Electronic Supplementary Information for

One-pot *ipso*-hydroxylation and *ortho*-/*para*-halogenation of (hetero)arylboronic acids under tungsten catalysis

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I. General Information

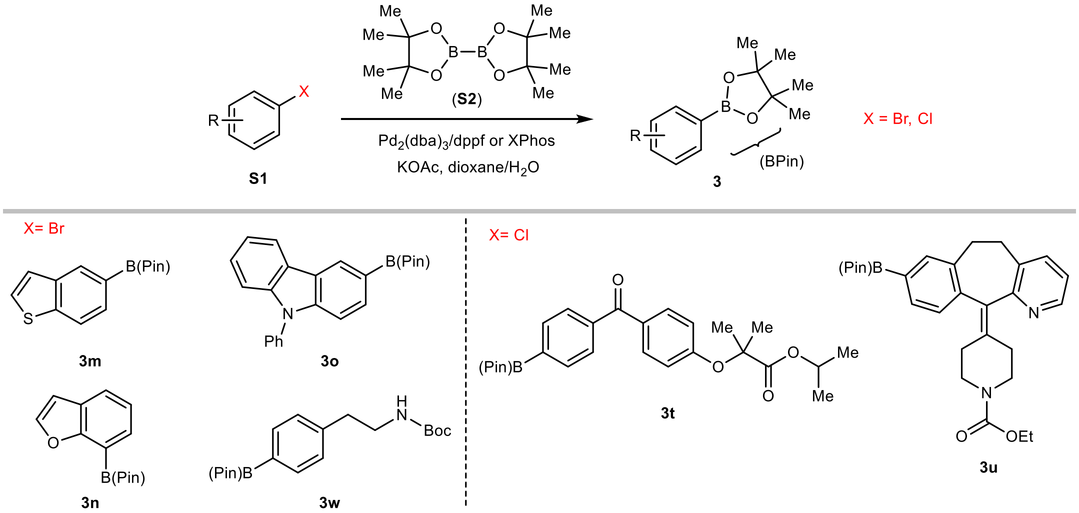
Glassware and stir bars were dried in an oven at 70 °C for at least 12h and then cooled in a desiccator cabinet over Drierite prior to use. Optimization and substrate screen were performed in 20 mL vials. All other reactions were performed in round-bottom flasks sealed with rubber septa. Plastic syringes or pipets were used to transfer liquid reagents. Reactions were stirred magnetically using Teflon-coated, magnetic stir bars. Analytical thin-layer chromatography (TLC) was performed using glass plates pre-coated with 0.25 mm of 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm and 320 nm). TLC plates were visualized by exposure to ultraviolet light and/or exposure to $KMnO_4$ stain (or phosphomolydic acid, PMA; cerium molybdate stain). Organic solutions were concentrated under reduced pressure using a rotary evaporator. Flash-column chromatography was performed on silica gel (300 or 400 mesh).

Nuclear magnetic resonance spectra were recorded at ambient temperature (unless otherwise stated) on Bruke 600 MHz spectrometers. All values for proton chemical shifts are reported in parts per million (δ) and referenced to the residual protium in $CDCl_3$ (δ 7.26) (or DMSO-D_6, δ 2.50). All values for carbon chemical shifts are reported in parts per million (δ) and referenced to the carbon resonances in $CDCl_3$ (δ 77.0) (or DMSO-D_6, 39.52). NMR data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad), coupling constant (Hz), and integration. Infrared spectroscopic data is reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were obtained using a liquid chromatography-electrospray ionization and Time-of-flight mass spectrometer.

All the starting materials, including (hetero)arenes halides, (hetero)aryl boronic acids/esters, diboronic esters, catalysts, bases, oxidants, metal halide, acids and solvents were commercially available. Unless noted, all the reaction solvents were not anhydrous.

II. Starting material synthesis

II-1. boronic ester **3m**, **3n**, **3o**, **3t**, **3u** and **3w** were prepared according to Mukaiyama-borylation

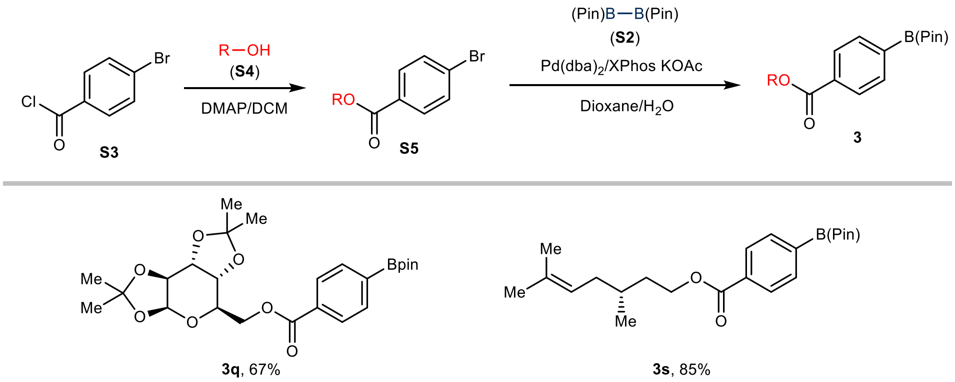


Scheme S1. Preparation of boronic esters **3m**, **3n**, **3o**, **3t**, **3u** and **3w**

To a round-bottom flask charged with (hetero)arylhalide **S1** (5 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) **S2** (1.905 g, 7.5 mmol, 1.5 equiv.), $Pd_2(dba)_3$ (114.5 mg, 0.125 mmol, 2.5mol %.), 1,1-

bis(diphenylphosphino)ferrocene (dppf, 166.3 mg, 6 mol%, or Xphos), KOAc (980 mg, 10 mmol, 2.0 equiv.), was added dioxane/ H_2O (20 mL/2.0 mL) under argon. The mixture was then vigorously stirred at around 100℃ for more 12 h. After competition, EtOAc (around 100 mL) was added, and the resulting mixture was washed with H_2O (30 mL), NH_4Cl (aq., 30 mL), brine (30 mL) and dried by Na_2SO_4. The desired product **1** was isolated after filtration, concentration, and flash chromatography (Scheme S1).

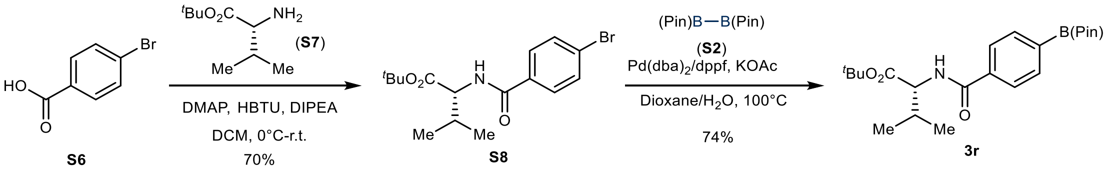
II-2. boronic ester **3q** to **3s** were prepared in a two-step procedure.



Scheme S2. Preparation of boronic esters **3q** and **3s**

To a round-bottom flask charged with alcohol (**S4**, 3.6 mmol, 1.2 equiv.) and DMAP (1.0998 g, 9 mmol, 3.0 equiv.) in anhydrous CH_2Cl_2 (20 mL) was added 4-bromobenzoyl chloride (**S3**, 658.5 mg, 3 mmol). The mixture was stirred at room temperature for 2 h, and then diluted with CH_2Cl_2. The resulting mixture was diluted with EtOAc (150 mL), then washed with H_2O (50 mL), NH_4Cl (50 mL), Na_2CO_3 (aq., 50 mL), NH_4Cl (20 mL), brine (50 mL), and dried by Na_2SO_4. The crude product **S5** was obtained after filtration and concentration under vacuum, which was directly used in the following borylation step without further purification.

Then to the round-bottom flask charged with crude **S5**, boronic ester **S2** (1.143 g, 4.5 mmol,1.5 equiv.), Pd(dba)$_2$ (86.3 mg, 0.15 mmol, 5mol %), Xphos (85.8 mg, 0.18 mmol, 6 mol %), and KOAc (588 mg, 6.0 mmol, 2.0 equiv.) was added dioxane/H_2O (20 mL/2 mL) under argon. The mixture was vigorously stirred at around 100℃ for 11 h, and then diluted with EtOAc (around 100 mL) after cooling to room temperature. The resulting mixture washed once with H_2O (30 mL), brine (30 mL), and dried by Na_2SO_4. After filtration and concentration under vacuum, the residue was purified by silica column (PE: EA = 10:1) to afford the desired products **3q** and **3s** (Scheme S2).



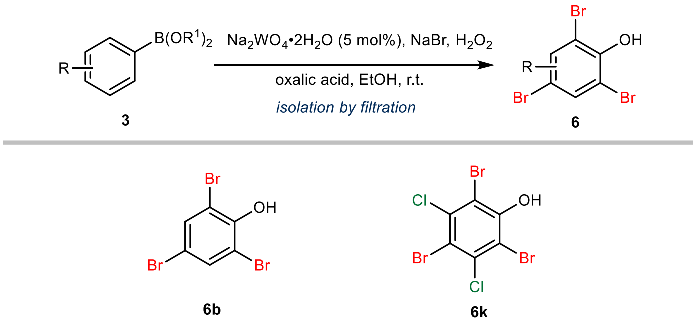
Scheme S3. Preparation of boronic esters **3r**

Boronic ester **3r** was prepared in a similarly fashion. To a round-bottom flask charged with4-bromobenzoic acid **S6** (2.41 g, 12 mmol,1.2 equiv.), DMAP (112 mg, 1.0 mmol, 10 mol%), HBTU (4.55 g, 12 mmol, 1.2 equiv.), and DIPEA (3.87g, 30 mmol, 3.0 equiv.) was added anhydrous CH_2Cl_2 (20 mL) under argon, followed by adding *tert*-butyl D-valinate (**S7**, 2.91 g, 10 mmol) after stirring for 10 minutes at 0°C. The reaction mixture was allowed to proceed for 14 h from 0℃ to room temperature, and diluted with EAOAc (200 mL). The resulting mixture diluted with EtOAc (150 mL), then washed with H_2O (50 mL), NH_4Cl (50 mL), Na_2CO_3 (aq., 50 mL), NH_4Cl (20 mL), brine (50 mL), and dried by Na_2SO_4. After filtration and concentration under vacuum, the crude mixture was purified by flash chromograph (PE: EA = 40: 1) to afford the product **S8** as white solid (2.73 g, 70% yield).

Then to the round-bottom flask charged with **S8** (1.18 g, 3.0 mmol), boronic ester **S2** (1.14 g, 4.5 mmol,1.5 equiv.), $Pd(dba)_2$ (86 mg, 0.15 mmol, 5mol %.), dppf (86 mg, 0.18 mmol, 6 mol %), and KOAc (588 mg, 6.0 mmol, 2.0 equiv.) was added dioxane/H_2O (20 mL/2.0 mL) under argon. The mixture was vigorously stirred at around 100℃ for 12 h, and then diluted with EtOAc (100 mL). The resulting mixture was then washed with H_2O (50 mL), NH_4Cl (aq., 50 mL), brine (50 mL), and dried by Na_2SO_4. After filtration and concentration under vacuum, the crude mixture was purified by flash chromograph (PE: EA = 20: 1) to afford desired product **3r** (0.98 g, 2.2 mmol, 74%) as a white solid (Scheme S3).

III. General procedure for ipso-hydroxylation-halogenation

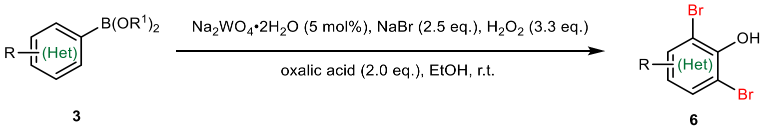
III-1. General procedure for *ipso*-hydroxylation-tribromination



Scheme S4. *ipso*-hydroxylation-tribromination of aryl boronic acid

To a 20 mL vial charged with aryl boronic acid or ester (**3**, 1.0 mmol, 1.0 equiv.), $Na_2WO_4•2H_2O$ (16.5 mg, 0.05 mmol, 5 mol %), NaBr (515 mg, 5 mmol, 5.0 equivalents), oxalic acid (180 mg, 2.0 mmol, 2.0 equivalent), and H_2O_2 (35% aq., 381 uL, 4.4 mmol, 4.4 equivalent) was added EtOH/H_2O (4.0 mL/0.3 mL). The mixture was stirred at room temperature for around 12 h, monitored by TLC analysis. Then the desired product **6** was isolated after filtration (Scheme S4).

III-2. General procedure for *ipso*-hydroxylation-dibromination

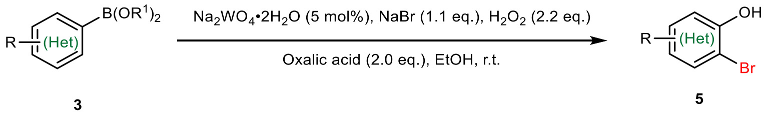


Scheme S5. *ipso*-hydroxylation-dibromination of (hetero)aryl boronic acid or ester

To a 20 mL vial charged with (hetero)aryl boronic acids or esters (**3**, 1.0 mmol, 1.0 equiv.), $Na_2WO_4•2H_2O$ (16.5 mg, 0.05 mmol, 5 mol %), NaBr (257.5 mg, 2.5 mmol, 2.5 equivalent), oxalic acid (180 mg, 2.0 mmol, 2.0 equivalent) in EtOH/H_2O (4.0 mL/0.3 mL) was added H_2O_2 (35% aq., 290 uL, 3.3 mmol, 3.3 equivalent) dropwise in the open air under room temperature. The mixture was stirred at room temperature for about 12 h, followed by diluted with around 25 mL EtOAc. The resulting mixture was then washed by H_2O (10 mL), brine (10 mL), and dried with Na_2SO_4. The desired product **6** was obtained by purification with flash chromatography after filtration and concentration

(Scheme S5).

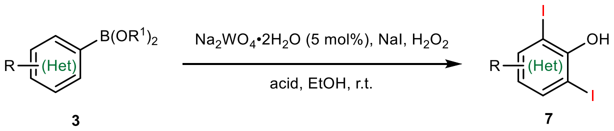
III-3. General procedure for selective *ipso*-hydroxylation-monobromination



Scheme S6. selective *ipso*-hydroxylation-monobromination of (hetero)aryl boronic acid or ester

To a 20 mL vial charged with (hetero)aryl boronic acids or esters (**1**, 1.0 mmol, 1.0 equiv.), Na_2WO_4•$2H_2O$ (16.5 mg, 0.05 mmol, 5 mol %), NaBr (113.3 mg, 1.1.0 mmol, 1.1 equivalent), oxalic acid (180 mg, 2.0 mmol, 2.0 equivalent) in EtOH/H_2O (4.0 mL/0.3 mL) was added H_2O_2 (35% aq., 190 uL, 2.2 mmol, 2.2 equivalent) dropwise in the open air under room temperature. The mixture was stirred at room temperature for around 12 h, and then diluted around 25 mL EtOAc. The resulting mixture was washed by H_2O (10 mL), brine (10 mL), and dried with Na_2SO_4. The desired product **5** was obtained by purification with flash chromatography after filtration and concentration (Scheme S6).

III-4. General procedure for selective *ipso*-hydroxylation-biiodination

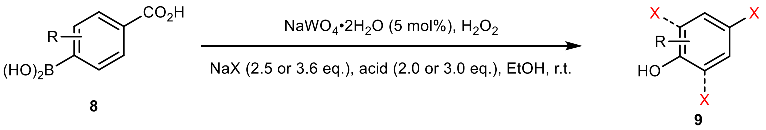


Scheme S7. *ipso*-hydroxylation-iodination of (hetero)aryl boronic acid or ester

To a 20 mL vial charged with (hetero)aryl boronic acids or esters (**3**, 1.0 mmol, 1.0 equiv.), Na_2WO_4•$2H_2O$ (16.5 mg, 0.05 mmol, 5 mol %), oxalic acid (180 mg, 2.0 mmol, 2.0 equivalent), NaI (374.5 mg, 2.5 mmol, 2.5 equivalent) in EtOH/H_2O (4.0 mL/0.3 mL) was added H_2O_2 (35% aq., 290 uL, 3.3 mmol, 3.3 equivalent) dropwise in the open air under room temperature. The mixture was stirred at room temperature for about 12 h, and then diluted with around 25 mL EtOAc. The resulting mixture was washed by H_2O (10 mL), brine (10 mL), and dried with Na_2SO_4. The desired product **7** was obtained by purification with flash chromatography after filtration and concentration (Scheme S7)

IV. General procedure for *ipso*-hydroxylation decarboxylative halogenation

IV-1 General procedure for *ipso*-hydroxylation decarboxylative halogenation

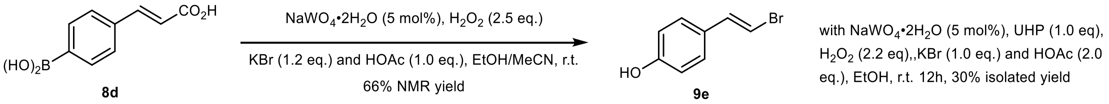


Scheme S8. *ipso*-hydroxylation decarboxylative halogenation

To a 20 mL vial charged with 4-boronobenzoic acid (**8**, 1.0 mmol, 1.0 equiv.), Na_2WO_4•$2H_2O$ (16.5 mg, 0.05 mmol, 5 mol %), oxalic acid (180 mg, 2.0 mmol, 2.0 equivalent), NaX (2.5 mmol, 2.5 equivalent) in EtOH/H_2O (4.0 mL/0.3 mL) was added H_2O_2 (35% aq., 290 uL, 3.3 mmol, 3.3 equivalent) in the open air at room temperature. The mixture was stirred at room temperature for around 12h, followed by diluting with around 25 mL EtOAc. The resulting mixture was then washed by H_2O (10 mL), brine (10 mL), and dried with Na_2SO_4. The desired product **9** was obtained by purification with flash chromatography after filtration and concentration (Scheme S8).

The reaction can be also performed under without tungstate catalyst, and the yields could be improved accoridn to H-NMR of crude products (products **9a**, **9b**, and **9c** with TMB as internal standard). To a 20 mL vial charged with 4-boronobenzoic acid (**8**, 1.0 equiv.), acid (2.0 equivalents or 3.0 equivalents), NaX (2.5 equivalents or 3.6 equivalents) in EtOH/H_2O was added H_2O_2 (35% aq., 3.5 equivalent or 4.5 equivalents) in the open air at room temperature. The mixture was stirred at room temperature for 12 or 24h, followed by diluting with around 5 mL EtOAc. The resulting mixture was then washed by H_2O (2 mL), brine (2 mL), and dried with Na_2SO_4. The yield was determined was ^{1}H NMR of crude product with TMB as internal standard

IV-2 General procedure for *ipso*-hydroxylation decarboxylative bromonination of (*E*)-3-(4-boronophenyl)acrylic acid



Scheme S9. Selective *ipso*-hydroxylation decarboxylative monobromination of (*E*)-3-(4-boronophenyl)acrylic acid

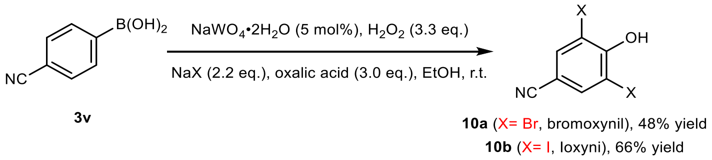
To a 20 mL vial charged with (*E*)-3-(4-boronophenyl)acrylic acid (**8d**, 39 mg, 0.2 mmol, 1.0 equivalent), Na_2WO_4•$2H_2O$ (3.3 mg, 0.01 mmol, 5 mol %), HOAc (12 mg, 0.2 mmol, 1.0 equivalent), KBr (28 mg, 0.24 mmol, 1.2 equivalent) in EtOH/MeCN/H_2O (1.0 mL/0.5/0.3 mL) was added H_2O_2 (35% aq., 50 uL, 0.5 mmol, 2.5 equivalents) in the open air at room temperature. The mixture was stirred at room temperature for around 12 h, followed by diluting with around 5 mL EtOAc. The resulting mixture was then washed by H_2O (2 mL), brine (2 mL), and dried with Na_2SO_4. The yield was determined was ^{1}H NMR of crude product with TMB as internal standard (Scheme S9).

When UHP and H_2O_2 was utilized instead of H_2O_2, the product was obtained in 30% yield as a white solid (22.3 mg, 0.5 mmol scale)

V. Synthetic application

V-1 Late-stage borylation-*ipso*-hydroxylation-halogenation of fenofibric acid and loratadine were performed as described previously. The borylation (see Scheme S1) and ipso-hydroxylation-halogenation (see Scheme S5, S6, S7) worked smoothly.

V-2 Preparation of bromoxynil (**10a**) and Ioxynil (**10b**)

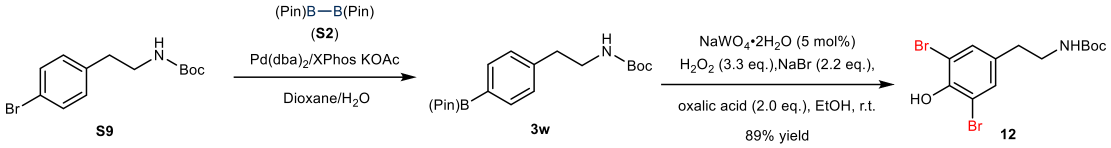


Scheme S10. Preparation of bromoxynil and Ioxynil

The bromoxynil and Ioxynil were prepared from (4-cyanophenyl)boronic acid (**3v**) according to procedure as described in **Scheme S5** and **S7** with Na_2WO_4•$2H_2O$ (16.5 mg, 0.05 mmol, 5 mol %), NaBr or NaI (2.5 mmol, 2.5 equivalent), oxalic acid (180 mg, 2.0 mmol, 2.0 equivalent), and H_2O_2 (35% aq., 290 uL, 3.3 mmol, 3.3 equivalents) in EtOH/H_2O (4.0 mL/0.3 mL) (Scheme S10).

V-2 Formal synthesis of ceratinamine

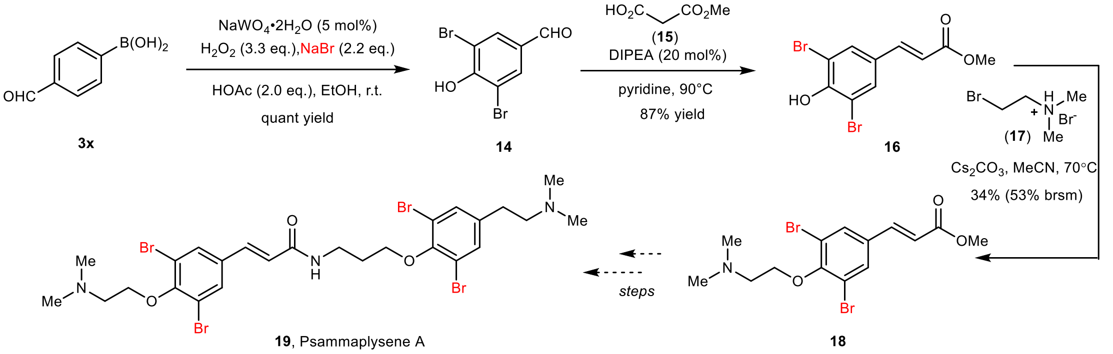
The ceratinamine can be prepared from key intermediate **12** according to reported literature.[1]



Scheme S11. Formal synthesis of ceratinamine

Compound **12** was prepared from *tert*-butyl (4-bromophenethyl)carbamate (**S9**) according to the procedures as described in **Scheme S1** and **Scheme S5** *via* Miyaura-borylation (see S1) and tungstate-catalyzed *ipso*-hydroxylation-dibromination (Scheme S11).

V-3 Formal synthesis of psammaplysene A



Scheme S12. Formal synthesis of psammaplysene A

The psammaplysene A can be prepared from key intermediate **18** according to reported literature,[2] which can be conveniently prepared from (4-formylphenyl) boronic acid (**3x**) in three steps.

To the round-bottom flask charged with (4-formylphenyl)boronic acid (**3x**) (696 mg, 3.0 mmol, 1.0 eqivalent), Na_2WO_4•$2H_2O$ (49.5 mg, 0.15 mmol, 5 mol %), NaBr (773 mg, 7.5 mmol, 2.5 equivalent), acetic acid (360 mg, 6.0 mmol, 2.0 equivalent) in EtOH/H_2O (4 mL/1 mL) was added H_2O_2 (35% aq., 857 uL, 9.9 mmol, 3.3 equivalents) in the open air at room temperature. The reaction proceeded at room temperature, monitored by TLC analysis. Additional H_2O_2 (35% aq., 460 uL after 12h, 200 uL after 20h, 200 uL after 32h, 200 uL after 44h) were added into the reaction before the completion of the reaction. After completion, the products decapitated as gray solid in the reaction solution, and quantitative yield of debromination product **14** (942 mg) were obtained.

The vinyl ester was introduced by condensation. To the solution of compound **14** (280 mg, 1.0 mmol, 1.0 equivalents) and 3-methoxy-3-oxopropanoic acid (**15**, 142 mg, 1.2 mmol, 1.2 equivalents) in pyridine (5 mL) was added DIPEA (26 mg, 0.2 mmol, 0.2 equivalent). The reaction mixture was then heated to 95℃ for 72h, and additional 3-methoxy-3-oxopropanoic acid were added in portions (150 mg + 150 mg + 160 mg). After competition of the reaction, the reaction mixture was cooled to room temperature and 5.0 mL HOAc were added, followed by adding 30 mL H_2O and 100 mL EtOAc. The resulting mixture was then washed by H_2O (30 mL ×7) until all pyridine were removed from organic layer, and dried by Na_2SO_4. The desired product **16** was isolated as white solid (290 mg, 87% yield) after filtration, concentration and purification *via* silica gel column (PE: DCM: EtOAc = 15:1: 1 to 10:1:1).

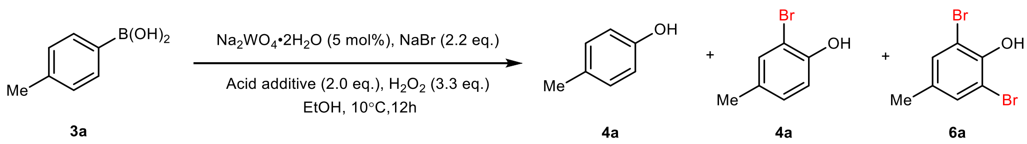
To the mixture of compound **16** (67 mg, 0.2 mmol, 1.0 equivalent), compound **17** (61 mg, 0.26 mmol, 1.3 equivalents), NaI (8 mg, 0.05 mmol, 25 mol%) and Cs_2CO_3 (200mg, 0.7 mmol, 3.5 equivalents) was added anhydrous MeCN (2 mL) at room temperature under argon. Next, the reaction mixture was heated to 65℃ for 24h. The undissolved solid was removed by filtration. The crude mixture was obtained after concertation and purified by silica gel column (PE: EtOAc = 4:1 to DCM: MeOH = 10:1) to afford the desired product **18** (yellow liquid, 28 mg, 34% yield; 22 mg of starting material **16** was recycled) (Scheme S12).

VI. Mechanism study

VI-1. Acid effects in halogenation

The acid effects were performed with substrates **3a** (1.0 mmol scale) at around 10℃ (room temperature in winter) for 12h according to the procedure as described in **Scheme S5**. And the reaction condition was the same (5 mol% $Na_2WO_4•2H_2O$, 2.2 equivalents NaBr, 3.3 equivalents of H_2O_2) with different acid additives (2.0 equivalents) (entry 1-5). One control experiment was performed at 30℃ (entry 6). The yield of products **4a**, **5a** and **6a** were determined by ^{1}H-NMR of crude mixture after removing all the solvents with TMB as internal standard (Table S1).

Table S1. Acid effects

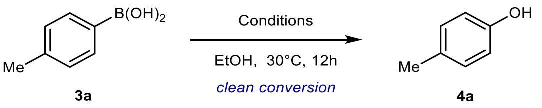


Entry	Acid additive	PKa[1]	Yield[a]		
			4a	4a	6a
1[b]	HOAc	4.86	19%	33%	23%
2[b]	HCO_2H	3.77	4%	45%	25%
3[b]	Citric Acid	3.09	0%	39%	38%
4[b]	$ClCH_2CO_2H$	2.86	0%	28%	57%
5[b]	Oxalic acid	2.83	0%	27%	68%
6[c]	HOAc	4.86	0%	21%	79%

a. Yields were determined by ^{1}H-NMR of crude mixture with 1,3,5-trimethoxylbenzene (TMB) as internal standard; b. the reactions were performed at 10°C; c. the reaction were performed at 30°C.

VI-2. Effects catalyst and acid in *ipso*-hydroxylation and halogenation

This reaction went through a two-steps cascade procedure. Thus, we would like to explore the effects and catalysts and acid additive in each step. The *ipso*-hydroxylation was performed with substrate **1a** (1.0 mmol, 1.0 equivalent) under the condition as described in **Scheme S5** yet without either catalyst (*Condition A*) or acid additive (*Condition B*). Clean conversions were obtained from both conditions (Scheme S13).



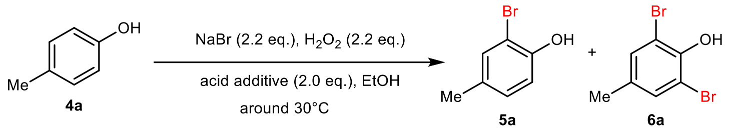
Condition A: oxalic acid (2.0 eq.), H_2O_2 (3.3 eq.)

Condition B: $Na_2WO_4•2H_2O$, H_2O_2 (3.3 eq.)

Scheme S13. Effects of acid and catalysis in *ipso*-hydroxylation

The experiments for investigation the effects of catalyst and acids in halogenation were performed with *p*-cresol (**2a**, 1.0 mmol, 1.0 equivalent) with NaBr (2.2 equivalents), acid additive (2.0 equivalents), H_2O_2 (2.2 equivalents) in EtOH at room temperature (around 30℃) for without catalyst 12h (Entry 1-3) or with $Na_2WO_4•2H_2O$ (5 mol%) for 6h (entry 4-5). The ration between starting material 2a and products 5a, 6a were determined by 1H-NMR of reaction crude mixture after removing all the solvents (Table S2).

Table S2. Effects of catalyst and acid in halogenation of phenols

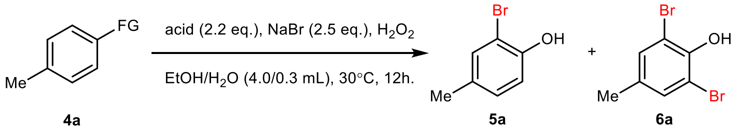


Entry	Catalyst	Acid additive	t/h	ratio by ^{1}H-NMR		
				4a	5a	6a
1	--	HOAc	12	23	55	22
2	--	$ClCH_2CO_2H$	12	0	31	68
3	--	Oxalic acid	12	0	18	79
4	Na_2WO_4-$2H_2O$ (5 mol%)	HOAc	6	20	40	40
5	Na_2WO_4-$2H_2O$(5 mol%)	Oxalic acid	6	0	21	79

VI-3. Background reactions

The background reactions were performed with either *p*-tolylboronic acid (**3a**) or *p*-cresol (**4a**) under the reaction as described in **Scheme S5** at 30℃ for 12h (1.0 mmol scale without tungstate catalyst). The ratio of products **5a** and **6a** was determined by ^{1}H NMR of crude products (Table S3).

Table S3. Background reaction between *p*-tolylboronic acid (**3a**) or *p*-cresol (**4a**)

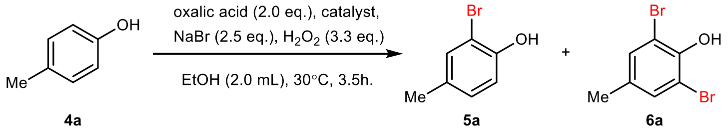


Entry	FG	H_2O_2 (eq.)	acid	Ratio by H-NMR		
				4a	5a	6a
1	$B(OH)_2$	3.3	HOAc	6	45	49
2			$ClCH_2CO_2H$	0	21	79
3			oxalic acid	0	16	84
4	OH	2.2	HOAc	23	48	29
5			$ClCH_2CO_2H$	0	30	70
6			oxalic acid	0	19	81

VI-4. Effects of boronic acids

During the mechanism study, the *p*-tolylboronic acid (**3a**) shower higher reaction rate than *p*-cresol (**4a**) under the same reaction condition. There, we hypothesized that the boronic acid could accelerate the reaction. The *p*-cresol (**4a**) was selected a model substrate under the condition as described in **Scheme S5** without utilizing tungstate catalyst, but boronic acids ($B(OH)_3$ or **3a**, 20 mol%) were added as catalyst. The ration of starting material and products were determined by ^{1}H-NMR of crude reaction mixture after removing all the solvent (Table S4).

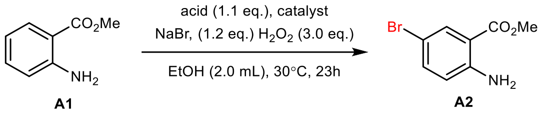
Table S4. Effects of boronic acid with phenol

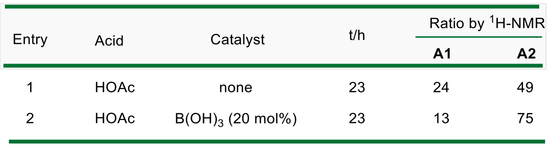


Entry	Catalyst	Ratio by H-NMR		
		4a	5a	6a
1	none	0	15	85
2	$B(OH)_3$ (20 mol%)	0	0	100
3	Tol—$B(OH)_2$ (**3a,** 20 mol%)	0	0	100

In order to figure out whether this rate-acceleration effects of boronic acids are specific to phenols, aniline **A1** was selected as another standard substrate as described in our previous research.[3] The reactions wre performed with aniline **A2** (1.0 mmol, 1.0 equivalent), NaBr (1.2 equivalent), H_2O_2 (3.0 equivalent) in EtOH. The ration between starting material and product was determined by H-NMR of reaction crude mixture after removing all the solvent (Table S5).

Table S5. Boronic acids promoted halogenation of aniline

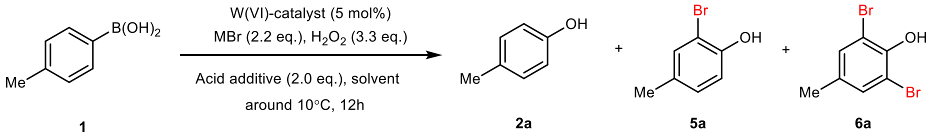




Entry	Acid	Catalyst	t/h	Ratio by ^{1}H-NMR	
				A1	**A2**
1	HOAc	none	23	24	49
2	HOAc	$B(OH)_3$ (20 mol%)	23	13	75

VII. Condition optimization

Table S6. Condition screening for ipso-hydroxylation-bromination 1

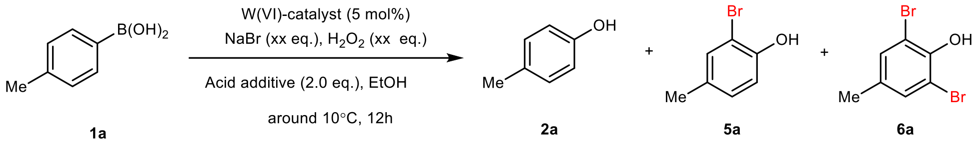


Entry	W(VI)-catalyst	MBr	Acid additive	Solvent	Conversion[a]	Yield[a]		
						2a	**3a**	**4a**
Catalyst screening								
1	Na_2WO_4-$2H_2O$	NaBr	HOAc	EtOH	100%	19%	33%	23%
2	K_2WO_4	NaBr	HOAc	EtOH	100%	0	9%	22%
3	$ZrWO_4$	NaBr	HOAc	EtOH	100%	0	40%	20%
4	$ZnWO_4$	NaBr	HOAc	EtOH	100%	0	32%	32%
5	$H_4[Si(W_3O_{10})_4]\bullet XH_2O$	NaBr	HOAc	EtOH	100%	7%	37%	26%
6	$Na_3O_{40}PW_{12}\bullet XH_2O$	NaBr	HOAc	EtOH	100%	47%	23%	5%
Bromide source screening								
7	Na_2WO_4-$2H_2O$	KBr	HOAc	EtOH	100%	40%	43%	7%
8	Na_2WO_4-$2H_2O$	LiBr	HOAc	EtOH	100%	21%	33%	12%
9	Na_2WO_4-$2H_2O$	$SrBr_2$-$6H_2O$	HOAc	EtOH	100%	0	13%	27%
Solvent source screening								
10	Na_2WO_4-$2H_2O$	NaBr	HOAc	^{i}PrOH	100%	31%	43%	14%
11	Na_2WO_4-$2H_2O$	NaBr	HOAc	THF/H_2O(5:1)	70%	2%	2%	18%
12	Na_2WO_4-$2H_2O$	NaBr	HOAc	Dioxane/H_2O(5:1)	100%	13%	15%	29%
13	Na_2WO_4-$2H_2O$	NaBr	HOAc	DCM/H_2O(5:1)	100%	24%	21%	12%
14	Na_2WO_4-$2H_2O$	NaBr	HOAc	MeCN	100%	43%	19%	9%
Acid additive screening								
15	Na_2WO_4-$2H_2O$	NaBr	$ClCH_2CO_2H$	EtOH	100%	0	28%	57%
16	Na_2WO_4-$2H_2O$	NaBr	HCO_2H	EtOH	100%	4%	45%	25%
17	Na_2WO_4-$2H_2O$	NaBr	$(CO_2H)_2$	EtOH	100%	0%	27%	68%
18	Na_2WO_4-$2H_2O$	NaBr	Citric Acid	EtOH	100%	0%	39%	38%

Unless noted, all the reactions were performed in 1.0 mmol scale (**1**), with 5 mol% of tungstate-catalyst, bromide salt (2.2 mmol, 2.2 equivalents), H_2O_2 (35% aq., 3.3 mmol, 3.3 equivalents), acid additive (2.0 mmol, 2.0 equivalents) in 4.0 mL solvents at room temperature. The condition optimization was carried out during the winter, the room temperature was around 10℃.

[a]. Conversion and yields were determined by ^{1}H-NMR of crude products with TMB as internal standard.

Table S7. Condition screening for ipso-hydroxylation-bromination 2



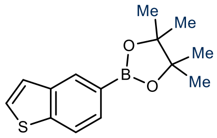
Entry	W(VI)-catalyst	NaBr (eq.)	Acid additive	H_2O_2 (eq.)	Yield[a]		
					2a	**5a**	**6a**
Catalyst confirmation							
1	Na_2WO_4-$2H_2O$	2.2	$ClCH_2CO_2H$	3.3	0%	17%	63%
2	$H_4[Si(W_3O_{10})_4]•XH_2O$	2.2	$ClCH_2CO_2H$	3.3	0%	8%	58%
3	Na_2WO_4-$2H_2O$	2.2	$(CO_2H)_2$	3.3	0%	21%	68%
4	$H_4[Si(W_3O_{10})_4]•XH_2O$	2.2	$(CO_2H)_2$	3.3	0%	16%	51%
5	Na_2WO_4-$2H_2O$	2.2	$(CO_2H)_2$	3.3	0%	17%	59%
Effects of H_2O_2 loading							
6	Na_2WO_4-$2H_2O$	2.2	$ClCH_2CO_2H$	3.3	0%	25%	59%
7	Na_2WO_4-$2H_2O$	2.2	$(CO_2H)_2$	3.3	0%	27%	66%
8	Na_2WO_4-$2H_2O$	2.2	$(CO_2H)_2$	4.0	0%	22%	68%
9	Na_2WO_4-$2H_2O$	2.2	$(CO_2H)_2$	5.0	0%	27%	79%
Effects of NaBr loading							
10	Na_2WO_4-$2H_2O$	3.3	$(CO_2H)_2$	4.0	0%	0%	73%
11	Na_2WO_4-$2H_2O$	3.3	$(CO_2H)_2$	5.0	0%	0%	77%
12	Na_2WO_4-$2H_2O$	2.5	$(CO_2H)_2$	3.3	0%	0%	98%
13	Na_2WO_4-$2H_2O$	2.5	$(CO_2H)_2$	2.2+1.1[b]	0%	0%	97%

Unless noted, all the reactions were performed in 1.0 mmol scale (**1**), with 5 mol% of tungstate-catalyst, bromide salt, H_2O_2 (35% aq.), acid additive (2.0 mmol, 2.0 equivalents) in 4.0 mL solvents at room temperature. The condition optimization was carried out during the winter, the room temperature was around 10℃.

[a]. 100% conversion, and yields were determined by ^{1}H-NMR of crude products with TMB as internal standard.

[b]. The H_2O_2 was added in two portions. 2.2 equivalents of H_2O_2 were added initially, followed by adding another 1.1 equivalent after 12h. And the reaction continued stirring for another 12h.

VIII. Analytic data of starting materials, intermediates and products

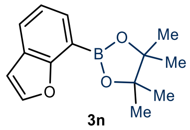


3m

2-(benzo[b]thiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3m**)[4] was prepared according to procedure **II-1** as described in **Scheme S1**, purified by flash column chromatography (PE: EtOAc = 30: 1), and obtained as a white solid (0.88g, 68% yield, 5.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.32 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.42 (dd, *J* = 5.5, 1.5 Hz, 1H), 7.35 (dd, *J* = 5.4, 1.5 Hz, 1H), 1.38 (s, 12H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 142.7, 139.2, 130.7, 129.7, 126.0, 124.1, 121.8, 83.8, 24.9

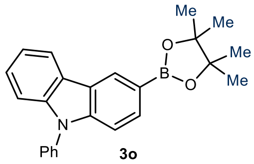


3n

2-(benzofuran-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3n**)[5] was prepared according to procedure **II-1** as described in **Scheme S1**, purified by flash column chromatography (PE: EtOAc = 50: 1), and obtained as a white solid (0.49g, 34% yield, 5.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.75 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.73 (d, *J* = 2.2 Hz, 1H), 7.71 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 2.2 Hz, 1H), 1.41 (s, 12H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.9, 145.3, 131.7, 126.8, 124.5, 122.3, 106.1, 83.9, 24.9

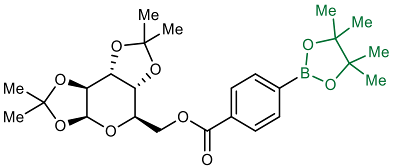


3o

9-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (**3o**)[6] was prepared according to procedure **II-1** as described in **Scheme S1**, purified by flash column chromatography (PE: EtOAc = 10: 1), and obtained as a white solid (0.45g, 61% yield, 2.0 mmol scale)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 8.19 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 7.3 Hz, 2H), 7.49 (d, *J* = 7.0 Hz, 1H), 7.39 (d, *J* = 12.3 Hz, 3H), 7.30 (t, *J* = 6.4 Hz, 1H), 1.41 (s, 12H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 143.0, 141.0, 137.5, 132.4, 129.9, 127.7, 127.6, 127.1, 125.9, 123.5, 123.1, 120.5, 120.3, 119.5, 109.7, 109.1, 83.6, 24.9

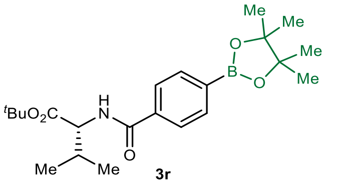


3q

((3a*S*,5*R*,5a*R*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**3q**)[7] was procedure **II-2** as described in **Scheme S2**, purified by flash column chromatography (PE: EtOAc = 10: 1), and obtained as white solid (0.96 g, 67% yield, 3.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.04 – 8.01 (m, 2H), 7.87 – 7.84 (m, 2H), 5.56 (d, *J* = 4.9 Hz, 1H), 4.65 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.54 (dd, *J* = 11.5, 4.8 Hz, 1H), 4.43 (dd, *J* = 11.5, 7.5 Hz, 1H), 4.37 – 4.31 (m, 2H), 4.18 (ddd, *J* = 7.1, 4.8, 1.8 Hz, 1H), 1.50 (s, 3H), 1.47 (s, 3H), 1.35 (s, 15H), 1.33 (s, 3H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.5, 134.6, 132.2, 128.7, 109.7, 108.8, 96.3, 84.1, 71.1, 70.7, 70.5, 66.1, 63.9, 25.98, 25.95, 25.0, 24.9, 24.5

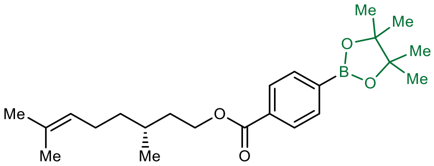


3r

***Tert*-butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)-*D*-valinate** (**3r**)[8] was prepared according to procedure **II-3** as described in **Scheme S3**, purified by flash column chromatography (PE : EtOAc = 20 : 1), and obtained as white solid (0.98g, 74% yield, 3.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 – 7.85 (m, 2H), 7.80 – 7.77 (m, 2H), 6.69 (d, *J* = 8.5 Hz, 1H), 4.68 (dd, *J* = 8.5, 4.4 Hz, 1H), 2.27 (heptd, *J* = 6.9, 4.4 Hz, 1H), 1.49 (s, 9H), 1.35 (s, 12H), 0.99 (dd, *J* = 11.7, 6.9 Hz, 6H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.3, 167.1, 136.6, 134.9, 132.5, 126.1, 84.1, 82.2, 57.6, 31.8, 28.0, 24.84, 24.82, 18.9, 17.8



3s

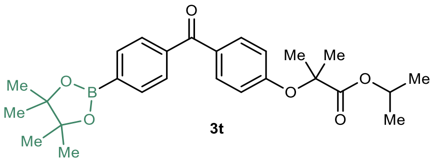
(*R*)-3,6-dimethylhept-5-en-1-yl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**3s**) was procedure **II-2** as described in **Scheme S2**, purified by flash column chromatography (PE: EtOAc = 10: 1), and obtained as a colorless liquid (0.98g, 85% yield, 3.0 mmol scale)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.03–8.00 (m, 2H), 7.87 (d, *J* = 7.9 Hz, 2H), 5.10 (tt, *J* = 7.2, 1.5 Hz, 1H), 4.41 – 4.32 (m, 2H), 2.01 (dtt, *J* = 21.9, 14.7, 7.0 Hz, 2H), 1.82 (dtd, *J* = 12.6, 7.2, 5.1 Hz, 1H), 1.71-1.63 (m, 1H), 1.67 (d, *J* = 1.7 Hz, 3H), 1.61-1.57 (m, 1H), 1.60 (s, 3H), 1.44 – 1.39 (m, 1H), 1.35 (s, 12H), 1.24 (dddd, *J* = 13.5, 9.3, 7.6, 6.0 Hz, 1H), 0.97 (d, *J* = 6.6 Hz, 3H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.7, 134.6, 133.8, 132.7, 131.3, 128.5, 124.5, 84.1, 63.6, 37.0, 35.5, 29.5, 25.7, 25.4, 24.8, 19.5, 17.6

HRMS for $C_{23}H_{35}BNaO_4^+$ ($[M+Na^+]$): 409.2521; found 409.2517

IR (KBr, cm^{-1}), cm^{-1}: 2928, 1724, 1401, 1360, 1269, 1113, 858



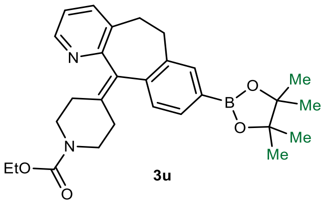
3t

Isopropyl 2-methyl-2-(4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)phenoxy)propanoate (3t)[9] was prepared according to procedure **II-1** as described in **Scheme S1**, purified by flash column chromatography (PE:

EtOAc = 30: 1), and obtained as a gray solid (2.44g, 95% yield, 5.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 – 7.88 (m, 2H), 7.76 – 7.73 (m, 2H), 7.72 – 7.69 (m, 2H), 6.87 – 6.83 (m, 2H), 5.08 (hept, *J* = 6.3 Hz, 1H), 1.36 (s, 6H), 1.26 (d, *J* = 5.1 Hz, 12H), 1.20 (d, *J* = 6.3 Hz, 6H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 195.7, 173.2, 159.6, 140.4, 134.5, 132.8, 132.1, 130.5, 128.7, 117.1, 84.2, 79.4, 69.3, 25.4, 24.9, 21.5

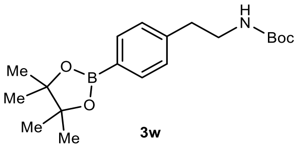


3u

Ethyl 4-(8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (3u)[10] was prepared according to procedure **II-1** as described in **Scheme S1**, purified by flash column chromatography (DCM: MeOH = 200: 1- 50:1)，and obtained as a yellow solid (0.88g, 38% yield, 5.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.37 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.65–7.58 (m, 2H), 7.41 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.06 (dd, *J* = 7.7, 4.8 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.79 (d, *J* = 27.9 Hz, 2H), 3.42 (tt, *J* = 11.9, 4.5 Hz, 1H), 3.34 (dt, *J* = 14.0, 5.5 Hz, 1H), 3.13 (dtd, *J* = 12.9, 8.9, 4.0 Hz, 2H), 2.88 – 2.81 (m, 2H), 2.48 (ddd, *J* = 14.2, 9.5, 4.5 Hz, 1H), 2.33 (tddd, *J* = 17.4, 12.9, 8.8, 4.5 Hz, 3H), 1.31 (d, *J* = 2.2 Hz, 12H), 1.24 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.5, 146.3, 142.8, 137.6, 136.9, 136.9, 135.3, 135.1, 133.7, 132.5, 128.6, 122.1, 83.7, 61.3, 44.8, 31.8, 31.5, 24.8, 24.7, 14.6

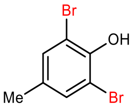


3w

***Tert*-butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenethyl)carbamate (3w)**[11] was prepared according to **II-1** procedure as described in **Scheme S1** , purified by flash column chromatography (PE: EtOAc = 50: 1), and obtained as white solid (0.88g, 84% yield, 3.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 7.9, 2.4 Hz, 2H), 7.13 (d, *J* = 7.4 Hz, 2H), 4.43 (s, 1H), 3.30 (t, *J* = 7.0 Hz, 2H), 2.73 (d, *J* = 7.4 Hz, 2H), 1.36 (s, 9H), 1.27 (d, *J* = 2.5 Hz, 12H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.8, 142.3, 135.1, 128.2, 126.8, 83.7, 79.2, 41.6, 36.3, 28.4, 24.8

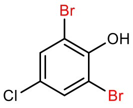


6a

2,6-dibromo-4-methylphenol (6a)[12] was prepared according to procedure **III-2** procedure as described in **Scheme S5**, purified by flash column chromatography (PE: EtOAc = 10: 1), and obtained as a yellow liquid (238 mg, 90% yield, 1.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 (s, 2H), 5.70 (s, 1H), 2.25 (s, 3H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.1, 132.4, 109.4, 20.0

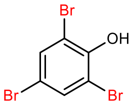


6b

2,6-dibromo-4-chlorophenol (**6b**)[10] was prepared according to prepared according to procedure **III-2** as described in **Scheme S5**, obtained as pale-yellows solid (272 mg, 96% yield, 1.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.46 (s, 2H), 5.85 (s, 1H)

^{13}C NMR (151 MHz, DMSO-D$_6$ + Chloroform-*d*) δ 149.7, 130.9, 124.5, 111.6



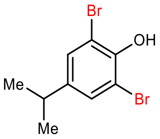
6c

2,4,6-tribromophenol (**6c**)[13] was prepared according to prepared according to procedure **III-1** as described in **Scheme S4** utilizing HOAc as acid additive, obtained as white solid (3.9g, quantitative yield, 10.0 mmol scale) by simple filtration.

