Support Information

for

Enantioselective Rhodium-Catalyzed Addition of Arylboronic Acids to *N*-Heteroaryl Ketones: Synthesis of α-Hydroxy Acids

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1. General information

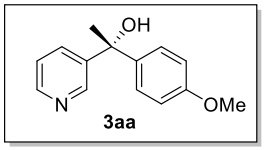
$[Rh(C_2H_4)_2Cl]_2$ was purchased from TCI chemical. Ligands (L5, L6, L7) were prepared according to a reported procedure[1]. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Solvents for chromatography were used as supplied by Adamas-beta®. All reactions were carried out under nitrogen atmosphere unless otherwise specified. Solvents were purified and dried according to standard methods prior to use.

^1H, ^{13}C and ^{19}F NMR data were recorded on a Bruker Avance III 400 NMR and 500 NMR spectrometers with $CDCl_3$ or DMSO-*d6* as the solvent. ^1H shifts were referenced to $CDCl_3$ at 7.26 ppm, to DMSO-*d6* at 2.54 ppm. ^{13}C shifts were referenced to $CDCl_3$ at 77 ppm, to DMSO at 40 ppm and obtained with ^1H decoupling. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), doublet-triplet (dt), doublet-quintet (dq), triplet-doublet (td), quintet (q), multiplet (m), and broad (br). MS was measured on Agilent 1100 Series LC/MSD (ESI) mass spectrometers. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Jiangyou silical gel (200-300 mesh). Infrared spectra were recorded on a Nicolet IS50 Fourier transform spectrometer (FT-IR) and were reported in wave numbers (cm^{-1}). Chiral HPLC analyses were performed on a Shimadzu Essentia SPD - 16 using a chiralcel OD-H, chiralcel AD-H, chiralpak AS-H, chiralpak IA, or chiralpak IC column. The optical rotations were measured on an Anton Paar Modular Circular Polarimeter.

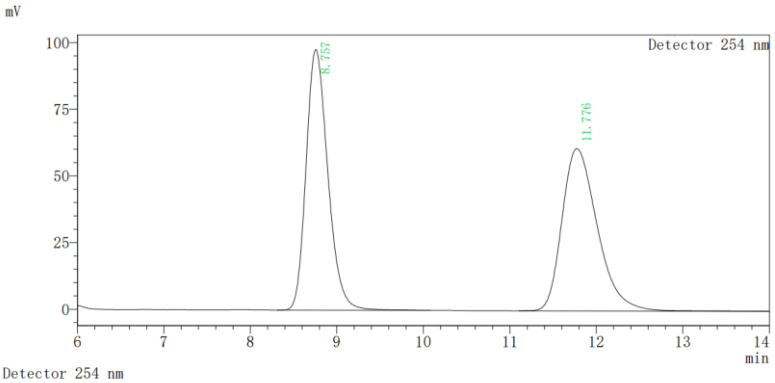
2. General procedure for asymmetric addition of arylboron reagents to *N*-Heteroaryl Ketones (General Procedure A).

To a screw-capped tube was charged N-heteroaryl ketones (0.20 mmol, 1.0 equiv), arylboron reagents (0.60 mmol, 3.0 equiv "B"), CsF (0.40 mmol, 2.0 equiv), (*S,S,S,S*)-WingPhos (5.3 mg, 0.0072 mmol, 3.6 mol %) and $[Rh(C_2H_4)_2Cl]_2$ (1.2 mg, 0.0030 mmol, 1.5 mol %). The tube was sealed then evacuated and backfilled with N_2 for three times. $B(OMe)_3$ (20.8 mg, 0.2 mmol, 1 equiv) was added to the above mixture via microsyringe, and degassed MTBE (3.5 mL) was added via syringe under N_2. The resulting mixture was stirred at 80 ºC under nitrogen for 16 h. After this time, the screw-capped tube was removed from the bath and allowed to cool to room temperature. The heterogenous mixture was diluted with EtOAc (10 mL) and filtered through celite, rinsing the celite plug with EtOAc/MeOH (24/1, v/v, 25 mL). The filtrate was concentrated, and the resulting residue was purified via flash chromatography on silica gel with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), affording the desired alcohol products. The enantiomeric excesses were determined by chiral HPLC on a chiralcel OD-H, chiralcel AD-H, chiralpak AS-H, or chiralpak IC column.

3. Analytical data of the products of enantioselective Rh-catalyzed addition of arylboronic acids to *N*-Heteroaryl Ketones.



(*R*)-1-(4-methoxyphenyl)-1-(pyridin-3-yl)ethan-1-ol (3aa): General Procedure A was followed using 1-(pyridin-3-yl)ethan -1-one (24.2 mg, 0.20 mmol), and (4-methoxyphenyl)boronic acid (91.2 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), the desired product was obtained as a colorless solid (41.5 mg, 90% yield, >99% ee). Chiral HPLC conditions: chiralpak AS-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol/ diethylamine: 80/20/0.03, 254 nm, 8.6 min (*R*), 11.8 min (*S*); $[\alpha]^{25}_{D}$ = -52.5° (c = 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 2.4 Hz, 1H), 8.36 - 8.35 (m, 1H), 7.71 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.33 - 7.28 (m, 2H), 7.20 - 7.17 (m, 1H), 6.86 - 6.81 (m, 2H), 3.78 (s, 3H), 3.49 (br.s, 1H), 1.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 146.7, 146.6, 144.4, 139.6, 133.8, 126.9, 122.8, 113.2, 73.7, 54.9, 30.4; IR (KBr, cm^{-1}) 3251, 2989, 2957, 2835, 1612, 1576, 1510, 1419, 1253, 1174, 1030, 920, 834, 816, 716; HRMS (ESI): *m/z* calcd. for $[M+H, C_{14}H_{16}NO_2]^+$: 230.1176; found: 230.1183.



Detector 254 nm

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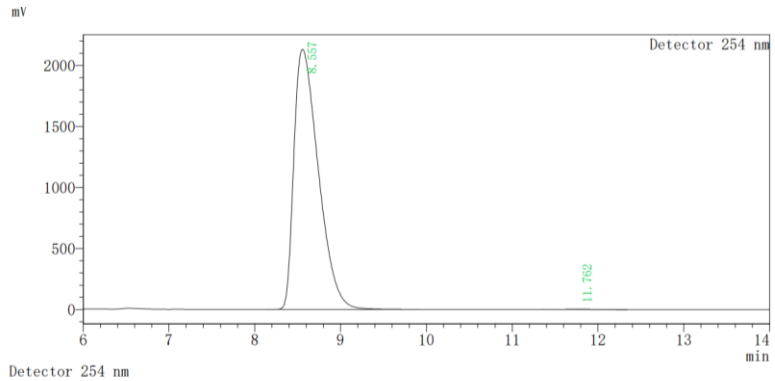
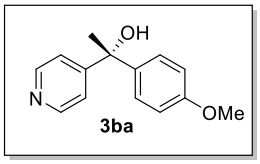
2	11.776	60835	38.377	1728379	50.222
Total		158518	100.000	3441457	100.000

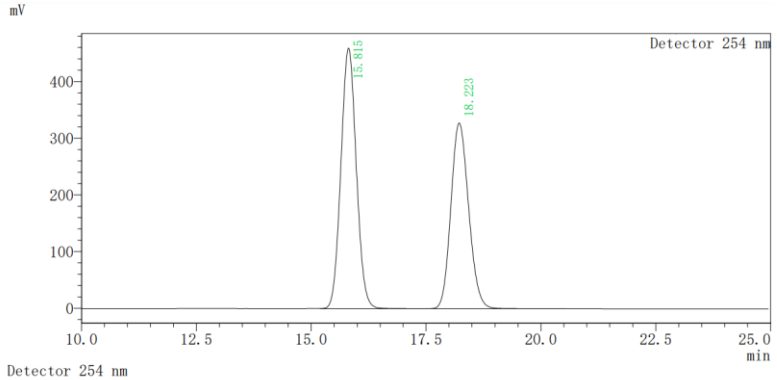


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	8.557	2130750	99.891	42205081	99.863
2	11.762	2330	0.109	58109	0.137
Total		2133080	100.000	42263190	100.000

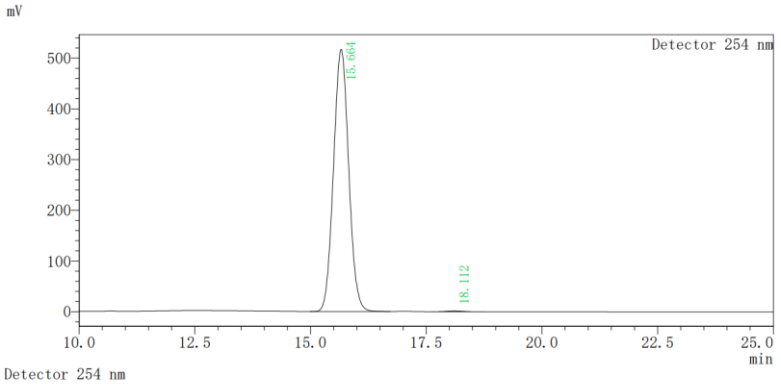


(*R*)-1-(4-methoxyphenyl)-1-(pyridin-4-yl)ethan-1-ol (3ba): General Procedure A was followed using 1-(pyridin-4-yl)ethan-1-one (24.2 mg, 0.20 mmol), and (4-methoxyphenyl)boronic acid (91.2 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), the desired product was obtained as a colorless solid (43.2 mg, 94% yield, >99% ee). Chiral HPLC conditions: chiralcel AD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol /diethylamine: 90/10/0.03, 254 nm, 15.7 min (*R*), 18.1 min (*S*); $[\alpha]^{25}_{D}$ = -25.0 ° (c = 0.74, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.48 - 8.42 (m, 2H), 7.40 - 7.36 (m, 2H), 7.36 - 7.31 (m, 2H), 6.91 - 6.78 (m, 2H), 5.84 (s, 1H), 3.71 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 158.7, 158.4, 149.7, 140.5, 127.3, 121.1, 113.7, 73.9, 55.5, 30.1; HRMS (FI): *m/z* calcd. for [M, $C_{14}H_{15}NO_2$]$^+$: 229.1097; found: 229.1093.



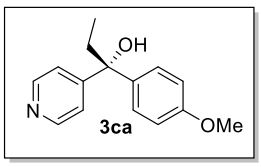
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	15.815	459357	58.371	10672388	54.733
2	18.223	327611	41.629	8826586	45.267
Total		786968	100.000	19498974	100.000

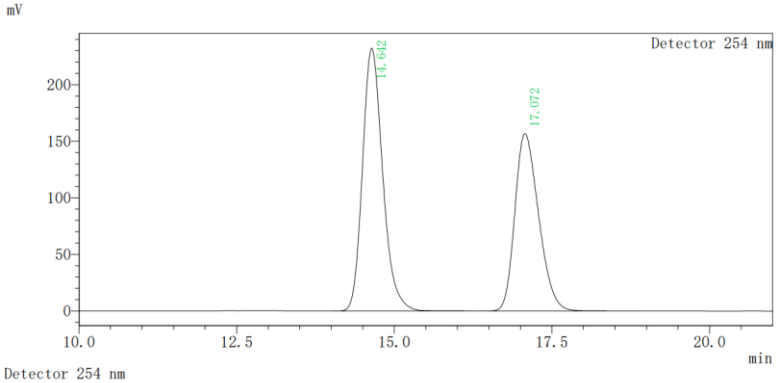


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	15.664	516913	99.737	11821689	99.705
2	18.112	1361	0.263	34938	0.295
Total		518273	100.000	11856627	100.000

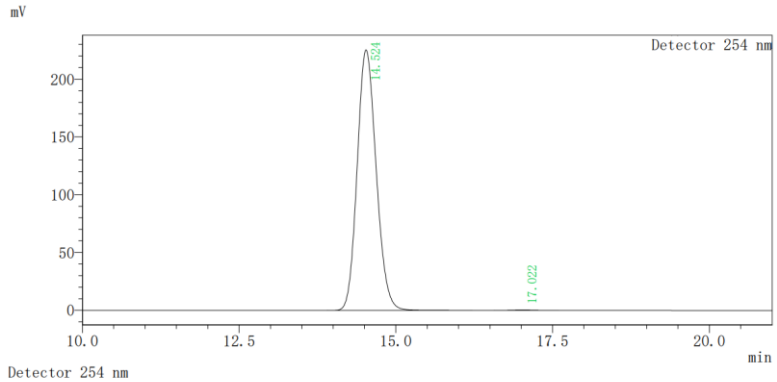


(*R*)-1-(4-methoxyphenyl)-1-(pyridin-4-yl)propan-1-ol (3ca): General Procedure A was followed using 1-(pyridin-4-yl)propan-1-one (27.0 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (91.2 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), the desired product was obtained as a colorless solid (44.8 mg, 92% yield, >99% ee). Chiral HPLC conditions: chiralcel AD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol /diethylamine: 90/10/0.03, 254 nm, 14.5 min (*R*), 17.0 min (*S*); $[\alpha]^{25}_{D}$ = -24.8 ° (c = 0.49, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.53 - 8.22 (m, 2H), 7.54 - 7.19 (m, 4H), 6.91 - 6.76 (m, 2H), 5.56 (s, 1H), 3.71 (s, 3H), 2.22 (q, *J* = 7.2 Hz, 2H), 0.74 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, DMSO) δ 158.2, 157.6, 149.6, 139.6, 127.4, 121.4, 113.7, 76.4, 55.4, 33.4, 8.5; IR (KBr, cm^{-1}): 3103, 2964, 2934, 2837, 1601, 1510, 1415, 1256, 1174, 1030, 985, 827, 816, 694; HRMS (ESI): *m/z* calcd. for $[M+H, C_{15}H_{18}NO_2]^+$: 244.1332; found: 244.1337.



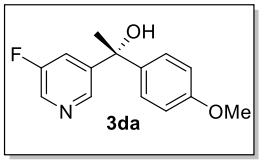
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	14.642	232431	59.719	5200303	55.796
2	17.072	156775	40.281	4119981	44.204
Total		389205	100.000	9320284	100.000

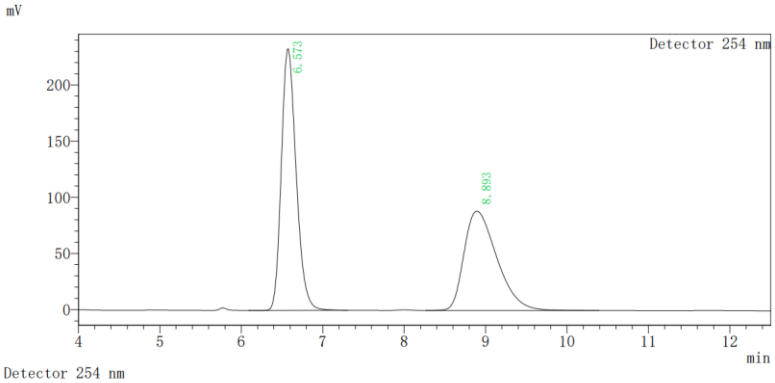


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	14.524	225512	99.837	4759937	99.810
2	17.022	368	0.163	9054	0.190
Total		225880	100.000	4768990	100.000

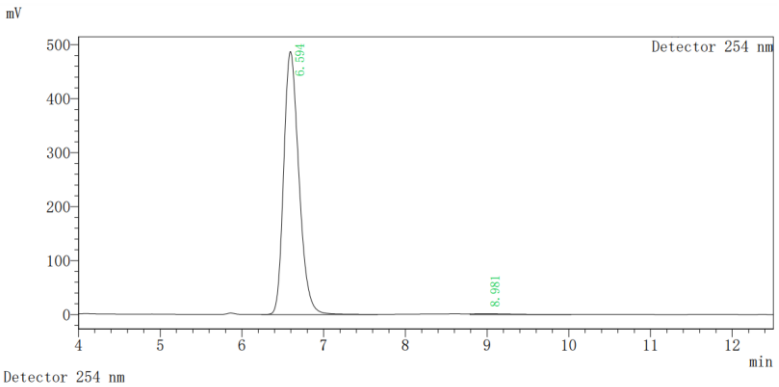


(*R*)-1-(5-fluoropyridin-3-yl)-1-(4-methoxyphenyl)ethan-1-ol (3da): General Procedure A was followed using 1-(5-fluoropyridin-3-yl)ethan-1-one (27.8 mg, 0.20 mmol), and (4-methoxyphenyl)boronic acid (91.2 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), the desired product was obtained as a colorless oil (47.3 mg, 95% yield, 99% ee). Chiral HPLC conditions: chiralpak AS-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol/diethylamine: 80/20/0.03, 254 nm, 6.6 min (*R*), 9.0 min (*S*); $[\alpha]^{25}_{D}$ = -22.1 ° (c = 0.78, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (t, *J* = 1.7 Hz, 1H), 8.14 (d, *J* = 2.7 Hz, 1H), 7.52 (dt, *J* = 9.8, 2.3 Hz, 1H), 7.36 - 7.25 (m, 2H), 6.91 - 6.79 (m, 2H), 4.32 (br.s, 0.88H), 3.79 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.2 (d, *J* = 256.2 Hz), 158.8, 146.5 (d, *J* = 2.8 Hz), 143.0 (d, *J* = 3.9 Hz), 138.7, 135.5 (d, *J* = 23.6 Hz), 127.0, 120.7 (d, *J* = 18.9 Hz), 113.7, 73.8, 55.2, 30.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -126.9 (s, 1F); IR (KBr, cm^{-1}): 3242, 2977, 2935, 2837, 1611, 1511, 1420, 1301, 1255, 1180, 1030, 897, 835, 709; HRMS (ESI): *m/z* calcd. for [M+H, $C_{14}H_{15}FNO_2$]$^+$: 248.1081; found: 248.1087.



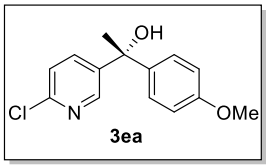
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.573	233012	72.462	2953225	54.317
2	8.893	88554	27.538	2483836	45.683
Total		321566	100.000	5437061	100.000

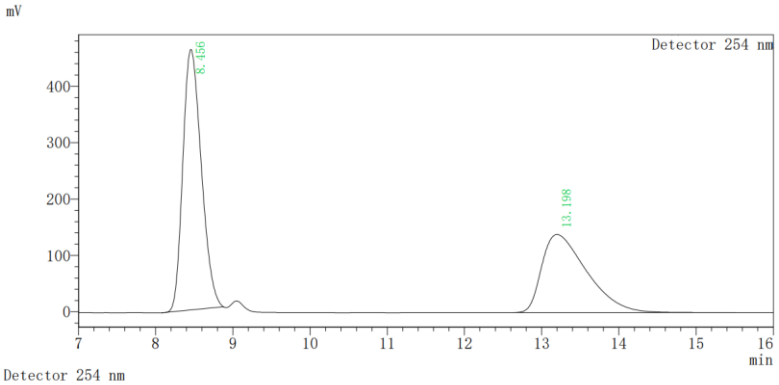


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.594	487326	99.732	6298669	99.253
2	8.981	1312	0.268	47418	0.747
Total		488637	100.000	6346087	100.000

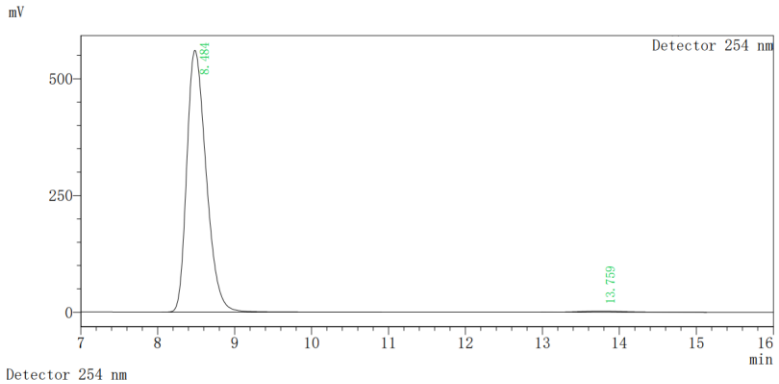


(*R*)-1-(6-chloropyridin-3-yl)-1-(4-methoxyphenyl)ethan-1-ol (3ea): General Procedure A was followed using 1-(6-chloropyridin-3-yl)ethan-1-one (31.0 mg, 0.20 mmol), and (4-methoxyphenyl)boronic acid (91.2 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), the desired product was obtained as a colorless solid (50.2 mg, 95% yield, 98% ee). Chiral HPLC conditions: chiralpak AS-H, 25 °C, flow rate: 1.0 mL/min, hexane/ isopropanol/diethylamine: 80/20/0.03, 254 nm, 8.5 min (*R*), 13.8 min (*S*); $[\alpha]^{25}_{D}$ = -46.2 ° (c = 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform -*d*) δ 8.37 (d, *J* = 2.5 Hz, 1H), 7.66 - 7.64 (m, 1H), 7.32 - 7.27 (m, 2H), 7.23 - 7.21 (m, 1H), 6.94 - 6.76 (m, 2H), 3.79 (s, 3H), 2.64 (br.s, 1H), 1.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 149.7, 147.3, 142.8, 138.7, 136.7, 127.1, 123.5, 113.8, 74.3, 55.3, 30.8; IR (KBr, cm^{-1}): 3361, 2975, 2934, 2836, 1608, 1583, 1511, 1461, 1372, 1251, 1108, 1028, 916, 832, 746; HRMS (ESI): *m/z* calcd. for [M+H, $C_{14}H_{15}ClNO_2]^+$: 264.0786; found: 264.0787.



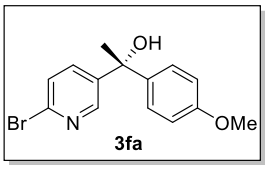
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	8.456	461807	76.938	7689082	57.851
2	13.198	138424	23.062	5602132	42.149
Total		600231	100.000	13291213	100.000



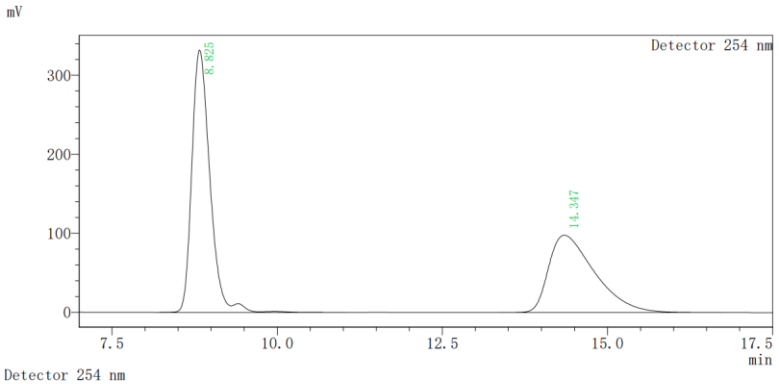
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	8.484	560780	99.509	9844257	98.907
2	13.759	2766	0.491	108751	1.093
Total		563546	100.000	9953008	100.000



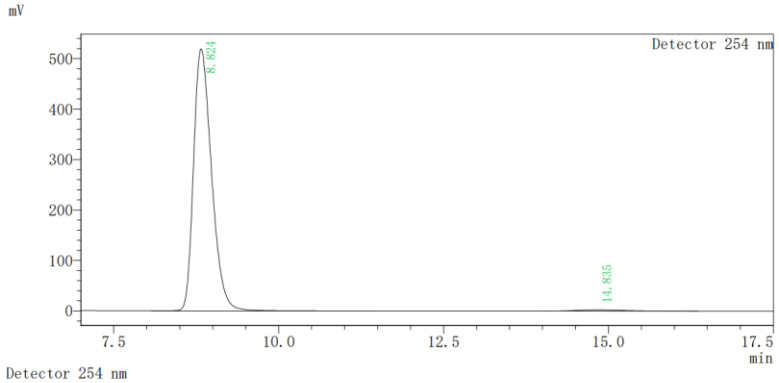
3fa

(*R*)-1-(6-bromopyridin-3-yl)-1-(4-methoxyphenyl)ethan-1-ol (3fa): General Procedure A was followed using 1-(6-bromopyridin-3-yl)ethan-1-one (39.8 mg, 0.20 mmol), and (4-methoxyphenyl)boronic acid (91.2 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), the desired product was obtained as a colorless oil (57.8 mg, 94% yield, 98% ee). Chiral HPLC conditions: chiralpak AS-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol/diethylamine: 80/20/0.03, 254 nm, 8.8 min (*R*), 14.8 min (*S*); $[\alpha]^{25}_{D}$ = -24.7 ° (c = 0.55, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 2.5 Hz, 1H), 7.56 - 7.54 (m, 1H), 7.40 - 7.38 (m, 1H), 7.33 - 7.27 (m, 2H), 6.92 - 6.81 (m, 2H), 3.80 (s, 3H), 2.32 (br.s, 1H), 1.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 147.7, 143.4, 139.8, 138.6, 136.6, 127.2, 127.0, 113.6, 74.0, 55.1, 30.5; HRMS (ESI): *m/z* calcd. for [M+H, $C_{14}H_{15}BrNO_2$]$^+$:308.0281; found: 308.0286.



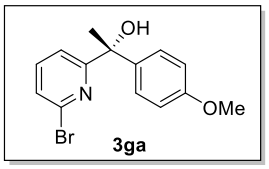
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	8.825	331918	77.238	6342907	57.292
2	14.347	97818	22.762	4728343	42.708
Total		429736	100.000	11071250	100.000

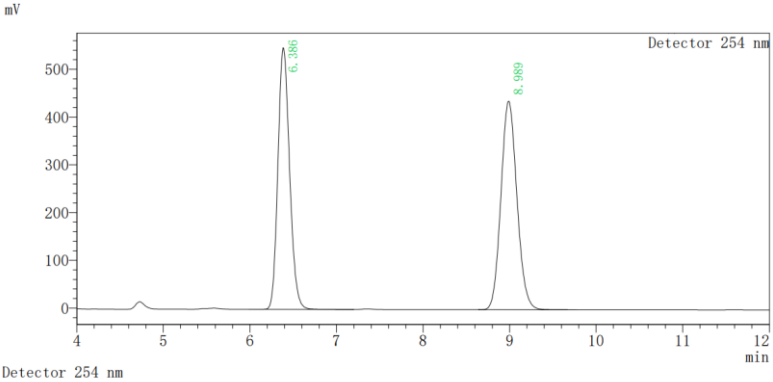


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	8.824	519513	99.555	9888753	98.907
2	14.835	2325	0.445	109247	1.093
Total		521838	100.000	9998001	100.000

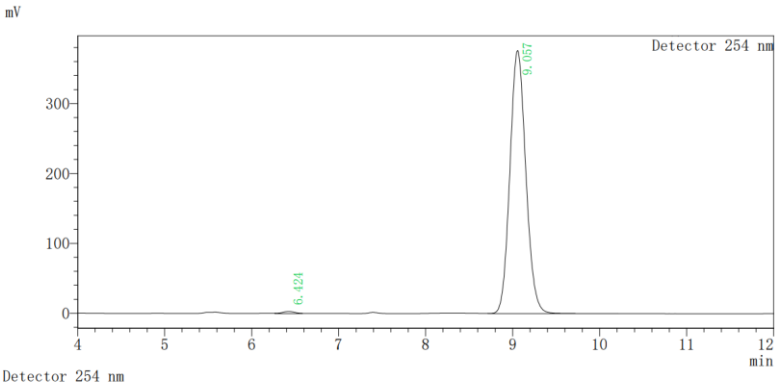


(*R*)-1-(6-bromopyridin-2-yl)-1-(4-methoxyphenyl)ethan-1-ol (3ga): General Procedure A was followed using 1-(6-bromopyridin-2-yl)ethan-1-one (39.8 mg, 0.20 mmol), and (4-methoxyphenyl)boronic acid (91.2 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), the desired product was obtained as a colorless oil (57.3 mg, 93% yield, 99% ee). Chiral HPLC conditions: chiralpak IC, 25 ºC, flow rate: 1.0 mL/min, hexane /isopropanol/diethylamine: 80/20/0.03, 254 nm, 6.4 min (*S*), 9.1 min (*R*); $[\alpha]^{25}_{D}$ = -115.0 ° (c = 0.92, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 - 7.45 (m, 1H), 7.41 - 7.31 (m, 3H), 7.21 - 7.19 (m, 1H), 6.88 - 6.81 (m, 2H), 4.95 (br.s, 1H), 3.78 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 158.6, 140.3, 139.1, 138.3, 127.1, 126.2, 119.0, 113.5, 75.0, 55.2, 29.4; HRMS (ESI): *m/z* calcd. for [M+Na, $C_{14}H_{14}BrNNaO_2$]$^+$: 330.0100; found: 330.0107.



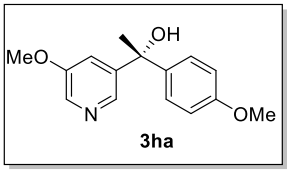
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.386	547739	55.649	5133806	47.784
2	8.989	436537	44.351	5610082	52.216
Total		984276	100.000	10743888	100.000



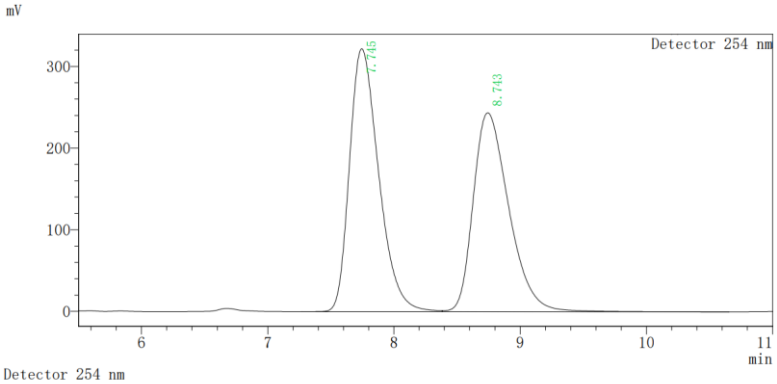
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.424	3094	0.815	30953	0.640
2	9.057	376451	99.185	4802197	99.360
Total		379545	100.000	4833150	100.000



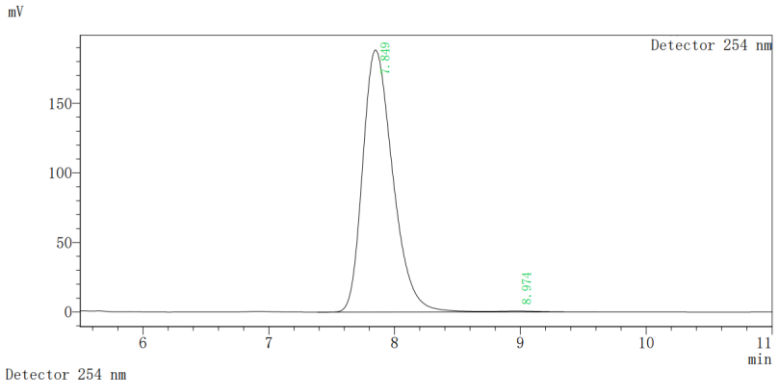
3ha

(*R*)-1-(4-methoxyphenyl)-1-(5-methoxypyridin-3-yl)ethan-1-ol (3ha): General Procedure A was followed using 1-(5-methoxypyridin-3-yl)ethan-1-one (30.2 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (91.2 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), the desired product was obtained as a colorless oil (46.6 mg, 90% yield, 99% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol/diethylamine: 80/20/0.03, 254 nm, 7.8 min (*R*), 9.0 min (*S*); $[\alpha]^{25}_{D}$ = -34.7 ° (c = 0.54, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 1.9 Hz, 1H), 7.87 (d, *J* = 2.8 Hz, 1H), 7.31 (t, *J* = 2.3 Hz, 1H), 7.28 - 7.23 (m, 2H), 6.86 - 6.66 (m, 2H), 4.95 (br.s, 1H), 3.72 (d, *J* = 7.5 Hz, 6H), 1.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 155.3, 145.4, 139.5, 139.2, 134.2, 127.0, 118.8, 113.4, 73.8, 55.3, 55.0, 30.5; IR (KBr, cm^{-1}): 3206, 2972, 2933, 2837, 1609, 1583, 1510, 1456, 1423, 1282, 1250, 1178, 1035, 874, 835, 713; HRMS (ESI): *m/z* calcd. for [M+H, $C_{15}H_{18}NO_3$]$^+$: 260.1281; found: 260.1287.



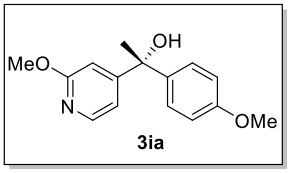
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	7.745	321957	56.906	5181526	52.010
2	8.743	243815	43.094	4780944	47.990
Total		565773	100.000	9962470	100.000



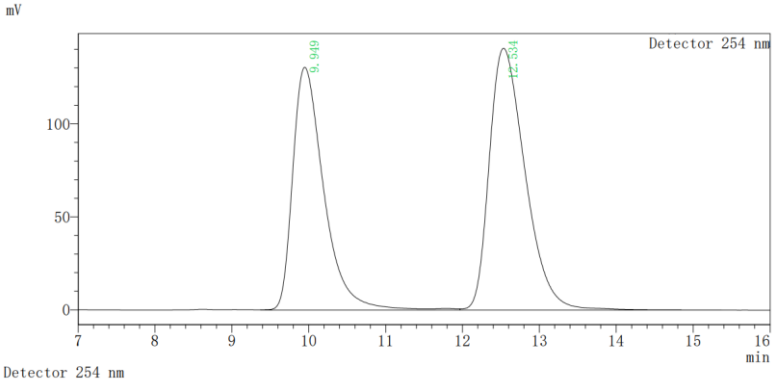
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	7.849	188445	99.619	3142158	99.409
2	8.974	720	0.381	18670	0.591
Total		189165	100.000	3160829	100.000



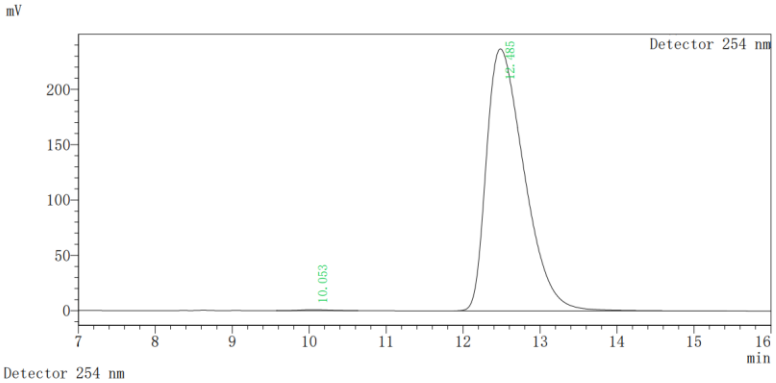
3ia

(*R*)-1-(4-methoxyphenyl)-1-(2-methoxypyridin-4-yl)etha n-1-ol (3ia): General Procedure A was followed using 1-(2-methoxypyridin-4-yl)ethan-1-one (30.2 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (91.2 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), the desired product was obtained as a colorless solid (48.0 mg, 92% yield, >99% ee). Chiral HPLC conditions: chiralpak AS-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol/diethylamine: 80/20/0.03, 254 nm, 10.1 min (*S*), 12.5 min (*R*); $[\alpha]^{25}_{D}$ = -52.6 ° (c = 0.40, $CHCl_3$);^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 - 7.99 (m, 1H), 7.32 - 7.27 (m, 2H), 6.85 - 6.80 (m, 4H), 3.89 (s, 3H), 3.76 (s, 3H), 2.66 (br.s, 1H), 1.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 160.1, 158.6, 146.4, 138.6, 127.0, 114.5, 113.5, 107.4, 74.9, 55.1, 53.4, 29.9; IR (KBr, cm^{-1}): 3183, 2972, 2935, 2840, 1602, 1512, 1463, 1382, 1299, 1246, 1165, 1029, 896, 840, 767; HRMS (ESI): *m/z* calcd. for [M+H, $C_{15}H_{18}NO_3$]$^+$: 260.1281; found: 260.1287.



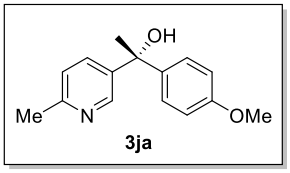
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	9.949	130373	48.108	3673166	44.579
2	12.534	140626	51.892	4566507	55.421
Total		270998	100.000	8239674	100.000



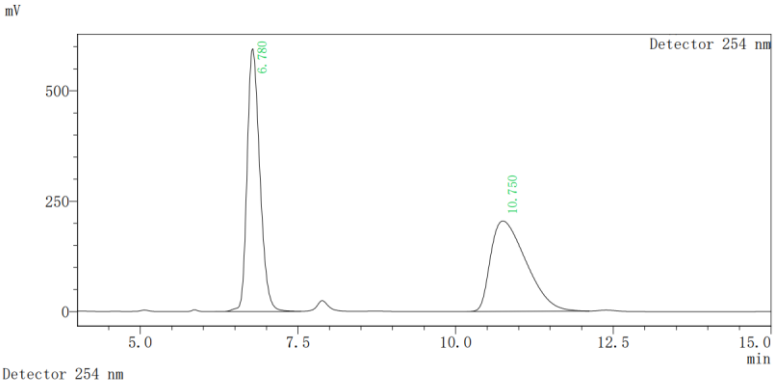
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	10.053	755	0.318	18037	0.223
2	12.485	236589	99.682	8062668	99.777
Total		237344	100.000	8080705	100.000



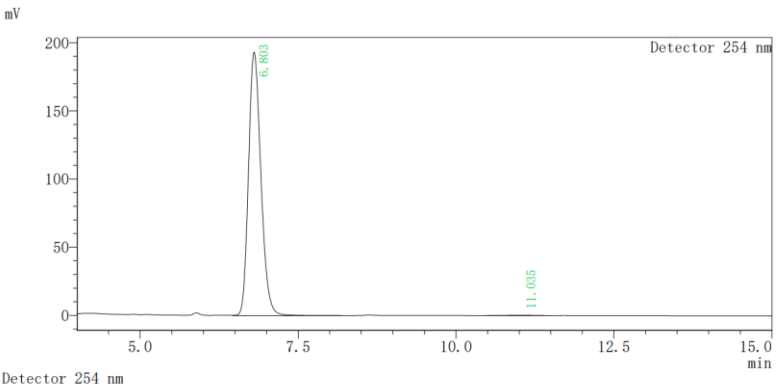
3ja

(*R*)-1-(4-methoxyphenyl)-1-(6-methylpyridin-3-yl)ethan-1-ol (3ja): General Procedure A was followed using 1-(6-methylpyridin-3-yl)ethan-1-one (27.0 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (91.2 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), the desired product was obtained as a colorless solid (31.4 mg, 64% yield, >99% ee). Chiral HPLC conditions: chiralpak AS-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol/diethylamine: 80/20/0.03, 254 nm, 6.8 min (*R*), 11.0 min (*S*); $[\alpha]^{25}_{D}$ = -23.3 ° (c = 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 2.2 Hz, 1H), 7.60 - 7.58 (m, 1H), 7.36 - 7.27 (m, 2H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.90 - 6.78 (m, 2H), 3.79 (s, 3H), 2.60 (br.s, 0.74H), 2.51 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 156.5, 146.5, 140.8, 139.6, 134.2, 127.0, 122.6, 113.6, 74.4, 55.2, 30.8, 23.8; IR (KBr, cm^{-1}): 3166, 3002, 2966, 2833, 1610, 1511, 1377, 1296, 1248, 1182, 1100, 1032, 924, 835, 767; HRMS (ESI): *m/z* calcd. for [M+H, $C_{15}H_{18}NO_2]^+$: 244.1332; found: 244.1337.



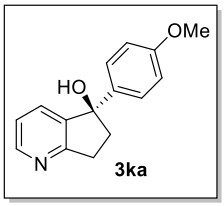
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.780	595011	74.390	8360407	51.104
2	10.750	204844	25.610	7999197	48.896
Total		799855	100.000	16359604	100.000

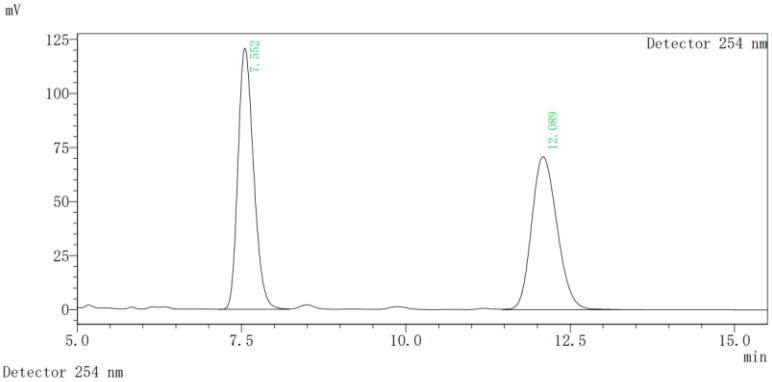


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.803	193088	99.890	2638978	99.740
2	11.035	213	0.110	6882	0.260
Total		193301	100.000	2645859	100.000

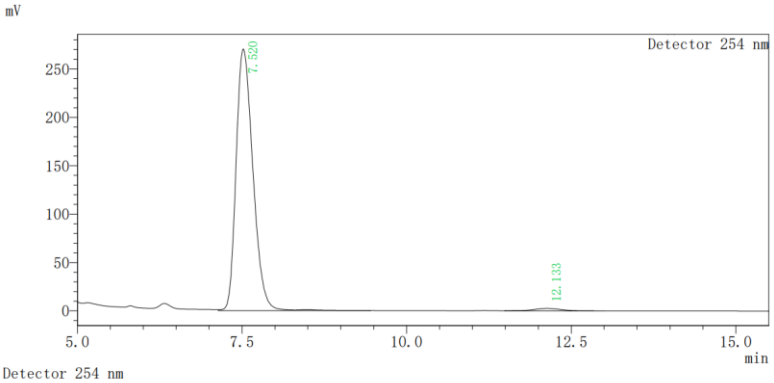


(*R*)-5-(4-methoxyphenyl)-6,7-dihydro-5H-cyclopenta[b]pyridin-5-ol (3ka): General Procedure A was followed using 6,7-dihydro-5H-cyclopenta[*b*]pyridin-5-one (26.6 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (91.2 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), the desired product was obtained as a colorless solid (32.3 mg, 67% yield, 97% ee). Chiral HPLC conditions: chiralpak AS-H, 25 °C, flow rate: 1.0 mL/min, hexane /isopropanol/diethylamine: 80/20/0.03, 254 nm, 7.5 min (*R*), 12.1 min (*S*); $[\alpha]^{25}_{D}$ = -10.2 ° (c = 0.54, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 4.7 Hz, 1H), 7.45 - 7.43 (m, 1H), 7.31 - 7.24 (m, 2H), 7.14 - 7.10 (m, 1H), 6.89 - 6.83 (m, 2H), 3.80 (s, 3H), 3.27 - 3.16 (m, 1H), 3.06 - 2.98 (m, 1H), 2.89 (br.s, 1H), 2.60 - 2.42 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 158.7, 149.4, 141.5, 138.1, 132.4, 126.7, 121.9, 113.5, 83.2, 55.2, 42.8, 31.6; IR (KBr, cm^{-1}): 3390, 3001, 2956, 2835, 1613, 1587, 1511, 1421, 1355, 1249, 1171, 1034, 917, 834, 716; HRMS (ESI): *m/z* calcd. for [M+H, $C_{15}H_{16}NO_2]^+$: 242.1176; found: 242.1174.



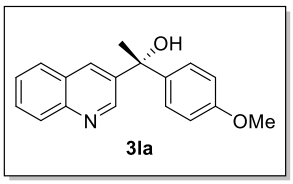
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	7.552	120701	63.037	1997607	51.162
2	12.089	70775	36.963	1906890	48.838
Total		191475	100.000	3904497	100.000



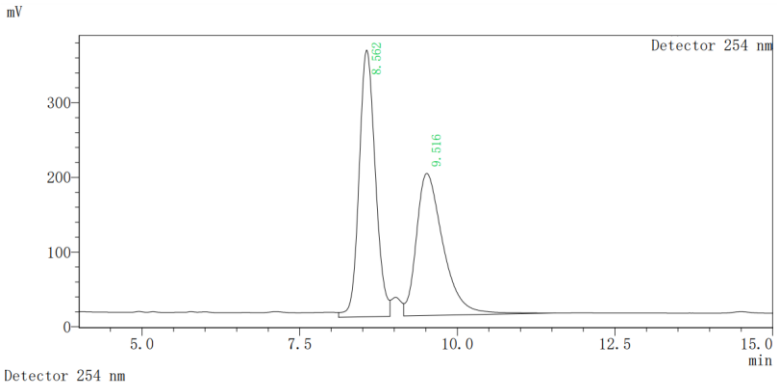
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	7.520	270329	99.059	4819991	98.529
2	12.133	2569	0.941	71950	1.471
Total		272898	100.000	4891942	100.000



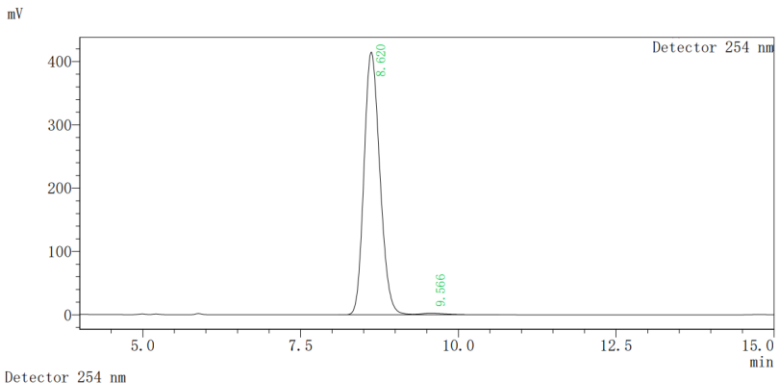
3la

(*R*)-1-(4-methoxyphenyl)-1-(quinolin-3-yl)ethan-1-ol (3la): General Procedure A was followed using 1-(quinolin-3-yl)ethan-1-one (34.2 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (91.2 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), the desired product was obtained as a colorless solid (52.3 mg, 93% yield, 98% ee). Chiral HPLC conditions: chiralpak AS-H, 25 ºC, flow rate: 1.0 mL/min, hexane /isopropanol/diethylamine: 80/20/0.03, 254 nm, 8.6 min (*R*), 9.6 min (*S*); $[\alpha]^{25}_{D}$ = -54.8 ° (c = 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (d, *J* = 2.3 Hz, 1H), 8.23 (d, *J* = 2.3 Hz, 1H), 8.01 - 7.99 (m, 1H), 7.73 - 7.71 (m, 1H), 7.65 - 7.56 (m, 1H), 7.51 - 7.44 (m, 1H), 7.34 - 7.28 (m, 2H), 6.83 - 6.75 (m, 2H), 4.61 (br.s, 1H), 3.74 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 149.6, 146.1, 141.3, 139.2, 131.8, 129.1, 128.3, 127.9, 127.4, 127.2, 126.6, 113.5, 74.3, 55.1, 30.5; IR (KBr, cm^{-1}): 3192, 2976, 2931, 2838, 1609, 1514, 1495, 1372, 1253, 1178, 1028, 914, 835, 757; HRMS (ESI): *m/z* calcd. for [M+H, $C_{18}H_{18}NO_2$]$^+$: 280.1332; found: 280.1335.



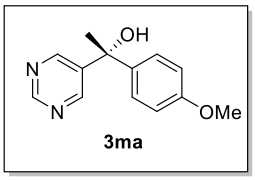
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	8.562	356881	65.204	6401452	53.152
2	9.516	190447	34.796	5642229	46.848
Total		547328	100.000	12043681	100.000

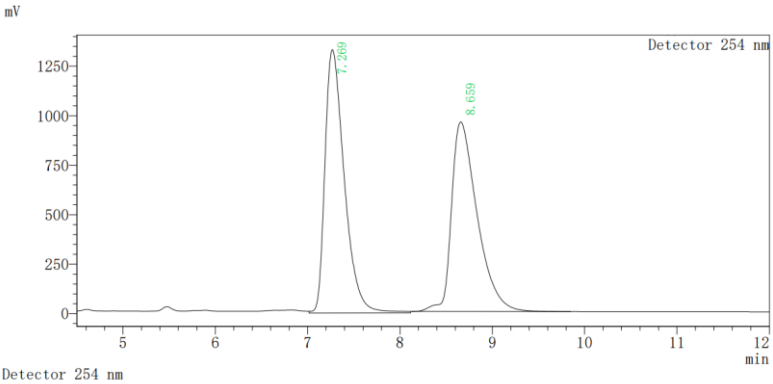


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	8.620	414869	99.443	7264090	99.075
2	9.566	2323	0.557	67835	0.925
Total		417191	100.000	7331925	100.000

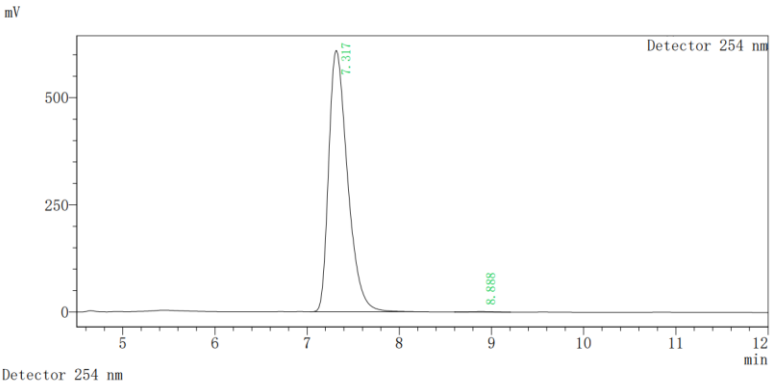


(*R*)-1-(4-methoxyphenyl)-1-(pyrimidin-5-yl)ethan-1-ol (3ma): General Procedure A was followed using 1-(pyrimidin -5-yl)ethan-1-one (24.4 mg, 0.20 mmol), (4-methoxyphenyl)-boronic acid (91.2 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (2/1 → 1/2, v/v), the desired product was obtained as a colorless solid (32.3 mg, 70% yield, >99% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol/diethylamine: 80/20/0.03, 254 nm, 7.3 min (*R*), 8.9 min (*S*); $[\alpha]^{25}_{D}$ = -10.6 ° (c = 0.42, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.93 (s, 1H), 8.67 (s, 2H), 7.35 - 7.27 (m, 2H), 6.91 - 6.81 (m, 2H), 3.77 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0, 156.4, 154.4, 141.7, 138.1, 127.0, 113.8, 73.0, 55.2, 30.4; IR (KBr, cm^{-1}): 3330, 2963, 2932, 2838, 1613, 1563, 1511, 1430, 1409, 1252, 1098, 1029, 910, 821, 726; HRMS (ESI): *m/z* calcd. for $[M+H, C_{13}H_{15}N_2O_2]^+$: 231.1128; found: 231.1133.



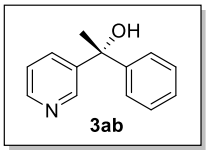
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	7.269	1328876	58.117	19354666	51.070
2	8.659	957696	41.883	18543513	48.930
Total		2286572	100.000	37898178	100.000

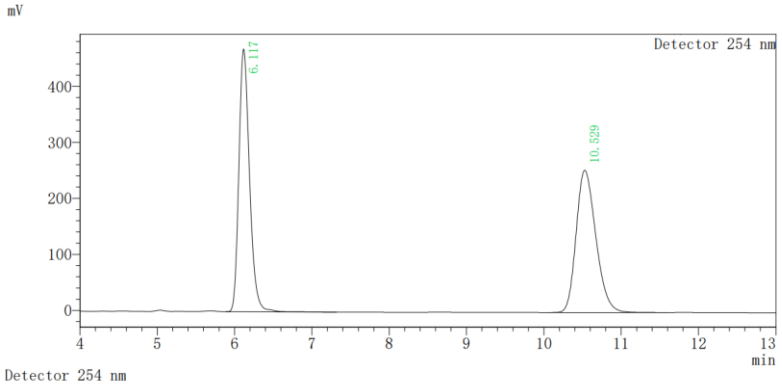


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	7.317	609751	99.834	8664852	99.815
2	8.888	1014	0.166	16071	0.185
Total		610765	100.000	8680924	100.000

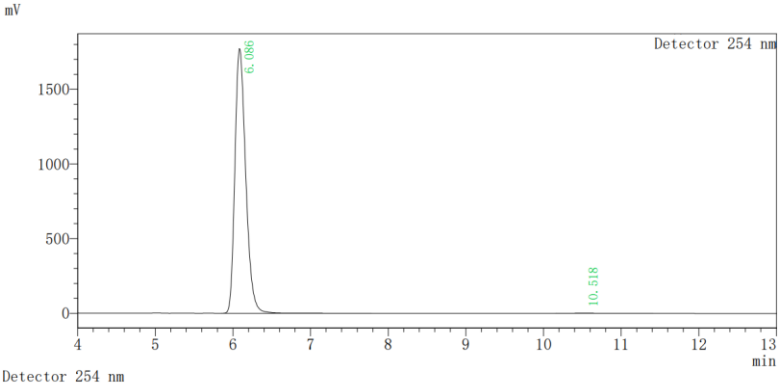


(*R*)-1-phenyl-1-(pyridin-3-yl)ethan-1-ol (3ab): General Procedure A was followed using 1-(pyridin-3-yl)ethan-1-one (24.2 mg, 0.20 mmol) and phenylboronic acid (73.2 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), the desired product was obtained as a colorless solid (33.5 mg, 84% yield, >99% ee). The absolute configuration was determined by comparing its optical rotation with reported data[2]. Chiral HPLC conditions: chiralpak IC, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol/diethylamine: 70/30/0.03, 254 nm, 6.1 min (*R*), 10.5 min (*S*); $[\alpha]^{25}_{D}$ = -22.5 ° (c = 0.22, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 2.0 Hz, 1H), 8.27 - 8.26 (m, 1H), 7.74 - 7.70 (m, 1H), 7.42 - 7.36 (m, 2H), 7.31 - 7.27 , 2H), 7.26 - 7.20 (m, 1H), 7.17 - 7.14 (m, 1H), 4.48 (br.s, 1H), 1.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 147.2, 147.1, 143.9, 133.9, 128.2, 127.1, 125.8, 123.0, 74.5, 30.5; HRMS (ESI): *m/z* calcd. for [M+H, $C_{13}H_{14}NO]^+$: 200.1070; found: 200.1074.



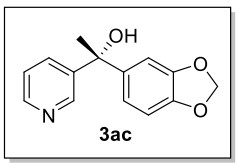
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.117	469529	64.912	4500892	50.041
2	10.529	253797	35.088	4493479	49.959
Total		723326	100.000	8994371	100.000

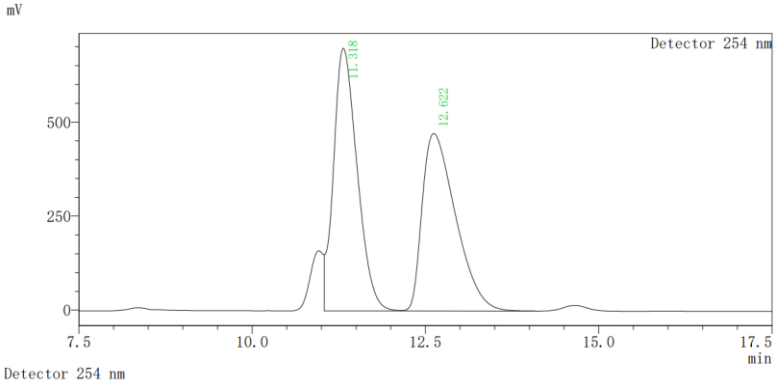


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.086	1772959	99.898	17247330	99.813
2	10.518	1807	0.102	32365	0.187
Total		1774766	100.000	17279695	100.000

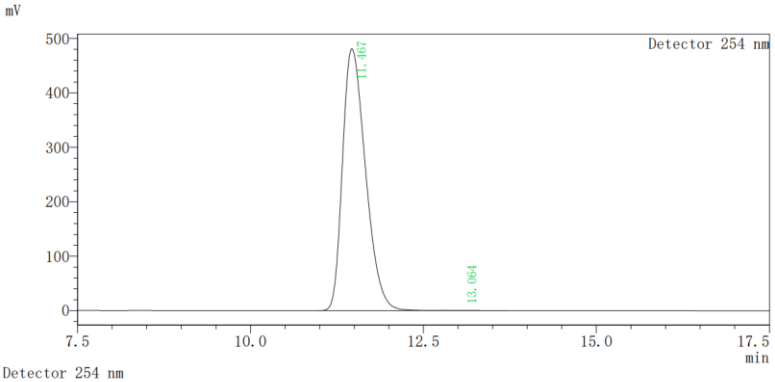


(*R*)-1-(benzo[d][1,3]dioxol-5-yl)-1-(pyridin-3-yl)ethan-1-ol (3ac): General Procedure A was followed using 1-(pyridin-3-yl)-ethan-1-one (24.2 mg, 0.20 mmol) and benzo[*d*][1,3]dioxol-5-yl-boronic acid (99.6 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (2/1 → 1/1, v/v), the desired product was obtained as a colorless solid (38.1 mg, 78% yield, >99% ee). Chiral HPLC conditions: chiralpak AS-H, 25 ºC, flow rate: 1.0 mL/min, hexane /isopropanol/diethylamine: 80/20/0.03, 254 nm, 11.5 min (*R*), 13.1 min (*S*); $[\alpha]^{25}_{D}$ = -28.8 ° (c = 0.44, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (d, *J* = 1.9 Hz, 1H), 8.25 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.71 (dt, *J* = 8.1, 2.0 Hz, 1H), 7.16 - 7.13 (m, 1H), 6.89 - 6.79 (m, 2H), 6.70 - 6.68 (m, 1H), 5.88 (s, 2H), 4.14 (br.s, 1H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 147.1, 146.9, 146.4, 144.1, 141.5, 133.8, 123.0, 118.9, 107.6, 106.9, 100.9, 74.2, 30.6; IR (KBr, cm^{-1}): 3224, 2980, 2896, 1489, 1441, 1377, 1251, 1104, 1087, 1040, 932, 799, 716; HRMS (ESI): *m/z* calcd. for [M+H, $C_{14}H_{14}NO_3]^+$: 244.0968; found: 244.0971.



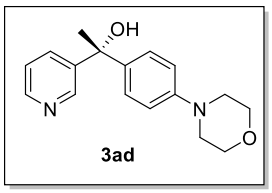
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	11.318	698303	59.685	16508732	51.077
2	12.622	471682	40.315	15812633	48.923
Total		1169984	100.000	32321365	100.000

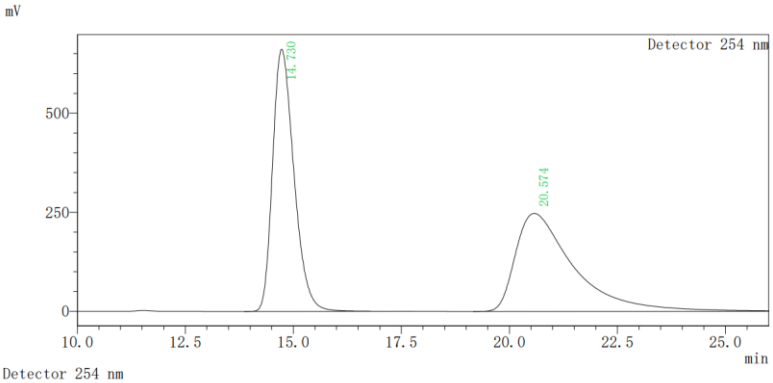


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	11.467	481033	99.909	11074387	99.864
2	13.064	440	0.091	15112	0.136
Total		481473	100.000	11089499	100.000

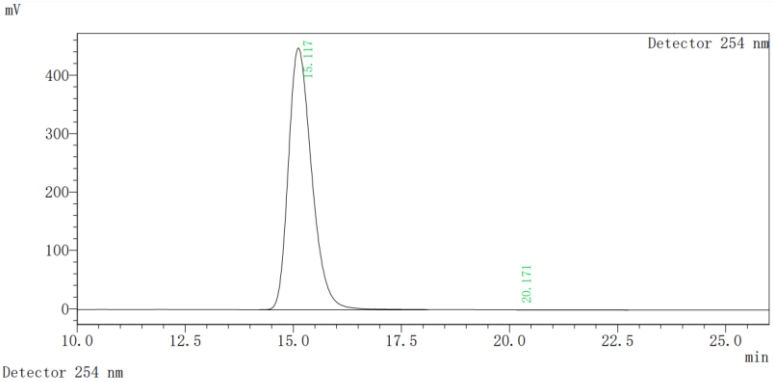


(*R*)-1-(4-morpholinophenyl)-1-(pyridin-3-yl)ethan-1-ol (3ad): General Procedure A was followed using 1-(pyridin-3-yl)ethan-1-one (24.2 mg, 0.20 mmol) and (4-morpholinophenyl)boronic acid (124.2 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), the desired product was obtained as a colorless solid (42.4 mg, 74% yield, >99% ee). Chiral HPLC conditions: chiralpak AS-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol/diethylamine: 80/20/0.03, 254 nm, 15.1 min (*R*), 20.2 min (*S*); $[\alpha]^{25}_{D}$ = -48.2 ° (c =0.08, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 2.3 Hz, 1H), 8.45 - 8.44 (m, 1H), 7.72 (m, 1H), 7.36 - 7.27 (m, 2H), 7.23 - 7.19 (m, 1H), 6.95 - 6.77 (m, 2H), 3.84 (t, *J* = 4.8 Hz, 4H), 3.14 (t, *J* = 5.2 Hz, 4H), 2.53 (s, 1H), 1.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 147.2, 147.0, 144.2, 138.5, 133.9, 126.8, 122.9, 115.1, 74.3, 66.7, 49.0, 30.1; IR (KBr, cm^{-1}): 3193, 2964, 2919, 2849, 1610, 1514, 1450, 1369, 1261, 1229, 1123, 1086, 926, 830, 711; HRMS (ESI): *m/z* calcd. for $[M+H, C_{17}H_{21}N_2O_2]^+$: 285.1598; found: 285.1605.



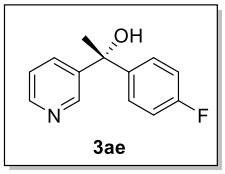
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	14.730	661286	72.779	22762686	49.506
2	20.574	247331	27.221	23216722	50.494
Total		908617	100.000	45979408	100.000

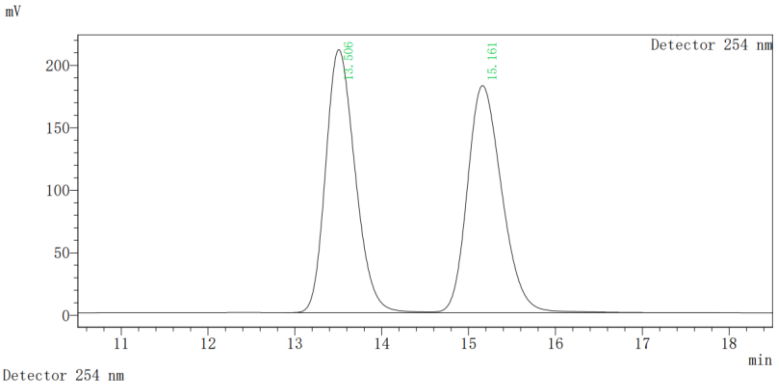


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	15.117	448331	99.979	16880404	99.950
2	20.171	92	0.021	8390	0.050
Total		448423	100.000	16888794	100.000

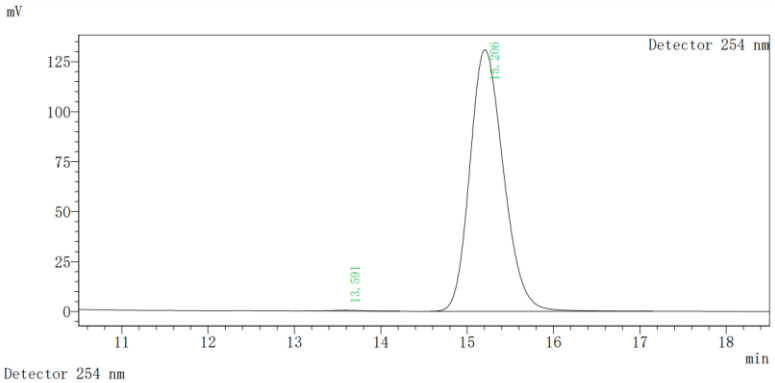


(*R*)-1-(4-fluorophenyl)-1-(pyridin-3-yl)ethan-1-ol (3ae): General Procedure A was followed using 1-(pyridin-3-yl)ethan-1-one (24.2 mg, 0.20 mmol) and (4-fluorophenyl)boronic acid (84.0 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/1, v/v), the desired product was obtained as a colorless oil (32.5 mg, 75% yield, >99% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol /diethylamine: 90/10/0.03, 254 nm, 13.6 min (*S*), 15.2 min (*R*); $[\alpha]^{25}_{D}$ = -9.0 ° (c = 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 8.24 (d, *J* = 4.8 Hz, 1H), 7.70 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.39 - 7.28 (m, 2H), 7.18 - 7.15(m, 1H), 7.03 - 6.87 (m, 2H), 4.87 (br.s, 1H), 1.89 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.0, 160.5, 147.2 (d, *J* = 40.3 Hz), 143.9, 143.1(d, *J* = 3.2 Hz), 133.9, 127.6 (d, *J* = 8.0 Hz), 123.1, 115.0 (d, *J* = 21.3 Hz), 74.1, 30.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.2 (s, 1F); IR (KBr, cm^{-1}): 3113, 2967, 2818, 1597, 1504, 1430, 1224, 1160, 1138, 1087, 1038, 924, 832, 711; HRMS (ESI): *m/z* calcd. for [M+H, $C_{13}H_{13}FNO]^+$: 218.0976; found: 218.0978.



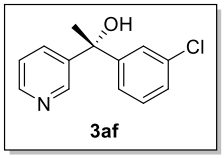
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	13.506	210499	53.662	4970200	49.764
2	15.161	181769	46.338	5017426	50.236
Total		392268	100.000	9987626	100.000

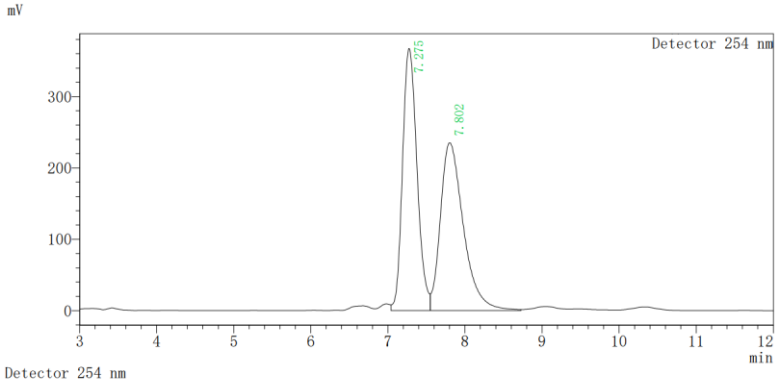


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	13.591	366	0.279	9618	0.271
2	15.206	130896	99.721	3541555	99.729
Total		131262	100.000	3551174	100.000

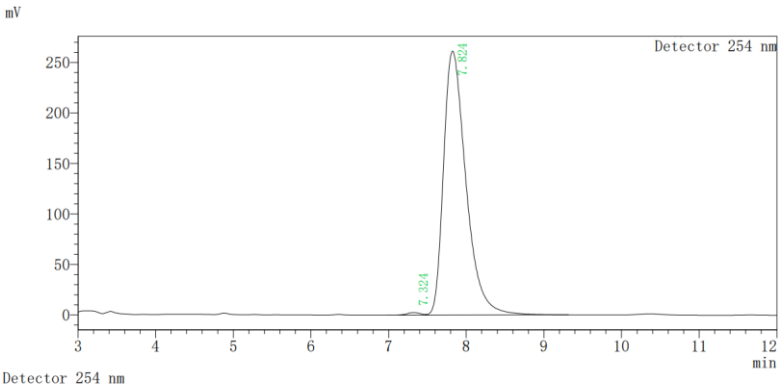


(*R*)-1-(3-chlorophenyl)-1-(pyridin-3-yl)ethan-1-ol (3af): General Procedure A was followed using 1-(pyridin-3-yl)ethan-1-one (24.2 mg, 0.20 mmol) and (3-chlorophenyl)boronic acid (93.8 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 2/1, v/v), the desired product was obtained as a colorless oil (27.7 mg, 59% yield, 99% ee). Chiral HPLC conditions: chiralpak AS-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol /diethylamine: 80/20/0.03, 254 nm, 7.3 min (*S*), 7.8 min (*R*); $[\alpha]^{25}_{D}$ = -0.3 ° (c = 0.30, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 2.3 Hz, 1H), 8.26 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.73 - 7.70 m, 1H), 7.42 (m, 1H), 7.25 - 7.15 (m, 4H), 4.91 (br.s, 1H), 1.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 147.5, 146.9, 143.4, 134.2, 134.1, 129.5, 127.2, 126.1, 124.0, 123.2, 74.1, 30.4; IR (KBr, cm^{-1}): 3179, 2978, 2928, 2854, 1593, 1572, 1474, 1419, 1191, 1079, 1027, 925, 787, 699; HRMS (ESI): *m/z* calcd. for $[M+H, C_{13}H_{13}ClNO]^+$: 234.0680; found: 234.0689.



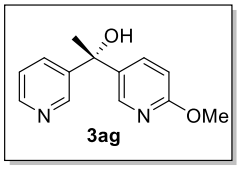
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	7.275	367442	60.956	4795656	49.583
2	7.802	235356	39.044	4876260	50.417
Total		602798	100.000	9671916	100.000

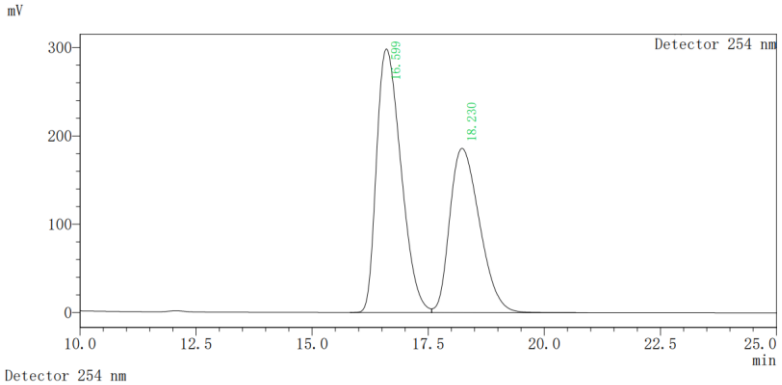


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	7.324	2615	0.990	33113	0.627
2	7.824	261396	99.010	5246068	99.373
Total		264011	100.000	5279181	100.000

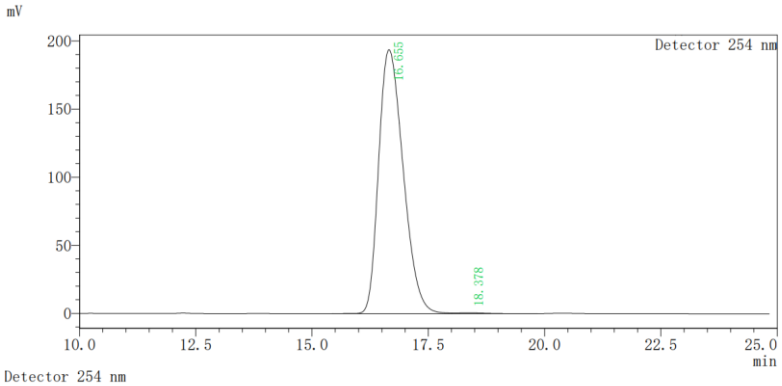


(*S*)-1-(6-methoxypyridin-3-yl)-1-(pyridin-3-yl)ethan-1-ol (3ag): General Procedure A was followed using 1-(pyridin-3-yl)-ethan-1-one (24.2 mg, 0.20 mmol) and (6-methoxypyridin-3-yl)-boronic acid (91.8 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (3/1 → 1/2, v/v), the desired product was obtained as a colorless solid (36.6 mg, 79% yield, >99% ee). Chiral HPLC conditions: chiralpak AS-H, 25 ºC, flow rate: 1.0 mL/min, hexane /isopropanol/diethylamine: 90/10/0.03, 254 nm, 16.7 min (*S*), 18.4 min (*R*); $[\alpha]^{25}_{D}$ = -6.3 ° (c = 0.28, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.53 (d, *J* = 1.8 Hz, 1H), 8.34 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.16 - 8.15 m, 1H), 7.73 - 7.70 m, 1H), 7.55 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.22 - 7.18 (m, 1H), 6.67 - 6.65 (m, 1H), 4.21 (br.s, 0.71H), 3.89 (s, 3H), 1.91 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 147.7, 147.0, 144.0, 143.4, 137.2, 135.5, 133.9, 123.1, 110.6, 73.2, 53.5, 30.5; IR (KBr, cm^{-1}): 3196, 2955, 2921, 1606, 1572, 1492, 1366, 1282, 1216, 1020, 919, 836, 709; HRMS (ESI): *m/z* calcd. for $[M+H, C_{13}H_{15}N_2O_2]^+$: 231.1128; found: 231.1133.



Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	16.599	298203	61.605	10961607	56.902
2	18.230	185851	38.395	8302527	43.098
Total		484054	100.000	19264134	100.000

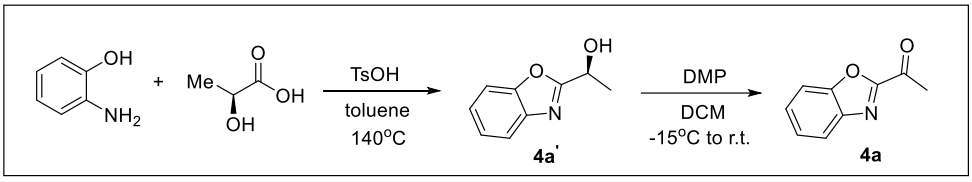


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	16.655	193728	99.697	7123939	99.627
2	18.378	588	0.303	26688	0.373
Total		194316	100.000	7150626	100.000

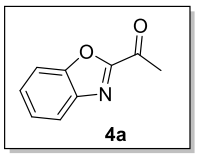
4. Synthesis of substrates for enantioselective Rh-catalyzed addition of arylboronic acids to α-Ketobenzoxazoles

α-Ketobenzoxazoles (except **4m**) were synthesized according to the followed scheme. Preparation of **4a** was shown as a representative example[3].

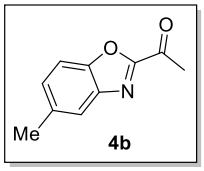


An oven-dried three-necked flask equipped with Dean-Stark apparatus was charged with 2-aminophenol (10.0 g, 91.66 mmol, 1.0 equiv) and TsOH (2.63 g, 13.75 mmol, 0.15 equiv), then fresh distilled toluene (160 mL) was added to the mixture. After stirring at room temperature for 5 minutes, the flask was moved to an oil bath, (*S*)-2-hydroxypropanoic acid (8.67 g, 96.24 mmol, 1.05 equiv) was added. The toluene collected in Dean-Stark apparatus was removed for 2 times at beginning of the reaction. The reaction was stirred at 140 ℃ overnight, then the three-necked flask was removed from the bath oil and allowed to cool to room temperature. reaction mixture was concentrated in vacuo then was diluted with DCM (40 mL) and filtered through celite, rinsing the celite plug with DCM (200 mL). The combined organic phase was added water (120 mL), the two phases were separated and the water phase was extracted with DCM (100 mL) for 2 times. subsequently, the combined organic phase was dried with anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography on a silica gel column with PE and EA (6/1, v/v) as the eluent to afford the alcohol product **4a'**.

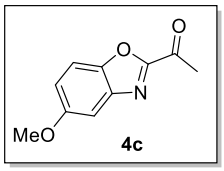
Alcohol **4a'** (5.82 g, 35.65 mmol, 1 equiv) was dissolved in DCM (150 mL), Dess-Martin Periodinane (18.20 g, 42.8 mmol, 1.2 equiv) was added in portions to above mixture at -15°C. The reaction was stirred for about 2 hours, TLC showed the transformation was completed, and reaction was quenched by adding saturated $NaHCO_3$ aqueous (20-40 mL) and saturated Na_2SO_3 aqueous (20-40 mL) at 0 ℃. The mixture was separated, and the water phase was extracted with DCM (80 mL x 2) and the combined organic extracts were washed with brine (100 mL), dried with anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude products were purified by flash chromatography on a silica gel column with PE and EA (12/1, v/v) as the eluent to afford the desired product **4a**.



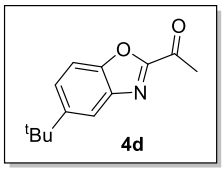
1-(benzo[d]oxazol-2-yl)ethan-1-one (4a): Aforementioned procedure was followed using 2-aminophenol (10.00 g, 91.66 mmol), (*S*)-2-hydroxypropanoic acid (8.67 g, 96.24 mmol), and TsOH (2.63 g, 13.75 mmol). **4a'** was obtained as an orange oil (6.98 g, 47% yield) by flash chromatography on silica gel with petroleum ether/ethyl acetate (6/1, v/v). Then, using **4a'** (5.82 g, 35.65 mmol) and DMP (18.20 g, 42.8 mmol), the **4a** was obtained as a white solid (4.94 g, 86% yield) by flash chromatography with petroleum ether/ethyl acetate (12/1, v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 - 7.89 (m, 1H), 7.67 - 7.65 (m, 1H), 7.56 - 7.52 (m, 1H), 7.48 - 7.44 (m, 1H), 2.82 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.4, 157.3, 150.8, 140.5, 128.5, 125.7, 122.2, 111.9, 26.9; HRMS (ESI): *m/z* calcd. for [M+Na, $C_9H_7NNaO_2$]$^+$: 184.0369; found: 184.0374.



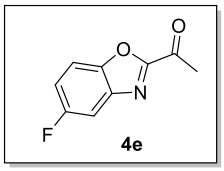
1-(5-methylbenzo[d]oxazol-2-yl)ethan-1-one (4b): Aforementioned procedure was followed using 2-amino-4-methyl-phenol (3.00 g, 24.36 mmol), (*S*)-2-hydroxypropanoic acid (2.30 g, 25.58 mmol), and TsOH (695.0 mg, 3.65 mmol). **4b'** was obtained as an orange oil (2.20 g, 51% yield) by flash chromatography on silica gel with petroleum ether/ethyl acetate (8/1 → 4/1, v/v). Then, using **4b'** (1.0 g, 5.65 mmol) and DMP (2.88 g, 6.78 mmol), the **4b** was obtained as a white solid (902.1 mg, 91% yield) by flash chromatography with petroleum ether/ethyl acetate (12/1, v/v) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 - 7.66 (m, 1H), 7.53 - 7.51 (m, 1H), 7.36 - 7.33 (m, 1H), 2.80 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.4, 157.4, 149.0, 140.7, 135.8, 130.0, 121.7, 111.2, 26.9, 21.4; HRMS (ESI): *m/z* calcd. for [M+Na, $C_{10}H_9NNaO_2$]$^+$: 198.0525; found: 198.0523.



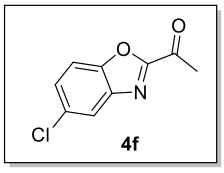
1-(5-methoxybenzo[d]oxazol-2-yl)ethan-1-one (4c): Aforementioned procedure was followed using 2-amino-4-methoxyphenol (5.00 g, 35.96 mmol) and (*S*)-2-hydroxypropanoic acid (3.40 g, 37.75 mmol) and TsOH (1025.94 mg, 5.40 mmol). **4c'** was obtained as an orange oil (2.92 g, 42% yield) by flash chromatography on silica gel with petroleum ether/ethyl acetate (8/1 → 4/1, v/v). Then, using **4c'** (1.17 g, 6.06 mmol) and DMP (3.08 g, 7.27 mmol), the **4c** was obtained as a white solid (952.9 mg, 92% yield) by flash chromatography with petroleum ether/ethyl acetate (12/1, v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 - 7.52 (m, 1H), 7.31 - 7.30 (m, 1H), 7.16 - 7.13 (dd, *J* = 9.1, 2.6 Hz, 1H), 3.88 (s, 3H), 2.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.3, 158.2, 158.0, 145.5, 141.4, 118.6, 112.2, 103.5, 55.9, 26.9; IR (KBr, cm^{-1}): 3075, 3029, 2917, 1707, 1529, 1350, 1123, 832; HRMS (ESI): *m/z* calcd. for [M+H, $C_{10}H_{10}NO_3$]$^+$: 192.0655; found: 192.0655.



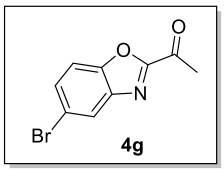
1-(5-(tert-butyl)benzo[d]oxazol-2-yl)ethan-1-one (4d): Aforementioned procedure was followed using 2-amino-4-(tert-butyl)phenol (4.15 g, 25.00 mmol), (*S*)-2-hydroxypropanoic acid (2.38 g, 26.42 mmol) and TsOH (713.3 mg, 3.75 mmol). **4d'** was obtained as an orange oil (3.63 g, 66% yield) by flash chromatography on silica gel with petroleum ether/ethyl acetate (8/1 → 4/1, v/v). Then, using **4d'** (3.62 g, 16.51 mmol) and DMP (8.40 g, 19.81 mmol), the **4d** was obtained as a white solid (3.08 g, 84% yield) by flash chromatography with petroleum ether/ethyl acetate (12/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 - 7.87 (m, 1H), 7.62 - 7.60 (m, 1H), 7.57 - 7.55 (m, 1H), 2.80 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.4, 157.5, 149.5, 148.9, 140.5, 126.8, 118.3, 111.0, 35.0, 31.6, 26.9; IR (KBr, cm^{-1}): 3078, 2962, 2869, 1707, 1529, 1475, 1106, 831; HRMS (ESI): *m/z* calcd. for [M+Na, $C_{13}H_{15}NNaO_2$]$^+$: 240.0995; found: 240.1001.



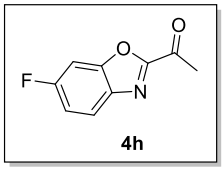
1-(5-fluorobenzo[d]oxazol-2-yl)ethan-1-one (4e): Aforementioned procedure was followed using 2-amino-4-fluoro-phenol (3.00 g, 23.61 mmol), (*S*)-2-hydroxypropanoic acid (2.23 g, 24.80 mmol) and TsOH (673.2 mg, 3.54 mmol). **4e'** was obtained as an orange oil (1.20 g, 28% yield) by flash chromatography on silica gel with petroleum ether/ethyl acetate (8/1 → 4/1, v/v). Then, using **4e'** (1.20 g, 6.64 mmol) and DMP (3.38 g, 7.97 mmol), the **4e** was obtained as a pink solid (1019.8 mg, 86% yield) by flash chromatography with petroleum ether/ethyl acetate (12/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 - 7.60 (m, 1H), 7.56 (dd, *J* = 8.0, 2.5 Hz, 1H), 7.33 - 7.26 (m, 1H), 2.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.1, 160.5 (d, *J* = 243.4 Hz), 158.6, 147.1 (d, *J* = 10.0 Hz), 141.2 (d, *J* = 13.2 Hz), 116.9 (d, *J* = 26.8 Hz), 112.5 (d, *J* = 9.9 Hz), 108.1 (d, *J* = 25.3 Hz), 26.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.1 (s, 1F); IR (KBr, cm^{-1}): 3097, 3067, 3027, 1707, 1533, 1475, 1124, 825; HRMS (ESI): *m/z* calcd. for [M+Na, $C_9H_6FNNaO_2$]$^+$: 202.0275; found: 202.0270.



