# Supporting Information

## Direct Bromocarboxylation of Arynes Using Allyl Bromides and Carbon Dioxide

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# 1.General information

All manipulations were carried out with standard Schlenk techniques in a $N_2$ glove box. $^1H$ and $^{13}C$ NMR spectra were recorded by using a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and $CDCl_3$ is used as a solvent with TMS as the internal standard. Mass spectra were recorded on a gas chromatograph-mass spectrometer with an FID and equipped with an AT.SE-30 capillary column (internal diameter: 0.32 mm, length: 30 m). The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide plates or as liquid films between two potassium bromide plates with an infrared spectrometer. Melting points were determined with a digital melting point measuring instrument. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF254) using UV light as a visualizing agent. Flash column chromatography was conducted using silica gel (200–300 mesh) with solvent as indicated.

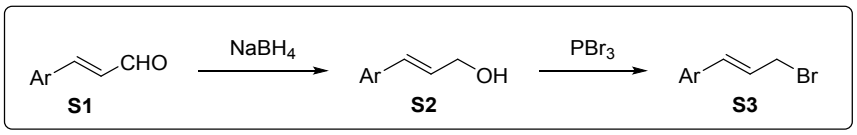
# 2. General procedure for the preparation of aryne precursors

Aryne precursors **1a, 1b, 1d, 1i** were commercially purchased and used without further purification. The other aryne precursors were prepared according to our previous work[1].

# 3. General procedure for the preparation of cinnamyl bromides

Cinnamyl bromide **2a** was commercially purchased and used without further purification. The other cinnamyl bromides were synthesized following literature procedures[2-6]. The synthetic methods are summarized in the following passages according to different starting materials used.

**(A) Synthesis of S3 from cinnamyl aldehyde S1**



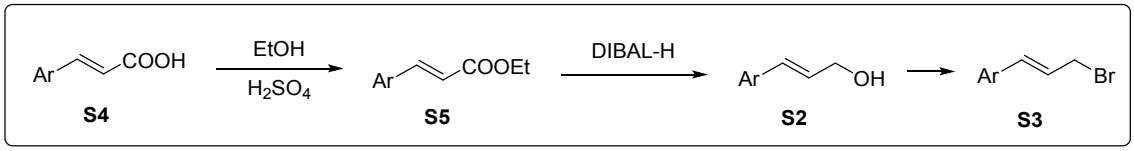
(1) General procedure for the preparation of **S2** from **S1**:

To a stirred solution of **S1** (5 mmol) in 25 mL MeOH at 0 °C was added $NaBH_4$ (5 mmol) slowly. The reaction was warmed to room temperature and stirred for 0.5 h. The reaction mixture was concentrated *in vacuo* and then extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and condensed to afford the crude **S2** and used for the next step without further purification.

(2) General procedure for the preparation of **S3** from **S2**:

To a stirred solution of the crude **S2** in 20 mL anhydrous $Et_2O$ at 0 °C under $N_2$ was added $PBr_3$ (0.4 equiv) dropwise. The reaction was stirred at 0 °C for about 0.5 h and quenched by the addition of saturated $NaHCO_3$ solution slowly. The layers were separated and the aqueous layer extracted with $Et_2O$. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* at room temperature to give **S3**.

**(B) Synthesis of S3 from cinnamic acid S4**




(1) General procedure for the preparation of **S5** from **S4**:

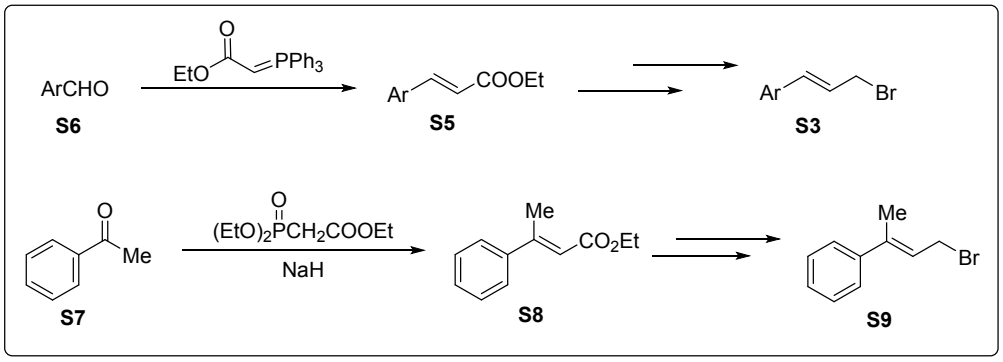
To a stirred solution of **S4** (2 g) in 20 mL EtOH was added concentrated $H_2SO_4$ (0.2 mL) dropwise. The reaction was heated at reflux for 12 h, the residue was then extracted with EtOAc. The combined organic layers were washed with brine, dried over $Na_2SO_4$, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford **S5**.

(2) General procedure for the preparation of **S2** from **S5**:

To a stirred solution of **S5** (5 mmol) in 25 mL anhydrous $CH_2Cl_2$ at -78 °C under $N_2$ was added 10 ml DIBAL-H (1.5 M in toluene) dropwise. The reaction was warmed to room temperature and stirred for 2 h. After completion, the reaction mixture was quenched by the addition of 10% aq. NaOH solution at 0 ˚C. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. The residue was then extracted with $CH_2Cl_2$. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash

chromatography on silica gel to afford **S2**. The procedure from **S2** to **S3** could be found in method (A, (2)).

**(C) Synthesis of S3 from benzaldehyde S6 or synthesis of S9 from acetophenone S7**



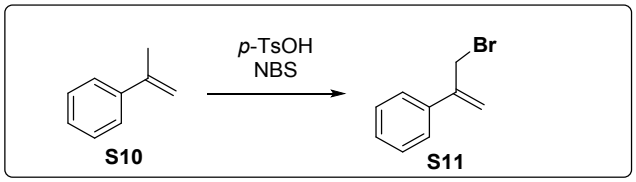

(1) General procedure for the preparation of **S5** from **S6**:

To a stirred solution of **S6** (2.0 g) in 20 mL $CH_2Cl_2$ at room temperature was added ethyl 2-(triphenylphosphoranylidene) acetate (1.5 equiv) slowly. The reaction was stirred at room temperature for 12 h. The solvent was removed *in vacuo* and the crude residue was purified by flash chromatography on silica gel to afford **S5**. The procedure from **S5** to **S3** has been mentioned in method B.

(2) General procedure for the preparation of **S8** from **S7**:

To a stirred solution of NaH (2.5 equiv) in 20 mL anhydrous THF, a solution of ethyl(diethoxyphosphoryl) acetate (1.2 equiv) in 4 mL anhydrous THF was added dropwise at 0 $^oC$ under $N_2$. After 1 h, acetophenone **S7** (10 mmol, 1.0 equiv) was added to the reaction mixture, and then stirred for 24 h at room temperature. After completion, the reaction mixture was quenched by $H_2O$ and extracted with EtOAc. The combined organic layers were dried over $Na_2SO_4$, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford **S8**. The procedure from **S8** to **S9** is similar to the synthesis of **S3**.

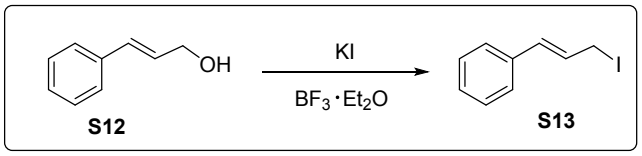
**(D) Synthesis of S11 from S10**




To a stirred solution of **S10** (10 mmol, 1 equiv) in 10 mL anhydrous THF was added NBS (11

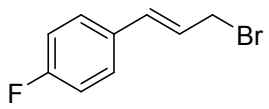
mmol, 1.96 g) and *p*-TsOH (1 mmol, 0.172 g). The reaction mixture was then stirred at 90 °C for 4 h. The solvent was removed *in vacuo* and the crude residue was purified by flash chromatography on silica gel to afford **S11**.

## 4. General procedure for the preparation of cinnamyl iodine S13

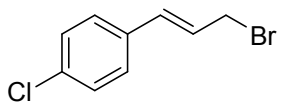



To a stirred solution of **S12** (5 mmol) in 10 mL anhydrous 1,4-dioxane was added $BF_3 \cdot Et_2O$ (5 mmol) and KI (5 mmol). The reaction was stirred for 20 min at room temperature. After completion, the reaction mixture was poured into cold water and extracted with $Et_2O$. The combined organic layers were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford **S13** in 38% isolated yield[7].

## 5. Characterization data for all starting materials

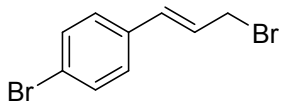



**(*E*)-1-(3-bromoprop-1-en-1-yl)-4-fluorobenzene (2c)** (Yellow solid, 355 mg, 83%) was prepared from corresponding cinnamyl aldehyde (2 mmol) according to the general method A. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 6.0 Hz, 2H), 7.02 (t, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 15.6 Hz, 1H), 6.35 – 6.27 (m, 1H), 4.14 (d, *J* = 7.6 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 246.6 Hz), 133.3, 131.9 (d, *J* = 3.3 Hz), 128.3 (d, *J* = 8.1 Hz), 124.9 (d, *J* = 2.2 Hz), 115.6 (d, *J* = 21.6 Hz), 33.2.

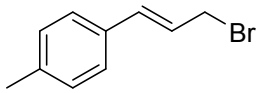



**(*E*)-1-(3-bromoprop-1-en-1-yl)-4-chlorobenzene (2d)** (Yellow solid, 778 mg, 68%) was prepared from corresponding cinnamyl aldehyde (5 mmol) according to the general method A. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 4H), 6.62 (d, *J* = 15.2 Hz, 1H), 6.43 – 6.36 (m, 1H), 4.17 (d, *J* = 7.2 Hz, 2H). $^{13}$C NMR

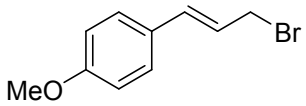
(100 MHz, $CDCl_3$) δ 134.3, 134.0, 133.2, 128.8, 127.9, 125.8, 33.0.



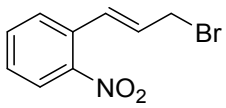

**(*E*)-1-bromo-4-(3-bromoprop-1-en-1-yl)benzene (2e)** (Yellow solid, 427 mg, 78%) was prepared from corresponding cinnamyl aldehyde (2 mmol) according to the general method A. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 6.8 Hz, 2H), 7.17 (s, 2H), 6.49 (d, *J* = 15.2 Hz, 1H), 6.33 – 6.28 (m, 1H), 4.05 (d, *J* = 6.4 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 134.7, 133.2, 131.8, 128.2, 125.9, 122.2, 32.9.



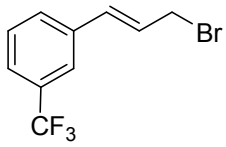

**(*E*)-1-(3-bromoprop-1-en-1-yl)-4-methylbenzene (2f)** (White solid, 755 mg, 72%) was prepared from corresponding cinnamyl aldehyde (5 mmol) according to the general method A. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 2H), 6.63 (d, *J* = 15.6 Hz, 1H), 6.40 – 6.32 (m, 1H), 4.18 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.3, 134.5, 133.0, 129.3, 126.6, 124.1, 33.8, 21.2.



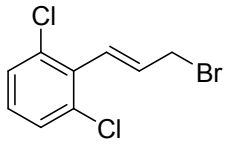

**(*E*)-1-(3-bromoprop-1-en-1-yl)-4-methoxybenzene (2g)** (White solid, 953 mg, 84%) was prepared from corresponding cinnamyl aldehyde (5 mmol) according to the general method A. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 15.2 Hz, 1H), 6.30 – 6.23 (m, 1H), 4.17 (d, *J* = 7.6 Hz, 2H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.8, 134.2, 128.5, 128.0, 123.0, 114.1, 55.3, 34.2.



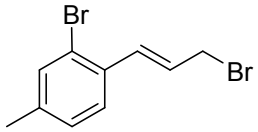

**(*E*)-1-(3-bromoprop-1-en-1-yl)-2-nitrobenzene (2h)** (Yellow solid, 813 mg, 67%) was prepared from corresponding cinnamyl aldehyde (5 mmol) according to the general method A. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.59 (s, 2H), 7.42 (d, *J* = 5.6 Hz, 1H), 7.12 (d, *J* = 15.2 Hz, 1H), 6.39 – 6.31 (m, 1H), 4.15 (d, *J* = 6.8 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.8, 133.3, 131.5, 130.4, 129.4, 128.9, 128.8, 124.7, 32.1.



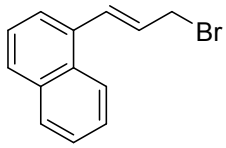

**(*E*)-1-(3-bromoprop-1-en-1-yl)-3-(trifluoromethyl)benzene (2i)** (Green oil, 931 mg, 71%) was prepared from corresponding cinnamic ester (5 mmol) according to the general method B. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 6.54 (d, *J* = 15.6 Hz, 1H), 6.39 – 6.31 (m, 1H), 4.03 (d, *J* = 7.2 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.6, 132.9, 131.1 (q, *J* = 32 Hz), 129.9, 129.2, 127.2, 124.8 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 273.3 Hz), 123.40 (d, *J* = 3.7 Hz), 32.5.




**(*E*)-2-(3-bromoprop-1-en-1-yl)-1,3-dichlorobenzene (2j)** (Yellow oil, 897 mg, 68%) was prepared from corresponding cinnamic ester (5 mmol) according to the general method B. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 8.0 Hz, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.35 – 6.27 (m, 1H), 4.00 (d, *J* = 7.6 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 134.4, 133.8, 132.9, 128.5, 128.4, 127.5, 32.3.

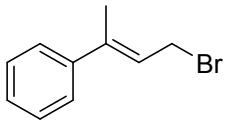



**(*E*)-2-bromo-1-(3-bromoprop-1-en-1-yl)-4-methylbenzene (2k)** (Yellow oil, 905 mg, 69%) was prepared from corresponding cinnamic alcohol (4.55 mmol) according to the general method C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 15.6 Hz, 1H), 6.32 – 6.25 (m, 1H), 4.15 (d, *J* = 7.6 Hz, 2H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.9, 133.3, 132.8, 132.6, 128.4, 127.0, 126.8, 123.6, 33.0, 20.8.

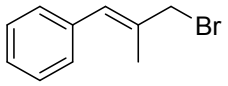



**(*E*)-1-(3-bromoprop-1-en-1-yl)naphthalene (2l)** (White solid, 733 mg, 73%) was prepared from corresponding cinnamic alcohol (4.1 mmol) according to the general method C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 1H), 7.85 (dd, *J* = 21.2, 7.2 Hz, 2H), 7.63 (d, *J* = 6.0 Hz, 1H), 7.53 (d, *J* =

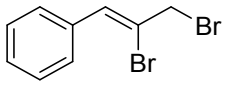
6.4 Hz,, 2H), 7.49 – 7.40 (m, 2H),, 6.49 – 6.42 (m, 1H),, 4.28 (d, $J$ = 6.8 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 133.5, 133.3, 131.5, 131.0, 128.6, 128.6, 128.2, 126.3, 125.9, 125.5, 124.2, 123.5, 76.7, 33.4.



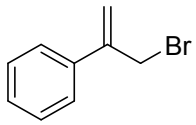

**(*E*)-(4-bromobut-2-en-2-yl)benzene (2m)** (Yellow oil, 904 mg, 86%) was prepared from corresponding cinnamic ester (5 mmol) according to the general method C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, $J$ = 7.6 Hz, 2H), 7.22 (t, $J$ = 7.2 Hz, 2H), 7.17 (t, $J$ = 6.8 Hz, 1H), 5.98 (t, $J$ = 8.4 Hz, 1H), 4.07 (d, $J$ = 8.4 Hz, 2H), 2.02 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.1, 141.4, 128.3, 127.7, 125.8, 122.7, 29.3, 15.5, 1.0.



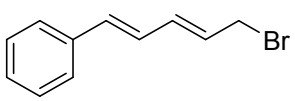

**(*E*)-(3-bromo-2-methylprop-1-en-1-yl)benzene (2n)** (Yellow oil, 681 mg, 65%) was prepared from corresponding cinnamyl alcohol (5 mmol) according to the general method A. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, $J$ = 7.6 Hz, 2H), 7.17 (t, $J$ = 8.0 Hz, 3H), 6.5 (s, 1H), 4.03 (s, 2H), 1.92 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.8, 134.3, 130.0, 128.9, 128.2, 127.1, 42.1, 16.4.




**(*Z*)-(2,3-dibromoprop-1-en-1-yl)benzene (2o)** (Yellow oil, 1027 mg, 75%) was prepared from corresponding cinnamyl aldehyde (5 mmol) according to the general method A. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, $J$ = 7.2 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.14 (s, 1H), 4.45 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 134.5, 132.1, 129.0, 128.7, 128.2, 120.7, 40.7.

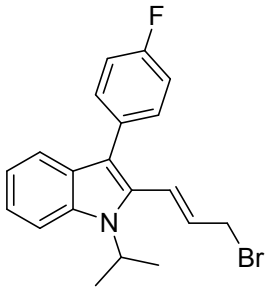



**(3-bromoprop-1-en-2-yl)benzene (2p)** (Yellow oil, 1529 mg, 78%) was prepared from 2-Phenyl-1-propene (10 mmol) according to the general method D. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, $J$ = 7.6 Hz, 2H), 7.37 – 7.28 (m, 3H), 5.53 (s, 1H), 5.45 (s, 1H), 4.35 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 144.2, 137.5, 128.4, 128.2, 126.0, 117.1, 34.1.

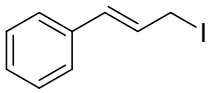



**((1*E*,3*E*)-5-bromopenta-1,3-dien-1-yl)benzene (2q)** (White solid, 838 mg, 88%) was prepared from

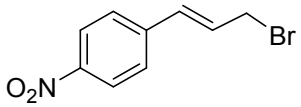
corresponding cinnamic alcohol (4.3 mmol) according to the general method C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 2H), 7.17 – 7.14 (m, 1H), 6.70 – 6.64 (m, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.39 – 6.33 (m, 1H), 5.94 – 5.86 (m, 1H), 4.01 (d, *J* = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.8, 135.2, 134.6, 129.0, 128.7, 128.1, 127.4, 126.6, 33.5.




**(*E*)-2-(3-bromoprop-1-en-1-yl)-3-(4-fluorophenyl)-1-isopropyl-1H-indole (6)** (pale green solid, 1669 mg, 90%) was prepared from corresponding cinnamyl aldehyde (5 mmol) according to the general method A. $^1$H NMR (400 MHz, $C_6D_6$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.21 – 7.10 (m, 5H), 6.95 (t, *J* = 8.4 Hz, 2H), 6.35 (d, *J* = 15.6 Hz, 1H), 5.80 – 5.72 (m, 1H), 4.50 – 4.43 (m, 1H), 3.49 (d, *J* = 7.6 Hz, 2H), 1.27 (s, 3H), 1.25 (s, 3H). $^{13}$C NMR (100 MHz, $C_6D_6$) δ 162.15 (d, *J* = 243.7 Hz), 136.2, 132.3 (d, *J* = 7.7 Hz), 132.3, 131.6 (d, *J* = 3.3 Hz), 131.4, 129.0, 124.0, 122.8, 120.5, 120.4, 116.7, 115.7 (d, *J* = 21.1 Hz), 112.0, 47.8, 32.8, 21.5. IR (KBr)/cm$^{-1}$ 3051, 2979, 2876, 1604, 1543, 1502, 1454, 1345, 1220, 1151, 1102, 960, 741, 562. HRMS-APCI (*m/z*): calcd for $C_{20}H_{20}BrFN^+$ $[M + H]^+$: 372.0758; found 372.0753.



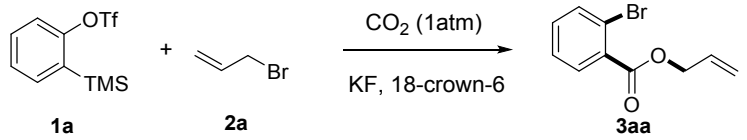

**(*E*)-(3-iodoprop-1-en-1-yl)benzene (2s)** (Yellow solid, 464 mg, 38%) was prepared from corresponding cinnamyl alcohol (5 mmol) according to references 7. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 4H), 7.32 – 7.29 (m, 1H), 6.64 (d, *J* = 15.2 Hz, 1H), 6.52 – 6.44 (m, 1H), 4.15 (d, *J* = 7.6 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 135.9, 133.1, 128.6, 128.1, 126.9, 126.6, 6.8.




**(*E*)-1-(3-bromoprop-1-en-1-yl)-4-nitrobenzene (2u)** (Yellow solid, 817 mg, 67%) was prepared from corresponding cinnamyl aldehyde (5 mmol) according to the general method A. $^1$H NMR (400 MHz, CDCl3) δ 8.06 (d, J = 7.6 Hz, 2H), 7.41 (d, J = 7.6 Hz, 2H), 6.60 (d, J = 15.6 Hz, 1H), 6.50 – 6.42 (m,

1H), 4.06 (d, J = 7.2 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl3) δ 147.1, 142.0, 131.8, 129.7, 127.1, 123.8, 31.9.

## 6. Reaction optimization for the synthesis of 3aa

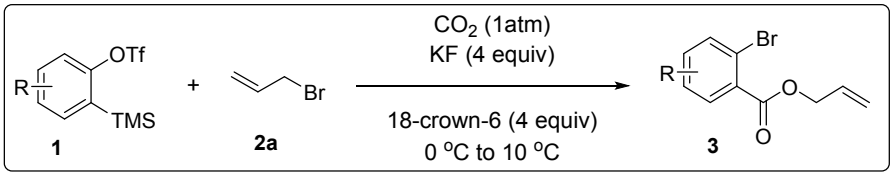



**1a** **2a** **3aa**

| Entry [a] | KF (eq.) | 18-crown-6 (eq.) | $CO_2$ | *T* (°C) | time (h) | yield (%) [b] |
|---|---|---|---|---|---|---|
| 1 | 4 | 4 | 1atm | 46 | 12 | 52 |
| 2 | 4 | 4 | 1atm | 10 | 12 | 69 |
| 3 | 4 | 4 | 1atm | 0 | 12 | 64 |
| 4 | 4 | 4 | 1atm | 0 to 5 | 12 | 71 |
| 5 | **4** | **4** | **1atm** | **0 to 10** | **12** | **79** |
| 6 | 4 | 4 | 1atm | 0 to rt | 12 | 65 |
| 7 | 4 | - | 1atm | 0 to 10 | 12 | n.d. |
| 8 | 4 | 4 | $N_2$ | 0 to 10 | 12 | n.d. |
| 9 | 4 | 4 | 1atm | 0 to10 | 24 | 80 |

Reaction conditions: [a]**1a** (0.2 mmol), $CO_2$ (1 atm), **2a** (0.5 mL), 12 h; [b] Yield based on **1a** and determined by $^1$H NMR analysis using $CH_3NO_2$ as an internal standard.

## 7. Three-component coupling of arynes, allyl bromide and $CO_2$

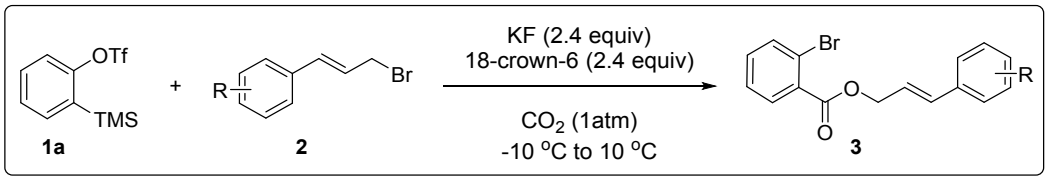



**1** **2a** **3**

In a $N_2$ glove box, a dried 25 mL Schlenk tube was charged with KF (4 equiv, 46.5 mg), 18-crown-6 (4 equiv, 211.5 mg) and **2a** (0.5 mL) and filled with a rubber plug. Then the sealed tube was removed from the $N_2$ glove box. The reaction mixture was stirred at 0 °C for 5 min and

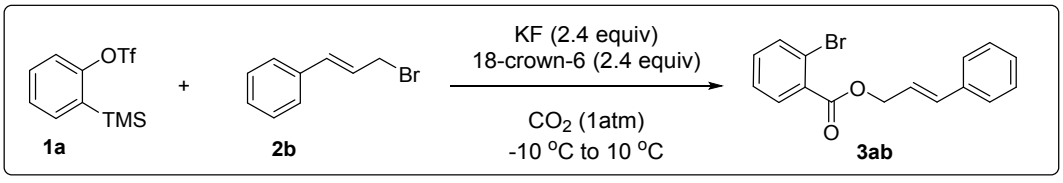
evacuated and backfilled with $CO_2$ (1 atm) for three times. To the stirring mixture was added the aryne precursor **1** (0.2 mmol, 49 μL) dropwise by a syringe. Then the reaction mixture was slowly warmed to 10 °C and kept stirring for 12 h. After the reaction was completed, the reaction mixture was quenched by $H_2O$ (10 mL) and extracted with ethyl acetate (30 mL). The organic layers were dried over $Na_2SO_4$ and the solvent was evaporated. The crude residue was then separated by column chromatography on silica gel to afford corresponding products **3**.

## 8. Three-component coupling of arynes, cinnamyl bromides and $CO_2$




In a $N_2$ glove box, a dried 25 mL Schlenk tube was charged with KF (2.4 equiv, 27.8 mg), 18-crown-6 (2.4 equiv, 126.8 mg). The reaction mixture was dissolved in anhydrous Ph-$CF_3$ (1 mL) and then added cinnamyl bromides **2** (0.2 mmol, 1 equiv). The sealed tube was filled with a rubber plug and removed from the $N_2$ glove box. The reaction mixture was stirred at -10 °C for 5 min and evacuated and backfilled with $CO_2$ (1 atm) for three times. To the stirring mixture was added the aryne precursor **1** (0.24 mmol, 59 μL) dropwise by a syringe. Then the reaction mixture was slowly warmed to 10 °C and kept stirring for 12 h. After the reaction was completed, the reaction mixture was quenched by $H_2O$ (10 mL) and extracted with ethyl acetate (30 mL). The organic layers were dried over $Na_2SO_4$ and the solvent was evaporated. The crude residue was then separated by column chromatography on silica gel to afford corresponding products **3**.

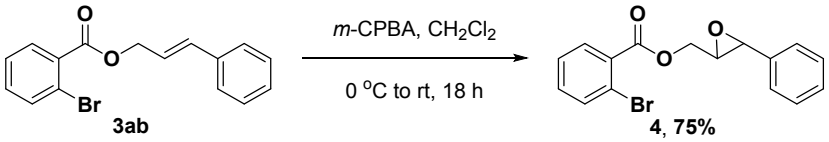
## 9. Procedure for the synthesis of 3ab in a 1 mmol scale



In a $N_2$ glove box, a dried 25 mL Schlenk tube was charged with KF (2.4 mmol), 18-crown-6 (2.4 mmol). The reaction mixture was dissolved in anhydrous Ph-$CF_3$ (5 mL) and then added cinnamyl bromides **2** (1 mmol). The sealed tube was filled with a rubber plug and removed from the $N_2$ glove box. The reaction mixture was stirred at -10 $^oC$ for 5 min and evacuated and backfilled with $CO_2$ (1 atm) for three times. To the stirring mixture was added the aryne precursor **1** (0.24 mmol, 59 μL) dropwise by a syringe and the Schlenk tube was linked to a $CO_2$ balloon. Then the reaction mixture was slowly warmed to 10 $^oC$ and kept stirring for 12 h. After the reaction was completed, the reaction mixture was quenched by $H_2O$ (30 mL) and extracted with ethyl acetate (90 mL). The organic layers were dried over $Na_2SO_4$ and the solvent was evaporated. The crude residue was then separated by column chromatography on silica gel to afford corresponding products **3ab** in 74% isolated yield.

