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Supplementary Information

Copper-Catalyzed Enantioselective Arylboronation of Activated Alkenes leading to Chiral 3,3'-Disubstituted Oxindoles

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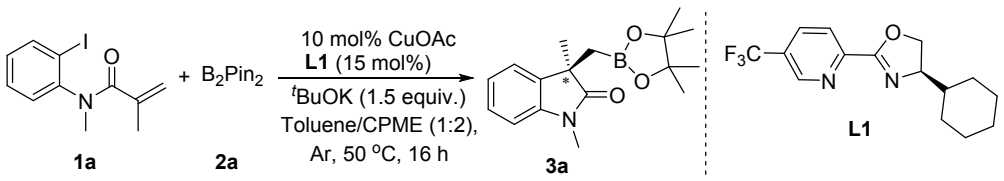
(A) Typical Experimental Procedure

(a) General

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 500 (500, 125, and 471 MHz) and advance spectrometer at room temperature in $CDCl_3$ (solvent signals, δ 7.26 and 77.0 ppm) using TMS as internal standard. High-resolution mass spectra (HRMS) was recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting Points were recorded on Hanon MP100 Apparatus. All the susbtrates **1** were prepared according to the known procedures.[1] Unless otherwise noted, all reactions were carried out using standard Schlenk techniques, and the starting materials and solvents were commercially available and were used without further purification. Column chromatography was performed on silica gel (200-300 mesh) using petroleum ether (PE)/ethyl acetate (EA).

(b) General procedure for synthesis of compounds 3.

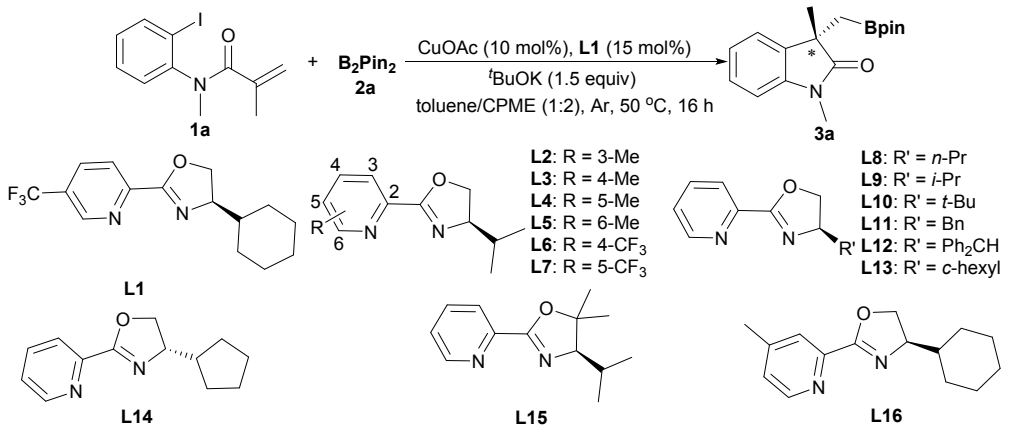


1a 2a 3a

To a Schlenk tube were added *N*-(2-iodophenyl)-*N*-methyl-2-methylacrylamide **1a** (0.1 mmol), B_2pin_2 **2a** (1.5 equiv), AcOCu (10 mol %), Ligand **L1** (15 mol%), ^{t}BuOK (1.5 equiv.), and Toluene/CPME (1:2) (1.0 mL). Then the tube is evacuated briefly under high vacuum and charged with argon through using standard Schlenk techniques; this process is repeated three times. The reaction mixture was stirred at 50 ^{o}C for 16 h. The reaction was quenched with water and extracted with ethyl acetate. The organic layer was washed with saturated NaCl solution, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired product **3a**.

(c) Screening of reaction conditions

Table S1 Screening of optimal reaction conditions[a]

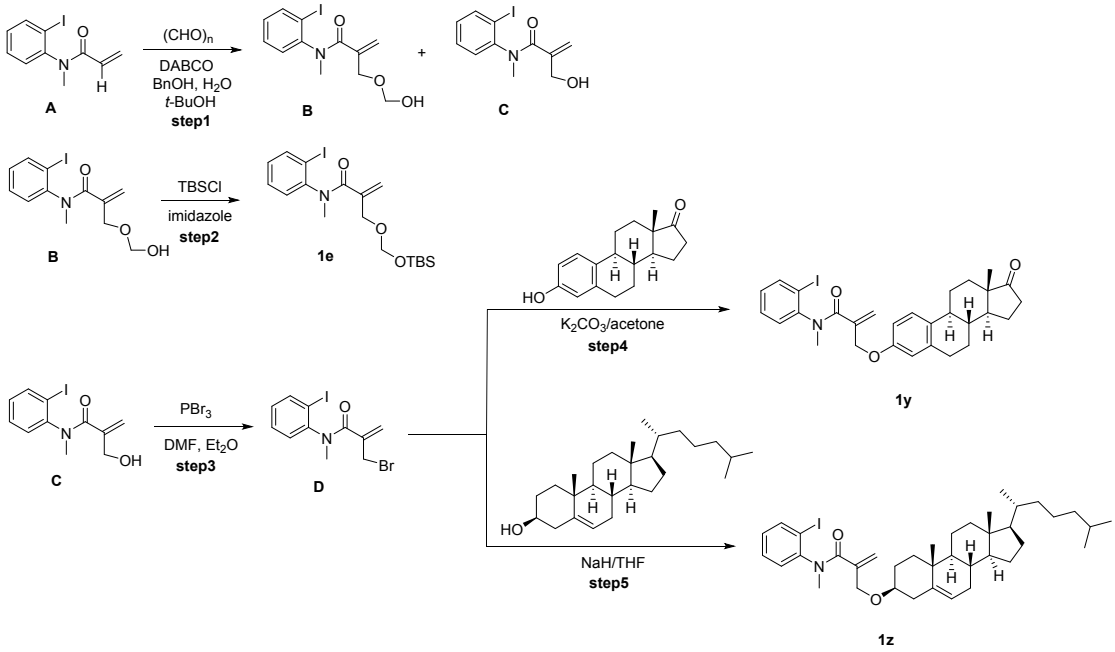


Entry	Variation from the standard conditions	Isolated yield (%)	er (%)
1	none	62	92:8
2	without CuOAc	0	—
3	without ^{t}BuOK	trace	—
4	CuCl instead of CuOAc	35	86:14
5	CuCN instead of CuOAc	33	88:12
6	CuTc instead of CuOAc	40	82:18
7	$Cu(CH_3CN)_4BF_4$ instead of CuOAc	42	88:12
8	$Cu(OAc)_2$ instead of CuOAc	41	91:9
9	CPME instead of toluene/CPME	46	92:8
10	toluene instead of toluene/CPME	66	90:10
11	dioxane instead of toluene/CPME	0	—
12	^{t}BuOLi instead of ^{t}BuOK	55	89:11
13	^{t}BuONa instead of ^{t}BuOK	58	88:12
14	MeONa instead of ^{t}BuOK	32	89:11
15	NaOH instead of ^{t}BuOK	46	88:12
16	Cs_2CO_3 instead of ^{t}BuOK	0	—
17	at 40 °C	34	92:8
18	at 60 °C	66	90:10
19	**L2** instead of **L1**	55	87:13
20	**L3** instead of **L1**	68	89:11
21	**L4** instead of **L1**	64	87:13
22	**L5** instead of **L1**	trace	—
23	**L6** instead of **L1**	50	86:14
24	**L7** instead of **L1**	63	89:11
25	**L8** instead of **L1**	45	63:37
26	**L9** instead of **L1**	56	87:13
27	**L10** instead of **L1**	22	76:24
28	**L11** instead of **L1**	63	73:27

29	**L12** instead of **L1**	48	67:33
30	**L13** instead of **L1**	60	89:11
31	**L14** instead of **L1**	50	23:77
32	**L15** instead of **L1**	50	51:49
33	**L16** instead of **L1**	72	89:11

[a] Standard reaction conditions: **1a** (0.1 mmol), **2a** (1.5 equiv), CuOAc (10 mol%), **L1** (15 mol%), ^{t}BuOK (1.5 equiv), anhydrous Toluene/CPME (1:2; 1.0 mL), 50 °C and 16 h. Methoxycyclopentane = CPME.

(d) Synthesis of compounds 1e, 1y and 1z.



Step 1: The substrate **A** (2.65 g, 9.2 mmol, 1.0 equiv), paraformaldehyde (4.3 g, 5.0 equiv), DABCO (1.0 g, 1.0 equiv) and BnOH (50 uL, 0.25 equiv) in *t*-BuOH (3 mL) / H_2O (12 mL) was stirred at 60 °C overnight. After the reaction was completed (monitored by TLC), the mixture was quenched with saturated brine and extracted with EtOAc (50 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 2/1) to give the desired products **B** (0.94 g, 29% yield) and **C** (1.16 g, 40% yield).

Step 2: The substrate **B** (0.88 g, 2.5 mmol, 1.0 equiv), was added to a solution of TBSCl (5 mmol, 0.75g) and imidazole (5 mmol, 340 mg) in dichloromethane(8 mL) at 0 °C. The reaction was warmed to room temperature and monitored by TLC. Upon completion the reaction was quenched with saturated NH_4Cl and extracted with ether (3×5 mL). The combined organics were washed with brine, dried over Na_2SO_4 and

concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to give the desired product **1e** (1.03g, 90% yield).

Preparation of **1y-1z**:

Step 3: To a solution of **C** (3.6 mmol) in DMF (2.0 mL)/Et_2O (1.0 mL) was added PBr_3 (0.17 mL, 0.5 equiv) dropwise at 0 °C. The mixture was stirred at room 10 mL) to the reaction mixture, the aqueous phase was further extracted with EtOAc (10 mL×3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 8/1) to get **D**.

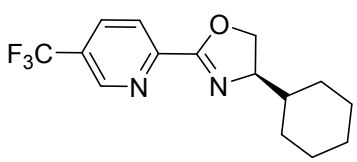
Step 4: Estrone (1 mmol) was added to a solution of **D** (1 mmol) and K_2CO_3 (2 mmol) in acetone 10 mL at 60 °C. The reaction was stirring for overnight and monitored by TLC. Upon completion the reaction was quenched with water and concentration, which was extracted with ethyl acetate (3×10 mL). The combined organics were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to give the desired product **1y**.

Step 5: Cholesterol (1 mmol) was slowly added to a solution of NaH **(**2 mmol) in THF 10 mL at 0 °C, and stirring for 30 mins at room temperature, **D** was also added at 0°C, the reaction was stirring for overnight and monitored by TLC. Upon completion the reaction was quenched with water and extracted with ethyl acetate (3×10 mL). The combined organics were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) to give the desired product **1z**.

(e) Ligands synthesis:

L5, L7, L9, L10, L11, L14 were commercial available, and the ligands synthesis were proceed as follows:

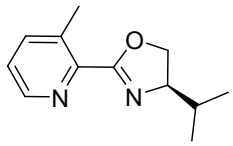
(*R*)-4-cyclohexyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (L1):



White solid, mp 128.9-129.9 °C; Preparation of $^{5\text{-}CF_3}PyOx^{c\text{-}hex}$ (*R*)-**L1**: D-valinol (1.55 g, 15 mmol) was added to a mixture of 5-(trifluoromethyl)picolinonitrile (1.72 g, 10 mmol) and $Zn(OTf)_2$ (363.5 mg, 5mmol) in toluene (20 mL). The solution was stirred under refluxing for 5 h, and then toluene

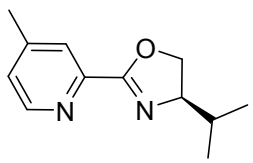
was removed in vacuum. The residue was purified by flash column chromatography with PE/EtOAc (v/v 2:1) to give the title compound as white solid (1.3 g, 44%). Optical Rotation: $[\alpha]_D^{20}$ = +23.6 (c = 0.3, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.01 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H) 4.53 (dd, *J* = 9.5 Hz, *J* = 8.0 Hz, 1H), 4.27 (t, *J* = 8.5 Hz, 1H), 4.21-4.16(m, 1H), 2.01-1.98 (m, 1H), 1.79-1.74 (m, 2H), 1.70-1.67 (m, 1H), 1.61-1.54 (m, 2H), 1.28-1.98 (m, 3H), 1.13-1.05 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 150.0, 146.6, 146.5, 133.9, 123.6, 76.7, 72.3, 71.3, 42.7, 29.5, 28.9, 26.4, 26.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.6. HRMS-ESI, m/z calcd. for $C_{15}H_{17}F_3N_2O$ $[M+H]^+$298.1293; found: 298.1295.

(*R*)-4-isopropyl-2-(3-methylpyridin-2-yl)-4,5-dihydrooxazole (L2):



White solid, mp 81.2-82.2 °C; Preparation of $^{3\text{-Me}}$PyOx$^{i\text{Pr}}$ (*R*)-**L2**: D-valinol (1.55 g, 15 mmol) was added to a mixture of 3-methylpicolinonitrile (1.18 g, 10 mmol) and $Zn(OTf)_2$ (363.5 mg, 5mmol) in toluene (20 mL). The solution was stirred under refluxing for 5 h, and then toluene was removed in vacuum. The residue was purified by flash column chromatography with PE/EtOAc (v/v 2:1) to give the title compound as white solid (1.1 g, 54%). Optical Rotation: $[\alpha]_D^{20}$ = +59.9 (c = 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 4.5 Hz, *J* =1.0 Hz, 1H), 7.56 (dd, *J* = 7.5 Hz, *J* =1.0 Hz, 1H), 7.24 (dd, *J* = 7.5 Hz, *J* = 4.5 Hz, 1H), 4.43 (dd, *J* = 9.5 Hz, *J* = 7.5 Hz, 1H), 4.20-4.11 (m, 1H), 2.60 (s, 3H), 1.88-1.83 (m, 1H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 146.7, 145.8, 139.1, 134.9, 124.6, 73.5, 69.7, 32.9, 20.5, 18.9, 18.4. HRMS-ESI, m/z calcd. for $C_{12}H_{16}N_2O$ $[M+H]^+$204.1263; found: 204.1263.

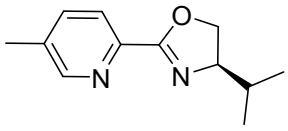
(*R*)-4-isopropyl-2-(4-methylpyridin-2-yl)-4,5-dihydrooxazole (L3):



Yellow oil. Preparation of $^{4\text{-Me}}$PyOx$^{i\text{Pr}}$ (*R*)-**L3**: D-valinol (1.55 g, 15 mmol) was added to a mixture of 4-methylpicolinonitrile (1.18 g, 10 mmol) and $Zn(OTf)_2$ (363.5 mg, 5mmol) in toluene (20 mL). The solution was stirred under refluxing for 5 h, and then toluene was removed in vacuum. The residue was purified by flash column chromatography with PE/EtOAc (v/v 2:1) to give the title compound as white solid (1.3 g, 64%). Optical Rotation: $[\alpha]_D^{20}$ = +167 (c = 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 5.0 Hz, 1H), 7.84(s, 1H), 7.13-7.12 (m, 1H), 4.43 (dd, *J* = 9.5 Hz, *J* = 8.0 Hz, 1H), 4.16-4.06 (m, 2H), 2.33 (s, 3H), 1.87-1.79 (m, 1H), 0.99 (d, *J* =

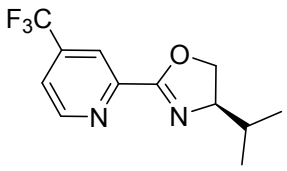
7.0 Hz, 3H), 0.88 (d, *J* =6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 149.3, 147.7, 146.5, 126.2, 124.6, 72.7, 70.5, 32.5, 20.8, 18.9, 18.0. HRMS-ESI, m/z calcd. for $C_{12}H_{16}N_2O$ $[M+H]^+$204.1263; found: 204.1265.

(*R*)-4-isopropyl-2-(5-methylpyridin-2-yl)-4,5-dihydrooxazole (L4):



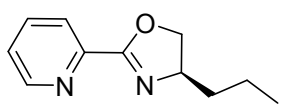
White solid, mp 80.8-81.8 °C; Preparation of $^{5\text{-Me}}$PyOx$^{i\text{Pr}}$ (*R*)-**L4**: D-valinol (1.55 g, 15 mmol) was added to a mixture of 5-methylpicolinonitrile (1.18 g, 10 mmol) and $Zn(OTf)_2$ (363.5 mg, 5mmol) in toluene (20 mL). The solution was stirred under refluxing for 5 h, and then toluene was removed in vacuum. The residue was purified by flash column chromatography with PE/EtOAc (v/v 2:1) to give the title compound as white solid (0.95 g, 46%). Optical Rotation: $[\alpha]_D^{20}$ = +108.3 (c = 0.3, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 5.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.55 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 4.47 (dd, *J* = 9.0 Hz, *J* = 8.0 Hz, 1H), 4.20-4.12 (m, 2H), 2.37 (s, 3H), 1.91-1.85 (m, 1H), 1.03 (d, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 150.1, 144.2, 136.9, 135.5, 123.4, 72.8, 70.6, 32.7, 19.0, 18.5, 18.1. HRMS-ESI, m/z calcd. for $C_{12}H_{16}N_2O$ $[M+H]^+$ 204.1263; found: 204.1263.

(*R*)-4-isopropyl-2-(4-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (L6):



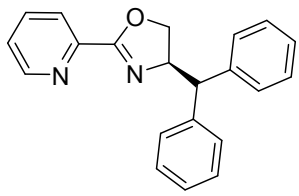
Yellow solid, mp 81.0-82.2 °C; Preparation of $^{4\text{-CF}_3}$PyOx$^{i\text{Pr}}$ (*R*)-**L6**: D-valinol (1.55 g, 15 mmol) was added to a mixture of 4-(trifluoromethyl)picolinonitrile (1.72 g, 10 mmol) and $Zn(OTf)_2$ (363.5 mg, 5mmol) in toluene (20 mL). The solution was stirred under refluxing for 5 h, and then toluene was removed in vacuum. The residue was purified by flash column chromatography with PE/EtOAc (v/v 2:1) to give the title compound as yellow solid (1.0 g, 39%). Optical Rotation: $[\alpha]_D^{20}$ = +89.2 (c = 0.5, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (d, *J* = 5.0 Hz, 1H), 8.25 (s,1H), 7.57 (d, *J* = 4.5 Hz, 1H), 4.51 (dd, *J* = 9.0 Hz, *J* = 8.0 Hz, 1H), 4.21 (t, *J* = 8.0 Hz, 1H), 4.18-4.14 (m, 1H), 1.89-1.84 (m, 1H), 1.02 (d, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 150.6, 148.1, 139.2, 138.9, 123.5, 121.3, 120.8, 119.7, 119.6, 73.0, 71.0, 32.6, 18.8, 18.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ -64.9. HRMS-ESI, m/z calcd. for $C_{12}H_{13}F_3N_2O$ $[M+H]^+$258.0980; found: 258.0982.

(*R*)-4-propyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (L8):



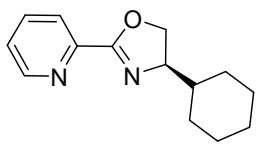
Yellow oil; Preparation of PyOx$^{n\text{Pr}}$ (*R*)-**L8**: D-Norvalinol (1.55 g, 15.0 mmol) was added to a mixture of 2-cyanopyridine (1.04 g, 10.0 mmol) and $Zn(OTf)_2$ (363.5 mg, 1.0 mmol) in toluene (20 mL). The solution was stirred under refluxing for 5 h, and then toluene was removed in vacuum. The residue was purified by flash column chromatography with PE/EtOAc (v/v 2:1) to give the title compound as yellow oil (1.2 g, 63%). Optical Rotation: $[\alpha]_D^{20}$ = +68.0 (c = 0.3, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65-8.62 (m, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.72-7.68 (m, 1H), 7.33-7.29 (m, 1H), 4.51 (dd, *J* = 9.5 Hz, *J* = 8.5 Hz, 1H), 4.32-4.25 (m, 1H), 4.05 (t, *J* = 8.5 Hz, 1H), 1.75 -1.68 (m, 1H), 1.54-1.40 (m, 1H), 1.38-1.33 (m, 1H), 0.91 (t, *J* =7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 149.5, 146.7, 136.4, 125.3, 123.7, 73.0, 66.7, 37.8, 19.0, 13.9. HRMS-ESI, m/z calcd. for $C_{11}H_{14}N_2O$ $[M+H]^+$ 190.1106; found: 190.1104.

(*R*)-4-benzhydryl-2-(pyridin-2-yl)-4,5-dihydrooxazole (L12):



White solid, mp 156.8-157.4 °C; Preparation of PyOx (*R*)-**L12**: (*R*)-Diphenylalaninol (3.4 g, 15.0 mmol) was added to a mixture of 2-cyanopyridine (1.04 g, 10.0 mmol) and $Zn(OTf)_2$ (363.5 mg, 1.0 mmol) in toluene (20 mL). The solution was stirred under refluxing for 5 h, and then toluene was removed in vacuum. The residue was purified by flash column chromatography with PE/EtOAc (v/v 2:1) to give the title compound as white solid (2.0 g, 64%). Optical Rotation: $[\alpha]_D^{20}$ = +41.6 (c = 0.2, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.0 Hz, 1H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.76-7.72 (m, 1H), 7.39-7.35 (m, 3H), 7.32-7.28 (m, 6H), 7.23-7.20 (m, 2H), 5.20 (q, *J* = 9.5 Hz, 1H), 4.54(t, *J* = 9.5 Hz, 1H), 4.20 (t, *J* = 8.5 Hz, 1H), 4.11 (d, *J* = 9.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3, 149.6, 136.5, 128.7, 128.6, 128.4, 126.8, 126.5, 125.5, 124.3, 72.0, 70.4, 58.9. HRMS-ESI, m/z calcd. for $C_{21}H_{18}N_2O$ $[M+H]^+$314.1419; found: 314.1421.

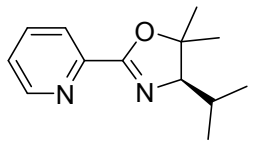
(*R*)-4-cyclohexyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (L13):



White solid; Preparation of PyOx$^{c\text{-hex}}$(*R*)-**L13**: D-2-Amino-2-cyclohexylethanol (2.1 g, 15.0 mmol) was added to a mixture of 2-cyanopyridine (1.04 g, 10.0 mmol) and $Zn(OTf)_2$ (363.5 mg, 1.0 mmol) in toluene (20 mL). The solution was stirred under refluxing for 5 h, and

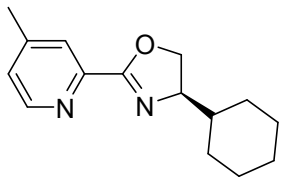
then toluene was removed in vacuum. The residue was purified by flash column chromatography with PE/EtOAc (v/v 2:1) to give the title compound as white solid (1.2 g, 52%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.5 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.78-7.74 (m, 1H), 7.39-7.35 (m, 1H), 4.49 (dd, *J* = 9.5 Hz, *J* = 8.5 Hz, 1H), 4.23 (t, *J* = 8.0 Hz,1H), 4.17-4.11 (m, 1H), 2.02-1.99 (d, *J* = 12.5 Hz, 1H), 1.77-1.73 (m, 2H), 1.69-1.66 (m, 2H), 1.63-1.60 (m, 1H), 1.59-1.55 (m, 1H), 1.27-1.19 (m, 3H), 1.17-1.02 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 149.7, 146.9, 136.5, 125.4, 123.9, 72.1, 71.0, 42.7, 29.6, 28.8, 26.5, 26.0.

(*R*)-4-isopropyl-5,5-dimethyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (L15):



White solid, mp 119.8-121.5 °C; Preparation of PyOx (*R*)-**L15**: (*R*)-Diphenylalaninol (3.4 g, 15.0 mmol) was added to a mixture of 2-cyanopyridine (1.04 g, 10.0 mmol) and $Zn(OTf)_2$ (363.5 mg, 1.0 mmol) in toluene (20 mL). The solution was stirred under refluxing for 5 h, and then toluene was removed in vacuum. The residue was purified by flash column chromatography with PE/EtOAc (v/v 2:1) to give the title compound as white solid (2.0 g, 64%). Optical Rotation: $[\alpha]_D^{20}$ = +26.1 (c = 0.2, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.5 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.86-7.82 (m, 1H), 7.43-7.40 (m, 1H), 3.95 (dd, *J* =10.5 Hz, *J* = 2.5 Hz, 1H), 2.29-2.23 (m, 1H), 1.34 (s, 3H), 1.27 (s, 3H), 1.05 (d, *J* =6.5 Hz, 3H), 0.98 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 149.9, 148.2, 137.3, 126.1, 122.4, 73.8, 60.8, 29.1, 28.4, 27.1, 22.5, 17.0. HRMS-ESI, m/z calcd. for $C_{13}H_{18}N_2O$ $[M+H]^+$218.1419; found: 218.1419.

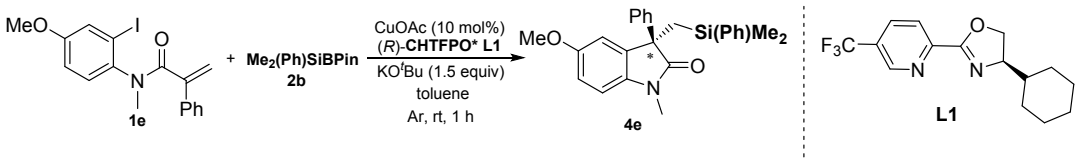
(*R*)-4-cyclohexyl-2-(4-methylpyridin-2-yl)-4,5-dihydrooxazole (L16):



White solid, mp 129.8-131.4 °C; Preparation of $^{4\text{-Me}}$PyOx$^{c\text{-hex}}$ (*R*)-**L26**: D-valinol (1.55 g, 15 mmol) was added to a mixture of 4-methylpicolinonitrile (1.18 g, 10 mmol) and $Zn(OTf)_2$ (363.5 mg, 5mmol) in toluene (20 mL). The solution was stirred under refluxing for 5 h, and then toluene was removed in vacuum. The residue was purified by flash column chromatography with PE/EtOAc (v/v 2:1) to give the title compound as white solid (1.6 g, 66%). Optical Rotation: $[\alpha]_D^{20}$ = +156.0 (c = 0.3, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51-8.48 (m, 1H), 7.86 (s, 1H), 7.15-7.14 (m, 1H), 4.44 (dd, *J* = 9.5 Hz, *J* = 8.0 Hz, 1H), 4.19 (t, *J* = 8.5 Hz, 1H), 4.12-4.07 (m, 1H), 2.35 (s, 3H), 1.97-1.92 (m, 1H), 1.75-1.70 (m, 2H), 1.66-1.62 (m, 1H), 1.60-1.56 (m,

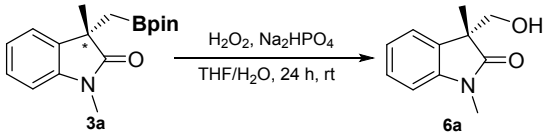
1H), 1.54-1.48 (m, 1H), 1.24-1.12 (m, 3H), 1.10-1.01 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 149.3, 147.8, 146.6, 126.2, 124.6, 71.9, 72.8, 70.8, 42.6, 29.5, 28.7, 26.4, 25.9, 20.8. HRMS-ESI, m/z calcd. for $C_{15}H_{20}N_2O$ $[M+H]^+$244.1576; found: 244.1578.

(e) Alkene Arylsilylation and Derivatization:



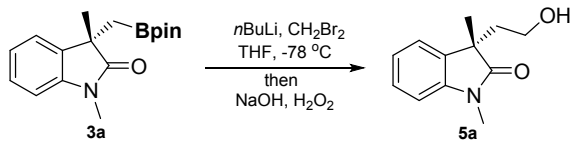
To a Schlenk tube were added *N*-(2-iodo-4-methoxyphenyl)-*N*-methyl-2-phenylacrylamide **1e** (0.1 mmol), Me_2(Ph)SiBPin **2b** (3.0 equiv), AcOCu (10 mol %), Ligand **L1** (15 mol%), ^{t}BuOK (1.5 equiv.), and Toluene (1.0 mL). Then the tube is evacuated briefly under high vacuum and charged with argon through using standard Schlenk techniques; this process is repeated three times. The reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with water and extracted with ethyl acetate. The organic layer was washed with saturated NaCl solution, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired product **4e**.

(*R*)-3-(hydroxymethyl)-1,3-dimethylindolin-2-one (6a)



3a (17.4 mg, 0.1 mmol) was dissolved in THF (0.5 mL). NaH_2PO_4 (0.5 M, 0.5 mL) was added. The reaction was cooled to 0 °C and H_2O_2 (30% wt% in H_2O, 0.25 mL) was added. The reaction was stirred at room temperature for 24 h. The reaction was di luted with water then extracted with EtOAc (3×5 mL). The organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The product **6** was isolated from the above residue by flash column chromatography using 40% EtOAc/ petroleum ether or MeOH/EtOAc/petroleum ether (about 2:49:49).

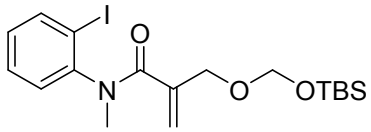
(*S*)-3-(2-hydroxyethyl)-1,3-dimethylindolin-2-one (5a)



3a (17.4 mg, 0.1 mmol) and dibromomethane (18 μL, 0.25 mmol, 2.5 equiv) was dissolved in THF (1.0 mL) and cooled to -78 °C. Then nBuLi (90 μL, 0.22 mmol, 2.2 equiv) was added dropwise. The reaction was warmed to room temperature and stirred for 1 h. The reaction was cooled to 0 °C then 2M NaOH (1 mL) followed by 30% H_2O_2 (1 mL) was added. The reaction was stirred for 2 h then extracted to ethyl acetate (3×5 mL). The residue was dried and purified by flash column chromatography (EtOAc/petroleum ether =1:4 to about 2:3) to afford **5a**.

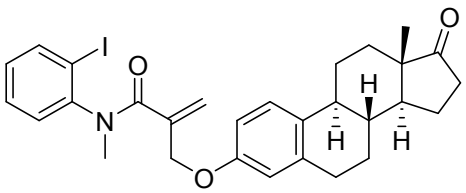
(B) Analytical data

2-((((tert-butyldimethylsilyl)oxy)methoxy)methyl)-N-(2-iodophenyl)-N-methylacrylamide (1e):



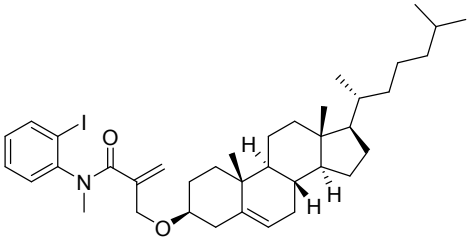
Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 5.23 (s, 1H), 5.14 (s, 1H), 4.82-4.78 (m, 2H), 4.29 (d, *J* = 13.5 Hz, 1H), 4.12 (d, *J* = 13.5 Hz, 1H), 3.23 (s, 3H), 0.87 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 146.7, 140.6, 140.0, 129.8, 129.4, 129.1, 118.9, 98.8, 89.4, 67.7, 36.9, 25.6, 18.0, -5.0, -5.1; HRMS-ESI, m/z calcd. for $C_{18}H_{29}INO_3Si$ $[M+H]^+$ 462.0956; found: 462.0960.

N-(2-iodophenyl)-N-methyl-2-((((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)methyl)acrylamide (1y):



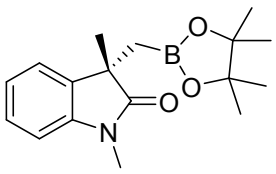
Yellow solid, mp 122.0-123.1 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 7.27-7.24 (m, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.69-6.65 (m, 1H), 6.62 (s, 1H), 5.37 (s, 1H), 5.22 (s, 1H), 4.79 (d, *J* = 13.0 Hz, 1H), 4.56 (d, *J* = 13.5 Hz, 1H), 3.28 (s, 3H), 2.86-2.84 (m, 2H), 2.49 (dd, *J* = 19.5 Hz, *J* = 8.5 Hz, 1H), 2.38-2.36 (m, 1H), 2.25-2.21(m, 1H), 2.17-2.09 (m, 1H), 2.07-2.03 (m, 1H), 2.02-1.97 (m, 1H), 1.96-1.93 (m, 1H), 1.66-1.55 (m, 2H), 1.54-1.50 (m, 1H), 1.49-1.46 (m, 2H), 1.44-1.39 (m, 1H), 0.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 220.8, 169.0, 156.2, 146.5, 140.0, 139.5, 137.6, 132.2, 129.7, 129.4, 129.3, 126.2, 119.6, 114.5, 112.3, 98.9, 68.0, 50.3, 47.9, 43.8, 38.2, 37.0, 35.8, 31.5, 29.5, 26.4, 25.8, 21.5, 13.7; HRMS-ESI, m/z calcd. for $C_{29}H_{33}INO_3$ $[M+H]^+$ 570.1500; found: 570.1503.

2-((((3S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)methyl)-N-(2-iodophenyl)-N-methylacrylamide (1z):

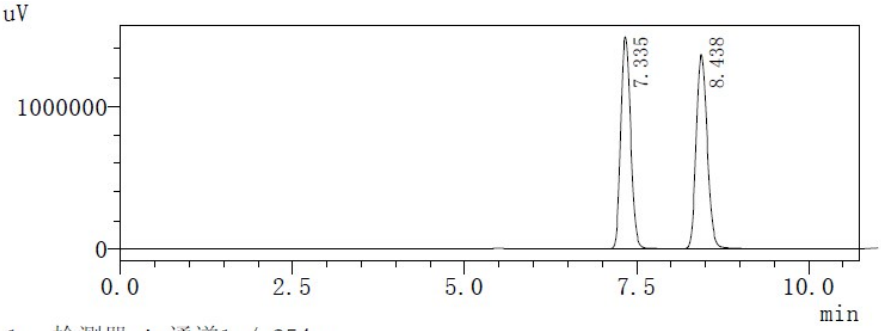


Yellow solid, mp 130.3-131.3 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 7.27-7.24 (m, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 7.26-7.24 (m, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 5.33 (s, 1H), 5.25 (s, 1H), 5.13 (s, 1H), 4.26 (d, *J* = 13.5 Hz, 1H), 4.03 (d, *J* = 13.5 Hz, 1H), 3.24 (s, 3H), 3.14-3.13 (m, 1H), 2.35-2.30 (m, 1H), 2.20-2.15 (m, 1H), 2.01-1.94 (m, 2H), 1.86-1.78 (m, 3H), 1.58-1.41 (m, 8H), 1.37-1.28 (m, 3H), 1.28-1.21 (m, 1H), 1.17-1.04 (m, 6H), 1.04-0.99 (m, 2H), 0.98 (s, 3H), 0.95-0.92 (m, 1H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 2.0 Hz, 3H), 0.85 (d, *J* = 2.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ169.8, 146.7, 141.7, 140.7, 140.6, 140.0, 130.0, 129.4, 129.2, 121.6, 121.6, 118.2, 99.0, 79.1, 68.1, 68.0, 56.7, 56.1, 50.1, 42.3, 39.7, 39.5, 39.1, 37.1, 36.9, 36.8, 36.1, 35.7, 31.9, 31.8, 28.3, 28.3, 28.2, 28.0, 24.2, 23.8, 22.8, 22.5, 21.0, 19.4, 18.7, 11.8; HRMS-ESI, m/z calcd. for $C_{38}H_{57}INO_2$ $[M+H]^+$ 686.3428; found: 686.3430.

(*S*)-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3a):



18.6 mg, 62% yield. Colorless foam; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.25-7.20 (m, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 3.19 (s, 3H), 1.43-1.33 (m, 2H), 1.40 (s, 3H), 1.02 (s, 6H), 0.95 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.7, 143.4, 135.8, 127.5, 122.6, 122.1, 107.6, 83.0, 45.5, 26.2, 25.6, 24.7, 24.3. $[\alpha]^{20}_{D}$ = -1.0 (c = 0.26 in CH_2Cl_2); 92:8 er [Chiralcel AD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λ_{max} 254 nm, t_R = 7.4 min and 8.5 min].

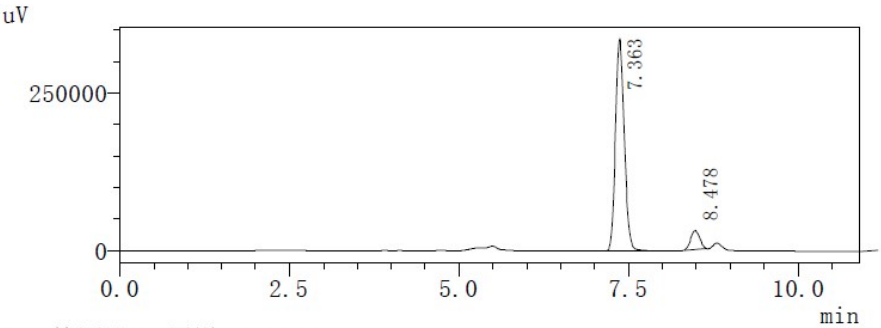


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	7.335	14832682	1481604	49.301	52.146
2	8.438	15253232	1359669	50.699	47.854
总计		30085915	2841273	100.000	100.000



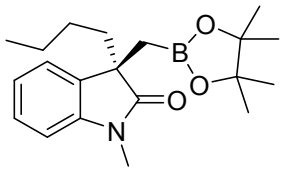
1 检测器 A 通道1 / 254nm

峰表

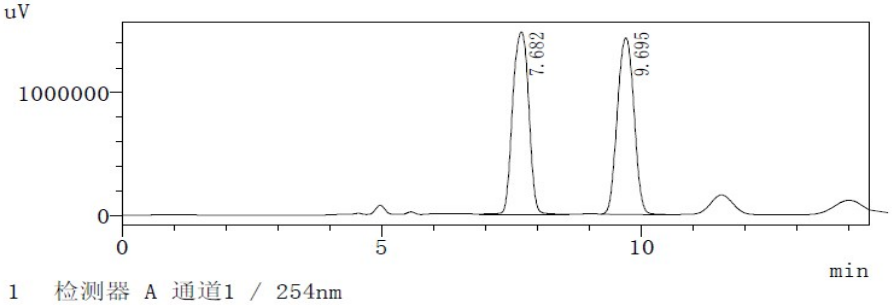
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	7.363	3033129	336380	91.632	91.831
2	8.478	277009	29921	8.368	8.169
总计		3310137	366302	100.000	100.000

(*S*)-3-butyl-1-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3b):



16.8 mg, 49% yield. Colorless foam; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.23-7.18 (m, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 3.19 (s, 3H), 1.94-1.87 (m, 1H), 1.79-1.72 (m, 1H), 1.40 (d, *J* = 15.5 Hz, 1H), 1.35 (d, *J* = 15.5 Hz, 1H), 1.22-1.18 (m, 2H), 1.70-1.14 (m, 2H), 0.97 (s, 6H), 0.89 (s, 6H), 0.75 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.1, 144.2, 134.2, 127.4, 122.8, 122.0, 107.4, 82.9, 49.6, 39.6, 26.4, 26.1, 24.7, 24.3, 22.8, 13.8. HRMS *m/z* (ESI) calcd for $C_{20}H_{31}BNO_3$ $[M+H]^+$: 344.2392, found: 344.2394. $[\alpha]^{20}_D$ = -5.3 (c = 0.3 in CH_2Cl_2); 87:13 er [Chiralcel AD-H column, n-hexane / i-PrOH = 95:5, 0.8 mL/min, λ_{max} 254 nm, t_R = 7.8 min and 9.8 min].

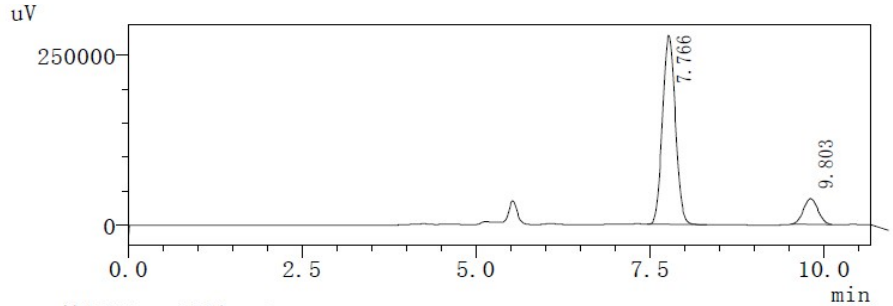


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	7.682	31924584	1483864	49.932	50.792
2	9.695	32011504	1437578	50.068	49.208
总计		63936089	2921442	100.000	100.000



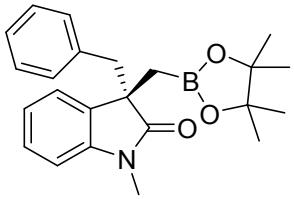
1 检测器 A 通道1 / 254nm

峰表

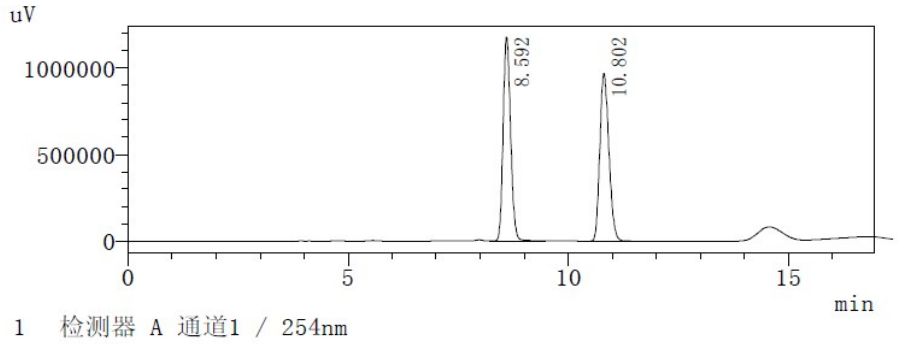
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	7.766	3594274	277736	86.704	87.956
2	9.803	551192	38031	13.296	12.044
总计		4145466	315767	100.000	100.000

(*S*)-3-benzyl-1-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3c):



18.1 mg, 48% yield. Colorless foam. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.16-7.12 (m, 1H), 7.12-7.09 (m, 1H), 7.06-7.02 (m, 3H), 6.98-6.94 (m, 1H), 6.87-6.84 (m, 2H), 6.57 (d, J = 7.5 Hz, 1H), 3.12-3.05 (m, 2H), 2.99 (s, 3H), 1.53 (d, J = 15.0 Hz, 1H), 1.45 (d, J = 15.5 Hz, 1H), 1.00 (s, 6H), 0.90 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 180.2, 143.9, 136.3, 133.0, 130.1, 127.5, 127.3, 126.3, 123.7, 121.6, 107.4, 83.0, 51.0, 45,3, 25.9, 24.7, 24.2. $[\alpha]^{20}_{D}$ = -3.3 (c = 0.2 in CH_2Cl_2); 89:11 er [Chiralcel AD-H column, n-hexane / i-PrOH = 95:5, 0.8 mL/min, λ_{max} 254 nm, t_R = 8.5 min and 10.7 min].

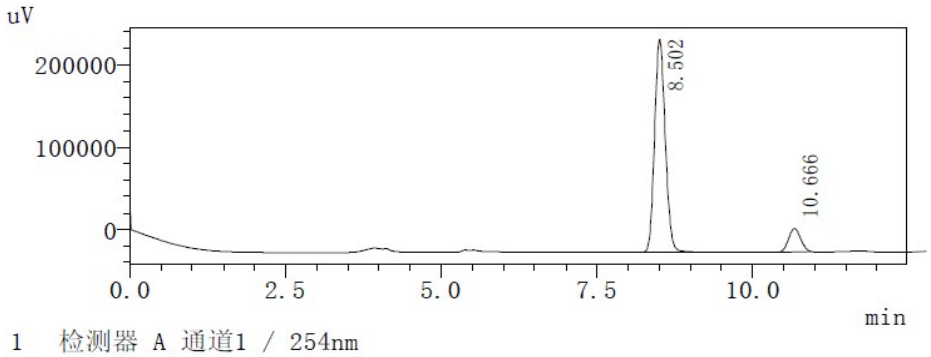


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	8.592	13880160	1173206	49.929	54.819
2	10.802	13919653	966941	50.071	45.181
总计		27799813	2140148	100.000	100.000



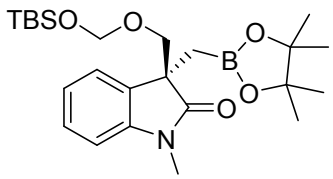
1 检测器 A 通道1 / 254nm

峰表

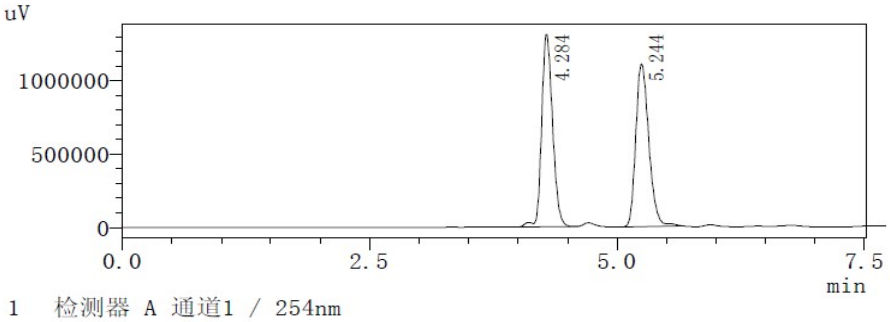
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	8.502	3071197	257993	88.973	90.160
2	10.666	380644	28157	11.027	9.840
总计		3451841	286150	100.000	100.000

(*S*)-3-((((tert-butyldimethylsilyl)oxy)methoxy)methyl)-1-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3d):



15.7 mg, 34% yield. Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.26 (m, 1H), 7.24-7.20 (m, 1H), 7.01-6.97 (m, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 4.68 (d, *J* = 5.5 Hz, 1H), 4.67 (d, *J* = 5.5 Hz, 1H), 3.89 (d, *J* = 9.0 Hz, 1H), 3.75 (d, *J* = 9.0 Hz, 1H), 3.19 (s, 3H), 1.38 (d, *J* = 15.5 Hz, 1H), 1.32 (d, *J* = 15.5 Hz, 1H), 1.00 (s, 6H), 0.91(s, 6H), 0.83 (s, 9H), -0.04 (s, 3H), -0.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.2, 144.5, 132.6, 127.7, 123.3, 122.0, 107.5, 90.3, 83.1, 73.0, 50.2, 26.2, 25.7, 25.0, 24.7, 24.3, 18.0, -5.1, -5.2; HRMS *m/z* (ESI) calcd for $C_{24}H_{41}BNO_5Si$ $[M+H]^+$: 462.2842, found: 462.2846. $[\alpha]^{20}_D$ = -0.6 (c = 0.25 in CH_2Cl_2); 88:12 er [Chiralcel AD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λ_{max} 254 nm, t_R = 4.3 min and 5.2 min].