The *ipso*-hydroxylation *decarboxylative bromination of 4-boronobenzoic acid* (**8a**) was performed according to procedure **IV-1** as described in Scheme S8, affording product **6c** as pale-yellow solid (137.9 mg, 42% yield, 1.0 mmol scale), or 71% yield (2.34g, 10.0 mmol scale, isolated by simple filtration).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 (s, 2H), 5.88 (s, 1H)

^{13}C NMR (151 MHz, Chloroform-d) δ 149.0, 134.2, 112.7, 110.4

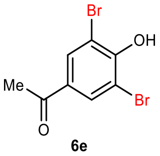


6d

2,6-dibromo-4-isopropylphenol (**6d**)[14] prepared according to procedure **III-2** as described in **Scheme S5**, and obtained as a yellow liquid (286 mg, 97% yield,1.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.29 (s, 2H), 5.72 (s, 1H), 2.81 (hept, *J* = 6.8 Hz, 1H), 1.21 (d, *J* = 6.8 Hz, 6H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.2, 143.5, 130.0, 109.6, 33.1, 23.9

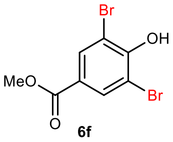


6e

1-(3,5-dibromo-4-hydroxyphenyl)ethan-1-one (**6e**)[15] was prepared according to procedure **III-2** as described in **Scheme S5**, purified by flash column chromatography (PE: EtOAc = 4: 1), and obtained as yellow solid (200 mg, 68% yield, 1.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.07 (s, 2H), 6.32 (s, 1H), 2.55 (s, 3H)

^{13}C NMR (151 MHz, Chloroform-d) δ 194.3, 153.3, 132.6, 131.9, 110.1, 26.2

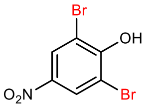


6f

Methyl 3,5-dibromo-4-hydroxybenzoate (**6f**)[3] was prepared according to procedure **III-2** as described in **Scheme S5**, purified by flash column chromatography (PE: EtOAc = 10: 1), and obtained as white solid (226 mg, 73% yield,1.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.15 (s, 2H), 6.29 (s, 1H), 3.90 (s, 3H)

^{13}C NMR (151 MHz, Chloroform-d) δ 164.5, 153.3, 133.6, 124.7, 109.7, 52.5

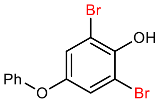


6g

2,6-dibromo-4-nitrophenol (**6g**)[10] was prepared according to procedure **III-2** as described in **Scheme S5**, purified by flash column chromatography (PE: EtOAc = 10: 1), and obtained as yellow solid (176 mg, 60% yield, 1.0 mmol scale)

^{1}H NMR (600 MHz, Chloroform-d) δ 8.41 (s, 2H), 6.50 (s, 1H)

^{13}C NMR (151 MHz, Chloroform-d) δ 155.0, 141.6, 127.9, 109.7

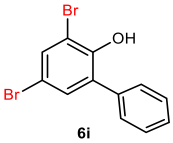


6h

2,6-dibromo-4-phenoxyphenol (**6h**)[16] was preared according to procedure **III-2** as described in **Scheme S5**, purified by flash column chromatography (PE: EtOAc = 40: 1), and obtained as a yellow solid (122 mg, 34% yield, 1.0 mmol scale, along with monobromination product (38% yield, 101 mg))

^{1}H NMR (600 MHz, Chloroform-d) δ 7.35 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.16 (s, 2H), 6.97 (dd, *J* = 8.4, 1.3 Hz, 2H), 5.70 (s, 1H)

^{13}C NMR (151 MHz, Chloroform-d) δ 157.0, 150.7, 145.8, 129.9, 123.7, 122.8, 118.4, 109.7

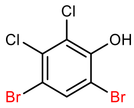


6i

3,5-dibromo-[1,1'-biphenyl]-2-ol (**6i**)[17] was prepared according to procedure **III-2** as described in **Scheme S5**, purified by flash column chromatography (PE: EtOAc = 40: 1), obtained as brown solid (269 mg, 82% yield, 1.0 mmol scale)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 4.5 Hz, 1H), 7.47 (dq, *J* = 13.3, 7.1 Hz, 4H), 7.40 (q, *J* = 5.9, 5.0 Hz, 2H), 5.66 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-d) δ 148.6, 135.9, 133.3, 132.7, 131.0, 129.0, 128.7, 128.3, 112.7, 111.5



6j

4,6-dibromo-2,3-dichlorophenol (**6j**) was prepared according to procedure **III-2** as described in **Scheme S5**, purified by flash column chromatography (PE: EtOAc = 40: 1), and obtained as a yellow solid (158 mg, 50% yield, 1.0 mmol scale).

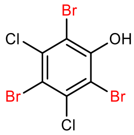
^{1}H NMR (600 MHz, Chloroform-d) δ 7.72 (s, 1H), 6.01 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.3, 134.1, 133.2, 121.0, 113.9, 108.5

HRMS for $C_6HBr_2Cl_2O^-$ ($[M-H]^-$): 318.7756; found 318.7761

IR (KBr, cm^{-1}): 3420, 1628, 1438, 1363, 1164, 798

M.p.: 82-87℃



6k

2,4,6-tribromo-3,5-dichlorophenol (**6k**) was prepared according to **III-1** as described in **Scheme S4**, obtained as a white solid by filtration (232 mg, 59% yield, 1.0 mmol scale)

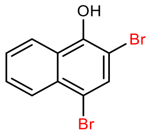
^{1}H NMR (600 MHz, Chloroform-d) δ 6.24 (s, 1H)

^{13}C NMR (151 MHz, Chloroform-*d* + DMSO-D_6) δ 152.1, 134.6, 113.4, 111.2

HRMS for $[M-H^-]$ $C_6Br_3Cl_2O^-$, 398.6861; found 396.6860

IR (KBr, cm^{-1}): 3415, 1631, 1361, 1281, 1262, 971

M.p.: 160-171.2℃

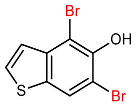


6l

2,4-dibromonaphthalen-1-ol (**6l**)[15] was prepared according to procedure **III-2** as described in **Scheme S5**, purified by flash column chromatography (PE: EtOAc = 30: 1), and obtained as a white solid (162 mg, 54% yield, 1.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (ddd, *J* = 8.4, 1.3, 0.7 Hz, 1H), 8.16 – 8.11 (m, 1H), 7.79 (s, 1H), 7.63 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.56 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 5.97 (s, 1H)

^{13}C NMR (151 MHz, Chloroform-d) δ 148.2, 131.9, 131.1, 128.1, 127.1, 126.9, 125.1, 122.8, 113.3, 103.2



6m

4,6-dibromobenzo[b]thiophen-5-ol (**6m**) was prepared according to procedure **III-2** as described in **Scheme S5**, purified by flash column chromatography (PE: EtOAc = 30: 1), and obtained as a yellow solid (127 mg, 82% yield, 0.5 mmol scale).

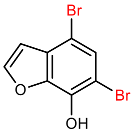
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.52 (d, *J* = 5.5 Hz, 1H), 7.34 (d, *J* = 5.5 Hz, 1H), 5.92 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.4, 139.8, 132.7, 129.2, 124.8, 123.7, 107.8, 103.1

HRMS for [M-H^{-}] $C_8H_5Br_2OS$, 306.8256; found 306.8255

IR (KBr, cm^{-1}): 3463, 1632, 1406, 1342, 1179, 750

M.p.: 87-88℃



6n

4,6-dibromobenzofuran-7-ol (**6n**) was prepared according to procedure **III-2** as described in **Scheme S5**, purified by flash column chromatography (PE: EtOAc = 40: 1), obtained as a yellow solid (116 mg, 79% yield, 0.5 mmol scale).

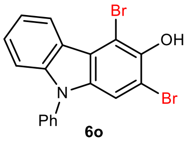
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 3.9 Hz, 1H), 7.51 – 7.46 (m, 1H), 6.77 (d, *J* = 3.9 Hz, 1H), 5.75 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 146.1, 142.6, 138.3, 130.3, 128.2, 107.5, 105.0, 104.4

HRMS for [M-H^{-}] $C_8H_3Br_2O_2^-$, 2980.8485; found 290.8501

IR (KBr, cm^{-1}): 3383, 1634, 1579, 1333, 1280 1174, 852

M.p.: 89-95℃



6o

2,4-dibromo-9-phenyl-9H-carbazol-3-ol (**6o**) was prepared according to procedure **III-2** as described in **Scheme S5**, purified by flash column chromatography (PE: EtOAc = 50: 1), obtained as white solid (72 mg, 57% yield, 0.3 mmol scale).

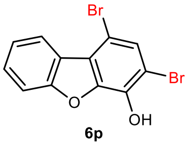
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 2.4 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.52 (dt, *J* = 7.1, 3.0 Hz, 5H), 7.27 (dd, *J* = 9.7, 3.8 Hz, 2H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 139.9, 136.8, 130.1, 129.5, 128.1, 126.9, 123.9, 123.2, 113.0, 111.5 (6 carbons were buried in other peaks)

HRMS for $C_{18}H_{11}Br_2NNaO^+$([M+Na]$^+$): 439.9079; found 439.9140

IR (KBr, cm^{-1}): 3413, 1595, 1471, 1437, 1277, 1231, 758

M.p.: 140-143℃



6p

1,3-dibromodibenzo[b,d]furan-4-ol (**6p**) was prepared according to procedure **III-2** as described in **Scheme S5**, purified by flash column chromatography (PE: EtOAc = 30: 1), and obtained as a yellow solid (115 mg, 67% yield, 0.5 mmol scale).

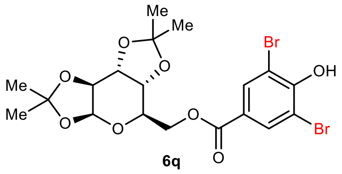
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.45 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.62 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.59 (s, 1H), 7.54 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.42 (ddd, *J* = 8.1, 7.3, 1.0 Hz, 1H), 5.83 (s, 1H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.3, 144.1, 138.3, 128.8, 128.3, 125.1, 123.7, 123.3, 122.5, 111.9, 107.6, 106.0

HRMS for $C_{12}H_5Br_2O_2^-$ ([M-H]$^-$) $C_{12}H_6Br_2NaO_2^+$: 340.8641; found 340.8647

IR (KBr, cm^{-1}): 3078, 1701, 1596, 1446, 1251, 1199, 839, 748

M.p.: 135-151℃



6q

((3*aS*,5*R*,5*aR*,8*aR*,8*bS*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 3,5-dibromo-4-hydroxybenzoate (**6q**) was prepared according procedure **III-2** as described in **Scheme S5**, purified by flash column chromatography (PE: EtOAc = 4: 1), obtained as white solid (119.2 mg,76% yield, 0.3 mmol scale).

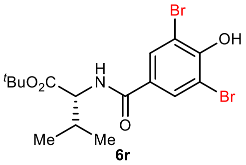
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.15 (s, 2H), 6.29 (s, 1H), 5.56 (d, *J* = 4.9 Hz, 1H), 4.66 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.51 (dd, *J* = 11.5, 4.6 Hz, 1H), 4.41 (dd, *J* = 11.5, 7.6 Hz, 1H), 4.35 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.31 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.17 (ddd, *J* = 6.9, 4.6, 1.7 Hz, 1H), 1.52 (s, 3H), 1.48 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.8, 153.3, 133.7, 124.6, 109.8, 109.7, 108.9, 96.3, 71.1, 70.7, 70.5, 66.0, 64.4, 26.00, 25.96, 24.9, 24.5

HRMS for $C_{19}H_{22}Br_2NaO_8^+$ ([M+Na$^+$]): 558.9553; found 558.9552

IR (KBr, cm^{-1}): 3420, 1628, 1438, 1363, 1164, 798,690

M.p.: 138-147℃



6r

***Tert*-butyl (3,5-dibromo-4-hydroxybenzoyl)-D-valinate** (**6r**) was prepared according to procedure **III-2** as described in **Scheme S5**, and obtained as white solid (115 mg, 79% yield, 0.3 mmol scale)

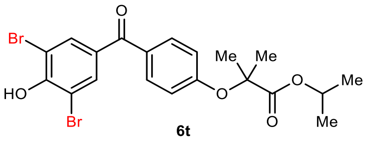
^{1}H NMR (600 MHz, Chloroform-d) δ 7.92 (s, 2H), 6.55 (d, *J* = 8.4 Hz, 1H), 6.26 (s, 1H), 4.63 (dd, *J* = 8.4, 4.4 Hz, 1H), 2.27 (td, *J* = 7.0, 4.4 Hz, 1H), 1.50 (s, 9H), 0.99 (d, *J* = 7.0 Hz, 6H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.4, 164.2, 152.2, 131.1, 128.7, 110.0, 82.6, 57.9, 31.7, 28.1, 18.9, 17.8

HRMS for [M+Na$^+$] $C_{16}H_{21}Br_2NNaO_4^+$, 473.9709; found 473.9713

IR (KBr, cm^{-1}): 3332, 2921, 1708, 1652, 1545, 1370, 1135, 732

M.p.: 130-141℃



6t

Isopropyl 2-(4-(3,5-dibromo-4-hydroxybenzoyl)phenoxy)-2-methylpropanoate (**6t**) was prepared according to procedure **III-2** as described in **Scheme S5**, purified by flash column chromatography (PE: EtOAc = 4: 1), and obtained as white solid (108 mg, 72% yield, 0.3 mmol scale).

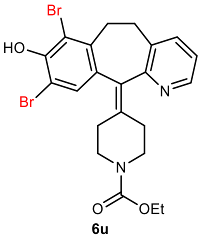
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (s, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.29 (s, 1H), 5.09 (p, *J* = 6.3 Hz, 1H), 1.67 (s, 6H), 1.21 (d, *J* = 6.3 Hz, 6H)

^{13}C NMR (151 MHz, Chloroform-d) δ 191.6, 173.1, 159.8, 152.6, 133.9, 132.6, 131.8, 129.7, 117.3, 109.8, 79.4, 69.4, 25.4, 21.5

HRMS for $C_{20}H_{20}Br_2NaO_5^+$([M+Na]$^+$): 522.9549; found 522.9534

IR (KBr, cm^{-1}): 3383, 1731, 1646, 1597, 1251, 1153, 1097, 767

M.p.: 149-152℃



6u

Ethyl 4-(7,9-dibromo-8-hydroxy-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (**6u**) was prepared according to procedure **III-2** as described in **Scheme S5**, purified by flash column chromatography (DCM: MeOH = 20: 1), obtained as yellow solid (65 mg, 42% yield, 0.3 mmol scale).

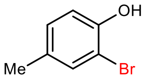
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.41 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.48 (d, *J* = 6.7 Hz, 1H), 7.34 (s, 1H), 7.13 (dd, *J* = 7.7, 4.8 Hz, 1H), 6.26 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 2H), 3.32 (dddd, *J* = 18.4, 15.8, 8.8, 4.3 Hz, 2H), 3.16 (dddd, *J* = 26.8, 13.2, 9.2, 4.1 Hz, 2H), 3.05 (ddd, *J* = 15.8, 9.2, 4.5 Hz, 1H), 2.92 – 2.84 (m, 1H), 2.49 (ddd, *J* = 14.2, 9.5, 4.7 Hz, 1H), 2.39 (tq, *J* = 9.1, 4.8 Hz, 2H), 2.28 (dt, *J* = 14.1, 4.8 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.1, 155.5, 148.8, 146.6, 138.1, 137.5, 137.2, 133.2, 133.1, 132.9, 131.9, 122.5, 113.1, 107.0, 61.4, 44.6, 44.6, 32.8, 30.4, 14.7

HRMS for $C_{22}H_{22}Br_2N_2NaO_3^+$ ([M+Na$^+$]): 544.9869; found 544.9884

IR (KBr, cm^{-1}): 3420, 2907, 1698, 1522, 1440, 1223, 1115, 783

M.p.: 189-210℃

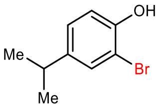


5a

2-bromo-4-methylphenol (**5a**)[18] was prepared according to procedure **III-3** as described in **Scheme S6**, purified by flash column chromatography (PE: EtOAc = 30: 1), and obtained as colorless liquid (155 mg, 83% yield, 1.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 2.4 Hz, 1H), 7.01 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.91 (dd, *J* = 8.4, 1.9 Hz, 1H), 5.36 (d, *J* = 2.0 Hz, 1H), 2.26 (d, *J* = 2.0 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.0, 132.1, 131.4, 129.7, 115.7, 109.8, 20.2

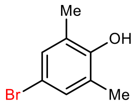


5b

2-bromo-4-isopropylphenol (**5b**)[19] was prepared according to procedure **III-3** as described in **Scheme S6**, purified by flash column chromatography (PE: EtOAc = 50: 1), and obtained as colorless liquid (175 mg, 82% yield, 1.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 2.1 Hz, 1H), 7.07 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 5.36 (s, 1H), 2.83 (hept, *J* = 6.9 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 6H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.1, 142.7, 129.6, 127.2, 115.8, 109.9, 33.2, 24.0

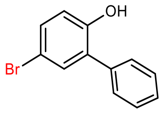


5c

4-bromo-2,6-dimethylphenol (**5c**)[10] was prepared according to procedure **III-3** as described in **Scheme S6**, obtained as a gray solid (214 mg, quantitative yield, 1.0 mmol scale)

^{1}H NMR (600 MHz, Chloroform-d) δ 7.03 (s, 2H), 4.5 (br, 1H), 2.14 (s, 6H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.3, 131.0, 125.2, 112.0, 15.7

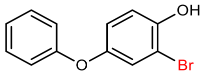


5d

5-bromo-[1,1'-biphenyl]-2-ol (**5d**)[20] was prepared according to procedure **III-3** as described in **Scheme S6**, purified by flash column chromatography (PE: EtOAc = 30: 1), and obtained as purple liquid (149 mg, 60% yield, 1.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.55 – 9.50 (m, 2H), 9.48 – 9.43 (m, 3H), 9.41 – 9.36 (m, 2H), 8.90 (d, *J* = 8.5 Hz, 1H), 7.26 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.6, 135.7, 132.6, 131.8, 130.0, 129.4, 128.9, 128.4, 117.6, 112.7



5e

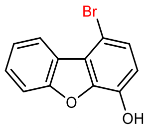
2-bromo-4-phenoxyphenol (**5e**) was prepared according to procedure **III-3** as described in **Scheme S6**, purified by flash column chromatography (PE: EtOAc = 20: 1), obtained as yellow liquid (118 mg, 75% yield, 0.6 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.32 (m, 2H), 7.17 (d, *J* = 2.8 Hz, 1H), 7.09 (m, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 6.95 (m, 3H), 5.37 (s, 1H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 157.7, 150.5, 148.6, 129.8, 123.1, 122.9, 120.5, 118.0, 116.5, 110.0

HRMS for $C_{12}H_8BrO_2^-$ ([M-H]$^-$): 262.9713; found 262.9691

IR (KBr, cm^{-1}): 2923, 1591, 1486, 1212, 903, 689

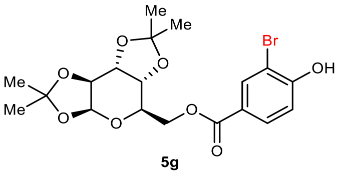


5f

1-bromodibenzo[b,d]furan-4-ol (**5f**)[21] was prepared according to procedure **III-3** as described in **Scheme S6**, purified by flash column chromatography (PE : EtOAc = 30 : 1), obtained as white solid (52 mg, 40% yield, 0.5 mmol scale)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.53 (t, *J* = 8.2 Hz, 1H), 7.42 (dd, *J* = 7.6, 2.4 Hz, 1H), 7.35 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.92 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.52 (s, 1H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.0, 144.5, 140.5, 127.9, 127.0, 124.8, 124.2, 123.0, 122.6, 114.6, 111.6, 106.0



5g

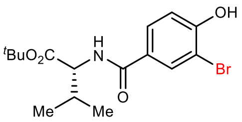
((3aS,5R,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 3-bromo-4-hydroxybenzoate (**5g**) was prepared according to procedure **III-3** as described in **Scheme S6**, purified by flash column chromatography (PE: EtOAc = 20: 1), and obtained as colorless liquid (57 mg, 43% yield, 0.3 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 6.01 (s, 1H), 5.56 (d, *J* = 5.0 Hz, 1H), 4.65 (d, *J* = 8.0 Hz, 1H), 4.51 (dd, *J* = 11.6, 4.8 Hz, 1H), 4.40 (dd, *J* = 11.6, 7.6 Hz, 1H), 4.35 (d, *J* = 4.6 Hz, 1H), 4.31 (d, *J* = 8.0 Hz, 1H), 4.17 (dd, *J* = 7.4, 4.7 Hz, 1H), 1.52 (s, 3H), 1.48 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.0, 156.4, 134.1, 131.1, 123.8, 115.8, 110.0, 109.7, 108.9, 96.3, 71.1, 70.7, 70.5, 66.1, 64.0, 26.0, 25.9, 24.9, 24.5

HRMS for [M+Na$^+$] $C_{19}H_{23}BrNaO_8^+$, 483.0448; found 483.0441

IR (KBr, cm^{-1}): 2990, 1720, 1599, 1209, 1068, 762



5h

***Tert*-butyl (3-bromo-4-hydroxybenzoyl)-*D*-valinate** (**5h**) was prepared according to procedure **III-3** as described in **Scheme S6**, purified by flash column chromatography (PE: EtOAc = 20: 1), and obtained as white solid (89 mg, 64% yield, 0.3 mmol scale).

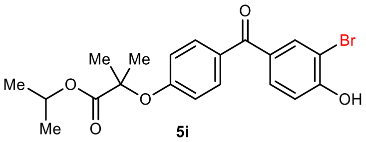
^{1}H NMR (600 MHz, Chloroform-d) δ 7.97 (s, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 6.37 (s, 1H), 4.64 (dd, *J* = 8.4, 4.4 Hz, 1H), 2.26 (heptd, *J* = 6.9, 4.4 Hz, 1H), 1.49 (s, 9H), 0.99 (d, *J* = 9.5 Hz, 3H), 0.98 (d, *J* = 9.5 Hz, 3H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.4, 165.5, 155.4, 131.6, 128.0, 127.9, 115.9, 110.4, 82. 5, 57.8, 31.8, 28.1, 18.9, 17.8

HRMS for [M+Na$^+$] $C_{16}H_{22}BrNNaO_4^+$, 394.0624; found 395.0624

IR (KBr, cm^{-1}): 3386, 2975, 1709, 1633, 1508, 1371, 1303, 1154, 1147, 840

M.p.: 113-116℃



5i

Isopropyl 2-(4-(3-bromo-4-hydroxybenzoyl)phenoxy)-2-methylpropanoate (**5i**) was prepared procedure **III-3** as described in **Scheme S6**, purified by flash column chromatography (PE: EtOAc = 20: 1), and obtained as white solid (45.7 mg, 36% yield, 0.3 mmol scale).

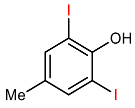
^{1}H NMR (600 MHz, Chloroform-d) δ 7.96 (s, 1H), 7.73 – 7.68 (m, 2H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 8.4, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.25 (s, 1H), 5.13 – 5.05 (m, 1H), 1.66 (s, 6H), 1.20 (d, *J* = 6.1 Hz, 6H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 193.1, 173.2, 159.5, 155.8, 134.4, 131.9, 131.8, 131.5, 130.4, 117.3, 115.6, 110.2, 79.4, 69.4, 25.4, 21.5

HRMS for [M+Na$^+$] $C_{20}H_{21}BrNaO_5^+$, 443.0465; found 443.0463

IR (KBr, cm^{-1}): 3451, 1634, 1597, 1274, 1254, 1143, 765

M.p.: 109-122℃

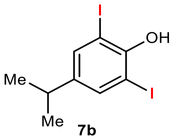


7a

2,6-diiodo-4-methylphenol (**7a**)[18] was prepared according to procedure **III-4** as described in **Scheme S7**, purified by flash column chromatography (PE: EtOAc = 30: 1), obtained as yellow solid (163.8 mg, 46% yield, 1.0 mmol scale). 35% yield (125 mg, 1.0 mmol) was obtained when $ClCH_2CO_2H$ was used instead of oxalic acid; and 33% yield (112 mg, 1.0 mmol) was obtained when HOAc was used instead of oxalic acid with UHP (1.0 equivalent) and H_2O_2 (3.3 equivalents)

^{1}H NMR (600MHz, Chloroform-*d*) δ 7.49 (s, 2H), 5.57 (s, 1H), 2.22 (s, 3H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.4, 139.6, 133.9, 81.9, 19.4

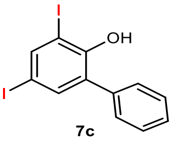


7b

2,6-diiodo-4-isopropylphenol (**7b**)[22] was prepared according to procedure **III-4** as described in **Scheme S7** utilizing HOAc/UHP instead of oxalic acid/H_2O_2 respectively, purified by flash column chromatography (PE: EtOAc = 50: 1), and obtained as yellow solid (152 mg, 40% yield, 1.0 mmol scale).

^{1}H NMR (600MHz, Chloroform-*d*) δ 7.51 (s, 2H), 5.59 (s, 1H), 2.77 (hept, *J* = 6.9 Hz, 1H), 1.19 (d, *J* = 6.9 Hz, 6H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.5, 145.0, 137.3, 82.2, 32.7, 23.9



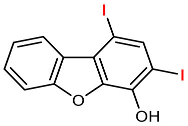
7c

3,5-diiodo-[1,1'-biphenyl]-2-ol (**7c**)[18] was prepared according to **III-4** as described in **Scheme S7**, purified by flash column chromatography (PE: EtOAc = 30: 1), and obtained as white solid (86 mg, 21% yield, 1.0 mmol scale).

When the reaction was preformed with [1,1'-biphenyl]-2-ylboronic acid (40 mg, 0.2 mmol, 1.0 eq.), HOAc (24 mg, 2.0 eq.), KI (88 mg, 2.5 eq.), H_2O_2 (35% aq., 68 μL, 3.5 eq.) in EtOH/H_2O (1.0 mL/0.5 mL) for 24h, ^{1}H-NMR of crude product showed 28% of **7c** and 42% yield of 5-iodo-[1,1'-biphenyl]-2-ol (mon-iodination) with TMB as internal standard.

^{1}H NMR (600MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.53 (s, 1H), 7.49 – 7.43 (m, 4H), 7.43 – 7.39 (m, 1H), 5.58 (s, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.7, 145.0, 139.3, 135.8, 130.6, 129.0, 128.9, 128.5, 86.8, 83.1



7d

1,3-diiododibenzo[b,d]furan-4-ol (**7d**) was prepared according to **III-4** as described in **Scheme S7** utilizing

$ClCH_2COOH$ instead of oxalic acid, and obtained as gray solid (163 mg, 75% yield, 0.5 mmol scale)

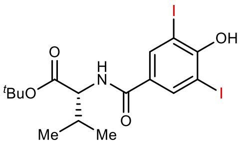
^{1}H NMR (600 MHz, DMSO-d_6) δ 11.19 (s, 1H), 8.62 – 8.57 (m, 1H), 8.03 (d, *J* = 2.3 Hz, 1H), 7.77 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.52 (td, *J* = 7.6, 2.1 Hz, 1H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 155.2, 144.0, 143.0, 140.9, 128.7, 126.9, 124.3, 122.8, 120.9, 111.9, 85.5, 74.8

HRMS for $C_{12}H_5I_2O_2^-$ ([M-H]$^-$): 434.8384; found 434.8416

IR (KBr, cm^{-1}): 3414, 1626, 1587, 1445, 1237, 1191, 748

M.p.: 157-172℃



7e

***Tert*-butyl (4-hydroxy-3,5-diiodobenzoyl)-D-valinate** (**7e**) was prepared according to **III-4** as described in **Scheme S7** utilizing $ClCH_2COOH$ instead of oxalic acid, purified by flash column chromatography (PE: EtOAc = 50: 1), and obtained as white solid (70 mg, 41% yield, 0.3 mmol scale).

24% yield (41 mg, 0.3 mmol scale) was obtained with UHP (1.0 equivalent), H_2O_2 (3.3 equivalents) and HOAc (2.0 equivalents)

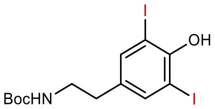
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.12 (s, 2H), 6.53 (d, *J* = 8.4 Hz, 1H), 6.11 (s, 1H), 4.62 (dd, *J* = 8.6, 4.5 Hz, 1H), 2.30 – 2.22 (m, 1H), 0.99 (d, *J* = 6.8, 3H), 0.98 (d, *J* = 6.8, 3H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.5, 163.9, 156.4, 138.4, 130.3, 82.7, 82.2, 58.0, 31.9, 28.2, 19.01, 18.0

HRMS for $C_{16}H_{21}I_2NNaO_4^+$ ([M+Na$^+$]): 567.9452; found 567.9462

IR (KBr, cm^{-1}): 3281, 2970, 1725, 1617, 1563, 1286, 1164, 844, 659

M.p.: 143-154℃

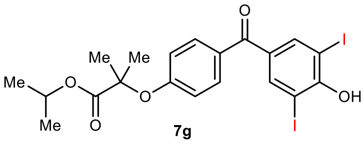


7f

***Tert*-butyl (4-hydroxy-3,5-diiodophenethyl)carbamate** (**7f**)[23] was prepared according to **III-4** as described in **Scheme S7** utilizing HOAc instead of oxalic acid, UHP (1.0 equivalent) and H_2O_2 (35% aq., 3.3 equivalents), purified by flash column chromatography (PE : EtOAc = 10 : 1), and obtained as white solid (90 mg, 46% yield, 0.4 mmol scale).

^{1}H NMR (600 MHz, Chloroform-d) δ 7.50 (s, 2H), 5.69 (s, 1H), 4.55 (s, 1H), 3.29 (t, *J* = 7.2 Hz, 2H), 2.66 (t, *J* = 7.2 Hz, 2H), 1.44 (s, 9H)

^{13}C NMR (151 MHz, Chloroform-d) δ 155.8, 152.2, 139.4, 135.1, 82.3, 79.5, 41.6, 34.2, 28.4



7g

Isopropyl 2-(4-(4-hydroxy-3,5-diiodobenzoyl)phenoxy)-2-methylpropanoate (**7g**) was prepared according to **III-4** as described in **Scheme S7** with HOAc (2.0 equivalents), UHP (1.0 equivalent) and H_2O_2 (3.3 equivalents) purified by flash column chromatography (PE : EtOAc = 10 : 1), and obtained as white solid (145 mg, 81% yield, 0.3 mmol scale).

45% yield (79 mg, 0.3 mmol) was obtained with $ClCH_2CO_2H$ (2.0 equivalent).

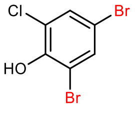
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.10 (s, 2H), 7.71 – 7.67 (m, 2H), 6.89 – 6.86 (m, 2H), 6.16 (s, 1H), 1.67 (s, 6H), 1.21 (s, 3H), 1.20 (s, 3H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 191.3, 173.1, 159.8, 156.6, 141.1, 134.1, 131.8, 129.8, 117.2, 81.8, 79.4, 69.4, 25.4, 21.5

HRMS for $C_{20}H_{20}I_2NaO_5^+$ ([M+Na]$^+$): 616.9292; found 616.9284

IR (KBr, cm^{-1}): 3401, 1731, 1644, 1597, 1253, 1149, 1101, 736

M.p.: 143-154℃



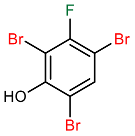
9a

2,4-dibromo-6-chlorophenol (**9a**)[24] was prepared according to procedure **IV-1** as described in **Scheme S8**, purified by flash column chromatography (PE: EtOAc = 2: 1), and obtained as white solid (90 mg, 28% yield, 1.0 mmol scale).

The reaction could be also performed with 4-borono-3-chlorobenzoic acid (40 mg, 0.2 mmol, 1.0 eq.), oxalic acid (36 mg, 0.4 mmol, 2.0 eq), NaBr (52 mg, 0.5 mmol, 2.5 eq.) and H_2O_2 (35% aq., 68μL, 3.5 eq.) in EtOH/H_2O (1.0 mL/0.25 mL) for 20h. 85% yield was obtained by H NMR of crude products with TMB as internal standard.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.55 (s, 1H), 7.45 (s, 1H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.2, 133.6, 131.4, 121.5, 112.2, 110.8



9b

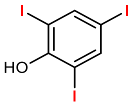
2,4,6-tribromo-3-fluorophenol (**9b**)[25] was prepared according to procedure **IV-1** as described in **Scheme S8**, purified by flash column chromatography (PE: EtOAc = 10: 1), and obtained as yellow solid (98 mg, 37% yield, 1.0 mmol scale).

The reaction could be also performed with 4-borono-2-fluorobenzoic acid (37 mg, 0.2 mmol, 1.0 eq.), oxalic acid (54 mg, 0.6 mmol, 3.0 eq), NaBr (75 mg, 0.72 mmol, 3.6 eq.) and H_2O_2 (35% aq., 90μL, 4.5 eq.) in EtOH/H_2O (1.0 mL/0.3 mL) for 24h. 71% yield was obtained by H NMR of crude products with TMB as internal standard.

^{1}H NMR (600 MHz, Chloroform-d) δ 7.67 (d, J = 7.2 Hz, 1H), 6.06 (s, 1H)

^{13}C NMR (151 MHz, Chloroform-d) δ 155.7 (d, J_{C-F} = 247.6 Hz), 150.2 (d, J^3_{C-F} = 3.2 Hz), 133.9, 104.6 (d, J^2_{C-F} = 4.5Hz), 100.2 (d, J^2_{C-F} = 24.2 Hz), 98.9 (d, J^2_{C-F} = 25.7 Hz)

^{19}F NMR (565 MHz, Chloroform-d) δ -96.43 (d, J = 6.9 Hz).



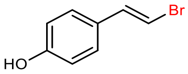
9c

2-chloro-4,6-diiodophenol (**9c**)[26] was prepared according to procedure **IV-1** as described in **Scheme S8**, and obtained as gray solid (60 mg, 14% yield, 1.0 mmol scale).

The reaction could be also performed with 4-boronobenzoic acid (83 mg, 0.5 mmol, 1.0 eq.), HOAc (90 mg, 1.5 mmol, 3.0 eq), KI (305 mg, 1.8 mmol, 3.6 eq.) and H_2O_2 (35% aq., 250μL, 5.0 eq.) in EtOH/H_2O (2.0 mL/0.3 mL) for 24h. 45% yield was obtained by H NMR of crude products.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.93 (s, 2H), 5.72 (s, 1H)

^{13}C NMR (151 MHz, CDCl$_3$) δ 153.9, 146.5, 83.50, 83.45



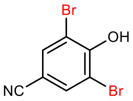
9d

(*E*)-2,6-dibromo-4-(2-bromovinyl)phenol (**9d**)[27] was prepared according to procedure **IV-2** as described in **Scheme S9**. The reaction was performed with (*E*)-3-(4-boronophenyl)acrylic acid (39 mg, 0.2 mmol, 1.0 eq.), Na$_2$WO$_4$•2H$_2$O (3.3 mg, 5mol%), oxalic acid (18 mg, 0.2 mmol, 1.0 eq), NaBr (26 mg, 0.25 mmol, 1.25 eq.) and H$_2$O$_2$ (35% aq., 50µL, 2.5eq.) in EtOH/MeCN/H$_2$O (1.0 mL/0.5 mL/0.3 mL) for 20h. 66% yield was obtained by ^{1}H-NMR of crude products with TMB as internal standard.

When the reaction was performed with (*E*)-3-(4-boronophenyl)acrylic acid (**8d**, 96 mg, 0.5 mmol, 1.0 eq.), Na$_2$WO$_4$•2H$_2$O (9.7 mg, 0.025 mmol, 5 mol %), HOAc (60 mg, 1.0 mmol, 2.0 eq.), KBr (59.5 mg, 0.5 mmol, 1.0 eq.), and UHP (47mg, 0.5 mmol, 1.0 eq.) in EtOH/H$_2$O (2.0 mL/0.3 mL) was added H$_2$O$_2$ (35% aq., 95 uL, 1.1.0 mmol, 2.2 eq.) in the open air. The mixture was stirred at room temperature for around 12 h. The desired product was obtained as white solid (22 mg, 30% yield) by flash column chromatography.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 – 7.16 (m, 2H), 7.03 (d, *J* = 14.0 Hz, 1H), 6.80 – 6.77 (m, 2H), 6.60 (d, *J* = 14.0 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 155.6, 136.4, 129.0, 127.6, 115.7, 104.1

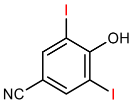


10a

3,5-dibromo-4-hydroxybenzonitrile (**10a**)[28] was prepared according to procedure **V-1** as described in **Scheme S10**, purified by flash column chromatography (PE: EtOAc = 10: 1), obtained as white solid (133.8 mg, 48% yield, 1.0 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 (s, 2H), 6.53 (s, 1H)

^{13}C NMR (151 MHz, CDCl$_3$) δ 153.6, 135.6, 116.2, 110.4, 106.5

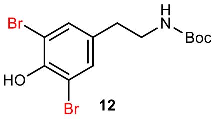


10b

4-hydroxy-3,5-diiodobenzonitrile (**10b**)[29] was prepared according to procedure **V-1** as described in **Scheme S10**, and obtained as white solid (245 mg, 66% yield, 1.0 mmol scale)

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.97 (s, 2H), 6.26 (s, 1H)

^{13}C NMR (151 MHz, CDCl$_3$) δ 157.6, 142.6, 115.6, 107.9, 82.0

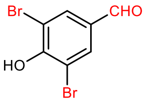


12

***Tert*-butyl (3,5-dibromo-4-hydroxyphenethyl)carbamate** (**12**)[1] was prepared according to procedure **III-2** as described in **Scheme S5** , purified by flash column chromatography (PE: EtOAc = 20: 1), and obtained as white solid (141 mg, 89% yield, 0.4 mmol scale).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.21 (s, 2H), 5.81 (br, 1H), 4.50 (s, 1H), 3.24 (t, *J* = 6.6 Hz, 2H), 2.63 (p, *J* = 5.7 Hz, 2H), 1.45–1.33 (m, 9H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 155.8, 148.0, 133.6, 132.2, 109.8, 79.5, 41.6, 34.7, 28.4

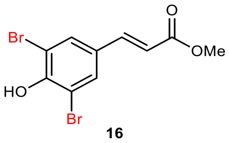


14

3,5-dibromo-4-hydroxybenzaldehyde (**14**)[24] was prepared according to procedure **III-2** as described in **Scheme S5**, obtained as gray solid (0.94g, quantitative yield, 3.0 mmol scale)

^{1}H NMR (600 MHz, DMSO-d_6) δ 9.60 (s, 1H), 7.94 (s, 2H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 189.6, 156.1, 133.7, 130.5, 112.0

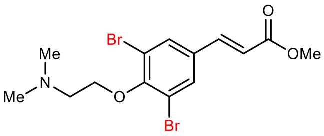


16

Methyl (*E*)-3-(3,5-dibromo-4-hydroxyphenyl)acrylate (**16**) [30] was prepared according to procedure **V-3** as described in Scheme **S11**, obtained as white solid (290 mg, 87% yield, 1.0 mmol scale)

^{1}H NMR (600 MHz, DMSO-d_6) δ 7.92 (s, 2H), 7.51 (d, J = 16.0 Hz, 1H), 6.56 (d, J = 16.0 Hz, 1H), 3.70 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d* + DMSO-d_6) δ 166.47, 152.04, 141.32, 131.26, 128.15, 116.96, 111.27, 51.23



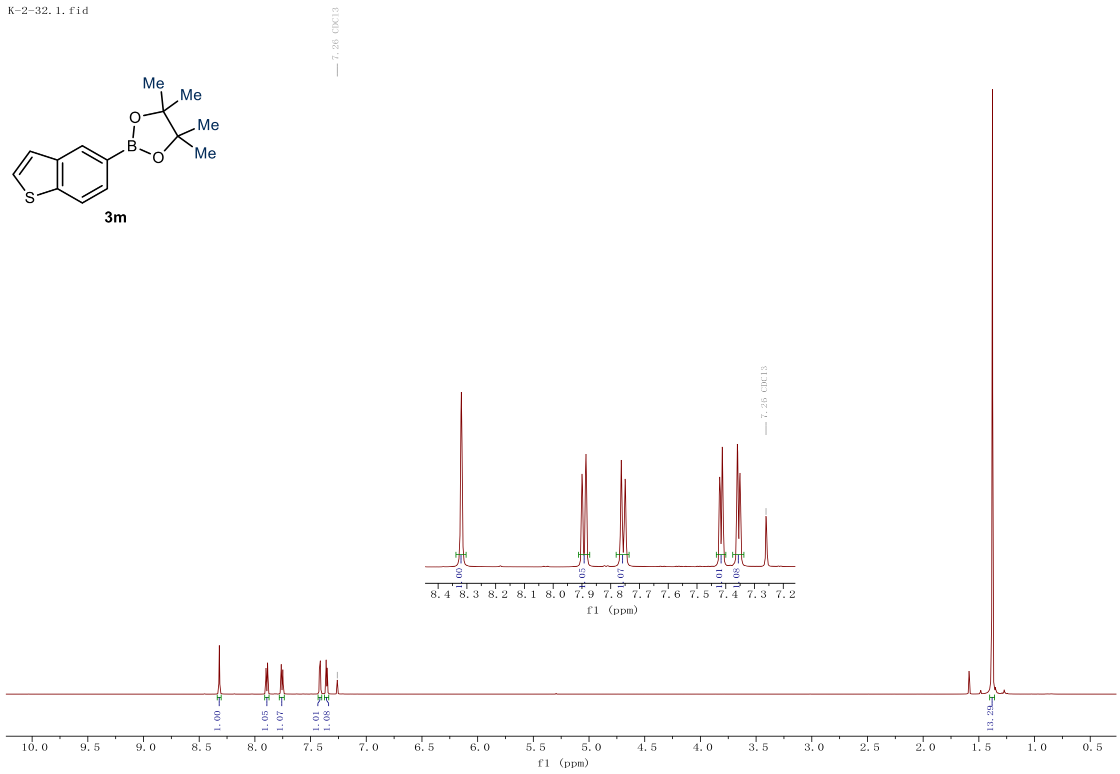
18

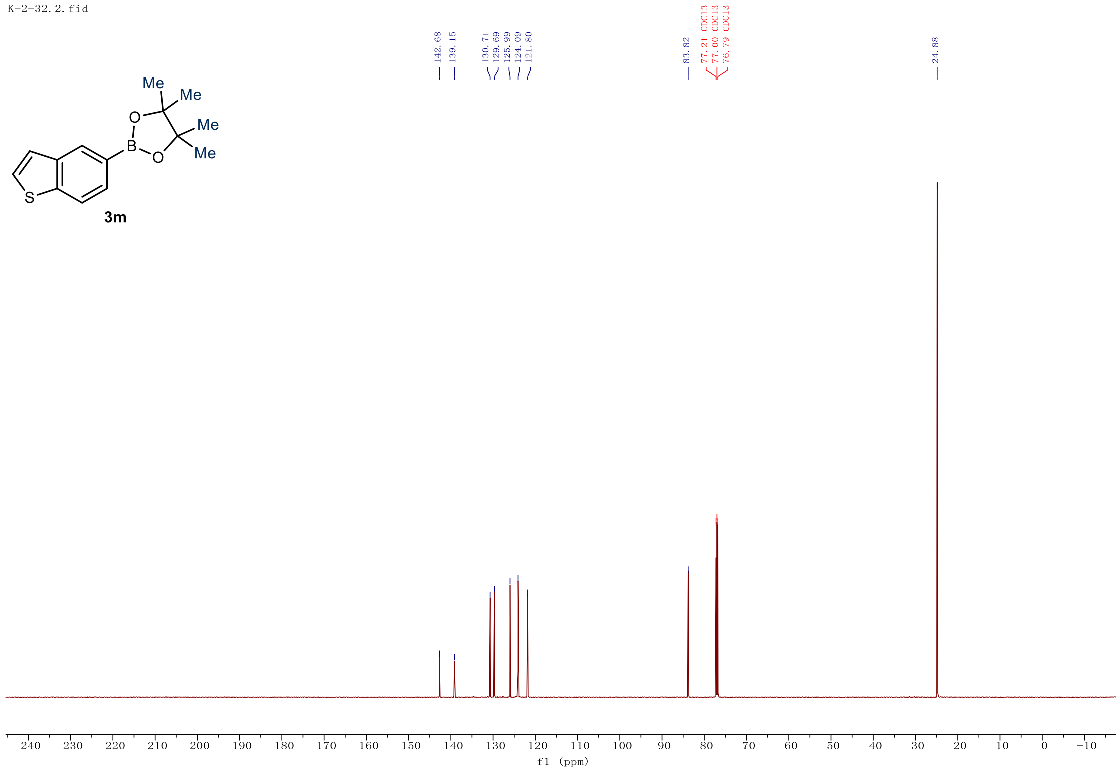
Methyl (*E*)-3-(3,5-dibromo-4-(2-(dimethylamino)ethoxy)phenyl)acrylate (**18**)[2] was prepared according to procedure **V-3** as described in Scheme **S11**, obtained as yellow liquid (28 mg, 34% yield, 0.2 mmol scale; 53% yield bases on recycled starting material **15** (22 mg))

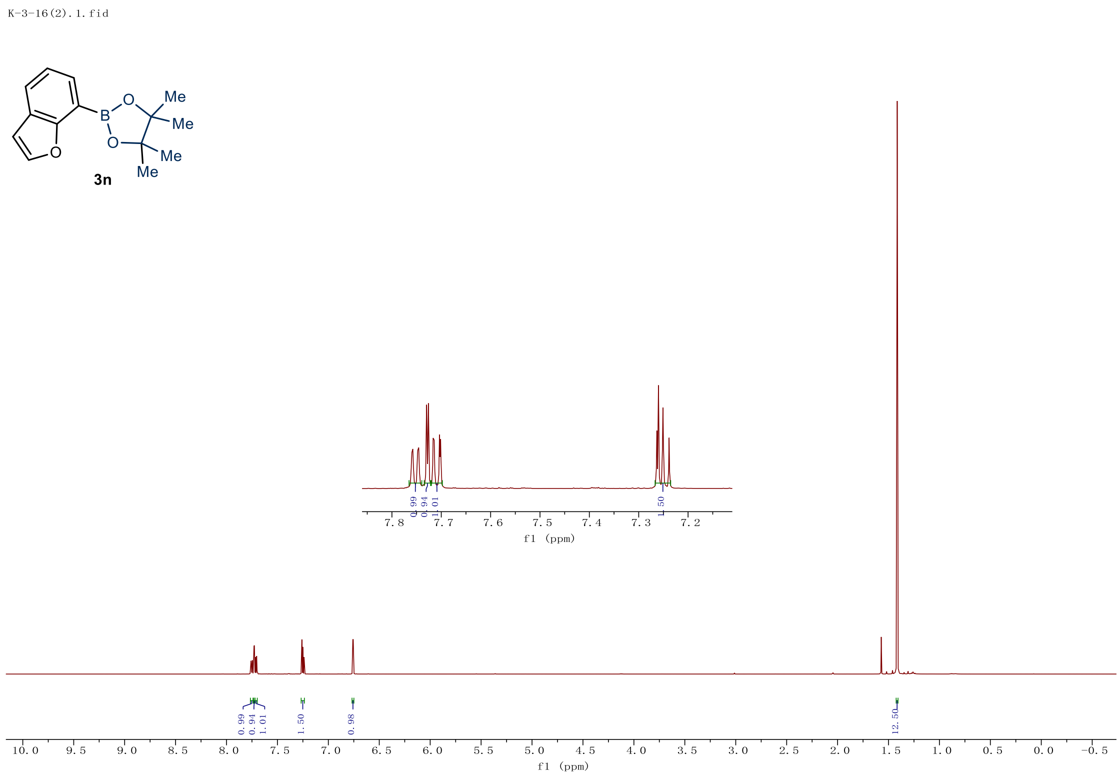
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.65 (s, 2H), 7.50 (d, *J* = 16.0 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 4.15 (t, *J* = 5.8 Hz, 2H), 3.80 (s, 3H), 2.89 (t, *J* = 5.8 Hz, 2H), 2.43 (s, 6H)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 166.7, 154.6, 141.2, 133.0, 132.0, 119.7, 118.8, 70.9, 58. 6, 51.9, 45.7

