# Supporting Information

## Cu(I)-Catalyzed Chemo- and Enantioselective Desymmetrizing C–O Bond Coupling of Acyl Radicals

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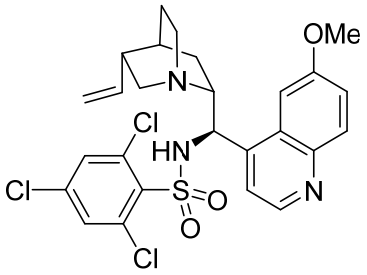



**L1**

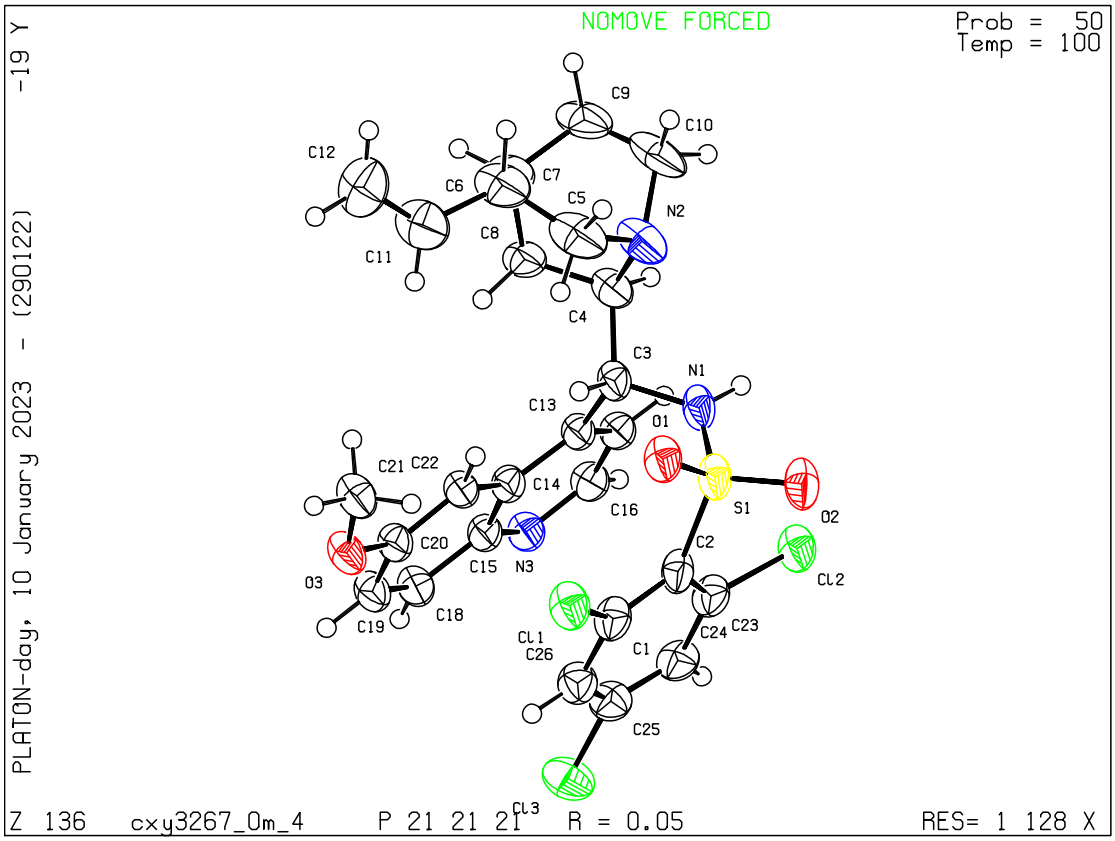
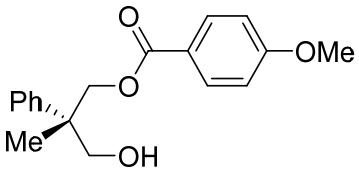



**Figure S1.** X-ray structure of **L1**.




**14**

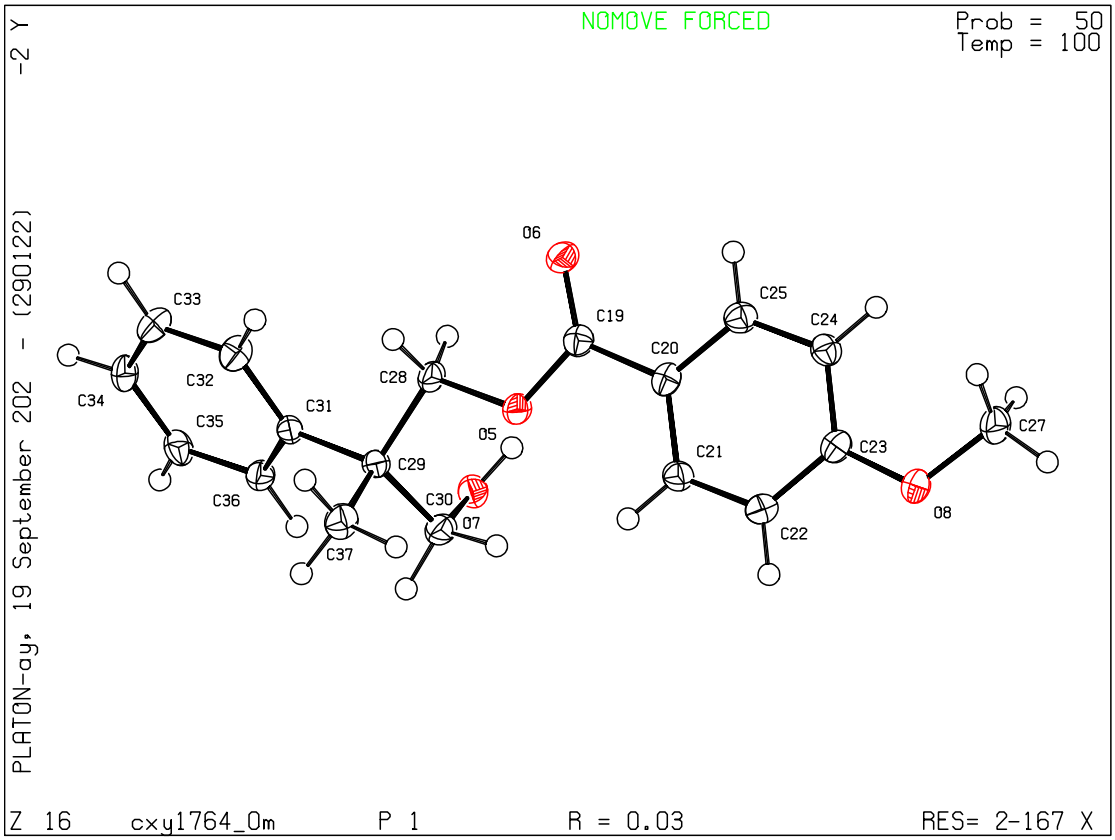
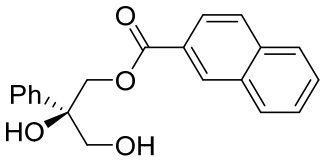



**Figure S2.** X-ray structure of **14**.




**41**

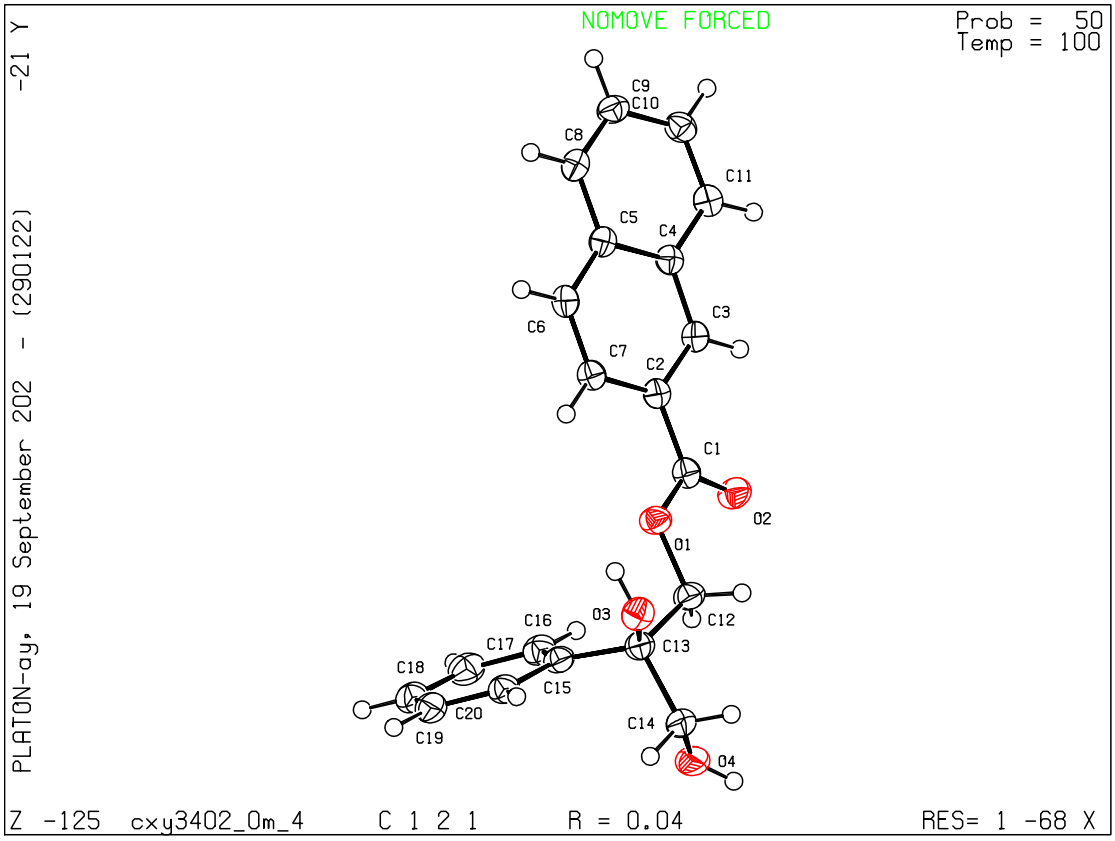
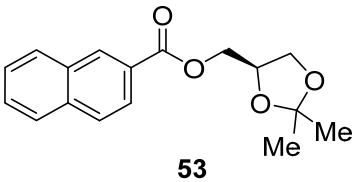



**Figure S3.** X-ray structure of **41**.




**53**

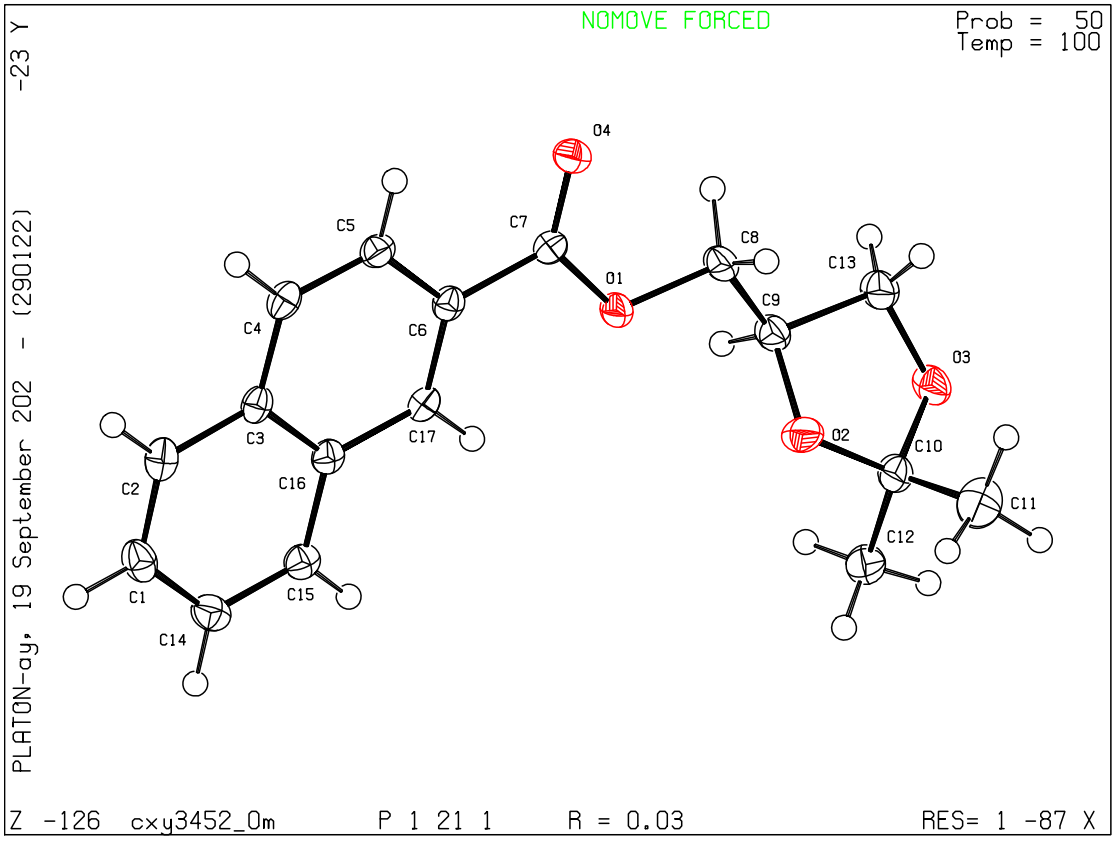
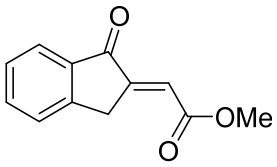



**Figure S4.** X-ray structure of **53**.




**56**

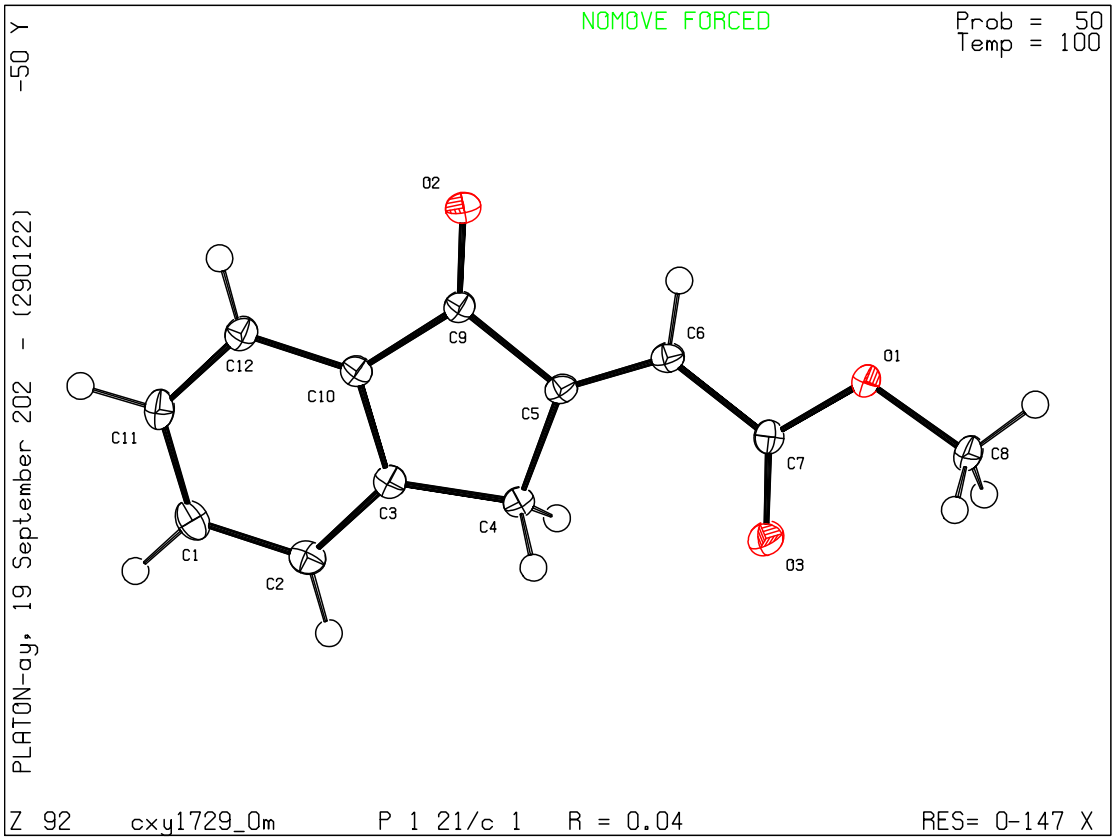



**Figure S5.** X-ray structure of **56**.

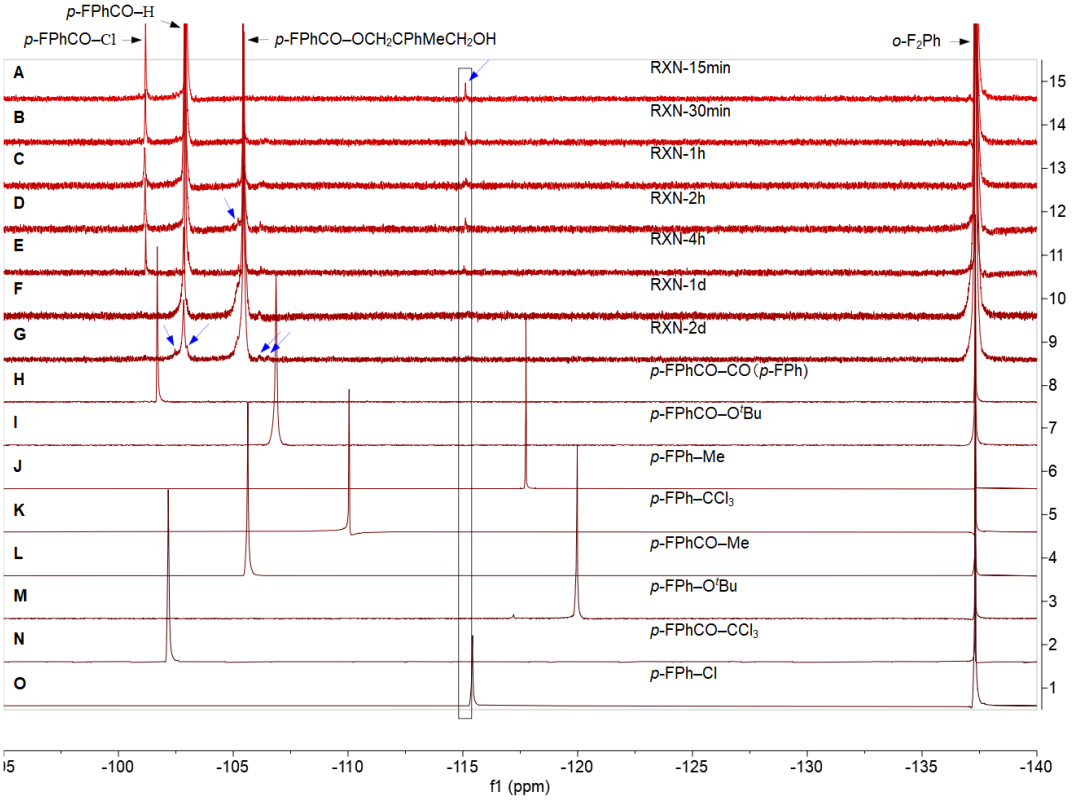



**Figure S6.** $^{19}F$ NMR spectroscopic analysis of the reaction mixtures with *p*-fluorophenyl aldehyde **A-6** in $CCl_4$. **A**–**G**, $^{19}F$ NMR spectra of the reaction mixtures in $CCl_4$ after stirring for the indicated reaction times. Peaks corresponding to unknown side products were indicated with blue arrows. **H**–**O**, $^{19}F$ NMR spectra of the authentic samples of speculated possible side products. For all $^{19}F$ NMR spectra shown here, *o*-difluorobenzene was added as an internal standard.

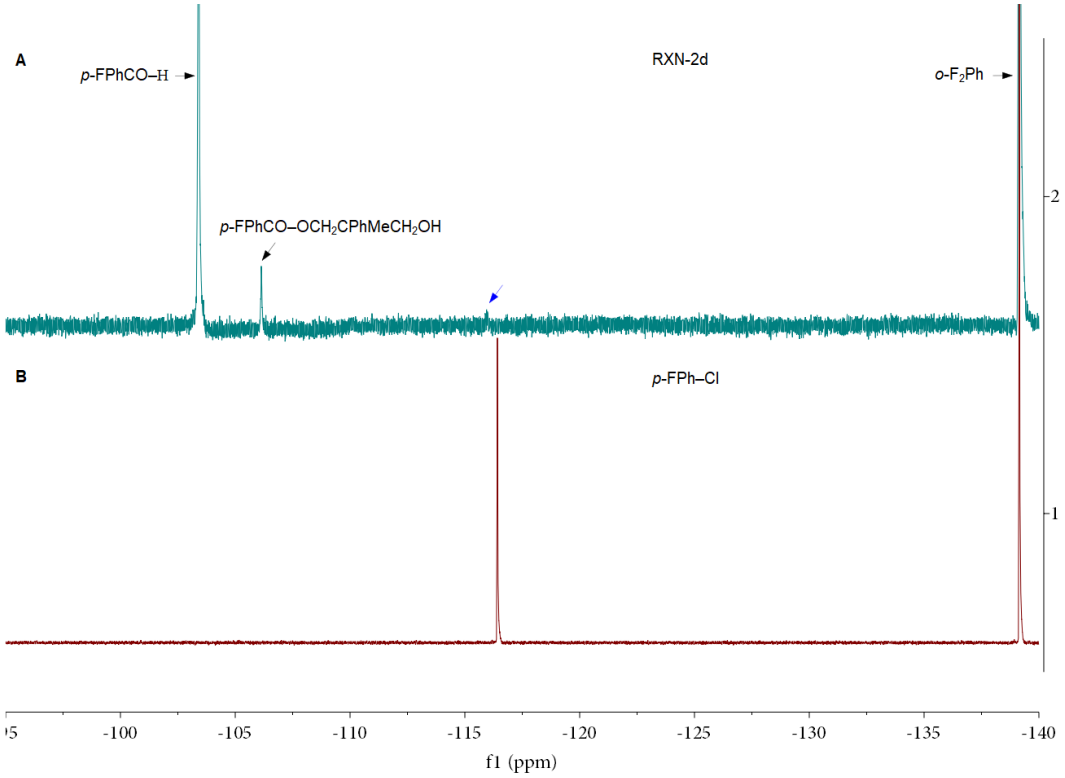
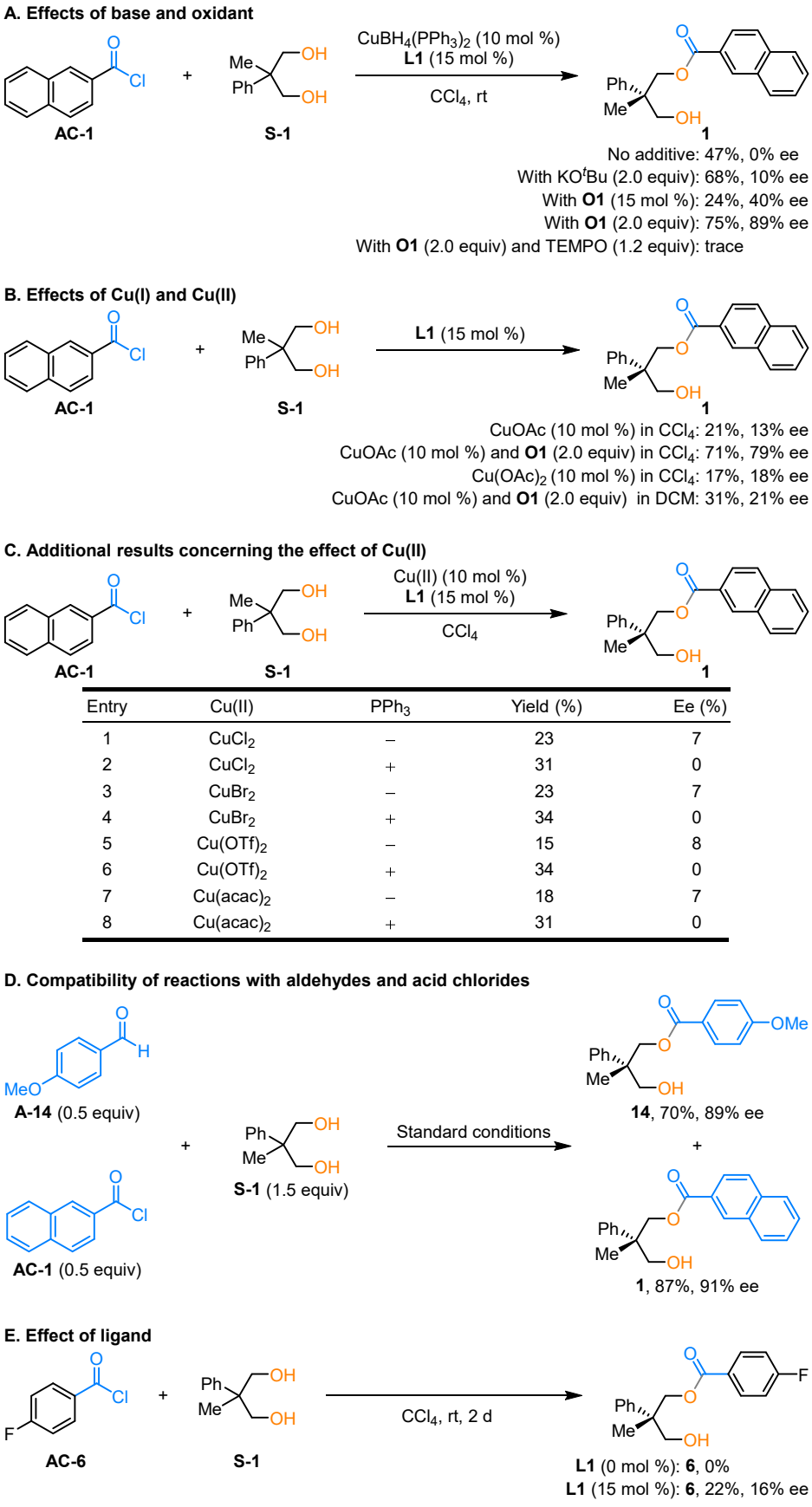



**Figure S7.** $^{19}F$ NMR spectroscopic analysis of the reaction mixture with *p*-fluorophenyl aldehyde **A-6** in $CH_2Cl_2$. **A**, The $^{19}F$ NMR spectrum of the reaction mixture in $CH_2Cl_2$ after stirring for 2 d. The peak corresponding to an unknown side product was indicated with a blue arrow. **B**, The $^{19}F$ NMR spectrum of the authentic sample of a speculated possible side product *p*-fluorochlorobenzene. For both $^{19}F$ NMR spectra shown here, *o*-difluorobenzene was added as an internal standard.

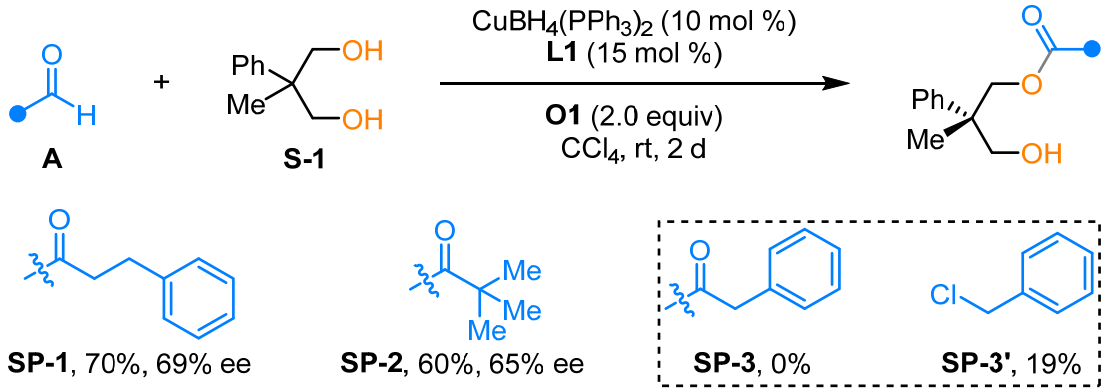



| Entry | Cu(II) | $PPh_3$ | Yield (%) | Ee (%) |
|---|---|---|---|---|
| 1 | $CuCl_2$ | – | 23 | 7 |
| 2 | $CuCl_2$ | + | 31 | 0 |
| 3 | $CuBr_2$ | – | 23 | 7 |
| 4 | $CuBr_2$ | + | 34 | 0 |
| 5 | $Cu(OTf)_2$ | – | 15 | 8 |
| 6 | $Cu(OTf)_2$ | + | 34 | 0 |
| 7 | $Cu(acac)_2$ | – | 18 | 7 |
| 8 | $Cu(acac)_2$ | + | 31 | 0 |

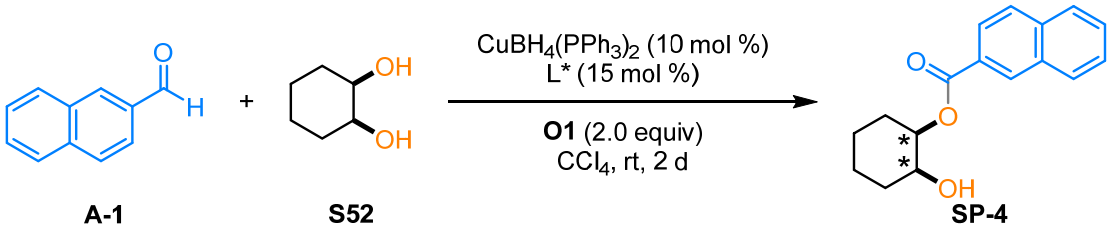
**Figure S8**. Results of control experiments with acid chlorides. **A**, In the presence of Cu(I) salt $CuBH_4(PPh_3)_2$ and chiral ligand **L1**, the reaction of acid chloride **AC-1** with

diol **S-1** provided ester **1** with no enantioselectivity. The addition of base KO$^t$Bu delivered still low enantioselectivity. By contrast, stoichiometric oxidant **O1** led to greatly improved enantiocontrol while a catalytic amount of **O1** only afforded a slightly increased ee value. The further addition of TEMPO completely inhibited the reaction, suggesting the involvement of radical species in the highly enantioselective formation of **1** in the presence of stoichiometric oxidant **O1** (for preliminary theoretical investigations, see Figure S14). **B**, Consistent with the aforementioned results, Cu(I) salt CuOAc also delivered marginal enantioselectivity in the absence of oxidant **O1** while the further addition of 2 equiv of **O1** resulted in greatly boosted enantioselectivity. Changing the solvent from carbon tetrachloride to dichloromethane totally abrogated this enantioselectivity enhancement. These results together indicated the indispensable roles of oxidant **O1** and carbon tetrachloride solvent in the Cu(I)/**L1**-catalyzed high enantioselective reaction of acid chloride **A-1** and diol **S-1**. Further, in the absence of oxidant **O1**, Cu(II) salt $Cu(OAc)_2$ was also incapable of inducing significant enantioselectivity. **C**, Without **O1**, many other common Cu(II) salts failed to elicit good enantioselectivity, too, regardless of the presence or absence of triphenylphosphine, further disproving the Cu(II)-catalyzed ionic esterification pathway (Lewis acid catalysis). **D**, The enantioselective reaction of acid chloride **AC-1** and **S-1** exhibited good compatibility with that of aldehyde **A-14** and **S-1** when carried out simultaneously in the same reaction flask. **E**, Acid chloride **AC-6** hardly reacted with **S-1** in the absence of any catalyst and the addition of ligand **L1** only led to ester **6** in low yield with marginal enantioselectivity. These results suggested that the non-enantioselective background reaction was very sluggish and free ligand **L1** was a very poor Lewis base catalyst for this esterification reaction.

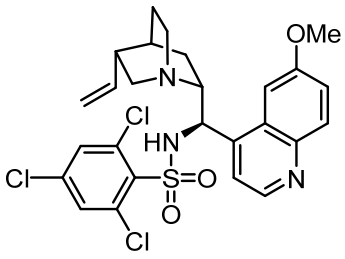
**Scheme S1. Results of Additional Alkyl Aldehydes.**



**Scheme S2. Catalytic Enantioselective Desymmetrizing Radical C–O Coupling of *cis*-1,2-Cyclohexadiol**

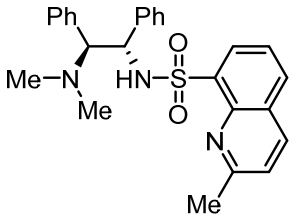



**A-1** **S52** **SP-4**



**L1**

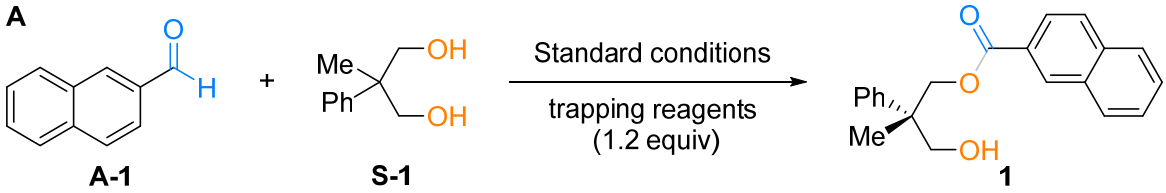
**SP-4**, 68%, 42% ee



**L8**

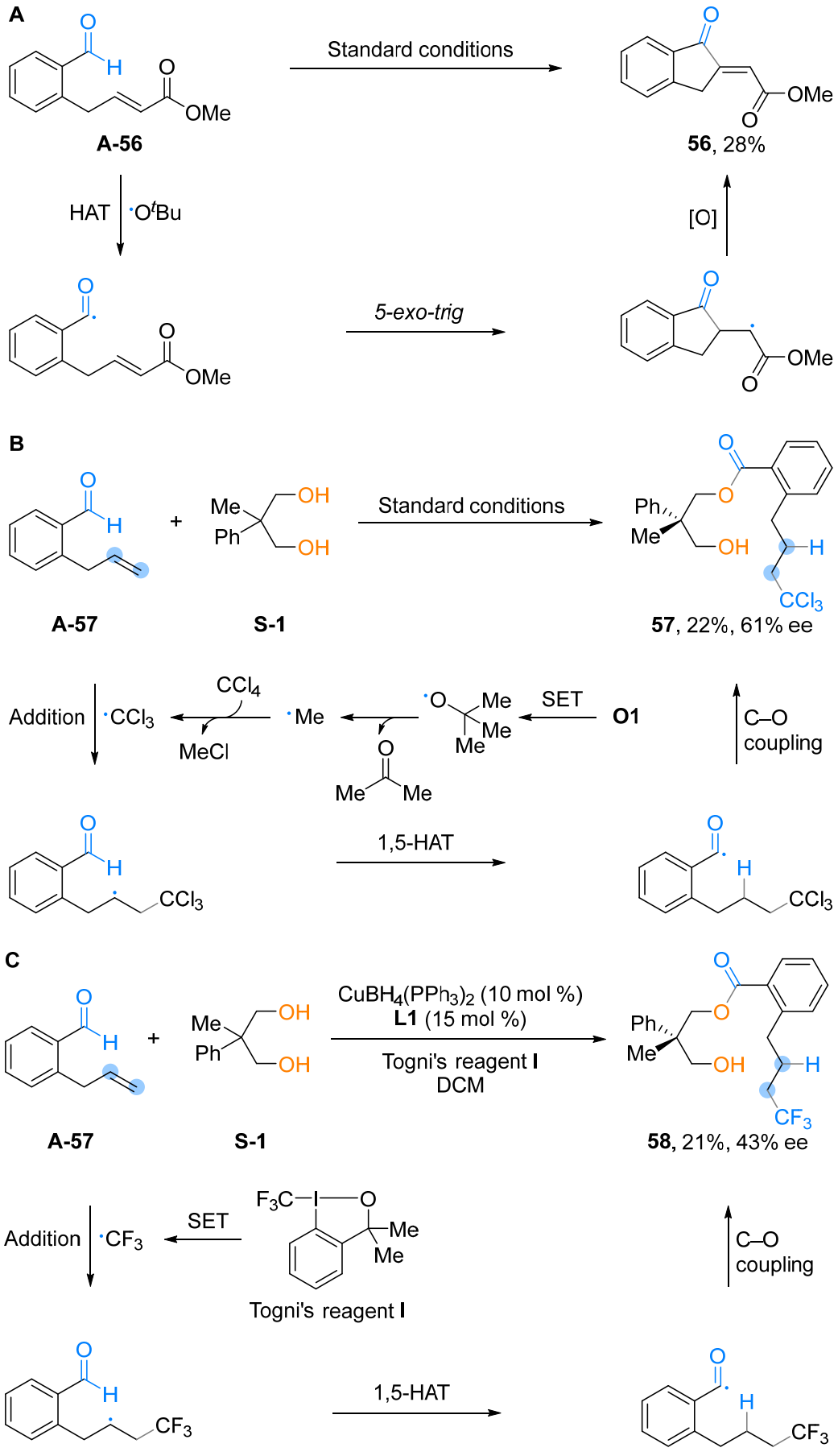
**SP-4**, 76%, 69% ee

**Scheme S3. Radical Inhibition Experiments**




| Trapping reagents | Yield of **1** | Ee of **1** |
|---|---|---|
| BHT | Trace | - |
| TEMPO | Trace | - |

**Scheme S4. Possible Reaction Mechanisms for the Formation of 56–58**



**Scheme S5. Control Experiments for Possible Product Kinetic Resolution and Oxidative Acetal Cleavage**

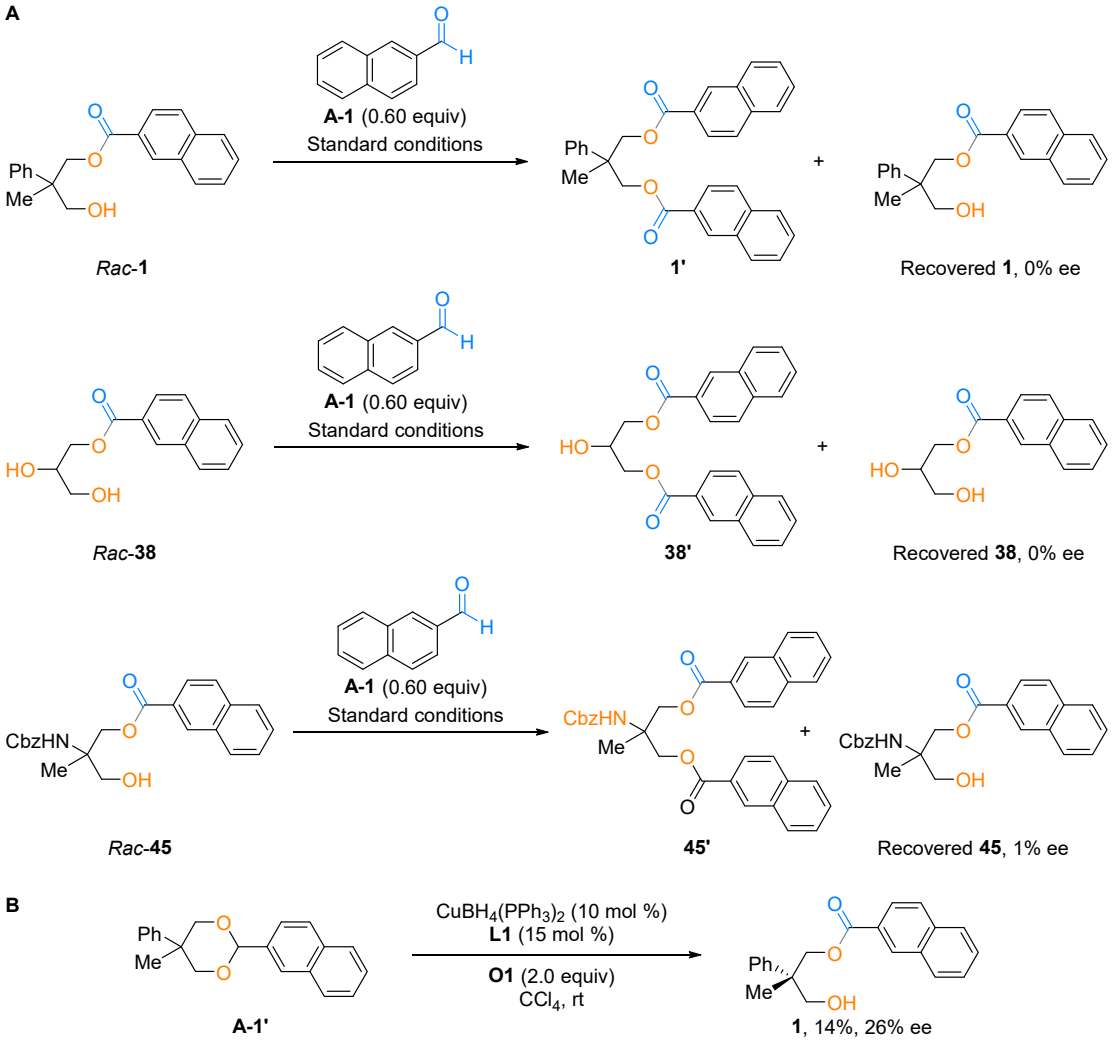
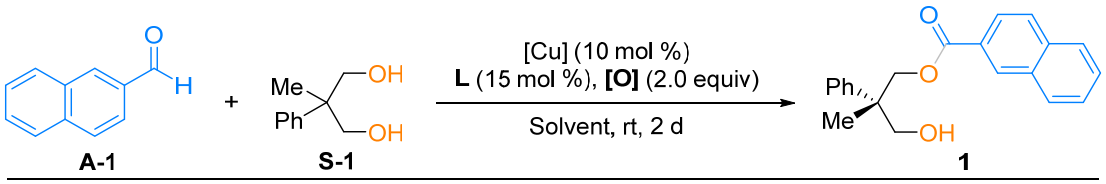
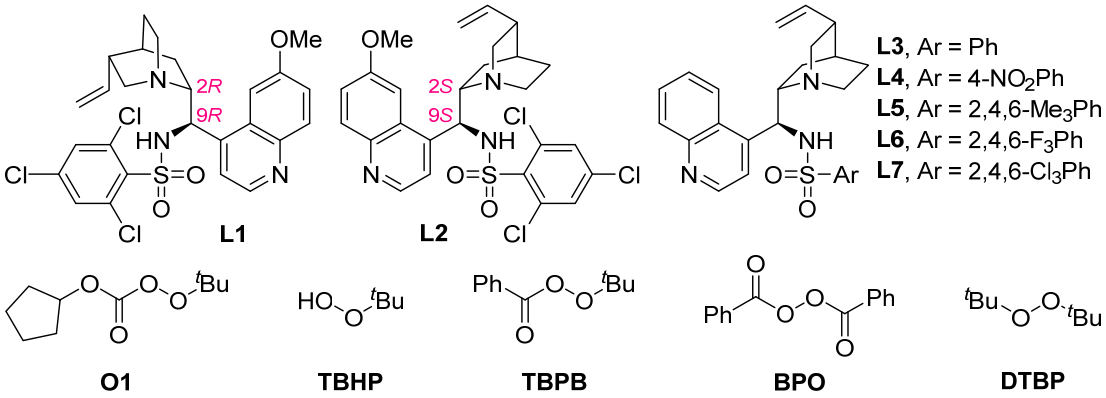


**Table S1. Optimization of Reaction Conditions for 2,2-Dicarbosubstituted 1,3-diols**[a]



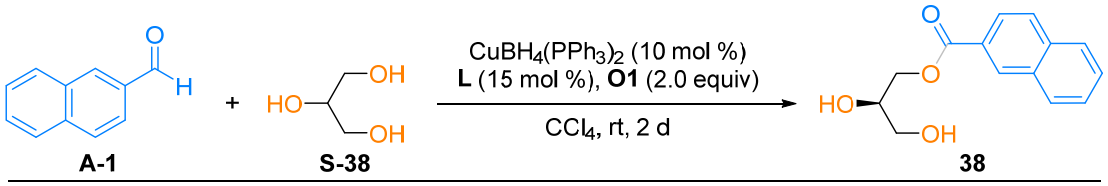




| Entry | L | [Cu] | [O] | Solvent | Yield (%) | Ee (%) |
|---|---|---|---|---|---|---|
| 1 | **L1** | $CuBH_4(PPh_3)_2$ | **O1** | MTBE | 9 | 61 |
| 2 | **L1** | $CuBH_4(PPh_3)_2$ | **O1** | EA | 8 | 85 |
| 3 | **L1** | $CuBH_4(PPh_3)_2$ | **O1** | *n*-Hexane | Trace | - |
| 4 | **L1** | $CuBH_4(PPh_3)_2$ | **O1** | $CH_2Cl_2$ | 6 | 75 |
| 5 | **L1** | $CuBH_4(PPh_3)_2$ | **O1** | $CHCl_3$ | Trace | - |
| 6 | **L1** | $CuBH_4(PPh_3)_2$ | **O1** | $CCl_4$ | 76 | 93 |
| 7 | **L2** | $CuBH_4(PPh_3)_2$ | **O1** | $CCl_4$ | 68 | −89 |
| 8 | **L3** | $CuBH_4(PPh_3)_2$ | **O1** | $CCl_4$ | 46 | −72 |
| 9 | **L4** | $CuBH_4(PPh_3)_2$ | **O1** | $CCl_4$ | 30 | −73 |
| 10 | **L5** | $CuBH_4(PPh_3)_2$ | **O1** | $CCl_4$ | 67 | −86 |
| 11 | **L6** | $CuBH_4(PPh_3)_2$ | **O1** | $CCl_4$ | 60 | −83 |
| 12 | **L7** | $CuBH_4(PPh_3)_2$ | **O1** | $CCl_4$ | 67 | −87 |
| 13 | **L1** | CuI | **O1** | $CCl_4$ | 14 | 78 |
| 14 | **L1** | $Cu_2O$ | **O1** | $CCl_4$ | 56 | 88 |
| 15 | **L1** | CuOAc | **O1** | $CCl_4$ | 26 | 83 |
| 16 | **L1** | CuTC | **O1** | $CCl_4$ | 54 | 81 |
| 17 | **L1** | CuCN | **O1** | $CCl_4$ | 48 | 58 |
| 18 | **L1** | $CuCF_3PPh_3(phen)$ | **O1** | $CCl_4$ | 7 | 50 |
| 19 | **L1** | $CuBH_4(PPh_3)_2$ | TBHP | $CCl_4$ | 30 | 38 |
| 20 | **L1** | $CuBH_4(PPh_3)_2$ | TBPB | $CCl_4$ | 17 | 69 |
| 21 | **L1** | $CuBH_4(PPh_3)_2$ | BPO | $CCl_4$ | Trace | - |
| 22 | **L1** | $CuBH_4(PPh_3)_2$ | DTBP | $CCl_4$ | Trace | - |
| 23 | **L1** (12%) | $CuBH_4(PPh_3)_2$ (10%) | **O1** | $CCl_4$ | 61 | 91 |
| 24 | **L1** (10%) | $CuBH_4(PPh_3)_2$ (10%) | **O1** | $CCl_4$ | 64 | 90 |
| 25 | **L1** (5.0%) | $CuBH_4(PPh_3)_2$ (10%) | **O1** | $CCl_4$ | 60 | 84 |
| 26 | **L1** (7.5%) | $CuBH_4(PPh_3)_2$ (5.0%) | **O1** | $CCl_4$ | 53 | 82 |

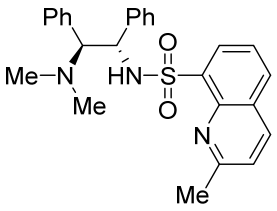
| | | | | | | |
|---|---|---|---|---|---|---|
| 27 | **L1** (3.0%) | $CuBH_4(PPh_3)_2$ (2.0%) | **O1** | $CCl_4$ | 17 | 49 |
| 28 | **L1** | $CuBH_4(PPh_3)_2$ | **O1** (1.0 equiv) | $CCl_4$ | 36 | 89 |
| 29 | **L1** | $CuBH_4(PPh_3)_2$ | **O1** (1.5 equiv) | $CCl_4$ | 47 | 90 |

[a]Reaction conditions: **A-1** (0.20 mmol), **S-1** (0.30 mmol), $CuBH_4(PPh_3)_2$ (10 mol %), **L** (15 mol %), **[O]** (2.0 equiv) in anhydrous solvent (4.0 mL) at rt for 2 d under argon. Yield was based on $^1$H NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard; ee values were based on chiral high-performance liquid chromatography (HPLC) analysis.

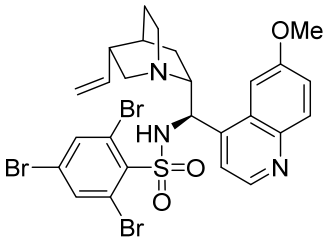
**Table S2. Optimization of Reaction Conditions for Glycerol**[a]



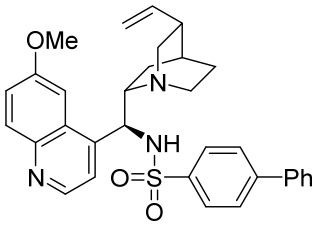

A-1 S-38 38



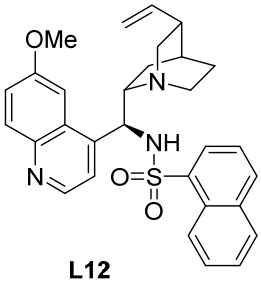
L8



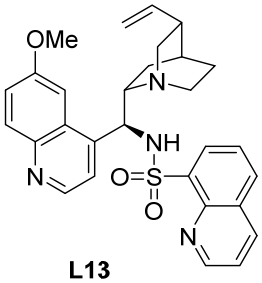
L10



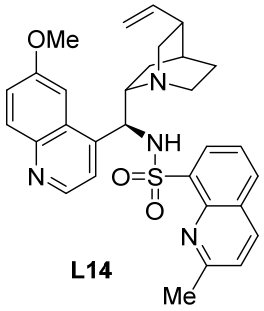
L11



L12



L13

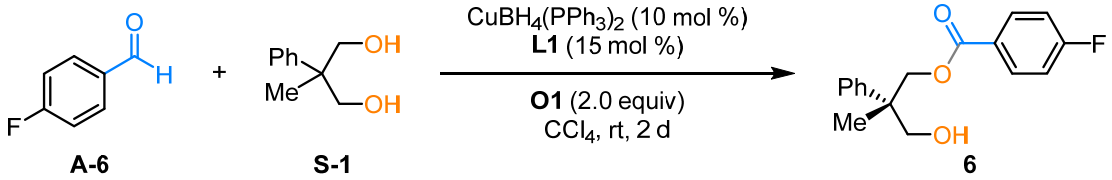


L14

| Entry | L | Yield (%) | Ee (%) |
|---|---|---|---|
| 1 | **L1** | 47 | −79 |
| 2 | **L8** | 71 | 95 |
| 3 | **L10** | 43 | −79 |
| 4 | **L11** | 25 | 50 |
| 5 | **L12** | 20 | 68 |
| 6 | **L13** | trace | - |
| 7 | **L14** | 20 | 64 |

[a]Reaction conditions: **A-1** (0.20 mmol), **S-38** (0.30 mmol), $CuBH_4(PPh_3)_2$ (10 mol %), **L** (15 mol %), **O1** (2.0 equiv) in anhydrous $CCl_4$ (4.0 mL) at rt for 2 d under argon. Yield was based on $^1H$ NMR analysis of the crude product using 1,3,5-trimethoxybenzene as an internal standard; ee values were based on chiral high-performance liquid chromatography (HPLC) analysis.

**Table S3. Product Ee Values in the Reaction**

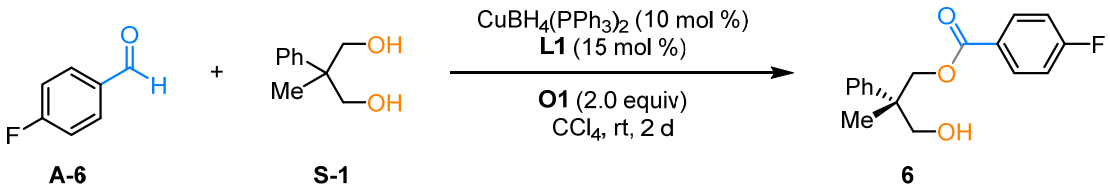



A-6 S-1 6

| Entry | Time (h) | Ee of **6** (%) |
|---|---|---|
| 1 | 0.25 | 91 |
| 2 | 0.5 | 92 |
| 3 | 1 | 91 |
| 4 | 2 | 92 |
| 5 | 8 | 92 |
| 6 | 24 | 92 |
| 7 | 48 | 92 |

Reaction conditions: **A-6** (0.025 mmol), **S-1** (1.5 equiv), $CuBH_4(PPh_3)_2$ (10 mol %), **L1** (15 mol %), and **O1** (2.0 equiv) in anhydrous carbon tetrachloride (0.50 mL) at rt for the indicated time under argon. Upon completion, the reaction mixture was purified by thin layer chromatography (petroleum ether/EtOAc = 3/1) and ee values were based on chiral HPLC analysis.

**Table S4. Generation of Acid Chlorides in the Reaction**




**A-6** **S-1** **6**

| Entry | Time (h) | **A-6** (%) | **AC-6** (%) | **6** (%) |
|---|---|---|---|---|
| 1 | 0.25 | 89 | 11 | 0 |
| 2 | 0.5 | 78 | 12 | 10 |
| 3 | 1 | 72 | 8 | 20 |
| 4 | 2 | 55 | 6 | 39 |
| 5 | 8 | 31 | 0.8 | 68 |
| 6 | 24 | 23 | 0 | 77 |
| 7 | 48 | 22 | 0 | 78 |

Reaction conditions: **A-6** (0.025 mmol), **S-1** (1.5 equiv.), $CuBH_4(PPh_3)_2$ (10 mol %), **L1** (15 mol %), and **O1** (2.0 equiv) in anhydrous carbon tetrachloride (0.50 mL) at rt for the indicated time under argon. Upon completion, *o*-difluorobenzene (0.50 mol/L in $CCl_4$, 50 μL, 1.0 equiv) was added and the reaction mixture was directedly analyzed by $^{19}F$ NMR spectroscopy.

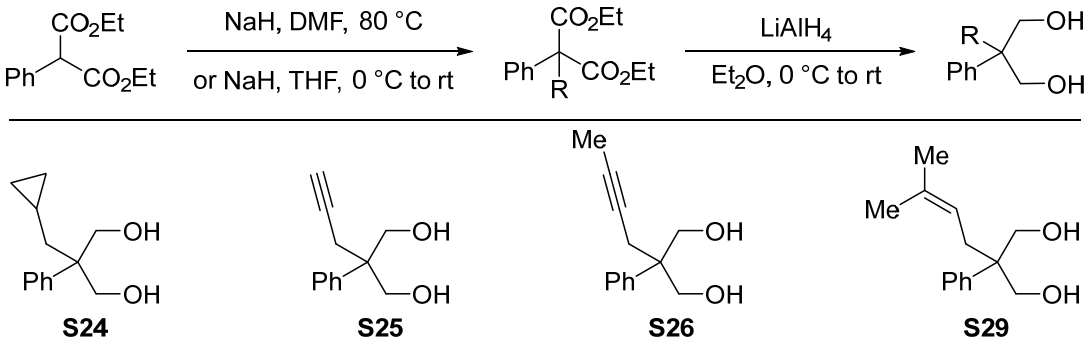
# 1. General information

All reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification unless otherwise stated. Extra dry solvents were purchased from J&K®. Chloroform ($CHCl_3$) was distilled from anhydrous calcium hydride ($CaH_2$) and stored under argon. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). $^{1}H$, $^{13}C$, $^{19}F$, and $^{31}P$-NMR spectra were recorded on Bruker Avance-400 spectrometers. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for $^{1}H$ NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for $^{13}C$ NMR are reported in terms of chemical shift (δ, ppm). Mass spectrometric data were obtained using Bruker Apex IV RTMS. Enantiomeric excess (ee) was determined using Agilent high-performance liquid chromatography (HPLC) with a Hitachi detector or SHIMADZU LC-20AD with an SPD-20AV detector; column conditions are reported in the experimental section below. Specific optical rotation was measured on a Rudolph-Autopol I. X-ray diffraction was measured on a 'Bruker APEX-II CCD diffractometer with Cu–Kα radiation.

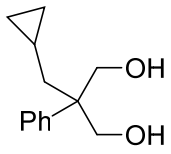
## 2. Synthesis of substrates

Glycerol (**S38**) and *cis*-1,2-cyclohexadiol (**S52**) was purchased from commercial sources and directly used. The following substrates were synthesized according to literature reports:
**S1** & **S22**,[1] **S23**,[2] **S27**,[3] **S28**,[4] **S32**,[5] **S39-S42**,[6] **S43**,[7] **S44**,[8] **S45**,[9] **S46**,[10] **S47**,[11] **S49**,[12] **S50**,[13] and **S51**.[14]

### 2.1 The synthesis of substrates S24–S26 and S29




**2-(Cyclopropylmethyl)-2-phenylpropane-1,3-diol (S24)**




**S24**

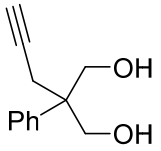
To a suspension of NaH (60% dispensed in mineral oil, 400.0 mg, 10.0 mmol, 2.0 equiv) in dry DMF (15 mL) at 0 °C was slowly added diethyl 2-phenylmalonate (196.0 mg, 5.0 mmol, 1.0 equiv). After stirring for 30 min, KI (830 mg, 5.0 mmol, 1.0 equiv) and cyclopropylmethyl chloride (1.81 g, 20.0 mmol, 4.0 equiv) were added dropwise. The reaction mixture was heated to 80 °C while stirring for 1 d. After completion of the reaction, the mixture was cooled to rt, quenched with saturated $NH_4Cl$ (aq.), and extracted with EtOAc (3x). The combined organic layer was washed with $H_2O$ (4x), dried over $Na_2SO_4$, and concentrated *in vacuo*. The residue was briefly purified by silica gel column chromatography to give the crude diester product.

To a suspension of $LiAlH_4$ (760.0 mg, 20 mmol, 4.0 equiv) in $Et_2O$ (15 mL) at 0 °C was slowly added a solution of the diester obtained above in $Et_2O$ (5 mL). Then the reaction mixture was warmed to rt and stirred for 2 h. Upon completion, the reaction was quenched by slowly, portionwise adding wet $Na_2SO_4$ (4.0 mL water in 32.0 g $Na_2SO_4$) at 0 °C. The resulting mixture was warmed to rt, stirred for additional 30 min, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 2/1) to yield product **S24** as a white solid

(577.1 mg, 56% yield over two steps).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 4H), 7.27 – 7.21 (m, 1H), 4.16 (d, *J* = 10.6 Hz, 2H), 4.00 (d, *J* = 10.7 Hz, 2H), 2.60 (br s, 2H), 1.55 (d, *J* = 6.1 Hz, 2H), 0.42 – 0.28 (m, 3H), −0.01 – −0.06 (m, 2H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 141.8, 128.6, 127.1, 126.5, 68.6, 48.3, 39.9, 5.8, 4.6.
**HRMS** (ESI) *m/z* calcd. for $C_{13}H_{18}NaO_2$ $[M + Na]^+$ 229.1199, found 229.1195.

**2-Phenyl-2-(prop-2-yn-1-yl)propane-1,3-diol (S25)**



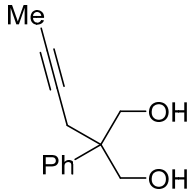

**S25**

To a suspension of NaH (60% dispensed in mineral oil, 240.0 mg, 6.0 mmol, 1.2 equiv) in dry THF (15 mL) at 0 °C was slowly added diethyl 2-phenylmalonate (196.0 mg, 5.0 mmol, 1.0 equiv). After stirring for 30 min, 2-propynyl bromide (0.71 g, 6.0 mmol, 1.2 equiv) was added dropwise. The reaction mixture was warmed to rt and stirred overnight. Upon completion, the reaction was quenched with saturated $NH_4Cl$ (aq.) and extracted with $CH_2Cl_2$ (3x). The combined organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo*. The residue was briefly purified by silica gel column chromatography to give the crude diester product.

To a suspension of $LiAlH_4$ (760.0 mg, 20 mmol, 4.0 equiv) in $Et_2O$ (15 mL) at 0 °C was slowly added a solution of the diester obtained above in $Et_2O$ (5 mL). Then the reaction mixture was warmed to rt and stirred for 2 h. Upon completion, the reaction was quenched by slow, portionwise addition of wet $Na_2SO_4$ (4.0 mL water in 32.0 g $Na_2SO_4$) at 0 °C. The resulting mixture was warmed to rt, stirred for additional 30 min, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 2/1) to yield product **S25** as a white solid (408.0 mg, 43% yield over two steps).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.34 (m, 4H), 7.32 – 7.25 (m, 1H), 4.10 (dd, *J* = 11.1, 5.7 Hz, 2H), 4.00 (dd, *J* = 11.1, 6.0 Hz, 2H), 2.76 (d, *J* = 2.6 Hz, 2H), 2.17 (t, *J* = 6.0 Hz, 2H), 1.99 (t, *J* = 2.6 Hz, 1H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 140.3, 128.8, 127.2, 126.7, 80.9, 71.3, 67.8, 47.4, 23.2.
**HRMS** (ESI) *m/z* calcd. for $C_{12}H_{15}O_2$ $[M + H]^+$ 191.1067, found 191.1064.

**2-(But-2-yn-1-yl)-2-phenylpropane-1,3-diol (S26)**

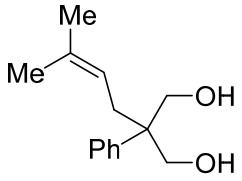



**S26**

The synthesis of substrate **S26** is similar to that of **S25**, and the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **S26** as a white solid (458.8 mg, 45% yield over two steps).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 4H), 7.26 – 7.19 (m, 1H), 3.96 (d, *J* = 11.0 Hz, 2H), 3.87 (d, *J* = 11.0 Hz, 2H), 3.09 (br s, 2H), 2.59 (d, *J* = 2.3 Hz, 2H), 1.68 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 140.8, 128.3, 126.7, 126.6, 78.4, 75.2, 67.3, 47.2, 23.5, 3.4.
**HRMS** (ESI) *m/z* calcd. for $C_{13}H_{16}NaO_2$ $[M + Na]^+$ 227.1043, found 227.1042.

**2-(3-Methylbut-2-en-1-yl)-2-phenylpropane-1,3-diol (S29)**

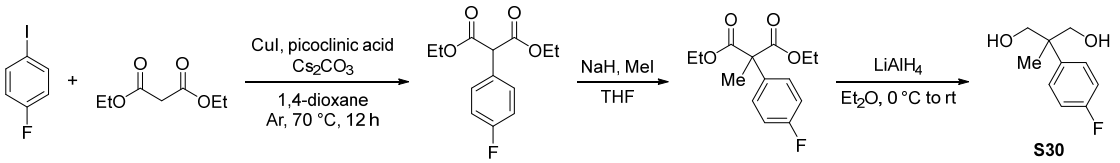



**S29**

The synthesis of substrate **S29** is similar to that of **S25**, and the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **S29** as a white solid (600.0 mg, 55% yield over two steps).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 4H), 7.28 – 7.21 (m, 1H), 4.88 (t, *J* = 7.2 Hz, 1H), 4.06 (dd, *J* = 11.0, 3.3 Hz, 2H), 3.91 (dd, *J* = 11.0, 3.4 Hz, 2H), 2.36 (d, *J* = 7.3 Hz, 2H), 2.32 – 2.11 (m, 2H), 1.61 (s, 3H), 1.55 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 141.4, 134.5, 128.6, 127.1, 126.5, 118.8, 68.5, 47.8, 32.9, 25.9, 17.9.
**HRMS** (ESI) *m/z* calcd. for $C_{14}H_{19}O$ $[M + H - H_2O]^+$ 203.1430, found 203.1427.

**2.2 Synthesis of substrate S30**




**S30**

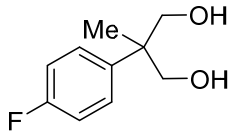
To a solution of CuI (48 mg, 0.25 mmol, 5.0 mol %), 2-picolinic acid (62 mg, 0.50 mmol, 10.0 mol %), $Cs_2CO_3$ (4.89 g, 15 mmol, 3.0 equiv), and diethyl malonate (1.52

mL, 10 mmol, 2.0 equiv) in 1,4-dioxane (5.0 mL) was added 1-fluoro-4-iodobenzene (1.11 g, 5.0 mmol, 1.0 equiv) under argon atmosphere. The mixture was sealed and placed in a preheated oil bath at 70 °C for stirring overnight. Then the reaction mixture was cooled to rt and partitioned between ethyl acetate (EtOAc, 3 × 20 mL) and saturated aqueous $NH_4Cl$ (10 mL). The organic portions were dried over $Na_2SO_4$, filtered, and concentrated by rotary evaporation. The thus-obtained crude product was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 20/1) to give diethyl 2-(4-fluorophenyl)malonate (0.74 g, 2.9 mmol, 58% yield).

To a solution of diethyl 2-(4-fluorophenyl)malonate (0.74 g, 2.9 mmol, 1.0 equiv) in dry THF (3 mL) was added NaH (60% dispensed in mineral oil, 0.15 g, 3.8 mmol, 1.3 equiv) portionwise at 0 °C under argon atmosphere. The resulting mixture was stirred at the same conditions for 30 min before the dropwise addition of methyl iodide (0.49 g, 3.5 mmol, 1.2 equiv). Then the reaction mixture was warmed to rt and stirred overnight. Upon completion, the reaction was quenched with saturated $NH_4Cl$ (aq.) and extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic layers were dried over $Na_2SO_4$, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 20/1) to give diethyl 2-(4-fluorophenyl)-2-methylmalonate (0.59 g, 2.2 mmol, 76% yield).

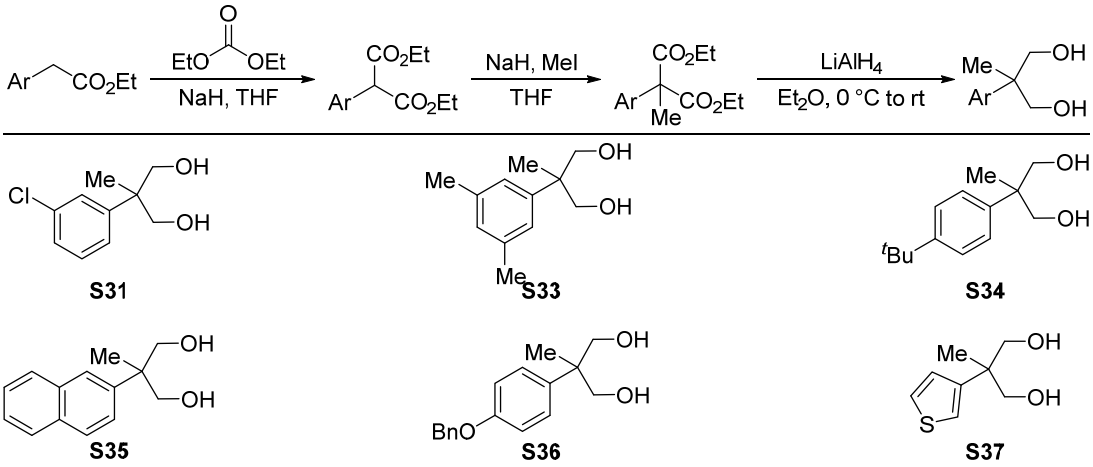
To a suspension of $LiAlH_4$ (0.25 g, 6.6 mmol, 3.0 equiv) in $Et_2O$ (15 mL) was slowly added a solution of diethyl 2-(4-fluorophenyl)-2-methylmalonate (0.59 g, 2.2 mmol) in $Et_2O$ (5 mL) at 0 °C. Then the reaction mixture was warmed to rt and stirred for 2 h. Upon completion, the reaction was quenched by slow, portionwise addition of wet $Na_2SO_4$ (2.0 mL water in 16.0 g $Na_2SO_4$) at 0 °C. The resulting mixture was warmed to rt, stirred for additional 30 min, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 2/1) to give the corresponding diol product **S30** (0.22 g, 1.2 mmol, 55% yield) as a white solid.

**2-(4-Fluorophenyl)-2-methylpropane-1,3-diol (S30)**




**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 2H), 7.05 (t, *J* = 8.7 Hz, 2H), 3.94 (d, *J* = 11.0 Hz, 2H), 3.81 (d, *J* = 11.0 Hz, 2H), 2.13 (br s, 2H), 1.27 (s, 3H).
**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ −116.3 (tt, *J* = 8.2, 5.3 Hz).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 161.5 (d, *J* = 245.5 Hz), 138.8 (d, *J* = 3.2 Hz), 128.3 (d, *J* = 7.7 Hz), 115.4 (d, *J* = 20.8 Hz), 69.9, 44.1, 20.9.
**HRMS** (ESI) *m/z* calcd. for $C_{10}H_{13}FNaO_2$ $[M + Na]^+$ 207.0792, found 207.0790.

## 2.3 The synthesis of substrates S31 and S33–S37




**General procedure I:**

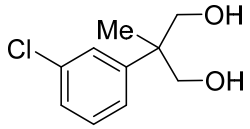
To a suspension of NaH (60% dispensed in mineral oil, 480.0 mg, 12.0 mmol, 2.4 equiv) in dry THF (15 mL) at 0 °C was slowly added the corresponding ester (5.0 mmol, 1.0 equiv). After stirring for 30 min, ethyl carbonate (1.7 g, 15 mmol, 3.0 equiv) was added dropwise. The mixture was warmed to rt and then heated to reflux while stirring under argon atmosphere for 24 h. After cooling to rt, the reaction was quenched by carefully adding saturated $NH_4Cl$ (aq.) and extracted with EtOAc (3x). The combined organic layer was dried over $Na_2SO_4$, filtered, and concentrated. The crude malonate diester product was used directly in the next step without further purification.

To a solution of the crude malonate diester obtained above in dry THF (15 mL) was added NaH (60% dispensed in mineral oil, 240.0 mg, 6.0 mmol, 1.2 equiv) portionwise at 0 °C under argon atmosphere. After stirring for 30 min, methyl iodide (852.0 mg, 6.0 mmol, 1.2 equiv) was added dropwise. The reaction mixture was warmed to rt and stirred overnight. Upon completion, the reaction was quenched with saturated $NH_4Cl$ (aq.) and extracted with $CH_2Cl_2$ (3x). The combined organic layer was dried over $Na_2SO_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography to give the α,α-disubstituted malonate diester product

.

To a suspension of $LiAlH_4$ (0.76 g, 20 mmol, 4.0 equiv) in $Et_2O$ (15 mL) at 0 °C was slowly added a solution of the α,α-disubstituted malonate diester obtained above in $Et_2O$ (5 mL). Then the reaction mixture was warmed to rt and stirred for 2 h. Upon completion, the reaction was quenched by slowly, portionwise adding wet $Na_2SO_4$ (4.0 mL water in 32.0 g $Na_2SO_4$) at 0 °C. The resulting mixture was warmed to rt, stirred for additional 30 min, filtered, and concentrated. The residue was purified by silica gel column chromatography to give the corresponding diol product.

**2-(3-Chlorophenyl)-2-methylpropane-1,3-diol (S31)**

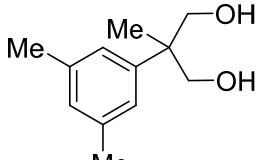



**S31**

According to **General procedure I** with ethyl 2-(3-chlorophenyl)acetate (0.99 g, 5.0 mmol, 1.0 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **S31** as a white solid (350.5 mg, 35% yield over three steps).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.42 (m, 1H), 7.35 – 7.27 (m, 2H), 7.24 (dt, *J* = 7.1, 1.9 Hz, 1H), 3.95 (d, *J* = 10.9 Hz, 2H), 3.83 (d, *J* = 11.0 Hz, 2H), 2.18 (br s, 2H), 1.27 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 145.4, 134.6, 129.8, 127.1, 126.9, 124.9, 69.9, 44.6, 20.8.
**HRMS** (ESI) *m/z* calcd. for $C_{10}H_{13}ClNaO_2$ $[M + Na]^+$ 223.0496, found 223.0493.

**2-(3,5-Dimethylphenyl)-2-methylpropane-1,3-diol (S33)**

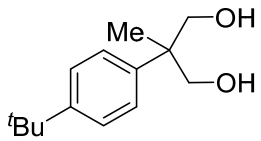



**S33**

According to **General procedure I** with ethyl 2-(3,5-dimethylphenyl)acetate (0.96 g, 5.0 mmol, 1.0 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **S33** as a white solid (475.8 mg, 49% yield over three steps).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.96 (s, 2H), 6.85 (s, 1H), 3.83 (d, *J* = 10.9 Hz, 2H), 3.67 (d, *J* = 11.0 Hz, 2H), 3.21 (br s, 2H), 2.29 (s, 6H), 1.23 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 143.0, 137.7, 128.1, 124.2, 69.3, 44.0, 21.4, 20.5.
**HRMS** (ESI) *m/z* calcd. for $C_{12}H_{18}NaO_2$ $[M + Na]^+$ 217.1199, found 217.1200.

**2-(4-(*tert*-Butyl)phenyl)-2-methylpropane-1,3-diol (S34)**

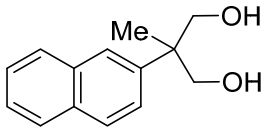



**S34**

According to **General procedure I** with ethyl 2-(4-(*tert*-butyl)phenyl)acetate (1.10 g, 5.0 mmol, 1.0 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **S34** as a white solid (488.2 mg, 44% yield over three steps).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 4H), 3.97 (dd, *J* = 11.0, 6.0 Hz, 2H), 3.84 (dd, *J* = 11.0, 5.9 Hz, 2H), 1.96 (t, *J* = 6.0 Hz, 2H), 1.32 (s, 9H), 1.31 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CD_3OD$) δ 152.4, 145.0, 130.1, 128.6, 71.7, 48.0, 37.6, 34.3, 23.1.
**HRMS** (ESI) *m/z* calcd. for $C_{14}H_{22}NaO_2$ $[M + Na]^+$ 245.1512, found 245.1508.

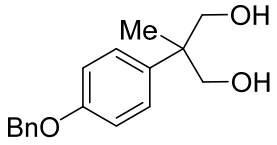
**2-Methyl-2-(naphthalen-2-yl)propane-1,3-diol (S35)**




**S35**

According to **General procedure I** with ethyl methyl 2-(naphthalen-2-yl)acetate (2.0 g, 10 mmol, 1.0 equiv), the reaction mixture was purified by column chromatography on silica gel to give product **S35** (0.53 g, 25% yield over three steps) as a white solid.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.74 (m, 4H), 7.58 – 7.51 (m, 1H), 7.51 – 7.40 (m, 2H), 4.04 (d, *J* = 11.0 Hz, 2H), 3.89 (d, *J* = 11.1 Hz, 2H), 2.32 (br s, 2H), 1.35 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 140.3, 133.4, 132.2, 128.4, 128.0, 127.4, 126.2, 125.9, 125.8, 124.7, 70.0, 44.8, 20.9.
**HRMS** (ESI) *m/z* calcd. for $C_{14}H_{16}NaO_2$ $[M + Na]^+$ 239.1043, found 239.1038.

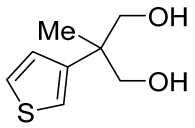
**2-(4-(Benzyloxy)phenyl)-2-methylpropane-1,3-diol (S36)**




**S36**

According to **General procedure I** with ethyl 2-(4-(benzyloxy)phenyl)acetate (1.35 g, 5.0 mmol, 1.0 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **S36** as a white solid (340.0 mg, 25% yield over three steps).
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.29 (m, 7H), 7.01 – 6.94 (m, 2H), 5.05 (s, 2H), 3.91 (dd, *J* = 10.9, 5.7 Hz, 2H), 3.79 (dd, *J* = 11.0, 5.6 Hz, 2H), 2.14 (t, *J* = 5.8 Hz, 2H), 1.27 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CD_3OD$) δ 157.4, 136.9, 135.0, 128.6, 128.0, 127.8, 127.4, 114.9, 70.2, 44.0, 20.8.
**HRMS** (ESI) *m/z* calcd. for $C_{17}H_{20}NaO_3$ $[M + Na]^+$ 295.1305, found 295.1300.

**2-Methyl-2-(thiophen-3-yl)propane-1,3-diol (S37)**

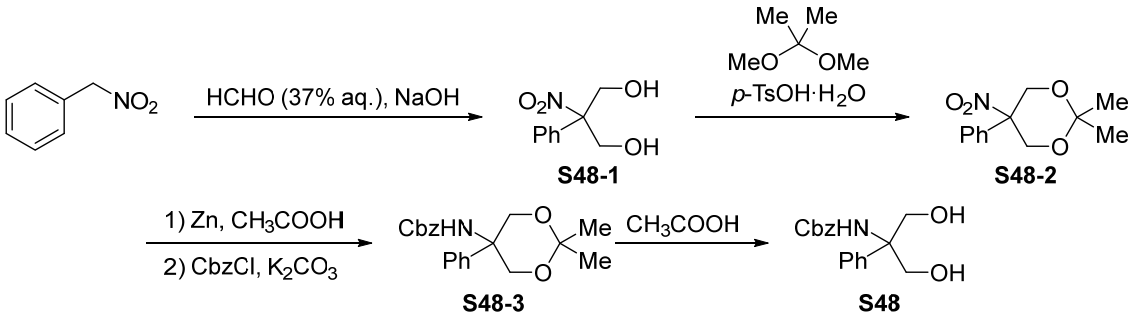



**S37**

According to **General procedure I** with ethyl 2-(thiophen-3-yl)acetate (0.85 g, 5.0 mmol, 1.0 equiv). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **S37** as a white solid (154.6 mg, 18% yield over three steps).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.21 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.13 (dd, *J* = 5.0, 1.4 Hz, 1H), 3.89 (dd, *J* = 10.9, 5.9 Hz, 2H), 3.80 (dd, *J* = 10.9, 6.0 Hz, 2H), 2.02 – 1.94 (m, 2H), 1.32 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 144.4, 126.1, 126.0, 121.0, 69.9, 43.5, 20.6.
**HRMS** (ESI) *m/z* calcd. for $C_8H_{12}NaO_2S$ $[M + Na]^+$ 195.0450, found 195.0449.

**2.4 The synthesis of substrate S48**




To a solution of phenylnitromethane (4.66 g, 34.0 mmol) in a mixture of EtOH (46 mL) and 1,4-dioxane (19 mL) were added aqueous NaOH (1.0 M, 0.19 mL, 0.19 mmol, 0.5 mol %) and formalin (37% aq., 5.6 mL, 68 mmol, 2.0 equiv) at rt, and the mixture was stirred under the same conditions for 5 h. After the evaporation of all volatile materials *in vacuo*, $H_2O$ (45 mL) was added. The mixture was extracted with EtOAc (3 × 45 mL) and the combined organic layer was dried, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to afford the diol **S48-1** (4.74 g, 71% yield).

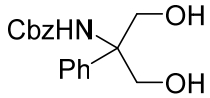
To a solution of **S48-1** (3.43 g, 17.4 mmol) in acetone (40 mL) were added *p*-TsOH·$H_2O$ (330.9 mg, 1.74 mmol, 0.10 equiv) and 2,2-dimethoxypropane (2.4 mL, 19 mmol, 1.1 equiv) at rt and the resulting mixture was stirred under the same conditions for 2 h. Upon completion, the reaction was quenched by adding $Et_3N$ (0.34 mL, 2.4 mmol, 0.14 equiv) and stirred at rt for 30 min. The resulting mixture was concentrated *in vacuo*. The residue was purified by column chromatography (petroleum ether/EtOAc = 5/1) to provide the acetonide **S48-2** (3.71 g, 90% yield).

To a solution of **S48-2** (1.427 g, 6.0 mmol) in $CH_3COOH$ (36 mL) were added zinc powders (1.56 g, 72.0 mmol, 12.0 equiv) at 15-min intervals within 3 h at rt. Upon completion, the reaction mixture was filtered and the filtrate was concentrated *in vacuo*. The residue was diluted with $CH_2Cl_2$ (30 mL), washed with saturated $NaHCO_3$ (30 mL), dried over $Na_2SO_4$, filtered, and concentrated *in vacuo* to provide the crude amine.

To a solution of the crude amine in THF/$H_2O$ (1/1 v/v, 10 mL) were successively added $K_2CO_3$ (1.59 g, 11.5 mmol, 2.0 equiv) and benzyl chloroformate (0.96 mL, 6.9 mmol, 1.2 equiv) at 0 °C while stirring. The resulting reaction mixture was stirred at rt for 3 h. Upon completion, the reaction was quenched by dropwise adding aqueous 3N HCl until the pH reached ~3. Next, the reaction mixture was extracted with EtOAc (2 × 15 mL). The combined organic layer was washed with water (1 × 15 mL) and brine (1 × 15 mL), dried over $Na_2SO_4$, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to afford **S48-3**.

A mixture of the thus-obtained **S48-3** (35 mL) in acetic acid and $H_2O$ (4/1 v/v, 35 mL) was heated at 60 °C for 1 h. Upon completion, all the volatile materials were removed *in vacuo* and the residue was purified by column chromatography (petroleum ether/EtOAc = 50/1 to 1/3) to offer product **S48** as a white solid (1.48 g, 86% over three steps).

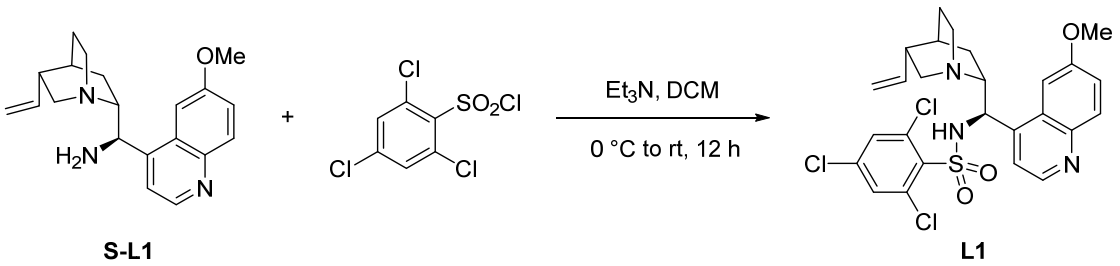
**Benzyl (1,3-dihydroxy-2-phenylpropan-2-yl) carbamate (S48)**




**S48**

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 10H), 5.91 (s, 1H), 5.11 (s, 2H), 4.00 (dd, *J* = 11.8, 5.0 Hz, 2H), 3.92 (dd, *J* = 11.8, 5.4 Hz, 2H), 3.31 (s, 2H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 156.8, 139.5, 136.1, 128.8, 128.6, 128.3, 128.2, 127.8, 126.0, 67.8, 67.2, 63.9.
**HRMS** (ESI) *m/z* calcd. for $C_{17}H_{20}NO_4$ $[M + H]^+$ 302.1387, found 302.1380.

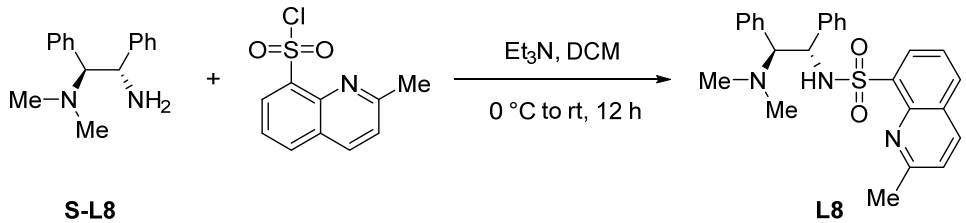
## 3. Synthesis of catalysts




To a solution of amine **S-L1** (1.62 g, 5.0 mmol, 1.0 equiv) in anhydrous $CH_2Cl_2$ (10 mL) were successively added 2,4,6-trichlorobenzenesulfonyl chloride (1.68 g, 6.0 mmol, 1.2 equiv) and $Et_3N$ (1.67 mL, 12.0 mmol, 2.0 equiv) under argon at 0 °C. The reaction mixture was stirred for 12 h at rt, and quenched by $H_2O$. The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phase was washed with brine, dried over $Na_2SO_4$, concentrated, and purified by silica gel flash column chromatography (eluent: $CH_2Cl_2$/MeOH = 20:1 to 10:1) to afford product **L1** as a white solid (2.60 g, 92% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.3 Hz, 1H × 0.6), 8.55 (d, *J* = 4.6 Hz, 1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.90 (d, *J* = 9.2 Hz, 1H × 0.6), 7.46 (d, *J* = 2.7 Hz, 1H × 0.6), 7.38 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.34 – 7.19 (m, 4H + 2H × 0.6), 6.94 (s, 2H × 0.6), 5.94 – 5.78 (m, 1H + 1H × 0.6), 5.20 – 4.97 (m, 3H + 2H × 0.6), 4.50 (d, *J* = 10.7 Hz, 1H × 0.6), 3.96 (s, 3H), 3.95 (s, 3H × 0.6), 3.41 (q, *J* = 9.3 Hz, 1H × 0.6), 3.05 – 2.80 (m, 5H + 2H × 0.6), 2.73 – 2.61 (m, 1H + 1H × 0.6), 2.37 – 2.24 (m, 1H + 1H × 0.6), 1.79 – 1.65 (m, 1H + 1H × 0.6), 1.63 – 1.45 (m, 2H + 2H × 0.6), 1.33 – 1.17 (m, 1H + 2H × 0.6), 1.06 – 0.82 (m, 1H + 2H × 0.6).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 158.0, 156.8, 147.3, 147.0, 144.7, 144.5, 142.8, 140.5, 139.7, 139.0, 137.7, 137.4, 136.0, 135.5, 134.2, 133.4, 131.9, 131.6, 130.6, 130.4, 128.2, 126.5, 124.8, 122.4, 120.6, 119.8, 115.1, 114.6, 103.2, 100.3, 62.6, 61.2, 55.9, 55.5, 55.4, 52.7, 49.3, 49.0, 46.3, 39.0, 38.4, 27.4, 27.2, 26.4, 25.6, 24.4.
**HRMS** (ESI) *m/z* calcd. for $C_{26}H_{27}Cl_3N_3O_3S$ $[M + H]^+$ 566.0833, found 566.0825.

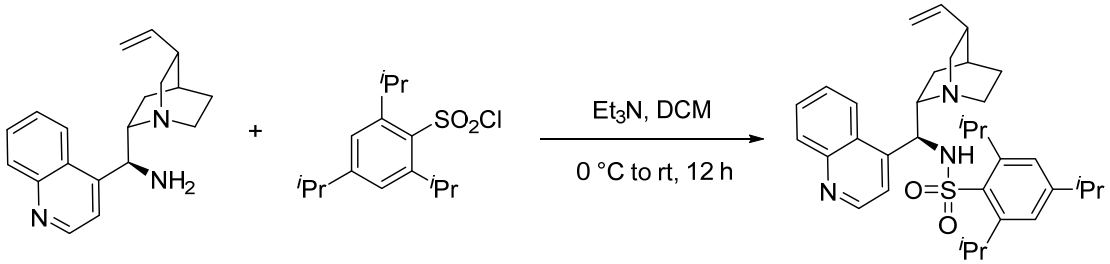
The structure of **L1** was further confirmed by X-ray diffraction analysis (Figure S1).




To a solution of amine **S-L8** (1.20 g, 5.0 mmol, 1.0 equiv) in anhydrous $CH_2Cl_2$ (10 mL) were successively added 2-methylquinoline-8-sulfonyl chloride (1.45 g, 6.0 mmol, 1.2 equiv) and $Et_3N$ (1.67 mL, 12.0 mmol, 2.0 equiv) under argon at 0 °C. The reaction

mixture was stirred for 12 h at rt and quenched by $H_2O$. The organic layer was separated, and the aqueous layer was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic phase was washed with brine, dried over $Na_2SO_4$, concentrated, and purified by silica gel flash column chromatography (eluent: $CH_2Cl_2$/MeOH = 20:1 to 10:1) to afford product **L8** as a white solid (1.80 g, 81% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 7.3, 1.5 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H + 1H), 7.97 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.19 – 7.05 (m, 5H), 7.05 – 6.93 (m, 3H), 6.80 (dd, *J* = 6.6, 2.9 Hz, 2H), 4.48 (d, *J* = 10.8 Hz, 1H), 3.63 (d, *J* = 10.8 Hz, 1H), 2.89 (s, 3H), 1.58 (s, 6H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 160.2, 143.3, 140.5, 136.5, 136.2, 132.7, 131.5, 130.6, 129.8, 128.1, 127.6, 127.5, 127.4, 126.9, 126.9, 124.6, 123.0, 73.9, 58.4, 40.2, 25.9.
**HRMS** (ESI) *m/z* calcd. for $C_{26}H_{28}N_3O_2S$ $[M + H]^+$ 446.1897, found 446.1890.

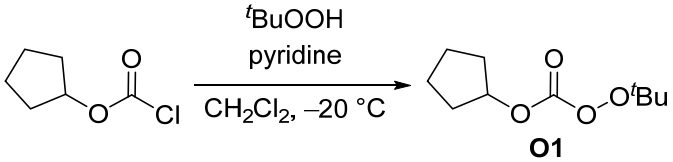



**S-L9** **L9**

To a solution of amine **S-L9** (1.47 g, 5.0 mmol, 1.0 equiv) in anhydrous $CH_2Cl_2$ (10 mL) were successively added 2,4,6-triisopropylbenzenesulfonyl chloride (1.82 g, 6.0 mmol, 1.2 equiv.) and $Et_3N$ (1.67 mL, 12.0 mmol, 2.0 equiv) under argon at 0 °C. The reaction mixture was stirred for 12 h at rt and was quenched by $H_2O$. The organic layer was separated and the aqueous layer was extracted with $CH_2Cl_2$ (3 ×). The combined organic phase was washed with brine, dried with anhydrous $Na_2SO_4$, concentrated, and purified over silica gel flash column chromatography (eluent: $CH_2Cl_2$:MeOH = 20:1 ~ 10:1) to afford the products **L9** as a white solid (1.68 g, 60% yield).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.80 (s, 1H×0.2), 8.50 (d, *J* = 4.4 Hz, 1H), 8.43 (d, *J* = 8.8 Hz, 1H×0.2), 8.28 (d, *J* = 8.4 Hz, 1H), 8.07 – 8.05 (m, 1H+1H×0.2), 7.71 (t, *J* = 7.6 Hz, 1H), 7.64 – 7.60 (m, 1H+1H×0.2), 7.34 – 7.30 (m, 2H×0.2), 7.18 (d, *J* = 4.8 Hz, 1H), 6.93 – 6.90 (m, 2H+2H×0.2), 5.68 – 5.53 (m, 1H+1H×0.2), 5.36 (d, *J* = 10.4 Hz, 1H), 4.95 – 4.82 (m, 2H+2H×0.2), 4.58 (d, *J* = 10.8 Hz, 1H×0.2), 3.91 – 3.78 (m, 2H+2H×0.2), 3.25 – 3.19 (m, 1H+2H×0.2), 3.11 – 3.03 (m, 1H), 2.83 – 2.65 (m, 4H+4H×0.2), 2.27 (s, 1H+1H×0.2), 1.67 – 1.53 (m, 3H+3H×0.2), 1.21 – 1.19 (m, 14H+14H×0.2), 1.05 – 1.03 (m, 1H+1H×0.2), 0.96 – 0.91 (m, 6H×0.2), 0.76 (d, *J* = 7.8 Hz, 6H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 149.7, 149.4, 141.2, 130.3, 129.1, 126.9, 123.1, 122.7, 120.0, 114.7, 61.9, 55.8, 52.6, 40.3, 39.6, 34.1, 29.6, 27.8, 27.4, 25.1, 24.9, 24.0, 23.7, 23.6.
**HRMS** (ESI) *m/z* calcd. for $C_{34}H_{46}N_3O_2S$ $[M+H]^+$ 560.3305, found 560.3306.

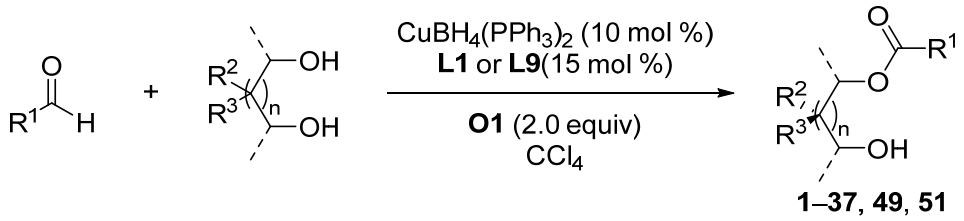
## 4. Synthesis of the oxidant




**O1**

**O1** was prepared from cyclopentyl carbonochloridate in 85% yield according to a literature procedure.[15]

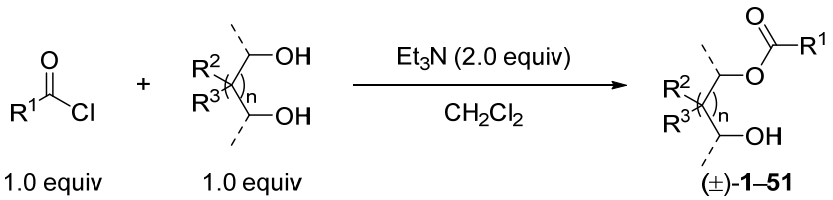
## 5. Cu-catalyzed enantioselective desymmetrizing radical C–O coupling with 2,2-dicarbofunctionalized 1,3-diols, 2-substituted-2-chloro-1,3-diols, and *meso* 1,4-diols




**General procedure A:**

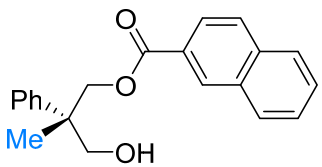
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (12.0 mg, 0.020 mmol, 10 mol %), **L1** or **L9** (0.030 mmol, 15 mol %), diol (0.30 mmol, 1.5 equiv), corresponding fresh aldehyde (0.20 mmol, 1.0 equiv), and anhydrous $CCl_4$ (4.0 mL). Then, **O1** (80.9 mg, 0.40 mmol, 2.0 equiv) was added to the mixture and the reaction mixture was stirred at rt. Upon completion (monitored by TLC), the reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel to afford the desired product.

The preparation of racemic product (±)-**1**–**51**:




To the mixture of diol (0.10 mmol, 1.0 equiv) and $Et_3N$ (27.7 μL, 0.20 mmol, 2.0 equiv) in dry $CH_2Cl_2$ (1.0 mL) was added the corresponding acyl chloride (0.10 mmol, 1.0 equiv) at rt. After stirring for 24 h, the reaction was quenched by adding saturated $NH_4Cl$ (aq.). Then, the mixture was extracted with $CH_2Cl_2$ (3x) and the combined organic layer was dried over $Na_2SO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography to afford the desired racemic product.

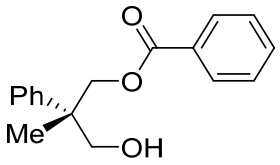
**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 2-naphthoate (1)**



According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum

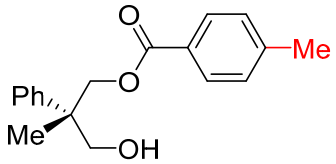
ether/EtOAc = 3/1) to yield product **1** as a colorless oil (46.1 mg, 72% yield, 93% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), $t_R$ (major) = 18.45 min, $t_R$ (minor) = 22.17 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.02 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.89 – 7.82 (m, 2H), 7.63 – 7.48 (m, 4H), 7.45 – 7.37 (m, 2H), 7.34 – 7.27 (m, 1H), 4.69 (d, *J* = 0.9 Hz, 2H), 3.91 (s, 2H), 2.52 (br s, 1H), 1.53 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.1, 142.8, 135.6, 132.5, 131.3, 129.4, 128.7, 128.4, 128.3, 127.8, 127.2, 126.9, 126.8, 126.6, 125.2, 69.2, 68.0, 44.2, 20.8.
**HRMS** (ESI) *m/z* calcd. for $C_{21}H_{20}NaO_3$ $[M + Na]^+$ 343.1305, found 343.1300.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl benzoate (2)**




According to **General procedure A** with benzaldehyde (21.2 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **2** as a colorless oil (46.8 mg, 86% yield, 92% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (major) = 11.37 min, $t_R$ (minor) = 14.87 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.04 – 7.93 (m, 2H), 7.61 – 7.51 (m, 1H), 7.49 – 7.34 (m, 6H), 7.32 – 7.26 (m, 1H), 4.60 (s, 2H), 3.84 (s, 2H), 1.46 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.9, 142.6, 133.2, 129.9, 129.7, 128.7, 128.5, 126.9, 126.5, 68.9, 68.0, 44.1, 20.8.
**HRMS** (ESI) *m/z* calcd. for $C_{17}H_{18}NaO_3$ $[M + Na]^+$ 293.1148, found 293.1144 .

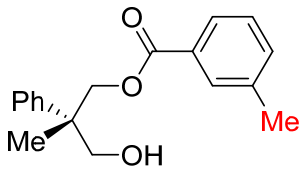
**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 4-methylbenzoate (3)**




According to **General procedure A** with *p*-tolualdehyde (24.0 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **3** as a colorless oil (46.0 mg, 81% yield, 93% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), $t_R$ (major) = 12.31 min, $t_R$ (minor) = 14.54 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.82 (m, 2H), 7.51 – 7.43 (m, 2H), 7.43 – 7.34 (m, 2H), 7.30 – 7.26 (m, 1H), 7.25 – 7.19 (m, 2H), 4.58 (s, 2H), 3.82 (s, 2H), 2.40 (s, 3H), 1.45 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.0, 144.0, 142.7, 129.7, 129.2, 128.7, 127.1, 126.9, 126.5, 68.7, 67.9, 44.1, 21.7, 20.8.

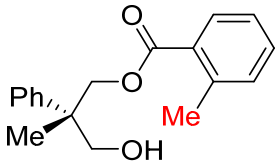
**HRMS** (ESI) *m/z* calcd. for $C_{18}H_{20}NaO_3$ $[M + Na]^+$ 307.1305, found 307.1299 .

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 3-methylbenzoate (4)**



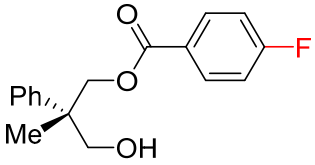

According to **General procedure A** with *m*-tolualdehyde (24.0 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **4** as a colorless oil (48.0 mg, 84% yield, 93% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), $t_R$ (major) = 10.31 min, $t_R$ (minor) = 14.40 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 2H), 7.50 – 7.43 (m, 2H), 7.41 – 7.35 (m, 3H), 7.34 – 7.26 (m, 2H), 4.59 (s, 2H), 3.83 (s, 2H), 2.39 (s, 3H), 1.46 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.1, 142.6, 138.3, 134.0, 130.2, 129.8, 128.7, 128.4, 126.9, 126.8, 126.6, 68.8, 67.9, 44.1, 21.3, 20.8.
**HRMS** (ESI) *m/z* calcd. for $C_{18}H_{20}NaO_3$ $[M + Na]^+$ 307.1305, found 307.1300.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 2-methylbenzoate (5)**



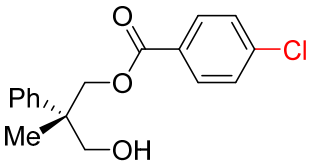

According to **General procedure A** with *o*-tolualdehyde (24.0 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **5** as a colorless oil (39.0 mg, 68% yield, 90% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), $t_R$ (major) = 10.15 min, $t_R$ (minor) = 15.72 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.42 – 7.33 (m, 3H), 7.31 – 7.17 (m, 3H), 4.59 (d, *J* = 2.1 Hz, 2H), 3.83 (d, *J* = 1.3 Hz, 2H), 2.52 (s, 3H), 1.46 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.9, 142.6, 140.4, 132.2, 131.8, 130.6, 129.3, 128.7, 126.9, 126.5, 125.8, 68.9, 68.1, 44.0, 21.8, 20.9.
**HRMS** (ESI) *m/z* calcd. for $C_{18}H_{20}NaO_3$ $[M + Na]^+$ 307.1305, found 307.1300.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 4-fluorobenzoate (6)**



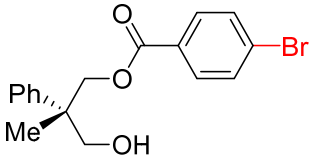
According to **General procedure A** with 4-fluorobenzaldehyde (24.8 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **6** as a colorless oil (46.0 mg, 80% yield, 93% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (major) = 9.67 min, $t_R$ (minor) = 11.41 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.08 – 7.90 (m, 2H), 7.48 – 7.42 (m, 2H), 7.42 – 7.34 (m, 2H), 7.32 – 7.27 (m, 1H), 7.14 – 7.05 (m, 2H), 4.60 (d, *J* = 1.3 Hz, 2H), 3.83 (s, 2H), 1.46 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 165.9, 165.9 (d, *J* = 254.2 Hz), 142.5, 132.2 (d, *J* = 9.3 Hz), 128.7, 127.0, 126.5, 126.2 (d, *J* = 3.1 Hz), 115.6 (d, *J* = 22.0 Hz), 69.0, 68.0, 44.1, 20.8.
**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ −105.2 (tt, *J* = 8.5, 5.4 Hz, 1F).
**HRMS** (ESI) *m/z* calcd. for $C_{17}H_{17}FNaO_3$ $[M + Na]^+$ 311.1054, found 311.1049.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 4-chlorobenzoate (7)**




According to **General procedure A** with 4-chlorobenzaldehyde (28.2 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **7** as a pale-yellow oil (49.0 mg, 80% yield, 94% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (major) = 11.57 min, $t_R$ (minor) = 12.54 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.0 – 7.8 (m, 2H), 7.5 – 7.4 (m, 2H), 7.4 – 7.3 (m, 4H), 7.3 – 7.3 (m, 1H), 4.6 (d, *J* = 2.0 Hz, 2H), 3.8 (s, 2H), 1.5 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.0, 142.4, 139.7, 131.0, 128.8, 128.7, 128.4, 127.0, 126.5, 69.1, 68.0, 44.1, 20.8.
**HRMS** (ESI) *m/z* calcd. for $C_{17}H_{17}ClNaO_3$ $[M + Na]^+$ 327.0758, found 327.0754.

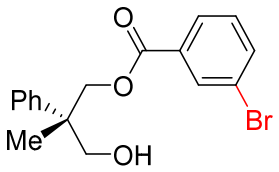
**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 4-bromobenzoate (8)**




According to **General procedure A** with 4-bromobenzaldehyde (37.0 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **8** as a light-yellow solid (52.2 mg, 75% yield, 93% ee).

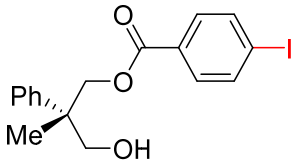
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm), $t_R$ (major) = 24.12 min, $t_R$ (minor) = 25.65 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 2H), 7.59 – 7.52 (m, 2H), 7.46 – 7.41 (m, 2H), 7.41 – 7.34 (m, 2H), 7.32 – 7.23 (m, 1H), 4.59 (d, *J* = 2.4 Hz, 2H), 3.82 (s, 2H), 1.45 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.1, 142.4, 131.8, 131.1, 128.8, 128.7, 128.3, 127.0, 126.5, 69.2, 68.0, 44.1, 20.8.
**HRMS** (ESI) *m/z* calcd. for $C_{17}H_{17}BrNaO_3$ $[M + Na]^+$ 371.0253, found 371.0248.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 3-bromobenzoate (9)**




According to **General procedure A** with 3-bromobenzaldehyde (37.0 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **9** as a pale-yellow oil (44.0 mg, 63% yield, 92% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (major) = 10.87 min, $t_R$ (minor) = 16.56 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.09 (t, *J* = 1.8 Hz, 1H), 7.89 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.73 – 7.63 (m, 1H), 7.49 – 7.42 (m, 2H), 7.42 – 7.34 (m, 2H), 7.34 – 7.27 (m, 2H), 4.60 (s, 2H), 3.84 (d, *J* = 1.9 Hz, 2H), 1.46 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 165.5, 142.3, 136.1, 132.6, 131.9, 130.0, 128.7, 128.2, 127.0, 126.5, 122.5, 69.3, 68.0, 44.1, 20.7.
**HRMS** (ESI) *m/z* calcd. for $C_{17}H_{17}BrNaO_3$ $[M + Na]^+$ 371.0253, found 371.0249.

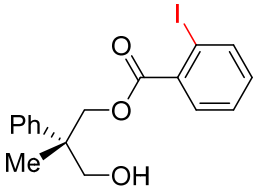
**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 4-iodobenzoate (10)**




According to **General procedure A** with 4-iodobenzaldehyde (46.4 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **10** as a pale-yellow oil (60.0 mg, 76% yield, 93% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), $t_R$ (major) = 18.42 min, $t_R$ (minor) = 20.44 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 2H), 7.71 – 7.58 (m, 2H), 7.49 – 7.33 (m, 4H), 7.32 – 7.26 (m, 1H), 4.59 (t, *J* = 2.2 Hz, 2H), 3.82 (s, 2H), 1.45 (s, 3H).

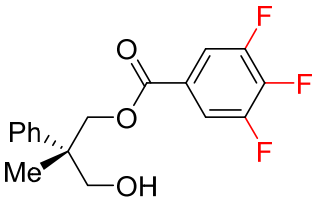
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.4, 142.4, 137.8, 131.0, 129.4, 128.7, 127.0, 126.5, 101.0, 69.2, 68.0, 44.1, 20.8.
**HRMS** (ESI) *m/z* calcd. for $C_{17}H_{17}INaO_3$ $[M + Na]^+$ 419.0115, found 419.0107.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 2-iodobenzoate (11)**




According to **General procedure A** with 2-iodobenzaldehyde (46.4 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **11** as a pale-yellow oil (16.0 mg, 20% yield, 90% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_R$ (major) = 8.30 min, $t_R$ (minor) = 13.60 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.65 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.41 – 7.33 (m, 3H), 7.31 – 7.26 (m, 1H), 7.20 – 7.05 (m, 1H), 4.63 (d, *J* = 1.0 Hz, 2H), 3.86 (d, *J* = 2.3 Hz, 2H), 1.46 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.8, 142.4, 141.4, 135.0, 132.8, 131.0, 128.7, 128.0, 127.0, 126.6, 94.1, 69.7, 68.1, 44.0, 20.9.
**HRMS** (ESI) *m/z* calcd. for $C_{17}H_{17}INaO_3$ $[M + Na]^+$ 419.0115, found 419.0107.