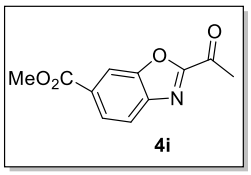
1-(5-chlorobenzo[d]oxazol-2-yl)ethan-1-one (4f): Aforementioned procedure was followed using 2-amino-4-chloro-phenol (5.74 g, 40.00 mmol), (*S*)-2-hydroxypropanoic acid (3.78 g, 42.00 mmol) and TsOH (1.14 g, 6.00 mmol). **4f'** was obtained as an orange oil (1.96 g, 25% yield) by flash chromatography on silica gel with petroleum ether/ethyl acetate (8/1 → 4/1, v/v). Then, using **4f'** (1.5 g, 7.61 mmol) and DMP (3.87 g, 9.13 mmol), the **4f** was obtained as a colorless solid (1.16 g, 78% yield) by flash chromatography with petroleum ether/ethyl acetate (12/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (m, 1H), 7.60 - 7.58 (m, 1H), 7.52 - 7.49 (m, 1H), 2.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.1, 158.1, 149.3, 141.5, 131.3, 129.0, 122.0, 112.7, 27.0; HRMS (ESI): *m/z* calcd. for [M+Na, $C_9H_6ClNNaO_2$]$^+$: 217.9979; found: 217.9976.



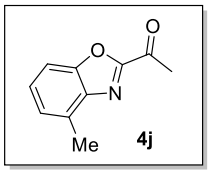
1-(5-bromobenzo[d]oxazol-2-yl)ethan-1-one (4g): Aforementioned procedure was followed using 2-amino-4-bromophenol (2.93 g, 15.58 mmol), (*S*)-2-hydroxypropanoic acid (1.47 g, 16.36 mmol) and TsOH (444.5 mg, 2.34 mmol). **4g'** was obtained as an orange oil (1.15 g, 31% yield) by flash chromatography on silica gel with petroleum ether/ethyl acetate (8/1 → 4/1, v/v). Then, using **4g'** (1.15 g, 4.77 mmol) and DMP (2.42 g, 5.73 mmol), the **4g** was obtained as a pink solid (869.8 mg, 76% yield) by flash chromatography with petroleum ether/ethyl acetate (12/1, v/v), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.6 Hz, 1H), 7.66 - 7.63 m, 1H), 7.56 - 7.53 (m, 1H), 2.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.1, 158.0, 149.7, 142.0, 131.7, 125.1, 118.5, 113.2, 27.0; HRMS (ESI): *m/z* calcd. for [M+Na, $C_9H_6BrNNaO_2]^+$: 261.9474; found: 261.9479.



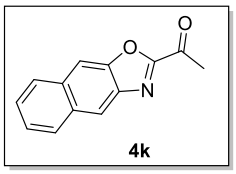
1-(6-fluorobenzo[d]oxazol-2-yl)ethan-1-one (4h): Aforementioned procedure was followed using 2-amino-5-fluorophenol (2.5 g, 19.67 mmol), (*S*)-2-hydroxypropanoic acid (1.86 g, 20.64 mmol) and TsOH (561.2 mg, 2.55 mmol). **4h'** was obtained as an orange oil (594 mg, 17% yield) by flash chromatography on silica gel with petroleum ether/ethyl acetate (8/1 → 4/1, v/v). Then, using **4h'** (500 mg, 2.76 mmol) and DMP (1.40 g, 3.31 mmol), the **4h** was obtained as a colorless solid (408.2 mg, 83% yield) by flash chromatography with petroleum ether/ethyl acetate (12/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.9, 4.9 Hz, 1H), 7.36 (dd, *J* = 7.7, 2.4 Hz, 1H), 7.22 (td, *J* = 9.2, 2.4 Hz, 1H), 2.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.8, 162.6 (d, *J* = 249.4 Hz), 157.95 (d, *J* = 4.0 Hz), 150.92 (d, *J* = 15.0 Hz), 136.82 (d, *J* = 1.7 Hz), 123.0 (d, *J* = 10.5 Hz), 114.5 (d, *J* = 25.3 Hz), 99.5 (d, *J* = 28.1 Hz), 26.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.9 (s, 1F); HRMS (ESI): *m/z* calcd. for [M+H, $C_9H_7FNO_2]^+$: 180.0455; found: 180.0451.



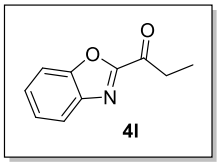
methyl 2-acetylbenzo[d]oxazole-6-carboxylate (4i): Aforementioned procedure was followed using 4-amino-3-hydroxybenzoate (2.5 g, 14.96 mmol), (*S*)-2-hydroxypropanoic acid (1.59 g, 15.71 mmol) and TsOH (426.8 mg, 2.24 mmol). **4i'** was obtained as an orange oil (731.3 mg, 22% yield) by flash chromatography on silica gel with petroleum ether/ethyl acetate (8/1 → 4/1, v/v). Then, using **4i'** (731.3 mg, 3.31 mmol) and DMP (1.68 g, 3.97 mmol), the **4i** was obtained as a colorless solid (627.2 mg, 87% yield) by flash chromatography with petroleum ether/ethyl acetate (12/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (m, 1H), 8.20 - 8.17 (m, 1H), 7.95 - 7.93 (m, 1H), 3.99 (s, 3H), 2.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.2, 165.9, 159.0, 150.4, 144.0, 130.4, 127.1, 122.0, 113.7, 52.6, 27.1; IR (KBr, cm^{-1}): 3106, 3010, 1704, 1425, 1290, 1122, 890, 774; HRMS (ESI): *m/z* calcd. for [M+Na, $C_{11}H_9NNaO_4]^+$: 242.0424; found: 242.0426.



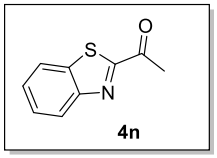
1-(4-methylbenzo[d]oxazol-2-yl)ethan-1-one (4j): Aforementioned procedure was followed using 2-amino-3-methyl-phenol (2.50 g, 20.30 mmol), (*S*)-2-hydroxypropanoic acid (1.92 g, 21.32 mmol) and TsOH (965.0 mg, 5.08 mmol). **4j'** was obtained as an orange oil (1.25 g, 35% yield) by flash chromatography on silica gel with petroleum ether/ethyl acetate (8/1 → 4/1, v/v). Then, using **4j'** (1.0 g, 5.65 mmol) and DMP (2.87 g, 6.78 mmol), the **4j** was obtained as a colorless solid (884.2 mg, 89% yield) by flash chromatography with petroleum ether/ethyl acetate (12/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.39 (m, 2H), 7.25 - 7,23 (m, 1H), 2.82 (s, 3H), 2.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.7, 156.7, 150.6, 140.1, 133.2, 128.3, 125.9, 109.0, 27.0, 16.4; IR (KBr, cm^{-1}): 3087, 2922, 1702, 1532, 1305, 1112, 789; HRMS (ESI): *m/z* calcd. for [M+Na, $C_{10}H_9NNaO_2]^+$: 198.0525; found: 198.0532.



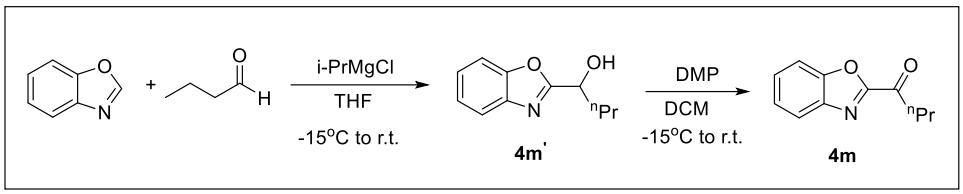
1-(naphtho[2,3-d]oxazol-2-yl)ethan-1-one (4k): solid, Aforementioned procedure was followed using 3-aminonaphthalen-2-ol (2.00 g, 12.56 mmol), (*S*)-2-hydroxypro-panoic acid (1.19 g, 13.19 mmol) and TsOH (597.0 mg, 3.14 mmol). **4k'** was obtained as an orange oil (523.7 mg, 20% yield) by flash chromatography on silica gel with petroleum ether/ethyl acetate (8/1 → 4/1, v/v). Then, using **4k'** (523.7 g, 2.46 mmol) and DMP (1.25 g, 2.95 mmol), the **4k** was obtained as a yellow solid (308.2 mg, 59% yield) by flash chromatography with petroleum ether/ethyl acetate (12/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.06 - 8.05 (m, 2H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.65 - 7.47 (m, 2H), 2.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.8, 158.7, 149.0, 140.0, 133.4, 131.7, 128.8, 128.0, 126.7, 125.2, 120.6, 107.8, 27.1; IR (KBr, cm^{-1}): 3061, 1706, 1537, 1305, 1265, 870, 753; HRMS (ESI): *m/z* calcd. for [M+Na, $C_{13}H_9NNaO_2]^+$: 234.0525; found: 234.0533.



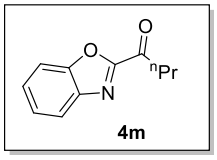
1-(benzo[d]oxazol-2-yl)propan-1-one (4l): Aforementioned procedure was followed using 2-aminophenol (2.99 g, 27.44 mmol), (*S*)-2-hydroxybutanoic acid (3.00 g, 28.82 mmol) and TsOH (782.9 mg, 4.12 mmol). **4l'** was obtained as an orange oil (1.74 g, 36% yield) by flash chromatography on silica gel with petroleum ether/ethyl acetate (8/1 → 4/1, v/v). Then, using **4l'** (1.73 g, 9.75 mmol) and DMP (4.96 g, 11.70 mmol), the **4l** was obtained as a white solid (1.46 g, 85% yield) by flash chromatography with petroleum ether/ethyl acetate (12/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.88 (m, 1H), 7.67 - 7.65 (m, 1H), 7.56 - 7.52 (m, 1H), 7.48 - 7.44 (m, 1H), 3.26 (q, *J* = 7.3 Hz, 2H), 1.30 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 157.1, 150.6, 140.4, 128.4, 125.6, 122.2, 111.9, 32.9, 7.7; HRMS (ESI): *m/z* calcd. for [M+Na, $C_{10}H_9NNaO_2]^+$: 198.0525; found: 198.0529.



1-(benzo[d]thiazol-2-yl)ethan-1-one (4n): Aforementioned procedure was followed using 2-aminobenzenethiol (5 g, 39.94 mmol), (*S*)-2-hydroxypropanoic acid (3.78 g, 41.94 mmol) and TsOH (1.14 g, 5.99 mmol). **4n'** was obtained as an orange oil (2.51 g, 35% yield) by flash chromatography on silica gel with petroleum ether/ethyl acetate (8/1 → 4/1, v/v). Then, using **4n'** (1.00 g, 5.58 mmol) and DMP (2.84 g, 6.69 mmol), the **4n** was obtained as a colorless solid (863.3 mg, 87% yield) by flash chromatography with petroleum ether/ethyl acetate (12/1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 - 8.11 (m, 1H), 8.11 - 7.87 (m, 1H), 7.61 - 7.56 (m, 1H), 7.56 - 7.50 (m, 1H), 2.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 166.4, 153.5, 137.3, 127.6, 126.9, 125.4, 122.4, 26.1; HRMS (ESI): *m/z* calcd. for $[M+Na, C_9H_7NNaOS]^+$: 200.0141; found: 200.0139.



Compound **4m'** was synthesized according the reference [4]. Benzo[*d*]oxazole (1.0 g, 8.39 mmol, 1 equiv) was dissolved in anhydrous THF (7 mL) under N_2, and the solution was cooled to -15 °C, i-PrMgCl (2M solution in THF, 4.2 mL, 8.39 mmol, 1 equiv) was added dropwise via syringe to the cooled mixture, and the mixture was stirred at -15 °C for about 30 minutes. After this time, butyraldehyde (603.5 mg, 8.39 mmol, 1 equiv) in 10 mL anhydrous THF (prepared in a separate, flame-dried round bottom flask under nitrogen) was added to the cooled mixture dropwise via constant pressure funnel and the mixture was stirred at -15 °C for about 20 minutes. After this time, the mixture was stirred and allowed to warm up to room temperature for about 3 h, TLC monitored the process of reaction. The reaction was quenched by adding saturated NH_4Cl (10-15 mL) at 0 °C. The organic layer was separated, water layer was extracted with EtOAc (20 mL x 2), and the combined organic extracts were washed with brine (30 mL), dried with anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude products were purified by flash chromatography on a silica gel column with PE/EA (8/1 → 4/1, v/v) as the eluent to afford the desired product **4m'** (545 mg, 34% yield, the reaction yield was not optimized). Following the aforementioned oxidation reaction procedure, **4m'** (545 mg, 2.85 mmol) and DMP (1.45 g, 3.42 mmol, 1.2 equiv) was used to provide **4m** as a white solid (404mg, 75% yield) after flash chromatography on a silica gel column with PE/EA (15/1, v/v).



1-(benzo[d]oxazol-2-yl)butan-1-one (4m): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.88 (m, 1H), 7.67 - 7.65 (m, 1H), 7.55 - 7.51 (m, 1H), 7.50 - 7.40 (m, 1H), 3.29 - 3.14 (m, 2H), 1.96 - 1.78 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 157.2, 150.6, 140.4, 128.3, 125.6, 122.1, 111.8, 41.3, 17.31 13.6;

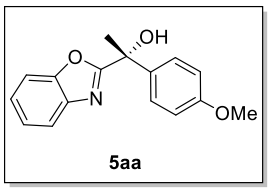
IR (KBr, cm^{-1}): 3092, 3023, 2959, 2875, 1706, 1532, 1350, 1023, 751; HRMS (ESI): *m/z* calcd. for [M+H, $C_{11}H_{12}NO_2]^+$: 190.0863; found: 190.0862.

5. General procedure of enantioselective Rh-catalyzed addition of arylboronic acids to α-Ketobenzoxazoles (General Procedure B).

To a flame-dried Schlenk tube equipped with a magnetic stirring bar was charged α-ketobenzoxazoles (0.20 mmol, 1 equiv), arylboronic acids (0.50 mmol, 2.5 equiv), CsF (0.40 mmol, 2 equiv), (*S*,*S*,*S*,*S*)-WingPhos (5.3 mg, 0.0072 mmol, 3.6 mol %) and $[Rh(C_2H_4)_2Cl]_2$ (1.2 mg, 0.0030 mmol, 1.5 mol %). The tube was sealed then evacuated and backfilled with N_2 for three times. Fresh distilled toluene (3.5 mL) was added via syringe and the resulting mixture was stirred at 60 ºC under nitrogen for 12 h. After this time, the Schlenk tube was removed from the bath and allowed to cool to room temperature. The heterogenous mixture was diluted with EtOAc (10 mL) and filtered through celite, rinsing the celite plug with EtOAc (25 mL). The filtrate was concentrated, and the resulting residue was purified via flash chromatography on silica gel with petroleum ether/ethyl acetate (8/1, v/v), affording the desired alcohol products. The enantiomeric excesses were determined by chiral HPLC on a chiralcel OD-H, chiralcel AD-H or chiralpak IA column.

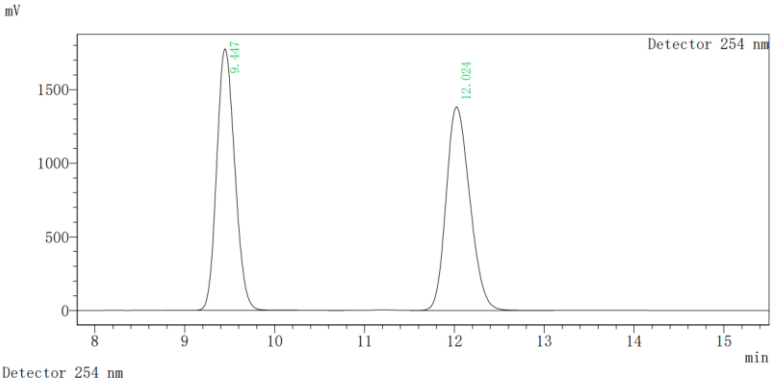
To perform the addition reaction by employing 0.3 mol% Rhodium, the procedure is: to a flame-dried Schlenk tube equipped with a magnetic stirring bar was charged α-ketobenzoxazoles (2.0 mmol, 1 equiv), arylboronic acids (6.0 mmol, 3.0 equiv), CsF (4.0 mmol, 2 equiv), (*S*,*S*,*S*,*S*)-WingPhos (5.3 mg, 0.0072 mmol, 0.36 mol %) and $[Rh(C_2H_4)_2Cl]_2$ (1.2 mg, 0.0030 mmol, 0.15 mol %) The tube was sealed then evacuated and backfilled with N_2 for three times. Fresh distilled toluene (35 mL) was added via syringe and the resulting mixture was stirred at 70 ºC under nitrogen for 16 h. Then the reaction mixture was cooled to room temperature, quenched by addition of EtOAc (30 mL) and water (20 mL). The organic phase was separated, the water phase was extracted with EtOAc (20 mL x 3), then combined the extracts, dried over sodium sulfate, concentrated and purified by flash column chromatography to provide the desired alcohol product. The enantiomeric excesses were determined by chiral HPLC on a chiralcel OD-H, or chiralcel AD-H.

6. Analytical data of the products of enantioselective Rh-catalyzed addition of arylboronic acids to α-Ketobenzoxazoles.



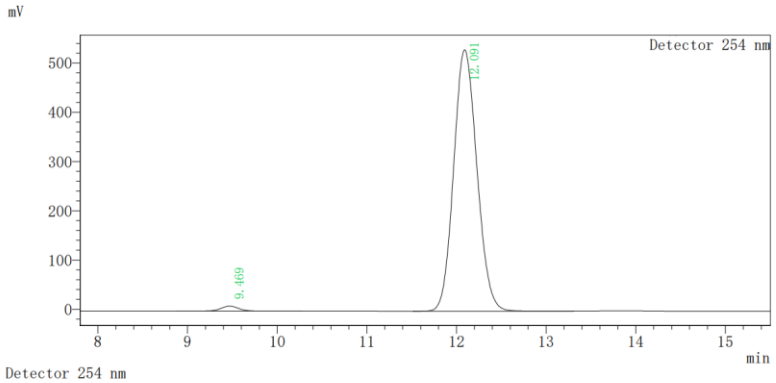
5aa

(*R*)-1-(benzo[d]oxazol-2-yl)-1-(4-methoxyphenyl)ethan-1-ol (5aa): General Procedure B was followed using **4a** (32.2 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (76.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless solid (50.9 mg, 94% yield, 97% ee). Chiral HPLC conditions: chiralcel AD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 80/20, 254 nm, 9.5 min (*S*), 12.1 min (*R*); $[\alpha]^{25}_{D}$ = 63.2 ° (c = 0.63, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 - 7.66 (m, 1H), 7.48 - 7.45 (m, 3H), 7.37 - 7.27 (m, 2H), 6.88 - 6.84 (m, 2H), 3.77 (s, 3H), 3.68 (br.s, 1H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 159.2, 151.0, 140.4, 135.9, 126.3, 125.1, 124.5, 120.1, 113.8, 110.8, 73.3, 55.2, 28.6; IR (KBr, cm^{-1}): 3378, 2992, 2934, 2836, 1610, 1511, 1455, 1302, 1248, 1178, 1031, 928, 831, 748; HRMS (ESI): *m/z* calcd. for [M+H, $C_{16}H_{16}NO_3$]$^+$: 270.1125; found: 270.1130.



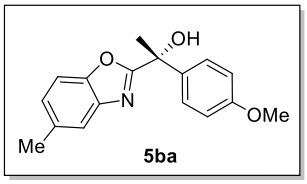
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	9.447	1775862	56.217	24866363	49.478
2	12.024	1383059	43.783	25390624	50.522
Total		3158920	100.000	50256987	100.000



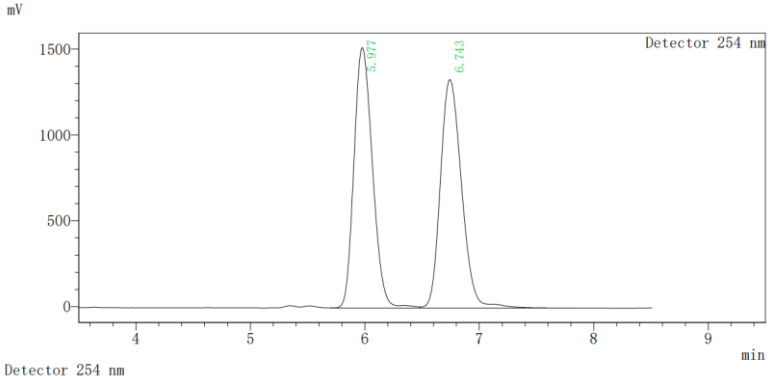
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	9.469	10050	1.858	140543	1.449
2	12.091	530805	98.142	9560863	98.551
Total		540855	100.000	9701406	100.000



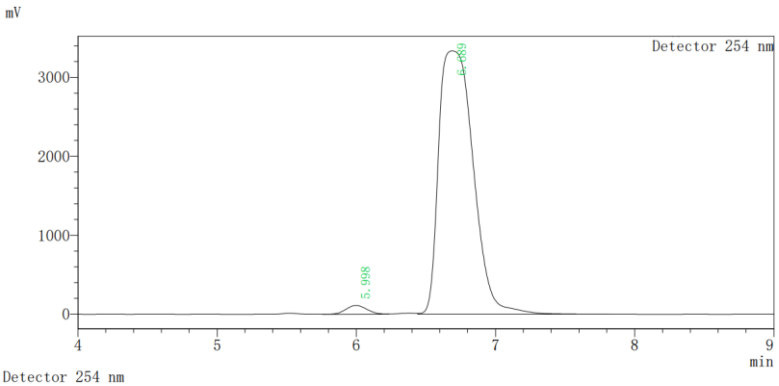
5ba

(*R*)-1-(4-methoxyphenyl)-1-(5-methylbenzo[d]oxazol-2-yl)ethan-1-ol (5ba): General Procedure B was followed using **4b** (35.0 mg, 0.20 mmol) and (4-methoxyphenyl) boronic acid (76.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless oil (51.1 mg, 90% yield, 96% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 80/20, 254 nm, 6.0 min (*S*), 6.7 min (*R*); $[\alpha]^{25}_{D}$ = 39.1 ° (c = 2.57, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 - 7.40 (m, 3H), 7.33 - 7.31 (m, 1H), 7.10 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.90 - 6.81 (m, 2H), 4.26 (br.s, 1H), 3.76 (s, 3H), 2.43 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 159.1, 149.2, 140.5, 136.1, 134.2, 126.3, 126.1, 119.9, 113.7, 110.1, 73.2, 55.1, 28.5, 21.3; IR (KBr, cm^{-1}): 3398, 2999, 2932, 2836, 1610, 1562, 1511, 1462, 1301, 1251, 1178, 1032, 958, 832, 801; HRMS (ESI): *m/z* calcd. for [M+H, $C_{17}H_{18}NO_3$]$^+$: 284.1281; found: 284.1285.



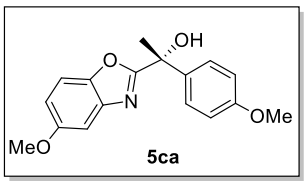
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	5.977	1516948	53.246	17012728	49.837
2	6.743	1331987	46.754	17124158	50.163
Total		2848935	100.000	34136886	100.000

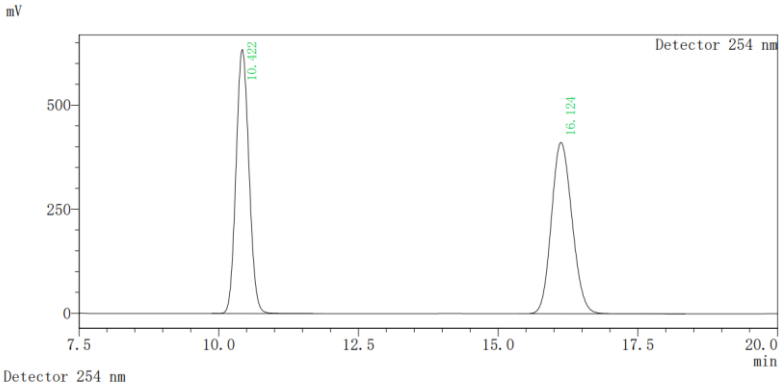


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	5.998	112258	3.256	1175301	1.998
2	6.689	3335164	96.744	57654606	98.002
Total		3447422	100.000	58829908	100.000

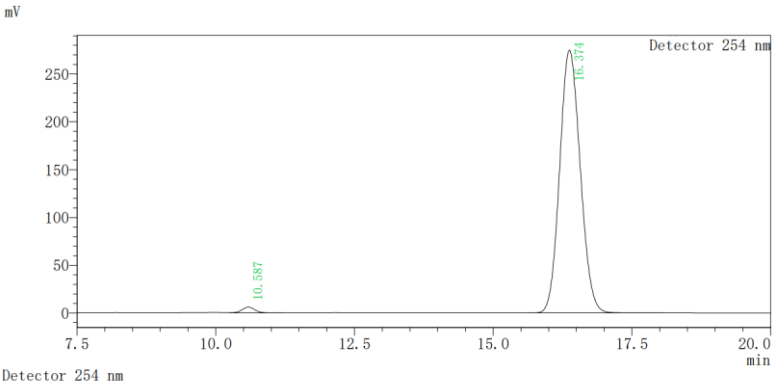


(*R*)-1-(5-methoxybenzo[d]oxazol-2-yl)-1-(4-methoxyphenyl)ethan-1-ol (5ca): General Procedure B was followed using **4c** (38.2 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid(76.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless oil (54.8 mg, 91% yield, 97% ee). Chiral HPLC conditions: chiralcel AD-H, 25 ºC, flow rate: 1.0 mL/min, hexane/isopropanol: 80/20, 254 nm, 10.6 min (*S*), 16.4 min (*R*); $[\alpha]^{25}_{D}$ = 33.0 ° (c = 0.26, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 -7.37 (m, 2H), 7.27 - 7.25 (m, 1H), 7.10 - 7.09 (m, 1H), 6.87 - 6.80 (m, 3H), 4.68 (br.s, 1H), 3.73 (d, *J* = 15.2 Hz, 6H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 158.9, 157.0, 145.4, 141.0, 136.0, 126.2, 113.5, 110.7, 102.9, 73.1, 55.7, 55.0, 28.5; IR (KBr, cm^{-1}): 3447, 2996, 2936, 2836, 1611, 1559, 1511, 1340, 1151, 1029, 949, 834, 807; HRMS (ESI): *m/z* calcd. for [M+H, $C_{17}H_{18}NO_4$]$^+$: 300.1230; found: 300.1234.



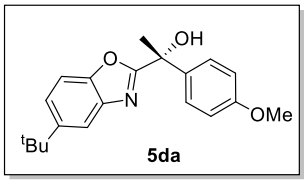
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	10.422	634167	60.637	10208076	49.130
2	16.124	411675	39.363	10569515	50.870
Total		1045842	100.000	20777591	100.000

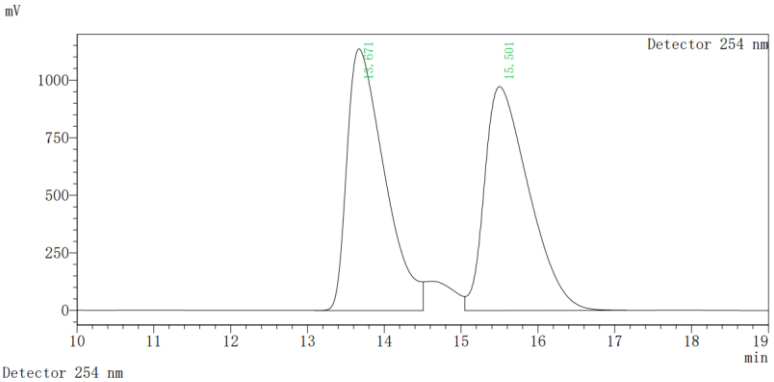


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	10.587	6054	2.155	96360	1.340
2	16.374	274877	97.845	7092518	98.660
Total		280932	100.000	7188879	100.000

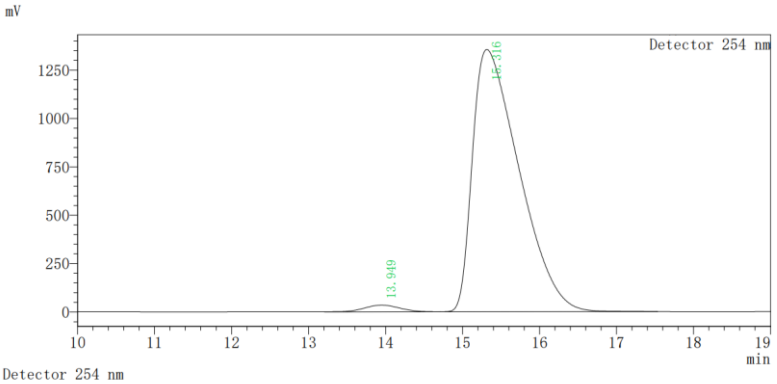


(*R*)-1-(5-(tert-butyl)benzo[d]oxazol-2-yl)-1-(4-methoxyphenyl)ethan-1-ol (5da): General Procedure B was followed using **4d** (43.4 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (76.0 mg, 0.50 mmol). After chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless oil (58.5 mg, 90% yield, 96% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 97/3, 254 nm, 13.9 min (*S*), 15.3 min (*R*); $[\alpha]^{25}_{D}$ = 36.0 ° (c = 1.50, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.73 (s, 1H), 7.48 - 7.45 (m, 2H), 7.38 (s, 2H), 6.87 - 6.85 m, 2H), 4.07 (br.s, 0.71H), 3.78 (s, 3H), 2.07 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 159.1, 149.0, 148.1, 140.2, 136.0, 126.3, 122.8, 116.6, 113.7, 110.0, 73.3, 55.2, 34.9, 31.7, 28.5; IR (KBr, cm^{-1}): 3393, 2961, 2869, 2836, 1611, 1562, 1511, 1481, 1365, 1251, 1179, 936, 833, 810; HRMS (ESI): *m/z* calcd. for [M+H, $C_{20}H_{24}NO_3$]$^+$: 326.1751; found: 326.1758.



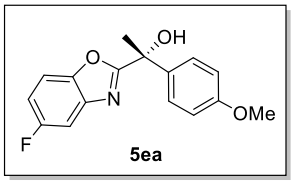
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	13.671	1135231	53.877	38465859	49.682
2	15.501	971859	46.123	38957663	50.318
Total		2107091	100.000	77423522	100.000



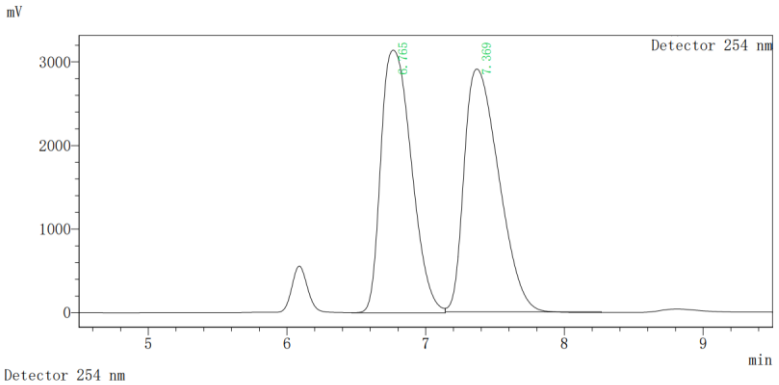
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	13.949	34685	2.495	1127766	1.939
2	15.316	1355264	97.505	57028036	98.061
Total		1389949	100.000	58155802	100.000



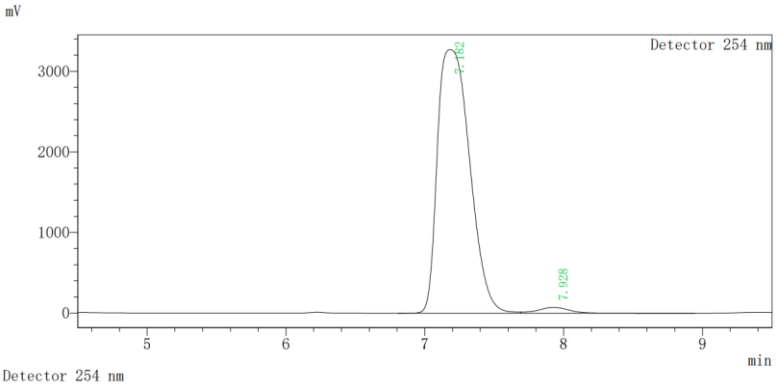
5ea

(*R*)-1-(5-fluorobenzo[d]oxazol-2-yl)-1-(4-methoxyphenyl) ethan-1-ol (5ea): General Procedure B was followed using **4e** (35.8 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (76.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless oil (55.4 mg, 89% yield, 96% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 85/15, 254 nm, 7.2 min (*R*), 7.9 min (*S*); $[\alpha]^{25}_{D}$ = 43.9 ° (c = 2.41, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 - 7.42 (m, 2H), 7.38 (m, 2H), 7.05 (td, *J* = 9.1, 2.5 Hz, 1H), 6.89 - 6.84 (m, 2H), 3.78 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 160.0 (d, *J* = 240.0 Hz), 159.3, 147.4 (d, *J* = 1.0 Hz), 141.2 (d, *J* = 13.0 Hz), 135.6, 126.3, 113.8, 112.9 (d, *J* = 26.0 Hz), 111.2 (d, *J* = 10.0 Hz), 106.6 (d, *J* = 26.0 Hz), 73.3, 55.2, 28.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -117.5 (s, 1F); IR (KBr): 3418, 2993, 2934, 2842, 1611, 1560, 1512, 1477, 1302, 1251, 1135, 1032, 959, 833, 806; HRMS (ESI): *m/z* calcd. for $[M+H, C_{16}H_{14}FNNaO_3]^+$: 310.0850; found: 310.0855.



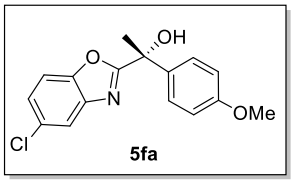
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.765	3141207	51.955	48357824	49.035
2	7.369	2904818	48.045	50260593	50.965
Total		6046026	100.000	98618417	100.000

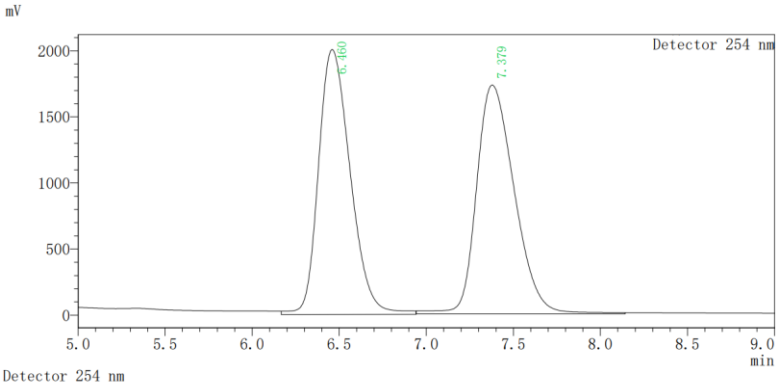


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	7.182	3271014	97.845	52996452	97.922
2	7.928	72028	2.155	1124534	2.078
Total		3343043	100.000	54120986	100.000

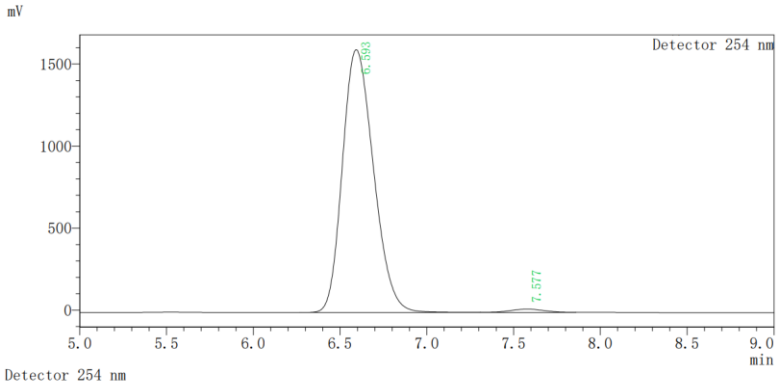


(*R*)-1-(5-chlorobenzo[d]oxazol-2-yl)-1-(4-methoxyphenyl) ethan-1-ol (5fa): General Procedure B was followed using **4f** (39.0 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (76.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless oil (52.3 mg, 86% yield, 96% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 80/20, 254 nm, 6.6 min (*R*), 7.7 min (*S*); $[\alpha]^{25}_{D}$ = 31.0 ° (c = 1.45, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 2.0 Hz, 1H), 7.48 - 7.40 (m, 2H), 7.39 - 7.37 (m, 1H), 7.30 - 7.29 (m, 1H), 6.90 - 6.83 (m, 2H), 3.78 (s, 3H), 3.40 (br.s, 1H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 159.3, 149.5, 141.5, 135.5, 130.0, 126.3, 125.5, 120.1, 113.8, 111.5, 73.3, 55.2, 28.5; IR (KBr, cm^{-1}): 3335, 2993, 2933, 2836, 1610, 1557, 1511, 1451, 1301, 1253, 1178, 1031, 920, 831, 705; HRMS (ESI): *m/z* calcd. for [M+H, $C_{16}H_{15}ClNO_3]^+$: 304.0735; found: 304.0737.



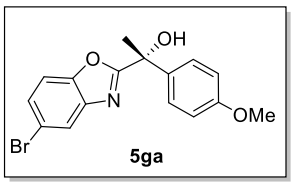
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.460	2004885	53.659	25508421	49.264
2	7.379	1731465	46.341	26270951	50.736
Total		3736350	100.000	51779372	100.000



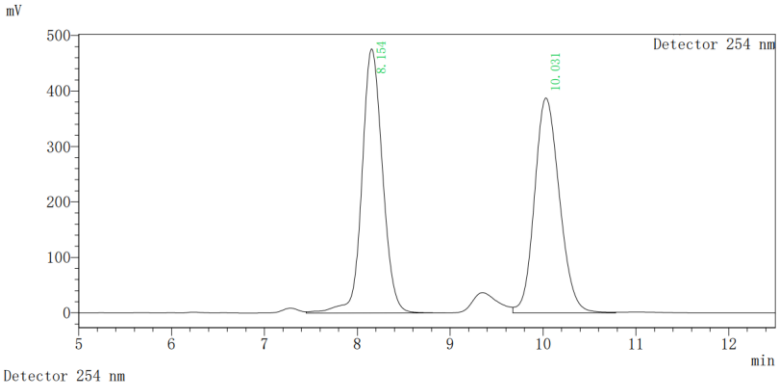
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.593	1602284	98.731	19999260	98.537
2	7.577	20601	1.269	296869	1.463
Total		1622885	100.000	20296129	100.000



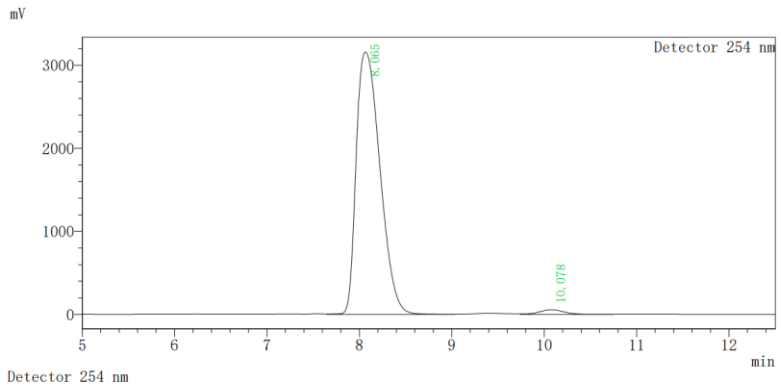
5ga

(*R*)-1-(5-bromobenzo[d]oxazol-2-yl)-1-(4-methoxyphenyl) ethan-1-ol (5ga): General Procedure B was followed using **4g** (47.8 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (76.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired prodcut was obtained as a yellow solid (58.7 mg, 84% yield, 96% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 85/15, 254 nm, 8.1 min (*R*), 10.1 min (*S*); $[\alpha]^{25}_{D}$ = 23.8 ° (c = 1.18, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 1.9 Hz, 1H), 7.47 - 7.40 (m, 3H), 7.36 - 7.34 (m, 1H), 6.91 - 6.82 (m, 2H), 3.78 (s, 3H), 3.52 (br.s, 1H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 159.3, 150.0, 142.0, 135.5, 128.2, 126.3, 123.2, 117.3, 113.8, 112.1, 73.3, 55.2, 28.5; IR (KBr, cm^{-1}): 3395, 2960, 2927, 2853, 1610, 1557, 1502, 1448, 1302, 1248, 1178, 1033, 908, 831, 802; HRMS (ESI): *m/z* calcd. for $[M+H, C_{16}H_{15}BrNO_3]^+$: 348.0230; found: 348.0233.



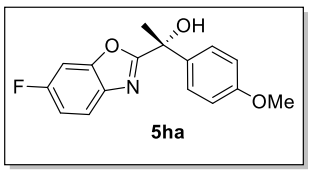
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	8.154	476078	55.102	7373990	50.371
2	10.031	387916	44.898	7265252	49.629
Total		863994	100.000	14639242	100.000

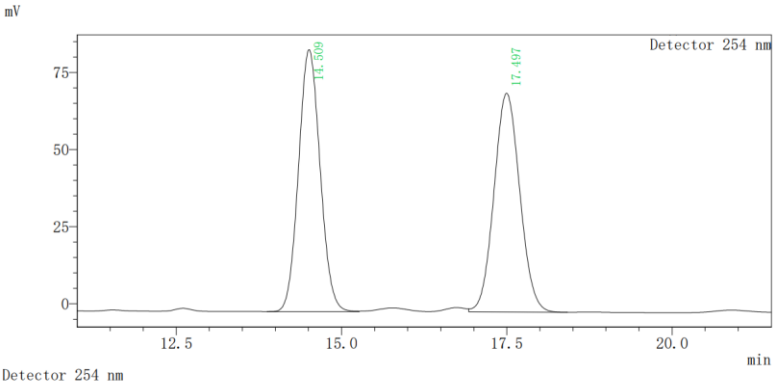


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	8.065	3158934	98.269	56292217	98.116
2	10.078	55656	1.731	1080730	1.884
Total		3214590	100.000	57372947	100.000

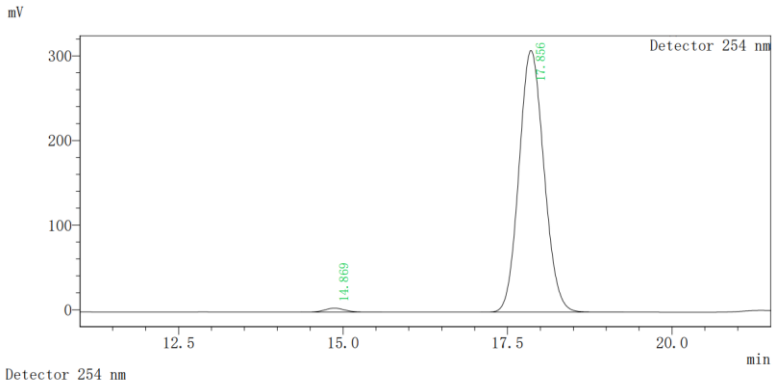


(*R*)-1-(6-fluorobenzo[d]oxazol-2-yl)-1-(4-methoxyphenyl)ethan-1-ol (5ha): General Procedure B was followed using **4h** (35.8 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (76.0 mg, 0.50 mmol). After chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless solid (51.7 mg, 90% yield, 97% ee). Chiral HPLC conditions: chiralcel AD-H, 25 ºC, flow rate: 1.0 mL/min, hexane/isopropanol: 90/10, 254 nm, 14.9 min (*S*), 17.9 min (*R*); $[\alpha]^{25}_{D}$ = 42.6 ° (c = 2.50, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.48 - 7.41 (m, 2H), 7.19 (dd, *J* = 7.9, 2.4 Hz, 1H), 7.07 (ddd, *J* = 9.5, 8.7, 2.4 Hz, 1H), 6.90 - 6.84 (m, 2H), 3.78 (s, 3H), 3.14 (br.s, 1H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.0 (d, *J* = 3.7 Hz), 160.6 (d, *J* = 244.5 Hz), 159.3, 156.0 (d, *J* = 14.7 Hz), 136.7, 135.6, 126.3, 120.5 (d, *J* = 10.0 Hz), 113.9, 112.5 (d, *J* = 24.7 Hz), 98.9 (d, *J* = 28.2 Hz), 73.3, 55.2, 28.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -114.8 (s, 1F); IR (KBr, cm^{-1}): 3263, 2960, 2927, 2854, 1617, 1541, 1509, 1483, 1250, 1177, 1079, 1031, 953, 832, 812; HRMS (ESI): *m/z* calcd. for [M+H, $C_{16}H_{15}FNO_3$]$^+$: 288.1030; found: 288.1031.



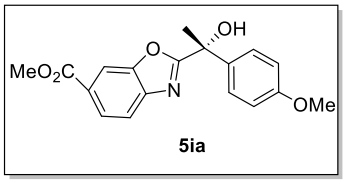
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	14.509	84911	54.500	1931172	50.050
2	17.497	70889	45.500	1927311	49.950
Total		155800	100.000	3858483	100.000



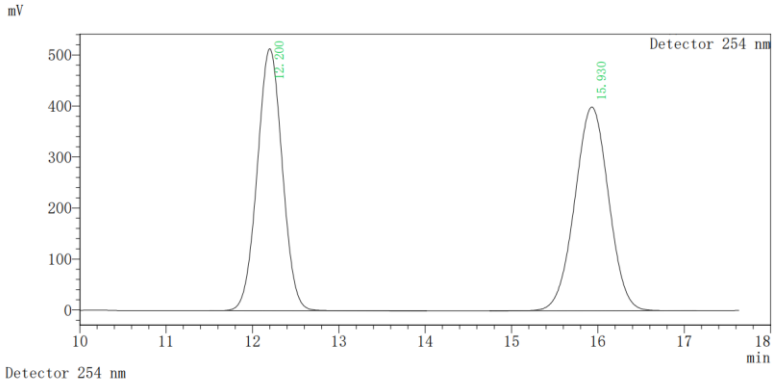
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	14.869	4717	1.502	101033	1.222
2	17.856	309374	98.498	8164615	98.778
Total		314091	100.000	8265648	100.000



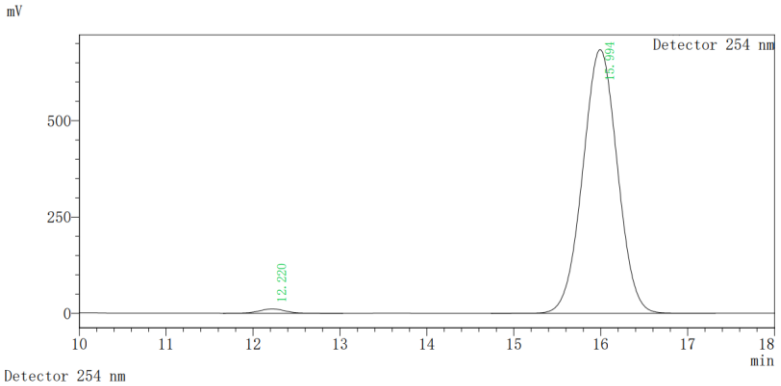
5ia

Methyl-(*R*)-2-(1-hydroxy-1-(4-methoxyphenyl)ethyl)benzo[d]oxazole-6-carboxylate (5ia): General Procedure B was followed using **4i** (43.8 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (76.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless oil (58.4 mg, 89% yield, 98% ee). Chiral HPLC conditions: chiralcel AD-H, 25 ºC, flow rate: 1.0 mL/min, hexane/isopropanol: 80/20, 254 nm, 12.2 min (*S*), 16.0 min (*R*); $[\alpha]^{25}_{D}$ = 65.8 ° (c = 2.65, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 1.5 Hz, 1H), 8.05 - 8.03 (m, 1H), 7.71 - 7.70 (m, 1H), 7.50 - 7.36 (m, 2H), 6.95 - 6.81 (m, 2H), 3.93 (s, 3H), 3.77 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 166.5, 159.3, 150.7, 144.3, 135.4, 127.3, 126.3, 126.2, 119.7, 113.8, 112.5, 73.4, 55.2, 52.4, 28.5; IR (KBr, cm^{-1}): 3445, 2996, 2953, 2836, 1720, 1607, 1511, 1434, 1295, 1254, 1178, 1074, 834, 775, 746; HRMS (ESI): *m/z* calcd. for $[M+H, C_{18}H_{18}NO_5]^+$: 328.1179; found: 328.1180.



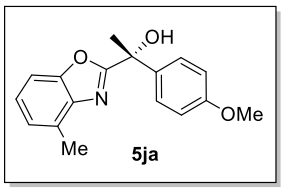
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	12.200	513544	56.268	10334757	48.696
2	15.930	399134	43.732	10888304	51.304
Total		912678	100.000	21223061	100.000



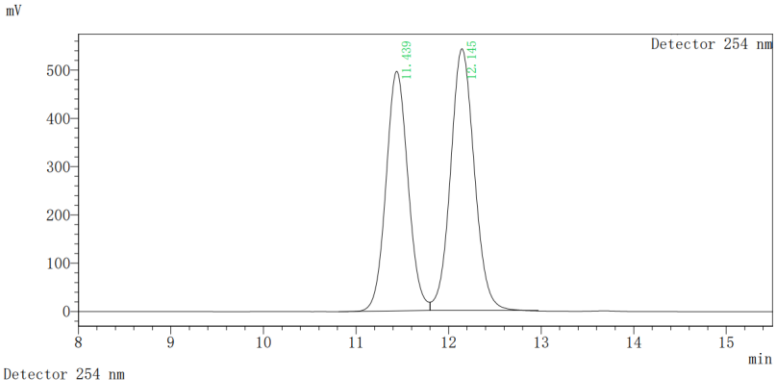
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	12.220	11277	1.622	230344	1.200
2	15.994	683968	98.378	18971343	98.800
Total		695245	100.000	19201686	100.000



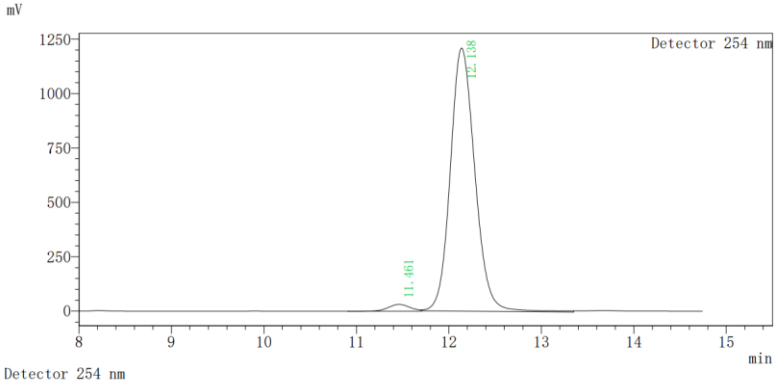
5ja

(*R*)-1-(4-methoxyphenyl)-1-(4-methylbenzo[d]oxazol-2-yl) ethan-1-ol (5ja): General Procedure B was followed using **4j** (35.0 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (76.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless oil (51.1 mg, 90% yield, 95% ee). Chiral HPLC conditions: chiralpak IA, 25 ^{o}C, flow rate: 1.0 mL/min, hexane/ isopropanol: 95/5, 254 nm, 11.5 min (*S*), 12.1 min (*R*); $[\alpha]^{25}_{D}$ =34.8 ° (c = 2.21, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 - 7.45 (m, 2H), 7.32 - 7.30 (m, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.14 -7.12 (m, 1H), 6.92 - 6.84 (m, 2H), 4.05 (br.s, 0.84H), 3.78 (s, 3H), 2.62 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 159.1, 150.9, 139.6, 136.0, 130.7, 126.3, 125.0, 124.7, 113.7, 108.0, 73.3, 55.2, 28.5, 16.5; IR (KBr, cm^{-1}): 3427, 2991, 2931, 2836, 1608, 1511, 1456, 1302, 1249, 1178, 1033, 832, 778, 757; HRMS (ESI): *m/z* calcd. for $[M+H, C_{17}H_{18}NO_3]^+$: 284.1281; found: 284.1286.



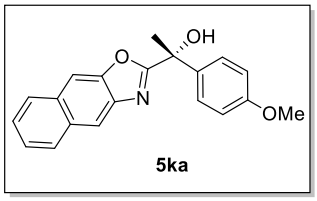
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	11.439	496267	47.795	8196123	45.851
2	12.145	542047	52.205	9679463	54.149
Total		1038315	100.000	17875585	100.000



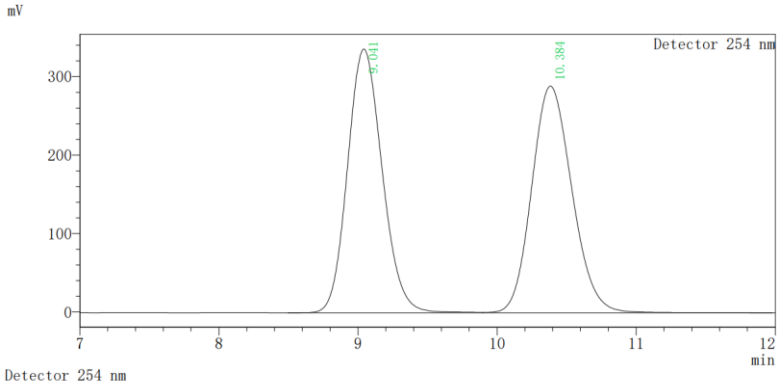
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	11.461	31513	2.541	514935	2.248
2	12.138	1208743	97.459	22389291	97.752
Total		1240256	100.000	22904225	100.000



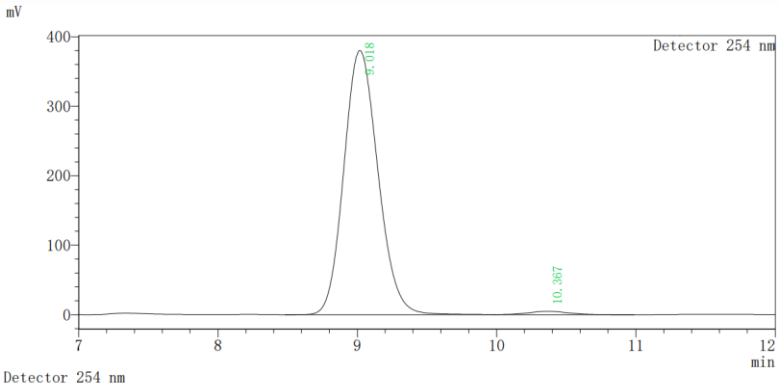
5ka

(*R*)-1-(4-methoxyphenyl)-1-(naphtho[2,3-d]oxazol-2-yl) ethan-1-ol (5ka): General Procedure B was followed using **4k** (42.2 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (76.0 mg, 0.50 mmol). After chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless solid (54.2 mg, 85% yield, 96% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 80/20, 254 nm, 9.0 min (*R*), 10.4 min (*S*); $[\alpha]^{25}_{D}$ = 56.5 ° (c = 1.16, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 8.02 - 7.95 (m, 1H), 7.95 - 7.88 (m, 1H), 7.85 (s, 1H), 7.58 - 7.42 (m, 4H), 6.93 - 6.84 (m, 2H), 3.91 (s, 1H), 3.78 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 159.3, 150.0, 140.4, 135.6, 131.6, 131.3, 128.5, 127.9, 126.4, 125.6, 124.8, 117.7, 113.9, 106.8, 73.4, 55.3, 28.4; IR (KBr, cm^{-1}): 3345, 3053, 2996, 2932, 2834, 1610, 1511, 1443, 1302, 1248, 1179, 1073, 1033, 865, 834, 742; HRMS (ESI): *m/z* calcd. for $[M+H, C_{20}H_{18}NO_3]^+$: 320.1281; found: 320.1282.



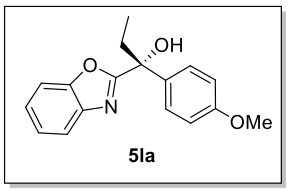
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	9.041	336096	53.784	5804148	49.950
2	10.384	288798	46.216	5815689	50.050
Total		624894	100.000	11619837	100.000



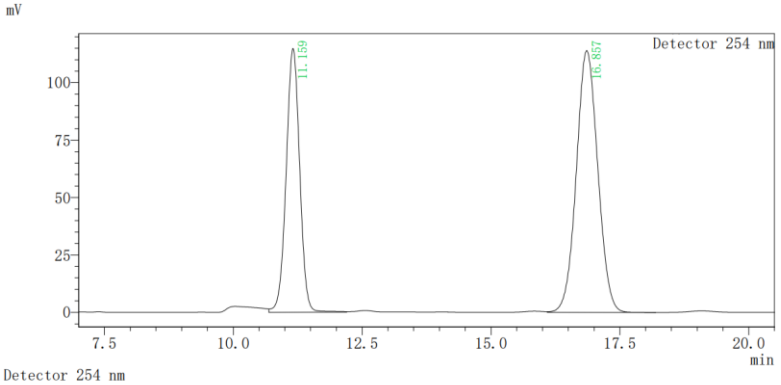
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	9.018	380412	98.732	6475901	98.390
2	10.367	4887	1.268	105951	1.610
Total		385299	100.000	6581851	100.000



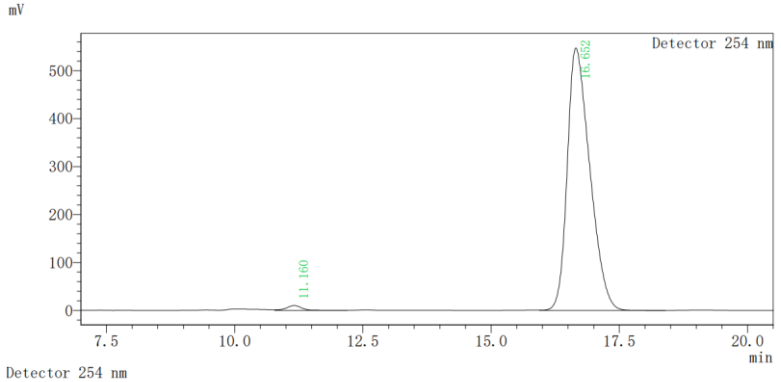
5la

(*R*)-1-(benzo[d]oxazol-2-yl)-1-(4-methoxyphenyl)propan-1-ol (5la): General Procedure B was followed using **4l** (35.0 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (76.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (10/1, v/v), the desired product was obtained as a colorless oil (47.4 mg, 83% yield, 97% ee). Chiral HPLC conditions: chiralcel AD-H, 25 ºC, flow rate: 1.0 mL/min, hexane/isopropanol: 85/15, 254 nm, 11.2 min (*R*), 16.7 min (*S*); $[\alpha]^{25}_{D}$ = 60.3 ° (c = 2.39, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 - 7.67 (m, 1H), 7.58 - 7.46 (m, 3H), 7.37 - 7.28 (m, 2H), 6.93 - 6.84 (m, 2H), 3.78 (s, 3H), 2.49 (dq, *J* = 14.5, 7.3 Hz, 1H), 2.35 (dq, *J* = 14.6, 7.4 Hz, 1H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 159.0, 151.2, 140.3, 134.7, 126.6, 125.0, 124.5, 120.0, 113.7, 110.8, 76.1, 55.2, 33.9, 7.9; IR (KBr, cm^{-1}): 3441, 2970, 2935, 2836, 1610, 1558, 1511, 1455, 1302, 1247, 1177, 1034, 1003, 880, 831, 748; HRMS (ESI): *m/z* calcd. for $[M+H, C_{17}H_{18}NO_3]^+$: 284.1281; found: 284.1284.



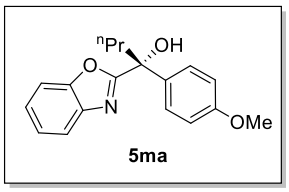
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	11.159	114842	50.188	2095992	38.826
2	16.857	113982	49.812	3302458	61.174
Total		228824	100.000	5398450	100.000

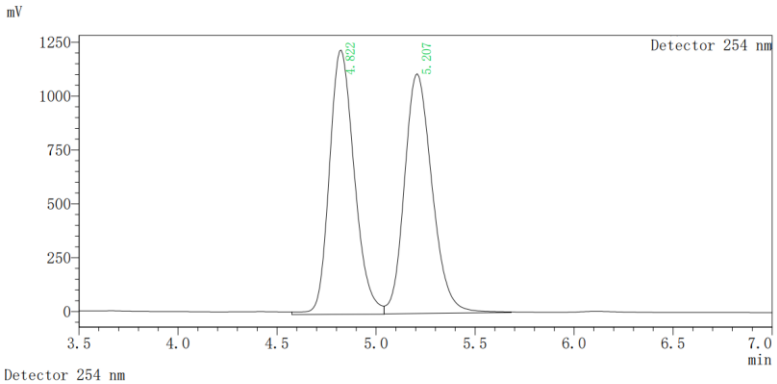


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	11.160	10190	1.829	217733	1.283
2	16.652	546951	98.171	16747824	98.717
Total		557141	100.000	16965557	100.000

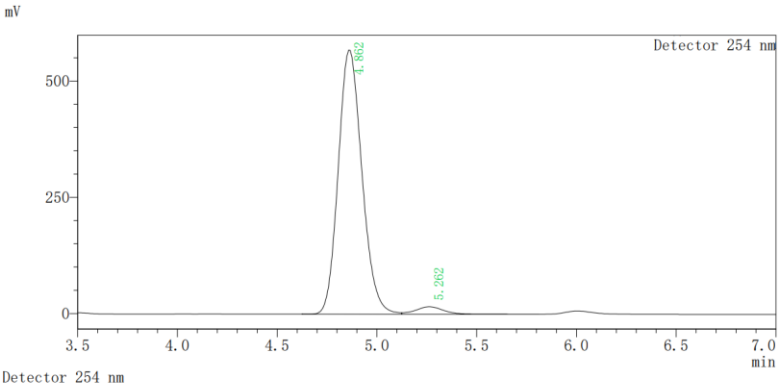


(*R*)-1-(benzo[d]oxazol-2-yl)-1-(4-methoxyphenyl)butan-1-ol (5ma): General Procedure B was followed using **4m** (37.8 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (121.6 mg, 0.8 mmol). After flash chromatography with petroleum ether/ethyl acetate (12/1, v/v), the desired product was obtained as a colorless oil (34.7 mg, 58% yield, 93% ee). Chiral HPLC conditions: chiralcel OD-H, 25 ºC, flow rate: 1.0 mL/min, hexane/isopropanol: 80/20, 230 nm, 4.9 min (*R*), 5.3 min (*S*); $[\alpha]^{25}_{D}$ = 63.5 ° (c = 0.88, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 - 7.68 (m, 1H), 7.59 - 7.51 (m, 2H), 7.51 - 7.47 (m, 1H), 7.36 - 7.28 (m, 2H), 6.95 - 6.81 (m, 2H), 3.93 (br.s, 0.8H), 3.78 (s, 3H), 2.43 (ddd, *J* = 13.7, 11.6, 4.8 Hz, 1H), 2.32 (ddd, *J* = 13.8, 11.7, 4.7 Hz, 1H), 1.50 - 1.48 (m, 1H), 1.34 - 1.30 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 159.0, 151.1, 140.3, 135.0, 126.6, 125.0, 124.4, 120.0, 113.6, 110.8, 75.8, 55.1, 43.2, 16.8, 14.1; IR (KBr, cm^{-1}): 3444, 2960, 2931, 2873, 1610, 1559, 1511, 1455, 1300, 1248, 1177, 1035, 830, 746; HRMS (ESI): *m/z* calcd. for [M+H, $C_{18}H_{20}NO_3$]$^+$: 298.1438; found: 298.1440.



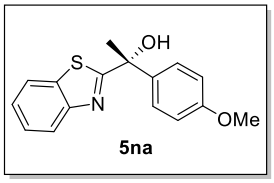
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	4.822	1226880	52.441	10787105	49.953
2	5.207	1112682	47.559	10807489	50.047
Total		2339562	100.000	21594594	100.000

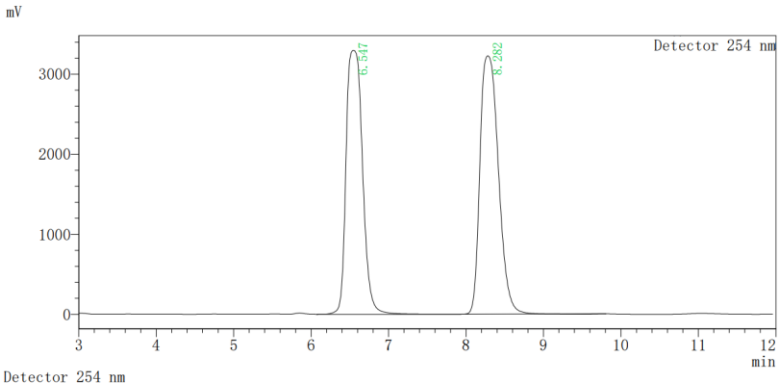


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	4.862	567680	97.244	4691899	96.779
2	5.262	16091	2.756	156156	3.221
Total		583771	100.000	4848056	100.000

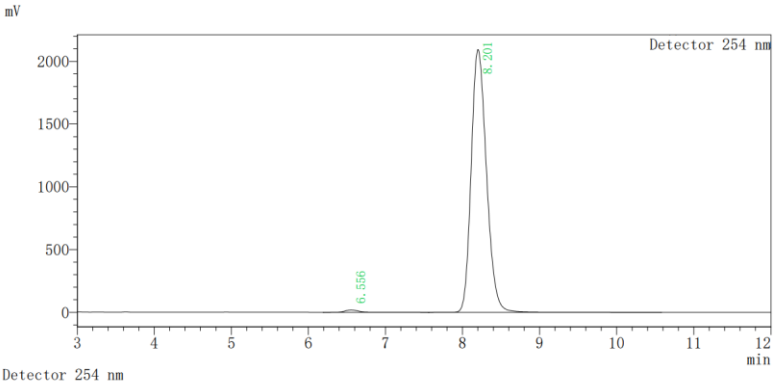


(*R*)-1-(benzo[d]thiazol-2-yl)-1-(4-methoxyphenyl)ethan-1-ol (5na): General Procedure B was followed using **4n** (35.4 mg, 0.20 mmol) and (4-methoxyphenyl)boronic acid (76.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (10/1, v/v), the desired product was obtained as a colorless oil (42.3 mg, 74% yield, 96% ee). Chiral HPLC conditions: chiralcel OD-H, 25 ºC, flow rate: 1.0 mL/min, hexane/ isopropanol: 80/20, 254 nm, 6.6 min (*S*), 8.2 min (*R*); $[\alpha]^{25}_{D}$ = -6.1 ° (c = 0.23, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.58 - 7.51 (m, 2H), 7.48 - 7.43 (m, 1H), 7.37 - 7.33 (m, 1H), 6.94 - 6.82 (m, 2H), 3.84 (s, 1H), 3.78 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.2, 159.1, 152.8, 137.2, 135.7, 126.8, 126.0, 125.0, 123.1, 121.7, 113.7, 76.2, 55.3, 30.3; IR (KBr, cm^{-1}): 3242, 2985, 2966, 2845, 1609, 1547, 1455, 1310, 1254, 1178, 1029, 917, 834, 763, 732; HRMS (ESI): *m/z* calcd. for [M+H, $C_{16}H_{16}NO_2S]^+$: 286.0896; found: 286.0901.



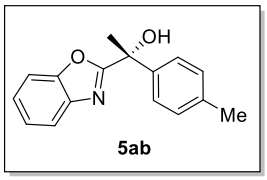
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.547	3296478	50.542	48560549	47.731
2	8.282	3225745	49.458	53176515	52.269
Total		6522223	100.000	101737064	100.000

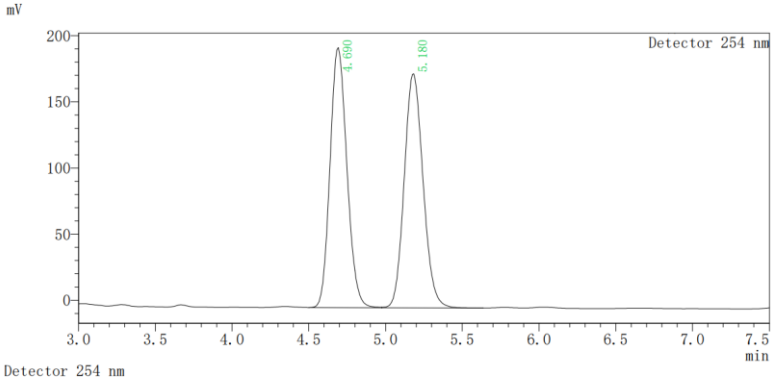


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.556	18668	0.884	242823	0.833
2	8.201	2094331	99.116	28916431	99.167
Total		2112999	100.000	29159253	100.000

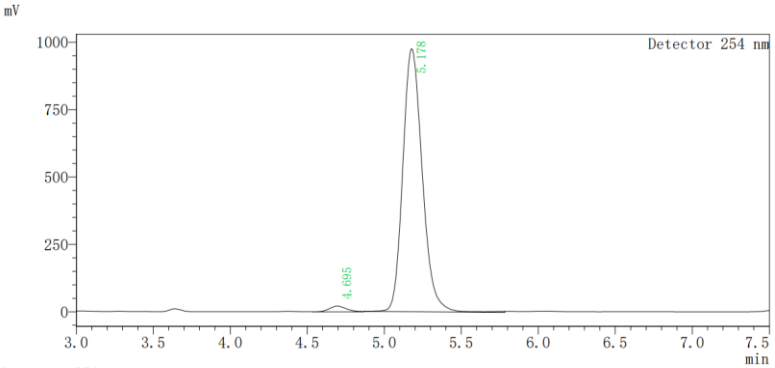


(*R*)-1-(benzo[d]oxazol-2-yl)-1-(p-tolyl)ethan-1-ol (5ab): General Procedure B was followed using **4a** (32.2 mg, 0.20 mmol) and *p*-tolylboronic acid (68.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (10/1, v/v), the desired product was obtained as a colorless oil (28.4 mg, 56% yield, 96% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 80/20, 254 nm, 4.7 min (*S*), 5.2 min (*R*); $[\alpha]^{25}_{D}$ = 62.4 ° (c = 1.39, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 - 7.67 (m, 1H), 7.51 - 7.43 (m, 3H), 7.36 - 7.28 (m, 2H), 7.17 - 7.15 (m, 2H), 4.32 (br.s, 1H), 2.34 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 150.9, 140.8, 140.3, 137.5, 129.0, 125.1, 124.9, 124.4, 120.1, 110.7, 73.5, 28.5, 20.9; IR (KBr, cm^{-1}): 3391, 3027, 2988, 2924, 1611, 1561, 1511, 1455, 1241, 1105, 1082, 929, 818, 748; HRMS (ESI): *m/z* calcd. for $[M+H, C_{16}H_{16}NO_2]^+$: 254.1176; found: 254.1182.



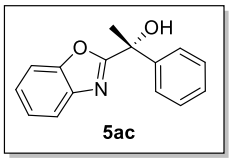
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	4.690	196626	52.636	1506583	49.871
2	5.180	176928	47.364	1514350	50.129
Total		373554	100.000	3020933	100.000

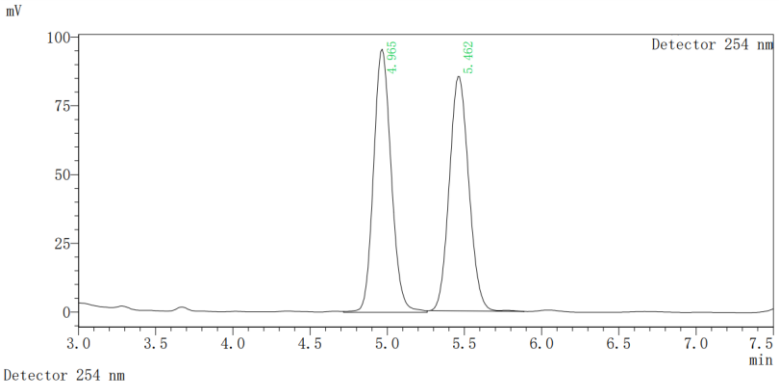


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	4.695	21063	2.114	168304	1.917
2	5.178	975276	97.886	8609005	98.083
Total		996339	100.000	8777309	100.000

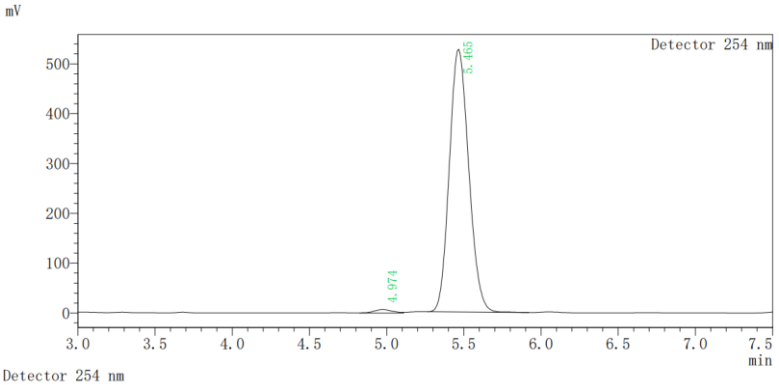


(*R*)-1-(benzo[d]oxazol-2-yl)-1-phenylethan-1-ol (5ac): General Procedure B was followed using **4a** (32.2 mg, 0.20 mmol) and phenylboronic acid (61.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (10/1, v/v), the desired product was obtained as a colorless oil (43.3 mg, 90% yield, 98% ee). The absolute configuration was determined based on **6c**. Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 80/20, 254 nm, 5.0 min (*S*), 5.5 min (*R*); $[\alpha]^{25}_{D}$ = 77.6 ° (c = 0.65, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 - 7.66 (m, 1H), 7.61 - 7.53 (m, 2H), 7.51 - 7.43 (m, 1H), 7.40 - 7.26 (m, 5H), 4.10 (br.s, 1H), 2.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 151.0, 143.7, 140.3, 128.4, 127.8, 125.2, 125.0, 124.5, 120.1, 110.8, 73.6, 28.6; HRMS (ESI): *m/z* calcd. for $[M+H, C_{15}H_{14}NO2]^+$: 240.1019; found: 240.1024.



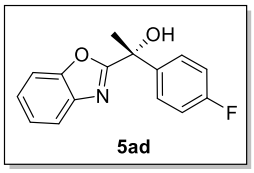
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	4.965	95667	52.875	762163	50.437
2	5.462	85265	47.125	748960	49.563
Total		180931	100.000	1511123	100.000



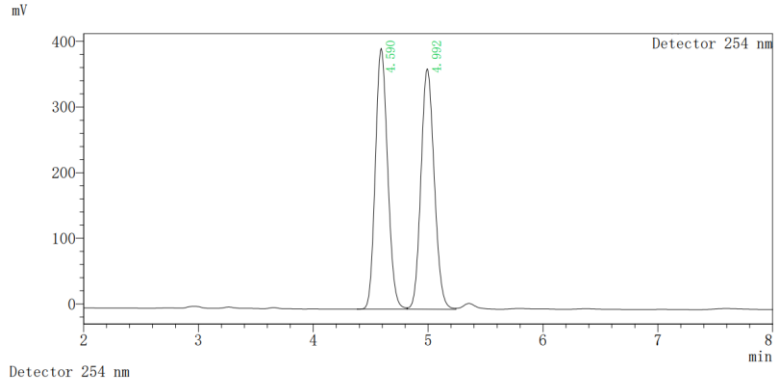
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	4.974	6956	1.302	57017	1.219
2	5.465	527241	98.698	4621324	98.781
Total		534197	100.000	4678341	100.000



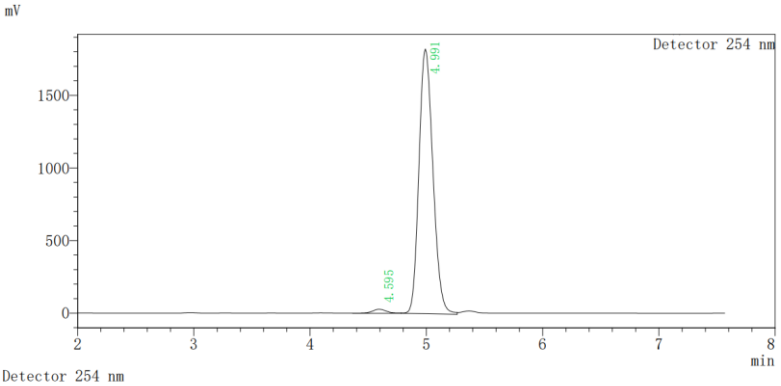
5ad

(*R*)-1-(benzo[d]oxazol-2-yl)-1-(4-fluorophenyl)ethan-1-ol (5ad): General Procedure B was followed using **4a** (32.2 mg, 0.20 mmol) and (4-fluorophenyl)boronic acid (70.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless oil (45.4 mg, 88% yield, 97% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/ isopropanol: 80/20, 254 nm, 4.6 min (*S*), 5.0 min (*R*); $[\alpha]^{25}_{D}$ = 62.5 ° (c = 1.66, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 - 7.69 (m, 1H), 7.58 - 7.45 (m, 3H), 7.39 - 7.30 (m, 2H), 7.06 - 7.00 (m, 2H), 4.06 (br.s, 1H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.1, 162.3 (d, *J* = 246.8 Hz), 151.1, 140.3, 139.5, 127.0 (d, *J* = 8.3 Hz), 125.4, 124.7, 120.2, 115.3 (d, *J* = 21.6 Hz), 110.9, 73.2, 28.8; IR (KBr, cm^{-1}): 3417, 3074, 2990, 2934, 1603, 1562, 1508, 1454, 1239, 1161, 1095, 928, 835, 748; HRMS (ESI): *m/z* calcd. for [M+H, $C_{15}H_{13}FNO_2]^+$: 258.0925; found: 258.0929.



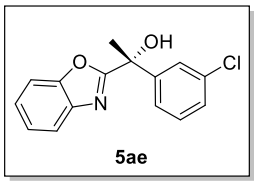
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	4.590	397525	52.026	2958098	49.990
2	4.992	366558	47.974	2959286	50.010
Total		764084	100.000	5917384	100.000



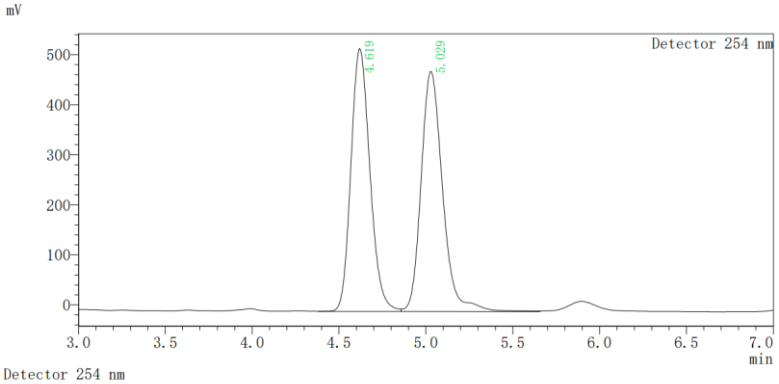
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	4.595	27605	1.492	237564	1.533
2	4.991	1822222	98.508	15254568	98.467
Total		1849827	100.000	15492132	100.000



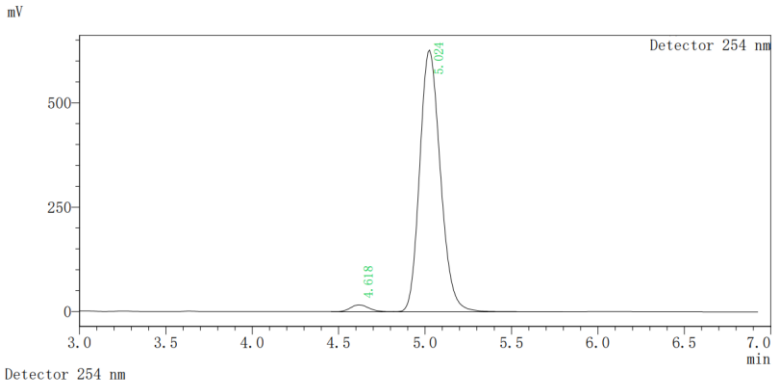
5ae

(*R*)-1-(benzo[d]oxazol-2-yl)-1-(3-chlorophenyl)ethan-1-ol (5ae): General Procedure B was followed using **4a** (32.2 mg, 0.20 mmol) and (3-chlorophenyl)boronic acid (78.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless solid (37.8 mg, 69% yield, 95% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 80/20, 254 nm, 4.6 min (*S*), 5.0 min (*R*); $[\alpha]^{25}_{D}$ = 80.5 ° (c = 1.06, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 - 7.62 (m, 1H), 7.53 - 7.52 (m, 1H), 7.45 - 7.40 (m, 1H), 7.37 - 7.32 (m, 1H), 7.29 - 7.25 (m, 2H), 7.22 - 7.16 (m, 2H), 3.63 (br.s, 1H), 1.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 151.1, 145.7, 140.2, 134.5, 129.8, 128.1, 125.4, 125.4, 124.7, 123.3, 120.3, 111.0, 73.2, 28.7; IR (KBr, cm^{-1}): 3325, 3078, 2991, 2925, 1595, 1564, 1454, 1241, 1138, 1082, 933, 798, 740; HRMS (ESI): *m/z* calcd. for [M+H, $C_{15}H_{13}ClNO_2]^+$: 274.0629; found: 274.0634.