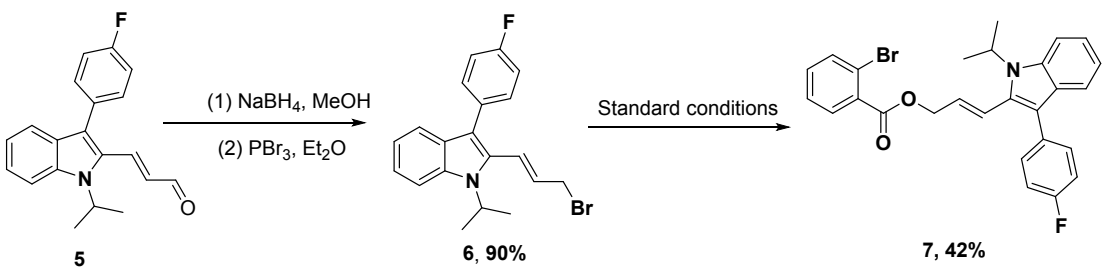
## 10. Synthetic applications

(1)




To a dried 25 mL Schlenk tube equipped with a magnetic stirring bar was added **3ab** (0.2 mmol, 63.2 mg) and dissolved in $CH_2Cl_2$ (2 mL), then *m*-CPBA (85%, 60 mg, 0.4 mmol) was added to the reaction mixture at 0 $^oC$ slowly. The tube was then filled with a rubber plug and stirred at room temperature for 18 h. After completion, the reaction mixture was quenched by the addition of saturated $NaHCO_3$ solution (10 mL) and extracted with $CH_2Cl_2$ (20 mL ×3). The organic layers were dried over $Na_2SO_4$ and the solvent was evaporated. The crude residue was then separated by column chromatography on silica gel to afford corresponding products **4** in 75% isolated yield.

(2)



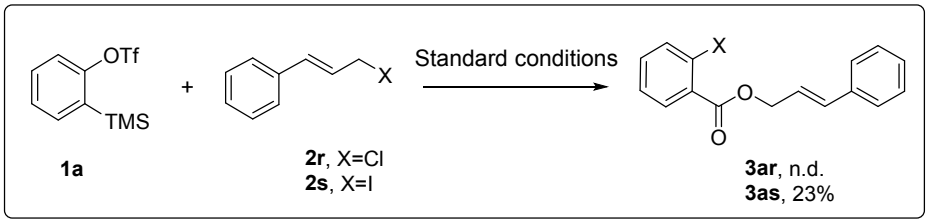
To a stirred solution of **5** (5 mmol) in 25 mL MeOH at 0 °C was added $NaBH_4$ (5 mmol) slowly. The reaction was warmed to room temperature and stirred for 0.5 h. The reaction mixture was concentrated *in vacuo* and then extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and condensed to afford the corresponding alcohol and used for the next step without further purification.

To a stirred solution of the corresponding alcohol in 20 mL anhydrous $Et_2O$ at 0 °C under $N_2$ was added $PBr_3$ (0.4 equiv) dropwise. The reaction was stirred at 0 °C for about 0.5 h and quenched by the addition of saturated $NaHCO_3$ solution. The layers were separated and the aqueous layer extracted with EtOAc. The combined organic layers were washed with brine, dried over anhydrous $Na_2SO_4$, filtered, and concentrated *in vacuo* at room temperature to afford **6** in 90% isolated yield.

Then, treatment of **6** with aryne precursor **1a** under the standard conditions resulted in the formation of **7** in 42% isolated yield.

## 11. Mechanistic experiments

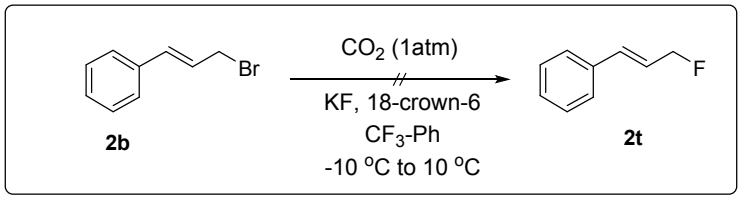
(a)




In a $N_2$ glove box, a dried 25 mL Schlenk tube was charged with KF (2.4 equiv, 27.8 mg), 18-crown-6 (2.4 equiv, 126.8 mg). The reaction mixture was dissolved in anhydrous Ph-$CF_3$ (1 mL) and then added corresponding **2r** or **2s** (0.2 mmol, 1 equiv). The sealed tube was filled with a rubber plug and removed from the $N_2$ glove box. The reaction mixture was stirred at -10 °C for 5 min and evacuated and backfilled with $CO_2$ (1 atm) for three times. To the stirring mixture was added the aryne precursor **1** (0.24 mmol, 59 μL) dropwise by a syringe. Then the reaction mixture was slowly warmed to 10 °C and kept stirring for 12 h. After the reaction was completed, the reaction mixture was filtrated and washed with ethyl acetate (30 mL). The organic layers were dried over $Na_2SO_4$ and the solvent was evaporated. The crude residue was then determined by $^1H$ NMR analysis using

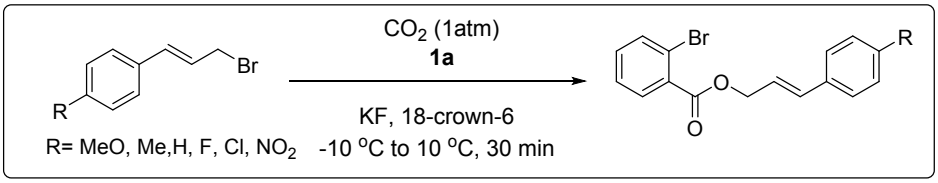
$CH_3NO_2$ as an internal standard.

(b)



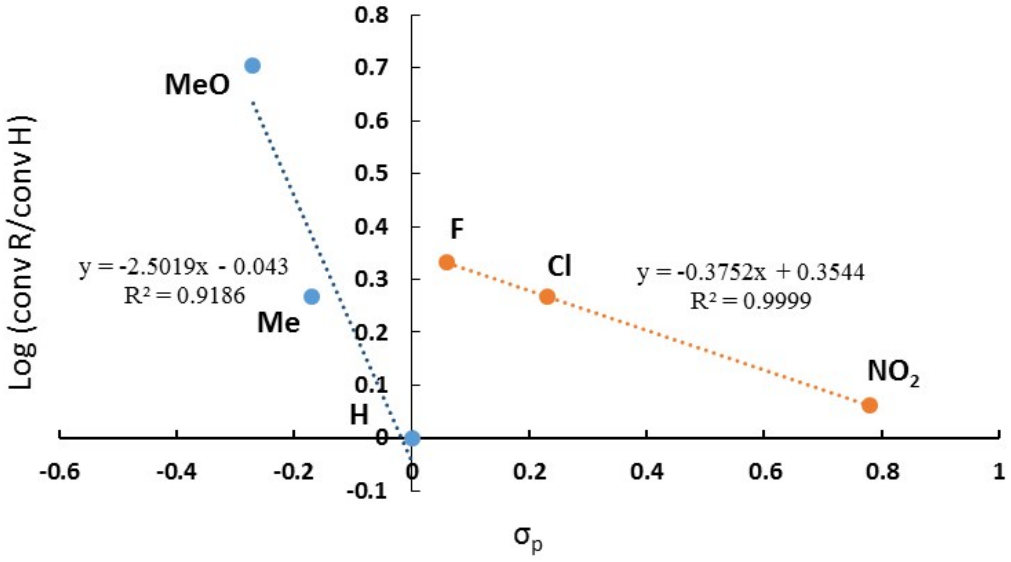

In a $N_2$ glove box, a dried 25 mL Schlenk tube was charged with KF (2.4 equiv, 27.8 mg), 18-crown-6 (2.4 equiv, 126.8 mg). The reaction mixture was dissolved in anhydrous Ph-$CF_3$ (1 mL) and then added corresponding **2b** (0.2 mmol, 1 equiv). The sealed tube was filled with a rubber plug and removed from the $N_2$ glove box. The reaction mixture was stirred at -10 °C for 5 min and evacuated and backfilled with $CO_2$ (1 atm) for three times. Then the reaction mixture was slowly warmed to 10 °C and kept stirring for 12 h. After the reaction was completed, the reaction mixture was filtrated and dissolved in $CDCl_3$. However, no obvious new signal was determined by $^{19}F$ NMR analysis.

(c)




In a $N_2$ glove box, a dried 25 mL Schlenk tube was charged with KF (2.4 equiv, 27.8 mg), 18-crown-6 (2.4 equiv, 126.8 mg). The reaction mixture was dissolved in anhydrous Ph-$CF_3$ (1 mL) and then added corresponding cinnamyl bromides **2** (0.2 mmol, 1 equiv). The sealed tube was filled with a rubber plug and removed from the $N_2$ glove box. The reaction mixture was stirred at -10 °C for 5 min and evacuated and backfilled with $CO_2$ (1 atm) for three times. To the stirring mixture was added the aryne precursor **1** (0.24 mmol, 59 μL) dropwise by a syringe. Then the reaction mixture was slowly warmed to 10 °C and kept stirring for 30 min. After the reaction was completed, the reaction mixture was filtrated and washed with ethyl acetate (30 mL). The organic layers were dried over $Na_2SO_4$ and the solvent was evaporated. The crude residue was then determined by $^1H$ NMR analysis using $CH_3NO_2$ as an internal standard. The corresponding log [conv R/conv H] and $\sigma_p$ values used to obtain the Hammett plot[8,9] are given below:

| | $\sigma_p$ | Yield | Starting material | Conversion | Log（conv R/conv H） |
|---|---|---|---|---|---|
| R=MeO | -0.27 | 6% | 34% | 66% | 0.705601 |
| R=Me | -0.17 | 4% | 76% | 24% | 0.266268 |
| R=H | 0 | 6% | 87% | 13% | 0 |
| R=F | 0.06 | 6% | 72% | 28% | 0.333215 |
| R=Cl | 0.23 | 4% | 76% | 24% | 0.266268 |
| R=$NO_2$ | 0.78 | 7% | 85% | 15% | 0.062148 |



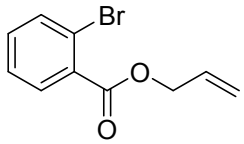

## 12. References


1. Jiang, H.; Zhang, Y.; Xiong, W.; Cen, J.; Wang, L.; Cheng, R.; Qi, C.; Wu, W. *Org. Lett*. **2019**, *21,* 345.
2. Li, X. T.; Gu, Q. S.; Dong, X. Y.; Meng, X.; Liu, X. Y. *Angew. Chem., Int. Ed*. **2018**, *57*, 7668.
3. Cho, H.; Shin, J.; Lee, S.; Jeon, H.; Park, S.; Kim, S. *Org. Lett*. **2018**, *20*, 6121.
4. West, T.; Daniels, D. S. B.; Slawin, A. M. Z.; Smith, A. *J. Am. Chem. Soc*. **2014**, *136*, 4476.
5. Wei, H.; Mao, F.; Ni, S.; Chen, F.; Li, B.; Qiu, X.; Hu, L.; Wang, M.; Zheng, X.; Zhu, J.; Lan, L.; Li, J. *Eur. J. Med. Chem*. **2018**, *145*, 235.
6. Nguyen, T. N. T.; Thiel, N.; Pape, F.; Teichert, J. *Org. Lett*. **2016**, *18*, 2455.
7. Bandgar, B. P.; Sadavarte, V. S.; Uppalla, L. S. *Tetrahedron Lett*. **2001**, *42*, 951.
8. Basnet, P.; Thapa, S.; Dickie, D. A.; Giri, R. *Chem. Commun*. **2016**, *52*, 11072.

9. Aihara, Y.; Chatani, N. *Chem. Sci*. **2013**, *4*, 664.

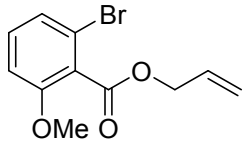
# 13. Characterization data for all products

### Allyl 2-bromobenzoate (3aa)



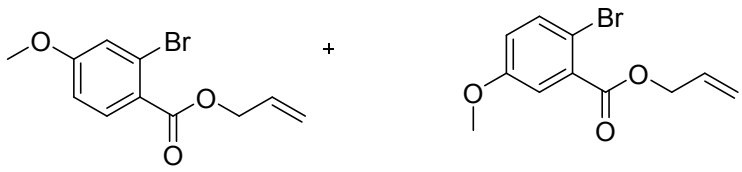
**3aa** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a yellow oil in 70% yield (33.6 mg). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.65 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.37 – 7.29 (m, 2H), 6.08 – 5.99 (m, 1H), 5.43 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.30 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.83 (d, *J* = 6.0, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.7, 134.3, 132.5, 132.1, 131.7, 131.3, 127.1, 121.6, 118.7, 66.1. IR (KBr)/cm$^{-1}$ 3080, 2932, 1730, 1585, 1439, 1364, 1254, 1119, 1032, 936, 745, 638. HRMS-ESI (*m/z*): calcd for $C_{10}H_9BrNaO_2^+$ [M + Na]$^+$: 262.9678; found 262.9681.

### Allyl 2-bromo-6-methoxybenzoate (3ba)



**3ba** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 30:1) as a yellow oil in 78% yield (42.1 mg). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 8.4 Hz, 1H), 7.14 – 7.12 (m, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.07 – 5.97 (m, 1H), 5.44 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.29 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.85 (dd, *J* = 6.0, 1.2 Hz, 2H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.8, 157.1, 131.6, 131.2, 125.8, 124.4, 119.6, 118.7, 109.9, 66.3, 56.1. IR (KBr)/cm$^{-1}$ 3091, 2947, 1735, 1580, 1451, 1360, 1268, 1105, 1034, 935, 839, 758. HRMS-ESI (*m/z*): calcd for $C_{11}H_{11}BrNaO_3^+$ [M + Na]$^+$: 292.9784; found 292.9788.

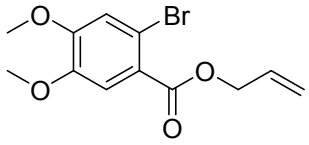
### Allyl 2-bromo-4-methoxybenzoate and allyl 2-bromo-5-methoxybenzoate (3ca and 3ca`)



**3ca** and **3ca`** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 30:1) as a yellow oil in 64% yield (regioisomer ratio= 1.3:1, 34.6 mg). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.8 Hz, 0.34H), 7.51 (d, *J* = 8.8 Hz, 0.64H), 7.32 (d, *J* = 2.8 Hz, 0.6H), 7.18 (s, 0.35H), 6.89 – 6.85 (m, 1H), 6.09 – 5.99 (m, 1H), 5.45 (d, *J* = 6.8 Hz, 0.55H), 5.40 (d, *J* = 6.8 Hz, 0.46H), 5.31 – 5.27 (m, 1H), 4.84 – 4.79 (m, 2H), 3.82 (s, 1.2H), 3.80 (s, 1.8H). $^{13}$C NMR

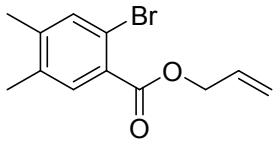
(100 MHz, $CDCl_3$) δ 165.5, 164.9, 162.3, 158.5, 134.9, 133.2, 132.6, 132.0, 131.7, 123.5, 123.2, 119.8, 118.8, 118.7, 118.3, 116.3, 112.9, 111.8, 66.1, 65.7, 55.5, 55.5. IR (KBr)/$cm^{-1}$ 3086, 2943, 1727, 1592, 1470, 1409, 1242, 1115, 1033, 937, 821, 765. HRMS-ESI (*m/z*): calcd for $C_{11}H_{11}BrNaO_3^+$ $[M + Na]^+$: 292.9784; found 292.9791.

## Allyl 2-bromo-4,5-dimethoxybenzoate (3da)



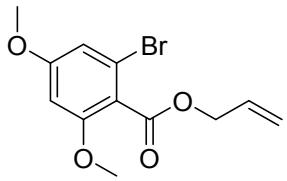
**3da** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow solid in 88% yield (52.8 mg, m.p. = 67- 68 °C). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.03 (s, 1H), 6.04 – 5.94 (m, 1H), 5.37 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.24 (dd, *J* = 10.4, 0.8 Hz, 1H), 4.76 (d, *J* = 6.0 Hz, 2H), 3.85 (s, 3H), 3.83 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 164.8, 151.9, 147.6, 131.9, 122.7, 118.3, 116.8, 114.0, 113.8, 65.8, 56.1, 55.9. IR (KBr)/$cm^{-1}$ 3085, 2940, 1721, 1592, 1508, 1450, 1368, 1260, 1191, 1115, 1025, 979, 764. HRMS-ESI (*m/z*): calcd for $C_{12}H_{13}BrNaO_4^+$ $[M + Na]^+$: 322.9889; found 322.9905.

## Allyl 2-bromo-4,5-dimethylbenzoate (3ea)



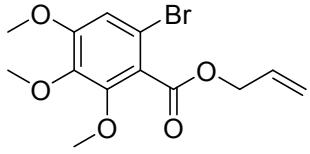
**3ea** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a yellow oil in 72% yield (38.6 mg). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.42 (s, 1H), 6.09 – 5.99 (m, 1H), 5.42 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.29 (d, *J* = 10.8 Hz, 1H), 4.81 (d, *J* = 5.6 Hz, 2H), 2.25 (s, 3H), 2.23 (s, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.7, 142.4, 135.8, 135.2, 132.5, 132.0, 128.8, 118.7, 118.5, 65.9, 19.5, 19.1. IR (KBr)/$cm^{-1}$ 3087, 2935, 1725, 1585, 1456, 1378, 1260, 1220, 936, 755. HRMS-ESI (*m/z*): calcd for $C_{12}H_{13}BrNaO_2^+$ $[M + Na]^+$: 269.0172; found 269.0178.

## Allyl 2-bromo-4,6-dimethoxybenzoate (3fa)



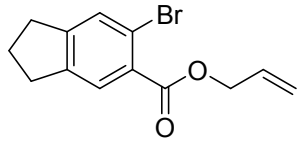
**3fa** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a pale yellow solid in 86% yield (51.6 mg, m.p. = 55- 56 °C). $^1H$ NMR (400 MHz, $CDCl_3$) δ 6.67 (s, 1H), 6.40 (s, 1H), 6.07 – 5.97 (m, 1H), 5.43 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.8 Hz, 1H), 4.82 (d, *J* = 6.0 Hz, 2H), 3.79 (s, 6H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.9, 161.6, 158.3, 131.8, 120.4, 118.8, 118.5, 108.9, 98.0, 66.1, 56.98, 55.62. IR (KBr)/$cm^{-1}$ 3091, 2946, 2847, 1733, 1590, 1460, 1270, 1157, 1104, 1135, 934, 825, 620. HRMS-ESI (*m/z*): calcd for $C_{12}H_{13}BrNaO_4^+$ $[M + Na]^+$: 322.9889; found 322.9894.

## Allyl 6-bromo-2,3,4-trimethoxybenzoate (3ga)



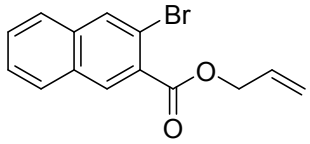
**3ga** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 70% yield (46.2 mg). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 1H), 6.05 – 5.95 (m, 1H), 5.41 (d, *J* = 17.2 Hz, 1H), 5.26 (d, *J* = 10.4 Hz, 1H), 4.80 (d, *J* = 6.0 Hz, 2H), 3.88 (s, 3H), 3.83 (s, 3H), 3.82 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.4, 154.9, 151.6, 141.5, 131.6, 123.9, 118.8, 112.8, 111.8, 66.3, 61.8, 60.8, 56.3. IR (KBr)/cm$^{-1}$ 3090, 2941, 1731, 1584, 1463, 1392, 1272, 1156, 1106, 1016, 929, 812, 736. HRMS-ESI (*m/z*): calcd for $C_{13}H_{15}BrNaO_5^+$ $[M + Na]^+$: 352.9995; found 353.0000.

## Allyl 6-bromo-2,3-dihydro-1H-indene-5-carboxylate (3ha)



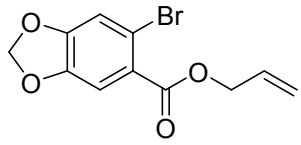
**3ha** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a yellow oil in 67% yield (37.5 mg). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.49 (s, 1H), 6.07 – 6.00 (m, 1H), 5.43 (d, *J* = 17.2 Hz, 1H), 5.29 (d, *J* = 10.4 Hz, 1H), 4.81 (d, *J* = 5.6 Hz, 2H), 2.93 – 2.85 (m, 4H), 2.14 – 2.06 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.1, 150.1, 143.7, 131.9, 130.1, 129.5, 127.0, 119.3, 118.6, 65.9, 32.7, 32.2, 25.4. IR (KBr)/cm$^{-1}$ 2935, 1810, 1724, 1584, 1448, 1383, 1258, 1107, 925, 755. HRMS-ESI (*m/z*): calcd for $C_{13}H_{13}BrNaO_2^+$ $[M + Na]^+$: 302.9991; found 302.9995.

## Allyl 3-bromo-2-naphthoate (3ia)



**3ia** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a yellow oil in 72% yield (41.8 mg). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.12 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.50 (m, 2H), 6.15 – 6.05 (m, 1H),, 5.48 (d, *J* = 17.2 Hz, 1H), 5.34 (d, *J* = 10.4 Hz, 1H), 4.90 (d, *J* = 5.6 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.7, 135.2, 133.0, 132.2, 131.8, 131.0, 129.1, 128.8, 128.6, 127.1, 126.7, 118.8, 117.0, 66.2. IR (KBr)/cm$^{-1}$ 3067, 2934, 1724, 1581, 1442, 1354, 1265, 1205, 1110, 974, 752, 579. HRMS-ESI (*m/z*): calcd for $C_{14}H_{11}BrNaO_2^+$ $[M + Na]^+$: 312.9835; found 312.9839.

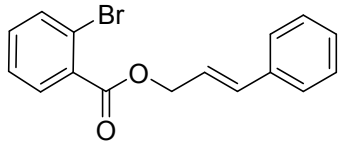
## Allyl 6-bromobenzo[d][1,3]dioxole-5-carboxylate (3ja)



**3ja** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a yellow oil in 74% yield (42.0 mg). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.05 (s, 1H), 6.05 – 5.95 (m, 3H), 5.39 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.27 (d, *J* = 10.4 Hz, 1H), 4.77 (d, *J* = 5.6 Hz, 2H). $^{13}$C

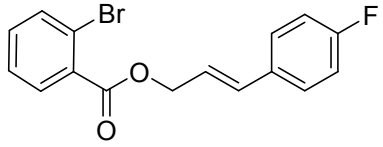
NMR (100 MHz, $CDCl_3$) δ 164.7, 150.9, 147.0, 131.8, 124.3, 118.5, 114.9, 114.3, 110.9, 102.4, 65.9. IR (KBr)/$cm^{-1}$ 3090, 2921, 1720, 1601, 1478, 1395, 1240, 1123, 1025, 927, 854, 759. HRMS-ESI (*m/z*): calcd for $C_{11}H_9BrNaO_4^+$ $[M + Na]^+$: 306.9576; found 306.9578.

## Cinnamyl 2-bromobenzoate (3ab)



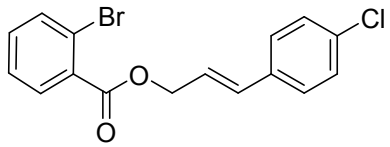

**3ab** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 74% yield (46.8 mg). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.31 (m, 4H), 7.28 – 7.24 (m, 1H), 6.76 (d, *J* = 15.6 Hz, 1H), 6.43 – 6.36 (m, 1H), 4.99 (d, *J* = 6.4 Hz, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.9, 136.1, 134.7, 134.3, 132.5, 132.1, 131.3, 128.6, 128.1, 127.1, 126.6, 122.7, 121.7, 66.1. IR (KBr)/$cm^{-1}$ 3044, 2934, 1722, 1583, 1440, 1370, 1253, 1113, 1030, 954, 738. HRMS-ESI (*m/z*): calcd for $C_{16}H_{13}BrNaO_2^+$ $[M + Na]^+$: 338.9991; found 338.9996.

## (*E*)-3-(4-fluorophenyl)allyl 2-bromobenzoate (3ac)




**3ac** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 70% yield (46.8 mg). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.31 (m, 4H), 7.02 (t, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 15.6 Hz, 1H), 6.36 – 6.29 (m, 1H), 4.98 (d, *J* = 6.4 Hz, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.9, 162.6 (d, *J* = 246 Hz), 134.4, 133.6, 132.6, 132.3 (d, *J* = 3.2 Hz), 132.1, 131.3, 128.2 (d, *J* = 8.1 Hz), 127.1, 122.4 (d, *J* = 2.1 Hz), 121.7, 115.5 (d, *J* = 21.5 Hz), 66.0. IR (KBr)/$cm^{-1}$ 3044, 2934, 1722, 1583, 1441, 1370, 1253, 1113, 1030, 954, 839, 738. HRMS-ESI (*m/z*): calcd for $C_{16}H_{12}BrFNaO_2^+$ $[M + Na]^+$: 356.9897; found 356.9901.

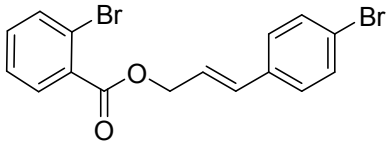
## (*E*)-3-(4-chlorophenyl)allyl 2-bromobenzoate (3ad)




**3ad** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 65% yield (45.5 mg). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.2 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.29 (m, 6H), 6.74 (d, *J* = 15.6 Hz, 1H), 6.44 – 6.37 (m, 1H), 5.02 (d, *J* = 6.0 Hz, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 165.8, 134.6, 134.3, 133.8, 133.3, 132.6, 132.0, 131.3, 128.8, 127.8, 127.1, 123.4, 121.7, 65.9. IR (KBr)/$cm^{-1}$ 2930, 1716, 1576, 1472, 1365,

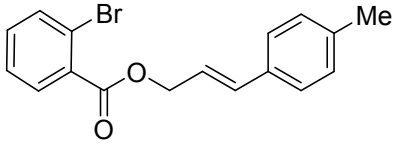
1243, 1110, 1023, 943, 831, 739. HRMS-ESI (*m/z*): calcd for $C_{16}H_{12}BrClNaO_2^+$ [M + Na]$^+$: 372.9601; found 372.9605.

## (*E*)-3-(4-bromophenyl)allyl 2-bromobenzoate (3ae)



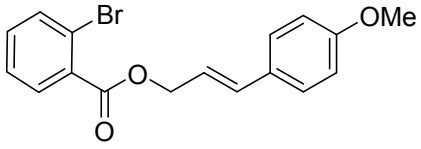

**3ae** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 64% yield (50.4 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 15.6 Hz, 1H), 6.42 – 6.35 (m, 1H), 4.98 (d, *J* = 6.0 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.8, 135.1, 134.4, 133.4, 132.6, 132.0, 131.7, 131.3, 128.2, 127.2, 123.5, 122.0, 121.7, 65.8. IR (KBr)/cm$^{-1}$ 3037, 2923, 1719, 1582, 1474, 1431, 1374, 1281, 1239, 1108, 1023, 952, 836, 792. HRMS-ESI (*m/z*): calcd for $C_{16}H_{12}Br_2NaO_2^+$ [M + Na]$^+$: 416.9096; found 416.9095.

