Supporting Information for

Seminormal-$BrCH_2CH_2OH$-mediated electrochemical epoxidation of unactivated olefins

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1. General Information

Unless otherwise noted, chemicals and materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to the general methods. Flash column chromatography was performed with silica gel (200–300 mesh). NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometer. Data were reported as chemical shifts in ppm relative to $CDCl_3$ (7.26 ppm) for ^1H NMR and $CDCl_3$ (77.2 ppm) for ^{13}C NMR. The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High resolution mass spectra (ESI HRMS) were recorded on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2. XINRUI® DJS-292B potentiostat made in China was used as a power supply device. The reticulated vitreous carbon (RVC) anode and Pt plate cathode are commercially available from Gaoss Union in China.

2. General Procedure for the Electrosynthesis

2.1 General Procedure for the Reaction

A 20 mL three-necked beaker-type cell was charged with alkene (0.2 mmol, 1 equiv.), $BrCH_2CH_2OH$ (50 mol%), K_3PO_4 (0.24 mmol, 1.2 equiv.), *n*-Bu_4NBF_4 (0.1 mmol, 0.5 equiv.). The cell was equipped with a reticulated vitreous carbon (RVC, 100 PPI, 1.2 cm x 0.8 cm x 0.8 cm) anode and a platinum plate (1 cm x 1 cm x 0.1 mm) cathode (Figure S1A and Figure S1B). MeCN/H_2O (6 mL/1 mL) was added. The electrolysis was carried out at room temperature using a constant current of 3 mA for 6 h (Figure S1C). After the reaction was completed, the reaction mixture was washed with 10 mL of saturated $NaHSO_3$ (aq.) and extracted with ethyl acetate (3 x 15 mL). The combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. Then the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether (1:30) to give the desired product. The reaction setup have been reported in our previous work.[1]

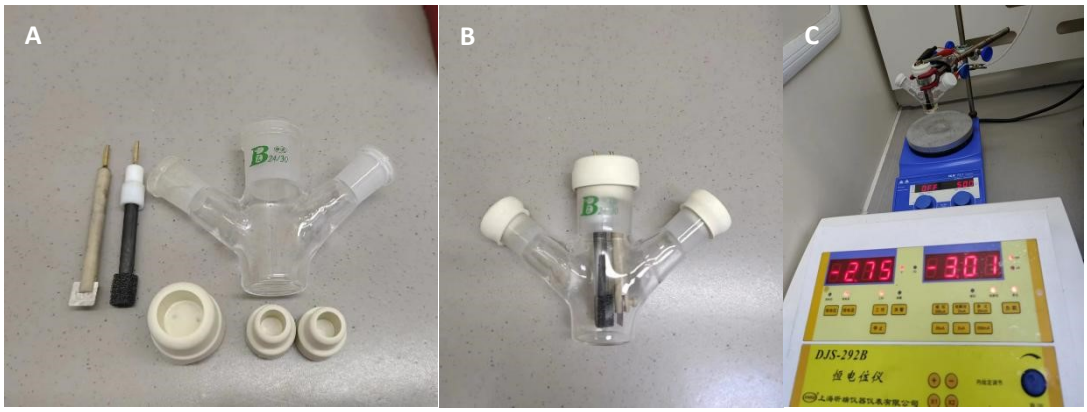
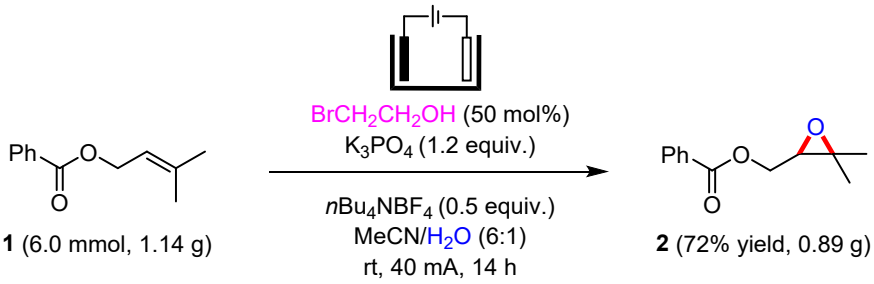


Figure S1. The reaction setup

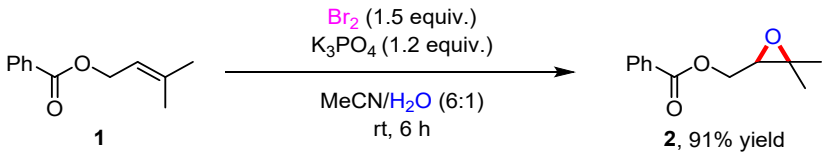
2.2 General Procedure for the Gram-Scale Synthesis of 2



A gram-scale electrolysis was conducted in a 100 mL three-necked round-bottomed flask with a piece of RVC (1.2 cm x 2 cm x 2 cm) as the anode, a Pt plate as the cathode (1.5 cm x 1.5 cm x 0.3 mm), and a constant current of 40 mA for 14 h at room temperature. The reaction mixture consisted 3-methylbut-2-en-1-yl benzoate (**1**, 1.14 g, 6 mmol, 1 equiv.), $BrCH_2CH_2OH$ (0.38 g, 50 mol%), K_3PO_4 (1.53 g, 0.24 mmol, 1.2 equiv.), *n*-Bu_4NBF_4 (0.99 g, 3 mmol, 0.5 equiv.) and MeCN/H_2O (78 mL/13 mL). After the reaction was completed, the reaction mixture was washed with 50 mL of saturated $NaHSO_3$ (aq.) and extracted with ethyl acetate (3 x 100 mL). The combined organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure. Then the residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether (1:30) to give the desired product **2** (0.89 g, 72% yield).

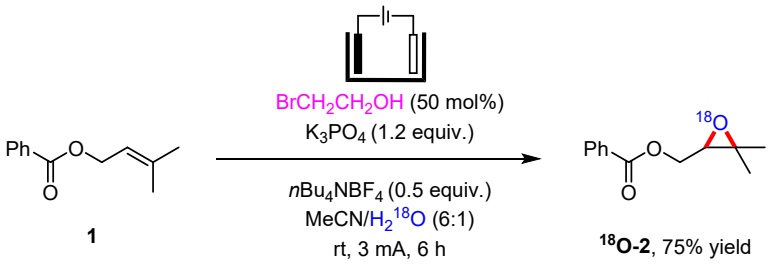
3. Mechanistic Studies

3.1 Epoxidation of 1 with Br_2



The epoxidation of 3-methylbut-2-en-1-yl benzoate (**1**) could be achieved in 91% yield with Br_2 as the activated reagent under the conditions of no electricity, indicating that the success of the reaction probably depends on the generation of Br_2 in situ.

3.2 Oxygen-Labeling Experiments



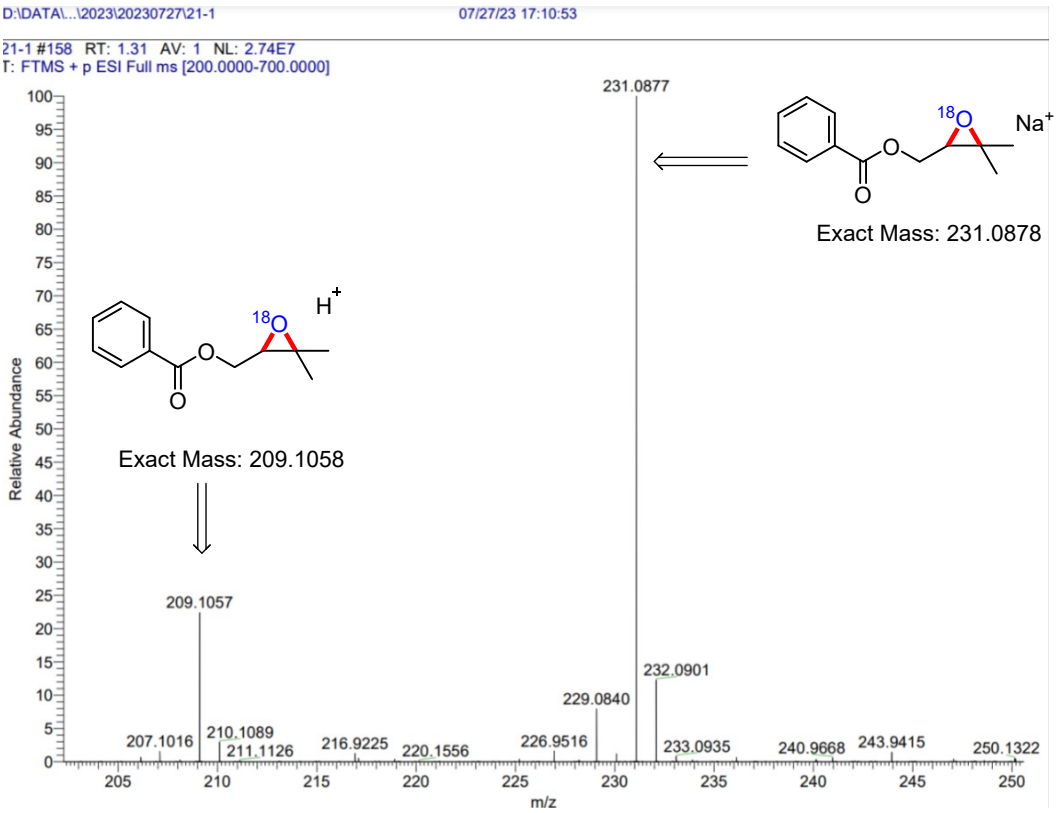
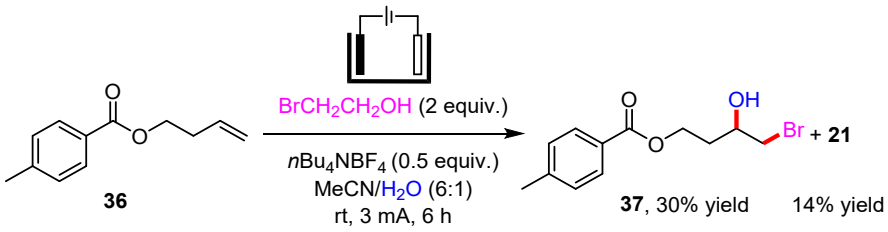


Figure S2 High resolution mass spectroscopy (HRMS) of **^{18}O-2**.

The oxygen-labeling experiment was conducted to understand the reaction mechanism. The product **^{18}O-2** was primarily obtained in 75% yield when using $H_2{}^{18}O$ instead of H_2O, indicating that the oxygen atom in epoxy group of product comes from water (Figure S2).

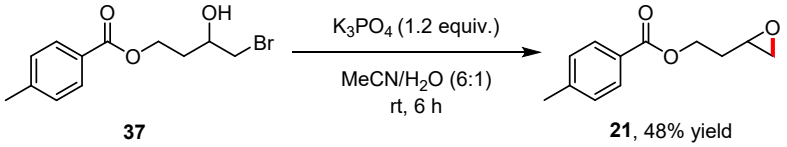
3.3 Bromohydroxylation of 36 without K_3PO_4



The bromohydroxylation product **37** was afforded in 30% yield by electrolyzing **36** in the absence of K_3PO_4 and epoxy product **21** was simultaneously detected in 14% yield, supporting that an electrochemical epoxidation involves a bromohydroxylation process.

4-Bromo-3-hydroxybutyl 4-methylbenzoate (37). Colourless oil (17.4 mg, 30% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 4.59–4.48 (m, 1H), 4.49–4.39 (m, 1H), 4.05–3.94 (m, 1H), 3.57 (dd, J = 10.4, 3.7 Hz, 1H), 3.46 (dd, J = 10.4, 6.6 Hz, 1H), 2.66 (d, J = 4.8 Hz, 1H), 2.41 (s, 3H), 2.14–2.00 (m, 1H), 2.02–1.88 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 144.0, 129.8, 129.3, 127.3, 68.2, 61.4, 39.8, 34.6, 21.8; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{12}H_{16}BrO_3^+$: 287.0277, Found: 287.0275.

3.4 Base-facilitated intramolecular epoxidation of 37



The epoxidation product **21** could be obtained in 48% yield from **37** with K_3PO_4 in a sulotion of $MeCN/H_2O$. The addition of K_3PO_4 could facilitate the conversion of the bromohydroxylation intermediate to the epoxidation product via an intramolecular nucleophilic substitution process with the release of Br^-.

3.5 Cyclic voltammetry studies

The cyclic voltammograms were recorded in an electrolyte of *n*-Bu_4NBF_4 (0.1 M) in MeCN (5 mL) using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and an Ag/AgCl reference electrode. The scan rate was 50 mV/s.

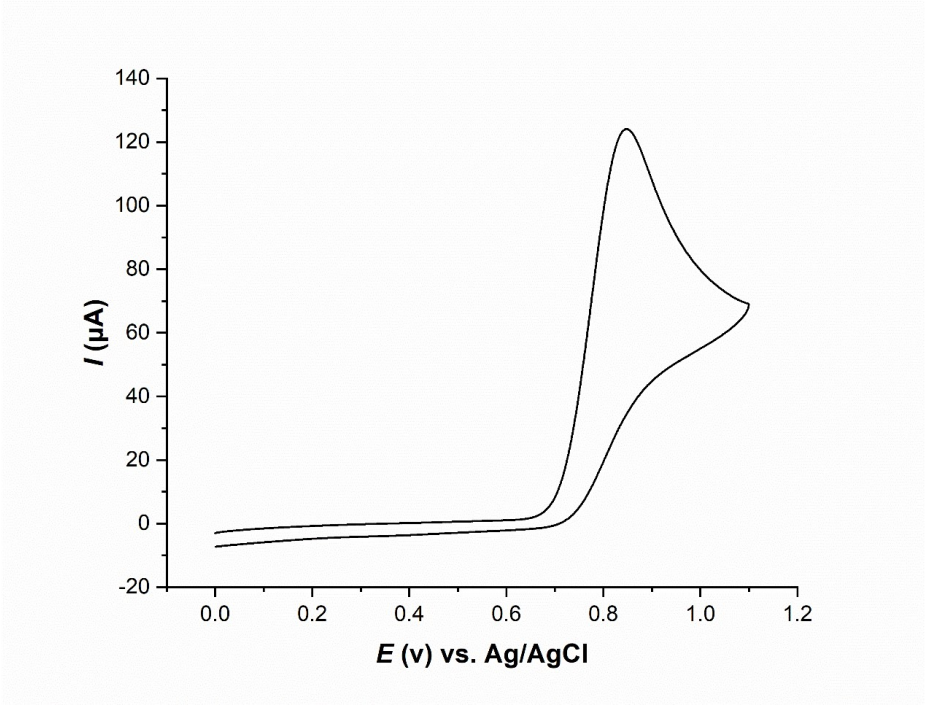


Figure S3. Cyclic voltammogram of *n*Bu_4NBr (10 mM) in an electrolyte of *n*Bu_4NBF_4 (0.1 M) in MeCN (5 mL). $E_{p/2}$ = 0.77 V.

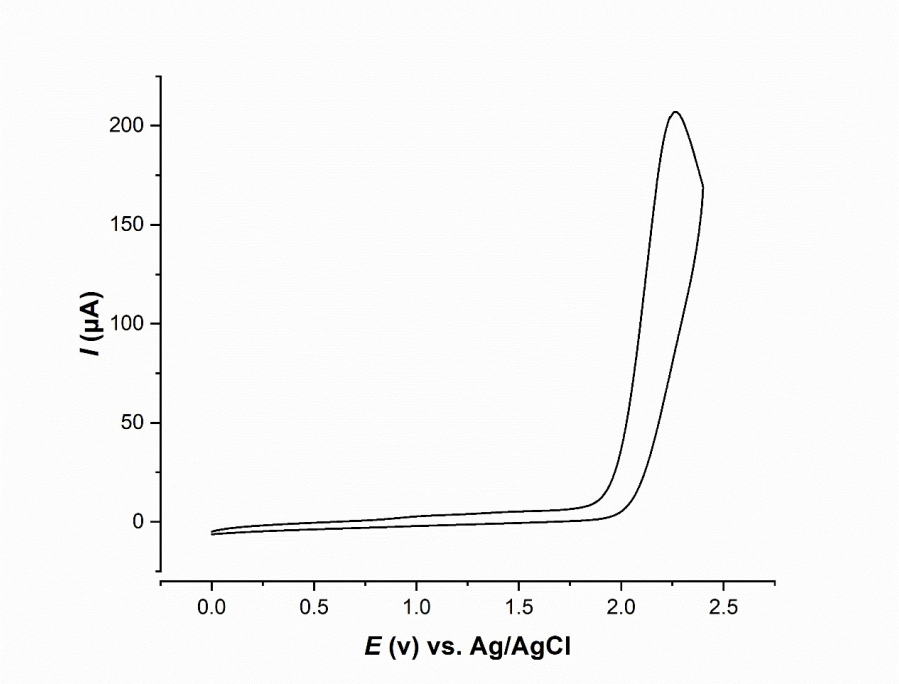


Figure S4. Cyclic voltammogram of 3-methylbut-2-en-1-yl benzoate (**1**, 10 mM) in an electrolyte of *n*Bu_4NBF_4 (0.1 M) in MeCN (5 mL). $E_{p/2}$ = 2.10 V.

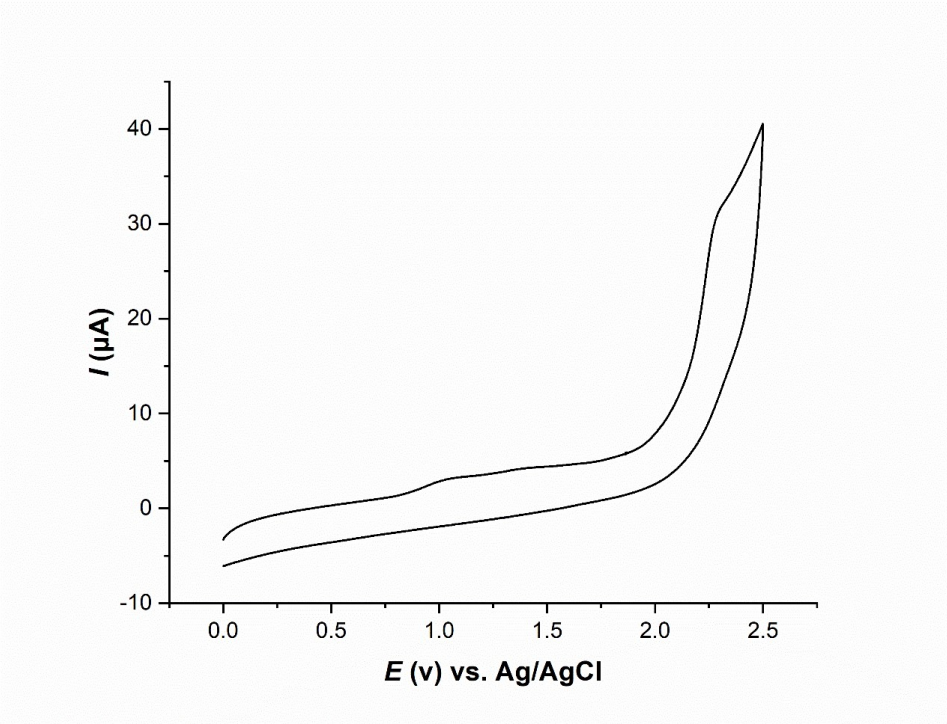
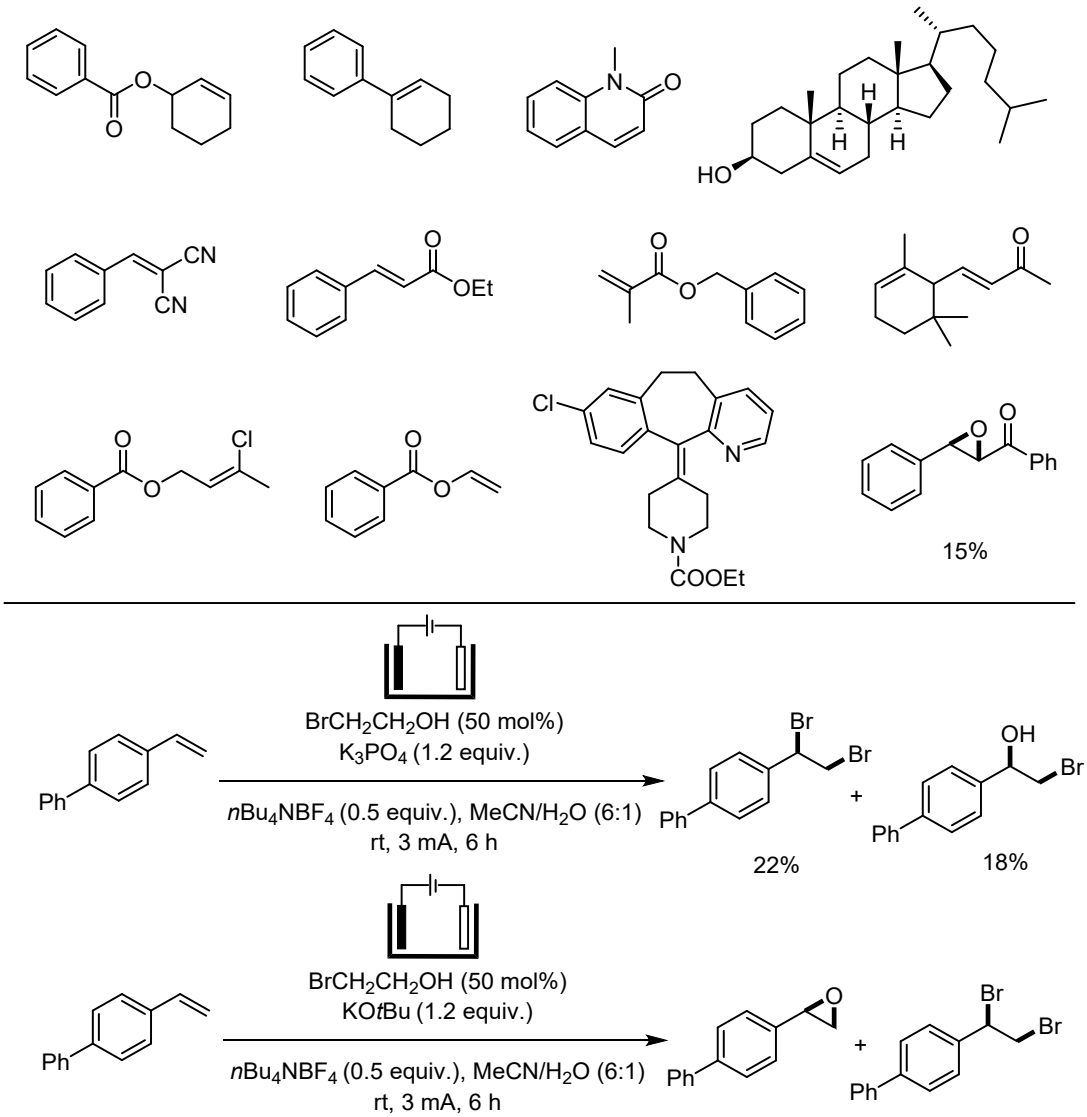


Figure S5. Cyclic voltammogram of (3,3-dimethyloxiran-2-yl)methyl benzoate (**2**, 10 mM) in an electrolyte of nBu$_4$NBF$_4$ (0.1 M) in MeCN (5 mL). $E_{p/2} \geq 2.17$ V.

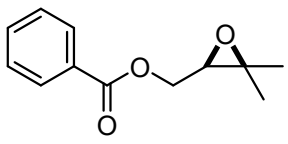
The cyclic voltammograms (CVs) of nBu$_4$NBr, alkene substrate **1** and epoxidation product **2** were tested in an electrolyte of nBu$_4$NBF$_4$ (0.1 M) in MeCN (5 mL). The oxidation potential of Br^- ($E_{p/2}$ = 0.77 V vs. Ag/AgCl) was significantly lower than that of the substrate **1** ($E_{p/2}$ = 2.10 V vs. Ag/AgCl) and product **2** ($E_{p/2} \geq 2.17$ V vs. Ag/AgCl) (Figure S3, Figure S4, and Figure S5,), indicating the anodic oxidation of Br^- were preferentially carried out. The cyclic voltammograms studies support our proposed mechanism.

4. Unsuccessful Substrates

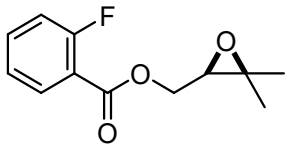


Scheme S1. Unsuccessful substrates in the reactions.

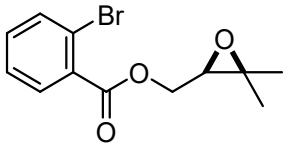
5. Characterization Data for the Electrolysis Products



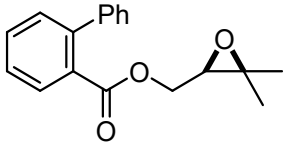
(3,3-Dimethyloxiran-2-yl)methyl benzoate (2).[2] Yellow oil (34.1 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–8.02 (m, 2H), 7.60–7.53 (m, 1H), 7.48–7.39 (m, 2H), 4.58 (dd, J = 12.1, 4.3 Hz, 1H), 4.27 (dd, J = 12.1, 6.7 Hz, 1H), 3.13 (dd, J = 6.7, 4.3 Hz, 1H), 1.37 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 133.3, 129.9 (2C), 128.5, 64.1, 60.7, 58.4, 24.7, 19.1.



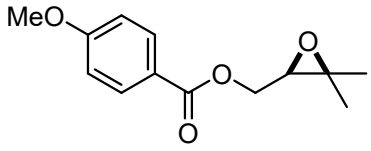
(3,3-Dimethyloxiran-2-yl)methyl 2-fluorobenzoate (3). Yellow oil (32.0 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.91 (m, 1H), 7.58–7.48 (m, 1H), 7.25–7.09 (m, 2H), 4.56 (dd, J = 12.1, 4.5 Hz, 1H), 4.31 (dd, J = 12.1, 6.7 Hz, 1H), 3.13 (dd, J = 6.7, 4.5 Hz, 1H), 1.37 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3 (d, $J_{C–F}$ = 3.7 Hz), 162.2 (d, $J_{C–F}$ = 260.9 Hz), 134.9 (d, $J_{C–F}$ = 8.9 Hz), 132.3, 124.1 (d, $J_{C–F}$ = 3.7 Hz), 118.4 (d, $J_{C–F}$ = 9.5 Hz), 117.2 (d, $J_{C–F}$ = 22.1 Hz), 64.3, 60.5, 58.5, 24.7, 19.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ −109.1; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{12}H_{14}FO_3^+$: 225.0921, Found: 225.0926.



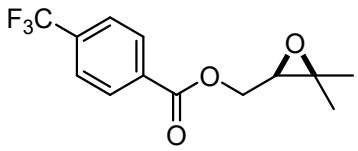
(3,3-Dimethyloxiran-2-yl)methyl 2-bromobenzoate (4). Yellow oil (48.4 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.80 (m, 1H), 7.69–7.63 (m, 1H), 7.41–7.28 (m, 2H), 4.57 (dd, J = 12.1, 4.5 Hz, 1H), 4.30 (dd, J = 12.1, 6.8 Hz, 1H), 3.14 (dd, J = 6.8, 4.5 Hz, 1H), 1.37 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 134.5, 132.9, 131.8, 131.6, 127.3, 121.9, 64.6, 60.4, 58.4, 24.7, 19.1; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{12}H_{14}BrO_3^+$: 285.0121, Found: 285.0120.



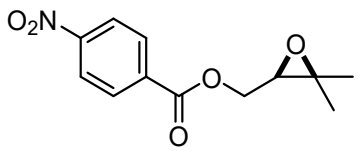
(3,3-Dimethyloxiran-2-yl)methyl [1,1'-biphenyl]-2-carboxylate (5). Yellow oil (35.6 mg, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.83 (m, 1H), 7.58–7.52 (m, 1H), 7.46–7.30 (m, 7H), 4.19–4.07 (m, 2H), 2.60 (t, J = 5.6 Hz, 1H), 1.26 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 142.8, 141.7, 131.6, 130.9, 130.6, 130.1, 128.5, 128.2, 127.4, 63.8, 60.1, 58.2, 24.6, 18.9; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{18}H_{19}O_3^+$: 283.1329, Found: 283.1334.



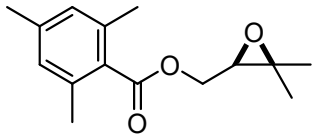
(3,3-Dimethyloxiran-2-yl)methyl 4-methoxybenzoate (6). Yellow oil (26.6 mg, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–7.98 (m, 2H), 6.97–6.86 (m, 2H), 4.57 (dd, J = 12.1, 4.3 Hz, 1H), 4.23 (dd, J = 12.1, 6.8 Hz, 1H), 3.86 (s, 3H), 3.13 (dd, J = 6.8, 4.3 Hz, 1H), 1.38 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 163.7, 132.0, 122.3, 113.8, 63.9, 60.9, 58.4, 55.6, 24.8, 19.2; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{13}H_{17}O_4^+$: 237.1121, Found: 237.1125.



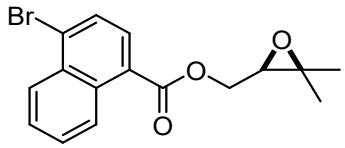
(3,3-Dimethyloxiran-2-yl)methyl 4-(trifluoromethyl)benzoate (7). White solid (37.7 mg, 69% yield); m.p. = 83.4−85.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24–8.14 (m, 2H), 7.77–7.67 (m, 2H), 4.64 (dd, J = 12.1, 4.0 Hz, 1H), 4.29 (dd, J = 12.1, 7.0 Hz, 1H), 3.15 (dd, J = 7.0, 4.0 Hz, 1H), 1.39 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 134.8 (q, $J_{C–F}$ = 32.8 Hz), 133.1, 130.3, 125.6 (q, $J_{C–F}$ = 3.7 Hz), 123.7 (q, $J_{C–F}$ = 272.9 Hz), 64.7, 60.5, 58.5, 24.7, 19.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ −63.1; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{14}H_{14}F_3O_3^+$: 275.0890, Found: 275.0888.



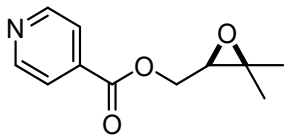
(3,3-Dimethyloxiran-2-yl)methyl 4-nitrobenzoate (8).[3] The title compound was obtained by eluting with ethyl acetate/petroleum ether (1:5) as a yellow oil (32.2 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.15 (m, 2H), 7.74–7.69 (m, 2H), 4.64 (dd, J = 12.1, 4.1 Hz, 1H), 4.29 (dd, J = 12.1, 7.0 Hz, 1H), 3.14 (dd, J = 7.0, 4.0 Hz, 1H), 1.39 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 150.8, 135.2, 131.1, 123.8, 65.1, 60.4, 58.5, 24.8, 19.2.



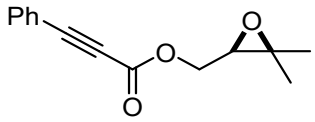
(3,3-Dimethyloxiran-2-yl)methyl 2,4,6-trimethylbenzoate (9). Yellow oil (27.1 mg, 54% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 2H), 4.50 (dd, J = 12.0, 4.9 Hz, 1H), 4.34 (dd, J = 12.0, 6.6 Hz, 1H), 3.11 (dd, J = 6.6, 4.9 Hz, 1H), 2.32 (s, 6H), 2.29 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 139.7, 135.4, 130.5, 128.6, 63.8, 60.5, 58.4, 24.7, 21.3, 20.0, 19.0; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{15}H_{21}O_3^+$: 249.1485, Found: 249.1488.



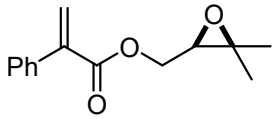
(3,3-Dimethyloxiran-2-yl)methyl 4-bromo-2-naphthoate (10). White solid (37.7 mg, 56% yield); m.p. = 77.7–78.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00–8.92 (m, 1H), 8.38–8.30 (m, 1H), 8.06 (d, J = 7.9 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.71–7.62 (m, 2H), 4.68 (dd, J = 12.1, 4.2 Hz, 1H), 4.36 (dd, J = 12.1, 6.9 Hz, 1H), 3.20 (dd, J = 6.9, 4.2 Hz, 1H), 1.42 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 132.6, 132.4, 130.6, 129.4, 129.1, 128.8, 128.0, 127.9, 126.7, 126.3, 64.5, 60.7, 58.5, 24.8, 19.2; HRMS (ESI) ([M + Na]$^+$) Calcd. for $C_{16}H_{15}BrNaO_2^+$: 341.0148, Found: 341.0152.



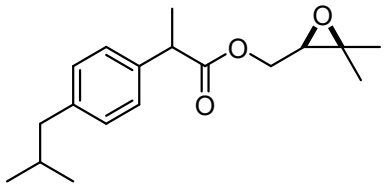
(3,3-Dimethyloxiran-2-yl)methyl isonicotinate (11). Yellow oil (30.0 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81–8.74 (m, 2H), 7.91–7.83 (m, 2H), 4.62 (dd, J = 12.1, 4.1 Hz, 1H), 4.29 (dd, J = 12.1, 7.0 Hz, 1H), 3.12 (dd, J = 7.0, 4.1 Hz, 1H), 1.37 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 150.8, 137.1, 123.1, 65.0, 60.4, 58.5, 24.7, 19.2; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{11}H_{14}NO_3^+$: 208.0968, Found: 208.0968.



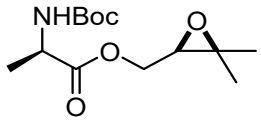
(3,3-Dimethyloxiran-2-yl)methyl 3-phenylpropiolate (12). Yellow oil (21.0 mg, 46% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.58 (m, 2H), 7.50–7.44 (m, 1H), 7.42–7.36 (m, 2H), 4.71 (dd, J = 12.2, 4.1 Hz, 1H), 4.52 (dd, J = 12.2, 8.4 Hz, 1H), 4.25 (dd, J = 8.4, 4.1 Hz, 1H), 1.44 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 133.3, 131.1, 128.8, 119.5, 87.7, 80.3, 71.8, 67.1, 62.6, 27.6, 27.0; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{14}H_{15}O_3^+$: 231.1016, Found: 231.1015.



