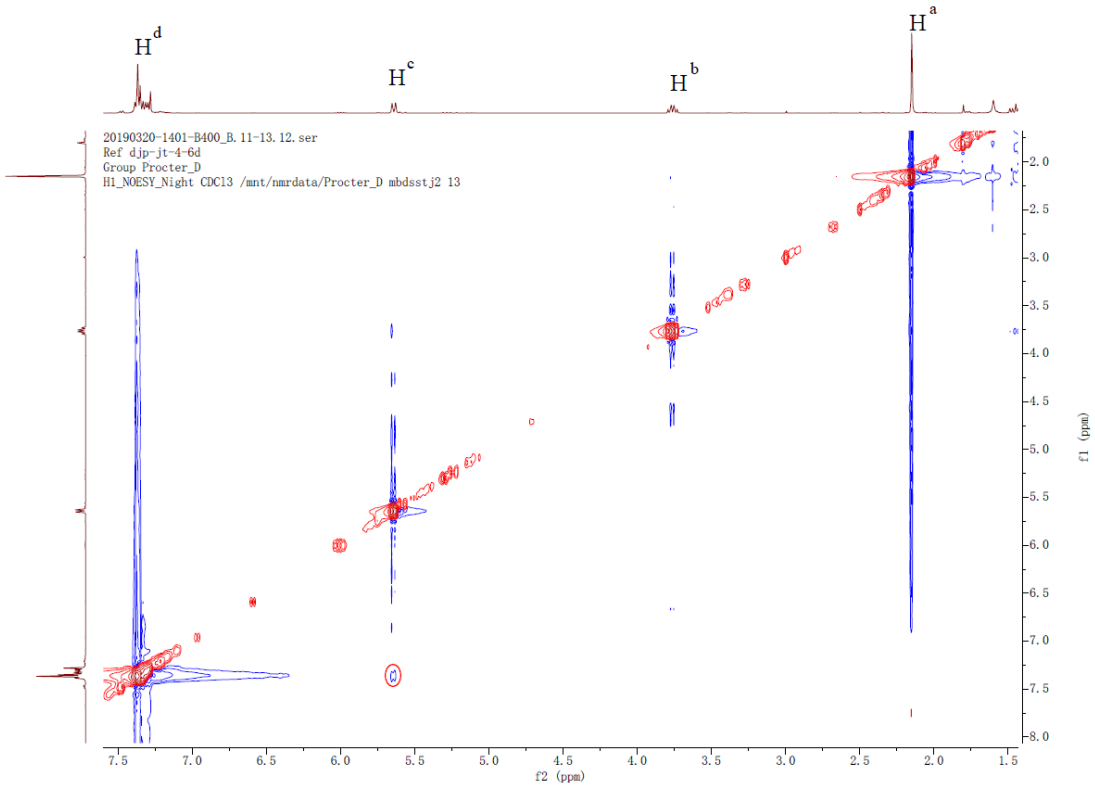


^{13}C NMR of compound **4y** (100 MHz, $CDCl_3$)

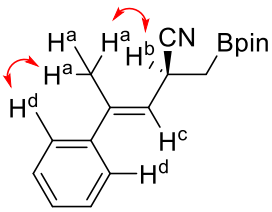


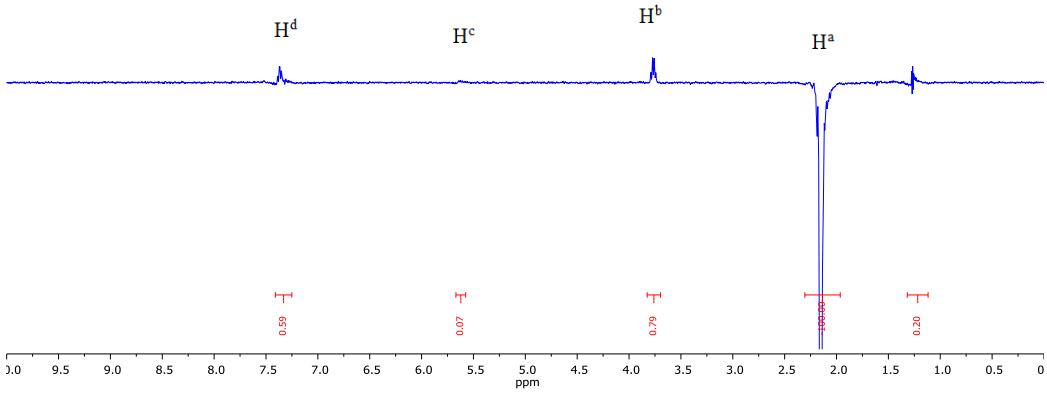
^{1}H NOESY of compound **4y** (400 MHz, $CDCl_3$)