## (*E*)-3-(p-tolyl)allyl 2-bromobenzoate (3af)



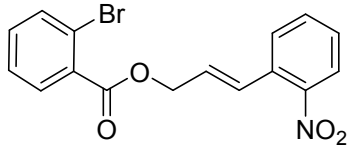

**3af** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 58% yield (38.3 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.37 – 7.31 (m, 4H), 7.15 (d, *J* = 7.2 Hz, 2H), 6.74 (d, *J* = 15.6 Hz, 1H), 6.40 – 6.33 (m, 1H), 4.99 (d, *J* = 6.4 Hz, 2H), 2.35 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.0, 138.1, 134.8, 134.3, 133.3, 132.5, 132.2, 131.3, 129.3, 127.1, 126.6, 122.0, 121.56, 66.3, 21.2. IR (KBr)/cm$^{-1}$ 3024, 2921, 1714, 1579, 1431, 1368, 1239, 1106, 1025, 947, 738. HRMS-ESI (*m/z*): calcd for $C_{17}H_{15}BrNaO_2^+$ [M + Na]$^+$: 353.0148; found 353.0153.

## (*E*)-3-(4-methoxyphenyl)allyl 2-bromobenzoate (3ag)



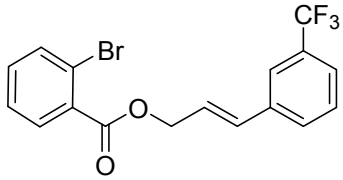

**3ag** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 30% yield (20.8 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.30 (m, 4H), 6.87 (d, *J* = 7.6 Hz, 2H), 6.71 (d, *J* = 15.6 Hz, 1H), 6.31 – 6.24 (m, 1H), 4.97 (d, *J* = 6.4 Hz, 2H), 3.81 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.0, 159.6, 134.6, 134.3, 132.5, 132.2, 131.3, 128.9, 127.9, 127.1, 121.7, 120.3, 114.0, 66.5, 55.3. IR (KBr)/cm$^{-1}$ 2920, 1717, 1590, 1502, 1442, 1244, 1110, 1026, 946, 836, 743, 634. HRMS-ESI (*m/z*): calcd for $C_{17}H_{15}BrNaO_3^+$ [M + Na]$^+$: 369.0097; found 369.0096.

## (*E*)-3-(2-nitrophenyl)allyl 2-bromobenzoate (3ah)



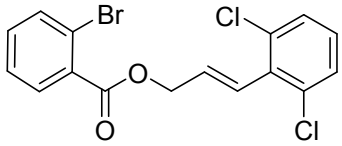

**3ah** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 5:1) as a yellow oil in 66% yield (47.6 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.44 – 7.32 (m, 3H), 7.29 – 7.25 (m, 1H), 6.40 – 6.36 (m, 1H), 5.04 (d, *J* = 5.2 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.7, 147.7, 134.3, 133.2, 132.7, 132.0, 131.7, 131.4, 129.2, 128.8, 128.6, 128.1, 127.2, 124.6, 121.7, 65.3. IR (KBr)/cm$^{-1}$ 3071, 2927, 2857, 1723, 1584, 1516, 1443, 1345, 1254, 1113, 1028, 953, 851, 739. HRMS-ESI (*m/z*): calcd for $C_{16}H_{12}BrNNaO_4^+$ [M + Na]$^+$: 383.9842; found 383.9849.

## (*E*)-3-(3-(trifluoromethyl)phenyl)allyl 2-bromobenzoate (3ai)



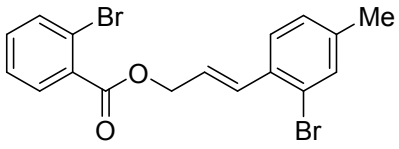

**3ai** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 61% yield (46.8 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 11.2 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.40 – 7.32 (m, 2H), 6.79 (d, *J* = 15.6 Hz, 1H), 6.51 – 6.44 (m, 1H), 5.02 (d, *J* = 5.6 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.8, 136.9, 134.4, 132.9, 132.7, 131.9, 131.4, 131.01 (q, *J* = 32 Hz), 129.7, 129.1, 127.2, 124.8, 124.6 (q, *J* = 3.6 Hz), 124.0 (q, *J* = 324.9 Hz), 123.3 (q, *J* = 3.6 Hz), 121.7, 65.6. IR (KBr)/cm$^{-1}$ 3060, 2942, 1729, 1588, 1441, 1327, 1255, 1121, 1034, 962, 899, 747. HRMS-ESI (*m/z*): calcd for $C_{17}H_{12}BrF_3NaO_2^+$ [M + Na]$^+$: 406.9865; found 406.9870.

## (*E*)-3-(2,6-dichlorophenyl)allyl 2-bromobenzoate (3aj)



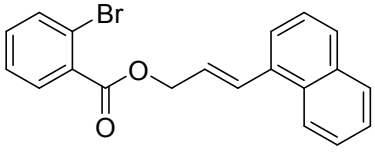

**3aj** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 64% yield (49.2 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.39 – 7.30 (m, 4H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.79 (d, *J* = 16.4 Hz, 1H), 6.49 – 6.43 (m, 1H), 5.06 (d, *J* = 5.6 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.7, 134.4, 134.3, 133.6, 132.6, 132.0, 131.6, 131.4, 128.5, 128.4, 127.4, 127.1, 121.8, 65.6. IR (KBr)/cm$^{-1}$ 2928, 1721, 1565, 1425, 1253, 1106, 1025, 954, 834, 752. HRMS-ESI (*m/z*): calcd for $C_{16}H_{11}BrCl_2NaO_2^+$ [M + Na]$^+$: 406.9212; found 406.9210.

## (*E*)-3-(2-bromo-4-methylphenyl)allyl 2-bromobenzoate (3ak)



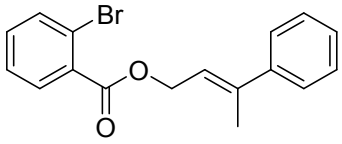

**3ak** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 71% yield (57.9 mg). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.30 (m, 3H), 7.10 – 7.06 (m, 2H), 6.34 – 6.27 (m, 1H), 5.01 (d, *J* = 6.0 Hz, 2H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.8, 139.7, 134.3, 133.3, 133.1, 132.9, 132.6, 132.0, 131.4, 128.4, 127.1, 126.8, 124.6, 123.6, 121.7, 65.9, 20.7. IR (KBr)/cm$^{-1}$ 3058, 2929, 1723, 1585, 1438, 1377, 1246, 1111, 1029, 956, 745, 692. HRMS-ESI (*m/z*): calcd for $C_{17}H_{14}Br_2NaO_2^+$ $[M + Na]^+$: 430.9253; found 430.9242.

## (*E*)-3-(naphthalen-1-yl)allyl 2-bromobenzoate (3al)



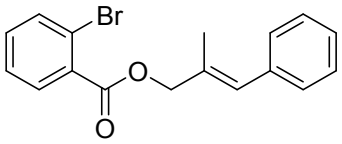

**3al** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 69% yield (50.5 mg). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 6.4 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 6.8 Hz, 1H), 7.58 – 7.45 (m, 4H), 7.40 – 7.32 (m, 2H), 6.49 – 6.42 (m, 1H), 5.14 (d, *J* = 6.0 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.9, 134.3, 133.9, 133.5, 132.5, 132.2, 131.9, 131.3, 131.1, 128.5, 128.4, 127.1, 126.2, 125.9, 125.8, 125.5, 124.1, 123.6, 121.7, 66.2. IR (KBr)/cm$^{-1}$ 3051, 2931, 1716, 1581, 1434, 1368, 1245, 1108, 1024, 949, 857, 749. HRMS-ESI (*m/z*): calcd for $C_{20}H_{15}BrNaO_2^+$ $[M + Na]^+$: 389.0148; found 389.0146.

## (*E*)-3-phenylbut-2-en-1-yl 2-bromobenzoate (3am)



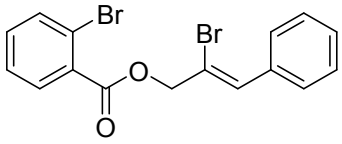

**3am** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 67% yield (44.2 mg). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 6.8 Hz, 2H), 7.40 – 7.29 (m, 5H), 6.08 (s, 1H), 5.10 (d, *J* = 6.8 Hz, 2H), 2.23 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.1, 142.4, 140.9, 134.3, 132.5, 132.3, 131.3, 128.3, 127.6, 127.1, 125.9, 121.6, 120.8, 62.7, 16.3. IR (KBr)/cm$^{-1}$ 2922, 1796, 1717, 1578, 1432, 1368, 1242, 1107, 1025, 925, 746, 691. HRMS-ESI (*m/z*): calcd for $C_{17}H_{15}BrNaO_2^+$ $[M + Na]^+$: 353.0148; found 353.0144.

## (*E*)-2-methyl-3-phenylallyl 2-bromobenzoate (3an)



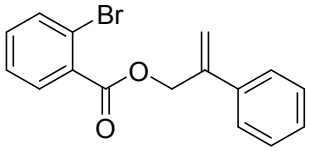
**3an** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 70% yield (46.2 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.33 (m, 7H), 6.69 (s, 1H), 4.95 (s, 2H), 2.04 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 166.0, 136.9, 134.3, 132.5, 132.3, 132.3, 131.3, 129.0, 128.9, 128.1, 127.1, 126.8, 121.6, 71.4, 15.8. IR (KBr)/cm$^{-1}$ 3063, 2925, 1727, 1586, 1440, 1369, 1280, 1248, 1115, 1030, 951, 852, 745, 696. HRMS-ESI (*m/z*): calcd for $C_{17}H_{15}BrNaO_2^+$ $[M + Na]^+$: 353.0148; found 353.0150.

## (*Z*)-2-bromo-3-phenylallyl 2-bromobenzoate (3ao)



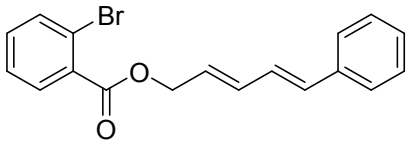
**3ao** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 62% yield (48.8 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 1H), 7.66 (t, *J* = 9.6 Hz, 3H), 7.38 – 7.32 (m, 5H), 7.19 (s, 1H), 5.16 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.2, 134.5, 134.5, 132.9, 131.9, 131.6, 131.4, 129.0, 128.6, 128.2, 127.2, 122.0, 118.4, 70.8. IR (KBr)/cm$^{-1}$ 3062, 2923, 1726, 1580, 1433, 1364, 1238, 1102, 1023, 946, 848, 740, 687. HRMS-ESI (*m/z*): calcd for $C_{16}H_{12}Br_2NaO_2^+$ $[M + Na]^+$: 412.9096; found 416.9097.

## 2-phenylallyl 2-bromobenzoate (3ap)



**3ap** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 54% yield (34.1 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.69 (m, 1H), 7.65 – 7.63 (m, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.40 – 7.30 (m, 5H), 5.63 (s, 1H), 5.50 (s, 1H), 5.26 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.8, 142.2, 138.0, 134.3, 132.7, 132.0, 131.3, 128.5, 128.1, 127.1, 126.1, 121.7, 115.9, 66.8. IR (KBr)/cm$^{-1}$ 3060, 2925, 1722, 1579, 1430, 1379, 1239, 1103, 1027, 907, 743, 693. HRMS-ESI (*m/z*): calcd for $C_{16}H_{13}BrNaO_2^+$ $[M + Na]^+$: 338.9991; found 338.9991.

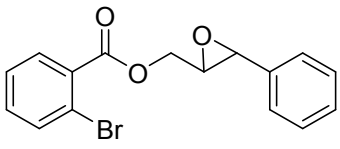
## (2*E*,4*E*)-5-phenylpenta-2,4-dien-1-yl 2-bromobenzoate (3aq)



**3aq** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 65% yield (44.5 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.36 – 7.30 (m, 4H), 7.24 – 7.22 (m, 1H), 6.83 – 6.76 (m, 1H), 6.62 – 6.52 (m, 2H), 6.00 – 5.95 (m, 1H), 4.92 (d, *J* = 6.0 Hz, 2H). $^{13}$C

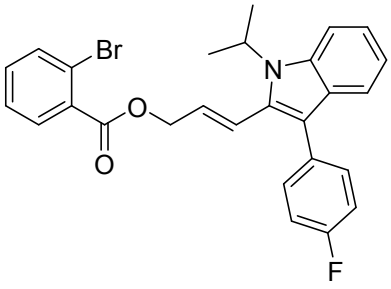
NMR (100 MHz, $CDCl_3$) δ 165.8, 136.8, 135.1, 134.3, 134.0, 132.5, 132.1, 131.3, 128.6, 127.8, 127.6, 127.1, 126.5, 126.3, 121.7, 65.8. IR (KBr)/$cm^{-1}$ 3036, 2930, 1726, 1588, 1443, 1256, 1119, 1033, 969, 837, 749, 696. HRMS-ESI (*m/z*): calcd for $C_{18}H_{15}BrNaO_2^+$ $[M + Na]^+$: 365.0148; found 365.0143.

## (3-phenyloxiran-2-yl)methyl 2-bromobenzoate (4)




**4** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 20:1) as a yellow oil in 75% yield (49.8 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.39 – 7.30 (m, 7H), 4.73 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.39 (dd, *J* = 12.0, 5.6 Hz, 1H), 3.92 (s, 1H), 3.41 – 3.39 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.6, 136.0, 134.3, 132.7, 131.5, 131.4, 128.4, 128.4, 127.1, 125.6, 121.7, 65.0, 58.9, 56.4. IR (KBr)/$cm^{-1}$ 3069, 2989, 1731, 1587, 1443, 1377, 1284, 1247, 1117, 1037, 969, 911, 794, 739. HRMS-ESI (*m/z*): calcd for $C_{16}H_{13}BrNaO_3^+$ $[M + Na]^+$: 354.9940; found 354.9948.

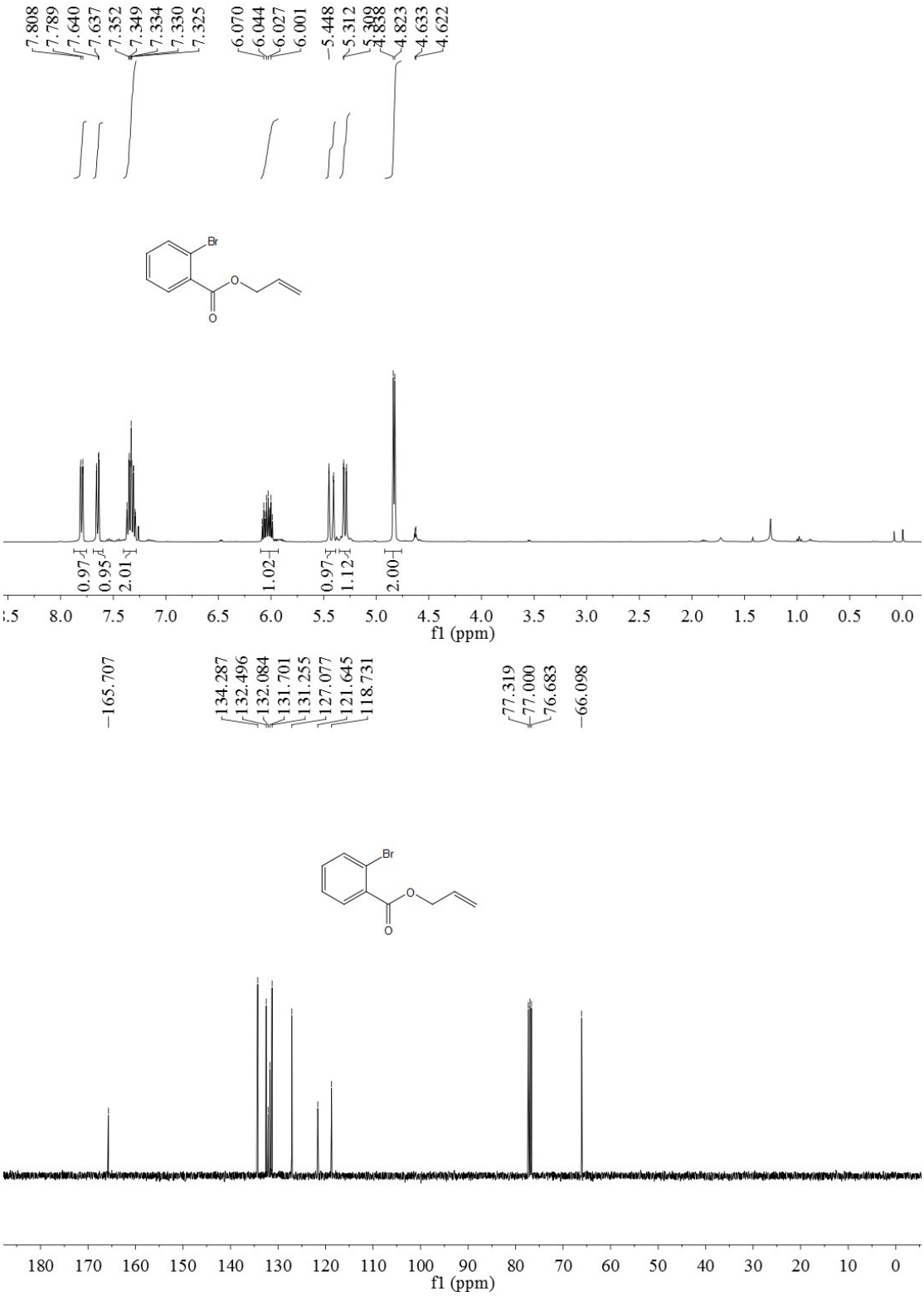
## (*E*)-3-(3-(4-fluorophenyl)-1-isopropyl-1H-indol-2-yl)allyl 2-bromobenzoate (7)



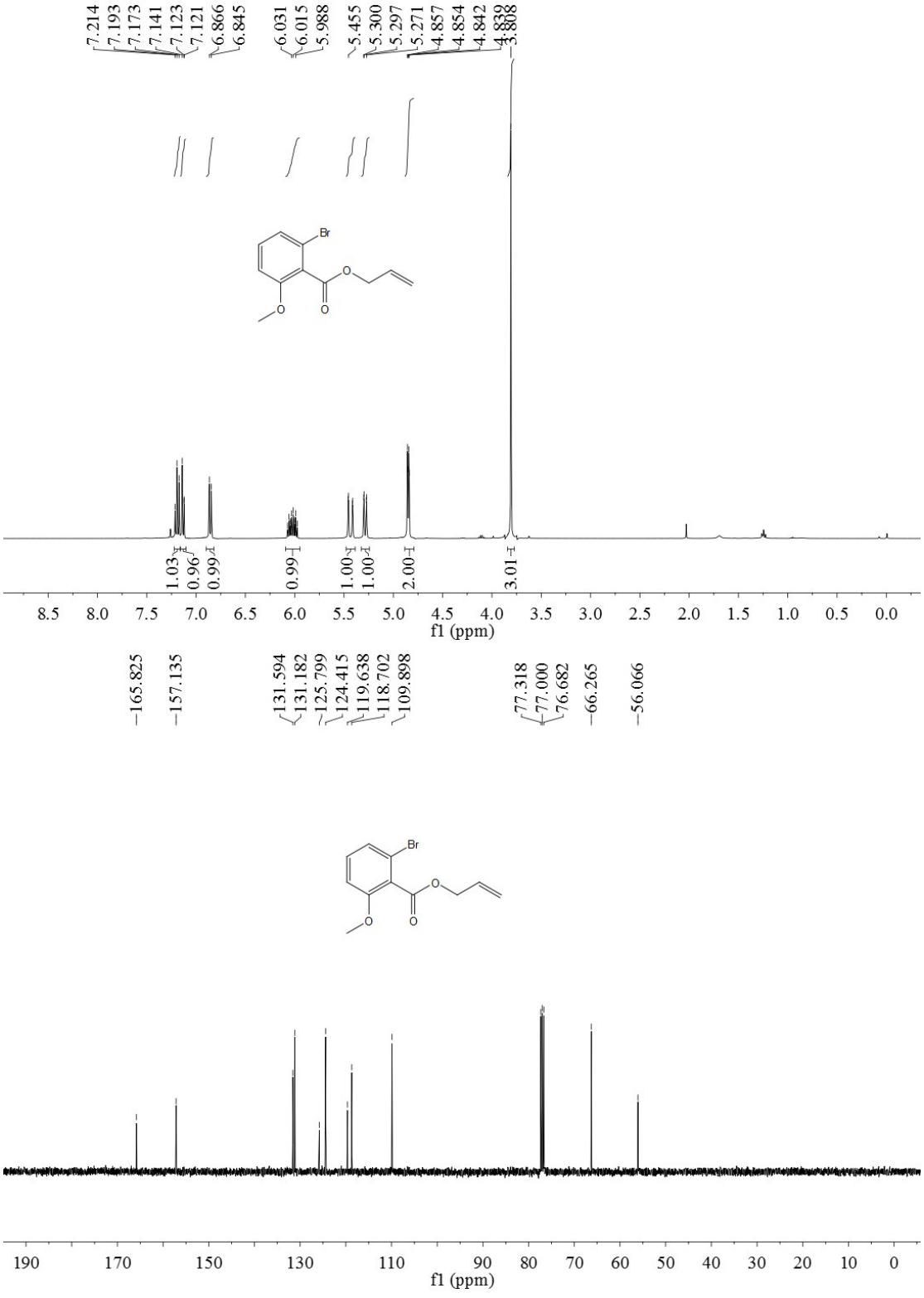

**7** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) as a brown oil in 42% yield (41.2 mg). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.43 – 7.37 (m, 2H), 7.29 – 7.25 (m, 1H),, 7.17 – 7.12 (m, 3H), 6.91 (d, *J* = 16.0 Hz, 1H), 5.98 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.99 – 4.91 (m, 3H), 1.74 (s, 3H), 1.73 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 165.7, 161.4 (d, *J* = 243.4 Hz), 135.3, 134.4, 132.7, 131.9, 131.8 (d, *J* = 7.8 Hz), 131.4, 131.2 (d, *J* = 3.3 Hz), 129.3, 128.2, 127.1, 123.8, 122.0, 121.6, 119.7, 119.6, 115.5, 115.3 (d, *J* = 21.0 Hz), 111.7, 65.7, 47.8, 21.7. IR (KBr)/$cm^{-1}$ 3052, 2980, 2935, 1729, 1592, 1544, 1500, 1454, 1345, 1288, 1239, 1113, 1028, 963, 835, 740, 644. HRMS-ESI (*m/z*): calcd for $C_{27}H_{24}BrFNO_2^+$ $[M + H]^+$: 492.0969; found 492.0975.

# 14. NMR spectra

## 3aa



**3ba**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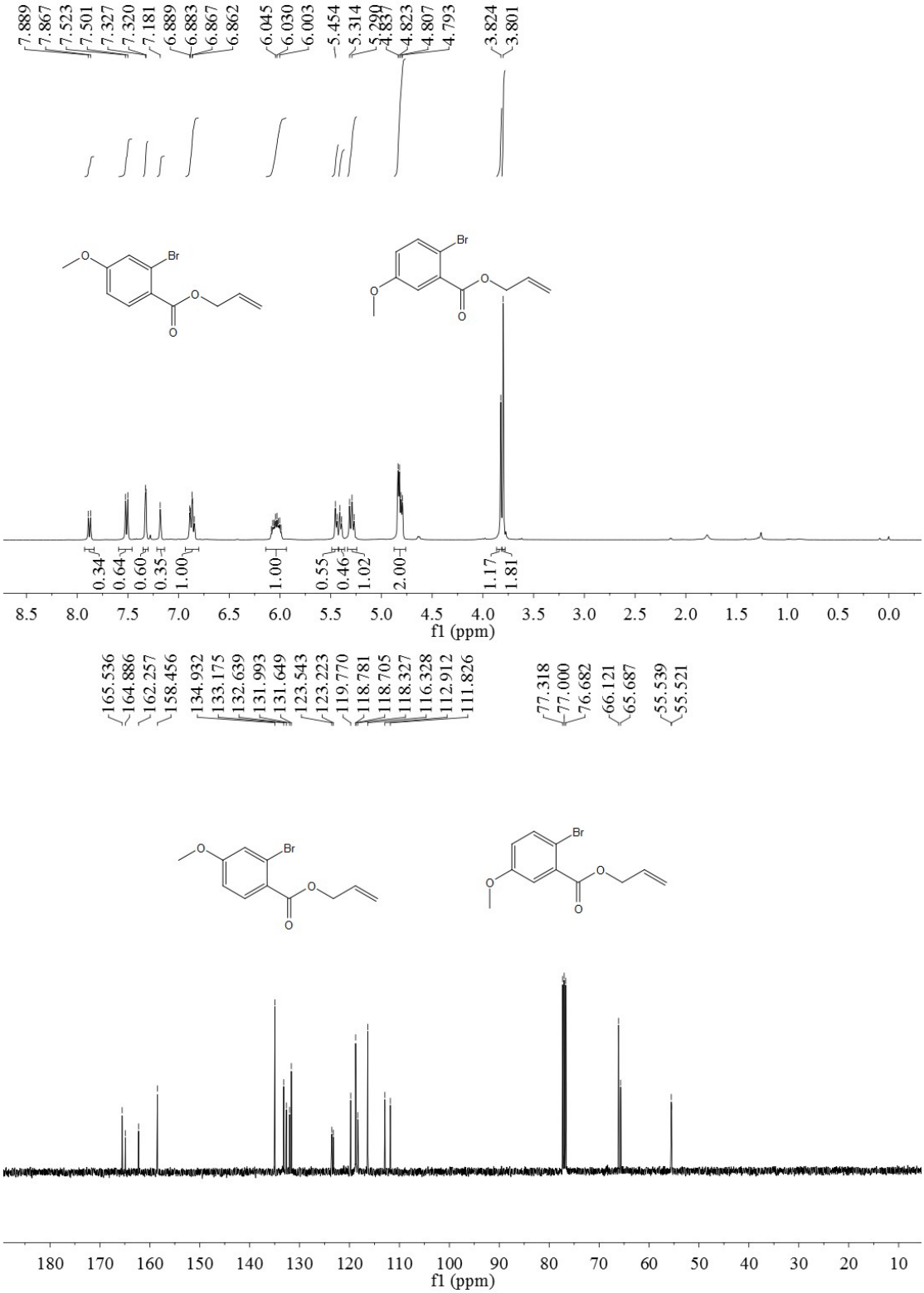
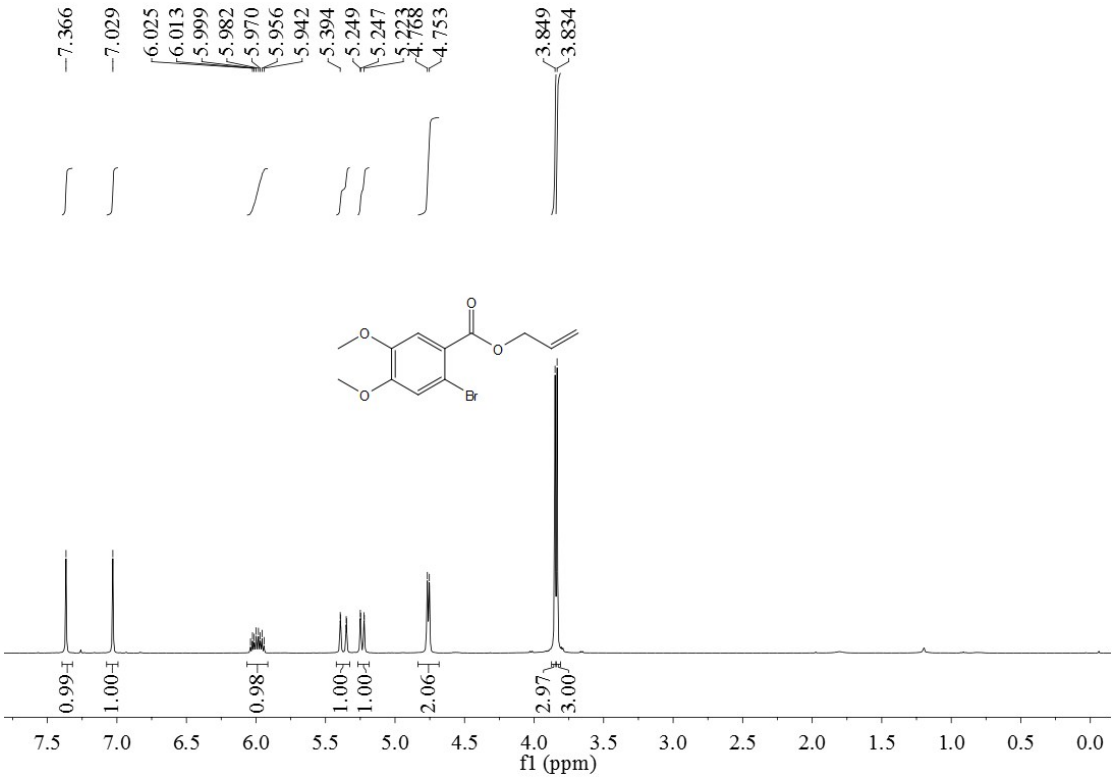
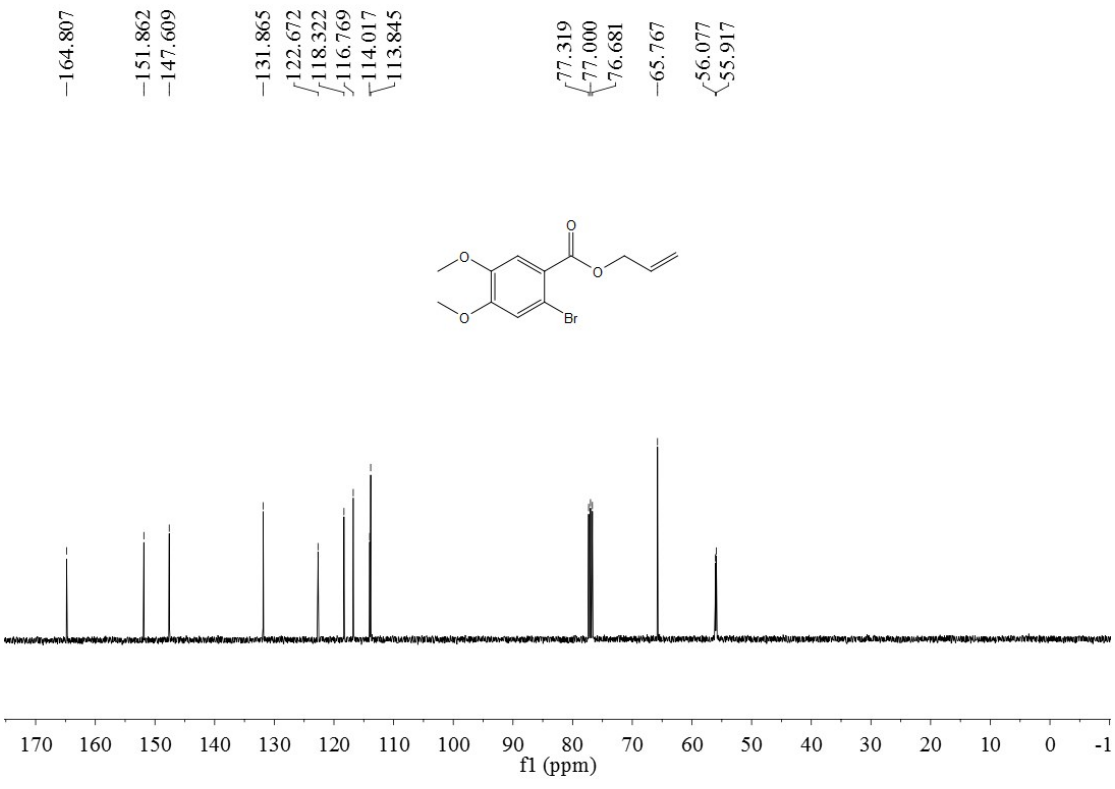
7.193
7.173
7.141
7.123
7.121
6.866
6.845
6.031
6.015
5.988
5.455
5.300
5.297
5.271
4.857
4.854
4.842
4.839
3.808
Br
O
O
O
1.03
0.96
0.99
0.99
1.00
1.00
2.00
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
165.825
157.135
131.594
131.182
125.799
124.415
119.638
118.702
109.898
77.318
77.000
76.682
66.265
56.066
Br
O
O
O
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

