Supplementary Information

Enantioselective Modular Synthesis of α-Aryl-α-Heteroaryl Aminonitriles with Parts per Million Organocatalyst Loading: Mechanistic Investigation for Stereochemical Origins

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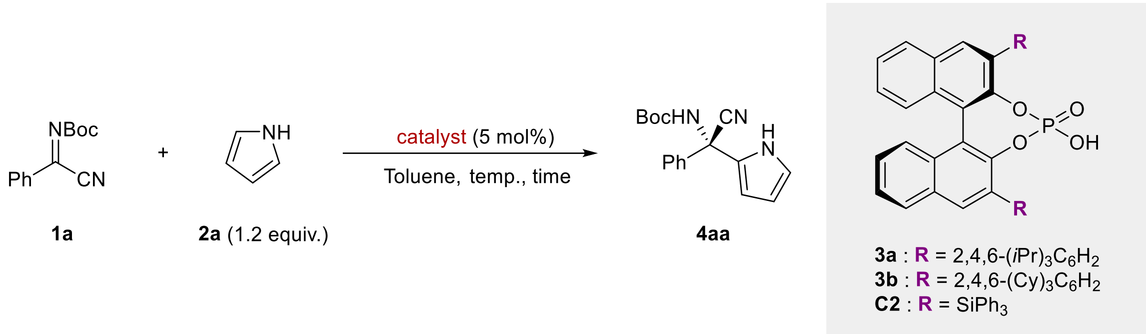
General Information:

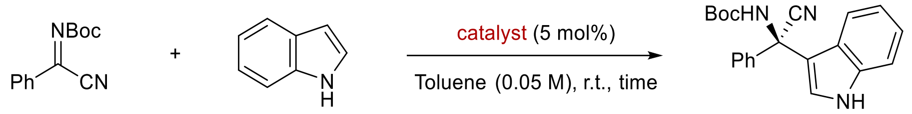
All reactions were performed in oven-dried glassware under a positive pressure of nitrogen. Solvents were transferred via syringe and were introduced into the reaction vessels through a rubber septum. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel (60-F254). The TLC plates were visualized with UV light. Column chromatography was carried out on a column packed with silica-gel 60N spherical neutral size 63-210 µm. The ^{1}H NMR (300 MHz) and ^{19}F NMR (282 MHz) spectra for solution in $CDCl_3$ were recorded on Varian Mercury 300, and ^{13}C NMR (125 MHz) spectra for solution in $CDCl_3$ were recorded on Bruker Avance 500. Chemical shifts (δ) are expressed in ppm downfield from internal TMS. HPLC analyses were performed on a SHIMADZU LC-2010A HT using 4.6 x 250 mm CHIRALPAK® IH-3, IBN-3, IC-3, IM, IF, and IK column. HRMS were recorded on a Waters SYNAPT G2 (ESI). ESI Mass spectra were recorded on a SHIMADZU LCMS-2020 using positive mode. Optical rotations were measured on a JASCO P-2200. Infrared spectra were recorded on a JASCO FT/IR-4600 spectrometer with ZnSe ATR unit. X-ray crystallographic analyses were conducted on X-ray generator or a Rigaku XtaLAB PRO MM007 DW diffractometer system equipped with a MicroMax007HFM-DW(Cu/Mo) X-ray generator and a HyPix-6000HE detector.

Optimization Study using pyrrole

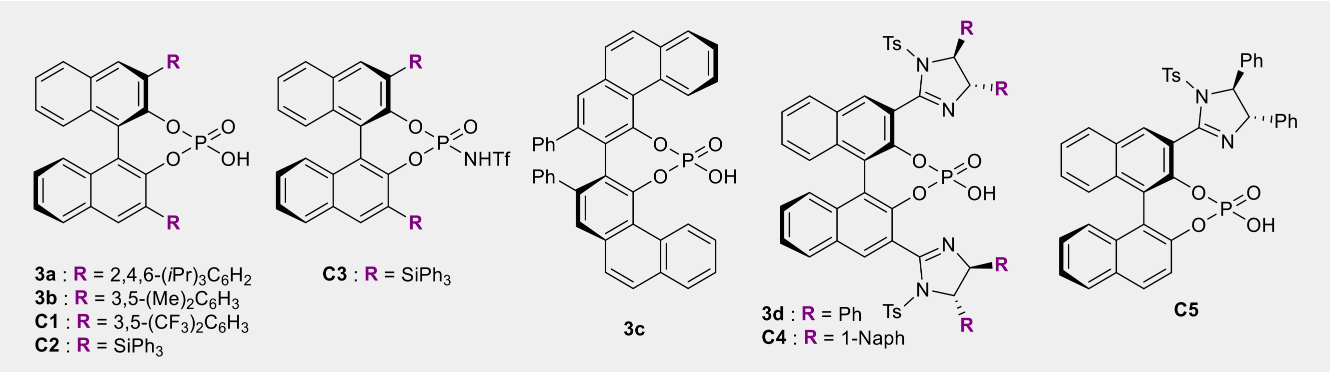


catalyst	solvent	temp. (°C)	time (h)	yield (%)	ee (%)
3a	Toluene	rt	3	99	97
3b	Toluene	rt	0.5	89	77
C2	Toluene	rt	96	92	40
3a	CH_2Cl_2	0	12	87	98
3a	THF	0	12	n.r.	-
3a	AcOEt	0	12	95	97
3a	Toluene	0	12	97	98
3a	Toluene	-20	12	90	98
3a	Toluene	-40	12	trace	-

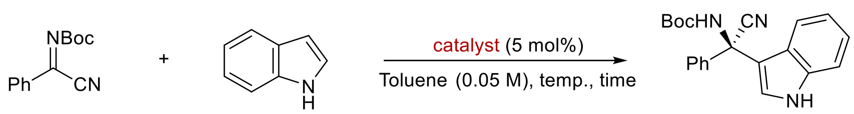
Optimization Study using indole



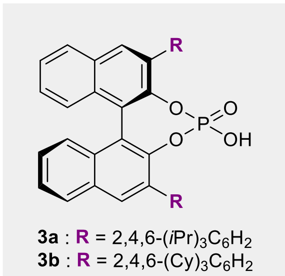
1a **5a** (1.2 equiv.) **6aa**



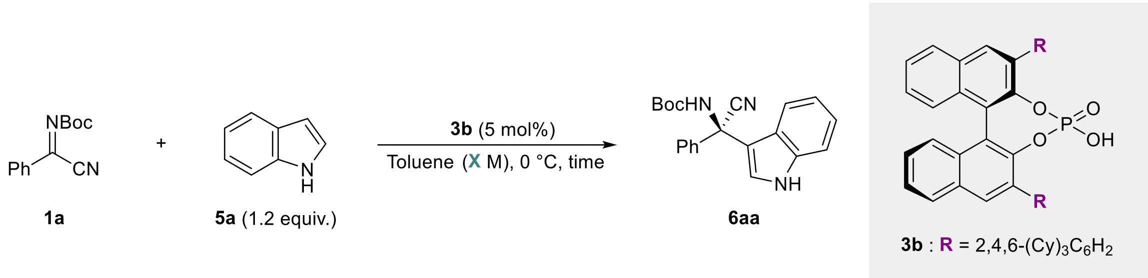
catalyst	time (h)	yield (%)	ee (%)
-	24	n.r.	-
3a	1	91	67
3b	1.5	94	25
C1	1.5	84	64
C2	96	92	40
C3	16	90	66
3c	1.5	84	-64
3d	24	19	9
C4	24	93	9
C5	24	n.r.	-



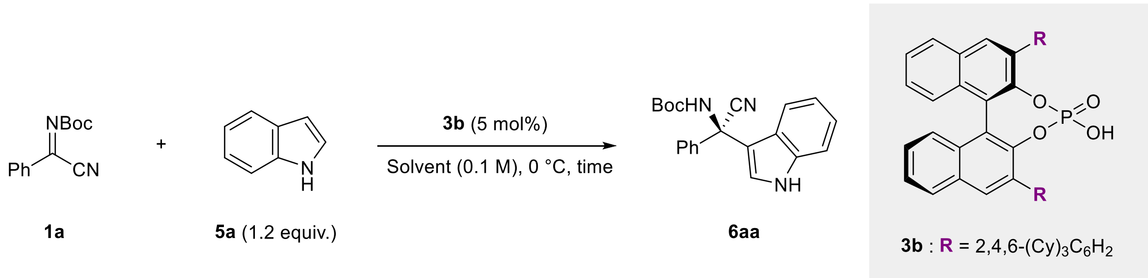
1a **5a** (1.2 equiv.) **6aa**



catalyst	temp.	time (h)	yield (%)	ee (%)
3a	r.t.	1	91	67
3a	0	12	99	72
3b	0	16	95	82
3b	-20	16	85	81

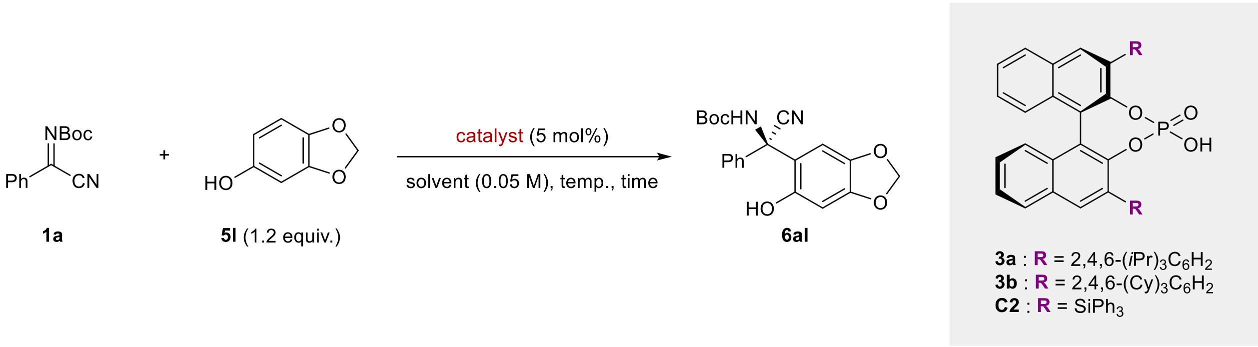


concentration (M)	time (h)	yield (%)	ee (%)
0.05	16	95	82
0.025	16	78	81
0.1	16	96	83
0.25	5	89	82

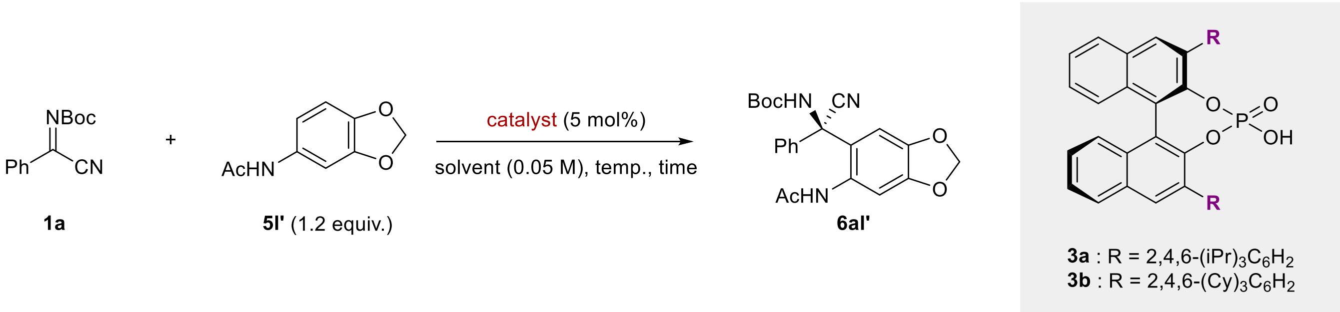


solvent	time (h)	yield (%)	ee (%)
Toluene	16	96	83
CH_2Cl_2	5	92	93
$(CH_2Cl)_2$	2	94	87
$CHCl_3$	2	93	90
CCl_4	2	97	89
MeCN	24	88	79
THF	24	n.r.	-
CH_2Cl_2	12	93	95

The reactions of iminonitriles with sesamols

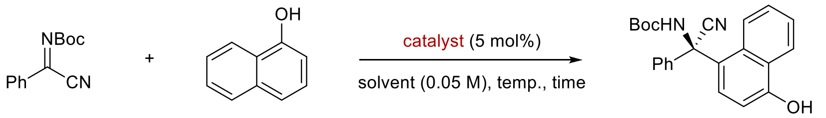


catalyst	solvent	temp.	time (h)	yield (%)	ee (%)
3a	Toluene	r.t.	12	84	29
3a	Toluene	-20	24	66	5
3a	CH_2Cl_2	0	6	92	29
3b	CH_2Cl_2	-20	6	90	23
C2	CH_2Cl_2	0	18	59	4

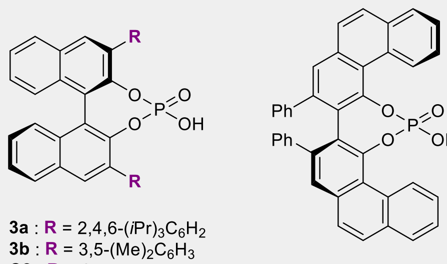


catalyst	solvent	temp.	time (h)	yield (%)	ee (%)
3a	Toluene	0	12	0	-
3b	CH_2Cl_2	-20	16	0	-

The reactions of iminonitriles with 1-naphthol



1a **5m** (1.2 equiv.) **6am**

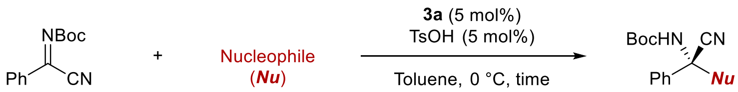


3a : **R** = 2,4,6-(iPr)$_3$C$_6$H$_2$
3b : **R** = 3,5-(Me)$_2$C$_6$H$_3$
C2 : **R** = SiPh$_3$

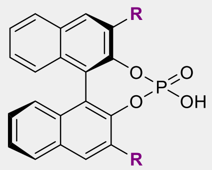
3c

catalyst	solvent	temp.	time (h)	yield (%)	ee (%)
3a	Toluene	0	168	77	23
3b	CH_2Cl_2	-20	168	84	50
3b	CH_2Cl_2	r.t.	48	64	37
C2	CH_2Cl_2	0	72	67	23
3c	CH_2Cl_2	0	48	97	-35

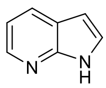
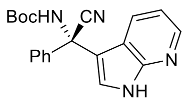
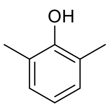
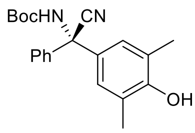
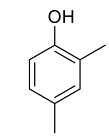
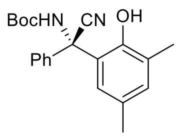
Othernucleophiles



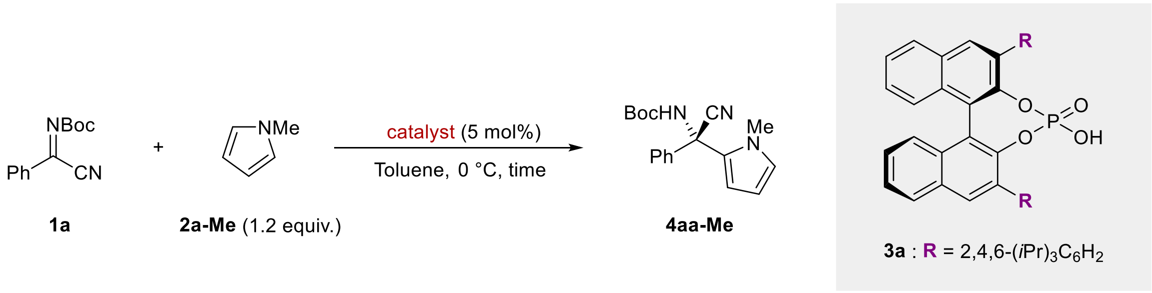
1a (1.2 equiv.)



3a : R = 2,4,6-(iPr)$_3$C$_6$H$_2$
3b : R = 2,4,6-(Cy)$_3$C$_6$H$_2$

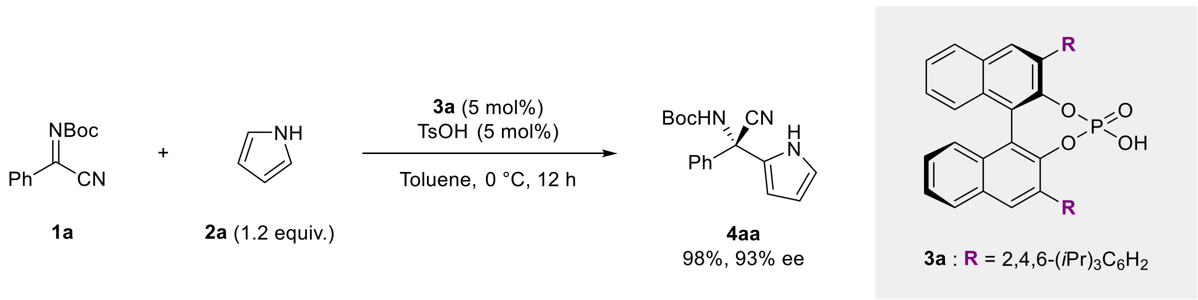
Run	Nucleophile	Product	condition	yield	ee (%)
1			catalyst **3b** in CH_2Cl_2, 12 h	22	2
2			catalyst **3a** in Toluene, 0 °C→r.t., 12 h	n.r.	-
3			catalyst **3a** in Toluene, 0 °C→r.t., 12 h	n.r.	-

The reaction using *N*-protected pyrrole.



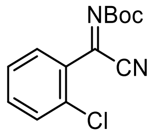
catalyst	time (h)	yield (%)	ee (%)
3a	12	0	-
TsOH	6	32	rac.

Since TsOH catalyzed the reaction, we hypothesized that strong acids can promote the reaction even without basic site through different reaction mechanism. We also investigated the reaction of pyrrole in the mixture of **3a**:TsOH = 1:1. The reaction maintained its enantioselectivity which implied that Bronsted acid-base dual activation is necessary to get enantioriched pyrrole adducts. However, in the case of emplying stronger acid, the reaction probably proceeds via different mechanism.



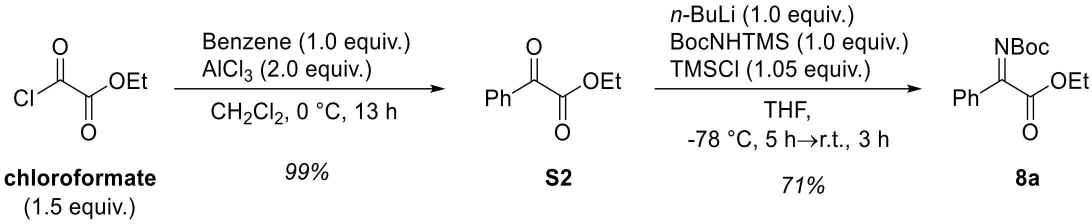
General Procedure for Preparation of α-Iminonitriles (1a-p)

Unknown α-iminonitriles (**1j**) were prepared according to the reported method.[1]



68% yield from corresponding benzoyl cyanide. Colorless oil. **m.p.**: 128.0-128.8 ˚C. **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.81 (br, 1H), 7.55-7.50 (m, 2H), 7.43-7.37 (m, 1H), 1.63 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 158.5, 141.3, 134.0, 132.6, 131.7, 131.4, 130.4, 127.4, 110.0, 85.6, 28.0; **IR** (ATR) 3460, 2981, 2223, 1736, 1589, 1371, 1146, 956, 727 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{13}H_{13}N_2ClNaO_2$ 287.0558; found 287.0559.

General Procedure for Preparation of Various Imines 8

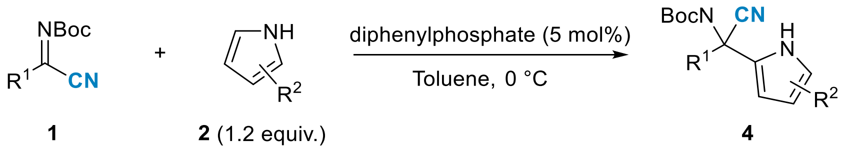


Imine **8a** was prepared according to the following procedure, and the analytical data for the compound was consistent with those reported in the literature.[2]

In a flame-dried round-bottomed flask, CH_2Cl_2 (20 mL) was added. Then benzene (0.89 mL, 10 mmol) was added, and the mixture was cooled to 0 ˚C. To this reaction mixture, chloroformate (1.5 equiv.) was added. After the solution was stirred for 10 minutes, $AlCl_3$ (2.0 equiv.) was added portion-wise. The reaction mixture was further stirred at 0 ˚C for 13 h. After the reaction was complete, cold water and 12 M HCl were added until the organic layer became colorless and clear. The mixture was subsequently extracted with CH_2Cl_2 3 times, the combined organic layer was washed with sat. $NaHCO_3$ aq., brine, finally dried over Na_2SO_4. After the solvent was removed under reduced pressure, ethyl benzoylformate **S2** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 95:5).

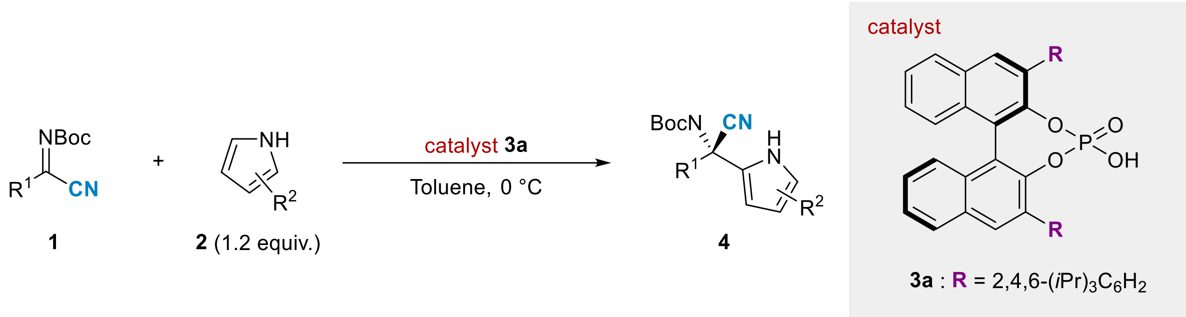
To the solution of freshly prepared BocNHTMS (1.0 equiv.) in THF (0.1 M), *n*-BuLi (1.0 equiv.) was added dropwise at −78 ˚C under Ar. To the reaction mixture, the solution of **S2** in THF (1.0 M) was added dropwise. After the reaction mixture was stirred for 5 h, TMSCl (1.05 equiv.) was added. Then the reaction was allowed to warm up to room temperature and was further stirred for 3 h. The reaction was quenched by adding sat. $NaHCO_3$ aq. and extracted with AcOEt which was dried over Na_2SO_4. After the reaction mixture was concentrated under reduced pressure, the obtained crude product was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 95:5) to afford ketiminoester.

General procedure for the synthesis of racemic products 4



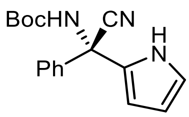
To the solution of iminonitrile **1** (1.0 equiv.) and diphenyl phosphate (5 mol%) in dry toluene (0.05 M), pyrrole **2** (1.2 equiv.) was added, then the mixture was stirred at 0 °C under argon atmosphere. The reaction mixture was concentrated under reduced pressure to give the residue, which was purified by silica-gel column chromatography to afford racemic products.

General procedure for the asymmetric synthesis of 4



To a flame-dried flask, catalyst **3a** (5 mol%) and α-iminonitrile **1** (1.0 equiv., 0.05 mmol) were dissolved in dry toluene (0.05 M) and cooled to 0 °C. Pyrrole **2** (1.2 equiv.) was added in one portion, and the solution was stirred at that temperature for 12 hours. The reaction mixture was concentrated under reduced pressure. Product **4** was purified by silica-gel column chromatography.

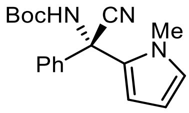
(*S*)-2-Phenyl-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4aa)



4aa (14.4 mg, 97% yield, 98% ee) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05 mmol), pyrrole **2a** (4.2 µL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 µmol). The crude **4aa** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

Colorless oil. **Optical Rotation**: $[\alpha]_D^{25.0}$ = −30.2 (98% ee, *c* 1.0, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.81 (br, 1H), 7.62-7.57 (m, 2H), 7.48-7.38 (m, 3H), 6.79-6.77 (m, 1H), 6.13-6.10 (m, 1H), 5.95 (s, 1H), 5.44 (s, 1H), 1.39 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.8, 137.1, 129.3, 129.1, 128.2, 125.9, 119.9, 118.3, 109.4, 108.9, 82.2, 57.1, 28.1; **IR** (ATR) 3410, 3347, 2980, 2366, 1693, 1488, 1152, 889, 732 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{17}H_{19}N_3NaO_2$ 320.1369; found 320.1379; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 95:5, 1.0 mL/min, 215 nm) 98% ee, t_R 8.0 (major), t_R 10.1 (minor) min.

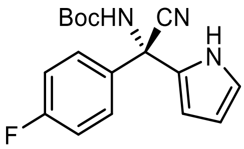
(*S*)-2-Phenyl-2-(1-methylpyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4aa-Me)



4aa-Me (5.0 mg, 32% yield) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05 mmol), pyrrole **2a-Me** (5.3 µL, 0.06 mmol) and TsOH (0.4 mg, 2.5 µmol). The crude **4aa-Me** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 80:20).

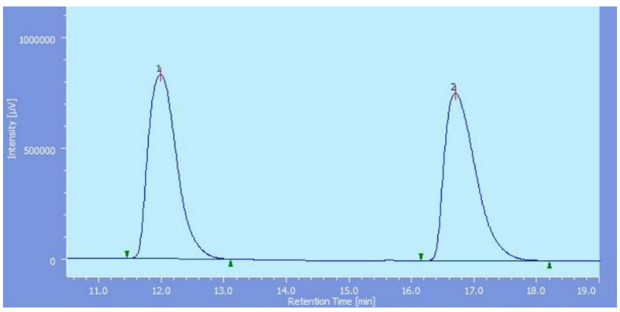
Pale yellow solid. **m.p.**: 132.1-132.8 °C.^{1}**H NMR** ($CDCl_3$, 300 MHz) δ 7.53-7.40 (m, 5H), 6.67 (t, J = 2.3 Hz, 1H), 5.97 (t, J = 3.4 Hz, 1H), 5.57 (s, 1H), 5.26 (s, 1H), 3.74 (s, 3H), 1.36 (s, 9H); ^{13}**C NMR** ($CDCl_3$, 125 MHz) δ 153.1, 129.0, 128.8, 128.7, 127.3, 126.4, 126.4, 118.0, 112.1, 107.0, 82.1, 56.8, 35.7, 28.0; **IR** (ATR) 3233, 2982, 2851, 2338, 1777, 1586, 1410, 1136,1051, 899, 730 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{18}H_{21}N_3NaO_2$ 334.1526; found 334.1530

(*S*)-2-(4-Fluorophenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4ba)

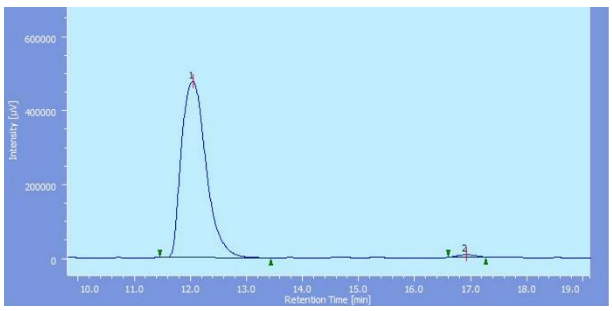


4ba (15.2 mg, 97% yield, 98% ee) was obtained by the general procedure using iminonitrile **1b** (12.4 mg, 0.05 mmol), pyrrole **2a** (4.2 µL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 µmol). The crude **4ba** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

Pale yellow oil. **Optical Rotation**: $[\alpha]_D^{25.0}$ = −53.3 (98% ee, *c* 0.157, $CHCl_3$); ^{1}**H NMR** ($CDCl_3$, 300 MHz) δ 8.81 (br, 1H), 7.60-7.51 (m, 2H), 7.17-7.10 (m, 2H), 6.81-6.78 (m, 1H), 6.13-6.10 (m, 1H), 5.92 (s, 1H), 5.48 (s, 1H), 1.39 (s, 9H); ^{13}**C NMR** ($CDCl_3$, 125 MHz) δ 163.0 (d, J_{C-F} = 248.2 Hz), 153.7, 127.9 (d, J_{C-F} = 8.5 Hz), 120.2, 118.2, 116.2 (d, J_{C-F} = 20.8 Hz), 115.9, 109.5, 108.9, 108.8, 82.4, 56.6, 28.1; ^{19}**F NMR** ($CDCl_3$, 376 MHz) δ −112.1; **IR** (ATR) 3336, 2923, 2320, 1716, 1507, 1372, 735 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{17}H_{18}FN_3NaO_2$ 338.1275; found 338.1285; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 97:3, 1.0 mL/min, 215 nm) 98% ee, t_R 12.0 (major), t_R 16.9 (minor) min.

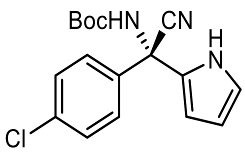


Peak	t_R (min)	Area (%)
1	12.0	50.0
2	16.7	50.0



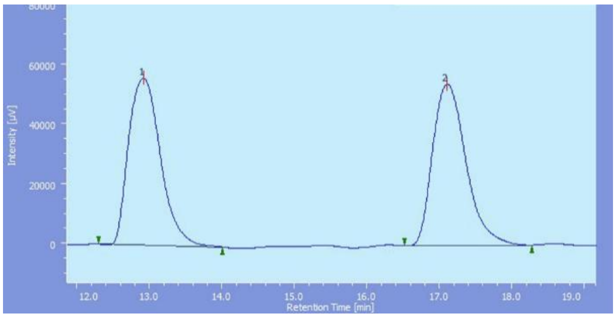
Peak	t_R (min)	Area (%)
1	12.0	99.0
2	16.9	1.0

(*S*)-2-(4-Chlorophenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4ca)

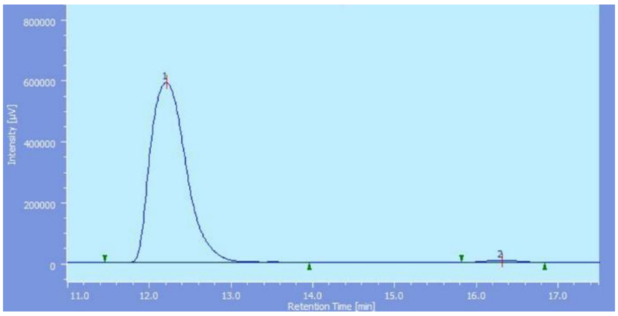


4ca (15.6 mg, 94% yield, 98% ee) was obtained by the general procedure using iminonitrile **1c** (13.2 mg, 0.05 mmol), pyrrole **2a** (4.2 μL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 μmol). The crude **4ca** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

Pale yellow oil. **Optical Rotation**: $[\alpha]_D^{25.0} = -33.5$ (98% ee, *c* 0.29, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.78 (br, 1H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 6.80-6.78 (m, 1H), 6.13-6.6.01 (m, 1H), 5.94 (s, 1H), 5.53 (br, 1H), 1.39 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 152.6, 134.8, 134.2, 128.2, 126.5, 126.3, 119.2, 117.1, 108.5, 108.0, 81.4, 55.7, 27.0; **IR** (ATR) 3345, 2979, 2318, 1699, 1490, 1159, 11240,816 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{17}H_{18}ClN_3NaO_2$ 354.0980; found 354.0987; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 97:3, 1.0 mL/min, 214 nm) 98% ee, t_R 12.4 (major), t_R 16.4 (minor) min.

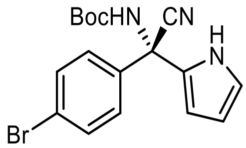


Peak	t_R (min)	Area (%)
1	12.9	50.0
2	17.1	50.0



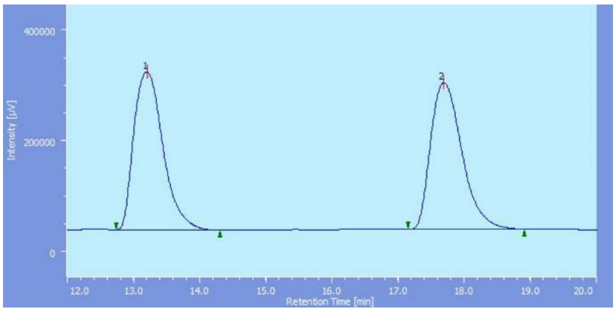
Peak	t_R (min)	Area (%)
1	12.4	99.0
2	16.4	1.0

(*S*)-2-(4-Bromophenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4da**)

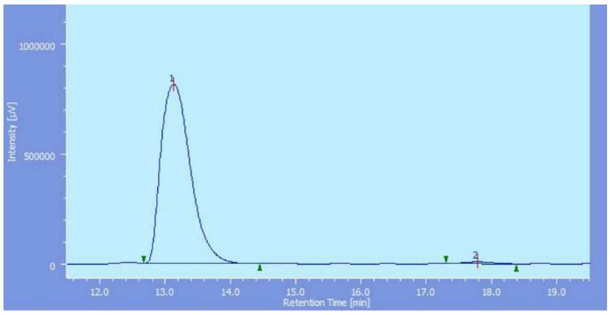


4da (17.8 mg, 95% yield, 98% ee) was obtained by the general procedure using iminonitrile **1d** (15.5 mg, 0.05 mmol), pyrrole **2a** (4.2 μL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 μmol). The crude **4da** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

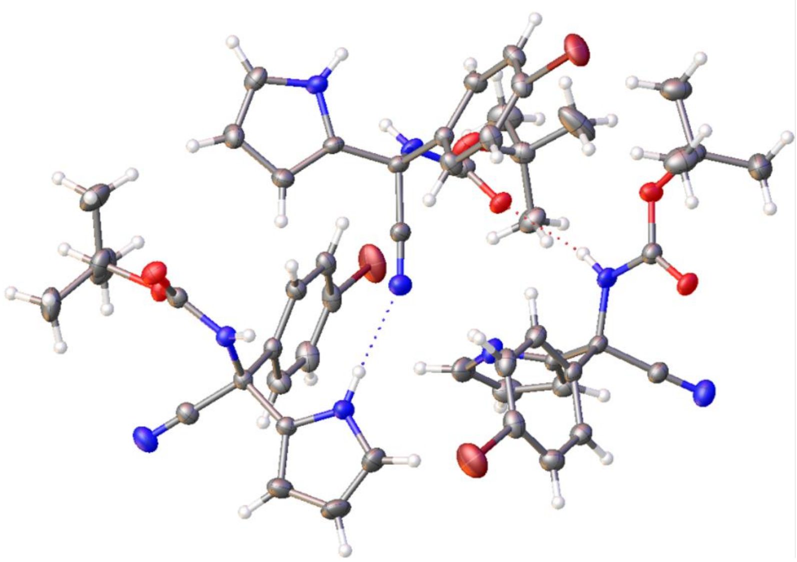
White solid. **m.p.**: 104.5-105.0 ˚C. **Optical Rotation**: $[\alpha]_D^{25.0} = -49.3$ (99% ee, *c* 0.74, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.80 (br, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.46 (d, *J* = 8.6 Hz, 1H), 6.80-6.78 (m, 1H), 6.12-6.09 (dd, *J* = 6.1, 3.0 Hz, 1H), 5.94 (s, 1H), 5.55 (br, 1H), 1.39 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.6, 132.2, 128.6, 127.6, 127.3, 123.4, 120.3, 118.1, 109.6, 109.0, 82.4, 56.8, 28.1; **IR** (ATR) 3333, 2977, 2247, 1702, 1486, 1367, 1158, 1010, 812, 731 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{17}H_{18}BrN_3NaO_2$ 398.0475; found 398.0477; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 97:3, 1.0 mL/min, 214 nm) 98% ee, t_R 13.2 (major), t_R 17.7 (minor) min.



Peak	t_R (min)	Area (%)
1	13.2	50.0
2	17.6	50.0



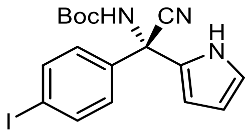
Peak	t_R (min)	Area (%)
1	13.2	99.0
2	17.7	1.0



Empirical Formula	$C_{17}H_{18}BrN_3O_2$
Formula weight	376.25
Temperature/K	123.15
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	20.10730(10)
b/Å	17.86380(10)
c/Å	15.33700(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5508.94(5)
Z	12
ρcalcg/cm^3	1.361
μ/mm^{-1}	3.151
F(000)	2304.0
Crystal size/mm^3	0.21 x 0.18 x 0.14
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.762 to 151.834
Index ranges	$-25 \leq h \leq 25$, $-17 \leq k \leq 21$, $-19 \leq l \leq 19$
Reflections collected	53680
Independent reflections	11206 [R_{int} = 0.0255, R_{sigma} = 0.0175]
Data/restraints/parameters	11206/0/631

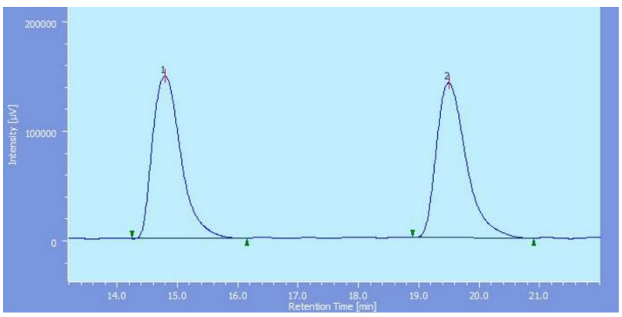
Goodness-of-fit on F2	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0265, wR_2 = 0.0667
Final R indexes [all data]	R_1 = 0.0268, wR_2 = 0.0668
Largest diff. peak/hole / e Å^{-3}	0.49/-0.72
Flack parameter	-0.014(3)

(*S*)-2-(4-Iodophenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4ea**)

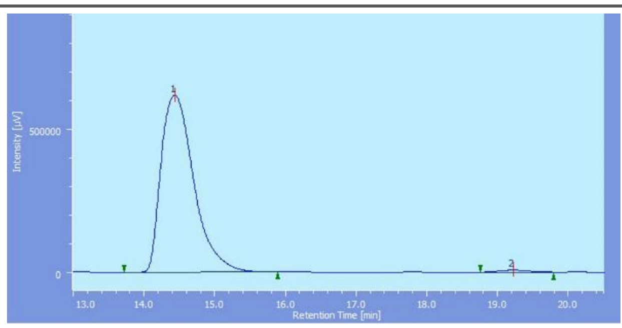


4ea (20.1 mg, 95% yield, 98% ee) was obtained by the general procedure using iminonitrile **1e** (17.8 mg, 0.05 mmol), pyrrole **2a** (4.2 μL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 μmol). The crude **4ea** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

Pale yellow oil. **Optical Rotation**: $[\alpha]_D^{25.0}$ = −30.9 (98% ee, *c* 0.21, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.74 (br, 1H), 7.79 (d, *J* = 6.4 Hz, 2H), 7.34 (d, *J* = 6.4 Hz, 2H), 6.79 (dd, *J* = 3.2, 2.1 Hz, 1H), 6.12 (dd, *J* = 4.5, 2.2 Hz, 1H), 5.95 (br, 1H), 5.46 (s, 1H), 1.40 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.5, 138.2, 131.0, 127.7, 127.4, 120.3, 118.0, 109.6, 1091, 95.2, 82.4, 56.9, 28.1; **IR** (ATR) 3331, 2977, 2852, 2309, 1698, 1158, 1006, 728 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{17}H_{18}IN_3NaO_2$ 446.0336; found 446.0341; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 97:3, 1.0 mL/min, 214 nm) 98% ee, t_R 14.5 (major), t_R 19.2 (minor) min.

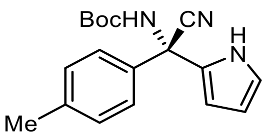


Peak	t_R (min)	Area (%)
1	14.8	50.0
2	19.5	50.0



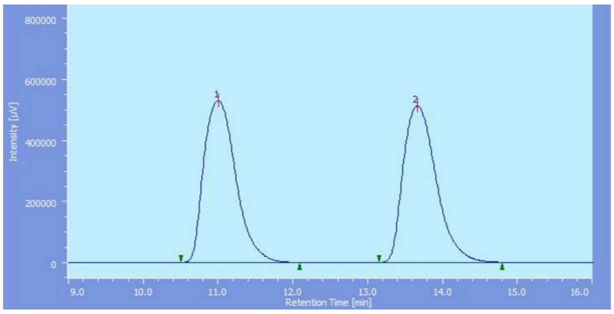
Peak	t_R (min)	Area (%)
1	14.5	99.0
2	19.2	1.0

(*S*)-2-(4-Methylphenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4fa**)

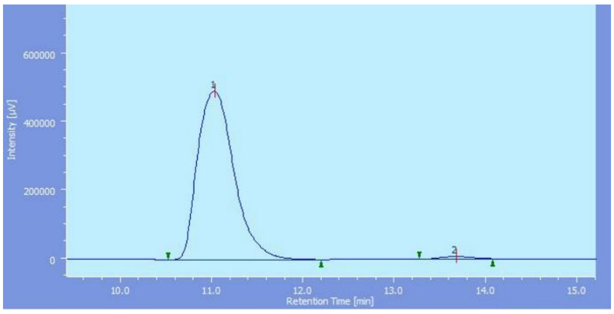


4fa (15.3 mg, 98% yield, 98% ee) was obtained by the general procedure using iminonitrile **1f** (12.2 mg, 0.05 mmol), pyrrole **2a** (4.2 μL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 μmol). The crude **4fa** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

Yellow oil. **Optical Rotation**: $[\alpha]_D^{25.0}$ = −13.3 (98% ee, *c* 0.21, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.84 (br, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 6.78-6.75 (m, 1H), 6.11 (dd, *J* = 6.1, 3.0 Hz, 1H), 5.95 (s, 1H), 5.41 (s, 1H), 2.38 (s, 3H), 1.40 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.9, 139.3, 134.0, 129.7, 128.4, 125.9, 119.8, 118.4, 109.3, 108.8, 82.0, 56.9, 28.1, 21.1; **IR** (ATR) 3344, 2978, 2243, 1702, 1480, 1240, 1003,808 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{18}H_{21}N_3NaO_2$ 334.1526; found 334.1528; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 97:3, 1.0 mL/min, 215 nm) 98% ee, t_R 11.0 (major), t_R 13.7 (minor) min.

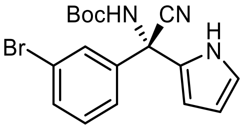


Peak	t_R (min)	Area (%)
1	11.0	50.0
2	13.7	50.0



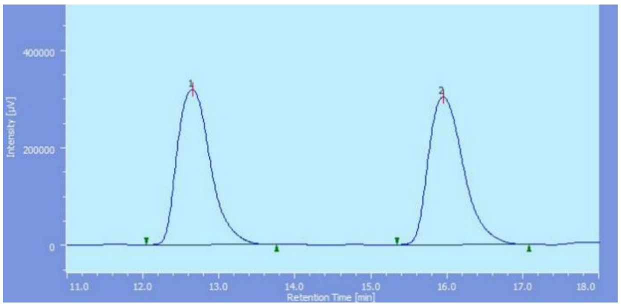
Peak	t_R (min)	Area (%)
1	11.0	98.6
2	13.7	1.4

(*S*)-2-(3-Bromophenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4ga**)

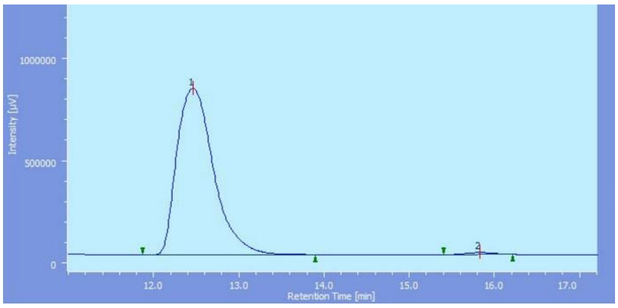


4ga (18.2 mg, 97% yield, 98% ee) was obtained by the general procedure using iminonitrile **1g** (15.5 mg, 0.05 mmol), pyrrole **2a** (4.2 µL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 µmol). The crude **4ga** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

White solid. **m.p.**: 102.0-103.0 ˚C. **Optical Rotation**: $[\alpha]_D^{25.0}$ = −29.6 (98% ee, *c* 0.693, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.71 (br, 1H), 8.74 (br, 1H), 7.74 (t, *J* = 2.0 Hz, 1H), 7.57-7.52 (m, 2H), 6.81-6.79 (m, 1H), 6.13 (dd, *J* = 6.2, 3.0 Hz, 1H), 5.98 (s, 1H), 5.45 (s, 1H), 1.40 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.5, 132.4, 130.6, 128.9, 127.2, 124.6, 124.5, 123.1, 120.3, 109.6, 109.1, 82.4, 56.7, 28.1; **IR** (ATR) 3336, 2978, 2321, 1706, 1473, 1157, 781 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{17}H_{18}BrN_3NaO$ 398.0475; found 398.1477; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 97:3, 1.0 mL/min, 215 nm) 98% ee, t_R 12.5 (major), t_R 15.8 (minor) min.

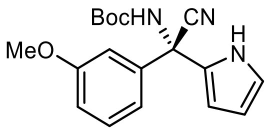


Peak	t_R (min)	Area (%)
1	12.6	50.0
2	15.9	50.0



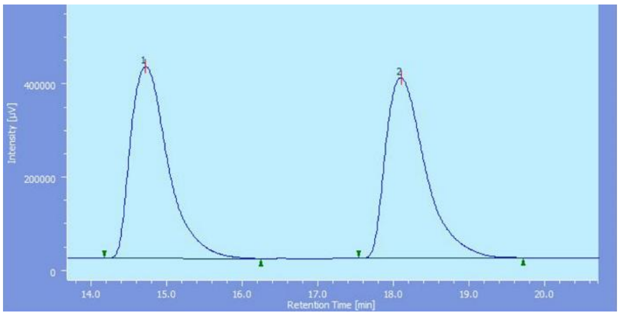
Peak	t_R (min)	Area (%)
1	12.5	98.8
2	15.8	1.2

(*S*)-2-(3-Methoxyphenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4ha**)

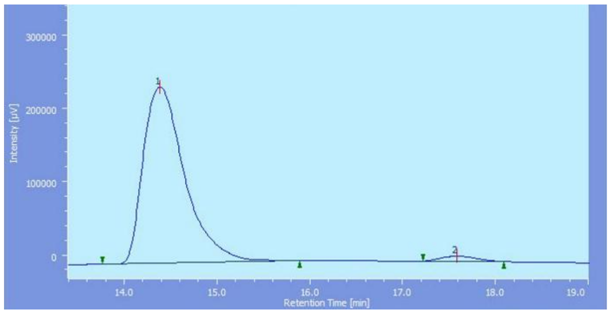


4ha (15.7 mg, 96% yield, 95% ee) was obtained by the general procedure using iminonitrile **1h** (13.0 mg, 0.05 mmol), pyrrole **2a** (4.2 µL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 µmol). The crude **4ha** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

Pale yellow oil. **Optical Rotation**: $[\alpha]_D^{25.0}$ = −79.6 (95% ee, *c* 0.317, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.77 (br, 1H), 7.36 (t, *J* = 8.1 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.13-7.11 (m, 1H), 6.95 (dd, *J* = 8.1, 2.5 Hz, 1H), 6.76 (dd, *J* = 4.5, 2.4 Hz, 1H), 6.12 (q, *J* = 3.0 Hz, 1H), 6.01 (br, 1H), 5.43 (br, 1H), 3.82 (s, 3H), 1.40 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 160.1, 153.8, 138.7, 130.2, 128.0, 119.9, 118.3, 118.1, 114.8, 111.7, 109.3, 108.9, 82.1, 57.1, 55.4, 28.1; **IR** (ATR) 3336, 2977, 2848, 2319, 1702, 1158, 739 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{18}H_{21}N_3NaO_2$ 350.1475; found 350.1482; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 97:3, 1.0 mL/min, 215 nm) 95% ee, t_R 14.4 (major), t_R 17.7 (minor) min.

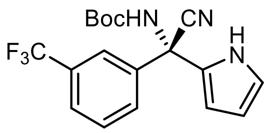


Peak	t_R (min)	Area (%)
1	14.7	50.0
2	18.1	50.0



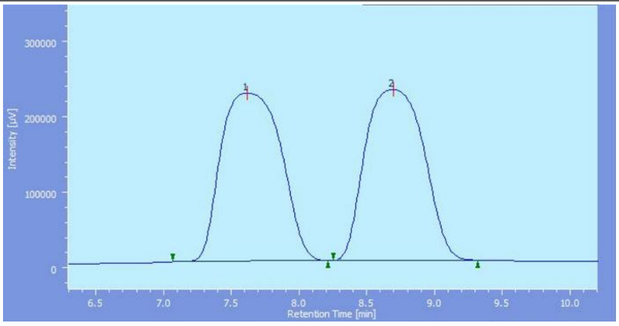
Peak	t_R (min)	Area (%)
1	14.4	97.6
2	17.7	2.4

(*S*)-2-(3-Methoxyphenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4ia**)

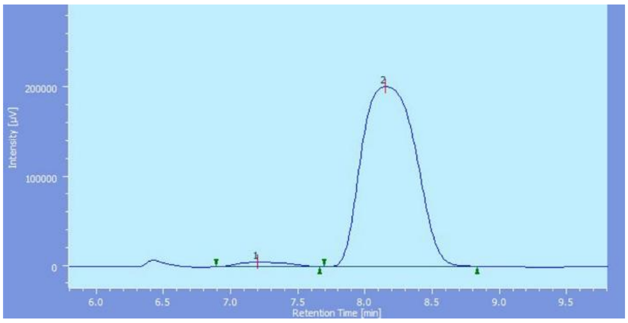


4ia (17.7 mg, 97% yield, 95% ee) was obtained by the general procedure using iminonitrile **1i** (14.9 mg, 0.05 mmol), pyrrole **2a** (4.2 µL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 µmol). The crude **4ia** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

Pale yellow oil. **Optical Rotation**: $[\alpha]_D^{25.0}$ = −73.0 (95% ee, *c* 0.223, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.71 (br, 1H), 7.84-7.79 (m, 2H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 6.82 (q, *J* = 2.3 Hz, 1H), 6.13 (q, *J* = 3.0 Hz, 1H), 5.92 (s, 1H), 5.52 (br, 1H), 4.15 (d, *J* = 12.6 Hz, 1H), 1.38 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.5, 131.5 (q, $J_{C\text{-}F}$ = 32.5 Hz), 129.7, 129.5, 127.0, 126.1, 123.6 (q, $J_{C\text{-}F}$ = 262.4 Hz), 122.6, 122.6, 120.6, 118.0, 109.8, 109.2, 82.6, 57.1, 28.0; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ −62.7; **IR** (ATR) 3336, 2924, 2319, 1704, 1328, 1162, 734 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{18}H_{18}F_3N_3NaO_2$ 388.1243; found 388.1244; **HPLC** (CHIRALPAK IK, Hexane/^{i}PrOH = 97:3, 1.0 mL/min, 215 nm) 95% ee, t_R 7.3 (major), t_R 8.2 (minor) min.

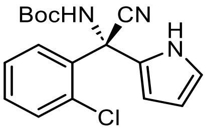


Peak	t_R (min)	Area (%)
1	7.6	50.0
2	8.7	50.0



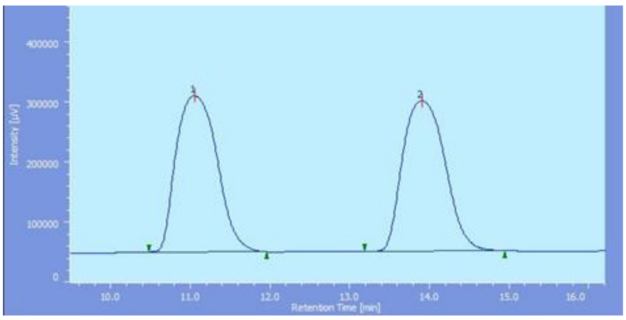
Peak	t_R (min)	Area (%)
1	7.3	2.3
2	8.2	97.7

(*S*)-2-(2-Chlorophenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4ja)

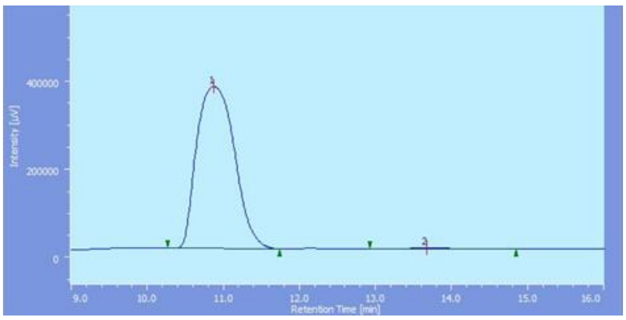


4ja (14.7 mg, 89% yield, 98% ee) was obtained by the general procedure using iminonitrile **1j** (13.2 mg, 0.05 mmol), pyrrole **2a** (4.2 μL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 μmol). The crude **4ja** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

Pale yellow oil. **Optical Rotation**: $[\alpha]_D^{25.0}$ = −4.9 (98% ee, *c* 0.56, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.62 (br, 1H), 7.61-7.57 (m, 1H), 7.46-7.34 (m, 3H), 6.82-6.80 (m, 1H), 6.19-6.10 (m, 2H), 5.66 (s, 1H), 1.39 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.5, 133.6, 132.3, 132.0, 130.6, 129.7, 127.2, 126.0, 119.8, 117.2, 109.3, 109.3, 82.1, 57.0, 28.1; **IR** (ATR) 3334, 2979, 2324, 1702, 1558, 1367, 1157, 889, 743 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{17}H_{18}ClN_3NaO_2$ 354.0980; found 354.0988; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 97:3, 1.0 mL/min, 215 nm) 98% ee, t_R 10.9 (major), t_R 13.7 (minor) min.

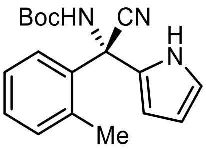


Peak	t_R (min)	Area (%)
1	11.1	50.0
2	14.0	50.0



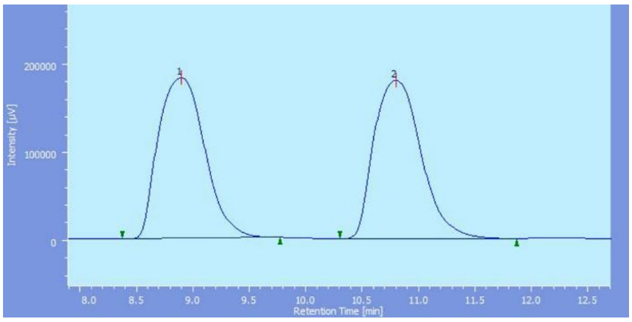
Peak	t_R (min)	Area (%)
1	10.9	99.2
2	13.7	0.8

(*S*)-2-(2-Methylphenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4ka)

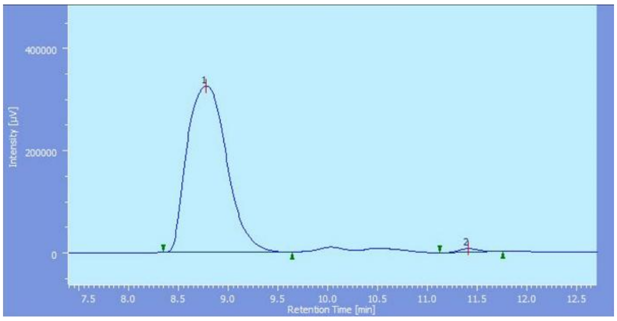


4ka (8.7 mg, 56% yield, 98% ee) was obtained by the general procedure using iminonitrile **1k** (12.2 mg, 0.05 mmol), pyrrole **2a** (4.2 μL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 μmol). The crude **4ka** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

Colorless oil. **Optical Rotation**: $[\alpha]_D^{25.0}$ = −71.2 (98% ee, *c* 0.177, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.51 (br, 1H), 7.52 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.35-7.19 (m, 3H), 6.78-6.76 (m, 1H), 6.18-6.15 (m, 1H), 6.12 (s, 1H), 5.34 (br, 1H), 2.31 (s, 3H), 1.41 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.7, 136.2, 134.2, 133.0, 131.0, 129.4, 127.3, 126.8, 126.4, 119.6, 118.0, 109.2, 82.1, 56.9, 28.1, 20.9; **IR** (ATR) 3336, 2978, 2852, 2320, 1698, 1367, 1159,737 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{18}H_{21}N_3NaO_2$ 334.1526; found 334.1532; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 97:3, 1.0 mL/min, 215 nm) 98% ee, t_R 8.8 (major), t_R 11.4 (minor) min.

