

Supporting Information

Cu-Catalyzed Enantioselective Decarboxylative Cyanation via the Synergistic Merger of Photocatalysis and Electrochemistry

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1. General Information

All reactions were carried out under an atmosphere of nitrogen in flame-dried sealed tube (vessel size: 10 mL, material: high borosilicate glass, thickness of glassware: 3 mm) with magnetic stirring (speed 1000 rpm). The $[\alpha]_D$ was recorded using PolAAR 3005 High Accuracy Polarimeter. ^1H NMR spectra, ^{13}C NMR spectra, and ^{19}F NMR spectra were recorded on a Bruker 400 MHz spectrometer in CDCl_3 . All signals are reported in δ units, parts per million (ppm), and were referenced to CDCl_3 (δ 7.26 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR) as the internal standard. Data for ^1H NMR spectra are reported as follows: chemical shift (ppm; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constant (Hz), and integration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak (CDCl_3 : 77.0 ppm). HRMS spectra were recorded on GCQTOF 7200 and Bruker McriOTOF11. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates.

THF was freshly distilled from CaH_2 ; HFIPA (AR grade), DMF (AR grade), CH_3OH (AR grade), DMA (AR grade) and DCE (AR grade) were purchased from Energy Chemical. Flash column chromatography was performed on silica gel 60 (particle size 200-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/dichloromethane or petroleum ether/ethyl acetate. Reagents were purchased from Aldrich, Bidepharm, Energy Chemical, J&K chemical, and were used as received. Ligands were purchased from Leyan.com. The carboxylic acids were synthesized according to published procedures¹. Nickel foam was purchased from TAOBAO (https://item.taobao.com/item.htm?spm=a1z09.2.0.0.3b142e8doL22fu&id=613462031143&_u=51bta621701); Carbon felt was purchased from Beijing Jinglong Special Carbon Technology Co., Ltd. Photoreactor was purchased from Wuhangeao.com. The enantiomeric excesses of the products were determined by chiral stationary phase Shimadzu HPLC using a Chiralpak AS-H, AD-H, IC, OD-H, OJ-H, OZ-3, IA.

2. Optimization of reaction conditions

2.1 Table S1. Screening of solvents for the Reaction^[a]

$\text{Cu}(\text{OTf})_2$ (5 mol%), L5 (6 mol%)
 $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (10 mol%)
 Cs_2CO_3 (0.2 equiv),
 ${}^n\text{Bu}_4\text{NPF}_6$ (2.0 equiv)

$\text{C}(+) - \text{Pt}(-), U_{\text{cell}} = 3.0 \text{ V},$
 $40 \text{ W}, 465 \text{ nm blue LED}$
 $\text{solvent (4 mL), rt, 6 h,}$

Entry	Solvent	Yield [%] ^[b]	ee [%] ^[c]
1	CH ₃ CN	13	90
2	DMF	NR	-
3	HFIPA	NR	-
5	MeOH	NR	-
6	DMA	NR	-
7	DCE	NR	-
8	THF	NR	-

[a] The reaction was performed using 0.2 mmol of **1a** and 0.4 mmol of **2a** for 6 h. [b] Yield was determined by GC using anisole as an internal standard. [c] Determined by HPLC using a chiral stationary phase. NR = no reaction.

2.2 Table S2. Screening of bases for the Reaction^[a]

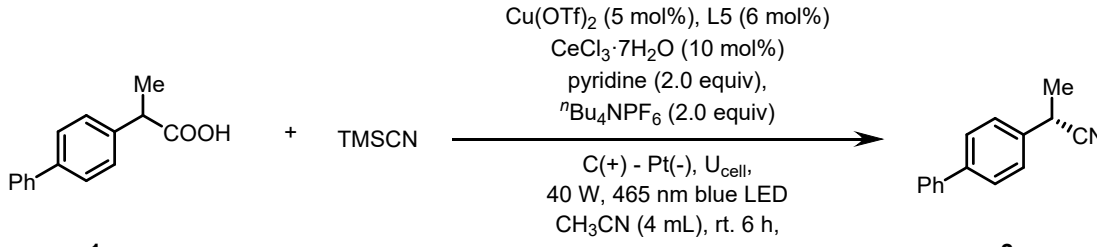
$\text{Cu}(\text{OTf})_2$ (5 mol%), ligand (6 mol%)
 $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (10 mol%)
 base (2.0 equiv),
 ${}^n\text{Bu}_4\text{NPF}_6$ (2.0 equiv)

$\text{C}(+) - \text{Pt}(-), U_{\text{cell}} = 3.0 \text{ V},$
 $40 \text{ W}, 465 \text{ nm blue LED}$
 $\text{CH}_3\text{CN (4 mL), rt, 6 h,}$

Entry	Base	Yield [%] ^[b]	ee [%] ^[c]
1	None	NR	-
2	DMAP	3	80
3	Quinoline	trace	-
4	2-isopropyl pyridine	22	92
5	Pyridine	28	92
6	2,6-diethylpyridine	24	90
7	2-Picoline	trace	-
8	2,6-Lutidine	7	90
9	2,6-dichloropyridine	NR	-
10	Cs_2CO_3 (0.2 equiv)	13	89

[a] The reaction was performed using 0.2 mmol of **1a** and 0.4 mmol of **2a** for 6 h. [b] Yield was determined by GC using anisole as an internal standard. [c] Determined by HPLC using a chiral stationary phase. NR = no reaction.

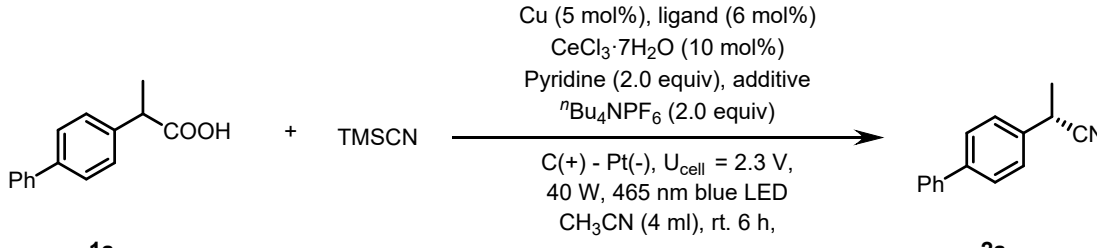
2.3 Table S3. Screening of the Voltage for the Reaction^[a]



Entry	U_{cell}	Yield [%] ^[b]	<i>ee</i> [%] ^[c]
1	2.1 V	31	88
2	2.2 V	33	87
3	2.3 V	61	86
4	2.4 V	44	90
5	2.5 V	45	90
6	2.6 V	13	92
7	2.7 V	50	89
8	2.8 V	6	87
9	2.9 V	7	90
10	3.0 V	6	90

[a] The reaction was performed using 0.2 mmol of **1a** and 0.4 mmol of **2a** for 6 h. [b] Yield was determined by GC using anisole as an internal standard. [c] Determined by HPLC using a chiral stationary phase.

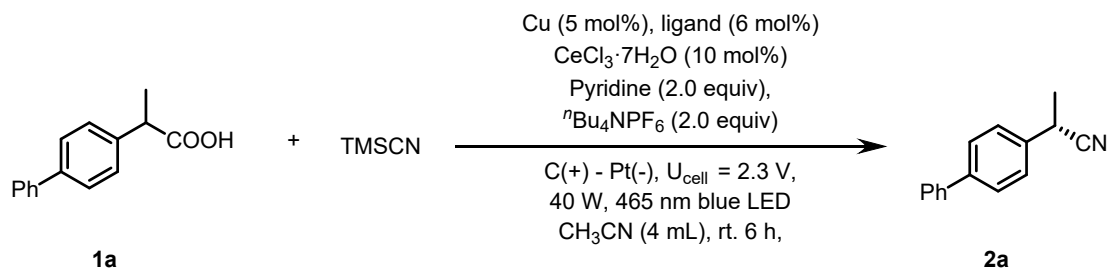
2.4 Table S5. Screening of additive for Reaction^[a]



Entry	additive	Yield [%] ^[b]	<i>ee</i> [%] ^[c]
1	H ₂ O (2 eq)	77	93
2	H ₂ O (4 eq)	35	92
3	H ₂ O (6 eq)	45	92
4	iPrOH (2 eq)	32	90
5	CH ₃ COOH (2 eq)	73	90

[a] The reaction was performed using 0.2 mmol of **1a** and 0.4 mmol of **2a** for 6 h. [b] Yield was determined by GC using anisole as an internal standard. [c] Determined by HPLC using a chiral stationary phase.

2.5 Table S4. Screening of Cu precursors for the Reaction^[a]

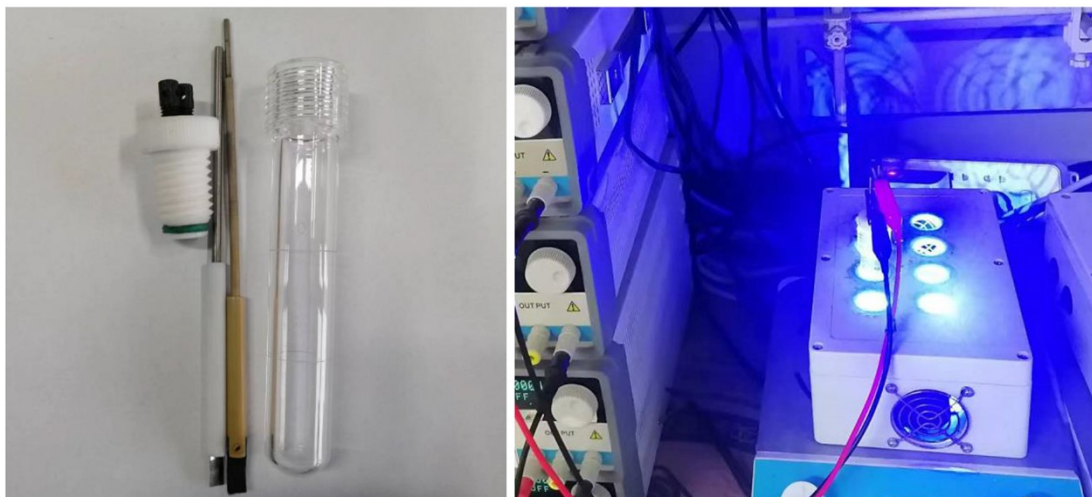


Entry	Cu	Yield [%] ^[b]	<i>ee</i> [%] ^[c]
1	CuI	3	80
2	CuTc	6	93
3	Cu(CH ₃ CN) ₄ BF ₆	7	93
4	Cu(OAc) ₂	11	92
5	Cu(OAc) ₂ ·H ₂ O	27	91
6	Cu(hfacac) ₂ ·H ₂ O	76	90
7	Cu(hfacac) ₂	69	90
8	Copper bis(2-ethylhexanoate)	6	94

[a] The reaction was performed using 0.2 mmol of **1a** and 0.4 mmol of **2a** for 6 h. [b] Yield was determined by GC using anisole as an internal standard. [c] Determined by HPLC using a chiral stationary phase.

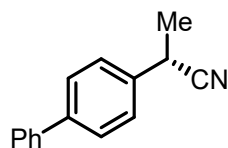
3. General procedure

In a nitrogen-filled glove box, an over-dried 10 mL tube charged with a stir bar, to a tube was added $\text{Cu}(\text{hfacac})_2 \cdot \text{H}_2\text{O}$ (5 mol%) and **L5** (6 mol%). CH_3CN (1.0 mL) was added to the tube, and stirred at room temperature for 1 h. $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (7.44 mg, 0.02 mmol), $n\text{Bu}_4\text{NPF}_6$ (155.0 mg, 0.4 mmol), phenylpropanoic acids (0.2 mmol), pyridine (32 mg, 0.4 mmol), H_2O (7.2 mg, 0.4 mmol), TMSCN (40.0 mg, 0.4 mmol) were added to the electrochemical cell. Then CH_3CN (3.0 mL) were added to the electrochemical cell. The tube was installed with a Pt foam ($1.0 \times 0.5 \text{ cm}^2$) as the cathode and carbon felt ($2.5 \times 0.5 \text{ cm}^2$) as the anode. The seal-tube was sealed and removed from the glovebox. The reaction mixture was electrolyzed under a constant voltage of 2.3-3.0 V until the complete consumption of the starting materials as detected by TLC (about 6 hours). After the reaction, the reaction was quenched by saturated aqueous $n\text{Bu}_4\text{NCl}$ solution. Then the aqueous layer was extracted with EtOAc (3 x 3 mL) and the combined organics were washed with sat. brine (4 x 10 mL), dried over anhydrous MgSO_4 , filtered and concentrated in vacuo. The crude product was purified by column chromatography to furnish the desired product.



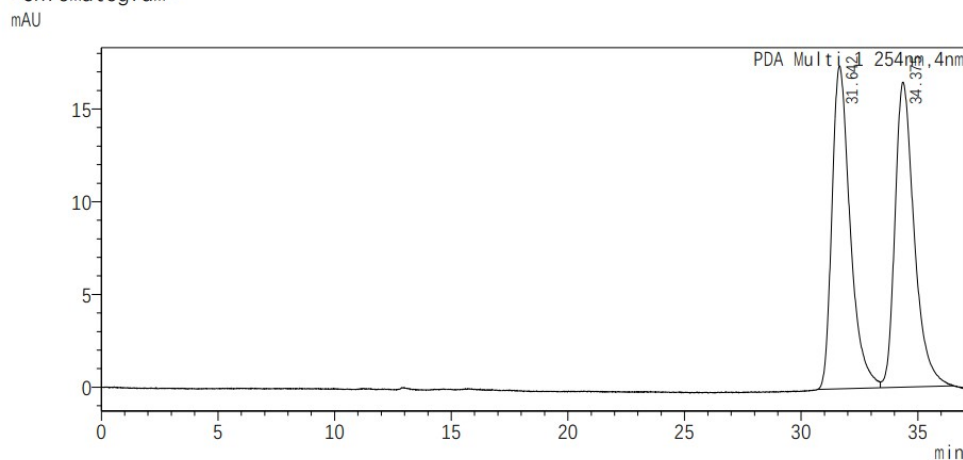
Characterization data of products:

(S)-2-([1,1'-Biphenyl]-4-yl)propanenitrile (**2a**)



Prepared according to general procedure, constant voltage is 2.3 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2a** as a white solid (31.5 mg, 76% yield) with 90% ee. m.p. 79.2-79.4 °C; $[\alpha]_D^{20} = -11.6$ (c 0.59, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.60 (dd, *J* = 13.1, 8.2 Hz, 4H), 7.49 – 7.40 (m, 4H), 7.37 (t, *J* = 7.3 Hz, 1H), 3.95 (q, *J* = 7.3 Hz, 1H), 1.69 (d, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 141.1, 140.3, 136.0, 128.9, 127.8, 127.6, 127.1, 127.1, 121.5, 30.9, 21.4. HRMS (EI): *m/z*: [M]⁺ Calcd for C₁₅H₁₃N: 207.1048, found 207.1042. HPLC (Daicel Chiralpak AS-H column, hexane/isopropanol = 99/1, flow rate 0.3 mL/min, 254 nm): t_R = 31.8 min (minor), t_R = 34.3 min (major).

<Chromatogram>



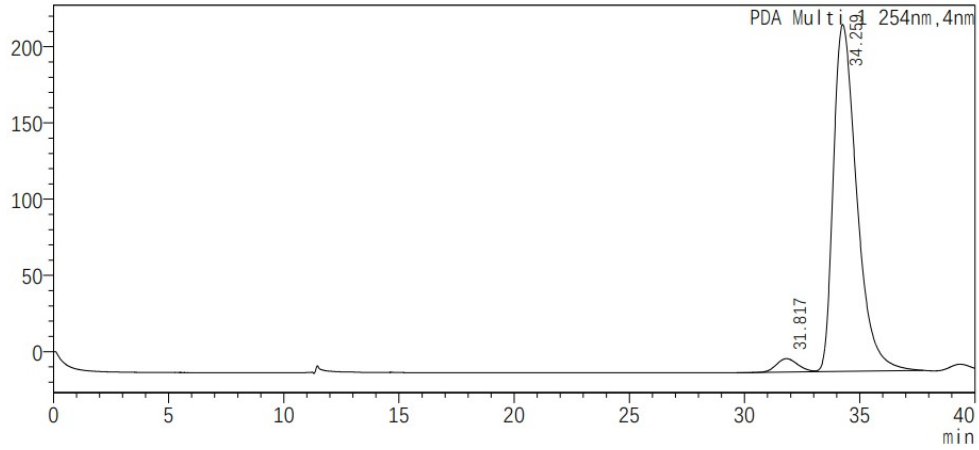
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PDA_Ch1_254nm

No.	Ret. Time(min)	Height (mAU)	Height%	Area(mAU*min)	Area%
1	31.642	17414	51.425	946432	50.030
2	34.375	16449	48.575	945283	49.970
Total		33863	100.000	1891716	100.000

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mAU



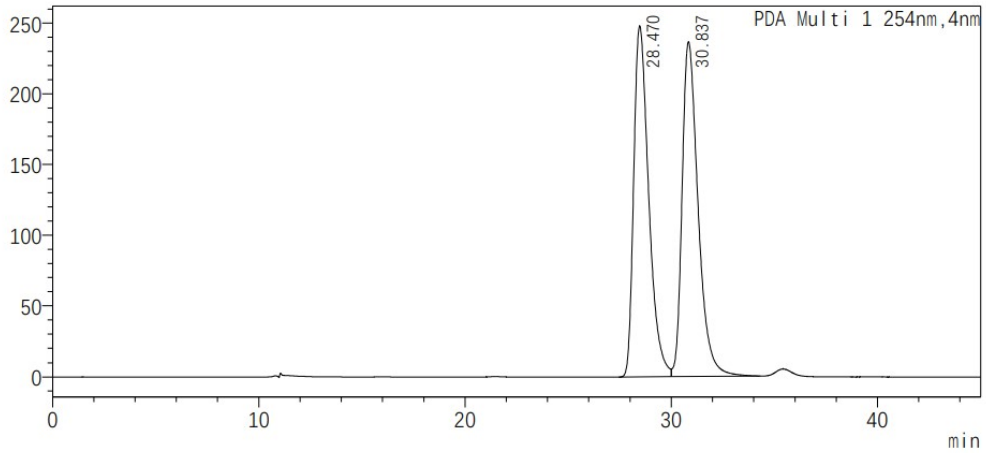
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PDA Ch1 254nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	31.817	8868	3.750	580310	3.478
2	34.259	227589	96.250	16104757	96.522
Total		236456	100.000	16685068	100.000

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mAU



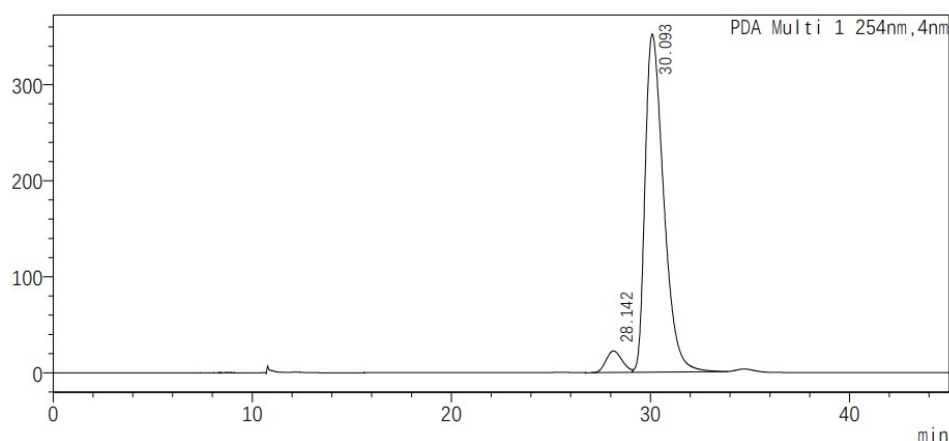
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PDA Ch1 254nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	28.470	248182	51.185	12524923	49.567
2	30.837	236693	48.815	12743796	50.433
Total		484875	100.000	25268719	100.000

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mAU

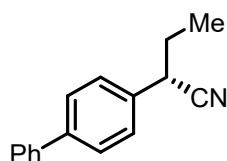


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PDA_Ch1_254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	28.142	22453	5.994	1262810	5.241
2	30.093	352118	94.006	22832790	94.759
Total		374571	100.000	24095600	100.000

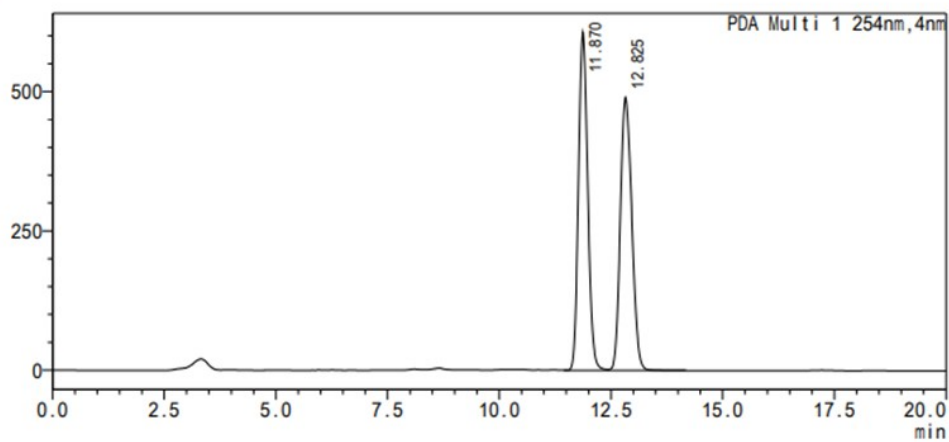
(S)-2-([1,1'-Biphenyl]-4-yl)butanenitrile (**2b**)



Prepared according to general procedure, constant voltage is 2.3 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2b** as a white solid (31.8 mg, 72% yield) with 90% ee. m.p. 76-77 °C; $[\alpha]_{\text{D}}^{20} = -17.2$ (c 0.52, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 7.60 (t, $J = 8.1$ Hz, 4H), 7.47 – 7.35 (m, 5H), 3.79 (t, $J = 7.2$ Hz, 1H), 1.98 (m, 2H) 1.12 (t, $J = 7.4$ Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 141.0, 140.3, 134.7, 128.8, 127.7, 127.7, 127.6, 127.1, 120.7, 38.6, 29.2, 11.5. **HRMS** (EI): m/z: [M]⁺ Calcd for C₁₈H₁₅N: 221.1204 C₁₆H₁₅N: 221.1204, found 221.1197. HPLC (Daicel Chiralpak AD-H column, hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 254 nm): $t_{\text{r}} = 17.9$ min (major), $t_{\text{r}} = 22.2$ min (minor).

<Chromatogram>

mAU



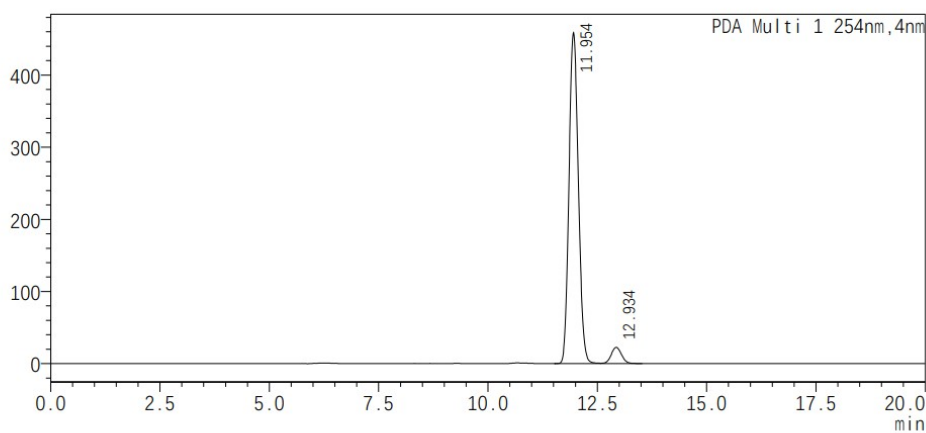
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PDA Ch1 254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	11.870	606781	55.340	8771219	50.086
2	12.825	489681	44.660	8741246	49.914
Total		1096461	100.000	17512465	100.000

<Chromatogram>

mAU

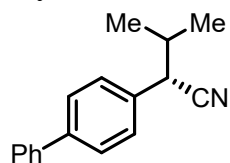


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PDA Ch1 254nm

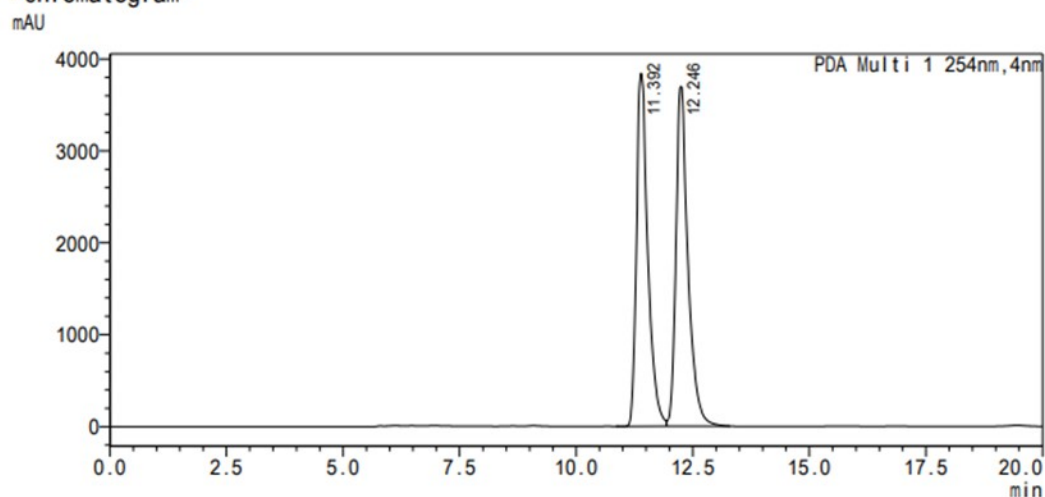
No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	11.954	458631	95.329	6850979	94.889
2	12.934	22474	4.671	368997	5.111
Total		481105	100.000	7219976	100.000

(S)-2-([1,1'-Biphenyl]-4-yl)-3-methylbutanenitrile (2c)



Prepared according to general procedure, constant voltage is 2.3 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2c** as a white solid (37.4 mg, 80% yield) with 86% ee. m.p. 56-57 °C; $[\alpha]_D^{20} = -15.4$ (c 0.54, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.62 (s, 1H), 7.61 – 7.57 (m, 3H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 3H), 3.71 (d, *J* = 6.2 Hz, 1H), 2.18 (m, *J* = 6.7 Hz, 1H), 1.10 (d, *J* = 6.8 Hz, 1H), 1.08 (d, *J* = 6.7 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 140.9, 140.3, 133.9, 128.8, 128.3, 127.6, 127.5, 127.0, 119.8, 44.8, 33.8, 20.8, 18.8. HRMS (EI): *m/z*: [M]⁺ Calcd for C₁₇H₁₇N: 235.1361, found 235.1358. HPLC (Daicel Chiralpak AD-H column, hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 254 nm): *t_r* = 11.1 min (major), *t_r* = 12.0 min (minor).