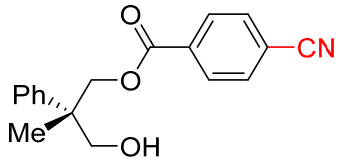
**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 3,4,5-trifluorobenzoate (12)**




According to **General procedure A** with 3,4,5-trifluorobenzaldehyde (32.0 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **12** as a pale-yellow oil (44.0 mg, 68% yield, 93% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (major) = 8.32 min, $t_R$ (minor) = 10.36 min.
**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 2H), 7.51 – 7.37 (m, 4H), 7.32 – 7.27 (m, 1H), 4.61 (q, *J* = 11.1 Hz, 2H), 3.96 – 3.72 (m, 2H), 1.46 (s, 3H).
**$^{13}$C NMR** (151 MHz, $CDCl_3$) δ 164.0, 151.0 (ddd, *J* = 252.2, 10.2, 3.5 Hz), 143.2 (dt, *J* = 259.9, 15.3 Hz), 142.1, 128.8, 127.1, 126.4, 125.9 (dt, *J* = 7.4, 3.6 Hz), 114.2 (dd, *J* = 17.5, 4.9 Hz), 69.8, 68.0, 44.0, 20.7.
**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ −132.2 – −132.6 (m, 2F), −152.2 (tt, *J* = 20.1, 6.6 Hz, 1F).

**HRMS** (ESI) *m/z* calcd. for $C_{17}H_{15}F_3NaO_3$ $[M + Na]^+$ 347.0866, found 347.0861.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 4-cyanobenzoate (13)**




According to **General procedure A** with 4-formylbenzonitrile (26.2 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **13** as a pale-yellow oil (40.0 mg, 68% yield, 84% ee).

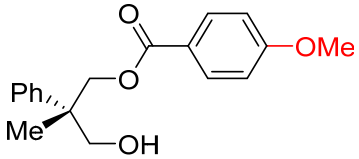
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_R$ (major) = 9.72 min, $t_R$ (minor) = 11.50 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.11 – 7.99 (m, 2H), 7.78 – 7.66 (m, 2H), 7.48 – 7.35 (m, 4H), 7.33 – 7.26 (m, 1H), 4.77 – 4.53 (m, 2H), 3.84 (d, *J* = 1.9 Hz, 2H), 1.47 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 165.1, 142.2, 133.8, 132.3, 130.1, 128.8, 127.1, 126.4, 117.9, 116.6, 69.7, 68.1, 44.0, 20.7.

**HRMS** (ESI) *m/z* calcd. for $C_{18}H_{17}NNaO_3$ $[M + Na]^+$ 318.1101, found 318.1097.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 4-methoxybenzoate (14)**




According to **General procedure A** with 4-methoxybenzaldehyde (27.2 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **14** as a light-yellow solid (46.0 mg, 76% yield, 92% ee).

**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_R$ (major) = 9.23 min, $t_R$ (minor) = 10.50 min.

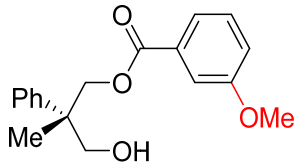
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.00 – 7.88 (m, 2H), 7.50 – 7.43 (m, 2H), 7.37 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.31 – 7.23 (m, 1H), 6.94 – 6.85 (m, 2H), 4.57 (s, 2H), 3.85 (s, 3H), 3.81 (s, 2H), 1.44 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.7, 163.6, 142.7, 131.7, 128.6, 126.9, 126.6, 122.3, 113.7, 68.6, 67.9, 55.5, 44.1, 20.8.

**HRMS** (ESI) *m/z* calcd. for $C_{18}H_{20}NaO_4$ $[M + Na]^+$ 323.1254, found 323.1249.

The structure of **14** was further confirmed by X-ray diffraction analysis (Figure S2).

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 3-methoxybenzoate (15)**




According to **General procedure A** with 3-methoxybenzaldehyde (27.2 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **15** as a pale-yellow oil (47.4 mg, 79% yield, 93% ee).

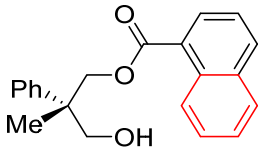
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (major) = 7.54 min, $t_R$ (minor) = 9.23 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.56 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.32 (d, *J* = 1.3 Hz, 4H), 7.09 (ddd, *J* = 8.3, 2.7, 1.0 Hz, 1H), 4.59 (d, *J* = 1.0 Hz, 2H), 3.83 (s, 2H), 3.82 (s, 3H), 1.45 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.8, 159.6, 142.6, 131.2, 129.5, 128.7, 126.9, 126.5, 122.0, 119.6, 114.2, 69.0, 68.0, 55.4, 44.1, 20.8.

**HRMS** (ESI) *m/z* calcd. for $C_{18}H_{20}NaO_4$ $[M + Na]^+$ 323.1254, found 323.1249.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 1-naphthoate (16)**




According to **General procedure A** with 1-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **16** as a light-yellow solid (44.0 mg, 69% yield, 85% ee).

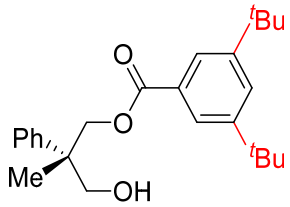
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_R$ (major) = 8.28 min, $t_R$ (minor) = 15.06 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.86 – 8.66 (m, 1H), 8.06 (dd, *J* = 7.3, 1.3 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.92 – 7.81 (m, 1H), 7.60 – 7.35 (m, 7H), 7.33 – 7.26 (m, 1H), 4.84 – 4.61 (m, 2H), 3.88 (s, 2H), 1.50 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.9, 142.7, 133.8, 133.6, 131.3, 130.3, 128.7, 128.6, 127.9, 127.0, 126.6, 126.3, 125.8, 124.5, 69.3, 68.2, 44.1, 21.0.

**HRMS** (ESI) *m/z* calcd. for $C_{21}H_{20}NaO_3$ $[M + Na]^+$ 343.1305, found 343.1301.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 3,5-di-tert-butylbenzoate (17)**




According to **General procedure A** with 3,5-di-*tert*-butylbenzaldehyde (46.8 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **17** as a pale-yellow oil (58.1 mg, 76% yield, 88% ee).

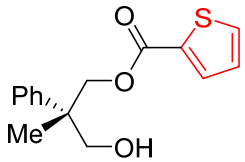
**HPLC** analysis: Chiralcel OD-3 (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min, λ = 254 nm), $t_R$ (major) = 8.87 min, $t_R$ (minor) = 9.92 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 1.9 Hz, 2H), 7.63 (t, *J* = 1.9 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.44 – 7.33 (m, 2H), 7.31 – 7.23 (m, 1H), 4.65 – 4.49 (m, 2H), 3.83 (s, 2H), 1.47 (s, 3H), 1.32 (s, 18H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.6, 151.2, 142.7, 129.2, 128.6, 127.4, 126.9, 126.6, 123.9, 68.9, 67.8, 44.2, 34.9, 31.3, 20.7.

**HRMS** (ESI) *m/z* calcd. for $C_{25}H_{34}NaO_3$ $[M + Na]^+$ 405.2400, found 405.2394.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl thiophene-2-carboxylate (18)**




According to **General procedure A** with thiophene-2-carbaldehyde (22.4 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **18** as a pale-yellow oil (44.0 mg, 80% yield, 94% ee).

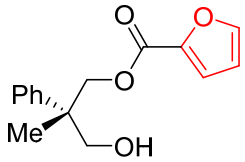
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), $t_R$ (major) = 14.68 min, $t_R$ (minor) = 19.05 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.70 (m, 1H), 7.64 – 7.52 (m, 1H), 7.50 – 7.33 (m, 4H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.15 – 7.01 (m, 1H), 4.55 (s, 2H), 3.83 (s, 2H), 1.44 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 162.5, 142.4, 133.7, 133.4, 132.8, 128.7, 127.9, 127.0, 126.6, 69.0, 67.9, 44.1, 20.6.

**HRMS** (ESI) *m/z* calcd. for $C_{15}H_{16}NaO_3S$ $[M + Na]^+$ 299.0712, found 299.0708.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl furan-2-carboxylate (19)**




According to **General procedure A** with furan-2-carbaldehyde (19.2 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **19** as a pale-yellow oil (30.0 mg, 58% yield, 92% ee).

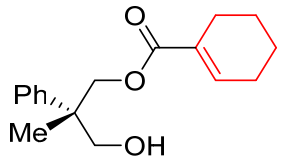
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), $t_R$ (major) = 16.06 min, $t_R$ (minor) = 20.39 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.41 – 7.33 (m, 2H), 7.31 – 7.22 (m, 2H), 7.13 (d, *J* = 3.4 Hz, 1H), 6.50 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.66 – 4.48 (m, 2H), 3.83 (s, 2H), 1.43 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 158.9, 146.6, 144.3, 142.4, 128.7, 127.0, 126.5, 118.3, 111.9, 68.9, 68.0, 44.0, 20.6.

**HRMS** (ESI) *m/z* calcd. for $C_{15}H_{16}NaO_4$ $[M + Na]^+$ 283.0941, found 283.0937.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl cyclohex-1-ene-1-carboxylate (20)**




According to **General procedure A** with cyclohex-1-ene-1-carbaldehyde (22.0 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **20** as a pale-yellow oil (34.0 mg, 62% yield, 86% ee).

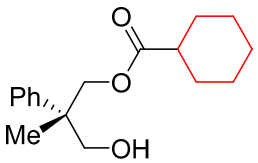
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (major) = 10.11 min, $t_R$ (minor) = 11.81 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 4H), 7.30 – 7.22 (m, 1H), 6.97 (tt, *J* = 3.8, 1.8 Hz, 1H), 4.46 – 4.35 (m, 2H), 3.76 (s, 2H), 2.27 – 2.14 (m, 4H), 1.70 – 1.53 (m, 4H), 1.38 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.9, 142.8, 140.7, 130.0, 128.6, 126.8, 126.5, 68.3, 67.9, 44.0, 25.9, 24.1, 22.0, 21.4, 20.8.

**HRMS** (ESI) *m/z* calcd. for $C_{17}H_{22}NaO_3$ $[M + Na]^+$ 297.1461, found 297.1457.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl cyclohexanecarboxylate (21)**




According to **General procedure A** with cyclohexanecarbaldehyde (22.4 mg, 0.20

mmol, 1.0 equiv) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **21** as a colorless oil (34.0 mg, 59% yield, 79% ee).

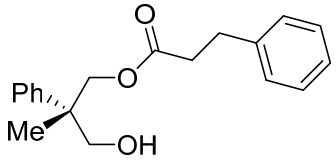
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (major) = 8.88 min, $t_R$ (minor) = 10.14 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 4H), 7.28 – 7.23 (m, 2H), 4.35 (d, *J* = 1.4 Hz, 2H), 3.73 (s, 2H), 2.38 – 2.23 (m, 1H), 1.91 – 1.80 (m, 2H), 1.77 – 1.67 (m, 2H), 1.66 – 1.58 (m, 1H), 1.47 – 1.36 (m, 2H), 1.35 (s, 3H), 1.32 – 1.14 (m, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 176.5, 142.6, 128.6, 126.8, 126.5, 68.1, 68.0, 43.9, 43.2, 29.0, 25.7, 25.4, 20.8.

**HRMS** (ESI) *m/z* calcd. for $C_{17}H_{24}NaO_3$ $[M + Na]^+$ 299.1618, found 299.1613.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 3-phenylpropanoate (SP-1)**




According to **General procedure A** with phenylpropyl aldehyde (16.8 mg, 0.2 mmol, 1.0 equiv.) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.3 mmol, 1.5 equiv.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **SP-1** as a pale-yellow oil (42.0 mg, 70% yield, 69% ee).

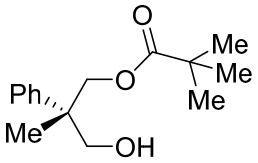
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (major) =11.00 min, $t_R$ (minor) = 12.30 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 4.3 Hz, 4H), 7.31 – 7.23 (m, 3H), 7.23 – 7.14 (m, 3H), 4.34 (s, 2H), 3.66 (s, 2H), 2.92 (t, *J* = 7.7 Hz, 2H), 2.72 – 2.58 (m, 2H), 1.30 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.3, 142.5, 140.3, 128.60, 128.55, 128.3, 126.9, 126.5, 126.4, 68.5, 67.8, 43.7, 35.8, 30.9, 20.6.

**HRMS** (ESI) *m/z* calcd. for $C_{19}H_{22}NaO_3$ $[M + Na]^+$ 321.1461, found 321.1460.

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl pivalate (SP-2)**



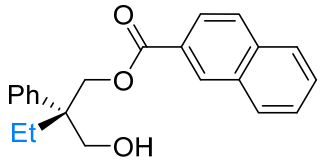

According to **General procedure A** with pivaldehyde (17.2 mg, 0.2 mmol, 1.0 equiv.) and 2-methyl-2-phenylpropane-1,3-diol (49.9 mg, 0.3 mmol, 1.5 equiv.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product **SP-2** as a pale-yellow oil (30.0 mg, 60% yield, 65% ee).

**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm), $t_R$ (major) =7.30 min, $t_R$ (minor) = 8.60 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 4H), 7.28 – 7.23 (m, 1H), 4.34 (s, 2H),

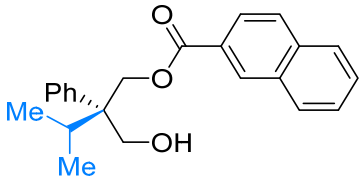
3.74 (d, $J$ = 0.9 Hz, 2H), 1.37 (s, 3H), 1.16 (s, 9H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 178.9, 142.6, 128.5, 126.8, 126.5, 68.4, 68.0, 44.0, 39.0, 27.2, 20.7.
**HRMS** (ESI) *m/z* calcd. for $C_{15}H_{22}NaO_3$ $[M + Na]^+$ 273.1461, found 273.1458.

**(*S*)-2-(Hydroxymethyl)-2-phenylbutyl 2-naphthoate (22)**



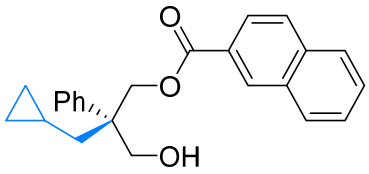

According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-ethyl-2-phenylpropane-1,3-diol (54.1 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **22** as a pale-yellow oil (30.8 mg, 76% yield, 93% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 0.8 mL/min, λ = 214 nm), $t_R$ (major) = 22.38 min, $t_R$ (minor) = 24.12 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.99 (dd, $J$ = 8.6, 1.7 Hz, 1H), 7.96 – 7.91 (m, 1H), 7.90 – 7.84 (m, 2H), 7.66 – 7.51 (m, 2H), 7.40 (d, $J$ = 4.3 Hz, 4H), 7.32 – 7.26 (m, 1H), 4.79 (s, 2H), 4.05 – 3.86 (m, 2H), 2.13 – 2.03 (m, 1H), 1.90 (q, $J$ = 7.5 Hz, 2H), 0.79 (t, $J$ = 7.5 Hz, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.2, 141.1, 135.6, 132.5, 131.3, 129.4, 128.7, 128.4, 128.3, 127.8, 127.2, 126.8, 126.7, 125.2, 66.4, 65.9, 47.4, 26.5, 7.9.
**HRMS** (ESI) *m/z* calcd. for $C_{21}H_{20}NaO_3$ $[M + Na]^+$ 357.1461, found 357.1455.

**(*S*)-2-(Hydroxymethyl)-3-methyl-2-phenylbutyl 2-naphthoate (23)**




According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-isopropyl-2-phenylpropane-1,3-diol (58.2 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **23** as a white solid (62.0 mg, 89% yield, 95% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (major) = 20.05 min, $t_R$ (minor) = 23.91 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.98 – 7.82 (m, 4H), 7.61 – 7.50 (m, 2H), 7.43 – 7.35 (m, 4H), 7.32 – 7.26 (m, 1H), 5.03 – 4.86 (m, 2H), 4.14 (s, 2H), 2.27 – 2.12 (m, 1H), 0.95 (d, $J$ = 6.9 Hz, 3H), 0.88 (d, $J$ = 6.9 Hz, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.2, 139.8, 135.6, 132.4, 131.3, 129.4, 128.4, 128.3, 127.8, 127.5, 127.2, 126.72, 126.66, 125.1, 65.6, 64.4, 49.7, 32.4, 18.1, 18.0.
**HRMS** (ESI) *m/z* calcd. for $C_{23}H_{24}NaO_3$ $[M + Na]^+$ 371.1618, found 371.1611.

**(*S*)-3-Cyclopropyl-2-(hydroxymethyl)-2-phenylpropyl 2-naphthoate (24)**




According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-(cyclopropylmethyl)-2-phenylpropane-1,3-diol (61.8 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **24** as a pale-yellow oil (54.0 mg, 75% yield, 95% ee).

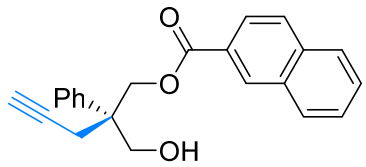
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (major) = 10.10 min, $t_R$ (minor) = 11.30 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.02 – 7.90 (m, 2H), 7.90 – 7.82 (m, 2H), 7.66 – 7.51 (m, 2H), 7.51 – 7.45 (m, 2H), 7.45 – 7.37 (m, 2H), 7.33 – 7.26 (m, 1H), 4.90 (s, 2H), 4.00 (s, 2H), 1.88 (dd, *J* = 14.2, 5.9 Hz, 1H), 1.73 (dd, *J* = 14.2, 7.1 Hz, 1H), 0.54 – 0.44 (m, 1H), 0.44 – 0.29 (m, 2H), 0.11 – 0.01 (m, 2H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.2, 141.7, 135.6, 132.5, 131.3, 129.4, 128.7, 128.4, 128.3, 127.8, 127.2, 126.8, 126.7, 125.1, 66.6, 66.0, 48.2, 39.4, 5.8, 5.0, 4.4.

**HRMS** (ESI) *m/z* calcd. for $C_{24}H_{24}NaO_3$ $[M + Na]^+$ 383.1618, found 383.1612.

**(*S*)-2-(Hydroxymethyl)-2-phenylpent-4-yn-1-yl 2-naphthoate (25)**




According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-phenyl-2-(prop-2-yn-1-yl)propane-1,3-diol (57.1 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **25** as a pale-yellow oil (42.0 mg, 61% yield, 93% ee).

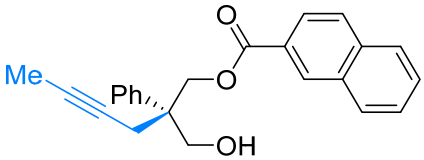
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (major) = 20.29 min, $t_R$ (minor) = 23.32 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.01 – 7.80 (m, 4H), 7.65 – 7.47 (m, 4H), 7.46 – 7.37 (m, 2H), 7.35 – 7.27 (m, 1H), 4.82 (s, 2H), 4.03 (s, 2H), 2.89 (t, *J* = 2.9 Hz, 2H), 2.00 (t, *J* = 2.7 Hz, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.9, 140.0, 135.7, 132.4, 131.3, 129.4, 128.7, 128.5, 128.3, 127.8, 127.4, 127.0, 126.80, 126.78, 125.1, 80.2, 71.7, 66.9, 66.0, 47.0, 24.0.

**HRMS** (ESI) *m/z* calcd. for $C_{23}H_{20}NaO_3$ $[M + Na]^+$ 367.1305, found 367.1299.

**(*S*)-2-(Hydroxymethyl)-2-phenylhex-4-yn-1-yl 2-naphthoate (26)**




According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-(but-2-yn-1-yl)-2-phenylpropane-1,3-diol (61.2 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **26** as a pale-yellow oil (52.0 mg, 73% yield, 86% ee).

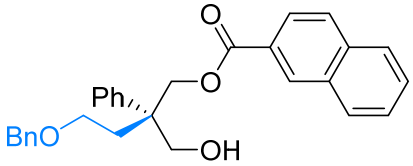
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (major) = 15.84 min, $t_R$ (minor) = 17.16 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.02 – 7.80 (m, 4H), 7.65 – 7.47 (m, 4H), 7.45 – 7.34 (m, 2H), 7.33 – 7.26 (m, 1H), 4.79 (s, 2H), 4.03 (s, 2H), 2.94 – 2.70 (m, 2H), 1.72 (t, *J* = 2.5 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.9, 140.5, 135.6, 132.4, 131.3, 129.4, 128.7, 128.4, 128.3, 127.8, 127.15, 127.12, 126.9, 126.7, 125.1, 79.1, 74.8, 67.3, 66.3, 47.1, 24.4, 3.6.

**HRMS** (ESI) *m/z* calcd. for $C_{24}H_{22}NaO_3$ $[M + Na]^+$ 381.1461, found 381.1455.

**(S)-4-(Benzyloxy)-2-(hydroxymethyl)-2-phenylbutyl 2-naphthoate (27)**




According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-(2-(benzyloxy)ethyl)-2-phenylpropane-1,3-diol (85.6 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **27** as a colorless oil (58.0 mg, 66% yield, 90% ee).

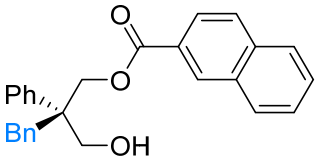
**HPLC** analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (major) = 9.93 min, $t_R$ (minor) = 21.52 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.97 – 7.78 (m, 4H), 7.64 – 7.48 (m, 2H), 7.45 – 7.21 (m, 11H), 4.76 – 4.62 (m, 2H), 4.43 (s, 2H), 4.13 – 3.95 (m, 2H), 3.61 – 3.51 (m, 1H), 3.50 – 3.42 (m, 1H), 2.37 – 2.14 (m, 2H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.8, 141.3, 137.6, 135.6, 132.4, 131.2, 129.4, 128.7, 128.5, 128.3, 128.2, 127.83, 127.76, 127.2, 126.8, 126.7, 125.1, 73.3, 68.2, 66.5, 65.6, 46.6, 34.1.

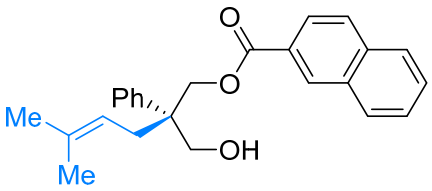
**HRMS** (ESI) *m/z* calcd. for $C_{29}H_{28}NaO_4$ $[M + Na]^+$ 463.1880, found 463.1874.

**(*S*)-2-Benzyl-3-hydroxy-2-phenylpropyl 2-naphthoate (28)**



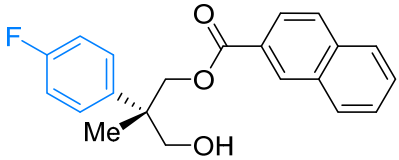
According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-benzyl-2-phenylpropane-1,3-diol (72.7 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **28** as a white solid (62.0 mg, 78% yield, 96% ee).
**HPLC** analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 214 nm), $t_R$ (major) = 11.58 min, $t_R$ (minor) = 17.99 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.03 – 7.82 (m, 4H), 7.65 – 7.49 (m, 2H), 7.42 – 7.25 (m, 5H), 7.17 – 7.04 (m, 3H), 6.90 – 6.78 (m, 2H), 4.84 – 4.63 (m, 2H), 3.98 (d, *J* = 2.5 Hz, 2H), 3.28 – 3.05 (m, 2H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.2, 140.7, 136.4, 135.7, 132.5, 131.3, 130.4, 129.4, 128.6, 128.5, 128.3, 127.9, 127.8, 127.1, 127.01, 126.96, 126.8, 126.5, 125.1, 65.8, 64.9, 48.2, 41.0.
**HRMS** (ESI) *m/z* calcd. for $C_{27}H_{24}NaO_3$ $[M + Na]^+$ 419.1618, found 419.1613.

**(*S*)-2-(Hydroxymethyl)-5-methyl-2-phenylhex-4-en-1-yl 2-naphthoate (29)**




According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-(3-methylbut-2-en-1-yl)-2-phenylpropane-1,3-diol (66.2 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **29** as a pale-yellow oil (56.0 mg, 75% yield, 93% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (major) = 14.18 min, $t_R$ (minor) = 15.59 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.02 – 7.82 (m, 4H), 7.64 – 7.49 (m, 2H), 7.48 – 7.34 (m, 4H), 7.33 – 7.24 (m, 2H), 5.03 – 4.89 (m, 1H), 4.82 – 4.67 (m, 2H), 3.95 (s, 2H), 2.70 – 2.47 (m, 2H), 1.62 (s, 1H), 1.56 (s, 2H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.1, 141.3, 135.6, 134.9, 132.5, 131.3, 129.4, 128.6, 128.4, 128.3, 127.8, 127.2, 126.9, 126.8, 126.7, 125.1, 118.5, 66.7, 66.2, 47.6, 32.7, 26.0, 18.0.
**HRMS** (ESI) *m/z* calcd. for $C_{25}H_{26}NaO_3$ $[M + Na]^+$ 397.1774, found 397.1769.

**(*S*)-2-(4-Fluorophenyl)-3-hydroxy-2-methylpropyl 2-naphthoate (30)**




According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-(4-fluorophenyl)-2-methylpropane-1,3-diol (55.2 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **30** as a white solid (42.0 mg, 62% yield,

87% ee).

**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (minor) = 17.13 min, $t_R$ (major) = 18.88 min.

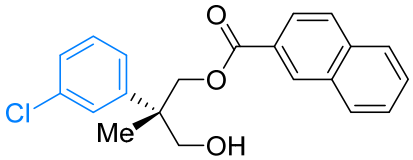
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.03 – 7.82 (m, 4H), 7.64 – 7.51 (m, 2H), 7.51 – 7.42 (m, 2H), 7.11 – 7.04 (m, 2H), 4.63 (s, 2H), 3.84 (s, 2H), 1.48 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.1, 161.7 (d, $J$ = 245.7 Hz), 138.4 (d, $J$ = 3.3 Hz), 135.7, 132.5, 131.3, 129.4, 128.5, 128.3 (d, $J$ = 2.9 Hz), 128.2, 127.8, 127.0, 126.8, 125.1, 115.4 (d, $J$ = 21.0 Hz), 69.0, 67.9, 43.8, 21.0.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ −115.9 – −116.1 (m, 1F).

**HRMS** (ESI) *m/z* calcd. for $C_{21}H_{19}FNaO_3$ $[M + Na]^+$ 361.1210, found 361.1204.

**(*S*)-2-(3-Chlorophenyl)-3-hydroxy-2-methylpropyl 2-naphthoate (31)**




According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-(m-tolyl)propane-1,3-diol (60.0 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **31** as a pale-yellow oil (42.0 mg, 59% yield, 87% ee).

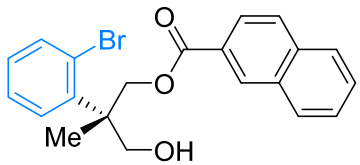
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (major) = 14.57 min, $t_R$ (minor) = 20.54 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.02 – 7.91 (m, 2H), 7.87 (d, $J$ = 8.6 Hz, 2H), 7.64 – 7.47 (m, 3H), 7.42 – 7.26 (m, 3H), 4.62 (d, $J$ = 2.6 Hz, 2H), 3.85 (s, 2H), 1.48 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.1, 145.0, 135.7, 134.6, 132.5, 131.3, 129.9, 129.4, 128.5, 128.4, 127.8, 127.17, 127.15, 126.9, 126.8, 125.1, 124.8, 68.7, 67.6, 44.3, 20.7.

**HRMS** (ESI) *m/z* calcd. for $C_{21}H_{19}ClNaO_3$ $[M + Na]^+$ 377.0915, found 377.0910.

**(*S*)-2-(2-Bromophenyl)-3-hydroxy-2-methylpropyl 2-naphthoate (32)**



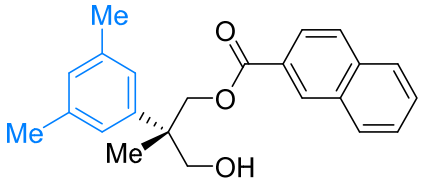

According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-(2-bromophenyl)-2-methylpropane-1,3-diol (73.5 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **32** as a pale-yellow oil (62.0 mg, 78% yield, 85% ee).

**HPLC** analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 80/20, flow rate 0.8 mL/min, λ = 230 nm), $t_R$ (major) = 9.93 min, $t_R$ (minor) = 15.69 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.96 – 7.79 (m, 4H), 7.65 (dd, $J$ = 7.9, 1.5

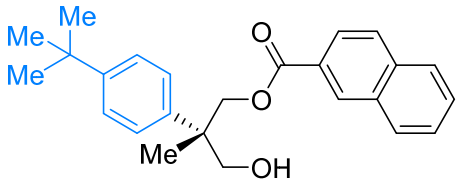
Hz, 1H), 7.61 – 7.50 (m, 3H), 7.37 – 7.30 (m, 1H), 7.17 – 7.10 (m, 1H), 4.98 (q, $J$ = 11.3 Hz, 2H), 4.20 (s, 2H), 1.67 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.0, 140.4, 136.2, 135.6, 132.4, 131.3, 130.4, 129.4, 128.7, 128.4, 128.3, 127.8, 127.6, 127.1, 126.7, 125.1, 122.4, 67.4, 65.9, 46.1, 19.9.
**HRMS** (ESI) *m/z* calcd. for $C_{21}H_{19}BrNaO_3$ $[M + Na]^+$ 421.0410, found 421.0405.

**(*S*)-2-(3,5-Dimethylphenyl)-3-hydroxy-2-methylpropyl 2-naphthoate (33)**




According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-(3,5-dimethylphenyl)-2-methylpropane-1,3-diol (52.2 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **33** as a white solid (46.0 mg, 70% yield, 94% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (major) = 11.81 min, $t_R$ (minor) = 20.99 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.02 (dd, $J$ = 8.6, 1.7 Hz, 1H), 7.98 – 7.83 (m, 3H), 7.66 – 7.48 (m, 2H), 7.09 (s, 2H), 6.93 (s, 1H), 4.63 (d, $J$ = 1.9 Hz, 2H), 3.86 (d, $J$ = 2.1 Hz, 2H), 2.34 (s, 6H), 1.48 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.1, 142.4, 138.1, 135.6, 132.5, 131.2, 129.4, 128.7, 128.4, 128.3, 127.8, 127.2, 126.8, 125.2, 124.4, 69.2, 68.0, 44.0, 21.6, 20.8.
**HRMS** (ESI) *m/z* calcd. for $C_{23}H_{24}NaO_3$ $[M + Na]^+$ 371.1618, found 371.1613.

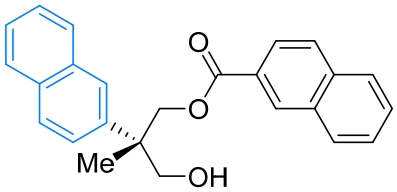
**(*S*)-2-(4-(*tert*-Butyl)phenyl)-3-hydroxy-2-methylpropyl 2-naphthoate (34)**




According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-(4-(*tert*-butyl)phenyl)-2-methylpropane-1,3-diol (66.7 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **34** as a white solid (60.0 mg, 80% yield, 90% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (major) = 11.71 min, $t_R$ (minor) = 13.20 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.01 (dd, $J$ = 8.6, 1.7 Hz, 1H), 7.93 (d, $J$ = 8.2 Hz, 1H), 7.87 (d, $J$ = 8.4 Hz, 2H), 7.65 – 7.50 (m, 2H), 7.41 (s, 4H), 4.74 – 4.57 (m, 2H), 3.86 (s, 2H), 1.49 (s, 3H), 1.33 (s, 9H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.1, 149.7, 139.4, 135.6, 132.5, 131.3, 129.4, 128.4, 128.3, 127.8, 127.2, 126.7, 126.2, 125.6, 125.2, 69.1, 68.0, 43.8, 34.4, 31.3, 20.8.

**HRMS** (ESI) *m/z* calcd. for $C_{25}H_{28}NaO_3$ $[M + Na]^+$ 399.1931, found 399.1926.

**(*S*)-3-Hydroxy-2-methyl-2-(naphthalen-2-yl)propyl 2-naphthoate (35)**




According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-(naphthalen-2-yl)propane-1,3-diol (64.8 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **35** as a white solid (54.8 mg, 74% yield, 94% ee).

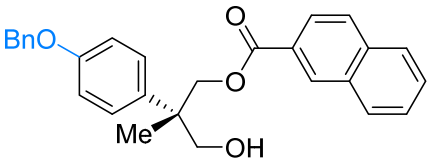
**HPLC** analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (major) = 11.89 min, $t_R$ (minor) = 16.67 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.99 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.95 – 7.78 (m, 7H), 7.66 – 7.44 (m, 5H), 4.77 (s, 2H), 3.97 (s, 2H), 1.59 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.1, 140.0, 135.6, 133.4, 132.5, 132.3, 131.3, 129.4, 128.4, 128.35, 128.31, 128.1, 127.8, 127.5, 127.1, 126.7, 126.2, 126.0, 125.7, 125.2, 124.6, 69.0, 68.0, 44.4, 20.9.

**HRMS** (ESI) *m/z* calcd. for $C_{25}H_{22}NaO_3$ $[M + Na]^+$ 393.1461, found 393.1455.

**(*S*)-2-(4-(Benzyloxy)phenyl)-3-hydroxy-2-methylpropyl 2-naphthoate (36)**




According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-(4-(benzyloxy)phenyl)-2-methylpropane-1,3-diol (81.6 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **36** as a white solid (58.0 mg, 68% yield, 94% ee).

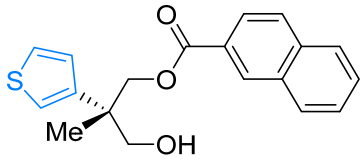
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (major) = 29.07 min, $t_R$ (minor) = 32.95 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.00 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 – 7.83 (m, 3H), 7.65 – 7.50 (m, 2H), 7.48 – 7.28 (m, 7H), 7.00 (d, *J* = 8.9 Hz, 2H), 5.06 (s, 2H), 4.62 (s, 2H), 3.84 (s, 2H), 1.47 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.1, 157.7, 137.0, 135.6, 134.8, 132.5, 131.3, 129.4, 128.6, 128.4, 128.3, 128.0, 127.8, 127.7, 127.5, 127.2, 126.8, 125.2, 114.9, 70.0, 69.2, 68.1, 43.6, 20.9.

**HRMS** (ESI) *m/z* calcd. for $C_{28}H_{26}NaO_4$ $[M + Na]^+$ 449.1723, found 449.1716 .

**(*S*)-3-Hydroxy-2-methyl-2-(thiophen-3-yl)propyl 2-naphthoate (37)**



According to **General procedure A** with 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv) and 2-methyl-2-(thiophen-3-yl)propane-1,3-diol (51.7 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product **37** as a white solid (46.0 mg, 71% yield, 90% ee).

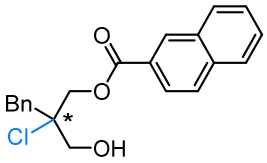
**HPLC** analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 95/5, flow rate 0.8 mL/min, λ = 214 nm), $t_R$ (major) = 37.10 min, $t_R$ (minor) = 41.04 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.01 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.98 – 7.91 (m, 1H), 7.91 – 7.81 (m, 2H), 7.65 – 7.49 (m, 2H), 7.38 – 7.31 (m, 1H), 7.27 – 7.22 (m, 2H), 7.23 – 7.17 (m, 1H), 4.59 (d, *J* = 1.6 Hz, 2H), 3.79 (s, 2H), 1.48 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.1, 144.1, 135.7, 132.5, 131.3, 129.4, 128.5, 128.3, 127.8, 127.1, 126.8, 126.3, 125.9, 125.1, 121.1, 68.8, 67.7, 43.0, 20.9.

**HRMS** (ESI) *m/z* calcd. for $C_{19}H_{18}NaO_3S$ $[M + Na]^+$ 349.0869, found 349.0862.

**2-Benzyl-2-chloro-3-hydroxypropyl 2-naphthoate (49)**



According to **General procedure A** with 2-naphthaldehyde (15.6 mg, 0.10 mmol, 1.0 equiv), 2-benzyl-2-chloropropane-1,3-diol (30.1 mg, 0.15 mmol, 1.5 equiv.), and **L9** (8.4 mg, 0.015 mmol, 15 mol %). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield product **49** as a colorless oil (25.5 mg, 72% yield, 85% ee).

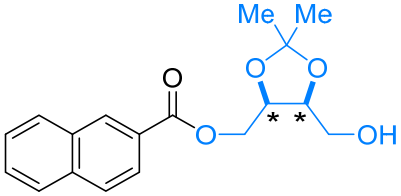
**HPLC** analysis: Chiralcel IA (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (minor) =16.08 min, $t_R$ (major) = 19.25 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 1.6 Hz, 1H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.95 – 7.86 (m, 2H), 7.67 – 7.53 (m, 2H), 7.39 – 7.27 (m, 5H), 4.61 (d, *J* = 11.8 Hz, 1H), 4.49 (d, *J* = 11.8 Hz, 1H), 3.77 (s, 2H), 3.29 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 166.7, 135.8, 134.6, 132.5, 131.6, 131.0, 129.5, 128.7, 128.5, 128.4, 127.9, 127.4, 126.9, 126.5, 125.1, 73.5, 66.2, 65.6, 41.7.

**HRMS** (ESI) *m/z* calcd. for $C_{21}H_{20}ClO_3$ $[M+H]^+$ 350.1095, found 350.1094.

**5-(Hydroxymethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl 2-naphthoate (51)**



According to **General procedure A** with 2-naphthaldehyde (15.6 mg, 0.10 mmol, 1.0

equiv) and *meso*-2,2-dimethyl-1,3-dioxolane-4,5-diyl)dimethanol (24.3 mg, 0.15 mmol, 1.5 equiv.). The reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product **51** as a white solid (19.0 mg, 60% yield, 87% ee).

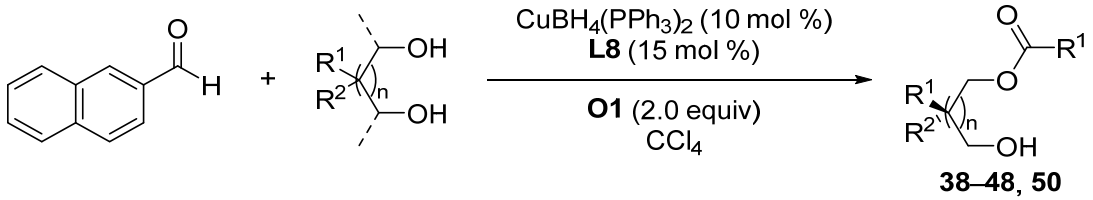
**HPLC** analysis: Chiralcel IA (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (minor) =14.59 min, $t_R$ (major) = 16.30 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.65 – 8.60 (m, 1H), 8.06 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.9 Hz, 2H), 7.64 – 7.51 (m, 2H), 4.65 – 4.53 (m, 2H), 4.54 – 4.45 (m, 1H), 4.47 – 4.37 (m, 1H), 3.94 – 3.80 (m, 2H), 1.54 (s, 3H), 1.43 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 166.5, 135.6, 132.5, 131.4, 129.4, 128.4, 128.3, 127.8, 126.9, 126.8, 125.2, 109.2, 77.2, 74.7, 63.5, 61.2, 27.7, 25.2.

**HRMS** (ESI) *m/z* calcd. for $C_{18}H_{20}NaO_5$ $[M+Na]^+$ 339.1203, found 339.1202.

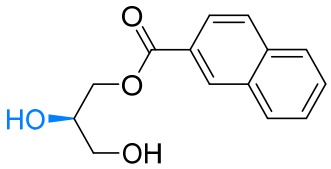
## 6. Cu-catalyzed enantioselective desymmetrizing radical C–O coupling with 1,2,3-triols, 2-amino 1,3-diols, and *meso* 1,2-diols




**General procedure B:**

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (12.0 mg, 0.020 mmol, 10 mol %), **L8** (0.030 mmol, 15 mol %), alcohol (0.30 mmol, 1.5 equiv), 2-naphthaldehyde (31.2 mg, 0.20 mmol, 1.0 equiv), and anhydrous $CCl_4$ (4.0 mL). Then, **O1** (80.9 mg, 0.40 mmol, 2.0 equiv) was added to the mixture and the reaction mixture was stirred at rt. Upon completion (monitored by TLC), the reaction mixture was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel to afford the desired product.

**(*R*)-2,3-Dihydroxypropyl 2-naphthoate (38)**



According to **General procedure B** with glycerol (27.6 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield product **38** as a white solid (35.0 mg, 71% yield, 95% ee).

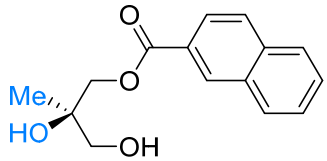
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (major) = 12.62 min, $t_R$ (minor) = 16.15 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.15 – 7.94 (m, 2H), 7.94 – 7.83 (m, 2H), 7.65 – 7.49 (m, 2H), 4.61 – 4.42 (m, 2H), 4.21 – 4.07 (m, 1H), 3.92 – 3.79 (m, 1H), 3.78 – 3.69 (m, 1H), 2.69 (d, *J* = 5.2 Hz, 1H), 2.20 (t, *J* = 6.1 Hz, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.2, 135.7, 132.4, 131.4, 129.4, 128.5, 128.3, 127.8, 126.82, 126.76, 125.1, 70.4, 65.9, 63.5.

**HRMS** (ESI) *m/z* calcd. for $C_{14}H_{14}NaO_4$ $[M + Na]^+$ 269.0784, found 269.0779.

**(*R*)-2,3-Dihydroxy-2-methylpropyl 2-naphthoate (39)**



According to **General procedure B** with 2-methylpropane-1,2,3-triol (31.8 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on

silica gel (petroleum ether/EtOAc = 1/1) to yield product **39** as a white solid (40.0 mg, 77% yield, 96% ee).

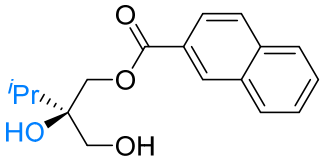
**HPLC** analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (minor) = 12.08 min, $t_R$ (major) = 17.08 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.13 – 7.93 (m, 2H), 7.93 – 7.84 (m, 2H), 7.69 – 7.47 (m, 2H), 4.49 (d, *J* = 11.3 Hz, 1H), 4.31 (d, *J* = 11.3 Hz, 1H), 3.63 (d, *J* = 11.5 Hz, 1H), 3.52 (d, *J* = 11.6 Hz, 1H), 1.33 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.4, 135.7, 132.4, 131.5, 129.4, 128.6, 128.4, 127.8, 126.9, 126.7, 125.1, 72.2, 68.5, 66.9, 21.5.

**HRMS** (ESI) *m/z* calcd. for $C_{15}H_{16}NaO_4$ $[M + Na]^+$ 283.0941, found 283.0937.

**(*R*)-2-Hydroxy-2-(hydroxymethyl)-3-methylbutyl 2-naphthoate (40)**




According to **General procedure B** with 2-isopropylpropane-1,2,3-triol (53.0 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **40** as a light-yellow solid (44.0 mg, 67% yield, 93% ee).

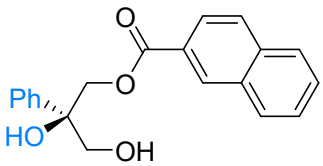
**HPLC** analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (minor) = 15.22 min, $t_R$ (major) = 17.44 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.07 – 7.93 (m, 2H), 7.89 (d, *J* = 8.7 Hz, 2H), 7.66 – 7.51 (m, 2H), 4.57 (d, *J* = 11.7 Hz, 1H), 4.40 (d, *J* = 11.7 Hz, 1H), 3.75 – 3.55 (m, 2H), 2.74 (br s, 1H), 2.12 – 1.94 (m, 1H), 1.74 (br s, 1H), 1.06 (dd, *J* = 7.0, 4.3 Hz, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 167.4, 135.7, 132.5, 131.4, 129.4, 128.6, 128.4, 127.8, 126.9, 126.8, 125.1, 75.3, 65.9, 64.1, 32.0, 17.0, 16.8.

**HRMS** (ESI) *m/z* calcd. for $C_{17}H_{20}NaO_4$ $[M + Na]^+$ 311.1254, found 311.1248.

**(*R*)-2,3-Dihydroxy-2-phenylpropyl 2-naphthoate (41)**




According to **General procedure B** with 2-phenylpropane-1,2,3-triol (50.5 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **41** as a white solid (44.0 mg, 68% yield, 97% ee).

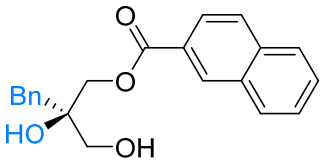
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (minor) = 36.48 min, $t_R$ (major) = 41.78 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.03 – 7.90 (m, 2H), 7.90 – 7.77 (m, 2H), 7.67 – 7.49 (m, 4H), 7.47 – 7.37 (m, 2H), 7.37 – 7.28 (m, 1H), 4.77 (d, *J* = 11.7 Hz,

1H), 4.66 (d, *J* = 11.7 Hz, 1H), 3.97 (dd, *J* = 11.7, 7.2 Hz, 1H), 3.86 (dd, *J* = 11.7, 6.1 Hz, 1H), 3.38 (s, 1H), 2.42 (t, *J* = 6.7 Hz, 1H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.3, 140.8, 135.7, 132.4, 131.5, 129.4, 128.6, 128.6, 128.3, 127.9, 127.8, 126.8, 126.7, 125.6, 125.1, 76.1, 68.9, 67.3.
**HRMS** (ESI) *m/z* calcd. for $C_{20}H_{18}NaO_4$ $[M + Na]^+$ 345.1097, found 345.1090.

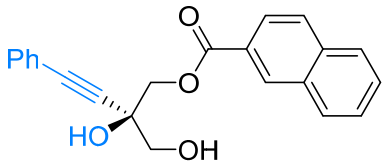
The structure of **41** was further confirmed by X-ray diffraction analysis (Figure S3).

**(*R*)-2-Benzyl-2,3-dihydroxypropyl 2-naphthoate (42)**




According to **General procedure B** with 2-benzylpropane-1,2,3-triol (54.4 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **42** as a white solid (48.0 mg, 71% yield, 97% ee).
**HPLC** analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (minor) = 11.92 min, $t_R$ (major) = 17.99 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.08 – 7.94 (m, 2H), 7.94 – 7.84 (m, 2H), 7.68 – 7.50 (m, 2H), 7.38 – 7.24 (m, 5H), 4.41 (d, *J* = 11.5 Hz, 1H), 4.27 (d, *J* = 11.5 Hz, 1H), 3.70 – 3.50 (m, 2H), 2.98 (s, 2H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.3, 135.8, 135.6, 132.5, 131.5, 130.6, 129.5, 128.63, 128.55, 128.4, 127.8, 127.0, 126.9, 126.7, 125.1, 74.0, 66.2, 65.3, 40.6.
**HRMS** (ESI) *m/z* calcd. for $C_{21}H_{20}NaO_4$ $[M + Na]^+$ 359.1254, found 359.1247.

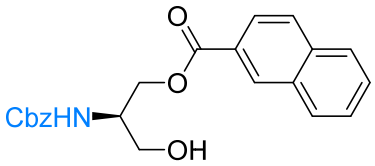
**(*R*)-2-Hydroxy-2-(hydroxymethyl)-4-phenylbut-3-yn-1-yl 2-naphthoate (43)**




According to **General procedure B** with 2-(phenylethynyl)propane-1,2,3-triol (57.7 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **43** as a white solid (59.0 mg, 85% yield, 89% ee).
**HPLC** analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (minor) = 17.79 min, $t_R$ (major) = 34.78 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.09 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.98 – 7.91 (m, 1H), 7.88 (dd, *J* = 8.4, 3.1 Hz, 2H), 7.66 – 7.50 (m, 2H), 7.47 – 7.39 (m, 2H), 7.35 – 7.23 (m, 3H), 4.72 (d, *J* = 11.3 Hz, 1H), 4.62 (d, *J* = 11.3 Hz, 1H), 3.99 – 3.76 (m, 2H), 3.38 (br s, 1H), 2.67 (br s, 1H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.1, 135.8, 132.5, 131.9, 131.6, 129.5, 128.9, 128.6, 128.37, 128.36, 127.8, 126.8, 126.7, 125.2, 121.7, 86.9, 86.7, 71.1, 67.4, 66.7.

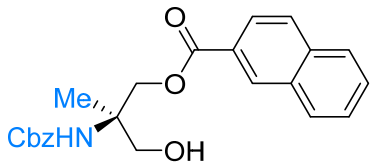
**HRMS** (ESI) *m/z* calcd. for $C_{22}H_{18}NaO_4$ $[M + Na]^+$ 369.1097, found 369.1096.

**(*R*)-2-(((Benzyloxy)carbonyl)amino)-3-hydroxypropyl 2-naphthoate (44)**



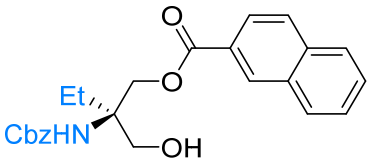

According to **General procedure B** with benzyl (1,3-dihydroxypropan-2-yl)carbamate (67.6 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **44** as a white solid (54.0 mg, 71% yield, 94% ee).
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (major) = 12.66 min, $t_R$ (minor) = 16.03 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.01 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.97 – 7.81 (m, 3H), 7.67 – 7.47 (m, 2H), 7.43 – 7.27 (m, 5H), 5.44 (d, *J* = 8.6 Hz, 1H), 5.11 (s, 2H), 4.53 (d, *J* = 5.9 Hz, 2H), 4.25 – 4.04 (m, 1H), 3.86 – 3.67 (m, 2H), 2.79 (br s, 1H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.2, 156.3, 136.2, 135.7, 132.4, 131.5, 129.4, 128.6, 128.4, 128.3, 128.2, 127.8, 126.8, 126.6, 125.1, 67.1, 63.3, 61.7, 51.9.
**HRMS** (ESI) *m/z* calcd. for $C_{22}H_{21}NNaO_5$ $[M + Na]^+$ 402.1312, found 402.1304.

**(*R*)-2-(((Benzyloxy)carbonyl)amino)-3-hydroxy-2-methylpropyl 2-naphthoate (45)**




According to **General procedure B** with benzyl (1,3-dihydroxy-2-methylpropan-2-yl)carbamate (71.7 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **45** as a white solid (63.7 mg, 81% yield, 98% ee).
**HPLC** analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (minor) = 16.57 min, $t_R$ (major) = 31.35 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.02 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.65 – 7.51 (m, 2H), 7.40 – 7.27 (m, 5H), 5.33 (s, 1H), 5.09 (s, 2H), 4.70 – 4.47 (m, 2H), 3.89 – 3.60 (m, 2H), 1.43 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.0, 155.9, 136.2, 135.7, 132.4, 131.4, 129.4, 128.61, 128.57, 128.4, 128.3, 128.2, 127.8, 126.8, 126.7, 125.1, 66.9, 66.7, 66.5, 56.9, 19.9.
**HRMS** (ESI) *m/z* calcd. for $C_{23}H_{23}NNaO_5$ $[M + Na]^+$ 416.1468, found 416.1461.

**(*R*)-2-(((Benzyloxy)carbonyl)amino)-2-(hydroxymethyl)butyl 2-naphthoate (46)**




According to **General procedure B** with benzyl (1-hydroxy-2-(hydroxymethyl)butan-2-yl)carbamate (76.0 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **46** as a colorless oil (53.0 mg, 65% yield, 95% ee).

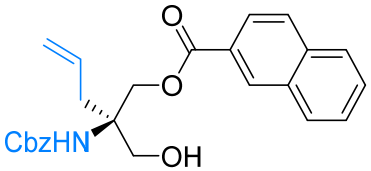
**HPLC** analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (minor) = 11.72 min, $t_R$ (major) = 19.22 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.02 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.92 – 7.85 (m, 2H), 7.65 – 7.51 (m, 2H), 7.39 – 7.26 (m, 5H), 5.18 (s, 1H), 5.10 (s, 2H), 4.69 – 4.44 (m, 2H), 3.79 (s, 3H), 1.99 (dq, *J* = 15.1, 7.6 Hz, 1H), 1.79 (dq, *J* = 14.8, 7.5 Hz, 1H), 0.97 (t, *J* = 7.5 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.0, 156.1, 136.2, 135.7, 132.4, 131.4, 129.4, 128.61, 128.57, 128.4, 128.3, 128.1, 127.8, 126.84, 126.73, 125.1, 66.9, 65.4, 59.5, 25.6, 7.6.

**HRMS** (ESI) *m/z* calcd. for $C_{24}H_{25}NNaO_5$ $[M + Na]^+$ 430.1625, found 430.1618.

**(*R*)-2-(((Benzyloxy)carbonyl)amino)-2-(hydroxymethyl)pent-4-en-1-yl 2-naphthoate (47)**




According to **General procedure B** with benzyl (1-hydroxy-2-(hydroxymethyl)pent-4-en-2-yl)carbamate (79.6 mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **47** as a pale-yellow oil (42.0 mg, 50% yield, 95% ee).

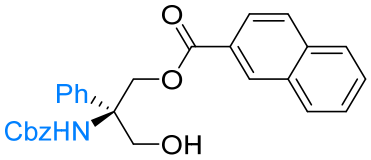
**HPLC** analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (minor) = 10.45 min, $t_R$ (major) = 18.12 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.02 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.95 (d, *J* = 8.7 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.67 – 7.51 (m, 2H), 7.41 – 7.27 (m, 5H), 5.98 – 5.73 (m, 1H), 5.25 (s, 1H), 5.20 (s, 1H), 5.18 – 5.13 (m, 1H), 5.10 (s, 2H), 4.70 – 4.47 (m, 2H), 3.94 – 3.69 (m, 3H), 2.84 – 2.68 (m, 1H), 2.57 – 2.41 (m, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.8, 156.0, 136.1, 135.7, 132.4, 131.8, 131.4, 129.5, 128.61, 128.59, 128.4, 128.3, 128.2, 127.8, 126.9, 126.7, 125.1, 120.2, 67.0, 65.3, 65.2, 58.8, 37.3.

**HRMS** (ESI) *m/z* calcd. for $C_{25}H_{25}NNaO_5$ $[M + Na]^+$ 442.1625, found 442.1617.

**(*R*)-2-(((Benzyloxy)carbonyl)amino)-3-hydroxy-2-phenylpropyl 2-naphthoate (48)**




According to **General procedure B** with benzyl (1,3-dihydroxy-2-phenylpropan-2-yl)carbamate (90.4mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **48** as a white solid (71.0 mg, 78% yield, 98% ee).

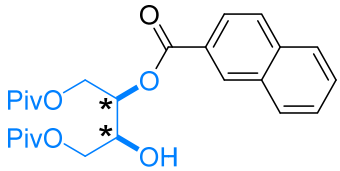
**HPLC** analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (minor) = 10.45 min, $t_R$ (major) = 18.12 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.00 – 7.81 (m, 4H), 7.65 – 7.46 (m, 4H), 7.44 – 7.20 (m, 8H), 5.86 (s, 1H), 5.10 (q, *J* = 12.2 Hz, 2H), 4.94 (d, *J* = 2.9 Hz, 2H), 4.24 – 3.97 (m, 2H), 3.67 (br s, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.9, 156.0, 139.3, 136.1, 135.7, 132.4, 131.5, 129.5, 128.8, 128.61, 128.58, 128.4, 128.3, 128.2, 128.0, 127.8, 126.8, 126.6, 126.1, 125.1, 67.3, 67.1, 66.7, 62.9.

**HRMS** (ESI) *m/z* calcd. for $C_{28}H_{25}NNaO_5$ $[M + Na]^+$ 478.1625, found 478.1617.

**2-((2-Naphthoyl)oxy)-3-hydroxybutane-1,4-diyl bis(2,2-dimethylpropanoate) (50)**




According to **General procedure B** with 2,3-dihydroxybutane-1,4-diyl bis(2,2-dimethylpropanoate) (87.1mg, 0.30 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield product **50** as a pale-yellow oil (65.8 mg, 74% yield, 85% ee).

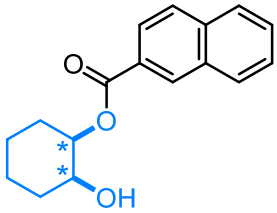
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (minor) = 21.30 min, $t_R$ (major) = 24.22 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.02 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.65 – 7.51 (m, 2H), 5.51 – 5.33 (m, 1H), 4.62 – 4.49 (m, 2H), 4.37 (dd, *J* = 11.8, 3.2 Hz, 1H), 4.26 (dd, *J* = 11.8, 5.5 Hz, 1H), 4.22 – 4.14 (m, 1H), 1.22 (s, 9H), 1.17 (s, 9H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 179.1, 178.6, 165.7, 135.7, 132.5, 131.4, 129.4, 128.5, 128.4, 127.8, 126.8, 126.7, 125.1, 72.0, 69.1, 65.2, 62.5, 38.95, 38.90, 27.2, 27.1.

**HRMS** (ESI) *m/z* calcd. for $C_{25}H_{32}NaO_7$ $[M + Na]^+$ 467.2040, found 467.2033.

**2-Hydroxycyclohexyl 2-naphthoate (SP-4)**



According to **General procedure A/B** with 2-naphthaldehyde (15.6 mg, 0.10 mmol, 1.0 equiv) and *cis*-1,2-cyclohexanediol **S52** (17.4 mg, 0.15 mmol, 1.5 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield product as a colorless oil (18.5 mg, 68% yield, 42% ee with **L1**; 20.5 mg, 76% yield, 69% ee with **L8**).

**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_R$ (minor) =9.01 min, $t_R$ (major) = 10.14 min.

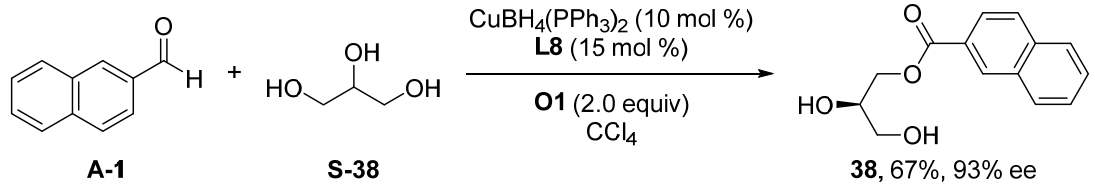
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.67 – 8.57 (m, 1H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.7 Hz, 2H), 7.65 – 7.51 (m, 2H), 5.29 (dt, *J* = 7.7, 2.8 Hz, 1H), 4.03 (dt, *J* = 7.7, 2.9 Hz, 1H), 2.17 – 1.67 (m, 8H), 1.56 – 1.38 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 166.4, 135.6, 132.5, 131.1, 129.4, 128.3, 128.2, 127.8, 127.6, 126.7, 125.2, 74.8, 69.7, 30.5, 27.4, 22.0.

**HRMS** (ESI) *m/z* calcd. for $C_{17}H_{19}O_3$ $[M+H]^+$ 271.1329, found 271.1327.

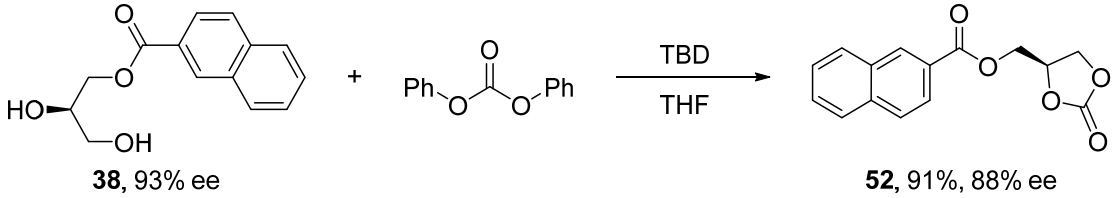
# 7. Synthetic transformations

## 7.1 Synthesis of chiral 38 on a 1-mmol scale



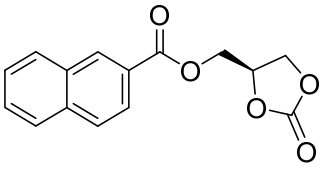

According to **General procedure B** with 2-naphthaldehyde **A-1** (156.0 mg, 1.0 mmol, 1.0 equiv) and glycerol **S-38** (138.0 mg, 1.52 mmol, 1.5 equiv), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield product **38** as a white solid (164.0 mg, 67% yield, 93% ee).

## 7.2 Synthesis of 52 from 38




To a solution of compound **38** (24.6 mg, 0.10 mmol, 1.0 equiv) and diphenyl carbonate (23.6 mg, 0.11 mmol, 1.1 equiv) in THF (1.0 mL) was added 1,5,7-triazabicylo[4.4.0]dec-5-ene (1 mg, 0.005 mmol, 5 mol %) and the reaction mixture was stirred at rt. Upon completion, the solvent was evaporated *in vacuo* and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **52** as a white solid (24.8 mg, 91% yield, 88% ee).

**(*S*)-(2-Oxo-1,3-dioxolan-4-yl)methyl 2-naphthoate (52)**



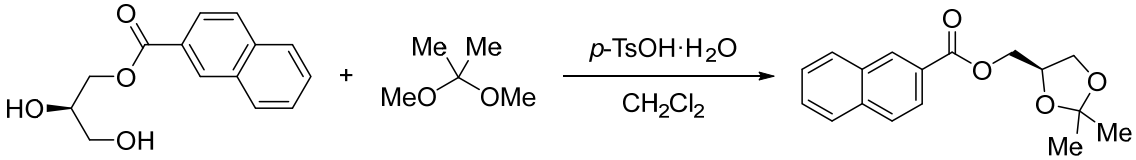
**HPLC** analysis: Chiralcel IC (*n*-Hexane/*i*-PrOH = 70/30, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (minor) = 20.75 min, $t_R$ (major) = 24.94 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.68 – 8.58 (m, 1H), 8.08 – 7.94 (m, 2H), 7.94 – 7.86 (m, 2H), 7.67 – 7.53 (m, 2H), 5.16 – 5.06 (m, 1H), 4.72 – 4.55 (m, 3H), 4.47 (dd, *J* = 8.8, 5.7 Hz, 1H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.2, 154.5, 135.8, 132.4, 131.7, 129.5, 128.8, 128.6, 127.8, 126.9, 126.0, 125.0, 74.0, 66.2, 63.8.

**HRMS** (ESI) *m/z* calcd. for $C_{15}H_{12}NaO_5$ $[M + Na]^+$ 295.0577, found 295.0573.

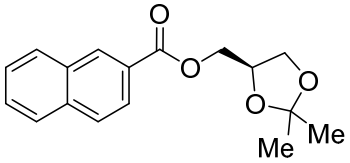
### 7.3 Synthesis of 53 from 38




**38**, 93% ee **53**, 87%, 93% ee

A mixture of **38** (24.6 mg, 0.10 mmol, 1.0 equiv), 2,2-dimethoxypropane (20.8 mg, 0.20 mmol, 2.0 equiv), and *p*-toluenesulfonic acid monohydrate (1 mg, 0.005 mmol, 5 mol %) in $CH_2Cl_2$ (1.0 mL) was stirred at rt for 2 h. Upon completion, the reaction was quenched with $K_2CO_3$ (2.0 mg) at rt, filtered, and evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield product **53** as a white solid (25.0 mg, 87% yield, 93% ee).

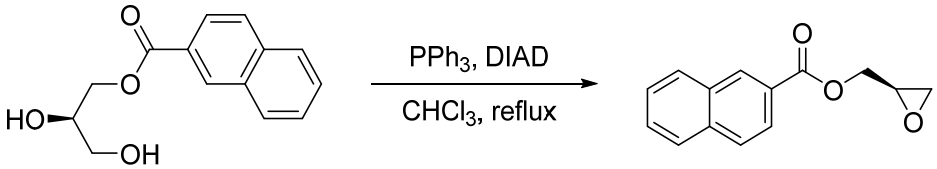
**(*R*)-(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl 2-naphthoate (53)**




**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 238 nm), $t_R$ (major) = 7.25 min, $t_R$ (minor) = 8.04 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.66 – 8.60 (m, 1H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.88 (dd, *J* = 8.3, 2.1 Hz, 2H), 7.64 – 7.50 (m, 2H), 4.56 – 4.38 (m, 3H), 4.19 (dd, *J* = 8.5, 6.3 Hz, 1H), 3.92 (dd, *J* = 8.5, 5.8 Hz, 1H), 1.49 (s, 3H), 1.41 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.6, 135.6, 132.5, 131.3, 129.4, 128.4, 128.2, 127.8, 127.0, 126.7, 125.3, 109.9, 73.8, 66.5, 65.2, 26.8, 25.4.
**HRMS** (ESI) *m/z* calcd. for $C_{17}H_{18}NaO_4$ $[M + Na]^+$ 309.1097, found 309.1091.

The structure of **53** was further confirmed by X-ray diffraction analysis (Figure S4).

### 7.4 Synthesis of 54 from 38

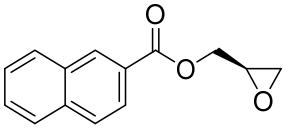



**38**, 93% ee **54**, 75%, 88% ee

A stirred mixture of **38** (24.6 mg, 0.10 mmol, 1.0 equiv), triphenylphosphine (27.5 mg, 0.105 mmol, 1.05 equiv) and diisopropyl azodicarboxylate (21.2 mg, 0.105 mmol, 1.05 equiv) in dry chloroform (1.0 mL) was refluxed for 8 h. After evaporation of the solvent at reduced pressure, the crude residue was purified by flash column chromatography on

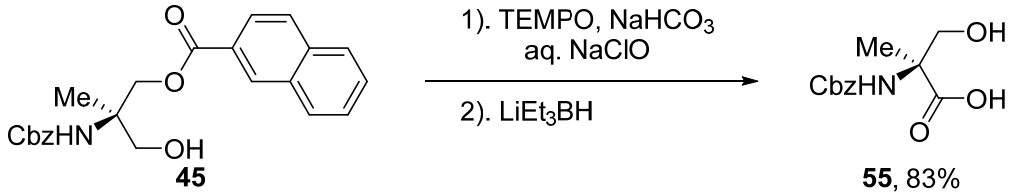
silica gel (petroleum ether/EtOAc = 5/1) to yield product **54** as a colorless oil (17.1 mg, 75% yield, 88% ee).

**(*R*)-Oxiran-2-ylmethyl 2-naphthoate (54)**



**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 230 nm), $t_R$ (minor) = 19.72 min, $t_R$ (major) = 20.98 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.72 – 8.58 (m, 1H), 8.08 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.03 – 7.93 (m, 1H), 7.89 (dd, *J* = 8.0, 2.7 Hz, 2H), 7.65 – 7.51 (m, 2H), 4.73 (dd, *J* = 12.3, 3.0 Hz, 1H), 4.23 (dd, *J* = 12.3, 6.3 Hz, 1H), 3.47 – 3.34 (m, 1H), 2.94 (dd, *J* = 4.9, 4.1 Hz, 1H), 2.78 (dd, *J* = 4.8, 2.6 Hz, 1H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 166.5, 135.7, 132.5, 131.4, 129.4, 128.4, 128.3, 127.8, 126.9, 126.8, 125.2, 65.7, 49.6, 44.8.
**HRMS** (ESI) *m/z* calcd. for $C_{14}H_{12}NaO_3$ $[M + Na]^+$ 251.0679, found 251.0674.

**7.5 Synthesis of 55 from chiral 45**

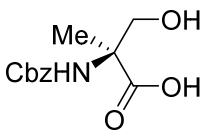



**45** **55**, 83%

To a solution of **45** (39.3 mg, 0.10 mmol, 1.0 equiv) in $CH_3CN$ (0.5 mL) and $H_2O$ (0.8 mL) were added 2,2,6,6-tetramethylpiperidinooxy (5.2 mg, 0.033 mmol, 0.33 equiv), $NaHCO_3$ (43.4 mg, 0.54 mmol, 5.4 equiv), and aq. NaClO (0.15 mL, activated chlorine 6%–14%). The reaction was allowed to stir at rt until the starting compound disappeared. Then the reaction was acidified with 1M HCl until the pH was 4–5 and was extracted with EtOAc (6x). The extract was dried over $Na_2SO_4$ and evaporated.

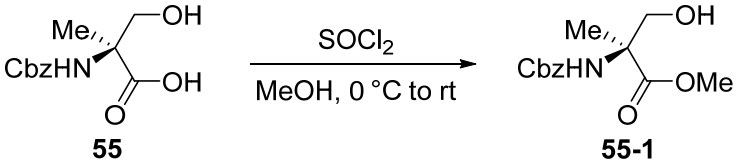
To a solution of the residue in anhydrous THF (1.0 mL) was slowly added $LiEt_3BH$ (1 M, 0.45 mL, 0.45 mmol, 4.5 equiv) at 0 ℃ under argon. After stirring at 0 ℃ for 30 min, the reaction mixture was treated with 1M HCl (10 mL) and then extracted with $CHCl_3$ (6x). The extract was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel ($CH_2Cl_2$/MeOH = 10/1 to 5/1) to yield product **55** as a pale-yellow oil (21.0 mg, 83% yield).

**(*S*)-2-(((Benzyloxy)carbonyl)amino)-3-hydroxy-2-methylpropanoic acid (55)**[11]



**$^1$H NMR** (400 MHz, MeOD) δ 7.42 – 7.21 (m, 5H), 5.04 (s, 2H), 3.96 (d, *J* = 10.8 Hz, 1H), 3.76 (d, *J* = 10.8 Hz, 1H), 1.41 (s, 3H).
**HRMS** (ESI) *m/z* calcd. for $C_{12}H_{15}NNaO_5$ $[M + Na]^+$ 276.0842, found 276.0839.

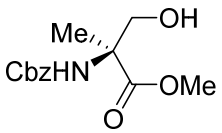
Determination of the ee value of **55**



**55** **55-1**

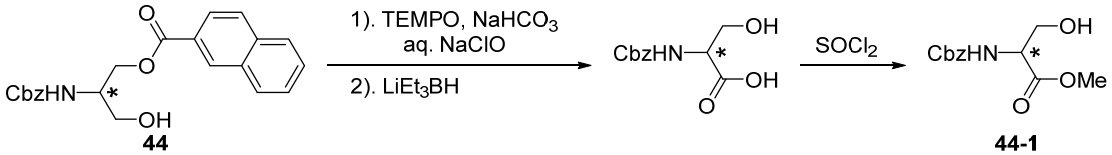
To a stirred solution of **55** (12.7 mg, 0.050 mmol, 1.0 equiv) in MeOH (0.5 mL) was added thionyl chloride (12.0 mg, 0.10 mmol, 2.0 equiv) dropwise at 0 ℃. The reaction was allowed to stir at rt until the starting compound disappeared. Then the solvent was evaporated *in vacuo* and the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield product **55-1** as a colorless oil (12.4 mg, 93% yield, 97% ee).

**(*S*)-Methyl 2-(((benzyloxy)carbonyl)amino)-3-hydroxy-2-methylpropanoate (55-1)**[16]



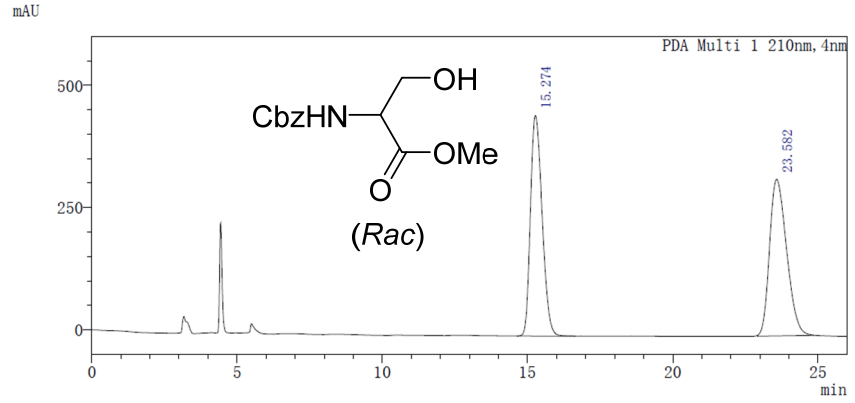

**HPLC** analysis: Chiralcel ODH (*n*-Hexane/*i*-PrOH = 85/15, flow rate 1.0 mL/min, λ = 210 nm), $t_R$ (major) = 17.82 min, $t_R$ (minor) = 20.08 min.
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 5H), 5.65 (br s, 1H), 5.10 (s, 2H), 4.10 – 4.00 (m, 1H), 3.89 – 3.78 (m, 1H), 3.78 (s, 3H), 2.90 (br s, 1H), 1.51 (s, 3H).
**HRMS** (ESI) *m/z* calcd. for $C_{13}H_{17}NNaO_5$ $[M + Na]^+$ 290.0999, found 290.0994.

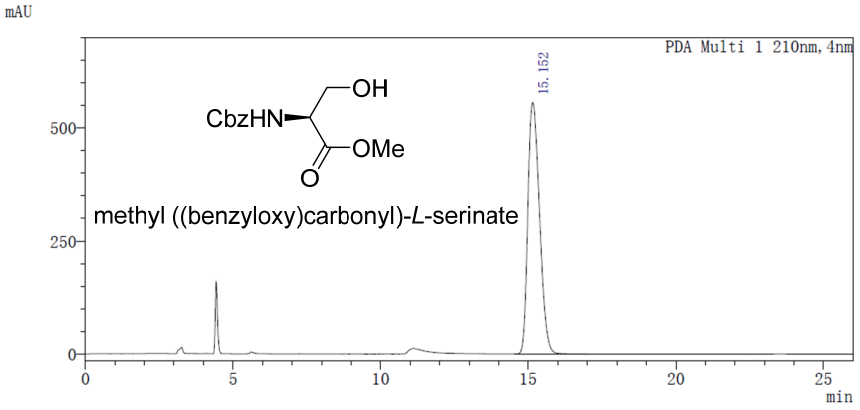
### 7.6 Determination of the Absolute Configuration of 44

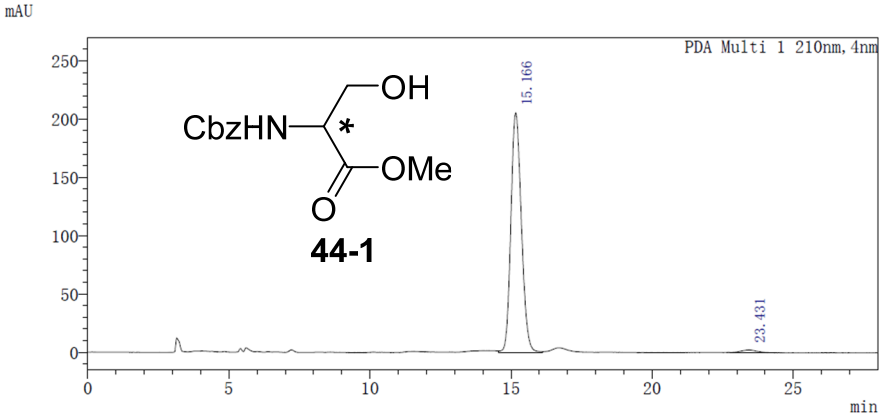


**44** **44-1**

**44-1** was prepared by following the same procedures as those for **55-1** using **44** as the starting material; the racemic product was prepared from commercially available *N*-benzyloxycarbonyl-*DL*-serine; methyl ((benzyloxy)carbonyl)-*L*-serinate was synthesized from commercially available *N*-(benzyloxycarbonyl)-*L*-serine.[17]
The HPLC spectra of **44-1** and methyl ((benzyloxy)carbonyl)-*L*-serinate indicate that these two compounds have the same absolute configuration.

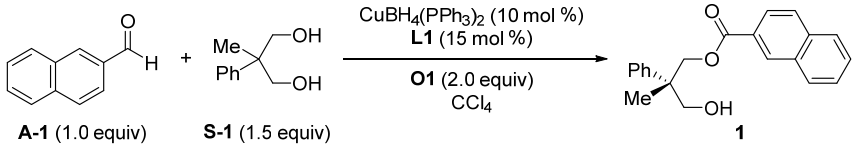

mAU
PDA Multi 1 210nm, 4nm
OH
CbzHN
OMe
O
(Rac)
15.274
23.582
500
250
0
0
5
10
15
20
25
min


mAU
PDA Multi 1 210nm, 4nm
OH
CbzHN
OMe
O
methyl ((benzyloxy)carbonyl)-L-serinate
15.152
500
250
0
0
5
10
15
20
25
min


mAU
PDA Multi 1 210nm, 4nm
OH
CbzHN
*
OMe
O
44-1
15.166
23.431
250
200
150
100
50
0
0
5
10
15
20
25
min

# 8. Mechanistic study

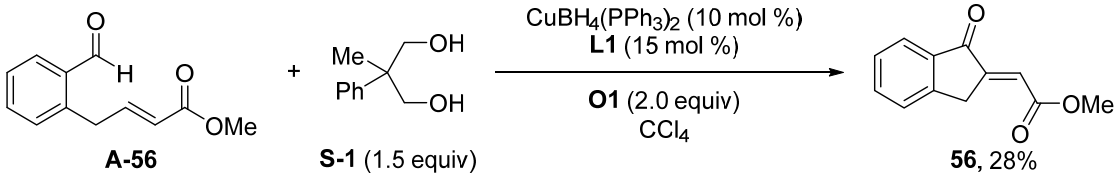
## 8.1 Radical inhibition experiments




| Trapping reagents | Yield of **1** | Ee of **1** |
|---|---|---|
| **BHT** (1.2 equiv) | Trace | - |
| **TEMPO** (1.2 equiv) | Trace | - |

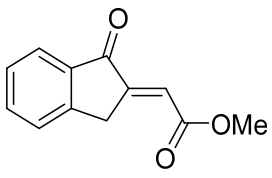
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (6.0 mg, 0.010 mmol, 10 mol %), **L1** (8.5 mg, 0.015 mmol, 15 mol %), 2-methyl-2-phenylpropane-1,3-diol (24.9 mg, 0.15 mmol, 1.5 equiv), fresh 2-naphthaldehyde (15.6 mg, 0.10 mmol, 1.0 equiv), the corresponding trapping reagents (1.2 equiv), and anhydrous $CCl_4$ (2.0 mL). Then, **O1** (40.5 mg, 0.20 mmol, 2.0 equiv) was added to the mixture and the reaction mixture was stirred at rt for 2 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo*. The residue was purified with column chromatography (petroleum ether/EtOAc = 3/1).

## 8.2 Radical trapping experiments




Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (6.0 mg, 0.010 mmol, 10 mol %), **L1** (8.5 mg, 0.015 mmol, 15 mol %), 2-methyl-2-phenylpropane-1,3-diol (24.9 mg, 0.15 mmol, 1.5 equiv), **A-56** (20.4 mg, 0.10 mmol, 1.0 equiv), and anhydrous $CCl_4$ (2.0 mL). Then, **O1** (40.5 mg, 0.20 mmol, 2.0 equiv) was added to the mixture and the reaction mixture was stirred at rt for 2 d. Then the reaction mixture was concentrated *in vacuo*. The residue was purified with column chromatography (petroleum ether/EtOAc = 10/1) to yield product **56** as a white solid (5.6 mg, 28% yield).

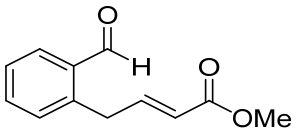
**Methyl (*E*)-2-(1-oxo-1,3-dihydro-2H-inden-2-ylidene)acetate (56)**



**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.4 Hz, 1H), 7.66 (td, *J* = 7.5, 1.2 Hz, 1H), 7.59 – 7.51 (m, 1H), 7.48 – 7.39 (m, 1H), 6.83 (t, *J* = 2.4 Hz, 1H), 4.14 (d, *J* = 2.2 Hz, 2H), 3.85 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 193.4, 166.6, 150.5, 149.8, 137.2, 135.9, 127.9, 126.5, 124.8, 120.7, 52.0, 32.4.
**HRMS** (ESI) *m/z* calcd. for $C_{12}H_{10}NaO_3$ $[M + Na]^+$ 225.0522, found 225.0519.

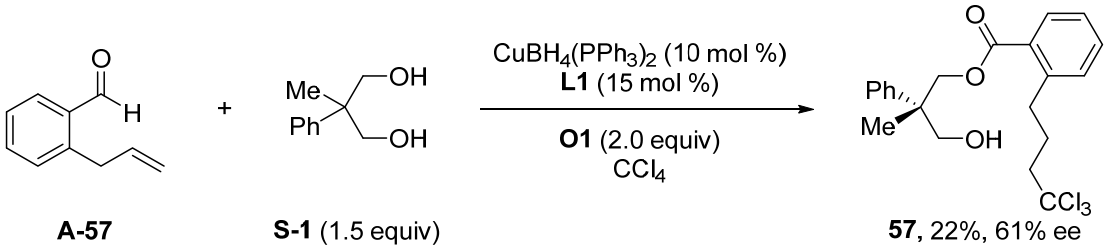
The structure of **56** was further confirmed by X-ray diffraction analysis (Figure S5).

**Methyl (*E*)-4-(2-formylphenyl)but-2-enoate (A-56)**




**A-56** was synthesized according to the literature report.[18]
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 10.15 (s, 1H), 7.84 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.56 (td, *J* = 7.5, 1.6 Hz, 1H), 7.47 (td, *J* = 7.5, 1.3 Hz, 1H), 7.28 (d, *J* = 7.6, 2H), 7.15 (dt, *J* = 15.6, 6.4 Hz, 1H), 5.73 (dt, *J* = 15.6, 1.7 Hz, 1H), 3.98 (dd, *J* = 6.4, 1.8 Hz, 2H), 3.70 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.5, 166.8, 147.0, 139.7, 134.1, 133.9, 133.8, 131.5, 127.6, 122.2, 51.5, 35.3.
**HRMS** (ESI) *m/z* calcd. for $C_{12}H_{12}NaO_3$ $[M + Na]^+$ 227.0679, found 227.0675.

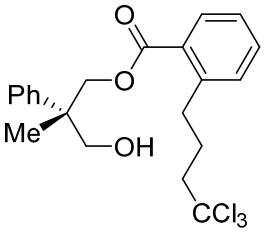
### 8.3 Observation of trichloromethyl radicals and formation of 57 from A-57




**A-57** **S-1** (1.5 equiv) **57**, 22%, 61% ee

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (6.0 mg, 0.010 mmol, 10 mol %), **L1** (8.5 mg, 0.015 mmol, 15 mol %), 2-methyl-2-phenylpropane-1,3-diol (24.9 mg, 0.15 mmol, 1.5 equiv), 2-allylbenzaldehyde **A-57** (14.6 mg, 0.10 mmol, 1.0 equiv), and anhydrous $CCl_4$ (2.0 mL). Then, **O1** (40.5 mg, 0.20 mmol, 2.0 equiv) was added to the mixture and the reaction mixture was stirred at rt for 2 d. The reaction mixture was concentrated *in vacuo.* The residue was purified with column chromatography (petroleum ether/EtOAc = 5/1) to yield product **57** as a pale-yellow oil (9.2 mg, 22% yield, 61% ee).

**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 2-(4,4,4-trichlorobutyl)benzoate (57)**



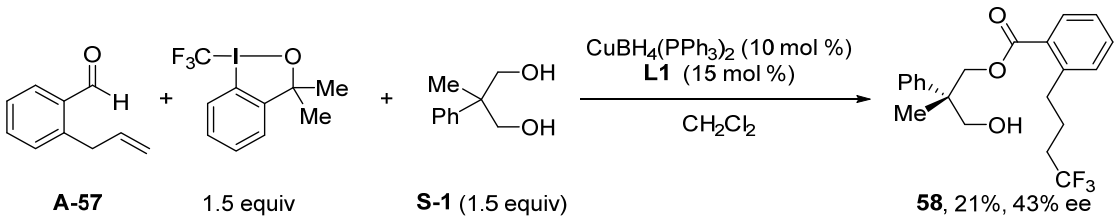
**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 226 nm), $t_R$ (major) = 8.16 min, $t_R$ (minor) = 10.50 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 1H), 7.51 – 7.42 (m, 3H), 7.42 – 7.35 (m, 2H), 7.34 – 7.22 (m, 4H), 4.69 – 4.51 (m, 2H), 3.84 (d, *J* = 1.3 Hz, 2H), 3.10 – 2.91 (m, 2H), 2.74 – 2.58 (m, 2H), 2.12 – 1.96 (m, 2H), 1.46 (s, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.6, 143.2, 142.5, 132.4, 131.0, 130.9, 129.1, 128.7, 127.0, 126.5, 126.4, 99.9, 69.1, 68.1, 54.6, 44.0, 32.7, 28.2, 20.9.

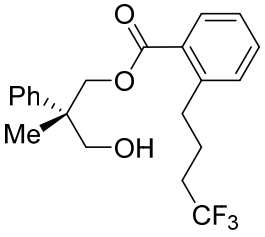
**HRMS** (ESI) *m/z* calcd. for $C_{21}H_{23}Cl_3NaO_3$ $[M + Na]^+$ 451.0605, found 451.0602.

## 8.4 Enantioselective C–O coupling of acyl radicals initiated by the generation of trifluoromethyl radicals with a known strategy[19]




Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (6.0 mg, 0.010 mmol, 10 mol %), **L1** (8.5 mg, 0.015 mmol, 15 mol %), 2-methyl-2-phenylpropane-1,3-diol (24.9 mg, 0.15 mmol, 1.5 equiv), 2-allylbenzaldehyde **A-57** (14.6 mg, 0.10 mmol, 1.0 equiv), Togni's reagent I (49.5 mg, 0.15 mmol, 1.5 equiv), and anhydrous $CH_2Cl_2$ (2.0 mL). The reaction mixture was stirred at rt for 2 d. Then the reaction mixture was concentrated *in vacuo*. The residue was purified with column chromatography (petroleum ether/EtOAc = 5/1) to yield product **58** as a pale-yellow oil (8.0 mg, 21% yield, 43% ee).

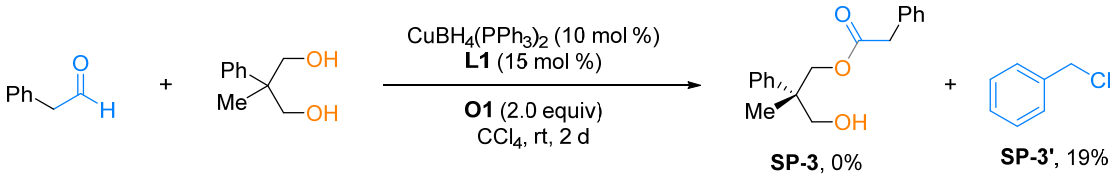
**(*S*)-3-Hydroxy-2-methyl-2-phenylpropyl 2-(4,4,4-trifluorobutyl)benzoate (58)**



**HPLC** analysis: Chiralcel IF (*n*-Hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), $t_R$ (major) = 6.44 min, $t_R$ (minor) = 7.82 min.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.48 – 7.41 (m, 3H), 7.40 – 7.34 (m, 2H), 7.30 – 7.20 (m, 3H), 4.69 – 4.50 (m, 2H), 3.83 (d, *J* = 1.7 Hz, 2H), 3.04 – 2.87 (m, 2H), 2.16 – 2.00 (m, 2H), 1.88 – 1.77 (m, 2H), 1.46 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 167.5, 143.2, 142.5, 132.4, 131.0, 130.9, 129.1, 128.7, 127.2 (q, *J* = 276.3 Hz), 127.0, 126.5, 126.4, 69.1, 68.2, 44.0, 33.4 (q, *J* = 28.5 Hz), 33.1, 23.7 (q, *J* = 2.7 Hz), 20.9.
**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ −66.2 (t, *J* = 10.8 Hz, 3F).
**HRMS** (ESI) *m/z* calcd. for $C_{21}H_{23}F_3NaO_3$ $[M + Na]^+$ 403.1492, found 403.1483.

### 8.5 The reaction with phenylacetaldehyde




According to **General procedure A** with phenylacetaldehyde (12.0 mg, 0.10 mmol, 1.0 equiv.) and 2-methyl-2-phenylpropane-1,3-diol (24.9 mg, 0.15 mmol, 1.5 equiv.). Upon completion, 1,3,5-trimethoxybenzene (16.8 mg, 0.10 mmol, 1.0 equiv) was added as an internal standard and the mixture was subjected for $^1$H NMR analysis, which indicated the formation of **SP-3'** in ca. 19% yield. Further purification and characterization of the reaction mixture revealed no formation of the desired product **SP-3**.

### 8.6 $^{19}$F NMR analysis of the reaction mixtures

$^{19}$F NMR analysis of the reaction mixtures under standard conditions (Figure S6)

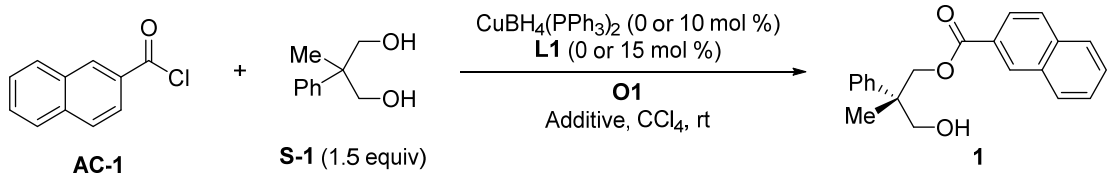
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (1.5 mg, 0.0025 mmol, 10 mol %), **L1** (2.13 mg, 0.00375 mmol, 15 mol %), 2-methyl-2-phenylpropane-1,3-diol (6.23 mg, 0.0375 mmol, 1.5 equiv), 4-fluorobenzaldehyde **A-6** (3.1 mg, 0.025 mmol, 1.0 equiv), and anhydrous $CCl_4$ (0.50 mL). Then, **O1** (10.1 mg, 0.050 mmol, 2.0 equiv) was added to the mixture and the reaction mixture was stirred at rt. Upon completion, *o*-difluorobenzenethe (50 μL, 0.50 mol/L in $CCl_4$, 1.0 equiv) was added. The reaction mixture was transferred to an NMR tube through a 0.22 μm filter and immediately analyzed by $^{19}$F NMR spectroscopy.

$^{19}$F NMR analysis of the reaction mixtures in $CH_2Cl_2$ (Figure S7)

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (1.5 mg, 0.0025 mmol, 10 mol %), **L1** (2.13 mg, 0.00375 mmol, 15 mol %), 2-methyl-2-phenylpropane-1,3-diol (6.23 mg, 0.0375 mmol, 1.5 equiv), 4-fluorobenzaldehyde **A-6** (3.1 mg, 0.025 mmol, 1.0 equiv),

and anhydrous $CH_2Cl_2$ (0.50 mL). Then, **O1** (10.1 mg, 0.050 mmol, 2.0 equiv) was added to the mixture and the reaction mixture was stirred at rt. After 2 d, *o*-difluorobenzenethe (50 μL, 0.50 mol/L in $CH_2Cl_2$, 1.0 equiv) was added. The reaction mixture was transferred to an NMR tube through a 0.22 μm filter and immediately analyzed by $^{19}F$ NMR spectroscopy.

## 8.7 Control experiments on the possible ionic enantioselective C–O bond formation catalyzed by Lewis acidic Cu(II) species




**AC-1** **S-1** (1.5 equiv) **1**

| Entry | $CuBH_4(PPh_3)_2$ (mol %) | **L1** (mol %) | **O1** (equiv) | Additive (equiv) | Yield | Ee |
|---|---|---|---|---|---|---|
| 1 | 10 | 15 | 2.0 | - | 75% | 89% |
| 2 | 10 | 15 | 0 | - | 47% | 0% |
| 3 | 10 | 15 | 0.15 | - | 24% | 40% |
| 4 | 10 | 15 | 2.0 | TEMPO (1.2) | trace | - |
| 5 | 10 | 15 | 0 | $KO^tBu$ (2.0) | 68% | 10% |
| 6 | 0 | 0 | 0 | - | 0% | - |
| 7 | 0 | 15 | 0 | - | 22% | 16% |

Control experiment with **O1**:

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (6.0 mg, 0.010 mmol, 10 mol %), **L1** (8.5 mg, 0.015 mmol, 15 mol %), 2-methyl-2-phenylpropane-1,3-diol (24.9 mg, 0.15 mmol, 1.5 equiv), 2-naphthoyl chloride (19.0 mg, 0.10 mmol, 1.0 equiv), and anhydrous $CCl_4$ (2.0 mL). Then, **O1** (40.5 mg, 0.20 mmol, 2.0 equiv) was added to the mixture and the reaction mixture was stirred at rt for 2 d. The reaction mixture was concentrated *in vacuo* and the residue was purified with column chromatography (petroleum ether/EtOAc = 3/1) to give product **1** (24.0 mg, 75% yield, 89% ee).

Control experiment without **O1**:

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (6.0 mg, 0.010 mmol, 10 mol %), **L1** (8.5 mg, 0.015 mmol, 15 mol %), 2-methyl-2-phenylpropane-1,3-diol (24.9 mg, 0.15 mmol, 1.5 equiv), 2-naphthoyl chloride (19.0 mg, 0.10 mmol, 1.0 equiv), and anhydrous $CCl_4$ (2.0 mL). The reaction mixture was stirred at rt for 2 d. The reaction mixture was concentrated *in vacuo* and the residue was purified with column chromatography (petroleum ether/EtOAc = 3/1) to give product **1** (15.1 mg, 47% yield, 0% ee).

Control experiment with a catalytic amount of **O1**:

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (6.0 mg, 0.010 mmol, 10 mol %), **L1** (8.5 mg, 0.015 mmol, 15 mol %), 2-methyl-2-phenylpropane-1,3-diol (24.9 mg, 0.15 mmol, 1.5 equiv), 2-naphthoyl chloride (19.0 mg, 0.10 mmol, 1.0 equiv), and anhydrous $CCl_4$ (2.0 mL). Then, **O1** (3.0 mg, 0.015 mmol, 15 mol %) was added to the mixture and the reaction mixture was stirred at rt for 2 d. The reaction mixture was concentrated *in vacuo* and the residue was purified with column chromatography (petroleum ether/EtOAc = 3/1) to give product **1** (7.8 mg, 24% yield, 40% ee).

Control experiment with TEMPO:

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (6.0 mg, 0.010 mmol, 10 mol %), **L1** (8.5 mg, 0.015 mmol, 15 mol %), 2-methyl-2-phenylpropane-1,3-diol (24.9 mg, 0.15 mmol, 1.5 equiv), 2-naphthoyl chloride (19.0 mg, 0.10 mmol, 1.0 equiv), TEMPO (18.8 mg, 0.12 mmol, 1.2 equiv), and anhydrous $CCl_4$ (2.0 mL). Then, **O1** (40.5 mg, 0.20 mmol, 2.0 equiv) was added to the mixture and the reaction mixture was stirred at rt for 2 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo*. The residue was purified with column chromatography (petroleum ether/EtOAc = 3/1).

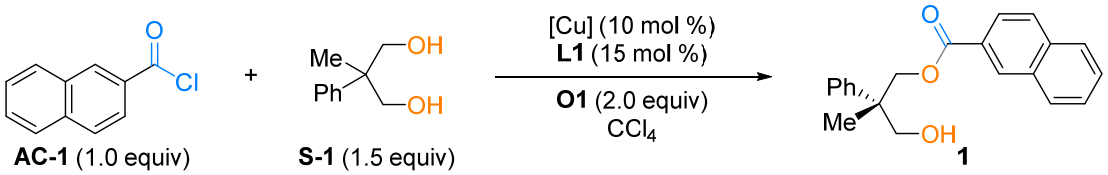
Control experiment with **O1** replaced by $KO^tBu$:

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (3.0 mg, 0.0050 mmol, 10 mol %), **L1** (4.25 mg, 0.0075 mmol, 15 mol %), 2-methyl-2-phenylpropane-1,3-diol (12.5 mg, 0.075 mmol, 1.5 equiv), 2-naphthoyl chloride (9.5 mg, 0.050 mmol, 1.0 equiv), and anhydrous $CCl_4$ (1.0 mL). Then, potassium *tert*-butoxide (11.2 mg, 0.10 mmol, 2.0 equiv) was added to the mixture and the reaction mixture was stirred at rt for 2 d. The reaction mixture was concentrated *in vacuo* and the residue was purified with column chromatography (petroleum ether/EtOAc = 3/1) to give product **1** (10.9 mg, 68% yield, 10% ee).

Control experiment without the catalyst and oxidant or with only **L1**:

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with **L1** (4.25 mg, 0.0075 mmol, 15 mol %) or without **L1**, 2-methyl-2-phenylpropane-1,3-diol (12.5 mg, 0.075 mmol, 1.5 equiv), 2-naphthoyl chloride (9.5 mg, 0.050 mmol, 1.0 equiv), and anhydrous $CCl_4$ (1.0 mL). The reaction mixture was stirred at rt for 2 d. The reaction mixture was concentrated *in vacuo* and the residue was purified with column chromatography (petroleum ether/EtOAc = 3/1) to give product **1** (3.6 mg, 22% yield, 16% ee with **L1**; 0% yield without **L1**).

## 8.8 Control experiments with $Cu(OAc)_2$ and CuOAc

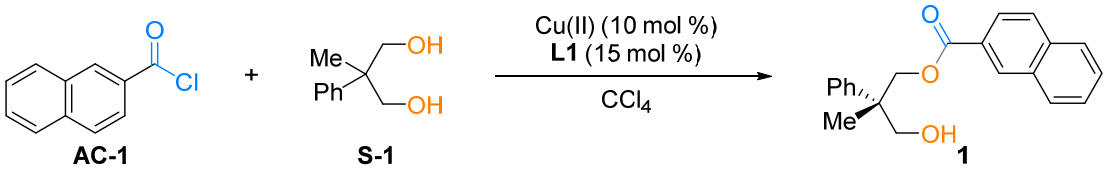



| Entry | [Cu] | **O1** | Yield (%) | Ee (%) |
|---|---|---|---|---|
| 1 | CuOAc | – | 21 | 13 |
| 2 | $Cu(OAc)_2$ | – | 17 | 18 |
| 3 | CuOAc | + | 71 | 79 |
| 4[a] | CuOAc | + | 31 | 21 |

[a]$CH_2Cl_2$ as solvent.

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with copper (I) acetate or copper (II) acetate (0.010 mmol, 10 mol %), **L1** (8.5 mg, 0.015 mmol, 15 mol %), 2-methyl-2-phenylpropane-1,3-diol (24.9 mg, 0.15 mmol, 1.5 equiv), 2-naphthoyl chloride (19.0 mg, 0.10 mmol, 1.0 equiv) and anhydrous $CCl_4$ (2.0 mL) (anhydrous $CH_2Cl_2$ (2.0 mL) as the solvent in entry 4). Then, the reaction mixture was stirred at rt for 2 d (for entries 3 and 4, **O1** (40.5 mg, 0.20 mmol, 2.0 equiv) was added into the mixture). The reaction mixture was concentrated *in vacuo* and the residue was purified with column chromatography (petroleum ether/EtOAc = 3/1) to give product **1**.

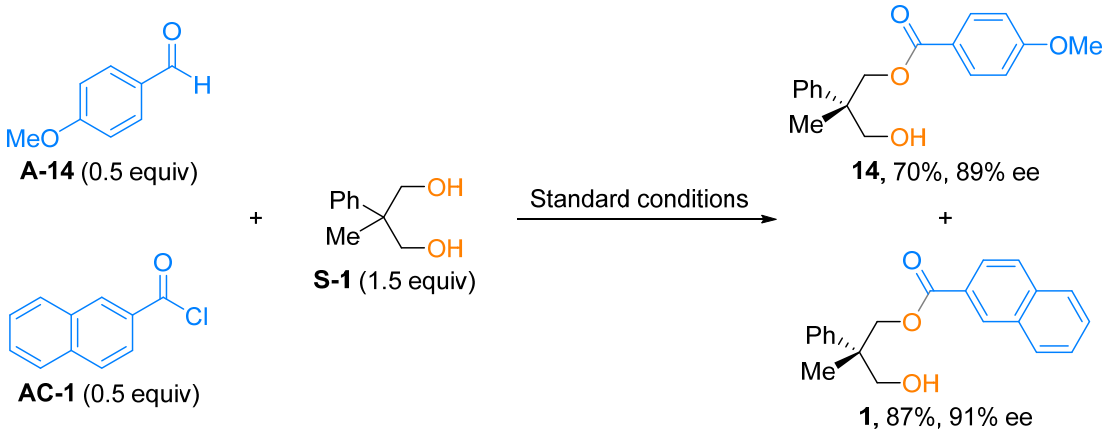
## 8.9 Control experiments with other Cu(II) salts




| Entry | Cu(II) | $PPh_3$ | Yield (%) | Ee (%) |
|---|---|---|---|---|
| 1 | $CuCl_2$ | – | 23 | 7 |
| 2 | $CuCl_2$ | + | 31 | 0 |
| 3 | $CuBr_2$ | – | 23 | 7 |
| 4 | $CuBr_2$ | + | 34 | 0 |
| 5 | $Cu(OTf)_2$ | – | 15 | 8 |
| 6 | $Cu(OTf)_2$ | + | 34 | 0 |
| 7 | $Cu(acac)_2$ | – | 18 | 7 |
| 8 | $Cu(acac)_2$ | + | 31 | 0 |

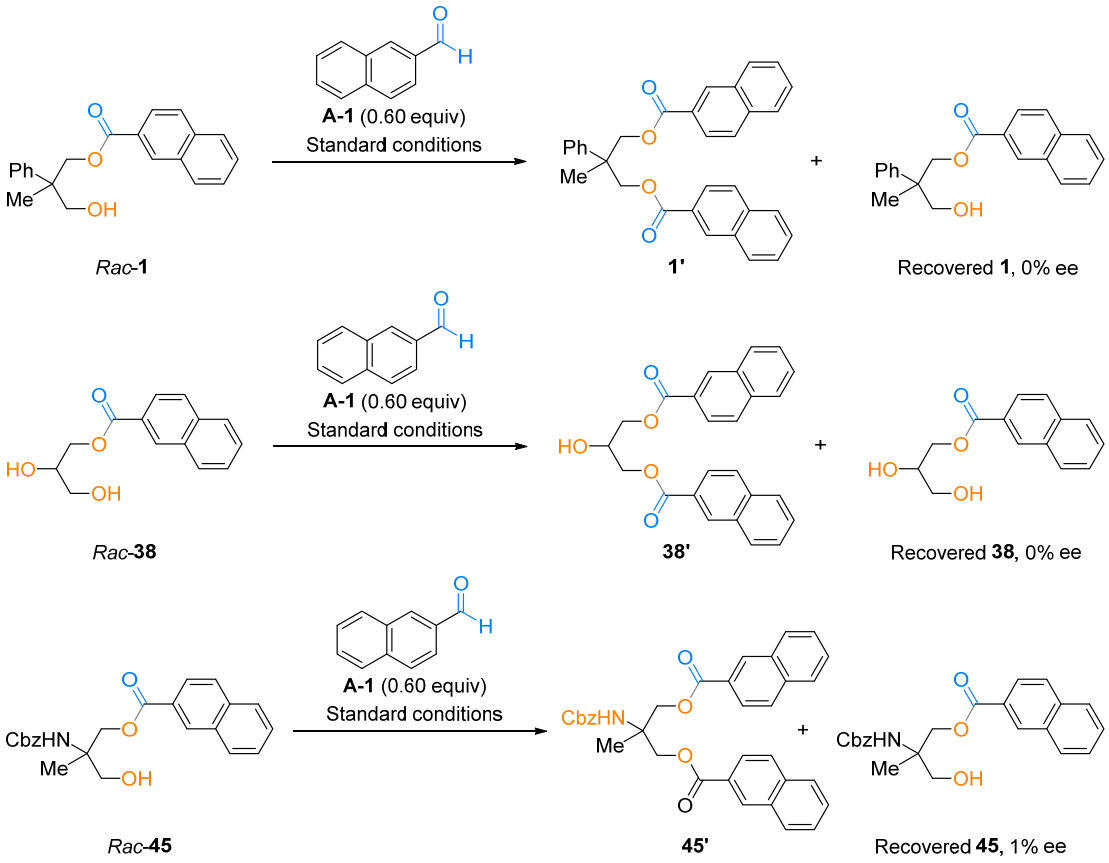
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with Cu (II) (0.010 mmol, 10 mol %), **L1** (8.5 mg, 0.015 mmol, 15 mol %), 2-methyl-2-phenylpropane-1,3-diol (24.9 mg, 0.15 mmol, 1.5 equiv), 2-naphthoyl chloride (19.0 mg, 0.10 mmol, 1.0 equiv), and anhydrous $CCl_4$ (2.0 mL). The reaction mixture was stirred at rt for 2 d. The reaction mixture was filtered through a plug of celite (rinsed with EtOAc) and concentrated *in vacuo*. Yield was based on $^1H$ NMR analysis of the crude products using 1,3,5-trimethoxybenzene as an internal standard. The residue was purified with column chromatography (petroleum ether/EtOAc = 3/1) to give product **1**.

## 8.10 Simultaneous reactions of acyl chloride AC-1 and aldehyde A-14 with S-1, respectively, in the same reaction flask



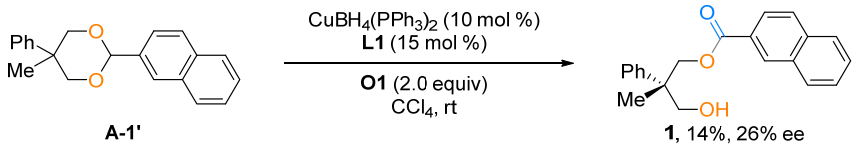
Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (6.0 mg, 0.010 mmol, 10 mol %), **L1** (8.5 mg, 0.015 mmol, 15 mol %), 2-methyl-2-phenylpropane-1,3-diol (24.9 mg, 0.15 mmol, 1.5 equiv), 2-naphthoyl chloride (9.5 mg, 0.050 mmol, 0.5 equiv), 4-methoxybenzaldehyde (6.8 mg, 0.050 mmol, 0.5 equiv), and anhydrous $CCl_4$ (2.0 mL). Then, **O1** (40.5 mg, 0.20 mmol, 2.0 equiv) was added to the mixture and the reaction mixture was stirred at rt for 2 d. The reaction mixture was concentrated *in vacuo* and the residue was purified with column chromatography (petroleum ether/EtOAc = 5/1) to give product **1** (14.0 mg, 87% yield, 91% ee) and **14** (10.5 mg, 70% yield, 89% ee).

### 8.11 Control experiments on the possible product kinetic resolution



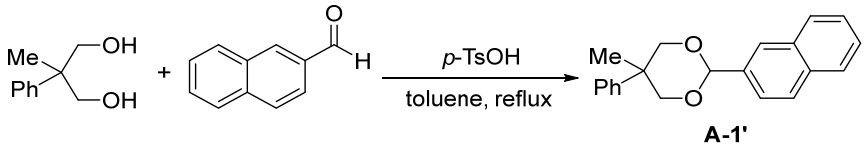

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (6.0 mg, 0.010 mmol, 10 mol %), **L1** (8.5 mg, 0.015 mmol, 15 mol %) or **L8** (6.7 mg, 0.015 mmol, 15 mol %), 2-naphthaldehyde (9.4 mg, 0.060 mmol, 0.6 equiv), corresponding racemic alcohol (0.10 mmol, 1.0 equiv), and anhydrous $CCl_4$ (2.0 mL). Then, **O1** (40.5 mg, 0.20 mmol, 2.0 equiv) was added to the mixture and the reaction mixture was stirred at rt for 1 d. The reaction mixture was concentrated *in vacuo* and the residue was purified with column chromatography (petroleum ether/EtOAc = 3/1).