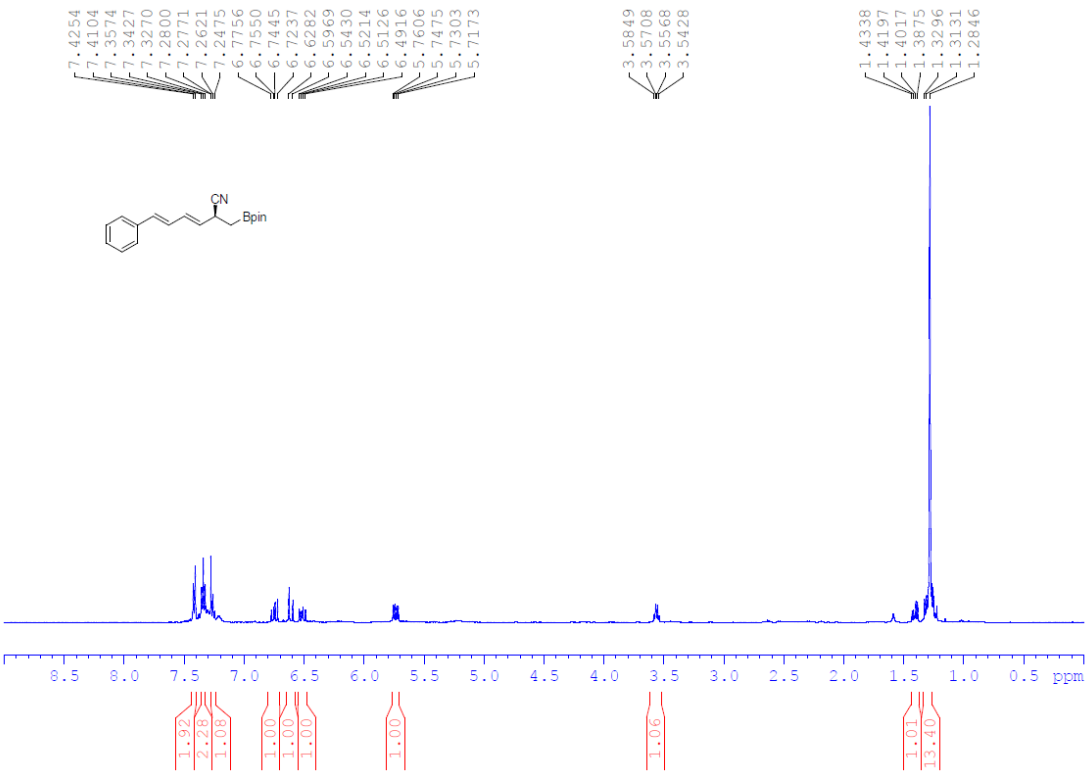


^{1}H nOe of compound **4y** (500 MHz, $CDCl_3$)

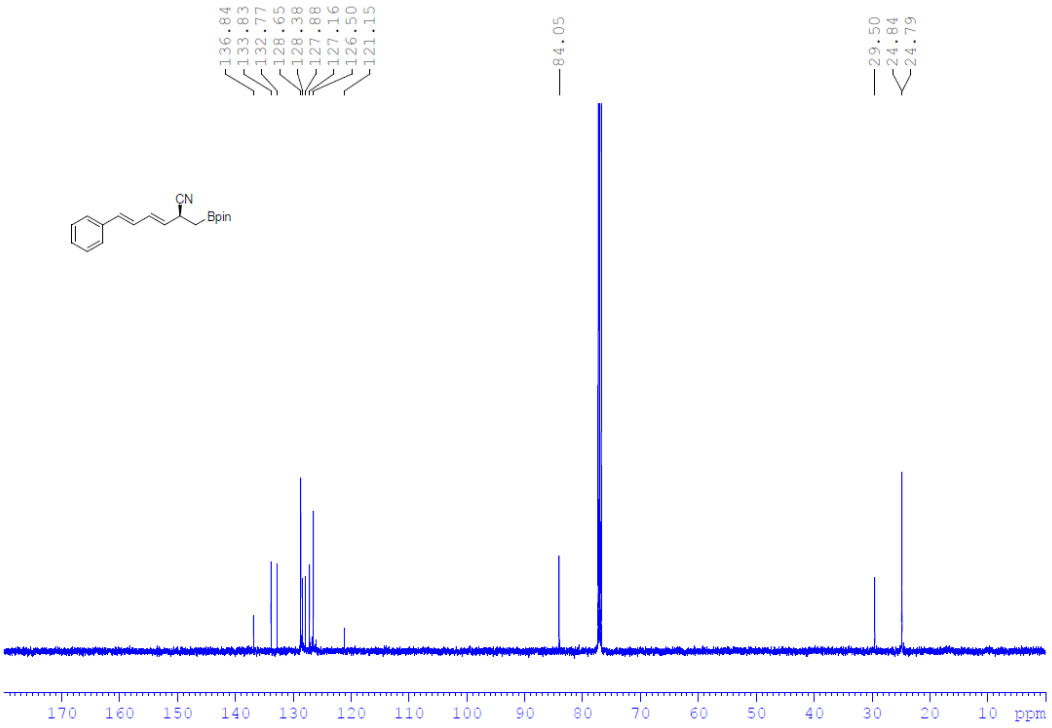




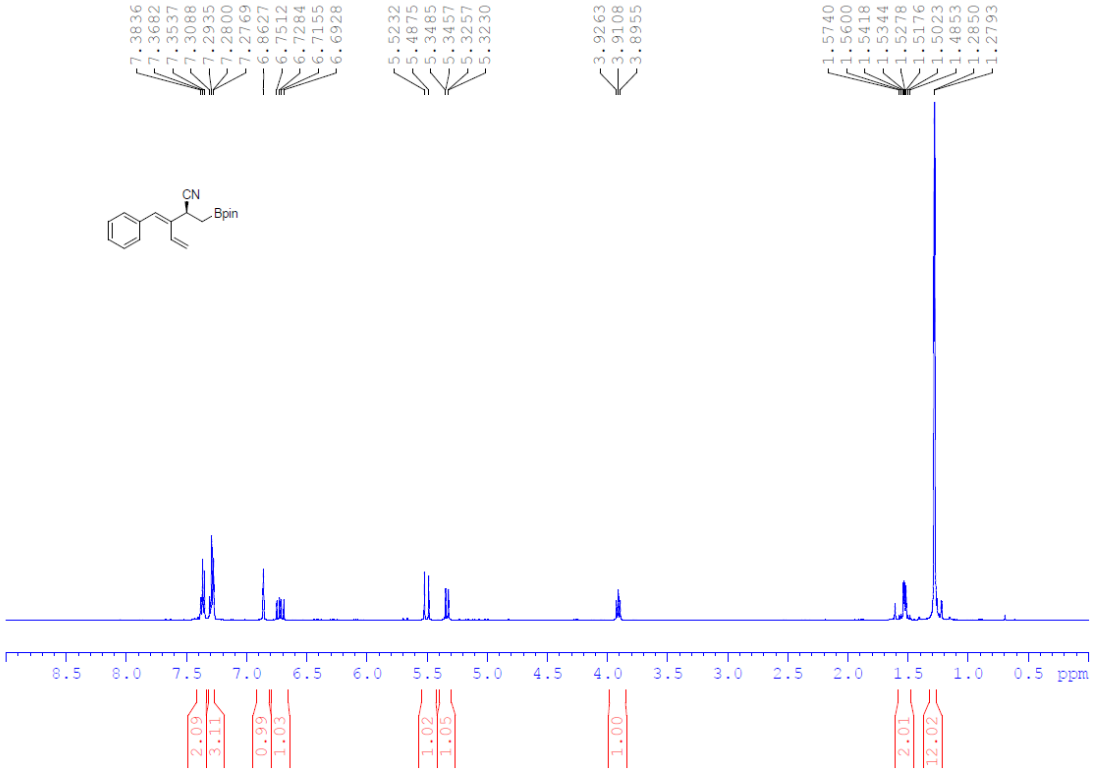
^{1}H NMR of compound **4z** (500 MHz, $CDCl_3$)