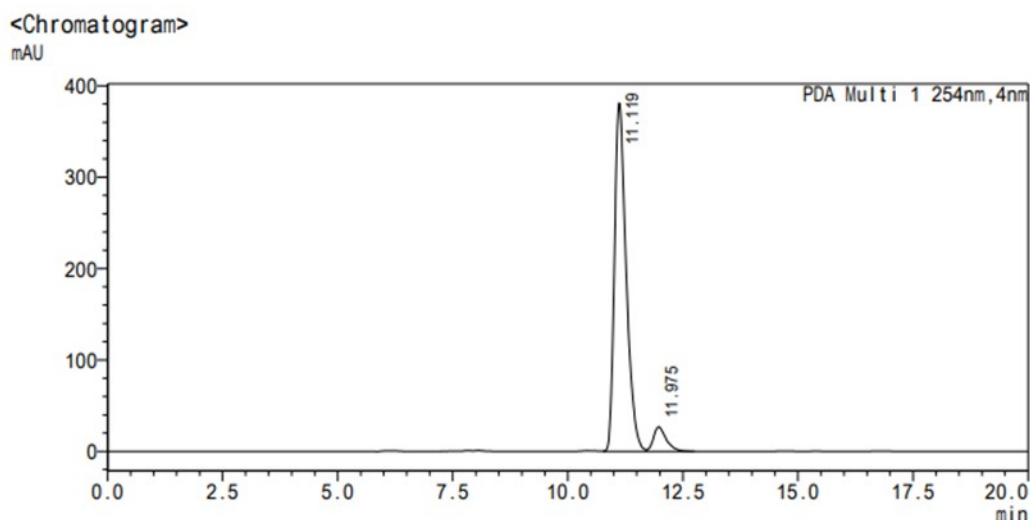
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<Peak Table>

PDA Ch1 254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	11.392	3838098	50.944	64821770	49.434
2	12.246	3695837	49.056	66306370	50.566
Total		7533935	100.000	131128140	100.000

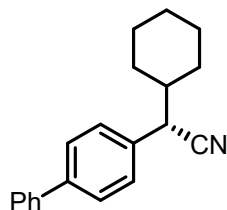


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PDA Ch1 254nm

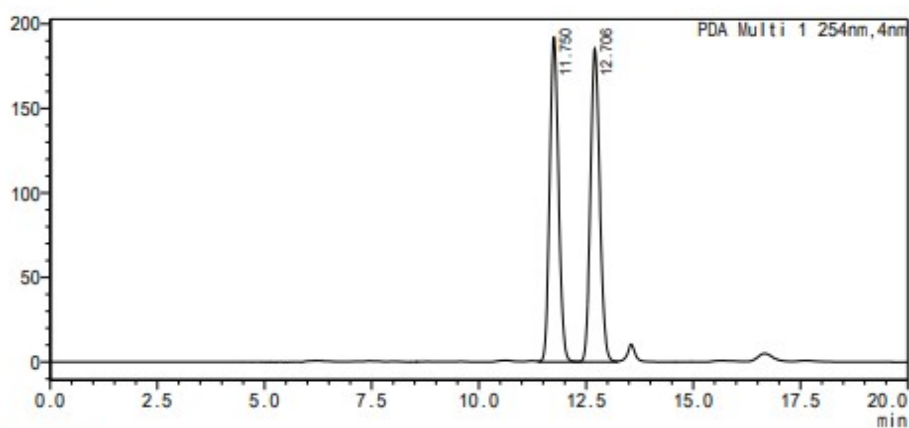
No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	11.119	380872	93.434	6756406	92.887
2	11.975	26768	6.566	517395	7.113
Total		407640	100.000	7273802	100.000

(S)-2-([1,1'-Biphenyl]-4-yl)-2-cyclohexylacetonitrile (2d)



Prepared according to general procedure, constant voltage is 2.3 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2d** as a white solid (19.3 mg, 35% yield) with 94% ee. m.p. 146.8-146.9 °C; $[\alpha]_D^{20} = -4.7$ (c 0.46, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.55 (m, 4H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.31 (m, 3H), 3.68 (d, *J* = 6.6 Hz, 1H), 1.89 (m, 1H), 1.83 – 1.65 (m, 6H), 1.21 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 140.9, 133.7, 128.8, 128.8, 128.4, 127.5, 127.5, 127.1, 120.1, 44.0, 42.8, 31.3, 29.6, 26.0, 25.8, 25.8. HRMS (EI): *m/z*: [M]⁺ Calcd for C₂₀H₂₁N: 275.1674, found 275.1672. HPLC (Daicel Chiralpak AD-H column, hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 254 nm): *t_r* = 11.6 min (major), *t_r* = 12.7 min (minor).

<Chromatogram>
mAU



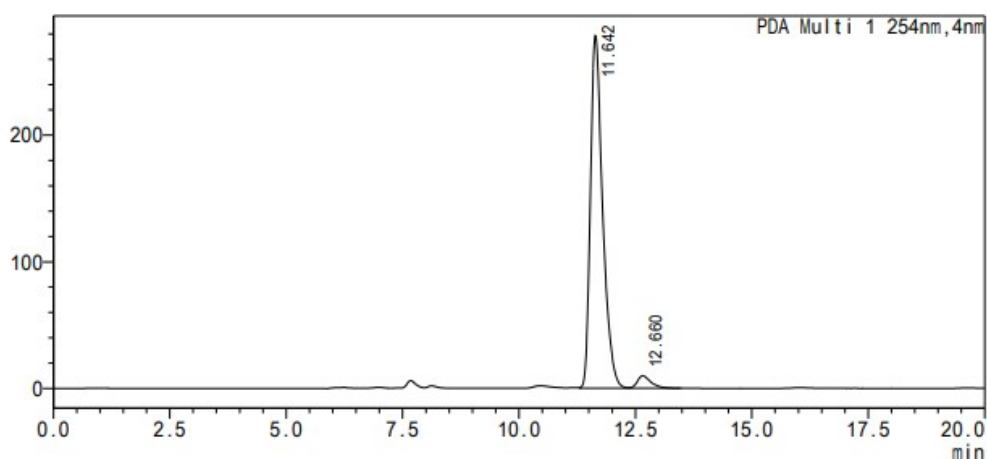
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PDA Ch1 254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	11.750	192095	50.898	2774981	49.664
2	12.706	185318	49.102	2812584	50.336
Total		377413	100.000	5587565	100.000

<Chromatogram>

mAU

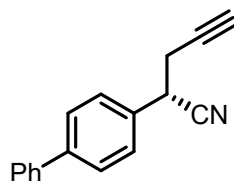


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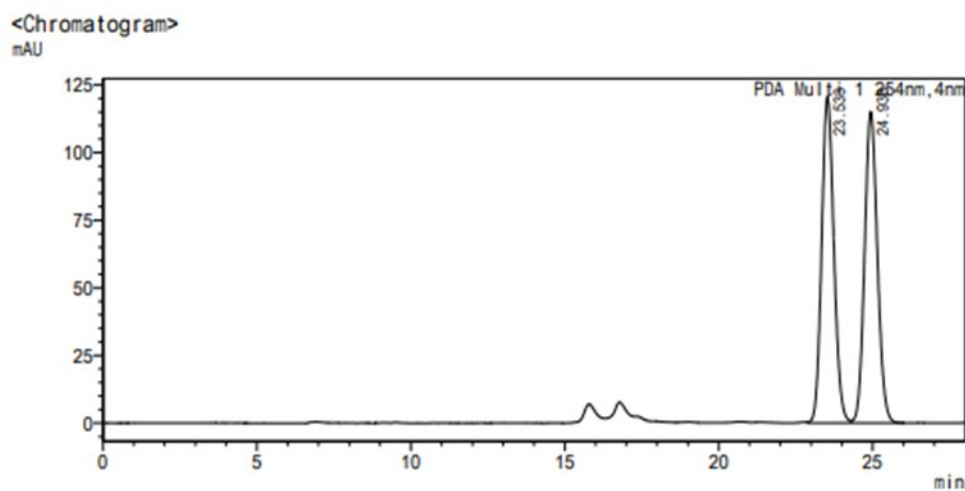
PDA Ch1 254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	11.642	278578	96.566	5086497	96.183
2	12.660	9906	3.434	201875	3.817
Total		288483	100.000	5288372	100.000

(S)-2-([1,1'-Biphenyl]-4-yl)pent-4-ynenitrile (2e)



Prepared according to general procedure, constant voltage is 2.3 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2e** as a white solid (24.5 mg, 53% yield) with 90% ee. m.p. 65-66 °C; $[\alpha]_D^{20} = -15.7$ (c 0.52, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.60 (m, 4H), 7.48 (m, 4H), 7.42 – 7.38 (m, 1H), 4.09 (t, *J* = 7.0 Hz, 1H), 2.93 – 2.80 (m, 2H), 2.22 (t, *J* = 2.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 141.7, 140.1, 133.1, 128.9, 127.8, 127.8, 127.7, 127.1, 119.4, 78.5, 72.5, 36.6, 25.9. HRMS (EI): m/z: [M]⁺ Calcd for C₁₇H₁₃N: 231.1048, found 231.1044. HPLC (Daicel Chiralpak IG column, hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 254 nm): t_r = 22.6 min (major), t_R = 24.0 min (minor).

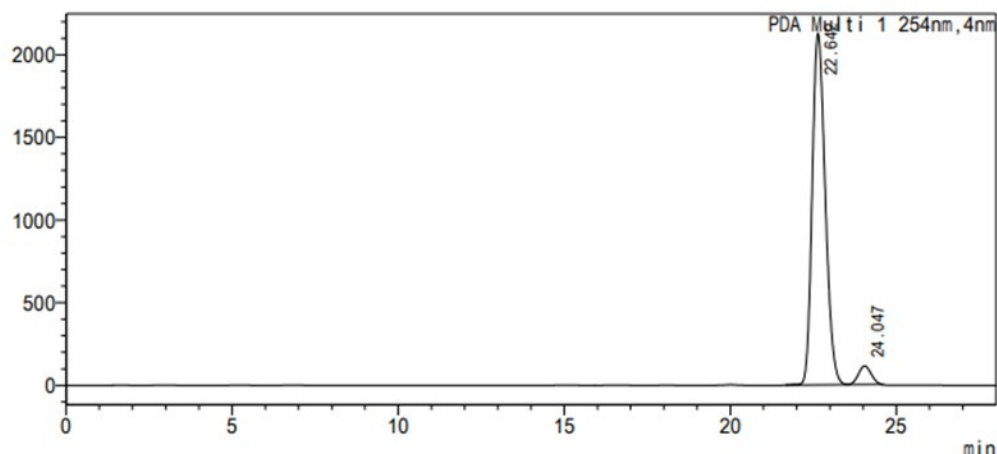


<Peak Table>

PDA Ch1 254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	23.533	120532	51.187	3321044	49.984
2	24.938	114943	48.813	3323117	50.016
Total		235475	100.000	6644160	100.000

<Chromatogram>
mAU

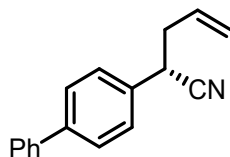


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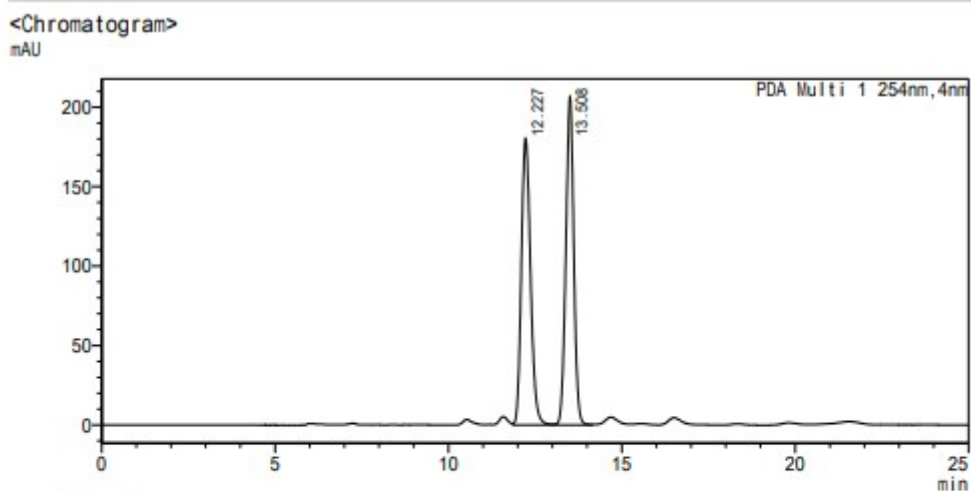
PDA Ch1 254nm

No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	22.642	2126298	94.981	58160528	95.078
2	24.047	112353	5.019	3010885	4.922
Total		2238651	100.000	61171412	100.000

(S)-2-([1,1'-Biphenyl]-4-yl)pent-4-enitrile (2f)



Prepared according to general procedure, constant voltage is 2.3 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2f** as a white solid (19.1 mg, 41% yield) with 90% ee. m.p. 92.1-92.7 °C; $[\alpha]_D^{20} = -18.8$ (c 0.5, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 7.60 (t, $J = 9.1$ Hz, 4H), 7.42 (m, 5H), 5.84 (td, $J = 17.3, 7.0$ Hz, 1H), 5.24-5.20 (m, 3H), 3.90 (t, $J = 7.2$ Hz, 1H), 2.69 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 141.2, 140.2, 134.1, 132.6, 128.9, 127.7, 127.7 127.6, 127.1, 120.2, 119.5, 39.8, 37.2. **HRMS** (EI): m/z: $[M]^+$ Calcd for C₁₇H₁₅N: 233.1204, found 233.1201. HPLC (Daicel Chiralpak AD-H column, hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 254 nm): $t_r = 12.1$ min (major), $t_r = 13.4$ min (minor).



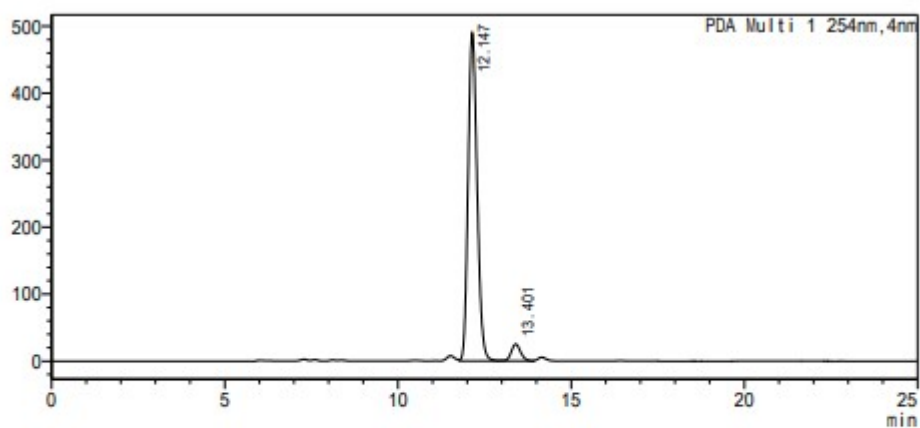
<Peak Table>

PDA Ch1 254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	12.227	180278	46.644	3318679	50.370
2	13.508	206222	53.356	3269897	49.630
Total		386500	100.000	6588576	100.000

<Chromatogram>

mAU

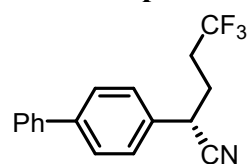


<Peak Table>

PDA Ch1 254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	12.147	489542	95.099	8894080	94.889
2	13.401	25227	4.901	479059	5.111
Total		514769	100.000	9373139	100.000

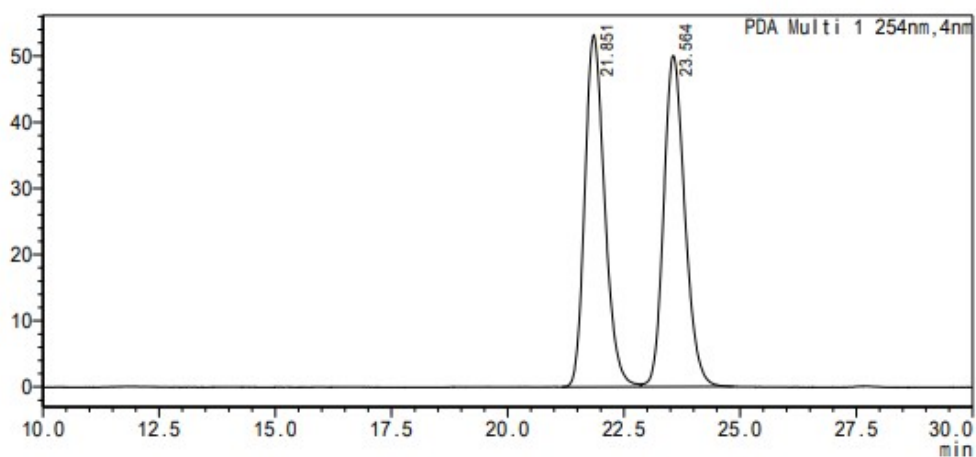
(S)-2-([1,1'-Biphenyl]-4-yl)-5,5,5-trifluoropentanenitrile (2g)



Prepared according to general procedure, constant voltage is 2.3 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2g** as a white solid

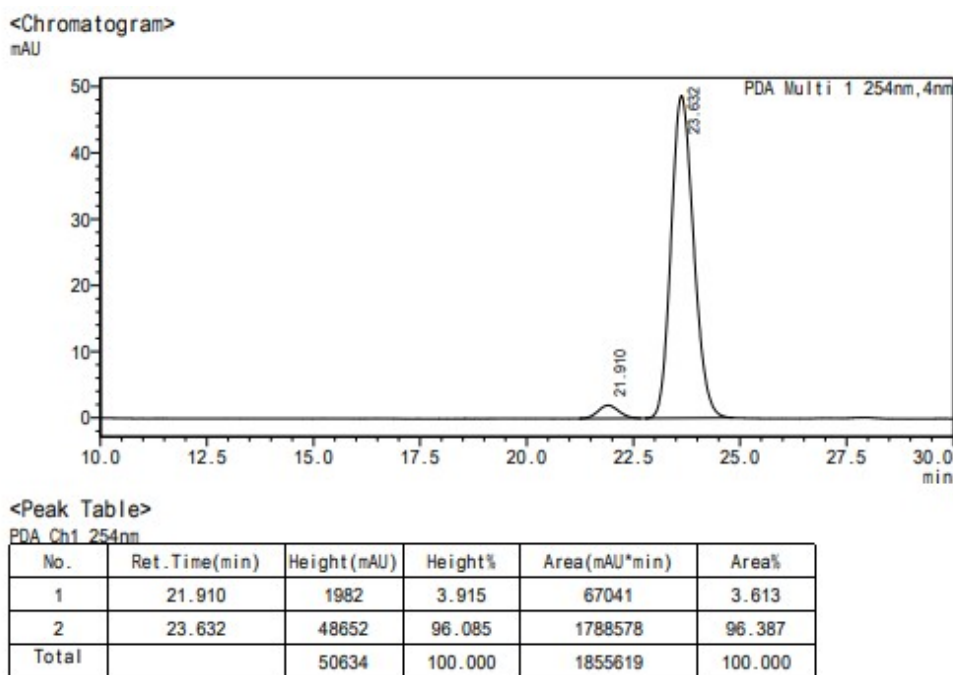
(40.5 mg, 70% yield) with 93% ee. m.p. 110.1-110.3 °C; $[\alpha]_D^{20} = -14.5$ (c 0.54, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.68 – 7.56 (m, 4H), 7.51 – 7.32 (m, 5H), 3.96 (t, *J* = 7.2 Hz, 1H), 2.40 – 2.16 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 141.8, 140.0, 133.0, 128.9, 128.1, 127.8, 127.6, 127.1, 126.4 (q, ¹*J*_{C-F} = 276.3 Hz), 119.5, 35.9, 31.2 (q, ²*J*_{C-F} = 29.4 Hz), 28.2 (q, ³*J*_{C-F} = 2.9 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -66.01. HRMS (EI): *m/z*: [M]⁺ Calcd for C₁₇H₁₄F₃N: 289.1078, found 289.1072. HPLC (Daicel Chiralpak IC column, hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min, 254 nm): *t*_r = 21.9 min (minor), *t*_r = 23.6 min (major).

<Chromatogram>
mAU

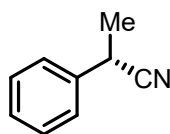


<Peak Table>
PDA Ch1 254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	21.851	53166	51.516	1580221	49.983
2	23.564	50037	48.484	1581309	50.017
Total		103203	100.000	3161530	100.000

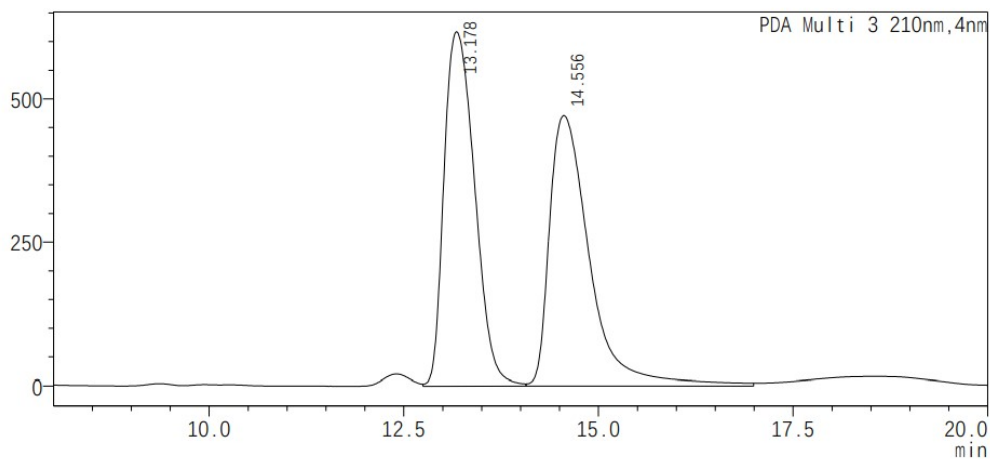


(S)-2-Phenylpropanenitrile (**2h**)



Prepared according to general procedure, constant voltage is 3.0 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2h** as a yellow liquid (23.3 mg, 89% yield) with 85% ee; $[\alpha]_{\text{D}}^{20} = -3.5$ (c 0.47, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.43 – 7.30 (m, 5H), 3.90 (q, $J = 7.2$ Hz, 1H), 1.61 (d, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.0, 129.0, 127.9, 126.6, 121.5, 31.1, 21.3. **HRMS** (EI): m/z : $[M]^+$ Calcd for $\text{C}_9\text{H}_9\text{N}$: 131.0735, found 131.0730. HPLC (Daicel Chiralpak AD-H column, hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 210 nm): $t_{\text{r}} = 13.1$ min (major), $t_{\text{r}} = 14.6$ min (minor).

<Chromatogram>
mAU



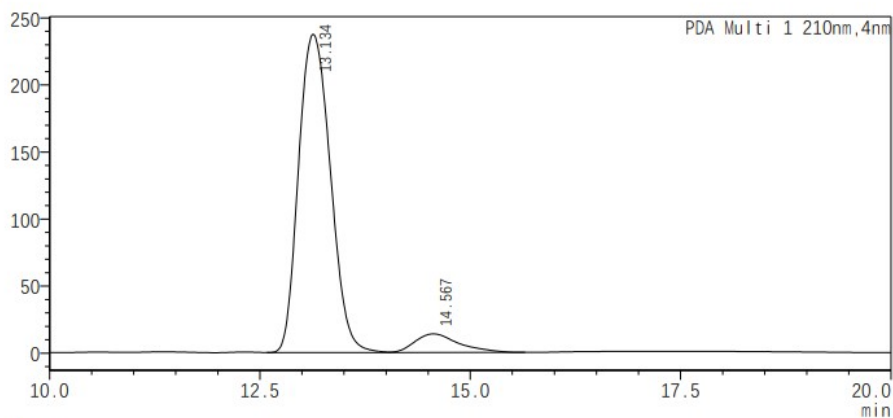
<Peak Table>

PDA Ch3 210nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	13.178	617520	56.718	16904546	49.985
2	14.556	471226	43.282	16914771	50.015
Total		1088746	100.000	33819317	100.000

<Chromatogram>

mAU

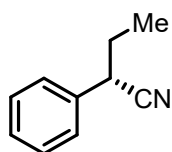


<Peak Table>

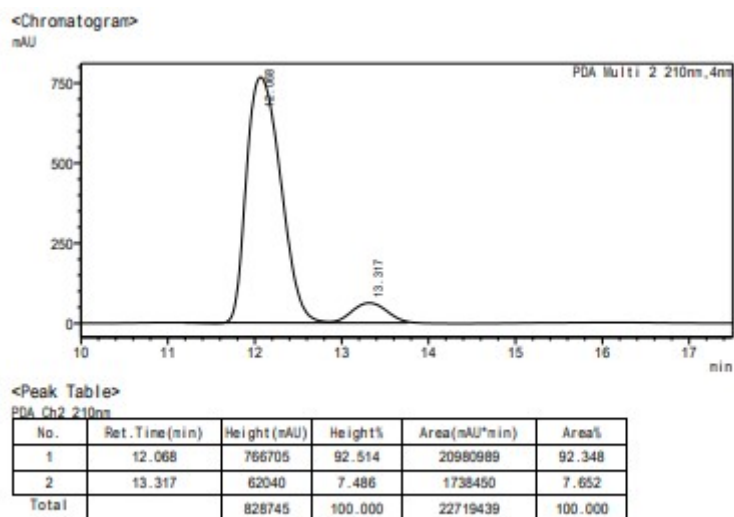
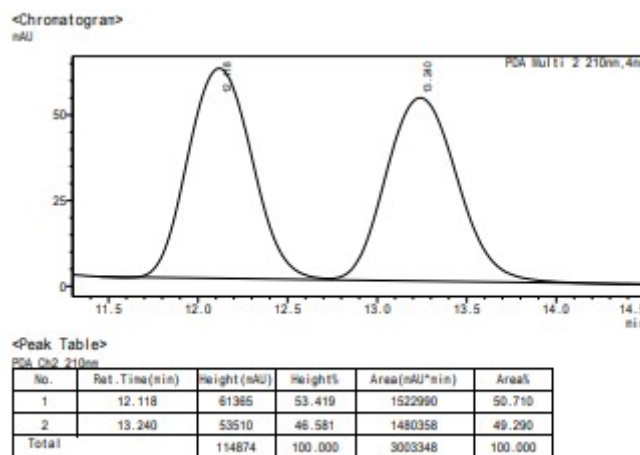
PDA Ch1 210nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	13.134	237263	94.482	6259743	92.550
2	14.567	13856	5.518	503909	7.450
Total		251119	100.000	6763651	100.000

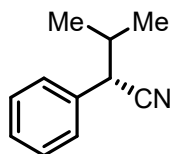
(S)-2-Phenylbutanenitrile (2i)



Prepared according to general procedure, constant voltage is 3.0 V, after a flash column chromatography (hexanes: EA = 20:1-10:1) afforded the product **2i** as a yellow liquid (19.4 mg, 67% yield) with 85% ee; $[\alpha]_D^{20} = -28.7$ (c 0.49, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.35 (m, 2H), 7.35 – 7.29 (m, 3H), 3.74 (t, *J* = 7.2 Hz, 1H), 1.99 – 1.90 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 135.7, 129.0, 128.0, 127.3, 120.7, 38.9, 29.2, 11.4. HRMS (EI): *m/z*: [M]⁺ Calcd for C₁₀H₁₁N: 145.0891, found 145.0885. HPLC (Daicel Chiralpak AS-H column, exane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min, 210 nm): *t_r* = 12.1 min (major), *t_r* = 13.3 min (minor).