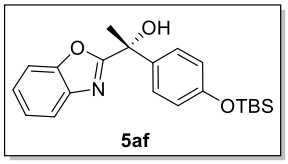
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	4.619	525265	52.276	3989458	49.132
2	5.029	479532	47.724	4130345	50.868
Total		1004797	100.000	8119803	100.000



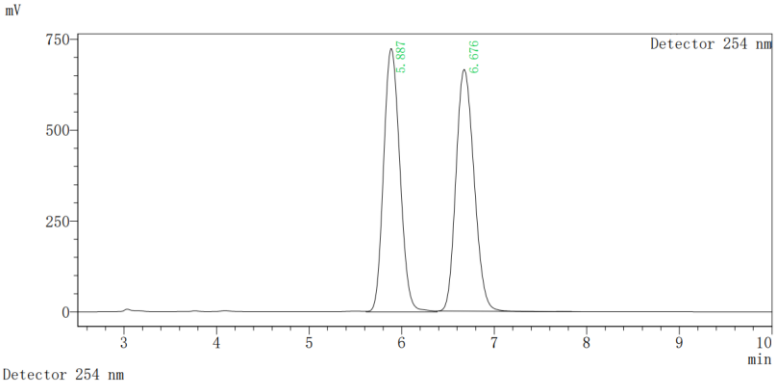
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	4.618	16951	2.634	128092	2.399
2	5.024	626605	97.366	5211053	97.601
Total		643556	100.000	5339146	100.000



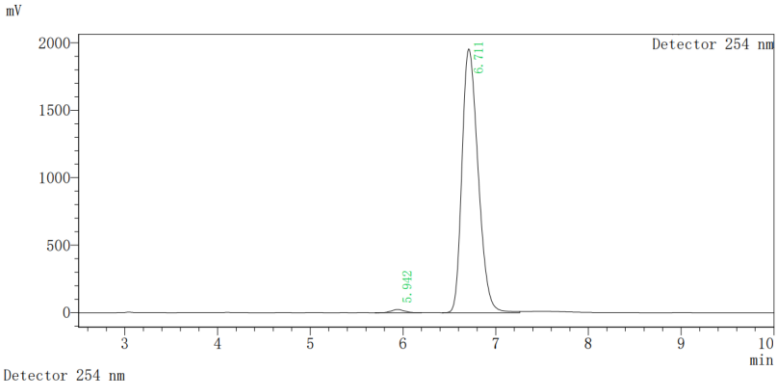
5af

(*R*)-1-(benzo[d]oxazol-2-yl)-1-(4-((tert-butyldimethylsilyl) oxy)phenyl)ethan-1-ol (5af): General Procedure B was followed using **4a** (32.2 mg, 0.20 mmol) and (4-((tert-butyldimethylsilyl)oxy)phenyl) boronic acid (126.2 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (10/1, v/v), the desired product was obtained as a colorless oil (66.7 mg, 90% yield, 98% ee). Chiral HPLC conditions: chiralcel OD-H, 25 ºC, flow rate: 1.0 mL/min, hexane/isopropanol: 95/5, 254 nm, 5.9 min (*S*), 6.7 min (*R*); $[\alpha]^{25}_{D}$ = 42.5 ° (c = 3.36, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 - 7.66 (m, 1H), 7.53 - 7.44 (m, 1H), 7.44 - 7.35 (m, 2H), 7.35 - 7.28 (m, 2H), 6.86 - 6.76 (m, 2H), 4.18 (br.s, 0.87H), 2.07 (s, 3H), 0.98 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 155.3, 151.0, 140.4, 136.4, 126.3, 125.1, 124.5, 120.1, 119.8, 110.8, 73.4, 28.6, 25.6, 18.1, -4.5; IR (KBr, cm^{-1}): 3349, 2956, 2930, 2858, 1607, 1509, 1455, 1362, 1267, 1173, 916, 839, 779, 741; HRMS (ESI): *m/z* calcd. for [M+H, $C_{21}H_{28}NO_3Si]^+$: 370.1833; found: 370.1839.



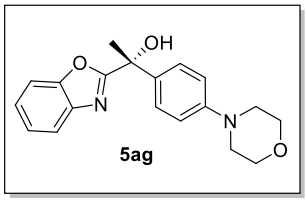
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	5.887	724429	52.133	8866236	49.509
2	6.676	665161	47.867	9041986	50.491
Total		1389590	100.000	17908222	100.000

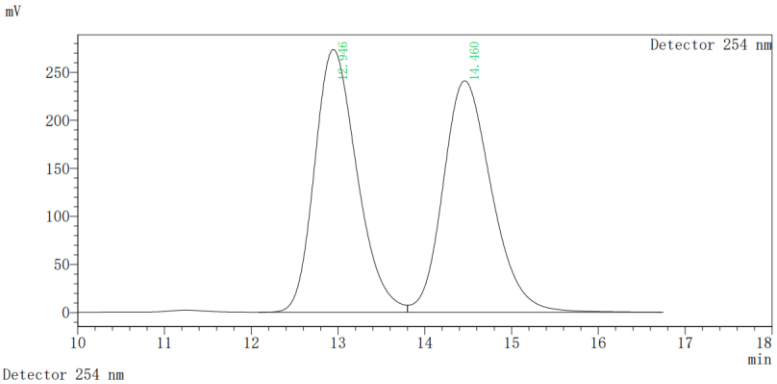


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	5.942	22864	1.157	225738	0.944
2	6.711	1954081	98.843	23679400	99.056
Total		1976945	100.000	23905138	100.000

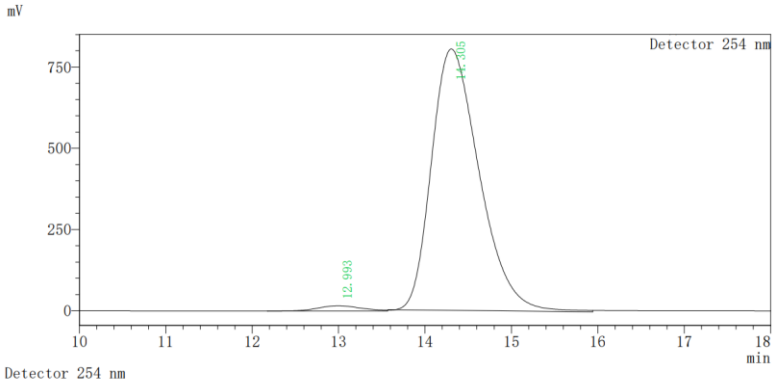


(*R*)-1-(benzo[d]oxazol-2-yl)-1-(4-morpholinophenyl)ethan-1-ol (5ag): General Procedure B was followed using **4a** (32.2 mg, 0.20 mmol) and (4-morpholinophenyl)boronic acid (103.6 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless oil (59.7 mg, 92% yield, 96% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/ isopropanol: 95/5, 254 nm, 13.0 min (*S*), 14.3 min (*R*); $[\alpha]^{25}_{D}$ = 41.3 ° (c = 1.43, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 - 7.66 (m, 1H), 7.52 - 7.39 (m, 3H), 7.37 - 7.26 (m, 2H), 6.93 - 6.76 (m, 2H), 3.93 (br.s, 1H), 3.95 - 3.58 (m, 4H), 3.25 - 2.83 (m, 4H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 151.0, 150.7, 140.4, 134.9, 126.0, 125.0, 124.4, 120.1, 115.2, 110.8, 73.2, 66.7, 48.9, 28.4; IR (KBr): 3390, 2963, 2855, 2824, 1610, 1514, 1453, 1377, 1238, 1119, 927, 825, 745; HRMS (ESI): *m/z* calcd. for $[M+H, C_{19}H_{21}N_2O_3]^+$: 325.1547; found: 325.1552.



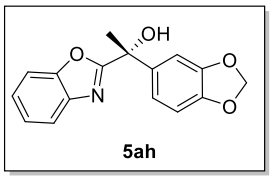
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	12.946	273414	53.165	9290630	49.841
2	14.460	240861	46.835	9349850	50.159
Total		514275	100.000	18640480	100.000

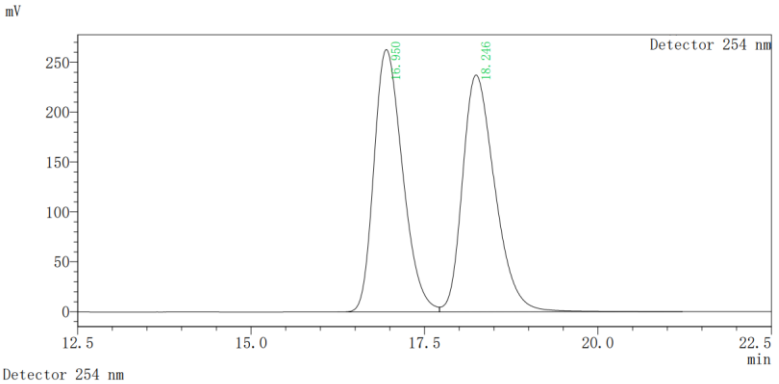


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	12.993	16201	1.975	556042	1.766
2	14.305	804054	98.025	30924789	98.234
Total		820255	100.000	31480832	100.000

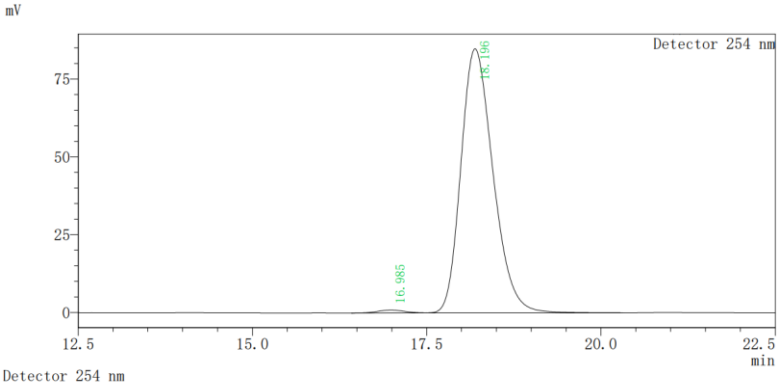


(*R*)-1-(benzo[d][1,3]dioxol-5-yl)-1-(benzo[d]oxazol-2-yl)ethan-1-ol (5ah): General Procedure B was followed using **4a** (32.2 mg, 0.20 mmol) and benzo[*d*][1,3]dioxol-5-ylboronic acid (83.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless oil (51.3 mg, 90% yield, 98% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/ isopropanol: 95/5, 254 nm, 17.0 min (*S*), 18.2 min (*R*); $[\alpha]^{25}_{D}$ = 56.8 ° (c = 2.29, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 - 7.67 (m, 1H), 7.54 - 7.43 (m, 1H), 7.38 - 7.29 (m, 2H), 7.07 - 7.06 (m, 1H), 7.01 - 6.98 (m, 1H), 6.76 - 6.74 (m, 1H), 5.93 (s, 2H), 3.66 (br.s, 1H), 2.05 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 151.0, 147.8, 147.2, 140.3, 137.8, 125.2, 124.6, 120.2, 118.4, 110.9, 108.0, 106.1, 101.2, 73.4, 28.7; IR (KBr, cm^{-1}): 3375, 3078, 2988, 2894, 1609, 1562, 1487, 1454, 1242, 1100, 1040, 934, 814, 749; HRMS (ESI): *m/z* calcd. for $[M+H, C_{16}H_{14}NO_4]^+$: 284.0917; found: 284.0920.



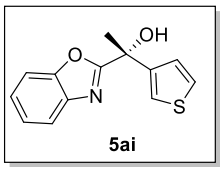
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	16.950	263106	52.571	7574827	49.550
2	18.246	237368	47.429	7712536	50.450
Total		500474	100.000	15287363	100.000

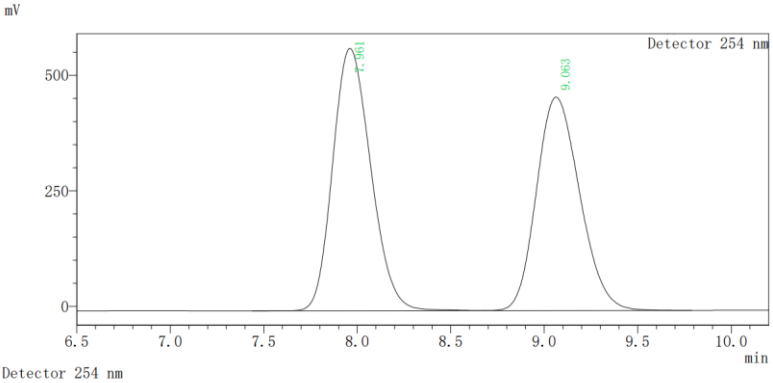


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	16.985	948	1.105	25818	0.939
2	18.196	84811	98.895	2723094	99.061
Total		85759	100.000	2748912	100.000

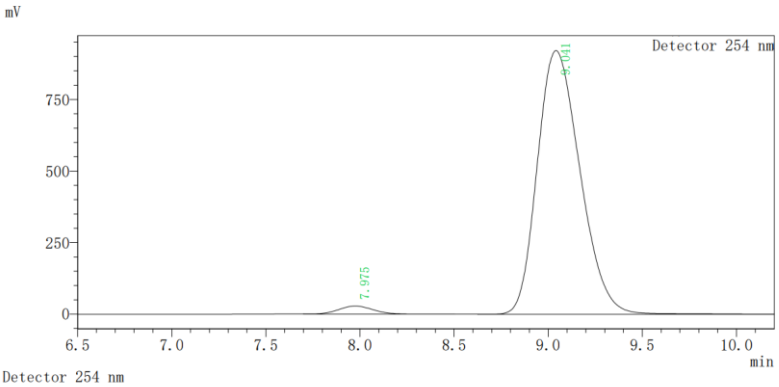


(*R*)-1-(benzo[d]oxazol-2-yl)-1-(thiophen-3-yl)ethan-1-ol (5ai): General Procedure B was followed using **4a** (32.2 mg, 0.20 mmol) and thiophen-3-ylboronic acid (76.8 mg, 0.60 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless solid (40.0 mg, 81% yield, 95% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 90/10, 254 nm, 8.0 min (*S*), 9.0 min (*R*); $[\alpha]^{25}_{D}$ = 27.3 ° (c = 0.42, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 - 7.68 (m, 1H), 7.56 - 7.47 (m, 1H), 7.38 - 7.31 (m, 3H), 7.30 - 7.28 (m, 1H), 7.22 - 7.20 (m, 1H), 3.43 (br.s, 1H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 151.1, 145.2, 140.4, 126.3, 125.7, 125.2, 124.6, 121.3, 120.2, 110.8, 71.9, 28.4; IR (KBr, cm^{-1}): 3392, 3091, 3024, 2961, 1604, 1533, 1350, 1300, 1120, 1099, 968, 892, 768, 754; HRMS (ESI): *m/z* calcd. for $[M+H, C_{13}H_{12}NO_2S]^+$: 246.0583; found: 246.0586.



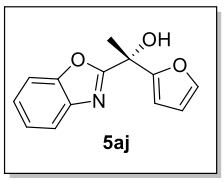
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	7.961	567422	55.145	8037257	51.961
2	9.063	461533	44.855	7430501	48.039
Total		1028955	100.000	15467758	100.000



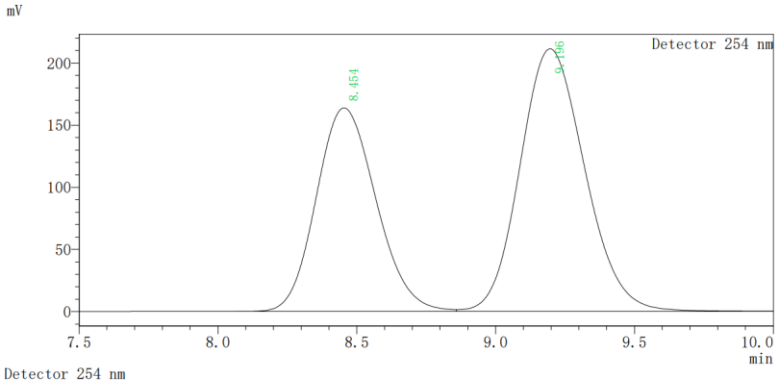
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	7.975	28662	3.018	369399	2.477
2	9.041	921150	96.982	14540948	97.523
Total		949813	100.000	14910348	100.000



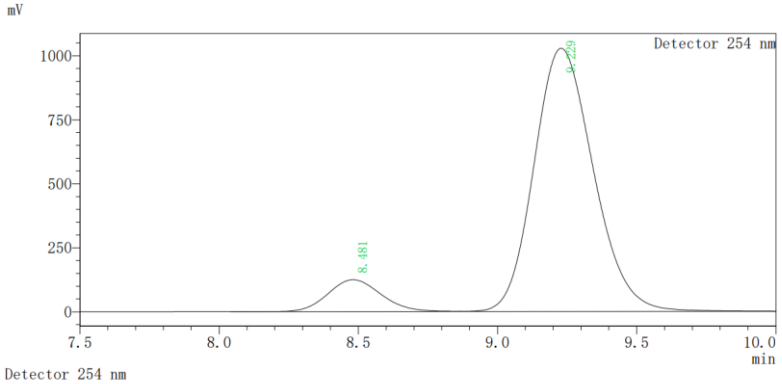
5aj

(*R*)-1-(benzo[d]oxazol-2-yl)-1-(furan-2-yl)ethan-1-ol (5aj): General Procedure B was followed using **4a** (32.2 mg, 0.20 mmol) and furan-2-ylboronic acid (78.4 mg, 0.70 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless solid (34.6 mg, 75% yield, 80% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 90/10, 230 nm, 8.5 min (*S*), 9.2 min (*R*); $[\alpha]^{25}_{D}$ = 3.0 ° (c = 1.13, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 - 7.69 (m, 1H), 7.56 - 7.49 (m, 1H), 7.41 - 7.31 (m, 3H), 6.40 - 6.38 (m, 1H), 6.36 - 6.35 (m, 1H), 2.87 (br.s, 1H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 154.9, 151.1, 142.7, 140.4, 125.3, 124.6, 120.3, 110.9, 110.4, 106.7, 69.7, 25.2; IR (KBr, cm^{-1}): 3317, 2995, 2929, 2859, 1611, 1563, 1455, 1241, 1158, 1129, 1084, 940, 830, 744; HRMS (ESI): *m/z* calcd. for [M+H, $C_{13}H_{12}NO_3$]$^+$: 230.0812; found: 230.0816.



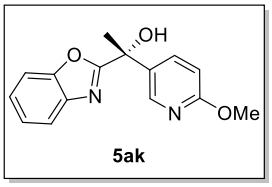
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	8.454	163675	43.669	2452749	41.727
2	9.196	211130	56.331	3425329	58.273
Total		374805	100.000	5878078	100.000



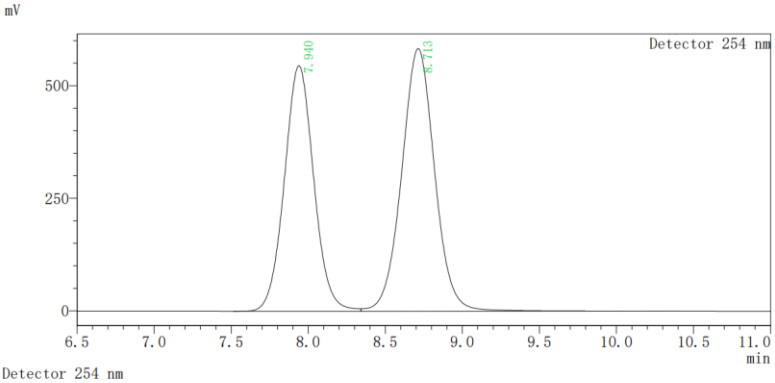
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	8.481	124313	10.790	1649942	9.749
2	9.229	1027779	89.210	15274933	90.251
Total		1152092	100.000	16924875	100.000



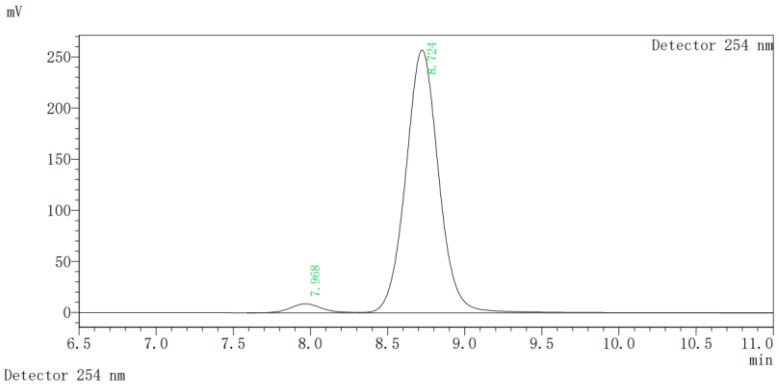
5ak

(*R*)-1-(benzo[d]oxazol-2-yl)-1-(6-methoxypyridin-3-yl)ethan-1-ol (5ak): General Procedure B was followed using **4a** (32.2 mg, 0.20 mmol) and (6-methoxypyridin-3-yl)boronic acid (76.5 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless oil (47.2 mg, 87% yield, 93% ee). Chiral HPLC conditions: chiralcel AD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 85/15, 254 nm, 8.0 min (*S*), 8.7 min (*R*); $[\alpha]^{25}_{D}$ = 40.5 ° (c = 2.2, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 2.6 Hz, 1H), 7.79 - 7.76 (m, 1H), 7.70 - 7.63 (m, 1H), 7.48 - 7.44 (m, 1H), 7.33 - 7.29 (m, 2H), 6.70 (d, *J* = 8.7 Hz, 1H), 4.59 (br.s, 0.82H), 3.89 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 163.7, 151.0, 143.9, 140.2, 136.3, 132.2, 125.4, 124.7, 120.1, 110.8, 110.5, 72.1, 53.5, 28.5; IR (KBr, cm^{-1}): 3332, 2991, 2947, 2848, 1607, 1493, 1455, 1381, 1289, 1123, 1083, 1024, 832, 748; HRMS (ESI): *m/z* calcd. for $[M+H, C_{15}H_{15}N_2O_3]^+$: 271.1077; found: 271.1074.



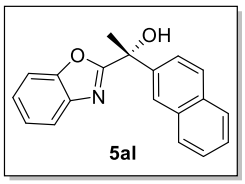
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	7.940	545473	48.338	7236290	45.435
2	8.713	582992	51.662	8690374	54.565
Total		1128466	100.000	15926663	100.000

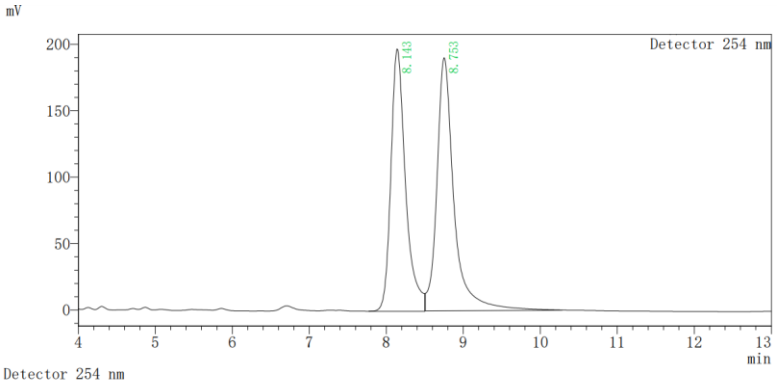


Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	7.968	8769	3.299	122598	3.110
2	8.724	257015	96.701	3818968	96.890
Total		265784	100.000	3941566	100.000

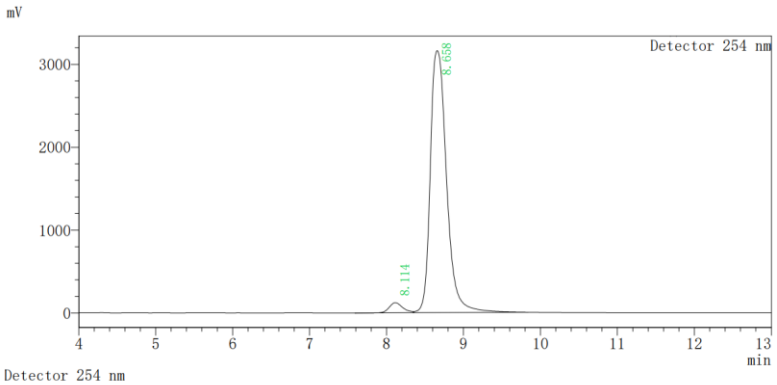


(*R*)-1-(benzo[d]oxazol-2-yl)-1-(naphthalen-2-yl)ethan-1-ol (5al): General Procedure B was followed using **4a** (32.2 mg, 0.20 mmol) and naphthalen-2-ylboronic acid (86.0 mg, 0.50 mmol). After flash chromatography with petroleum ether/ethyl acetate (8/1, v/v), the desired product was obtained as a colorless solid (40.7 mg, 70% yield, 94% ee). Chiral HPLC conditions: chiralpak IA, 25 ^{o}C, flow rate: 1.0 mL/min, hexane/isopropanol: 85/15, 254 nm, 8.1 min (*S*), 8.7 min (*R*); $[\alpha]^{25}_{D}$ = 90.6 ° (c = 0.78, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.88 - 7.72 (m, 4H), 7.70 - 7.60 (m, 1H), 7.49 - 7.46 (m, 3H), 7.35 - 7.32 (m, 2H), 4.20 (br.s, 1H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 151.1, 141.0, 140.4, 133.0, 132.8, 128.3, 127.5, 126.2, 125.2, 124.6, 123.7, 123.2, 120.2, 110.9, 73.8, 28.6; IR (KBr, cm^{-1}): 3345, 3056, 2985, 2933, 2836, 1602, 1562, 1454, 1371, 1241, 1127, 1085, 931, 858, 818, 745; HRMS (ESI): *m/z* calcd. for [M+H, $C_{19}H_{16}NO_2]^+$: 290.1176; found: 290.1184.



Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	8.143	197368	50.887	2609957	46.979
2	8.753	190489	49.113	2945627	53.021
Total		387857	100.000	5555583	100.000



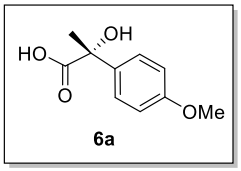
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	8.114	122089	3.719	1489588	3.107
2	8.658	3161188	96.281	46449730	96.893
Total		3283277	100.000	47939319	100.000

7. General procedure of hydrolysis of chiral tertiary alcohol for synthesis of chiral α-Hydroxy Acids (General Procedure C).

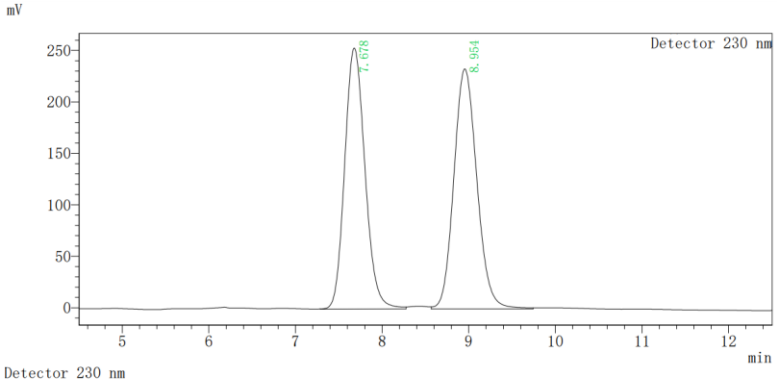
To a Schlenk tube was added **5aa** (103.7 mg, 0.39 mmol, 1.0 equiv), KOH (480.3 mg, 7.71 mmol, 20 equiv, 90 wt%), and glycol (3.9 mL). The resulting mixture was stirred at 150 ºC under nitrogen for 16 h. Then cooled to room temperature, ether (6 mL) was added to the mixture. Reaction mixture pH was adjusted to 1 by adding aqueous HCl (~2.6 mL, 3M) at -15 ºC. The mixture was added water (6 mL) and extracted with ether (10-20 mL x 3), the combined organic phase was washed with water (20 mL), and brine (15 mL), dried over sodium sulfate, filtered, and concentrated to provide the desired product with high purity. The enantiomeric excesses were determined by chiral HPLC on a chiralpak AS-H or chiralcel AD-H column.

8. Analytical data of chiral α-Hydroxy Acids



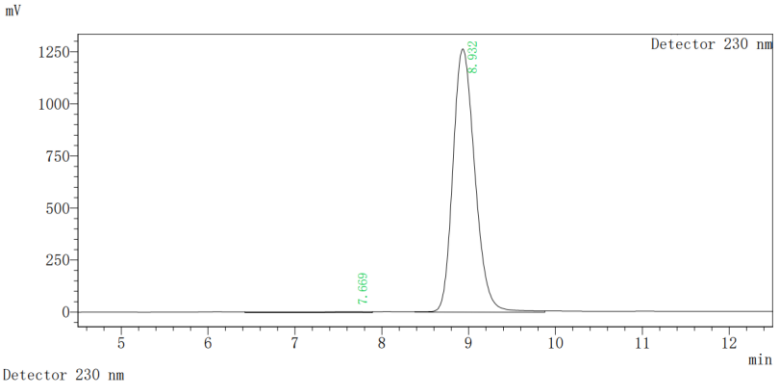
6a

(*R*)-2-hydroxy-2-(4-methoxyphenyl)propanoic acid (6a): General Procedure C was followed using **5aa** (103.7 mg, 0.39 mmol). After extraction, the desired product was obtained as solid (68.3 mg, 89% yield, 97% ee). Chiral HPLC conditions: chiralpak AS-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol /trifluoroacetic acid: 80/20/0.1, 230 nm, 7.7 min (*S*), 8.9 min (*R*); $[\alpha]^{25}_{D}$ = -27.0 ° (c = 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.56 (br.s, 1H), 7.43 - 7.41 (m, 2H), 6.89 - 6.87 (m, 2H), 5.67 (br.s, 1H), 3.73 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 176.8, 158.8, 136.9, 126.9, 113.7, 74.9, 55.5, 27.8; HRMS (ESI): *m/z* calcd. for $[M+2Na-H, C_{10}H_{11}Na_2O_4]^+$: 241.0447; found: 241.0453.



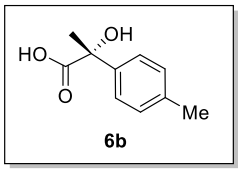
Detector 230 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	7.678	253547	52.084	4135369	48.924
2	8.954	233260	47.916	4317325	51.076
Total		486807	100.000	8452694	100.000

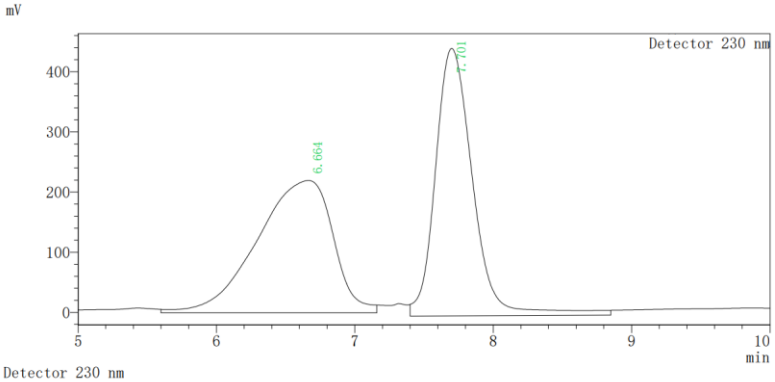


Detector 230 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	7.669	5472	0.431	349742	1.548
2	8.932	1263580	99.569	22236964	98.452
Total		1269052	100.000	22586706	100.000

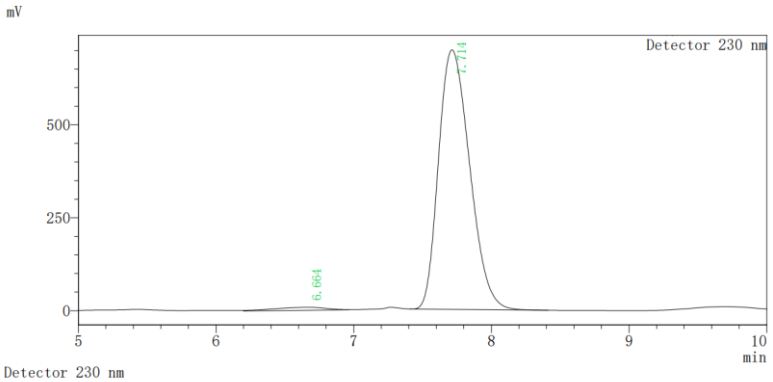


(*R*)-2-hydroxy-2-(p-tolyl)propanoic acid (6b): General Procedure C was followed using **5ab** (92.4 mg, 0.36 mmol). After extraction, the desired product was obtained as solid (58.6 mg, 90% yield, 96% ee). Chiral HPLC conditions: chiralpak AS-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol/ trifluoroacetic acid: 85/15/0.1, 230 nm, 6.7 min (*S*), 7.7 min (*R*); $[\alpha]^{25}_{D}$ = -16.7 ° (c = 0.66, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.60 (br.s, 1H), 7.39 - 7.37 (m, 2H), 7.14 - 7.12 (m, 2H), 5.68 (br.s, 1H), 2.27 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 176.7, 141.9, 136.6, 128.9, 125.6, 75.2, 27.8, 21.1; HRMS (ESI): *m/z* calcd. for [M+2Na-H, $C_{10}H_{11}Na_2O_3$]$^+$: 225.0498; found: 225.0501.



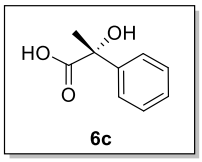
Detector 230 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.664	220057	33.101	8412979	50.076
2	7.701	444751	66.899	8387514	49.924
Total		664809	100.000	16800494	100.000

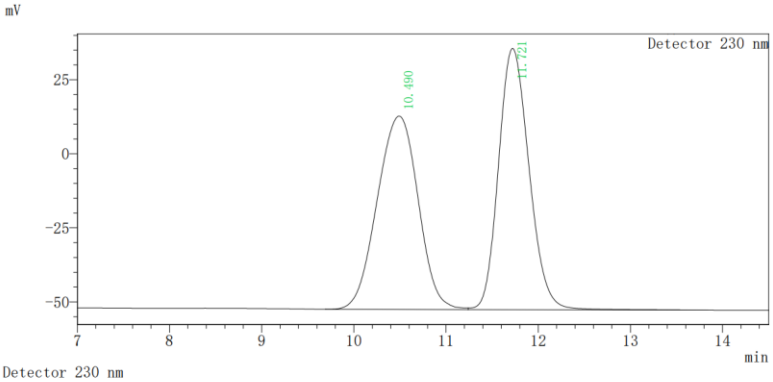


Detector 230 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.664	8025	1.136	215381	1.919
2	7.714	698147	98.864	11005933	98.081
Total		706173	100.000	11221314	100.000

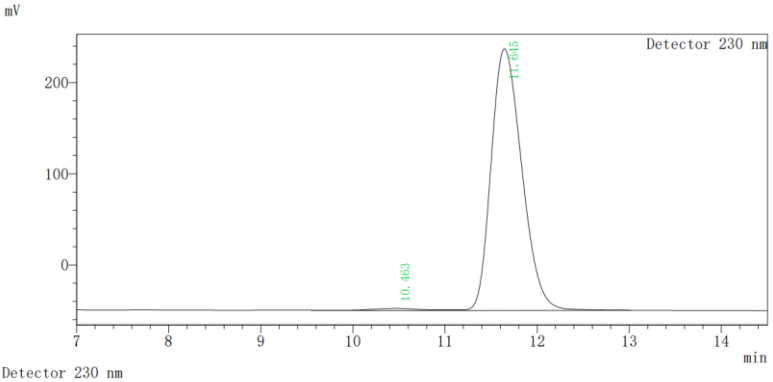


(*R*)-2-hydroxy-2-phenylpropanoic acid (6c): General Procedure C was followed using **5ac** (416 mg, 1.7 mmol). After extraction, the desired product was obtained as solid (257 mg, 91% yield, 97% ee). The absolute configuration was determined by comparing its optical rotation with reported data[5]. Chiral HPLC conditions: chiralpak AS-H, 25 ^{o}C, flow rate: 1.0 mL/min, hexane/isopropanol/trifluoroacetic acid: 90/10/0.1, 230 nm, 10.5 min (*S*), 11.6 min (*R*); $[\alpha]^{25}D$ = -24.2 ° (c = 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.62 (br.s, 1H), 7.55 - 7.47 (m, 2H), 7.37 - 7.30 (m, 2H), 7.28 - 7.22 (m, 1H), 5.77 (br.s, 1H), 1.61 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 176.6, 144.9, 128.3, 127.5, 125.7, 75.3, 27.8; HRMS (ESI): *m/z* calcd. for $[M+2Na-H, C_9H_9Na_2O_3]^+$: 211.0342; found: 211.0345.



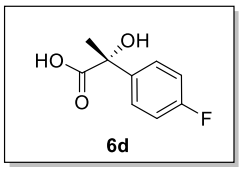
Detector 230 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	10.490	65289	42.540	2020584	49.831
2	11.721	88190	57.460	2034257	50.169
Total		153479	100.000	4054841	100.000

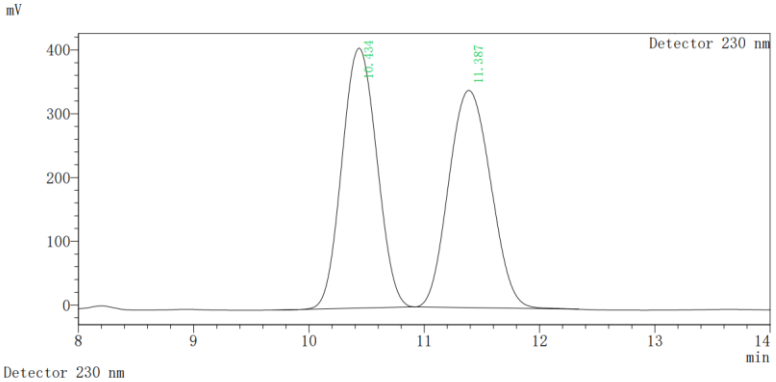


Detector 230 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	10.463	2232	0.773	86987	1.298
2	11.645	286714	99.227	6615456	98.702
Total		288947	100.000	6702444	100.000

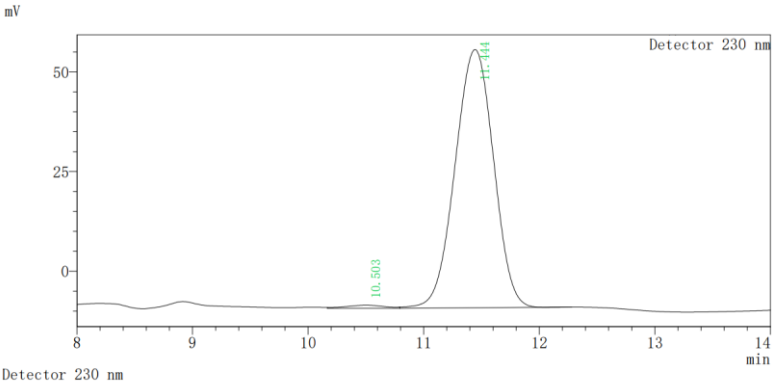


(*R*)-2-(4-fluorophenyl)-2-hydroxypropanoic acid (6d): General Procedure C was followed using **5ad** (84.2 mg, 0.32 mmol). After extraction, the desired product was obtained as solid (54.2 mg, 87% yield, 97% ee). Chiral HPLC conditions: chiralcel AD-H, 25 °C, flow rate: 1.0 mL/min, hexane /isopropanol/trifluoroacetic acid: 90/10/0.1, 230 nm, 10.5 min (*S*), 11.4 min (*R*); $[\alpha]^{25}_{D}$ = -11.0 ° (c = 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.56 - 7.52 (m, 2H), 7.15 (t, *J* = 8.7 Hz, 1H), 3.51 (br.s, 1H), 1.61 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 176.4 , 161.8 (d, *J* = 242.9 Hz), 141.1 (d, *J* = 3.0 Hz), 127.8 (d, *J* = 8.1 Hz), 115.0 (d, *J* = 21.2 Hz), 75.0, 27.9; HRMS (ESI): *m/z* calcd. for [M+2Na-H, $C_9H_8FNa_2O_3]^+$: 229.0247; found: 229.0246.



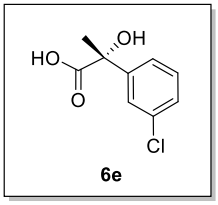
Detector 230 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	10.434	407669	54.478	8546701	49.767
2	11.387	340651	45.522	8626736	50.233
Total		748321	100.000	17173437	100.000



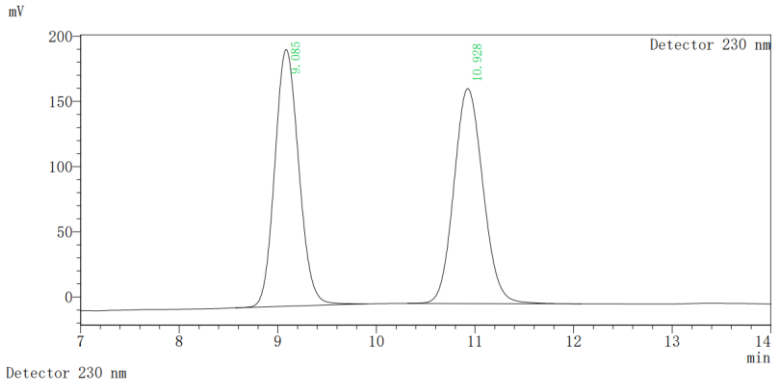
Detector 230 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	10.503	816	1.243	19177	1.263
2	11.444	64786	98.757	1499036	98.737
Total		65602	100.000	1518213	100.000



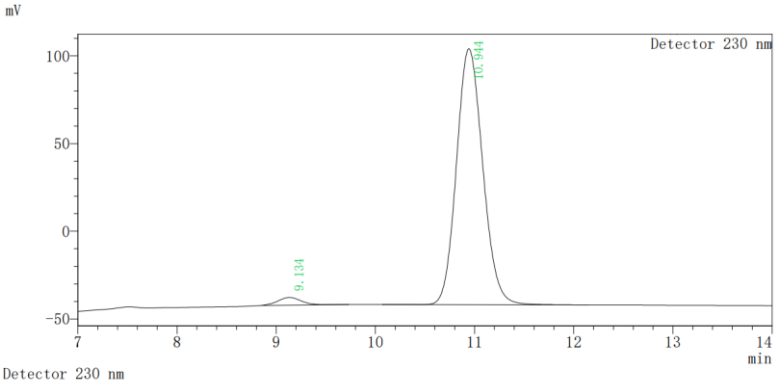
6e

(*R*)-2-(3-chlorophenyl)-2-hydroxypropanoic acid (6e): General Procedure C was followed using **5ae** (65.0 mg, 0.24 mmol). After extraction, the desired product was obtained as solid (43.6 mg, 91% yield, 95% ee). Chiral HPLC conditions: chiralcel AD-H, 25 ºC, flow rate: 1.0 mL/min, hexane/isopropanol/ trifluoroacetic acid: 90/10/0.1, 230 nm, 9.1 min (*S*), 10.9 min (*R*); $[\alpha]^{25}_{D}$ = -24.7 ° (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.58 (t, *J* = 1.9 Hz, 1H), 7.50 (dt, *J* = 7.5, 1.6 Hz, 1H), 7.45 - 7.34 (m, 2H), 3.48 (br.s, 1H), 1.65 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 176.0, 147.4, 133.3, 130.4, 127.6, 125.7, 124.6, 75.2, 27.8; HRMS (ESI): *m/z* calcd. For $[M+Na, C_9H_9ClNaO_3]^+$: 223.0132; found: 223.0129.



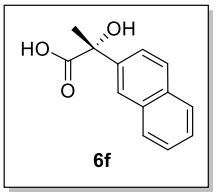
Detector 230 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	9.085	196913	54.430	3333164	49.620
2	10.928	164863	45.570	3384196	50.380
Total		361776	100.000	6717359	100.000

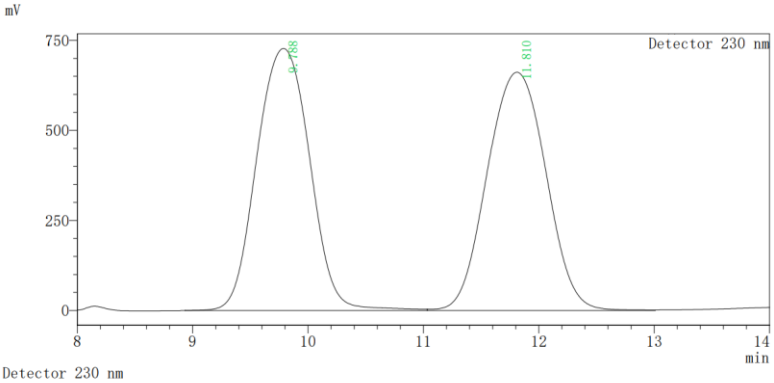


Detector 230 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	9.134	4453	2.961	74632	2.697
2	10.944	145938	97.039	2692933	97.303
Total		150391	100.000	2767565	100.000

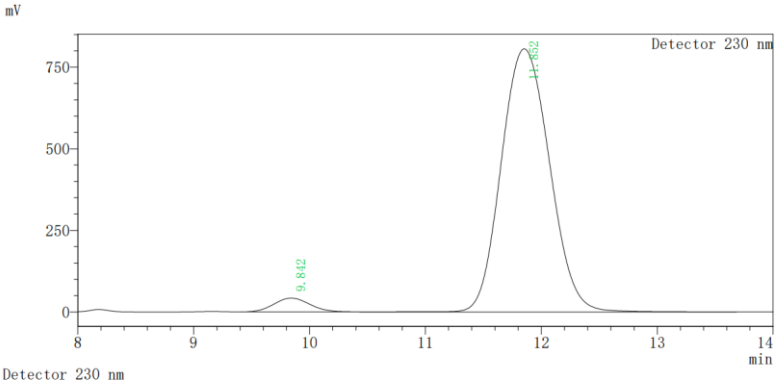


(*R*)-2-hydroxy-2-(naphthalen-2-yl)propanoic acid (6f): General Procedure C was followed using **5al** (66.4 mg, 0.24 mmol). After extraction, the desired product was obtained as solid (46.8 mg, 94% yield, 93% ee). Chiral HPLC conditions: chiralpak AS-H, 25 °C, flow rate: 1.0 mL/min, hexane /isopropanol/trifluoroacetic acid: 85/15/0.1, 230 nm, 9.8 min (*S*), 11.9 min (*R*); $[\alpha]^{25}_{D}$ = -8.1 ° (c = 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.56 (br, 0.89H), 8.04 (s, 1H), 7.96 - 7.82 (m, 3H), 7.68 - 7.65 (m, 1H), 7.50 (m, 2H), 6.05 (br, 0.74H), 1.74 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 176.5, 142.4, 133.0, 132.6, 128.6, 127.9, 127.8, 126.6, 126.4, 124.5, 124.1, 75.6, 27.8; HRMS (ESI): *m/z* calcd. for [M+Na, $C_{13}H_{12}NaO_3]^+$: 239.0679; found: 239.0676.



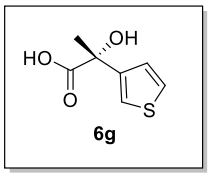
Detector 230 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	9.788	727463	52.374	23281934	49.847
2	11.810	661521	47.626	23425013	50.153
Total		1388984	100.000	46706947	100.000

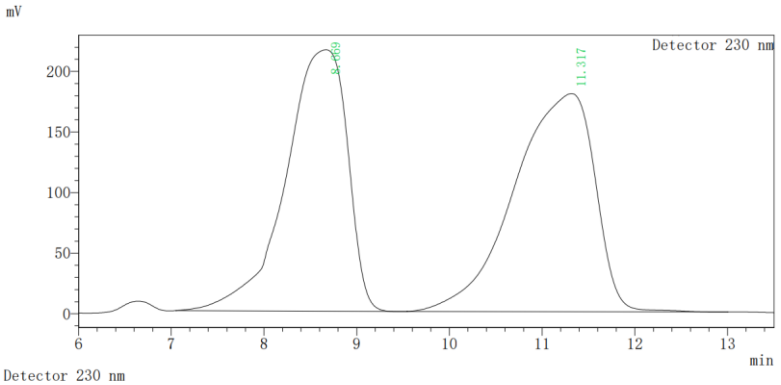


Detector 230 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	9.842	42169	4.972	900995	3.710
2	11.852	806021	95.028	23383346	96.290
Total		848190	100.000	24284341	100.000

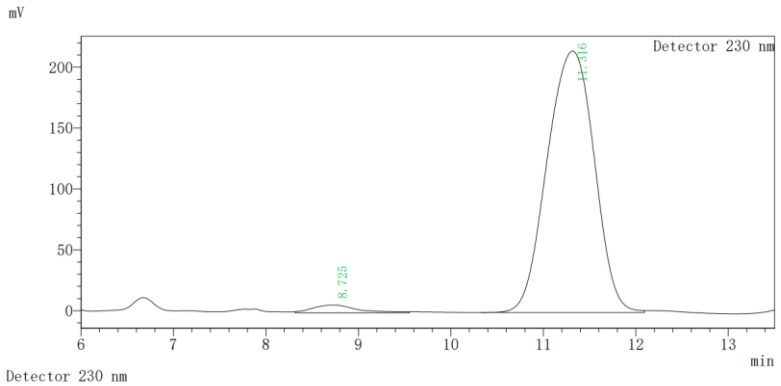


(*R*)-2-hydroxy-2-(thiophen-3-yl)propanoic acid (6g): General Procedure C was followed using **5ai** (87.4 mg, 0.36 mmol). After extraction, the desired product was obtained as solid (53.7 mg, 87% yield, 94% ee). Chiral HPLC conditions: chiralpak AS-H, 25 ºC, flow rate: 1.0 mL/min, hexane/isopropanol/trifluoroacetic acid: 85/15/0.1, 230 nm, 8.7 min (*S*), 11.3 min (*R*); $[\alpha]^{25}_{D}$ = -9.7 ° (c = 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.62 (br.s, 1H), 7.45 (m, 1H), 7.40 - 7.39 (m, 1H), 7.13 (dd, *J* = 5.0, 1.3 Hz, 1H), 5.73 (br.s, 1H), 1.60 (s, 3H); ^{13}C NMR (101 MHz, DMSO) δ 176.3, 146.6, 127.0, 126.2, 121.4, 74.0, 27.8; HRMS (ESI): *m/z* calcd. for $[M+2Na-H, C_7H_7Na_2O_3S]^+$: 216.9906; found: 216.9909.



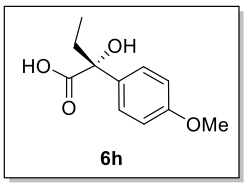
Detector 230 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	8.669	215647	54.488	10014306	47.819
2	11.317	180119	45.512	10928012	52.181
Total		395766	100.000	20942318	100.000

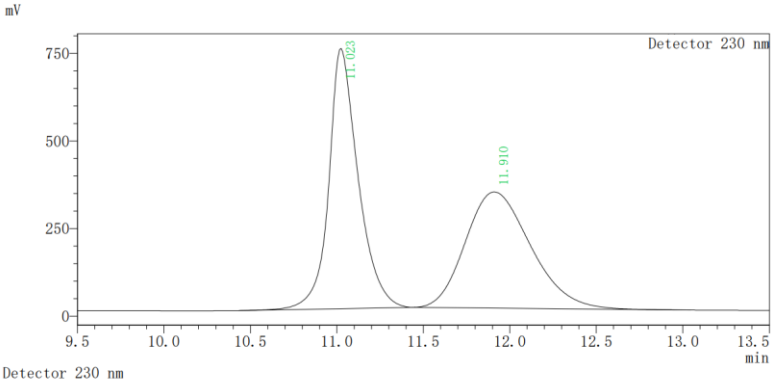


Detector 230 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	8.725	6351	2.873	217776	2.778
2	11.316	214698	97.127	7620703	97.222
Total		221049	100.000	7838480	100.000

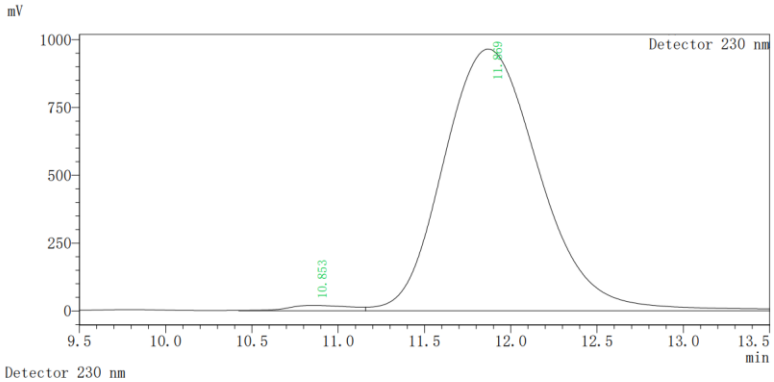


(*R*)-2-hydroxy-2-(4-methoxyphenyl)butanoic acid (6h): General Procedure C was followed using **5la** (95.2 mg, 0.32 mmol). After extraction, the desired product was obtained as a colorless solid (12.8 mg, 19% yield, 97% ee). Chiral HPLC conditions: chiralpak AS-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol /trifluoroacetic acid: 90/10/0.1, 230 nm, 10.9 min (*S*), 11.9 min (*R*); $[\alpha]^{25}_{D}$ = -41.4 ° (c = 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.62 (br.s, 1H), 7.52 - 7.33 (m, 2H), 6.97 - 6.77 (m, 2H), 5.41 (br.s, 1H), 3.73 (s, 3H), 2.07 (dq, *J* = 14.3, 7.2 Hz, 1H), 1.83 (dq, *J* = 14.3, 7.3 Hz, 1H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, DMSO) δ 176.5, 158.8, 135.6, 127.3, 113.7, 77.9, 55.5, 32.8, 8.7; HRMS (ESI): *m/z* calcd. for $[M+Na, C_{11}H_{14}NaO_4]^+$: 233.0784; found: 233.0786.



Detector 230 nm

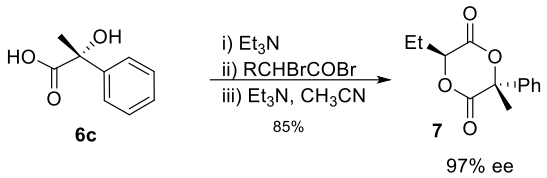
No.	Ret.Time(min)	Height	Height%	Area	Area%
1	11.023	742748	69.120	8791007	50.206
2	11.910	331829	30.880	8718770	49.794
Total		1074577	100.000	17509777	100.000



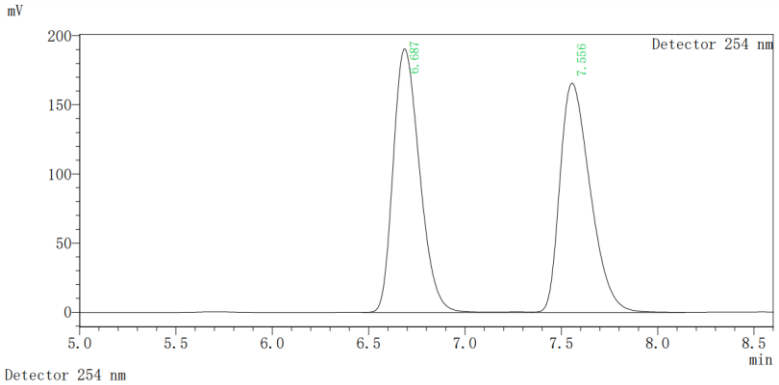
Detector 230 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	10.853	20309	2.061	527601	1.376
2	11.869	964945	97.939	37807471	98.624
Total		985253	100.000	38335072	100.000

9. Transformations of chiral α-Hydroxy Acid.

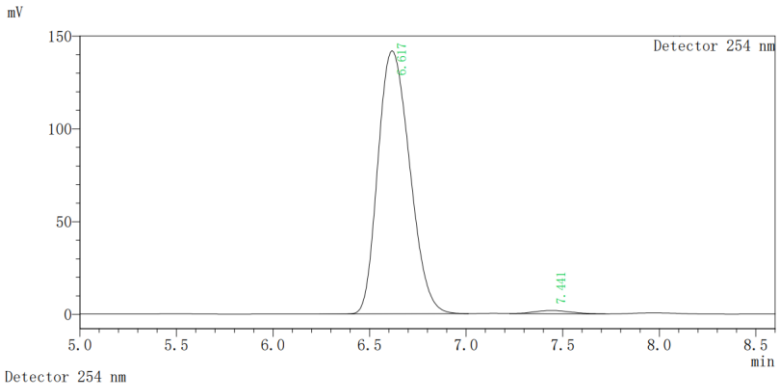


Compound **7** was synthesized according reported literature[6]. 2-Bromobutanoyl bromide (151.7mg, 0.66 mmol) was added to a stirred solution of (*R*)-**6c** (100mg, 0.6mmol) and Et_3N (67 mg, 0.66 mmol) in MeCN (2 mL) at 0-5°C under an N_2 atmosphere and the mixture was stirred for 30 min. Et_3N (67mg, 0.66 mmol) was added to the mixture at the same temperature, then the reaction was stirred at 50-55°C for 3 h and at 70-75°C for 30 min. The mixture was allowed to cool to r.t. then aq HCl (1M, 1mL) was added and the mixture was diluted with EtOAc (10 mL) and water (8 mL). Organic layer was separated, the water layer was extracted with EtOAc (10 mL x 2). The combined organic phase was washed with H_2O (15 mL), brine (15 mL), dried over sodium sulfate, concentrated, and purified by flash chromatography with petroleum ether/ethyl acetate (40/1 → 30/1, v/v) to afford the desired product **7** as white solid (119mg, 85% yield, 97% ee). Chiral HPLC conditions: chiralpak IC, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 98/2, 254 nm, 6.6 min (*R*), 7.4 min (*S*); $[\alpha]^{25}_D$ = -77.9 ° (c = 0.82, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 - 7.37 (m, 5H), 4.27 (q, *J* = 11.04 Hz, 1H), 2.12 - 1.75 (m, 5.39H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 167.0, 137.1, 129.7, 129.4, 123.8, 84.2, 77.0, 28.1, 23.5, 8.5; IR (KBr, cm^{-1}): 3061, 2976, 1734, 1448, 1259, 1101, 799, 698; HRMS (FI): *m/z* calcd. for [M, $C_{13}H_{14}O_4$]$^+$: 234.0887; found: 234.0889.



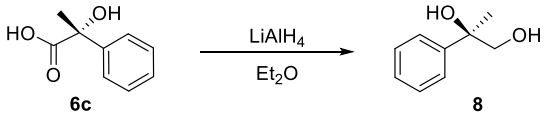
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.687	190494	53.454	1816767	49.959
2	7.556	165875	46.546	1819718	50.041
Total		356369	100.000	3636486	100.000



Detector 254 nm

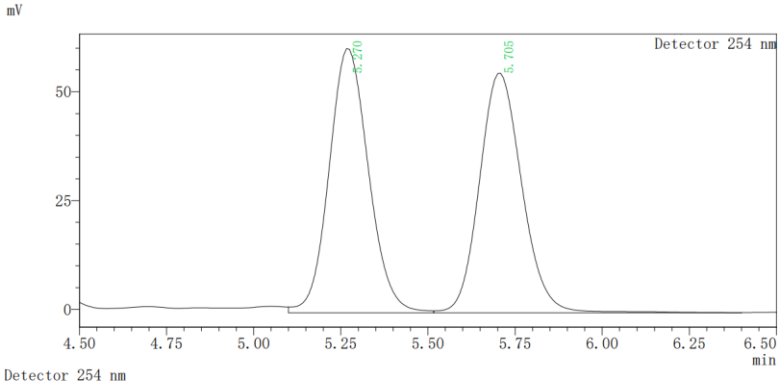
No.	Ret.Time(min)	Height	Height%	Area	Area%
1	6.617	141782	98.760	1624992	98.572
2	7.441	1780	1.240	23538	1.428
Total		143562	100.000	1648530	100.000



6c **8**

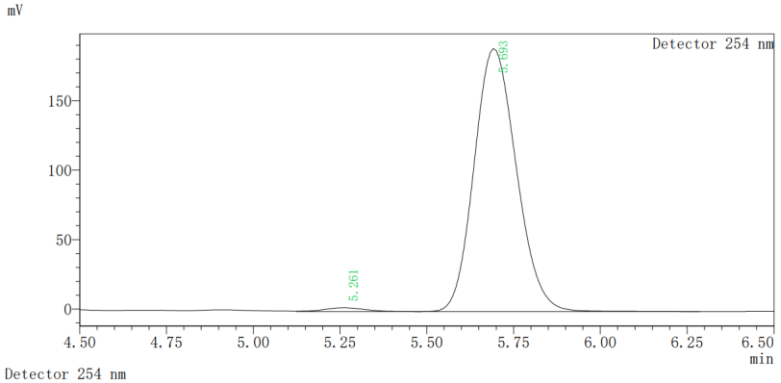
97% ee

Compound **8** was synthesized according reported literature[7]. To a suspension of $LiAlH_4$ (189.7 mg, 5 mmol) in extra dry diethyl ether (5 mL) at 0°C was added slowly a solution of α-hydroxy acid **6c** (332.3 mg, 2 mmol) in diethyl ether (10 mL) under N_2 atmosphere. The reaction was stirred at room temperature for 2 h, then quenched by consecutive addition of 0.25 mL H_2O, 0.25 mL NaOH aq (15 wt%) and 0.6 mL H_2O. The solid in mixture was filtered and washed with ether (50 mL). The collective organic phase was dried over anhydrous sodium sulfate, filtered, and concentrated to provide crude product, which was purified by flash chromatography with petroleum ether/ethyl acetate (4/1 → 2/1, v/v) to afford diol **8** as colorless oil (276 mg, 91% yield 97% ee). Chiral HPLC conditions: chiralcel AD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 80/20, 254 nm, 5.3 min (*S*), 5.7 min (*R*); $[\alpha]^{25}_D$ = -7.7 ° (c = 1.15, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 - 7.27 (m, 2H), 7.23 - 7.20 (m, 2H), 7.17 - 7.10 (m, 1H), 3.54 (d, *J* = 11.2 Hz, 1H), 3.40 (d, *J* = 11.3 Hz, 1H), 3.31 (br.s, 0.88H), 1.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 128.2, 126.9, 125.0, 74.8, 70.6, 25.8; HRMS (FI): *m/z* calcd. for [M, $C_9H_{12}O_2$]$^+$: 152.0832; found: 152.0829.



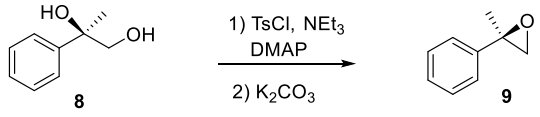
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	5.270	60666	52.428	477521	50.565
2	5.705	55047	47.572	466853	49.435
Total		115713	100.000	944375	100.000



Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	5.261	2780	1.447	23605	1.452
2	5.693	189375	98.553	1601949	98.548
Total		192155	100.000	1625554	100.000

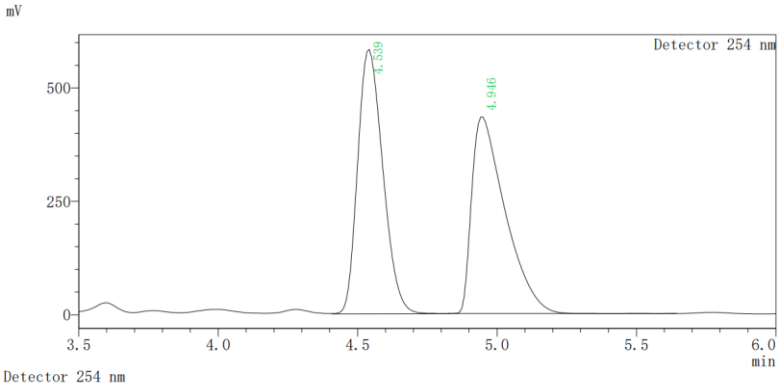


8 97% ee

9 97% ee

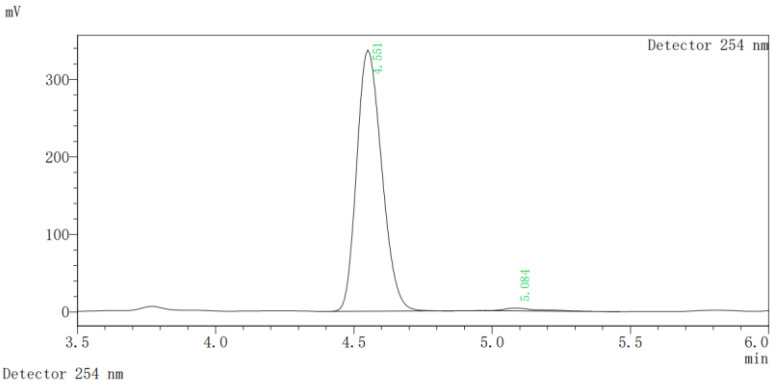
Compound **9** was synthesized according reported literature[7a, 8]. To a solution of **8** (232 mg, 1.52 mmol) in extra dry CH_2Cl_2 (16 mL) was added Et_3N (200 mg, 1.97 mmol) and the mixture was cooled to 0°C. Subsequently, tosyl chloride (348.8 mg, 1.83 mmol) and DMAP (18.5 mg, 0.15 mmol) were added to the reaction mixture, the reaction was stirred at the same temperature overnight. After starting material was completely consumed, water (15 mL) was added to the reaction. The mixture was extracted with CH_2Cl_2 (20 mL x 2), and combined organic phase was dried over anhydrous sodium sulfate, filtered, concentrated. Crude product was purified by flash column chromatography with petroleum ether/ethyl acetate (10/1 → 4/1, v/v) to provide the tosylate in 85% yield (395 mg).

Tosylate (97 mg, 0.31 mmol) was dissolved in methanol (4 mL), and potassium carbonate (87.5 mg, 0.62 mmol) was added in one portion. The reaction was stirred at room temperature for about 30 min., TLC showed starting material disappeared. The reaction mixture was diluted with water (15 mL) and extracted with diethyl ether (15 mL x 3). The combined organic layer was washed with saturated sodium chloride solution (20 mL), dried over anhydrous sodium sulfate, filtered and concentrated to give **9** as colorless oil (36.8 mg, 87%, 97% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 80/20, 254 nm, 4.6 min (*R*), 5.1 min (*S*); $[\alpha]^{25}D$ = -21.4 ° (c = 0.1, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.40 - 7.27 (m, 5H), 2.98 (d, *J* = 5.4 Hz, 1H), 2.81 (d, *J* = 5.4 Hz, 1H), 1.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 128.3, 127.4, 125.3, 57.0, 56.7, 21.8; HRMS (FI): m/z calcd. for [M, $C_9H_{10}O]^+$: 134.0726; found: 134.0725.



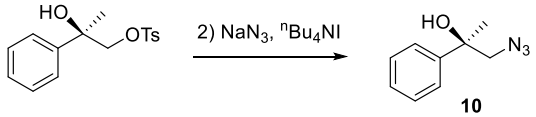
Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
1	4.539	582551	57.352	3661026	50.365
2	4.946	433188	42.648	3607989	49.635
Total		1015739	100.000	7269015	100.000



Detector 254 nm

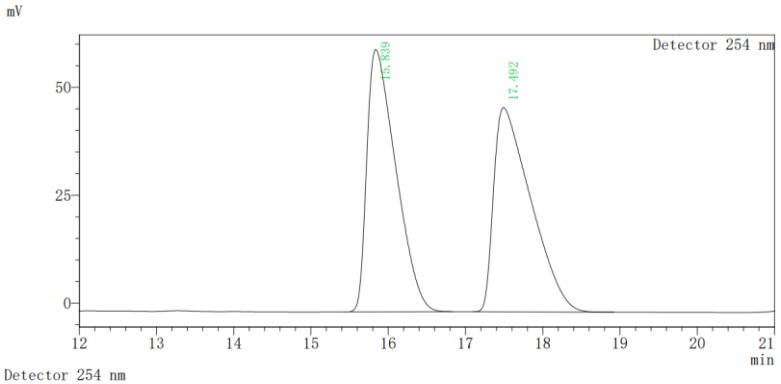
No.	Ret.Time(min)	Height	Height%	Area	Area%
1	4.551	336964	98.926	2116447	98.507
2	5.084	3659	1.074	32080	1.493
Total		340623	100.000	2148527	100.000



10

97% ee

Compound **10** was synthesized according the reported literature[7a]. To a solution of tosylate (155mg, 0.5 mmol) in extra dry DMF (4 mL) was added sodium azide (82 mg, 1.25 mmol) and $^{n}Bu_4NI$ (9.2 mg, 0.025 mmol) at room temperature under N_2. Subsequently, the reaction mixture was heated to 80°C and stirred at that temperature for about 5 h. Then, the solution was cooled to room temperature, water (15 mL) was added and the mixture was extracted with diethyl ether (20 mL x 3). The combined organic phase was washed with water (15 mL), dried over sodium sulfate, filtered off, and concentrated. Purification by flash column chromatography with petroleum ether/ethyl acetate (10/1, v/v) provided the azidoalcohol **10** as colorless oil (75.2 mg, 85%, 97% ee). Chiral HPLC conditions: chiralcel OD-H, 25 °C, flow rate: 1.0 mL/min, hexane/isopropanol: 97/3, 254 nm, 15.6 min (*R*), 17.9 min (*S*); $[\alpha]^{25}_{D}$ = -33.4 ° (c = 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 - 7.43 (m, 2H), 7.41 - 7.37 (m, 2H), 7.36 -7.27 (m, 1H), 3.60 (d, *J* = 12.3 Hz, 1H), 3.45 (d, *J* = 12.3 Hz, 1H), 2.57 (br.s, 1H), 1.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 128.4, 127.4, 124.8, 74.5, 62.0, 27.0; HRMS (FI): *m/z* calcd. for [M, $C_9H_{11}ON_3$]$^+$: 177.0897; found: 177.0901.



Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
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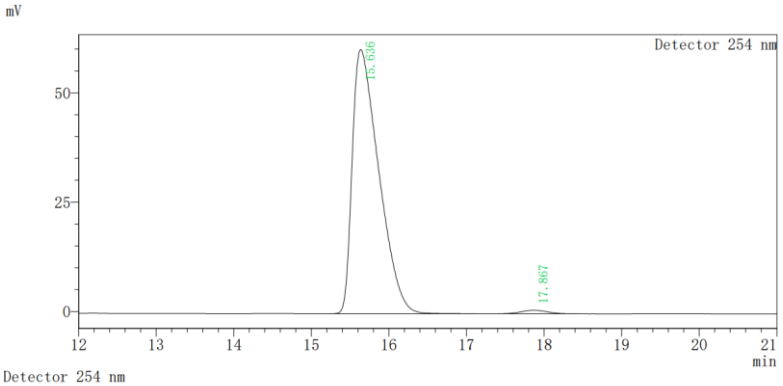
2	17.492	47336	43.790	1585057	50.017
Total		108097	100.000	3169051	100.000



Detector 254 nm

No.	Ret.Time(min)	Height	Height%	Area	Area%
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2	17.867	810	1.324	18751	1.289
Total		61203	100.000	1455034	100.000

10. References

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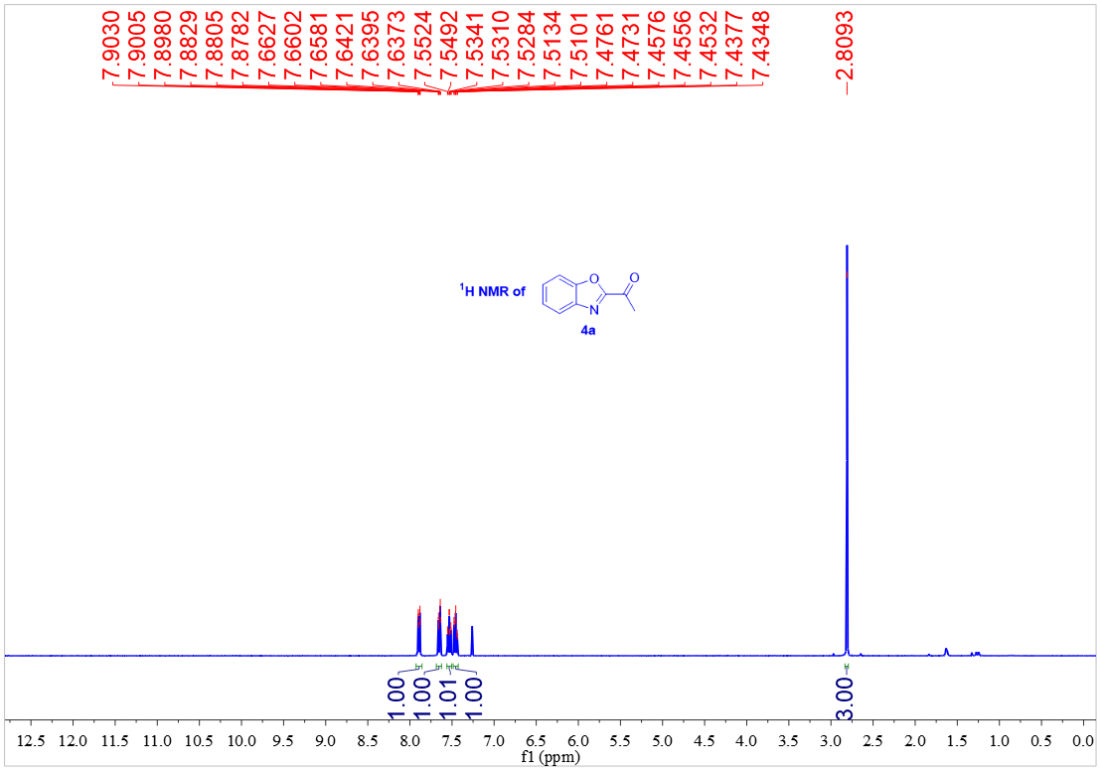
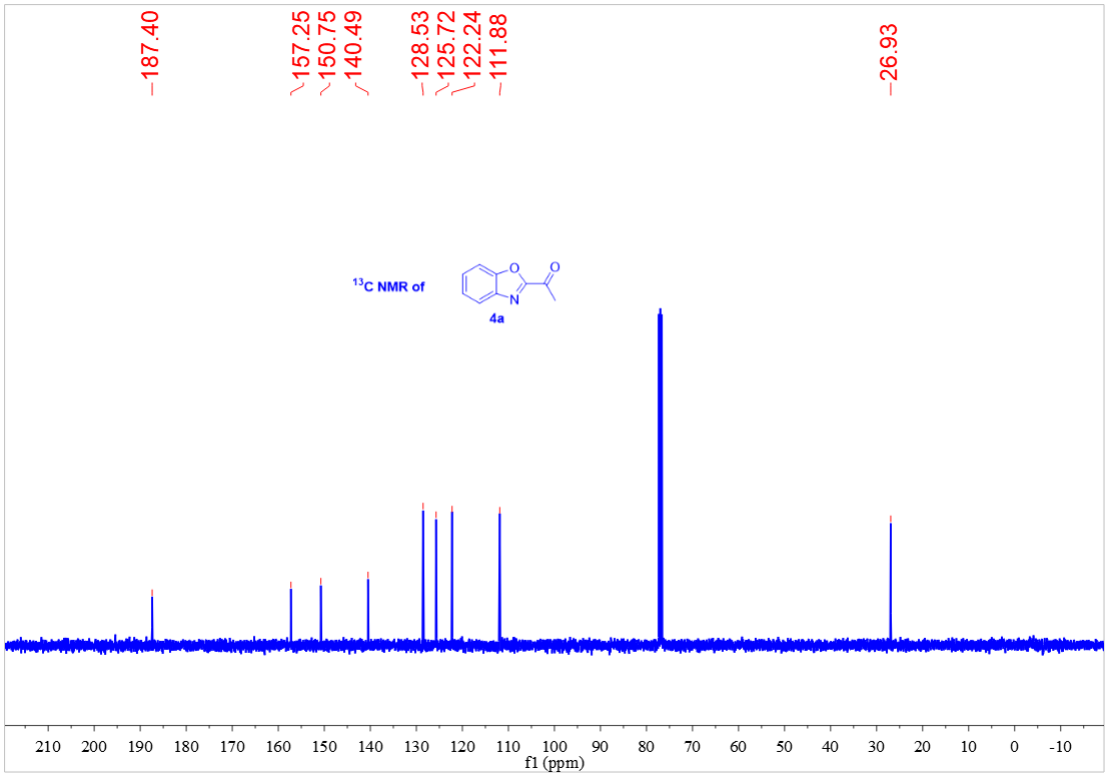
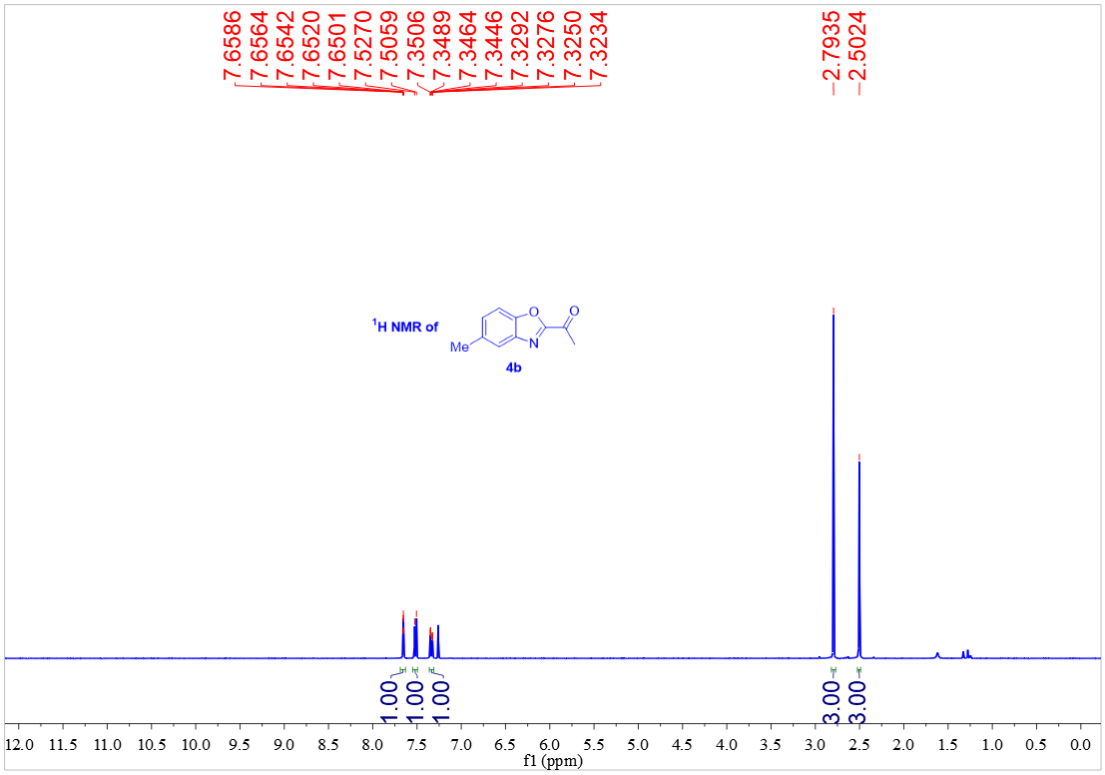
11. NMR Spectra