**3ca and 3ca`**

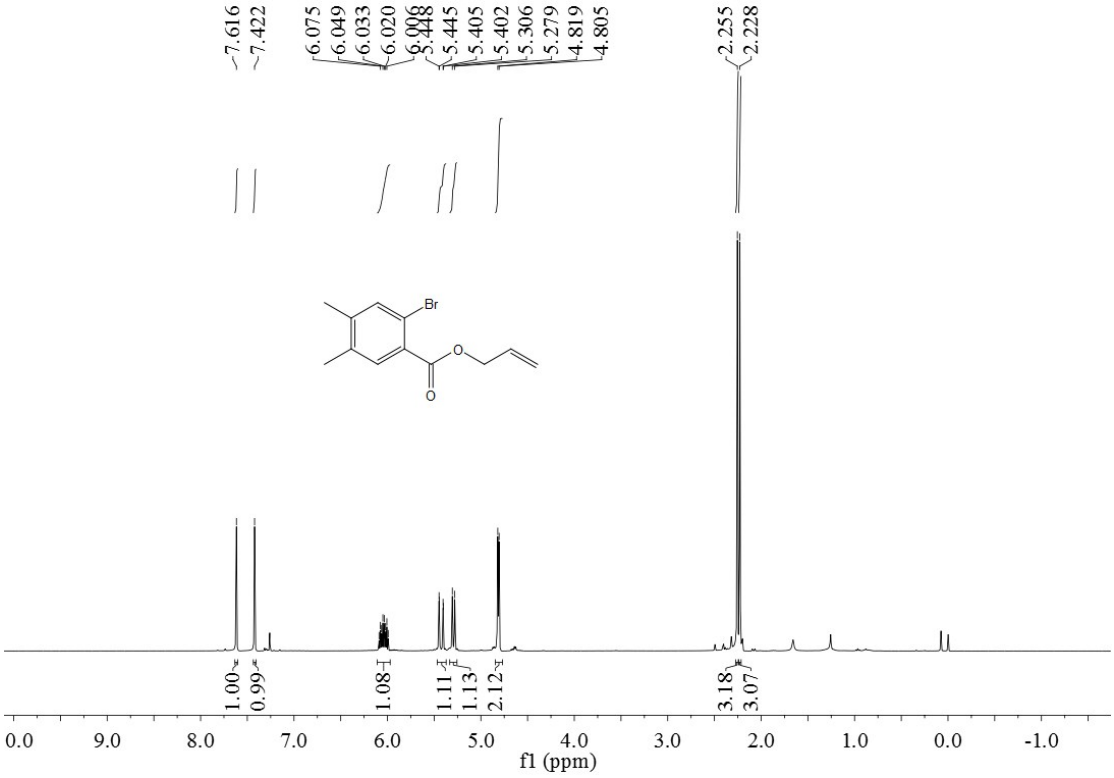

7.889
7.867
7.523
7.501
7.327
7.320
7.181
6.889
6.883
6.867
6.862
6.045
6.030
6.003
5.454
5.314
4.823
4.807
4.793
3.824
3.801
Br
O
O
O
0.34
0.64
0.60
0.35
1.00
1.00
0.55
0.46
1.02
2.00
1.17
1.81
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
165.536
164.886
162.257
158.456
134.932
133.175
132.639
131.993
131.649
123.543
123.223
119.770
118.781
118.705
118.327
116.328
112.912
111.826
77.318
77.000
76.682
66.121
65.687
55.539
55.521
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

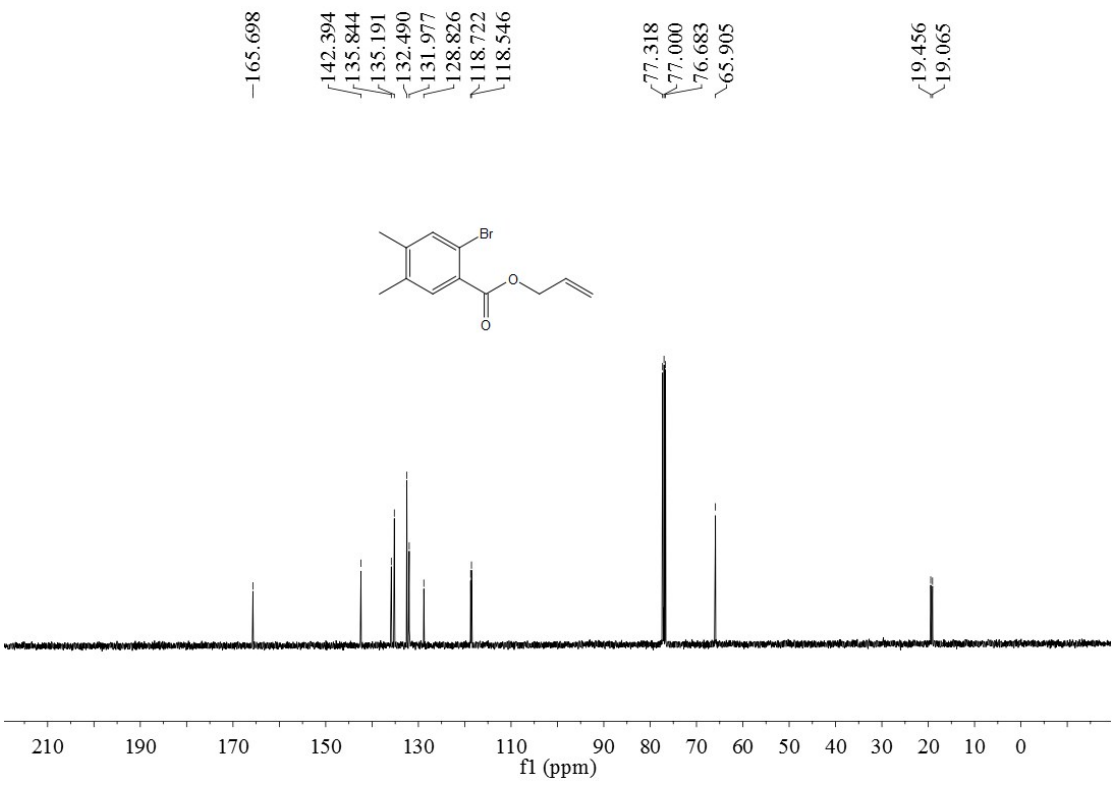
**3da**


7.366
7.029
6.025
6.013
5.999
5.982
5.970
5.956
5.942
5.394
5.249
5.247
5.223
4.768
4.753
3.849
3.834
O
O
O
Br
0.99
1.00
0.98
1.00
1.00
2.06
2.97
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

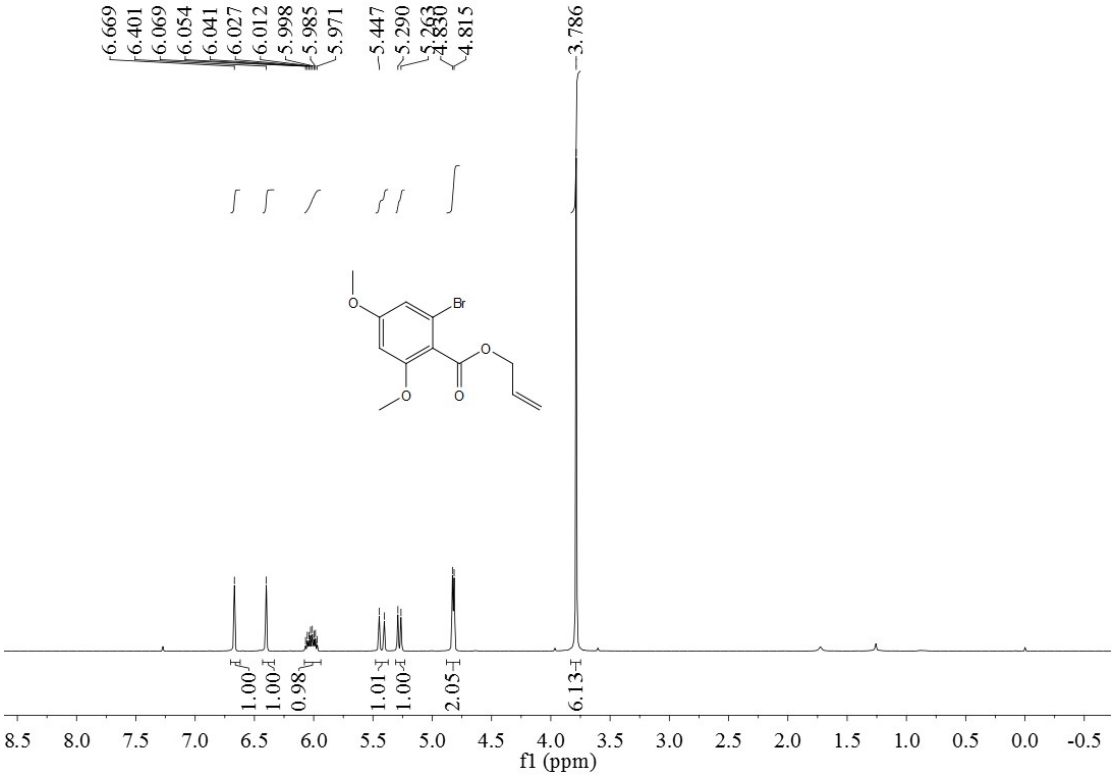

164.807
151.862
147.609
131.865
122.672
118.322
116.769
114.017
113.845
77.319
77.000
76.681
65.767
56.077
55.917
O
O
O
Br
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

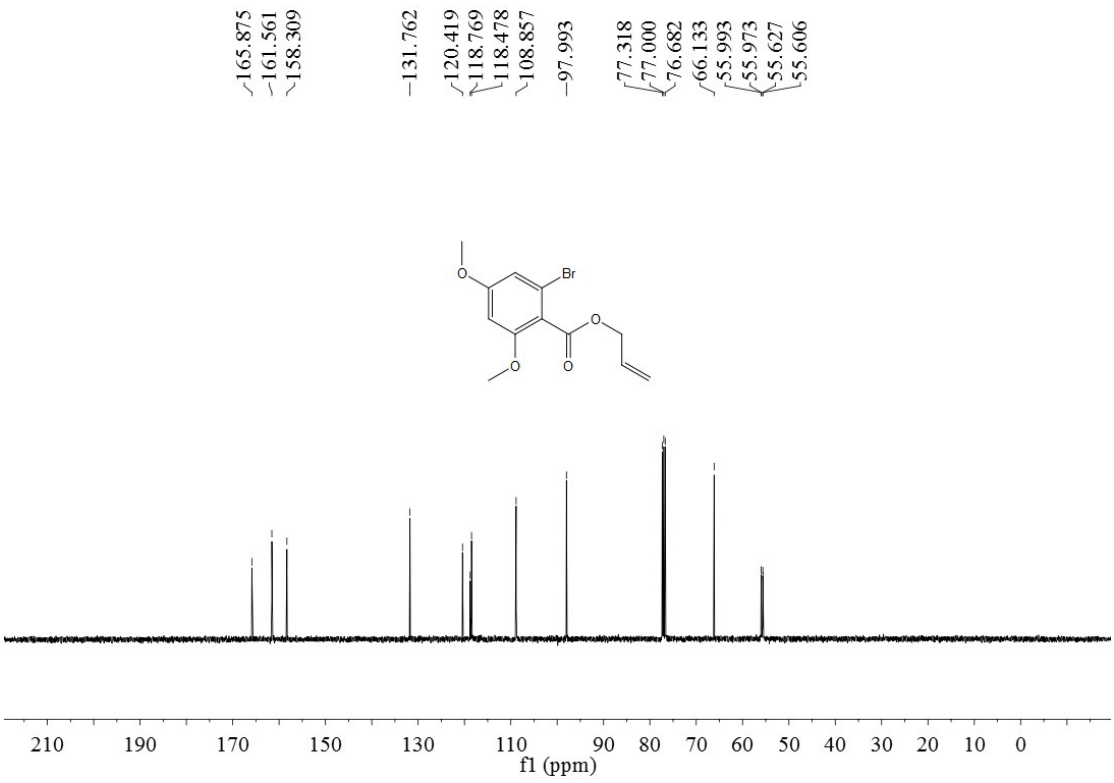
**3ea**


7.616
7.422
6.075
6.049
6.033
6.020
6.006
5.448
5.445
5.405
5.402
5.306
5.279
4.819
4.805
2.255
2.228
Br
O
O
1.00
0.99
1.08
1.11
1.13
2.12
3.18
3.07
0.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


165.698
142.394
135.844
135.191
132.490
131.977
128.826
118.722
118.546
77.318
77.000
76.683
65.905
19.456
19.065
Br
O
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**3fa**


6.669
6.401
6.069
6.054
6.041
6.027
6.012
5.998
5.985
5.971
5.447
5.290
5.263
5.250
4.830
4.815
3.786
Br
O
O
O
O
1.00
1.00
0.98
1.01
1.00
2.05
6.13
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)


165.875
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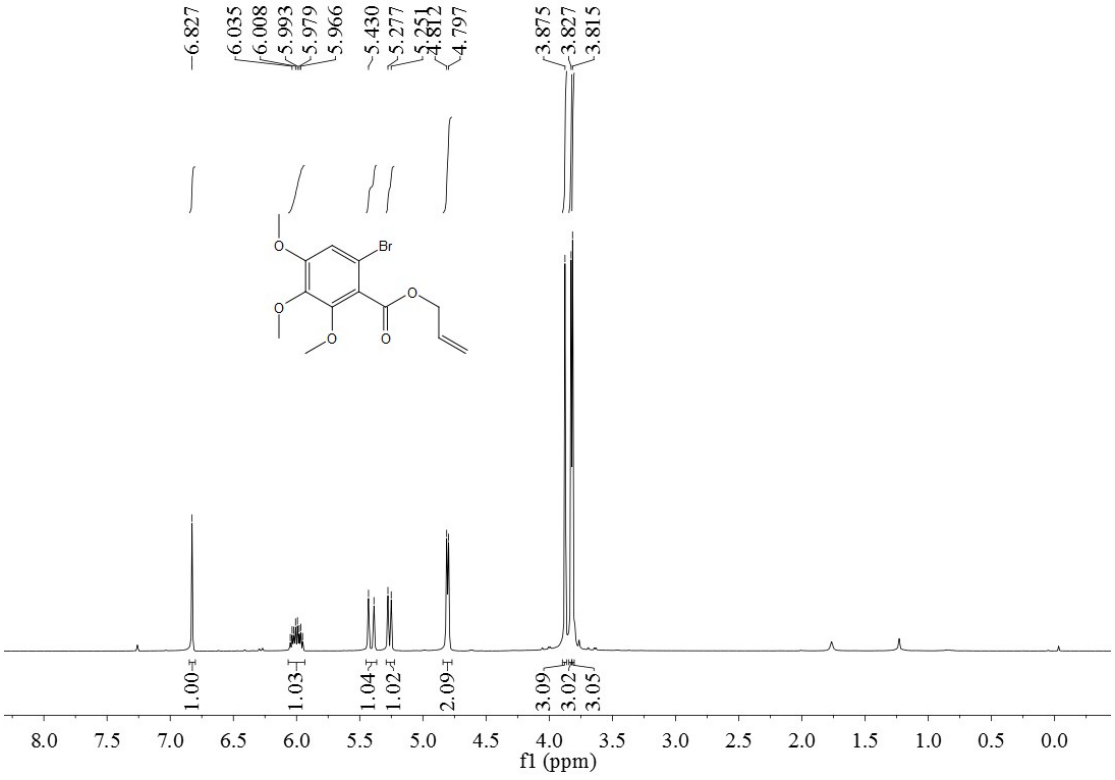
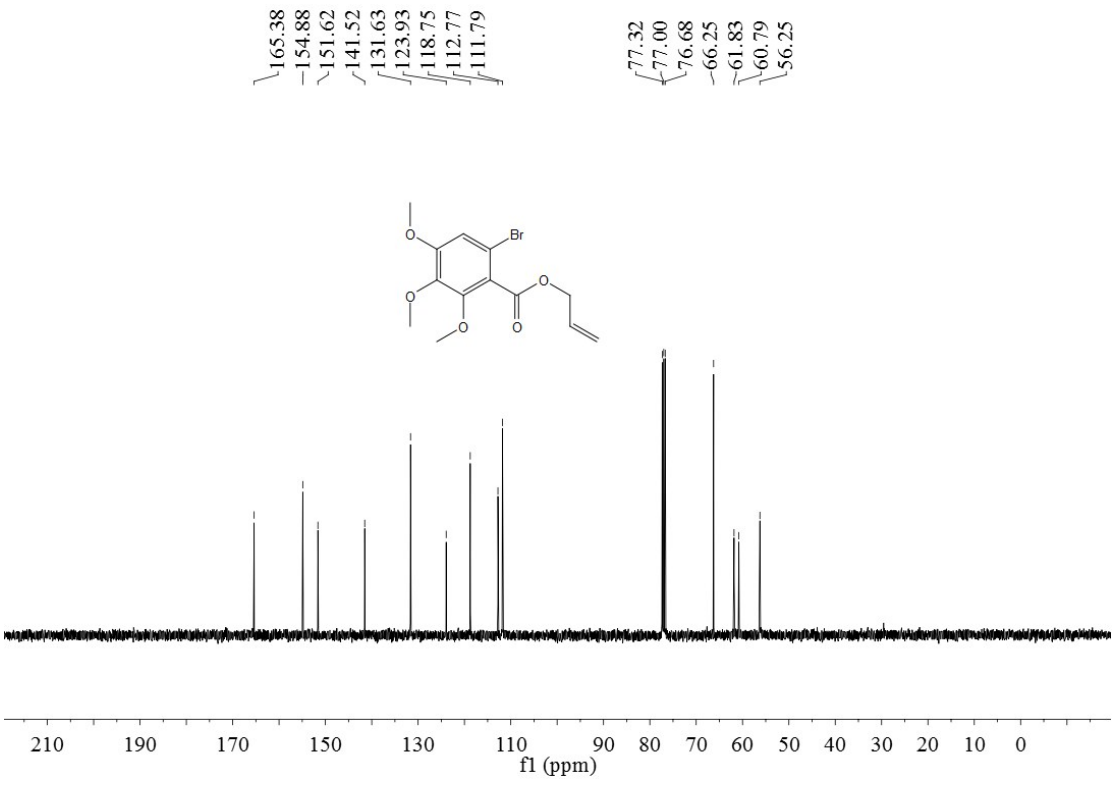
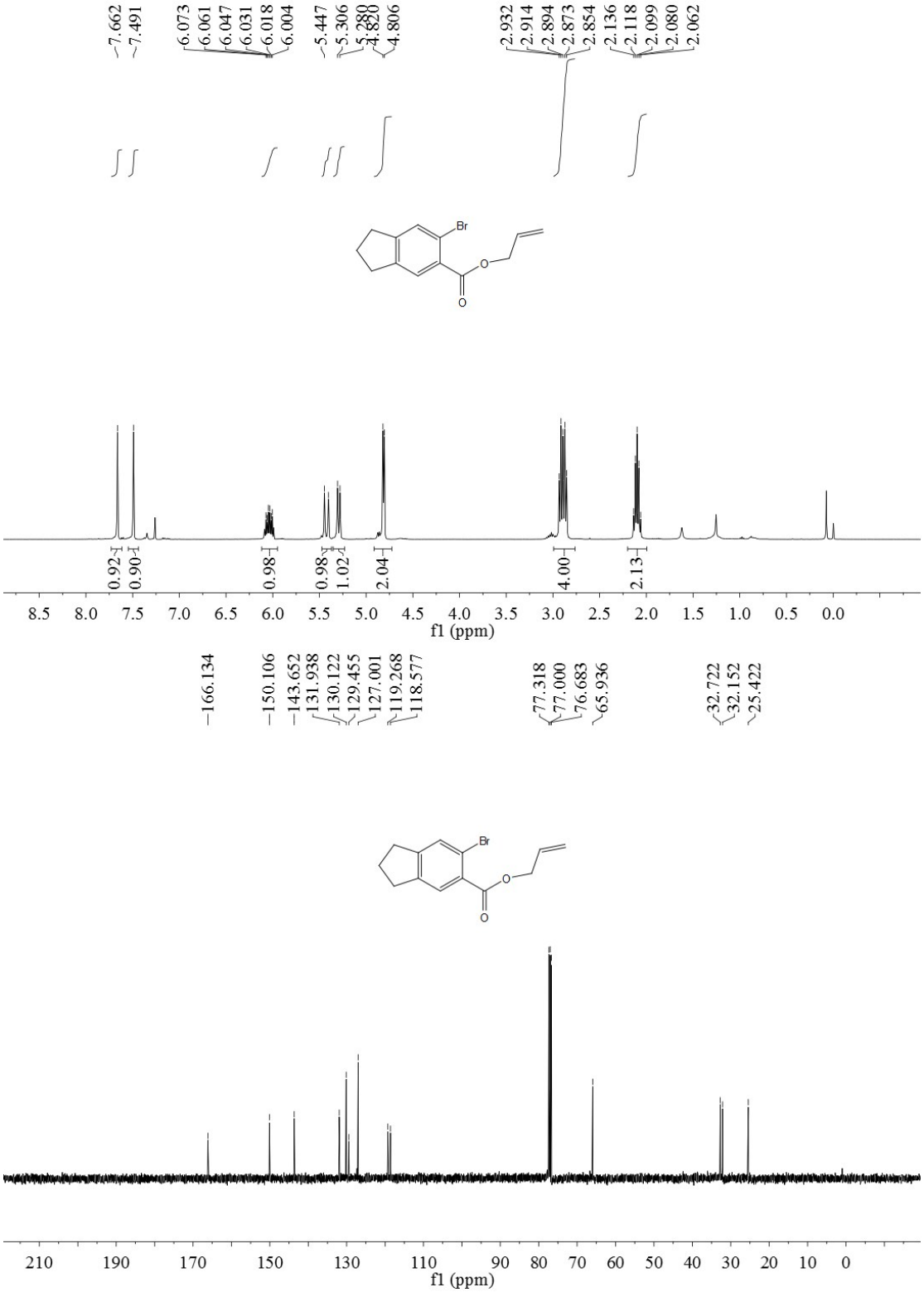
158.309
131.762
120.419
118.769
118.478
108.857
97.993
77.318
77.000
76.682
66.133
55.993
55.973
55.627
55.606
Br
O
O
O
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

**3ga**


6.827
6.035
6.008
5.993
5.979
5.966
5.430
5.277
5.251
4.812
4.797
3.875
3.827
3.815
Br
1.00
1.03
1.04
1.02
2.09
3.09
3.02
3.05
f1 (ppm)


165.38
154.88
151.62
141.52
131.63
123.93
118.75
112.77
111.79
77.32
77.00
76.68
66.25
61.83
60.79
56.25
Br
f1 (ppm)