IX. NMR spectra of starting materials, intermediates and products



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Me
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O
O
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7.7
7.6
7.5
7.4
7.3
7.2
f1 (ppm)
0.99
0.94
1.01
1.50
0.98
12.50
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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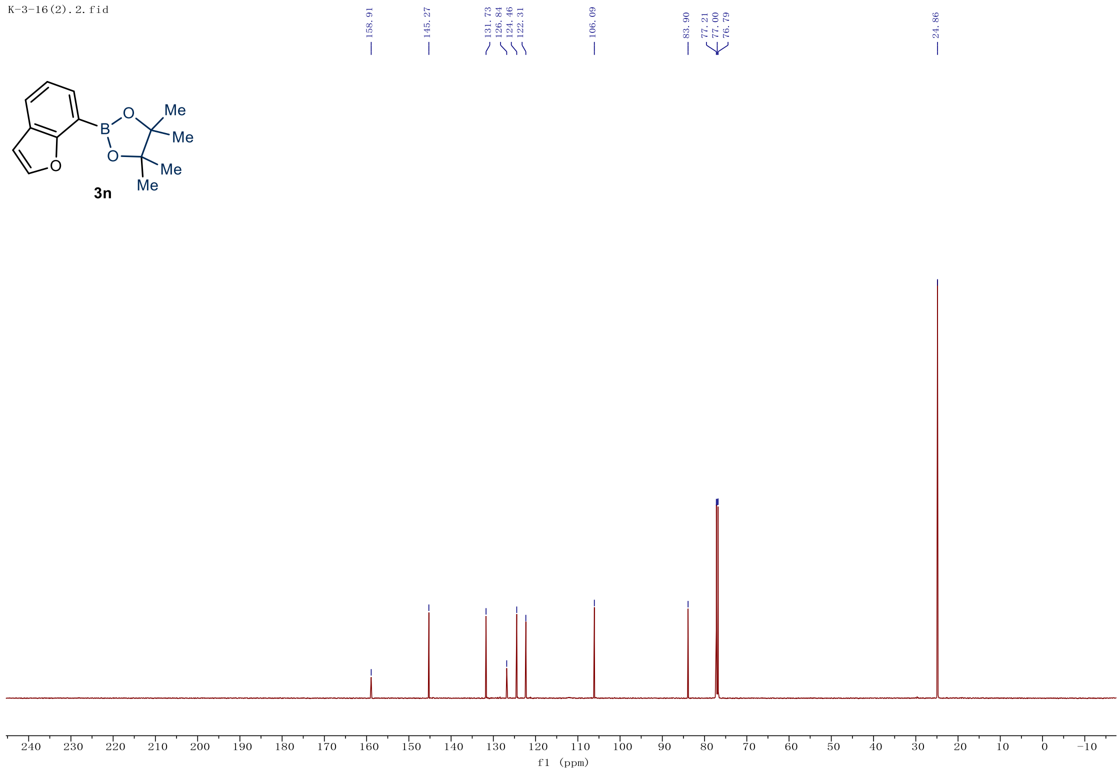
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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Me
Me
B
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O
O
3n
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230
220
210
200
190
180
170
160
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140
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120
110
100
90
80
70
60
50
40
30
20
10
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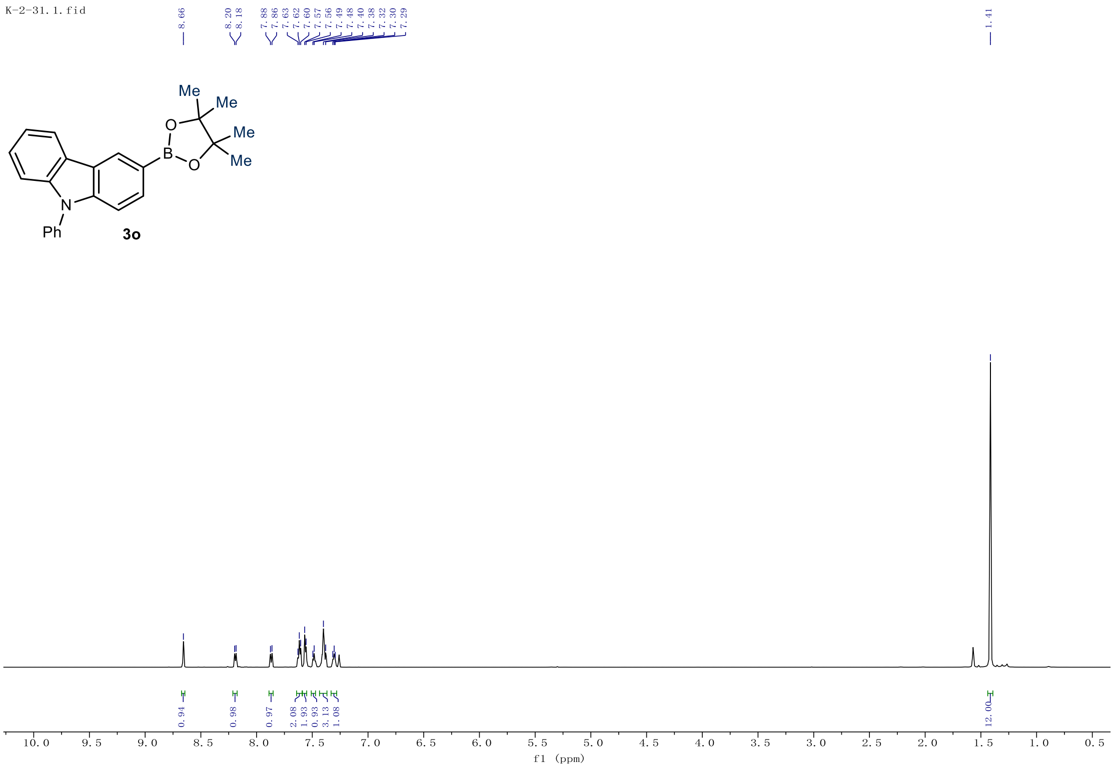
f1 (ppm)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7.32
7.30
7.29
1.41
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Me
Me
Me
O
B
O
N
Ph
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0.98
0.97
2.08
1.93
0.93
3.13
1.08
12.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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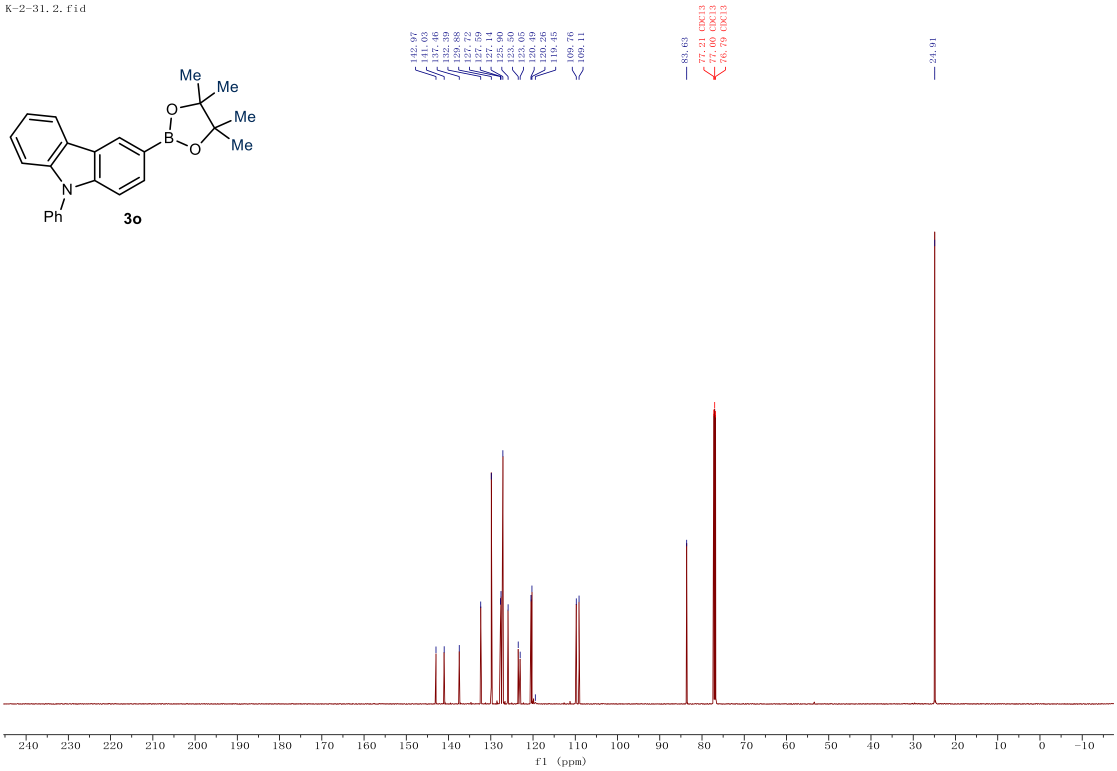
0.5
f1 (ppm)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127.14
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123.05
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120.26
119.45
109.76
109.11
83.63
77.21 CDCl3
77.00 CDCl3
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24.91
Me
Me
Me
Me
O
B
O
N
Ph
3o
240
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190
180
170
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80
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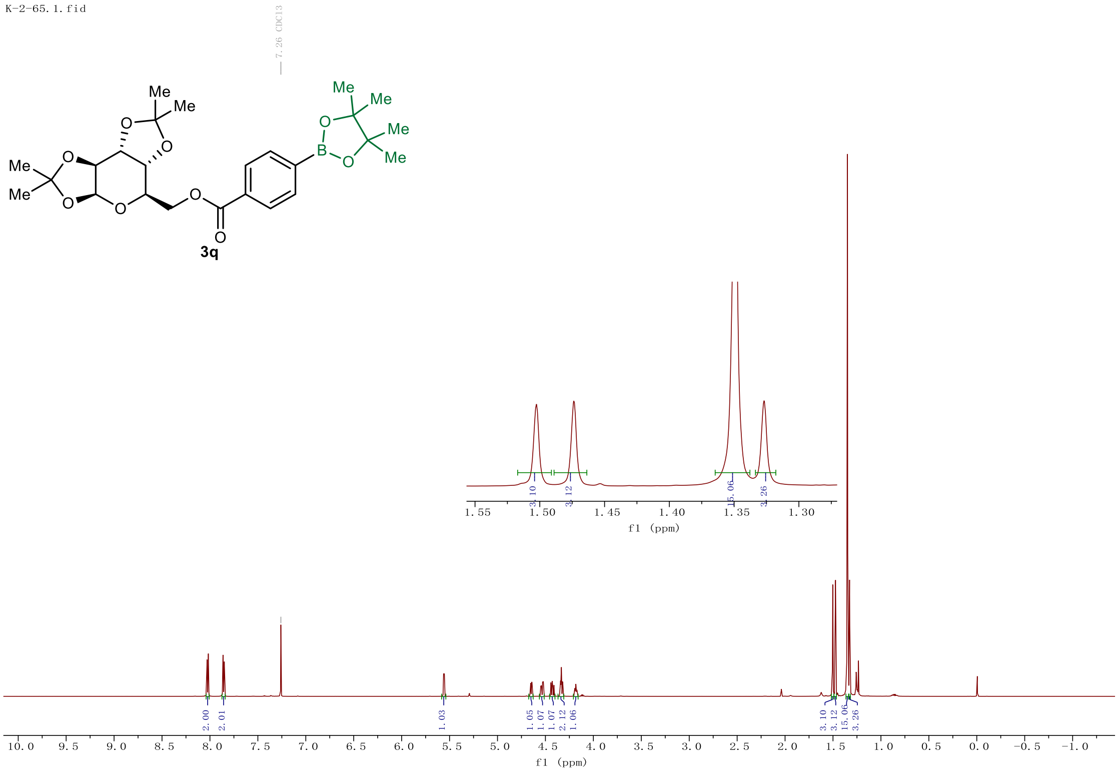
50
40
30
20
10
0
-10
f1 (ppm)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Me
Me
Me
Me
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3.12
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3.26
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1.50
1.45
1.40
1.35
1.30
f1 (ppm)
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2.01
1.03
1.05
1.07
1.07
2.12
1.06
3.10
3.12
15.06
3.26
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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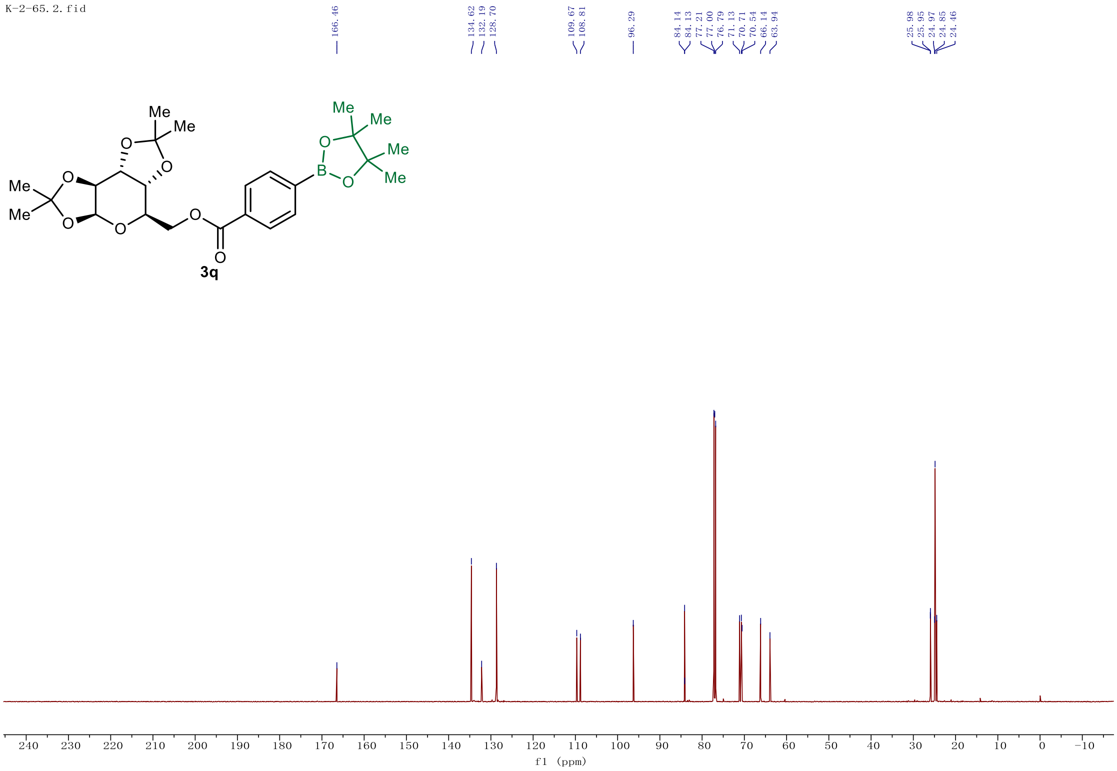
f1 (ppm)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77.00
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70.71
70.54
66.14
63.94
25.98
25.95
24.97
24.85
24.46
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Me
O
O
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B
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180
170
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30
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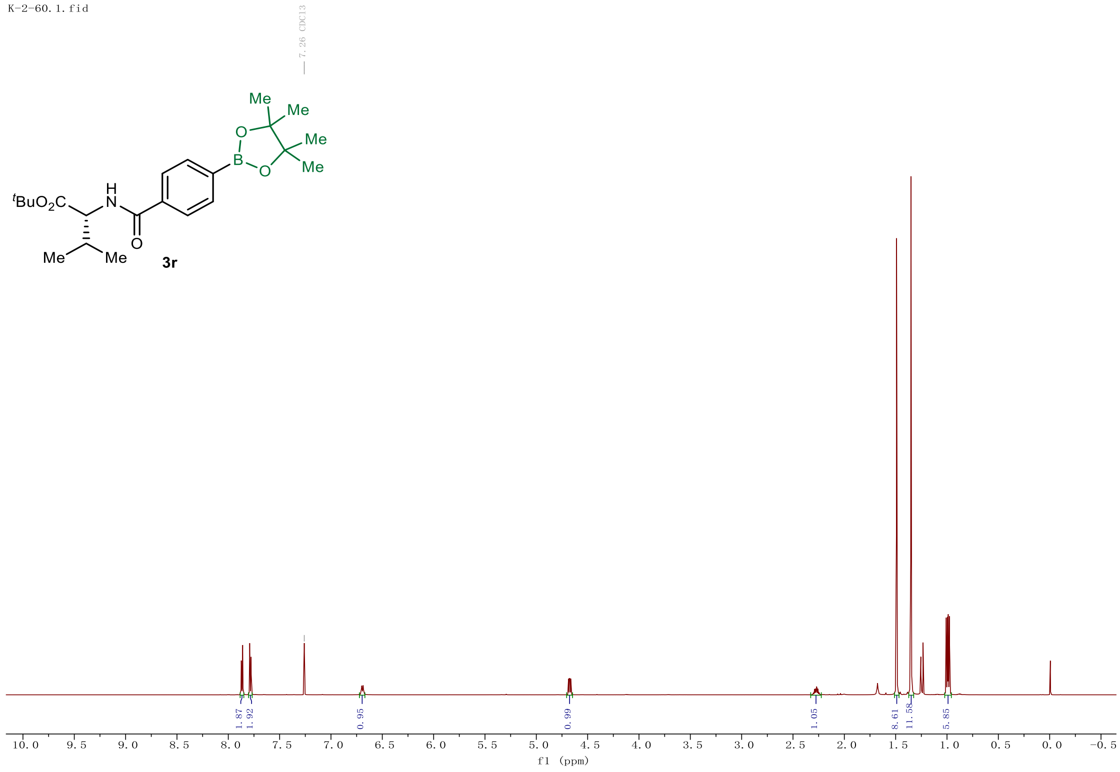
f1 (ppm)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Me
Me
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B
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O
Me
Me
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0.99
1.05
8.61
11.58
5.85
10.0
9.5
9.0
8.5
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7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
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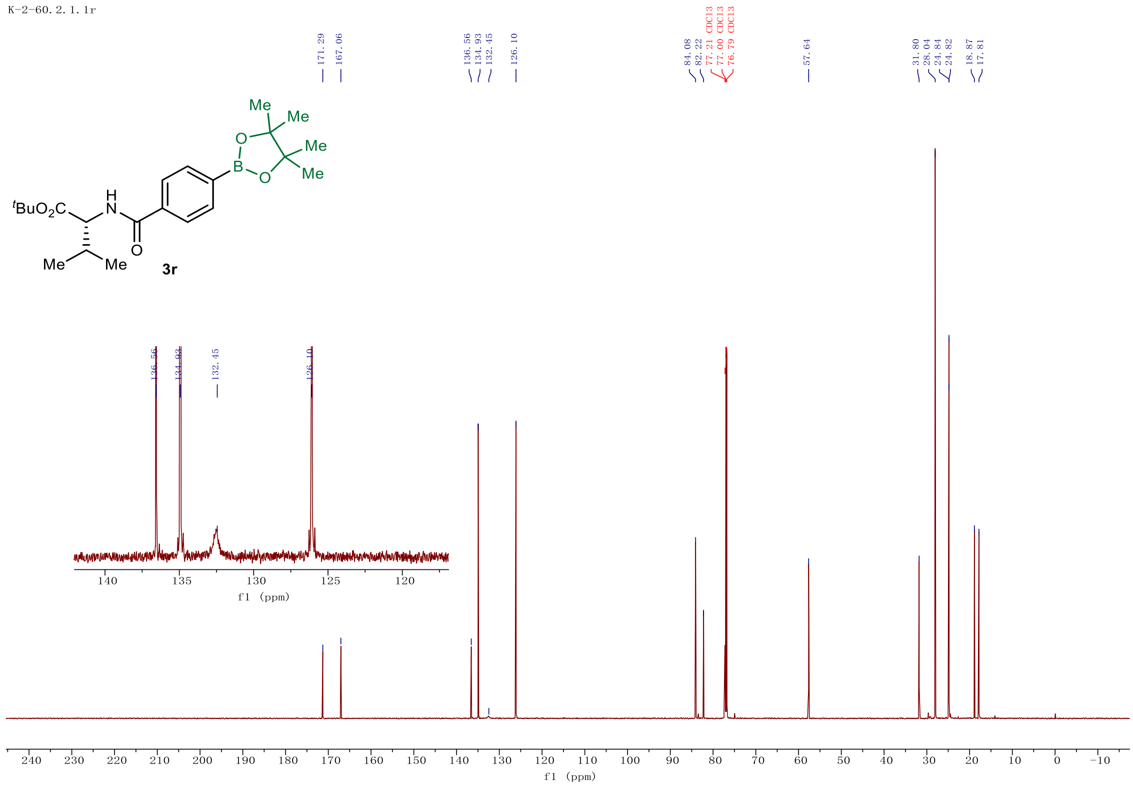
f1 (ppm)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77.00 CDCl3
76.79 CDCl3
57.64
31.80
28.04
24.84
24.82
18.87
17.81
Me
Me
Me
Me
O
B
O
^{t}BuO$_2$C
H
N
O
Me
Me
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136.56
134.93
132.45
126.10
140
135
130
125
120
f1 (ppm)
240
230
220
210
200
190
180
170
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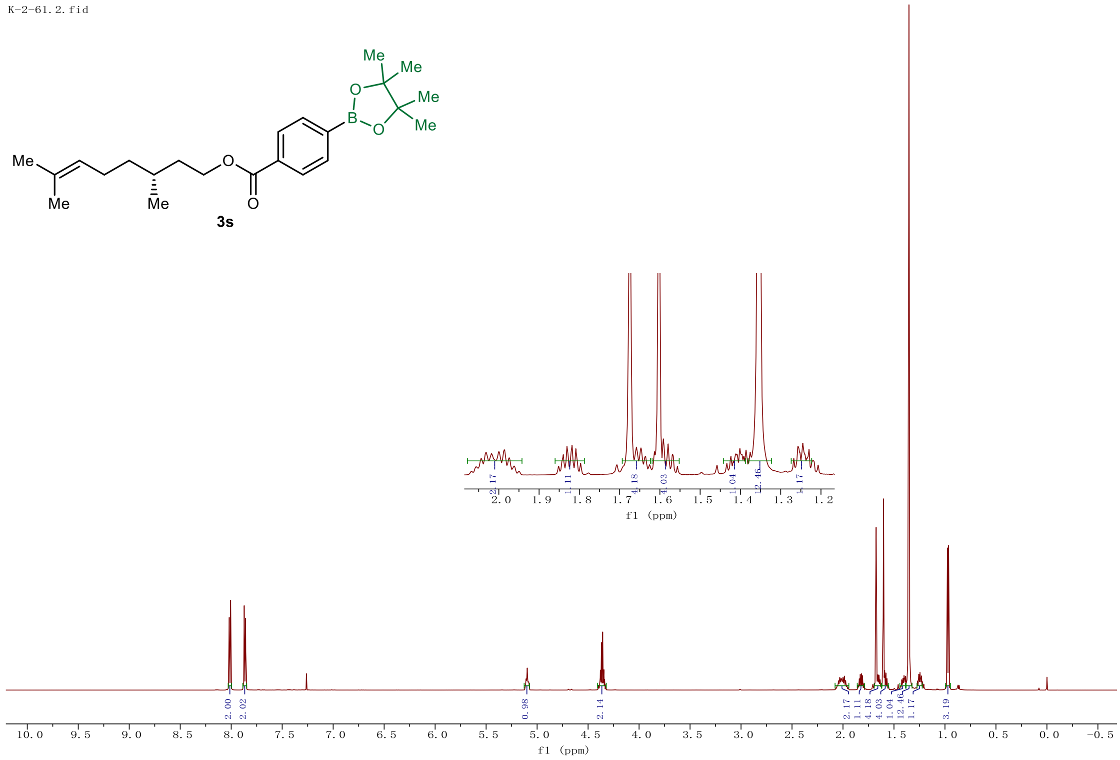
f1 (ppm)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4.18
1.03
1.04
12.46
1.17
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
f1 (ppm)
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2.14
2.17
1.11
4.18
4.03
1.04
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1.17
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9.0
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8.0
7.5
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6.5
6.0
5.5
5.0
4.5
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3.0
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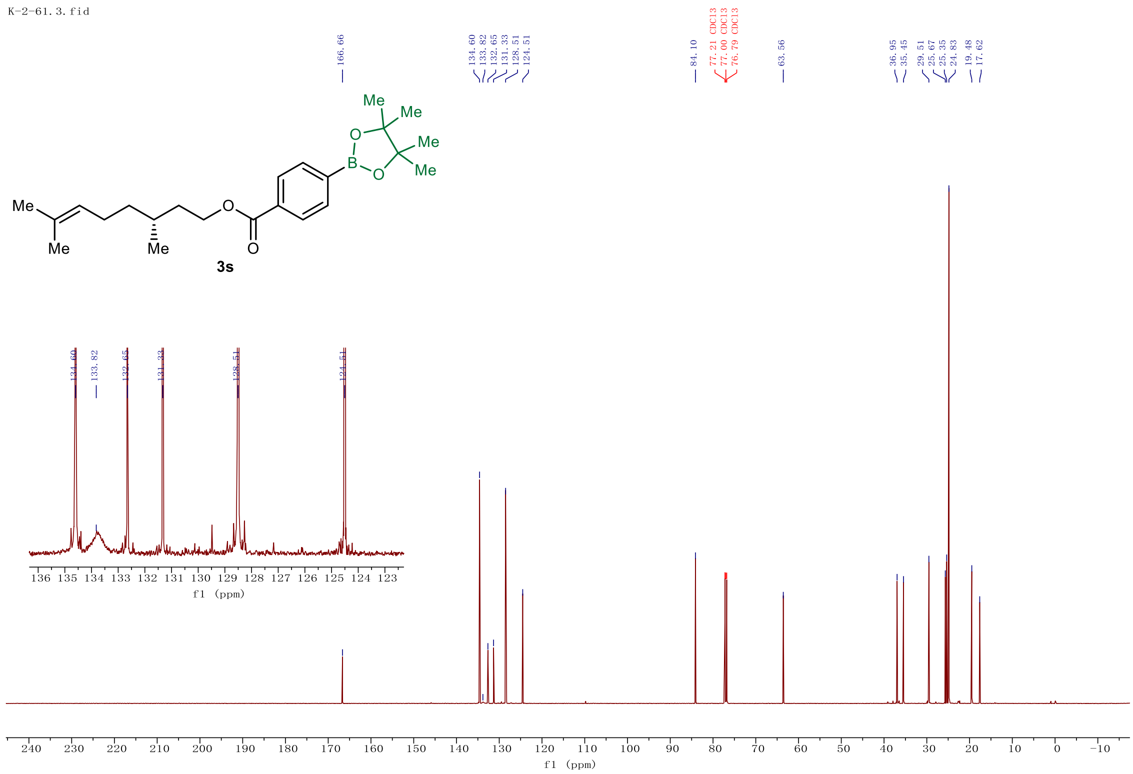
f1 (ppm)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77.00 CDCl3
76.79 CDCl3
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35.45
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25.67
25.35
24.83
19.48
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Me
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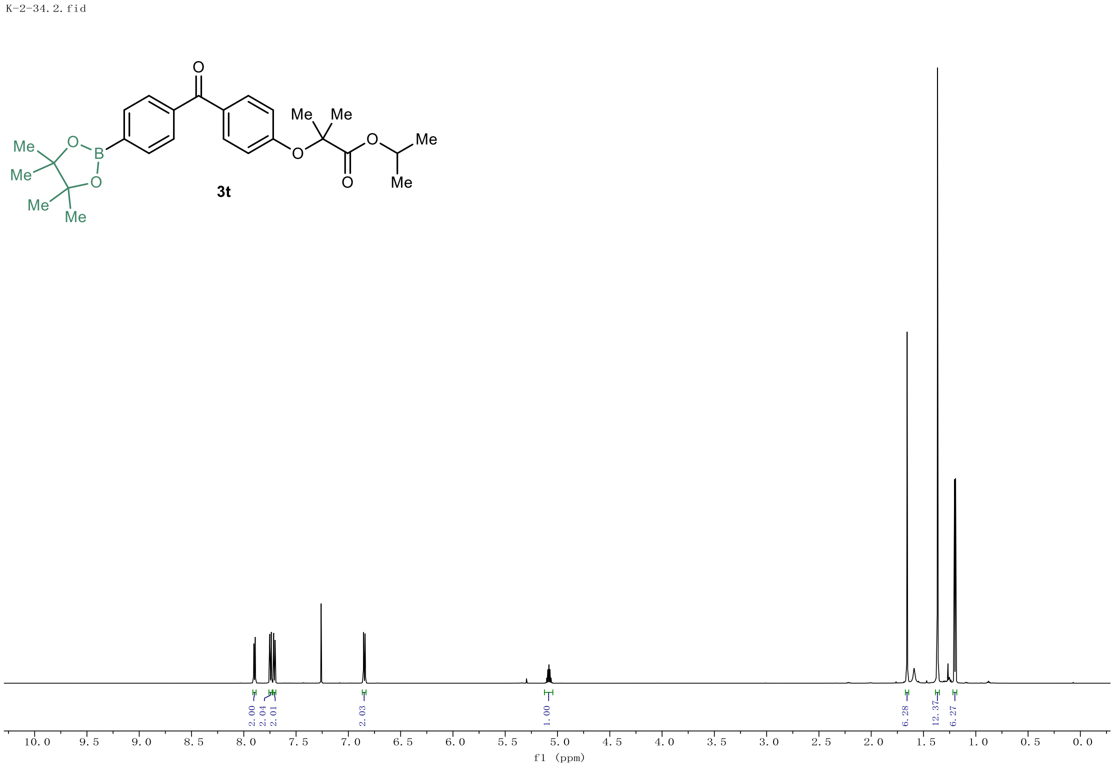
f1 (ppm)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6.0
5.5
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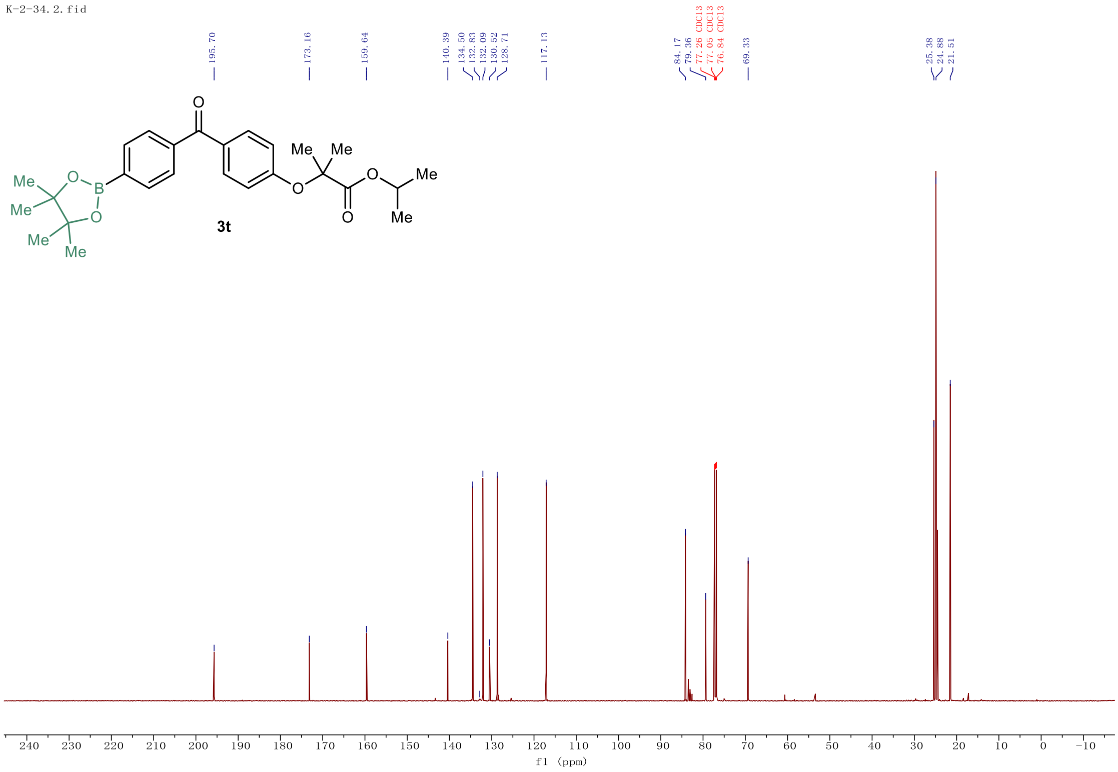
f1 (ppm)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77.05 CDCl3
76.84 CDCl3
69.33
25.38
24.88
21.51
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Me
Me
O
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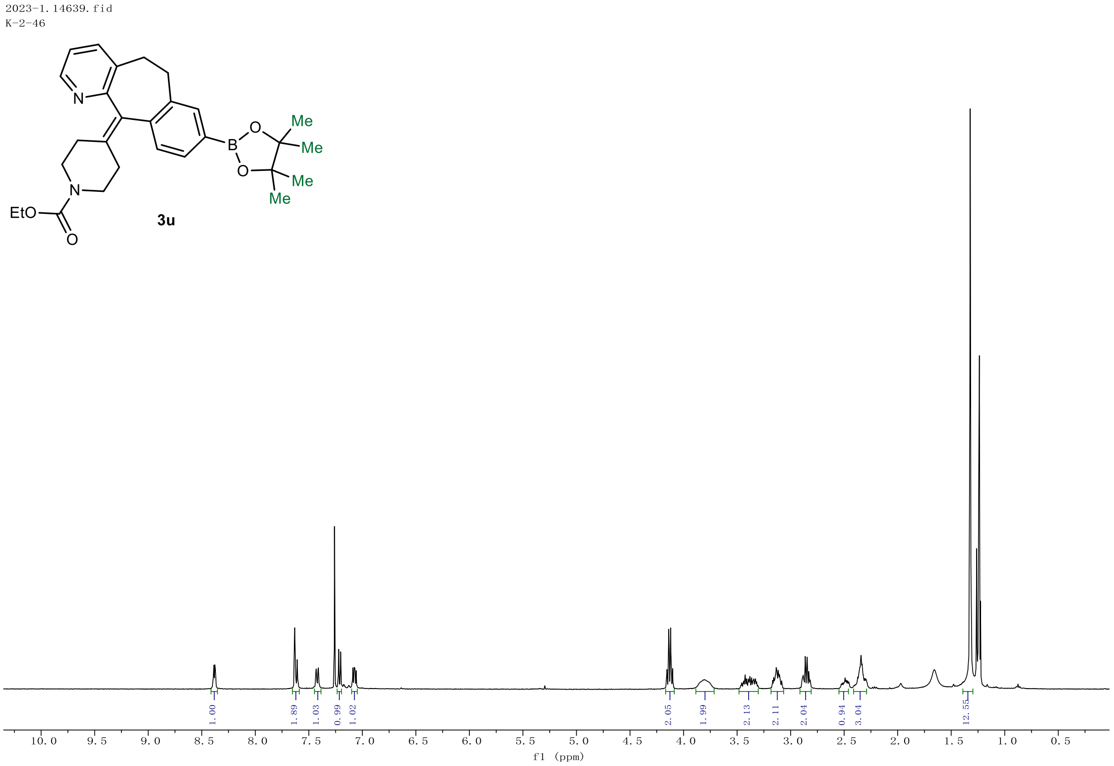
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EtO
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1.03
0.99
1.02
2.05
1.99
2.13
2.11
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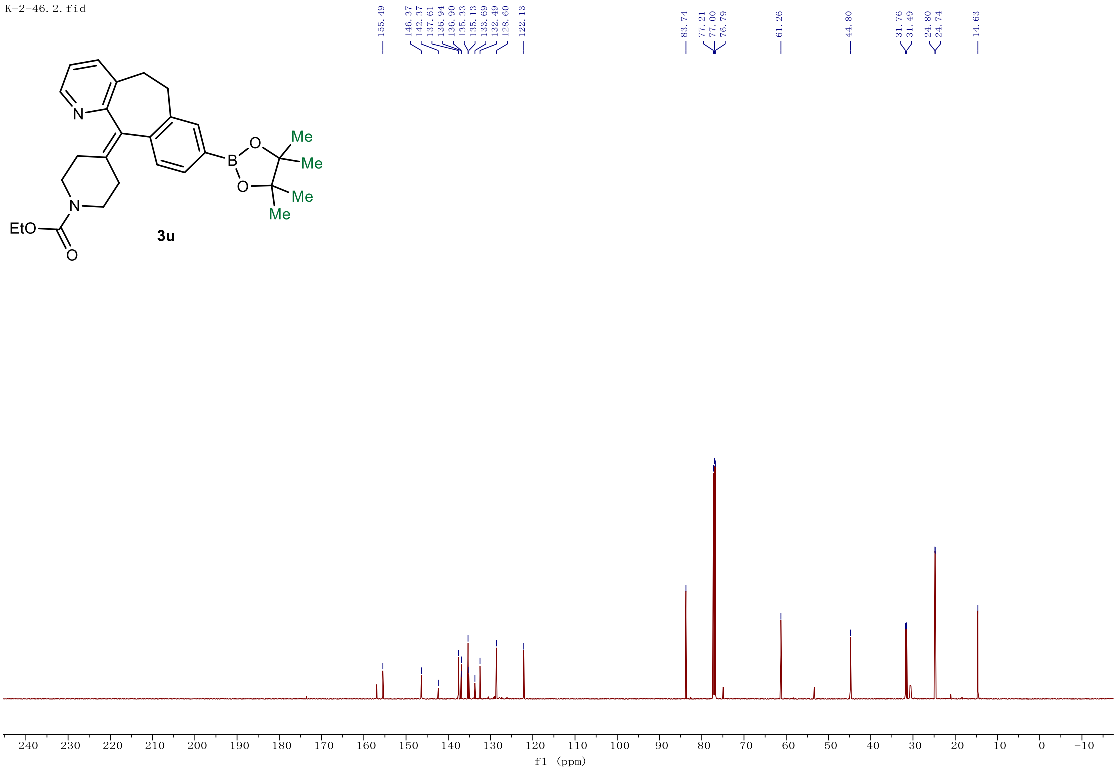
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180
170
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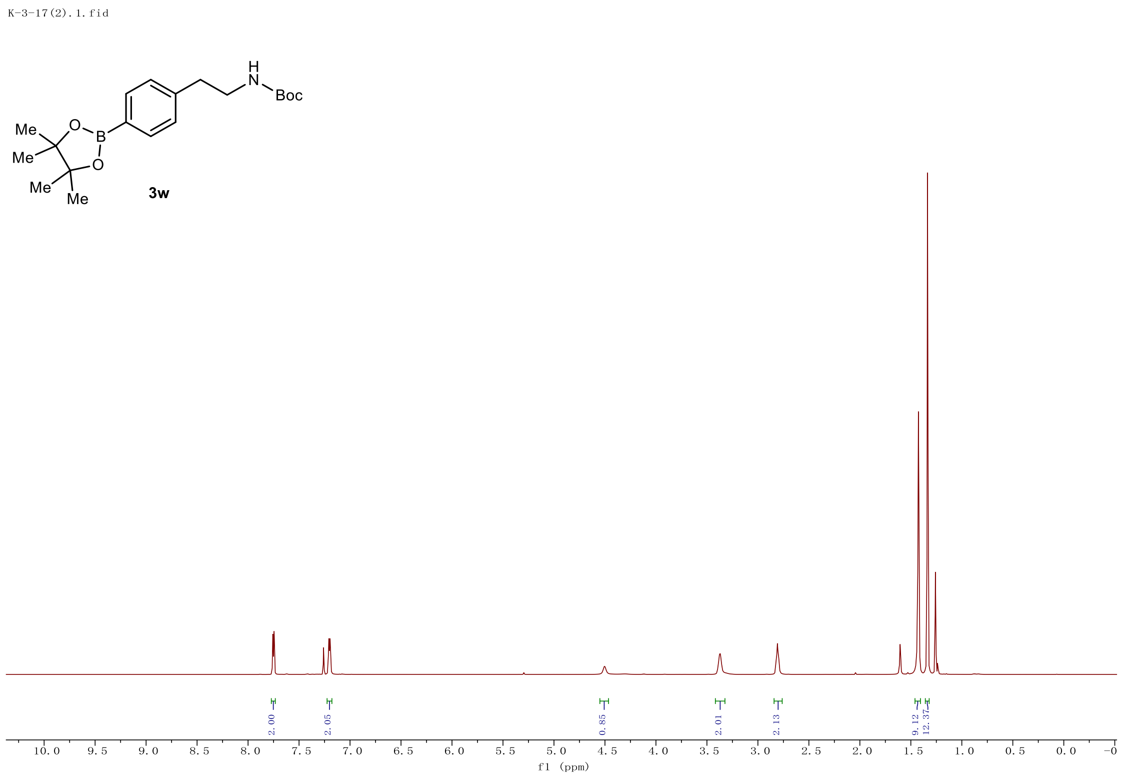
f1 (ppm)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9.0
8.5
8.0
7.5
7.0
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5.0
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2.0
1.5
1.0
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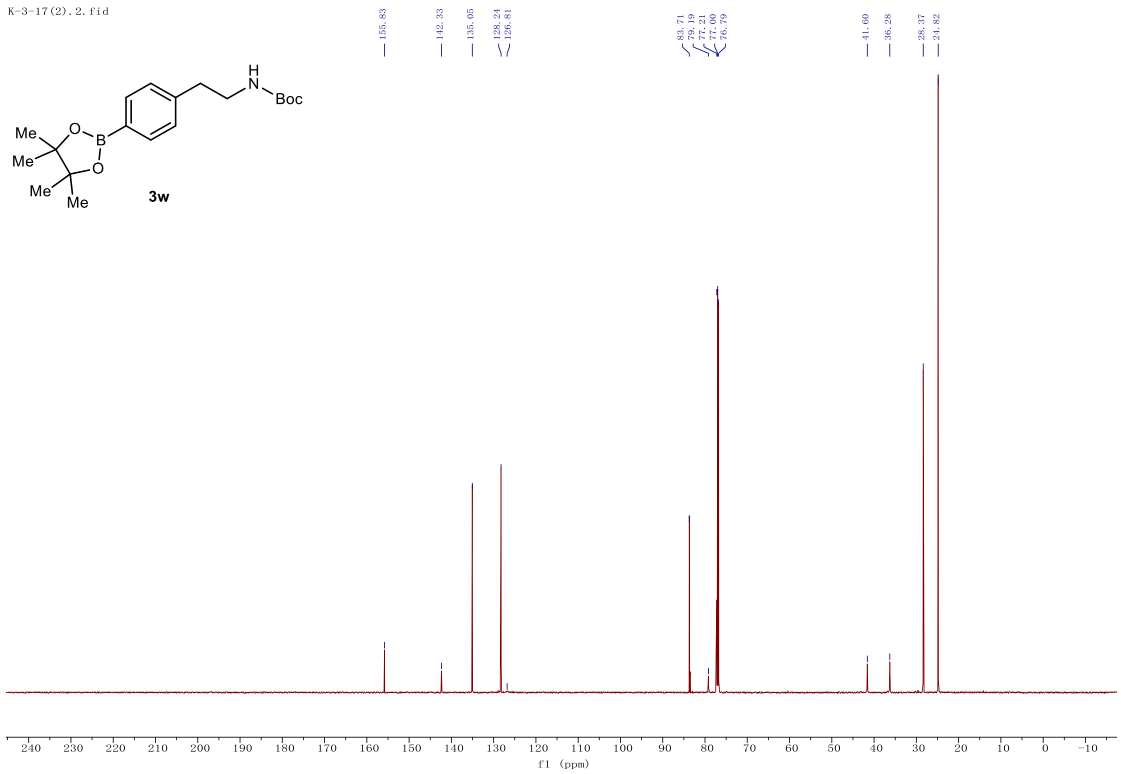
f1 (ppm)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28.37
24.82
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Boc
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B
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Me
Me
Me
Me
3w
240
230
220
210
200
190
180
170
160
150
140
130
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70
60
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40
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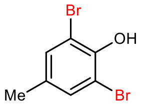
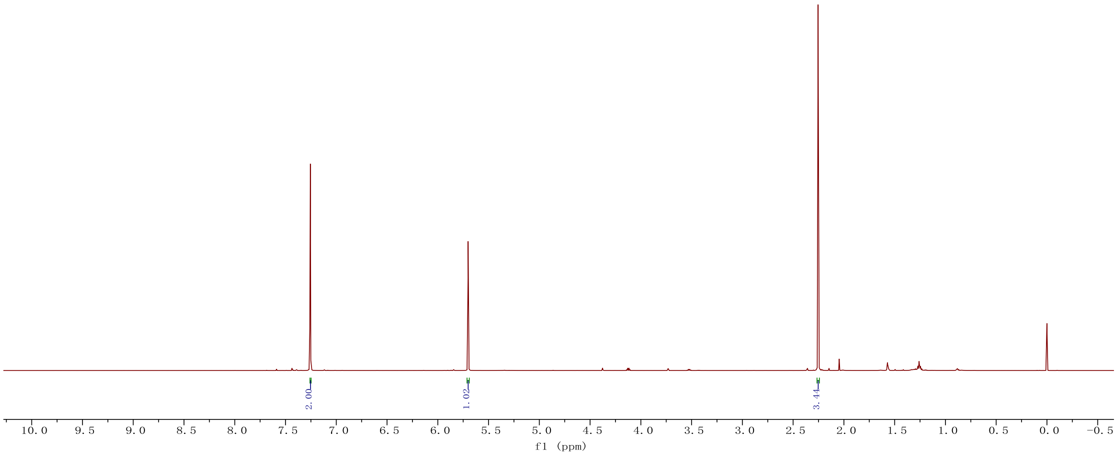
f1 (ppm)

K-2-66.1.fid



6a



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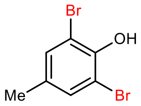

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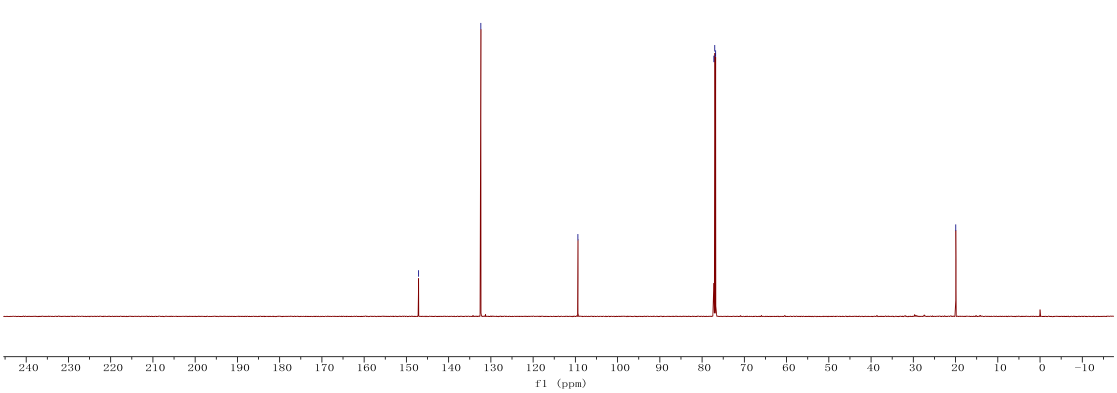