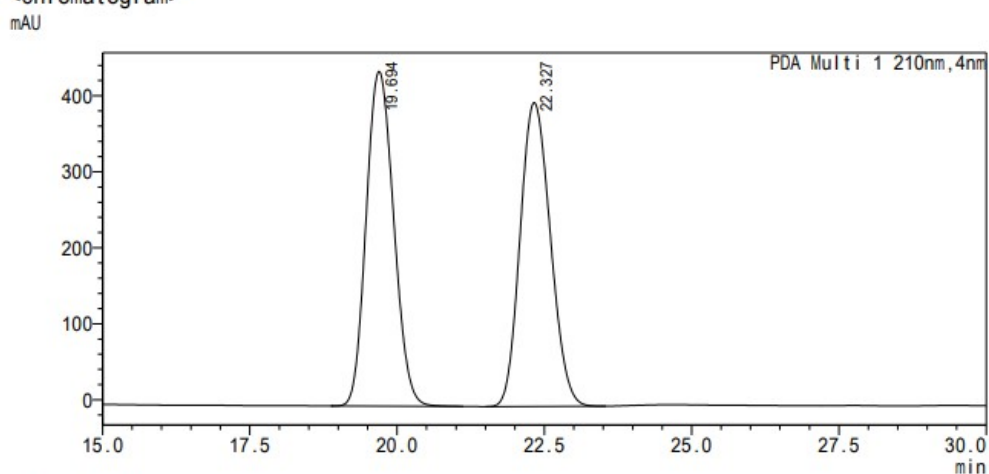


(S)-3-Methyl-2-phenylbutanenitrile (2j)



Prepared according to general procedure, constant voltage is 3.0 V, after a flash column chromatography (hexanes: EA = 20:1-10:1) afforded the product **2j** as a yellow liquid (16.2 mg, 51% yield) with 85% ee; $[\alpha]_D^{20} = -8.9$ (c 0.45, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.26 (m, 5H), 3.66 (t, *J* = 6.3 Hz, 1H), 2.13 (m, 2H), 1.05 (t, *J* = 7.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 134.9, 128.8, 127.9, 119.8, 45.1, 33.8, 20.8, 18.8. HRMS (EI): *m/z*: [M]⁺ Calcd for C₁₁H₁₃N: 159.1048, found 159.1044. HPLC (Daicel Chiralpak IC column, exane/isopropanol = 99/1, flow rate 0.5 mL/min, 210 nm): *t_r* = 20.3 min (minor), *t_r* = 23.2 min (major).

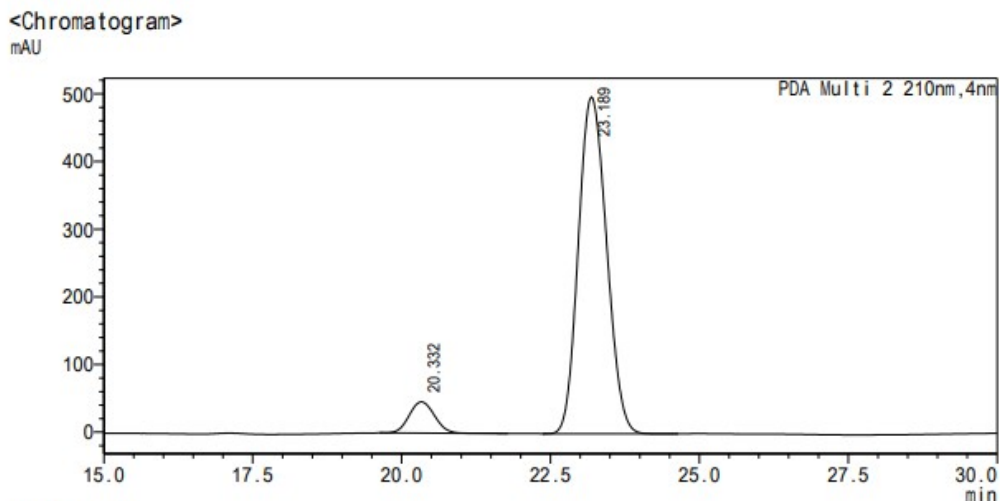
<Chromatogram>



<Peak Table>

PDA Ch1 210nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	19.694	440228	52.405	14295978	50.020
2	22.327	399815	47.595	14284491	49.980
Total		840042	100.000	28580469	100.000

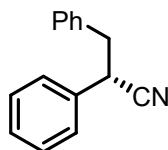


<Peak Table>

PDA Ch2 210nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	20.332	46165	8.492	1366632	7.691
2	23.189	497454	91.508	16403661	92.309
Total		543619	100.000	17770293	100.000

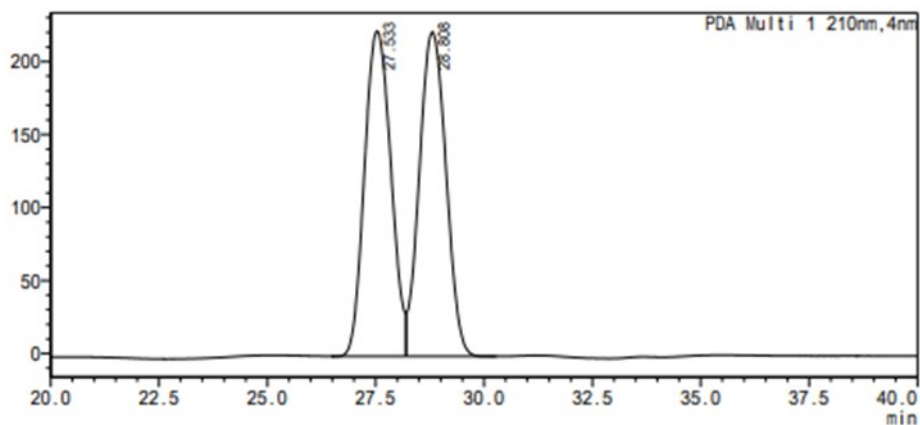
(S)-2,3-Diphenylpropanenitrile (2k)



Prepared according to general procedure, constant voltage is 3.0 V, after a flash column chromatography (hexanes: EA = 20:1-10:1) afforded the product **2k** as a white solid (22.0 mg, 53% yield) with 84% ee. m.p. 57-58 °C; $[\alpha]_D^{20} = -4.4$ (c 0.53, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 7.41 – 7.23 (m, 8H), 7.15 (d, $J = 8.1$ Hz, 2H), 4.01 (t, $J = 7.4$ Hz, 1H), 3.17 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 136.3, 135.2, 129.19, 129.0, 128.6, 128.2, 127.5, 127.4, 120.3, 42.2, 39.8. **HRMS** (EI): m/z: [M]⁺ Calcd for C₁₅H₁₃N: 207.1048, found 207.1045. HPLC (Daicel Chiralpak AD-H column, hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 210 nm): $t_r = 27.5$ min (major), $t_r = 28.6$ min (minor).

<Chromatogram>

mAU



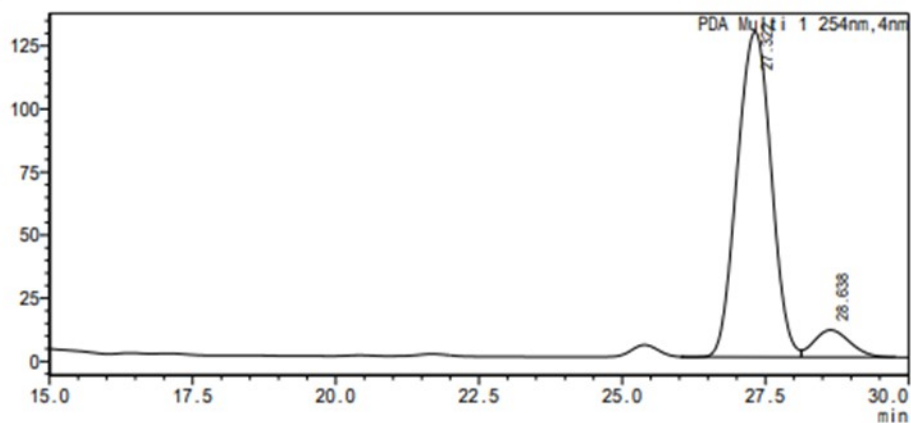
<Peak Table>

PDA Ch1 210nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	27.533	222713	50.053	9439585	49.821
2	28.808	222238	49.947	9507514	50.179
Total		444951	100.000	18947099	100.000

<Chromatogram>

mAU

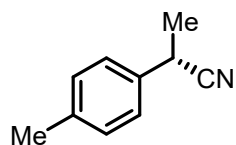


<Peak Table>

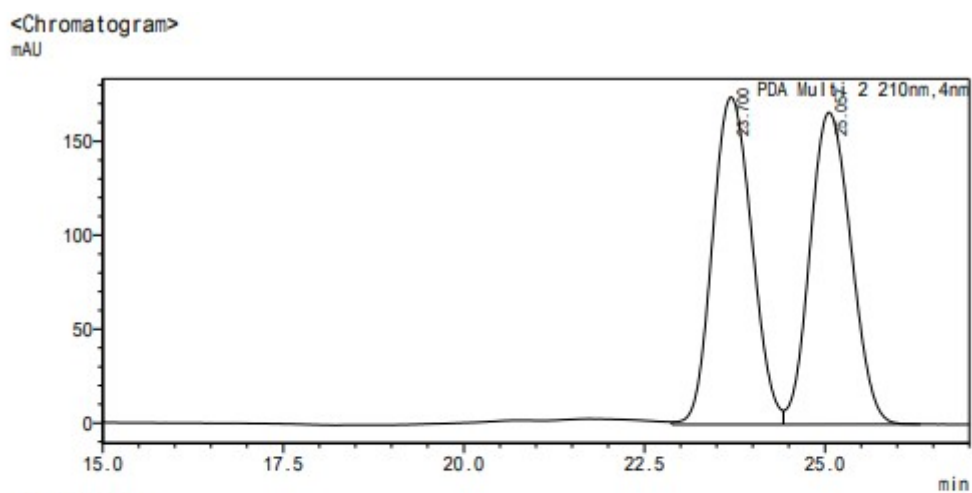
PDA Ch1 254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	27.322	128961	92.314	5321932	91.931
2	28.638	10738	7.686	467098	8.069
Total		139698	100.000	5789030	100.000

(S)-2-(p-Tolyl)propanenitrile (2l)



Prepared according to general procedure, constant voltage is 3.0 V, after a flash column chromatography (hexanes: EA = 20:1-10:1) afforded the product **2I** as a yellow liquid (17.4 mg, 60% yield) with 88% ee; $[\alpha]_D^{20} = -18.5$ (c 0.25, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.26 – 7.18 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 3.86 (q, *J* = 7.3 Hz, 1H), 2.35 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 137.8, 134.1, 129.7, 126.5, 121.7, 30.8, 21.5, 21.0. HRMS (EI): *m/z*: [M]⁺ Calcd for C₁₀H₁₁N: 145.0891, found 145.0886. HPLC (Daicel Chiralpak IE column, hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 210 nm): *t_r* = 24.6 min (minor), *t_r* = 26.0 min (major).

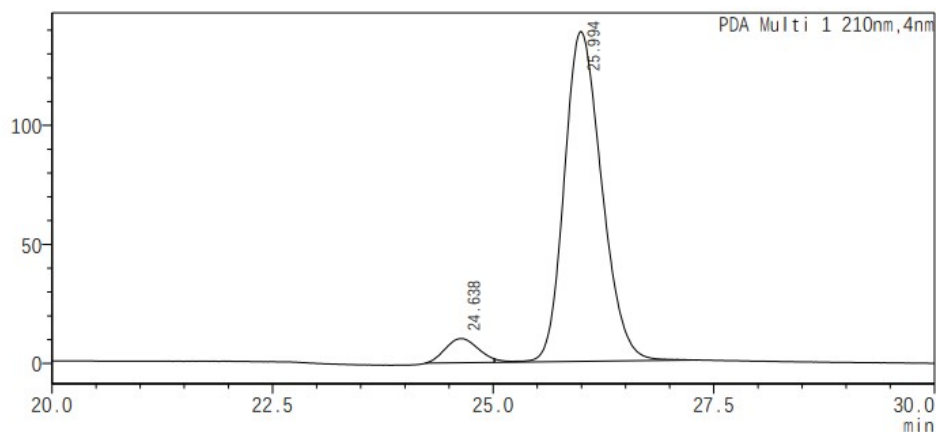


<Peak Table>

PDA Ch2 210nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	23.700	174205	51.210	6595560	50.173
2	25.057	165975	48.790	6550034	49.827
Total		340180	100.000	13145594	100.000

<Chromatogram>
mAU

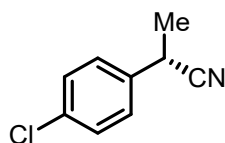


<Peak Table>

PDA Ch1 210nm

No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	24.638	10160	6.832	261169	5.998
2	25.994	138563	93.168	4093210	94.002
Total		148724	100.000	4354379	100.000

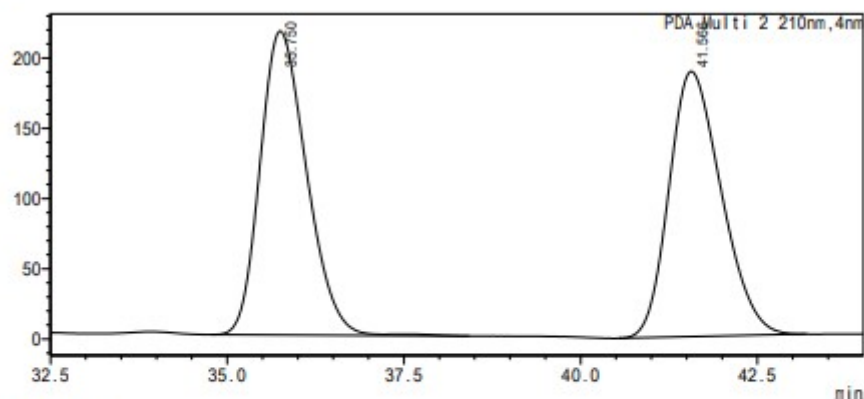
(S)-2-(4-Chlorophenyl)propanenitrile (**2m**)



Prepared according to general procedure, constant voltage is 3.0 V, after a flash column chromatography (hexanes: EA = 20:1-10:1) afforded the product **2m** as a yellow liquid (23.1 mg, 70% yield) with 88% ee; $[\alpha]_D^{20} = -19.5$ (c 0.59, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.39 – 7.33 (m, 2H), 7.31 – 7.27 (m, 2H), 3.88 (q, $J = 7.3$ Hz, 1H), 1.63 (d, $J = 7.3$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 135.5, 134.0, 129.3, 128.1, 121.1, 30.7, 21.3. **HRMS** (EI): m/z : $[\text{M}]^+$ Calcd for $\text{C}_9\text{H}_8\text{ClN}$: 165.0345, found 165.0340. HPLC (Daicel Chiralpak OJ-H column, hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 210 nm): $t_r = 34.5$ min (minor), $t_r = 39.7$ min (major).

<Chromatogram>

mAU



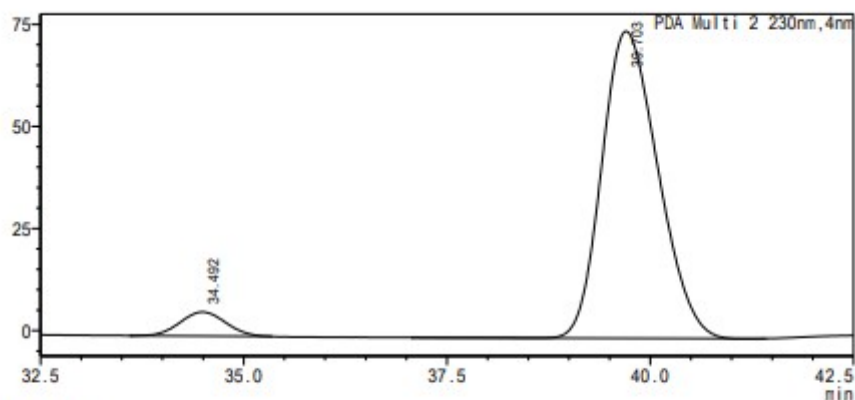
<Peak Table>

PDA Ch2 210nm

No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	35.750	216261	53.396	9906803	50.501
2	41.566	188755	46.604	9710397	49.499
Total		405016	100.000	19617200	100.000

<Chromatogram>

mAU

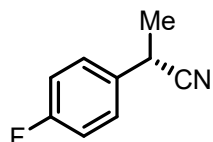


<Peak Table>

PDA Ch2 230nm

No.	Ret. Time (min)	Height (mAU)	Height%	Area (mAU*min)	Area%
1	34.492	5884	7.258	229950	5.998
2	39.703	75189	92.742	3603722	94.002
Total		81073	100.000	3833672	100.000

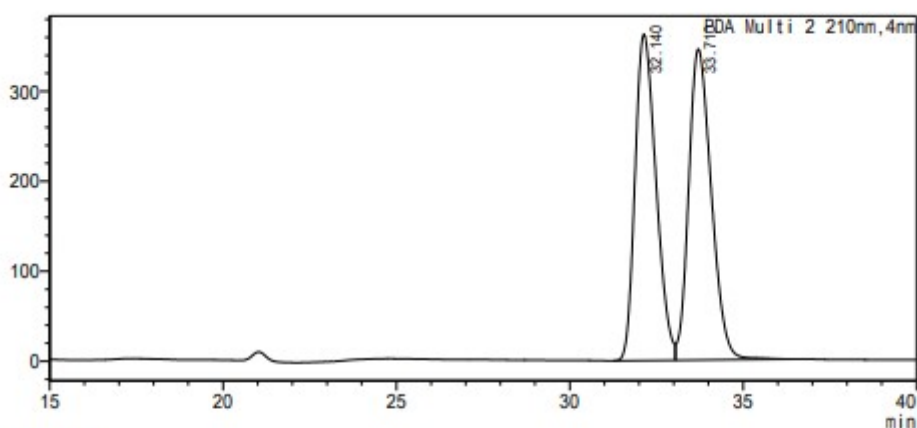
(S)-2-(4-Fluorophenyl)propanenitrile (**2n**)



Prepared according to general procedure, constant voltage is 3.0 V, after a flash column chromatography (hexanes: EA = 20:1-10:1) afforded the product **2n** as a yellow liquid (12.0 mg, 40% yield) with 81% ee; $[\alpha]_D^{20} = -12.5$ (c 0.25, CHCl_3); $^1\text{H NMR}$ (400 MHz,

CDCl₃) δ 7.38 – 7.28 (m, 2H), 7.13 – 7.00 (m, 2H), 3.89 (q, *J* = 7.3 Hz, 1H), 1.63 (d, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 162.4 (d, ¹*J*_{C-F} = 247.3 Hz), 132.8 (d, ⁴*J*_{C-F} = 3.6 Hz), 128.4 (d, ³*J*_{C-F} = 8.0 Hz), 121.4, 116.1 (d, ²*J*_{C-F} = 22.5 Hz), 30.6, 21.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -113.88. HRMS (EI): *m/z*: [M]⁺ Calcd for C₉H₈FN: 149.0641, found 149.0634. HPLC (Daicel Chiralpak OJ-H column, hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 210 nm): *t*_r = 32.0 min (minor), *t*_r = 33.3 min (major).

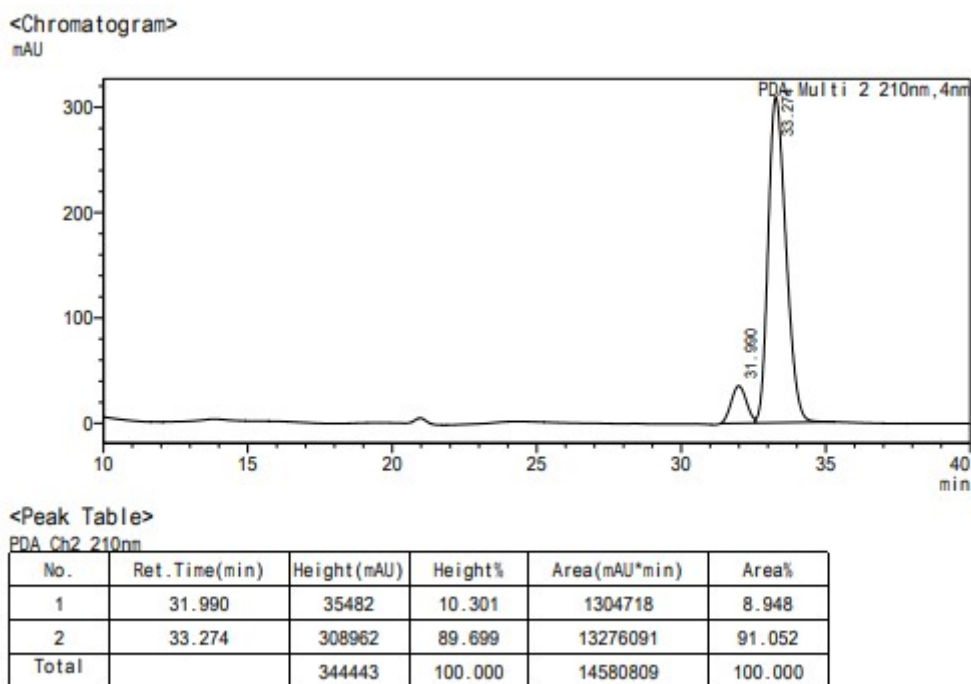
<Chromatogram>
mAU



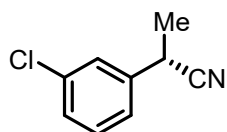
<Peak Table>

PDA_Ch2 210nm

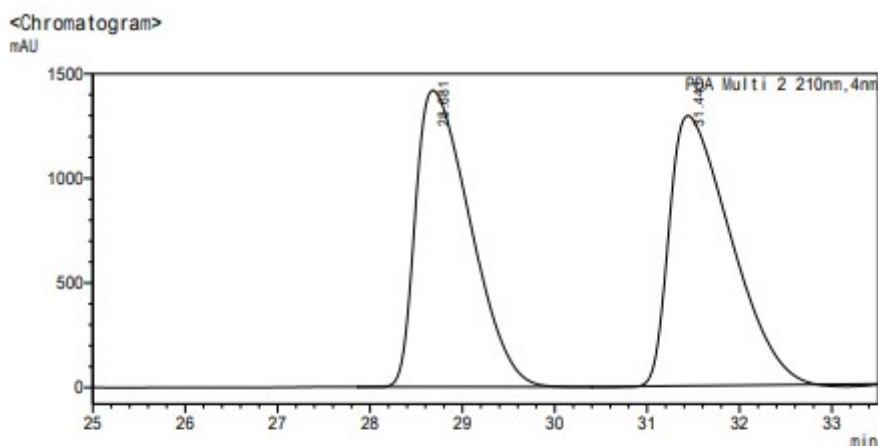
No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	32.140	362610	51.202	15257503	49.307
2	33.710	345592	48.798	15686181	50.693
Total		708202	100.000	30943684	100.000



(S)-2-(3-Chlorophenyl)propanenitrile (2o)

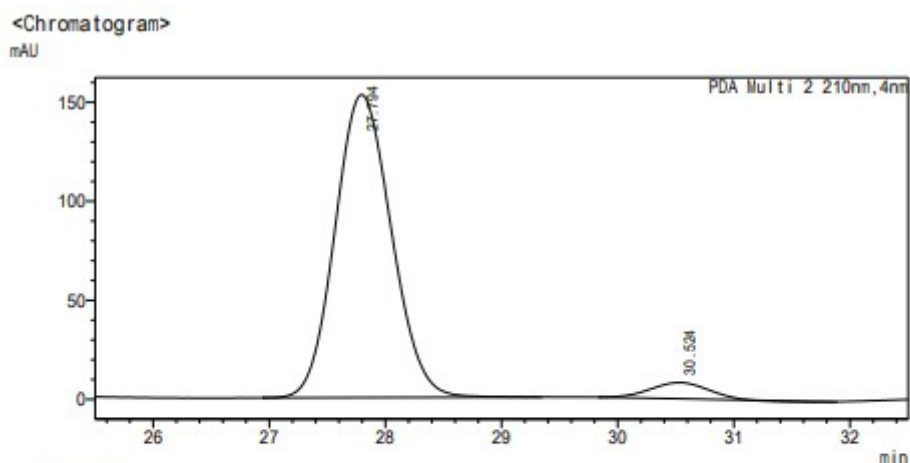


Prepared according to general procedure, constant voltage is 3.0 V, after a flash column chromatography (hexanes: EA = 20:1-10:1) afforded the product **2o** as a yellow liquid (13.2 mg, 40% yield) with 90% ee; $[\alpha]_D^{20} = -19.3$ (c 0.50, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.35 (t, *J* = 2.1 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.27 – 7.24 (m, 1H), 3.88 (q, *J* = 7.3 Hz, 1H), 1.65 (d, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 138.9, 135.0, 130.4, 128.4, 127.0, 124.9, 120.9, 30.9, 21.2. HRMS (EI): *m/z*: [M]⁺ Calcd for C₉H₈ClN: 165.0345, found 165.0343. HPLC (Daicel Chiralpak OJ-H column, hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 210 nm): *t_r* = 27.8 min (major), *t_r* = 30.5 min (minor).



<Peak Table>
PDA Ch2 210nm

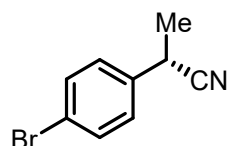
No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	28.681	1418097	52.322	58124104	49.452
2	31.443	1292223	47.678	59412571	50.548
Total		2710320	100.000	117536675	100.000



<Peak Table>
PDA Ch2 210nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	27.794	152894	94.947	5156324	94.999
2	30.524	8136	5.053	271436	5.001
Total		161030	100.000	5427760	100.000

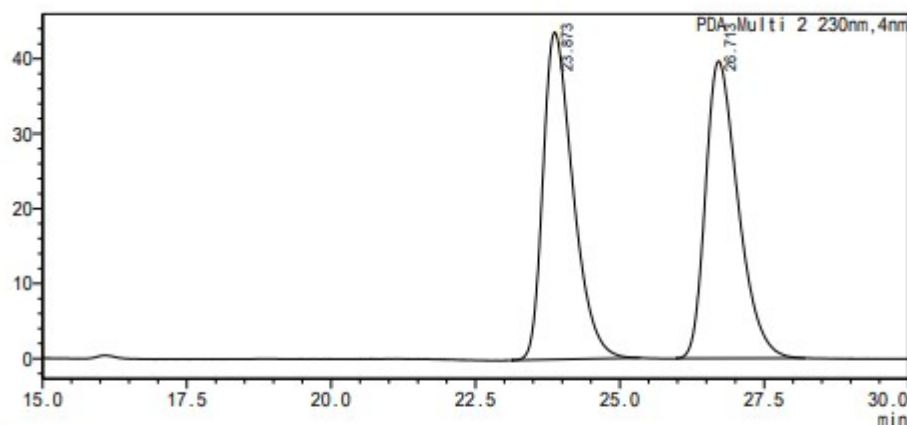
(S)-2-(4-Bromophenyl)propanenitrile (2p)



Prepared according to general procedure, constant voltage is 3.0 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2p** as a yellow liquid (21.3 mg, 51% yield) with 90% ee; $[\alpha]_D^{20} = -12.6$ (c 0.48, CHCl_3); $^1\text{H NMR}$ (400 MHz,

CDCl₃) δ 7.56 – 7.48 (m, 2H), 7.26 – 7.18 (m, 2H), 3.87 (q, *J* = 7.2 Hz, 1H), 1.63 (d, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 136.0, 132.3, 128.4, 122.1, 121.0, 30.8, 21.3. HRMS (EI): *m/z*: [M]⁺ Calcd for C₉H₈BrN: 208.9840, found 208.9833. HPLC (Daicel Chiralpak AD-H column, hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min, 230nm): *t_r* = 23.9 min (major), *t_r* = 26.9 min (minor).