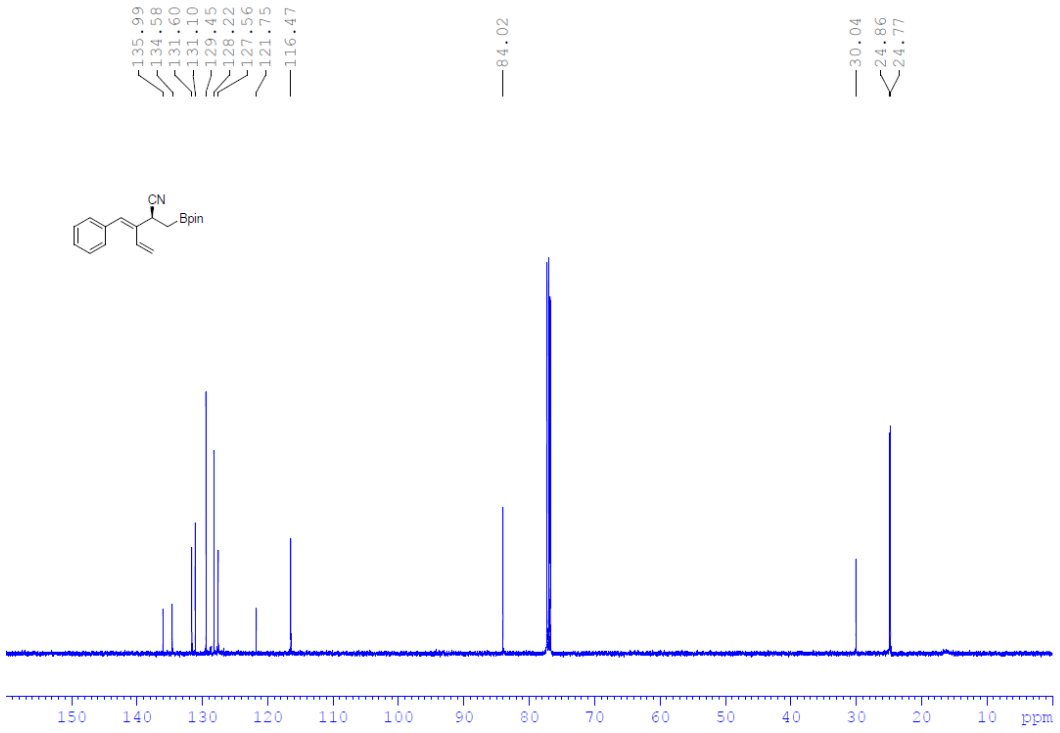
^{13}C NMR of compound **4z** (125 MHz, $CDCl_3$)



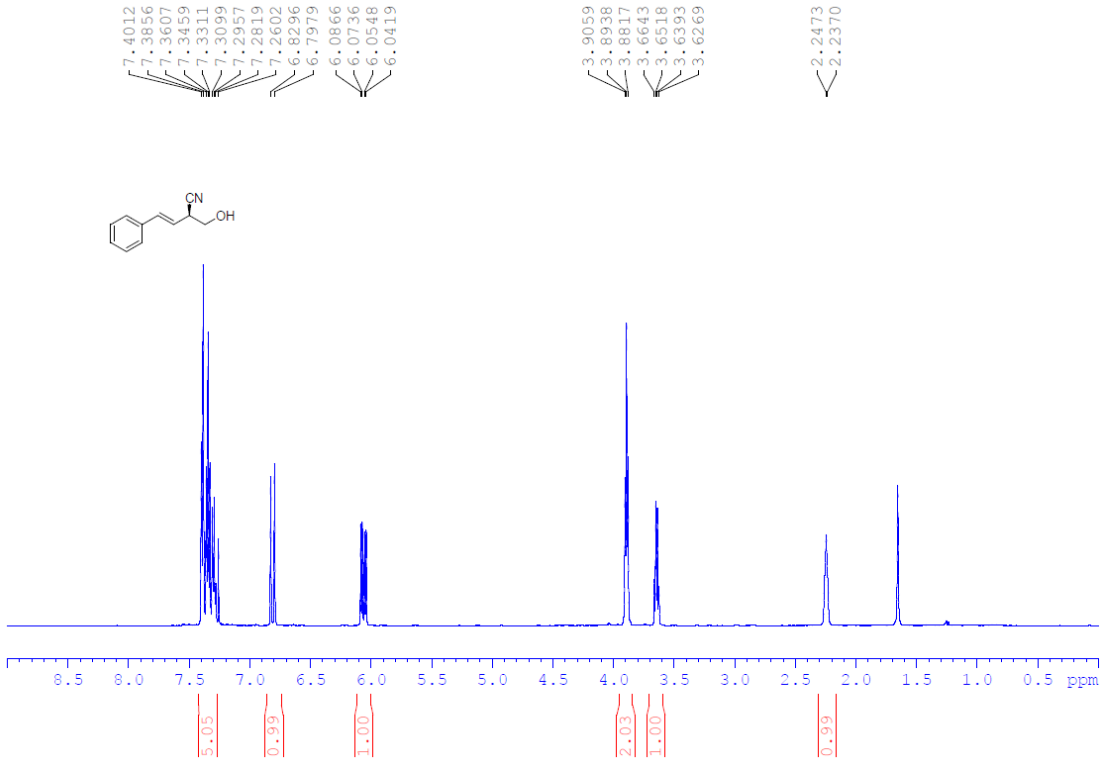
^{1}H NMR of compound **9** (500 MHz, $CDCl_3$)