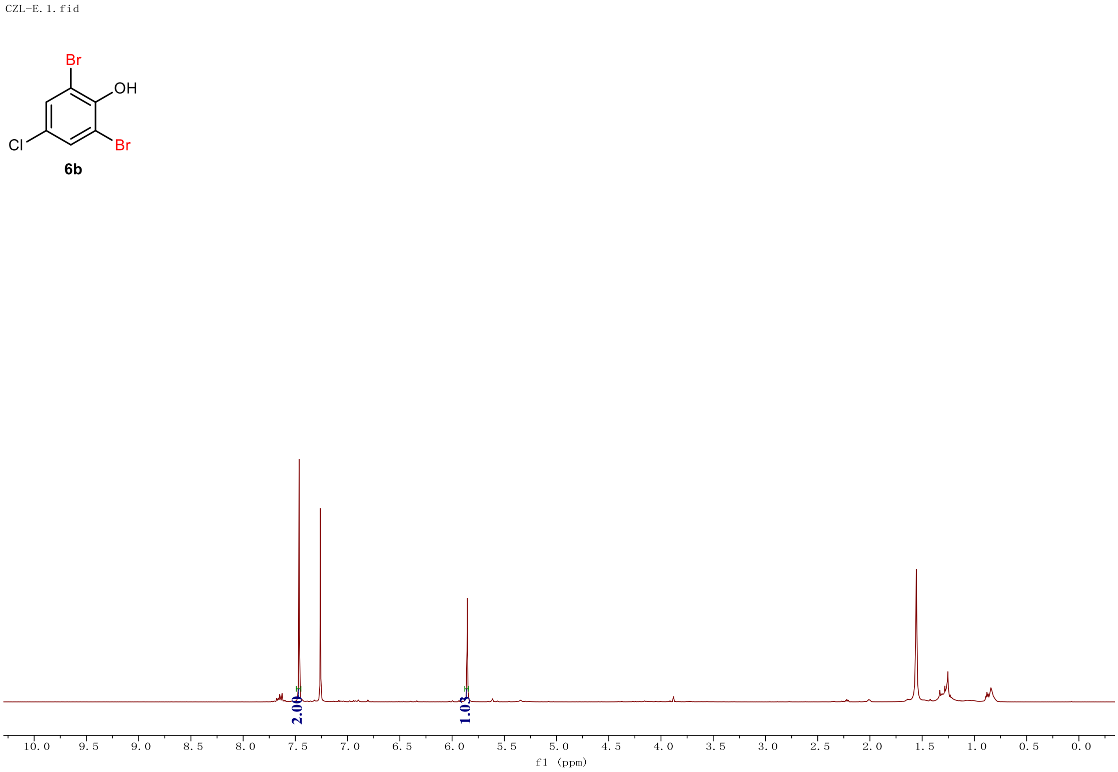
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Br
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6.5
6.0
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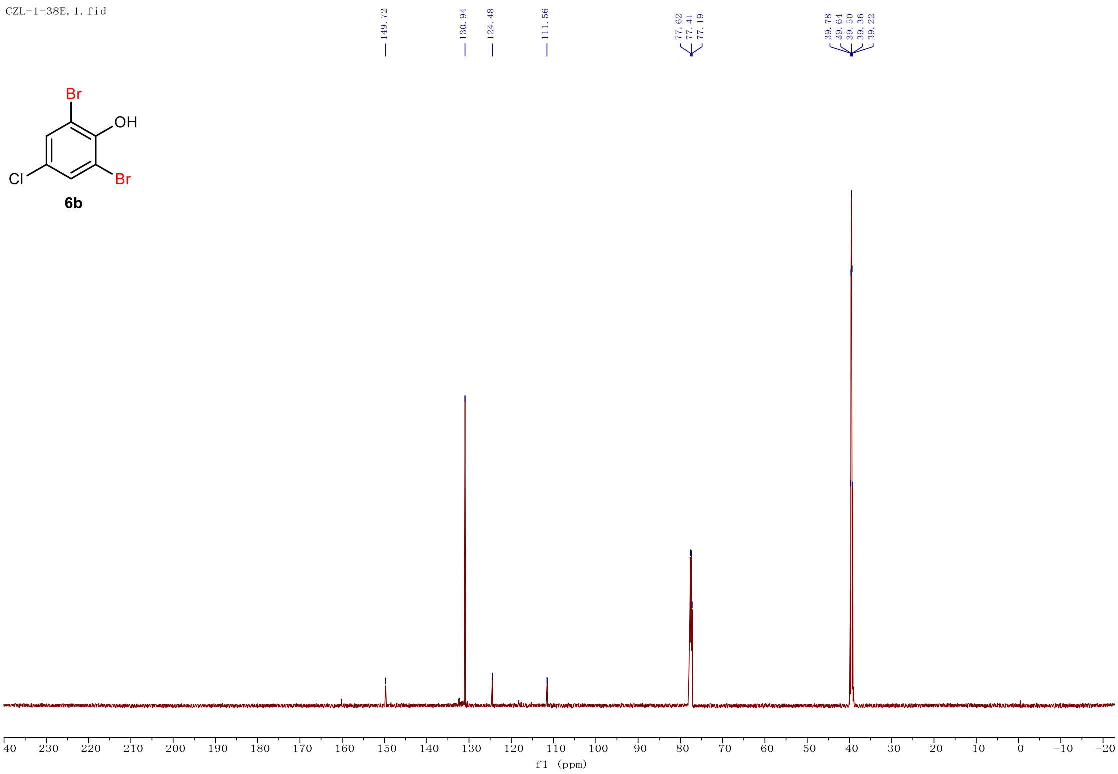
0.0
f1 (ppm)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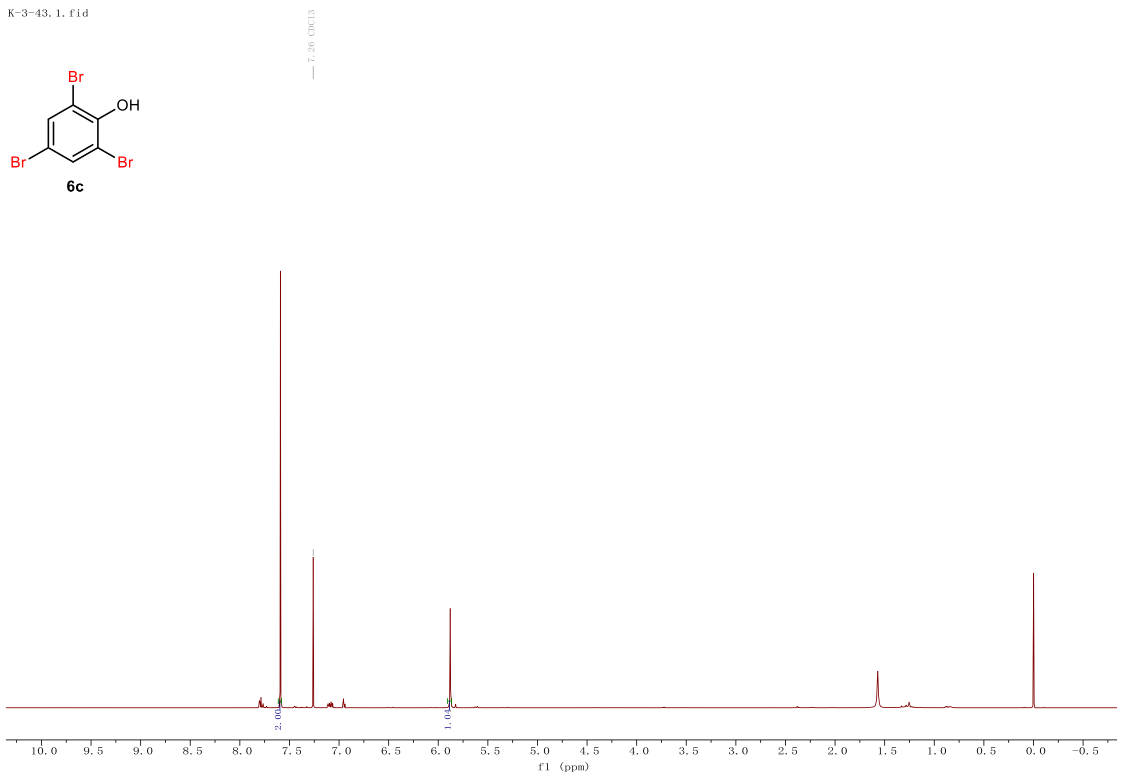
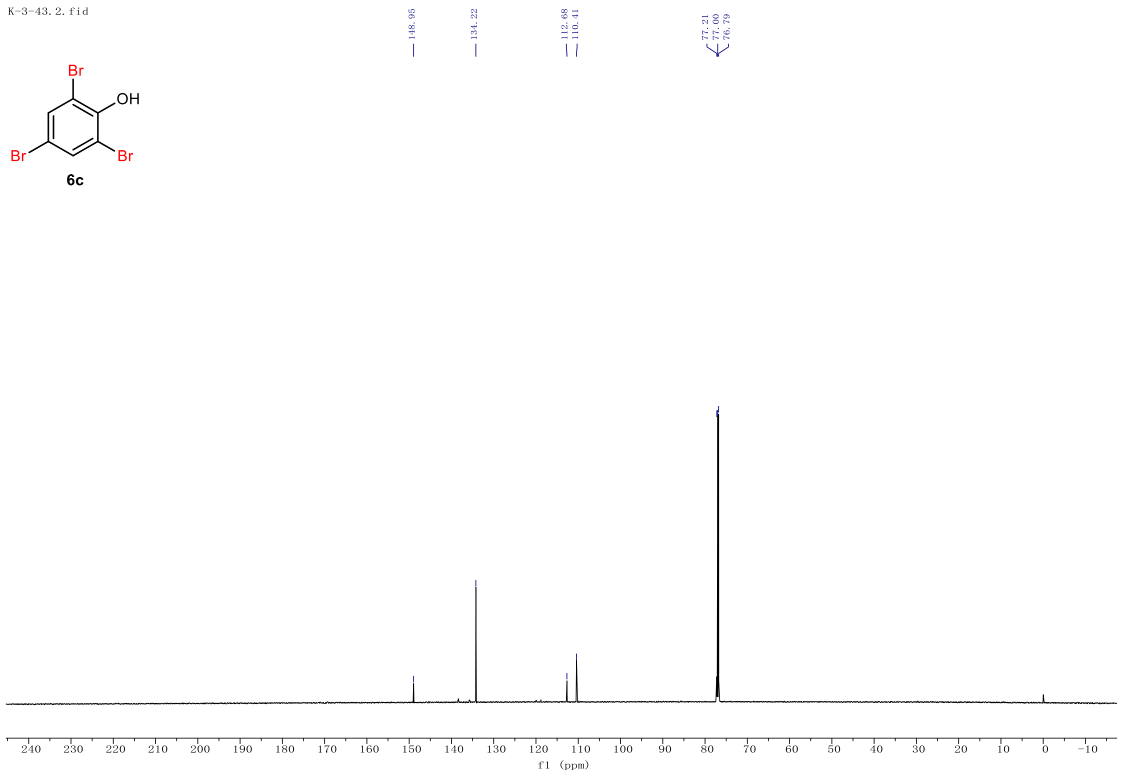
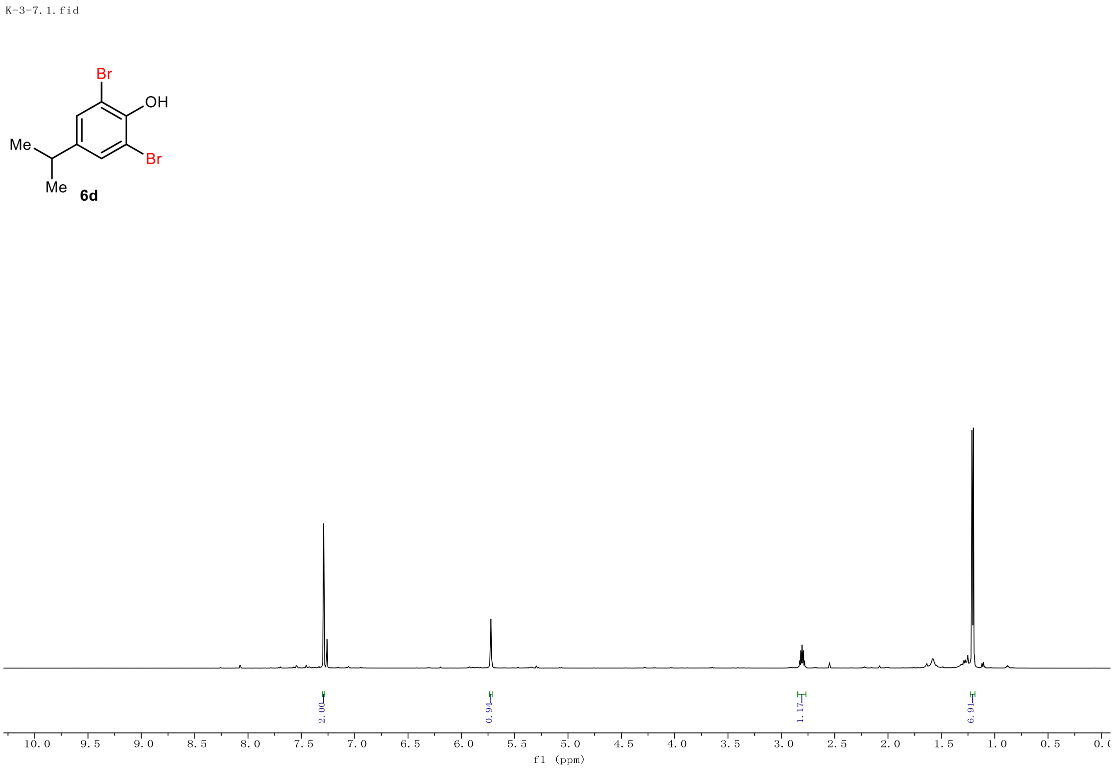
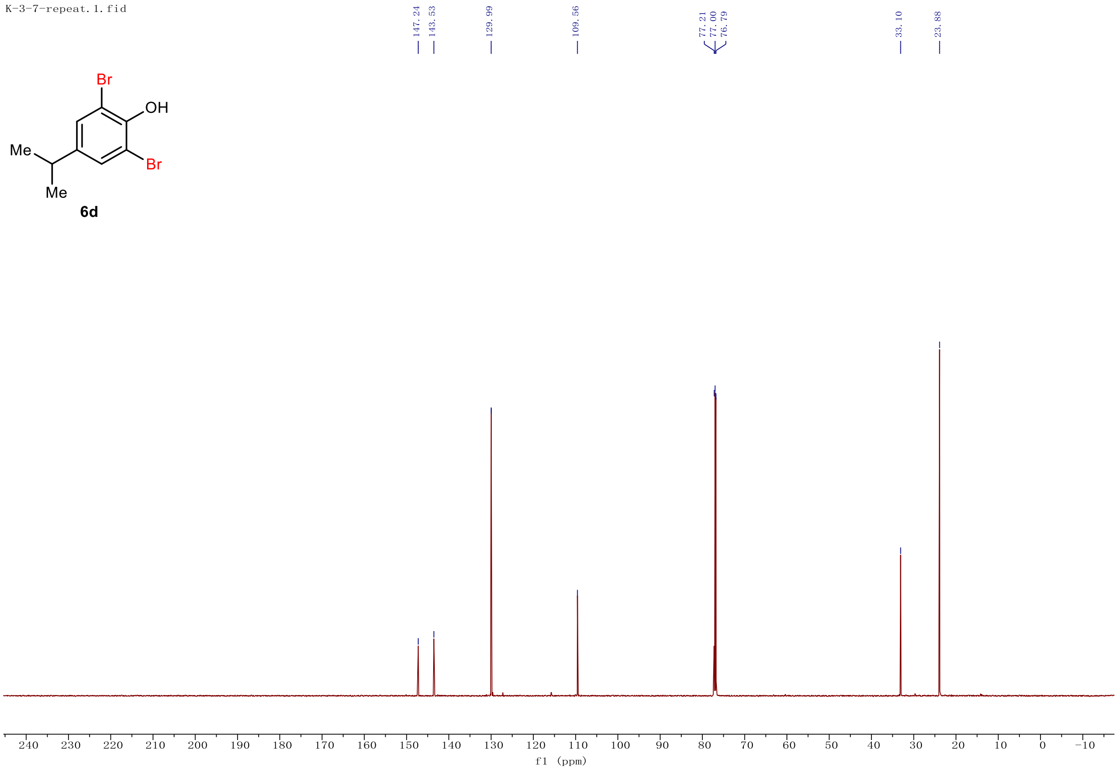
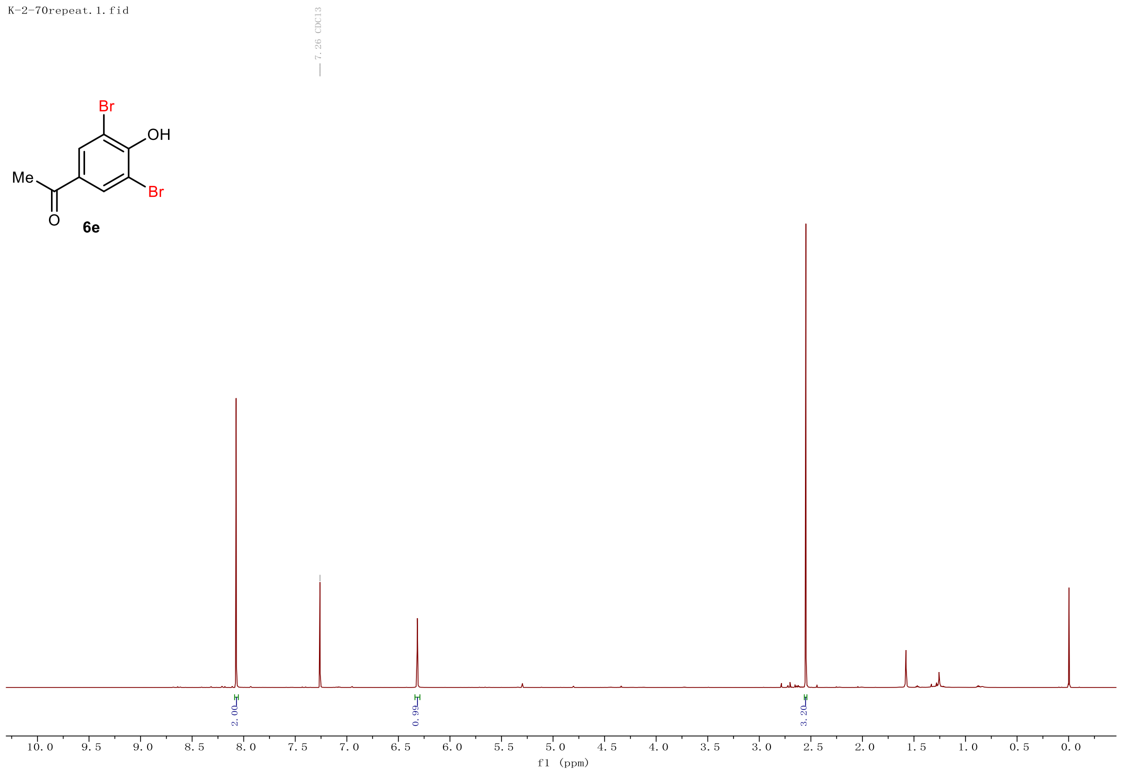
39.50
39.36
39.22
Br
OH
Cl
Br
6b
40
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

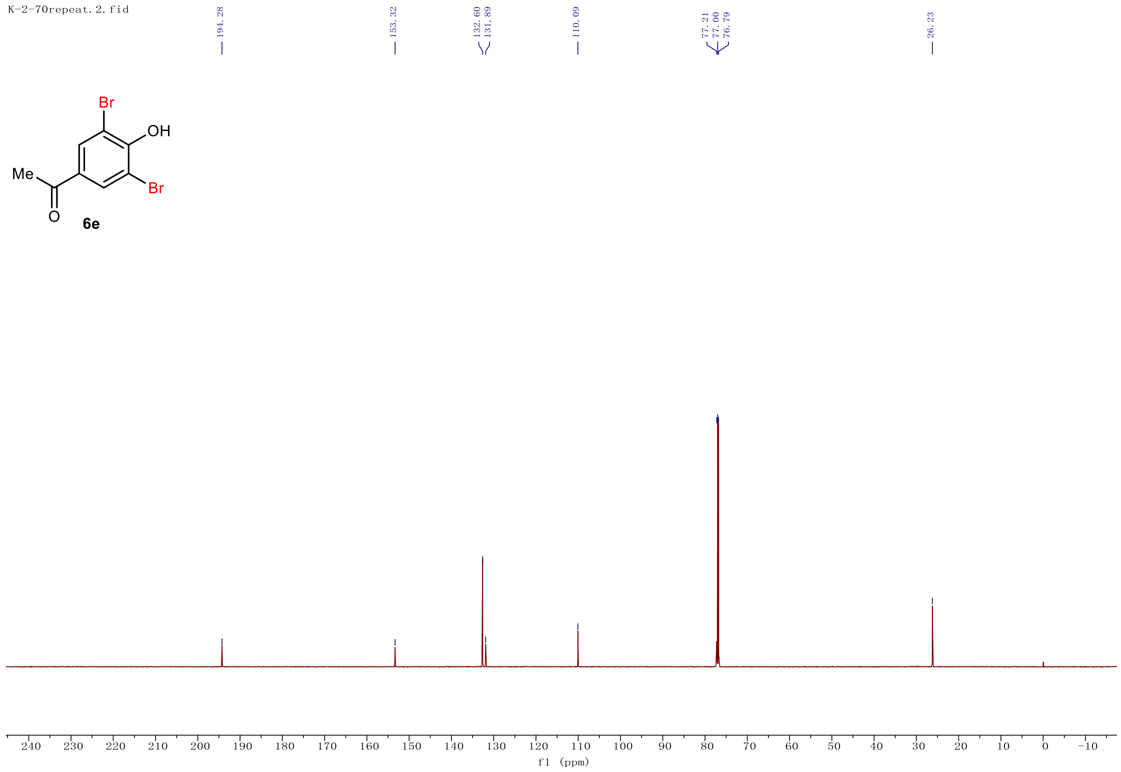

K-3-43.1.fid
7.26 CDCl3
Br
OH
Br
Br
6c
2.00
1.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

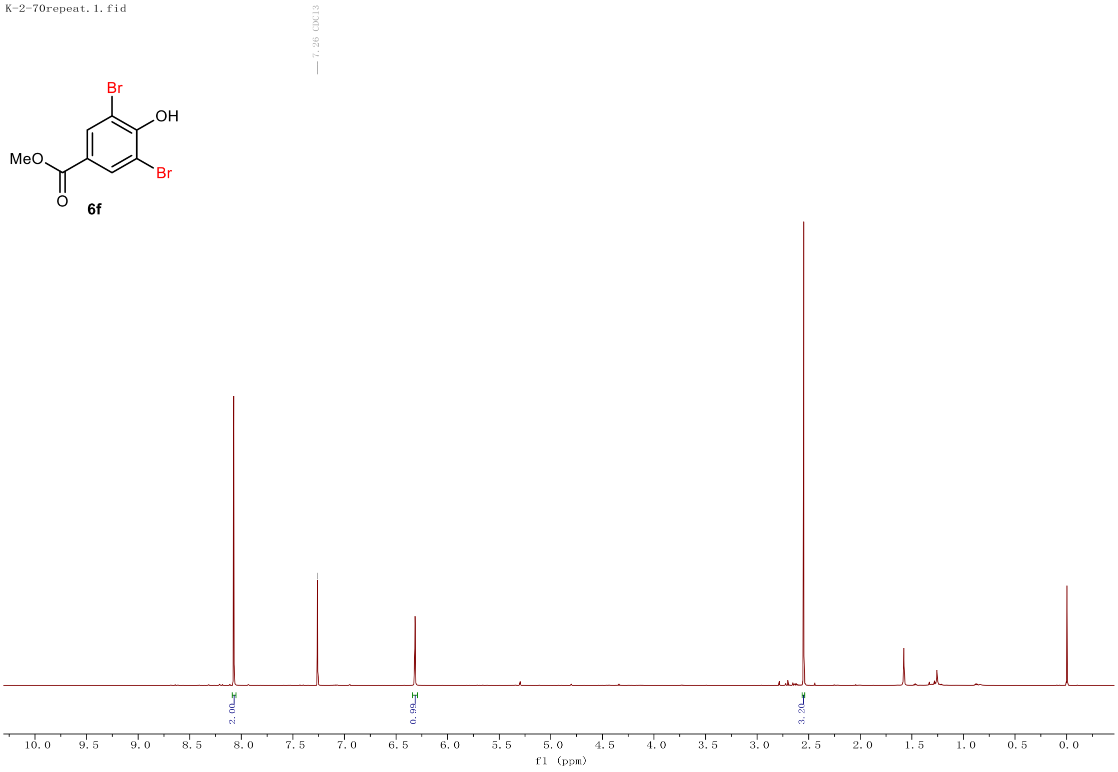

K-3-43.2.fid
148.95
134.22
112.68
110.41
77.21
77.00
76.79
Br
OH
Br
Br
6c
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

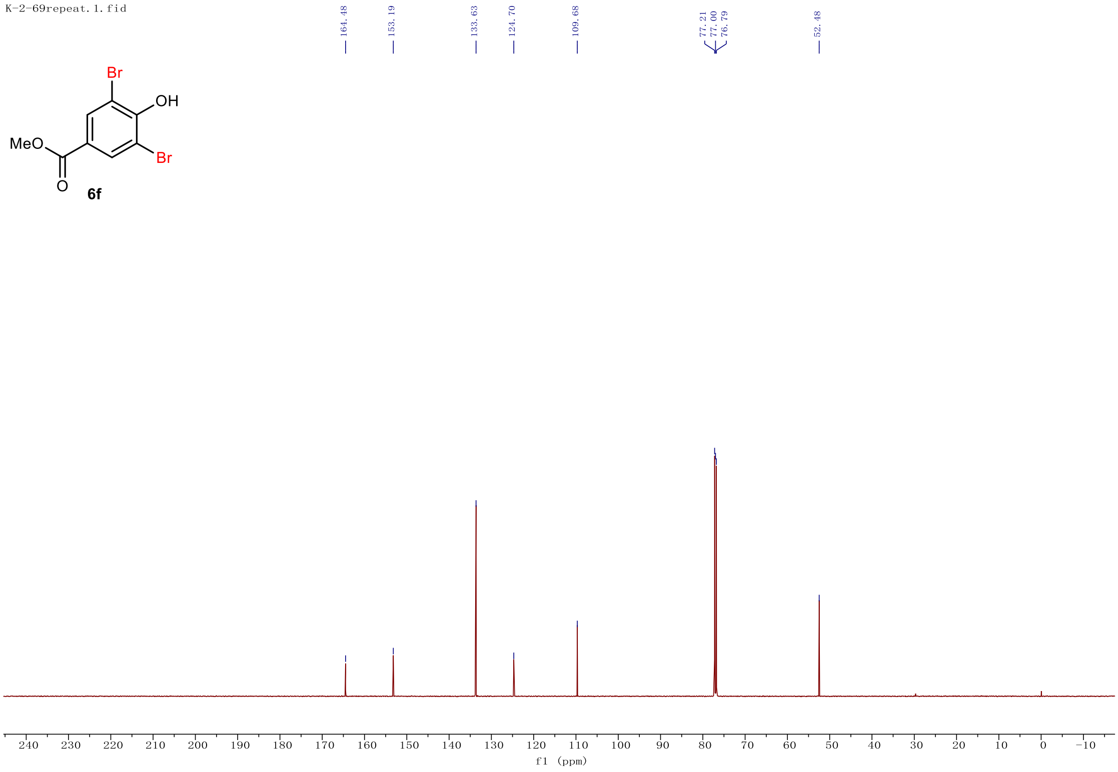

K-3-7.1.fid
Br
OH
Me
Br
Me
6d
2.00
0.94
1.17
6.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

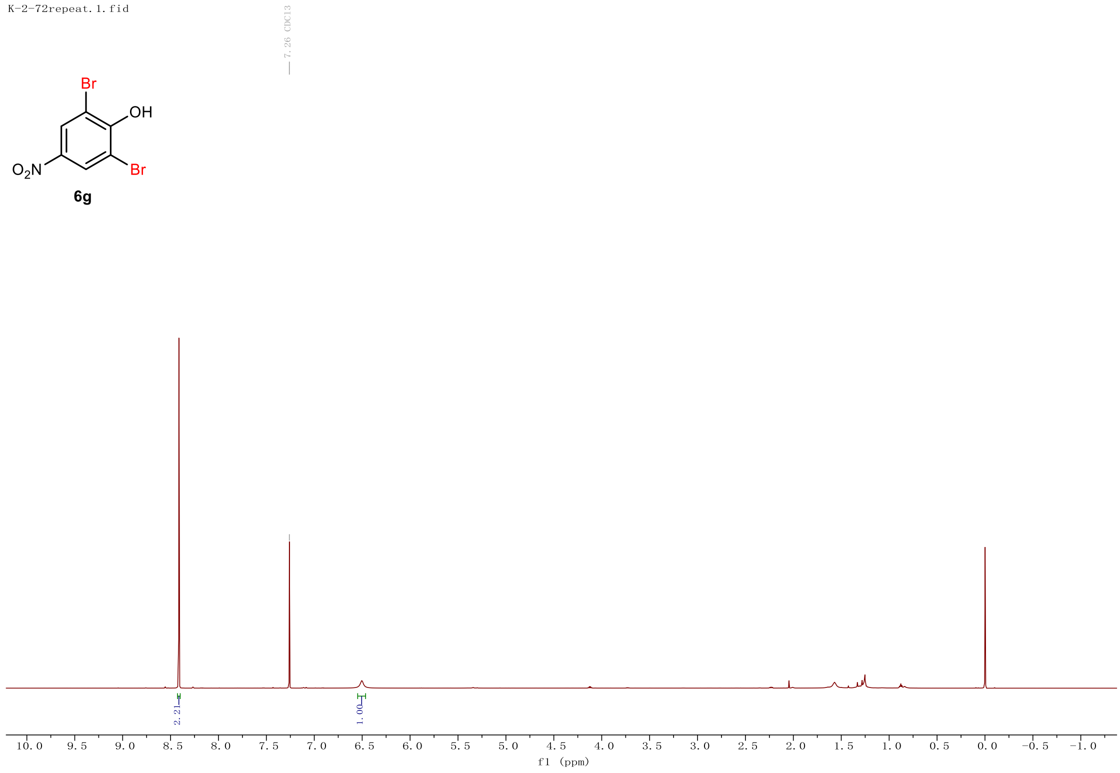

K-3-7-repeat.1.fid
147.24
143.53
129.99
109.56
77.21
77.00
76.79
33.10
23.88
Br
OH
Me
Br
Me
6d
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

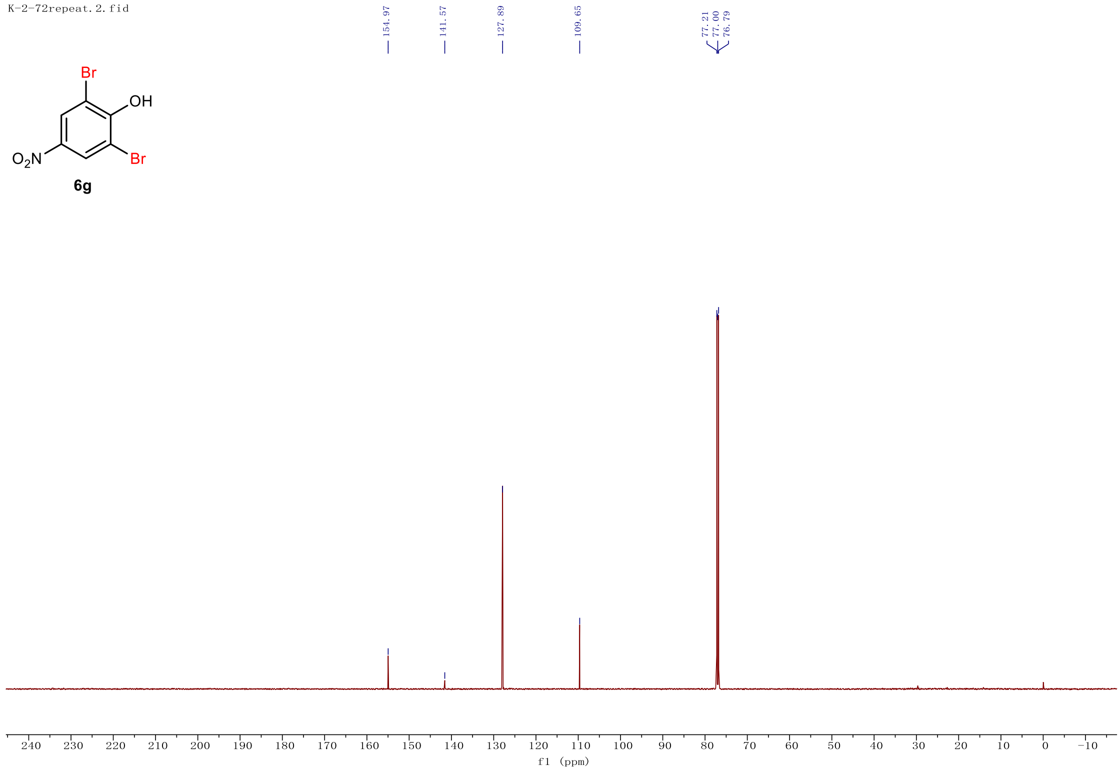

K-2-70repeat.1.fid
7.26 CDCl3
Br
OH
Me
Br
O
6e
2.00
0.99
3.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


K-2-70repeat.2.fid
194.28
153.32
132.60
131.89
110.09
77.21
77.00
76.79
26.23
Br
OH
Me
Br
O
6e
240
230
220
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)

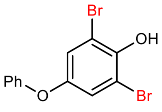

K-2-70repeat.1.fid
7.26 CDCl3
Br
OH
MeO
Br
O
6f
2.00
0.99
3.20
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


K-2-69repeat.1.fid
164.48
153.19
133.63
124.70
109.68
77.21
77.00
76.79
52.48
Br
OH
MeO
Br
O
6f
240
230
220
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)

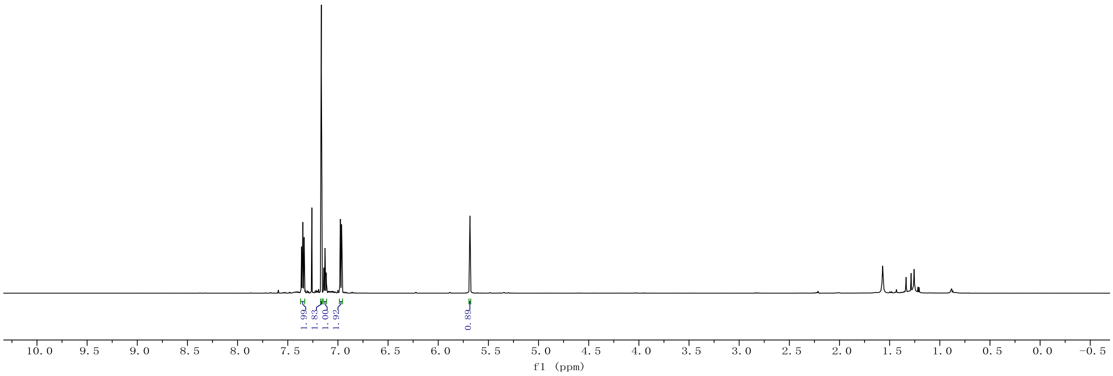

K-2-72repeat.1.fid
7.26 CDCl3
Br
OH
O2N
Br
6g
2.21
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0
f1 (ppm)


K-2-72repeat.2.fid
154.97
141.57
127.89
109.65
77.21
77.00
76.79
Br
OH
O2N
Br
6g
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

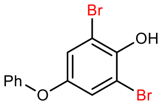
K-3-67.3.fid



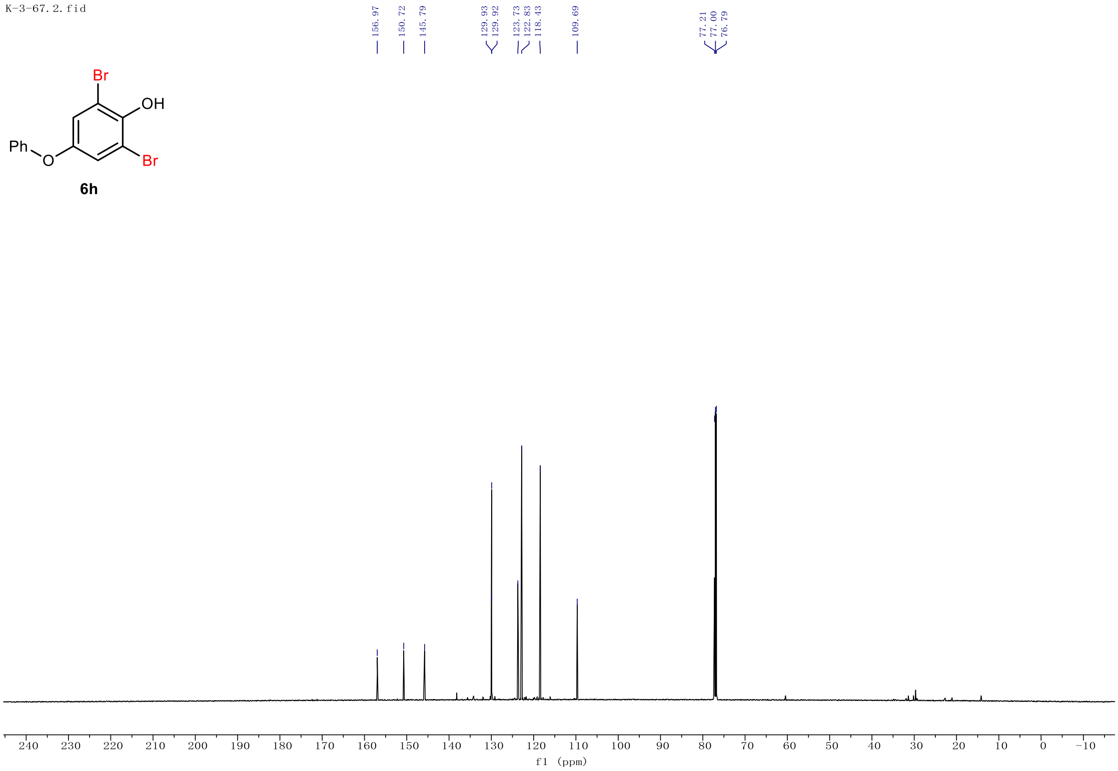
6h

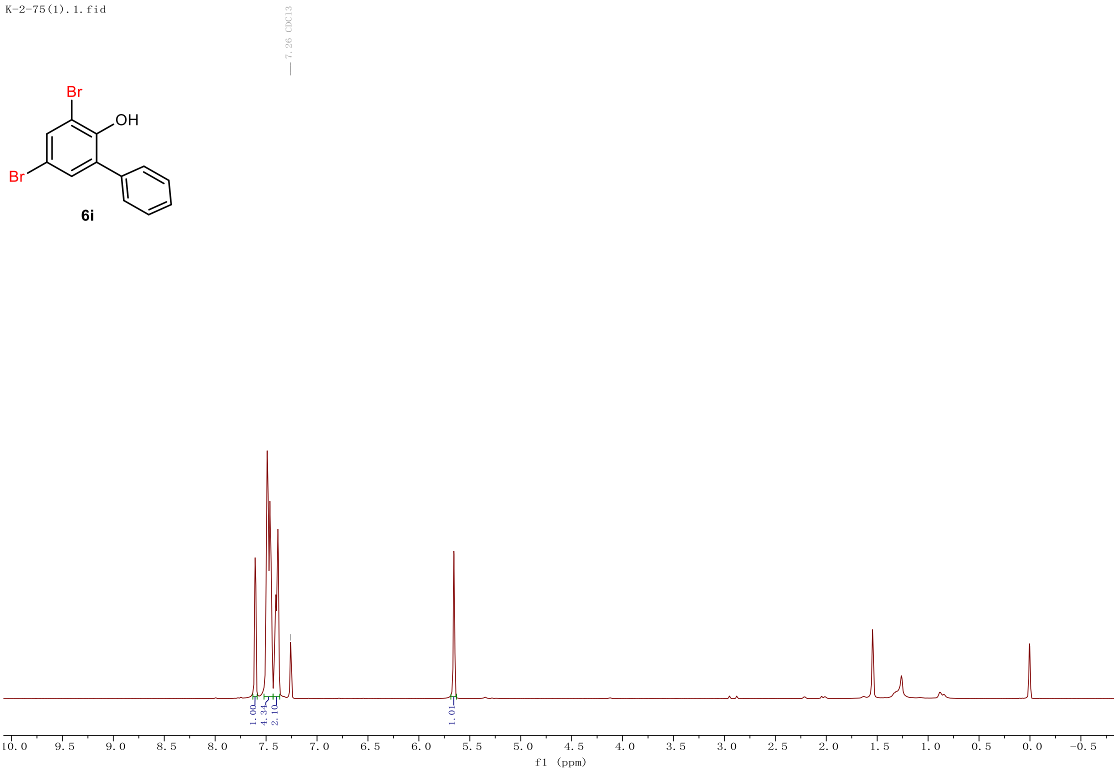


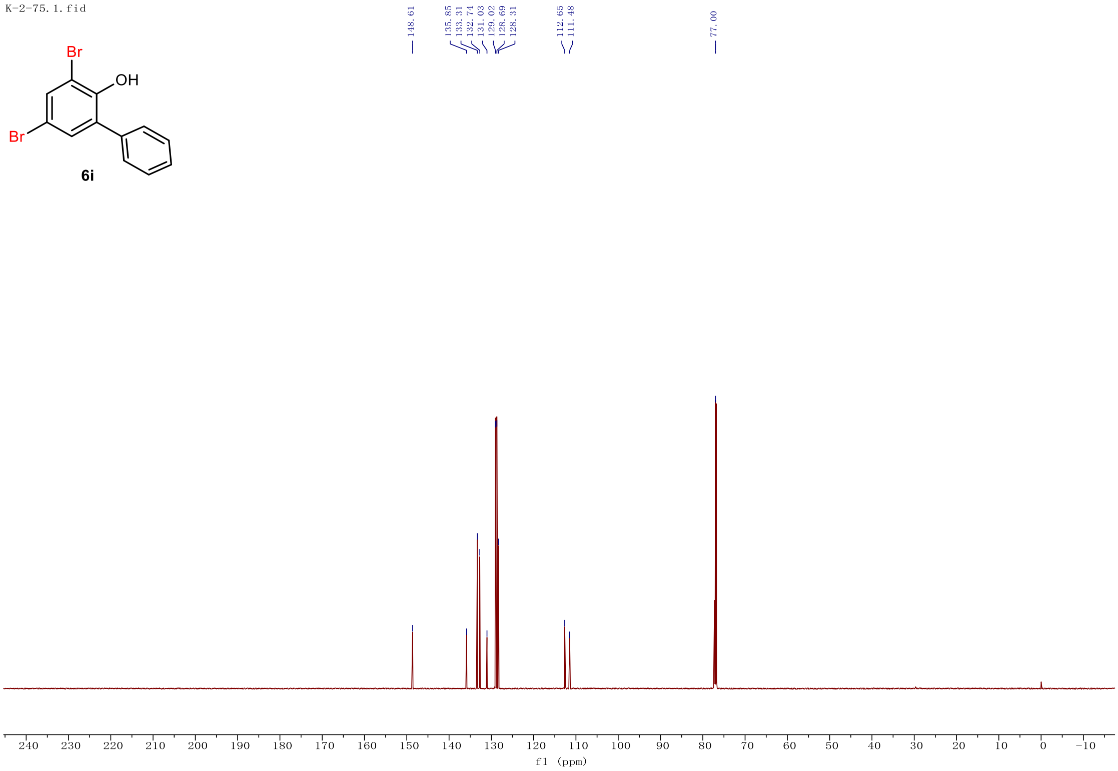
K-3-67.2.fid

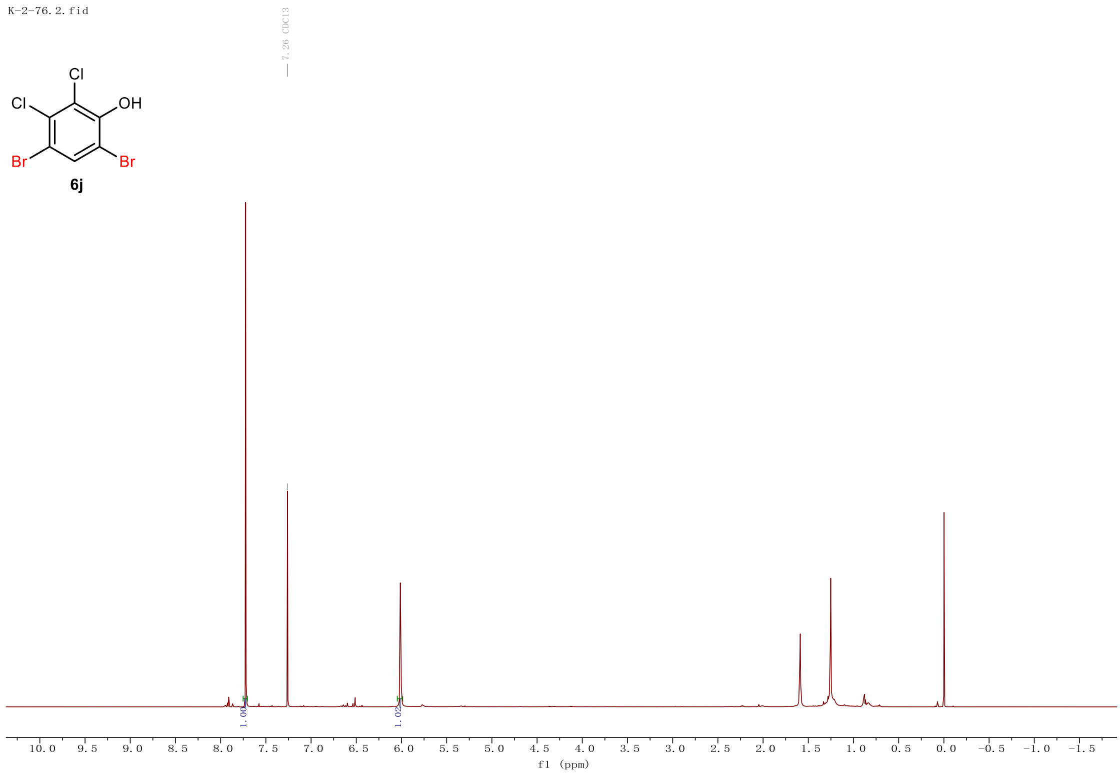


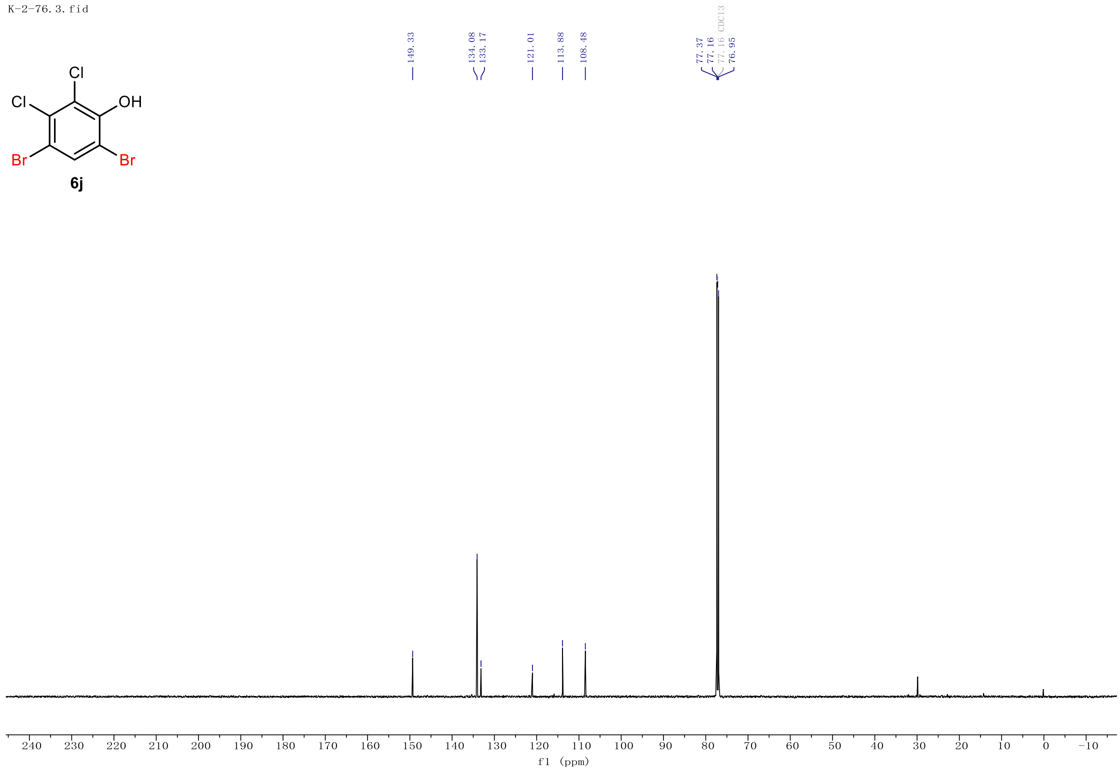
6h

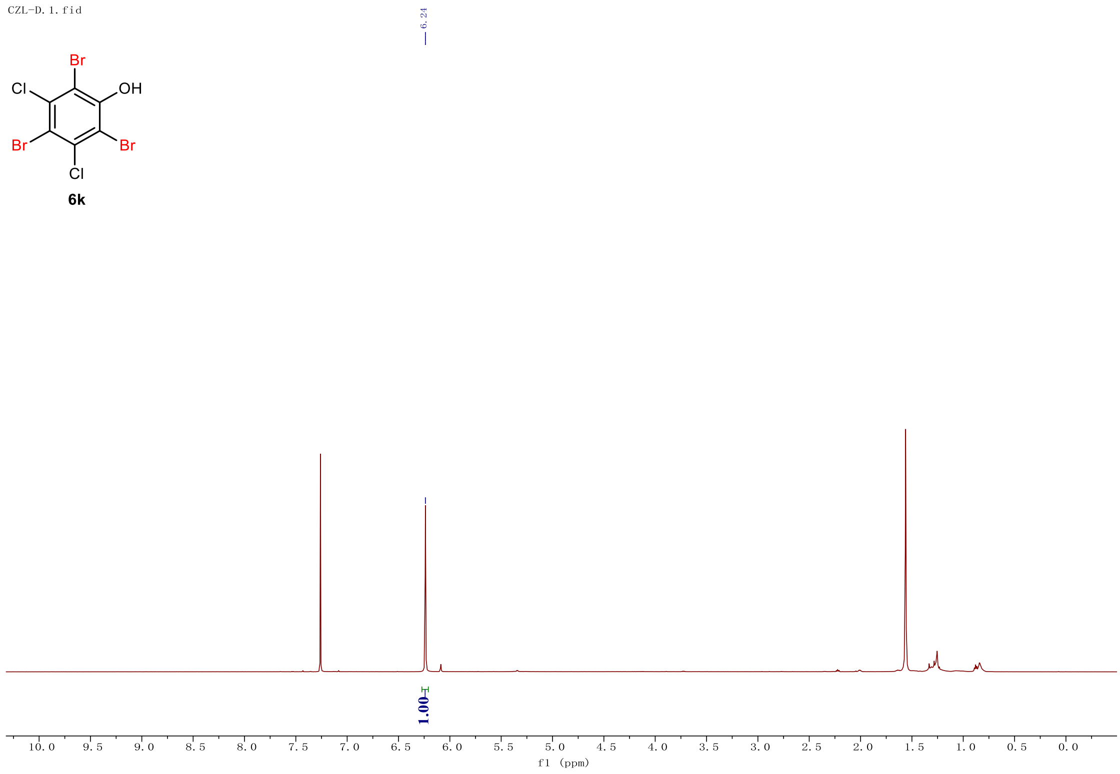


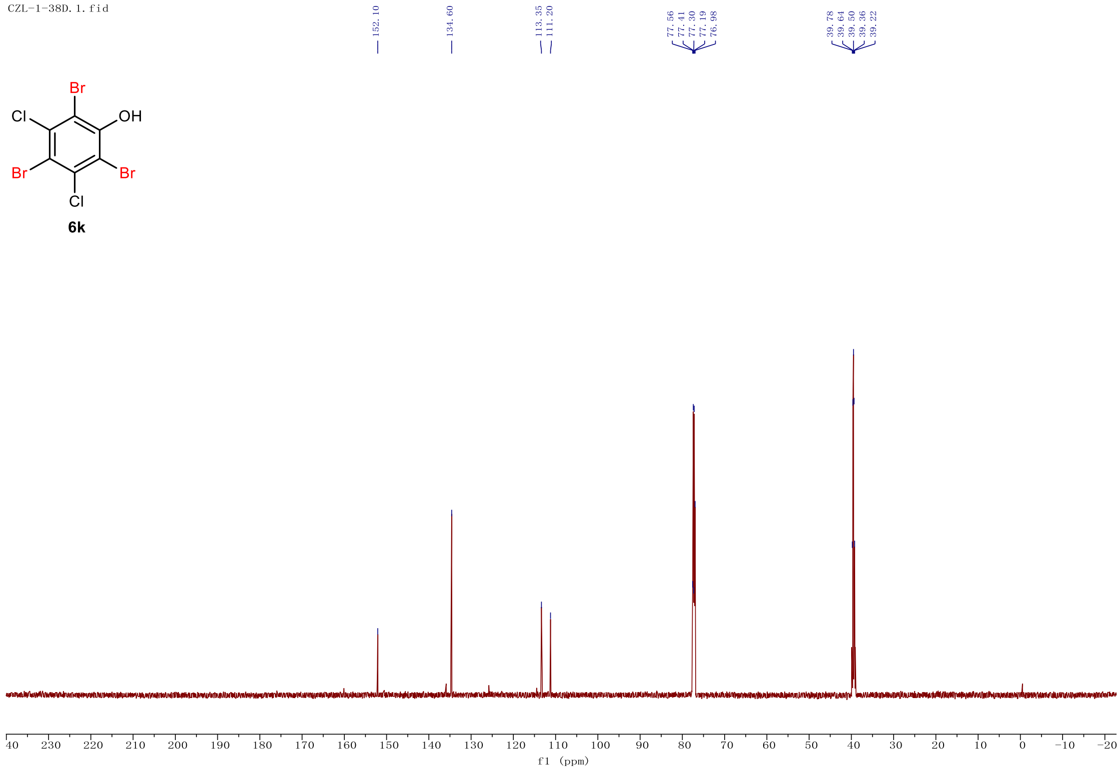

K-2-75(1).1.fid
7.26 CDCl3
Br
OH
Br
6i
1.00
4.34
2.10
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