<Chromatogram>
mAU

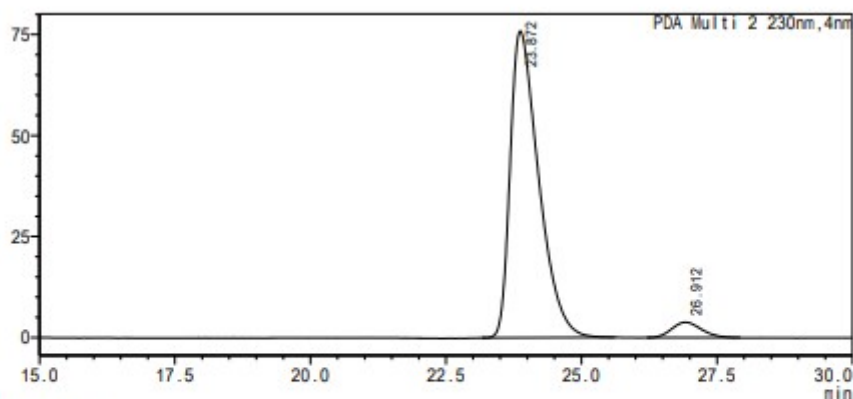


<Peak Table>

PDA Ch2 230nm

No.	Ret. Time(min)	Height (mAU)	Height%	Area(mAU*min)	Area%
1	23.873	43641	52.387	1578819	50.296
2	26.713	39664	47.613	1560209	49.704
Total		83306	100.000	3139028	100.000

<Chromatogram>
mAU

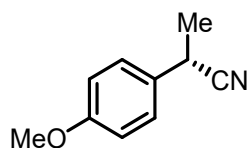


<Peak Table>

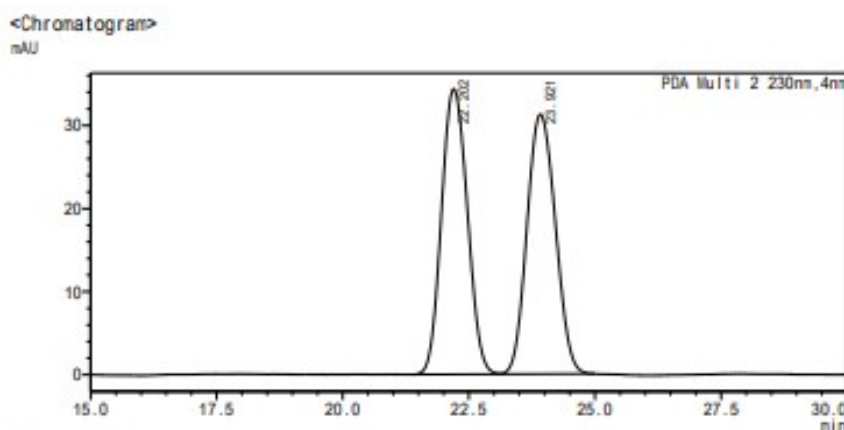
PDA Ch2 230nm

No.	Ret. Time(min)	Height (mAU)	Height%	Area(mAU*min)	Area%
1	23.872	75884	95.222	2782263	95.018
2	26.912	3808	4.778	145886	4.982
Total		79692	100.000	2928149	100.000

(S)-2-(4-Methoxyphenyl)propanenitrile (2q)

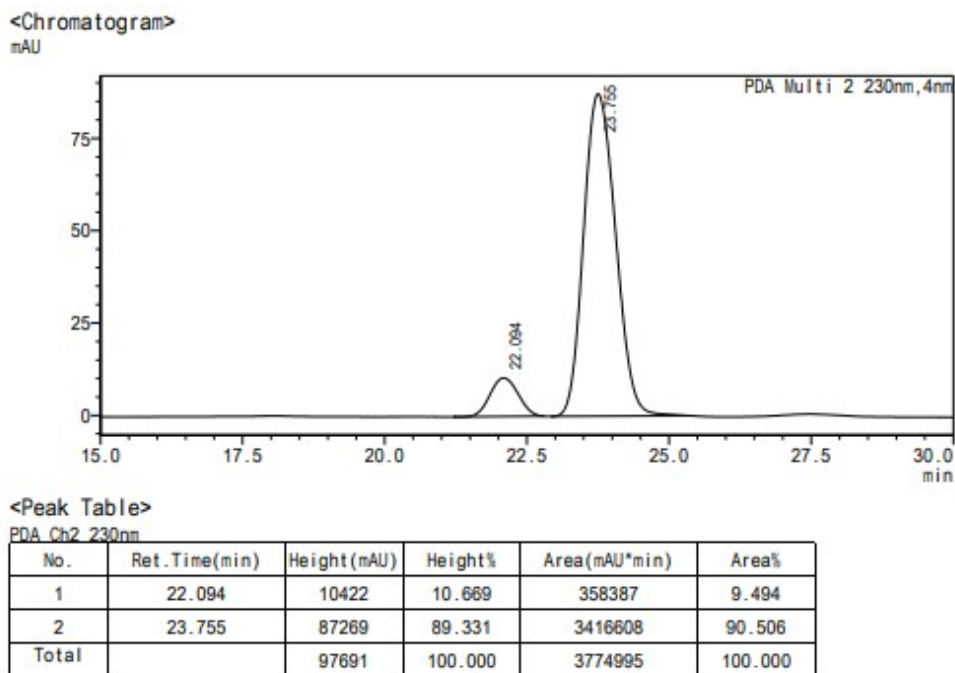


Prepared according to general procedure, constant voltage is 3.0 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2q** as a yellow liquid (19.0 mg, 58% yield) with 81% ee; $[\alpha]_D^{20} = -9.2$ (c 0.50, CHCl_3); **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.30 – 7.27 (m, 2H), 7.00 – 6.87 (m, 2H), 3.88 (q, $J = 7.3$ Hz, 1H), 3.83 (s, 3H), 1.64 (d, $J = 7.2$ Hz, 3H). **$^{13}\text{C NMR}$** (101 MHz, CDCl_3) δ 159.3, 129.1, 127.8, 121.8, 114.5, 55.3, 30.5, 21.5. **HRMS** (EI): m/z : $[\text{M}]^+$ Calcd for $\text{C}_{10}\text{H}_{11}\text{NO}$: 161.0841, found 161.0834. HPLC (Daicel Chiralpak OZ-3 column, hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min, 230 nm): $t_r = 22.1$ min (minor), $t_r = 23.8$ min (major).

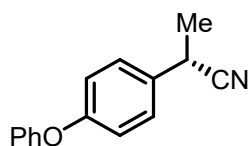


<Peak Table>
PDA Ch2 230nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	22.202	34324	52.353	1226186	50.020
2	23.921	31239	47.647	1225223	49.980
Total		65562	100.000	2451409	100.000

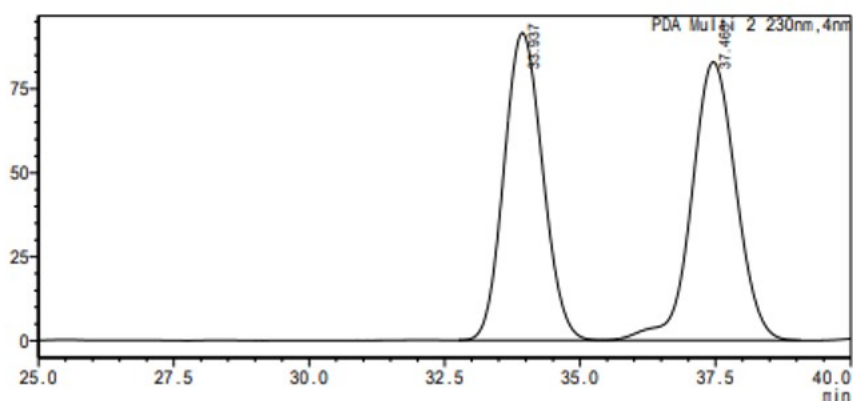


(S)-2-(4-Phenoxyphenyl)propanenitrile (2r)



Prepared according to general procedure, constant voltage is 3.0 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2r** as a yellow liquid (25.9 mg, 58% yield) with 88% ee; $[\alpha]_{\text{D}}^{20} = -5.9$ (c 0.50, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.35 (q, $J = 8.5$ Hz, 3H), 7.18 – 7.07 (m, 2H), 7.02 (d, $J = 8.6$ Hz, 3H), 6.94 (d, $J = 6.9$ Hz, 1H), 3.86 (q, $J = 7.3$ Hz, 1H), 1.64 (d, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 158.0, 156.6, 138.9, 130.5, 129.9, 123.8, 121.3, 119.2, 118.0, 117.1, 31.1, 21.3. **HRMS** (EI): m/z : $[\text{M}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{NO}$: 223.0997, found 223.0994. HPLC (Daicel Chiralpak IC column, hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 230 nm): $t_{\text{r}} = 33.9$ min (minor), $t_{\text{r}} = 37.2$ min (major).

<Chromatogram>
nAU

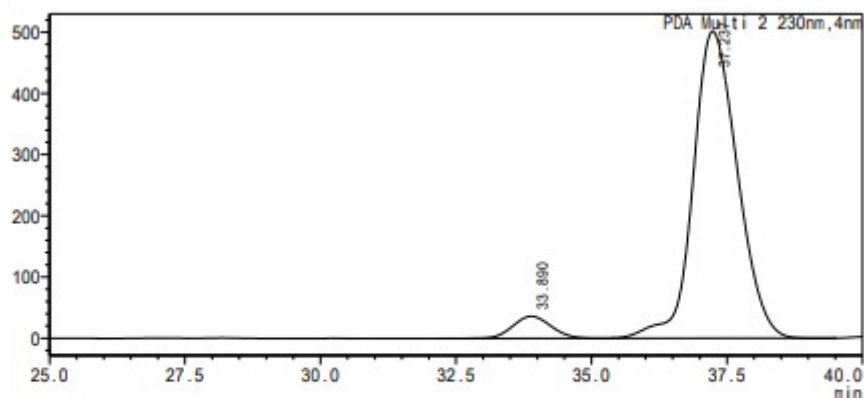


<Peak Table>

PDA Ch2 230nm

No.	Ret. Time(min)	Height (mAU)	Height%	Area(mAU*min)	Area%
1	33.937	91498	52.480	4545694	49.064
2	37.463	82849	47.520	4719115	50.936
Total		174347	100.000	9264810	100.000

<Chromatogram>
nAU

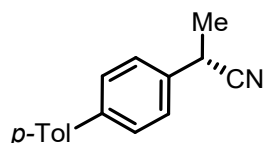


<Peak Table>

PDA Ch2 230nm

No.	Ret. Time(min)	Height (mAU)	Height%	Area(mAU*min)	Area%
1	33.890	36016	6.698	1758747	5.808
2	37.237	501702	93.302	28525122	94.192
Total		537718	100.000	30283868	100.000

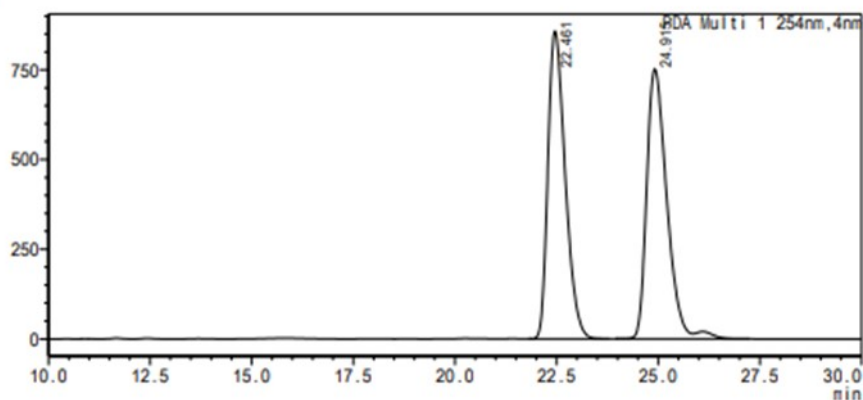
(S)-2-(4'-Methyl-[1,1'-biphenyl]-4-yl)propanenitrile (2s)



Prepared according to general procedure, constant voltage is 2.3 V, after a flash column chromatography (hexanes: EA = 20:1-10:1) afforded the product **2s** as a white solid (32.3mg, 73% yield) with 90% ee. m.p. 109-110 °C; $[\alpha]_D^{20} = -13.0$ (c 0.50, CHCl₃); **1H**

NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 6.8 Hz, 2H), 3.93 (q, *J* = 7.2 Hz, 1H), 2.39 (s, 3H), 1.67 (d, *J* = 7.3 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 133.3, 133.0, 132.8, 129.0, 127.8, 127.7, 126.7, 126.4, 126.4, 124.8, 120.7, 39.0, 29.0, 11.5. **HRMS** (EI): *m/z*: [M]⁺ Calcd for C₁₆H₁₅N: 221.1204, found 221.1198. **HPLC** (Daicel Chiralpak IC column, hexane/isopropanol = 99/1, flow rate 1.0 mL/min, 254 nm): *t_r* = 21.8 min (minor), *t_r* = 24.0 min (major).

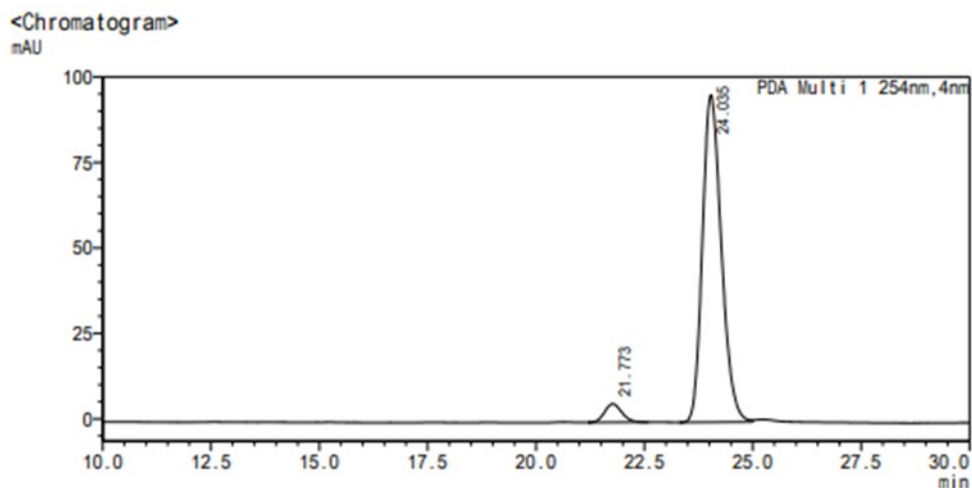
<Chromatogram>
nAU



<Peak Table>

PDA Ch1 254nm

No.	Ret. Time(min)	Height (nAU)	Height%	Area(nAU*min)	Area%
1	22.461	857143	53.274	25353567	49.321
2	24.915	751792	46.726	26051871	50.679
Total		1608935	100.000	51405437	100.000

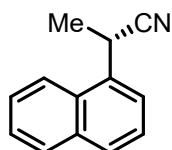


<Peak Table>

PDA Ch1 254nm

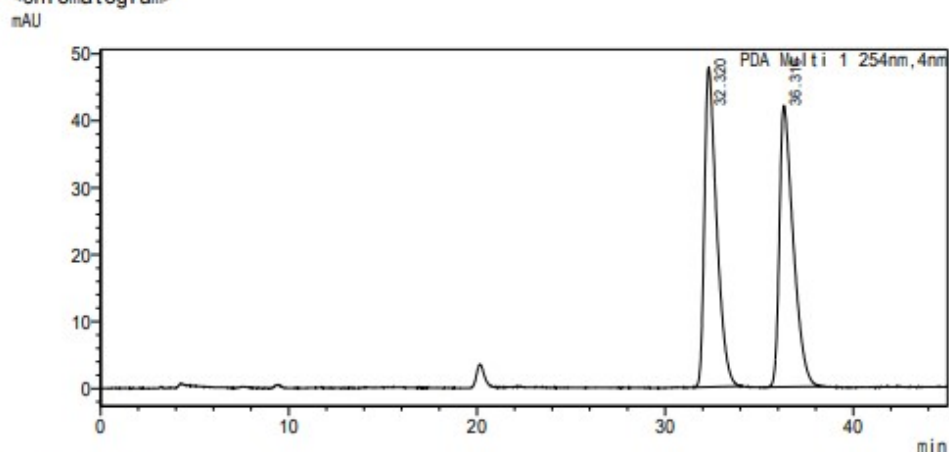
No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	21.773	5386	5.329	149543	4.873
2	24.035	95679	94.671	2919371	95.127
Total		101065	100.000	3068914	100.000

(S)-2-(Naphthalen-1-yl)propanenitrile (2t)



Prepared according to general procedure, constant voltage is 3.0 V, after a flash column chromatography (hexanes: EA = 20:1-10:1) afforded the product **2t** as a white solid (23.1 mg, 64% yield) with 94% ee. m.p. 87-88 °C; $[\alpha]_D^{20} = -43.0$ (c 0.50, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 7.98 – 7.89 (m, 2H), 7.87 – 7.80 (m, 1H), 7.70 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.63 – 7.42 (m, 3H), 4.63 (q, *J* = 7.2 Hz, 1H), 1.79 (d, *J* = 7.2 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 134.0, 132.7, 129.8, 129.3, 128.9, 126.9, 126.1, 125.6, 124.7, 122.1, 121.8, 28.2, 20.6. **HRMS** (EI): *m/z*: [M]⁺ Calcd for C₁₃H₁₁N: 181.0891, found 181.0884. HPLC (Daicel Chiralpak OJ-H column, hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min, 254 nm): *t_r* = 31.3 min (major), *t_r* = 36.2 min (minor).

<Chromatogram>

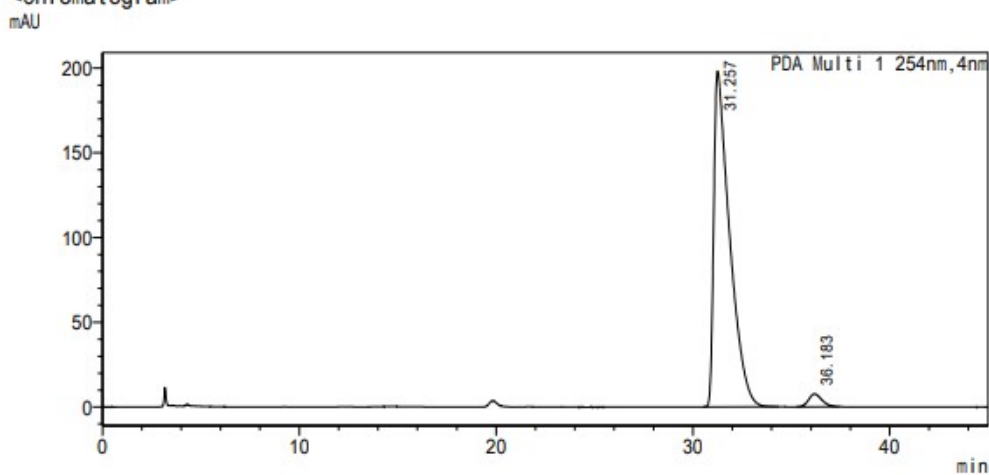


<Peak Table>

PDA Ch1 254nm

No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	32.320	47755	53.190	2151675	49.980
2	36.316	42027	46.810	2153424	50.020
Total		89782	100.000	4305100	100.000

<Chromatogram>

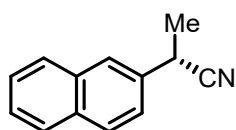


<Peak Table>

PDA Ch1 254nm

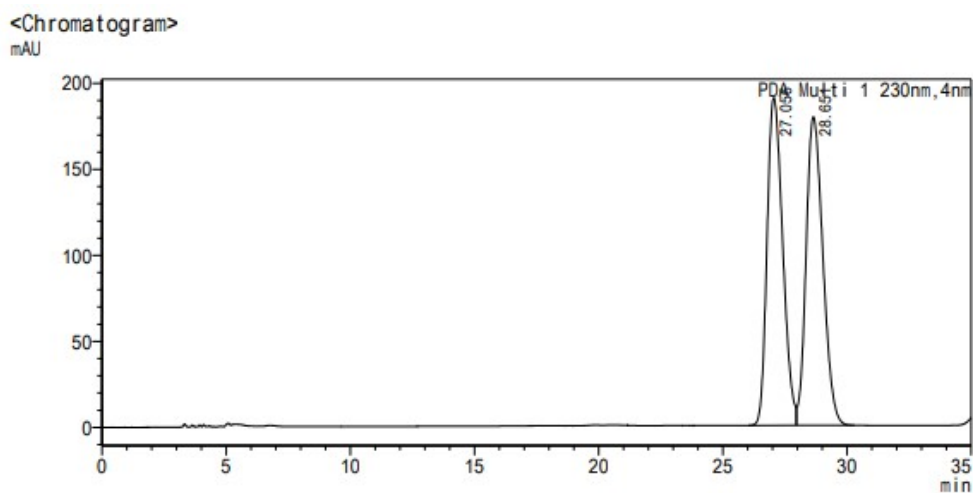
No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	31.257	198022	96.322	11076602	96.907
2	36.183	7561	3.678	353479	3.093
Total		205583	100.000	11430081	100.000

(S)-2-(Naphthalen-2-yl)propanenitrile (2u)



Prepared according to general procedure, constant voltage is 3.0 V, after a flash column chromatography (hexanes: EA = 20:1-10:1) afforded the product **2u** as a white solid

(29.0mg, 80% yield) with 92% ee. m.p. 86-87 °C; $[\alpha]_D^{20} = -24.0$ (c 0.50, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 7.92 – 7.82 (m, 4H), 7.56 – 7.48 (m, 2H), 7.43 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 1H), 1.73 (d, *J* = 7.3 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 134.3, 133.3, 132.8, 129.1, 127.8, 127.7, 126.7, 126.5, 125.6, 124.4, 121.5, 31.4, 21.4. **HRMS** (EI): *m/z*: [M]⁺ Calcd for C₁₃H₁₁N: 181.0891, found 181.0884. HPLC (Daicel Chiralpak IC column, hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min, 230 nm): *t_r* = 27.2 min (minor), *t_r* = 28.7 min (major).

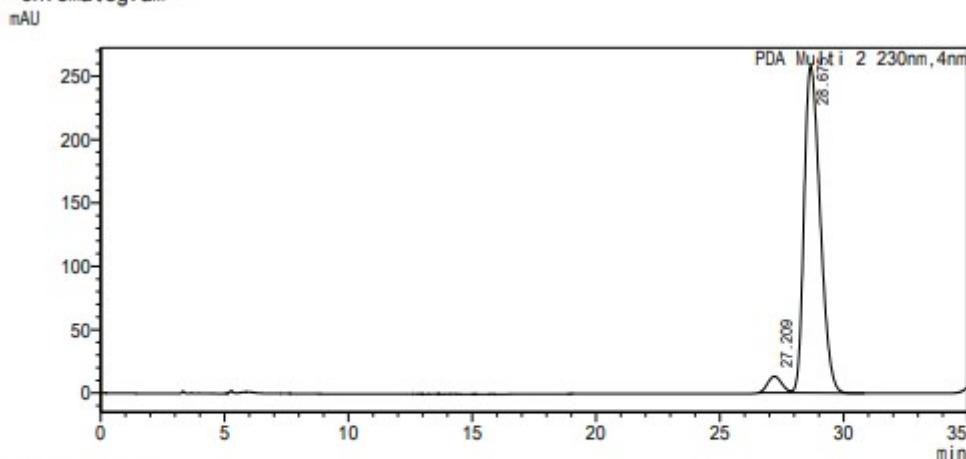


<Peak Table>

PDA Ch1 230nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	27.056	190543	51.529	8336715	49.751
2	28.651	179234	48.471	8420031	50.249
Total		369777	100.000	16756746	100.000

<Chromatogram>

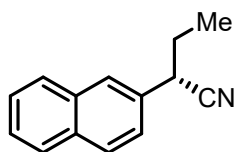


<Peak Table>

PDA Ch2 230nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	27.209	12918	4.772	512070	4.223
2	28.675	257775	95.228	11613371	95.777
Total		270693	100.000	12125441	100.000

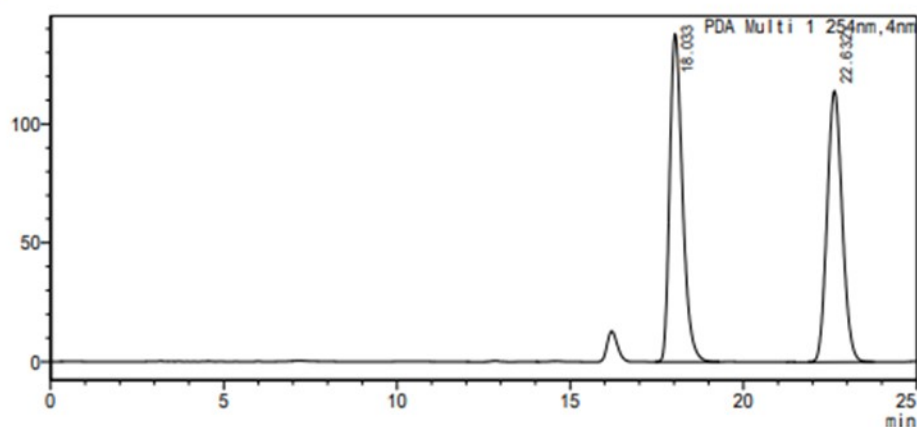
(S)-2-(Naphthalen-2-yl)butanenitrile (2v)



Prepared according to general procedure, constant voltage is 2.3 V, after a flash column chromatography (hexanes: EA = 20:1-10:1) afforded the product **2v** as a white solid (23.8 mg 61% yield) with 90% ee. m.p. 58-59 °C; $[\alpha]_D^{20} = -29.8$ (c 0.52, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 7.88 – 7.82 (m, 4H), 7.55 – 7.49 (m, 2H), 7.40 (dd, $J = 8.5, 1.9$ Hz, 1H), 3.91 (t, $J = 7.1$ Hz, 1H), 2.04 (m, 2H), 1.11 (t, $J = 7.4$ Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 133.3, 133.0, 132.8, 129.0, 127.9, 127.7, 126.7, 126.5, 126.4, 124.8, 39.1, 29.1, 11.5. **HRMS** (EI): m/z : $[M]^+$ Calcd for C₁₄H₁₃N: 195.1048, found 195.1042. HPLC (Daicel Chiralpak AD-H column, hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min, 254 nm): $t_r = 17.9$ min (major), $t_r = 22.2$ min (minor).