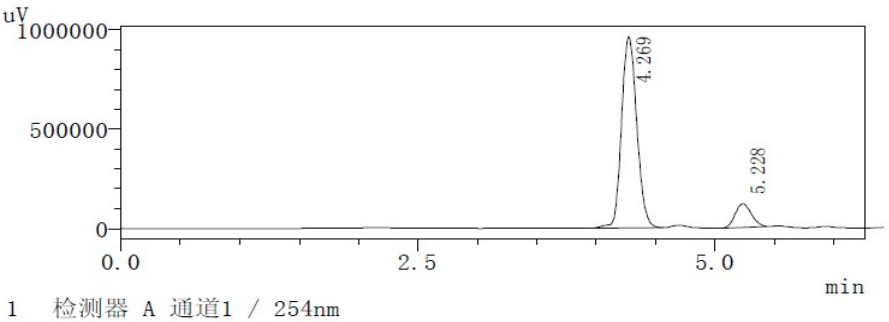


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	4.284	10108776	1310883	49.833	54.145
2	5.244	10176521	1110185	50.167	45.855
总计		20285298	2421068	100.000	100.000



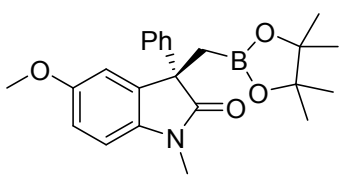
1 检测器 A 通道1 / 254nm

峰表

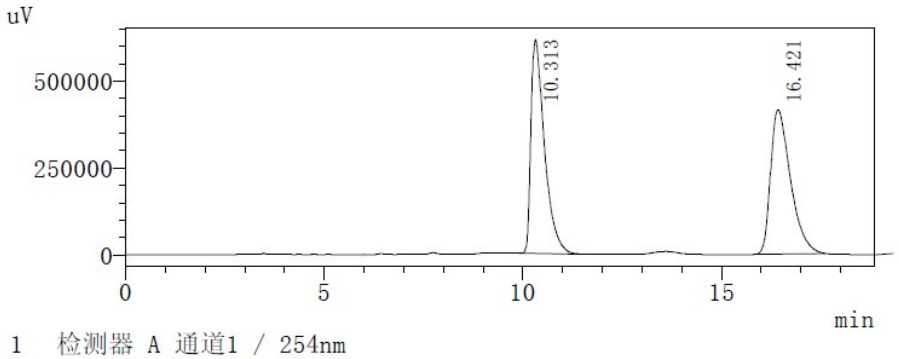
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	4.269	8590452	962237	88.499	89.031
2	5.228	1116436	118551	11.501	10.969
总计		9706889	1080788	100.000	100.000

(*S*)-5-methoxy-1-methyl-3-phenyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3e):



24.7 mg, 63% yield. Colorless foam; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.32-7.30 (m, 2H), 7.27-7.23 (m, 2H), 7.21-7.17 (m, 1H), 6.98 (d, *J* = 2.5 Hz, 1H), 6.85-6.82 (m, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 3.77 (s, 3H), 3.17 (s, 3H), 1.91 (d, *J* = 15 Hz, 1H), 1.87 (d, *J* = 15.5 Hz, 1H), 0.99 (s, 6H), 0.89 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 179.3, 155.9, 141.7, 138.0, 135.5, 128.3, 126.9, 126.6, 112.8, 120.0, 108.2, 83.0, 77.3, 55.8, 53.5, 26.6, 25.0, 24.6, 24.2. $[\alpha]^{20}_{D}$ = -6.0 (c = 0.26 in CH_2Cl_2); 87:13 er [Chiralcel OD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λ_{max} 254 nm, t_R = 10.5 min and 16.6 min].

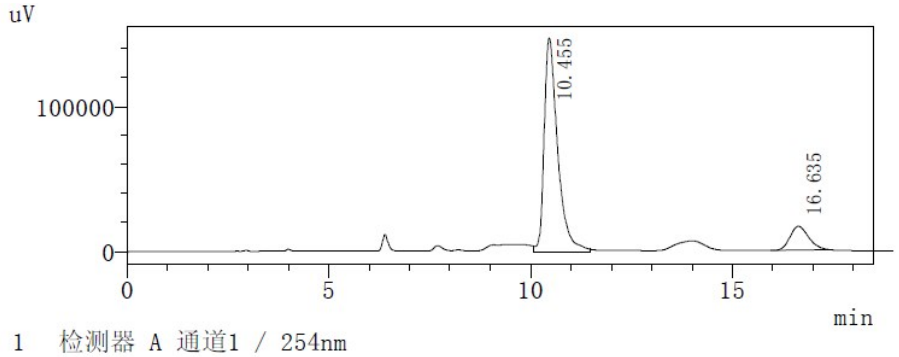


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	10.313	14653091	616216	50.188	59.712
2	16.421	14543166	415757	49.812	40.288
总计		29196257	1031973	100.000	100.000



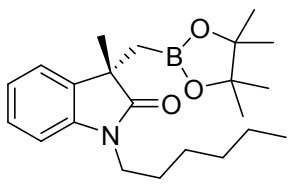
1 检测器 A 通道1 / 254nm

峰表

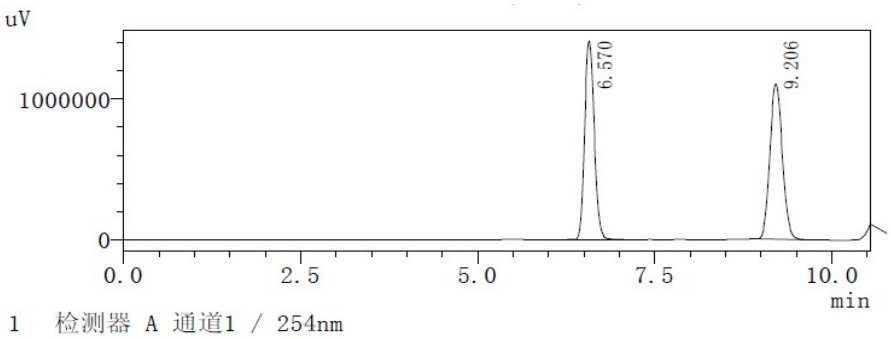
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	10.455	3425802	147507	86.622	89.974
2	16.635	529101	16437	13.378	10.026
总计		3954903	163944	100.000	100.000

(*S*)-1-hexyl-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3f):



25.9 mg, 70% yield. Colorless foam; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.24 (d, *J* = 7.5, 1H), 7.20-7.17 (m, 1H), 6.97 (t, *J* = 7.5, 1H), 6.79 (d, *J* = 8.0, 1H), 3.72-3.60 (m, 2H), 1.71-1.63 (m, 2H), 1.41 (d, *J* = 15.5 Hz, 1H), 1.37 (s, 3H), 1.34 (d, *J* = 16.0 Hz, 1H), 1.33-1.29 (m, 4H), 1.23-1.18 (m, 2H), 1.01 (s, 6H), 0.91 (s, 6H), 0.87 (t, *J* =6.5 Hz, 3H).^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.4, 142.8, 136.0, 127.3, 122.7, 121.8, 107.9, 83.4, 83.0, 77.3, 76.7, 45.3, 40.0, 31.5, 27.2, 26.6, 26.1, 25.0, 24.7, 24.2, 22.5, 14.0. HRMS *m/z* (ESI) calcd for $C_{22}H_{35}BNO_3$ $[M+H]^+$: 372.2705, found: 372.2703. $[\alpha]^{20}_D$ = -2.2 (c = 0.2 in CH_2Cl_2); 91:9 er [Chiralcel AD-H column, n-hexane / i-PrOH = 95:5, 0.8 mL/min, λ_{max} 254 nm, t_R = 6.6 min and 9.2 min].

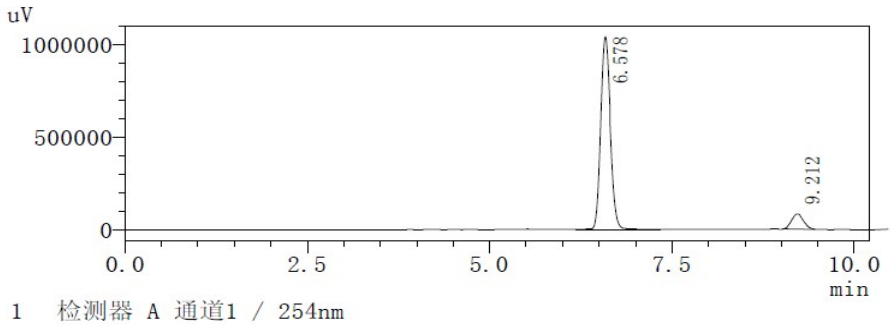


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	6.570	13360336	1408519	49.762	56.095
2	9.206	13488070	1102417	50.238	43.905
总计		26848406	2510937	100.000	100.000



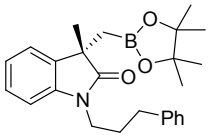
1 检测器 A 通道1 / 254nm

峰表

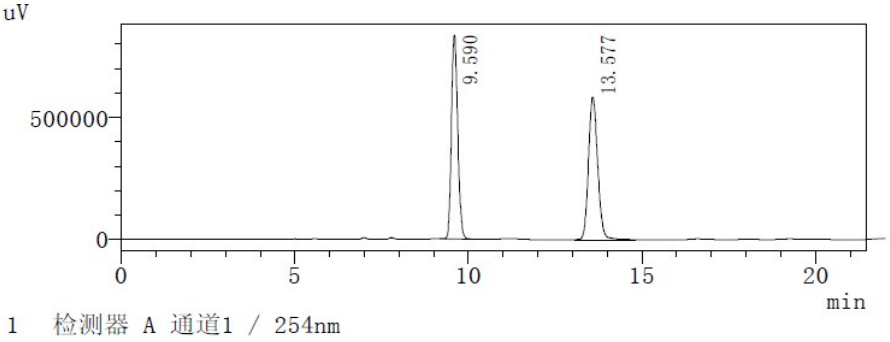
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	6.578	9527459	1040914	91.009	92.648
2	9.212	941241	82603	8.991	7.352
总计		10468699	1123517	100.000	100.000

(*S*)-3-methyl-1-(3-phenylpropyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3g):



21.8 mg, 54% yield. White foam. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.30-7.27 (m, 2H), 7.24-7.22 (m, 3H), 7.21-7.16 (m, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.5 Hz, 1H), 3.79-3.66 (m, 2H), 2.78-2.67 (m, 2H), 2.09-1.95 (m, 2H), 1.44 (d, *J* = 15.5 Hz, 1H), 1.39 (s, 3H), 1.36 (d, *J* = 15.5 Hz, 1H), 0.99 (s, 6H), 0.90 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.5, 142.6, 141.3, 136.0, 128.4, 127.4, 126.0, 122.7, 121.9, 107.8, 83.0, 45.3, 39.5, 33.2, 28.8, 26.2, 24.7, 24.2. HRMS *m/z* (ESI) calcd for $C_{25}H_{33}BNO_3$ $[M+H]^+$: 406.2548, found: 406.2550. $[\alpha]^{20}_{D}$ = +12.6 (c = 0.2 in CH_2Cl_2); 91:9 er [Chiralcel AD-H column, n-hexane / i-PrOH = 95:5, 0.8 mL/min, λ_{max} 254 nm, t_R = 9.6min and 13.6 min].

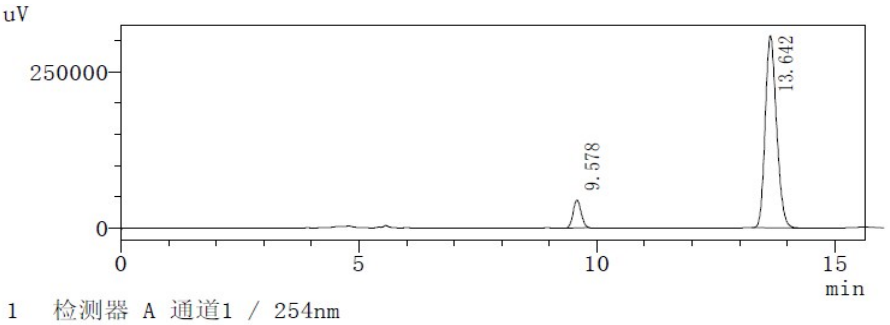


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	9.590	10525136	836941	49.550	58.807
2	13.577	10716371	586260	50.450	41.193
总计		21241506	1423201	100.000	100.000



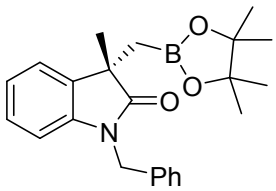
1 检测器 A 通道1 / 254nm

峰表

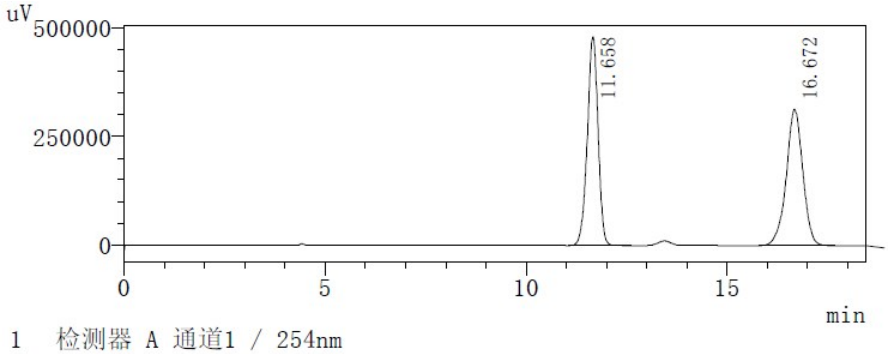
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	9.578	524546	44878	9.326	12.734
2	13.642	5100157	307557	90.674	87.266
总计		5624703	352435	100.000	100.000

(*S*)-1-benzyl-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3h):



28.2 mg, 76% yield. Colorless foam; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.36-7.34 (m, 2H), 7.32-7.29 (m, 2H), 7.28 - 7.26 (m, 1H), 7.25-7.21 (m, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 4.96 (d, *J* = 16.0 Hz, 1H), 4.85 (d, *J* = 15.5 Hz, 1H), 1.50 (d, *J* = 15.5 Hz, 1H), 1.47 (s, 3H), 1.43 (d, *J* = 15.5 Hz, 1H), 1.05 (s, 6H), 0.92 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.8, 142.4, 136.3, 135.8, 128.6, 127.4, 122.6, 122.2, 108.8, 83.1, 45.5, 43.9, 26.4, 24.7, 24.3. $[\alpha]^{20}_{D}$ = -1.2 (c = 0.2 in CH_2Cl_2); 91:9 er [Chiralcel AD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λ_{max} 254 nm, t_R = 11.7 min and 16.8 min].

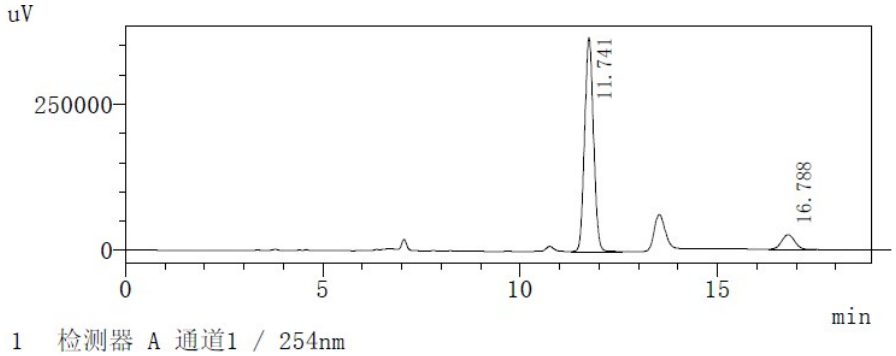


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	11.658	8888563	479356	49.825	60.471
2	16.672	8951106	313342	50.175	39.529
总计		17839669	792698	100.000	100.000



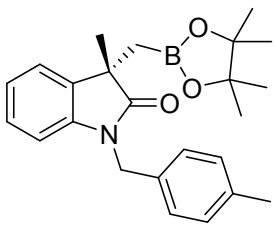
1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

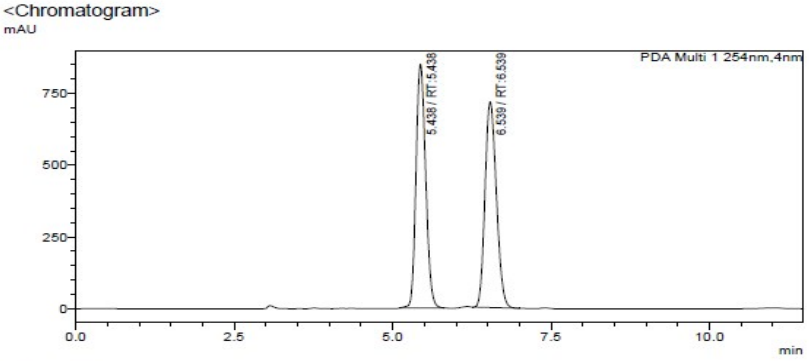
峰#	RT(min)	Area	Height	Area%	Height%
1	11.741	5743393	366550	90.866	93.536
2	16.788	577319	25331	9.134	6.464
总计		6320712	391881	100.000	100.000

(*S*)-3-methyl-1-(4-methylbenzyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3i):



21.1 mg, 54% yield. Light yellow foam; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.27-7.26 (m, 1H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.12-7.07 (m, 3H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.67 (t, *J* = 8.0 Hz, 1H), 4.93 (d, *J* = 15.5 Hz, 1H), 4.79 (d, *J* = 16.0 Hz, 1H), 2.31 (s, 3H), 1.48 (d, *J* = 15.5 Hz, 1H), 1.46 (s, 3H), 1.42 (d, *J* = 15.5 Hz, 1H), 1.06 (s, 6H), 0.93 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.7, 142.5, 137.0, 135.9, 133.3, 129.3, 127.4, 122.6, 122.1, 108.8, 83.1, 45.5, 43.7, 26.3, 24.7, 24.3, 21.1. HRMS *m/z* (ESI) calcd for $C_{24}H_{31}BNO_3$ $[M+H]^+$: 392.2392, found: 392.2393. $[\alpha]^{20}_D$ = -5.6 (c = 0.25 in CH_2Cl_2); 89:11 er [Chiralcel OD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λ_{max} 254 nm, t_R = 5.4 min and 6.5 min].

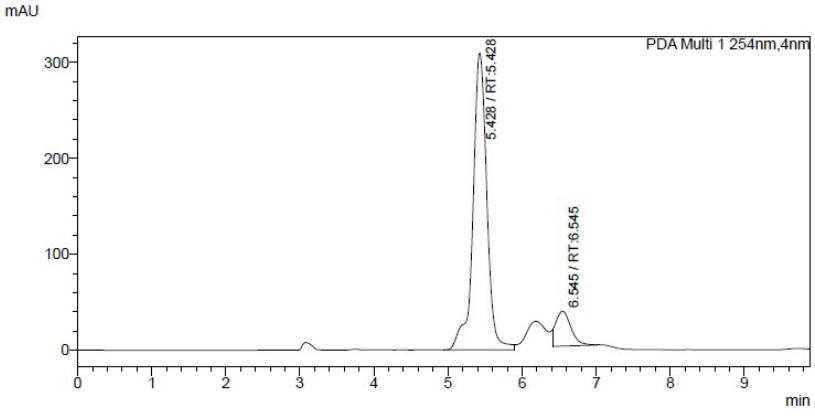
<Chromatogram>



<Column Performance>

PDA

Ret. Time	Area	Height	Area%
5.438	9006076	850197	50.184
6.539	8939856	717427	49.816
	17945932	1567625	100.000

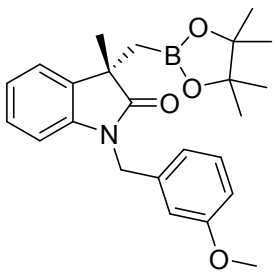


<Column Performance>

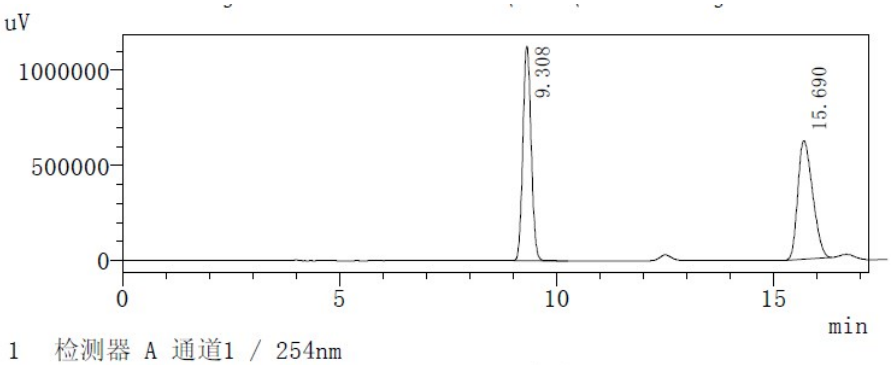
PDA

Ret. Time	Area	Height	Area%
5.428	4043240	309711	88.682
6.545	516040	36322	11.318
	4559280	346033	100.000

(*S*)-1-(3-methoxybenzyl)-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3j):



30.9 mg, 76% yield. Colorless solid mp; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.28-7.26 (m, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.88 (s, 1H), 6.79- 6.77 (m, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 4.97 (d, *J* = 15.5 Hz, 1H), 4.75 (d, *J* = 15.5 Hz, 1H), 3.77 (s, 3H), 1.47 (d, *J* = 15.5 Hz, 1H), 1.46 (s, 3H), 1.41 (d, *J* = 15.0 Hz, 1H), 1.05 (s, 6H), 0.93 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.7, 159.8, 142.4, 137.9, 135.8, 129.6, 127.4, 122.6, 122.1, 119.6, 122.6, 113.1, 112.7, 108.7, 83.1, 55.1, 45.5, 43.8, 26.2, 24.7, 24.2. HRMS *m/z* (ESI) calcd for $C_{24}H_{31}BNO_4$ $[M+H]^+$: 408.2341, found: 408.2343. $[\alpha]^{20}_D$ =+2.0 (c = 0.3 in CH_2Cl_2); 92:8 er [Chiralcel AD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λ_{max} 254 nm, t_R = 9.4 min and 16.1 min].

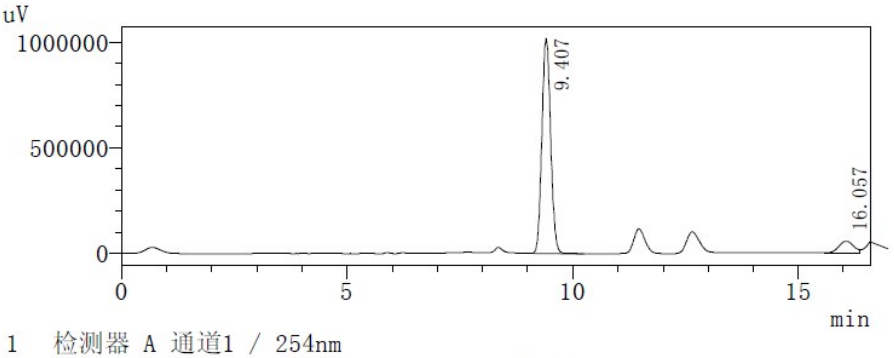


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	9.308	14995836	1124946	50.367	64.395
2	15.690	14777403	622004	49.633	35.605
总计		29773239	1746951	100.000	100.000



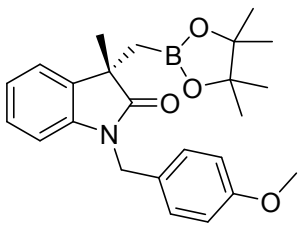
1 检测器 A 通道1 / 254nm

峰表

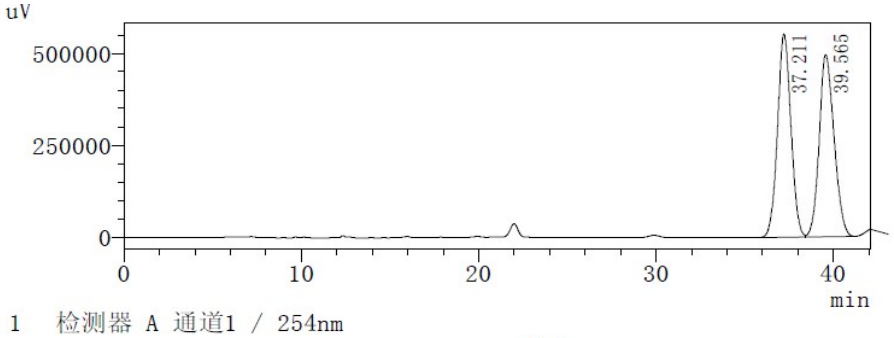
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	9.407	13718406	1017645	91.597	94.753
2	16.057	1258549	56348	8.403	5.247
总计		14976955	1073993	100.000	100.000

(*S*)-1-(4-methoxybenzyl)-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3k):



23.6 mg, 58% yield. Colorless foam; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.29-7.26 (m, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 7.5 Hz, 1H), 4.89 (d, *J* = 15.5 Hz, 1H), 4.78 (d, *J* = 15.5 Hz, 1H), 3.77 (s, 3H), 1.48 (d, *J* = 15.5 Hz, 1H), 1.45 (s, 3H), 1.41 (d, *J* = 15.5 Hz, 1H), 1.05 (s, 6H), 0.92 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.7, 158.9, 142.5, 135.9, 128.7, 128.4, 127.3, 122.6, 122.1, 114.0, 108.8, 83.1, 55.2, 45.4, 43.4, 26.3, 24.7, 24.3. HRMS *m/z* (ESI) calcd for $C_{24}H_{31}BNO_4$ $[M+H]^+$: 408.2341, found: 408.2341. $[\alpha]^{20}_D$ = -2.8 (c = 0.2 in CH_2Cl_2); 92:8 er [Chiralcel AD-H column, n-hexane / i-PrOH = 97:3, 0.7 mL/min, λ_{max} 254 nm, t_R = 37.4 min and 39.9 min].

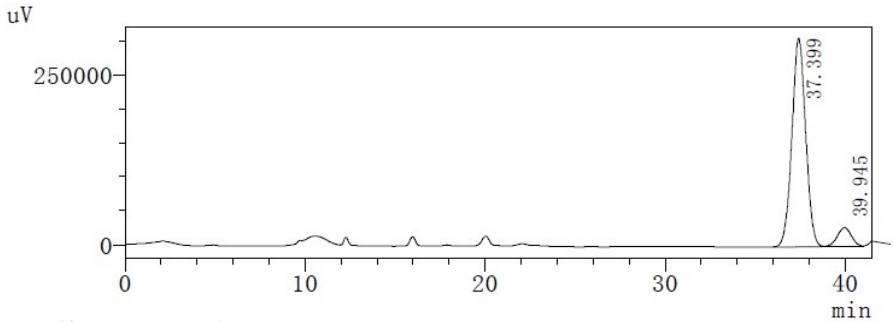


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	37.211	28983275	551777	50.108	52.738
2	39.565	28858448	494481	49.892	47.262
总计		57841722	1046258	100.000	100.000



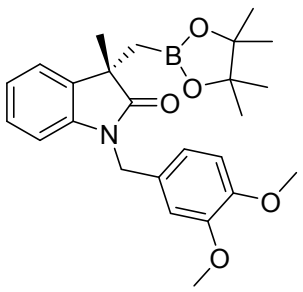
1 检测器 A 通道1 / 254nm

峰表

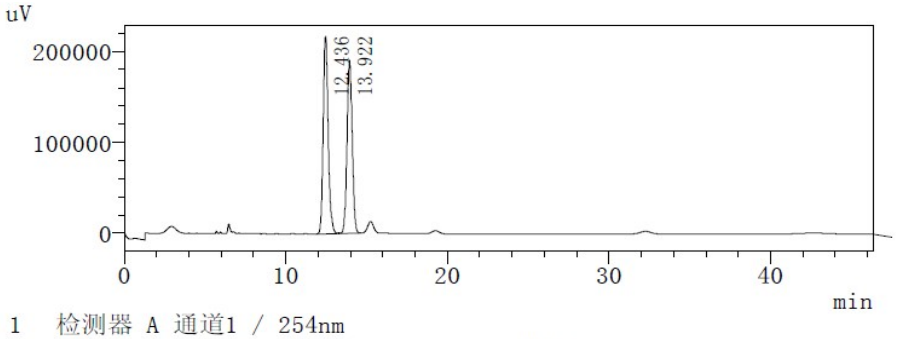
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	37.399	16310868	307354	91.938	91.873
2	39.945	1430373	27188	8.062	8.127
总计		17741242	334542	100.000	100.000

(*S*)-1-(3,4-dimethoxybenzyl)-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3l):



29.7 mg, 68% yield. Light yellow foam; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.28-7.26 (m, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.91-6.88 (m, 2H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.72 (d, *J* = 7.5 Hz, 1H), 4.93 (d, *J* = 15.0 Hz, 1H), 4.71 (d, *J* = 15.5 Hz, 1H), 3.83 (s, 3H), 1.46 (s, 3H), 1.44 (d, *J* = 15.5 Hz, 1H), 1.39 (d, *J* = 15.0 Hz, 1H), 1.04 (s, 6H), 0.92 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.7, 149.1, 148.3, 142.3, 135.8, 128.9, 127.3, 122.7, 122.1, 119.7, 111.0, 110.8, 108.7, 83.1, 55.9, 55.8, 55.8, 45.5, 43.6, 25.9, 24.7, 24.2. HRMS *m/z* (ESI) calcd for $C_{25}H_{33}BNO_5$ $[M+H]^+$: 438.2446, found: 438.2442. $[\alpha]^{20}_D$ = -3.2 (c = 0.3 in CH_2Cl_2); 93:7 er [Chiralcel AD-H column, n-hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, t_R = 12.4 min and 14.0 min].

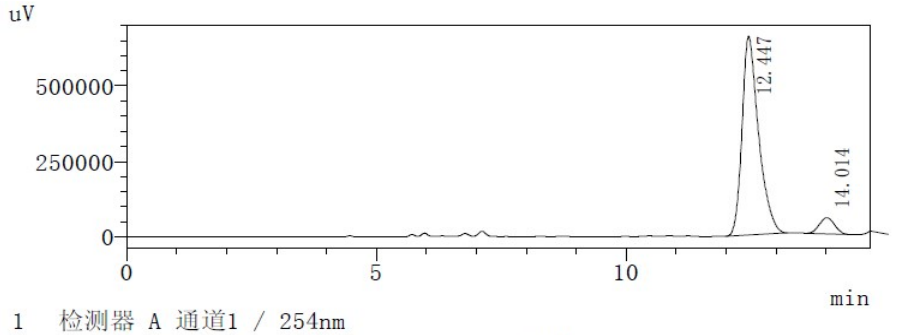


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	12.436	4611335	217041	51.960	53.243
2	13.922	4263370	190605	48.040	46.757
总计		8874705	407646	100.000	100.000



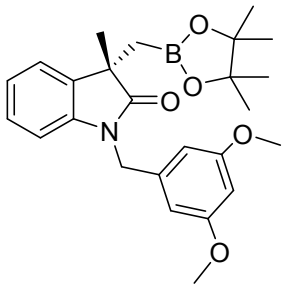
1 检测器 A 通道1 / 254nm

峰表

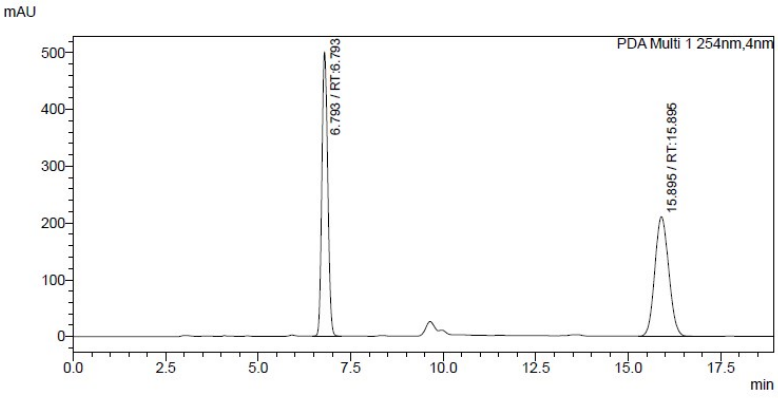
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	12.447	15143781	658567	93.064	92.509
2	14.014	1128582	53326	6.936	7.491
总计		16272362	711893	100.000	100.000

(*S*)-1-(3,5-dimethoxybenzyl)-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3m):

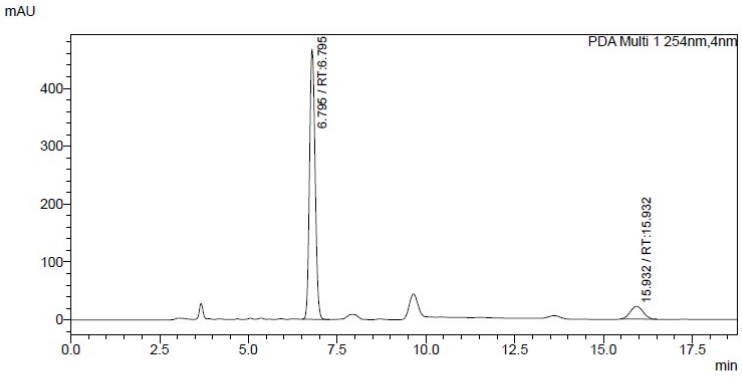


15.7 mg, 36% yield. White foam; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.27 (d, *J* = 8.0 Hz, 1H), 7.11-7.08 (m, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6. 47 (s, 1H), 6.46 (s, 1H), 6.33-6.32 (m, 1H), 4.98 (d, *J* = 15.5 Hz, 1H), 4.64 (d, *J* = 15.5 Hz, 1H), 3.73 (s, 6H), 1.46 (s, 3H), 1.44 (d, *J* = 15.5 Hz, 1H), 1.39 (d, *J* = 15.5 Hz, 1H), 1.05 (s, 6H), 0.94 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.7, 160.9, 142.3, 138.7, 127.4, 122.6, 122.1, 108.7, 105.4, 99.0, 83.0, 77.3, 76.7, 55.2, 45.4, 43.8, 25.9, 24.7, 24.2. HRMS *m/z* (ESI) calcd for $C_{25}H_{33}BNO_5$ $[M+H]^+$: 438.2446, found: 438.2444. $[\alpha]^{20}_D$ = -1.7 (c = 0.2 in CH_2Cl_2); 90:10 er [Chiralcel AD-H column, n-hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, t_R = 6.8 min and 15.9 min].



<Column Performance>
PDA

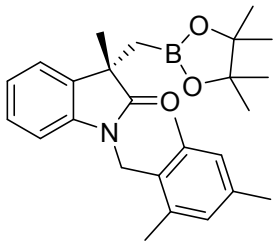
Ret. Time	Area	Height	Area%
6.793	5499380	500579	49.997
15.895	5499961	210603	50.003
	10999341	711182	100.000



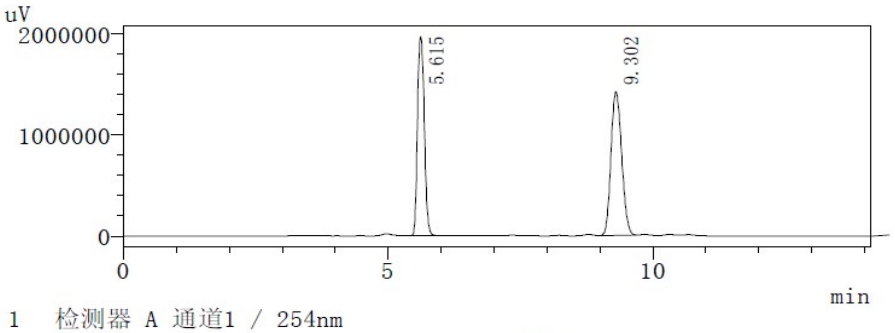
<Column Performance>
PDA

Ret. Time	Area	Height	Area%
6.795	5113024	466614	90.199
15.932	555577	22135	9.801
	5668601	488750	100.000

(*S*)-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-(2,4,6-trimethylbenzyl)indolin-2-one (3n):



33.1 mg, 79% yield. White solid; mp ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.24 (d, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.85 (s, 2H), 6.35 (d, *J* = 8.0 Hz, 1H), 5.18 (d, *J* = 15.5 Hz, 1H), 4.72 (d, *J* = 15.5 Hz, 1H), 2.34 (s, 6H), 2.26 (s, 3H), 1.44 (s, 3H), 3.94 (d, *J* = 7.0 Hz, 1H), 3.52-3.45 (m, 1H), 3.40-3.36 (m, 1H), 3.16 (t, *J* = 11.0 Hz, 1H), 2.71 (t, *J* = 8.0 Hz, 1H), 2.38 (s, 3H), 1.40 (d, *J* =4.0 Hz, 2H), 1.08 (s, 6H), 1.00 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.3, 142.8, 137.3, 137.1, 136.0, 129.6, 128.8, 127.4, 122.6, 121.8, 128.1, 109.1, 83.1, 45.1, 39.8, 25.6, 25.0, 24,8 24.5, 20.9, 20.4. HRMS m/z (ESI) calcd for $C_{25}H_{35}BNO_3$ [M+H]+: 420.2705, found: 420.2705. $[\alpha]^{20}_D$ = -45.2 (c = 0.5 in CH_2Cl_2); 91:9 er [Chiralcel AD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λmax 254 nm, t_R = 5.6 min and 9.3 min].

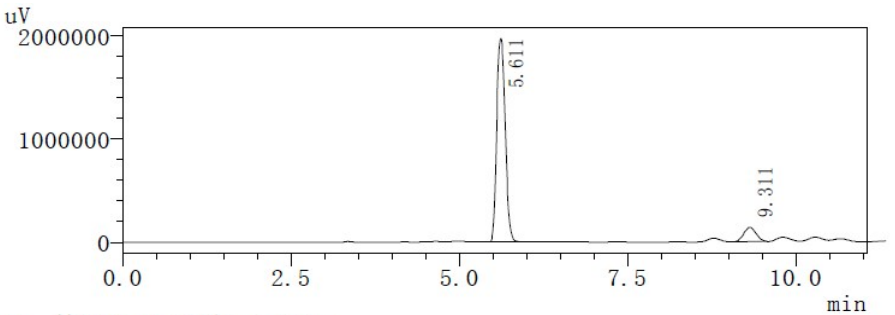


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	5.615	17614180	1969965	46.766	58.016
2	9.302	20050531	1425609	53.234	41.984
总计		37664711	3395574	100.000	100.000



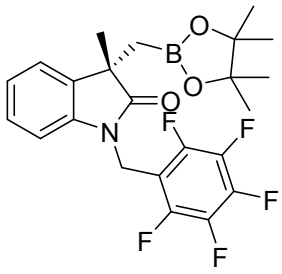
1 检测器 A 通道1 / 254nm

峰表

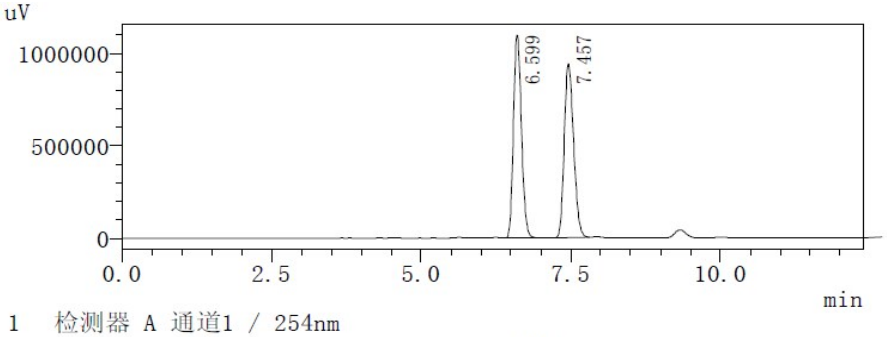
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	5.611	17397289	1972686	90.971	93.493
2	9.311	1726761	137290	9.029	6.507
总计		19124050	2109976	100.000	100.000

(*S*)-3-methyl-1-((perfluorophenyl)methyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3o):



28.0 mg, 60% yield. Light yellow foam; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.28 (d, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 5.15 (d, *J* = 15.5 Hz, 1H), 4.82 (d, *J* = 15.5 Hz, 1H), 1.43 (d, *J* = 15.0 Hz, 1H), 1.42 (s, 3H), 1.38 (d, *J* = 16.0 Hz, 1H), 1.04 (s, 6H), 0.93 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.0, 141.4, 135.7, 127.6, 123.0, 122.6, 107.5, 83.1, 45.3, 32.1, 25.8, 24.7, 24.3. ^{19}F NMR ($CDCl_3$, 470 MHz): δ (ppm) -141.15, -141.17, -141.20, -141.22, -153.93, -153.98, -161.35, -161.38, -161.40. HRMS m/z (ESI) calcd for $C_{23}H_{24}BF_5NO_3$ $[M+H]^+$: 468.1764, found: 468.1767. $[\alpha]^{20}_D$ = -5.1 (c = 0.22 in CH_2Cl_2); 88:12 er [Chiralcel AD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λmax 254 nm, t_R = 6.6 min and 7.5 min].

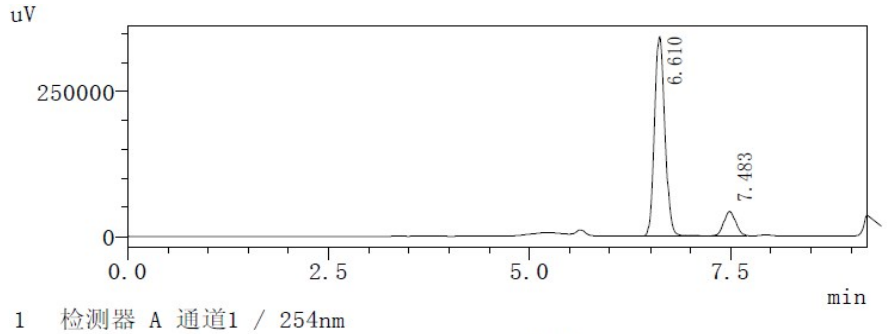


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	6.599	10223079	1097477	50.051	53.817
2	7.457	10202291	941800	49.949	46.183
总计		20425370	2039276	100.000	100.000



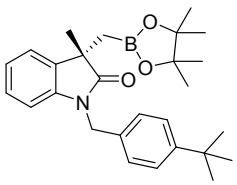
1 检测器 A 通道1 / 254nm

峰表

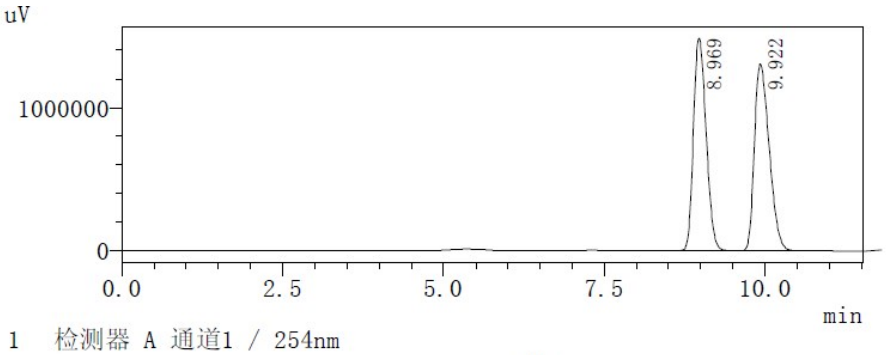
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	6.610	3117962	344091	88.085	89.247
2	7.483	421771	41458	11.915	10.753
总计		3539733	385549	100.000	100.000

(*S*)-1-(4-(tert-butyl)benzyl)-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3p):



27.7 mg, 64% yield. Colorless foam; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.33-7.26 (m, 5H), 7.15-7.09 (m, 1H), 6.99-6.95 (m, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.93 (d, *J* = 15.5 Hz, 1H), 4.79 (d, *J* = 15.5 Hz, 1H), 1.48 (d, *J* = 15.5 Hz, 1H), 1.46 (s, 3H), 1.42 (d, *J* = 15.5 Hz, 1H), 1.28 (s, 6H), 1.26 (s, 3H), 1.04 (s, 6H), 0.91 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.7, 150.2, 142.6, 135.8, 133.3, 127.3, 127.2, 125.5, 122.6, 122.0, 108.7, 83.0, 45.4, 43.5, 34.4, 31.3, 26.2, 25.0, 24.7, 24.3. HRMS *m/z* (ESI) calcd for $C_{27}H_{37}BNO_3$ $[M+H]^+$: 434.2861, found: 434.2865. $[\alpha]^{20}_D$ = -2.9 (c = 0.2 in CH_2Cl_2); 92:8 er [Chiralcel AD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λ_{max} 254 nm, t_R = 9.0 min and 9.9 min].

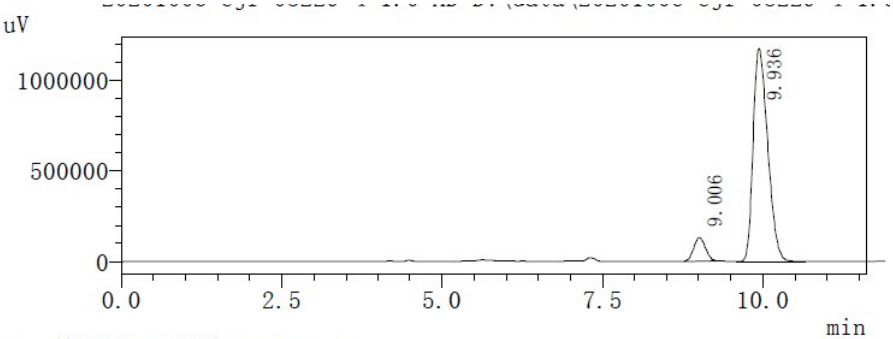


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	8.969	20274603	1481307	49.240	53.176
2	9.922	20900120	1304379	50.760	46.824
总计		41174723	2785685	100.000	100.000



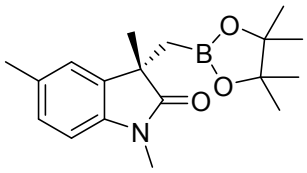
1 检测器 A 通道1 / 254nm

峰表

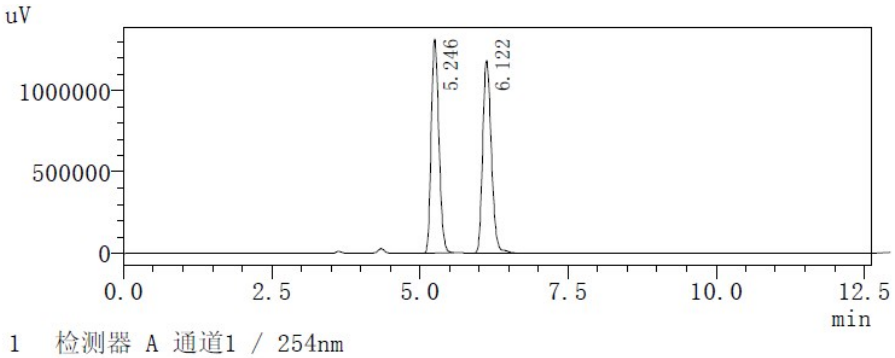
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	9.006	1620728	128780	8.024	9.886
2	9.936	18578358	1173894	91.976	90.114
总计		20199087	1302674	100.000	100.000

(*S*)-1,3,5-trimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3q):



20.7 mg, 66% yield. Yellow foam. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.09 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 3.17 (s, 3H), 2.32 (s, 3H), 1.40 (s, 3H), 1.38 (d, *J* = 15.5 Hz, 1H), 1.32 (d, *J* = 15.5 Hz, 1H), 1.03 (s, 6H), 0.97 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.6, 150.0, 135.9, 131.5, 127.6, 123.6, 107.4, 83.0, 45.5, 26.2, 25.5, 24.7, 24.4, 21.1. $[\alpha]^{20}_{D}$ =+8.0 (c = 0.2 in CH_2Cl_2); 92:8 er [Chiralcel AD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λ_{max} 254 nm, t_R =5.3min and 6.1min].