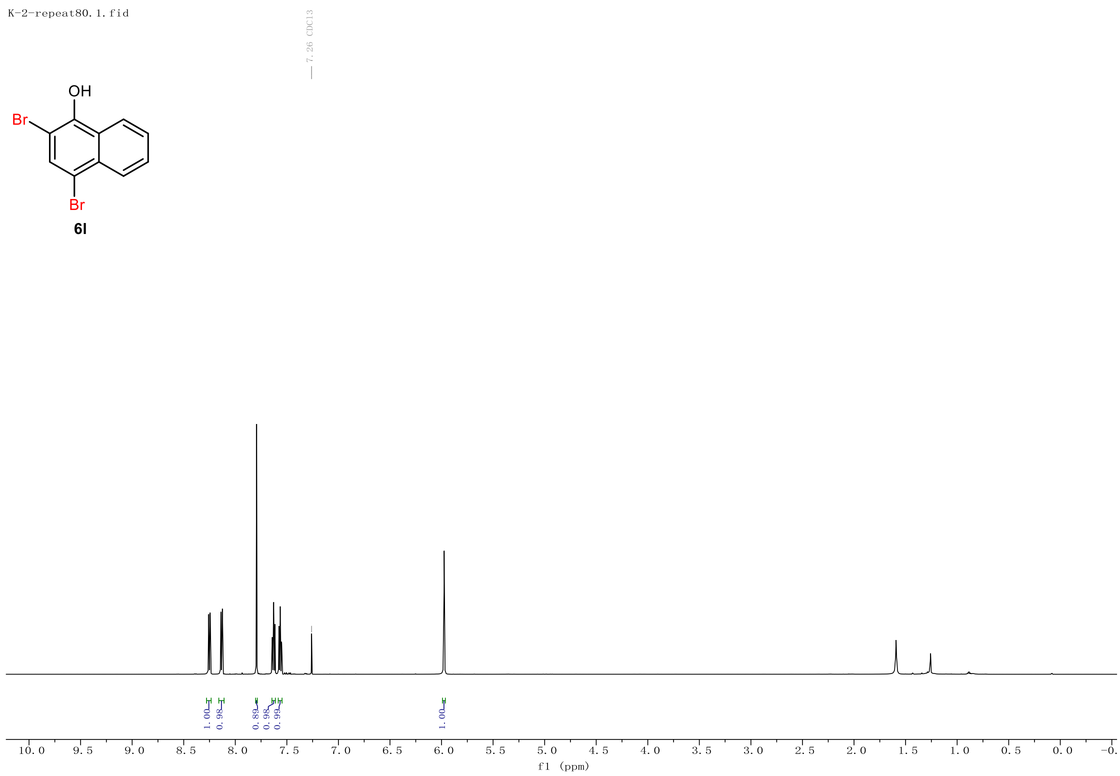

K-2-75.1.fid
148.61
135.85
133.31
132.74
131.03
129.02
128.69
128.31
112.65
111.48
77.00
Br
OH
Br
6i
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

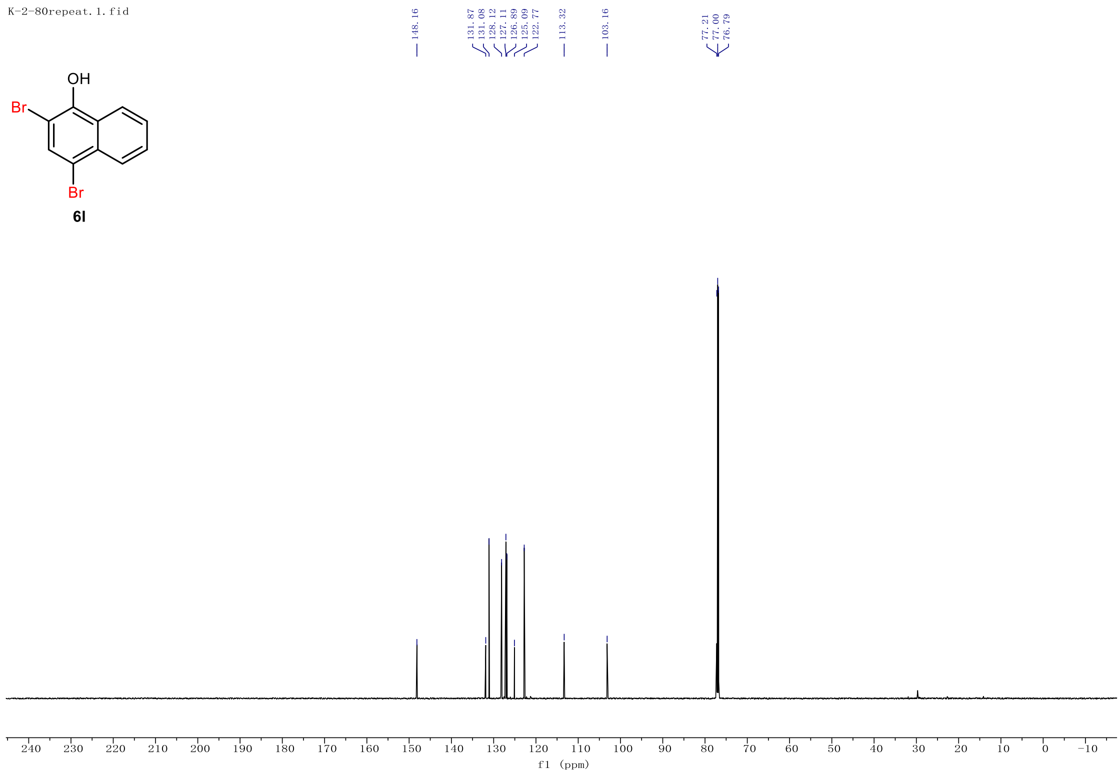

K-2-76.2.fid
7.26 CDCl3
Cl
Cl
OH
Br
Br
6j
1.00
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)


K-2-76.3.fid
149.33
134.08
133.17
121.01
113.88
108.48
77.37
77.16
77.16 CDCl3
76.95
Cl
Cl
OH
Br
Br
6j
240
230
220
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)

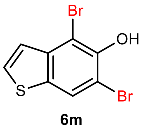

CZL-D.1.fid
6.24
Br
Cl
OH
Br
Br
Cl
6k
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


CZL-1-38D.1.fid
152.10
134.60
113.35
111.20
77.56
77.41
77.30
77.19
76.98
39.78
39.64
39.50
39.36
39.22
Br
Cl
OH
Br
Br
Cl
6k
40
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

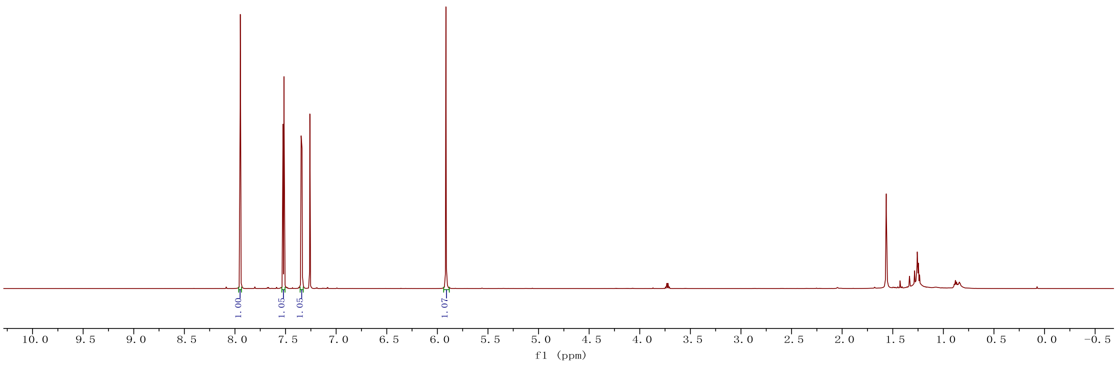

K-2-repeat80.1.fid
7.26 CDCl3
OH
Br
Br
6l
1.00
0.98
0.89
0.98
0.99
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


K-2-80repeat.1.fid
148.16
131.87
131.08
128.12
127.11
126.89
125.09
122.77
113.32
103.16
77.21
77.00
76.79
OH
Br
Br
6l
240
230
220
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)

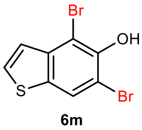
K-2-81.1.fid



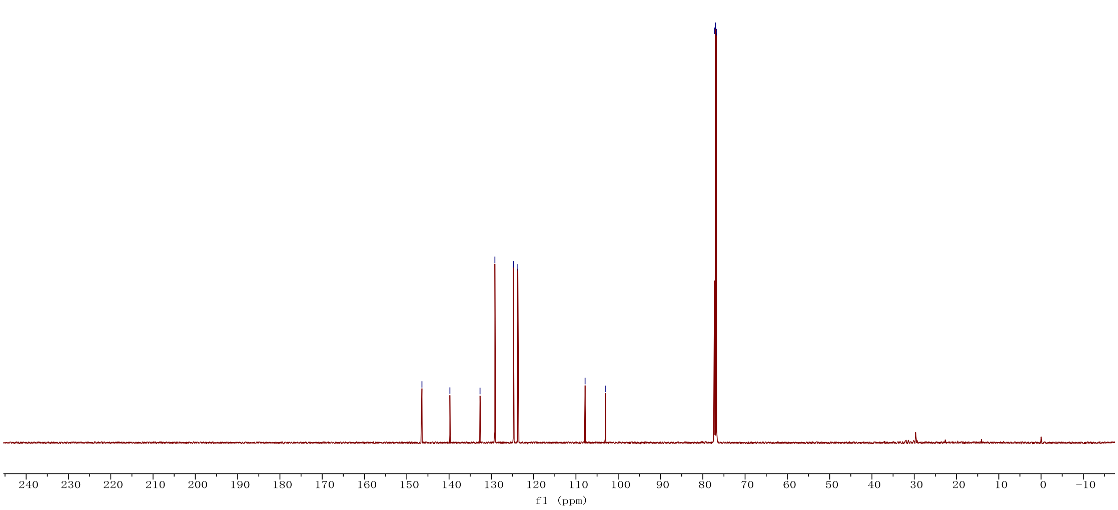
6m

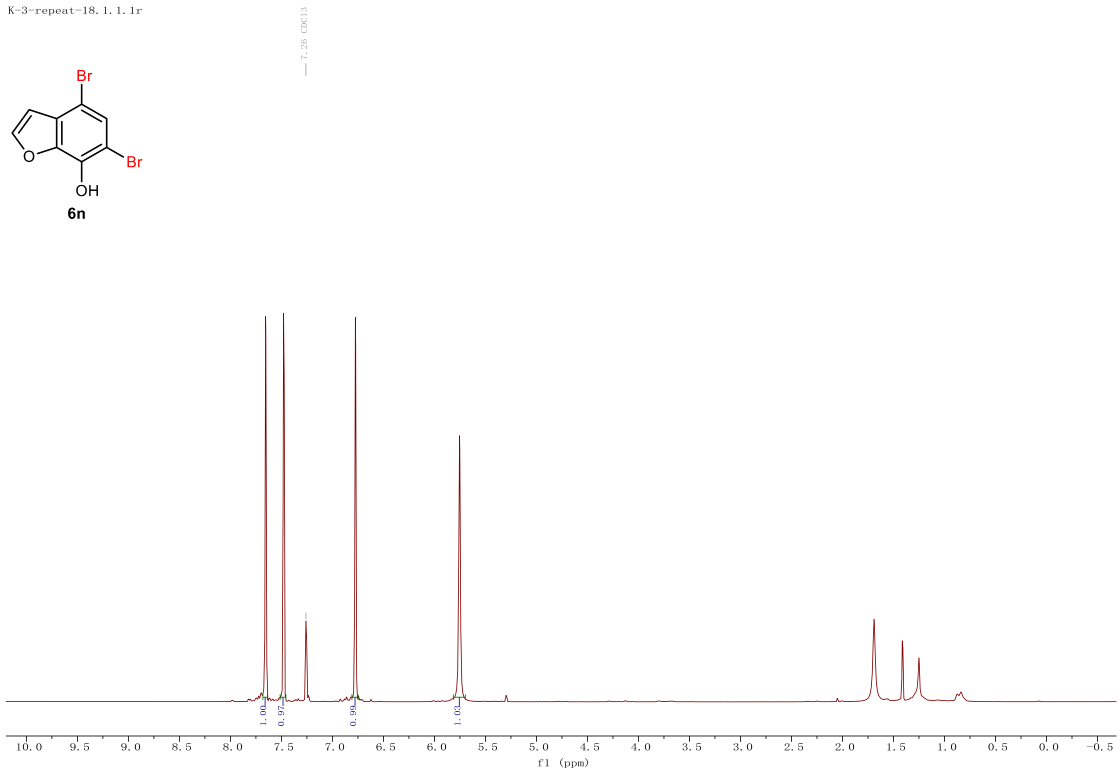


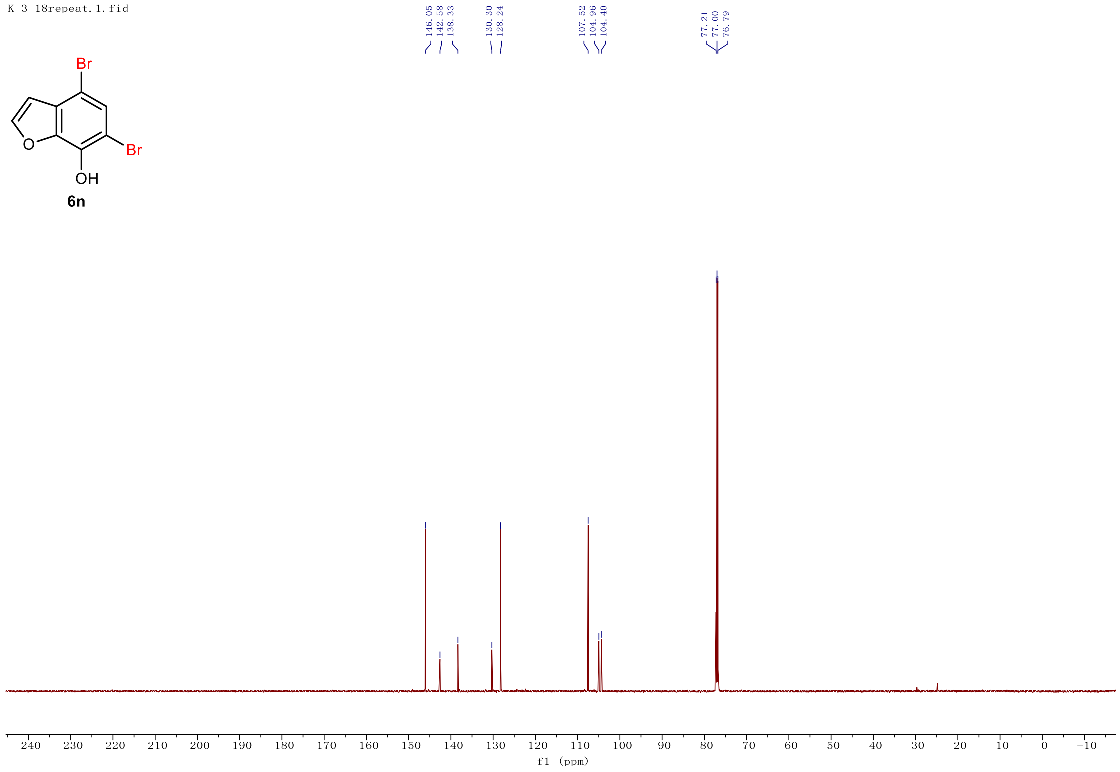
K-2-81.2.fid

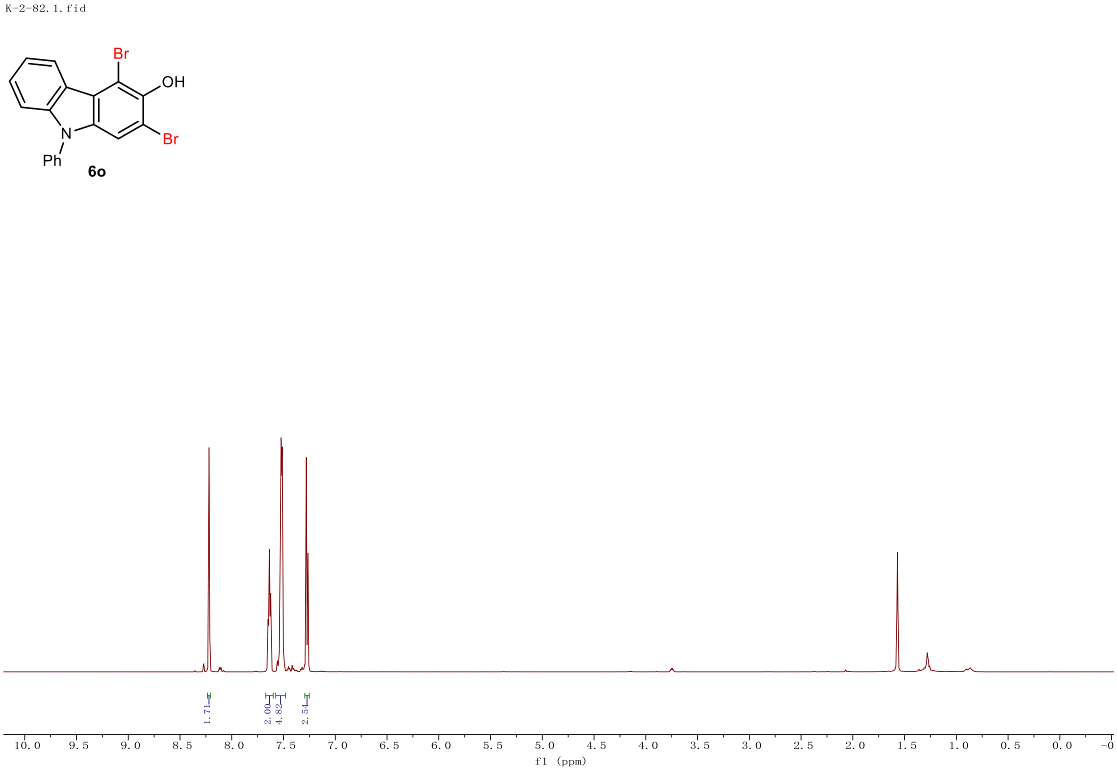


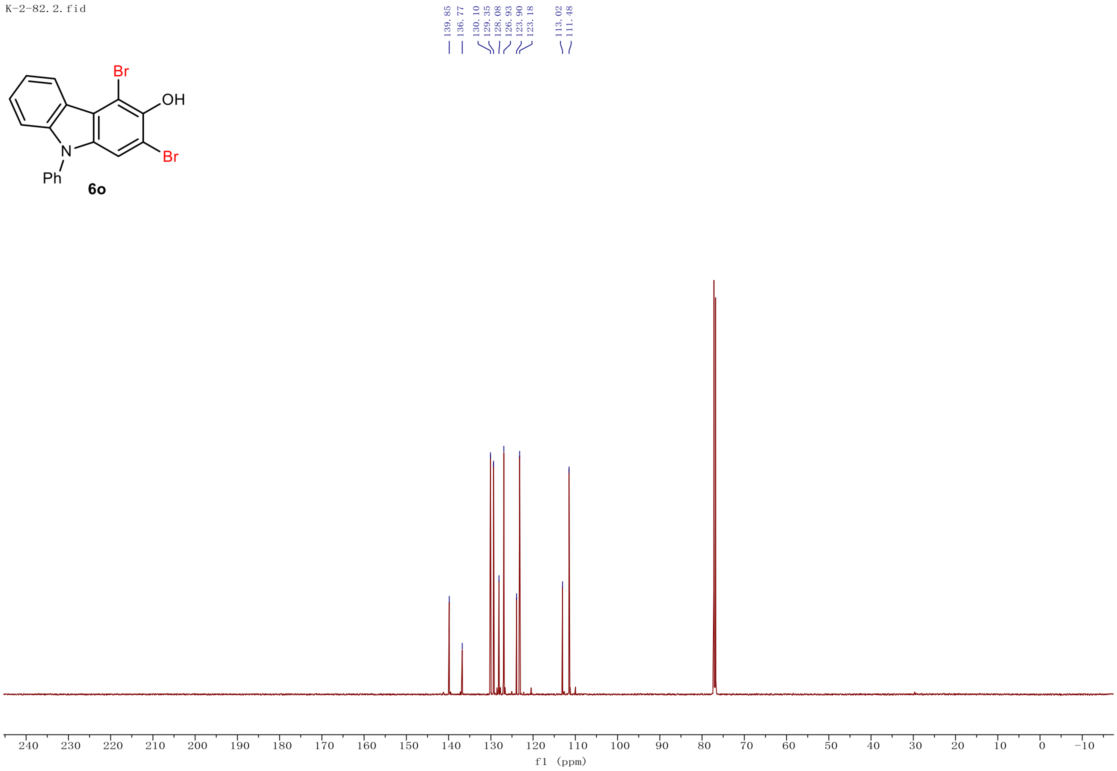
6m

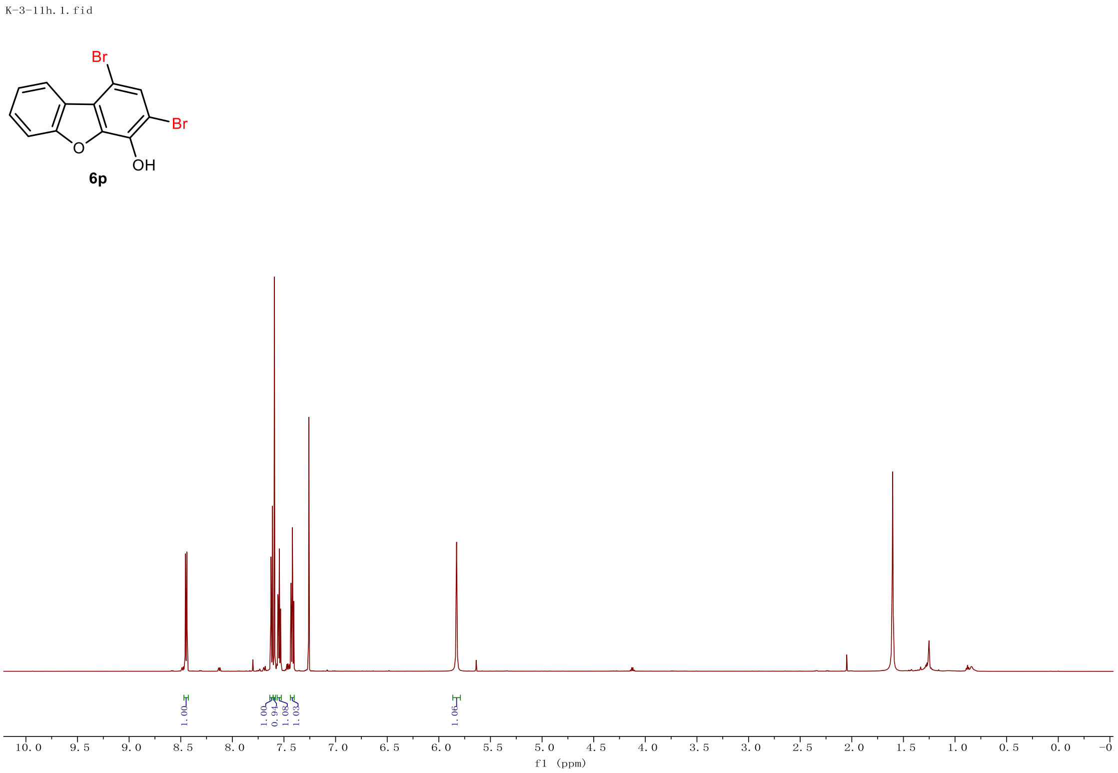



K-3-repeat-18.1.1.1r
Br
Br
O
OH
6n
7.26 CDCl3
1.00
0.97
0.99
1.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

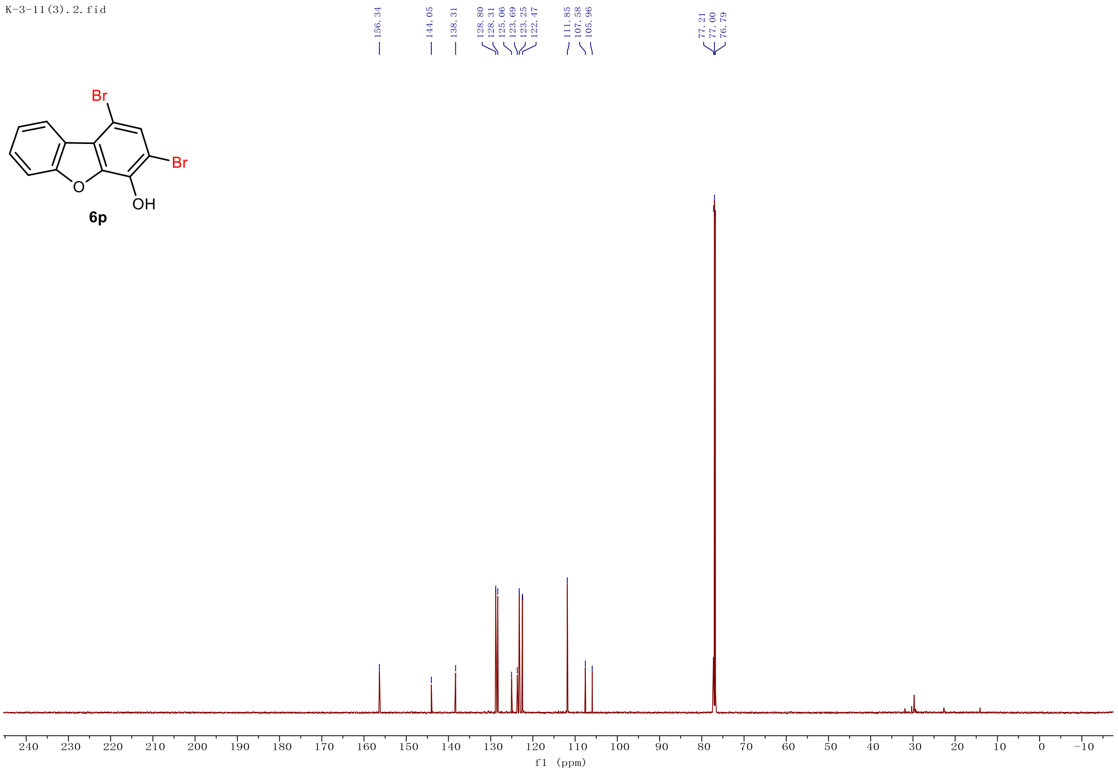

K-3-18repeat.1.fid
146.05
142.58
138.33
130.30
128.24
107.52
104.96
104.40
77.21
77.00
76.79
Br
Br
O
OH
6n
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


K-2-82.1.fid
Br
OH
N
Br
Ph
6o
1.71
2.00
4.82
2.54
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 -0
f1 (ppm)


K-2-82.2.fid
139.85
136.77
130.10
129.35
128.08
126.93
123.90
123.18
113.02
111.48
Br
OH
N
Br
Ph
6o
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

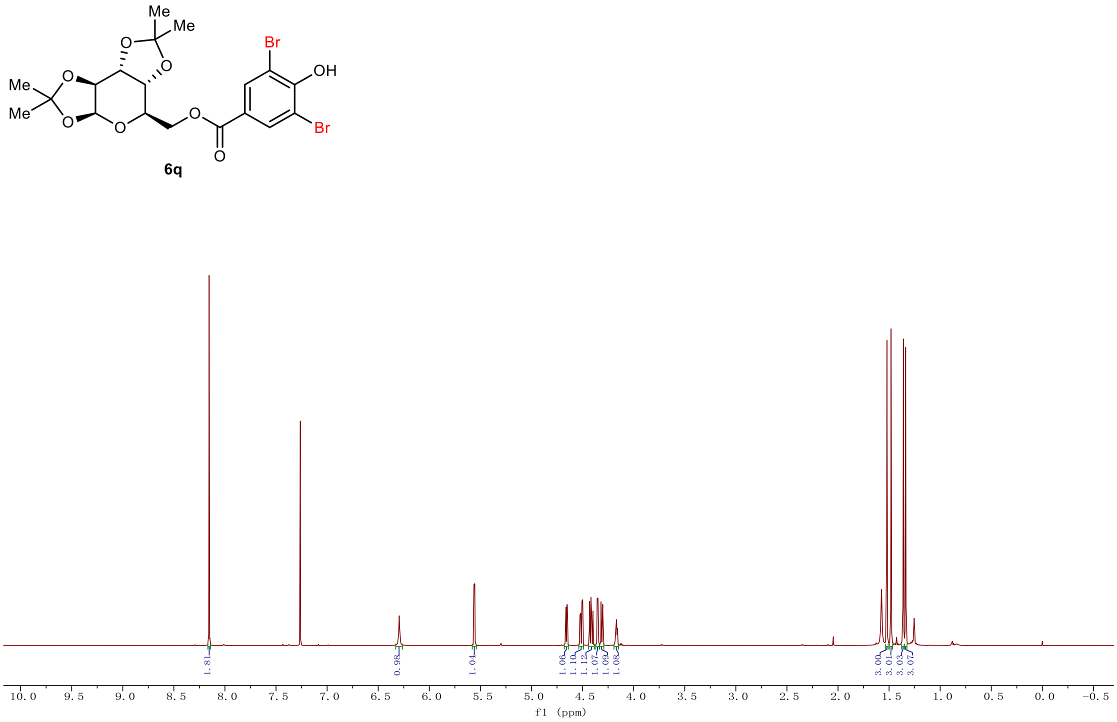

K-3-11h.1.fid
Br
Br
O
OH
1.00
1.00
0.94
1.08
1.03
1.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

6p


K-3-11(3).2.fid
156.34
144.05
138.31
128.80
128.31
125.06
123.69
123.25
122.47
111.85
107.58
105.96
77.21
77.00
76.79
Br
Br
O
OH
240
230
220
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)

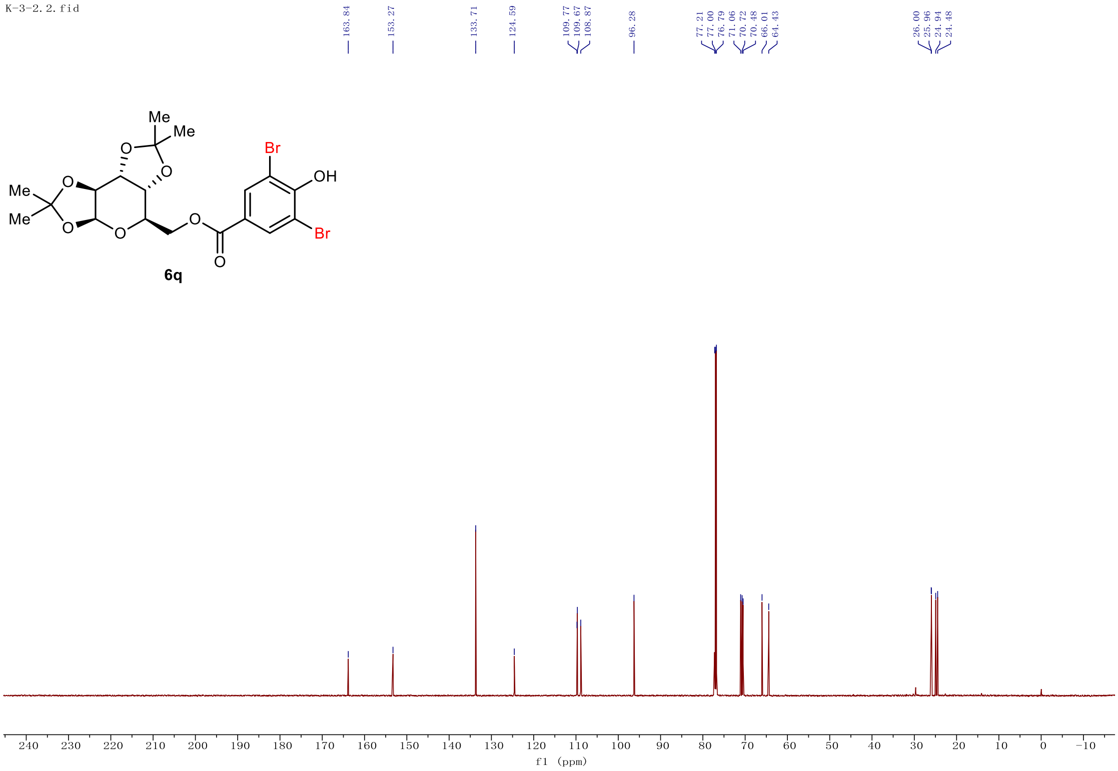
6p

K-3-2.1.fid

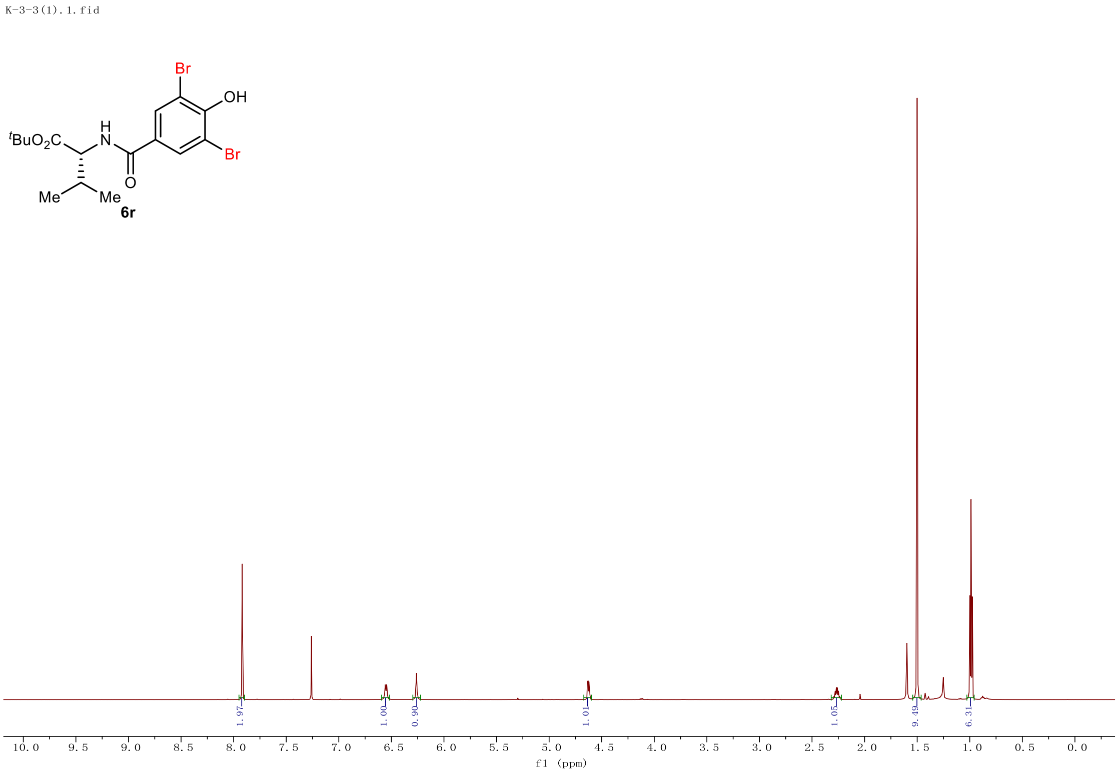


6q

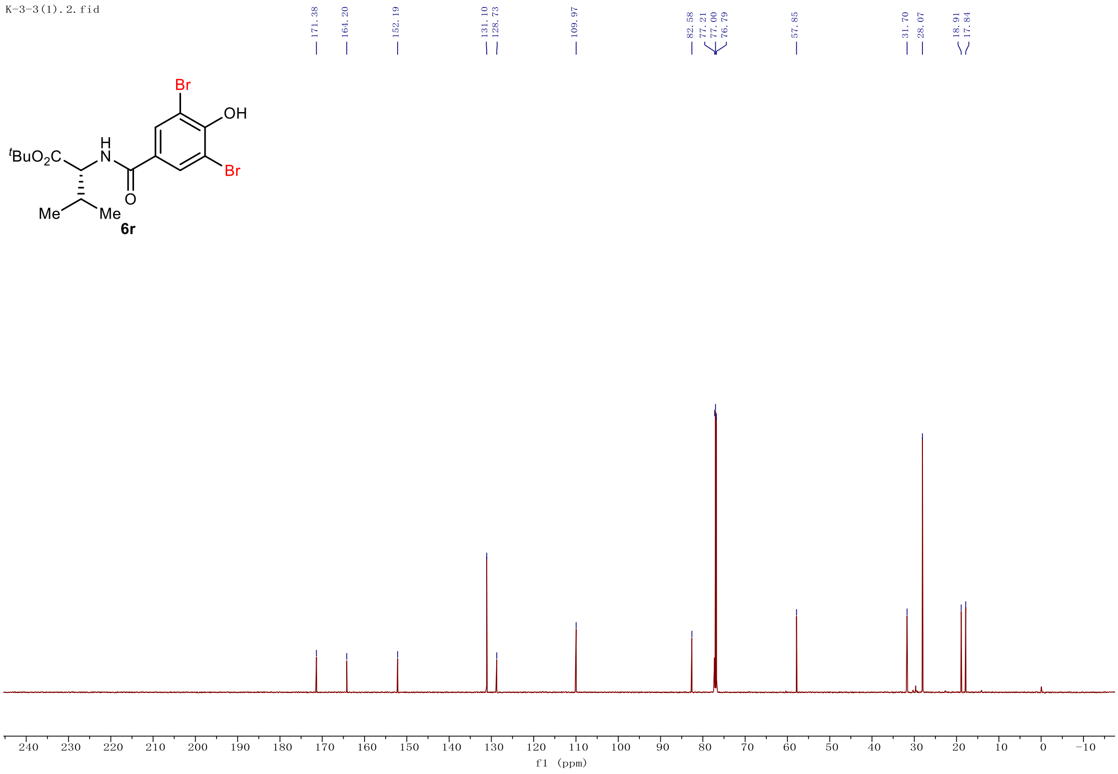
K-3-2.2.fid



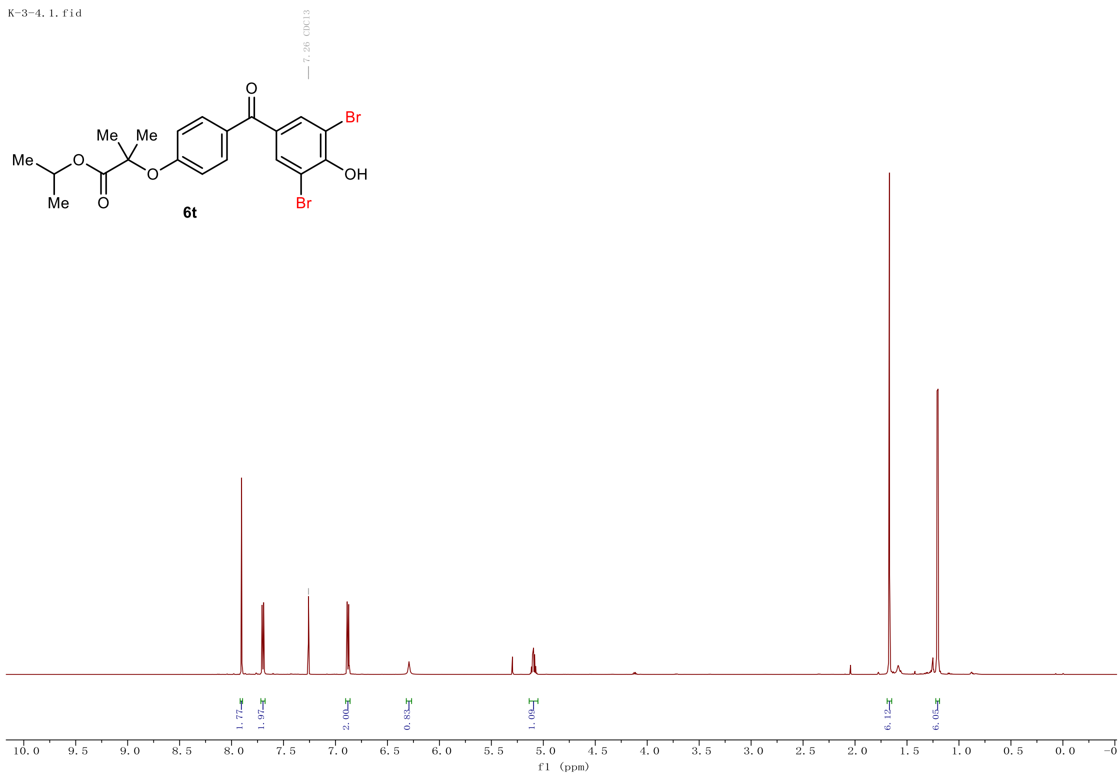
6q

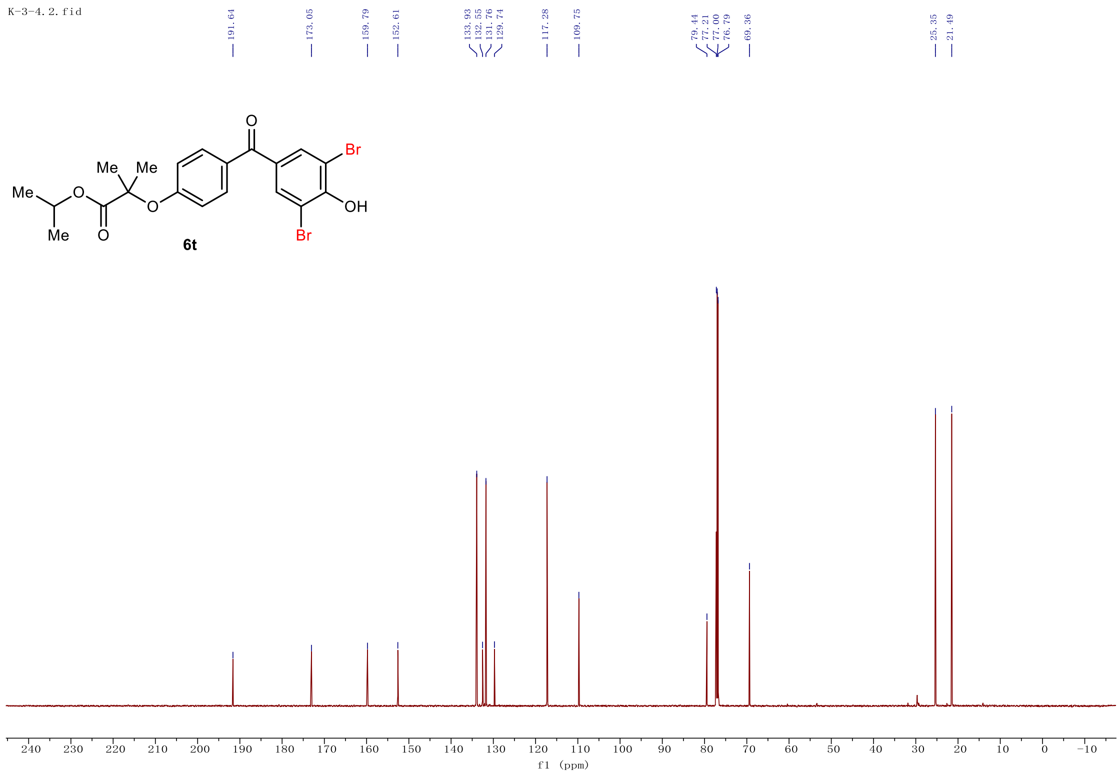

K-3-3(1).1.fid
Br
OH
Br
^{t}BuO$_2$C
H
N
O
Me
Me
1.97
1.00
0.90
1.01
1.05
9.49
6.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

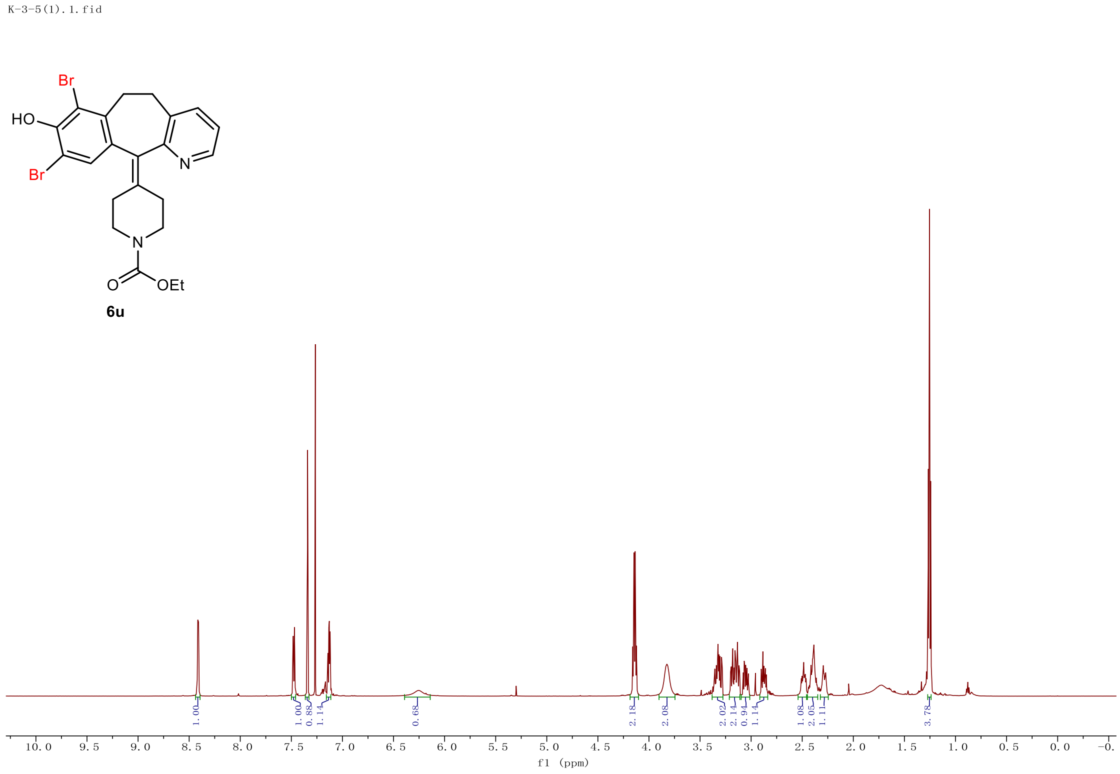
6r


K-3-3(1).2.fid
171.38
164.20
152.19
131.10
128.73
109.97
82.58
77.21
77.00
76.79
57.85
31.70
28.07
18.91
17.84
Br
OH
Br
^{t}BuO$_2$C
H
N
O
Me
Me
240
230
220
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)

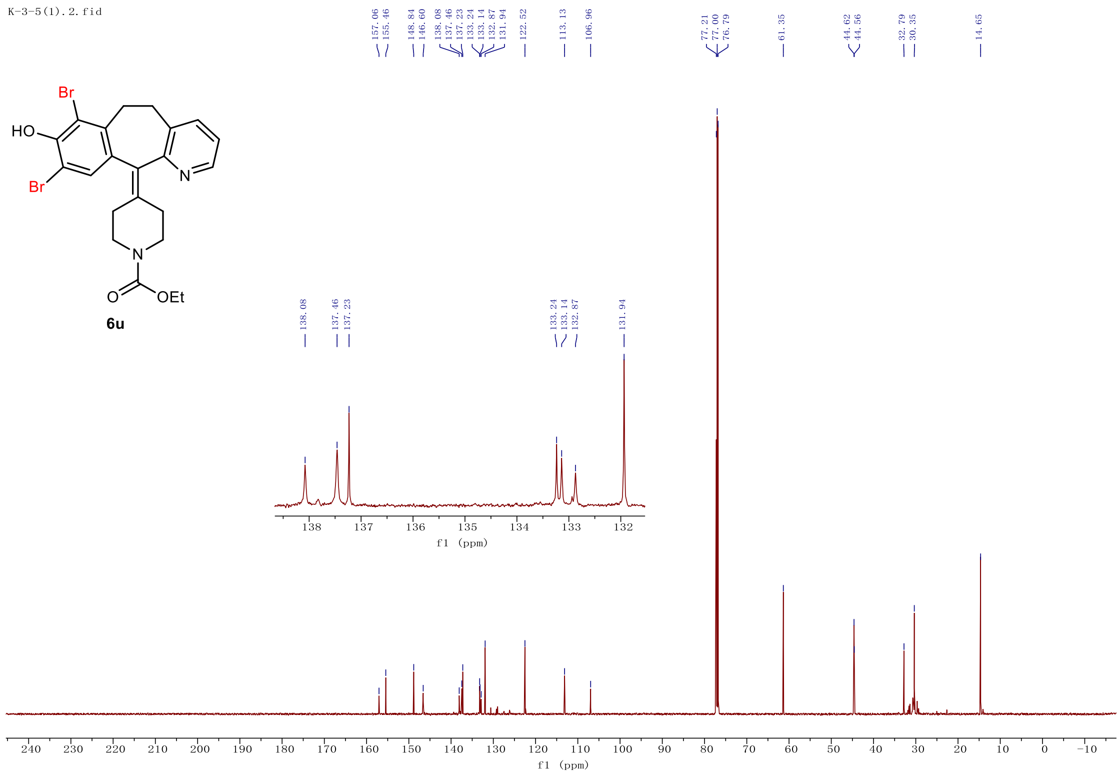
6r


K-3-4.1.fid
7.26 CDCl3
Me
Me
Me
Me
O
O
O
O
Br
OH
Br
6t
1.77
1.97
2.00
0.83
1.09
6.12
6.05
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
-0
f1 (ppm)