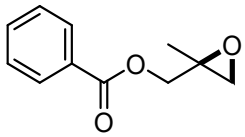
(3,3-Dimethyloxiran-2-yl)methyl 2-phenylacrylate (13). Colourless oil (31.7 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.40 (m, 2H), 7.39–7.33 (m, 3H), 6.42 (d, J = 1.1 Hz, 1H), 5.95 (d, J = 1.1 Hz, 1H), 4.49 (dd, J = 12.1, 4.2 Hz, 1H), 4.20 (dd, J = 12.1, 6.8 Hz, 1H), 3.07 (dd, J = 6.8, 4.2 Hz, 1H), 1.36 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 141.0, 136.6, 128.4 (2C), 128.3, 127.6, 64.2, 60.6, 58.4, 24.7, 19.1; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{14}H_{17}O_3^+$: 233.1172, Found: 233.1170.



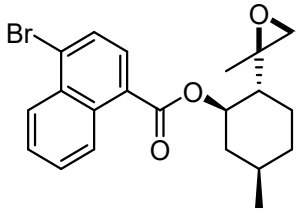
3,3-Dimethyloxiran-2-yl)methyl 2-(4-isobutylphenyl)propanoate (14). Yellow oil (33.0 mg, 57% yield, dr = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.18 (m, 2H), 7.13–7.06 (m, 2H), 4.35–4.23 (m, 1H), 4.10–4.00 (m, 1H), 3.79–3.70 (m, 1H), 3.04–2.83 (m, 1H), 2.44 (d, J = 7.2 Hz, 2H), 1.90–1.75 (m, 1H), 1.53–1.48 (m, 3H), 1.30 (s, 3H), 1.25 (d, J = 1.8 Hz, 3H), 0.90 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 140.8, 137.6, 129.5, 127.3, 63.8, 60.5, 58.3, 45.2, 45.1, 30.3, 24.7, 22.5, 19.0, 18.7, 18.6; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{18}H_{27}O_3^+$: 291.1955, Found: 291.1958.



3,3-Dimethyloxiran-2-yl)methyl (*tert*-butoxycarbonyl)-*D*-alaninate (15). The title compound was obtained by eluting with ethyl acetate/petroleum ether (1:3) as a yellow oil (27.5 mg, 51% yield, dr = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.05 (s, 1H), 4.42–4.33 (m, 1H), 4.14–4.04 (m, 1H), 3.03–2.93 (m, 1H), 1.79–1.72 (m, 1H), 1.43 (s, 9H), 1.40 (d, J = 7.2 Hz, 3H), 1.34 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 155.2, 80.1, 64.3, 60.4, 60.3, 58.4, 49.4, 28.4, 24.6, 19.1, 19.0, 18.7; HRMS (ESI) ([M + Na]$^{+}$) Calcd. For $C_{13}H_{23}NNaO_4^{+}$: 280.1519, Found: 280.1516.

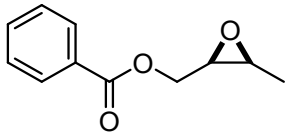


(2-Methyloxiran-2-yl)methyl benzoate (16).[4] Yellow oil (28.4 mg, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.03 (m, 2H), 7.60–7.54 (m, 1H), 7.48–7.42 (m, 2H), 4.49 (d, J = 12.0 Hz, 1H), 4.20 (d, J = 12.0 Hz, 1H), 2.86 (d, J = 4.7 Hz, 1H), 2.72 (d, J = 4.7 Hz, 1H), 1.47 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 133.4, 129.9, 128.6, 67.8, 55.1, 52.1, 18.7.

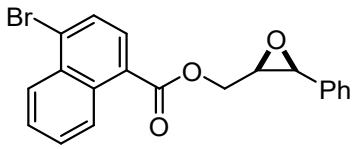


(*1R,2R,5R*)-5-Methyl-2-(2-methyloxiran-2-yl)cyclohexyl 4-bromo-1-naphthoate (17). The title compound was obtained by eluting with ethyl acetate/petroleum ether (1:50) as a white solid (58.4 mg, 72% yield, dr > 19:1); m.p. = 120.6−122.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00–8.90 (m, 1H), 8.37–8.27 (m, 1H), 8.22 (d, J = 7.9 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.70–7.58 (m, 2H), 5.23–5.12 (m, 1H), 2.55 (s, 2H), 2.31–2.21 (m, 1H), 1.89–1.62 (m, 3H), 1.48–1.37 (m, 2H), 1.30 (s, 3H), 1.17 (q, J = 11.9 Hz, 1H), 1.04–0.92 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 132.6, 132.3, 130.4, 129.4, 128.6, 128.4, 127.8 (2C), 127.6, 126.3,

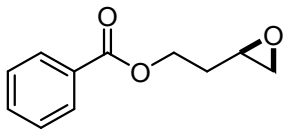
74.3, 58.1, 52.3, 49.3, 40.5, 33.9, 31.4, 28.3, 22.0, 17.4; HRMS (ESI) ([M + Na]$^+$) Calcd. for $C_{21}H_{23}BrNaO_3^+$: 425.0723, Found: 425.0732.



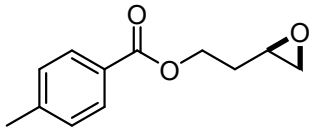
3-Methyloxiran-2-yl)methyl benzoate (18).[5] Yellow oil (20.0 mg, 52% yield, dr = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–8.02 (m, 2H), 7.61–7.54 (m, 1H), 7.50–7.40 (m, 2H), 4.61 (dd, J = 12.2, 3.2 Hz, 1H), 4.18 (dd, J = 12.2, 6.1 Hz, 1H), 3.11–2.97 (m, 2H), 1.37 (d, J = 5.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 133.3, 129.9, 129.8, 128.5, 65.2, 56.5, 52.7, 17.4.



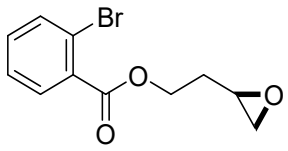
3-Phenyloxiran-2-yl)methyl 4-bromo-1-naphthoate (19). Colourless oil (41.0 mg, 54% yield, dr > 19:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01–8.93 (m, 1H), 8.38–8.32 (m, 1H), 8.08 (d, J = 7.9 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.73–7.62 (m, 2H), 7.42–7.28 (m, 5H), 4.84 (dd, J = 12.2, 3.2 Hz, 1H), 4.43 (dd, J = 12.2, 5.9 Hz, 1H), 3.94 (d, J = 2.0 Hz, 1H), 3.50–3.42 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 136.2, 132.6, 132.3, 130.6, 129.4, 129.0, 128.8, 128.7 (2C), 127.9, 127.8, 126.4, 126.3, 125.8, 65.0, 59.5, 56.7; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{20}H_{16}BrO_3^+$: 383.0277, Found: 383.0273.



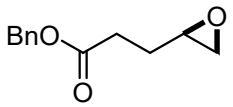
2-(Oxiran-2-yl)ethyl benzoate (20). Yellow oil (24.2 mg, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.00 (m, 2H), 7.61–7.52 (m, 1H), 7.49–7.40 (m, 2H), 4.53–4.43 (m, 2H), 3.16–3.06 (m, 1H), 2.86–2.78 (m, 1H), 2.60–2.52 (m, 1H), 2.15–1.92 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 133.2, 130.2, 129.7, 128.5, 62.0, 49.8, 47.0, 32.2; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{11}H_{13}O_3^+$: 193.0859, Found: 193.0852.



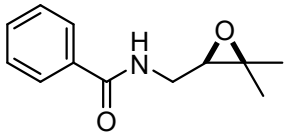
2-(Oxiran-2-yl)ethyl 4-methylbenzoate (21). Yellow oil (24.1 mg, 59% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 4.50–4.41 (m, 2H), 3.15–3.06 (m, 1H), 2.84–2.79 (m, 1H), 2.58–2.54 (m, 1H), 2.41 (s, 3H), 2.11–1.90 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 143.9, 129.8, 129.3, 127.5, 61.8, 49.8, 47.1, 32.2, 21.8; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{12}H_{15}O_3^+$: 207.1016, Found: 207.1013.



2-(Oxiran-2-yl)ethyl 2-bromobenzoate (22). Colourless oil (25.9 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.76 (m, 1H), 7.70–7.61 (m, 1H), 7.42–7.28 (m, 2H), 4.54–4.46 (m, 2H), 3.17–3.08 (m, 1H), 2.86–2.79 (m, 1H), 2.57 (dd, J = 4.9, 2.7 Hz, 1H), 2.15–2.02 (m, 1H), 2.02–1.88 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 134.5, 132.8, 132.2, 131.5, 127.4, 121.7, 62.7, 49.8, 47.1, 32.0; HRMS (ESI) ([M + Na]$^+$) Calcd. for $C_{11}H_{11}BrNaO_3^+$: 292.9784, Found: 292.9796.

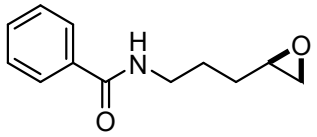


Benzyl-3-(oxiran-2-yl)propanoate (23).[6] Yellow oil (22.5 mg, 55% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.30 (m, 5H), 5.13 (s, 2H), 3.04–2.95 (m, 1H), 2.75 (t, J = 4.4 Hz, 1H), 2.56–2.46 (m, 3H), 2.07–1.93 (m, 1H), 1.87–1.73 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 136.0, 128.8, 128.5, 128.4, 66.6, 51.4, 47.2, 30.6, 27.8.

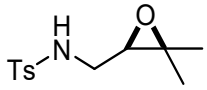


***N*-((3,3-Dimethyloxiran-2-yl)methyl)benzamide (24).**[7] Yellow oil (37.8 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.85 (m, 2H), 7.48–7.34 (m, 3H), 4.16 (dd, J = 9.5, 5.4 Hz,

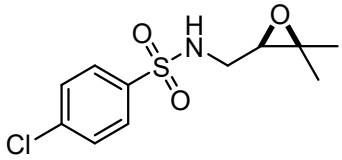
1H), 4.01 (dd, J = 17.5, 5.4 Hz, 1H), 3.84 (dd, J = 17.5, 9.5 Hz, 1H), 1.57 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 133.4, 130.9, 128.2, 127.3, 51.0, 50.1, 27.5, 22.3.



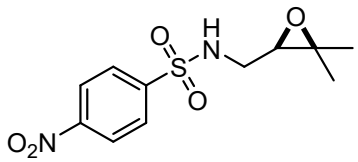
***N*-(3-(Oxiran-2-yl)propyl)benzamide (25).** Colorless oil (23.8 mg, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.73 (m, 2H), 7.55–7.40 (m, 3H), 6.22 (s, 1H), 4.33–4.14 (m, 1H), 3.91–3.83 (m, 1H), 3.63 (t, J = 10.1 Hz, 1H), 3.57–3.49 (m, 2H), 2.34–2.22 (m,1H), 1.98–1.73 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 134.7, 131.7, 128.8, 127.0, 52.3, 39.2, 36.2, 33.5, 27.3.



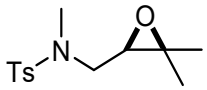
***N*-((3,3-Dimethyloxiran-2-yl)methyl)-4-methylbenzenesulfonamide (26).**[8] Colorless oil (30.7 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.29–5.14 (m, 1H), 3.28–3.16 (m, 1H), 3.03–2.91 (m, 1H), 2.88–2.80 (m, 1H), 2.41 (s, 3H), 1.24 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 136.9, 129.9, 127.2, 61.9, 59.2, 42.8, 24.6, 21.7, 18.8.



4-Chloro-*N*-((3,3-dimethyloxiran-2-yl)methyl)benzenesulfonamide (27). Yellow oil (28.4 mg, 52% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.72 (m, 2H), 7.47–7.40 (m, 2H), 5.21–5.09 (m, 1H), 3.30–3.18 (m, 1H), 2.95–2.84 (m, 1H), 2.83–2.75 (m, 1H), 1.21 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 138.5, 129.7, 128.7, 61.9, 59.4, 43.0, 24.6, 18.9; HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{11}H_{14}ClNNaO_3S^+$: 298.0275, Found: 298.0281.

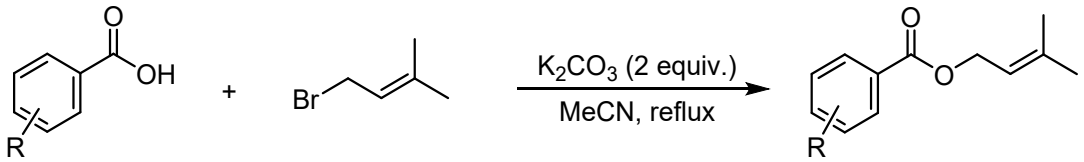


***N*-((3,3-Dimethyloxiran-2-yl)methyl)-4-nitrobenzenesulfonamide (28).** Colourless oil (23.5 mg, 41% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40–8.35 (m, 2H), 8.10–8.05 (m, 2H), 5.31–5.28 (m, 1H), 3.49–3.37 (m, 1H), 3.05–2.93 (m, 1H), 2.87 (dd, J = 7.6, 4.0 Hz, 1H), 1.29 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 146.0, 128.4, 124.6, 61.8, 59.5, 43.1, 24.6, 18.9; HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{11}H_{14}N_2NaO_5S^+$: 309.0516, Found: 309.0524.

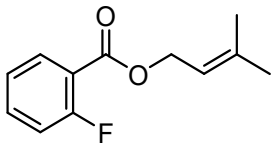


***N*-((3,3-Dimethyloxiran-2-yl)methyl)-*N*,4-dimethylbenzenesulfonamide (29).** Colourless oil (28.7 mg, 54% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.64 (m, 2H), 7.34–7.29 (m, 2H), 3.64–3.54 (m, 1H), 2.91–2.87 (m, 1H), 2.81 (s, 3H), 2.80–2.74 (m, 1H), 2.43 (s, 3H), 1.30 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 134.3, 129.9, 127.5, 62.0, 57.6, 49.8, 35.7, 24.6, 21.6, 18.9; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{13}H_{20}NO_3S^+$: 270.1158, Found: 270.1155.

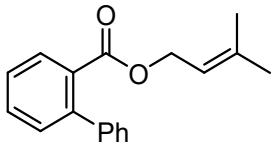
6. Synthesis and Characterization of Unknown Substrates



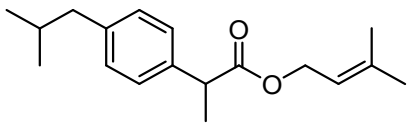
A round-bottom flask was charged with 1-bromo-3-methylbut-2-ene (5 mmol, 1 equiv.), carboxylic acid (6 mmol, 1.2 equiv.), K_2CO_3 (1.38 g, 10 mmol, 2 equiv.) and MeCN (25 mL). The solution was refluxed for 12 h. After the reaction was completed, H_2O (50 mL) was added and the resulting mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layers dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether (1:50) to afford product.



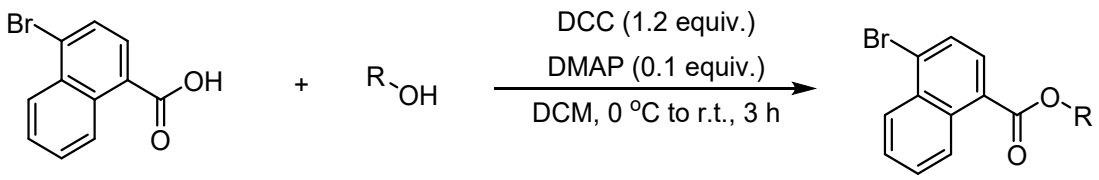
3-Methylbut-2-en-1-yl 2-fluorobenzoate (S1). Yellow oil (662 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.86 (m, 1H), 7.53–7.43 (m, 1H), 7.22–7.05 (m, 2H), 5.51–5.40 (m, 1H), 4.82 (d, J = 7.2 Hz, 2H), 1.77 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5 (d, $J_{C–F}$ = 3.6 Hz), 162.0 (d, $J_{C–F}$ = 259.7 Hz), 139.5, 134.4 (d, $J_{C–F}$ = 9.2 Hz), 132.1, 123.9 (d, $J_{C–F}$ = 3.8 Hz), 119.1 (d, $J_{C–F}$ = 9.7 Hz), 118.5, 117.0 (d, $J_{C–F}$ = 22.3 Hz), 62.3, 25.9, 18.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ −109.7; HRMS (ESI) ([M + Na]$^+$) Calcd. for $C_{12}H_{13}FNaO_2^+$: 231.0792, Found: 231.0799.



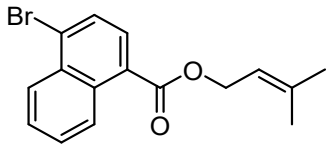
3-Methylbut-2-en-1-yl [1,1'-biphenyl]-2-carboxylate (S2). Yellow oil (950 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 7.7, 1.4 Hz, 1H), 7.57–7.48 (m, 1H), 7.44–7.32 (m, 7H), 5.13–5.02 (m, 1H), 4.58 (d, J = 7.3 Hz, 2H), 1.71 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 142.3, 141.4, 139.1, 131.5, 131.1, 130.6, 129.7, 128.5, 128.1, 127.2, 61.9, 25.8, 18.0; HRMS (ESI) ([M + H]$^+$) Calcd. for $C_{18}H_{19}O_2^+$: 267.1380, Found: 267.1375.



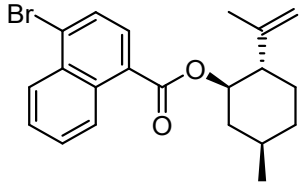
3-Methylbut-2-en-1-yl 2-(4-isobutylphenyl)acetate (S3). Yellow oil (1.24 g, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 8.1 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 5.37–5.27 (m, 1H), 4.67–4.50 (m, 2H), 3.71 (q, J = 7.2 Hz, 1H), 2.53–2.40 (m, 2H), 1.95–1.80 (m, 1H), 1.74 (s, 3H), 1.66 (s, 3H), 1.50 (d, J = 7.2 Hz, 3H), 0.92 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 140.4, 138.9, 138.0, 129.3, 127.2, 118.7, 61.7, 45.2, 45.1, 30.2, 25.7, 22.4, 18.7, 18.0; HRMS (ESI) ([M + Na]$^+$) Calcd. for $C_{18}H_{26}NaO_2^+$: 297.1825, Found: 297.1836.



The mixture of 4-bromo-1-naphthoic acid (5 mmol, 1 equiv.) in CH_2Cl_2 (30 mL) was added dicyclohexylcarbodiimide (DCC, 6 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 0.5 mmol, 0.1 equiv), then the corresponding enol (6 mmol, 1.2 equiv) was added dropwise at 0 ℃. The solution was warmed up to room temperature and stirred for 3 h. Then the mixture was filtered and washed with CH_2Cl_2 (3 × 50 mL) and concentrated. The residue was chromatographed through silica gel eluting with ethyl acetate/petroleum ether (1:50) to afford product.

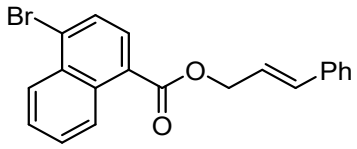


3-Methylbut-2-en-1-yl 4-bromo-1-naphthoate (S4). Yellow oil (1.03 g, 65 yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99–8.89 (m, 1H), 8.37–8.27 (m, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.70–7.59 (m, 2H), 5.60–5.48 (m, 1H), 4.91 (d, J = 7.2 Hz, 2H), 1.81 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 139.7, 132.5, 132.3, 130.1, 129.0, 128.7, 128.5, 127.8, 127.7, 127.6, 126.4, 118.6, 62.3, 26.0, 18.3; HRMS (ESI) ([M + Na]$^+$) Calcd. for $C_{16}H_{15}BrNaO_2^+$: 341.0148, Found: 341.0162



(1*R*,2*S*,5*R*)-5-methyl-2-(prop-1-en-2-yl)cyclohexyl 4-bromo-1-naphthoate (S5). Colourless oil (1.46 g, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90–8.83 (m, 1H), 8.35–8.28 (m, 1H), 7.91 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.68–7.57 (m, 2H), 5.23–5.12 (m, 1H), 4.90–4.79 (m, 2H), 2.41–2.21 (m, 2H), 1.84–1.78 (m, 1H), 1.77 (s, 3H), 1.74–1.66 (m, 1H), 1.58–1.43 (m, 1H), 1.28–1.14 (m, 1H), 1.11–0.99 (m, 1H), 0.99 (d, J = 6.5 Hz, 3H),

0.92–0.78 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 146.4, 132.4, 132.2, 129.8, 129.0, 128.3, 127.7, 127.6, 126.5, 112.3, 74.7, 51.2, 40.6, 34.2, 31.6, 30.7, 22.2, 19.5; HRMS (ESI) ($[M + H]^+$) Calcd. for $C_{21}H_{24}BrO_2^+$: 387.0954, Found: 387.0951.



Cinnamyl 4-bromo-1-naphthoate (S6). White solid (1.58 g, 86% yield); m.p.= 63.1−64.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04–8.94 (m, 1H), 8.39–8.31 (m, 1H), 8.06 (d, J = 7.9 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.72–7.62 (m, 2H), 7.49–7.41 (m, 2H), 7.39–7.32 (m, 2H), 7.32–7.27 (m, 1H), 6.80 (d, J = 15.7 Hz, 1H), 6.53–6.41 (m, 1H), 5.08 (dd, J = 6.5, 1.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 136.3, 134.8, 132.6, 132.3, 130.3, 129.0, 128.8, 128.7, 128.3, 127.8 (2C), 127.1, 126.8, 126.4, 123.1, 66.0; HRMS (ESI) ($[M + Na]^+$) Calcd. for $C_{20}H_{15}BrNaO_2^+$: 389.0148, Found: 389.0161.

7. References

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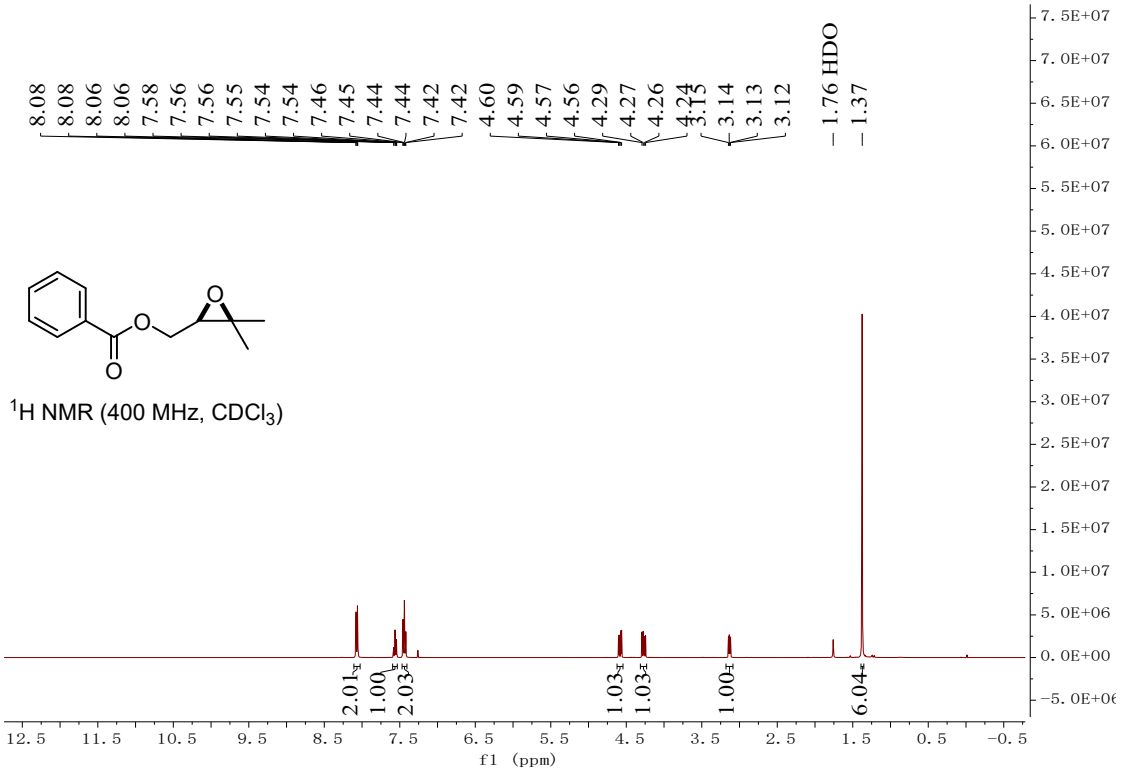
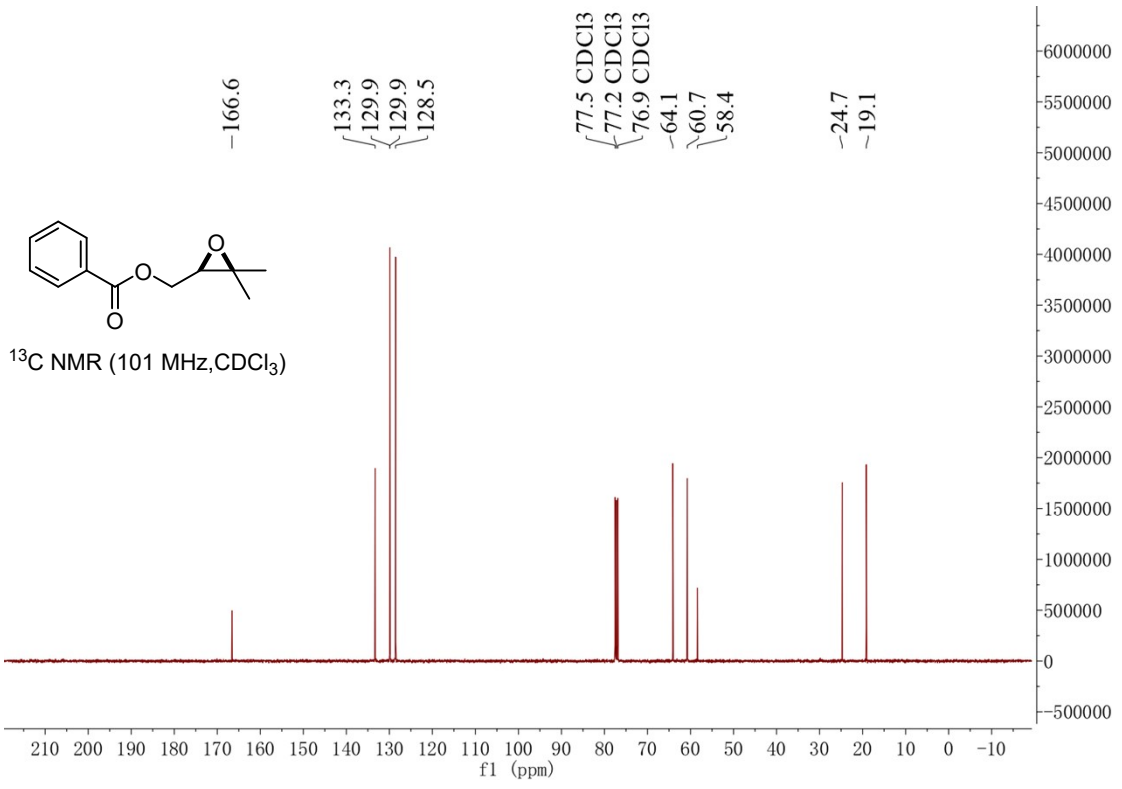
8. NMR Spectra of the Products

Compound 2

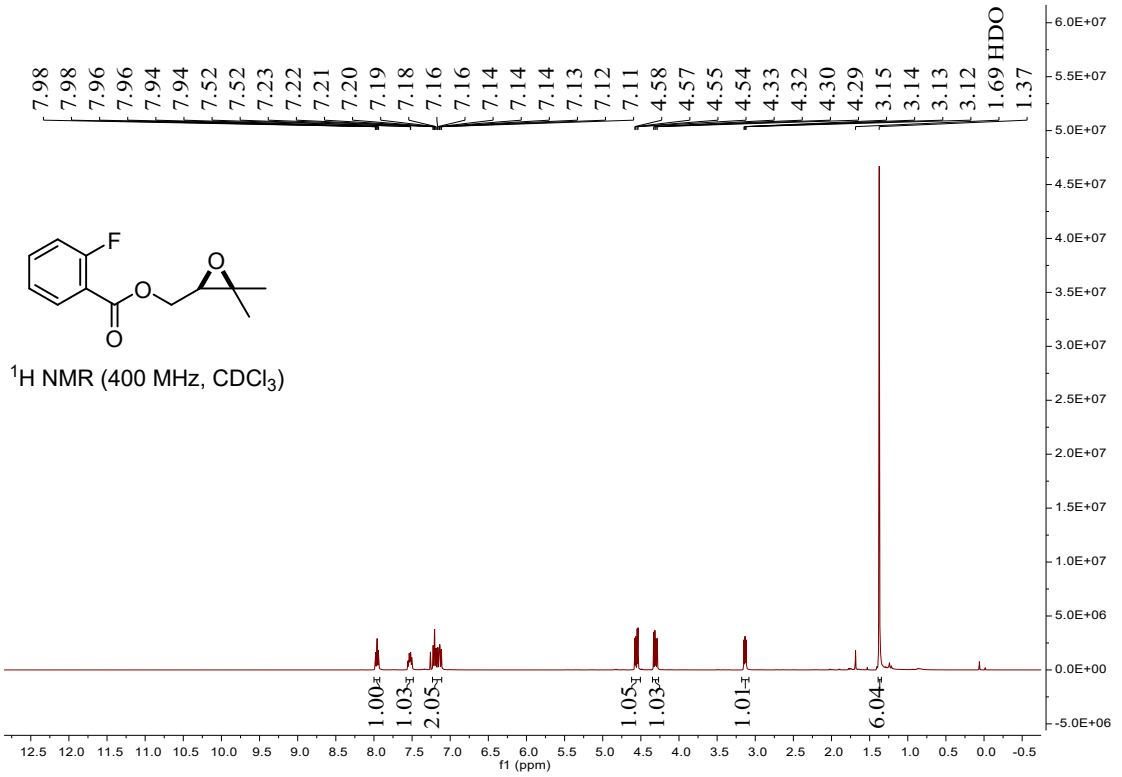


^{1}H NMR (400 MHz, $CDCl_3$)

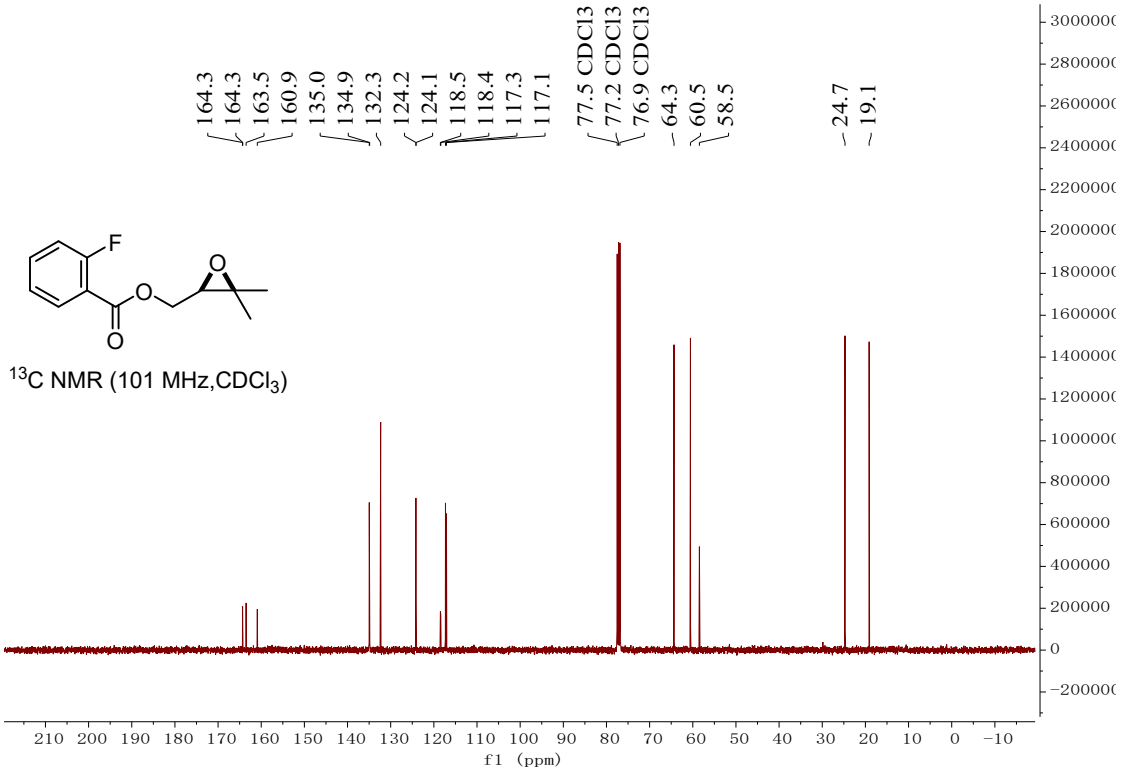


^{13}C NMR (101 MHz,$CDCl_3$)