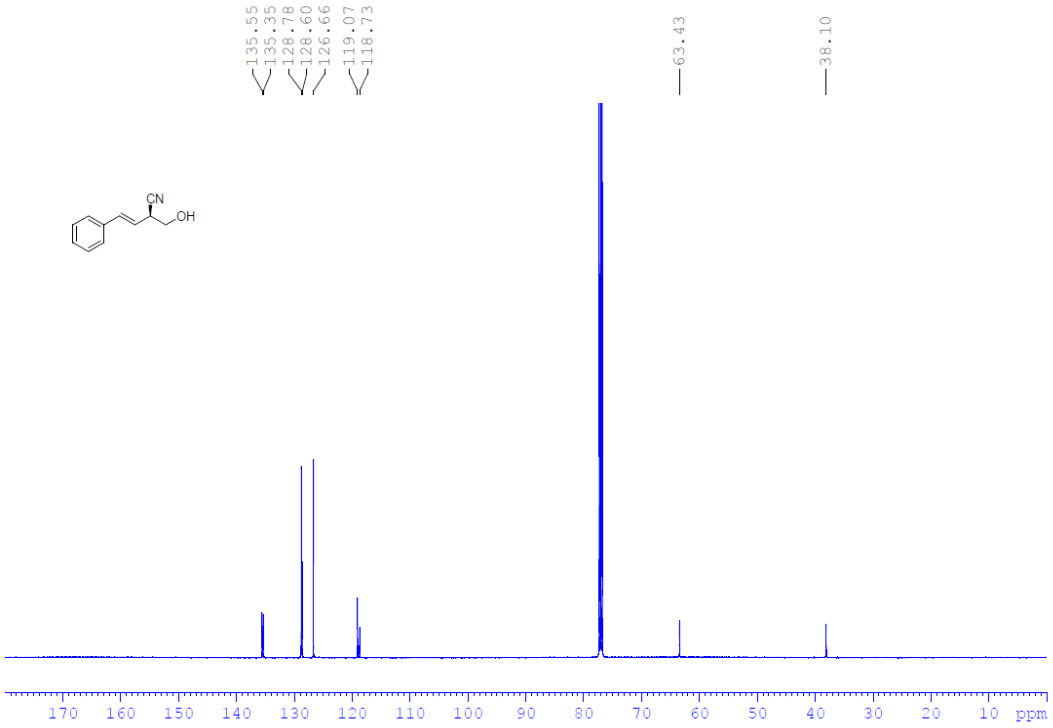
^{13}C NMR of compound **9** (125 MHz, $CDCl_3$)



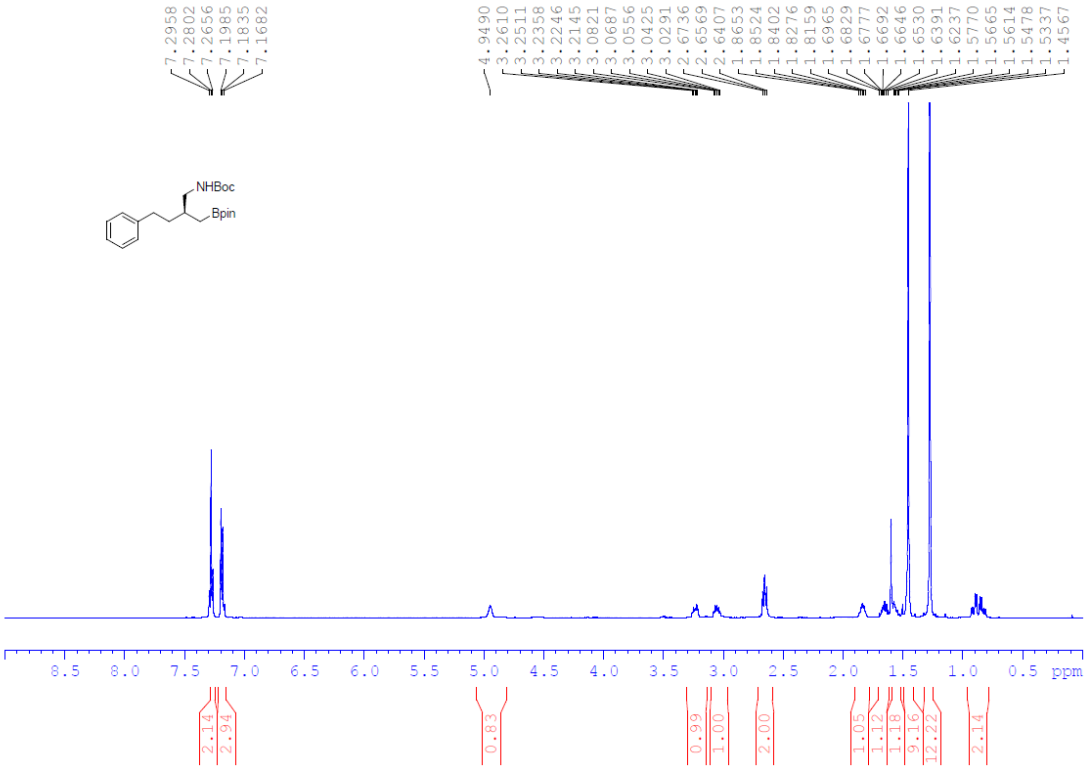
^{1}H NMR of compound **10** (500 MHz, $CDCl_3$)



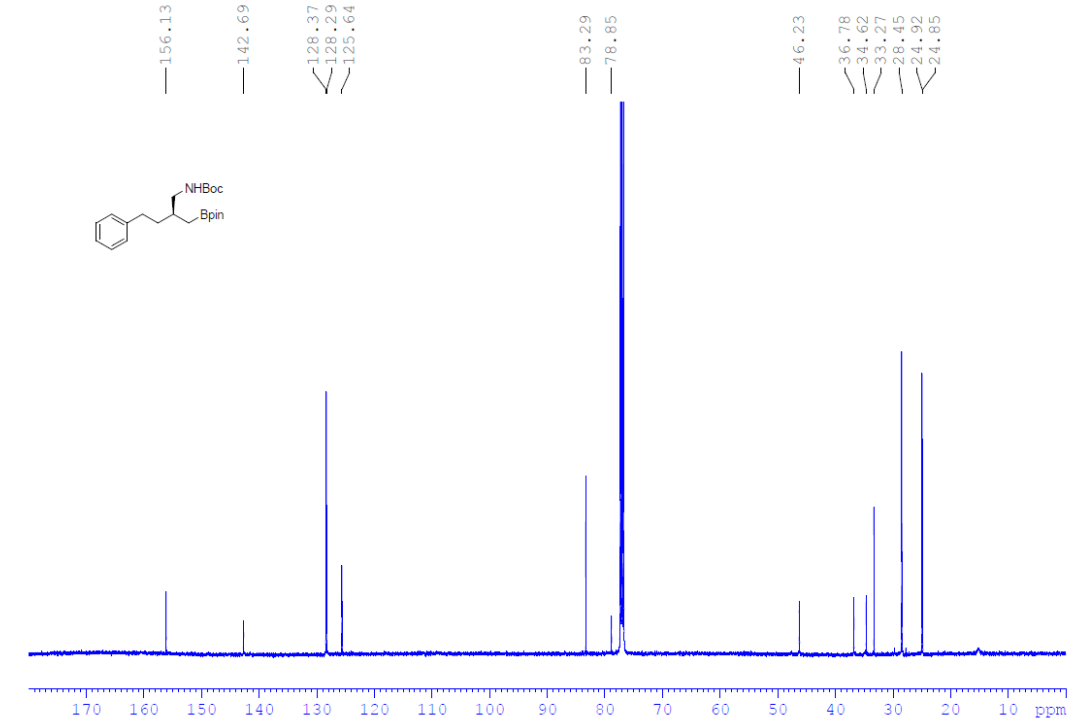
^{13}C NMR of compound **10** (125 MHz, $CDCl_3$)