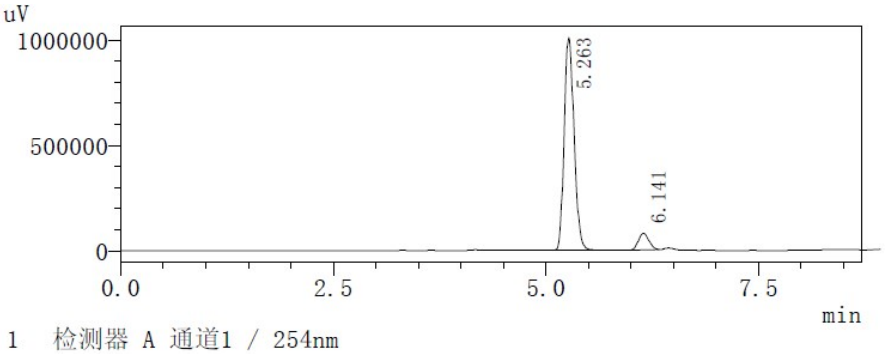


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	5.246	11669357	1311037	49.253	52.614
2	6.122	12023187	1180754	50.747	47.386
总计		23692543	2491791	100.000	100.000



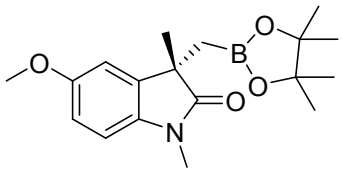
1 检测器 A 通道1 / 254nm

峰表

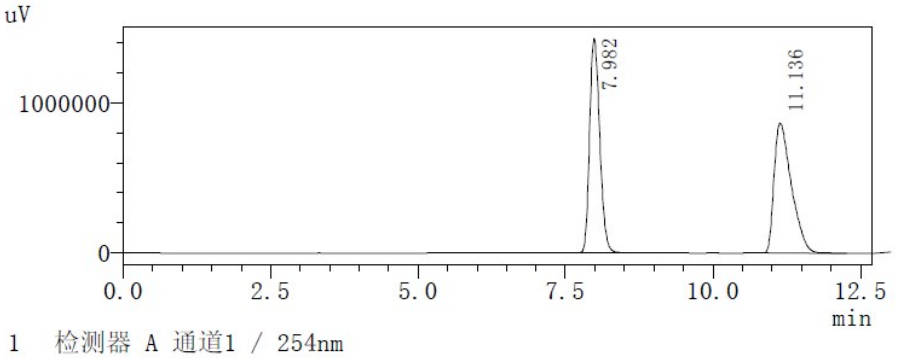
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	5.263	8196980	1011797	92.207	92.725
2	6.141	692770	79378	7.793	7.275
总计		8889749	1091175	100.000	100.000

(*S*)-5-methoxy-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3r):



21.2 mg, 64% yield. Colorless foam; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 6.93 (d, J = 2.5 Hz, 1H), 6.75 (d, J = 8.0 Hz, J = 2.5 Hz, 1H), 6.68 (d, J = 8.5 Hz, 1H), 3.78 (s, 3H), 3.16 (s, 3H), 1.39 (s, 3H), 1.36 (d, J = 15.5 Hz, 1H), 1.32 (d, J = 15.5 Hz, 1H), 1.06 (s, 6H), 0.99 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.4, 155.9, 137.2, 136.9, 111.9, 110.3, 107.9, 83.0, 55.9, 45.9, 26.3, 25.4, 24.8, 24.4. $[\alpha]^{20}_{D}$ = 11.1 (c = 0.3 in CH_2Cl_2); 90:10 er [Chiralcel AD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λ_{max} 254 nm, t_R = 7.9 min and 11.2 min].

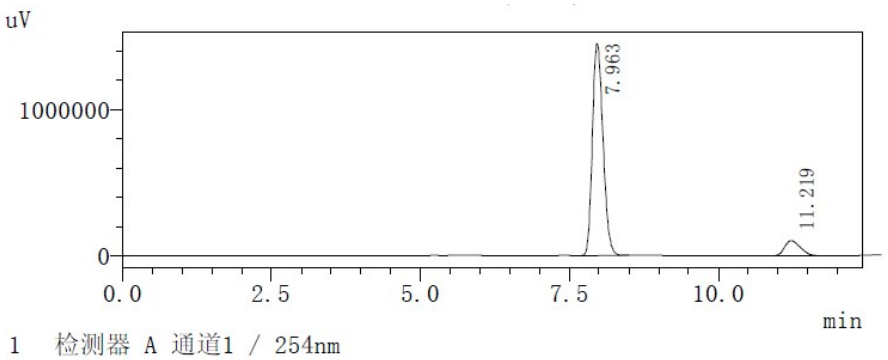


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	7.982	17031841	1426045	49.094	62.250
2	11.136	17660428	864801	50.906	37.750
总计		34692269	2290845	100.000	100.000



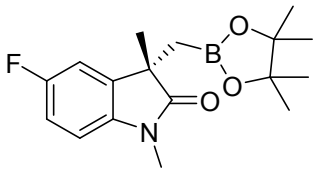
1 检测器 A 通道1 / 254nm

峰表

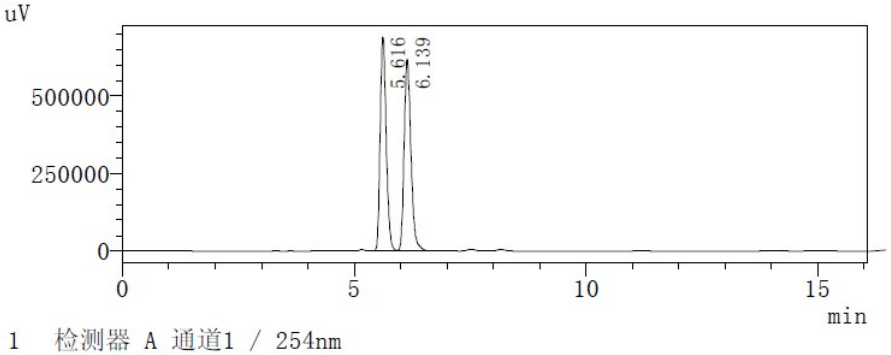
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	7.963	17970106	1447966	90.144	93.281
2	11.219	1964827	104305	9.856	6.719
总计		19934933	1552271	100.000	100.000

(*S*)-5-fluoro-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3s):



19.4 mg, 61% yield. Colorless foam. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.05 (dd, *J* = 8.5 Hz, *J* = 2.5 Hz, 1H), 6.94-6.90 (m, 1H), 6.70 (dd, *J* = 8.5 Hz, *J* = 4.0 Hz, 1H), 3.18 (s, 3H), 1.40 (s, 3H), 1.38 (d, *J* = 15.5 Hz, 1H), 1.33 (d, *J* = 15.5 Hz, 1H), 1.07 (s, 6H), 1.00 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.3, 160.2, 139.3, 137.5, 137.5, 113.5, 113.3, 111.1, 110.9, 107.9, 107.9, 83.1, 45.9, 26.3, 25.3, 24.9, 24.7, 24.7, 24.4. ^{19}F NMR ($CDCl_3$, 470 MHz): δ (ppm) -121.5. HRMS *m/z* (ESI) calcd for $C_{17}H_{24}BFNO_3$ $[M+H]^+$: 320.1828, found: 320.1831. $[\alpha]^{20}_D$ = +2.2 (c = 0.1 in CH_2Cl_2); 90:10 er [Chiralcel OD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λ_{max} 254 nm, t_R = 5.6 min and 6.1 min].

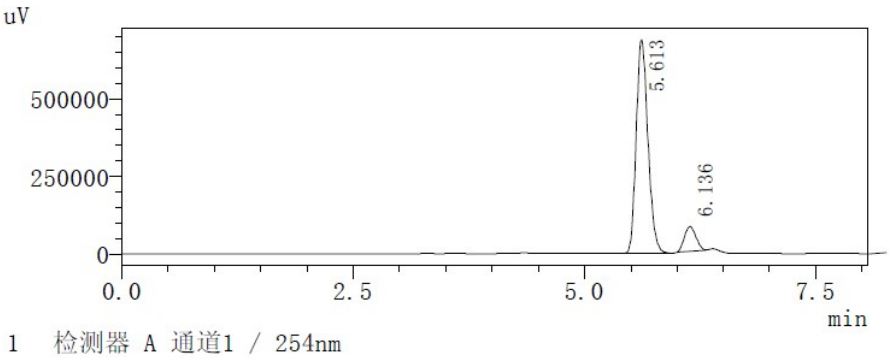


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	5.616	6245441	689228	49.559	52.702
2	6.139	6356518	618547	50.441	47.298
总计		12601959	1307775	100.000	100.000



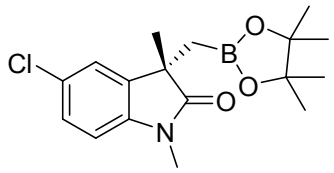
1 检测器 A 通道1 / 254nm

峰表

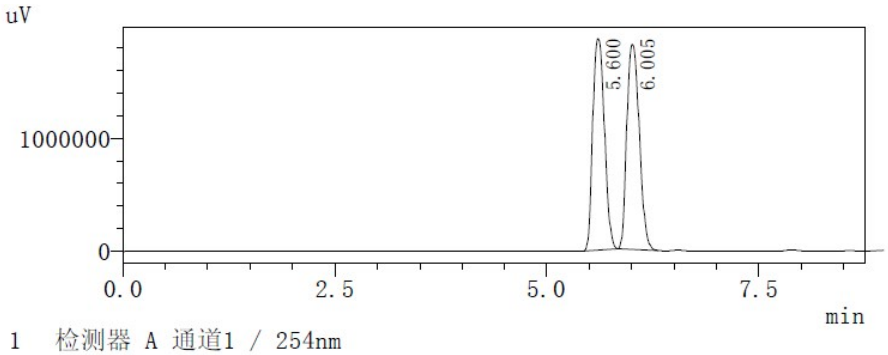
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	5.613	6081090	689711	89.787	89.652
2	6.136	691714	79612	10.213	10.348
总计		6772804	769324	100.000	100.000

(*S*)-5-chloro-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3t):



16.4 mg, 49% yield. Colorless solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.27 (d, *J* = 7.0 Hz, 1H), 7.19 (dd, *J* = 8.5 Hz, *J* = 2.5 Hz, 1H), 6.70 (d, *J* = 8.5 Hz, 1H), 3.17 (s, 3H), 1.39 (s, 3H), 1.37 (d, *J* = 15.5 Hz, 1H), 1.33 (d, *J* = 15.5 Hz, 1H), 1.07 (s, 6H), 0.99 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.2, 141.9, 137.5, 127.5, 127.3, 123.4, 108.5, 83.2, 45.7, 26.3, 25.2, 25.0, 24.7, 24.4. $[\alpha]^{20}_{D}$ = +1.18 (c = 0.2 in CH_2Cl_2); 85:15 er [Chiralcel AD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λ_{max} 254 nm, t_R = 5.6 min and 6.0 min].

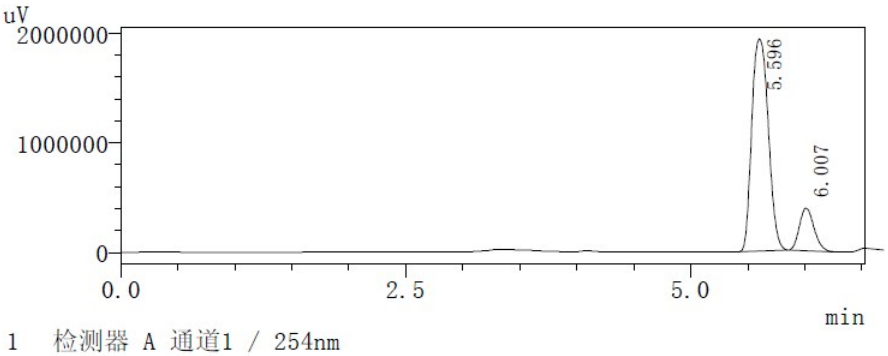


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	5.600	17866987	1864362	49.104	50.791
2	6.005	18518852	1806299	50.896	49.209
总计		36385840	3670660	100.000	100.000



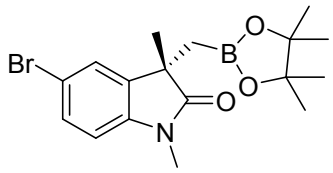
1 检测器 A 通道1 / 254nm

峰表

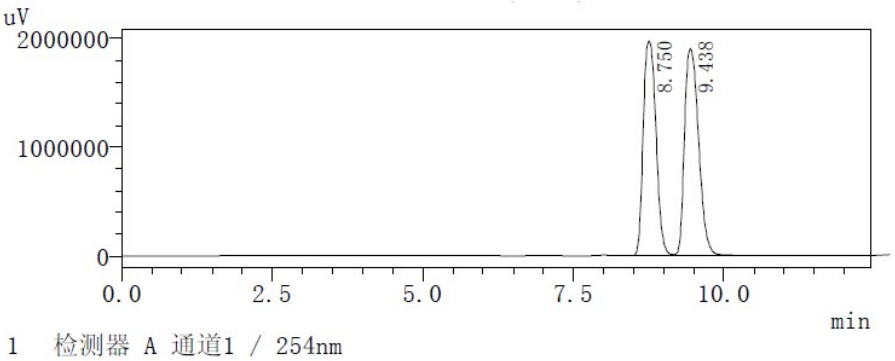
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	5.596	19561347	1938627	85.173	83.334
2	6.007	3405196	387714	14.827	16.666
总计		22966543	2326341	100.000	100.000

(*S*)-5-bromo-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3u):



15.2 mg, 40% yield. Yellow foam. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.41 (d, *J* = 1.5 Hz, 1H), 7.34 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 3.16 (s, 3H), 1.39 (s, 3H), 1.36 (d, *J* = 16.5 Hz, 1H), 1.33 (d, *J* = 16.0 Hz, 1H), 1.07 (s, 6H), 1.00 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.1, 142.4, 137.9, 130.2, 126.1, 114.8, 109.0, 83.2, 45.6, 26.3, 25.2, 25.0, 24.7, 24.4. $[\alpha]^{20}_{D}$ = 10.7 (c = 0.3 in CH_2Cl_2); 88:12 er [Chiralcel AD-H column, n-hexane / i-PrOH = 97:3, 1.0 mL/min, λ_{max} 254 nm, t_R = 8.8 min and 9.5 min].

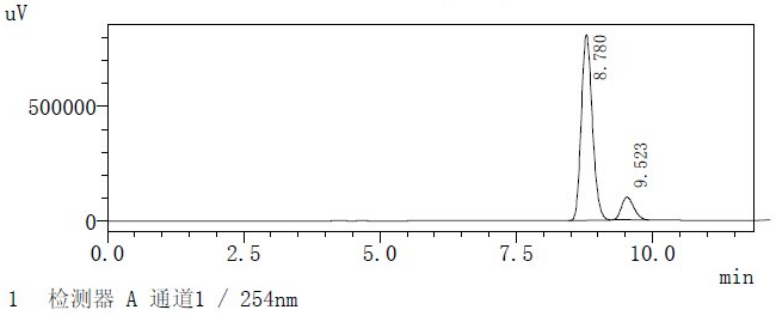


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	8.750	29134488	1976304	48.290	50.895
2	9.438	31198451	1906793	51.710	49.105
总计		60332939	3883097	100.000	100.000



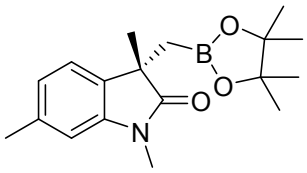
1 检测器 A 通道1 / 254nm

峰表

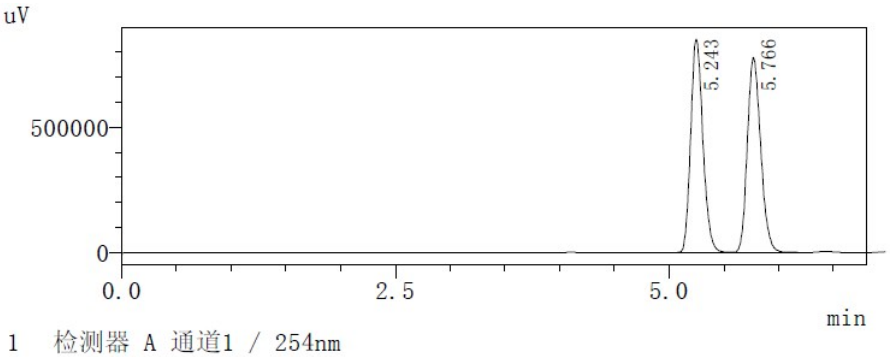
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	8.780	11438640	810005	88.157	89.161
2	9.523	1536657	98466	11.843	10.839
总计		12975297	908471	100.000	100.000

(*S*)-1,3,6-trimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3v):



21.1 mg, 67% yield. Colorless foam; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.14 (d, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.0 Hz, 1H), 6.60 (s, 1H), 3.17 (s, 3H), 2.36 (s, 3H),1.38 (s, 3H), 1.36 (d, *J* = 15.5 Hz, 1H), 1.32 (d, *J* = 15.0 Hz, 1H), 1.04 (s, 6H), 0.97 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 182.0, 143.4, 137.5, 132.9, 122.5, 122.4, 108.6, 83.0, 45.2, 26.1, 25.5, 25.0, 24.7, 24.3, 21.7. HRMS *m/z* (ESI) calcd for $C_{18}H_{27}BNO_3$ $[M+H]^+$: 316.2079, found: 316.2081. $[\alpha]^{20}_D$ = -1.0 (c = 0.2 in CH_2Cl_2); 88:12 er [Chiralcel AD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λ_{max} 254 nm, t_R = 5.3 min and 5.8 min].

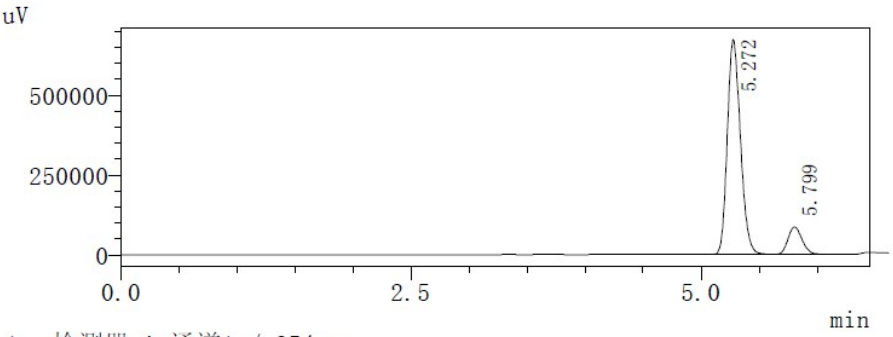


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	5.243	6621001	850563	50.006	52.187
2	5.766	6619491	779286	49.994	47.813
总计		13240492	1629849	100.000	100.000



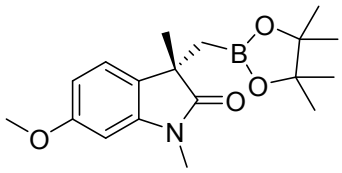
1 检测器 A 通道1 / 254nm

峰表

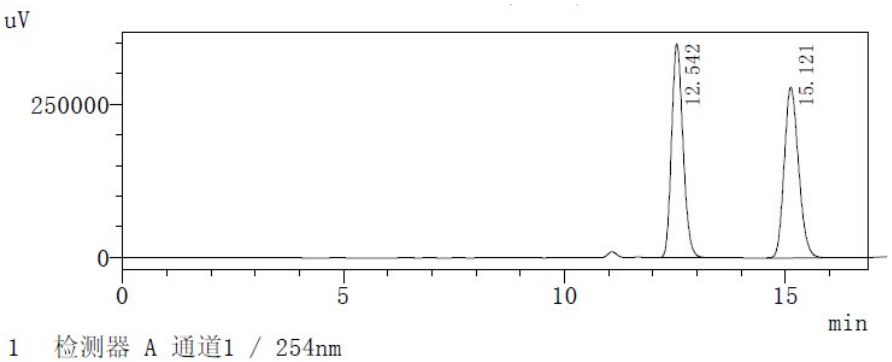
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	5.272	5288509	673105	88.017	88.696
2	5.799	720009	85782	11.983	11.304
总计		6008518	758887	100.000	100.000

(*S*)-6-methoxy-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3w):



21.1 mg, 48% yield. Yellow foam; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.15 (d, *J* = 8.0 Hz, 1H), 6.51 (dd, *J* = 8.5 Hz, *J* = 2.5 Hz, 1H), 6.39 (d, *J* = 2.5 Hz, 1H), 3.81 (s, 3H), 3.17 (s, 3H), 1.37 (s, 3H), 1.37 (d, *J* = 15.5 Hz, 1H), 1.32 (d, *J* = 15.5 Hz, 1H), 1.05 (s, 6H), 0.98 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 182.2, 159.8, 144.6, 128.0, 123.1, 105.7, 95.8, 83.0, 55.5, 45.0, 26.2, 25.7, 24.8, 24.4. $[\alpha]^{20}_{D}$ = -3.7 (c = 0.3 in CH_2Cl_2); 85:15 er [ChiralcelAD-H column, n-hexane / i-PrOH = 97:3, 0.7 mL/min, λ_{max} 254 nm, t_R = 12.8 min and 15.4 min].

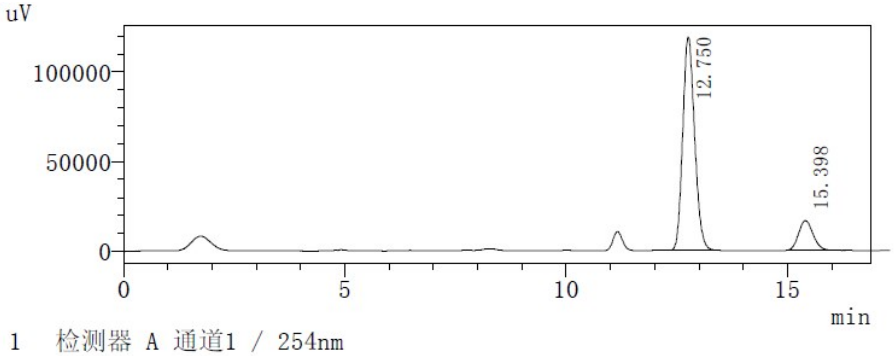


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	12.542	6269624	348546	49.983	55.639
2	15.121	6273981	277895	50.017	44.361
总计		12543605	626441	100.000	100.000



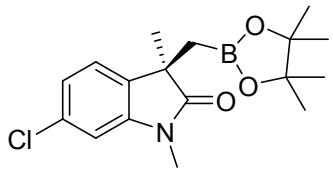
1 检测器 A 通道1 / 254nm

峰表

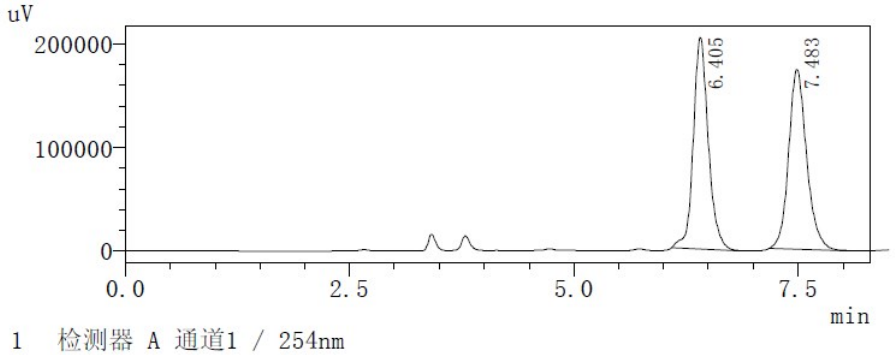
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	12.750	2223963	118986	85.440	87.740
2	15.398	378990	16625	14.560	12.260
总计		2602953	135611	100.000	100.000

(*S*)-6-chloro-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3x):



21.4 mg, 64% yield. Yellow solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.17 (d, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 6.79 (d, *J* = 1.5 Hz, 1H), 3.17 (s, 3H), 1.39 (d, *J* = 15.0 Hz, 1H), 1.38 (s, 3H), 1.33 (d, *J* = 15.5 Hz, 1H), 1.05 (s, 6H), 0.97 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 181.6, 144.7, 134.2, 133.2, 123.5, 121.8, 108.3, 83.2, 65.6, 45.2, 26.3, 25.5, 24.8, 24.3. $[\alpha]^{20}_{D}$ = +4.3 (c = 0.2 in CH_2Cl_2); 95:5 er [Chiralcel OD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λ_{max} 254 nm, t_R = 6.4min and 7.3 min].

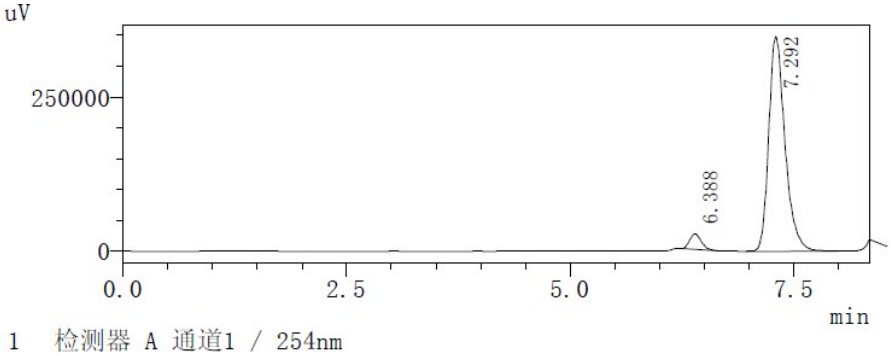


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	6.405	2366698	203667	49.349	54.006
2	7.483	2429174	173450	50.651	45.994
总计		4795872	377117	100.000	100.000



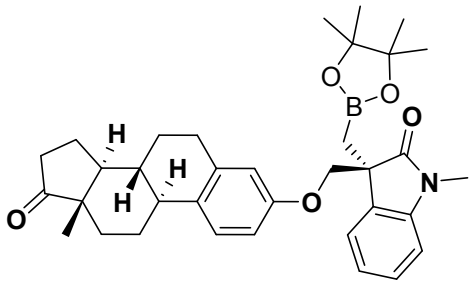
1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

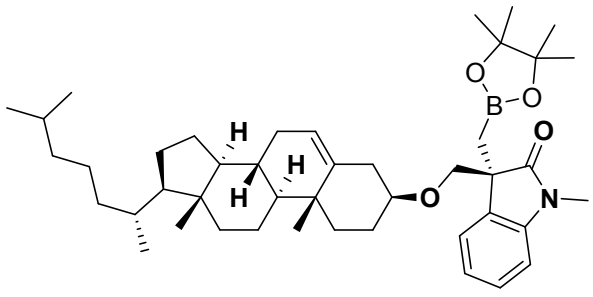
峰#	RT(min)	Area	Height	Area%	Height%
1	6.388	229740	25412	4.964	6.809
2	7.292	4398743	347806	95.036	93.191
总计		4628483	373218	100.000	100.000

(*S*)-1-methyl-3-((((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)methyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3y):



26.0 mg, 46% yield. Yellow foam. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.36 (d, *J* = 7.5 Hz, 1H), 7.24 (dd, *J* = 7.5 Hz, *J* =1.0 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.62-6.58 (m, 1H), 6.53 (s, 1H), 4.19 (dd, *J* = 9.0 Hz, *J* = 6.5 Hz, 1H), 4.07 (dd, *J* = 8.5 Hz, *J* = 5.0 Hz, 1H), 3.23 (s, 3H), 2.84-2.80 (m, 2H), 2.48 (dd, *J* = 19.5 Hz, *J* = 9.0 Hz, 1H), 2.37-2.33 (m, 1H), 2.22-2.17 (m, 1H), 2.16-2.08 (m, 1H), 2.06-2.00 (m, 1H), 1.98-1.91(m, 2H), 1.66-1.57 (m, 2H), 1.54-1.48 (m, 2H), 1.48-1.41(m, 4H), 1.39-1.34 (m, 1H), 1.00 (s, 6H), 0.91 (s, 6H), 0.88(s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 230.0, 178.7, 156.8, 144.3, 137.5, 132.2, 132.2, 127.9, 126.1, 123.8, 122.2, 114.9, 114.8, 112.5, 112.3, 107.6, 83.1, 72.9, 50.4, 50.0, 47.9, 43.9, 38.3, 35.8, 31.5, 29.5, 26.5, 26.3, 25.9, 24.8, 24.7, 24.5, 21.5, 13.8. HRMS *m/z* (ESI) calcd for $C_{35}H_{45}BNO_5$ $[M+H]^+$: 570.3385, found: 570.3391. $[\alpha]^{20}_D$ = +12.2 (c = 0.2 in CH_2Cl_2).

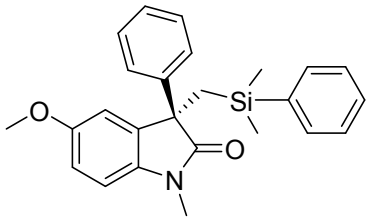
(*S*)-3-((((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)methyl)-1-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3z):



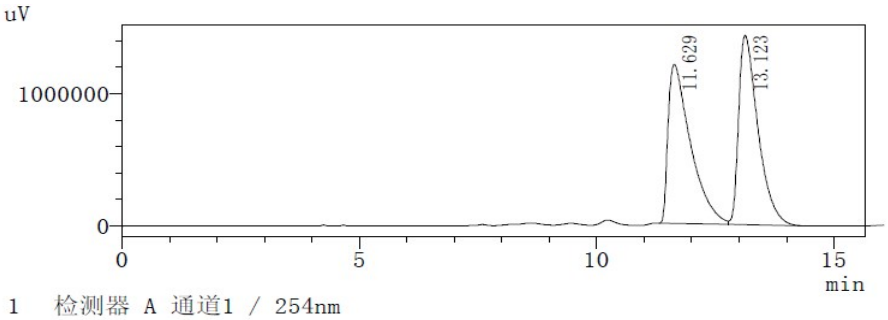
30.1 mg, 44% yield. Colorless foam; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.29 (d, *J* = 7.0 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 5.26-5.21 (m, 1H), 3.71 (t, *J* = 8.0 Hz, 1H), 3.64 (dd, *J* = 9.0 Hz, *J* = 7.0 Hz, 1H), 3.19 (s, 3H), 3.02-2.97 (m, 1H), 2.19-2.08(m, 1H), 2.37-2.33 (m, 1H), 2.22-2.17 (m, 1H), 2.16-2.08 (m, 1H), 2.06-2.00 (m, 1H), 2.06-1.90 (m, 3H), 1.84-1.78(m, 1H), 1.77-1.71 (m, 2H), 1.66-1.62 (m, 1H), 1.58-1.53 (m, 1H),

150-1.47 (m, 3H), 1.44-1.34 (m, 5H), 1.34-1.30 (m, 2H), 1.23-1.18 (m, 2H), 1.15-1.02 (m, 7H), 0.97 (s, 6H), 0.96-0.94 (m, 2H), 0.91(s, 3H), 0.89 (d, J = 7.0 Hz, 3H), 0.88 (s, 6H), 0.86 (d, J = 2.0 Hz, 3H) 0.85 (d, J = 2.5 Hz, 3H), 0.64 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 179.4, 144.4, 141.0, 133.1, 127.5, 123.6, 121.9, 121.9, 121.3, 107.3, 83.0, 80.2, 80.1, 73.6, 73.5, 56.7, 56.1, 50.8, 50.1, 42.3, 39.7, 39.5, 39.0, 38.8, 37.1, 36.7, 36.2, 35.7, 31.8, 28.3, 28.2, 28.1, 28.0, 26.2, 24.7, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8. HRMS *m/z* (ESI) calcd for $C_{44}H_{69}BNO_4$ $[M+H]^+$: 686.5314, found: 686.5318. $[\alpha]^{20}_D$ = -8.9 (c = 0.2 in CH_2Cl_2).

(*S*)-3-((dimethyl(phenyl)silyl)methyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4e):



30.5 mg, 76% yield. Yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.33-7.31 (m, 2H), 7.29-7.26 (m, 2H), 7.25-7.23 (m, 3H), 7.22-7.19 (m, 3H), 6.81 (dd, J = 8.5 Hz, J = 2.5 Hz, 1H), 6.69 (d, J = 8.5 Hz, 1H), 6.61 (d, J = 2.5 Hz, 1H), 3.67 (s, 3H), 2.92 (s, 3H), 2.21 (d, J = 14.5 Hz, 1H), 1.76 (d, J = 14.0 Hz, 1H),0.05 (s, 3H), -0.01 (S, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 178.3, 155.7, 143.1, 138.2, 137.0, 134.4, 133.5, 128.7, 128.3, 127.4, 126.9, 126.4, 112.9, 112.4, 108.5, 55.6, 54.1, 26.2, 25.7, -2.1, -2.5. $[\alpha]^{20}_D$ = -7.5 (c = 0.25 in CH_2Cl_2); 61:39 er [Chiralcel OD-H column, n-hexane / i-PrOH = 95:5, 1.0 mL/min, λ_{max} 254 nm, t_R = 11.6 min and 13.0 min].

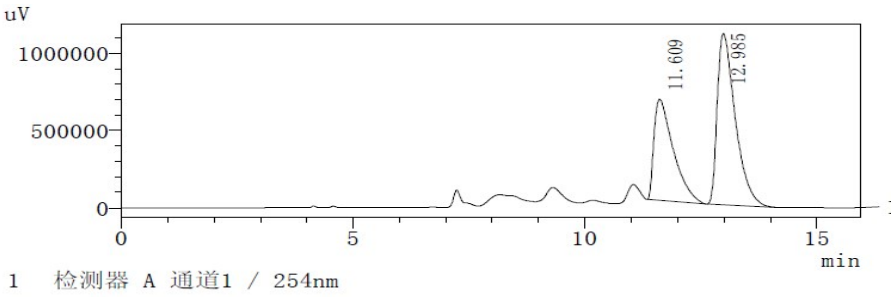


1 检测器 A 通道1 / 254nm

峰表

检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	11.629	39560581	1200419	49.370	45.643
2	13.123	40570952	1429573	50.630	54.357
总计		80131533	2629993	100.000	100.000



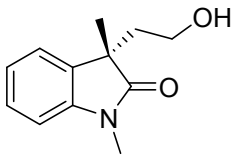
1 检测器 A 通道1 / 254nm

峰表

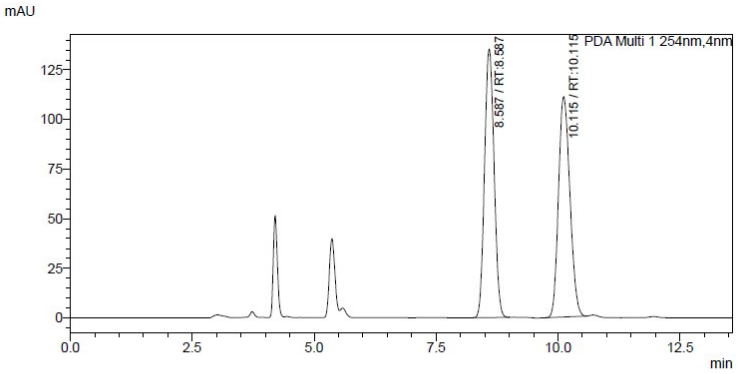
检测器 A Ch1 254nm

峰#	RT(min)	Area	Height	Area%	Height%
1	11.609	19079942	655315	38.810	37.123
2	12.985	30081910	1109951	61.190	62.877
总计		49161852	1765266	100.000	100.000

(*S*)-3-(2-hydroxyethyl)-1,3-dimethylindolin-2-one (5a):



11.5 mg, 56% yield. White solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.31 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 6.0 Hz, 1H), 7.10, (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 3.85 (d, *J* = 10.5 Hz, 1H), 3.74 (d, *J* = 11.0 Hz, 1H), 3.23 (s, 3H), 2.25-2.20 (m, 1H), 1.62-1.54 (m, 1H), 1.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 179.9, 143.7, 131.7, 128.4, 122.8, 122.7, 108.3, 67.7, 49.8, 37.3, 26.2, 19.0. $[\alpha]^{20}_{D}$ = +18.4 (c = 0.2 in CH_2Cl_2); 88:12 er [ChiralcAD-H column, n-hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, t_R = 8.6 min and 10.1 min].



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Ret. Time	Area	Height	Area%
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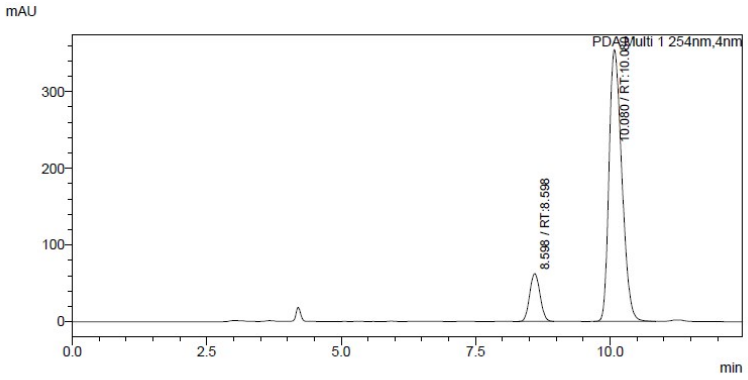
10.115	1810885	111138	49.646
	3647578	246455	100.000



<Column Performance>
PDA

Ret. Time	Area	Height	Area%
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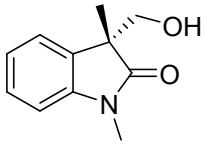
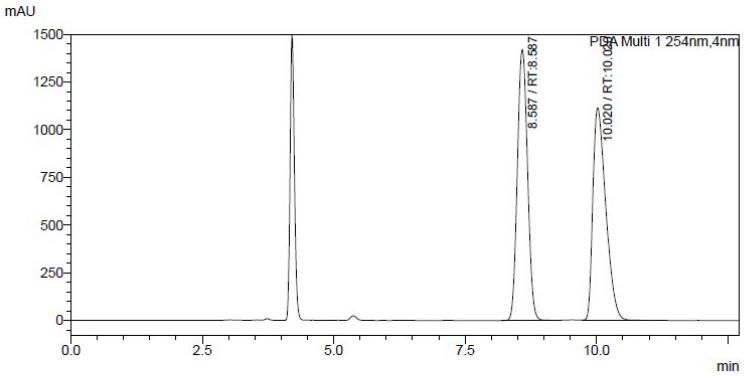
10.080	5852588	354388	87.516
	6687485	416784	100.000

(*R*)-3-(hydroxymethyl)-1,3-dimethylindolin-2-one (6a):



13.0 mg, 68% yield. White solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.31 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.09, (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.5 Hz, 1H), 3.85 (t, *J* = 9.0 Hz, 1H), 3.74 (dd, *J* = 10.5 Hz, *J* = 2.5 Hz, 1H), 3.23 (s, 3H), 2.32-2.29 (m, 1H), 1.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 179.9, 143.6, 131.7, 128.3, 122.7, 122.7, 108.3, 67.6, 49.8, 26.2, 19.0. $[\alpha]^{20}_{D}$ = +23.3 (c = 0.2 in CH_2Cl_2); 89:11 er [Chiralcel AD-H column, n-hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, t_R = 8.6 min and 10.0 min].



<Column Performance>
PDA

Ret. Time	Area	Height	Area%
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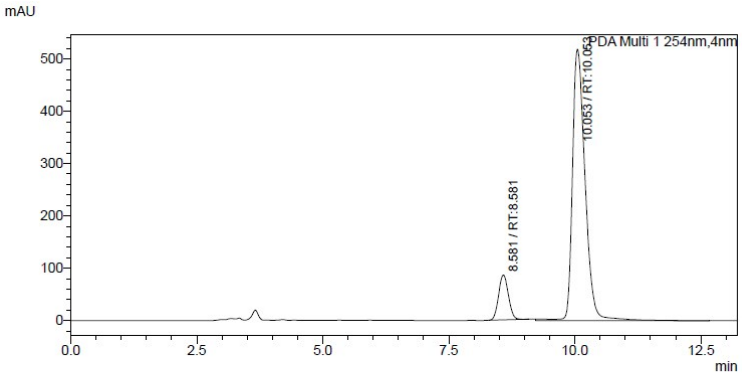
10.020	19060303	1115430	49.947
	38160891	2537571	100.000



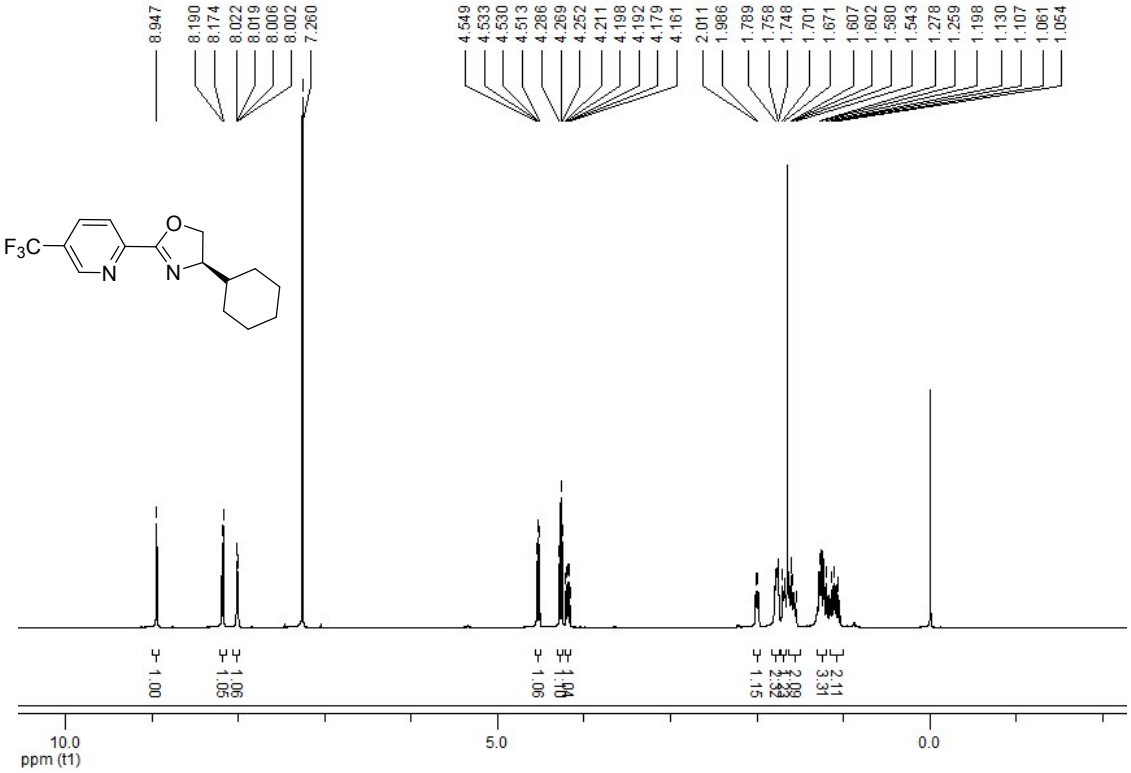
<Column Performance>

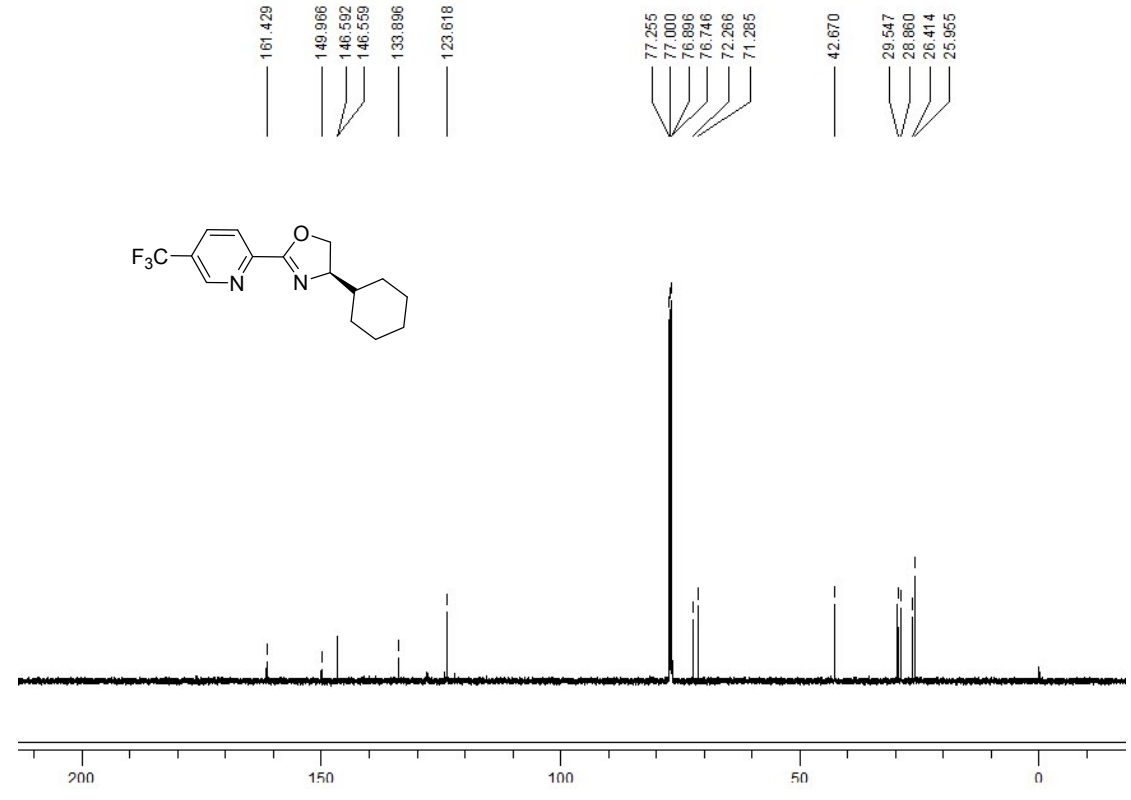
PDA

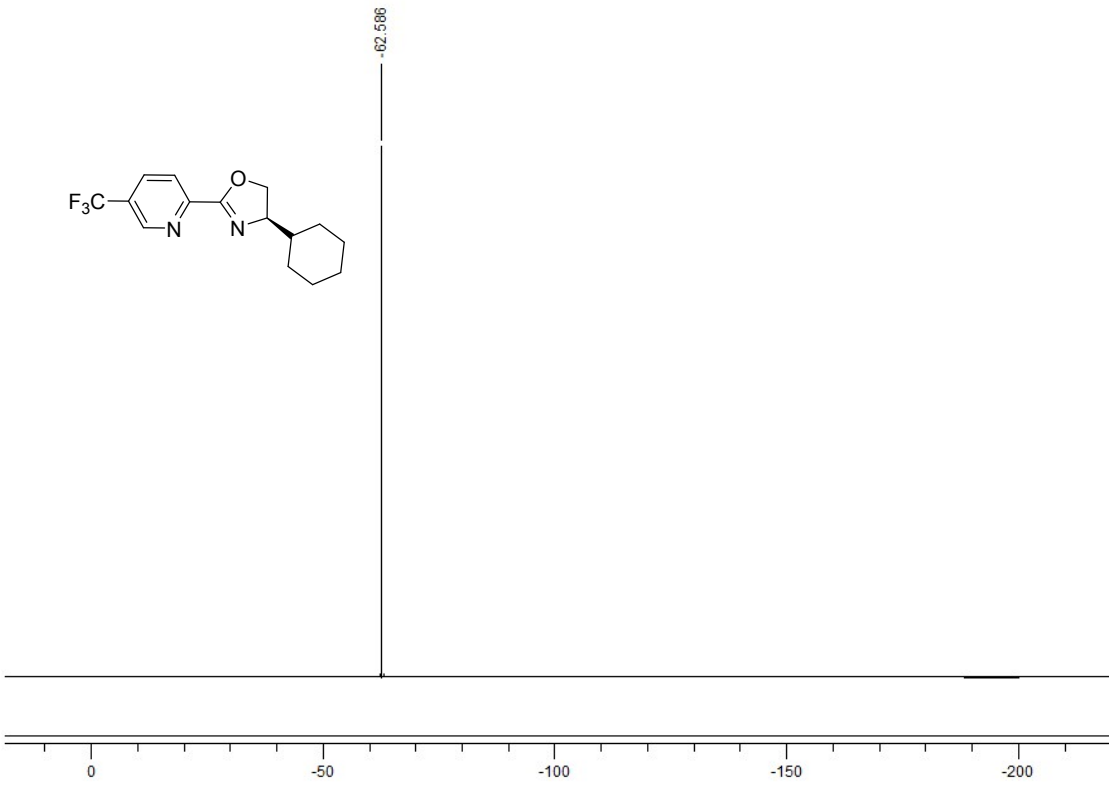
Ret. Time	Area	Height	Area%
8.581	1155532	85477	11.266
10.053	9101576	518551	88.734
	10257108	604028	100.000