## 8.12 Control experiment on the possible oxidative acetal cleavage



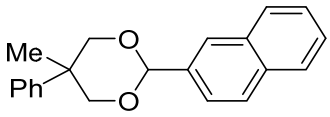

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with $CuBH_4(PPh_3)_2$ (6.0 mg, 0.010 mmol, 10 mol %), **L1** (8.5 mg, 0.015 mmol, 15 mol %), **A-1'** (30.4 mg, 0.10 mmol, 1.0 equiv), and anhydrous $CCl_4$ (2.0 mL). Then, **O1** (40.5 mg, 0.20 mmol, 2.0 equiv) was added to the mixture and the reaction mixture was stirred at rt for 2 d. The reaction mixture was concentrated *in vacuo* and the residue was purified with column chromatography (petroleum ether/EtOAc = 3/1) to give product **1** (4.5 mg, 14% yield, 26% ee).

Synthesis of compound **A-1'**




To a solution of 2-methyl-2-phenylpropane-1,3-diol (166 mg, 1.0 mmol, 1.0 equiv) and 2-naphthaldehyde (234 mg, 1.5 mmol, 1.5 equiv) in toluene (5.0 mL) was added *p*-toluenesulfonic acid (9.5 mg, 0.050 mmol, 5 mol %). The reaction was allowed to stir at 120 °C until the starting material disappeared. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 20/1) to give product **A-1'** as a pale-yellow solid (214 mg, 70% yield).

**5-Methyl-2-(naphthalen-2-yl)-5-phenyl-1,3-dioxane (A-1')**




**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 7.95 (m, 1H), 7.95 – 7.81 (m, 3H), 7.69 (dd, $J$ = 8.6, 1.7 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.43 – 7.35 (m, 2H), 7.34 – 7.24 (m, 4H), 5.67 (s, 1H), 4.20 (s, 4H), 1.74 (s, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 143.2, 135.7, 133.7, 133.1, 128.8, 128.4, 128.3, 127.8, 127.0, 126.4, 126.1, 125.6, 125.3, 123.8, 102.1, 76.3, 36.8, 22.9.
**HRMS** (ESI) *m/z* calcd. for $C_{21}H_{20}NaO_2$ $[M + Na]^+$ 327.1356, found 327.1350.

# 9. Computational study

## 9.1 Computational Details

All density functional theory (DFT) calculations were performed using Gaussian 16 program[20] with default parameters. Geometry optimizations were conducted with B3LYP functional,[21] employing the D3 version of Grimme's dispersion corrections[22] with Becke-Johnson damping.[23] LANL2DZ basis set[24] was used for copper and 6-31G(d) basis set was used for all other atoms. (5d,7f) keyword in Gaussian 16 software is used. Single-point energies and solvent effects at $CCl_4$ (tetrachloromethane) were evaluated with B3LYP functional and D3 version of Grimme's dispersion corrections with Becke-Johnson damping. SDD basis set[25] was used for copper and 6-311+G(d,p) basis set was used for all other atoms. The solvation energies were calculated with a self-consistent reaction field (SCRF) using the SMD implicit solvent model.[26] Frequency analysis was also performed at the same level of theory as geometry optimization to confirm whether optimized stationary points were either local minimum or transition state, as well as to evaluate zero-point vibrational energies and thermal corrections for enthalpies and free energies at 298.15 K. Mulliken spin distribution was acquired at the same level of theory as geometry optimization.

In addition, geometry optimization, frequency analysis, and single point energy of open-shell local minimums were calculated with unrestricted DFT methods, while the same computations for close-shell transition states and local minima were performed with restricted DFT methods. Wavefunction stability test at the same level of theory as geometry optimizations was employed to ensure that the SCF converged wavefunction was stable.

To correct the Gibbs free energies under 1 atm to the standard state in solution (1 mol/L), a correction of $RT\ln(c_s/c_g)$ is added to energies of all species. $c_s$ stands for the standard molar concentration in solution (1 mol/L), $c_g$ stands for the standard molar concentration in gas phase (about 0.040876 mol/L), and $R$ is the gas constant. For calculated intermediates at the standard state of 1 mol/L at 298.15 K, the correction value equaling to 1.89 kcal/mol was used. For solvent $CCl_4$ (tetrachloromethane) with density of 1554.96 g/L at 298.15 K and molecular weight of 153.82 g/mol, the correction value equaling to 3.26 kcal/mol was used.

The 3D diagrams of optimized structures shown in the main text and below here in Supporting Information for computations were generated with CYLview software.[27]

## 9.2 Discussions on C–O Bond Formation Mechanism

The proposed C–O bond formation mechanism between LCu(II)Alkoxyl intermediate **Int10** and benzoyl radical **Int4** includes the following three possible pathways: sequential SET and ion-type C–O bond formation (path A in Figure S9), radical-substitution-type C–O bond formation (path B in Figure S9) and reductive elimination (path C in Figure S9).

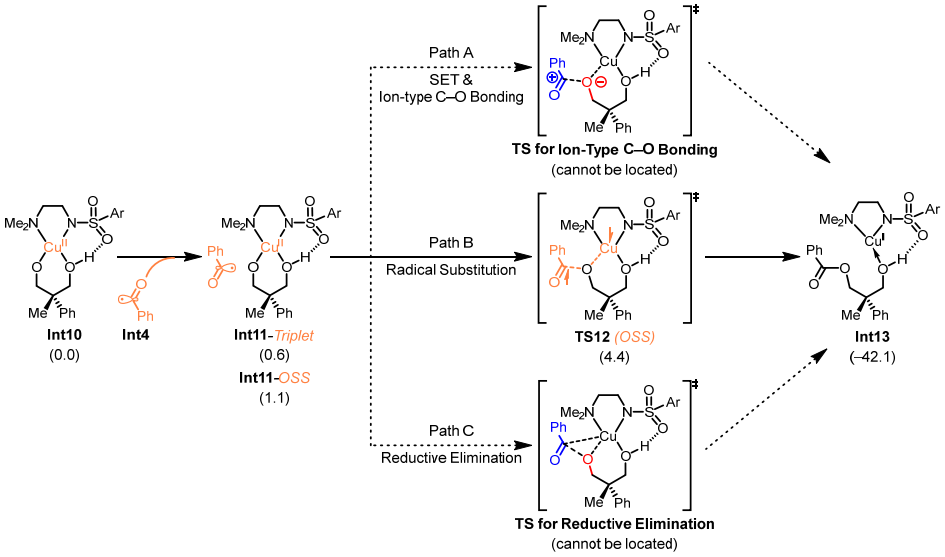



**Figure S9.** Results of the preliminary DFT calculations on the C–O coupling mechanism. Calculations were carried out at the B3LYP-D3(BJ)/6-311+G(d, p)-SDD-SMD(Tetrachloromethane)// B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level of theory. Free energies in kcal/mol relative to **Int4** and **Int10** were shown in parentheses. Ar = 2,4,6-trichlorophenyl.

Regarding path A, sequential SET and ion-type C–O bond formation, the proposed pre-intermediate of the ion-type C–O bond formation transition state has an unstable wavefunction (UHF to RHF wavefunction instability). Further optimization of this structure leads to an open-shell singlet diradical species **Int11**-*OSS*, which is the pre-intermediate of radical-substitution-type C–O bond formation transition state. Thus, we believe that sequential SET and ion-type C–O bond formation is not an operative pathway for the C–O bond formation. (Figure S10)

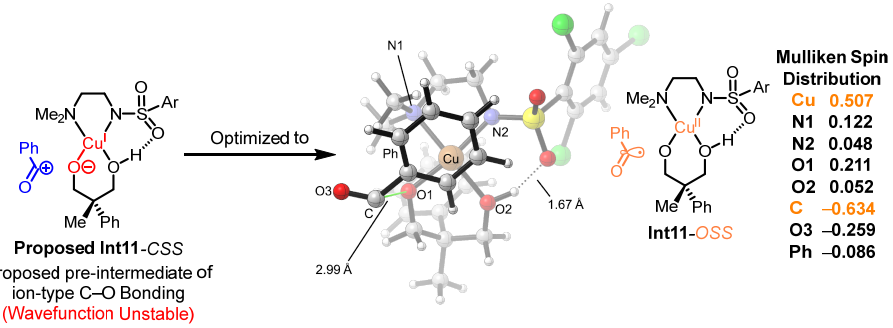



**Figure S10.** Results of the DFT study on the ion-type C–O bond formation mechanism. The proposed pre-intermediate of the ion-type C–O bond formation transition state has an unstable wavefunction and was further optimized to open-shell singlet diradical species **Int11**-*OSS*. Ar = 2,4,6-trichlorophenyl.

Regarding path B, the radical substitution pathway via **TS12** is operative for the C–O bond formation with a free energy barrier of 4.4 kcal/mol. **TS12** is an open-shell diradical singlet C–O bond formation transition state, whose nature of radical substitution is confirmed by the computed Mulliken spin distribution. Significant radical characters are identified on the carbons of the forming C–O bond, the coordinating nitrogen and oxygen atoms, and the copper center (Figure S11).

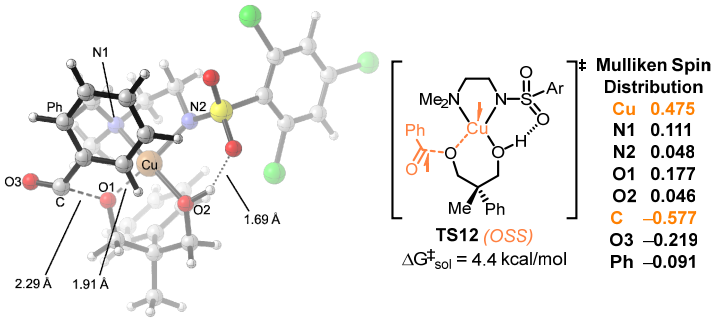



**Figure S11.** Located open-shell singlet radical-substitution-type C–O bond formation transition state **TS12**. Ar = 2,4,6-trichlorophenyl.

Regarding path C, the reductive elimination, attempts on locating the C–O reductive elimination transition state unfortunately fail despite extensive efforts. Both the proposed pre-intermediate structures and the transition state structures of the reductive elimination are optimized to an analogue of the C–O bond formation product **Int13**. This is probably due to the shallow shape of the free energy surface of the C–O bond formation. Considering both the unfruitful optimizations of the pre-intermediate and transition structures, we believe the reductive elimination transition state cannot be located, and thus, the reductive elimination may not be operative. (Figure S12)

Therefore, the reaction most likely undergoes an outer-sphere singlet radical-substitution-type C–O bond formation via **TS12**.

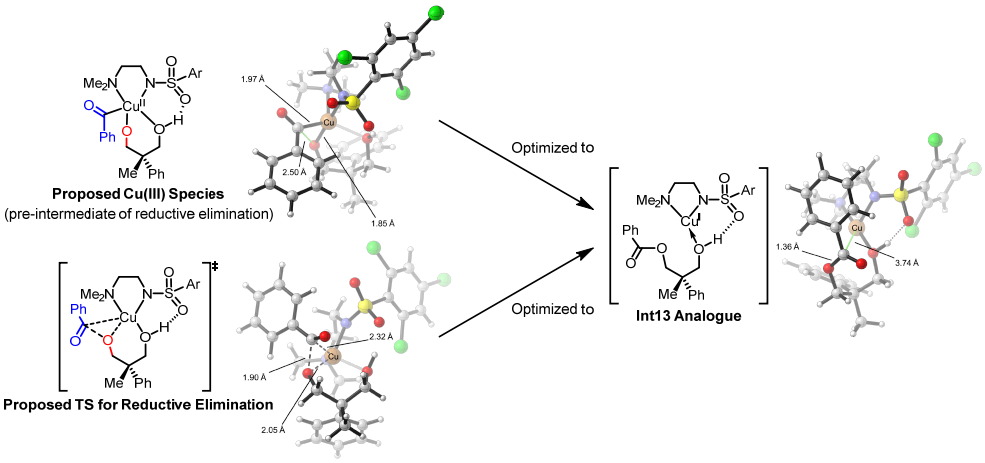



**Figure S12.** Attempts on locating the C–O reductive elimination transition state. The proposed pre-intermediate and transition state structures of the reductive elimination were both optimized to an analogue of the C–O bond formation product **Int13** despite extensive efforts. Ar = 2,4,6-trichlorophenyl.

On the basis of these results, we have proposed two radical substitution-type C–O coupling transition states **TS-Major** and **TS-Minor** (Figure S13) that likely lead to the two product enantiomers, respectively. Regarding the disfavored transition state **TS-Minor**, the vinyl, quinoline, and 2,4,6-trichlorophenyl groups in the ligand **L1** likely provide the steric hindrance that disfavors the approach of the attacking acyl radical.

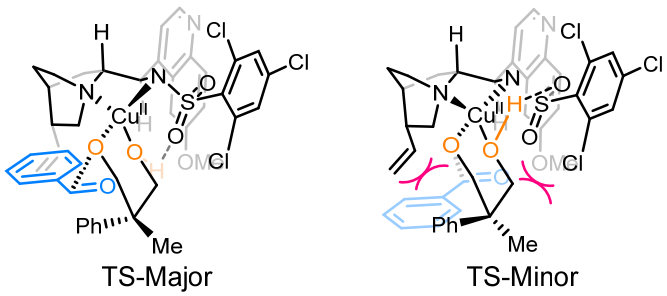



**Figure S13.** Proposed transition states leading to the two product enantiomers.

### 9.3 Discussions on Possible XAT Species

Preliminary DFT computations on proposed XAT processes are discussed in this section. The XAT between benzoyl chloride (**Int1**) and trichloromethyl radical (**Int2**) has a reaction barrier of 25.0 kcal/mol and an endergonic free energy change of 19.4 kcal/mol. (**TS3**, Figure S14A) These results correspond to a $k_{act}$ around $10^{-5}$ L/mol/s ($k_{act}$ = $k_B T(h^{-1})\exp(-\Delta G^{\ddagger}/RT)$, Erying Equation) and a $K_{eq}$ around $10^{-15}$ ($K_{eq}$ = $\exp(-\Delta G/RT)$), respectively, indicating that XAT between benzoyl chloride and trichloromethyl radical was not consistent with the observed reaction rate. Accordingly, this reaction is unlikely involved in the regeneration of acyl radicals from acid chlorides.

Next, we examined the XAT reaction of methyl radicals (**Int6**) with benzoyl chlorides (Figure S14B). Although the reaction barrier was lower than that of trichloromethyl radicals (18.8 kcal/mol via **TS7** *vs* 25.0 kcal/mol via **TS3**), the reaction proved to be uncompetitive to the XAT reaction of methyl radicals with carbon tetrachloride (**Int5**) given the much lower reaction barrier of the latter (**TS9**, free energy barrier: 8.4 kcal/mol, Figure S14C).

All in all, although our experimental results indicated the likely involvement of radical species in the enantioselective reaction of acid chlorides with diols, we have thus far been unable to elucidate its mechanism. Further experimental and theoretical studies on these processes are ongoing in our laboratories.

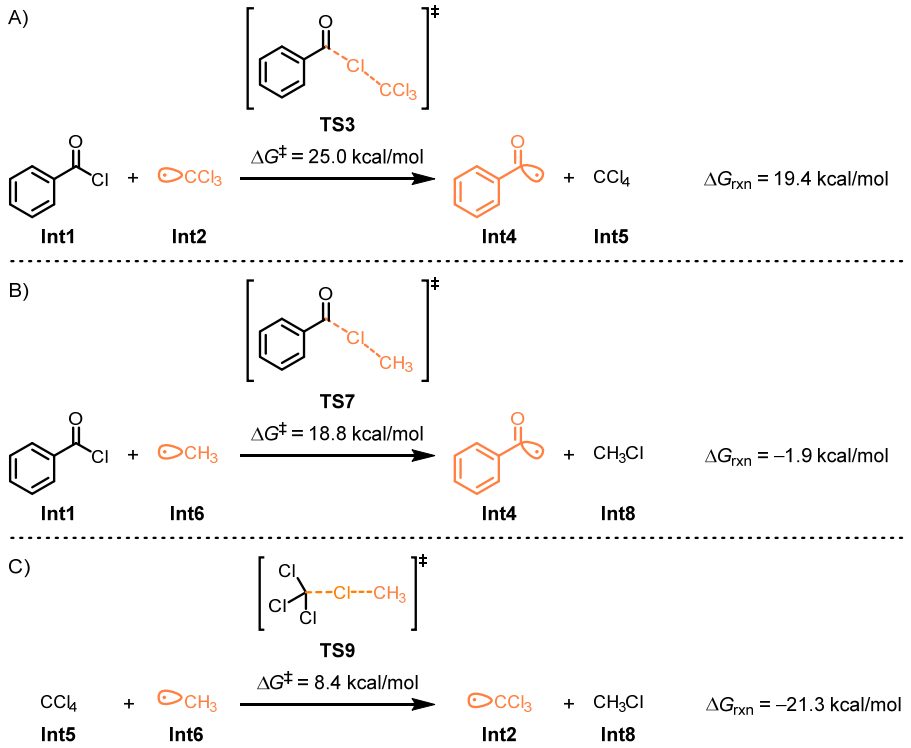



**Figure S14.** Results of DFT calculations on possible XAT processes.

## 9.4 Table of Energies

**Table S5. Energies in Figures S9 to S12 and S14.** Zero-point correction (***ZPE***), thermal correction to enthalpy (***TCH***), thermal correction to Gibbs free energy (***TCG***), energies (***E***), enthalpies (***H***), and Gibbs free energies (***G***) (in Hartree) of the structures calculated at B3LYP-D3(BJ)/6-311+G(d,p)-SDD-SMD(Tetrachloromethane)//B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level of theory.

| Structure | ***ZPE*** | ***TCH*** | ***TCG*** | ***E*** | ***H*** | ***G*** | Imaginary Frequency |
|---|---|---|---|---|---|---|---|
| **Int1** | 0.101469 | 0.109761 | 0.068385 | −805.347377 | −805.237616 | −805.278992 | |
| **Int2** | 0.007127 | 0.012540 | −0.021677 | −1418.734576 | −1418.722036 | −1418.756253 | |
| **TS3** | 0.107734 | 0.122160 | 0.061089 | −2224.053439 | −2223.931279 | −2223.992350 | 290.8*i* |
| **Int4** | 0.097913 | 0.105179 | 0.066670 | −345.048649 | −344.943470 | −344.981979 | |
| **Int5** | 0.009350 | 0.015923 | −0.020289 | −1879.004256 | −1878.988333 | −1879.024545 | |
| **Int6** | 0.029834 | 0.033884 | 0.011045 | −39.854956 | −39.821072 | −39.843911 | |
| **TS7** | 0.134840 | 0.146350 | 0.094646 | −845.184649 | −845.038299 | −845.090003 | 422.4*i* |
| **Int8** | 0.038118 | 0.042077 | 0.015481 | −500.159413 | −500.117336 | −500.143932 | |
| **TS9** | 0.042629 | 0.052471 | 0.004709 | −1918.854611 | −1918.802140 | −1918.849902 | 441.1*i* |
| **Int10** | 0.436054 | 0.468534 | 0.372045 | −3164.276342 | −3163.807808 | −3163.904297 | |
| **Int11**-*OSS* | 0.535384 | 0.576069 | 0.459953 | −3509.341426 | −3508.765357 | −3508.881473 | |
| **Int11**-*Triplet* | 0.535393 | 0.576076 | 0.459014 | −3509.341380 | −3508.765304 | −3508.882366 | |
| **TS12** | 0.535109 | 0.574942 | 0.462570 | −3509.338902 | −3508.763960 | −3508.876332 | 195.2*i* |
| **Int13** | 0.538412 | 0.578538 | 0.463511 | −3509.413903 | −3508.835365 | −3508.950392 | |

## 9.5 Cartesian Coordinates of Computed Species

### Int1

Charge = 0, Multiplicity = 1

| | | | |
|---|---|---|---|
| C | 2.39076400 | -0.11634500 | 0.00000000 |
| C | 1.09772500 | -0.63409700 | 0.00000000 |
| C | 0.00000000 | 0.23675400 | 0.00000000 |
| C | 0.20846900 | 1.62735500 | 0.00000000 |
| C | 1.50191800 | 2.13654300 | 0.00000000 |
| C | 2.59485800 | 1.26502100 | 0.00000000 |
| H | 3.23999100 | -0.79266200 | 0.00000000 |
| H | 0.93700300 | -1.70498700 | 0.00000000 |
| H | -0.65308000 | 2.28556400 | 0.00000000 |
| H | 1.66015000 | 3.21068900 | 0.00000000 |
| H | 3.60549300 | 1.66315400 | 0.00000000 |
| C | -1.41088300 | -0.21046100 | 0.00000000 |
| O | -2.37471300 | 0.49462900 | 0.00000000 |
| Cl | -1.65229100 | -2.02631800 | 0.00000000 |

### Int2

Charge = 0, Multiplicity = 2

| | | | |
|---|---|---|---|
| C | 0.00000000 | 0.00000000 | 0.27511600 |
| Cl | 0.00000000 | 1.70124100 | -0.03236700 |
| Cl | -1.47331800 | -0.85062000 | -0.03236700 |
| Cl | 1.47331800 | -0.85062000 | -0.03236700 |

### TS3

Charge = 0, Multiplicity = 2

| | | | |
|---|---|---|---|
| C | 3.32618000 | 1.84128000 | -0.00006800 |
| C | 2.29869400 | 0.90109700 | -0.00010800 |
| C | 2.61585800 | -0.46391600 | -0.00004000 |
| C | 3.95967000 | -0.88608800 | 0.00005700 |
| C | 4.97608500 | 0.06106900 | 0.00009800 |
| C | 4.65897800 | 1.42383800 | 0.00004200 |
| H | 3.08701200 | 2.90000800 | -0.00011600 |
| H | 1.26085500 | 1.21025600 | -0.00020200 |
| H | 4.18068900 | -1.94832000 | 0.00009800 |
| H | 6.01403000 | -0.25769100 | 0.00017500 |
| H | 5.45574600 | 2.16205900 | 0.00008300 |
| C | 1.57884500 | -1.50196200 | -0.00004600 |

| | | | |
|---|---|---|---|
| O | 1.65748400 | -2.68306700 | -0.00004300 |
| Cl | -0.58851600 | -0.66237500 | 0.00004800 |
| C | -2.43520400 | 0.15561700 | 0.00001900 |
| Cl | -3.26451100 | -0.37280200 | 1.47437500 |
| Cl | -3.27910100 | -0.40539000 | -1.45378200 |
| Cl | -2.22862800 | 1.92366200 | -0.02060700 |

## Int4

Charge = 0, Multiplicity = 2

| | | | |
|---|---|---|---|
| C | 1.63447500 | -1.16916100 | 0.00000000 |
| C | 1.33541000 | 0.19193600 | 0.00000000 |
| C | 0.00000000 | 0.61237700 | 0.00000000 |
| C | -1.04041400 | -0.33262900 | 0.00000000 |
| C | -0.73699600 | -1.68991400 | 0.00000000 |
| C | 0.59913500 | -2.10678500 | 0.00000000 |
| H | 2.66869900 | -1.49994100 | 0.00000000 |
| H | 2.12271100 | 0.93970100 | 0.00000000 |
| H | -2.06807400 | 0.01700800 | 0.00000000 |
| H | -1.53555900 | -2.42627300 | 0.00000000 |
| H | 0.83226200 | -3.16788900 | 0.00000000 |
| C | -0.29983500 | 2.06187200 | 0.00000000 |
| O | -1.37133600 | 2.59140200 | 0.00000000 |

## Int5

Charge = 0, Multiplicity = 1

| | | | |
|---|---|---|---|
| Cl | -1.03341100 | 1.03341100 | -1.03341100 |
| Cl | 1.03341100 | -1.03341100 | -1.03341100 |
| Cl | 1.03341100 | 1.03341100 | 1.03341100 |
| C | 0.00000000 | 0.00000000 | 0.00000000 |
| Cl | -1.03341100 | -1.03341100 | 1.03341100 |

## Int6

Charge = 0, Multiplicity = 2

| | | | |
|---|---|---|---|
| C | 0.00000000 | 0.00000000 | 0.00015100 |
| H | 0.00000000 | 1.08284100 | -0.00030200 |
| H | -0.93776800 | -0.54142000 | -0.00030200 |
| H | 0.93776800 | -0.54142000 | -0.00030200 |

## TS7

Charge = 0, Multiplicity = 2

| | | | |
|---|---|---|---|
| C | -1.97388900 | -1.74371200 | 0.00011200 |
| C | -0.76726400 | -1.04732500 | 0.00012600 |
| C | -0.77728500 | 0.35299500 | 0.00001200 |
| C | -1.99811000 | 1.05235000 | -0.00010900 |
| C | -3.19733700 | 0.34951600 | -0.00013800 |
| C | -3.18538000 | -1.04901700 | -0.00002600 |
| H | -1.96922900 | -2.82940200 | 0.00020400 |
| H | 0.17995900 | -1.57204400 | 0.00022500 |
| H | -1.98237900 | 2.13713200 | -0.00019100 |
| H | -4.14092700 | 0.88706200 | -0.00024700 |
| H | -4.12324400 | -1.59719600 | -0.00004500 |
| C | 0.45957200 | 1.15728400 | 0.00005200 |
| O | 0.57325100 | 2.33934200 | 0.00016100 |
| Cl | 2.26265800 | 0.01870300 | -0.00004500 |
| C | 4.11294500 | -1.12482400 | -0.00007800 |
| H | 4.86463600 | -0.34176100 | -0.01474300 |
| H | 4.03375500 | -1.71098300 | -0.91067700 |
| H | 4.04673300 | -1.68910800 | 0.92525100 |

## Int8

Charge = 0, Multiplicity = 1

| | | | |
|---|---|---|---|
| C | 0.00000000 | 0.00000000 | -1.13877700 |
| H | 0.00000000 | 1.03396800 | -1.48480900 |
| H | 0.89544300 | -0.51698400 | -1.48480900 |
| H | -0.89544300 | -0.51698400 | -1.48480900 |
| Cl | 0.00000000 | 0.00000000 | 0.66394600 |

## TS9

Charge = 0, Multiplicity = 2

| | | | |
|---|---|---|---|
| Cl | 1.45499800 | 0.00031200 | -0.00069200 |
| C | -0.55857600 | 0.00001700 | -0.00001300 |
| Cl | -1.08743900 | -0.46186600 | 1.62506700 |
| Cl | -1.08850800 | -1.17639200 | -1.21207000 |
| Cl | -1.08873600 | 1.63792700 | -0.41229300 |
| C | 3.73024800 | 0.00002900 | -0.00003400 |
| H | 3.91176900 | 1.00711000 | -0.35838800 |
| H | 3.91165800 | -0.81393900 | -0.69294900 |
| H | 3.91120100 | -0.19314500 | 1.05140500 |

## Int10

Charge = 0, Multiplicity = 2

| | | | |
|---|---|---|---|
| C | 0.70199200 | -1.68269400 | 1.25267100 |
| H | 0.83460200 | -2.75045700 | 1.03235600 |
| N | 0.25829000 | -0.92211400 | 0.07637200 |
| C | -0.34544100 | -1.46304400 | 2.33527900 |
| N | -1.69725700 | -1.76862300 | 1.82221200 |
| H | -0.34389700 | -0.40606300 | 2.61554100 |
| C | -2.74928100 | -1.15204300 | 2.64926500 |
| C | -1.94285800 | -3.21619400 | 1.67988300 |
| H | -3.70135400 | -1.29275200 | 2.13836900 |
| H | -2.55622200 | -0.08189900 | 2.73607300 |
| H | -2.91438700 | -3.34692200 | 1.19995500 |
| H | -1.17269500 | -3.66742300 | 1.05011200 |
| S | 1.27573800 | -0.99832500 | -1.16677300 |
| C | 2.77535300 | -0.13023000 | -0.55549500 |
| C | 3.96090700 | -0.79853300 | -0.18617100 |
| C | 2.77518900 | 1.27357300 | -0.40964900 |
| C | 5.09930700 | -0.10470600 | 0.23351500 |
| C | 3.90163900 | 1.98091400 | 0.00481400 |
| C | 5.06162500 | 1.27957300 | 0.31077200 |
| O | 0.75462300 | -0.13676600 | -2.26049800 |
| O | 1.67749100 | -2.35557500 | -1.54635400 |
| Cu | -1.75121900 | -1.01976800 | -0.13557000 |
| H | 1.66640100 | -1.31381600 | 1.63039600 |
| H | -1.93838400 | -3.71067100 | 2.66295900 |
| H | -0.12422700 | -2.06394400 | 3.23028500 |
| H | -2.76946100 | -1.60643700 | 3.65155100 |
| H | 5.99460500 | -0.65173100 | 0.49915000 |
| H | 3.86389400 | 3.05910300 | 0.09141100 |
| Cl | 4.13706400 | -2.53808400 | -0.16352800 |
| Cl | 6.48387000 | 2.15415900 | 0.82648600 |
| Cl | 1.36195000 | 2.26583700 | -0.68978100 |
| C | -3.87465700 | 0.82972400 | -1.37062200 |
| C | -4.40150100 | -0.60914400 | -1.03272400 |
| H | -5.40815400 | -0.49114900 | -0.59296600 |
| H | -4.54078400 | -1.13288200 | -1.99808200 |
| C | -2.75175100 | 0.69656900 | -2.40804100 |
| H | -3.19361500 | 0.42393300 | -3.37270200 |
| H | -2.21414400 | 1.64417600 | -2.53261900 |
| O | -3.60940600 | -1.31977300 | -0.14843800 |
| C | -3.41576300 | 1.50239300 | -0.07484500 |
| C | -4.34969000 | 1.74856400 | 0.94466700 |

| | | | |
|---|---|---|---|
| C | -2.07912200 | 1.84154300 | 0.17531500 |
| C | -3.97009200 | 2.32710300 | 2.15262300 |
| H | -5.38944900 | 1.47373400 | 0.79655800 |
| C | -1.68807500 | 2.40798500 | 1.39357400 |
| H | -1.31383200 | 1.66120200 | -0.56840300 |
| C | -2.63210300 | 2.66035800 | 2.38581900 |
| H | -4.71854100 | 2.51125000 | 2.91861300 |
| H | -0.64097200 | 2.64934900 | 1.55022500 |
| H | -2.33414200 | 3.10865700 | 3.32944800 |
| C | -4.99945400 | 1.64168200 | -2.04042000 |
| H | -5.40570400 | 1.09414200 | -2.89900400 |
| H | -5.82142500 | 1.83256900 | -1.34597800 |
| H | -4.63152800 | 2.61115600 | -2.39544000 |
| O | -1.82921000 | -0.33979100 | -2.04203300 |
| H | -0.89466800 | -0.14909800 | -2.32479600 |

## **Int11-***OSS*

Charge = 0, Multiplicity = 1

| | | | |
|---|---|---|---|
| C | 0.82517800 | -1.04666200 | 1.65552100 |
| H | 0.61608000 | -2.12274100 | 1.71326800 |
| N | 0.55384100 | -0.50711400 | 0.31595000 |
| C | -0.03547100 | -0.25679900 | 2.63148500 |
| N | -1.44792100 | -0.24811600 | 2.19865200 |
| H | 0.30228900 | 0.78338400 | 2.63829000 |
| C | -2.21467500 | 0.81808000 | 2.86722100 |
| C | -2.10995700 | -1.54956600 | 2.40222000 |
| H | -3.19916700 | 0.86517100 | 2.40328700 |
| H | -1.71140400 | 1.77314300 | 2.71601000 |
| H | -3.13104500 | -1.47660600 | 2.02815400 |
| H | -1.59091200 | -2.33127000 | 1.84636100 |
| S | 1.47362500 | -1.13421400 | -0.83793300 |
| C | 3.15928800 | -0.49914500 | -0.46301900 |
| C | 4.15673300 | -1.28123700 | 0.15695000 |
| C | 3.50682500 | 0.83606200 | -0.75757500 |
| C | 5.43918800 | -0.78371100 | 0.40338800 |
| C | 4.78117000 | 1.34759700 | -0.52250700 |
| C | 5.74235400 | 0.52234700 | 0.04822800 |
| O | 1.09498300 | -0.52261200 | -2.13880300 |
| O | 1.57428300 | -2.59751700 | -0.83142600 |
| Cu | -1.38811900 | 0.04227800 | 0.12312800 |
| H | 1.87715100 | -0.90975400 | 1.94251800 |
| H | -2.12582800 | -1.81205500 | 3.47113500 |
| H | 0.05346100 | -0.66125300 | 3.65129400 |

| | | | |
|---|---|---|---|
| H | -2.29883400 | 0.61150900 | 3.94498300 |
| H | 6.18049200 | -1.41752300 | 0.87254100 |
| H | 5.00912200 | 2.37468400 | -0.77664800 |
| Cl | 3.91080700 | -2.91913100 | 0.72185700 |
| Cl | 7.34620900 | 1.14779100 | 0.34531600 |
| Cl | 2.37482900 | 2.00135700 | -1.40956000 |
| C | -2.81072000 | 2.35133600 | -1.39510800 |
| C | -3.76551200 | 1.22965400 | -0.85745100 |
| H | -4.67041300 | 1.72749700 | -0.46916000 |
| H | -4.09366800 | 0.63497200 | -1.73244600 |
| C | -1.81594400 | 1.71590600 | -2.37796200 |
| H | -2.34228700 | 1.48084800 | -3.30983000 |
| H | -0.99626800 | 2.40525300 | -2.61223900 |
| O | -3.23001700 | 0.44416400 | 0.14795700 |
| C | -2.12513800 | 3.03157700 | -0.20861400 |
| C | -2.89246300 | 3.75018200 | 0.72195800 |
| C | -0.74745900 | 2.93662300 | 0.02496500 |
| C | -2.30420000 | 4.37118100 | 1.82093200 |
| H | -3.96793400 | 3.81997500 | 0.59189000 |
| C | -0.15082100 | 3.54822900 | 1.13213700 |
| H | -0.11228400 | 2.37723200 | -0.64721400 |
| C | -0.92510300 | 4.27625800 | 2.03256400 |
| H | -2.92460600 | 4.92698300 | 2.51866000 |
| H | 0.92216100 | 3.45188400 | 1.27378200 |
| H | -0.46635600 | 4.76120000 | 2.88955100 |
| C | -3.63336900 | 3.36976400 | -2.20803800 |
| H | -4.21838200 | 2.85690300 | -2.98044800 |
| H | -4.33089100 | 3.91867500 | -1.57094900 |
| H | -2.98356200 | 4.10284100 | -2.69976200 |
| O | -1.28811000 | 0.48891000 | -1.85495300 |
| H | -0.37152500 | 0.26590000 | -2.16614200 |
| C | -3.70968000 | -2.72761600 | -0.49218600 |
| C | -2.75628900 | -2.28982300 | -1.41919100 |
| C | -1.53326200 | -2.94776700 | -1.52085300 |
| C | -1.27477300 | -4.06613300 | -0.72237700 |
| C | -2.24737700 | -4.53775600 | 0.16569500 |
| C | -3.46209200 | -3.86613300 | 0.29028900 |
| H | -2.96264100 | -1.41256300 | -2.01940500 |
| H | -0.77270700 | -2.58521800 | -2.20243800 |
| H | -0.30805200 | -4.55303500 | -0.79176500 |
| H | -2.04876500 | -5.41688600 | 0.77290800 |
| H | -4.21653400 | -4.19340900 | 0.99938600 |
| C | -4.95687100 | -1.95211500 | -0.31684800 |
| O | -5.74606100 | -2.03170000 | 0.57823200 |

**Int11**-*Triplet*

Charge = 0, Multiplicity = 3

| | | | |
|---|---|---|---|
| C | 0.82468100 | -1.06400900 | 1.63927600 |
| H | 0.60066200 | -2.13777000 | 1.68423800 |
| N | 0.55563800 | -0.50369400 | 0.30783000 |
| C | -0.02144000 | -0.27380500 | 2.62749100 |
| N | -1.43585300 | -0.24445300 | 2.20191600 |
| H | 0.32925800 | 0.76199700 | 2.64174800 |
| C | -2.18386600 | 0.83313000 | 2.87344500 |
| C | -2.11576200 | -1.53609500 | 2.40876000 |
| H | -3.17096700 | 0.89149100 | 2.41641500 |
| H | -1.66951800 | 1.78135300 | 2.71607000 |
| H | -3.13501200 | -1.45060700 | 2.03215000 |
| H | -1.60588200 | -2.32628400 | 1.85646100 |
| S | 1.47485000 | -1.11439200 | -0.85526000 |
| C | 3.16277600 | -0.49255500 | -0.46882800 |
| C | 4.15670000 | -1.28967300 | 0.13770300 |
| C | 3.51651900 | 0.84575400 | -0.74122200 |
| C | 5.44156700 | -0.80240000 | 0.39182400 |
| C | 4.79347100 | 1.34708700 | -0.49825100 |
| C | 5.75090000 | 0.50789400 | 0.05819600 |
| O | 1.09866300 | -0.47943900 | -2.14566700 |
| O | 1.57082800 | -2.57801700 | -0.87356000 |
| Cu | -1.38768800 | 0.04521300 | 0.12557300 |
| H | 1.87936700 | -0.94535800 | 1.92411600 |
| H | -2.13670100 | -1.79481000 | 3.47848300 |
| H | 0.06780000 | -0.68852400 | 3.64310100 |
| H | -2.26299800 | 0.63029500 | 3.95229700 |
| H | 6.17998200 | -1.44741200 | 0.85013700 |
| H | 5.02622900 | 2.37715300 | -0.73541300 |
| Cl | 3.90343200 | -2.93540000 | 0.67608000 |
| Cl | 7.35787300 | 1.12054100 | 0.36481800 |
| Cl | 2.38982800 | 2.02680500 | -1.37283900 |
| C | -2.82975800 | 2.34419500 | -1.39164100 |
| C | -3.77697600 | 1.22457300 | -0.83640700 |
| H | -4.67782000 | 1.72409600 | -0.44060400 |
| H | -4.11448100 | 0.62423600 | -1.70396600 |
| C | -1.84486700 | 1.70416000 | -2.38116400 |
| H | -2.38171900 | 1.45983200 | -3.30458300 |
| H | -1.03066300 | 2.39447900 | -2.63095400 |
| O | -3.22913300 | 0.44632500 | 0.16750100 |
| C | -2.13231900 | 3.03198100 | -0.21654600 |

| | | | |
|---|---|---|---|
| C | -2.89046800 | 3.75407100 | 0.71881200 |
| C | -0.75211100 | 2.93959000 | 0.00264700 |
| C | -2.29123400 | 4.38035500 | 1.80879900 |
| H | -3.96732900 | 3.82229500 | 0.59980800 |
| C | -0.14439900 | 3.55636000 | 1.10090200 |
| H | -0.12368800 | 2.37775100 | -0.67391600 |
| C | -0.90991600 | 4.28745500 | 2.00630100 |
| H | -2.90474600 | 4.93872800 | 2.51056500 |
| H | 0.92999400 | 3.46117600 | 1.23170000 |
| H | -0.44262300 | 4.77640300 | 2.85637600 |
| C | -3.66260300 | 3.35645600 | -2.20177700 |
| H | -4.25496700 | 2.83816200 | -2.96491000 |
| H | -4.35422600 | 3.90795700 | -1.56048900 |
| H | -3.01931900 | 4.08770300 | -2.70466900 |
| O | -1.30497800 | 0.48277500 | -1.85617400 |
| H | -0.38585900 | 0.27113400 | -2.16840100 |
| C | -3.72018200 | -2.74086100 | -0.47918000 |
| C | -2.77202400 | -2.29313900 | -1.40671800 |
| C | -1.54075100 | -2.93586900 | -1.50629200 |
| C | -1.26851600 | -4.04913900 | -0.70531400 |
| C | -2.23530100 | -4.53056200 | 0.18400900 |
| C | -3.45832700 | -3.87392400 | 0.30675400 |
| H | -2.98918300 | -1.42042000 | -2.00976000 |
| H | -0.78500200 | -2.56655200 | -2.18951000 |
| H | -0.29596200 | -4.52431200 | -0.77429200 |
| H | -2.02579300 | -5.40562500 | 0.79343100 |
| H | -4.20880300 | -4.20883200 | 1.01647700 |
| C | -4.97826100 | -1.98252700 | -0.30902800 |
| O | -5.76508400 | -2.06510500 | 0.58788700 |

## **Proposed Int11**-*CSS*

Charge = 0, Multiplicity = 1

| | | | |
|---|---|---|---|
| C | -1.24581200 | -0.08411300 | 2.06832600 |
| H | -0.96863200 | 0.75519100 | 2.72139500 |
| N | -0.78060200 | 0.12161000 | 0.69473400 |
| C | -0.58343400 | -1.38952700 | 2.52164800 |
| N | 0.87553600 | -1.32839600 | 2.30862000 |
| H | -0.98163500 | -2.19638500 | 1.90115300 |
| C | 1.43084700 | -2.60481300 | 1.84618200 |
| C | 1.59756800 | -0.84123700 | 3.48988100 |
| H | 2.49941400 | -2.48223000 | 1.66595900 |
| H | 0.95880600 | -2.88191700 | 0.90195100 |
| H | 2.63607000 | -0.64755500 | 3.20971100 |

| | | | |
|---|---|---|---|
| H | 1.15832700 | 0.09782200 | 3.83172000 |
| S | -1.65534400 | 1.02127900 | -0.31253700 |
| C | -3.25439400 | 0.12395100 | -0.35420200 |
| C | -4.47998300 | 0.68504900 | 0.05826300 |
| C | -3.29231700 | -1.20647100 | -0.82949700 |
| C | -5.67975900 | -0.02689400 | -0.03261000 |
| C | -4.48058200 | -1.92674200 | -0.92446900 |
| C | -5.66795400 | -1.32185600 | -0.52914700 |
| O | -1.06015400 | 0.84739100 | -1.66415100 |
| O | -1.89640300 | 2.40242800 | 0.11436800 |
| Cu | 1.14702000 | 0.26609500 | 0.70287100 |
| C | 3.54338400 | -0.59210100 | -1.51898500 |
| C | 3.67123200 | 0.56927800 | -0.49016500 |
| H | 4.73790100 | 0.69839200 | -0.24261000 |
| H | 3.38103900 | 1.49903100 | -1.01097300 |
| C | 2.17676600 | -0.51567400 | -2.21236900 |
| H | 2.04909500 | 0.49847700 | -2.61388200 |
| H | 2.13651600 | -1.20898400 | -3.06427900 |
| O | 2.99125500 | 0.40388600 | 0.71098900 |
| C | 3.78567000 | -1.95241300 | -0.86253000 |
| C | 4.77301400 | -2.09289800 | 0.12438600 |
| C | 3.08701200 | -3.10253500 | -1.25123900 |
| C | 5.04852000 | -3.33076100 | 0.70367300 |
| H | 5.32736000 | -1.22351000 | 0.45966700 |
| C | 3.35813000 | -4.34467900 | -0.67453500 |
| H | 2.29833700 | -3.03526900 | -1.99096000 |
| C | 4.33962500 | -4.46636300 | 0.30793600 |
| H | 5.81519900 | -3.40544700 | 1.47028300 |
| H | 2.79329100 | -5.21699300 | -0.99265100 |
| H | 4.54862900 | -5.43127200 | 0.76130100 |
| C | 4.61269800 | -0.36286300 | -2.60907900 |
| H | 4.49182700 | 0.62258900 | -3.07747700 |
| H | 5.61721200 | -0.41346400 | -2.17777400 |
| H | 4.54575700 | -1.12651700 | -3.39126400 |
| H | -2.33738800 | -0.19214100 | 2.11488600 |
| H | 1.56963700 | -1.57566100 | 4.31287100 |
| H | -0.82631000 | -1.61257400 | 3.57184300 |
| H | 1.28029700 | -3.41050700 | 2.58481100 |
| H | -6.60372100 | 0.43631500 | 0.28844300 |
| H | -4.47062900 | -2.94237300 | -1.29837300 |
| Cl | -4.64680400 | 2.28366000 | 0.74075400 |
| Cl | -7.16579000 | -2.21352600 | -0.64628300 |
| Cl | -1.86224600 | -2.08621400 | -1.31516000 |
| O | 1.12883200 | -0.82209300 | -1.29533400 |

| | | | |
|---|---|---|---|
| H | 0.28789100 | -0.42320800 | -1.60823700 |
| C | 1.29359500 | 2.14176500 | 1.28135300 |
| C | 1.61137300 | 3.16814000 | 0.28101000 |
| C | 1.32087200 | 2.99408800 | -1.07595100 |
| C | 2.23669600 | 4.34203100 | 0.73488000 |
| C | 1.64747500 | 4.00171300 | -1.98061700 |
| H | 0.80502700 | 2.10252000 | -1.40932500 |
| C | 2.57716400 | 5.33232000 | -0.17938400 |
| H | 2.44919100 | 4.45454900 | 1.79258200 |
| C | 2.28143000 | 5.16325500 | -1.53635900 |
| H | 1.40424400 | 3.87826600 | -3.03125200 |
| H | 3.06648200 | 6.23907300 | 0.16338800 |
| H | 2.54271300 | 5.94270200 | -2.24635900 |
| O | 1.15705800 | 2.25674400 | 2.46045600 |

## TS12

Charge = 0, Multiplicity = 1

| | | | |
|---|---|---|---|
| C | -0.84066500 | 0.81638600 | 1.79760300 |
| H | -0.78896600 | 1.89934000 | 1.96621700 |
| N | -0.56582400 | 0.46439700 | 0.39832400 |
| C | 0.18034100 | 0.07736100 | 2.65420300 |
| N | 1.55164600 | 0.31564600 | 2.15684600 |
| H | -0.00129800 | -0.99867200 | 2.58718900 |
| C | 2.52030200 | -0.61251900 | 2.76710900 |
| C | 1.98117300 | 1.70988300 | 2.37895300 |
| H | 3.47276400 | -0.50215600 | 2.24937000 |
| H | 2.16911700 | -1.63574200 | 2.63854800 |
| H | 3.02403300 | 1.80348400 | 2.08111000 |
| H | 1.38250600 | 2.39715800 | 1.77937300 |
| S | -1.48665800 | 1.23001500 | -0.66734800 |
| C | -3.15179000 | 0.49819300 | -0.38970400 |
| C | -4.18510400 | 1.16056800 | 0.30397000 |
| C | -3.43674900 | -0.81126900 | -0.83041600 |
| C | -5.44468300 | 0.58182200 | 0.48396000 |
| C | -4.68580800 | -1.40403900 | -0.66313600 |
| C | -5.68588200 | -0.69012100 | -0.01343200 |
| O | -1.09682800 | 0.80816400 | -2.03737600 |
| O | -1.61052700 | 2.67530300 | -0.45821500 |
| Cu | 1.37247900 | -0.00093200 | 0.08500300 |
| H | -1.84584300 | 0.49179700 | 2.10429400 |
| H | 1.88503900 | 1.97452600 | 3.44333000 |
| H | 0.09547800 | 0.38207800 | 3.70884300 |
| H | 2.63629200 | -0.39717300 | 3.84040800 |

| | | | |
|---|---|---|---|
| H | -6.21599600 | 1.12659900 | 1.01285100 |
| H | -4.86549100 | -2.40674800 | -1.02881600 |
| Cl | -4.01178900 | 2.73699800 | 1.04206400 |
| Cl | -7.26009800 | -1.41750700 | 0.20094600 |
| Cl | -2.24869700 | -1.84830700 | -1.59835400 |
| C | 2.71005100 | -2.33475700 | -1.47033700 |
| C | 3.69425200 | -1.16864100 | -1.12607400 |
| H | 4.64354100 | -1.61974600 | -0.79611900 |
| H | 3.91264200 | -0.63991800 | -2.07201700 |
| C | 1.59467000 | -1.78941600 | -2.37597100 |
| H | 2.00774900 | -1.60811700 | -3.37511000 |
| H | 0.77523500 | -2.51219600 | -2.47096400 |
| O | 3.24430600 | -0.29325900 | -0.13882900 |
| C | 2.17903000 | -2.96153700 | -0.17787800 |
| C | 3.07394900 | -3.59070200 | 0.70298600 |
| C | 0.82585600 | -2.93143600 | 0.18484400 |
| C | 2.63264800 | -4.19367900 | 1.87799000 |
| H | 4.13417900 | -3.60598600 | 0.47074800 |
| C | 0.37785300 | -3.52774700 | 1.36851900 |
| H | 0.09478600 | -2.44034300 | -0.44289300 |
| C | 1.27641500 | -4.16935900 | 2.21755700 |
| H | 3.34971900 | -4.67940100 | 2.53397600 |
| H | -0.68065000 | -3.49007700 | 1.61177800 |
| H | 0.93062300 | -4.64080100 | 3.13297700 |
| C | 3.46598800 | -3.39099900 | -2.30230800 |
| H | 3.94043800 | -2.92347600 | -3.17289000 |
| H | 4.24876200 | -3.87661000 | -1.71500100 |
| H | 2.78474100 | -4.17147600 | -2.65983600 |
| O | 1.10990600 | -0.54845500 | -1.86300000 |
| H | 0.20518000 | -0.26909200 | -2.15491200 |
| C | 3.47018000 | 2.57759900 | -0.53416700 |
| C | 2.47110700 | 2.30903300 | -1.47996700 |
| C | 1.43126500 | 3.21514600 | -1.67224300 |
| C | 1.40853200 | 4.41496100 | -0.95479600 |
| C | 2.43918100 | 4.71652700 | -0.06058500 |
| C | 3.46685400 | 3.79986000 | 0.15577800 |
| H | 2.49009100 | 1.37480600 | -2.02606100 |
| H | 0.62422100 | 2.97356500 | -2.35477600 |
| H | 0.58459100 | 5.10793300 | -1.09327900 |
| H | 2.43014100 | 5.65717500 | 0.48357800 |
| H | 4.25541900 | 4.00103500 | 0.87453400 |
| C | 4.53647300 | 1.58905700 | -0.24087300 |
| O | 5.28090700 | 1.57869100 | 0.69756700 |

## Proposed Cu-III-Species

Charge = 0, Multiplicity = 1

| | | | |
|---|---|---|---|
| C | -1.24581200 | -0.08411300 | 2.06832600 |
| H | -0.96863200 | 0.75519100 | 2.72139500 |
| N | -0.78060200 | 0.12161000 | 0.69473400 |
| C | -0.58343400 | -1.38952700 | 2.52164800 |
| N | 0.87553600 | -1.32839600 | 2.30862000 |
| H | -0.98163500 | -2.19638500 | 1.90115300 |
| C | 1.43084700 | -2.60481300 | 1.84618200 |
| C | 1.59756800 | -0.84123700 | 3.48988100 |
| H | 2.49941400 | -2.48223000 | 1.66595900 |
| H | 0.95880600 | -2.88191700 | 0.90195100 |
| H | 2.63607000 | -0.64755500 | 3.20971100 |
| H | 1.15832700 | 0.09782200 | 3.83172000 |
| S | -1.65534400 | 1.02127900 | -0.31253700 |
| C | -3.25439400 | 0.12395100 | -0.35420200 |
| C | -4.47998300 | 0.68504900 | 0.05826300 |
| C | -3.29231700 | -1.20647100 | -0.82949700 |
| C | -5.67975900 | -0.02689400 | -0.03261000 |
| C | -4.48058200 | -1.92674200 | -0.92446900 |
| C | -5.66795400 | -1.32185600 | -0.52914700 |
| O | -1.06015400 | 0.84739100 | -1.66415100 |
| O | -1.89640300 | 2.40242800 | 0.11436800 |
| Cu | 1.14702000 | 0.26609500 | 0.70287100 |
| C | 3.54338400 | -0.59210100 | -1.51898500 |
| C | 3.67123200 | 0.56927800 | -0.49016500 |
| H | 4.73790100 | 0.69839200 | -0.24261000 |
| H | 3.38103900 | 1.49903100 | -1.01097300 |
| C | 2.17676600 | -0.51567400 | -2.21236900 |
| H | 2.04909500 | 0.49847700 | -2.61388200 |
| H | 2.13651600 | -1.20898400 | -3.06427900 |
| O | 2.99125500 | 0.40388600 | 0.71098900 |
| C | 3.78567000 | -1.95241300 | -0.86253000 |
| C | 4.77301400 | -2.09289800 | 0.12438600 |
| C | 3.08701200 | -3.10253500 | -1.25123900 |
| C | 5.04852000 | -3.33076100 | 0.70367300 |
| H | 5.32736000 | -1.22351000 | 0.45966700 |
| C | 3.35813000 | -4.34467900 | -0.67453500 |
| H | 2.29833700 | -3.03526900 | -1.99096000 |
| C | 4.33962500 | -4.46636300 | 0.30793600 |
| H | 5.81519900 | -3.40544700 | 1.47028300 |
| H | 2.79329100 | -5.21699300 | -0.99265100 |
| H | 4.54862900 | -5.43127200 | 0.76130100 |

| | | | |
|---|---|---|---|
| C | 4.61269800 | -0.36286300 | -2.60907900 |
| H | 4.49182700 | 0.62258900 | -3.07747700 |
| H | 5.61721200 | -0.41346400 | -2.17777400 |
| H | 4.54575700 | -1.12651700 | -3.39126400 |
| H | -2.33738800 | -0.19214100 | 2.11488600 |
| H | 1.56963700 | -1.57566100 | 4.31287100 |
| H | -0.82631000 | -1.61257400 | 3.57184300 |
| H | 1.28029700 | -3.41050700 | 2.58481100 |
| H | -6.60372100 | 0.43631500 | 0.28844300 |
| H | -4.47062900 | -2.94237300 | -1.29837300 |
| Cl | -4.64680400 | 2.28366000 | 0.74075400 |
| Cl | -7.16579000 | -2.21352600 | -0.64628300 |
| Cl | -1.86224600 | -2.08621400 | -1.31516000 |
| O | 1.12883200 | -0.82209300 | -1.29533400 |
| H | 0.28789100 | -0.42320800 | -1.60823700 |
| C | 1.29359500 | 2.14176500 | 1.28135300 |
| C | 1.61137300 | 3.16814000 | 0.28101000 |
| C | 1.32087200 | 2.99408800 | -1.07595100 |
| C | 2.23669600 | 4.34203100 | 0.73488000 |
| C | 1.64747500 | 4.00171300 | -1.98061700 |
| H | 0.80502700 | 2.10252000 | -1.40932500 |
| C | 2.57716400 | 5.33232000 | -0.17938400 |
| H | 2.44919100 | 4.45454900 | 1.79258200 |
| C | 2.28143000 | 5.16325500 | -1.53635900 |
| H | 1.40424400 | 3.87826600 | -3.03125200 |
| H | 3.06648200 | 6.23907300 | 0.16338800 |
| H | 2.54271300 | 5.94270200 | -2.24635900 |
| O | 1.15705800 | 2.25674400 | 2.46045600 |

## Proposed Reductive Elimination TS

Charge = 0, Multiplicity = 1

| | | | |
|---|---|---|---|
| C | -1.10559500 | 1.07876600 | 1.44142400 |
| H | -0.71593300 | 2.07528500 | 1.69501900 |
| N | -0.68622400 | 0.68014600 | 0.10792400 |
| C | -0.56908500 | 0.01075500 | 2.40414600 |
| N | 0.88462000 | -0.21180200 | 2.22465700 |
| H | -1.07573400 | -0.92799000 | 2.16866200 |
| C | 1.24966600 | -1.60646300 | 2.50731900 |
| C | 1.67266500 | 0.70174500 | 3.05947800 |
| H | 2.32276500 | -1.73425200 | 2.36331800 |
| H | 0.72706800 | -2.26413400 | 1.80976200 |
| H | 2.73202700 | 0.59219900 | 2.81078500 |
| H | 1.37700200 | 1.73353700 | 2.86026400 |

| | | | |
|---|---|---|---|
| S | -1.66493200 | 0.72684500 | -1.13074500 |
| C | -3.14393500 | -0.23353500 | -0.57847600 |
| C | -4.42093900 | 0.32259200 | -0.36404500 |
| C | -3.01061500 | -1.61162100 | -0.30016500 |
| C | -5.50670700 | -0.45385100 | 0.05343600 |
| C | -4.07999800 | -2.40199300 | 0.11449900 |
| C | -5.32613600 | -1.80984500 | 0.27988700 |
| O | -1.05231900 | -0.06310700 | -2.23047300 |
| O | -2.15337200 | 2.06029300 | -1.51537900 |
| Cu | 1.25961000 | 0.25135100 | 0.07988200 |
| C | 3.65069300 | -1.09220900 | -1.69446600 |
| C | 3.83167000 | 0.43102400 | -1.49355900 |
| H | 4.88894600 | 0.64955700 | -1.28834900 |
| H | 3.58799300 | 0.91564200 | -2.44910500 |
| C | 2.29414900 | -1.38829200 | -2.36755900 |
| H | 2.13702100 | -0.66163200 | -3.17313100 |
| H | 2.31459800 | -2.38793800 | -2.82358000 |
| O | 3.08170400 | 1.01970300 | -0.45045100 |
| C | 3.83807900 | -1.88033000 | -0.39546700 |
| C | 4.61857800 | -1.37837700 | 0.65658700 |
| C | 3.31880800 | -3.17639100 | -0.26061300 |
| C | 4.89228300 | -2.15074100 | 1.78723200 |
| H | 5.01570900 | -0.37171600 | 0.60379800 |
| C | 3.58506000 | -3.94973000 | 0.86876900 |
| H | 2.69218700 | -3.58993700 | -1.04282000 |
| C | 4.38128200 | -3.44403800 | 1.89741400 |
| H | 5.50551800 | -1.73629100 | 2.58309000 |
| H | 3.16857500 | -4.95055700 | 0.94308100 |
| H | 4.59269000 | -4.04638900 | 2.77634500 |
| C | 4.74913800 | -1.52936400 | -2.69217300 |
| H | 4.64871300 | -0.99506800 | -3.64543800 |
| H | 5.74448800 | -1.32342700 | -2.28607300 |
| H | 4.68381300 | -2.60327100 | -2.89206100 |
| H | -2.19757700 | 1.12826500 | 1.55246700 |
| H | 1.53328700 | 0.49228000 | 4.13435300 |
| H | -0.79395700 | 0.26793400 | 3.45194400 |
| H | 0.99197500 | -1.89516900 | 3.54117300 |
| H | -6.47389300 | 0.00925600 | 0.20001500 |
| H | -3.93404500 | -3.45726000 | 0.30601600 |
| Cl | -4.79923400 | 2.02074500 | -0.55569100 |
| Cl | -6.68105500 | -2.78686300 | 0.79954900 |
| Cl | -1.48178000 | -2.45391900 | -0.42446300 |
| O | 1.22675000 | -1.32437800 | -1.42953300 |
| H | 0.39807800 | -0.99967900 | -1.86118200 |

| | | | |
|---|---|---|---|
| C | 1.42349400 | 3.12477200 | -0.19196000 |
| C | 2.29408200 | 3.39277200 | 0.87407800 |
| C | 1.95176000 | 4.37639900 | 1.79769300 |
| C | 0.74813600 | 5.07526500 | 1.66720800 |
| C | -0.11637400 | 4.79792200 | 0.60370800 |
| C | 0.21502200 | 3.82852700 | -0.33739500 |
| H | 3.21267100 | 2.82701700 | 0.95237800 |
| H | 2.62431300 | 4.59717800 | 2.62114000 |
| H | 0.48285700 | 5.83584500 | 2.39593600 |
| H | -1.05647900 | 5.33222800 | 0.50863300 |
| H | -0.46872500 | 3.57054700 | -1.13787800 |
| C | 1.73651300 | 2.12754100 | -1.20752200 |
| O | 1.56979800 | 1.99419400 | -2.36640100 |

## Int13-Analogue

Charge = 0, Multiplicity = 1

| | | | |
|---|---|---|---|
| C | -1.21064600 | 1.17592200 | 1.88469400 |
| H | -0.67645300 | 2.03110800 | 2.32061800 |
| N | -0.74343200 | 0.92512700 | 0.53199700 |
| C | -0.97290900 | -0.09932000 | 2.70108000 |
| N | 0.42136500 | -0.61474500 | 2.59053300 |
| H | -1.62809400 | -0.88035700 | 2.30439900 |
| C | 0.46161700 | -2.01446400 | 3.04995400 |
| C | 1.34676400 | 0.20187000 | 3.39892700 |
| H | 1.48244400 | -2.38838700 | 2.97517500 |
| H | -0.18135600 | -2.62307500 | 2.40956600 |
| H | 2.35938300 | -0.19187800 | 3.28428400 |
| H | 1.33336300 | 1.23337000 | 3.04527500 |
| S | -1.63948200 | 1.32732100 | -0.69325600 |
| C | -3.10832100 | 0.19539500 | -0.61093900 |
| C | -4.42852000 | 0.61828500 | -0.35467900 |
| C | -2.92273100 | -1.20022200 | -0.71605700 |
| C | -5.49230300 | -0.28367700 | -0.24324900 |
| C | -3.96563700 | -2.11676400 | -0.61037400 |
| C | -5.25062800 | -1.64187400 | -0.37681000 |
| O | -0.92663500 | 0.91461700 | -1.93759500 |
| O | -2.17445000 | 2.69396400 | -0.68559600 |
| Cu | 0.90518200 | -0.37229700 | 0.58661300 |
| C | 3.55387400 | -1.21157200 | -1.84773500 |
| C | 4.36485400 | 0.10197200 | -1.86780400 |
| H | 5.39713700 | -0.09649900 | -1.56789700 |

| | | | |
|---|---|---|---|
| H | 4.35733800 | 0.51447400 | -2.87860800 |
| C | 2.10097600 | -0.96287300 | -2.30474700 |
| H | 2.11236300 | -0.41635900 | -3.25345900 |
| H | 1.59549700 | -1.92536200 | -2.46193900 |
| O | 3.88208300 | 1.09684500 | -0.95807400 |
| C | 3.55277900 | -1.90098100 | -0.47759200 |
| C | 4.16106300 | -1.35465600 | 0.66059100 |
| C | 2.95044600 | -3.16470700 | -0.35433300 |
| C | 4.20547100 | -2.06597000 | 1.86353500 |
| H | 4.60649300 | -0.36970800 | 0.61695300 |
| C | 2.98524400 | -3.87288300 | 0.84450300 |
| H | 2.46509500 | -3.61361400 | -1.21656200 |
| C | 3.62852500 | -3.33098200 | 1.95984500 |
| H | 4.70430800 | -1.62715200 | 2.72375500 |
| H | 2.52230800 | -4.85400100 | 0.90363400 |
| H | 3.67655700 | -3.88886400 | 2.89093000 |
| C | 4.22066500 | -2.13459700 | -2.91773100 |
| H | 5.08268400 | -1.64552300 | -3.38383400 |
| H | 4.57266100 | -3.06945600 | -2.47695900 |
| H | 3.52078900 | -2.38495300 | -3.72240400 |
| H | -2.28218300 | 1.41387300 | 1.94804900 |
| H | 1.06709900 | 0.17778800 | 4.46533100 |
| H | -1.22313500 | 0.05567600 | 3.76343100 |
| H | 0.11594900 | -2.10093400 | 4.09369500 |
| H | -6.49184800 | 0.08558500 | -0.05326400 |
| H | -3.77288000 | -3.17727300 | -0.70921100 |
| Cl | -4.89981800 | 2.29009800 | -0.13449100 |
| Cl | -6.57601900 | -2.77640900 | -0.23942400 |
| Cl | -1.34798200 | -1.93673300 | -0.97484800 |
| O | 1.39727900 | -0.19465000 | -1.34234400 |
| H | 0.56844100 | 0.21861600 | -1.71990700 |
| C | 2.32692200 | 2.76189100 | -0.36061700 |
| C | 2.83230500 | 2.77610000 | 0.94714400 |
| C | 2.17406500 | 3.50577900 | 1.93457100 |
| C | 0.99321100 | 4.19077000 | 1.62910600 |
| C | 0.47632100 | 4.15502000 | 0.33313200 |
| C | 1.15011300 | 3.45424800 | -0.66386400 |
| H | 3.74001300 | 2.23033800 | 1.17755400 |
| H | 2.57992300 | 3.54118500 | 2.94222100 |
| H | 0.47437700 | 4.74798300 | 2.40460300 |
| H | -0.46401000 | 4.64057000 | 0.09984500 |
| H | 0.75144500 | 3.39847200 | -1.66990600 |
| C | 2.97227800 | 1.98601200 | -1.44694300 |
| O | 2.72676600 | 2.10629400 | -2.62957100 |

## Int13

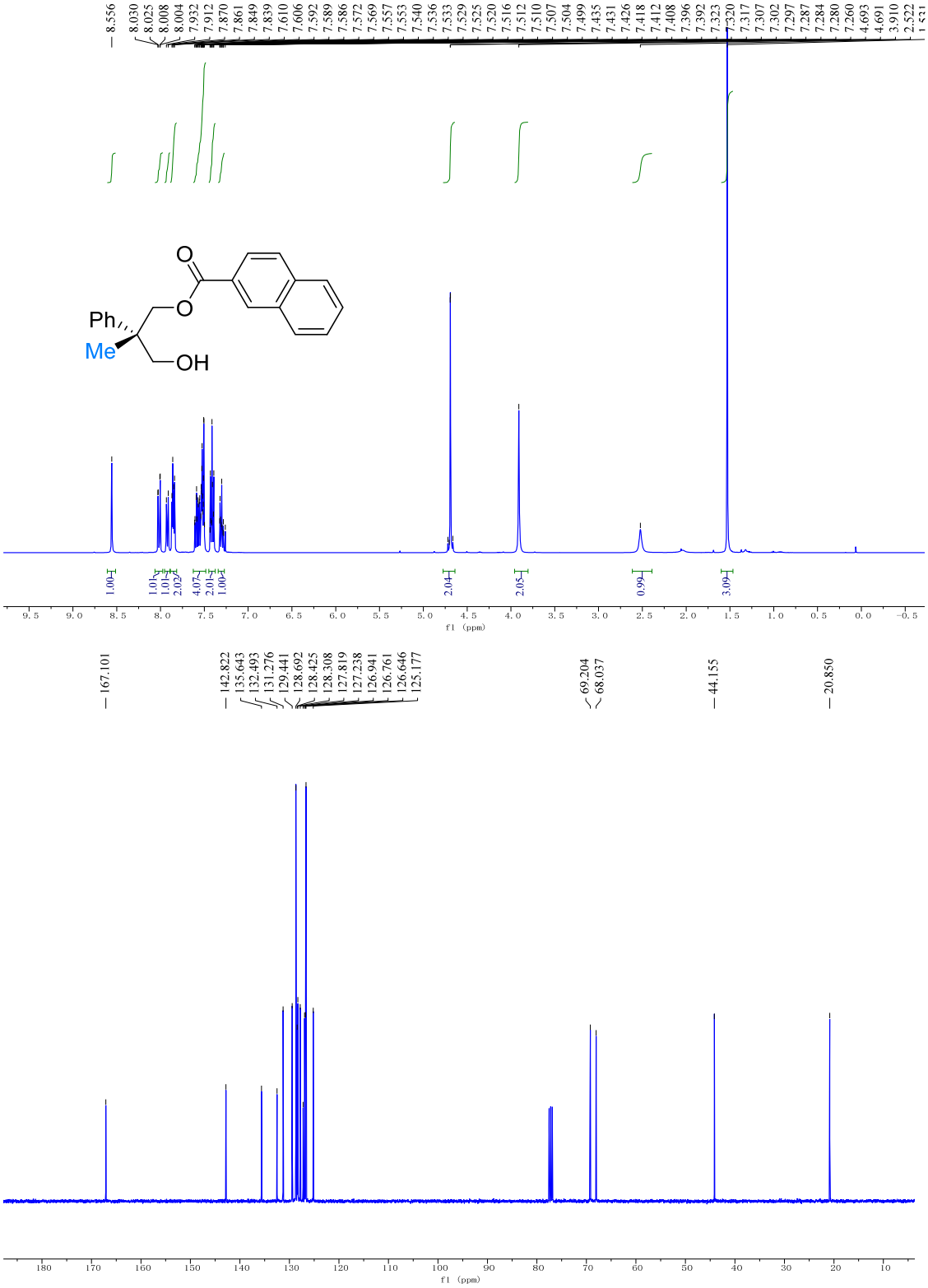
Charge = 0, Multiplicity = 1

| | | | |
|---|---|---|---|
| C | -1.09037300 | 0.76254000 | 1.75591200 |
| H | -1.11129100 | 1.85912400 | 1.69059800 |
| N | -0.85387700 | 0.12524100 | 0.46049400 |
| C | 0.00837100 | 0.30316800 | 2.71737100 |
| N | 1.36614800 | 0.62099500 | 2.21506300 |
| H | -0.05014700 | -0.78339000 | 2.82485200 |
| C | 2.38843100 | -0.08058900 | 3.00494900 |
| C | 1.60833800 | 2.07246600 | 2.27129100 |
| H | 3.37403000 | 0.12719200 | 2.57950400 |
| H | 2.21021100 | -1.15524900 | 2.96164300 |
| H | 2.62069400 | 2.28537100 | 1.92769500 |
| H | 0.91259200 | 2.59669400 | 1.61759700 |
| S | -1.59394800 | 0.77591800 | -0.77958000 |
| C | -3.37165000 | 0.38951500 | -0.51010600 |
| C | -4.35921200 | 1.34871700 | -0.21308900 |
| C | -3.79221900 | -0.95841400 | -0.51345800 |
| C | -5.69211200 | 0.99403800 | 0.01677400 |
| C | -5.11499100 | -1.33193000 | -0.28949400 |
| C | -6.05687600 | -0.34267800 | -0.03227900 |
| O | -1.24611000 | 0.00198300 | -2.00628800 |
| O | -1.46482000 | 2.23894500 | -0.89597500 |
| Cu | 1.21817100 | -0.12143500 | 0.21895400 |
| H | -2.05582000 | 0.45172800 | 2.18631700 |
| H | 1.49226500 | 2.44720400 | 3.30206600 |
| H | -0.14521300 | 0.75878700 | 3.70999900 |
| H | 2.38150600 | 0.24676700 | 4.05863000 |
| H | -6.42370300 | 1.76201300 | 0.23225000 |
| H | -5.39690000 | -2.37665100 | -0.31212100 |
| Cl | -4.04578000 | 3.06557300 | -0.08001300 |
| Cl | -7.72342700 | -0.79490000 | 0.25060900 |
| Cl | -2.69560200 | -2.30140800 | -0.77517300 |
| C | 2.92069700 | -2.35533500 | -1.41166900 |
| C | 4.11387900 | -1.40084000 | -1.22925700 |
| H | 4.85895900 | -1.80192500 | -0.53831400 |
| H | 4.61074900 | -1.22954900 | -2.19026100 |
| C | 1.90003900 | -1.74793500 | -2.39594000 |
| H | 2.41688600 | -1.53509300 | -3.34116600 |
| H | 1.12045900 | -2.48969700 | -2.60852200 |
| O | 3.62970500 | -0.14338100 | -0.73925700 |
| C | 2.28652000 | -2.73326400 | -0.06491200 |

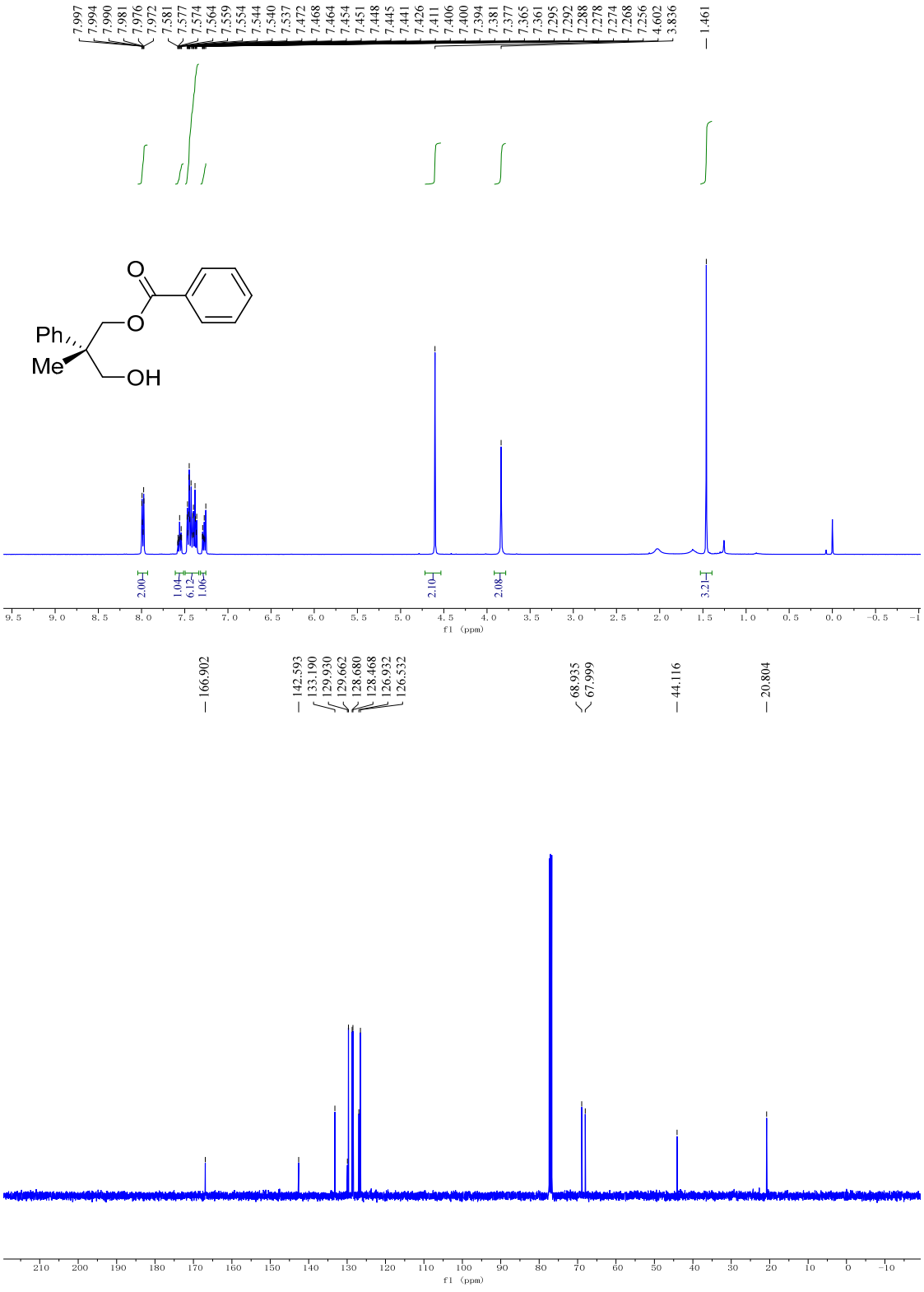
| | | | |
|---|---|---|---|
| C | 3.09966100 | -3.20445300 | 0.98106000 |
| C | 0.89604700 | -2.72763600 | 0.14220300 |
| C | 2.55143200 | -3.66428000 | 2.17599500 |
| H | 4.17801800 | -3.23345000 | 0.85792300 |
| C | 0.34470300 | -3.17180500 | 1.34983000 |
| H | 0.21500800 | -2.38769400 | -0.62605800 |
| C | 1.16634500 | -3.64768700 | 2.36794100 |
| H | 3.20703100 | -4.03418200 | 2.95943400 |
| H | -0.73273000 | -3.13189700 | 1.47408000 |
| H | 0.73796700 | -4.00161400 | 3.30128600 |
| C | 3.46894500 | -3.64154000 | -2.07260900 |
| H | 3.89168800 | -3.42698200 | -3.06115600 |
| H | 4.25126800 | -4.09710000 | -1.45842300 |
| H | 2.66805800 | -4.37766300 | -2.19132200 |
| O | 1.32019700 | -0.54818200 | -1.89826000 |
| H | 0.35716800 | -0.45608600 | -2.13175900 |
| C | 3.81103200 | 2.17922100 | -0.50164800 |
| C | 2.50439400 | 2.34048400 | -0.98946800 |
| C | 1.85203400 | 3.56409900 | -0.84296400 |
| C | 2.50667900 | 4.62742800 | -0.21713500 |
| C | 3.81824600 | 4.47594800 | 0.24683200 |
| C | 4.47523100 | 3.25613600 | 0.09903500 |
| H | 2.01447700 | 1.51883000 | -1.49885900 |
| H | 0.83014500 | 3.66435300 | -1.19582100 |
| H | 1.99711700 | 5.57891400 | -0.09299600 |
| H | 4.32609500 | 5.30935300 | 0.72352800 |
| H | 5.49338300 | 3.11770100 | 0.44839600 |
| C | 4.51793400 | 0.87806000 | -0.62245600 |
| O | 5.72014900 | 0.71305700 | -0.61931700 |

# 10. NMR spectra

## 1



**2**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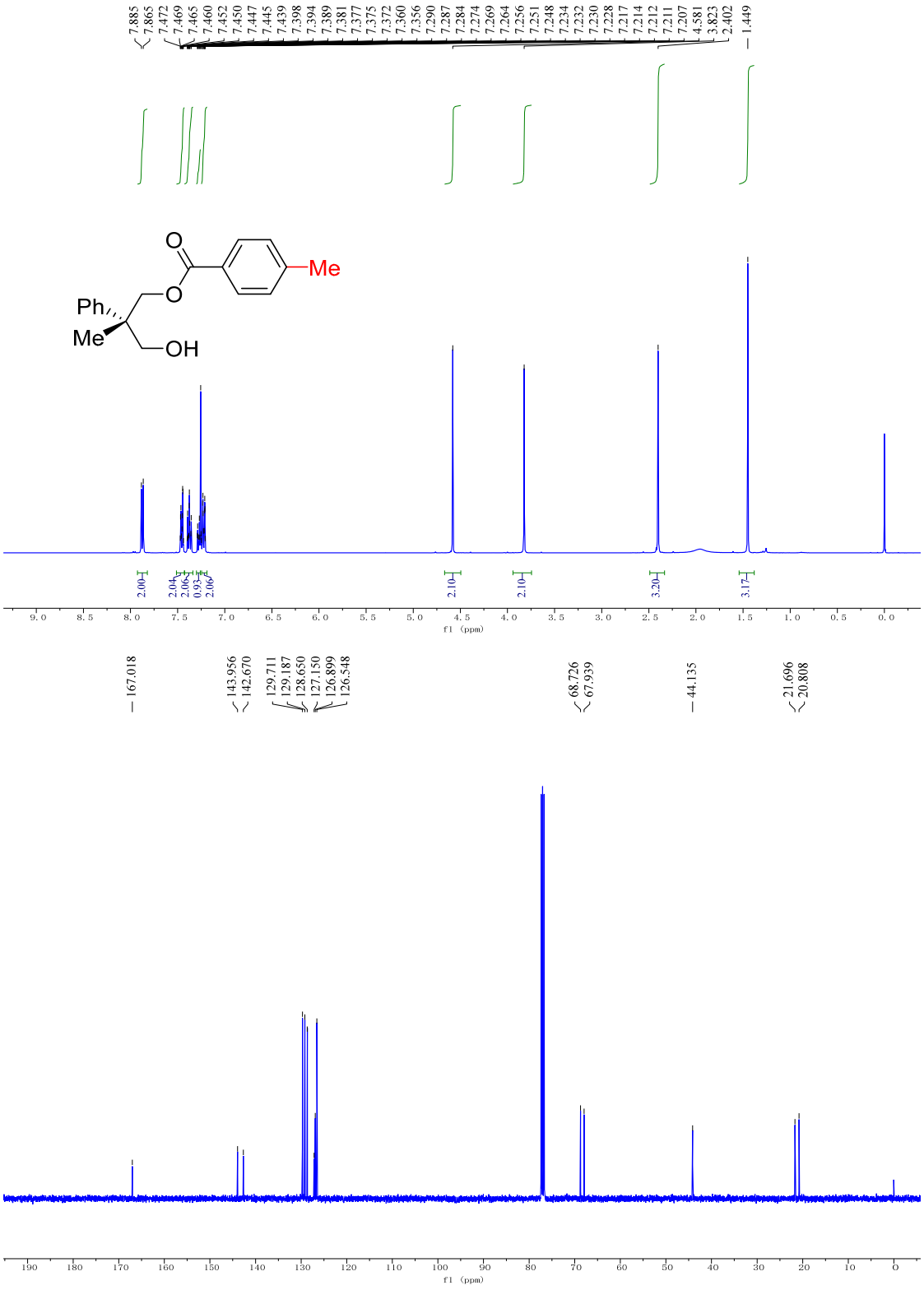
7.994
7.990
7.981
7.976
7.972
7.581
7.577
7.574
7.564
7.559
7.554
7.544
7.540
7.537
7.472
7.468
7.464
7.454
7.451
7.448
7.445
7.441
7.426
7.411
7.406
7.400
7.394
7.381
7.377
7.365
7.361
7.295
7.292
7.288
7.278
7.274
7.268
7.256
4.602
3.836
1.461
O
O
Ph
Me
OH
2.00
1.04
6.12
1.06
2.10
2.08
3.21
f1 (ppm)
166.902
142.593
133.190
129.930
129.662
128.680
128.468
126.932
126.532
68.935
67.999
44.116
20.804
f1 (ppm)

**3**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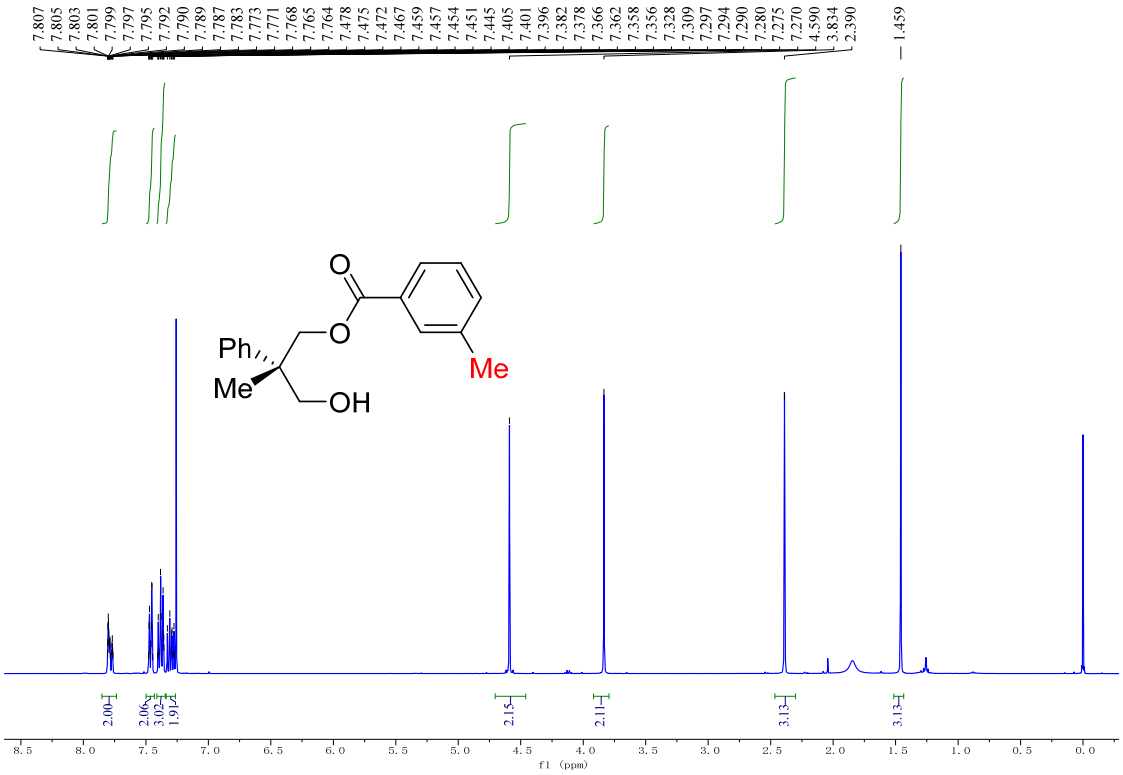
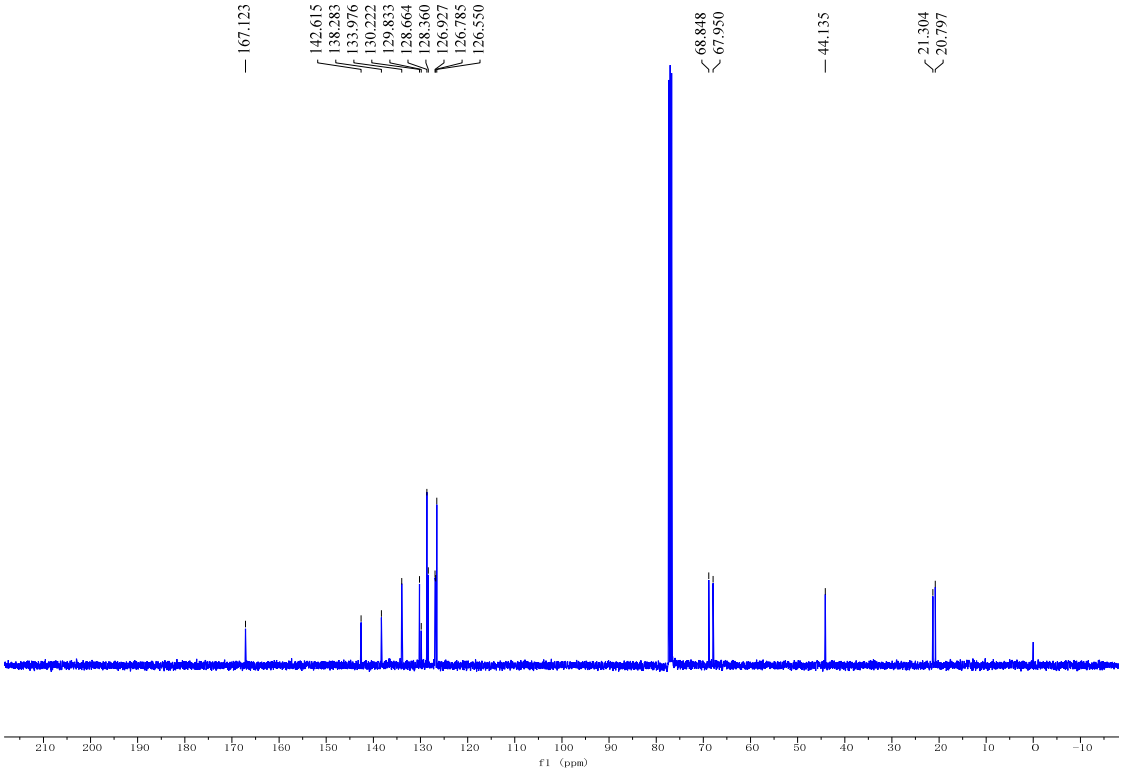
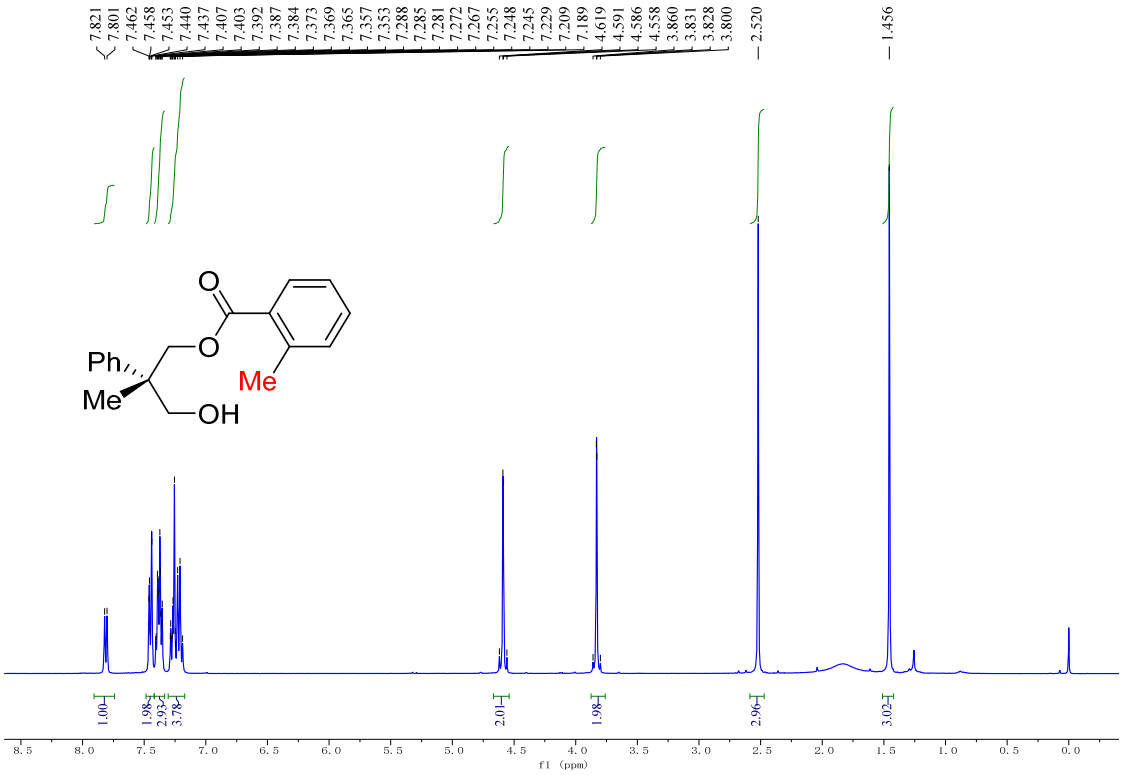
7.865
7.472
7.469
7.465
7.460
7.452
7.450
7.447
7.445
7.439
7.398
7.394
7.389
7.381
7.377
7.375
7.372
7.360
7.356
7.290
7.287
7.284
7.274
7.269
7.264
7.256
7.251
7.248
7.234
7.232
7.230
7.228
7.217
7.214
7.212
7.211
7.207
4.581
3.823
2.402
1.449
O
O
Me
Ph
Me
OH
2.00
2.04
2.06
0.93
2.06
2.10
2.10
3.20
3.17
f1 (ppm)
167.018
143.956
142.670
129.711
129.187
128.650
127.150
126.899
126.548
68.726
67.939
44.135
21.696
20.808
f1 (ppm)

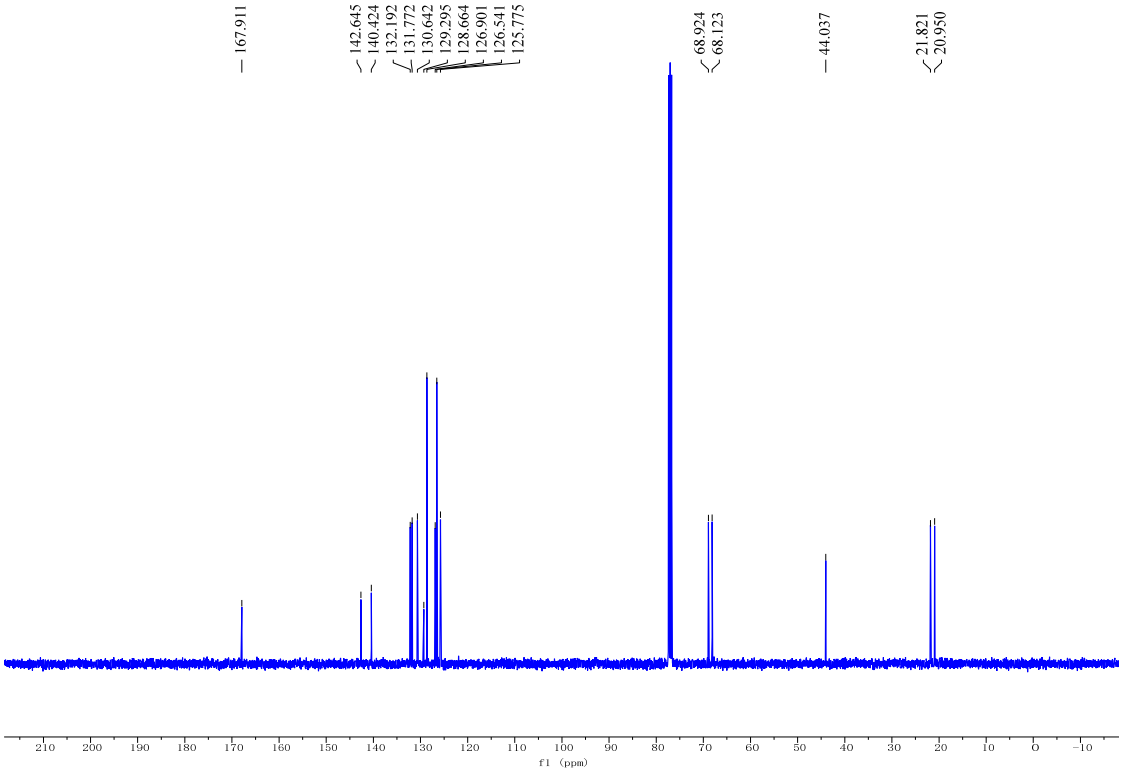
**4**


7.807
7.805
7.803
7.801
7.799
7.797
7.795
7.792
7.790
7.789
7.787
7.783
7.773
7.771
7.768
7.765
7.764
7.478
7.475
7.472
7.467
7.459
7.457
7.454
7.451
7.445
7.405
7.401
7.396
7.382
7.378
7.366
7.362
7.358
7.356
7.328
7.309
7.297
7.294
7.290
7.280
7.275
7.270
4.590
3.834
2.390
1.459
O
O
Ph
Me
OH
Me
2.00
2.06
3.02
1.91
2.15
2.11
3.13
3.13
f1 (ppm)


167.123
142.615
138.283
133.976
130.222
129.833
128.664
128.360
126.927
126.785
126.550
68.848
67.950
44.135
21.304
20.797
f1 (ppm)

**5**


7.821
7.801
7.462
7.458
7.453
7.440
7.437
7.407
7.403
7.392
7.387
7.384
7.373
7.369
7.365
7.357
7.353
7.288
7.285
7.281
7.272
7.267
7.255
7.248
7.245
7.229
7.209
7.189
4.619
4.591
4.586
4.558
3.860
3.831
3.828
3.800
2.520
1.456
O
O
Ph
Me
Me
OH
1.00
1.98
2.93
3.78
2.01
1.98
2.96
3.02
f1 (ppm)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142.645
140.424
132.192
131.772
130.642
129.295
128.664
126.901
126.541
125.775
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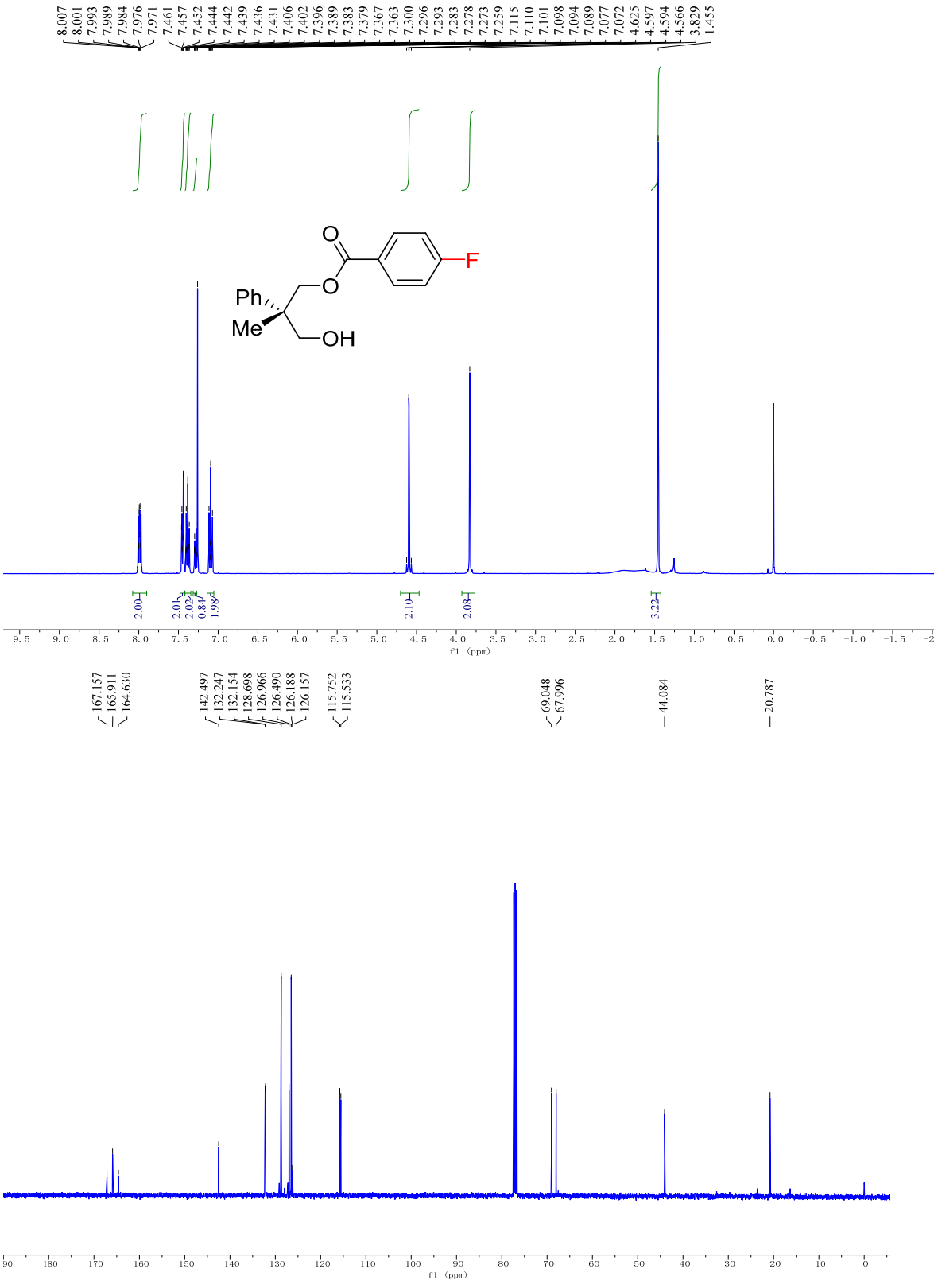
68.123
44.037
21.821
20.950
f1 (ppm)

**6**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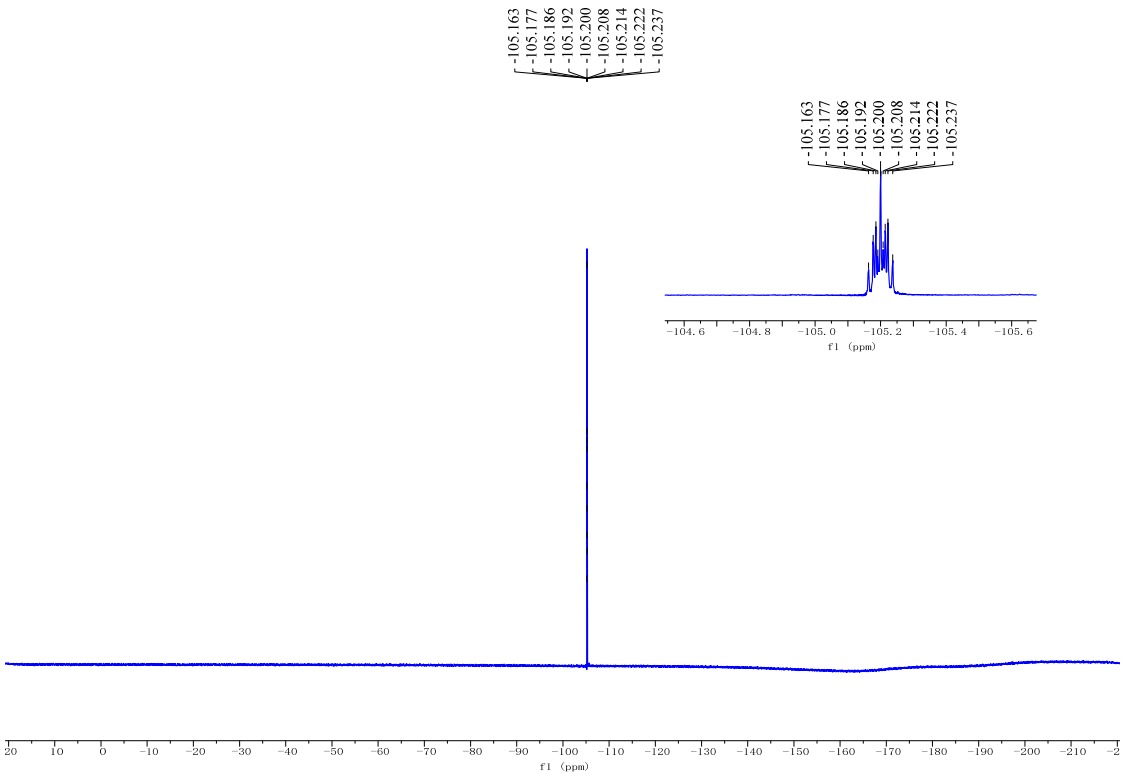
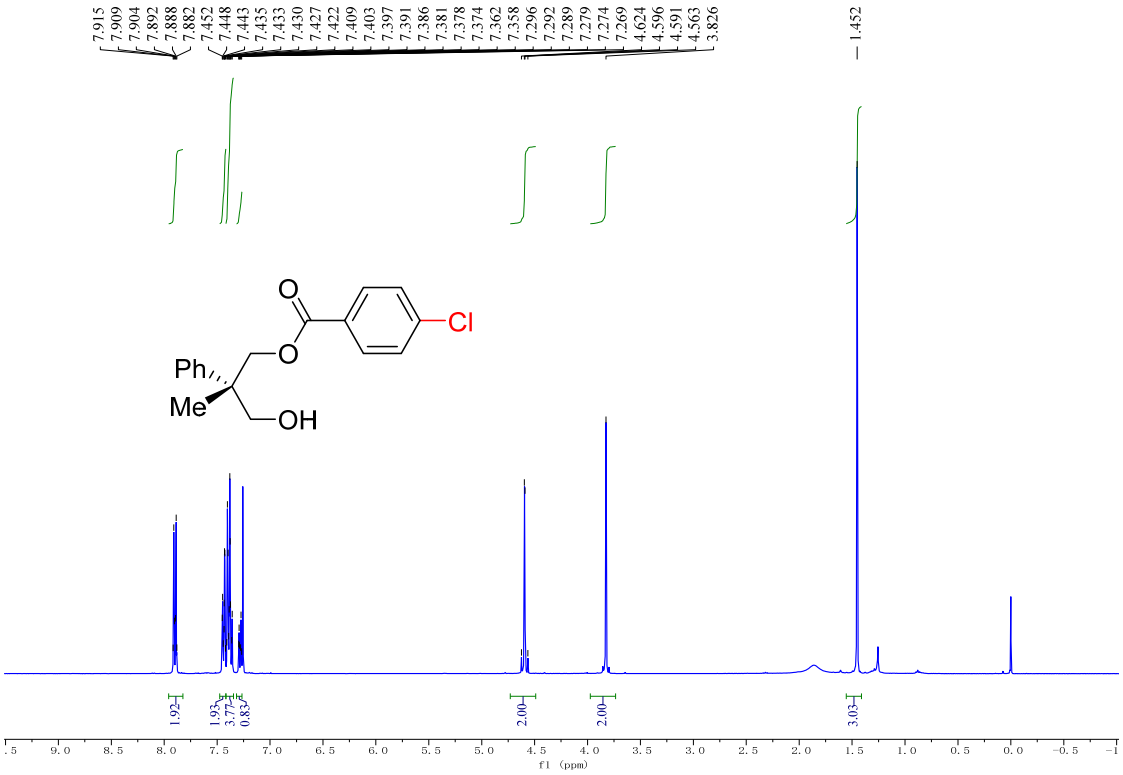
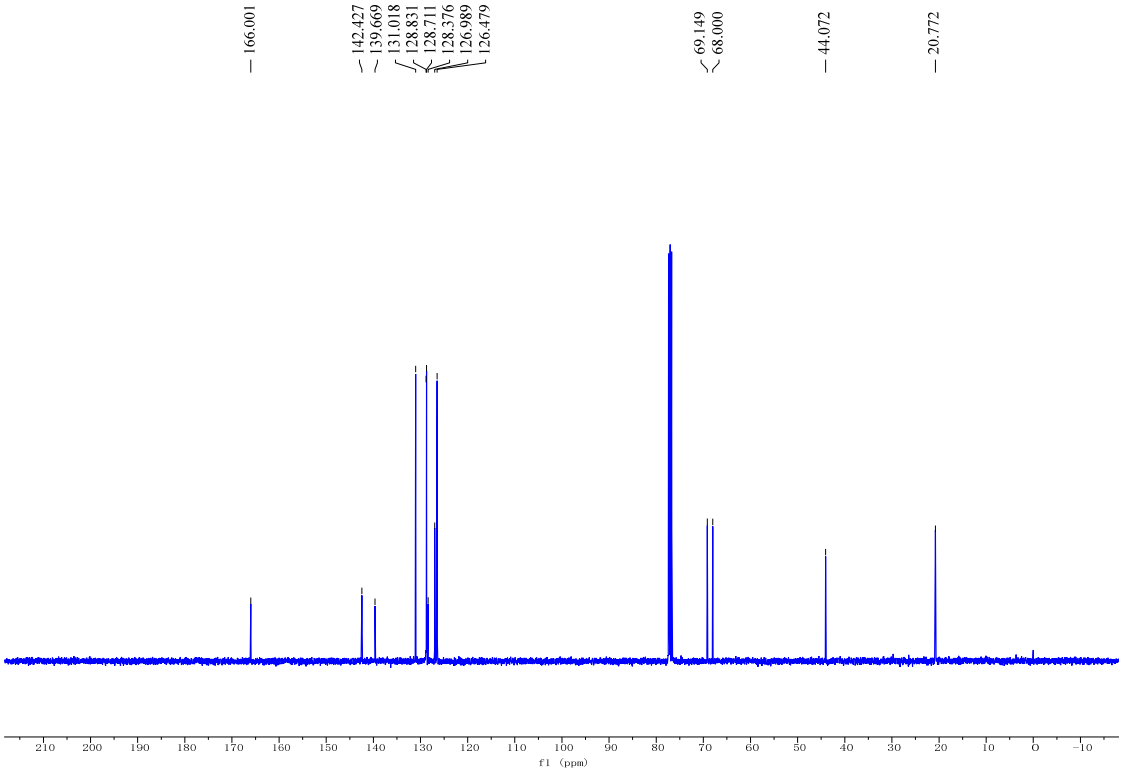
8.001
7.993
7.989
7.984
7.976
7.971
7.461
7.457
7.452
7.444
7.442
7.439
7.436
7.431
7.406
7.402
7.396
7.389
7.383
7.379
7.367
7.363
7.300
7.296
7.293
7.283
7.278
7.273
7.259
7.115
7.110
7.101
7.098
7.094
7.089
7.077
7.072
4.625
4.597
4.594
4.566
3.829
1.455
O
O
F
Ph
Me
OH
2.00
2.01
2.02
0.84
1.98
2.10
2.08
3.22
f1 (ppm)
167.157
165.911
164.630
142.497
132.247
132.154
128.698
126.966
126.490
126.188
126.157
115.752
115.533
69.048
67.996
44.084
20.787
f1 (ppm)