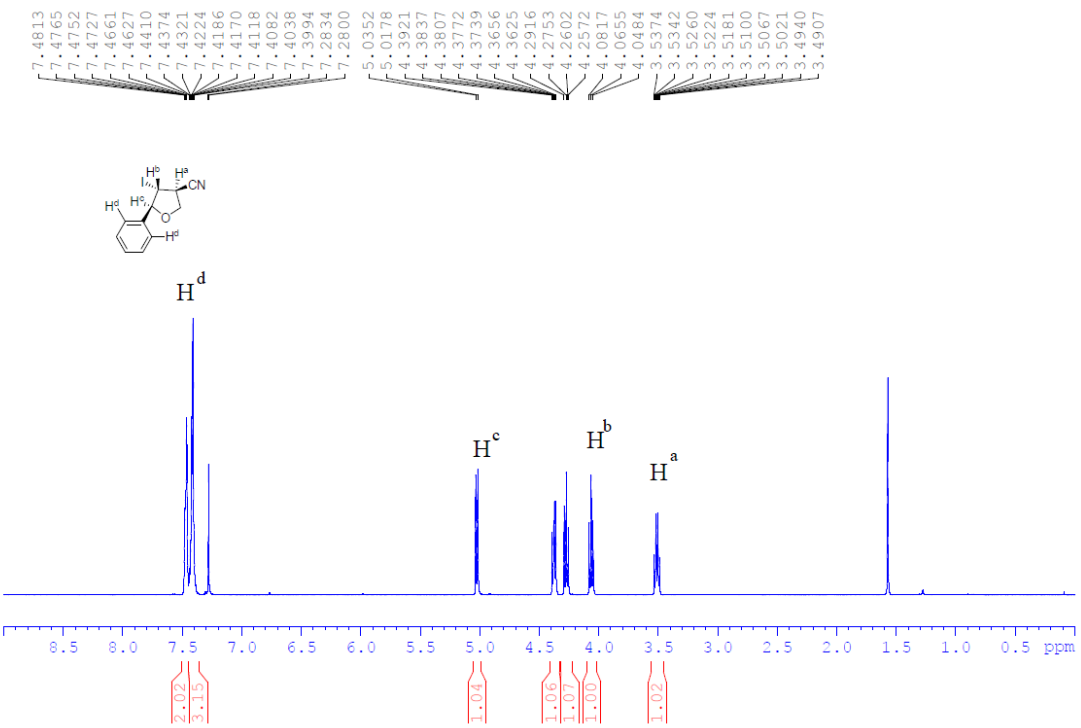
^{1}H NMR of compound **14** (500 MHz, $CDCl_3$)



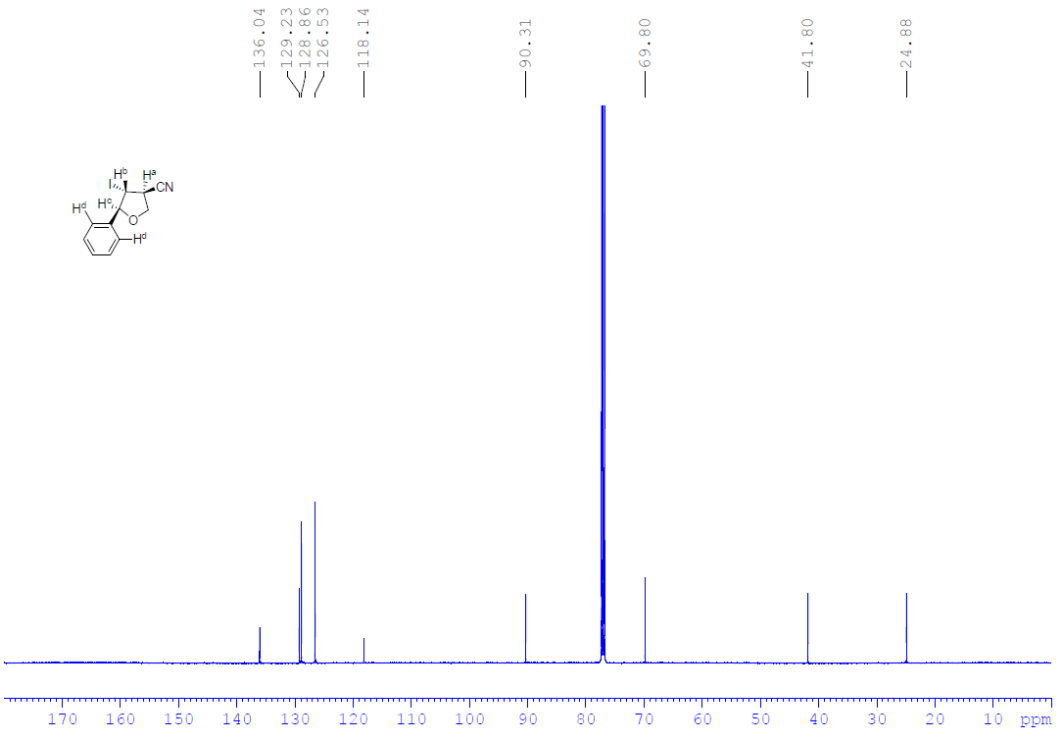
^{13}C NMR of compound **14** (125 MHz, $CDCl_3$)