(D) NMR Spectra

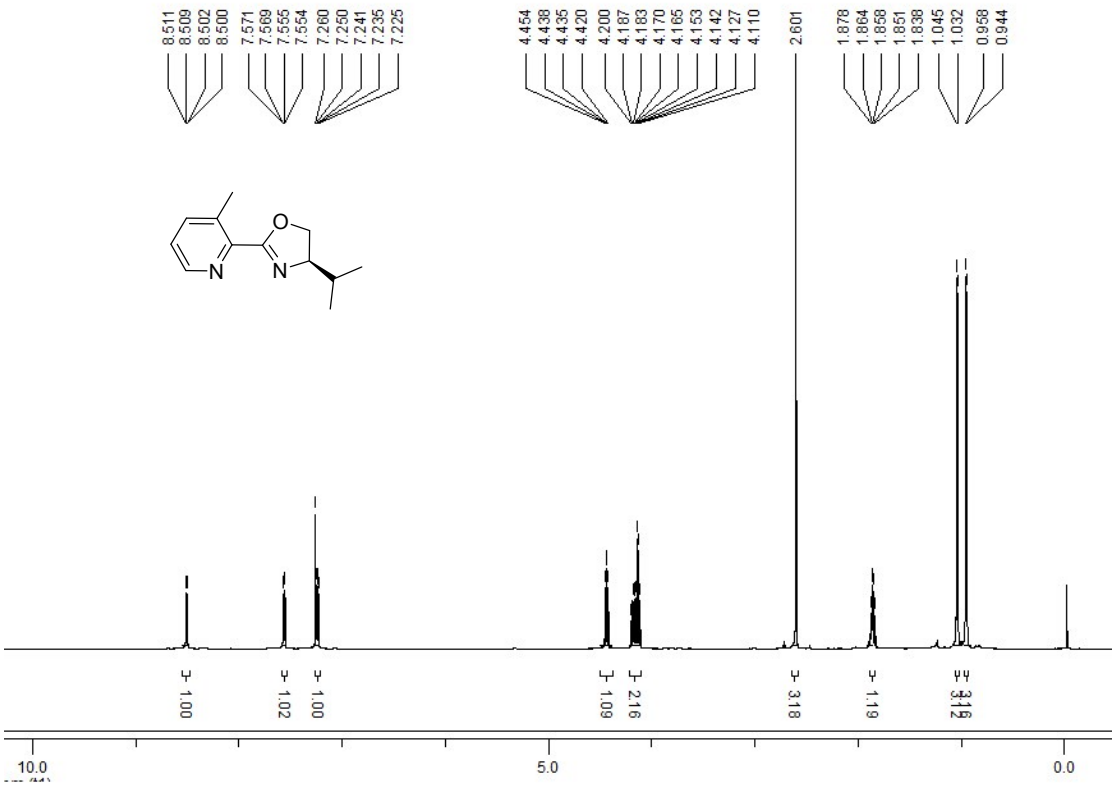
(R)-4-cyclohexyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (L1):

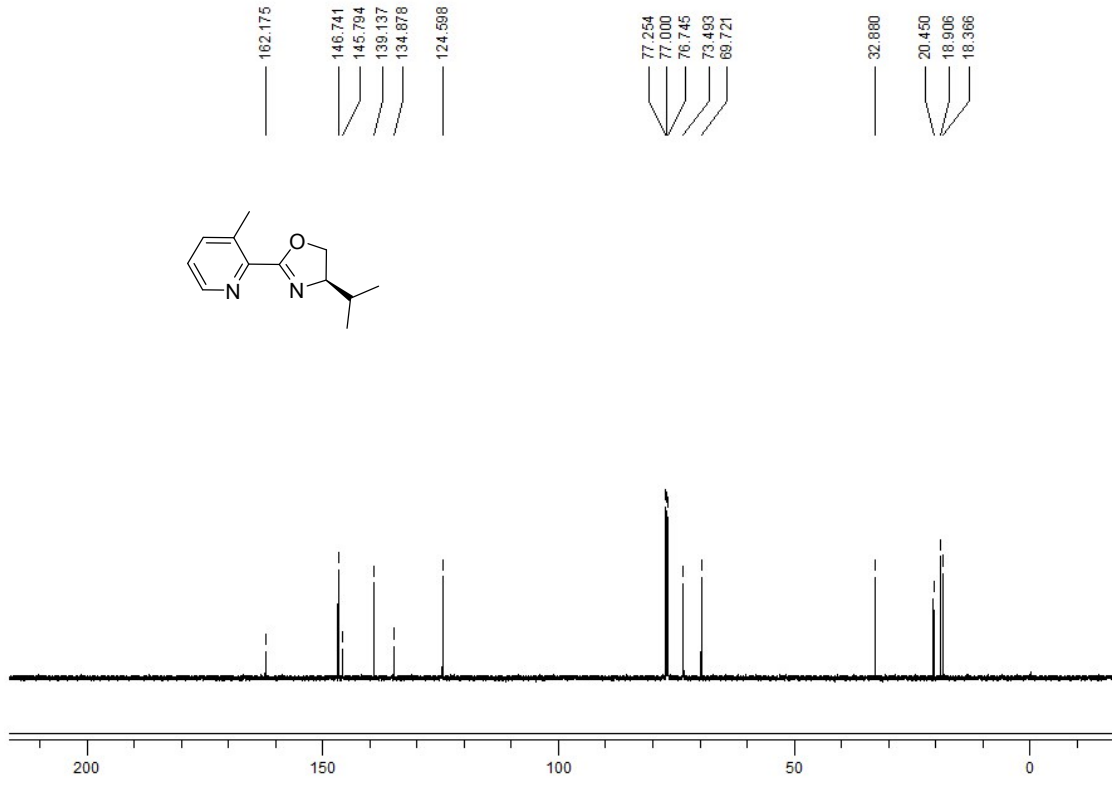




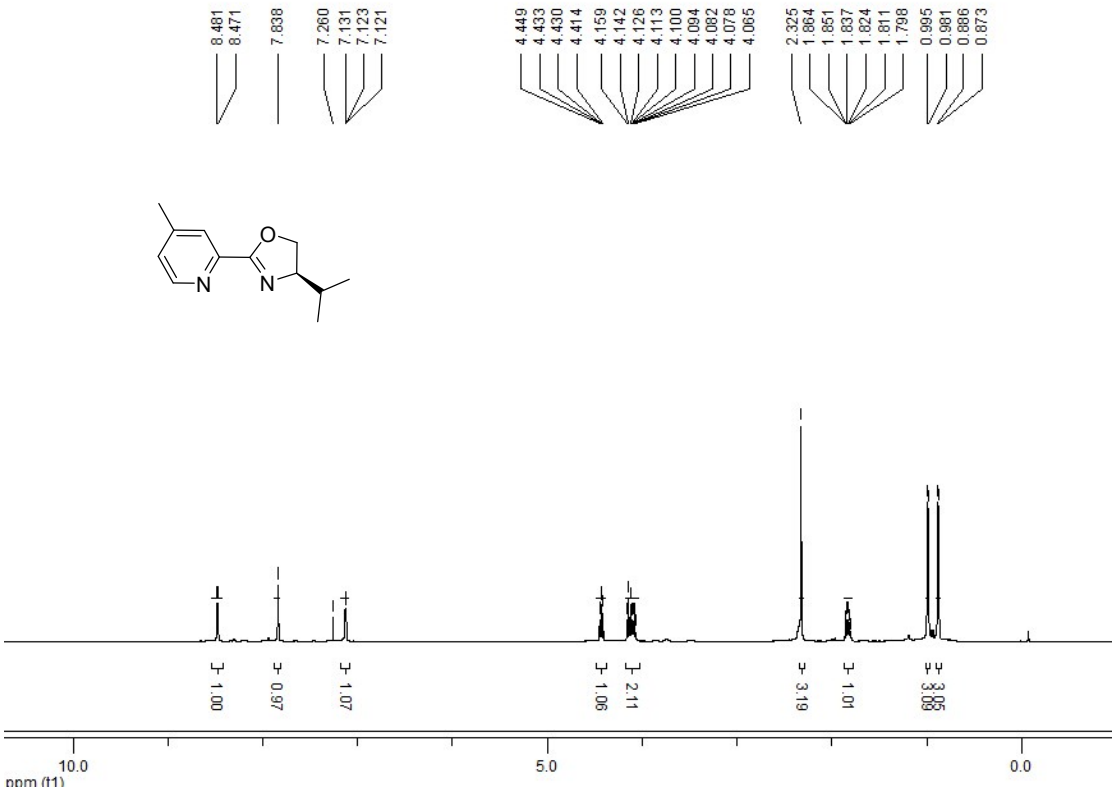

-62.586
F3C
N
O
N
0
-50
-100
-150
-200

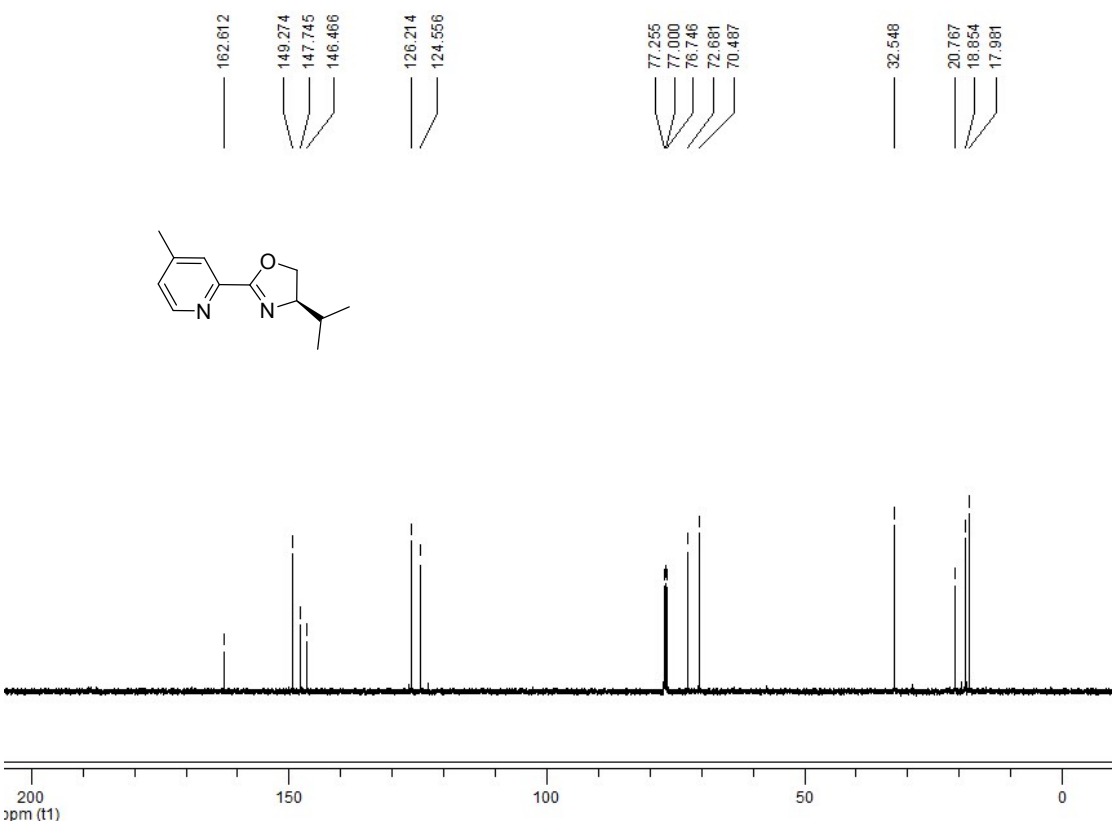
(R)-4-isopropyl-2-(3-methylpyridin-2-yl)-4,5-dihydrooxazole (L2):



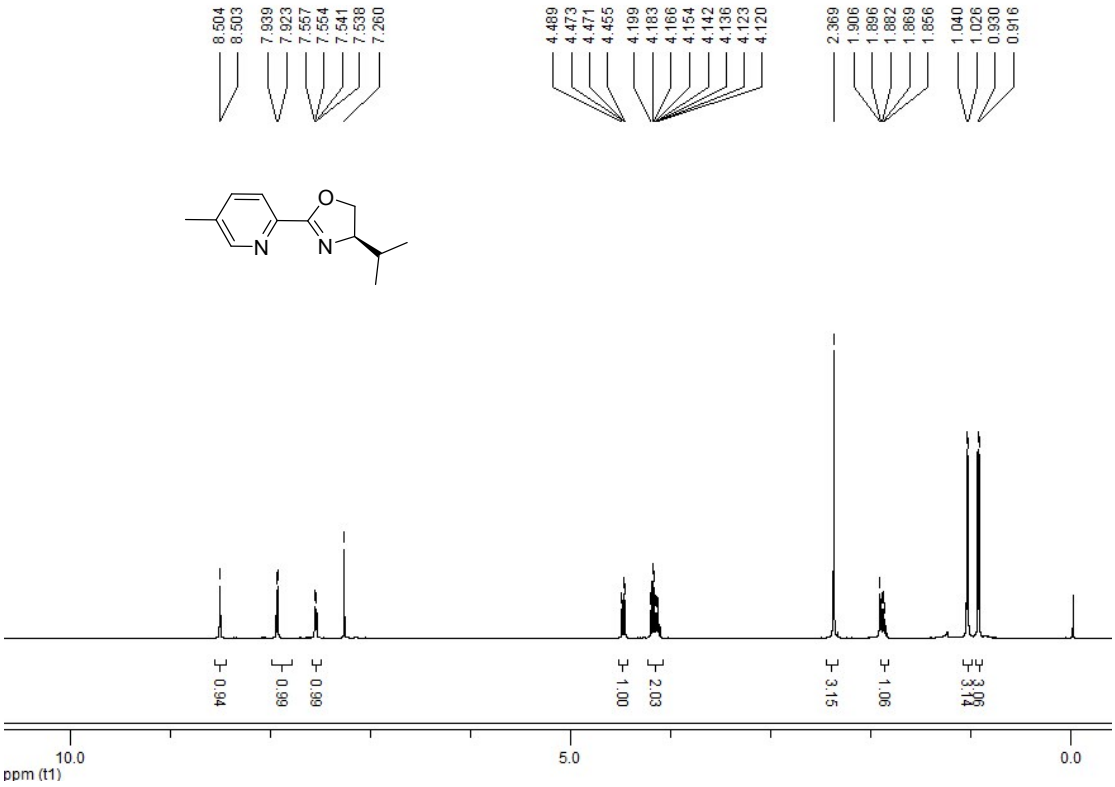


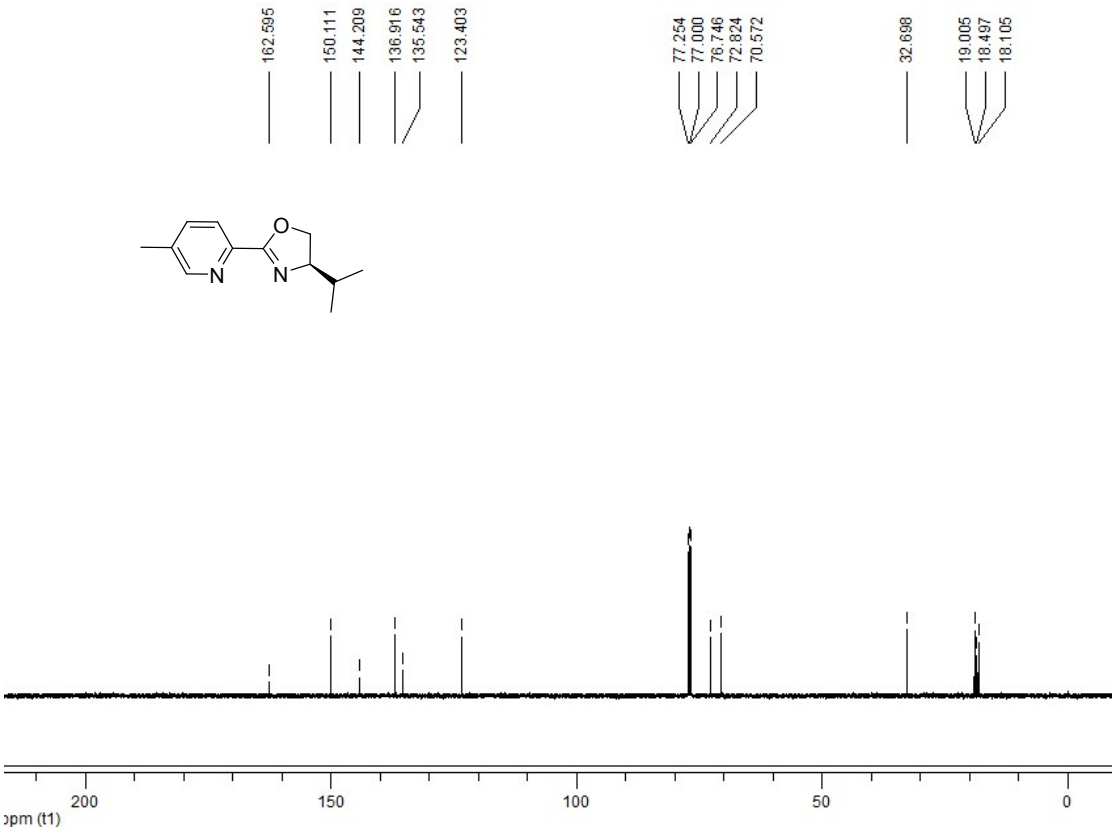
(R)-4-isopropyl-2-(4-methylpyridin-2-yl)-4,5-dihydrooxazole (L3):



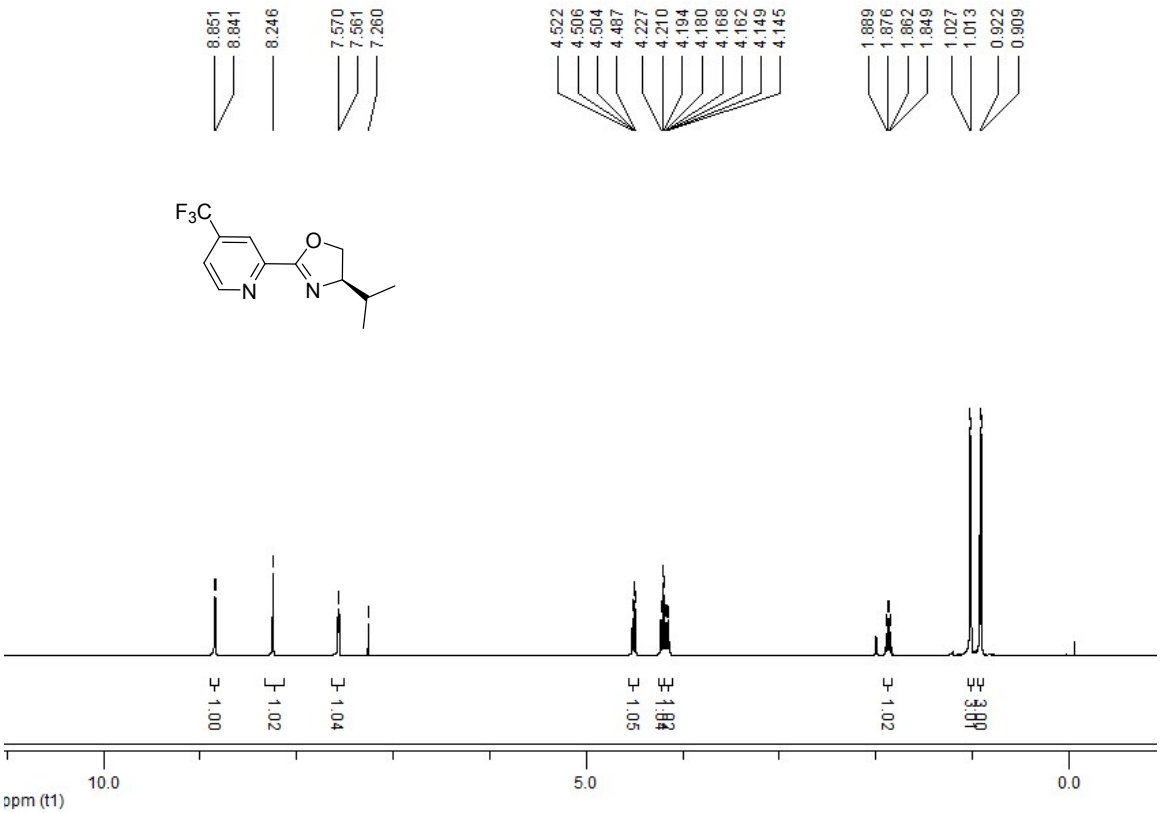


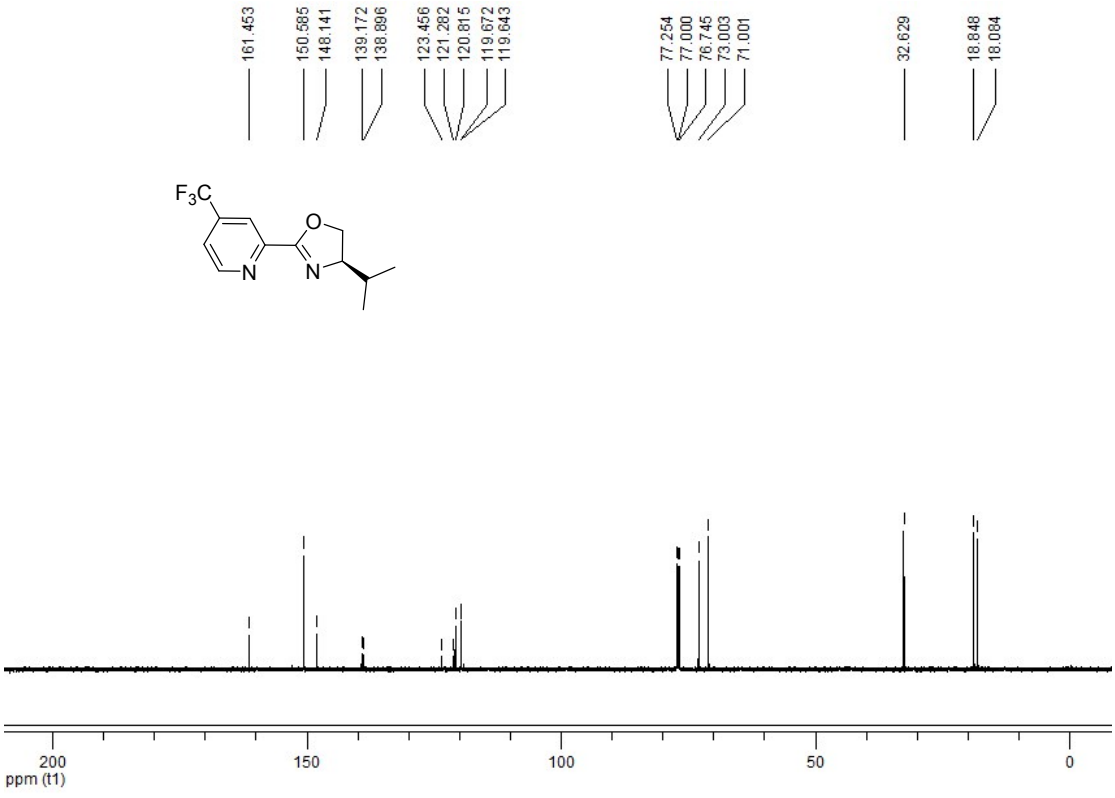
(R)-4-isopropyl-2-(5-methylpyridin-2-yl)-4,5-dihydrooxazole (L4):

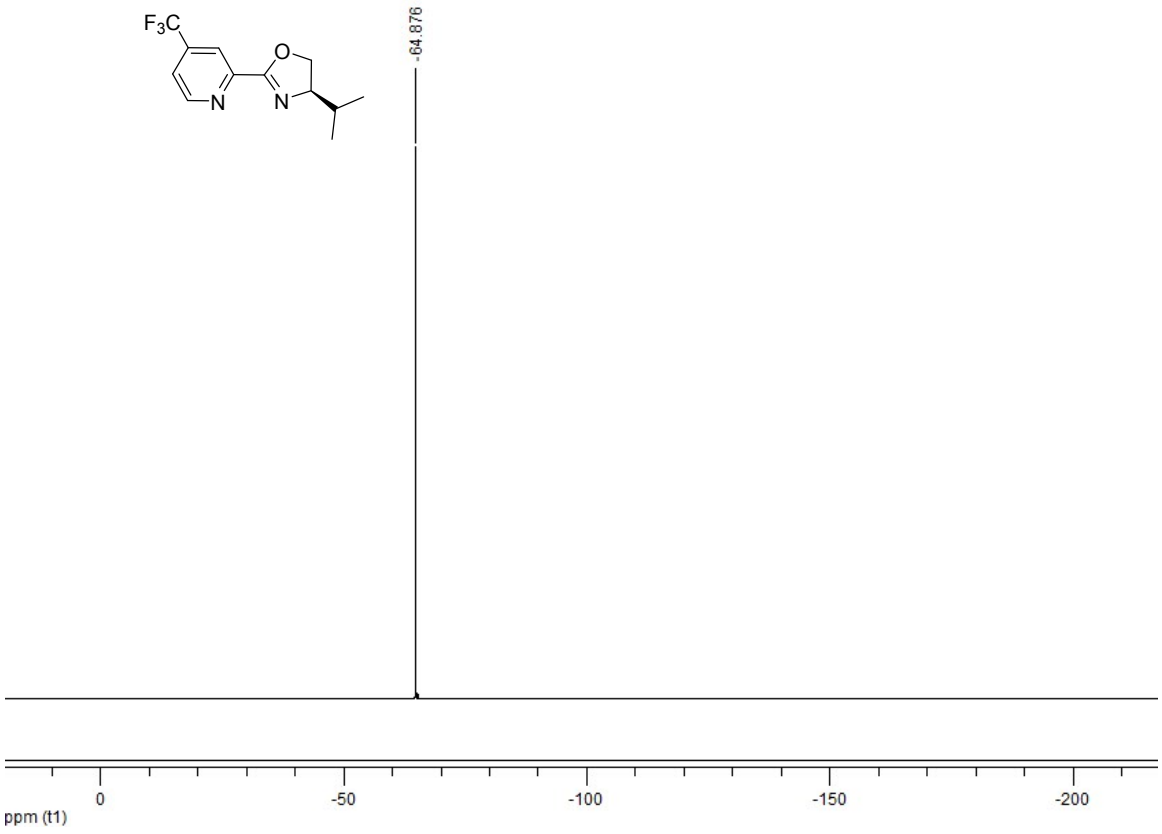




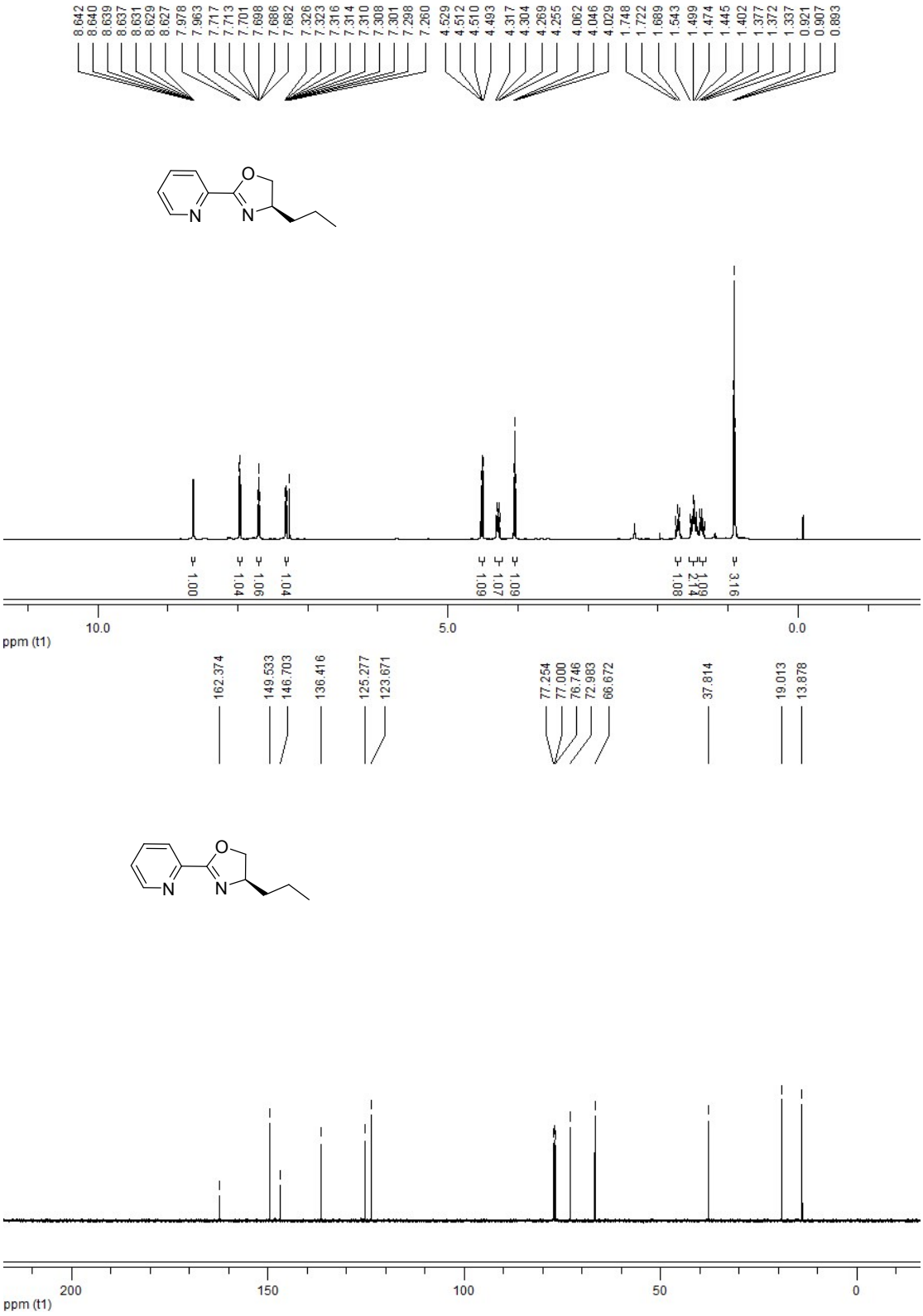
(R)-4-isopropyl-2-(4-(trifluoromethyl)pyridin-2-yl)-4,5-dihydrooxazole (L6) :



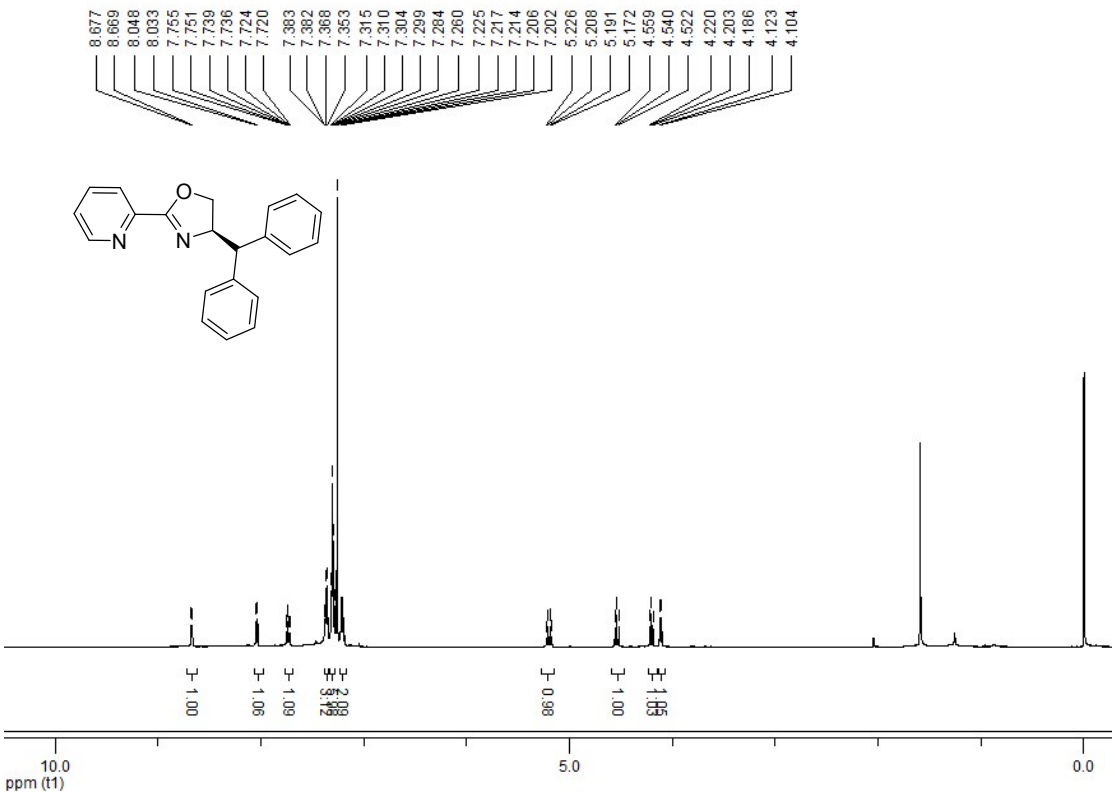


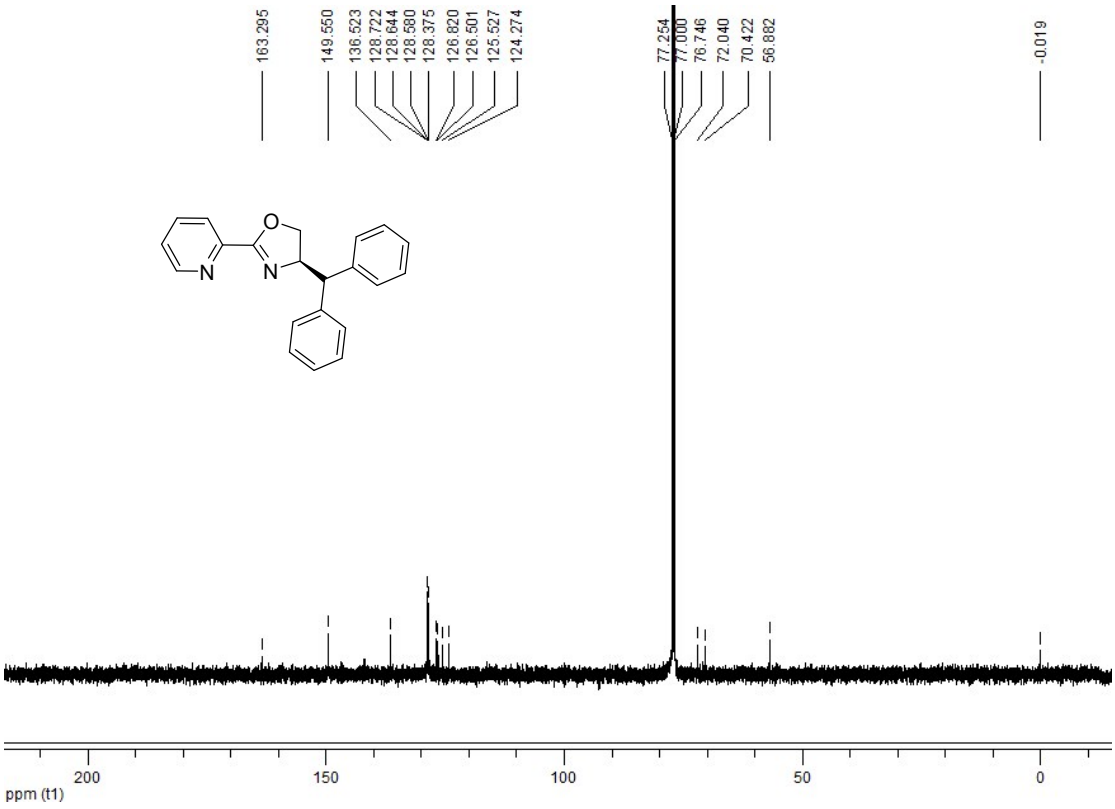

F3C
O
N
N
-64.876
0
-50
-100
-150
-200
ppm (t1)

(R)-4-propyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (L8):



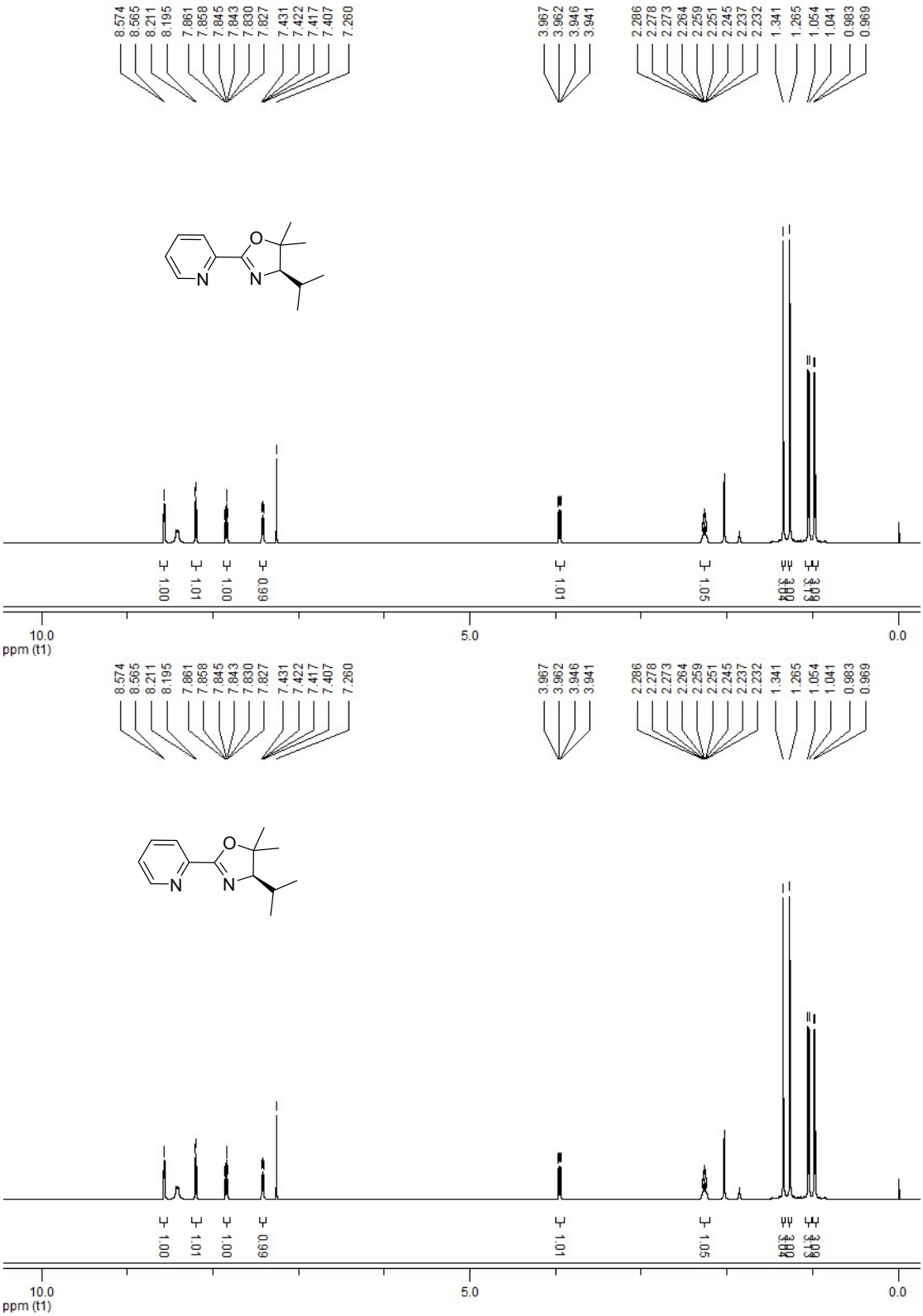
(R)-4-benzhydryl-2-(pyridin-2-yl)-4,5-dihydrooxazole (L12):



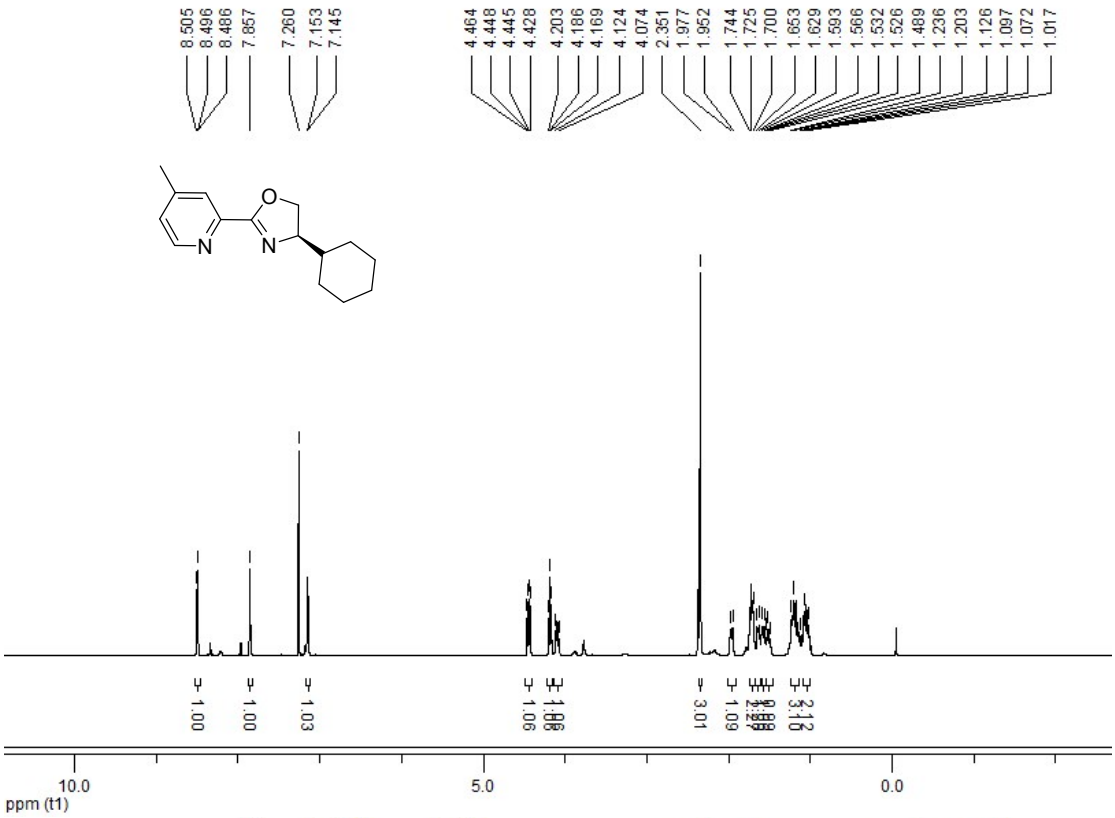


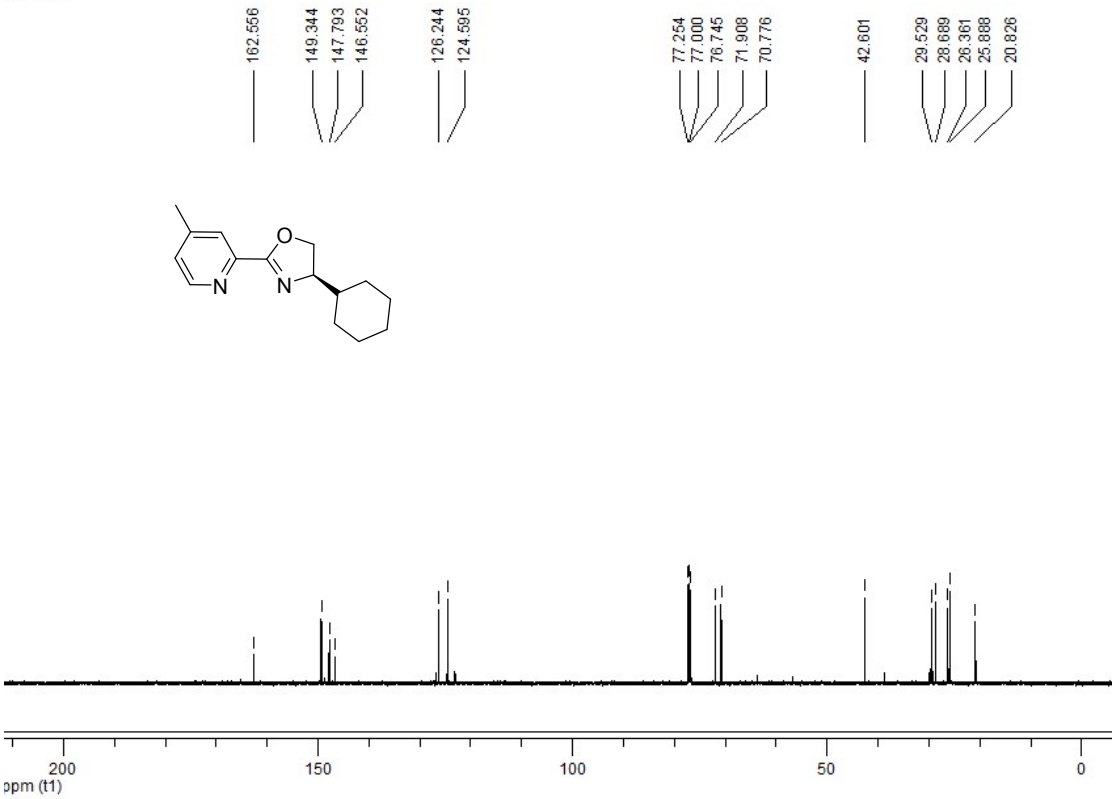
(R)-4-cyclohexyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (L13):

(R)-4-isopropyl-5,5-dimethyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (L15):