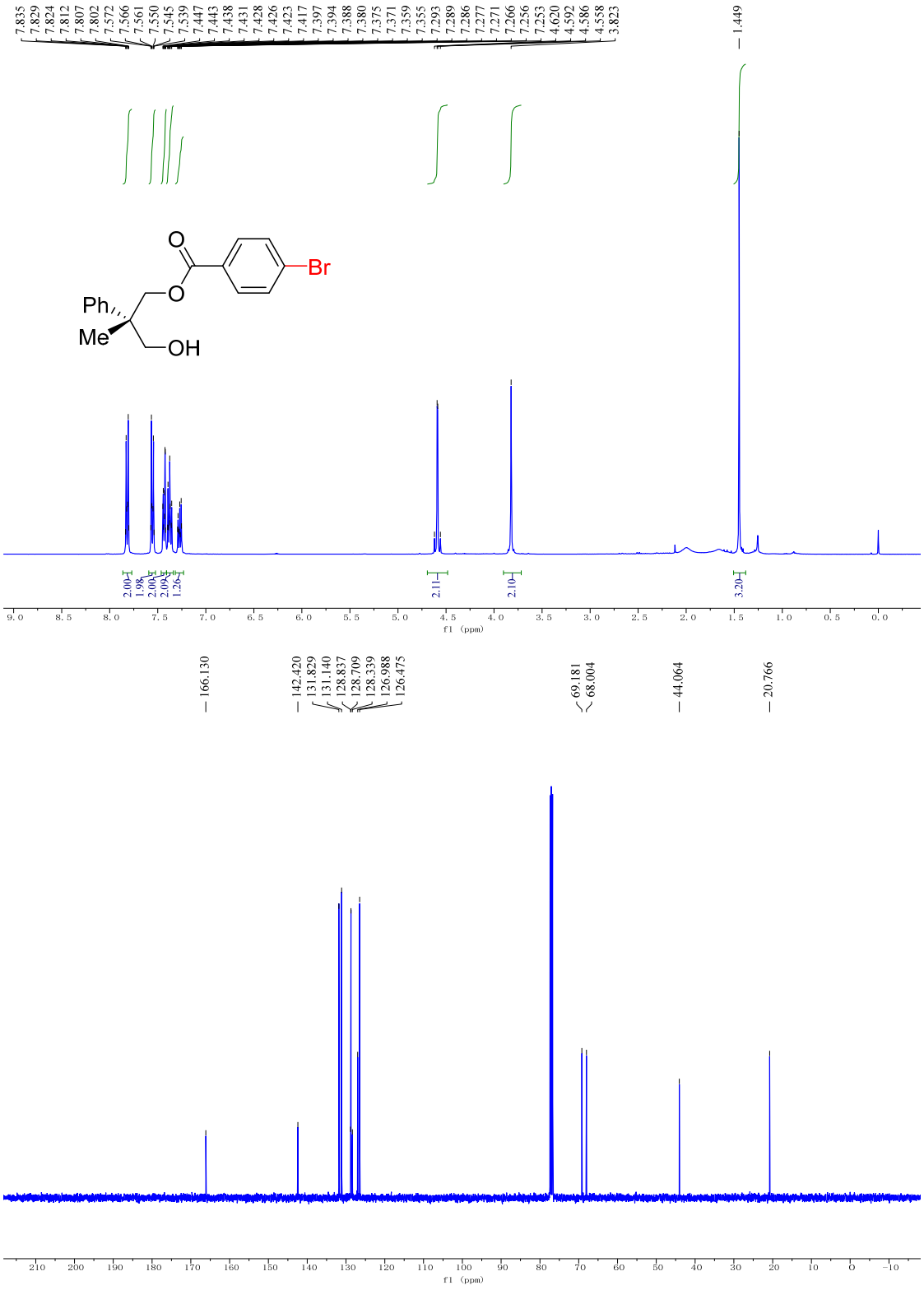

-105.163
-105.177
-105.186
-105.192
-105.200
-105.208
-105.214
-105.222
-105.237
-104.6
-104.8
-105.0
-105.2
-105.4
-105.6
f1 (ppm)
f1 (ppm)

**7**

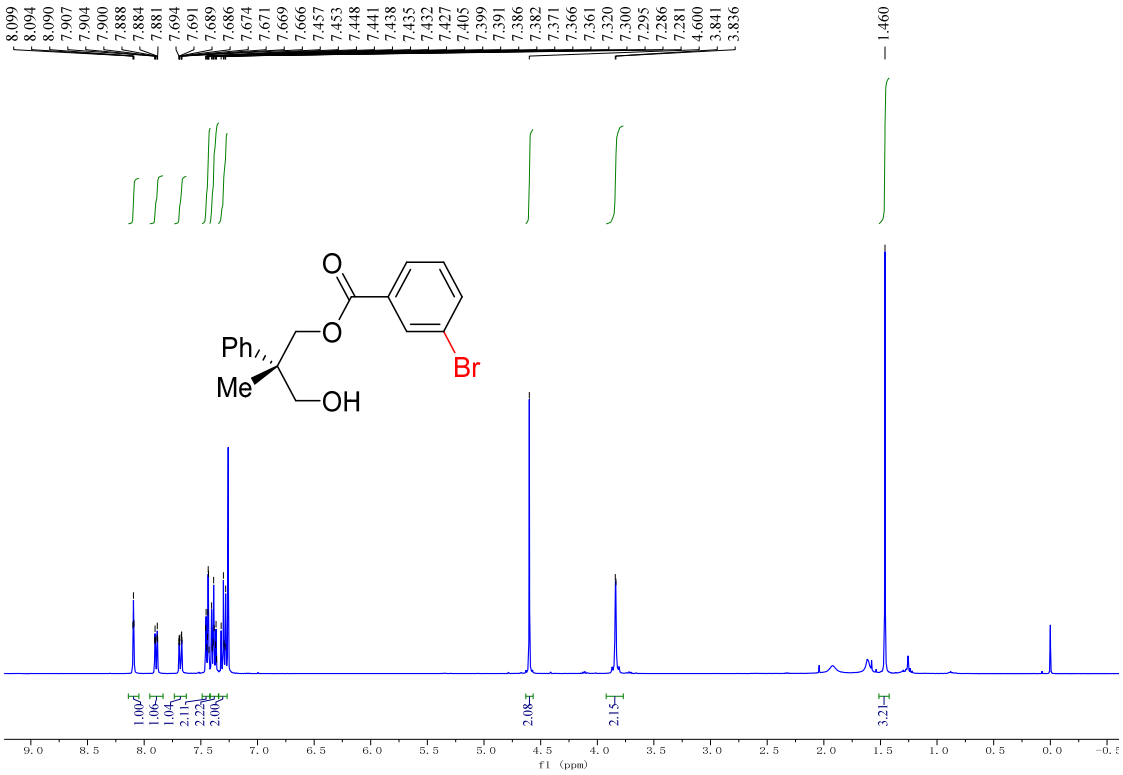

7.915
7.909
7.904
7.892
7.888
7.882
7.452
7.448
7.443
7.435
7.433
7.430
7.427
7.422
7.409
7.403
7.397
7.391
7.386
7.381
7.378
7.374
7.362
7.358
7.296
7.292
7.289
7.279
7.274
7.269
4.624
4.596
4.591
4.563
3.826
1.452
O
O
Cl
Ph
Me
OH
1.92
1.93
3.77
0.83
2.00
2.00
3.03
f1 (ppm)

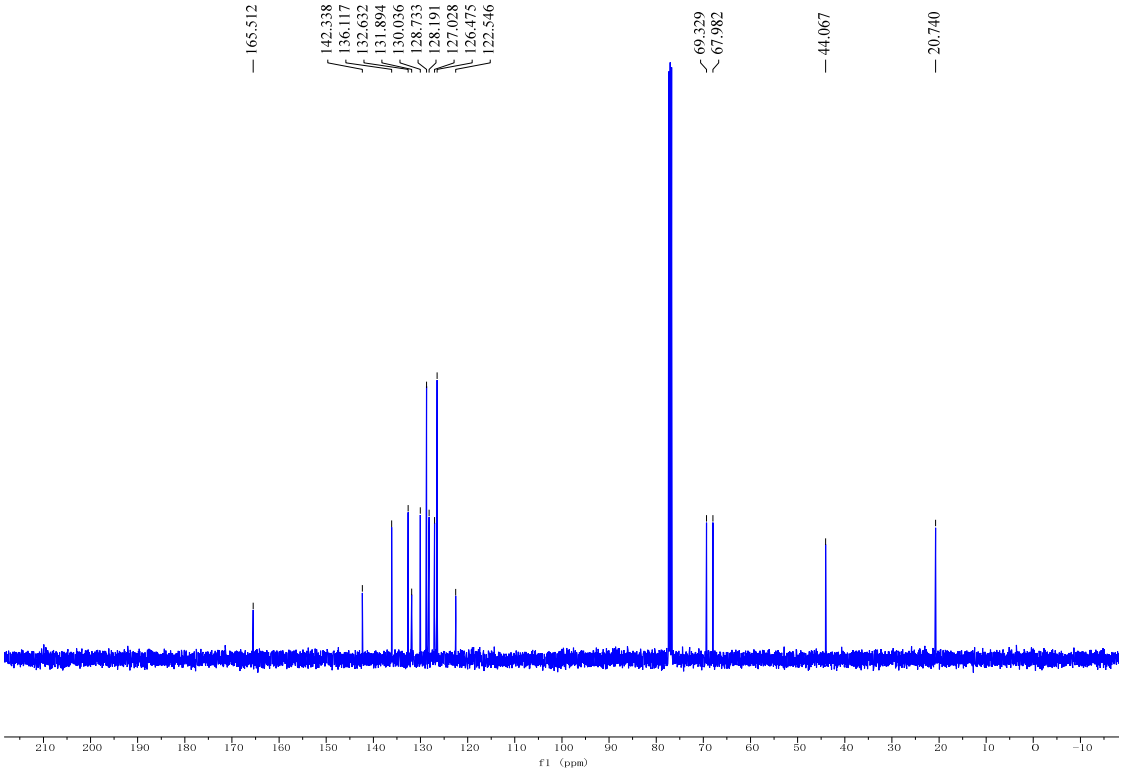

166.001
142.427
139.669
131.018
128.831
128.711
128.376
126.989
126.479
69.149
68.000
44.072
20.772
f1 (ppm)

**8**

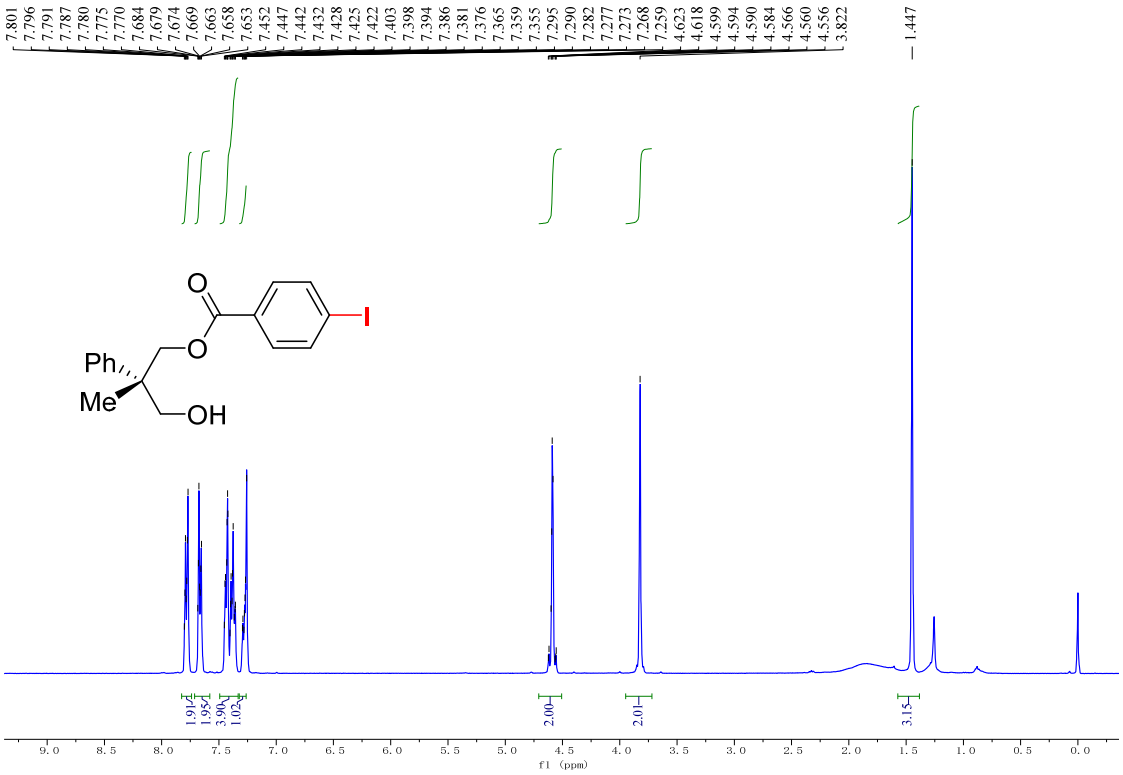

7.835
7.829
7.824
7.812
7.807
7.802
7.572
7.566
7.561
7.550
7.545
7.539
7.447
7.443
7.438
7.431
7.428
7.426
7.423
7.417
7.397
7.394
7.388
7.380
7.375
7.371
7.359
7.355
7.293
7.289
7.286
7.277
7.271
7.266
7.256
7.253
4.620
4.592
4.586
4.558
3.823
1.449
O
O
Br
Ph
Me
OH
2.00
1.98
2.00
2.09
1.26
2.11
2.10
3.20
f1 (ppm)
166.130
142.420
131.829
131.140
128.837
128.709
128.339
126.988
126.475
69.181
68.004
44.064
20.766
f1 (ppm)

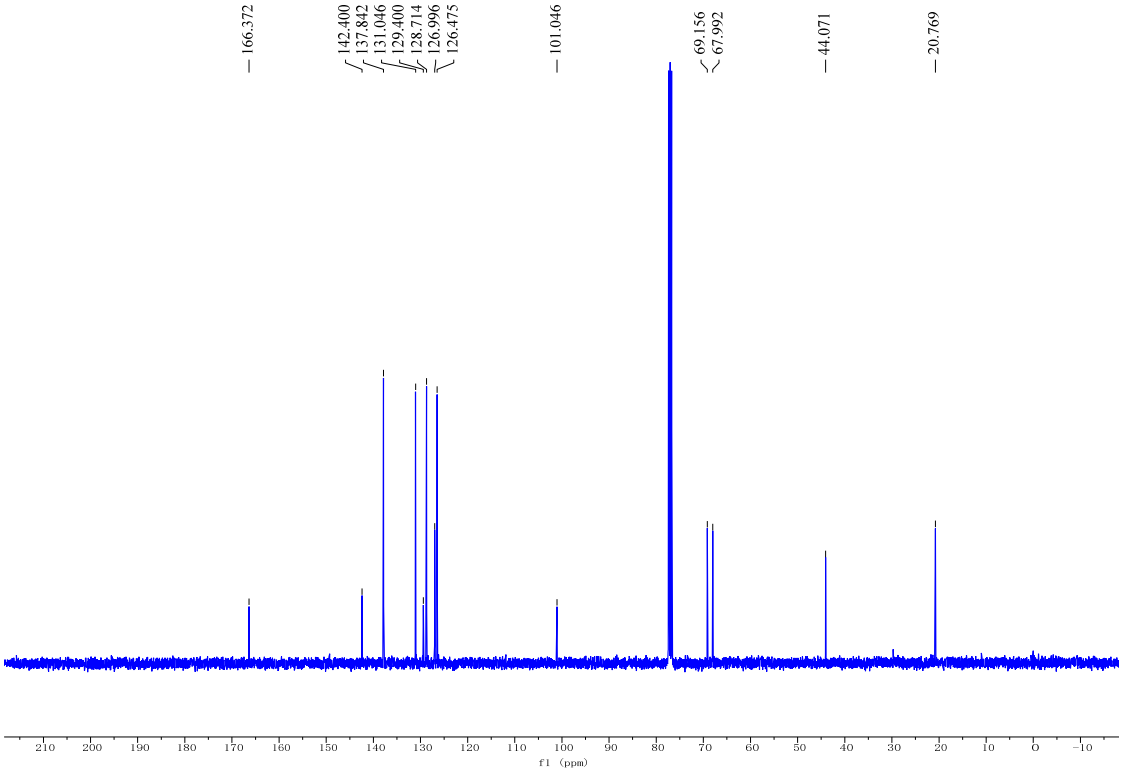
**9**


8.099
8.094
8.090
7.907
7.904
7.900
7.888
7.884
7.881
7.694
7.691
7.689
7.686
7.674
7.671
7.669
7.666
7.457
7.453
7.448
7.441
7.438
7.435
7.432
7.427
7.405
7.399
7.391
7.386
7.382
7.371
7.366
7.361
7.320
7.300
7.295
7.286
7.281
4.600
3.841
3.836
1.460
O
O
Ph
Me
OH
Br
1.00
1.06
1.04
2.11
2.22
2.00
2.08
2.15
3.21
f1 (ppm)

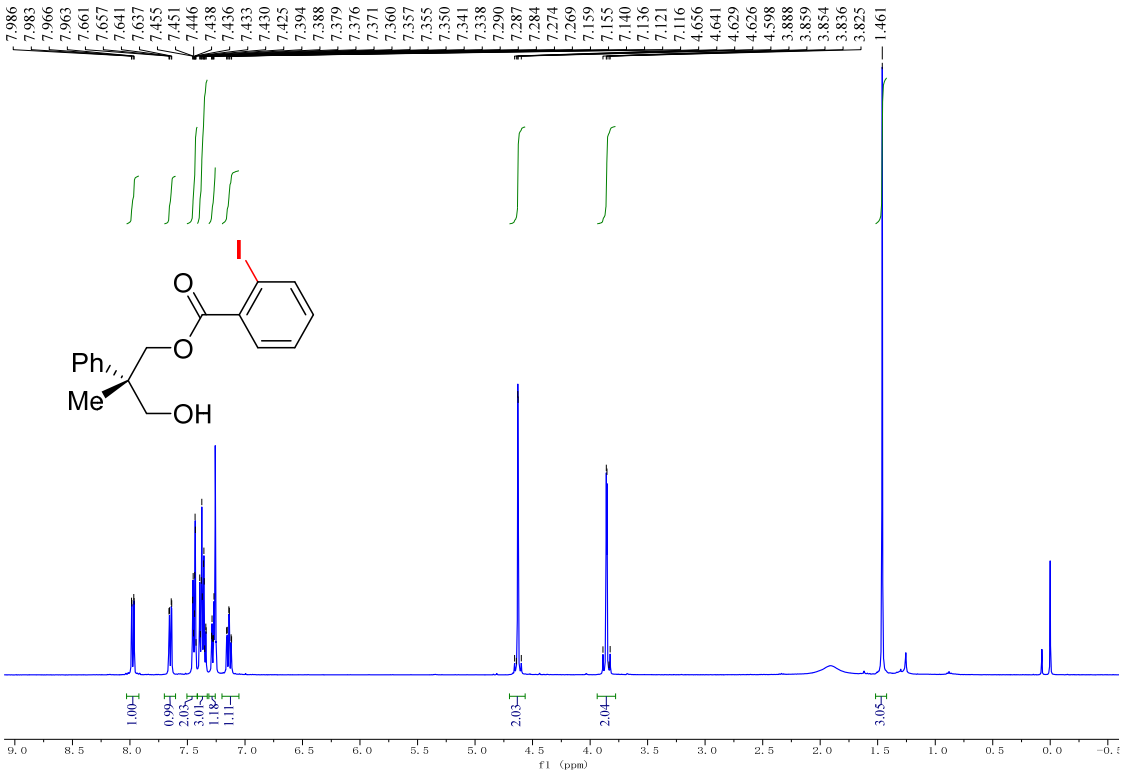

165.512
142.338
136.117
132.632
131.894
130.036
128.733
128.191
127.028
126.475
122.546
69.329
67.982
44.067
20.740
f1 (ppm)

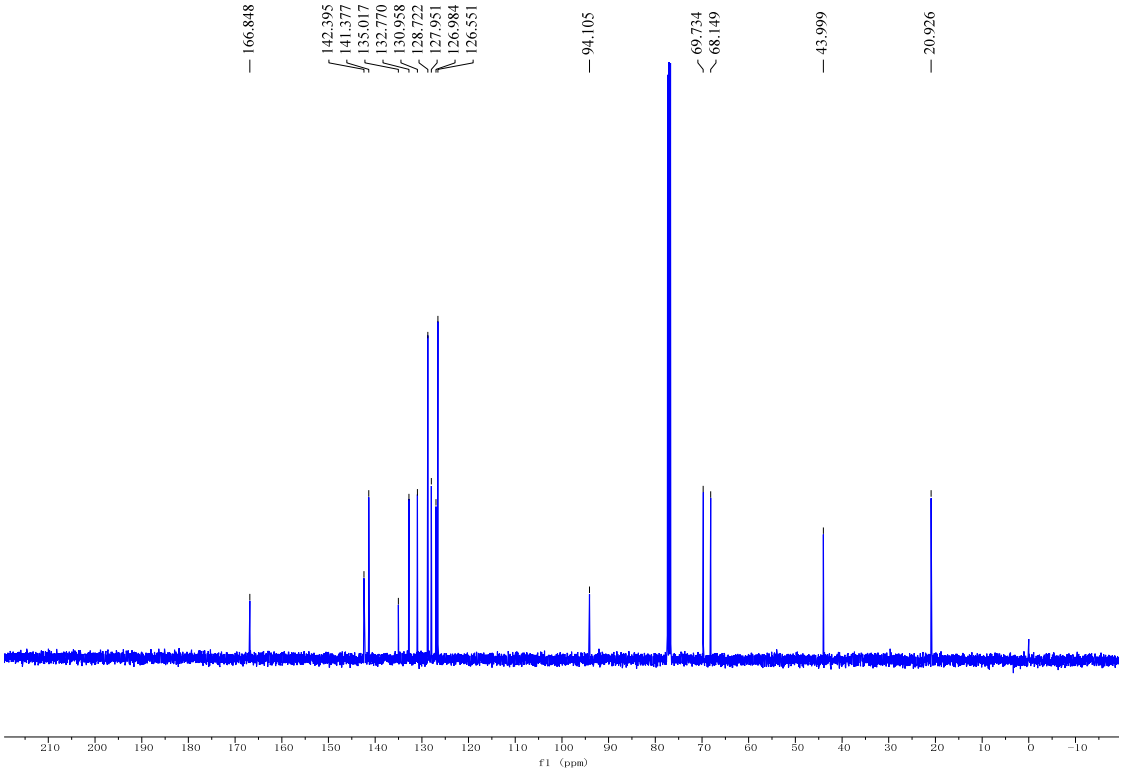
**10**


7.801
7.796
7.791
7.787
7.780
7.775
7.770
7.684
7.679
7.674
7.669
7.663
7.658
7.653
7.452
7.447
7.442
7.432
7.428
7.425
7.422
7.403
7.398
7.394
7.386
7.381
7.376
7.365
7.359
7.355
7.295
7.290
7.282
7.277
7.273
7.268
7.259
4.623
4.618
4.599
4.594
4.590
4.584
4.566
4.560
4.556
3.822
1.447
O
O
I
Ph
Me
OH
1.91
1.95
3.90
1.02
2.00
2.01
3.15
f1 (ppm)

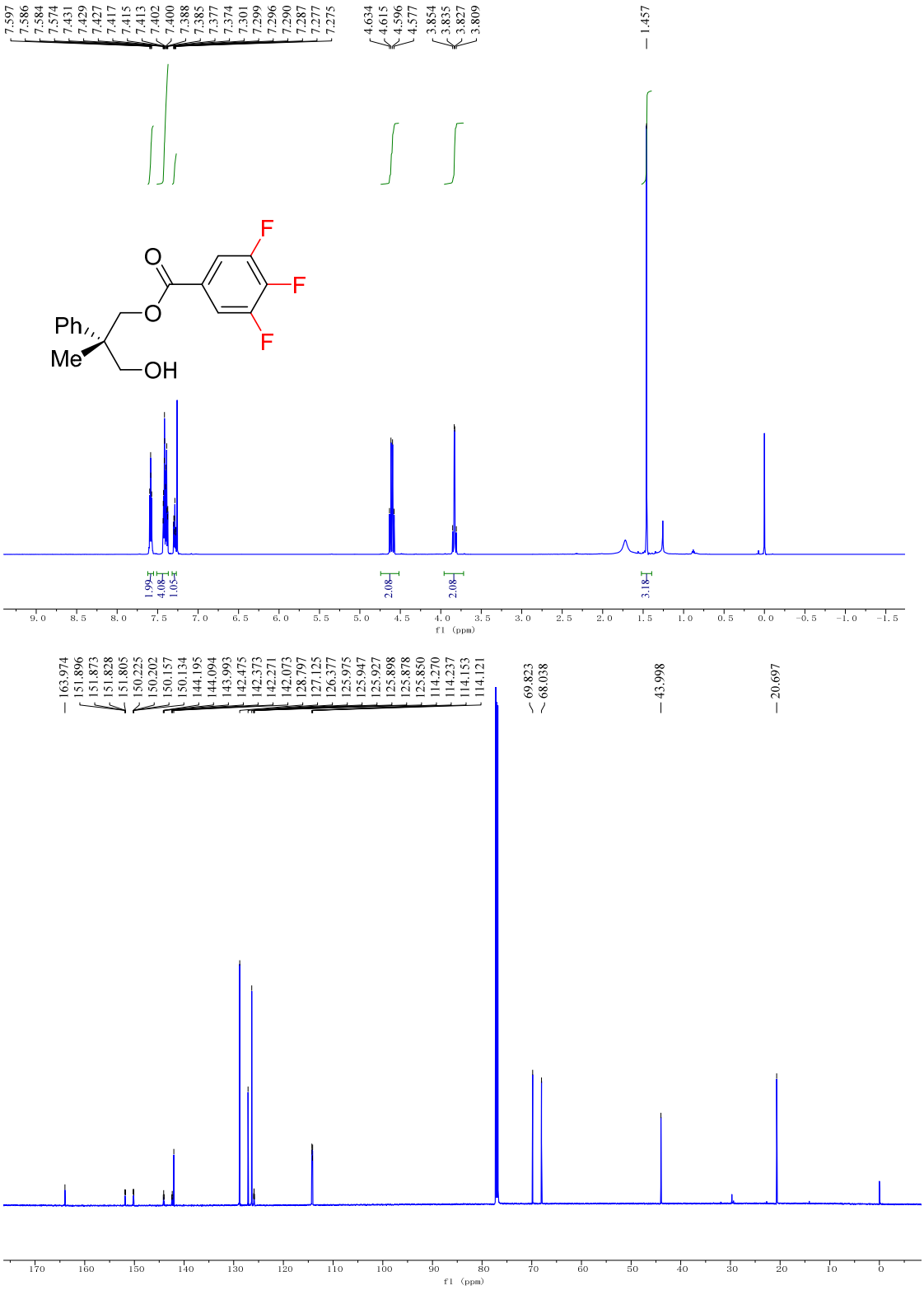

166.372
142.400
137.842
131.046
129.400
128.714
126.996
126.475
101.046
69.156
67.992
44.071
20.769
f1 (ppm)

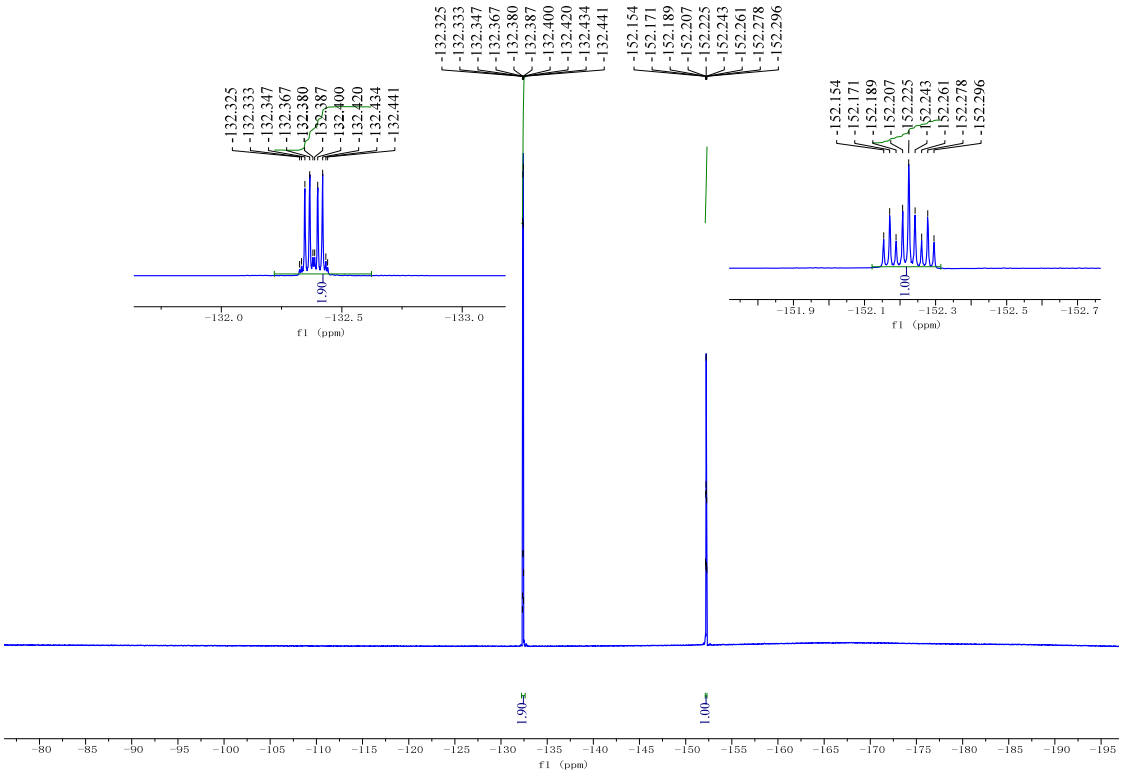
**11**


7.986
7.983
7.966
7.963
7.661
7.657
7.641
7.637
7.455
7.451
7.446
7.438
7.436
7.433
7.430
7.425
7.394
7.388
7.379
7.376
7.371
7.360
7.357
7.355
7.350
7.341
7.338
7.290
7.287
7.284
7.274
7.269
7.159
7.155
7.140
7.136
7.121
7.116
4.656
4.641
4.629
4.626
4.598
3.888
3.859
3.854
3.836
3.825
1.461
I
O
O
Ph
Me
OH
1.00
0.99
2.03
3.01
1.18
1.11
2.03
2.04
3.05
f1 (ppm)

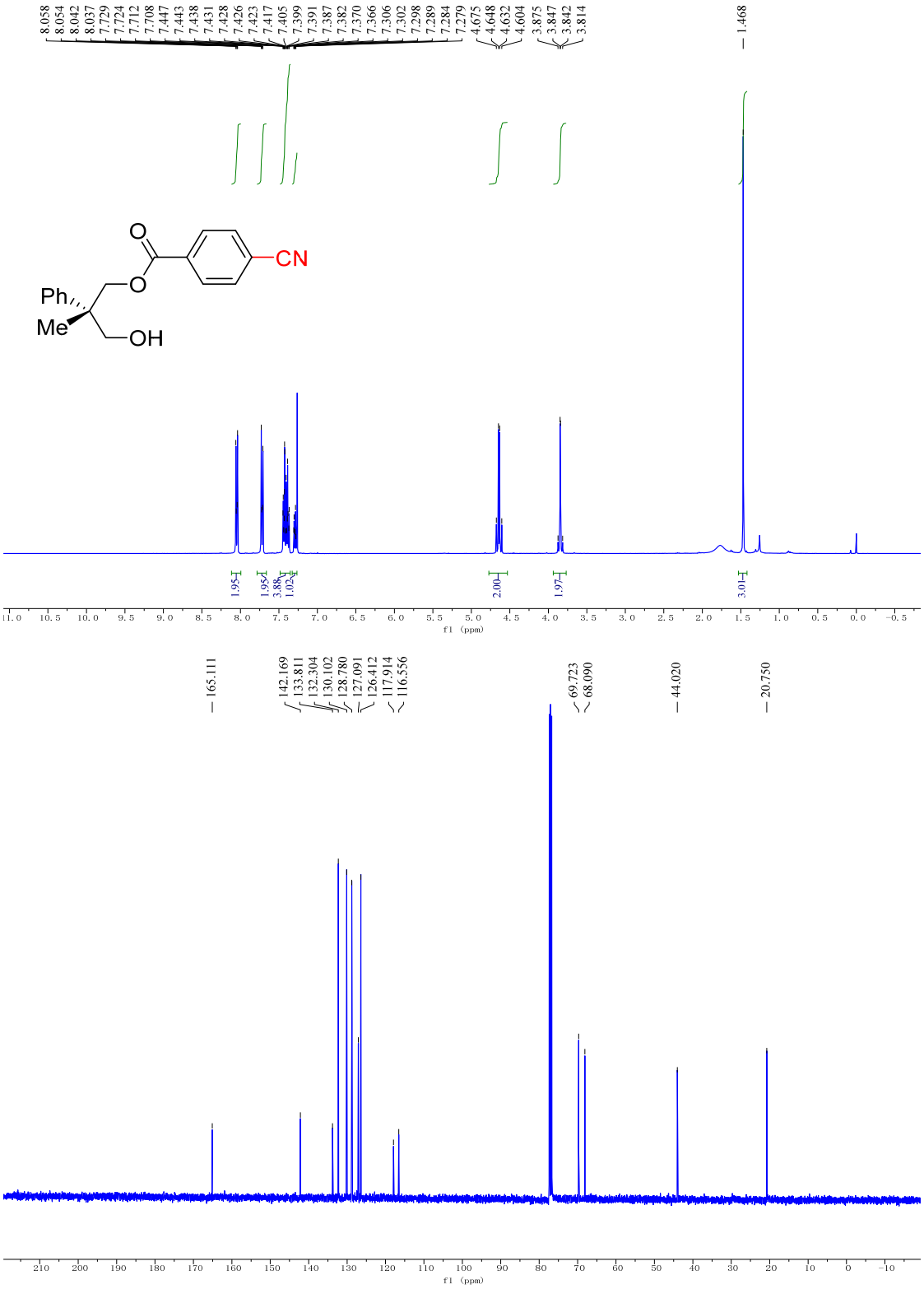

166.848
142.395
141.377
135.017
132.770
130.958
128.722
127.951
126.984
126.551
94.105
69.734
68.149
43.999
20.926
f1 (ppm)

**12**

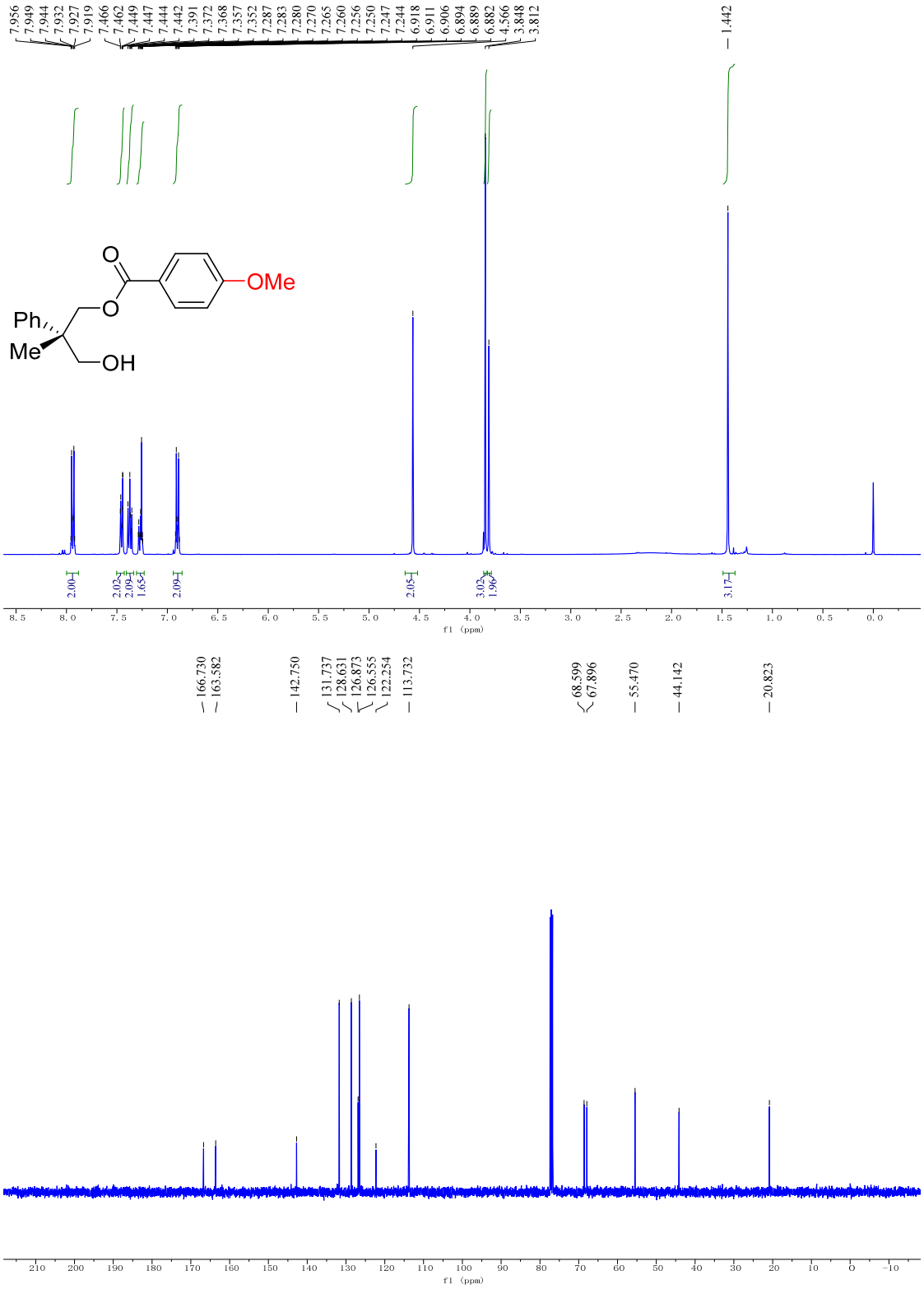

7.597
7.586
7.584
7.574
7.431
7.429
7.427
7.417
7.415
7.413
7.402
7.400
7.388
7.385
7.377
7.374
7.301
7.299
7.296
7.290
7.287
7.277
7.275
4.634
4.615
4.596
4.577
3.854
3.835
3.827
3.809
1.457
F
F
F
O
O
Ph
Me
OH
1.99
4.08
1.05
2.08
2.08
3.18
f1 (ppm)
163.974
151.896
151.873
151.828
151.805
150.225
150.202
150.157
150.134
144.195
144.094
143.993
142.475
142.373
142.271
142.073
128.797
127.125
126.377
125.975
125.947
125.927
125.898
125.878
125.850
114.270
114.237
114.153
114.121
69.823
68.038
43.998
20.697
f1 (ppm)


-132.325
-132.333
-132.347
-132.367
-132.380
-132.387
-132.400
-132.420
-132.434
-132.441
-152.154
-152.171
-152.189
-152.207
-152.225
-152.243
-152.261
-152.278
-152.296
1.90
1.00
f1 (ppm)

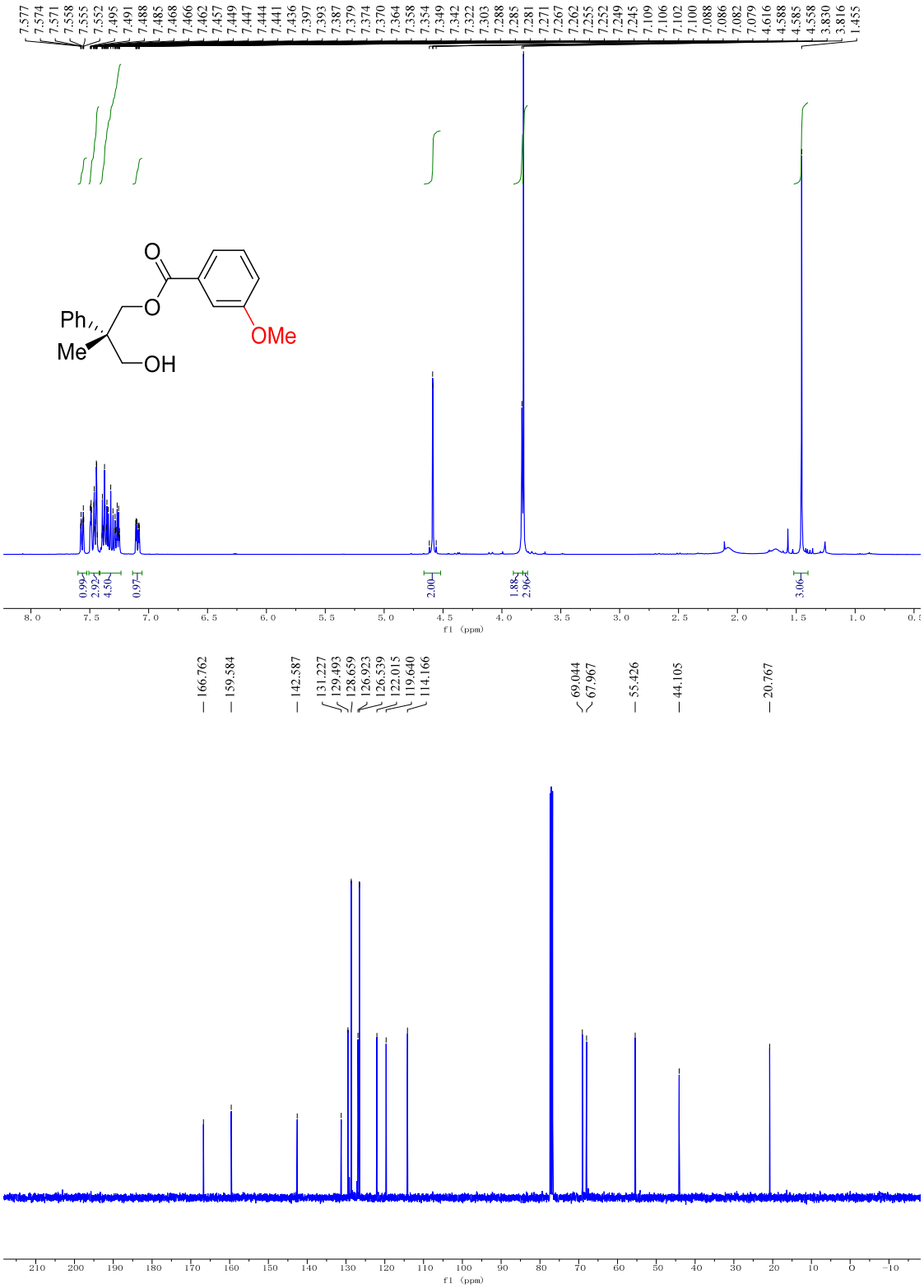
**13**


8.058
8.054
8.042
8.037
7.729
7.724
7.712
7.708
7.447
7.443
7.438
7.431
7.428
7.426
7.423
7.417
7.405
7.399
7.391
7.387
7.382
7.370
7.366
7.306
7.302
7.298
7.289
7.284
7.279
4.675
4.648
4.632
4.604
3.875
3.847
3.842
3.814
1.468
O
O
CN
Ph
Me
OH
1.95
1.95
3.88
1.02
2.00
1.97
3.01
f1 (ppm)
165.111
142.169
133.811
132.304
130.102
128.780
127.091
126.412
117.914
116.556
69.723
68.090
44.020
20.750
f1 (ppm)

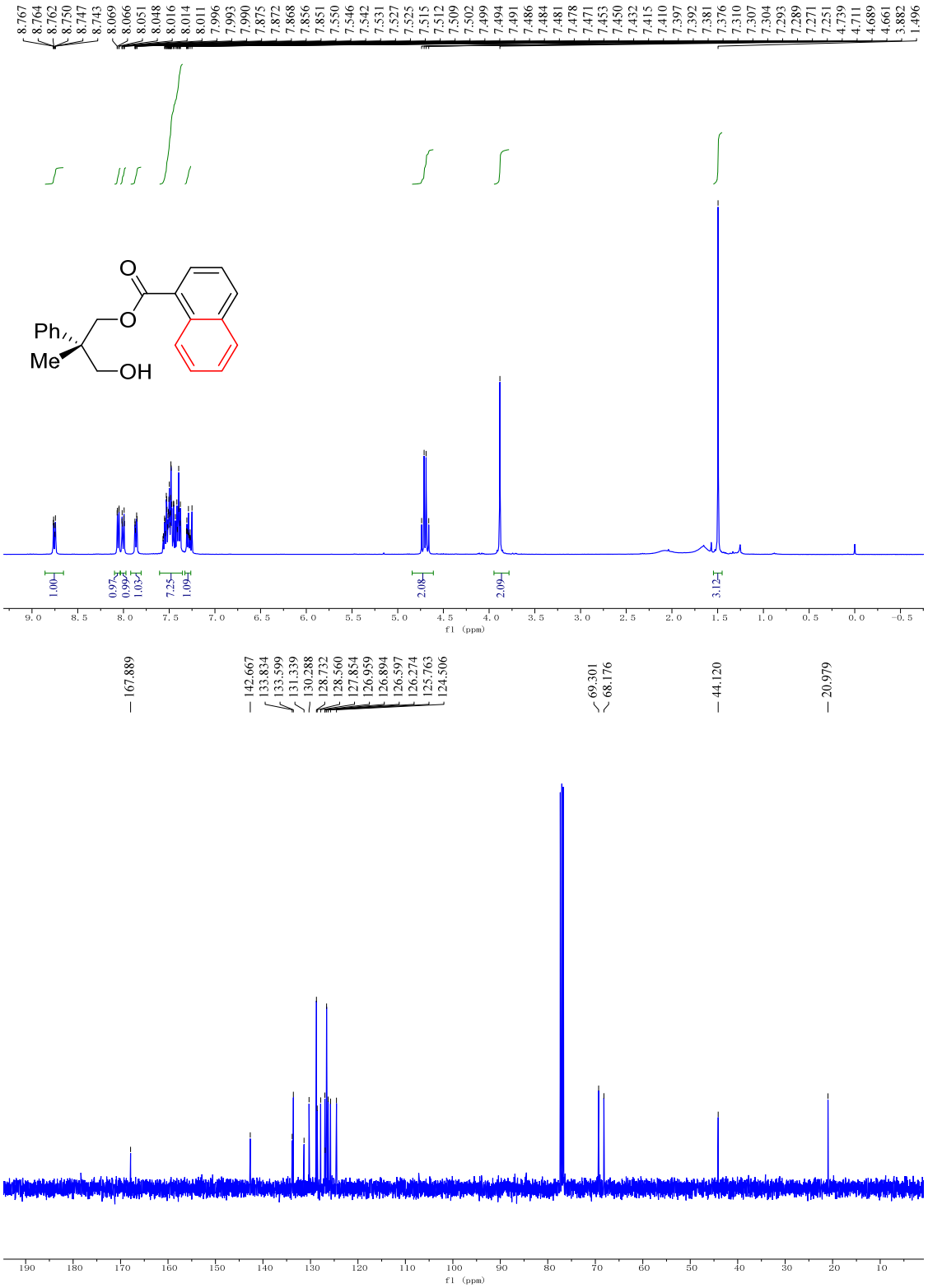
**14**


7.956
7.949
7.944
7.932
7.927
7.919
7.466
7.462
7.449
7.447
7.444
7.442
7.391
7.372
7.368
7.357
7.352
7.287
7.283
7.280
7.270
7.265
7.260
7.256
7.250
7.247
7.244
6.918
6.911
6.906
6.894
6.889
6.882
4.566
3.848
3.812
1.442
O
O
OMe
Ph
Me
OH
2.00
2.02
2.09
1.65
2.09
2.05
3.02
1.96
3.17
f1 (ppm)
166.730
163.582
142.750
131.737
128.631
126.873
126.555
122.254
113.732
68.599
67.896
55.470
44.142
20.823
f1 (ppm)

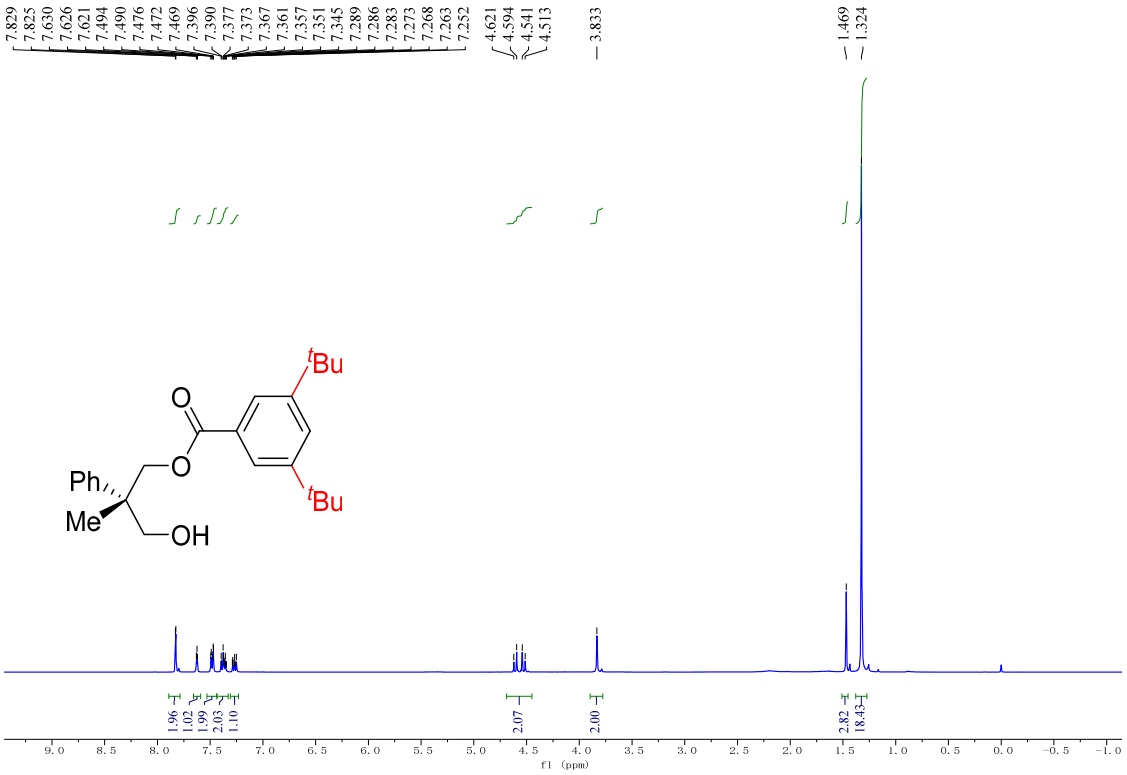
**15**

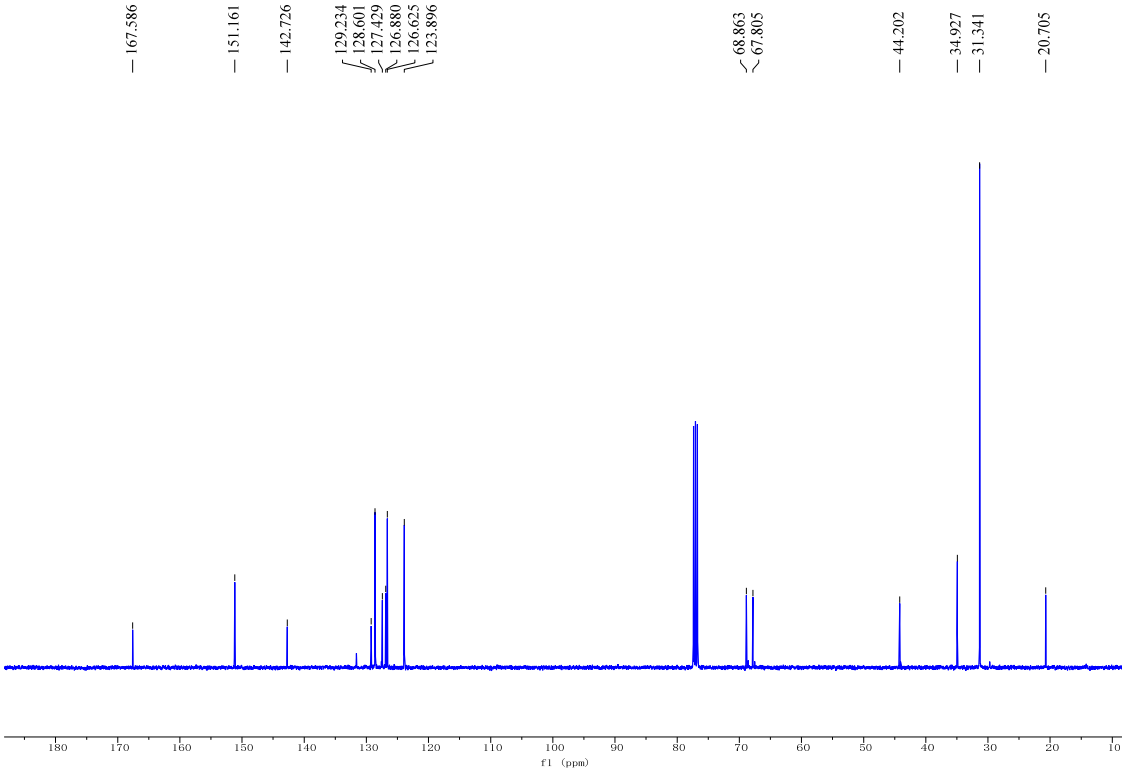

7.577
7.574
7.571
7.558
7.555
7.552
7.495
7.491
7.488
7.485
7.468
7.466
7.462
7.457
7.449
7.447
7.444
7.441
7.436
7.397
7.393
7.387
7.379
7.374
7.370
7.364
7.358
7.354
7.349
7.342
7.322
7.303
7.288
7.285
7.281
7.271
7.267
7.262
7.255
7.252
7.249
7.245
7.109
7.106
7.102
7.100
7.088
7.086
7.082
7.079
4.616
4.588
4.585
4.558
3.830
3.816
1.455
O
O
Ph
Me
OH
OMe
0.99
2.92
4.50
0.97
2.00
1.88
2.96
3.06
f1 (ppm)
166.762
159.584
142.587
131.227
129.493
128.659
126.923
126.539
122.015
119.640
114.166
69.044
67.967
55.426
44.105
20.767
f1 (ppm)

**16**

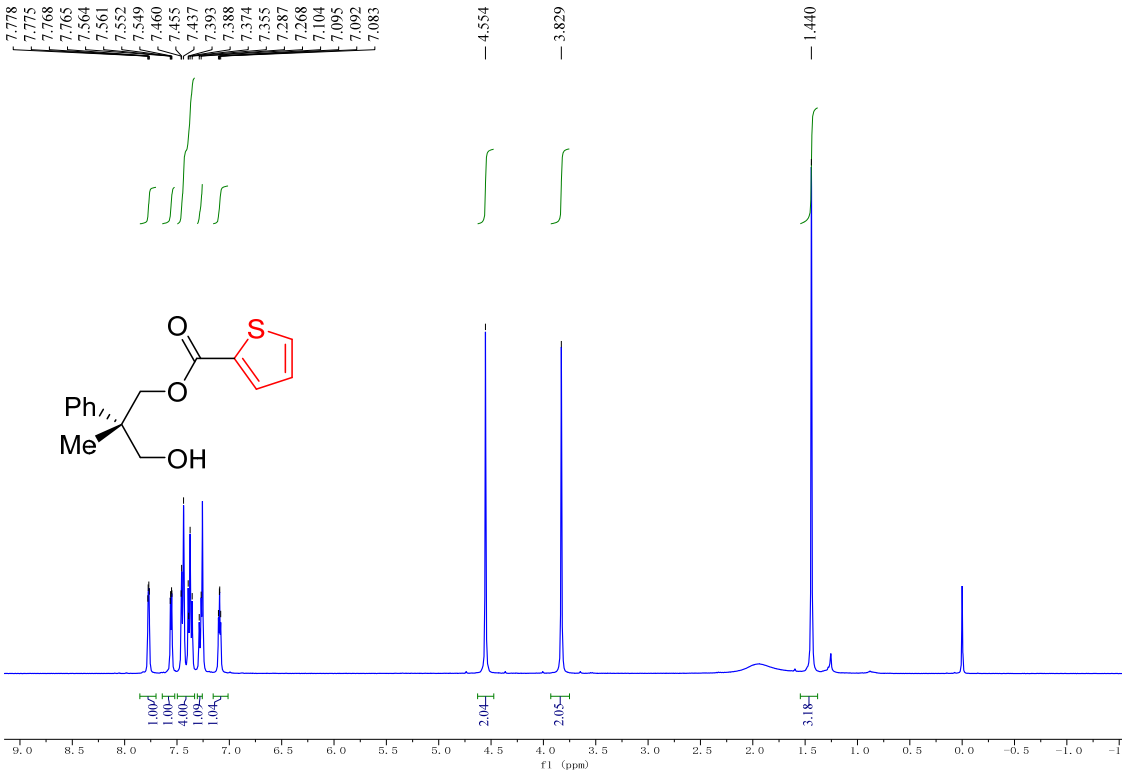

8.767
8.764
8.762
8.750
8.747
8.743
8.069
8.066
8.051
8.048
8.016
8.014
8.011
7.996
7.993
7.990
7.875
7.872
7.868
7.856
7.851
7.550
7.546
7.542
7.531
7.527
7.525
7.515
7.512
7.509
7.502
7.499
7.494
7.491
7.486
7.484
7.481
7.478
7.471
7.453
7.450
7.432
7.415
7.410
7.397
7.392
7.381
7.376
7.310
7.307
7.304
7.293
7.289
7.271
7.251
4.739
4.711
4.689
4.661
3.882
1.496
O
O
Ph
Me
OH
1.00
0.97
0.99
1.03
7.25
1.09
2.08
2.09
3.12
f1 (ppm)
167.889
142.667
133.834
133.599
131.339
130.288
128.732
128.560
127.854
126.959
126.894
126.597
126.274
125.763
124.506
69.301
68.176
44.120
20.979
f1 (ppm)

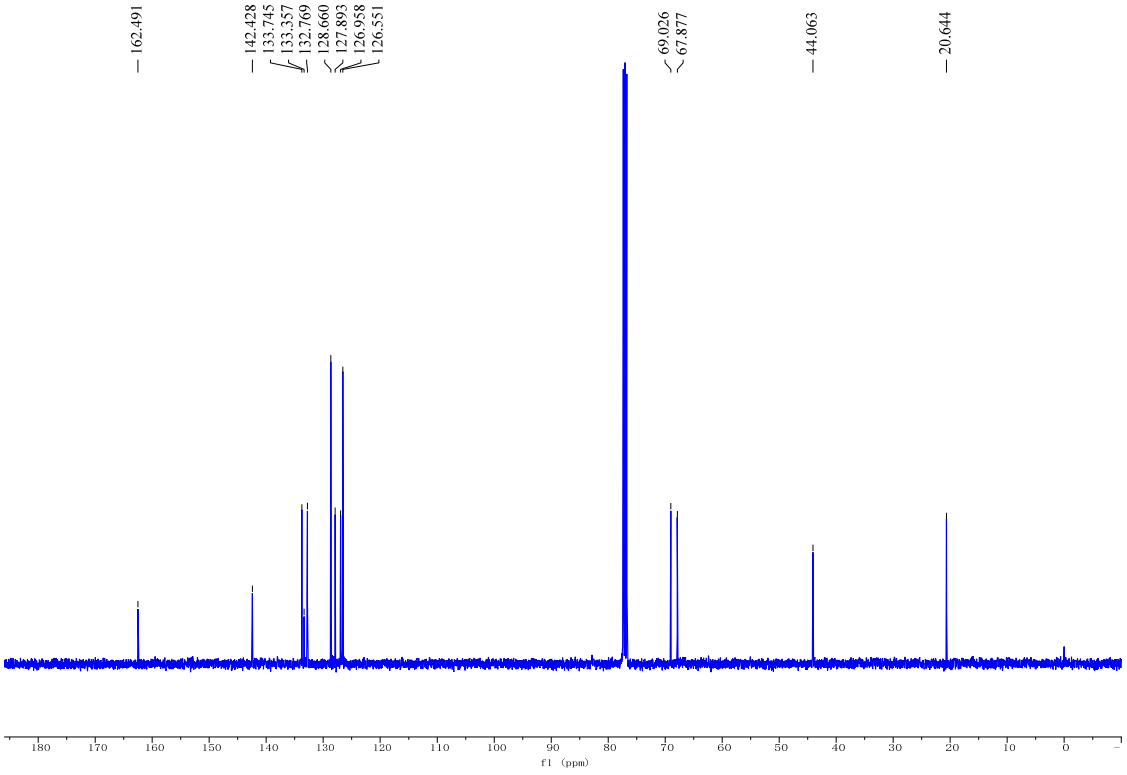
**17**


7.829
7.825
7.630
7.626
7.621
7.494
7.490
7.476
7.472
7.469
7.396
7.390
7.377
7.373
7.367
7.361
7.357
7.351
7.345
7.289
7.286
7.283
7.273
7.268
7.263
7.252
4.621
4.594
4.541
4.513
3.833
1.469
1.324
tBu
tBu
O
O
Ph
Me
OH
1.96
1.02
1.99
2.03
1.10
2.07
2.00
2.82
18.43
f1 (ppm)

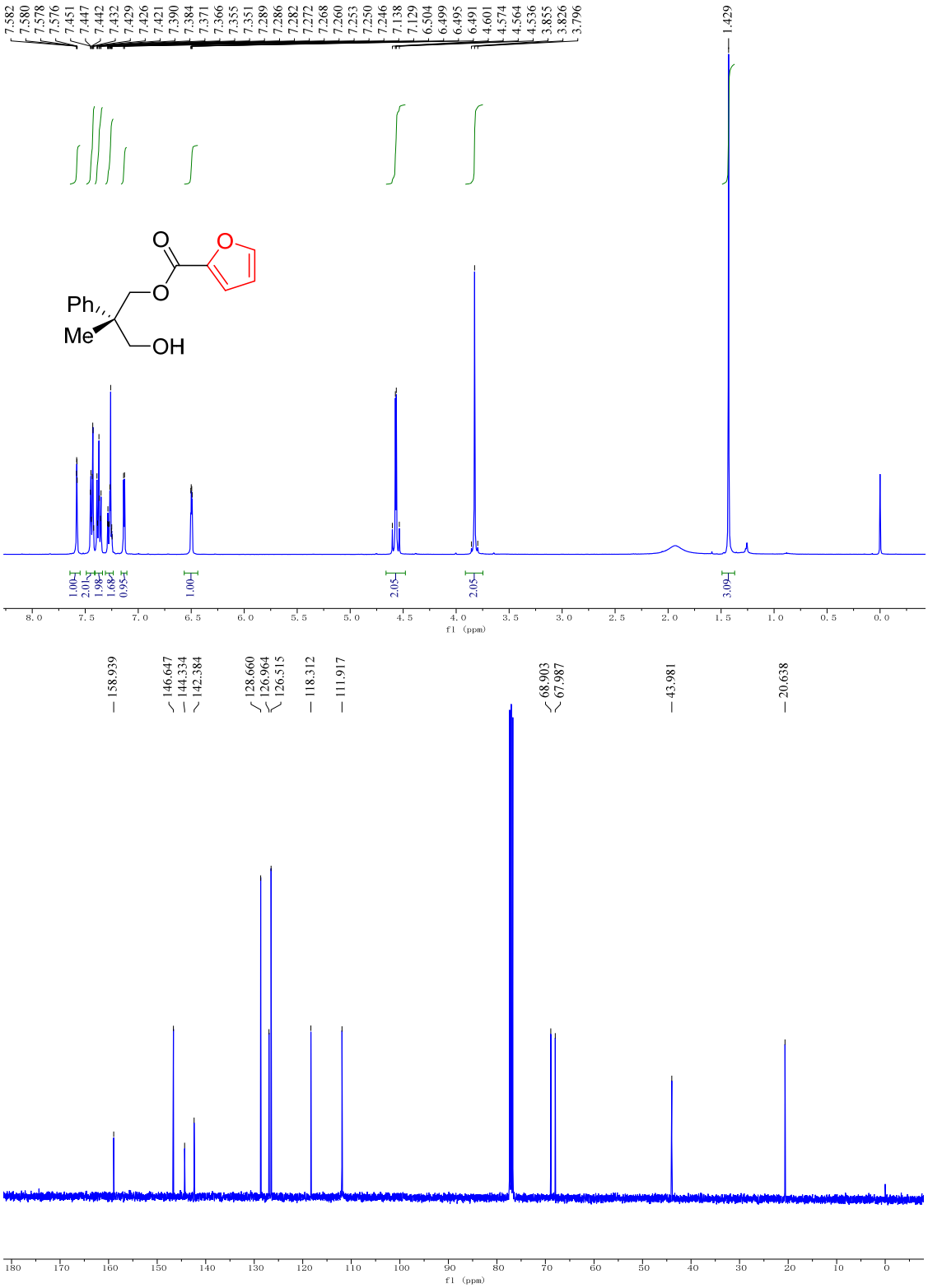

167.586
151.161
142.726
129.234
128.601
127.429
126.880
126.625
123.896
68.863
67.805
44.202
34.927
31.341
20.705
f1 (ppm)

**18**

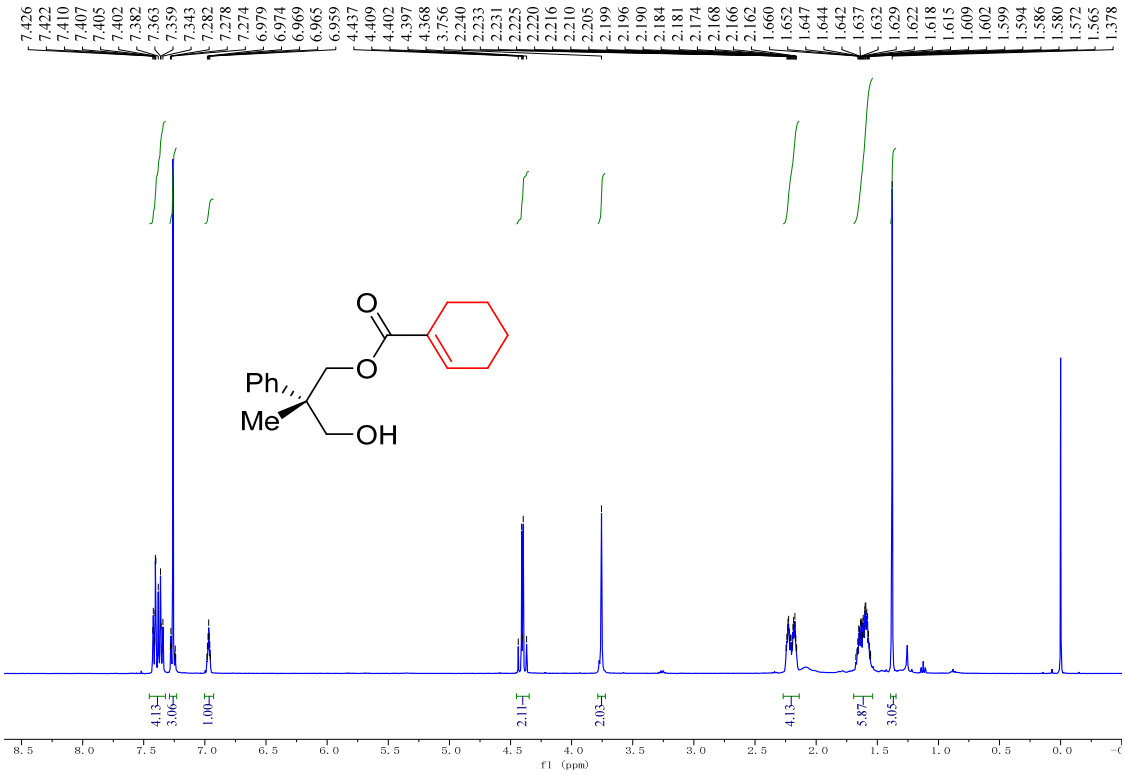

7.778
7.775
7.768
7.765
7.564
7.561
7.552
7.549
7.460
7.455
7.437
7.393
7.388
7.374
7.355
7.287
7.268
7.104
7.095
7.092
7.083
4.554
3.829
1.440
O
S
O
Ph
Me
OH
1.00
1.00
4.00
1.09
1.04
2.04
2.05
3.18
f1 (ppm)

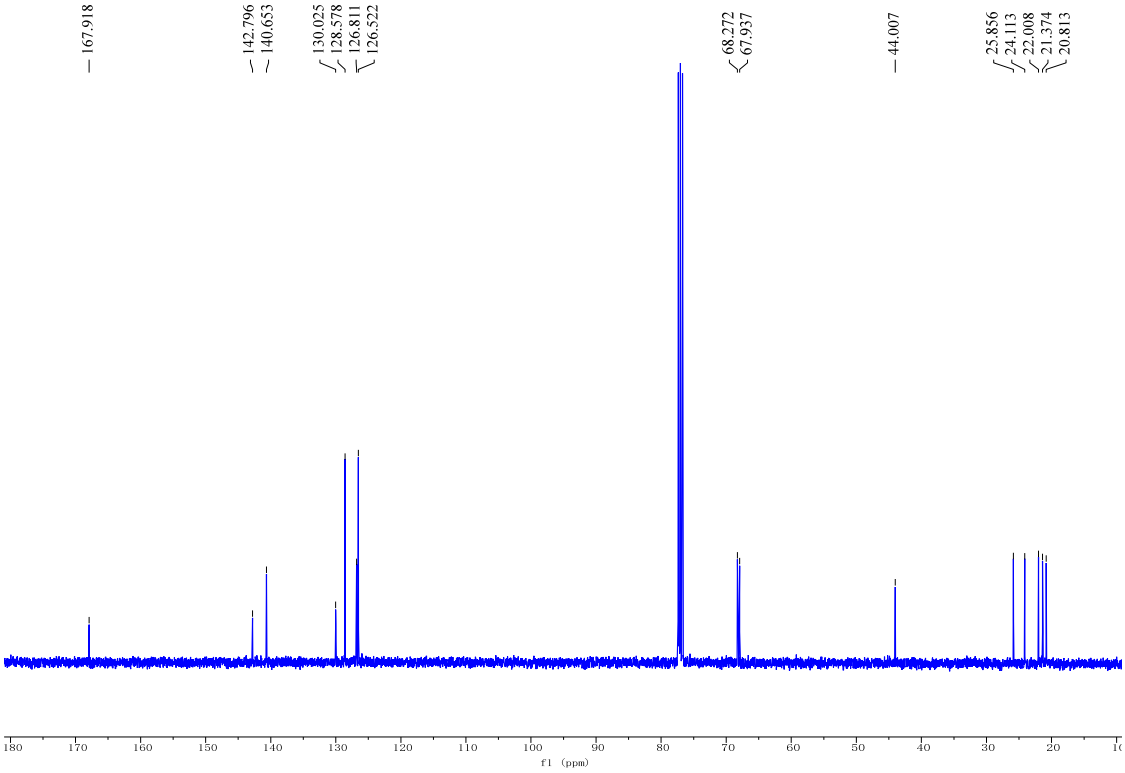

162.491
142.428
133.745
133.357
132.769
128.660
127.893
126.958
126.551
69.026
67.877
44.063
20.644
f1 (ppm)

**19**

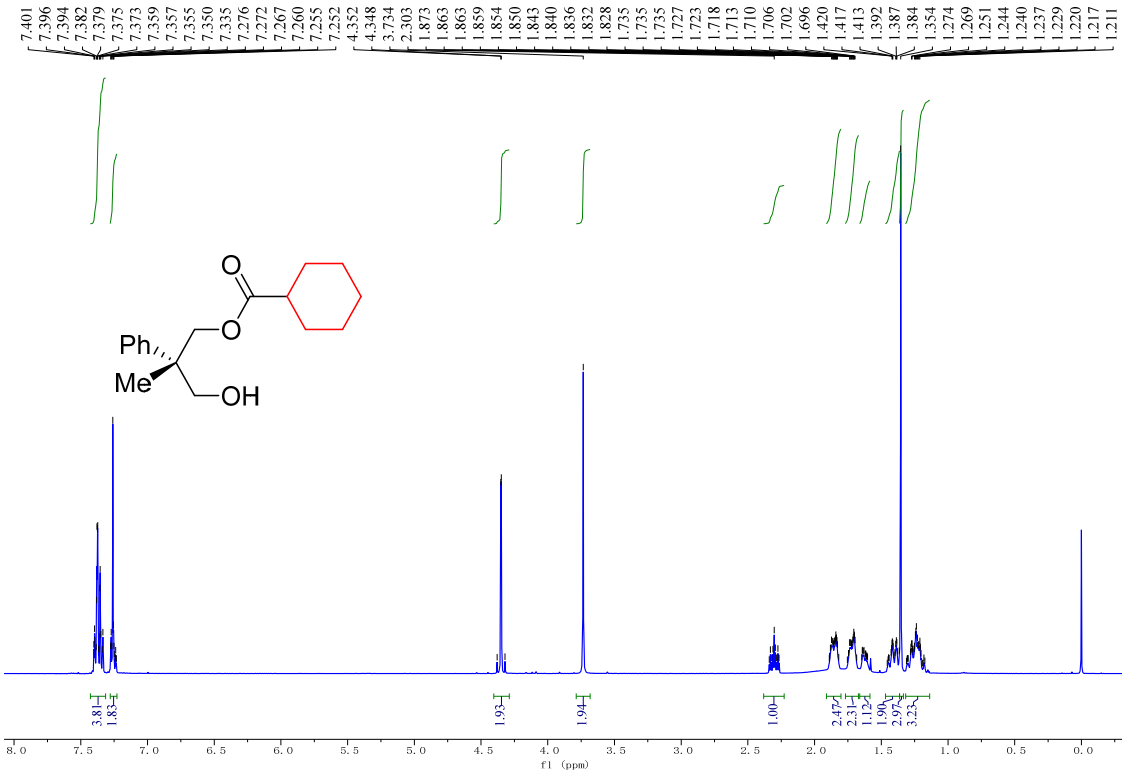

7.582
7.580
7.578
7.576
7.451
7.447
7.442
7.432
7.429
7.426
7.421
7.390
7.384
7.371
7.366
7.355
7.351
7.289
7.286
7.282
7.272
7.268
7.260
7.253
7.250
7.246
7.138
7.129
6.504
6.499
6.495
6.491
4.601
4.574
4.564
4.536
3.855
3.826
3.796
1.429
O
O
O
Ph
Me
OH
1.00
2.01
1.98
1.68
0.95
1.00
2.05
2.05
3.09
f1 (ppm)
158.939
146.647
144.334
142.384
128.660
126.964
126.515
118.312
111.917
68.903
67.987
43.981
20.638
f1 (ppm)

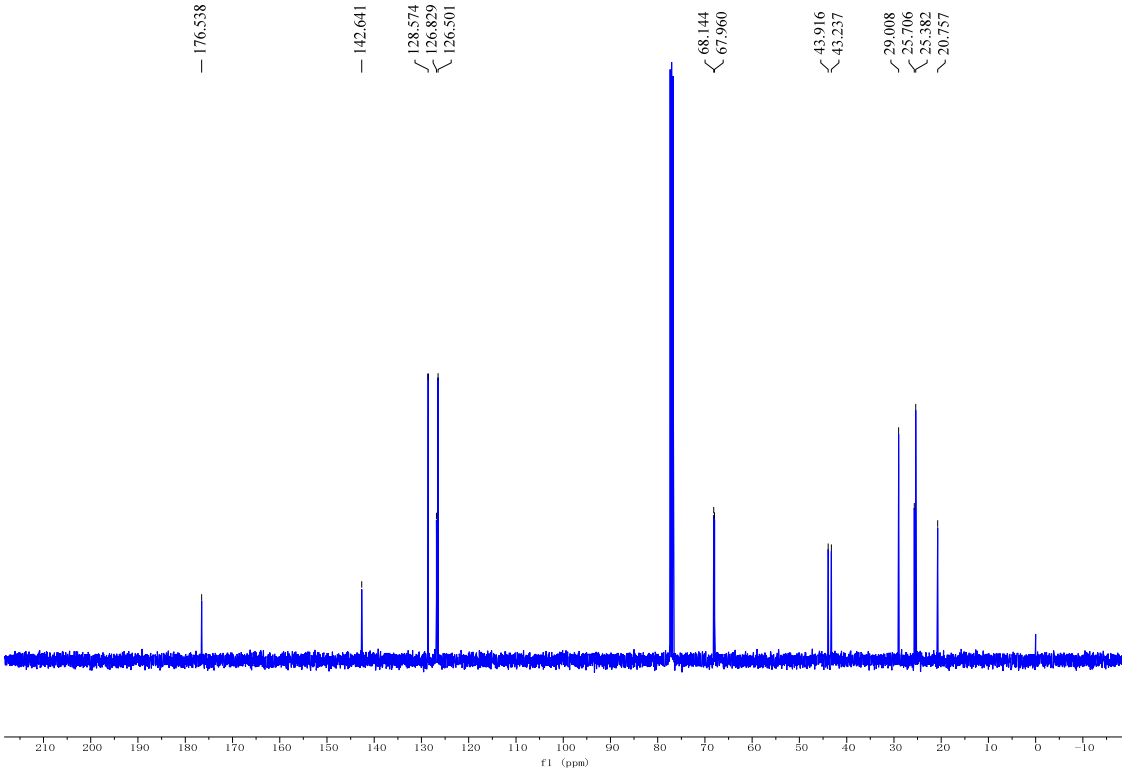
**20**


7.426
7.422
7.410
7.407
7.405
7.402
7.382
7.363
7.359
7.343
7.282
7.278
7.274
6.979
6.974
6.969
6.965
6.959
4.437
4.409
4.402
4.397
4.368
3.756
2.240
2.233
2.231
2.225
2.220
2.216
2.210
2.205
2.199
2.196
2.190
2.184
2.181
2.174
2.168
2.166
2.162
1.660
1.652
1.647
1.644
1.642
1.637
1.632
1.629
1.622
1.618
1.615
1.609
1.602
1.599
1.594
1.586
1.580
1.572
1.565
1.378
O
O
Ph
Me
OH
4.13
3.06
1.00
2.11
2.03
4.13
5.87
3.05
f1 (ppm)

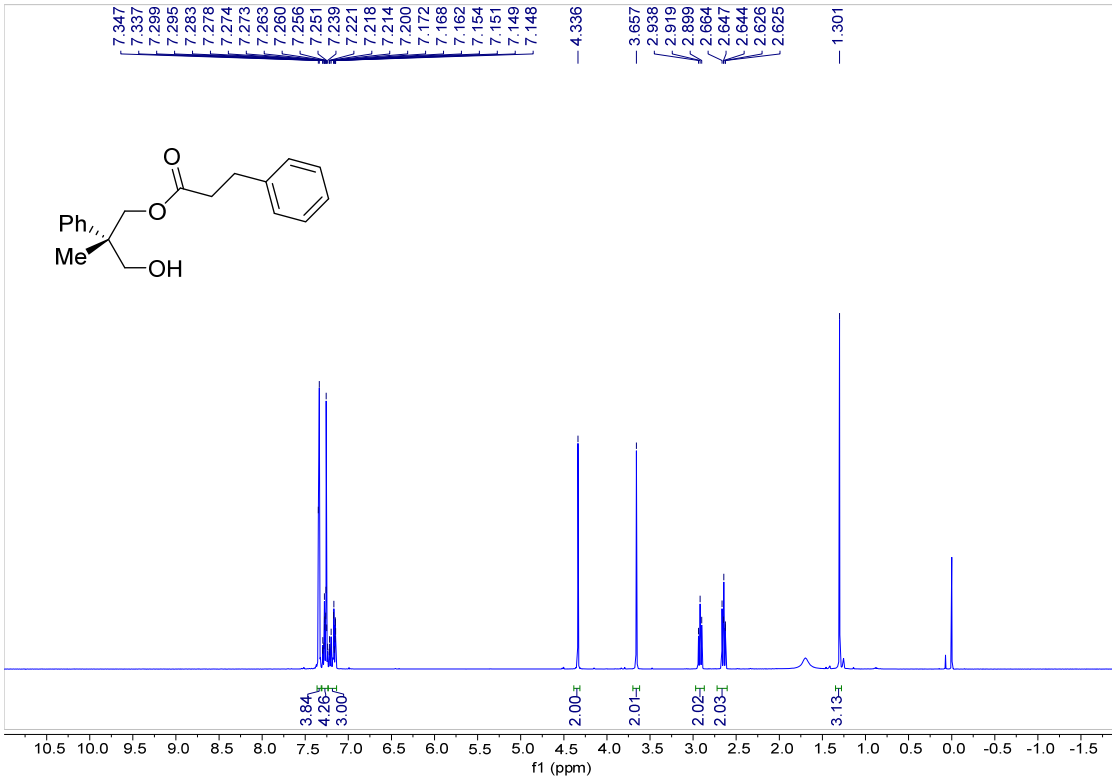

167.918
142.796
140.653
130.025
128.578
126.811
126.522
68.272
67.937
44.007
25.856
24.113
22.008
21.374
20.813
f1 (ppm)

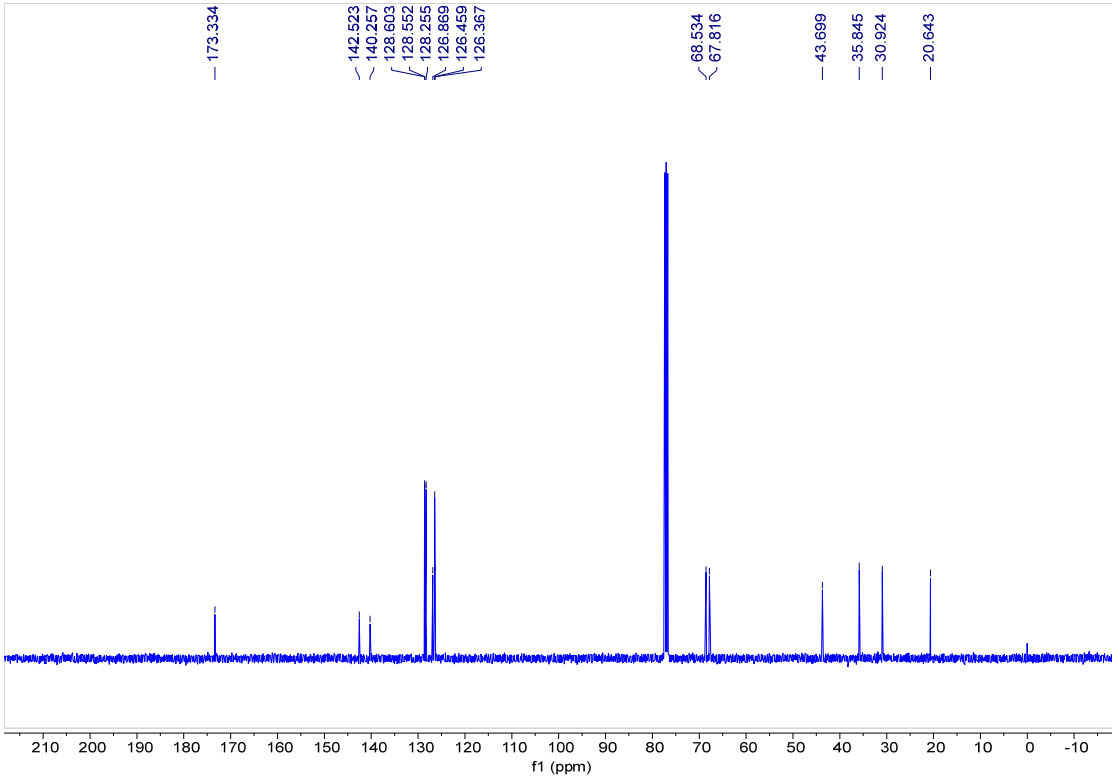
**21**


7.401
7.396
7.394
7.382
7.379
7.375
7.373
7.359
7.357
7.355
7.350
7.335
7.276
7.272
7.267
7.260
7.255
7.252
4.352
4.348
3.734
2.303
1.873
1.863
1.863
1.859
1.854
1.850
1.843
1.840
1.836
1.832
1.828
1.735
1.735
1.735
1.727
1.723
1.718
1.713
1.710
1.706
1.702
1.696
1.420
1.417
1.413
1.392
1.387
1.384
1.354
1.274
1.269
1.251
1.244
1.240
1.237
1.229
1.220
1.217
1.211
O
O
Ph
Me
OH
3.81
1.83
1.93
1.94
1.00
2.47
2.31
1.12
1.90
2.97
3.23
f1 (ppm)

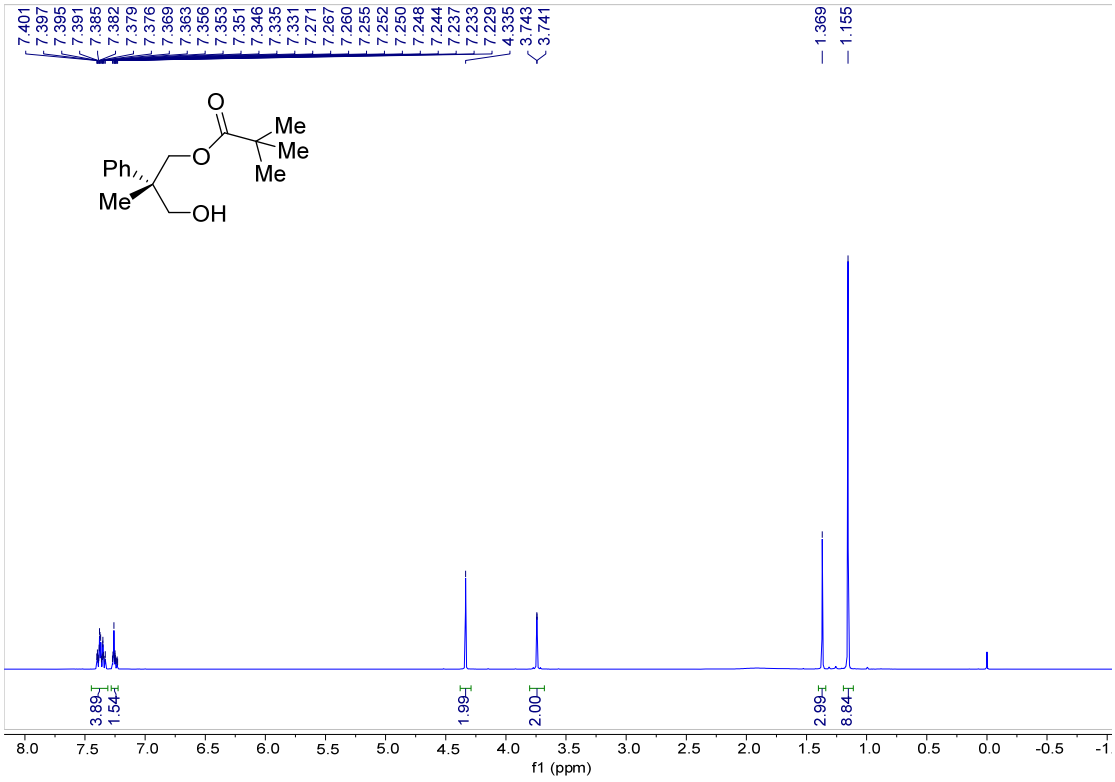

176.538
142.641
128.574
126.829
126.501
68.144
67.960
43.916
43.237
29.008
25.706
25.382
20.757
f1 (ppm)

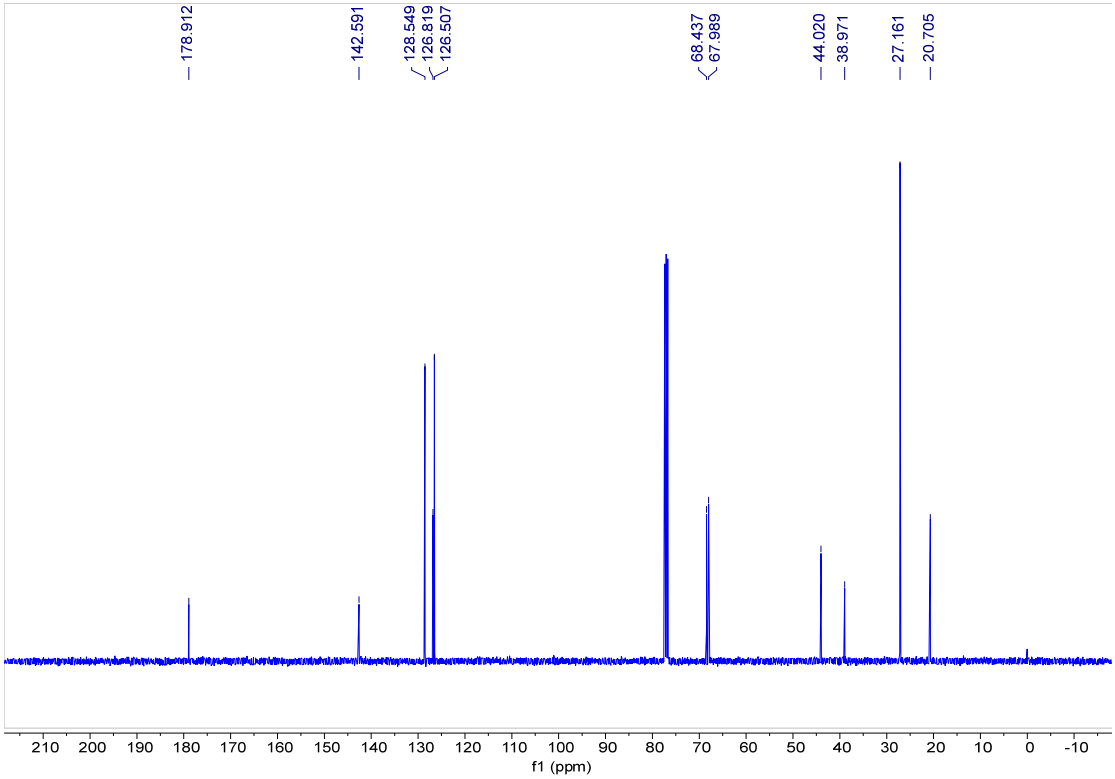
**SP-1**


7.347
7.337
7.299
7.295
7.283
7.278
7.274
7.273
7.263
7.260
7.256
7.251
7.239
7.221
7.218
7.214
7.200
7.172
7.168
7.162
7.154
7.151
7.149
7.148
4.336
3.657
2.938
2.919
2.899
2.664
2.647
2.644
2.626
2.625
1.301
O
O
Ph
Me
OH
3.84
4.26
3.00
2.00
2.01
2.02
2.03
3.13
f1 (ppm)

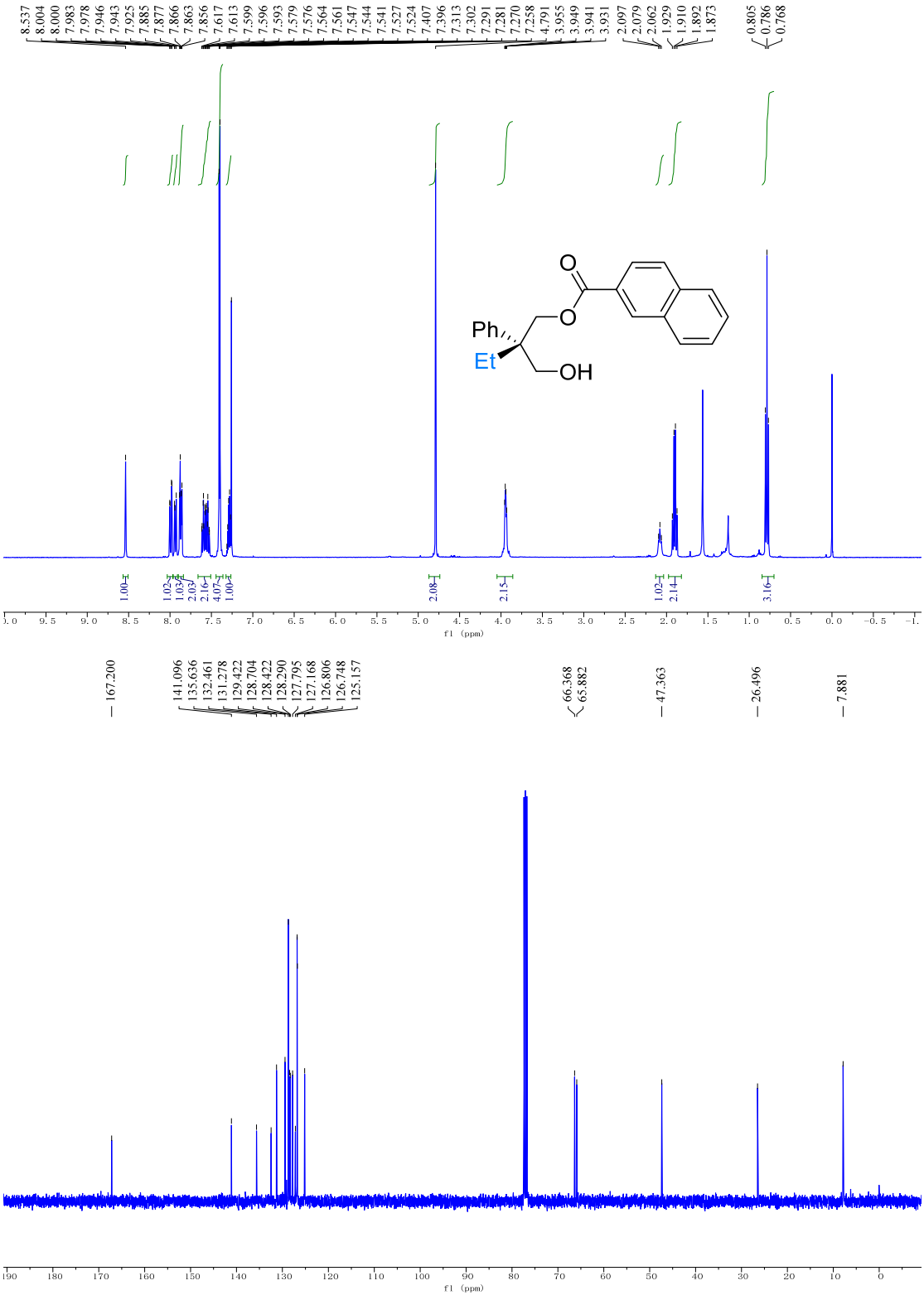

173.334
142.523
140.257
128.603
128.552
128.255
126.869
126.459
126.367
68.534
67.816
43.699
35.845
30.924
20.643
f1 (ppm)

**SP-2**

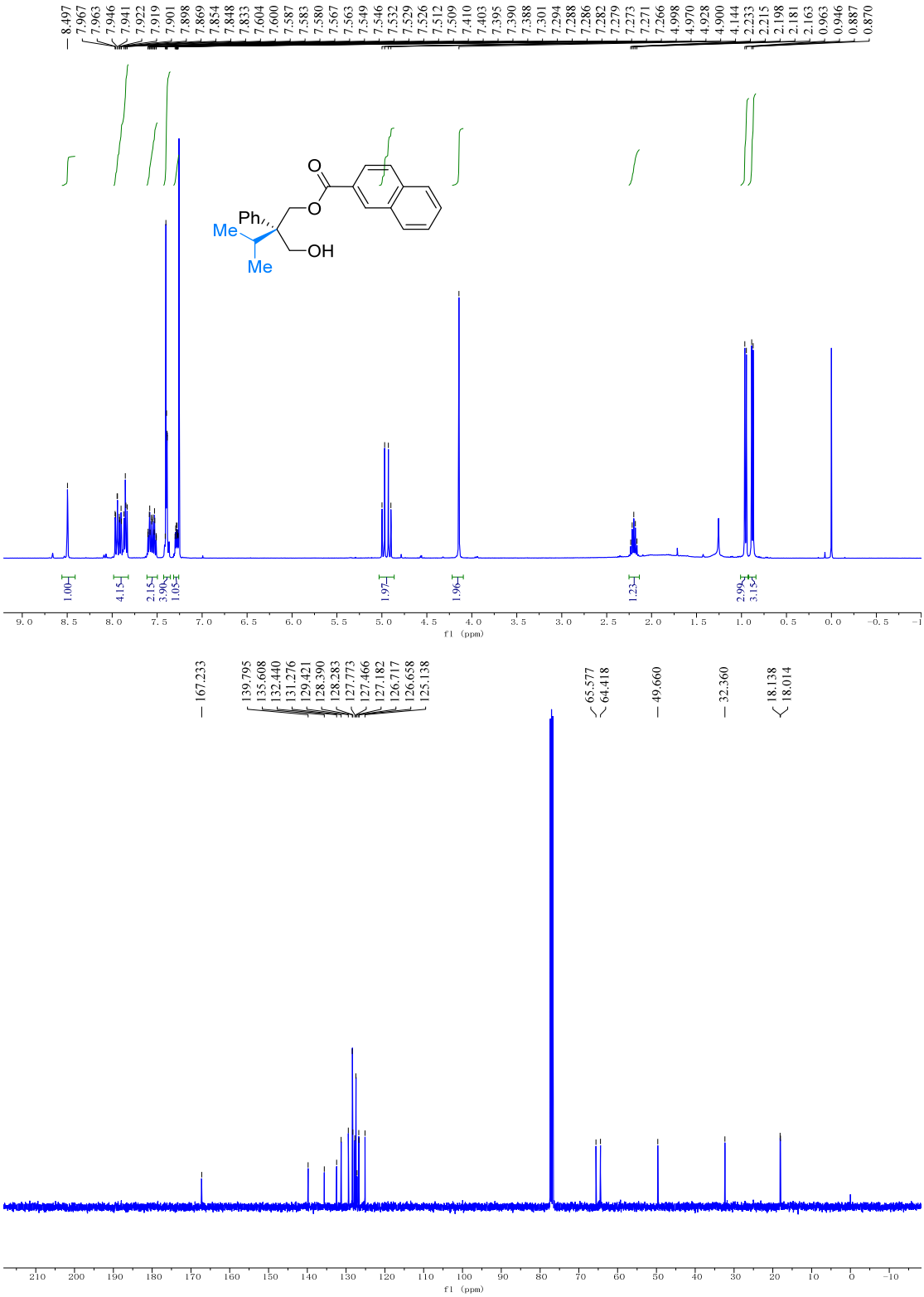

7.401
7.397
7.395
7.391
7.385
7.382
7.379
7.376
7.369
7.363
7.356
7.353
7.351
7.346
7.335
7.331
7.271
7.267
7.260
7.255
7.252
7.250
7.248
7.244
7.237
7.233
7.229
4.335
3.743
3.741
1.369
1.155
O
Me
Me
Me
O
Ph
Me
OH
3.89
1.54
1.99
2.00
2.99
8.84
f1 (ppm)


178.912
142.591
128.549
126.819
126.507
68.437
67.989
44.020
38.971
27.161
20.705
f1 (ppm)

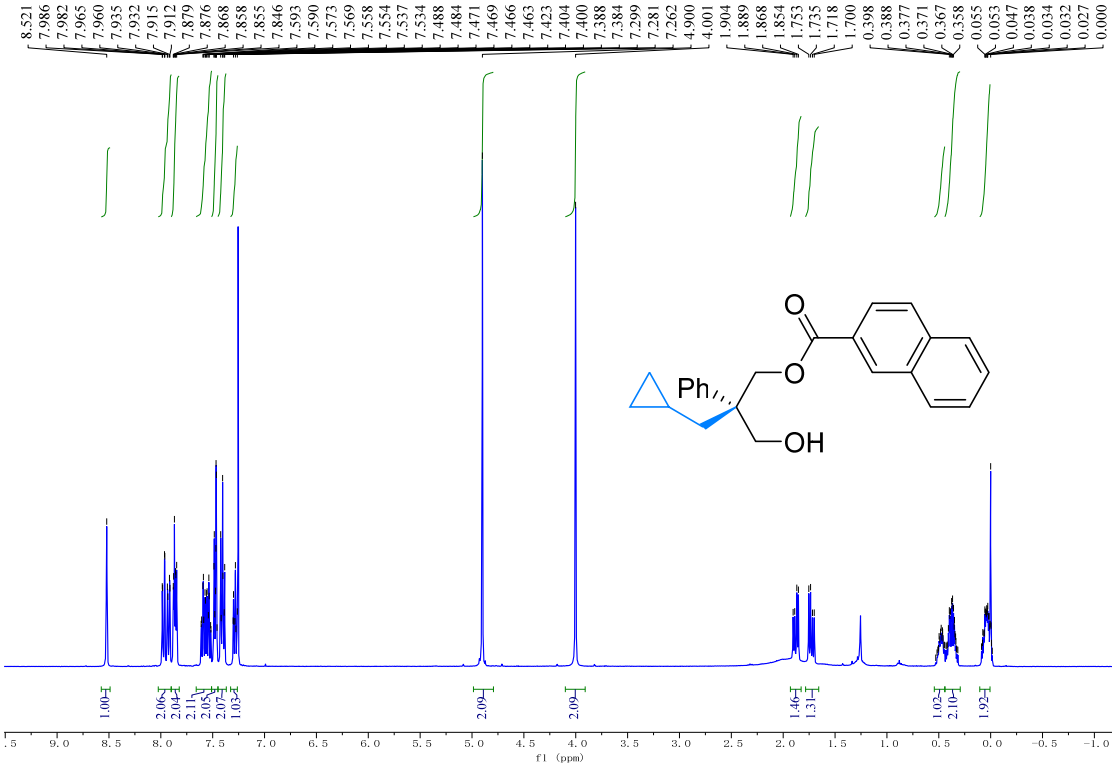
**22**

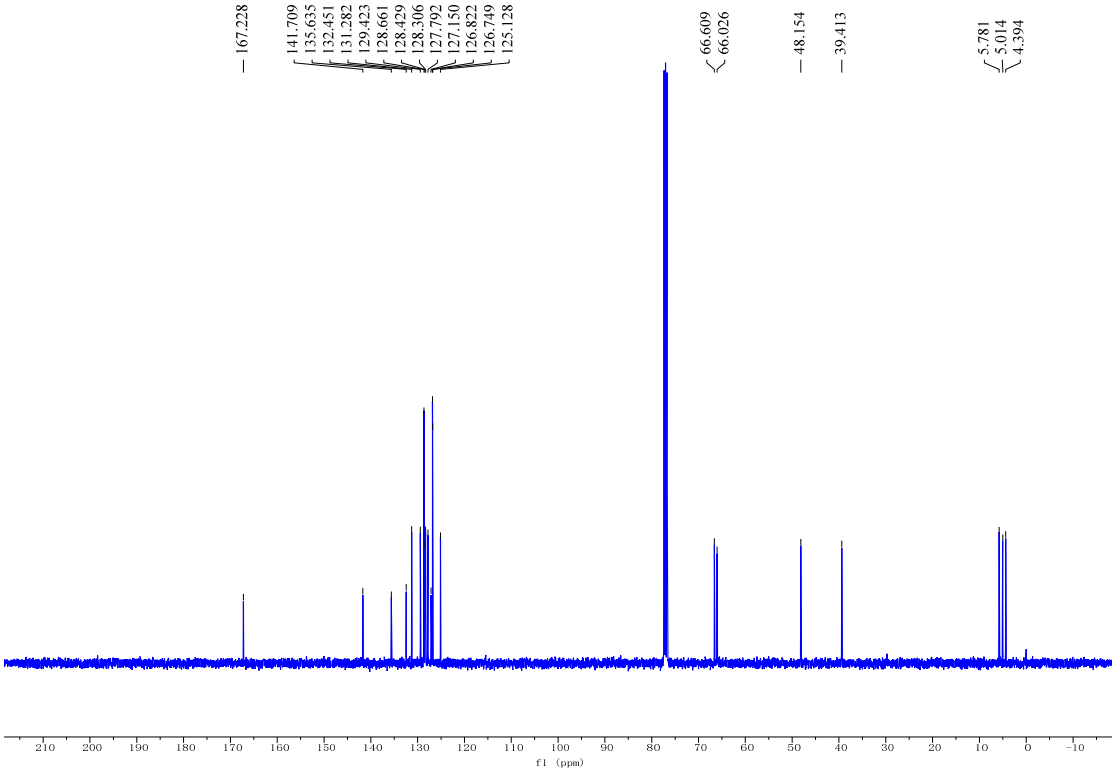

8.537
8.004
8.000
7.983
7.978
7.946
7.943
7.925
7.885
7.877
7.866
7.863
7.856
7.617
7.613
7.599
7.596
7.593
7.579
7.576
7.564
7.561
7.547
7.544
7.541
7.527
7.524
7.407
7.396
7.313
7.302
7.291
7.281
7.270
7.258
4.791
3.955
3.949
3.941
3.931
2.097
2.079
2.062
1.929
1.910
1.892
1.873
0.805
0.786
0.768
O
O
Ph
Et
OH
1.00
1.02
1.03
2.03
2.16
4.07
1.00
2.08
2.15
1.02
2.14
3.16
f1 (ppm)
167.200
141.096
135.636
132.461
131.278
129.422
128.704
128.422
128.290
127.795
127.168
126.806
126.748
125.157
66.368
65.882
47.363
26.496
7.881
f1 (ppm)