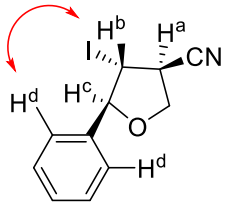
^{1}H NMR of compound **11a** (500 MHz, $CDCl_3$)

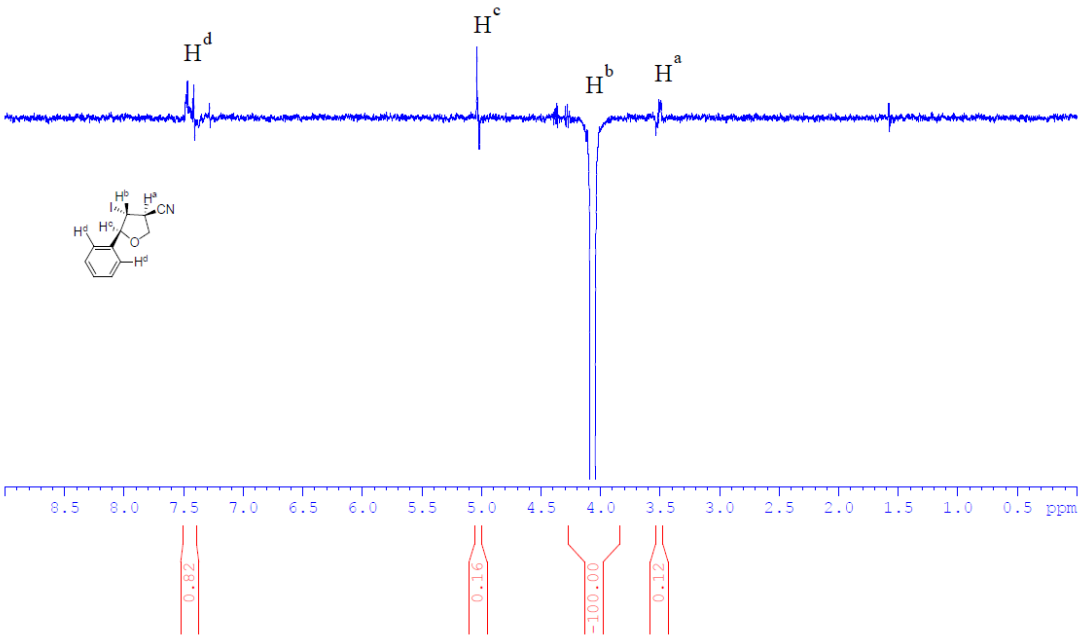


^{13}C NMR of compound **11a** (125 MHz, $CDCl_3$)

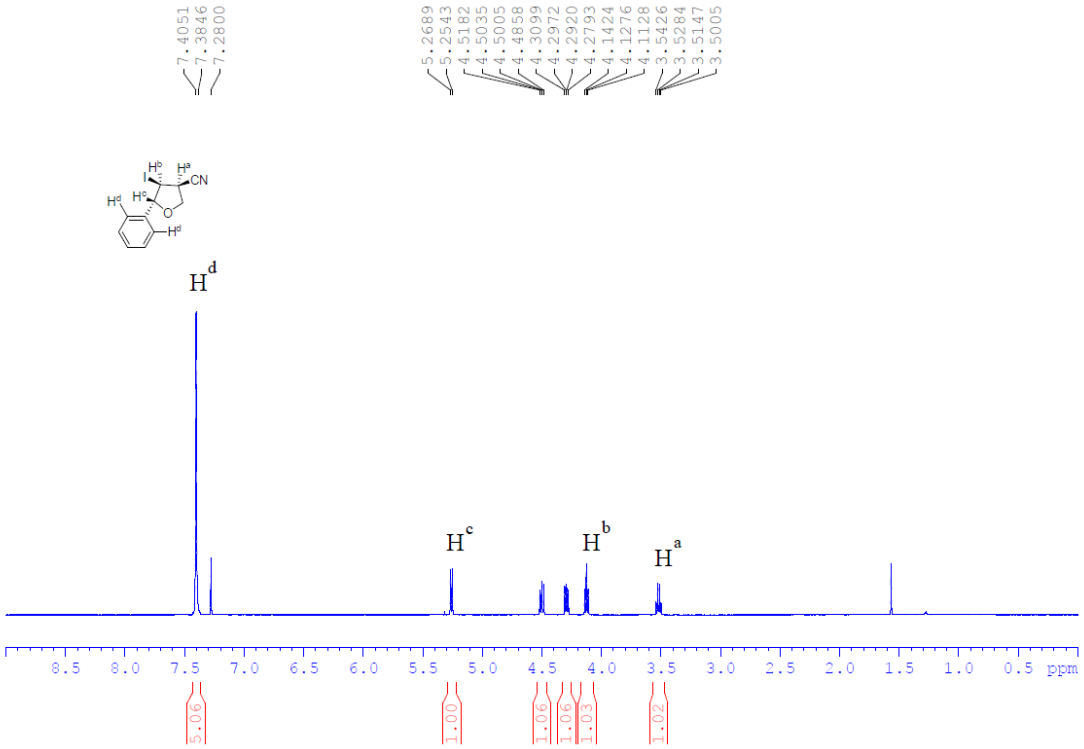


^{1}H nOe of compound **11a** (500 MHz, $CDCl_3$)