<Chromatogram>

mAU



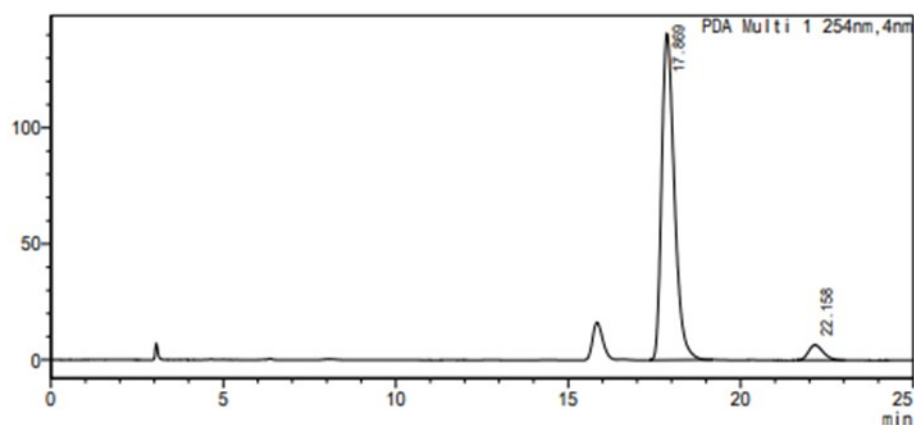
<Peak Table>

PDA Ch1 254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	18.033	137891	54.725	3533826	50.589
2	22.632	114080	45.275	3451576	49.411
Total		251971	100.000	6985401	100.000

<Chromatogram>

mAU

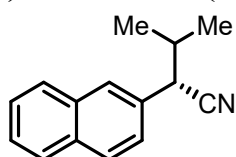


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PDA Ch1 254nm

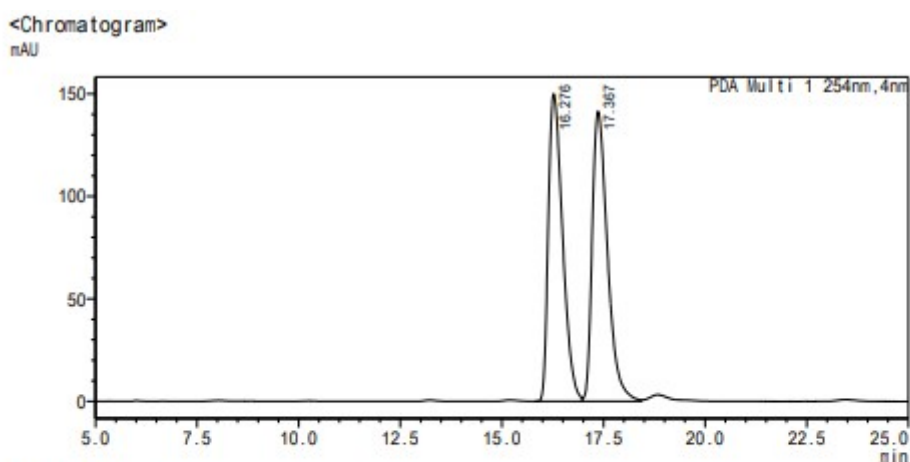
No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	17.869	140570	95.524	3616990	94.865
2	22.158	6586	4.476	195782	5.135
Total		147156	100.000	3812772	100.000

(S)-3-Methyl-2-(naphthalen-2-yl)butanenitrile (2w)



Prepared according to general procedure, constant voltage is 2.3 V, after a flash column chromatography (hexanes: EA = 20:1-10:1) afforded the product **2w** as a yellow

liquid (22.2 mg, 53% yield) with 86% ee; $[\alpha]_D^{20} = -27.3$ (c 0.82, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.89 – 7.83 (m, 3H), 7.81 (d, $J = 1.7$ Hz, 1H), 7.57 – 7.46 (m, 2H), 7.38 (dd, $J = 8.5, 1.9$ Hz, 1H), 3.84 (d, $J = 6.2$ Hz, 1H), 2.24 (m, 2H), 1.11 (d, $J = 6.7$ Hz, 3H), 1.07 (d, $J = 6.7$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 133.1, 132.8, 132.3, 128.7, 127.9, 127.7, 127.0, 126.6, 126.4, 125.3, 119.8, 45.3, 33.7, 20.9, 18.8. **HRMS** (EI): m/z : $[\text{M}]^+$ Calcd for $\text{C}_{15}\text{H}_{15}\text{N}$: 209.1204, found 209.1199. HPLC (Daicel Chiralpak AD-H column, hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min, 254 nm): $t_r = 16.2$ min (major), $t_r = 17.4$ min (minor).



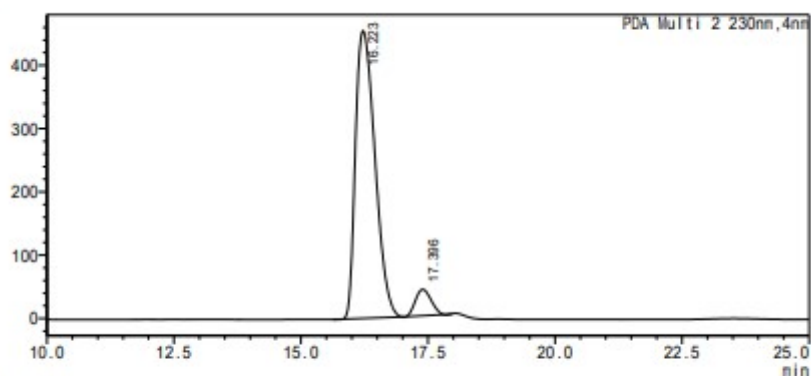
<Peak Table>

PDA Ch1 254nm

No.	Ret. Time(min)	Height (mAU)	Height%	Area(mAU*min)	Area%
1	16.276	149804	51.455	3656269	49.719
2	17.367	141329	48.545	3697554	50.281
Total		291133	100.000	7353823	100.000

<Chromatogram>

nAU

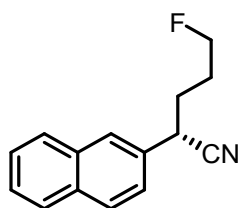


<Peak Table>

PDA Ch2 230nm

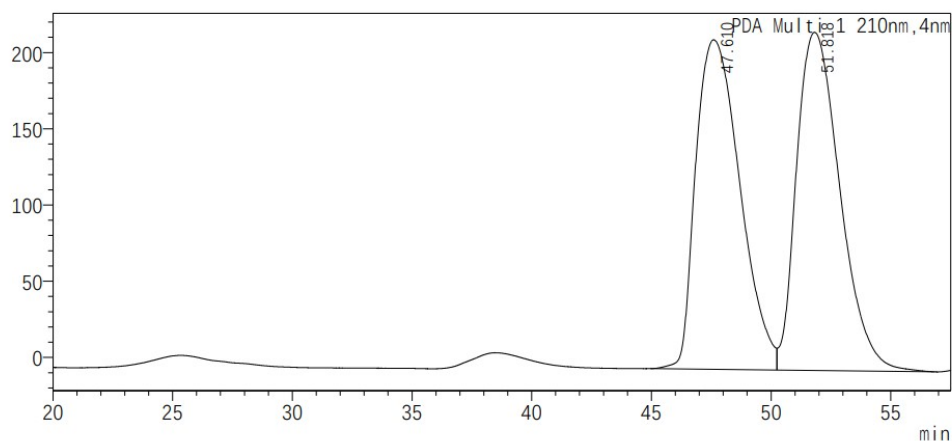
No.	Ret. Time(min)	Height (mAU)	Height%	Area(mAU*min)	Area%
1	16.223	454487	91.603	12159286	93.185
2	17.396	41661	8.397	889268	6.815
Total		496147	100.000	13048554	100.000

(S)-5-Fluoro-2-(naphthalen-2-yl)pentanenitrile (2x)



Prepared according to general procedure, constant voltage is 2.3 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2x** as a yellow liquid (24.5 mg, 54% yield) with 92% ee; $[\alpha]_D^{20} = -32.5$ (c 0.50, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 7.92 – 7.82 (m, 4H), 7.57 – 7.49 (m, 2H), 7.42 (dd, $J = 8.5, 2.0$ Hz, 1H), 4.56 (q, $J = 5.9$ Hz, 1H), 4.44 (q, $J = 6.0$ Hz, 1H), 4.04 (t, $J = 7.3$ Hz, 1H), 2.20 – 2.12 (m, 2H), 1.98 – 1.85 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 133.3, 132.8, 132.6, 129.2, 127.8, 127.7, 126.8, 126.58, 126.4, 124.6, 120.4, 83.0 (d, $^1J_{C-F} = 166.4$ Hz), 37.1, 31.8 (d, $^3J_{C-F} = 4.4$ Hz), 27.8 (d, $^2J_{C-F} = 20.3$ Hz). **HRMS** (EI): m/z: [M]⁺ Calcd for C₁₅H₁₄FN: 227.1110, found 227.1106. HPLC (Daicel Chiralpak AD-H column, hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min, 210 nm): $t_r = 45.9$ min (major), $t_R = 50.7$ min (minor).

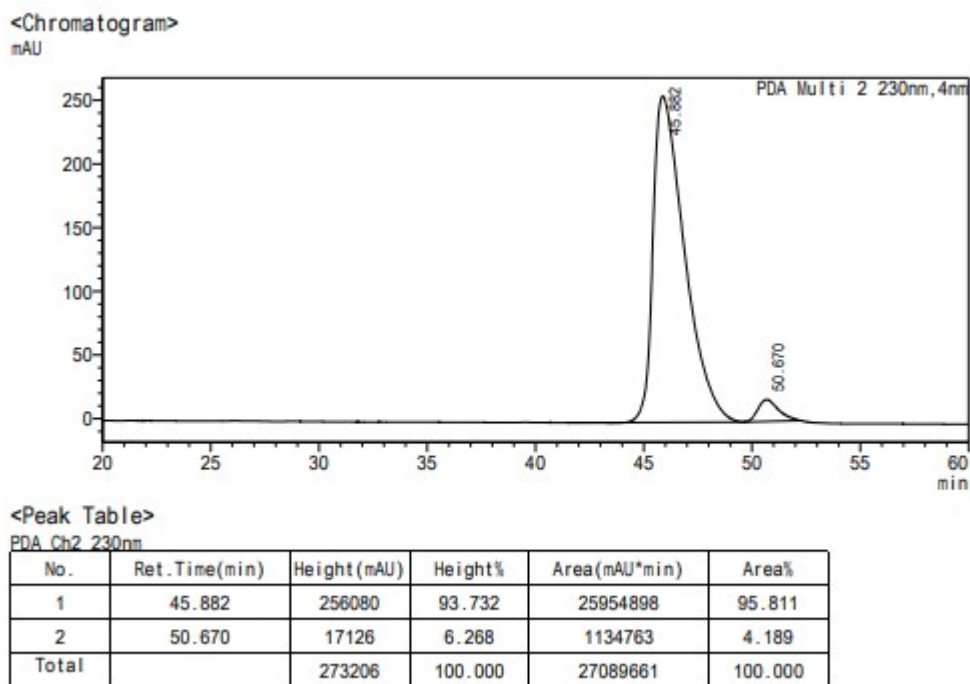
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mAU



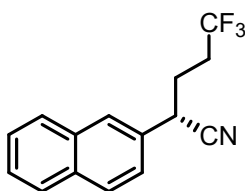
<Peak Table>

PDA Ch1 210nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	47.610	216170	49.357	27792674	49.807
2	51.818	221802	50.643	28007972	50.193
Total		437972	100.000	55800646	100.000

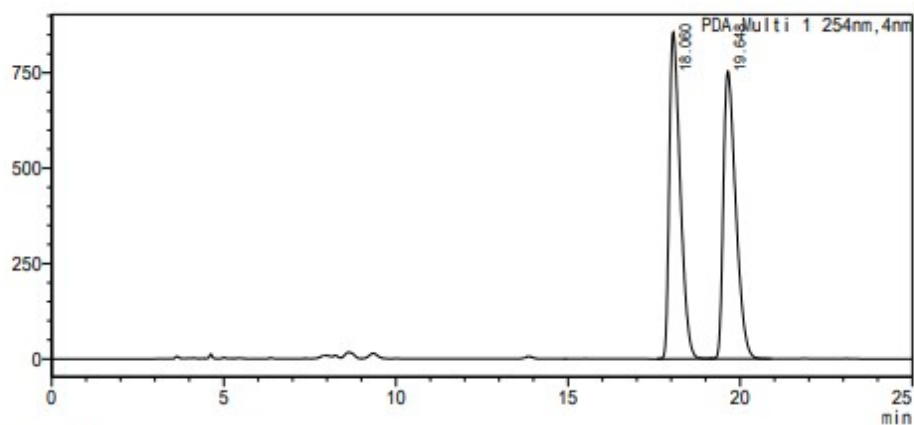


(S)-5,5,5-Trifluoro-2-(naphthalen-2-yl)pentanenitrile (2y)



Prepared according to general procedure, constant voltage is 2.3 V, after a flash column chromatography (hexanes: EA = 20:1-10:1) afforded the product **2y** as a white solid (31.6 mg, 60% yield) with 93% ee. m.p. 55-56 °C; $[\alpha]_D^{20} = -21.6$ (c 0.50, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 7.95 – 7.80 (m, 4H), 7.60 – 7.50 (m, 2H), 7.40 (dd, $J = 8.5, 1.9$ Hz, 1H), 4.13 – 4.04 (m, 1H), 2.37 – 2.20 (m, 4H). **¹³C NMR** (101 MHz, CDCl₃) δ 133.3, 133.0, 131.3, 129.6, 127.9, 127.8, 127.0, 126.9, 126.5, 126.4 (q, $^1J_{C-F} = 276.3$ Hz), 124.2, 119.5, 53.4, 36.3, 31.1 (q, $^2J_{C-F} = 29.8$ Hz), 28.1 (q, $^3J_{C-F} = 3.3$ Hz). **¹⁹F NMR** (376 MHz, CDCl₃) δ -65.70. **HRMS** (EI): m/z: [M]⁺ Calcd for C₁₅H₁₂F₃N: 263.0922, found 263.0917. HPLC (Daicel Chiralpak OZ-3 column, hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min, 254 nm): $t_r = 18.2$ min (major), $t_r = 20.0$ min (minor).

<Chromatogram>
mAU

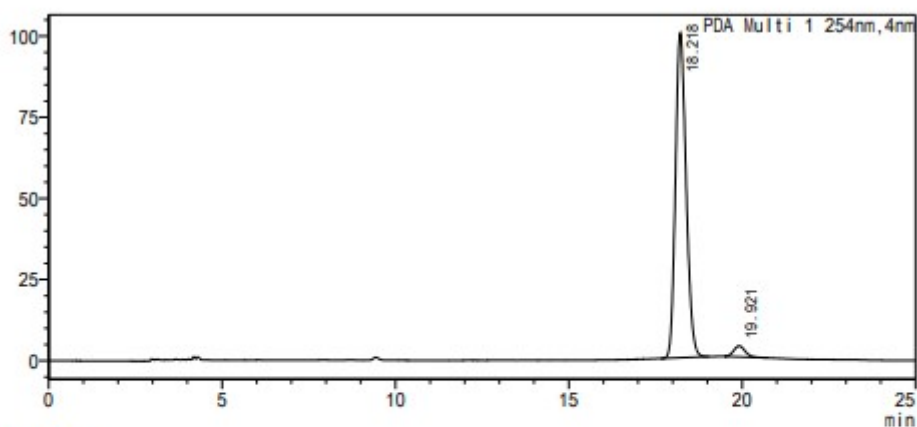


<Peak Table>

PDA Ch1 254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	18.060	855441	53.129	18894507	49.965
2	19.648	754678	46.871	18920696	50.035
Total		1610118	100.000	37815203	100.000

<Chromatogram>
mAU

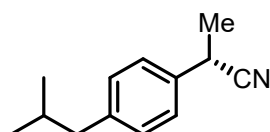


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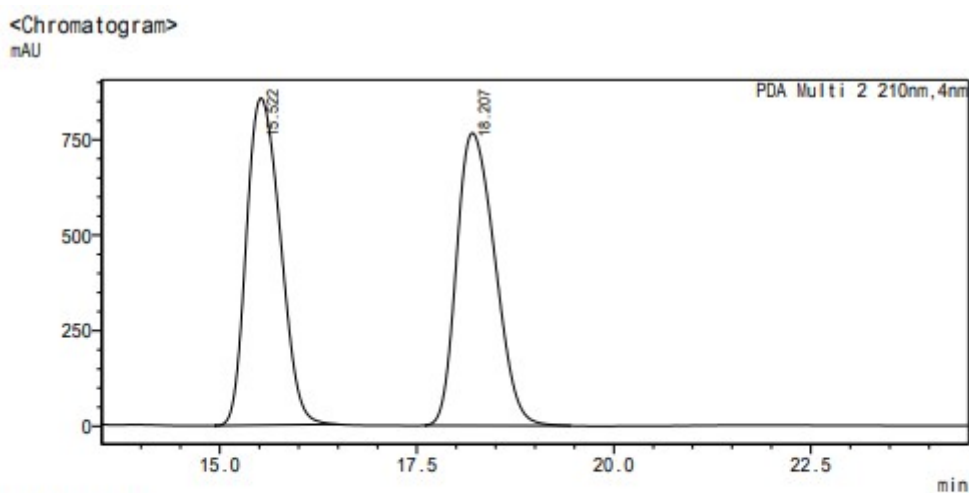
PDA Ch1 254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	18.218	99956	96.731	2136214	96.449
2	19.921	3378	3.269	78651	3.551
Total		103334	100.000	2214865	100.000

(S)-2-(4-sobutylphenyl)propanenitrile (2z)



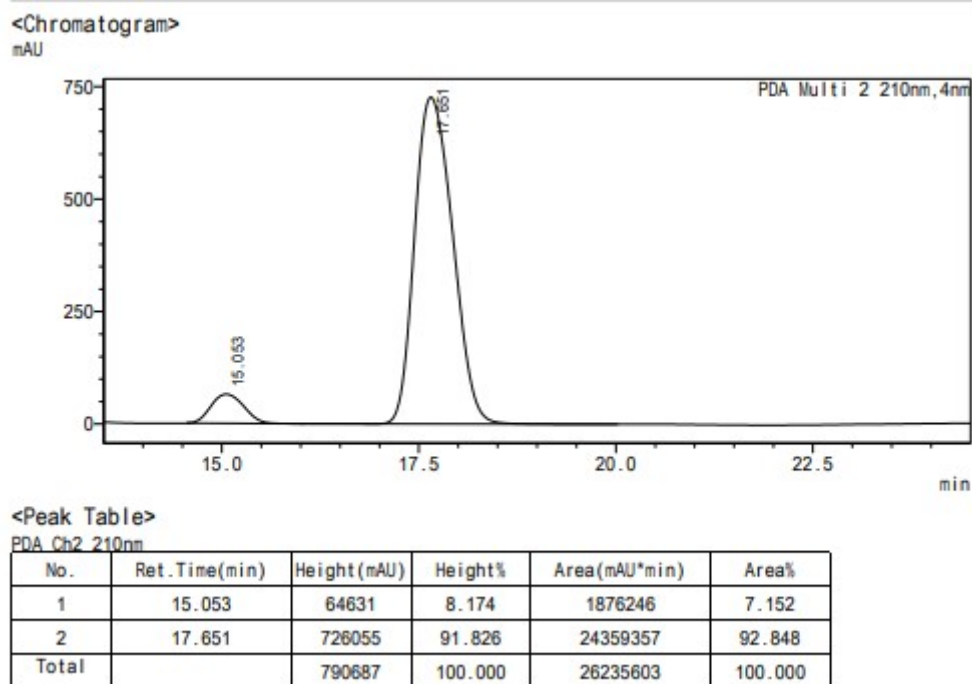
Prepared according to general procedure, constant voltage is 3.0 V, after a flash column chromatography (hexanes: EA = 20:1-10:1) afforded the product **2z** as a yellow liquid (24.3 mg, 86% yield) with 86% ee; $[\alpha]_D^{20} = -13.6$ (c 0.52, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.28 – 7.23 (m, 2H), 7.18 – 7.13 (m, 2H), 3.87 (q, *J* = 7.3 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.92 – 1.81 (m, 1H), 1.63 (d, *J* = 7.3 Hz, 3H), 0.91 (s, 3H), 0.89 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 141.6, 134.3, 129.8, 126.4, 121.8, 44.9, 30.9, 30.1, 22.3, 21.4. HRMS (EI): *m/z*: [M]⁺ Calcd for C₁₃H₁₇N: 187.1361, found 187.1357. HPLC (Daicel Chiralpak OJ-H column, hexane/isopropanol = 99.5/0.5, flow rate 1.0 mL/min, 210 nm): *t_r* = 15.1 min (minor), *t_R* = 17.7 min (major).



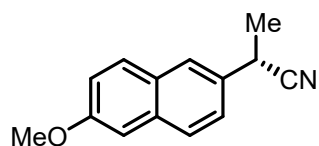
<Peak Table>

PDA_Ch2_210nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	15.522	855901	52.782	25628097	49.783
2	18.207	765677	47.218	25851391	50.217
Total		1621577	100.000	51479488	100.000



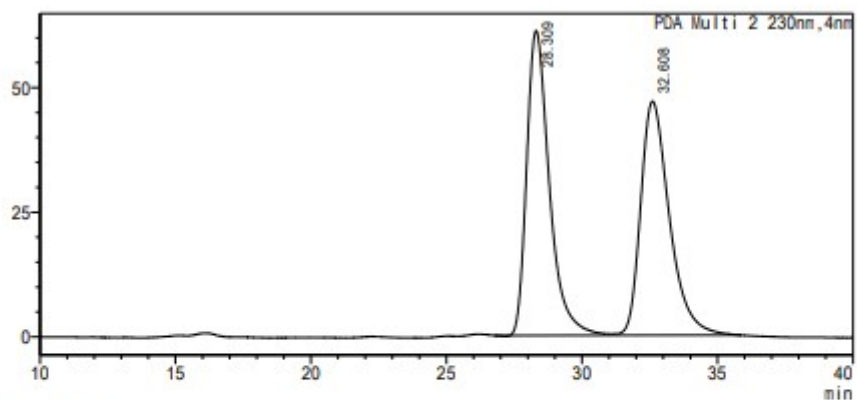
(S)-2-(6-Methoxynaphthalen-2-yl)propanenitrile (2aa)



Prepared according to general procedure, constant voltage is 3.0 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2aa** as a white solid (27.4 mg, 65% yield) with 91 er. m.p. 84.3-84.6 °C; $[\alpha]_D^{20} = -31.6$ (c 0.47, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 7.80 – 7.70 (m, 3H), 7.39 (dd, $J = 8.3, 2.1$ Hz, 1H), 7.19 (dd, $J = 8.9, 2.5$ Hz, 1H), 7.14 (d, $J = 2.7$ Hz, 1H), 4.03 (q, $J = 7.2$ Hz, 1H), 3.93 (s, 3H), 1.71 (d, $J = 7.2$ Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 158.1, 134.0, 132.0, 129.3, 128.8, 127.9, 125.4, 124.9, 121.7, 119.6, 105.7, 55.3, 31.2, 21.4. **HRMS** (EI): m/z: [M]⁺ Calcd for C₁₄H₁₃NO: 211.0997, found 211.0991. HPLC (Daicel Chiralpak AS-H column, hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 230 nm): $t_r = 28.0$ min (major), $t_r = 32.5$ min (minor).

<Chromatogram>

mAU



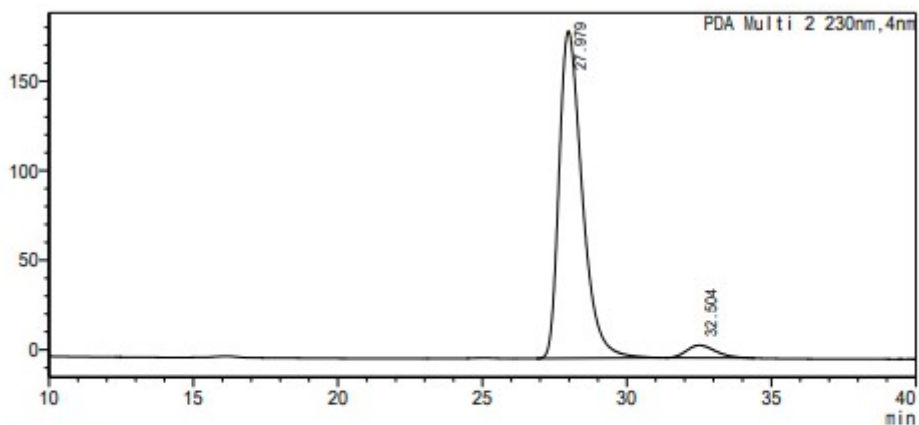
<Peak Table>

PDA Ch2 230nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	28.309	61130	56.576	3556099	50.587
2	32.608	46919	43.424	3473610	49.413
Total		108049	100.000	7029709	100.000

<Chromatogram>

mAU

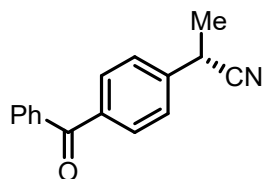


<Peak Table>

PDA Ch2 230nm

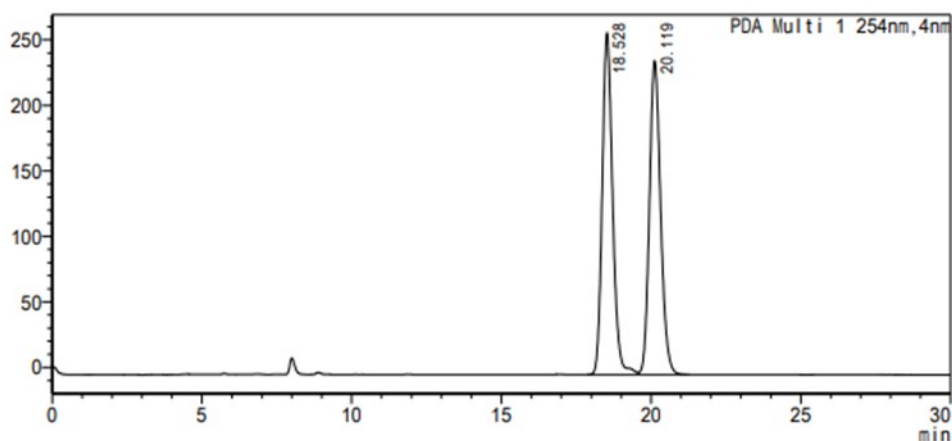
No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	27.979	182518	96.281	10159323	95.344
2	32.504	7050	3.719	496093	4.656
Total		189567	100.000	10655416	100.000

(S)-2-(4-Benzoylphenyl)propanenitrile (2ab)



Prepared according to general procedure, constant voltage is 2.3 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2ab** as a white solid (33.4 mg, 71% yield) with 85% ee. m.p. 54-55 °C; $[\alpha]_D^{20} = -12.1$ (c 0.50, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.76 (m, 3H), 7.76 – 7.70 (m, 1H), 7.66 – 7.56 (m, 2H), 7.51 (q, *J* = 7.3 Hz, 3H), 3.98 (q, *J* = 7.2 Hz, 1H), 1.68 (d, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 195.9, 138.5, 137.5, 137.1, 132.7, 130.5, 130.0, 129.8, 129.1, 128.4, 128.1, 121.0, 31.1, 21.3. HRMS (EI): *m/z*: [M]⁺ Calcd for C₁₈H₁₃NO: 235.0997, found 235.0992. HPLC (Daicel Chiralpak IG column, hexane/isopropanol = 80/20, flow rate 0.7 mL/min, 254 nm): *t_r* = 21.6 min (minor), *t_r* = 23.5 min (major).