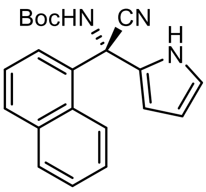


Peak	t_R (min)	Area (%)
1	8.9	50.0
2	10.8	50.0



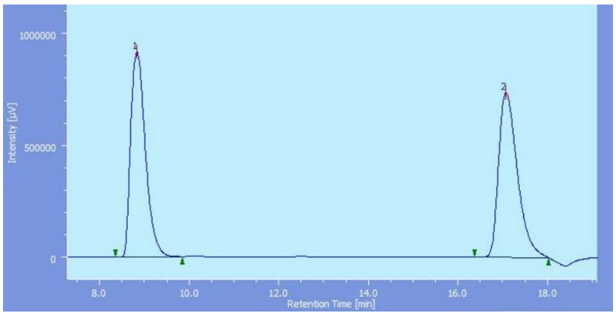
Peak	t_R (min)	Area (%)
1	8.8	99.0
2	11.4	1.0

(*S*)-2-(1-Naphtyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4la**)

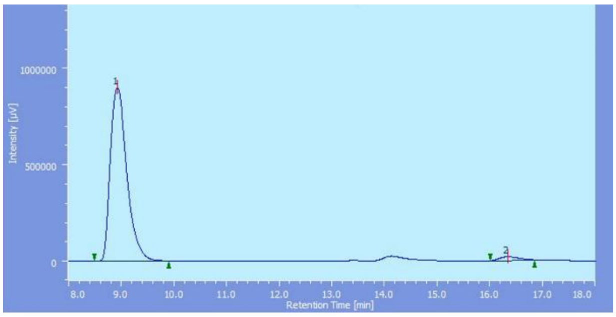


4la (16.0 mg, 92% yield, 95% ee) was obtained by the general procedure using iminonitrile **1l** (14.0 mg, 0.05 mmol), pyrrole **2a** (4.2 µL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 µmol). The crude **4la** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

Pale yellow oil. **Optical Rotation**: $[\alpha]_D^{25.0}$ = +23.8 (95% ee, *c* 0.290, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 9.22 (br, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.96-7.90 (m, 3H), 7.78 (s, 1H), 7.54-7.45 (m, 4H), 6.81-6.79 (m, 1H), 6.12 (s, 1H), 5.98 (br, 1H), 5.56 (s, 1H), 4.29 (d, *J* = 12.6 Hz, 1H), 4.15 (d, *J* = 12.6 Hz, 1H), 1.41 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 154.2, 134.8, 131.2, 129.3, 129.3, 127.5, 126.7, 126.7, 126.2, 125.5, 124.9, 119.6, 118.0, 111.9, 109.9, 108.9, 82.2, 57.4, 28.2; **IR** (ATR) 3290, 2928, 2319, 1702, 1157, 748 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{21}N_3NaO_2$ 370.1526; found 370.1527; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 95:5, 1.0 mL/min, 215 nm) 95% ee, t_R 8.9 (major), t_R 16.6 (minor) min.

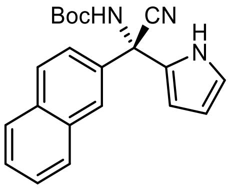


Peak	t_R (min)	Area (%)
1	8.8	50.0
2	17.1	50.0



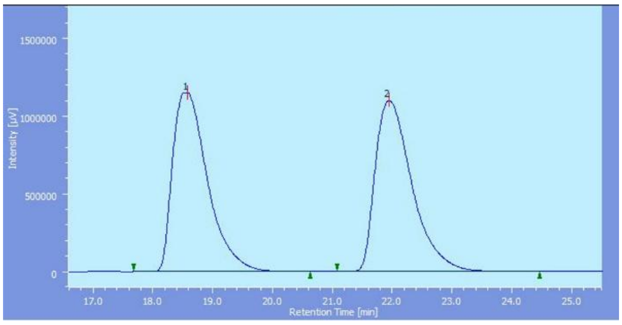
Peak	t_R (min)	Area (%)
1	8.9	97.7
2	16.6	2.3

(*S*)-2-(2-Naphtyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4ma**)

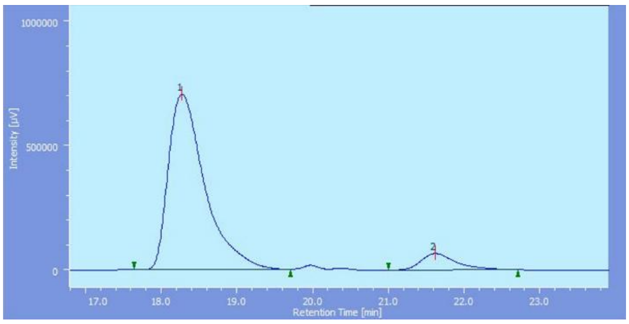


4ma (15.8 mg, 91% yield, 81% ee) was obtained by the general procedure using iminonitrile **1m** (14.0 mg, 0.05 mmol), pyrrole **2a** (4.2 µL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 µmol). The crude **4ma** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

Pale yellow oil. **Optical Rotation**: $[\alpha]_D^{25.0} = -15.1$ (81% ee, *c* 0.347, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.82 (br, 1H), 8.12 (d, J = 2.0 Hz, 1H), 7.94-7.87 (m, 3H), 7.64-7.52 (m, 3H), 6.77 (dd, J = 4.3, 2.8 Hz, 1H), 6.12 (m, 1H), 6.00 (br, 1H), 5.61 (s, 1H), 1.38 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.9, 133.3, 132.9, 129.2, 128.5, 128.0, 127.7, 127.2, 127.0, 125.6, 123.0, 120.0, 118.4, 109.4, 108.9, 82.2, 57.3, 28.1; **IR** (ATR) 3354, 2978, 2318, 1698, 1366, 1157, 752 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{21}N_3NaO_2$ 370.1526; found 370.1538; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 97:3, 1.0 mL/min, 215 nm) 81% ee, t_R 18.2 (major), t_R 21.6 (minor) min.

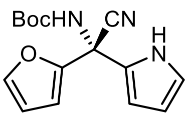


Peak	t_R (min)	Area (%)
1	18.6	50.0
2	21.9	50.0



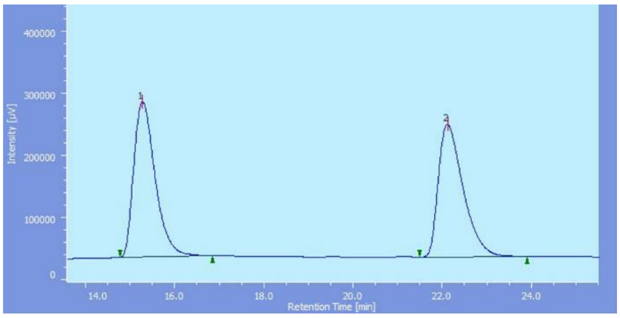
Peak	t_R (min)	Area (%)
1	18.2	91.7
2	21.6	8.3

(*S*)-2-(2-Furyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4na**)

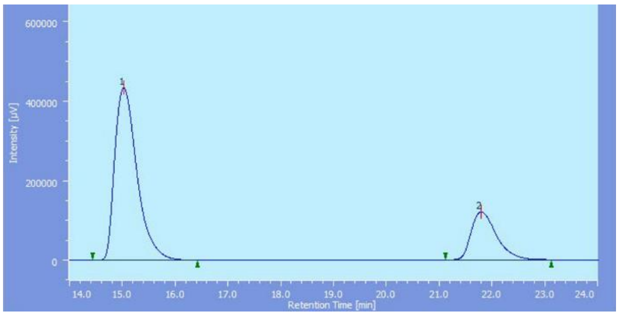


4na (13.5 mg, 94% yield, 52% ee) was obtained by the general procedure using iminonitrile **1n** (11.1 mg, 0.05 mmol), pyrrole **2a** (4.2 μL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 μmol). The crude **4na** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

Dark brown oil. **Optical Rotation**: $[\alpha]_D^{25.0}$ = −6.4 (52% ee, *c* 0.270, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 9.10 (br, 1H), 7.48-7.46 (m, 1H), 6.80 (dd, *J* = 4.7, 2.3 Hz, 1H),.6.54 (dd, *J* = 3.4, 0.9 Hz, 1H), 6.44 (dd, *J* = 3.4, 1.9 Hz, 1H), 6.14 (dd, *J* = 6.0, 3.4 Hz, 1H), 5.53 (s, 1H), 1.43 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.8, 147.9, 143.6, 126.3, 119.9, 116.5, 111.1, 109.6, 108.7, 108.7, 82.3, 52.1, 28.1; **IR** (ATR) 3334, 2918, 2320, 1716, 1488, 1157, 880, 733 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{15}H_{17}N_3NaO_3$ 310.1162; found 310.1165; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 97:3, 1.0 mL/min, 215 nm) 52% ee, t_R 15.0 (major), t_R 21.8 (minor) min.

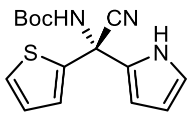


Peak	t_R (min)	Area (%)
1	15.3	50.0
2	22.1	50.0



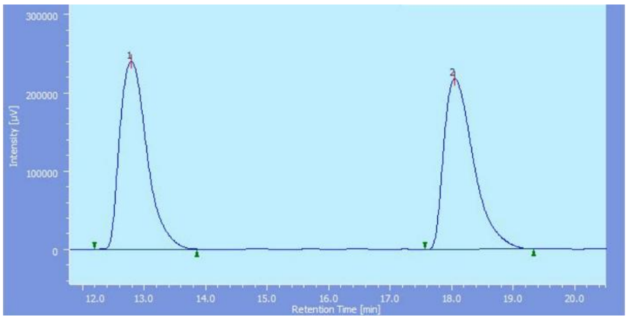
Peak	t_R (min)	Area (%)
1	15.0	78.2
2	21.8	21.8

(*S*)-2-(2-Thienyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4oa**)

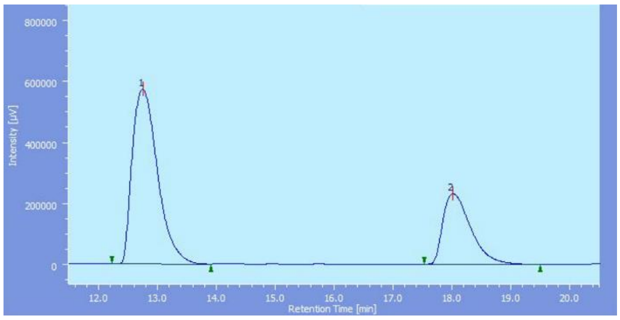


4oa (14.0 mg, 92% yield, 39% ee) was obtained by the general procedure using iminonitrile **1o** (11.8 mg, 0.05 mmol), pyrrole **2a** (4.2 μL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 μmol). The crude **4oa** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

Brown amorphous solid. **Optical Rotation**: $[\alpha]_D^{25.0}$ = +2.0 (39% ee, *c* 0.28, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.89 (br, 1H), 7.32 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.29 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.03-7.01 (m, 1H), 6.81-6.78 (m, 1H), 6.19 (s, 1H), 6.17-6.14 (m, 1H), 5.51 (br, 1H), 1.42 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.6, 141.2, 127.9, 127.2, 126.9, 119.8, 117.7, 108.9, 82.4, 53.8, 28.1; **IR** (ATR) 3344, 2979, 2317, 1669, 1234, 1151, 1002, 665 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{15}H_{217}N_3NaO_2S$ 326.0934; found 326.0937; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 97:3, 1.0 mL/min, 215 nm) 39% ee, t_R 12.8 (major), t_R 18.0 (minor) min.

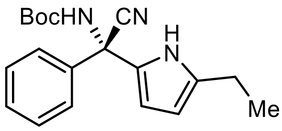


Peak	t_R (min)	Area (%)
1	12.7	50.0
2	18.0	50.0



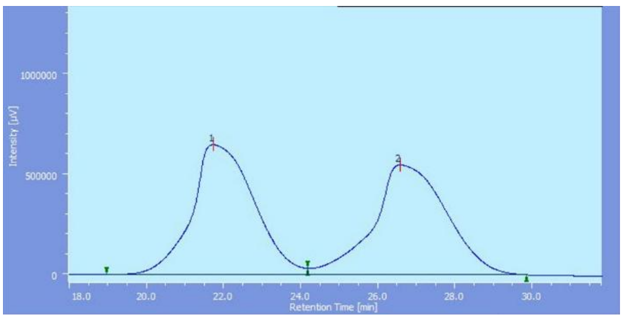
Peak	t_R (min)	Area (%)
1	12.8	69.5
2	18.0	30.5

(*S*)-2-Phenyl-2-(5-ethyl-1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4ab**)

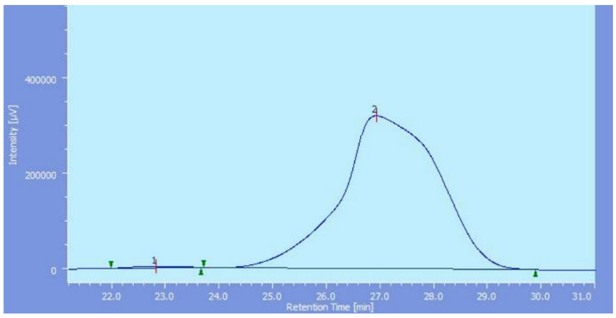


4ab (15.9 mg, 98% yield, 99% ee) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05 mmol), pyrrole **2b** (10.0 µL in 6M Toluene solution, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 µmol). The crude **4ab** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 80:20).

Yellow oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = +8.5 (99% ee, *c* 0.29, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.57 (br, 1H), 7.62-7.59 (m, 2H), 7.48-7.38 (m, 3H), 5.78-5.73 (m, 2H), 5.45 (s, 1H), 2.57 (q, *J* = 7.6 Hz, 1H), 1.38 (s, 9H), 1.22 (t, *J* = 7.6 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 152.8, 135.8, 128.1, 127.9, 124.9, 117.5, 108.7, 103.8, 81.0, 56.2, 27.0, 19.8, 12.3; **IR** (ATR) 3330, 2974, 2239, 1702, 1450, 1366, 1159, 756, 697 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{19}H_{23}N_3NaO_2$ 348.1682; found 348.1681; **HPLC** (CHIRALPAK IC-3, Hexane/^{i}PrOH = 99:1, 1.0 mL/min, 215 nm) 99% ee, t_R 22.8 (major), t_R 26.9 (minor) min.

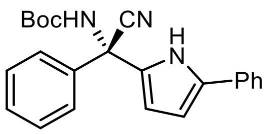


Peak	t_R (min)	Area (%)
1	21.7	50.0
2	26.6	50.0



Peak	t_R (min)	Area (%)
1	22.8	0.4
2	26.9	99.6

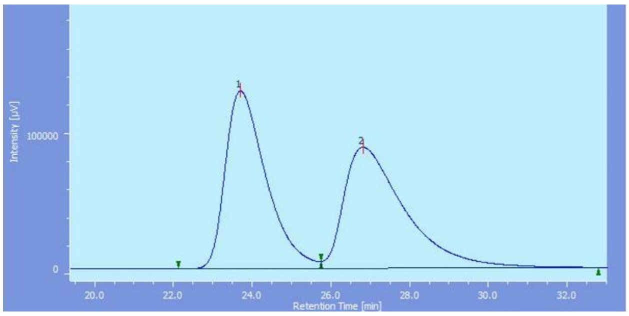
(*S*)-2-Phenyl-2-(5-phenyl-1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4ac**)



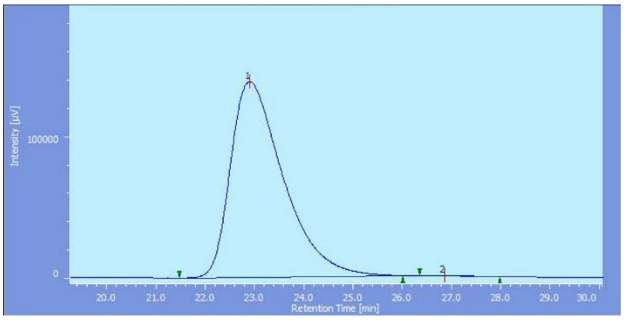
4ac (17.7 mg, 95% yield, 99.6% ee) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05

mmol), pyrrole **2c** (8.6 mg, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 μmol). The crude **4ac** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 80:20).

Pale yellow oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = −48.2 (99% ee, *c* 0.64, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 9.25 (br, 1H), 7.80 (m, *J* = 8.2 Hz, 2H), 7.46-7.34 (m, 7H), 7.27-7.22 (m, 1H), 6.35 (t, *J* = 3.2 Hz, 2H), 5.89 (s, 1H), 5.57 (s, 1H), 1.41 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 154.0, 138.2, 136.9, 134.7, 131.7, 129.0, 128.2, 127.9, 127.2, 124.2, 117.9, 111.5, 106.0, 95.4, 82.6, 57.0, 28.1; **IR** (ATR) 3341, 2978, 2309, 1708, 1482, 1368, 1160, 967, 757 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{23}N_3NaO_2$ 396.1682; found 396.1688; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 95:5, 1.0 mL/min, 215 nm) 99.6% ee, t_R 22.9 (major), t_R 26.8 (minor) min.

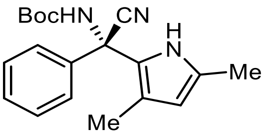


Peak	t_R (min)	Area (%)
1	23.2	50.0
2	26.8	50.0



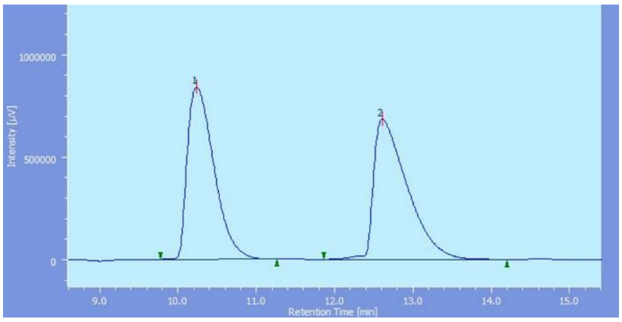
Peak	t_R (min)	Area (%)
1	22.9	99.8
2	26.8	0.2

(*S*)-2-Phenyl-2-(3,5-dimethyl-1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4ad)

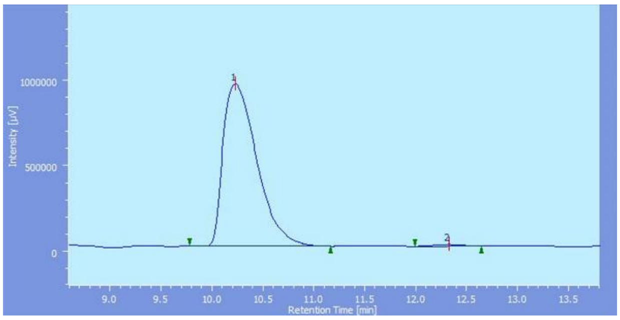


4ad (15.8 mg, 97% yield, 99.6% ee) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05 mmol), pyrrole **2d** (6.2 μL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 μmol). The crude **4ad** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 80:20).

Yellow oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = −19.0 (99% ee, *c* 0.50, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.62-7.58 (m, 2H), 7.51-7.43 (m, 3H), 7.05 (br, 1H), 5.72 (d, *J* = 3.0 Hz, 1H), 5.27 (s, 1H), 2.12 (s, 3H), 2.07 (s, 3H), 1.34 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.1, 137.2, 129.2, 129.2, 127.6, 126.2, 119.9, 118.7, 118.2, 110.9, 81.8, 56.8, 28.0, 12.8, 11.8; **IR** (ATR) 3341, 2978, 2929, 2239, 1701, 1366, 1158, 1052, 753 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{19}H_{23}N_3NaO_2$ 348.1682; found 348.1687; **HPLC** (CHIRALPAK IH-3, Hexane/^{i}PrOH = 95:5, 1.0 mL/min, 215 nm) 99.6% ee, t_R 23.0 (major), t_R 26.8 (minor) min.

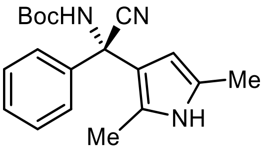


Peak	t_R (min)	Area (%)
1	10.2	49.8
2	12.6	50.2



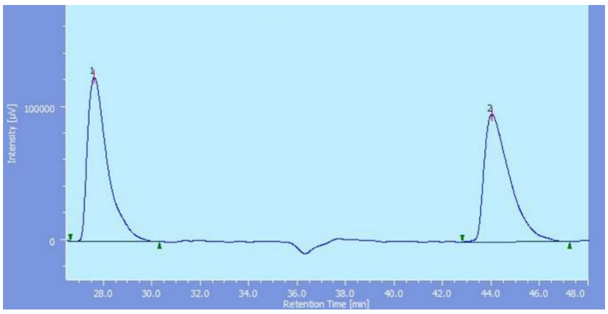
Peak	t_R (min)	Area (%)
1	10.2	99.8
2	12.3	0.2

(*S*)-2-Phenyl-2-(2,5-dimethyl-1*H*-pyrrol-3-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4ae**)

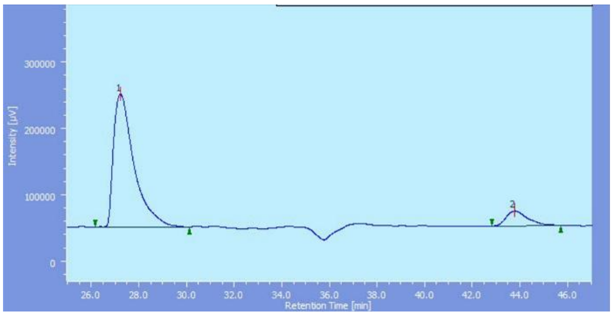


4ae (14.0 mg, 86% yield, 80% ee) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05 mmol), pyrrole **2a** (6.1 μL, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 μmol). The crude **4ae** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 80:20).

Yellow oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = −26.9 (80% ee, *c* 0.49, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.88 (br, 1H), 7.56-7.48 (m, 2H), 7.42-7.31 (m, 3H), 5.27 (s, 1H), 5.23 (s, 1H), 2.19 (s, 3H), 2.08 (s, 3H), 1.33 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.4, 139.5, 128.5, 128.1, 125.9, 125.1, 124.0, 119.5, 117.4, 106.0, 81.4, 56.9, 28.1, 12.6, 12.3; **IR** (ATR) 3353, 2977, 2238, 1701, 1367, 1248, 1158, 1099, 1052, 697 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{19}H_{23}N_3NaO_2$ 348.1682; found 348.1696; **HPLC** (CHIRALPAK IH-3, Hexane/^{i}PrOH = 95:5, 1.0 mL/min, 215 nm) 80% ee, t_R 23.0 (major), t_R 26.8 (minor) min.

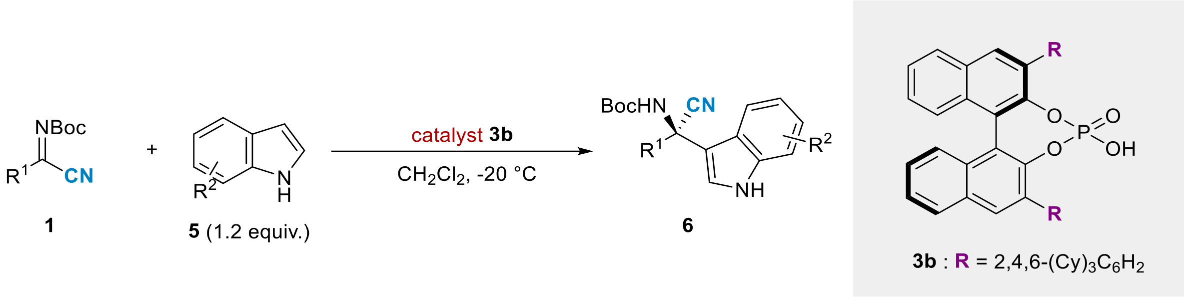


Peak	t_R (min)	Area (%)
1	27.6	50.0
2	44.0	50.0



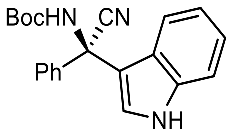
Peak	t_R (min)	Area (%)
1	27.3	89.8
2	43.9	10.2

General procedure for the asymmetric synthesis of 6



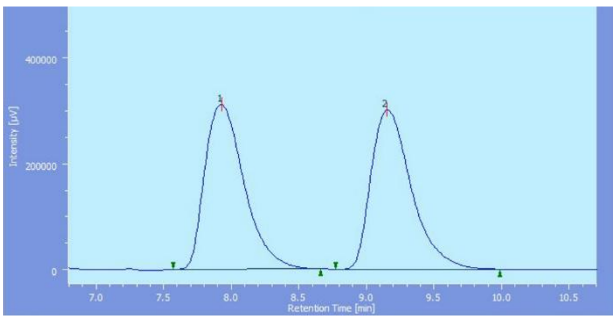
To a flame-dried flask, catalyst **3b** (5 mol%) and α-iminonitrile **1** (1.0 equiv., 0.05 mmol) were dissolved in dry CH_2Cl_2 (0.1 M) and cooled to 0 ˚C. Indole **5** (1.2 equiv.) was added in one portion, and the solution was stirred at that temperature for 12 hours. The reaction mixture was concentrated under reduced pressure. Product **6** was purified by silica-gel column chromatography.

(*R*)-2-(1*H*-Indol-3-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6aa)

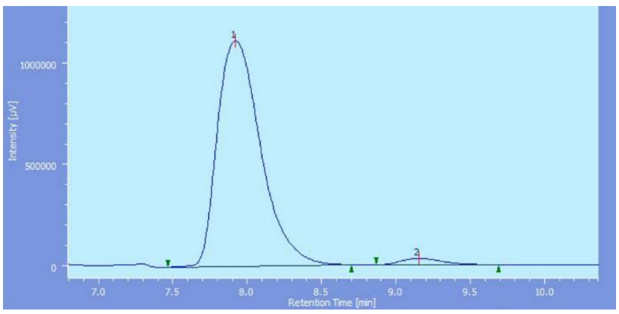


6aa (16.2 mg, 93% yield, 95% ee) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05 mmol), indole **5a** (7.0 mg, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 μmol). The crude **6aa** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 70:30).

White solid. **m.p.**: 193.5-194.0 ˚C. **Optical Rotation:** $[\alpha]_D^{25.0}$ = −232.2 (95% ee, *c* 0.18, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.20 (br, 1H), 7.86 (s, 1H), 7.67-7.64 (m, 2H), 7.46-7.38 (m, 4H), 7.30-7.20 (m, 2H), 6.60 (br, 1H), 5.49 (br, 1H), 1.36 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.3, 138.4, 136.9, 128.7, 128.6, 125.9, 124.9, 123.8, 123.3, 120.9, 119.6, 119.1, 115.0, 111.8, 81.5, 56.9, 28.1; **IR** (ATR) 3336, 2978, 2245, 1702, 1480, 1367, 1158, 742, 698 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{21}N_3NaO_2$ 370.1526; found 370.1531; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 85:15, 1.0 mL/min, 215 nm) 95% ee, t_R 7.9 (major), t_R 9.2 (minor) min.

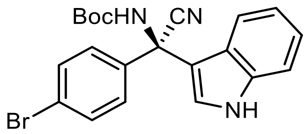


Peak	t_R (min)	Area (%)
1	7.9	50.0
2	9.2	50.0



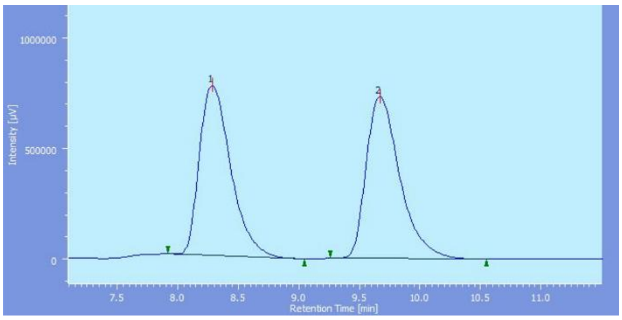
Peak	t_R (min)	Area (%)
1	7.9	97.5
2	9.2	2.5

(*R*)-2-(1*H*-Indol-3-yl)-2-(4-bromophenyl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**6ba**)

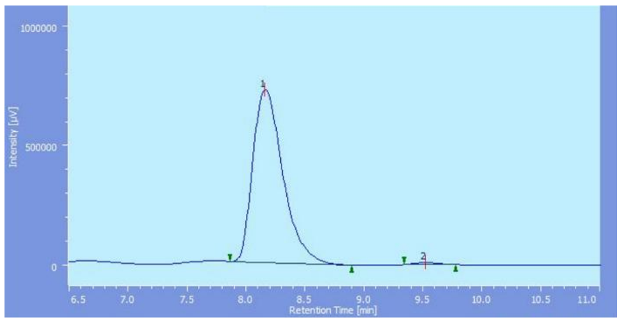


6ba (19.8 mg, 93% yield, 98% ee) was obtained by the general procedure using iminonitrile **1d** (15.5 mg, 0.05 mmol), indole **5a** (7.0 mg, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 μmol). The crude **6ba** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 80:20).

Purple oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = +65.5 (98% ee, *c* 0.50, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.30 (br, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.60-7.48 (m, 4H), 7.40-7.27 (m, 2H), 7.25-7.19 (m, 1H), 6.60 (s, 1H), 5.51 (br, 1H), 1.39 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.2, 137.5, 136.9, 131.8, 127.7, 124.7, 123.5, 122.7, 121.1, 119.4, 118.7, 114.5, 111.9, 111.7, 82.0, 56.6, 28.1; **IR** (ATR) 3349, 2979, 2248, 1701, 1485, 1367, 1158, 1010, 813, 743 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{20}BrN_3NaO_2$ 448.0631; found 448.0636; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 85:15, 1.0 mL/min, 215 nm) 98% ee, t_R 8.1 (major), t_R 9.5 (minor) min.

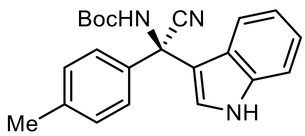


Peak	$t_{R\ (min)}$	Area (%)
1	8.3	50.0
2	9.7	50.0



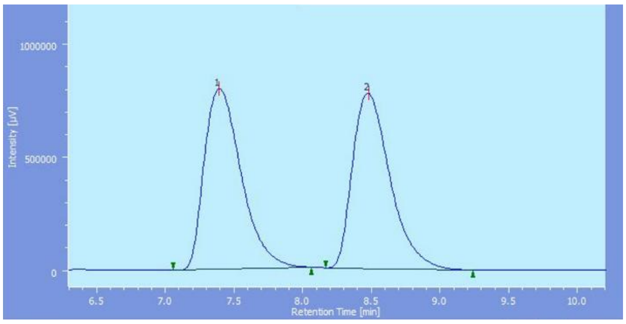
Peak	$t_{R\ (min)}$	Area (%)
1	8.1	99.1
2	9.5	0.9

(*R*)-2-(1*H*-Indol-3-yl)-2-(4-methylphenyl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**6ca**)

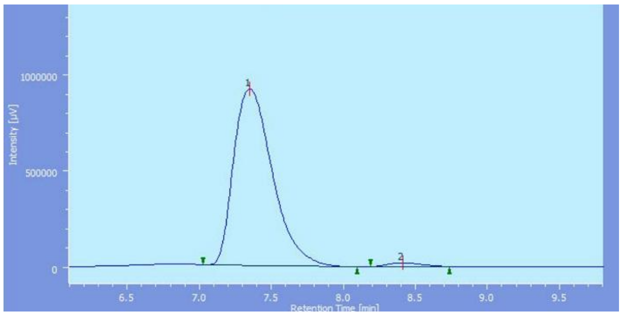


6ca (17.2 mg, 95% yield, 96% ee) was obtained by the general procedure using iminonitrile **1f** (12.2 mg, 0.05 mmol), indole **5a** (7.0 mg, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 μmol). The crude **6ca** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 70:30).

Pale brown oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = −14.8 (96% ee, *c* 0.34, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.30 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.51-7.49 (m, 3H), 7.37-7.16 (m, 4H), 6.61 (s, 1H), 5.47 (br, 1H), 2.37 (s, 3H), 1.37 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.4, 138.4, 136.9, 135.4, 129.3, 125.8, 124.9, 123.8, 123.2, 120.8, 119.6, 119.2, 115.1, 111.8, 81.6, 56.7, 28.1, 21.1; **IR** (ATR) 3345, 2979, 2239, 1701, 1479, 1367, 1159, 1049, 808, 743 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{22}H_{23}N_3NaO_2$ 384.1682; found 384.1680; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 85:15, 1.0 mL/min, 215 nm) 96% ee, t_R 7.4 (major), t_R 8.4 (minor) min.

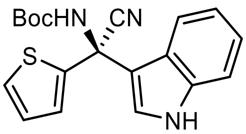


Peak	t_R (min)	Area (%)
1	7.4	50.0
2	8.5	50.0



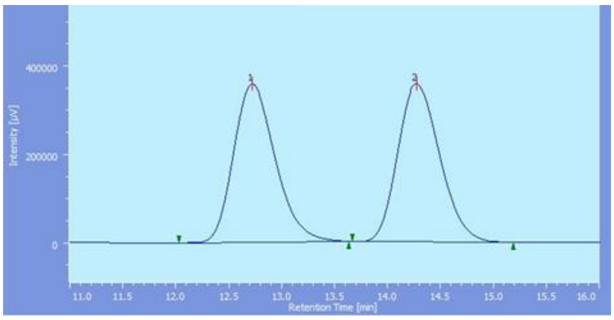
Peak	t_R (min)	Area (%)
1	7.4	98.2
2	8.4	1.8

(*R*)-2-(1*H*-Indol-3-yl)-2-(2-thienyl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**6da**)

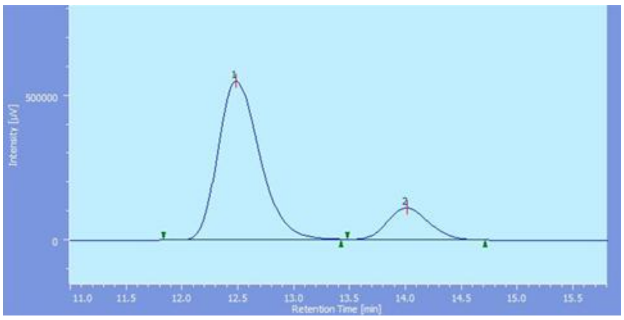


6da (17.3 mg, 98% yield, 67% ee) was obtained by the general procedure using iminonitrile **1n** (11.8 mg, 0.05 mmol), indole **5a** (7.0 mg, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 μmol). The crude **6da** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 70:30).

Brown oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = +2.3 (67% ee, *c* 0.45, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.45 (br, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.38-7.27 (m, 3H), 7.24-7.16 (m, 2H), 7.01-6.96 (m, 2H), 5.57 (br, 1H), 1.41 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.2, 143.3, 136.9, 126.9, 126.7, 126.1, 124.5, 123.5, 123.2, 120.8, 119.6, 118.5, 114.7, 111.9, 81.8, 53.6, 28.1; **IR** (ATR) 3727, 3346, 2360, 2293, 1699, 1459, 1367, 1157, 1024, 840, 703 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{19}H_{19}N_3NaO_2S$ 376.1090; found 376.1098; **HPLC** (CHIRALPAK IM, Hexane/^{i}PrOH = 88:12, 1.0 mL/min, 215 nm) 67% ee, t_R 12.5 (major), t_R 14.0 (minor) min.

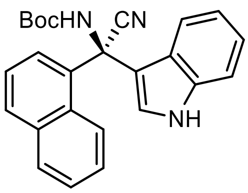


Peak	t_R (min)	Area (%)
1	12.7	50.0
2	14.3	50.0



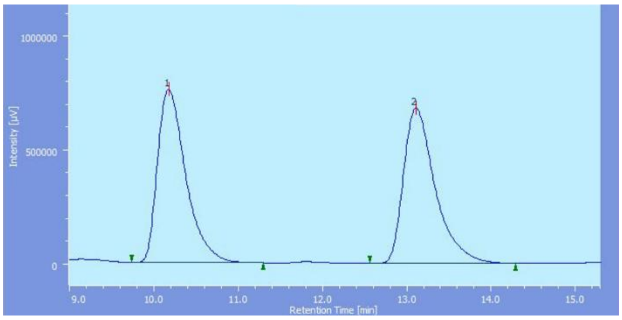
Peak	t_R (min)	Area (%)
1	12.5	83.5
2	14.0	16.5

(*R*)-2-(1*H*-Indol-3-yl)-2-(1-naphtyl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**6ea**)

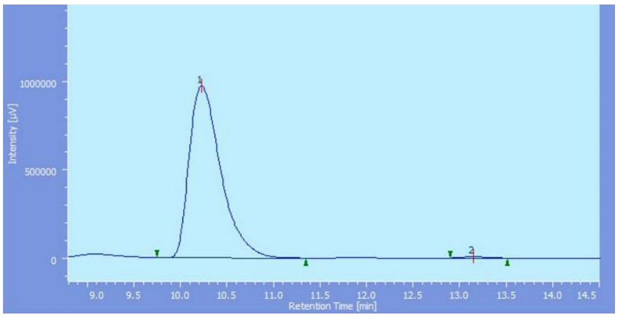


6ea (14.5 mg, 73% yield, 99% ee) was obtained by the general procedure using iminonitrile **1l** (14.0 mg, 0.05 mmol), indole **5a** (7.0 mg, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 μmol). The crude **6ea** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

Yellow oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = +33.1 (99% ee, *c* 0.23, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.51 (s, 1H), 8.29 (d, *J* = 8.5 Hz, 2H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.77-7.72 (m, 2H), 7.49-7.37 (m, 4H), 7.33-7.12 (m, 2H), 6.70 (s 1H), 5.68 (br, 1H), 1.31 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 174.1, 154.9, 136.8, 128.4, 128.0, 127.3, 126.2, 125.2, 122.4, 120.0, 116.2, 111.6, 80.0, 66.2, 28.3; **IR** (ATR) 3344, 2925, 2854, 2318, 1708, 1482, 1367, 1160, 744 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{25}H_{23}N_3NaO_2$ 420.1682; found 420.1683; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 88:12, 1.0 mL/min, 215 nm) 99% ee, t_R 10.2 (major), t_R 13.1 (minor) min.

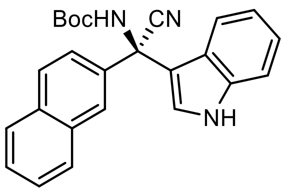


Peak	t_R (min)	Area (%)
1	10.2	50.0
2	13.1	50.0



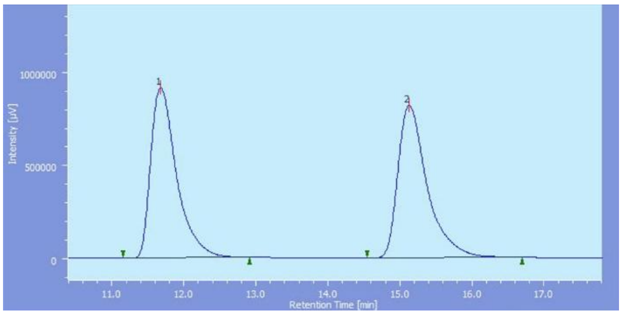
Peak	t_R (min)	Area (%)
1	10.2	99.4
2	13.1	0.6

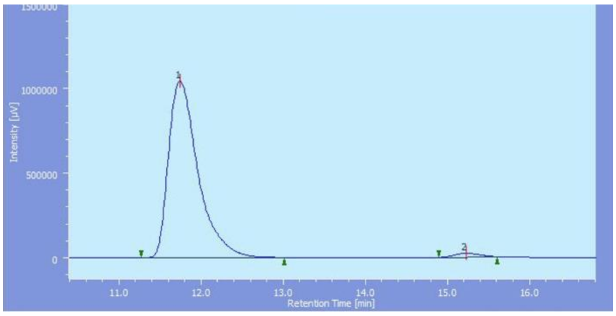
(*R*)-2-(1*H*-Indol-3-yl)-2-(2-naphtyl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**6fa**)



6fa (16.3 mg, 82% yield, 97% ee) was obtained by the general procedure using iminonitrile **1m** (14.0 mg, 0.05 mmol), indole **5a** (7.0 mg, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 μmol). The crude **6fa** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 75:25).

Pale yellow oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = +63.8 (97% ee, *c* 0.23, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.26 (s, 1H), 8.17 (s, 1H), 7.90-7.85 (m, 5H), 7.68-7.65 (m, 1H), 7.55-7.52 (m, 2H), 7.37-7.34 (m, 1H), 7.28-7.18 (m, 1H), 6.54 (s, 1H), 5.60 (br, 1H), 1.33 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.4, 136.9, 133.2, 133.0, 128.7, 128.6, 128.4, 127.7, 126.8, 126.7, 125.4, 125.0, 123.8, 123.8, 123.4, 121.0, 119.6, 119.1, 114.9, 111.9, 81.7, 57.0, 28.1; **IR** (ATR) 3314, 2926, 2237, 1701, 1479, 1366, 1157, 1051, 744 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{25}H_{23}N_3NaO_2$ 420.1682; found 420.1689; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 88:12, 1.0 mL/min, 215 nm) 97% ee, t_R 11.7 (major), t_R 15.2 (minor) min.

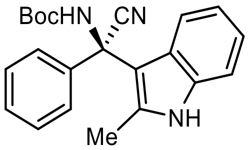




Peak	t_R (min)	Area (%)
1	11.6	50.0
2	15.1	50.0

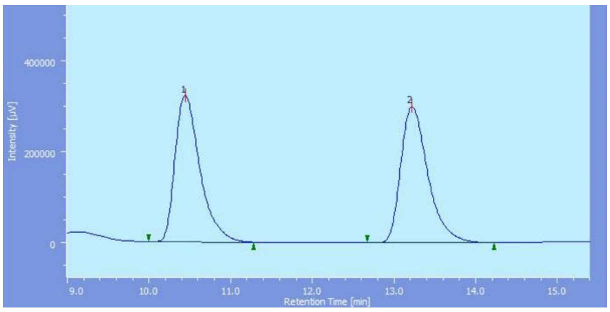
Peak	t_R (min)	Area (%)
1	11.7	98.3
2	15.2	1.7

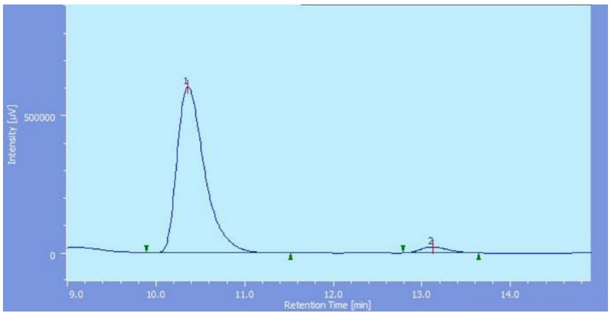
(*R*)-2-(2-Methyl-1*H*-indol-3-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6ab)



6ab (17.2 mg, 95% yield, 93% ee) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05 mmol), indole **5b** (7.9 mg, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 μmol). The crude **6ab** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 70:30).

Yellow oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = +9.0 (93% ee, *c* 0.34, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.04 (br, 1H), 7.67-7.63 (m, 2H), 7.47-7.23 (m, 5H), 7.16-7.02 (m, 3H), 5.43 (br, 1H),1.99 (s, 3H), 1.36 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.3, 138.7, 134.6, 133.7, 128.9, 128.8, 126.6, 125.9, 125.8, 122.0, 120.4, 119.3, 110.6, 108.1, 81.5, 57.5, 28.1, 13.2; **IR** (ATR) 3339, 2979, 2310, 1701, 1482, 1367, 1256, 1159, 890, 742 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{22}H_{23}N_3NaO_2$ 384.1682; found 384.1689; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 88:12, 1.0 mL/min, 215 nm) 93% ee, t_R 10.4 (major), t_R 13.1 (minor) min.

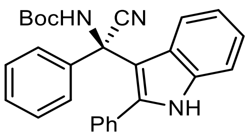




Peak	t_R (min)	Area (%)
1	10.4	49.9
2	13.2	50.1

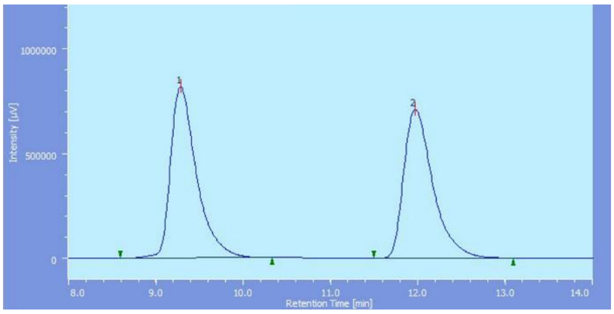
Peak	t_R (min)	Area (%)
1	10.4	96.5
2	13.1	3.5

(*R*)-2-Phenyl-2-(2-phenyl-1*H*-indol-3-yl) -2-(*tert*-butoxycarbonylamino)acetonitrile (6ac)

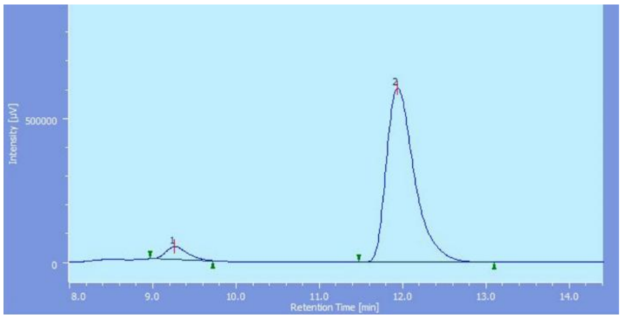


6ac (19.3 mg, 91% yield, 89% ee) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05 mmol), indole **5c** (11.6 mg, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 μmol). The crude **6ac** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 78:22).

Yellow oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = +19.3 (89% ee, *c* 0.57, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.30 (br, 1H), 7.58-7.55 (m, 3H), 7.37-7.20 (m, 10H), 7.14-7.09 (m, 1H), 5.32 (s, 1H), 1.26 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 152.9, 138.9, 136.8, 135.3, 132.2, 129.8, 129.0, 128.8, 128.7, 128.2, 127.2, 126.1, 122.9, 120.8, 120.5, 119.0, 11.1, 109.0, 81.2, 57.6, 28.0; **IR** (ATR) 3316, 2978, 2239, 1697, 1487, 1366, 1156, 1001, 743, 664 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{27}H_{25}N_3NaO_2$ 446.1839; found 446.1846; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 88:12, 1.0 mL/min, 215 nm) 89% ee, t_R 9.3 (major), t_R 11.9 (minor) min.

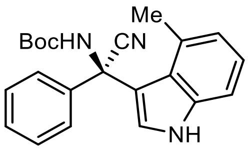


Peak	t_R (min)	Area (%)
1	9.3	50.0
2	12.0	50.0



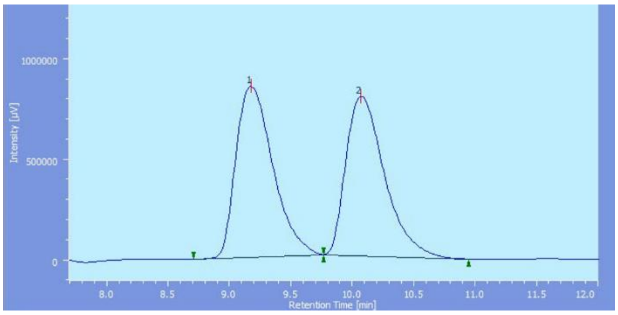
Peak	t_R (min)	Area (%)
1	9.3	5.4
2	11.9	94.6

(*R*)-2-(4-Methyl-1*H*-indol-3-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6ad)

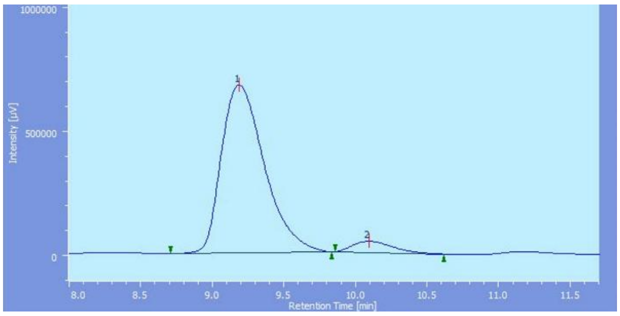


6ad (17.5 mg, 97% yield, 89% ee) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05 mmol), indole **5d** (7.5 µL, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 µmol). The crude **6ad** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 70:30).

Pale yellow oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = −27.4 (89% ee, *c* 0.05, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.30 (br, 1H), 7.65-7.62 (m, 2H), 7.44-7.41 (m, 3H), 7.20-7.11 (m, 2H), 7.00 (d, *J* = 6.7 Hz, 1H), 6.26 (br, 1H), 5.52 (br, 1H), 2.86 (s, 3H), 1.36 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 152.8, 139.3, 137.9, 130.4, 128.8, 128.6, 126.7, 126.4, 123.6, 123.4, 123.3, 120.2, 115.8, 109.6, 81.6, 57.2, 28.2, 22.4; **IR** (ATR) 3337, 2980, 2309, 1692, 1482, 1366, 1157, 1050, 889, 747 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{22}H_{23}N_3NaO_2$ 384.1682; found 384.1689; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 88:12, 1.0 mL/min, 215 nm) 89% ee, t_R 9.2 (major), t_R 10.2 (minor) min.

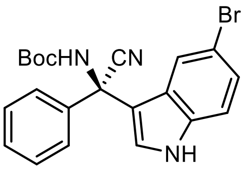


Peak	t_R (min)	Area (%)
1	9.2	50.0
2	10.8	50.0



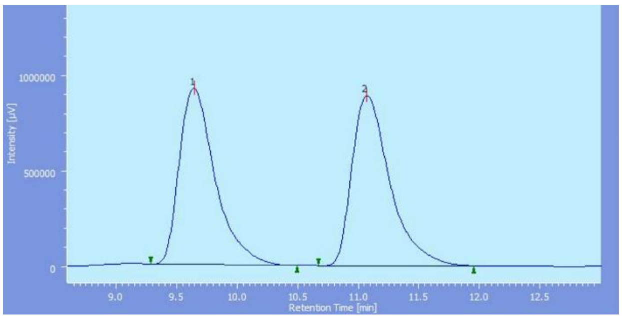
Peak	t_R (min)	Area (%)
1	9.2	94.3
2	10.2	5.7

(*R*)-2-(5-Bromo-1*H*-indol-3-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6ae)

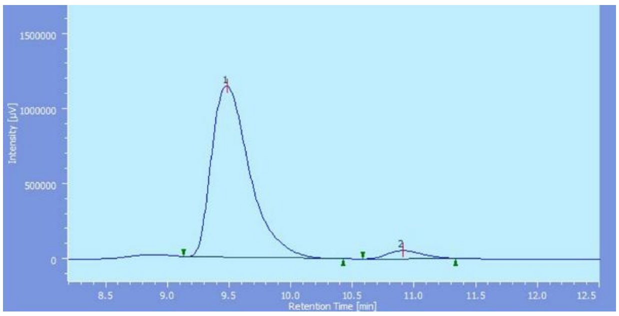


6ae (20.7 mg, 97% yield, 92% ee) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05 mmol), indole **5e** (11.8 mg, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 μmol). The crude **6ae** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 70:30).

Pale brown oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = +52.2 (92% ee, *c* 0.30, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.54 (br, 1H), 7.89 (s, 1H), 7.60-7.55 (m, 2H), 7.45-7.37 (m, 3H), 7.31-7.28 (m, 1H), 7.17 (d, *J* = 8.7 Hz, 1H), 5.45 (br, 1H), 1.37 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.4, 138.2, 135.5, 128.9, 128.9, 126.2, 126.1, 125.9, 125.7, 125.4, 121.9, 119.0, 114.1, 113.4, 81.9, 56.8, 28.1; **IR** (ATR) 3320, 2979, 2242, 1701, 1482, 1366, 1049, 1001, 924, 747 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{20}BrN_3NaO_2$ 448.0631; found 448.0626; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 88:12, 1.0 mL/min, 215 nm) 92% ee, t_R 9.4 (major), t_R 10.9 (minor) min.

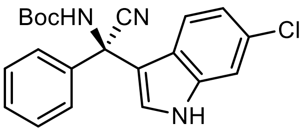


Peak	t_R (min)	Area (%)
1	9.2	50.0
2	10.8	50.0



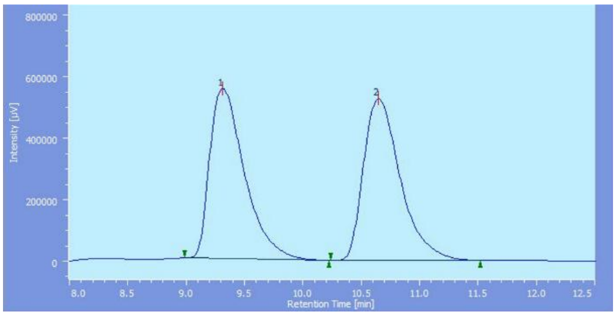
Peak	t_R (min)	Area (%)
1	9.4	96.0
2	10.9	4.0

(*R*)-2-(6-Chloro-1*H*-indol-3-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6af)

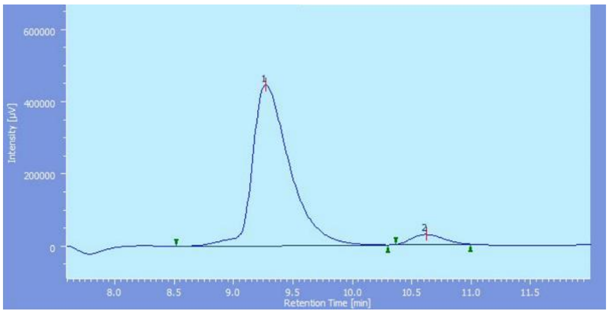


6af (18.5 mg, 97% yield, 90% ee) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05 mmol), indole **5f** (9.1 mg, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 μmol). The crude **6af** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 70:30).

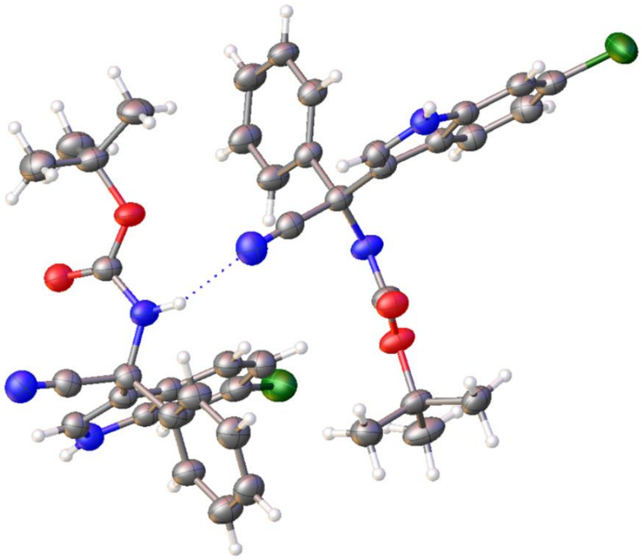
White solid. **m.p.**: 211.0-212.0 ˚C. **Optical Rotation:** $[\alpha]_D^{25.0}$ = +21.7 (90% ee, *c* 0.53, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.33 (br, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.62-7.59 (m, 2H), 7.43-7.40 (m, 3H), 7.35-7.34 (m, 1H), 7.16 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.63 (s, 1H), 5.44 (br, 1H), 1.36 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.3, 137.3, 130.1, 129.3, 128.8, 128.5, 125.9, 125.4, 122.4, 121.7, 120.5, 119.0, 115.1, 111.8, 81.8, 56.9, 28.1; **IR** (ATR) 3352, 3266, 2927, 2248, 1693, 1483, 1364, 1154, 1059, 905, 809, 690 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{20}ClN_3NaO_2$ 404.1136; found 404.1142; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 88:12, 1.0 mL/min, 215 nm) 90% ee, t_R 9.3 (major), t_R 10.6 (minor) min.