**3ha**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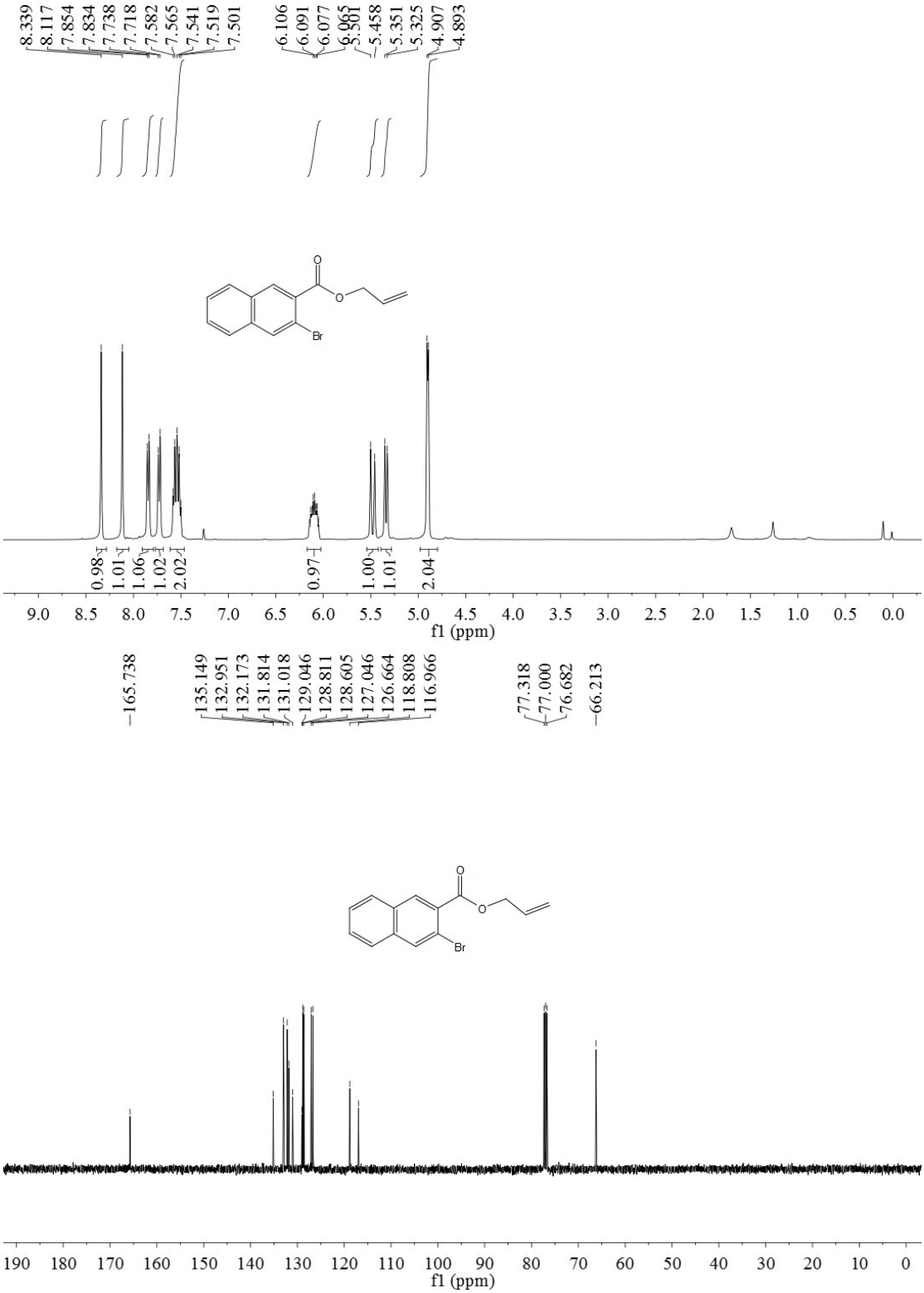
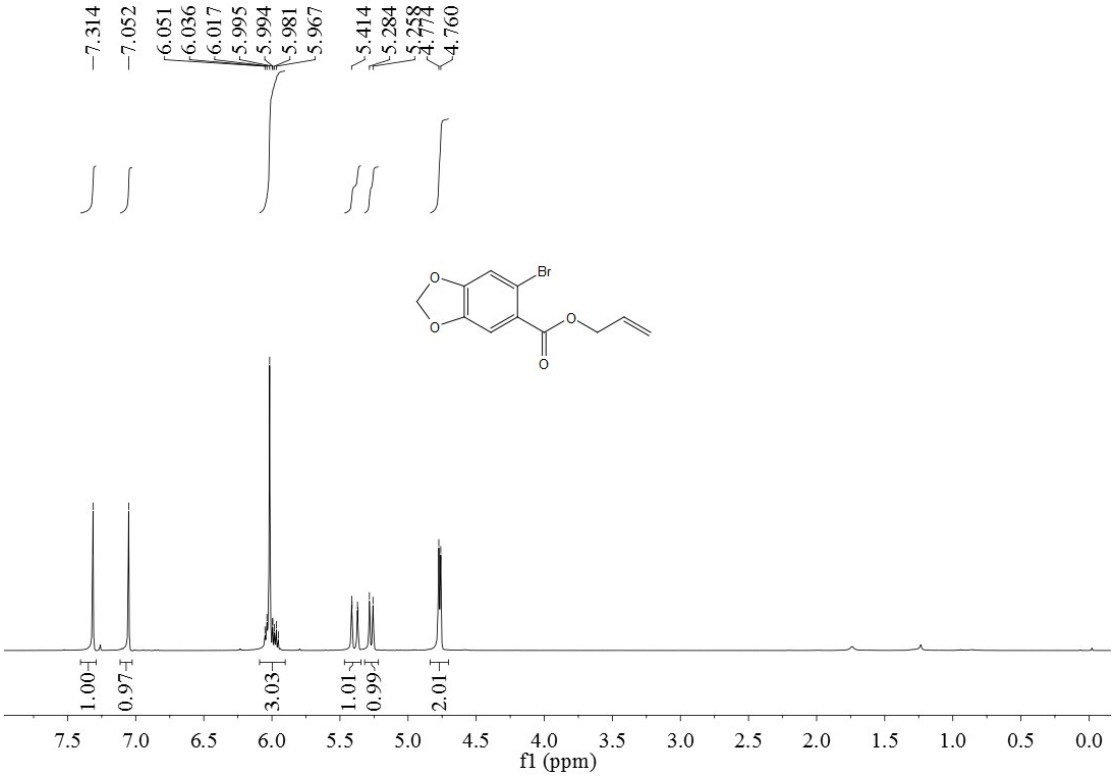
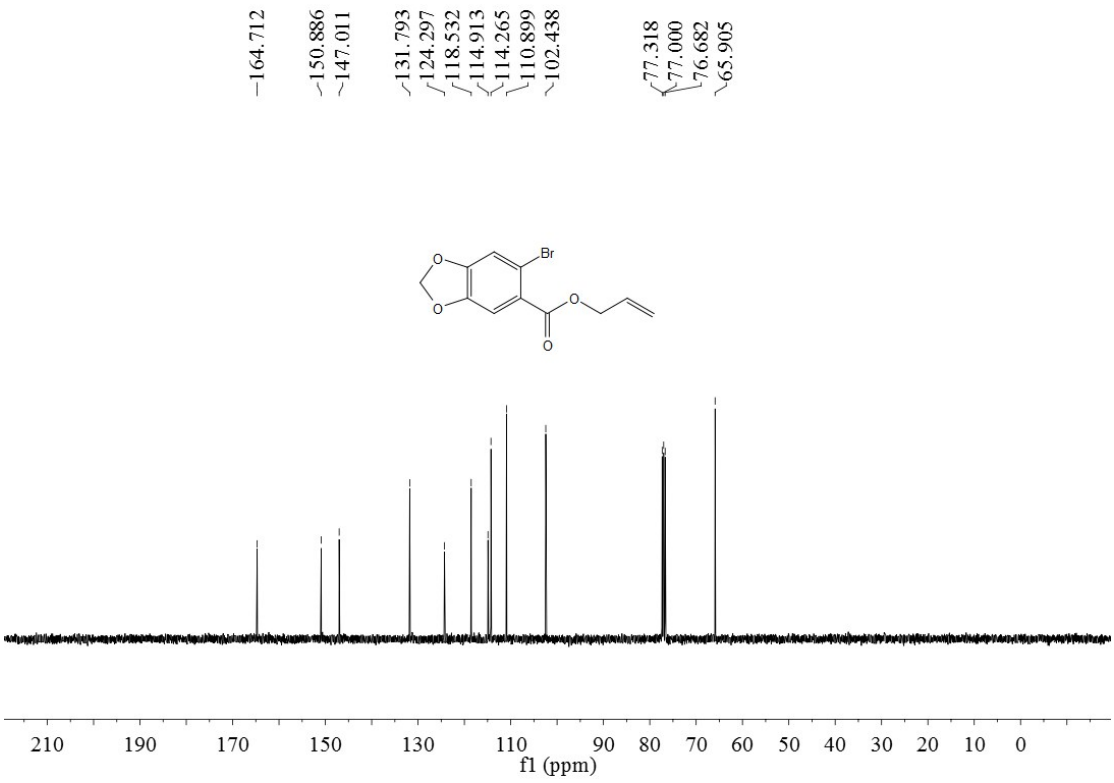
6.047
6.031
6.018
6.004
5.447
5.306
5.280
4.820
4.806
2.932
2.914
2.894
2.873
2.854
2.136
2.118
2.099
2.080
2.062
Br
O
O
0.92
0.90
0.98
0.98
1.02
2.04
4.00
2.13
f1 (ppm)
166.134
150.106
143.652
131.938
130.122
129.455
127.001
119.268
118.577
77.318
77.000
76.683
65.936
32.722
32.152
25.422
Br
O
O
f1 (ppm)

**3ia**

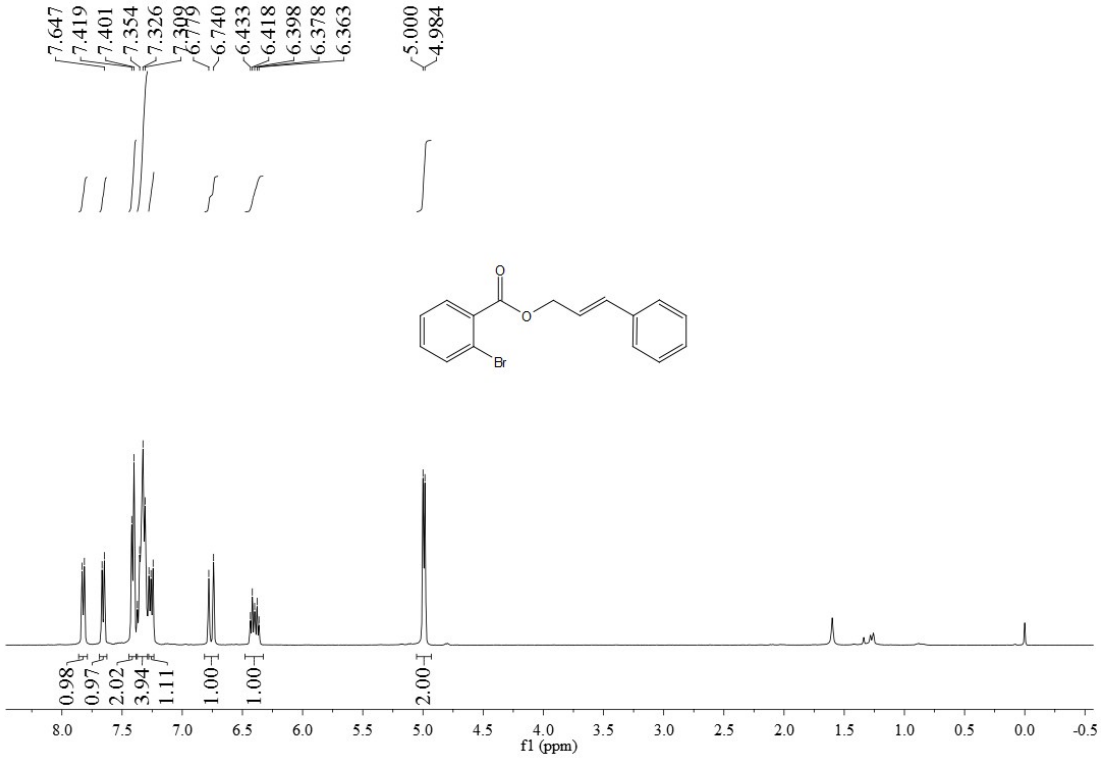

8.339
8.117
7.854
7.834
7.738
7.718
7.582
7.565
7.541
7.519
7.501
6.106
6.091
6.077
6.065
5.501
5.458
5.351
5.325
4.907
4.893
O
O
Br
0.98
1.01
1.06
1.02
2.02
0.97
1.00
1.01
2.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
165.738
135.149
132.951
132.173
131.814
131.018
129.046
128.811
128.605
127.046
126.664
118.808
116.966
77.318
77.000
76.682
66.213
O
O
Br
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

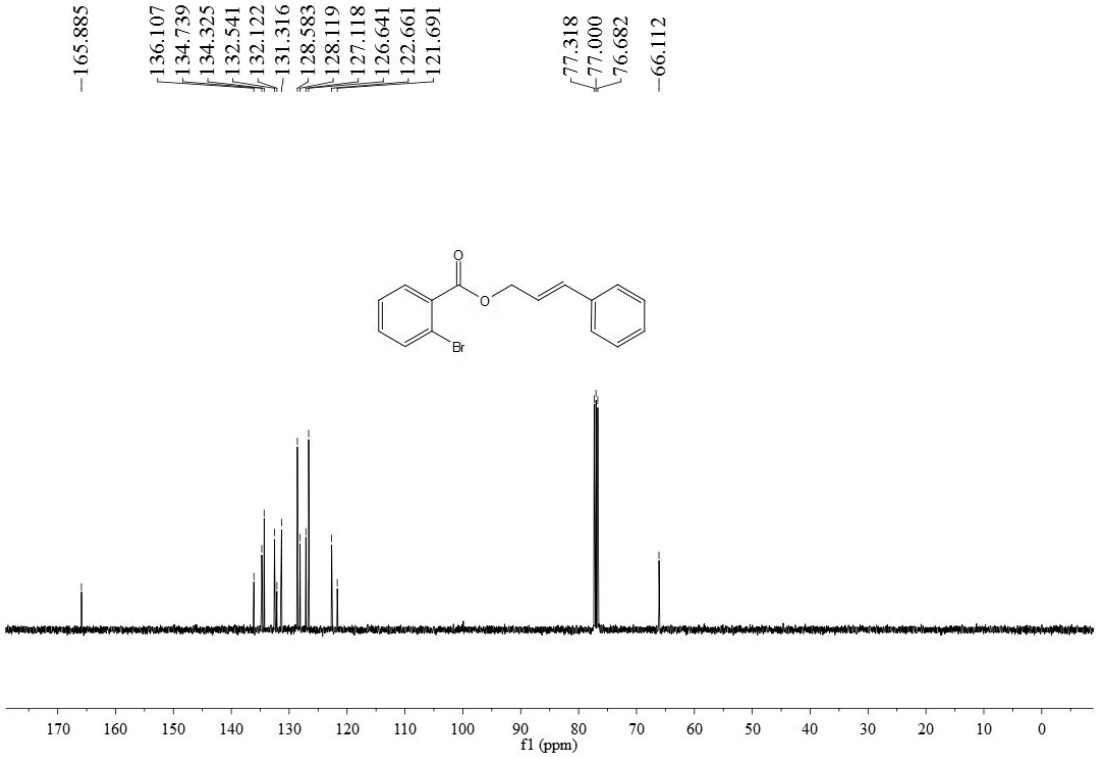
**3ja**


7.314
7.052
6.051
6.036
6.017
5.995
5.994
5.981
5.967
5.414
5.284
5.258
4.774
4.760
Br
O
O
O
O
1.00
0.97
3.03
1.01
0.99
2.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

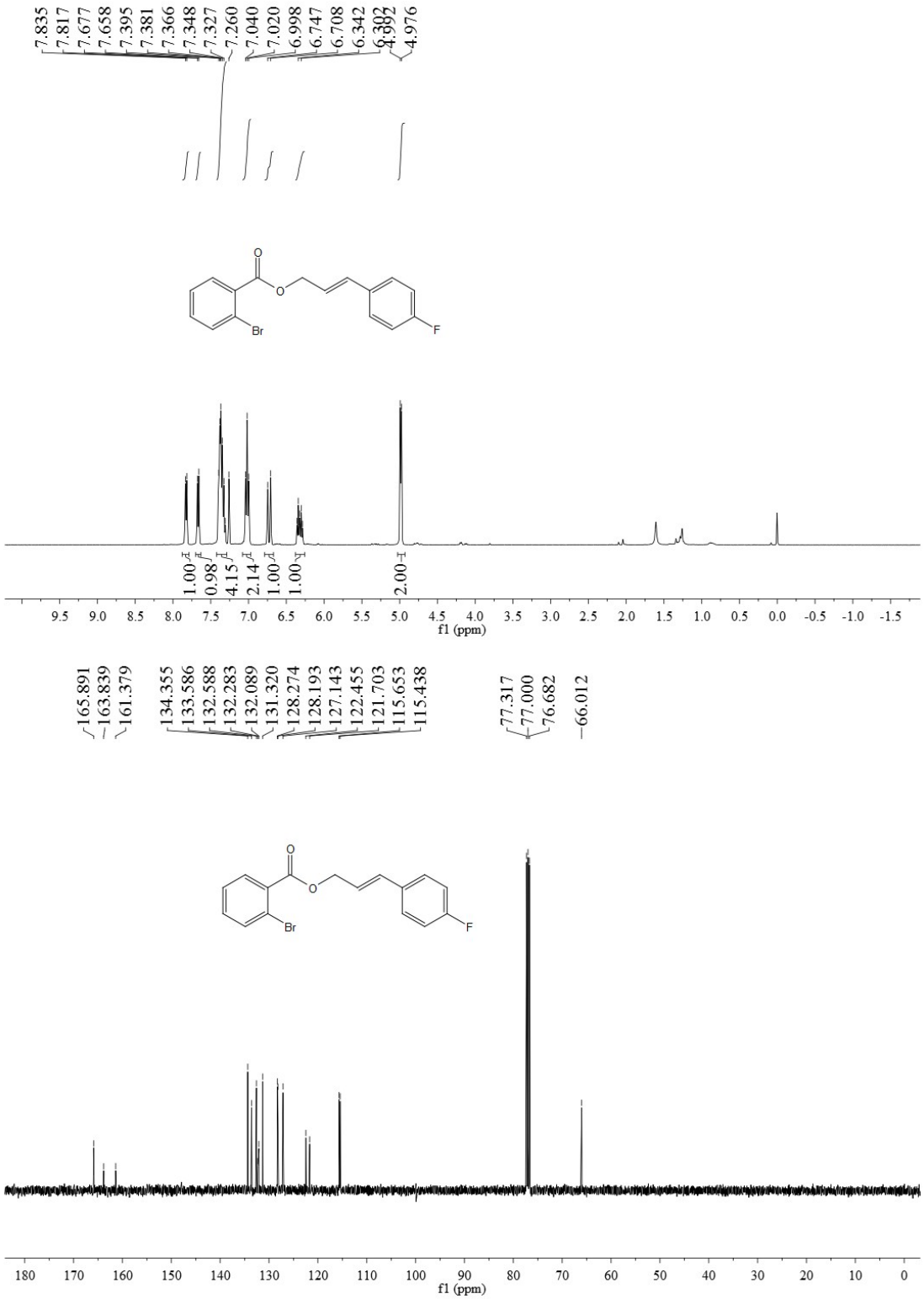

164.712
150.886
147.011
131.793
124.297
118.532
114.913
114.265
110.899
102.438
77.318
77.000
76.682
65.905
Br
O
O
O
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**3ab**

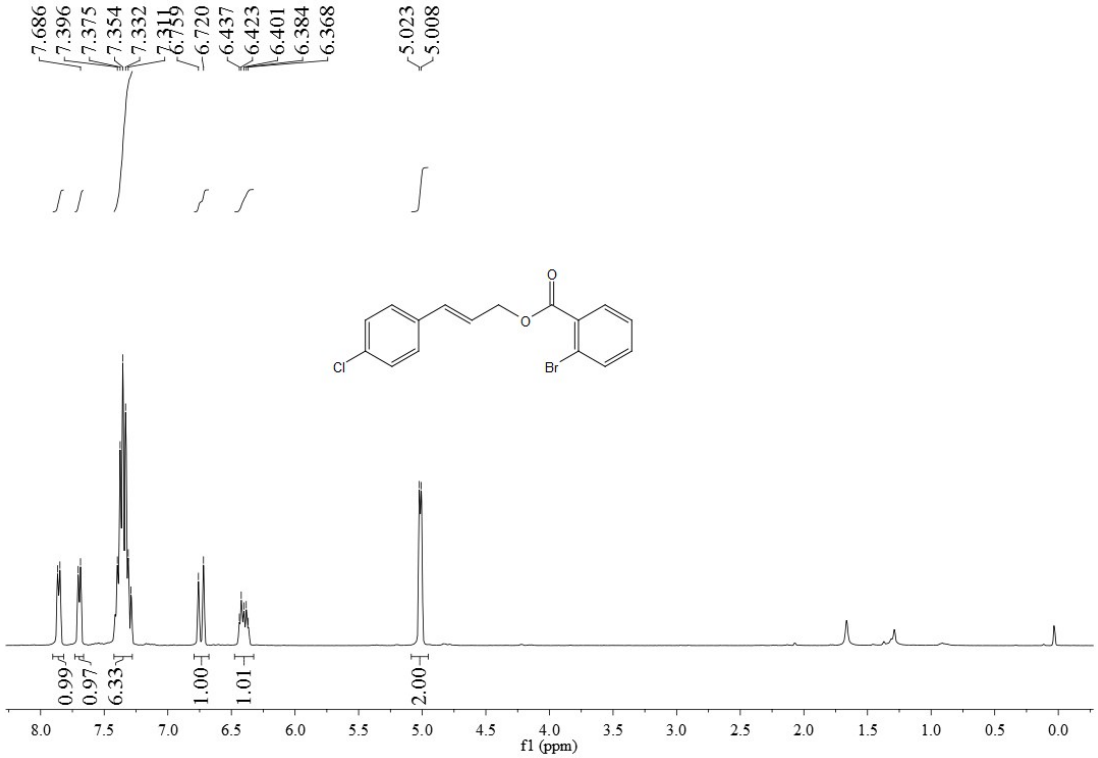

7.647
7.419
7.401
7.354
7.326
7.309
6.779
6.740
6.433
6.418
6.398
6.378
6.363
5.000
4.984
O
O
Br
0.98
0.97
2.02
3.94
1.11
1.00
1.00
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

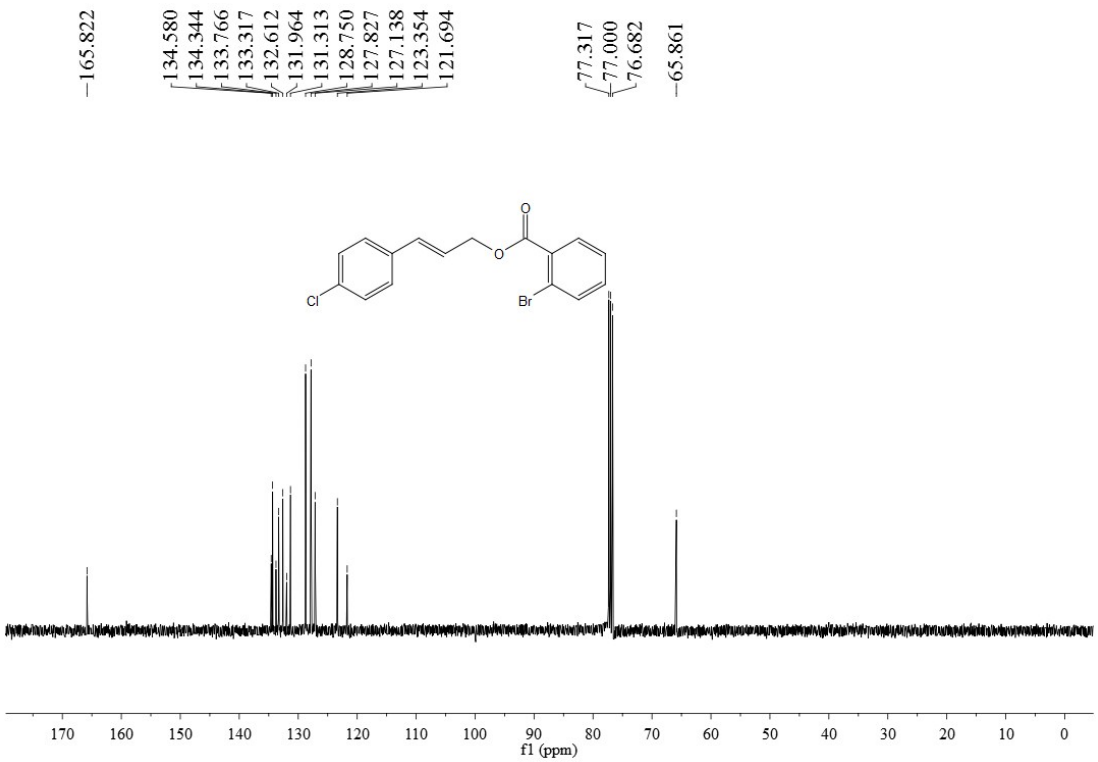

165.885
136.107
134.739
134.325
132.541
132.122
131.316
128.583
128.119
127.118
126.641
122.661
121.691
77.318
77.000
76.682
66.112
O
O
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**3ac**

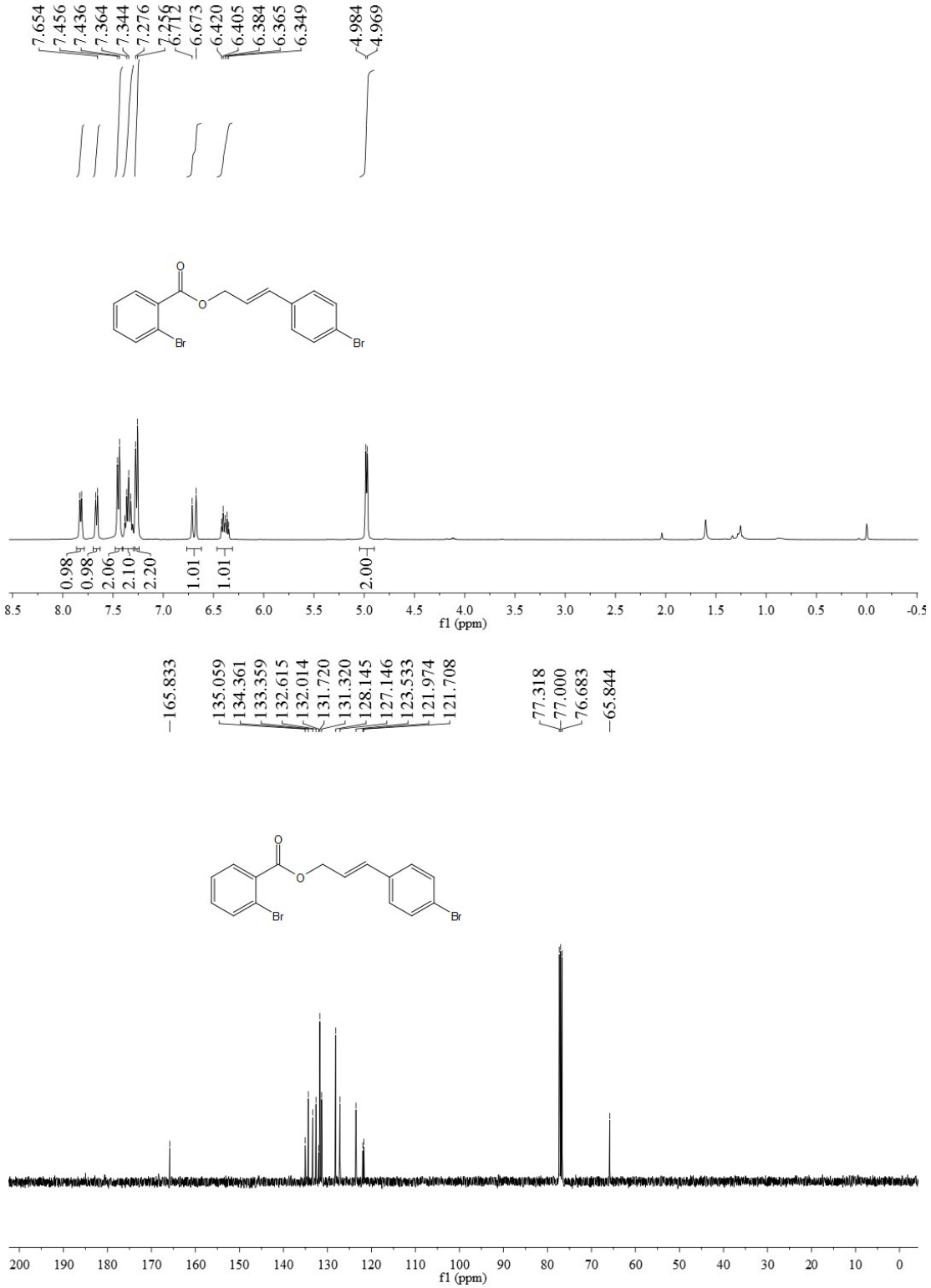

7.835
7.817
7.677
7.658
7.395
7.381
7.366
7.348
7.327
7.260
7.040
7.020
6.998
6.747
6.708
6.342
6.302
4.992
4.976
O
O
Br
F
1.00
0.98
4.15
2.14
1.00
1.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)
165.891
163.839
161.379
134.355
133.586
132.588
132.283
132.089
131.320
128.274
128.193
127.143
122.455
121.703
115.653
115.438
77.317
77.000
76.682
66.012
O
O
Br
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