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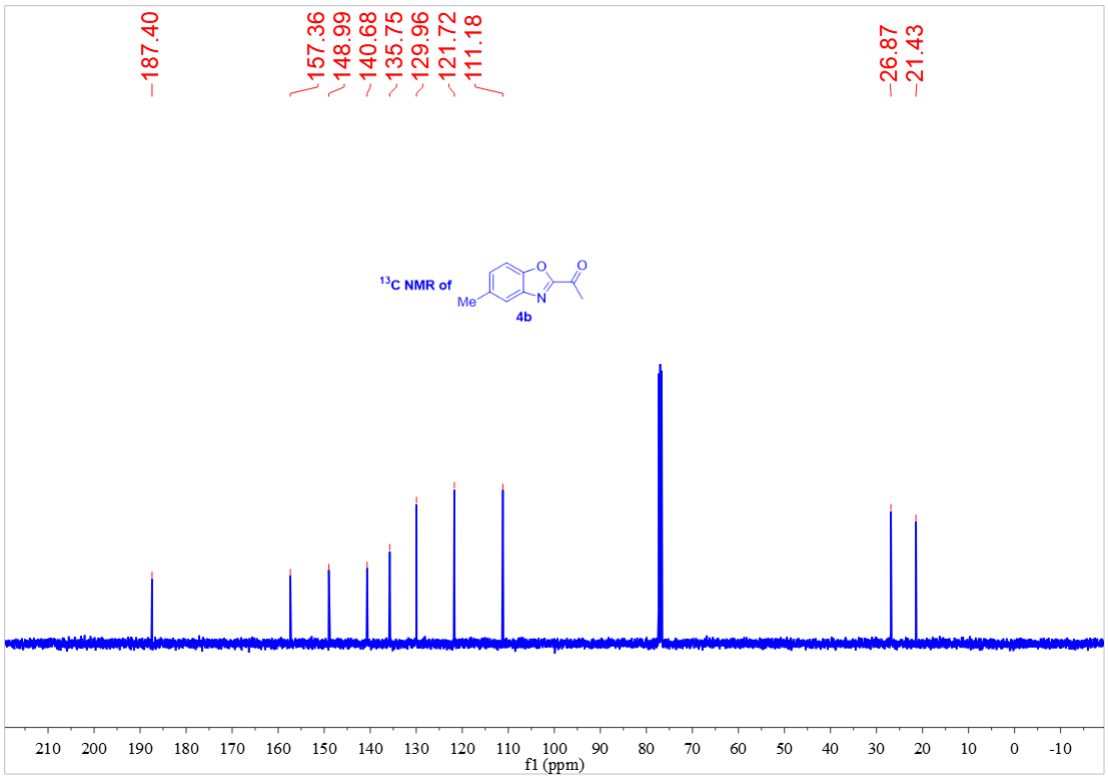
7.3446
7.3292
7.3276
7.3250
7.3234
2.7935
2.5024
1H NMR of
Me
4b
1.00
1.00
1.00
3.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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129.96
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21.43
13C NMR of
Me
4b
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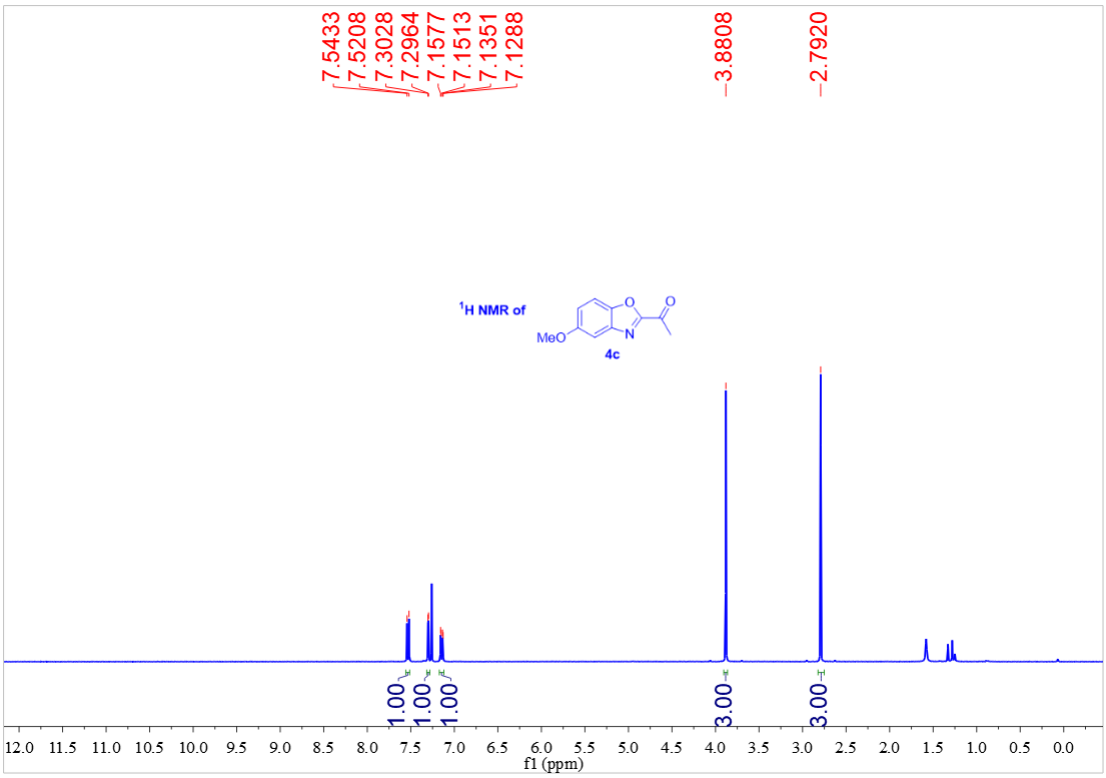
f1 (ppm)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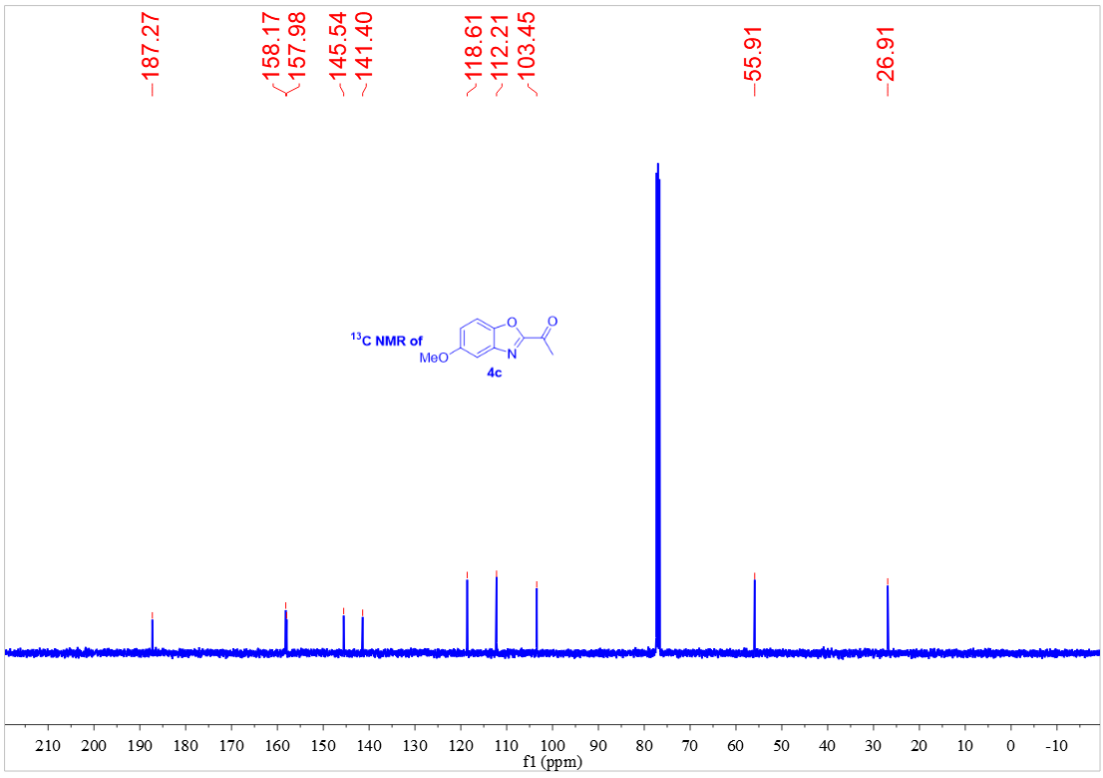
7.2964
7.1577
7.1513
7.1351
7.1288
3.8808
2.7920
1H NMR of
MeO
4c
1.00
1.00
1.00
3.00
3.00
f1 (ppm)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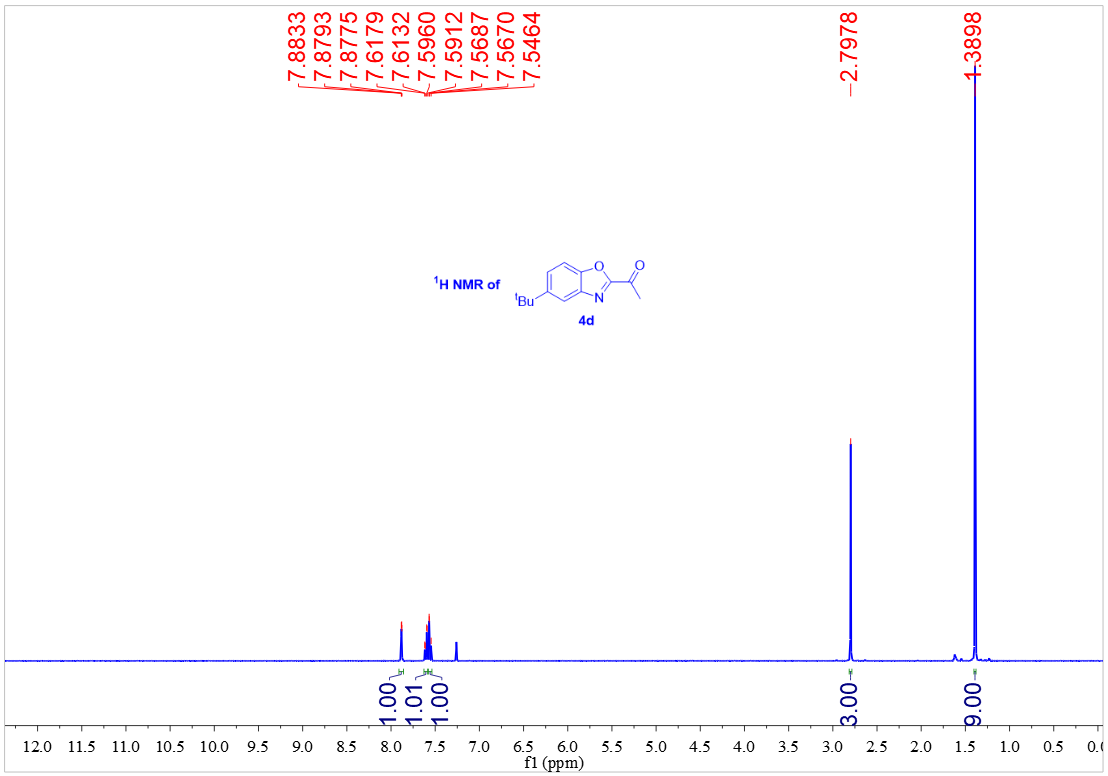
26.91
13C NMR of
MeO
4c
f1 (ppm)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^{1}H NMR of
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1.00
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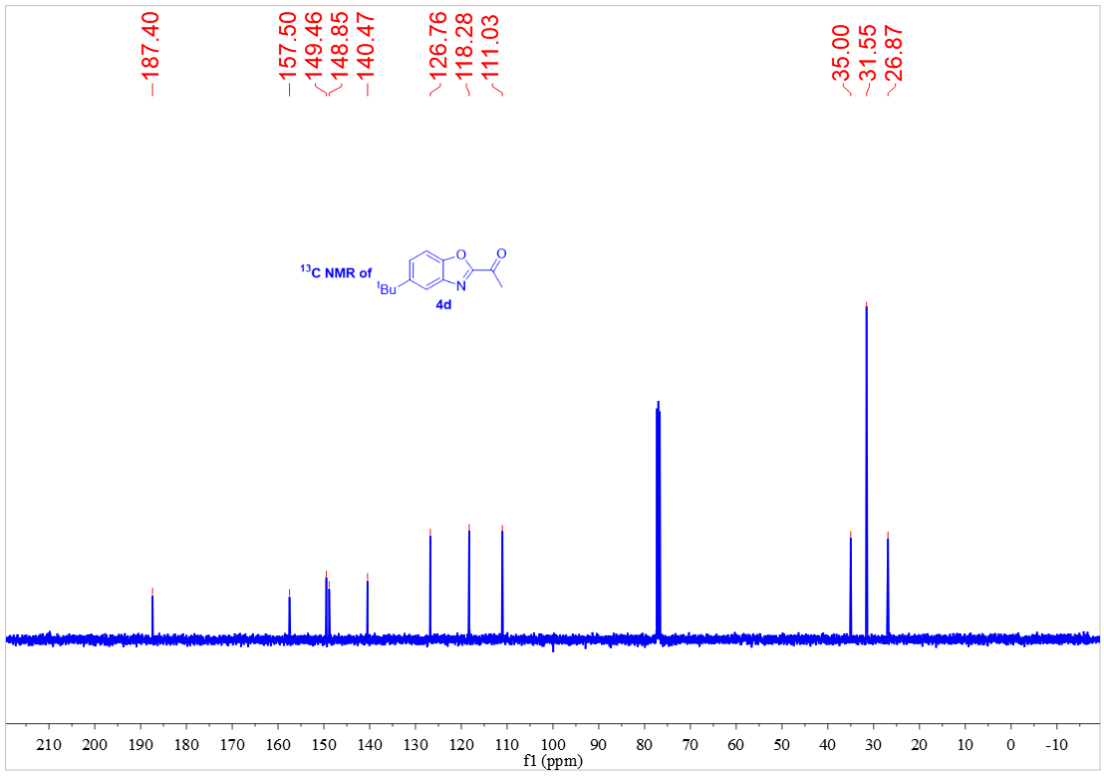
9.00
f1 (ppm)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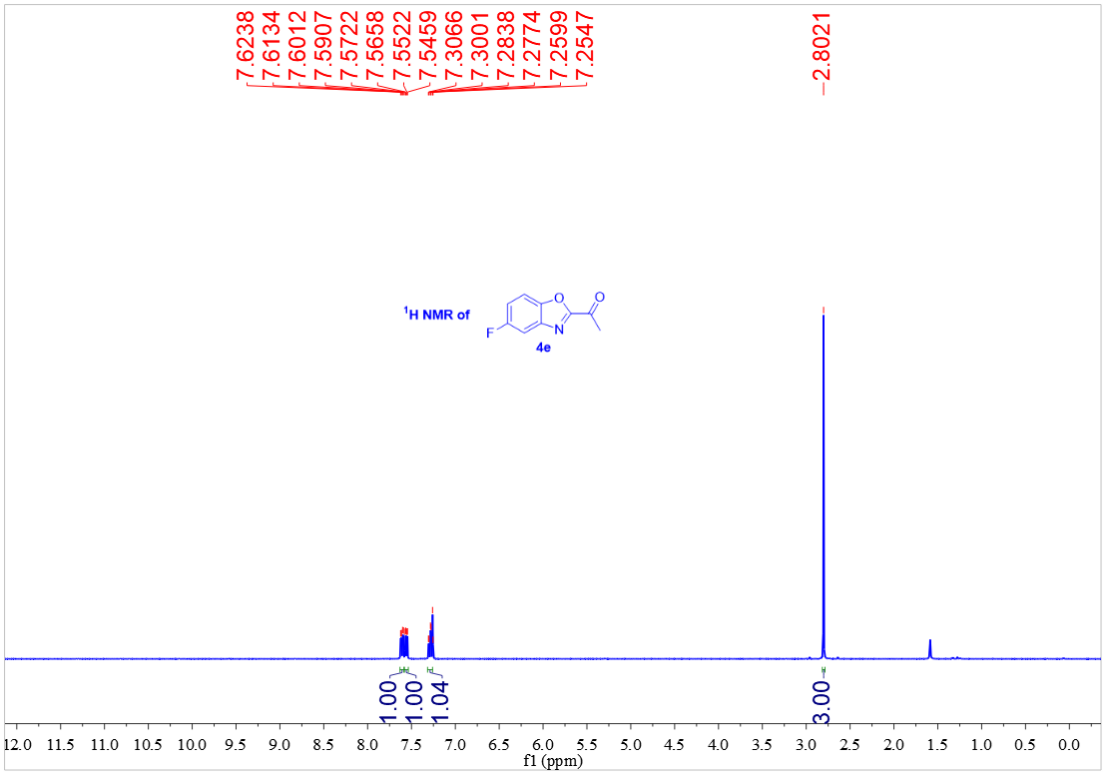
f1 (ppm)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4e
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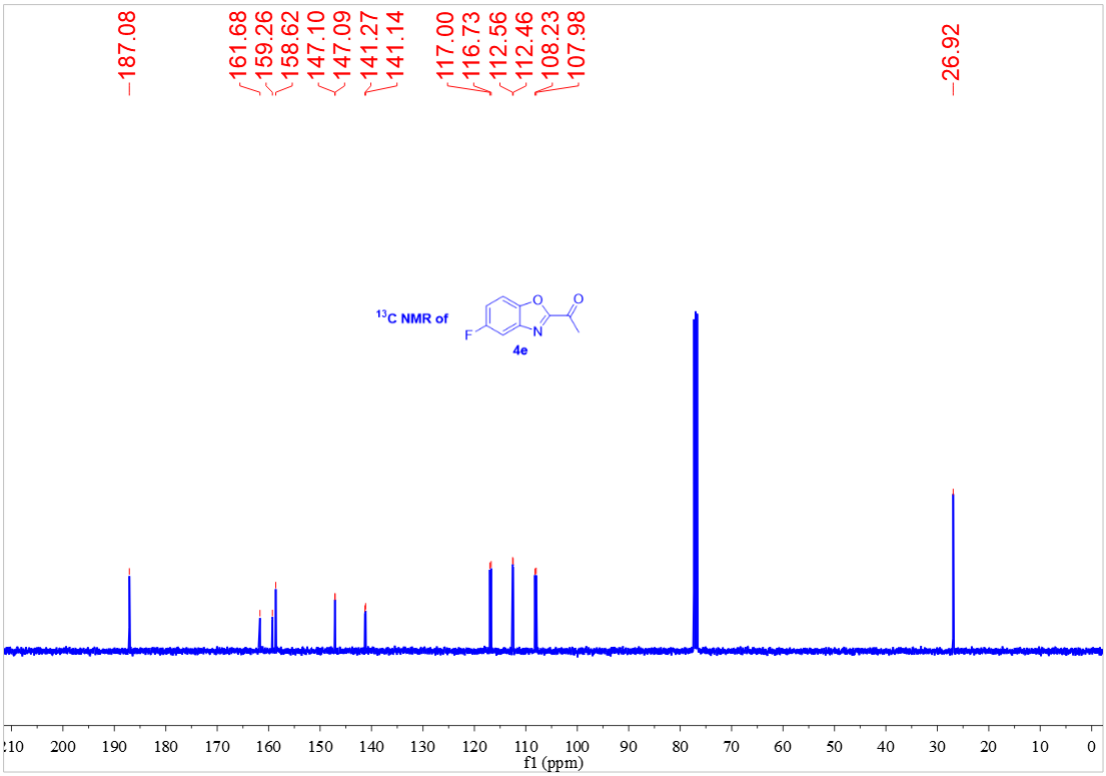
1.00
1.04
3.00
f1 (ppm)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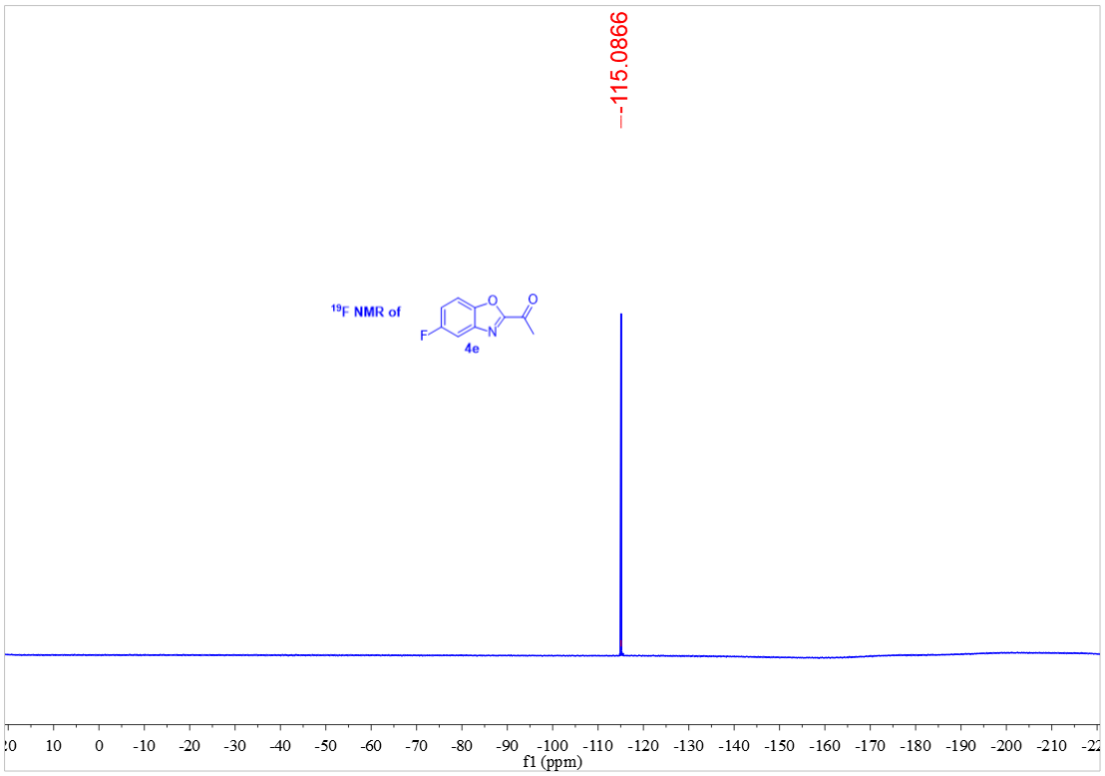
26.92
^{13}C NMR of
4e
f1 (ppm)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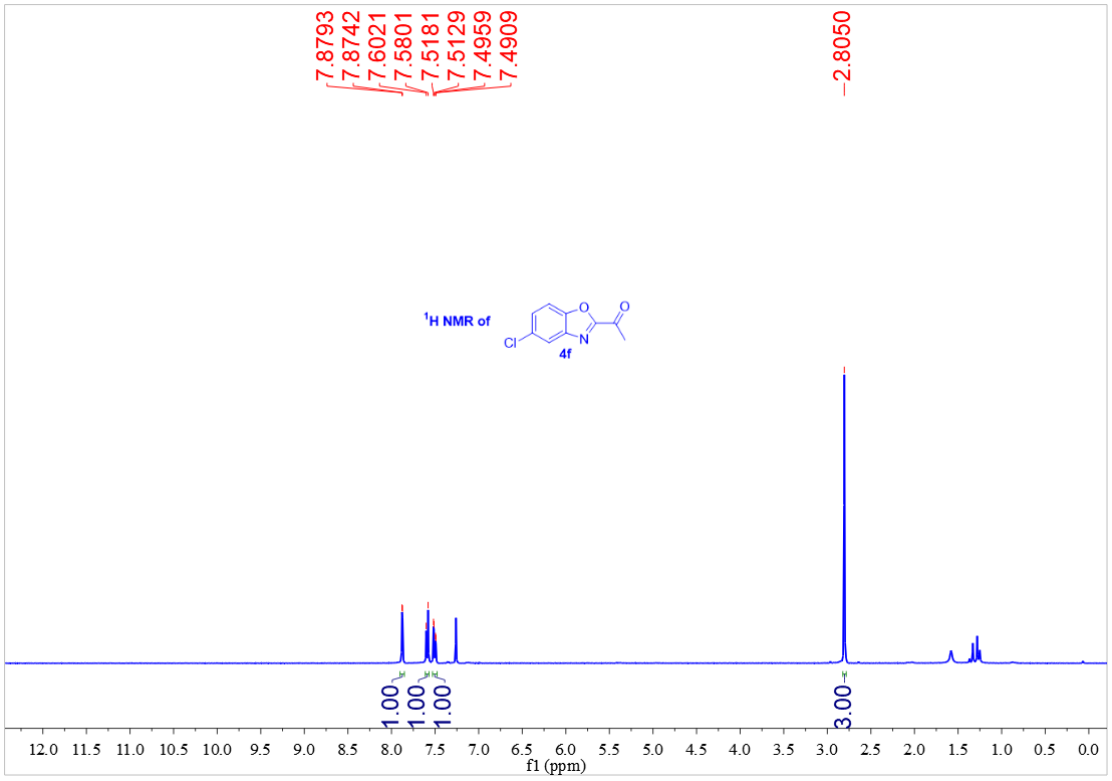
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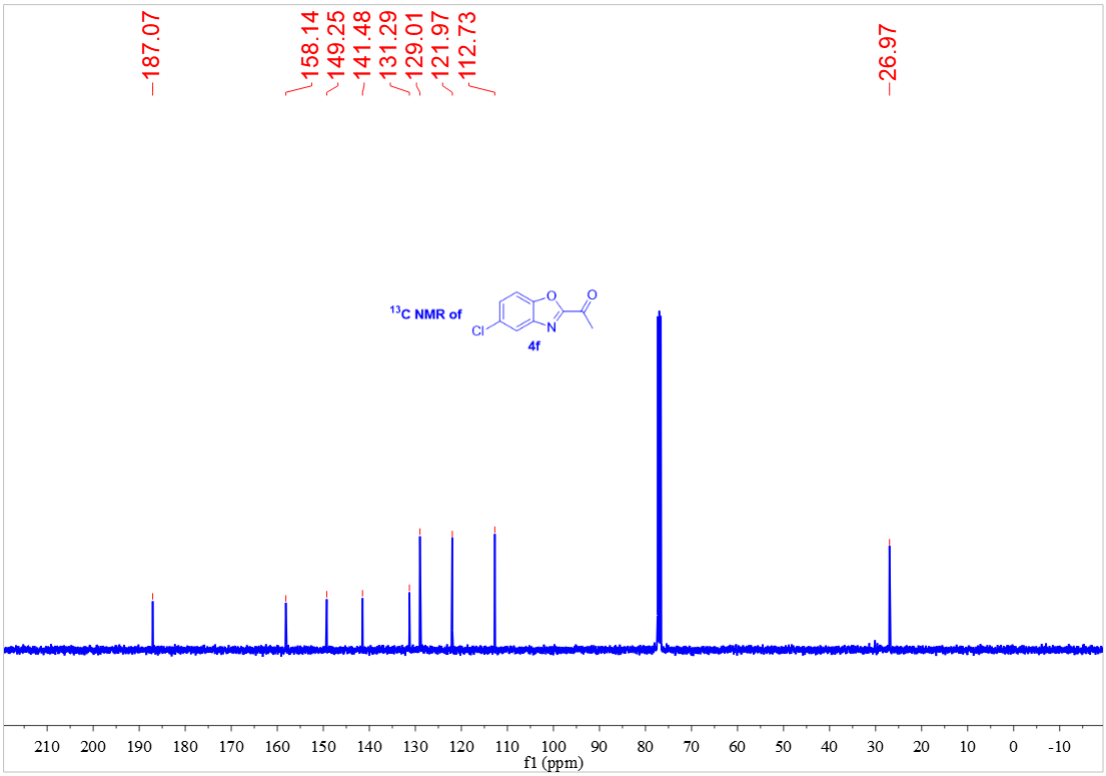
1.00
1.00
3.00
f1 (ppm)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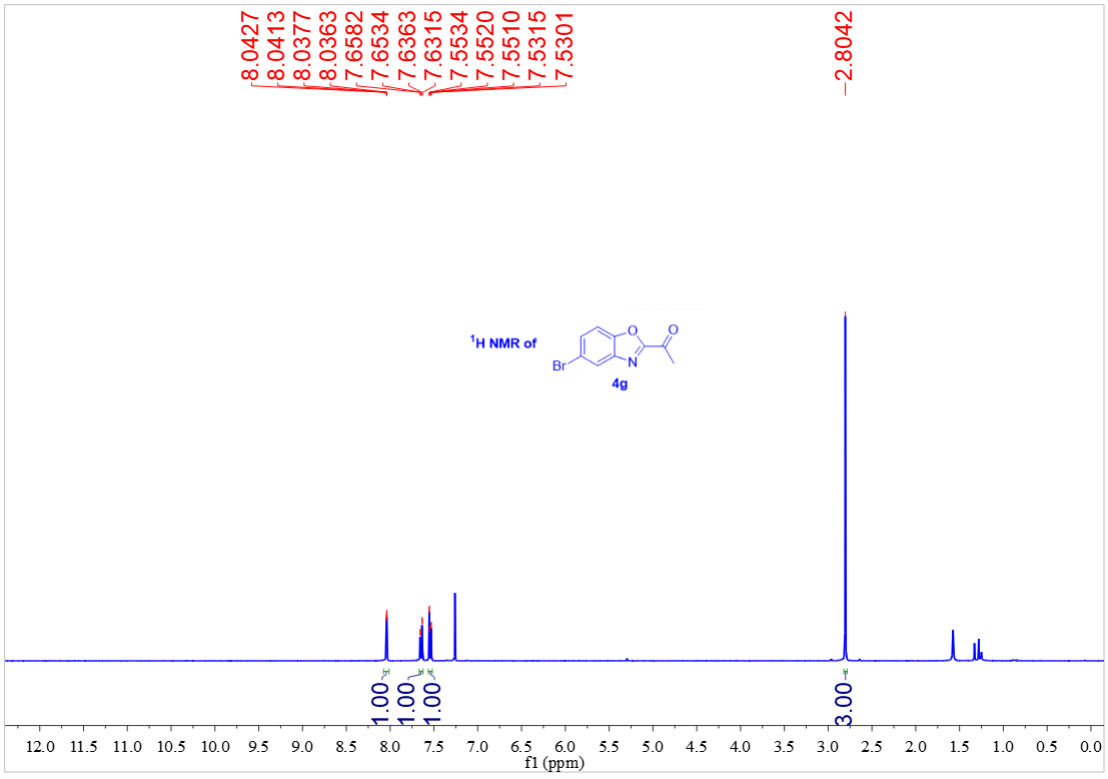
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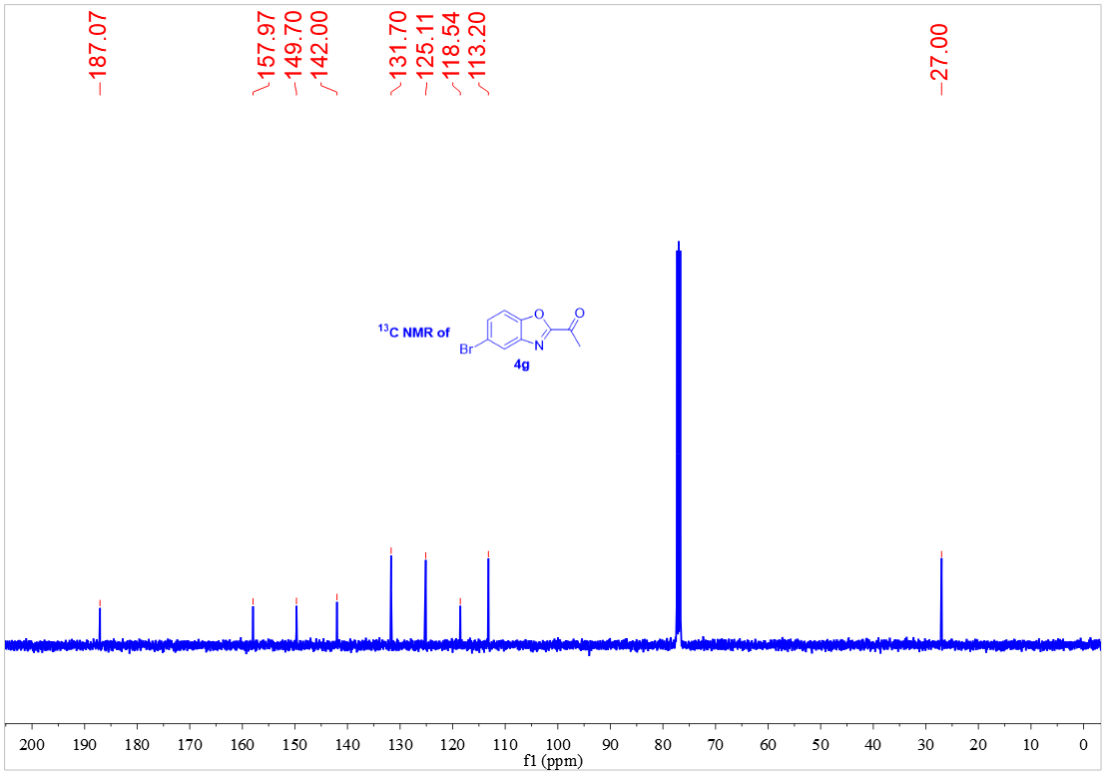
1.00
1.00
3.00
f1 (ppm)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27.00
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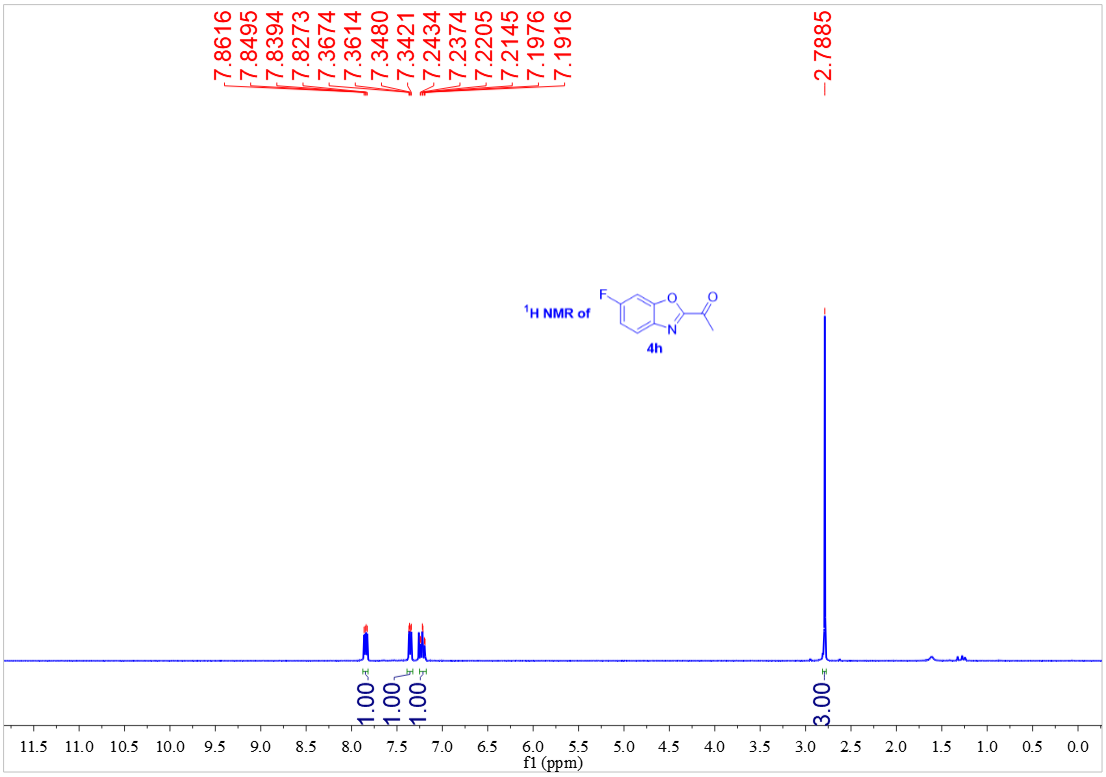
f1 (ppm)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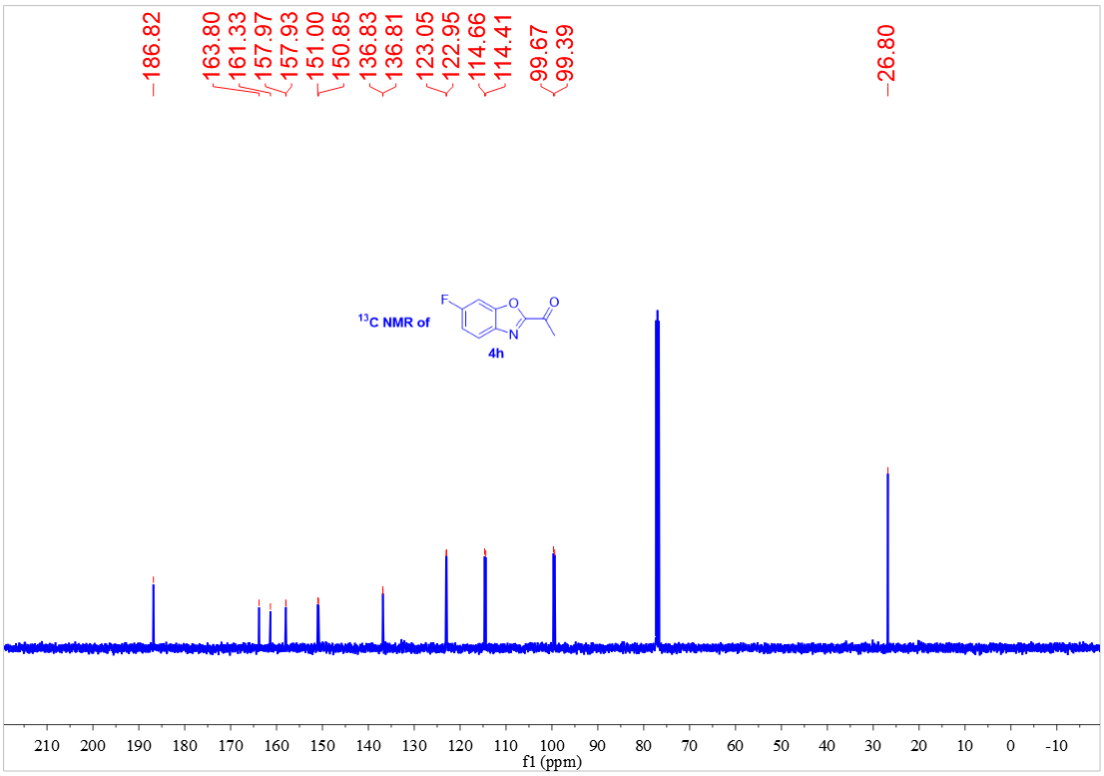
1.00
1.00
3.00
f1 (ppm)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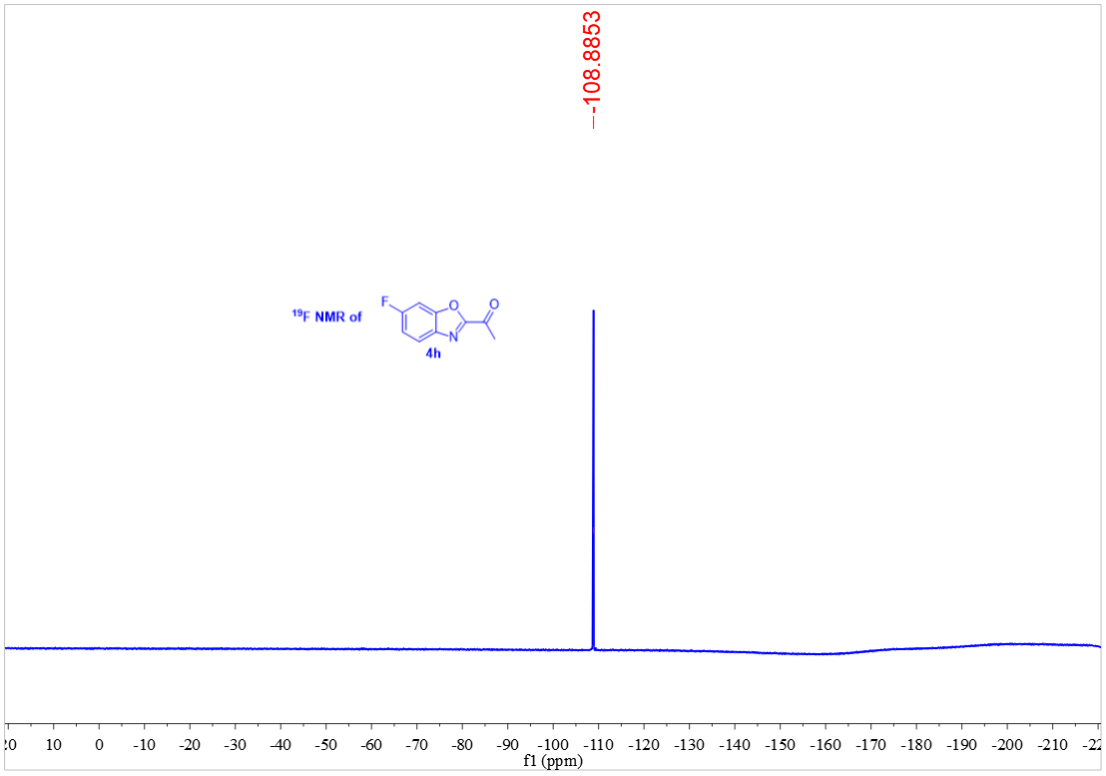
13C NMR of
4h
f1 (ppm)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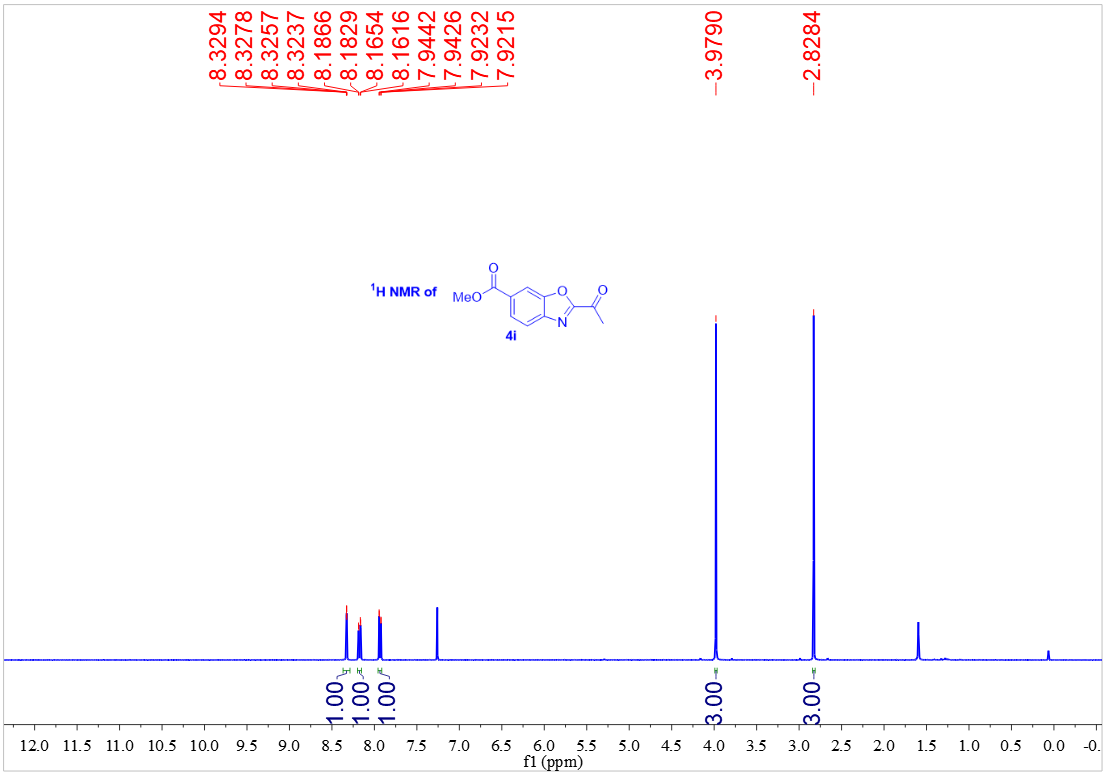
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O
O
N
4i
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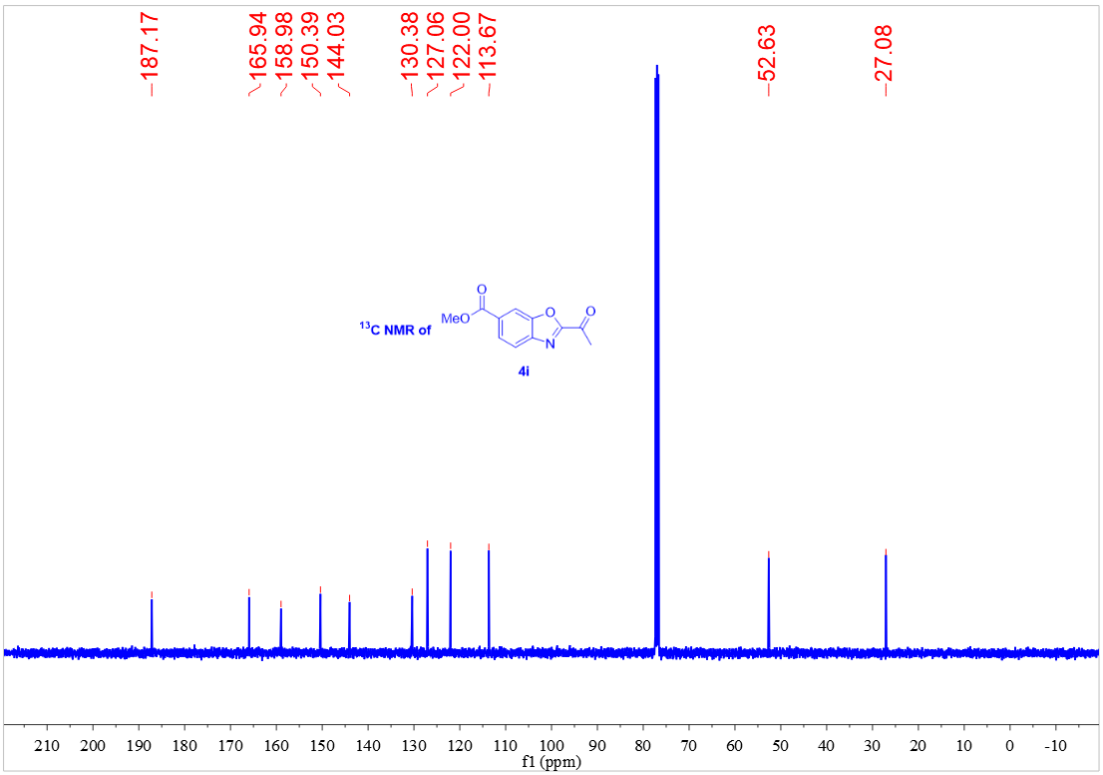
1.00
3.00
3.00
f1 (ppm)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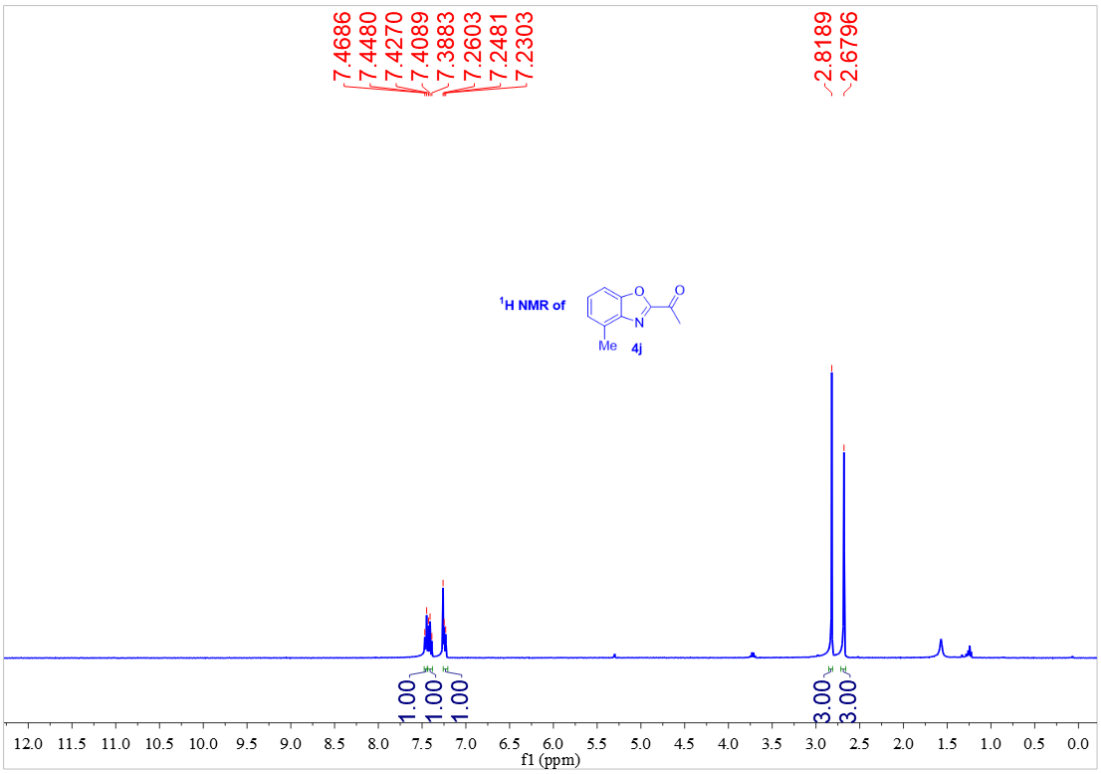
O
O
N
4i
f1 (ppm)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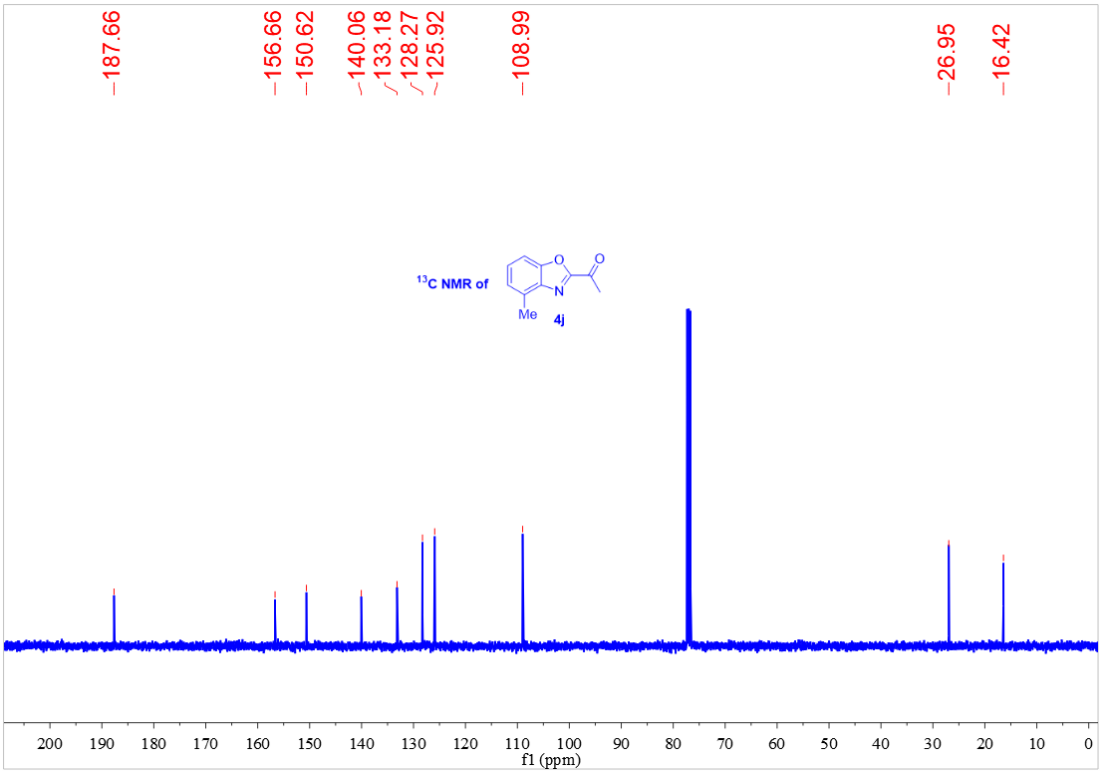
Me
4j
1.00
1.00
1.00
3.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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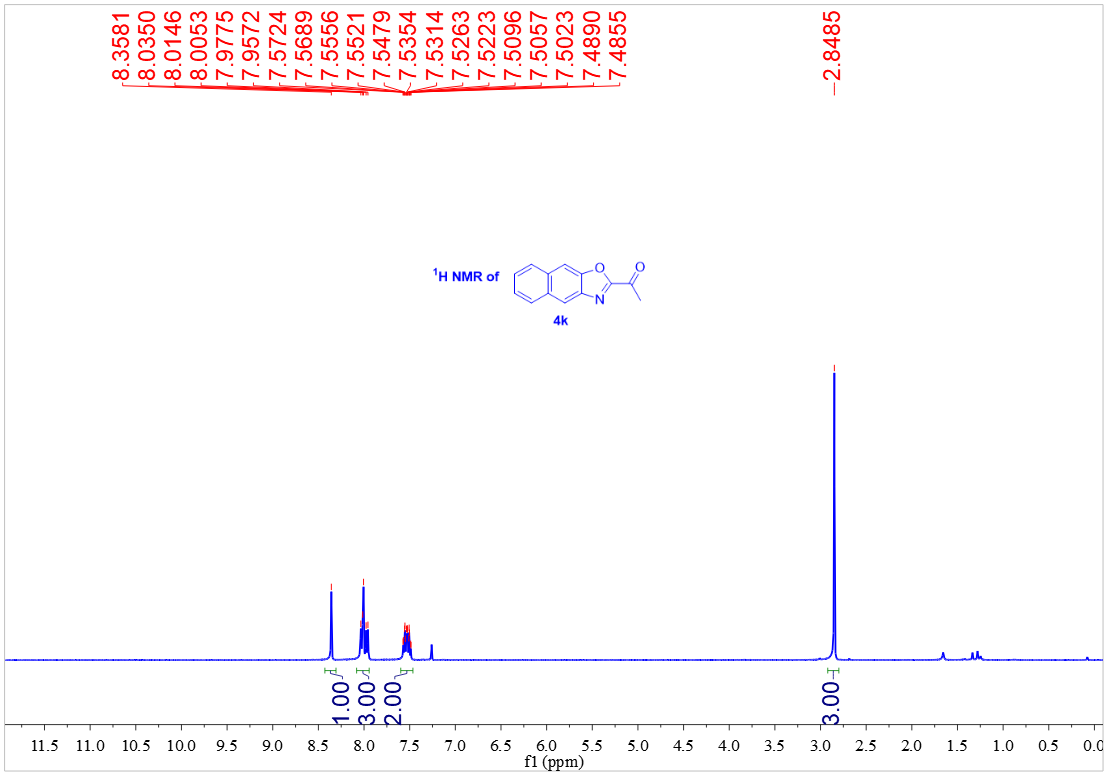
f1 (ppm)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4k
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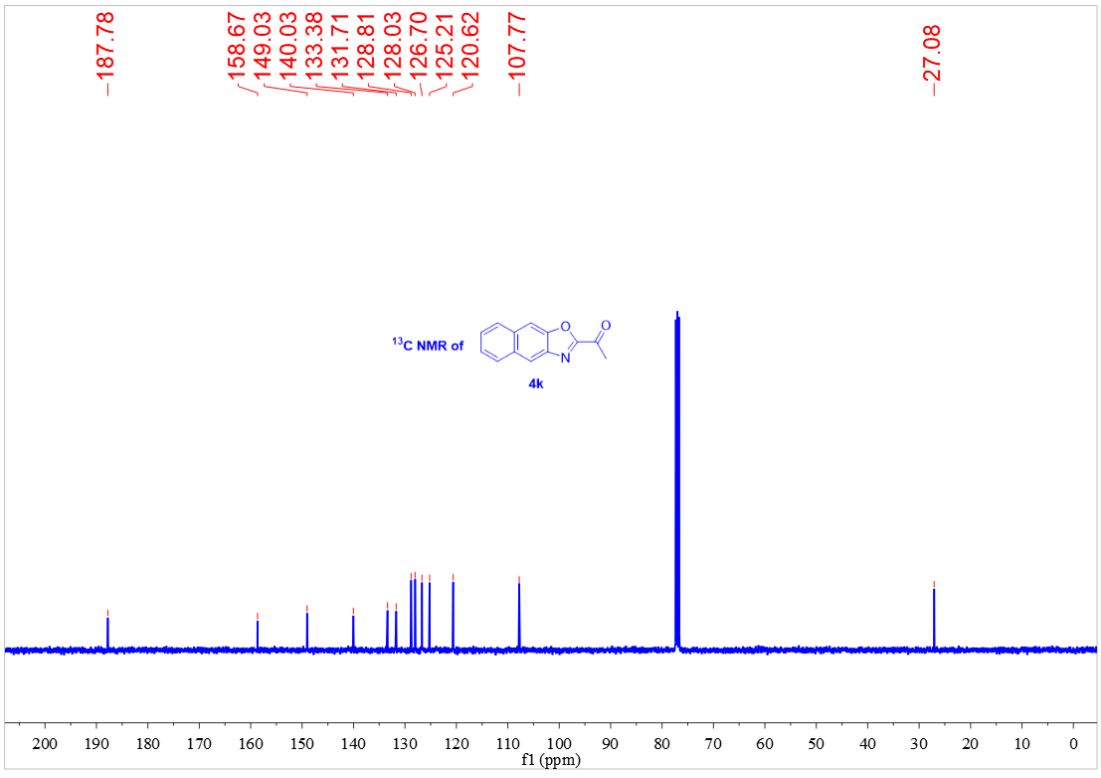
2.00
3.00
f1 (ppm)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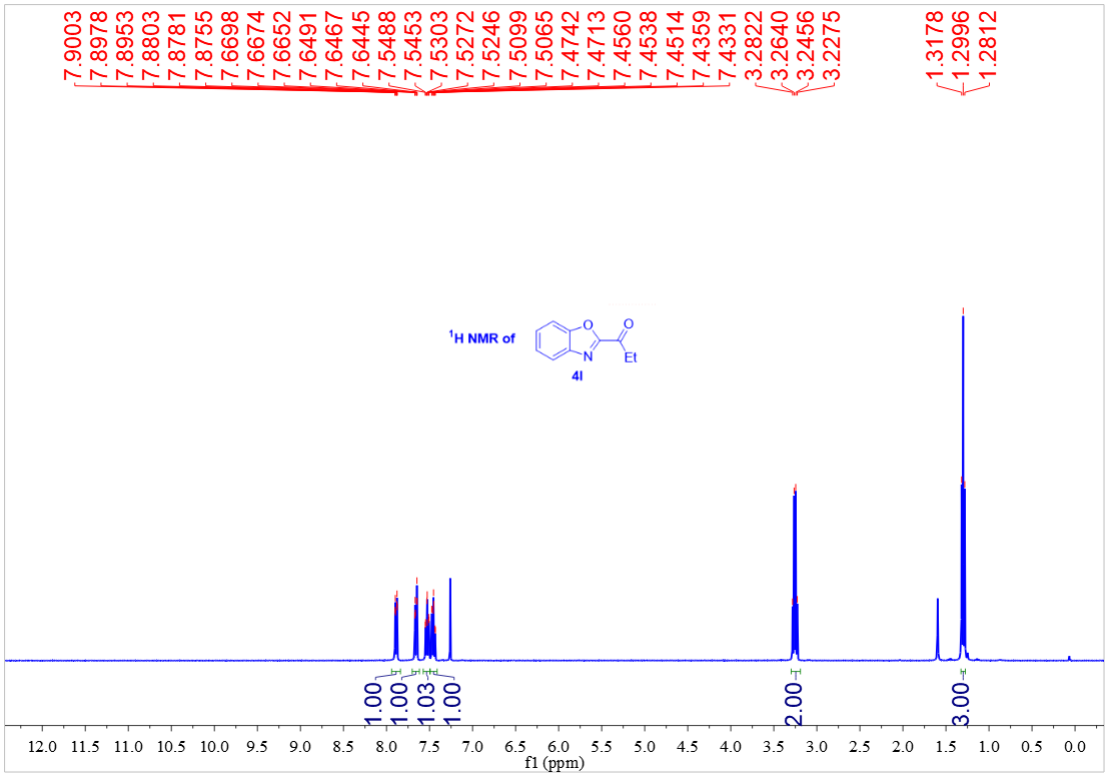
4k
f1 (ppm)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4l
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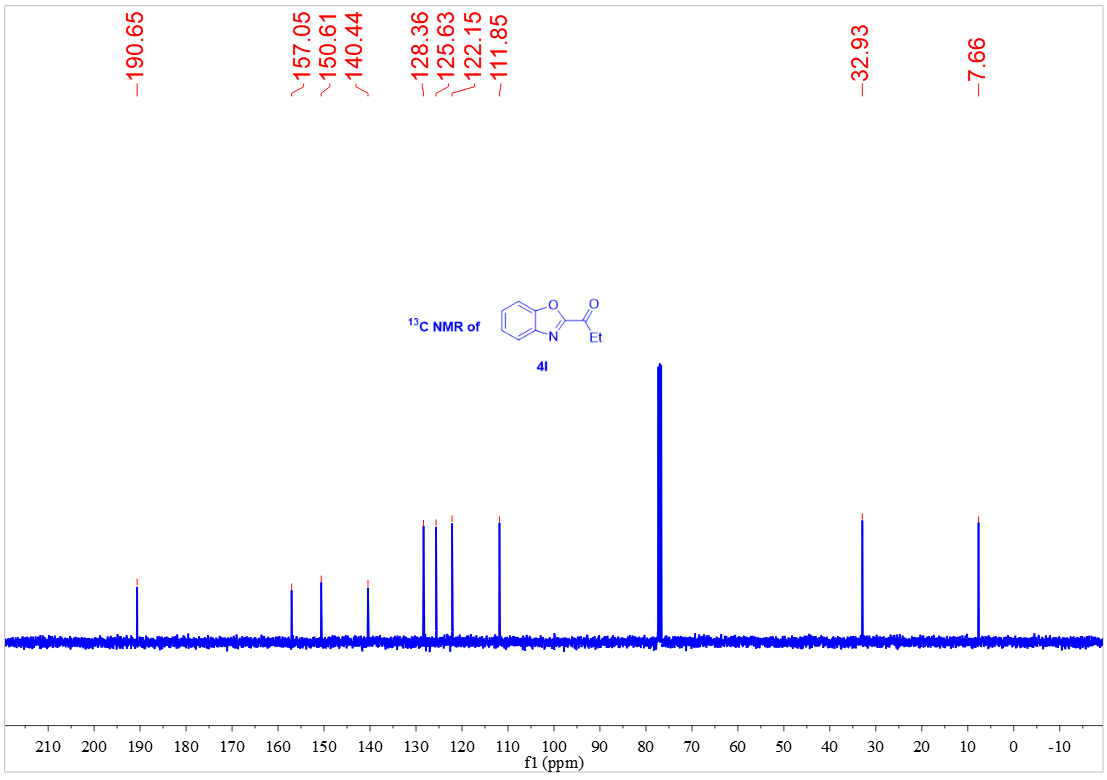
1.03
1.00
2.00
3.00
f1 (ppm)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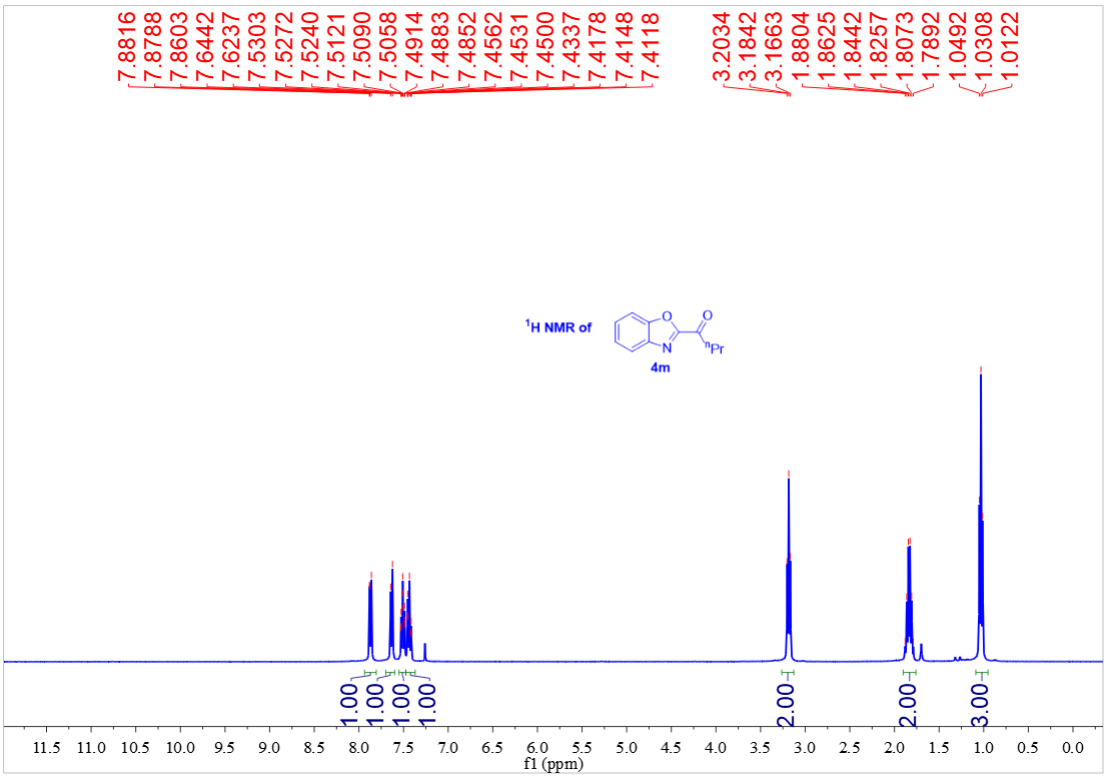
f1 (ppm)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1.7892
1.0492
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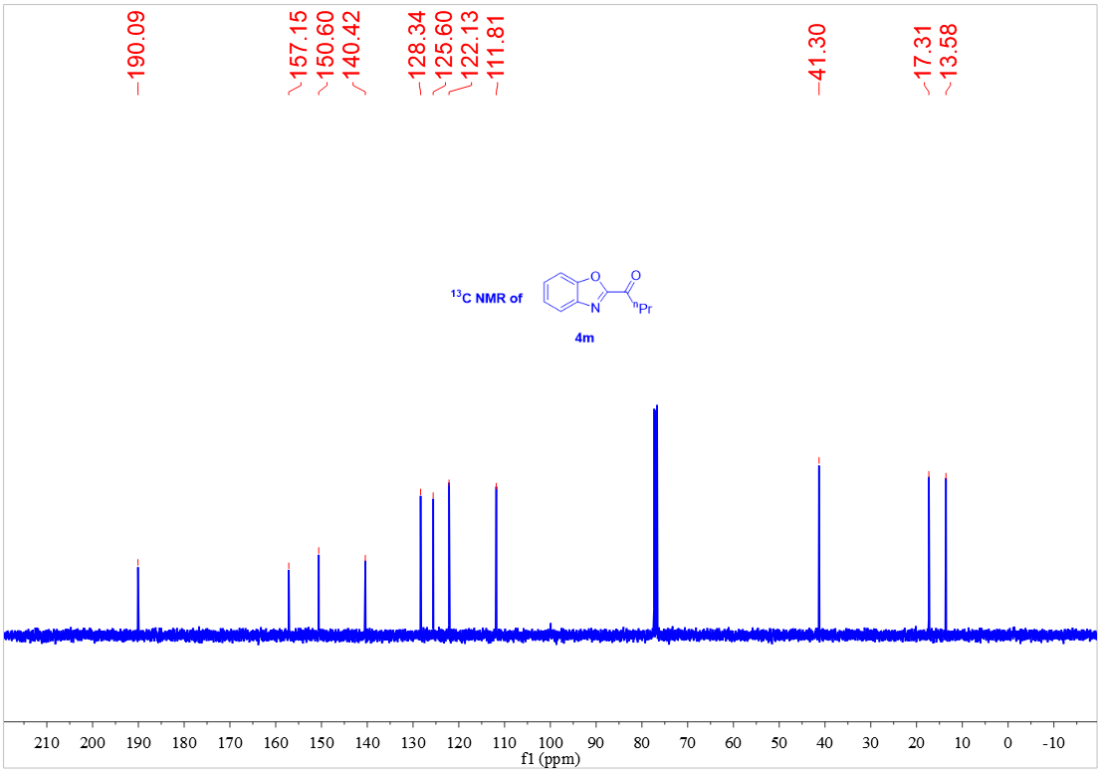
3.00
f1 (ppm)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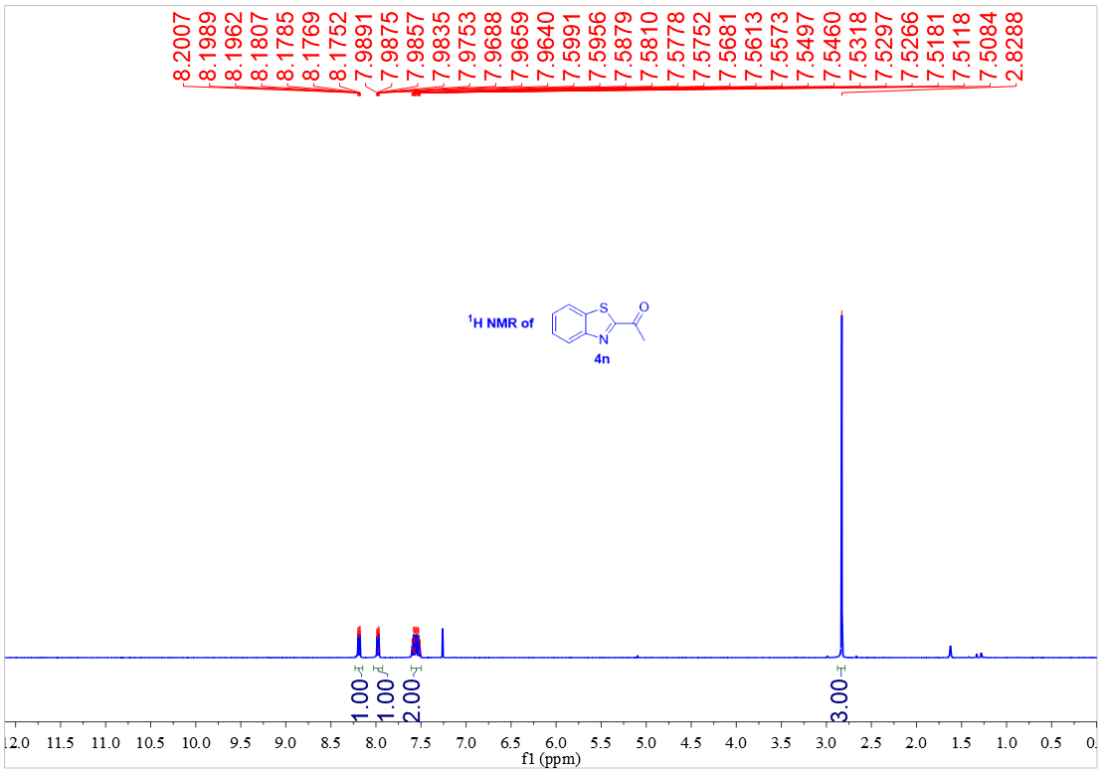
4m
f1 (ppm)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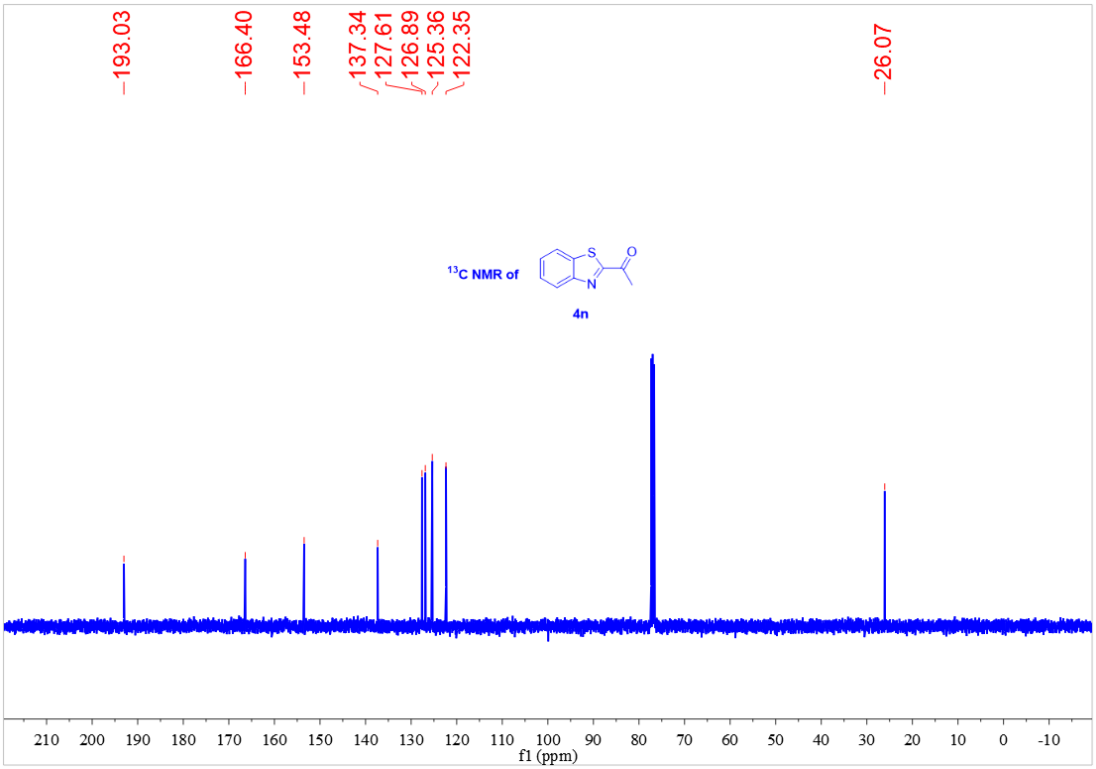
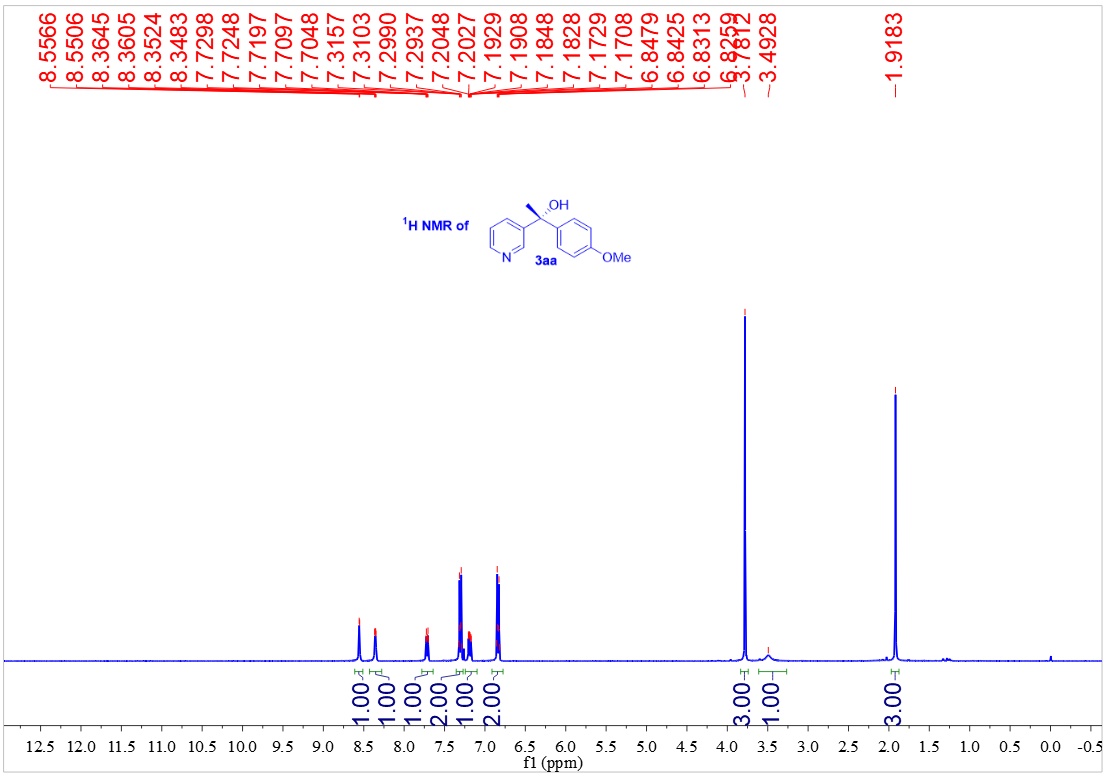
8.1989
8.1962
8.1807
8.1785
8.1769
8.1752
7.9891
7.9875
7.9857
7.9835
7.9753
7.9688
7.9659
7.9640
7.5991
7.5956
7.5879
7.5810
7.5778
7.5752
7.5681
7.5613
7.5573
7.5497
7.5460
7.5318
7.5297
7.5266
7.5181
7.5118
7.5084
2.8288
1H NMR of
4n
1.00
1.00
2.00
3.00
f1 (ppm)


193.03
166.40
153.48
137.34
127.61
126.89
125.36
122.35
26.07
13C NMR of
4n
f1 (ppm)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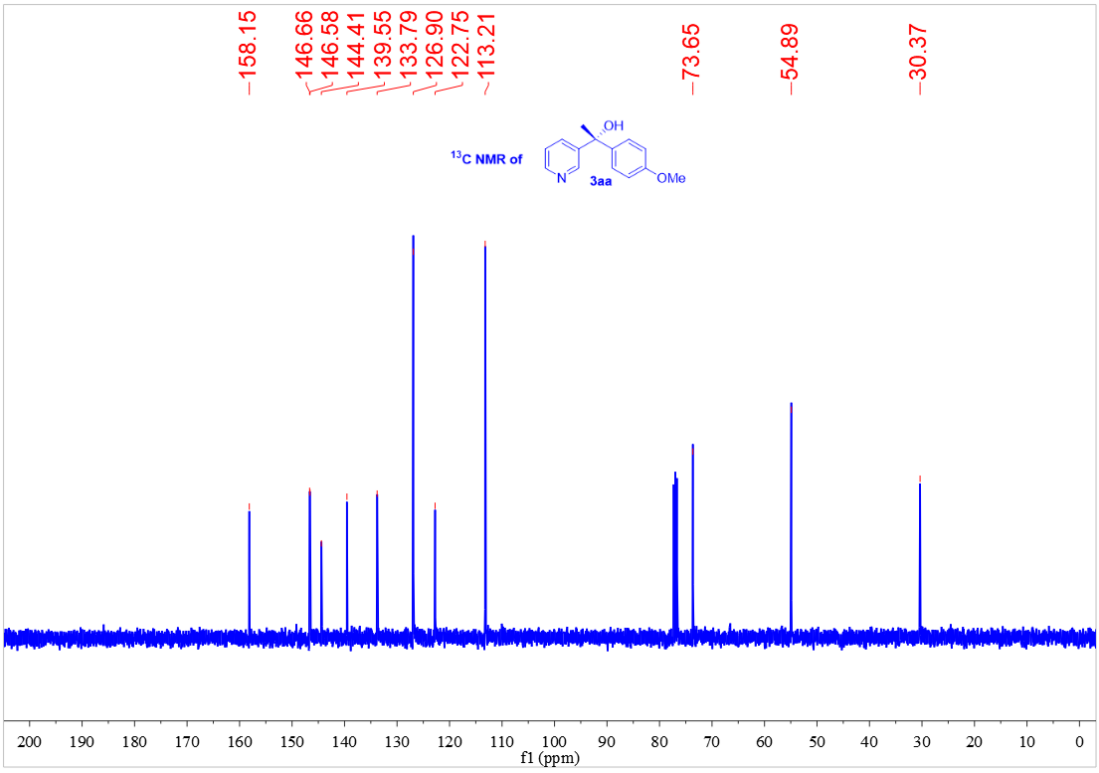
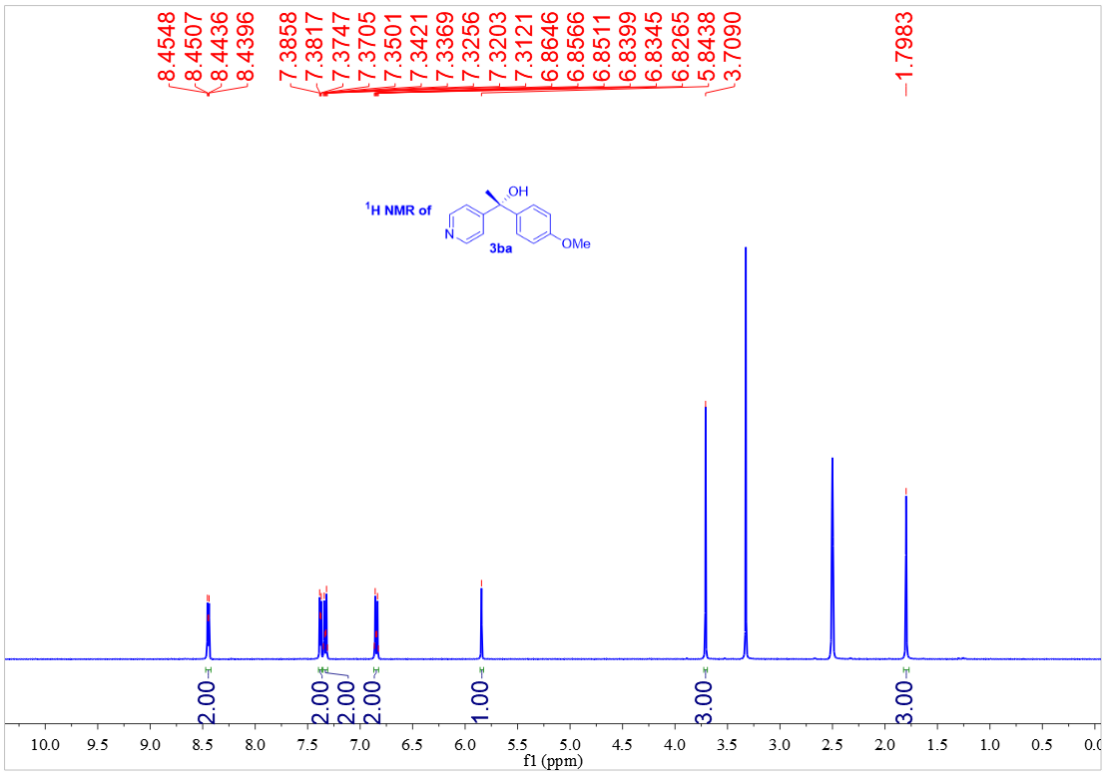
8.5506
8.3645
8.3605
8.3524
8.3483
7.7298
7.7248
7.7197
7.7097
7.7048
7.3157
7.3103
7.2990
7.2937
7.2048
7.2027
7.1929
7.1908
7.1848
7.1828
7.1729
7.1708
6.8479
6.8425
6.8313
3.7812
3.4928
1.9183
1H NMR of
3aa
OH
OMe
1.00
1.00
1.00
2.00
1.00
2.00
3.00
1.00
3.00
f1 (ppm)


158.15
146.66
146.58
144.41
139.55
133.79
126.90
122.75
113.21
73.65
54.89
30.37
13C NMR of
3aa
OH
OMe
f1 (ppm)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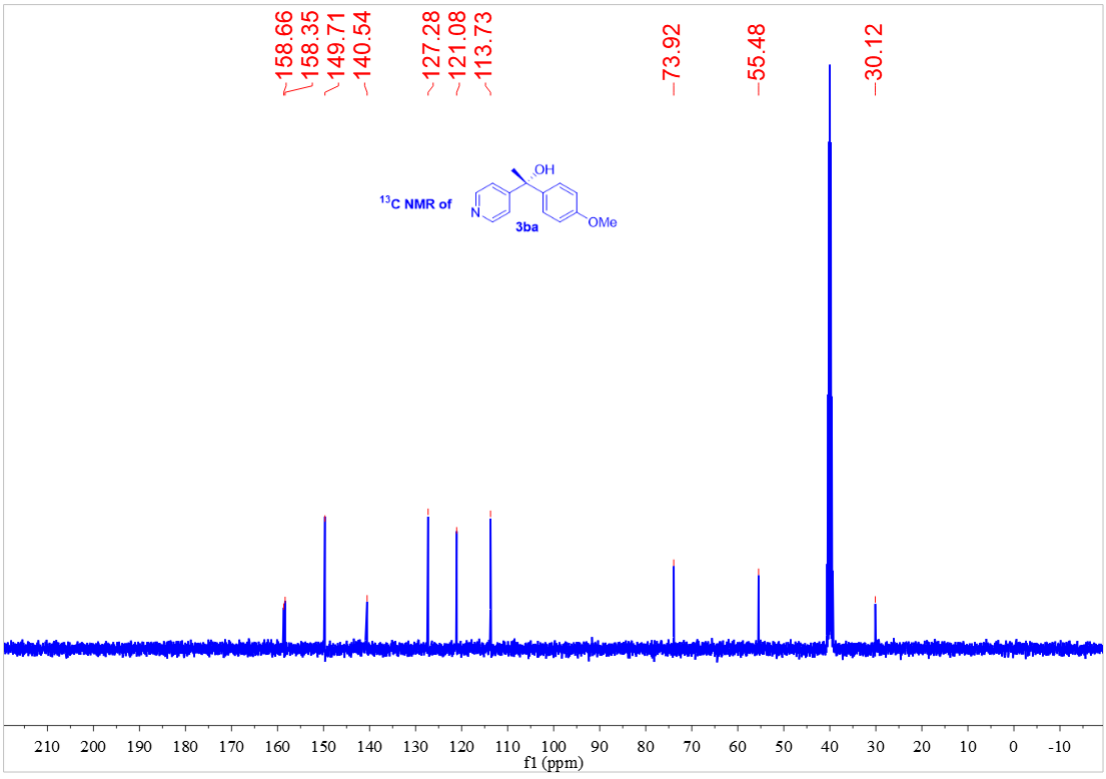
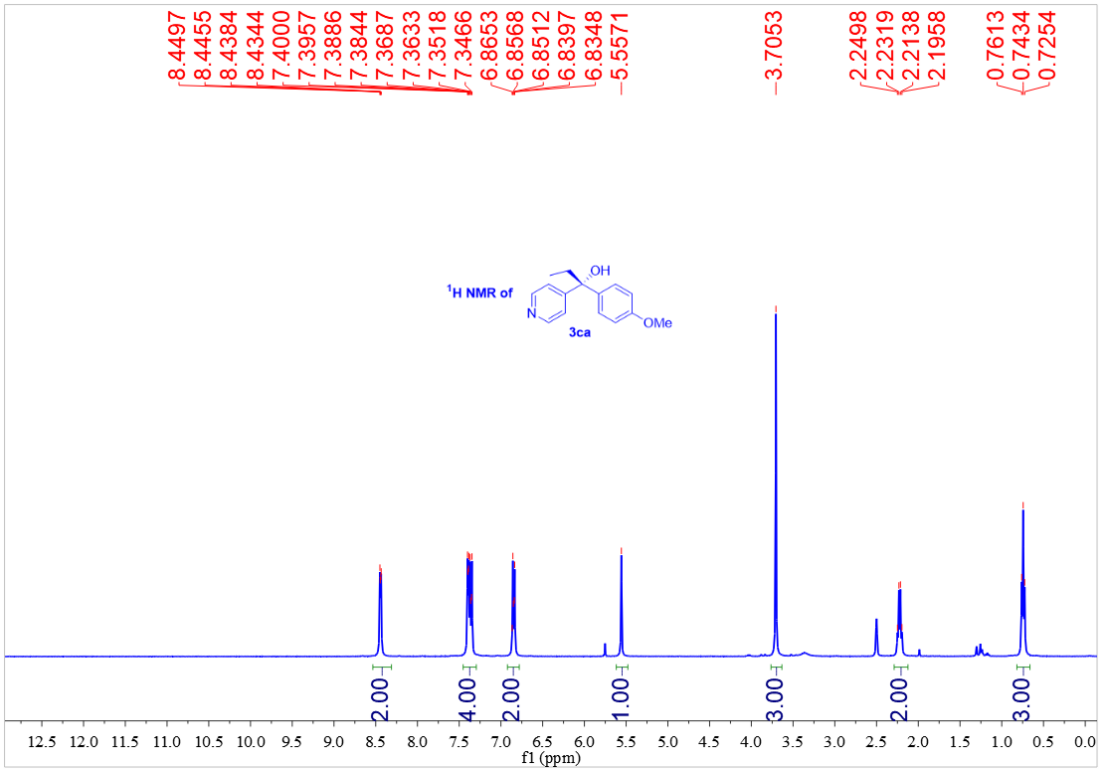
8.4436
8.4396
7.3858
7.3817
7.3747
7.3705
7.3501
7.3421
7.3369
7.3256
7.3203
7.3121
6.8646
6.8566
6.8511
6.8399
6.8345
6.8265
5.8438
3.7090
1.7983
1H NMR of
OH
N
OMe
3ba
2.00
2.00
2.00
2.00
1.00
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