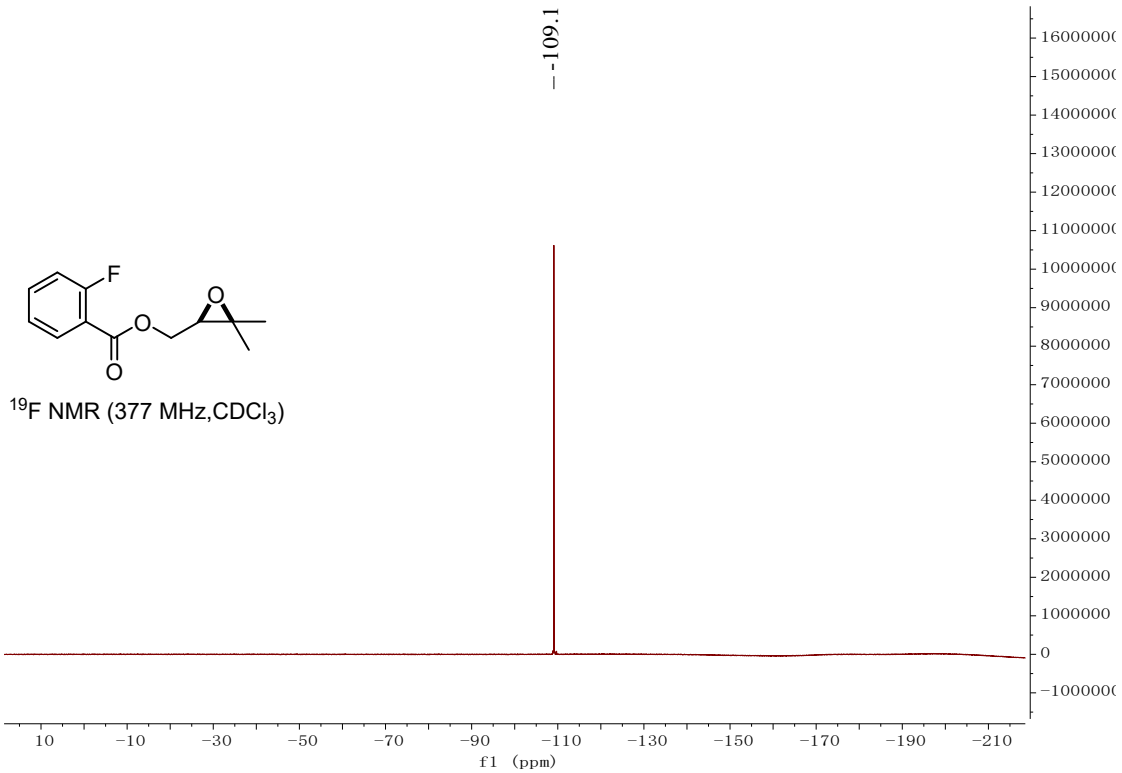
Compound 3



^{1}H NMR (400 MHz, $CDCl_3$)

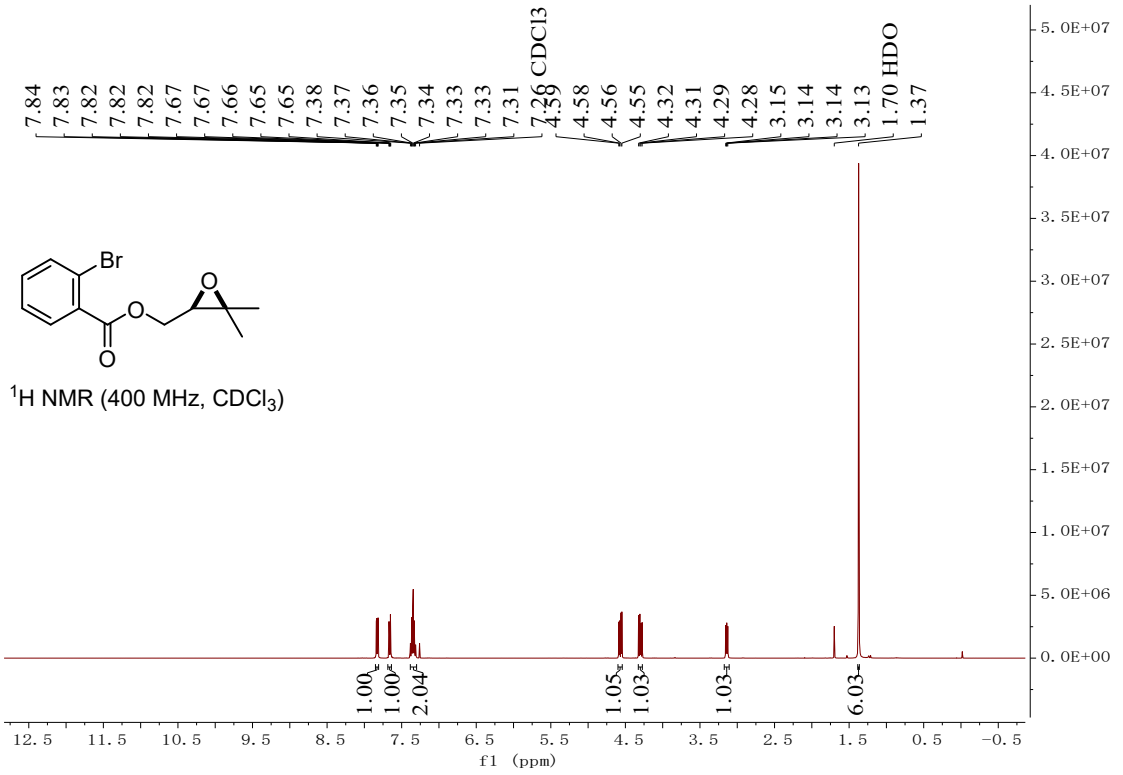


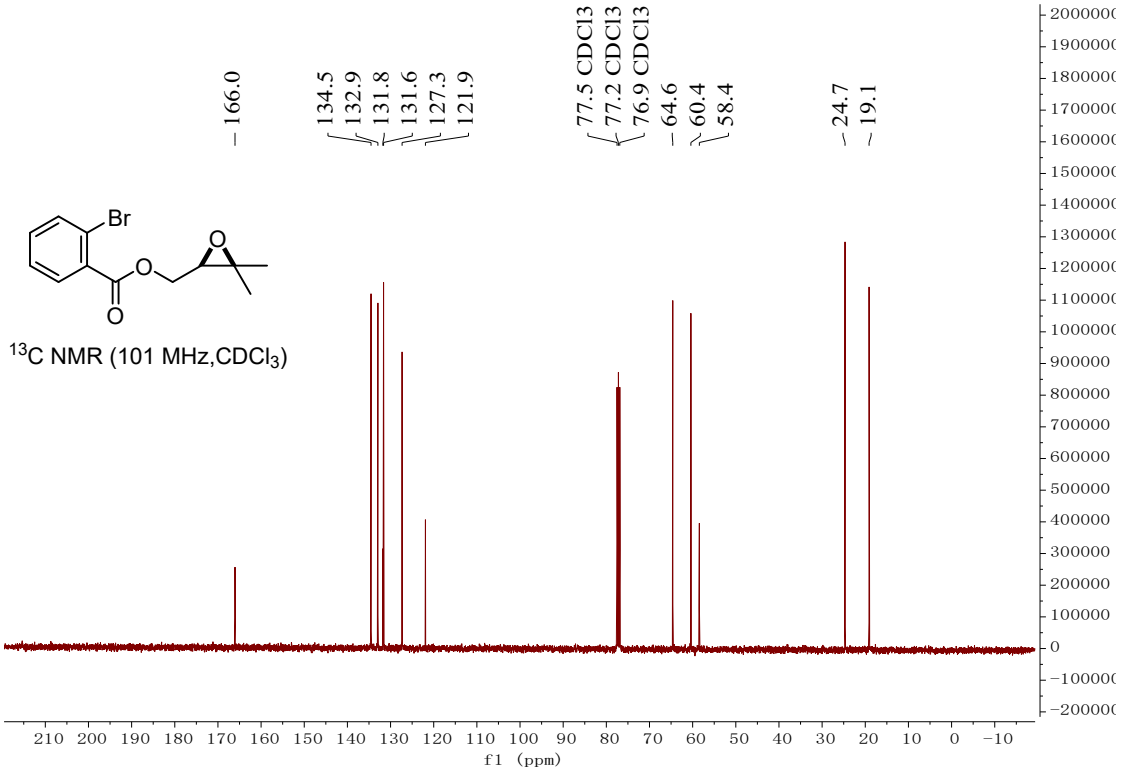
^{13}C NMR (101 MHz,$CDCl_3$)



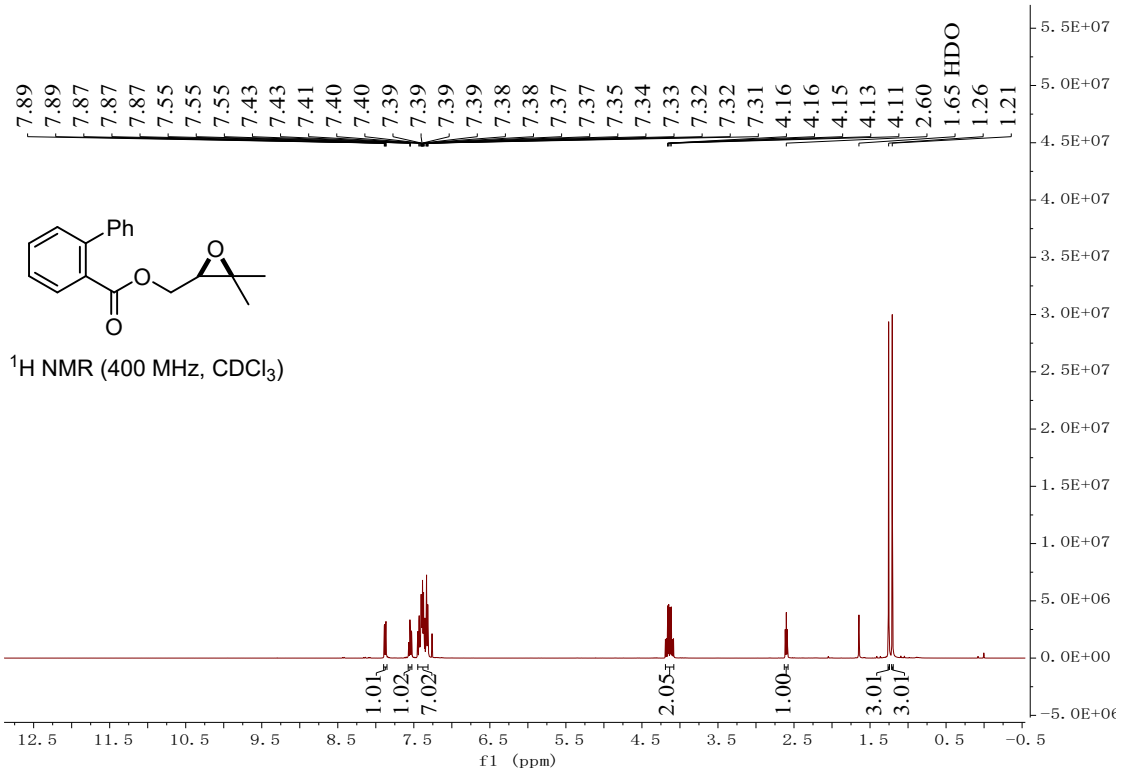
^{19}F NMR (377 MHz,$CDCl_3$)

Compound 4

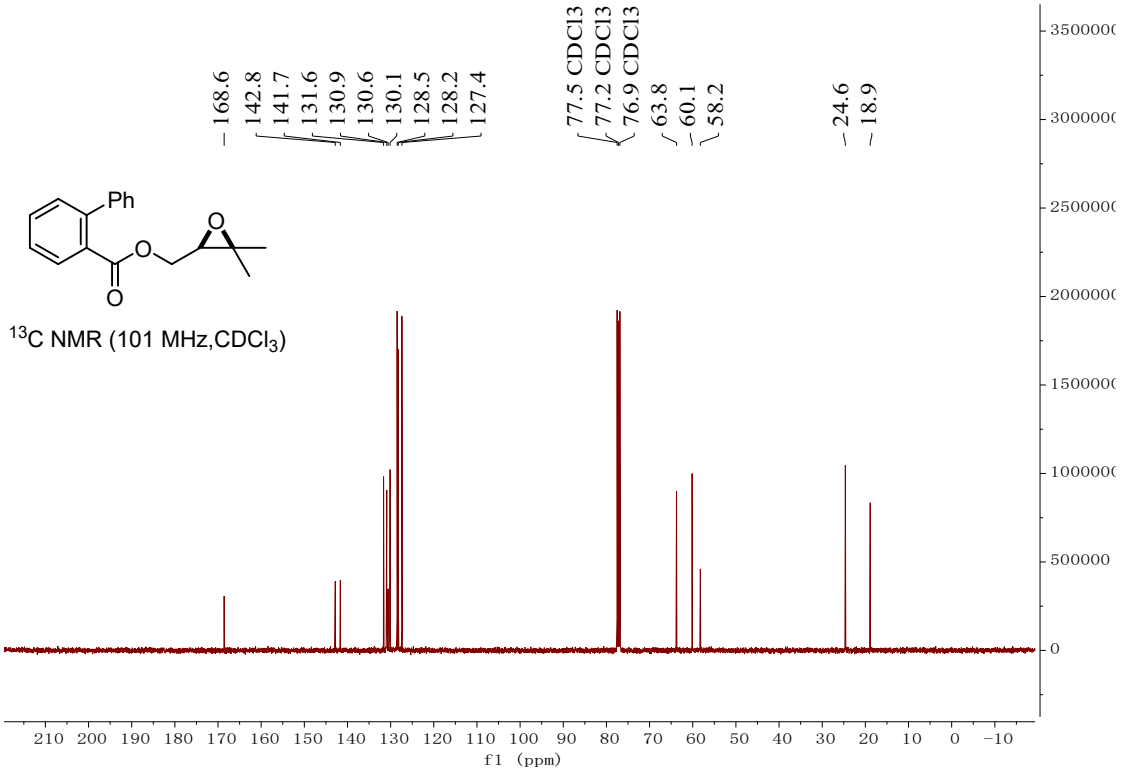

7.84
7.83
7.82
7.82
7.82
7.67
7.67
7.66
7.65
7.65
7.38
7.37
7.36
7.35
7.34
7.33
7.33
7.31
7.26 CDCl3
4.59
4.58
4.56
4.55
4.32
4.31
4.29
4.28
3.15
3.14
3.14
3.13
1.70 HDO
1.37
Br
O
O
O
1H NMR (400 MHz, CDCl3)
1.00
1.00
2.04
1.05
1.03
1.03
6.03
f1 (ppm)


166.0
134.5
132.9
131.8
131.6
127.3
121.9
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
64.6
60.4
58.4
24.7
19.1
Br
O
O
O
13C NMR (101 MHz,CDCl3)
f1 (ppm)

Compound 5

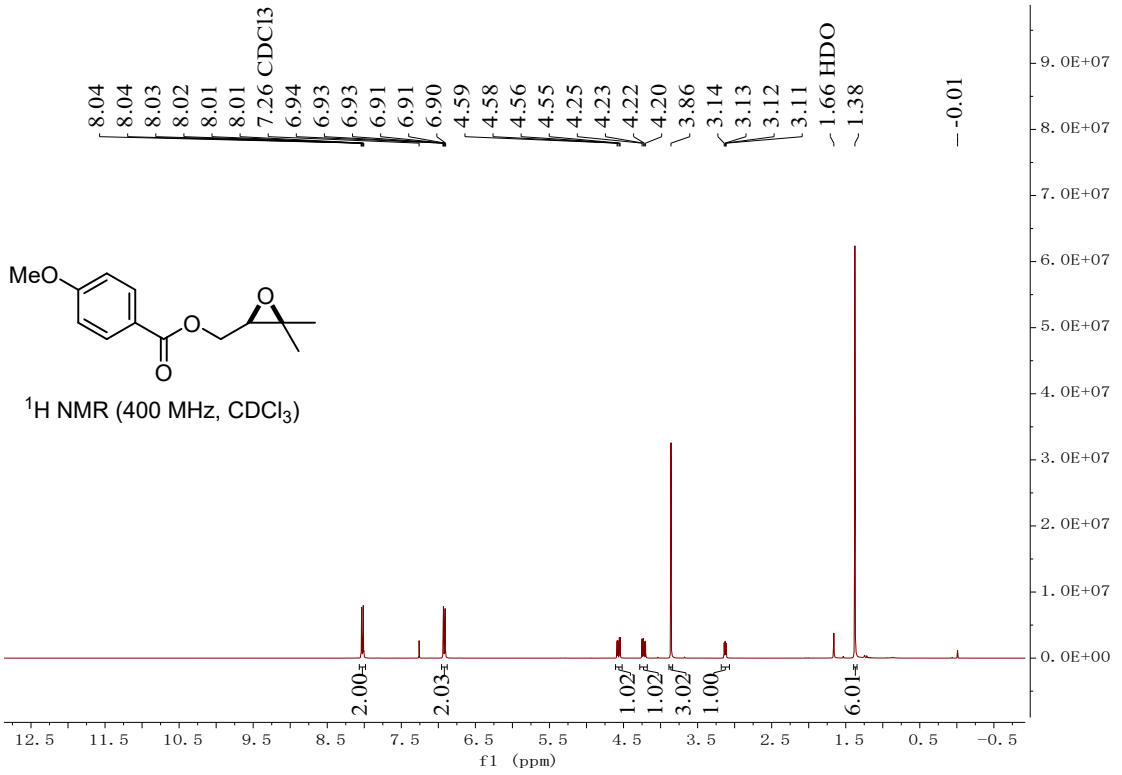


^{1}H NMR (400 MHz, $CDCl_3$)

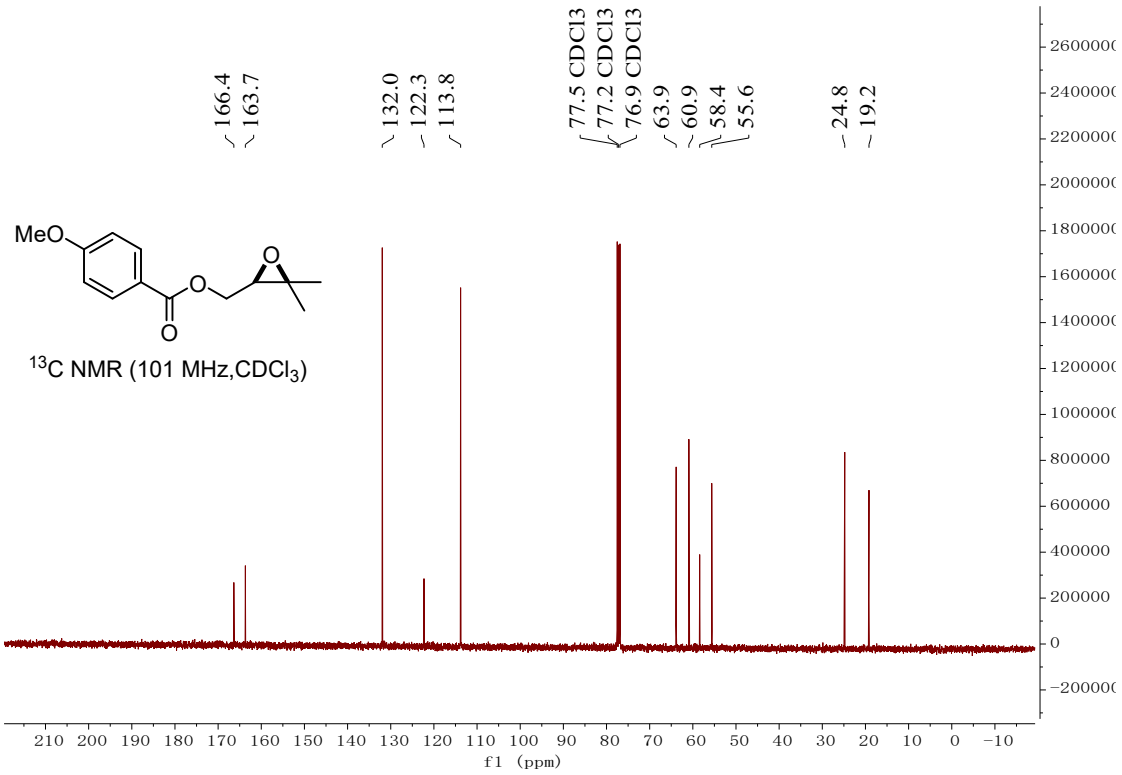


^{13}C NMR (101 MHz,$CDCl_3$)

Compound 6

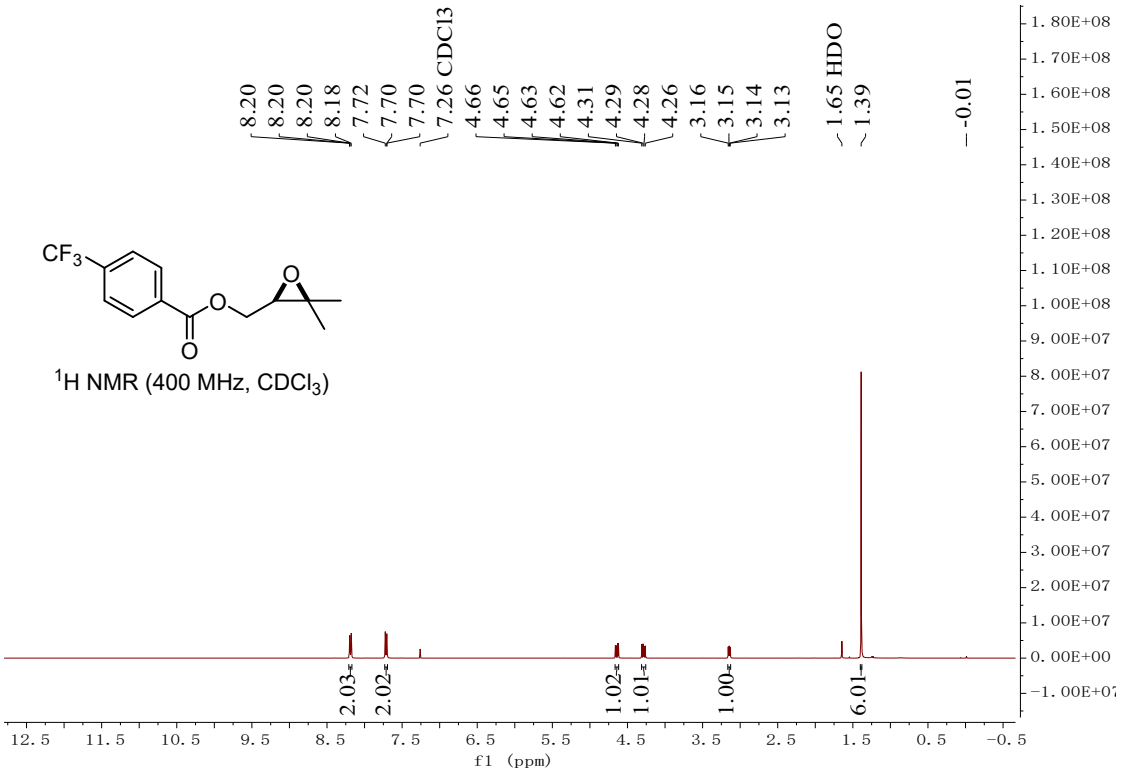


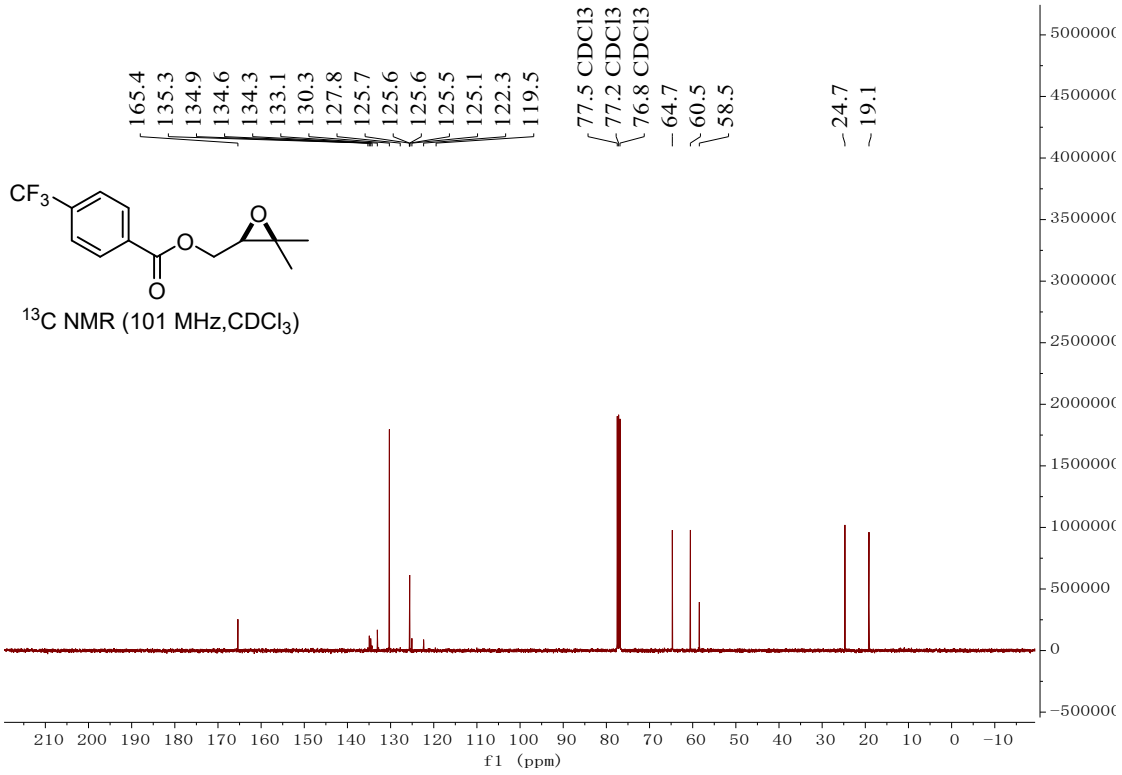
^{1}H NMR (400 MHz, $CDCl_3$)

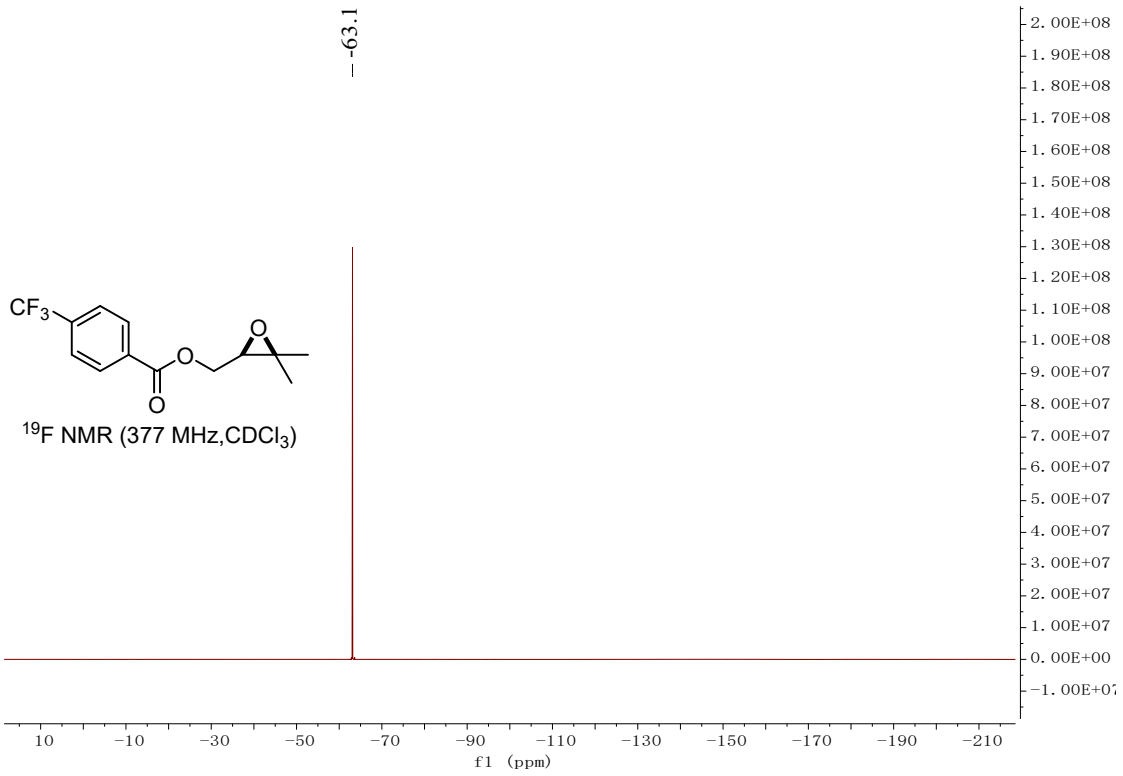


^{13}C NMR (101 MHz,$CDCl_3$)

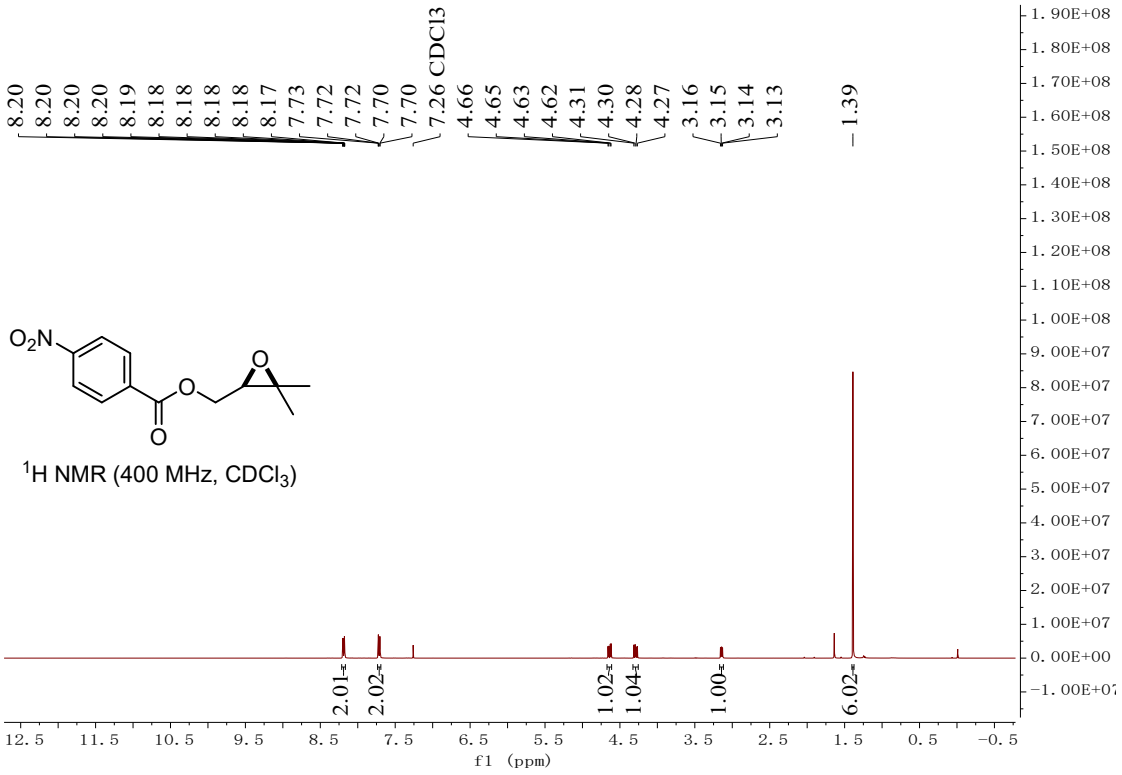
Compound 7

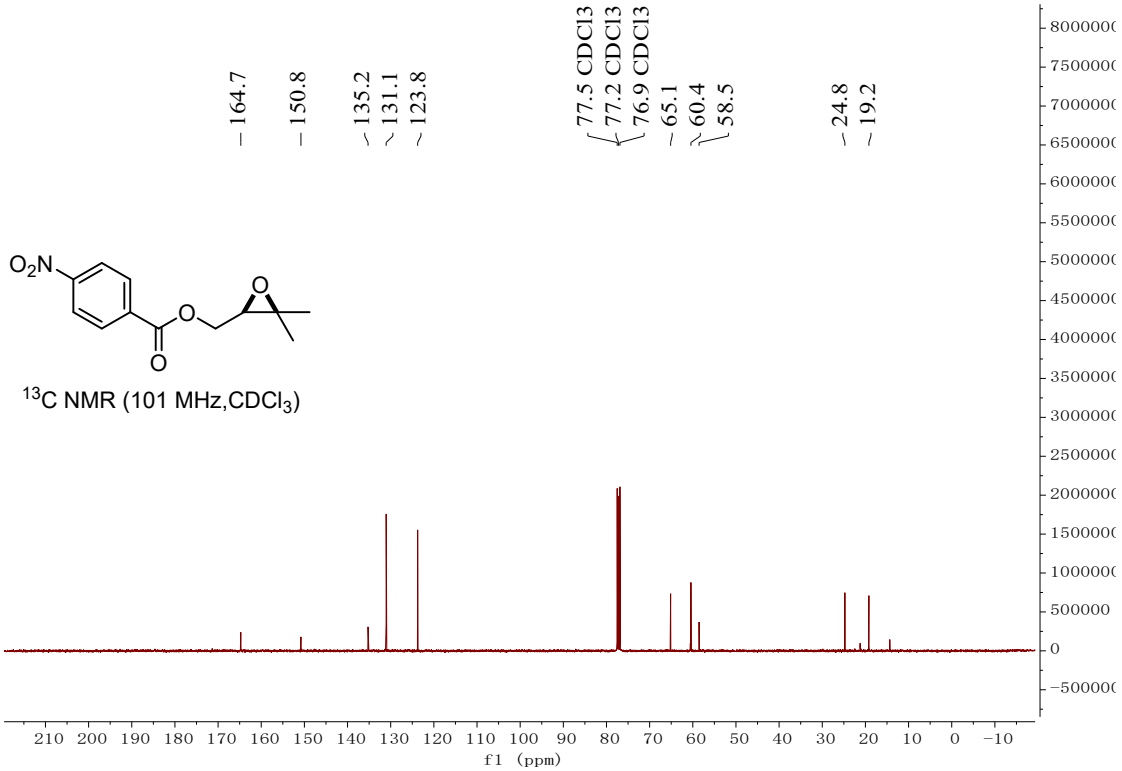

8.20
8.20
8.20
8.18
7.72
7.70
7.70
7.26 CDCl3
4.66
4.65
4.63
4.62
4.31
4.29
4.28
4.26
3.16
3.15
3.14
3.13
1.65 HDO
1.39
-0.01
CF3
O
O
O
1H NMR (400 MHz, CDCl3)
2.03
2.02
1.02
1.01
1.00
6.01
f1 (ppm)