Peak	t_R (min)	Area (%)
1	9.3	50.0
2	10.6	50.0



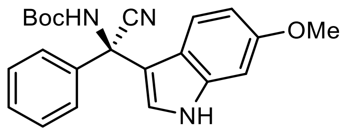
Peak	t_R (min)	Area (%)
1	9.3	94.9
2	10.6	5.1



Empirical Formula	$C_{21}H_{20}N_3O_2Cl$
Formula weight	381.85
Temperature/K	153.15
Crystal system	triclinic
Space group	P_1
a/Å	9.7777(3)
b/Å	10.8697(2)
c/Å	11.3717(3)
α/°	62.837
β/°	64.591
γ/°	74.964
Volume/Å^3	968.24(5)

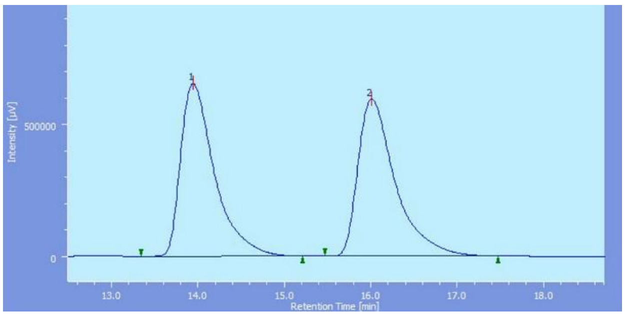
Z	2
ρcalcg/cm^3	1.310
μ/mm^{-1}	1.914
F(000)	400.0
Crystal size/mm^3	0.084 x 0.61 x 0.044
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.174 to 153.05
Index ranges	$-12 \le h \le 12$, $-13 \le k \le 13$, $-14 \le l \le 14$
Reflections collected	73028
Independent reflections	7705 [R_{int} = 0.0784, R_{sigma} = 0.0394]
Data/restraints/parameters	7705/3/493
Goodness-of-fit on F2	1.083
Final R indexes [I>=2σ (I)]	R_1 = 0.0532, wR_2 = 0.1392
Final R indexes [all data]	R_1 = 0.0588, wR_2 = 0.1448
Largest diff. peak/hole / e Å^{-3}	0.22/-0.726
Flack parameter	-0.010(18)

(*R*)-2-(6-Methoxy-1*H*-indol-3-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (**6ag**)

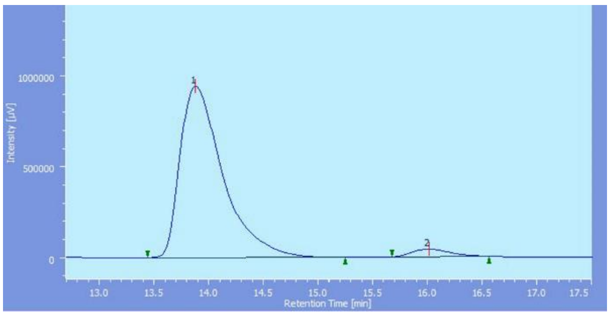


6ag (18.5 mg, 98% yield, 92% ee) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05 mmol), indole **5g** (8.9 mg, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 μmol). The crude **6ag** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 70:30).

Pale brown oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = −18.6 (92% ee, *c* 0.16, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.08 (br, 1H), 7.70-7.61 (m, 3H), 7.45-7.42 (m, 3H), 6.88-6.82 (m, 2H), 6.48 (s, 1H), 5.46 (br, 1H), 3.83 (s, 3H), 1.36 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 157.1, 153.4, 138.4, 137.8, 128.6, 128.6, 125.9, 123.7, 120.1, 119.3, 118.1, 114.9, 110.9, 95.0, 81.7, 57.1, 55.6, 28.1; **IR** (ATR) 3315, 2978, 2309, 1708, 1630, 1482, 1367, 1159, 889, 694 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{22}H_{23}N_3NaO_2$ 400.1632; found 400.1638; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 88:12, 1.0 mL/min, 215 nm) 92% ee, t_R 13.9 (major), t_R 16.0 (minor) min.

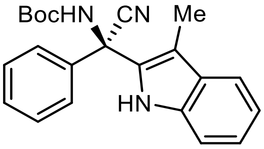


Peak	t_R (min)	Area (%)
1	13.9	50.0
2	16.0	50.0



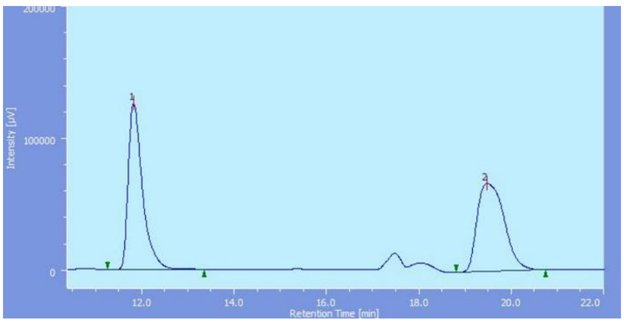
Peak	t_R (min)	Area (%)
1	13.9	96.2
2	16.0	3.8

(*R*)-2-(3-Methyl-1*H*-indol-2-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6ah)

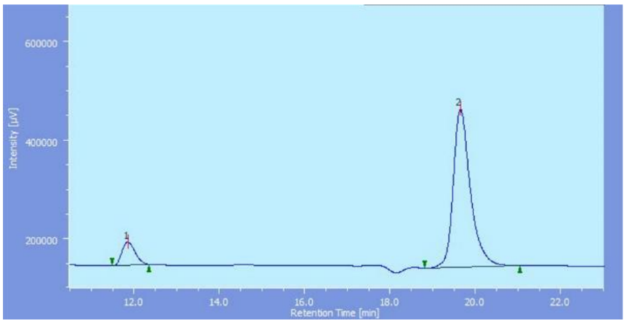


6ah (16.1 mg, 89% yield, 81% ee) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05 mmol), indole **5h** (7.9 mg, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 μmol). The crude **6ah** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 70:30).

Colorless oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = +16.5 (81% ee, *c* 0.04, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.76 (br, 1H), 7.59-7.56 (m, 3H), 7.49-7.44 (m, 3H), 7.24-7.11 (m, 3H), 5.51 (s, 1H), 2.38 (s, 3H), 1.36 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.0, 136.7, 134.5, 129.7, 129.5, 129.4, 127.9, 126.3, 123.4, 120.0, 119.1, 117.8, 111.1, 110.7, 82.3, 57.3, 28.0, 28.0; **IR** (ATR) 3341, 2978, 2249, 1702, 1452, 1367, 1156, 1051, 908, 730 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{22}H_{23}N_3NaO_2$ 384.1682; found 384.1683; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 95:5, 1.0 mL/min, 215 nm) 81% ee, t_R 13.9 (major), t_R 16.0 (minor) min.

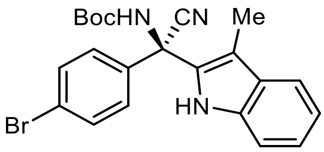


Peak	t_R (min)	Area (%)
1	11.6	50.0
2	15.2	50.0



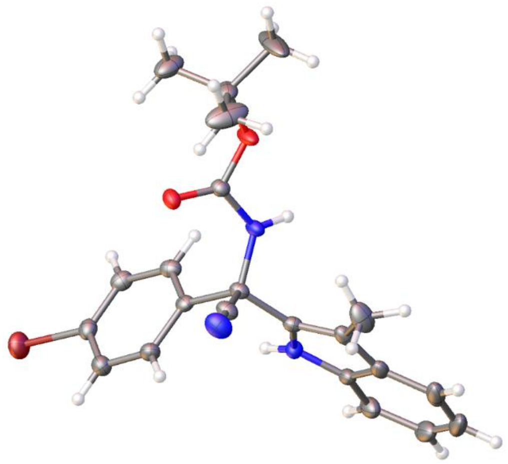
Peak	t_R (min)	Area (%)
1	13.9	10.2
2	16.0	89.8

(*R*)-2-(3-Methyl-1*H*-indol-2-yl)-2-(4-bromophenyl)-2-(*tert*-butoxycarbonylamino)acetonitrile (6ai)

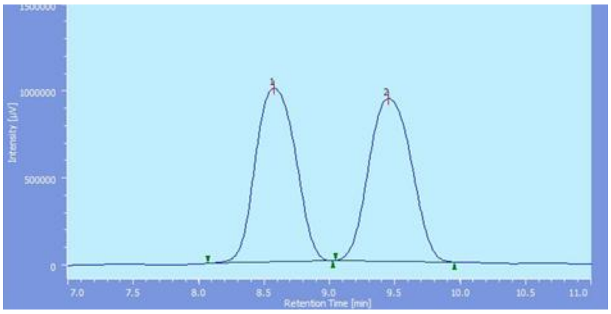


6ai (18.3 mg, 83% yield, 85% ee) was obtained by the general procedure using iminonitrile **1d** (15.5 mg, 0.05 mmol), 2-methylindole **5i** (7.9 mg, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 μmol). The crude **6ai** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 80:20).

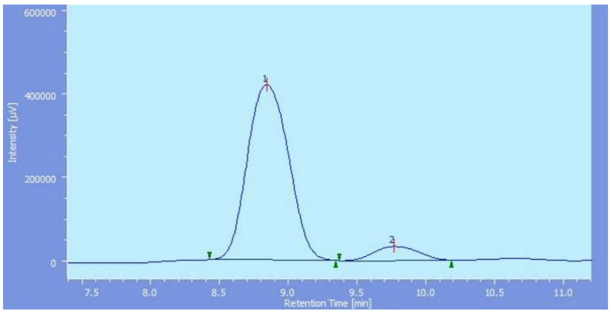
White solid. **Optical Rotation:** $[\alpha]_D^{25.0}$ = −180.05 (83% ee, *c* 0.08, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.76 (br, 1H), 7.62-7.55 (m, 3H), 7.46-7.43 (m, 2H), 7.26-7.11 (m, 3H), 5.50 (br, 1H), 2.36 (s, 3H), 1.37 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 153.1, 135.9, 134.6, 132.5, 129.4, 128.0, 127.3, 123.9, 123.6, 120.2, 119.2, 117.5, 111.2, 111.0, 82.7, 56.99, 28.1, 9.2; **IR** (ATR) 3724, 3047, 2298, 1765, 1504, 1428, 1372, 1206, 1054, 930, 797 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{22}H_{22}N_3NaO_2$ 462.0788; found 462.0776; **HPLC** (CHIRALPAK IK, Hexane/^{i}PrOH = 95:5, 1.0 mL/min, 215 nm) 85% ee, t_R 8.8 (major), t_R 9.8 (minor) min.



Empirical Formula	$C_{22}H_{22}N_3O_2Br$
Formula weight	440.33
Temperature/K	103(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.35120(10)
b/Å	11.21500(10)
c/Å	19.5965(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2055.16(4)
Z	2
ρcalcg/cm^3	1.423
μ/mm^{-1}	2.904
F(000)	904.0
Crystal size/mm^3	0.156 x 0.129 x 0.081
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.026 to 151.508
Index ranges	$-11 \leq h \leq 11$, $-12 \leq k \leq 14$, $-24 \leq l \leq 24$
Reflections collected	23219
Independent reflections	4135 [R_{int} = 0.0174, R_{sigma} = 0.0112]
Data/restraints/parameters	4135/0/257
Goodness-of-fit on F2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0217, wR_2 = 0.0547
Final R indexes [all data]	R_1 = 0.0217, wR_2 = 0.0547
Largest diff. peak/hole / e Å^{-3}	0.25/-0.38
Flack parameter	-0.023(3)

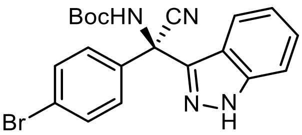


Peak	t_R (min)	Area (%)
1	8.6	50.0
2	9.5	50.0



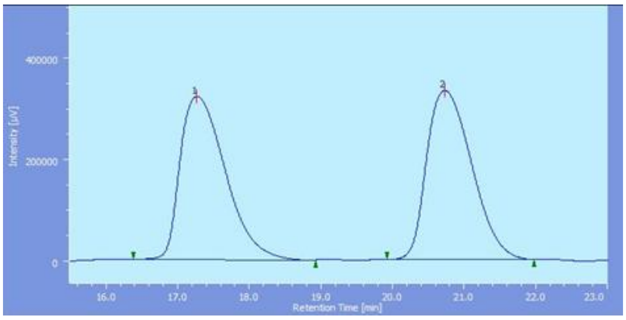
Peak	t_R (min)	Area (%)
1	8.8	92.3
2	9.8	7.8

(*R*)-2-(1*H*-Indazol-3-yl)-2-(4-bromophenyl)-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6ak)

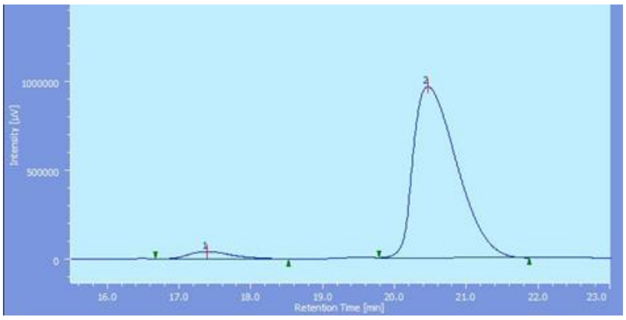


6ak (16.0 mg, 75% yield, 92% ee) was obtained by the general procedure using iminonitrile **1a** (15.5 mg, 0.05 mmol), indazole **5k** (7.1 mg, 0.06 mmol) and catalyst **3a** (1.9 mg, 2.5 μmol). The crude **6ak** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 80:20).

White solid. **Optical Rotation:** $[\alpha]_D^{25.0}$ = 21.0 (92% ee, *c* 0.59, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.15 (s, 1H), 7.78-7.75 (m, 1H), 7.55-7.51 (m, 2H), 7.33-7.28 (m, 3H), 7.25-7.15 (m, 2H), 6.72 (s, 1H), 1.37 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 152.5, 138.2, 135.5, 135.1, 132.5, 128.0, 127.8, 126.1, 125.0, 122.3, 121.7, 115.4, 111.0, 82.9, 72.1, 28.0; **IR** (ATR) 3301, 2982, 2310, 1867, 1707, 1488, 1370, 1244, 1011, 825 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{20}H_{19}N_4NaO_2$ 449.0584; found 449.0589; **HPLC** (CHIRALPAK IBN-3, Hexane/^{i}PrOH = 98:2, 1.0 mL/min, 215 nm) 92% ee, t_R 17.4 (minor), t_R 20.5 (major) min.

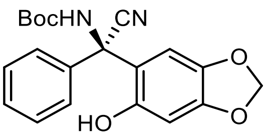


Peak	t_R (min)	Area (%)
1	17.3	50.0
2	20.7	50.0



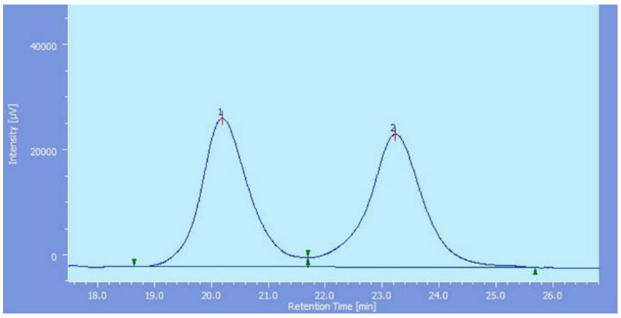
Peak	t_R (min)	Area (%)
1	17.4	3.9
2	20.5	96.1

(*R*)-2-(6-Hydroxybenzo[*d*][1,3]dioxol-5-yl)-2-(4-bromophenyl)-2-(*tert*-butoxycarbonylamino)acetonitrile (6al)

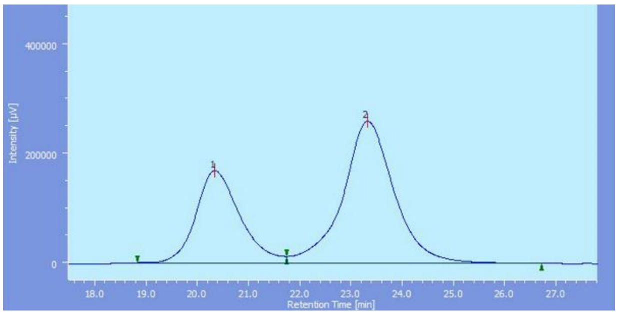


6al (16.9 mg, 92% yield, 29% ee) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05 mmol), sesamol **5l** (8.3 mg, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 μmol). The crude **6al** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 80:20).

Colorless oil. **Optical Rotation:** $[\alpha]_D^{25.0} = -10.0$ (29% ee, *c* 0.43, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.43-7.31 (m, 5H), 6.80 (s, 1H), 6.61 (s, 1H), 5.97 (dd, *J* = 4.1, 1.4 Hz, 2H), 5.61 (s, 1H), 1.35 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 154.0, 149.4, 148.6, 144.1, 140.0, 129.2, 129.1, 128.7, 125.7, 121.0, 104.6, 101.7, 93.8, 81.0, 65.3, 28.2; **IR** (ATR) 3361, 2980, 2774, 2261, 1708, 1477, 1288, 1157, 1028, 936, 750 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{20}H_{20}N_2NaO_5$ 391.1264; found 391.1269; **HPLC** (CHIRALPAK IH-3, Hexane/^{i}PrOH = 90:10, 1.0 mL/min, 215 nm) 29% ee, t_R 20.3 (major), t_R 23.3 (minor) min.

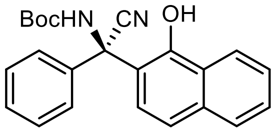


Peak	t_R (min)	Area (%)
1	20.2	50.0
2	23.2	50.0



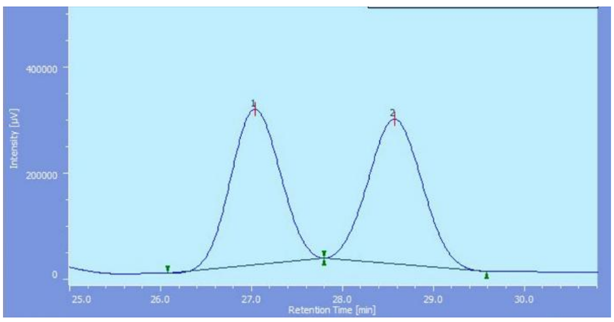
Peak	t_R (min)	Area (%)
1	20.3	35.6
2	23.3	64.4

(*R*)-2-(1-Hydroxynaphtalen-2-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6am)

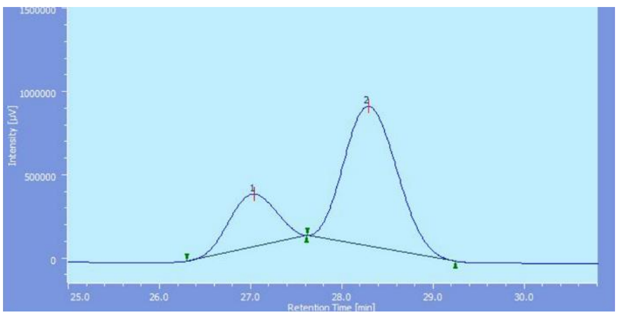


6am (15.7 mg, 84% yield, 50% ee) was obtained by the general procedure using iminonitrile **1a** (11.5 mg, 0.05 mmol), 1-naphthol **5m** (8.7 mg, 0.06 mmol) and catalyst **3b** (2.5 mg, 2.5 μmol). The crude **6am** was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 80:20).

Yellow oil. **Optical Rotation:** $[\alpha]_D^{25.0} = -26.1$ (50% ee, *c* 0.17, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.08 (br, 1H), 7.87 (d, *J* = 7.4 Hz, 2H) , 7.65-7.26 (m, 10H), 5.66 (br, 1H), 1.25 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 171.2, 154.1, 150.6, 140.0, 134.7, 129.1, 128.7, 128.2, 127.0, 126.5, 126.3, 125.3, 123.8, 123.3, 121.5, 119.8, 80.8, 65.5, 28.1; **IR** (ATR) 3421, 2978, 2317, 1701, 1602, 1507, 1368, 1099, 969, 823, 774 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{23}H_{22}N_2NaO_3$ 397.1523; found 397.1524; **HPLC** (CHIRALPAK IK, Hexane/^{i}PrOH = 95:5, 1.0 mL/min, 215 nm) 50% ee, t_R 27.0 (major), t_R 28.3 (minor) min.

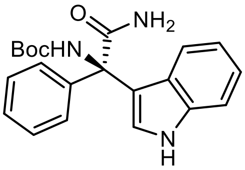


Peak	t_R (min)	Area (%)
1	27.0	50.0
2	28.5	50.0



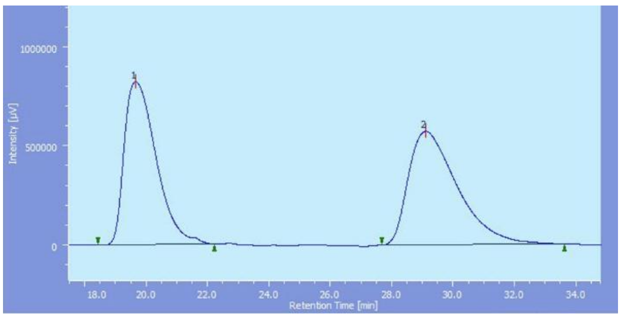
Peak	t_R (min)	Area (%)
1	27.0	24.9
2	28.3	75.1

(*R*)-2-(1*H*-Indol-3-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetamide (**7**)

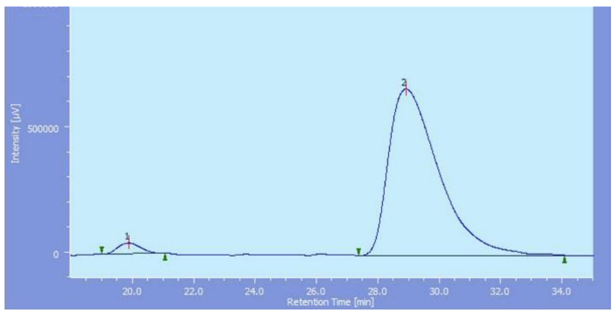


In a round bottomed flask, $InCl_3$ (4.6 mg, 30 mol%) and acetaldoxime (17.0 μL, 5.0 equiv.) were added to a solution of **6aa** (17.4 mg, 0.05 mmol) in benzene. The mixture was stirred at 0 °C for 10 min and warmed up to room temperature. After stirring 48 h, the crude mixture was concentrated under reduced pressure, the resulting mixture was purified by silica-gel column chromatography (eluent: Hexane/AcOEt, 60:40).

Colorless oil. **Optical Rotation:** $[\alpha]_D^{25.0}$ = −248.2 (95% ee, *c* 0.057, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.63 (br, 1H), 7.59-7.56 (m, 2H), 7.43-7.35 (m, 4H), 7.05-7.01 (m, 3H), 6.67 (br, 1H), 6.58 (br, 1H), 6.39 (m, 1H), 5.67 (br, 1H), 1.35 (s, 9H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 174.3, 154.9, 140.0, 136.8, 128.4, 128.0, 127.3, 126.5, 125.1, 122.2, 119.8, 119.7, 115.7, 111.7, 80.0, 66.1, 28.3; **IR** (ATR) 3372, 2960, 2924, 2355, 1692, 1462, 1261, 1165, 1033, 804 cm^{-1}; **HRMS** (ESI) m/z: $[M+Na]^+$ calculated for $C_{21}H_{23}N_3NaO_3$ 388.1632; found 395.1632; **HPLC** (CHIRALPAK IH, Hexane/^{i}PrOH = 85:15, 1.0 mL/min, 215 nm) 94% ee, t_R 19.9 (major), t_R 28.9 (minor) min.



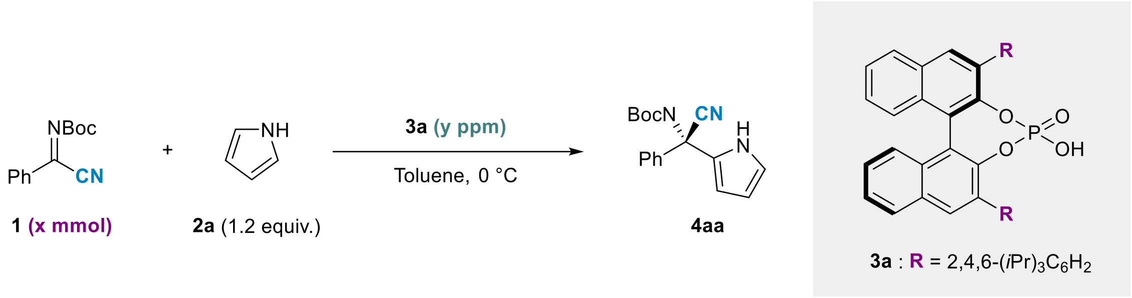
Peak	t_R (min)	Area (%)
1	19.7	50.0
2	29.1	50.0



Peak	t_R (min)	Area (%)
1	19.9	97.3
2	28.9	2.7

Asymmetric Friedel-Crafts Reaction of 1a with 2a with low catalyst loading
The reactions were performed using **1a**, **2a**, and catalyst **3a** in toluene. Most of these experiments were following general procedures.

Catalyst addition:
The reaction with 100 ppm of catalyst: 10.0 μL of the solution of 1.3 mg of catalyst **3a** in 0.5 mL Toluene.
The reaction with 50 ppb of catalyst: 5.0 μL of the solution of 1.3 mg of catalyst **3a** in 50 mL Toluene.



x mmol	y ppm	time	Yield (%)	Ee (%)	TON	TOF (h^{-1})
0.25	100	10 h	90	97	9,000	900
2.5	0.05 (= 50 ppb)	7 d	54	94	10,800,000	64,286

The TON was calculated by the following equation.
TON = The yield of the product / catalyst equivalent

The TOF was calculated by TON divided by the reaction time (h).
TOF = TON / reaction time (h)

DFT calculations

The calculation was performed using Gaussian 09 revision E.01.4) Geometry optimizations were performed using B3LYP functional with 6-31G(d,p) basis set for all the atoms under the conditions of tight convergence criteria (opt=tight) with an ultrafine integration grid (int=(grid=ultrafine)). After optimization of structures, frequency calculations were performed at the same level of the theory to confirm that the obtained structures were either a stationary point (no imaginary frequencies) or a transition state (one imaginary frequency). Single point energy calculations for the optimized geometry were performed using M06-2X functional with 6-311G+(d,p) basis set for all the atoms in CPCM solvation model (toluene or CH_2Cl_2). 3D Model were visualized by CYLview5) and GaussView. NBO analysis was carried out using NBO version 3.1.6)

Calculated Structures

Pyr-(*S*)-O-TS

M06-2X/6-311G+(d,p)/CPCM(toluene)//B3LYP/6-31G(d)

single point energy: -3555.54120093 a.u.
number of imaginary frequencies: 1 (273.6056*i*)

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C	-3.83786	0.55371	0.68858
C	-4.62267	1.07358	1.69806
C	-4.29022	2.27015	2.38008
C	-3.15353	3.02729	1.95259
C	-2.39635	2.56398	0.81966
C	-5.06072	2.72679	3.48344
C	-4.70969	3.86749	4.16675
C	-3.56291	4.59636	3.77282
C	-2.80804	4.19092	2.69420
C	-1.32859	3.40644	0.20758
C	-1.60627	4.74192	-0.25322
C	-0.51872	5.55222	-0.71242
C	0.78885	5.00758	-0.74676
C	1.05290	3.69352	-0.41728
C	-0.04491	2.91111	0.04163
C	-2.91743	5.29080	-0.31044
C	-3.13171	6.57553	-0.75873
C	-2.04897	7.38774	-1.16997
C	-0.77081	6.88096	-1.14940
O	0.21539	1.59235	0.42396
P	-0.36253	0.37303	-0.47811
O	-1.91086	0.79887	-0.73322
H	-5.51956	0.53780	1.99612
H	-5.92828	2.14528	3.78602

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H	-3.27140	5.48303	4.32923
H	-1.92793	4.75672	2.41148
H	1.60806	5.64126	-1.07575
H	-3.76121	4.68168	-0.00902
H	-4.14452	6.96684	-0.80178
H	-2.23187	8.40201	-1.51384
H	0.06992	7.48419	-1.48339
C	-4.23796	-0.72616	0.01343
C	-4.18926	-1.95202	0.72373
C	-4.76134	-0.69550	-1.30069
C	-4.68811	-3.10749	0.11192
C	-5.23718	-1.88431	-1.86509
C	-5.22370	-3.09847	-1.17887
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C	3.03174	2.98305	-1.81639
C	4.53538	2.46818	0.48142
C	4.36846	2.57397	-1.89869
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C	-4.73974	-2.30564	3.17864
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H	-1.74836	-2.99571	1.52394
H	-2.08902	-3.12056	3.25979
H	-2.95180	-4.15441	2.11530
H	-5.49439	-1.51220	3.15858
H	-5.25438	-3.25528	2.98885
H	-4.32092	-2.34823	4.19146
C	-5.79887	-4.35597	-1.81804
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C	-4.75035	-5.47469	-1.95530
H	-6.11959	-4.08246	-2.83259

H	-7.80900	-4.07585	-0.99745
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H	-6.91309	1.05300	-1.45204
H	-6.41801	1.90461	-2.92881
H	-6.84897	0.18867	-2.99556
H	-3.01909	0.29941	-3.23185
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H	-4.13291	1.46873	-3.96688
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C	2.24542	1.99417	-4.03221
C	2.84114	4.45479	-3.87387
H	1.23220	3.46467	-2.87059
H	1.77061	1.15085	-3.52506
H	1.67245	2.21136	-4.94213
H	3.25251	1.69028	-4.34007
H	2.82284	5.35872	-3.25412
H	3.88058	4.28541	-4.17936
H	2.25600	4.65328	-4.77997
C	2.65498	3.09134	2.03519
C	3.40305	4.21937	2.77336
C	2.66563	1.78837	2.85632
H	1.61132	3.40722	1.95181
H	3.36441	5.15675	2.20725
H	2.95413	4.39805	3.75819
H	4.45882	3.96785	2.92868
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C	6.95076	0.98211	-2.01153

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H	7.30561	3.86878	-0.07209
H	8.55959	2.94427	-0.92598
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H	7.99690	0.66017	-1.94479
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N	2.71054	-1.53006	-2.09196
C	3.52320	-1.68177	-3.18715
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H	3.33491	-1.12854	-4.09616
C	4.28856	-2.99557	-1.51818
H	2.66952	-2.32770	-0.10997
H	5.31511	-2.91474	-3.51586
H	4.88232	-3.69525	-0.94473
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H	0.76732	-3.44892	3.99132
C	3.00887	-4.55506	2.78797
H	2.94696	-4.85674	3.83862
H	3.54091	-5.33115	2.23003
H	3.58608	-3.62692	2.72753
C	0.80770	-5.66253	2.23918
H	-0.21059	-5.51842	1.87441
H	1.29883	-6.41572	1.61537
H	0.76134	-6.03984	3.26681

Pyr-(*R*)-O-TS

M06-2X/6-311G+(d,p)/CPCM(toluene)//B3LYP/6-31G(d)

single point energy: -3555.53667068 a.u.
number of imaginary frequencies: 1 (209.8161*i*)

C	-2.69654	1.31305	0.29950
C	-3.83786	0.55371	0.68858
C	-4.62267	1.07358	1.69806
C	-4.29022	2.27015	2.38008
C	-3.15353	3.02729	1.95259
C	-2.39635	2.56398	0.81966
C	-5.06072	2.72679	3.48344
C	-4.70969	3.86749	4.16675
C	-3.56291	4.59636	3.77282
C	-2.80804	4.19092	2.69420
C	-1.32859	3.40644	0.20758
C	-1.60627	4.74192	-0.25322
C	-0.51872	5.55222	-0.71242
C	0.78885	5.00758	-0.74676
C	1.05290	3.69352	-0.41728
C	-0.04491	2.91111	0.04163
C	-2.91743	5.29080	-0.31044
C	-3.13171	6.57553	-0.75873
C	-2.04897	7.38774	-1.16997
C	-0.77081	6.88096	-1.14940
O	0.21539	1.59235	0.42396
P	-0.36253	0.37303	-0.47811

O	-1.91086	0.79887	-0.73322
H	-5.51956	0.53780	1.99612
H	-5.92828	2.14528	3.78602
H	-5.30090	4.20348	5.01413
H	-3.27140	5.48303	4.32923
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H	1.60806	5.64126	-1.07575
H	-3.76121	4.68168	-0.00902
H	-4.14452	6.96684	-0.80178
H	-2.23187	8.40201	-1.51384
H	0.06992	7.48419	-1.48339
C	-4.23796	-0.72616	0.01343
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C	-4.76134	-0.69550	-1.30069
C	-4.68811	-3.10749	0.11192
C	-5.23718	-1.88431	-1.86509
C	-5.22370	-3.09847	-1.17887
H	-4.66373	-4.04206	0.66665
H	-5.64999	-1.85973	-2.87128
C	2.44694	3.15268	-0.53738
C	3.20877	2.88724	0.62530
C	3.03174	2.98305	-1.81639
C	4.53538	2.46818	0.48142
C	4.36846	2.57397	-1.89869
C	5.14379	2.31474	-0.76735
H	5.12583	2.27174	1.37451
H	4.81142	2.45008	-2.88222
O	-0.32272	-0.77717	0.60508
C	-3.62504	-2.06113	2.14196
C	-2.54058	-3.14825	2.26081
C	-4.73974	-2.30564	3.17864
H	-3.14565	-1.10946	2.38810
H	-1.74836	-2.99571	1.52394
H	-2.08902	-3.12056	3.25979
H	-2.95180	-4.15441	2.11530
H	-5.49439	-1.51220	3.15858
H	-5.25438	-3.25528	2.98885
H	-4.32092	-2.34823	4.19146
C	-5.79887	-4.35597	-1.81804

C	-7.04429	-4.85757	-1.06197
C	-4.75035	-5.47469	-1.95530
H	-6.11959	-4.08246	-2.83259
H	-7.80900	-4.07585	-0.99745
H	-7.48408	-5.72482	-1.56944
H	-6.79165	-5.16232	-0.03927
H	-3.87698	-5.13007	-2.51958
H	-4.40137	-5.81630	-0.97356
H	-5.17528	-6.34096	-2.47679
C	-4.87691	0.59097	-2.11785
C	-6.35105	0.95308	-2.38752
C	-4.07332	0.51436	-3.42996
H	-4.45414	1.41076	-1.53119
H	-6.91309	1.05300	-1.45204
H	-6.41801	1.90461	-2.92881
H	-6.84897	0.18867	-2.99556
H	-3.01909	0.29941	-3.23185
H	-4.46211	-0.26465	-4.09662
H	-4.13291	1.46873	-3.96688
C	2.27166	3.23574	-3.12062
C	2.24542	1.99417	-4.03221
C	2.84114	4.45479	-3.87387
H	1.23220	3.46467	-2.87059
H	1.77061	1.15085	-3.52506
H	1.67245	2.21136	-4.94213
H	3.25251	1.69028	-4.34007
H	2.82284	5.35872	-3.25412
H	3.88058	4.28541	-4.17936
H	2.25600	4.65328	-4.77997
C	2.65498	3.09134	2.03519
C	3.40305	4.21937	2.77336
C	2.66563	1.78837	2.85632
H	1.61132	3.40722	1.95181
H	3.36441	5.15675	2.20725
H	2.95413	4.39805	3.75819
H	4.45882	3.96785	2.92868
H	2.08597	1.00792	2.35401
H	3.68530	1.41442	3.00719
H	2.22338	1.95994	3.84584

C	6.61854	1.93821	-0.85435
C	7.49444	3.20653	-0.92431
C	6.95076	0.98211	-2.01153
H	6.86899	1.42058	0.08273
H	7.30561	3.86878	-0.07209
H	8.55959	2.94427	-0.92598
H	7.28463	3.77291	-1.83988
H	6.31358	0.09204	-1.99620
H	6.82586	1.46860	-2.98629
H	7.99690	0.66017	-1.94479
H	-0.22900	-1.69389	0.20969
N	1.56908	-3.31100	0.75170
C	2.81887	-3.59955	0.87461
C	3.43742	-3.36796	2.19518
C	4.67729	-3.93834	2.53062
C	2.76314	-2.56933	3.13769
C	5.22784	-3.72111	3.79163
H	5.20641	-4.55209	1.80856
C	3.31872	-2.35750	4.39338
H	1.81505	-2.12105	2.86230
C	4.55080	-2.93345	4.72407
H	6.18529	-4.16687	4.04444
H	2.79500	-1.73777	5.11504
H	4.98261	-2.76389	5.70666
C	0.71983	-3.88099	-0.20024
O	-0.16215	-3.20502	-0.72513
C	3.37187	-4.90519	0.52944
N	3.85952	-5.94177	0.33628
O	0.49474	0.06152	-1.64621
H	1.84345	-1.26960	-1.67543
N	2.61508	-1.93508	-1.71129
C	2.75431	-2.94748	-2.62700
C	3.52771	-2.29331	-0.46178
C	3.90871	-3.64393	-2.32674
H	2.02992	-3.08124	-3.41769
C	4.48727	-3.02211	-1.18180
H	3.98239	-0.94130	0.04942
H	4.29774	-4.49643	-2.86748
H	5.40264	-3.30982	-0.68153

O	0.91676	-5.17592	-0.38757
C	0.14071	-5.98826	-1.37259
C	-1.31725	-6.06018	-0.91940
H	-1.38316	-6.44079	0.10569
H	-1.80233	-5.08357	-0.96872
H	-1.86236	-6.74980	-1.57310
C	0.82904	-7.34957	-1.26849
H	0.35158	-8.05726	-1.95400
H	1.88831	-7.26774	-1.52910
H	0.75170	-7.74676	-0.25137
C	0.30301	-5.38984	-2.77033
H	-0.21818	-4.43553	-2.86198
H	1.36143	-5.23323	-3.00021
H	-0.11221	-6.08758	-3.50604

Pyr-(*S*)-N-TS

M06-2X/6-311G+(d,p)/CPCM(toluene)//B3LYP/6-31G(d)

single point energy: -3555.54872570 a.u.
number of imaginary frequencies: 1 (281.3437*i*)

C	1.81077	-2.88771	0.03478
C	3.13229	-2.82002	0.56186
C	3.55974	-3.89181	1.31891
C	2.71741	-4.98853	1.62870
C	1.39978	-5.04090	1.07189
C	0.97837	-3.98746	0.18591
C	3.15530	-6.02983	2.49096
C	2.31919	-7.06918	2.82574
C	1.00185	-7.10256	2.31147
C	0.55518	-6.11917	1.45653
C	-0.32181	-4.06484	-0.54368
C	-0.63697	-5.18568	-1.39014
C	-1.95486	-5.28771	-1.94115
C	-2.89788	-4.26238	-1.68142
C	-2.57421	-3.12467	-0.97052
C	-1.25826	-3.04734	-0.42841
C	0.30910	-6.19058	-1.73494
C	-0.03945	-7.24903	-2.54467
C	-1.35450	-7.36787	-3.05231

C	-2.28843	-6.40254	-2.75726
O	-0.94605	-1.93090	0.33877
P	0.18939	-0.85961	-0.14281
O	1.36742	-1.81129	-0.73646
H	4.57373	-3.88855	1.70908
H	4.16386	-5.97850	2.89416
H	2.66103	-7.85561	3.49297
H	0.33270	-7.90950	2.59772
H	-0.46054	-6.15664	1.08093
H	-3.90185	-4.36389	-2.08582
H	1.32334	-6.11244	-1.36171
H	0.70557	-7.99786	-2.79960
H	-1.61829	-8.21219	-3.68325
H	-3.29785	-6.46850	-3.15642
C	4.07981	-1.68850	0.27902
C	4.44056	-0.78535	1.30941
C	4.70449	-1.59625	-0.98652
C	5.44944	0.15230	1.06233
C	5.69517	-0.62611	-1.18225
C	6.10046	0.24609	-0.16988
H	5.73339	0.82937	1.86263
H	6.18912	-0.56628	-2.15034
C	-3.58197	-2.02911	-0.78667
C	-4.16107	-1.79647	0.48266
C	-3.99751	-1.25800	-1.90111
C	-5.13420	-0.79830	0.60863
C	-4.97845	-0.27758	-1.71703
C	-5.56136	-0.02676	-0.47278
H	-5.58582	-0.62383	1.58284
H	-5.29753	0.30627	-2.57724
O	0.72394	-0.28602	1.19211
C	3.77888	-0.80078	2.68858
C	3.29950	0.59763	3.12430
C	4.71556	-1.39825	3.75823
H	2.89085	-1.43601	2.62833
H	2.66843	1.06046	2.36164
H	2.71316	0.51870	4.04742
H	4.13979	1.27185	3.32929
H	5.01827	-2.42134	3.51039

H	5.62796	-0.79837	3.86277
H	4.21672	-1.42160	4.73475
C	7.25343	1.21603	-0.39984
C	8.54392	0.69389	0.26411
C	6.94569	2.65150	0.06032
H	7.43418	1.24856	-1.48371
H	8.79695	-0.30947	-0.09579
H	9.38953	1.35888	0.04949
H	8.42721	0.63811	1.35315
H	6.03376	3.03637	-0.40701
H	6.81307	2.70723	1.14702
H	7.77436	3.32063	-0.20115
C	4.37140	-2.54110	-2.14110
C	5.59013	-3.39158	-2.54976
C	3.79039	-1.78440	-3.35092
H	3.60099	-3.23890	-1.80145
H	5.97908	-3.96035	-1.69779
H	5.31348	-4.10378	-3.33677
H	6.40655	-2.77020	-2.93638
H	2.89317	-1.22607	-3.06627
H	4.51685	-1.07748	-3.76995
H	3.51705	-2.48859	-4.14629
C	-3.41968	-1.44590	-3.30544
C	-2.71233	-0.17306	-3.80757
C	-4.49379	-1.91455	-4.30584
H	-2.65775	-2.22772	-3.25980
H	-1.90717	0.10141	-3.12029
H	-2.27975	-0.34796	-4.80108
H	-3.40666	0.67215	-3.89070
H	-4.97060	-2.84415	-3.97481
H	-5.28463	-1.16513	-4.43030
H	-4.04780	-2.09465	-5.29153
C	-3.80759	-2.62897	1.71448
C	-5.00766	-3.48493	2.16759
C	-3.27442	-1.76451	2.87202
H	-3.01012	-3.32514	1.44113
H	-5.35936	-4.13525	1.35864
H	-4.72657	-4.11969	3.01668
H	-5.85134	-2.85985	2.48368

H	-2.40261	-1.18276	2.55866
H	-4.03708	-1.06863	3.24212
H	-2.97391	-2.40090	3.71313
C	-6.64915	1.02513	-0.29674
C	-7.95003	0.61536	-1.01461
C	-6.19326	2.42539	-0.74595
H	-6.87136	1.08186	0.77772
H	-8.30378	-0.36052	-0.66466
H	-8.74263	1.35171	-0.83401
H	-7.79847	0.54546	-2.09851
H	-5.28724	2.73711	-0.21413
H	-5.97562	2.45055	-1.82026
H	-6.97621	3.16761	-0.54953
H	-0.07371	1.21450	1.81524
N	-0.27474	2.00993	2.18521
C	-0.18305	3.20571	1.49742
C	0.98199	3.22715	0.51202
C	1.49469	4.42898	0.00460
C	1.54171	2.01443	0.08981
C	2.54552	4.41838	-0.91152
H	1.08614	5.37873	0.33757
C	2.58732	2.00605	-0.83415
H	1.16365	1.08919	0.50721
C	3.09175	3.20629	-1.33859
H	2.93980	5.35901	-1.28655
H	3.01208	1.05568	-1.14472
H	3.91046	3.19876	-2.05345
C	-0.98583	1.86103	3.29744
O	-1.09720	0.74465	3.87664
C	-0.25477	4.47369	2.26297
N	-0.28028	5.49440	2.81744
O	-0.24274	0.17503	-1.12685
H	-1.16527	1.82428	-0.82618
N	-1.54185	2.79151	-0.74308
C	-1.51892	3.68174	-1.71642
C	-1.73826	3.32234	0.48385
C	-2.01183	4.93360	-1.24515
H	-1.14710	3.42066	-2.69915
C	-2.31775	4.75843	0.08043

H	-2.56090	2.82973	1.08682
H	-2.09941	5.83361	-1.83786
H	-2.71569	5.49547	0.76590
O	-1.63849	2.94976	3.77618
C	-2.30614	2.98882	5.09560
C	-3.49272	2.02184	5.12338
H	-4.16411	2.21242	4.27845
H	-3.16195	0.98413	5.07740
H	-4.06225	2.17347	6.04779
C	-2.78171	4.44199	5.17702
H	-3.25489	4.62683	6.14723
H	-1.94008	5.13046	5.05710
H	-3.51675	4.65513	4.39288
C	-1.28116	2.68972	6.19328
H	-0.90952	1.66643	6.11594
H	-0.43631	3.38321	6.12407
H	-1.74961	2.81887	7.17552

Pyr-(*R*)-N-TS

M06-2X/6-311G+(d,p)/CPCM(toluene)//B3LYP/6-31G(d)

single point energy: -3555.54131537 a.u.
number of imaginary frequencies: 1 (253.0845*i*)

C	2.71898	-1.31708	0.15759
C	3.92556	-0.68483	0.57703
C	4.80246	-1.44403	1.32508
C	4.50306	-2.76414	1.74315
C	3.28954	-3.38007	1.30138
C	2.42627	-2.64953	0.40990
C	5.37962	-3.47944	2.60328
C	5.06030	-4.74149	3.04664
C	3.84058	-5.33669	2.64788
C	2.98131	-4.67763	1.79645
C	1.24731	-3.30898	-0.22271
C	1.39662	-4.52383	-0.98101
C	0.22244	-5.22472	-1.40469
C	-1.05261	-4.68311	-1.10776
C	-1.20951	-3.45600	-0.49571
C	-0.02536	-2.77287	-0.09141

C	2.66174	-5.05287	-1.35920
C	2.75701	-6.22211	-2.08112
C	1.59483	-6.93441	-2.45983
C	0.35474	-6.44033	-2.12920
O	-0.18780	-1.56215	0.57266
P	0.37671	-0.16170	-0.03648
O	1.83825	-0.57378	-0.62851
H	5.75205	-1.00878	1.62241
H	6.30290	-2.99887	2.91797
H	5.73273	-5.27605	3.71193
H	3.57553	-6.32230	3.02087
H	2.04742	-5.14627	1.50964
H	-1.93732	-5.24234	-1.40162
H	3.56261	-4.51685	-1.08495
H	3.73559	-6.59849	-2.36649
H	1.68507	-7.86024	-3.02124
H	-0.54896	-6.96463	-2.43079
C	4.30550	0.71680	0.19201
C	4.35453	1.73738	1.17572
C	4.72936	0.99123	-1.12878
C	4.86364	2.99085	0.81936
C	5.21893	2.26765	-1.42990
C	5.31275	3.27779	-0.47256
H	4.91367	3.76619	1.57894
H	5.55814	2.47618	-2.44243
C	-2.58256	-2.90120	-0.25779
C	-3.09731	-2.81347	1.05758
C	-3.40012	-2.53770	-1.35811
C	-4.41330	-2.37371	1.24001
C	-4.70701	-2.09871	-1.11421
C	-5.24231	-2.02044	0.17479
H	-4.81545	-2.32454	2.24947
H	-5.33234	-1.83081	-1.96258
O	0.54139	0.65509	1.27645
C	3.89044	1.51567	2.61741
C	2.96443	2.63726	3.12677
C	5.08669	1.35405	3.57827
H	3.31123	0.58758	2.64306
H	2.13601	2.82559	2.44021

H	2.54617	2.35694	4.10081
H	3.50799	3.57948	3.26853
H	5.73401	0.51806	3.29461
H	5.70337	2.26121	3.59076
H	4.73447	1.17476	4.60143
C	5.91718	4.63087	-0.82682
C	7.25120	4.86106	-0.08989
C	4.94381	5.79636	-0.57577
H	6.13720	4.61289	-1.90333
H	7.96374	4.05586	-0.29984
H	7.70605	5.81002	-0.39916
H	7.10205	4.89999	0.99572
H	4.01349	5.66099	-1.13717
H	4.68222	5.87886	0.48558
H	5.39444	6.74821	-0.88221
C	4.71523	-0.06153	-2.23669
C	6.13844	-0.37719	-2.73757
C	3.79306	0.34761	-3.40121
H	4.31440	-0.99078	-1.82286
H	6.78282	-0.71091	-1.91643
H	6.11087	-1.17185	-3.49318
H	6.60973	0.50045	-3.19527
H	2.77369	0.52534	-3.04534
H	4.14848	1.26064	-3.89374
H	3.75943	-0.44605	-4.15766
C	-2.92067	-2.61322	-2.81044
C	-2.84514	-1.22130	-3.46414
C	-3.78475	-3.57404	-3.65007
H	-1.90369	-3.01162	-2.81331
H	-2.13772	-0.58696	-2.92215
H	-2.50189	-1.30764	-4.50273
H	-3.82385	-0.72581	-3.47558
H	-3.81894	-4.57472	-3.20445
H	-4.81787	-3.21834	-3.74105
H	-3.37633	-3.66756	-4.66350
C	-2.30199	-3.24367	2.29008
C	-2.93598	-4.48229	2.95481
C	-2.13100	-2.09570	3.30313
H	-1.29979	-3.53788	1.96848

H	-3.02071	-5.31402	2.24628
H	-2.32370	-4.81671	3.80092
H	-3.94084	-4.26552	3.33614
H	-1.62738	-1.23950	2.84494
H	-3.09726	-1.75920	3.69874
H	-1.52531	-2.42982	4.15403
C	-6.68845	-1.60700	0.42136
C	-7.67973	-2.56537	-0.26606
C	-6.95814	-0.14742	0.01271
H	-6.86159	-1.67807	1.50372
H	-7.50919	-3.60133	0.04630
H	-8.71315	-2.29809	-0.01467
H	-7.58233	-2.52621	-1.35754
H	-6.32091	0.54238	0.57644
H	-6.76937	0.00625	-1.05702
H	-8.00274	0.12291	0.20929
H	-0.14340	2.10517	0.62007
N	-0.52813	3.16534	0.21018
C	-1.68725	3.88898	0.44787
C	-1.95325	4.05098	1.95607
C	-2.75483	5.07990	2.46600
C	-1.39545	3.11657	2.83886
C	-2.99981	5.16994	3.83790
H	-3.16704	5.83173	1.79933
C	-1.64664	3.20741	4.20715
H	-0.75185	2.34266	2.43662
C	-2.45105	4.23188	4.71232
H	-3.61367	5.98113	4.22005
H	-1.20201	2.48009	4.88127
H	-2.64012	4.30393	5.78008
C	0.13302	3.19815	-0.94228
O	1.17642	2.51448	-1.13733
C	-1.87501	5.19509	-0.23449
N	-2.06772	6.25147	-0.67788
O	-0.41546	0.42802	-1.15591
H	-1.71447	1.70241	-1.35969
N	-2.47354	2.29184	-1.48990
C	-3.34302	2.65881	-2.40610
C	-2.86249	2.73646	-0.14629

C	-4.47230	3.27717	-1.78875
H	-3.15562	2.48742	-3.45911
C	-4.24828	3.24188	-0.43901
H	-2.84171	1.85268	0.52743
H	-5.31725	3.70003	-2.31422
H	-4.88831	3.63402	0.33924
O	-0.36753	3.96962	-1.93743
C	0.26256	4.09805	-3.26366
C	1.66332	4.69528	-3.10252
H	1.60981	5.65078	-2.56979
H	2.31591	4.01539	-2.55169
H	2.10266	4.87762	-4.08964
C	-0.66964	5.08643	-3.97242
H	-0.27418	5.32878	-4.96464
H	-1.66858	4.65373	-4.09967
H	-0.76883	6.00865	-3.39299
C	0.27776	2.75124	-3.99542
H	1.01138	2.06636	-3.57122
H	-0.70868	2.27712	-3.94231
H	0.51631	2.91629	-5.05280

Ind-(*R*)-O-TS

M06-2X/6-311G+(d,p)/CPCM(CH_2Cl_2)//B3LYP/6-31G(d,p)

single point energy: -4409.48955945 a.u.
number of imaginary frequencies: 1 (292.8480*i*)

C	3.22446	0.03611	0.19568
C	3.88854	1.23828	0.57556
C	4.89612	1.12884	1.51240
C	5.22696	-0.10138	2.13281
C	4.56359	-1.29830	1.71340
C	3.59639	-1.22099	0.65018
C	6.19989	-0.16609	3.16679
C	6.48778	-1.35628	3.79290
C	5.80435	-2.53408	3.40940
C	4.87144	-2.50754	2.39625
C	3.01665	-2.45354	0.04244
C	3.86097	-3.48109	-0.50955
C	3.25888	-4.70128	-0.95533

C	1.85097	-4.84716	-0.89065
C	1.01895	-3.82738	-0.47500
C	1.64365	-2.62813	-0.02828
C	5.26655	-3.33298	-0.67043
C	6.03218	-4.34651	-1.20343
C	5.43918	-5.56787	-1.60055
C	4.07959	-5.73585	-1.48105
O	0.81740	-1.60564	0.44564
P	0.67615	-0.23653	-0.41430
O	2.21639	0.14305	-0.76423
H	5.44539	2.02078	1.80068
H	6.70267	0.75136	3.46324
H	7.22748	-1.39310	4.58786
H	6.01383	-3.46897	3.92207
H	4.35161	-3.41774	2.12099
H	1.40991	-5.78599	-1.21466
H	5.73803	-2.40118	-0.38172
H	7.10238	-4.20327	-1.32521
H	6.05617	-6.36183	-2.01208
H	3.60514	-6.65949	-1.80370
C	3.57385	2.57060	-0.03998
C	3.00023	3.60206	0.74524
C	3.93657	2.82919	-1.38292
C	2.82336	4.86712	0.17373
C	3.72939	4.11155	-1.90287
C	3.18469	5.14893	-1.14631
H	2.39425	5.65806	0.78386
H	4.01653	4.31358	-2.93238
C	-0.46999	-4.00946	-0.49898
C	-1.18931	-4.15947	0.71029
C	-1.14951	-4.10524	-1.73889
C	-2.56544	-4.40449	0.65130
C	-2.52520	-4.36572	-1.73631
C	-3.25625	-4.52400	-0.55738
H	-3.11827	-4.52944	1.58029
H	-3.03732	-4.44550	-2.69050
O	0.16110	0.72209	0.73155
H	-0.53477	1.38580	0.44927
N	-3.04705	1.76929	1.66103

C	-4.21610	1.24105	1.77084
C	-4.62916	0.49856	2.97882
C	-5.96356	0.10128	3.16950
C	-3.66770	0.19597	3.96107
C	-6.33120	-0.57994	4.32768
H	-6.71131	0.32782	2.41604
C	-4.04240	-0.48308	5.11388
H	-2.63827	0.49491	3.79772
C	-5.37397	-0.87192	5.30057
H	-7.36472	-0.88191	4.46893
H	-3.29592	-0.71524	5.86755
H	-5.66209	-1.40425	6.20293
C	-2.70294	2.71563	0.68922
O	-1.60446	2.67018	0.14103
C	-5.35313	2.14702	1.64268
N	-6.29241	2.82993	1.60852
O	-0.11824	-0.29514	-1.66455
O	-3.62124	3.65190	0.52216
C	-3.47632	4.78559	-0.44555
C	-2.29845	5.65941	-0.01506
H	-2.41474	5.97766	1.02672
H	-1.34741	5.13509	-0.12360
H	-2.27201	6.55625	-0.64352
C	-4.80862	5.51472	-0.27123
H	-4.84745	6.37653	-0.94538
H	-5.64472	4.84949	-0.50637
H	-4.92618	5.87321	0.75662
C	-3.32507	4.23224	-1.86103
H	-2.38725	3.69003	-1.98668
H	-4.15206	3.56113	-2.11103
H	-3.33900	5.06697	-2.57080
C	-3.97926	0.12724	-1.46677
C	-5.10780	-0.07735	-0.61961
C	-6.33676	0.50915	-0.97418
C	-6.41503	1.26189	-2.13945
C	-5.28609	1.44497	-2.96740
C	-4.05651	0.88336	-2.64314
C	-3.32394	-1.15432	0.25215
C	-4.50515	-0.40541	0.76679