158.66
158.35
149.71
140.54
127.28
121.08
113.73
73.92
55.48
30.12
13C NMR of
OH
N
OMe
3ba
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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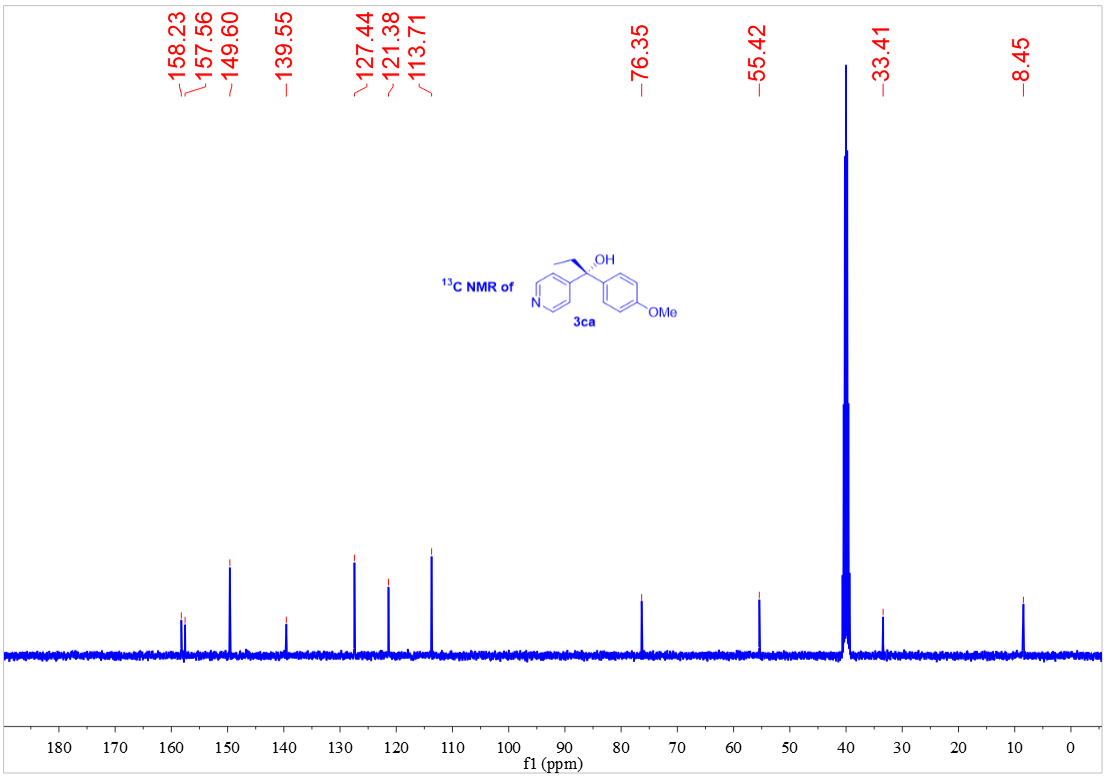
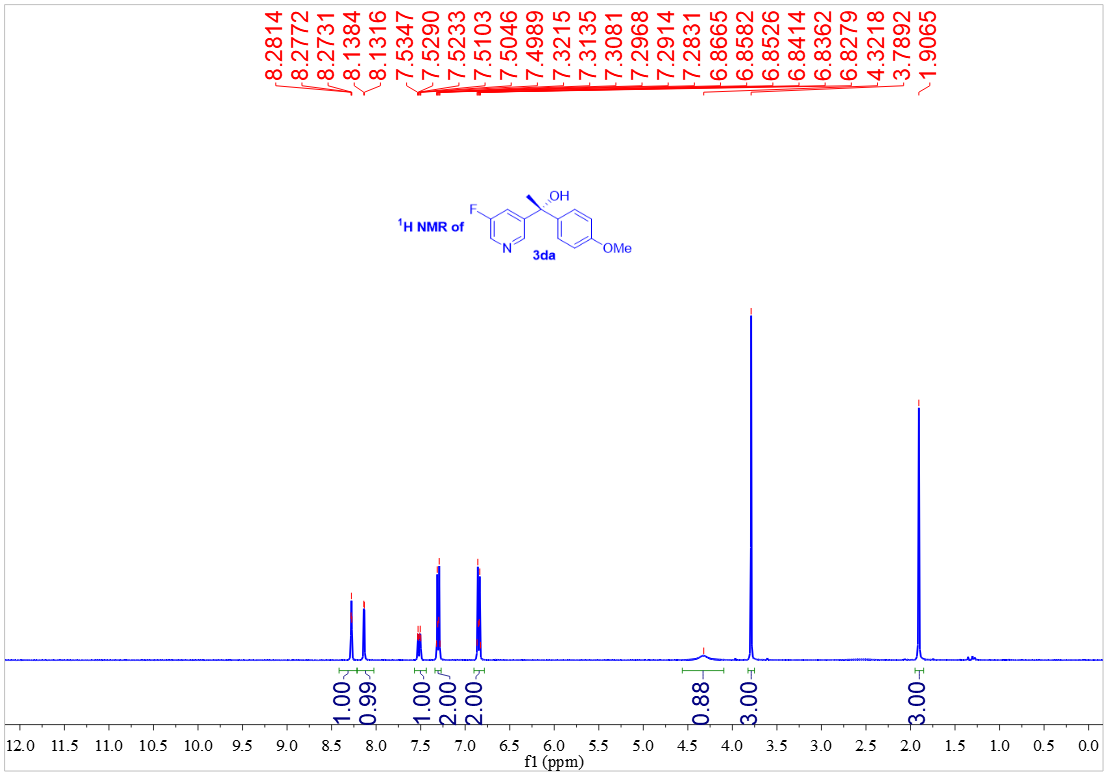
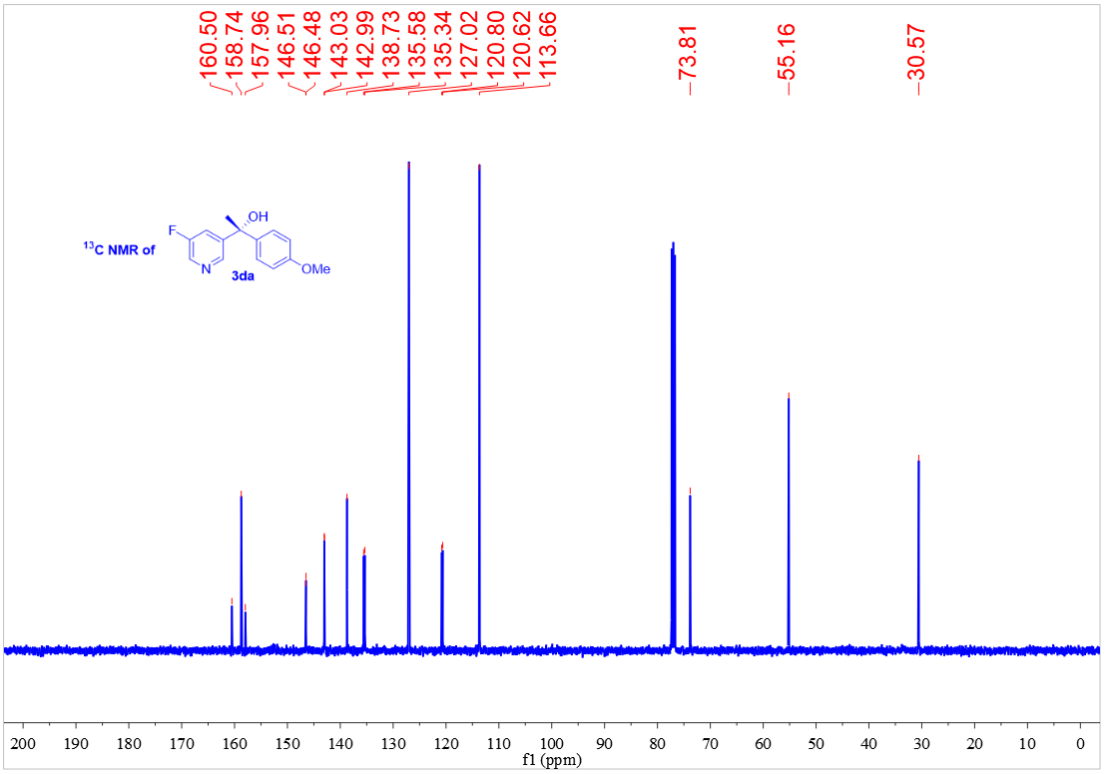
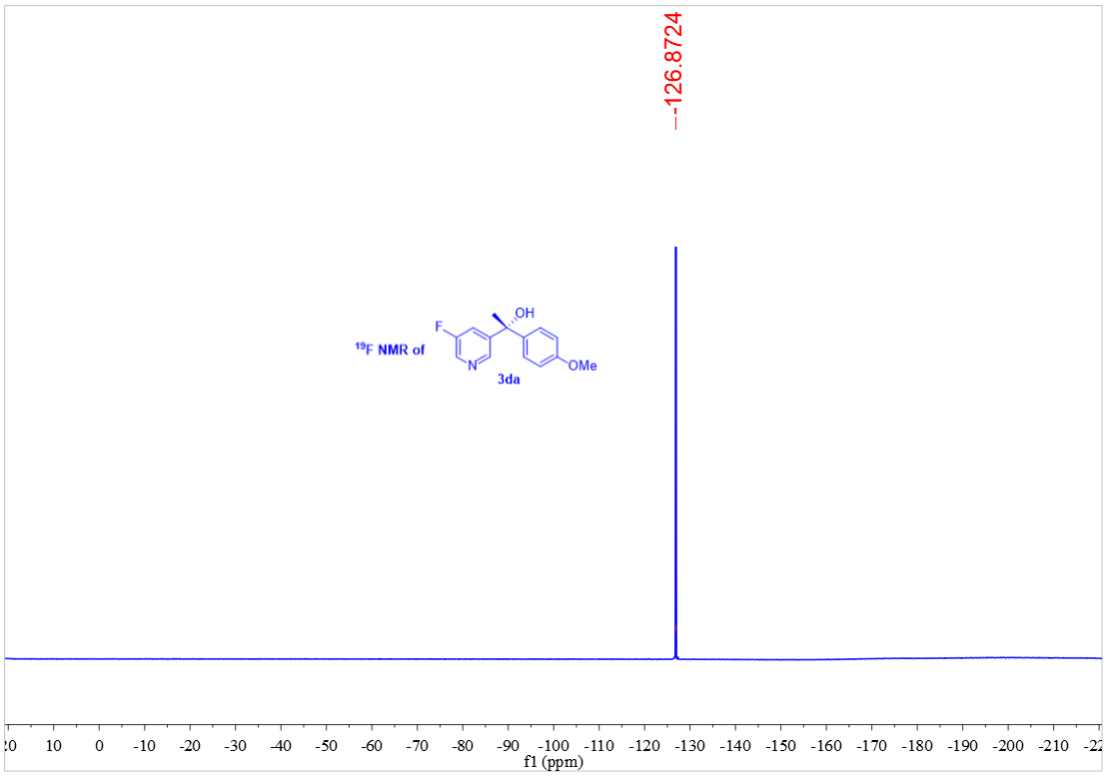
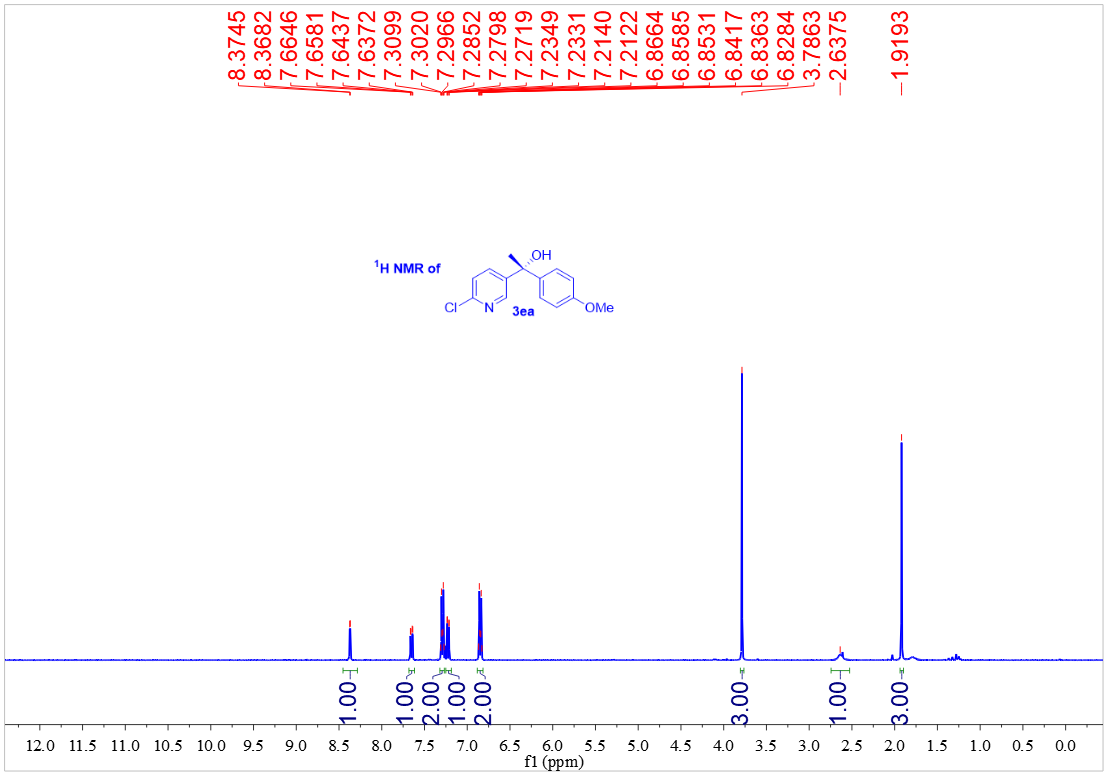
8.4455
8.4384
8.4344
7.4000
7.3957
7.3886
7.3844
7.3687
7.3633
7.3518
7.3466
6.8653
6.8568
6.8512
6.8397
6.8348
5.5571
3.7053
2.2498
2.2319
2.2138
2.1958
0.7613
0.7434
0.7254
1H NMR of
3ca
OH
OMe
2.00
4.00
2.00
1.00
3.00
2.00
3.00
f1 (ppm)


158.23
157.56
149.60
139.55
127.44
121.38
113.71
76.35
55.42
33.41
8.45
13C NMR of
3ca
OH
OMe
f1 (ppm)


8.2814
8.2772
8.2731
8.1384
8.1316
7.5347
7.5290
7.5233
7.5103
7.5046
7.4989
7.3215
7.3135
7.3081
7.2968
7.2914
7.2831
6.8665
6.8582
6.8526
6.8414
6.8362
6.8279
4.3218
3.7892
1.9065
1H NMR of
3da
OH
F
N
OMe
1.00
0.99
1.00
2.00
2.00
0.88
3.00
3.00
f1 (ppm)


160.50
158.74
157.96
146.51
146.48
143.03
142.99
138.73
135.58
135.34
127.02
120.80
120.62
113.66
73.81
55.16
30.57
13C NMR of
3da
OH
F
N
OMe
f1 (ppm)


-126.8724
^{19}F NMR of
3da
f1 (ppm)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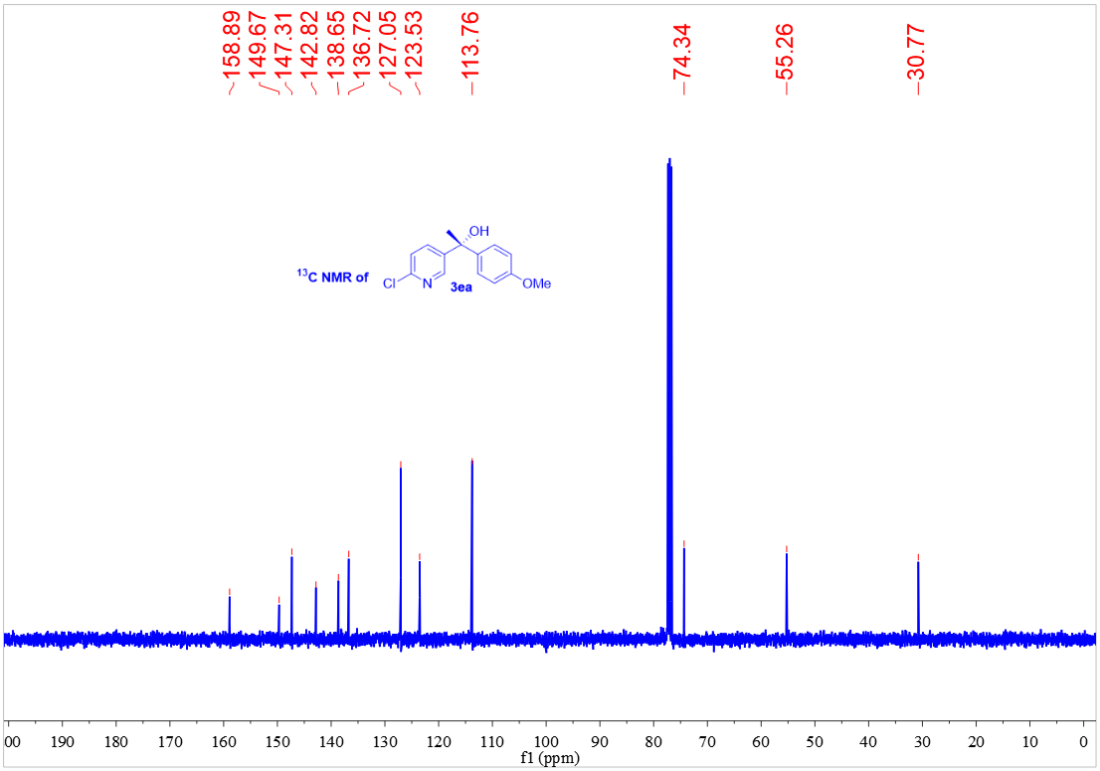
8.3682
7.6646
7.6581
7.6437
7.6372
7.3099
7.3020
7.2966
7.2852
7.2798
7.2719
7.2349
7.2331
7.2140
7.2122
6.8664
6.8585
6.8531
6.8417
6.8363
6.8284
3.7863
2.6375
1.9193
^{1}H NMR of
3ea
1.00
1.00
2.00
1.00
2.00
3.00
1.00
3.00
f1 (ppm)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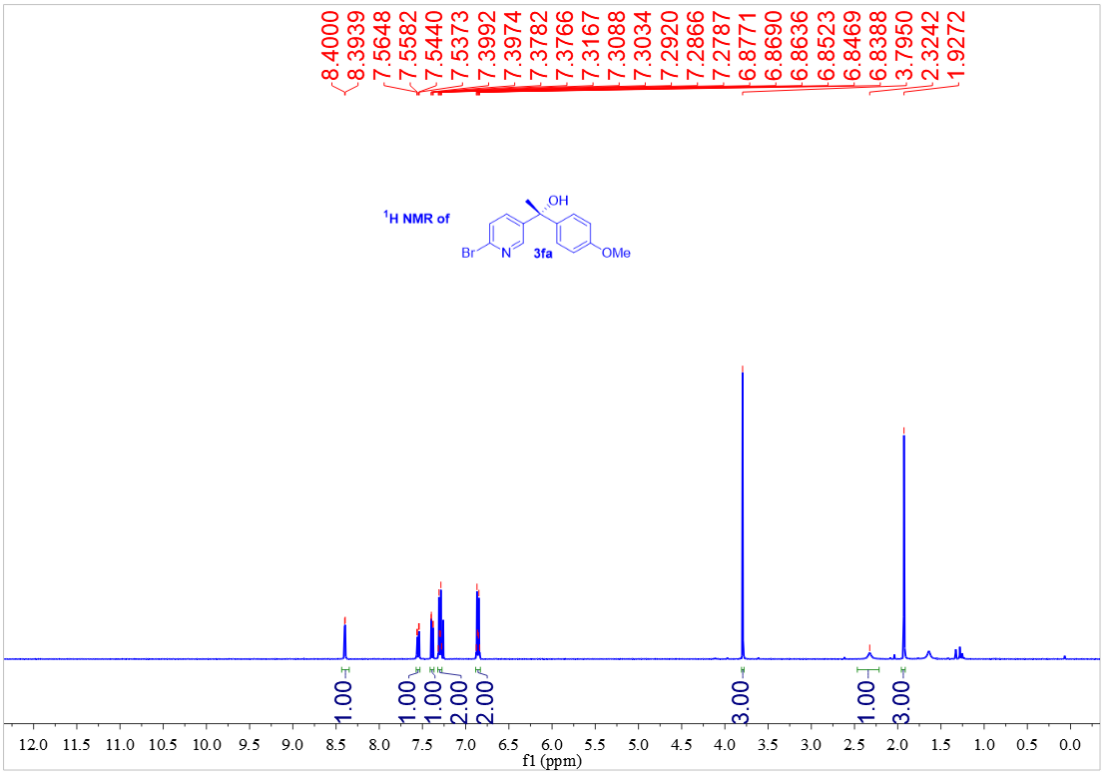
149.67
147.31
142.82
138.65
136.72
127.05
123.53
113.76
74.34
55.26
30.77
13C NMR of
OH
Cl
N
3ea
OMe
f1 (ppm)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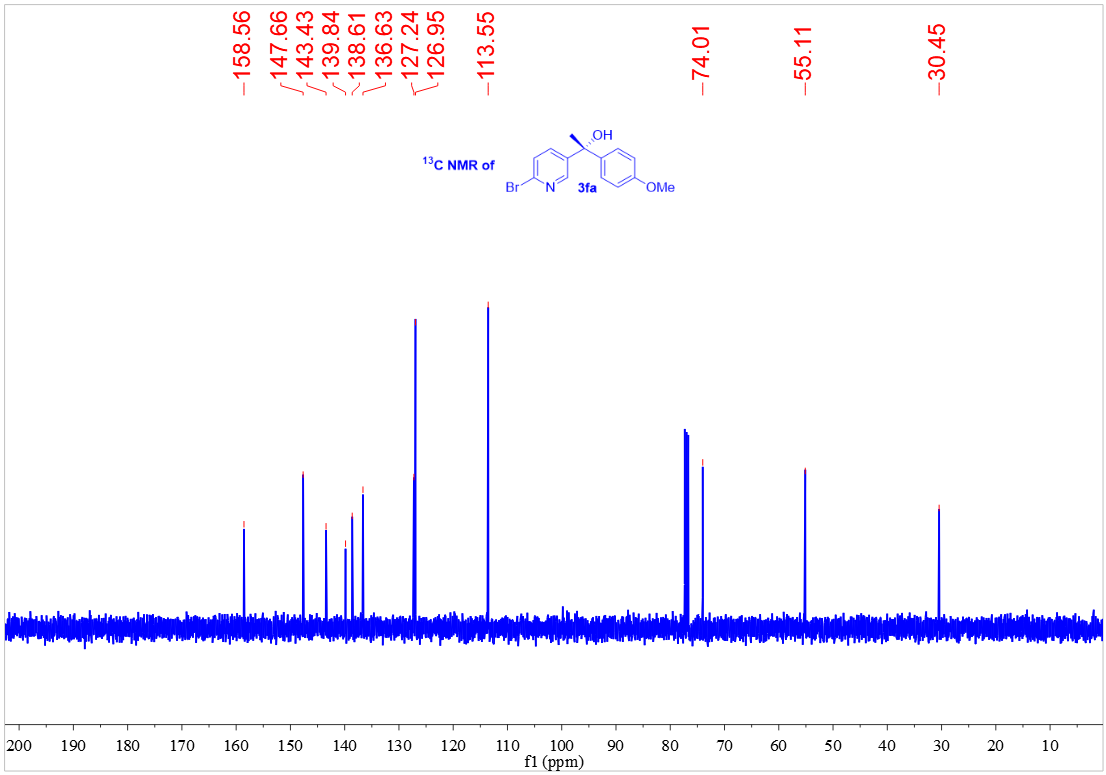
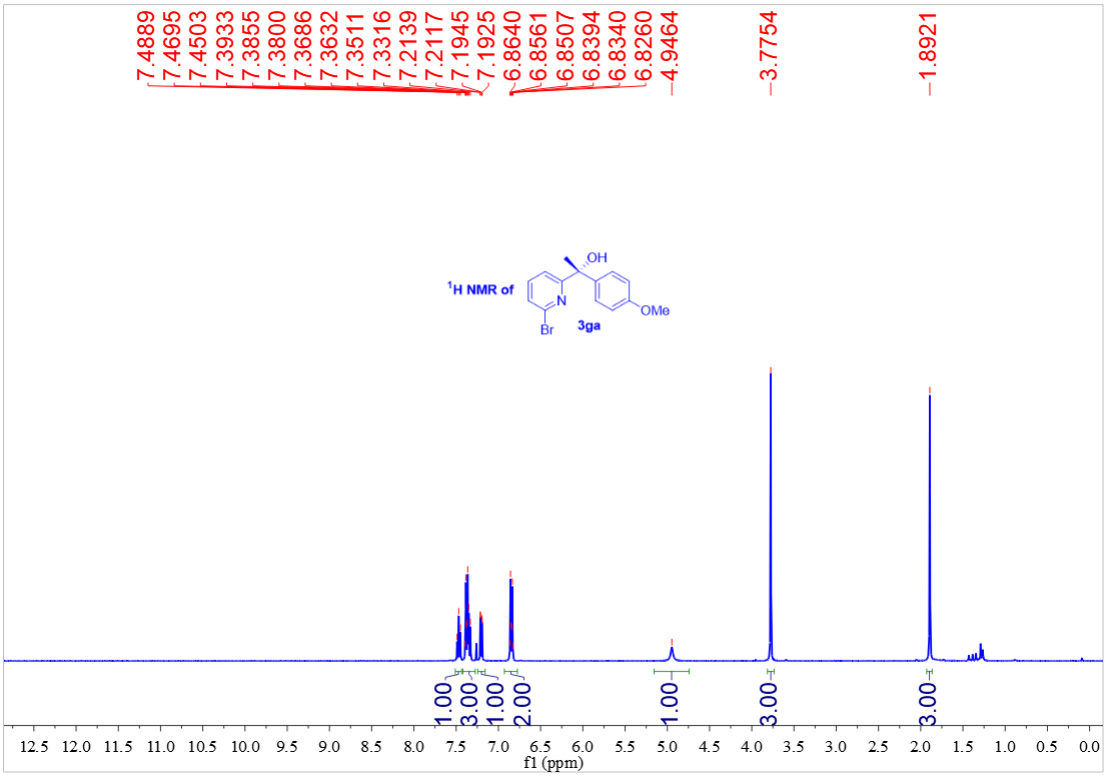
8.3939
7.5648
7.5582
7.5440
7.5373
7.3992
7.3974
7.3782
7.3766
7.3167
7.3088
7.3034
7.2920
7.2866
7.2787
6.8771
6.8690
6.8636
6.8523
6.8469
6.8388
3.7950
2.3242
1.9272
1H NMR of
OH
Br
N
3fa
OMe
1.00
1.00
1.00
2.00
2.00
3.00
1.00
3.00
f1 (ppm)


158.56
147.66
143.43
139.84
138.61
136.63
127.24
126.95
113.55
74.01
55.11
30.45
13C NMR of
OH
Br
N
3fa
OMe
f1 (ppm)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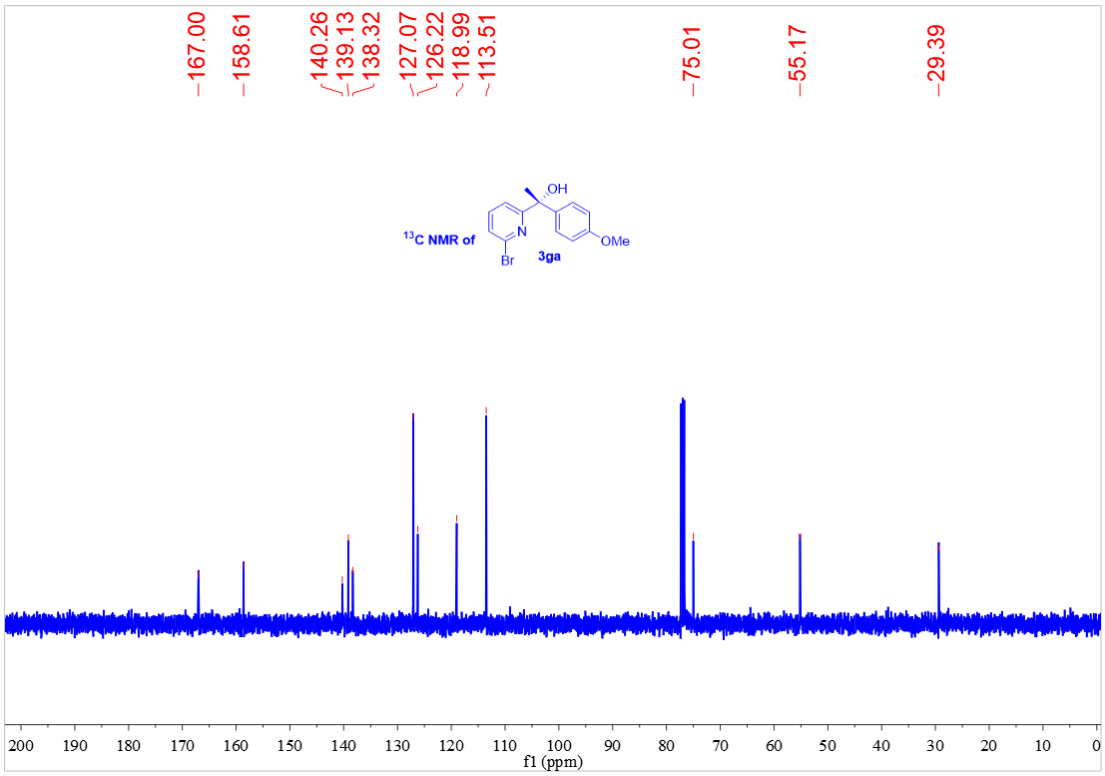
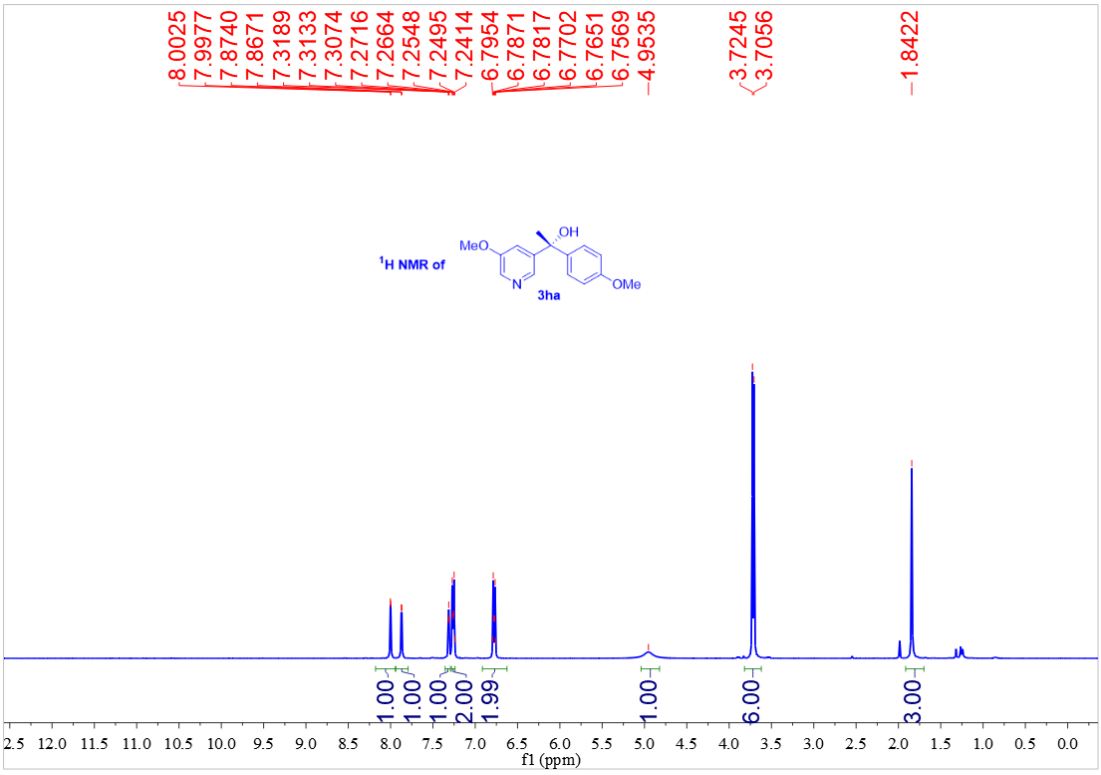
7.4695
7.4503
7.3933
7.3855
7.3800
7.3686
7.3632
7.3511
7.3316
7.2139
7.2117
7.1945
7.1925
6.8640
6.8561
6.8507
6.8394
6.8340
6.8260
4.9464
3.7754
1.8921
1H NMR of
OH
N
Br
3ga
OMe
1.00
3.00
1.00
2.00
1.00
3.00
3.00
f1 (ppm)


167.00
158.61
140.26
139.13
138.32
127.07
126.22
118.99
113.51
75.01
55.17
29.39
OH
N
Br
OMe
13C NMR of 3ga
f1 (ppm)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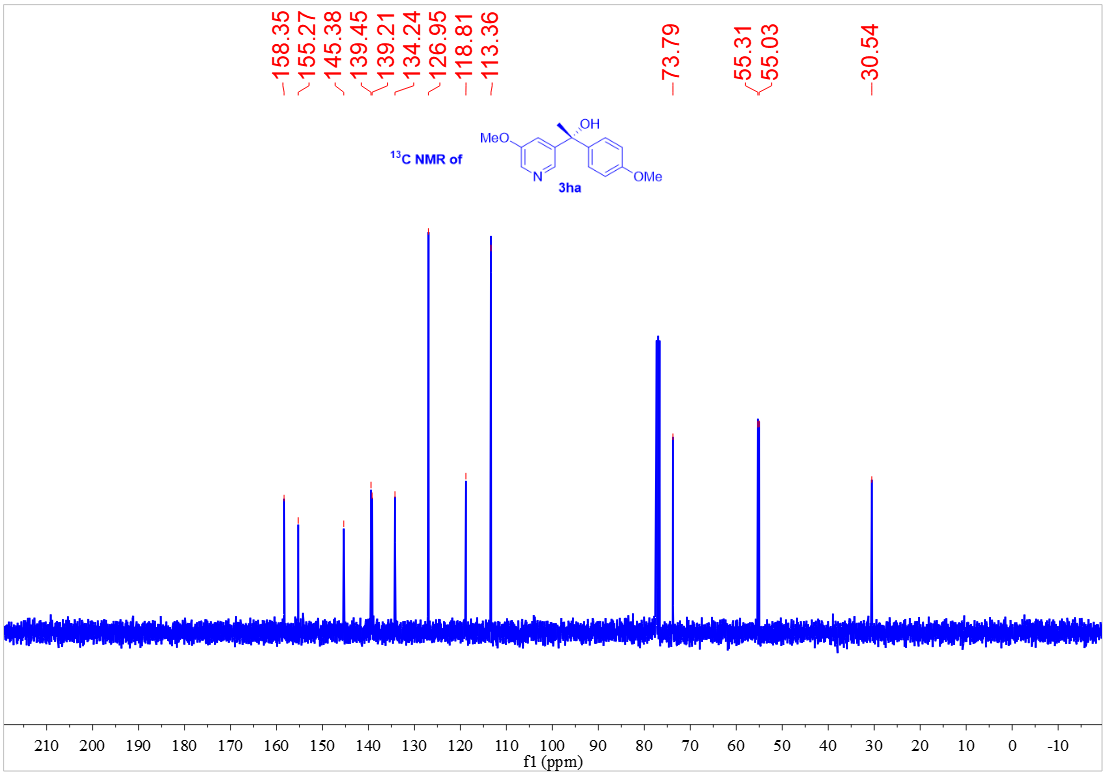
7.8740
7.8671
7.3189
7.3133
7.3074
7.2716
7.2664
7.2548
7.2495
7.2414
6.7954
6.7871
6.7817
6.7702
6.7651
6.7569
4.9535
3.7245
3.7056
1.8422
MeO
OH
N
OMe
1H NMR of 3ha
1.00
1.00
1.00
2.00
1.99
1.00
6.00
3.00
f1 (ppm)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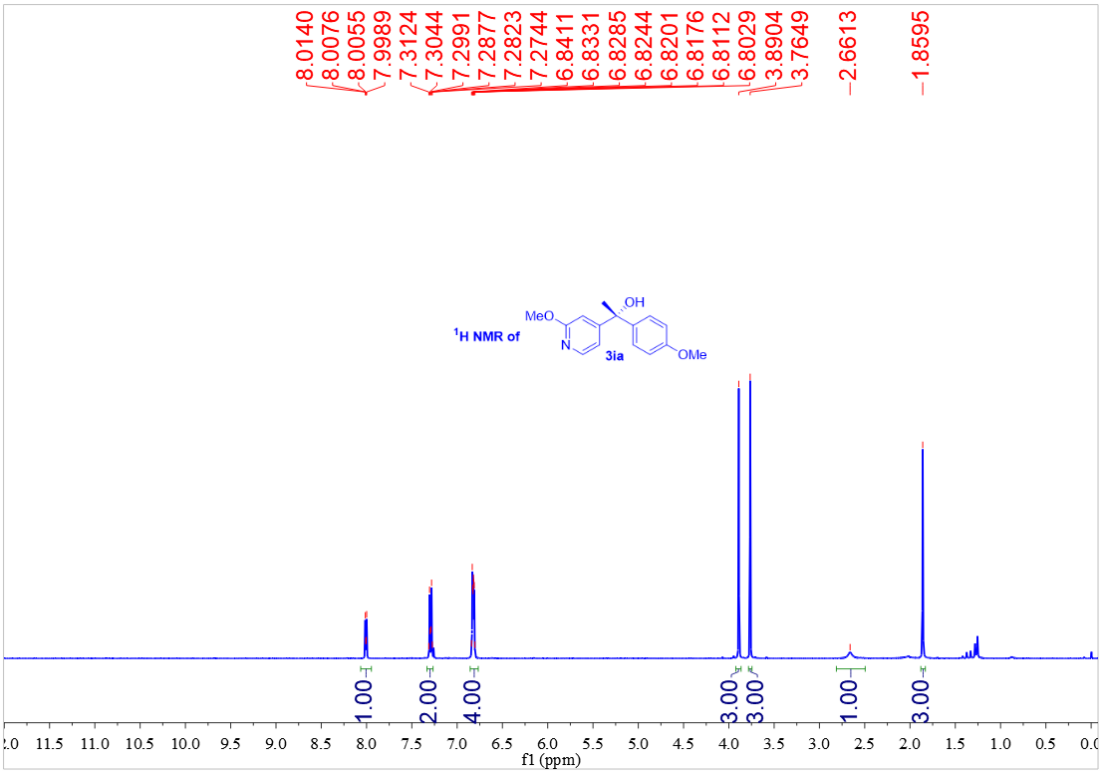
155.27
145.38
139.45
139.21
134.24
126.95
118.81
113.36
73.79
55.31
55.03
30.54
13C NMR of
MeO
OH
N
OMe
3ha
f1 (ppm)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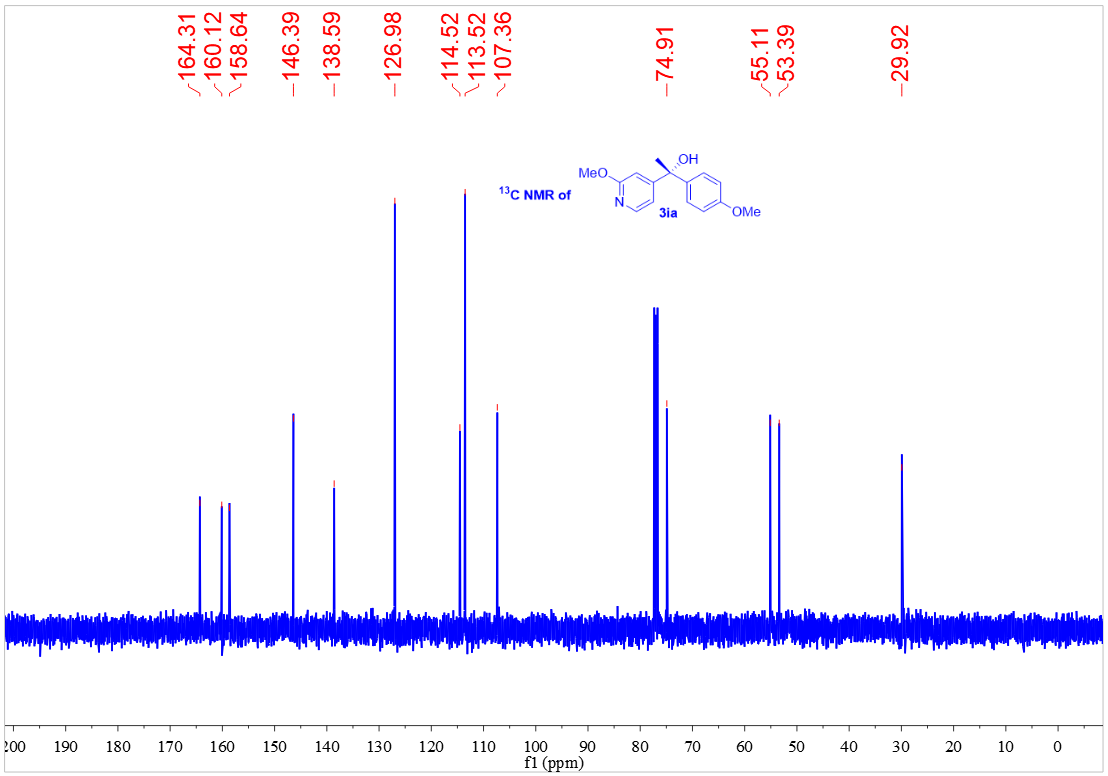
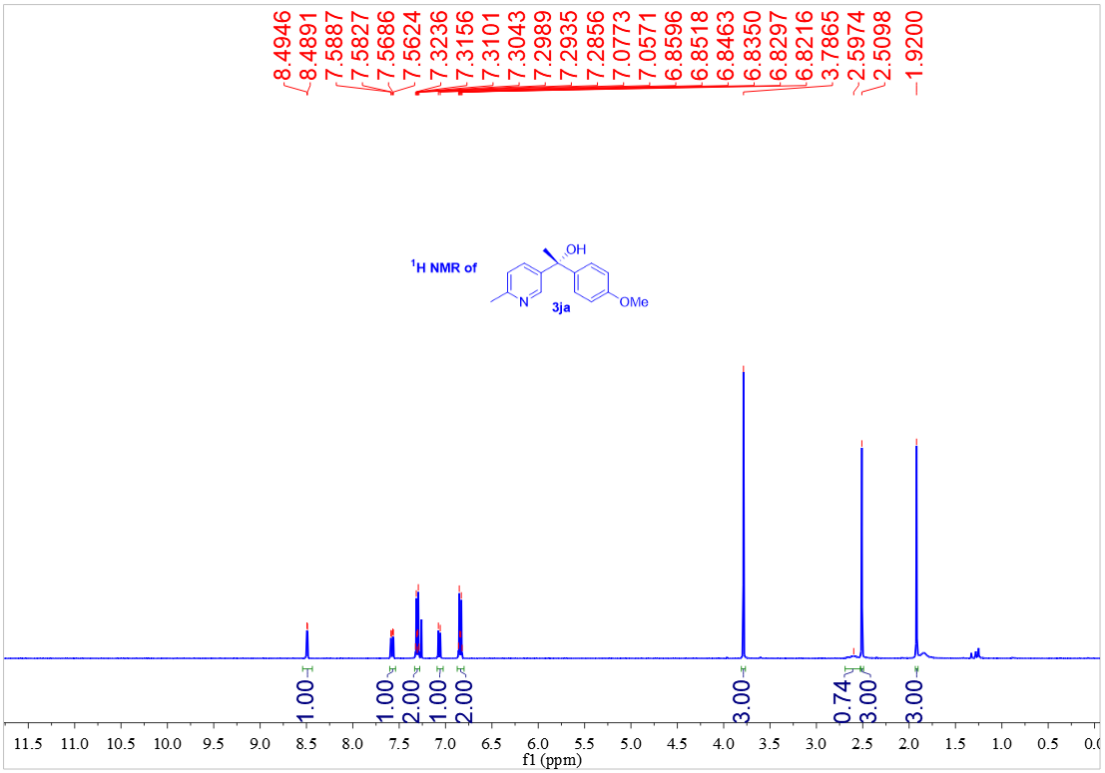
7.2877
7.2823
7.2744
6.8411
6.8331
6.8285
6.8244
6.8201
6.8176
6.8112
6.8029
3.8904
3.7649
2.6613
1.8595
1H NMR of
MeO
OH
N
OMe
3ia
1.00
2.00
4.00
3.00
3.00
1.00
3.00
f1 (ppm)


164.31
160.12
158.64
146.39
138.59
126.98
114.52
113.52
107.36
74.91
55.11
53.39
29.92
^{13}C NMR of
MeO
OH
N
OMe
3ia
f1 (ppm)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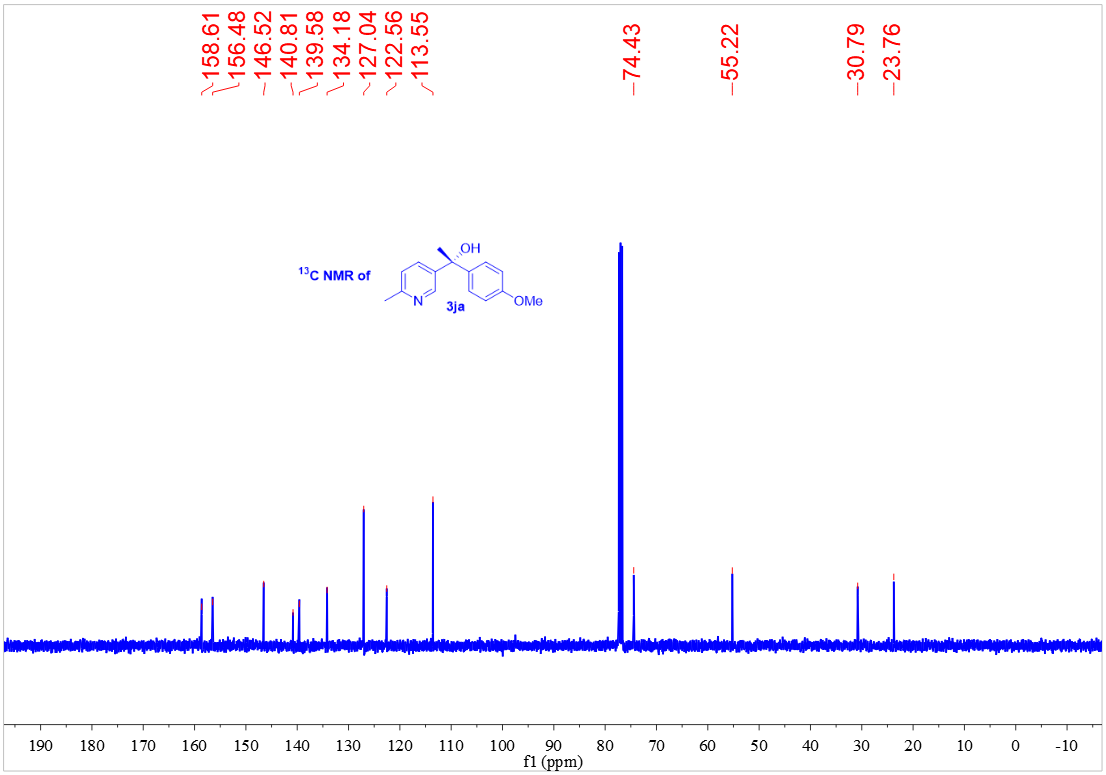
7.3156
7.3101
7.3043
7.2989
7.2935
7.2856
7.0773
7.0571
6.8596
6.8518
6.8463
6.8350
6.8297
6.8216
3.7865
2.5974
2.5098
1.9200
^{1}H NMR of
OH
N
OMe
3ja
1.00
1.00
2.00
1.00
2.00
3.00
0.74
3.00
3.00
f1 (ppm)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156.48
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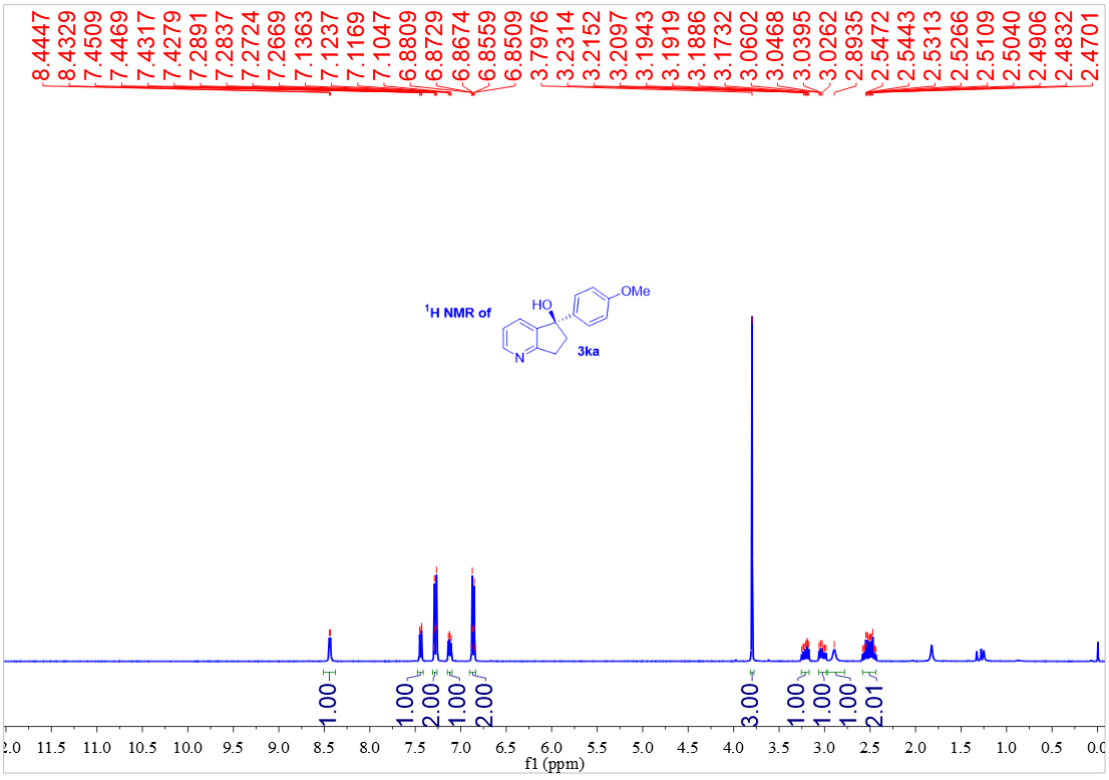
140.81
139.58
134.18
127.04
122.56
113.55
74.43
55.22
30.79
23.76
13C NMR of
OH
OMe
N
3ja
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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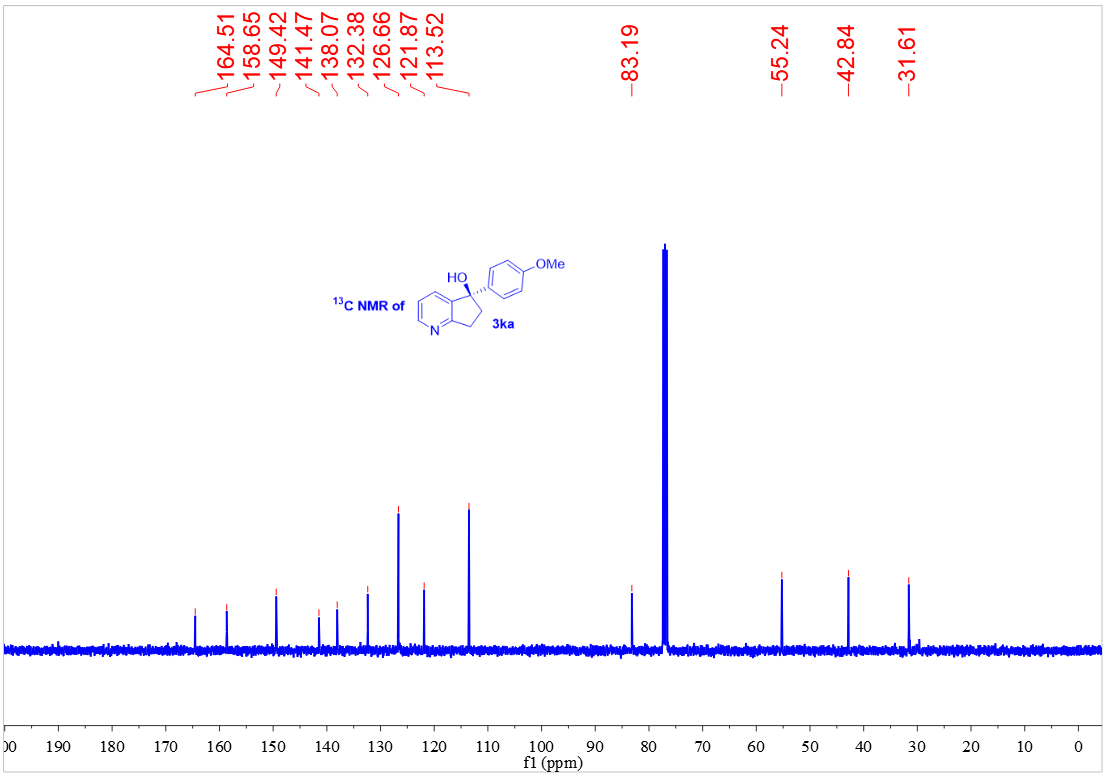
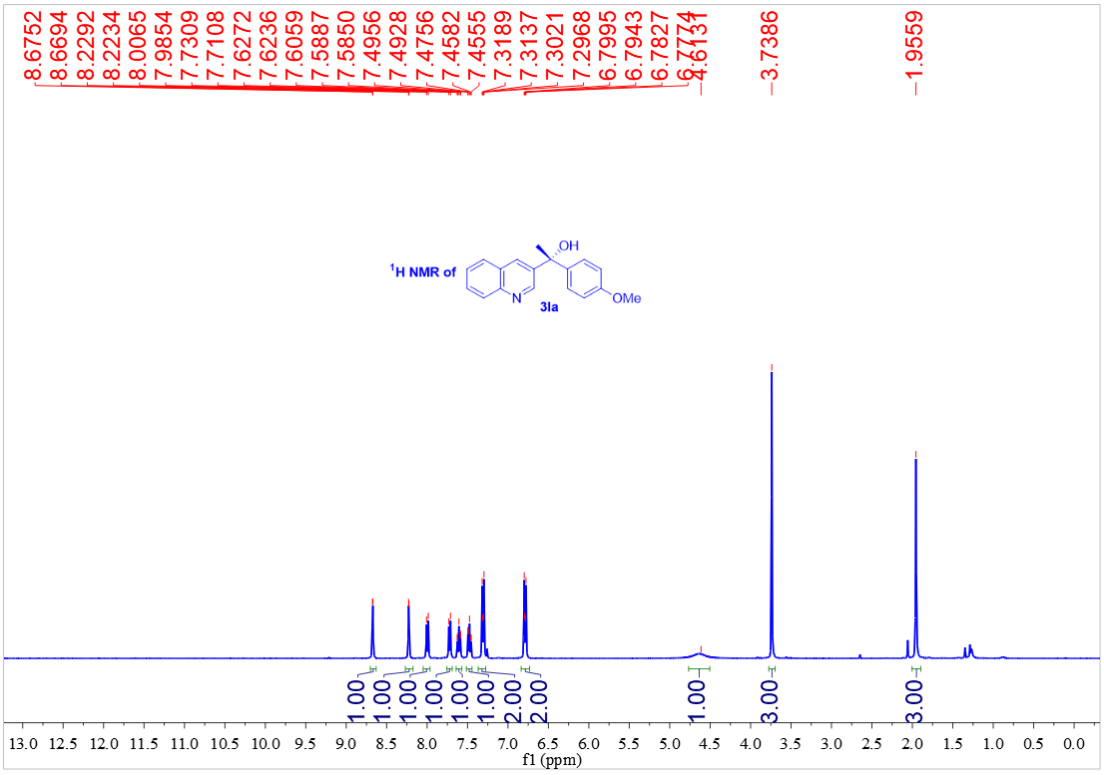
7.1363
7.1237
7.1169
7.1047
6.8809
6.8729
6.8674
6.8559
6.8509
3.7976
3.2314
3.2152
3.2097
3.1943
3.1919
3.1886
3.1732
3.0602
3.0468
3.0395
3.0262
2.8935
2.5472
2.5443
2.5313
2.5266
2.5109
2.5040
2.4906
2.4832
2.4701
1H NMR of
HO
OMe
N
3ka
1.00
1.00
2.00
1.00
2.00
3.00
1.00
1.00
1.00
2.01
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.51
158.65
149.42
141.47
138.07
132.38
126.66
121.87
113.52
83.19
55.24
42.84
31.61
HO
OMe
13C NMR of
3ka
N
f1 (ppm)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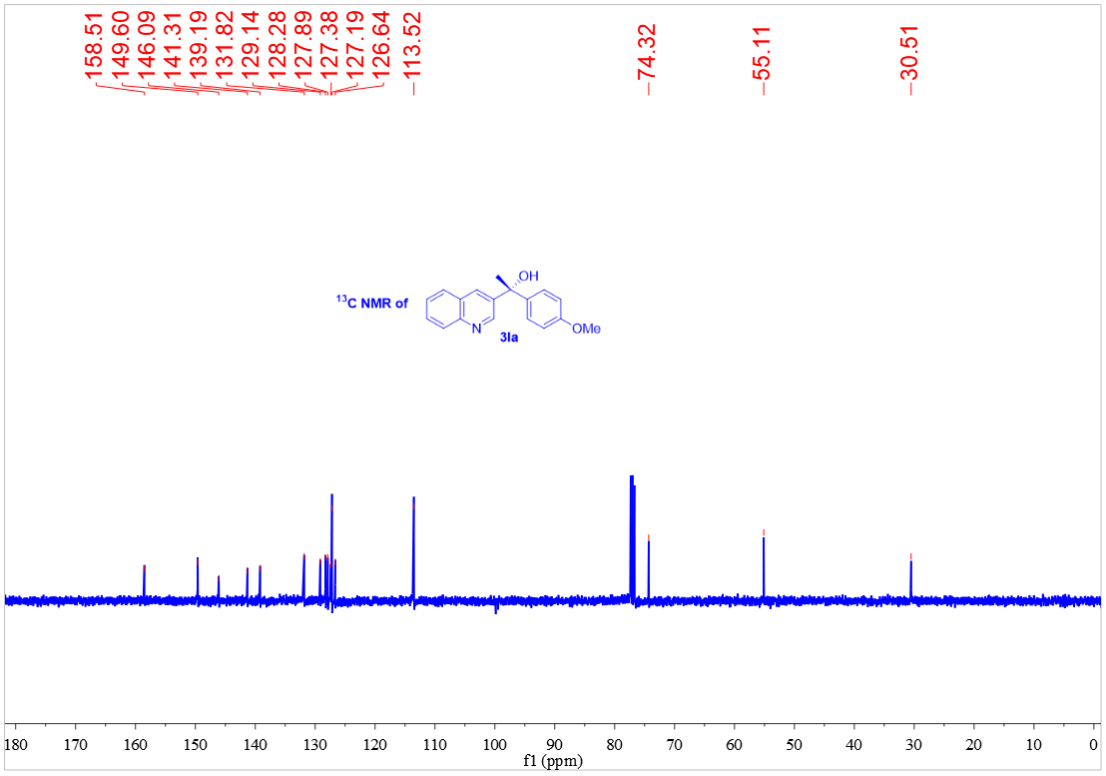
8.6694
8.2292
8.2234
8.0065
7.9854
7.7309
7.7108
7.6272
7.6236
7.6059
7.5887
7.5850
7.4956
7.4928
7.4756
7.4582
7.4555
7.3189
7.3137
7.3021
7.2968
6.7995
6.7943
6.7827
6.7774
6.6131
3.7386
1.9559
1H NMR of
OH
OMe
N
3la
1.00
1.00
1.00
1.00
1.00
1.00
2.00
2.00
1.00
3.00
3.00
f1 (ppm)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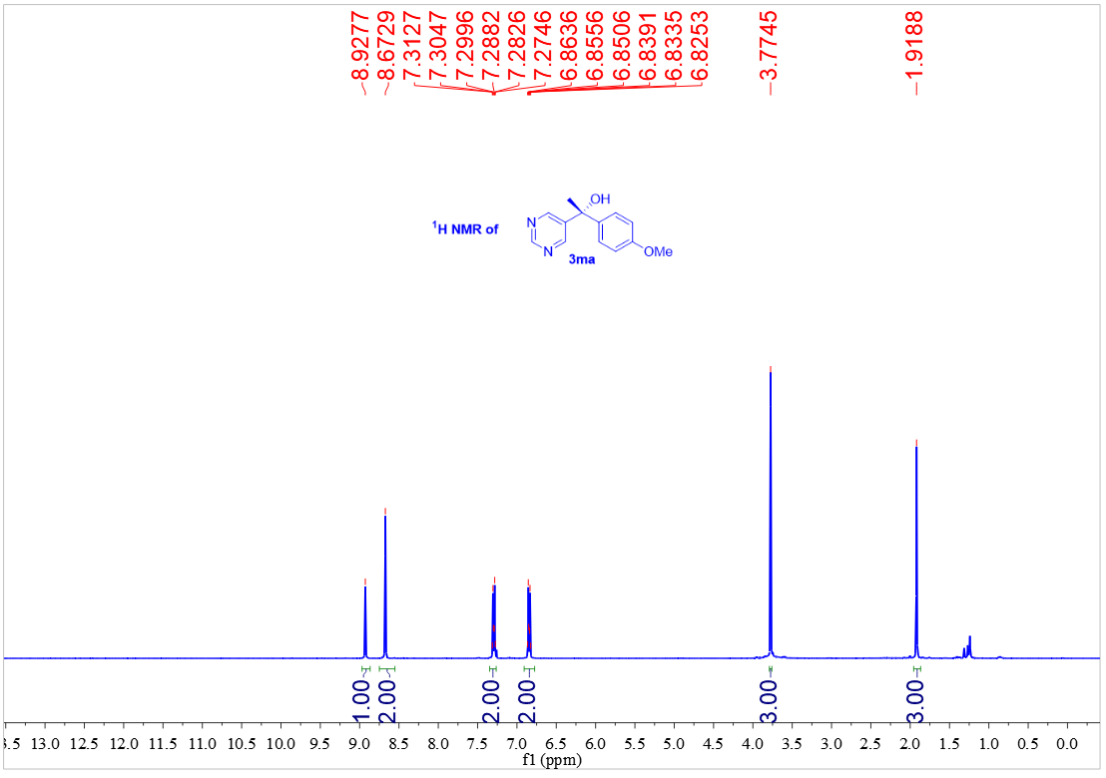
149.60
146.09
141.31
139.19
131.82
129.14
128.28
127.89
127.38
127.19
126.64
113.52
74.32
55.11
30.51
13C NMR of
OH
N
OMe
3la
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.2826
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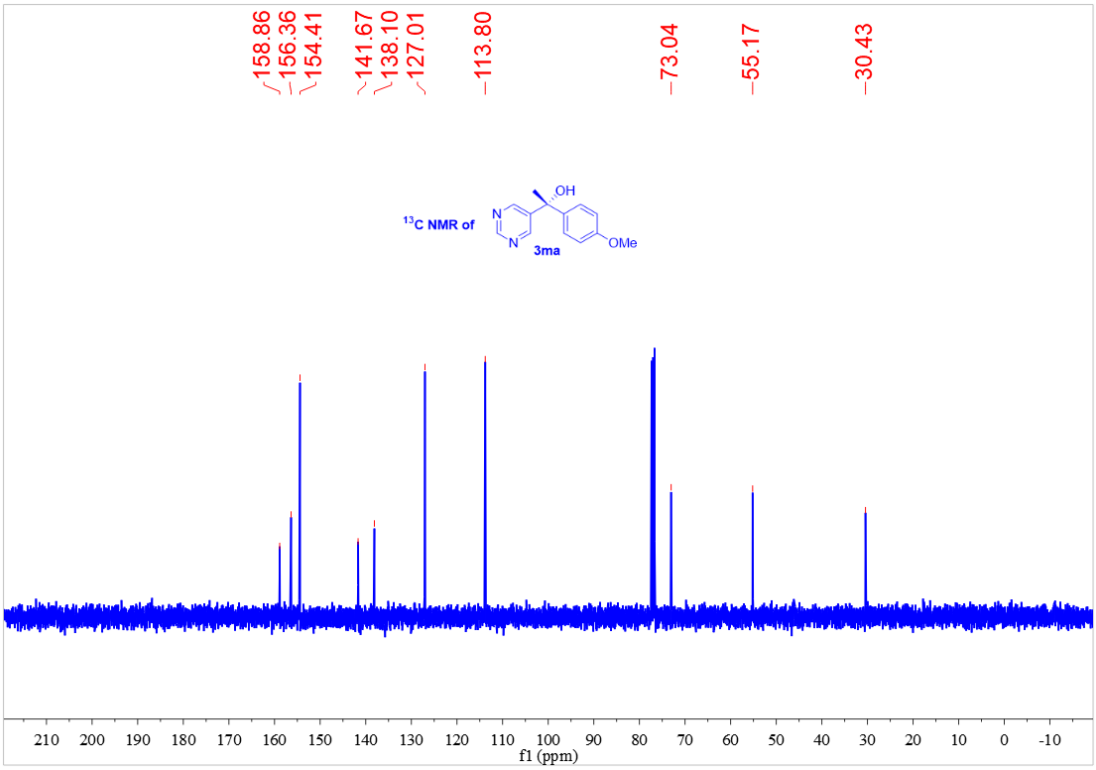
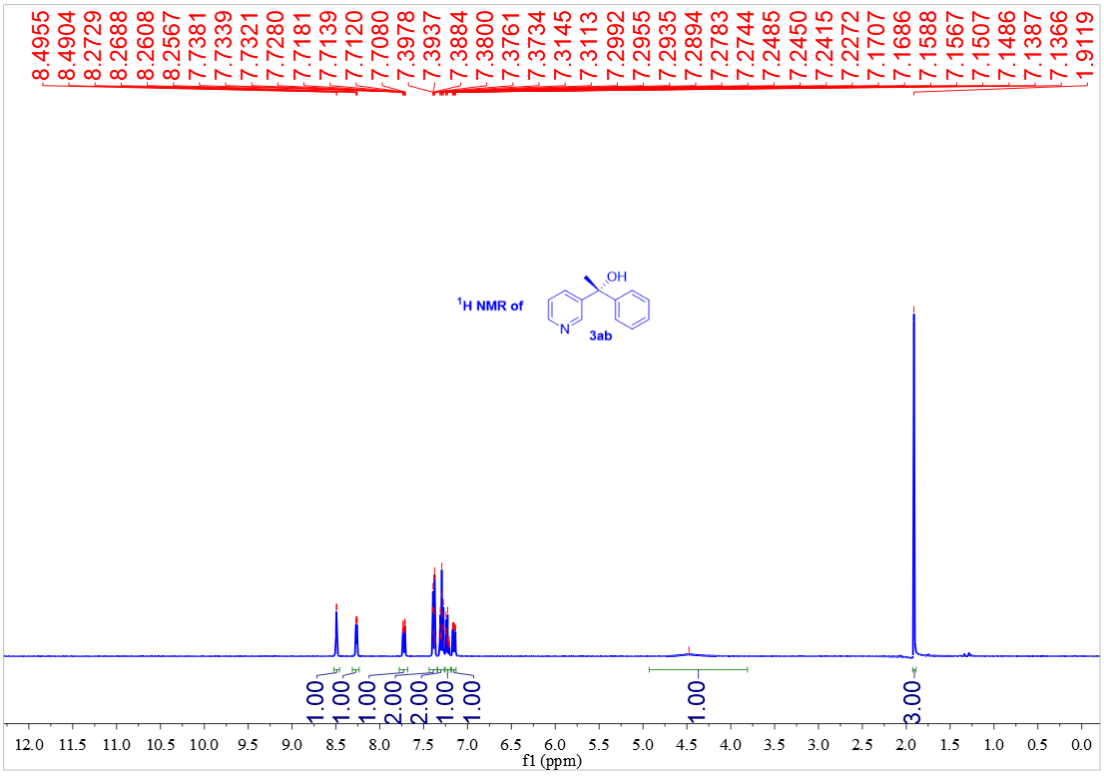
6.8636
6.8556
6.8506
6.8391
6.8335
6.8253
3.7745
1.9188
1H NMR of
OH
N
N
OMe
3ma
1.00
2.00
2.00
2.00
3.00
3.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


158.86
156.36
154.41
141.67
138.10
127.01
113.80
73.04
55.17
30.43
13C NMR of
OH
N
N
OMe
3ma
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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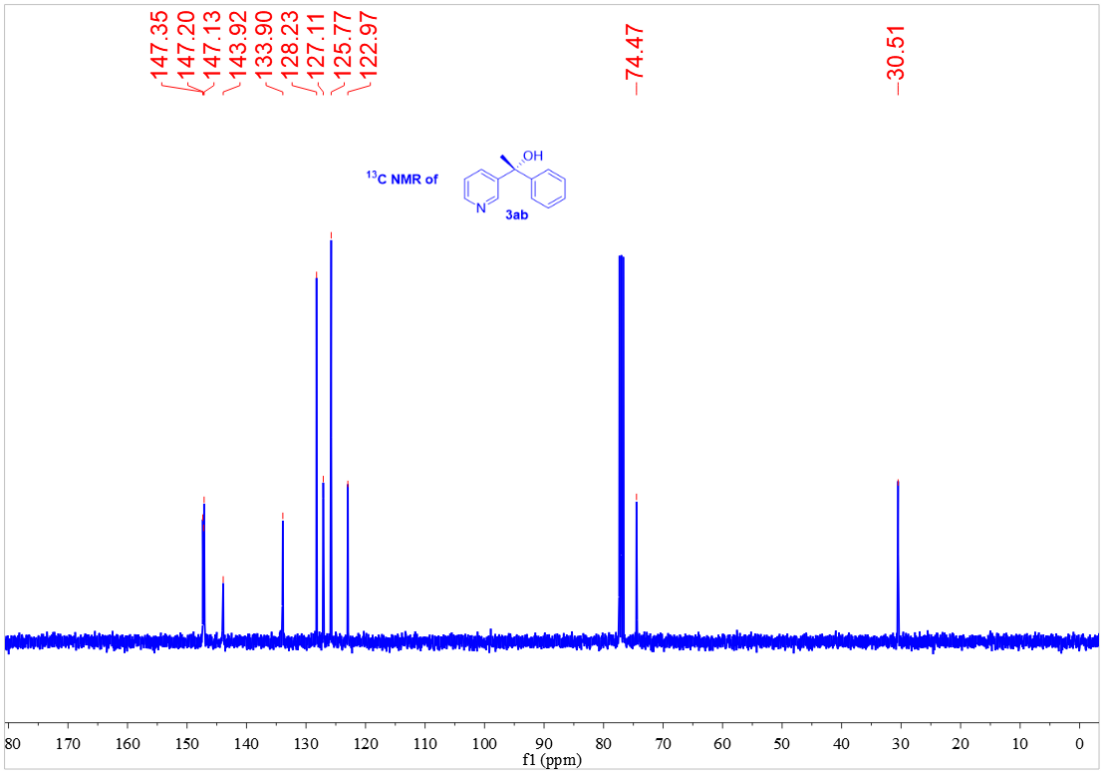
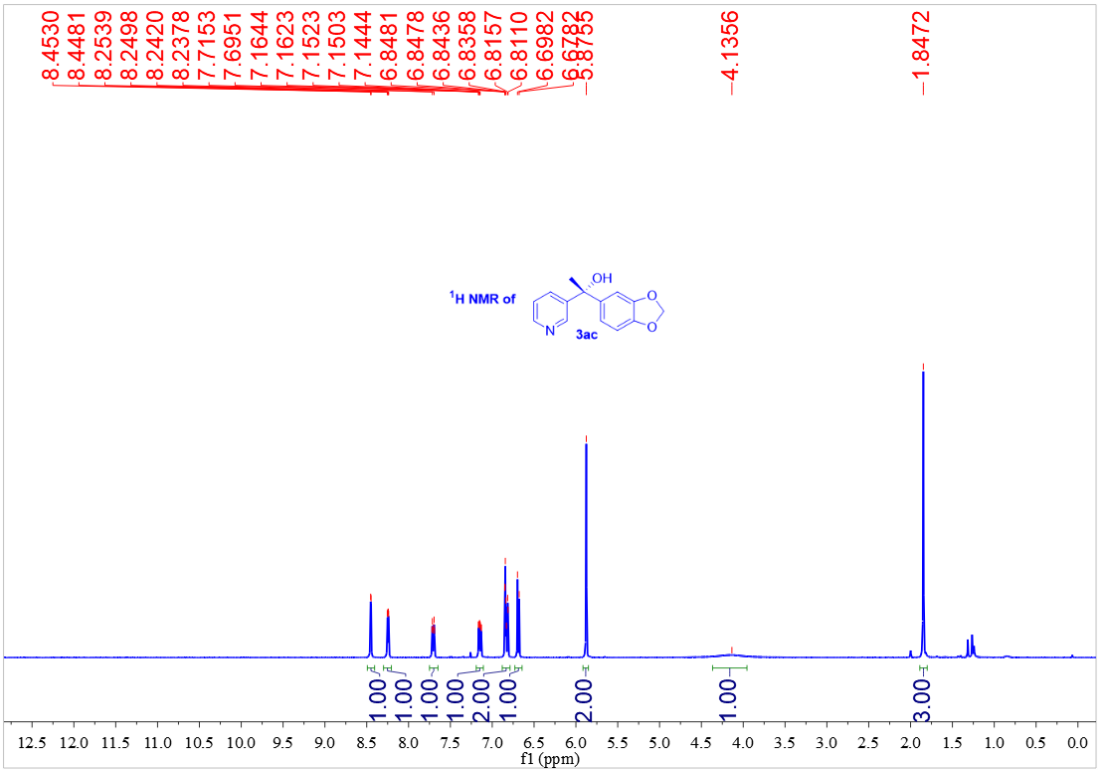
7.7280
7.7181
7.7139
7.7120
7.7080
7.3978
7.3937
7.3884
7.3800
7.3761
7.3734
7.3145
7.3113
7.2992
7.2955
7.2935
7.2894
7.2783
7.2744
7.2485
7.2450
7.2415
7.2272
7.1707
7.1686
7.1588
7.1567
7.1507
7.1486
7.1387
7.1366
1.9119
1H NMR of
OH
N
3ab
1.00
1.00
1.00
2.00
2.00
1.00
1.00
1.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


147.35
147.20
147.13
143.92
133.90
128.23
127.11
125.77
122.97
74.47
30.51
13C NMR of
OH
N
3ab
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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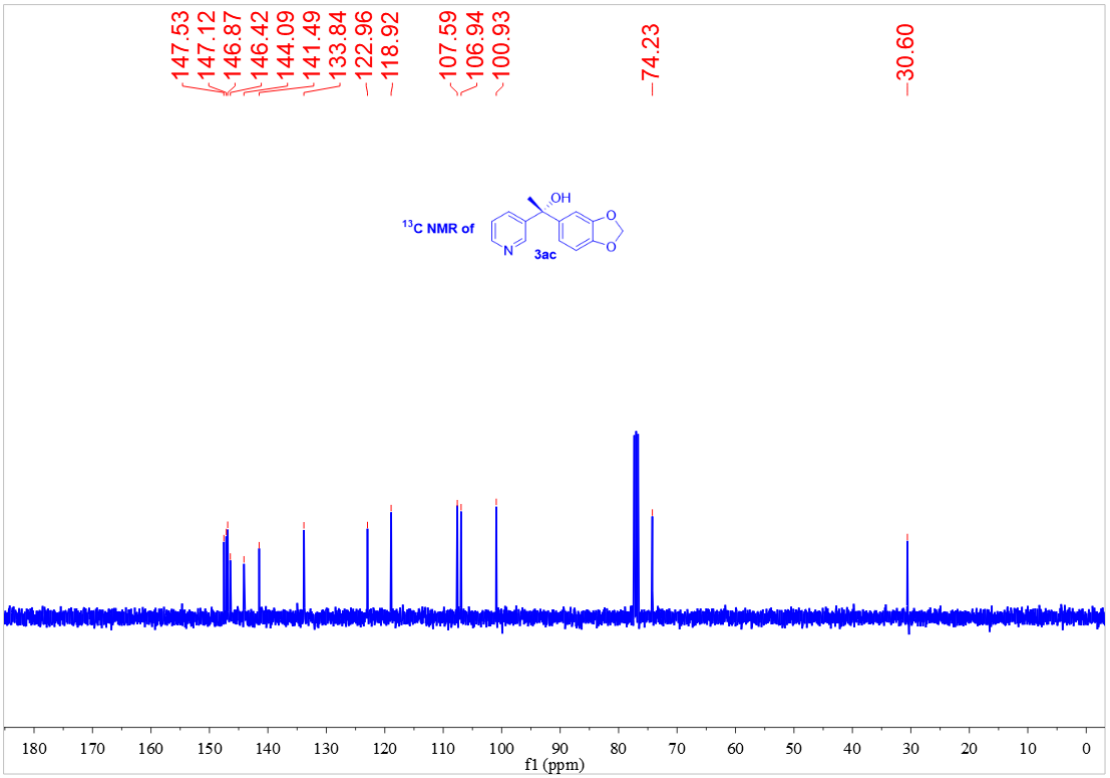
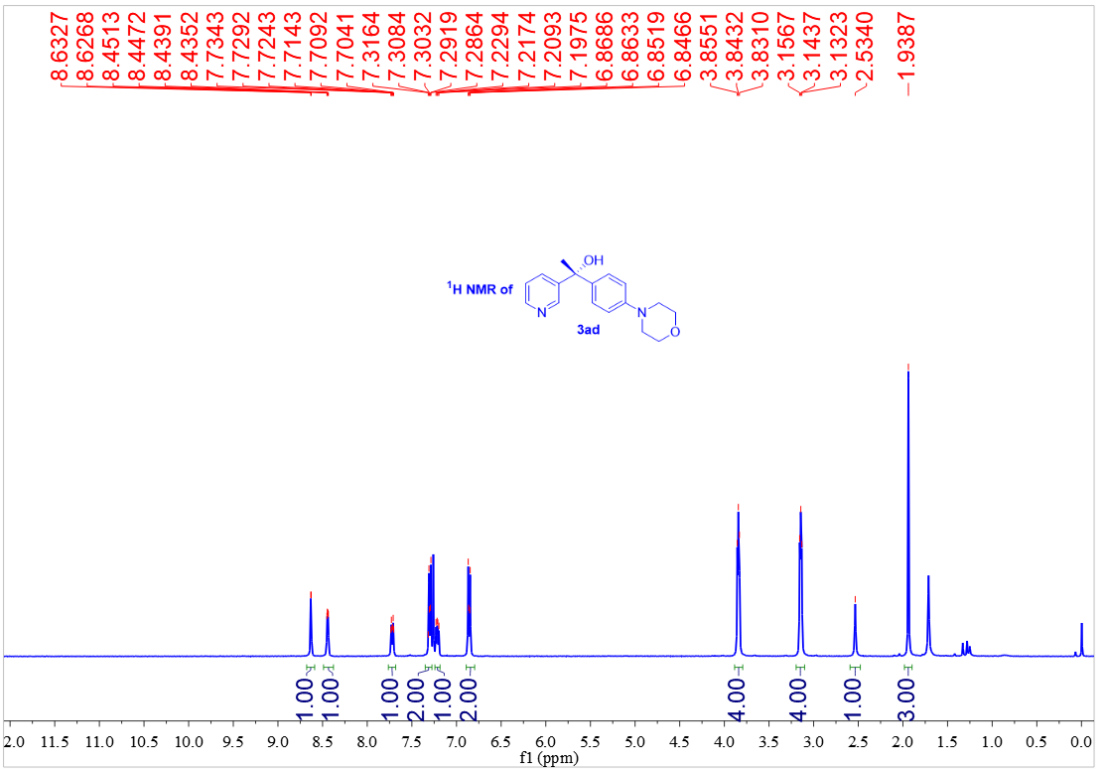
8.4481
8.2539
8.2498
8.2420
8.2378
7.7153
7.6951
7.1644
7.1623
7.1523
7.1503
7.1444
6.8481
6.8478
6.8436
6.8358
6.8157
6.8110
6.6982
6.6782
5.8755
4.1356
1.8472
1H NMR of
OH
N
O
O
3ac
1.00 1.00 1.00 1.00 2.00 1.00 2.00 1.00 3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