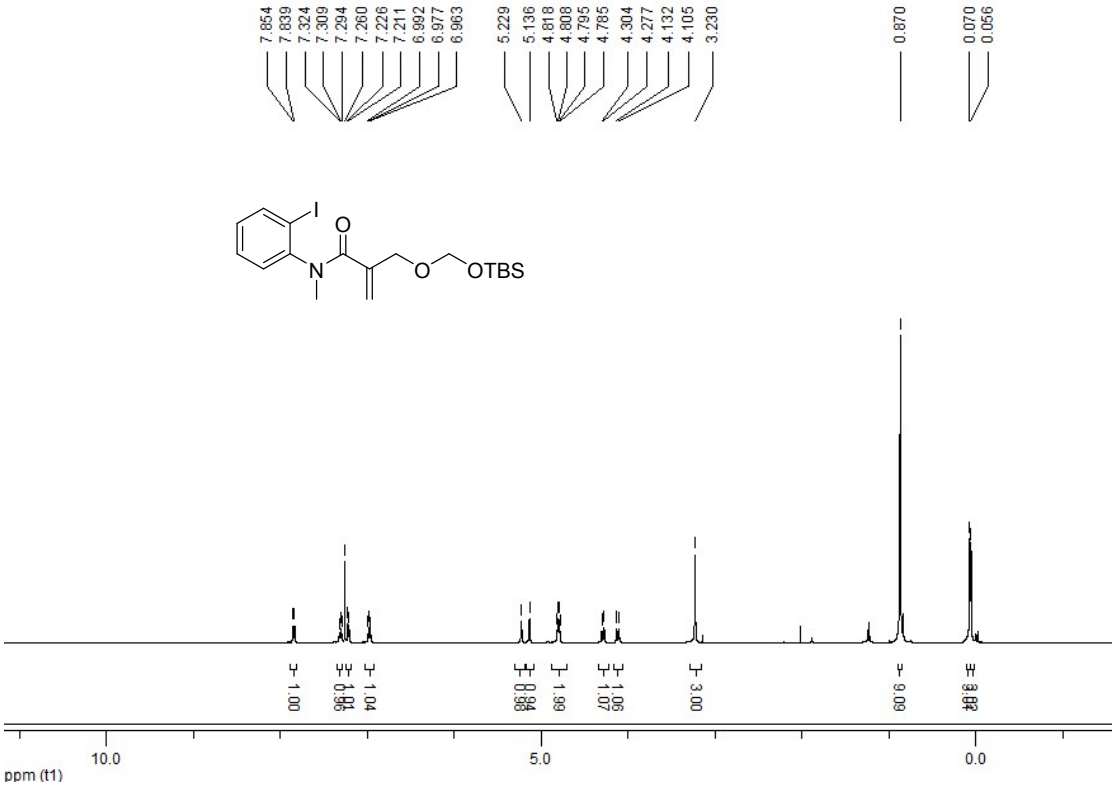


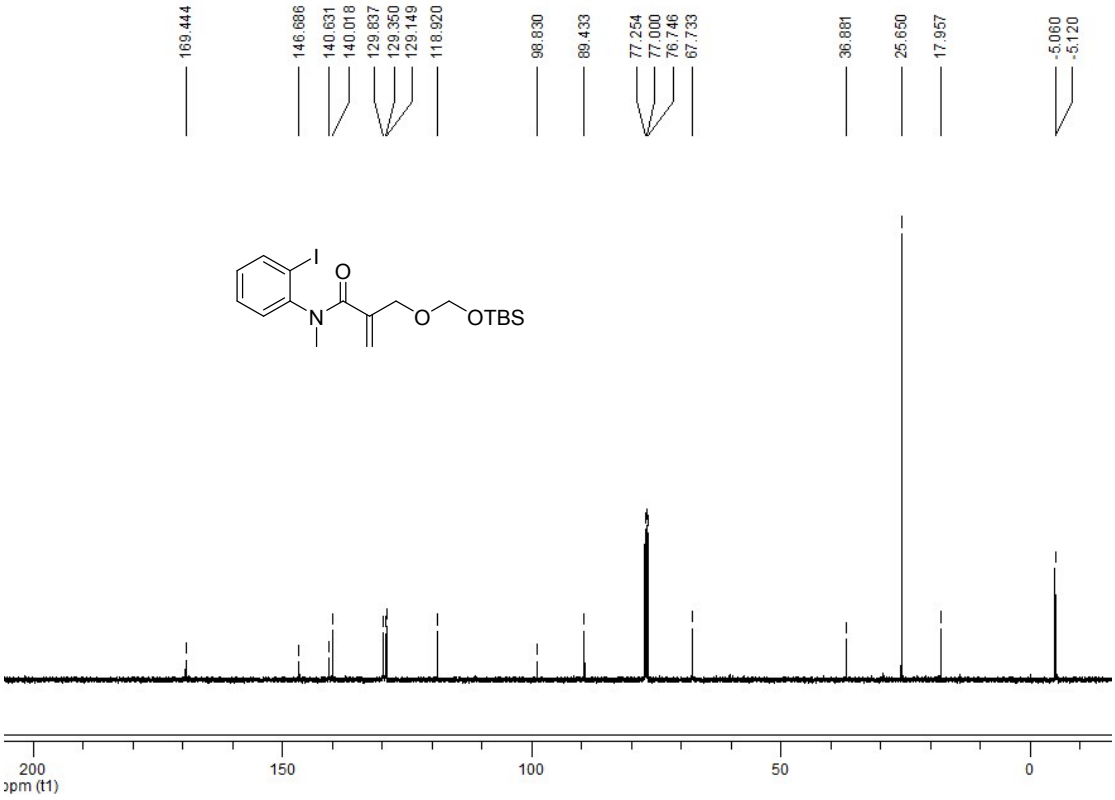
(R)-4-cyclohexyl-2-(4-methylpyridin-2-yl)-4,5-dihydrooxazole (L16):



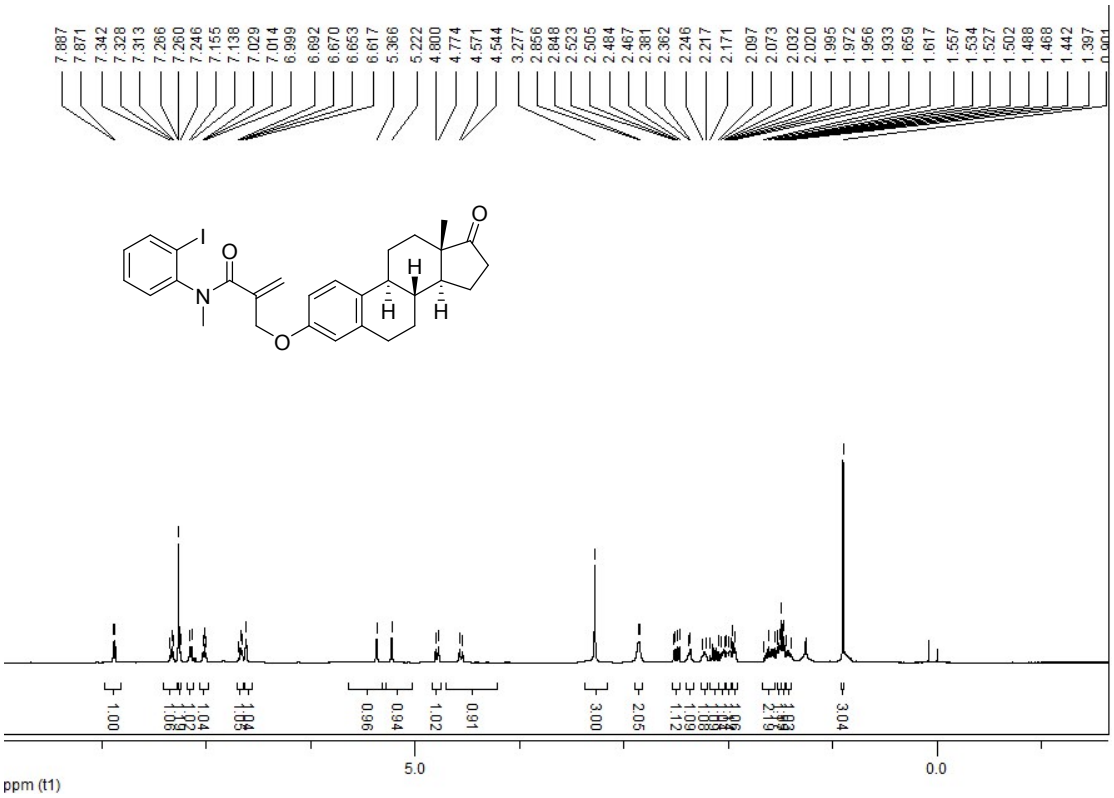


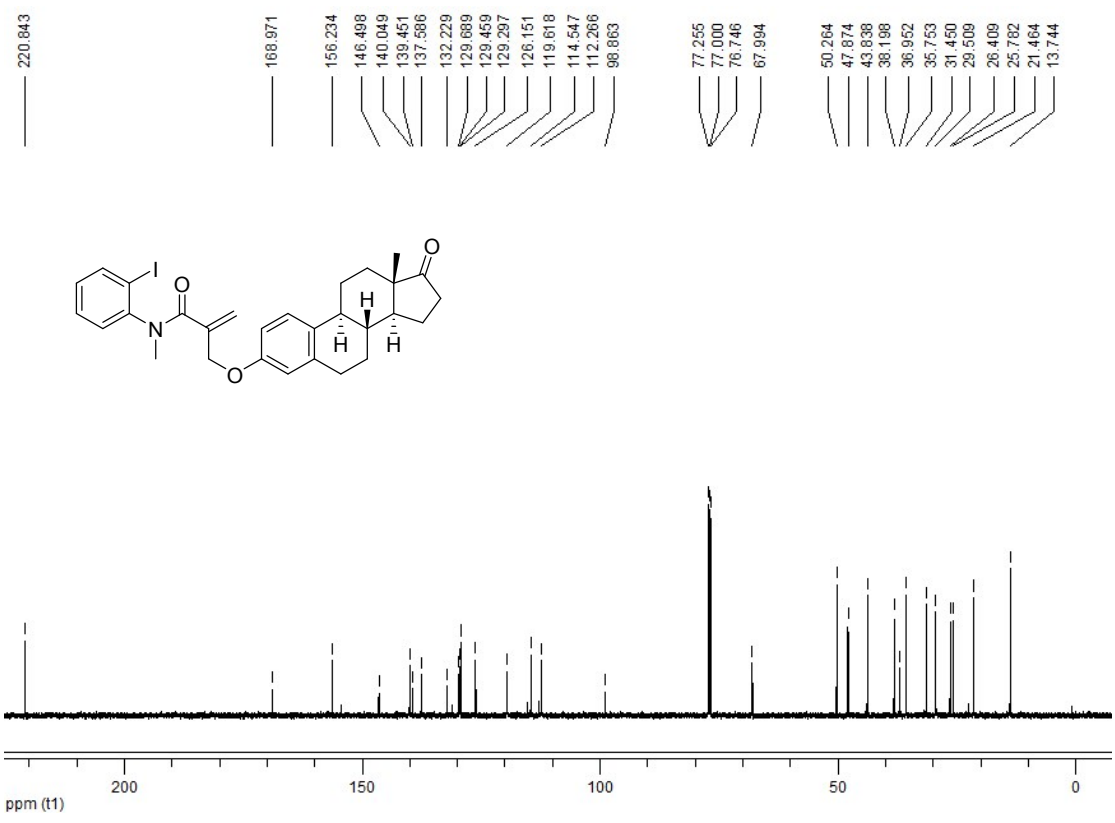
2-((((tert-butyldimethylsilyl)oxy)methoxy)methyl)-N-(2-iodophenyl)-N-methylacrylamide (1e):



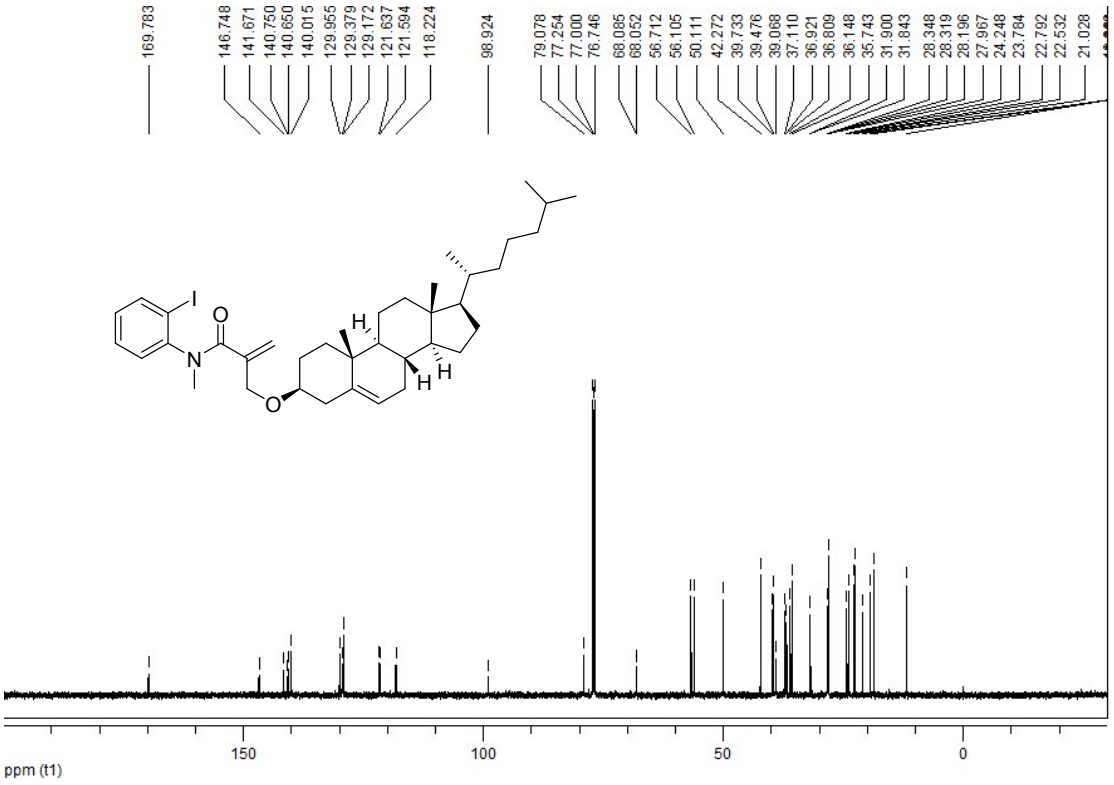


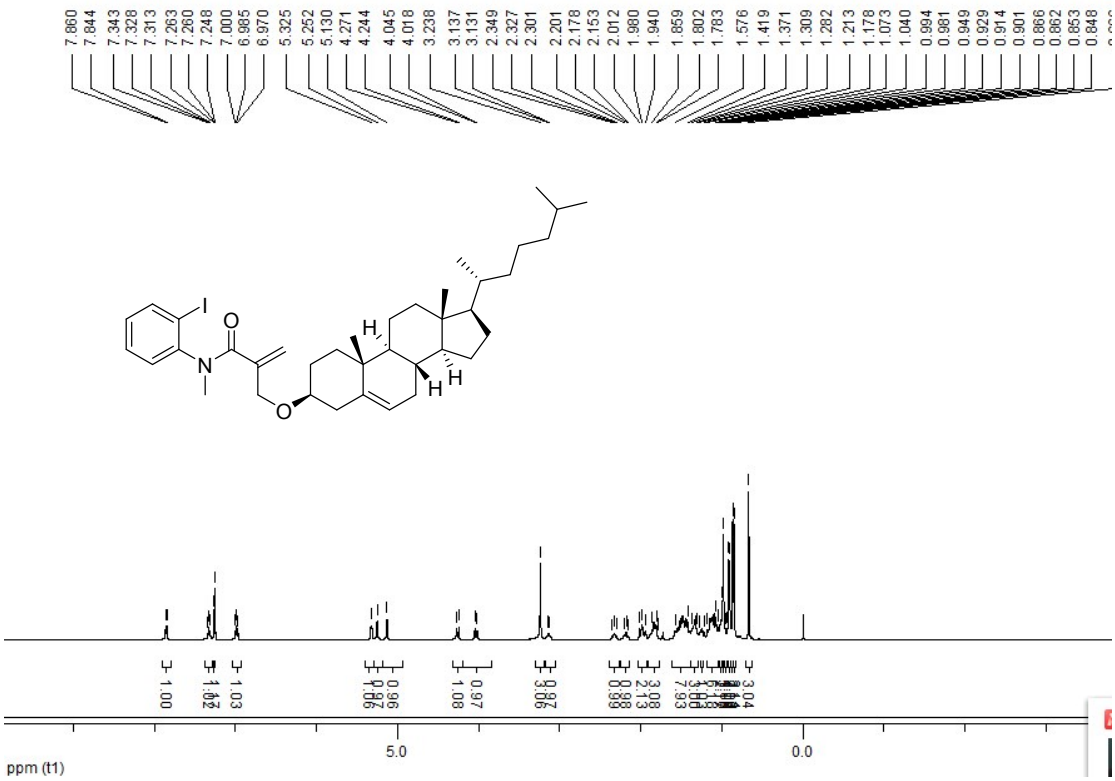
N-(2-iodophenyl)-N-methyl-2-((((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)methyl)acrylamide (1y):



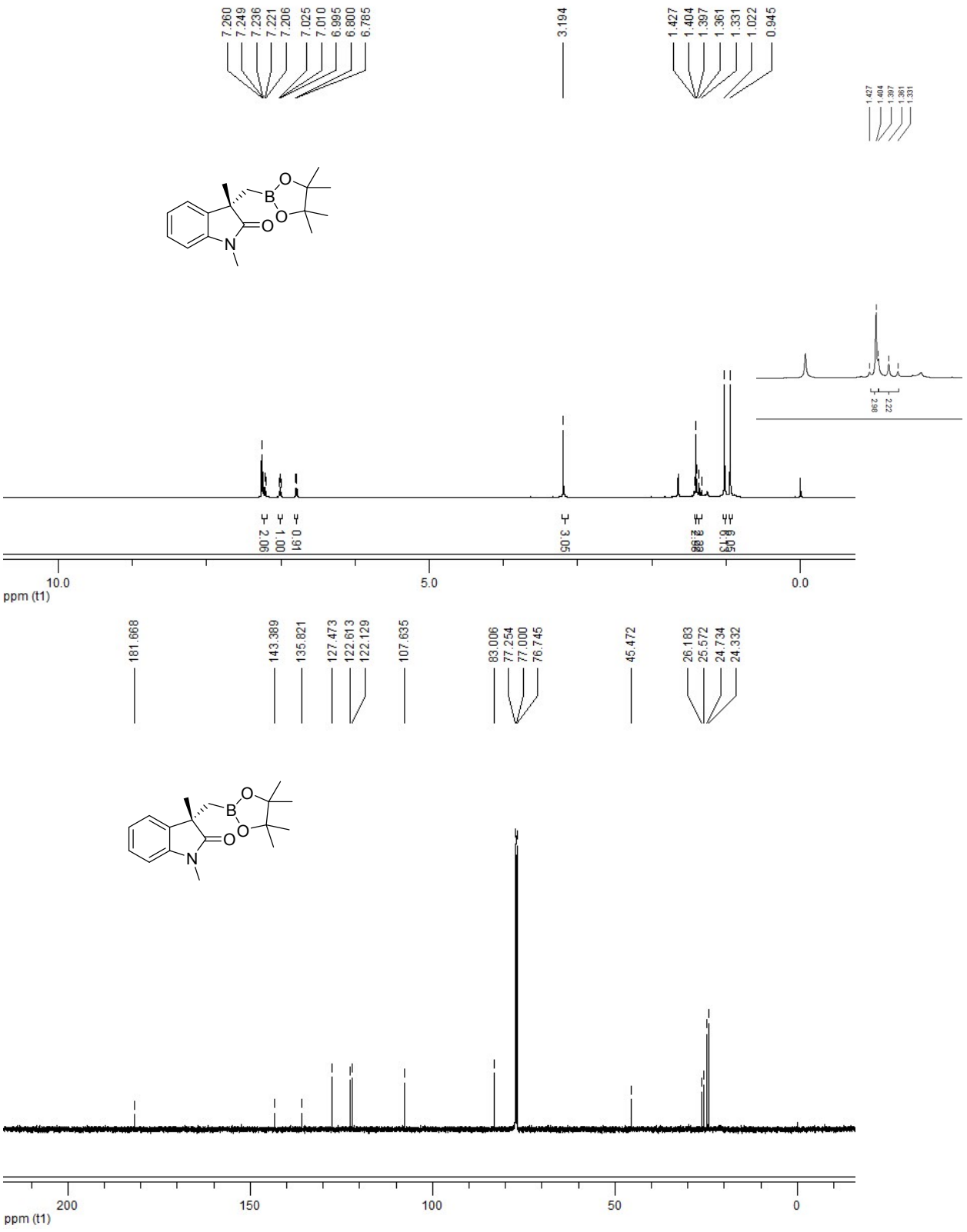


2-((((3S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)methyl)-N-(2-iodophenyl)-N-methylacrylamide (1z):

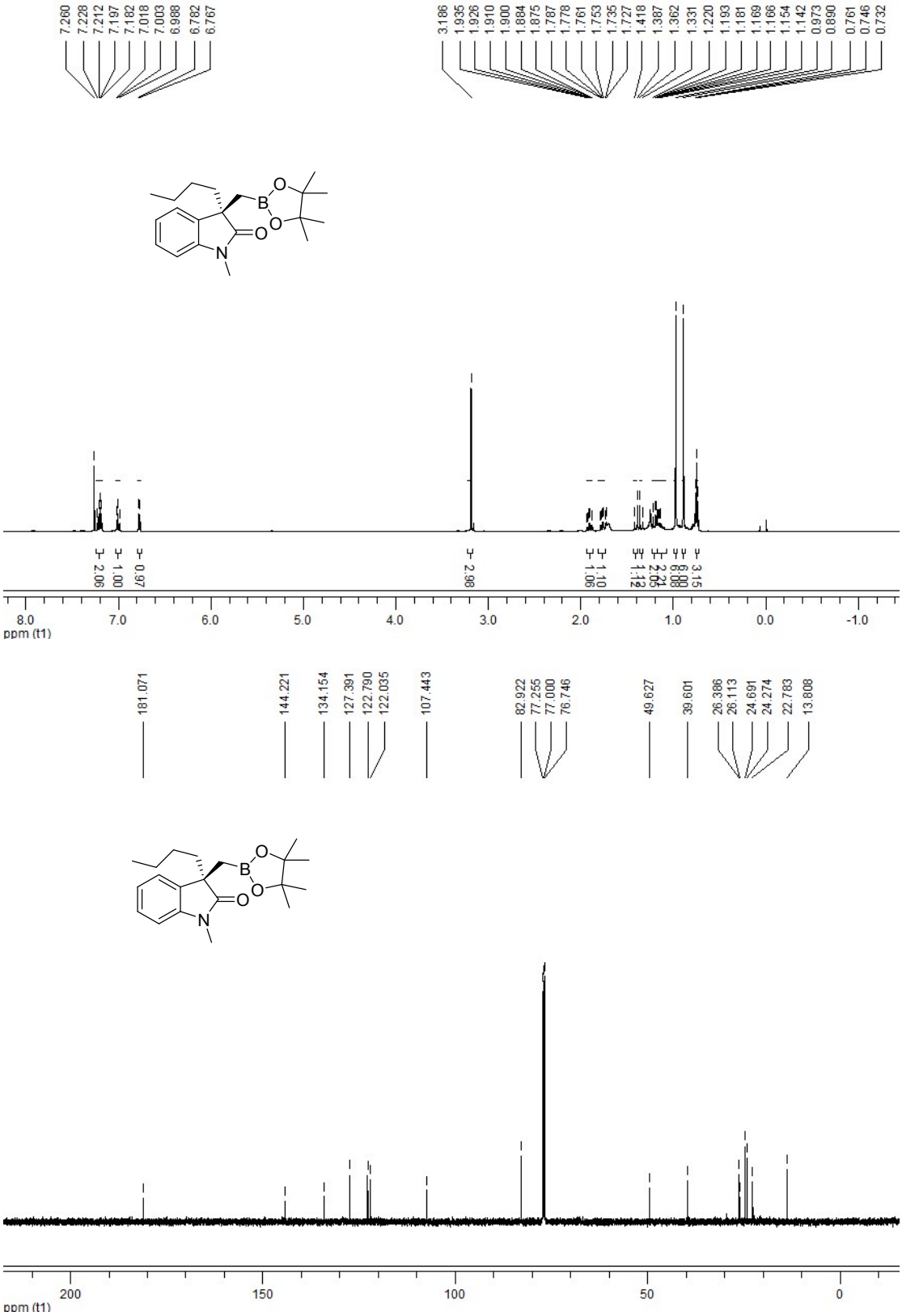




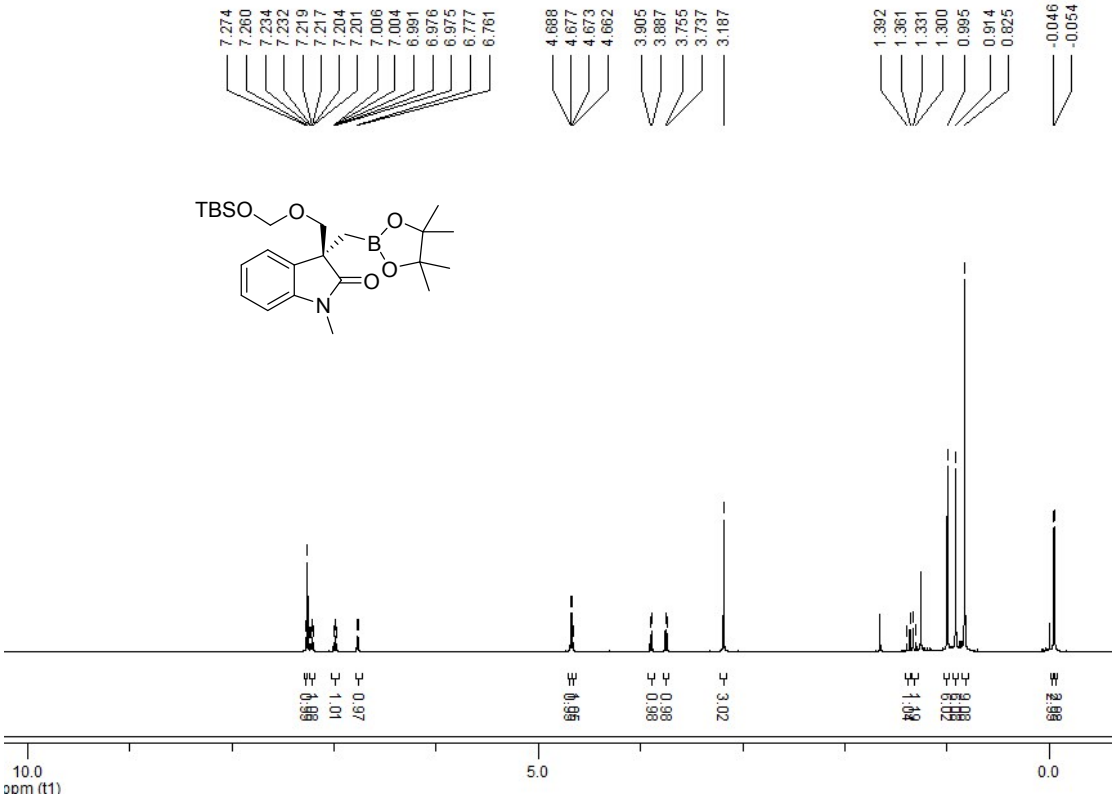
(S)-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3a):

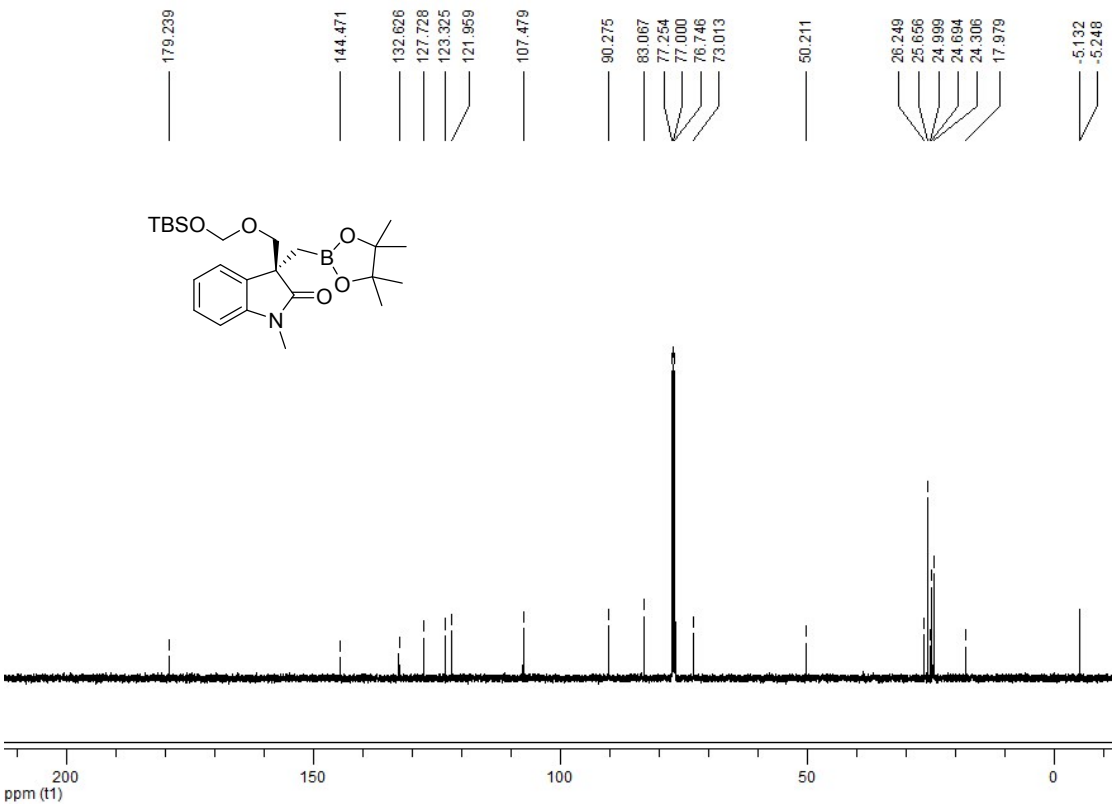


(S)-3-butyl-1-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3b):

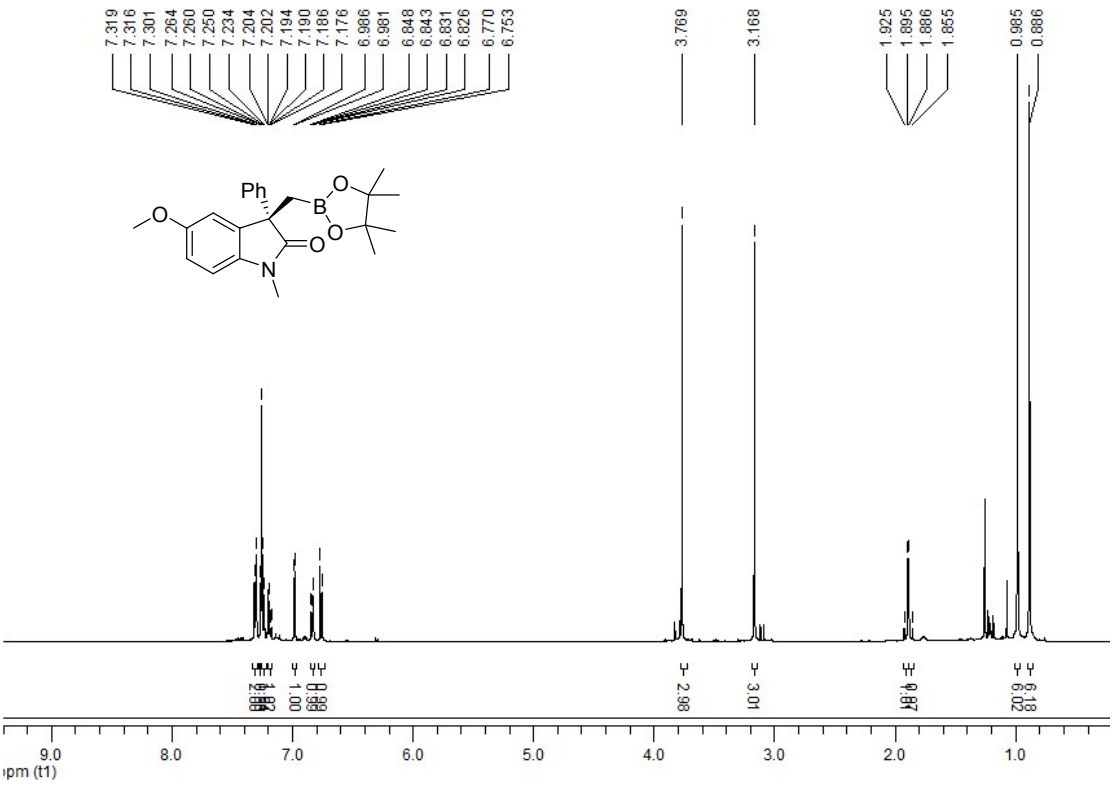


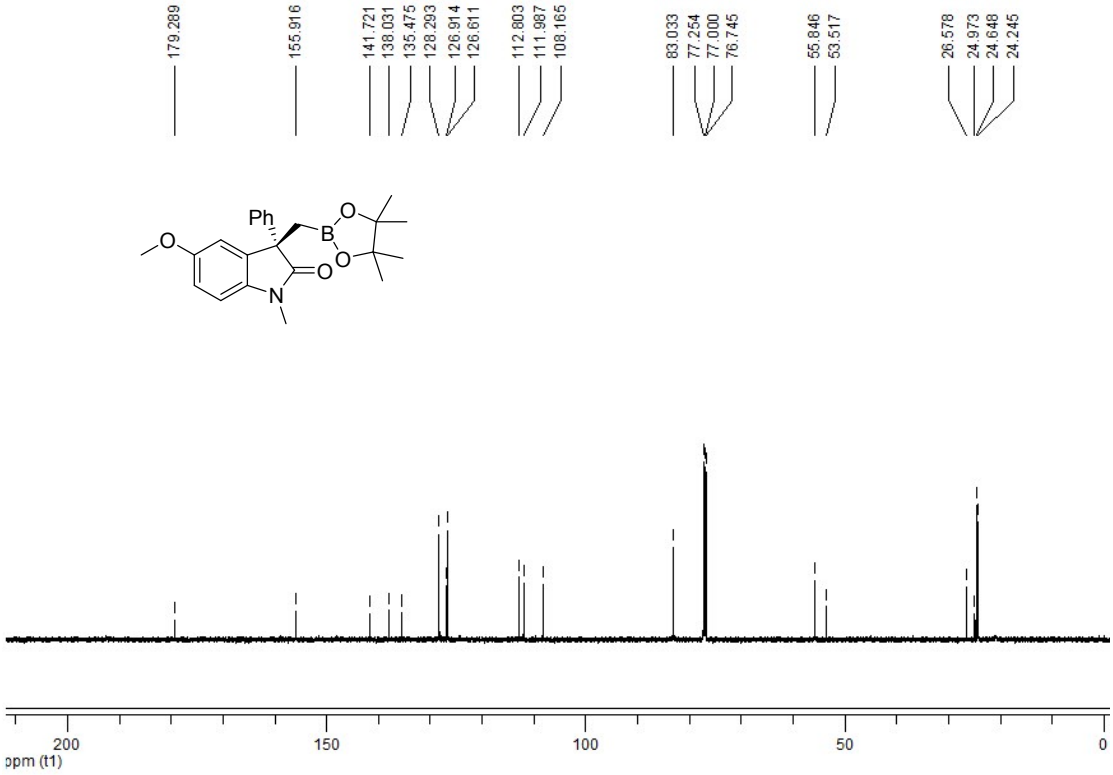
(S)-3-((((tert-butyldimethylsilyl)oxy)methoxy)methyl)-1-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3d):



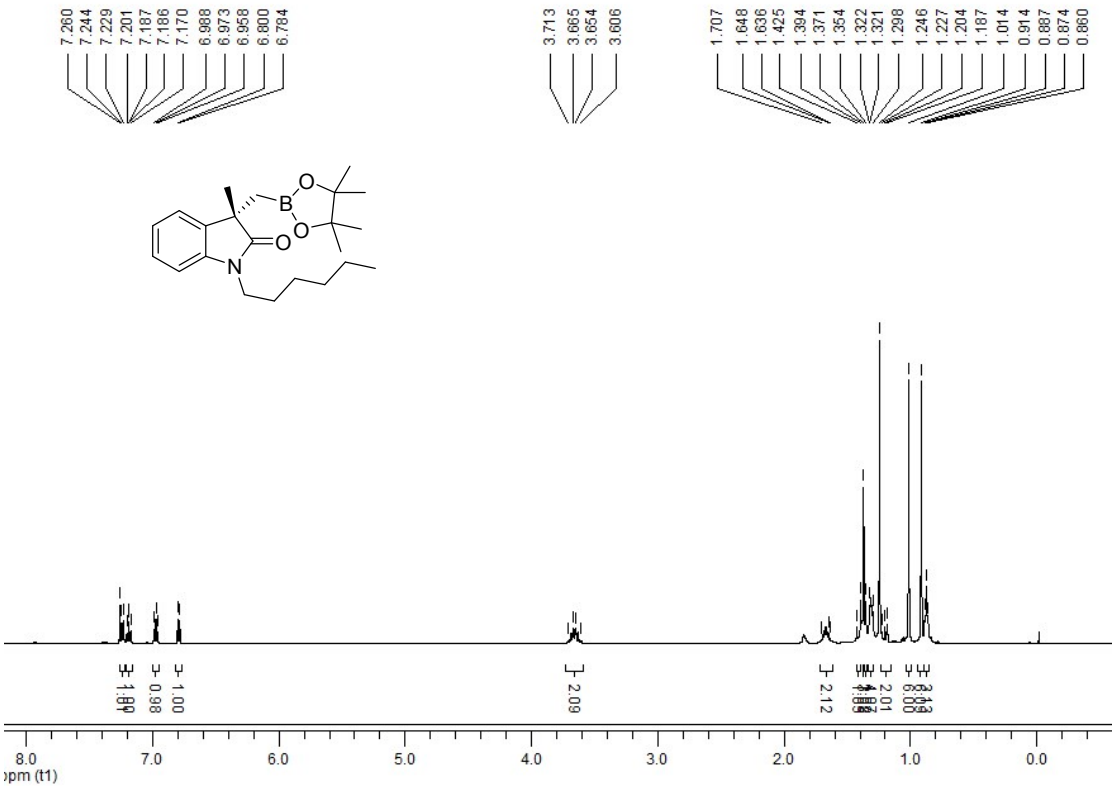


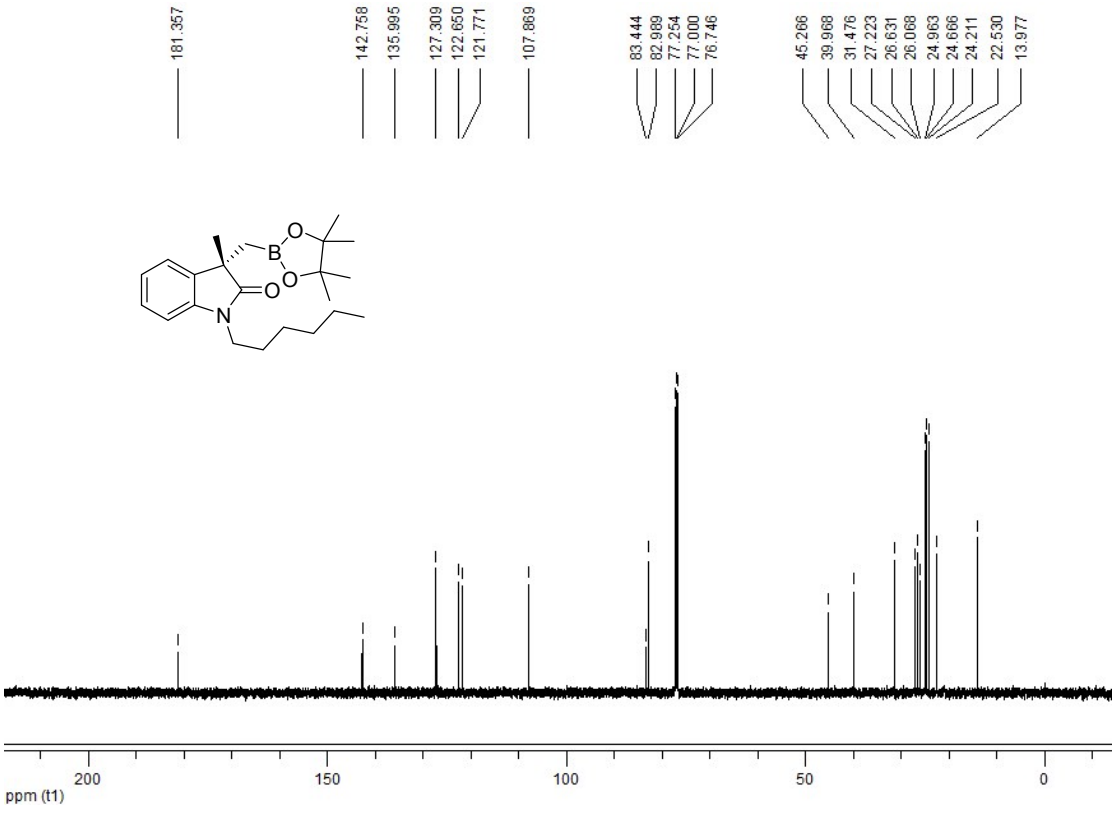
(S)-5-methoxy-1-methyl-3-phenyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3e):



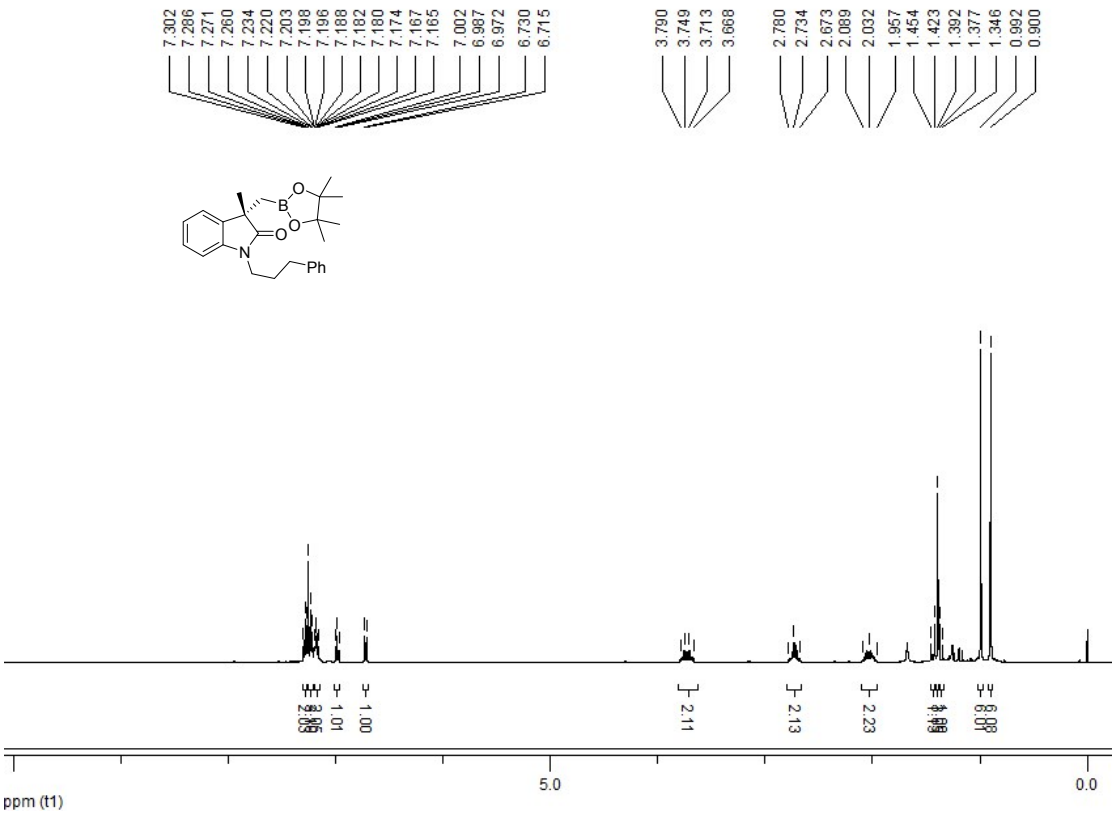


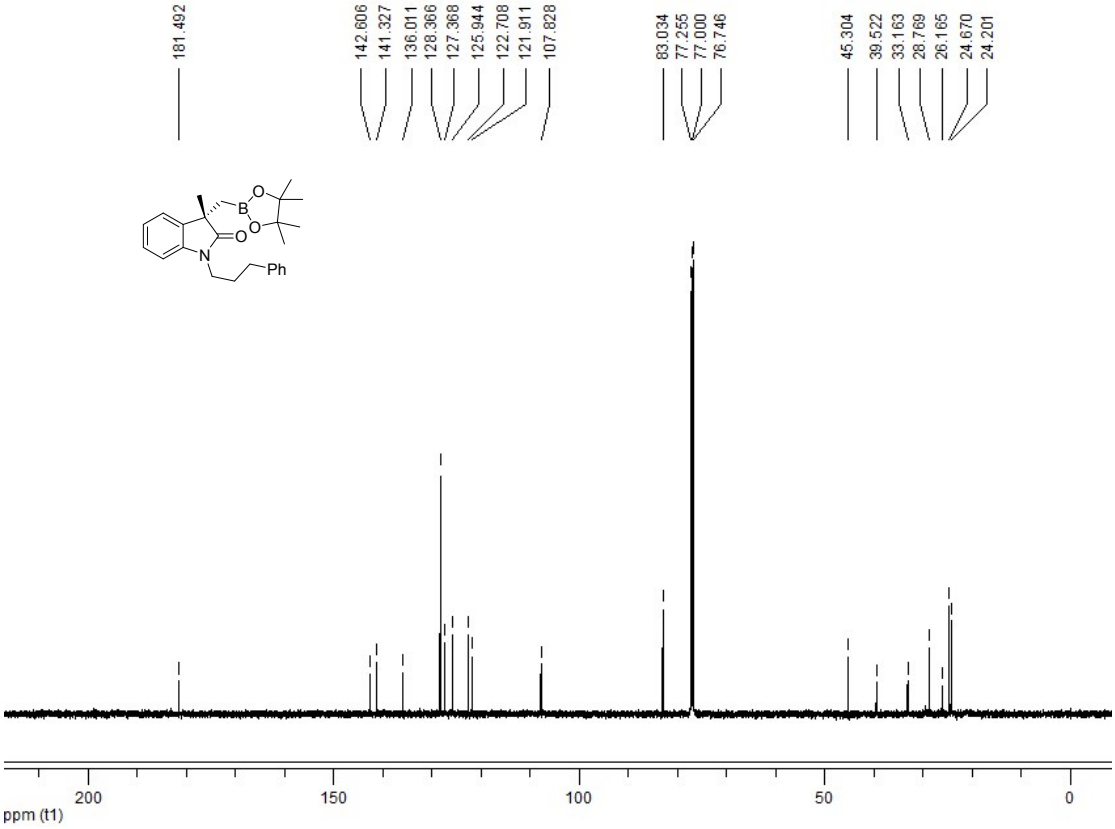
(S)-1-hexyl-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3f):