H	-7.21236	0.37262	-0.34431
H	-7.36130	1.71500	-2.42405
H	-5.38098	2.03362	-3.87630
H	-3.18525	1.01977	-3.27810
H	-1.95035	-0.51697	-1.24818
H	-2.62590	-1.74621	0.82891
H	-5.28311	-1.31464	1.24870
N	-2.91199	-0.54097	-0.90908
C	2.57509	3.39193	2.21041
C	3.73193	3.73025	3.12857
C	1.36311	4.24896	2.51560
H	2.30659	2.30965	2.33188
C	3.33160	3.61704	4.58544
H	4.08100	4.77538	2.91826
H	4.59049	3.04015	2.92057
C	0.96231	4.13511	3.97231
H	1.59370	5.32002	2.27477
H	0.50662	3.93398	1.86472
C	2.11886	4.47200	4.89119
H	4.18787	3.93353	5.23593
H	3.10287	2.54572	4.82693
H	0.10408	4.82552	4.18046
H	0.61246	3.09000	4.18169
H	1.80907	4.31663	5.95725
H	2.38653	5.55484	4.77225
C	3.01258	6.55390	-1.75298
C	2.10993	7.38430	-0.86336
C	4.37066	7.20564	-1.91848
H	2.53314	6.43036	-2.75948
C	1.97953	8.80273	-1.37970
H	2.52822	7.40365	0.17732
H	1.09579	6.90964	-0.80995
C	4.24027	8.62380	-2.43560
H	4.90199	7.21617	-0.93059
H	4.99283	6.60238	-2.62941
C	3.33680	9.45457	-1.54733
H	1.35854	9.40601	-0.66773
H	1.44647	8.79253	-2.36668
H	5.25430	9.09864	-2.48858

H	3.82282	8.60365	-3.47665
H	3.21043	10.47626	-1.99091
H	3.81657	9.58078	-0.54123
C	4.60003	1.77426	-2.28765
C	4.28449	2.07815	-3.73812
C	6.09536	1.76234	-2.04192
H	4.16912	0.77560	-2.01346
C	4.98685	1.11173	-4.66992
H	4.60532	3.12609	-3.97741
H	3.17705	2.01934	-3.90165
C	6.79761	0.79529	-2.97319
H	6.50680	2.79441	-2.19647
H	6.29904	1.47410	-0.97802
C	6.48164	1.09763	-4.42377
H	4.78412	1.40120	-5.73368
H	4.57413	0.07993	-4.51686
H	7.90505	0.85442	-2.81002
H	6.47704	-0.25250	-2.73272
H	6.96319	0.32798	-5.08130
H	6.91432	2.09513	-4.69968
C	-0.44119	-3.95052	-3.09755
C	-0.08926	-5.31854	-3.64568
C	-1.33736	-3.18977	-4.05394
H	0.49964	-3.36532	-2.92282
C	0.53607	-5.21748	-5.02202
H	-1.01690	-5.94666	-3.70316
H	0.62189	-5.83125	-2.94709
C	-0.71165	-3.08802	-5.43006
H	-2.32738	-3.71144	-4.13195
H	-1.52909	-2.16128	-3.65159
C	-0.35821	-4.45543	-5.97843
H	0.72626	-6.24618	-5.42461
H	1.52701	-4.69755	-4.94388
H	-1.42293	-2.57575	-6.12878
H	0.21541	-2.45900	-5.37202
H	0.15923	-4.34161	-6.96630
H	-1.29866	-5.04060	-6.15586
C	-4.75227	-4.88941	-0.55878
C	-5.44505	-4.18973	-1.71042

C	-4.90770	-6.39366	-0.65684
H	-5.18777	-4.53200	0.41115
C	-6.90448	-4.58673	-1.79981
H	-4.92810	-4.45207	-2.67079
H	-5.36559	-3.07948	-1.57755
C	-6.36720	-6.79069	-0.74541
H	-4.36401	-6.76625	-1.56454
H	-4.44020	-6.87892	0.23893
C	-7.06107	-6.09053	-1.89595
H	-7.37122	-4.10245	-2.69653
H	-7.44872	-4.21251	-0.89309
H	-6.44668	-7.90085	-0.87875
H	-6.88331	-6.52893	0.21562
H	-8.15030	-6.35543	-1.89477
H	-6.62792	-6.44916	-2.86657
C	-0.50713	-4.11962	2.09037
C	-1.45372	-3.51571	3.10773
C	-0.09052	-5.52029	2.49176
H	0.40385	-3.47176	1.99783
C	-0.85330	-3.53309	4.49868
H	-2.41566	-4.09280	3.10995
H	-1.69471	-2.46046	2.81615
C	0.51065	-5.53752	3.88241
H	-0.98424	-6.19763	2.46329
H	0.65589	-5.91596	1.75503
C	-0.43470	-4.93265	4.90018
H	-1.60055	-3.13874	5.23529
H	0.03929	-2.85427	4.52782
H	0.75122	-6.59276	4.17419
H	1.47302	-4.96105	3.87924
H	0.06357	-4.90210	5.90387
H	-1.34503	-5.58119	4.99528

Ind-(*S*)-O-TS

M06-2X/6-311G+(d,p)/CPCM(CH_2Cl_2)//B3LYP/6-31G(d,p)

single point energy: -4409.48339211 a.u.
number of imaginary frequencies: 1 (224.8188*i*)

C	1.07431	2.63649	-0.70599

C	2.33563	2.70916	-1.36179
C	2.49284	3.70398	-2.30445
C	1.44093	4.58954	-2.65277
C	0.19876	4.52167	-1.94280
C	0.05531	3.55785	-0.88317
C	1.59827	5.54455	-3.69345
C	0.56517	6.38139	-4.04787
C	-0.67481	6.29147	-3.37315
C	-0.85244	5.39012	-2.34655
C	-1.14291	3.55080	0.00815
C	-1.51627	4.71983	0.76026
C	-2.74485	4.70363	1.49597
C	-3.53974	3.52989	1.49902
C	-3.14164	2.36603	0.87421
C	-1.91322	2.40742	0.15533
C	-0.70497	5.88562	0.84055
C	-1.10385	6.98020	1.57560
C	-2.33777	6.97572	2.26678
C	-3.13675	5.85686	2.22786
O	-1.51844	1.24741	-0.51274
P	-0.17583	0.44608	-0.06171
O	0.90530	1.61156	0.22992
H	3.45146	3.81077	-2.80534
H	2.55110	5.59104	-4.21434
H	0.69508	7.10205	-4.85064
H	-1.49696	6.93675	-3.66983
H	-1.81108	5.32832	-1.84481
H	-4.48229	3.54001	2.03953
H	0.24793	5.90552	0.32531
H	-0.46033	7.85429	1.62886
H	-2.64379	7.84848	2.83685
H	-4.07796	5.83024	2.77129
C	3.47682	1.80781	-0.98541
C	3.89578	0.76663	-1.84947
C	4.17652	2.05207	0.21991
C	5.01196	0.00371	-1.48886
C	5.27519	1.24467	0.53641
C	5.71476	0.21741	-0.29979
H	5.33817	-0.78955	-2.15579

H	5.81486	1.42797	1.46339
C	-3.98866	1.12966	0.95037
C	-4.72358	0.69905	-0.18205
C	-4.10110	0.42773	2.17325
C	-5.54443	-0.42791	-0.06788
C	-4.94381	-0.68942	2.23052
C	-5.67045	-1.14119	1.12878
H	-6.10913	-0.75227	-0.93831
H	-5.03334	-1.23207	3.16840
O	0.29822	-0.19204	-1.42800
H	-0.25680	-0.94461	-1.78560
N	0.48663	-3.76798	-2.10919
C	0.76579	-5.02928	-1.79282
C	1.98391	-5.64662	-2.33807
C	2.33280	-6.96600	-2.00620
C	2.81179	-4.89644	-3.19375
C	3.50480	-7.52294	-2.51431
H	1.71021	-7.55333	-1.33715
C	3.96792	-5.46547	-3.71069
H	2.52989	-3.87952	-3.44439
C	4.31772	-6.77828	-3.36906
H	3.78486	-8.53033	-2.22440
H	4.60075	-4.88976	-4.38004
H	5.22794	-7.21700	-3.76944
C	-0.75864	-3.34787	-2.57420
O	-1.14308	-2.18466	-2.48157
C	-0.24498	-6.08163	-1.81202
N	-1.08513	-6.88211	-1.86238
O	-0.31722	-0.45089	1.10694
O	-1.38308	-4.33093	-3.20068
C	-2.68681	-4.13795	-3.90395
C	-2.94441	-5.53265	-4.47595
H	-2.14155	-5.82683	-5.15923
H	-3.00739	-6.27448	-3.67380
H	-3.88987	-5.53723	-5.02797
C	-2.52138	-3.10471	-5.01966
H	-3.43698	-3.07982	-5.62104
H	-2.34234	-2.10528	-4.62008
H	-1.69095	-3.37975	-5.67881

C	-3.75656	-3.75172	-2.88204
H	-3.78479	-4.47890	-2.06365
H	-3.57785	-2.75950	-2.46471
H	-4.73693	-3.75137	-3.37187
C	1.98607	-3.57320	1.51058
C	2.04820	-4.97015	1.22520
C	3.10246	-5.72742	1.77090
C	4.04822	-5.09462	2.56703
C	3.96755	-3.71040	2.83422
C	2.94129	-2.93242	2.31048
C	0.24389	-4.08775	0.19377
C	0.92048	-5.26692	0.10613
H	3.16983	-6.79544	1.57615
H	4.86230	-5.67198	2.99746
H	4.71889	-3.24409	3.46607
H	2.88005	-1.86705	2.51432
H	0.55919	-2.09837	0.89600
H	-0.65119	-3.88355	-0.37732
H	0.46041	-6.16191	0.66746
N	0.88048	-3.06503	0.86411
C	-4.69323	1.45290	-1.50756
C	-4.23861	0.57298	-2.69400
C	-6.05634	2.11469	-1.82381
H	-3.96651	2.26861	-1.42514
C	-4.19212	1.37188	-4.00601
H	-4.93540	-0.26914	-2.81382
H	-3.25518	0.14222	-2.47429
C	-6.00881	2.91167	-3.13667
H	-6.83141	1.33774	-1.89538
H	-6.34990	2.76782	-0.99264
C	-5.54116	2.03999	-4.31126
H	-3.89733	0.71393	-4.83486
H	-3.41230	2.14410	-3.93177
H	-6.99559	3.34370	-3.35027
H	-5.31645	3.75865	-3.01904
H	-5.47115	2.64069	-5.22723
H	-6.29473	1.26188	-4.50499
C	-6.55111	-2.37475	1.23893
C	-8.03508	-2.08954	0.91367

C	-6.02830	-3.54372	0.37145
H	-6.51077	-2.70977	2.28632
C	-8.90356	-3.34772	1.06837
H	-8.11632	-1.71842	-0.11823
H	-8.40753	-1.28636	1.56215
C	-6.89817	-4.80131	0.52207
H	-6.02216	-3.22968	-0.68315
H	-4.98668	-3.76282	0.63738
C	-8.37481	-4.51085	0.21498
H	-9.94363	-3.12121	0.80128
H	-8.91341	-3.65167	2.12591
H	-6.52213	-5.59836	-0.13275
H	-6.81021	-5.17951	1.55149
H	-8.98270	-5.41022	0.37897
H	-8.47919	-4.25320	-0.85030
C	-3.34482	0.83637	3.43280
C	-4.29585	1.36490	4.53363
C	-2.46167	-0.30246	3.99400
H	-2.66642	1.65725	3.17617
C	-3.52456	1.80900	5.78605
H	-5.00914	0.57354	4.80526
H	-4.89608	2.19755	4.14329
C	-1.68958	0.14515	5.24410
H	-3.08940	-1.16741	4.25150
H	-1.76722	-0.63134	3.21383
C	-2.63161	0.68450	6.33012
H	-4.22720	2.14753	6.55891
H	-2.89755	2.67686	5.53259
H	-1.09623	-0.69216	5.63234
H	-0.97198	0.92969	4.96346
H	-2.05507	1.04206	7.19318
H	-3.26736	-0.13542	6.69762
C	3.18091	0.46113	-3.16209
C	3.96532	0.98564	-4.38936
C	2.86973	-1.04098	-3.35372
H	2.21548	0.97928	-3.14738
C	3.20354	0.73379	-5.70025
H	4.94566	0.48772	-4.42823
H	4.17032	2.05768	-4.27606

C	2.08569	-1.28780	-4.65147
H	3.80634	-1.61430	-3.39658
H	2.30941	-1.41381	-2.49077
C	2.84045	-0.74872	-5.87529
H	3.79916	1.08257	-6.55470
H	2.28056	1.33250	-5.69832
H	1.88749	-2.36118	-4.76850
H	1.10412	-0.79583	-4.57905
H	2.24432	-0.88774	-6.78680
H	3.76347	-1.33172	-6.01436
C	6.91075	-0.63716	0.08509
C	6.51927	-2.11311	0.33318
C	8.06127	-0.55324	-0.94414
H	7.30089	-0.24236	1.03598
C	7.72985	-2.96256	0.74960
H	6.08062	-2.52852	-0.58571
H	5.73582	-2.16508	1.09927
C	9.27007	-1.40239	-0.52096
H	7.69935	-0.90319	-1.92194
H	8.35878	0.49444	-1.08074
C	8.87397	-2.86522	-0.27050
H	7.42417	-4.00855	0.88262
H	8.09153	-2.61944	1.73089
H	10.05518	-1.34465	-1.28606
H	9.70233	-0.98322	0.40014
H	9.74270	-3.44107	0.07322
H	8.55291	-3.31951	-1.22046
C	3.80120	3.18247	1.17284
C	3.36038	2.67042	2.56399
C	4.93725	4.22381	1.31787
H	2.94519	3.71955	0.75034
C	2.95589	3.82979	3.48837
H	4.18399	2.10879	3.02730
H	2.52680	1.96863	2.44803
C	4.52904	5.38073	2.24350
H	5.83481	3.73578	1.72349
H	5.21408	4.60753	0.32731
C	4.07882	4.86953	3.62002
H	2.67947	3.43986	4.47677

H	2.05644	4.31717	3.08346
H	5.36219	6.08781	2.35060
H	3.70333	5.93963	1.77864
H	3.75069	5.70772	4.24865
H	4.93763	4.41134	4.13311

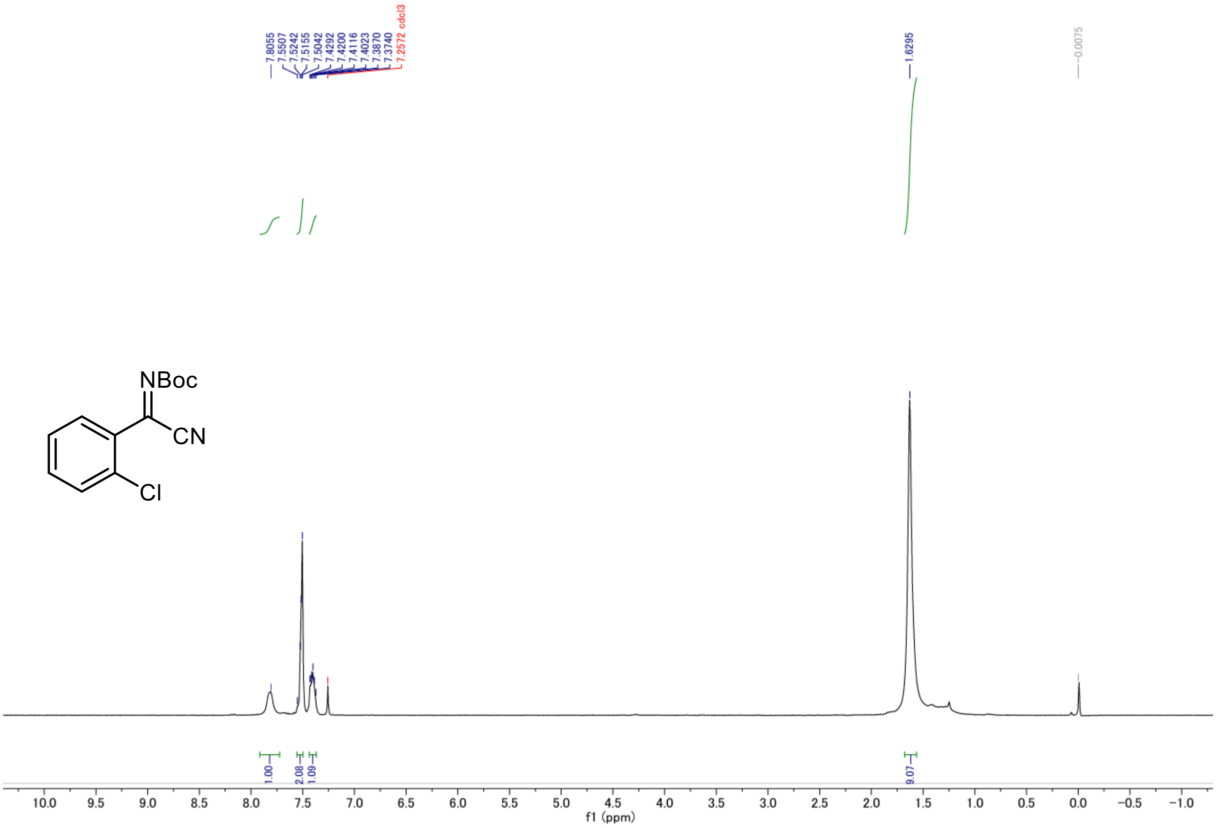
References

1. Oyamada, Y.; Fujii, M.; Takehara, T.; Suzuki, T.; Nakamura, S. Catalytic Enantioselective Construction of an α-Thio-Substituted α-Aminonitriles-Bearing Tetrasubstituted Carbon Center. *ACS Catal.* **2024**, *14*, 3411–3419.
2. Takizawa, S.; Rémond, E.; Arteaga, F.; Yoshida, Y.; Sridharan, V.; Bayardon, J.; Juge, S.; Sasai, H. P-Chirogenic Organocatalysts: Application to the Aza-Morita–Baylis–Hillman (Aza-MBH) Reaction of Ketimines. *Chem. Commun.* **2013**, *49*, 8392–8394.

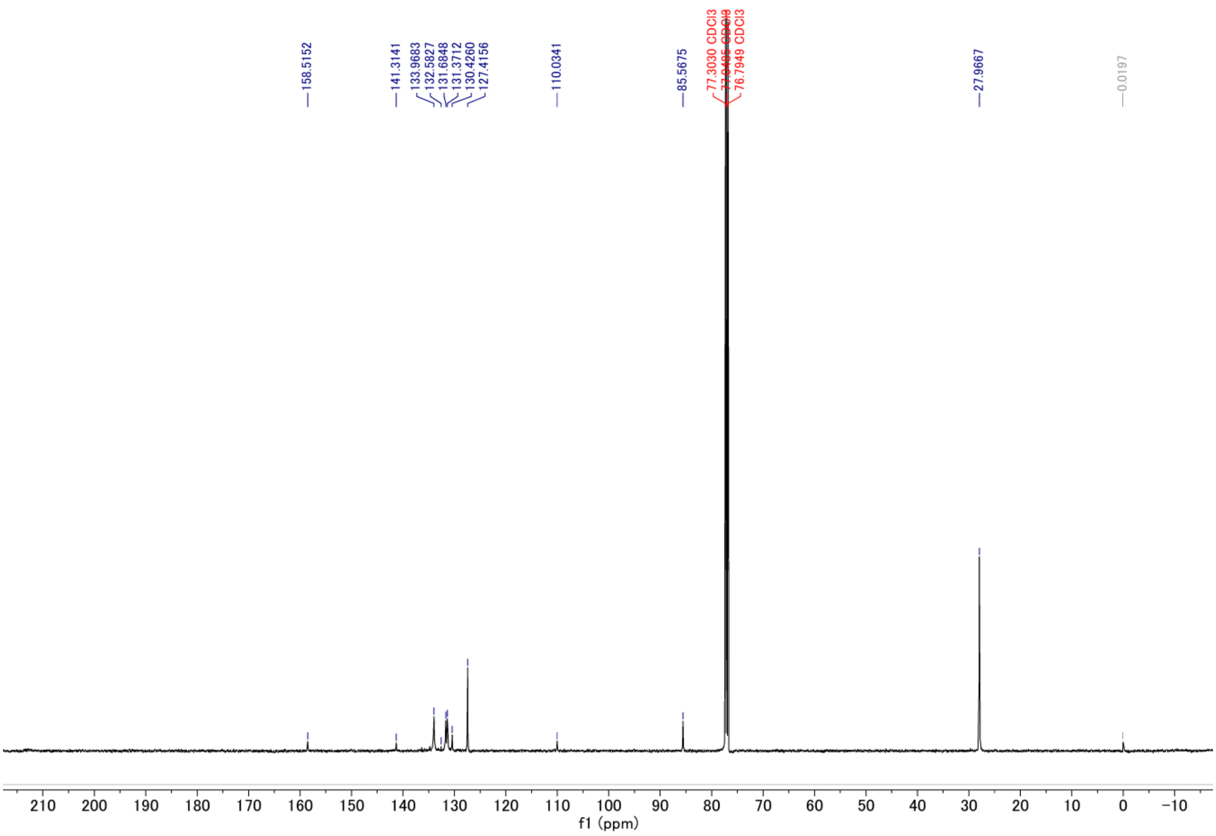
Spectral Data for Materials

(*Z*)-2-[(*tert*-Butoxycarbonylimino)]-2-(2-chlorophenyl)acetonitrile (1j)

^{1}H NMR ($CDCl_3$, 300 MHz)



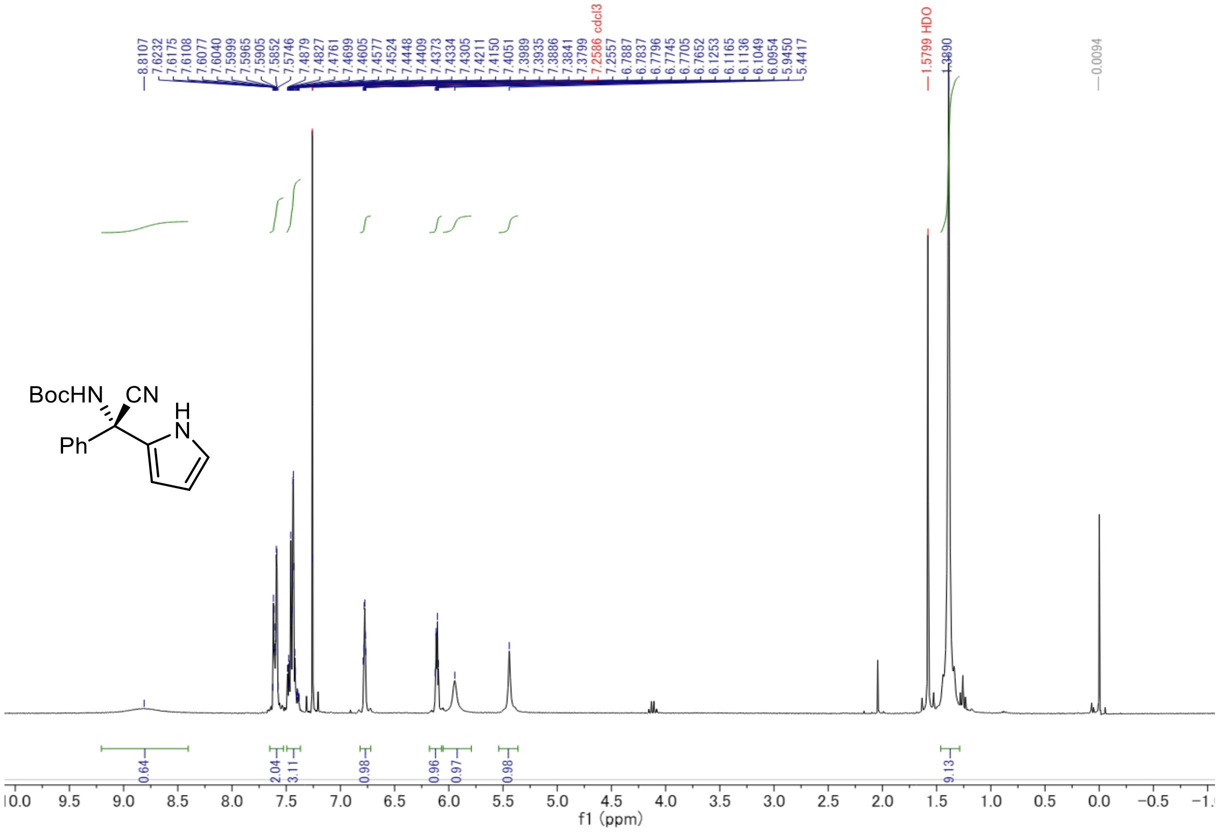
^{13}C NMR ($CDCl_3$, 125 MHz)



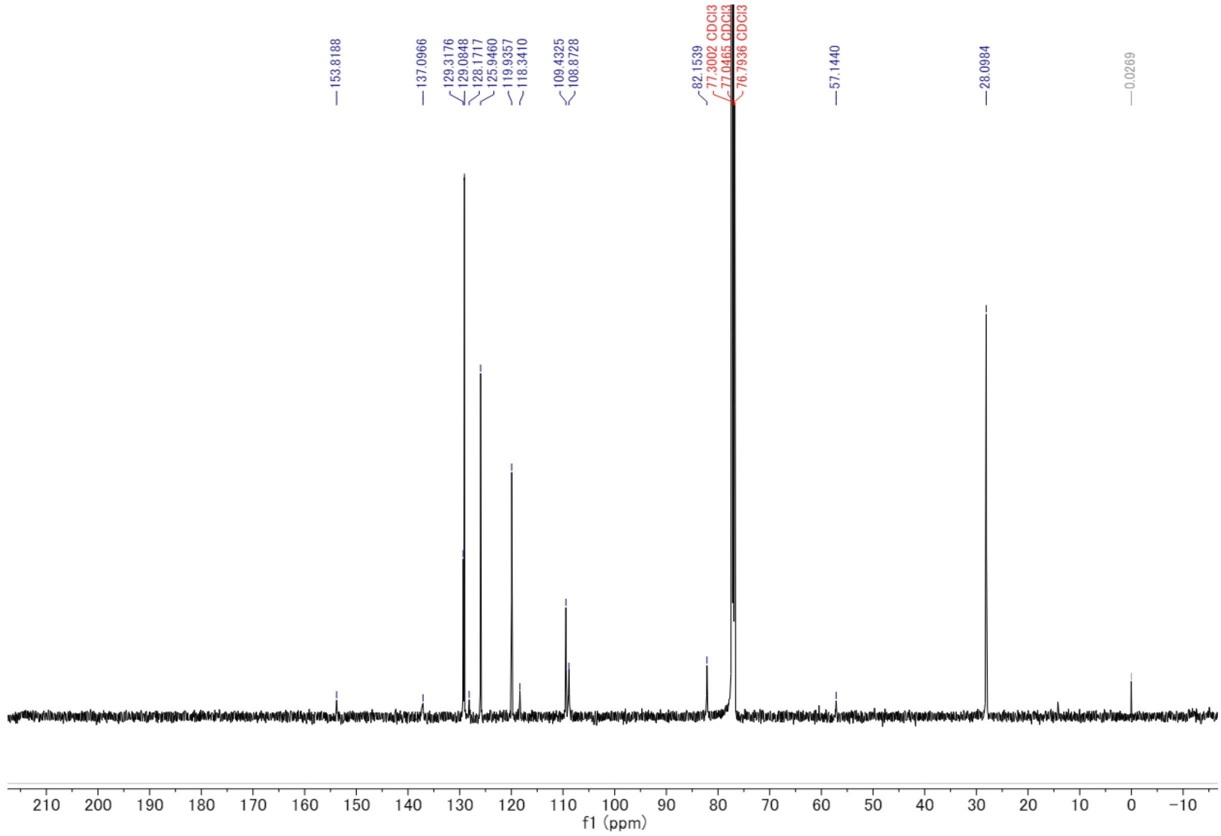
Spectral Data for Isolated Products

(*S*)-2-Phenyl-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4aa)

^{1}H NMR ($CDCl_3$, 300 MHz)

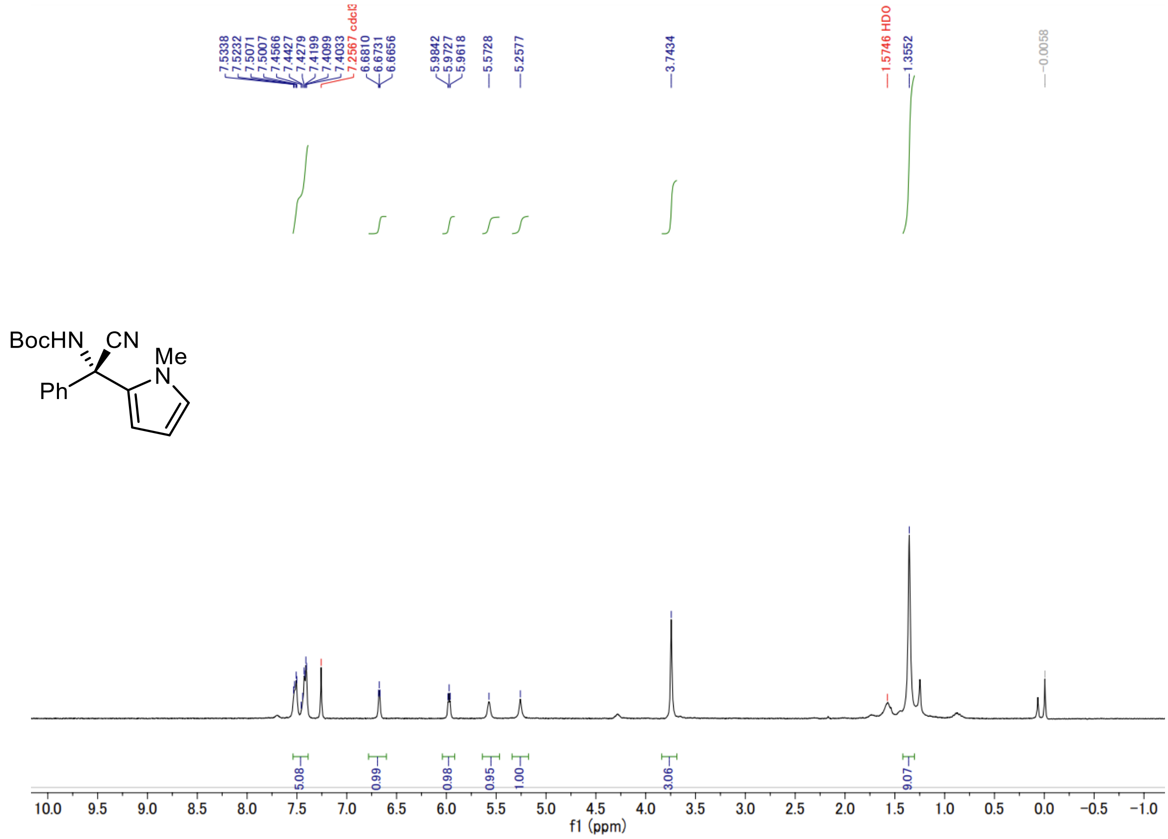


^{13}C NMR ($CDCl_3$, 125 MHz)

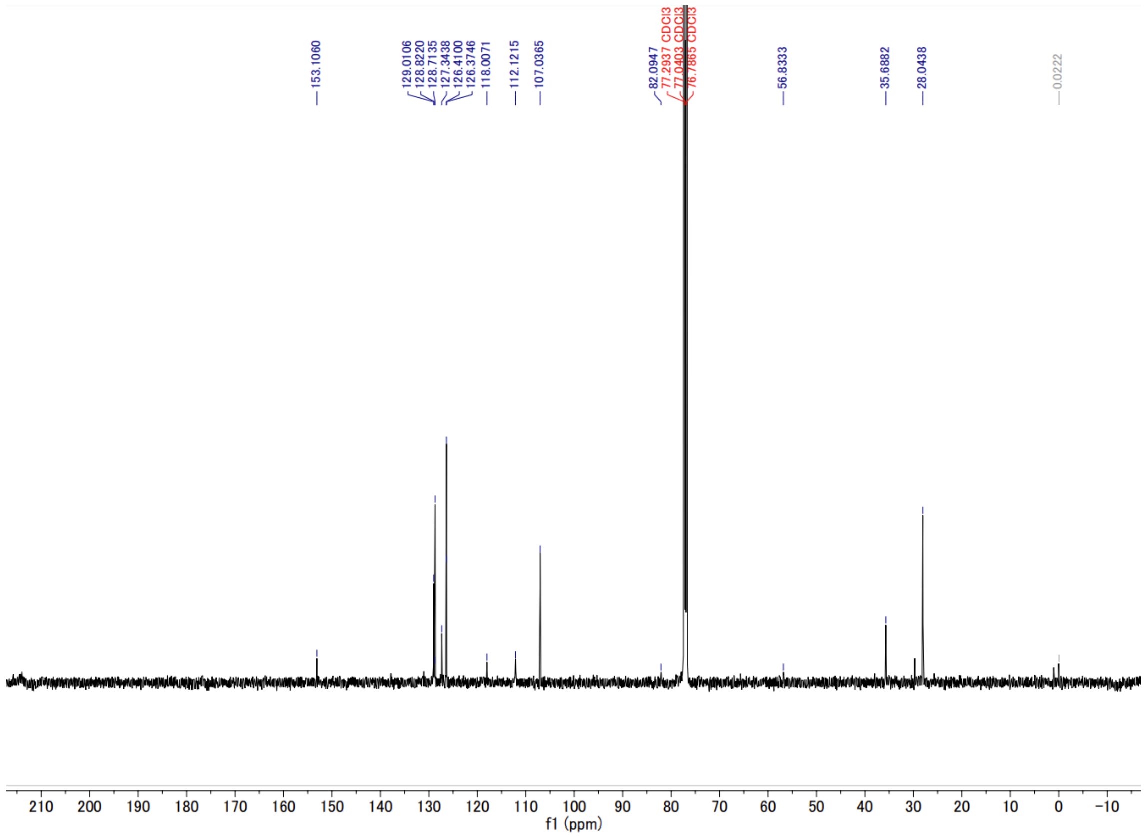


(*S*)-2-Phenyl-2-(1-methyl-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4aa-Me)

^{1}H NMR ($CDCl_3$, 300 MHz)

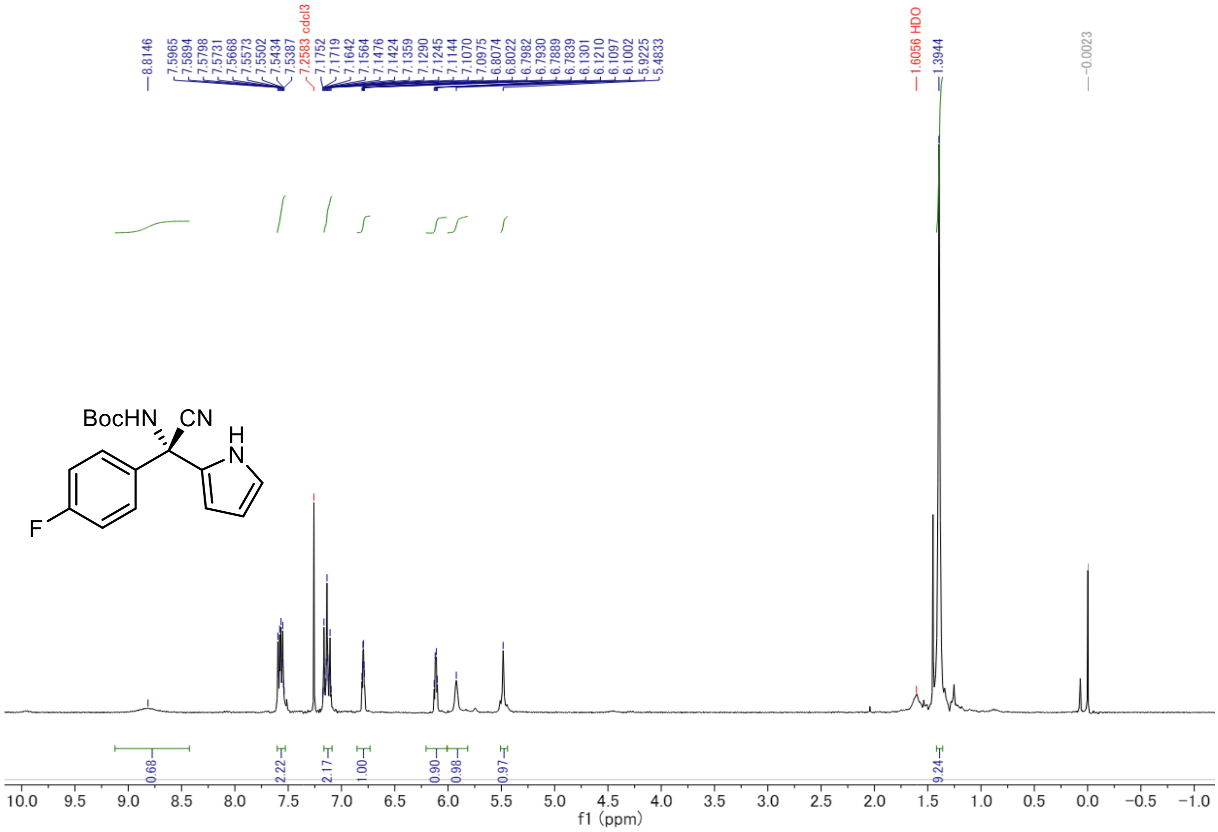


^{13}C NMR ($CDCl_3$, 125 MHz)

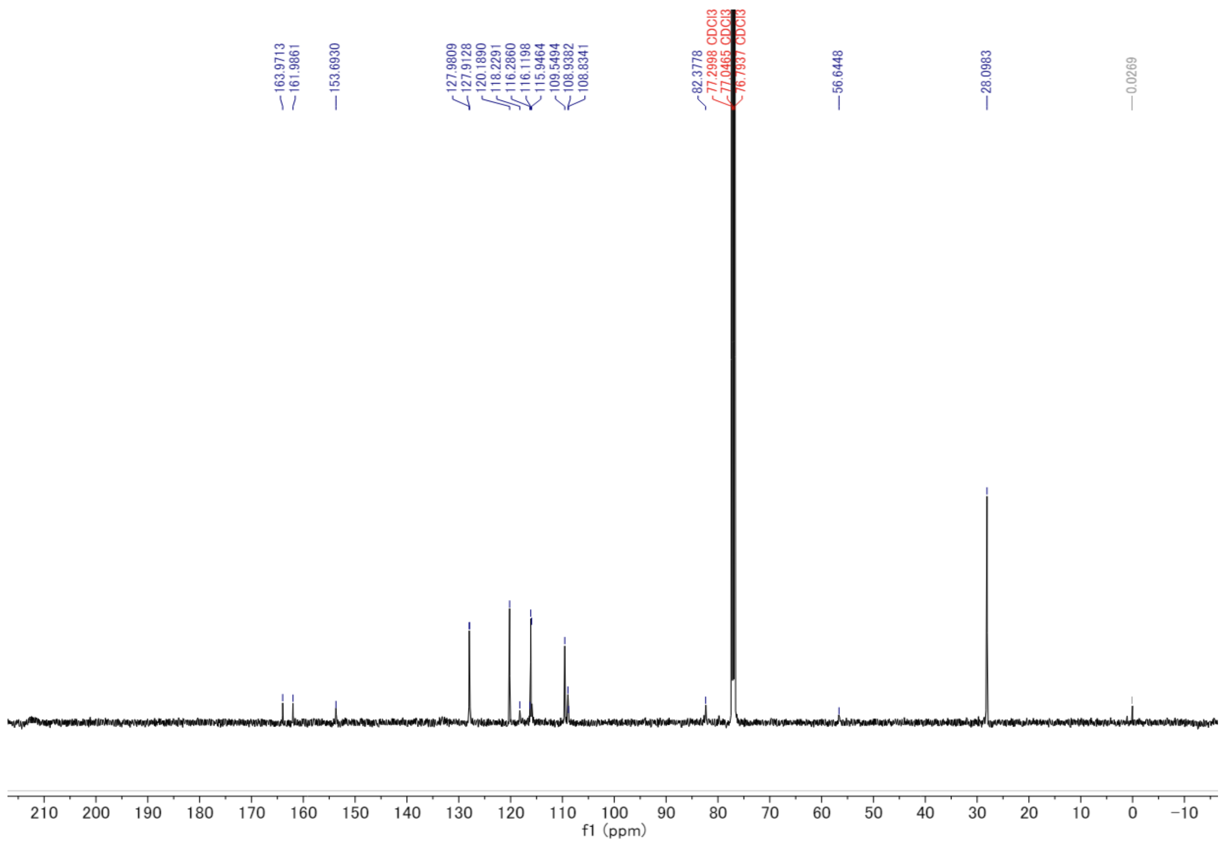


(*S*)-2-(4-Fluorophenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4ba**)

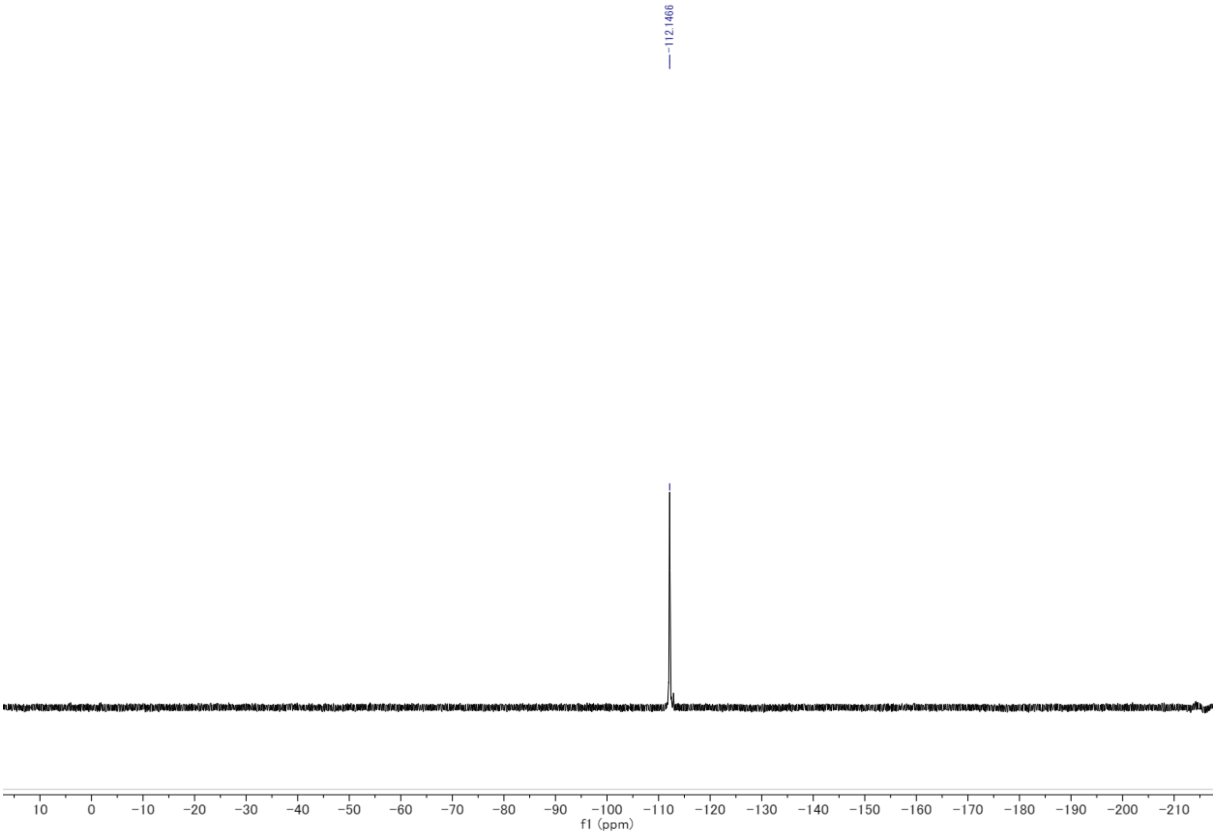
^{1}H NMR ($CDCl_3$, 300 MHz)



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

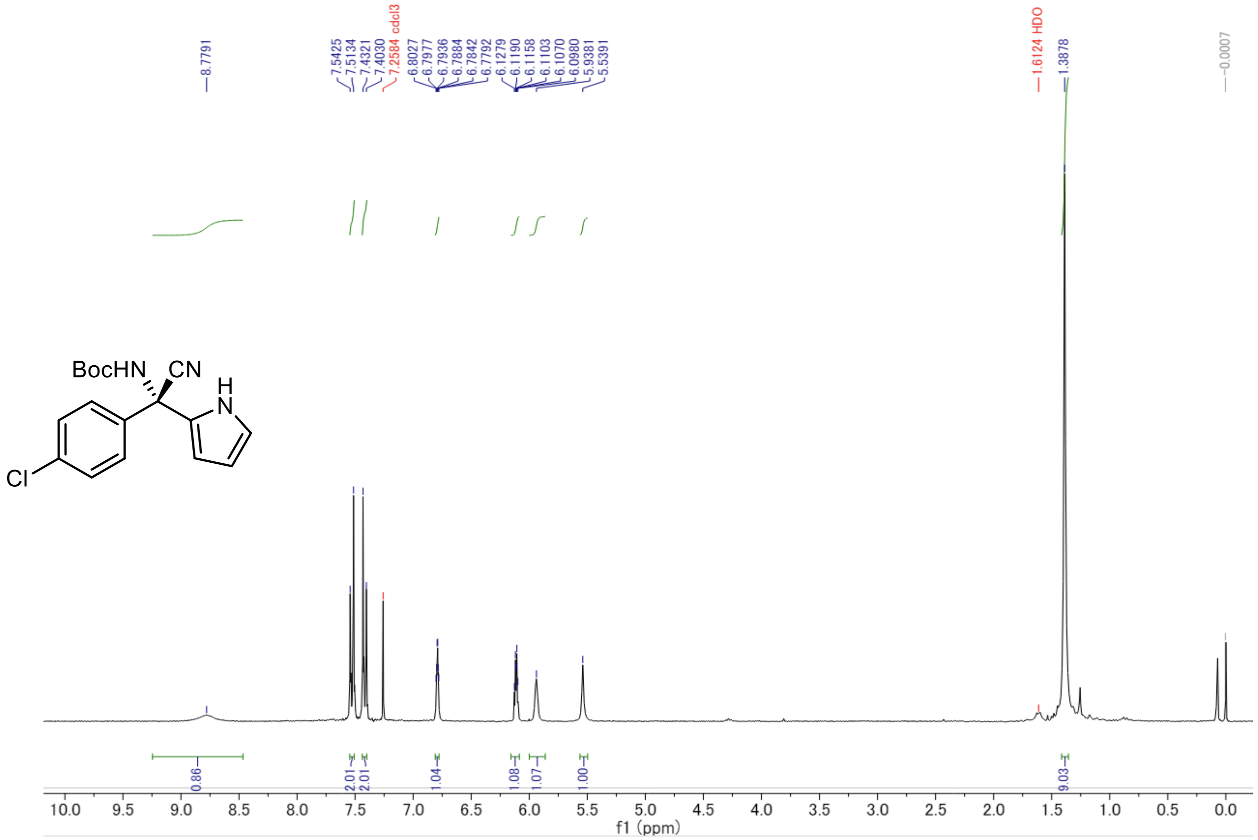


^{19}F NMR ($CDCl_3$, 376 MHz)

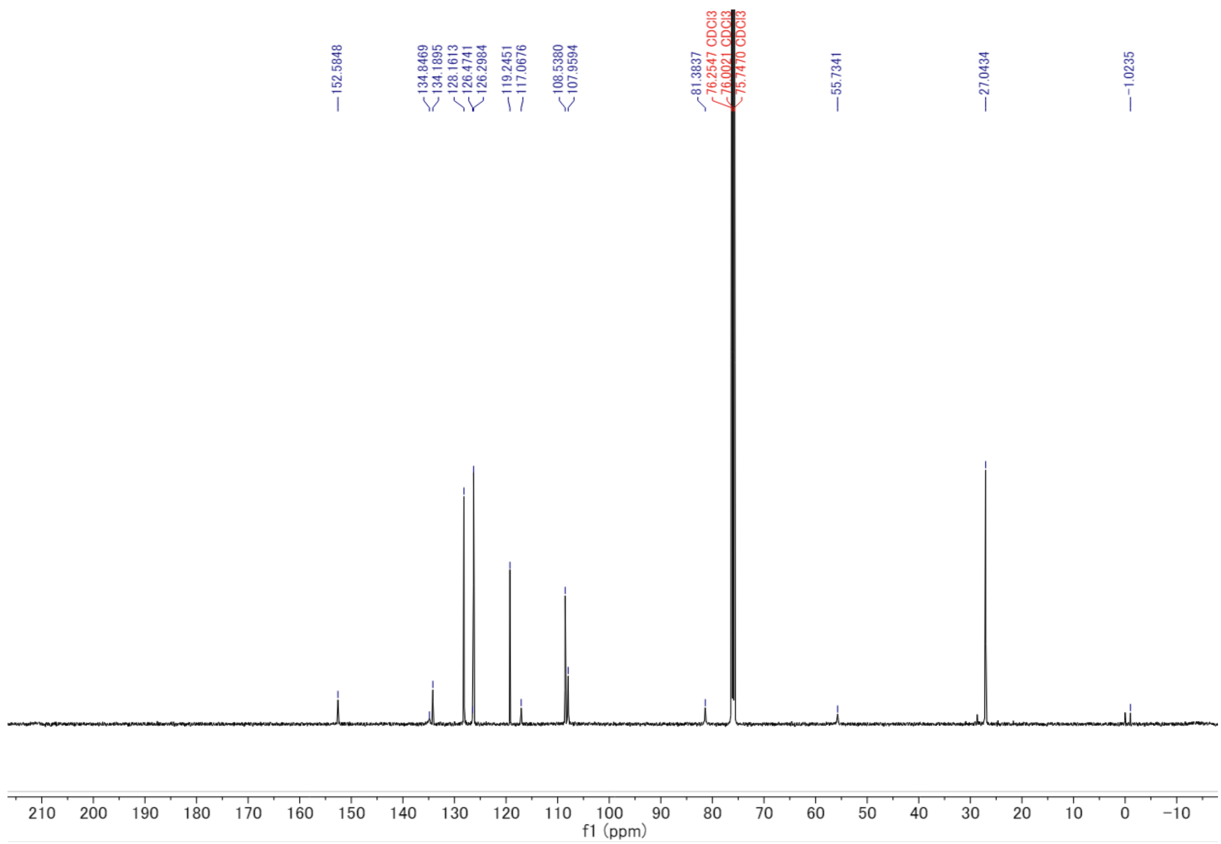


(*S*)-2-(4-Chlorophenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4ca**)

^{1}H NMR ($CDCl_3$, 300 MHz)

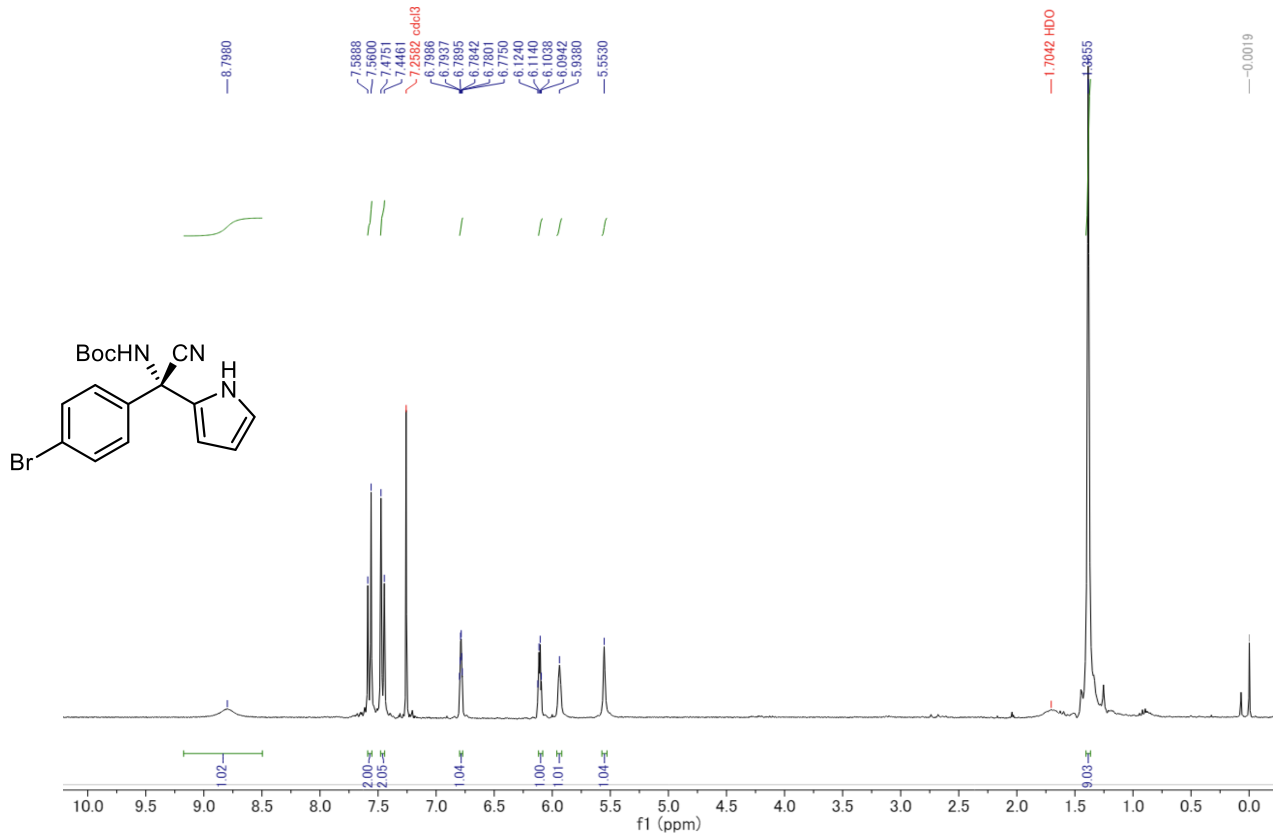


^{13}C NMR ($CDCl_3$, 125 MHz)