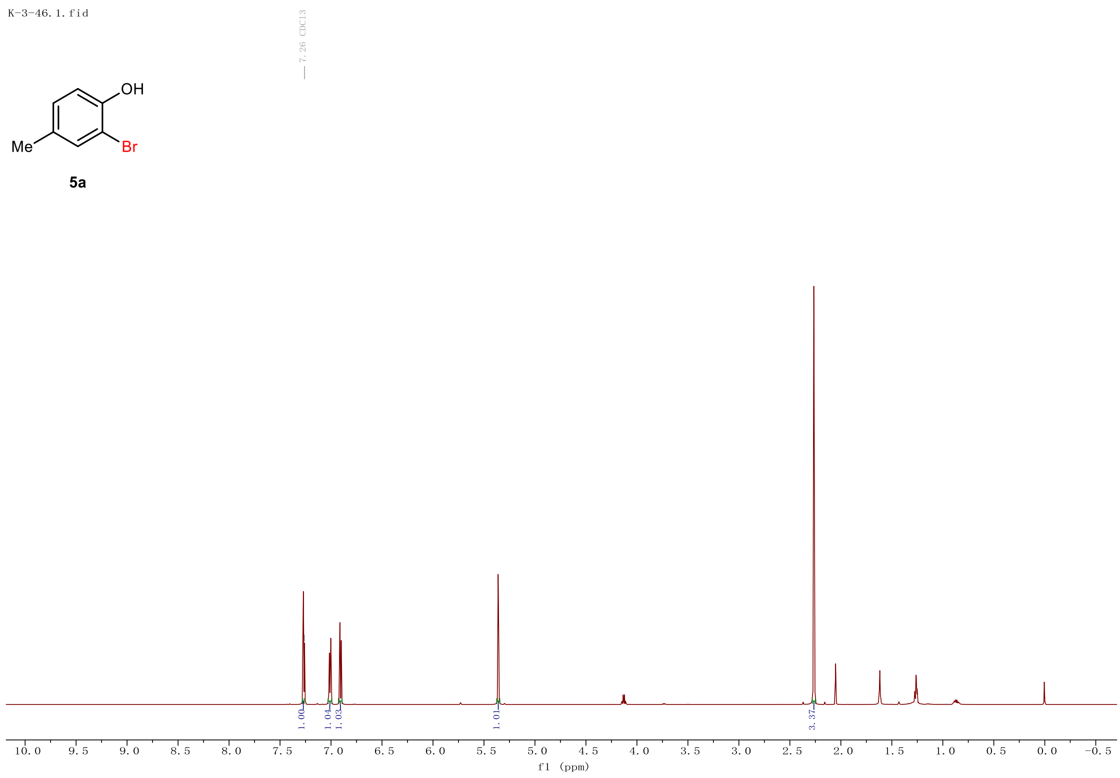

K-3-4.2.fid
191.64
173.05
159.79
152.61
133.93
132.55
131.76
129.74
117.28
109.75
79.44
77.21
77.00
76.79
69.36
25.35
21.49
Me
Me
Me
Me
O
O
O
O
Br
OH
Br
6t
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


K-3-5(1).1.fid
Br
HO
Br
N
N
O
OEt
1.00
1.00
0.88
1.14
0.68
2.18
2.08
2.02
2.14
0.94
1.14
1.08
2.05
1.11
3.78
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
-0.
f1 (ppm)

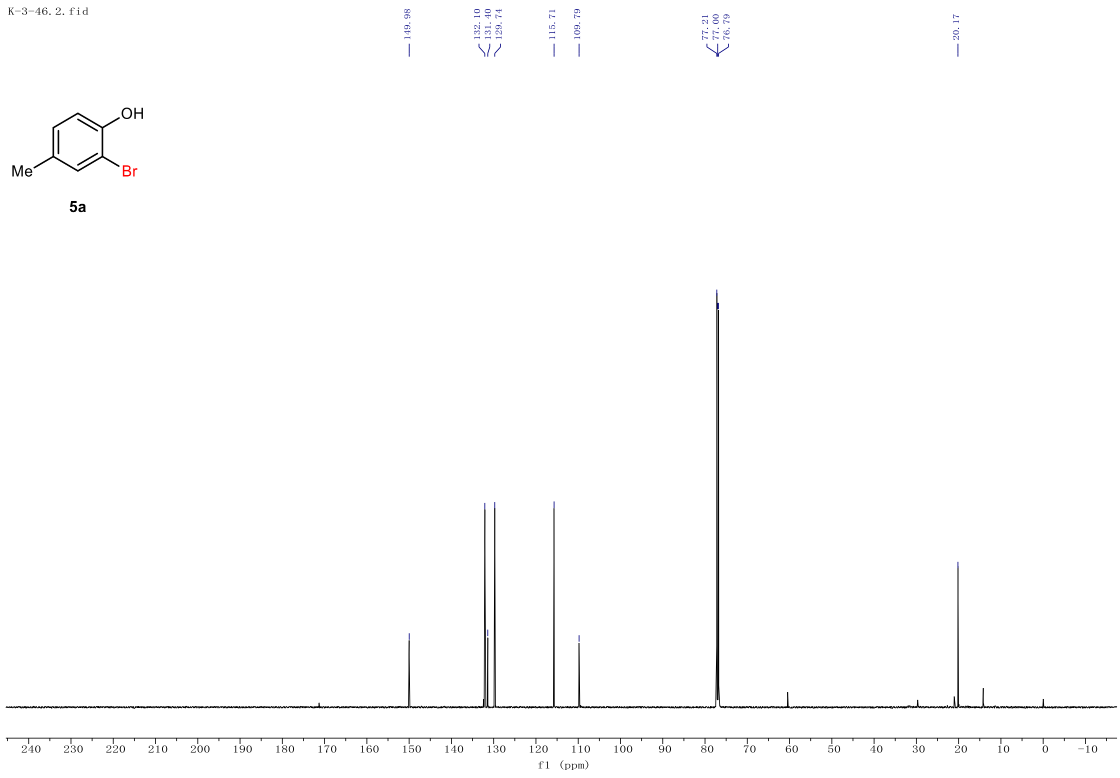
6u


K-3-5(1).2.fid
157.06
155.46
148.84
146.60
138.08
137.46
137.23
133.24
133.14
132.87
131.94
122.52
113.13
106.96
77.21
77.00
76.79
61.35
44.62
44.56
32.79
30.35
14.65
Br
HO
Br
N
N
O
OEt
138.08
137.46
137.23
133.24
133.14
132.87
131.94
138
137
136
135
134
133
132
f1 (ppm)
240
230
220
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)

6u

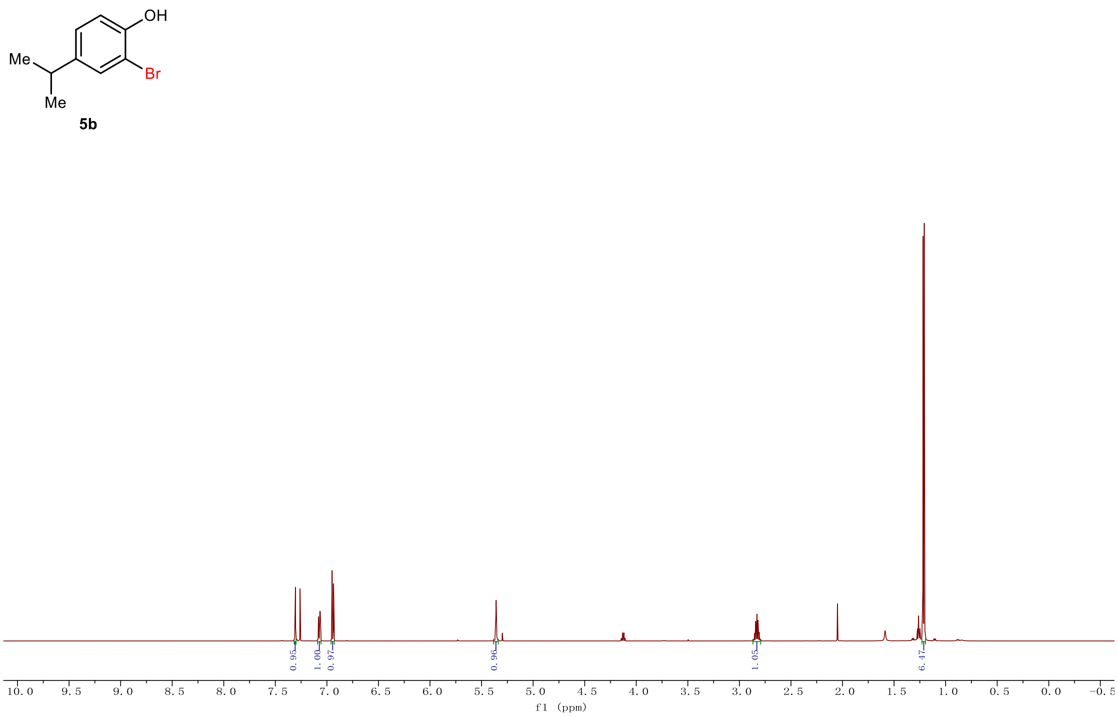

K-3-46.1.fid
7.26 CDCl3
OH
Me
Br
1.00
1.04
1.03
1.01
3.37
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

5a

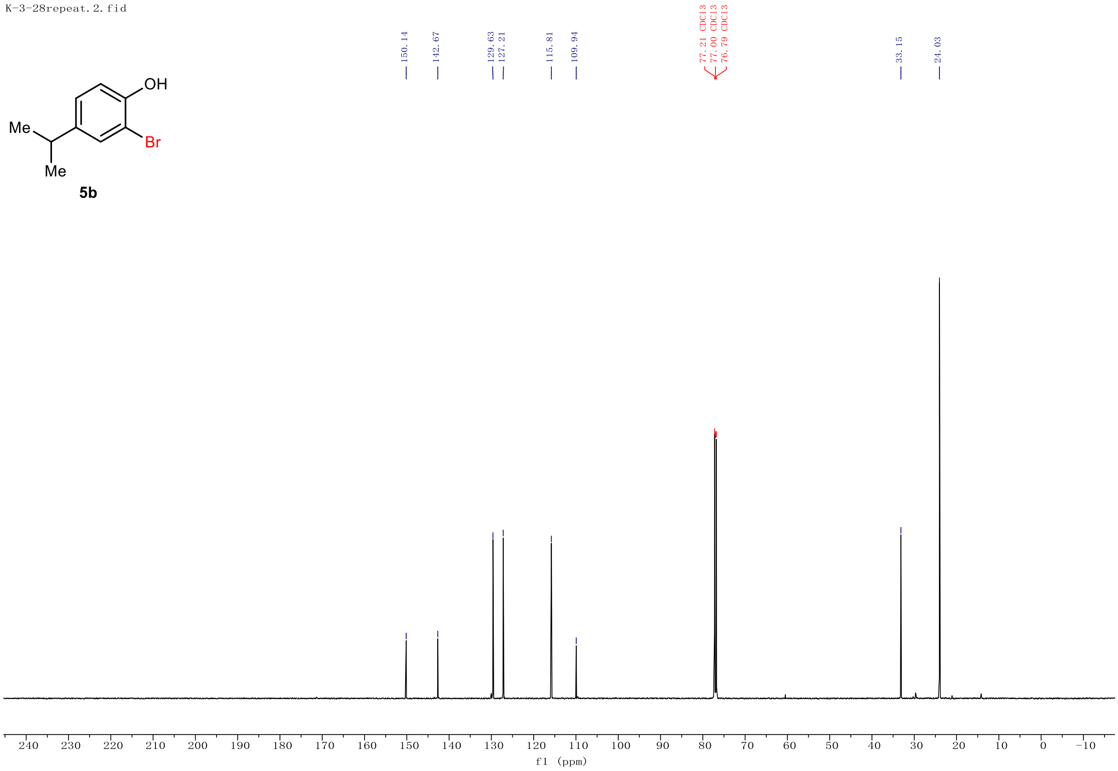

K-3-46.2.fid
149.98
132.10
131.40
129.74
115.71
109.79
77.21
77.00
76.79
20.17
OH
Me
Br
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

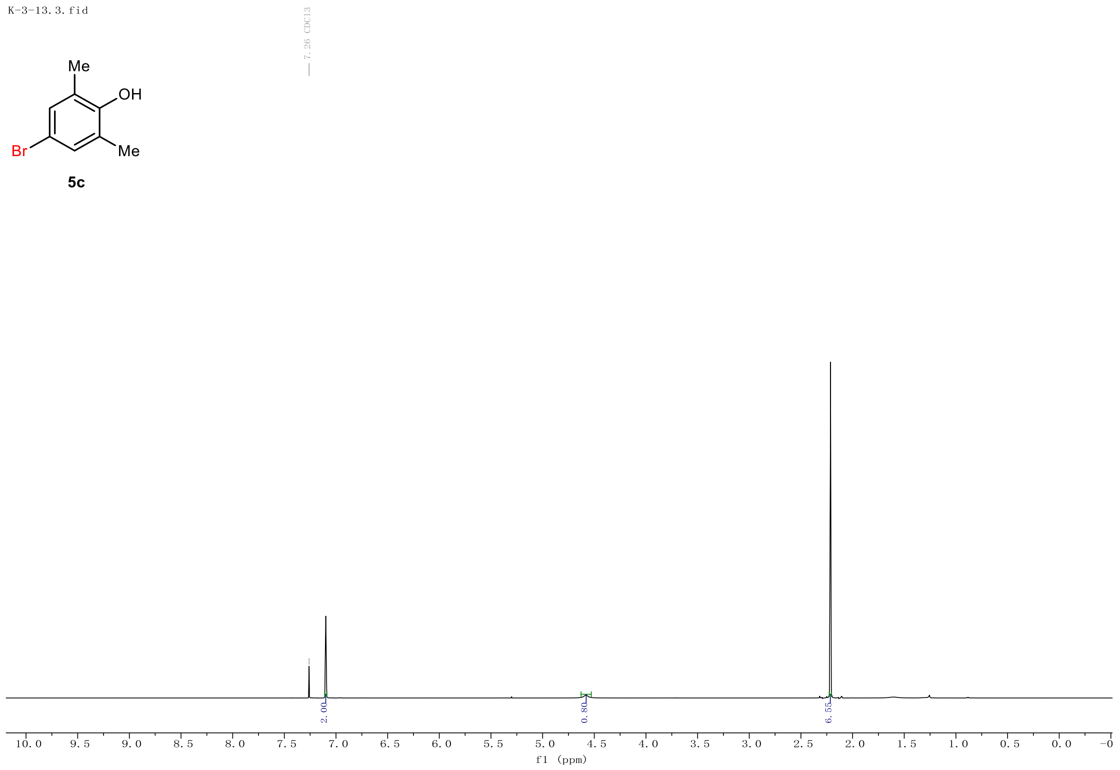
5a

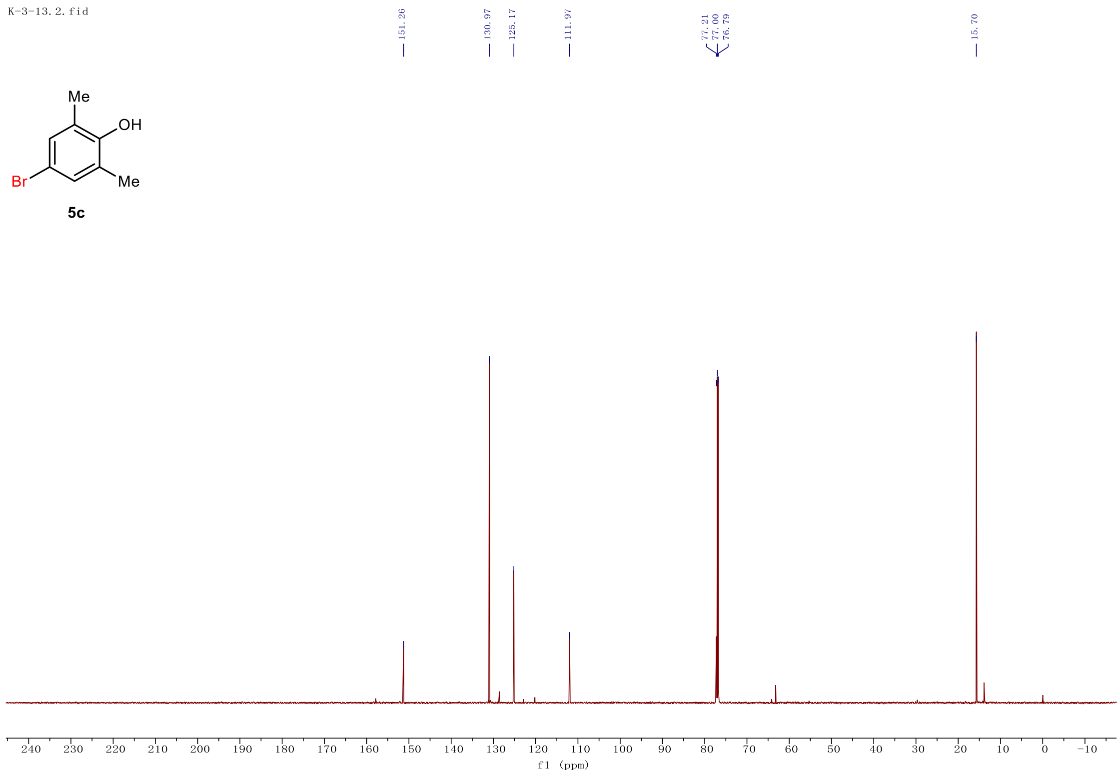
K-3-28.1.fid

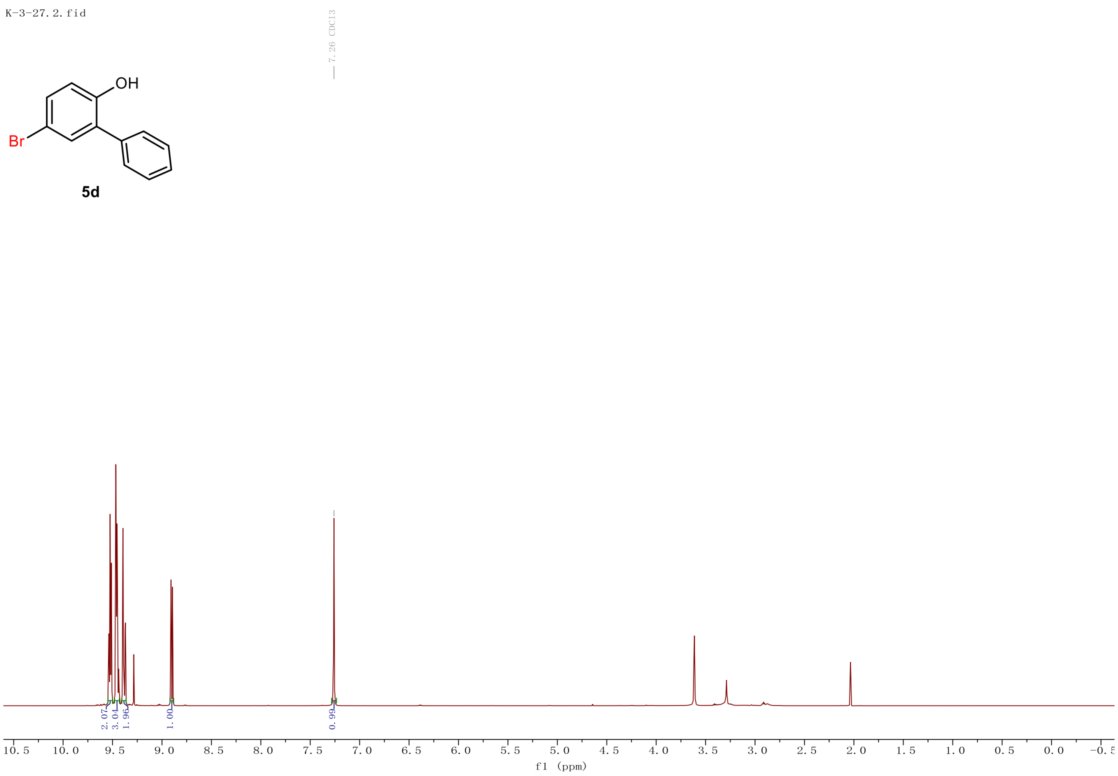


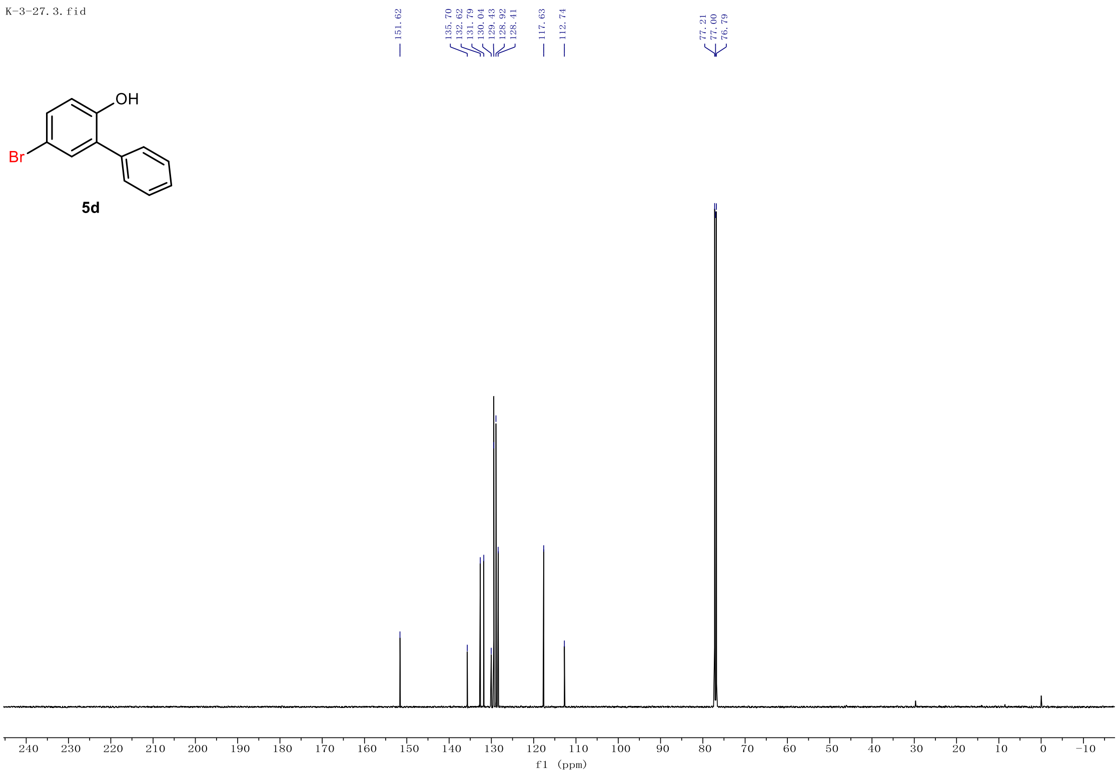
K-3-28repeat.2.fid

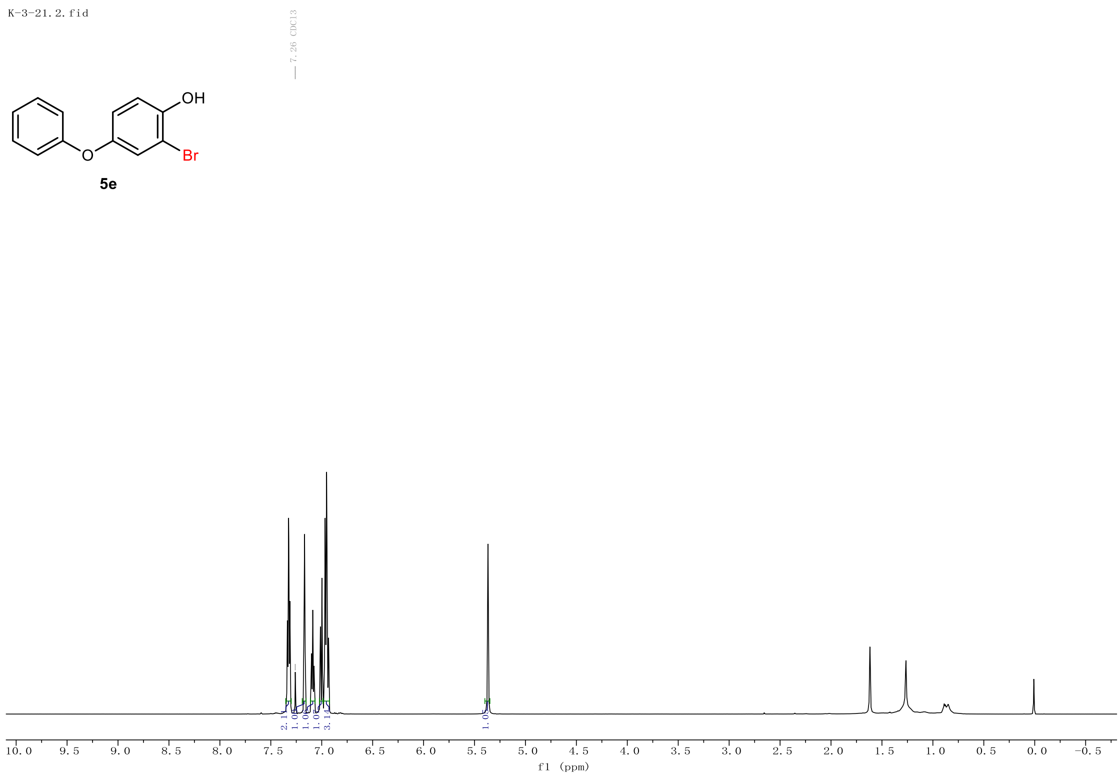



K-3-13.3.fid
7.26 CDCl3
Me
OH
Br
Me
5c
2.00
0.80
6.55
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)

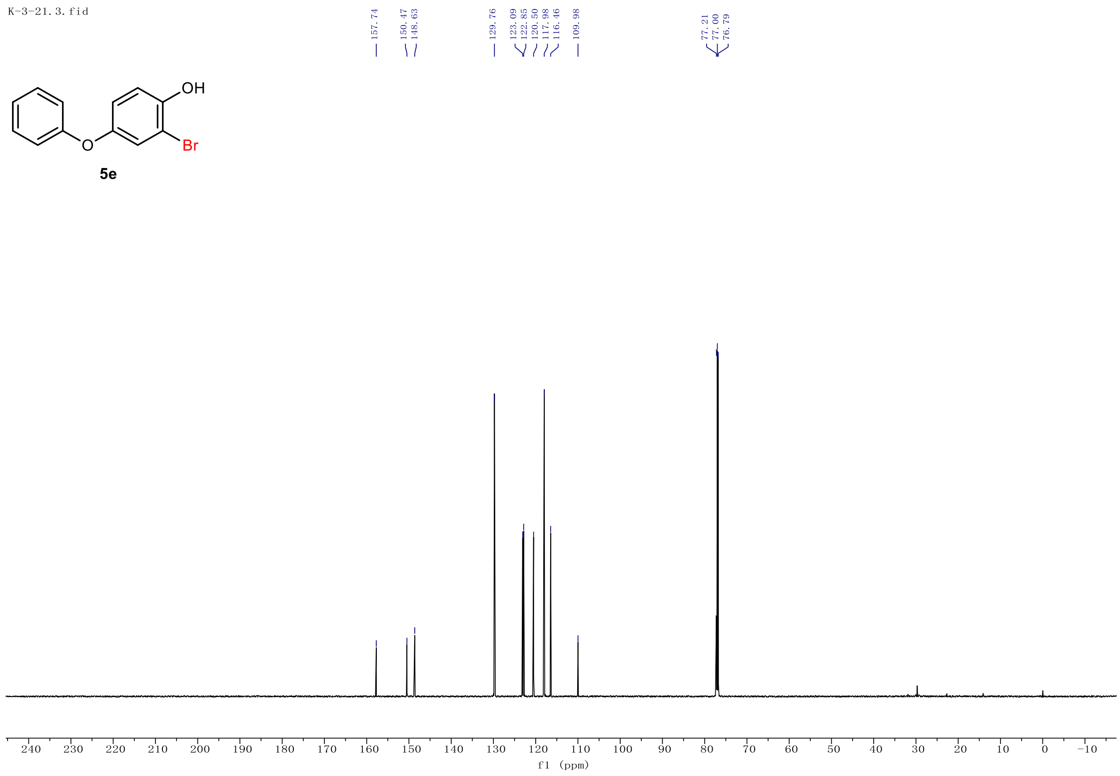

K-3-13.2.fid
151.26
130.97
125.17
111.97
77.21
77.00
76.79
15.70
Me
OH
Br
Me
5c
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


K-3-27.2.fid
7.26 CDCl3
OH
Br
5d
2.07
3.04
1.96
1.00
0.99
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
-0.5
f1 (ppm)

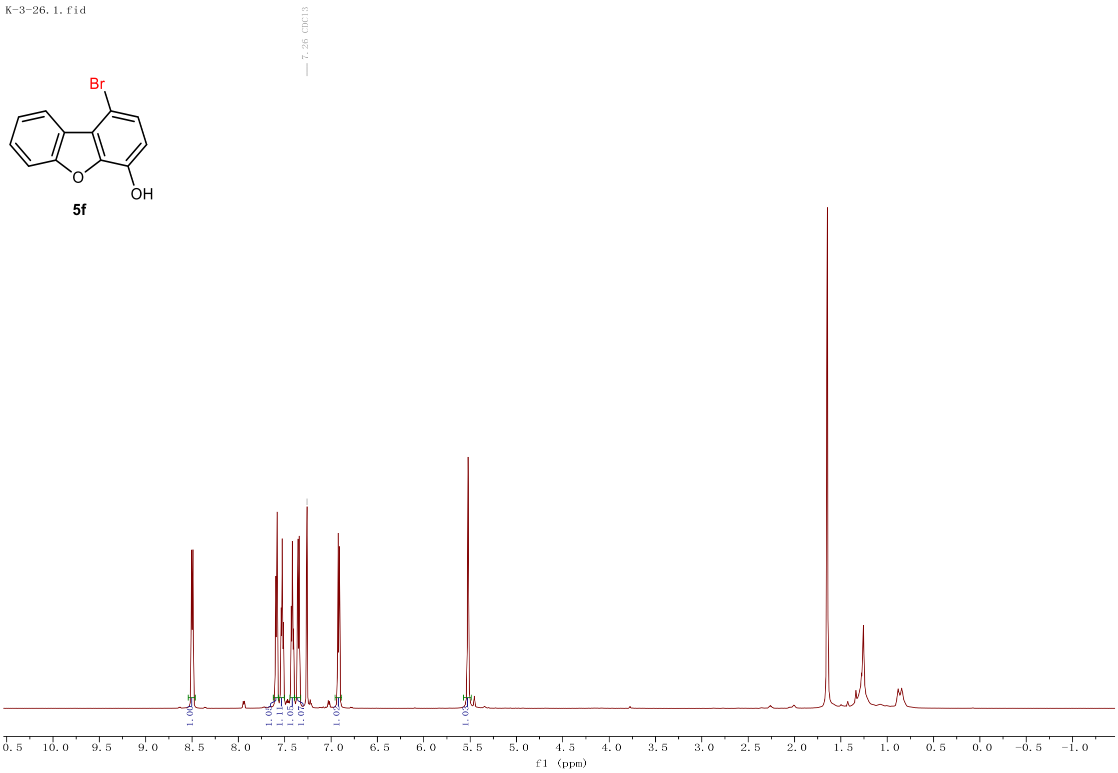

K-3-27.3.fid
151.62
135.70
132.62
131.79
130.04
129.43
128.92
128.41
117.63
112.74
77.21
77.00
76.79
OH
Br
5d
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

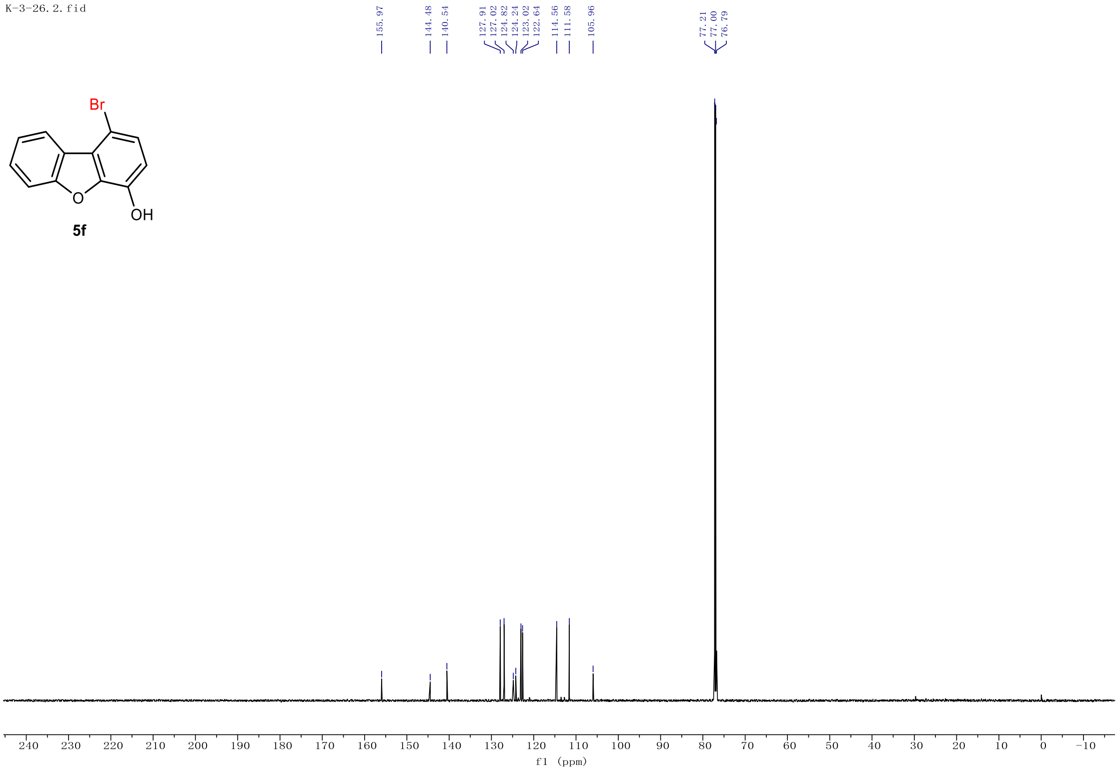

K-3-21.2.fid
7.26 CDCl3
OH
O
Br
2.11
1.06
1.06
1.07
3.14
1.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

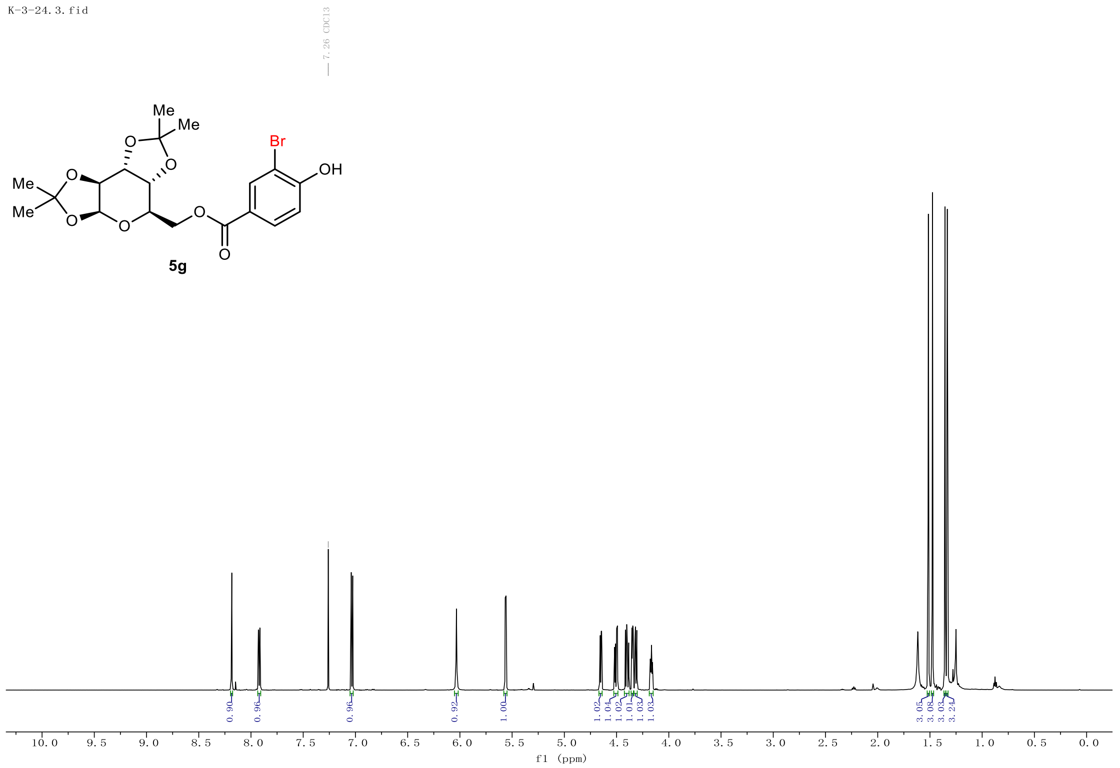
5e

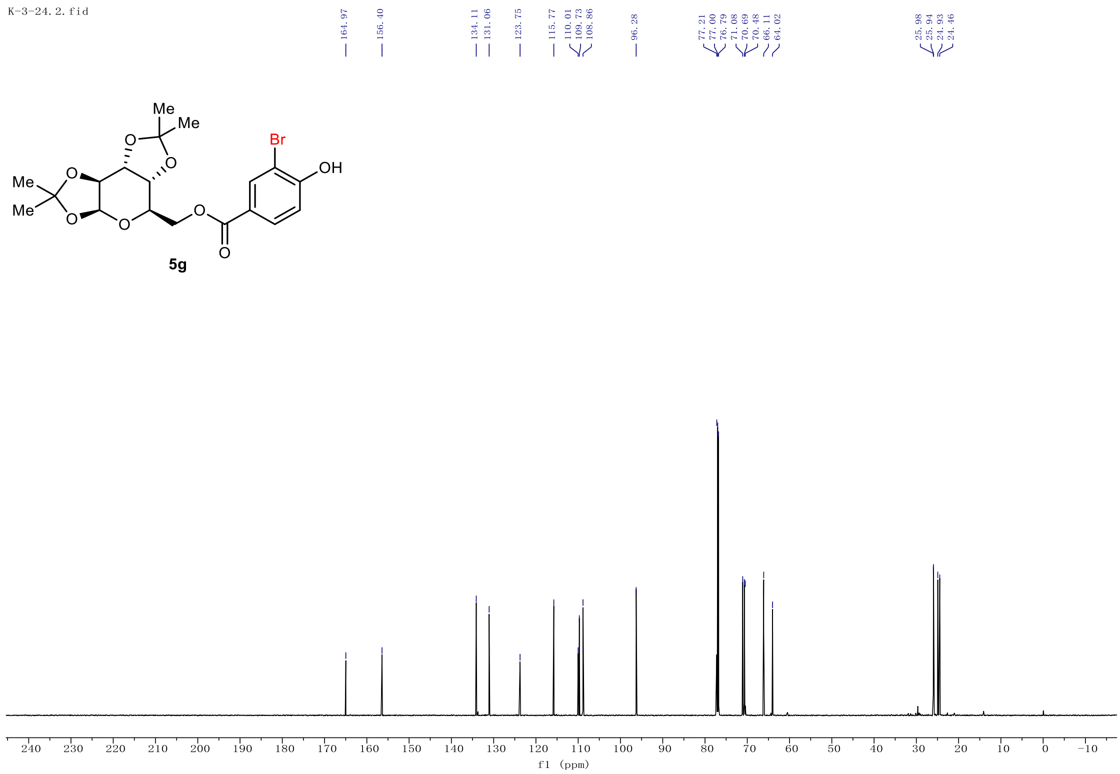

K-3-21.3.fid
157.74
150.47
148.63
129.76
123.09
122.85
120.50
117.98
116.46
109.98
77.21
77.00
76.79
OH
O
Br
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

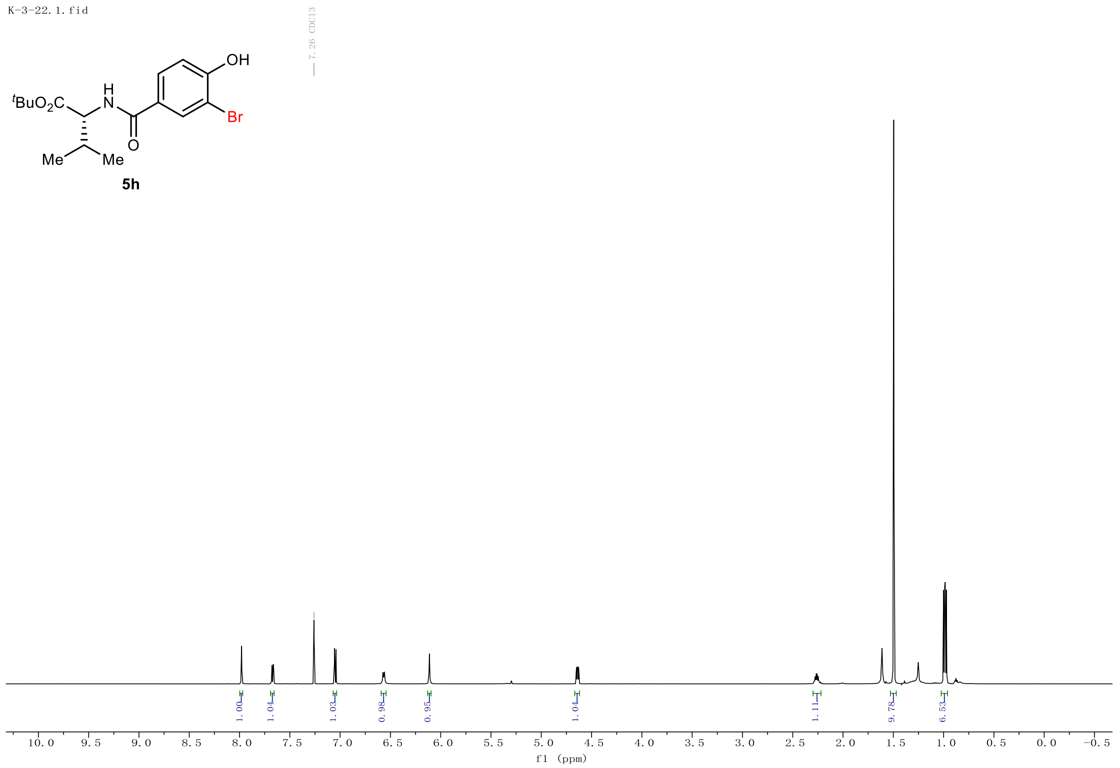
5e

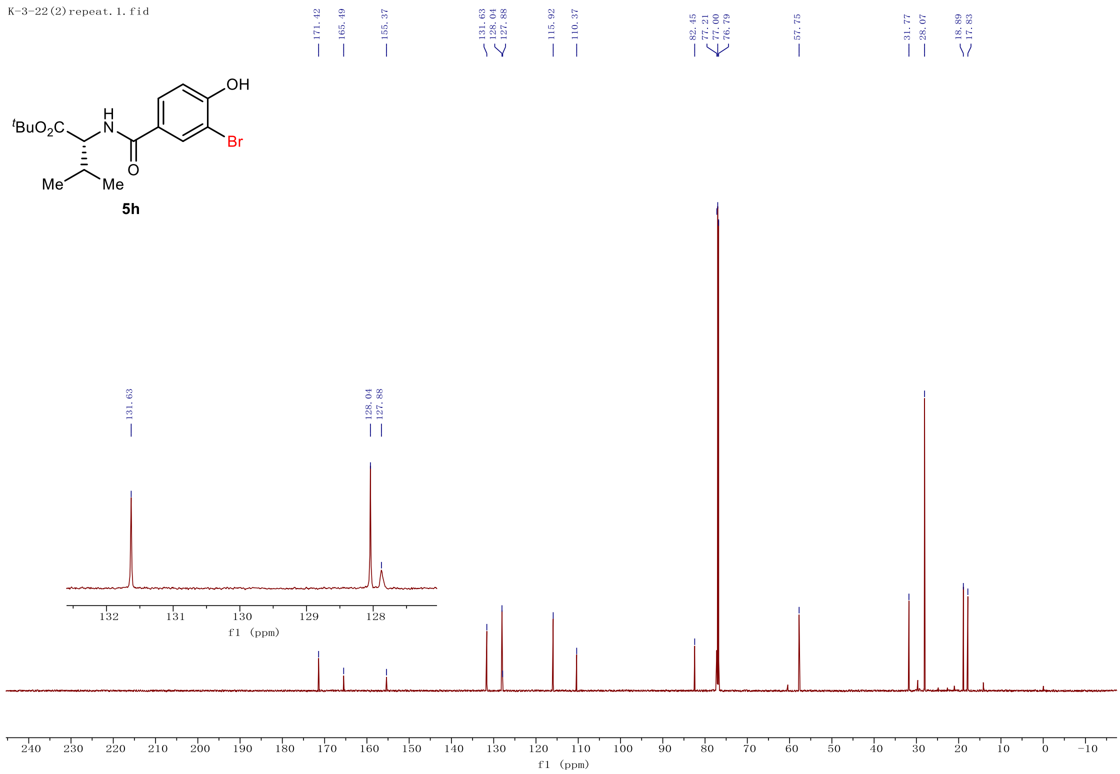

K-3-26.1.fid
7.26 CDCl3
Br
O
OH
5f
1.00
1.03
1.11
1.05
1.07
1.02
1.03
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)


K-3-26.2.fid
155.97
144.48
140.54
127.91
127.02
124.82
124.24
123.02
122.64
114.56
111.58
105.96
77.21
77.00
76.79
Br
O
OH
5f
240
230
220
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)

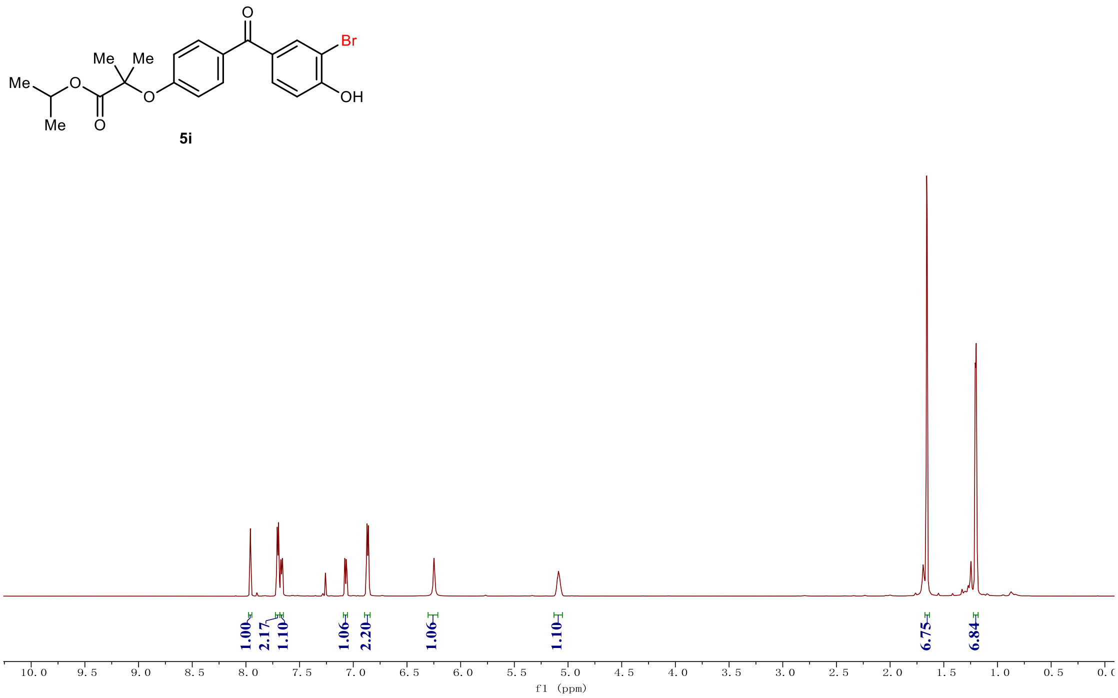

K-3-24.3.fid
7.26 CDCl3
Me
Me
Br
OH
Me
Me
O
O
O
O
O
O
O
5g
0.90
0.96
0.96
0.92
1.00
1.02
1.04
1.02
1.01
1.03
1.03
3.05
3.08
3.03
3.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


K-3-24.2.fid
164.97
156.40
134.11
131.06
123.75
115.77
110.01
109.73
108.86
96.28
77.21
77.00
76.79
71.08
70.69
70.48
66.11
64.02
25.98
25.94
24.93
24.46
Me
Me
Br
OH
Me
Me
O
O
O
O
O
O
O
5g
240
230
220
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)


K-3-22.1.fid
7.26 CDCl3
OH
Br
H
N
O
^{t}BuO$_2$C
Me
Me
5h
1.00
1.04
1.03
0.98
0.95
1.04
1.11
9.78
6.53
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
-0.5
f1 (ppm)

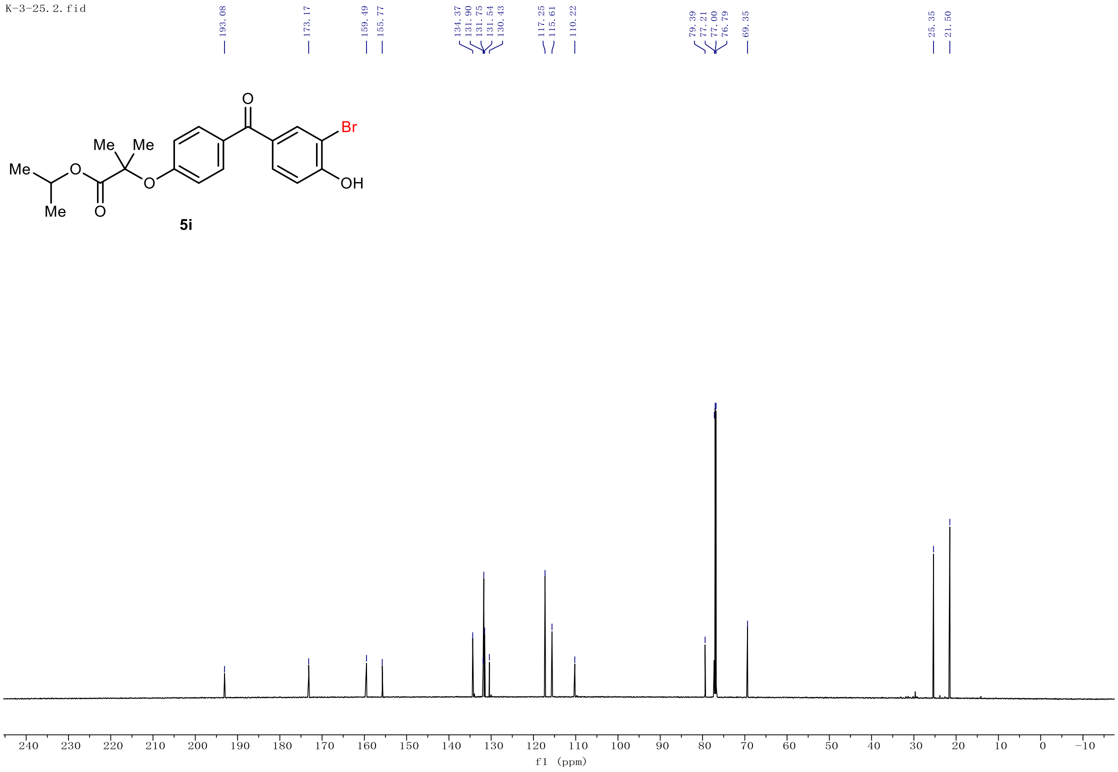

K-3-22(2)repeat.1.fid
171.42
165.49
155.37
131.63
128.04
127.88
115.92
110.37
82.45
77.21
77.00
76.79
57.75
31.77
28.07
18.89
17.83
OH
Br
H
N
O
^{t}BuO$_2$C
Me
Me
5h
131.63
128.04
127.88
132
131
130
129
128
f1 (ppm)
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