147.53
147.12
146.87
146.42
144.09
141.49
133.84
122.96
118.92
107.59
106.94
100.93
74.23
30.60
13C NMR of
OH
N
O
O
3ac
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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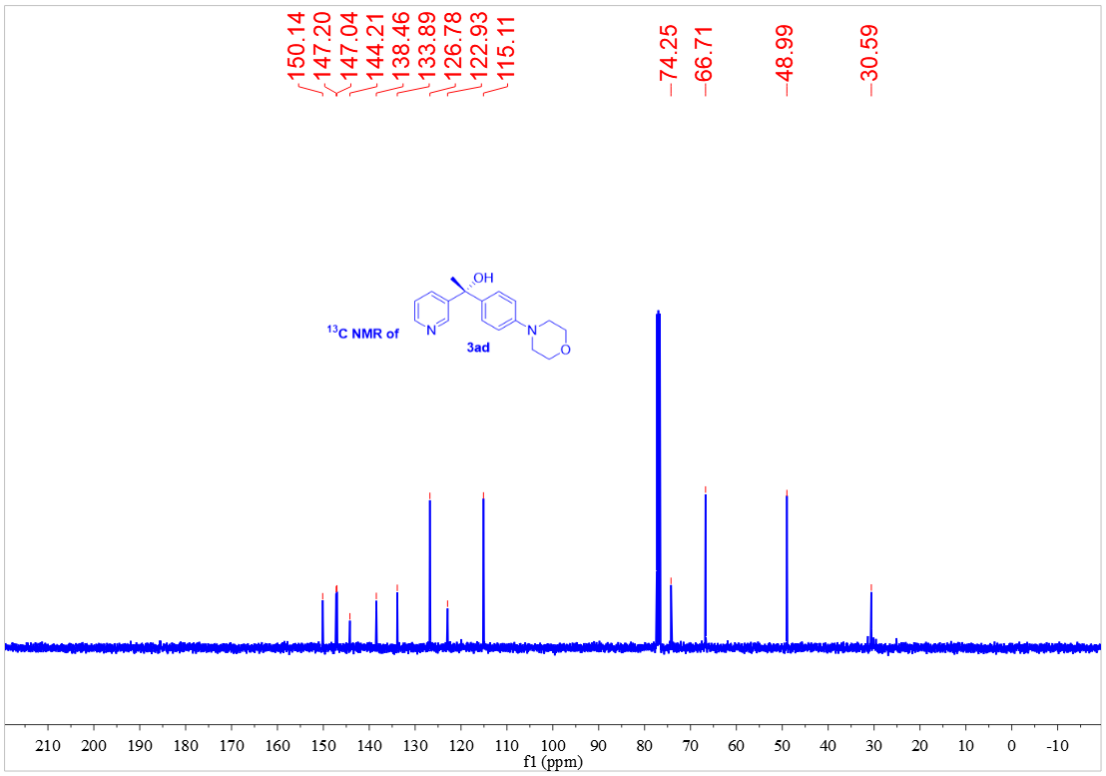
8.4391
8.4352
7.7343
7.7292
7.7243
7.7143
7.7092
7.7041
7.3164
7.3084
7.3032
7.2919
7.2864
7.2294
7.2174
7.2093
7.1975
6.8686
6.8633
6.8519
6.8466
3.8551
3.8432
3.8310
3.1567
3.1437
3.1323
2.5340
1.9387
1H NMR of
OH
N
N
O
3ad
1.00
1.00
1.00
2.00
1.00
2.00
4.00
4.00
1.00
3.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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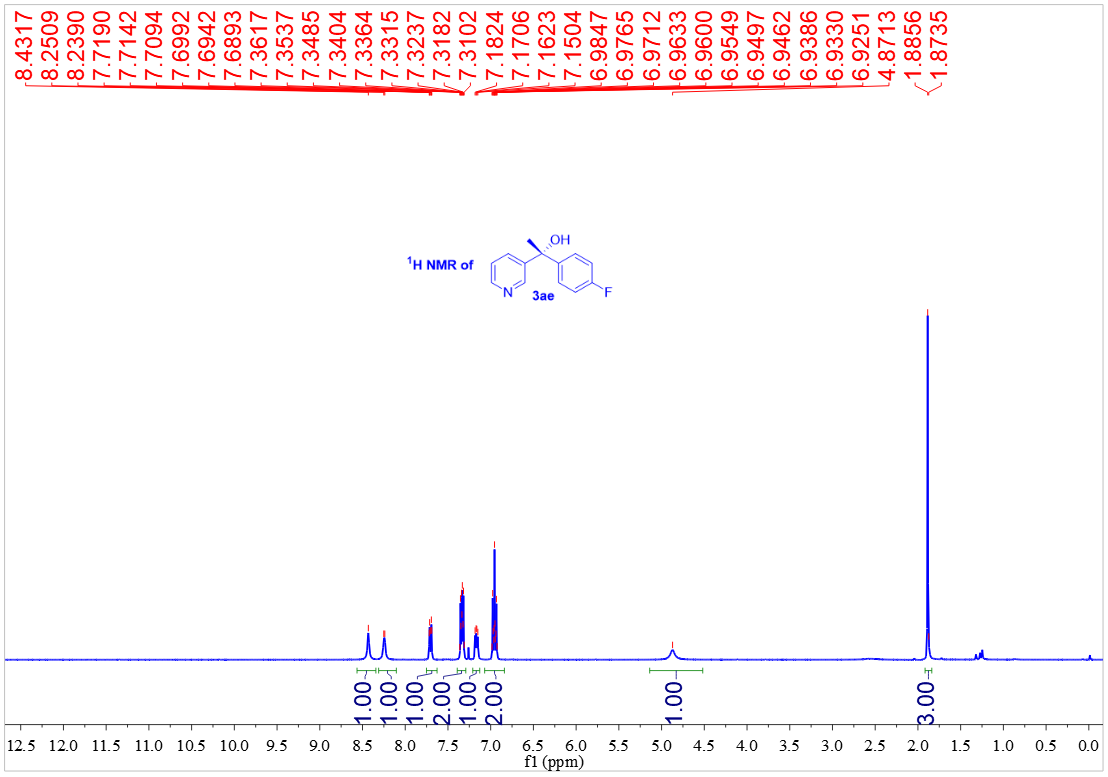
147.20
147.04
144.21
138.46
133.89
126.78
122.93
115.11
74.25
66.71
48.99
30.59
OH
N
O
13C NMR of
3ad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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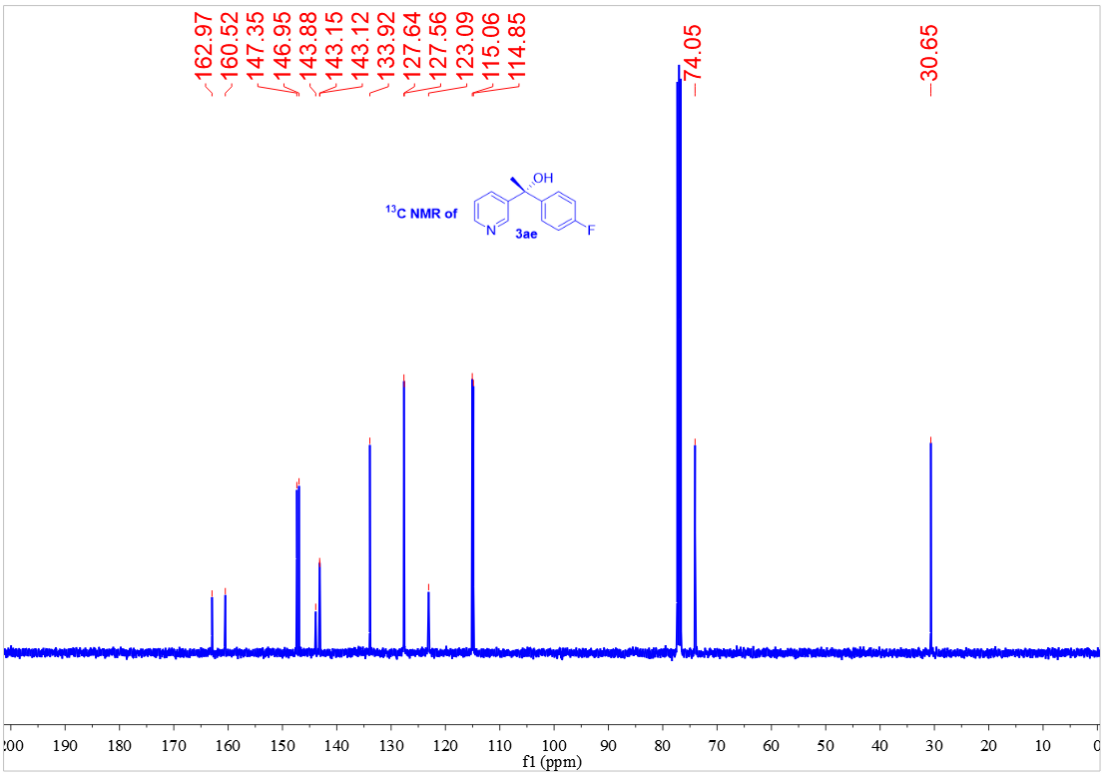
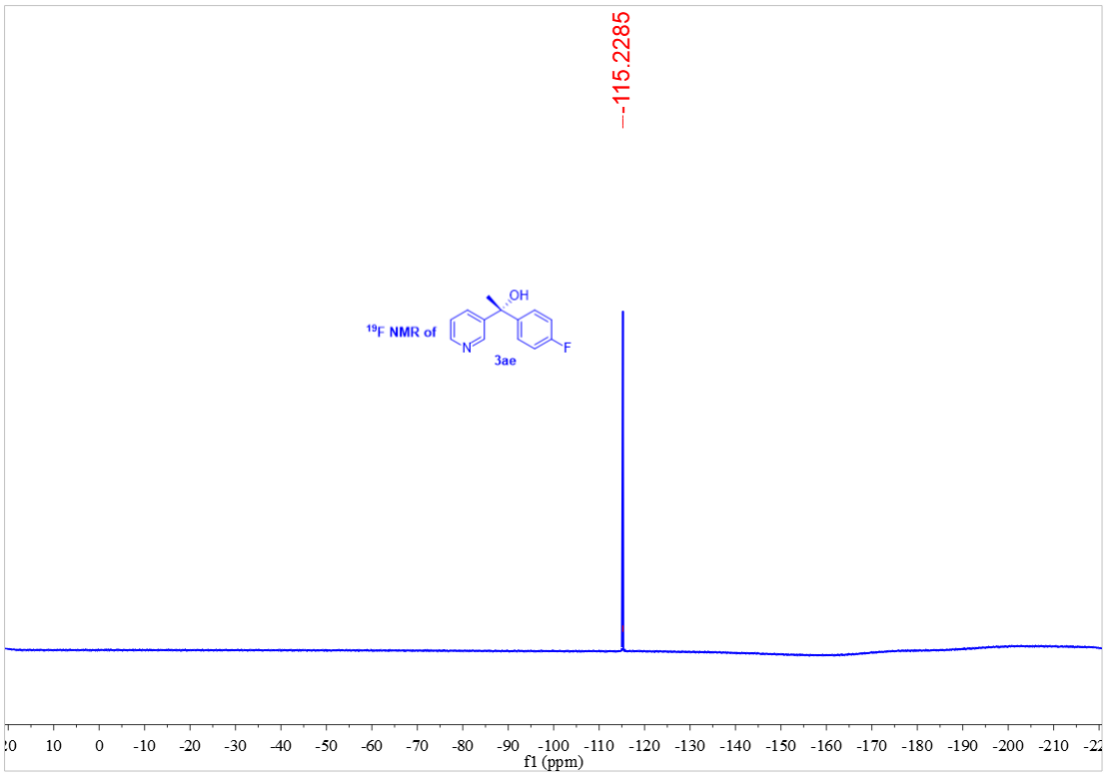
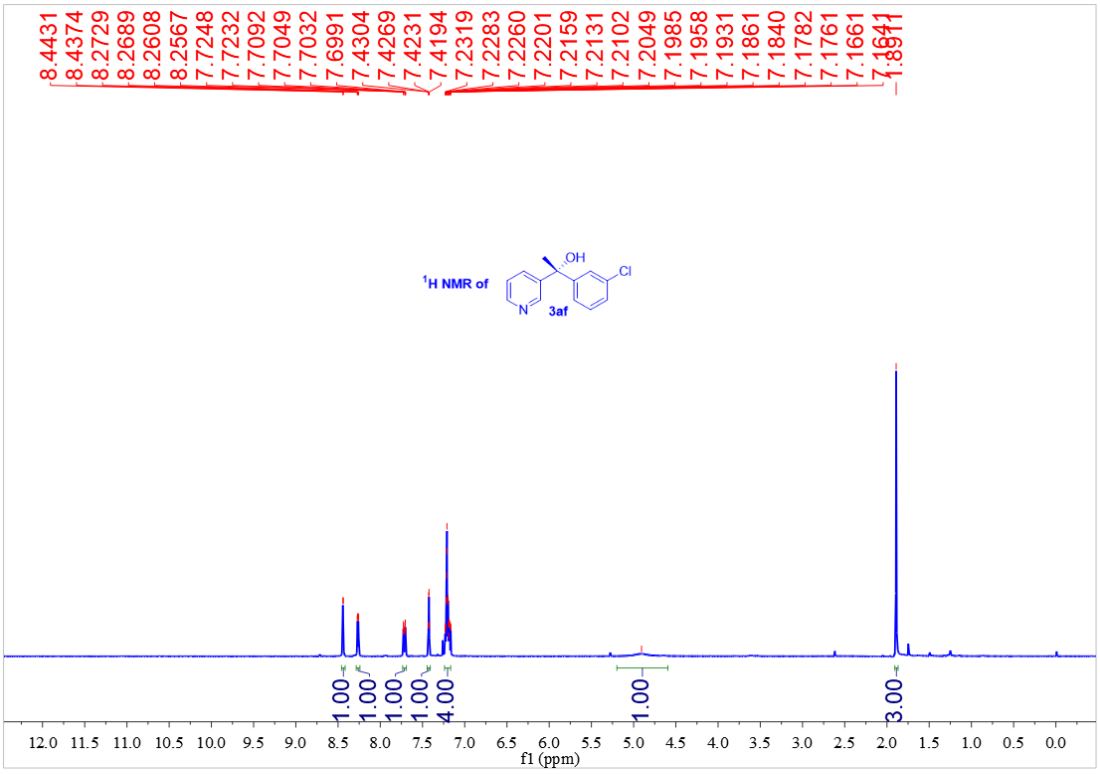
7.7142
7.7094
7.6992
7.6942
7.6893
7.3617
7.3537
7.3485
7.3404
7.3364
7.3315
7.3237
7.3182
7.3102
7.1824
7.1706
7.1623
7.1504
6.9847
6.9765
6.9712
6.9633
6.9600
6.9549
6.9497
6.9462
6.9386
6.9330
6.9251
4.8713
1.8856
1.8735
OH
N
F
1H NMR of
3ae
1.00
1.00
1.00
2.00
1.00
2.00
1.00
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


162.97
160.52
147.35
146.95
143.88
143.15
143.12
133.92
127.64
127.56
123.09
115.06
114.85
74.05
30.65
13C NMR of
3ae
OH
N
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-115.2285
19F NMR of
3ae
OH
N
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)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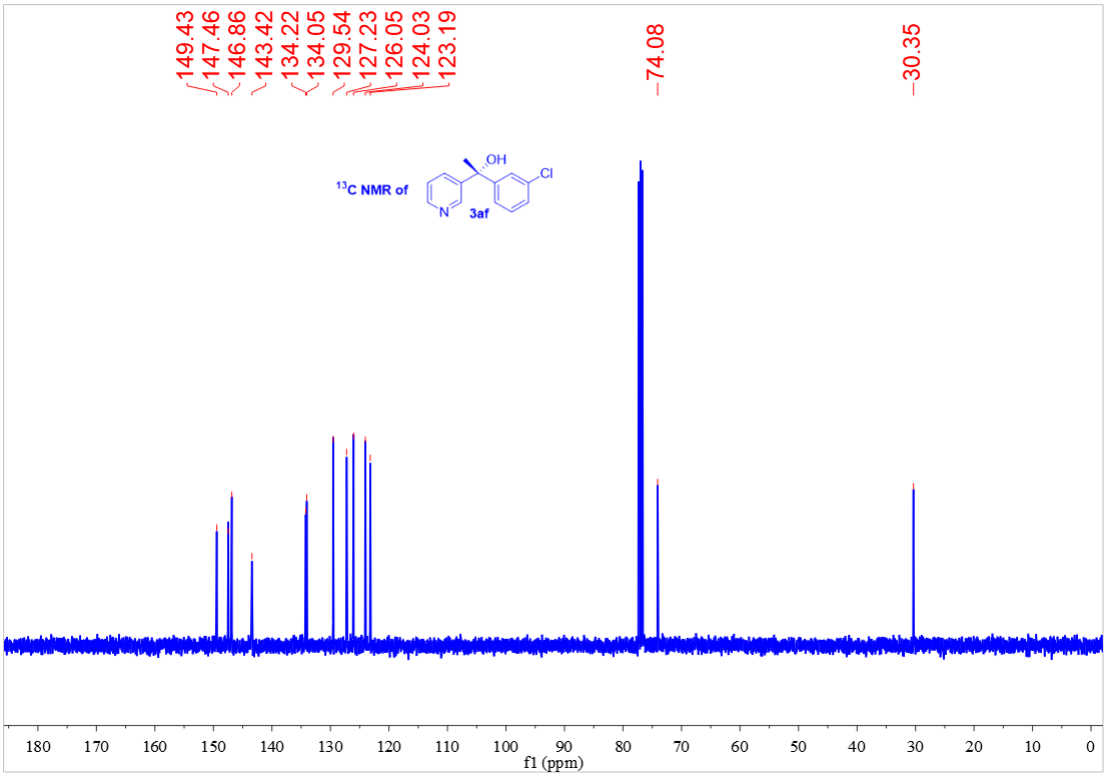
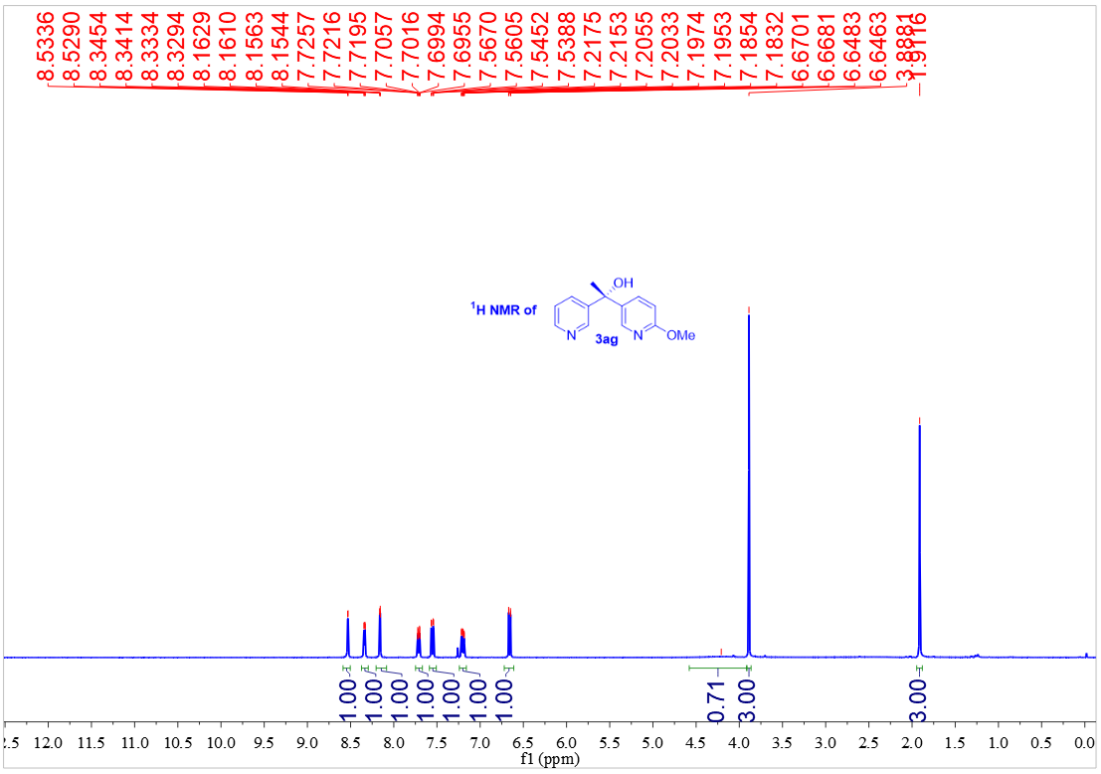
8.2689
8.2608
8.2567
7.7248
7.7232
7.7092
7.7049
7.7032
7.6991
7.4304
7.4269
7.4231
7.4194
7.2319
7.2283
7.2260
7.2201
7.2159
7.2131
7.2102
7.2049
7.1985
7.1958
7.1931
7.1861
7.1840
7.1782
7.1761
7.1661
1.8911
1H NMR of
OH
Cl
N
3af
1.00
1.00
1.00
1.00
4.00
1.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