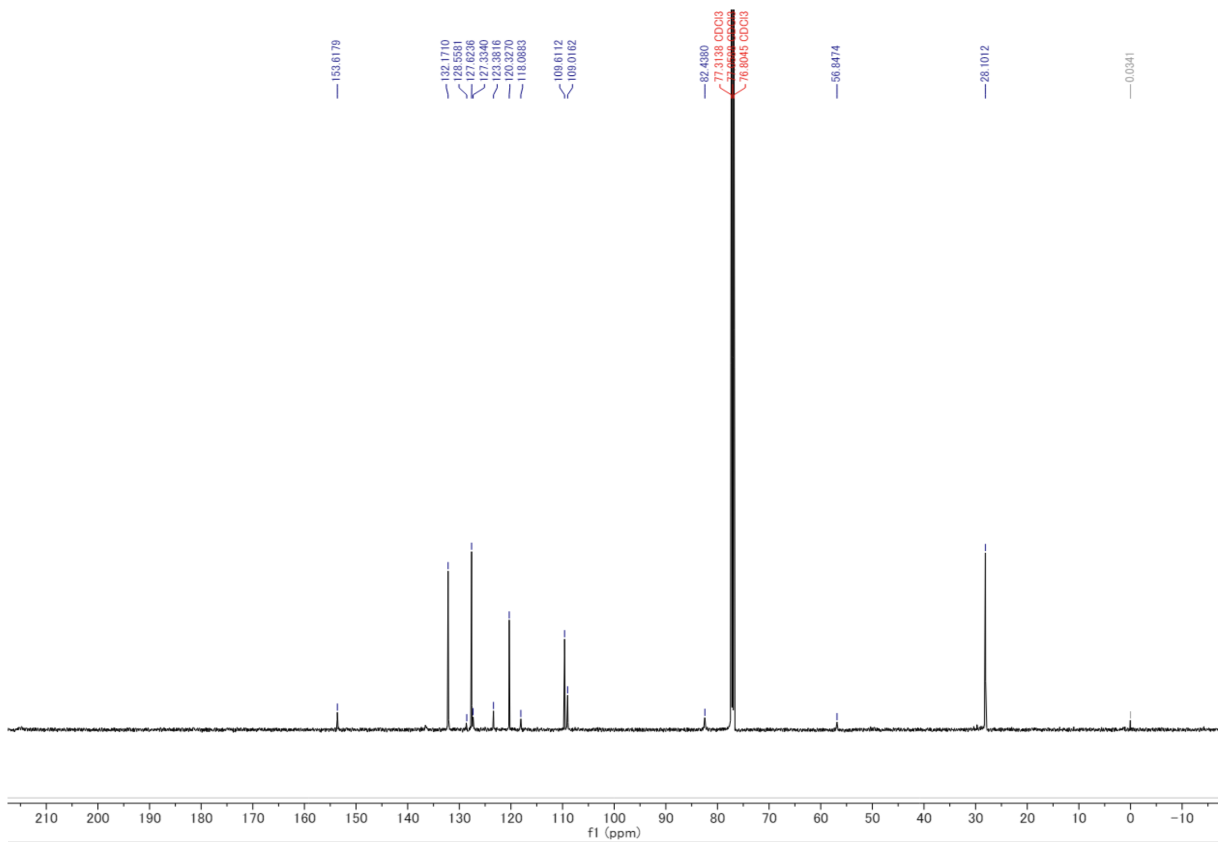


(*S*)-2-(4-Bromophenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4da)

^{1}H NMR ($CDCl_3$, 300 MHz)

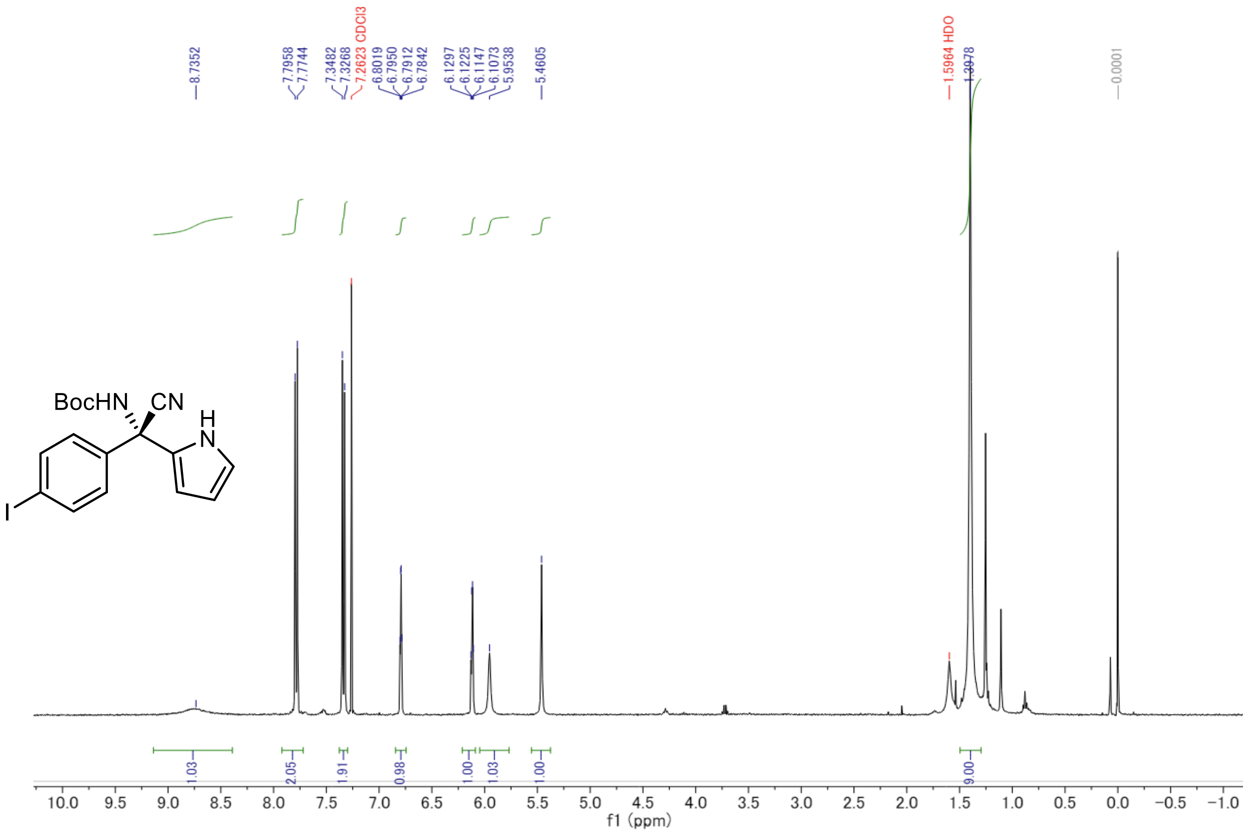


^{13}C NMR ($CDCl_3$, 125 MHz)

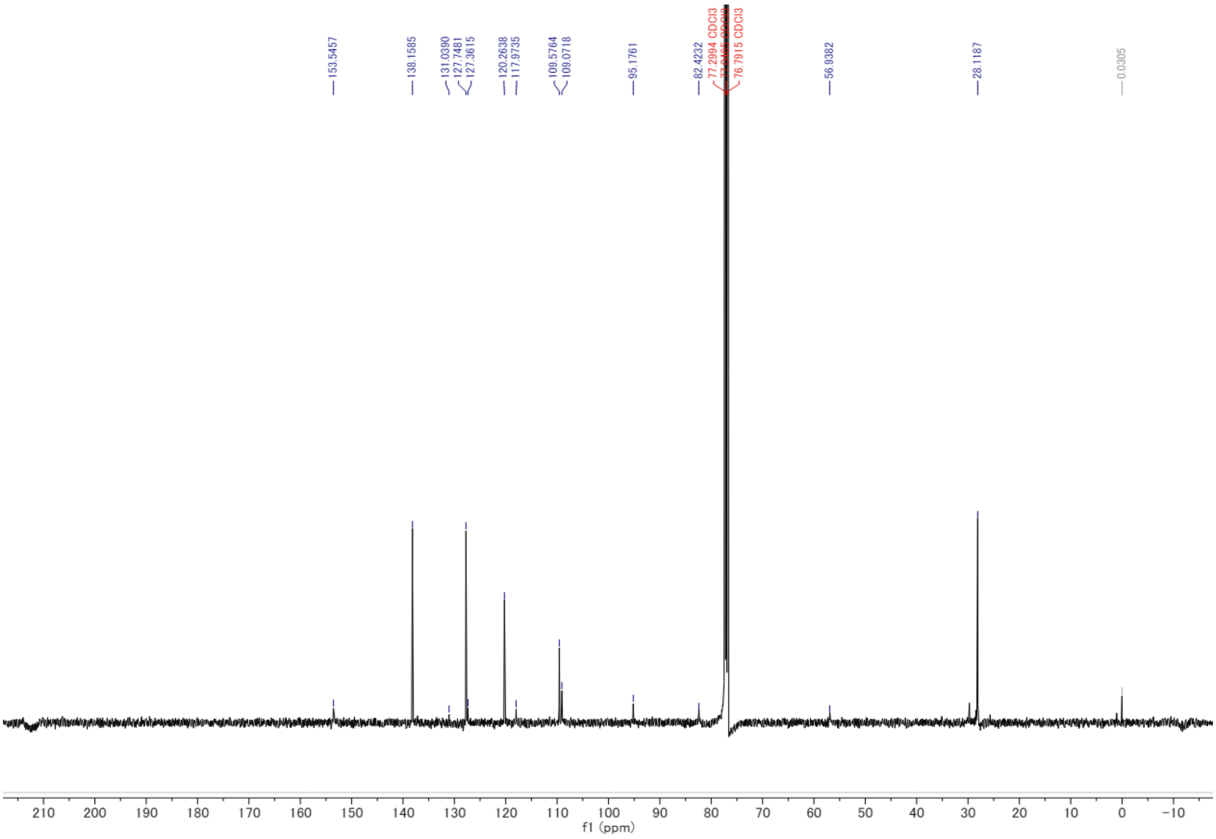


(*S*)-2-(4-Iodophenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4ea)

^{1}H NMR ($CDCl_3$, 300 MHz)

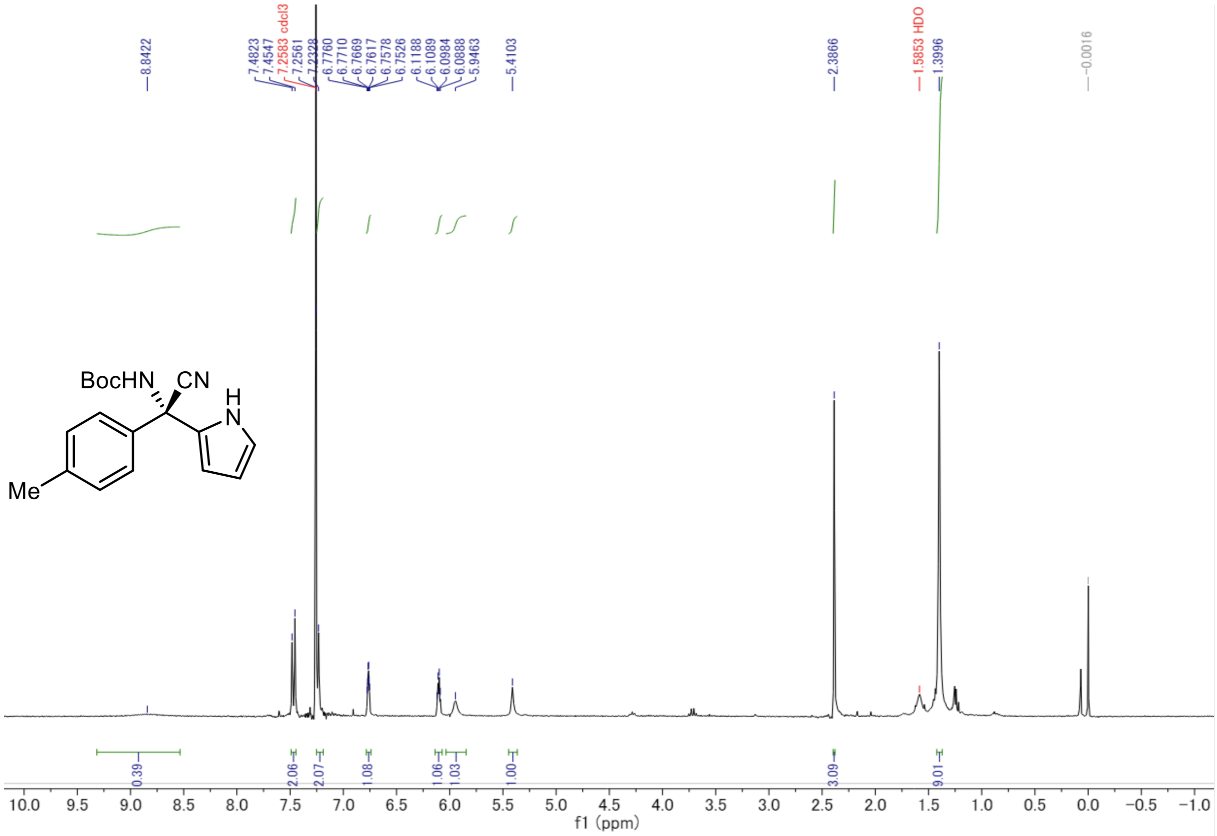


^{13}C NMR ($CDCl_3$, 125 MHz)

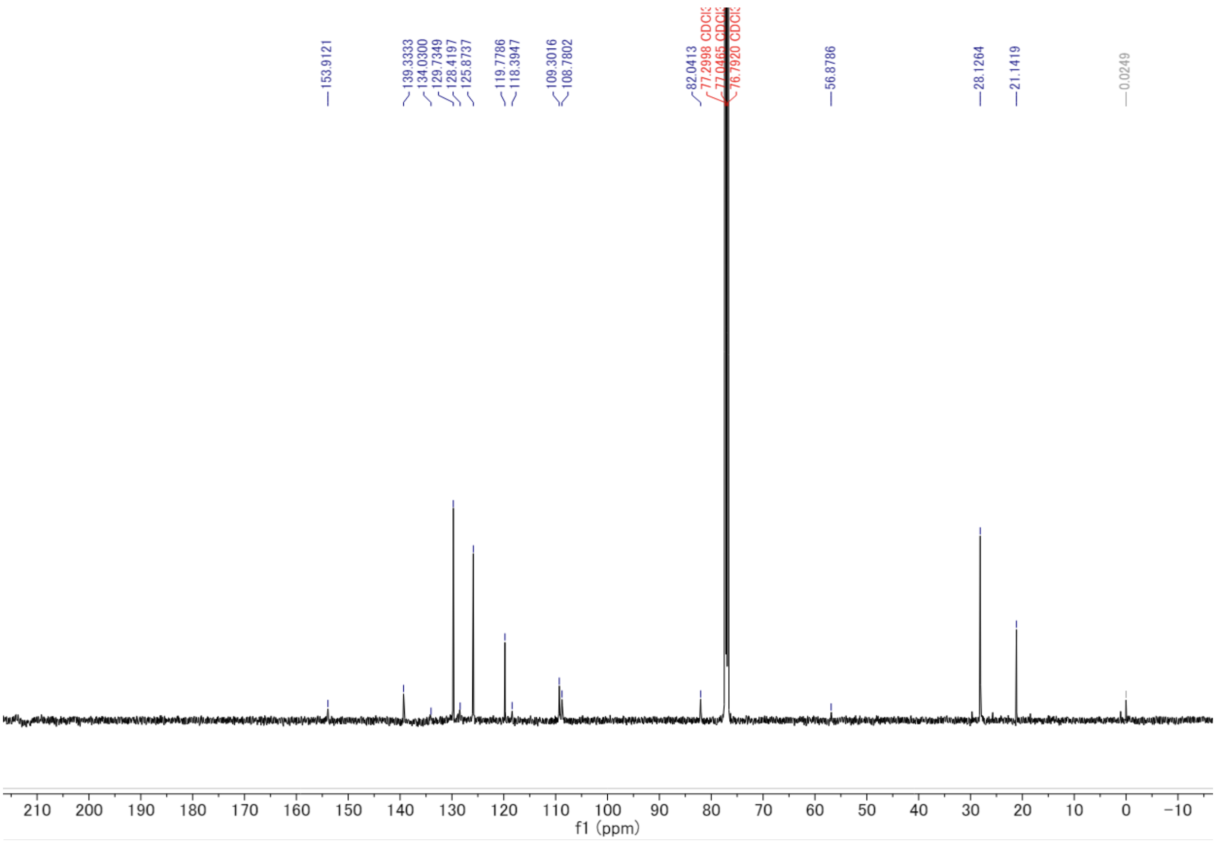


(*S*)-2-(4-Methylphenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4fa)

^{1}H NMR (CDCl$_3$, 300 MHz)

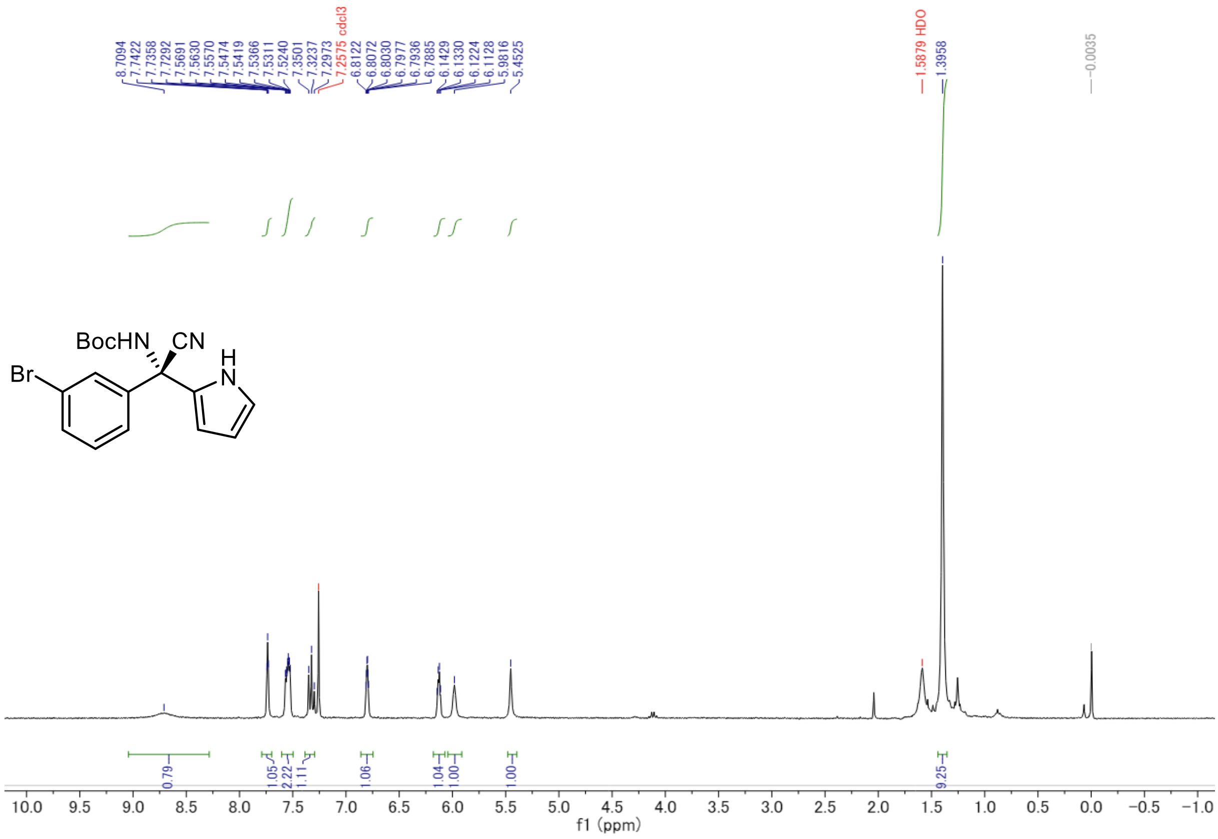


^{13}C NMR (CDCl$_3$, 125 MHz)

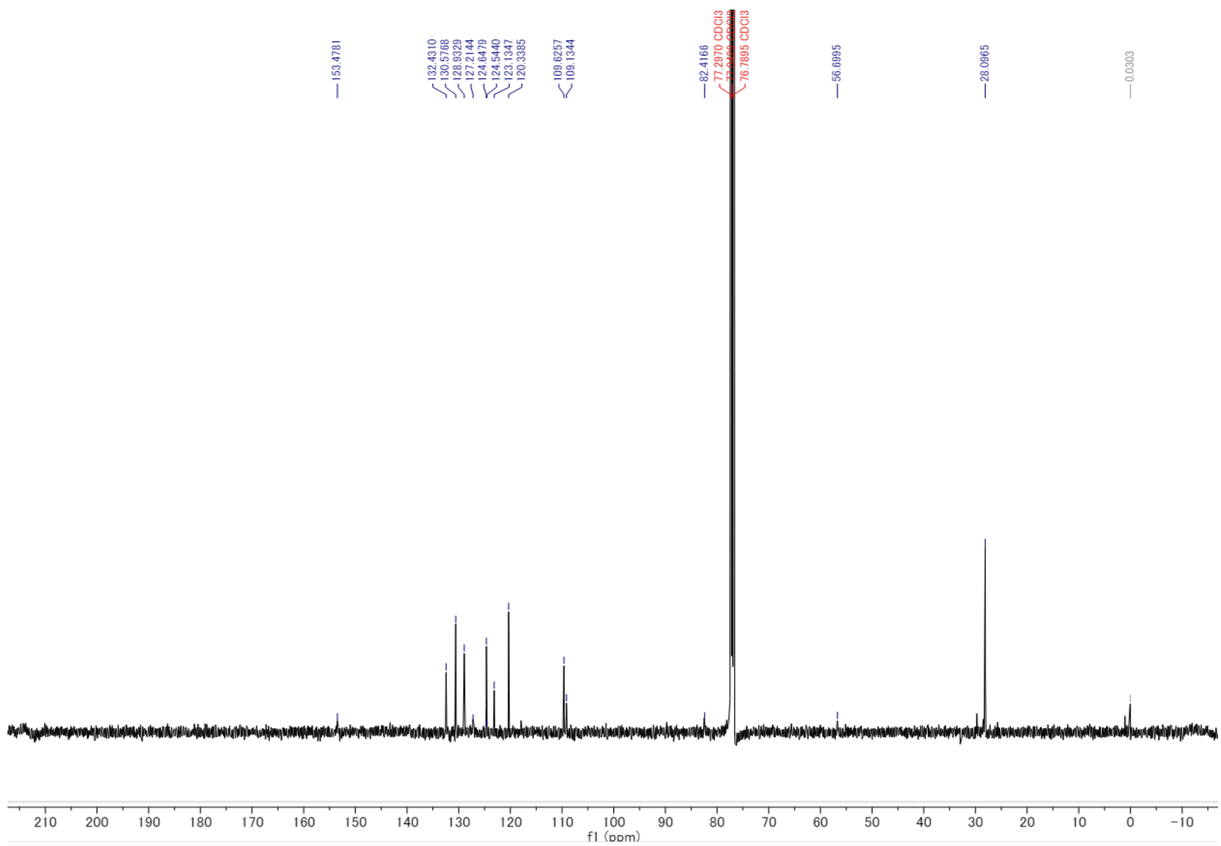


(*S*)-2-(3-Bromophenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4ga**)

^{1}H NMR ($CDCl_3$, 300 MHz)

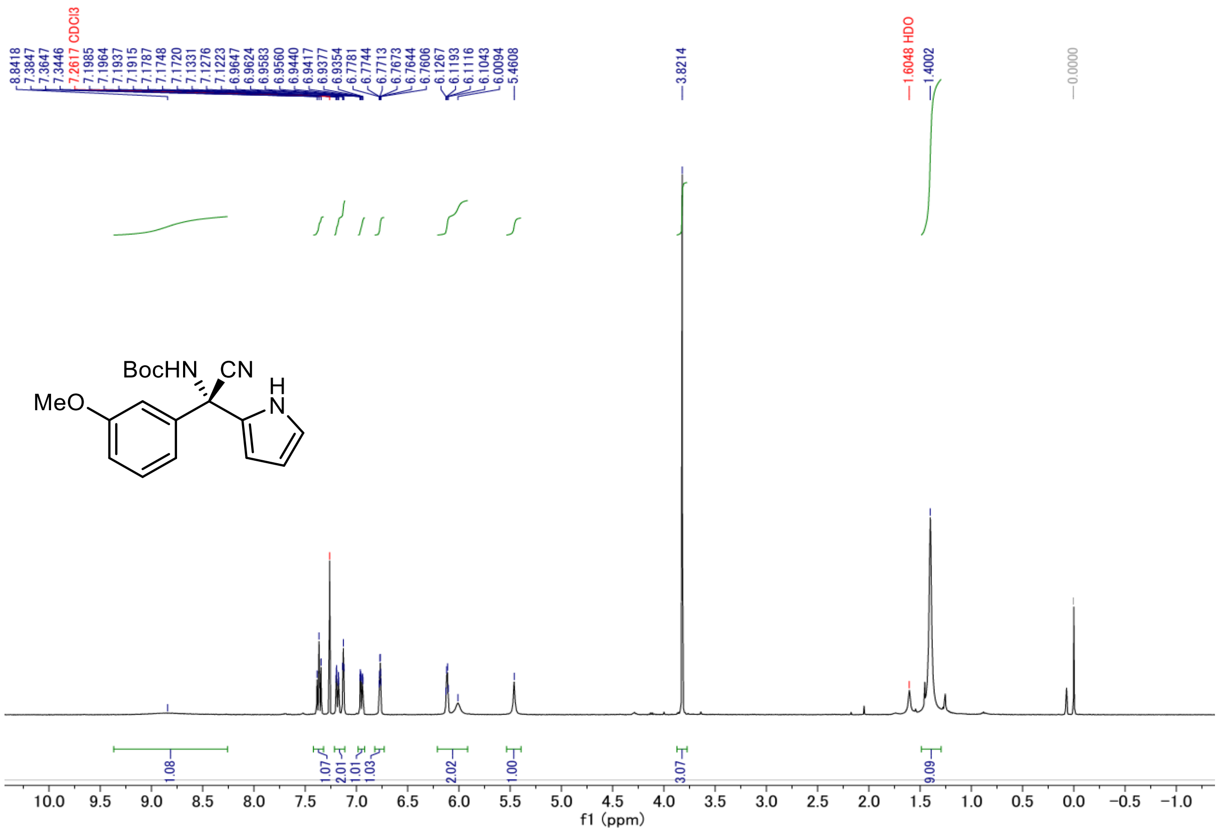


^{13}C NMR ($CDCl_3$, 125 MHz)

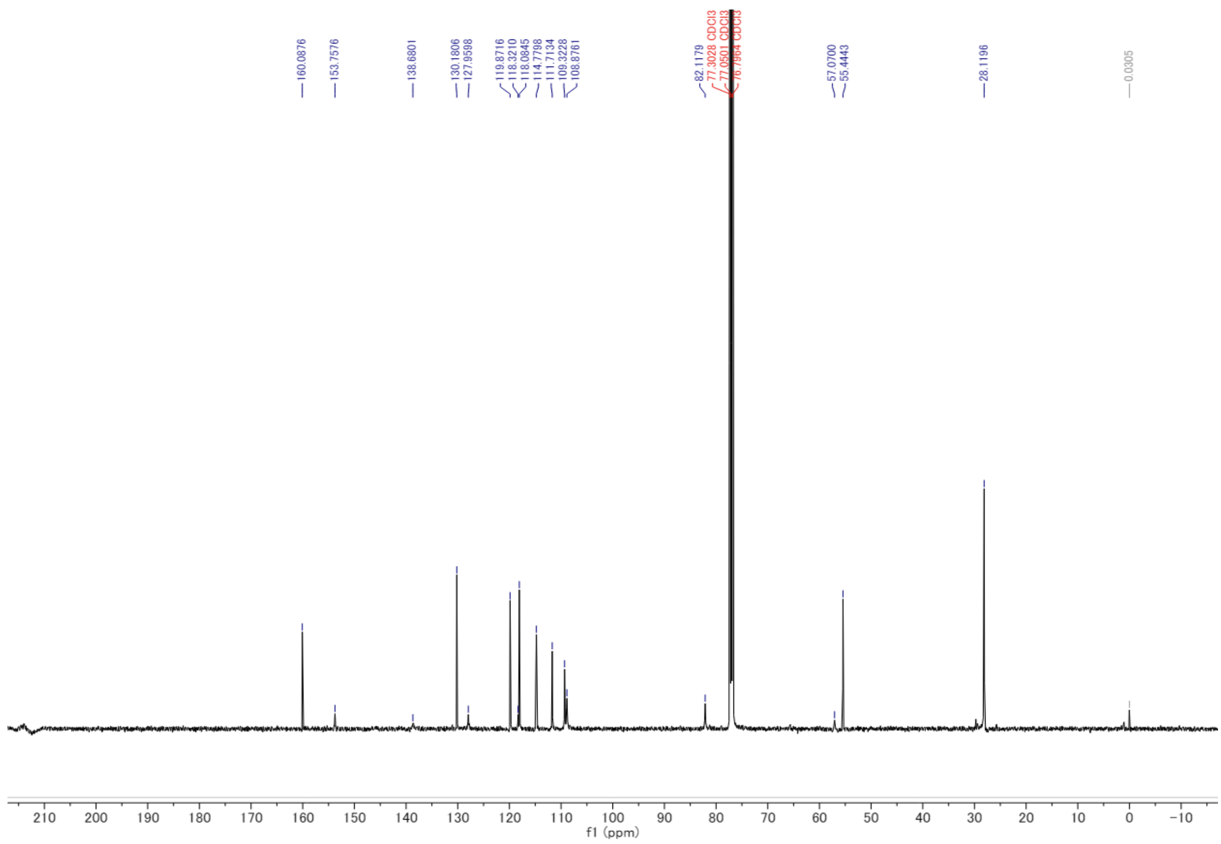


(*S*)-2-(3-Methoxyphenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4ha)

[1]H NMR ($CDCl_3$, 300 MHz)

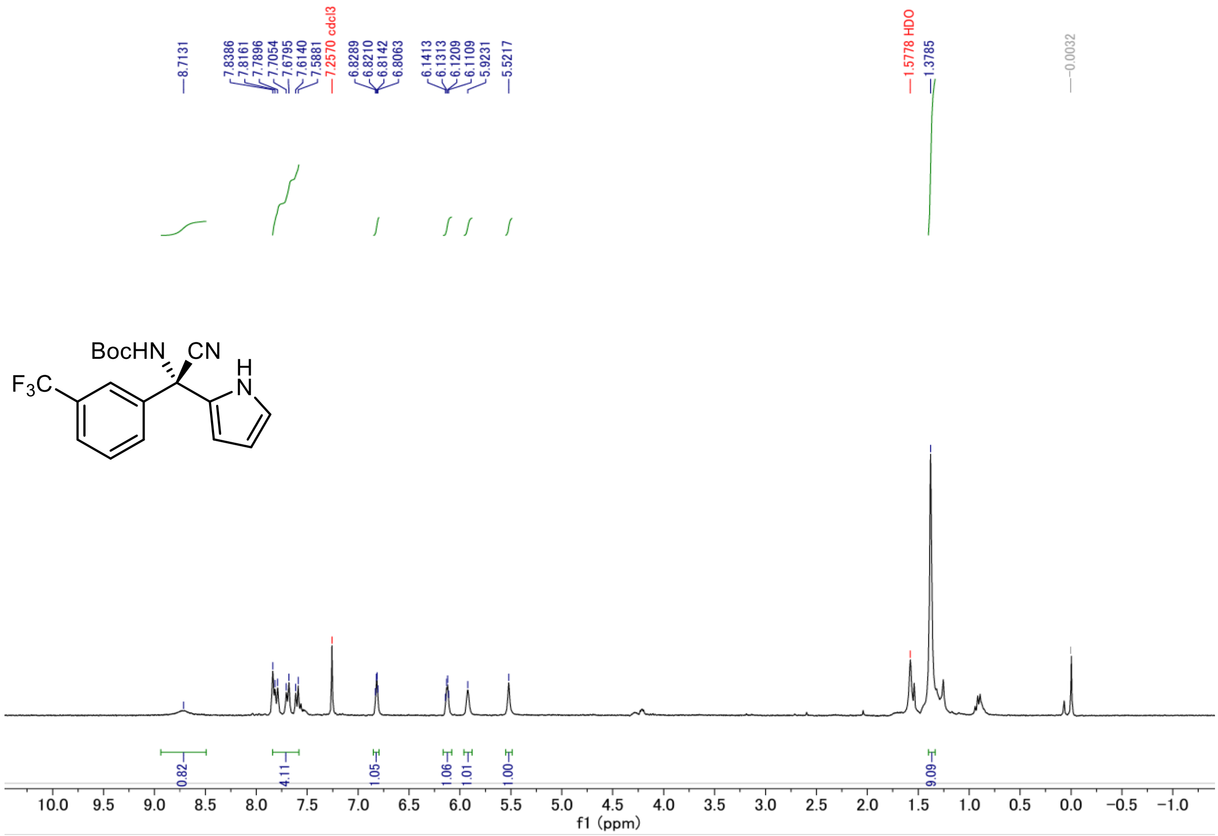


[13]C NMR ($CDCl_3$, 125 MHz)

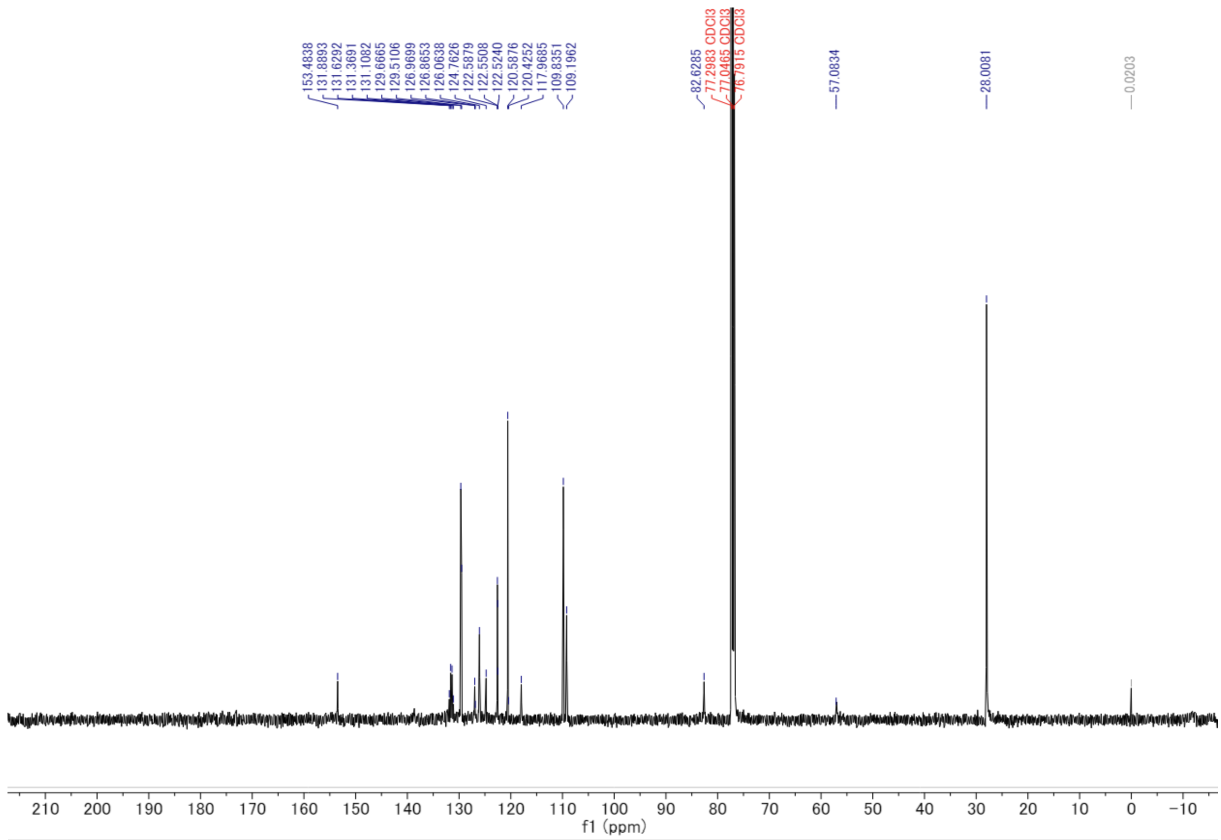


(*S*)-2-(3-Methoxyphenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4ia)

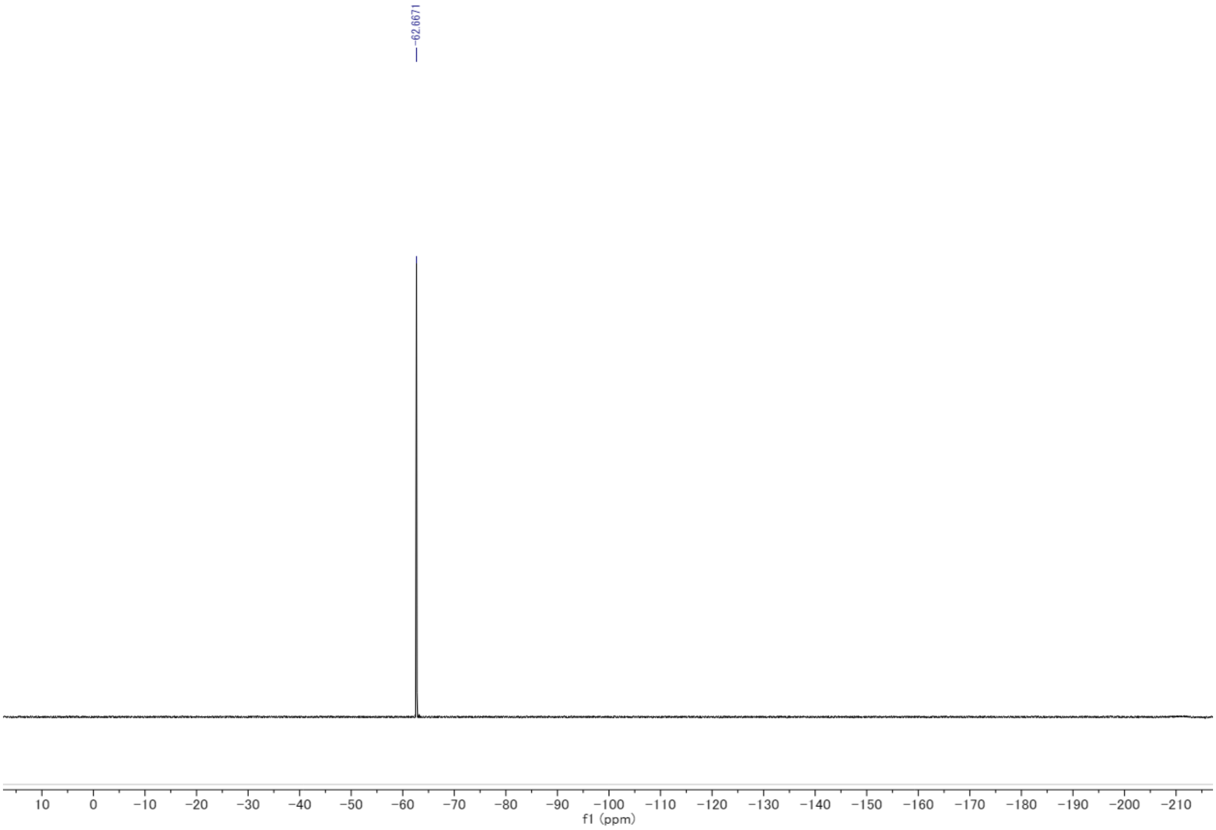
^{1}H NMR ($CDCl_3$, 300 MHz)



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

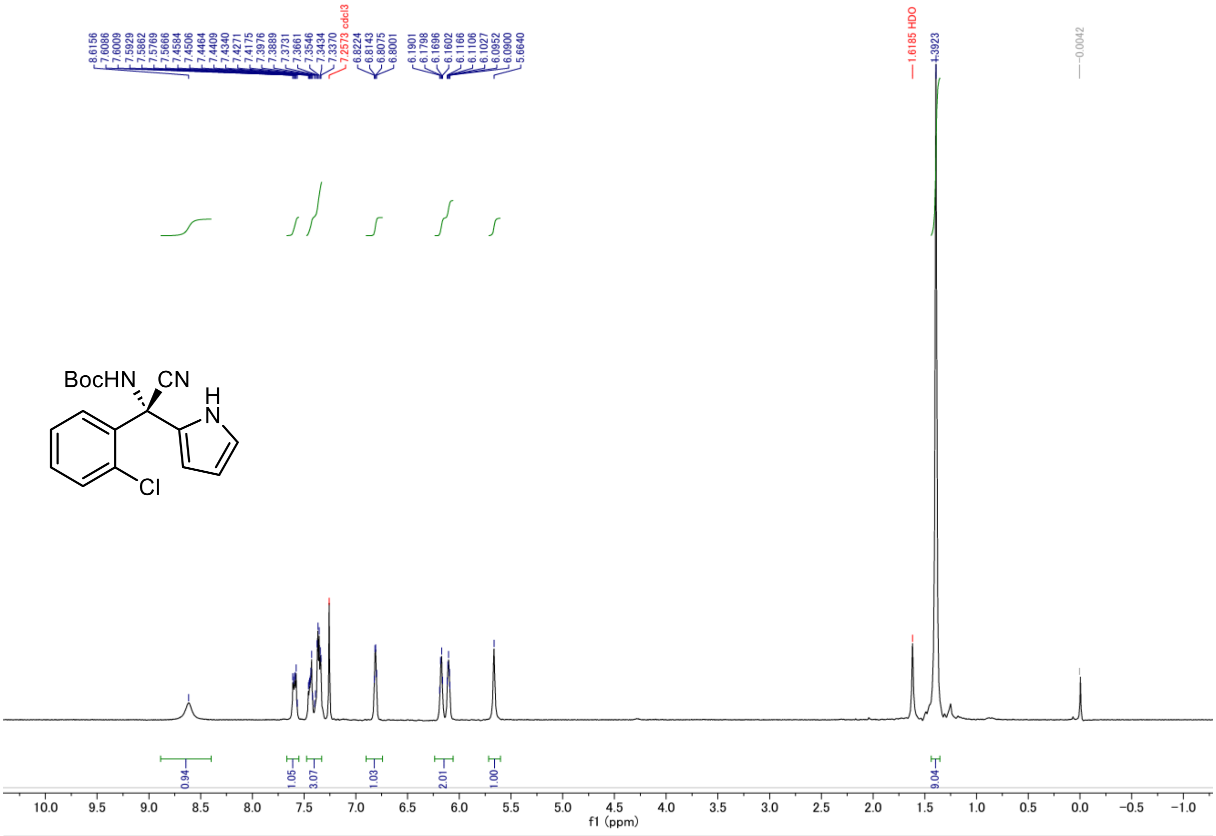


^{19}F NMR ($CDCl_3$, 376 MHz)

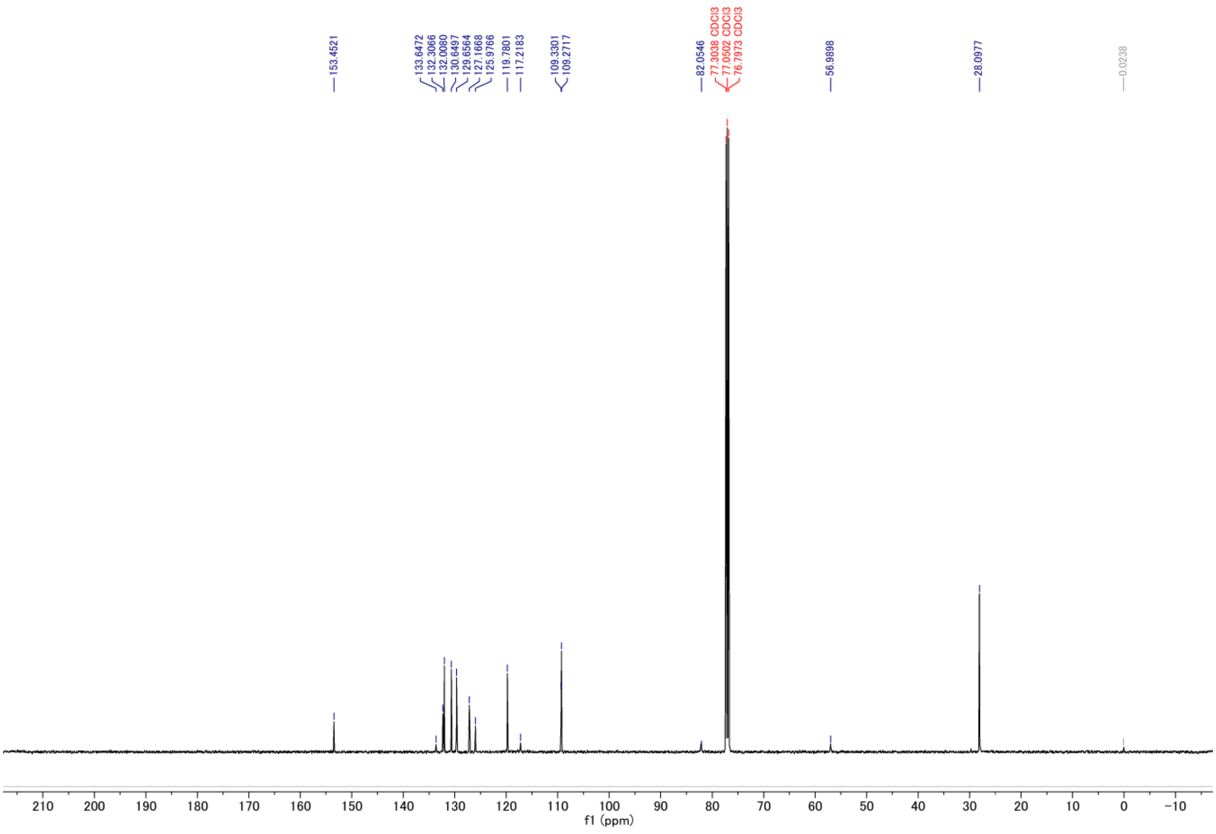


(*S*)-2-(2-Bromophenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4ja)

[1]H NMR ($CDCl_3$, 300 MHz)

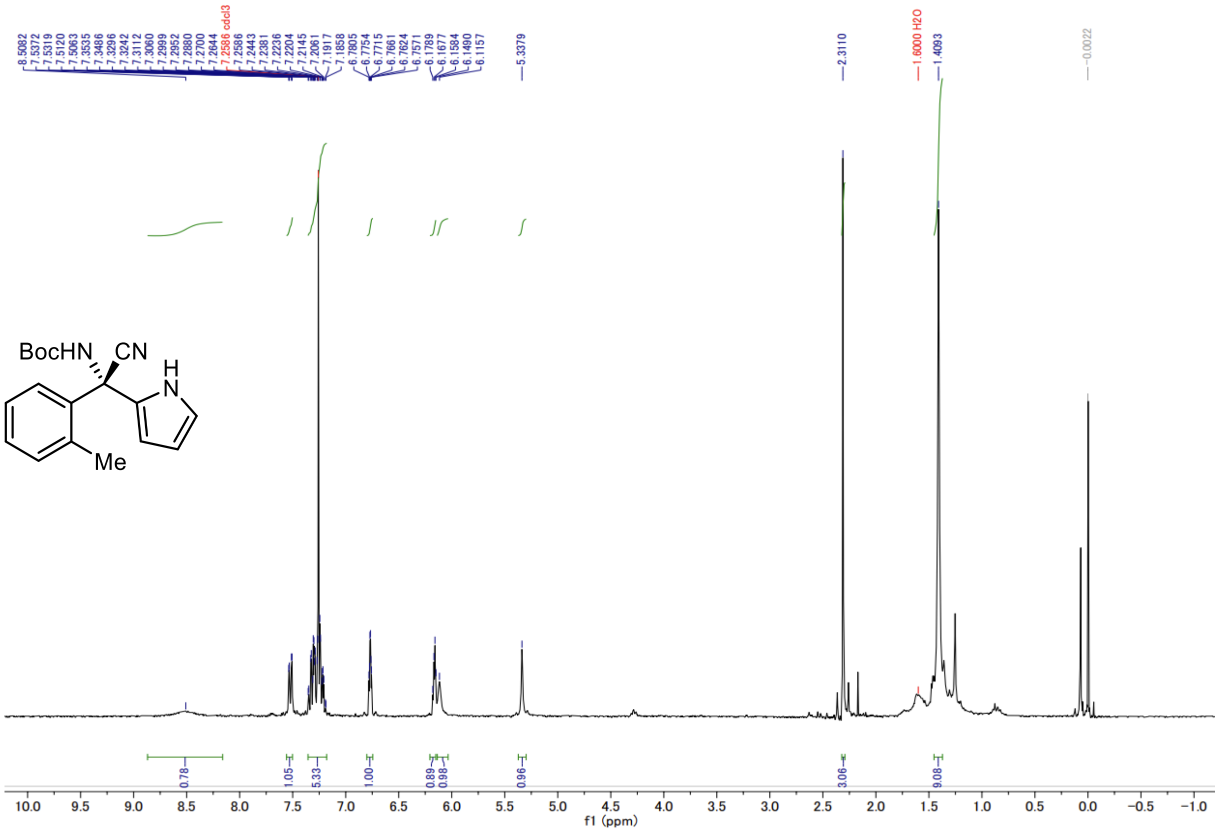


[13]C NMR ($CDCl_3$, 125 MHz)

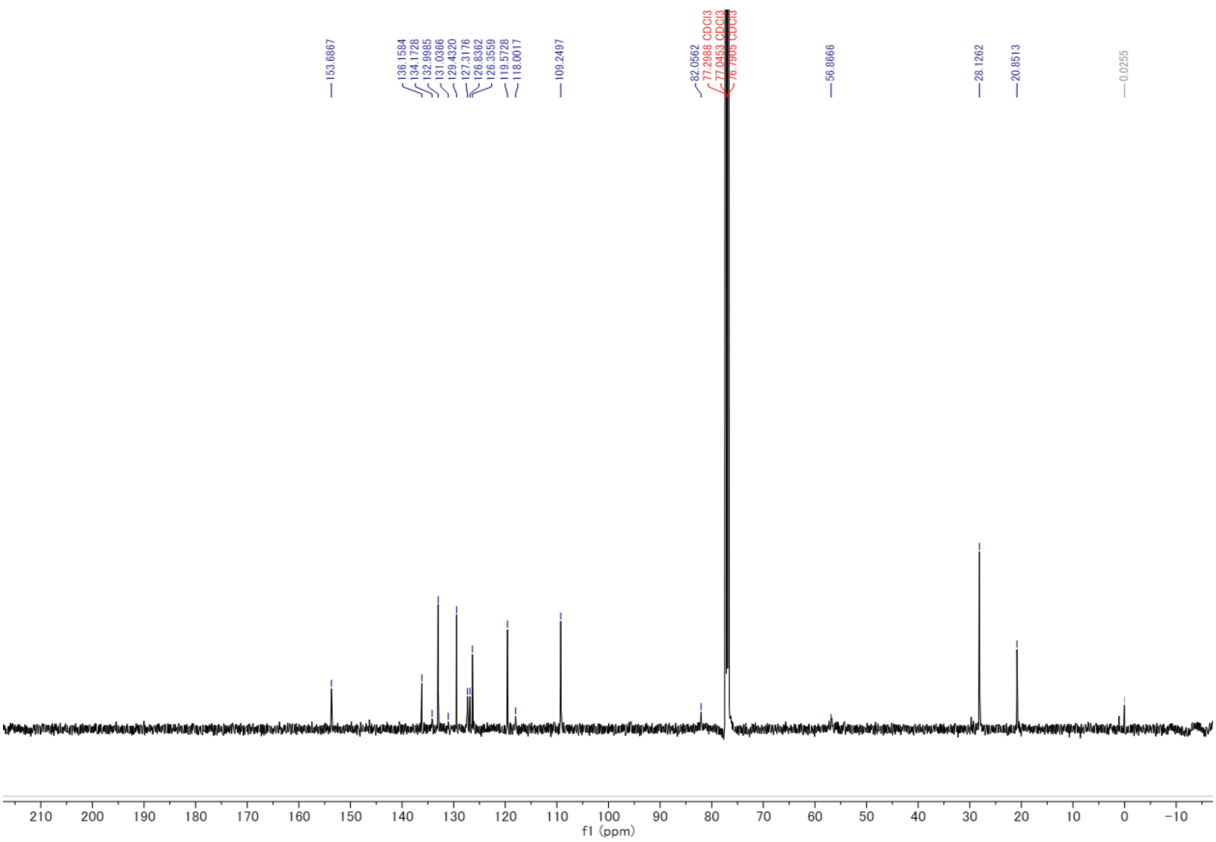


(*S*)-2-(2-Methylphenyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4ka)

^{1}H NMR ($CDCl_3$, 300 MHz)

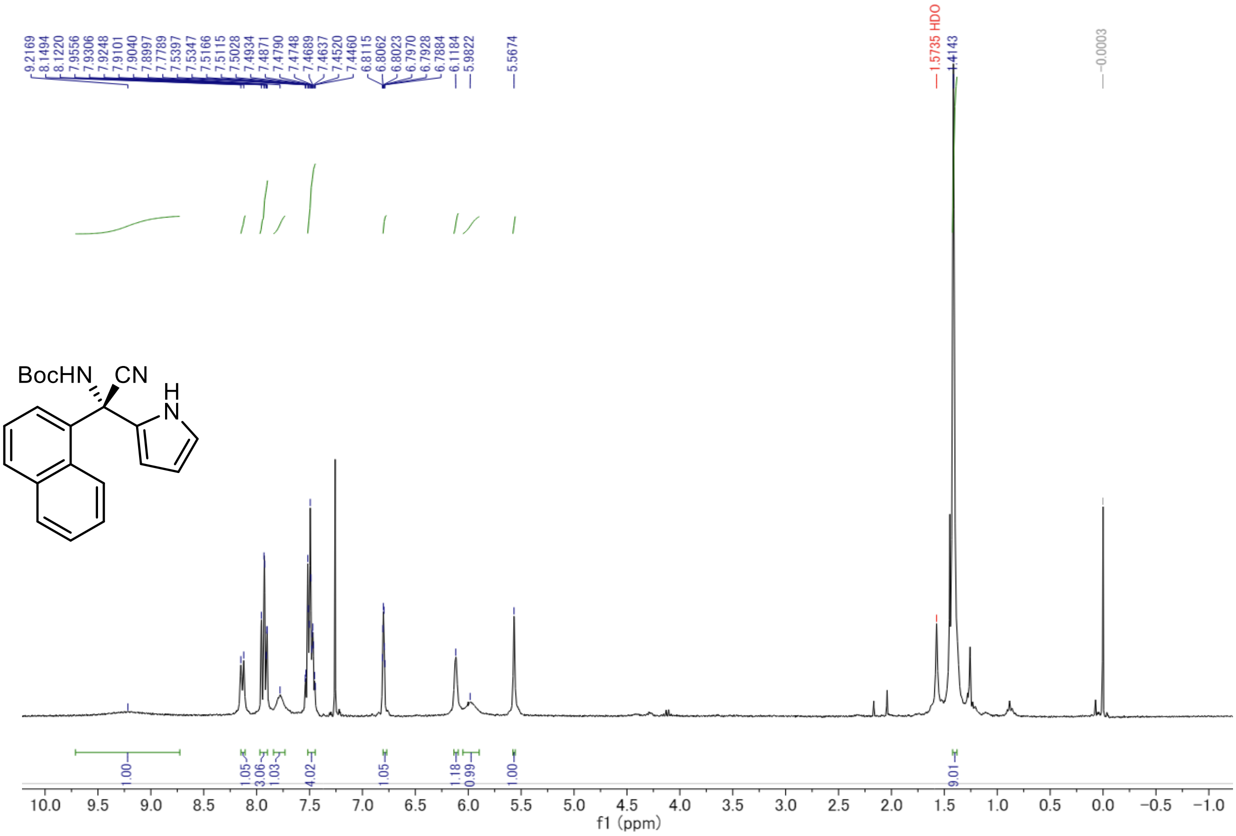


^{13}C NMR ($CDCl_3$, 125 MHz)