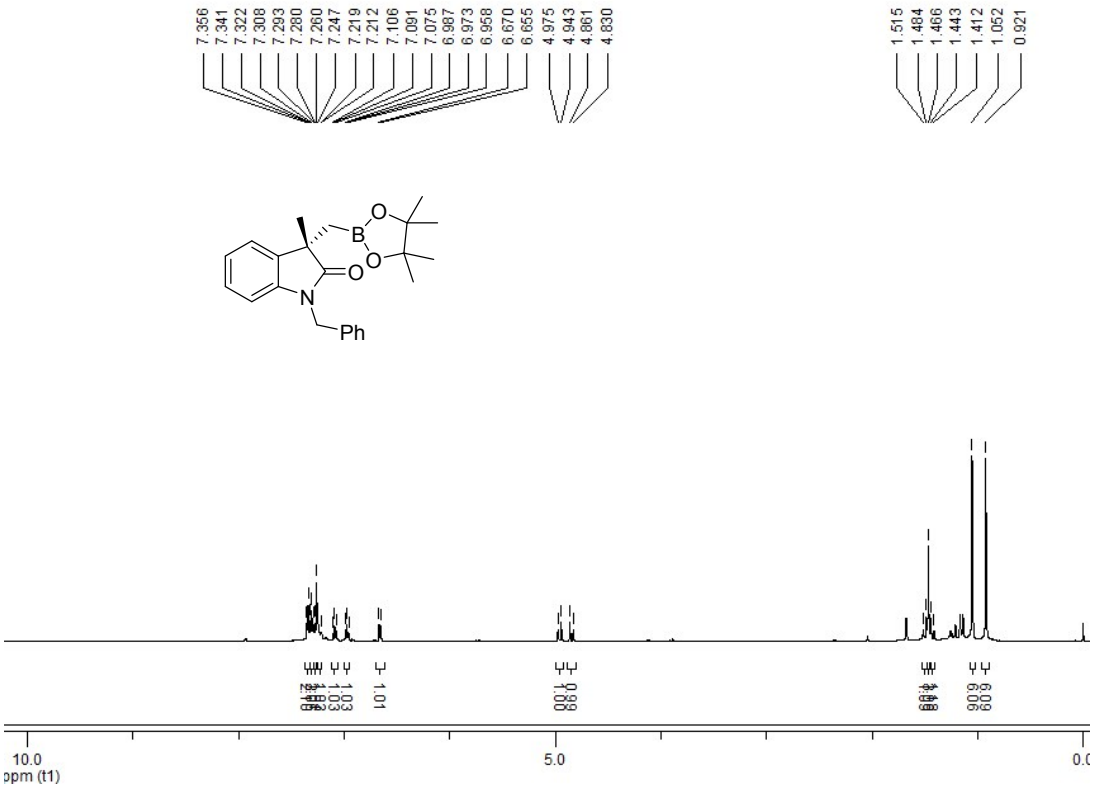


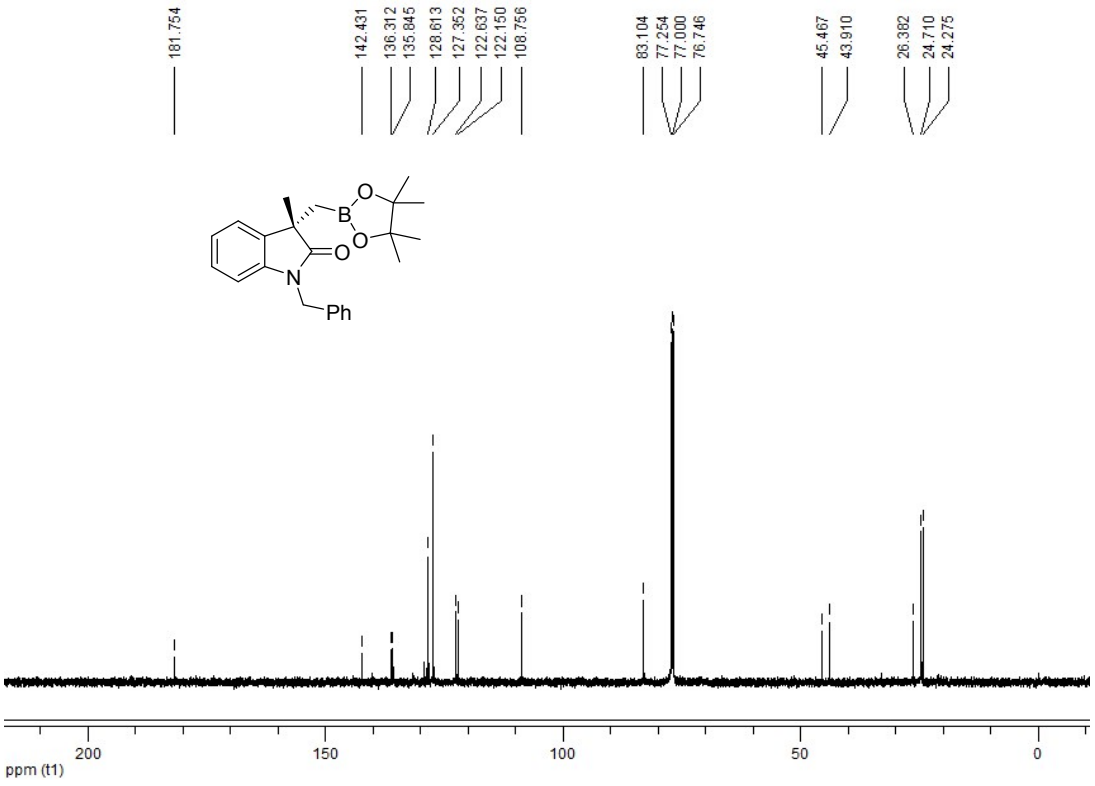
(S)-3-methyl-1-(3-phenylpropyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3g):



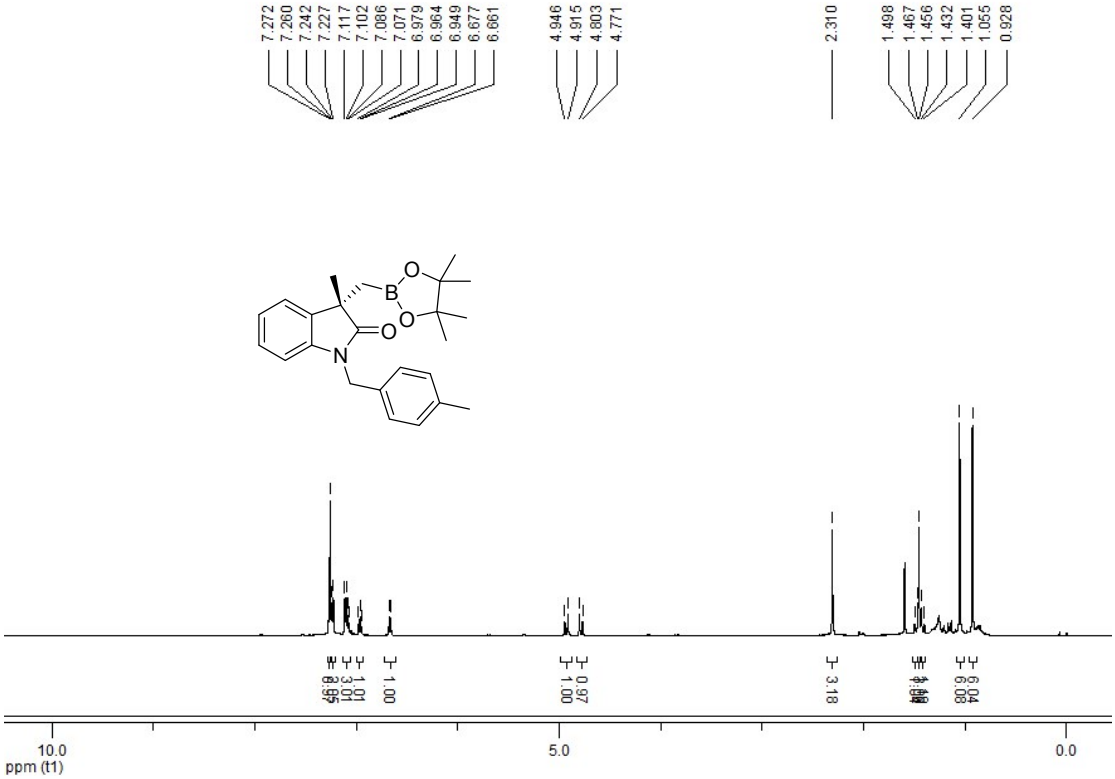


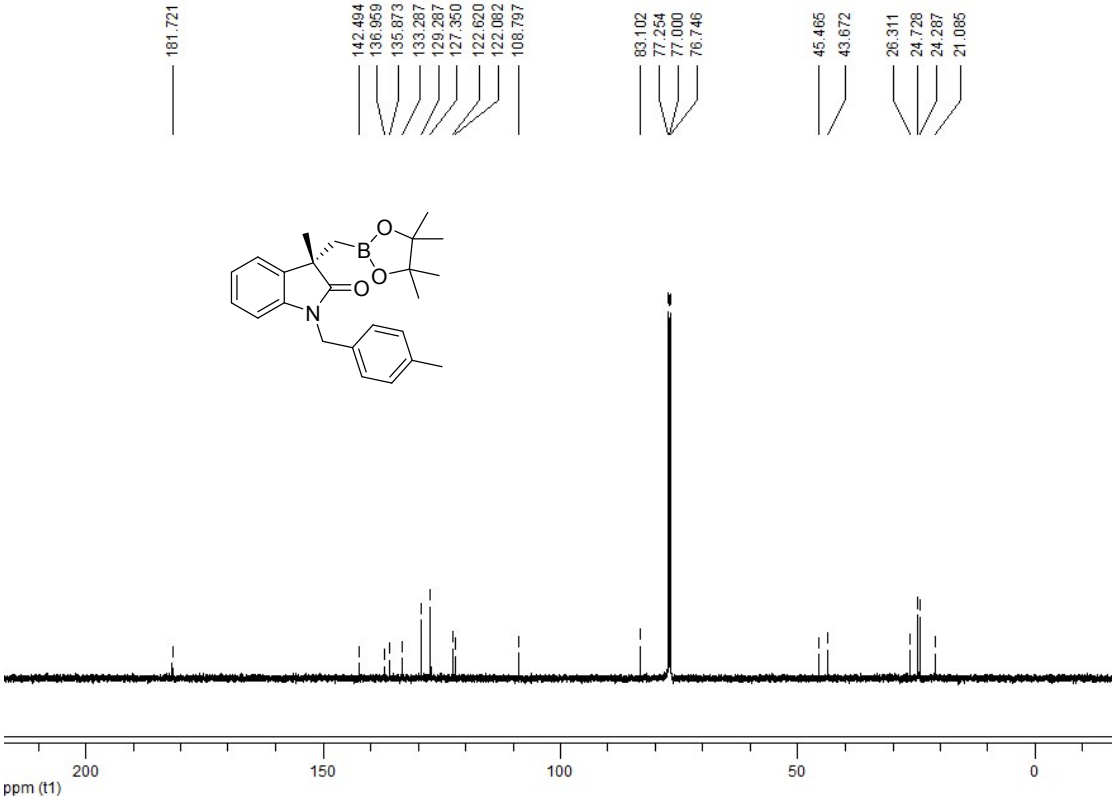
(S)-1-benzyl-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3h):



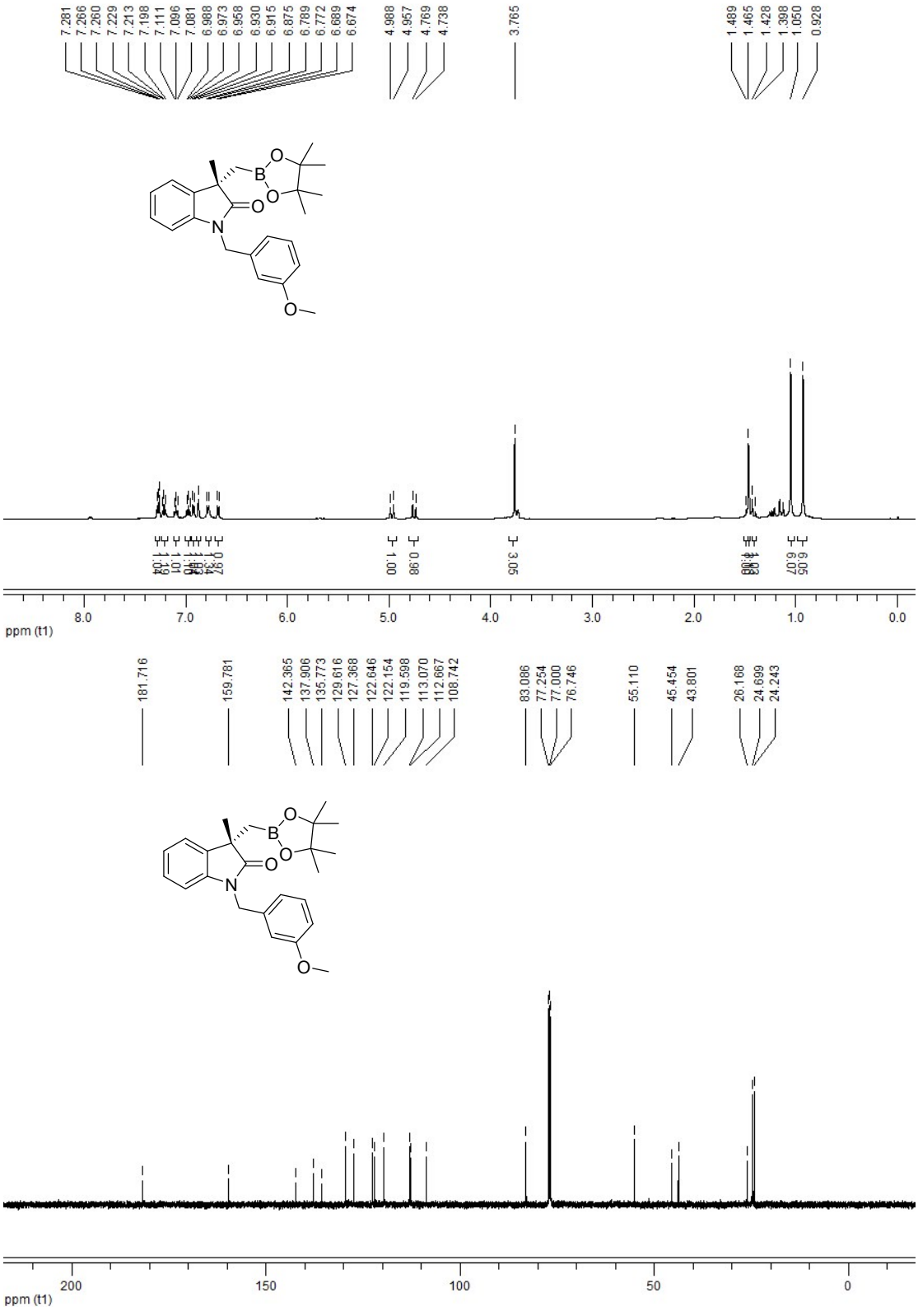


(S)-3-methyl-1-(4-methylbenzyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3i):

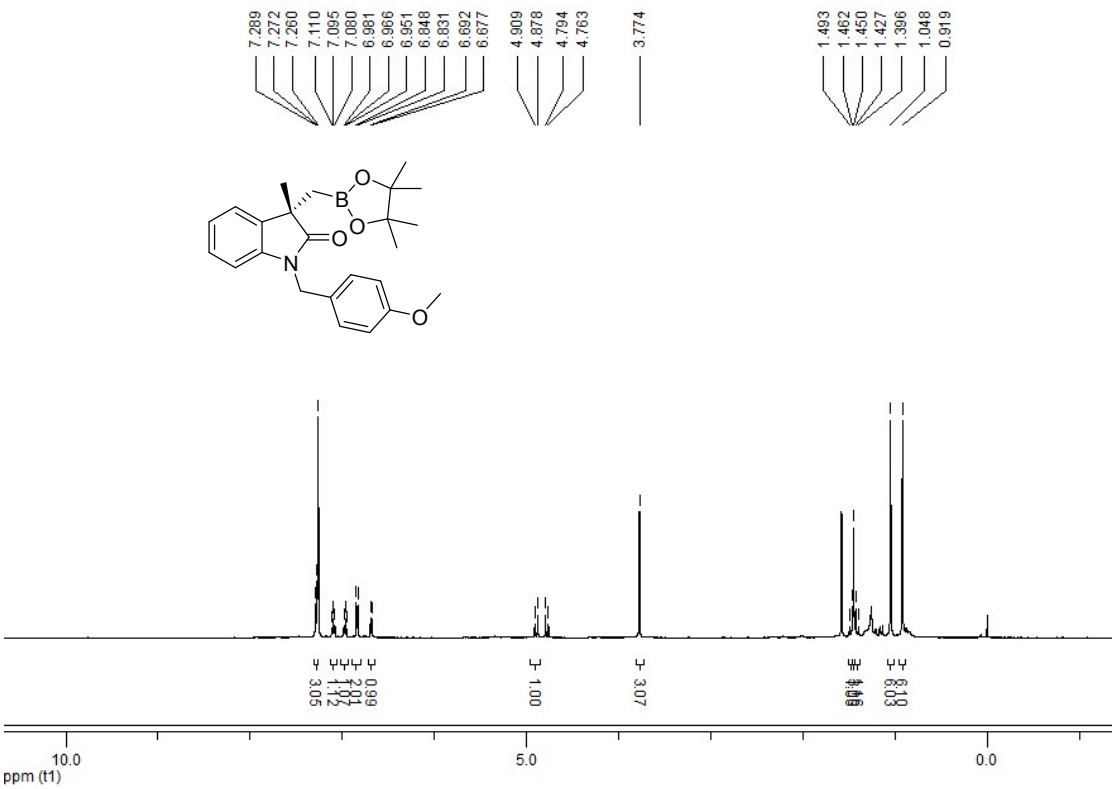


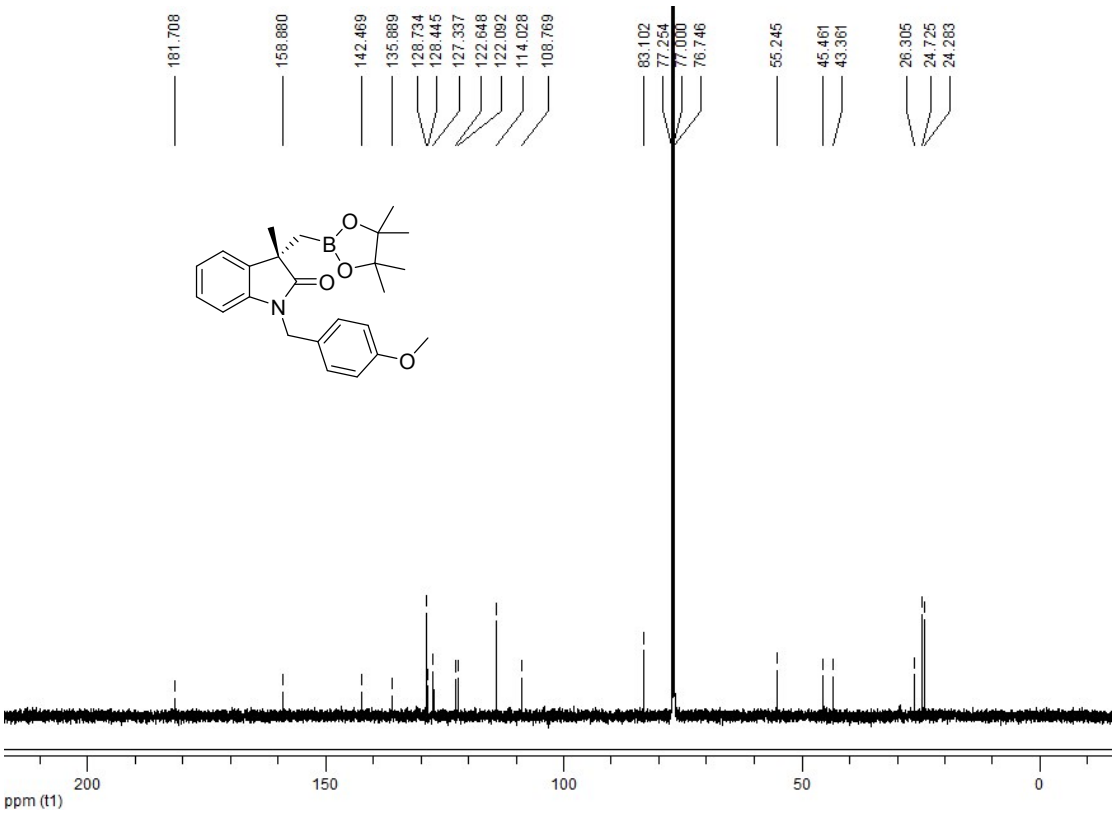


(S)-1-(3-methoxybenzyl)-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3j):

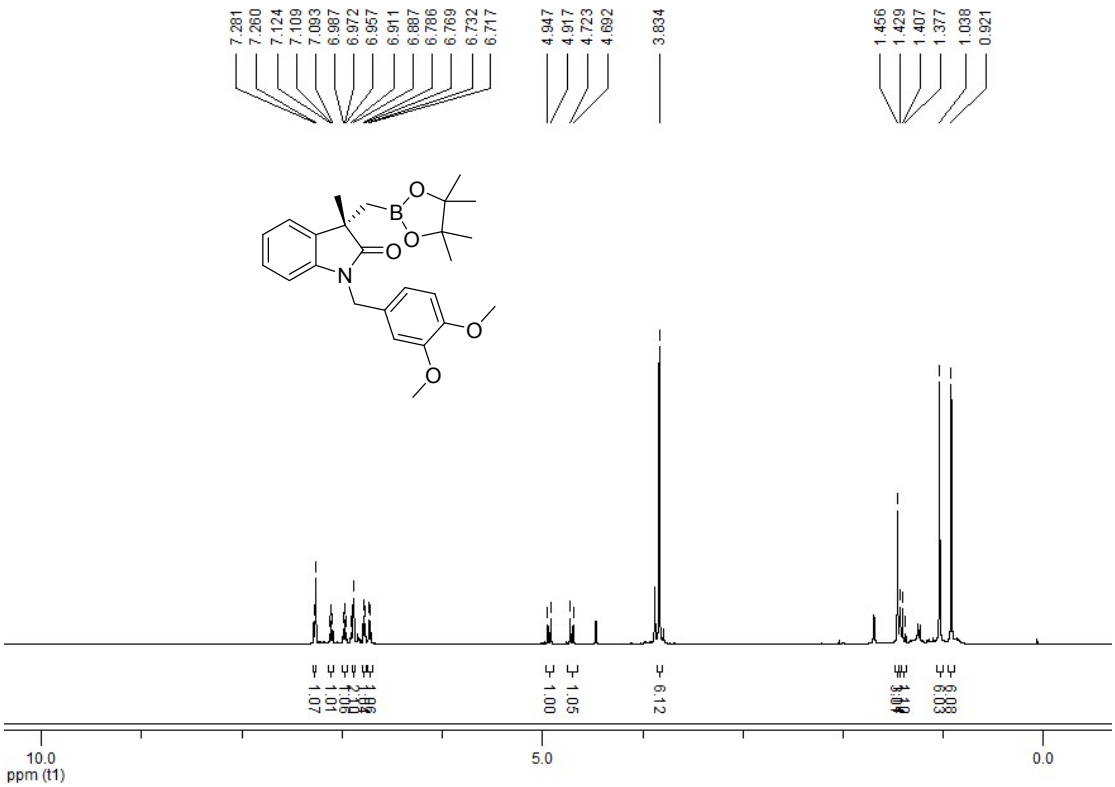


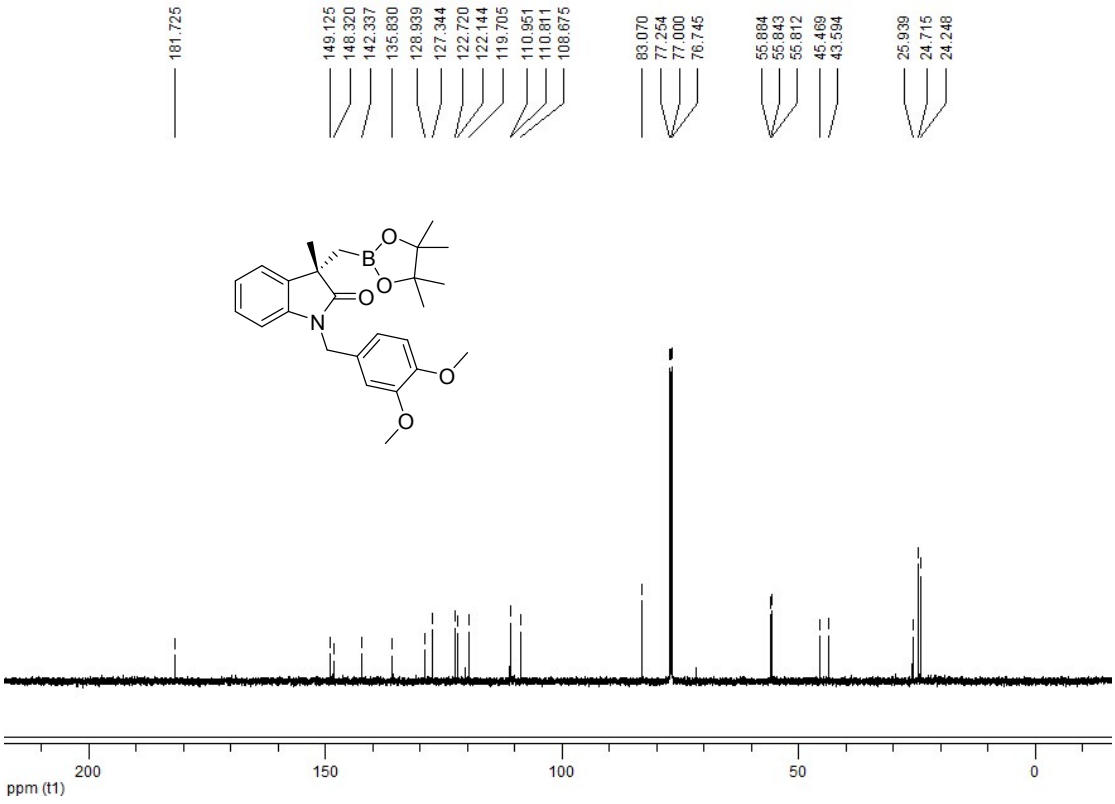
(S)-1-(4-methoxybenzyl)-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3k):



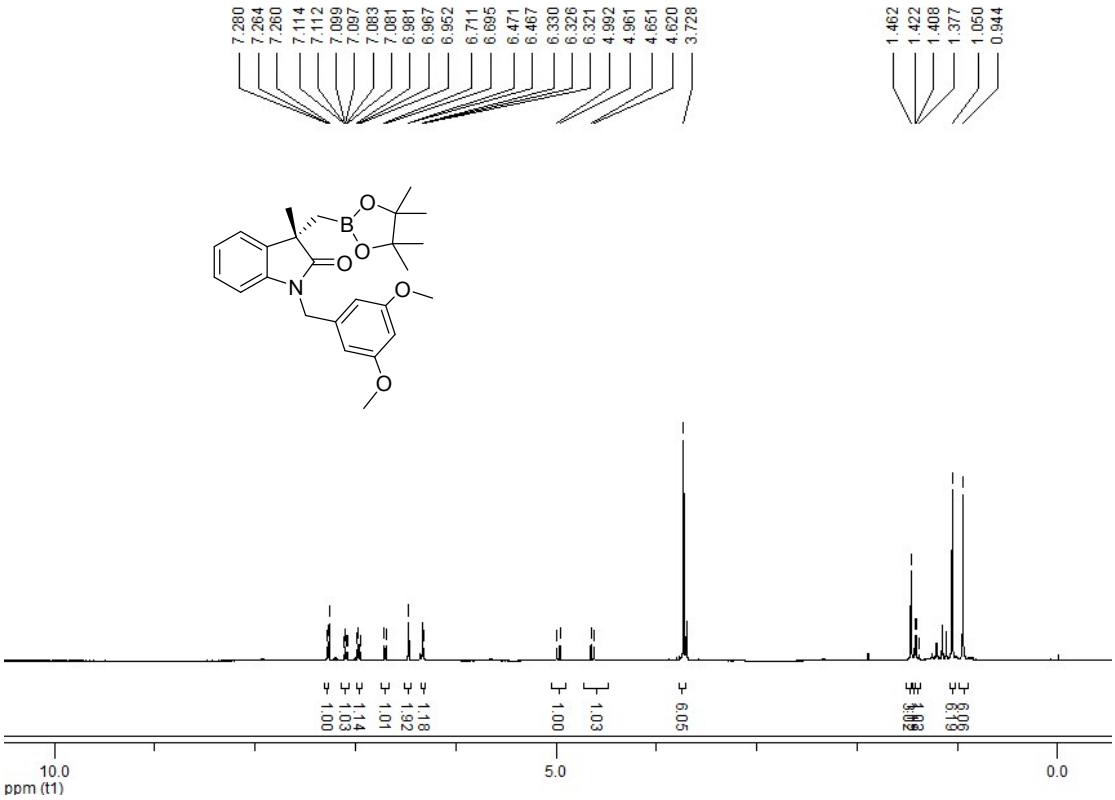


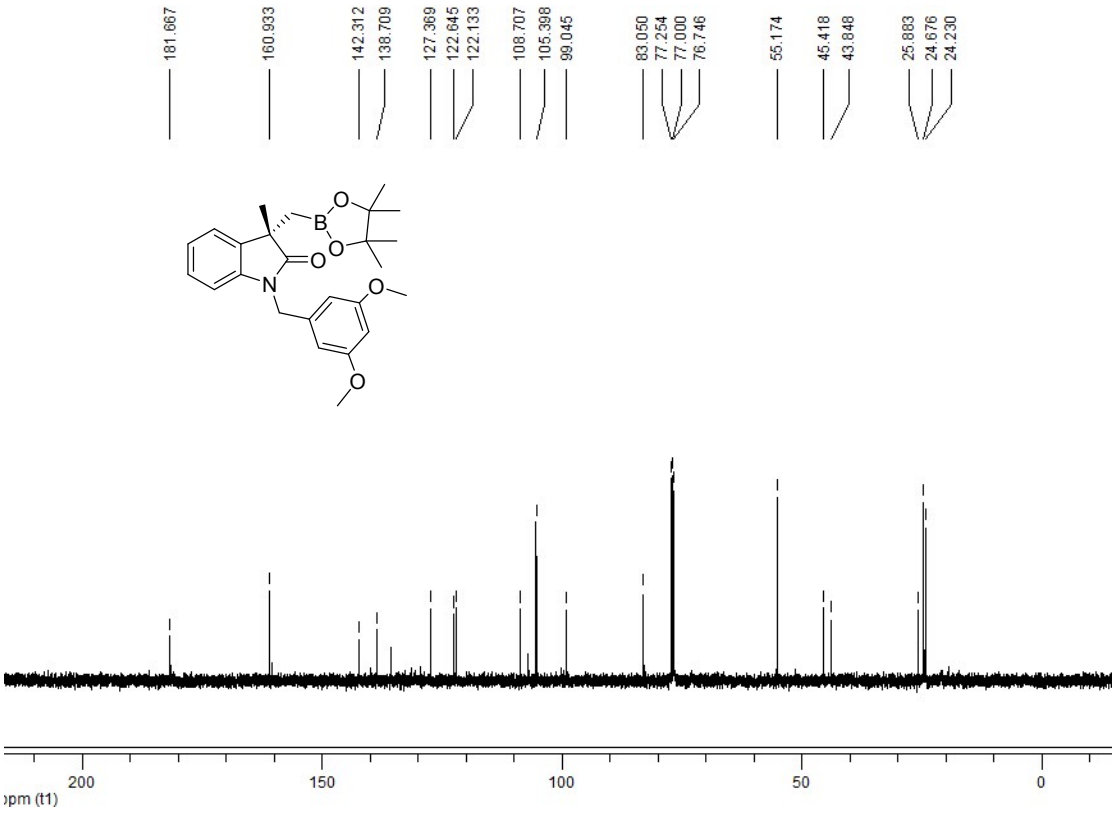
(S)-1-(3,4-dimethoxybenzyl)-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3l):



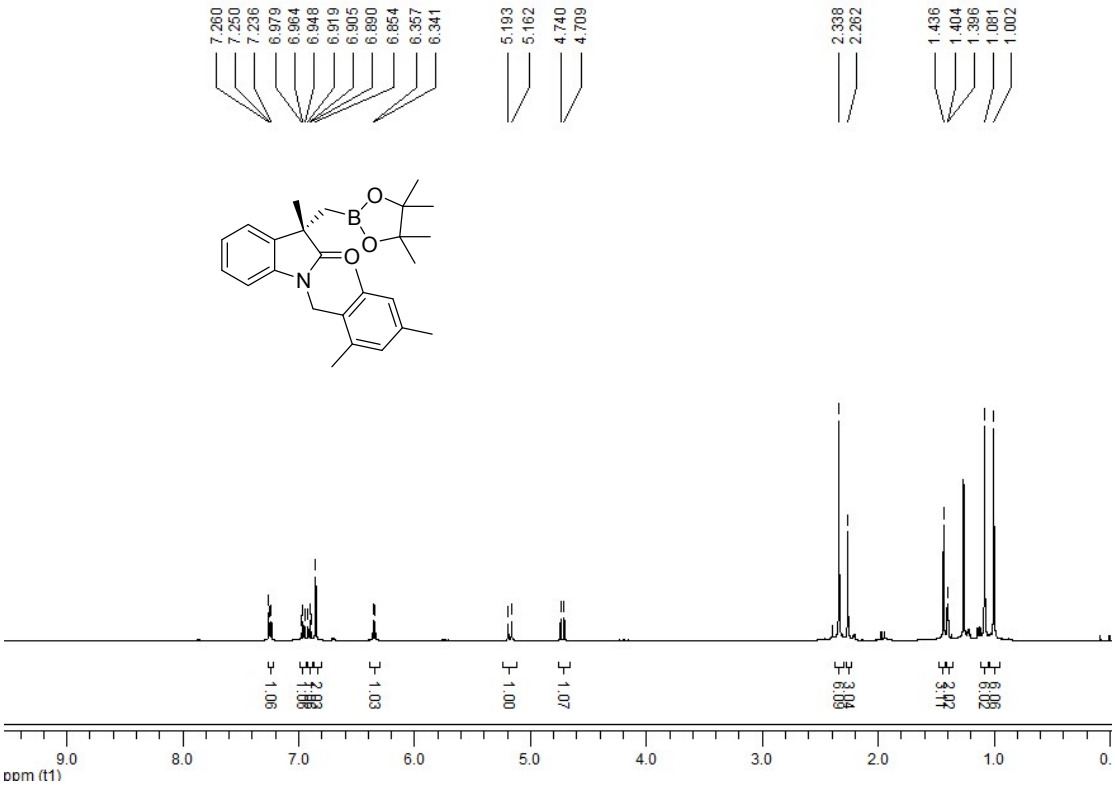


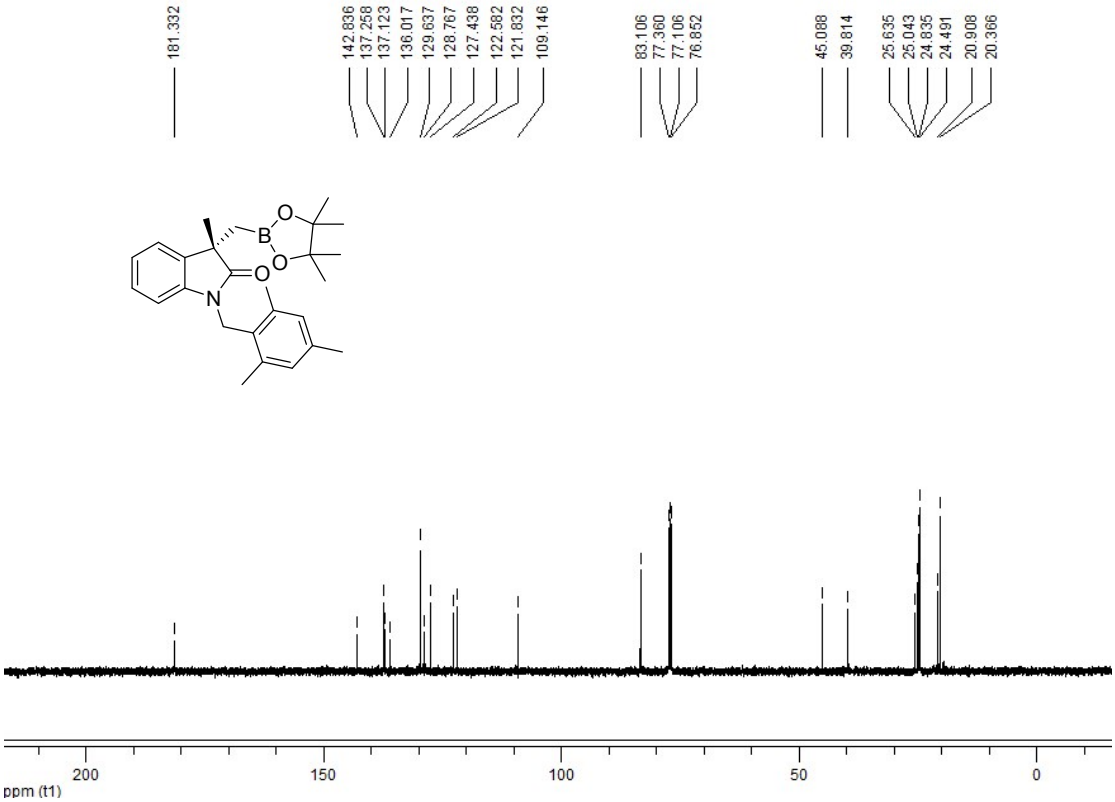
(S)-1-(3,5-dimethoxybenzyl)-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3m):



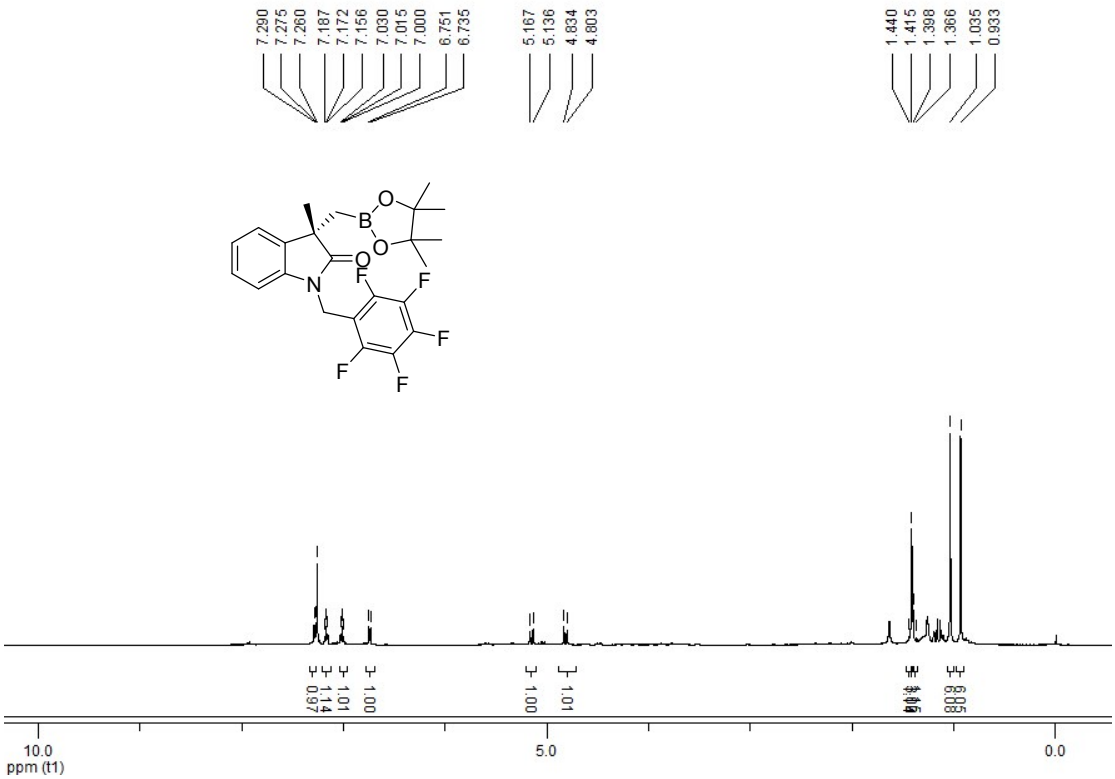


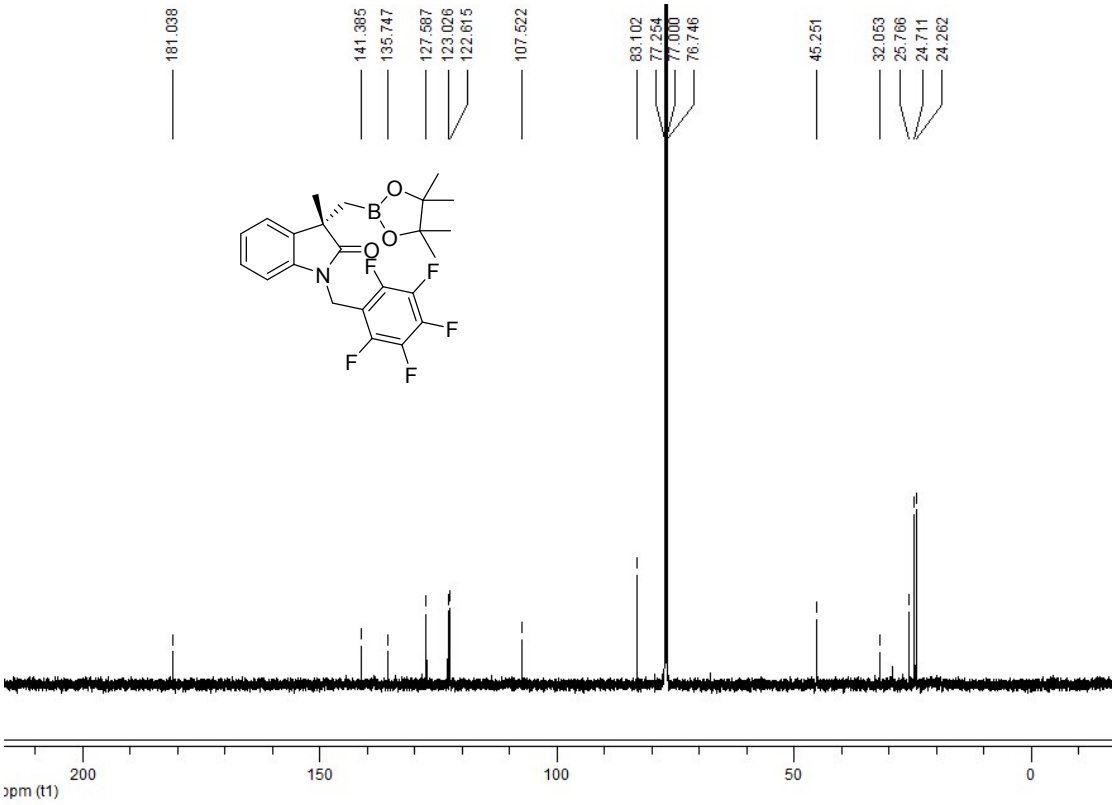
(S)-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-(2,4,6-trimethylbenzyl)indolin-2-one (3n):

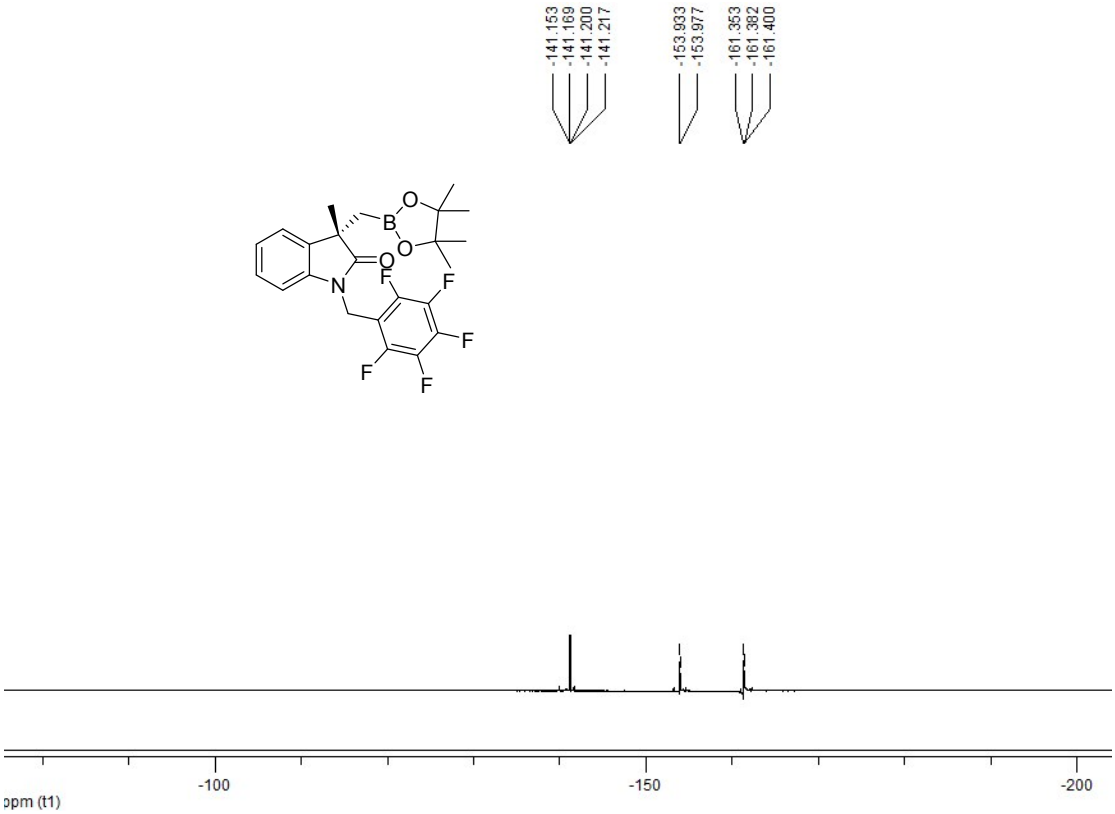




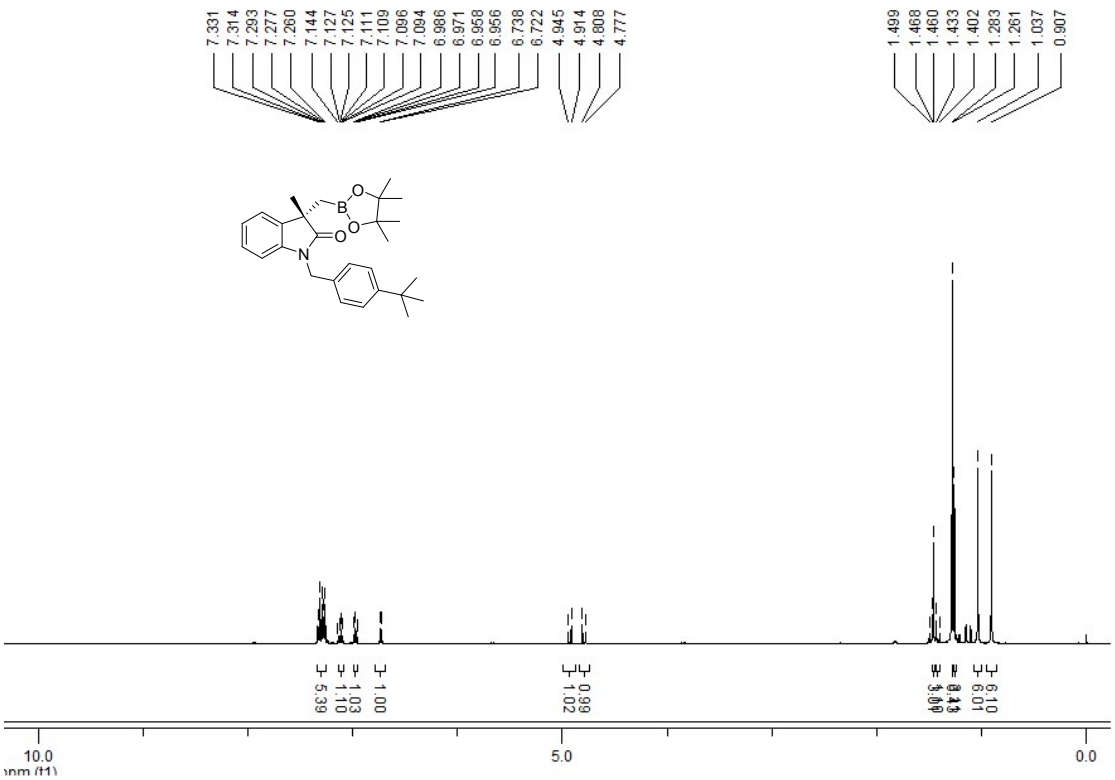
(S)-3-methyl-1-((perfluorophenyl)methyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3o):