149.43
147.46
146.86
143.42
134.22
134.05
129.54
127.23
126.05
124.03
123.19
74.08
30.35
13C NMR of
OH
Cl
N
3af
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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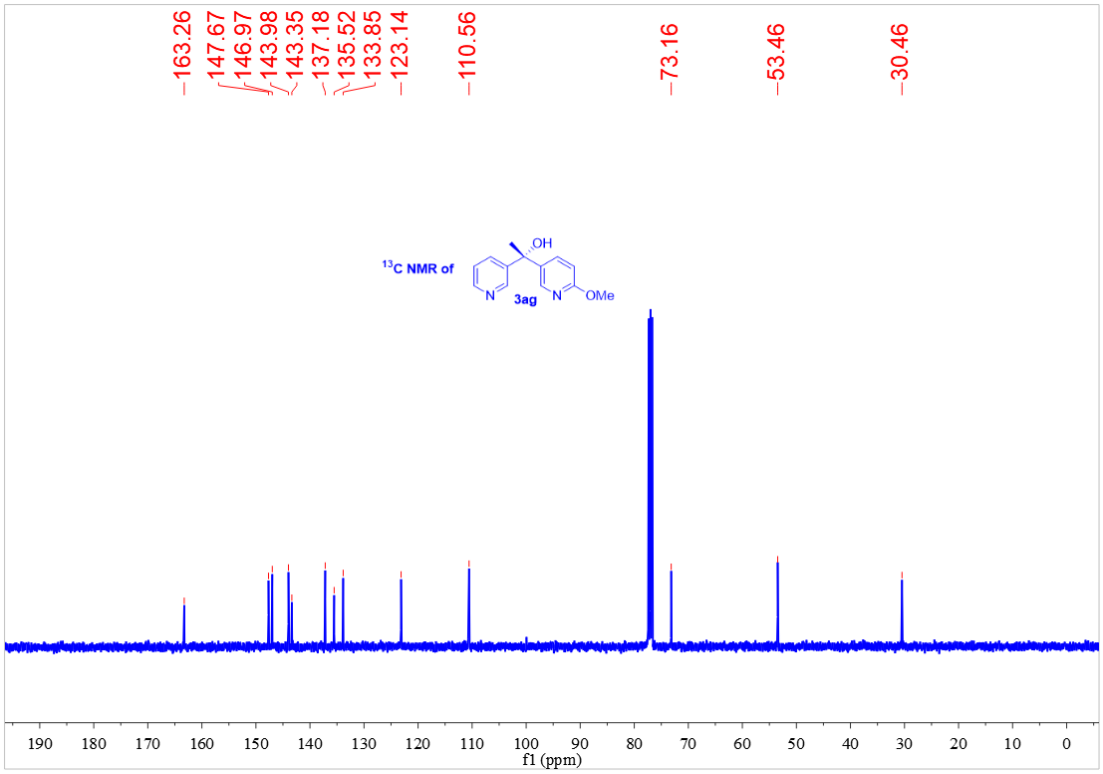
8.3334
8.3294
8.1629
8.1610
8.1563
8.1544
7.7257
7.7216
7.7195
7.7057
7.7016
7.6994
7.6955
7.5670
7.5605
7.5452
7.5388
7.2175
7.2153
7.2055
7.2033
7.1974
7.1953
7.1854
7.1832
6.6701
6.6681
6.6483
6.6463
3.8881
1.9116
^{1}H NMR of
3ag
OH
OMe
1.00
1.00
1.00
1.00
1.00
1.00
1.00
0.71
3.00
3.00
f1 (ppm)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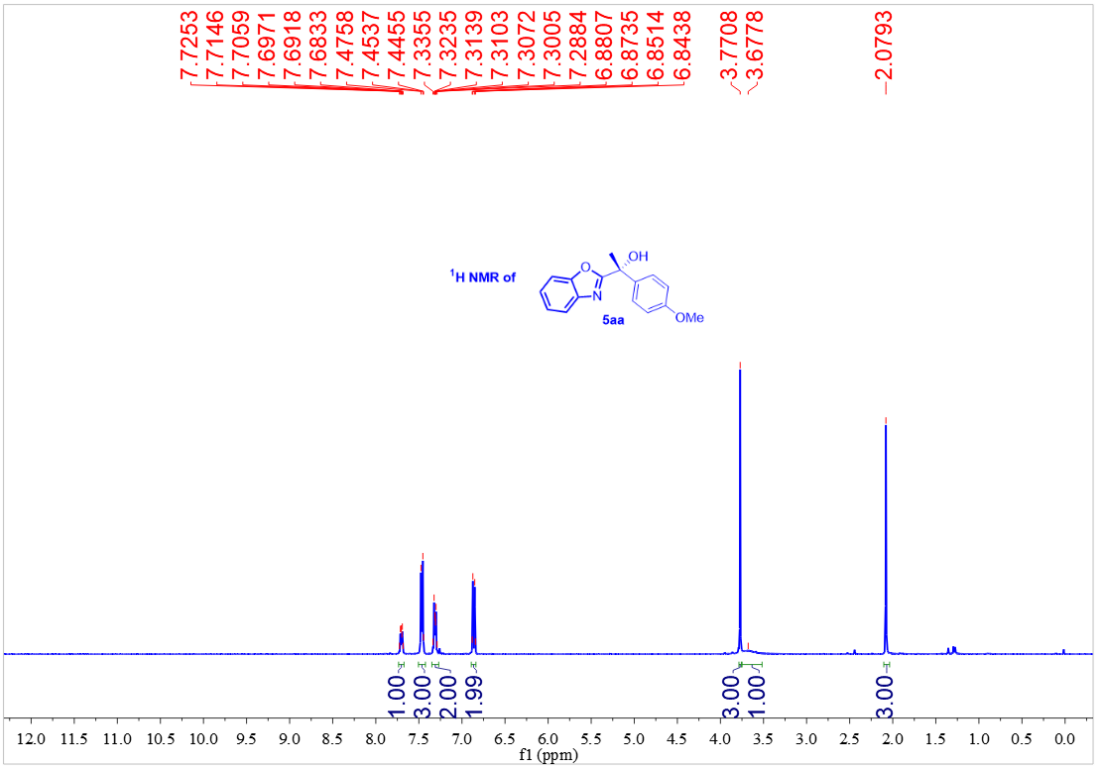
146.97
143.98
143.35
137.18
135.52
133.85
123.14
110.56
73.16
53.46
30.46
^{13}C NMR of
3ag
OH
OMe
f1 (ppm)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7.6918
7.6833
7.4758
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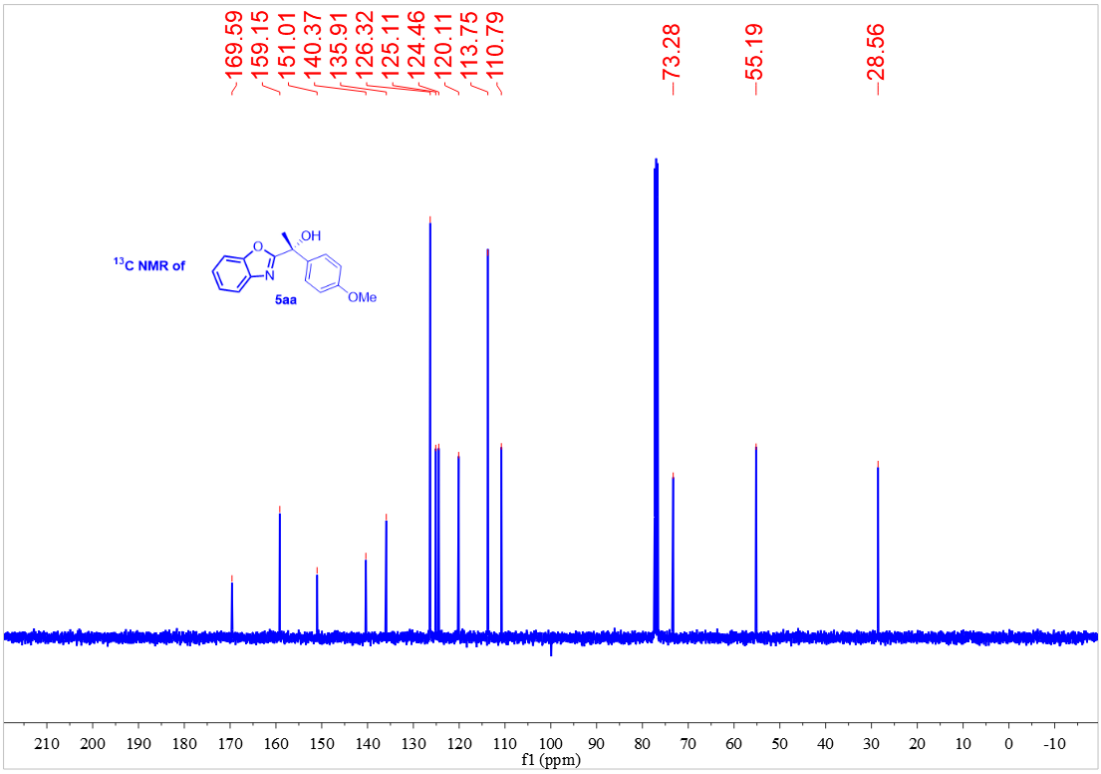
7.4455
7.3355
7.3235
7.3139
7.3103
7.3072
7.3005
7.2884
6.8807
6.8735
6.8514
6.8438
3.7708
3.6778
2.0793
1H NMR of
5aa
OH
OMe
1.00
3.00
2.00
1.99
3.00
1.00
3.00
f1 (ppm)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140.37
135.91
126.32
125.11
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120.11
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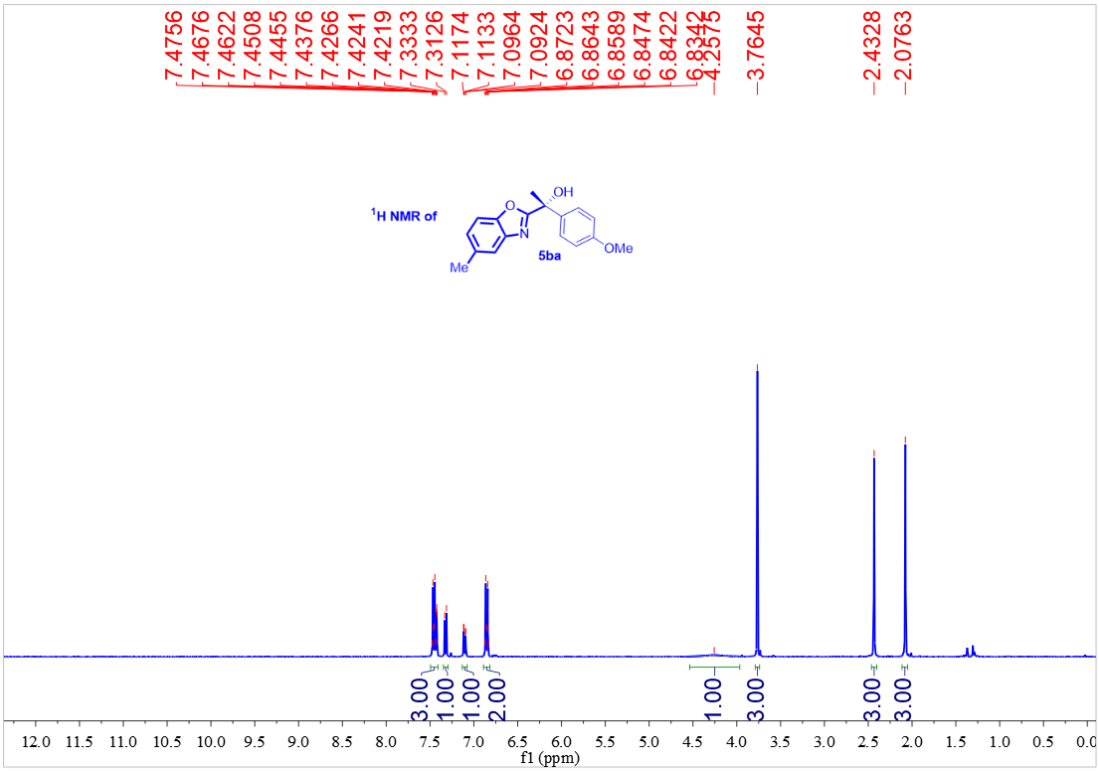
110.79
73.28
55.19
28.56
13C NMR of
5aa
OH
OMe
f1 (ppm)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7.4266
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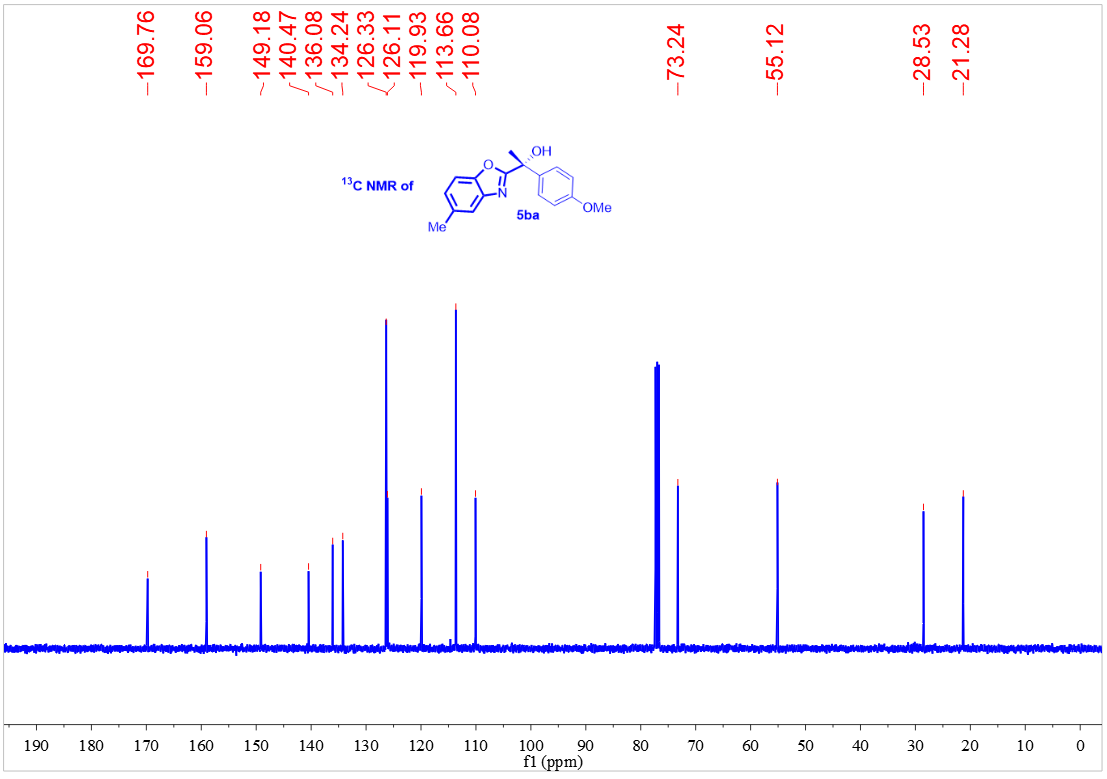
7.3333
7.3126
7.1174
7.1133
7.0964
7.0924
6.8723
6.8643
6.8589
6.8474
6.8422
6.8342
4.2575
3.7645
2.4328
2.0763
1H NMR of
OH
O
N
OMe
Me
5ba
3.00
1.00
1.00
2.00
1.00
3.00
3.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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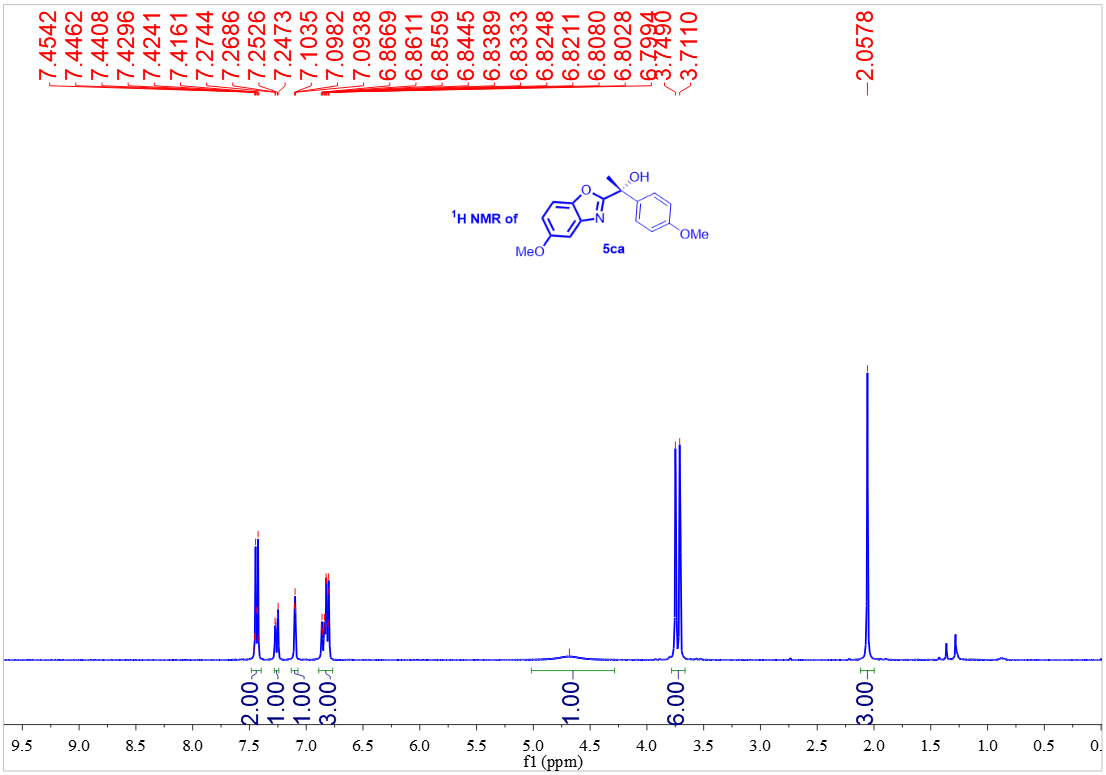
140.47
136.08
134.24
126.33
126.11
119.93
113.66
110.08
73.24
55.12
28.53
21.28
13C NMR of
OH
O
N
OMe
Me
5ba
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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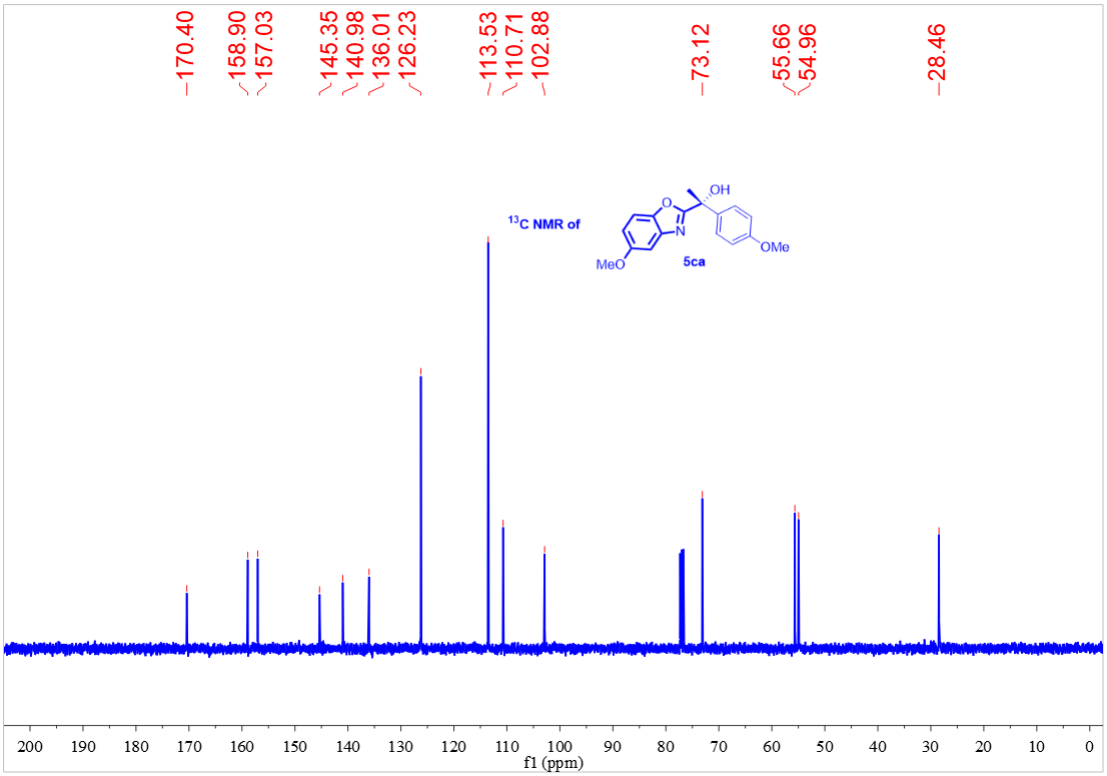
7.2473
7.1035
7.0982
7.0938
6.8669
6.8611
6.8559
6.8445
6.8389
6.8333
6.8248
6.8211
6.8080
6.8028
3.7994
3.7490
3.7110
2.0578
^{1}H NMR of
5ca
2.00
1.00
1.00
3.00
1.00
6.00
3.00
f1 (ppm)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140.98
136.01
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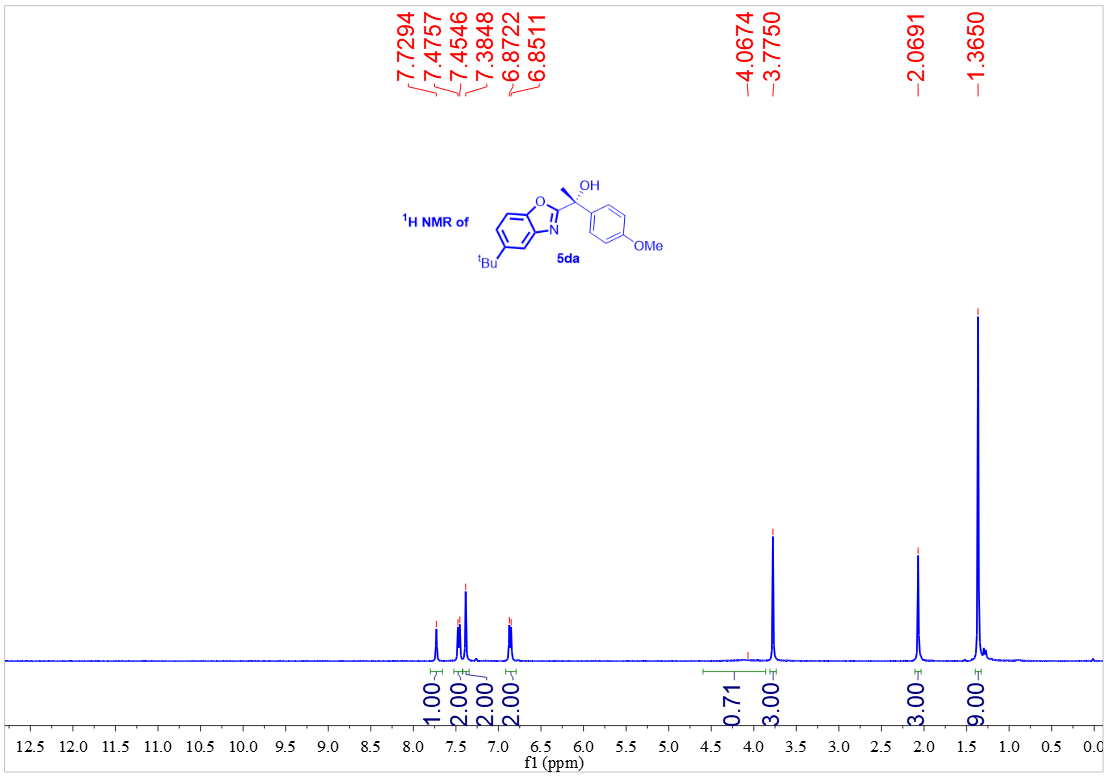
110.71
102.88
73.12
55.66
54.96
28.46
^{13}C NMR of
5ca
f1 (ppm)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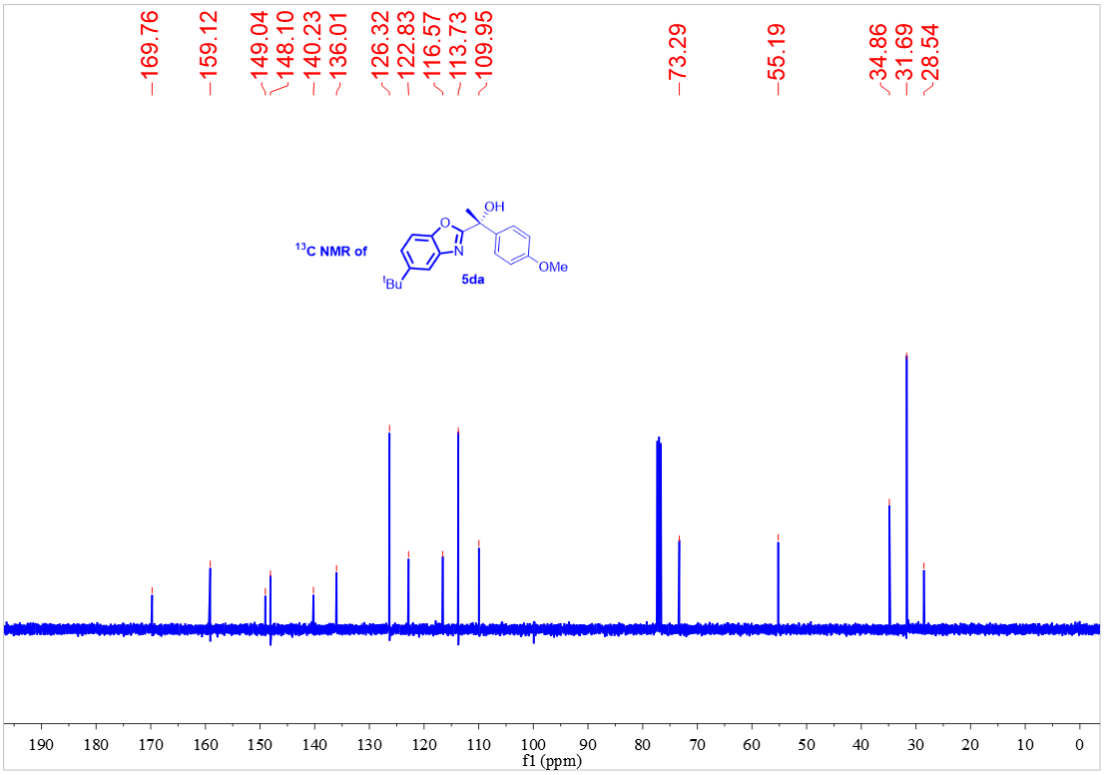
7.4757
7.4546
7.3848
6.8722
6.8511
4.0674
3.7750
2.0691
1.3650
1H NMR of
5da
1.00
2.00
2.00
2.00
0.71
3.00
3.00
9.00
f1 (ppm)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136.01
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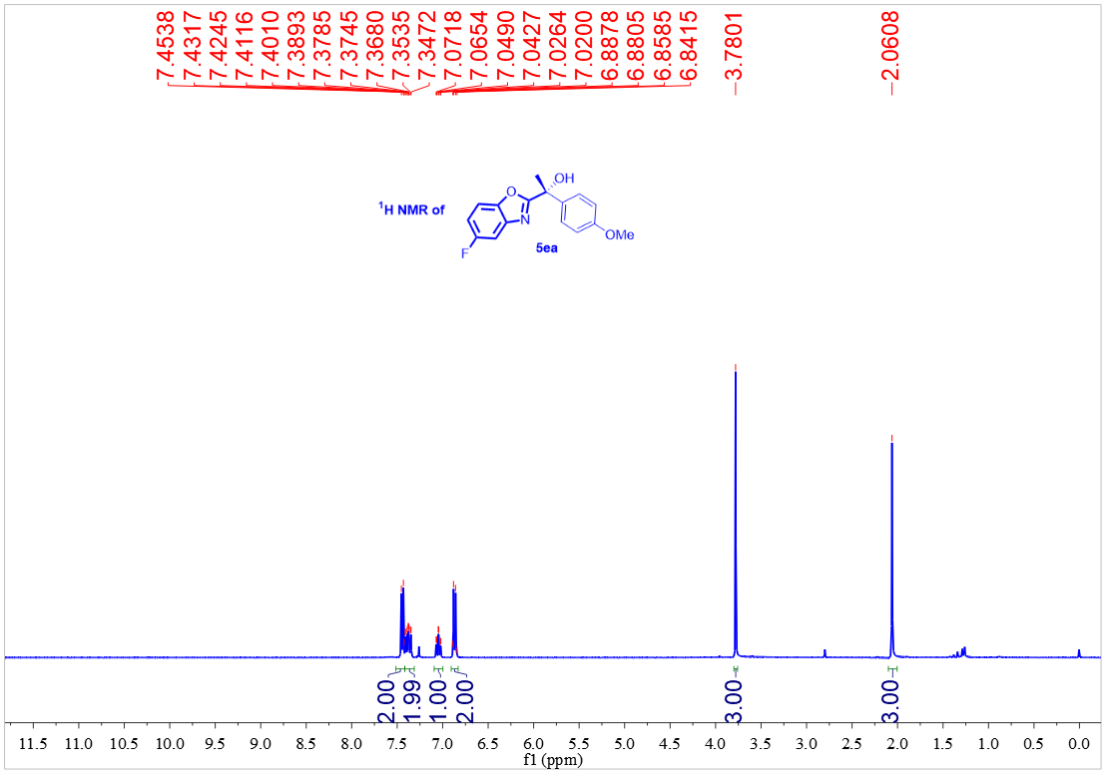
34.86
31.69
28.54
13C NMR of
5da
f1 (ppm)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7.3785
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7.3680
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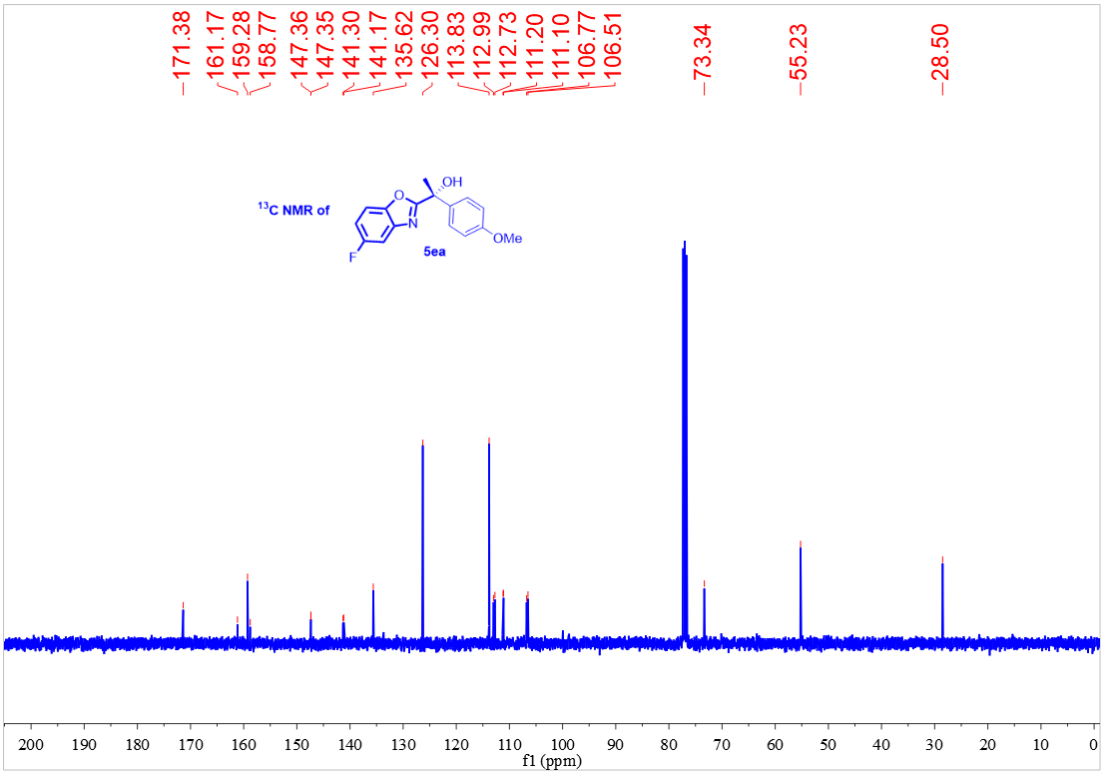
7.3472
7.0718
7.0654
7.0490
7.0427
7.0264
7.0200
6.8878
6.8805
6.8585
6.8415
3.7801
2.0608
1H NMR of
5ea
OH
OMe
F
2.00
1.99
1.00
2.00
3.00
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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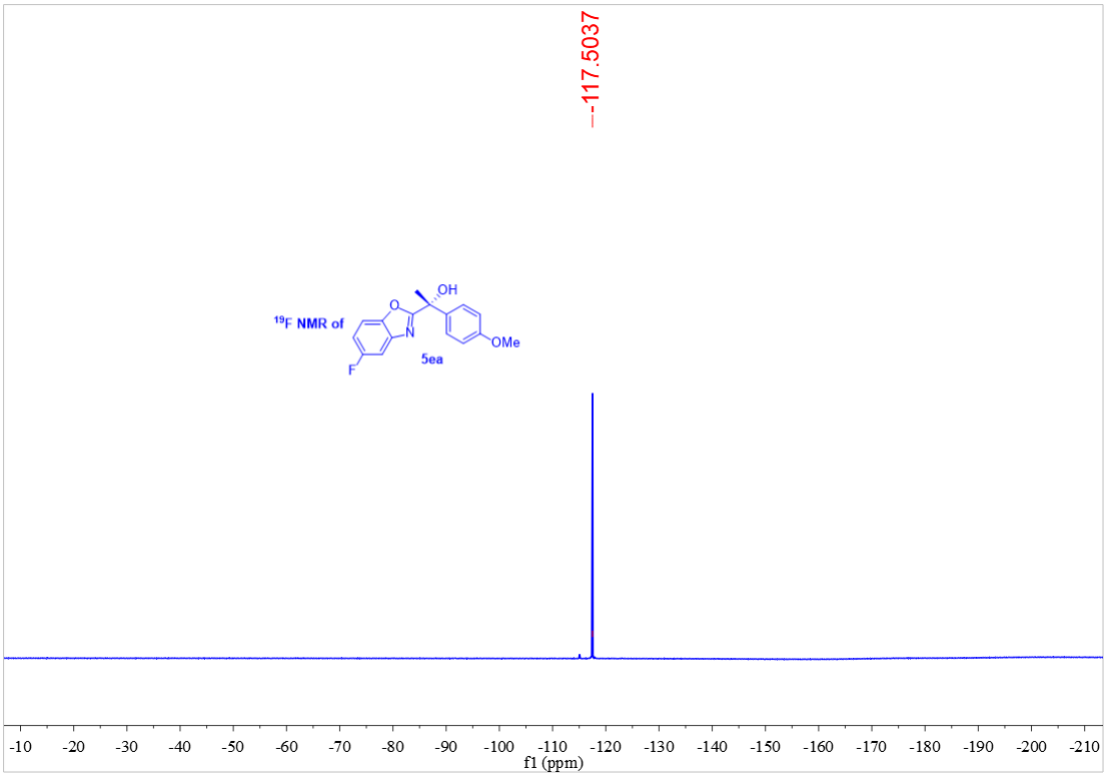
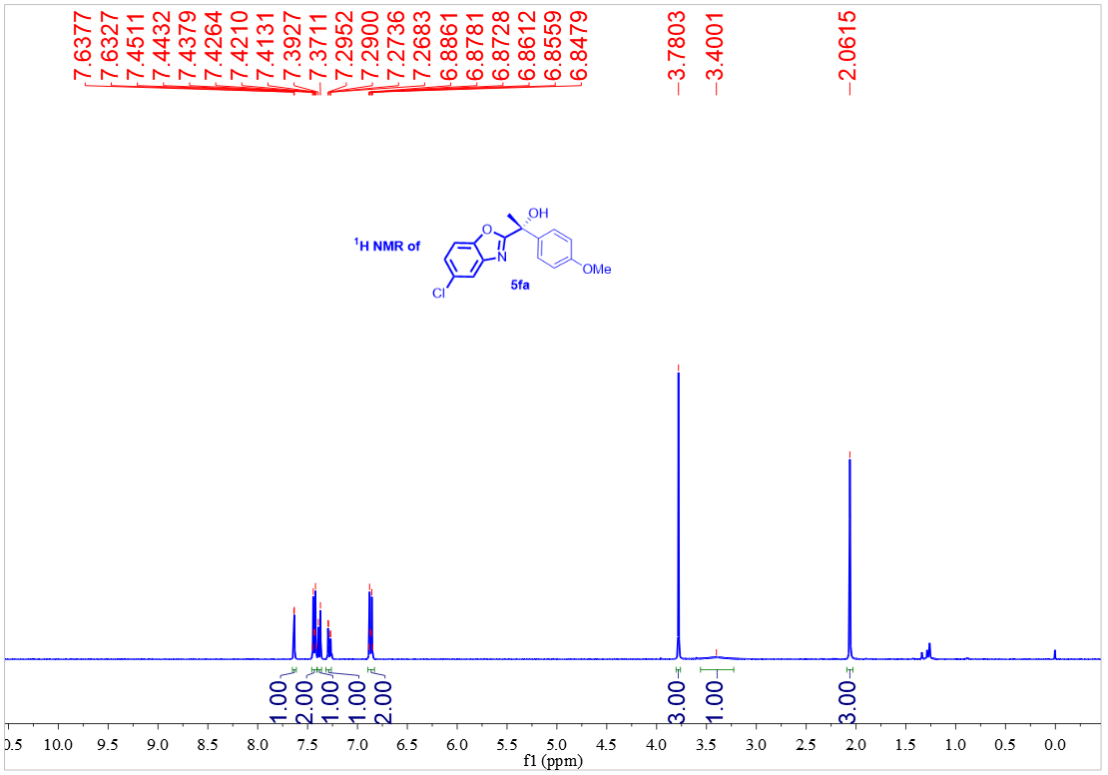
126.30
113.83
112.99
112.73
111.20
111.10
106.77
106.51
73.34
55.23
28.50
13C NMR of
5ea
OH
OMe
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-117.5037
19F NMR of
5ea
OH
OMe
F
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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7.3711
7.2952
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7.2683
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6.8781
6.8728
6.8612
6.8559
6.8479
3.7803
3.4001
2.0615
1H NMR of
5fa
OH
OMe
Cl
1.00
2.00
1.00
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3.00
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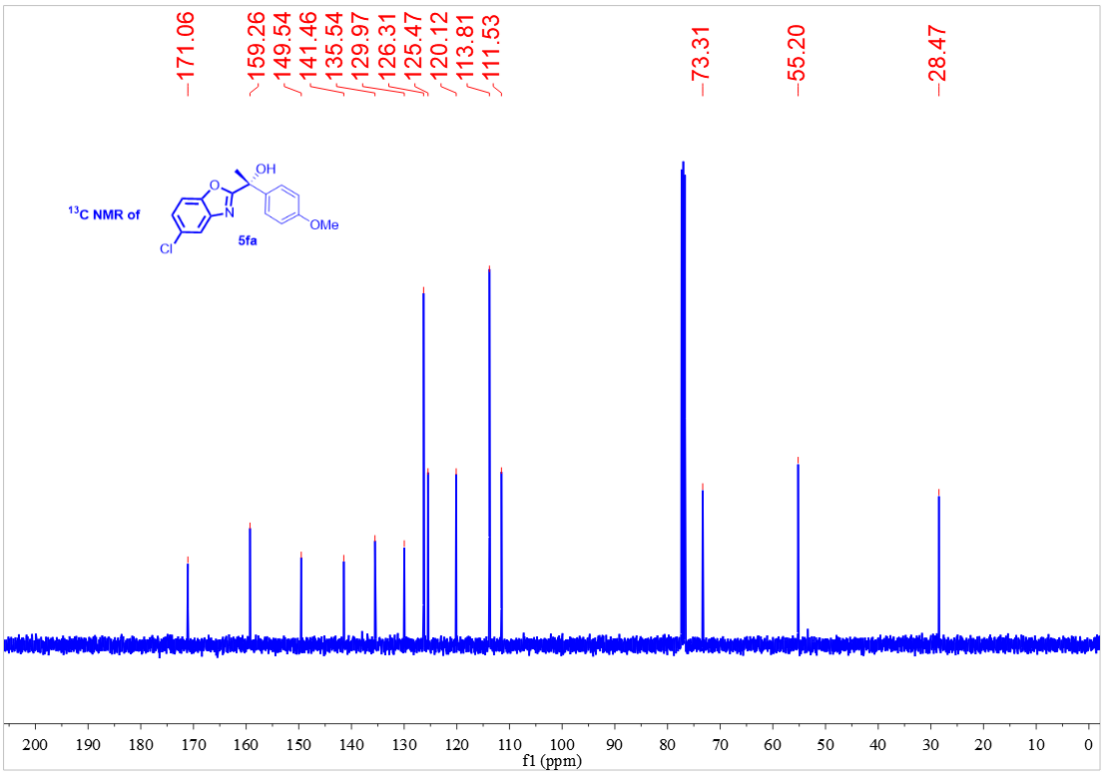
3.00
f1 (ppm)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55.20
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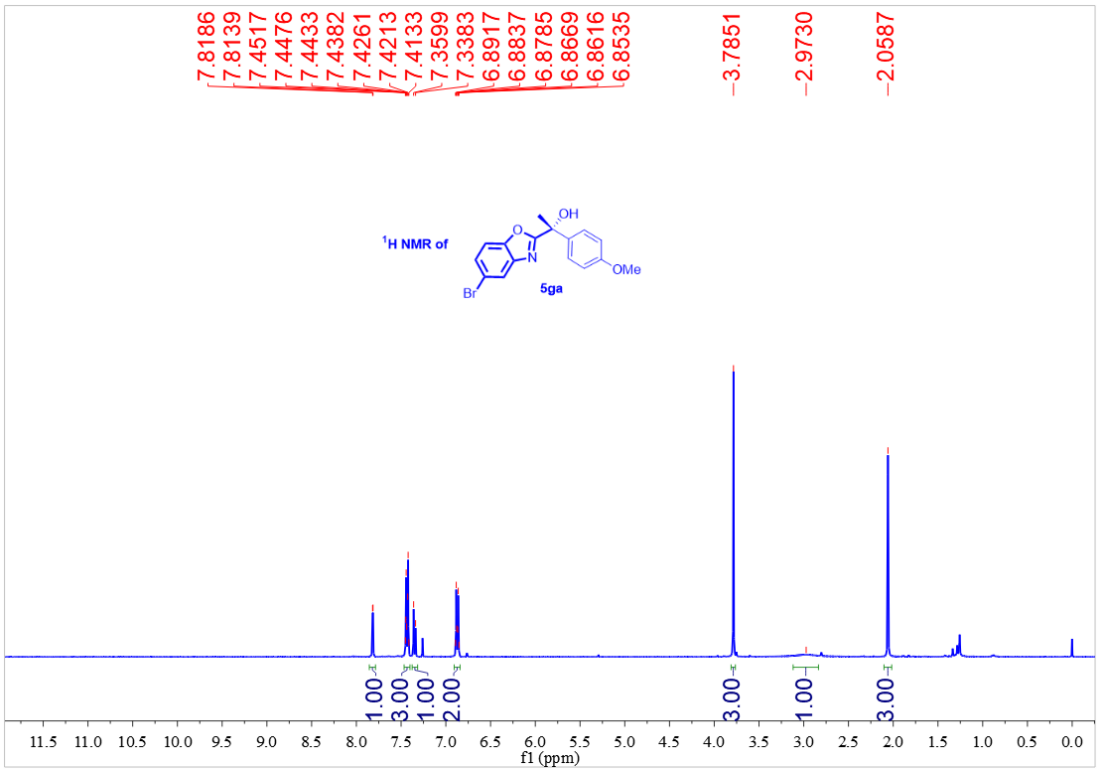
13C NMR of
5fa
OH
OMe
Cl
f1 (ppm)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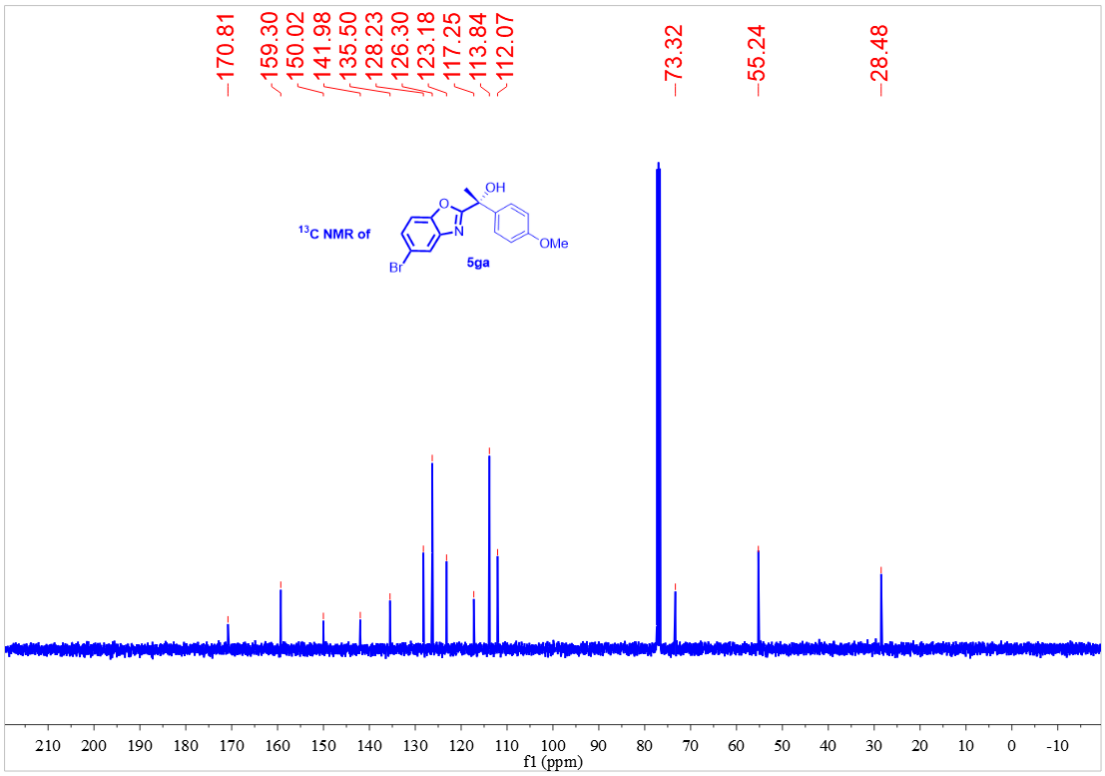
7.3383
6.8917
6.8837
6.8785
6.8669
6.8616
6.8535
3.7851
2.9730
2.0587
1H NMR of
5ga
OH
OMe
Br
1.00
3.00
1.00
2.00
3.00
1.00
3.00
f1 (ppm)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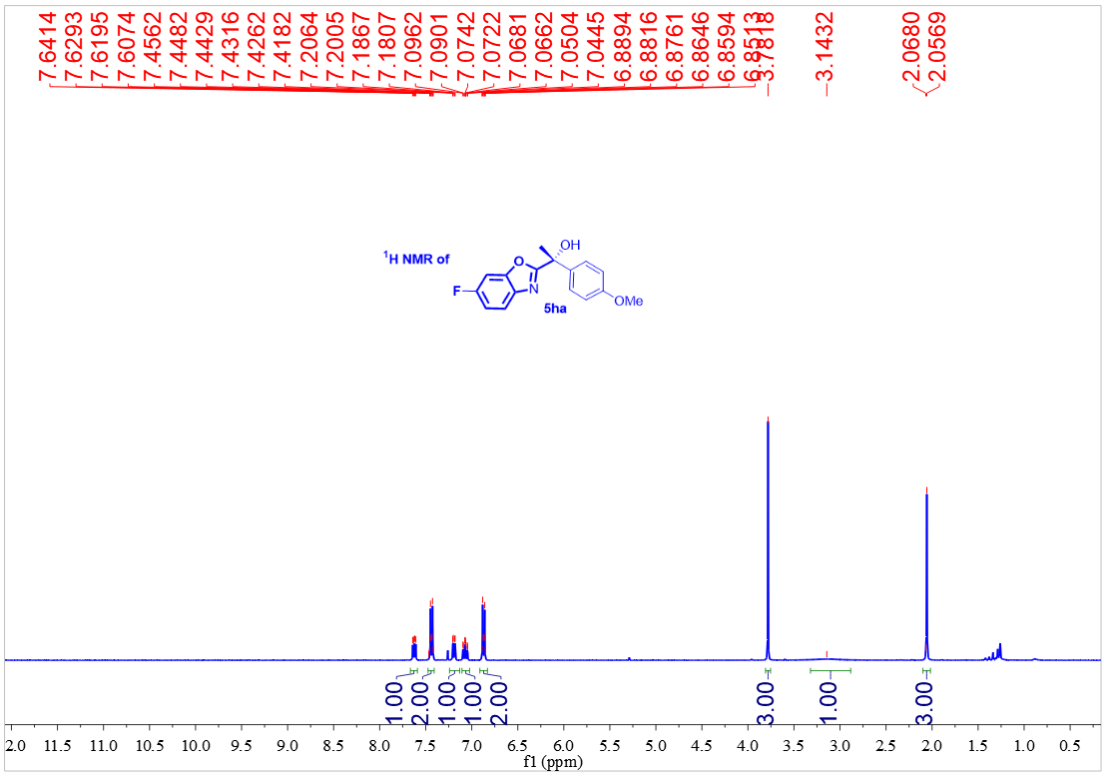
128.23
126.30
123.18
117.25
113.84
112.07
73.32
55.24
28.48
13C NMR of
OH
O
N
OMe
Br
5ga
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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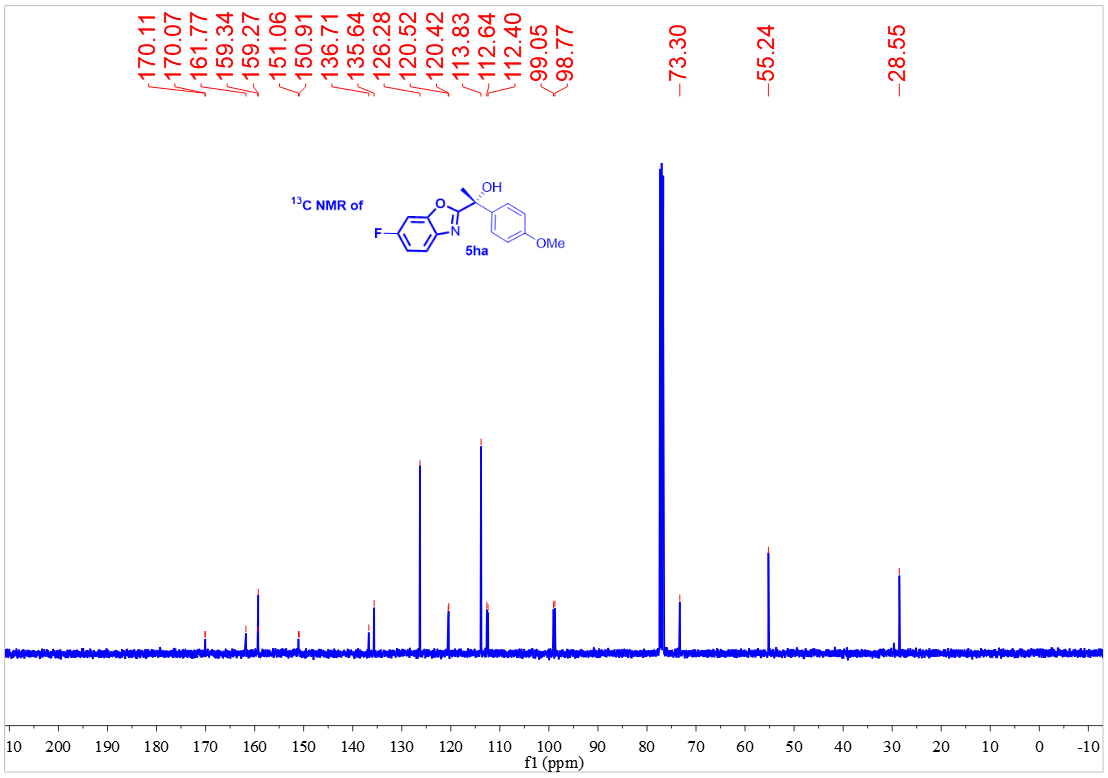
7.2005
7.1867
7.1807
7.0962
7.0901
7.0742
7.0722
7.0681
7.0662
7.0504
7.0445
6.8894
6.8816
6.8761
6.8646
6.8594
6.8513
3.7818
3.1432
2.0680
2.0569
1H NMR of
OH
O
N
F
OMe
5ha
1.00
2.00
1.00
1.00
2.00
3.00
1.00
3.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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112.64
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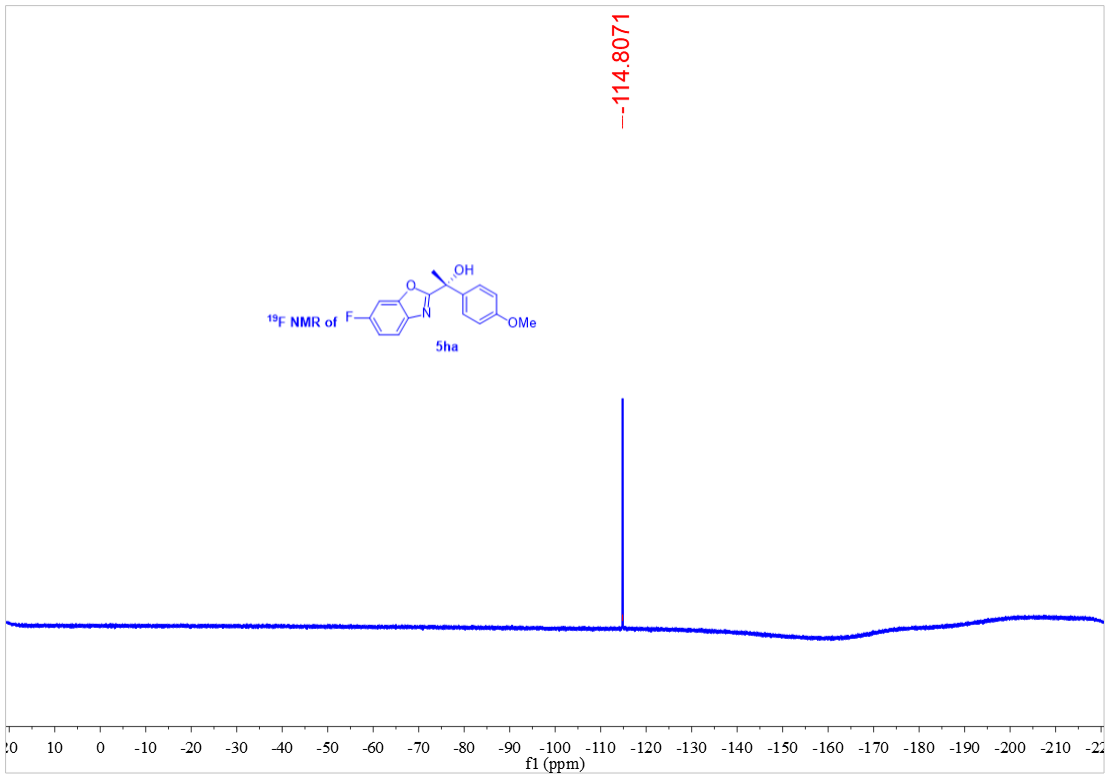
73.30
55.24
28.55
13C NMR of
OH
F
O
N
OMe
5ha
f1 (ppm)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OH
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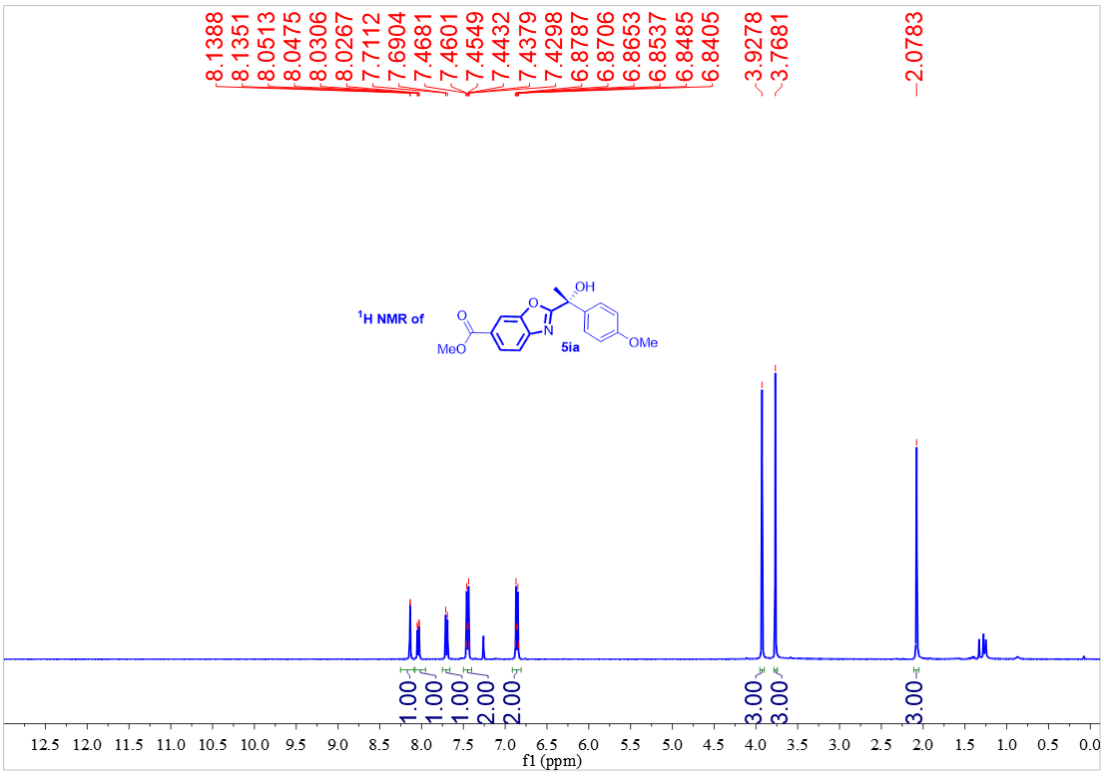
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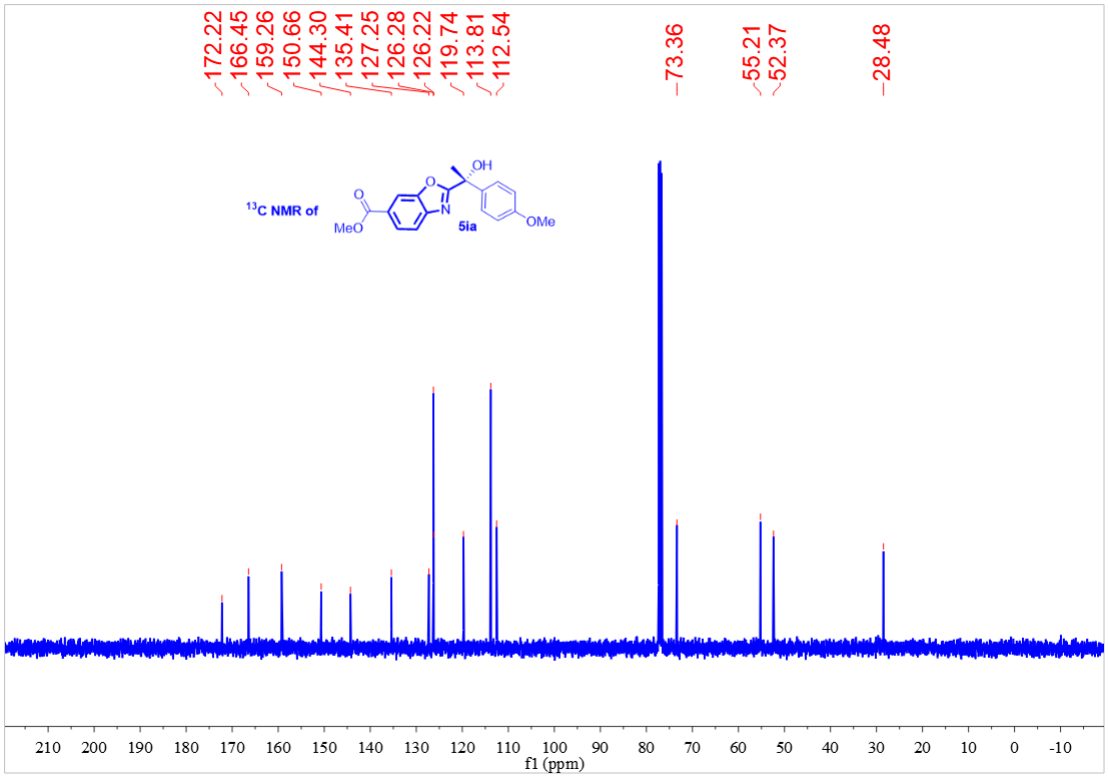
7.4432
7.4379
7.4298
6.8787
6.8706
6.8653
6.8537
6.8485
6.8405
3.9278
3.7681
2.0783
1H NMR of
MeO
OH
OMe
5ia
1.00
1.00
1.00
2.00
2.00
3.00
3.00
3.00
f1 (ppm)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144.30
135.41
127.25
126.28
126.22
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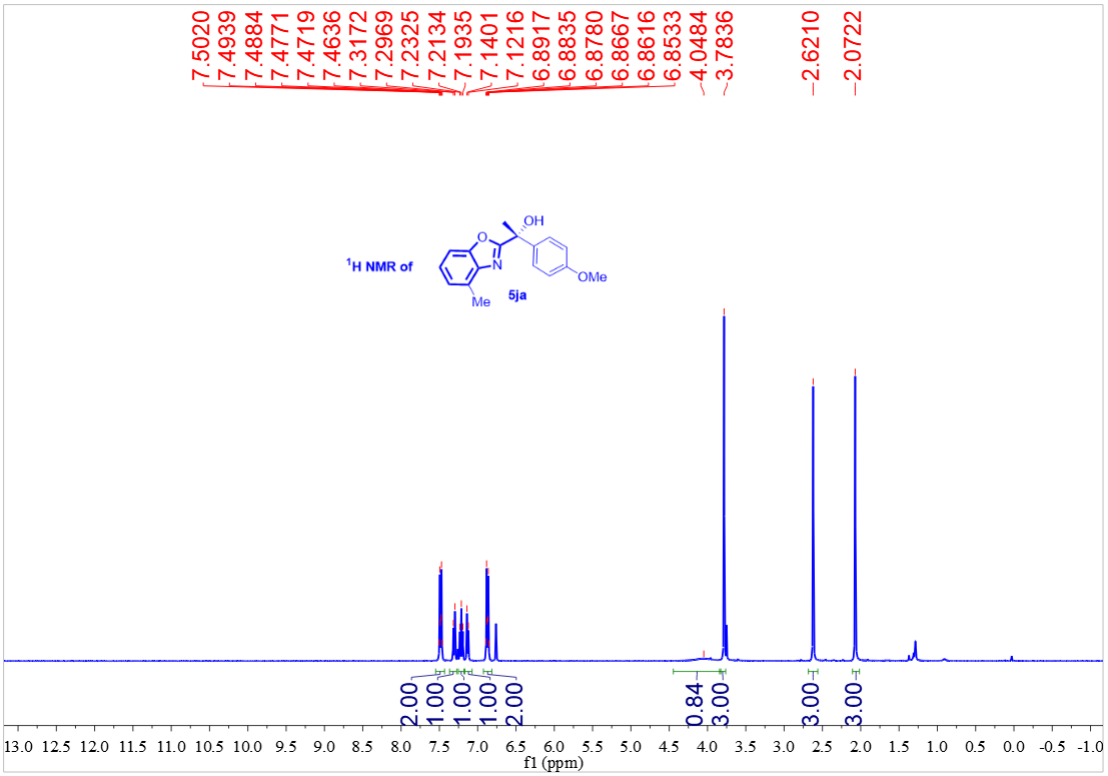
73.36
55.21
52.37
28.48
13C NMR of
MeO
OH
OMe
5ia
f1 (ppm)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7.1935
7.1401
7.1216
6.8917
6.8835
6.8780
6.8667
6.8616
6.8533
4.0484
3.7836
2.6210
2.0722
1H NMR of
OH
OMe
Me
5ja
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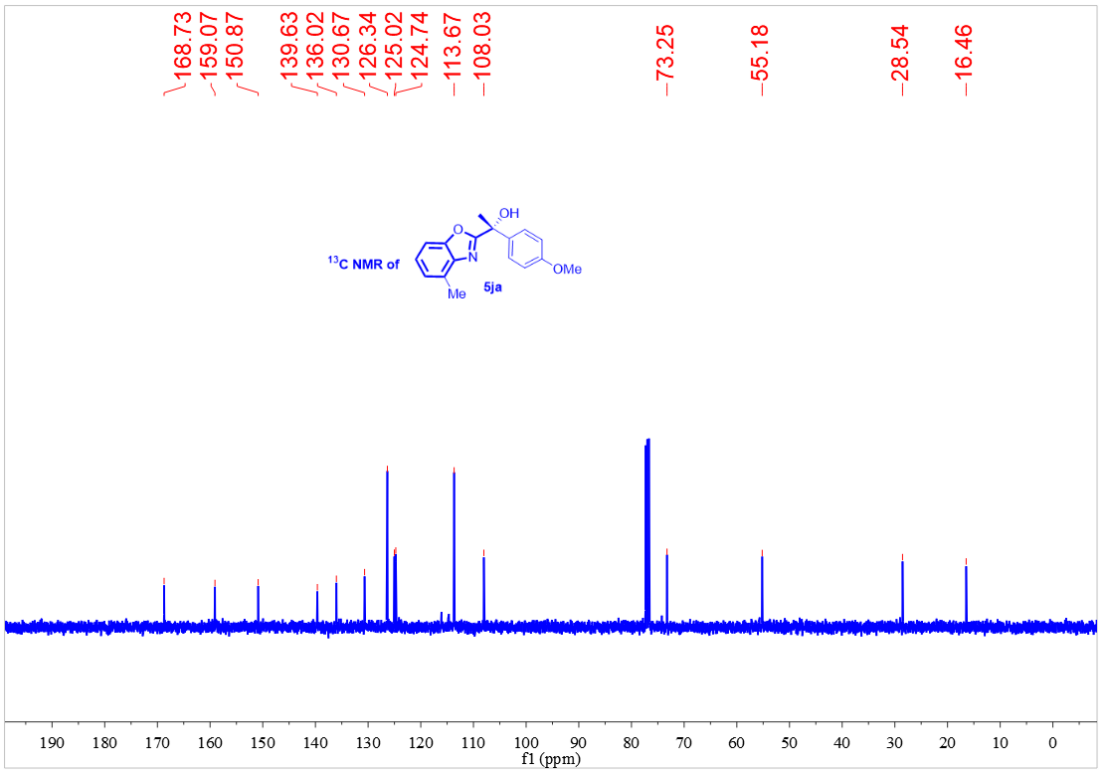
1.00
1.00
1.00
2.00
0.84
3.00
3.00
3.00
f1 (ppm)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139.63
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130.67
126.34
125.02
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113.67
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73.25
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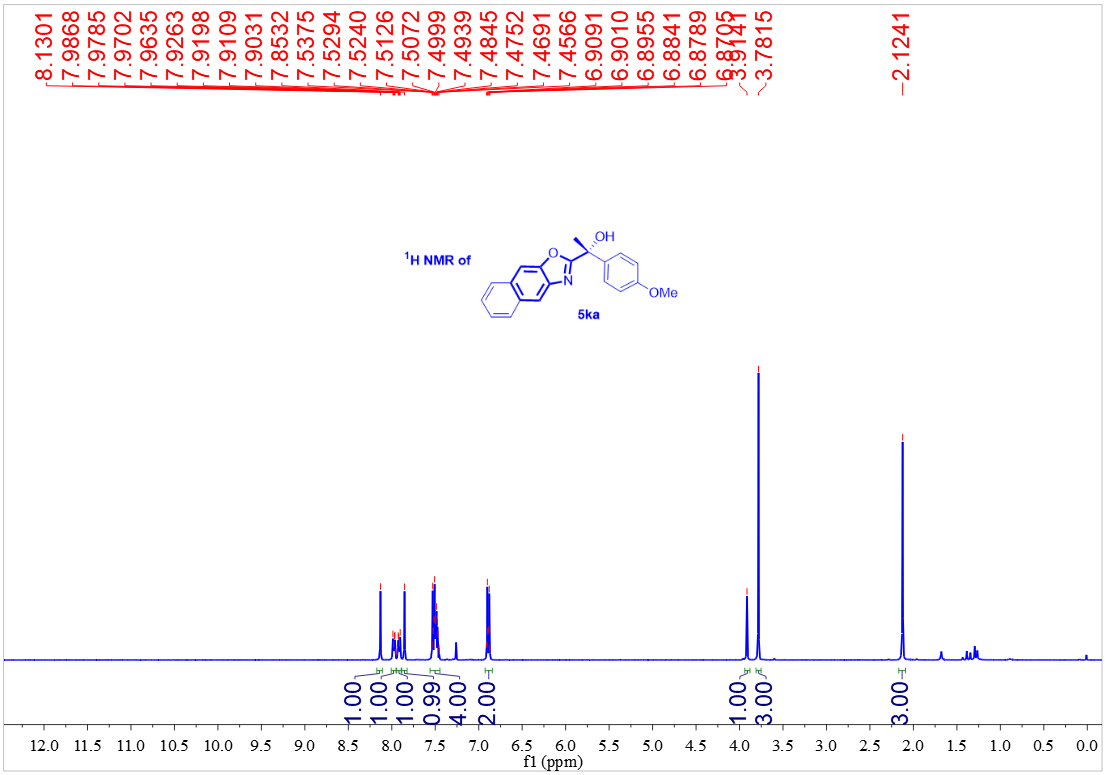
28.54
16.46
13C NMR of
OH
OMe
Me
5ja
f1 (ppm)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7.9198
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7.8532
7.5375
7.5294
7.5240
7.5126
7.5072
7.4999
7.4939
7.4845
7.4752
7.4691
7.4566
6.9091
6.9010
6.8955
6.8841
6.8789
3.9141
3.7815
2.1241
1H NMR of
OH
OMe
5ka
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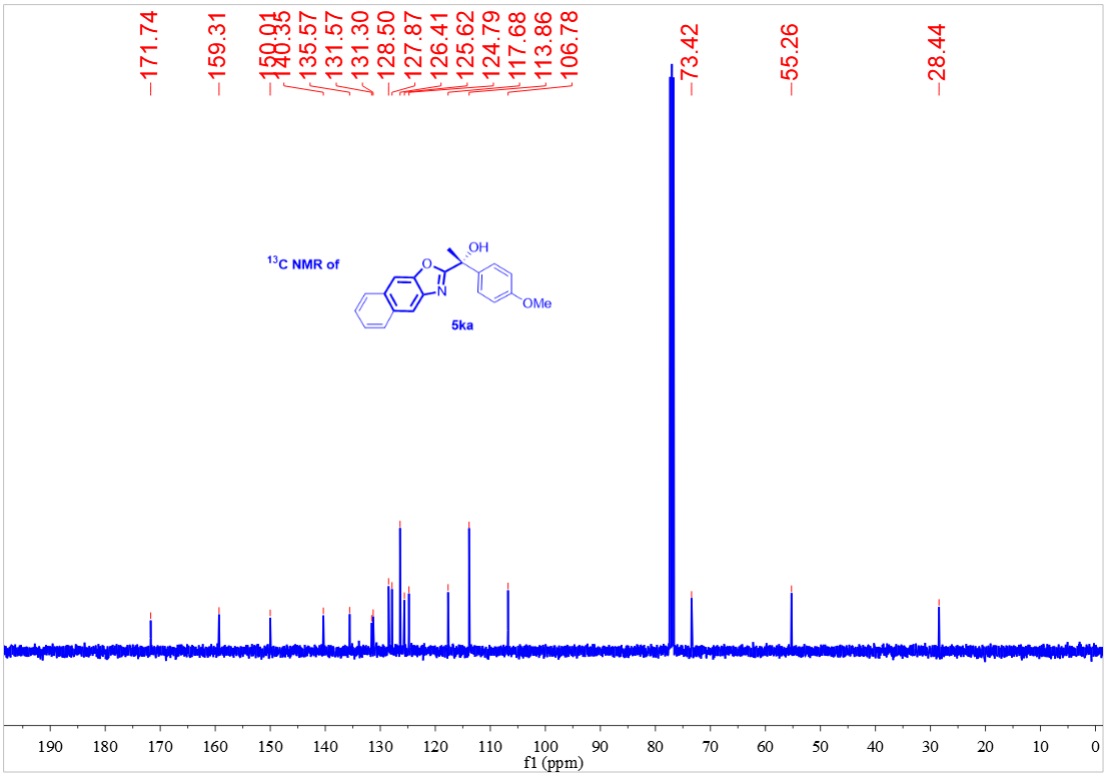
1.00
1.00
0.99
4.00
2.00
1.00
3.00
3.00
f1 (ppm)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125.62
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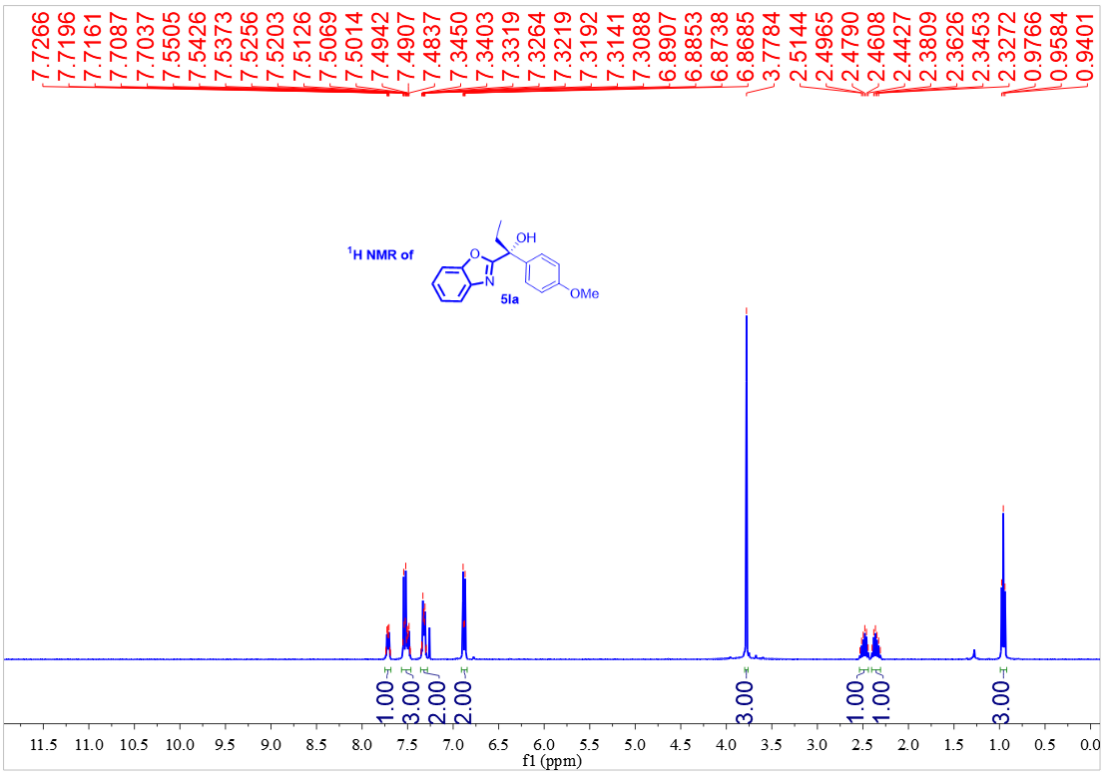
113.86
106.78
73.42
55.26
28.44
13C NMR of
OH
OMe
5ka
f1 (ppm)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7.5069
7.5014
7.4942
7.4907
7.4837
7.3450
7.3403
7.3319
7.3264
7.3219
7.3192
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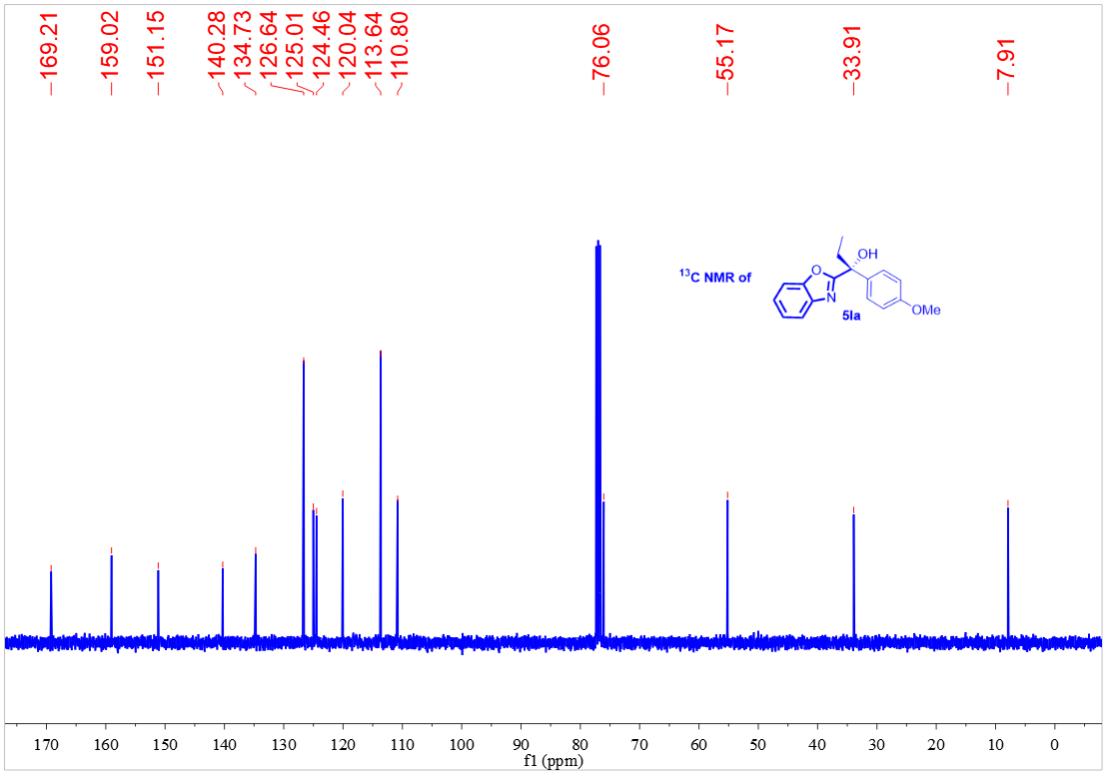
7.3088
6.8907
6.8853
6.8738
6.8685
3.7784
2.5144
2.4965
2.4790
2.4608
2.4427
2.3809
2.3626
2.3453
2.3272
0.9766
0.9584
0.9401
^{1}H NMR of
OH
O
N
OMe
5la
1.00
3.00
2.00
2.00
3.00
1.00
1.00
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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151.15
140.28
134.73
126.64
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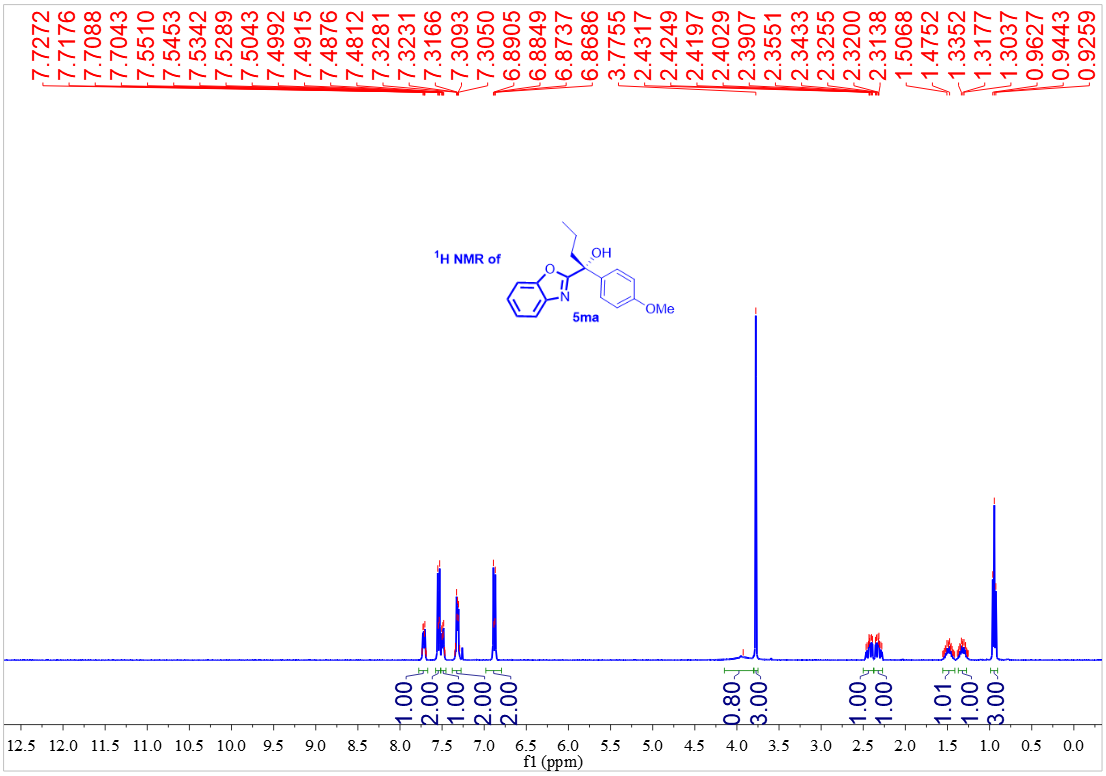
124.46
120.04
113.64
110.80
76.06
55.17
33.91
7.91
^{13}C NMR of
OH
O
N
OMe
5la
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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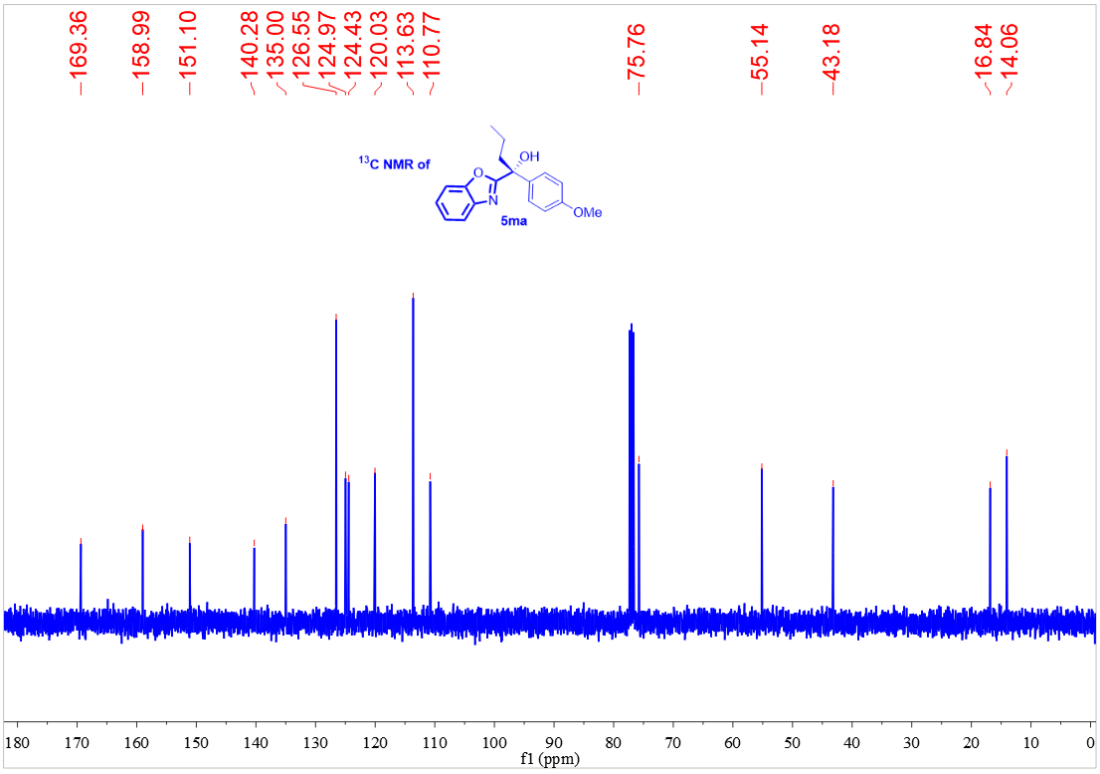
7.4915
7.4876
7.4812
7.3281
7.3231
7.3166
7.3093
7.3050
6.8905
6.8849
6.8737
6.8686
3.7755
2.4317
2.4249
2.4197
2.4029
2.3907
2.3551
2.3433
2.3255
2.3200
2.3138
1.5068
1.4752
1.3352
1.3177
1.3037
0.9627
0.9443
0.9259
1H NMR of
OH
OMe
5ma
1.00
2.00
1.00
2.00
2.00
0.80
3.00
1.00
1.00
1.01
1.00
3.00
f1 (ppm)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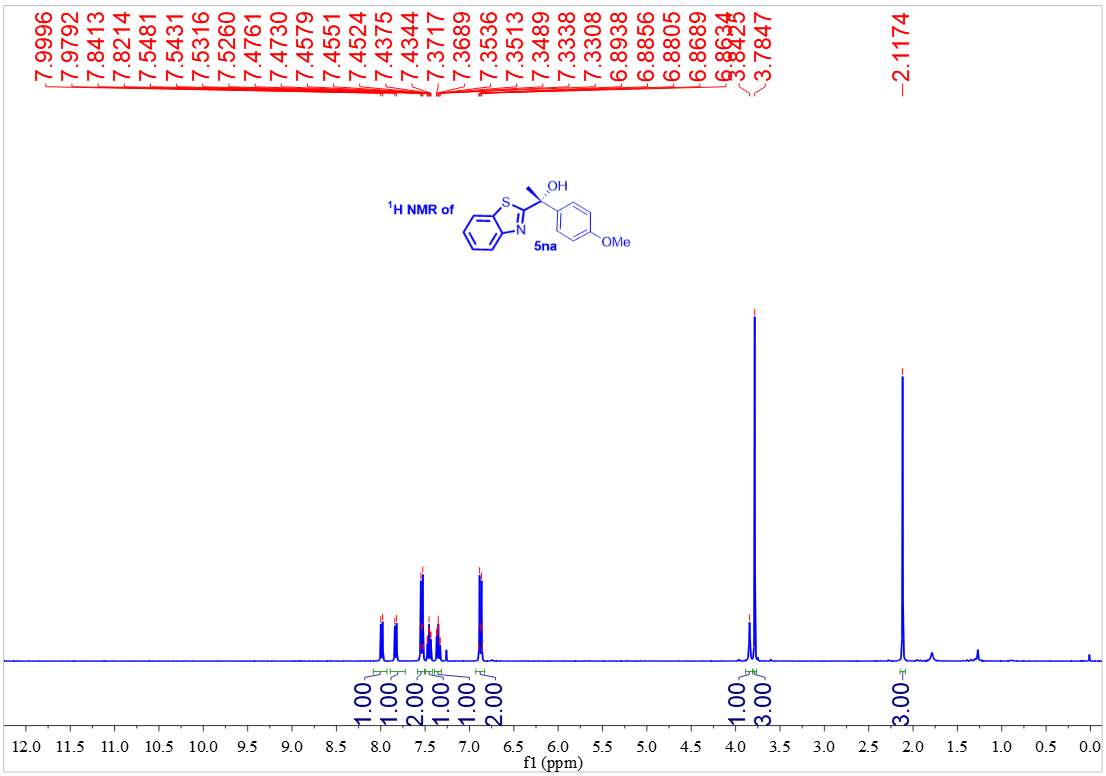
14.06
13C NMR of
OH
OMe
5ma
f1 (ppm)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7.4551
7.4524
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7.4344
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7.3308
6.8938
6.8856
6.8805
6.8689
6.8634
3.8425
3.7847
2.1174
1H NMR of
5na
OH
OMe
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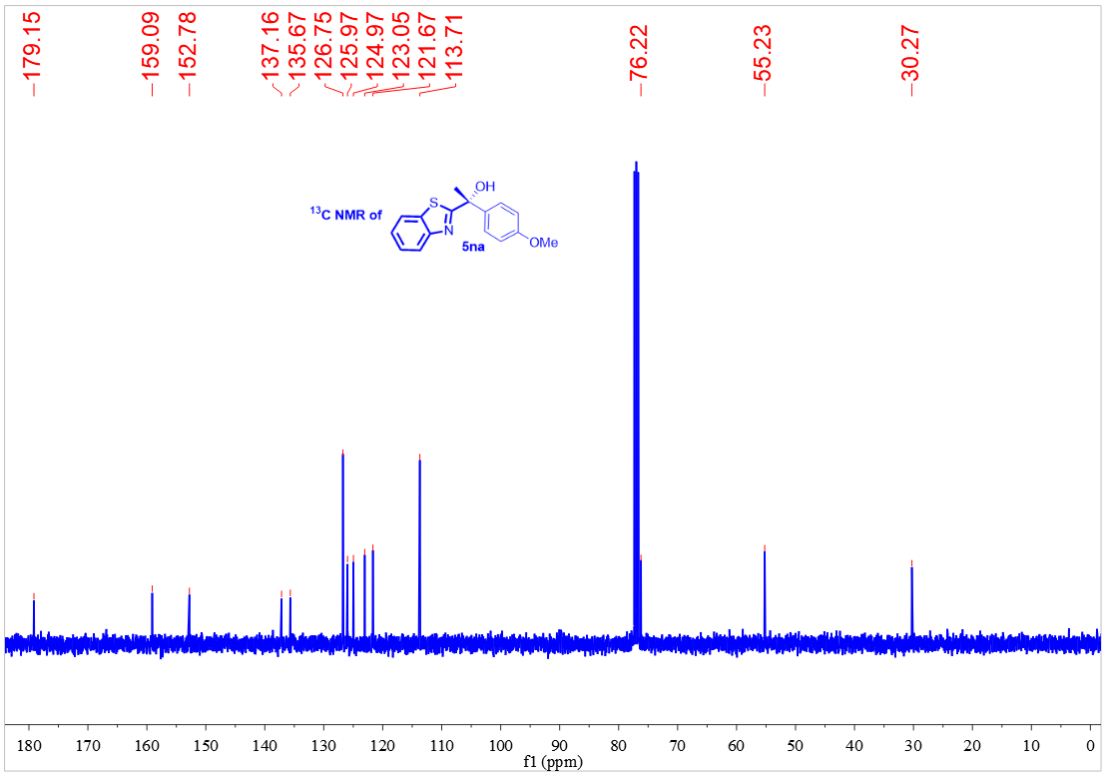
1.00
2.00
1.00
1.00
2.00
1.00
3.00
3.00
f1 (ppm)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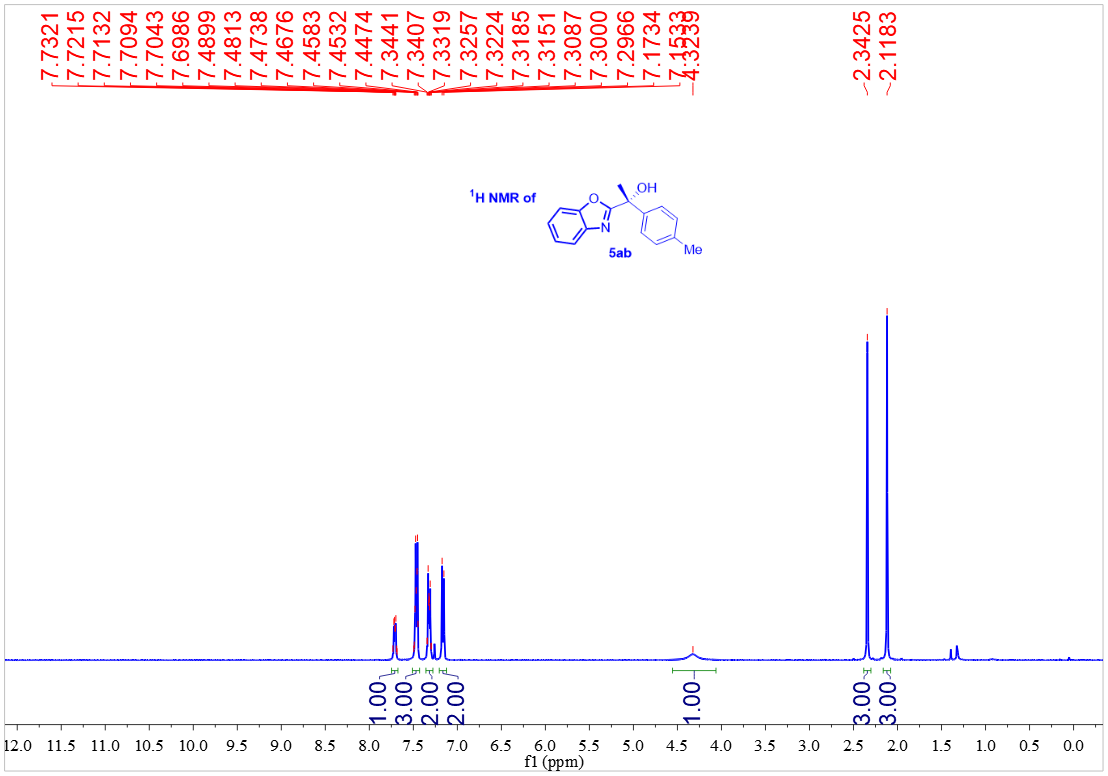
55.23
30.27
13C NMR of
5na
OH
OMe
f1 (ppm)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7.4474
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7.3087
7.3000
7.2966
7.1734
7.1533
4.3239
2.3425
2.1183
1H NMR of
5ab
OH
Me
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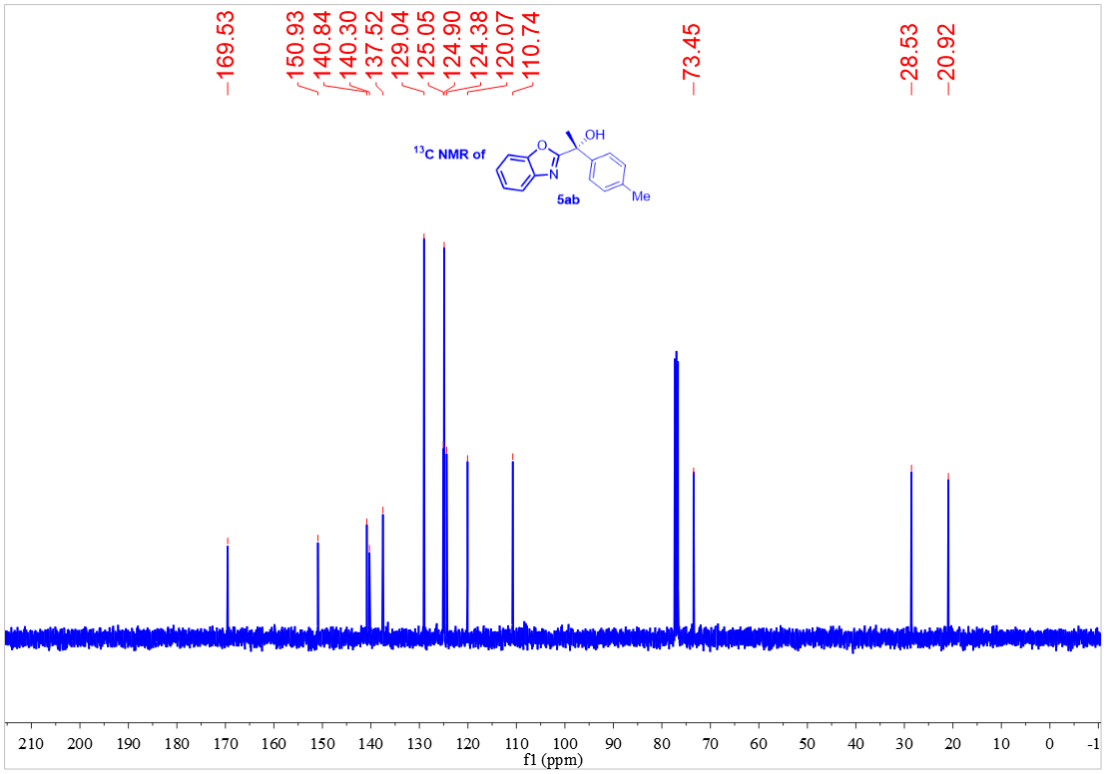
3.00
2.00
2.00
1.00
3.00
3.00
f1 (ppm)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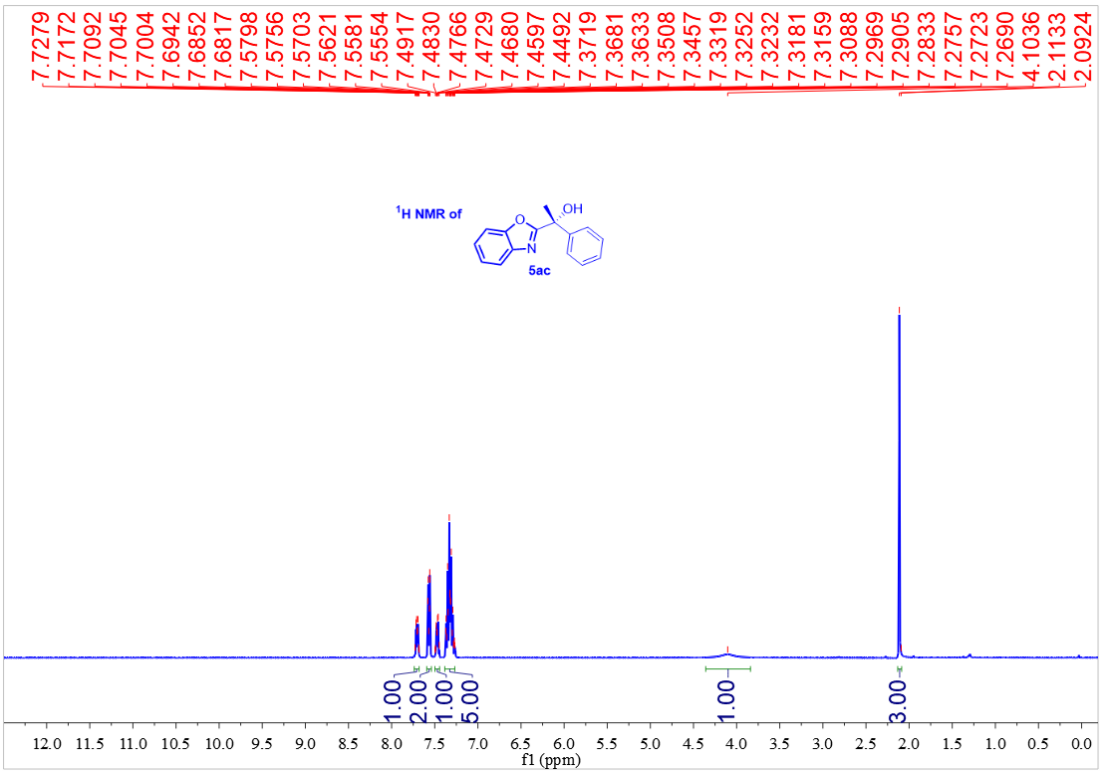
13C NMR of
5ab
OH
Me
f1 (ppm)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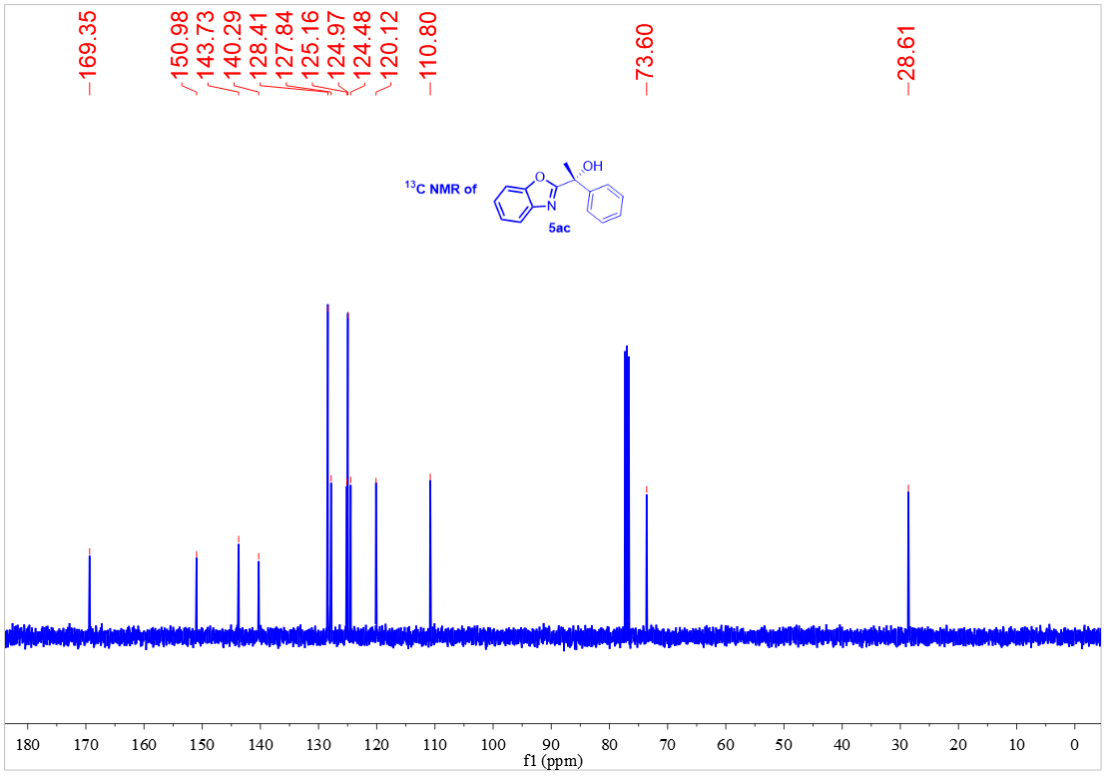
7.2905
7.2833
7.2757
7.2723
7.2690
4.1036
2.1133
2.0924
1H NMR of
OH
O
N
5ac
1.00
2.00
1.00
5.00
1.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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13C NMR of
OH
O
N
5ac
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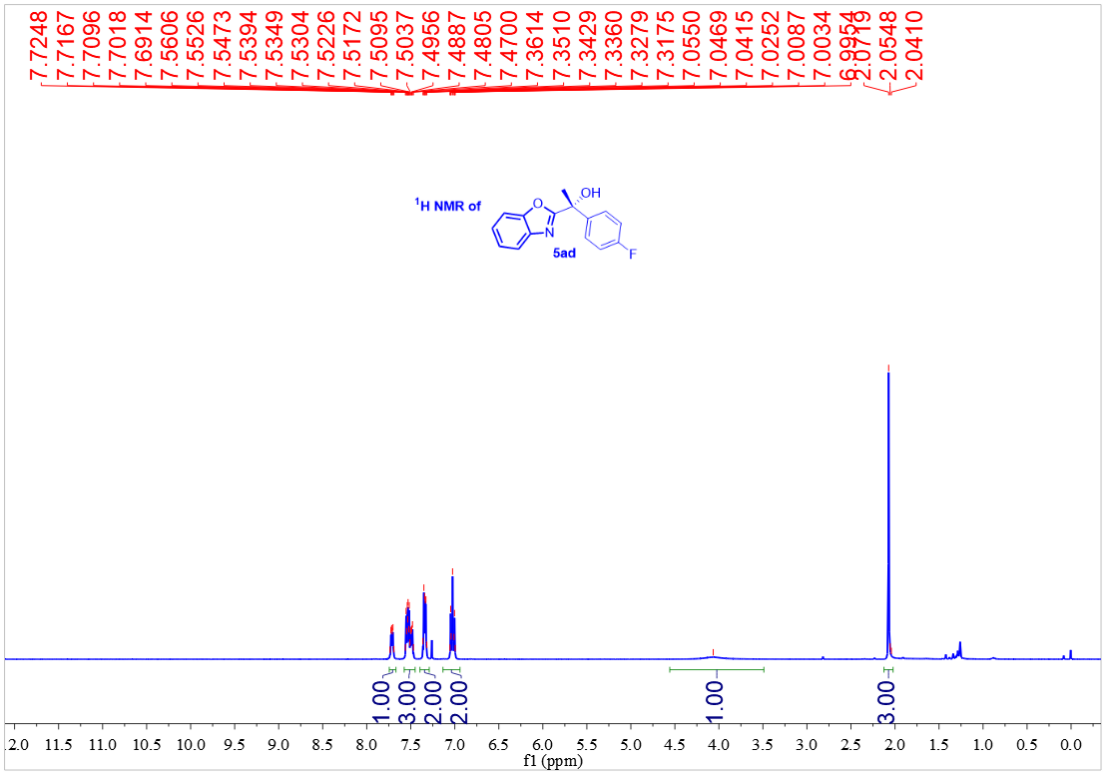
f1 (ppm)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7.3175
7.0550
7.0469
7.0415
7.0252
7.0087
7.0034
6.9954
2.0548
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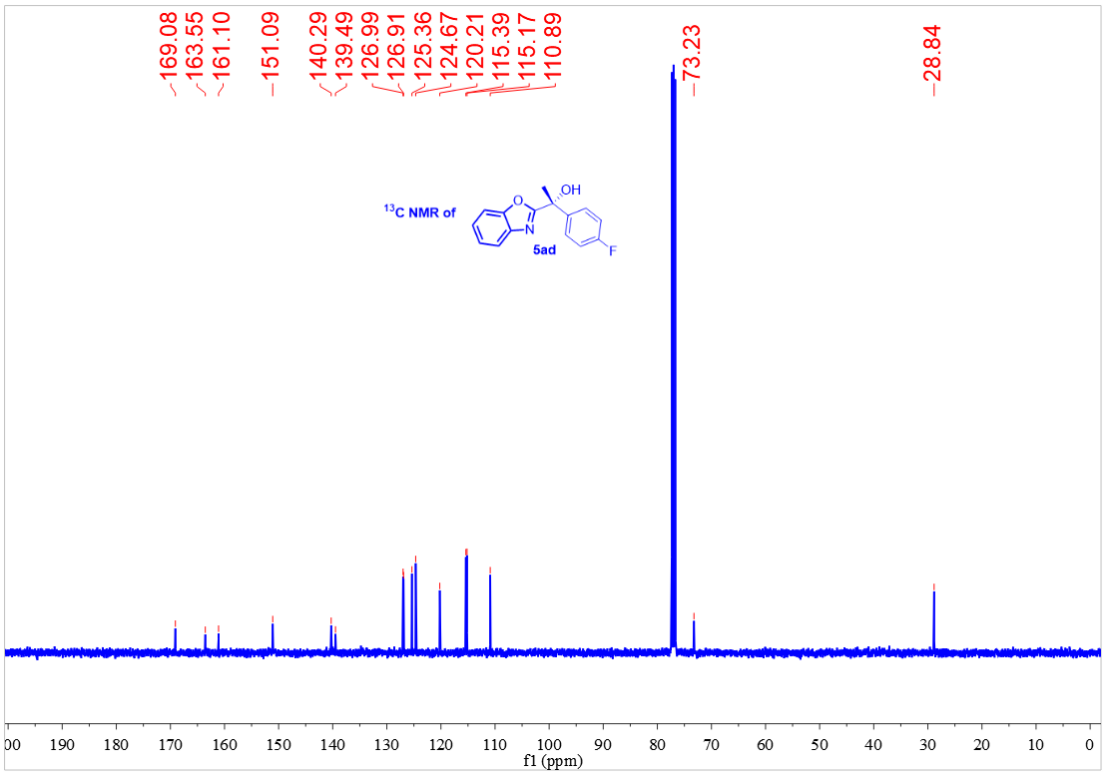
1H NMR of
5ad
OH
F
1.00
3.00
2.00
2.00
1.00
3.00
f1 (ppm)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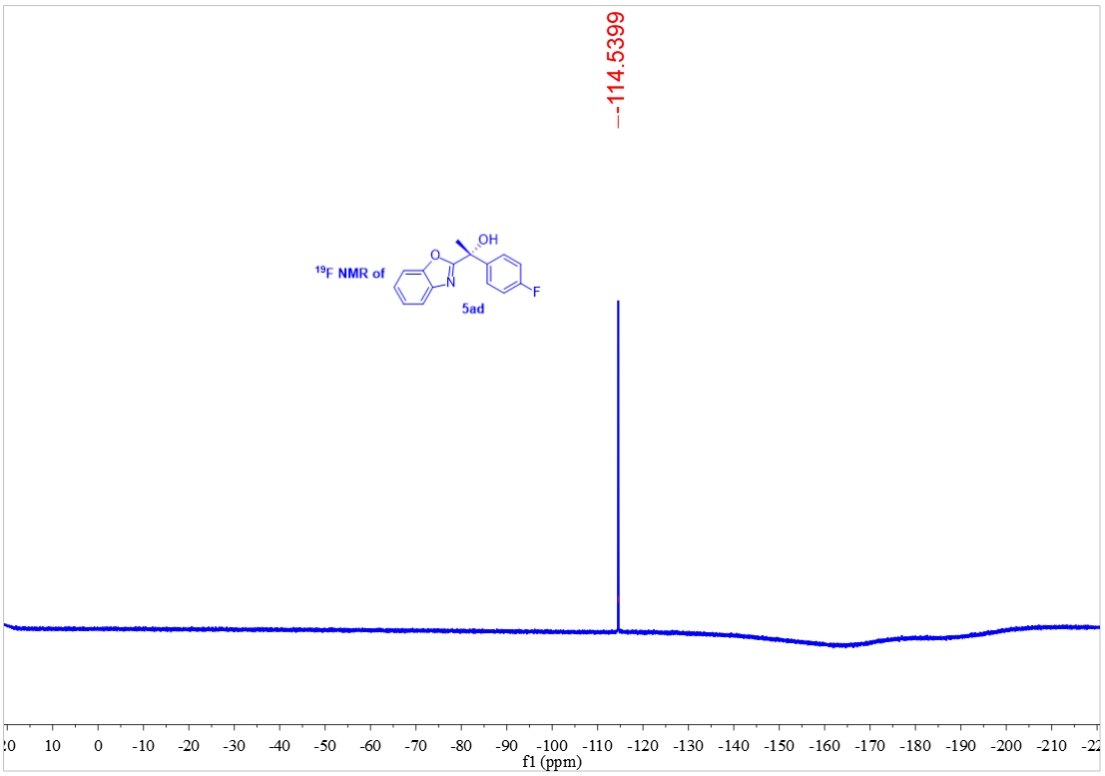
13C NMR of
5ad
OH
F
f1 (ppm)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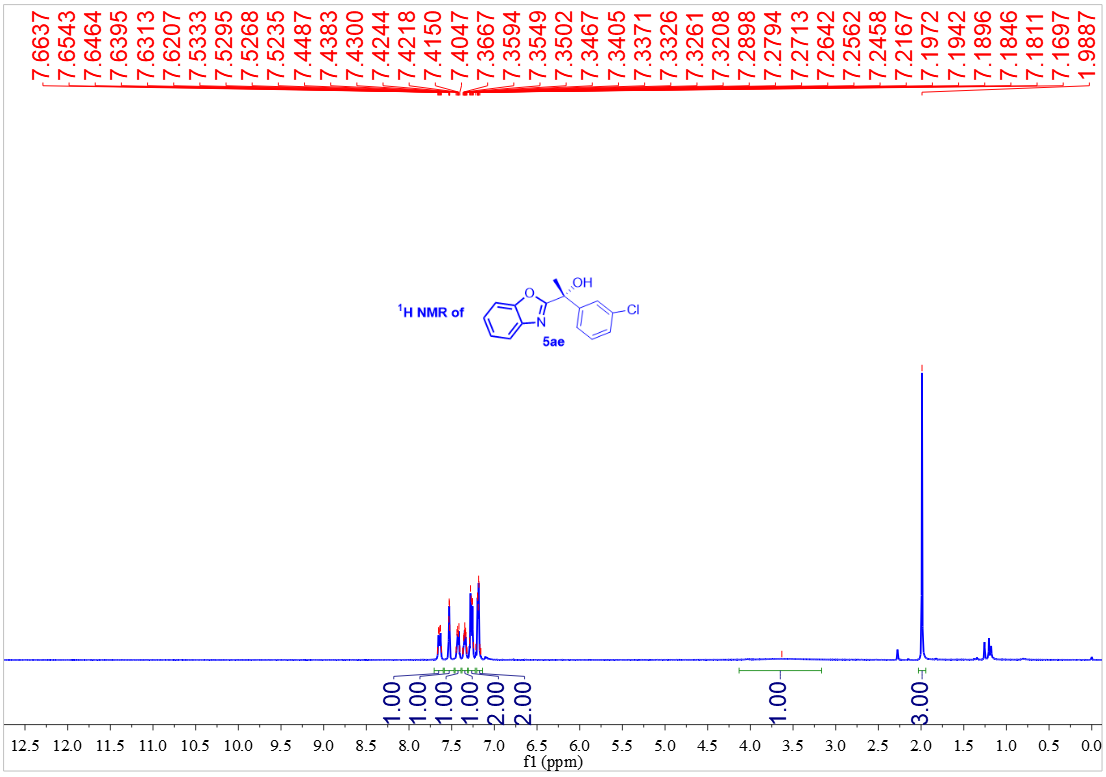
19F NMR of
OH
F
5ad
f1 (ppm)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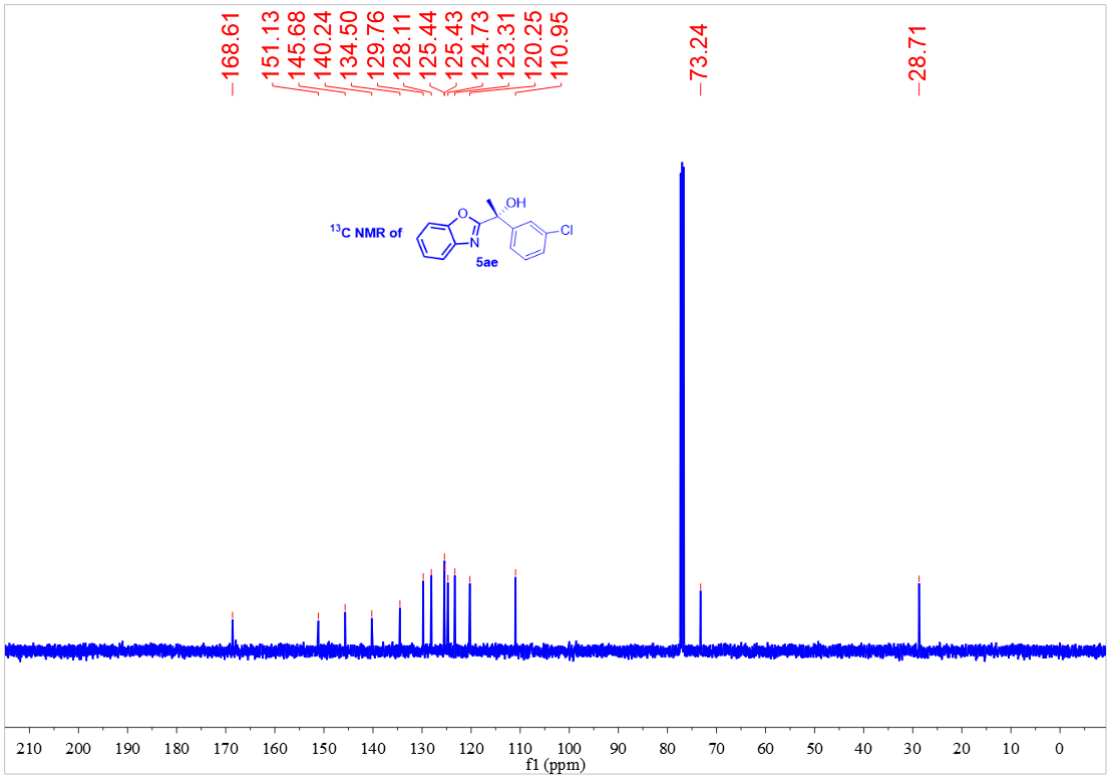
7.1972
7.1942
7.1896
7.1846
7.1811
7.1697
1.9887
1H NMR of
OH
Cl
5ae
1.00
1.00
1.00
1.00
2.00
2.00
1.00
3.00
f1 (ppm)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145.68
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129.76
128.11
125.44
125.43
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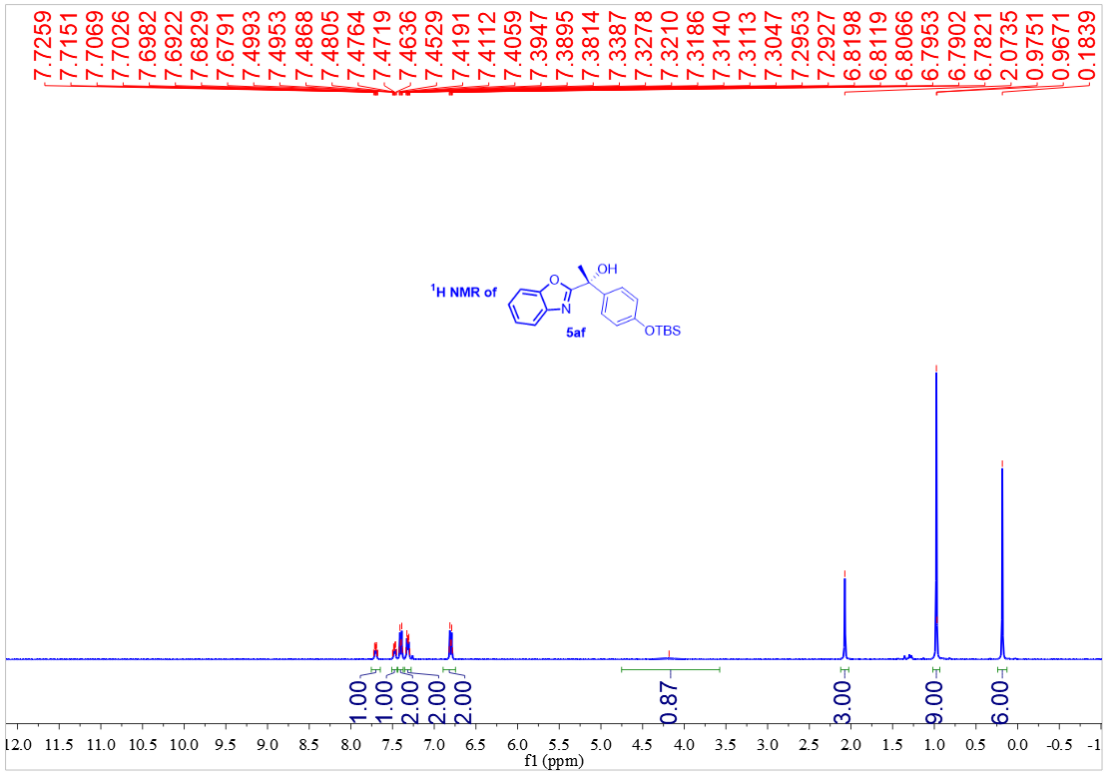
123.31
120.25
110.95
73.24
28.71
13C NMR of
5ae
OH
Cl
f1 (ppm)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7.6982
7.6922
7.6829
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7.4993
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7.4868
7.4805
7.4764
7.4719
7.4636
7.4529
7.4191
7.4112
7.4059
7.3947
7.3895
7.3814
7.3387
7.3278
7.3210
7.3186
7.3140
7.3113
7.3047
7.2953
7.2927
6.8198
6.8119
6.8066
6.7953
6.7902
6.7821
2.0735
0.9751
0.9671
0.1839
1H NMR of
5af
OH
OTBS
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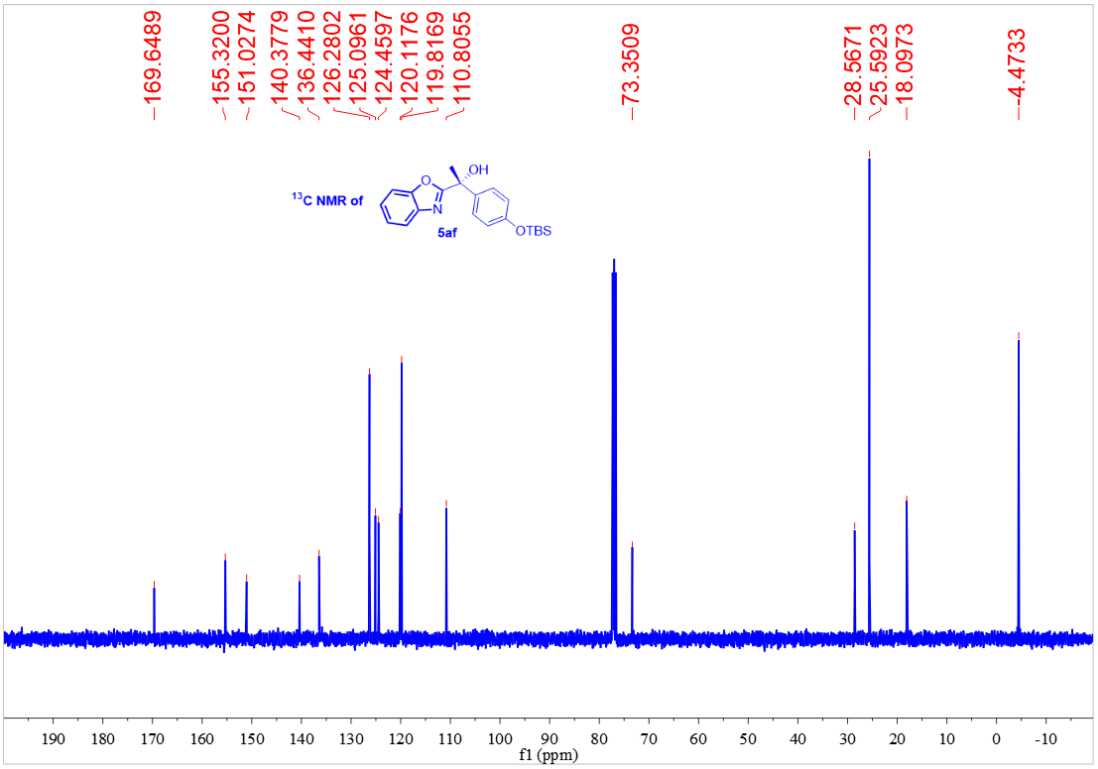
1.00
2.00
2.00
2.00
0.87
3.00
9.00
6.00
f1 (ppm)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151.0274
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136.4410
126.2802
125.0961
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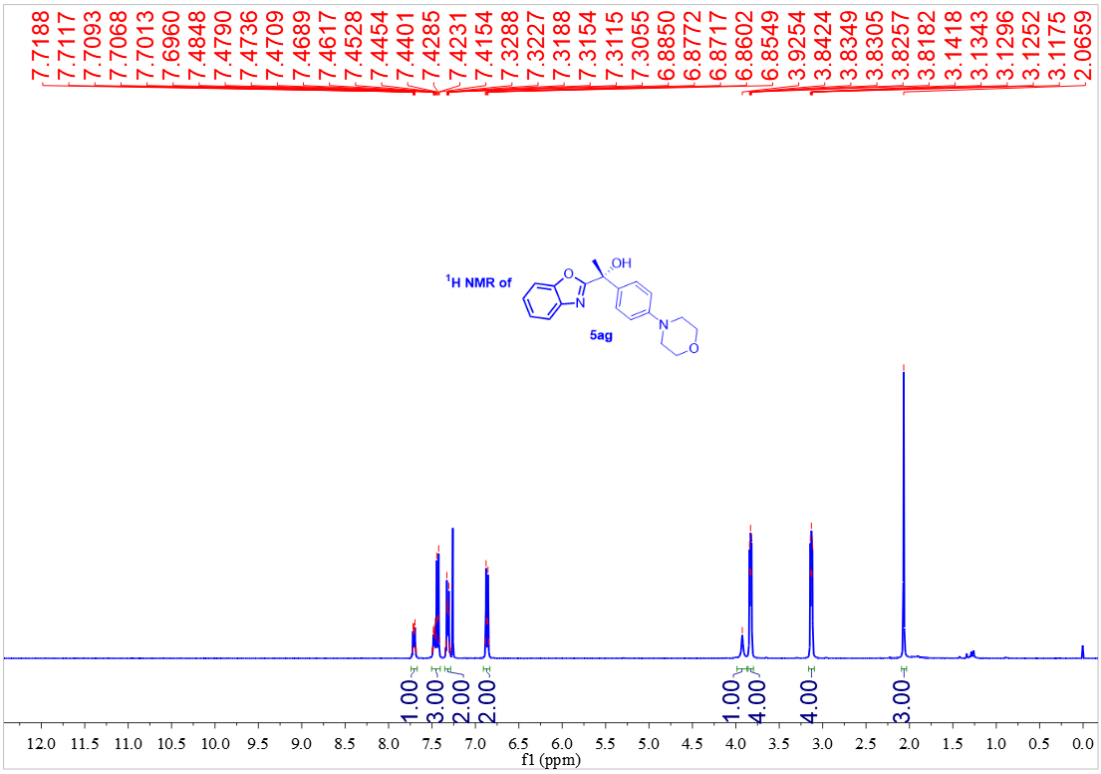
120.1176
119.8169
110.8055
73.3509
28.5671
25.5923
18.0973
-4.4733
13C NMR of
5af
OH
OTBS
f1 (ppm)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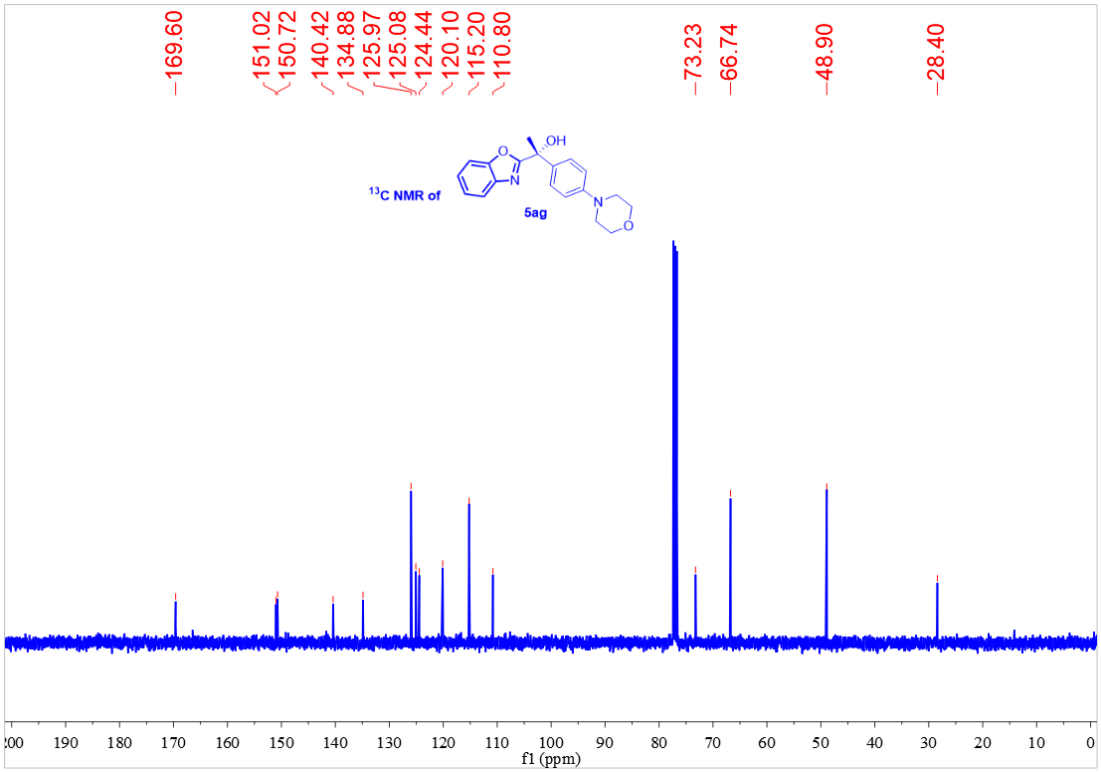
7.4689
7.4617
7.4528
7.4454
7.4401
7.4285
7.4231
7.4154
7.3288
7.3227
7.3188
7.3154
7.3115
7.3055
6.8850
6.8772
6.8717
6.8602
6.8549
3.9254
3.8424
3.8349
3.8305
3.8257
3.8182
3.1418
3.1343
3.1296
3.1252
3.1175
2.0659
1H NMR of
5ag
OH
1.00
3.00
2.00
2.00
1.00
4.00
4.00
3.00
f1 (ppm)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125.97
125.08
124.44
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115.20
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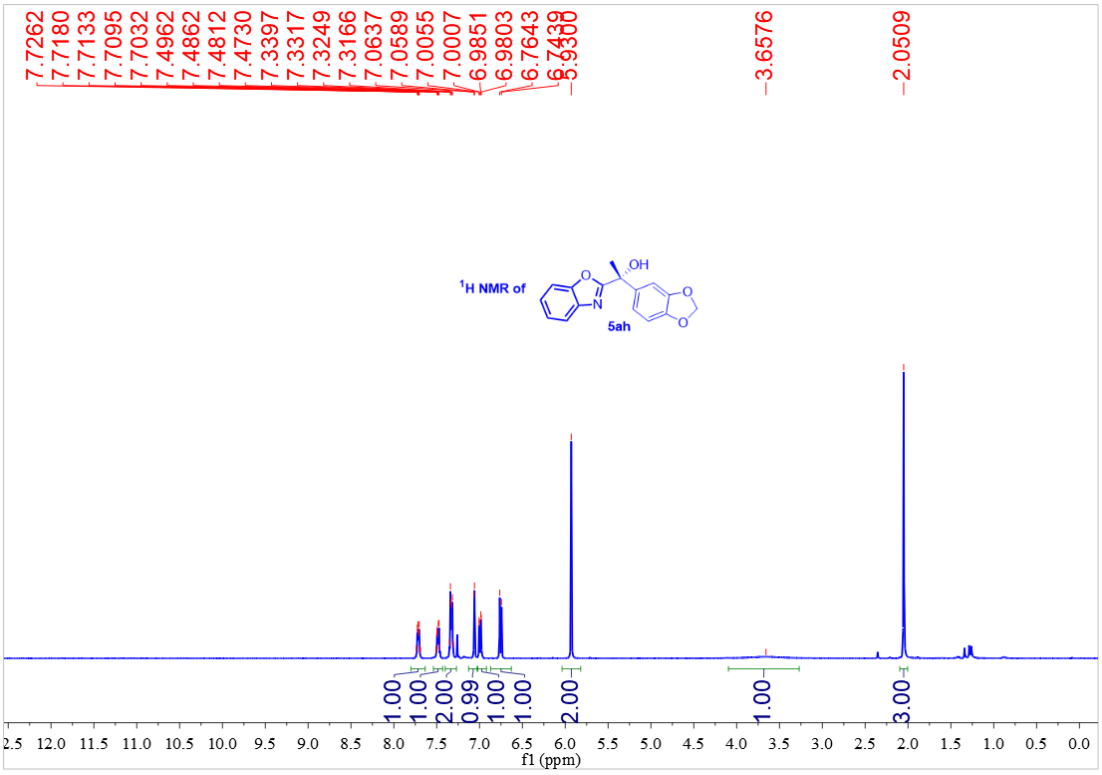
73.23
66.74
48.90
28.40
13C NMR of
5ag
OH
f1 (ppm)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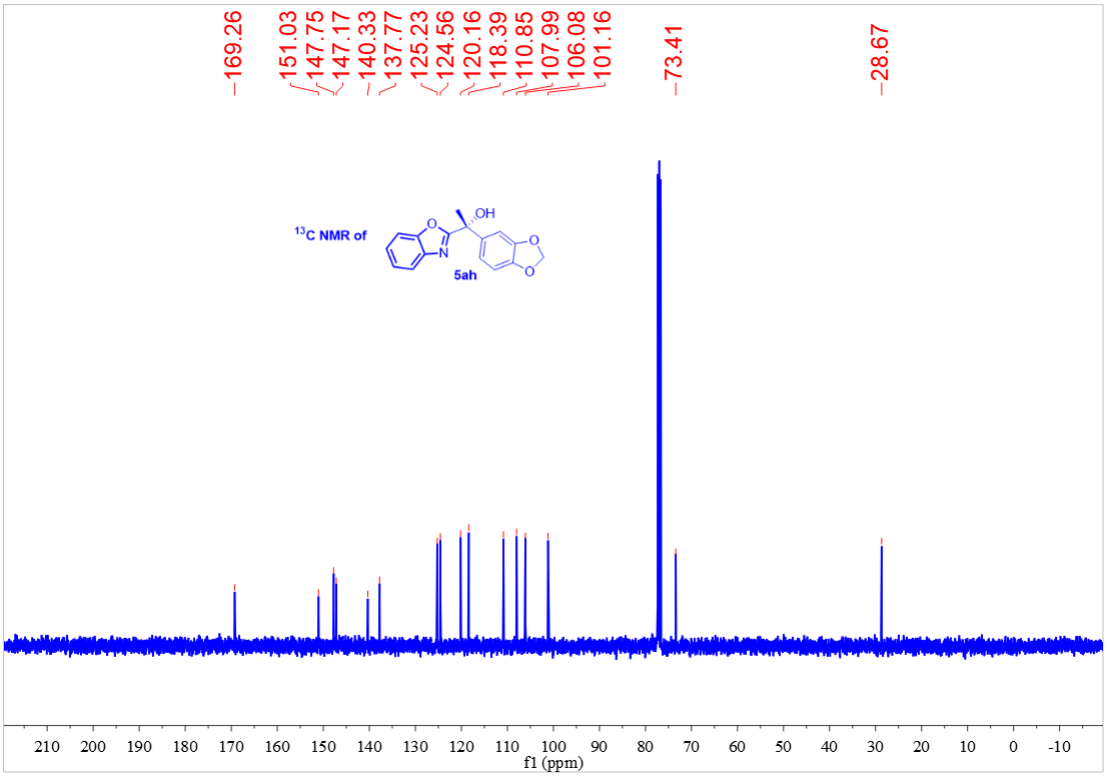
7.7032
7.4962
7.4862
7.4812
7.4730
7.3397
7.3317
7.3249
7.3166
7.0637
7.0589
7.0055
7.0007
6.9851
6.9803
6.7643
3.6576
2.0509
1H NMR of
5ah
OH
1.00
1.00
2.00
0.99
1.00
1.00
2.00
1.00
3.00
f1 (ppm)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147.75
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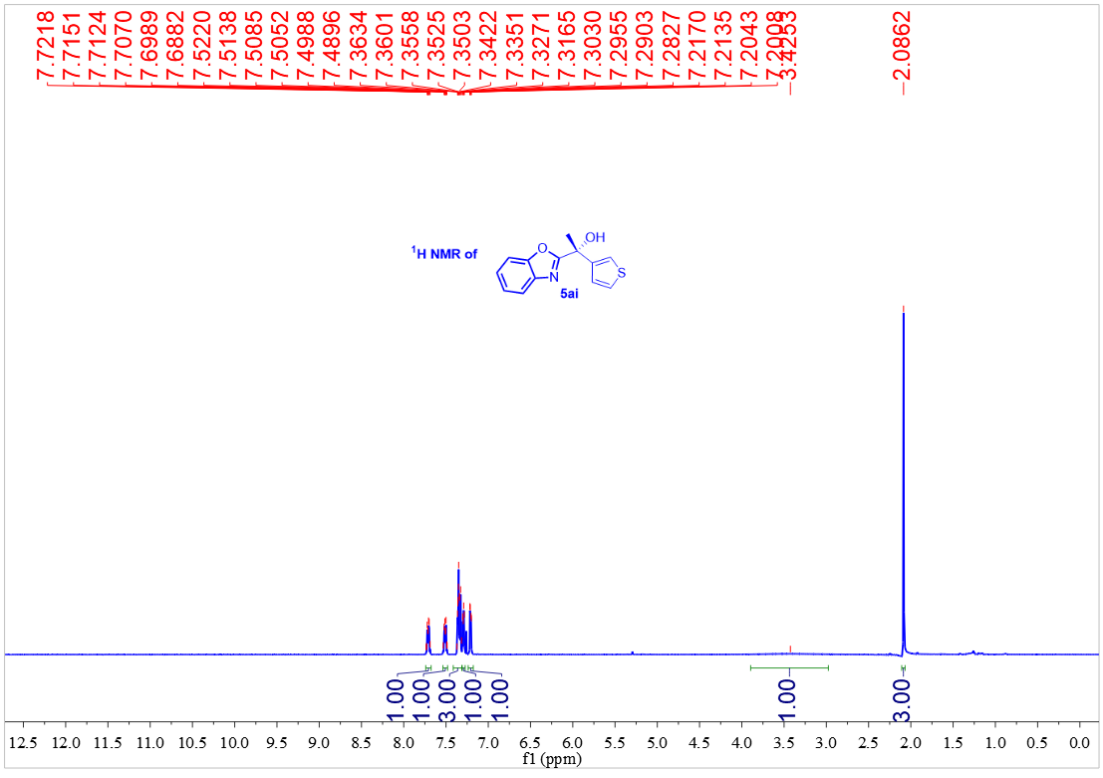
140.33
137.77
125.23
124.56
120.16
118.39
110.85
107.99
106.08
101.16
73.41
28.67
13C NMR of
OH
O
N
O
O
5ah
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.7151
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7.6989
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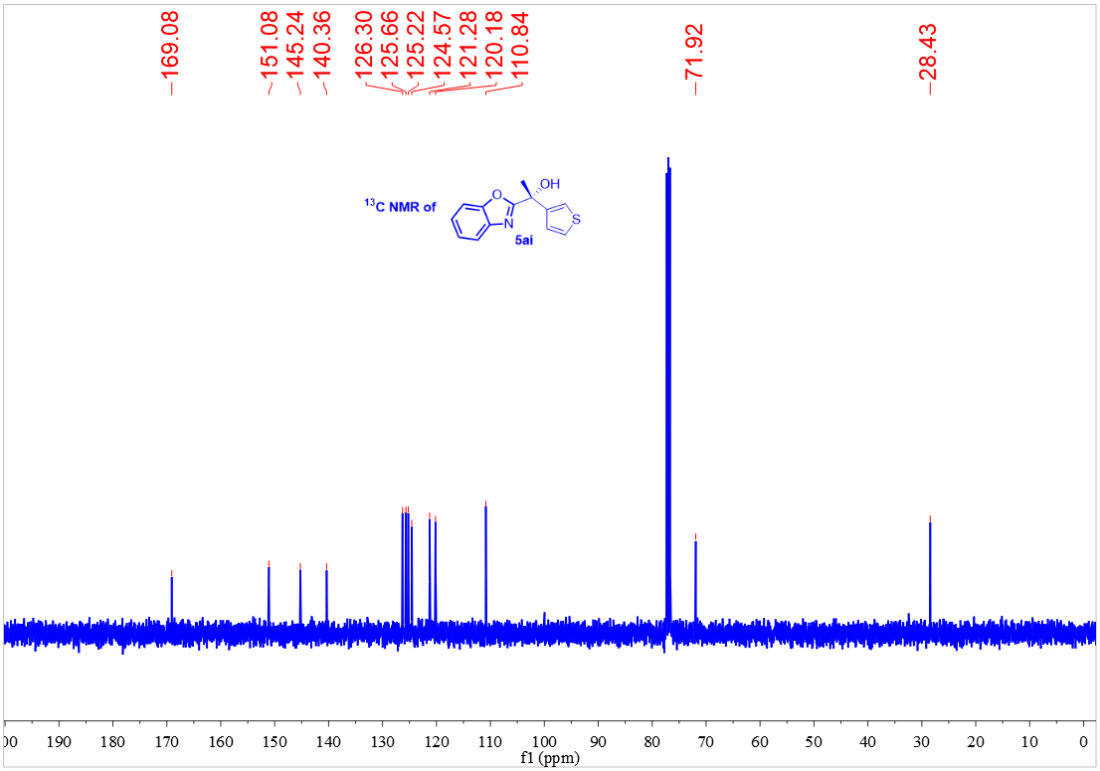
7.5220
7.5138
7.5085
7.5052
7.4988
7.4896
7.3634
7.3601
7.3558
7.3525
7.3503
7.3422
7.3351
7.3271
7.3165
7.3030
7.2955
7.2903
7.2827
7.2170
7.2135
7.2043
7.2008
3.4253
2.0862
1H NMR of
OH
O
N
S
5ai
1.00
1.00
3.00
1.00
1.00
1.00
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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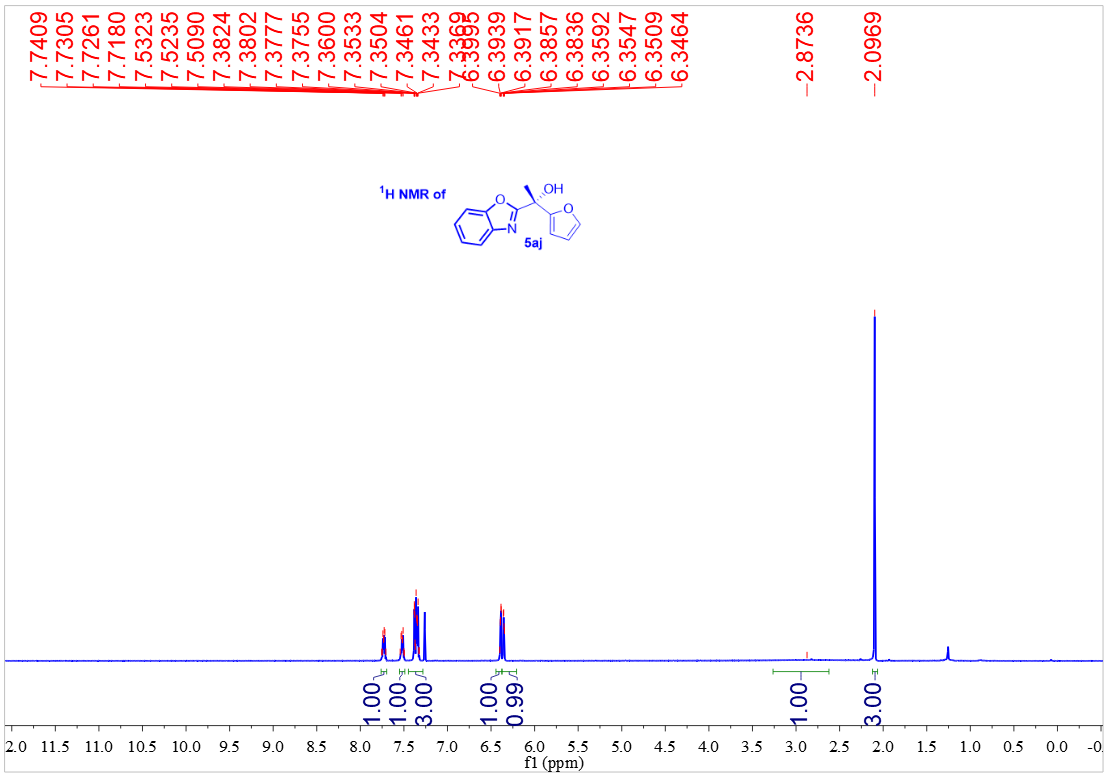
151.08
145.24
140.36
126.30
125.66
125.22
124.57
121.28
120.18
110.84
71.92
28.43
13C NMR of
OH
O
N
S
5ai
f1 (ppm)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7.7305
7.7261
7.7180
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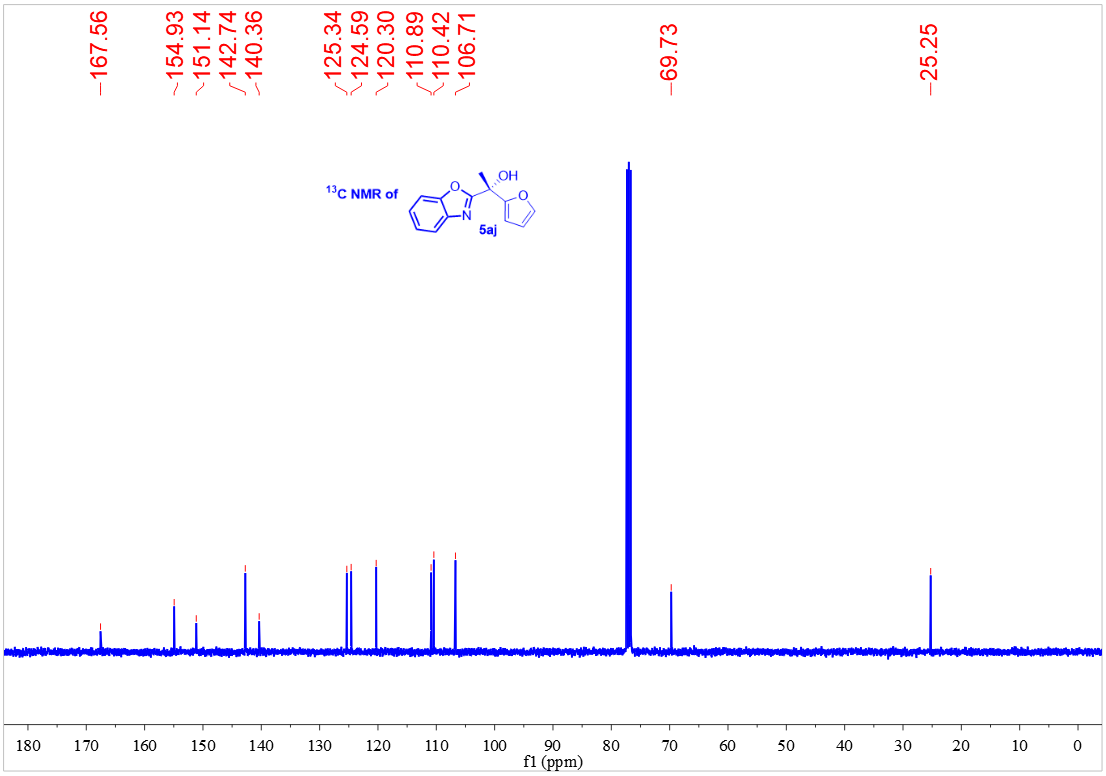
7.5235
7.5090
7.3824
7.3802
7.3777
7.3755
7.3600
7.3533
7.3504
7.3461
7.3433
6.3939
6.3917
6.3857
6.3836
6.3592
6.3547
6.3509
6.3464
2.8736
2.0969
1H NMR of
OH
O
N
O
5aj
1.00
1.00
3.00
1.00
0.99
1.00
3.00
f1 (ppm)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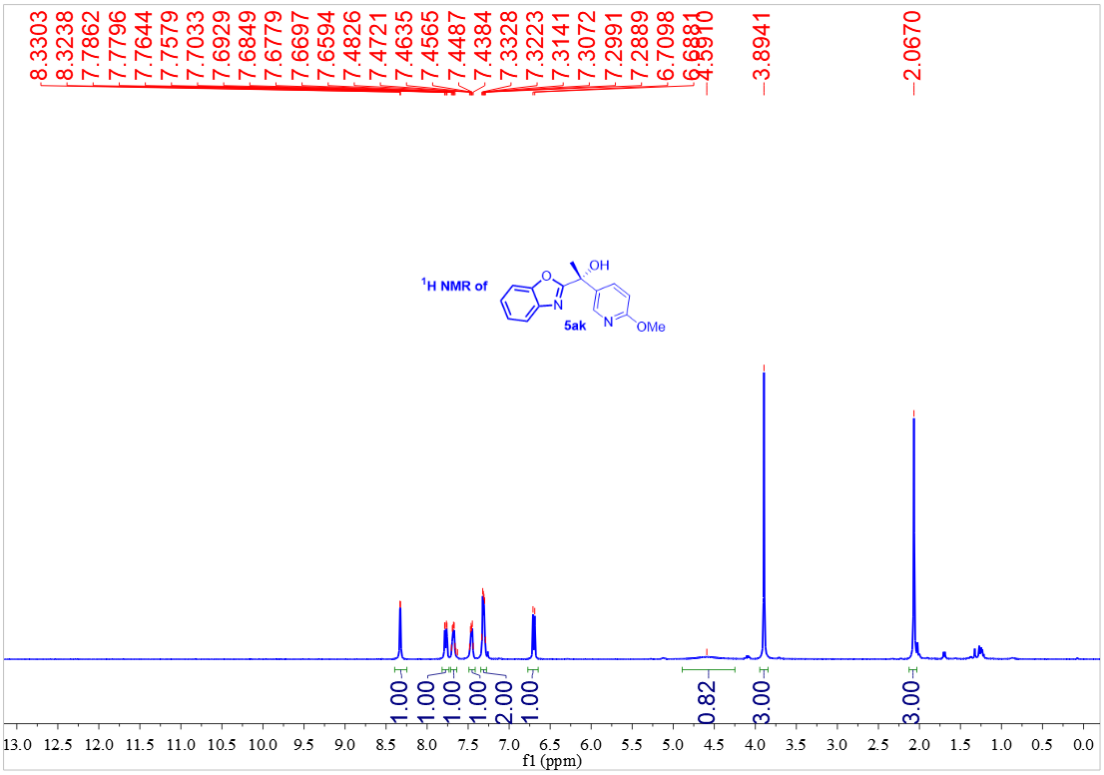
154.93
151.14
142.74
140.36
125.34
124.59
120.30
110.89
110.42
106.71
69.73
25.25
13C NMR of
5aj
f1 (ppm)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8.3238
7.7862
7.7796
7.7644
7.7579
7.7033
7.6929
7.6849
7.6779
7.6697
7.6594
7.4826
7.4721
7.4635
7.4565
7.4487
7.4384
7.3328
7.3223
7.3141
7.3072
7.2991
7.2889
6.7098
6.6881
4.5910
3.8941
2.0670
1H NMR of
5ak
OMe
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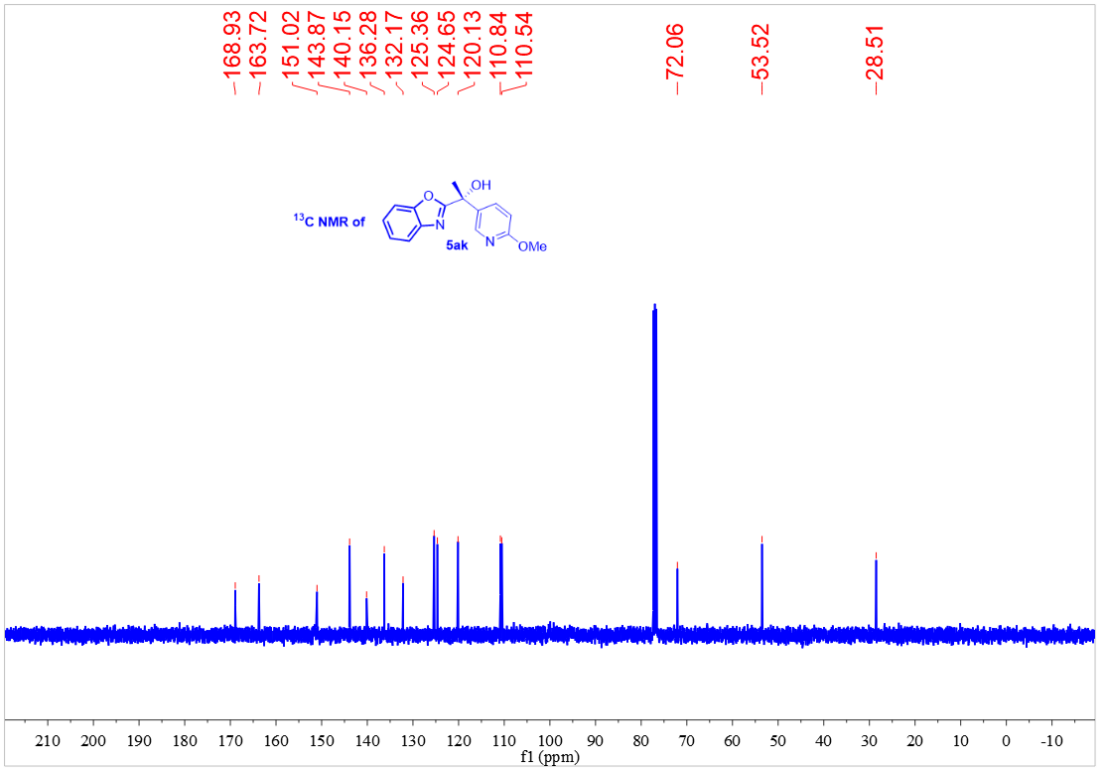
1.00
1.00
1.00
2.00
1.00
0.82
3.00
3.00
f1 (ppm)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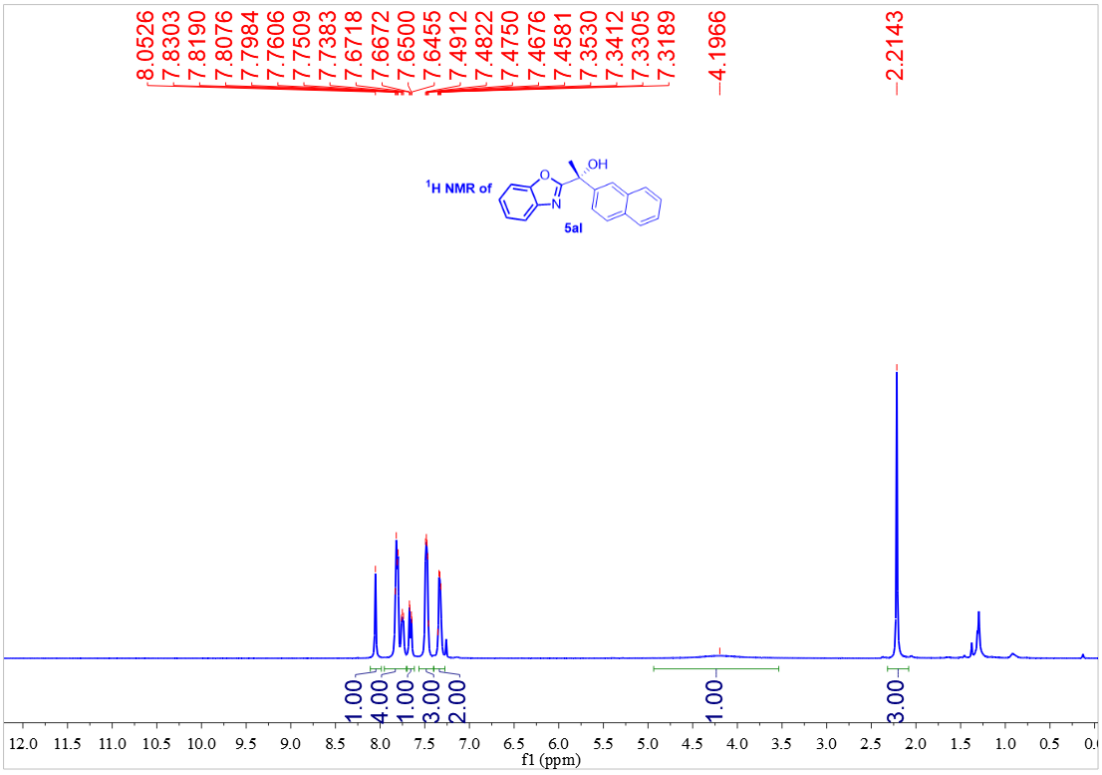
163.72
151.02
143.87
140.15
136.28
132.17
125.36
124.65
120.13
110.84
110.54
72.06
53.52
28.51
13C NMR of
5ak
OH
OMe
f1 (ppm)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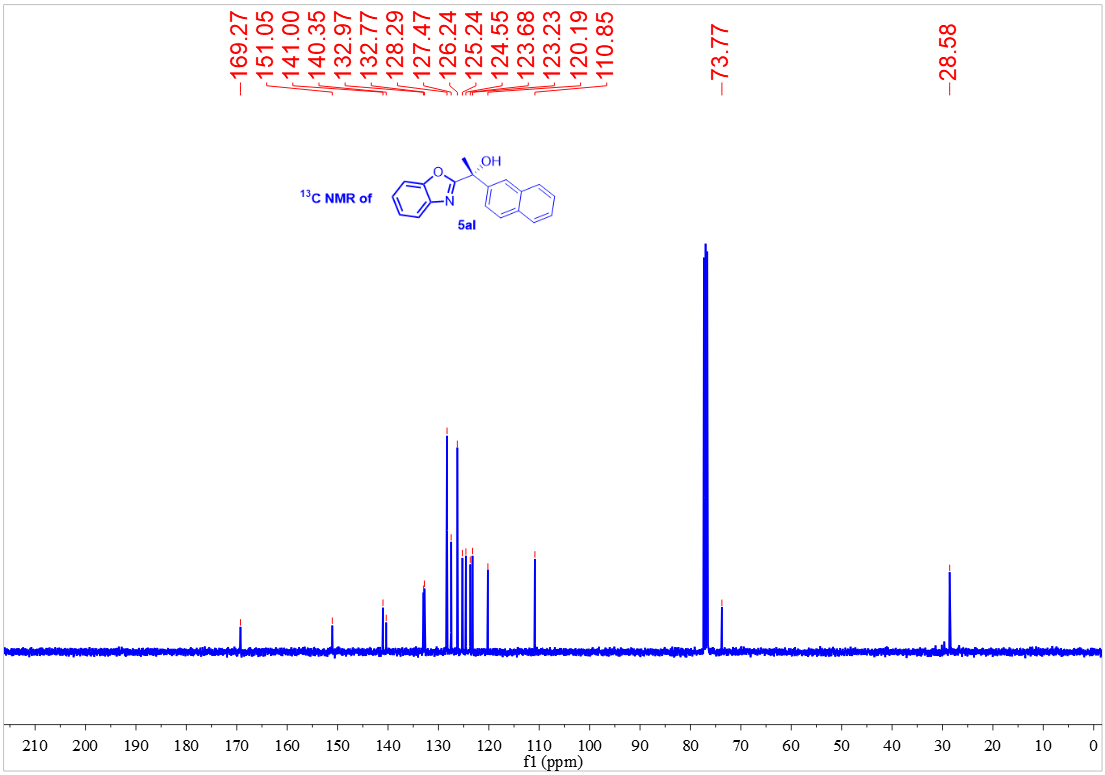
7.8303
7.8190
7.8076
7.7984
7.7606
7.7509
7.7383
7.6718
7.6672
7.6500
7.6455
7.4912
7.4822
7.4750
7.4676
7.4581
7.3530
7.3412
7.3305
7.3189
4.1966
2.2143
1H NMR of
5al
OH
1.00
4.00
1.00
3.00
2.00
1.00
3.00
f1 (ppm)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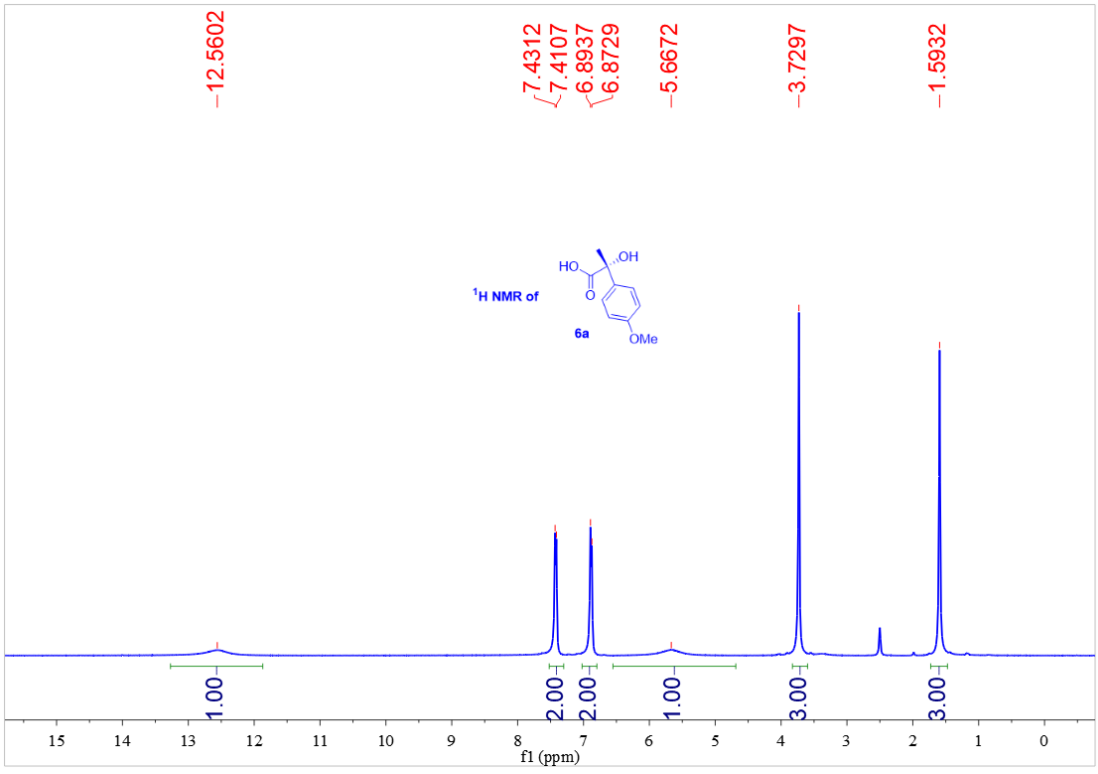
141.00
140.35
132.97
132.77
128.29
127.47
126.24
125.24
124.55
123.68
123.23
120.19
110.85
73.77
28.58
13C NMR of
OH
O
N
5al
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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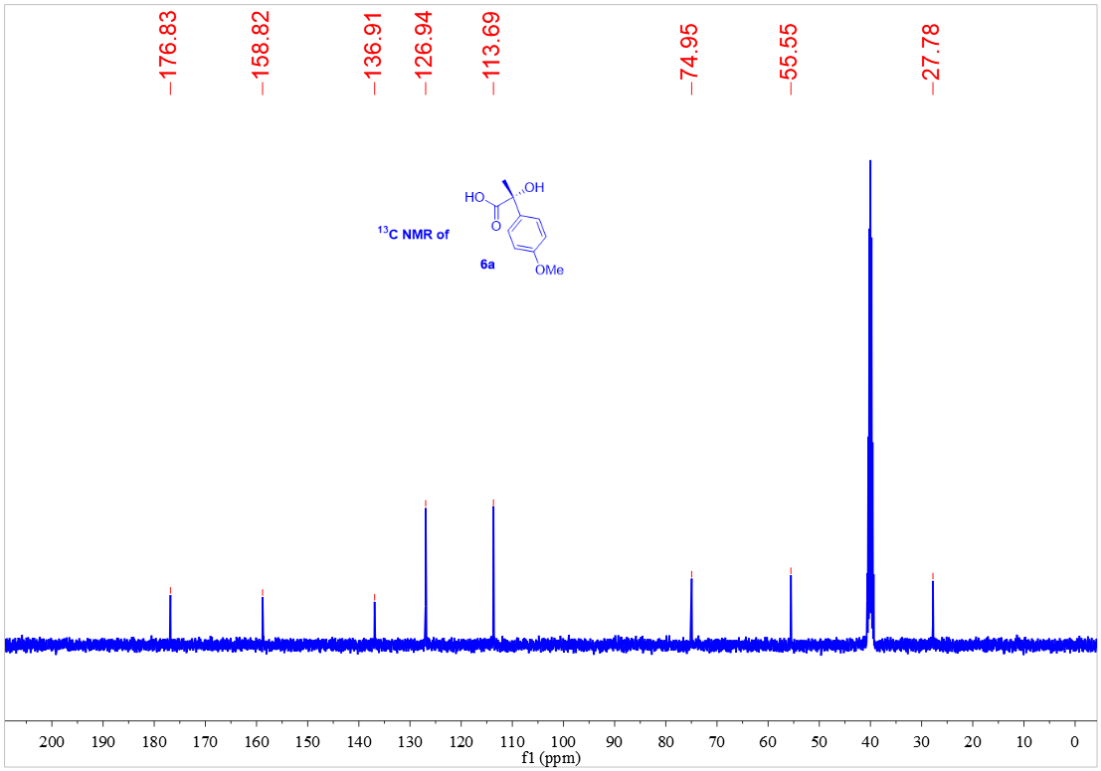
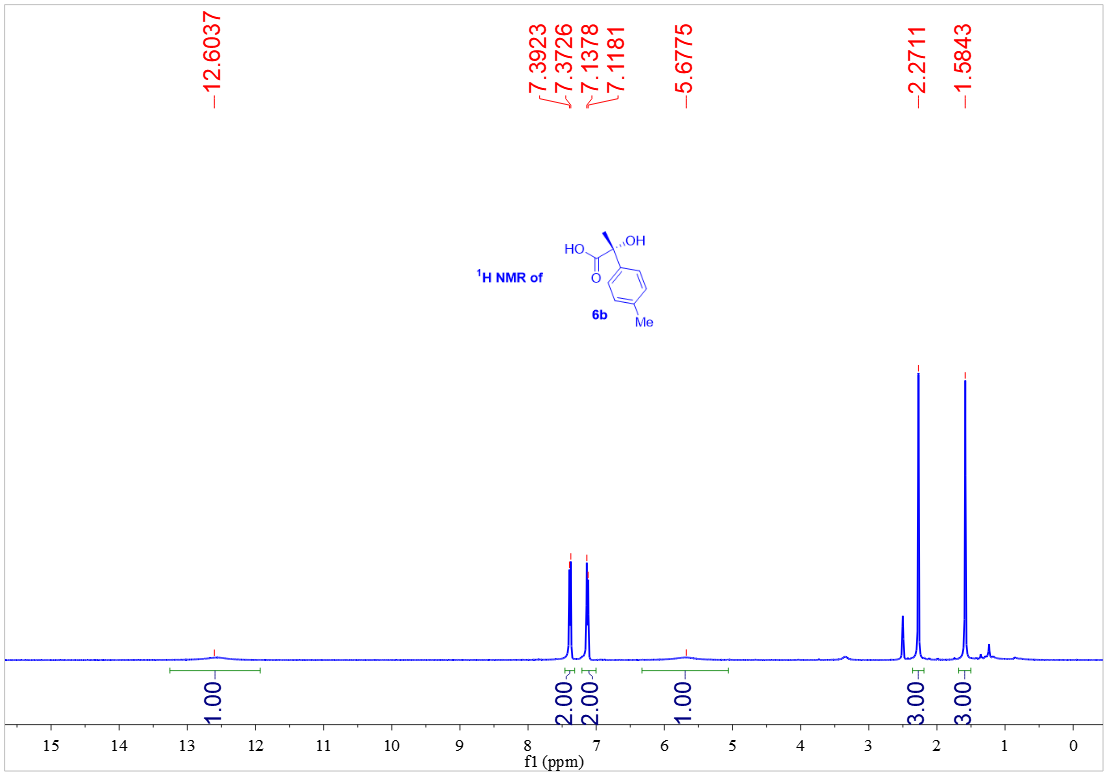
7.4312
7.4107
6.8937
6.8729
5.6672
3.7297
1.5932
1H NMR of
HO
OH
O
6a
OMe
1.00
2.00
2.00
1.00
3.00
3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