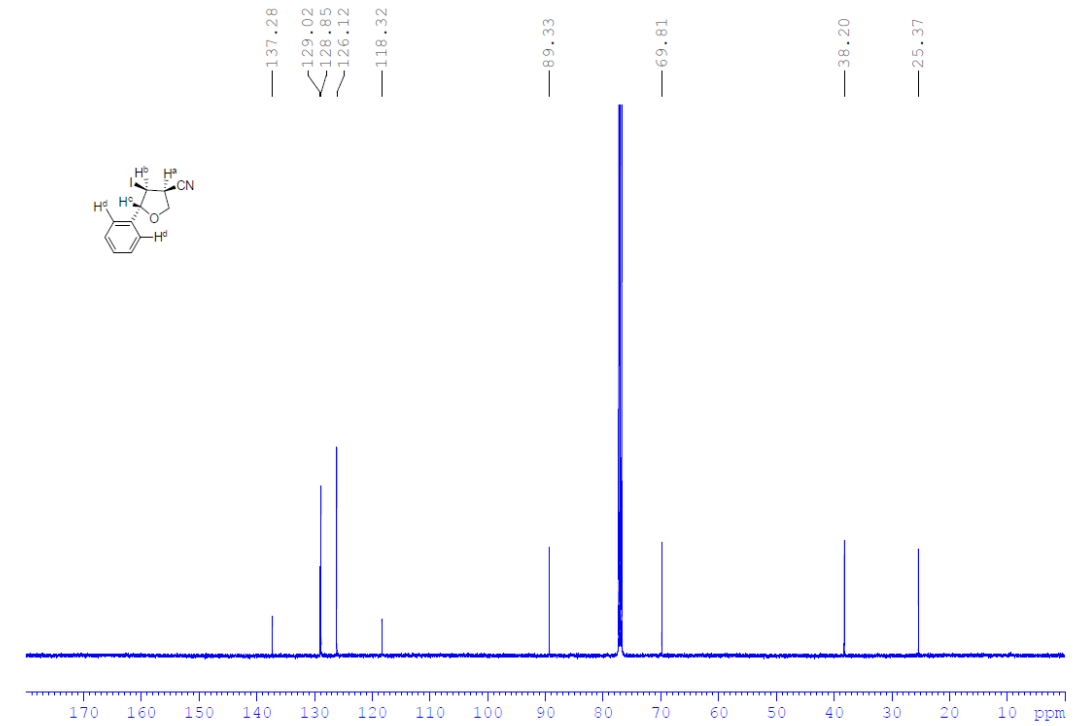




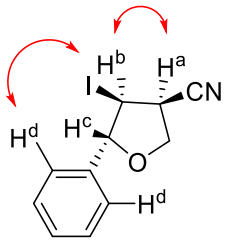
^{1}H NMR of compound **11a'** (500 MHz, $CDCl_3$)

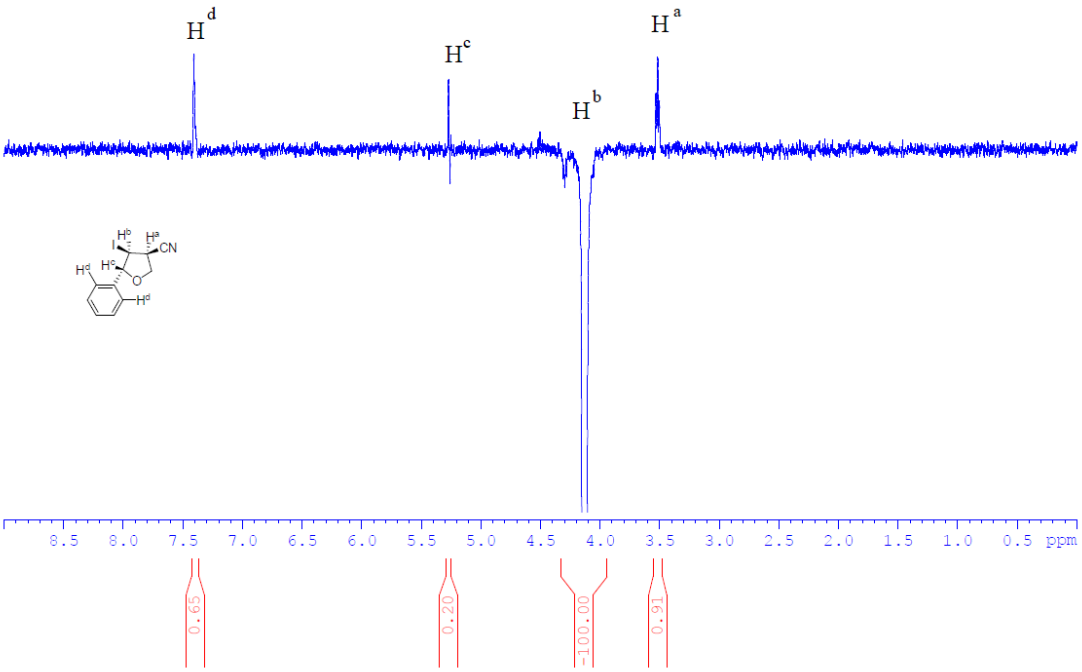


^{13}C NMR of compound **11a'** (125 MHz, $CDCl_3$)

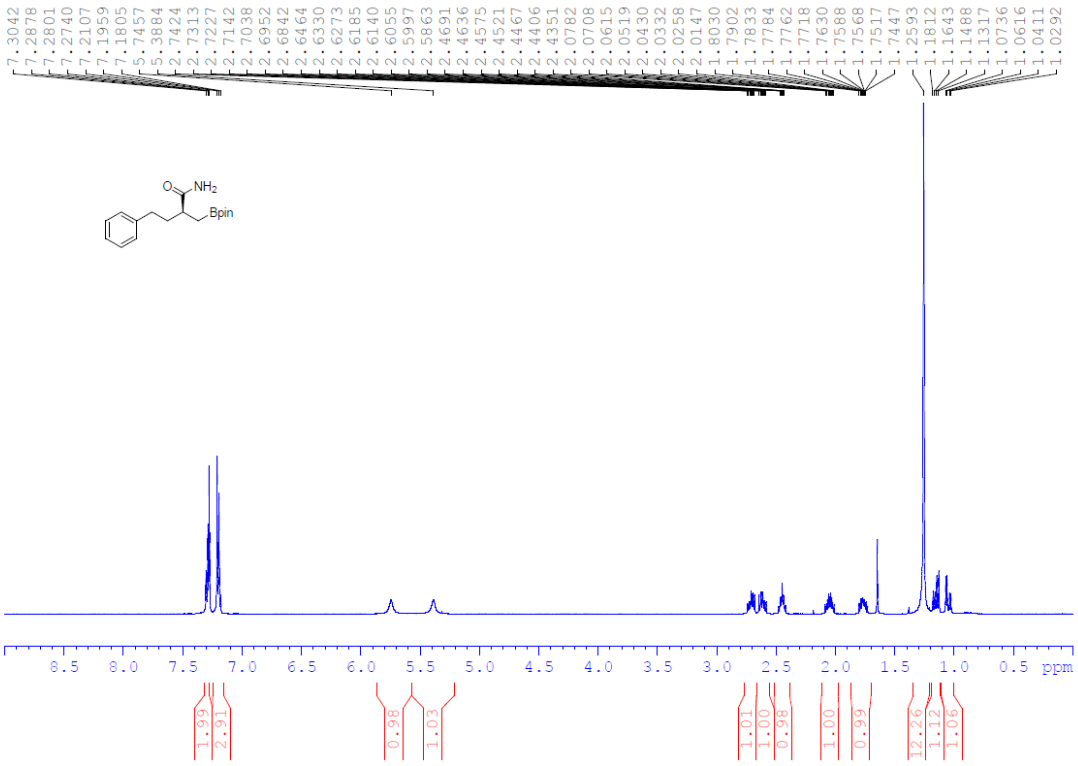


^{1}H nOe of compound **11a'** (500 MHz, $CDCl_3$)