<Chromatogram>
mAU

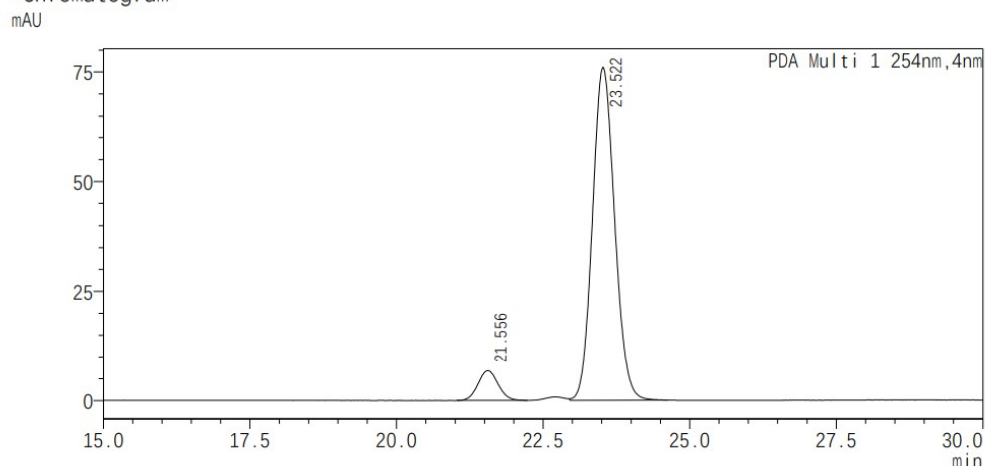


<Peak Table>

PDA Ch1 254nm

No.	Ret. Time(min)	Height (mAU)	Height%	Area(mAU*min)	Area%
1	18.528	260152	52.055	6296753	50.361
2	20.119	239611	47.945	6206572	49.639
Total		499763	100.000	12503325	100.000

<Chromatogram>

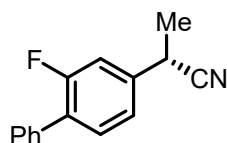


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PDA Ch1 254nm

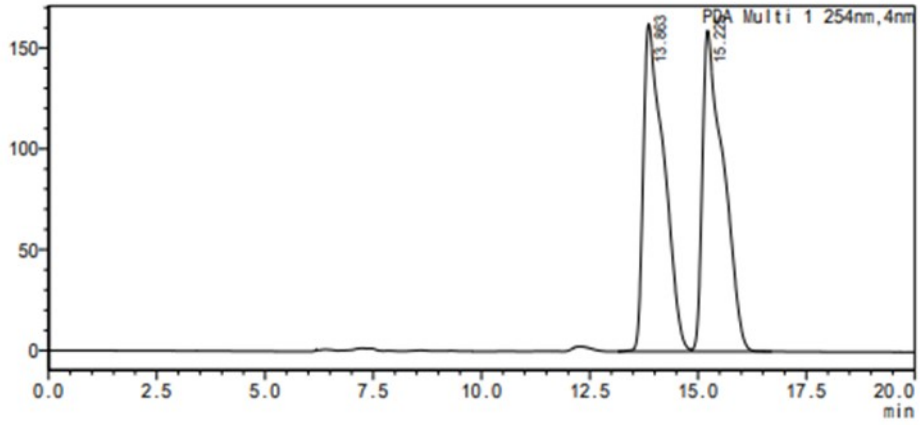
No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	21.556	6843	8.260	162917	7.538
2	23.522	75998	91.740	1998369	92.462
Total		82841	100.000	2161287	100.000

(S)-2-(2-Fluoro-[1,1'-biphenyl]-4-yl)propanenitrile (**2ac**)



Prepared according to general procedure, constant voltage is 2.3 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2ac** as a yellow liquid (27.5 mg, 64% yield) with 90% ee; $[\alpha]_{\text{D}}^{20} = -9.4$ (c 0.58, CHCl_3); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.54 (dd, $J = 6.8, 1.6$ Hz, 2H), 7.51 – 7.43 (m, 3H), 7.42 – 7.36 (m, 1H), 7.25 – 7.13 (m, 2H), 3.94 (q, $J = 7.3$ Hz, 1H), 1.69 (d, $J = 7.3$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 159.8 (d, $^1J_{\text{C-F}} = 248.1$ Hz), 138.1 (d, $^3J_{\text{C-F}} = 7.6$ Hz), 134.9, 131.5 (d, $^4J_{\text{C-F}} = 3.8$ Hz), 129.0 (d, $^4J_{\text{C-F}} = 2.9$ Hz), 128.9, 128.5, 128.0, 122.7 (d, $^4J_{\text{C-F}} = 3.5$ Hz), 121.0, 114.8 (d, $^2J_{\text{C-F}} = 24.3$ Hz), 30.7, 21.2. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -116.23. **HRMS** (EI): m/z : $[\text{M}]^+$ Calcd for $\text{C}_{15}\text{H}_{12}\text{FN}$: 225.0954, found 225.0949. HPLC (Daicel Chiralpak AS-H column, hexane/isopropanol = 90/10, flow rate 0.5 mL/min, 254 nm): $t_{\text{r}} = 13.8$ min (minor), $t_{\text{r}} = 15.1$ min (major).

<Chromatogram>
mAU



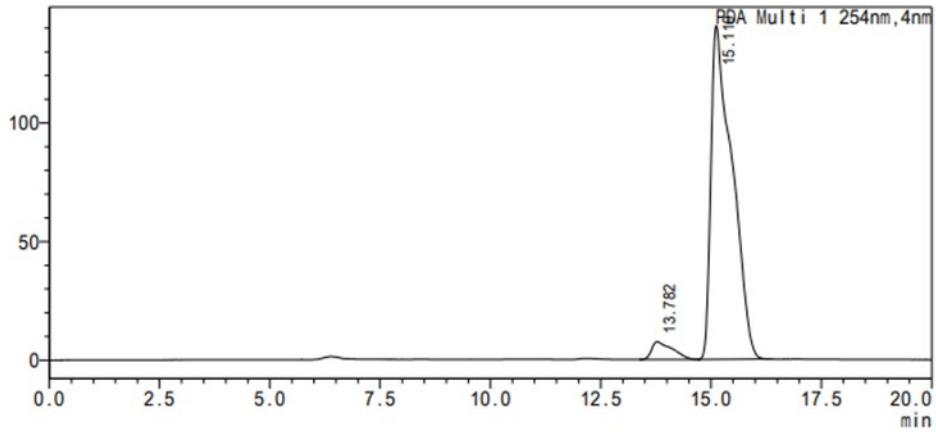
<Peak Table>

PDA Ch1 254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	13.863	162191	50.488	5361499	49.992
2	15.225	159057	49.512	5363136	50.008
Total		321248	100.000	10724634	100.000

<Chromatogram>

mAU

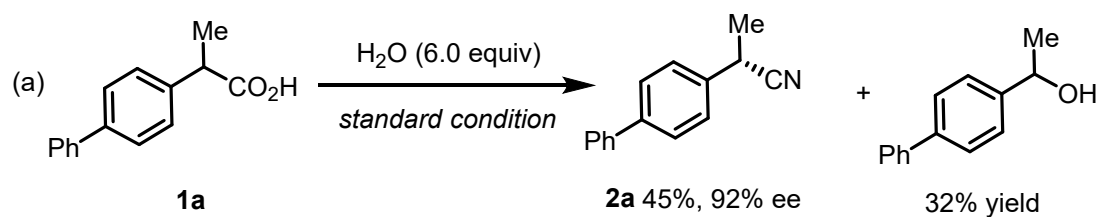


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PDA Ch1 254nm

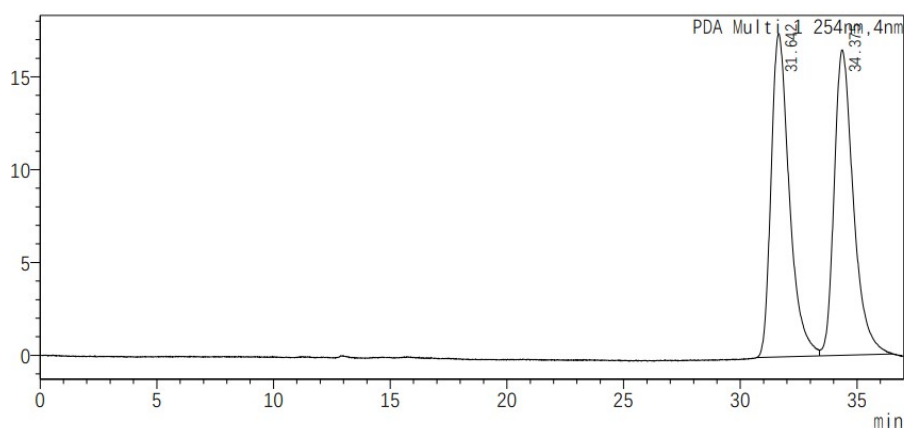
No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	13.782	7505	5.067	243356	4.918
2	15.119	140624	94.933	4704590	95.082
Total		148129	100.000	4947947	100.000

4. Mechanistic studies



Prepared according to general procedure, but adding 6 equivalents of water, constant voltage is 2.3 V, after a flash column chromatograph (hexanes: EA = 20:1-10:1) afforded the product **2a** and the product 1-(4-biphenyl)ethanol as a white solid. ^1H NMR (400 MHz, CDCl_3) δ 7.60 (dd, $J = 13.1, 8.2$ Hz, 4H), 7.49 – 7.40 (m, 4H), 7.37 (t, $J = 7.3$ Hz, 1H), 3.95 (q, $J = 7.3$ Hz, 1H), 1.69 (d, $J = 7.3$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.1, 140.3, 136.0, 128.9, 127.8, 127.6, 127.1, 127.1, 121.5, 30.9, 21.4. HRMS (EI): m/z : $[\text{M}]^+$ Calcd for $\text{C}_{14}\text{H}_{14}\text{O}$: 198.1045, found 198.1036.

<Chromatogram>
mAU

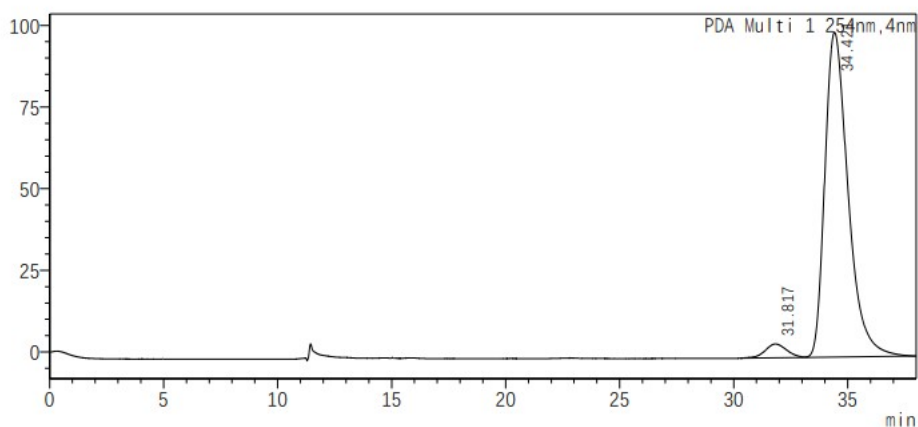


<Peak Table>

PDA_Ch1_254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	31.642	17414	51.425	946432	50.030
2	34.375	16449	48.575	945283	49.970
Total		33863	100.000	1891716	100.000

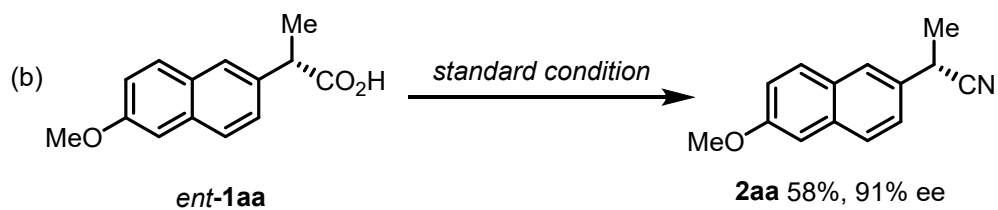
<Chromatogram>
mAU



<Peak Table>

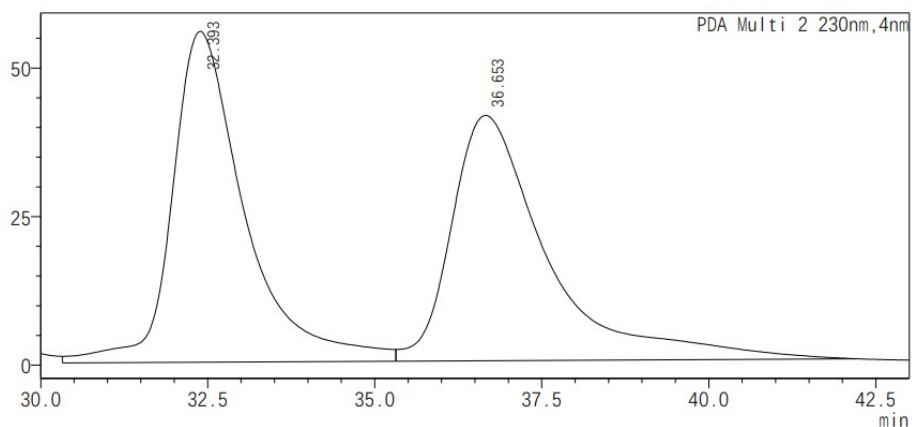
PDA Ch1 254nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	31.817	4219	4.071	275260	3.759
2	34.421	99431	95.929	7048239	96.241
Total		103650	100.000	7323499	100.000



Prepared according to general procedure, the reaction of ent-1aa (0.2 mmol) gave 2aa (24.5mg, 58% yield, 91% ee) as a white solid. HPLC (Daicel Chiralpak AS-H column, hexane/isopropanol = 99/1, flow rate 0.5 mL/min, 230 nm): t_r = 32.3 min (major), t_r = 36.8 min (minor).

<Chromatogram>
mAU



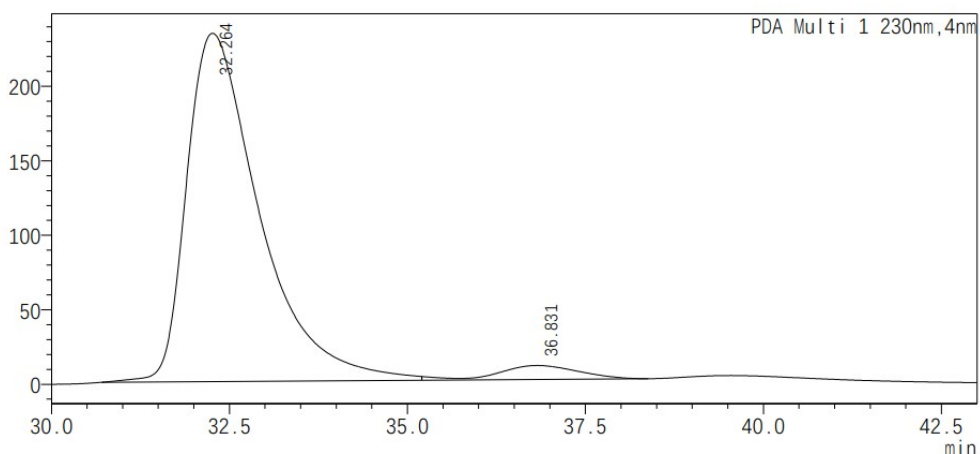
<Peak Table>

PDA Ch2 230nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	32.393	55677	57.433	4213843	50.492
2	36.653	41265	42.567	4131720	49.508
Total		96942	100.000	8345564	100.000

<Chromatogram>

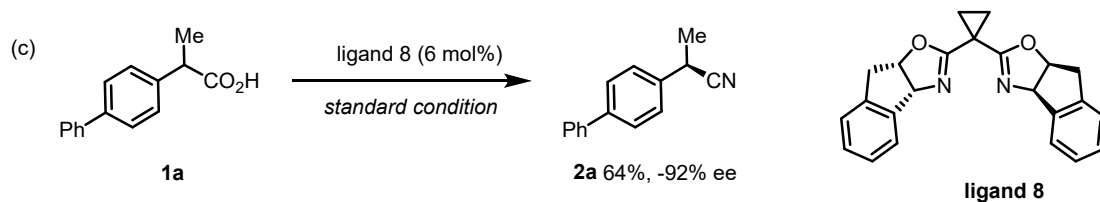
mAU



<Peak Table>

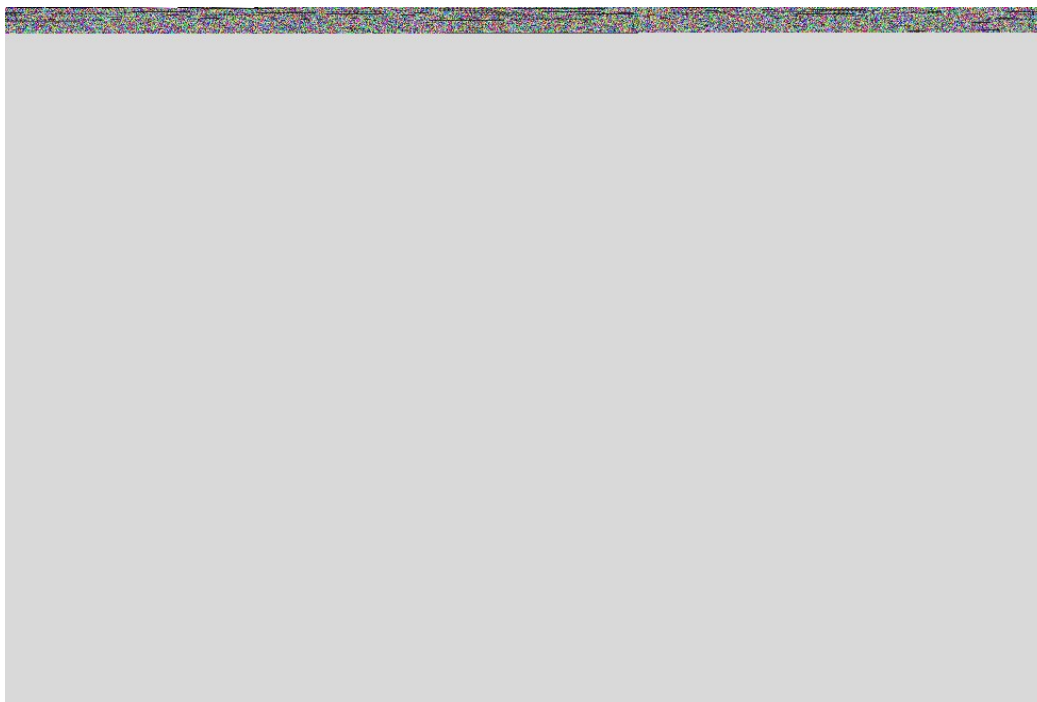
PDA Ch1 230nm

No.	Ret. Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	32.264	233721	96.136	16610732	95.702
2	36.831	9393	3.864	745946	4.298
Total		243114	100.000	17356677	100.000

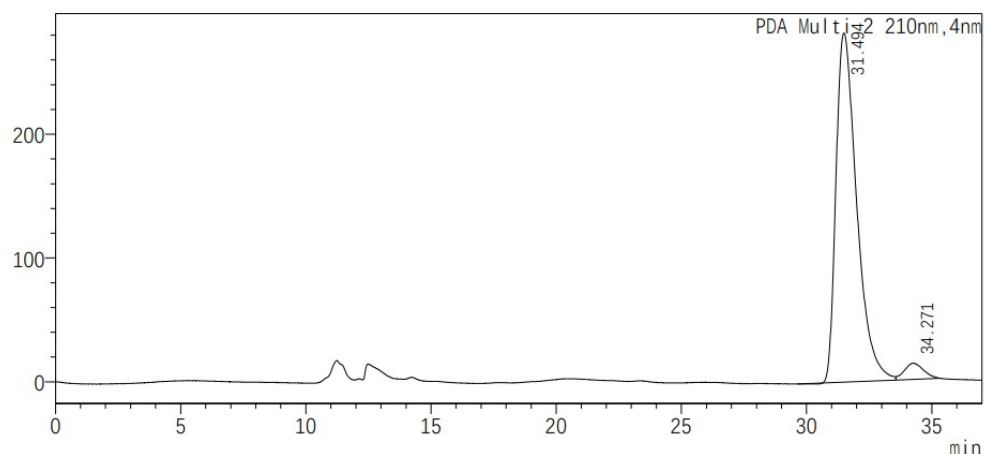


Prepared according to general procedure, the reaction of **1a** (0.2 mmol) with **ligand 8** gave (*R*)-**2a** (26.5 mg, 64% yield, -92% ee) as a white solid. m.p. 79.2-79.4 °C; $[\alpha]_D^{20}$

= 13 (c 0.50, CHCl₃); **¹H NMR** (400 MHz, CDCl₃) δ 7.60 (dd, *J* = 13.1, 8.2 Hz, 4H), 7.49 – 7.40 (m, 4H), 7.37 (t, *J* = 7.3 Hz, 1H), 3.95 (q, *J* = 7.3 Hz, 1H), 1.69 (d, *J* = 7.3 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 141.1, 140.3, 136.0, 128.9, 127.8, 127.6, 127.1, 127.1, 121.5, 30.9, 21.4. **HRMS** (EI): *m/z*: [M]⁺ Calcd for C₁₅H₁₃N: 207.1048, found 207.1046. HPLC (Daicel Chiralpak AS-H column, hexane/isopropanol = 99/1, flow rate 0.3 mL/min, 254 nm): *t_r* = 31.5 (major), *t_r* = 34.3 min (minor).



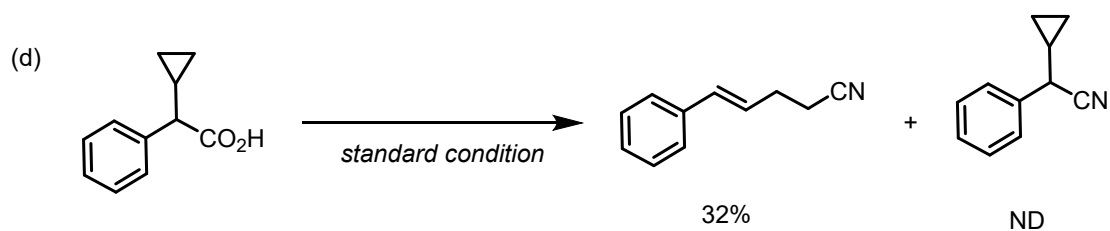
<Chromatogram>
mAU



<Peak Table>

PDA Ch2 210nm

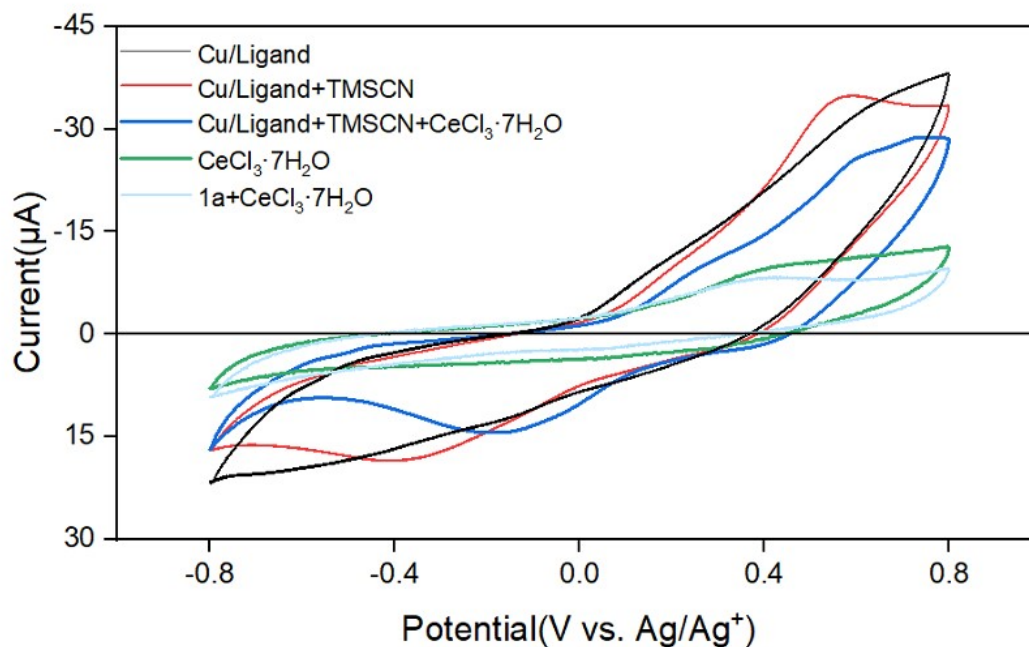
No.	Ret.Time(min)	Height(mAU)	Height%	Area(mAU*min)	Area%
1	31.494	281838	95.591	16212464	95.925
2	34.271	13000	4.409	688721	4.075
Total		294838	100.000	16901185	100.000



Prepared according to general procedure, the reaction of 2-cyclopropyl-2-phenylacetic acid (0.2 mmol) gave ring opening product (E)-5-phenylpent-4-enitrile (10.0 mg, 32% yield) as light yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 – 7.28 (m, 4H), 7.28 – 7.21 (m, 1H), 6.53 (d, $J = 16.0$ Hz, 1H), 6.19 (dt, $J = 16.0, 6.8$ Hz, 1H), 2.63 – 2.46 (m, 4H).

(e) Cyclic voltammetry

The cyclic voltammograms were recorded in a solution of 0.1 M $^n\text{Bu}_4\text{NPF}_6$ CH_3CN solution using a graphite carbon rod working electrode, a platinum sheet auxiliary electrode and a Ag/AgCl reference electrode. The scan rate was 0.1 V/s. Cyclic voltammetry curves of Cu (1.0 mM), Ligand (1.2 mM), TMSCN (4.0 mM), $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (1.0 mM), 1a (2.0 mM) in 0.1 M $^n\text{Bu}_4\text{NPF}_6$ CH_3CN solution.