**3ad**

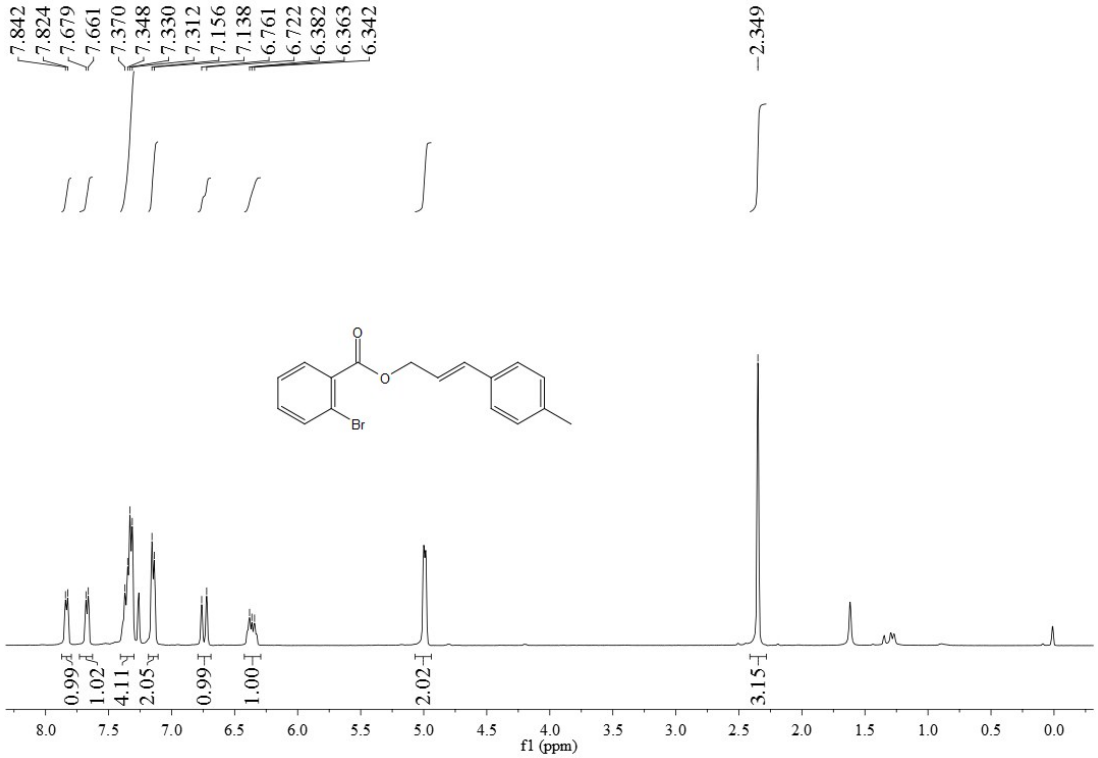

7.686
7.396
7.375
7.354
7.332
7.311
6.759
6.720
6.437
6.423
6.401
6.384
6.368
5.023
5.008
O
O
Cl
Br
0.99
0.97
6.33
1.00
1.01
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

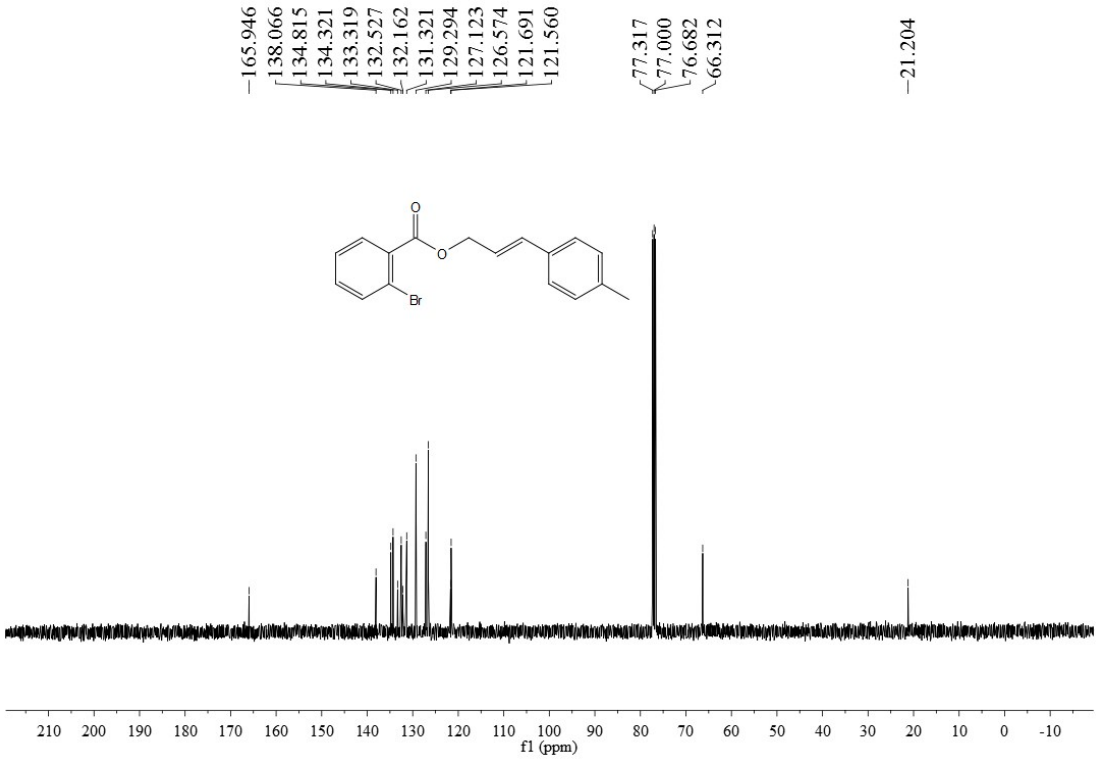

165.822
134.580
134.344
133.766
133.317
132.612
131.964
131.313
128.750
127.827
127.138
123.354
121.694
77.317
77.000
76.682
65.861
O
O
Cl
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**3ae**

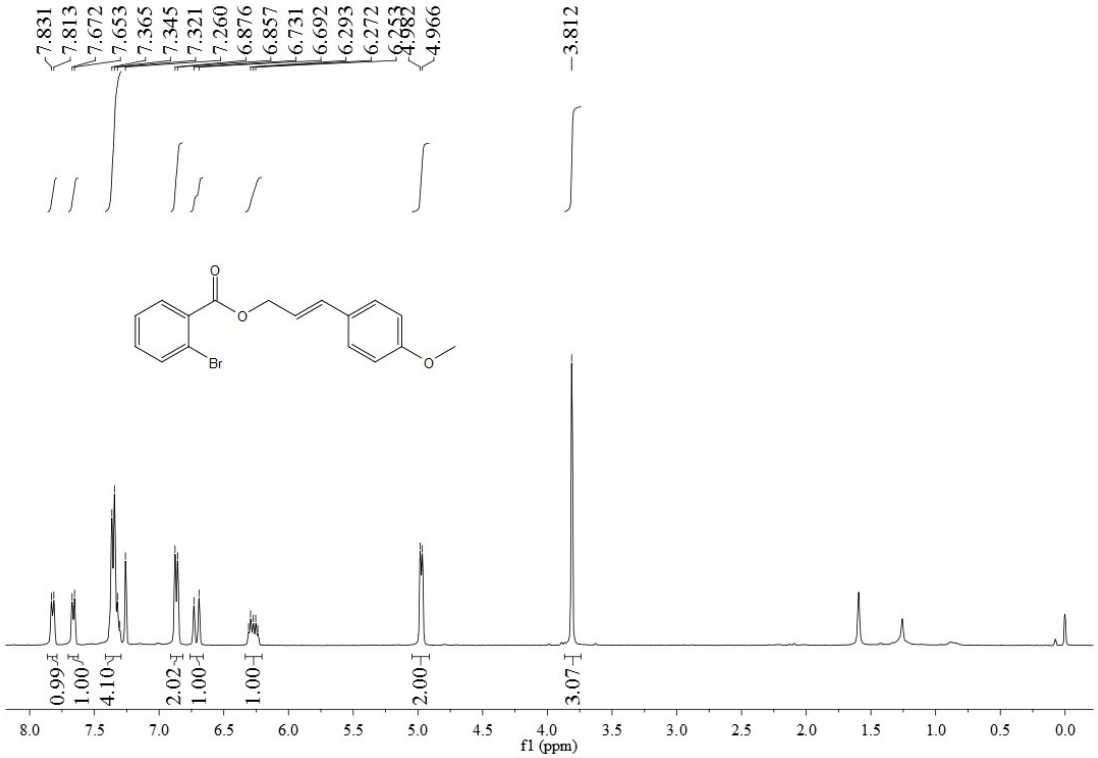

7.654
7.456
7.436
7.364
7.344
7.276
7.256
6.712
6.673
6.420
6.405
6.384
6.365
6.349
4.984
4.969
O
O
Br
Br
0.98
0.98
2.06
2.10
2.20
1.01
1.01
2.00
f1 (ppm)
165.833
135.059
134.361
133.359
132.615
132.014
131.720
131.320
128.145
127.146
123.533
121.974
121.708
77.318
77.000
76.683
65.844
O
O
Br
Br
f1 (ppm)

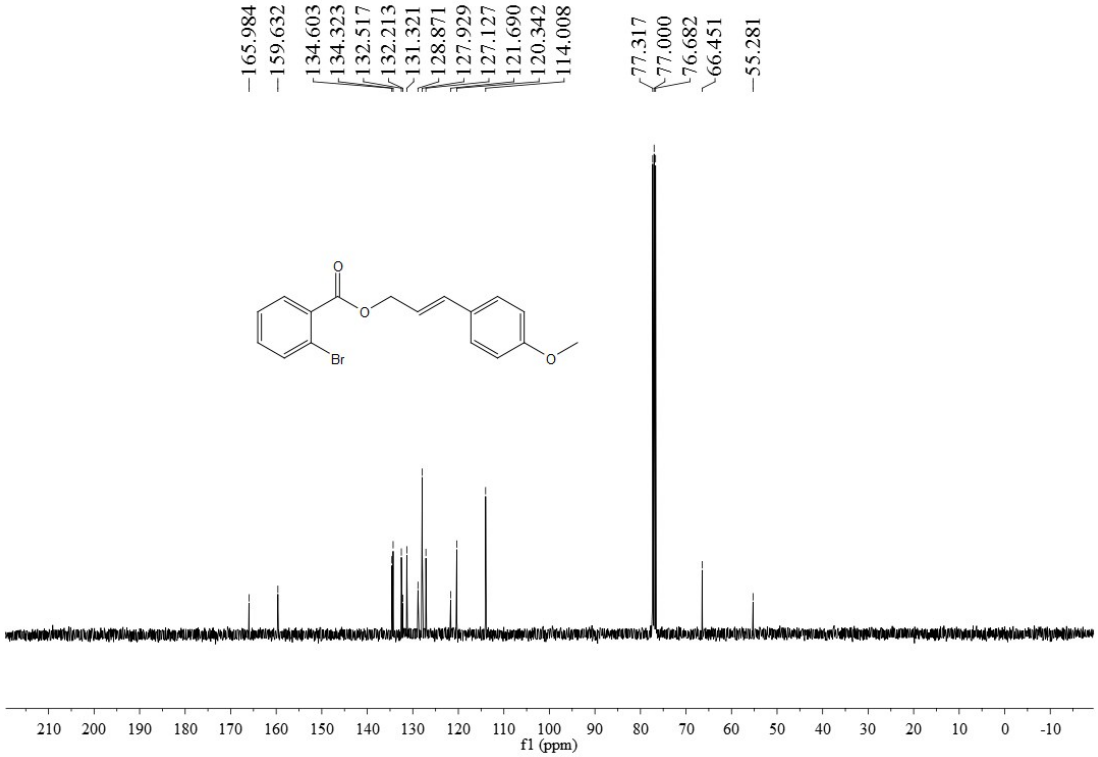
**3af**


7.842
7.824
7.679
7.661
7.370
7.348
7.330
7.312
7.156
7.138
6.761
6.722
6.382
6.363
6.342
2.349
O
O
Br
0.99
1.02
4.11
2.05
0.99
1.00
2.02
3.15
f1 (ppm)

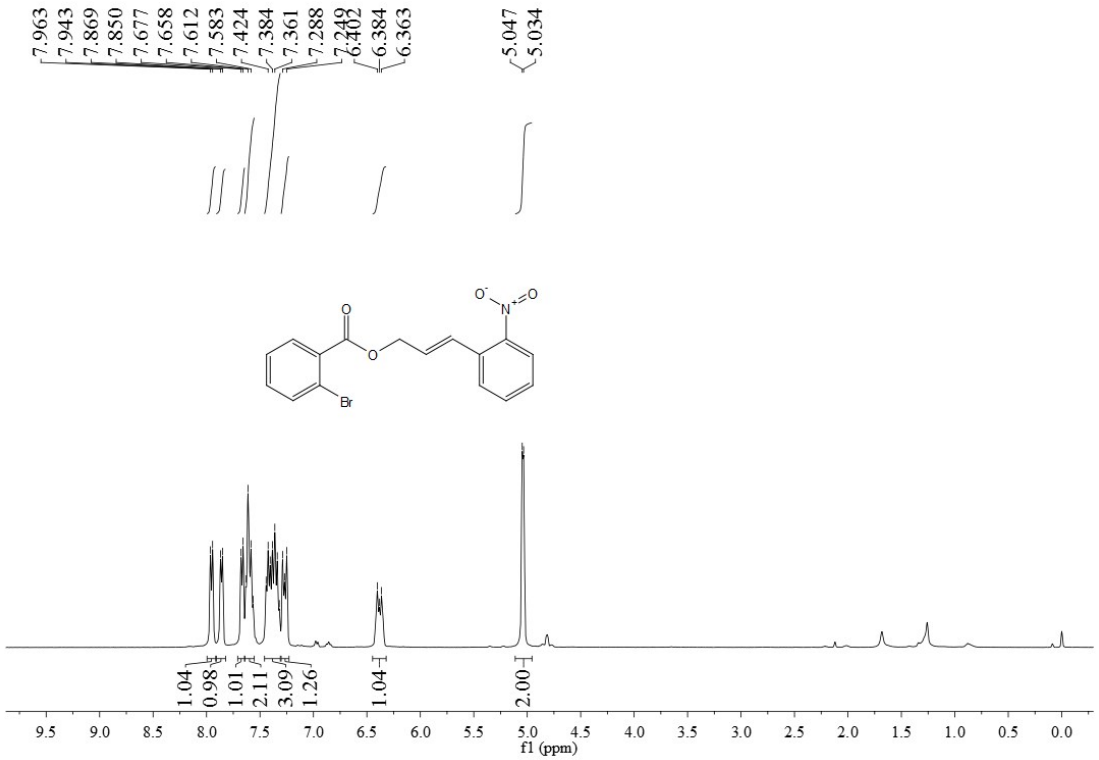

165.946
138.066
134.815
134.321
133.319
132.527
132.162
131.321
129.294
127.123
126.574
121.691
121.560
77.317
77.000
76.682
66.312
21.204
O
O
Br
f1 (ppm)

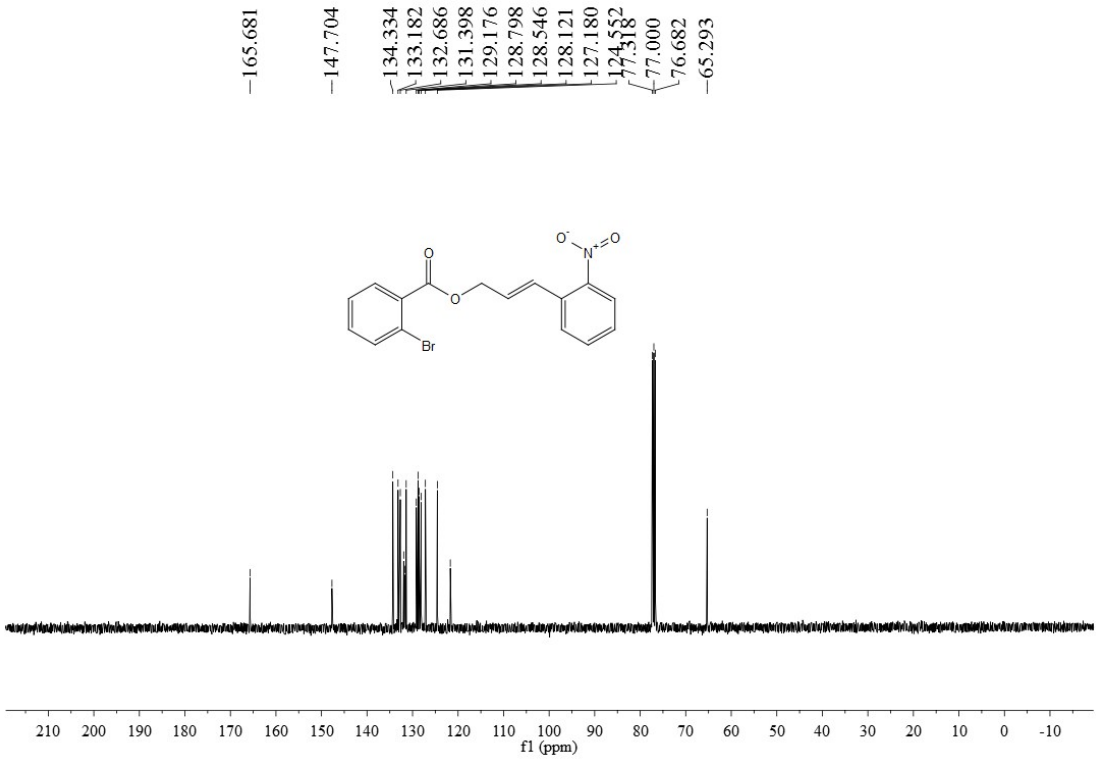
**3ag**


7.831
7.813
7.672
7.653
7.365
7.345
7.321
7.260
6.876
6.857
6.731
6.692
6.293
6.272
6.253
4.982
4.966
3.812
O
O
Br
O
0.99
1.00
4.10
2.02
1.00
1.00
2.00
3.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

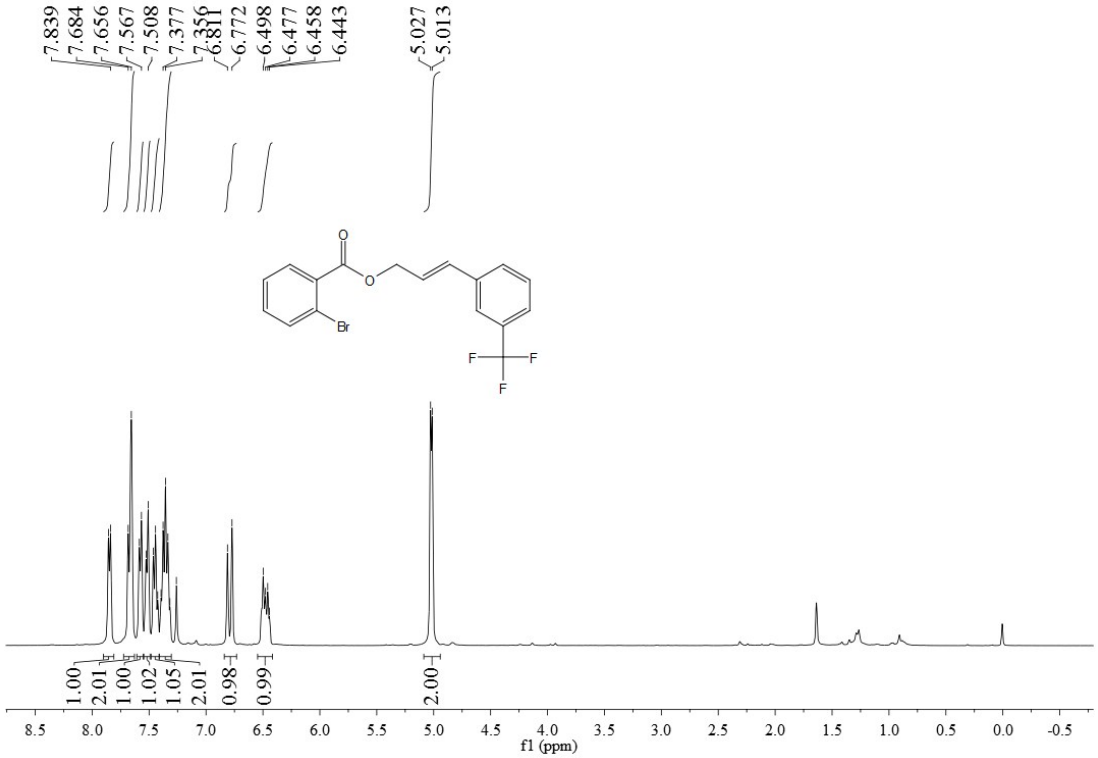

165.984
159.632
134.603
134.323
132.517
132.213
131.321
128.871
127.929
127.127
121.690
120.342
114.008
77.317
77.000
76.682
66.451
55.281
O
O
Br
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

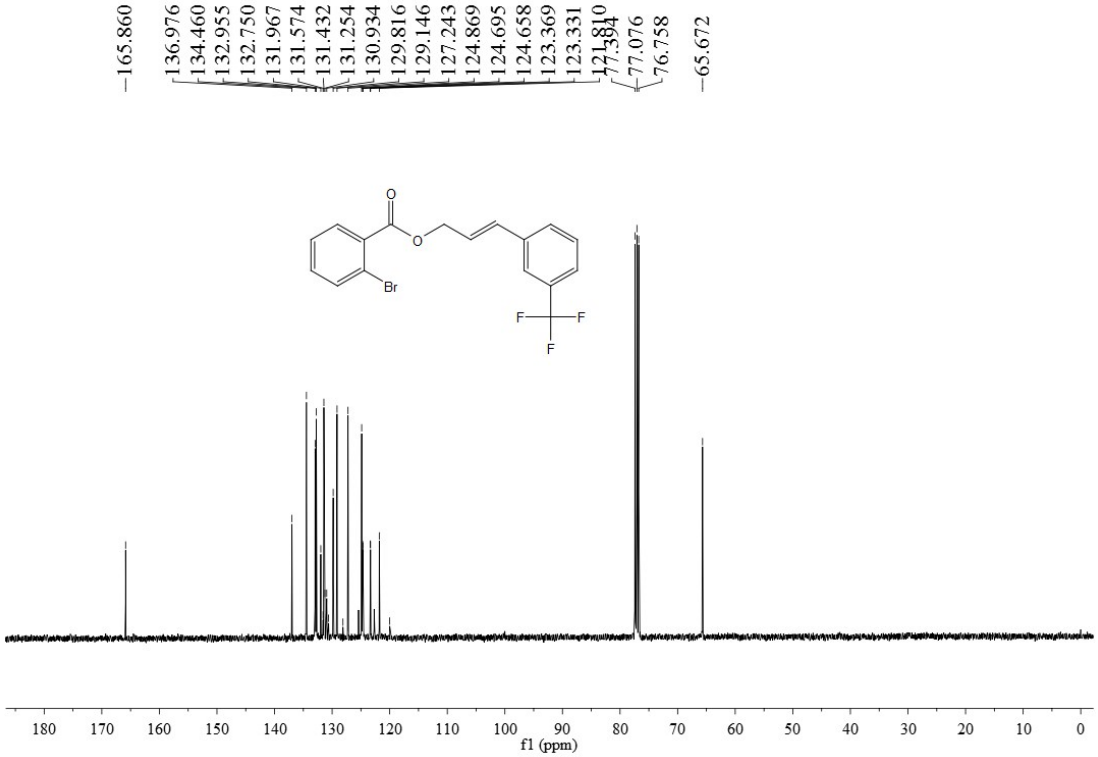
**3ah**


7.963
7.943
7.869
7.850
7.677
7.658
7.612
7.583
7.424
7.384
7.361
7.288
7.249
6.402
6.384
6.363
5.047
5.034
1.04
0.98
1.01
2.11
3.09
1.26
1.04
2.00
f1 (ppm)

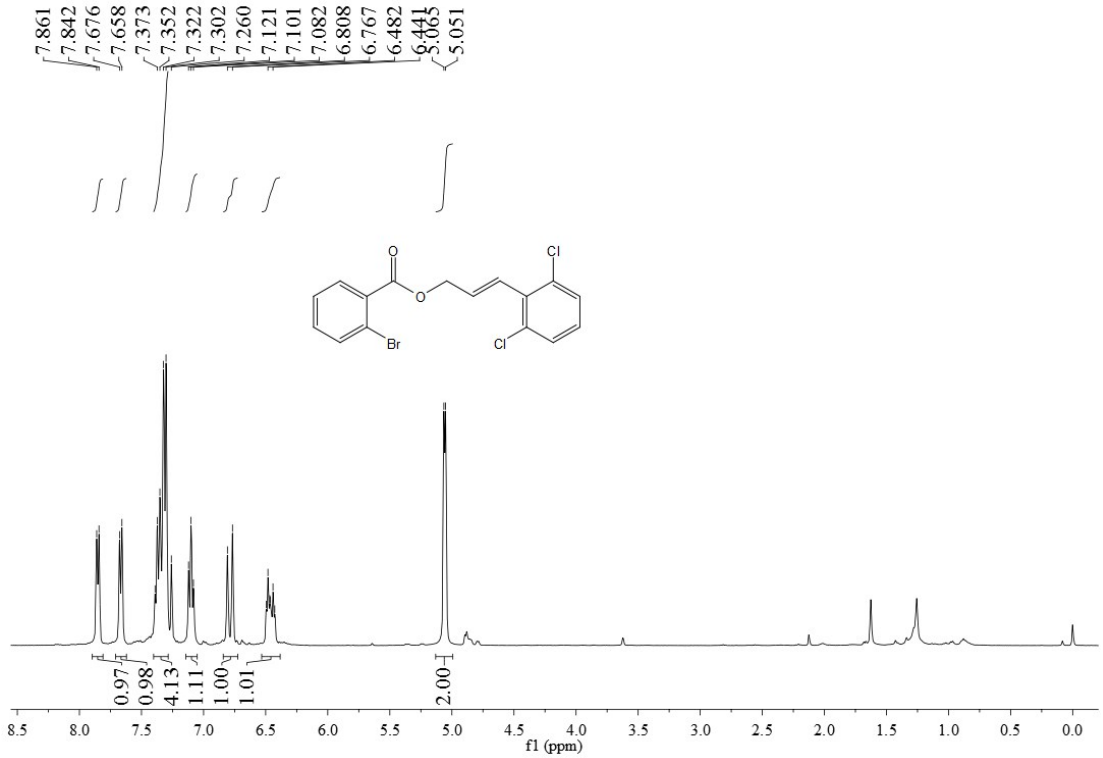

165.681
147.704
134.334
133.182
132.686
131.398
129.176
128.798
128.546
128.121
127.180
124.552
77.318
77.000
76.682
65.293
f1 (ppm)