K-3-25.1.fid

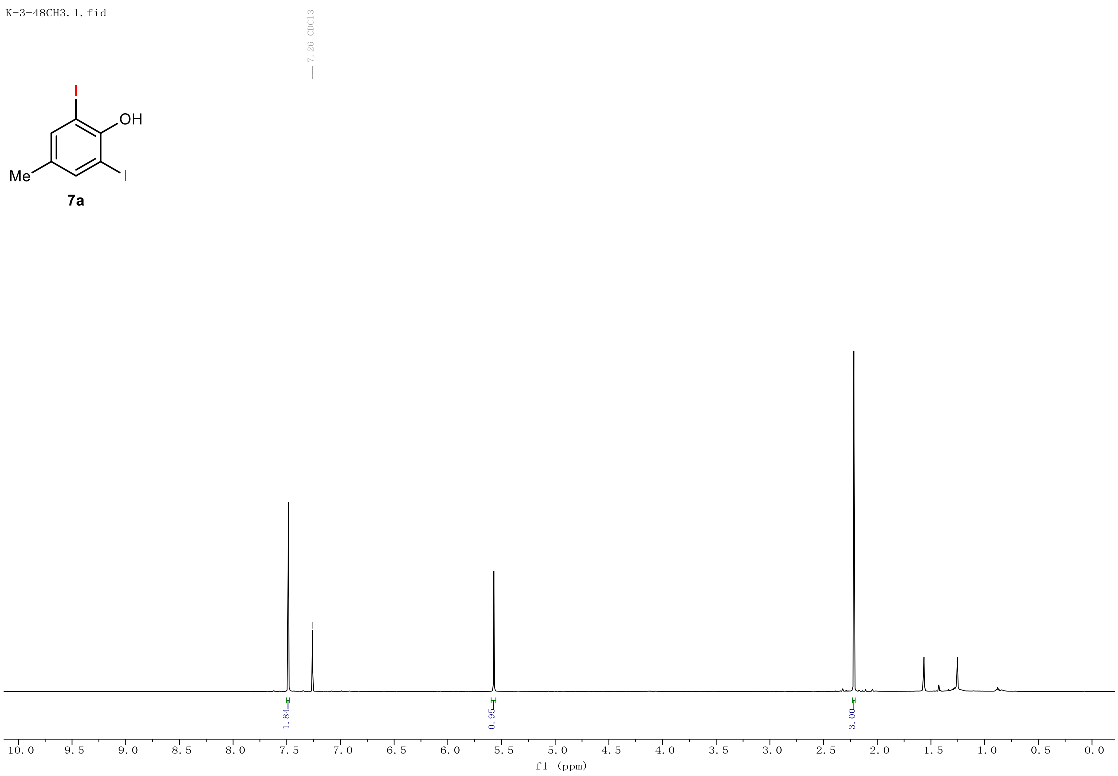


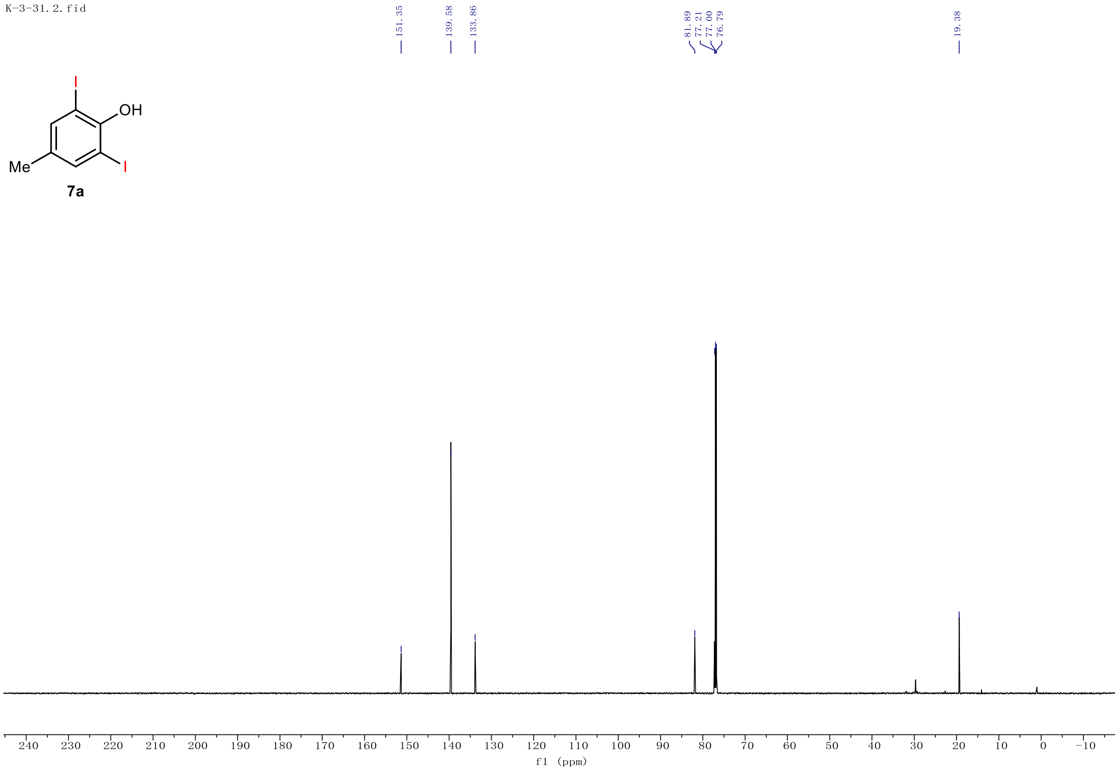
5i

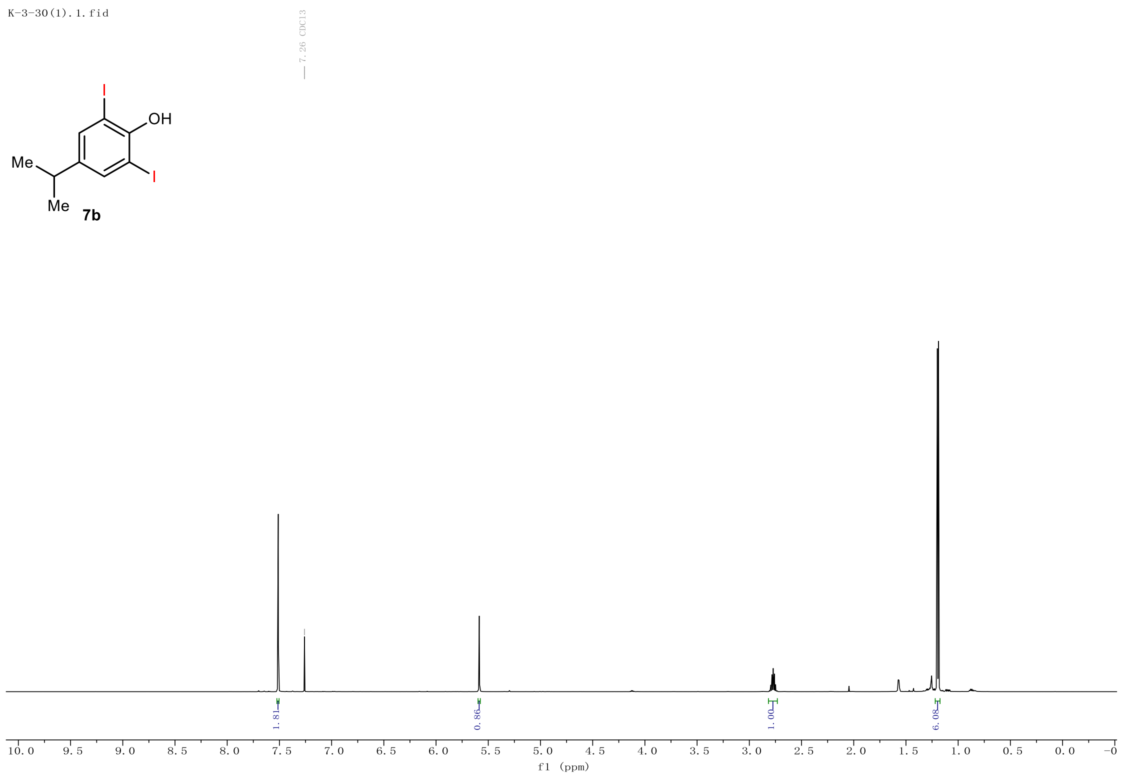
K-3-25.2.fid



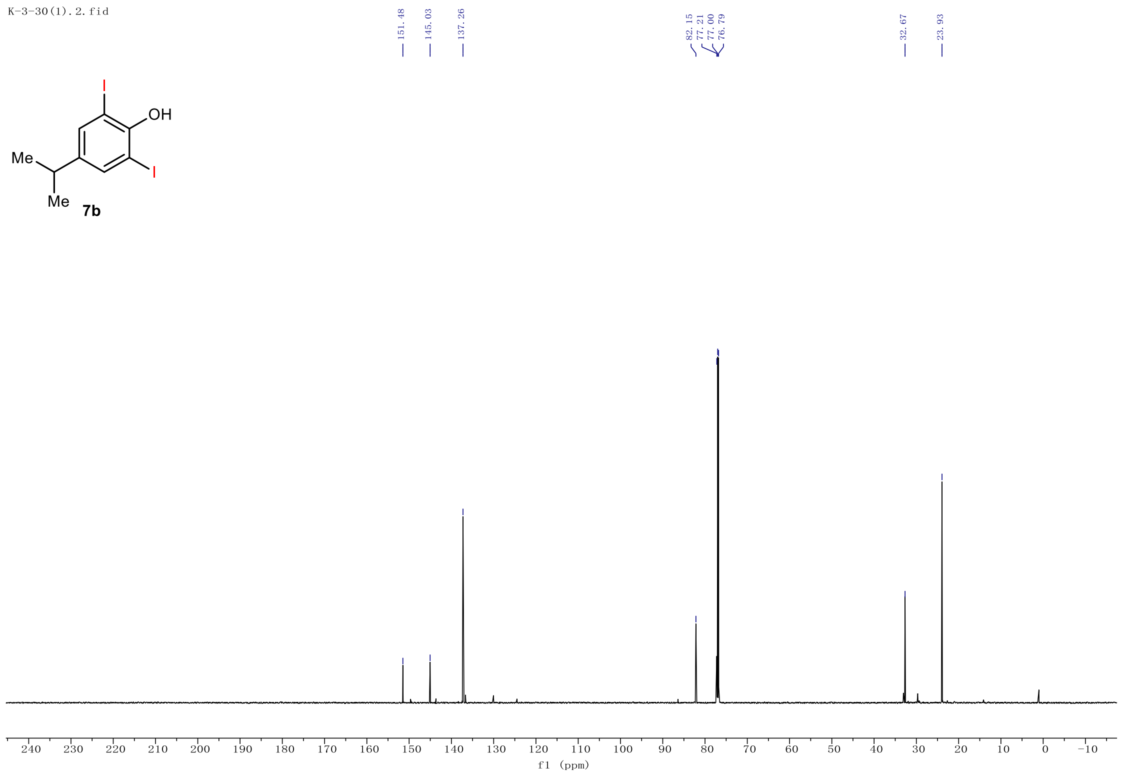
5i


K-3-48CH3.1.fid
7.26 CDCl3
I
OH
Me
I
7a
1.84
0.95
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
0.0
f1 (ppm)

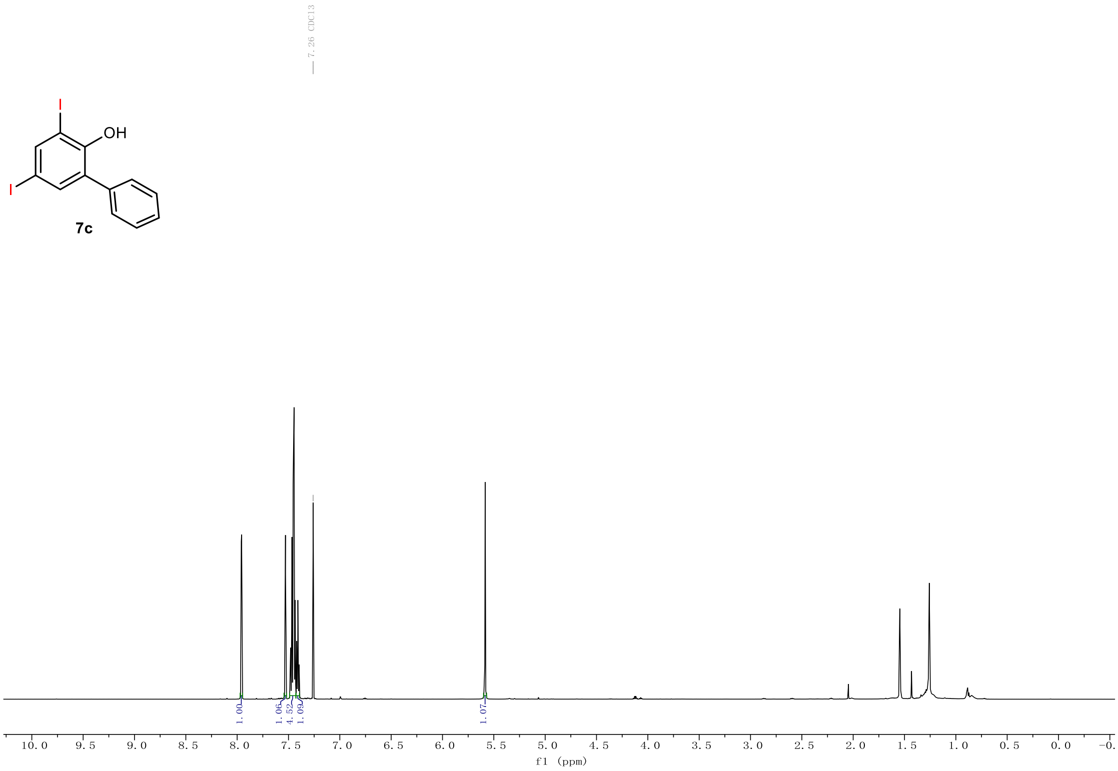

K-3-31.2.fid
151.35
139.58
133.86
81.89
77.21
77.00
76.79
19.38
I
OH
Me
I
7a
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

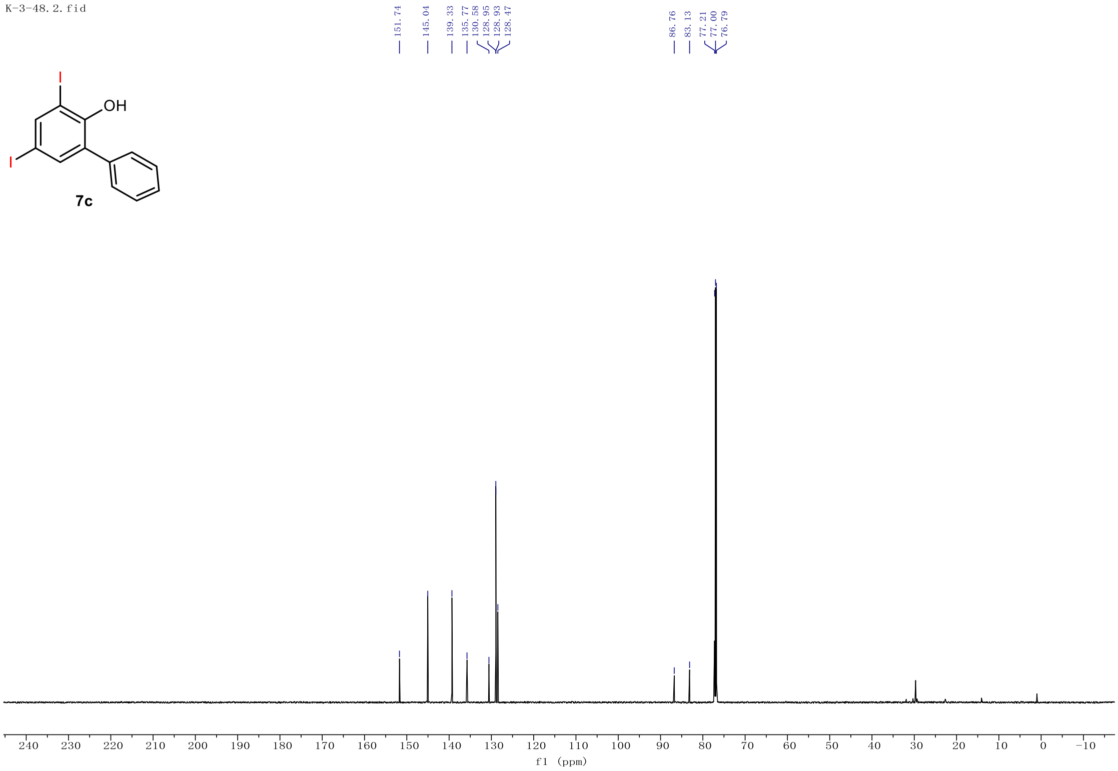

K-3-30(1).1.fid
7.26 CDCl3
OH
I
I
Me
Me
1.81
0.86
1.00
6.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)

7b

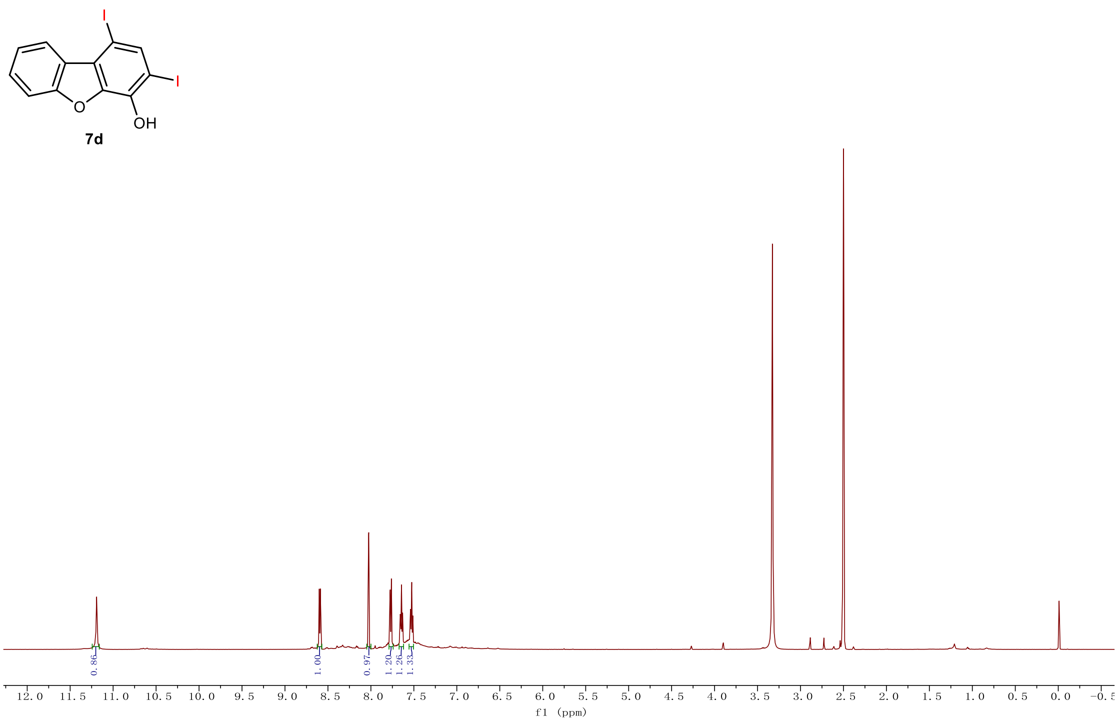

K-3-30(1).2.fid
151.48
145.03
137.26
82.15
77.21
77.00
76.79
32.67
23.93
OH
I
I
Me
Me
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

7b


7.26 CDCl3
I
OH
I
7c
1.00
1.06
4.52
1.09
1.07
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
-0.
f1 (ppm)

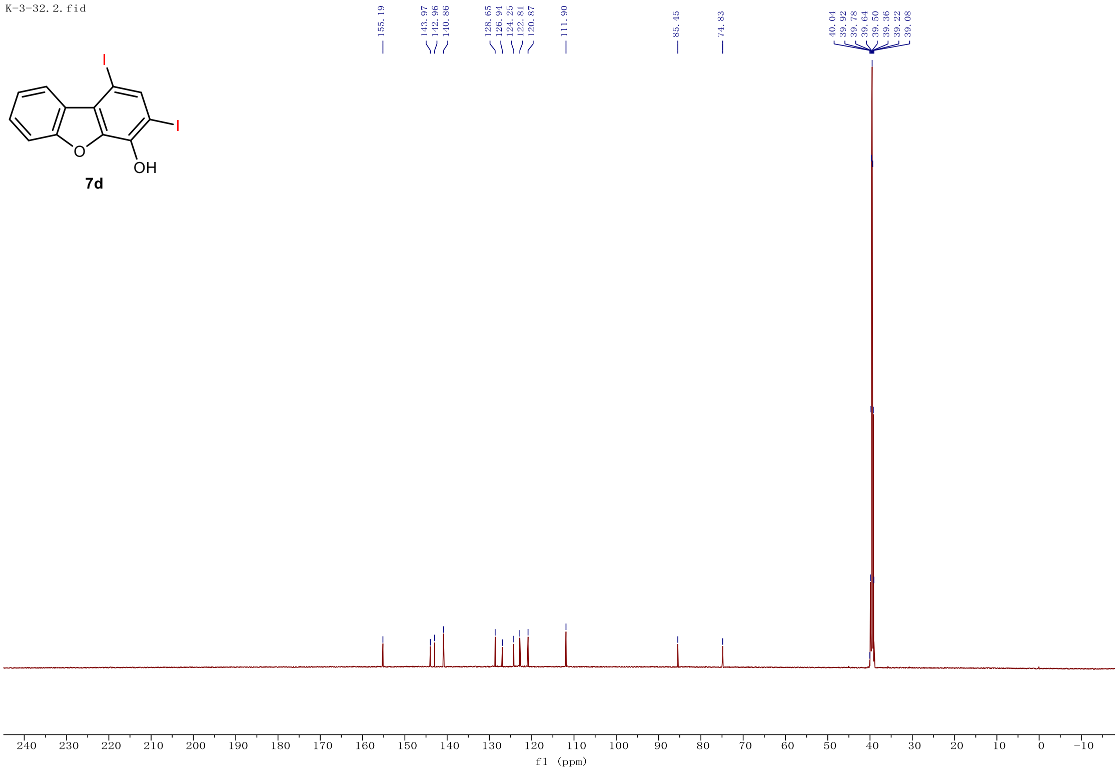

K-3-48.2.fid
151.74
145.04
139.33
135.77
130.58
128.95
128.93
128.47
86.76
83.13
77.21
77.00
76.79
I
OH
I
7c
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

K-3-32.1.fid

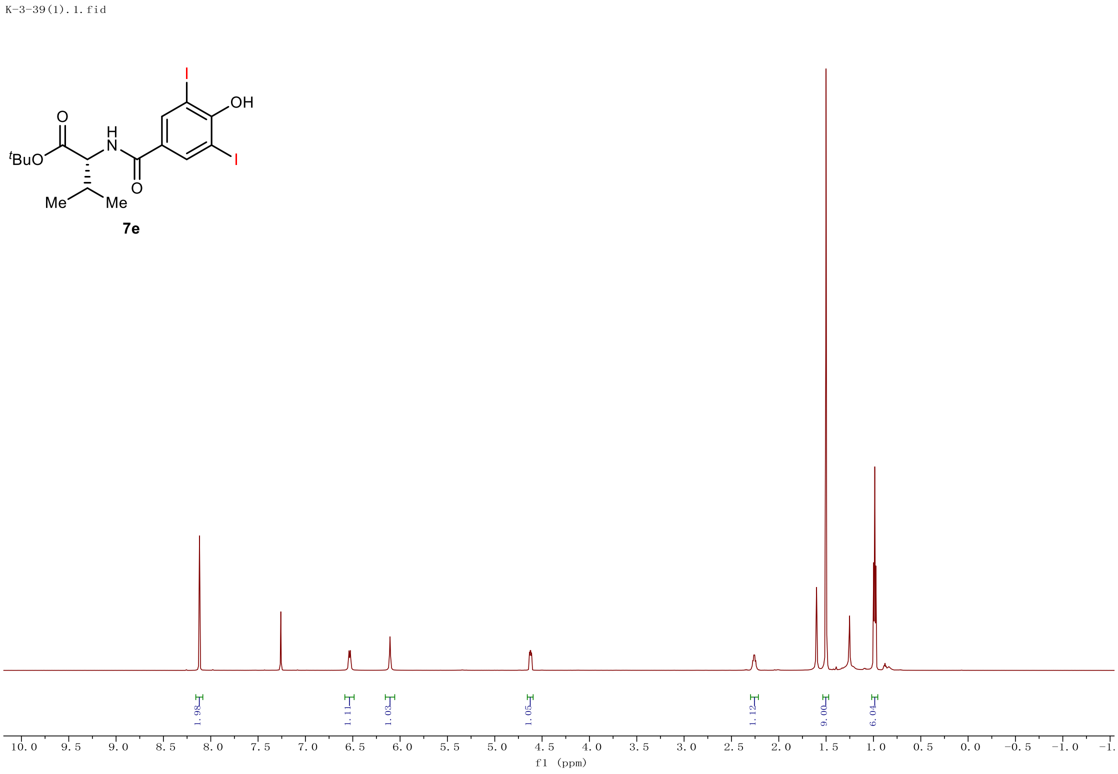


7d

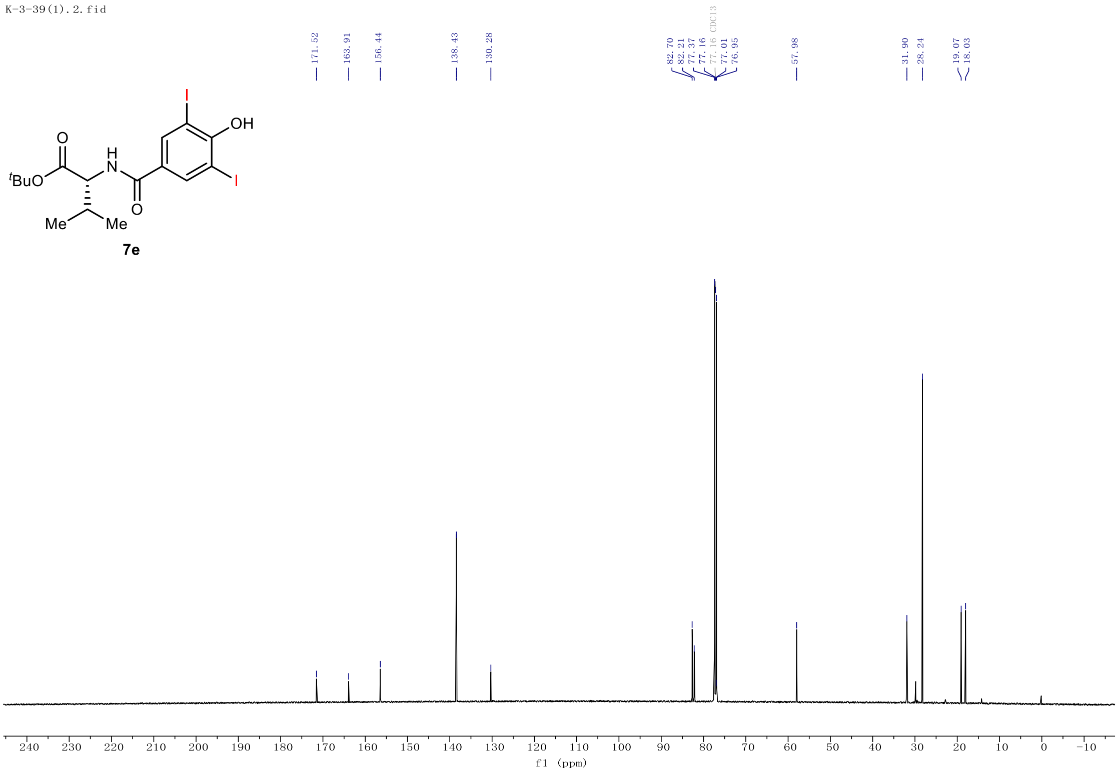
K-3-32.2.fid



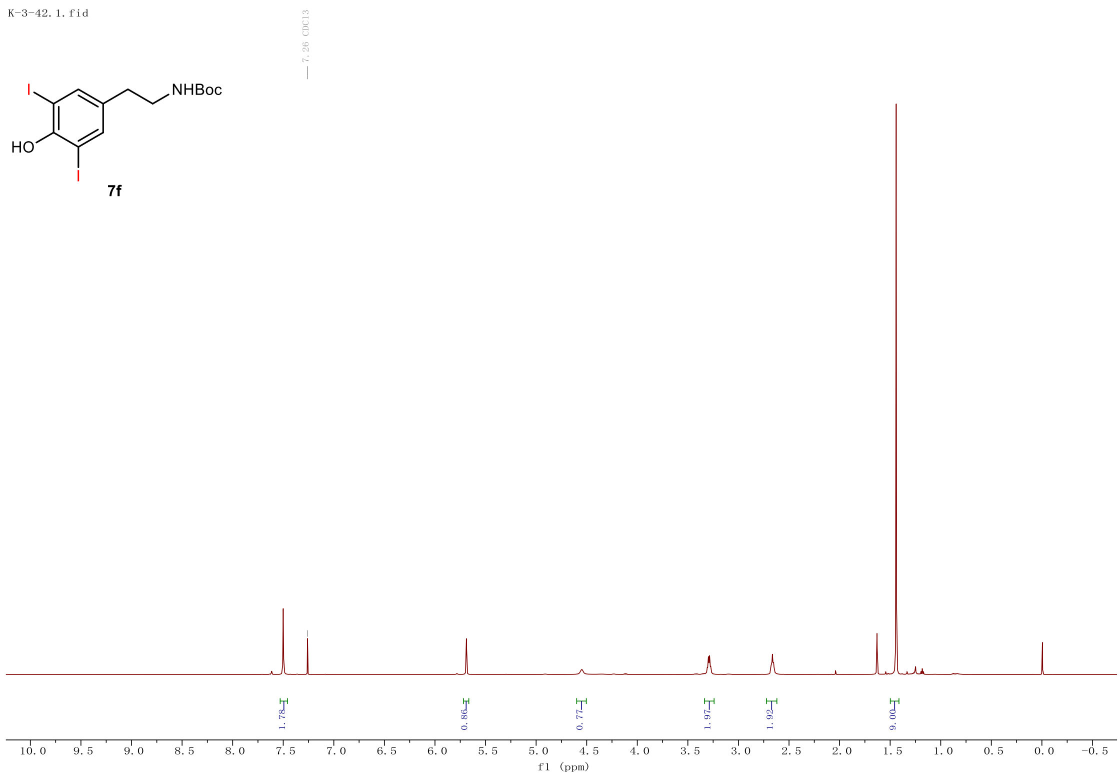
7d


K-3-39(1).1.fid
I
OH
I
O
H
N
tBuO
O
Me
Me
1.98
1.11
1.03
1.05
1.12
9.00
6.04
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
-0.5
-1.0
f1 (ppm)

7e


K-3-39(1).2.fid
171.52
163.91
156.44
138.43
130.28
82.70
82.21
77.37
77.16
77.16 CDCl3
77.01
76.95
57.98
31.90
28.24
19.07
18.63
I
OH
I
O
H
N
tBuO
O
Me
Me
240
230
220
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)

7e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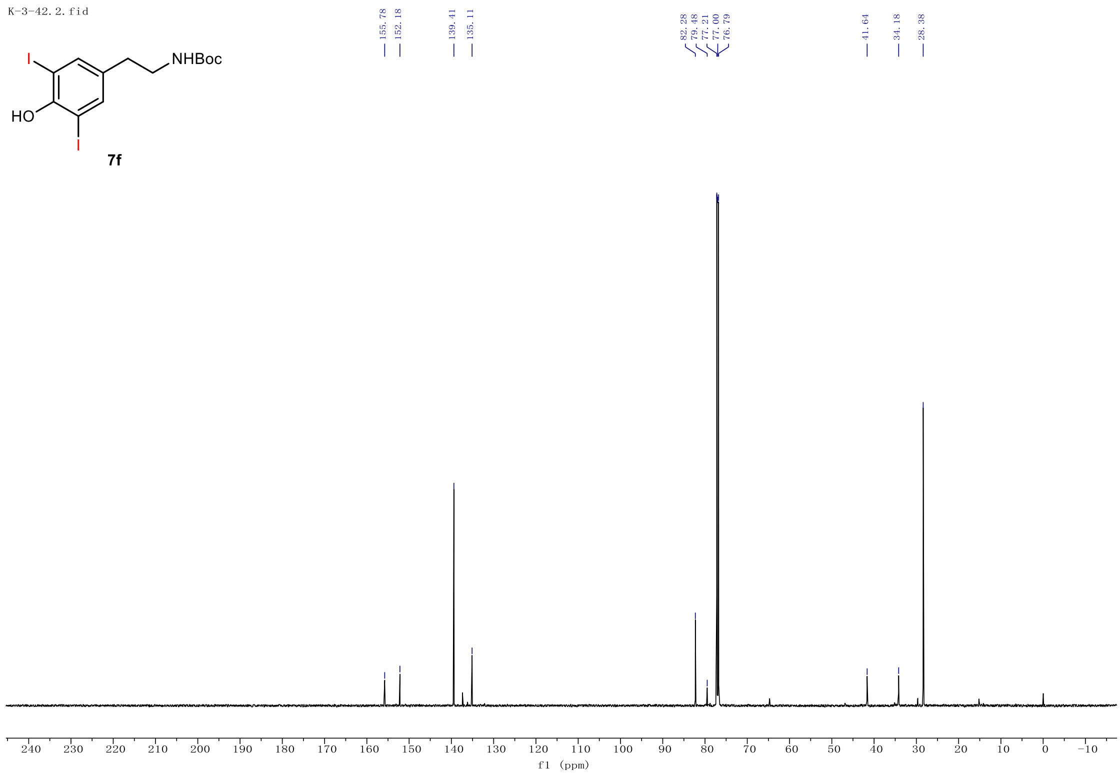
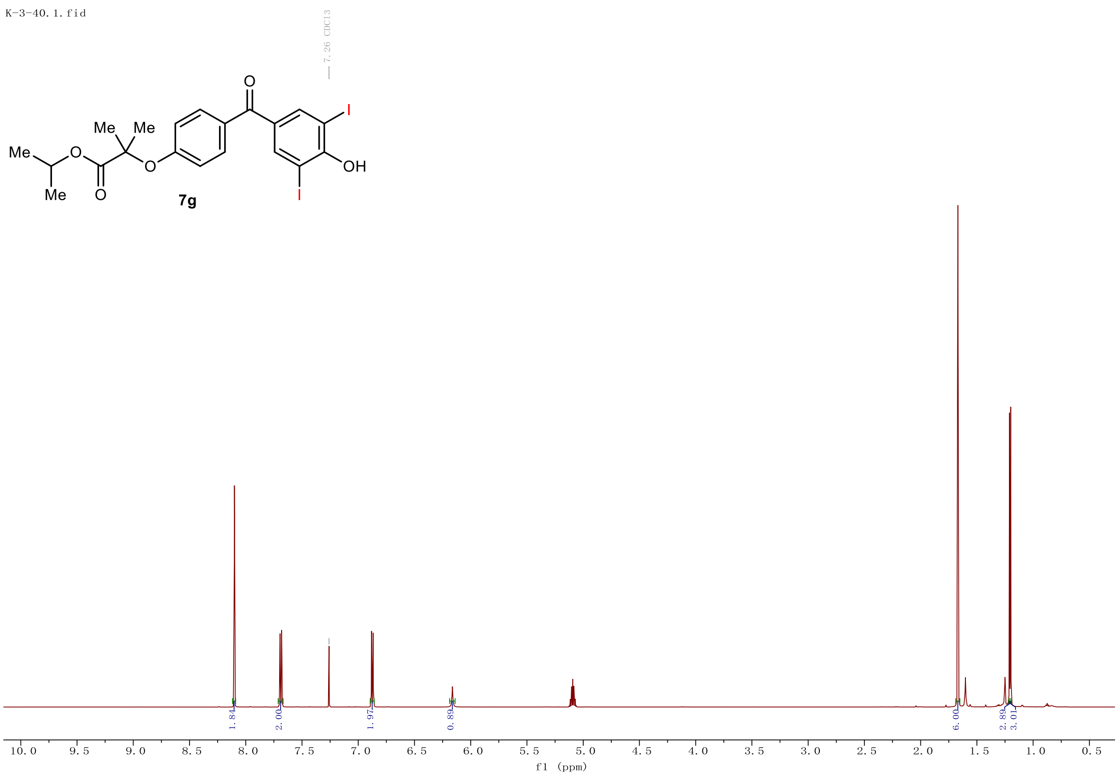
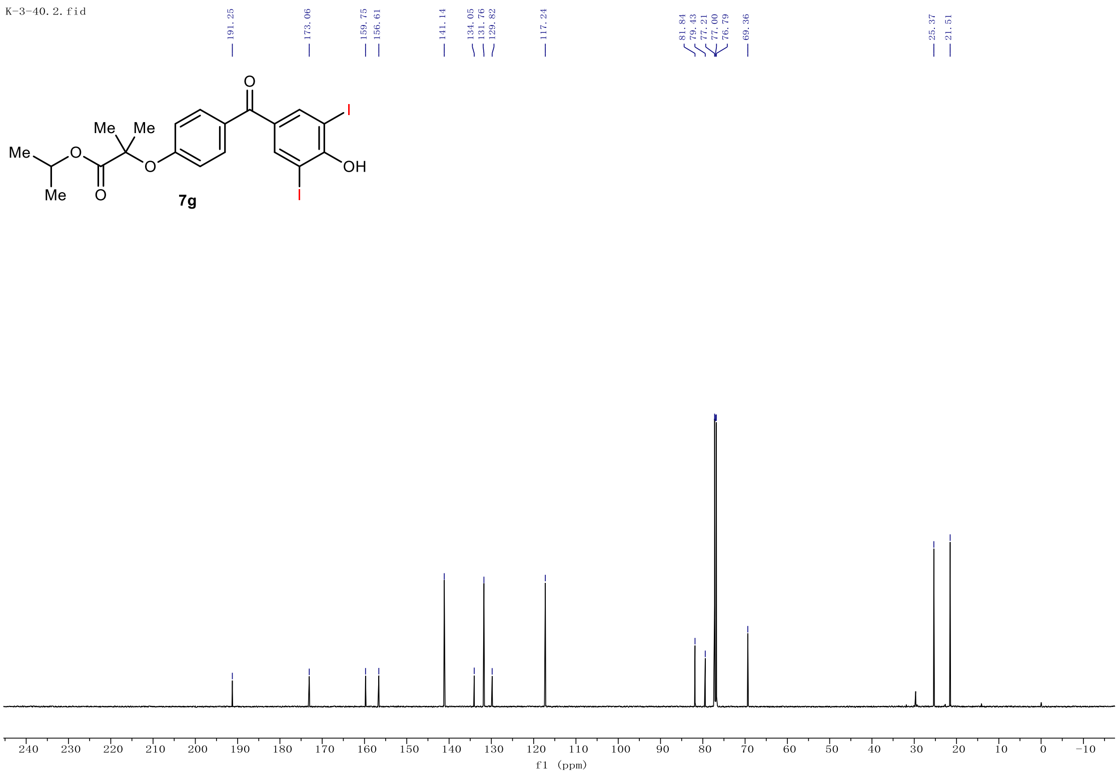
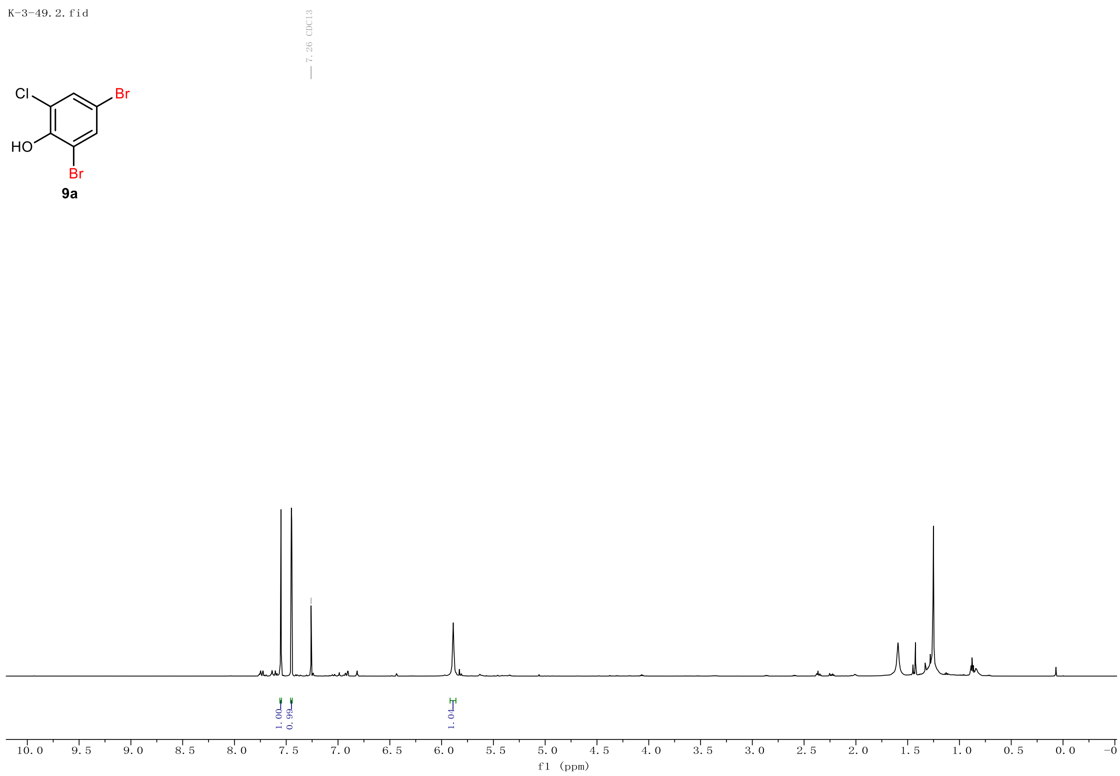
7.26 CDCl3
NHBoc
HO
I
I
7f
1.78
0.86
0.77
1.97
1.92
9.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

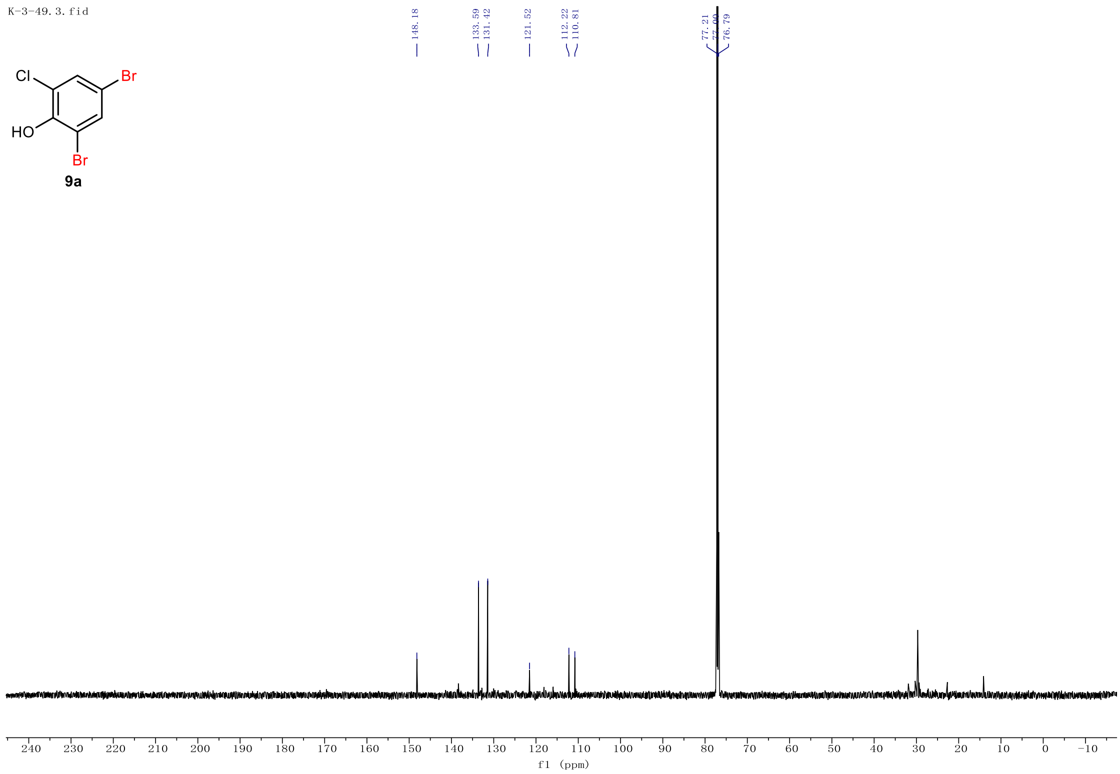

K-3-42.2.fid
155.78
152.18
139.41
135.11
82.28
79.48
77.21
77.00
76.79
41.64
34.18
28.38
NHBoc
HO
I
I
7f
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


K-3-40.1.fid
7.26 CDCl3
Me
Me
Me
Me
O
O
O
O
I
OH
I
7g
1.84
2.00
1.97
0.89
6.00
2.89
3.01
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)

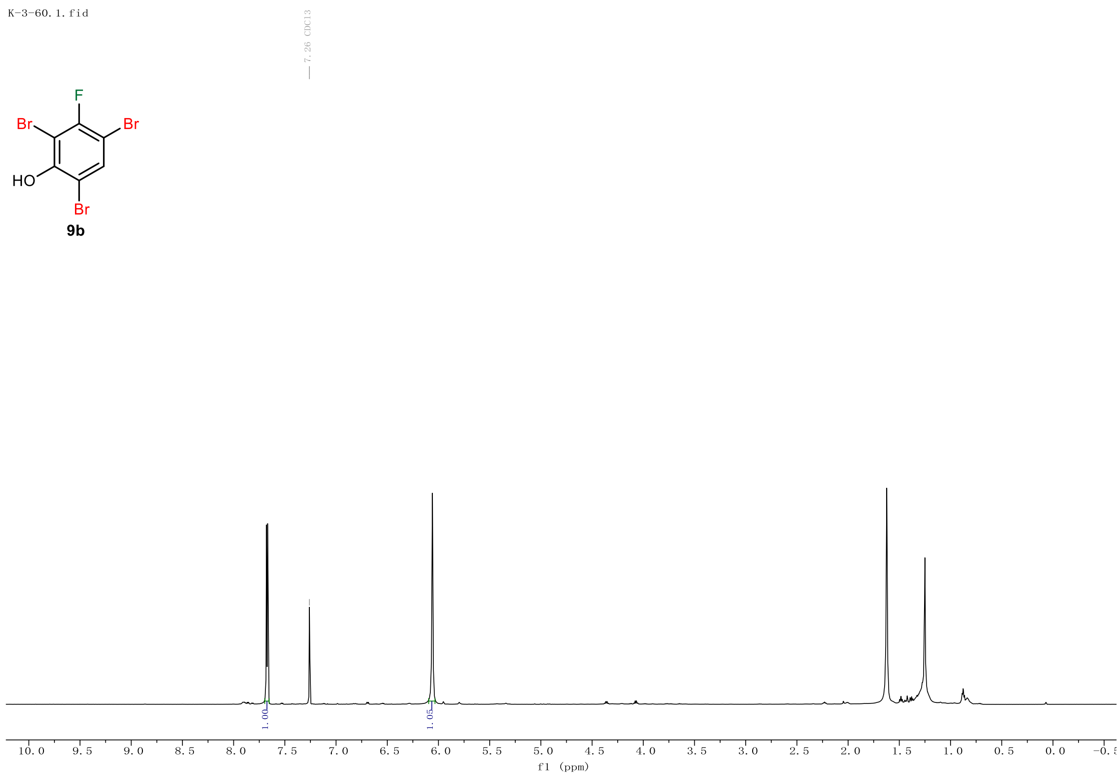

K-3-40.2.fid
191.25
173.06
159.75
156.61
141.14
134.05
131.76
129.82
117.24
81.84
79.43
77.21
77.00
76.79
69.36
25.37
21.51
Me
Me
Me
Me
O
O
O
O
I
OH
I
7g
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