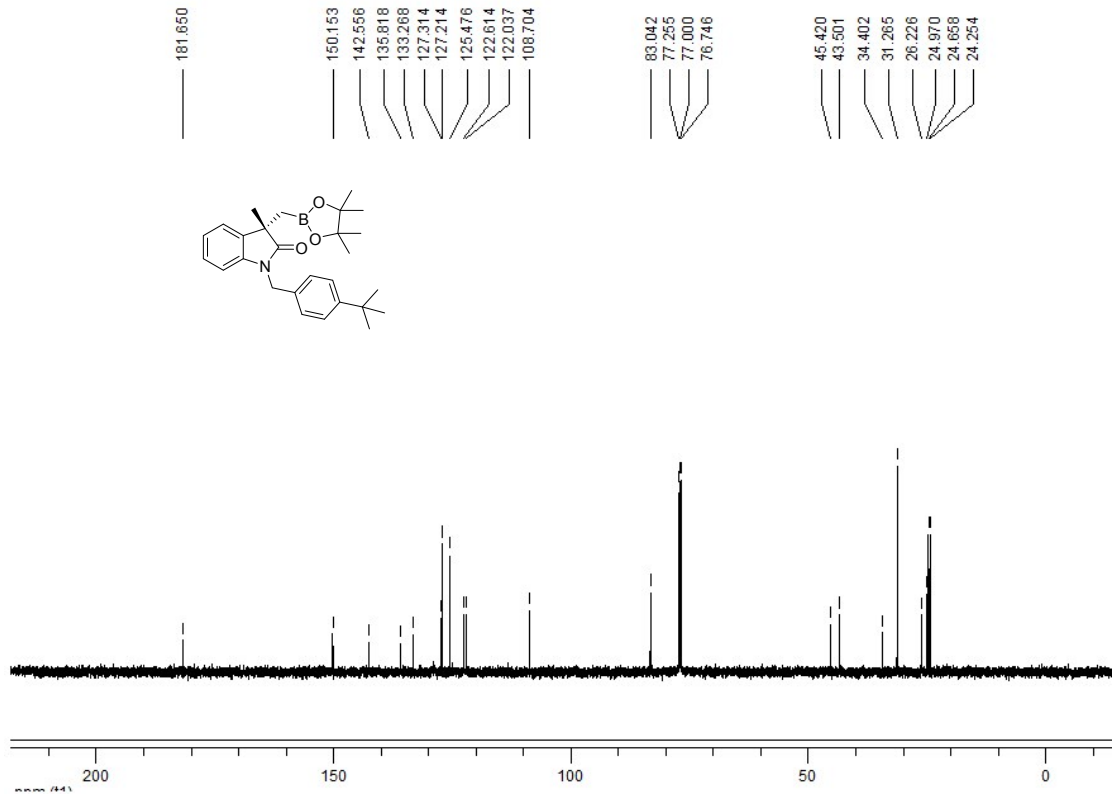




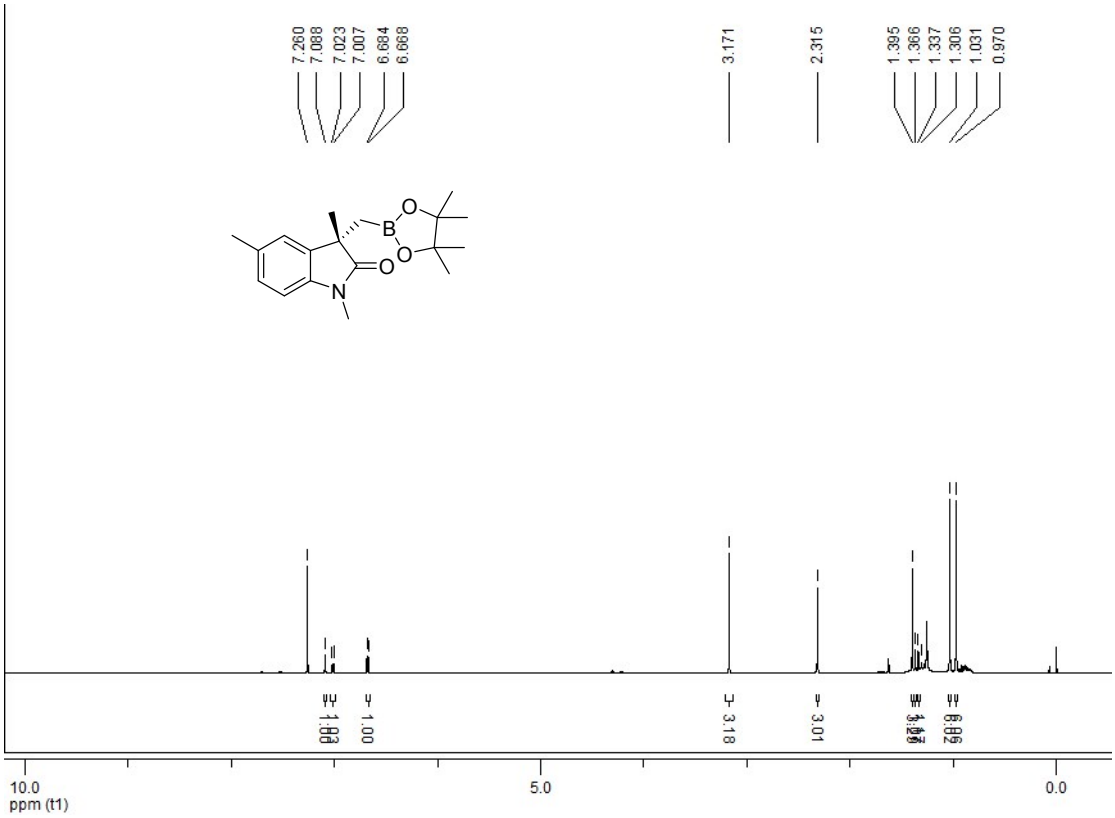

-141.153
-141.169
-141.200
-141.217
-153.933
-153.977
-161.353
-161.382
-161.400
O
B
O
O
N
F
F
F
F
F
-100
-150
-200
ppm (t1)

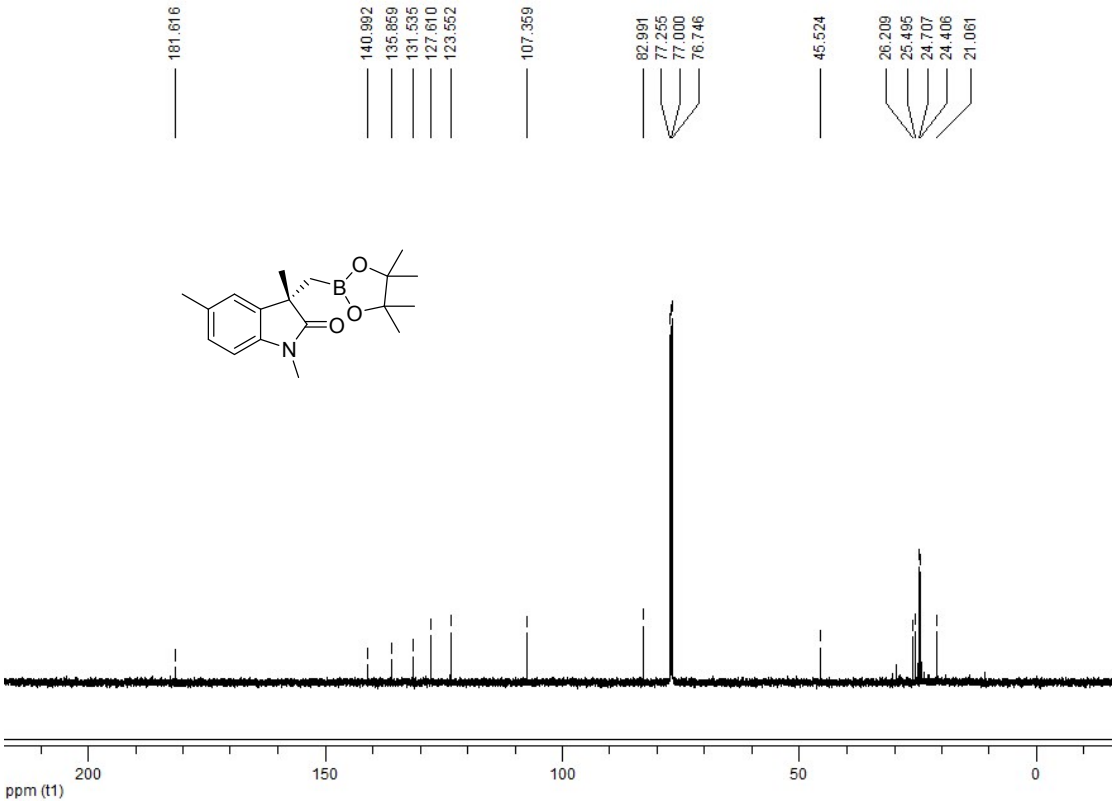
(S)-1-(4-(tert-butyl)benzyl)-3-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3p):



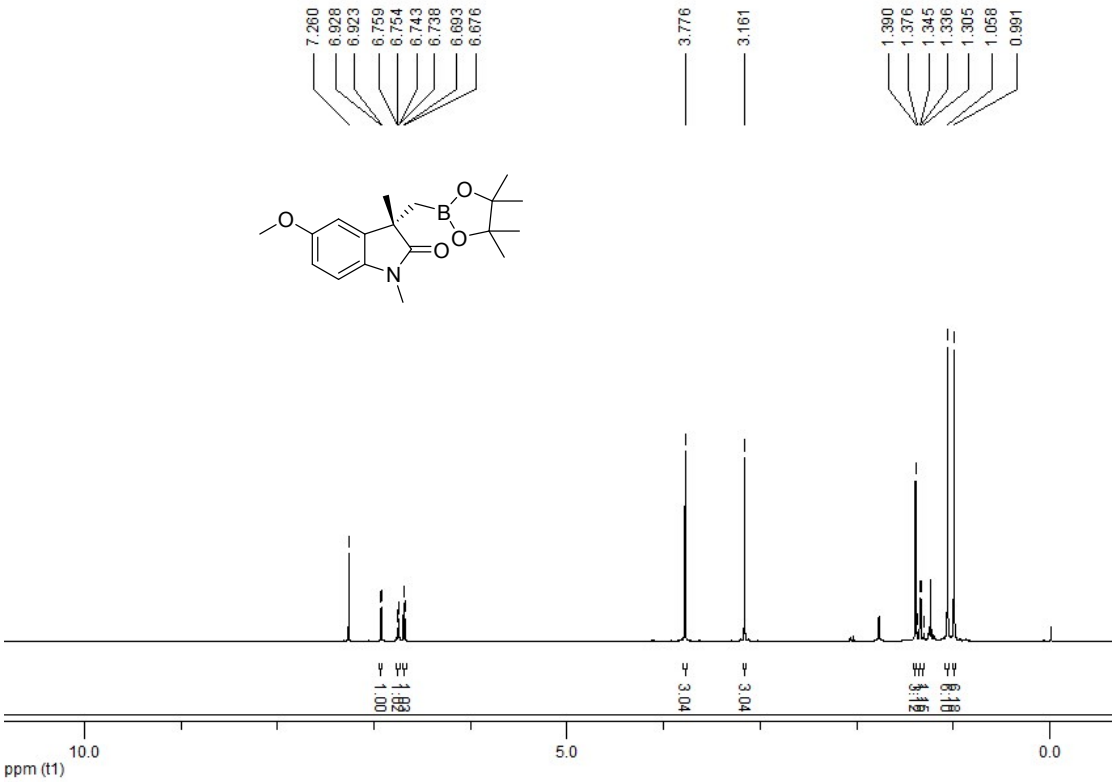


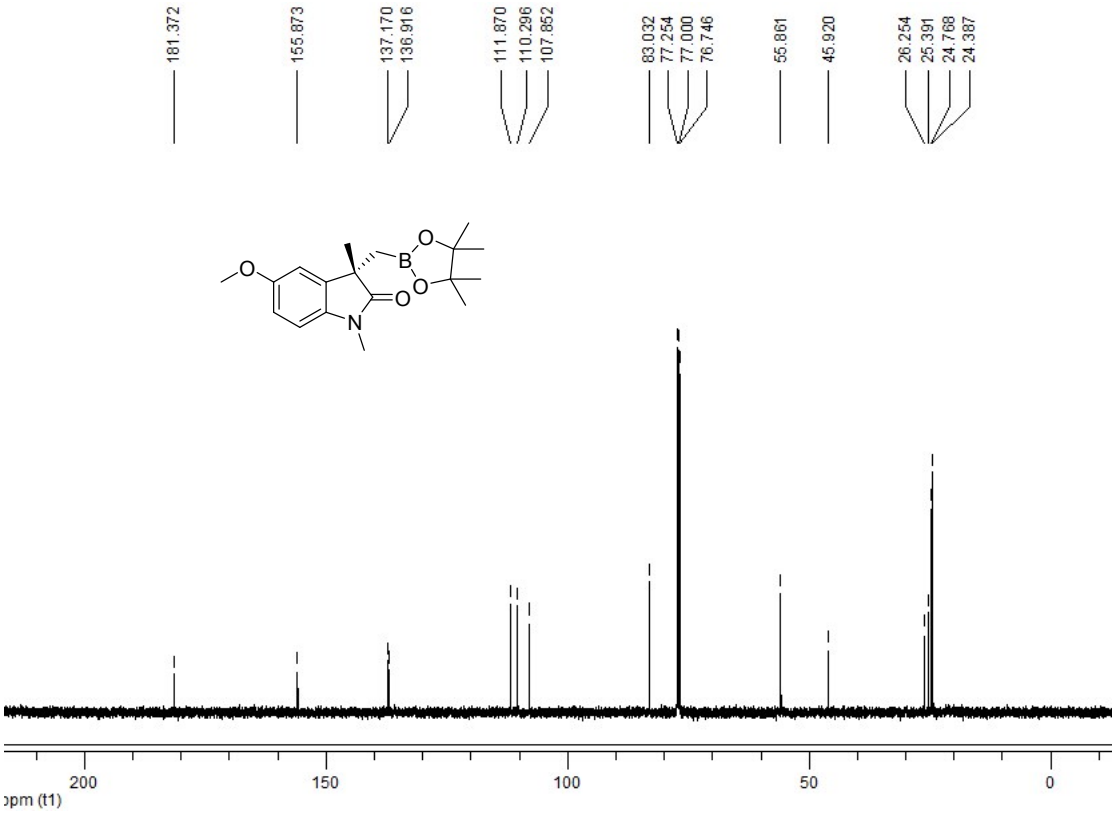
(S)-1,3,5-trimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3q):



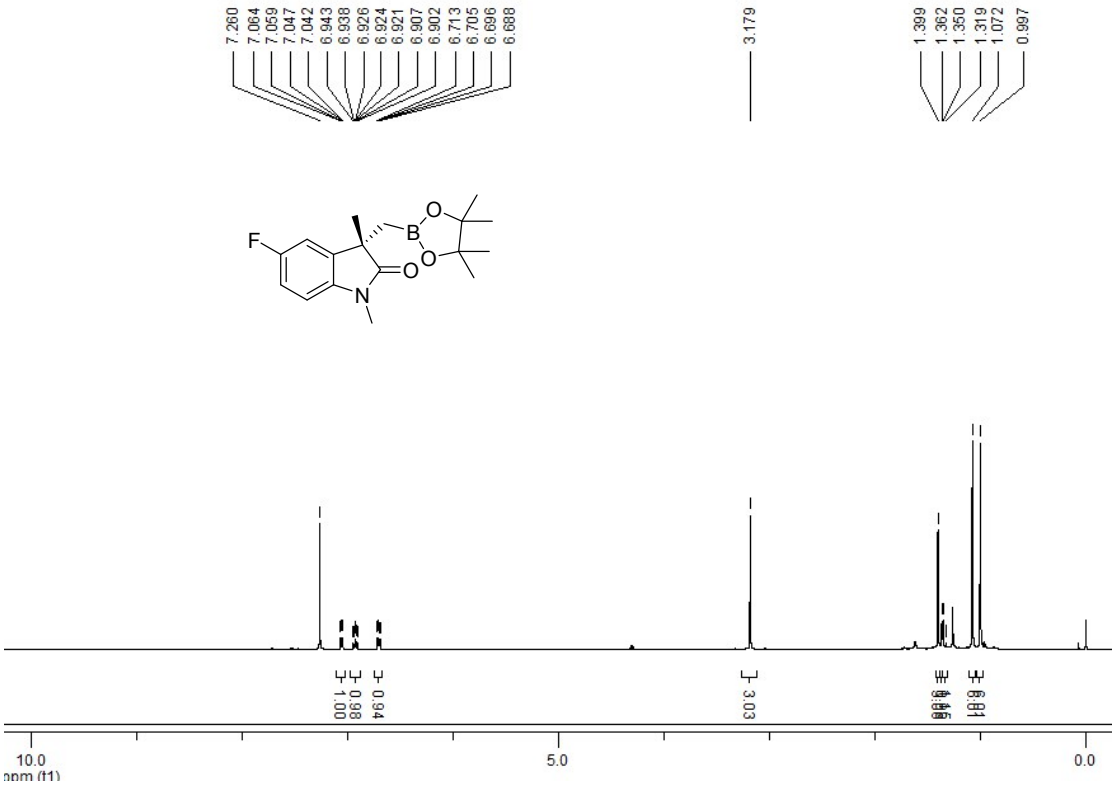


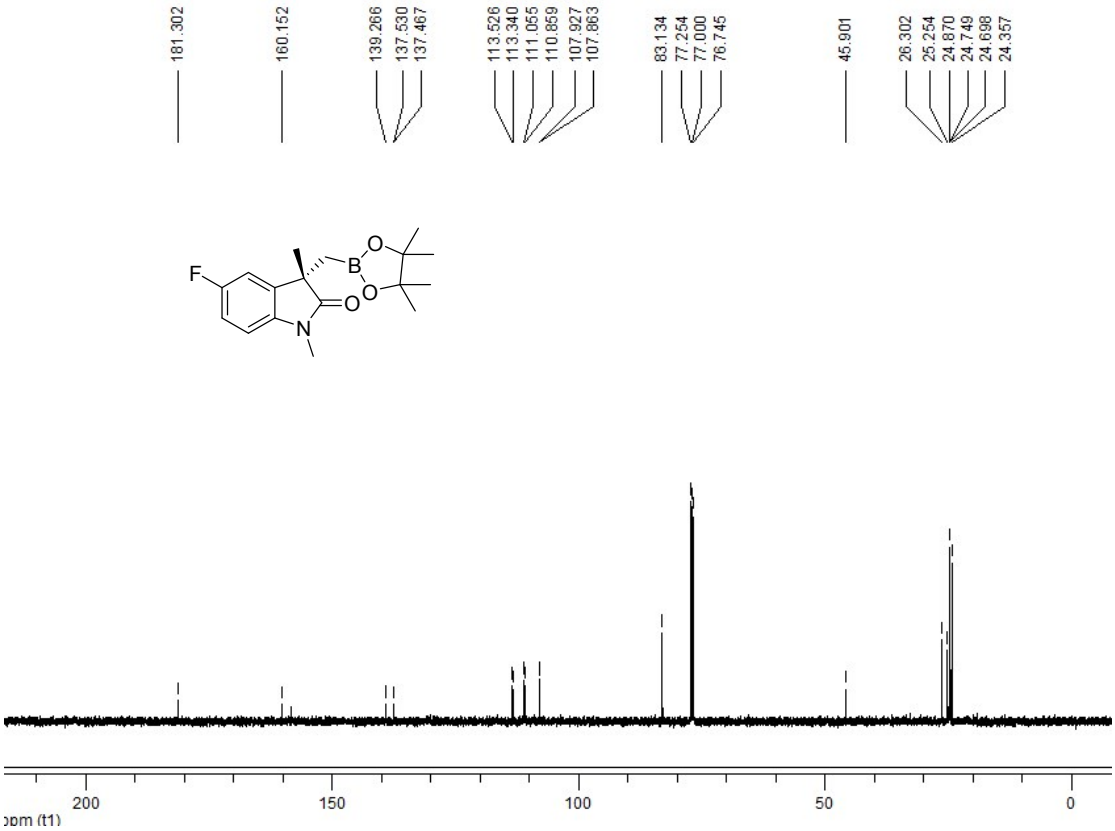
(S)-5-methoxy-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3r):

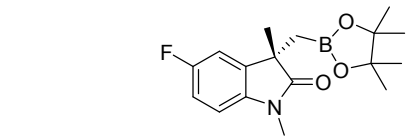




(S)-5-fluoro-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3s):

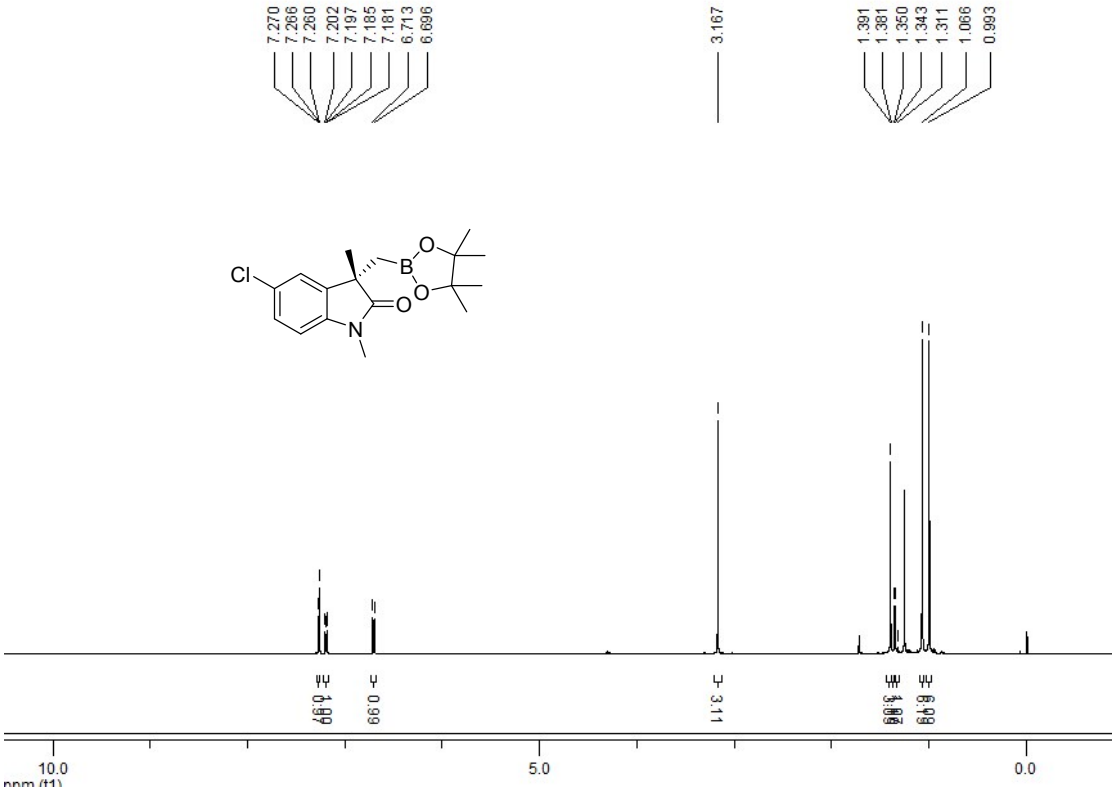


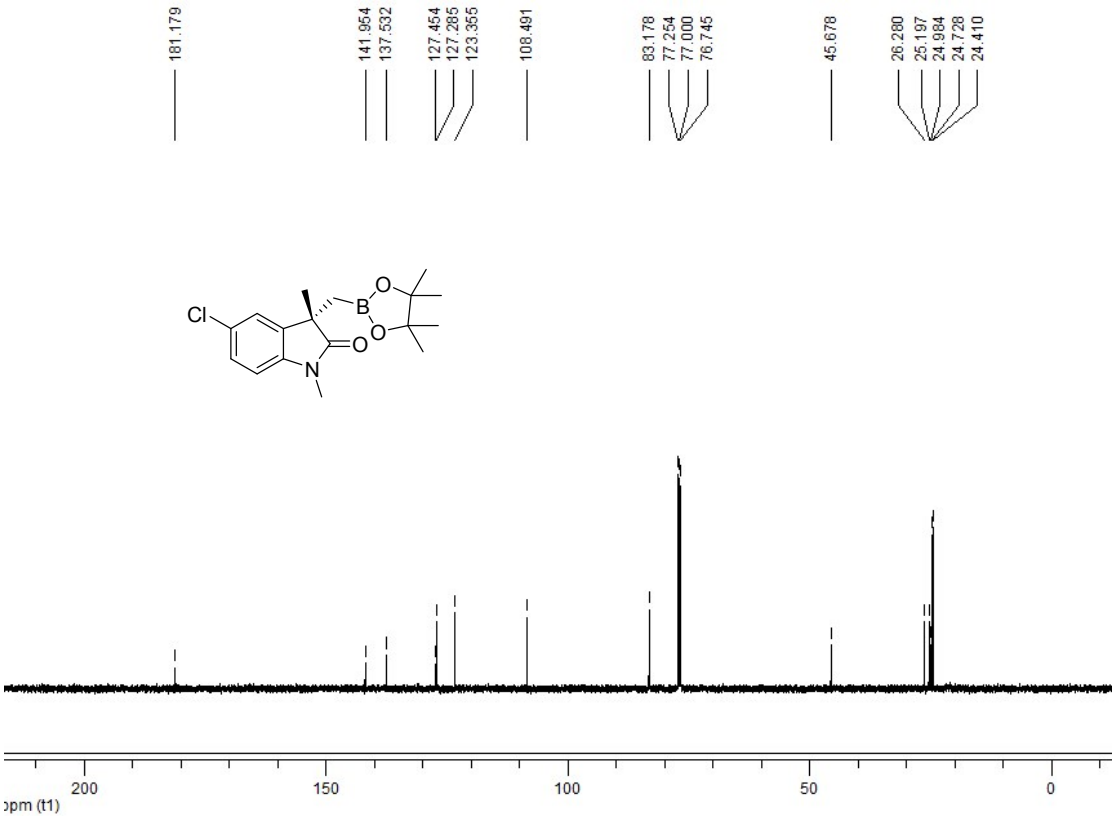



F
B
O
O
O
N

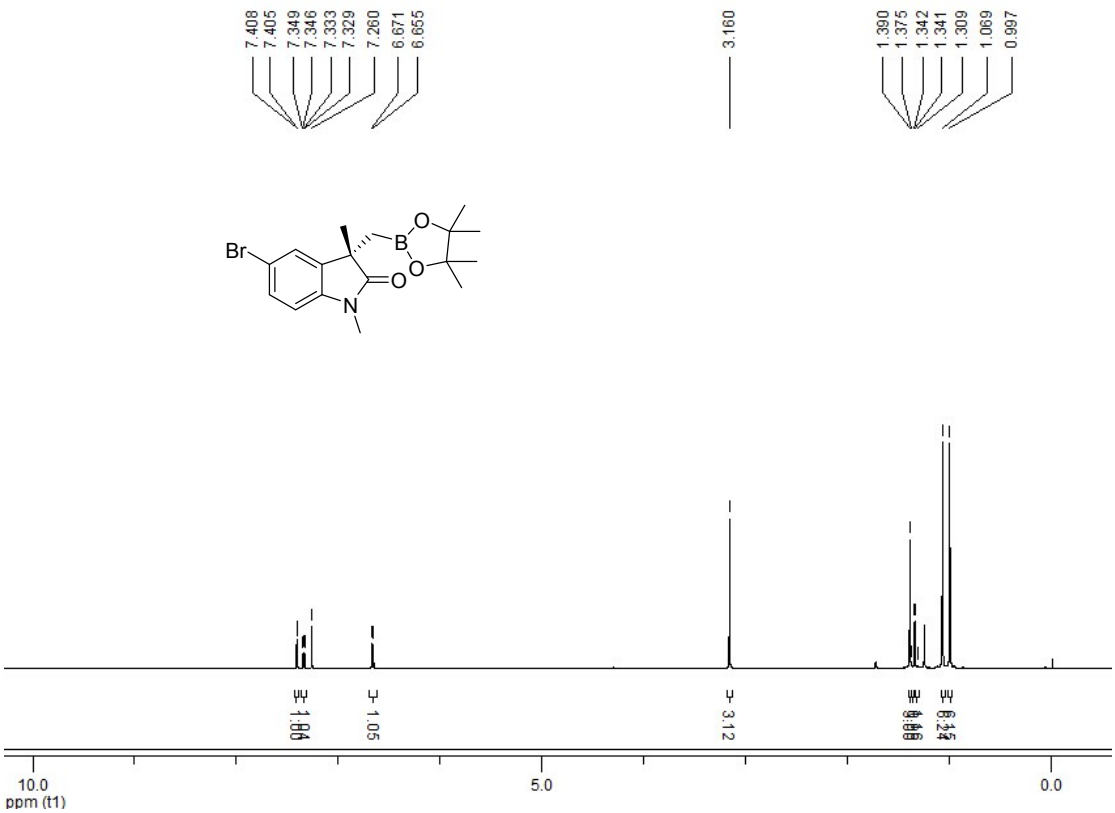
-121.482
0
-50
-100
-150
-200
ppm (t1)

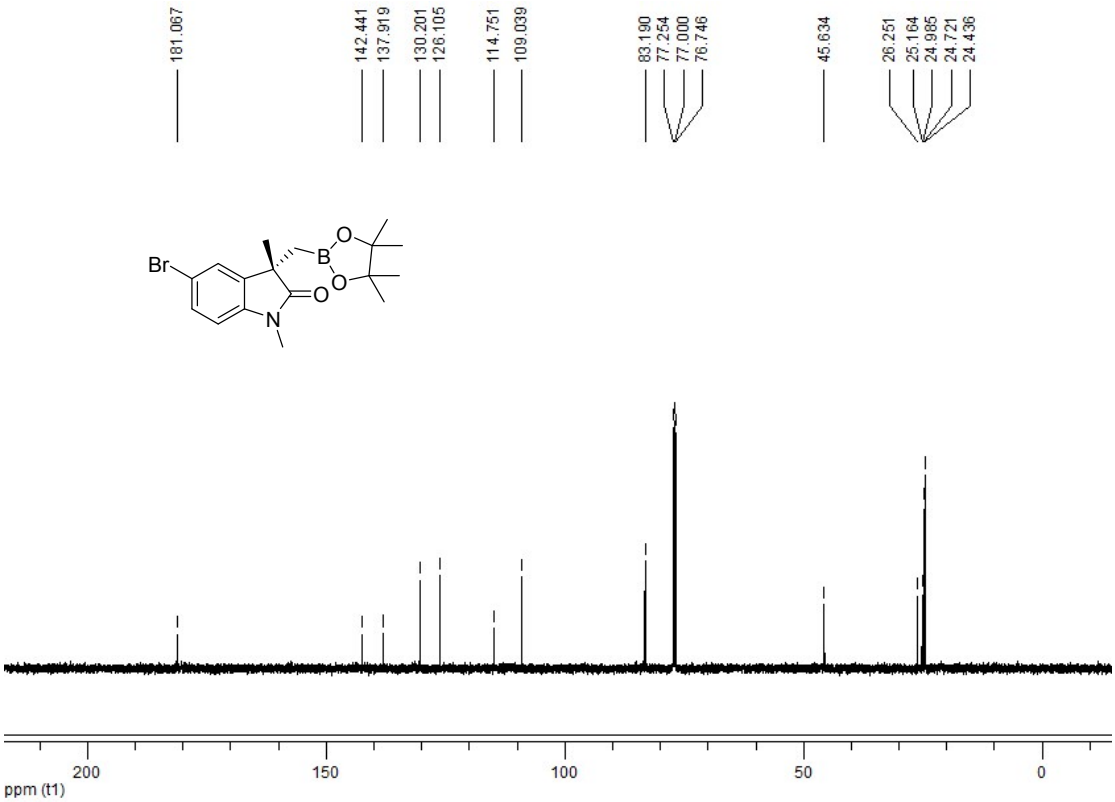
S)-5-chloro-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3t):



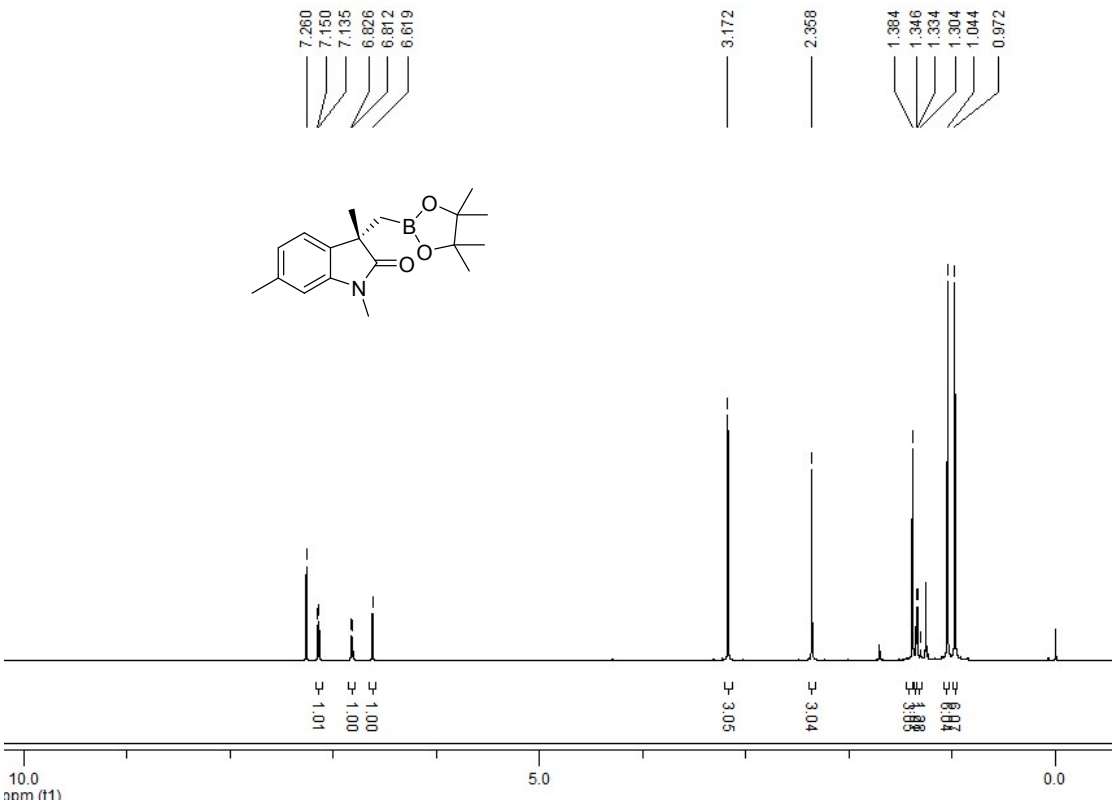


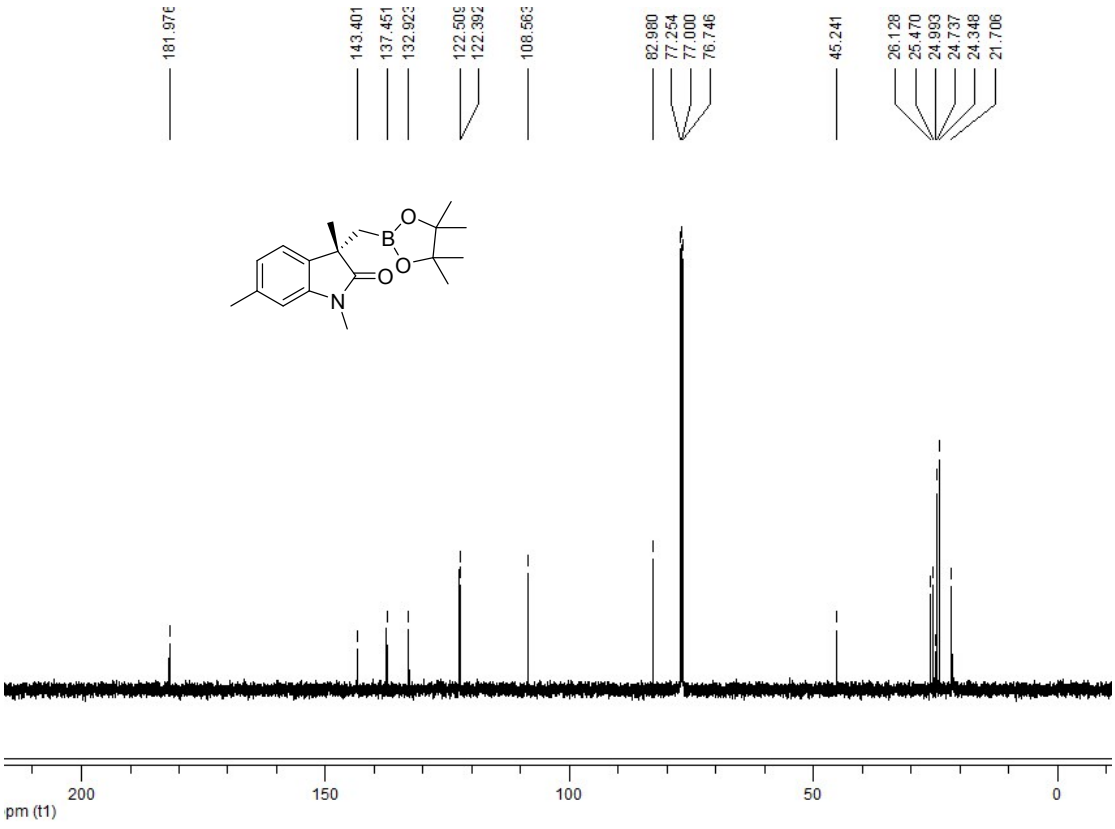
(S)-5-bromo-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3u):



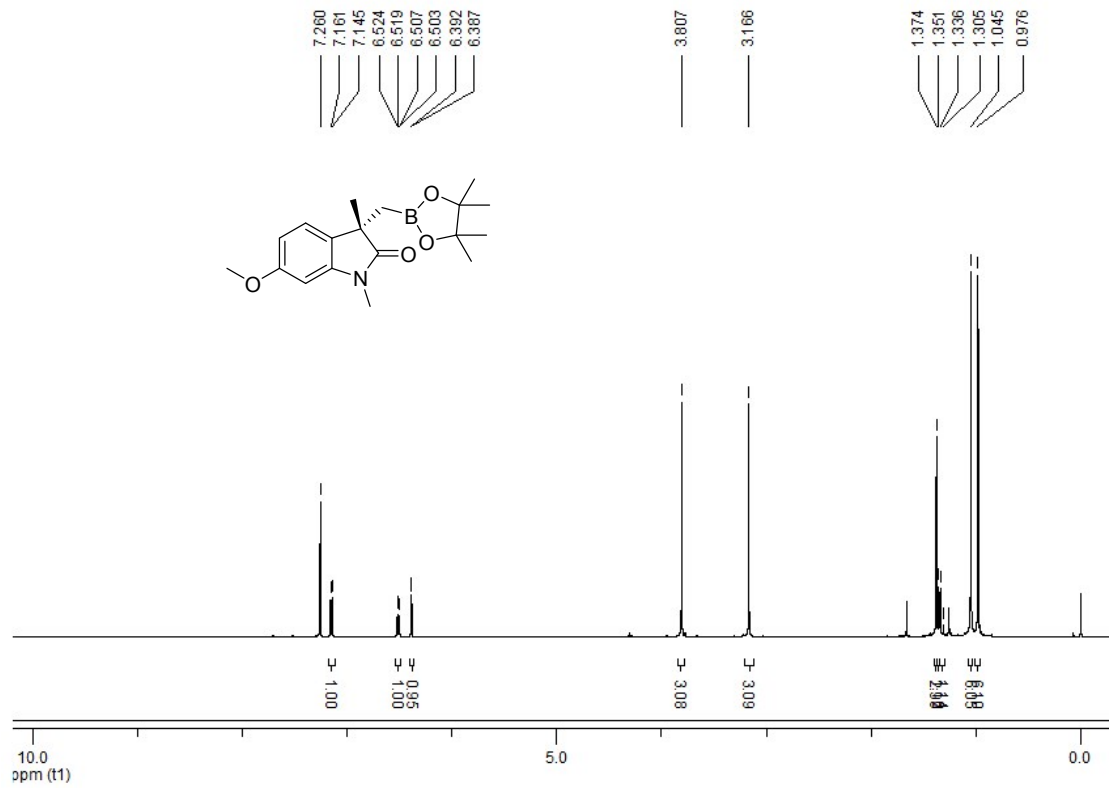


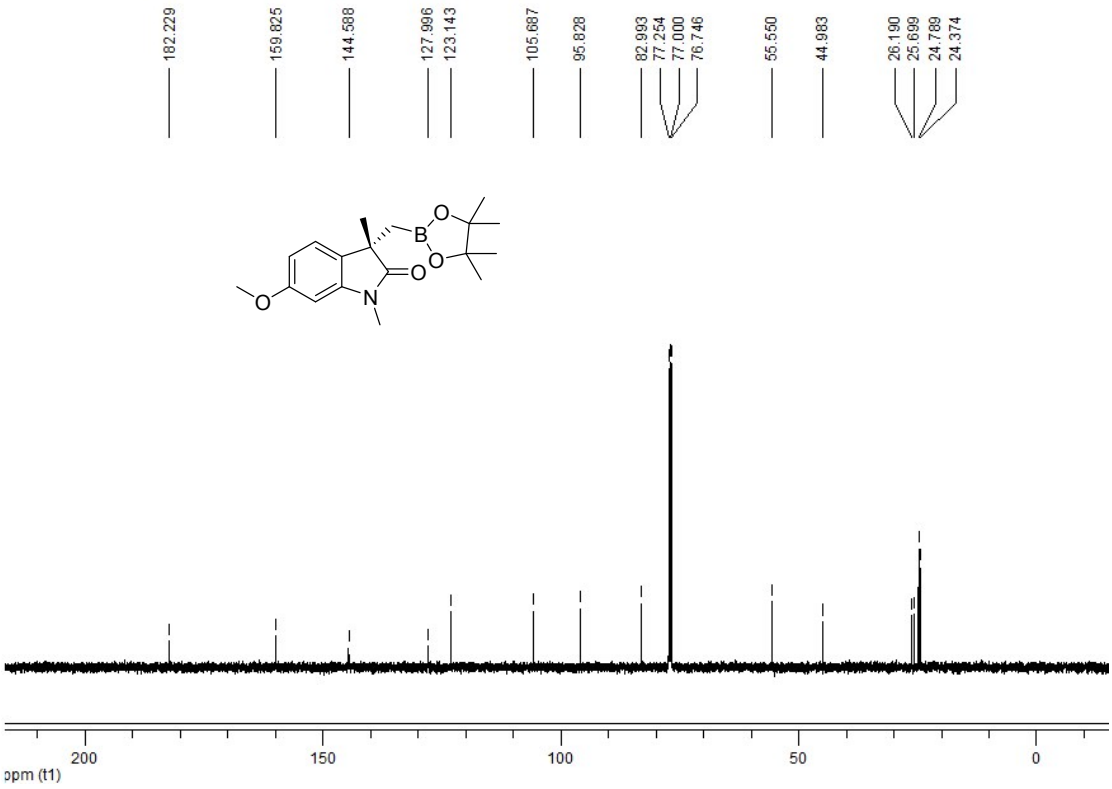
(S)-1,3,6-trimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3v):