**23**

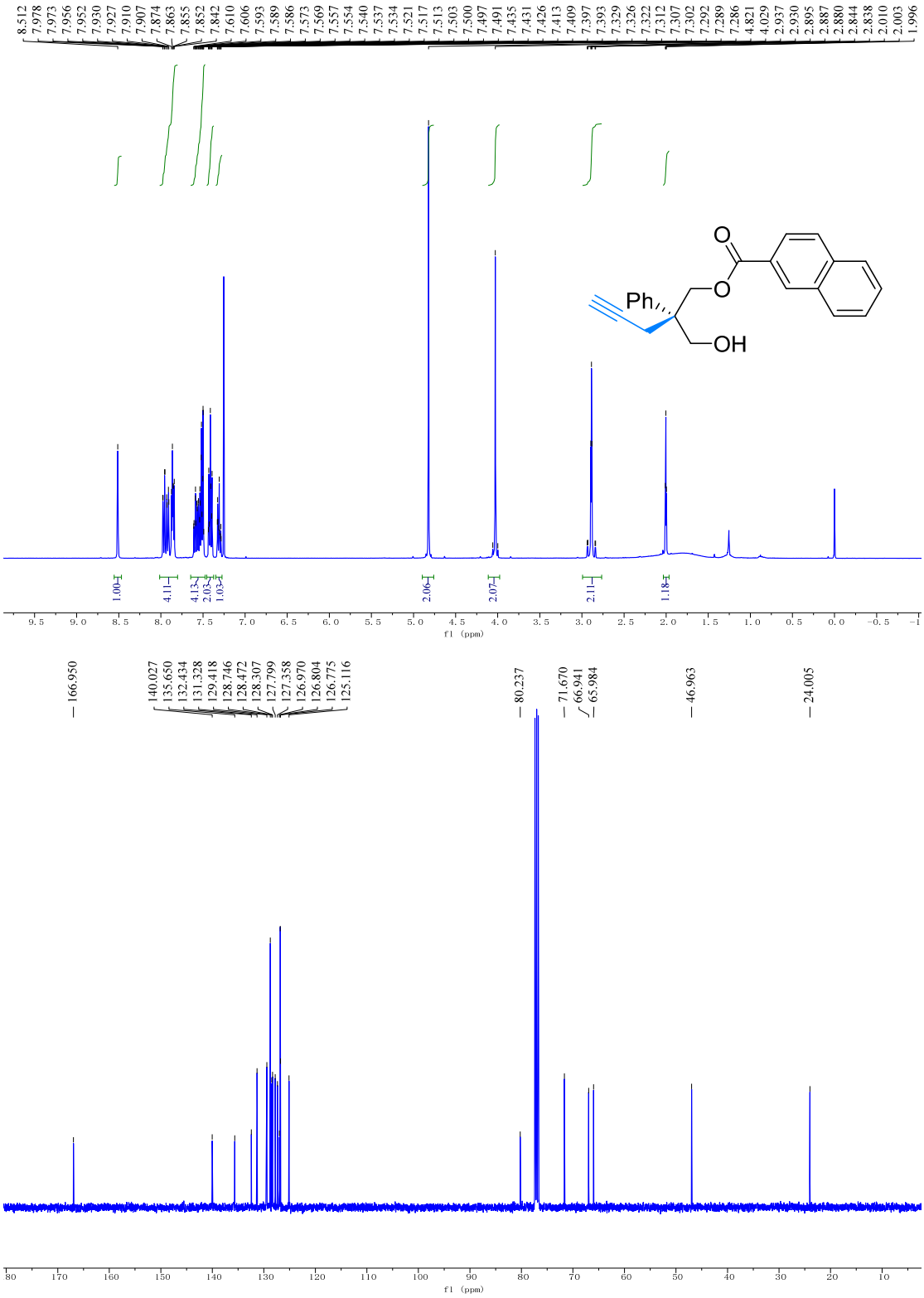

8.497
7.967
7.963
7.946
7.941
7.922
7.919
7.901
7.898
7.869
7.854
7.848
7.833
7.604
7.600
7.587
7.583
7.580
7.567
7.563
7.549
7.546
7.532
7.529
7.526
7.512
7.509
7.410
7.403
7.395
7.390
7.388
7.301
7.294
7.288
7.286
7.282
7.279
7.273
7.271
7.266
4.998
4.970
4.928
4.900
4.144
2.233
2.215
2.198
2.181
2.163
0.963
0.946
0.887
0.870
O
O
Ph
Me
Me
OH
1.00
4.15
2.15
3.90
1.05
1.97
1.96
1.23
2.99
3.15
f1 (ppm)
167.233
139.795
135.608
132.440
131.276
129.421
128.390
128.283
127.773
127.466
127.182
126.717
126.658
125.138
65.577
64.418
49.660
32.360
18.138
18.014
f1 (ppm)

**24**

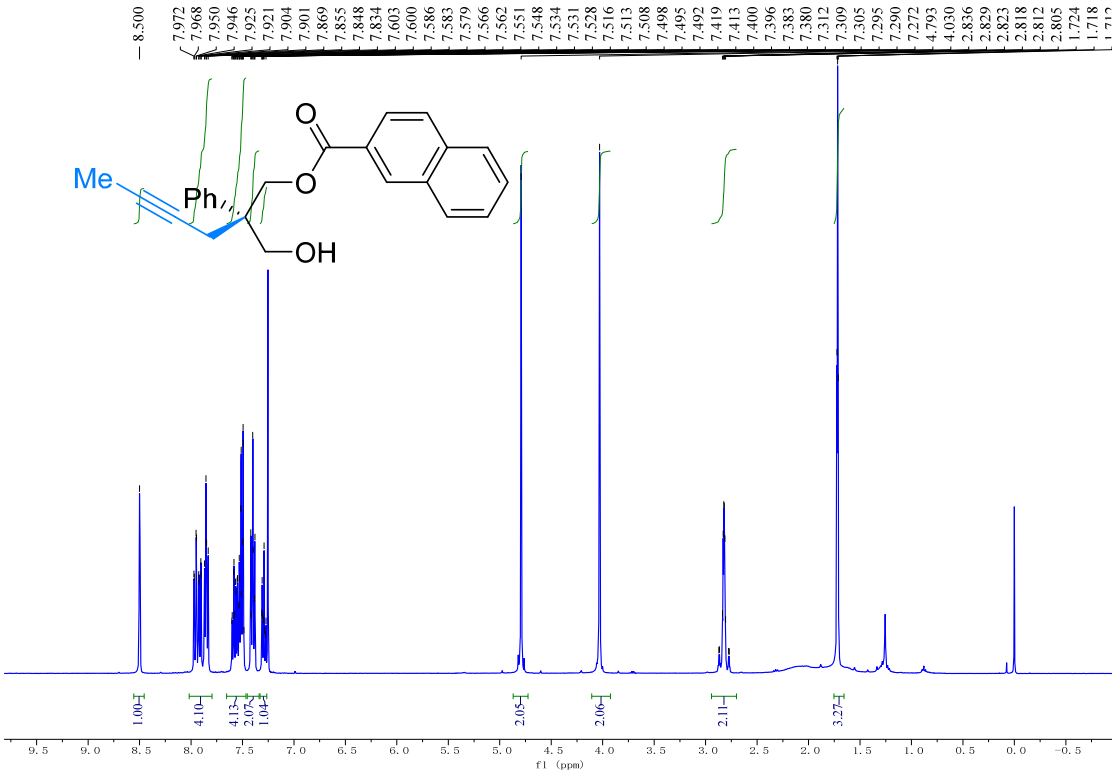

8.521
7.986
7.982
7.965
7.960
7.935
7.932
7.915
7.912
7.879
7.876
7.868
7.858
7.855
7.846
7.593
7.590
7.573
7.569
7.558
7.554
7.537
7.534
7.488
7.484
7.471
7.469
7.466
7.463
7.423
7.404
7.400
7.388
7.384
7.299
7.281
7.262
4.900
4.001
1.904
1.889
1.868
1.854
1.753
1.735
1.718
1.700
0.398
0.388
0.377
0.371
0.367
0.358
0.055
0.053
0.047
0.038
0.034
0.032
0.027
0.000
O
O
Ph
OH
1.00
2.06
2.04
2.11
2.05
2.07
1.03
2.09
2.09
1.46
1.31
1.02
2.10
1.92
f1 (ppm)

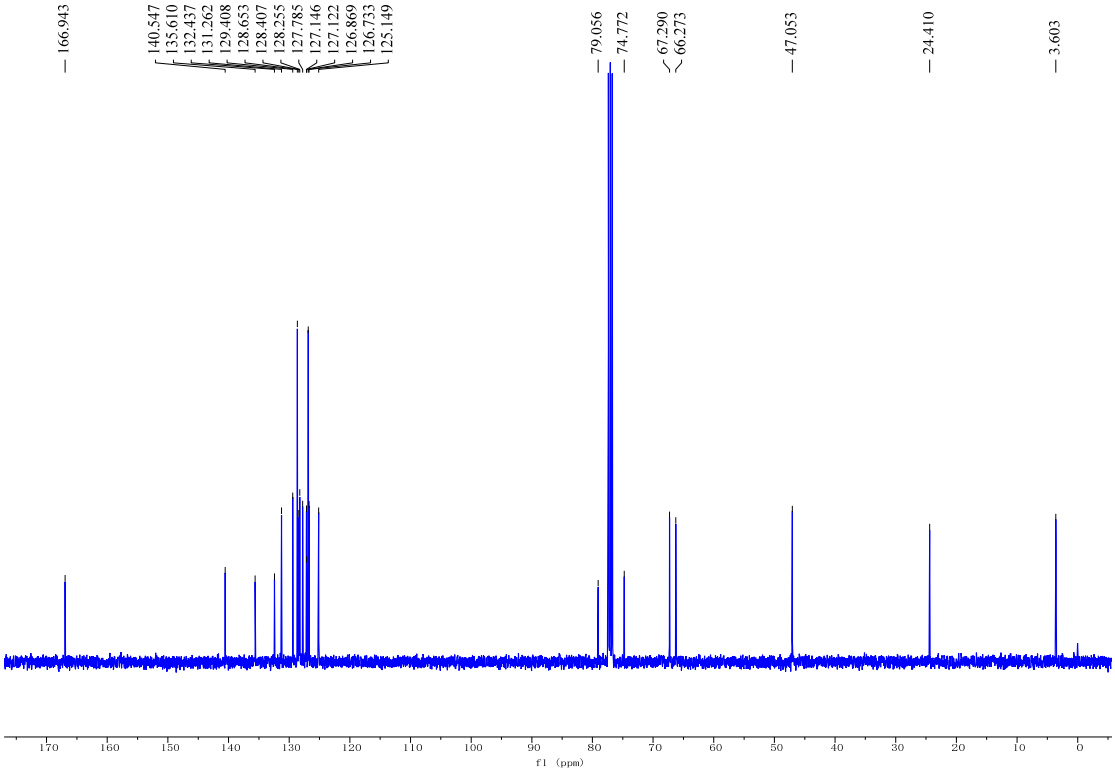

167.228
141.709
135.635
132.451
131.282
129.423
128.661
128.429
128.306
127.792
127.150
126.822
126.749
125.128
66.609
66.026
48.154
39.413
5.781
5.014
4.394
f1 (ppm)

**25**

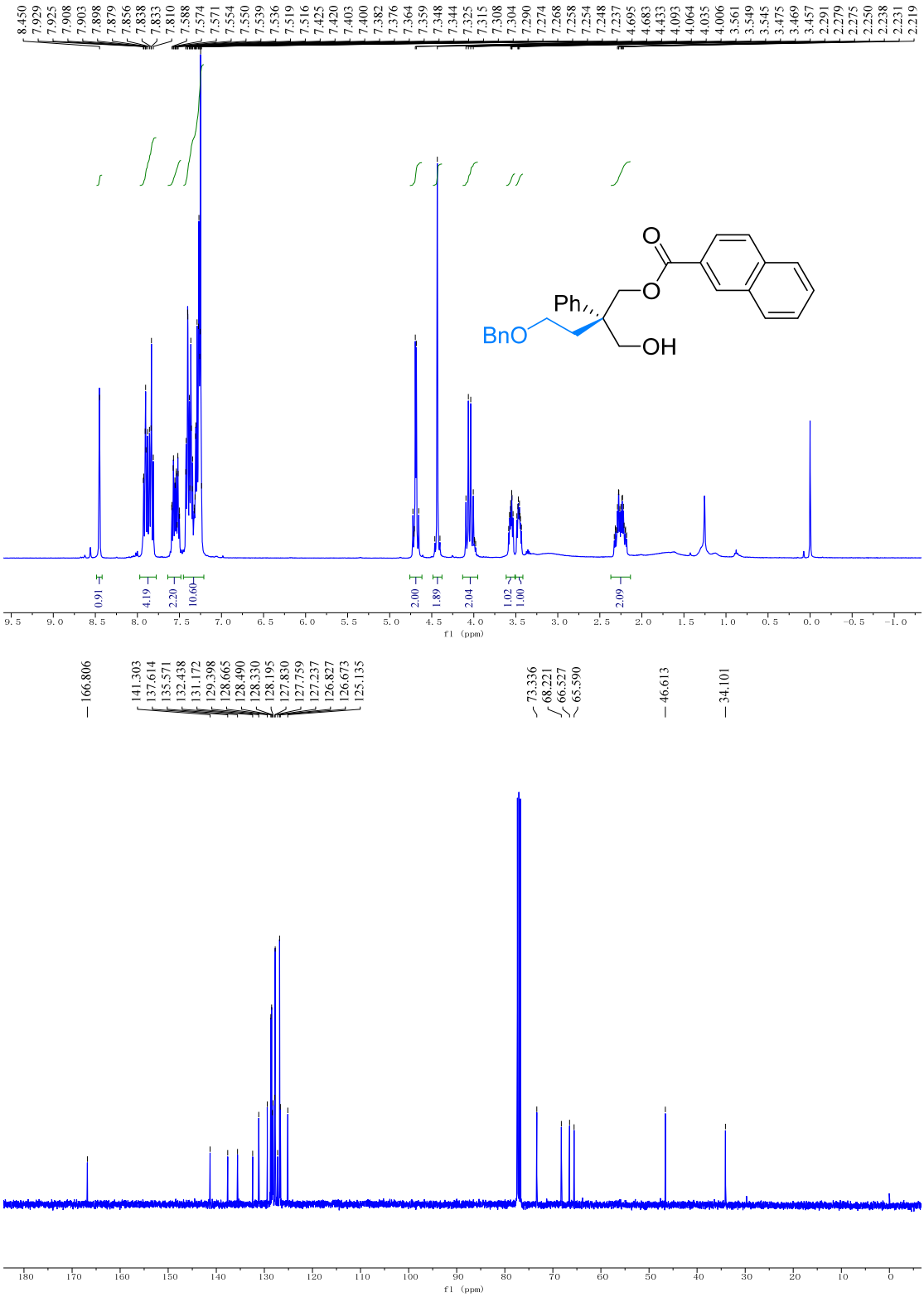

8.512
7.978
7.973
7.956
7.952
7.930
7.927
7.910
7.907
7.874
7.863
7.855
7.852
7.842
7.610
7.606
7.593
7.589
7.586
7.573
7.569
7.557
7.554
7.540
7.537
7.534
7.521
7.517
7.513
7.503
7.500
7.497
7.491
7.435
7.431
7.426
7.413
7.409
7.397
7.393
7.329
7.326
7.322
7.312
7.307
7.302
7.292
7.289
7.286
4.821
4.029
2.937
2.930
2.895
2.887
2.880
2.844
2.838
2.010
2.003
1.996
O
O
Ph
OH
1.00
4.11
4.13
2.03
1.03
2.06
2.07
2.11
1.18
f1 (ppm)
166.950
140.027
135.650
132.434
131.328
129.418
128.746
128.472
128.307
127.799
127.358
126.970
126.804
126.775
125.116
80.237
71.670
66.941
65.984
46.963
24.005
f1 (ppm)

**26**


8.500
7.972
7.968
7.950
7.946
7.925
7.921
7.904
7.901
7.869
7.855
7.848
7.834
7.603
7.600
7.586
7.583
7.579
7.566
7.562
7.551
7.548
7.534
7.531
7.528
7.516
7.513
7.508
7.498
7.495
7.492
7.419
7.413
7.400
7.396
7.383
7.380
7.312
7.309
7.305
7.295
7.290
7.272
4.793
4.030
2.836
2.829
2.823
2.818
2.812
2.805
1.724
1.718
O
O
Me
Ph
OH
1.00
4.10
4.13
2.07
1.04
2.05
2.06
2.11
3.27
f1 (ppm)


166.943
140.547
135.610
132.437
131.262
129.408
128.653
128.407
128.255
127.785
127.146
127.122
126.869
126.733
125.149
79.056
74.772
67.290
66.273
47.053
24.410
3.603
f1 (ppm)

**27**


8.450
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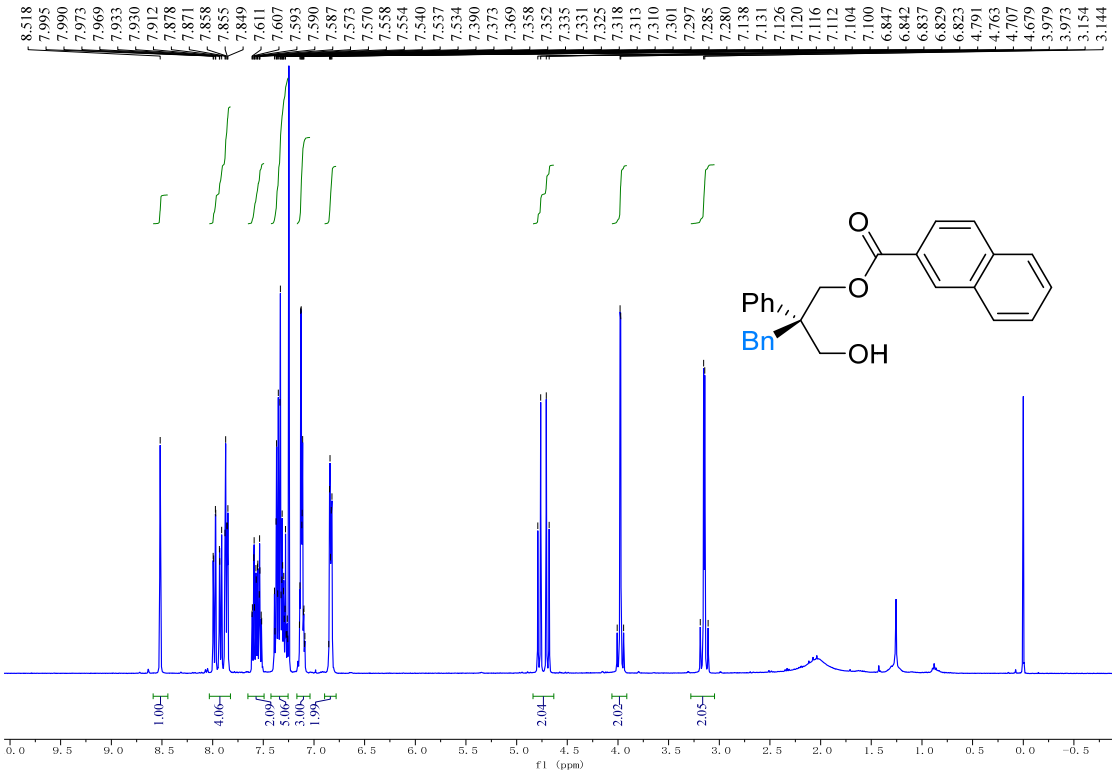
7.925
7.908
7.903
7.898
7.879
7.856
7.838
7.833
7.810
7.588
7.574
7.571
7.554
7.550
7.539
7.536
7.519
7.516
7.425
7.420
7.403
7.400
7.382
7.376
7.364
7.359
7.348
7.344
7.325
7.315
7.308
7.304
7.290
7.274
7.268
7.258
7.254
7.248
7.237
4.695
4.683
4.433
4.093
4.064
4.035
4.006
3.561
3.549
3.545
3.475
3.469
3.457
2.291
2.279
2.275
2.250
2.238
2.231
2.219
O
O
Ph
BnO
OH
0.91
4.19
2.20
10.60
2.00
1.89
2.04
1.02
1.00
2.09
f1 (ppm)
166.806
141.303
137.614
135.571
132.438
131.172
129.398
128.665
128.490
128.330
128.195
127.830
127.759
127.237
126.827
126.673
125.135
73.336
68.221
66.527
65.590
46.613
34.101
f1 (ppm)

**28**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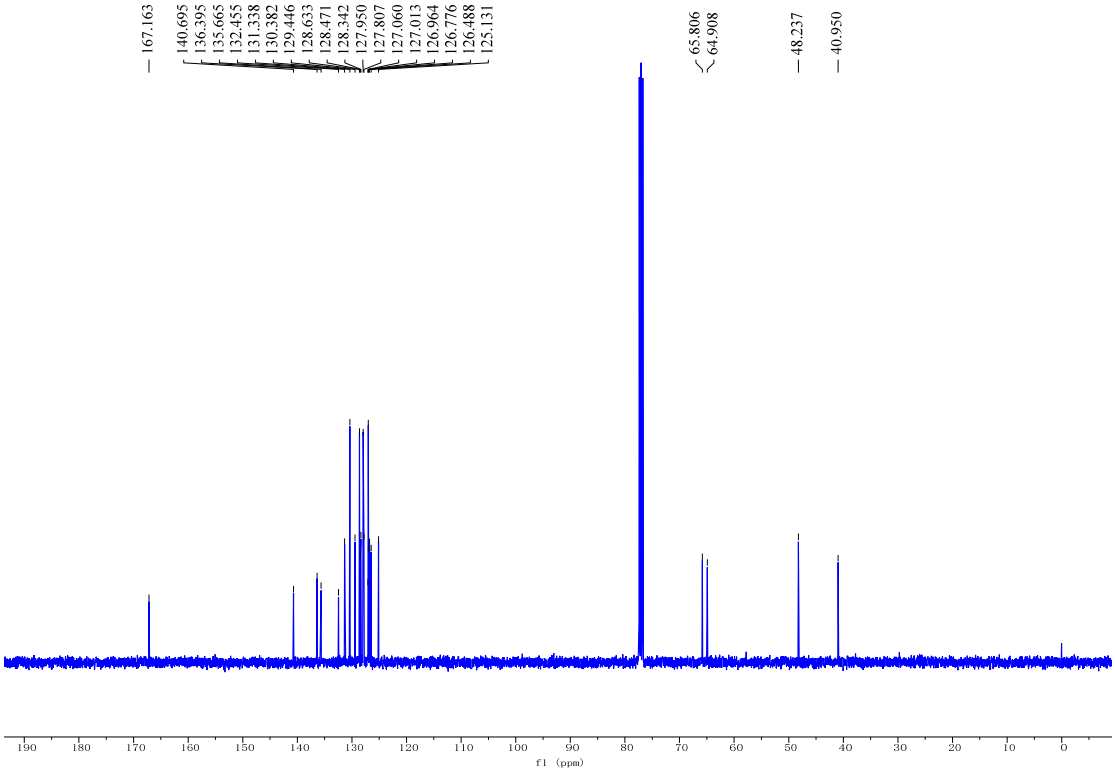
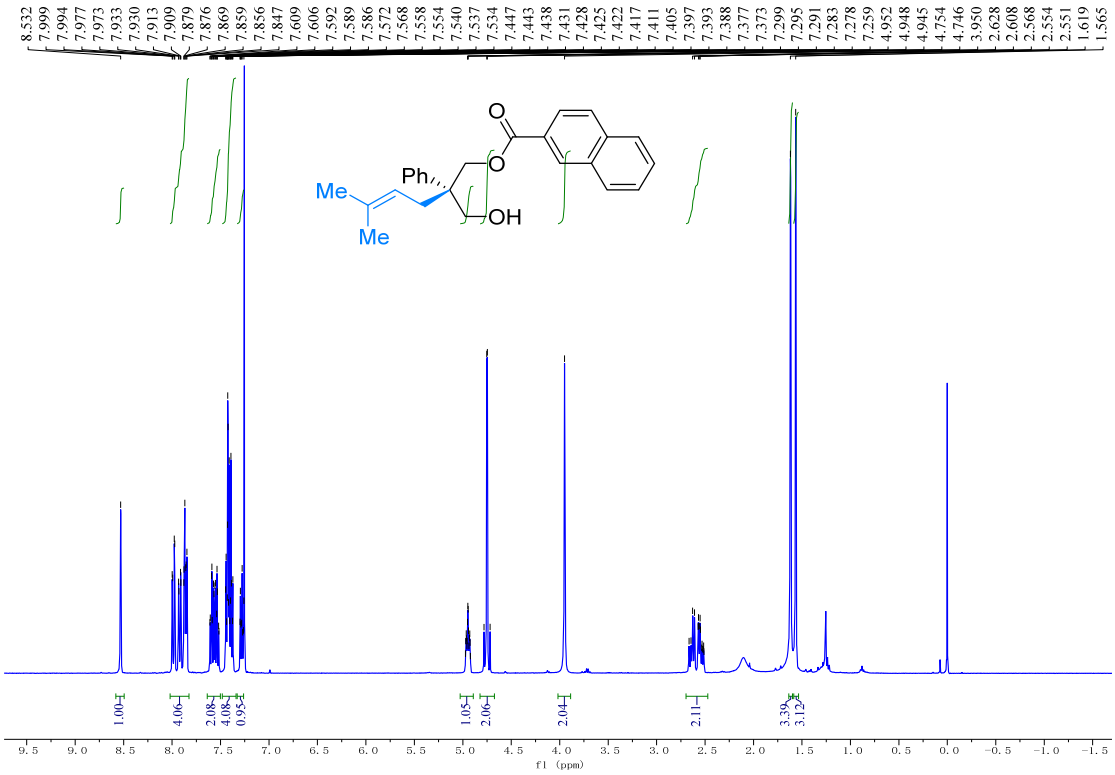
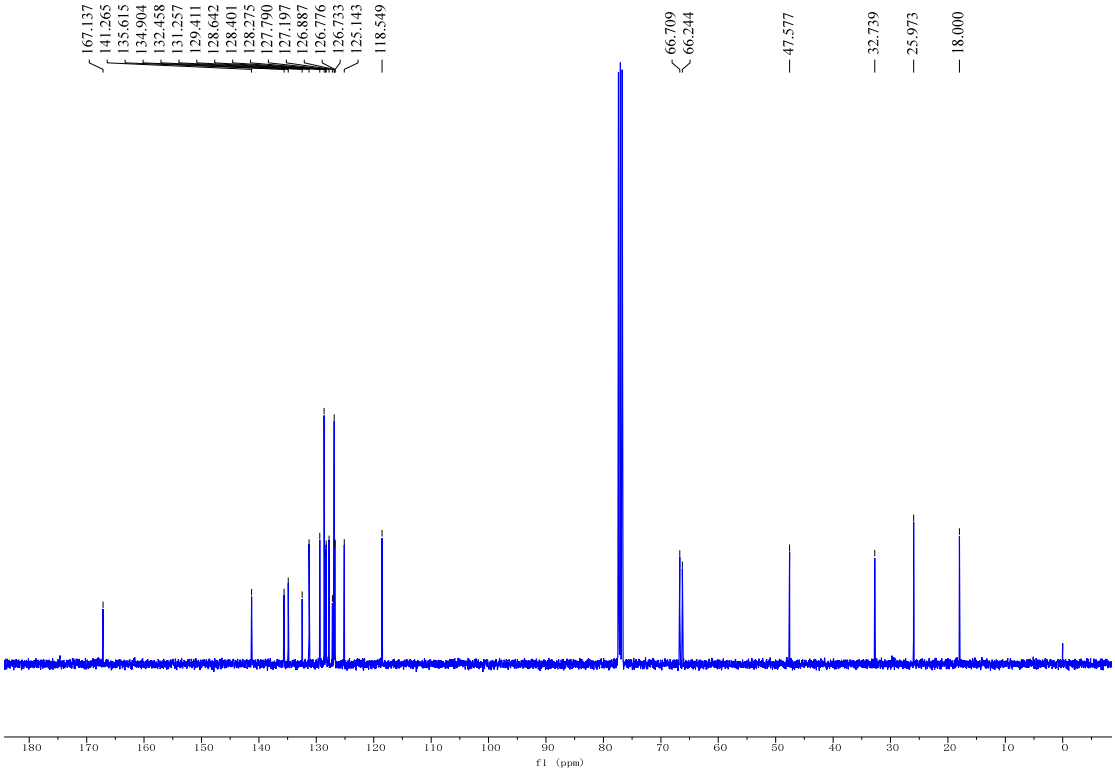
7.995
7.990
7.973
7.969
7.933
7.930
7.912
7.878
7.871
7.858
7.855
7.849
7.611
7.607
7.593
7.590
7.587
7.573
7.570
7.558
7.554
7.540
7.537
7.534
7.390
7.373
7.369
7.358
7.352
7.335
7.331
7.325
7.318
7.313
7.310
7.301
7.297
7.285
7.280
7.138
7.131
7.126
7.120
7.116
7.112
7.104
7.100
6.847
6.842
6.837
6.829
6.823
4.791
4.763
4.707
4.679
3.979
3.973
3.154
3.144
O
O
Ph
Bn
OH
1.00
4.06
2.09
5.06
3.00
1.99
2.04
2.02
2.05
f1 (ppm)

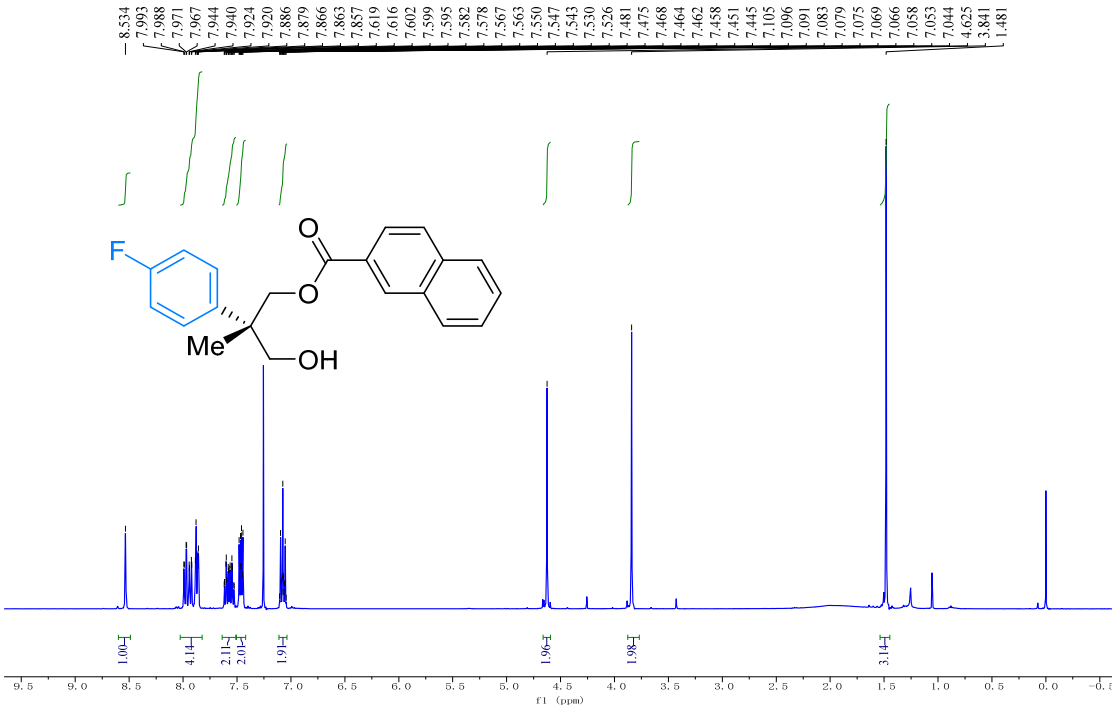

167.163
140.695
136.395
135.665
132.455
131.338
130.382
129.446
128.633
128.471
128.342
127.950
127.807
127.060
127.013
126.964
126.776
126.488
125.131
65.806
64.908
48.237
40.950
f1 (ppm)

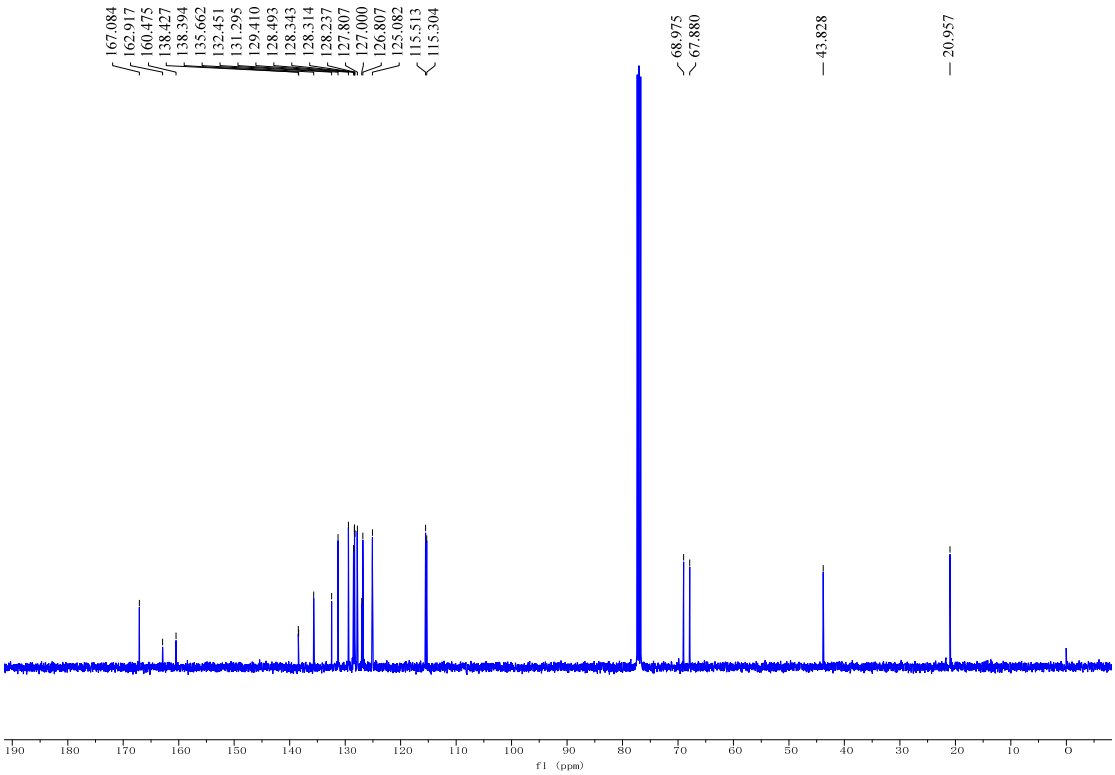
**29**

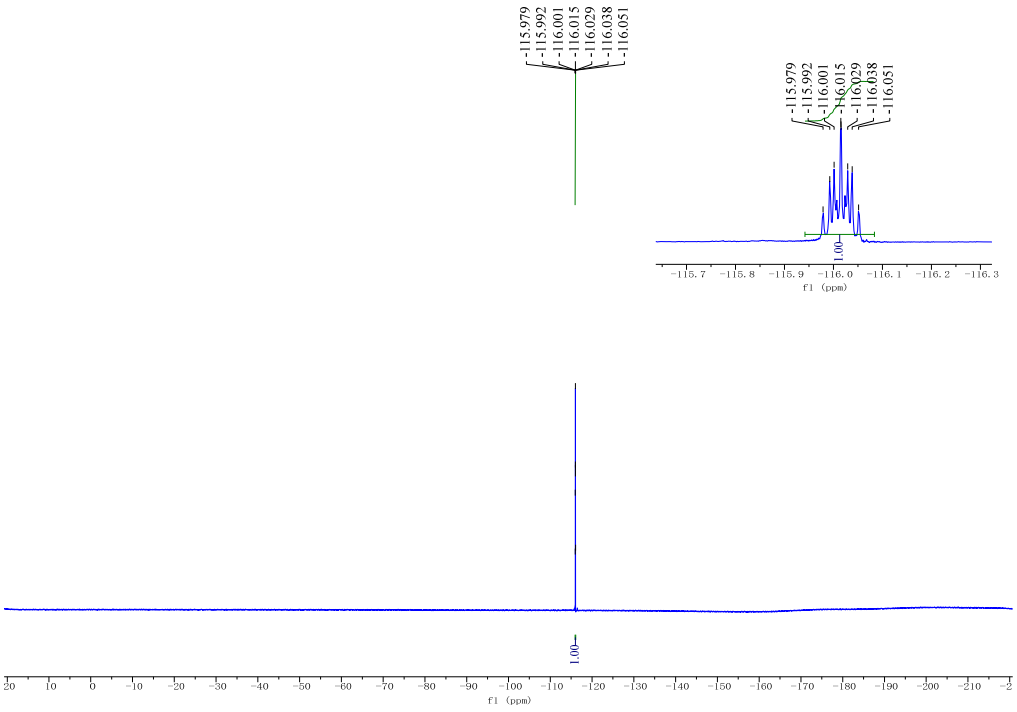

8.532
7.999
7.994
7.977
7.973
7.933
7.930
7.913
7.909
7.879
7.876
7.869
7.859
7.856
7.847
7.609
7.606
7.592
7.589
7.586
7.572
7.568
7.558
7.554
7.540
7.537
7.534
7.447
7.443
7.438
7.431
7.428
7.425
7.422
7.417
7.411
7.405
7.397
7.393
7.388
7.377
7.373
7.299
7.295
7.291
7.283
7.278
7.259
4.952
4.948
4.945
4.754
4.746
3.950
2.628
2.608
2.568
2.554
2.551
1.619
1.565
Me
Me
Ph
O
O
OH
1.00
4.06
2.08
4.08
0.95
1.05
2.06
2.04
2.11
3.39
3.12
f1 (ppm)


167.137
141.265
135.615
134.904
132.458
131.257
129.411
128.642
128.401
128.275
127.790
127.197
126.887
126.776
126.733
125.143
118.549
66.709
66.244
47.577
32.739
25.973
18.000
f1 (ppm)

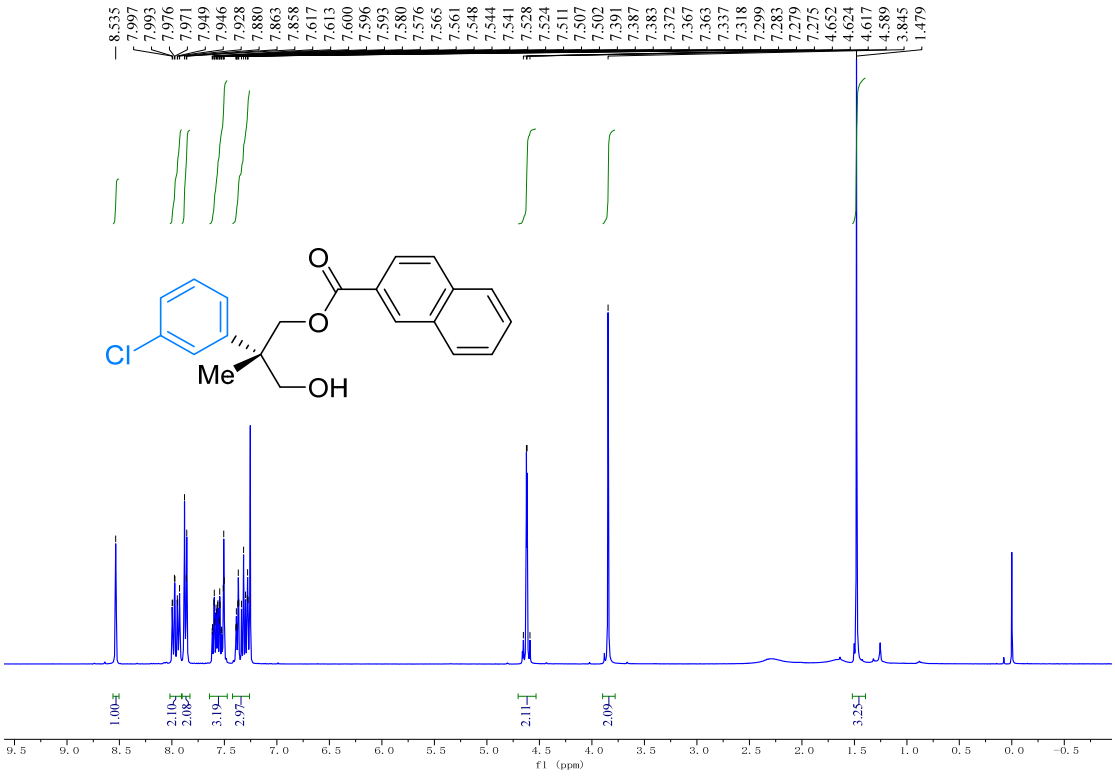
**30**

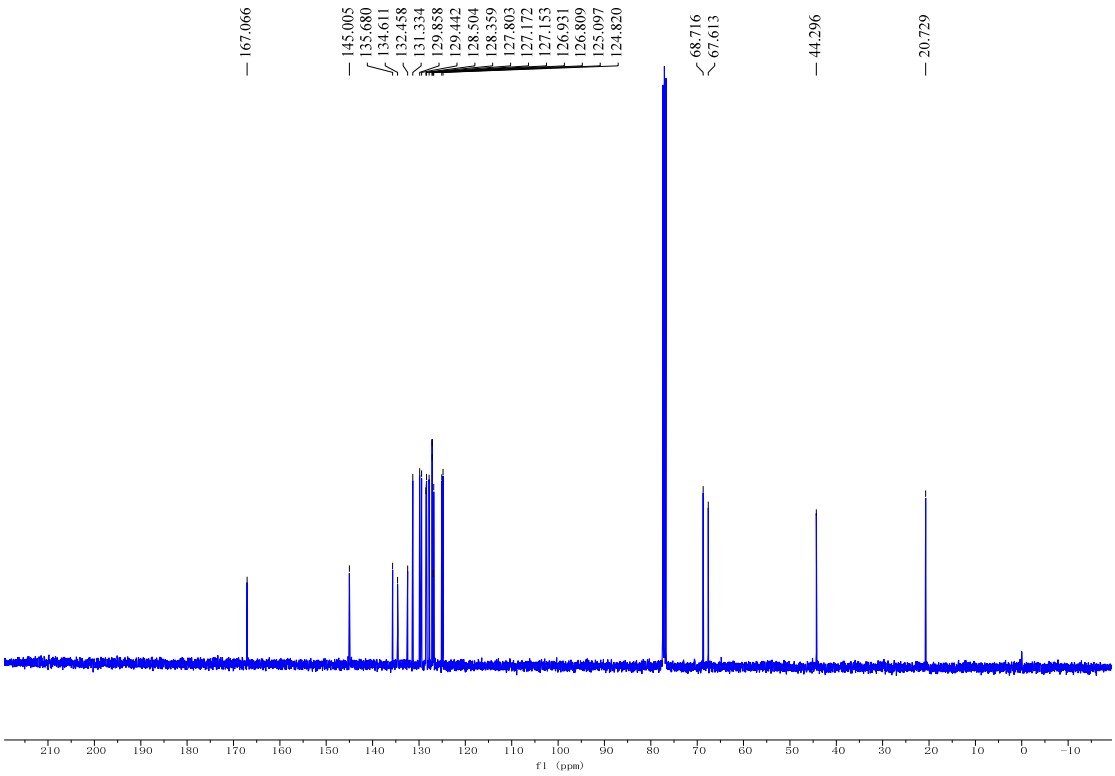

8.534
7.993
7.988
7.971
7.967
7.944
7.940
7.924
7.920
7.886
7.879
7.866
7.863
7.857
7.619
7.616
7.602
7.599
7.595
7.582
7.578
7.567
7.563
7.550
7.547
7.543
7.530
7.526
7.481
7.475
7.468
7.464
7.462
7.458
7.451
7.445
7.105
7.096
7.091
7.083
7.079
7.075
7.069
7.066
7.058
7.053
7.044
4.625
3.841
1.481
F
O
O
Me
OH
1.00
4.14
2.11
2.01
1.91
1.96
1.98
3.14
f1 (ppm)


167.084
162.917
160.475
138.427
138.394
135.662
132.451
131.295
129.410
128.493
128.343
128.314
128.237
127.807
127.000
126.807
125.082
115.513
115.304
68.975
67.880
43.828
20.957
f1 (ppm)

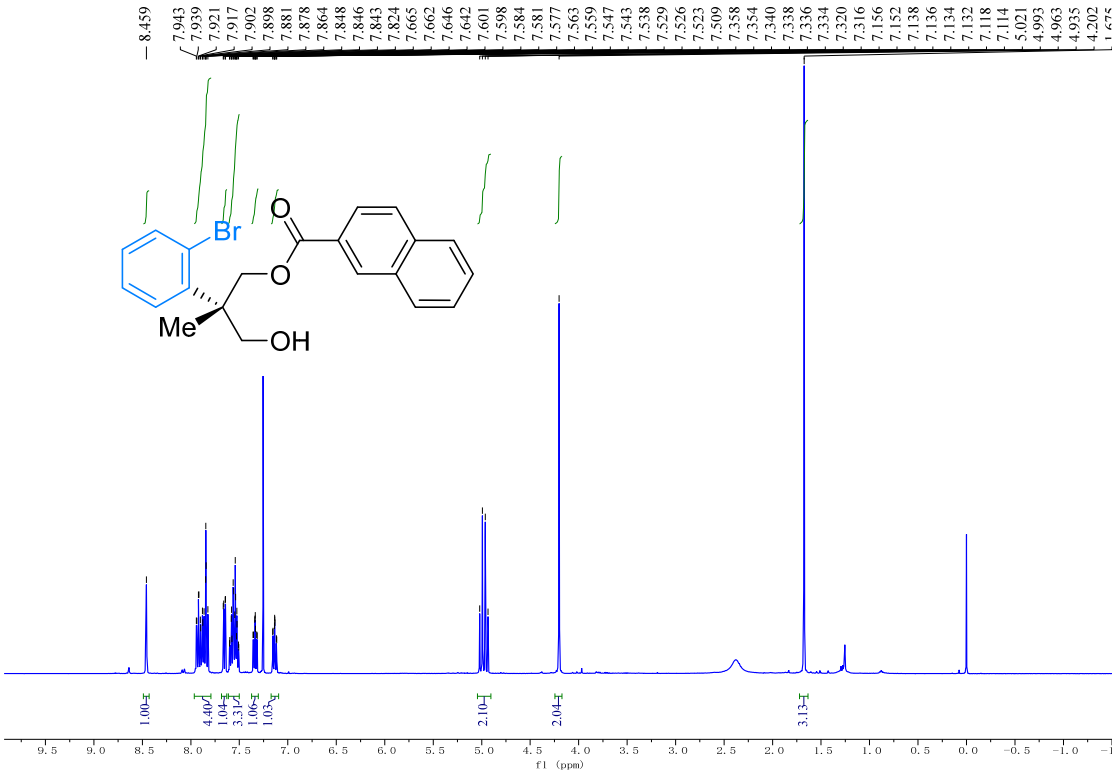

-115.979
-115.992
-116.001
-116.015
-116.029
-116.038
-116.051
1.00
-115.7 -115.8 -115.9 -116.0 -116.1 -116.2 -116.3
f1 (ppm)
1.00
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

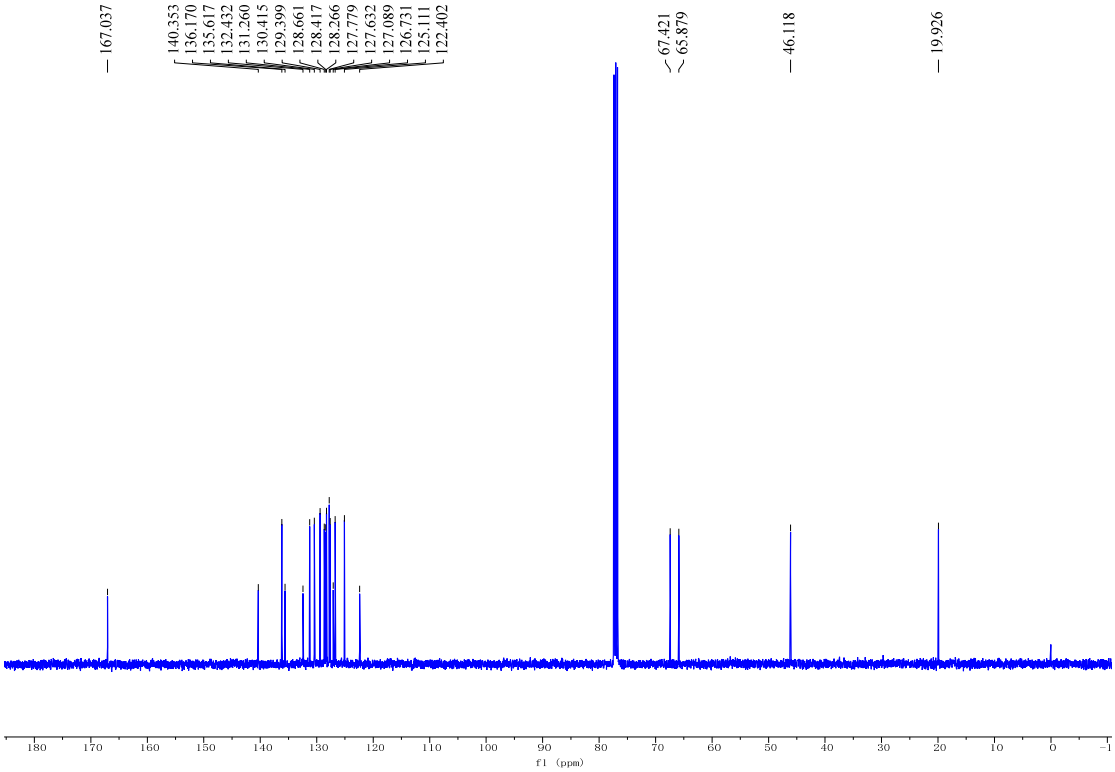
**31**


8.535
7.997
7.993
7.976
7.971
7.949
7.946
7.928
7.880
7.863
7.858
7.617
7.613
7.600
7.596
7.593
7.580
7.576
7.565
7.561
7.548
7.544
7.541
7.528
7.524
7.511
7.507
7.502
7.391
7.387
7.383
7.372
7.367
7.363
7.337
7.318
7.299
7.283
7.279
7.275
4.652
4.624
4.617
4.589
3.845
1.479
O
O
Cl
Me
OH
1.00
2.10
2.08
3.19
2.97
2.11
2.09
3.25
f1 (ppm)

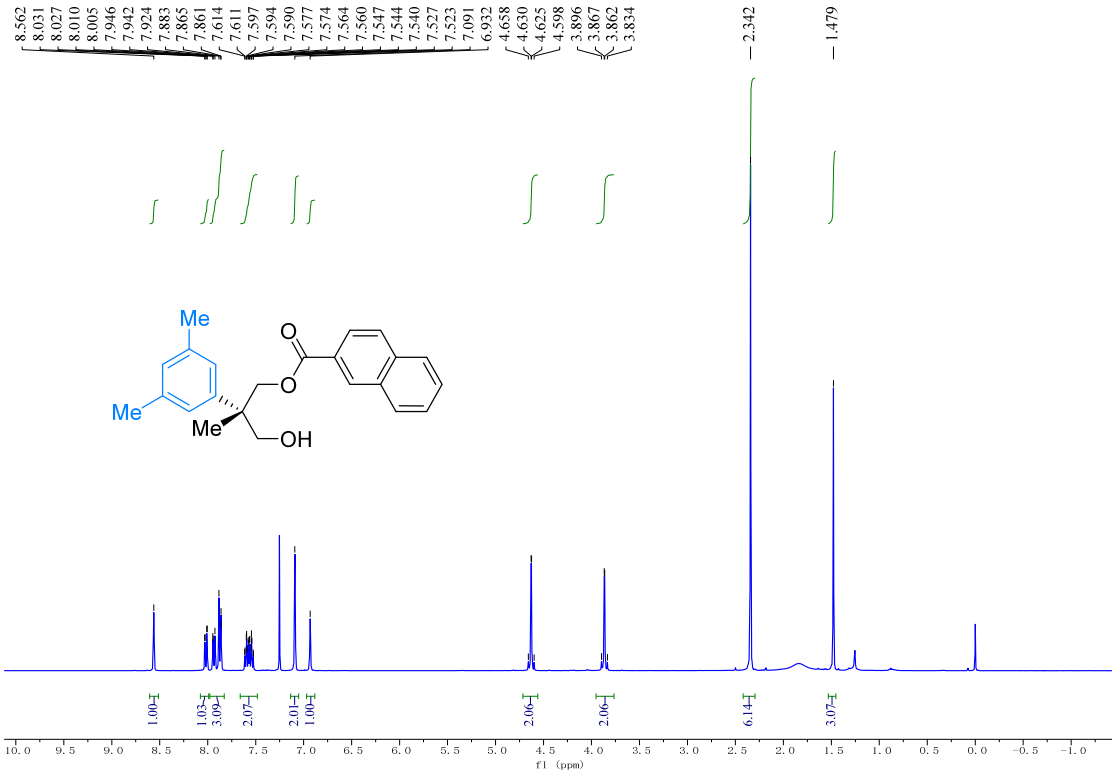

167.066
145.005
135.680
134.611
132.458
131.334
129.858
129.442
128.504
128.359
127.803
127.172
127.153
126.931
126.809
125.097
124.820
68.716
67.613
44.296
20.729
f1 (ppm)

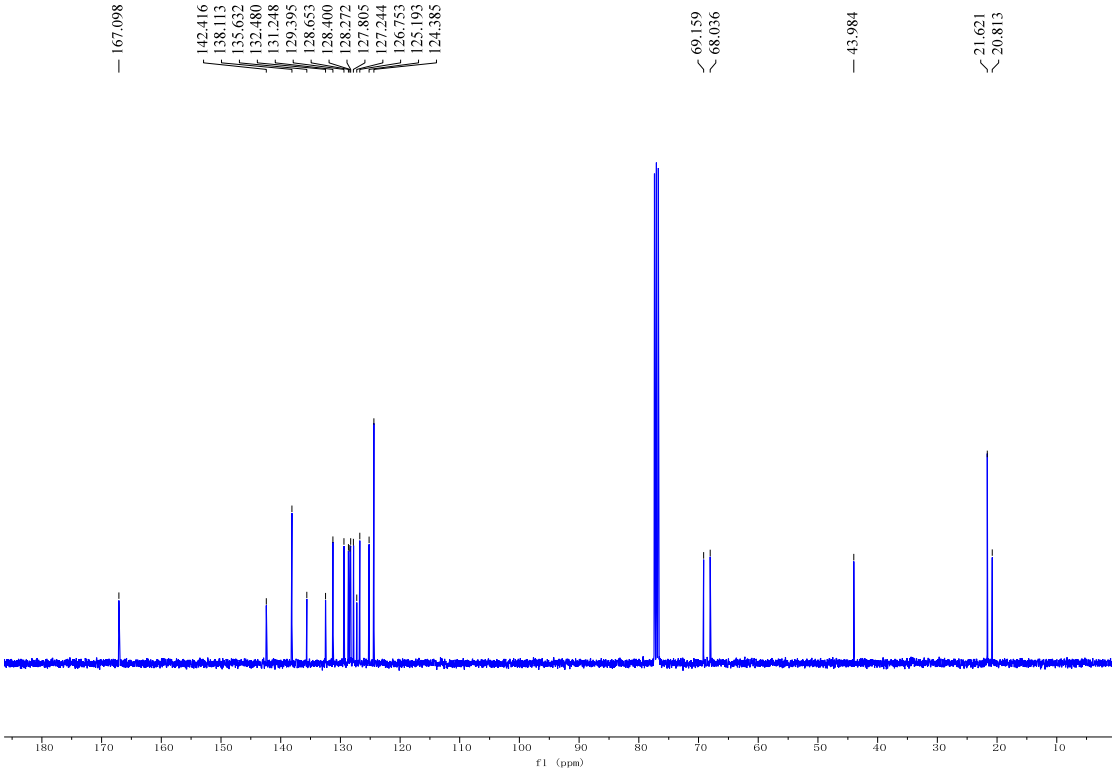
**32**


8.459
7.943
7.939
7.921
7.917
7.902
7.898
7.881
7.878
7.864
7.848
7.846
7.843
7.824
7.665
7.662
7.646
7.642
7.601
7.598
7.584
7.581
7.577
7.563
7.559
7.547
7.543
7.538
7.529
7.526
7.523
7.509
7.358
7.354
7.340
7.338
7.336
7.334
7.320
7.316
7.156
7.152
7.138
7.136
7.134
7.132
7.118
7.114
5.021
4.993
4.963
4.935
4.202
Br
O
O
Me
OH
1.00
4.40
1.04
3.31
1.06
1.03
2.10
2.04
3.13
f1 (ppm)

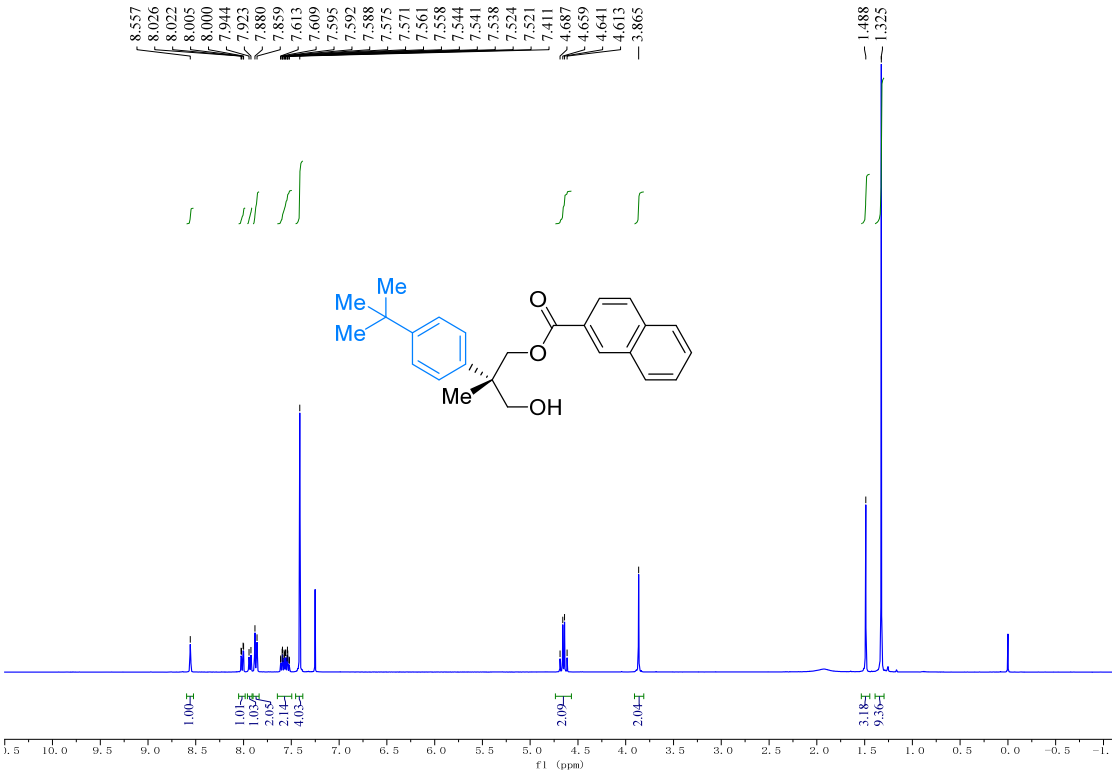

167.037
140.353
136.170
135.617
132.432
131.260
130.415
129.399
128.661
128.417
128.266
127.779
127.632
127.089
126.731
125.111
122.402
67.421
65.879
46.118
19.926
f1 (ppm)

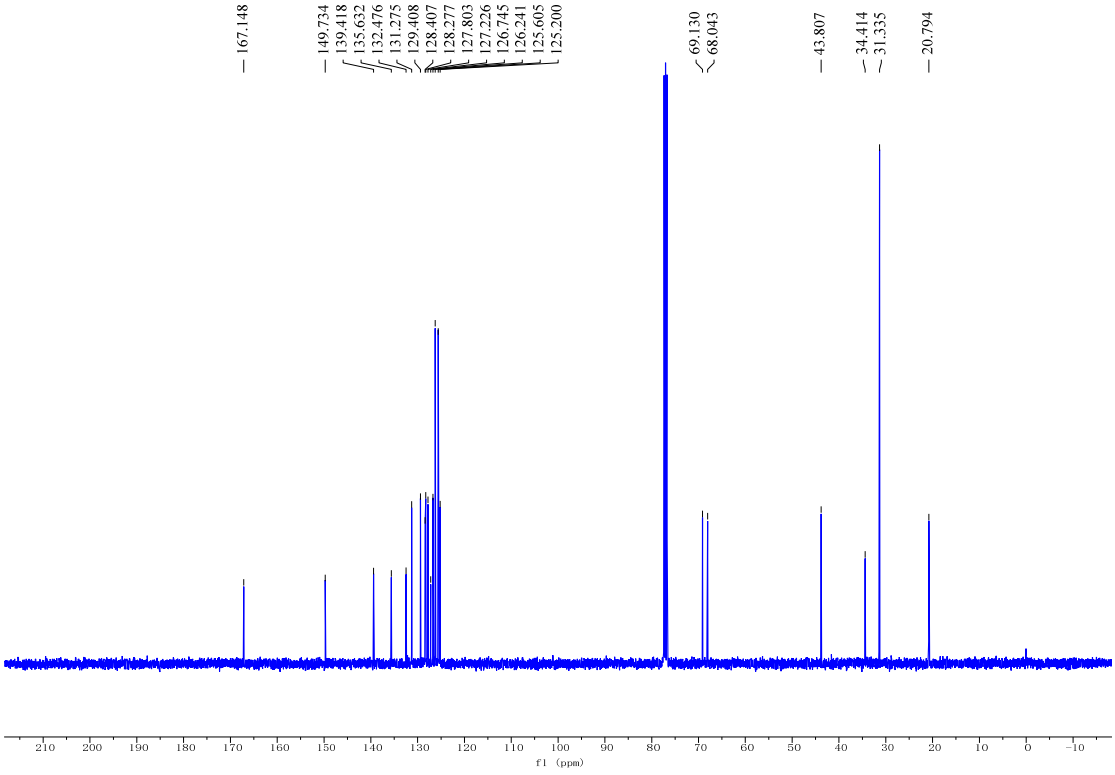
**33**


8.562
8.031
8.027
8.010
8.005
7.946
7.942
7.924
7.883
7.865
7.861
7.614
7.611
7.597
7.594
7.590
7.577
7.574
7.564
7.560
7.547
7.544
7.540
7.527
7.523
7.091
6.932
4.658
4.630
4.625
4.598
3.896
3.867
3.862
3.834
2.342
1.479
Me
Me
Me
O
O
OH
1.00
1.03
3.09
2.07
2.01
1.00
2.06
2.06
6.14
3.07
f1 (ppm)

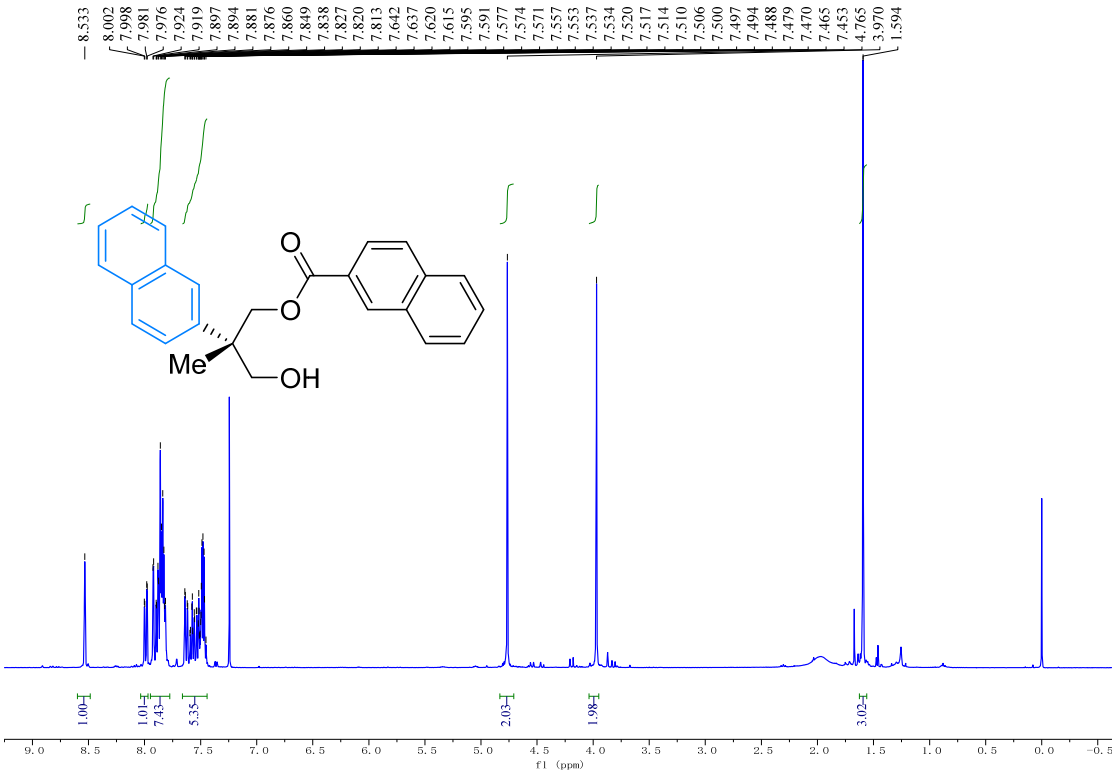

167.098
142.416
138.113
135.632
132.480
131.248
129.395
128.653
128.400
128.272
127.805
127.244
126.753
125.193
124.385
69.159
68.036
43.984
21.621
20.813
f1 (ppm)

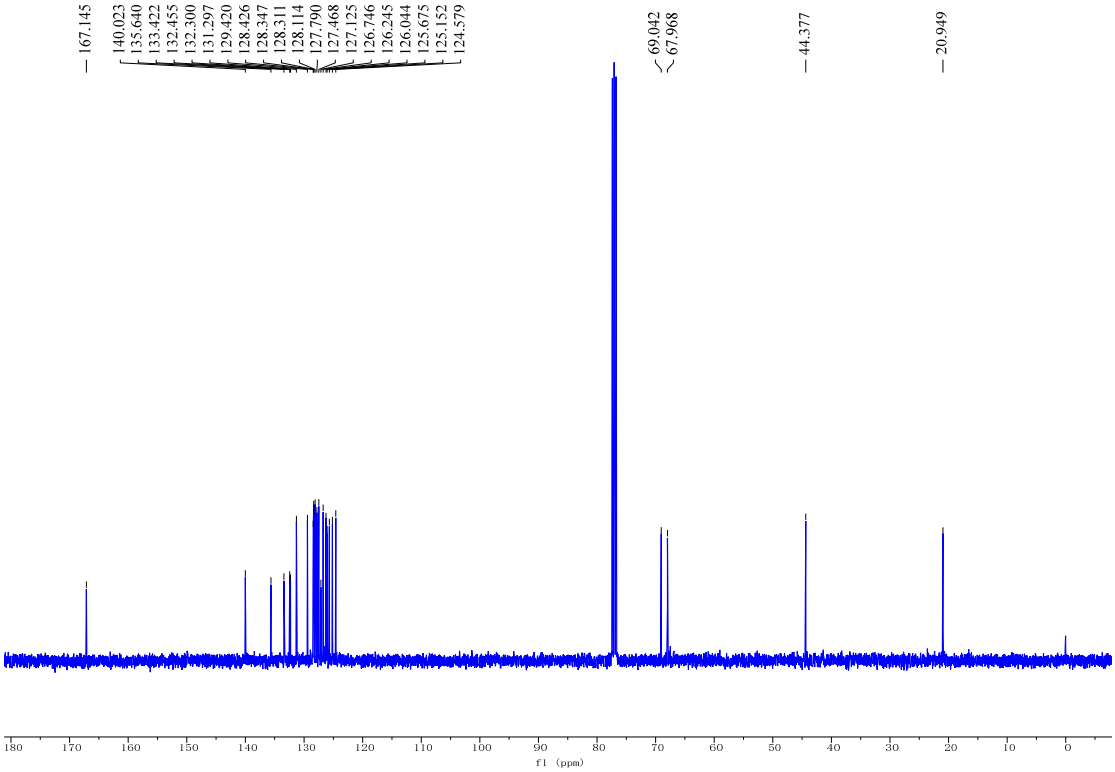
**34**


8.557
8.026
8.022
8.005
8.000
7.944
7.923
7.880
7.859
7.613
7.609
7.595
7.592
7.588
7.575
7.571
7.561
7.558
7.544
7.541
7.538
7.524
7.521
7.411
4.687
4.659
4.641
4.613
3.865
1.488
1.325
Me
Me
Me
O
O
OH
1.00
1.01
1.03
2.05
2.14
4.03
2.09
2.04
3.18
9.36
f1 (ppm)

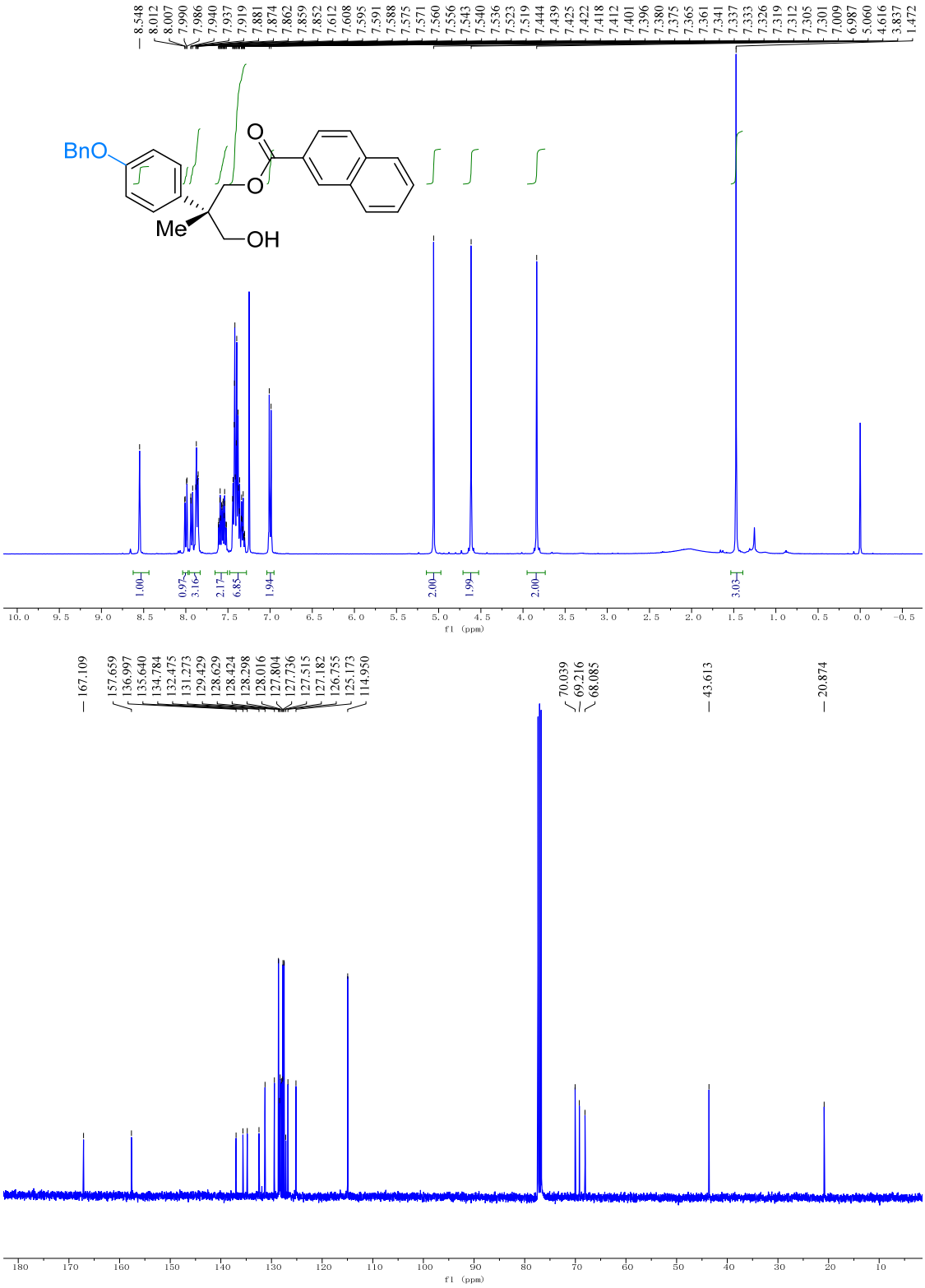

167.148
149.734
139.418
135.632
132.476
131.275
129.408
128.407
128.277
127.803
127.226
126.745
126.241
125.605
125.200
69.130
68.043
43.807
34.414
31.335
20.794
f1 (ppm)

**35**

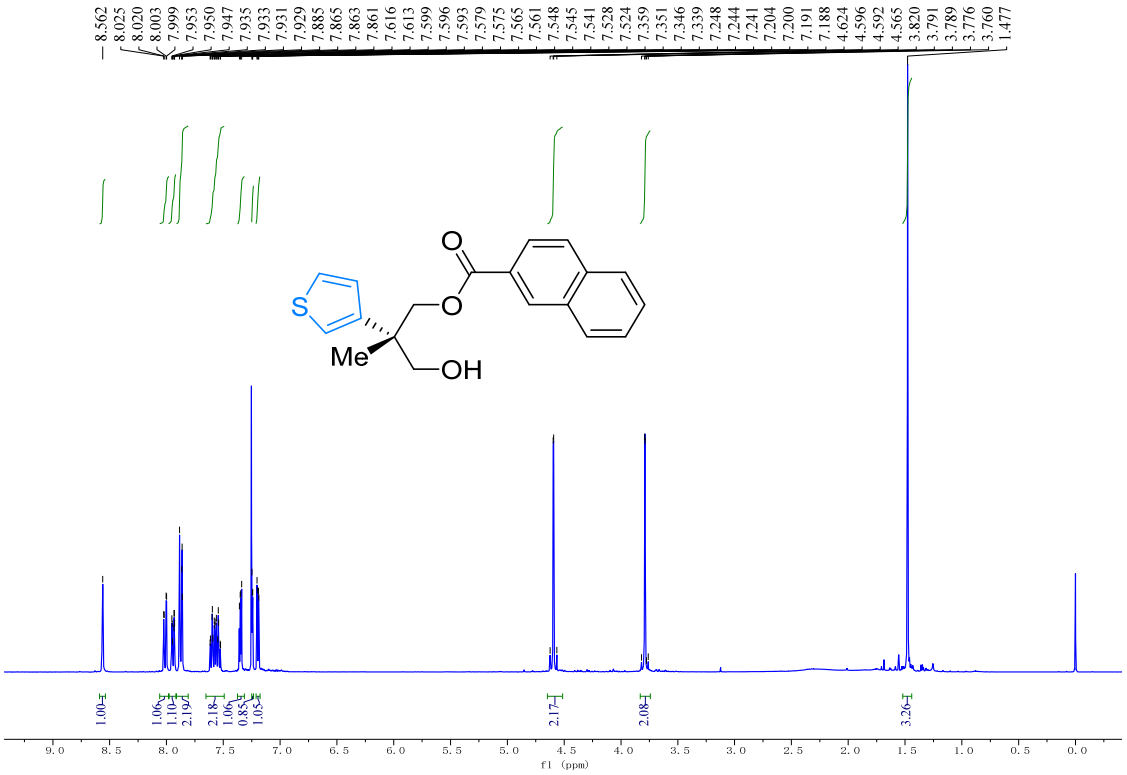

8.533
8.002
7.998
7.981
7.976
7.924
7.919
7.897
7.894
7.881
7.876
7.860
7.849
7.838
7.827
7.820
7.813
7.642
7.637
7.620
7.615
7.595
7.591
7.577
7.574
7.571
7.557
7.553
7.537
7.534
7.520
7.517
7.514
7.510
7.506
7.500
7.497
7.494
7.488
7.479
7.470
7.465
7.453
4.765
3.970
1.594
O
O
Me
OH
1.00
1.01
7.43
5.35
2.03
1.98
3.02
f1 (ppm)


167.145
140.023
135.640
133.422
132.455
132.300
131.297
129.420
128.426
128.347
128.311
128.114
127.790
127.468
127.125
126.746
126.245
126.044
125.675
125.152
124.579
69.042
67.968
44.377
20.949
f1 (ppm)

**36**


8.548
8.012
8.007
7.990
7.986
7.940
7.937
7.919
7.881
7.874
7.862
7.859
7.852
7.612
7.608
7.595
7.591
7.588
7.575
7.571
7.560
7.556
7.543
7.540
7.536
7.523
7.519
7.444
7.439
7.425
7.422
7.418
7.412
7.401
7.396
7.380
7.375
7.365
7.361
7.341
7.337
7.333
7.326
7.319
7.312
7.305
7.301
7.009
6.987
5.060
4.616
3.837
1.472
BnO
O
O
Me
OH
1.00
0.97
3.16
2.17
6.85
1.94
2.00
1.99
2.00
3.03
f1 (ppm)
167.109
157.659
136.997
135.640
134.784
132.475
131.273
129.429
128.629
128.424
128.298
128.016
127.804
127.736
127.515
127.182
126.755
125.173
114.950
70.039
69.216
68.085
43.613
20.874
f1 (ppm)

**37**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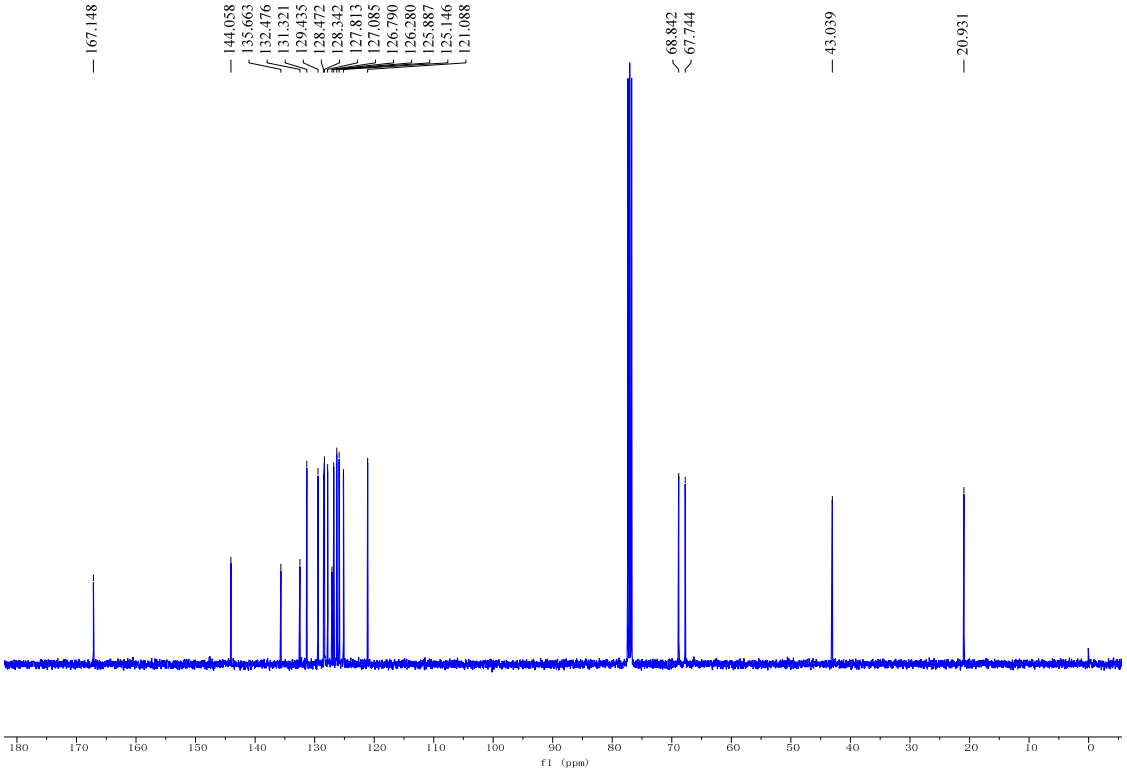
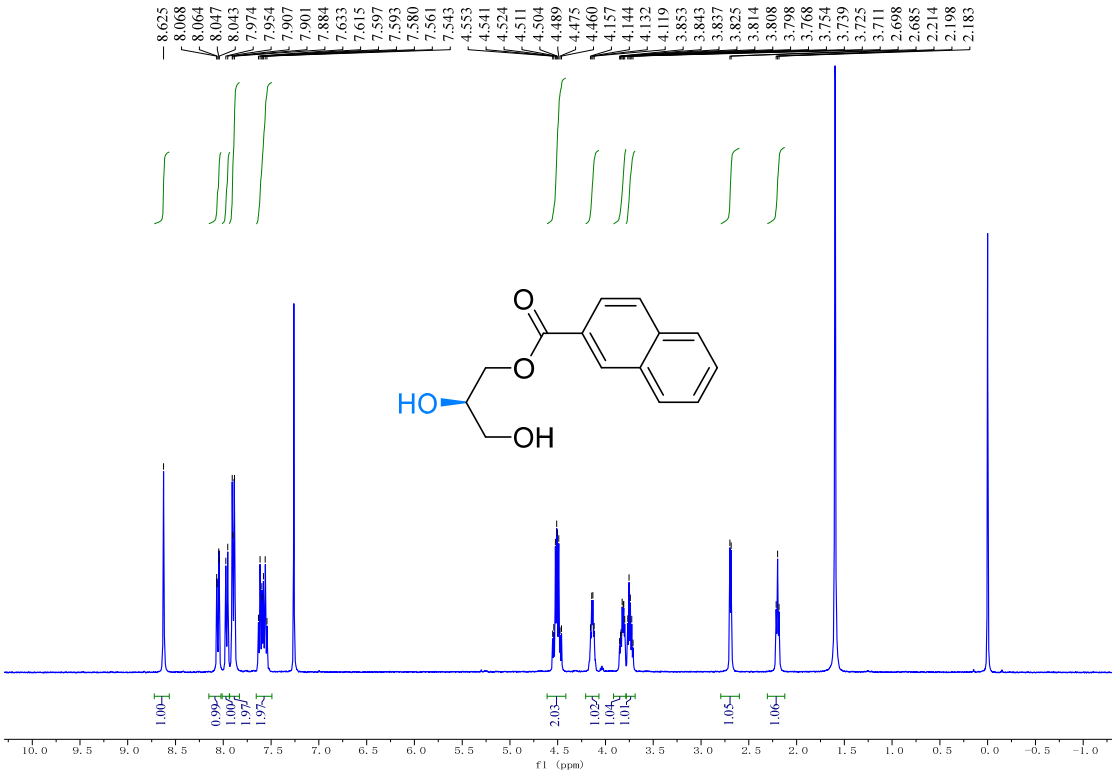
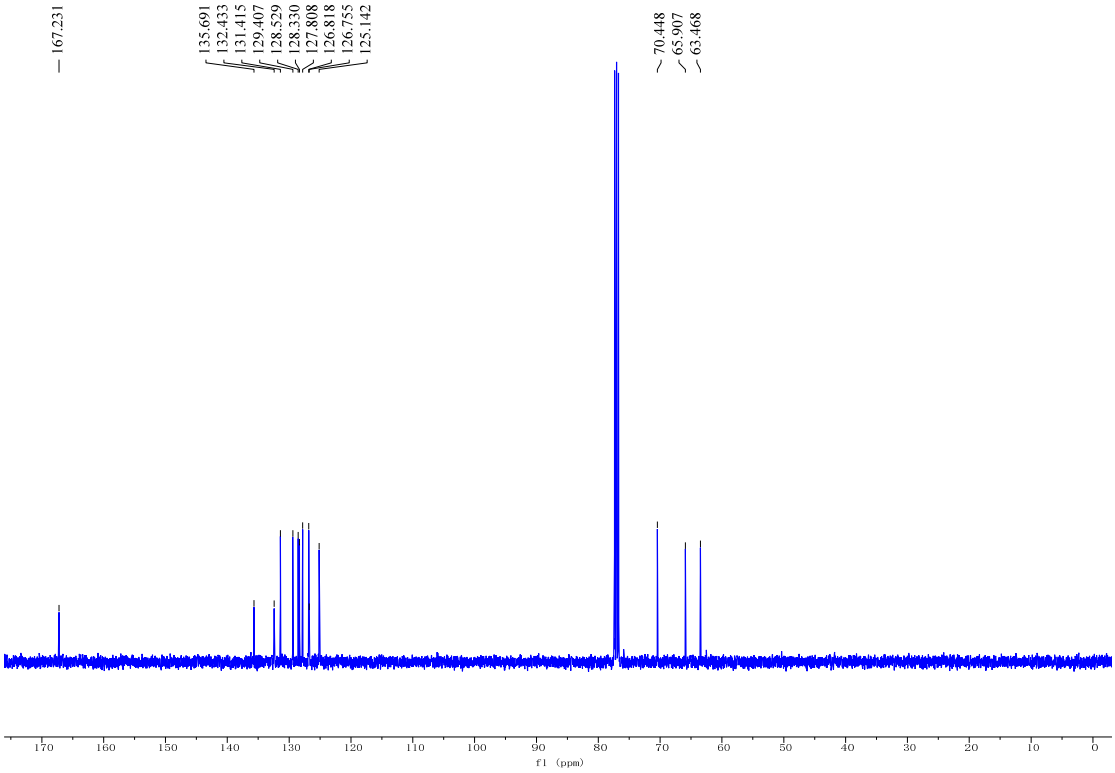
8.025
8.020
8.003
7.999
7.953
7.950
7.947
7.935
7.933
7.931
7.929
7.885
7.865
7.863
7.861
7.616
7.613
7.599
7.596
7.593
7.579
7.575
7.565
7.561
7.548
7.545
7.541
7.528
7.524
7.359
7.351
7.346
7.339
7.248
7.244
7.241
7.204
7.200
7.191
7.188
4.624
4.596
4.592
4.565
3.820
3.791
3.789
3.776
3.760
1.477
O
O
S
Me
OH
1.00
1.06
1.10
2.19
2.18
1.06
0.85
1.05
2.17
2.08
3.26
f1 (ppm)

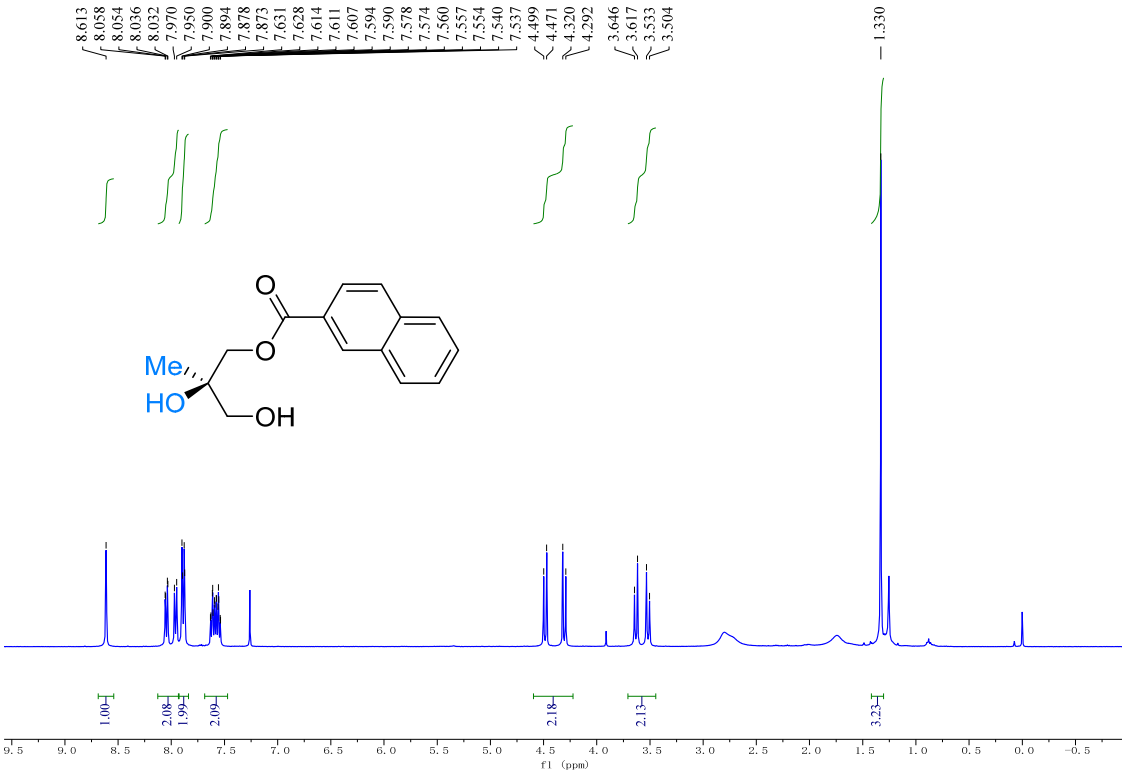

167.148
144.058
135.663
132.476
131.321
129.435
128.472
128.342
127.813
127.085
126.790
126.280
125.887
125.146
121.088
68.842
67.744
43.039
20.931
f1 (ppm)

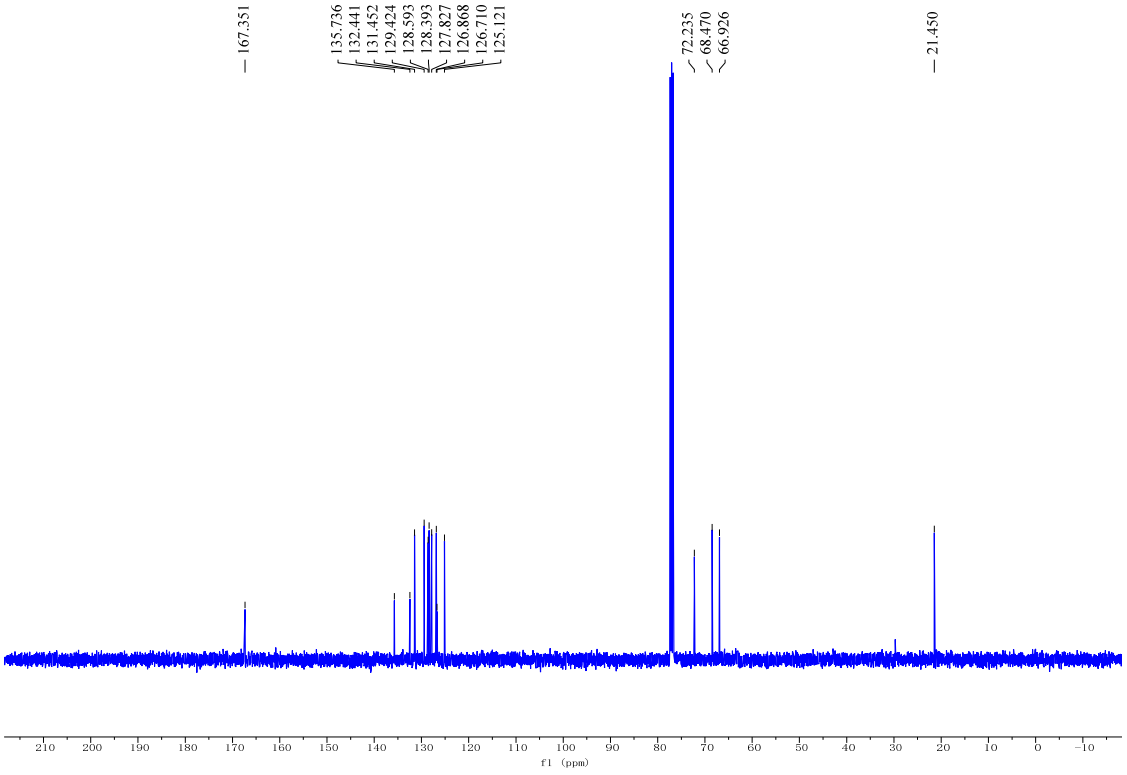
**38**


8.625
8.068
8.064
8.047
8.043
7.974
7.954
7.907
7.901
7.884
7.633
7.615
7.597
7.593
7.580
7.561
7.543
4.553
4.541
4.524
4.511
4.504
4.489
4.475
4.460
4.157
4.144
4.132
4.119
3.853
3.843
3.837
3.825
3.814
3.808
3.798
3.768
3.754
3.739
3.725
3.711
2.698
2.685
2.214
2.198
2.183
O
O
HO
OH
1.00
0.99
1.00
1.97
1.97
2.03
1.02
1.04
1.01
1.05
1.06
f1 (ppm)

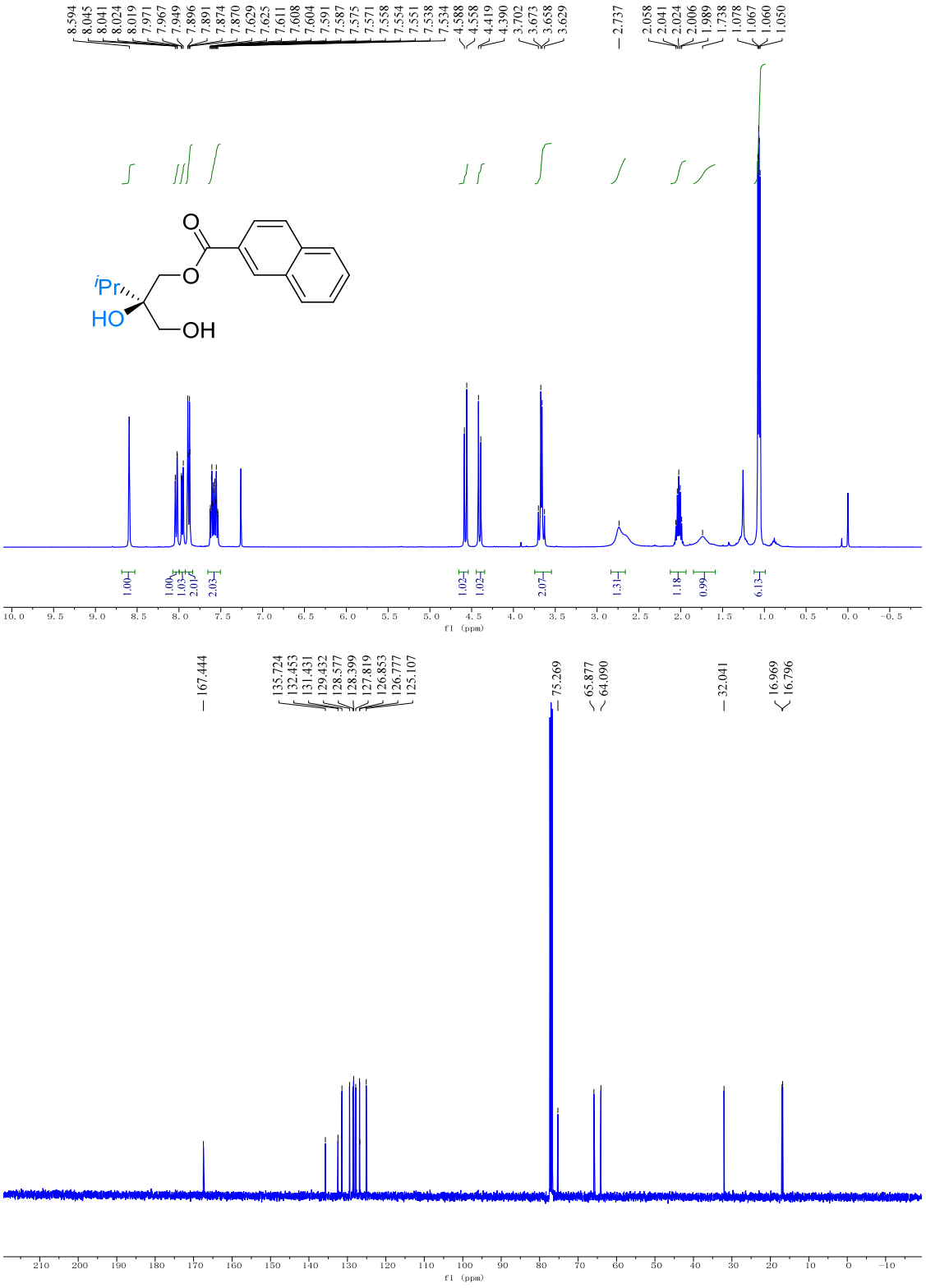

167.231
135.691
132.433
131.415
129.407
128.529
128.330
127.808
126.818
126.755
125.142
70.448
65.907
63.468
f1 (ppm)

**39**

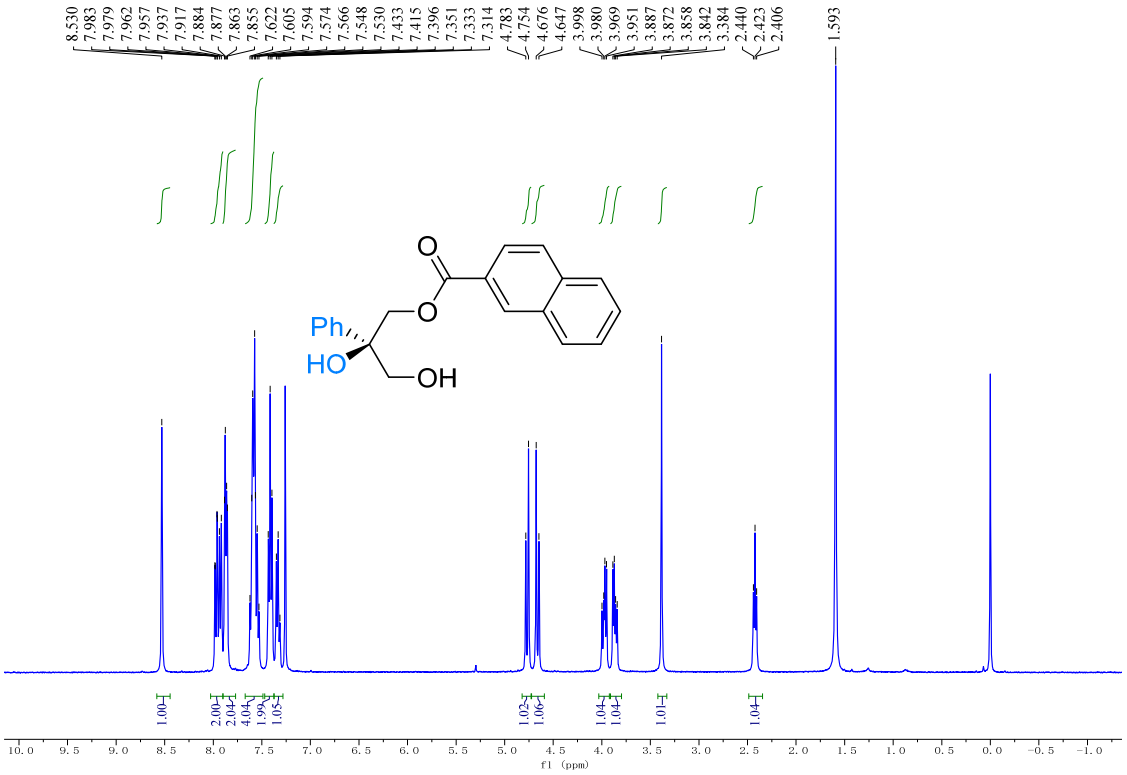

8.613
8.058
8.054
8.036
8.032
7.970
7.950
7.900
7.894
7.878
7.873
7.631
7.628
7.614
7.611
7.607
7.594
7.590
7.578
7.574
7.560
7.557
7.554
7.540
7.537
4.499
4.471
4.320
4.292
3.646
3.617
3.533
3.504
1.330
O
O
Me
HO
OH
1.00
2.08
1.99
2.09
2.18
2.13
3.23
f1 (ppm)

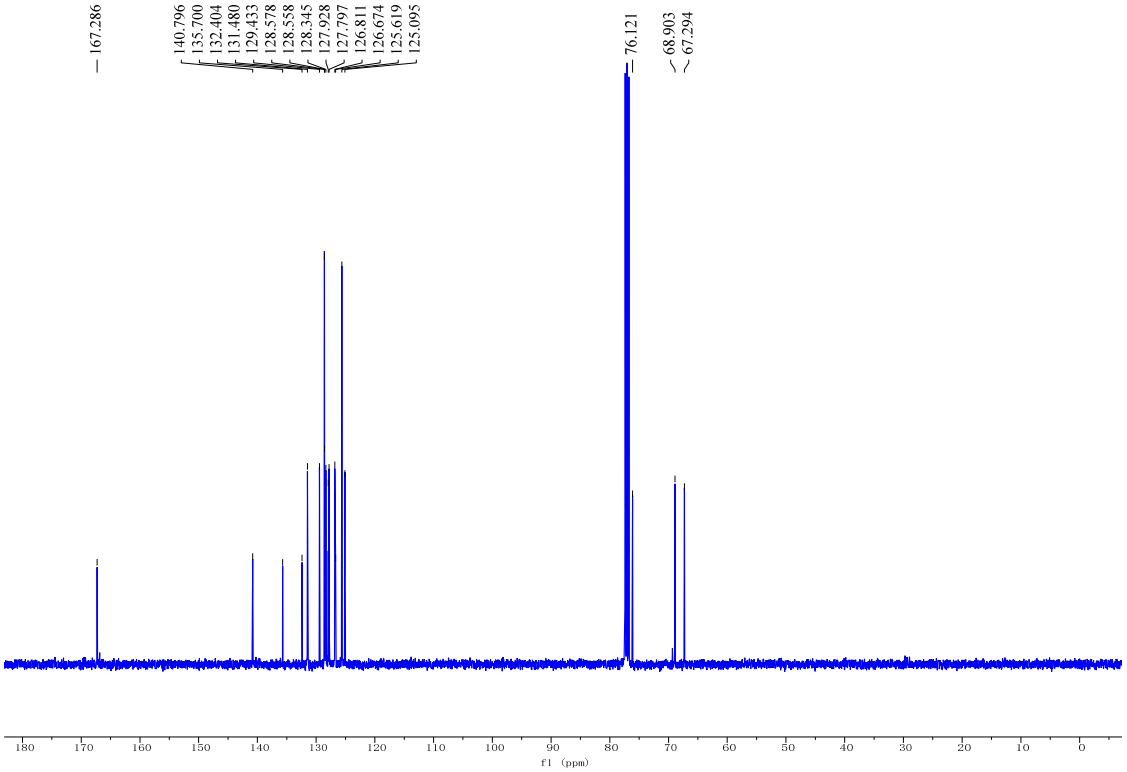

167.351
135.736
132.441
131.452
129.424
128.593
128.393
127.827
126.868
126.710
125.121
72.235
68.470
66.926
21.450
f1 (ppm)

**40**

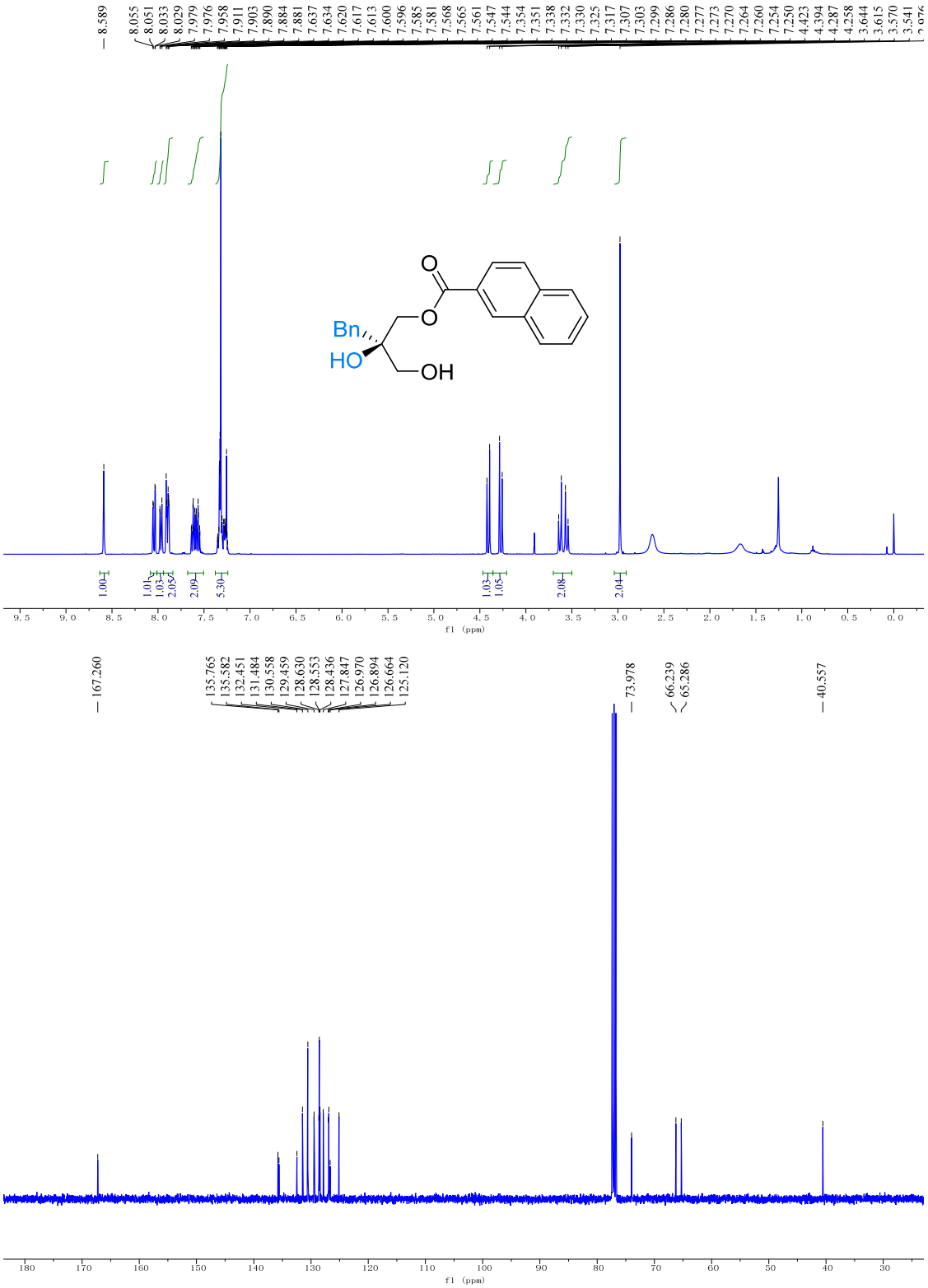

8.594
8.045
8.041
8.024
8.019
7.971
7.967
7.949
7.896
7.891
7.874
7.870
7.629
7.625
7.611
7.608
7.604
7.591
7.587
7.575
7.571
7.558
7.554
7.551
7.538
7.534
4.588
4.558
4.419
4.390
3.702
3.673
3.658
3.629
2.737
2.058
2.041
2.024
2.006
1.989
1.738
1.078
1.067
1.060
1.050
O
O
iPr
HO
OH
1.00
1.00
1.03
2.01
2.03
1.02
1.02
2.07
1.31
1.18
0.99
6.13
f1 (ppm)
167.444
135.724
132.453
131.431
129.432
128.577
128.399
127.819
126.853
126.777
125.107
75.269
65.877
64.090
32.041
16.969
16.796
f1 (ppm)

**41**


8.530
7.983
7.979
7.962
7.957
7.937
7.917
7.884
7.877
7.863
7.855
7.622
7.605
7.594
7.574
7.566
7.548
7.530
7.433
7.415
7.396
7.351
7.333
7.314
4.783
4.754
4.676
4.647
3.998
3.980
3.969
3.951
3.887
3.872
3.858
3.842
3.384
2.440
2.423
2.406
1.593
O
O
Ph
HO
OH
1.00
2.00
2.04
4.04
1.99
1.05
1.02
1.06
1.04
1.04
1.01
1.04
f1 (ppm)


167.286
140.796
135.700
132.404
131.480
129.433
128.578
128.558
128.345
127.928
127.797
126.811
126.674
125.619
125.095
76.121
68.903
67.294
f1 (ppm)