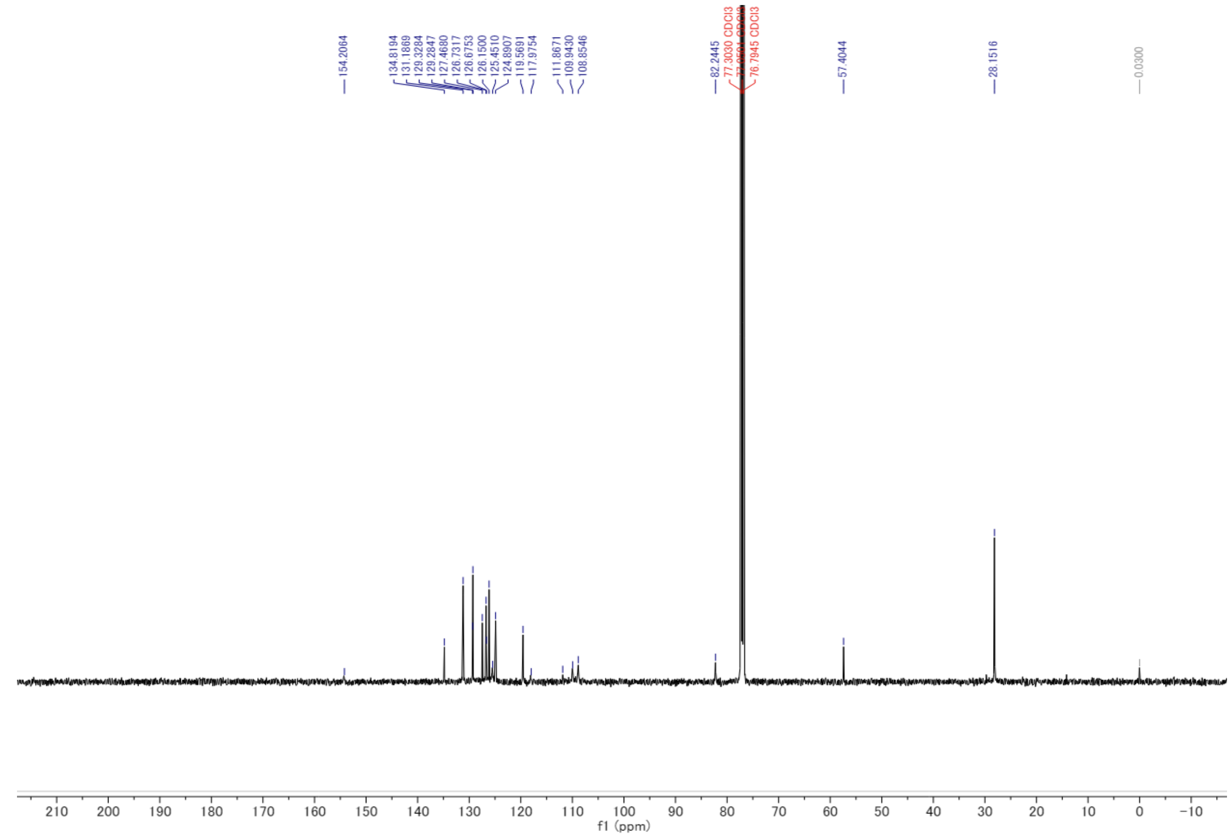


(*S*)-2-(1-Naphtyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4la)

^{1}H NMR ($CDCl_3$, 300 MHz)

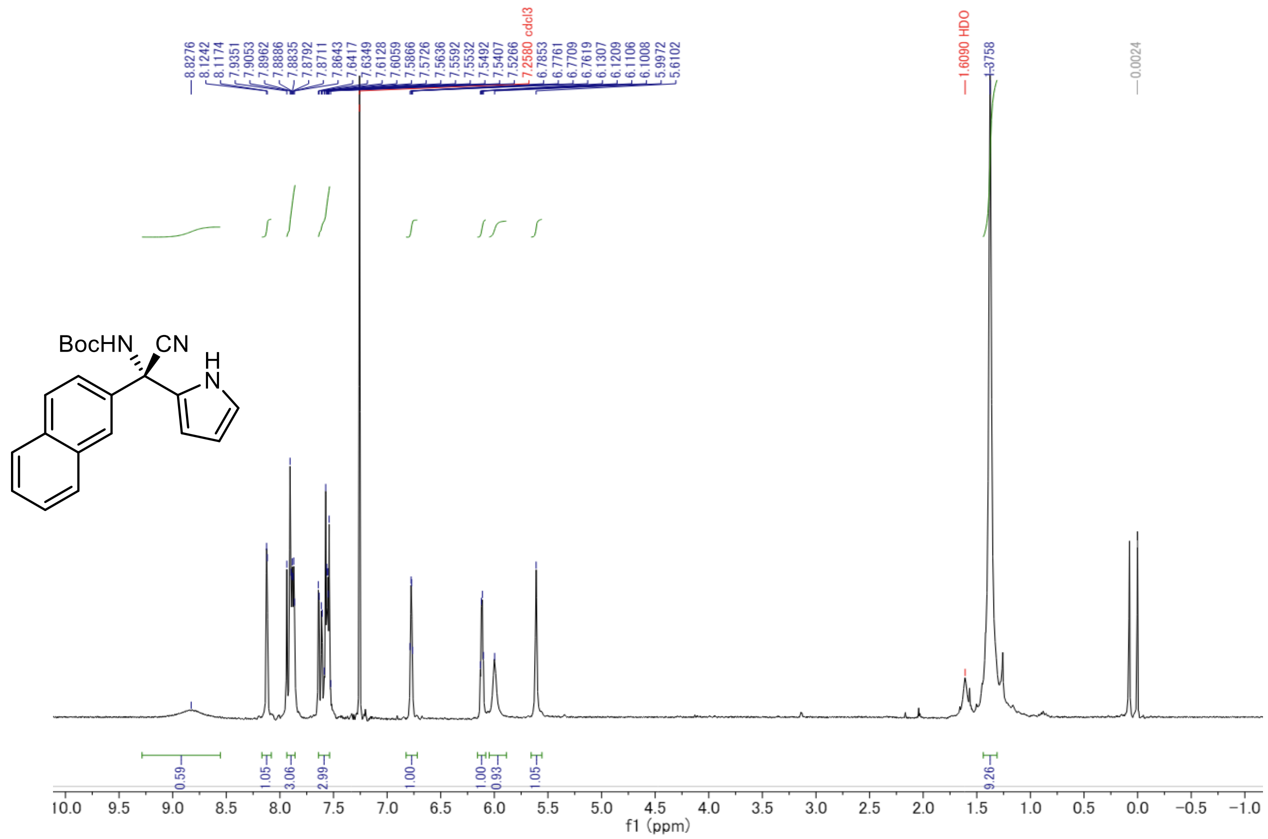


^{13}C NMR ($CDCl_3$, 125 MHz)

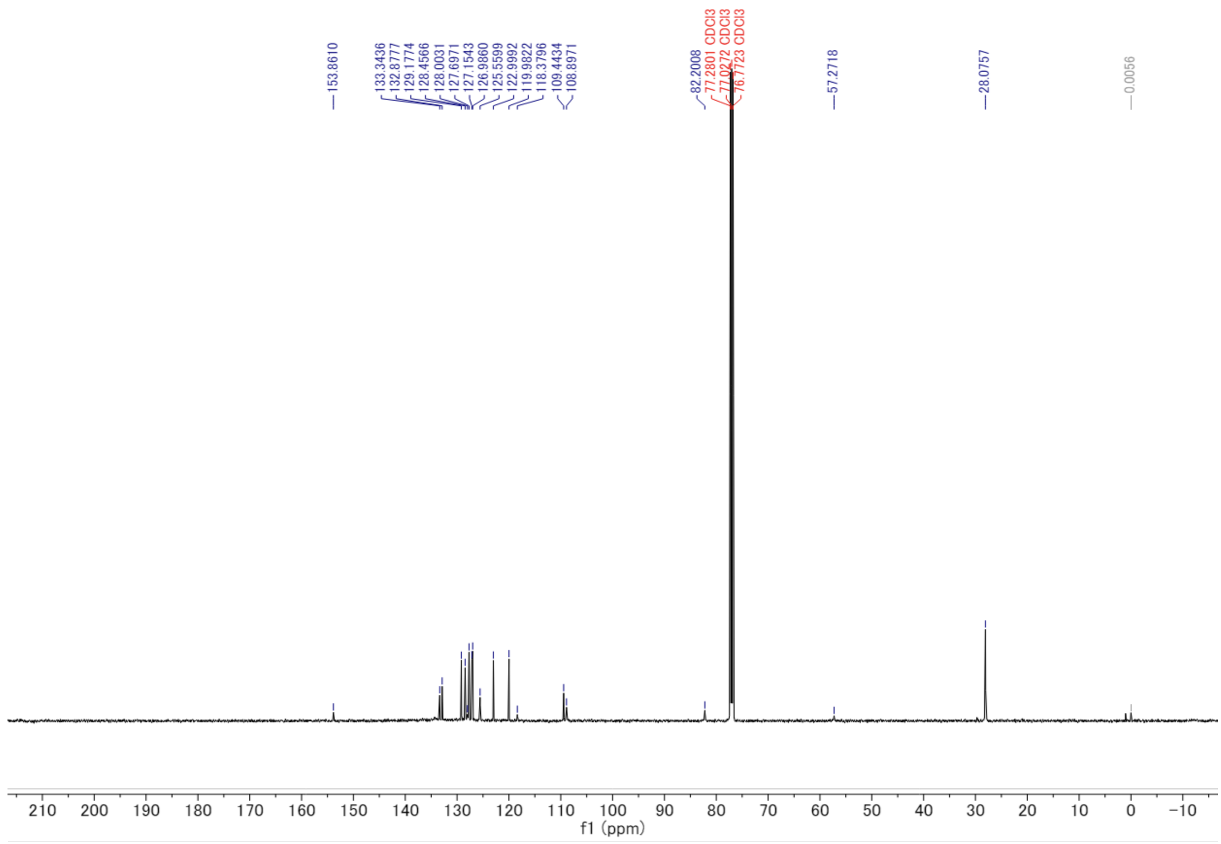


(*S*)-2-(2-Naphtyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4ma)

^{1}H NMR ($CDCl_3$, 300 MHz)

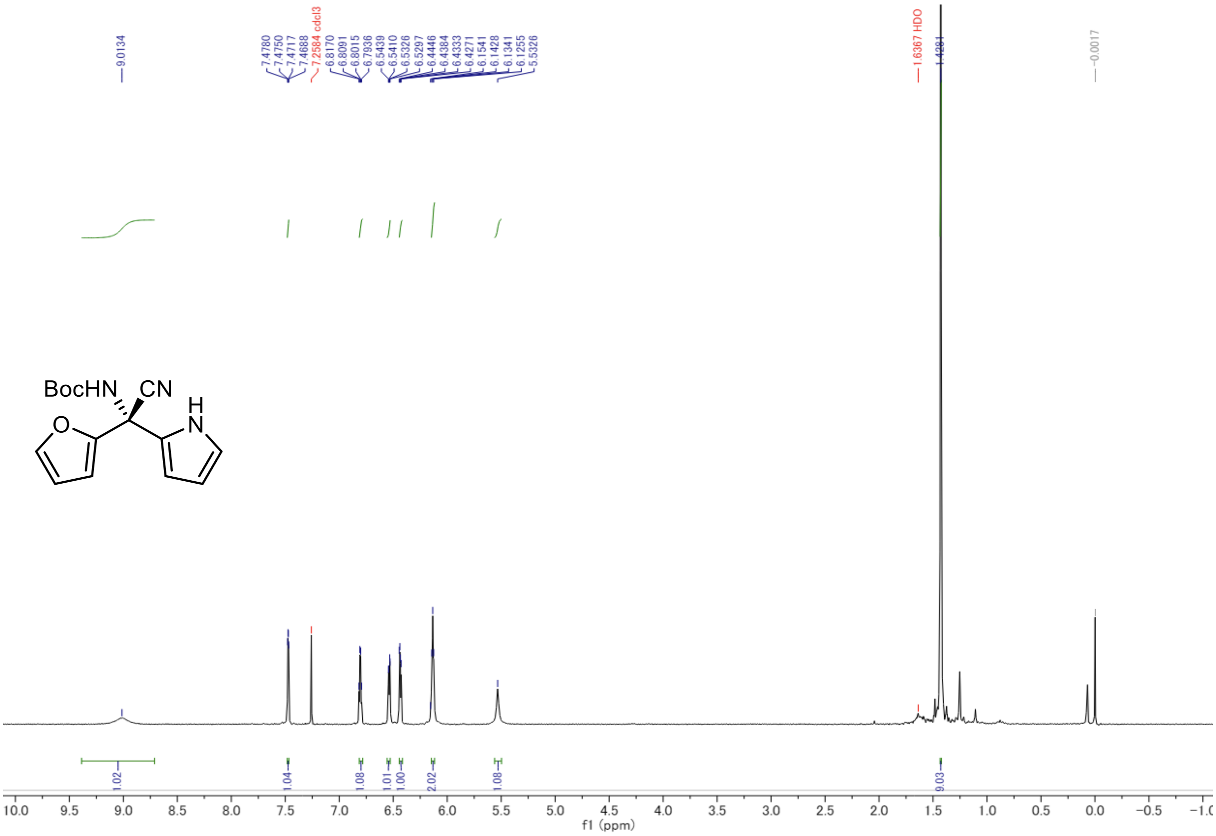


^{13}C NMR ($CDCl_3$, 125 MHz)

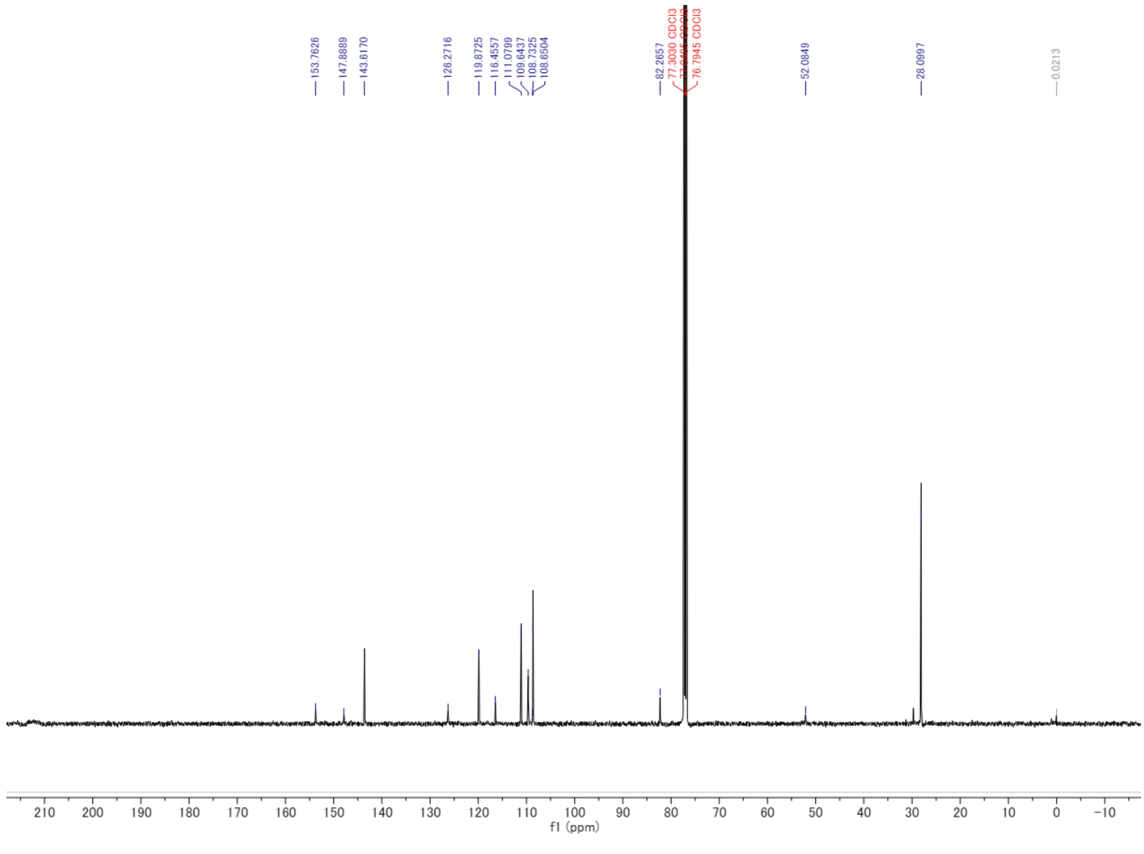


(*S*)-2-(2-Furyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4na**)

[1]H NMR ($CDCl_3$, 400 MHz)

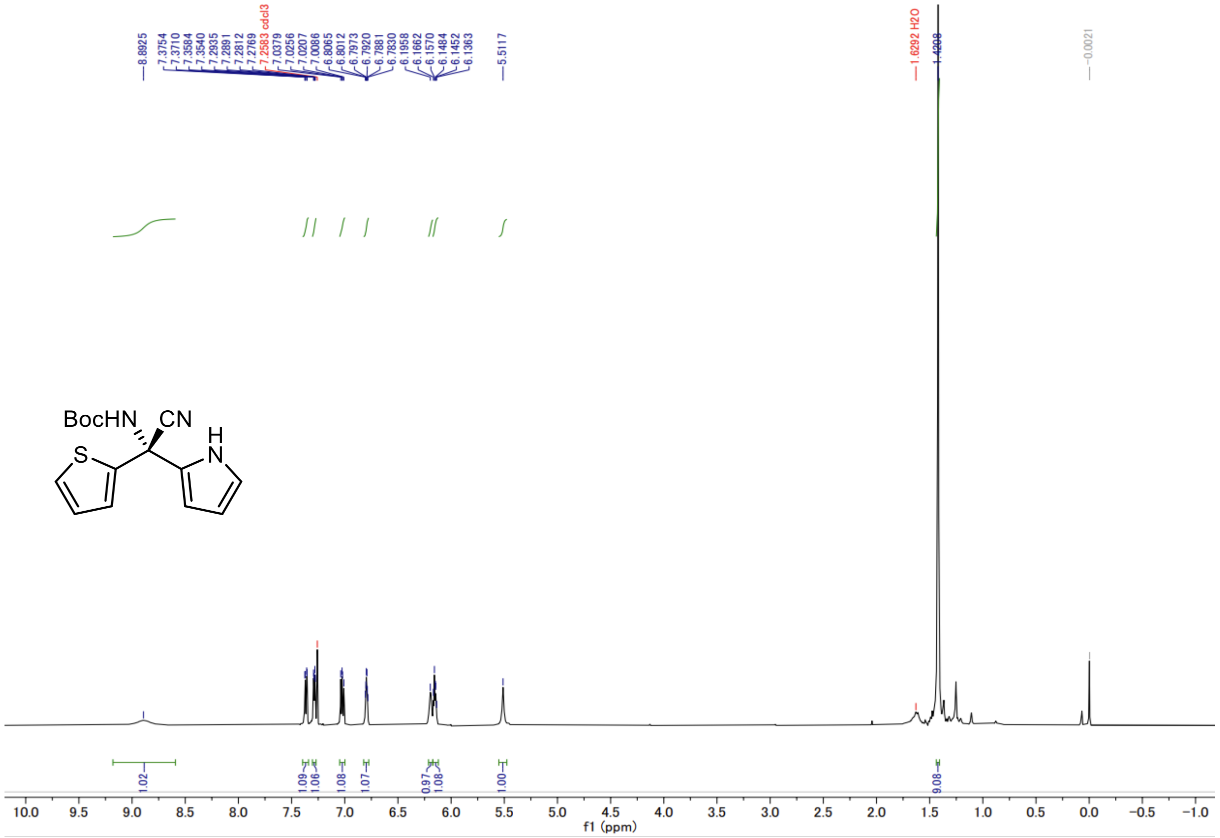


[13]C NMR ($CDCl_3$, 125 MHz)

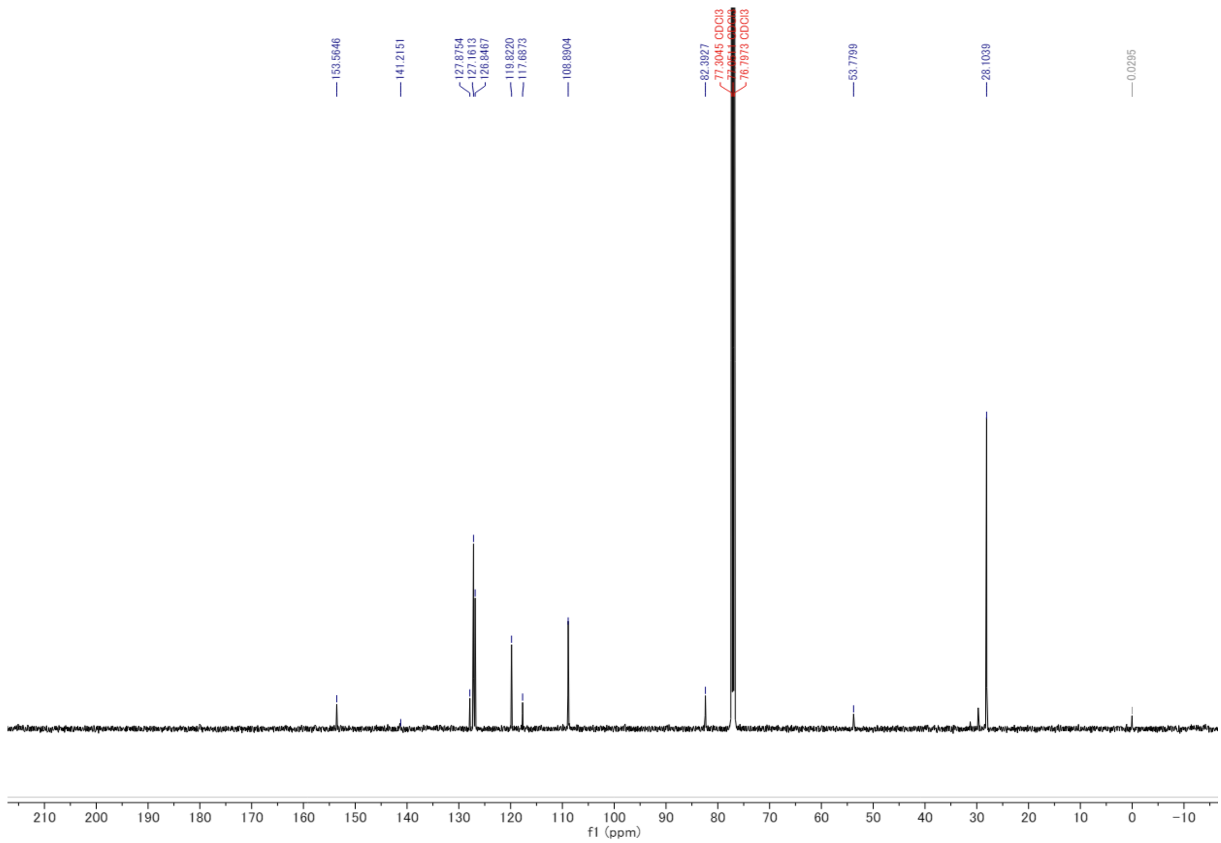


(*S*)-2-(2-Thienyl)-2-(1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4oa)

^{1}H NMR (CDCl$_3$, 300 MHz)

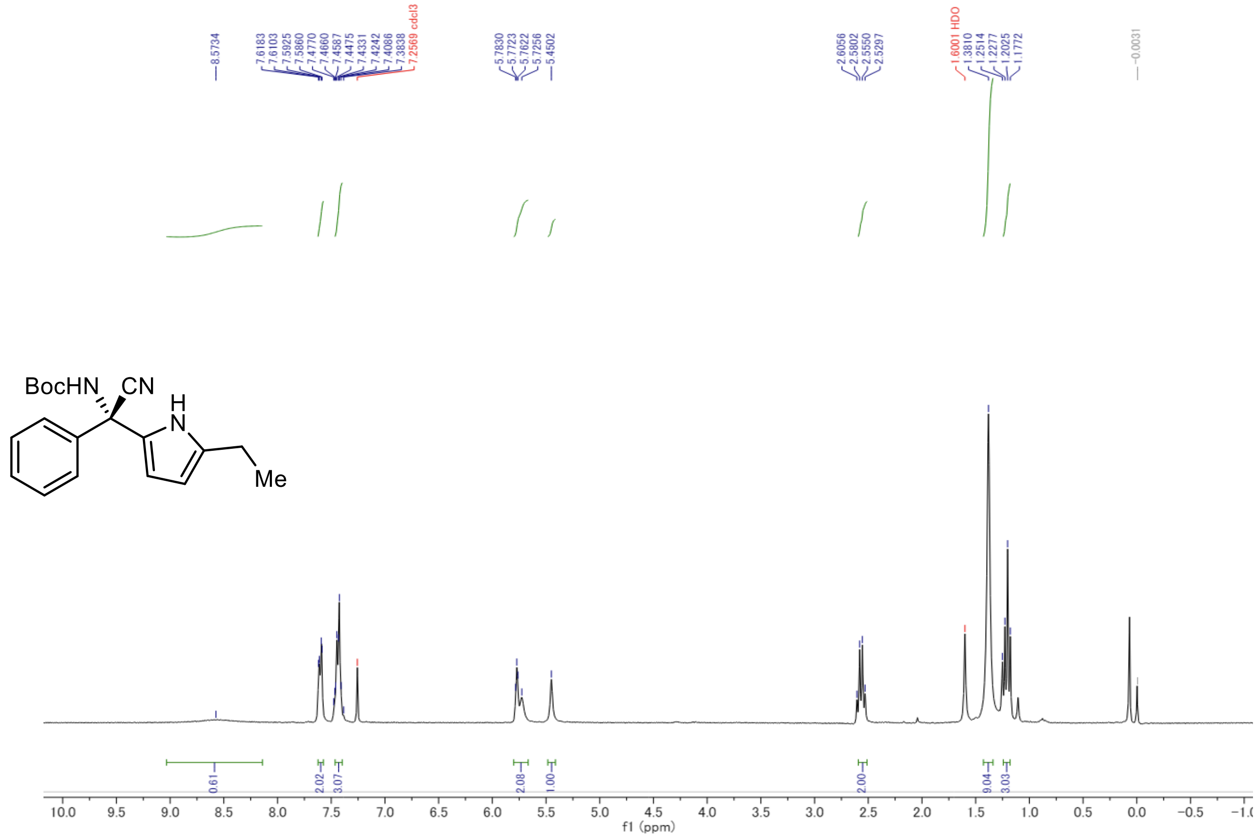


^{13}C NMR (CDCl$_3$, 125 MHz)

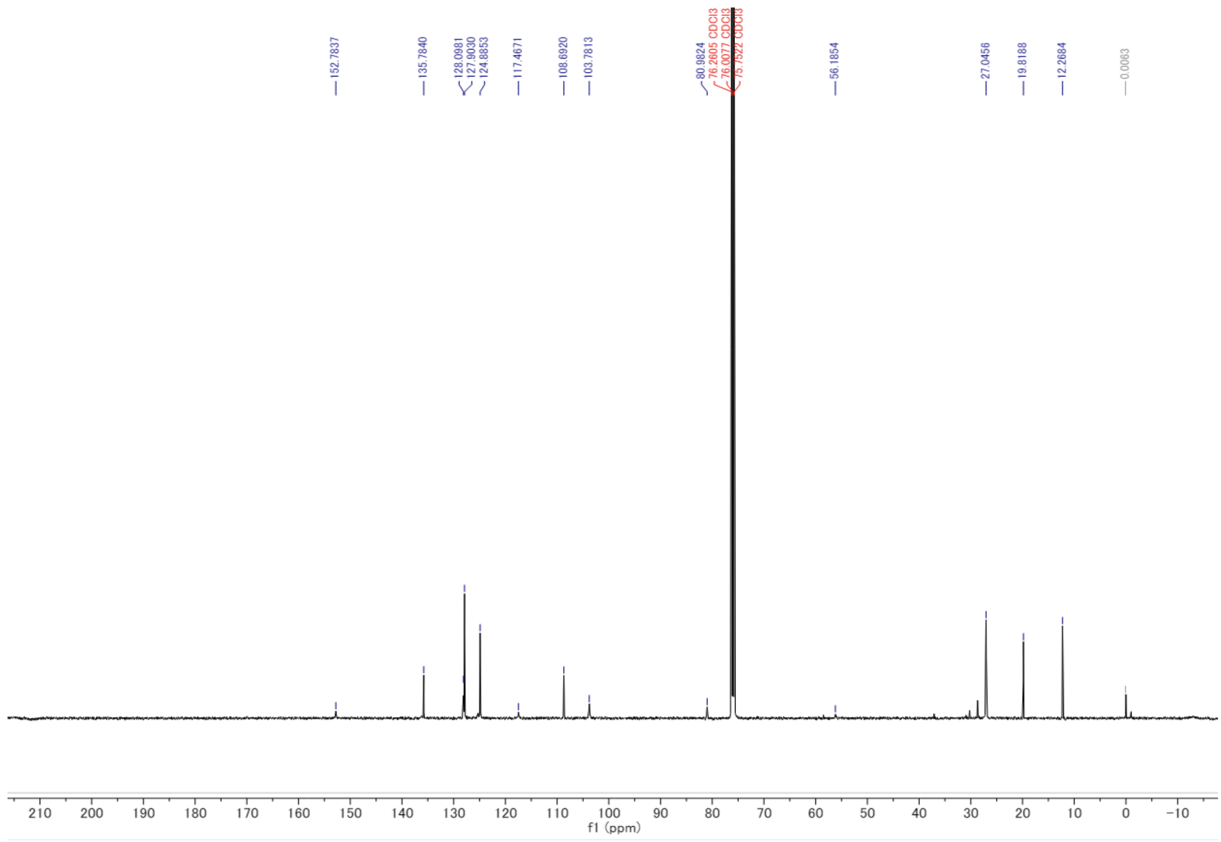


(*S*)-2-Phenyl-2-(5-ethyl-1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4ab)

^{1}H NMR ($CDCl_3$, 300 MHz)

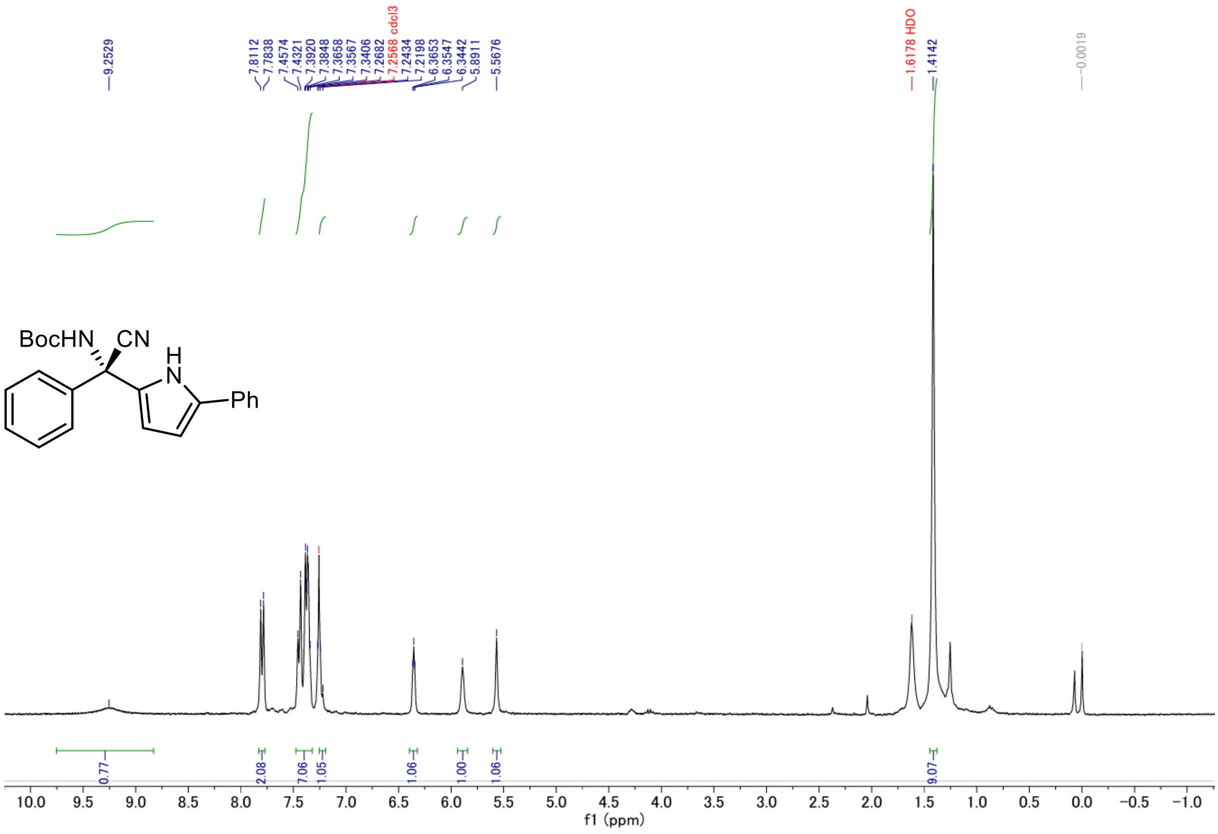


^{13}C NMR ($CDCl_3$, 125 MHz)

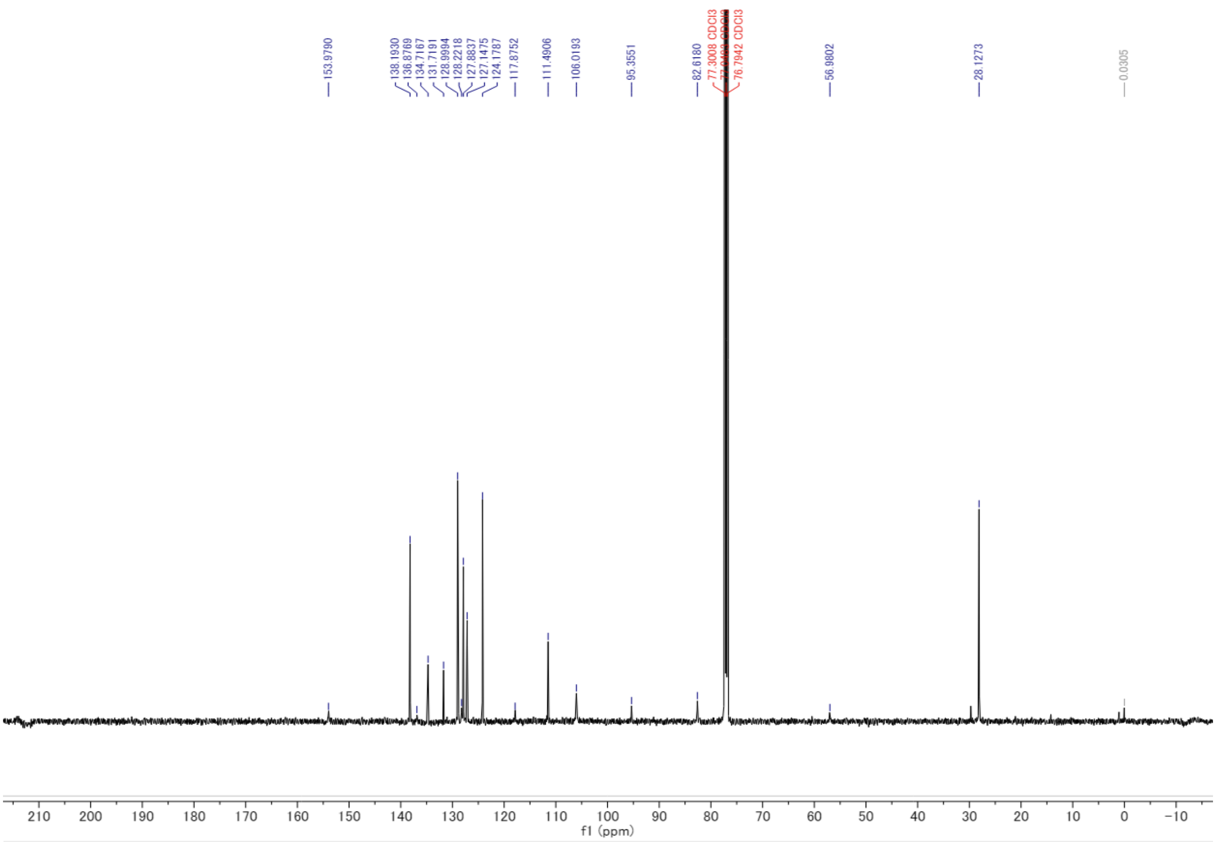


(*S*)-2-Phenyl-2-(5-phenyl-1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (**4ac**)

^{1}H NMR ($CDCl_3$, 300 MHz)

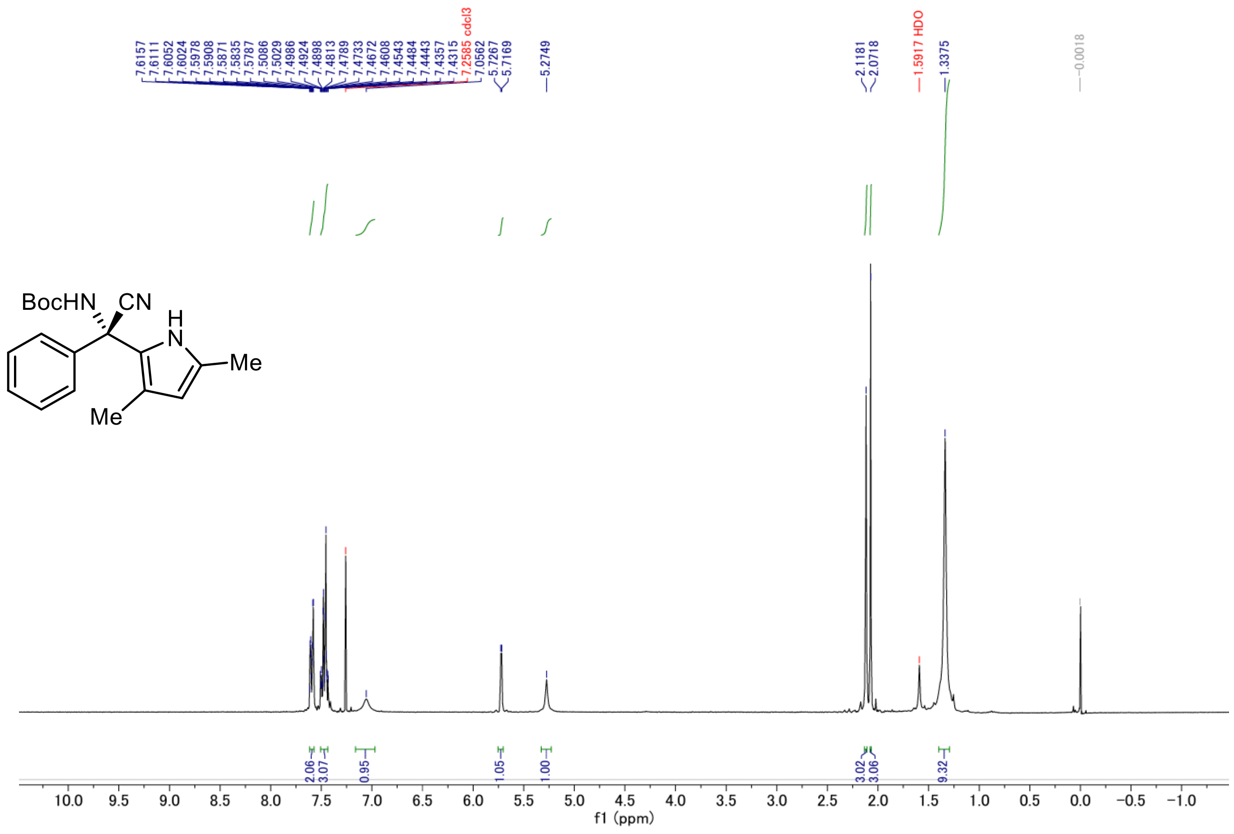


^{13}C NMR ($CDCl_3$, 125 MHz)

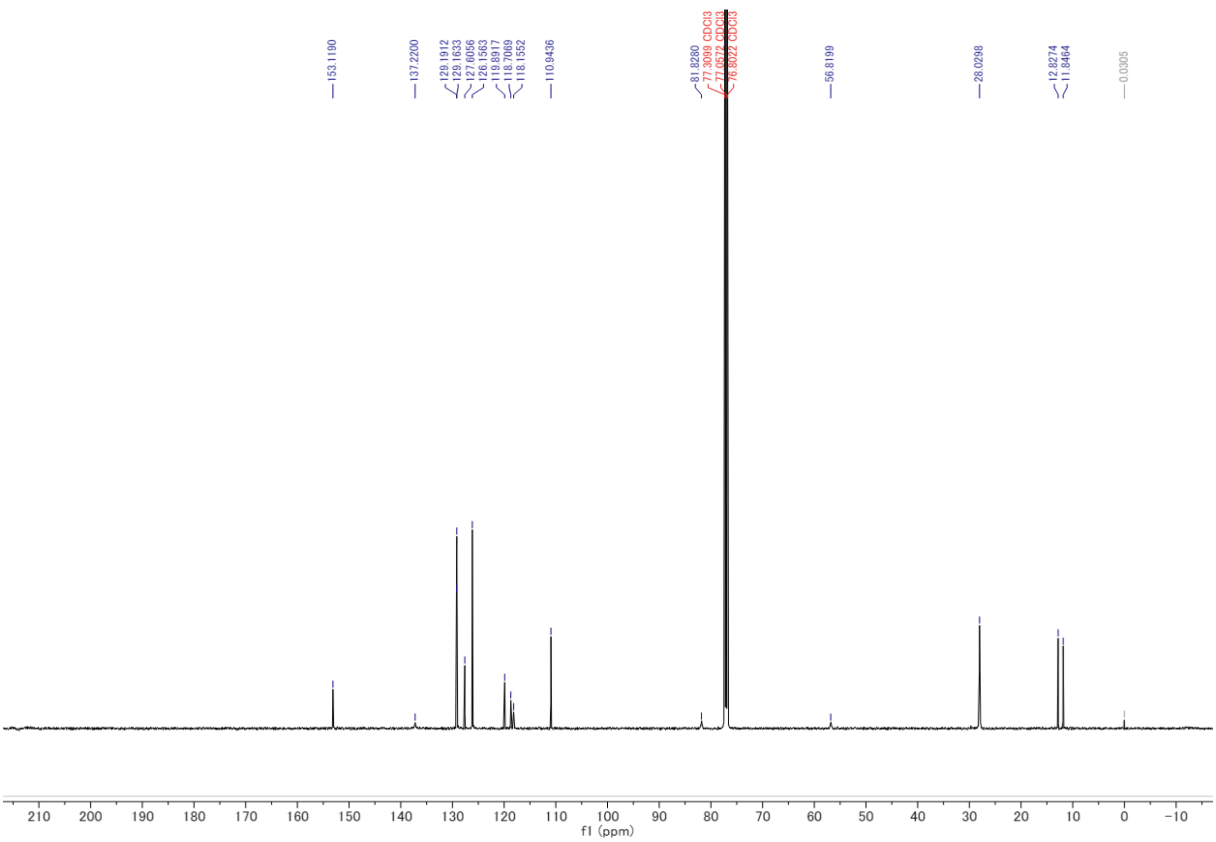


(*S*)-2-Phenyl-2-(3,5-dimethyl-1*H*-pyrrol-2-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4ad)

^{1}H NMR ($CDCl_3$, 300 MHz)

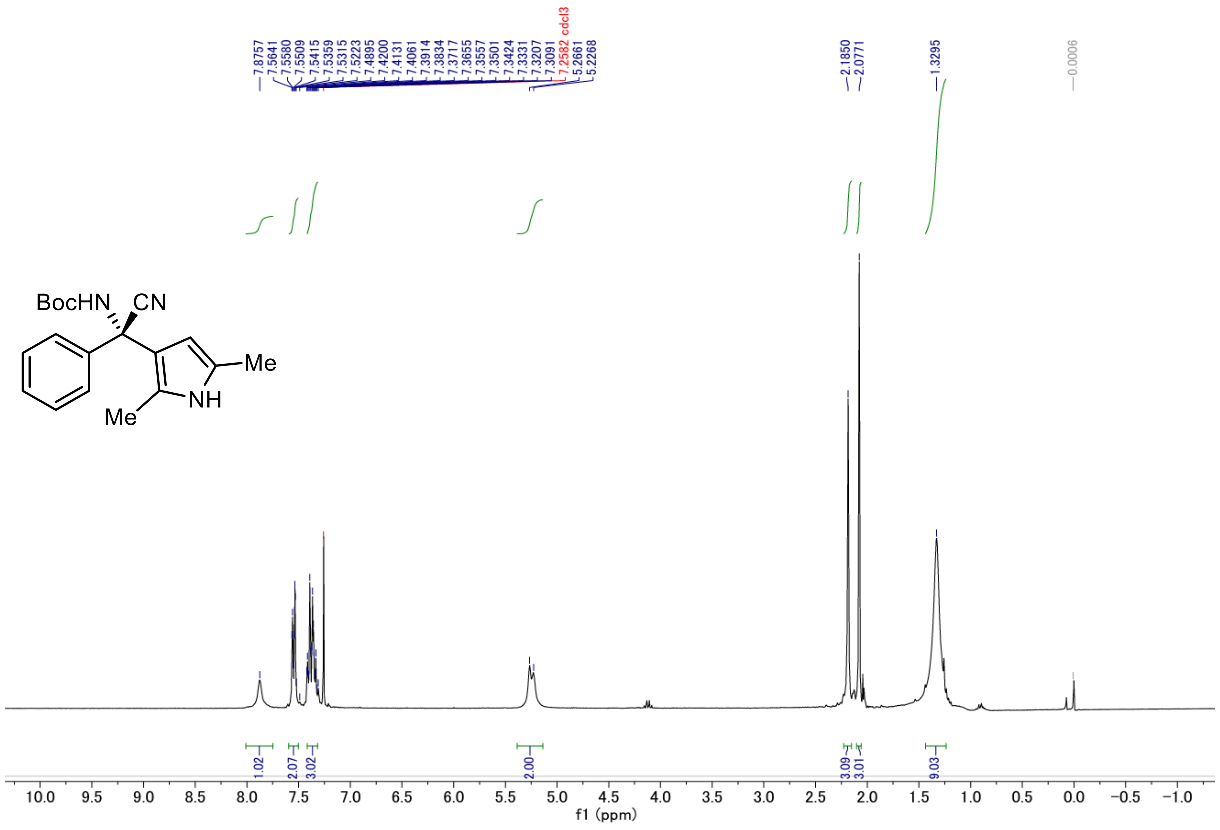


^{13}C NMR ($CDCl_3$, 125 MHz)

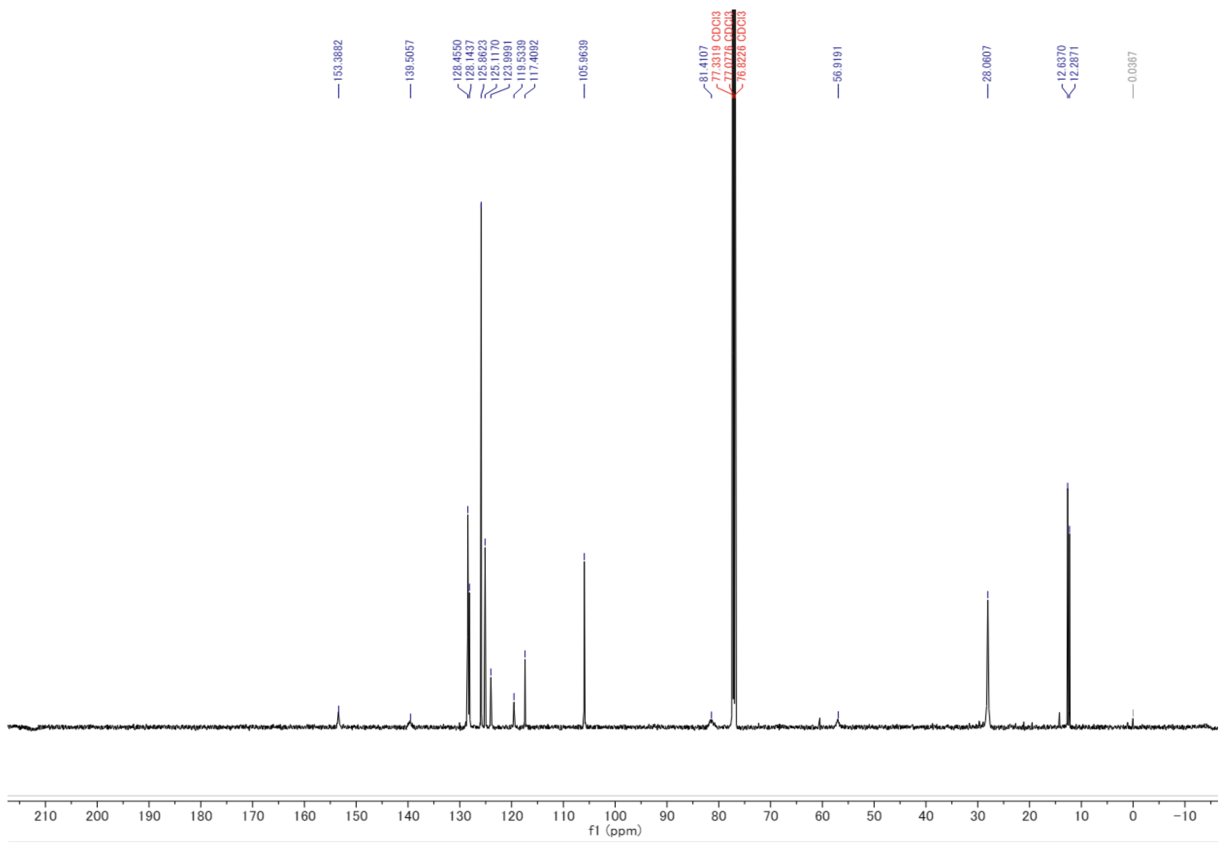


(*S*)-2-Phenyl-2-(2,5-dimethyl-1*H*-pyrrol-3-yl)-2-(*tert*-butoxycarbonylamino)acetonitrile (4ae)

^{1}H NMR (CDCl$_3$, 300 MHz)

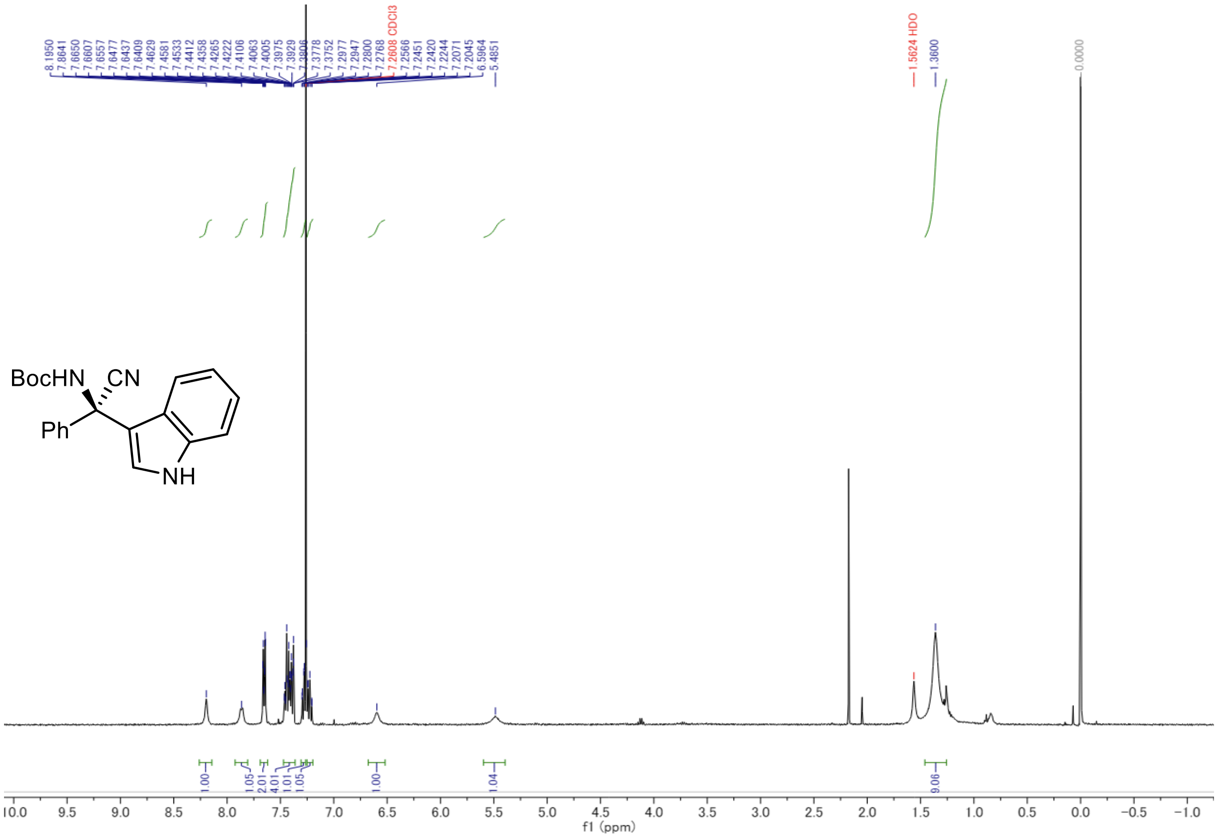


^{13}C NMR (CDCl$_3$, 125 MHz)

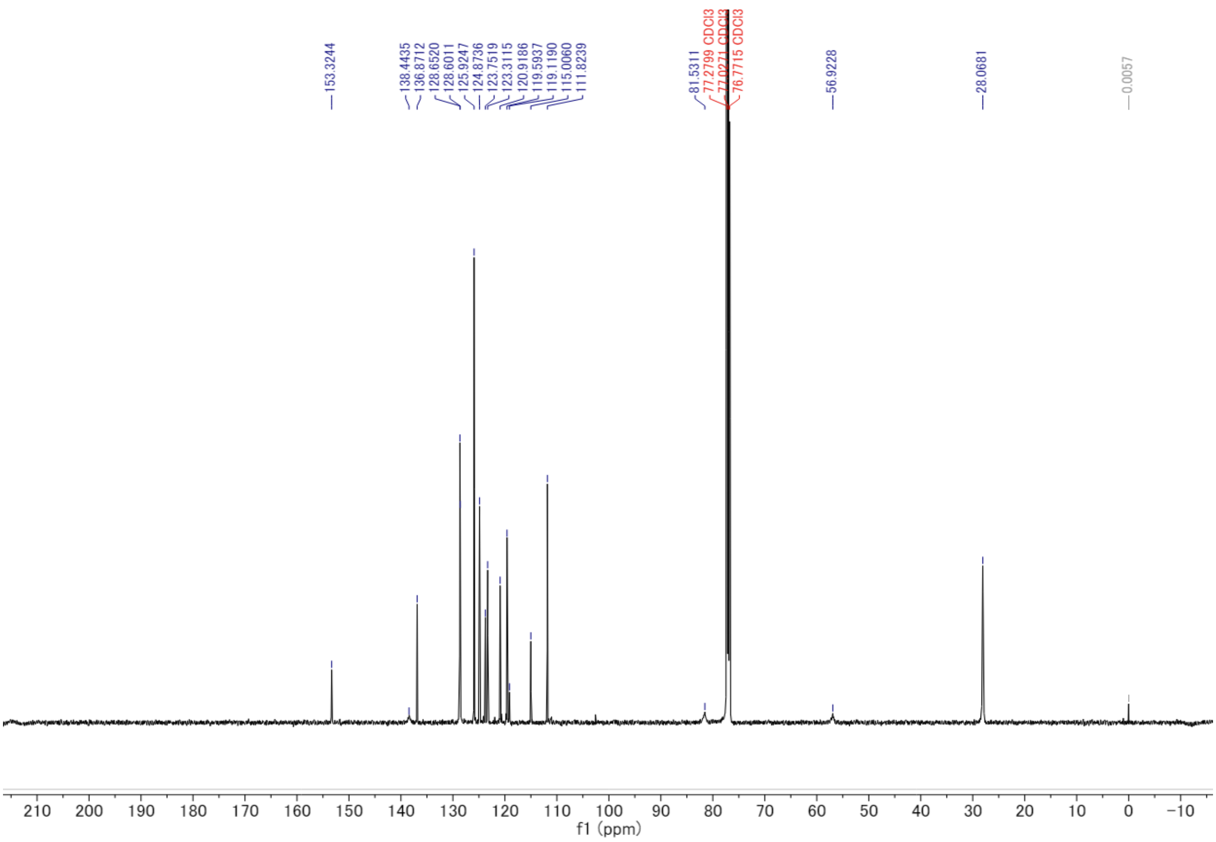


(*R*)-2-(1*H*-Indol-3-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6aa)

^{1}H NMR ($CDCl_3$, 300 MHz)