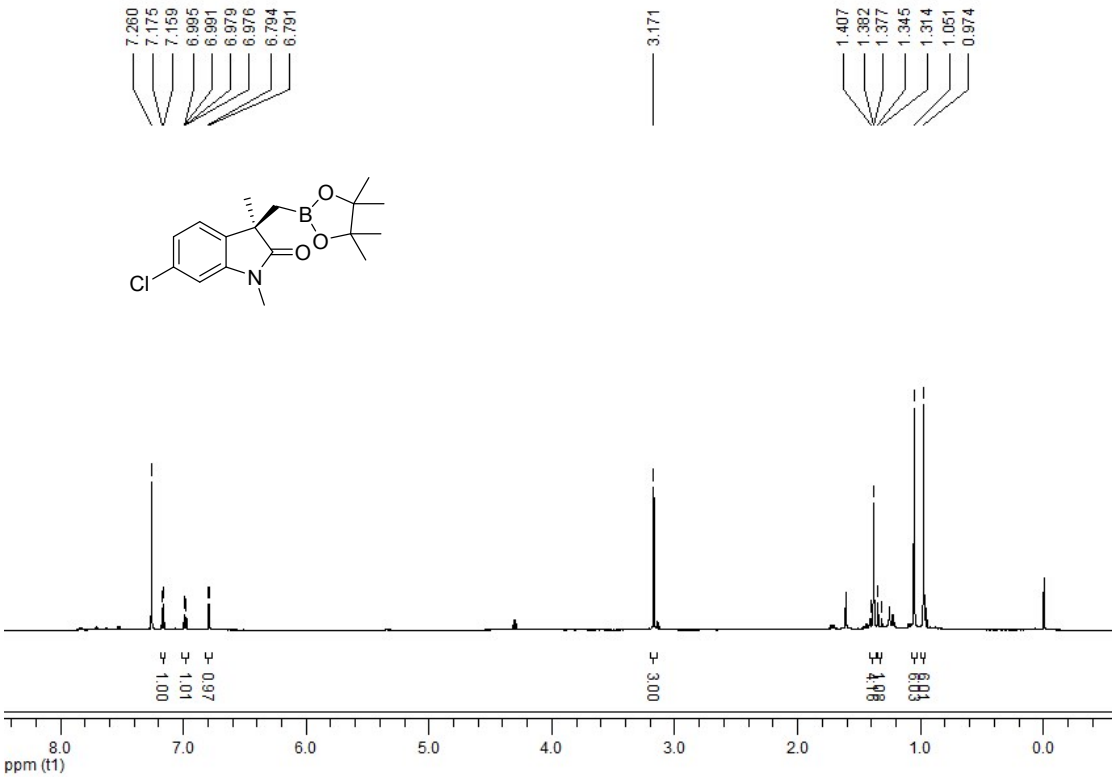


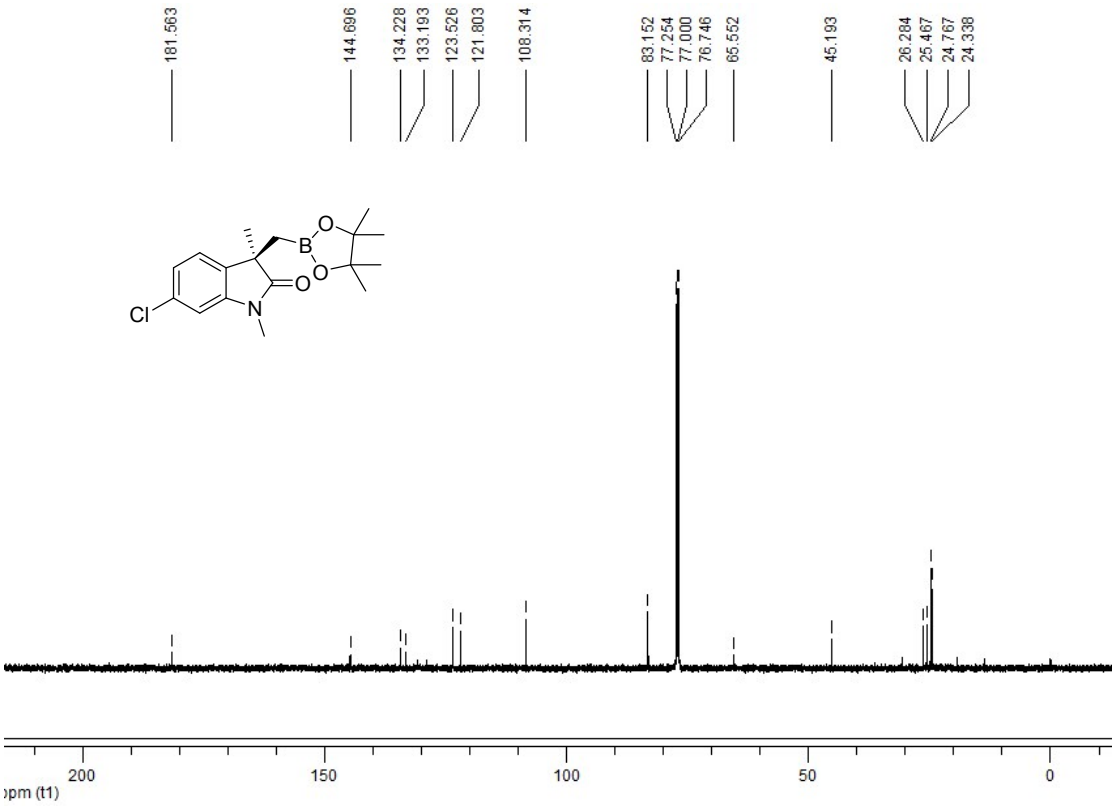
(S)-6-methoxy-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3w):



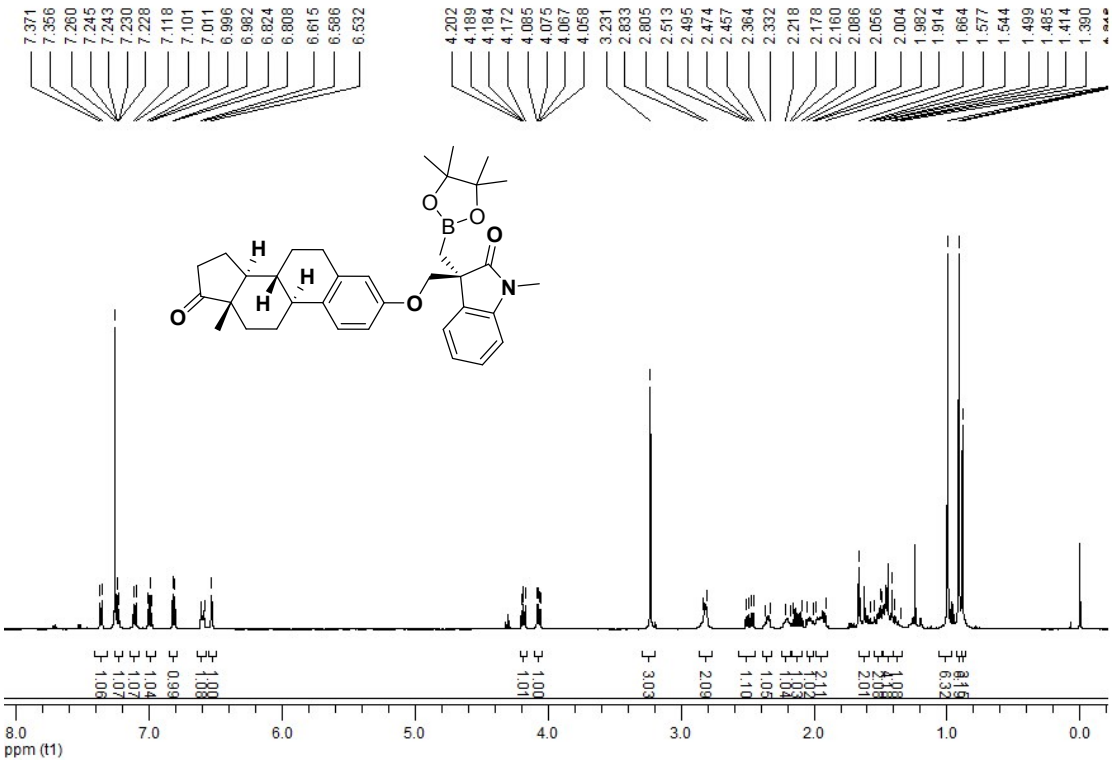


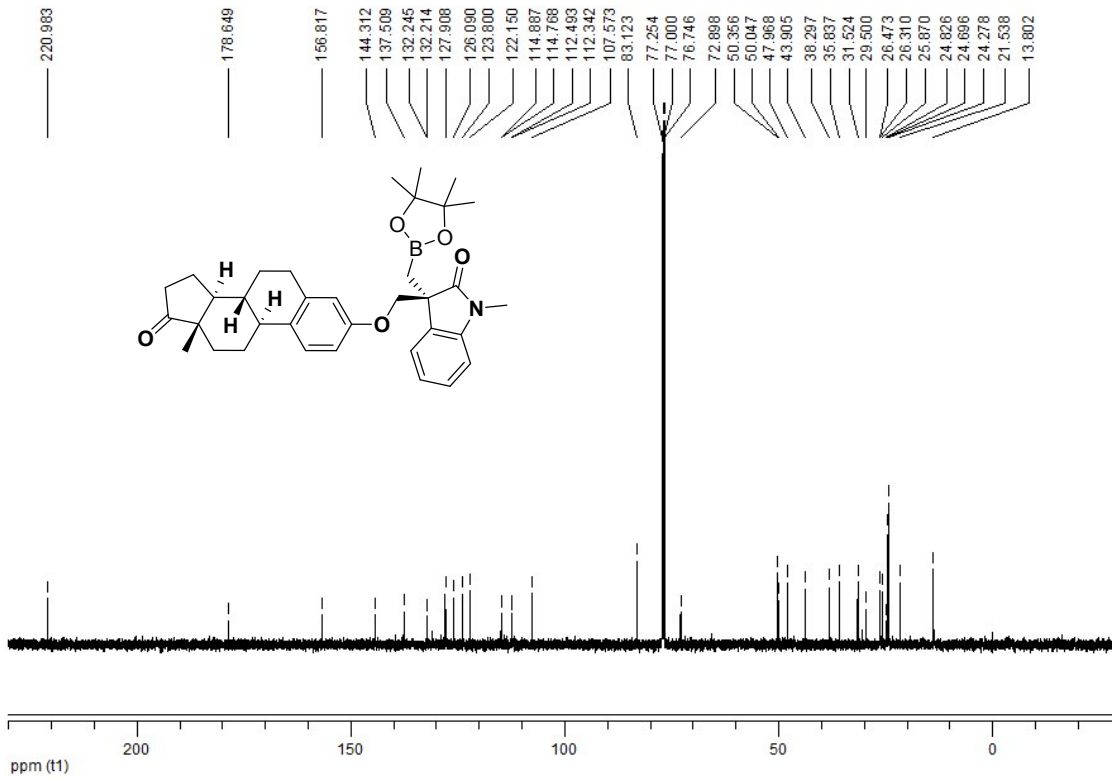
(S)-6-chloro-1,3-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3x):



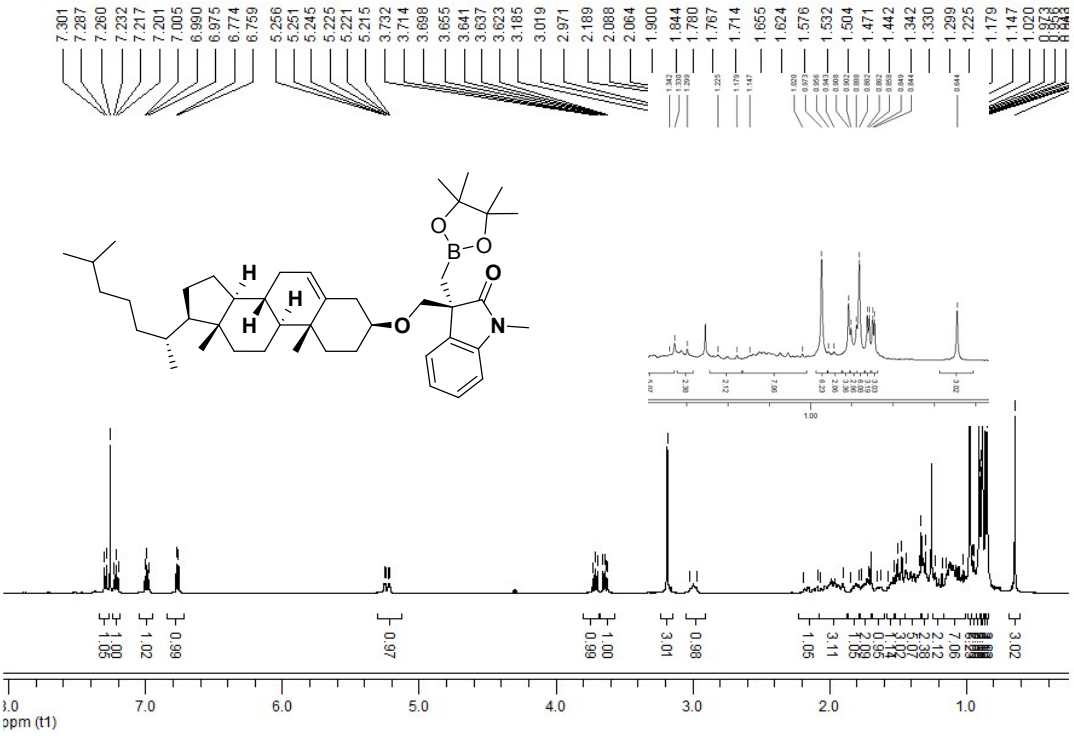


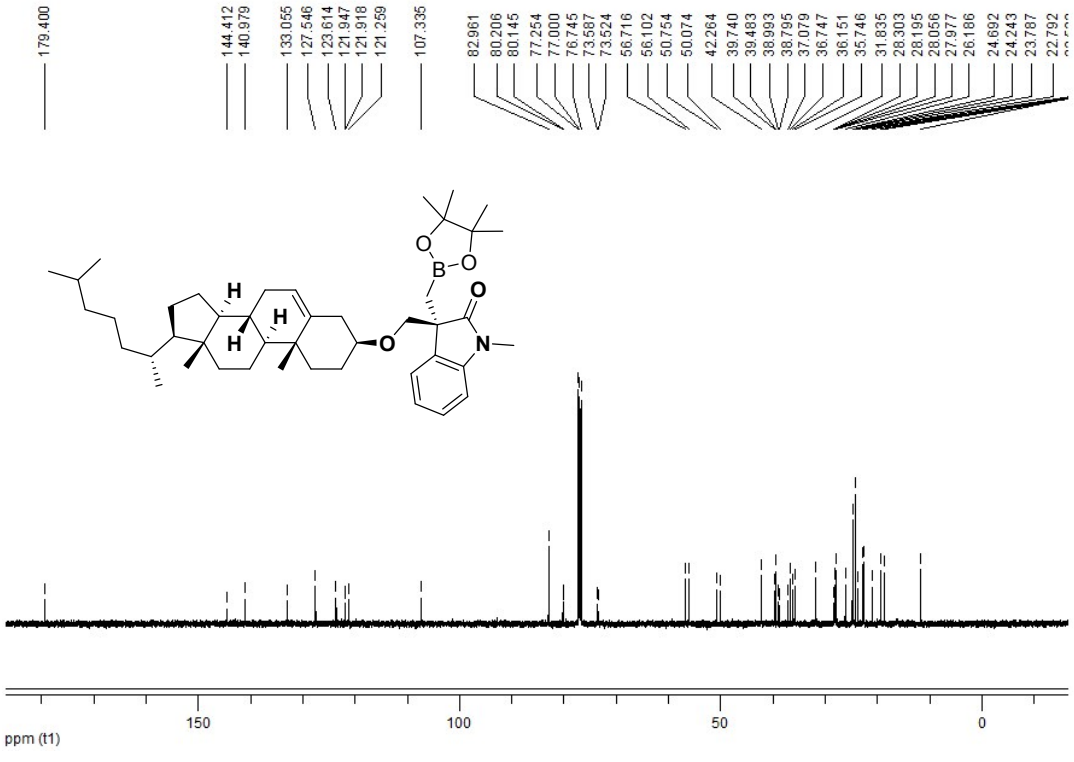
(S)-1-methyl-3-((((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)methyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3y):



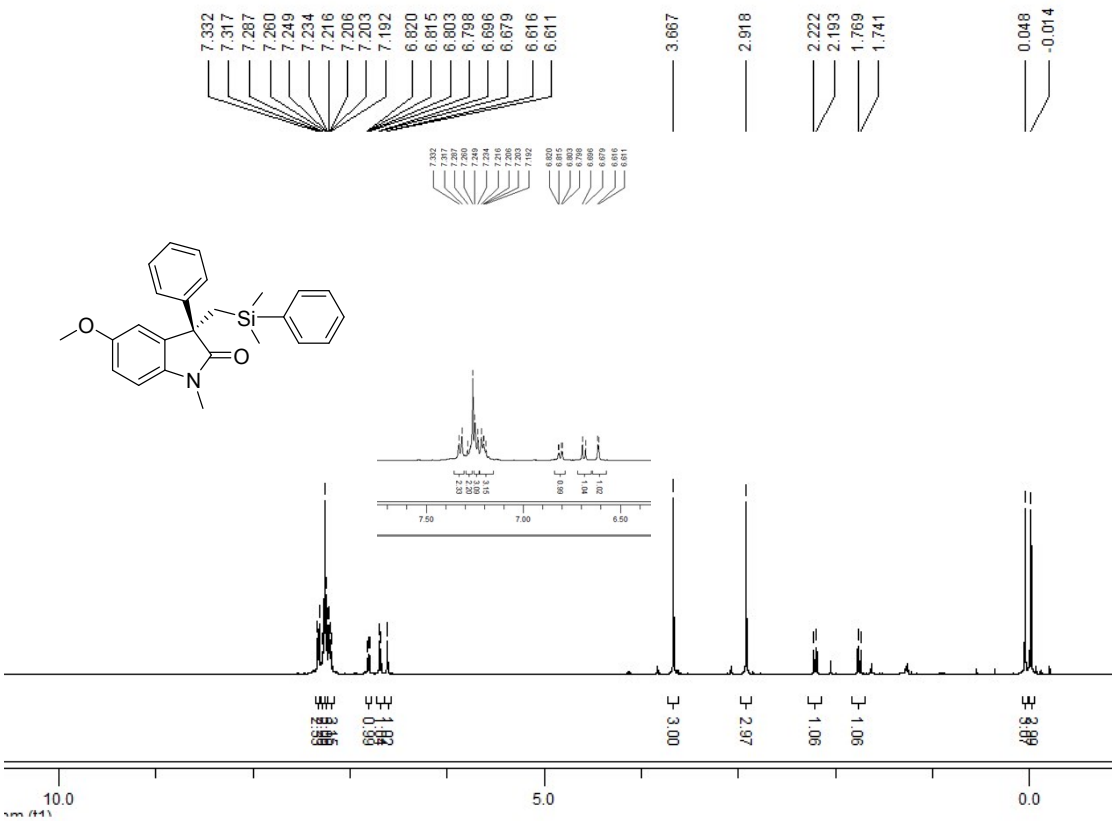


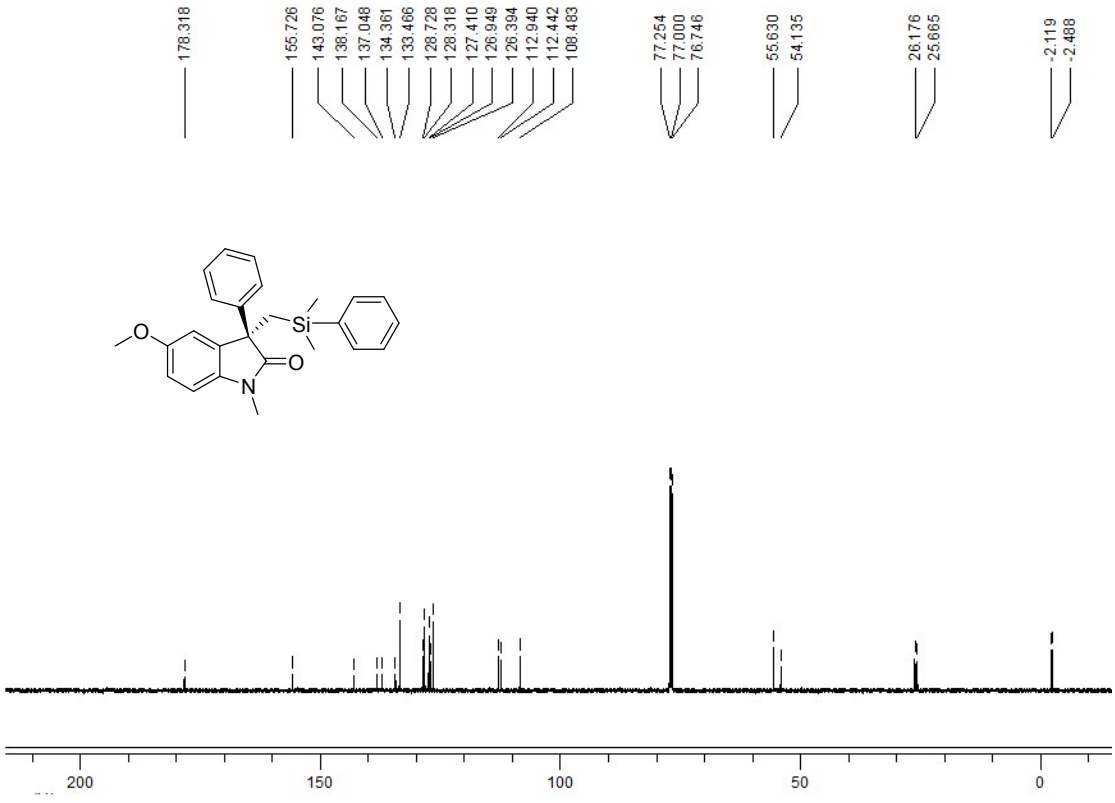
(S)-3-((((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)methyl)-1-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)indolin-2-one (3z):



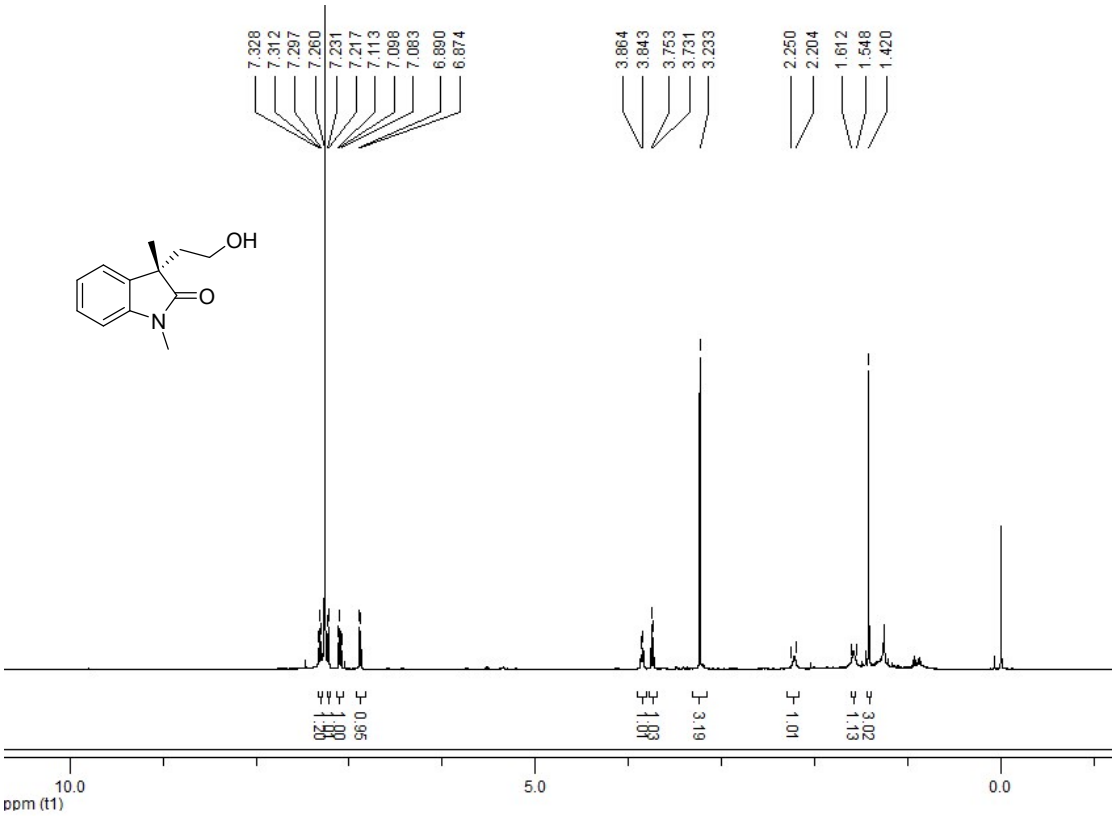


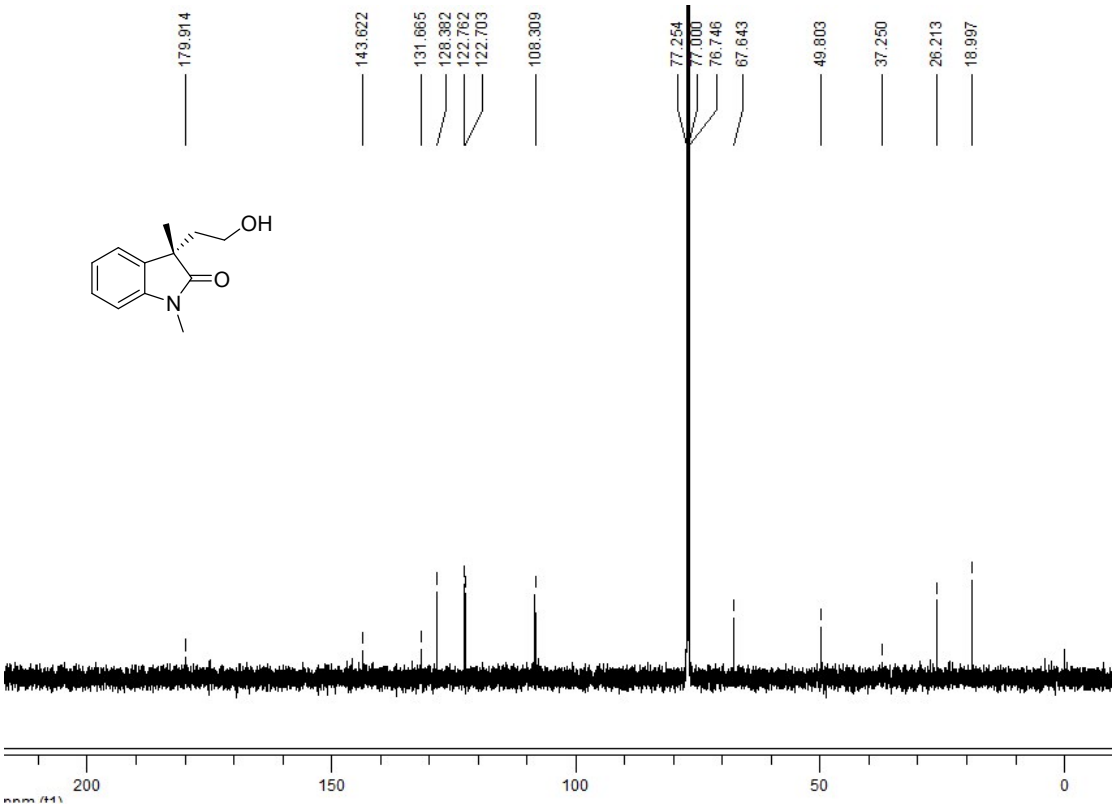
(S)-3-((dimethyl(phenyl)silyl)methyl)-5-methoxy-1-methyl-3-phenylindolin-2-one (4e):



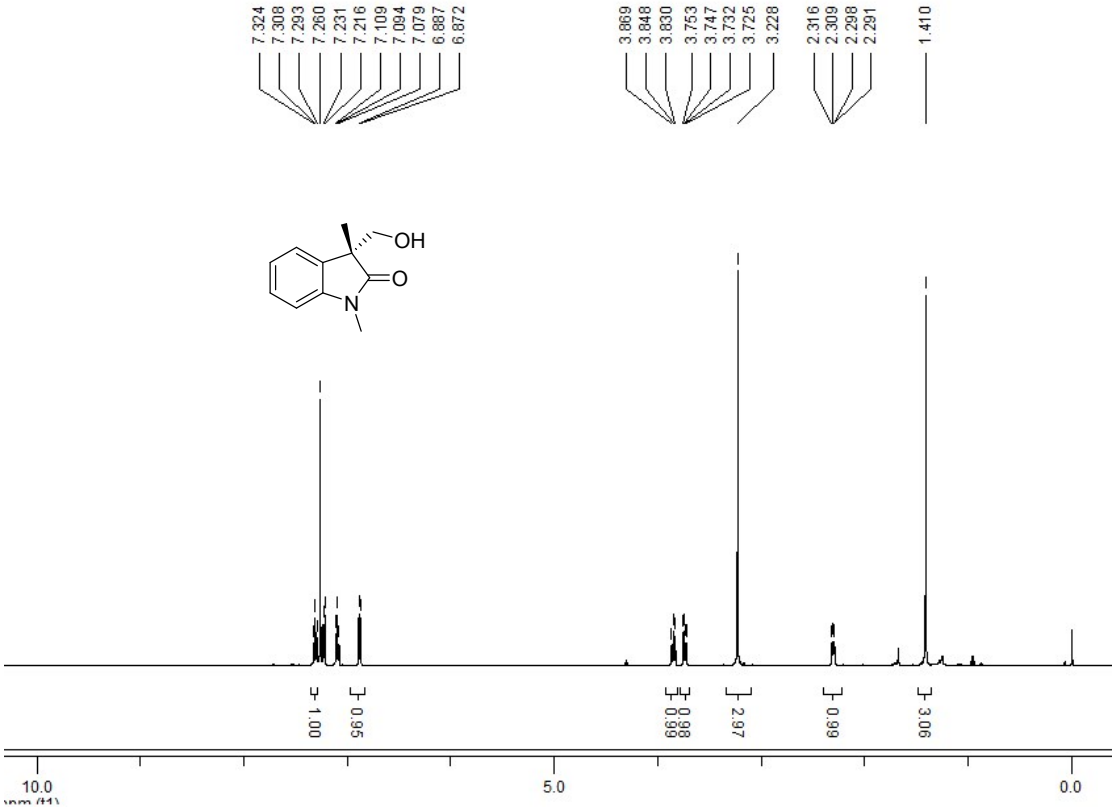


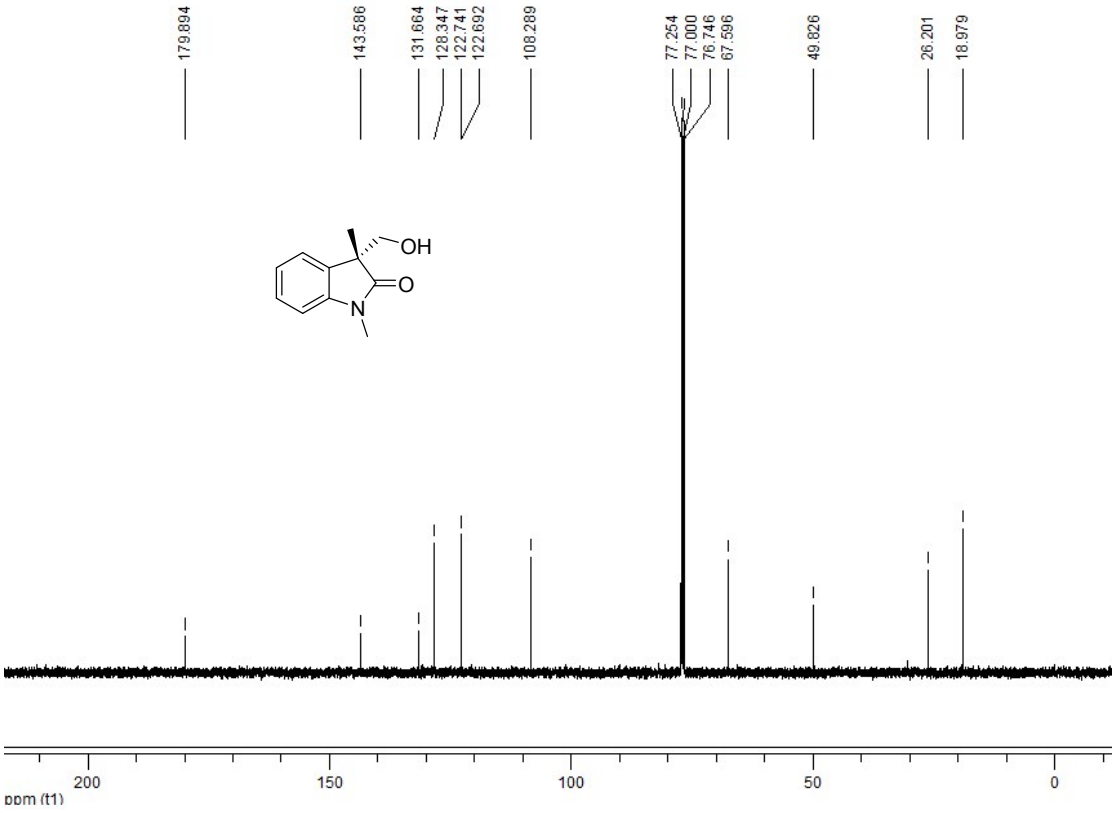
(S)-3-(2-hydroxyethyl)-1,3-dimethylindolin-2-one (5a):



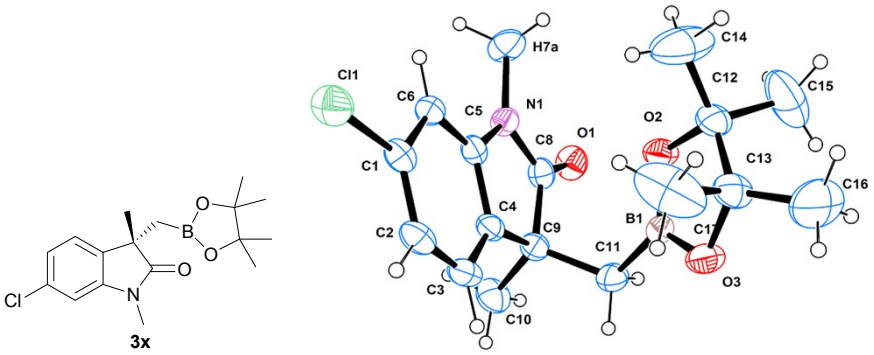


(R)-3-(hydroxymethyl)-1,3-dimethylindolin-2-one (6a):





(D) The X-ray Single-Crystal Diffraction Analysis of 3x (CCDC 2053886)



The thermal ellipsoid plot of 3x with 30% displacement ellipsoids

Table S2. Crystal data and structure refinement for A.

Identification code	A	
Empirical formula	C17 H23 B Cl N O3	
Formula weight	335.62	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.213(3) Å	α= 90°.
	b = 10.603(2) Å	β= 114.903(3)°.
	c = 14.382(3) Å	γ = 90°.
Volume	1827.6(7) $Å^3$	
Z	4	
Density (calculated)	1.220 Mg/m^3	
Absorption coefficient	0.221 mm^{-1}	
F(000)	712	
Crystal size	0.180 x 0.170 x 0.160 mm^3	
Theta range for data collection	2.565 to 25.498°.	
Index ranges	-16<=h<=16, -11<=k<=12, -16<=l<=17	
Reflections collected	13771	
Independent reflections	3395 [R(int) = 0.0342]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3395 / 0 / 214	
Goodness-of-fit on F^2	1.034	

Final R indices [I>2sigma(I)]	R1 = 0.0640, wR2 = 0.1714
R indices (all data)	R1 = 0.0901, wR2 = 0.1915
Extinction coefficient	n/a
Largest diff. peak and hole	0.704 and -0.326 e.Å^{-3}

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for A. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	7182(3)	4317(3)	6644(3)	47(1)
C(1)	7004(2)	8936(3)	6127(2)	50(1)
C(2)	6141(3)	8283(3)	5388(2)	55(1)
C(3)	6331(2)	7096(3)	5088(2)	53(1)
C(4)	7387(2)	6595(3)	5533(2)	44(1)
C(5)	8238(2)	7268(3)	6291(2)	43(1)
C(6)	8077(2)	8446(3)	6612(2)	46(1)
C(7)	10250(3)	6918(3)	7512(3)	73(1)
C(8)	9063(3)	5430(3)	6163(2)	50(1)
C(9)	7847(3)	5357(3)	5366(2)	49(1)
C(10)	7842(3)	5260(4)	4299(3)	70(1)
C(11)	7273(3)	4207(3)	5597(2)	57(1)
C(12)	7693(3)	4712(4)	8342(3)	67(1)
C(13)	6448(3)	4497(4)	7802(3)	67(1)
C(14)	8160(5)	5794(7)	9000(4)	139(3)
C(15)	8287(5)	3516(7)	8986(4)	143(3)
C(16)	5885(6)	3716(8)	8265(5)	168(3)
C(17)	5857(5)	5823(7)	7578(4)	146(3)
Cl(1)	6760(1)	10450(1)	6471(1)	70(1)
N(1)	9232(2)	6575(2)	6639(2)	48(1)
O(1)	9774(2)	4625(2)	6341(2)	66(1)
O(2)	8041(2)	4727(2)	7506(2)	59(1)
O(3)	6257(2)	4055(3)	6784(2)	66(1)

Table S4. Bond lengths [Å] and angles [°] for A.

B(1)-O(3)	1.349(4)
B(1)-O(2)	1.352(4)
B(1)-C(11)	1.565(5)
C(1)-C(2)	1.374(4)
C(1)-C(6)	1.390(4)
C(1)-Cl(1)	1.749(3)
C(2)-C(3)	1.388(5)
C(2)-H(2)	0.9300
C(3)-C(4)	1.373(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.389(4)
C(4)-C(9)	1.507(4)
C(5)-C(6)	1.379(4)
C(5)-N(1)	1.401(3)
C(6)-H(6)	0.9300
C(7)-N(1)	1.448(4)
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-O(1)	1.214(4)
C(8)-N(1)	1.365(4)
C(8)-C(9)	1.533(4)
C(9)-C(10)	1.536(4)
C(9)-C(11)	1.545(4)
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(14)	1.449(6)
C(12)-O(2)	1.457(4)
C(12)-C(13)	1.512(5)
C(12)-C(15)	1.571(7)
C(13)-C(16)	1.448(6)
C(13)-O(3)	1.454(4)
C(13)-C(17)	1.575(7)

C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600

O(3)-B(1)-O(2)	113.1(3)
O(3)-B(1)-C(11)	124.8(3)
O(2)-B(1)-C(11)	122.1(3)
C(2)-C(1)-C(6)	122.6(3)
C(2)-C(1)-Cl(1)	119.3(2)
C(6)-C(1)-Cl(1)	118.1(2)
C(1)-C(2)-C(3)	119.8(3)
C(1)-C(2)-H(2)	120.1
C(3)-C(2)-H(2)	120.1
C(4)-C(3)-C(2)	119.2(3)
C(4)-C(3)-H(3)	120.4
C(2)-C(3)-H(3)	120.4
C(3)-C(4)-C(5)	119.6(3)
C(3)-C(4)-C(9)	131.4(3)
C(5)-C(4)-C(9)	109.0(2)
C(6)-C(5)-C(4)	122.7(3)
C(6)-C(5)-N(1)	127.6(3)
C(4)-C(5)-N(1)	109.7(3)
C(5)-C(6)-C(1)	116.1(3)
C(5)-C(6)-H(6)	122.0
C(1)-C(6)-H(6)	122.0
N(1)-C(7)-H(7A)	109.5
N(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
N(1)-C(7)-H(7C)	109.5

H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
O(1)-C(8)-N(1)	124.8(3)
O(1)-C(8)-C(9)	126.6(3)
N(1)-C(8)-C(9)	108.6(2)
C(4)-C(9)-C(8)	101.7(2)
C(4)-C(9)-C(10)	112.7(3)
C(8)-C(9)-C(10)	108.3(3)
C(4)-C(9)-C(11)	112.6(3)
C(8)-C(9)-C(11)	109.5(3)
C(10)-C(9)-C(11)	111.5(3)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-B(1)	113.1(3)
C(9)-C(11)-H(11A)	109.0
B(1)-C(11)-H(11A)	109.0
C(9)-C(11)-H(11B)	109.0
B(1)-C(11)-H(11B)	109.0
H(11A)-C(11)-H(11B)	107.8
C(14)-C(12)-O(2)	109.6(3)
C(14)-C(12)-C(13)	121.8(4)
O(2)-C(12)-C(13)	103.3(3)
C(14)-C(12)-C(15)	106.6(5)
O(2)-C(12)-C(15)	104.0(3)
C(13)-C(12)-C(15)	110.2(4)
C(16)-C(13)-O(3)	111.9(4)
C(16)-C(13)-C(12)	120.5(4)
O(3)-C(13)-C(12)	104.8(3)
C(16)-C(13)-C(17)	107.4(5)
O(3)-C(13)-C(17)	102.8(3)
C(12)-C(13)-C(17)	108.0(4)
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5

C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(12)-C(15)-H(15A)	109.5
C(12)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(12)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(13)-C(16)-H(16A)	109.5
C(13)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(13)-C(17)-H(17A)	109.5
C(13)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(13)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(8)-N(1)-C(5)	110.9(2)
C(8)-N(1)-C(7)	123.7(3)
C(5)-N(1)-C(7)	124.5(3)
B(1)-O(2)-C(12)	108.6(2)
B(1)-O(3)-C(13)	107.5(2)

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for A. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	52(2)	39(2)	48(2)	-2(2)	20(2)	-6(2)
C(1)	47(2)	56(2)	44(2)	10(1)	17(1)	10(1)
C(2)	41(2)	72(2)	46(2)	10(2)	11(1)	13(2)
C(3)	45(2)	68(2)	38(2)	0(2)	10(1)	-2(2)
C(4)	43(2)	54(2)	33(1)	4(1)	14(1)	-1(1)
C(5)	39(2)	48(2)	42(2)	11(1)	16(1)	4(1)
C(6)	41(2)	47(2)	45(2)	4(1)	11(1)	1(1)
C(7)	38(2)	63(2)	93(3)	-3(2)	3(2)	2(2)
C(8)	50(2)	51(2)	52(2)	7(1)	26(2)	3(1)
C(9)	56(2)	52(2)	39(2)	-3(1)	22(1)	-3(1)
C(10)	87(3)	81(3)	52(2)	-1(2)	37(2)	3(2)
C(11)	64(2)	57(2)	48(2)	-11(2)	23(2)	-11(2)
C(12)	76(2)	88(3)	44(2)	-10(2)	31(2)	-20(2)
C(13)	61(2)	96(3)	51(2)	-7(2)	31(2)	-9(2)
C(14)	129(5)	196(7)	115(4)	-91(4)	73(4)	-71(4)
C(15)	125(5)	186(7)	108(4)	80(4)	41(4)	39(4)
C(16)	157(6)	268(9)	111(4)	-37(5)	88(4)	-123(6)
C(17)	144(5)	182(6)	96(4)	-16(4)	33(4)	81(5)
Cl(1)	63(1)	65(1)	72(1)	0(1)	20(1)	20(1)
N(1)	37(1)	44(1)	56(2)	3(1)	14(1)	1(1)
O(1)	62(1)	55(1)	80(2)	4(1)	30(1)	13(1)
O(2)	53(1)	80(2)	44(1)	-10(1)	21(1)	-16(1)
O(3)	58(1)	90(2)	53(1)	-17(1)	24(1)	-25(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for A.

	x	y	z	U(eq)
H(2)	5431	8636	5090	67
H(3)	5751	6644	4592	63
H(6)	8652	8887	7122	56
H(7A)	10857	6418	7514	110
H(7B)	10162	6769	8132	110
H(7C)	10406	7795	7468	110
H(10A)	8228	5971	4188	105
H(10B)	7085	5252	3786	105
H(10C)	8209	4496	4254	105
H(11A)	7691	3452	5604	68
H(11B)	6530	4117	5051	68
H(14A)	7849	6553	8625	208
H(14B)	8955	5801	9228	208
H(14C)	7985	5744	9582	208
H(15A)	9037	3470	9044	214
H(15B)	7885	2772	8649	214
H(15C)	8301	3575	9657	214
H(16A)	6107	2853	8269	252
H(16B)	5093	3786	7876	252
H(16C)	6083	3990	8956	252
H(17A)	5187	5782	6955	220
H(17B)	6350	6444	7509	220
H(17C)	5674	6053	8135	220

Table S7. Torsion angles [°] for A.

C(6)-C(1)-C(2)-C(3)	-1.1(5)
Cl(1)-C(1)-C(2)-C(3)	178.2(2)
C(1)-C(2)-C(3)-C(4)	-0.5(4)
C(2)-C(3)-C(4)-C(5)	1.6(4)
C(2)-C(3)-C(4)-C(9)	-179.5(3)
C(3)-C(4)-C(5)-C(6)	-1.2(4)
C(9)-C(4)-C(5)-C(6)	179.6(3)
C(3)-C(4)-C(5)-N(1)	179.4(2)
C(9)-C(4)-C(5)-N(1)	0.2(3)
C(4)-C(5)-C(6)-C(1)	-0.3(4)
N(1)-C(5)-C(6)-C(1)	179.0(3)
C(2)-C(1)-C(6)-C(5)	1.5(4)
Cl(1)-C(1)-C(6)-C(5)	-177.8(2)
C(3)-C(4)-C(9)-C(8)	-177.3(3)
C(5)-C(4)-C(9)-C(8)	1.7(3)
C(3)-C(4)-C(9)-C(10)	66.9(4)
C(5)-C(4)-C(9)-C(10)	-114.0(3)
C(3)-C(4)-C(9)-C(11)	-60.2(4)
C(5)-C(4)-C(9)-C(11)	118.8(3)
O(1)-C(8)-C(9)-C(4)	178.1(3)
N(1)-C(8)-C(9)-C(4)	-3.1(3)
O(1)-C(8)-C(9)-C(10)	-62.9(4)
N(1)-C(8)-C(9)-C(10)	115.8(3)
O(1)-C(8)-C(9)-C(11)	58.8(4)
N(1)-C(8)-C(9)-C(11)	-122.5(3)
C(4)-C(9)-C(11)-B(1)	-47.9(4)
C(8)-C(9)-C(11)-B(1)	64.5(3)
C(10)-C(9)-C(11)-B(1)	-175.7(3)
O(3)-B(1)-C(11)-C(9)	134.4(3)
O(2)-B(1)-C(11)-C(9)	-43.7(4)
C(14)-C(12)-C(13)-C(16)	-93.5(6)
O(2)-C(12)-C(13)-C(16)	143.0(5)
C(15)-C(12)-C(13)-C(16)	32.4(6)
C(14)-C(12)-C(13)-O(3)	139.3(4)
O(2)-C(12)-C(13)-O(3)	15.8(4)
C(15)-C(12)-C(13)-O(3)	-94.8(4)

C(14)-C(12)-C(13)-C(17)	30.2(5)
O(2)-C(12)-C(13)-C(17)	-93.3(4)
C(15)-C(12)-C(13)-C(17)	156.1(4)
O(1)-C(8)-N(1)-C(5)	-177.7(3)
C(9)-C(8)-N(1)-C(5)	3.5(3)
O(1)-C(8)-N(1)-C(7)	-8.2(5)
C(9)-C(8)-N(1)-C(7)	173.0(3)
C(6)-C(5)-N(1)-C(8)	178.2(3)
C(4)-C(5)-N(1)-C(8)	-2.4(3)
C(6)-C(5)-N(1)-C(7)	8.8(5)
C(4)-C(5)-N(1)-C(7)	-171.8(3)
O(3)-B(1)-O(2)-C(12)	2.0(4)
C(11)-B(1)-O(2)-C(12)	-179.7(3)
C(14)-C(12)-O(2)-B(1)	-142.5(4)
C(13)-C(12)-O(2)-B(1)	-11.3(4)
C(15)-C(12)-O(2)-B(1)	103.9(4)
O(2)-B(1)-O(3)-C(13)	8.8(4)
C(11)-B(1)-O(3)-C(13)	-169.5(3)
C(16)-C(13)-O(3)-B(1)	-147.5(5)
C(12)-C(13)-O(3)-B(1)	-15.3(4)
C(17)-C(13)-O(3)-B(1)	97.5(4)

Symmetry transformations used to generate equivalent atoms:

Table S8. Hydrogen bonds for A [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(6)-H(6)...O(1)#1	0.93	2.44	3.355(4)	167.9
C(2)-H(2)...Cl(1)#2	0.93	2.98	3.874(3)	161.7

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y+1/2,-z+3/2 #2 -x+1,-y+2,-z+1

(E) References

1 (*a*) R.-X. Liang, R.-Y. Chen, C. Zhong, J.-W. Zhu, Z.-Y. Cao and Y.-X. Jia, *Org. Lett.,* 2020, **22**, 3215; (*b*) W. Kong, Q Wang and J. Zhu, *Angew. Chem. Int. Ed.*, 2016, **55**, 9714; (*c*) M.-B. Zhou, X.-C. Huang, Y. Y. Liu, R.-J. Song and J.-H. Li, *Chem. Eur. J.,* 2014, **20,** 1843.