165.4
135.3
134.9
134.6
134.3
133.1
130.3
127.8
125.7
125.6
125.6
125.5
125.1
122.3
119.5
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
64.7
60.5
58.5
24.7
19.1
CF3
O
O
O
13C NMR (101 MHz,CDCl3)
f1 (ppm)

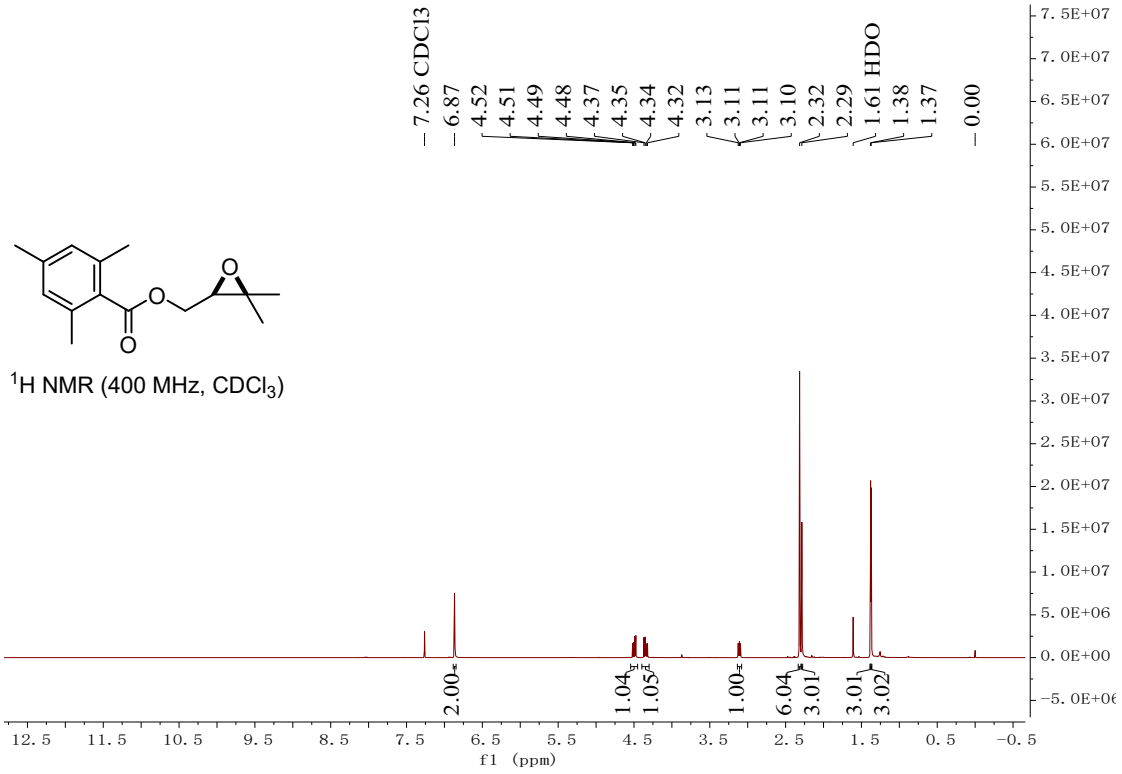

-63.1
CF3
O
O
O
19F NMR (377 MHz,CDCl3)
2.00E+08
1.90E+08
1.80E+08
1.70E+08
1.60E+08
1.50E+08
1.40E+08
1.30E+08
1.20E+08
1.10E+08
1.00E+08
9.00E+07
8.00E+07
7.00E+07
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
-1.00E+07
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

Compound 8

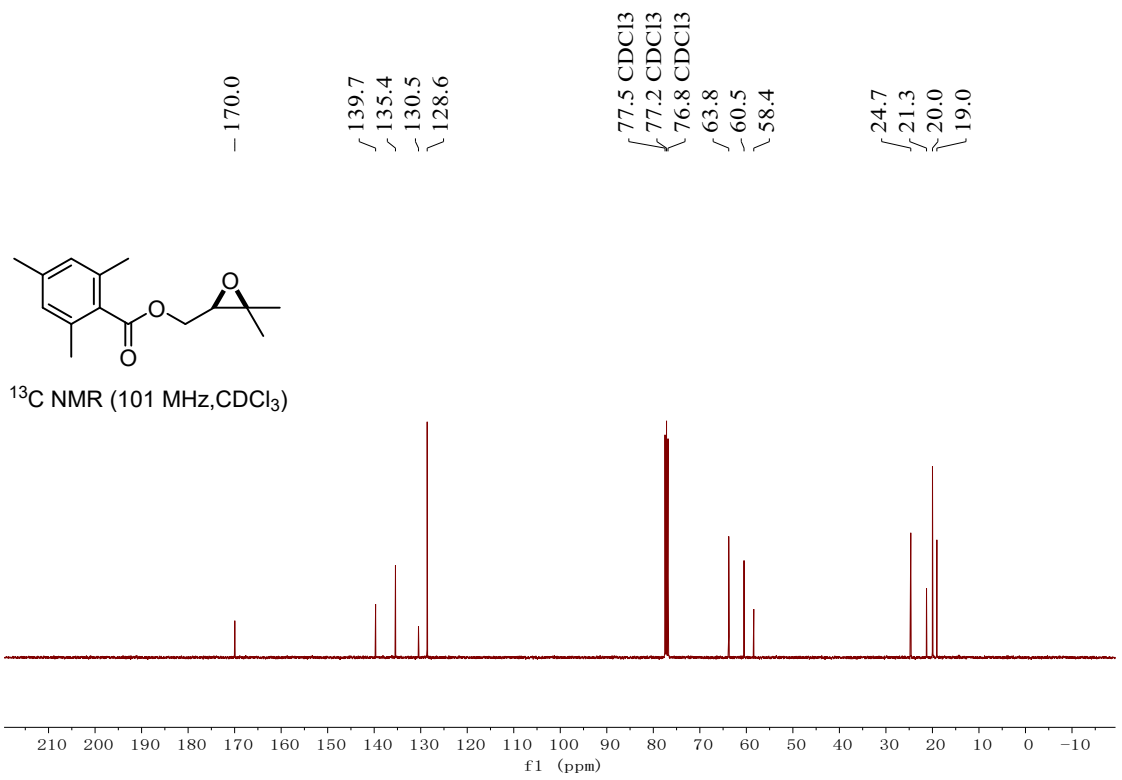

8.20
8.20
8.20
8.20
8.19
8.18
8.18
8.18
8.18
8.17
7.73
7.72
7.72
7.70
7.70
7.26 CDCl3
4.66
4.65
4.63
4.62
4.31
4.30
4.28
4.27
3.16
3.15
3.14
3.13
1.39
O2N
O
O
O
1H NMR (400 MHz, CDCl3)
2.01
2.02
1.02
1.04
1.00
6.02
f1 (ppm)


164.7
150.8
135.2
131.1
123.8
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
65.1
60.4
58.5
24.8
19.2
O2N
O
O
O
13C NMR (101 MHz,CDCl3)
f1 (ppm)

Compound 9

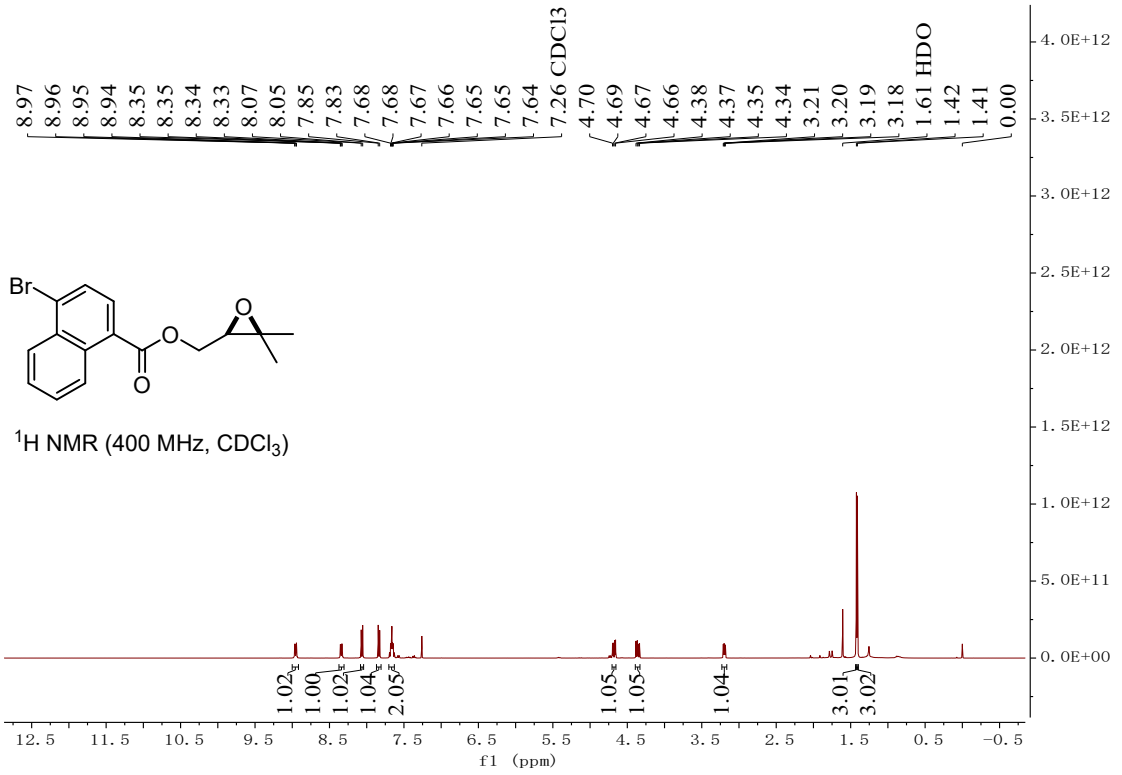


^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz,$CDCl_3$)

Compound 10


8.97
8.96
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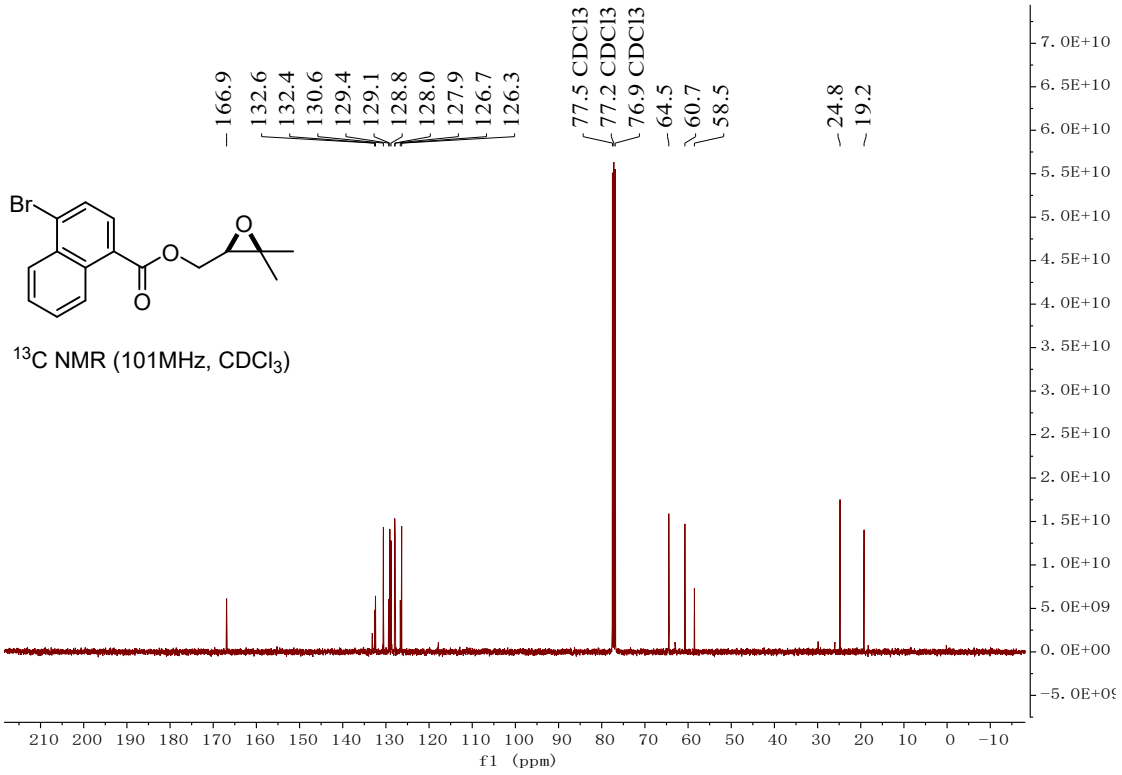
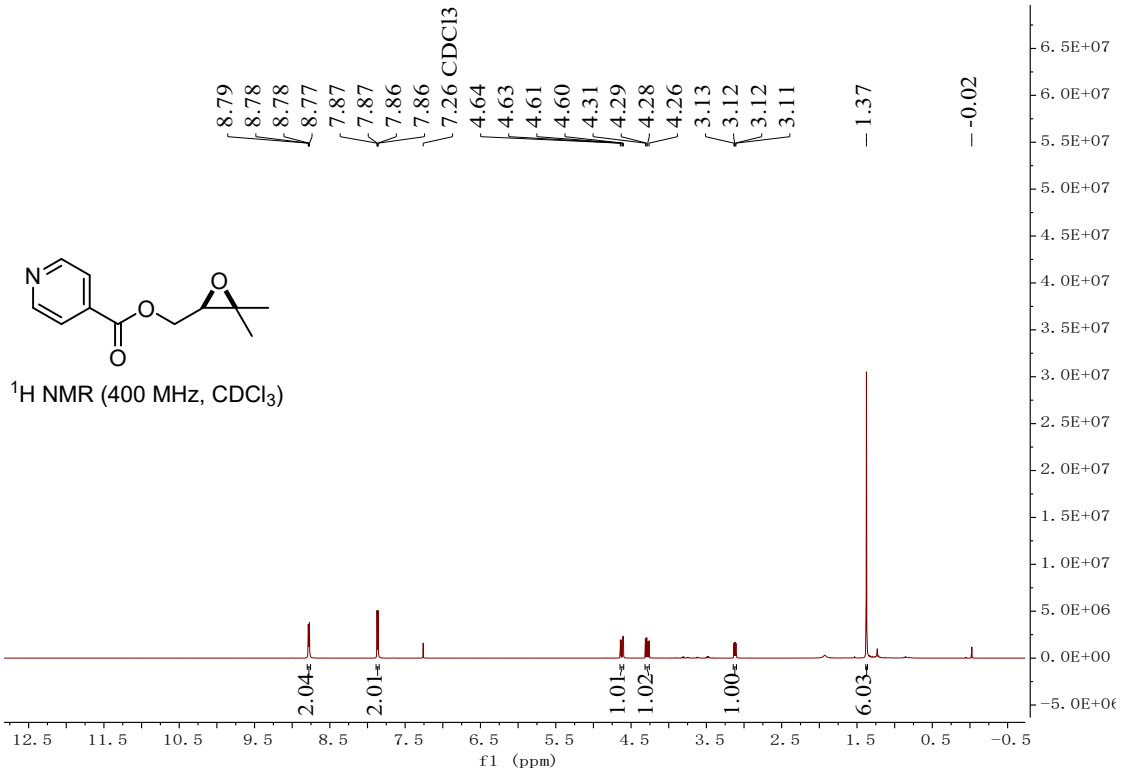
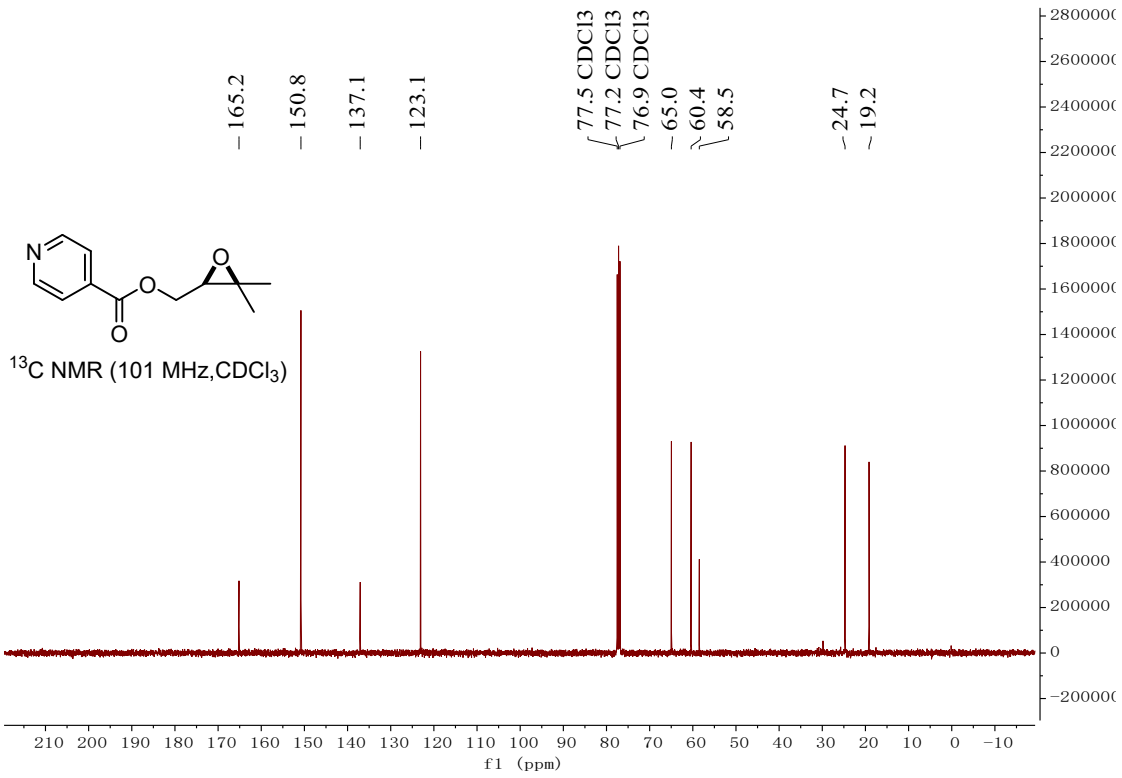
8.35
8.34
8.33
8.07
8.05
7.85
7.83
7.68
7.68
7.67
7.66
7.65
7.65
7.64
7.26 CDCl3
4.70
4.69
4.67
4.66
4.38
4.37
4.35
4.34
3.21
3.20
3.19
3.18
1.61 HDO
1.42
1.41
0.00
Br
O
O
O
1H NMR (400 MHz, CDCl3)
1.02
1.00
1.02
1.04
2.05
1.05
1.05
1.04
3.01
3.02
f1 (ppm)


166.9
132.6
132.4
130.6
129.4
129.1
128.8
128.0
127.9
126.7
126.3
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
64.5
60.7
58.5
24.8
19.2
Br
O
O
O
13C NMR (101MHz, CDCl3)
f1 (ppm)

Compound 11

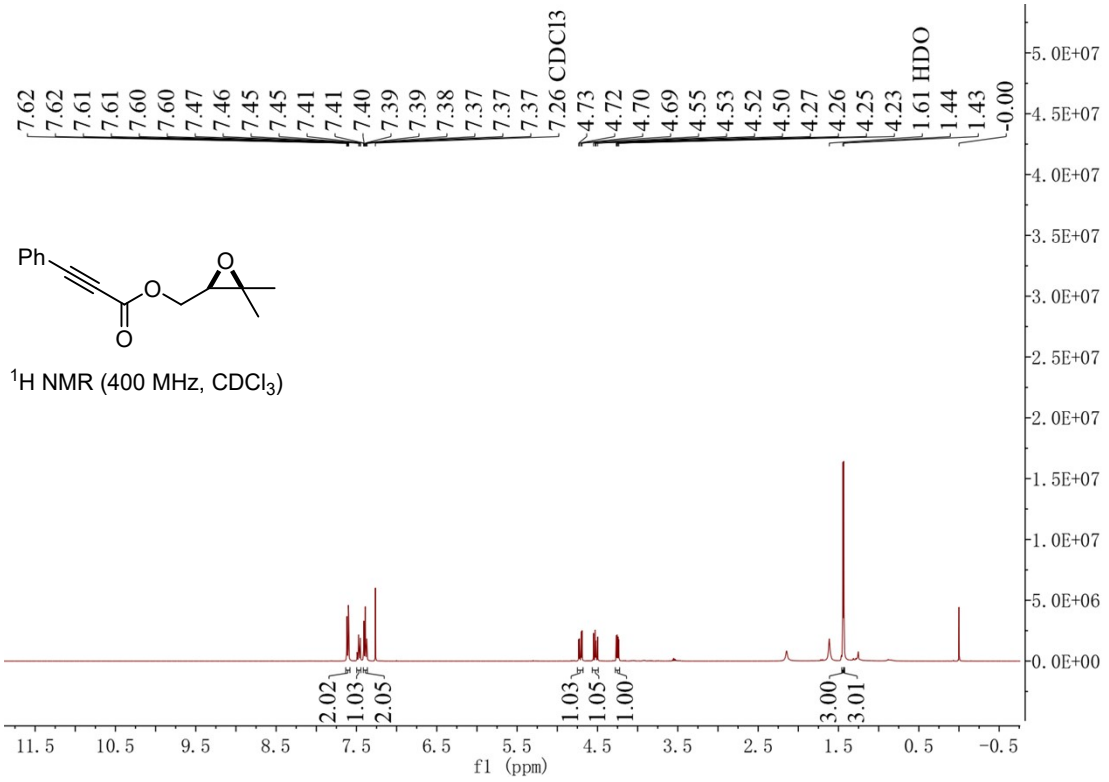


^{1}H NMR (400 MHz, $CDCl_3$)

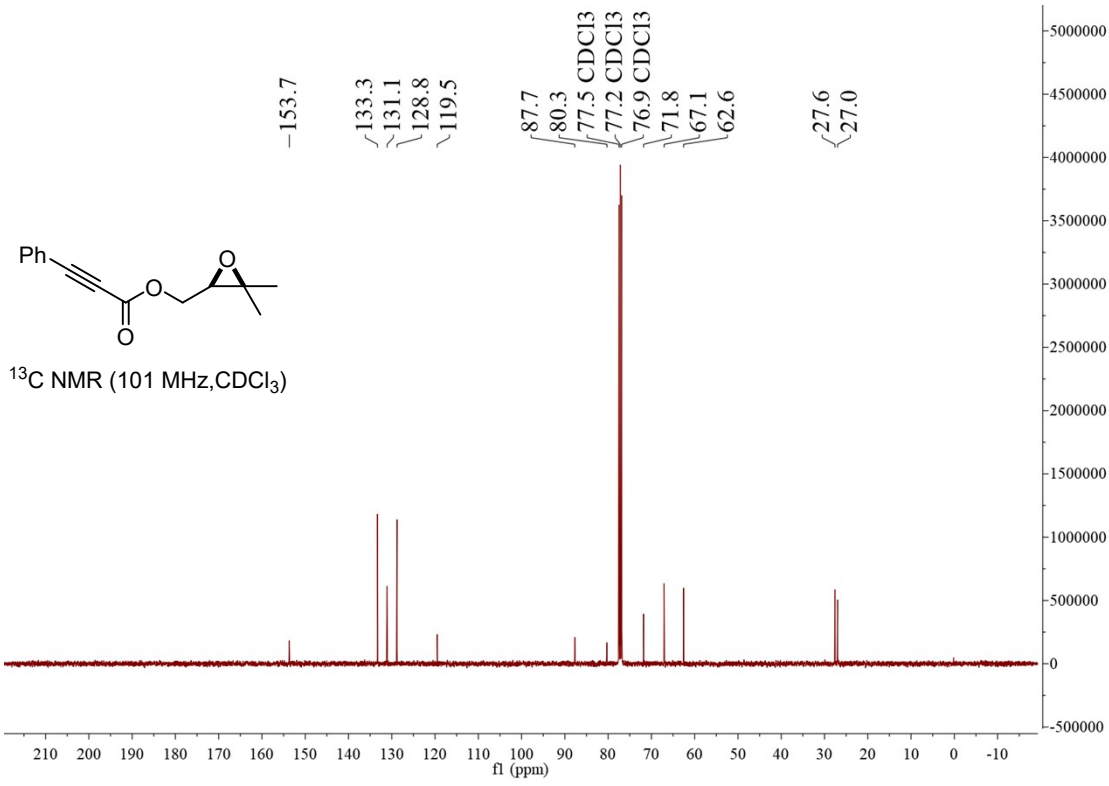


^{13}C NMR (101 MHz,$CDCl_3$)

Compound 12

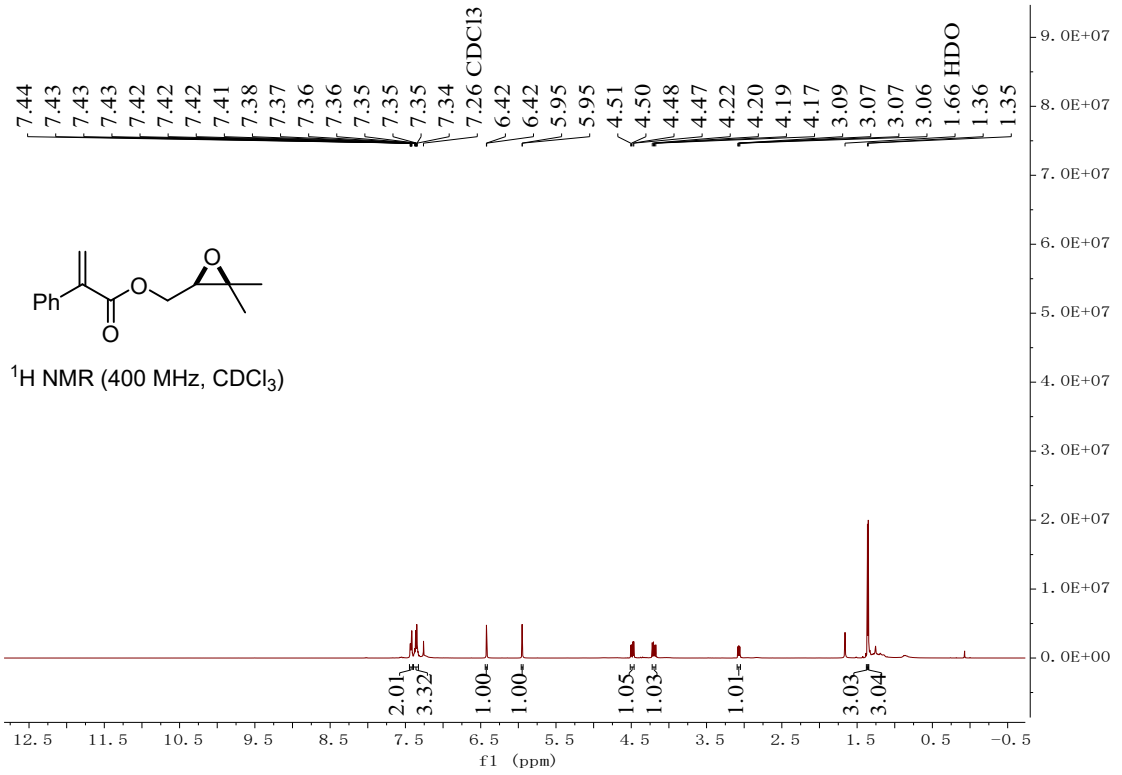


^{1}H NMR (400 MHz, $CDCl_3$)

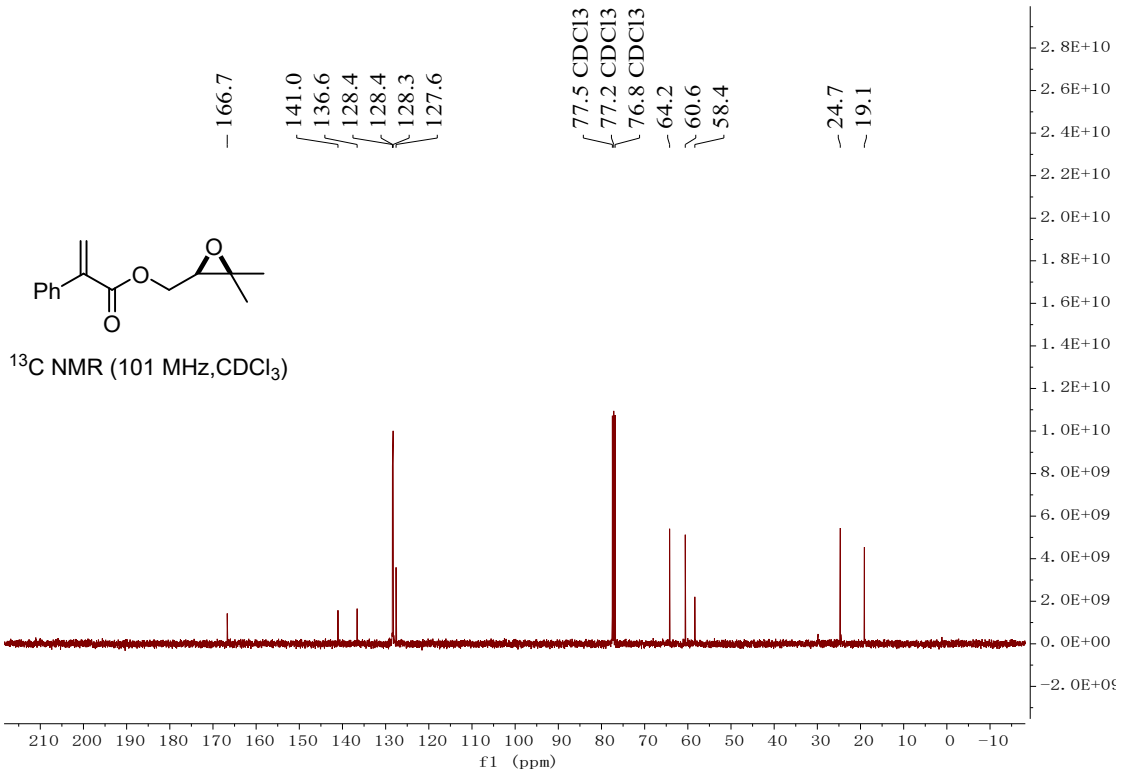


^{13}C NMR (101 MHz,$CDCl_3$)

Compound 13

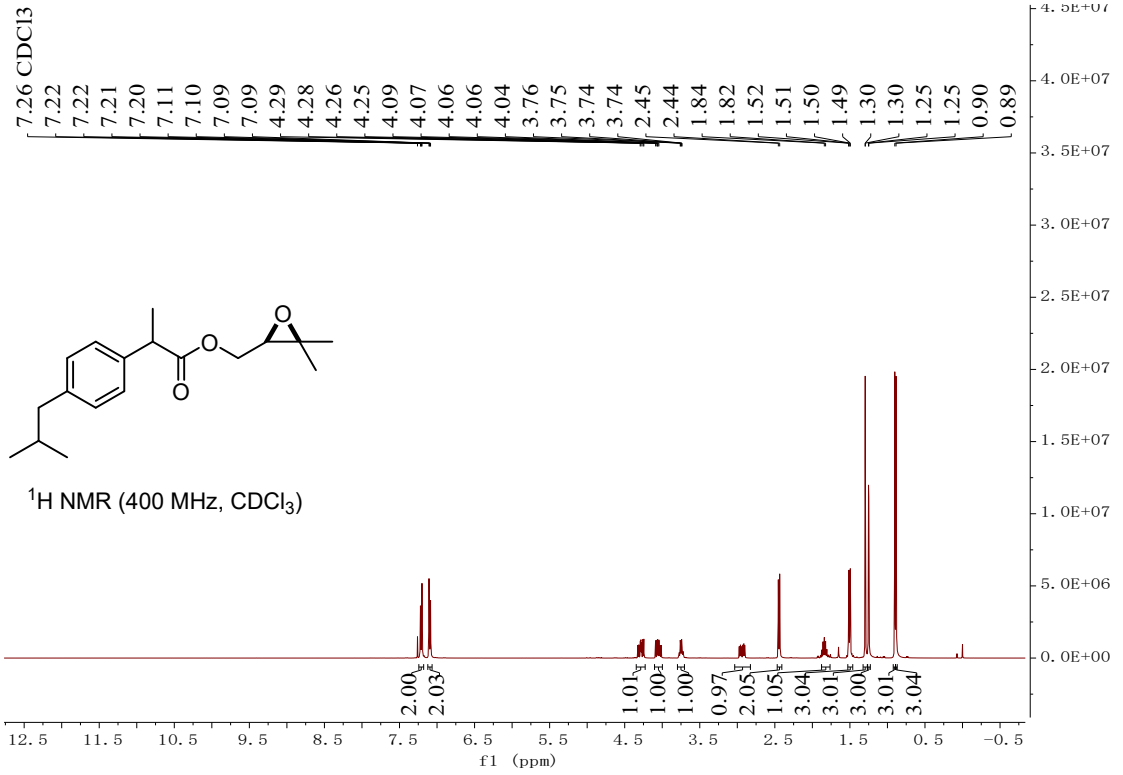


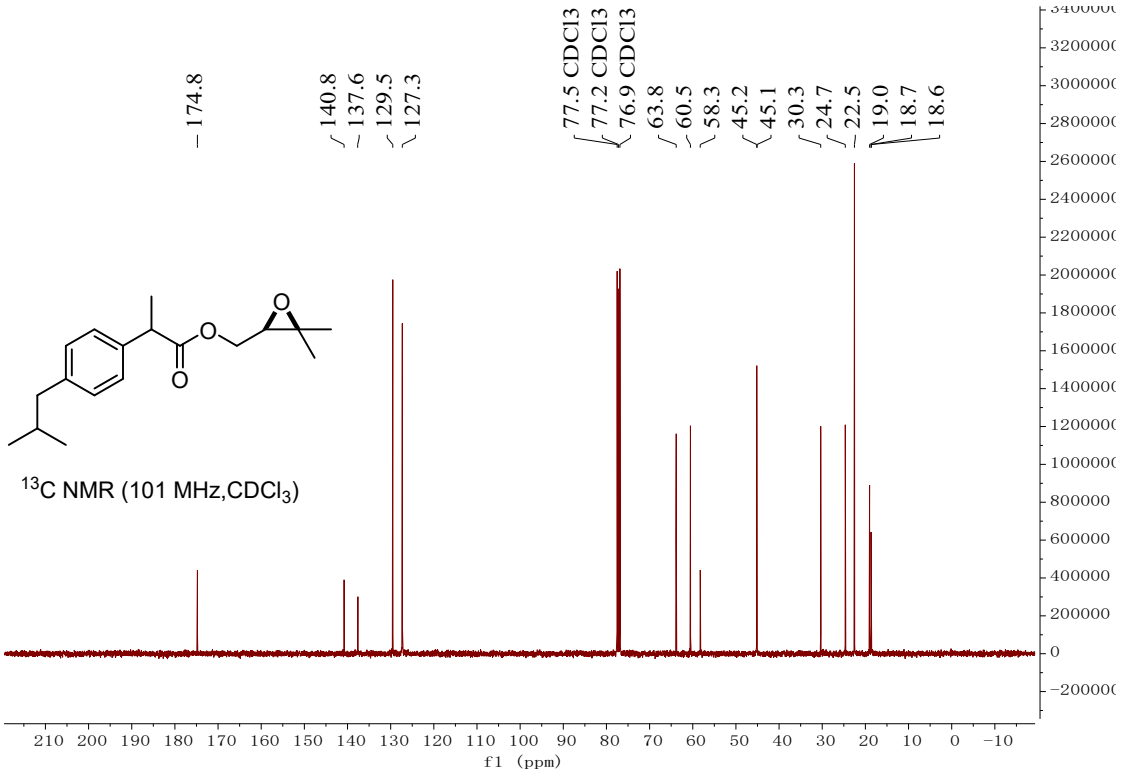
^{1}H NMR (400 MHz, $CDCl_3$)