**42**


8.589
8.055
8.051
8.033
8.029
7.979
7.976
7.958
7.911
7.903
7.890
7.884
7.881
7.637
7.634
7.620
7.617
7.613
7.600
7.596
7.585
7.581
7.568
7.565
7.561
7.547
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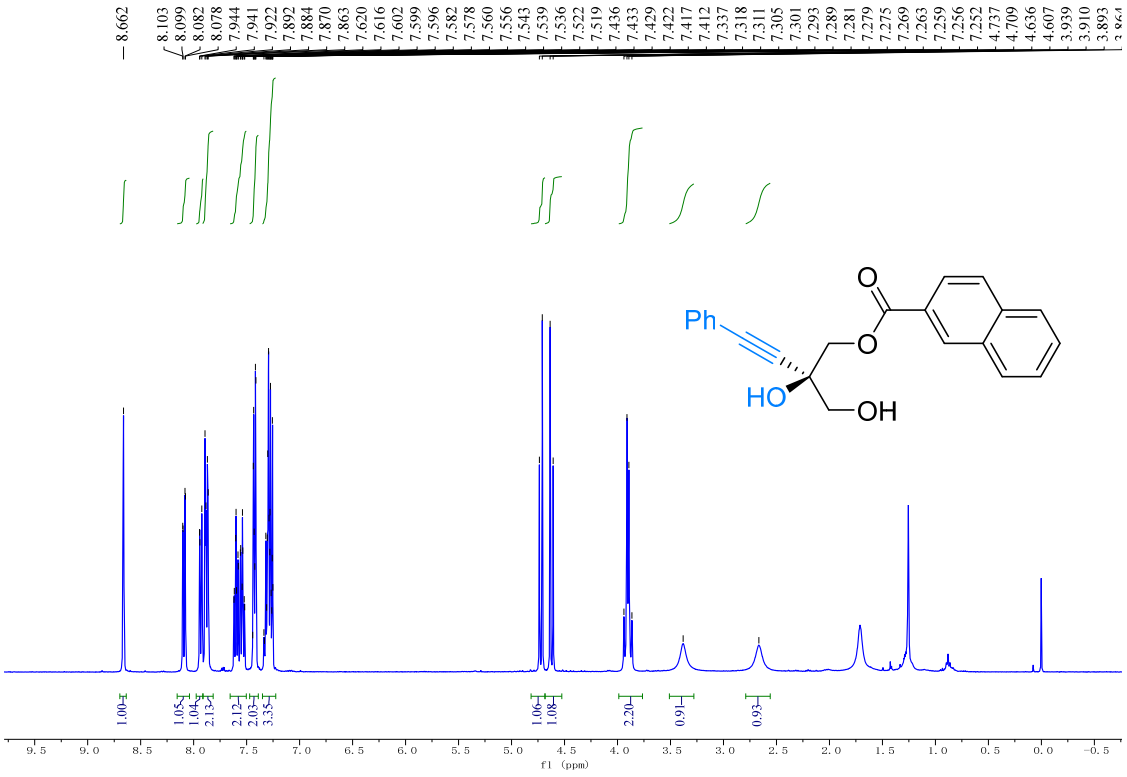
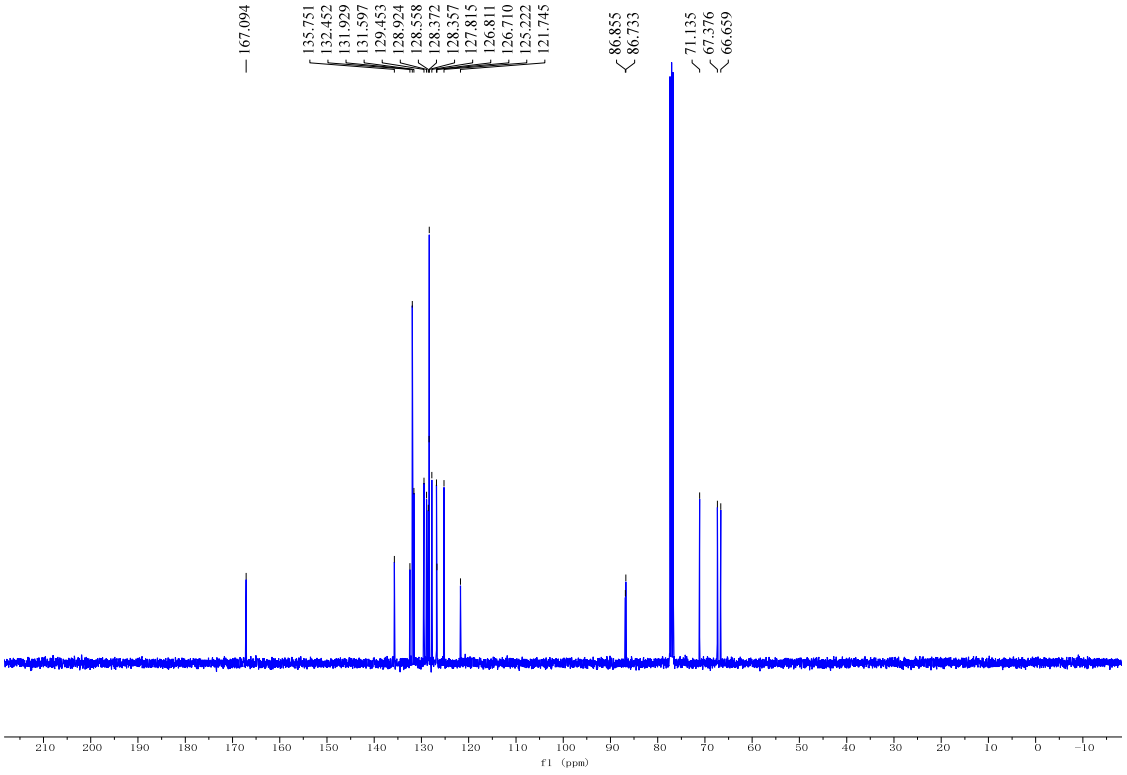
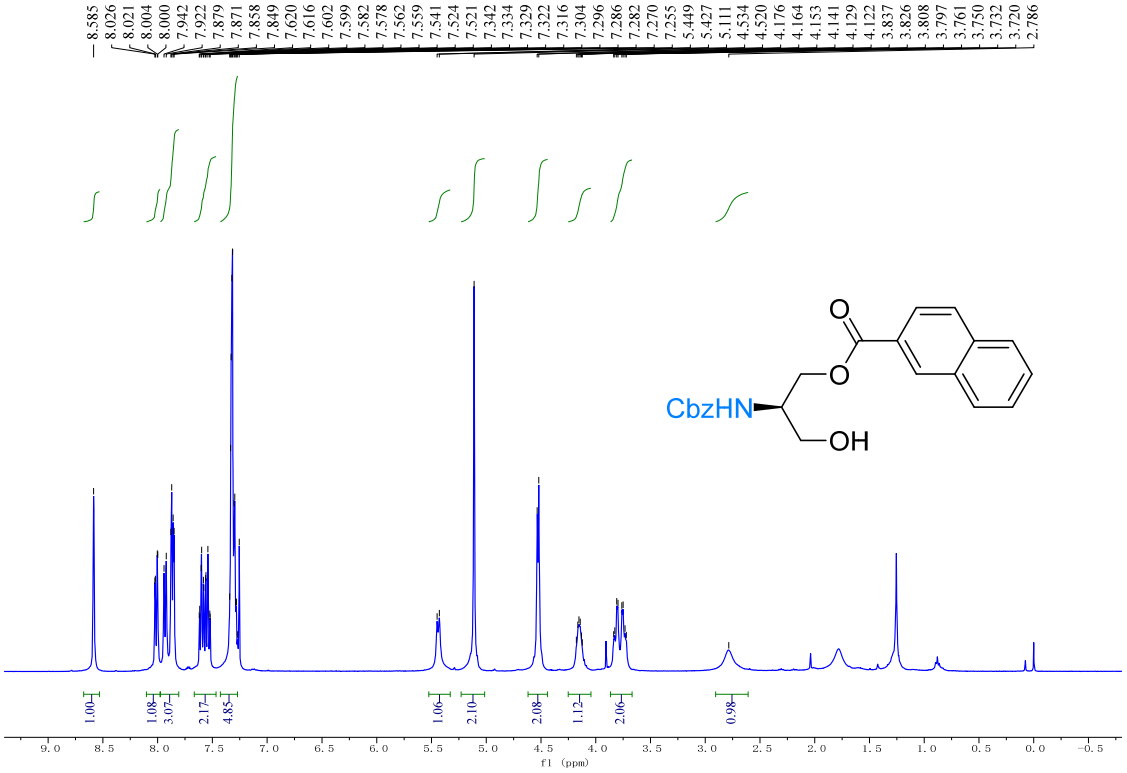
7.354
7.351
7.338
7.332
7.330
7.325
7.317
7.307
7.303
7.299
7.286
7.280
7.277
7.273
7.270
7.264
7.260
7.254
7.250
4.423
4.394
4.287
4.258
3.644
3.615
3.570
3.541
O
O
Bn
HO
OH
1.00
1.01
1.03
2.05
2.09
5.30
1.03
1.05
2.08
2.04
f1 (ppm)
167.260
135.765
135.582
132.451
131.484
130.558
129.459
128.630
128.553
128.436
127.847
126.970
126.894
126.664
125.120
73.978
66.239
65.286
40.557
f1 (ppm)

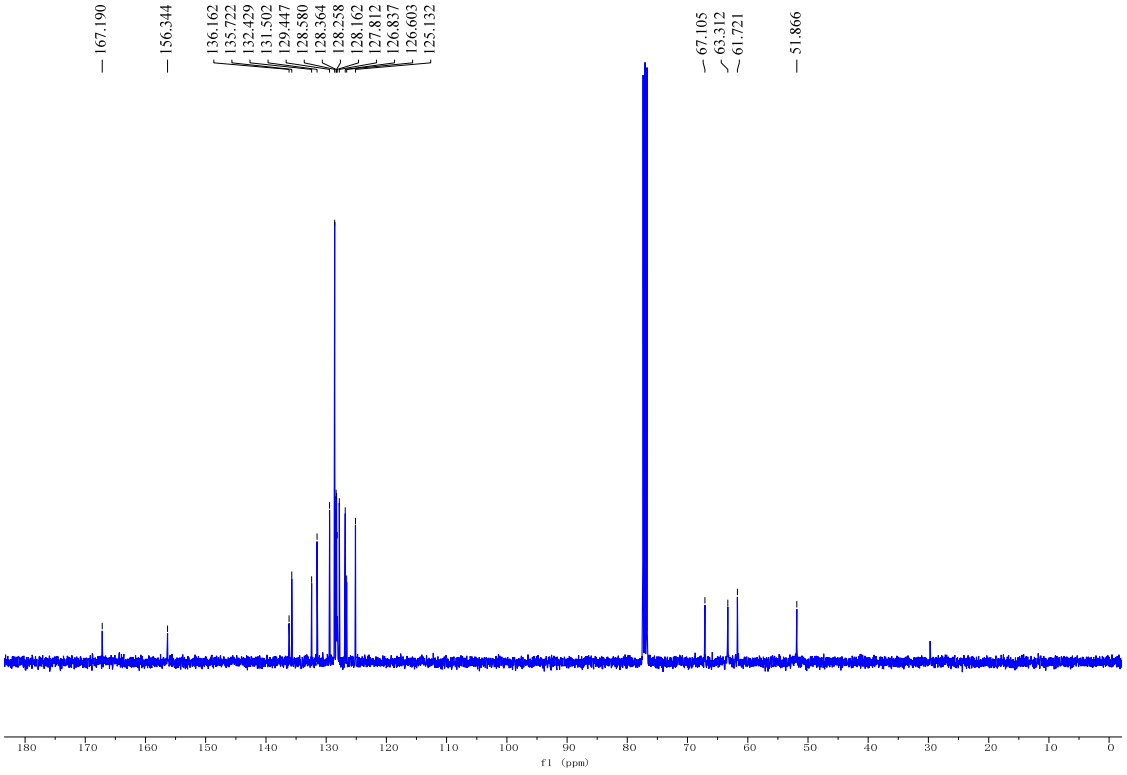
**43**


8.662
8.103
8.099
8.082
8.078
7.944
7.941
7.922
7.892
7.884
7.870
7.863
7.620
7.616
7.602
7.599
7.596
7.582
7.578
7.560
7.556
7.543
7.539
7.536
7.522
7.519
7.436
7.433
7.429
7.422
7.417
7.412
7.337
7.318
7.311
7.305
7.301
7.293
7.289
7.281
7.279
7.275
7.269
7.263
7.259
7.256
7.252
4.737
4.709
4.636
4.607
3.939
3.910
3.893
Ph
O
O
HO
OH
1.00
1.05
1.04
2.13
2.12
2.03
3.35
1.06
1.08
2.20
0.91
0.93
f1 (ppm)

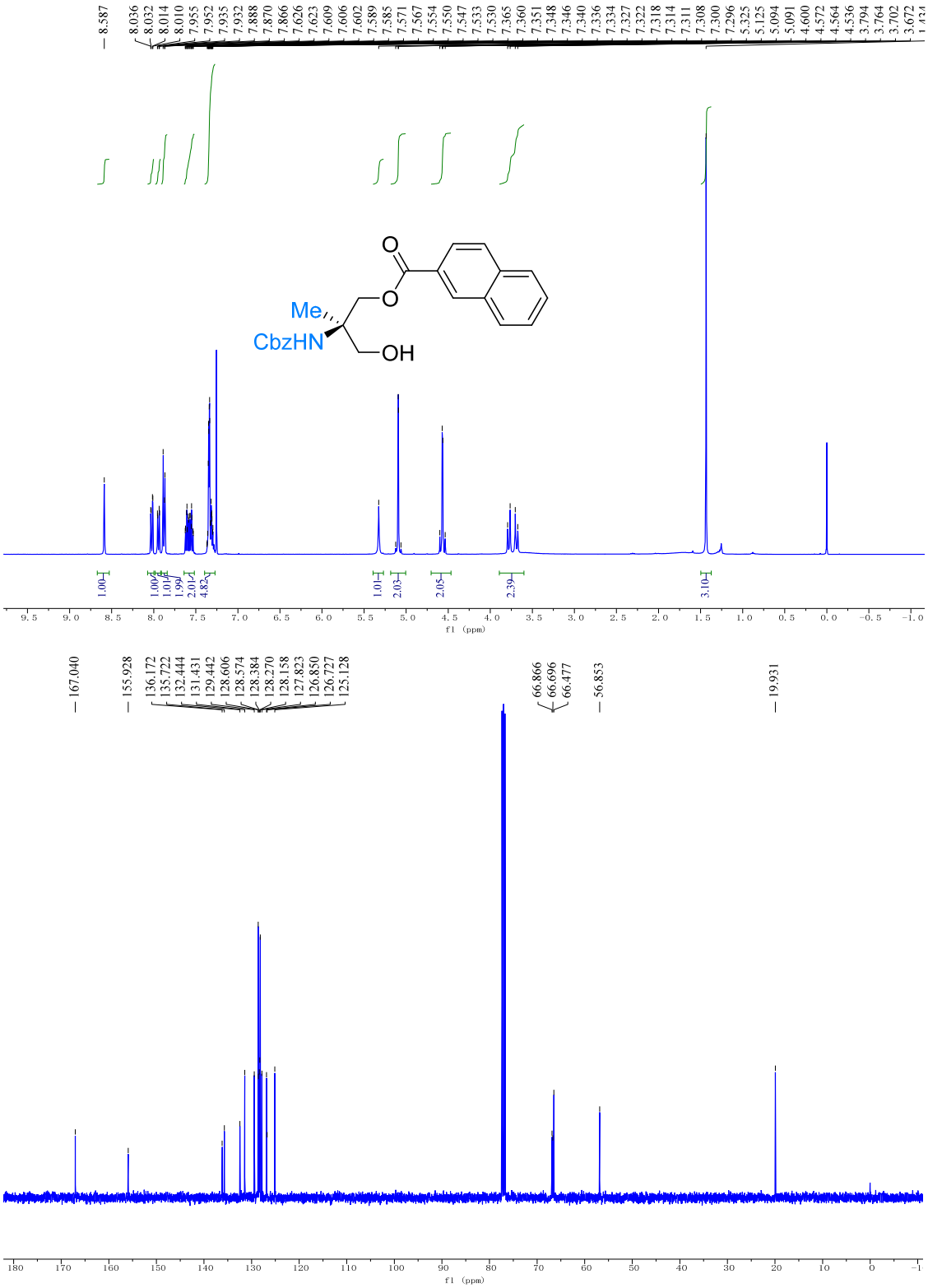

167.094
135.751
132.452
131.929
131.597
129.453
128.924
128.558
128.372
128.357
127.815
126.811
126.710
125.222
121.745
86.855
86.733
71.135
67.376
66.659
f1 (ppm)

**44**

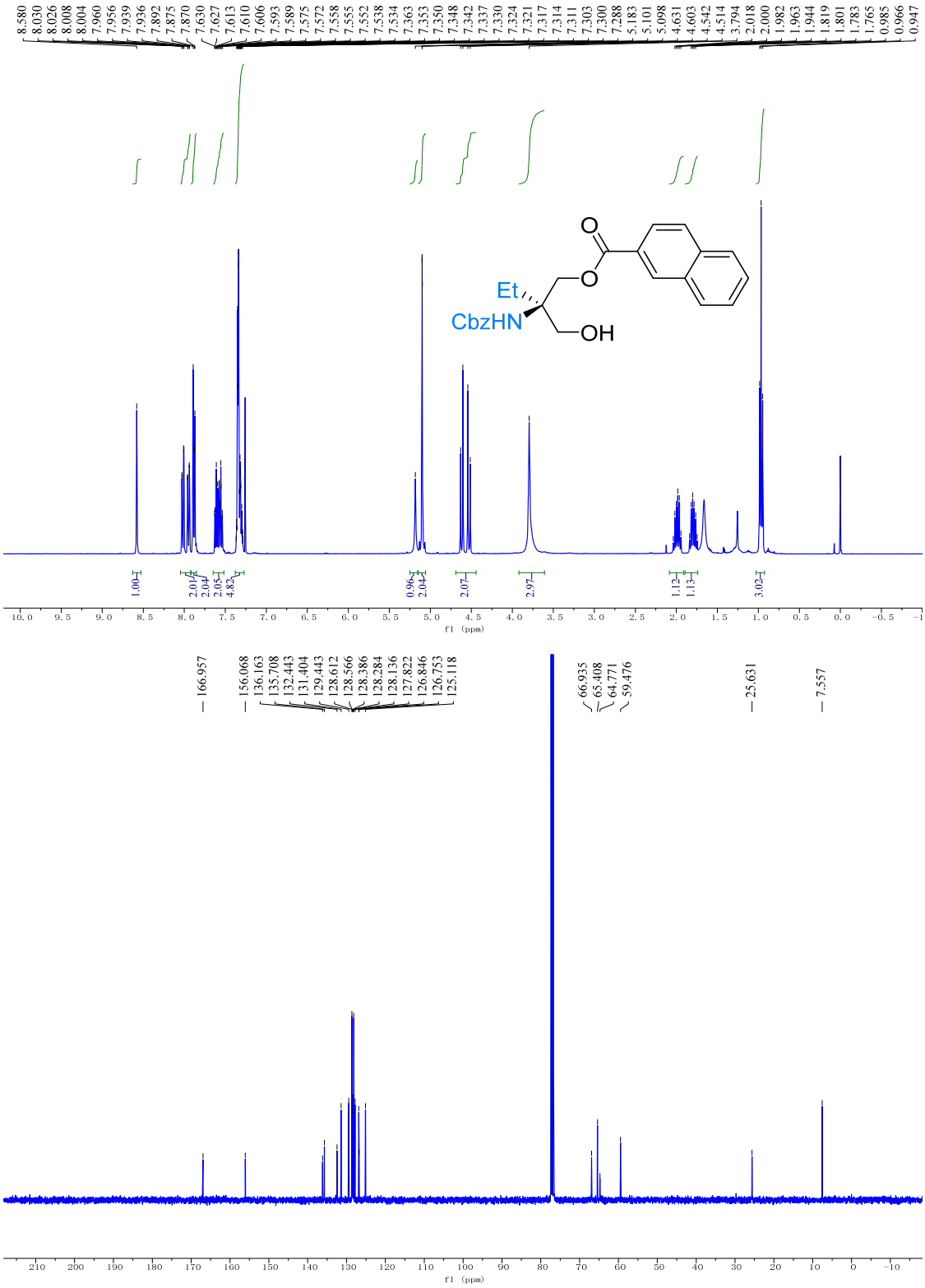

8.585
8.026
8.021
8.004
8.000
7.942
7.922
7.879
7.871
7.858
7.849
7.620
7.616
7.602
7.599
7.582
7.578
7.562
7.559
7.541
7.524
7.521
7.342
7.334
7.329
7.322
7.316
7.304
7.296
7.286
7.282
7.270
7.255
5.449
5.427
5.111
4.534
4.520
4.176
4.164
4.153
4.141
4.129
4.122
3.837
3.826
3.808
3.797
3.761
3.750
3.732
3.720
2.786
O
O
CbzHN
OH
1.00
1.08
3.07
2.17
4.85
1.06
2.10
2.08
1.12
2.06
0.98
f1 (ppm)


167.190
156.344
136.162
135.722
132.429
131.502
129.447
128.580
128.364
128.258
128.162
127.812
126.837
126.603
125.132
67.105
63.312
61.721
51.866
f1 (ppm)

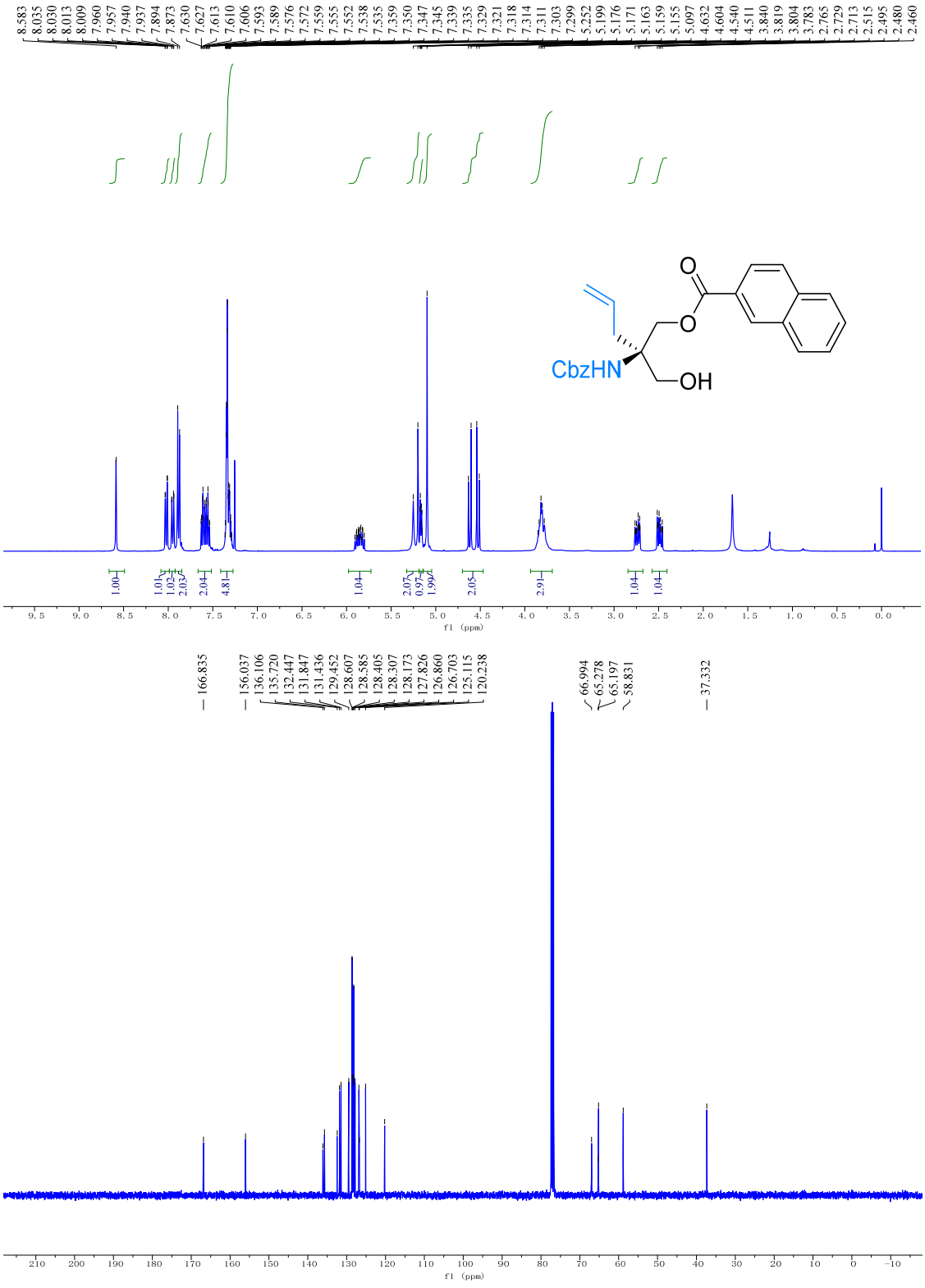
**45**


8.587
8.036
8.032
8.014
8.010
7.955
7.952
7.935
7.932
7.888
7.870
7.866
7.626
7.623
7.609
7.606
7.602
7.589
7.585
7.571
7.567
7.554
7.550
7.547
7.533
7.530
7.365
7.360
7.351
7.348
7.346
7.340
7.336
7.334
7.327
7.322
7.318
7.314
7.311
7.308
7.300
7.296
5.325
5.125
5.094
5.091
4.600
4.572
4.564
4.536
3.794
3.764
3.702
3.672
O
O
Me
CbzHN
OH
1.00
1.00
1.01
1.99
2.01
4.82
1.01
2.03
2.05
2.39
3.10
f1 (ppm)
167.040
155.928
136.172
135.722
132.444
131.431
129.442
128.606
128.574
128.384
128.270
128.158
127.823
126.850
126.727
125.128
66.866
66.696
66.477
56.853
19.931
f1 (ppm)

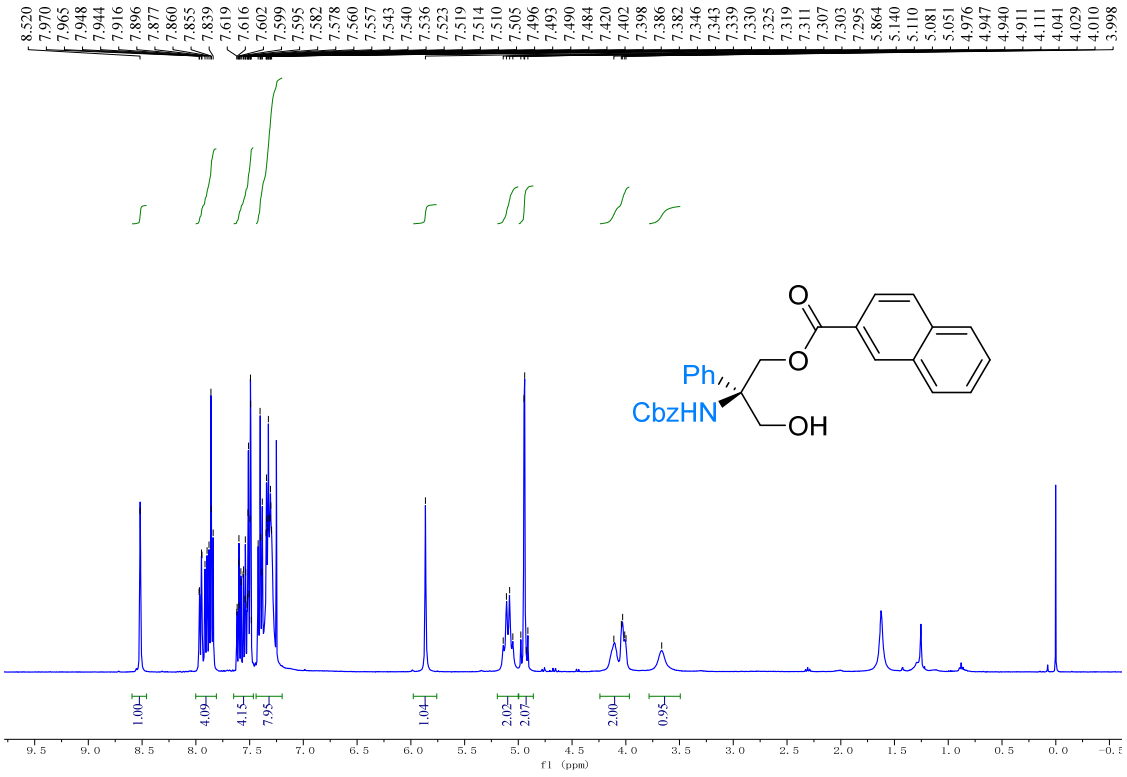
**46**

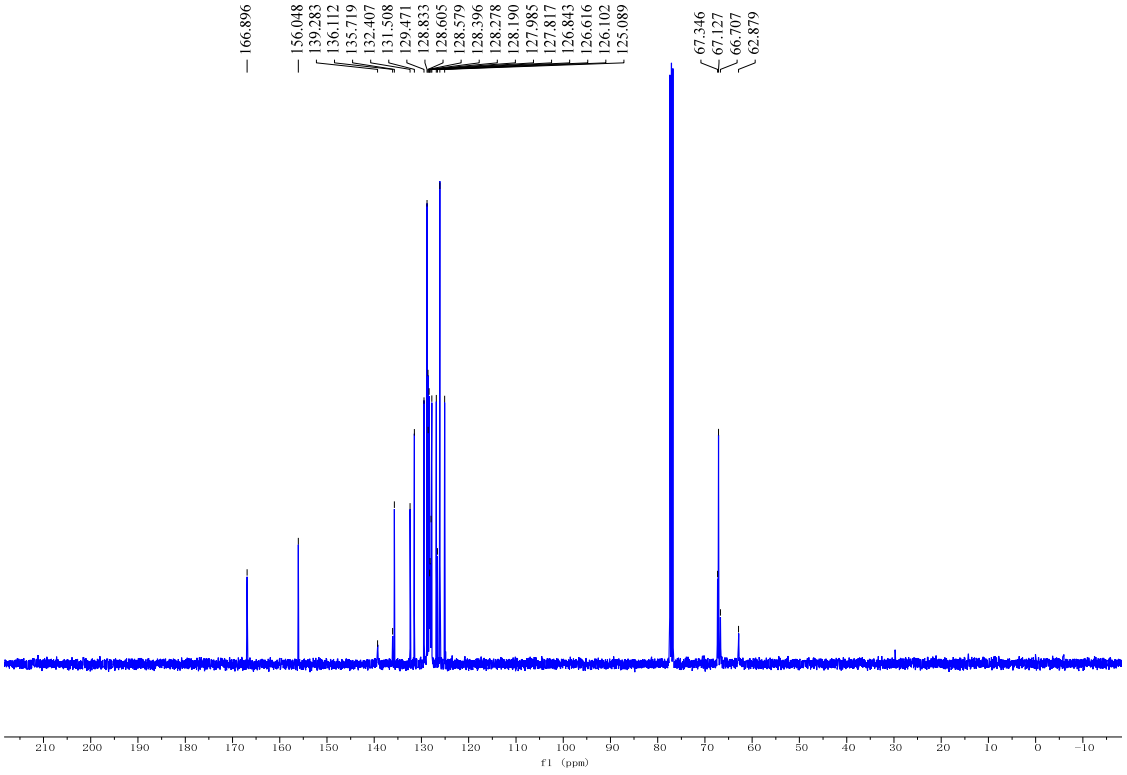

8.580
8.030
8.026
8.008
8.004
7.960
7.956
7.939
7.936
7.892
7.875
7.870
7.630
7.627
7.613
7.610
7.606
7.593
7.589
7.575
7.572
7.558
7.555
7.552
7.538
7.534
7.363
7.353
7.350
7.348
7.342
7.337
7.330
7.324
7.321
7.317
7.314
7.311
7.303
7.300
7.288
5.183
5.101
5.098
4.631
4.603
4.542
4.514
3.794
2.018
2.000
1.982
1.963
1.944
1.819
1.801
1.783
1.765
0.985
0.966
0.947
O
O
Et
CbzHN
OH
1.00
2.01
2.04
2.05
4.82
0.96
2.04
2.07
2.97
1.12
1.13
3.02
f1 (ppm)
166.957
156.068
136.163
135.708
132.443
131.404
129.443
128.612
128.566
128.386
128.284
128.136
127.822
126.846
126.753
125.118
66.935
65.408
64.771
59.476
25.631
7.557
f1 (ppm)

**47**

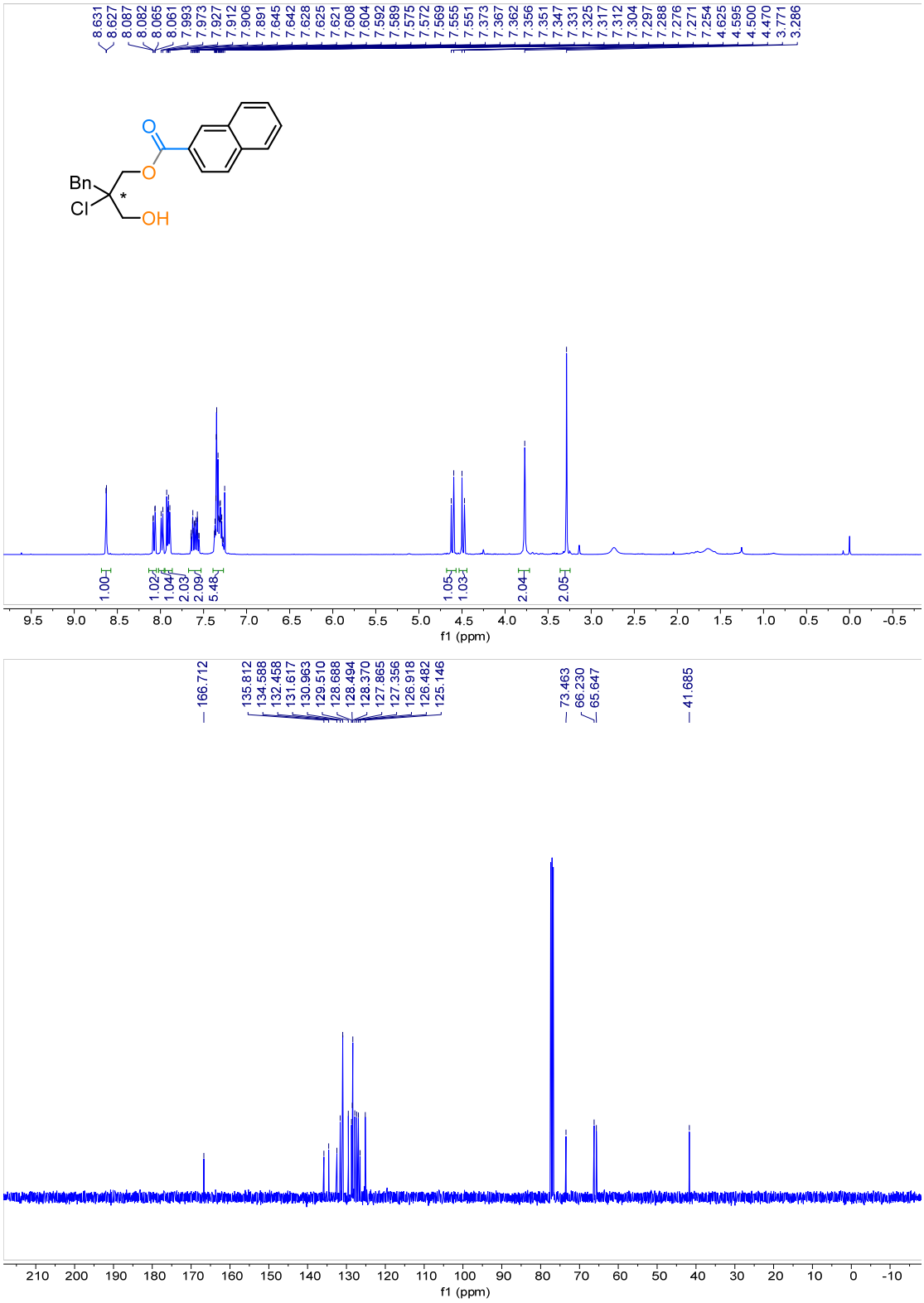

8.583
8.035
8.030
8.013
8.009
7.960
7.957
7.940
7.937
7.894
7.873
7.630
7.627
7.613
7.610
7.606
7.593
7.589
7.576
7.572
7.559
7.555
7.552
7.538
7.535
7.359
7.350
7.347
7.345
7.339
7.335
7.329
7.321
7.318
7.314
7.311
7.303
7.299
5.252
5.199
5.176
5.171
5.163
5.159
5.155
5.097
4.632
4.604
4.540
4.511
3.840
3.819
3.804
3.783
2.765
2.729
2.713
2.515
2.495
2.480
2.460
O
O
CbzHN
OH
1.00
1.01
1.02
2.03
2.04
4.81
1.04
2.07
0.97
1.99
2.05
2.91
1.04
1.04
f1 (ppm)
166.835
156.037
136.106
135.720
132.447
131.847
131.436
129.452
128.607
128.585
128.405
128.307
128.173
127.826
126.860
126.703
125.115
120.238
66.994
65.278
65.197
58.831
37.332
f1 (ppm)

**48**

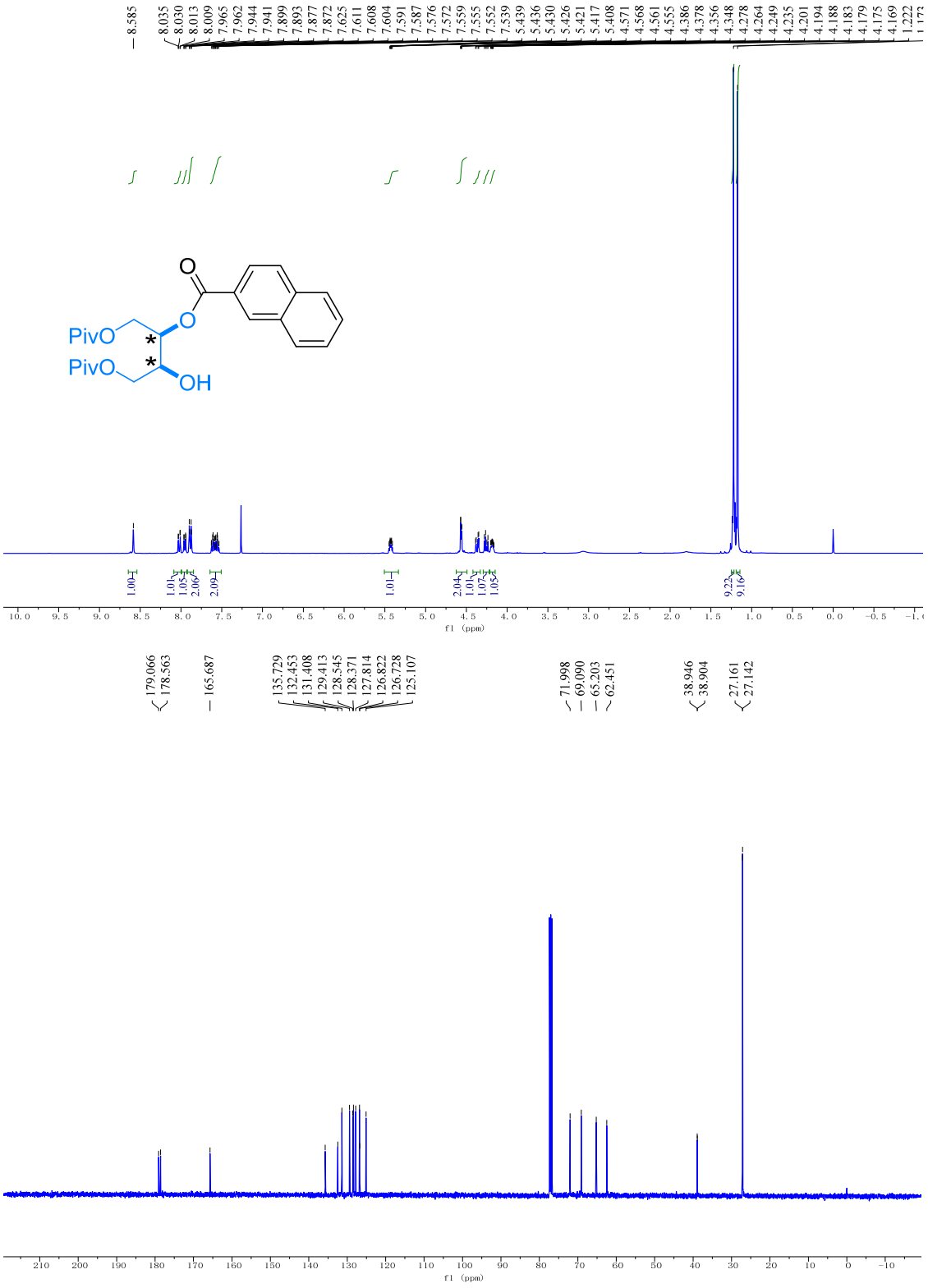

8.520
7.970
7.965
7.948
7.944
7.916
7.896
7.877
7.860
7.855
7.839
7.619
7.616
7.602
7.599
7.595
7.582
7.578
7.560
7.557
7.543
7.540
7.536
7.523
7.519
7.514
7.510
7.505
7.496
7.493
7.490
7.484
7.420
7.402
7.398
7.386
7.382
7.346
7.343
7.339
7.330
7.325
7.319
7.311
7.307
7.303
7.295
5.864
5.140
5.110
5.081
5.051
4.976
4.947
4.940
4.911
4.111
4.041
4.029
4.010
3.998
O
O
Ph
CbzHN
OH
1.00
4.09
4.15
7.95
1.04
2.02
2.07
2.00
0.95
f1 (ppm)


166.896
156.048
139.283
136.112
135.719
132.407
131.508
129.471
128.833
128.605
128.579
128.396
128.278
128.190
127.985
127.817
126.843
126.616
126.102
125.089
67.346
67.127
66.707
62.879
f1 (ppm)

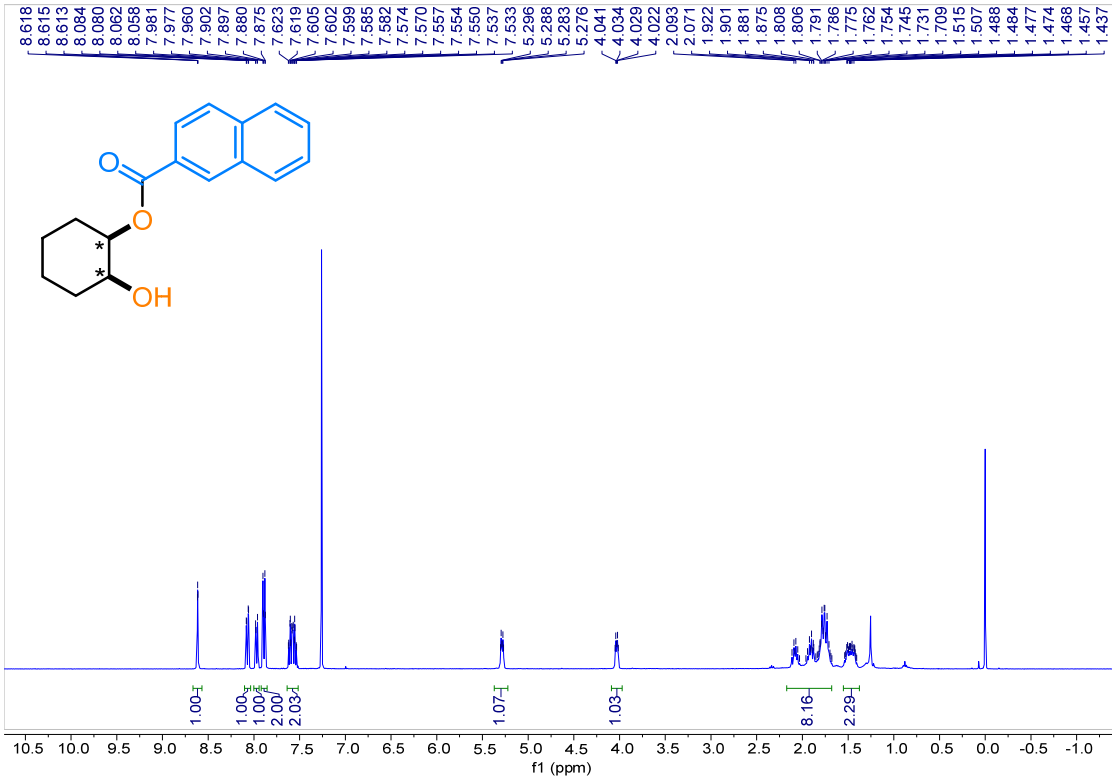
**49**

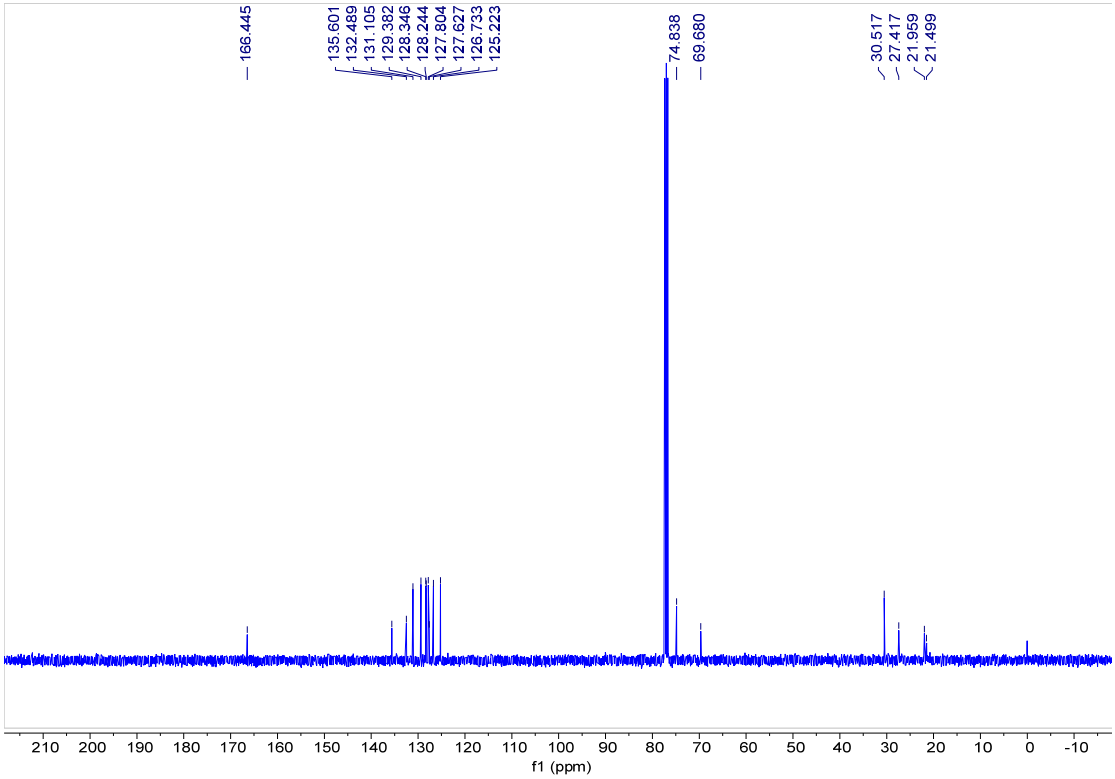

8.631
8.627
8.087
8.082
8.065
8.061
7.993
7.973
7.927
7.912
7.906
7.891
7.645
7.642
7.628
7.625
7.621
7.608
7.604
7.592
7.589
7.575
7.572
7.569
7.555
7.551
7.373
7.367
7.362
7.356
7.351
7.347
7.331
7.325
7.317
7.312
7.304
7.297
7.288
7.276
7.271
7.254
4.625
4.595
4.500
4.470
3.771
3.286
O
O
Bn
Cl
*
OH
1.00
1.02
1.04
2.03
2.09
5.48
1.05
1.03
2.04
2.05
f1 (ppm)
166.712
135.812
134.588
132.458
131.617
130.963
129.510
128.688
128.494
128.370
127.865
127.356
126.918
126.482
125.146
73.463
66.230
65.647
41.685
f1 (ppm)

**50**

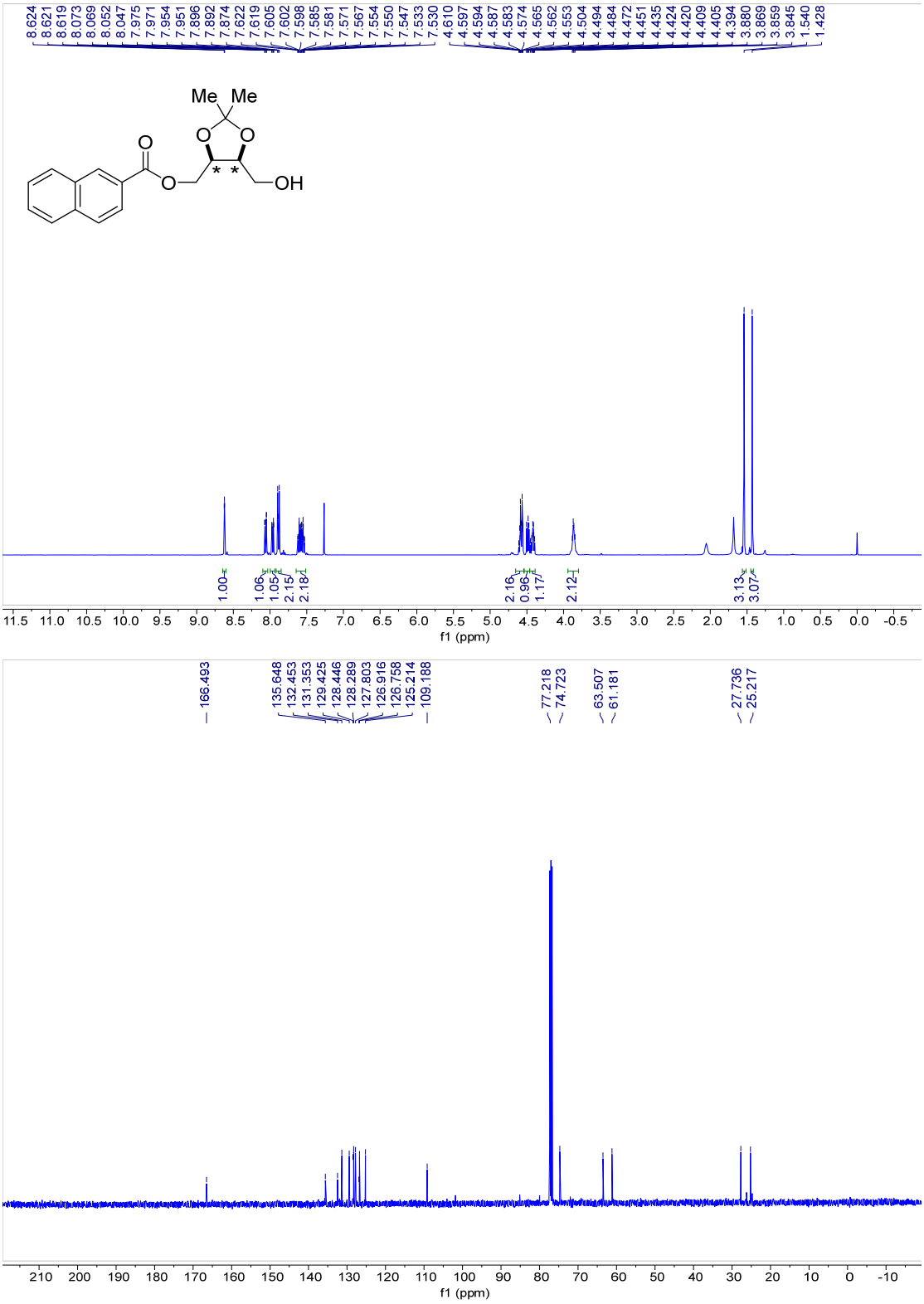

8.585
8.035
8.030
8.013
8.009
7.965
7.962
7.944
7.941
7.899
7.893
7.877
7.872
7.625
7.611
7.608
7.604
7.591
7.587
7.576
7.572
7.559
7.555
7.552
7.539
7.439
5.436
5.430
5.426
5.421
5.417
5.408
4.571
4.568
4.561
4.555
4.386
4.378
4.356
4.348
4.278
4.264
4.249
4.235
4.201
4.194
4.188
4.183
4.179
4.175
4.169
1.222
PivO
PivO
OH
1.00
1.01
1.05
2.06
2.09
1.01
2.04
1.01
1.07
1.05
9.22
9.16
f1 (ppm)
179.066
178.563
165.687
135.729
132.453
131.408
129.413
128.545
128.371
127.814
126.822
126.728
125.107
71.998
69.090
65.203
62.451
38.946
38.904
27.161
27.142
f1 (ppm)

**SP-4**


8.618
8.615
8.613
8.084
8.080
8.062
8.058
7.981
7.977
7.960
7.902
7.897
7.880
7.875
7.623
7.619
7.605
7.602
7.599
7.585
7.582
7.574
7.570
7.557
7.554
7.550
7.537
7.533
5.296
5.288
5.283
5.276
4.041
4.034
4.029
4.022
2.093
2.071
1.922
1.901
1.881
1.875
1.808
1.806
1.791
1.786
1.775
1.762
1.754
1.745
1.731
1.709
1.515
1.507
1.488
1.484
1.477
1.474
1.468
1.457
1.437
O
O
*
*
OH
1.00
1.00
1.00
2.00
2.03
1.07
1.03
8.16
2.29
f1 (ppm)


166.445
135.601
132.489
131.105
129.382
128.346
128.244
127.804
127.627
126.733
125.223
74.838
69.680
30.517
27.417
21.959
21.499
f1 (ppm)

**51**


8.624
8.621
8.619
8.073
8.069
8.052
8.047
7.975
7.971
7.954
7.951
7.896
7.892
7.874
7.622
7.619
7.605
7.602
7.598
7.585
7.581
7.571
7.567
7.554
7.550
7.547
7.533
7.530
4.610
4.597
4.594
4.587
4.583
4.574
4.565
4.562
4.553
4.504
4.494
4.484
4.472
4.451
4.435
4.424
4.420
4.409
4.405
4.394
3.880
3.869
3.859
3.845
1.540
1.428
Me Me
O
O
O
O
* *
OH
1.00
1.06
1.05
2.15
2.18
2.16
0.96
1.17
2.12
3.13
3.07
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
166.493
135.648
132.453
131.353
129.425
128.446
128.289
127.803
126.916
126.758
125.214
109.188
77.218
74.723
63.507
61.181
27.736
25.217
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)

**52**


8.610
8.607
8.605
8.037
8.032
8.015
8.011
7.987
7.967
7.917
7.903
7.895
7.883
7.644
7.641
7.627
7.624
7.620
7.607
7.603
7.589
7.586
7.572
7.569
7.566
7.552
7.549
5.135
5.125
5.120
5.116
5.113
5.110
5.103
5.095
5.090
5.081
4.687
4.679
4.671
4.666
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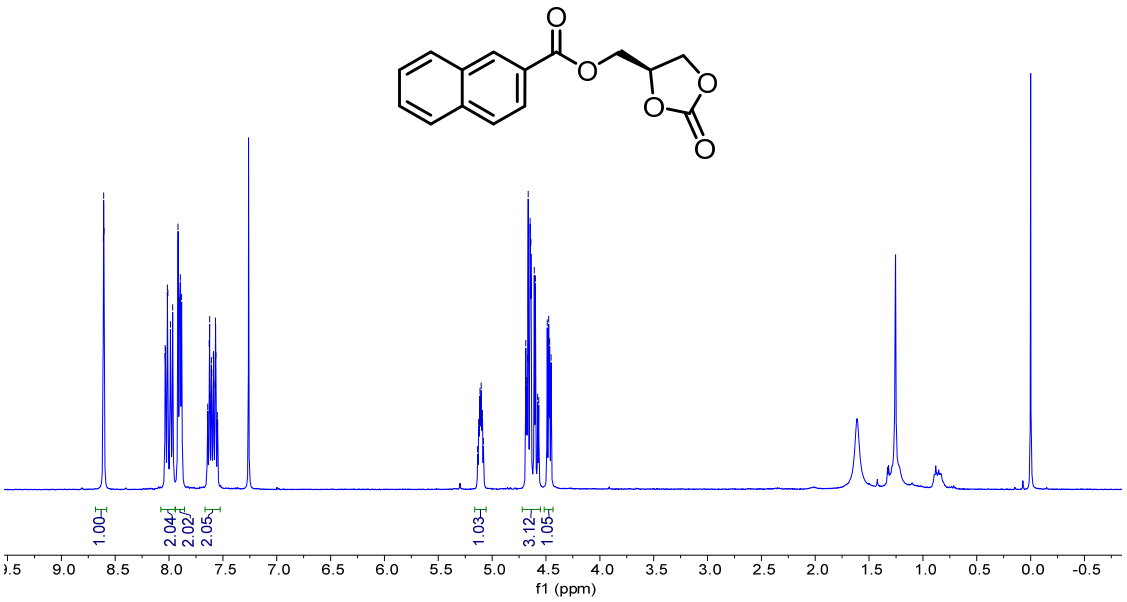
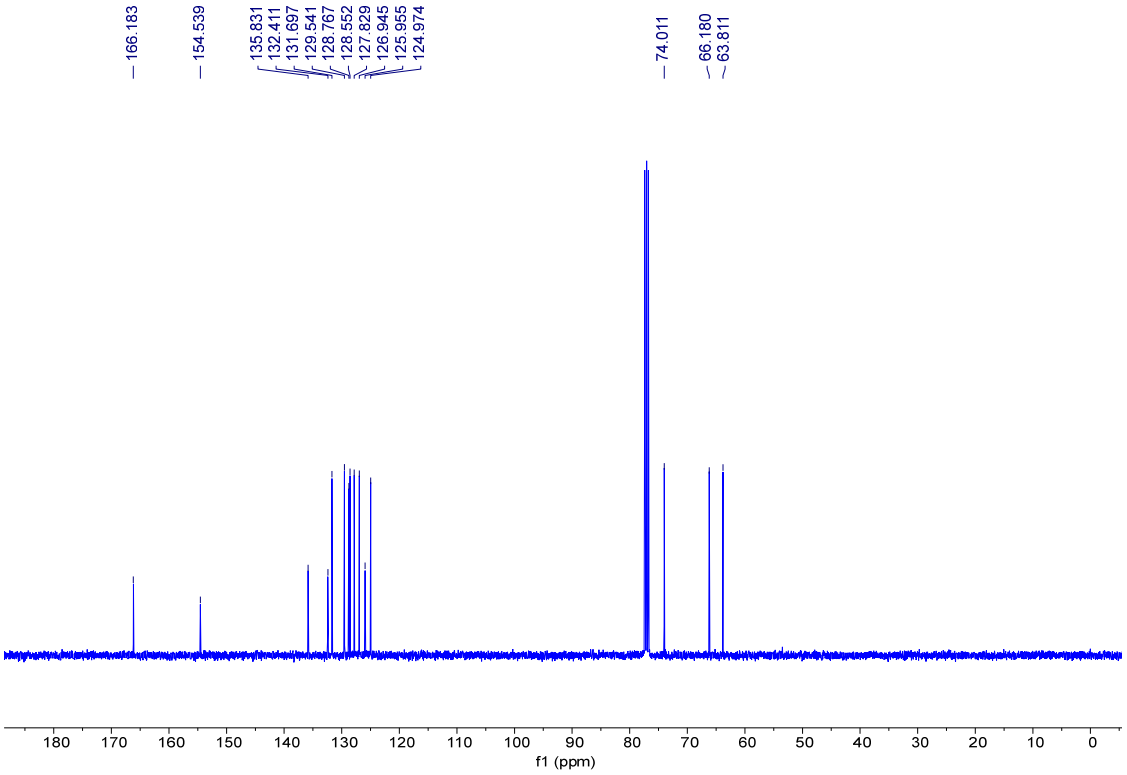
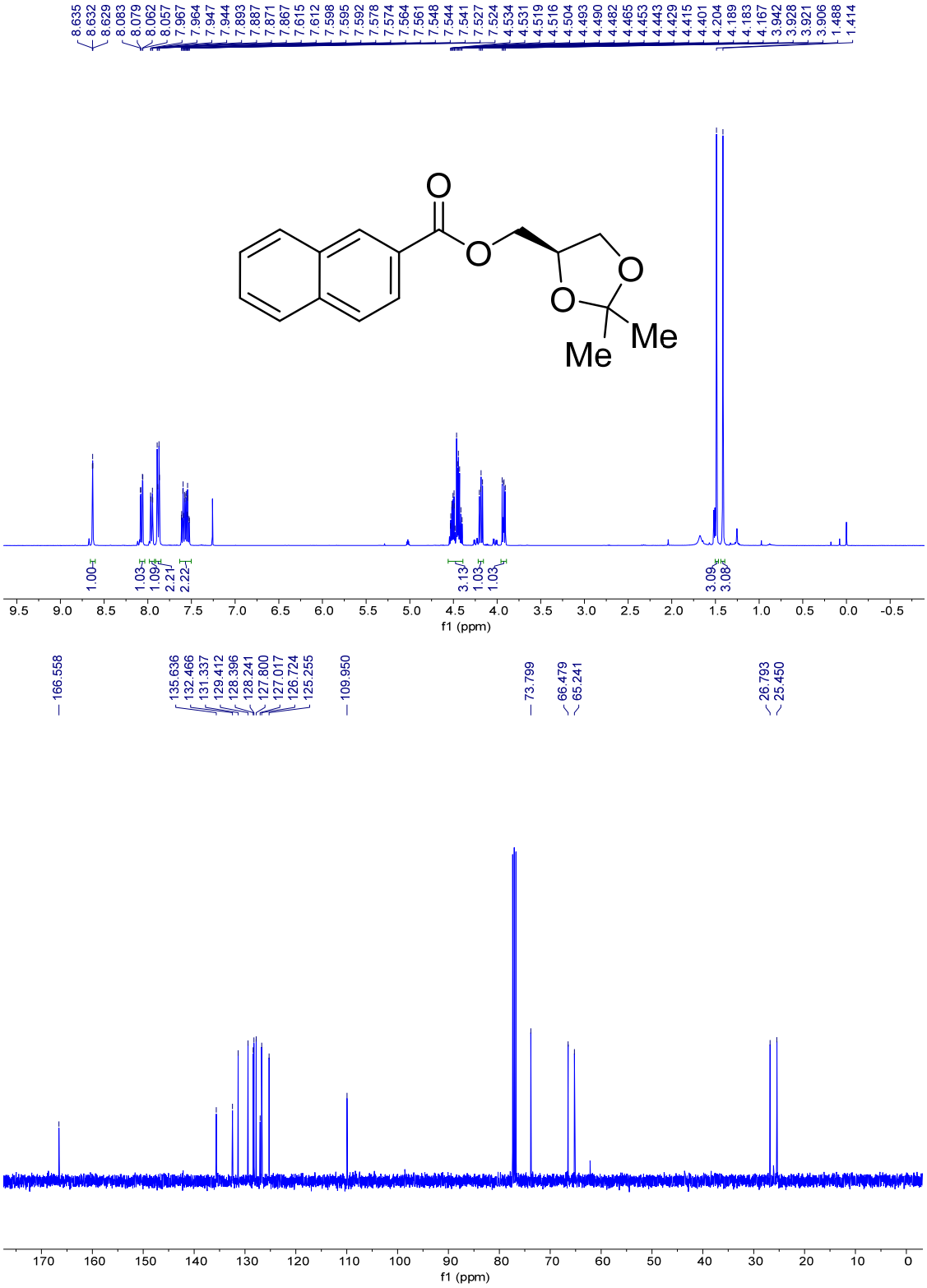
4.578
4.567
4.489
4.474
4.467
4.452


O
O
O
O
O
1.00
2.04
2.02
2.05
1.03
3.12
1.05
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)

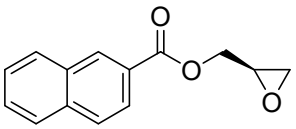

166.183
154.539
135.831
132.411
131.697
129.541
128.767
128.552
127.829
126.945
125.955
124.974
74.011
66.180
63.811
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

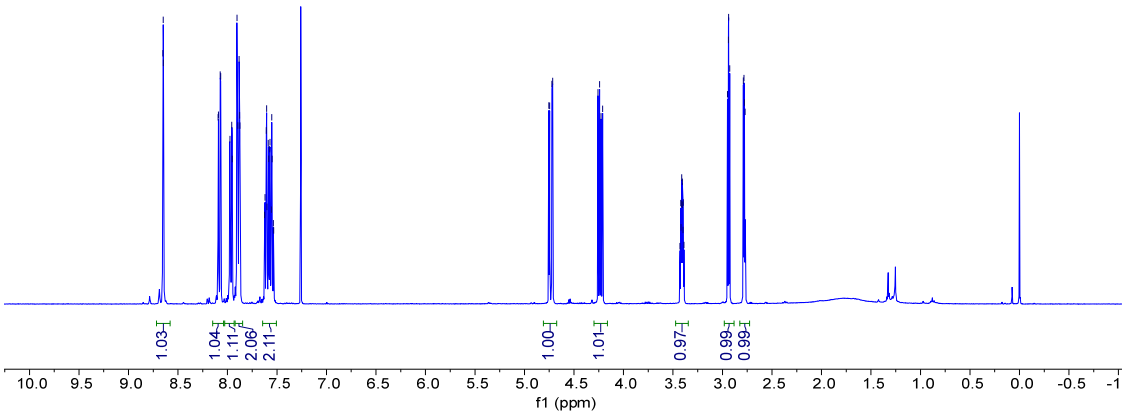
**53**

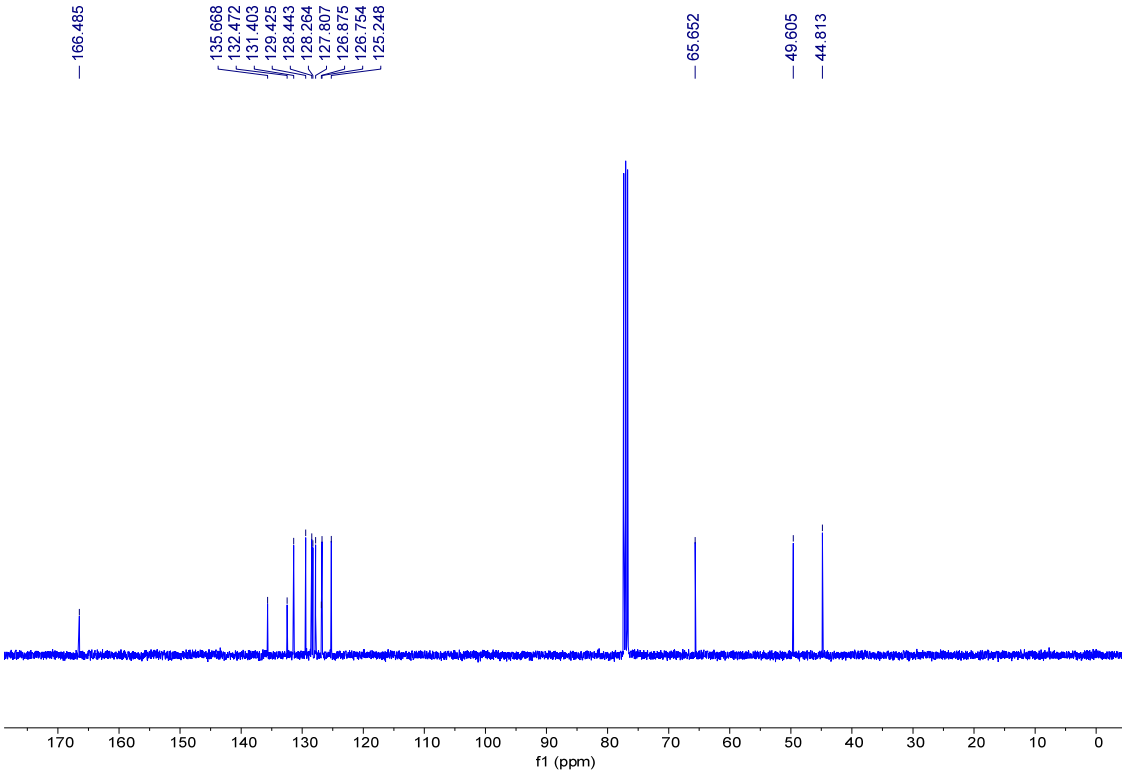

8.635
8.632
8.629
8.083
8.079
8.062
8.057
7.967
7.964
7.947
7.944
7.893
7.887
7.871
7.867
7.615
7.612
7.598
7.595
7.592
7.578
7.574
7.564
7.561
7.548
7.544
7.541
7.527
7.524
4.534
4.531
4.519
4.516
4.504
4.493
4.490
4.482
4.465
4.453
4.443
4.429
4.415
4.401
4.204
4.189
4.183
4.167
3.942
3.928
3.921
3.906
1.488
1.414
O
O
O
O
Me
Me
1.00
1.03
1.09
2.21
2.22
3.13
1.03
1.03
3.09
3.08
f1 (ppm)
166.558
135.636
132.466
131.337
129.412
128.396
128.241
127.800
127.017
126.724
125.255
109.950
73.799
66.479
65.241
26.793
25.450
f1 (ppm)

**54**

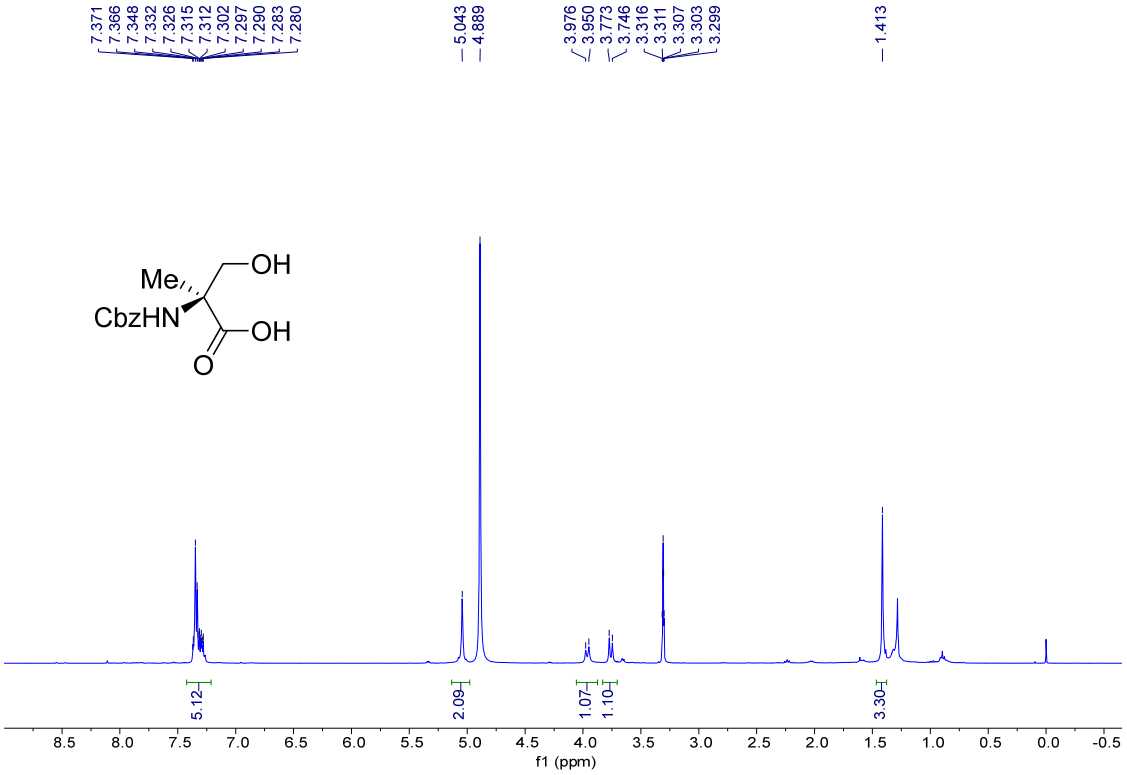

8.653
8.649
8.647
8.095
8.091
8.073
8.069
7.975
7.956
7.953
7.904
7.896
7.883
7.878
7.875
7.625
7.621
7.608
7.604
7.601
7.588
7.584
7.574
7.570
7.557
7.553
7.550
7.536
7.533
4.754
4.746
4.723
4.715
4.257
4.241
4.226
4.211
3.422
3.418
3.414
3.412
3.406
3.403
3.399
3.396
3.389
2.950
2.939
2.938
2.927
2.790
2.783
2.778


O
O
O

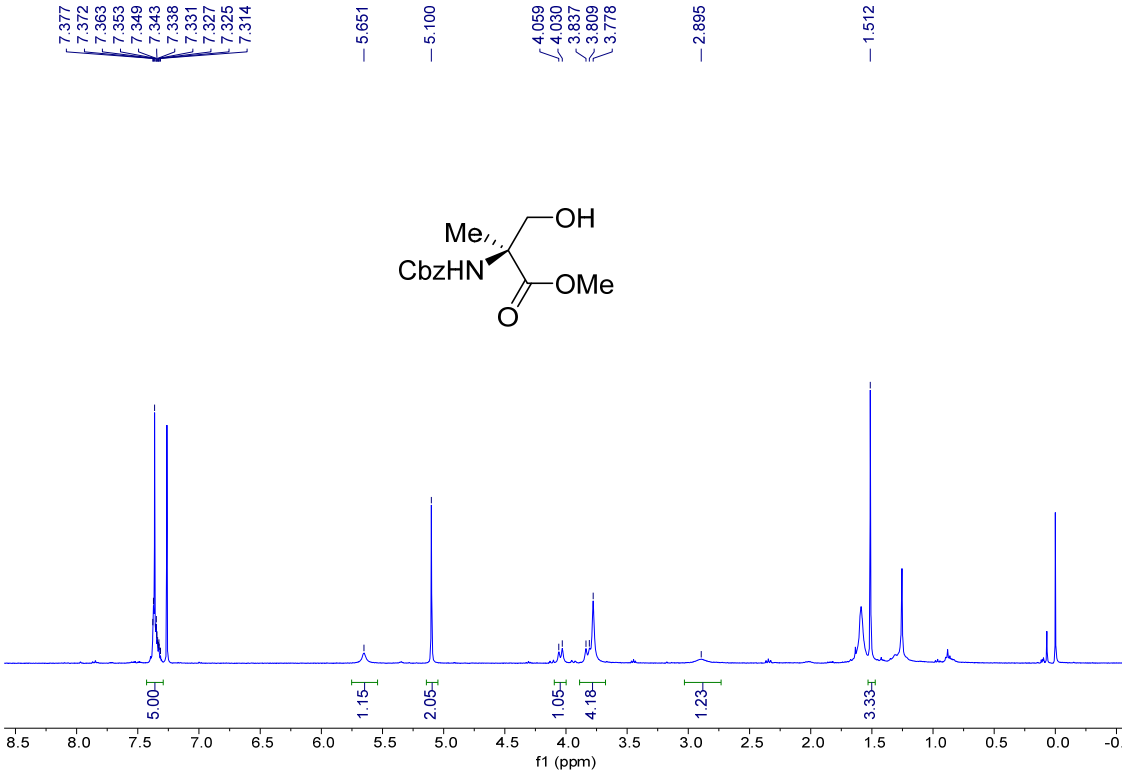

1.03
1.04
1.11
2.06
2.11
1.00
1.01
0.97
0.99
0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


166.485
135.668
132.472
131.403
129.425
128.443
128.264
127.807
126.875
126.754
125.248
65.652
49.605
44.813
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

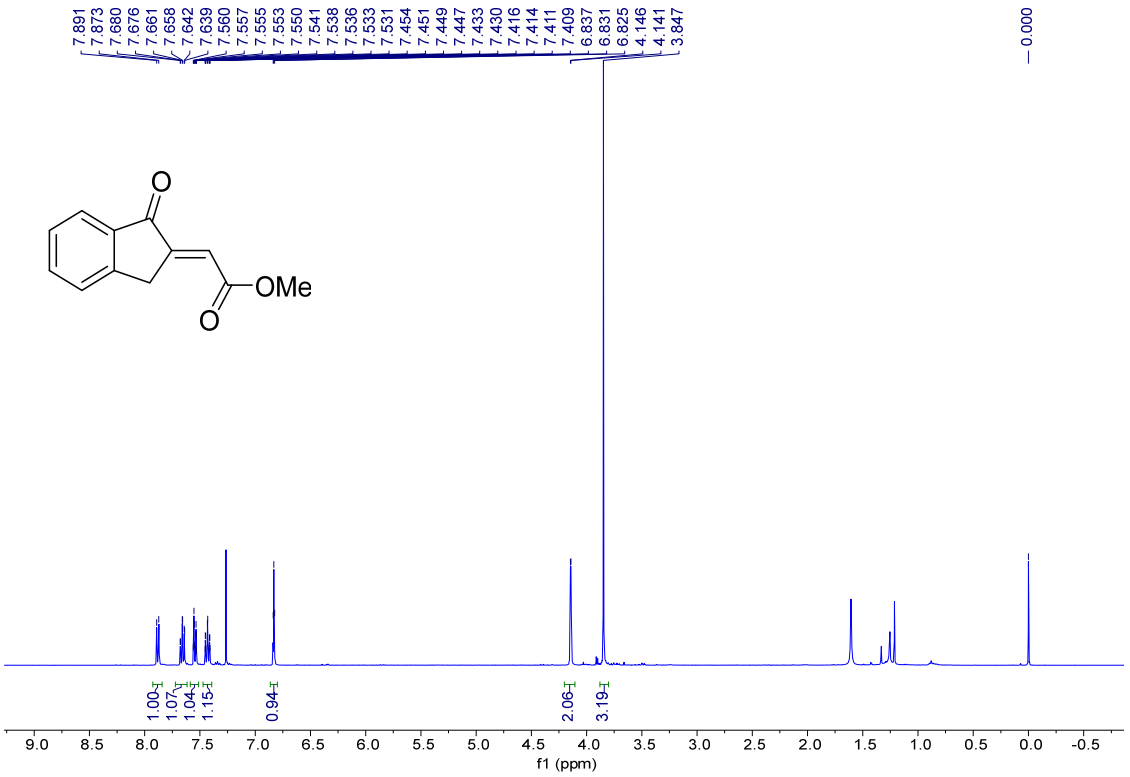
**55**

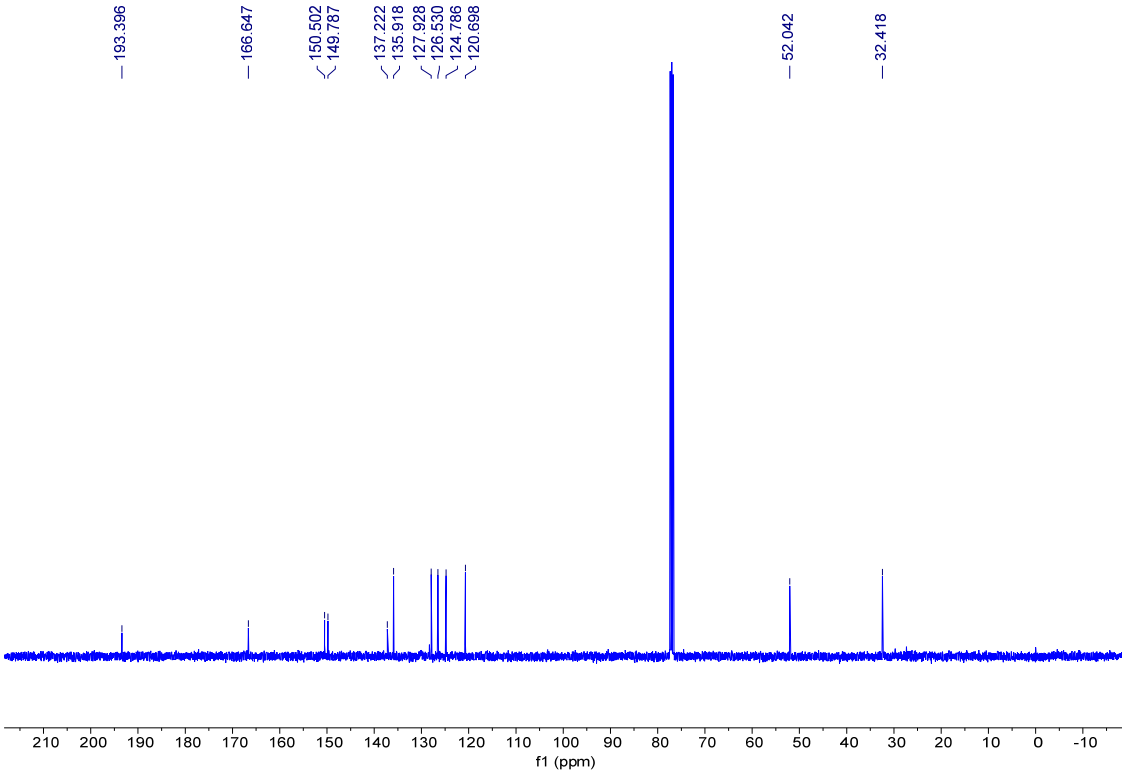

7.371
7.366
7.348
7.332
7.326
7.315
7.312
7.302
7.297
7.290
7.283
7.280
5.043
4.889
3.976
3.950
3.773
3.746
3.316
3.311
3.307
3.303
3.299
1.413
Me
OH
CbzHN
OH
O
5.12
2.09
1.07
1.10
3.30
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

**55-1**

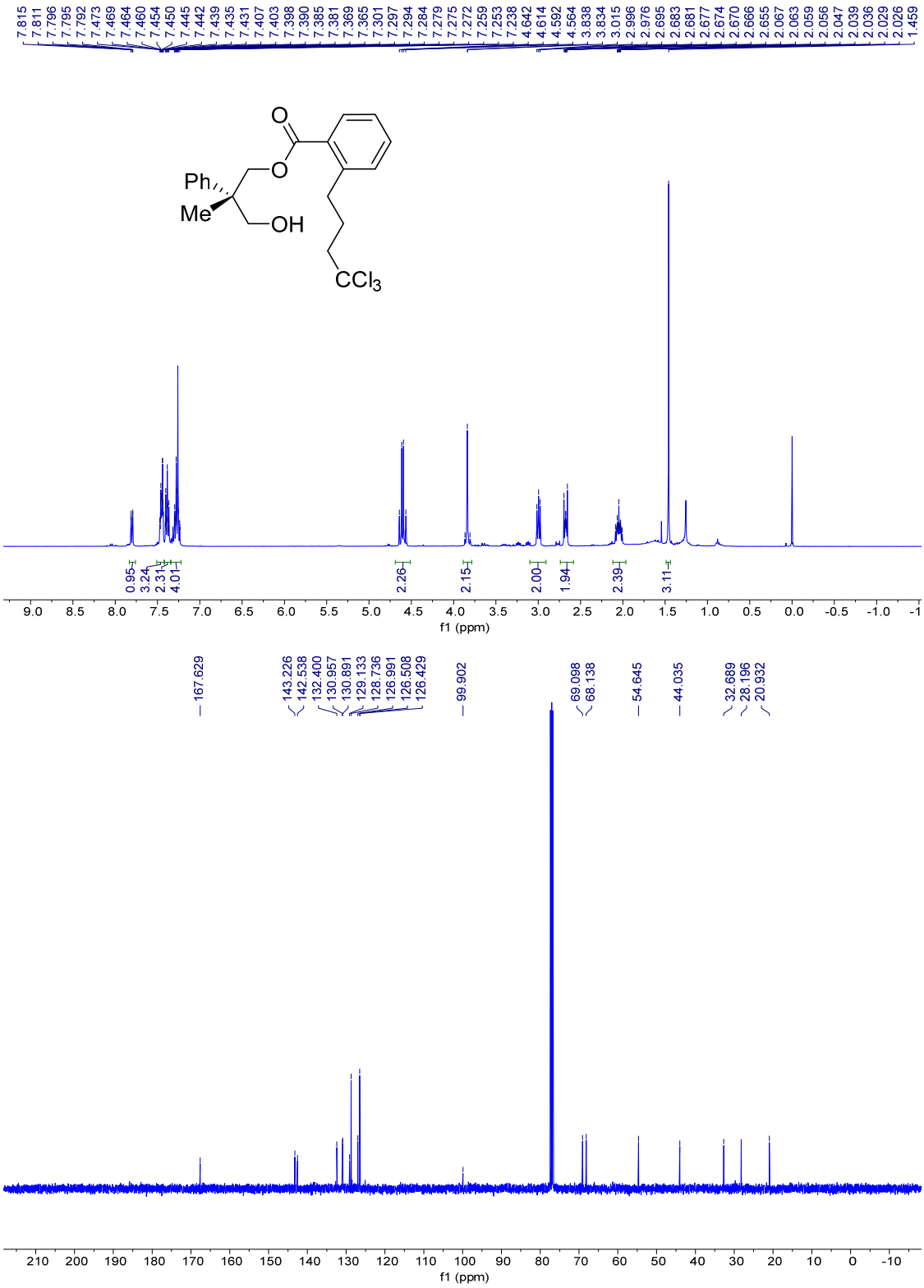

7.377
7.372
7.363
7.353
7.349
7.343
7.338
7.331
7.327
7.325
7.314
5.651
5.100
4.059
4.030
3.837
3.809
3.778
2.895
1.512
Me
OH
CbzHN
OMe
O
5.00
1.15
2.05
1.05
4.18
1.23
3.33
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

**56**

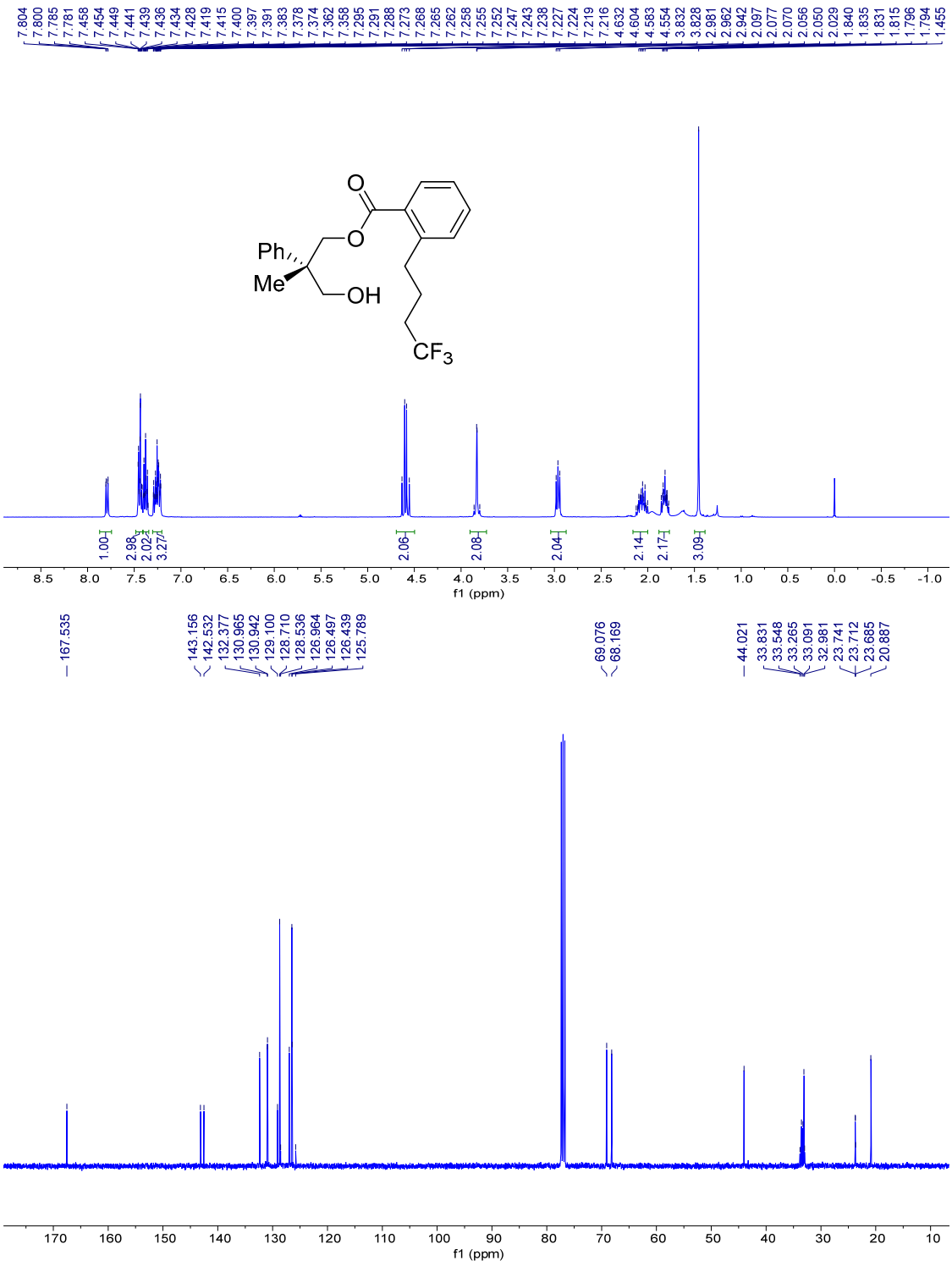

7.891
7.873
7.680
7.676
7.661
7.658
7.642
7.639
7.560
7.557
7.555
7.553
7.550
7.541
7.538
7.536
7.533
7.531
7.454
7.451
7.449
7.447
7.433
7.430
7.416
7.414
7.411
7.409
6.837
6.831
6.825
4.146
4.141
3.847
0.000
O
OMe
O
1.00
1.07
1.04
1.15
0.94
2.06
3.19
f1 (ppm)

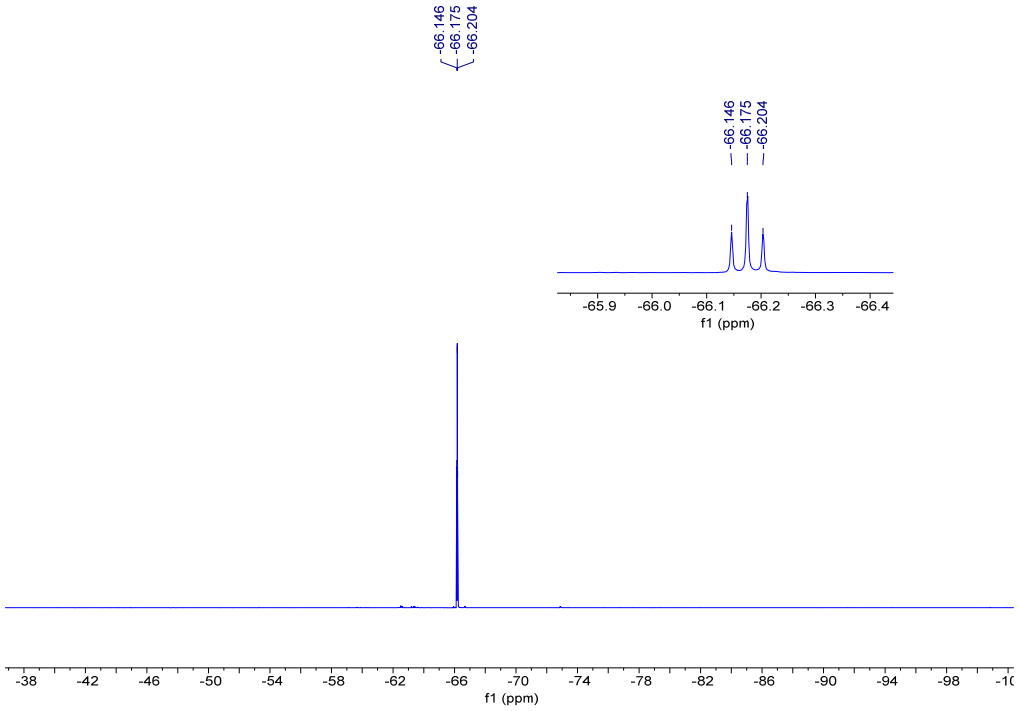

193.396
166.647
150.502
149.787
137.222
135.918
127.928
126.530
124.786
120.698
52.042
32.418
f1 (ppm)

**57**

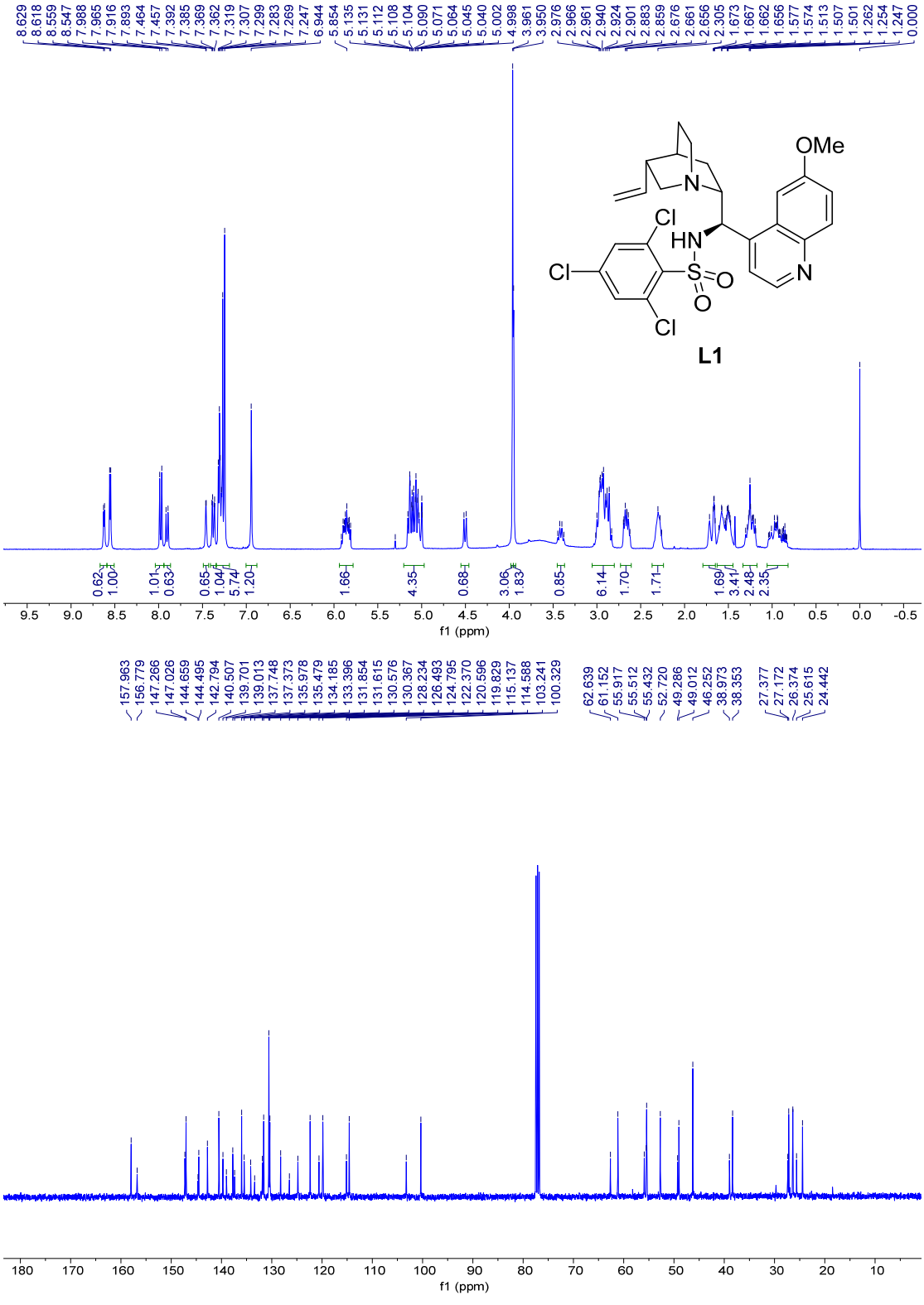

7.815 7.811 7.796 7.795 7.792 7.473 7.469 7.464 7.460 7.454 7.450 7.445 7.442 7.439 7.435 7.431 7.407 7.403 7.398 7.390 7.385 7.381 7.369 7.365 7.301 7.297 7.294 7.284 7.279 7.275 7.272 7.259 7.253 7.238 4.642 4.614 4.592 4.564 3.838 3.834 3.015 2.996 2.976 2.695 2.683 2.681 2.677 2.674 2.670 2.666 2.655 2.067 2.063 2.059 2.056 2.047 2.039 2.036 2.029 2.026 1.459
O
O
Ph
Me
OH
CCl3
0.95 3.24 2.31 4.01 2.26 2.15 2.00 1.94 2.39 3.11
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
f1 (ppm)
167.629 143.226 142.538 132.400 130.957 130.891 129.133 128.736 126.991 126.508 126.429 99.902 69.098 68.138 54.645 44.035 32.689 28.196 20.932
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)

**58**

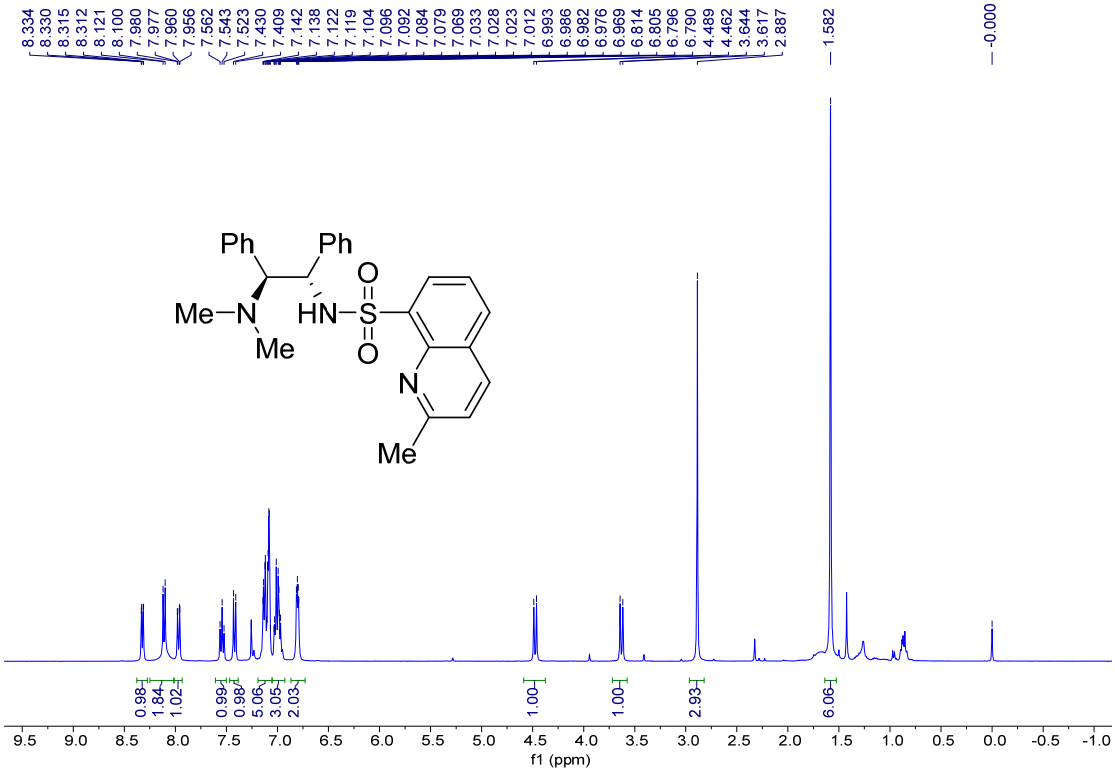

7.804 7.800 7.785 7.781 7.458 7.454 7.449 7.441 7.439 7.436 7.434 7.428 7.419 7.415 7.400 7.397 7.391 7.383 7.378 7.374 7.362 7.358 7.295 7.291 7.288 7.273 7.268 7.265 7.262 7.258 7.255 7.252 7.247 7.243 7.238 7.227 7.224 7.219 7.216 4.632 4.604 4.583 4.554 3.832 3.828 2.981 2.962 2.942 2.097 2.077 2.070 2.056 2.050 2.029 1.840 1.835 1.831 1.815 1.796 1.794 1.455
O
O
Ph
Me
OH
CF3
1.00 2.98 2.02 3.27 2.06 2.08 2.04 2.14 2.17 3.09
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)
167.535
143.156 142.532 132.377 130.965 130.942 129.100 128.710 128.536 126.964 126.497 126.439 125.789
69.076 68.169
44.021 33.831 33.548 33.265 33.091 32.981 23.741 23.712 23.685 20.887
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

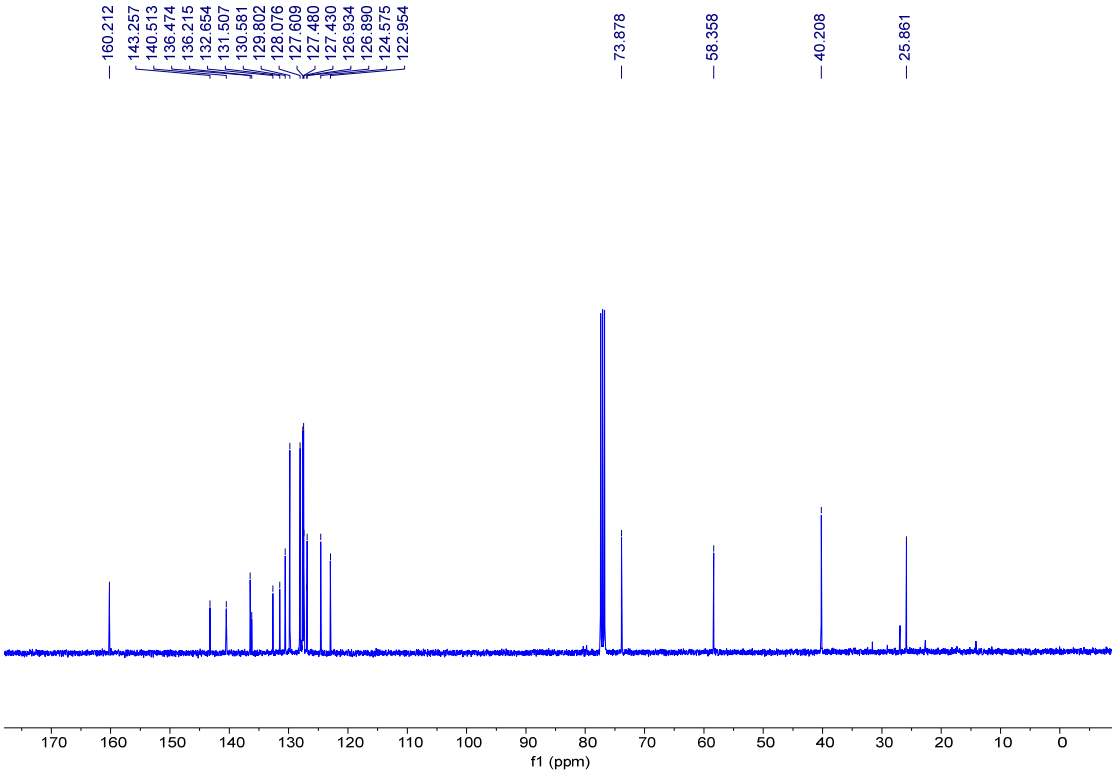

-66.146
-66.175
-66.204
-66.146
-66.175
-66.204
-65.9
-66.0
-66.1
-66.2
-66.3
-66.4
f1 (ppm)
-38
-42
-46
-50
-54
-58
-62
-66
-70
-74
-78
-82
-86
-90
-94
-98
f1 (ppm)

**L1**

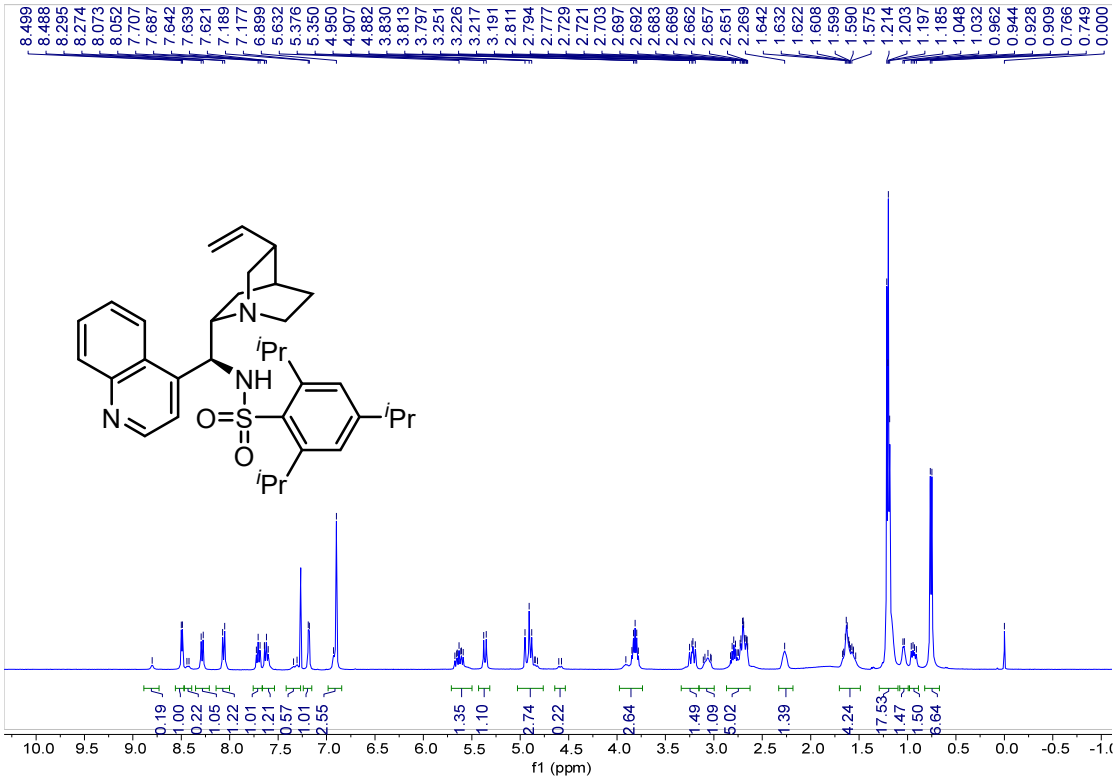

8.629 8.618 8.559 8.547 7.988 7.965 7.916 7.893 7.464 7.457 7.392 7.385 7.369 7.362 7.319 7.307 7.299 7.283 7.269 7.247 6.944 5.854 5.135 5.131 5.112 5.108 5.104 5.090 5.071 5.064 5.045 5.040 5.002 4.998 3.961 3.950 2.976 2.966 2.961 2.940 2.924 2.901 2.883 2.859 2.676 2.661 2.656 2.305 1.673 1.667 1.662 1.656 1.577 1.574 1.513 1.507 1.501 1.262 1.254 1.247 0.000
OMe
N
Cl
HN
Cl
S
O
O
N
Cl
L1
0.62 1.00 1.01 0.63 0.65 1.04 5.74 1.20 1.66 4.35 0.68 3.06 1.83 0.85 6.14 1.70 1.71 1.69 3.41 2.48 2.35
f1 (ppm)
157.963 156.779 147.266 147.026 144.659 144.495 142.794 140.507 139.701 139.013 137.748 137.373 135.978 135.479 134.185 133.396 131.854 131.615 130.576 130.367 128.234 126.493 124.795 122.370 120.596 119.829 115.137 114.588 103.241 100.329
62.639 61.152 55.917 55.512 55.432 52.720 49.286 49.012 46.252 38.973 38.353
27.377 27.172 26.374 25.615 24.442
f1 (ppm)