5. DFT Calculations

All the density functional theory (DFT) calculations were performed using Gaussian 09 program.² Geometry optimizations were performed with the M06-L functional³ using a combined basis set (SDD effective core potential⁴ for copper and 6-31G(d) basis⁵ for the other atoms). Harmonic frequency calculations were performed for each stationary point to ensure that it is either an energy minimum (no imaginary frequency) or a transition state (only one imaginary frequency). For each transition state, intrinsic reaction coordinate (IRC) analysis was performed to ensure that it connects the correct reactant and product. The single-point energy calculations were further performed with the M06-L functional and a combined basis set (SDD effective core potential for copper and the 6-311++G(2df,2p) basis set⁶ for all other atoms), using a self-consistent reaction field (SCRF) method called IEFPCM⁷ in order to obtain energies in solution. The single-point energies corrected by the thermal correction to Gibbs free energies (TCG, obtained from frequency calculations) were used as the Gibbs free energies reported in this work, corresponding to the reference state of 1 mol/L, 298.15 K. The independent gradient model (IGM) was conducted with Multiwfn and VMD.⁸ The 3-D images of the calculated structures were prepared using CYLview.⁹

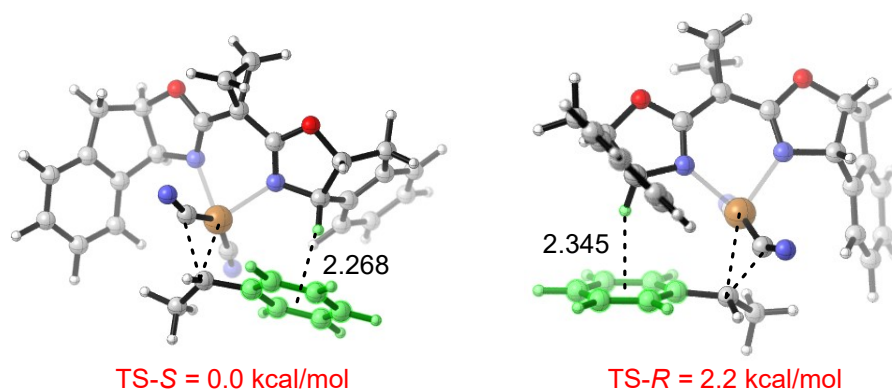


Figure S1. Optimized structures and IGM analysis of the transition states TS-S and TS-R for forming (*S*)-**2i** and (*R*)-**2i**.

We have conducted DFT calculations on the C-C reductive elimination to understand the role of the ligand **L5** on enantioselectivity. The calculation is performed at the M06-L/SDD-6-311+G*// M06-L /SDD-6-31G* level of theory. The solvent effect (acetonitrile) was also taken into account by using IEFPCM method. Reductive

elimination from the Cu(III) intermediate could deliver the cyanation product with the transition state (**TS-S** and **TS-R**) at 0 and 2.2 kcal/mol respectively. the IGM analysis showed that C-H $\cdots\pi$ interaction between the benzylic proton of the ligand and the aryl group of the substrate play a significant role on lowering the energy of the transition state.

Table S6. Energy data (hartrees).

Geometry	$E_{M06-L/6-31G(d)}$	TCG	$E_{M06-L/6-311+G(d,p)}$	$TCG+E_{M06-L/6-311+G(d,p)}$	TCG+ $G_{(corr-B3-LYP)}$	Imaginary Frequency
TS-S	-1841.113473	0.482642	-1842.00581108		0	
TS-R	-1841.109622	0.483395	-1842.00310556		2.2	

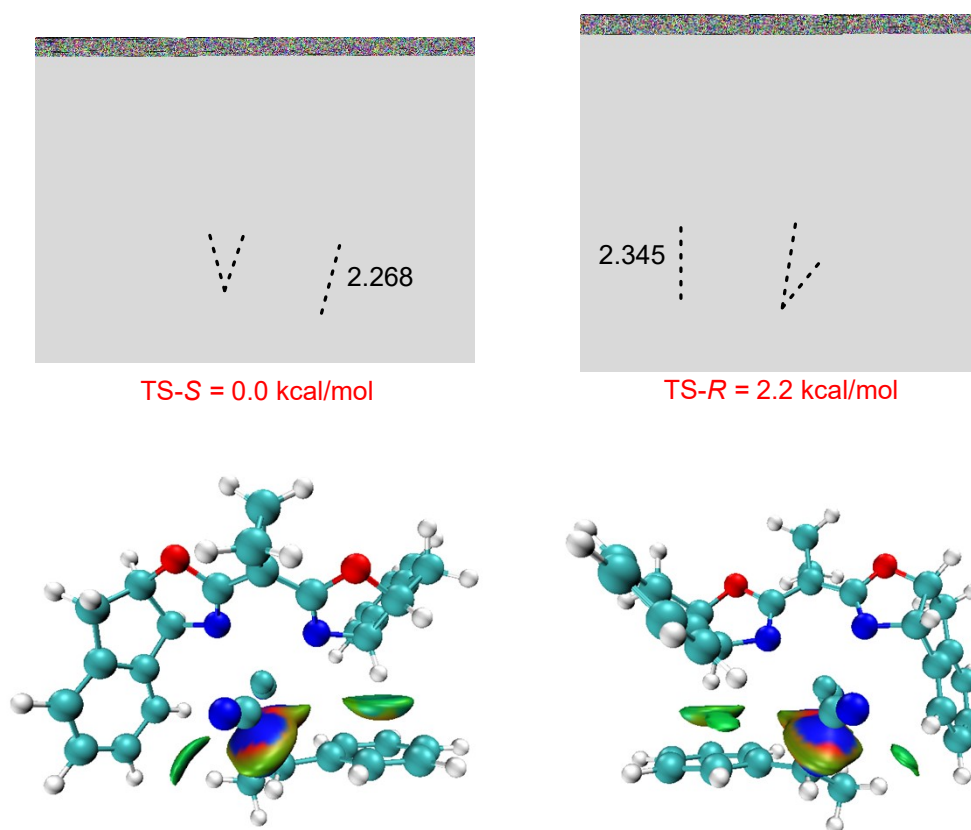


Figure S2. Optimized structures and IGM analysis of the transition states **TS-S** and **TS-R** for forming (*S*)-**2i** and (*R*)-**2i**. For IGM analysis, blue, attraction; green, weak interaction; red, steric effect.

TS-S

O	1.94125100	-2.35099500	-1.54699500
O	-2.42858300	-3.05785700	0.08189400
N	1.11465700	-0.61483500	-0.36747400
N	-1.52522400	-1.08642400	0.68482400
C	2.54864800	-0.32616000	-0.54411200
H	2.66383300	0.69486600	-0.91784400
C	3.35256000	-0.57312000	0.70399500
C	3.21404000	0.04143000	1.94515500
H	2.44845900	0.80182300	2.10275600
C	4.05967400	-0.34782300	2.98224100
H	3.96432500	0.11666700	3.96209800
C	5.02908800	-1.33219400	2.77277200
H	5.68301100	-1.62733200	3.59164000
C	5.16687500	-1.94122000	1.52593200
H	5.92509800	-2.70751100	1.36889400
C	4.32067300	-1.55703100	0.48832700
C	4.29975400	-2.03996800	-0.93564900
H	4.26976900	-3.13200900	-1.03133500
H	5.19032400	-1.70693100	-1.48538900
C	3.04868200	-1.39932100	-1.53099500
H	3.17224100	-1.05406200	-2.56230800
C	0.91031700	-1.76517700	-0.90573000
C	-0.33347400	-2.55494500	-0.91216900
C	-0.20007900	-4.04925500	-1.20862700
H	0.81634800	-4.41242100	-1.31539200
H	-0.87972300	-4.69217800	-0.65938800
C	-0.74973800	-3.17403800	-2.25494500
H	-1.81874400	-3.18881000	-2.44817100
H	-0.12281800	-2.90977600	-3.10156800

C	-2.80246200	-1.14846900	1.42132900
H	-2.57787200	-1.14314000	2.49589600
C	-3.75835900	-0.06292400	1.01764100
C	-3.67533800	1.29811800	1.29692300
H	-2.85868500	1.68880900	1.90617700
C	-4.64967900	2.14990700	0.77634300
H	-4.60609200	3.21706300	0.98909100
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H	-6.43942100	2.31545900	-0.41019900
C	-5.76852000	0.27453300	-0.27818400
H	-6.58371600	-0.11727700	-0.88537000
C	-4.79773200	-0.57814200	0.24142300
C	-4.69141500	-2.06925000	0.08936500
H	-4.55421600	-2.37371700	-0.95691100
H	-5.59132800	-2.58654100	0.44426700
C	-3.45798000	-2.45534100	0.91617900
H	-3.67244300	-3.18425400	1.69991400
C	-1.42704400	-2.16325700	-0.00906800
Cu	-0.48511400	0.72860500	0.30376200
C	-0.14269000	1.41786200	2.10826500
N	0.00355000	1.83852400	3.19845200
C	-1.30572400	0.94173700	-1.40450800
N	-1.90323600	0.54837800	-2.34405000
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H	-0.90601400	2.93106900	-2.00522100
C	0.98732300	2.82443100	-1.08247100
C	1.79223000	3.13858600	0.02633900
C	1.60517400	2.62842500	-2.33036700
C	3.16768800	3.26904500	-0.11778500
H	1.33517000	3.27034800	1.00549800

C	2.98231500	2.75603100	-2.47096900
H	0.98818800	2.38074800	-3.19420100
C	3.76811100	3.07987100	-1.36453300
H	3.77737300	3.51809400	0.74844600
H	3.44314400	2.60670800	-3.44513400
H	4.84605000	3.18115200	-1.47137100
C	-1.23543600	3.60687400	-0.00685700
H	-1.18564700	4.65744500	-0.33202400
H	-2.29204200	3.32330600	0.01159700
H	-0.84014800	3.53822100	1.00872500

TS-R

O	1.92361700	-2.42723800	-1.49143300
O	-2.41196900	-3.09423100	0.24726500
N	1.09632900	-0.64841200	-0.37520700
N	-1.54417300	-1.06250900	0.68797500
C	2.52111400	-0.35380600	-0.60300300
H	2.62105000	0.66047000	-1.00443600
C	3.35728900	-0.58432500	0.62934900
C	3.21195300	-0.00557200	1.88671800
H	2.41432300	0.71223200	2.07733700
C	4.08558300	-0.38210600	2.90484800
H	3.98430700	0.05771000	3.89530400
C	5.08678300	-1.32619900	2.66358500
H	5.76194400	-1.61351500	3.46784300
C	5.22262800	-1.91193800	1.40554100
H	5.99749000	-2.65640100	1.22635500
C	4.34903900	-1.53855000	0.38716200
C	4.30314300	-2.01981000	-1.03640800
H	4.32942900	-3.11156800	-1.13476900
H	5.15147600	-1.63647100	-1.61954300

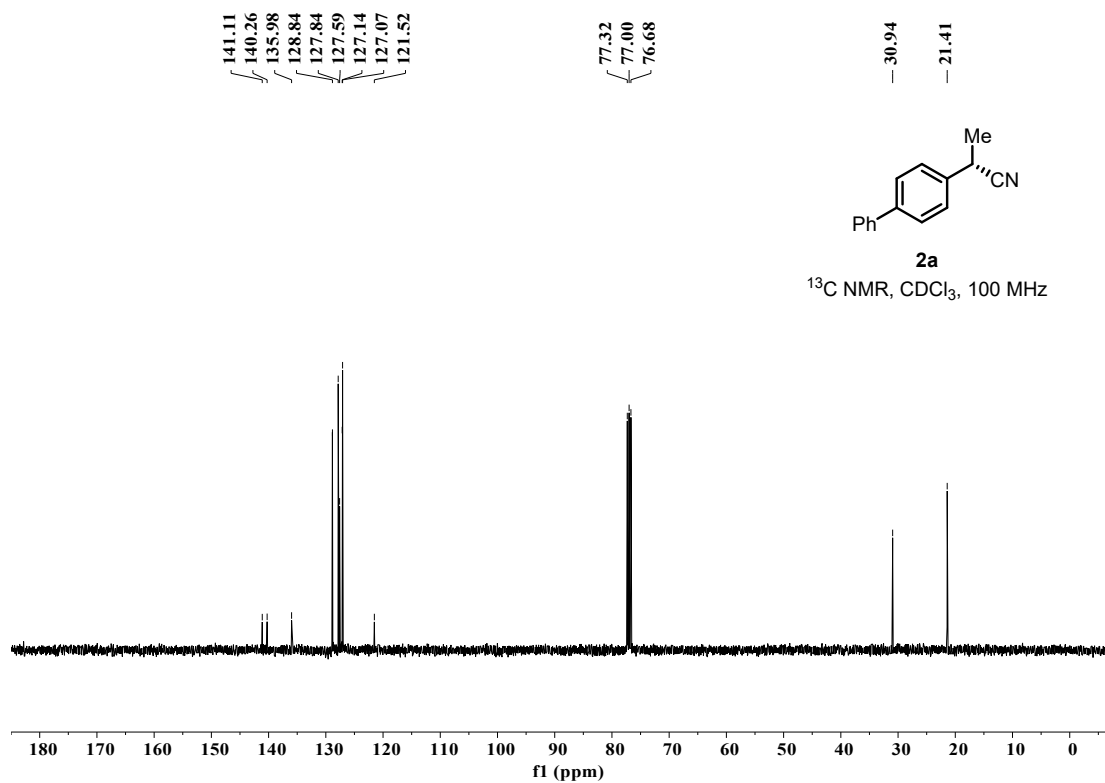
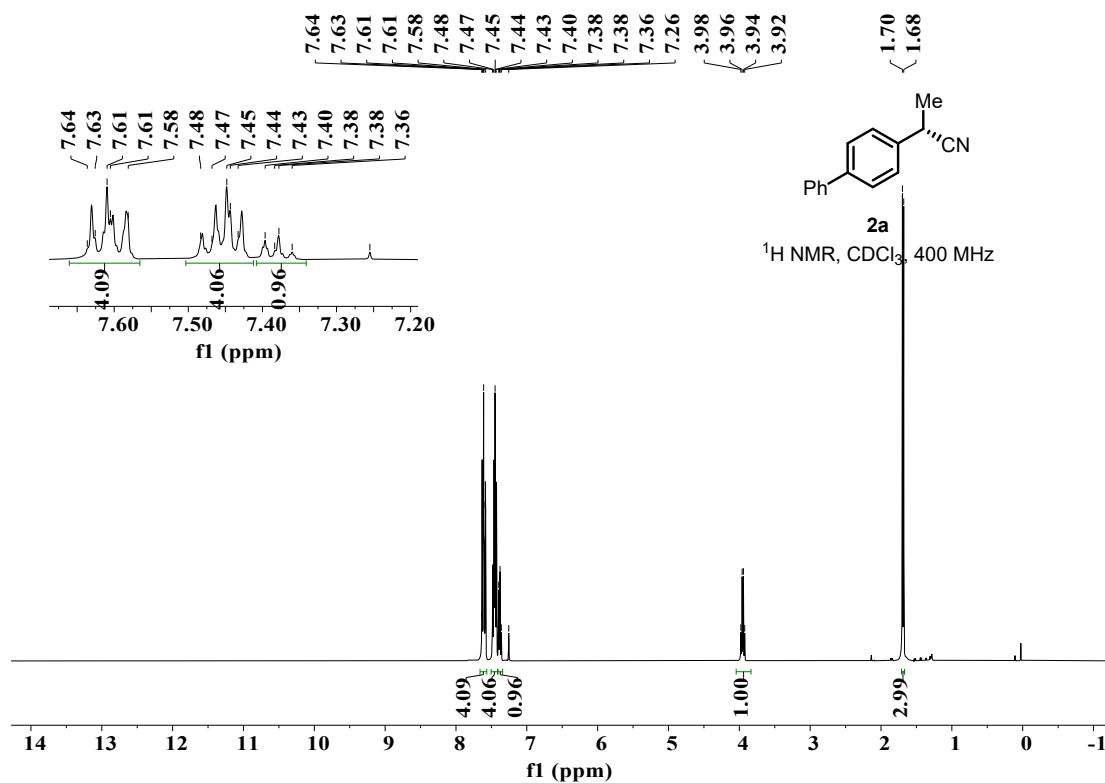
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H	3.05009500	-1.13500300	-2.62832000
C	0.89888700	-1.82645000	-0.85294500
C	-0.33518100	-2.62809300	-0.80182900
C	-0.19474400	-4.13231300	-1.02741200
H	0.82274300	-4.49459700	-1.12766000
H	-0.86499400	-4.75370400	-0.44310800
C	-0.75931400	-3.31321900	-2.11133000
H	-1.82953500	-3.34647600	-2.29517400
H	-0.13982300	-3.08741200	-2.97426100
C	-2.81553700	-1.09899300	1.44153100
H	-2.57770300	-1.05957900	2.51253500
C	-3.77647700	-0.02957900	1.01158400
C	-3.72988000	1.33004300	1.30145700
H	-2.95330400	1.72552100	1.95685600
C	-4.69764100	2.16832000	0.74917600
H	-4.68025600	3.23515400	0.96609300
C	-5.69645800	1.64328600	-0.07334300
H	-6.44829300	2.30658800	-0.49713700
C	-5.74984100	0.27632800	-0.34574300
H	-6.54030100	-0.12734500	-0.97738700
C	-4.78175700	-0.56114900	0.20186800
C	-4.64096700	-2.04944500	0.05217100
H	-4.40478000	-2.33826900	-0.98126400
H	-5.55866900	-2.58661000	0.32029400
C	-3.47127700	-2.41873400	0.97783800
H	-3.75741500	-3.09043000	1.78905400
C	-1.42670200	-2.19022200	0.08235700
Cu	-0.57066600	0.73383800	0.04867800
C	-0.22826800	1.43704300	1.77280400

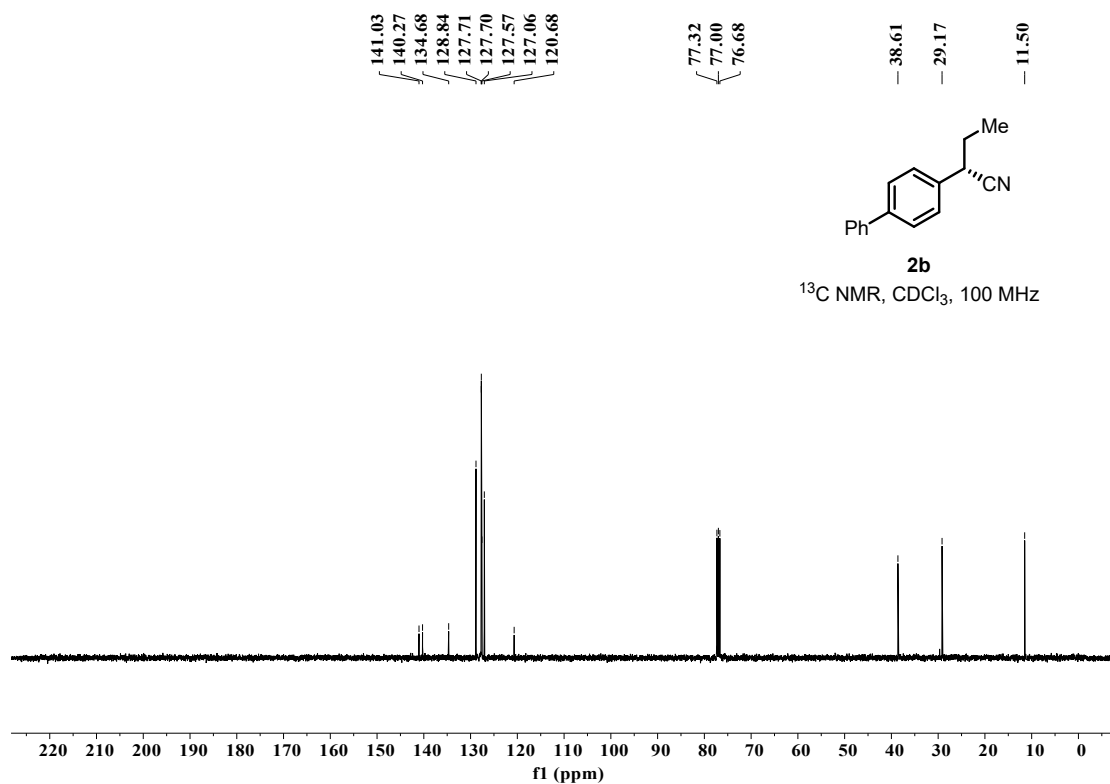
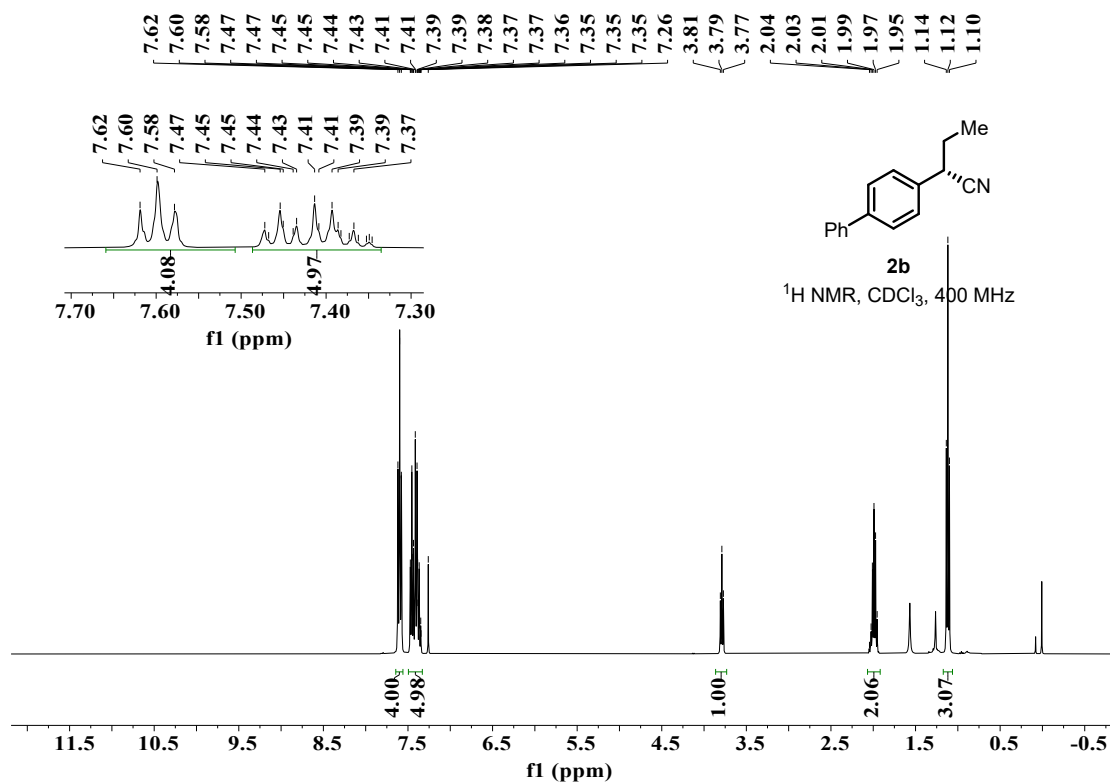
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C	-1.43927300	0.88168000	-1.71754700
N	-1.99351300	0.89936600	-2.75644200
C	0.07380100	3.02412500	0.55377600
H	0.35014600	3.44943100	1.51713800
C	1.26482400	2.95266400	-0.31198400
C	1.18191400	2.89897900	-1.71374300
C	2.53340300	3.04819600	0.28481700
C	2.33390100	2.94540100	-2.48821700
H	0.20888000	2.80942100	-2.19265800
C	3.68591700	3.08905600	-0.49198200
H	2.60570600	3.10023200	1.37127300
C	3.58920900	3.03787500	-1.88170200
H	2.25444400	2.90998700	-3.57269100
H	4.65961600	3.16645600	-0.01253500
H	4.48836700	3.07018000	-2.49328100
C	-1.19974000	3.64566200	0.06175400
H	-1.53584400	3.26939200	-0.90710400
H	-2.00870300	3.50946700	0.78481600
H	-1.02196200	4.72831800	-0.02528300

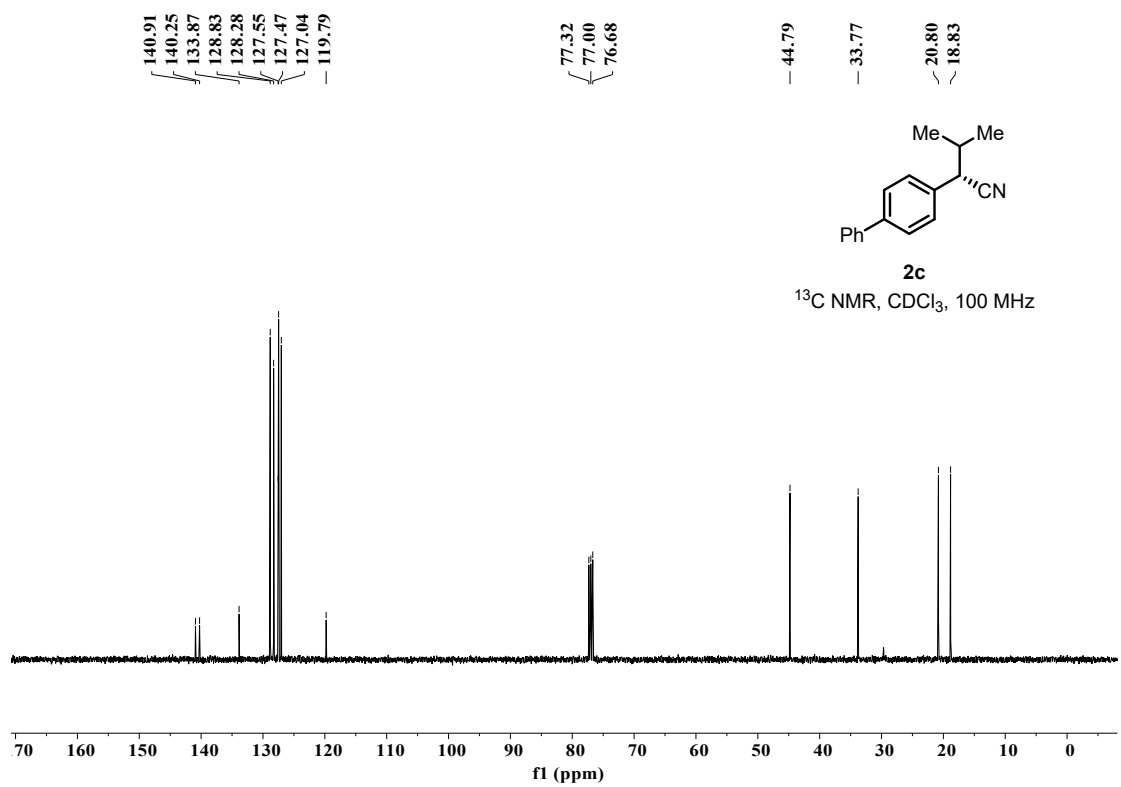
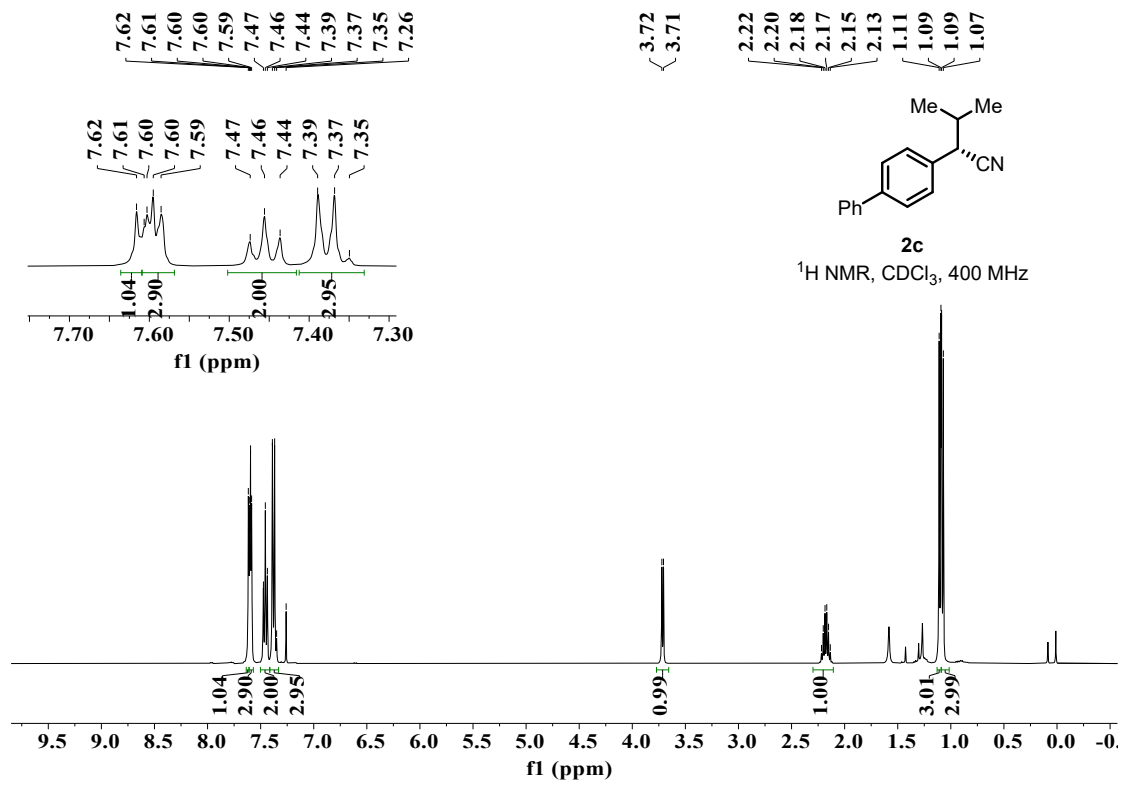
6. References:

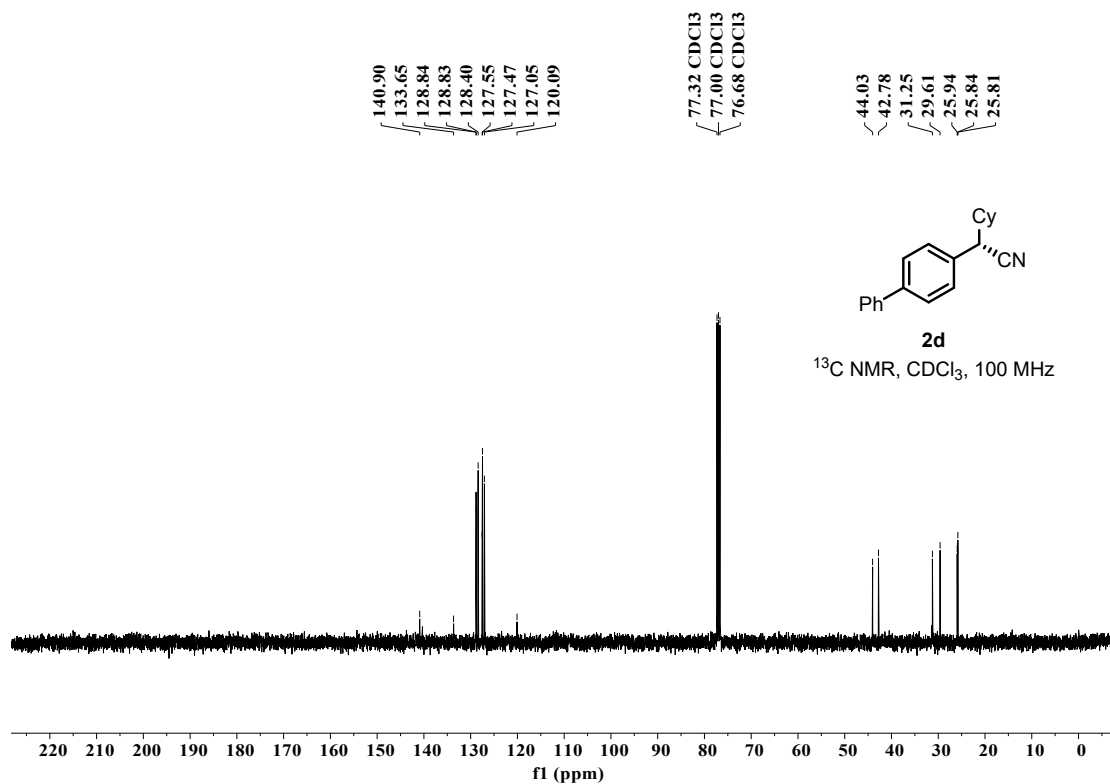
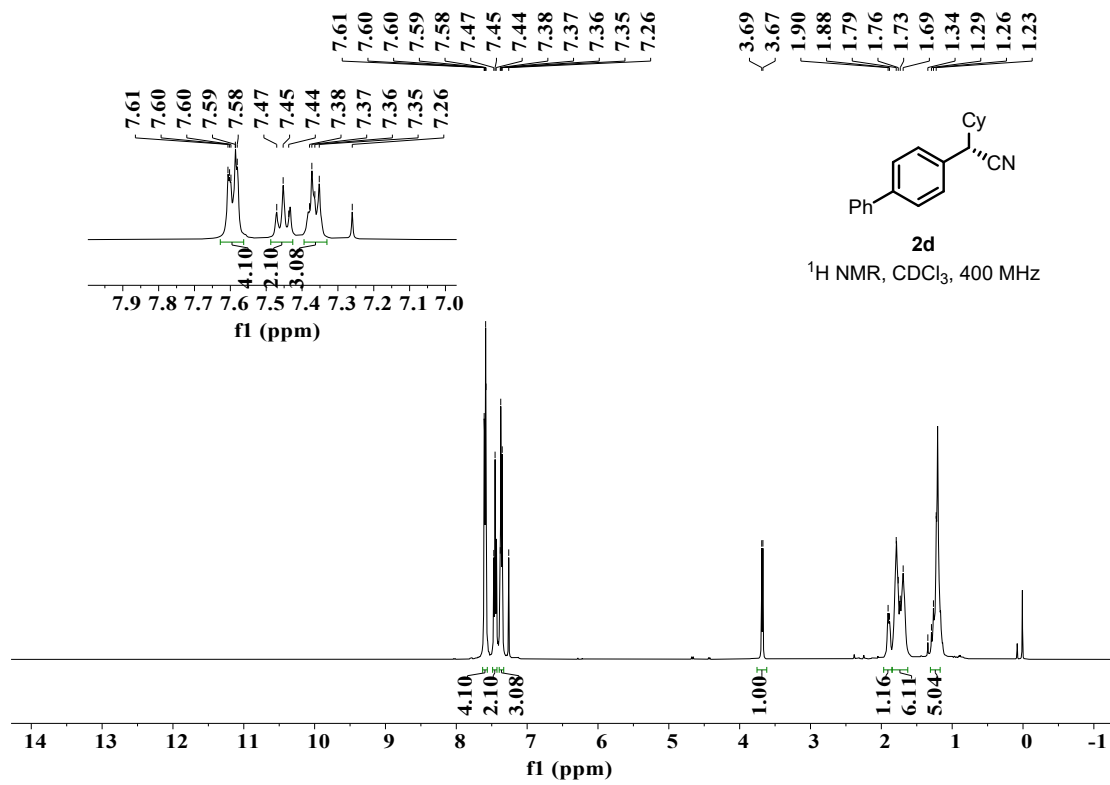
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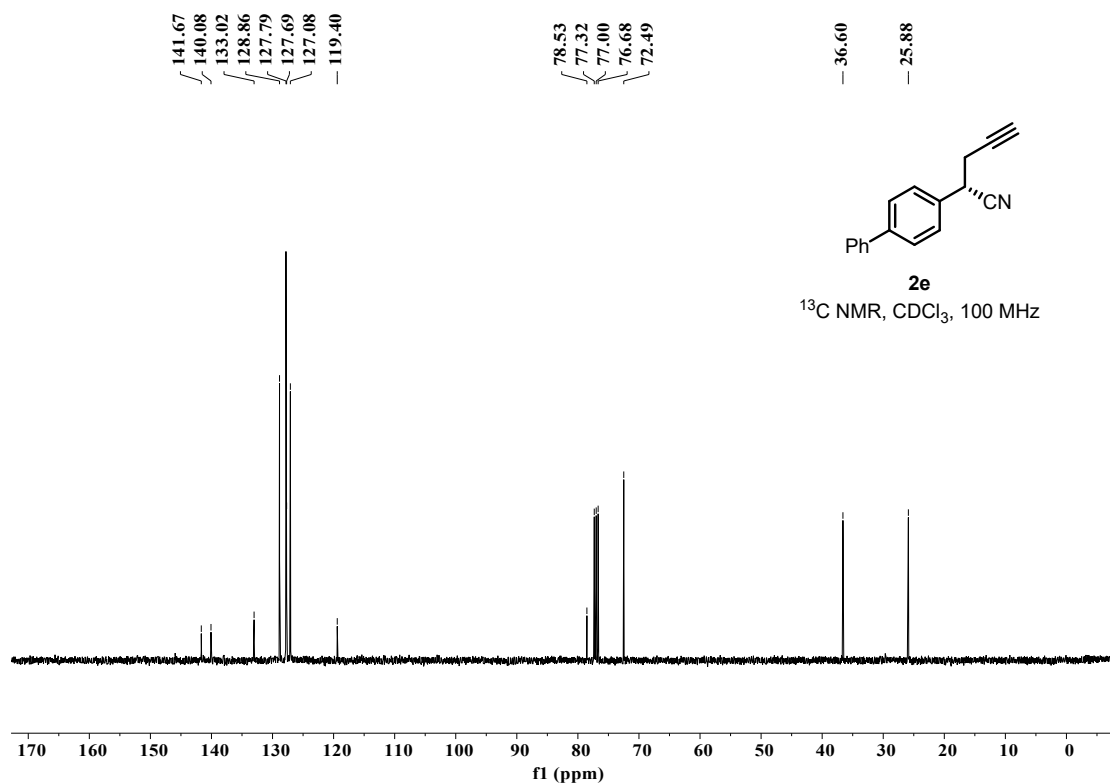
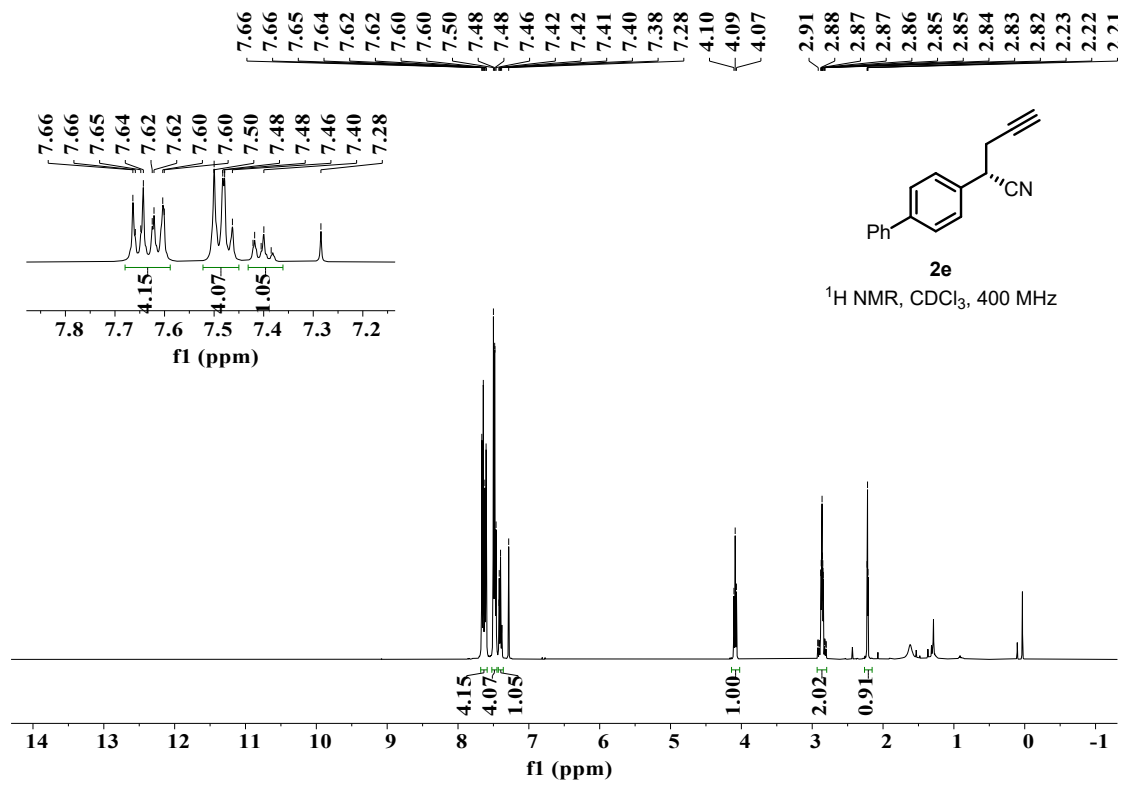
7. NMR spectra of products:

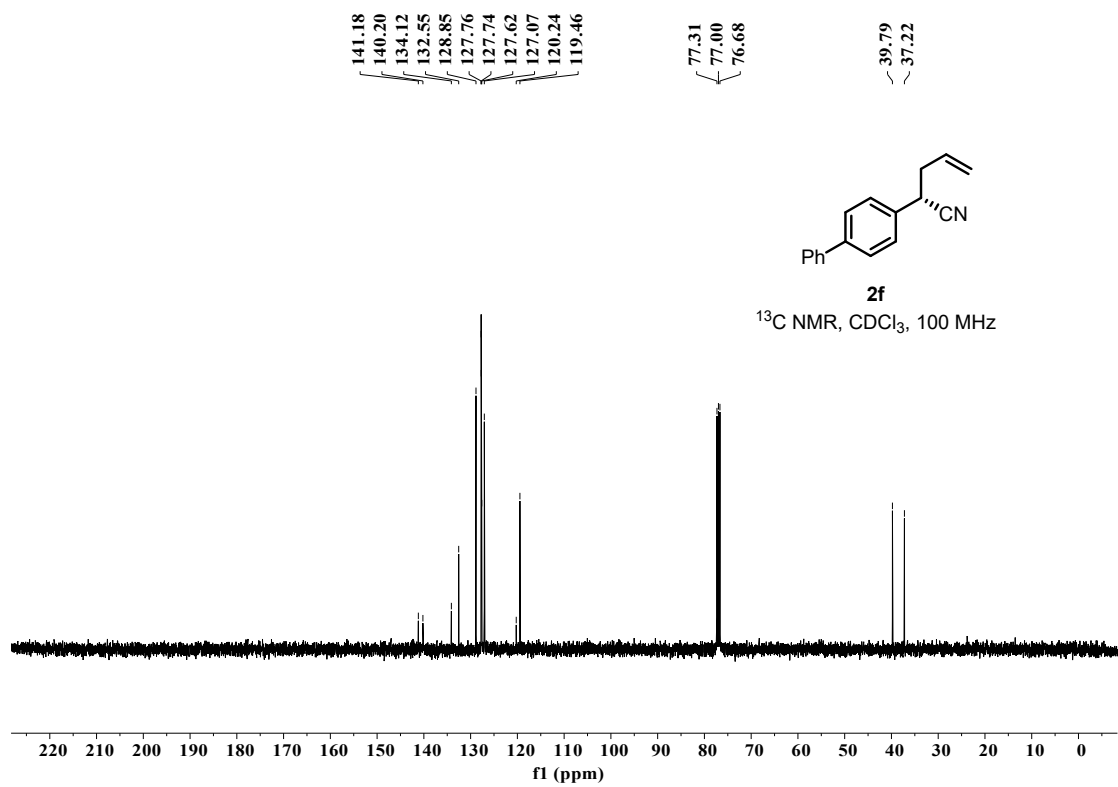
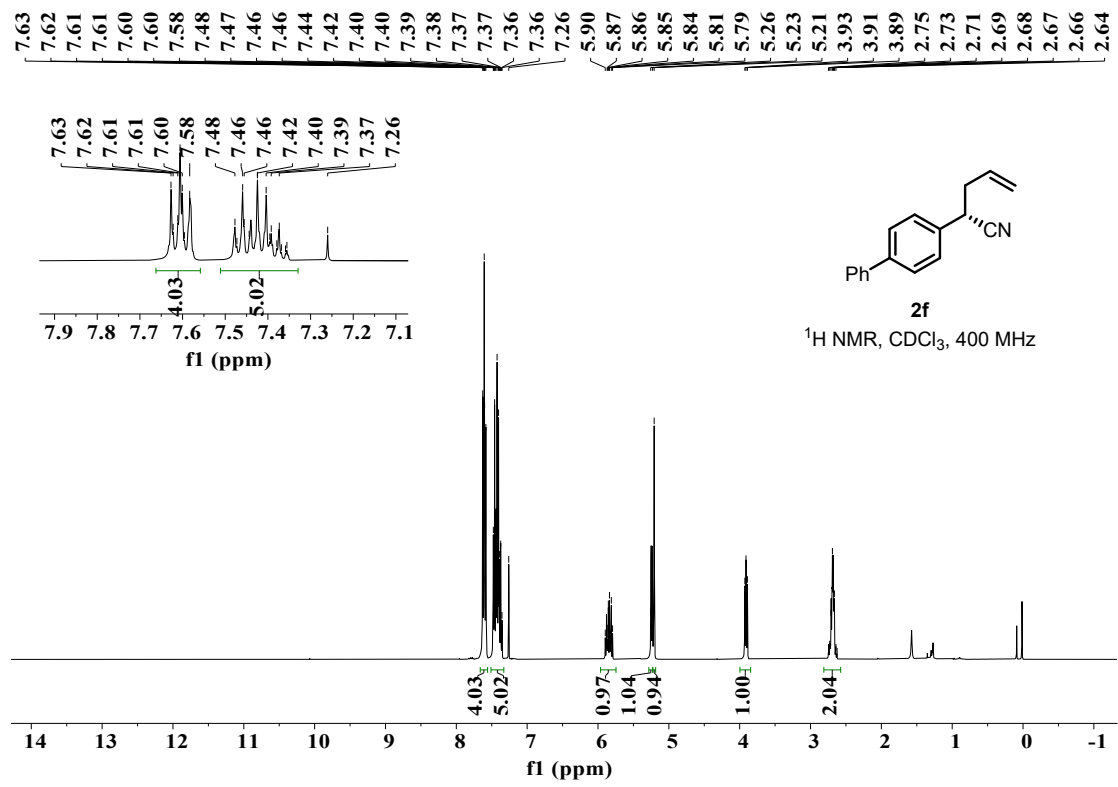


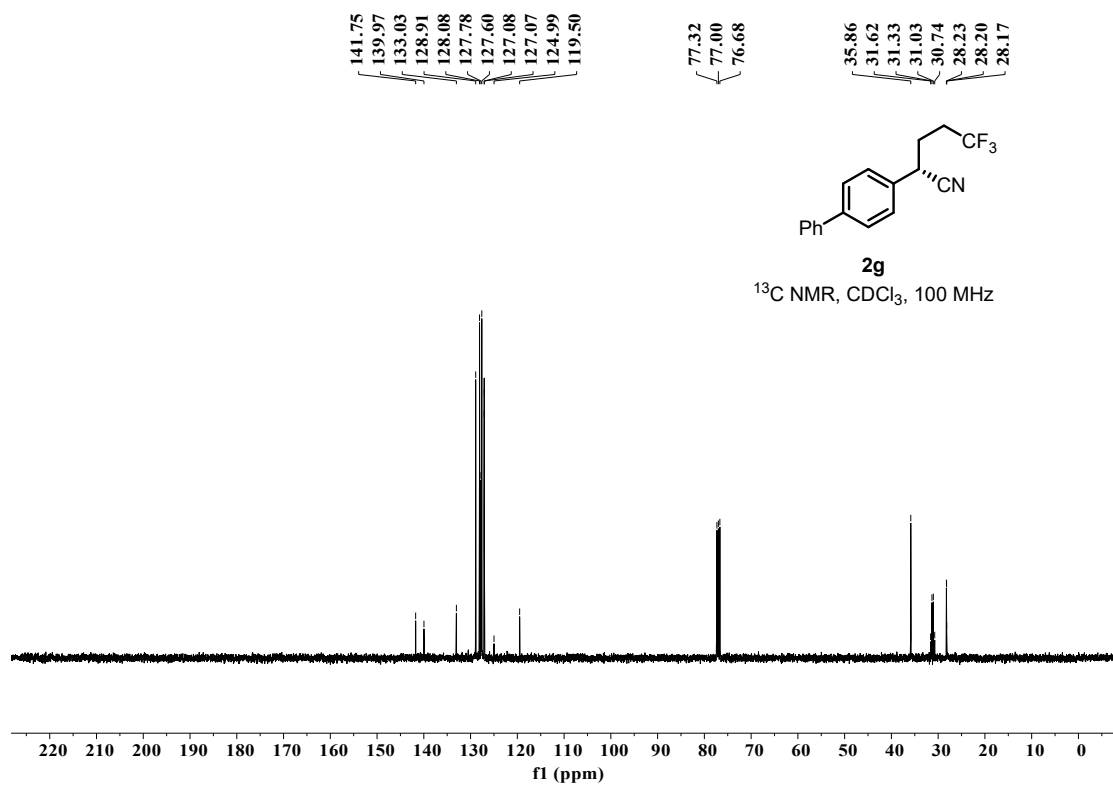
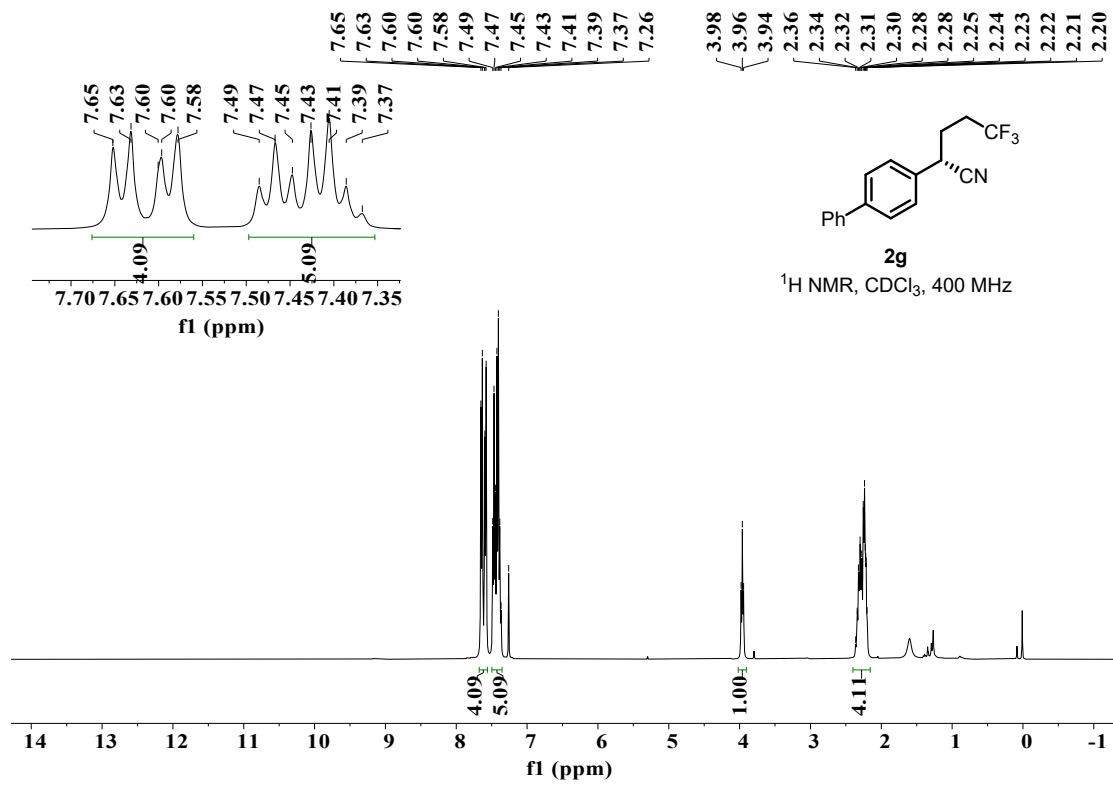




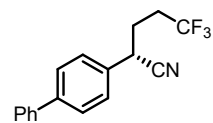






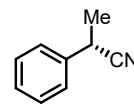
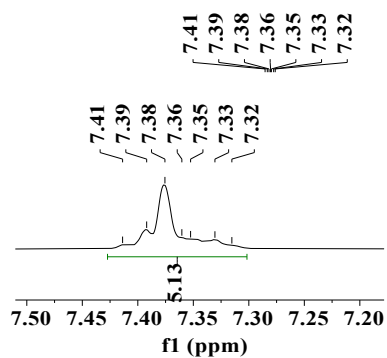
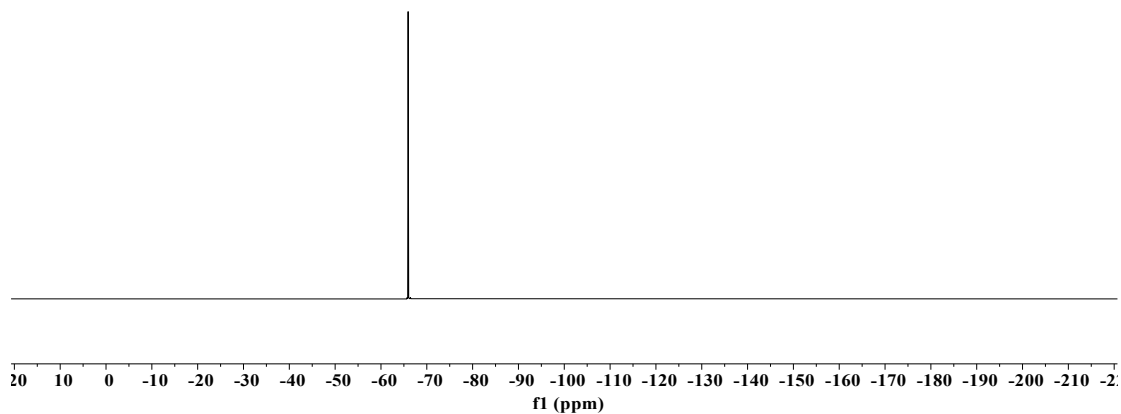


--66.01



2g

¹⁹F NMR, CDCl₃, 376 MHz



2h

¹H NMR, CDCl₃, 400 MHz