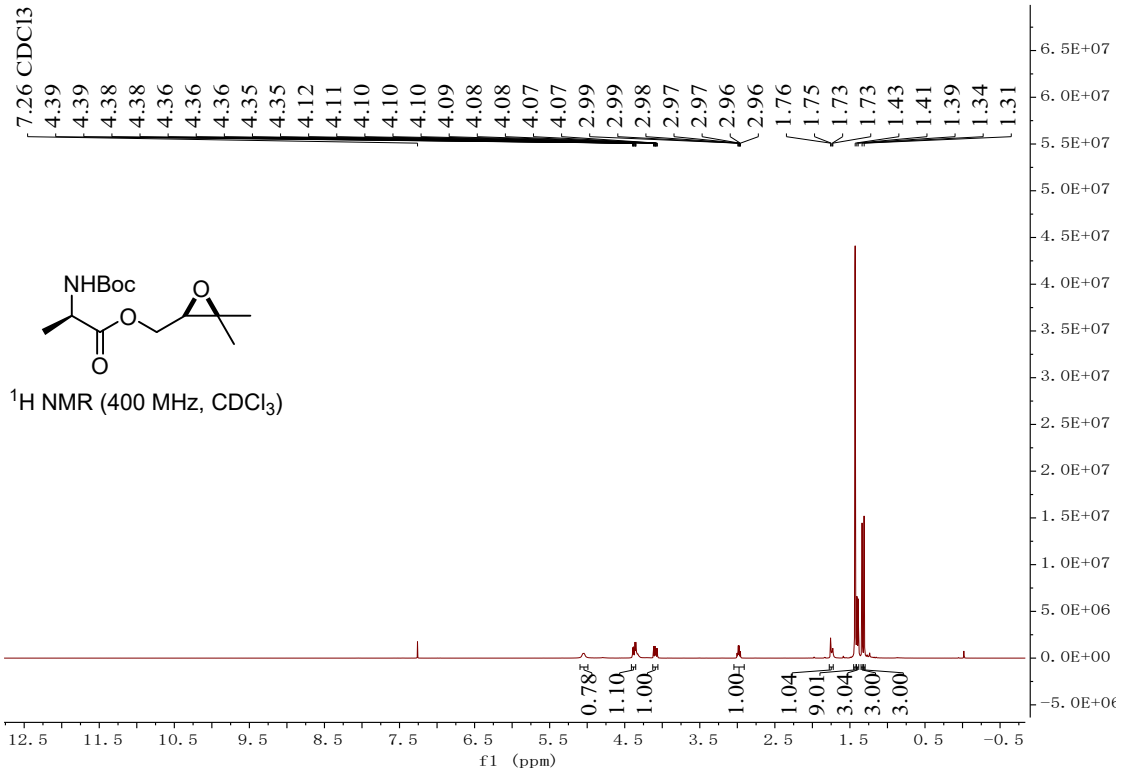
^{13}C NMR (101 MHz,$CDCl_3$)

Compound 14

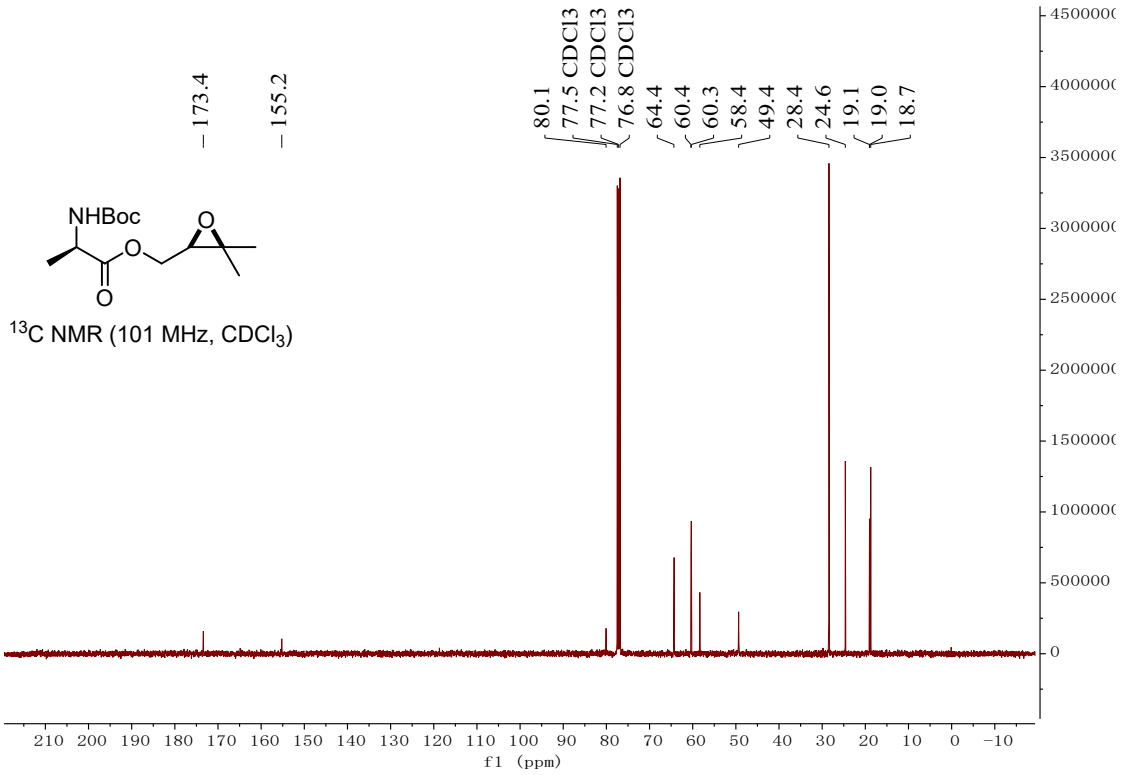

7.26 CDCl3
7.22
7.22
7.21
7.20
7.11
7.10
7.09
7.09
4.29
4.28
4.26
4.25
4.09
4.07
4.06
4.06
4.04
3.76
3.75
3.74
3.74
2.45
2.44
1.84
1.82
1.52
1.51
1.50
1.49
1.30
1.30
1.25
1.25
0.90
0.89
O
O
O
1H NMR (400 MHz, CDCl3)
2.00
2.03
1.01
1.00
1.00
0.97
2.05
1.05
3.04
3.01
3.00
3.01
3.04
f1 (ppm)


174.8
140.8
137.6
129.5
127.3
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
63.8
60.5
58.3
45.2
45.1
30.3
24.7
22.5
19.0
18.7
18.6
O
O
O
13C NMR (101 MHz,CDCl3)
f1 (ppm)

Compound 15

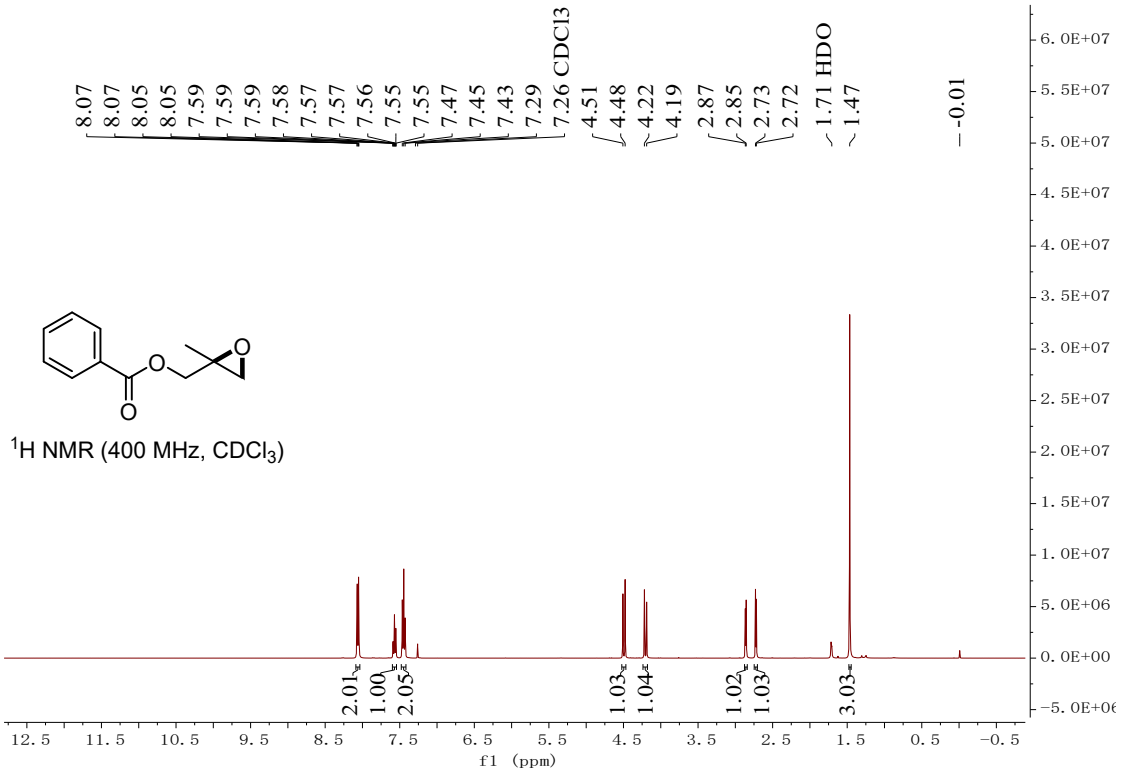


^{1}H NMR (400 MHz, $CDCl_3$)

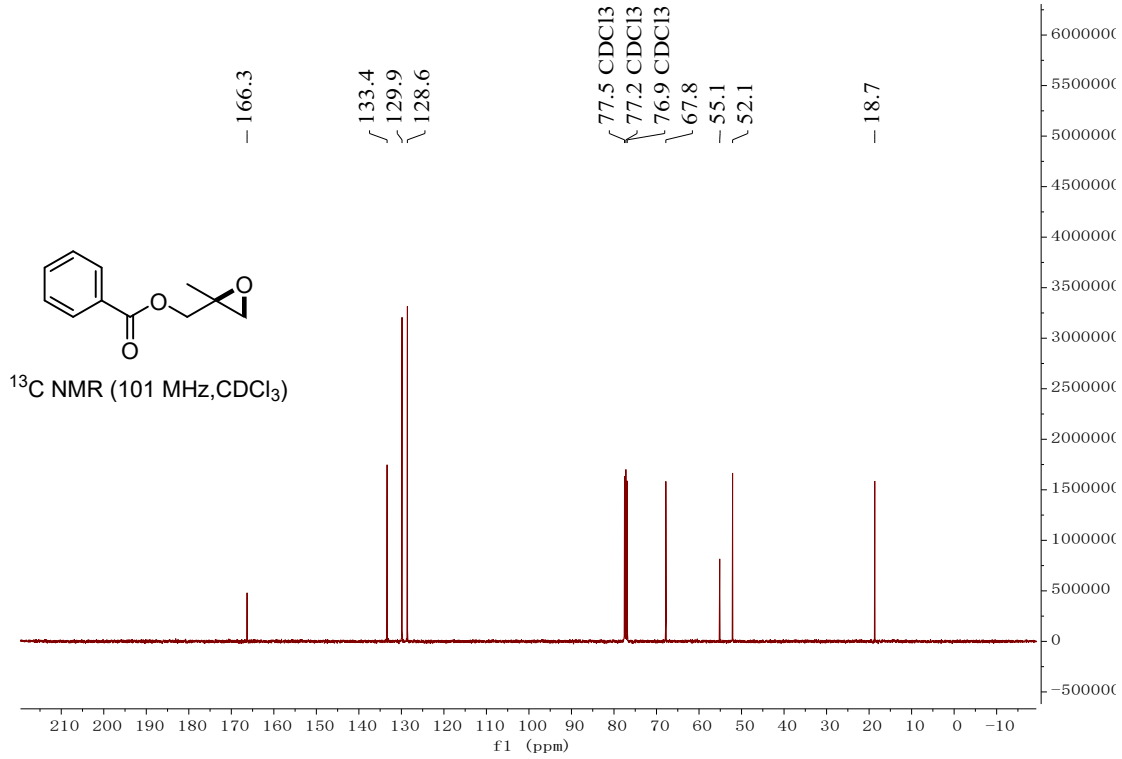


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 16

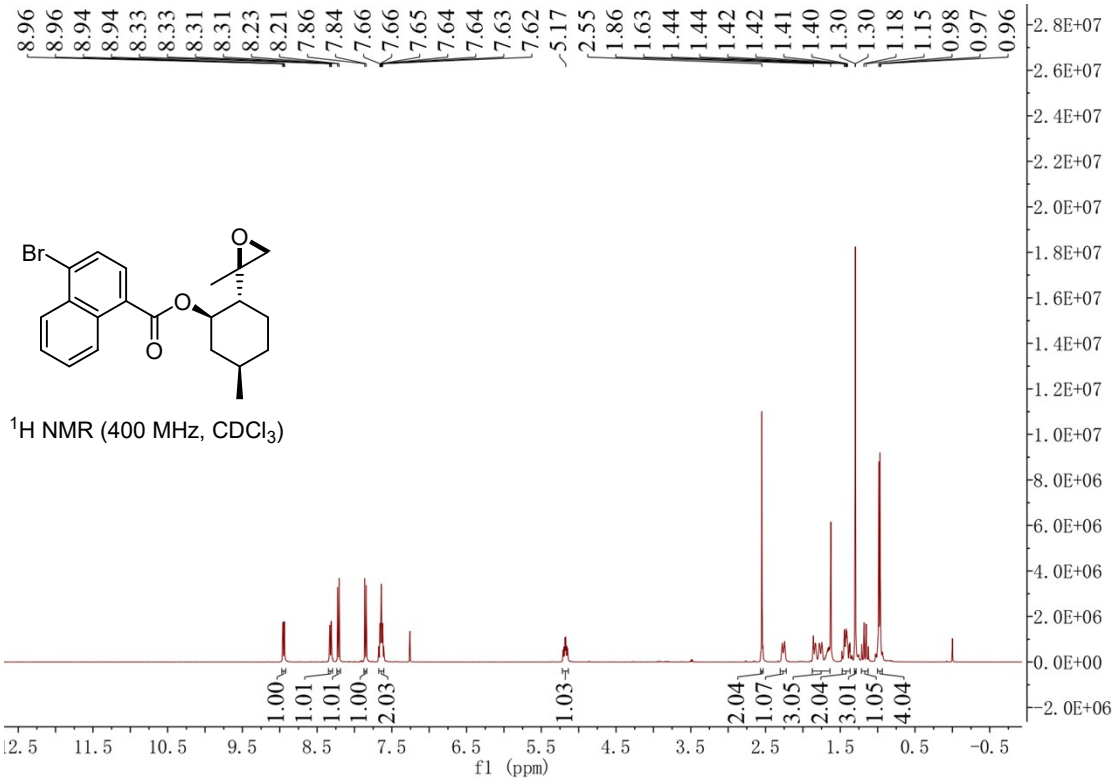


^{1}H NMR (400 MHz, $CDCl_3$)

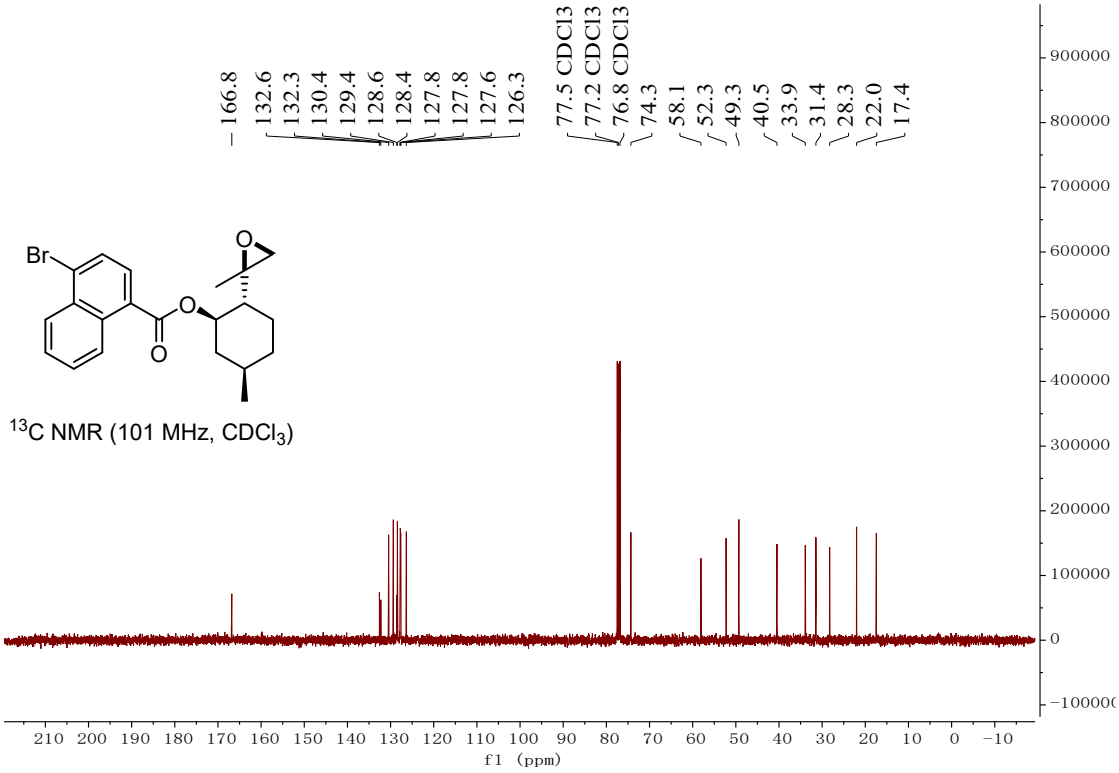


^{13}C NMR (101 MHz,$CDCl_3$)

Compound 17

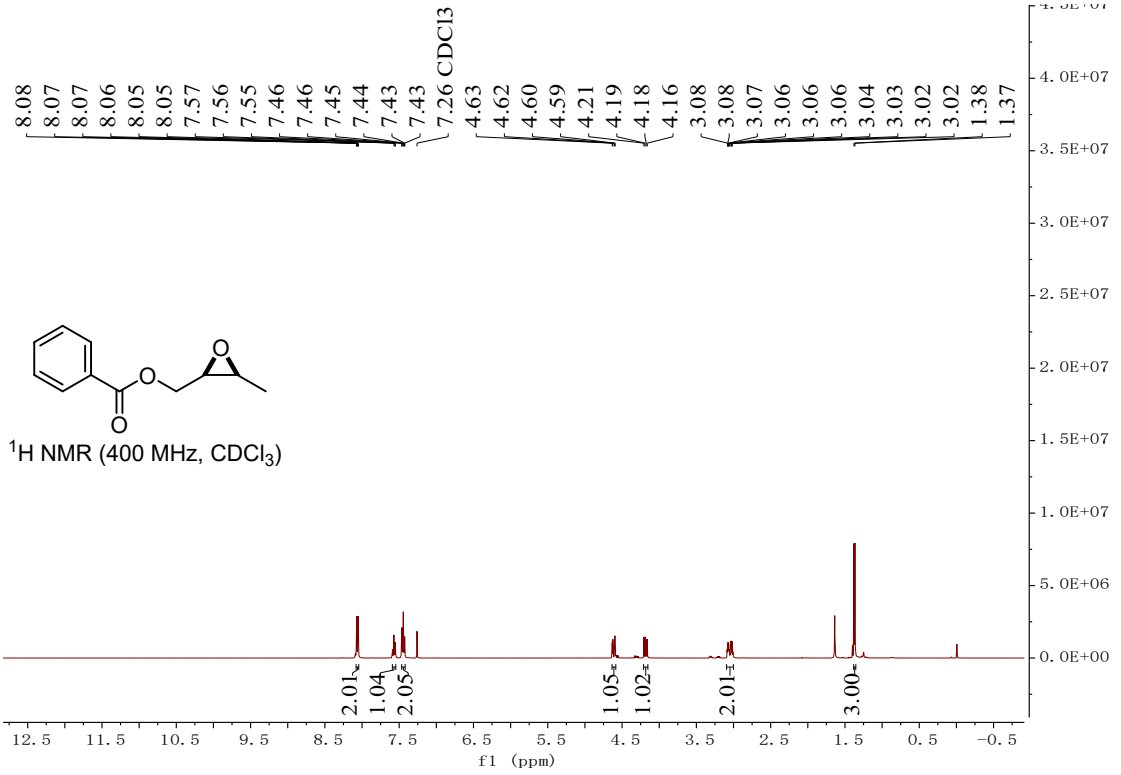


^{1}H NMR (400 MHz, $CDCl_3$)

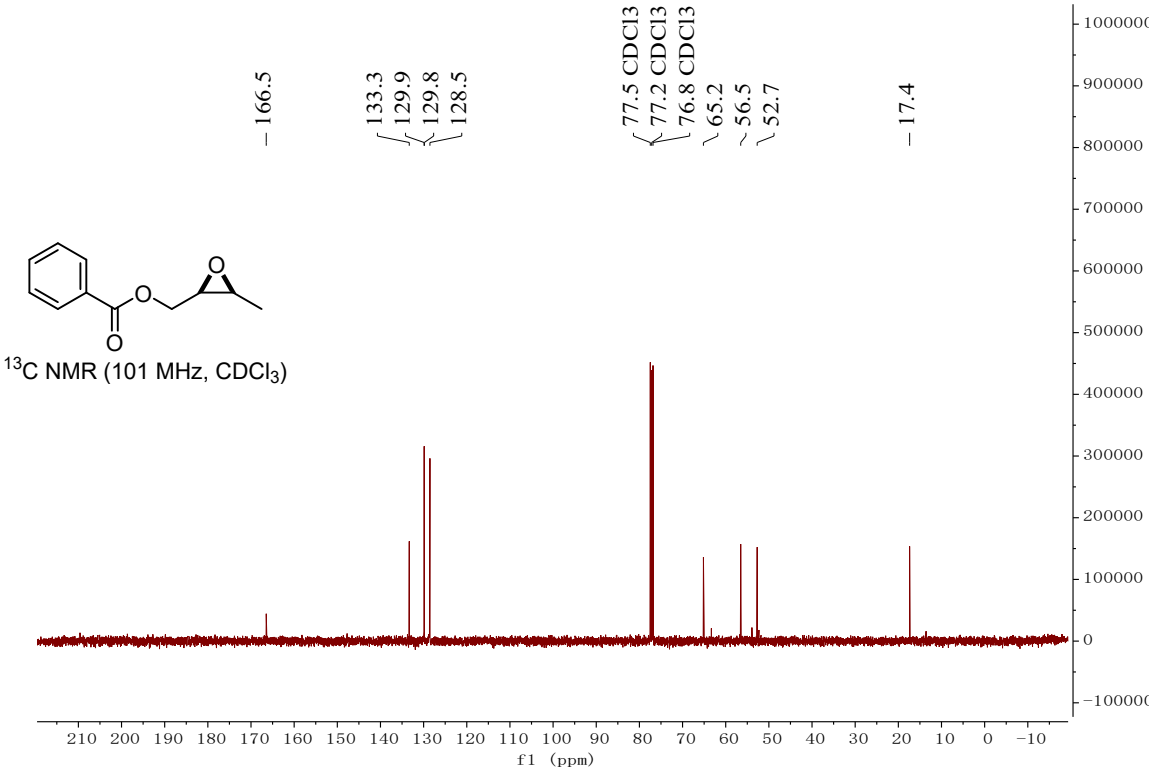


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 18

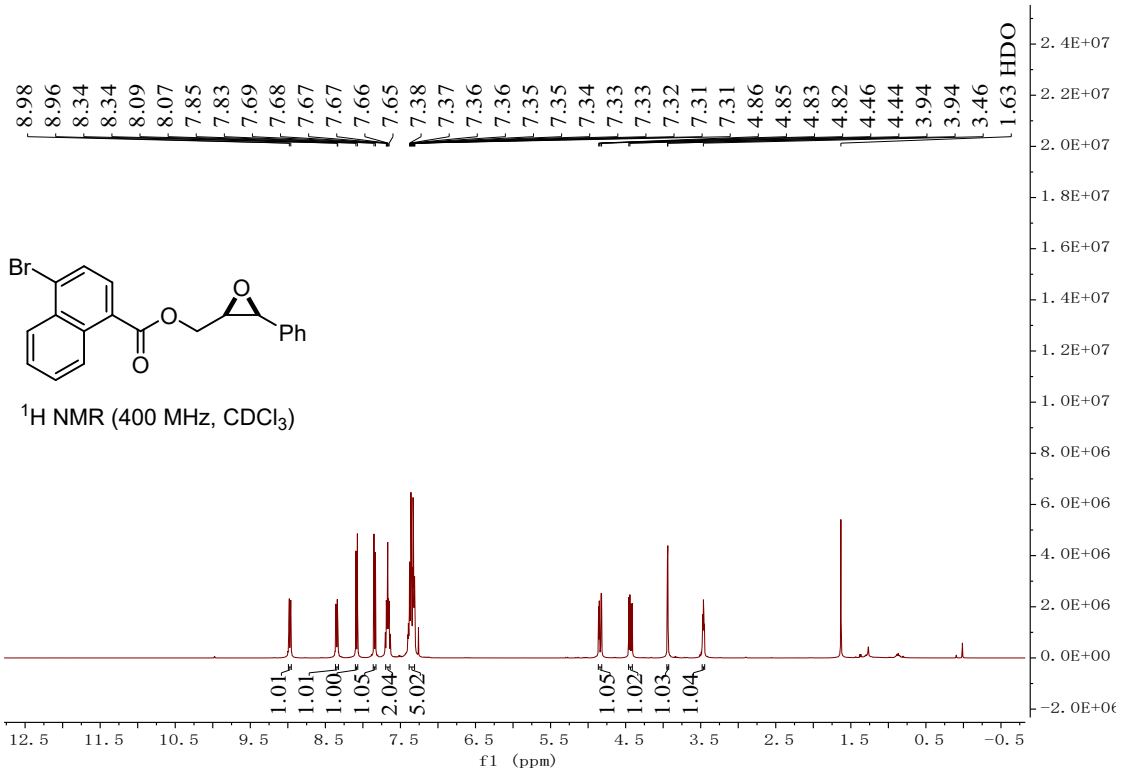


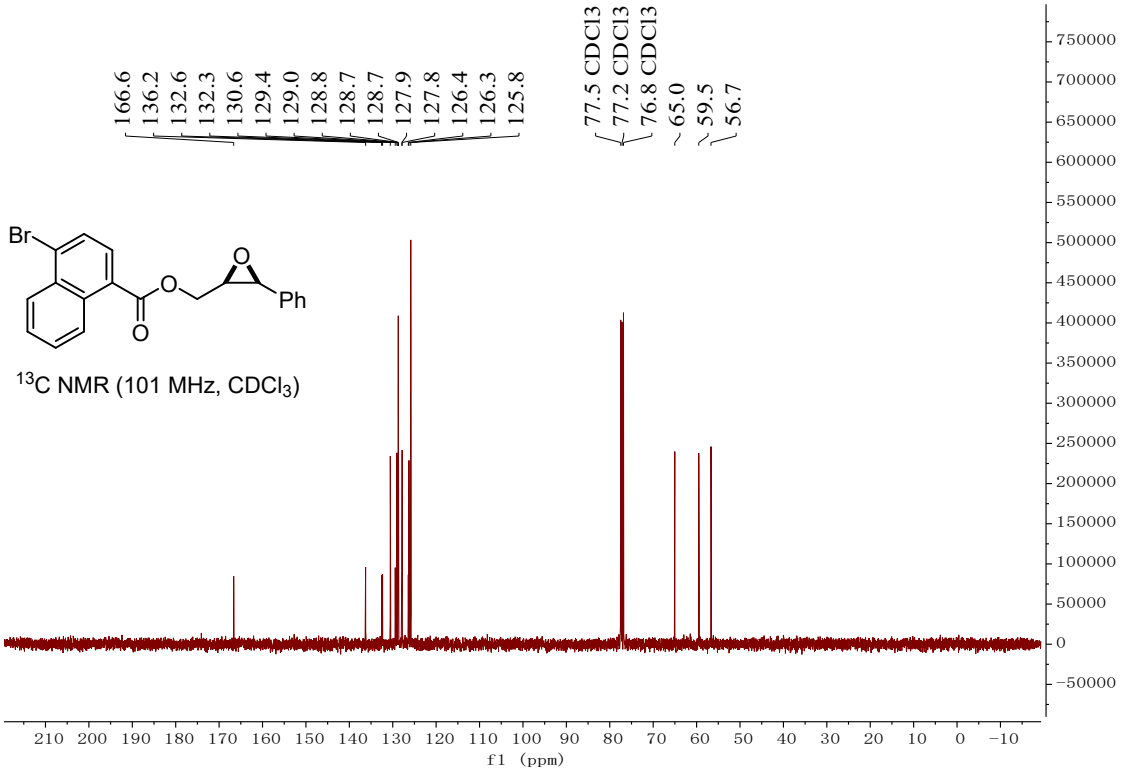
^{1}H NMR (400 MHz, $CDCl_3$)



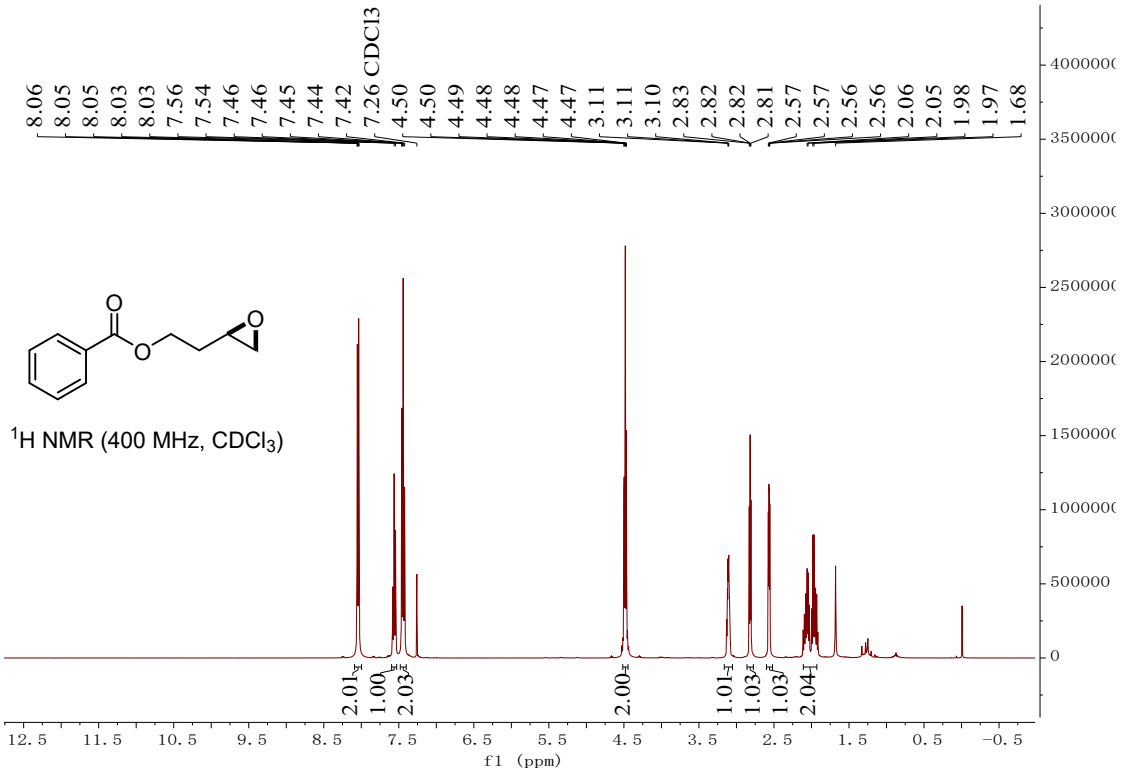
^{13}C NMR (101 MHz, $CDCl_3$)