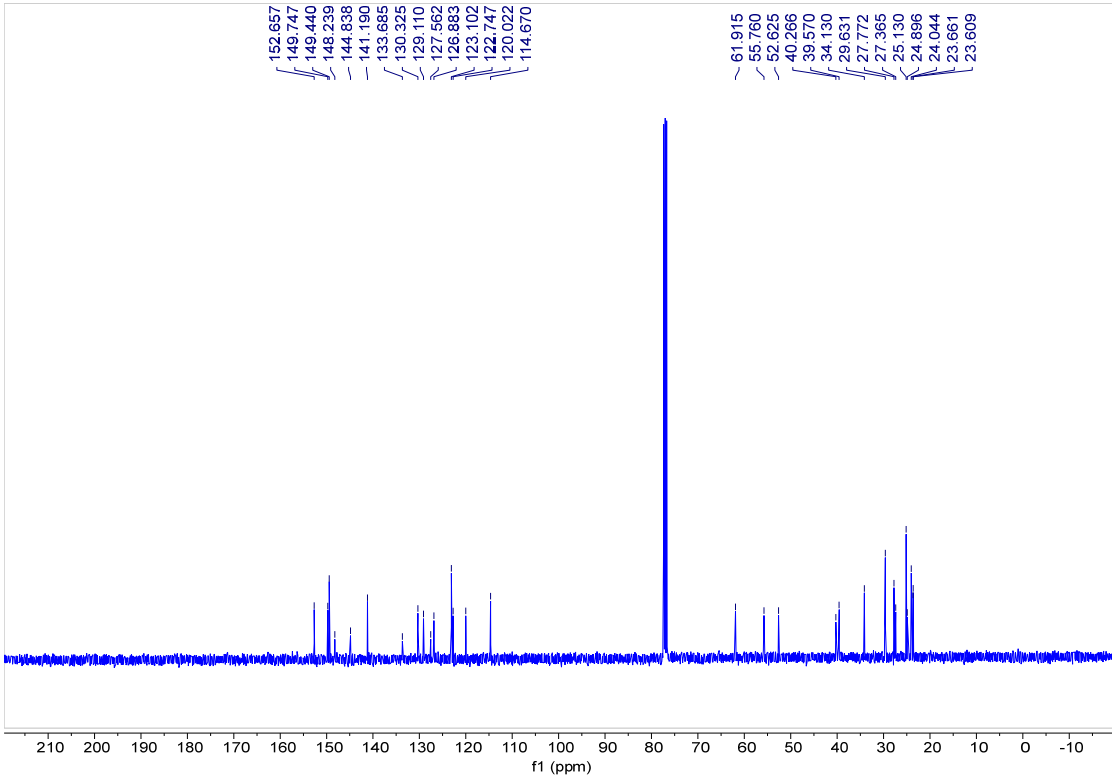
**L8**


8.334
8.330
8.315
8.312
8.121
8.100
7.980
7.977
7.960
7.956
7.562
7.543
7.523
7.430
7.409
7.142
7.138
7.122
7.119
7.104
7.096
7.092
7.084
7.079
7.069
7.033
7.028
7.023
7.012
6.993
6.986
6.982
6.976
6.969
6.814
6.805
6.796
6.790
4.489
4.462
3.644
3.617
2.887
1.582
-0.000
Ph
Ph
Me
N
Me
HN
S
O
O
N
Me
0.98
1.84
1.02
0.99
0.98
5.06
3.05
2.03
1.00
1.00
2.93
6.06
f1 (ppm)


160.212
143.257
140.513
136.474
136.215
132.654
131.507
130.581
129.802
128.076
127.609
127.480
127.430
126.934
126.890
124.575
122.954
73.878
58.358
40.208
25.861
f1 (ppm)

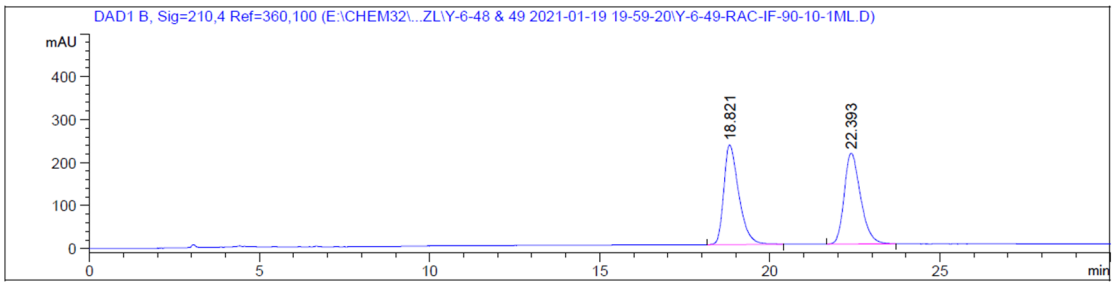
**L9**


8.499
8.488
8.295
8.274
8.073
8.052
7.707
7.687
7.642
7.639
7.621
7.189
7.177
6.899
5.632
5.376
5.350
4.950
4.907
4.882
3.830
3.813
3.797
3.251
3.226
3.217
3.191
2.811
2.794
2.777
2.729
2.721
2.703
2.697
2.692
2.683
2.669
2.662
2.657
2.651
2.269
1.642
1.632
1.622
1.608
1.599
1.590
1.575
1.214
1.203
1.197
1.185
1.048
1.032
0.962
0.944
0.928
0.909
0.766
0.749
0.000
N
iPr
NH
O=S
O
iPr
iPr
N
0.19
1.00
0.22
1.05
1.22
1.01
1.21
0.57
1.01
2.55
1.35
1.10
2.74
0.22
2.64
1.49
1.09
5.02
1.39
4.24
17.53
1.47
1.50
6.64
f1 (ppm)


152.657
149.747
149.440
148.239
144.838
141.190
133.685
130.325
129.110
127.562
126.883
123.102
122.747
120.022
114.670
61.915
55.760
52.625
40.266
39.570
34.130
29.631
27.772
27.365
25.130
24.896
24.044
23.661
23.609
f1 (ppm)

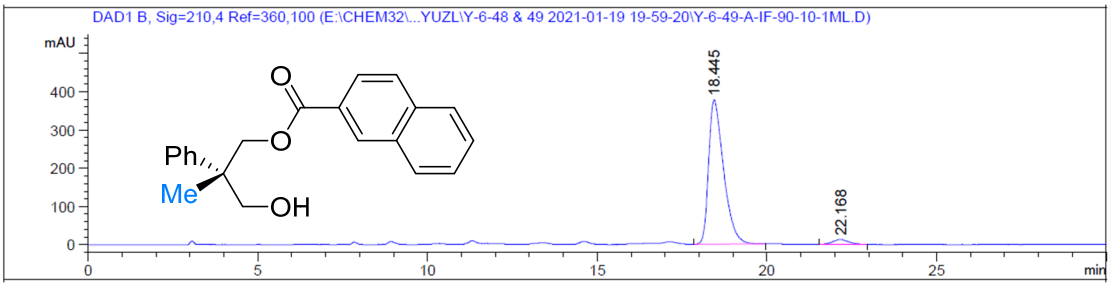
# 11. HPLC spectra

## 1




Signal 2: DAD1 B, Sig=210,4 Ref=360,100

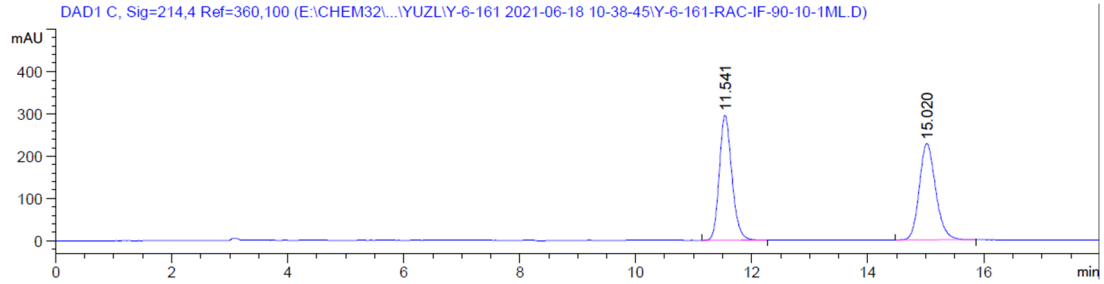
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.821 | BB | 0.4655 | 7092.12402 | 231.46718 | 50.0352 |
| 2 | 22.393 | BB | 0.5045 | 7082.15674 | 211.58578 | 49.9648 |
| Totals : | | | | 1.41743e4 | 443.05296 | |




Signal 2: DAD1 B, Sig=210,4 Ref=360,100

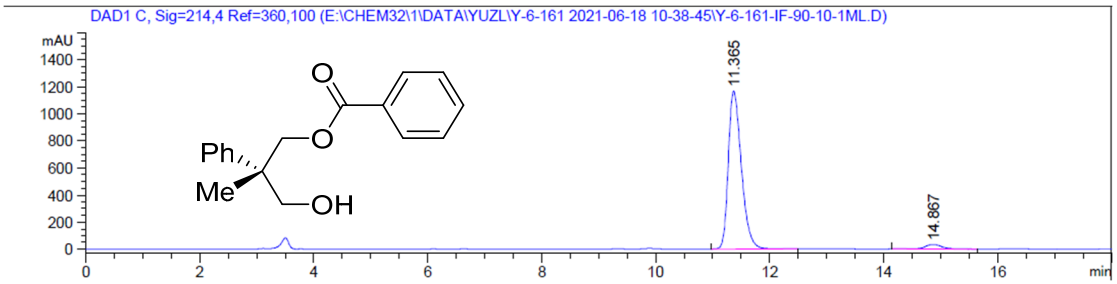
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.445 | BB | 0.4598 | 1.15674e4 | 377.22275 | 96.6831 |
| 2 | 22.168 | BB | 0.4199 | 396.84653 | 12.31530 | 3.3169 |
| Totals : | | | | 1.19643e4 | 389.53805 | |

**2**




Signal 3: DAD1 C, Sig=214,4 Ref=360,100

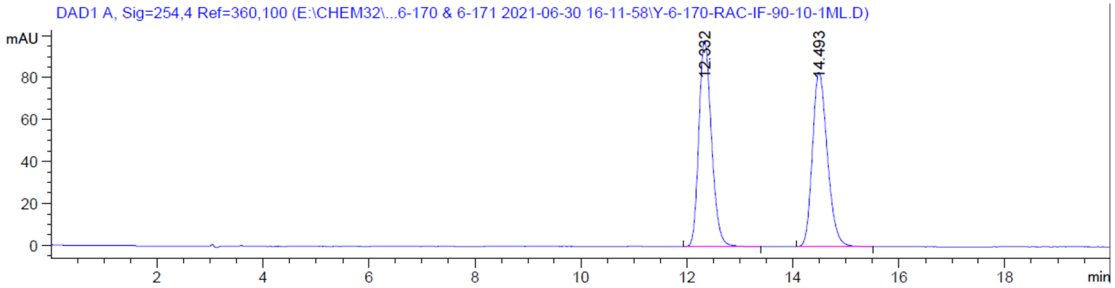
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.541 | BB | 0.2299 | 4450.62988 | 295.17331 | 49.9589 |
| 2 | 15.020 | BB | 0.3024 | 4457.95068 | 227.76067 | 50.0411 |
| Totals : | | | | 8908.58057 | 522.93398 | |




Signal 3: DAD1 C, Sig=214,4 Ref=360,100

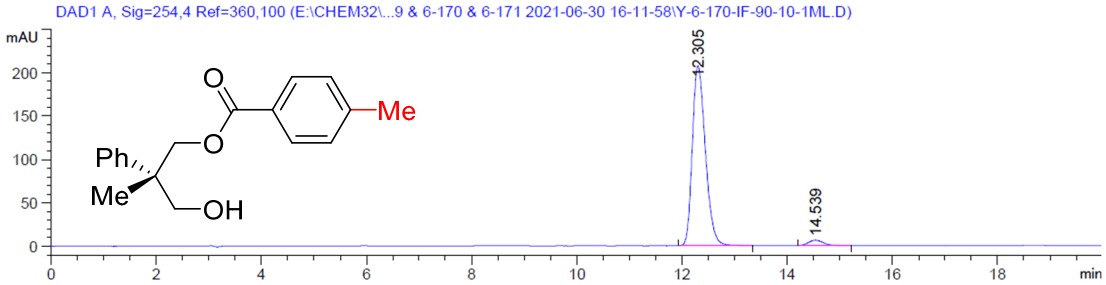
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.365 | BB | 0.2433 | 1.85304e4 | 1166.44739 | 96.2438 |
| 2 | 14.867 | VB R | 0.3011 | 723.20459 | 34.61361 | 3.7562 |
| Totals : | | | | 1.92536e4 | 1201.06099 | |

**3**




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

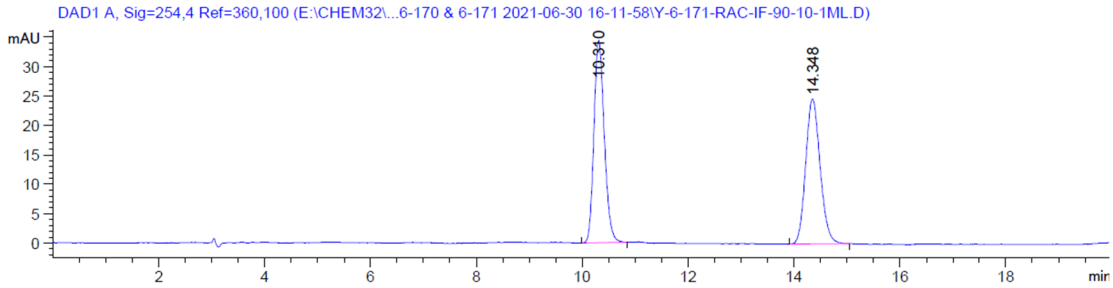
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.332 | BB | 0.2559 | 1633.44995 | 98.27419 | 50.0202 |
| 2 | 14.493 | BB | 0.3051 | 1632.13000 | 83.12865 | 49.9798 |
| Totals : | | | | 3265.57996 | 181.40284 | |




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

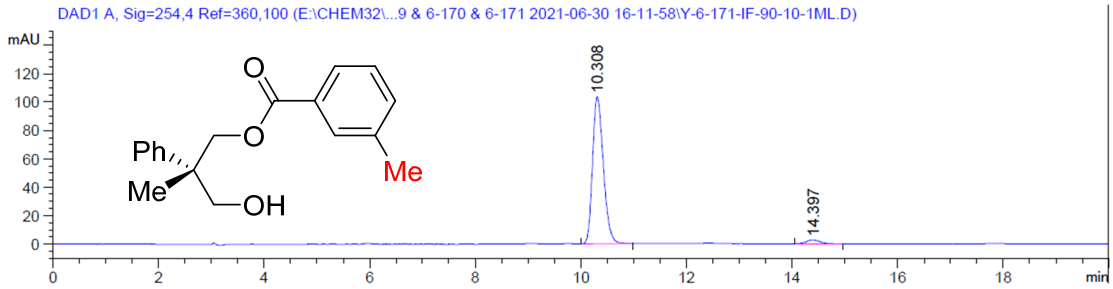
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.305 | BB | 0.2667 | 3563.46313 | 207.09471 | 96.7043 |
| 2 | 14.539 | BB | 0.2756 | 121.44368 | 6.28055 | 3.2957 |
| Totals : | | | | 3684.90681 | 213.37526 | |

**4**




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

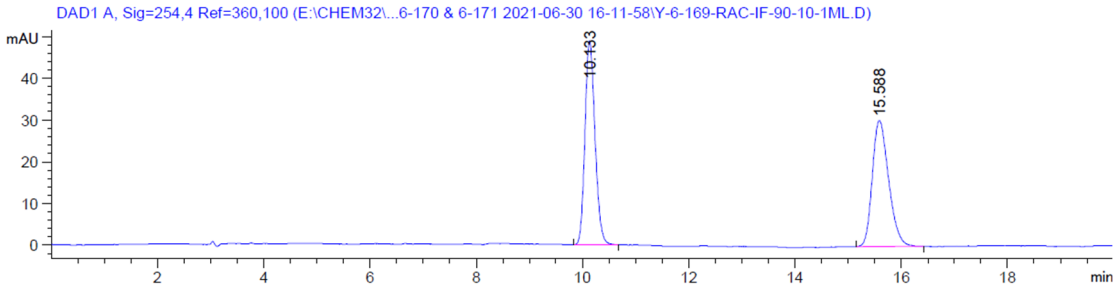
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.310 | BB | 0.2088 | 468.31921 | 34.40042 | 49.9613 |
| 2 | 14.348 | BB | 0.2938 | 469.04407 | 24.66986 | 50.0387 |
| Totals : | | | | 937.36328 | 59.07028 | |




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

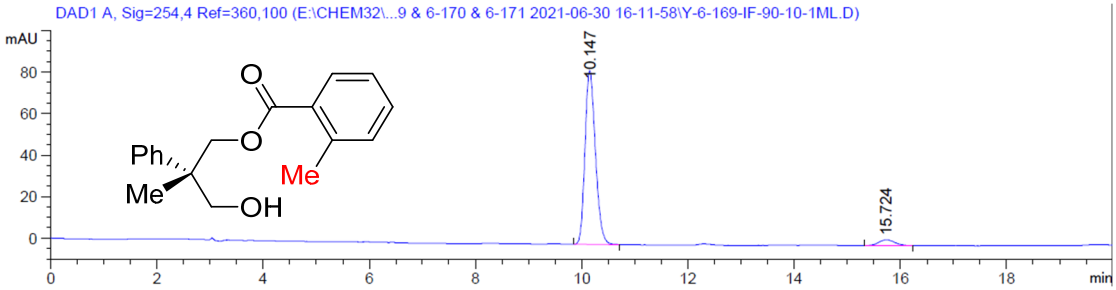
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.308 | BB | 0.2196 | 1467.21558 | 103.37952 | 96.6240 |
| 2 | 14.397 | BB | 0.2439 | 51.26311 | 2.69549 | 3.3760 |
| Totals : | | | | 1518.47869 | 106.07501 | |

**5**




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

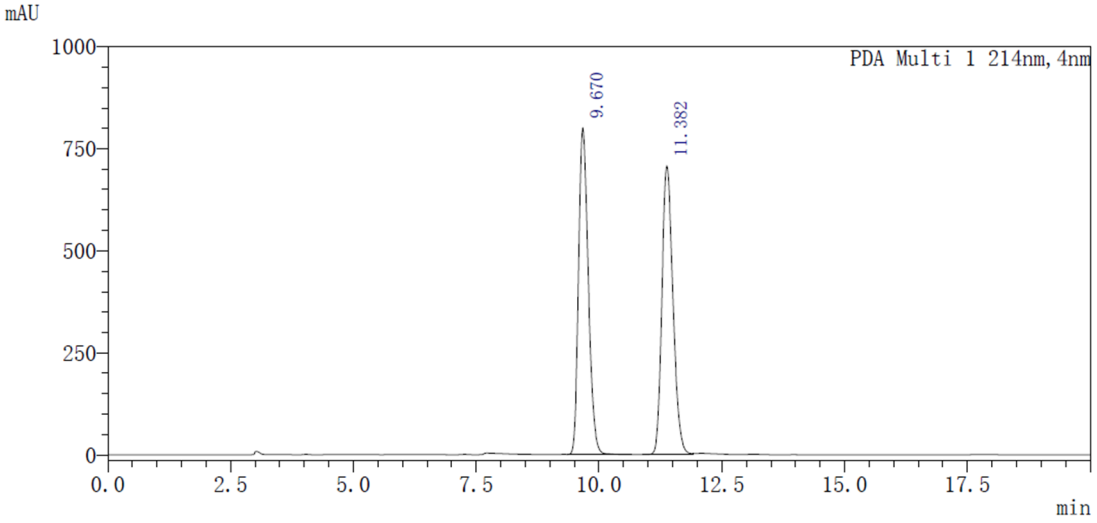
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.133 | BB | 0.2031 | 643.51324 | 49.02430 | 49.8515 |
| 2 | 15.588 | BB | 0.3317 | 647.34808 | 30.23992 | 50.1485 |
| Totals : | | | | 1290.86133 | 79.26421 | |




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

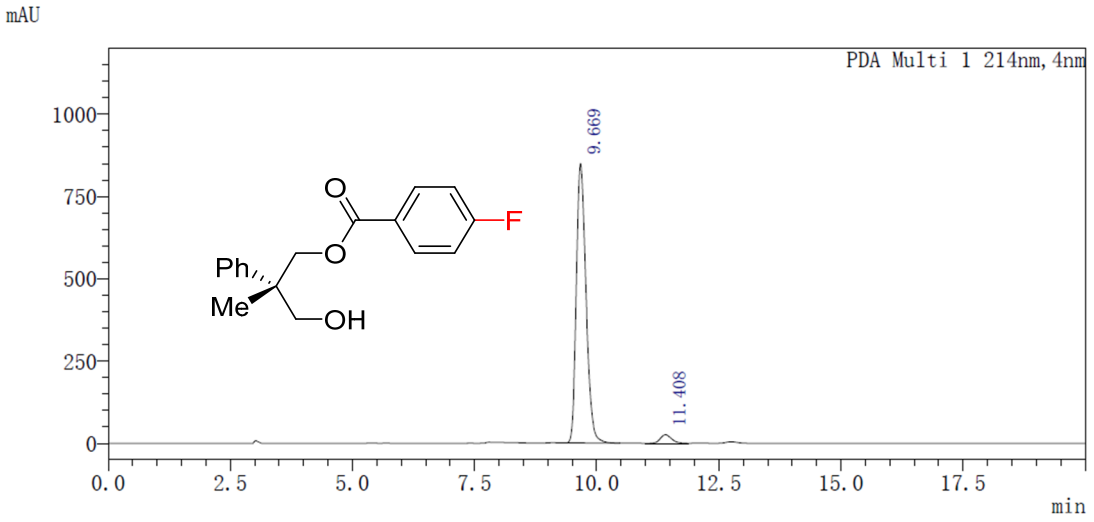
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.147 | BB | 0.2108 | 1137.92139 | 83.59083 | 95.0238 |
| 2 | 15.724 | BB | 0.2672 | 59.59121 | 2.81260 | 4.9762 |
| Totals : | | | | 1197.51260 | 86.40343 | |

**6**




PDA Ch1 214nm

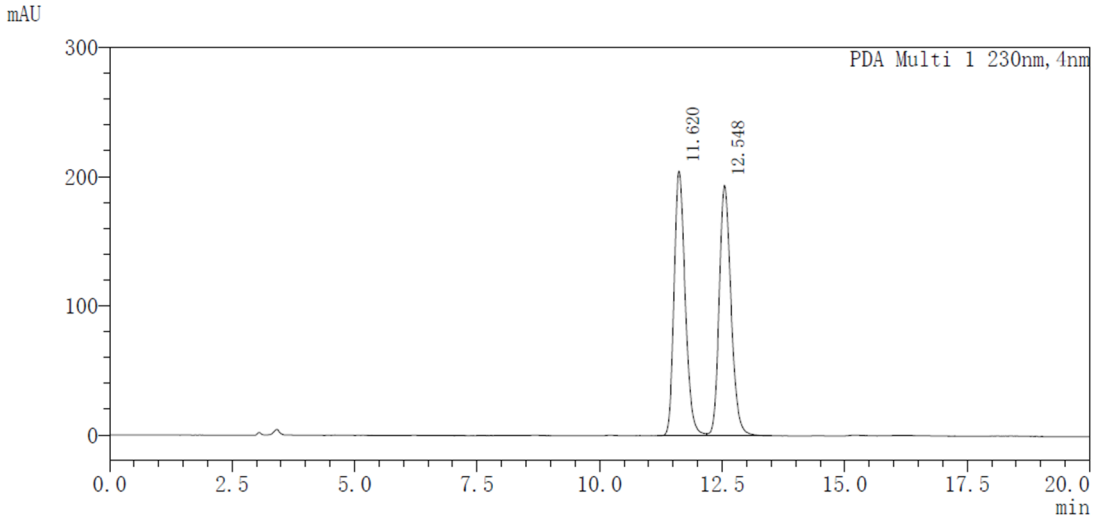
| T | Hight | Area | Area% |
|---|---|---|---|
| 9.670 | 800608 | 11104403 | 50.000 |
| 11.382 | 707456 | 11104442 | 50.000 |




PDA Ch1 214nm

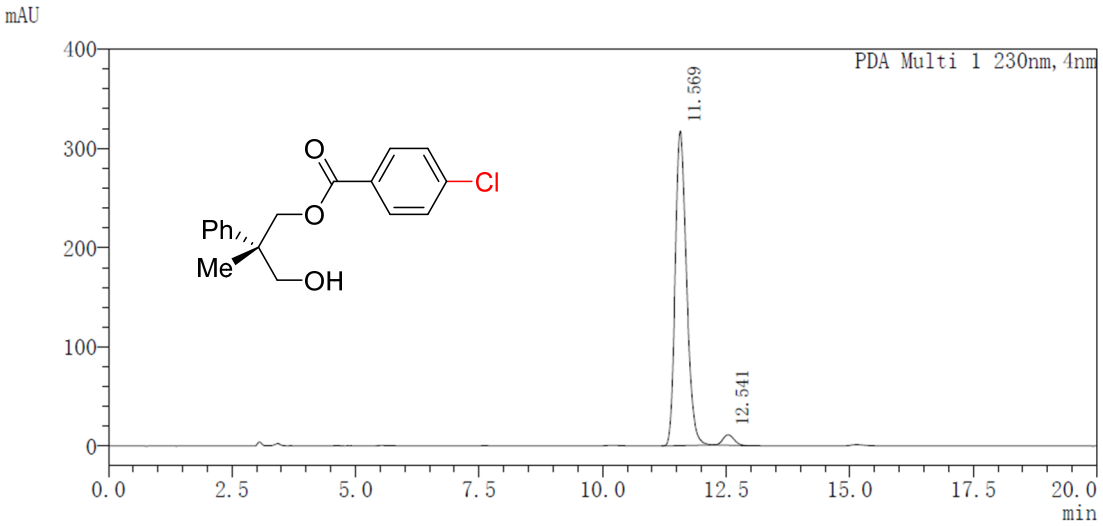
| T | Hight | Area | Area% |
|---|---|---|---|
| 9.669 | 848975 | 11742426 | 96.524 |
| 11.408 | 26290 | 422805 | 3.476 |

**7**




PDA Ch1 230nm

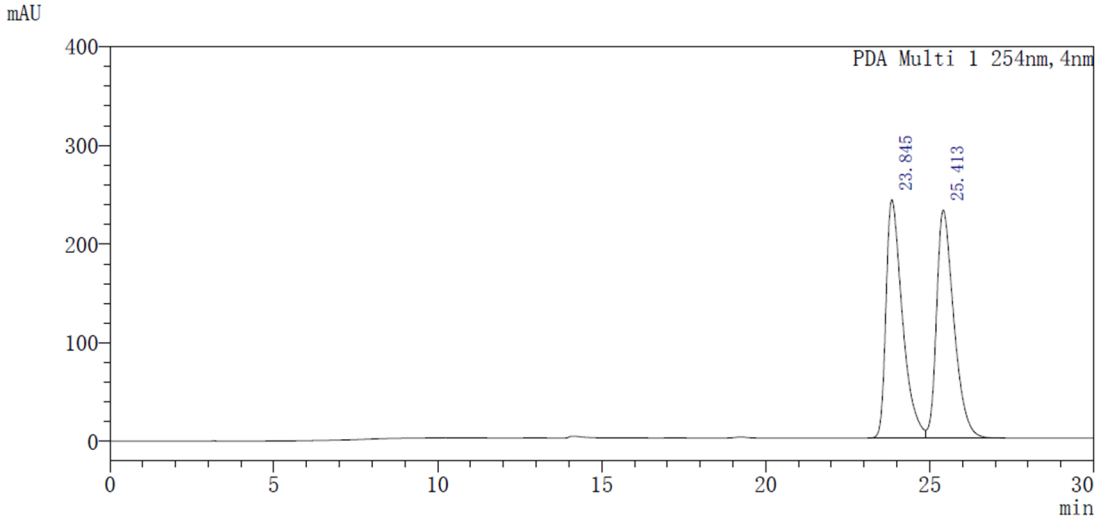
| T | Hight | Area | Area% |
|---|---|---|---|
| 11.620 | 204986 | 3247589 | 49.850 |
| 12.548 | 194003 | 3267154 | 50.150 |




PDA Ch1 230nm

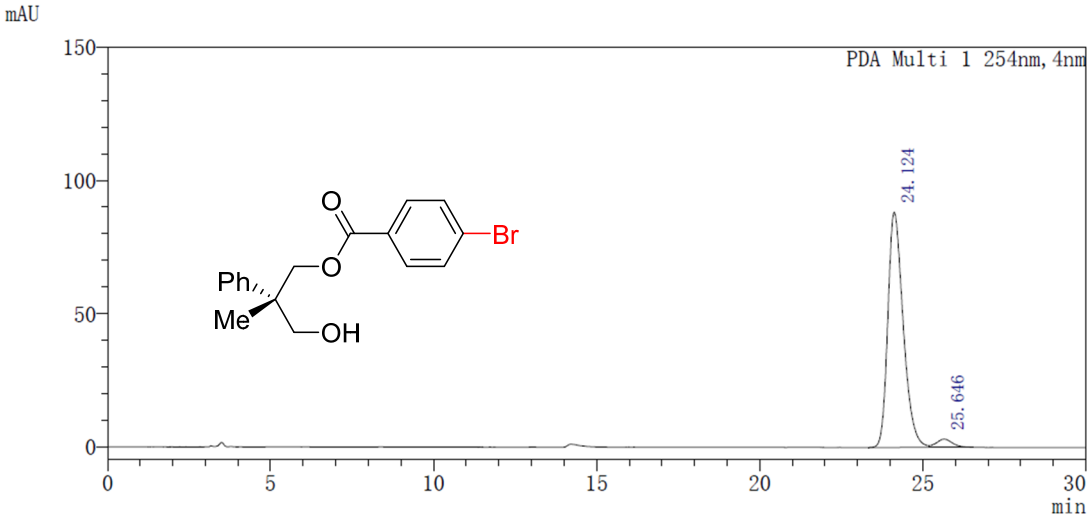
| T | Hight | Area | Area% |
|---|---|---|---|
| 11.569 | 316894 | 5050458 | 96.761 |
| 12.541 | 10654 | 169042 | 3.239 |

**8**




PDA Ch1 254nm

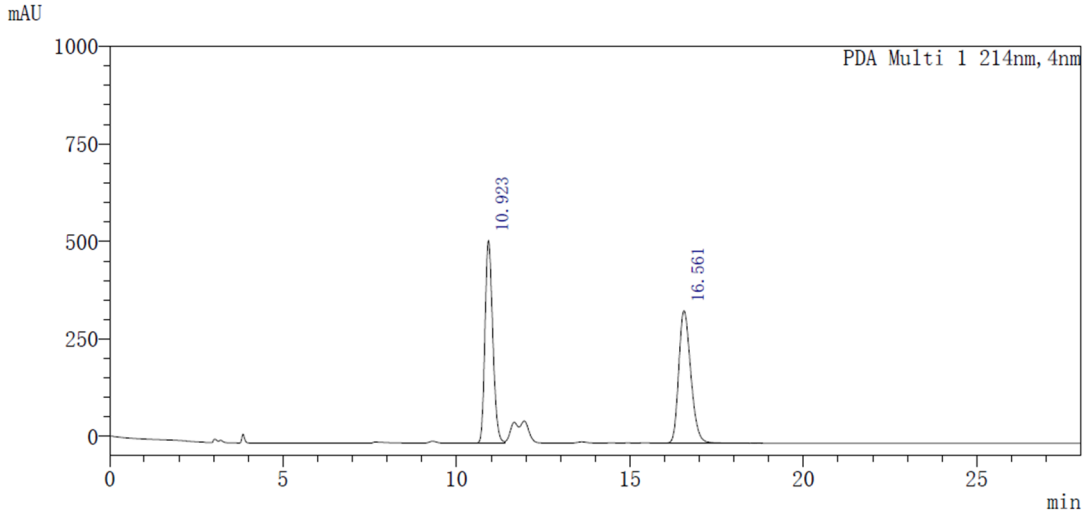
| T | Hight | Area | Area% |
|---|---|---|---|
| 23.845 | 241471 | 8395626 | 49.775 |
| 25.413 | 230947 | 8471453 | 50.225 |




PDA Ch1 254nm

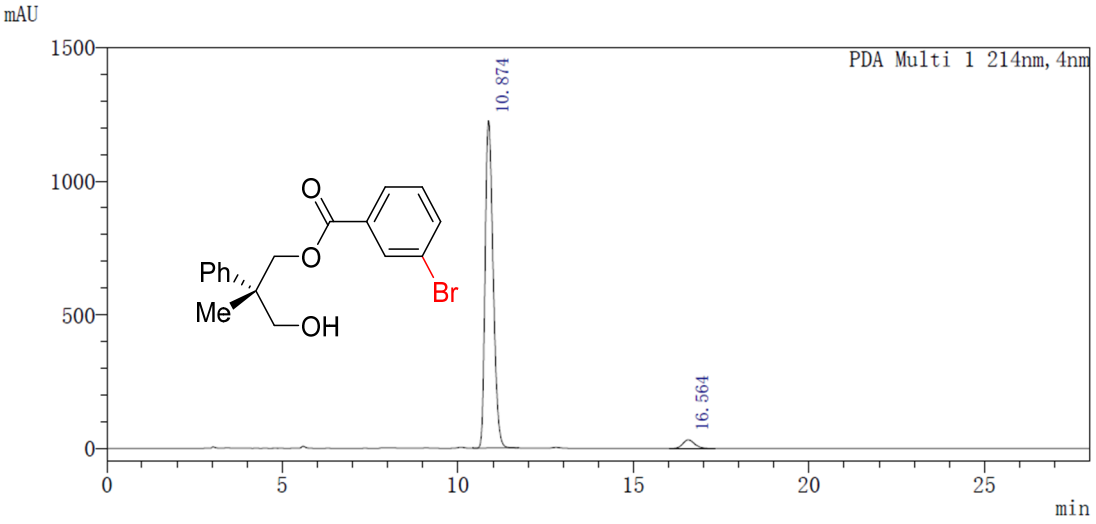
| T | Hight | Area | Area% |
|---|---|---|---|
| 24.124 | 88350 | 2896320 | 96.489 |
| 25.646 | 3064 | 105406 | 3.511 |

**9**




PDA Ch1 214nm

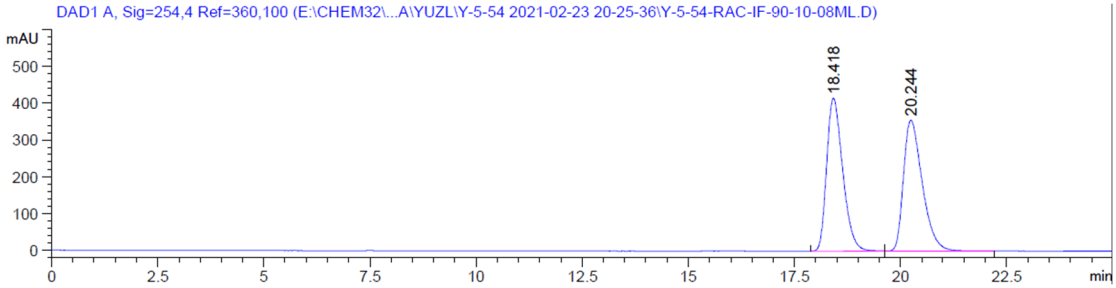
| T | Hight | Area | Area% |
|---|---|---|---|
| 10.923 | 518787 | 8071359 | 49.622 |
| 16.561 | 339622 | 8194453 | 50.378 |




PDA Ch1 214nm

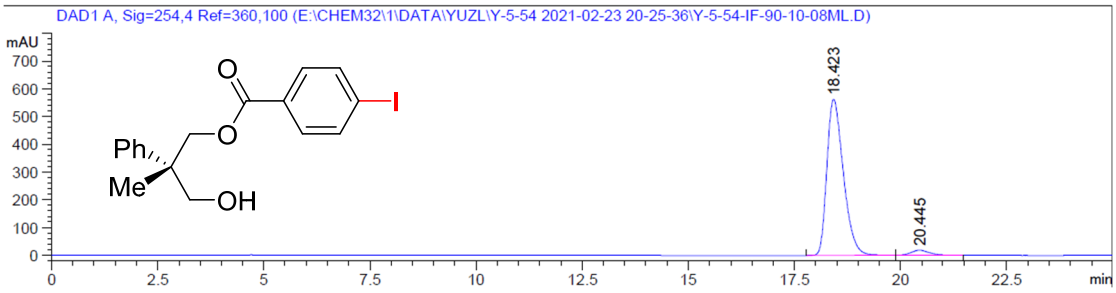
| T | Hight | Area | Area% |
|---|---|---|---|
| 10.874 | 1225796 | 19408993 | 96.331 |
| 16.564 | 31906 | 739198 | 3.669 |

**10**




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

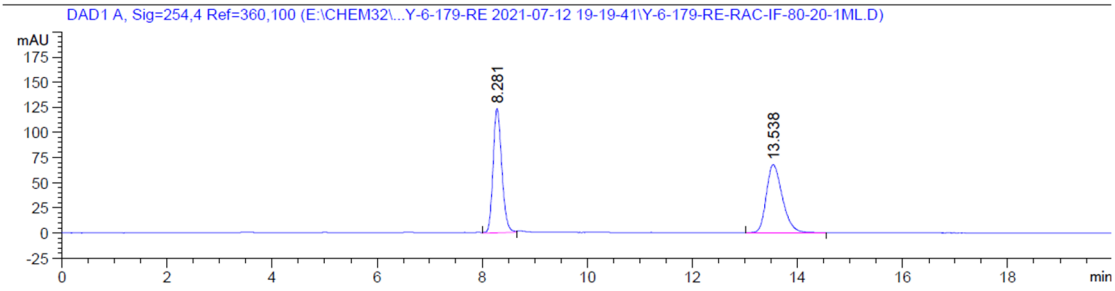
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.418 | BB | 0.4066 | 1.09332e4 | 416.08795 | 49.9579 |
| 2 | 20.244 | BB | 0.4749 | 1.09516e4 | 355.99442 | 50.0421 |
| Totals : | | | | 2.18848e4 | 772.08237 | |




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

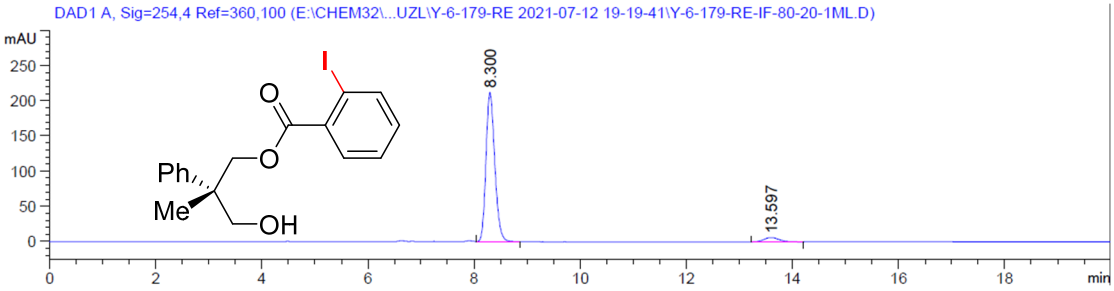
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.423 | BB | 0.4140 | 1.51478e4 | 562.74408 | 96.5879 |
| 2 | 20.445 | BB | 0.4602 | 535.11853 | 17.72374 | 3.4121 |
| Totals : | | | | 1.56829e4 | 580.46782 | |

**11**




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

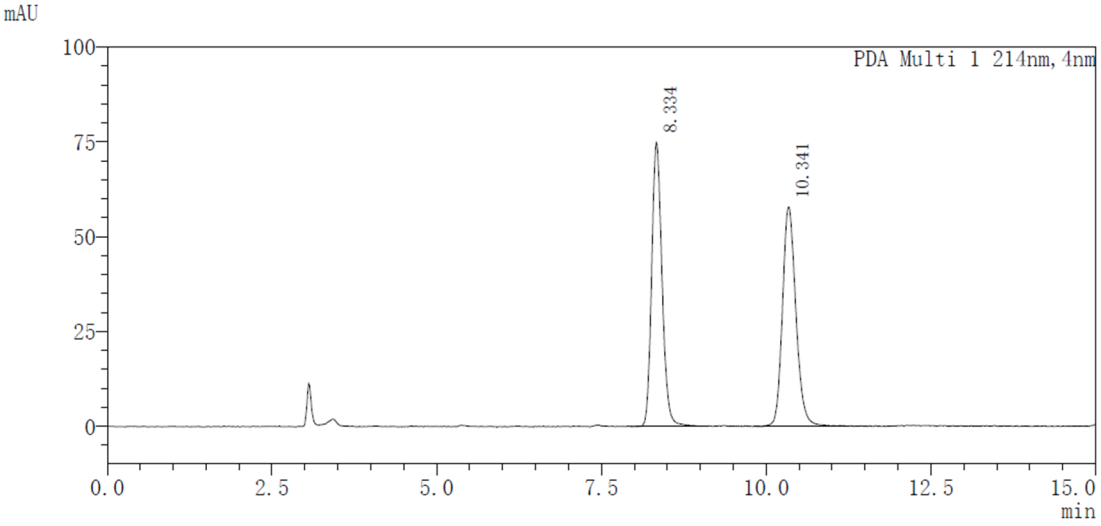
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.281 | MM R | 0.1917 | 1424.37561 | 123.85420 | 49.8840 |
| 2 | 13.538 | BB | 0.3266 | 1431.00183 | 67.69056 | 50.1160 |
| Totals : | | | | 2855.37744 | 191.54476 | |




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

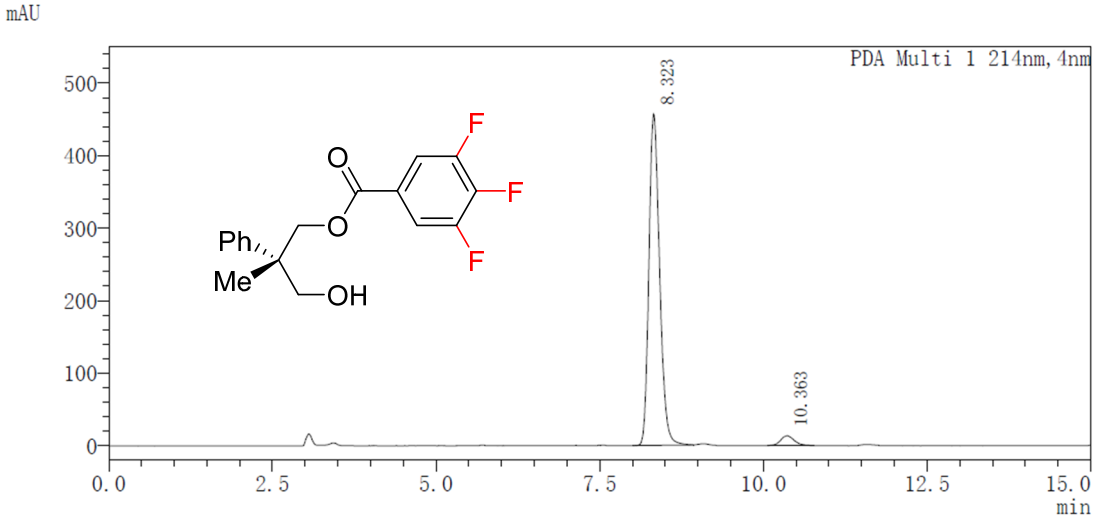
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.300 | FM R | 0.1922 | 2446.06421 | 212.06801 | 95.0871 |
| 2 | 13.597 | BB | 0.2980 | 126.38103 | 6.24697 | 4.9129 |
| Totals : | | | | 2572.44524 | 218.31497 | |

**12**




PDA Ch1 214nm

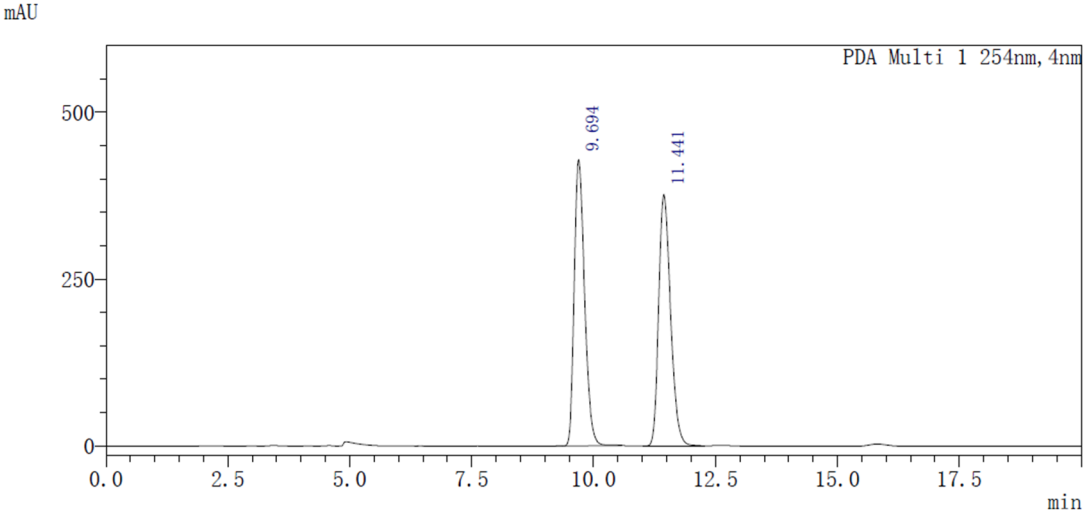
| T | Hight | Area | Area% |
|---|---|---|---|
| 8.334 | 74852 | 814635 | 49.872 |
| 10.341 | 57769 | 818805 | 50.128 |




PDA Ch1 214nm

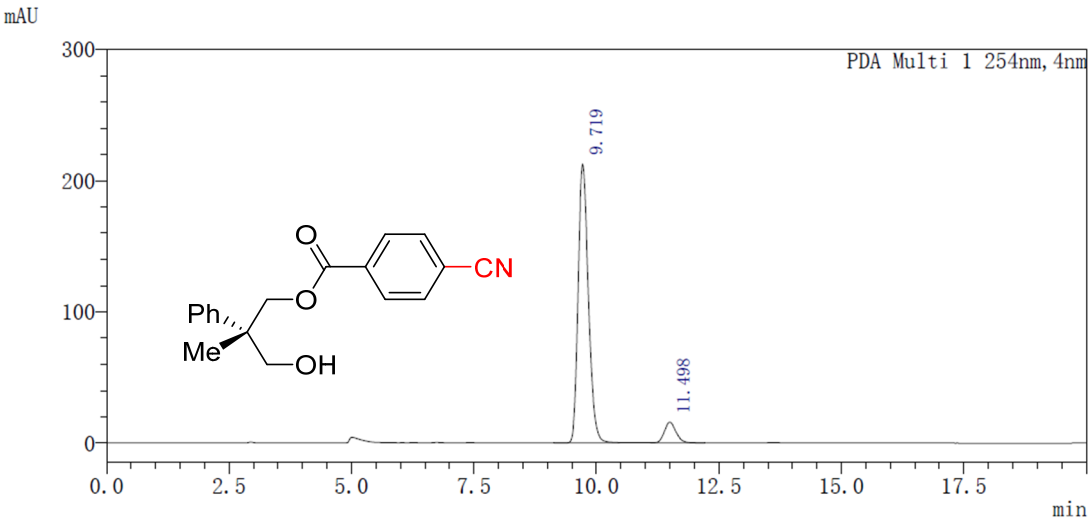
| T | Hight | Area | Area% |
|---|---|---|---|
| 8.323 | 456394 | 5185570 | 96.470 |
| 10.363 | 13394 | 189771 | 3.530 |

**13**




PDA Ch1 254nm

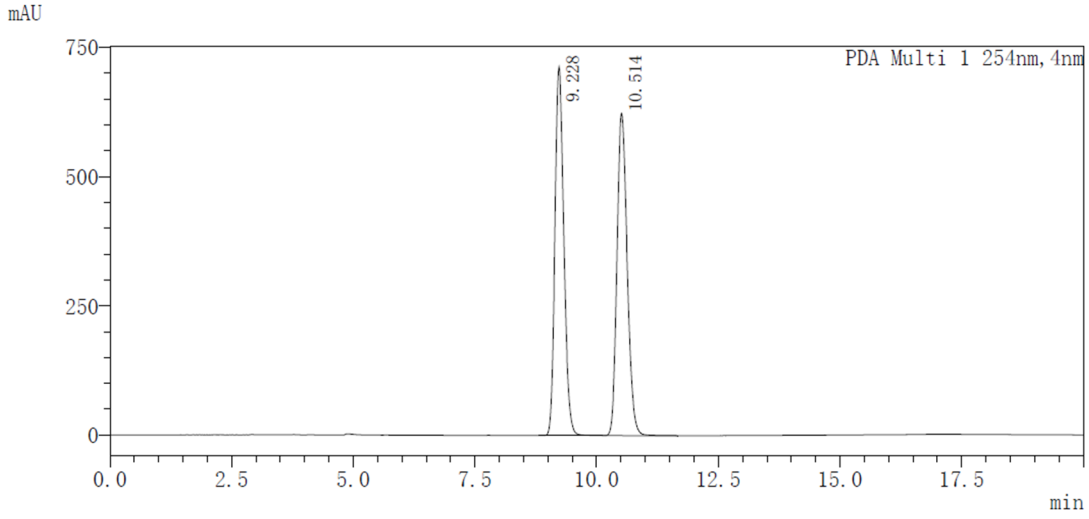
| T | Hight | Area | Area% |
|---|---|---|---|
| 9.694 | 428395 | 6354936 | 49.929 |
| 11.441 | 376365 | 6372902 | 50.071 |




PDA Ch1 254nm

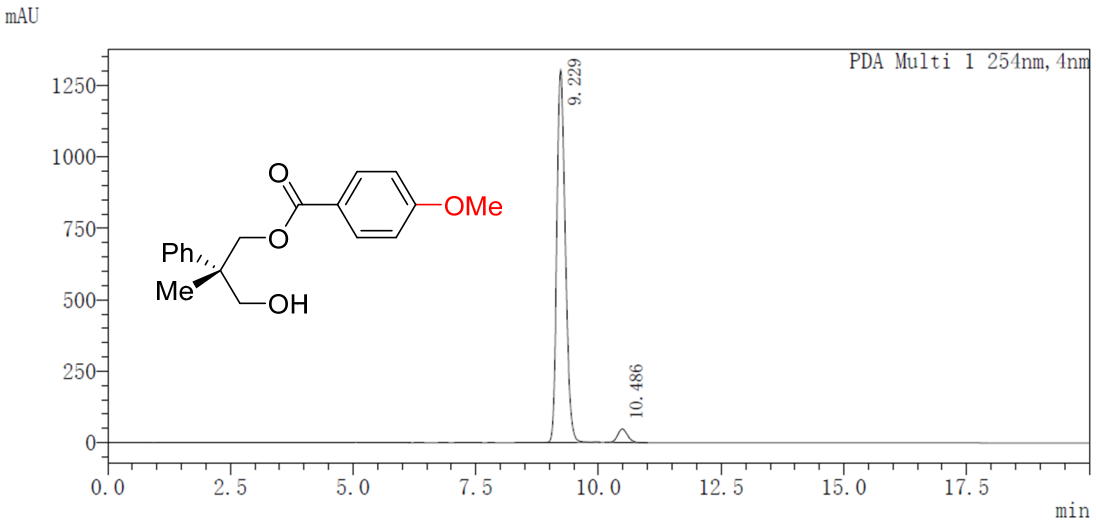
| T | Hight | Area | Area% |
|---|---|---|---|
| 9.719 | 212234 | 3093702 | 92.228 |
| 11.498 | 15740 | 260720 | 7.772 |

**14**




PDA Ch1 254nm

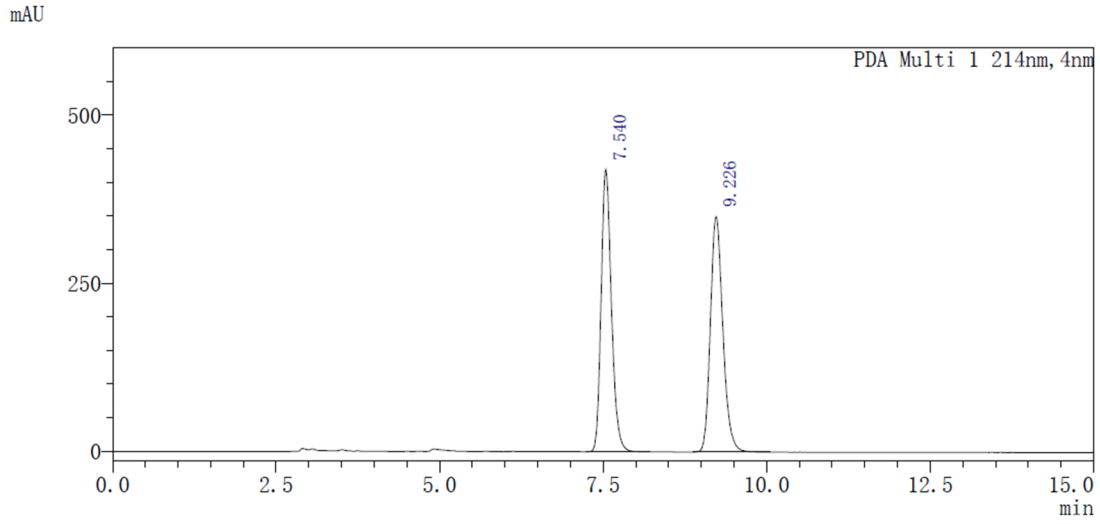
| T | Hight | Area | Area% |
|---|---|---|---|
| 9.228 | 713080 | 9083051 | 49.928 |
| 10.514 | 623293 | 9109180 | 50.072 |




PDA Ch1 254nm

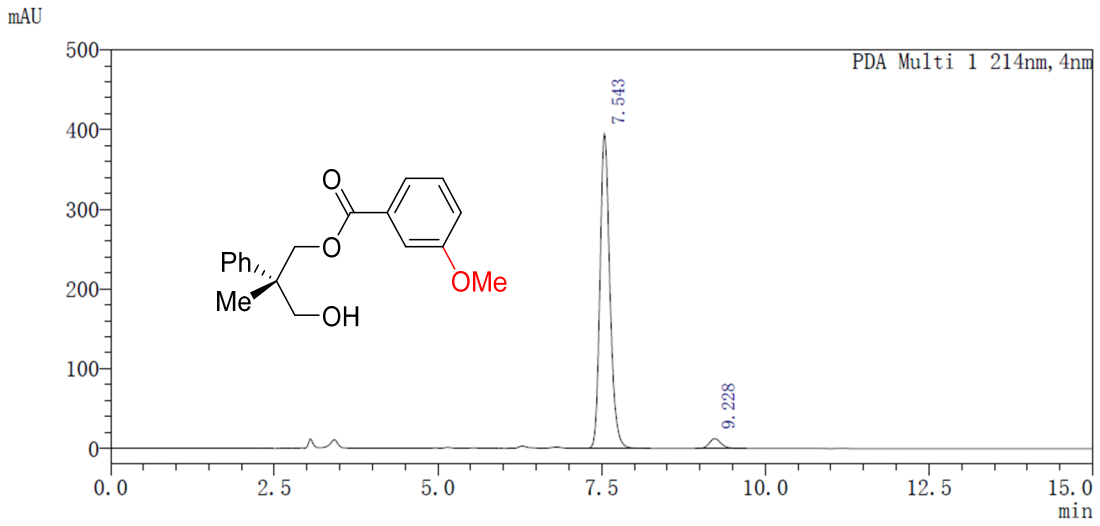
| T | Hight | Area | Area% |
|---|---|---|---|
| 9.229 | 1302355 | 15762771 | 95.976 |
| 10.486 | 47535 | 660855 | 4.024 |

**15**




PDA Ch1 214nm

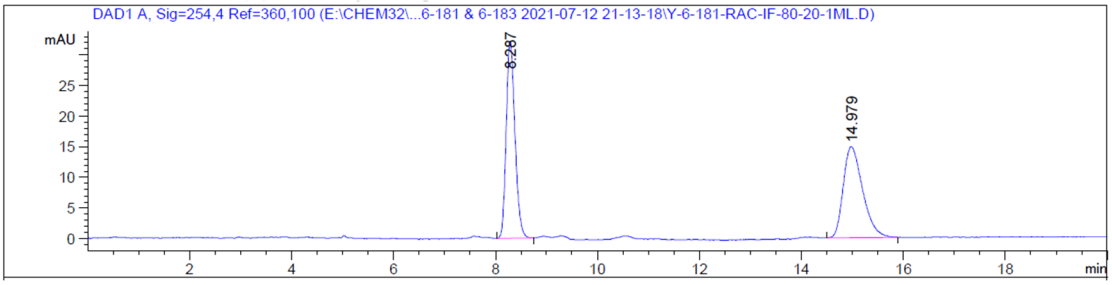
| T | Hight | Area | Area% |
|---|---|---|---|
| 7.540 | 419953 | 4592606 | 49.759 |
| 9.226 | 350293 | 4637014 | 50.241 |




PDA Ch1 214nm

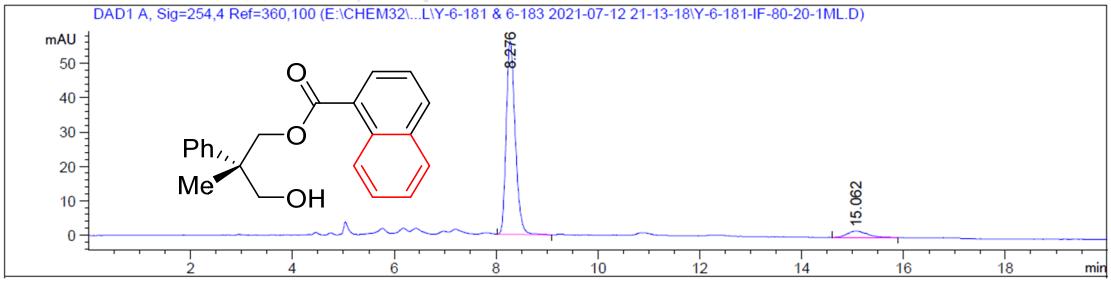
| T | Hight | Area | Area% |
|---|---|---|---|
| 7.543 | 394795 | 4148127 | 96.302 |
| 9.228 | 12581 | 159296 | 3.698 |

**16**




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

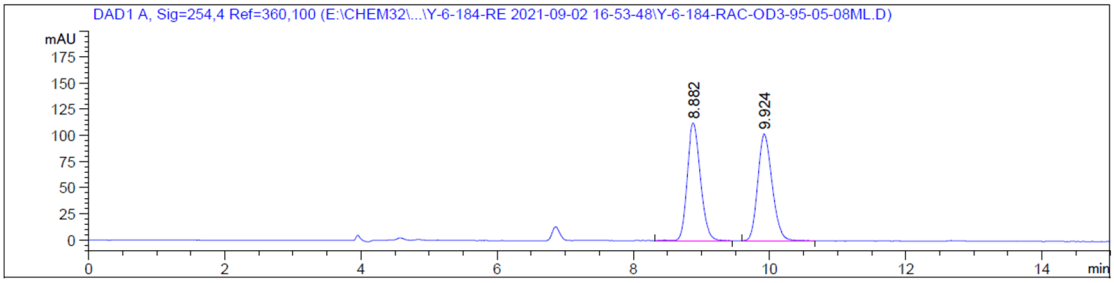
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.287 | BB | 0.1851 | 383.56494 | 32.17307 | 49.4535 |
| 2 | 14.979 | BB | 0.3920 | 392.04233 | 14.84985 | 50.5465 |
| Totals : | | | | 775.60727 | 47.02292 | |




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

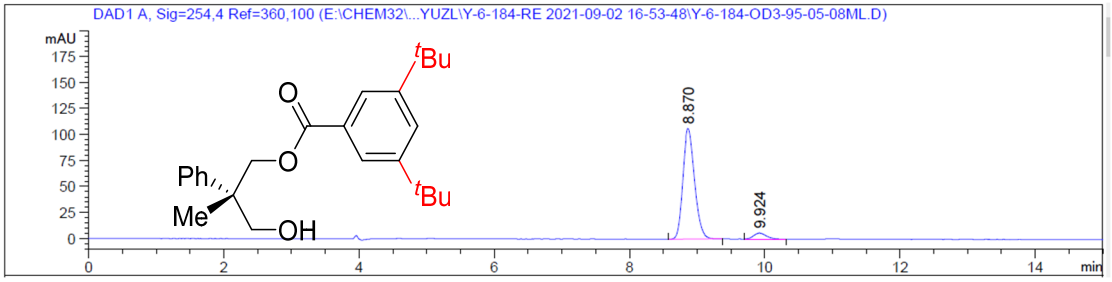
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.276 | BB | 0.1888 | 687.56091 | 56.16941 | 92.6722 |
| 2 | 15.062 | BB | 0.3307 | 54.36721 | 1.96563 | 7.3278 |
| Totals : | | | | 741.92813 | 58.13504 | |

**17**




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

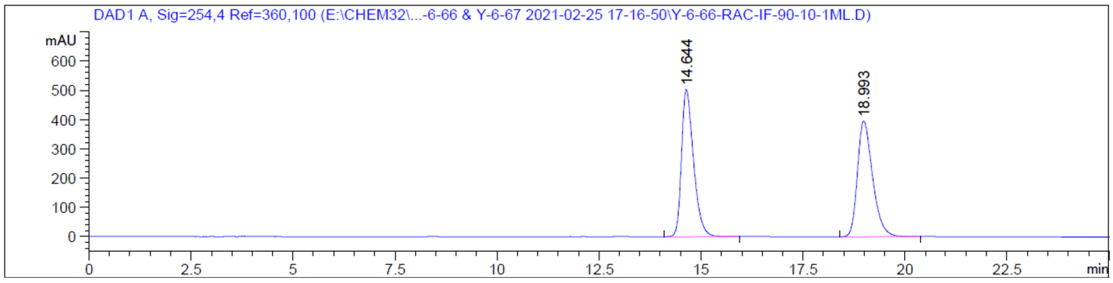
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.882 | VB R | 0.2088 | 1514.27246 | 112.65430 | 50.1301 |
| 2 | 9.924 | BB | 0.2280 | 1506.41003 | 102.15164 | 49.8699 |
| Totals : | | | | 3020.68250 | 214.80595 | |




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

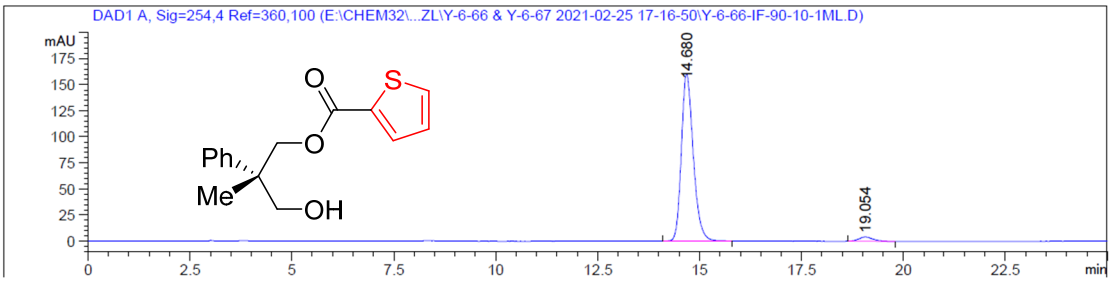
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.870 | BB | 0.1856 | 1276.99780 | 106.72684 | 94.2120 |
| 2 | 9.924 | BB | 0.2069 | 78.45339 | 5.98542 | 5.7880 |
| Totals : | | | | 1355.45119 | 112.71226 | |

**18**




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

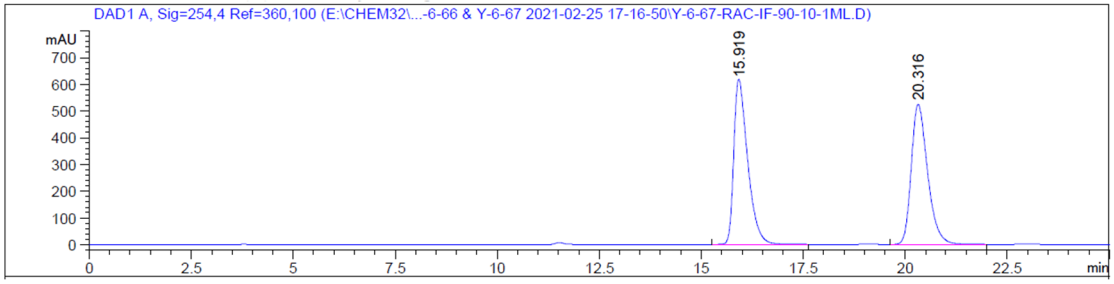
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.644 | BB | 0.3096 | 1.03291e4 | 502.96863 | 50.2244 |
| 2 | 18.993 | BB | 0.3918 | 1.02368e4 | 395.76633 | 49.7756 |
| Totals : | | | | 2.05659e4 | 898.73495 | |




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

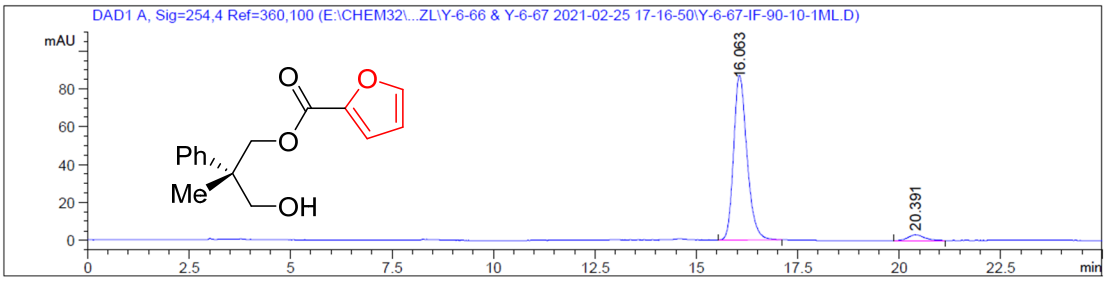
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.680 | BB | 0.3085 | 3250.46704 | 160.35411 | 96.8449 |
| 2 | 19.054 | BB | 0.3265 | 105.89628 | 4.16715 | 3.1551 |
| Totals : | | | | 3356.36332 | 164.52127 | |

**19**




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

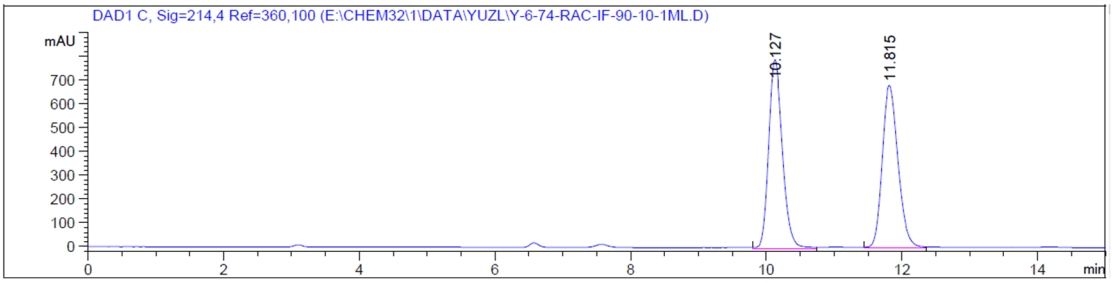
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.919 | BB | 0.3558 | 1.46185e4 | 618.48370 | 49.9666 |
| 2 | 20.316 | BB | 0.4233 | 1.46380e4 | 525.03961 | 50.0334 |
| Totals : | | | | 2.92565e4 | 1143.52332 | |




Signal 1: DAD1 A, Sig=254,4 Ref=360,100

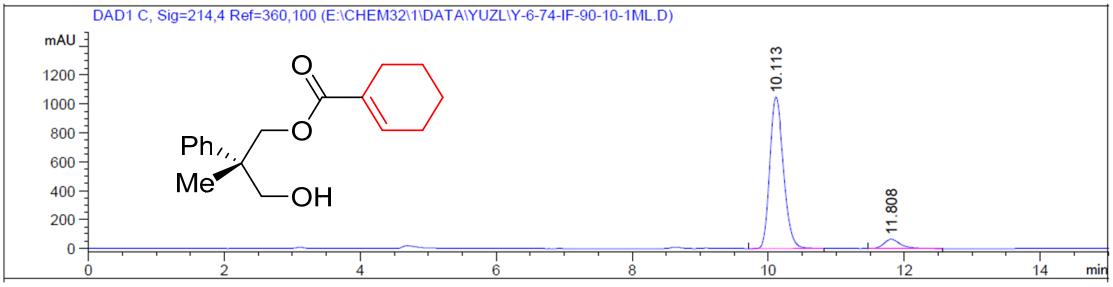
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.063 | BB | 0.3491 | 1994.12415 | 87.11172 | 95.8835 |
| 2 | 20.391 | BB | 0.3370 | 85.61294 | 3.11142 | 4.1165 |
| Totals : | | | | 2079.73708 | 90.22314 | |

**20**




Signal 3: DAD1 C, Sig=214,4 Ref=360,100

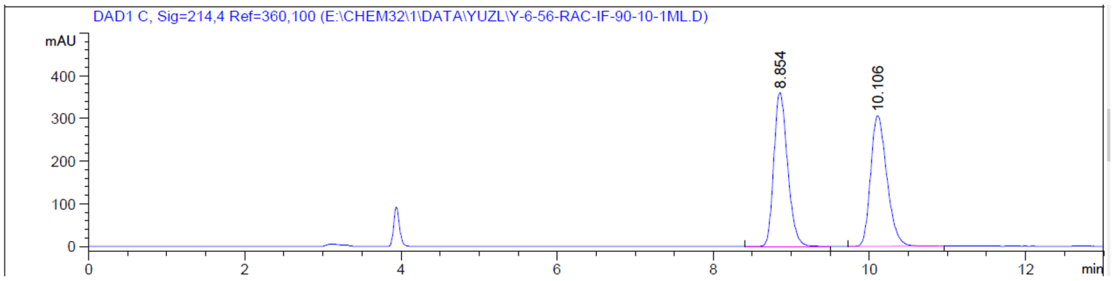
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.127 | MM R | 0.2341 | 1.11544e4 | 794.26135 | 50.2879 |
| 2 | 11.815 | MM R | 0.2690 | 1.10267e4 | 683.19043 | 49.7121 |
| Totals : | | | | 2.21811e4 | 1477.45178 | |




Signal 3: DAD1 C, Sig=214,4 Ref=360,100

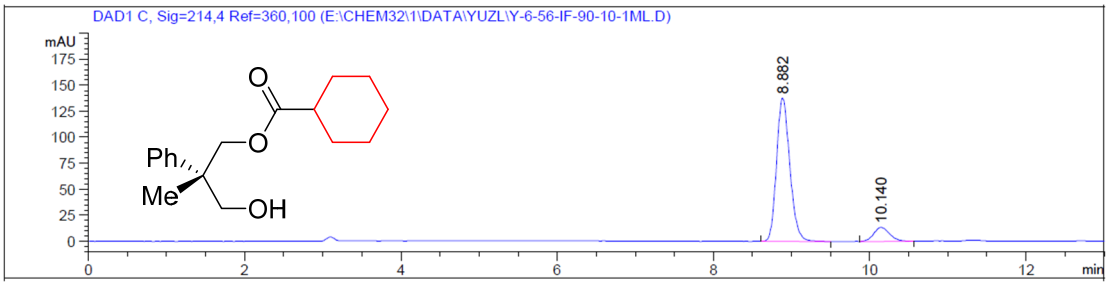
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.113 | BB | 0.2180 | 1.45710e4 | 1049.05383 | 92.9759 |
| 2 | 11.808 | BV R | 0.2550 | 1100.80603 | 65.19671 | 7.0241 |
| Totals : | | | | 1.56718e4 | 1114.25054 | |

**21**




Signal 3: DAD1 C, Sig=214,4 Ref=360,100

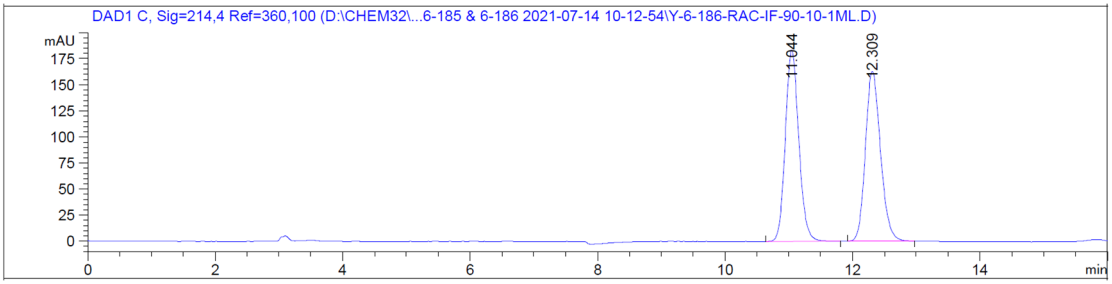
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.854 | BB | 0.1911 | 4417.39697 | 360.19217 | 49.9004 |
| 2 | 10.106 | BV R | 0.2233 | 4435.02246 | 305.69449 | 50.0996 |
| Totals : | | | | 8852.41943 | 665.88666 | |




Signal 3: DAD1 C, Sig=214,4 Ref=360,100

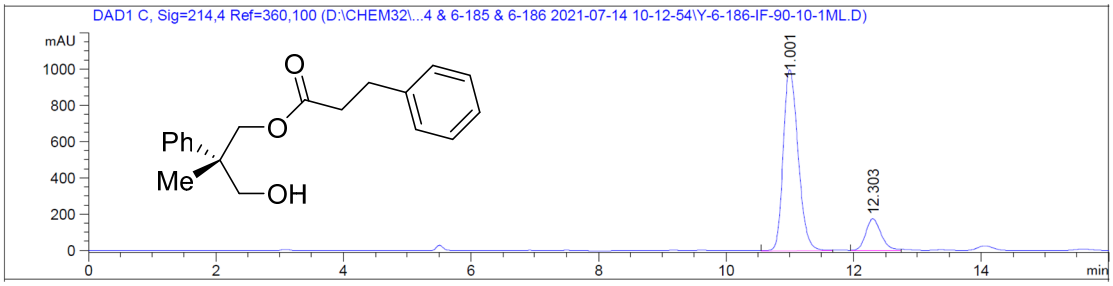
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.882 | BB | 0.1819 | 1631.71301 | 138.05721 | 89.5252 |
| 2 | 10.140 | BB | 0.2215 | 190.91646 | 13.45651 | 10.4748 |
| Totals : | | | | 1822.62947 | 151.51372 | |

## SP-1




Signal 3: DAD1 C, Sig=214,4 Ref=360,100

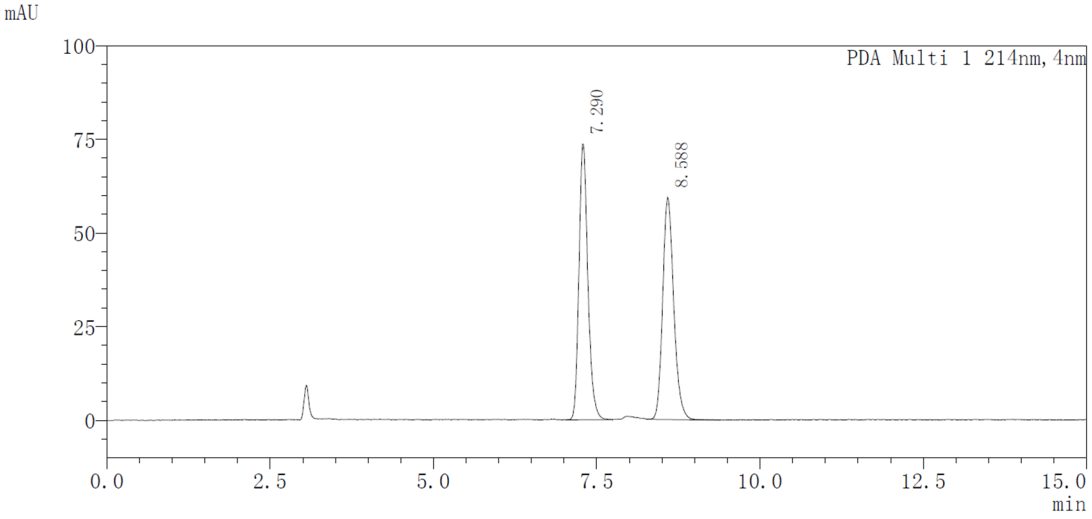
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.044 | BV R | 0.2270 | 2690.99194 | 183.58548 | 50.1247 |
| 2 | 12.309 | BB | 0.2538 | 2677.60352 | 162.88426 | 49.8753 |
| Totals : | | | | 5368.59546 | 346.46974 | |




Signal 3: DAD1 C, Sig=214,4 Ref=360,100

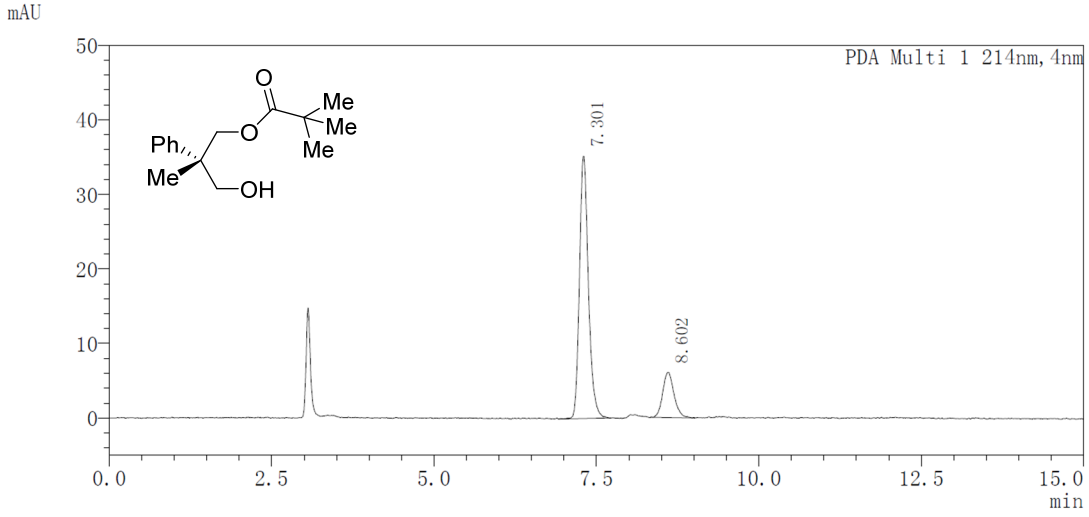
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.001 | MM R | 0.2701 | 1.61704e4 | 997.82214 | 84.5188 |
| 2 | 12.303 | MF R | 0.2829 | 2961.90503 | 174.50294 | 15.4812 |
| Totals : | | | | 1.91323e4 | 1172.32509 | |

SP-2




PDA Ch1 214nm

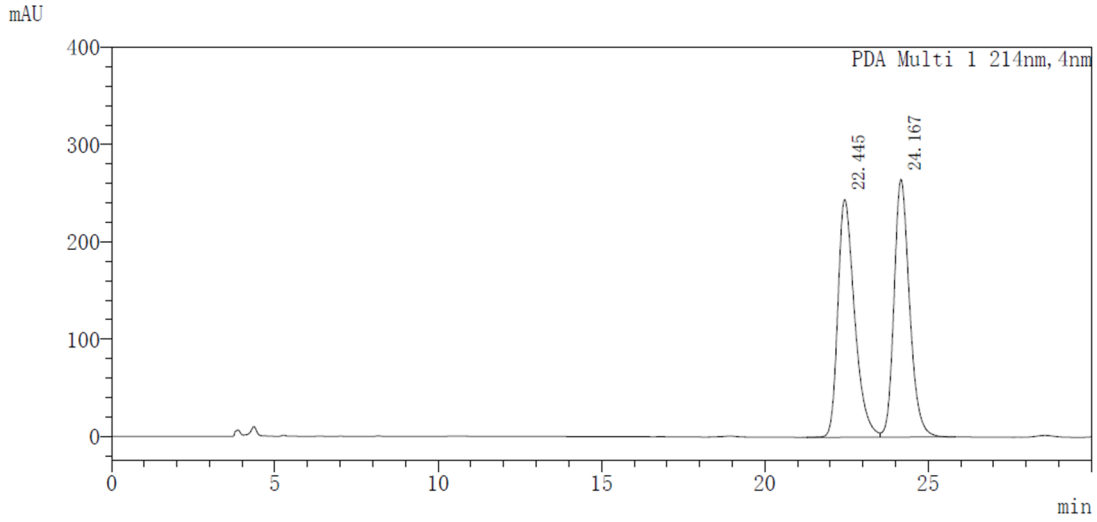
| T | Hight | Area | Area% |
|---|---|---|---|
| 7.290 | 73626 | 699825 | 50.055 |
| 8.588 | 59290 | 698280 | 49.945 |




PDA Ch1 214nm

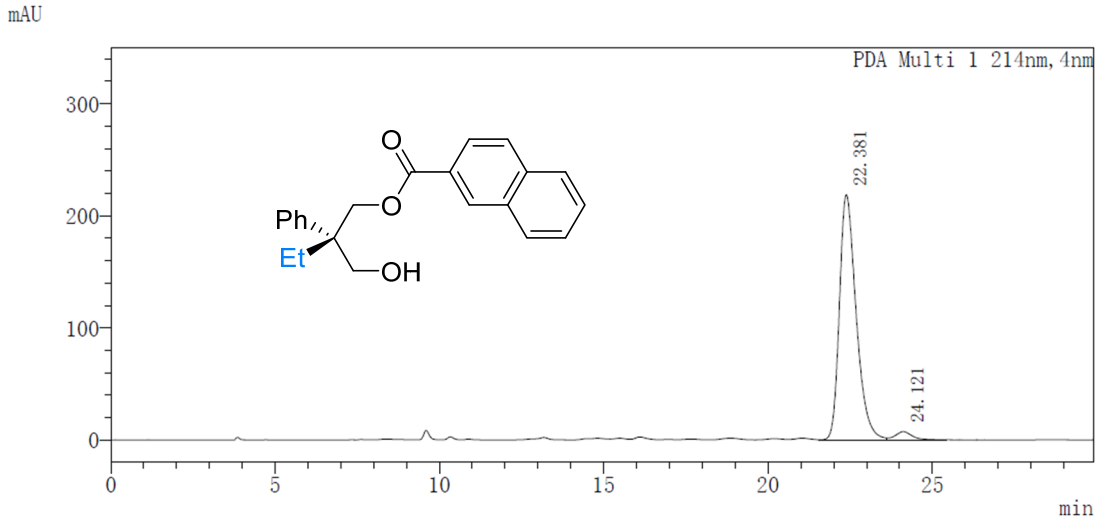
| T | Hight | Area | Area% |
|---|---|---|---|
| 7.301 | 35189 | 337024 | 82.256 |
| 8.602 | 6055 | 72701 | 17.744 |

**22**




PDA Ch1 214nm

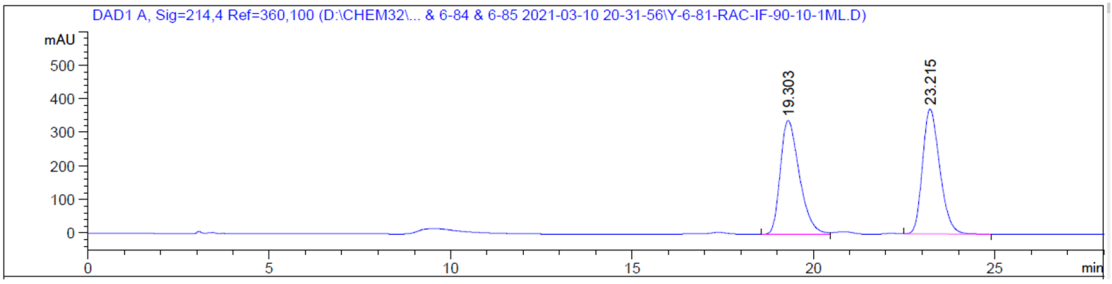
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 22.445 | 8740266 | 49.983 |
| 2 | 24.167 | 8746249 | 50.017 |




PDA Ch1 214nm

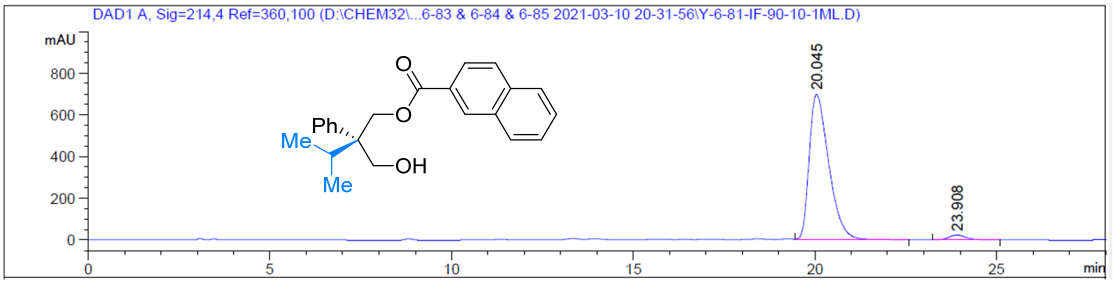
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 22.381 | 7716968 | 96.738 |
| 2 | 24.121 | 260185 | 3.262 |

**23**




Signal 1: DAD1 A, Sig=214,4 Ref=360,100

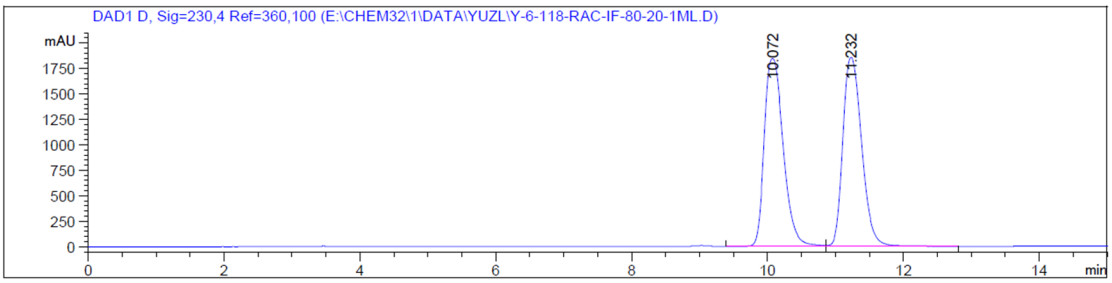
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 19.303 | BV | 0.5639 | 1.24636e4 | 339.83795 | 50.2714 |
| 2 | 23.215 | BB | 0.5127 | 1.23291e4 | 371.94122 | 49.7286 |
| Totals : | | | | 2.47927e4 | 711.77917 | |



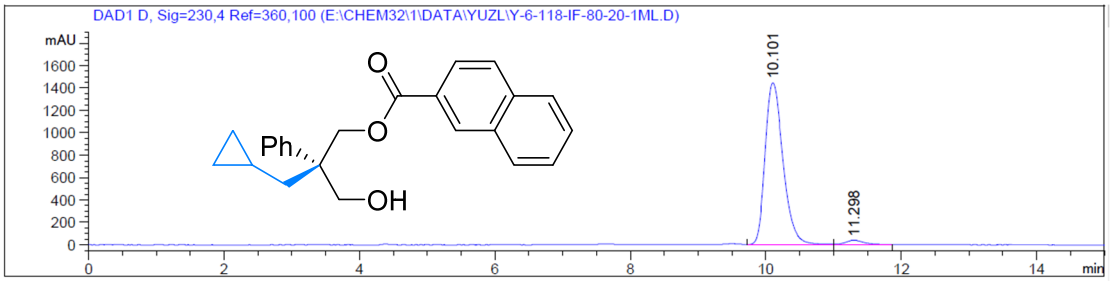

Signal 1: DAD1 A, Sig=214,4 Ref=360,100

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 20.045 | VB | 0.5732 | 2.60245e4 | 697.69598 | 97.2829 |
| 2 | 23.908 | BB | 0.4886 | 726.85822 | 22.87988 | 2.7171 |
| Totals : | | | | 2.67514e4 | 720.57586 | |

**24**



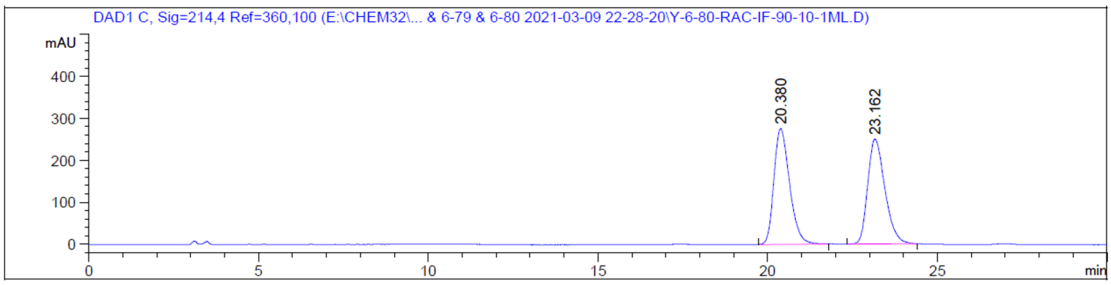

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.072 | VV R | 0.3001 | 3.57526e4 | 1843.69702 | 50.0188 |
| 2 | 11.232 | VB | 0.3005 | 3.57257e4 | 1856.78235 | 49.9812 |




Signal 4: DAD1 D, Sig=230,4 Ref=360,100

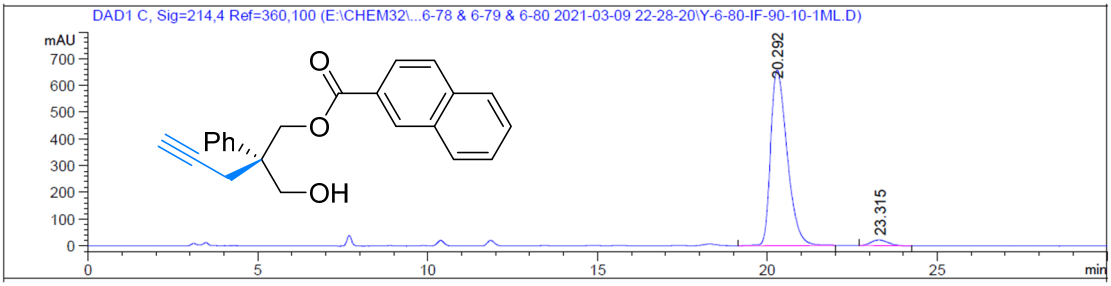
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.101 | MM R | 0.3047 | 2.64277e4 | 1445.55627 | 97.4091 |
| 2 | 11.298 | MM R | 0.3085 | 702.93396 | 37.96986 | 2.5909 |
| Totals : | | | | 2.71306e4 | 1483.52613 | |

**25**




Signal 3: DAD1 C, Sig=214,4 Ref=360,100

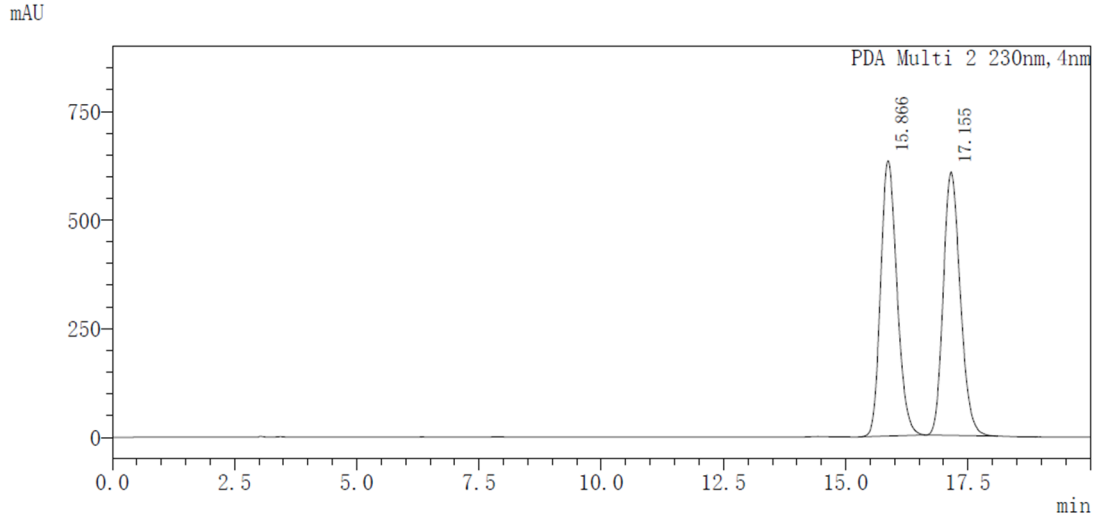
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 20.380 | BB | 0.4851 | 8813.44336 | 275.55588 | 50.0630 |
| 2 | 23.162 | BB | 0.5313 | 8791.27344 | 249.36247 | 49.9370 |
| Totals : | | | | 1.76047e4 | 524.91835 | |




Signal 3: DAD1 C, Sig=214,4 Ref=360,100

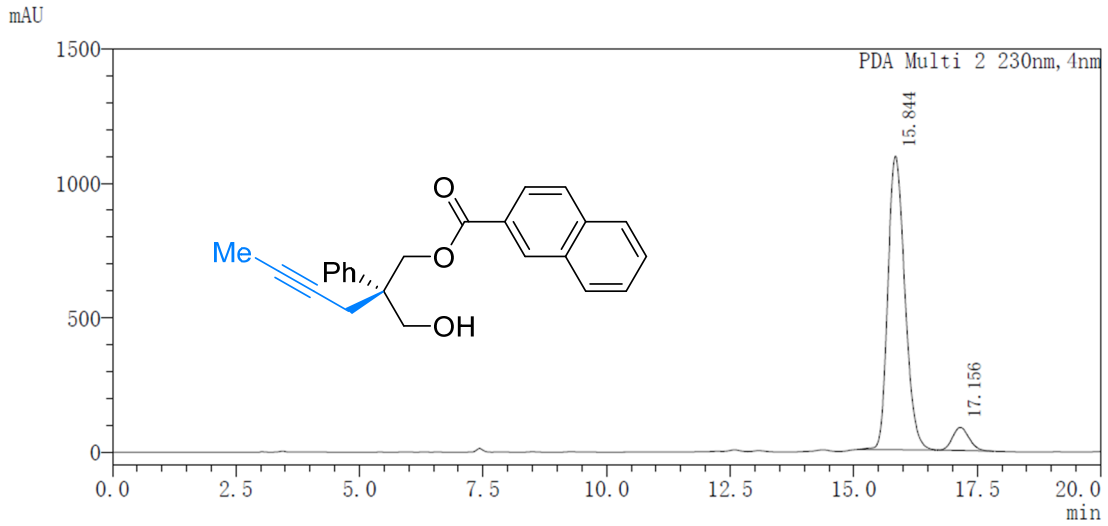
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 20.292 | VV R | 0.5152 | 2.21312e4 | 656.69611 | 96.7152 |
| 2 | 23.315 | BB | 0.4211 | 751.65027 | 21.54066 | 3.2848 |
| Totals : | | | | 2.28828e4 | 678.23677 | |

**26**




PDA Ch2 230nm

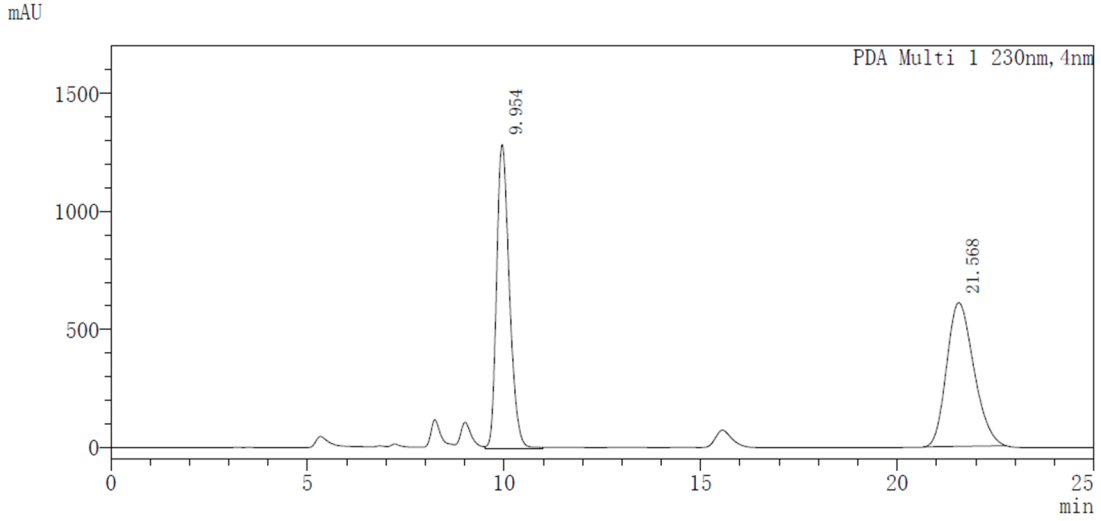
| T | Hight | Area | Area% |
|---|---|---|---|
| 15.866 | 633647 | 14761282 | 50.068 |
| 17.155 | 606099 | 14721154 | 49.932 |




PDA Ch2 230nm

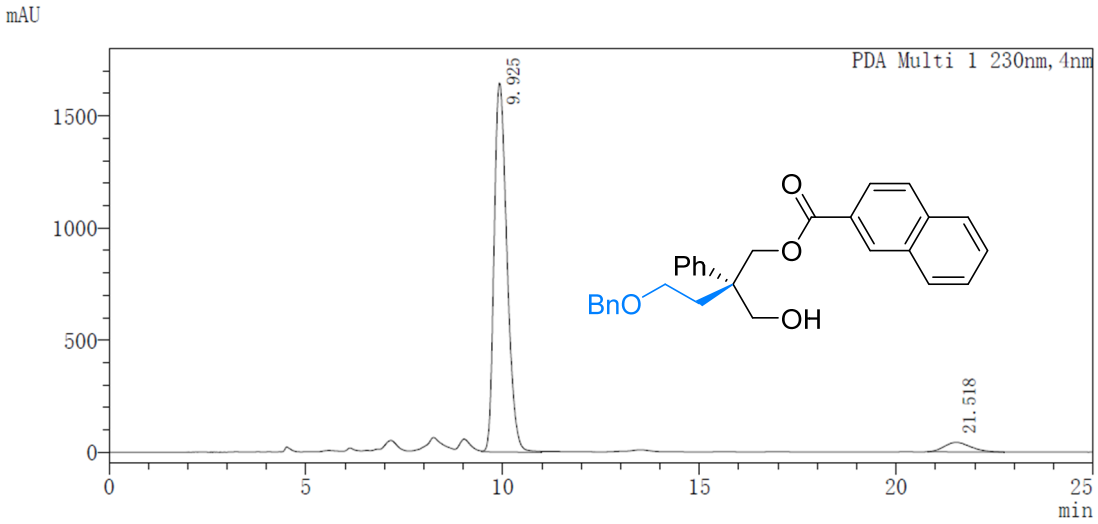
| T | Hight | Area | Area% |
|---|---|---|---|
| 15.844 | 1092614 | 26135304 | 92.868 |
| 17.156 | 86230 | 2006990 | 7.132 |

**27**




PDA Ch1 230nm

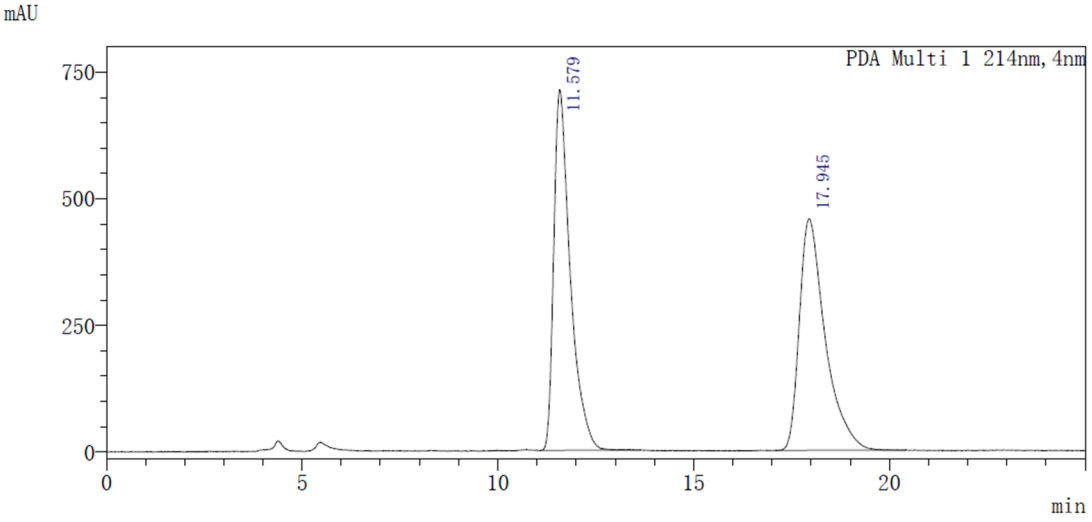
| T | Hight | Area | Area% |
|---|---|---|---|
| 9.954 | 1285251 | 29108389 | 49.853 |
| 21.568 | 608386 | 29279890 | 50.147 |




PDA Ch1 230nm

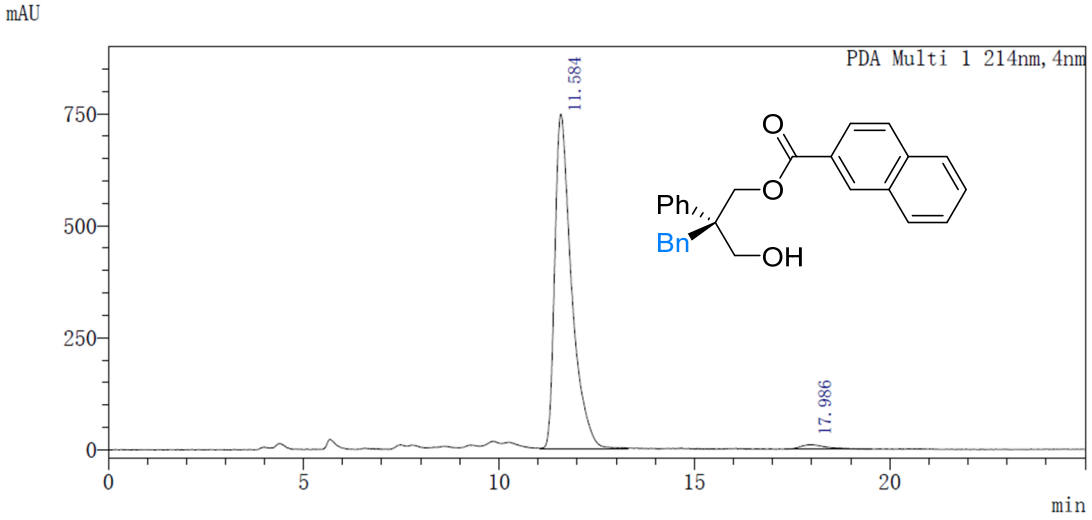
| T | Hight | Area | Area% |
|---|---|---|---|
| 9.925 | 1645528 | 37490793 | 94.990 |
| 21.518 | 42219 | 1977346 | 5.010 |

**28**




PDA Ch1 214nm

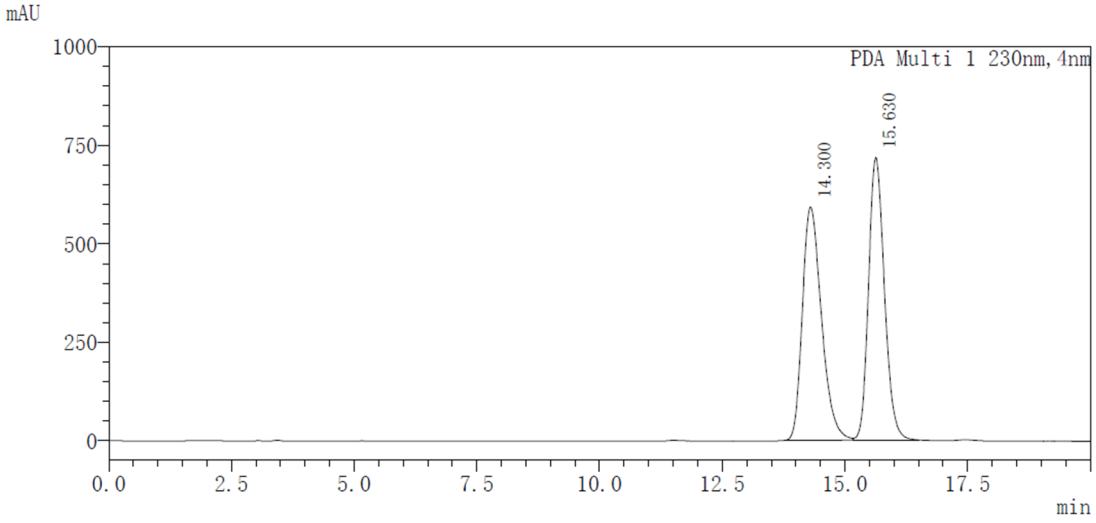
| T | Hight | Area | Area% |
|---|---|---|---|
| 11.579 | 711753 | 20896190 | 49.926 |
| 17.945 | 457176 | 20957939 | 50.074 |




PDA Ch1 214nm

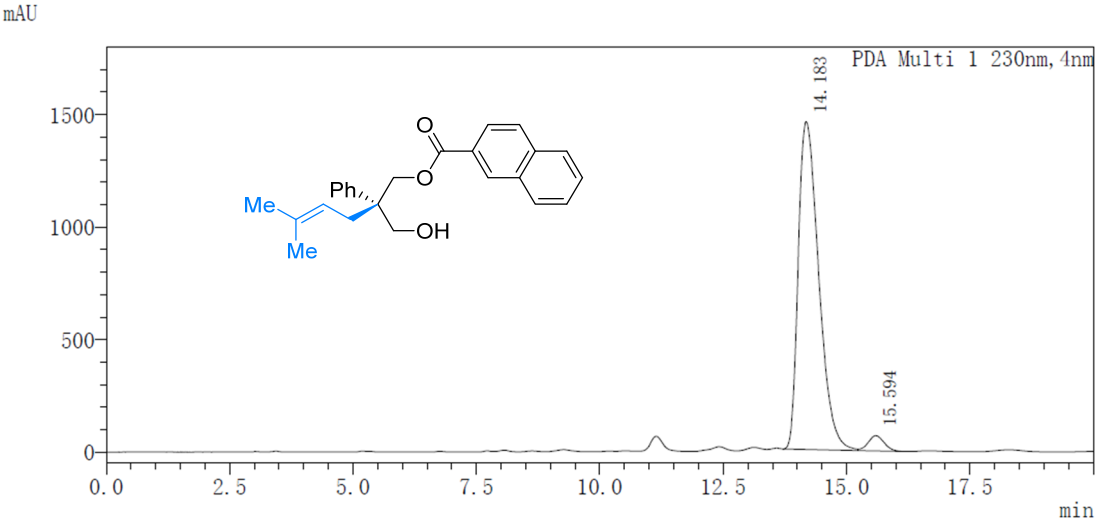
| T | Hight | Area | Area% |
|---|---|---|---|
| 11.584 | 746294 | 22309170 | 98.123 |
| 17.986 | 9820 | 426721 | 1.877 |