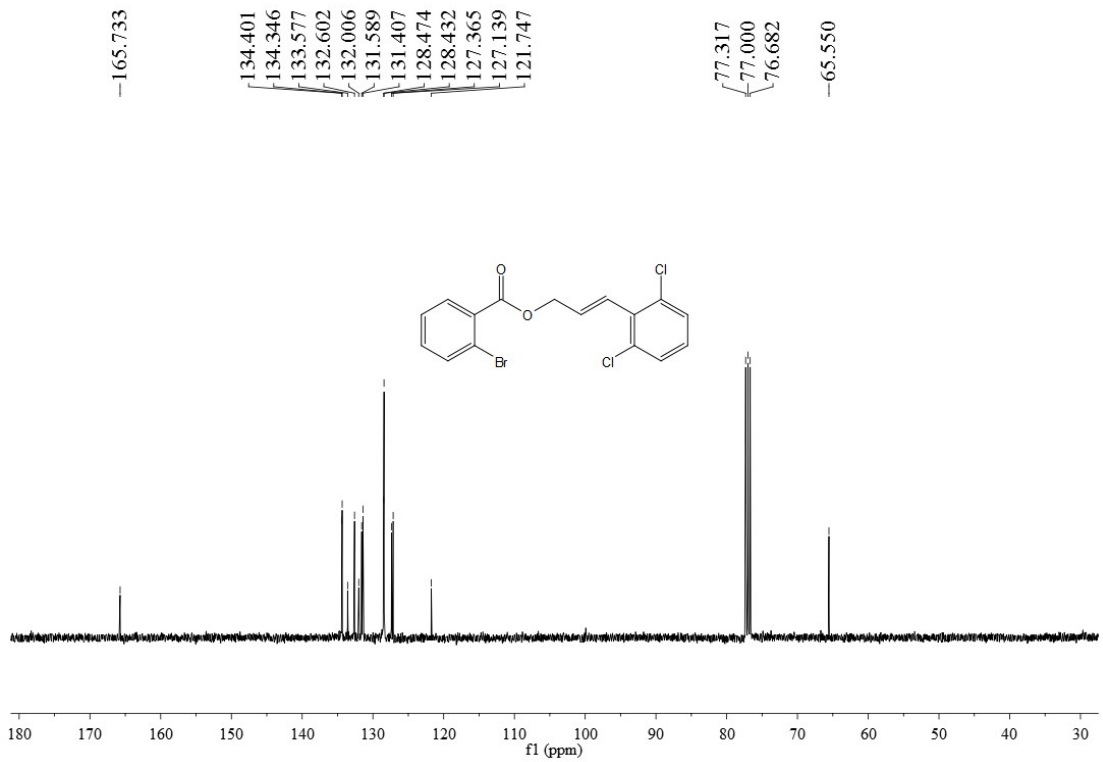
**3ai**


7.839
7.684
7.656
7.567
7.508
7.377
7.356
6.811
6.772
6.498
6.477
6.458
6.443
5.027
5.013
O
O
Br
F
F
F
1.00
2.01
1.00
1.02
1.05
2.01
0.98
0.99
2.00
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)

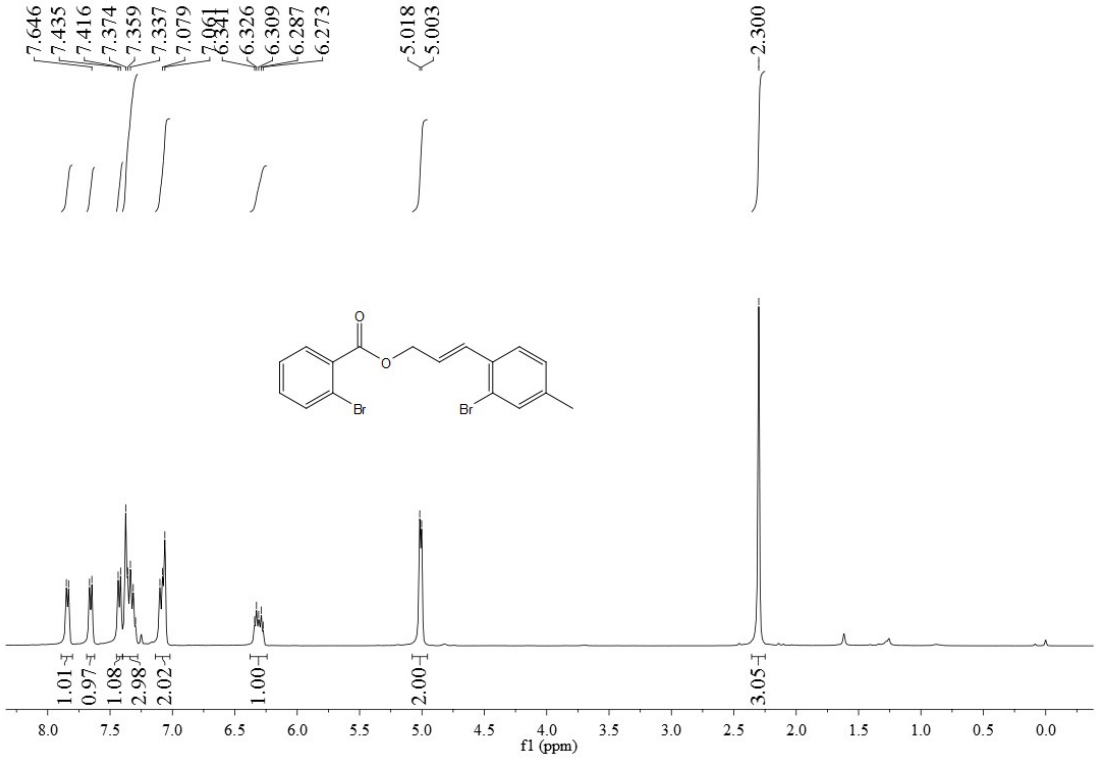

165.860
136.976
134.460
132.955
132.750
131.967
131.574
131.432
131.254
130.934
129.816
129.146
127.243
124.869
124.695
124.658
123.369
123.331
121.810
77.394
77.076
76.758
65.672
O
O
Br
F
F
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

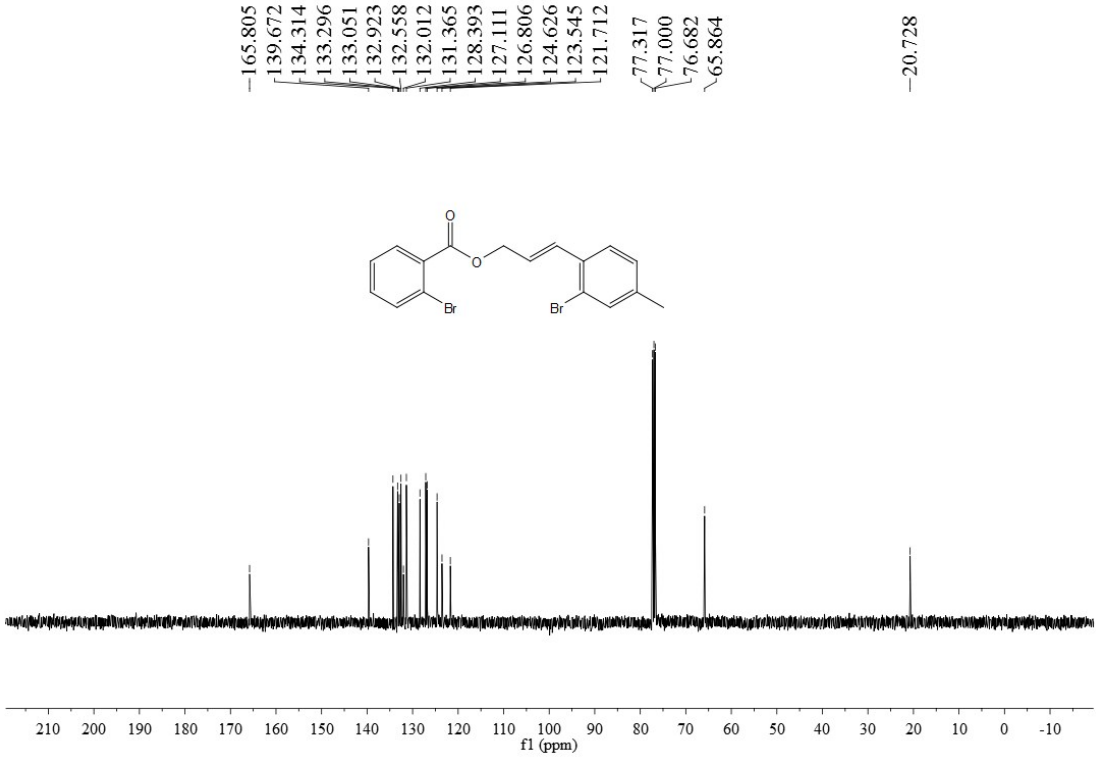
**3aj**


7.861
7.842
7.676
7.658
7.373
7.352
7.322
7.302
7.260
7.121
7.101
7.082
6.808
6.767
6.482
6.441
5.065
5.051
O
O
Cl
Br
Cl
0.97
0.98
4.13
1.11
1.00
1.01
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

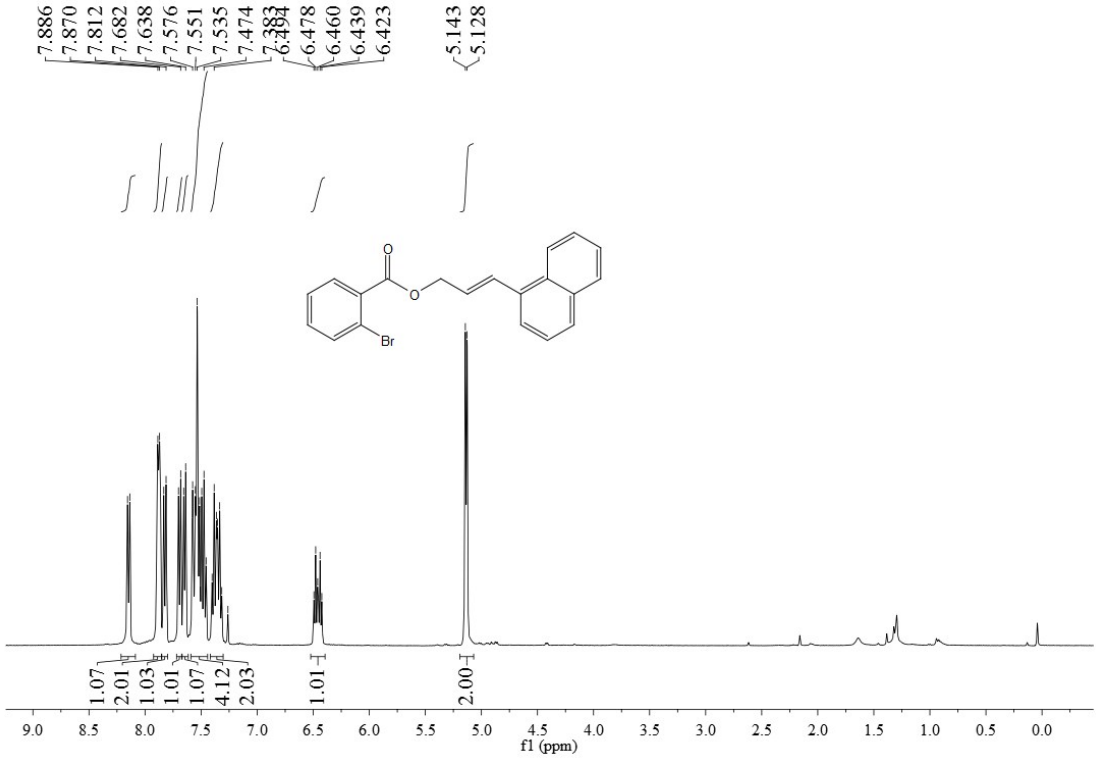

165.733
134.401
134.346
133.577
132.602
132.006
131.589
131.407
128.474
128.432
127.365
127.139
121.747
77.317
77.000
76.682
65.550
O
O
Cl
Br
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

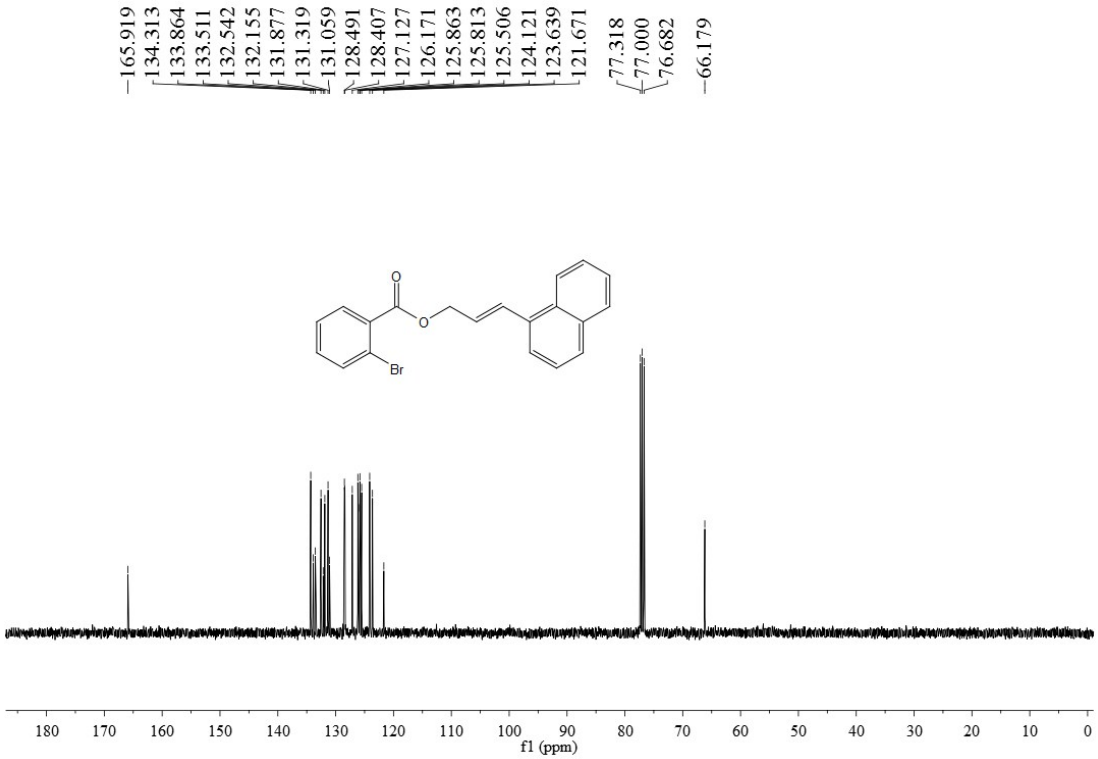
**3ak**


7.646
7.435
7.416
7.374
7.359
7.337
7.079
6.326
6.309
6.287
6.273
5.018
5.003
2.300
O
O
Br
Br
1.01
0.97
1.08
2.98
2.02
1.00
2.00
3.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

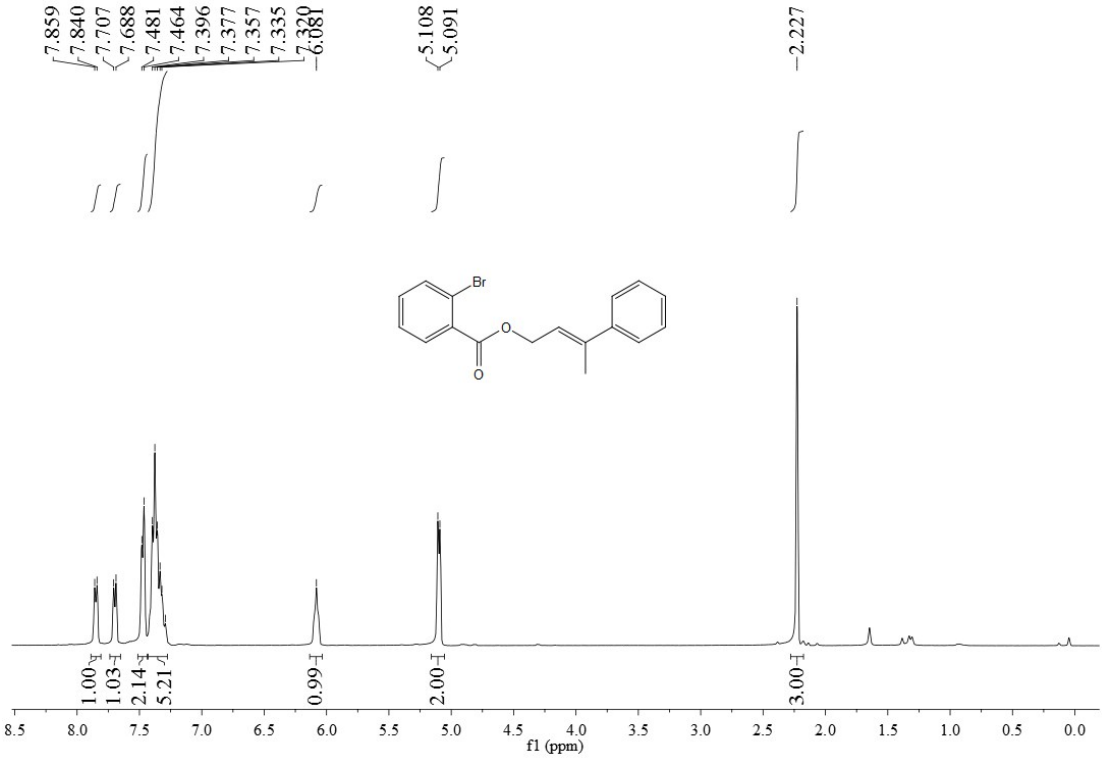

165.805
139.672
134.314
133.296
133.051
132.923
132.558
132.012
131.365
128.393
127.111
126.806
124.626
123.545
121.712
77.317
77.000
76.682
65.864
20.728
O
O
Br
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

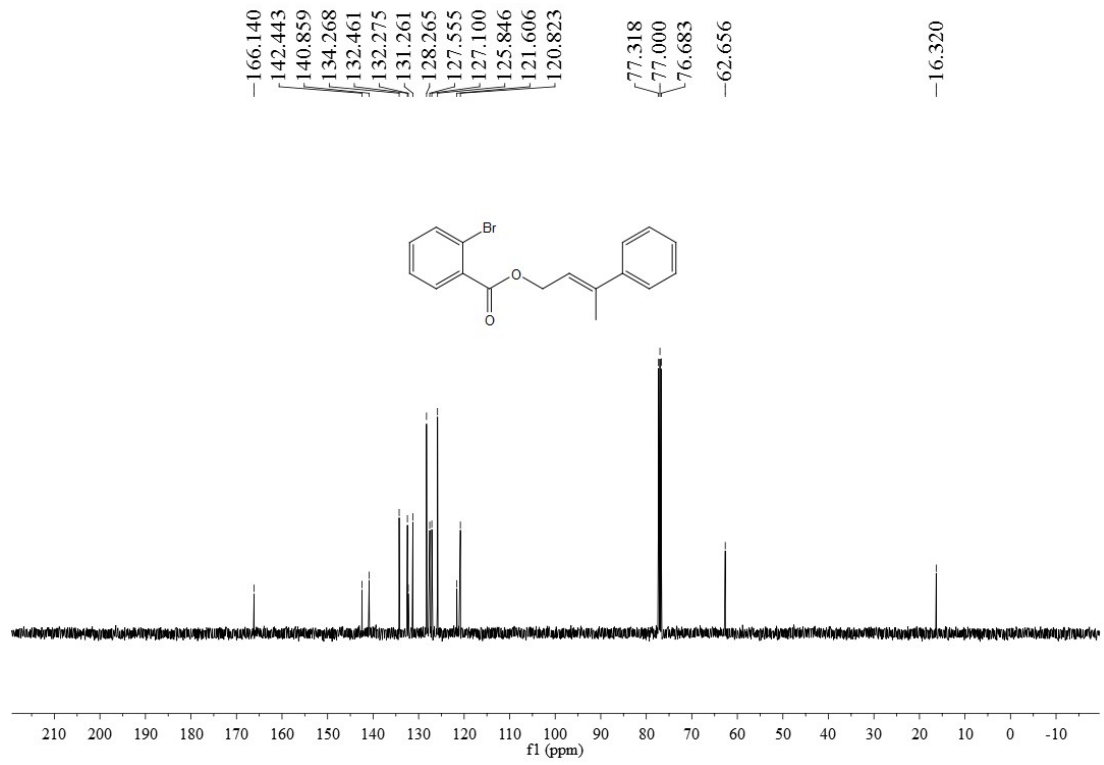
**3al**


7.886
7.870
7.812
7.682
7.638
7.576
7.551
7.535
7.474
6.478
6.460
6.439
6.423
5.143
5.128
O
O
Br
1.07
2.01
1.03
1.01
1.07
4.12
2.03
1.01
2.00
f1 (ppm)

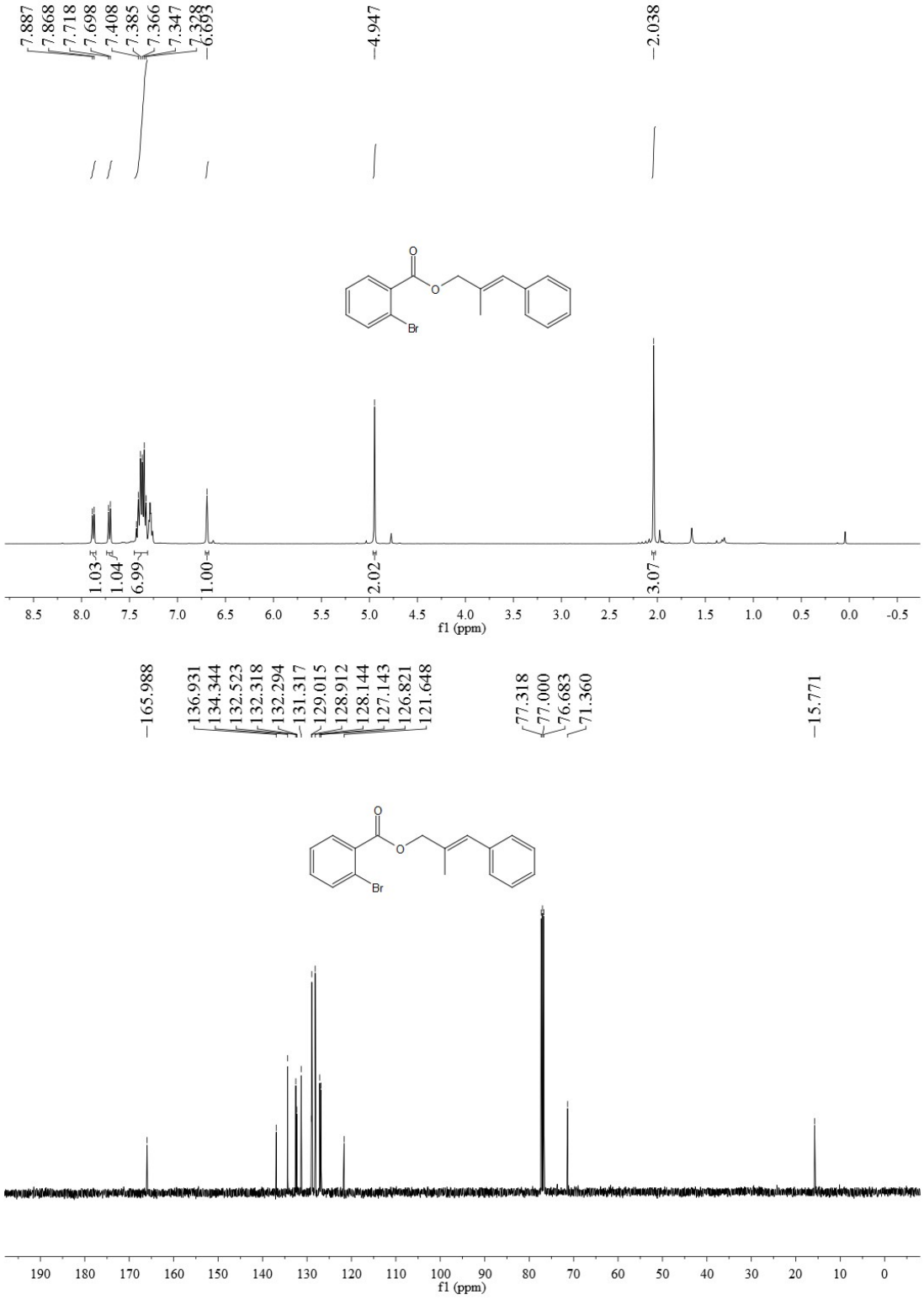

165.919
134.313
133.864
133.511
132.542
132.155
131.877
131.319
131.059
128.491
128.407
127.127
126.171
125.863
125.813
125.506
124.121
123.639
121.671
77.318
77.000
76.682
66.179
O
O
Br
f1 (ppm)

**3am**

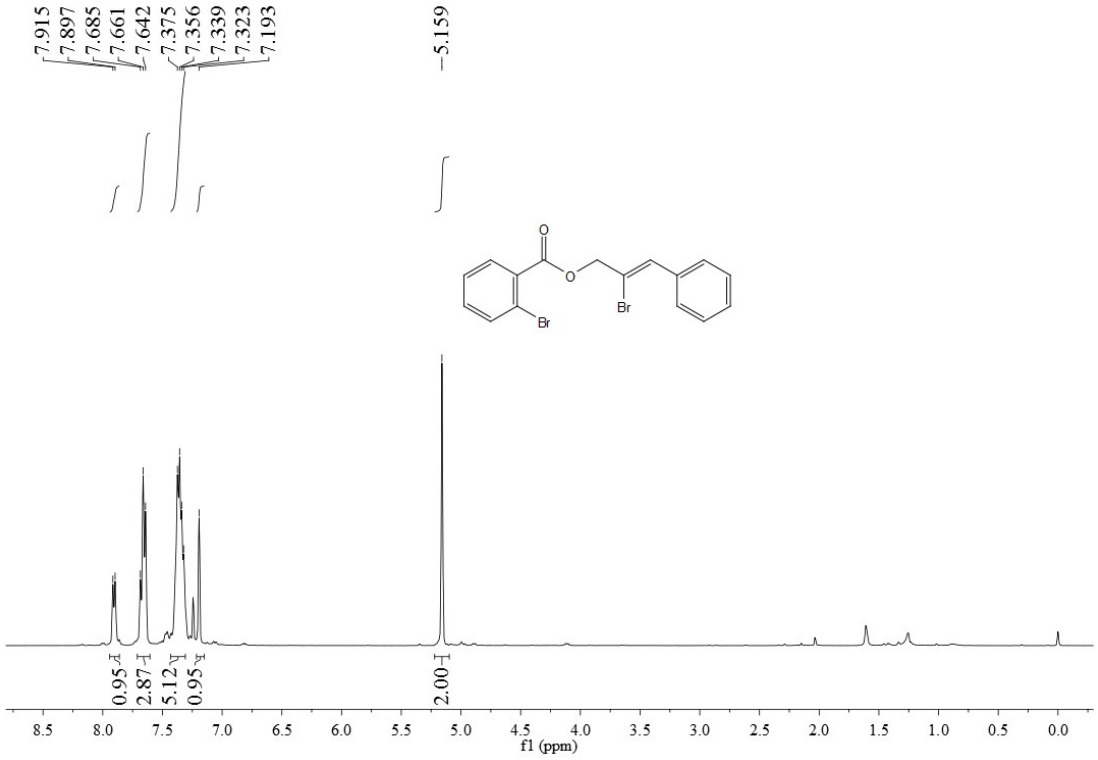

7.859
7.840
7.707
7.688
7.481
7.464
7.396
7.377
7.357
7.335
7.320
6.081
5.108
5.091
2.227
Br
O
O
1.00
1.03
2.14
5.21
0.99
2.00
3.00
f1 (ppm)