Compound 19

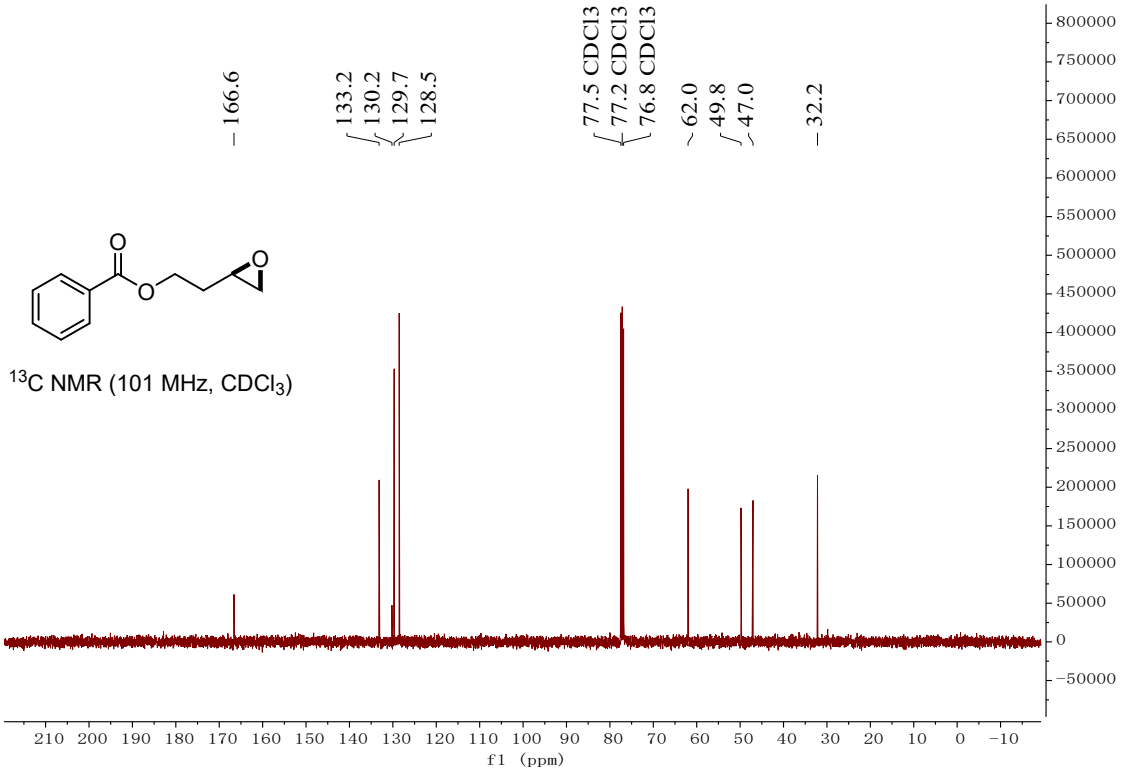

8.98
8.96
8.34
8.34
8.09
8.07
7.85
7.83
7.69
7.68
7.67
7.67
7.66
7.65
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.32
7.31
7.31
4.86
4.85
4.83
4.82
4.46
4.44
3.94
3.94
3.46
1.63 HDO
Br
O
O
O
Ph
1H NMR (400 MHz, CDCl3)
1.01
1.01
1.00
1.05
2.04
5.02
1.05
1.02
1.03
1.04
f1 (ppm)


166.6
136.2
132.6
132.3
130.6
129.4
129.0
128.8
128.7
128.7
127.9
127.8
126.4
126.3
125.8
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
65.0
59.5
56.7
Br
O
O
O
Ph
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 20

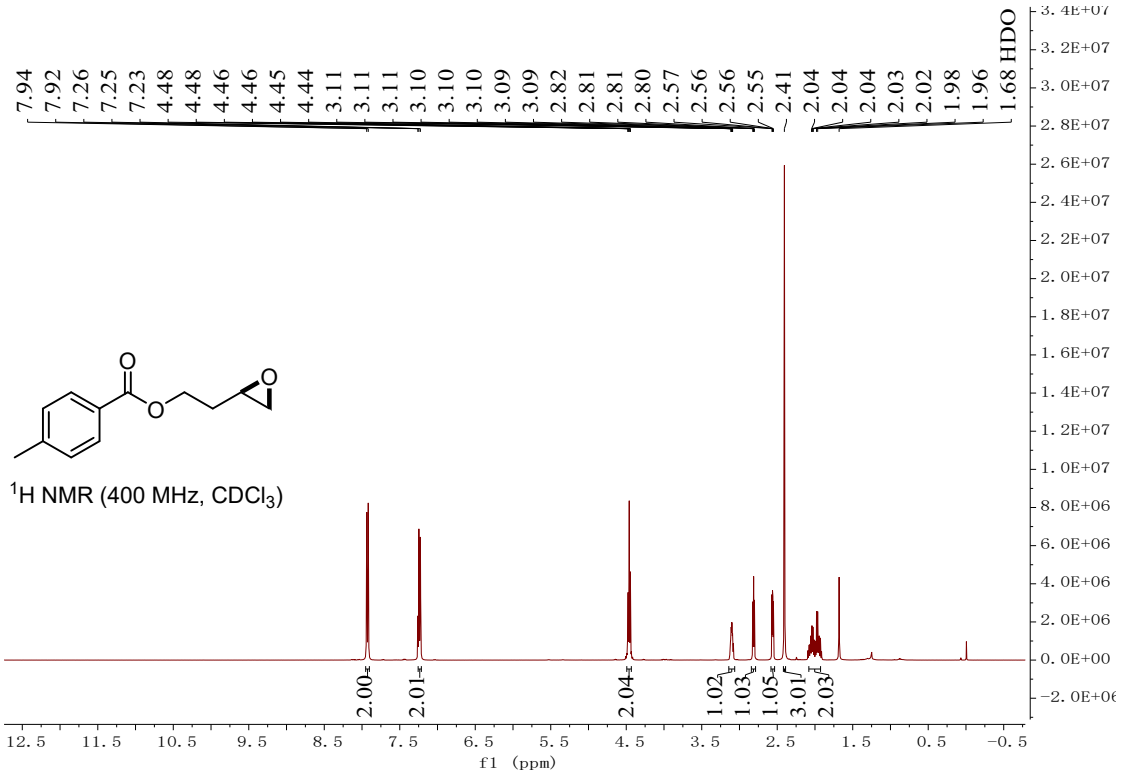


^{1}H NMR (400 MHz, $CDCl_3$)

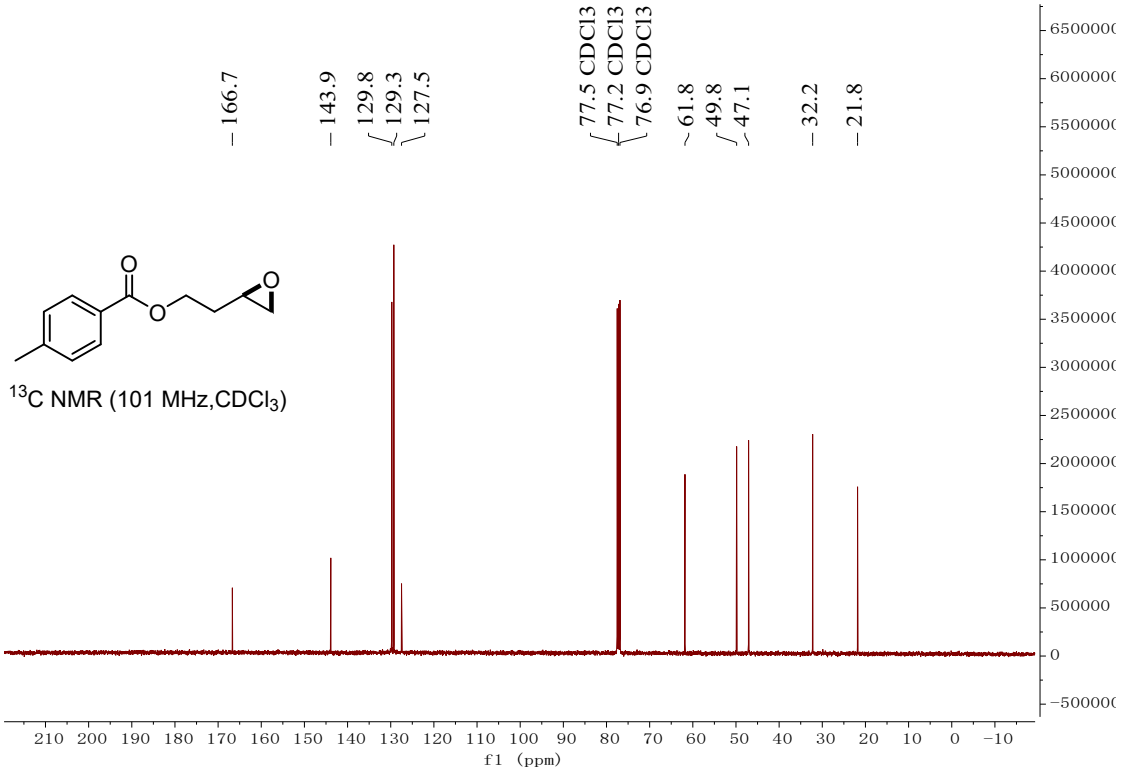


^{13}C NMR (101 MHz, $CDCl_3$)

Compound 21

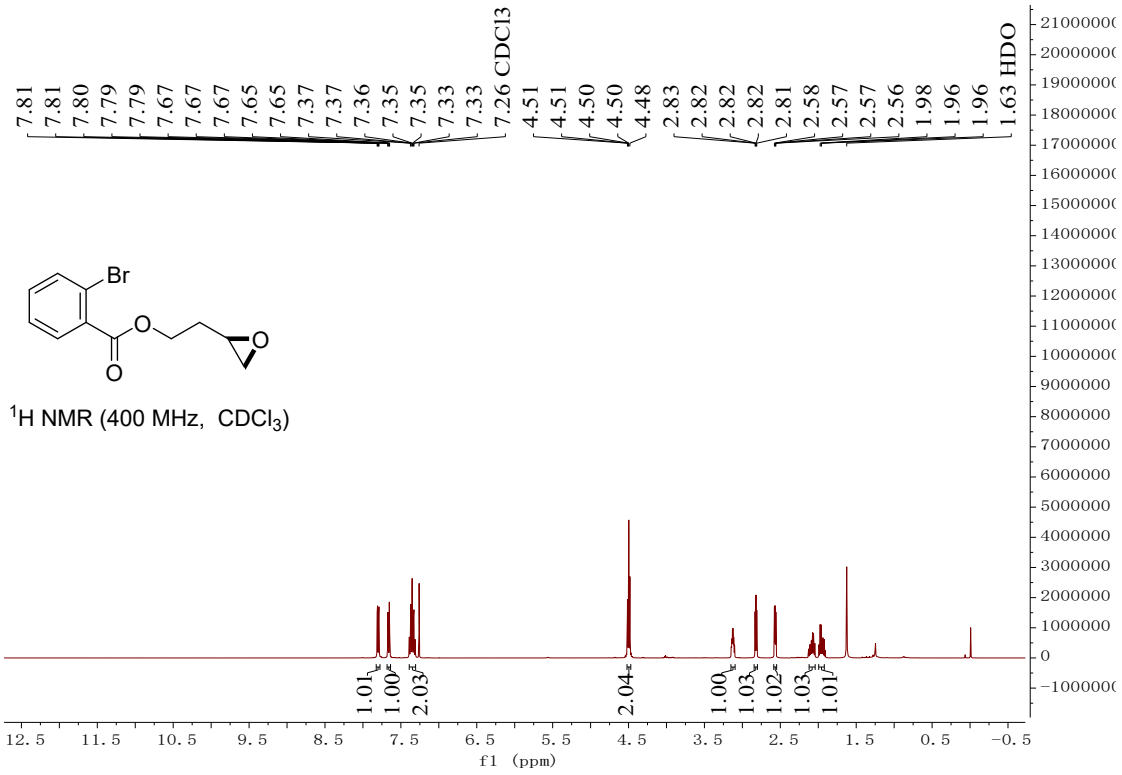


^{1}H NMR (400 MHz, $CDCl_3$)

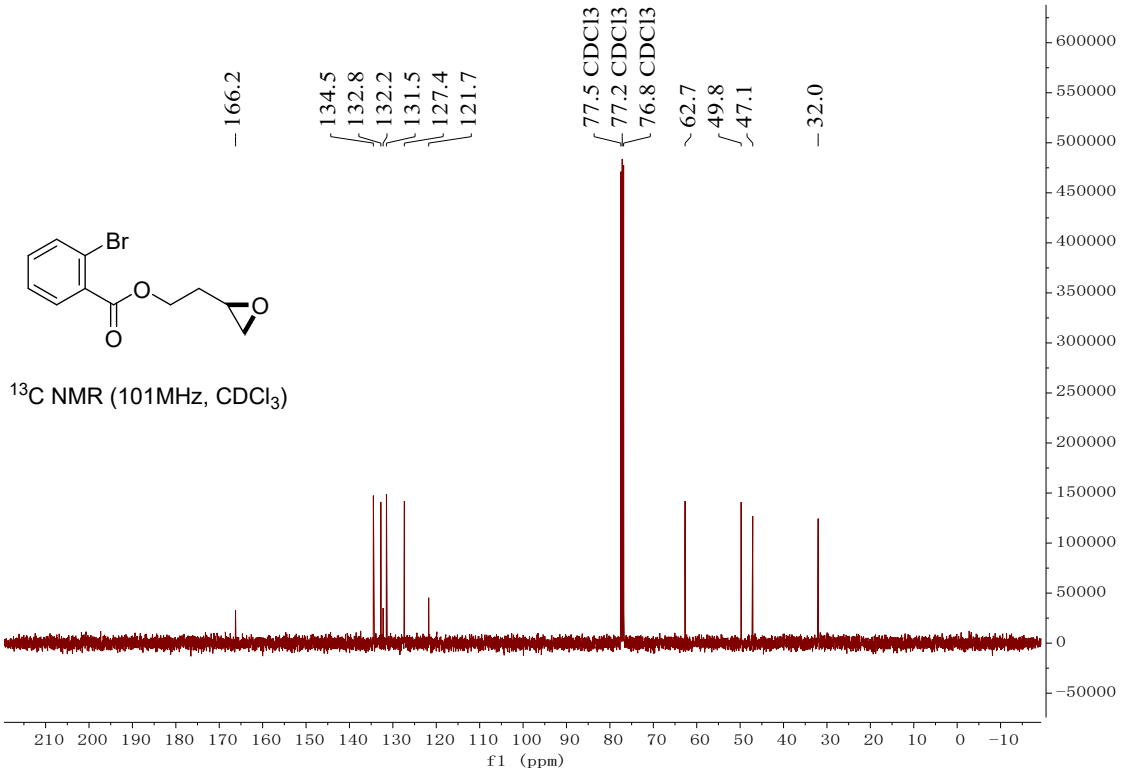


^{13}C NMR (101 MHz,$CDCl_3$)

Compound 22

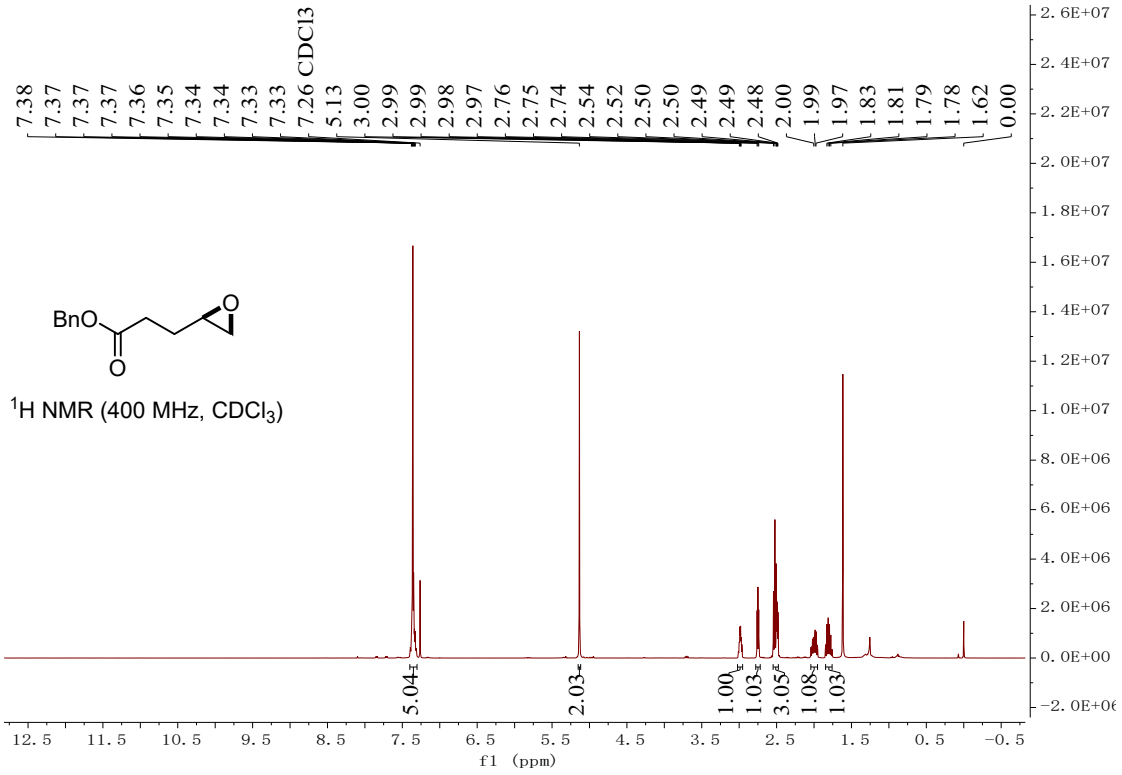


^{1}H NMR (400 MHz, $CDCl_3$)

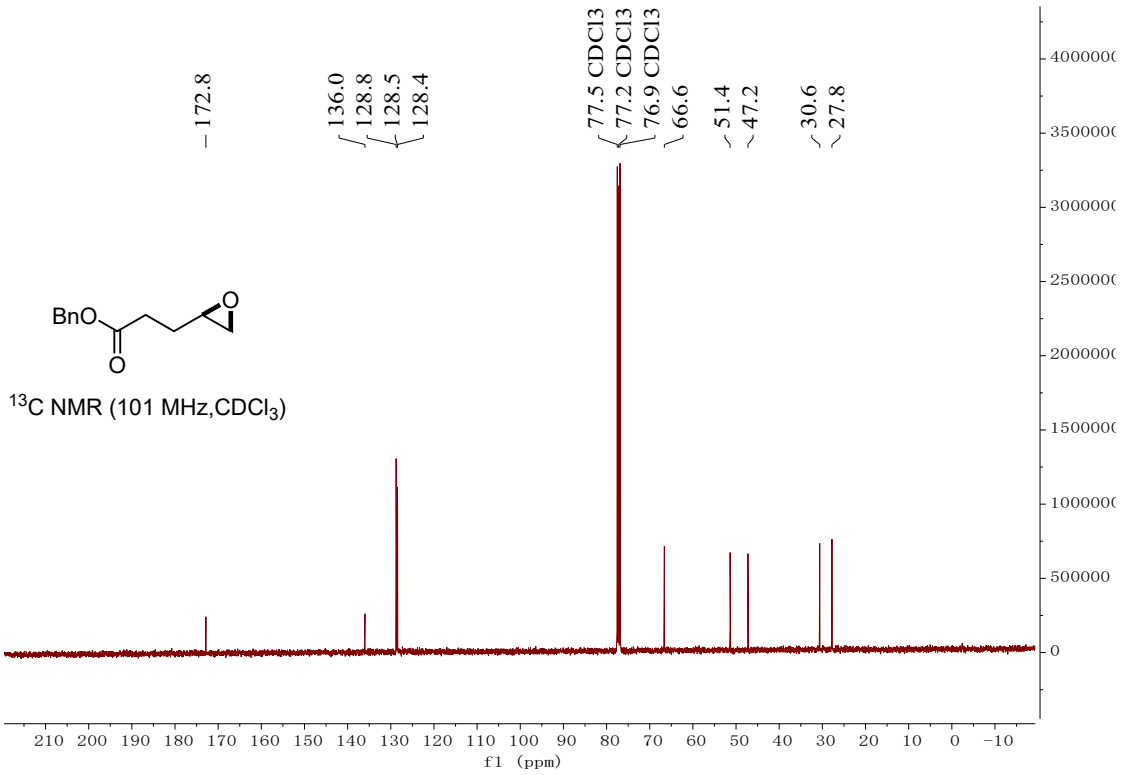


^{13}C NMR (101MHz, $CDCl_3$)

Compound 23

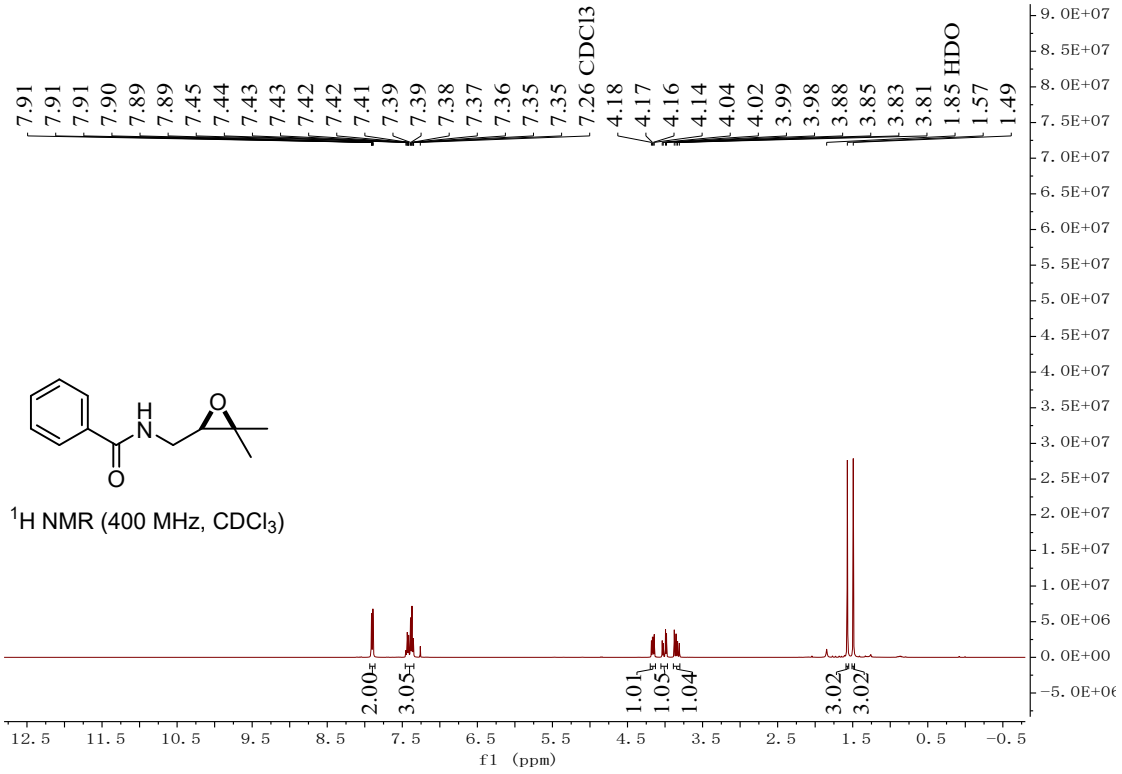


^{1}H NMR (400 MHz, $CDCl_3$)

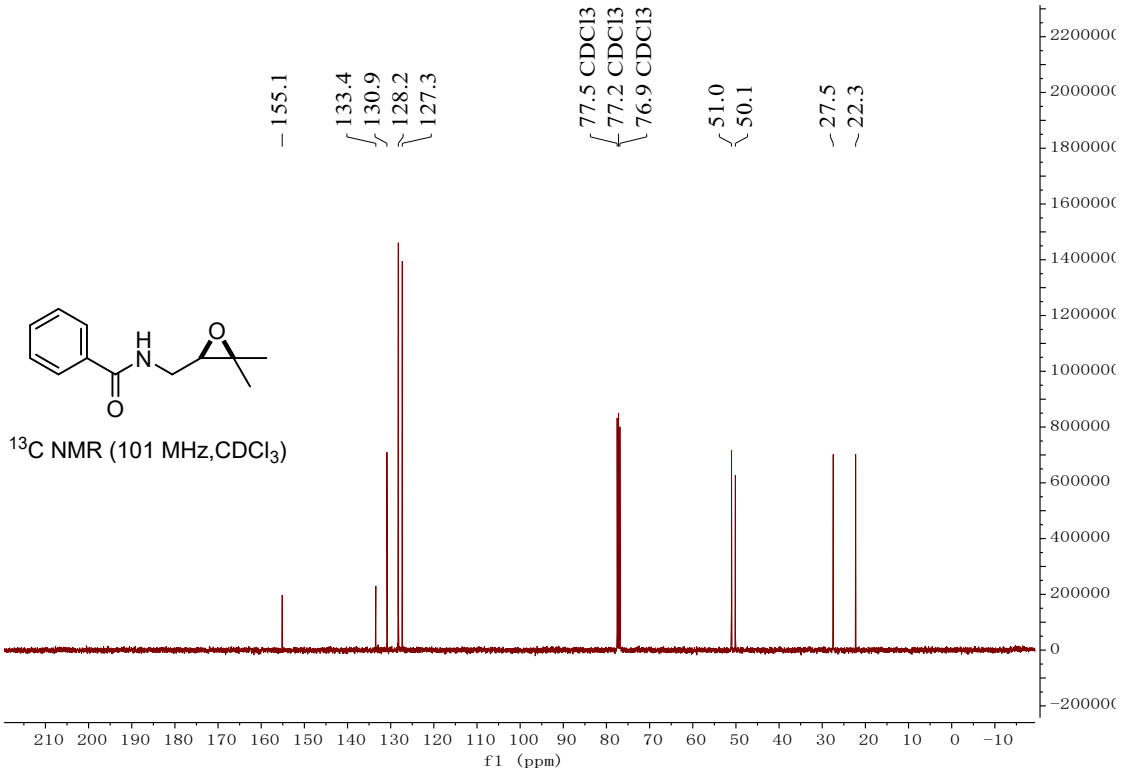


^{13}C NMR (101 MHz,$CDCl_3$)

Compound 24

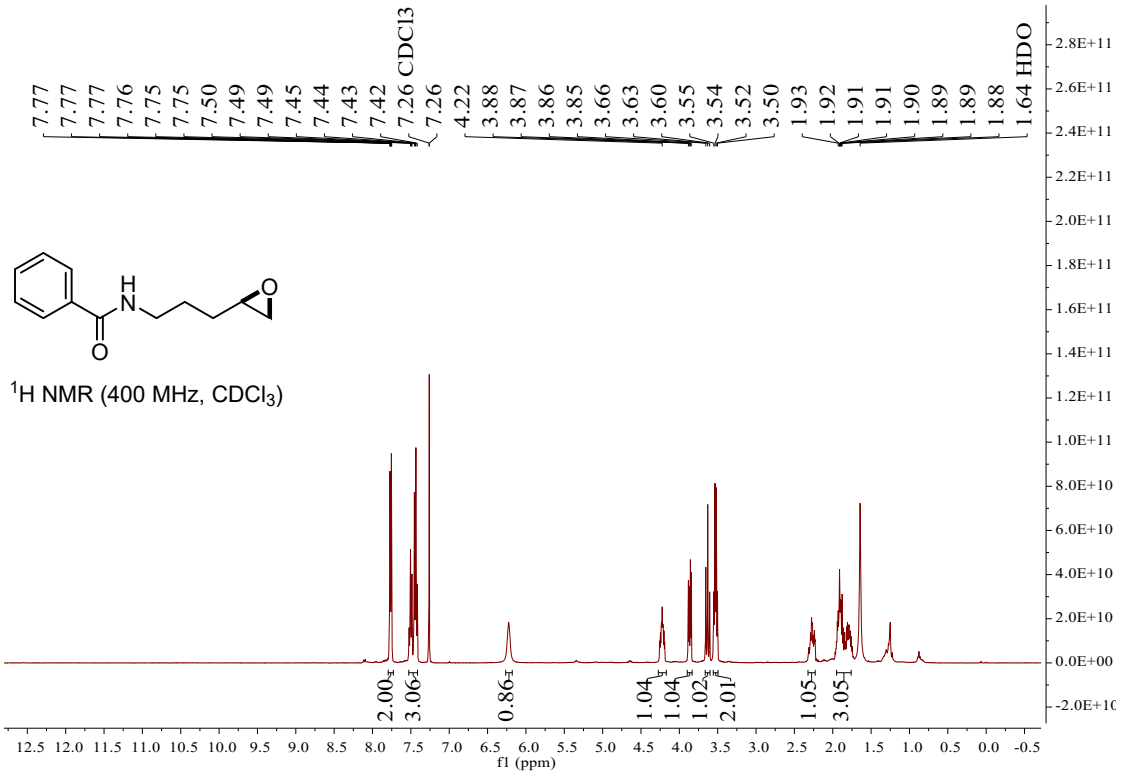


^{1}H NMR (400 MHz, $CDCl_3$)

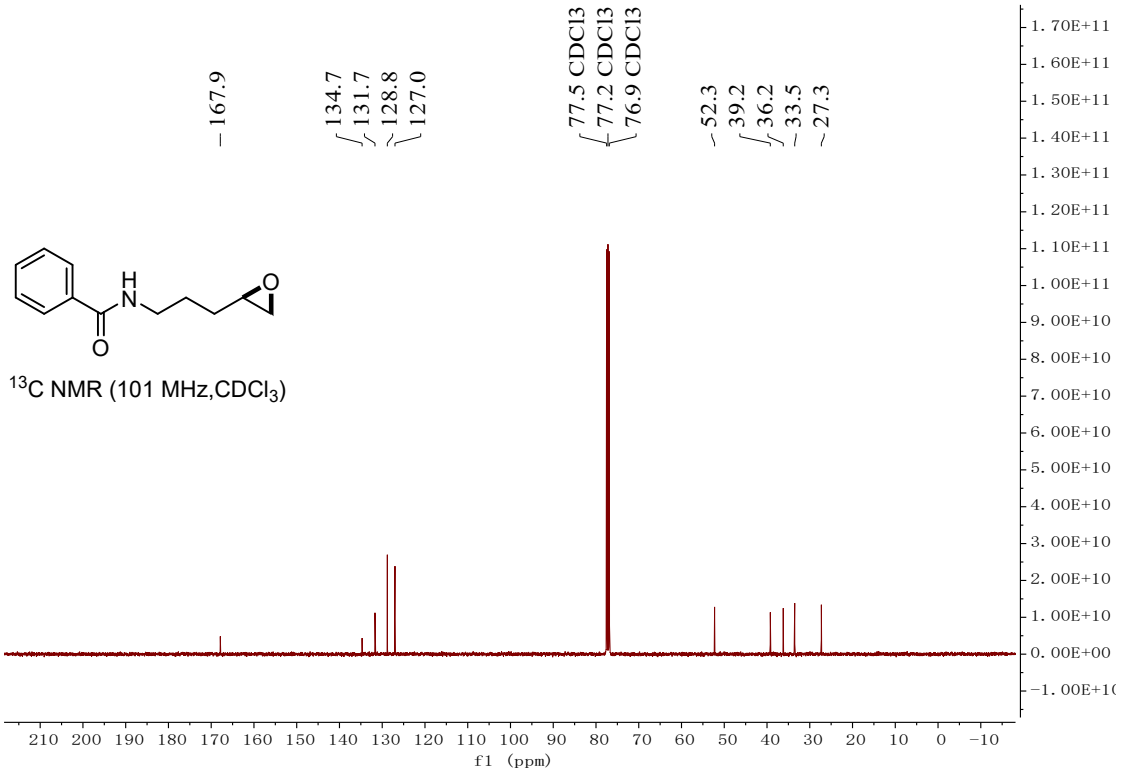


^{13}C NMR (101 MHz,$CDCl_3$)