176.83
158.82
136.91
126.94
113.69
74.95
55.55
27.78
^{13}C NMR of
6a
HO
O
OH
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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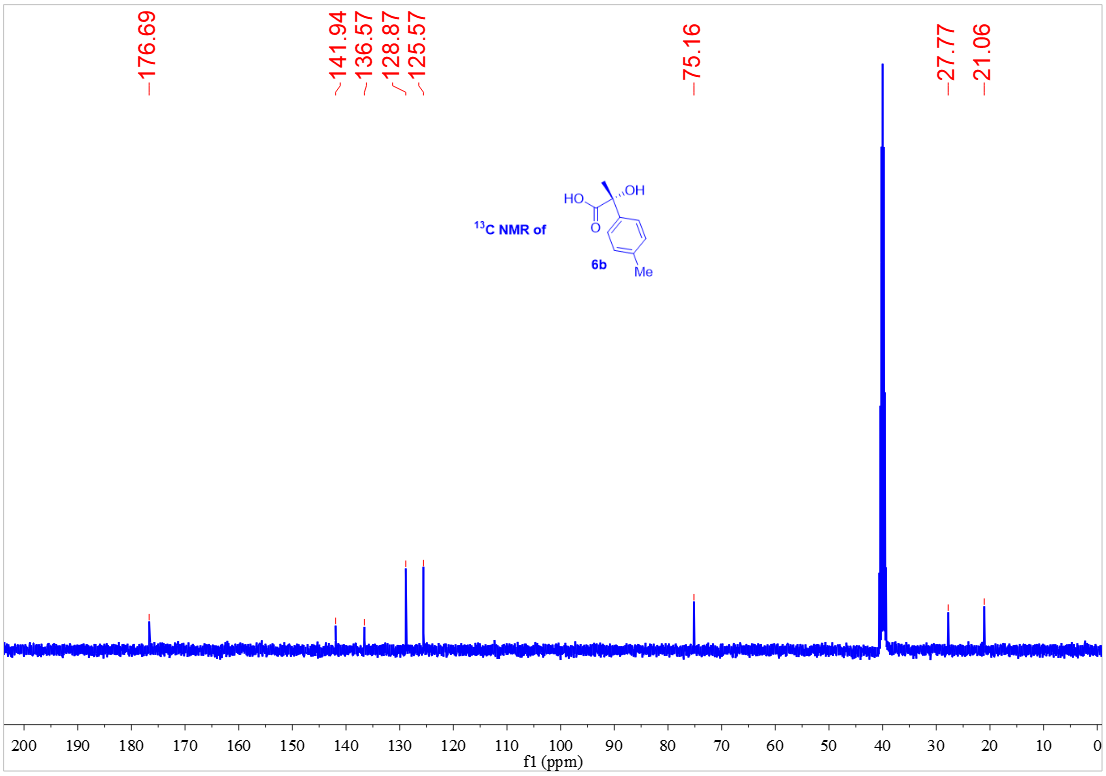
7.3726
7.1378
7.1181
5.6775
2.2711
1.5843
^{1}H NMR of
6b
HO
O
OH
Me
1.00
2.00
2.00
1.00
3.00
3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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141.94
136.57
128.87
125.57
75.16
27.77
21.06
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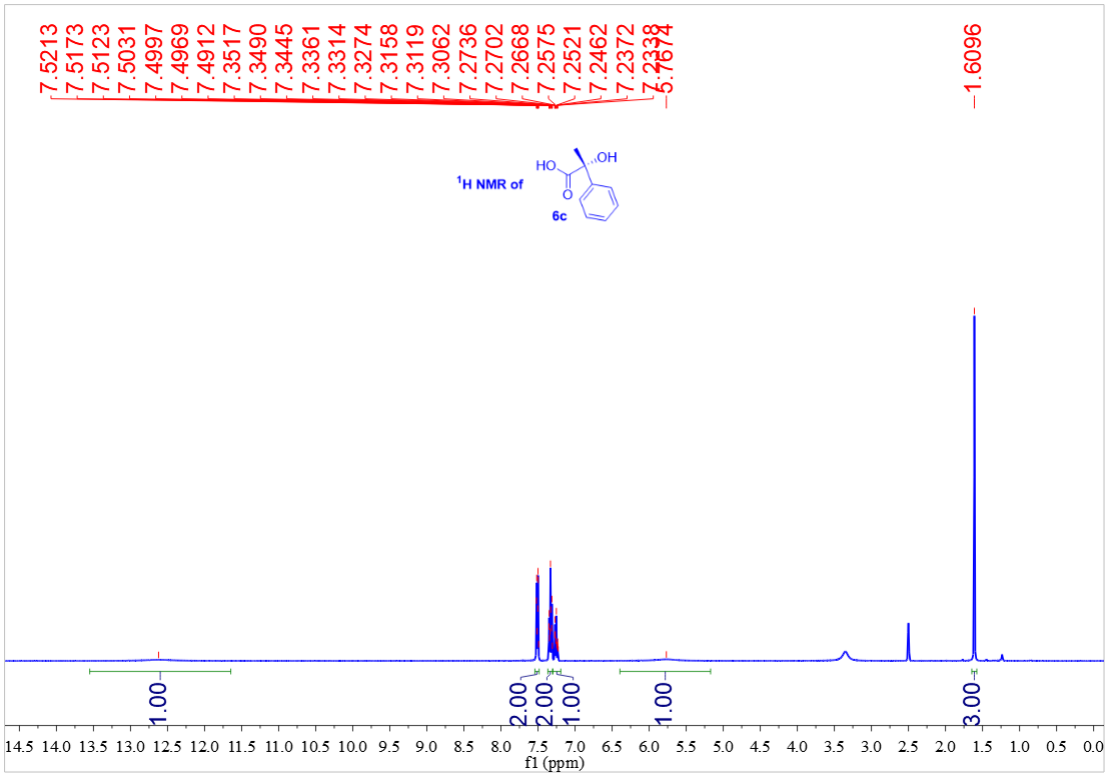
6b
HO
OH
O
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.4912
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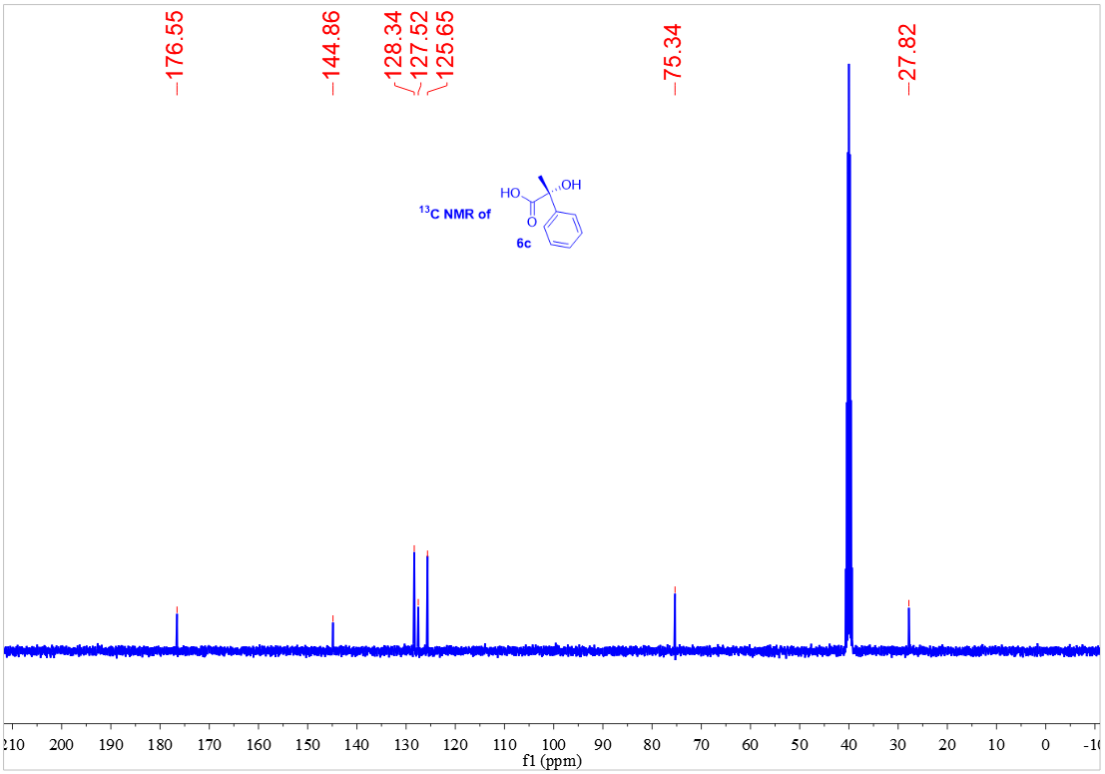
7.3490
7.3445
7.3361
7.3314
7.3274
7.3158
7.3119
7.3062
7.2736
7.2702
7.2668
7.2575
7.2521
7.2462
7.2372
1.6096
^{1}H NMR of
6c
HO
OH
O
1.00
2.00
2.00
1.00
1.00
3.00
14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.52
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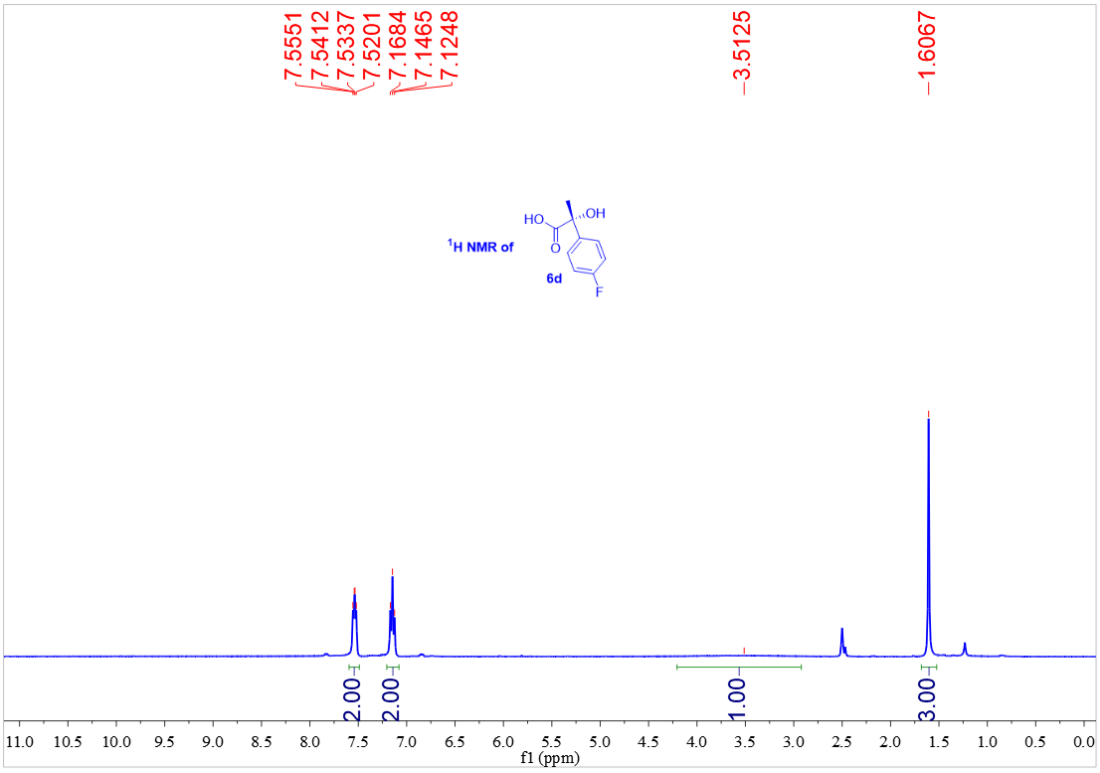
75.34
27.82
HO
OH
O
13C NMR of
6c
f1 (ppm)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7.5412
7.5337
7.5201
7.1684
7.1465
7.1248
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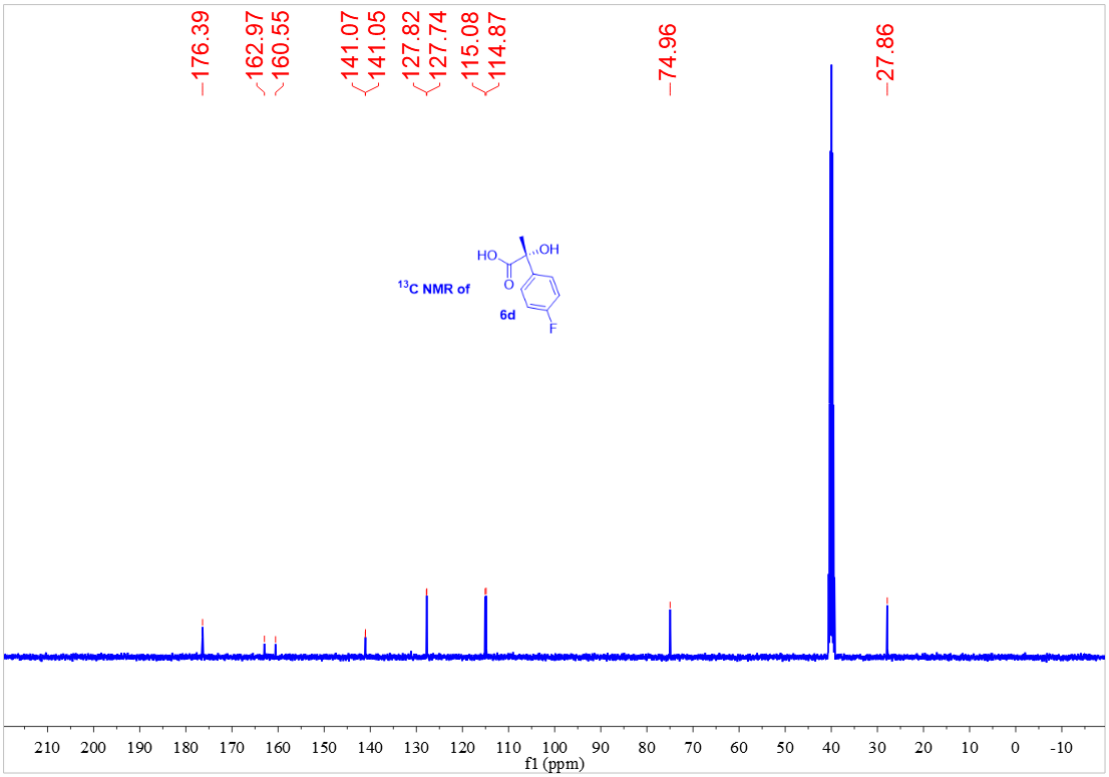
HO
OH
O
1H NMR of
6d
F
2.00
2.00
1.00
3.00
f1 (ppm)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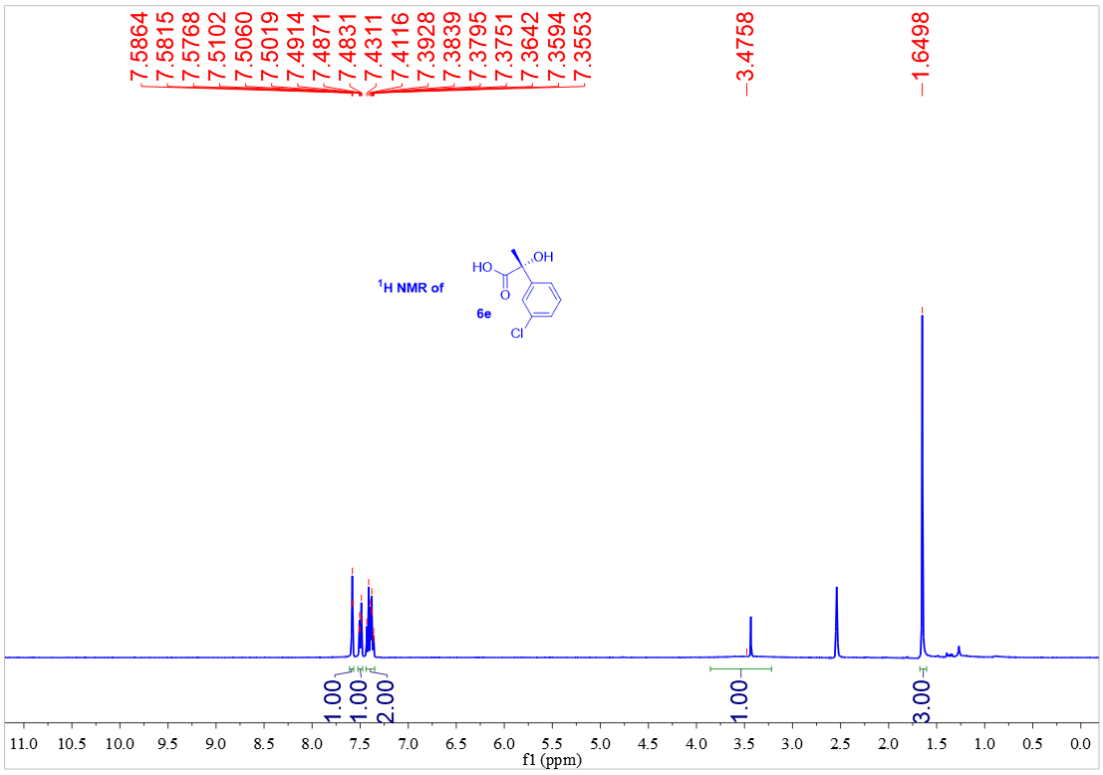
162.97
160.55
141.07
141.05
127.82
127.74
115.08
114.87
74.96
27.86
13C NMR of
6d
HO
OH
O
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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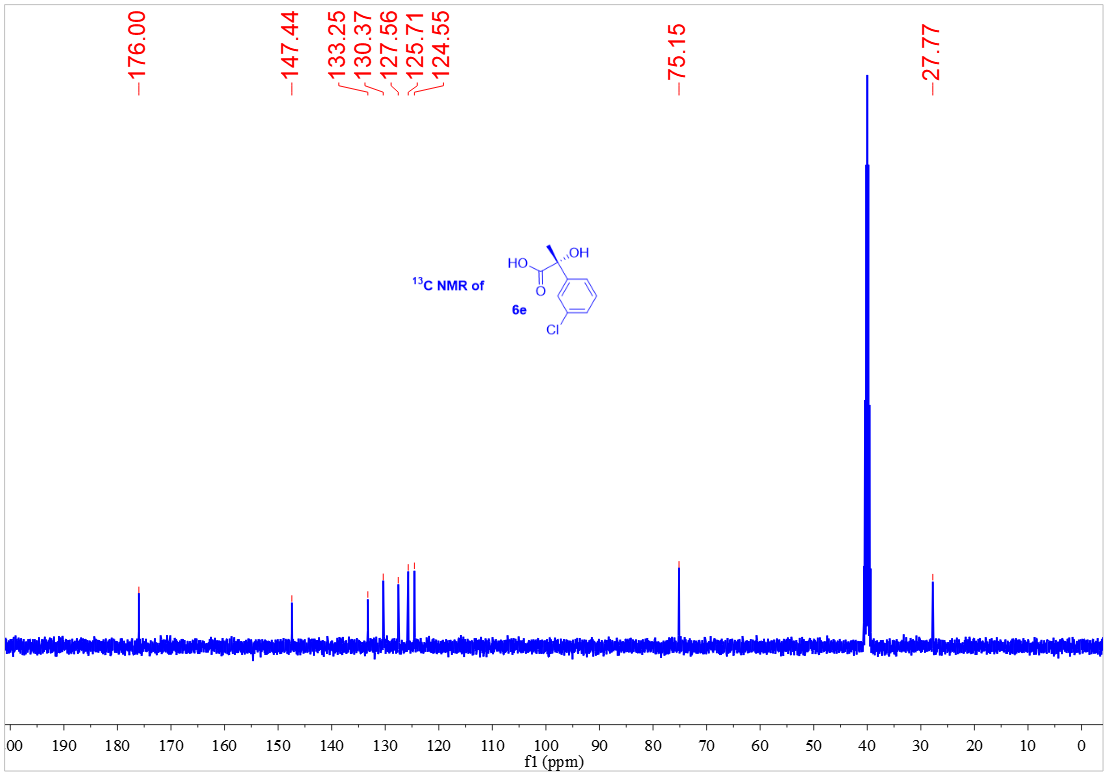
7.4871
7.4831
7.4311
7.4116
7.3928
7.3839
7.3795
7.3751
7.3642
7.3594
7.3553
3.4758
1.6498
1H NMR of
6e
HO
OH
O
Cl
1.00
1.00
2.00
1.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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130.37
127.56
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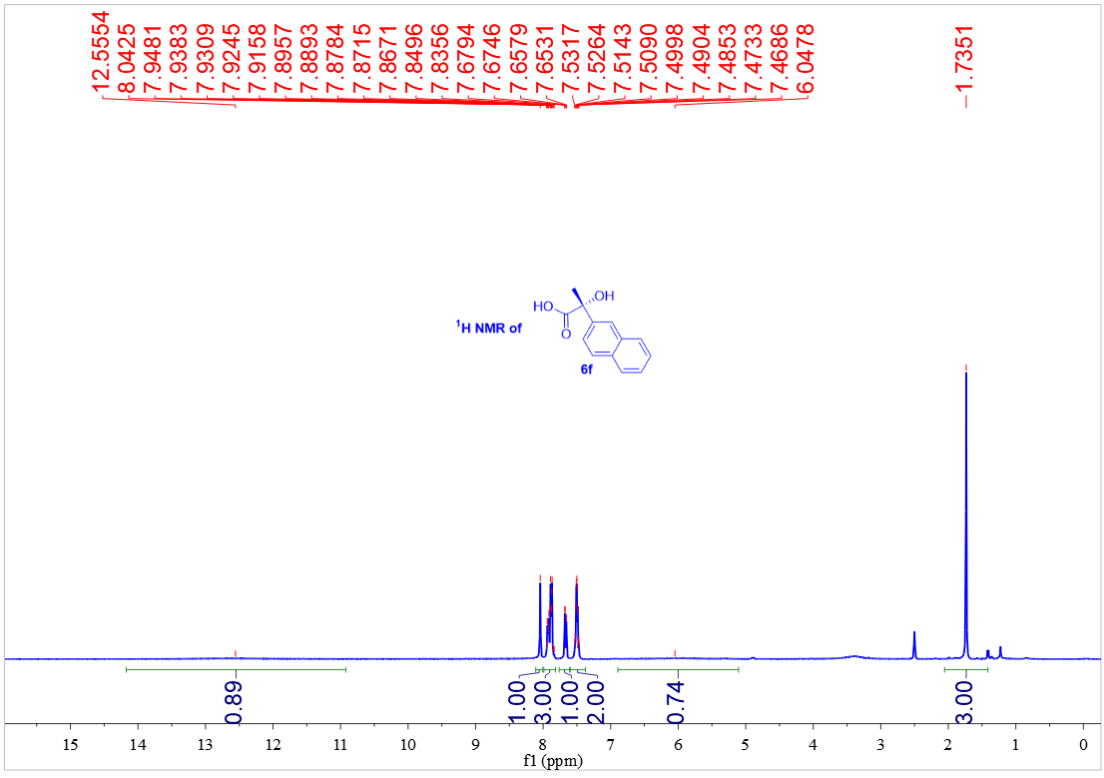
124.55
75.15
27.77
^{13}C NMR of
6e
HO
OH
O
Cl
f1 (ppm)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7.8671
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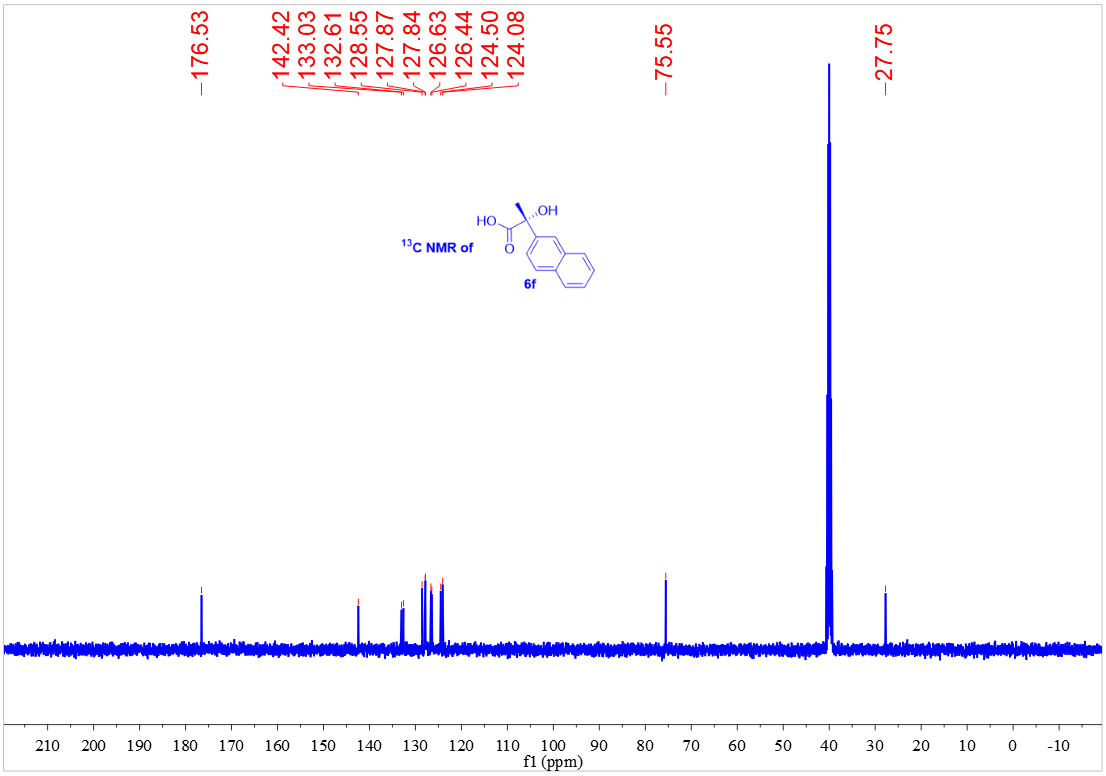
7.6746
7.6579
7.6531
7.5317
7.5264
7.5143
7.5090
7.4998
7.4904
7.4853
7.4733
7.4686
6.0478
1.7351
^{1}H NMR of
6f
HO
OH
O
0.89
1.00
3.00
1.00
2.00
0.74
3.00
f1 (ppm)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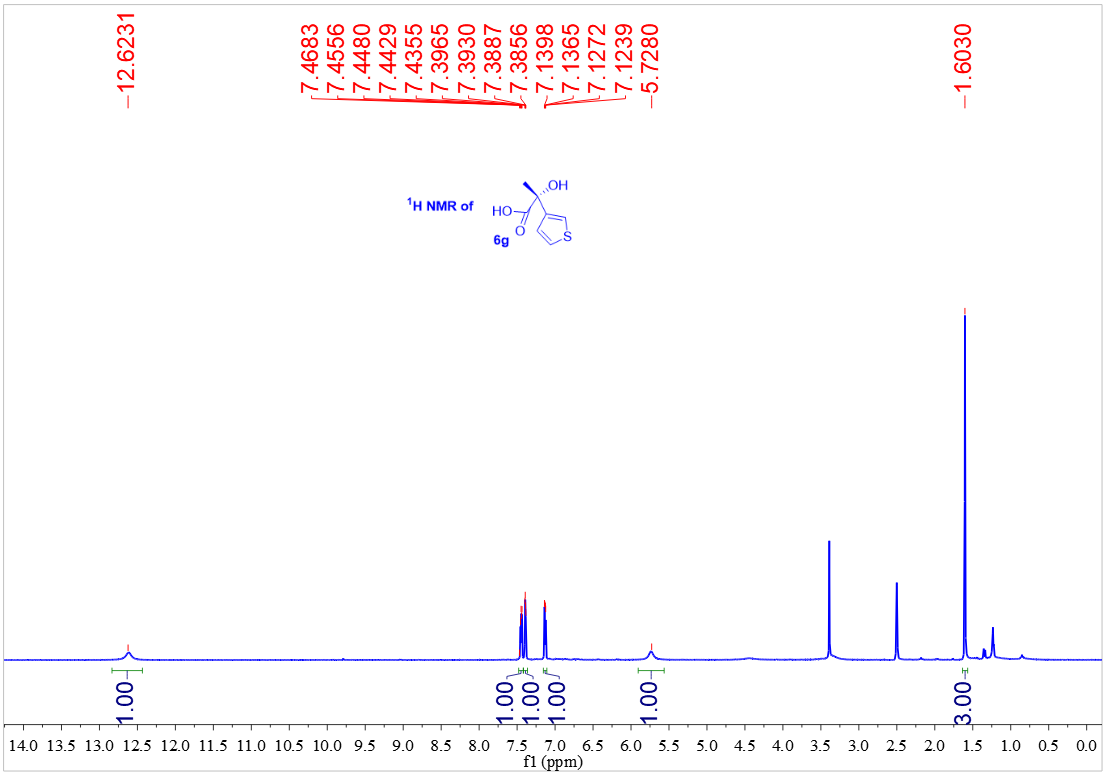
124.50
124.08
75.55
27.75
^{13}C NMR of
6f
f1 (ppm)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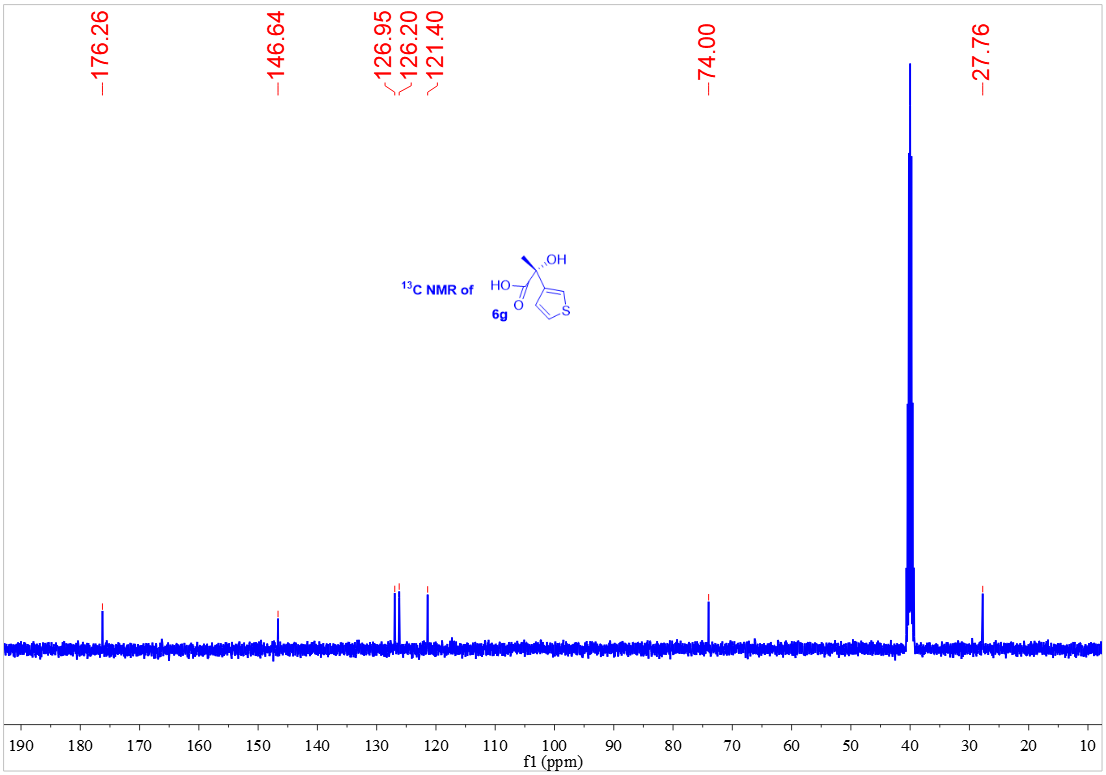
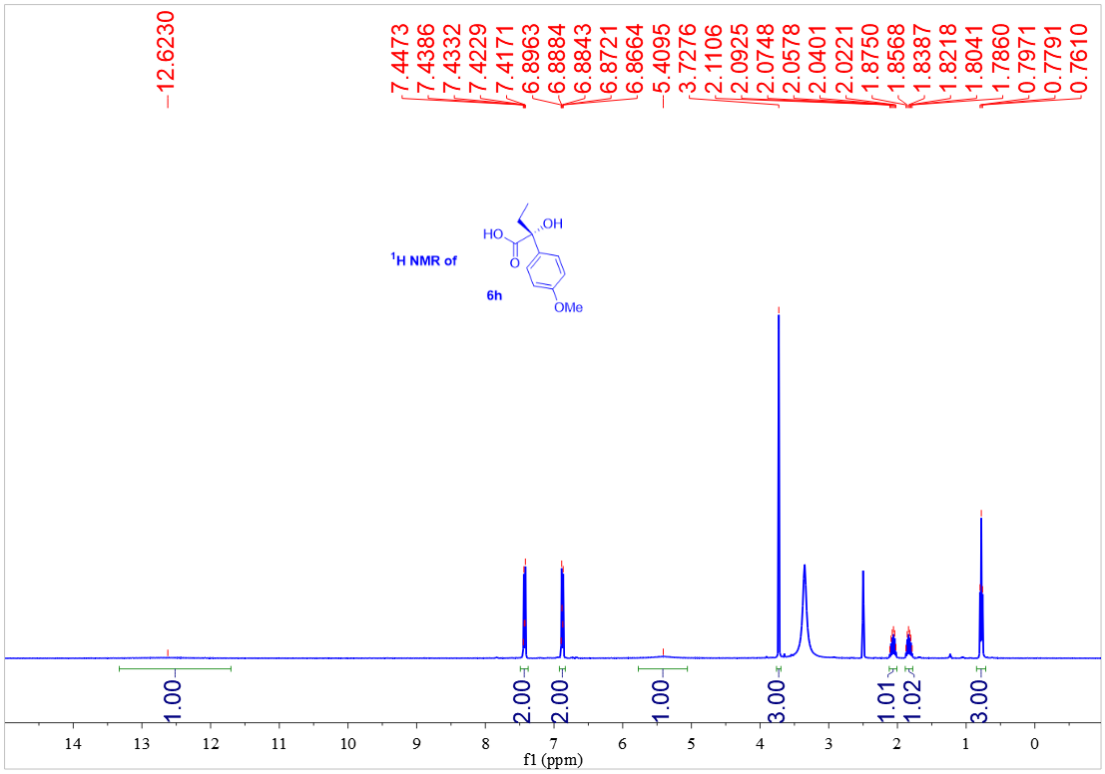
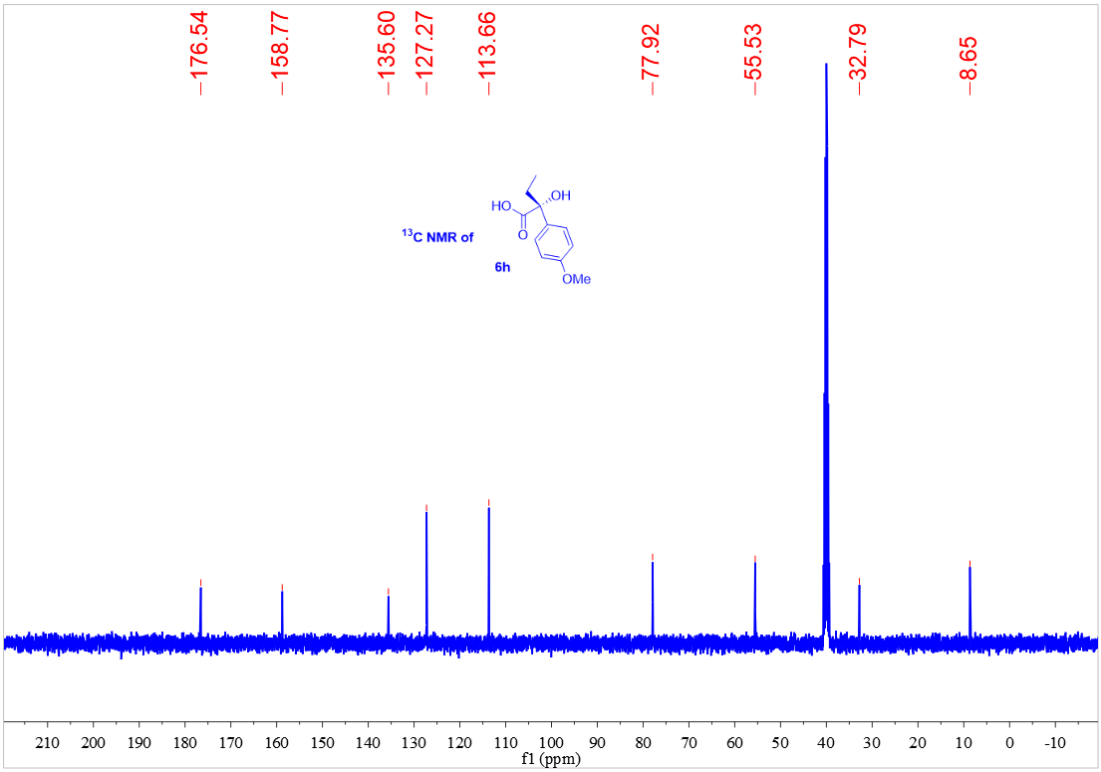
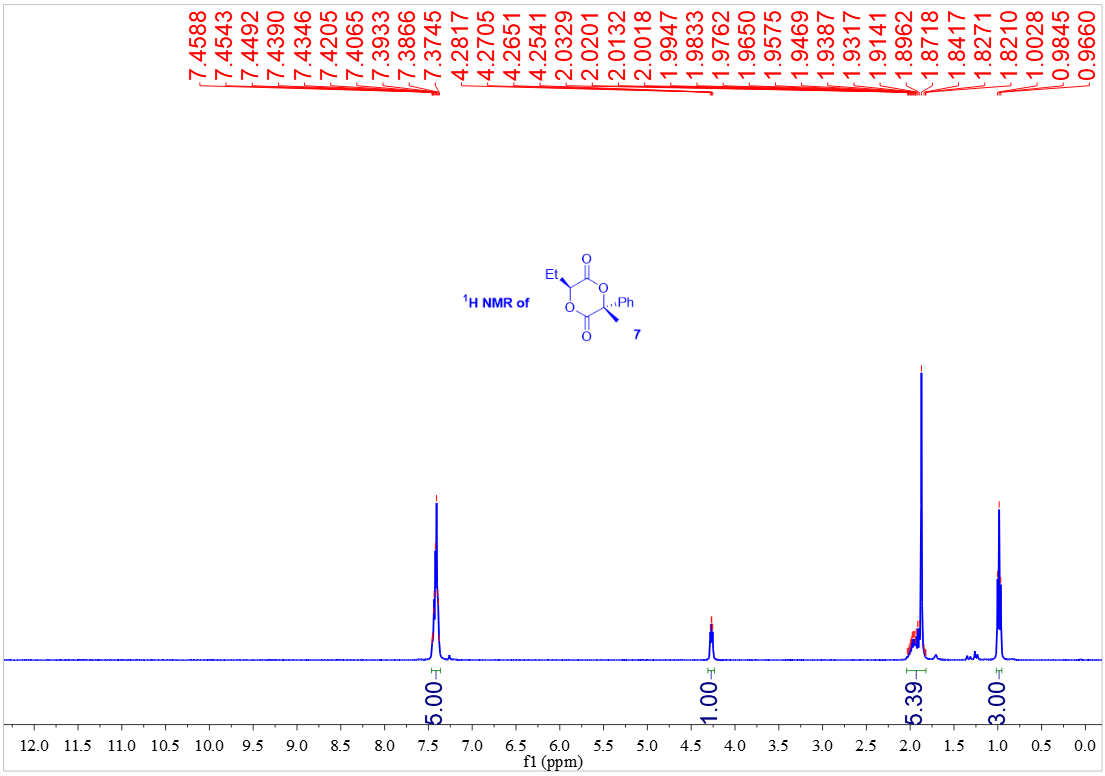
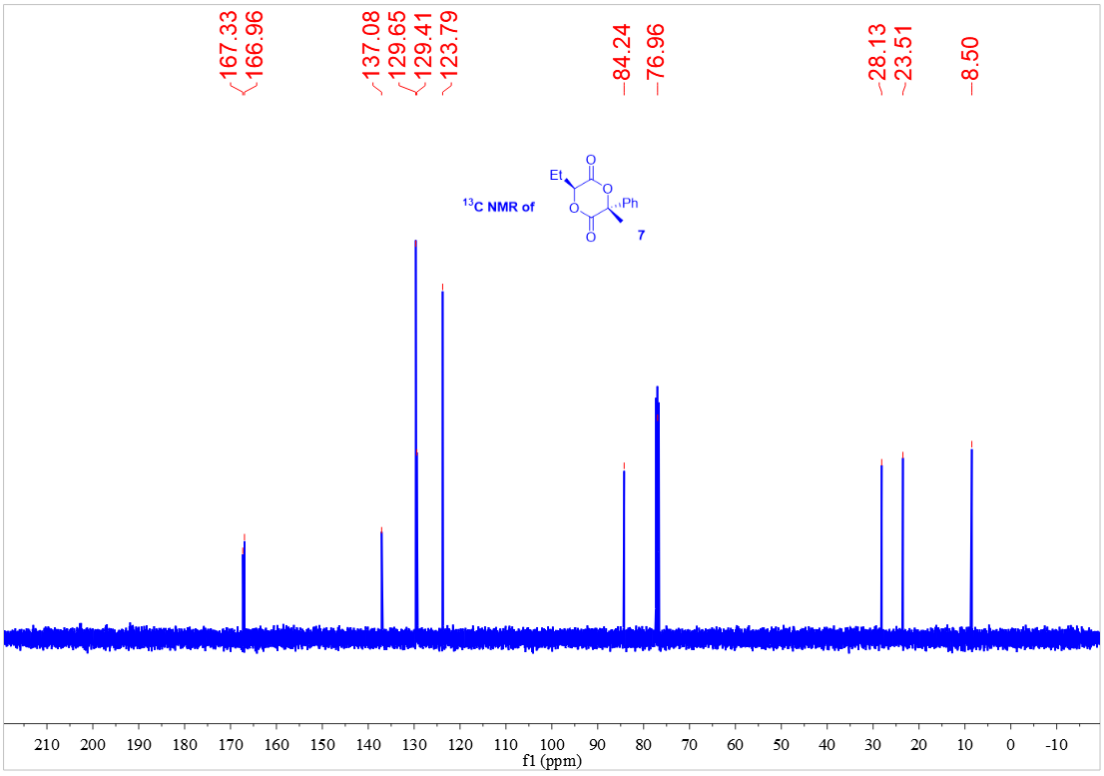
7.1365
7.1272
7.1239
5.7280
1.6030
^{1}H NMR of
6g
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

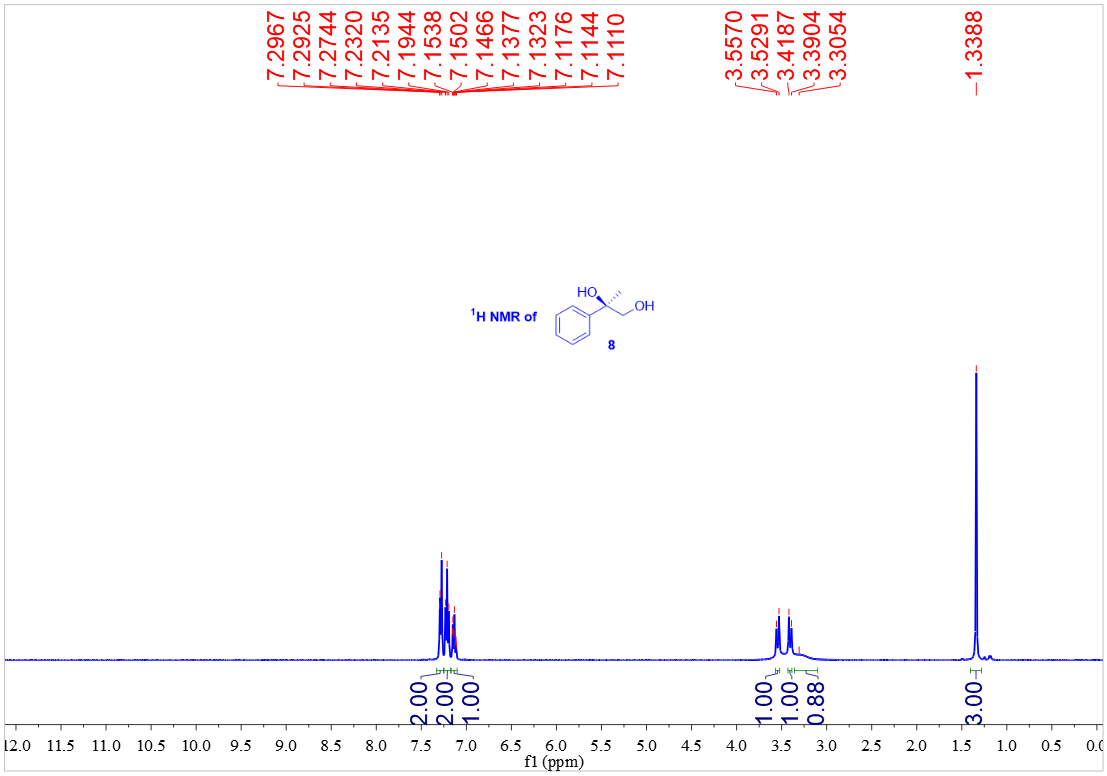

176.26
146.64
126.95
126.20
121.40
74.00
27.76
13C NMR of
6g
OH
HO
O
S
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

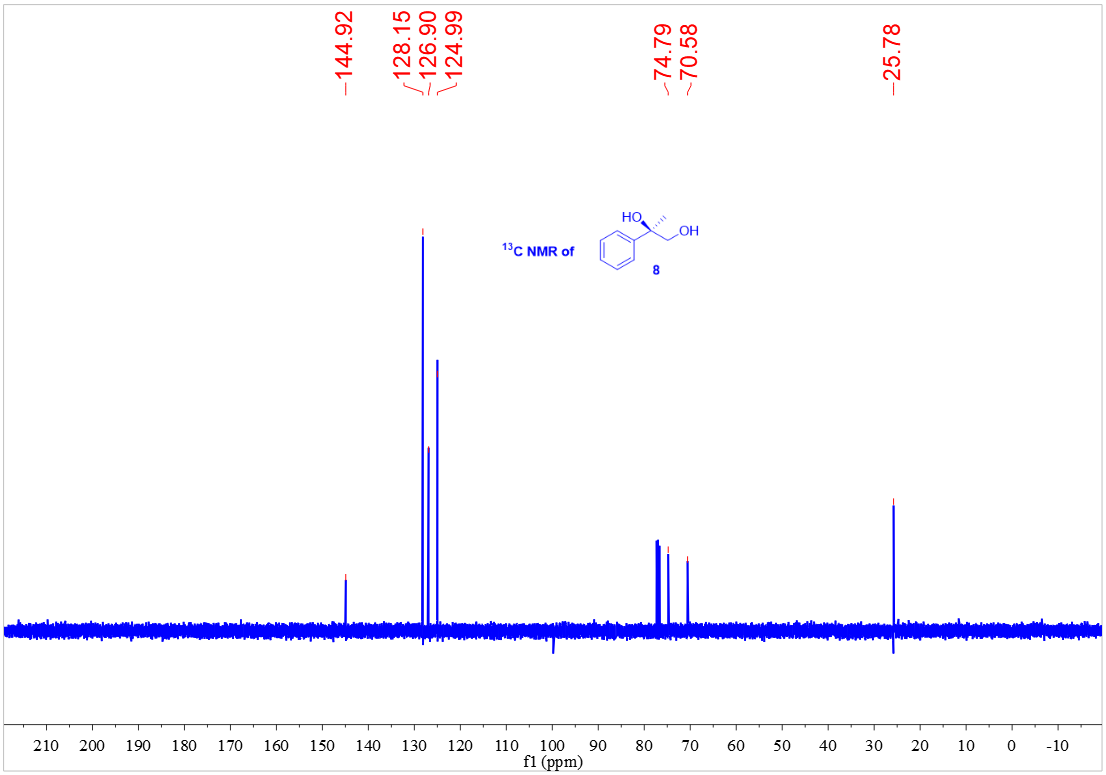

12.6230
7.4473
7.4386
7.4332
7.4229
7.4171
6.8963
6.8884
6.8843
6.8721
6.8664
5.4095
3.7276
2.1106
2.0925
2.0748
2.0578
2.0401
2.0221
1.8750
1.8568
1.8387
1.8218
1.8041
1.7860
0.7971
0.7791
0.7610
1H NMR of
6h
OH
HO
O
OMe
1.00
2.00
2.00
1.00
3.00
1.01
1.02
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

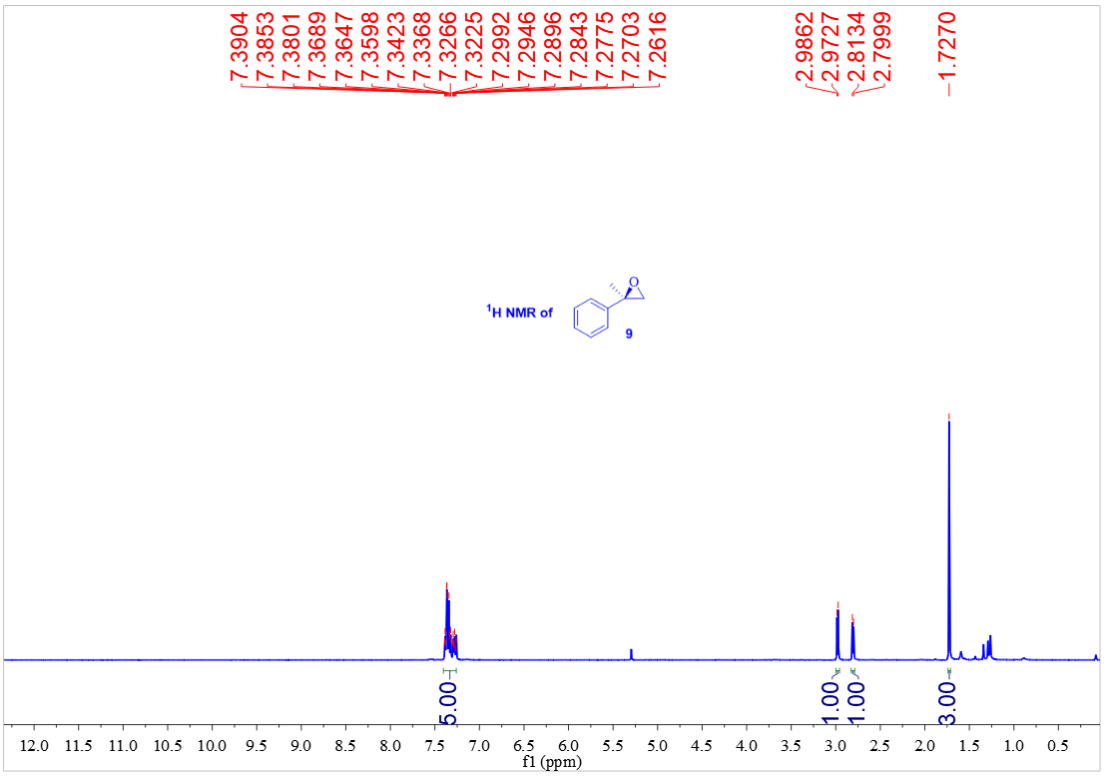

176.54
158.77
135.60
127.27
113.66
77.92
55.53
32.79
8.65
^{13}C NMR of
6h
HO
OH
O
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

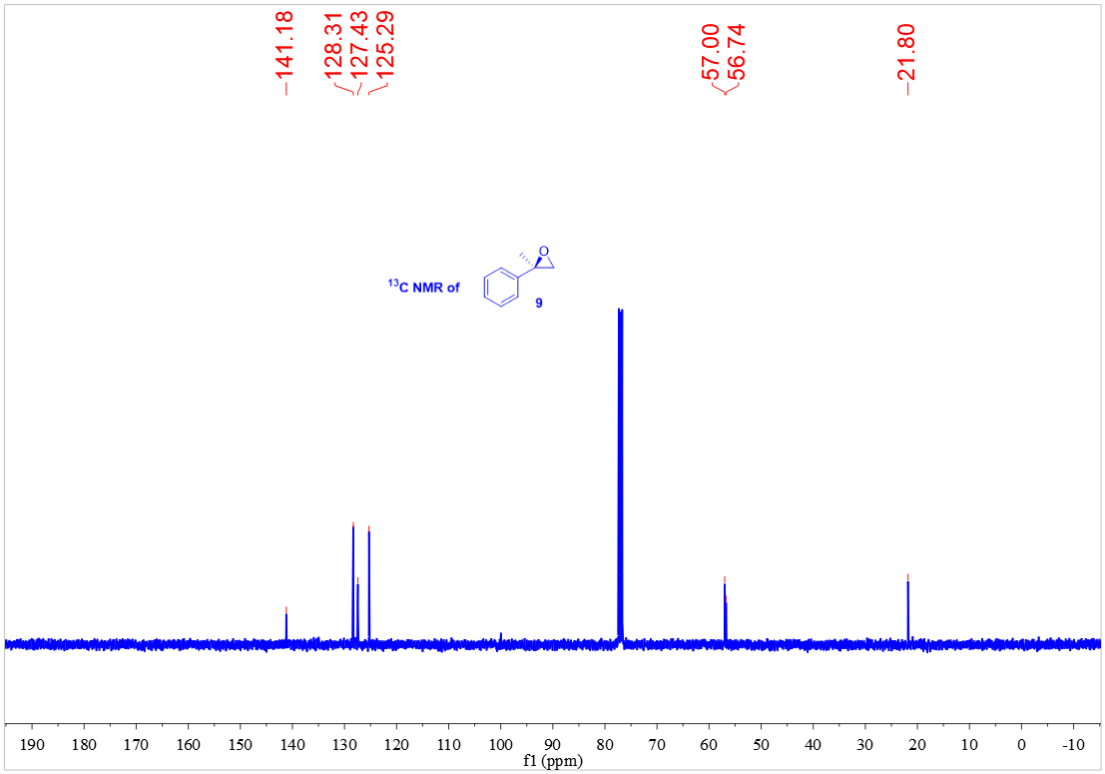

7.4588
7.4543
7.4492
7.4390
7.4346
7.4205
7.4065
7.3933
7.3866
7.3745
4.2817
4.2705
4.2651
4.2541
2.0329
2.0201
2.0132
2.0018
1.9947
1.9833
1.9762
1.9650
1.9575
1.9469
1.9387
1.9317
1.9141
1.8962
1.8718
1.8417
1.8271
1.8210
1.0028
0.9845
0.9660
^{1}H NMR of
7
Et
Ph
O
5.00
1.00
5.39
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.33
166.96
137.08
129.65
129.41
123.79
84.24
76.96
28.13
23.51
8.50
13C NMR of
7
f1 (ppm)


7.2967
7.2925
7.2744
7.2320
7.2135
7.1944
7.1538
7.1502
7.1466
7.1377
7.1323
7.1176
7.1144
7.1110
3.5570
3.5291
3.4187
3.3904
3.3054
1.3388
1H NMR of
8
2.00
2.00
1.00
1.00
1.00
0.88
3.00
f1 (ppm)


144.92
128.15
126.90
124.99
74.79
70.58
25.78
^{13}C NMR of
HO
OH
8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.3904
7.3853
7.3801
7.3689
7.3647
7.3598
7.3423
7.3368
7.3266
7.3225
7.2992
7.2946
7.2896
7.2843
7.2775
7.2703
7.2616
2.9862
2.9727
2.8134
2.7999
1.7270
^{1}H NMR of
O
9
5.00
1.00
1.00
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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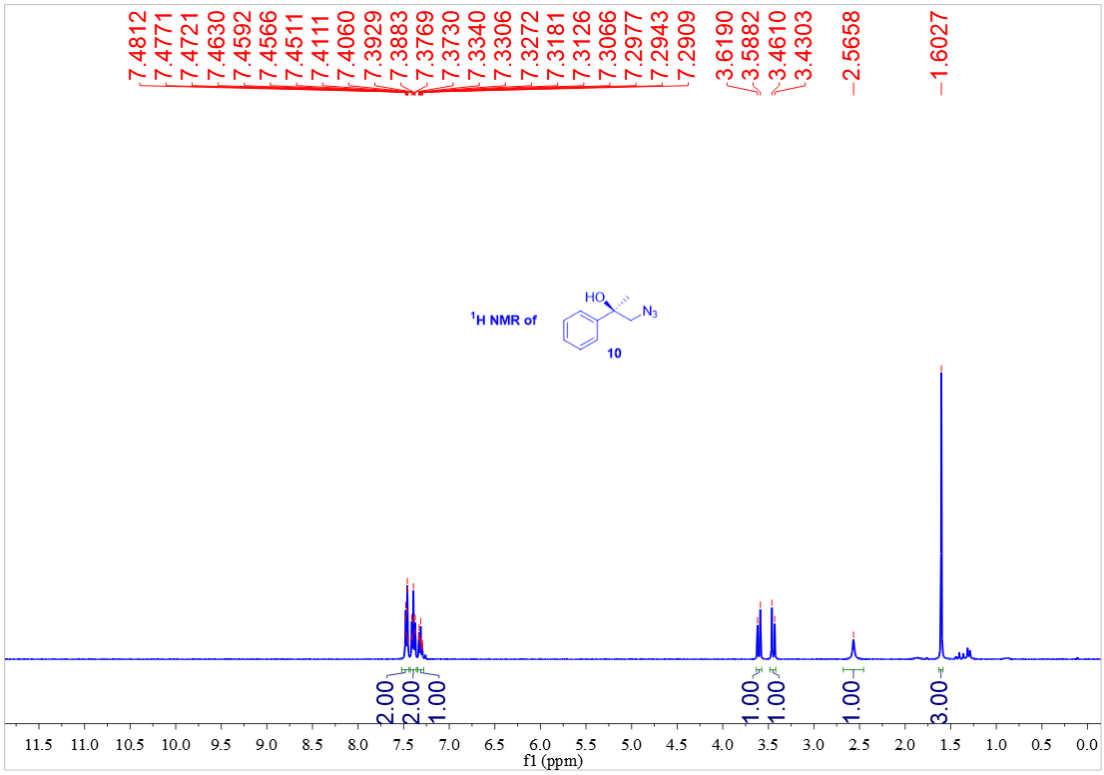
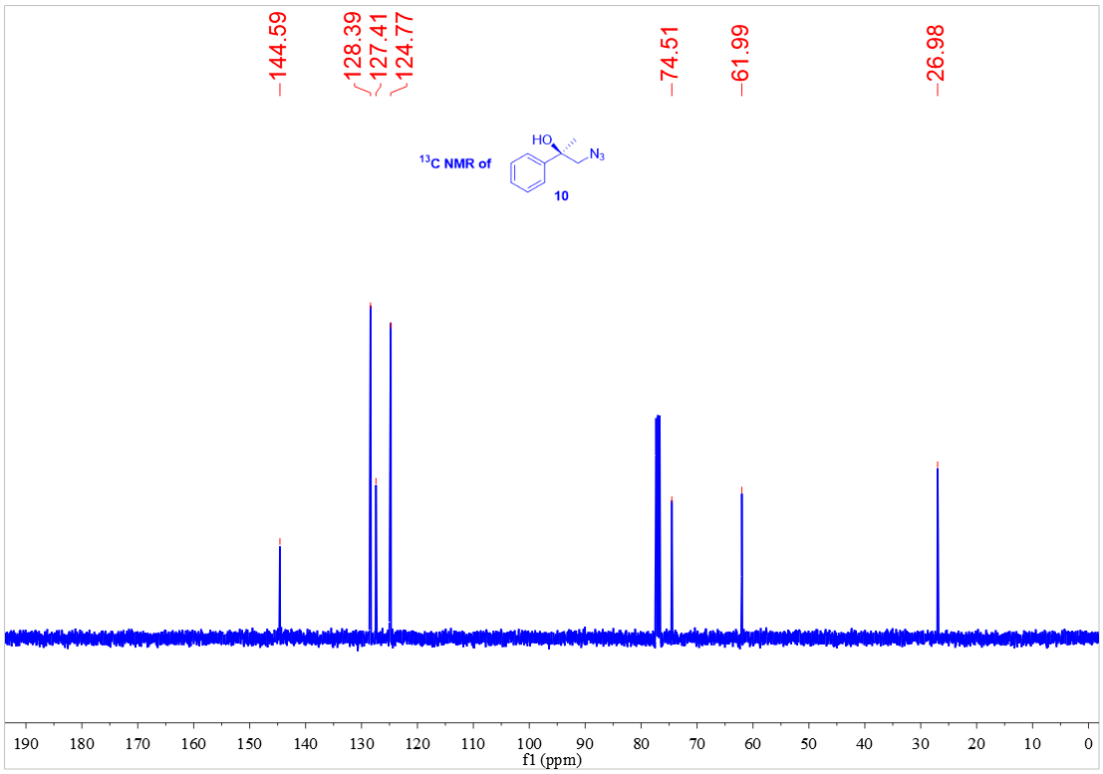
128.31
127.43
125.29
57.00
56.74
21.80
13C NMR of
9
f1 (ppm)


7.4812
7.4771
7.4721
7.4630
7.4592
7.4566
7.4511
7.4111
7.4060
7.3929
7.3883
7.3769
7.3730
7.3340
7.3306
7.3272
7.3181
7.3126
7.3066
7.2977
7.2943
7.2909
3.6190
3.5882
3.4610
3.4303
2.5658
1.6027
1H NMR of
HO
N3
10
2.00
2.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)


144.59
128.39
127.41
124.77
74.51
61.99
26.98
13C NMR of
HO
N3
10
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)