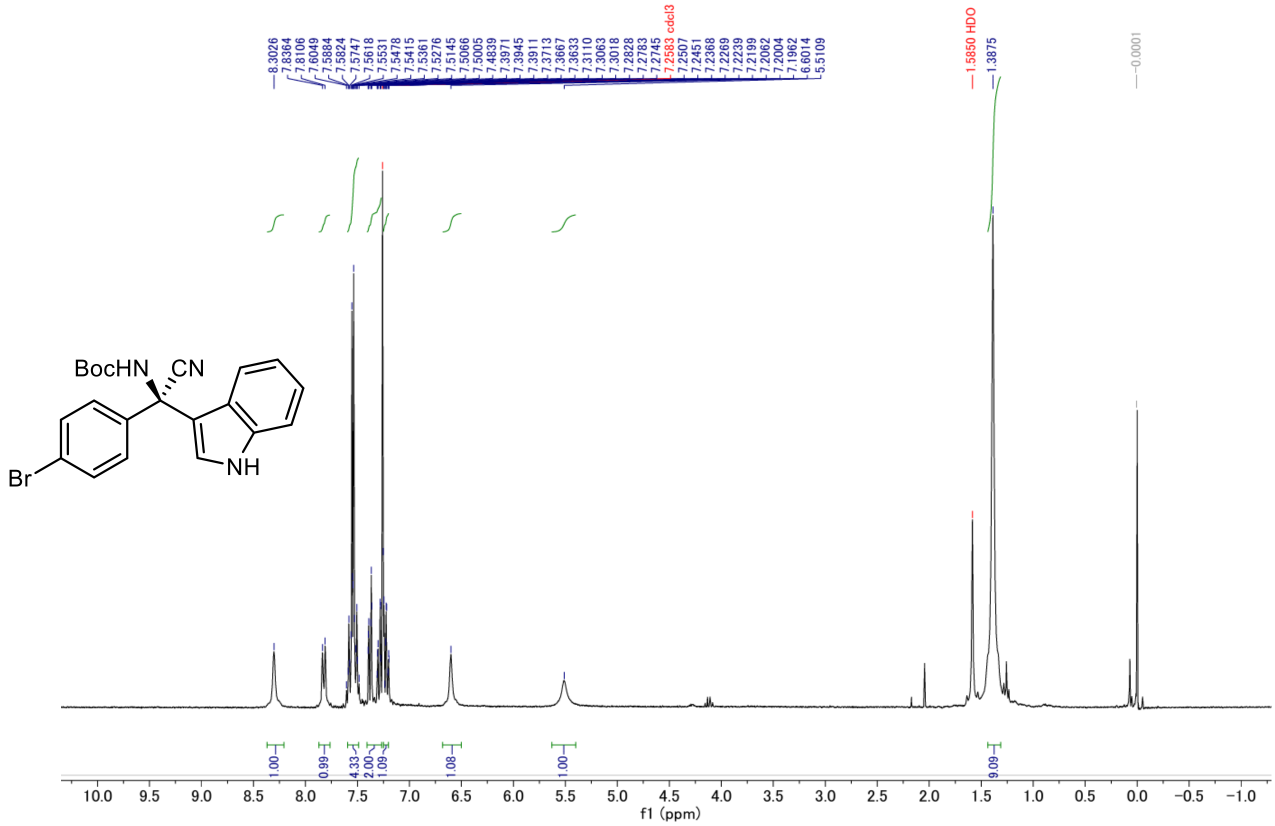


^{13}C NMR ($CDCl_3$, 125 MHz)

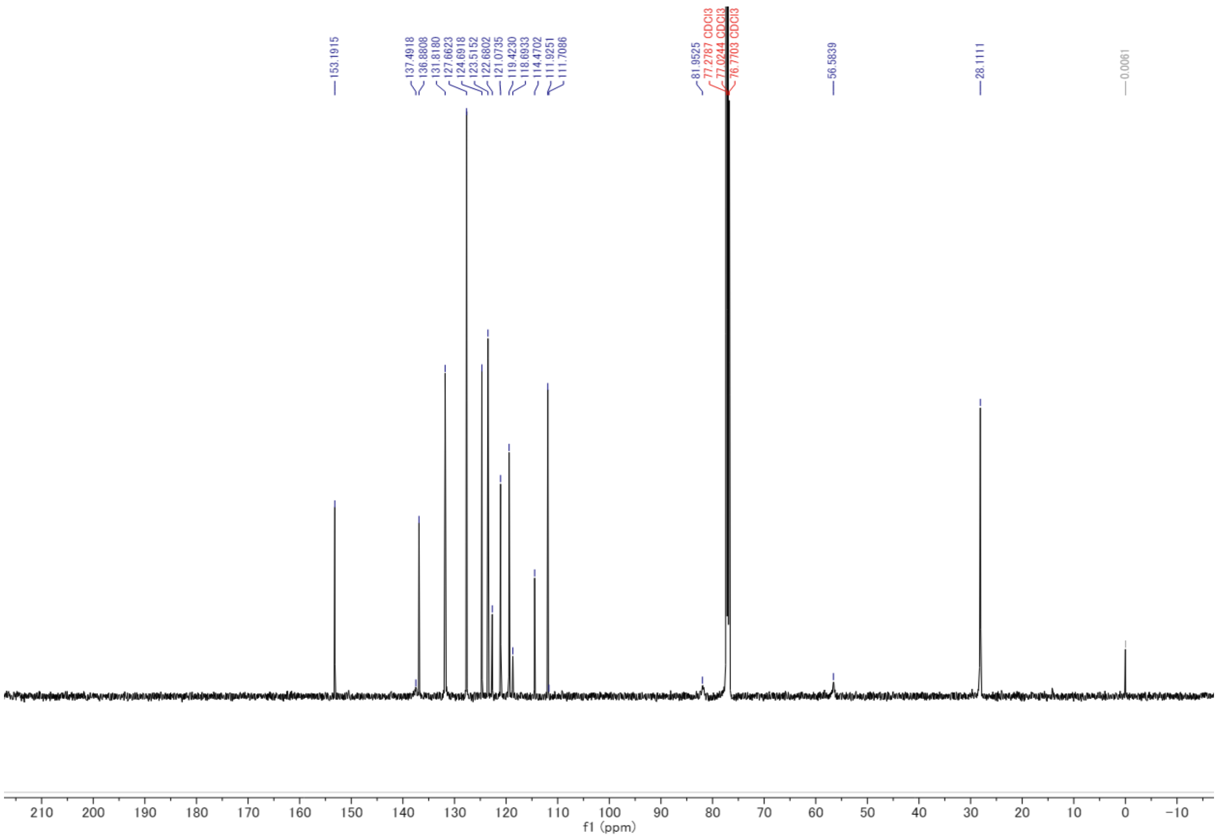


(*R*)-2-(1*H*-Indol-3-yl)-2-(4-bromophenyl)-2-(*tert*-butoxycarbonylamino)acetonitrile (6ba)

[1]H NMR ($CDCl_3$, 300 MHz)

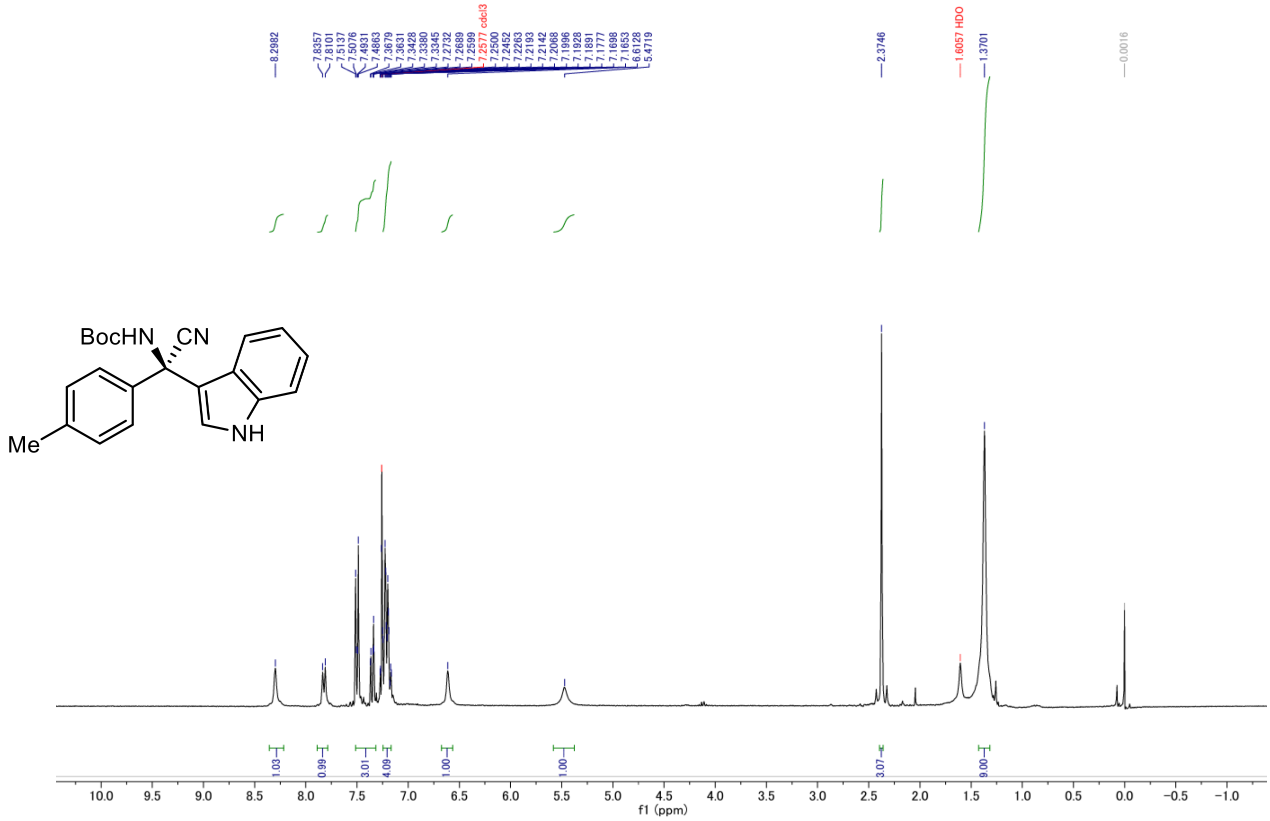


[13]C NMR ($CDCl_3$, 125 MHz)

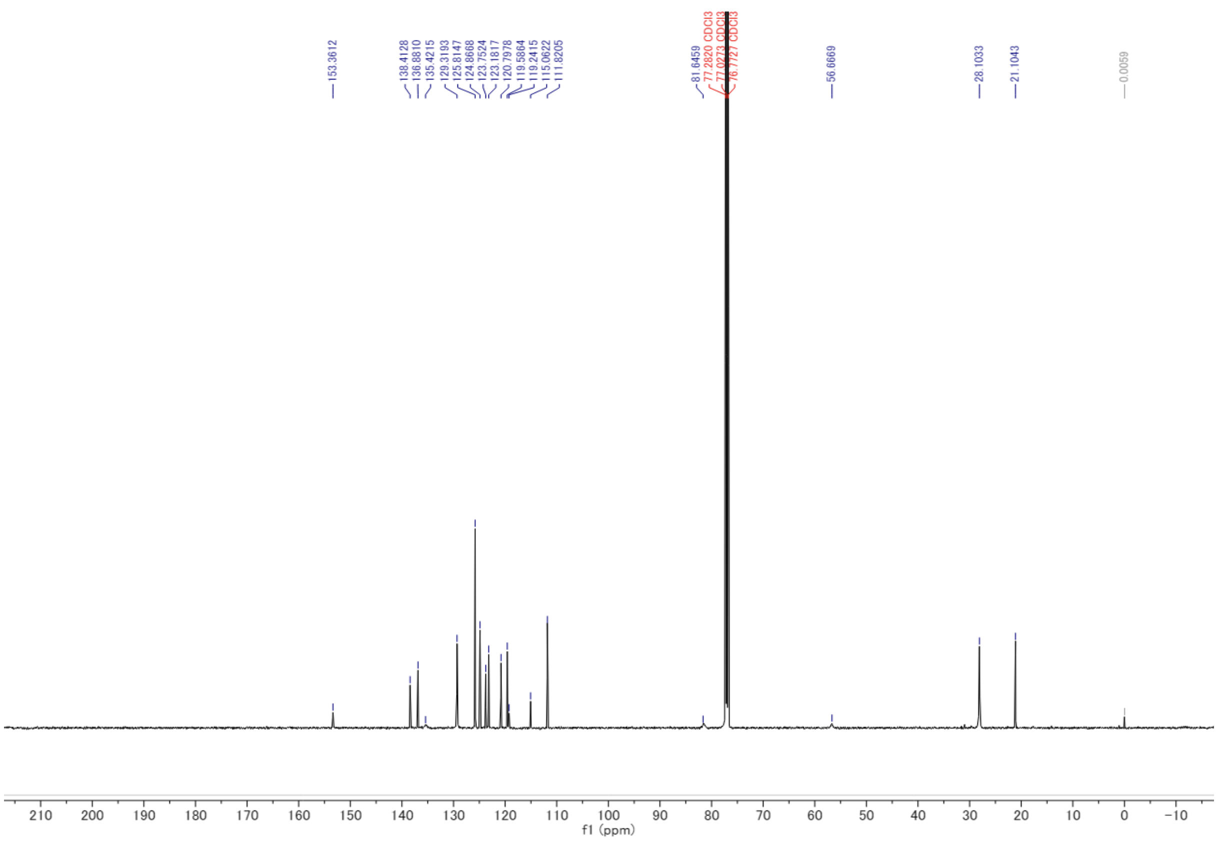


(*R*)-2-(1*H*-Indol-3-yl)-2-(4-methylphenyl)-2-(*tert*-butoxycarbonylamino)acetonitrile (6ca)

^{1}H NMR ($CDCl_3$, 300 MHz)

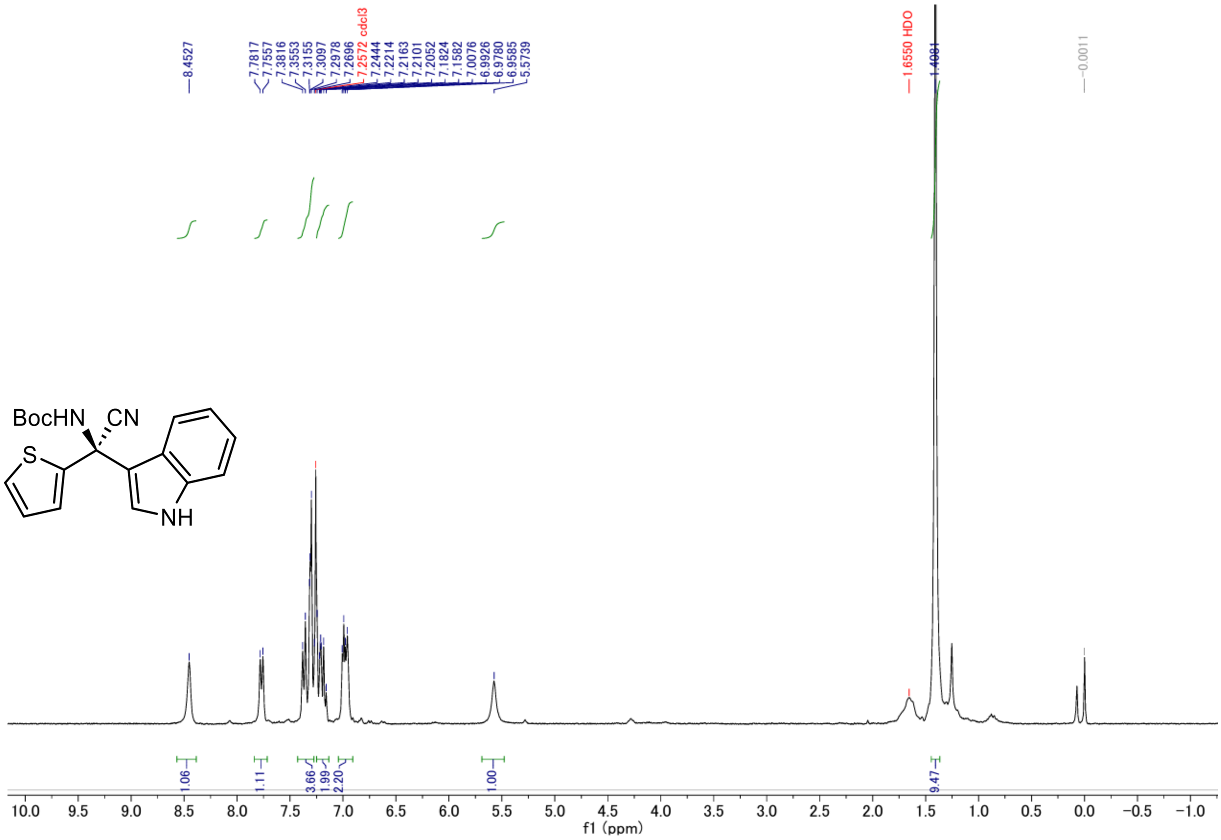


^{13}C NMR ($CDCl_3$, 125 MHz)

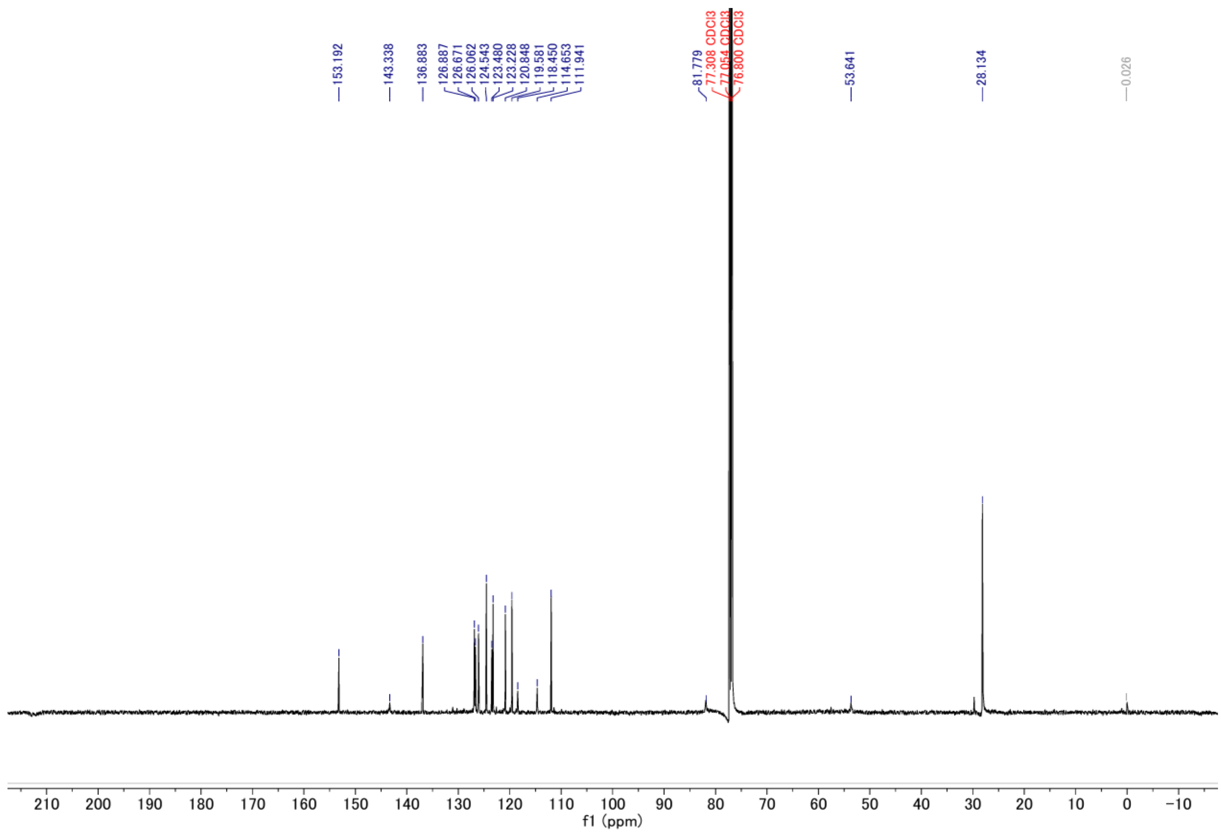


(*R*)-2-(1*H*-Indol-3-yl)-2-(2-thienyl)-2-(*tert*-butoxycarbonylamino)acetonitrile (6da)

^{1}H NMR ($CDCl_3$, 300 MHz)

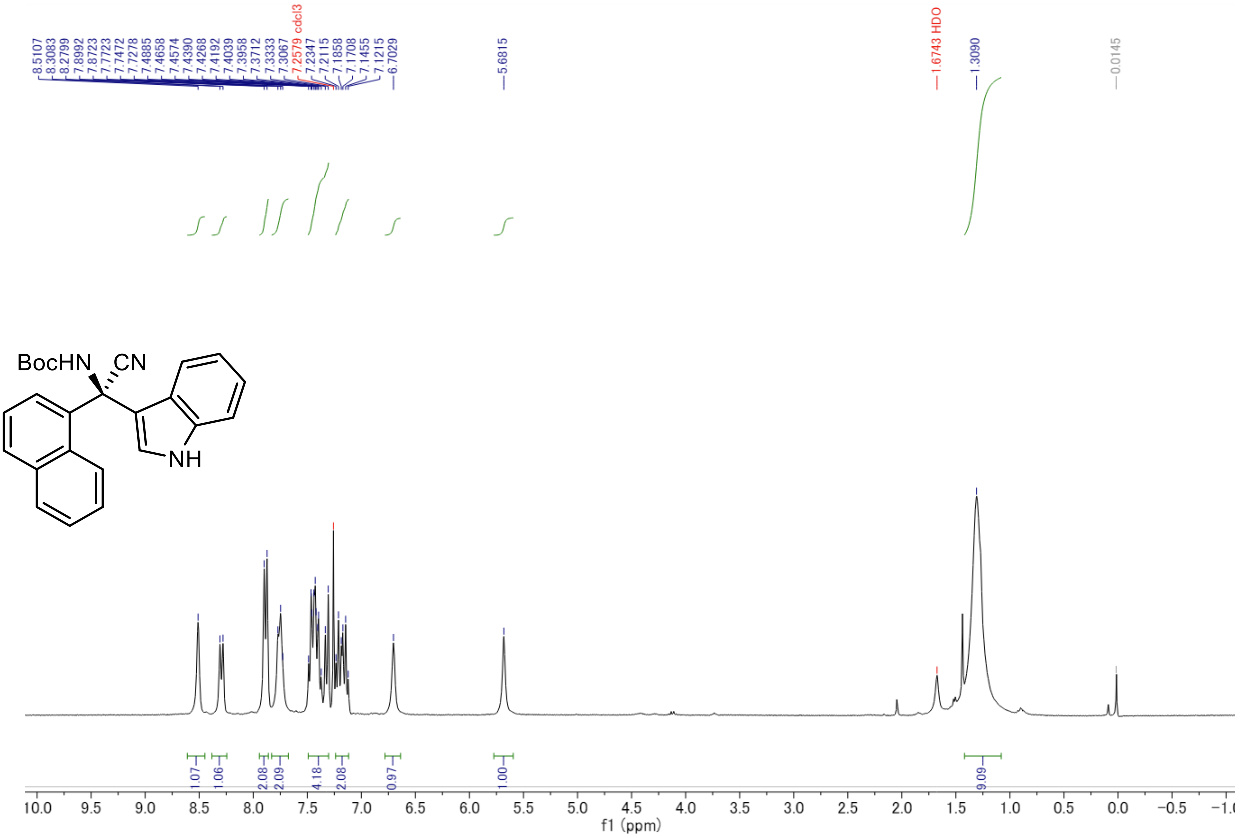


^{13}C NMR ($CDCl_3$, 125 MHz)

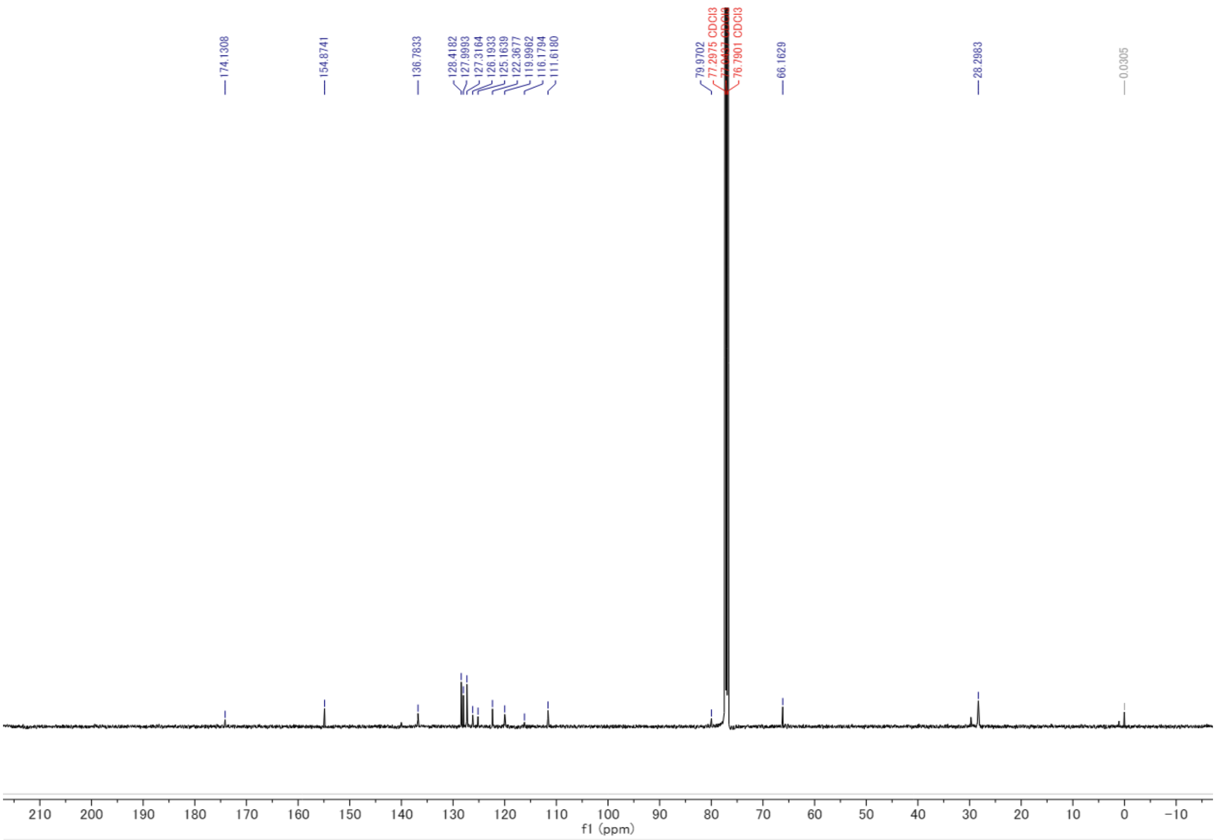


(*R*)-2-(1*H*-Indol-3-yl)-2-(1-naphtyl)-2-(*tert*-butoxycarbonylamino)acetonitrile (6ea)

^{1}H NMR ($CDCl_3$, 300 MHz)

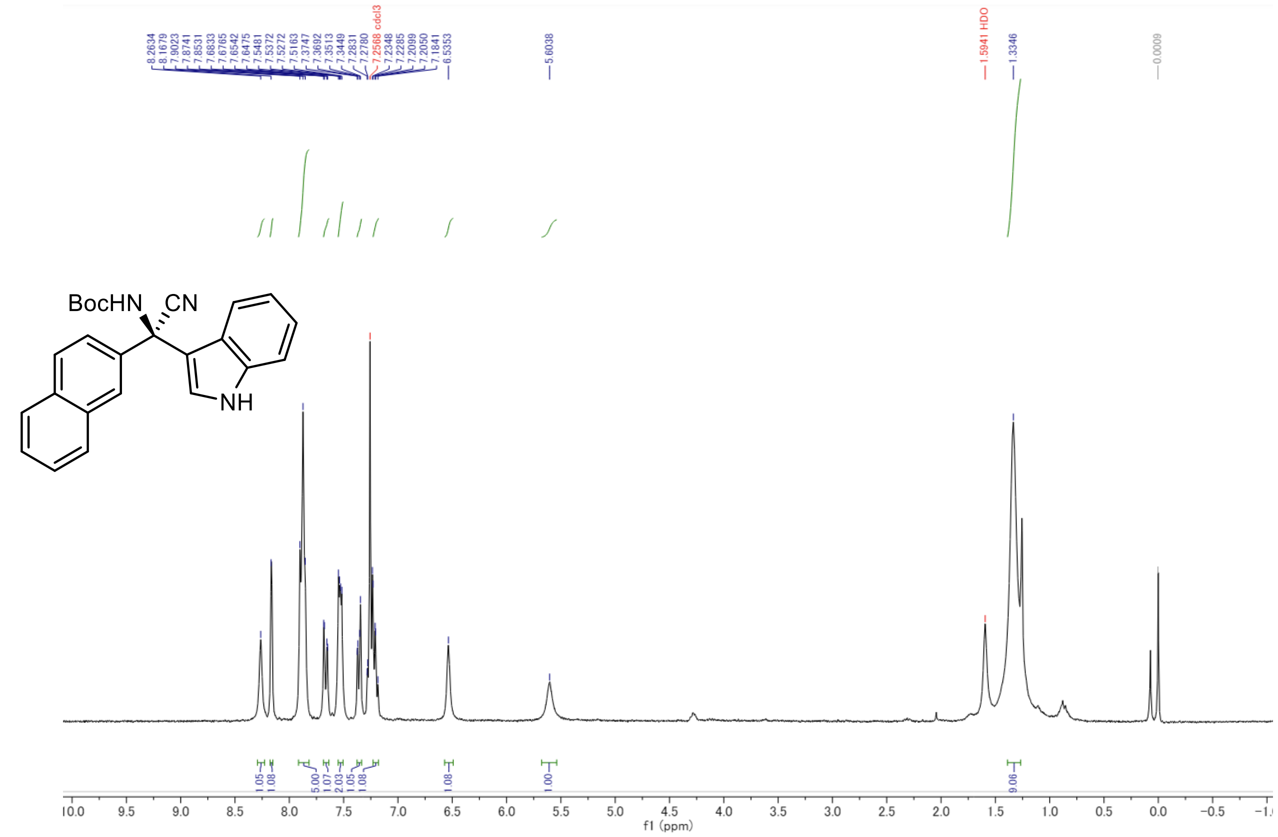


^{13}C NMR ($CDCl_3$, 125 MHz)

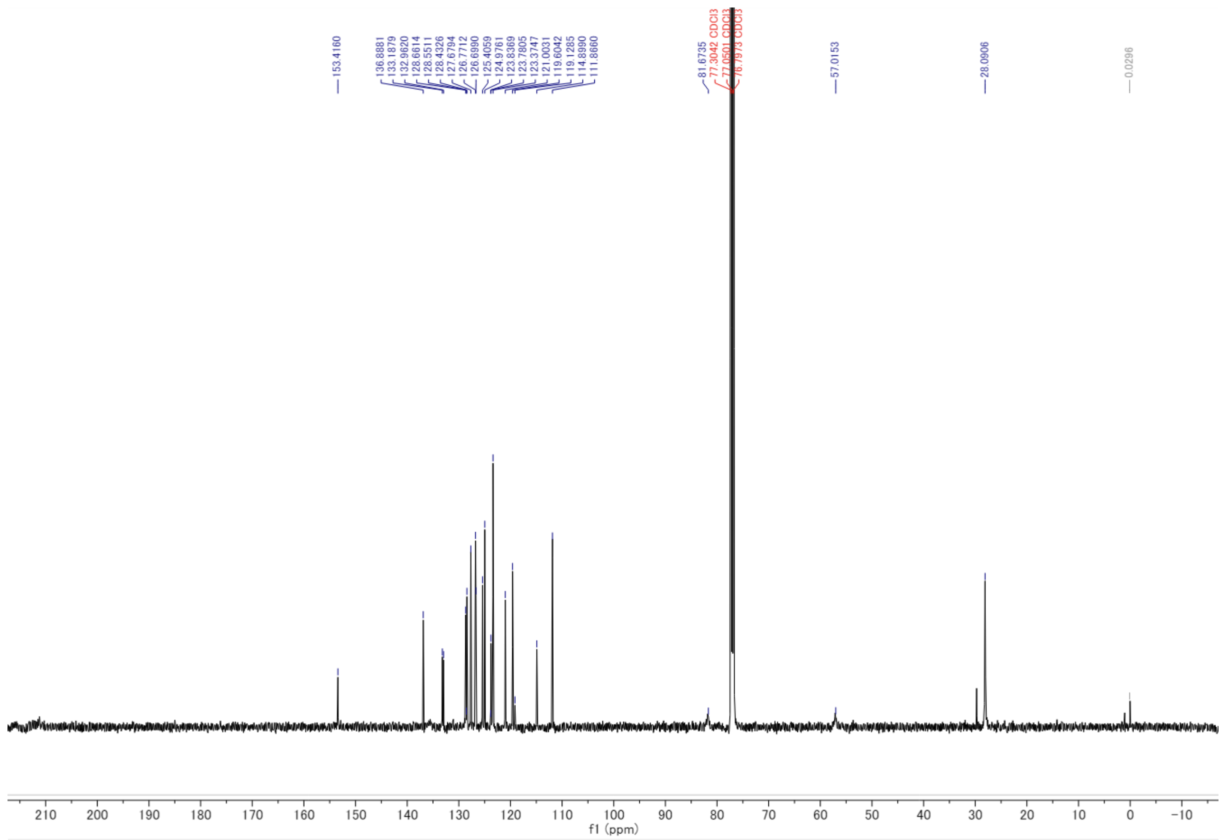


(*R*)-2-(1*H*-Indol-3-yl)-2-(2-naphtyl)-2-(*tert*-butoxycarbonylamino)acetonitrile (6fa)

^{1}H NMR ($CDCl_3$, 300 MHz)

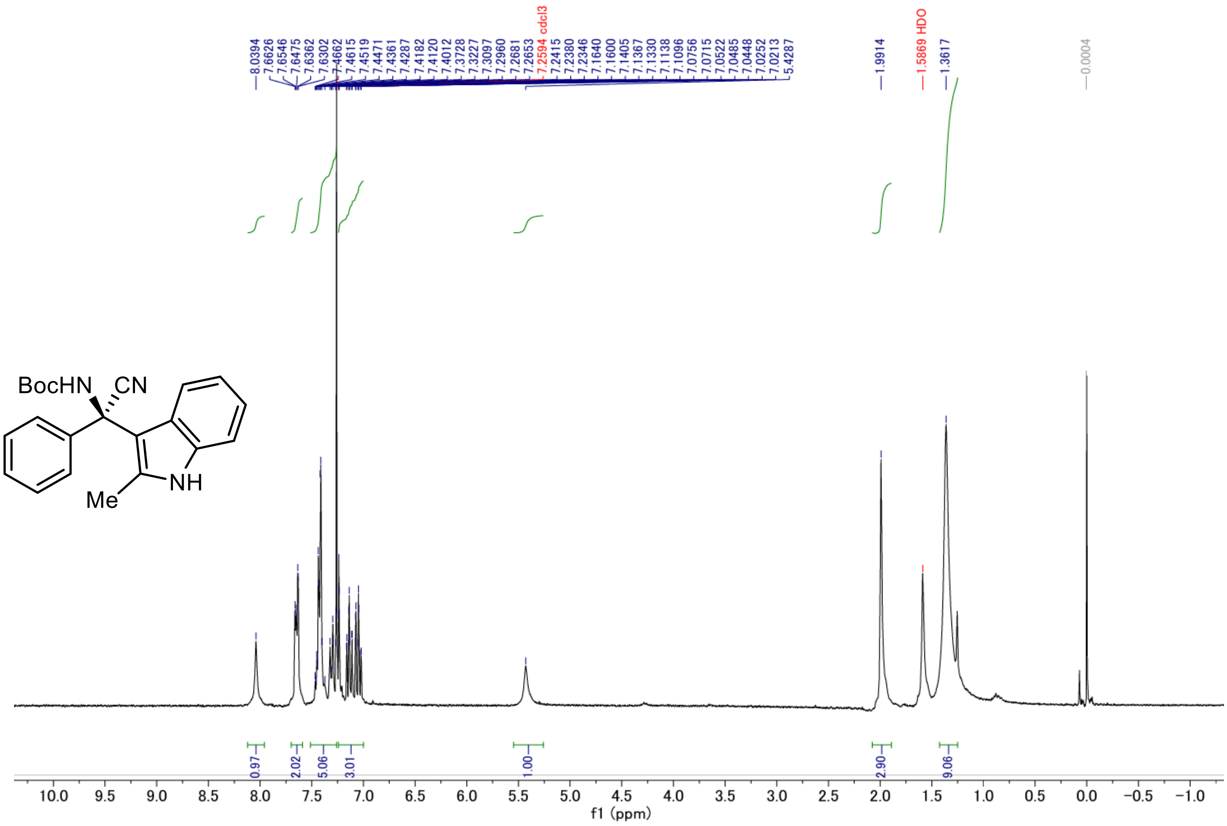


^{13}C NMR ($CDCl_3$, 125 MHz)

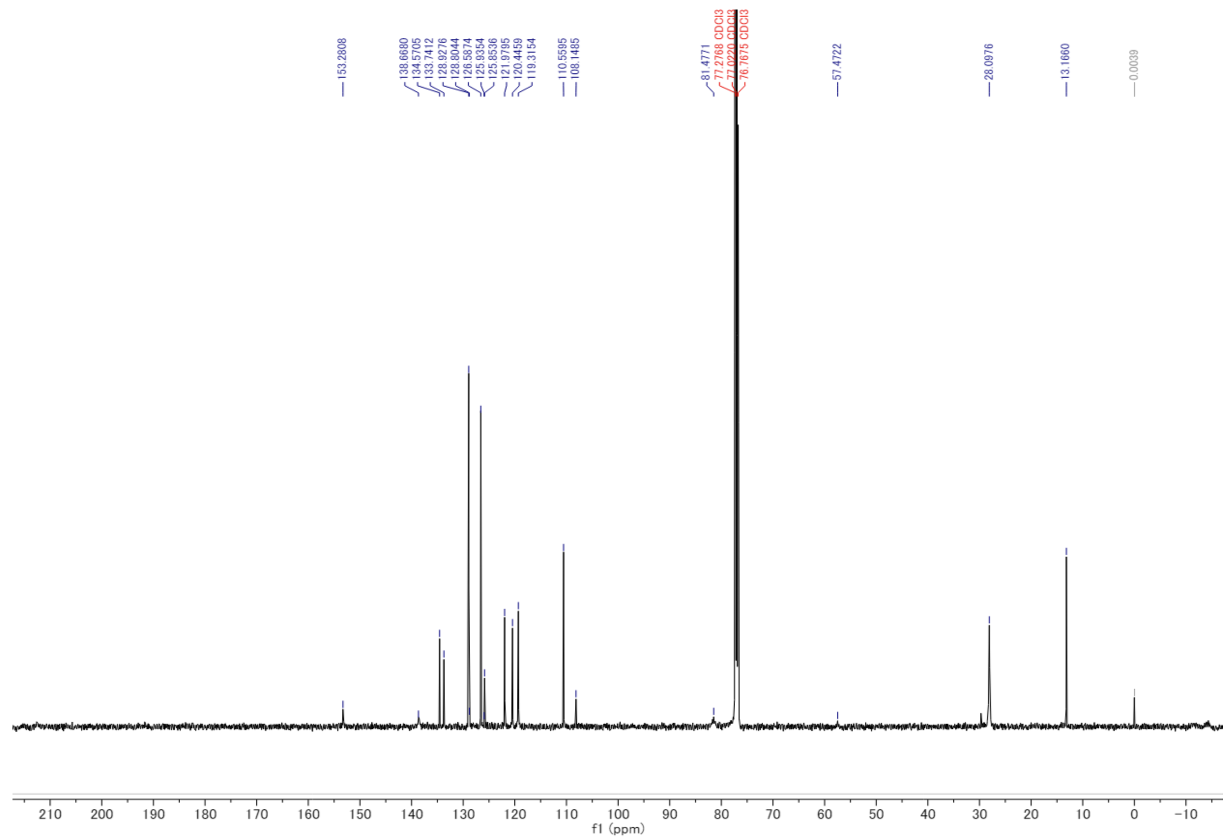


(*R*)-2-(2-Methyl-1*H*-indol-3-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6ab)

^{1}H NMR ($CDCl_3$, 300 MHz)

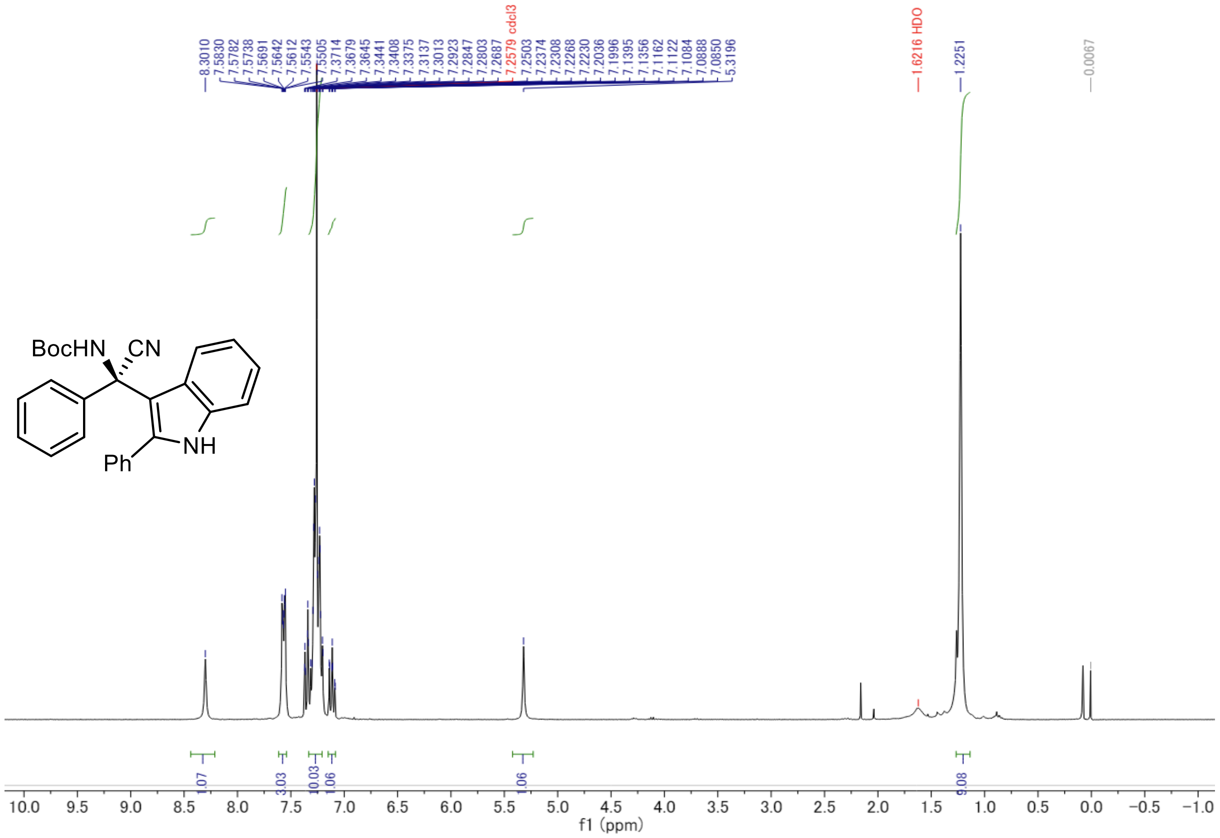


^{13}C NMR ($CDCl_3$, 125 MHz)

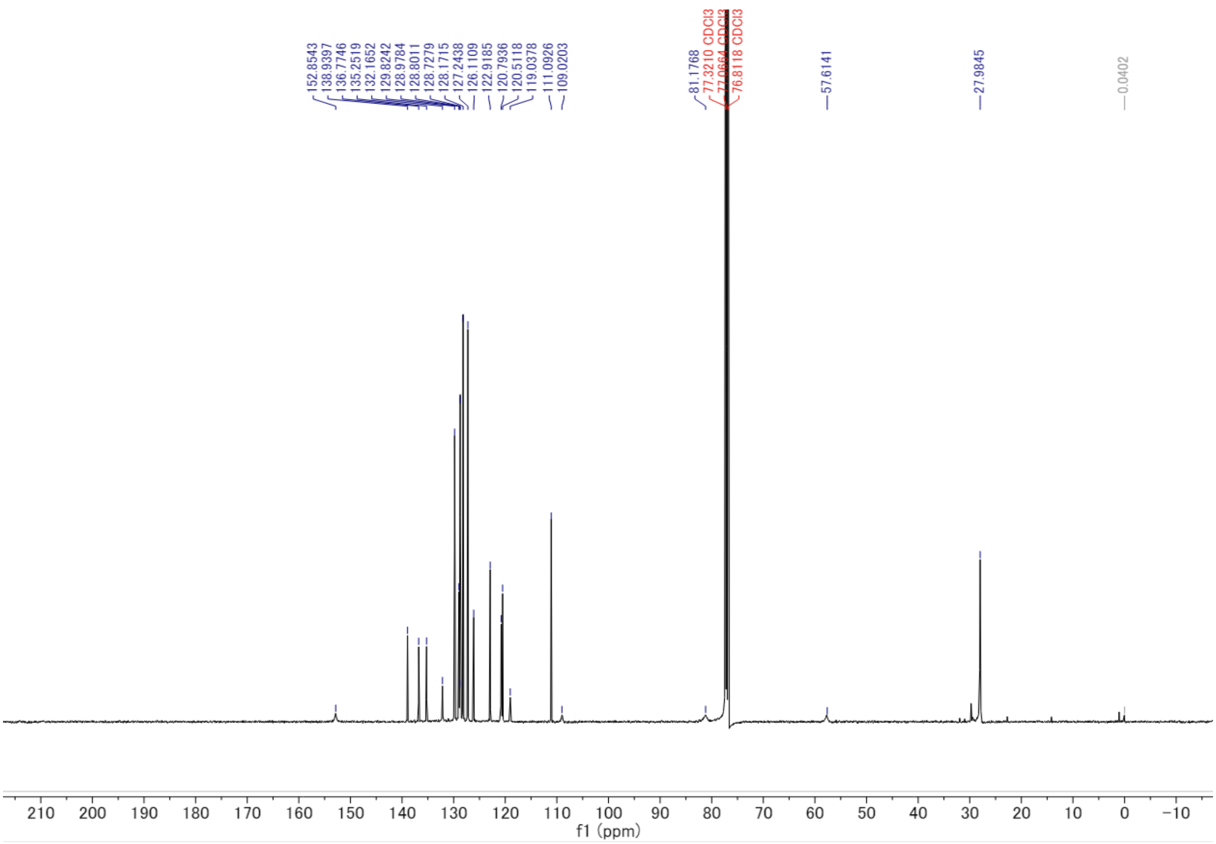


(*R*)-2-Phenyl-2-(2-Phenyl-1*H*-indol-3-yl) -2-(*tert*-butoxycarbonylamino)acetonitrile (**6ac**)

^{1}H NMR ($CDCl_3$, 300 MHz)

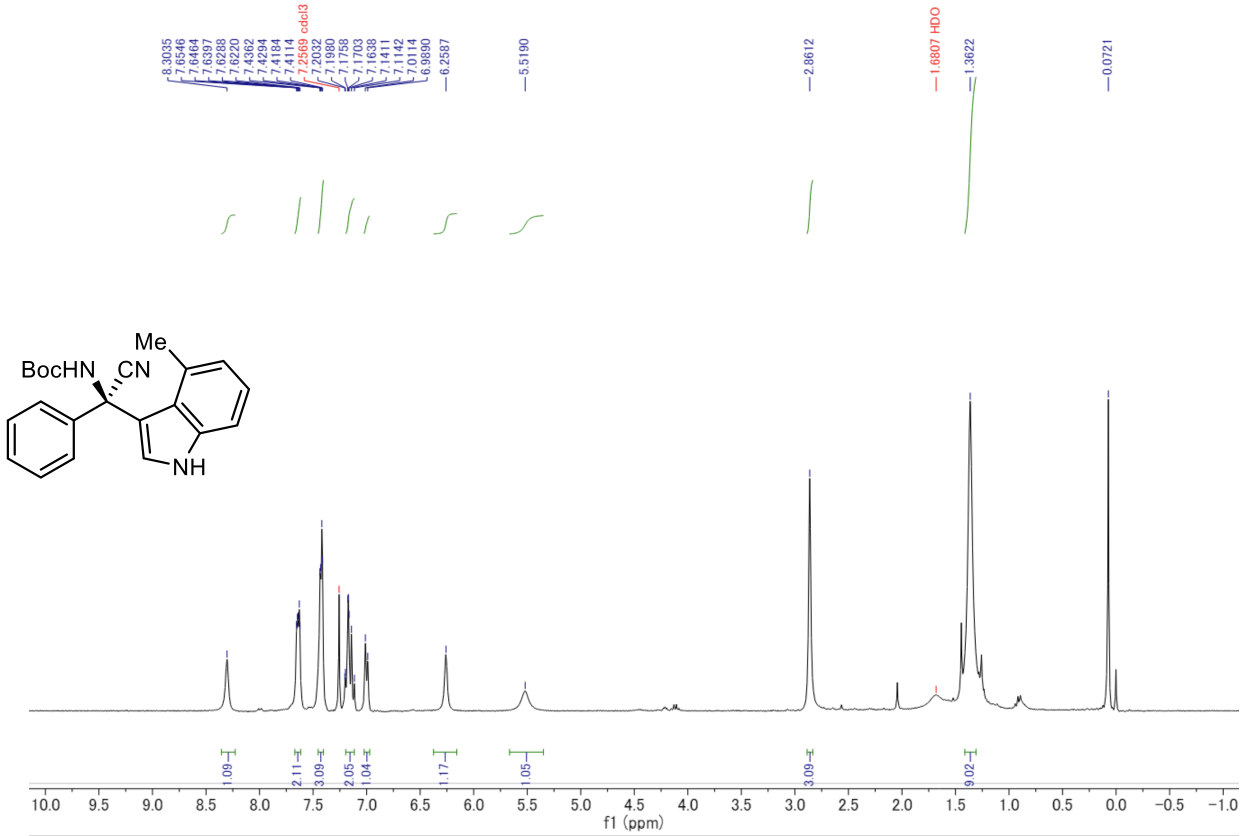


^{13}C NMR ($CDCl_3$, 125 MHz)

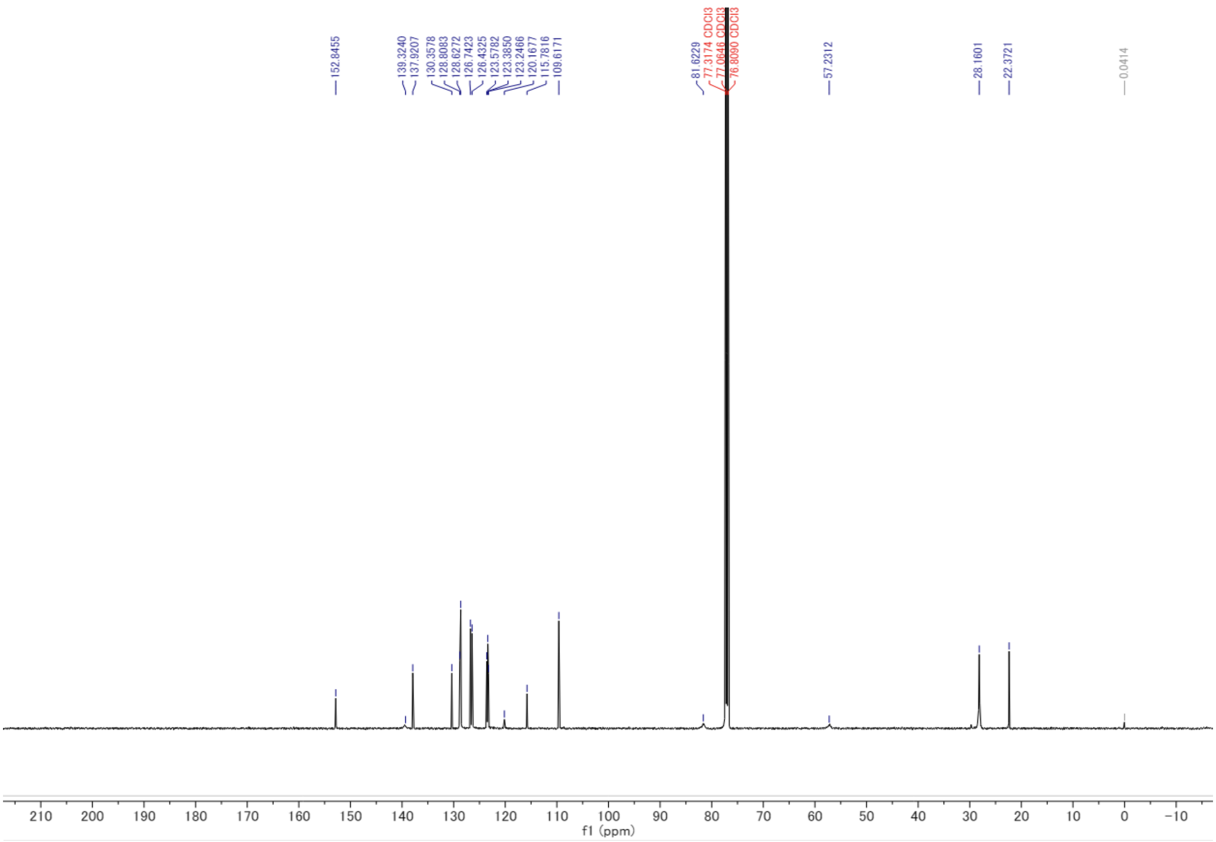


(*R*)-2-(4-Methyl-1*H*-indol-3-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6ad)

^{1}H NMR ($CDCl_3$, 300 MHz)

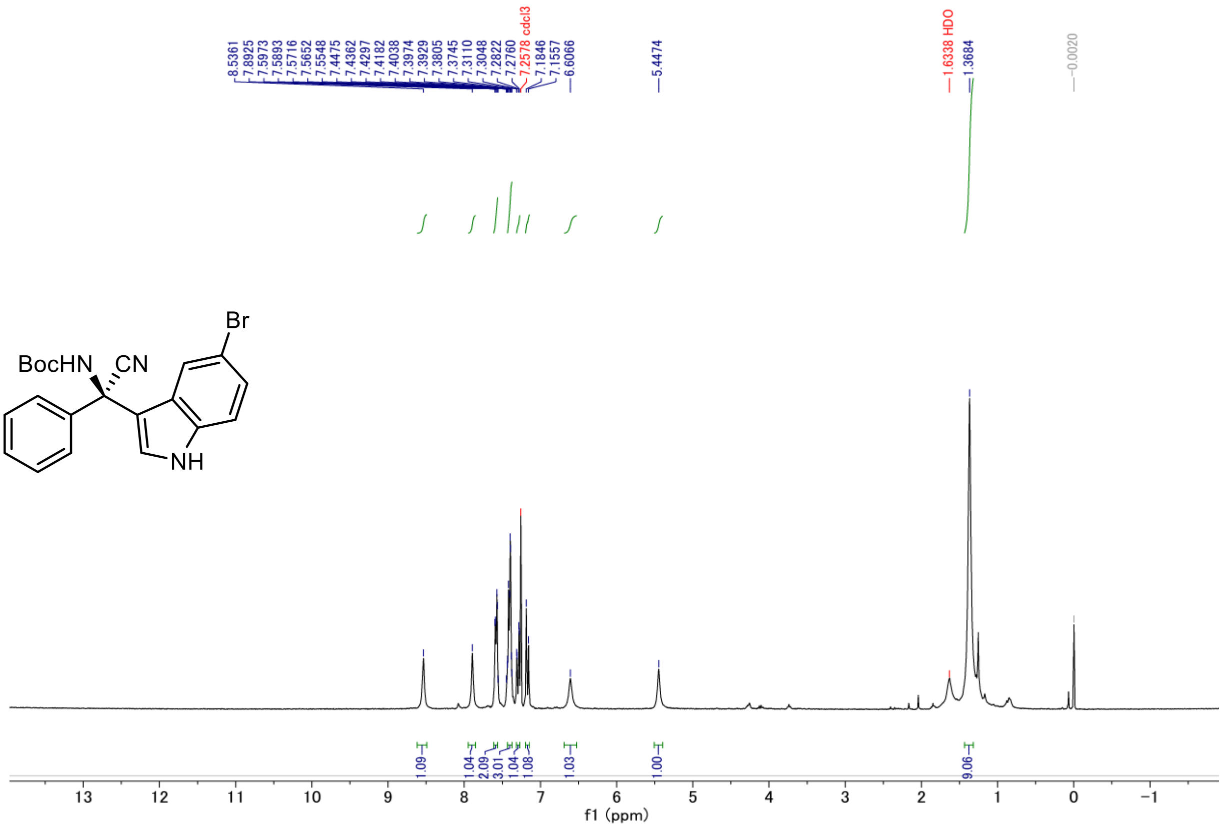


^{13}C NMR ($CDCl_3$, 125 MHz)