Compound 25

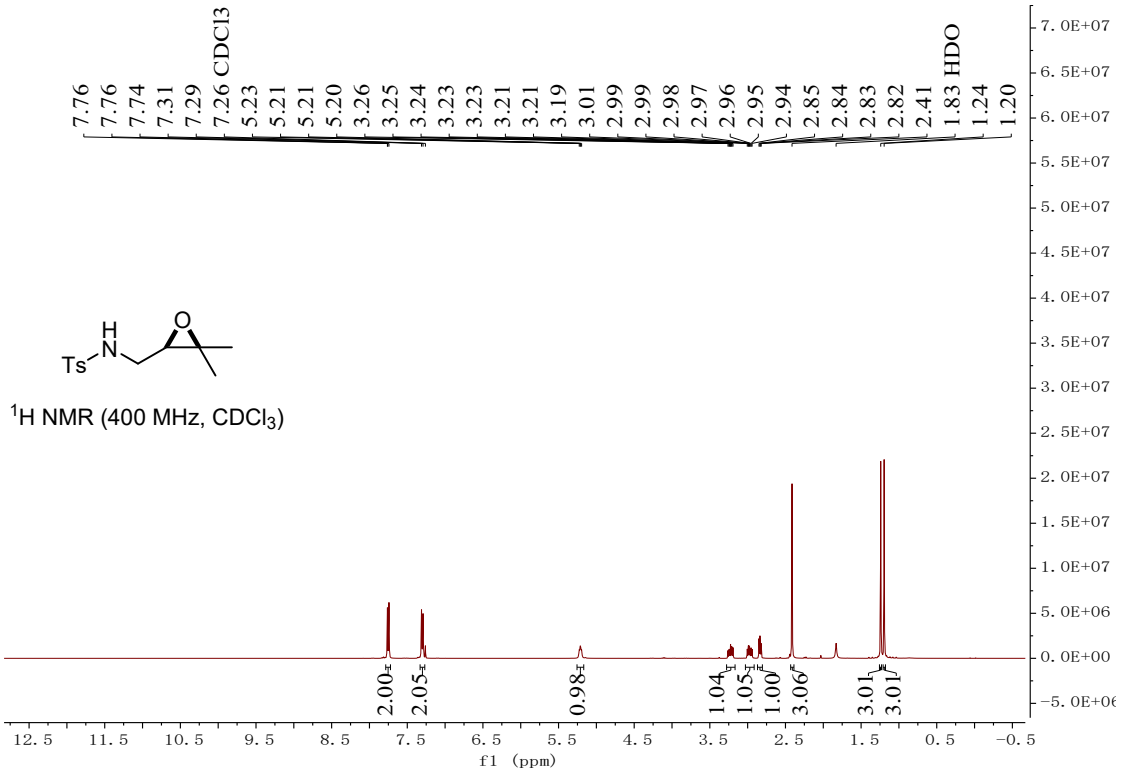


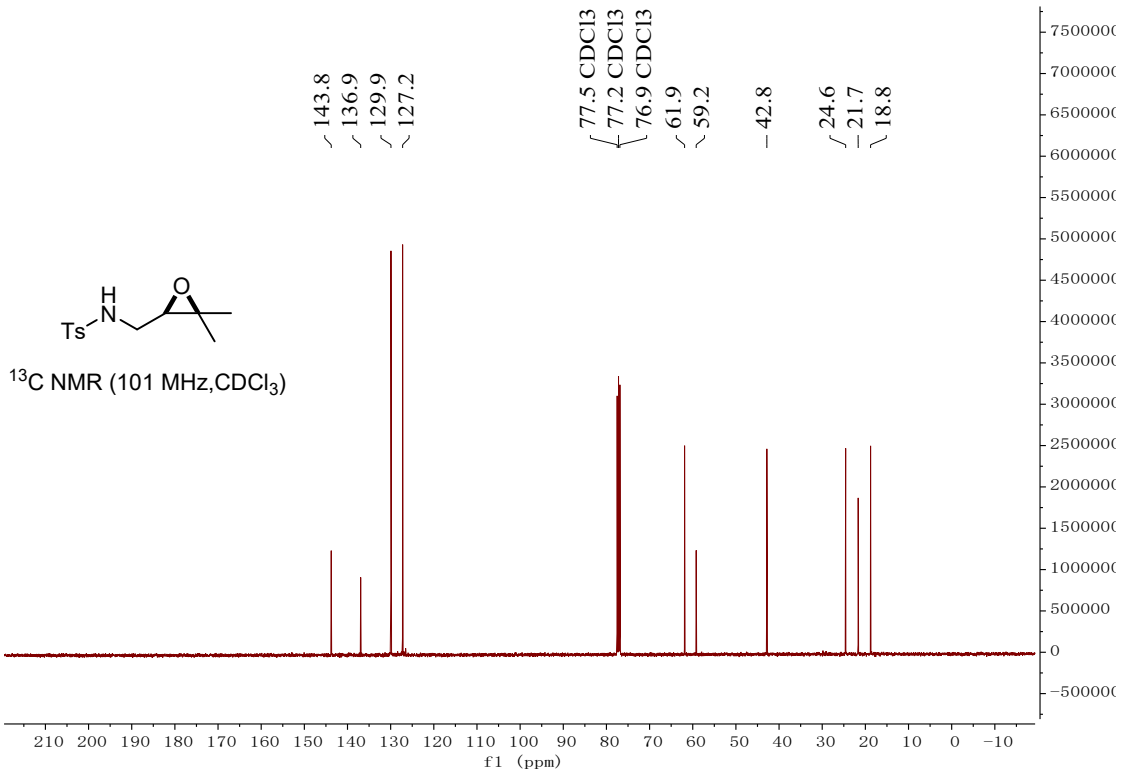
^{1}H NMR (400 MHz, $CDCl_3$)



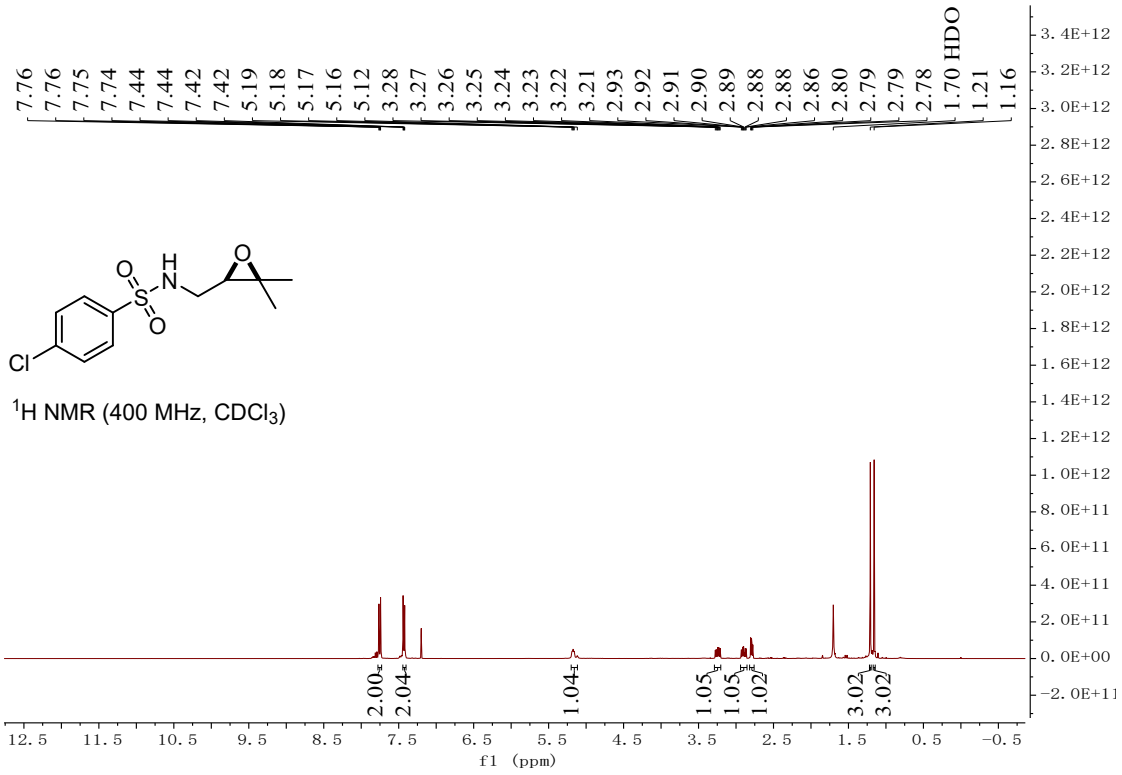
^{13}C NMR (101 MHz,$CDCl_3$)

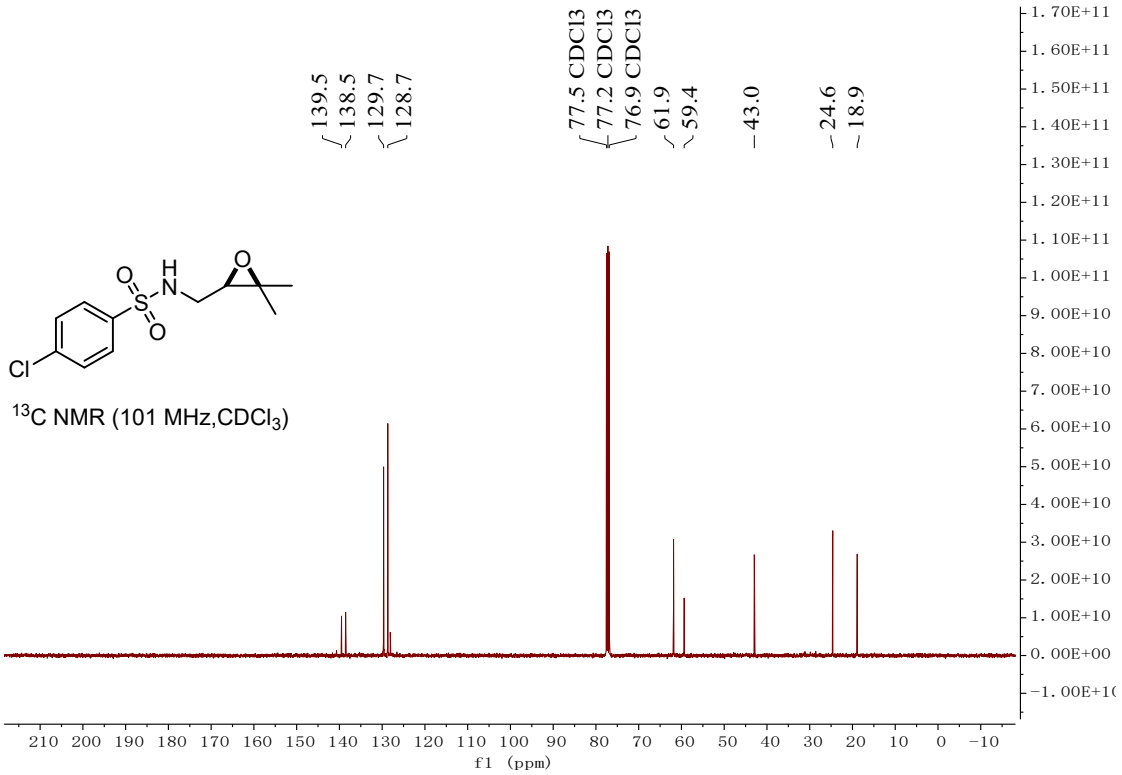
Compound 26


7.76
7.76
7.74
7.31
7.29
7.26 CDCl3
5.23
5.21
5.21
5.20
3.26
3.25
3.24
3.23
3.23
3.21
3.21
3.19
3.01
2.99
2.99
2.98
2.97
2.96
2.95
2.94
2.85
2.84
2.83
2.82
2.41
1.83 HDO
1.24
1.20
Ts
H
N
O
1H NMR (400 MHz, CDCl3)
2.00
2.05
0.98
1.04
1.05
1.00
3.06
3.01
3.01
f1 (ppm)

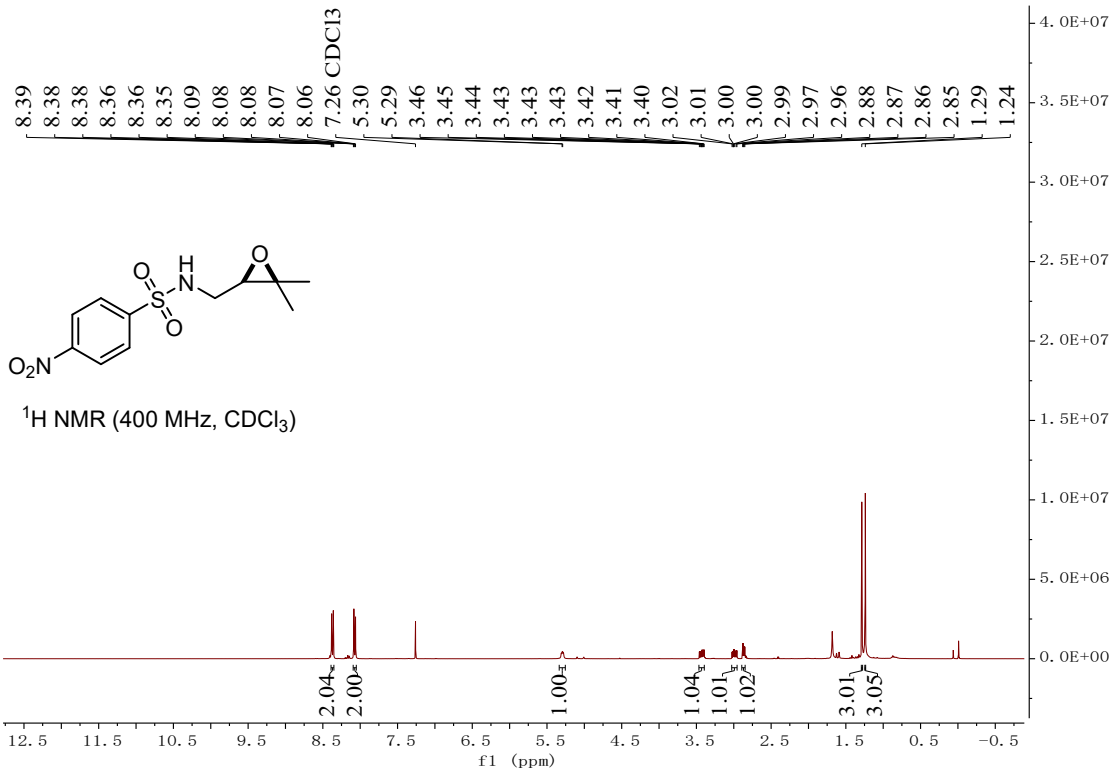

143.8
136.9
129.9
127.2
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
61.9
59.2
42.8
24.6
21.7
18.8
Ts
H
N
O
13C NMR (101 MHz,CDCl3)
f1 (ppm)

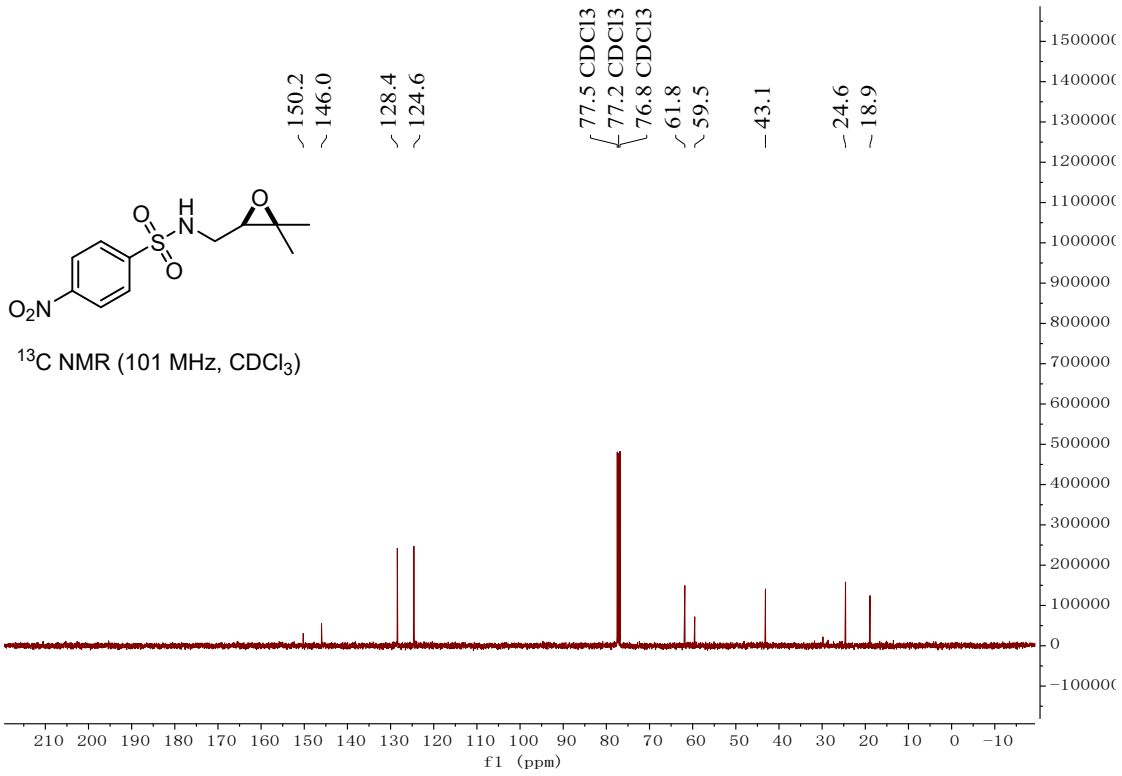
Compound 27


7.76
7.76
7.75
7.74
7.44
7.44
7.42
7.42
5.19
5.18
5.17
5.16
5.12
3.28
3.27
3.26
3.25
3.24
3.23
3.22
3.21
2.93
2.92
2.91
2.90
2.89
2.88
2.88
2.86
2.80
2.79
2.79
2.78
1.70 HDO
1.21
1.16
Cl
^{1}H NMR (400 MHz, CDCl$_3$)
2.00
2.04
1.04
1.05
1.05
1.02
3.02
3.02
f1 (ppm)

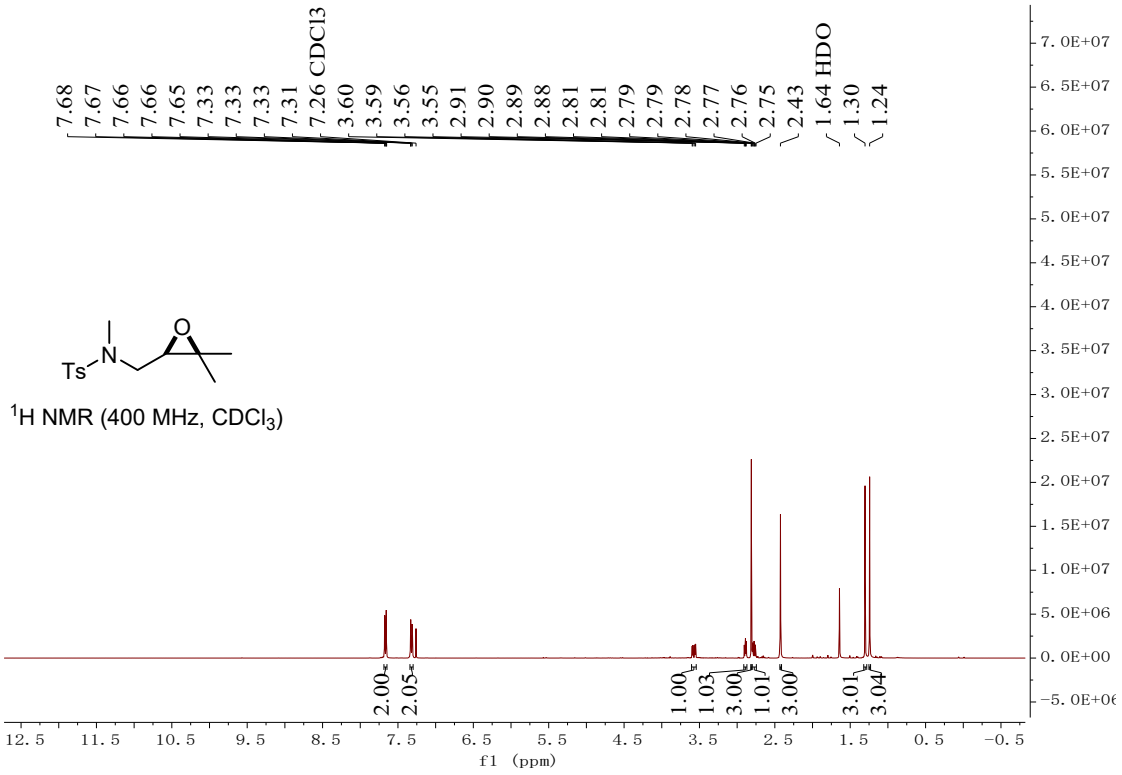

139.5
138.5
129.7
128.7
77.5 CDCl3
77.2 CDCl3
76.9 CDCl3
61.9
59.4
43.0
24.6
18.9
Cl
^{13}C NMR (101 MHz,CDCl$_3$)
f1 (ppm)

Compound 28

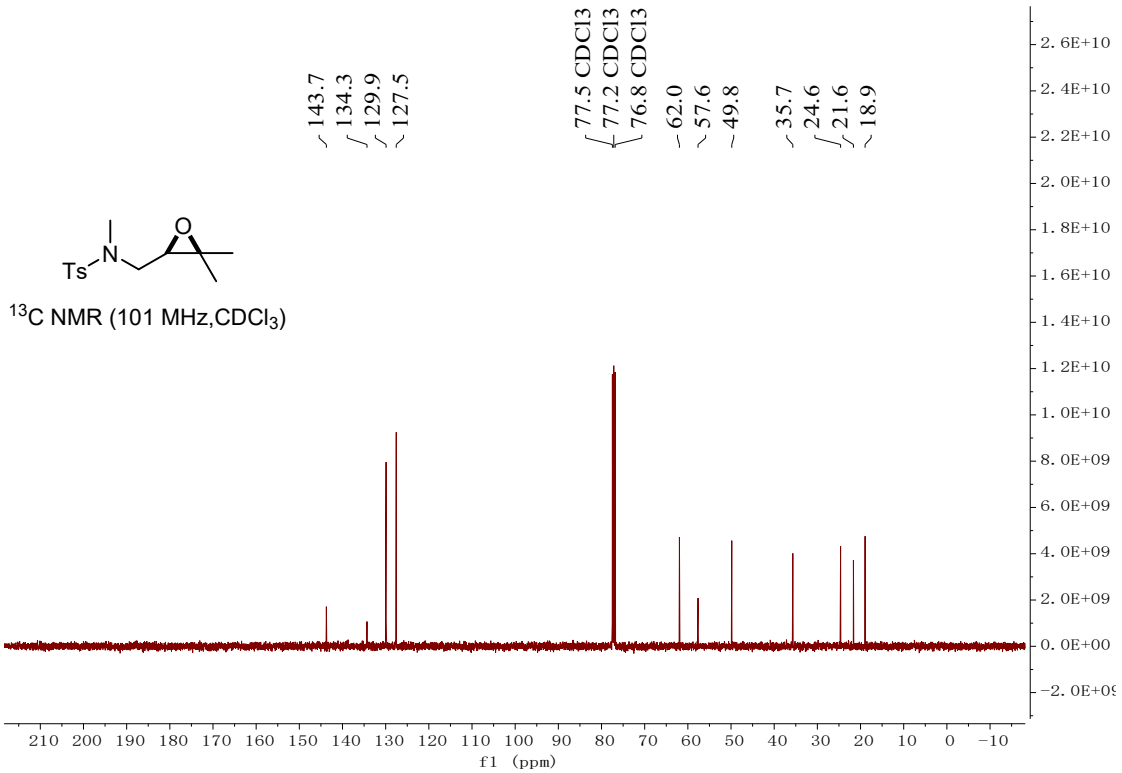

8.39
8.38
8.38
8.36
8.36
8.35
8.09
8.08
8.08
8.07
8.06
7.26 CDCl3
5.30
5.29
3.46
3.45
3.44
3.43
3.43
3.43
3.42
3.41
3.40
3.02
3.01
3.00
3.00
2.99
2.97
2.96
2.88
2.87
2.86
2.85
1.29
1.24
4.0E+07
3.5E+07
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
O
H
N
O
S
O
O2N
1H NMR (400 MHz, CDCl3)
2.04
2.00
1.00
1.04
1.01
1.02
3.01
3.05
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5
f1 (ppm)


150.2
146.0
128.4
124.6
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
61.8
59.5
43.1
24.6
18.9
O2N
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound 29

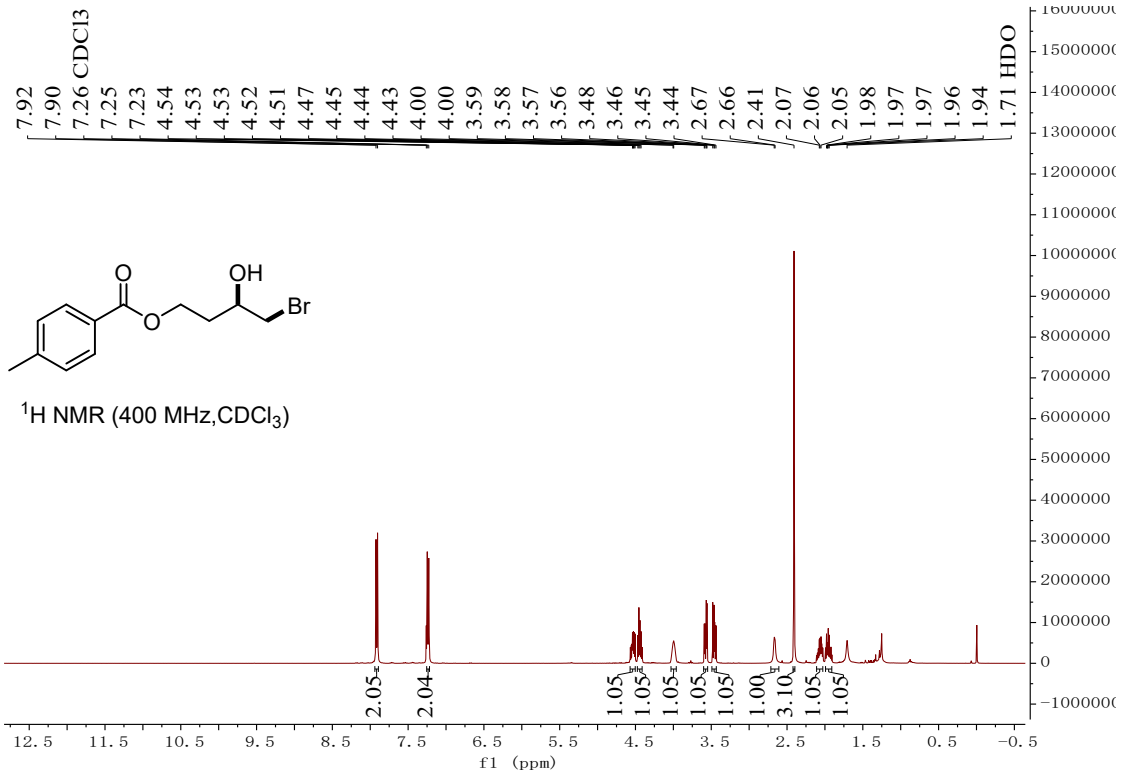


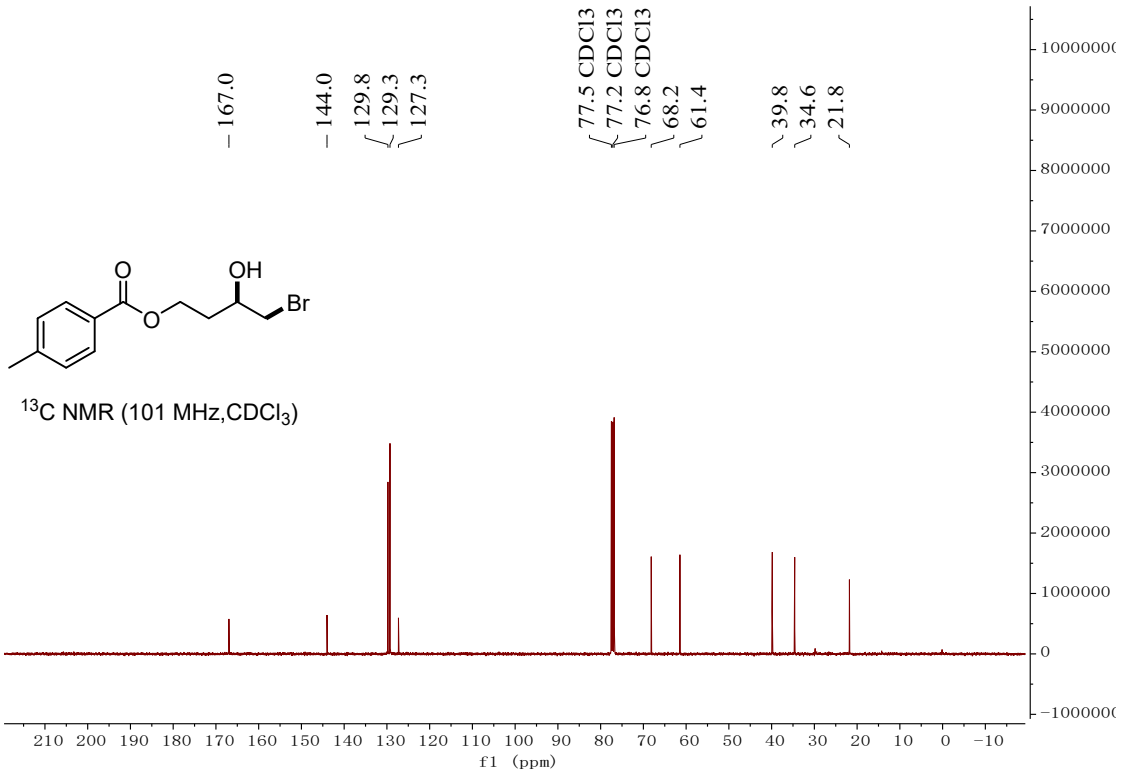
^{1}H NMR (400 MHz, $CDCl_3$)



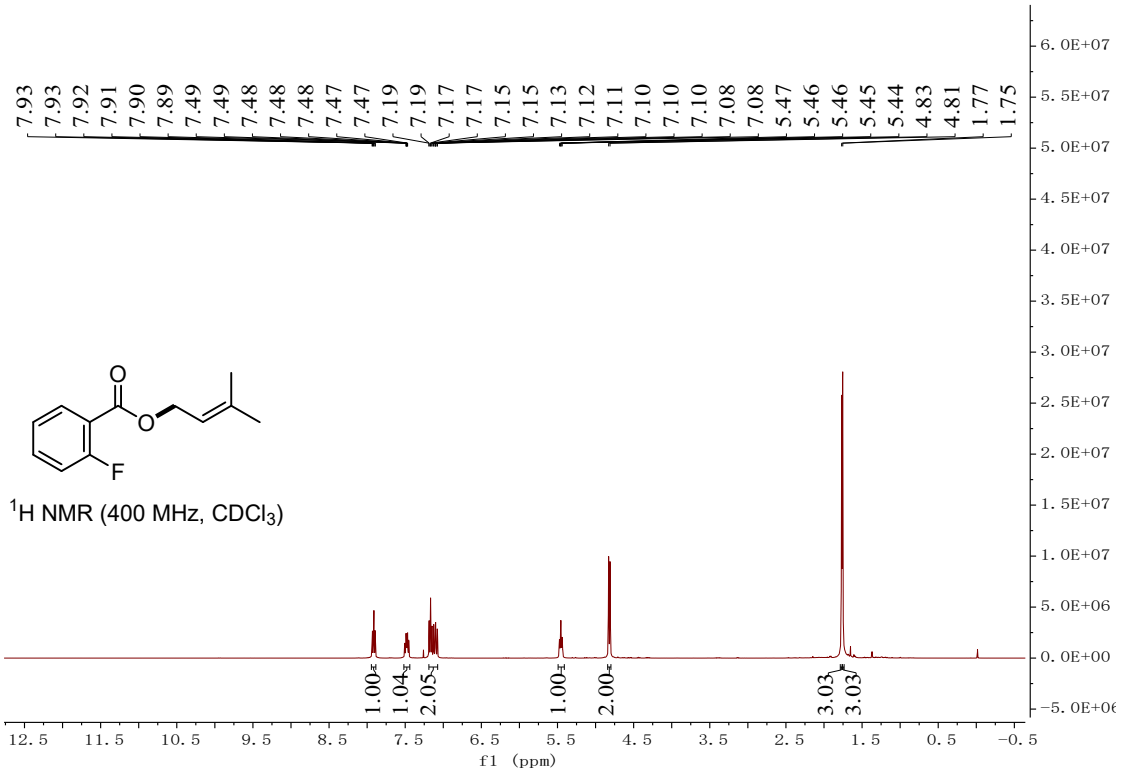
^{13}C NMR (101 MHz,$CDCl_3$)

Compound 37

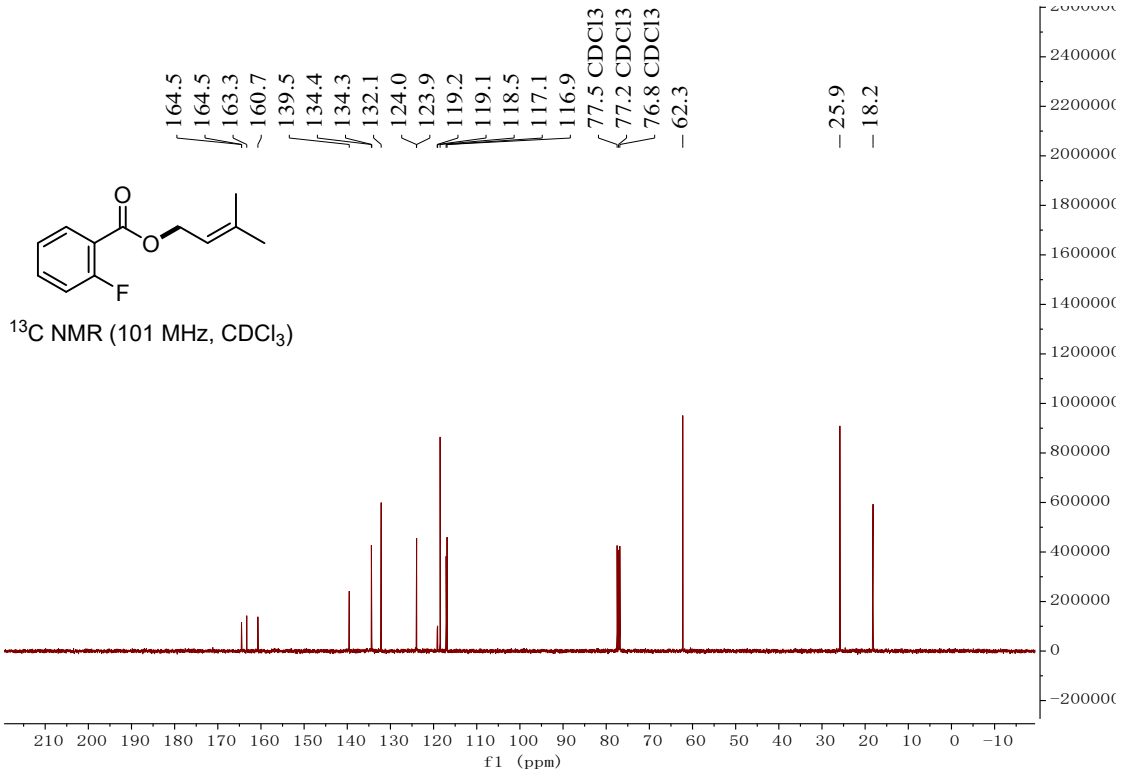

7.92
7.90
7.26 CDCl3
7.25
7.23
4.54
4.53
4.53
4.52
4.51
4.47
4.45
4.44
4.43
4.00
4.00
3.59
3.58
3.57
3.56
3.48
3.46
3.45
3.44
2.67
2.66
2.41
2.07
2.06
2.05
1.98
1.97
1.97
1.96
1.94
1.71 HDO
O
OH
O
Br
1H NMR (400 MHz,CDCl3)
2.05
2.04
1.05
1.05
1.05
1.05
1.05
1.00
3.10
1.05
1.05
f1 (ppm)