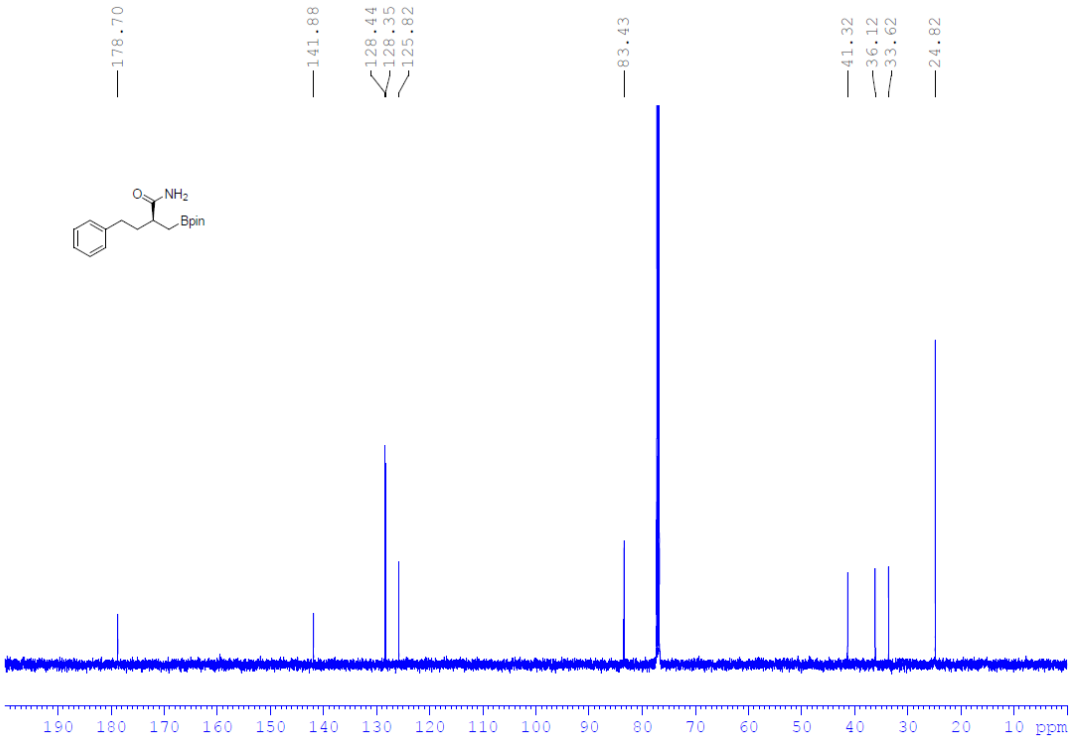




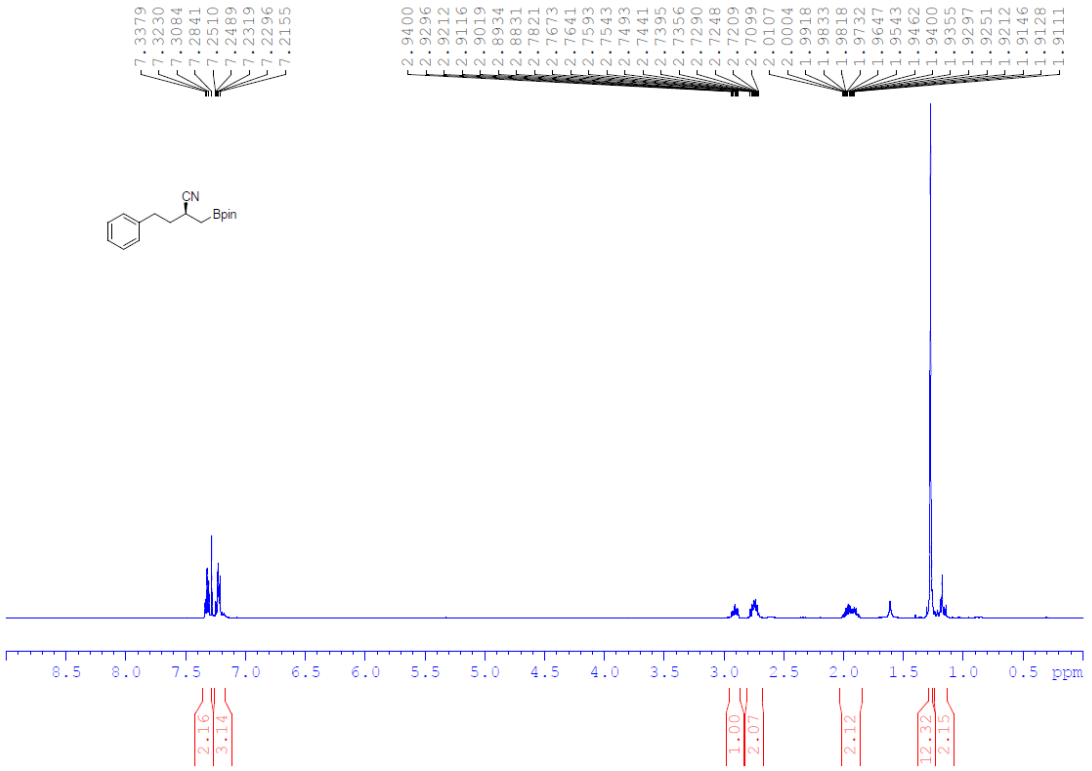
^{1}H NMR of compound **13** (500 MHz, $CDCl_3$)



^{13}C NMR of compound **13** (125 MHz, $CDCl_3$)



^{1}H NMR of compound **12** (500 MHz, $CDCl_3$)



^{13}C NMR of compound **12** (125 MHz, $CDCl_3$)