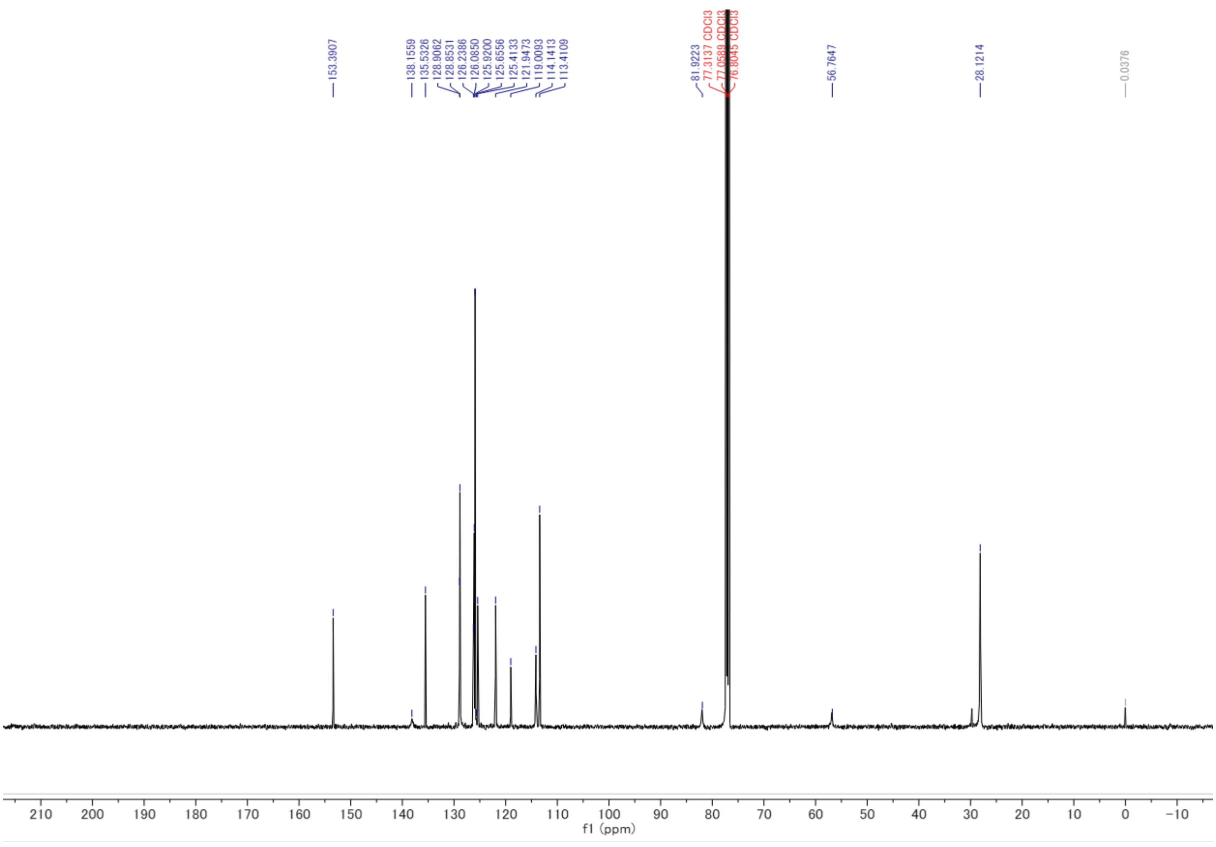


(*R*)-2-(5-Bromo-1*H*-indol-3-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6ae)

^{1}H NMR ($CDCl_3$, 300 MHz)

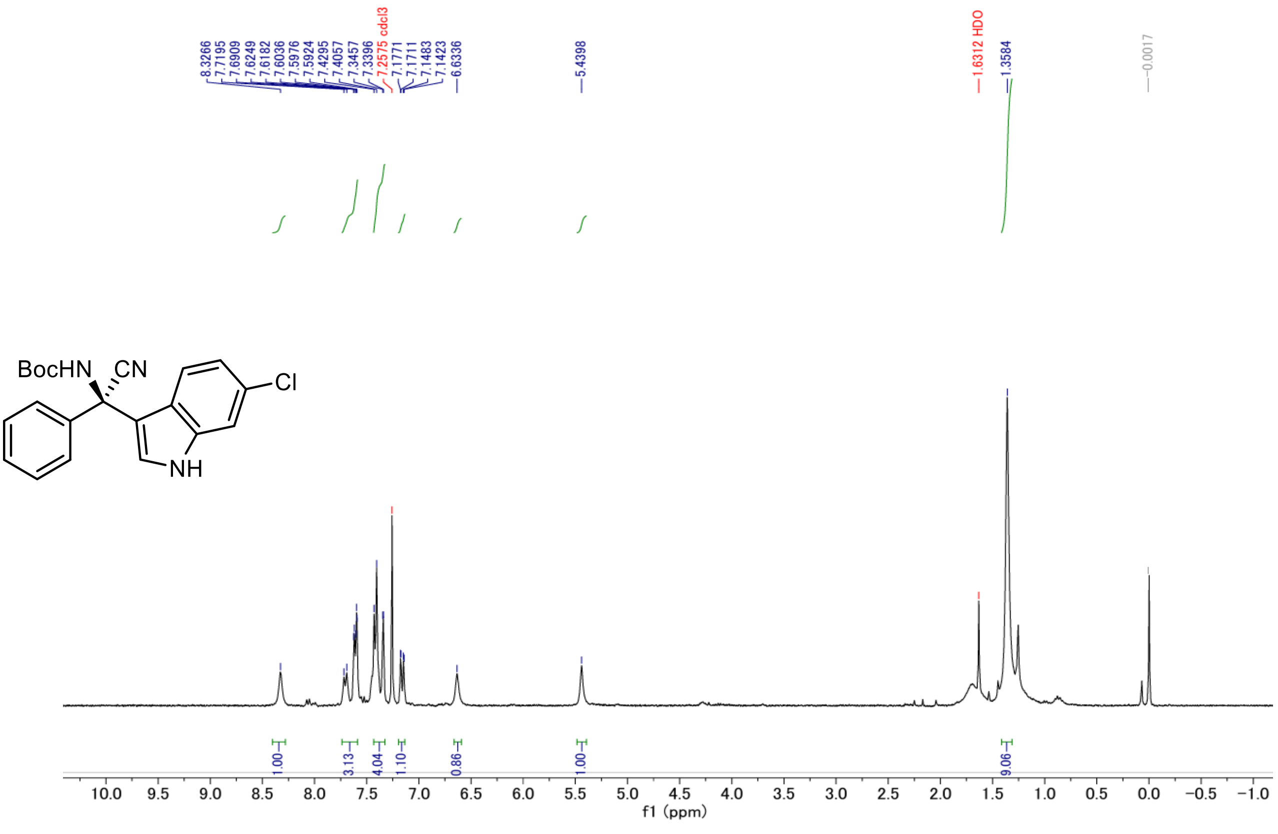


^{13}C NMR ($CDCl_3$, 125 MHz)

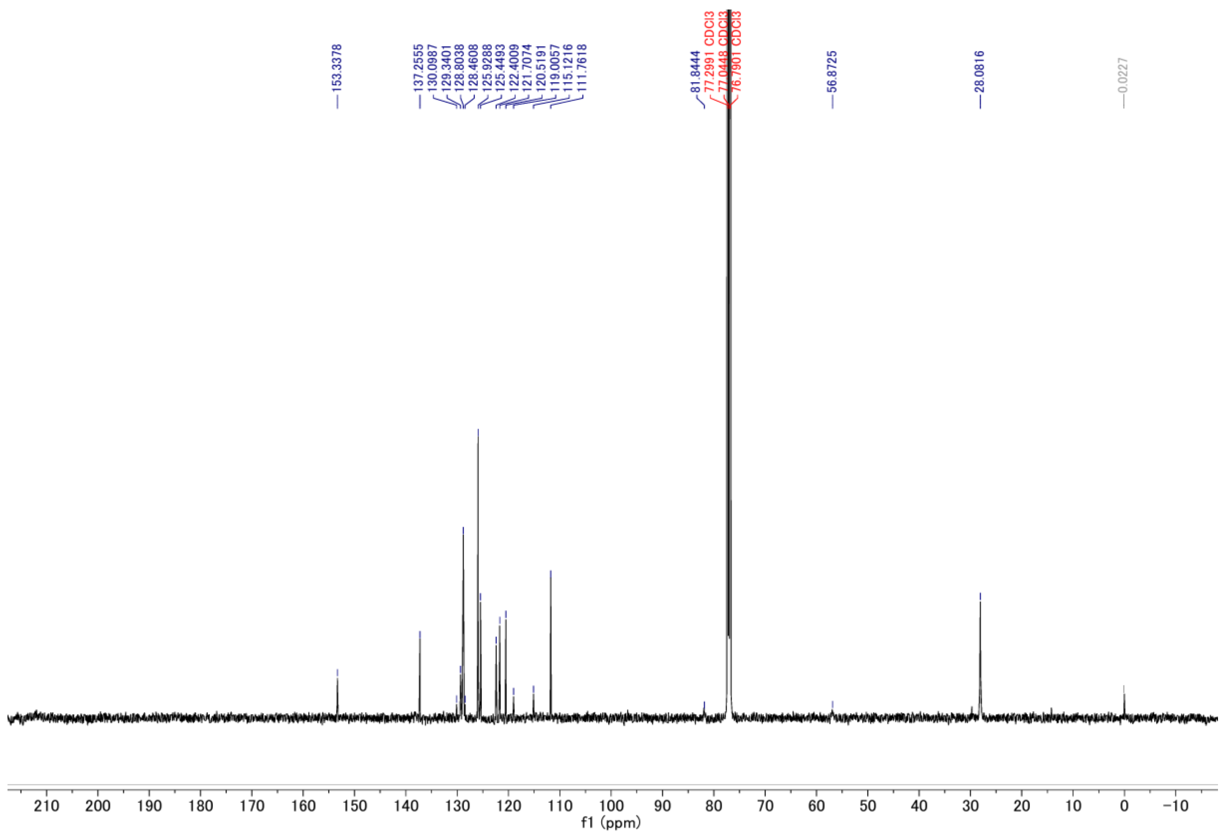


(*R*)-2-(6-Chloro-1*H*-indol-3-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6af)

^{1}H NMR ($CDCl_3$, 300 MHz)

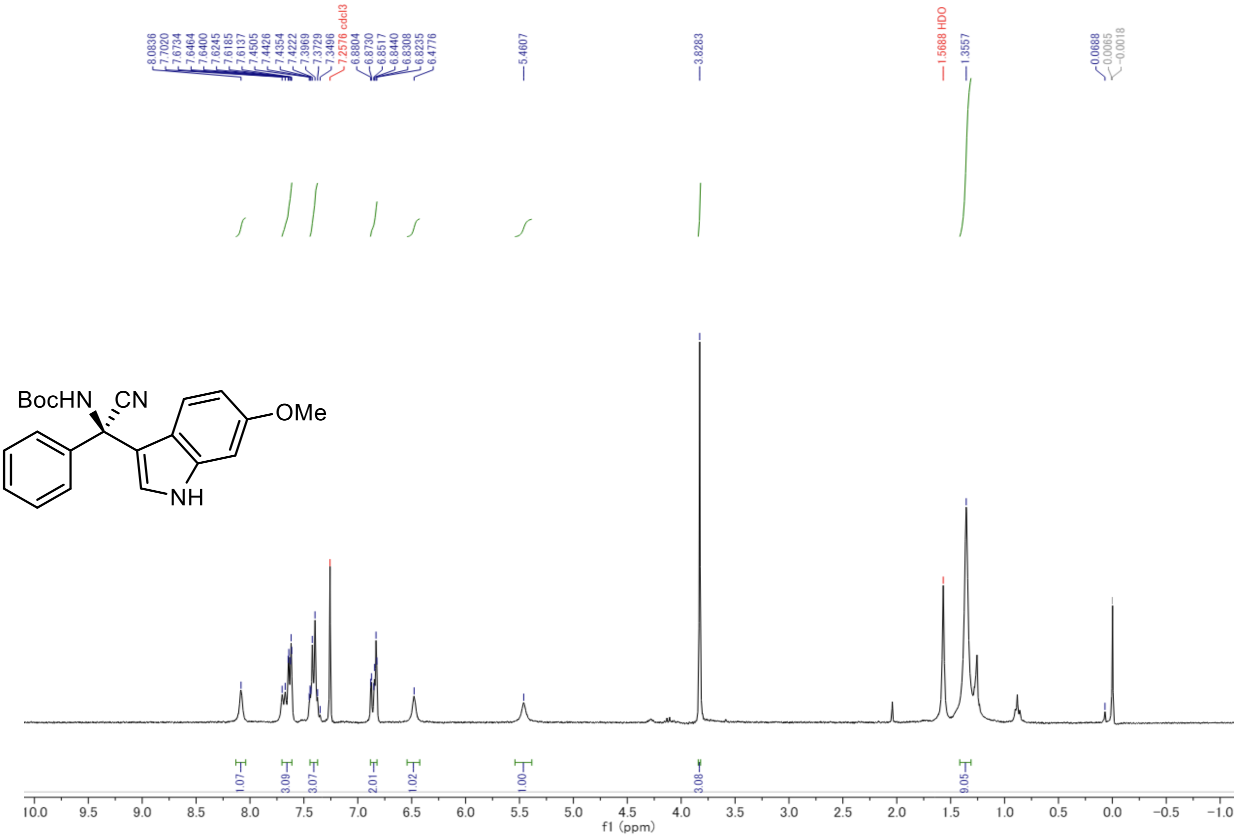


^{13}C NMR ($CDCl_3$, 125 MHz)

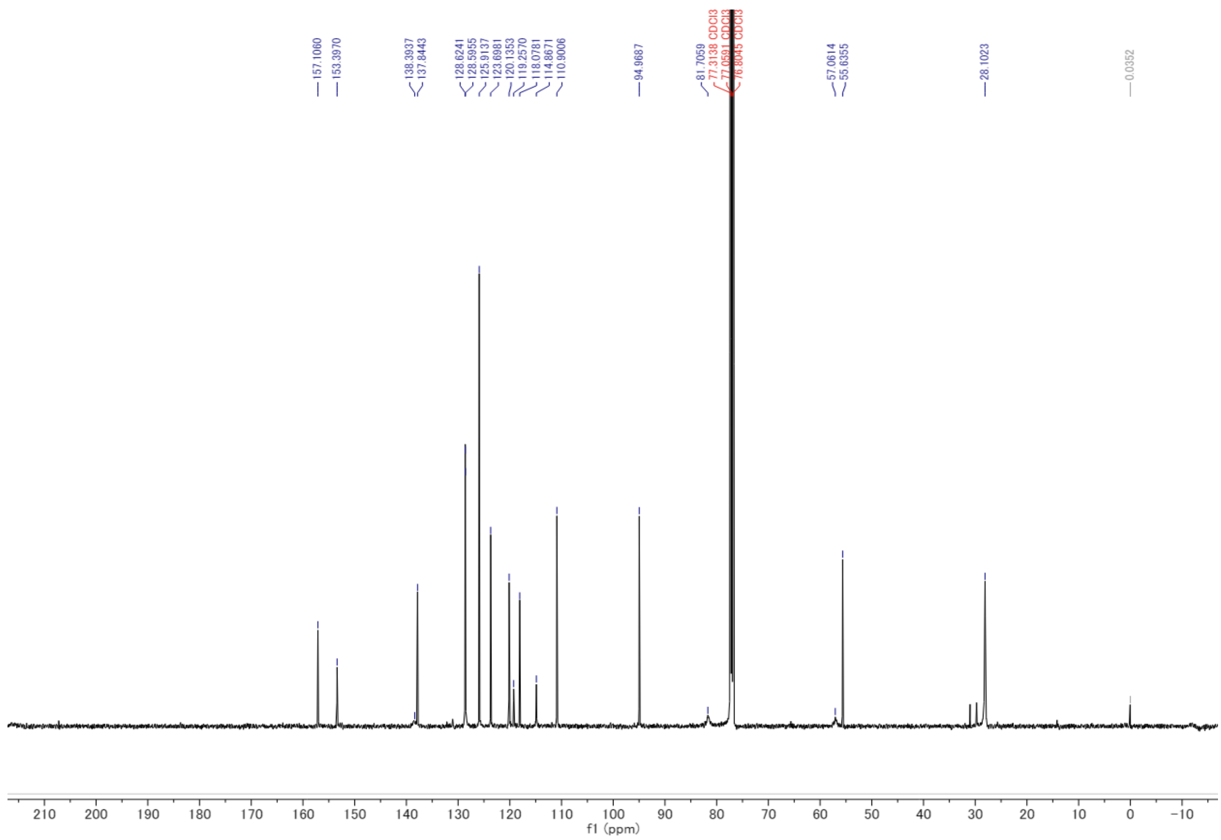


(*R*)-2-(6-Methoxy-1*H*-indol-3-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6ag)

^{1}H NMR ($CDCl_3$, 300 MHz)

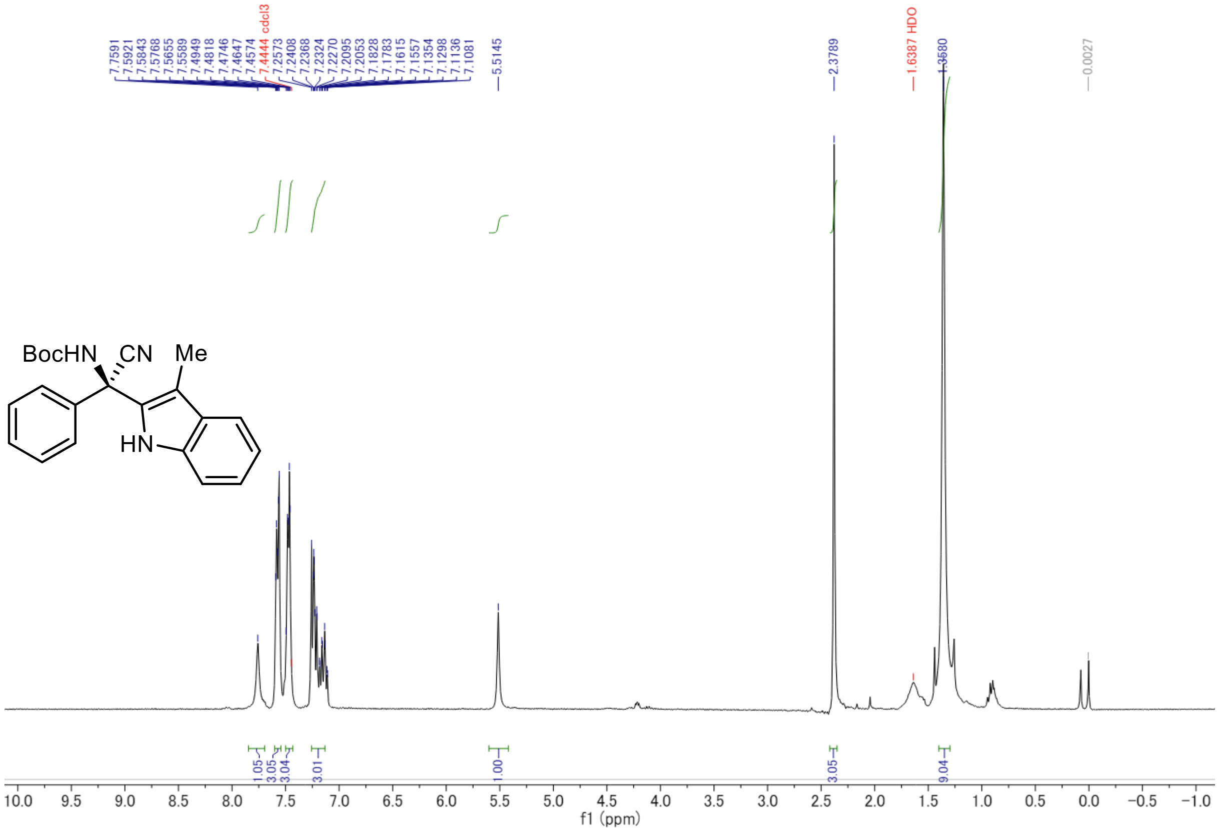


^{13}C NMR ($CDCl_3$, 125 MHz)

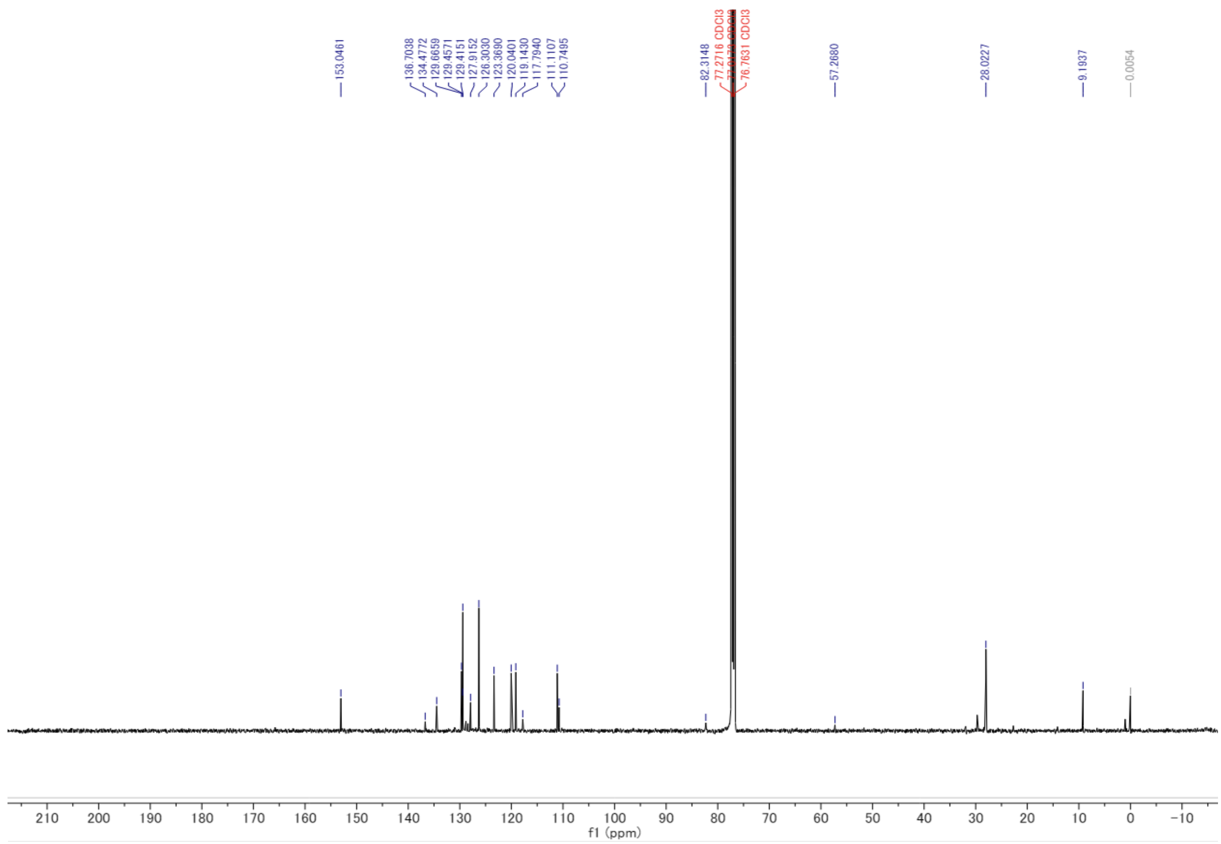


(*R*)-2-(3-Methyl-1*H*-indol-2-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6ah)

^{1}H NMR (CDCl$_3$, 300 MHz)

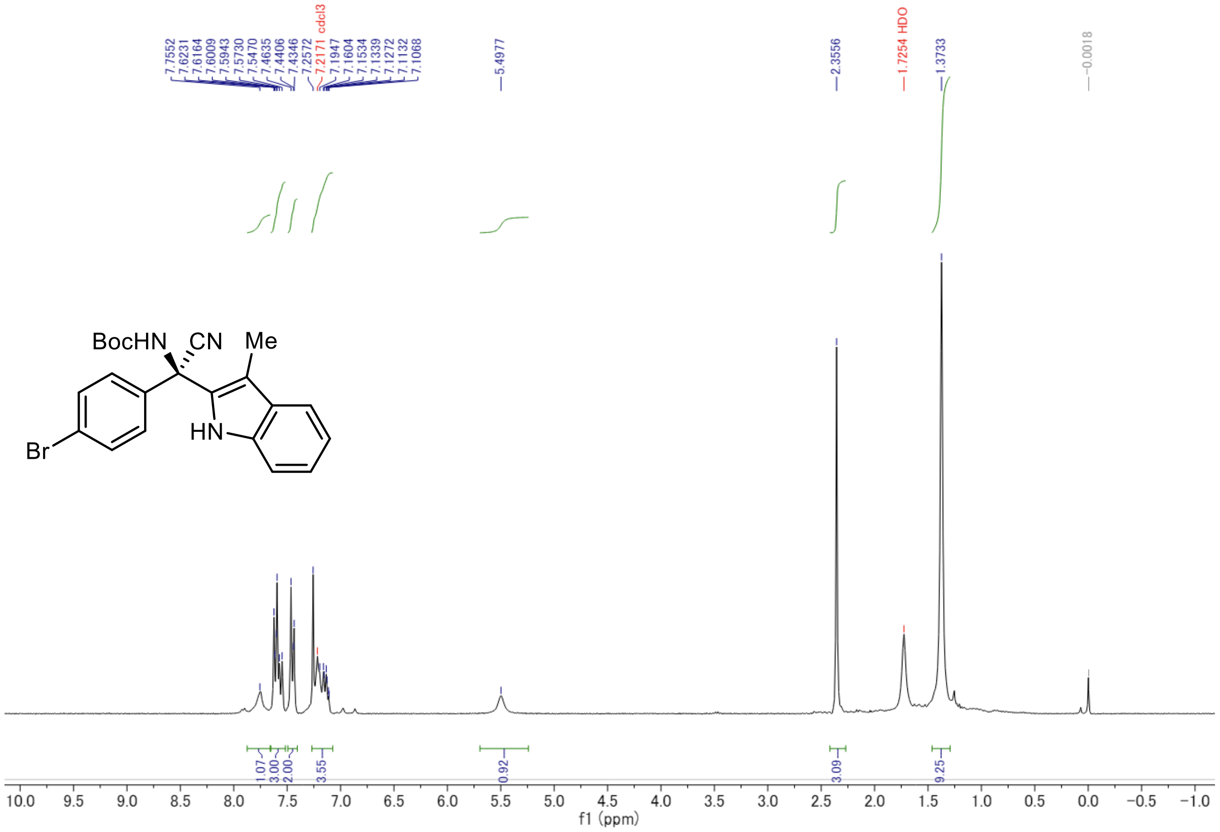


^{13}C NMR (CDCl$_3$, 125 MHz)

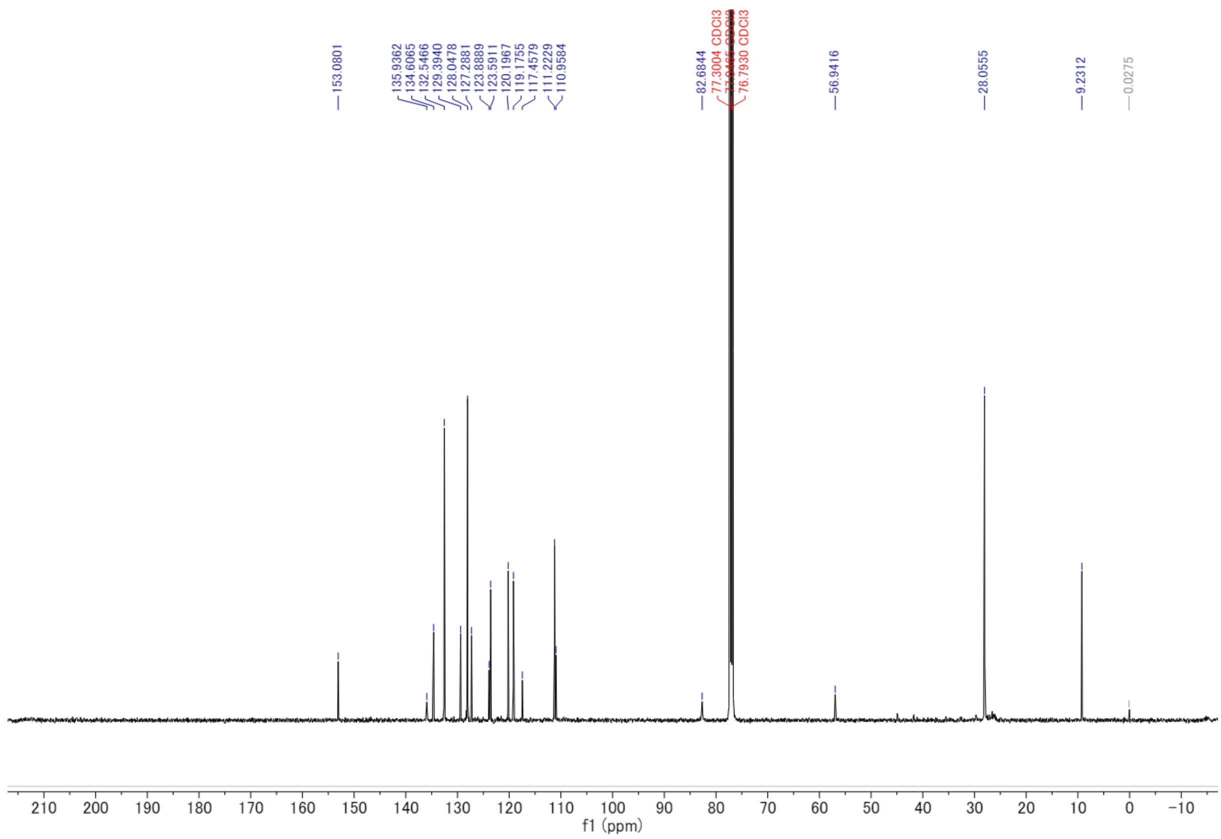


(*R*)-2-(3-Methyl-1*H*-indol-2-yl)-2-(4-bromophenyl)-2-(*tert*-butoxycarbonylamino)acetonitrile (6ai)

^{1}H NMR ($CDCl_3$, 300 MHz)

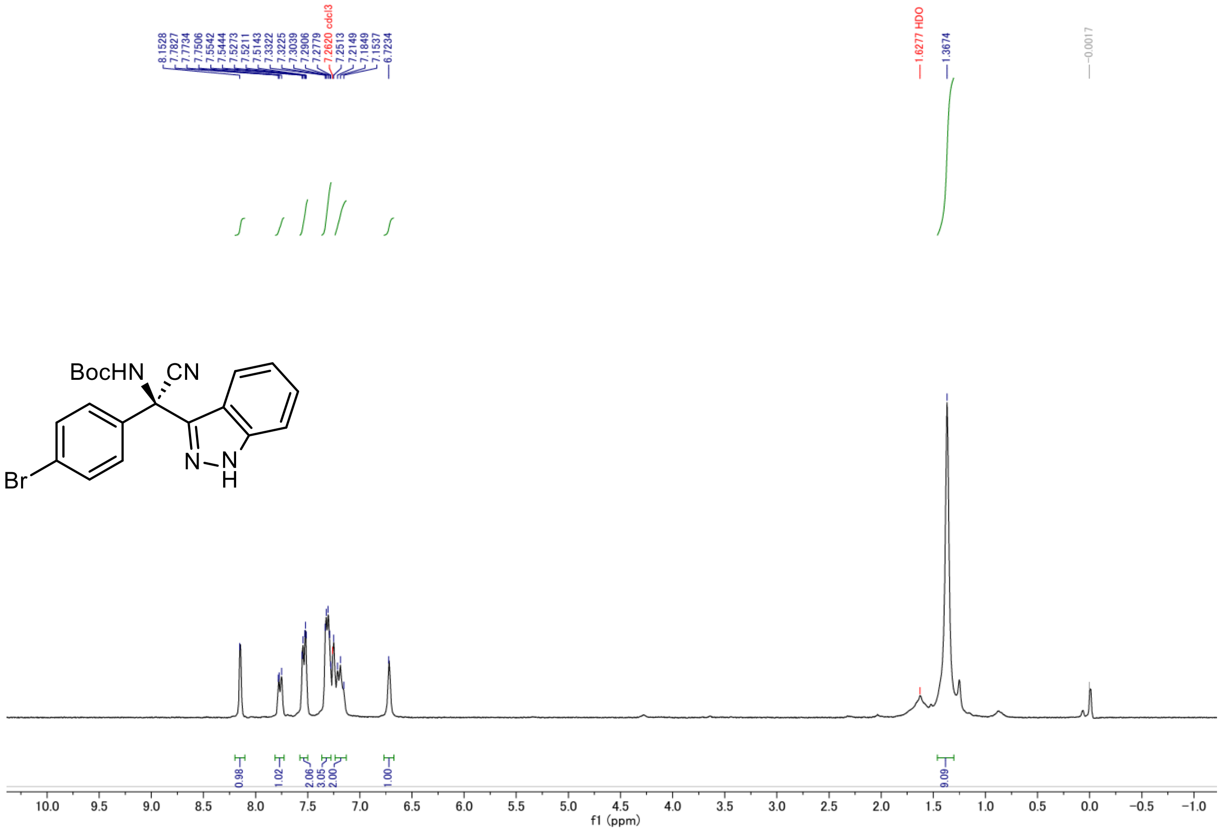


^{13}C NMR ($CDCl_3$, 125 MHz)

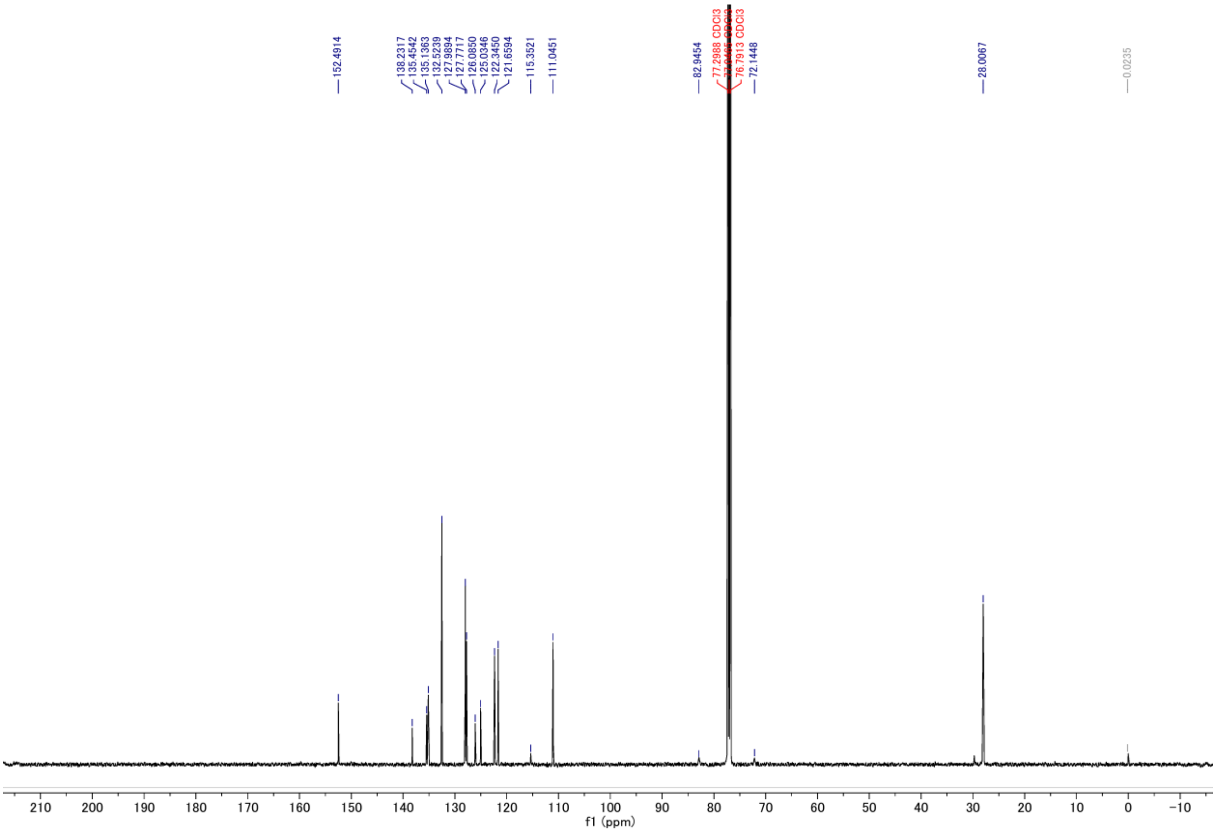


(*R*)-2-(1*H*-Indazol-3-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6ak)

^{1}H NMR ($CDCl_3$, 300 MHz)

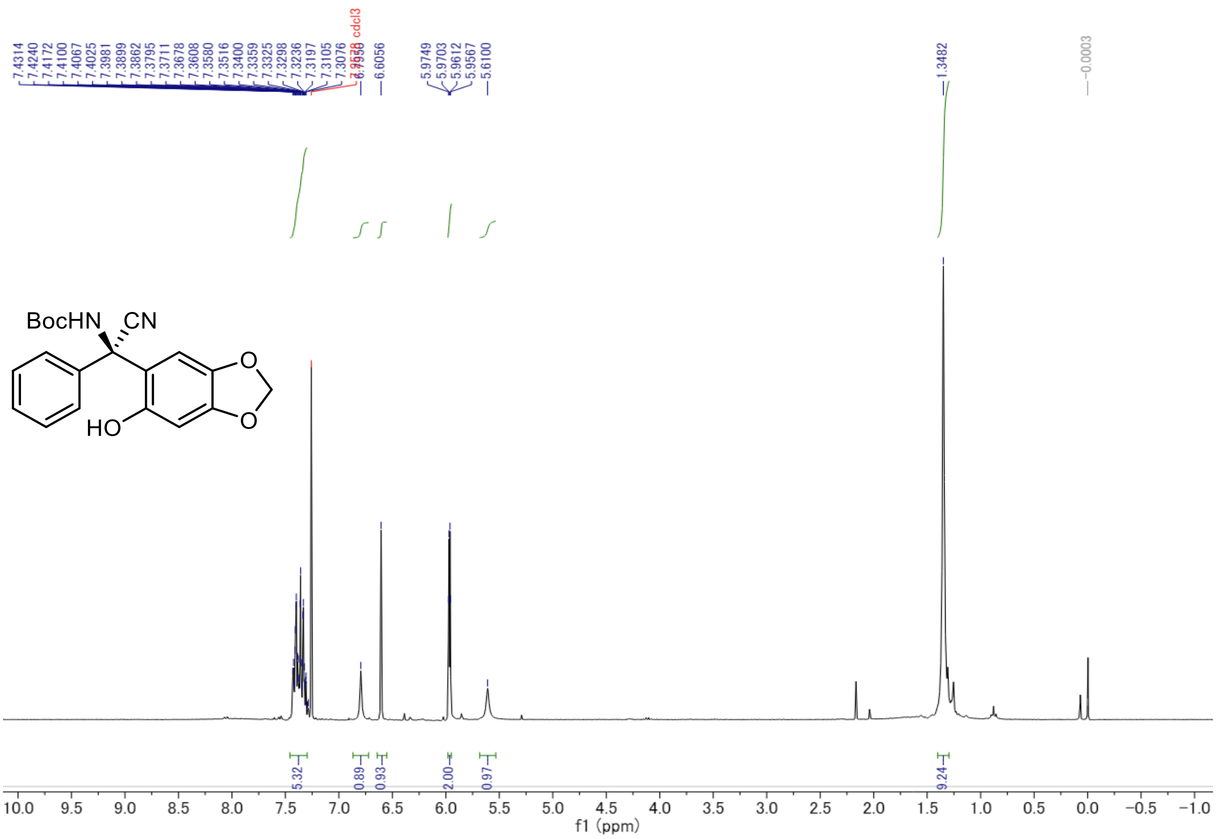


^{13}C NMR ($CDCl_3$, 125 MHz)

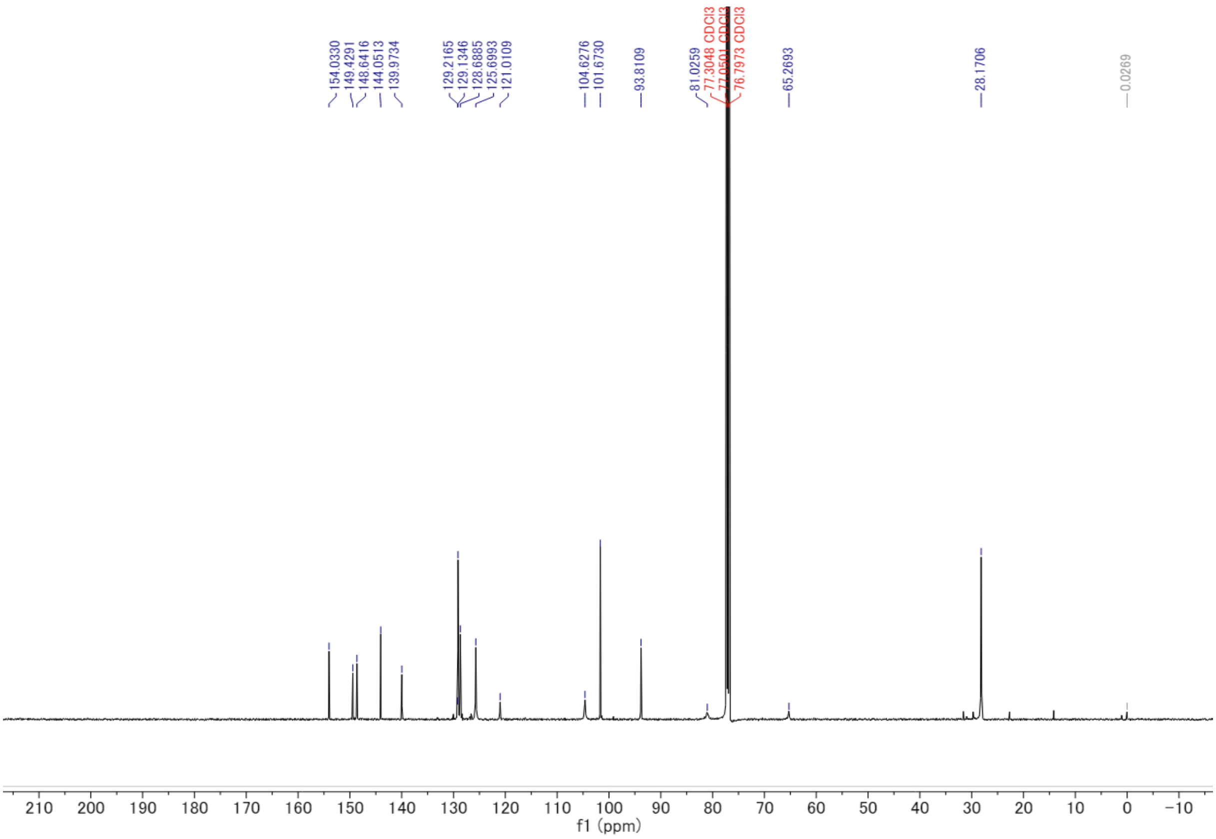


(*R*)-2-(6-Hydroxybenzo[*d*][1,3]dioxol-5-yl)-2-(4-bromophenyl)-2-(*tert*-butoxycarbonylamino)acetonitrile (6al)

^{1}H NMR ($CDCl_3$, 300 MHz)

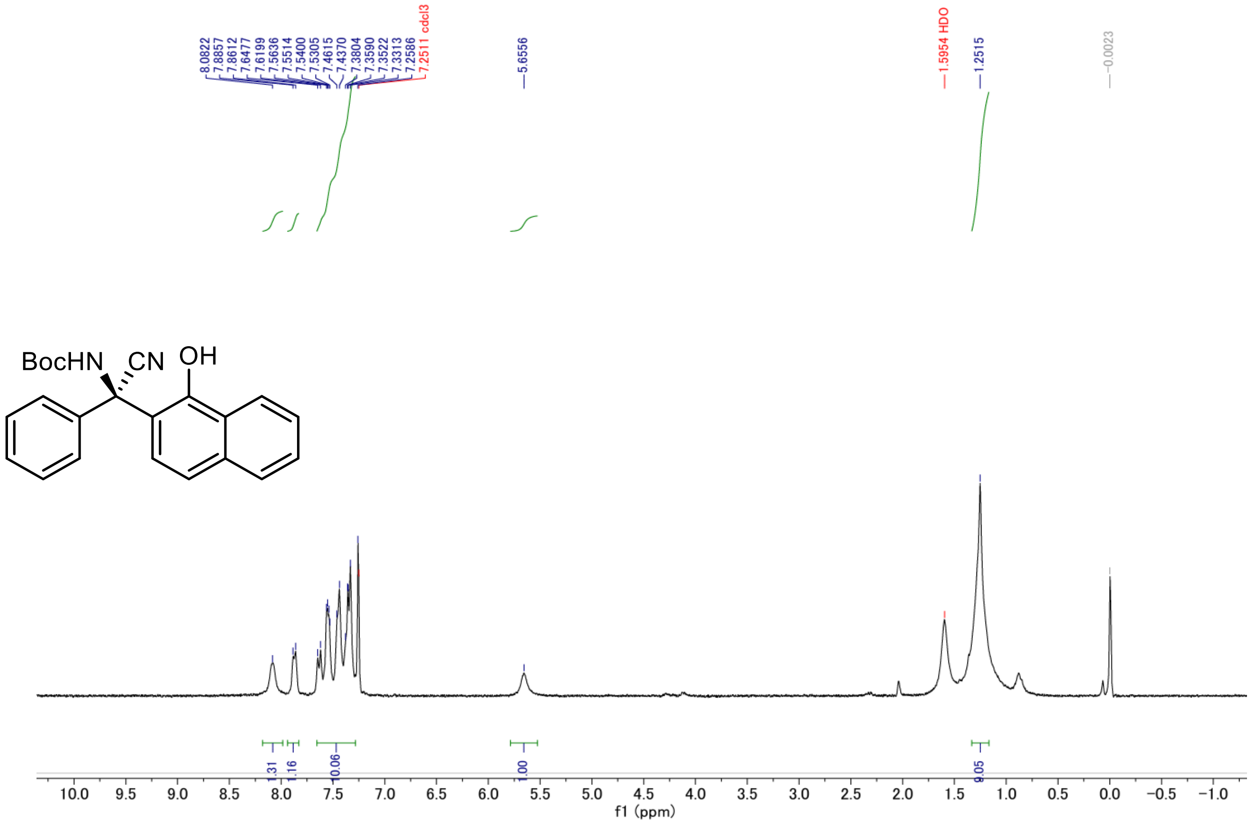


^{13}C NMR ($CDCl_3$, 125 MHz)

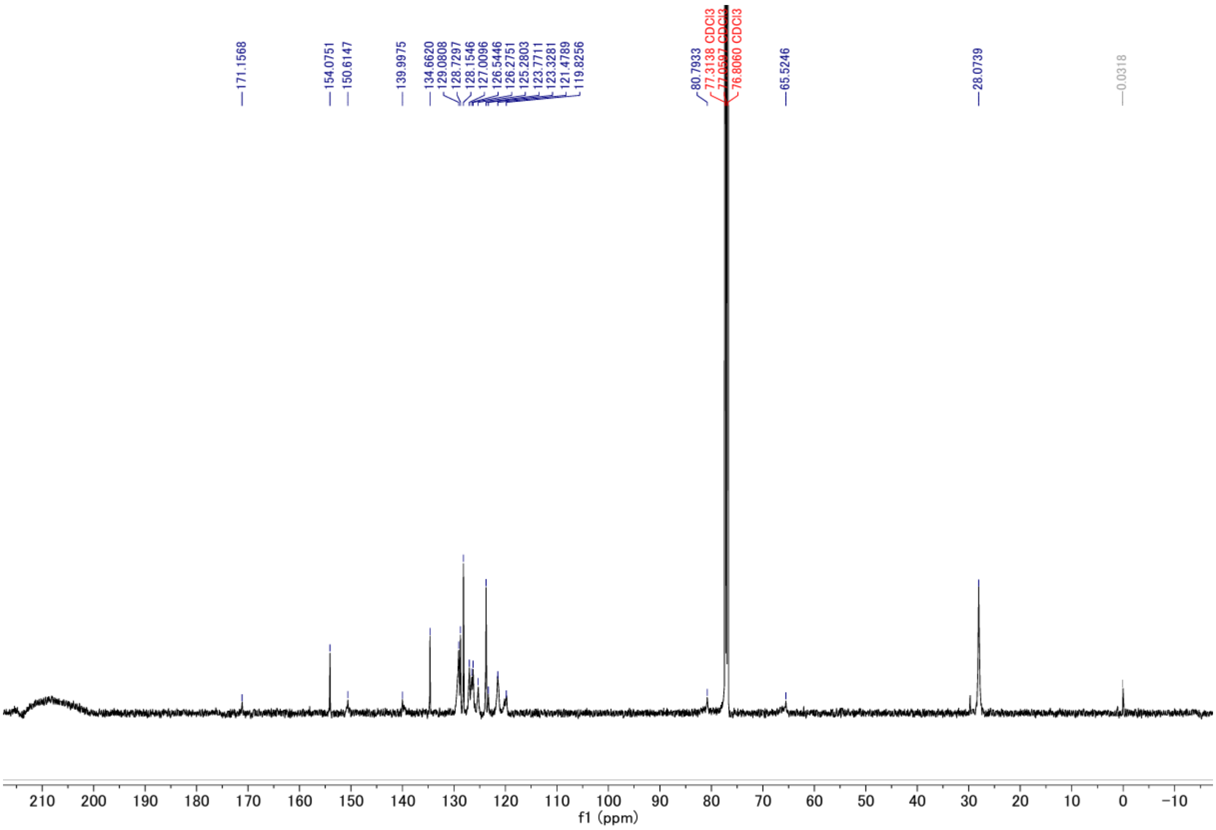


(*R*)-2-(1-Hydroxynaphtalen-2-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetonitrile (6am)

^{1}H NMR ($CDCl_3$, 300 MHz)

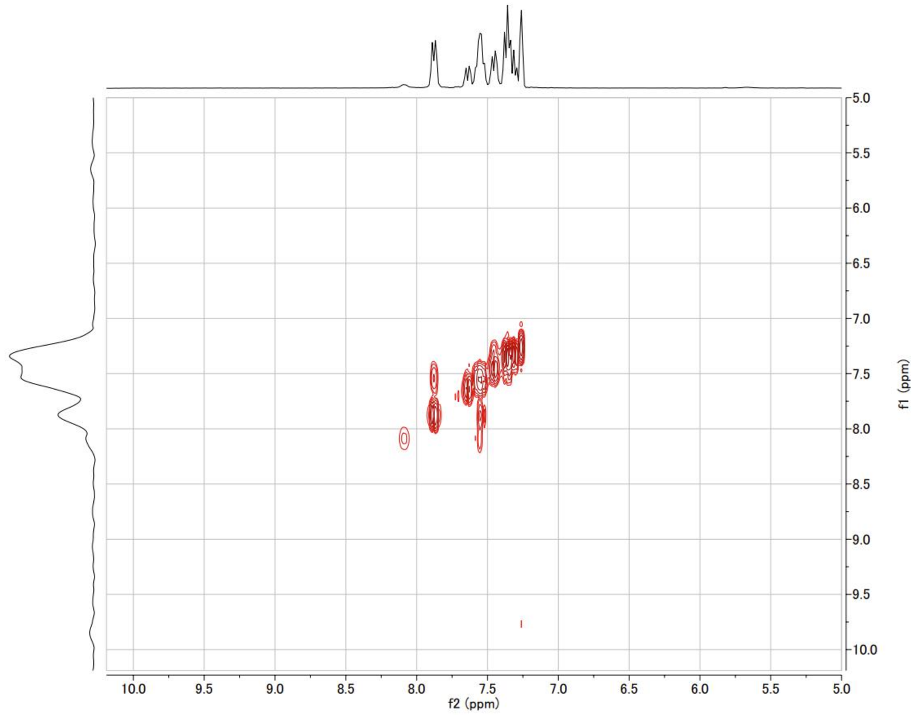


^{13}C NMR ($CDCl_3$, 125 MHz)



H-H COSY NMR ($CDCl_3$, 125 MHz)

In order to confirm the reaction position of 1-naphthol (2-position) with iminonitrile, we conduct H-H COSY NMR.



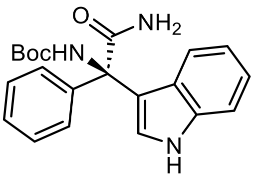
We also compared out spectrum to Friedel-Crafts products of 1-naphthol in the following literature, we conclude 2-position of naphthol is functionalized in this study.

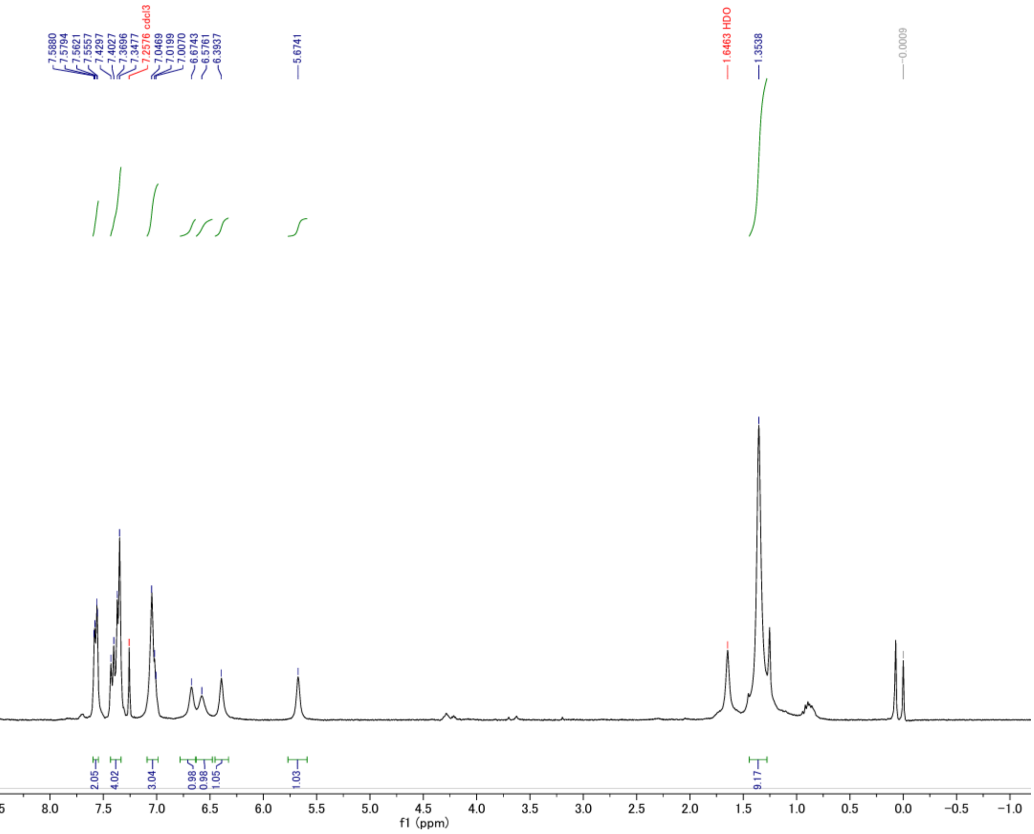
P. E. Georghiou, M. Ashram, *J. Org. Chem.* **1995**, *60*, 2909–2911.

J. Hill, W. Tam, *J. Org. Chem.* **2019**, *84*, 8309–8314.

(*R*)-2-(1*H*-Indol-3-yl)-2-phenyl-2-(*tert*-butoxycarbonylamino)acetamide (7)

^{1}H NMR ($CDCl_3$, 300 MHz)





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