167.0
144.0
129.8
129.3
127.3
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
68.2
61.4
39.8
34.6
21.8
O
OH
O
Br
13C NMR (101 MHz,CDCl3)
f1 (ppm)

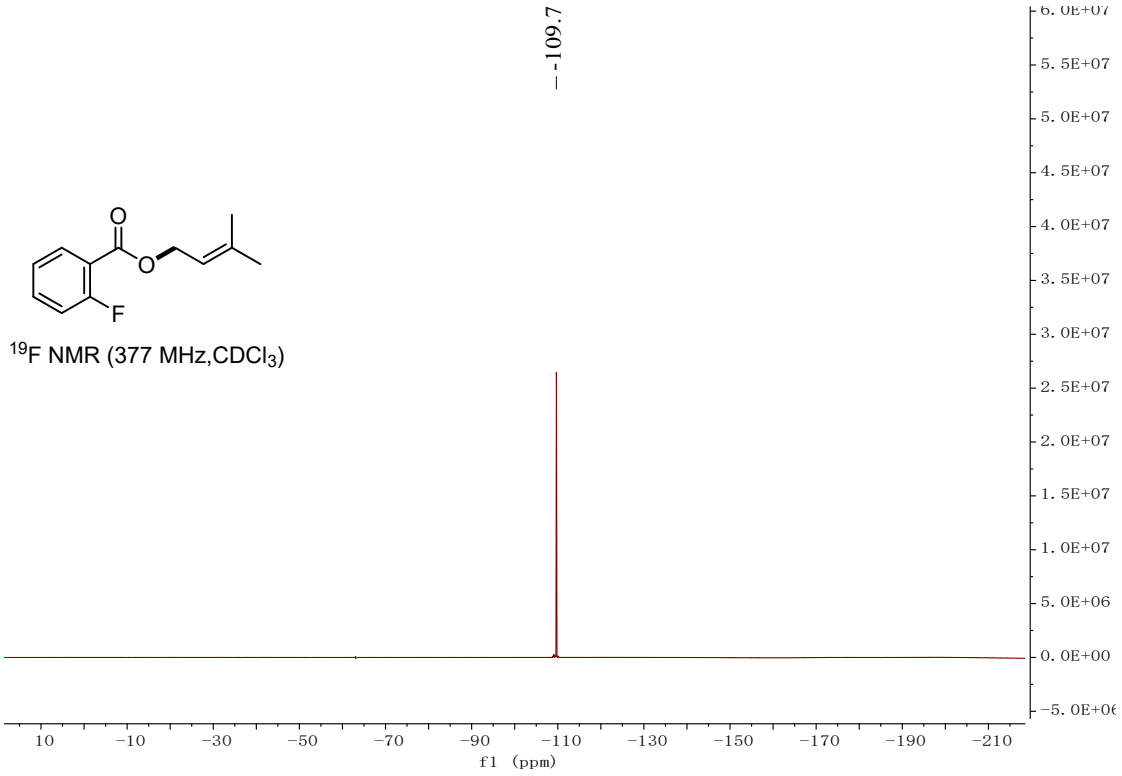
Compound S1



^{1}H NMR (400 MHz, $CDCl_3$)

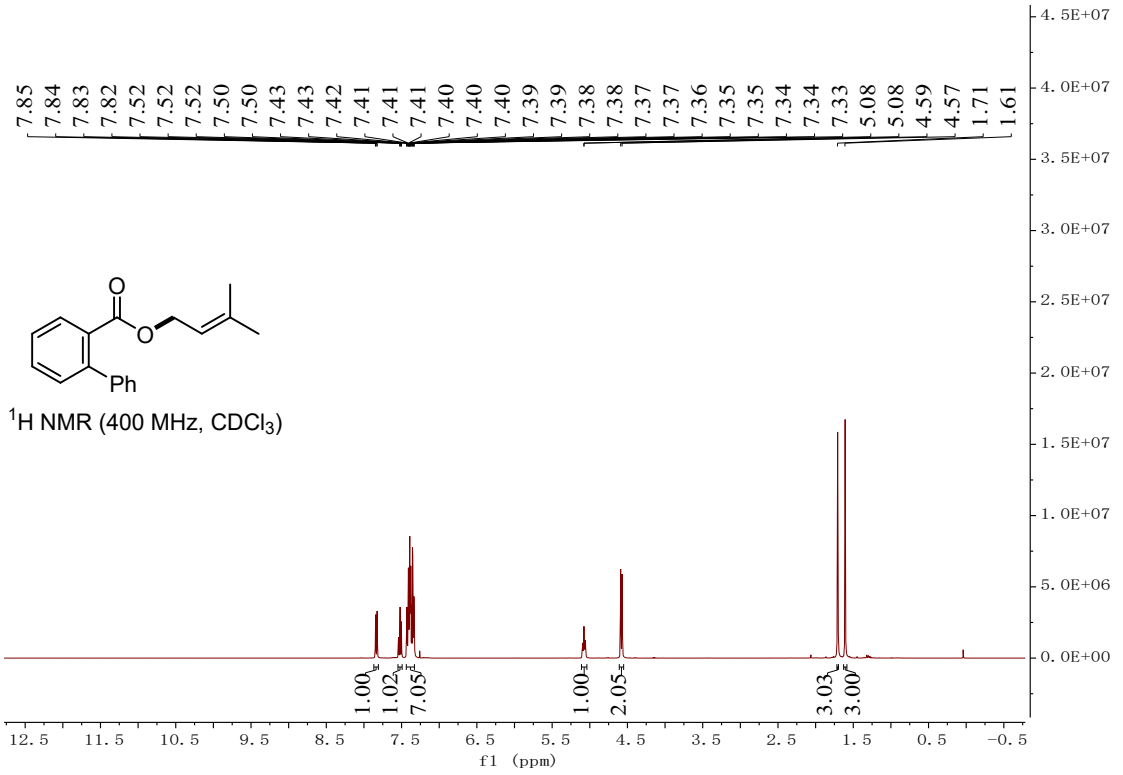


^{13}C NMR (101 MHz, $CDCl_3$)

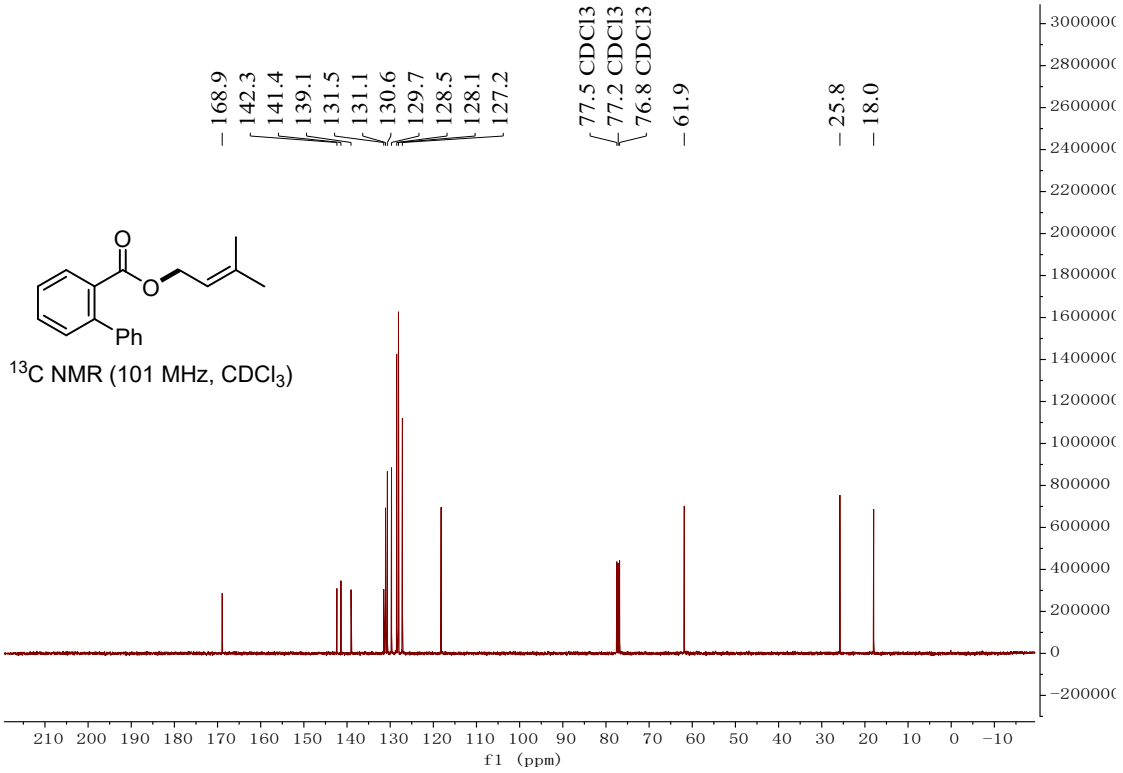


^{19}F NMR (377 MHz,$CDCl_3$)

Compound S2

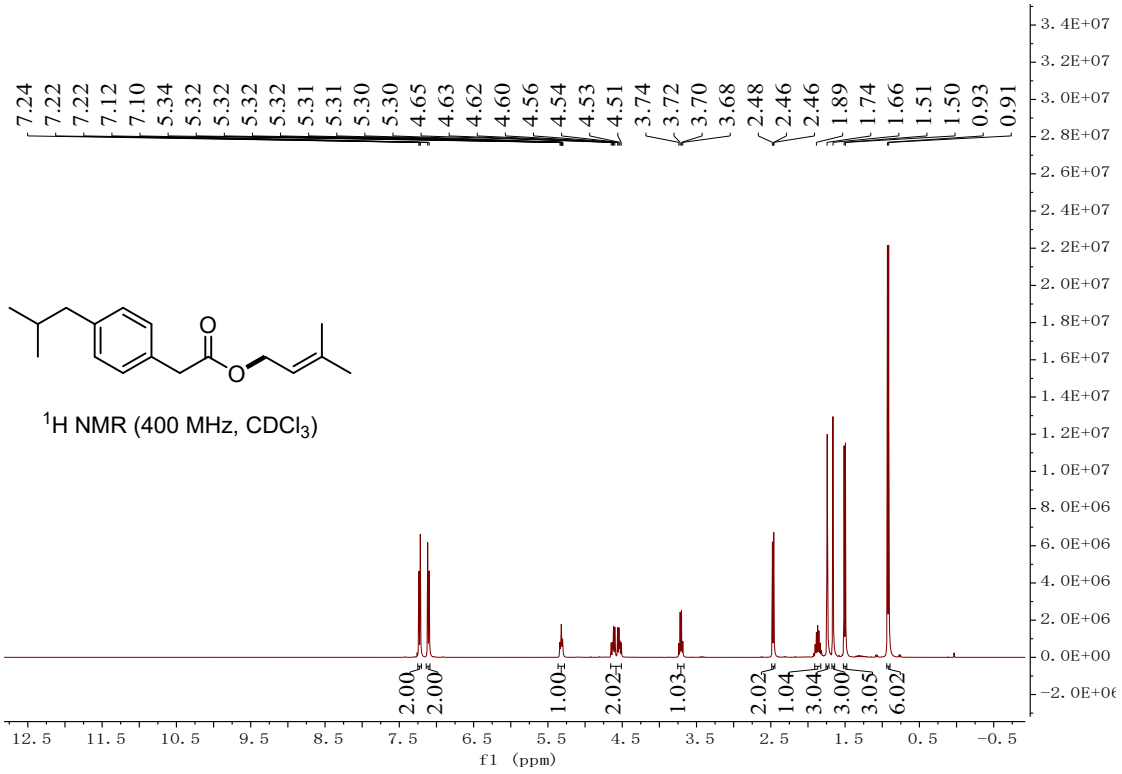


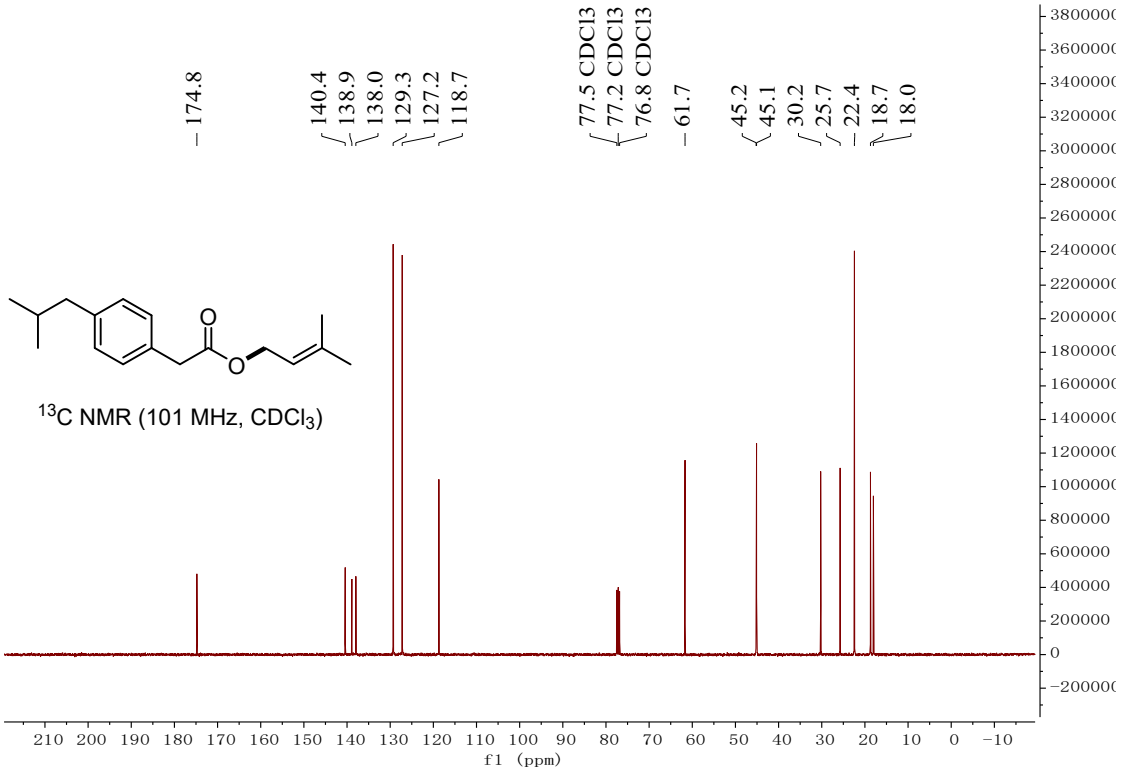
^{1}H NMR (400 MHz, $CDCl_3$)



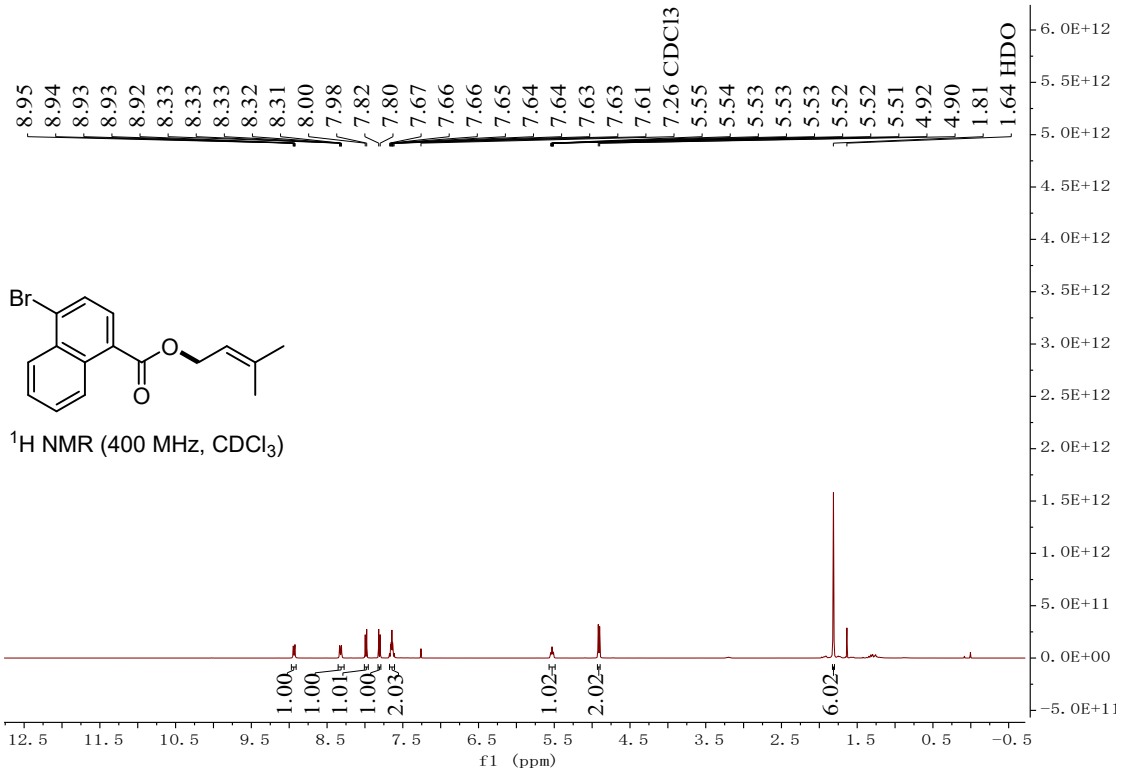
^{13}C NMR (101 MHz, $CDCl_3$)

Compound S3

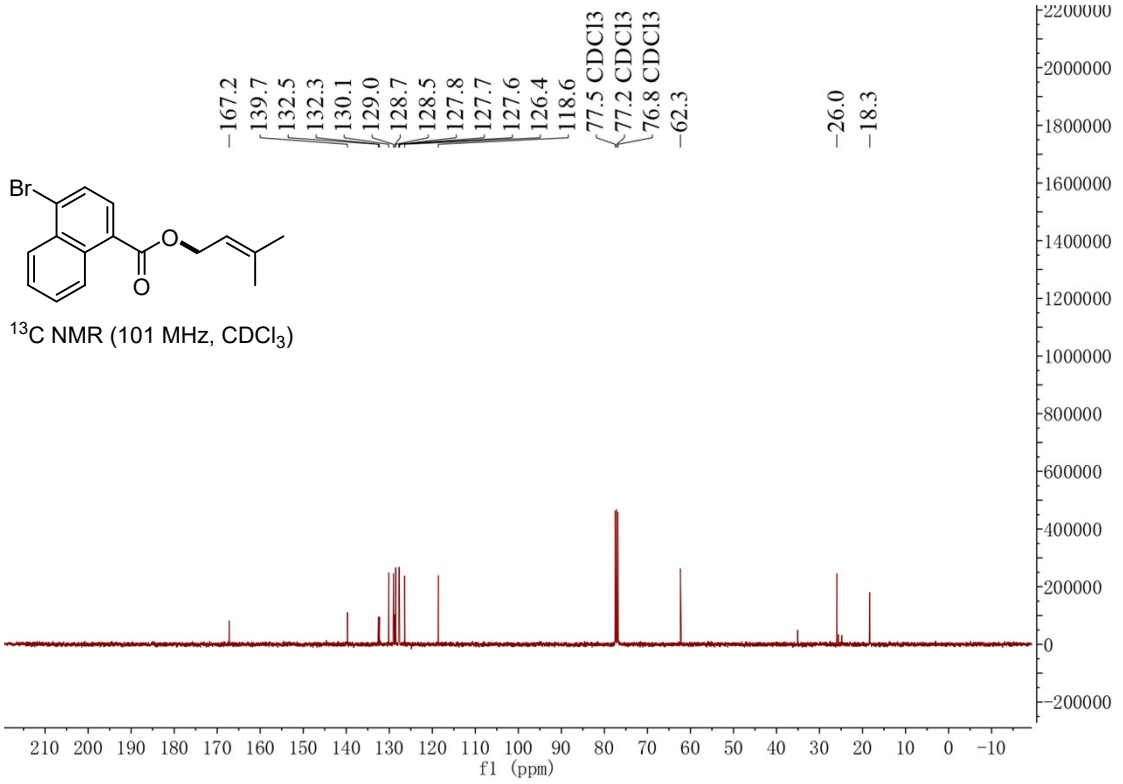

7.24
7.22
7.22
7.12
7.10
5.34
5.32
5.32
5.32
5.32
5.31
5.31
5.30
5.30
4.65
4.63
4.62
4.60
4.56
4.54
4.53
4.51
3.74
3.72
3.70
3.68
2.48
2.46
2.46
1.89
1.74
1.66
1.51
1.50
0.93
0.91
O
O
1H NMR (400 MHz, CDCl3)
2.00
2.00
1.00
2.02
1.03
2.02
1.04
3.04
3.00
3.05
6.02
f1 (ppm)


174.8
140.4
138.9
138.0
129.3
127.2
118.7
77.5 CDCl3
77.2 CDCl3
76.8 CDCl3
61.7
45.2
45.1
30.2
25.7
22.4
18.7
18.0
O
O
13C NMR (101 MHz, CDCl3)
f1 (ppm)

Compound S4

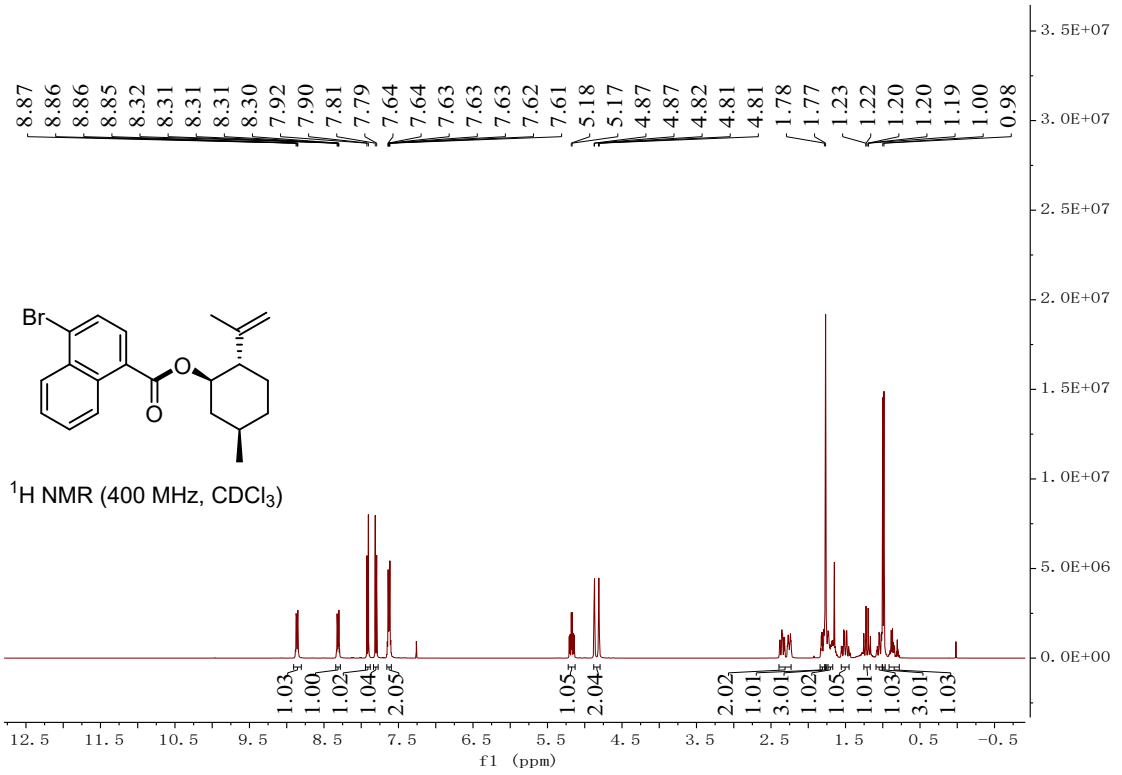


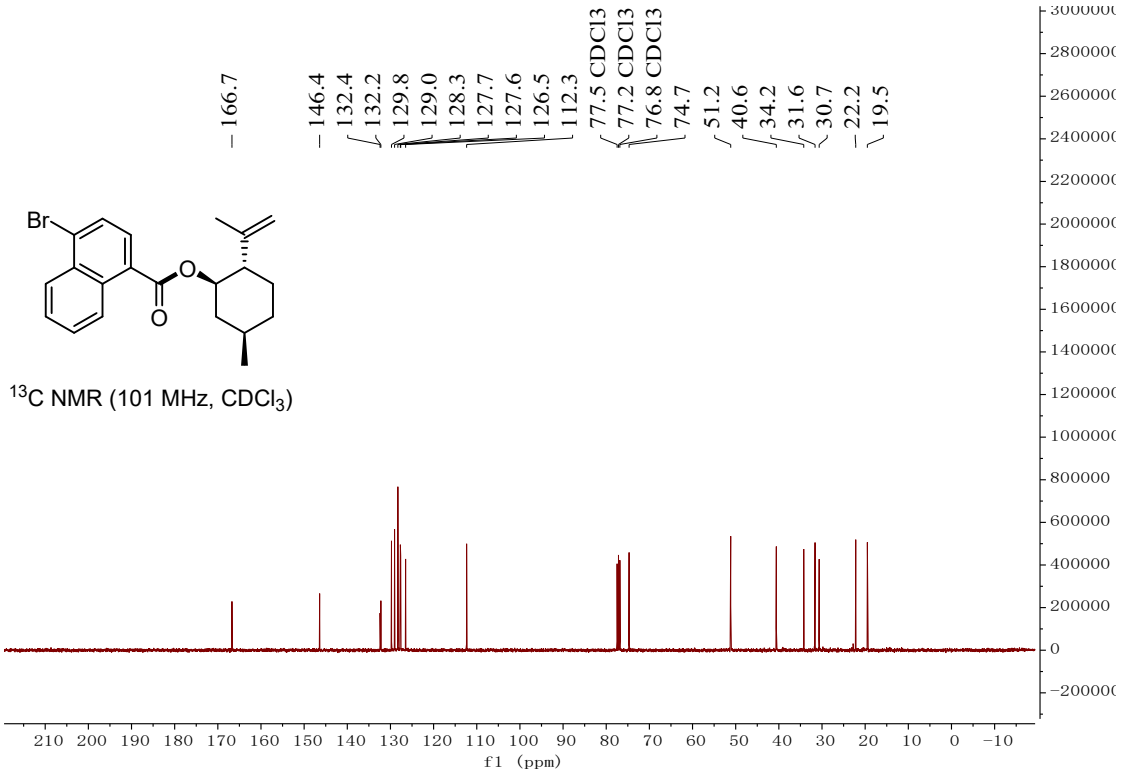
^{1}H NMR (400 MHz, $CDCl_3$)



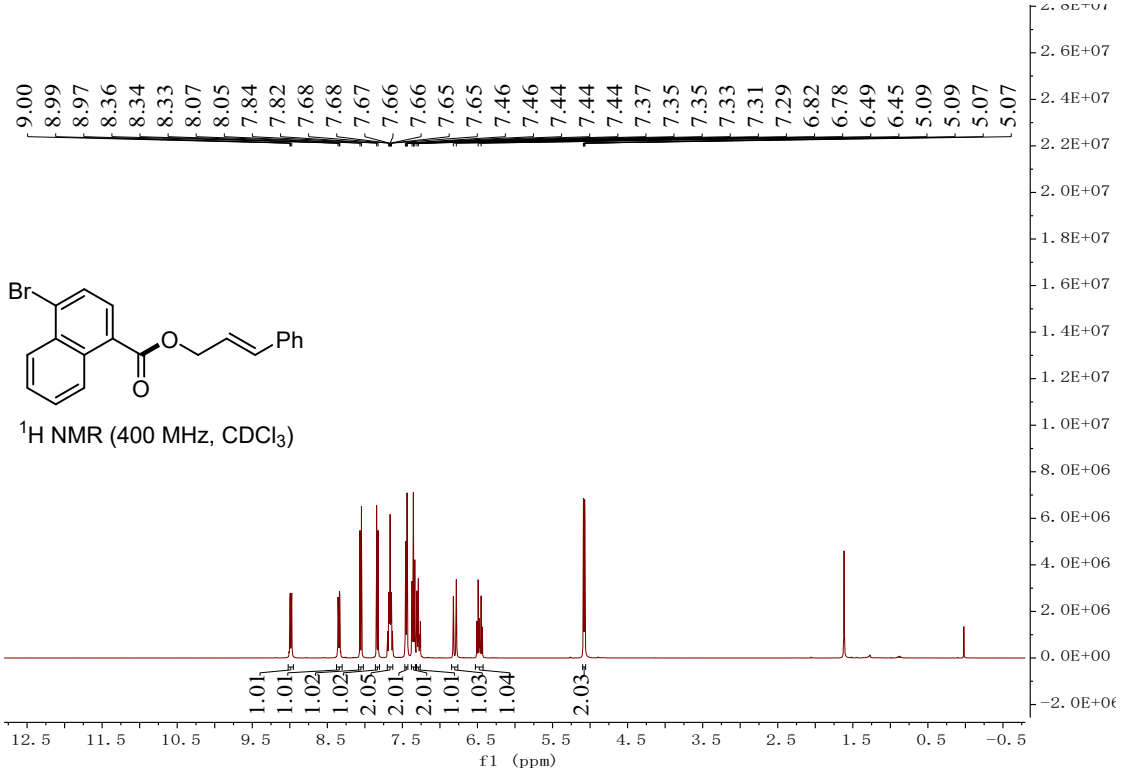
^{13}C NMR (101 MHz, $CDCl_3$)

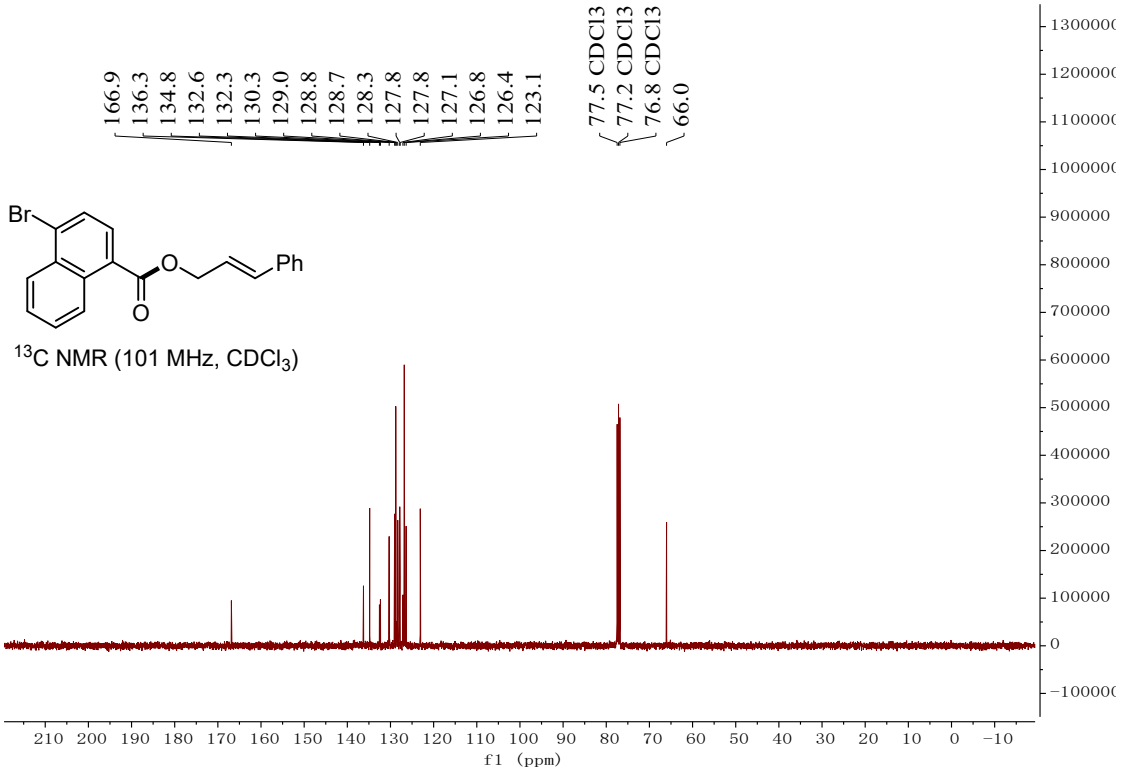
Compound S5


Br
O
O
^{1}H NMR (400 MHz, $CDCl_3$)
8.87 8.86 8.86 8.85 8.32 8.31 8.31 8.31 8.30 7.92 7.90 7.81 7.79 7.64 7.64 7.63 7.63 7.63 7.62 7.61 5.18 5.17 4.87 4.87 4.82 4.81 4.81 1.78 1.77 1.23 1.22 1.20 1.20 1.19 1.00 0.98
1.03 1.00 1.02 1.04 2.05 1.05 2.04 2.02 1.01 3.01 1.02 1.05 1.01 1.03 3.01 1.03
f1 (ppm)


Br
O
O
^{13}C NMR (101 MHz, $CDCl_3$)
166.7 146.4 132.4 132.2 129.8 129.0 128.3 127.7 127.6 126.5 112.3 77.5 CDCl3 77.2 CDCl3 76.8 CDCl3 74.7 51.2 40.6 34.2 31.6 30.7 22.2 19.5
f1 (ppm)

Compound S6


9.00 8.99 8.97 8.36 8.34 8.33 8.07 8.05 7.84 7.82 7.68 7.68 7.67 7.66 7.66 7.65 7.65 7.46 7.46 7.44 7.44 7.44 7.37 7.35 7.35 7.33 7.31 7.29 6.82 6.78 6.49 6.45 5.09 5.09 5.07 5.07
Br
O
O
Ph
1H NMR (400 MHz, CDCl3)
1.01 1.01 1.02 1.02 2.05 2.01 2.01 1.01 1.03 1.04 2.03
f1 (ppm)


166.9 136.3 134.8 132.6 132.3 130.3 129.0 128.8 128.7 128.3 127.8 127.8 127.1 126.8 126.4 123.1
77.5 CDCl3 77.2 CDCl3 76.8 CDCl3 66.0
Br
O
O
Ph
13C NMR (101 MHz, CDCl3)
f1 (ppm)