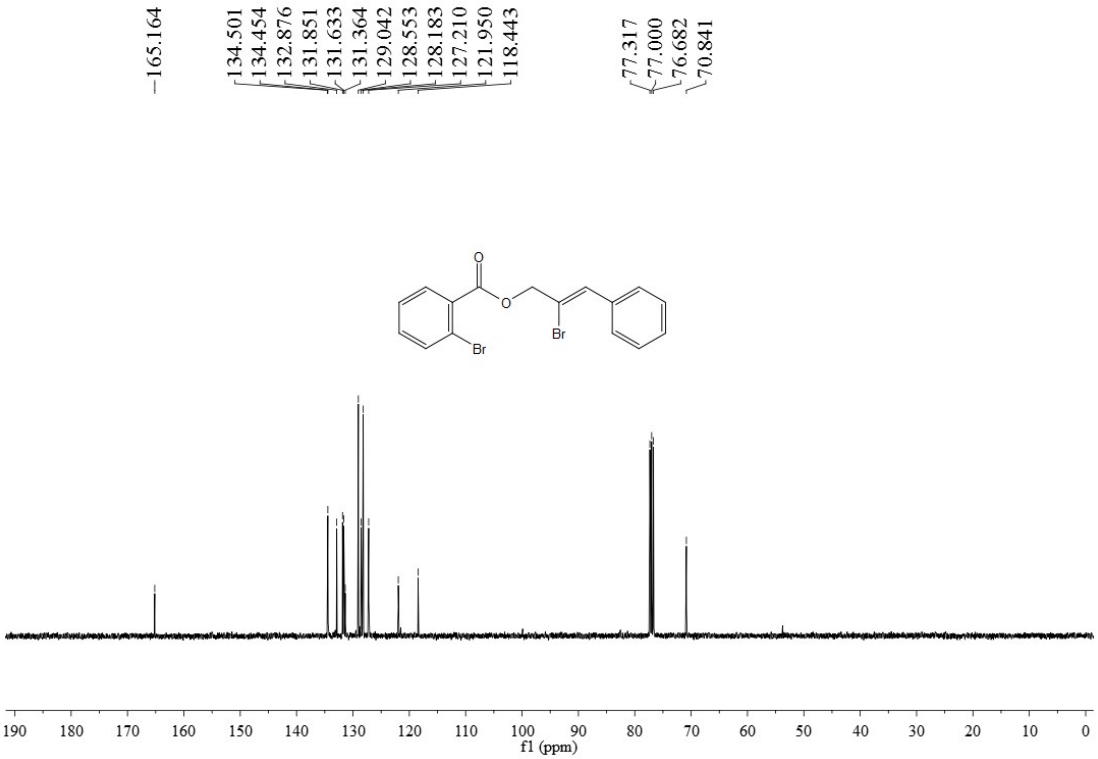

166.140
142.443
140.859
134.268
132.461
132.275
131.261
128.265
127.555
127.100
125.846
121.606
120.823
77.318
77.000
76.683
62.656
16.320
Br
O
O
f1 (ppm)

**3an**

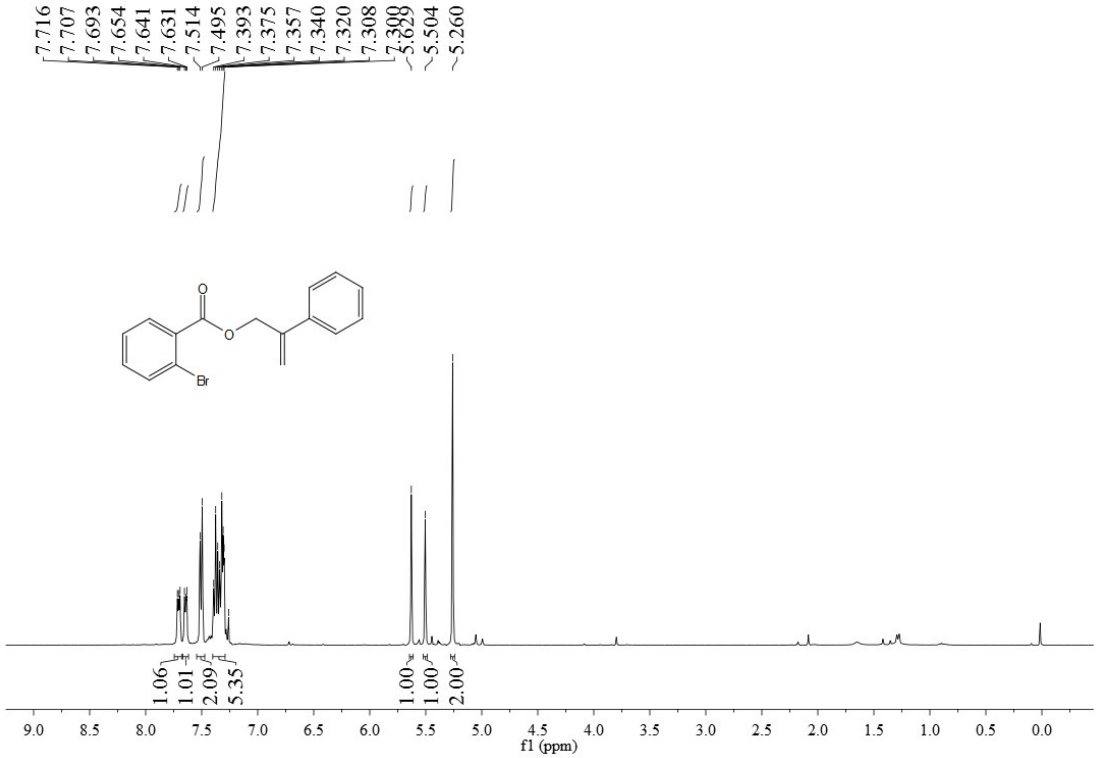

7.887
7.868
7.718
7.698
7.408
7.385
7.366
7.347
7.328
6.693
4.947
2.038
O
O
Br
1.03
1.04
6.99
1.00
2.02
3.07
f1 (ppm)
165.988
136.931
134.344
132.523
132.318
132.294
131.317
129.015
128.912
128.144
127.143
126.821
121.648
77.318
77.000
76.683
71.360
15.771
O
O
Br
f1 (ppm)

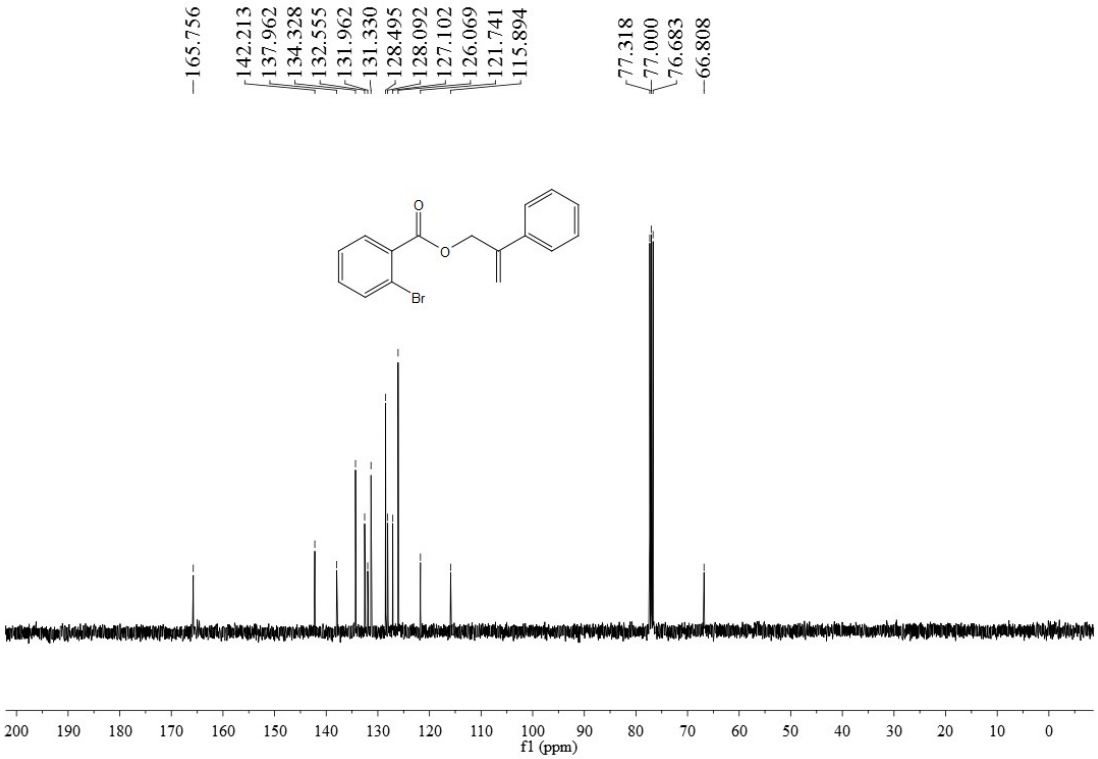
**3ao**


7.915
7.897
7.685
7.661
7.642
7.375
7.356
7.339
7.323
7.193
5.159
O
O
Br
Br
0.95
2.87
5.12
0.95
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

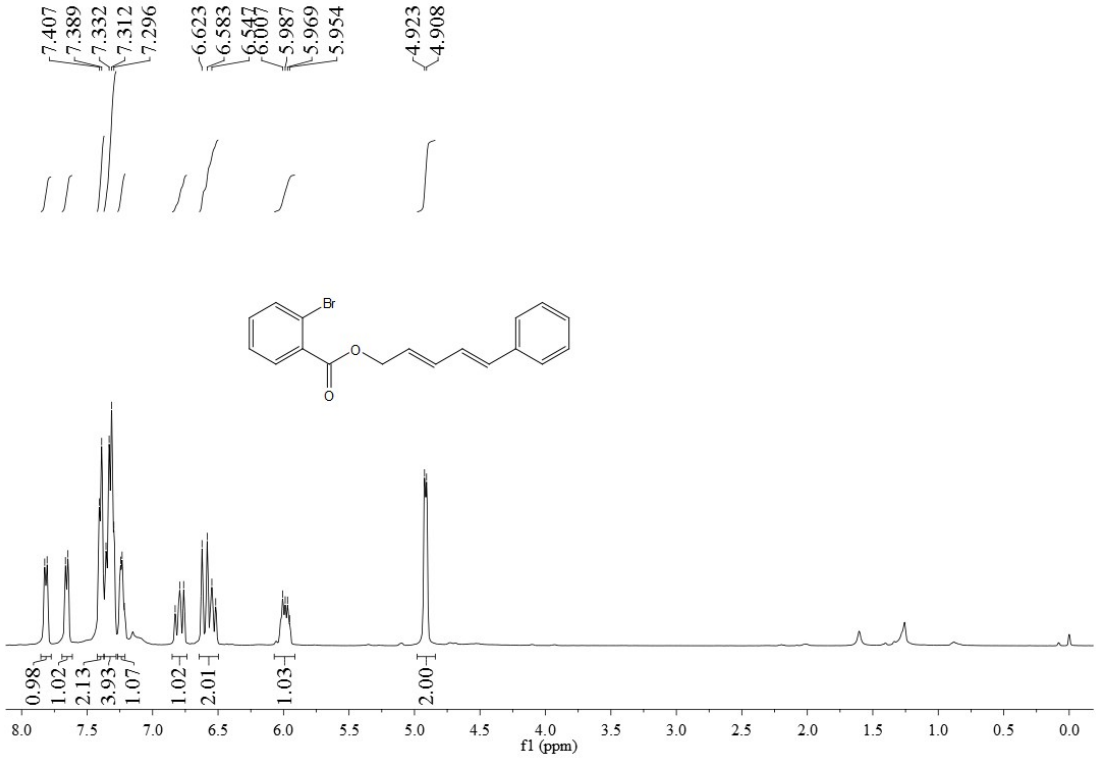

165.164
134.501
134.454
132.876
131.851
131.633
131.364
129.042
128.553
128.183
127.210
121.950
118.443
77.317
77.000
76.682
70.841
O
O
Br
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

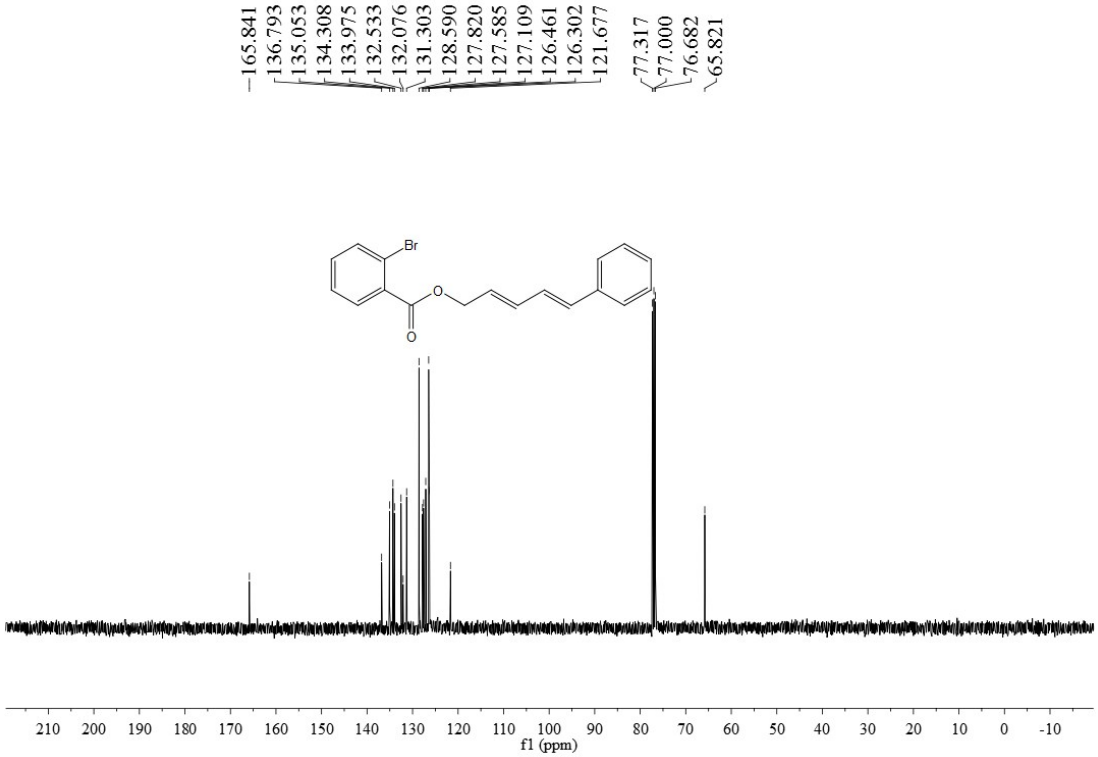
**3ap**


7.716
7.707
7.693
7.654
7.641
7.631
7.514
7.495
7.393
7.375
7.357
7.340
7.320
7.308
5.504
5.260
O
O
Br
1.06
1.01
2.09
5.35
1.00
1.00
2.00
f1 (ppm)

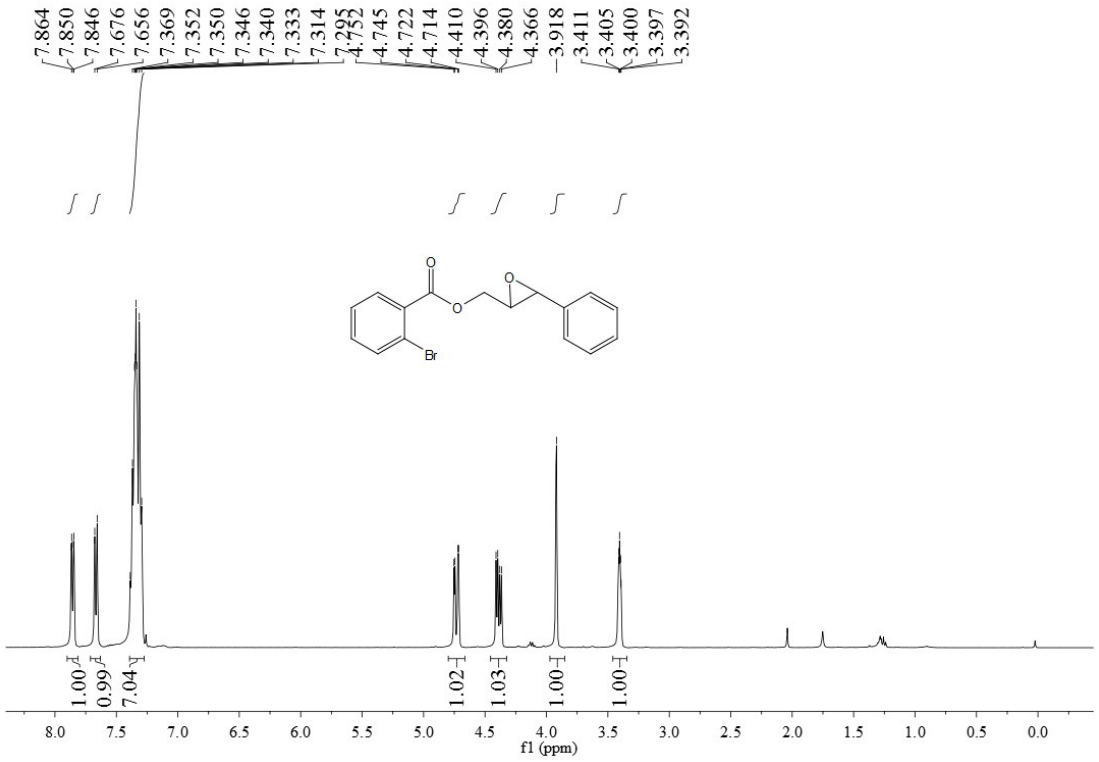

165.756
142.213
137.962
134.328
132.555
131.962
131.330
128.495
128.092
127.102
126.069
121.741
115.894
77.318
77.000
76.683
66.808
O
O
Br
f1 (ppm)

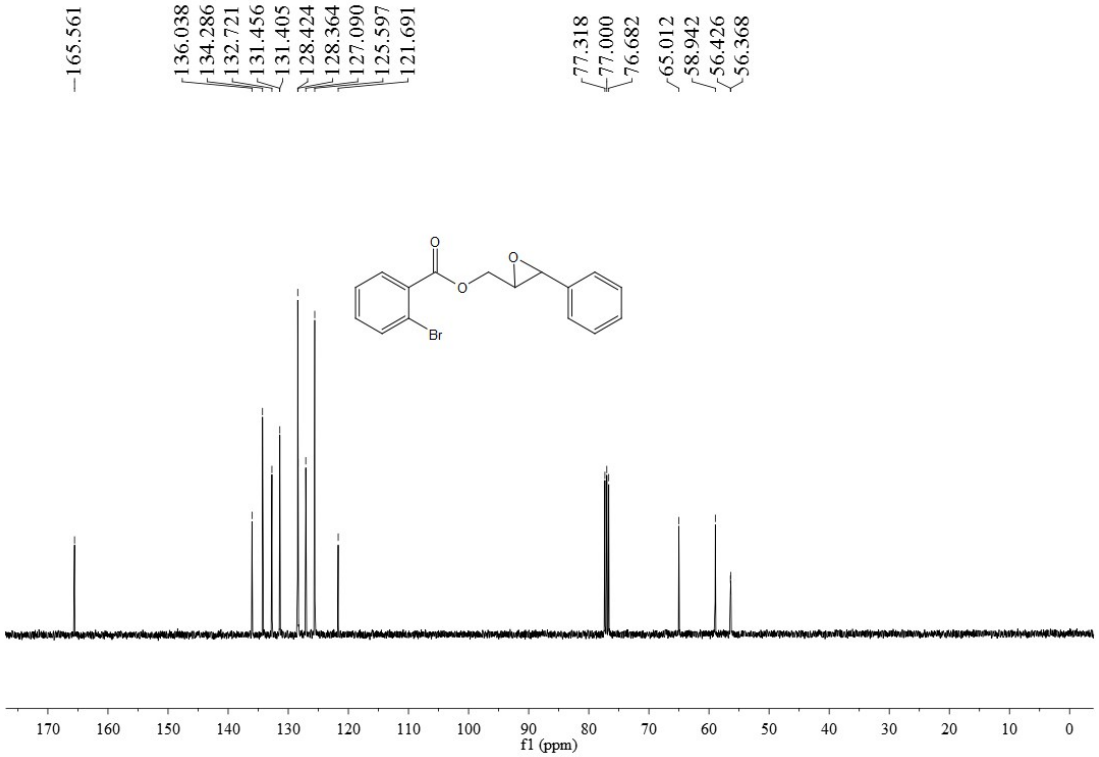
**3aq**


7.407
7.389
7.332
7.312
7.296
6.623
6.583
6.547
6.007
5.987
5.969
5.954
4.923
4.908
Br
O
O
0.98
1.02
2.13
3.93
1.07
1.02
2.01
1.03
2.00
f1 (ppm)

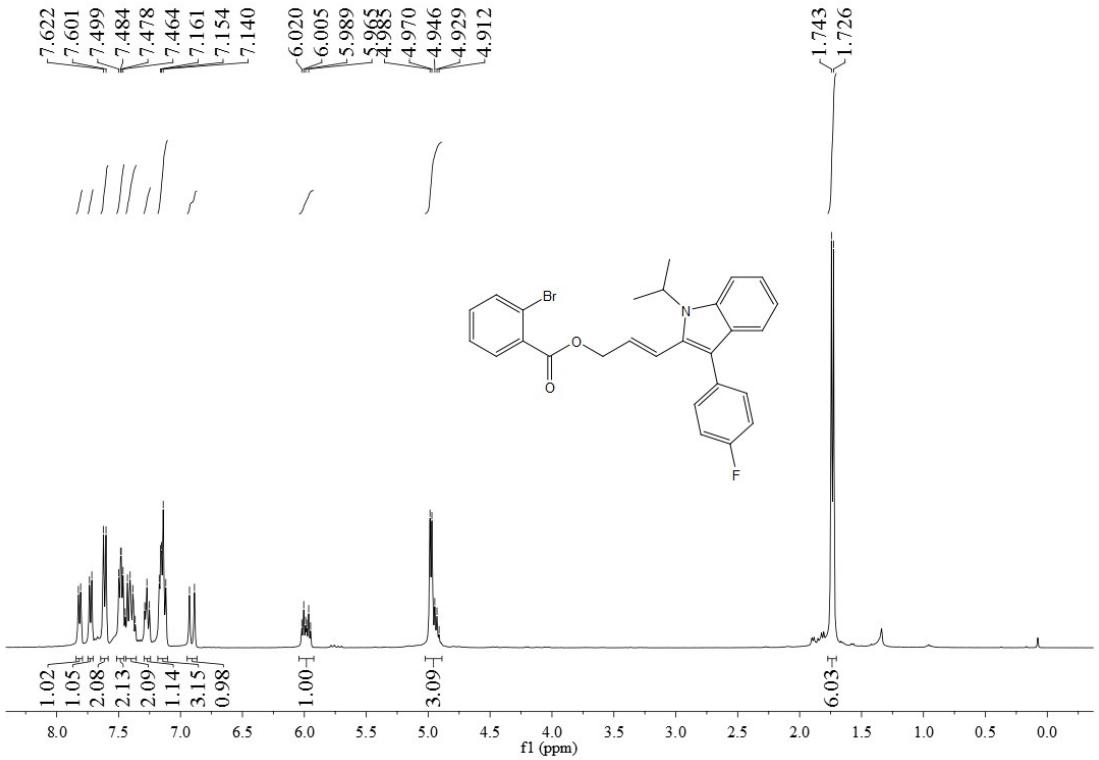

165.841
136.793
135.053
134.308
133.975
132.533
132.076
131.303
128.590
127.820
127.585
127.109
126.461
126.302
121.677
77.317
77.000
76.682
65.821
Br
O
O
f1 (ppm)

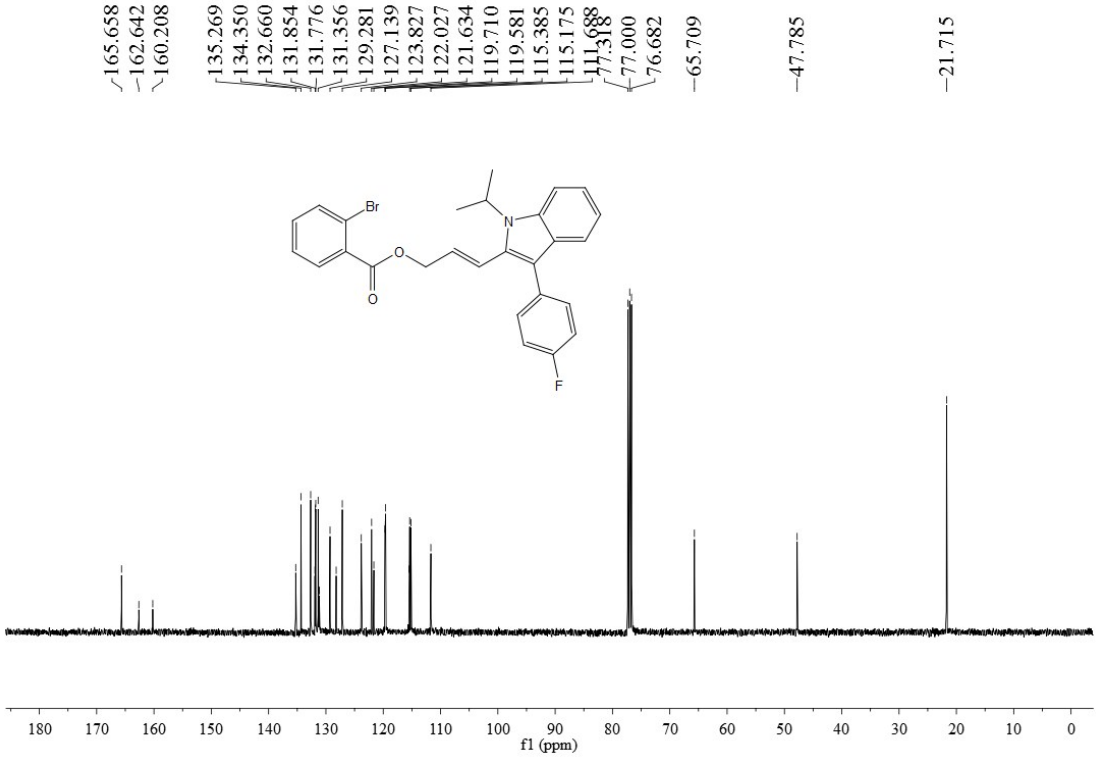
**4**


7.864
7.850
7.846
7.676
7.656
7.369
7.352
7.350
7.346
7.340
7.333
7.314
7.295
4.752
4.745
4.722
4.714
4.410
4.396
4.380
4.366
3.918
3.411
3.405
3.400
3.397
3.392
O
O
O
Br
1.00
0.99
7.04
1.02
1.03
1.00
1.00
f1 (ppm)


165.561
136.038
134.286
132.721
131.456
131.405
128.424
128.364
127.090
125.597
121.691
77.318
77.000
76.682
65.012
58.942
56.426
56.368
O
O
O
Br
f1 (ppm)

**7**


7.622
7.601
7.499
7.484
7.478
7.464
7.161
7.154
7.140
6.020
6.005
5.989
5.965
4.985
4.970
4.946
4.929
4.912
1.743
1.726
Br
O
O
N
F
1.02
1.05
2.08
2.13
2.09
1.14
3.15
0.98
1.00
3.09
6.03
f1 (ppm)


165.658
162.642
160.208
135.269
134.350
132.660
131.854
131.776
131.356
129.281
127.139
123.827
122.027
121.634
119.710
119.581
115.385
115.175
111.688
77.318
77.000
76.682
65.709
47.785
21.715
Br
O
O
N
F
f1 (ppm)