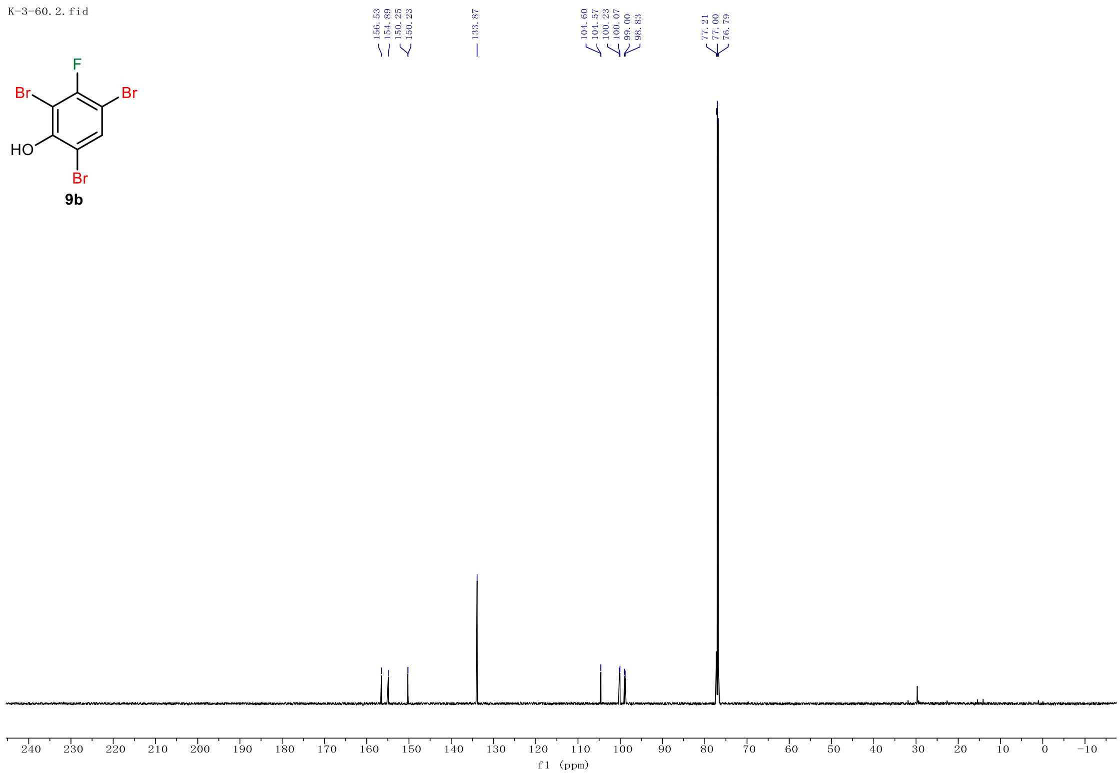

K-3-49.2.fid
7.26 CDCl3
Cl
Br
HO
Br
1.00
0.99
1.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

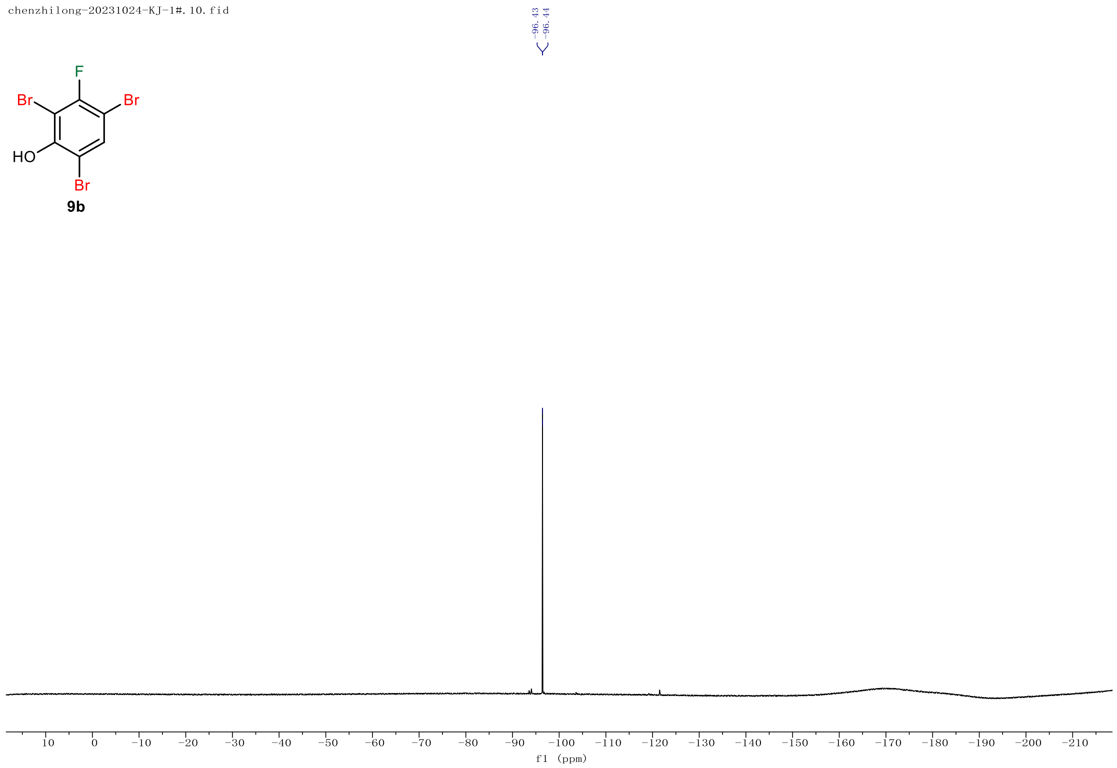
9a

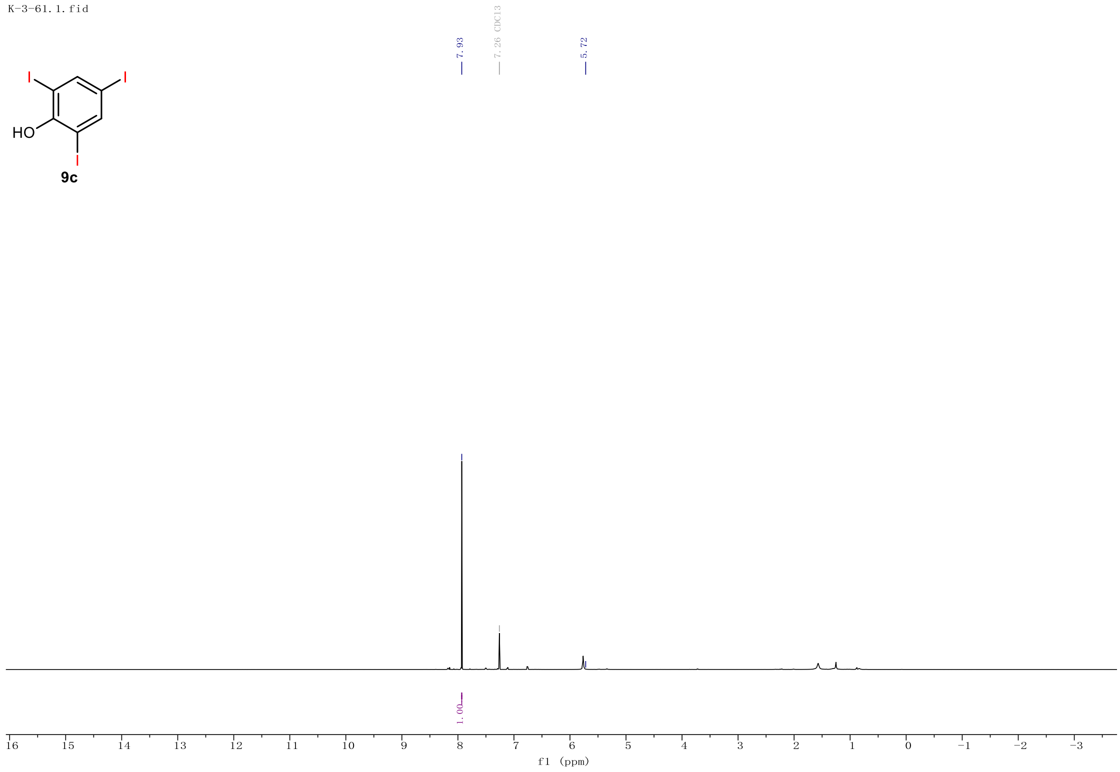

K-3-49.3.fid
148.18
133.59
131.42
121.52
112.22
110.81
77.21
77.00
76.79
Cl
Br
HO
Br
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

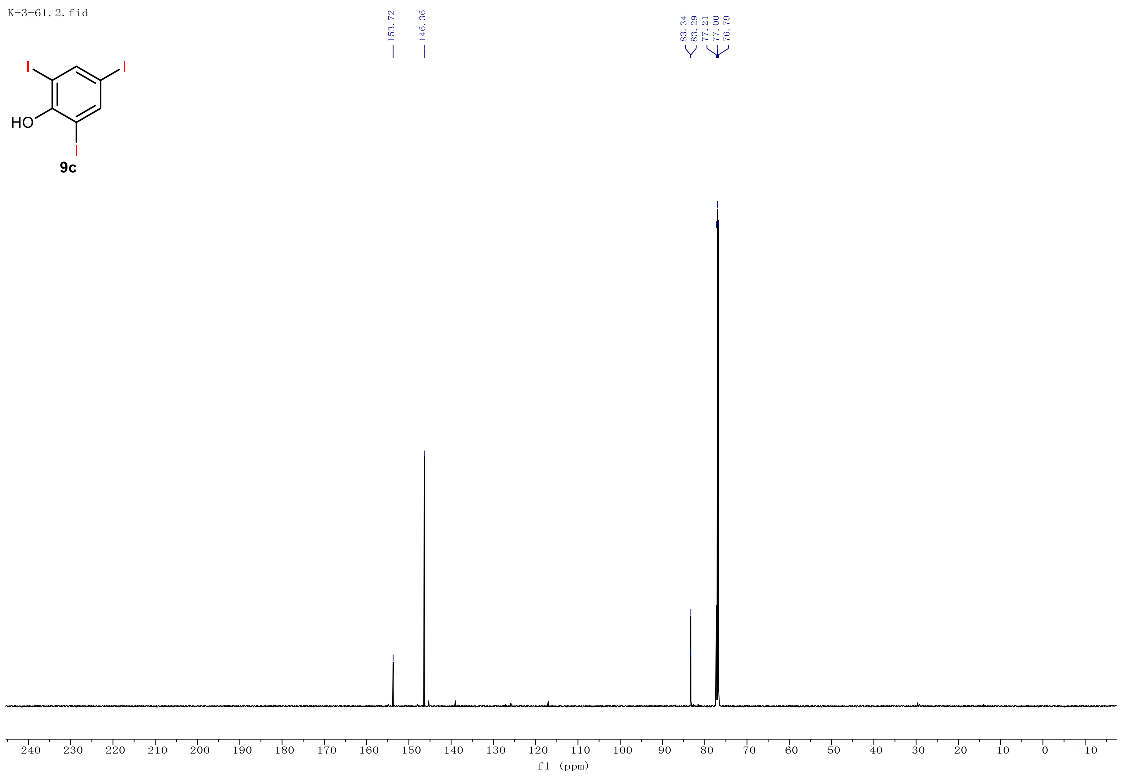
9a

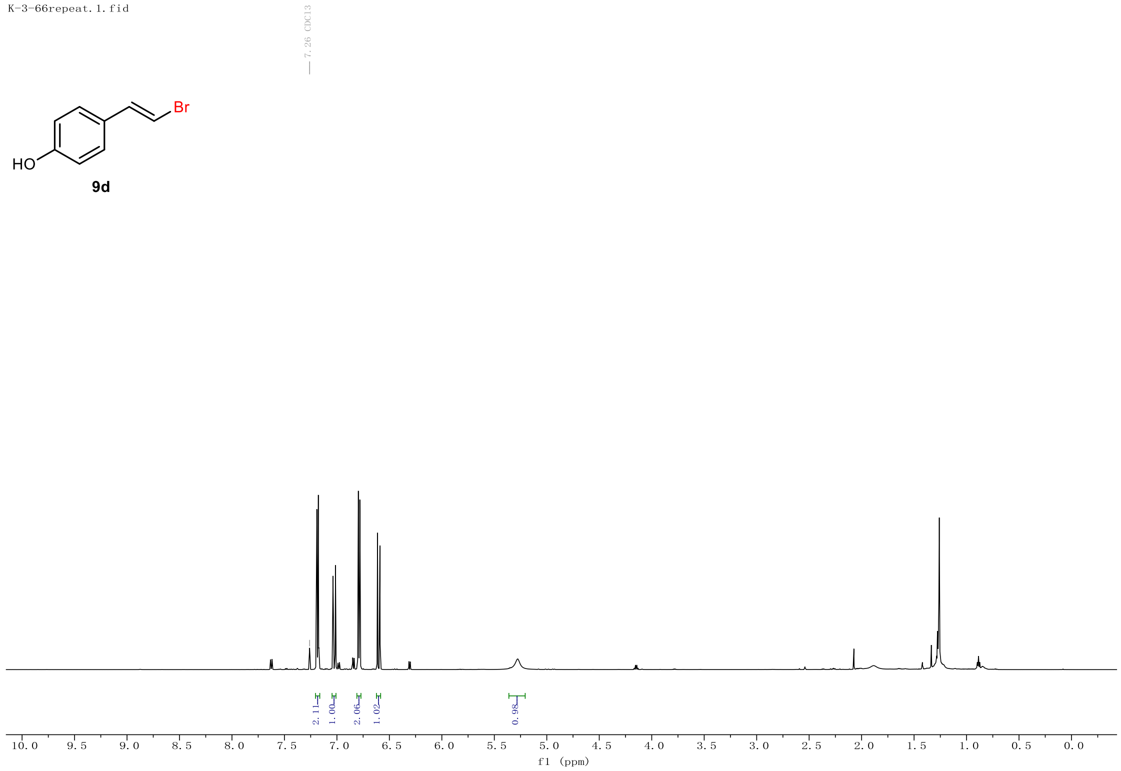

K-3-60.1.fid
7.26 CDCl3
F
Br
Br
HO
Br
9b
1.00
1.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

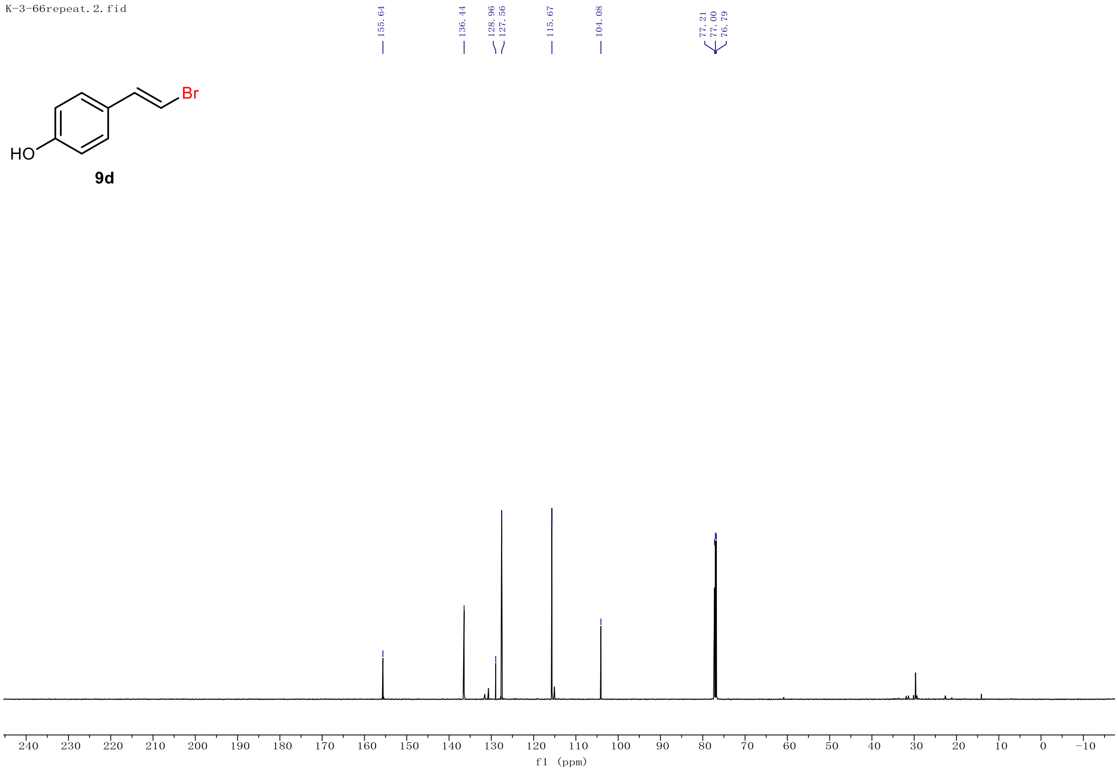

K-3-60.2.fid
156.53
154.89
150.25
150.23
133.87
104.60
104.57
100.23
100.07
99.00
98.83
77.21
77.00
76.79
F
Br
Br
HO
Br
9b
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

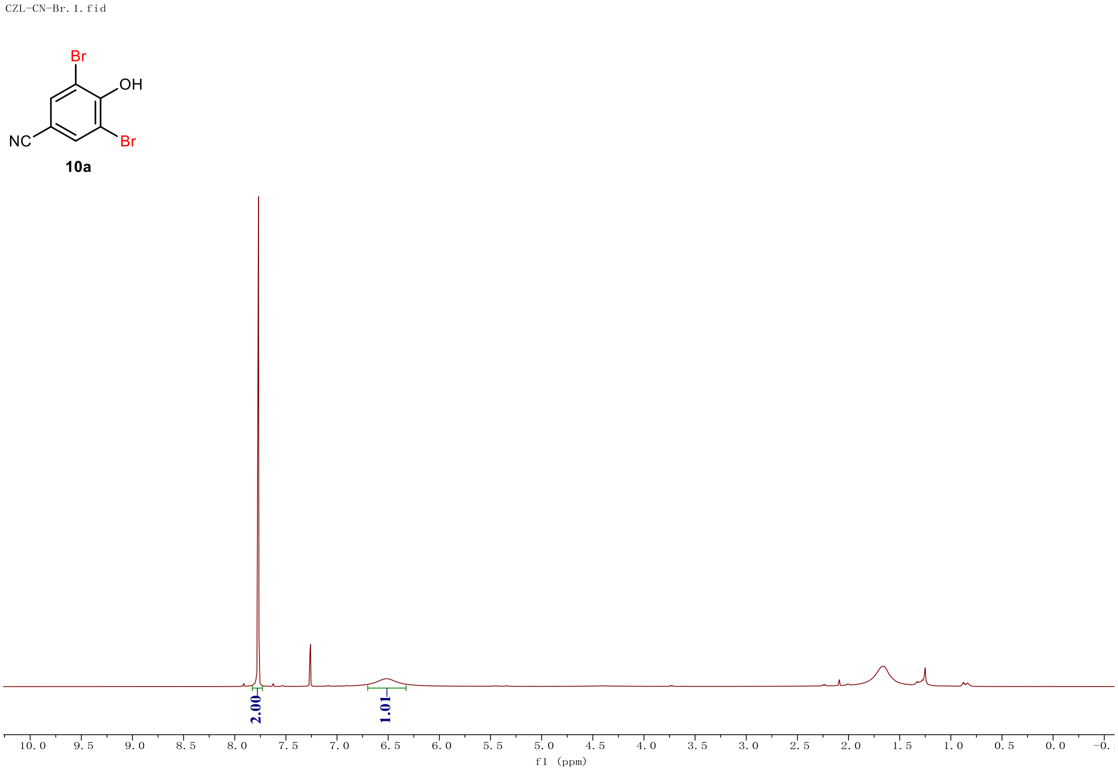

chenzhilong-20231024-KJ-1#.10.fid
-96.43
-96.44
F
Br
Br
HO
Br
9b
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

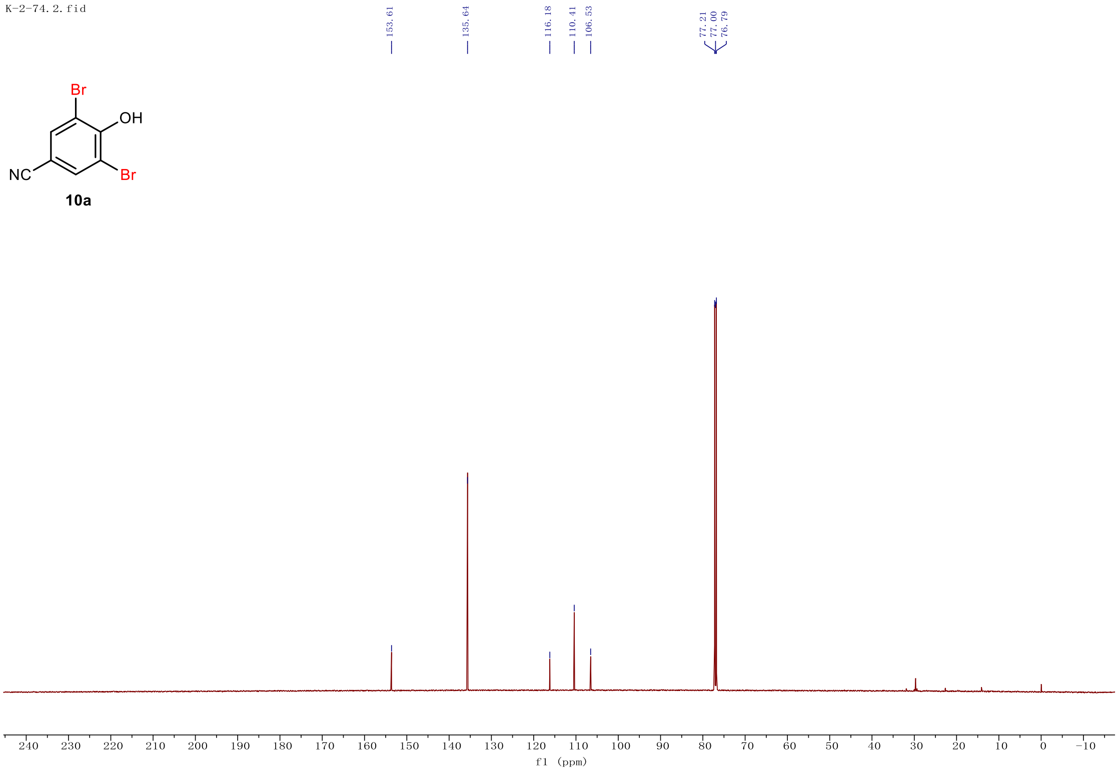

K-3-61.1.fid
7.93
7.26 CDCl3
5.72
I
I
HO
I
9c
1.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)


K-3-61.2.fid
153.72
146.36
83.34
83.29
77.21
77.00
76.79
I
I
HO
I
9c
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

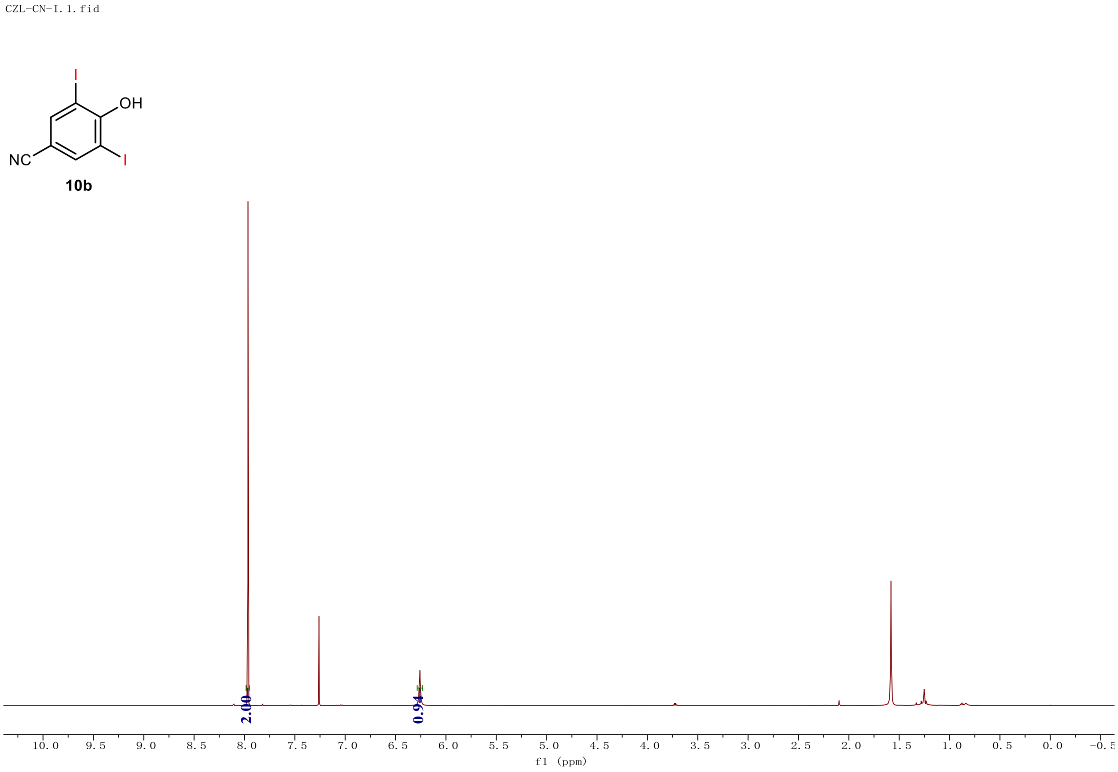

K-3-66repeat.1.fid
7.26 CDCl3
Br
HO
9d
2.11
1.00
2.06
1.02
0.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


K-3-66repeat.2.fid
155.64
136.44
128.96
127.56
115.67
104.08
77.21
77.00
76.79
Br
HO
9d
240
230
220
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)

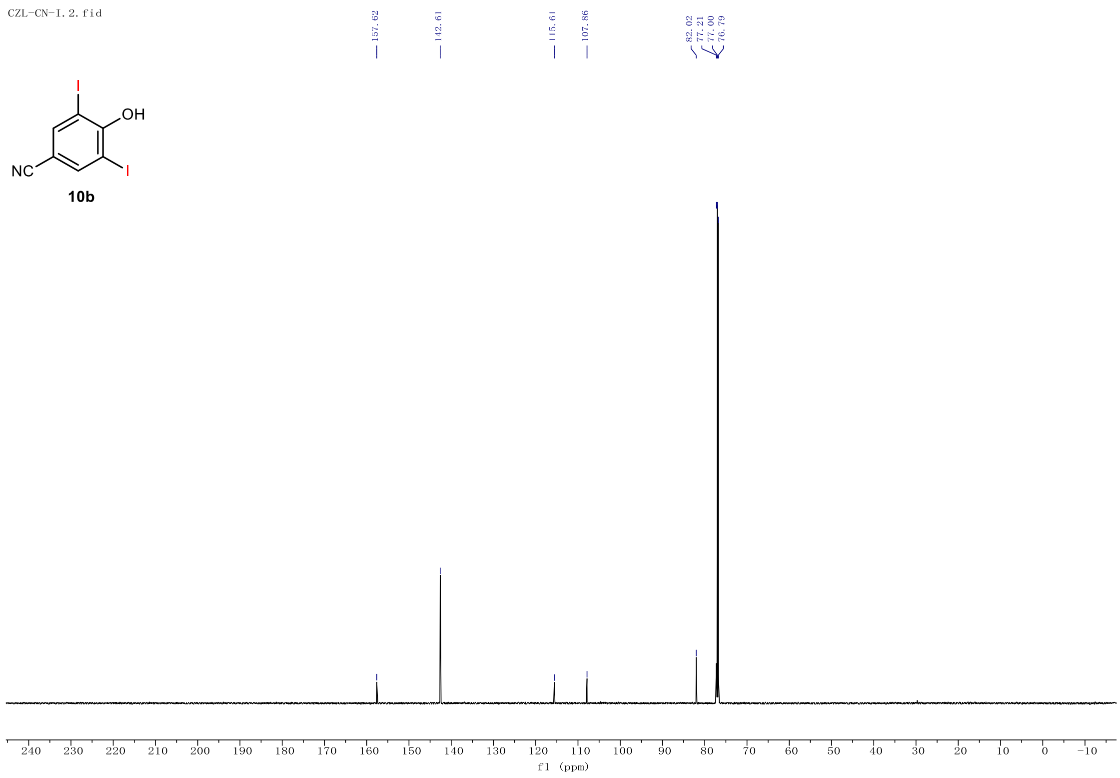

CZL-CN-Br.1.fid
Br
OH
NC
Br
10a
2.00
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


K-2-74.2.fid
153.61
135.64
116.18
110.41
106.53
77.21
77.00
76.79
Br
OH
NC
Br
240
230
220
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)

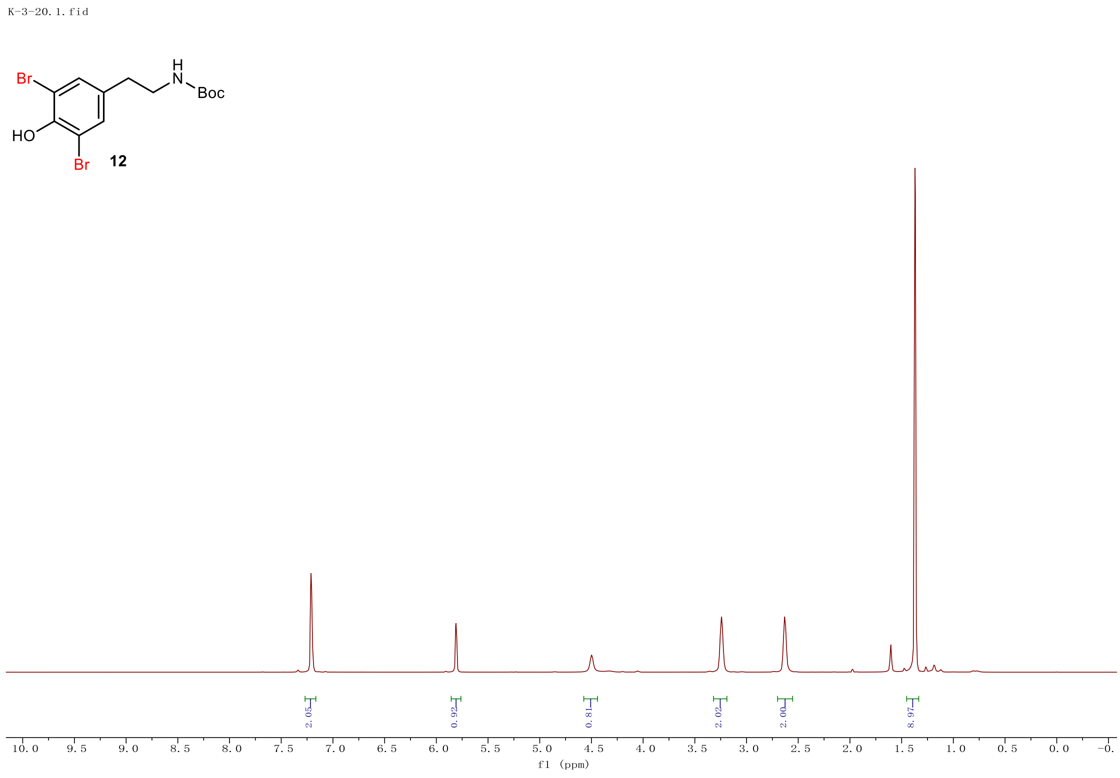
10a


CZL-CN-I.1.fid
I
OH
NC
I
2.00
0.94
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
-0.5
f1 (ppm)

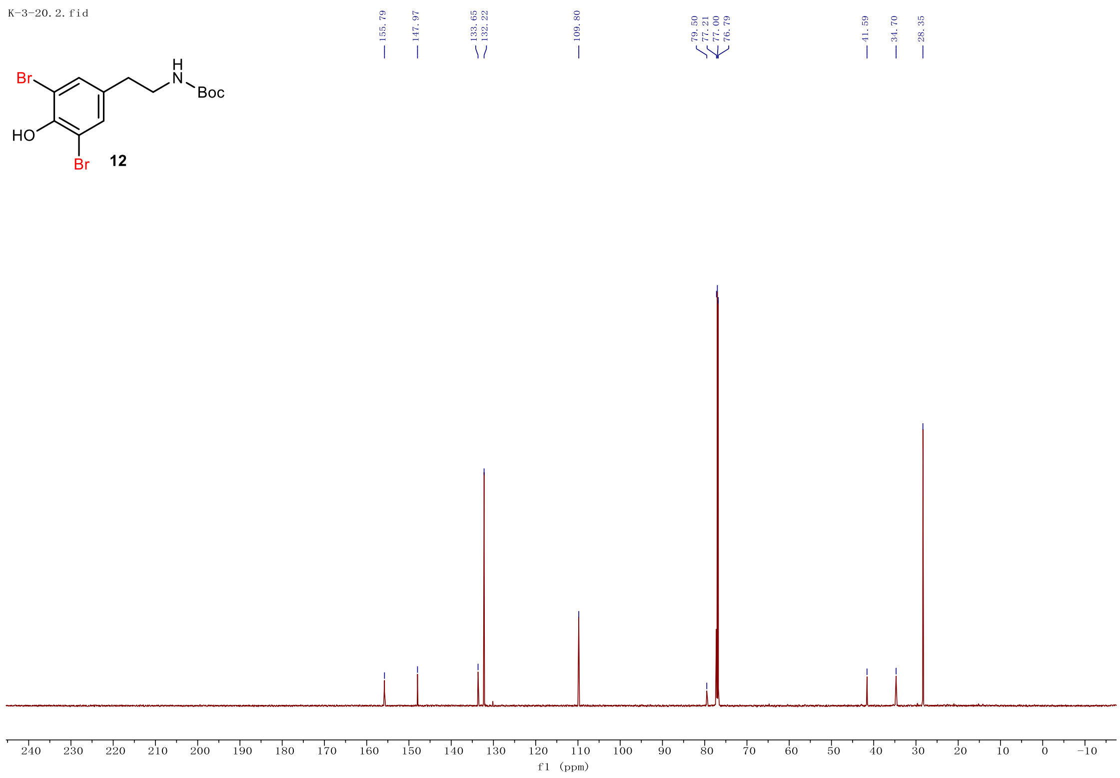
10b

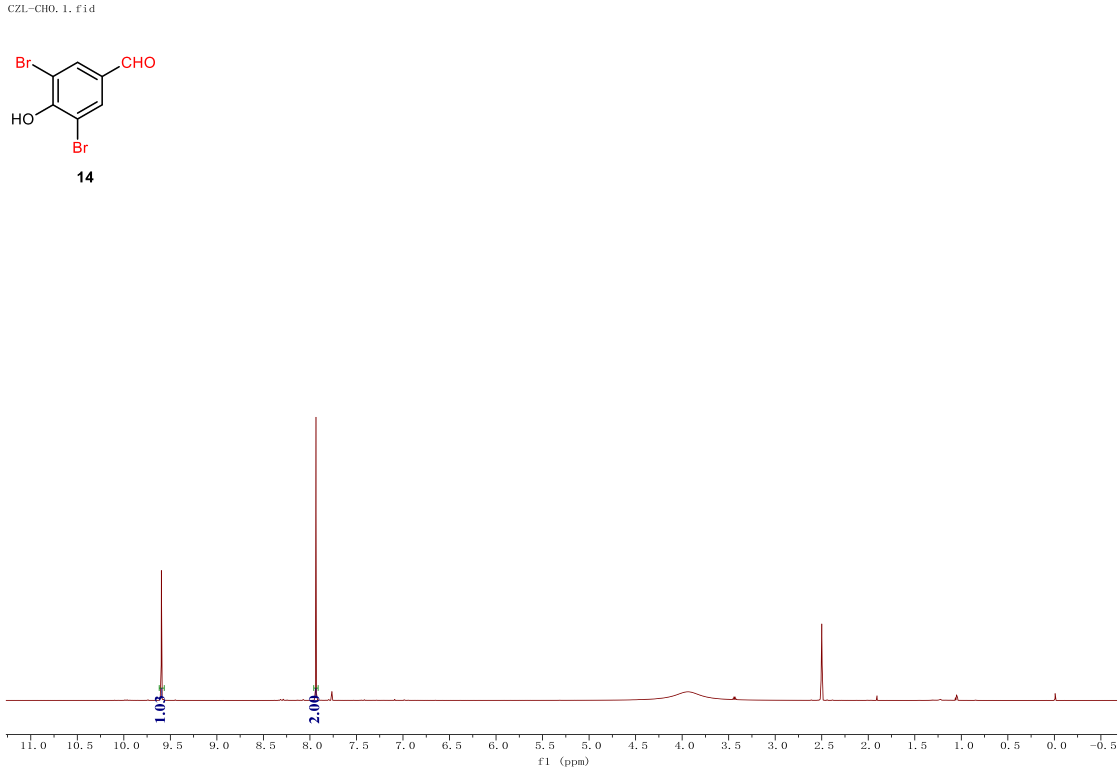

CZL-CN-I.2.fid
157.62
142.61
115.61
107.86
82.02
77.21
77.00
76.79
I
OH
NC
I
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

10b


K-3-20.1.fid
Br
HO
Br
H
N
Boc
2.05
0.92
0.81
2.02
2.00
8.97
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
-0.
f1 (ppm)

12


K-3-20.2.fid
Br
HO
Br
H
N
Boc
12
155.79
147.97
133.65
132.22
109.80
79.50
77.21
77.00
76.79
41.59
34.70
28.35
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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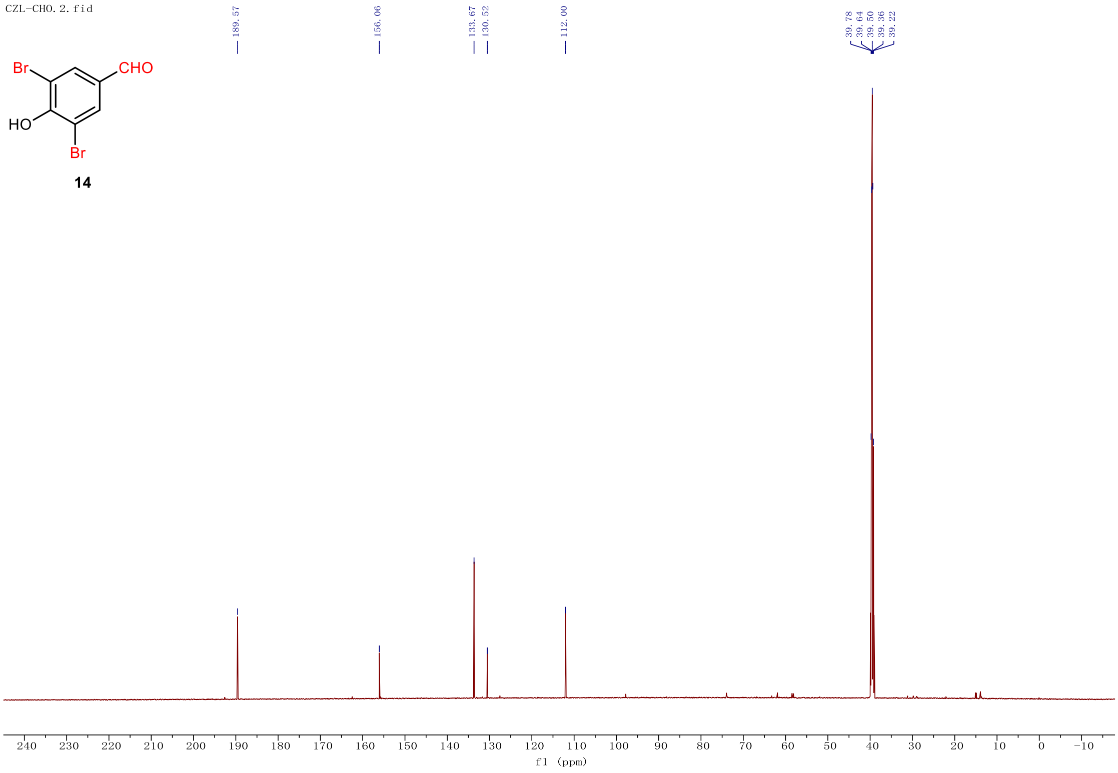
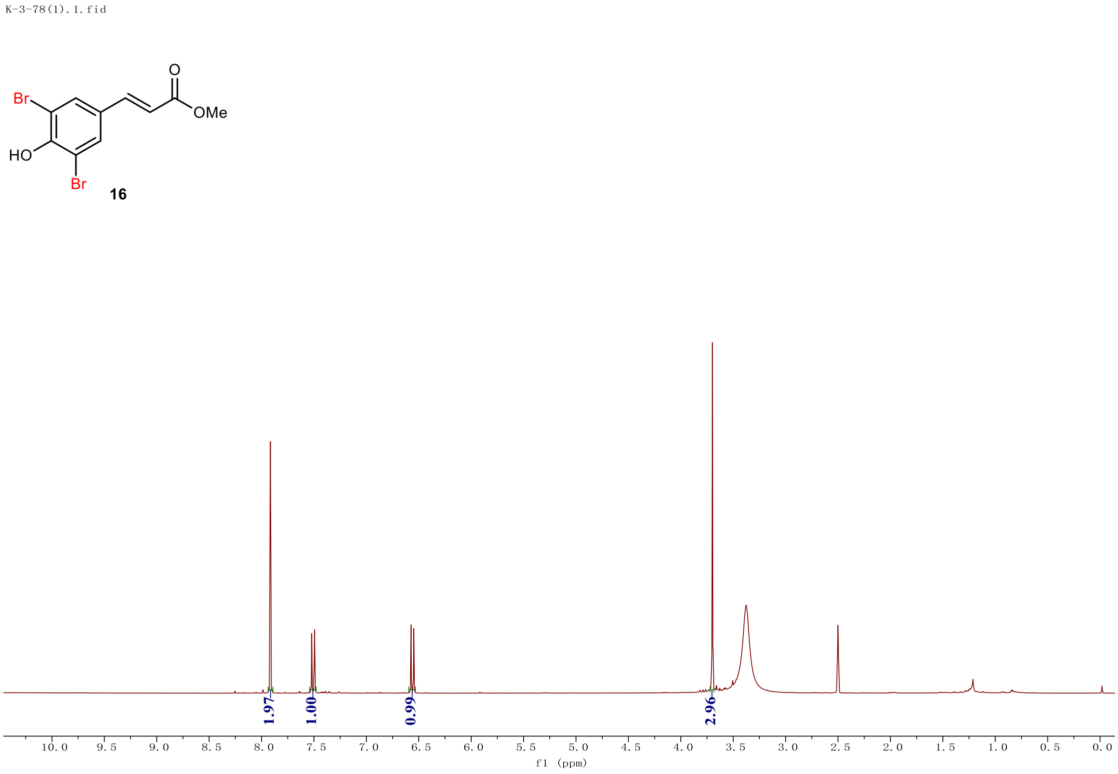
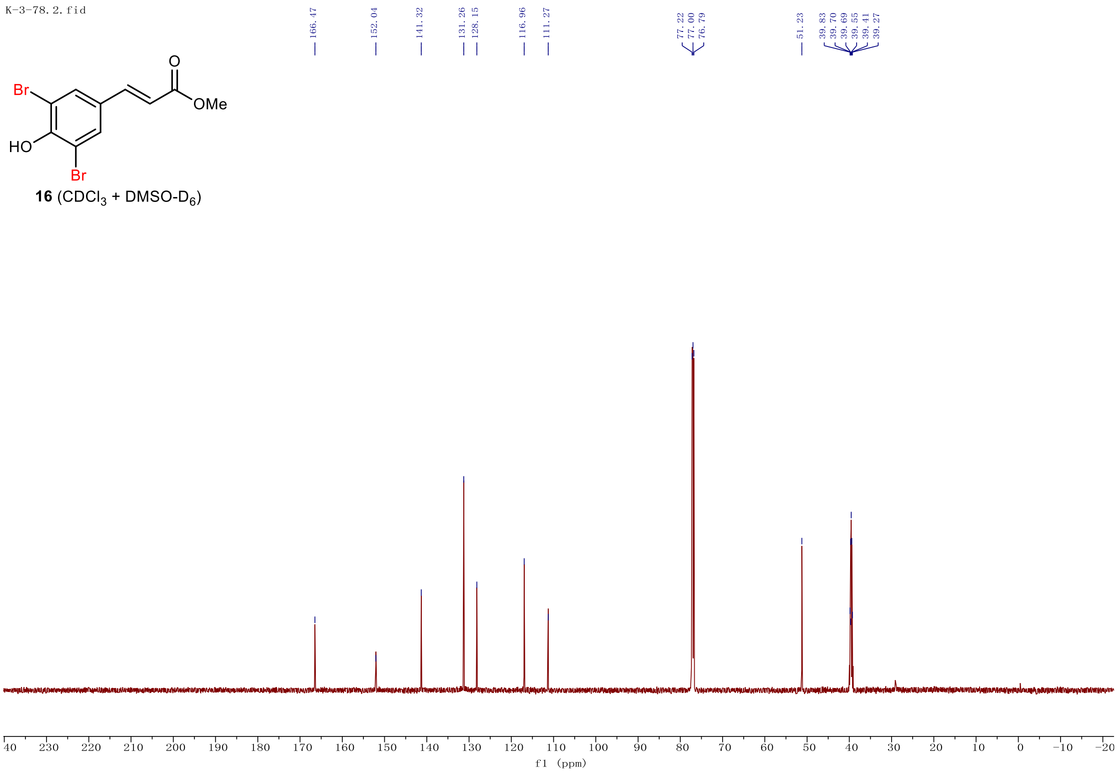
Br
CHO
HO
Br
14
1.03
2.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


CZL-CHO.2.fid
Br
CHO
HO
Br
189.57
156.06
133.67
130.52
112.00
39.78
39.64
39.50
39.36
39.22
240
230
220
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)

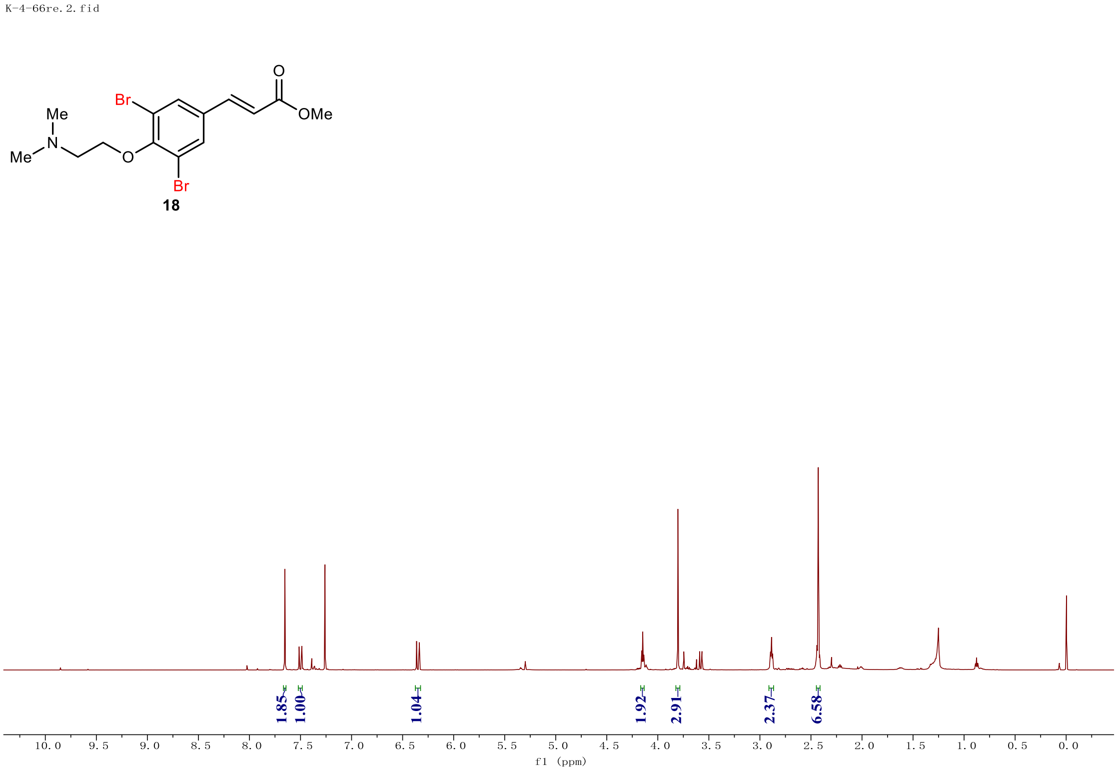
14


K-3-78(1).1.fid
Br
O
OMe
HO
Br
1.97
1.00
0.99
2.96
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)

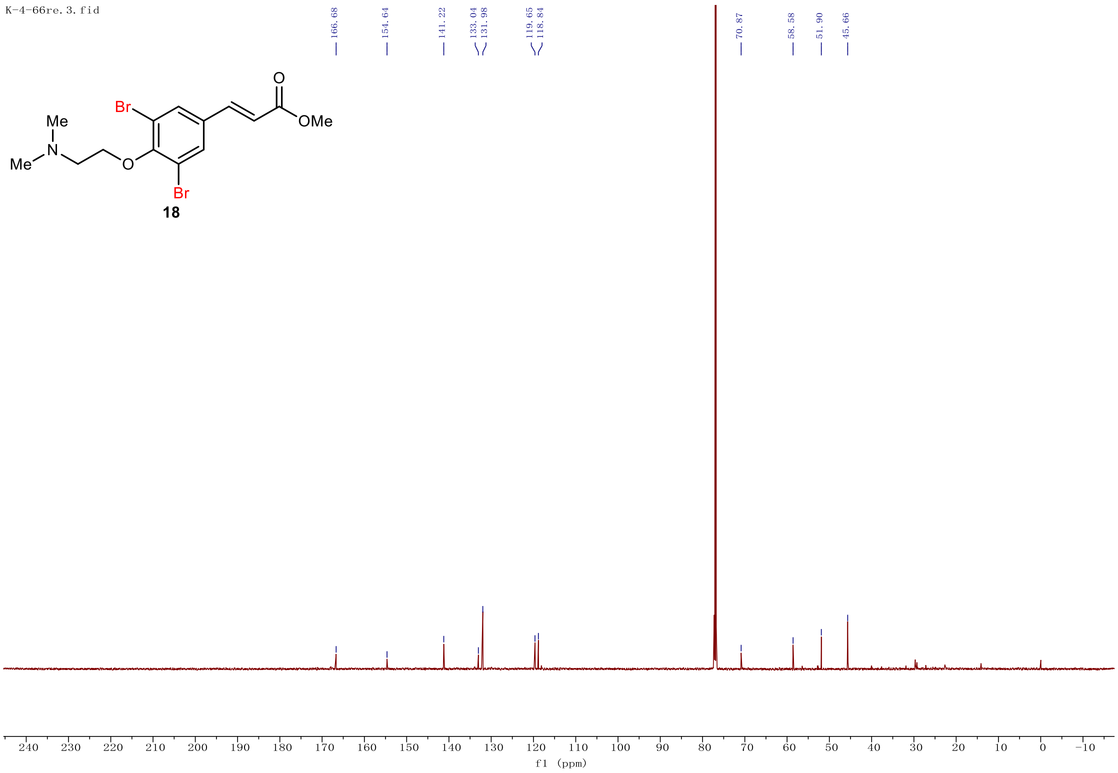
16



16 ($CDCl_3$ + DMSO-D_6)



18



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