**29**




PDA Ch1 230nm

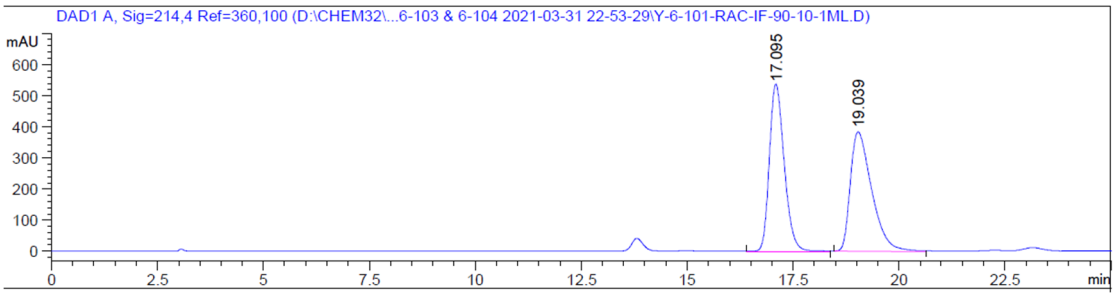
| T | Hight | Area | Area% |
|---|---|---|---|
| 14.300 | 592867 | 16093852 | 49.907 |
| 15.630 | 717690 | 16153694 | 50.093 |




PDA Ch1 230nm

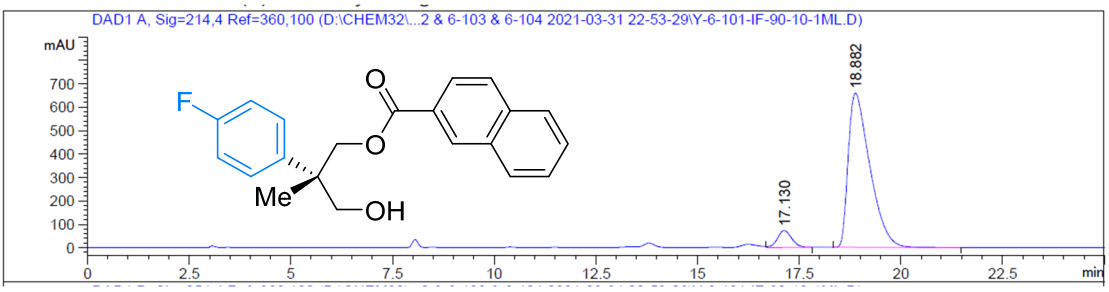
| T | Hight | Area | Area% |
|---|---|---|---|
| 14.183 | 1457263 | 41950514 | 96.497 |
| 15.594 | 67966 | 1522844 | 3.503 |

**30**




Signal 1: DAD1 A, Sig=214,4 Ref=360,100

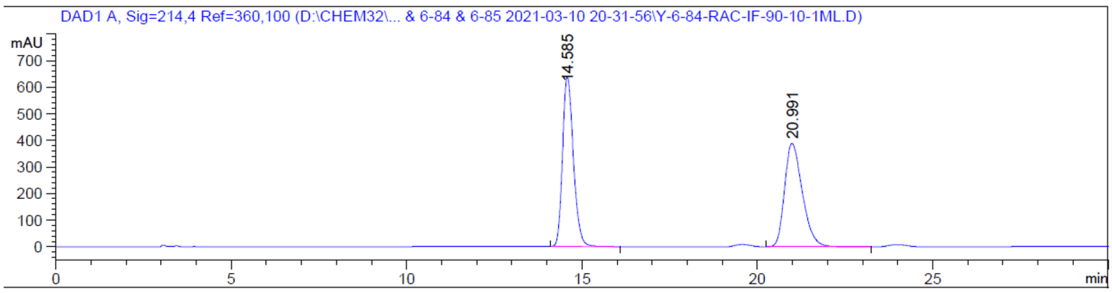
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.095 | MM R | 0.4091 | 1.32250e4 | 538.72211 | 49.6436 |
| 2 | 19.039 | MM R | 0.5835 | 1.34149e4 | 383.18976 | 50.3564 |
| Totals : | | | | 2.66399e4 | 921.91187 | |




Signal 1: DAD1 A, Sig=214,4 Ref=360,100

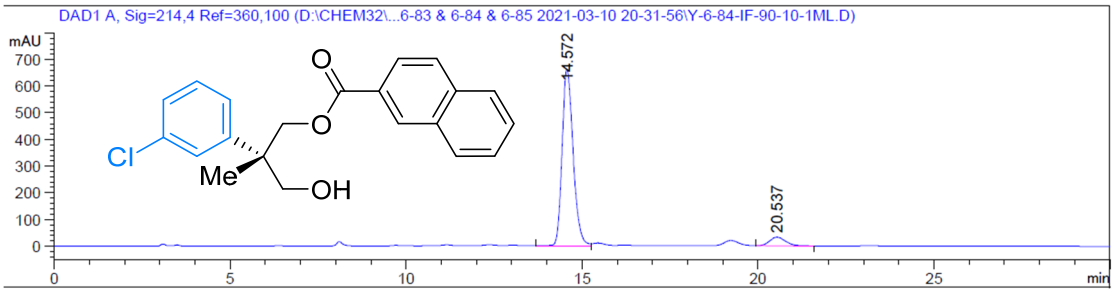
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.130 | VB | 0.3747 | 1729.35962 | 71.36333 | 6.6327 |
| 2 | 18.882 | BB | 0.5597 | 2.43437e4 | 657.93695 | 93.3673 |
| Totals : | | | | 2.60731e4 | 729.30029 | |

**31**




Signal 1: DAD1 A, Sig=214,4 Ref=360,100

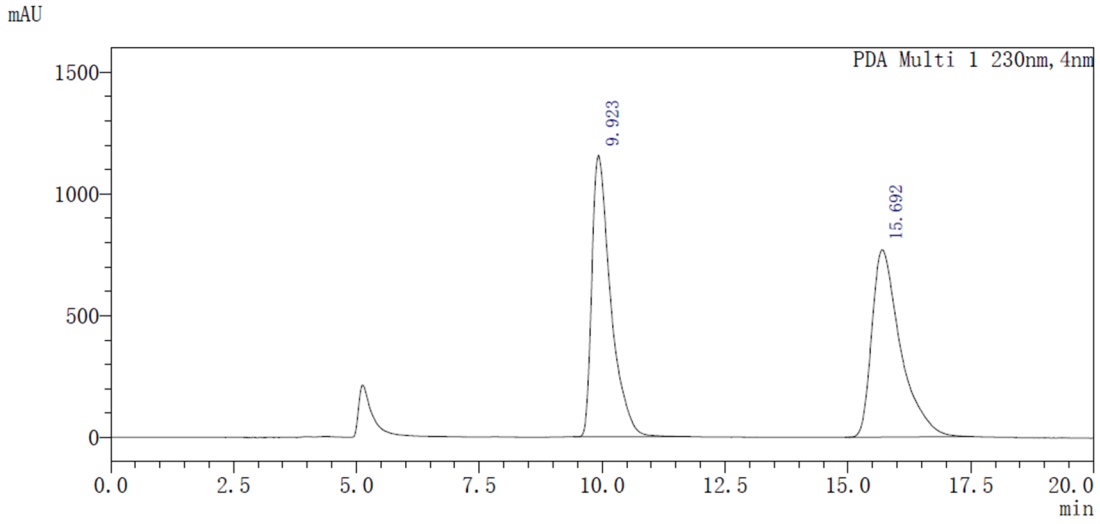
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.585 | BB | 0.3295 | 1.36467e4 | 638.06464 | 49.9124 |
| 2 | 20.991 | BB | 0.5452 | 1.36946e4 | 388.53964 | 50.0876 |
| Totals : | | | | 2.73413e4 | 1026.60428 | |




Signal 1: DAD1 A, Sig=214,4 Ref=360,100

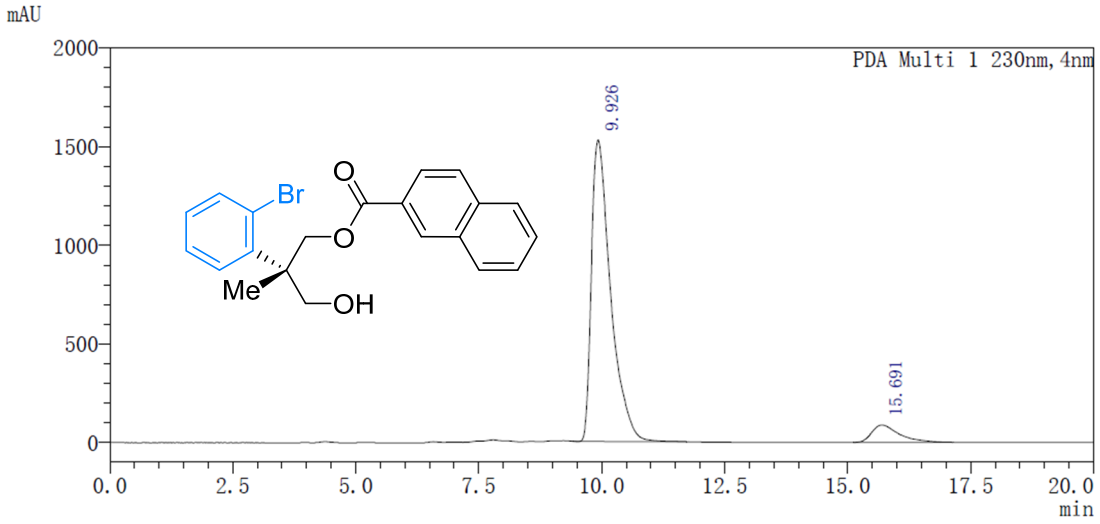
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.572 | BV | 0.3361 | 1.44125e4 | 661.67725 | 93.4088 |
| 2 | 20.537 | BB | 0.4846 | 1016.99640 | 32.36177 | 6.5912 |
| Totals : | | | | 1.54295e4 | 694.03901 | |

**32**




PDA Ch1 230nm

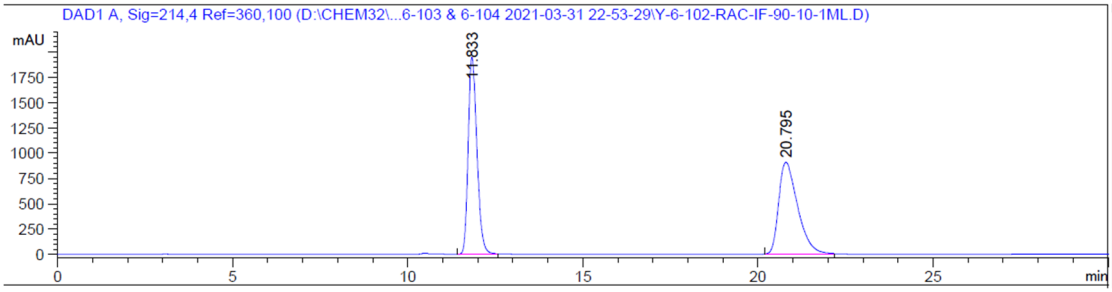
| T | Hight | Area | Area% |
|---|---|---|---|
| 9.923 | 1156383 | 30811650 | 49.787 |
| 15.692 | 769235 | 31075167 | 50.213 |




PDA Ch1 230nm

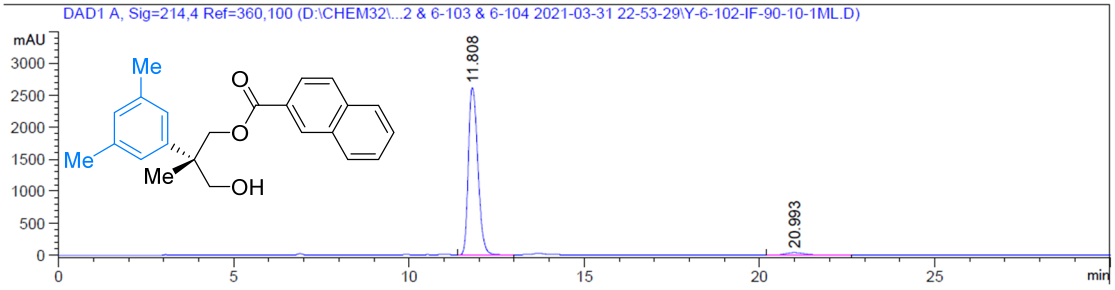
| T | Hight | Area | Area% |
|---|---|---|---|
| 9.926 | 1528562 | 41494874 | 92.495 |
| 15.691 | 88351 | 3367077 | 7.505 |

**33**




Signal 1: DAD1 A, Sig=214,4 Ref=360,100

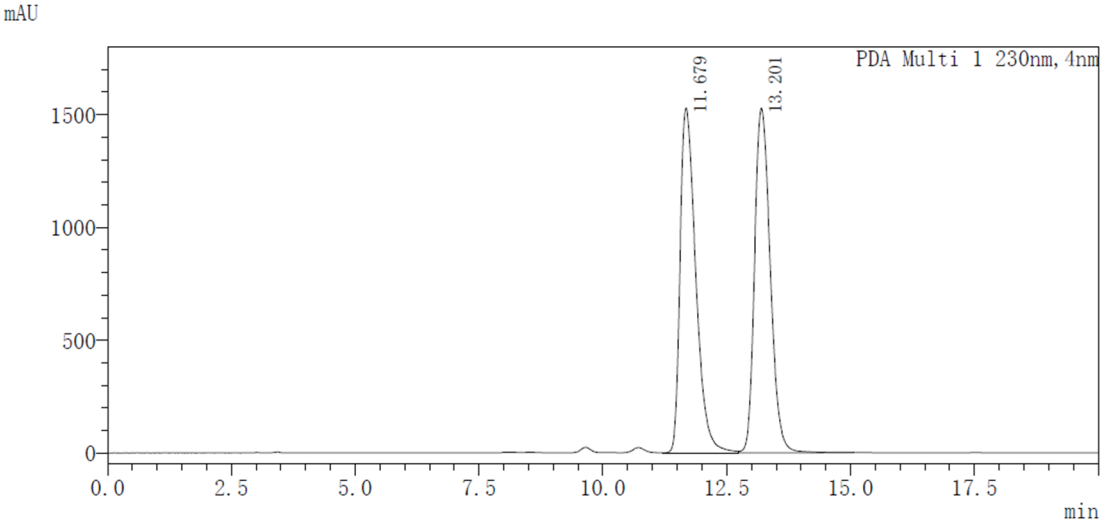
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.833 | BV | 0.2696 | 3.40208e4 | 1949.02246 | 49.7148 |
| 2 | 20.795 | MM R | 0.6308 | 3.44111e4 | 909.23828 | 50.2852 |
| Totals : | | | | 6.84319e4 | 2858.26074 | |




Signal 1: DAD1 A, Sig=214,4 Ref=360,100

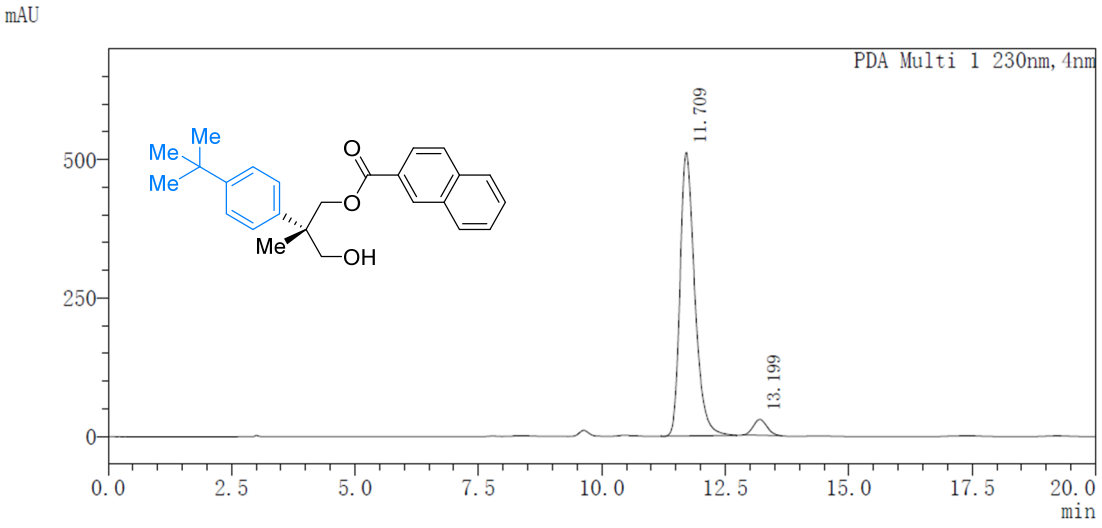
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 11.808 | BB | 0.2941 | 4.92453e4 | 2610.79663 | 97.1645 |
| 2 | 20.993 | BB | 0.5809 | 1437.11658 | 37.85955 | 2.8355 |
| Totals : | | | | 5.06824e4 | 2648.65619 | |

**34**




PDA Ch1 230nm

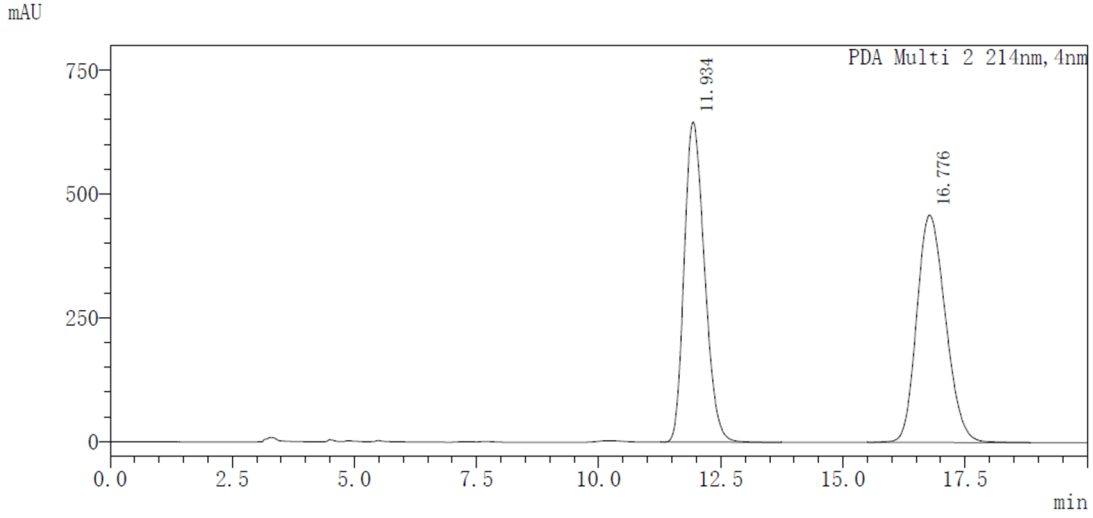
| T | Hight | Area | Area% |
|---|---|---|---|
| 11.679 | 1528230 | 33667628 | 49.986 |
| 13.201 | 1527808 | 33686713 | 50.014 |




PDA Ch1 230nm

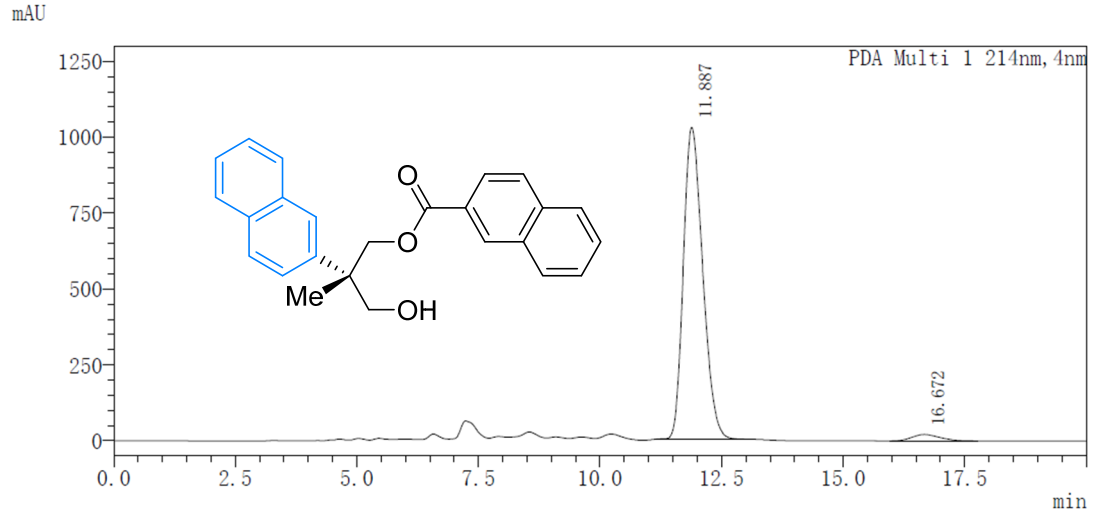
| T | Hight | Area | Area% |
|---|---|---|---|
| 11.709 | 511804 | 10588466 | 95.096 |
| 13.199 | 28429 | 546003 | 4.904 |

**35**




PDA Ch2 214nm

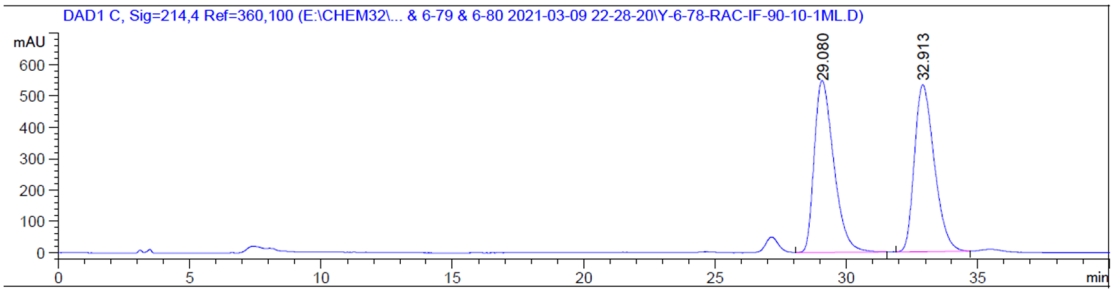
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 11.934 | 18715619 | 49.911 |
| 2 | 16.776 | 18782713 | 50.089 |




PDA Ch1 214nm

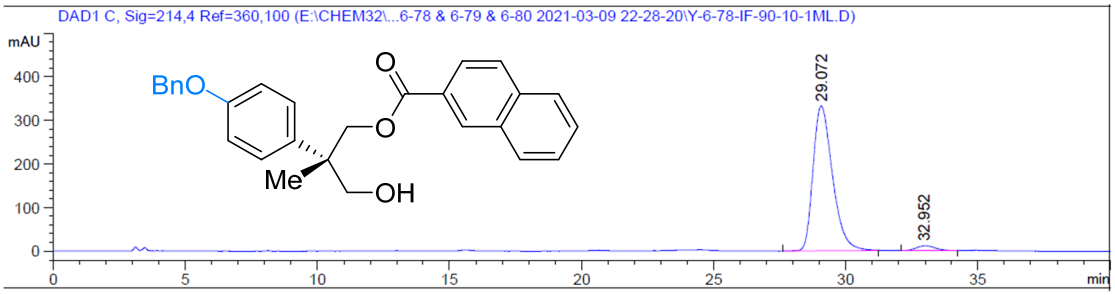
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 11.887 | 28467984 | 97.227 |
| 2 | 16.672 | 812023 | 2.773 |

**36**




Signal 3: DAD1 C, Sig=214,4 Ref=360,100

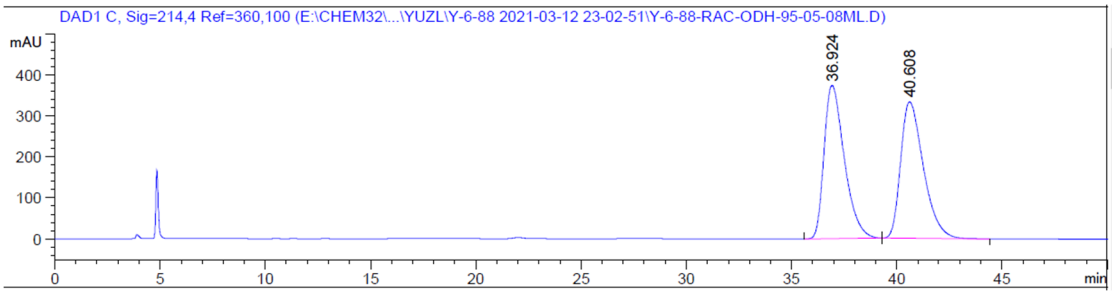
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 29.080 | BB | 0.7596 | 2.82578e4 | 547.98065 | 50.2224 |
| 2 | 32.913 | BB | 0.6969 | 2.80075e4 | 531.38977 | 49.7776 |




Signal 3: DAD1 C, Sig=214,4 Ref=360,100

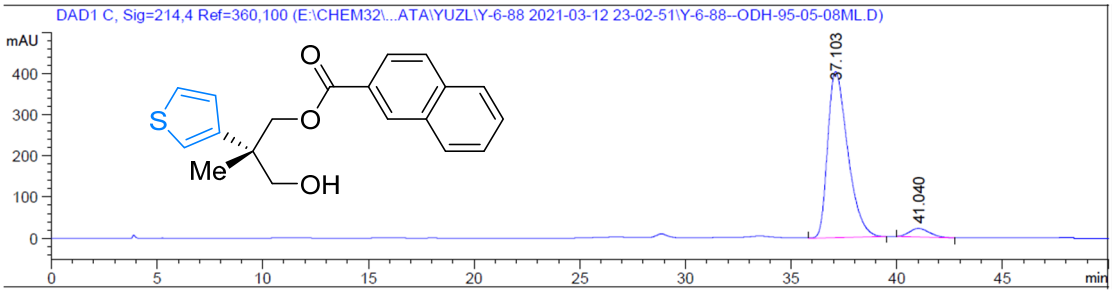
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 29.072 | VV R | 0.7583 | 1.70300e4 | 332.05759 | 96.8178 |
| 2 | 32.952 | BV R | 0.6001 | 559.74548 | 11.14227 | 3.1822 |

**37**




Signal 3: DAD1 C, Sig=214,4 Ref=360,100

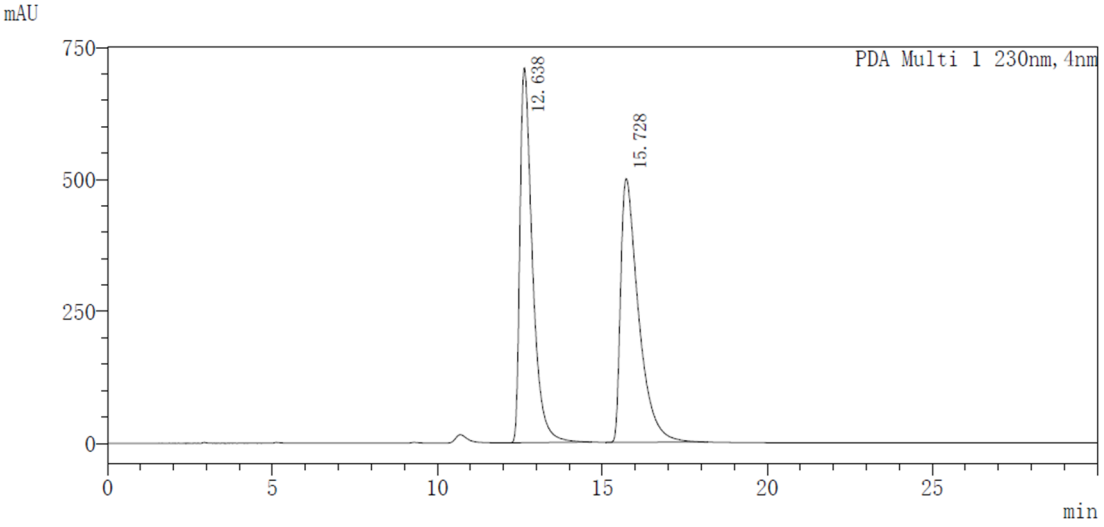
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 36.924 | BB | 1.0210 | 2.50399e4 | 374.02655 | 49.9963 |
| 2 | 40.608 | BB | 1.1518 | 2.50436e4 | 332.84494 | 50.0037 |




Signal 3: DAD1 C, Sig=214,4 Ref=360,100

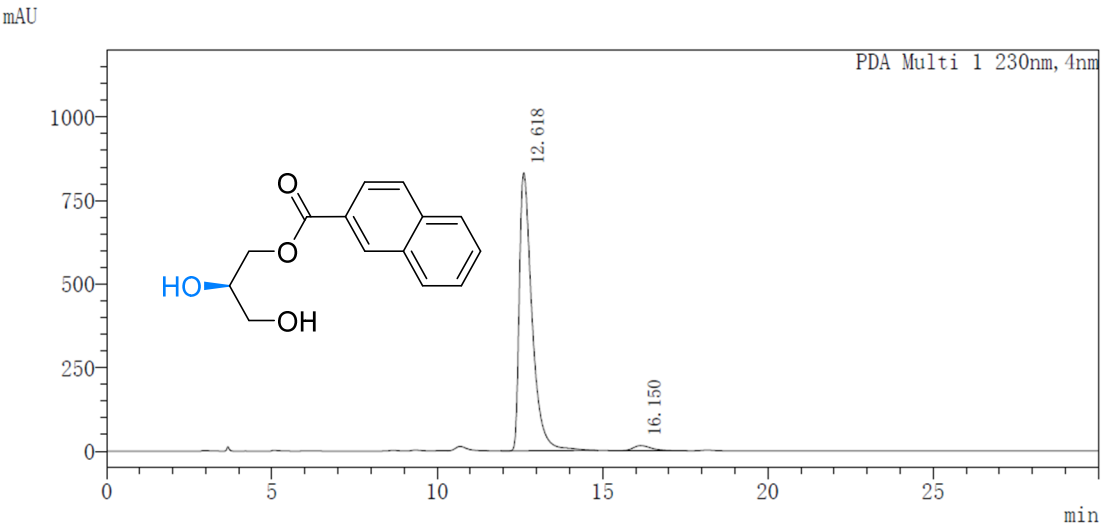
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 37.103 | MM R | 1.0998 | 2.66017e4 | 403.11874 | 95.0809 |
| 2 | 41.040 | MM R | 1.1070 | 1376.27942 | 20.72047 | 4.9191 |

**38**




PDA Ch1 230nm

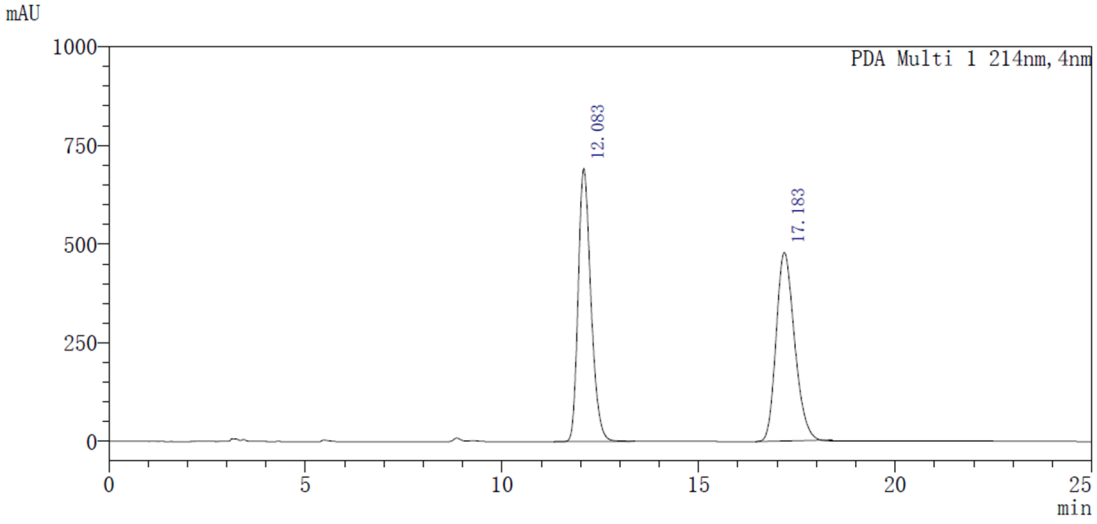
| T | Hight | Area | Area% |
|---|---|---|---|
| 12.638 | 710370 | 18703878 | 49.774 |
| 15.728 | 499909 | 18873618 | 50.226 |




PDA Ch1 230nm

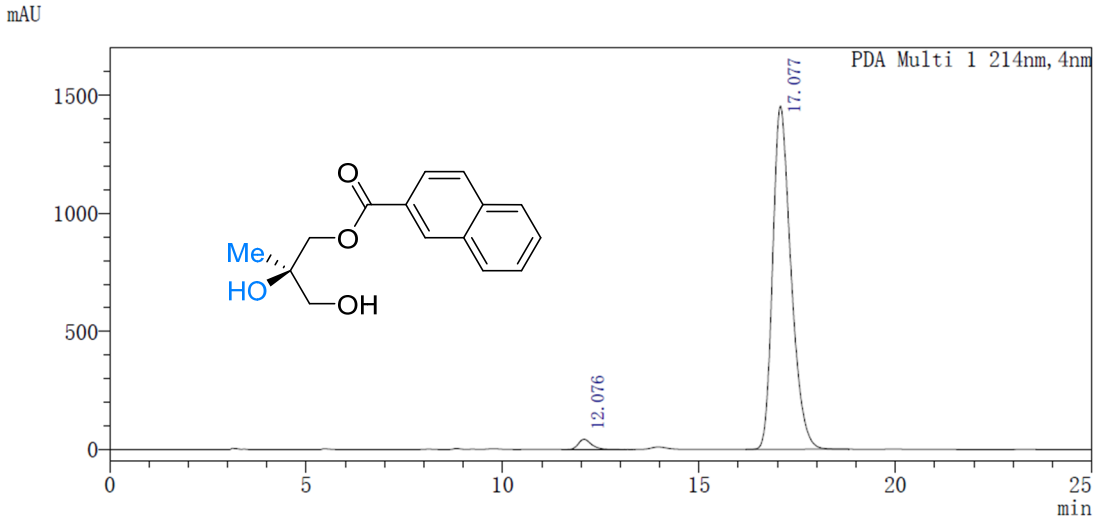
| T | Hight | Area | Area% |
|---|---|---|---|
| 12.618 | 831412 | 22226163 | 97.537 |
| 16.150 | 15091 | 561278 | 2.463 |

**39**




PDA Ch1 214nm

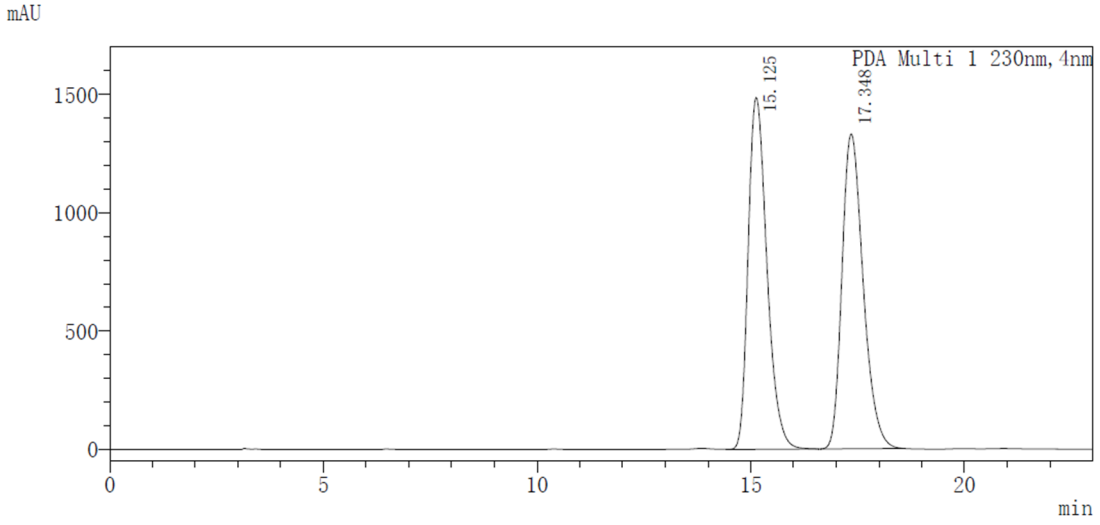
| T | Hight | Area | Area% |
|---|---|---|---|
| 12.083 | 691286 | 15593495 | 50.032 |
| 17.183 | 478011 | 15573344 | 49.968 |




PDA Ch1 214nm

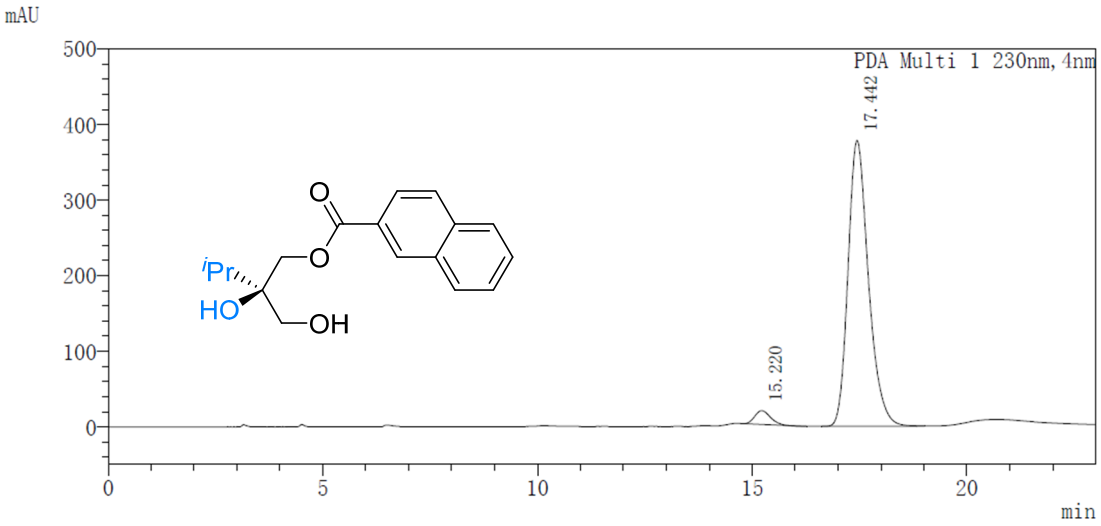
| T | Hight | Area | Area% |
|---|---|---|---|
| 12.076 | 43361 | 1017127 | 2.116 |
| 17.077 | 1451881 | 47052073 | 97.884 |

**40**




PDA Ch1 230nm

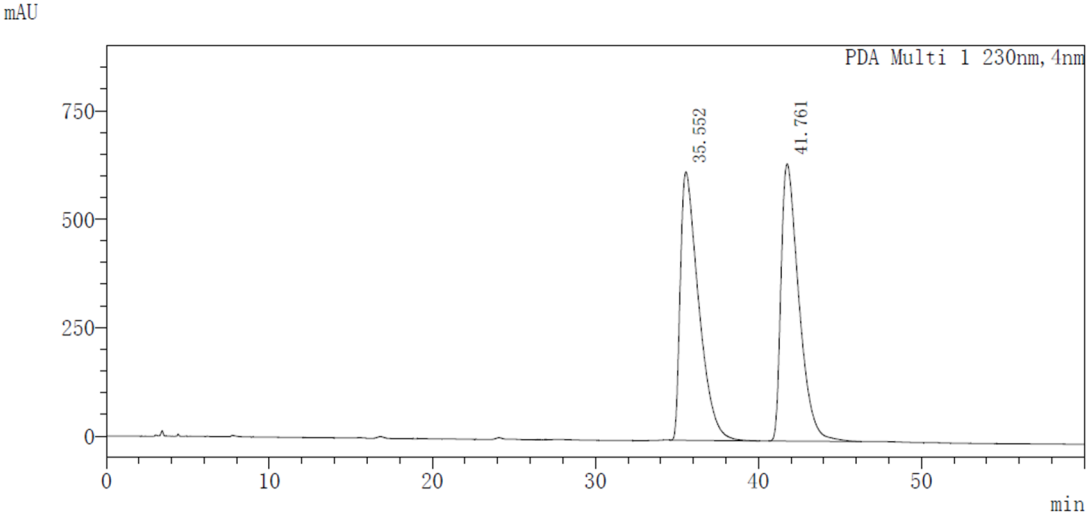
| T | Hight | Area | Area% |
|---|---|---|---|
| 15.125 | 1484768 | 45355586 | 49.717 |
| 17.348 | 1328751 | 45871839 | 50.283 |




PDA Ch1 230nm

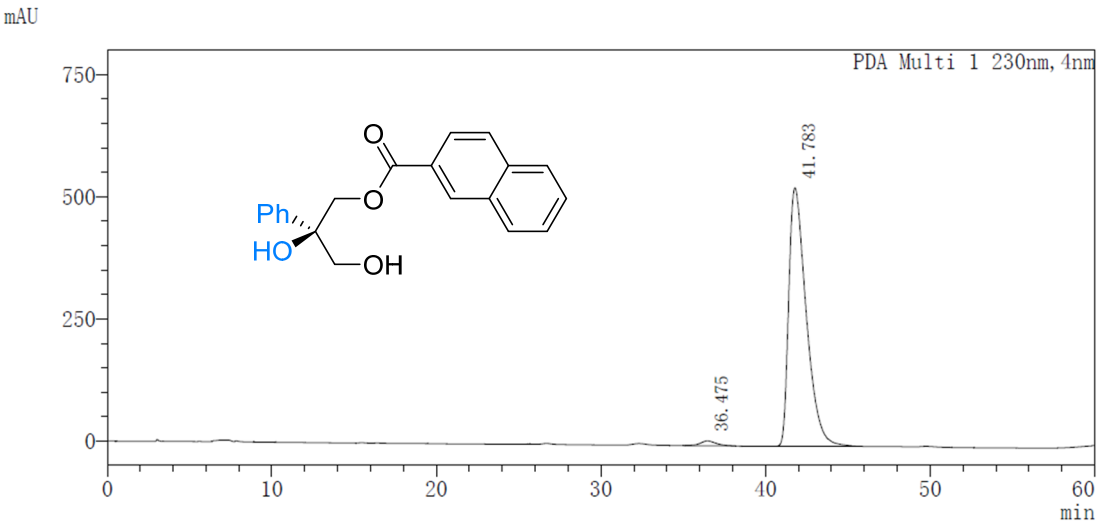
| T | Hight | Area | Area% |
|---|---|---|---|
| 15.220 | 18290 | 459254 | 3.537 |
| 17.442 | 378472 | 12525391 | 96.463 |

**41**




PDA Ch1 230nm

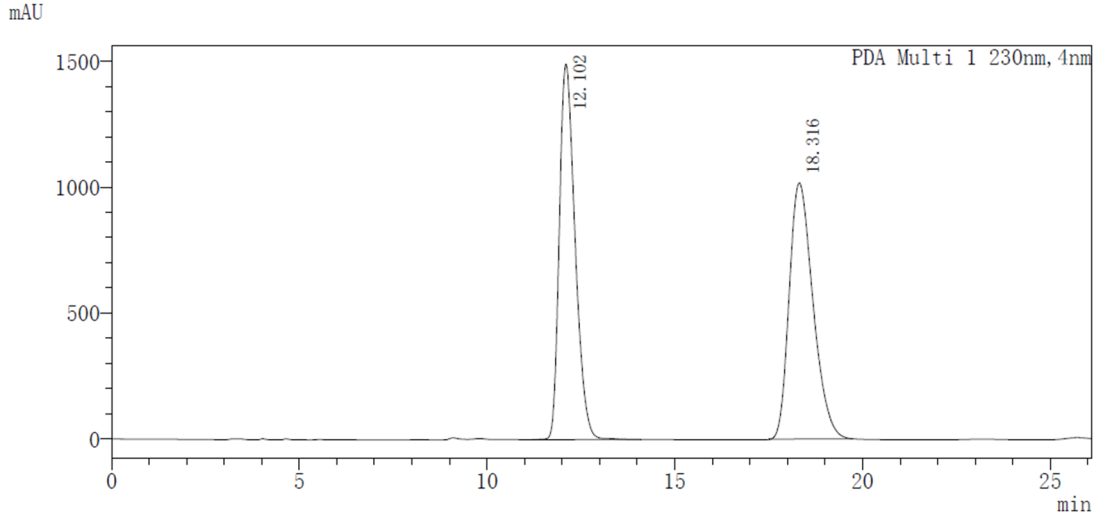
| T | Hight | Area | Area% |
|---|---|---|---|
| 35.552 | 618602 | 48439203 | 49.891 |
| 41.761 | 639438 | 48651347 | 50.109 |




PDA Ch1 230nm

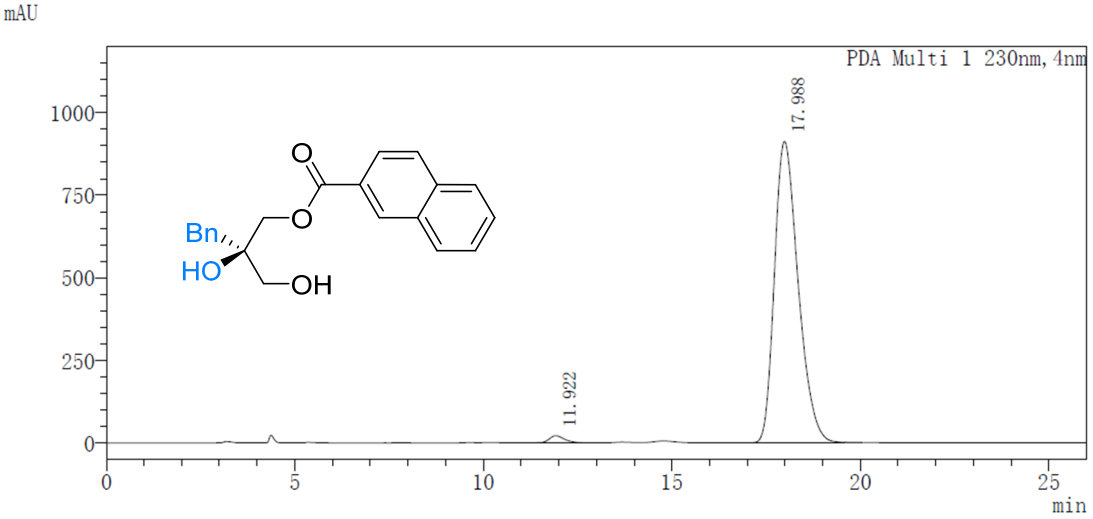
| T | Hight | Area | Area% |
|---|---|---|---|
| 36.475 | 10011 | 674312 | 1.698 |
| 41.783 | 529129 | 39026805 | 98.302 |

**42**




PDA Ch1 230nm

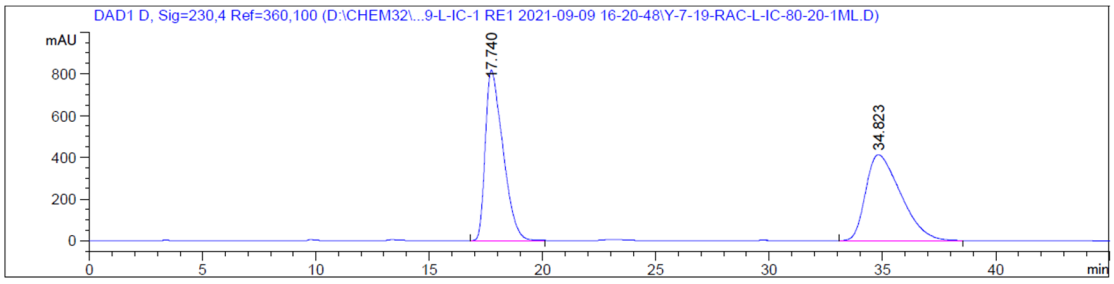
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 12.102 | 43564077 | 49.259 |
| 2 | 18.316 | 44875181 | 50.741 |




PDA Ch1 230nm

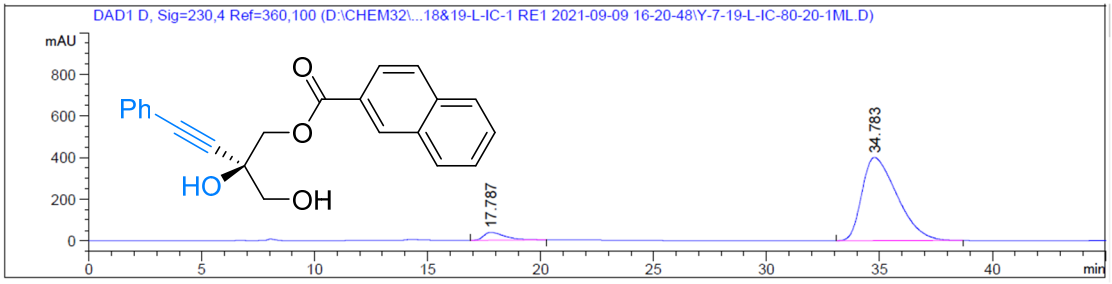
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 11.922 | 631272 | 1.555 |
| 2 | 17.988 | 39959537 | 98.445 |

**43**




Signal 4: DAD1 D, Sig=230,4 Ref=360,100

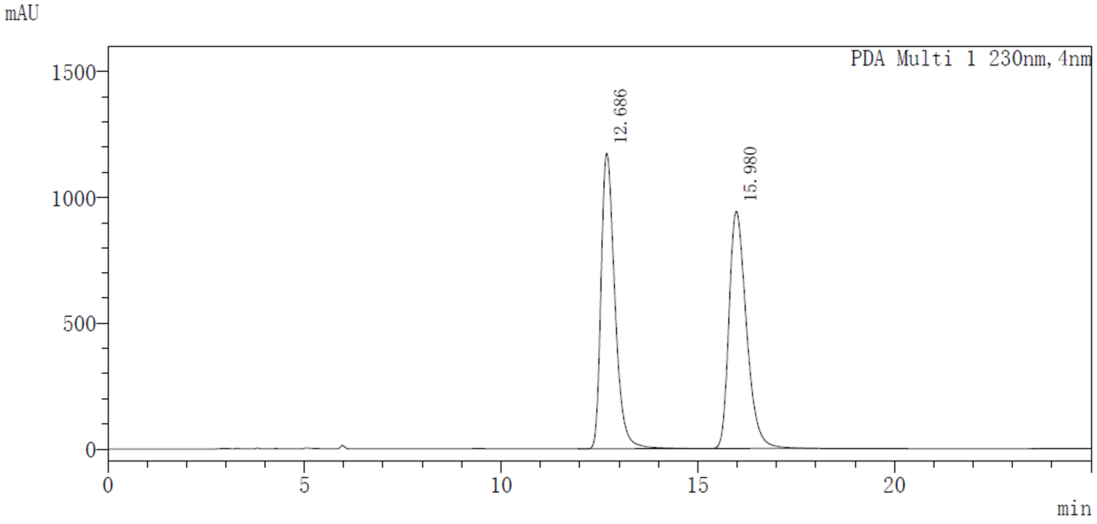
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.740 | BB | 0.7538 | 4.39730e4 | 817.20239 | 49.9349 |
| 2 | 34.823 | BB | 1.2634 | 4.40876e4 | 411.69104 | 50.0651 |




Signal 4: DAD1 D, Sig=230,4 Ref=360,100

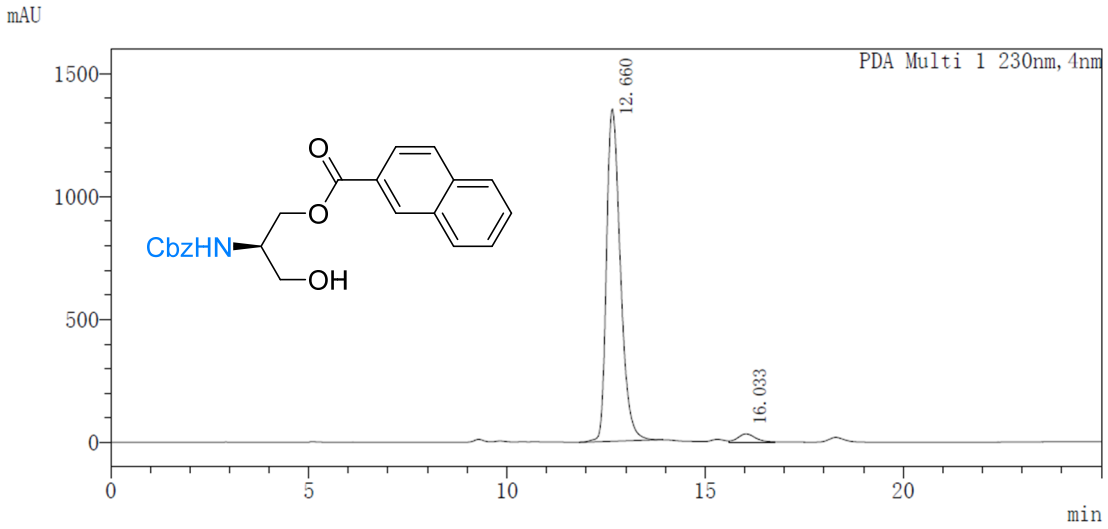
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.787 | BB | 0.7696 | 2459.97046 | 37.88008 | 5.3871 |
| 2 | 34.783 | BB | 1.4009 | 4.32040e4 | 399.73822 | 94.6129 |

**44**




PDA Ch1 230nm

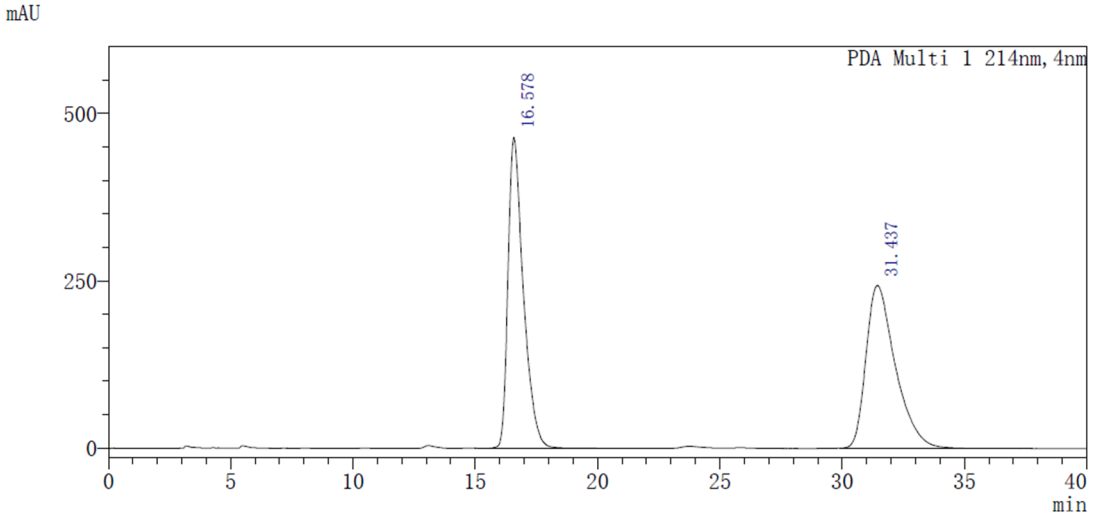
| T | Hight | Area | Area% |
|---|---|---|---|
| 12.686 | 1175205 | 28685965 | 49.644 |
| 15.980 | 942978 | 29096898 | 50.356 |




PDA Ch1 230nm

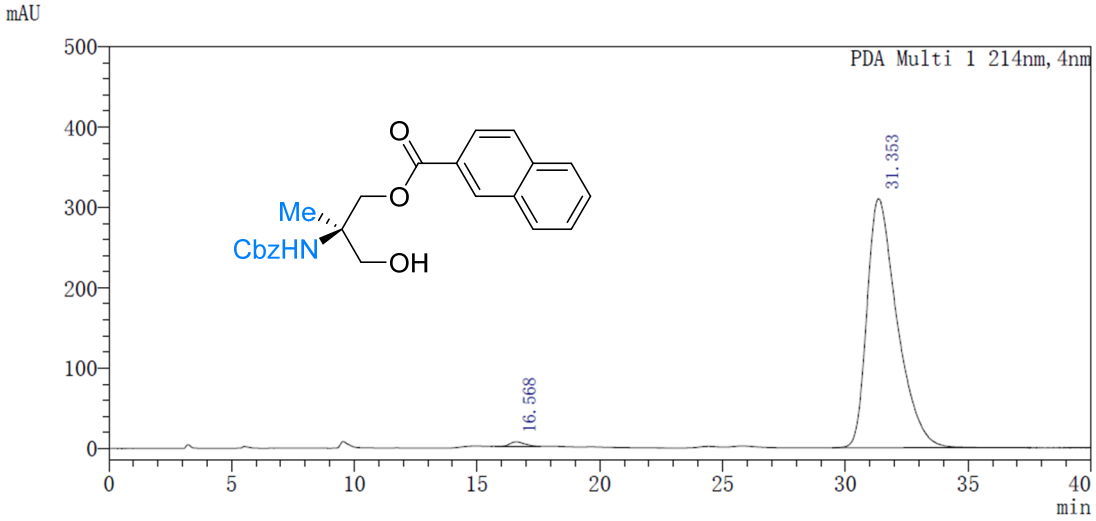
| T | Hight | Area | Area% |
|---|---|---|---|
| 12.660 | 1351225 | 32949114 | 96.998 |
| 16.033 | 33577 | 1019629 | 3.002 |

**45**




PDA Ch1 214nm

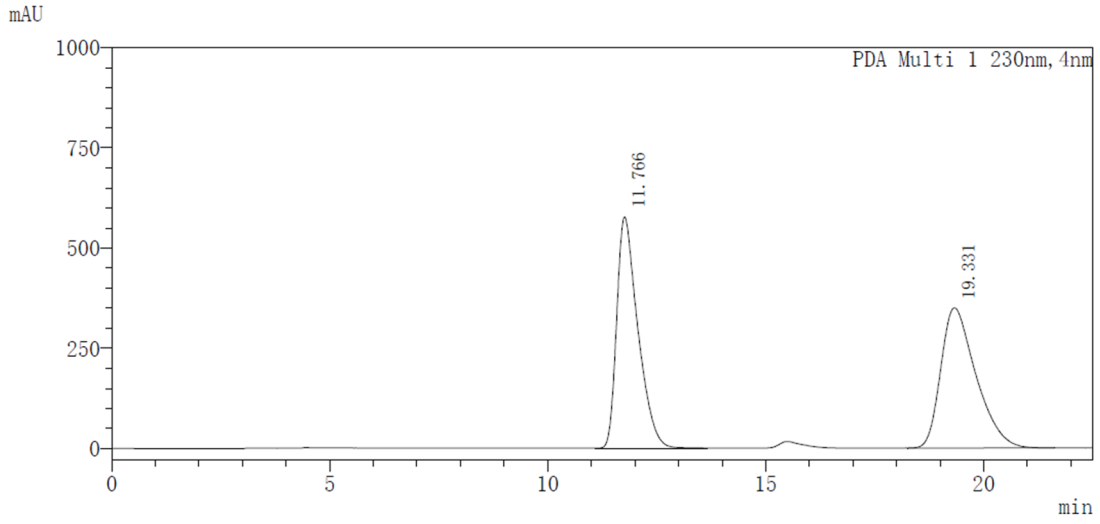
| T | Hight | Area | Area% |
|---|---|---|---|
| 16.578 | 464375 | 20264127 | 49.965 |
| 31.437 | 243558 | 20292487 | 50.035 |




PDA Ch1 214nm

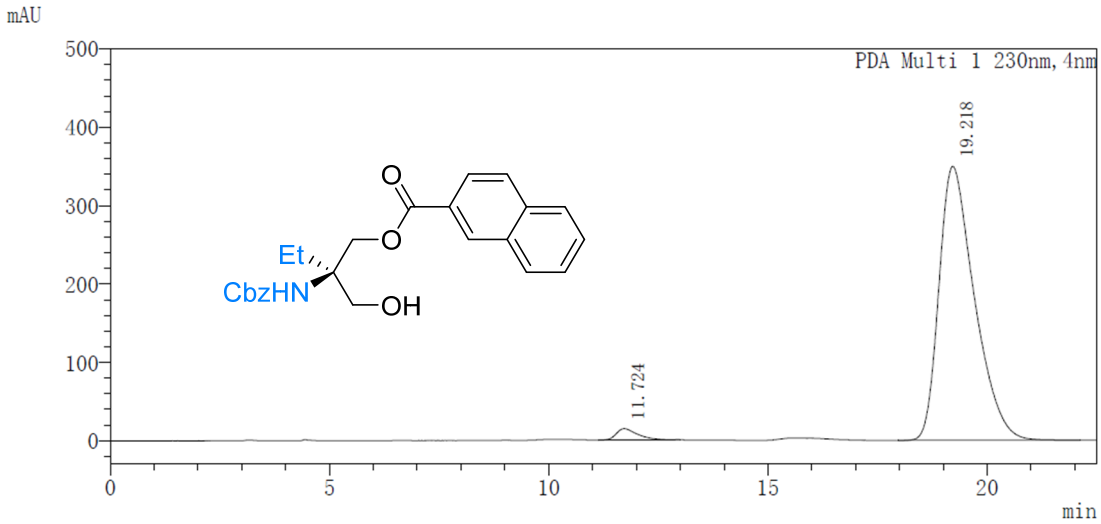
| T | Hight | Area | Area% |
|---|---|---|---|
| 16.568 | 5688 | 226251 | 0.849 |
| 31.353 | 309902 | 26408385 | 99.151 |

**46**




PDA Ch1 230nm

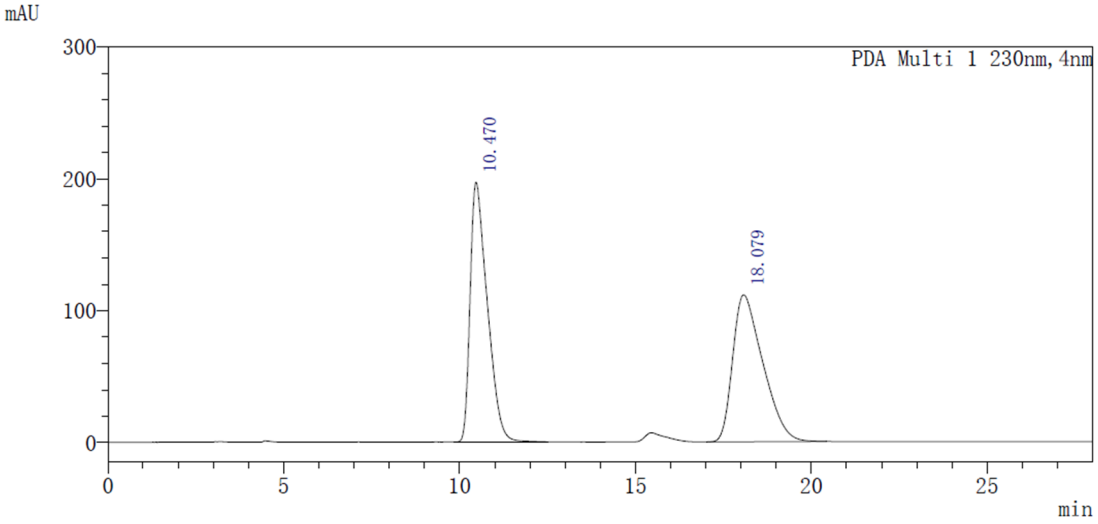
| T | Hight | Area | Area% |
|---|---|---|---|
| 11.766 | 576904 | 19454624 | 49.779 |
| 19.331 | 349802 | 19627205 | 50.221 |




PDA Ch1 230nm

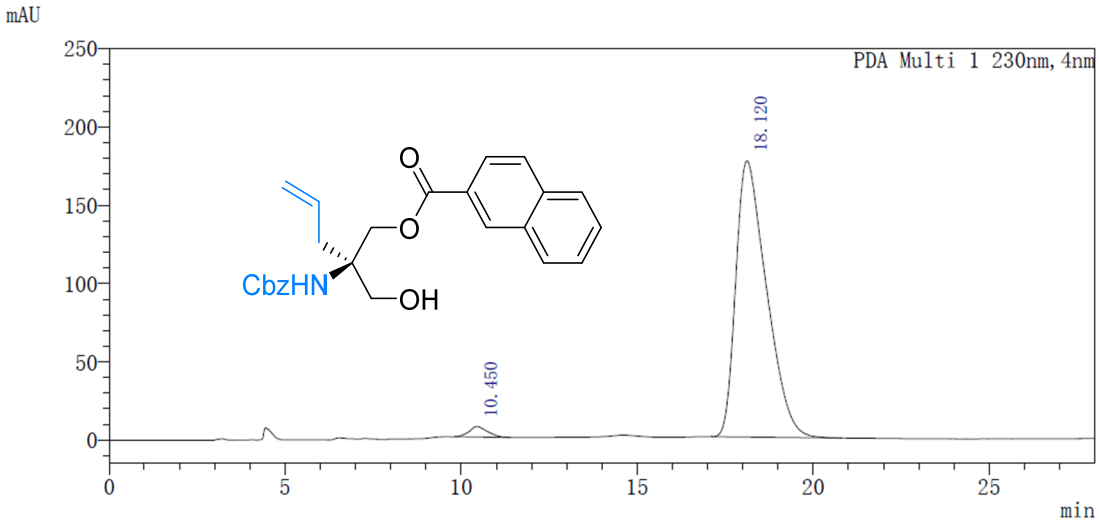
| T | Hight | Area | Area% |
|---|---|---|---|
| 11.724 | 14469 | 487224 | 2.423 |
| 19.218 | 349426 | 19624869 | 97.577 |

**47**




PDA Ch1 230nm

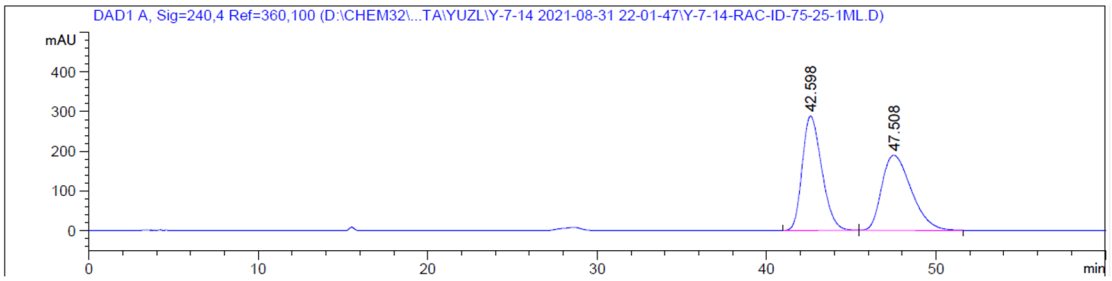
| T | Hight | Area | Area% |
|---|---|---|---|
| 10.470 | 196982 | 6680509 | 50.127 |
| 18.079 | 111491 | 6646746 | 49.873 |




PDA Ch1 230nm

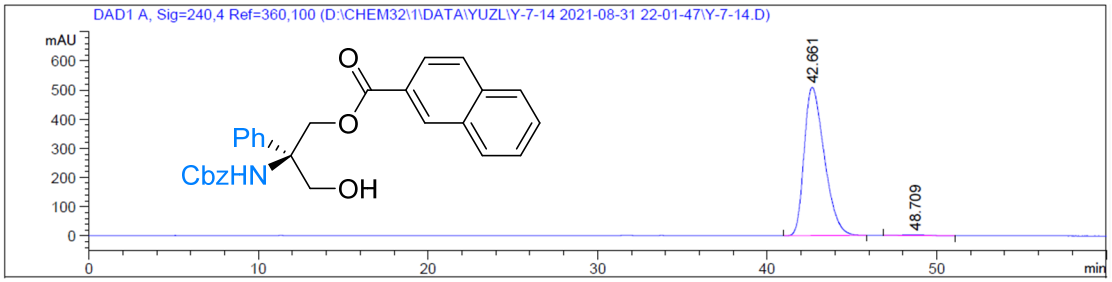
| T | Hight | Area | Area% |
|---|---|---|---|
| 10.450 | 6759 | 244179 | 2.226 |
| 18.120 | 176526 | 10726141 | 97.774 |

**48**




Signal 1: DAD1 A, Sig=240,4 Ref=360,100

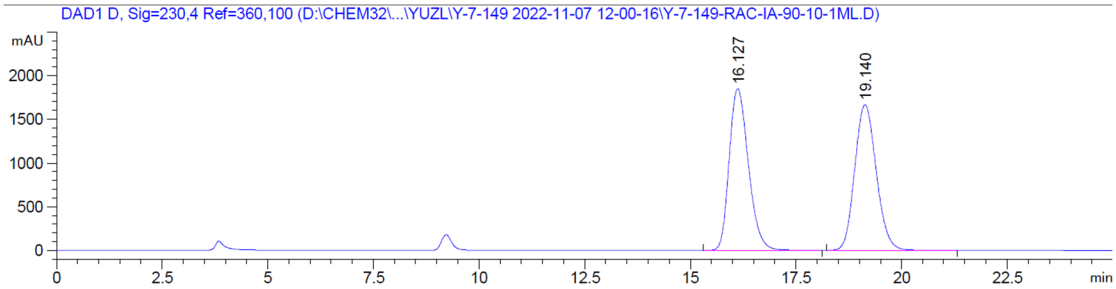
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 42.598 | BB | 1.1754 | 2.31248e4 | 288.42746 | 50.2080 |
| 2 | 47.508 | BB | 1.4512 | 2.29333e4 | 189.06421 | 49.7920 |




Signal 1: DAD1 A, Sig=240,4 Ref=360,100

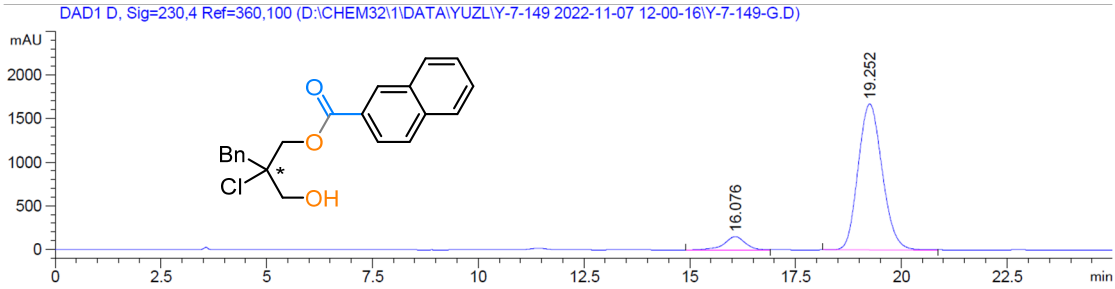
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 42.661 | BB | 1.1711 | 4.21642e4 | 508.64670 | 99.1679 |
| 2 | 48.709 | MM R | 2.0594 | 353.79117 | 2.86323 | 0.8321 |

**49**




Signal 4: DAD1 D, Sig=230,4 Ref=360,100

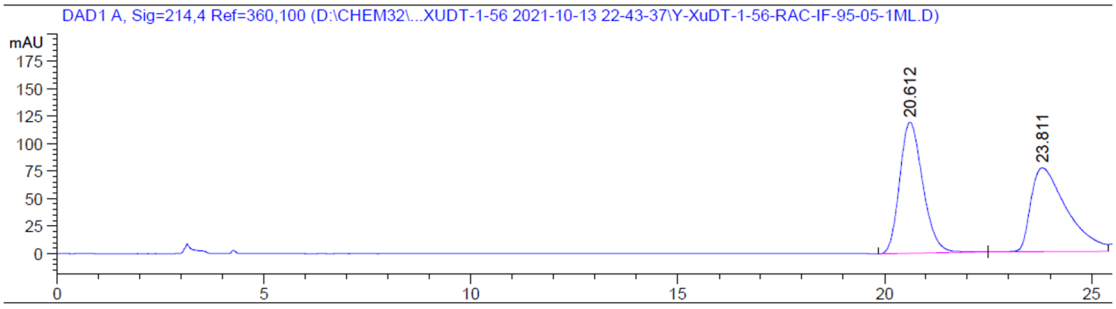
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.127 | BB | 0.4463 | 5.84222e4 | 1850.80847 | 49.7344 |
| 2 | 19.140 | BB | 0.5477 | 5.90461e4 | 1665.04810 | 50.2656 |
| Totals : | | | | 1.17468e5 | 3515.85657 | |




Signal 4: DAD1 D, Sig=230,4 Ref=360,100

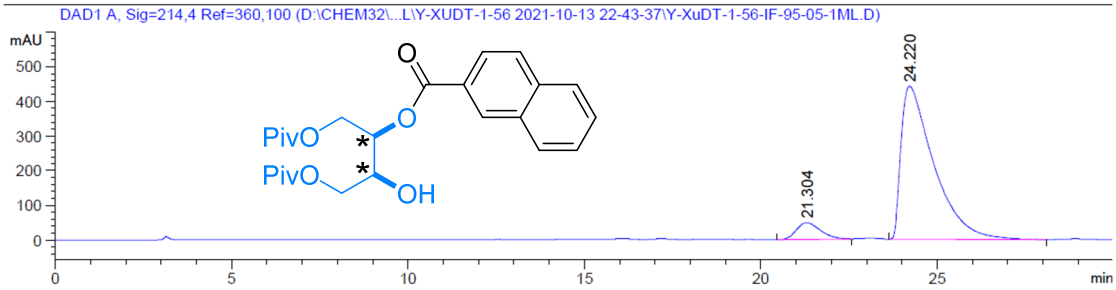
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.076 | MF R | 0.5856 | 5373.36914 | 152.94269 | 7.5040 |
| 2 | 19.252 | MF R | 0.6590 | 6.62337e4 | 1675.01343 | 92.4960 |
| Totals : | | | | 7.16070e4 | 1827.95612 | |

**50**




Signal 1: DAD1 A, Sig=214,4 Ref=360,100

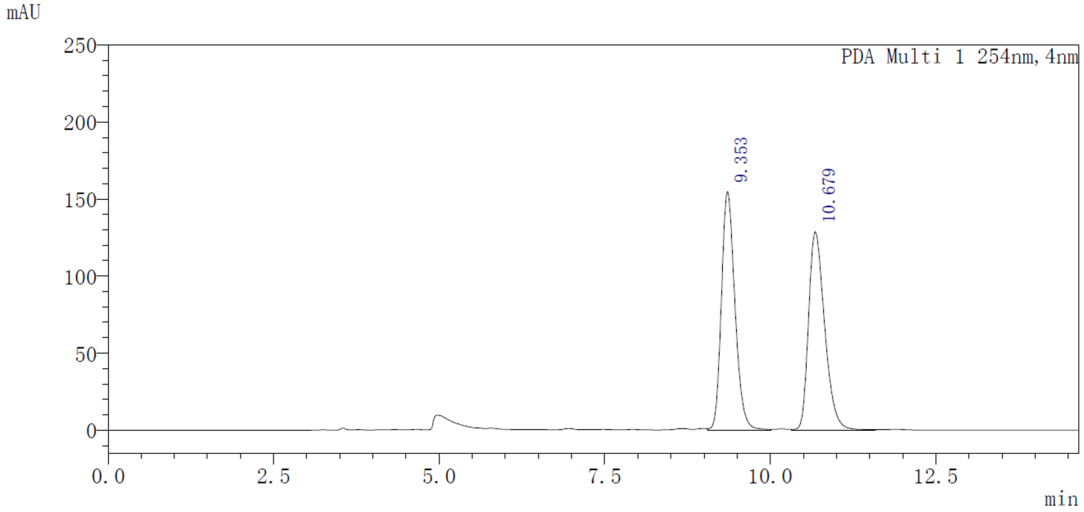
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 20.612 | BB | 0.6010 | 4665.12988 | 119.61897 | 50.2401 |
| 2 | 23.811 | BV | 0.8904 | 4620.53760 | 76.30984 | 49.7599 |




Signal 1: DAD1 A, Sig=214,4 Ref=360,100

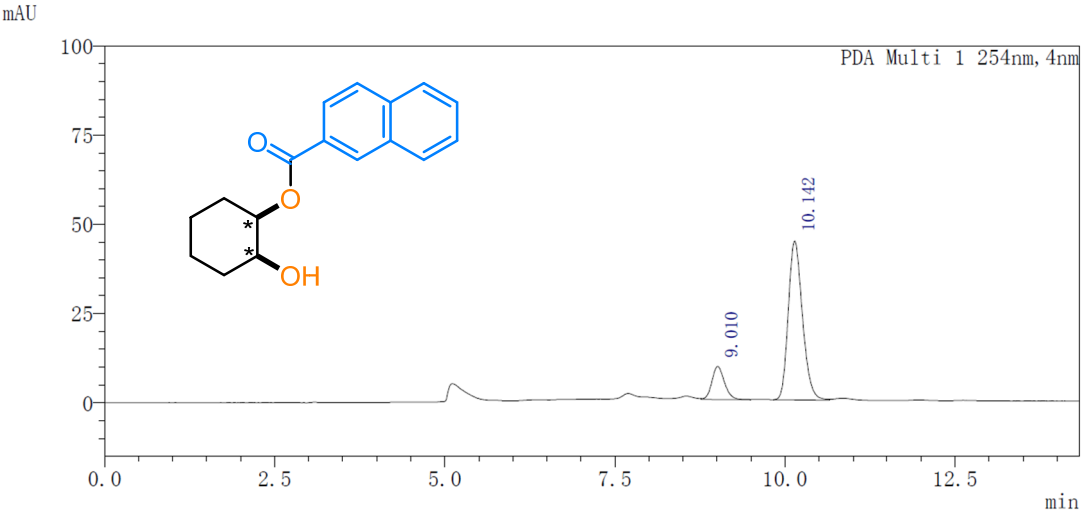
| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 21.304 | BB | 0.7234 | 2268.98120 | 48.18225 | 7.3804 |
| 2 | 24.220 | BB | 0.9317 | 2.84744e4 | 440.77148 | 92.6196 |

**SP-4**




PDA Ch1 254nm

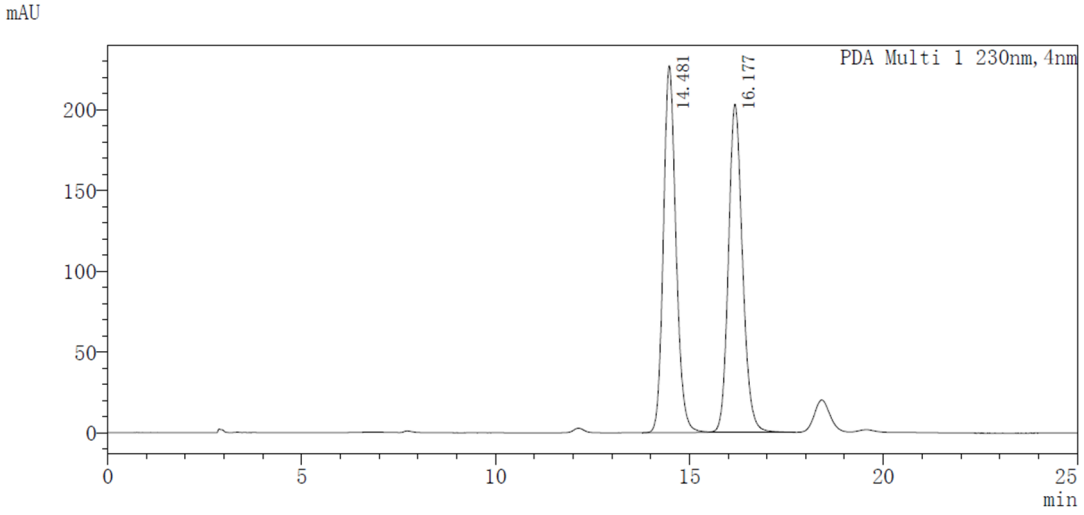
| T | Hight | Area | Area% |
|---|---|---|---|
| 9.353 | 154582 | 2202445 | 50.286 |
| 10.679 | 128558 | 2177433 | 49.714 |




PDA Ch1 254nm

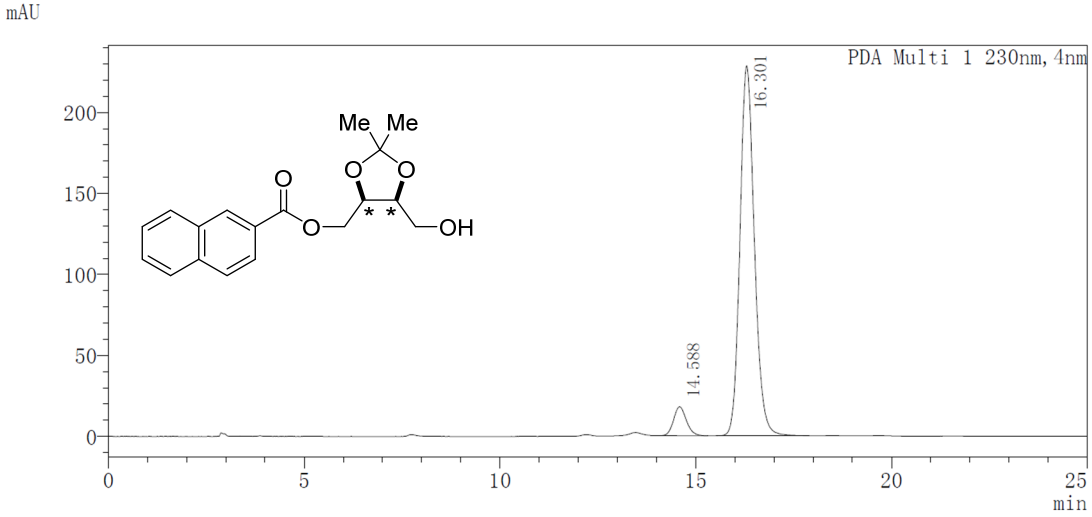
| T | Hight | Area | Area% |
|---|---|---|---|
| 9.010 | 9287 | 118179 | 15.487 |
| 10.142 | 44560 | 644888 | 84.513 |

**51**




PDA Ch1 230nm

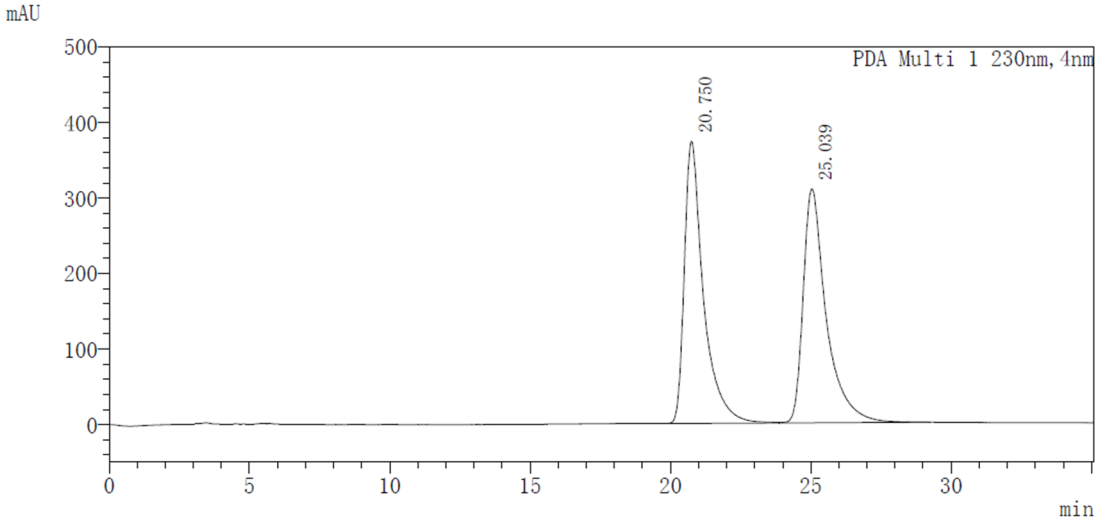
| T | Hight | Area | Area% |
|---|---|---|---|
| 14.481 | 227084 | 5138793 | 49.936 |
| 16.177 | 203236 | 5151993 | 50.064 |




PDA Ch1 230nm

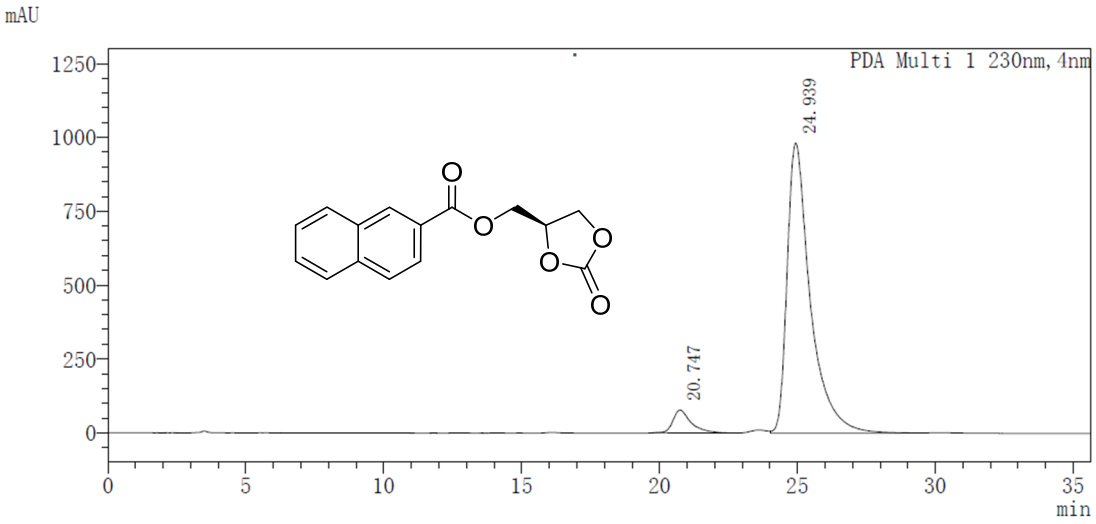
| T | Hight | Area | Area% |
|---|---|---|---|
| 14.588 | 17867 | 404767 | 6.471 |
| 16.301 | 228328 | 5850151 | 93.529 |

**52**




PDA Ch1 230nm

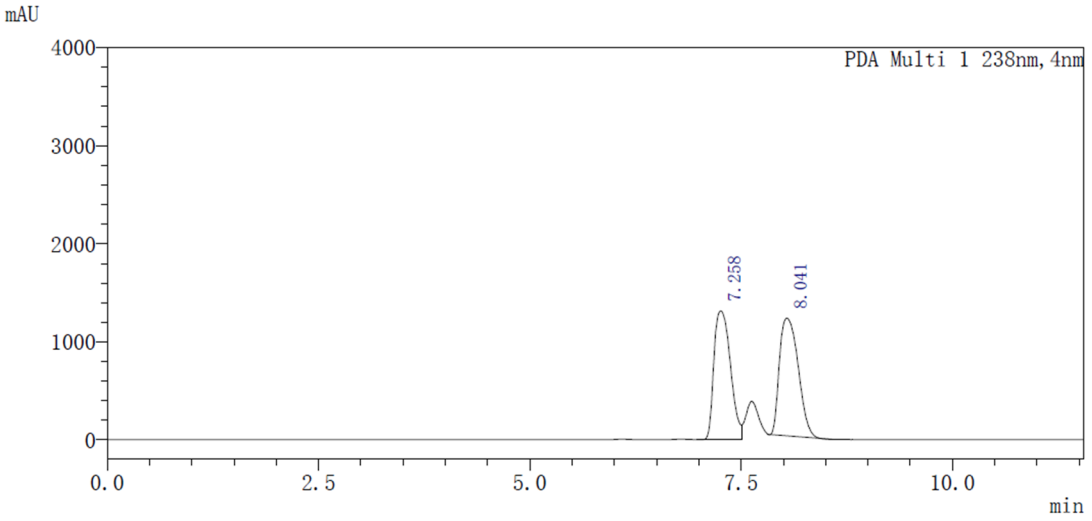
| T | Hight | Area | Area% |
|---|---|---|---|
| 20.750 | 373594 | 17712581 | 49.949 |
| 25.039 | 310126 | 17748922 | 50.051 |




PDA Ch1 230nm

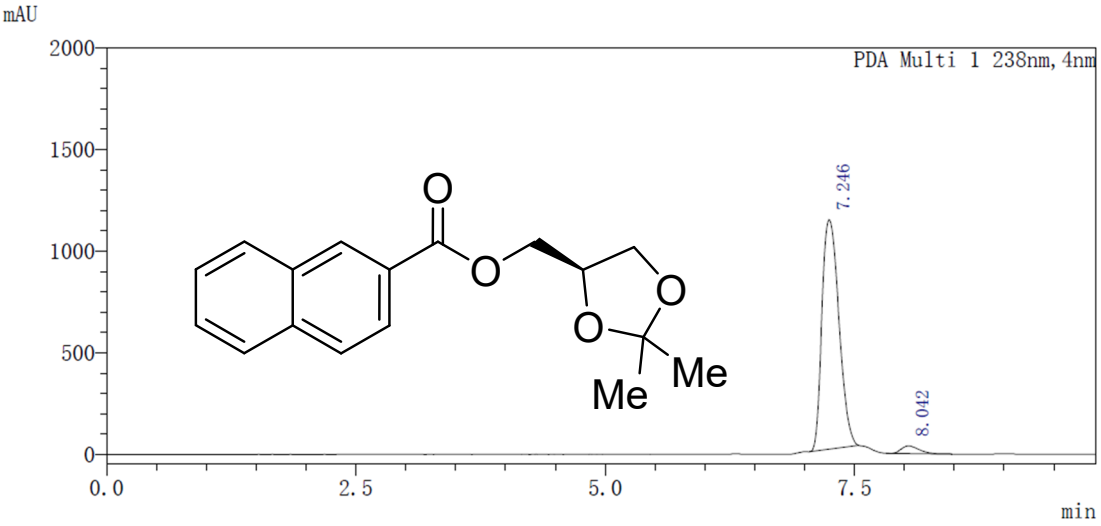
| T | Hight | Area | Area% |
|---|---|---|---|
| 20.747 | 77109 | 3558545 | 5.822 |
| 24.939 | 982182 | 57567062 | 94.178 |

**53**




PDA Ch1 238nm

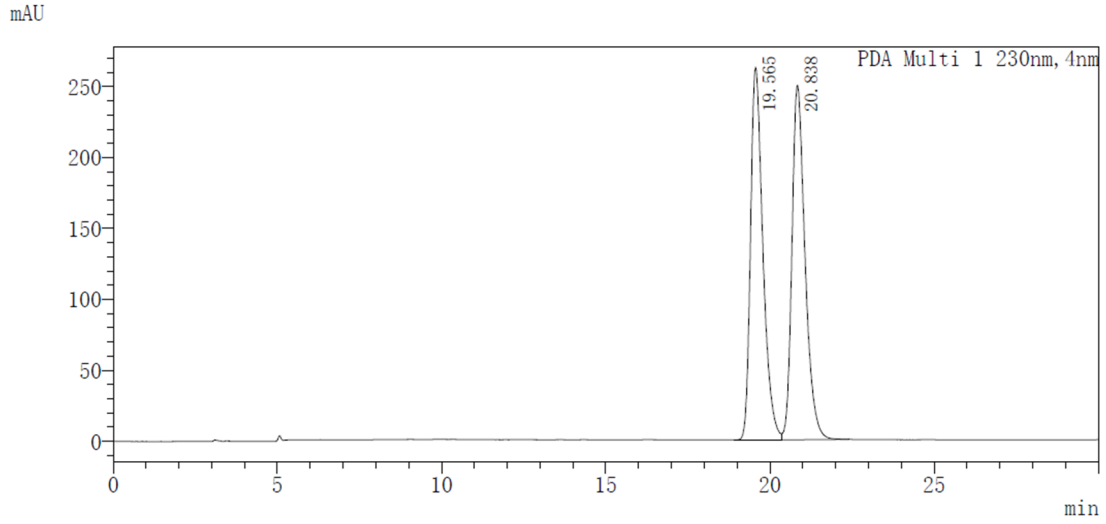
| T | Hight | Area | Area% |
|---|---|---|---|
| 7.258 | 1315338 | 17975876 | 49.245 |
| 8.041 | 1200671 | 18527083 | 50.755 |




PDA Ch1 238nm

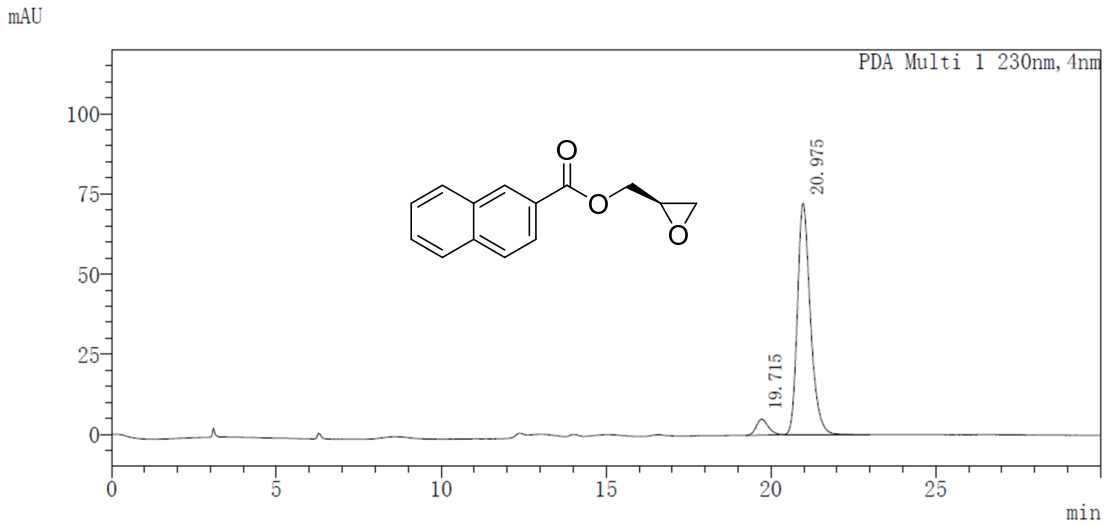
| T | Hight | Area | Area% |
|---|---|---|---|
| 7.246 | 1130769 | 13376039 | 96.666 |
| 8.042 | 37824 | 461362 | 3.334 |

**54**




PDA Ch1 230nm

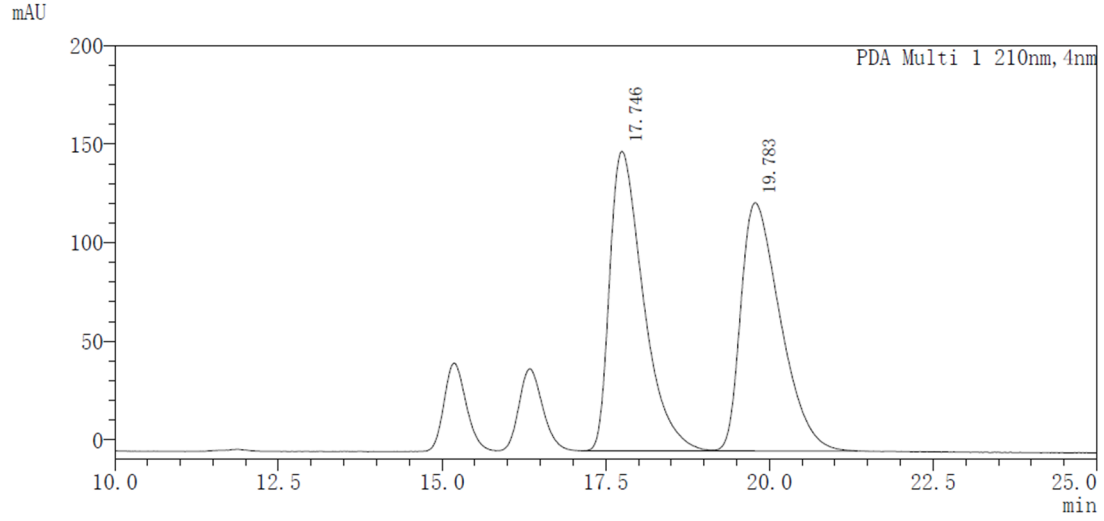
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 19.565 | 6885587 | 49.787 |
| 2 | 20.838 | 6944619 | 50.213 |




PDA Ch1 230nm

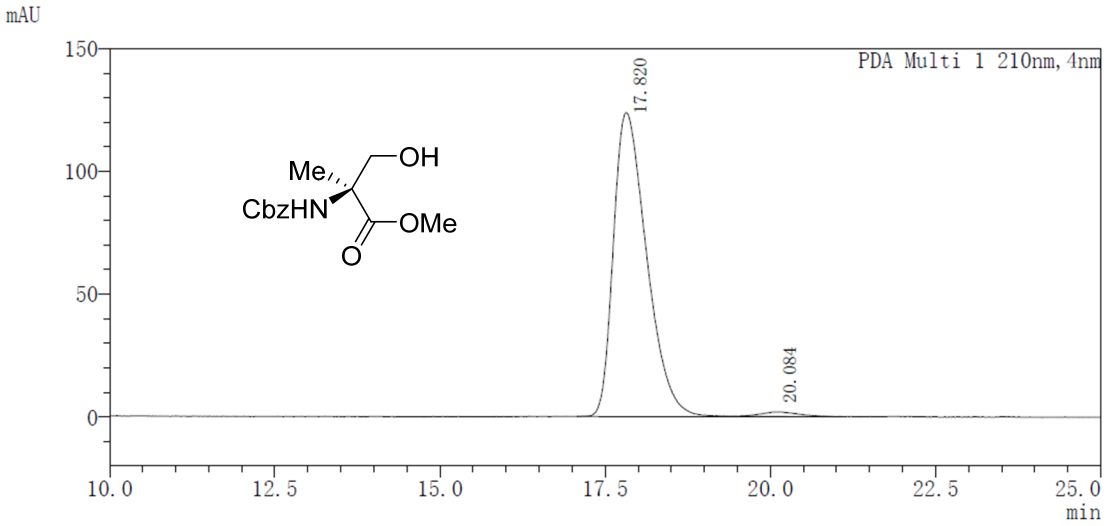
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 19.715 | 123908 | 5.913 |
| 2 | 20.975 | 1971533 | 94.087 |

**55-1**




PDA Ch1 210nm

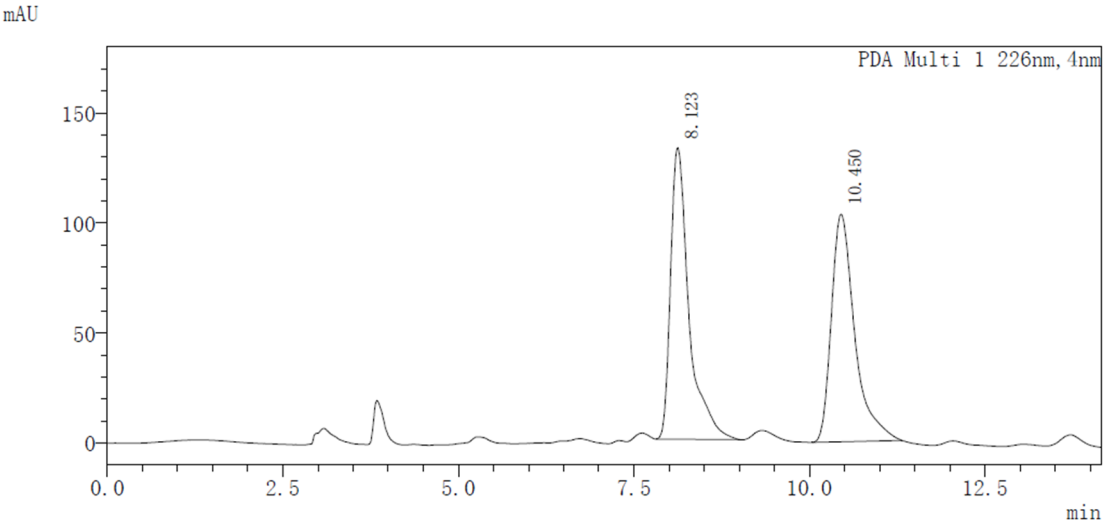
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 17.746 | 5449114 | 50.710 |
| 2 | 19.783 | 5296560 | 49.290 |




PDA Ch1 210nm

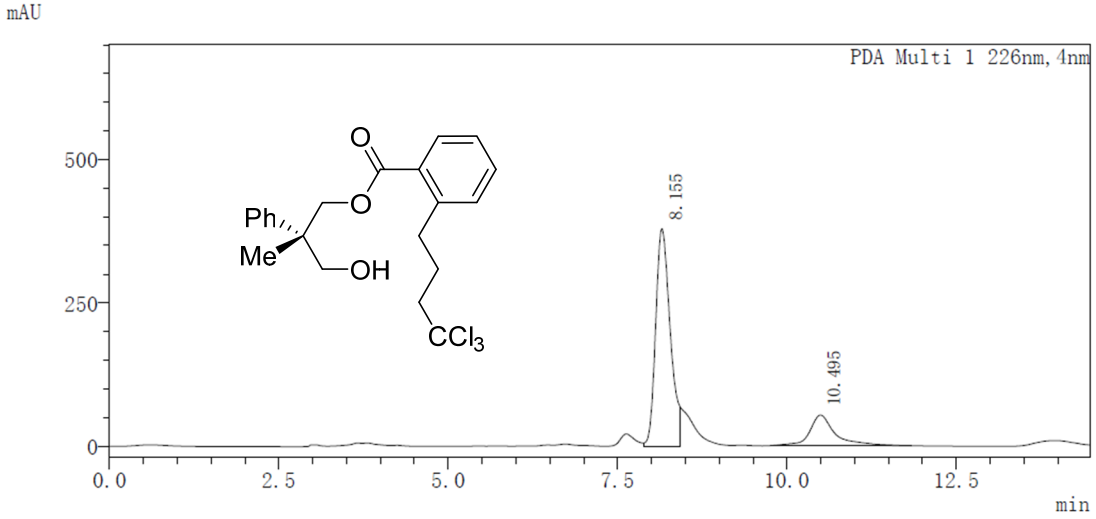
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 17.820 | 4343313 | 98.331 |
| 2 | 20.084 | 73735 | 1.669 |

**57**




PDA Ch1 226nm

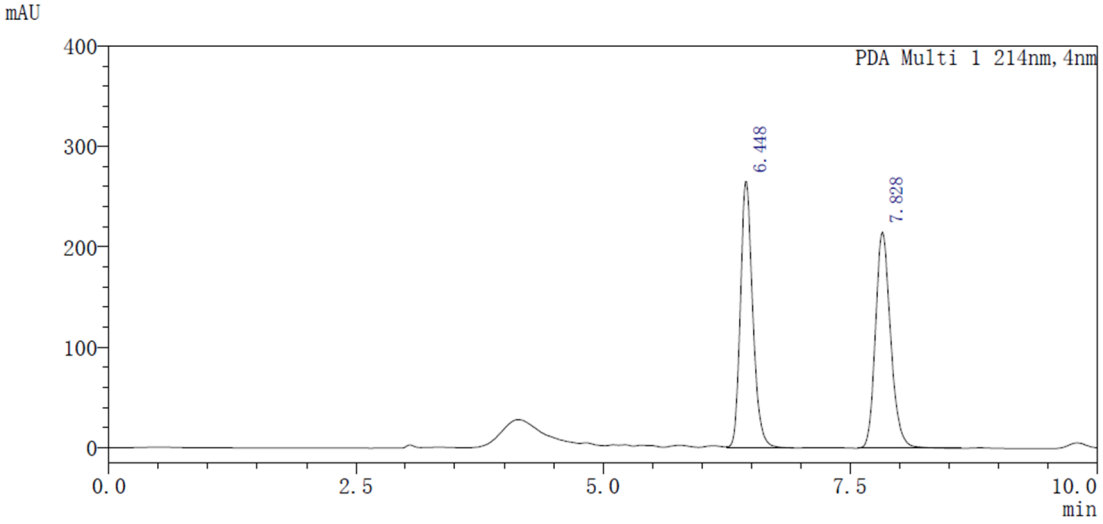
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 8.123 | 2416176 | 50.202 |
| 2 | 10.450 | 2396699 | 49.798 |




PDA Ch1 226nm

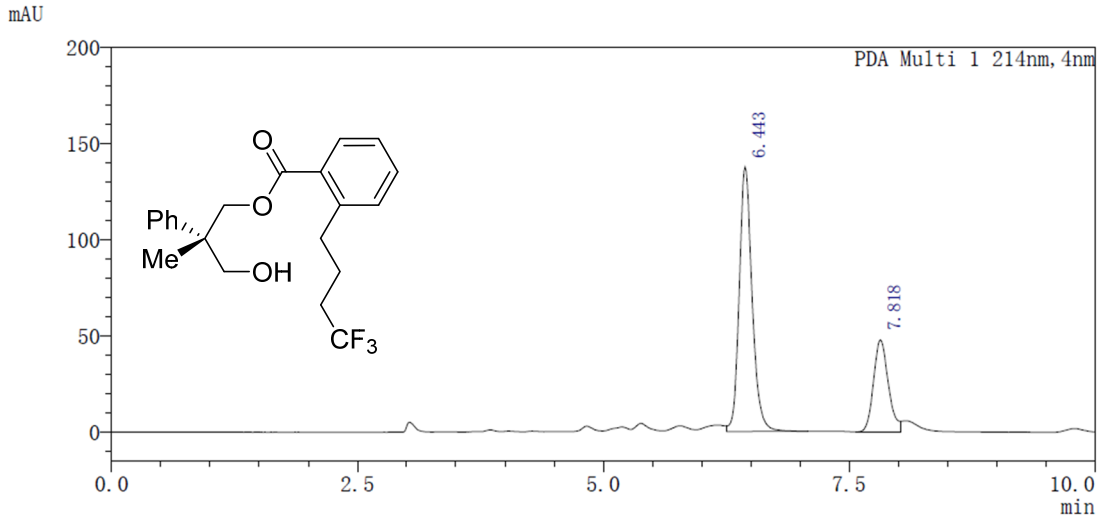
| Peak# | Ret. Time | Area | Area% |
|---|---|---|---|
| 1 | 8.155 | 5716315 | 80.570 |
| 2 | 10.495 | 1378553 | 19.430 |

**58**




PDA Ch1 214nm

| T | Hight | Area | Area% |
|---|---|---|---|
| 6.448 | 265410 | 2316945 | 50.175 |
| 7.828 | 214970 | 2300765 | 49.825 |




PDA Ch1 214nm

| T | Hight | Area | Area% |
|---|---|---|---|
| 6.443 | 137593 | 1253006 | 71.461 |
| 7.818 | 47752 | 500400 | 28.539 |

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