Palladium-Catalyzed Reductive Electrocarboxylation of Allyl Esters with Carbon Dioxide

(Supporting Information)

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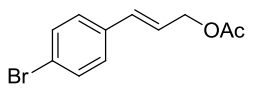
1 General Information

All the electrochemical reduction were performed in an undivided cell equipped with one platinum electrode (1.0×1.0 cm^2) and a magnesium rod as sacrificial anode unless otherwise noted. Solvents and commercially available reagents were used without purification. Column chromatography was performed using either 100-200 Mesh or 300-400 Mesh silica gel. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I_2 chamber.

All the platinum electrode were purchased from Ida Hengsheng Technology Co., Ltd, Tianjin, China. The potentiostat (E36105A, KEYSIGHT) was purchased from Shiqiang Telecom Co., Ltd, Shengzhen, China. The All commercial reagents were purchased from TCI, Sigma-Aldrich, Adamas-beta, 9-Ding chemistry and Energy Chemical of the highest purity grade. They were used without further purification unless specified.

^1H NMR and ^{13}C NMR spectra were recorded on Agilent AV 400, Varian Inova 400 (400 MHz and 100 MHz, respectively).^{19}F NMR spectra were recorded on Agilent AV 400, Varian Inova 400 (376 MHz) instrument and are reported relative to the $CFCl_3$ as the internal standard. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Infrared spectra were obtained on a Bio-Rad FTS-185 instrument. High resolution mass spectra were recorded at the Center for Mass Spectrometry, Shanghai Institute of Organic Chemistry. Analytical and spectral data of all those known compounds are exactly matching with the reported values.

2 Structures of Starting Materials



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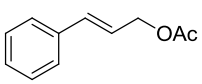

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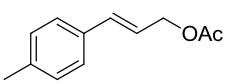

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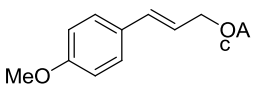

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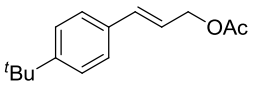

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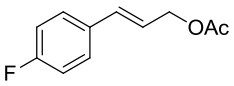

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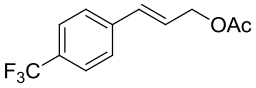

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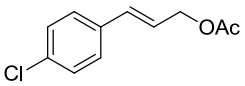

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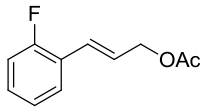

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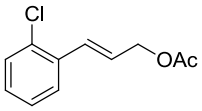

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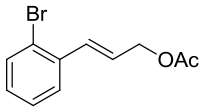

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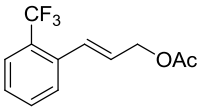

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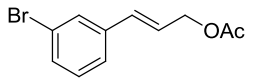

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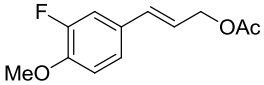

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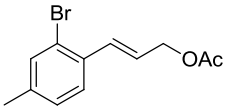

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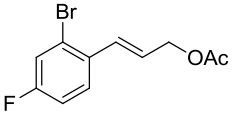

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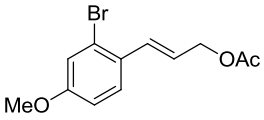

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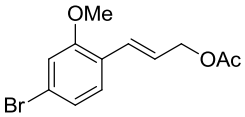

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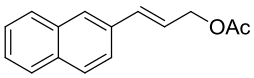

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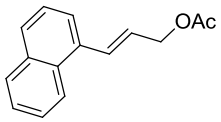

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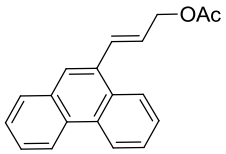
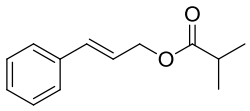


1u

Cinnamyl ester (3a-3g)



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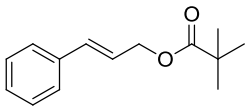

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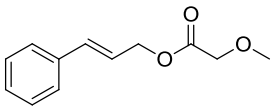

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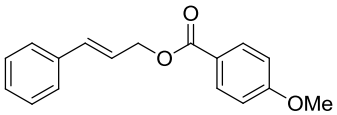

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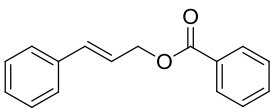

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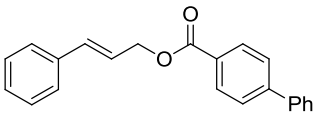

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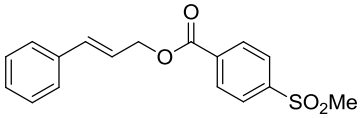
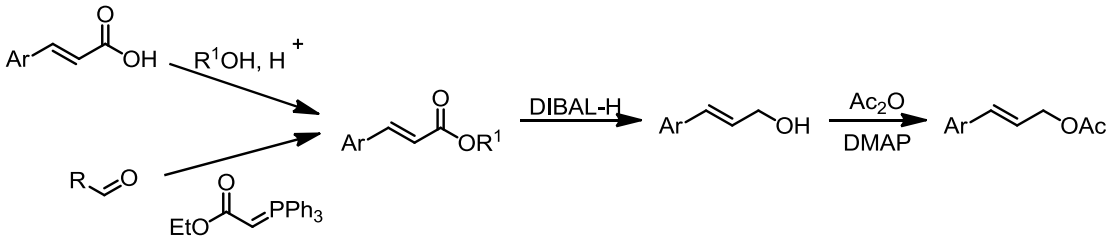


3g

3 Synthesis and Characterization of Starting Materials

General scheme 1 for the synthesis of 1a, 1c-1u



General Procedure A: Synthesis of α, β-Unsaturated Esters from Aldehydes:
To a stirred solution of the aldehyde (1.0 equiv) in CH_2Cl_2 (10 mL/g aldehyde) was added ethyl 2- (triphenylphosphoranylidene)acetate (1.05 equiv). The reaction was stirred overnight at rt, concentrated *in vacuo*, the residue triturated with PE / Et_2O (9:1), and the solids removed by filtration. The solvent was removed *in vacuo* and the crude residue purified by flash chromatography on silica gel to leave the pure α,β-unsaturated esters.

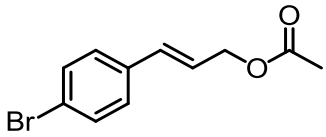
General Procedure B: Synthesis of α, β-Unsaturated Esters from Acids:
To a stirred solution of the α,β-unsaturated acid (1.0 equiv) in ethanol (10 mL / g acid) was added conc. H_2SO_4 (0.1 mL / g acid). The reaction was heated at reflux for 3 h, allowed to cool, and concentrated *in vacuo*. The residue was neutralised with $NaHCO_3$ (sat. aq.), extracted with EtOAc (3 equal volume) and the combined organics washed with brine (equal volume). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo* to leave the pure α,β-unsaturated esters.

General Procedure C: Synthesis of allyl alcohol
To a stirred solution of the α, β-unsaturated ester (1.0 equiv) in anhydrous CH_2Cl_2 (0.2 M) at −78 °C under N_2 was added DIBAL-H (1.0-1.2 M in toluene *or* hexane, 2.2 equiv) dropwise. The reaction was stirred for 1.5 h at −78 °C, and quenched with NaOH (10% aq.) (equal volume). The resultant mixture was allowed to warm to rt and stirred for 1 h. The layers were separated and the aqueous layer extracted with CH_2Cl_2 (2 equal volume). The combined organics were washed with brine (equal volume), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to leave the pure allylic alcohols.

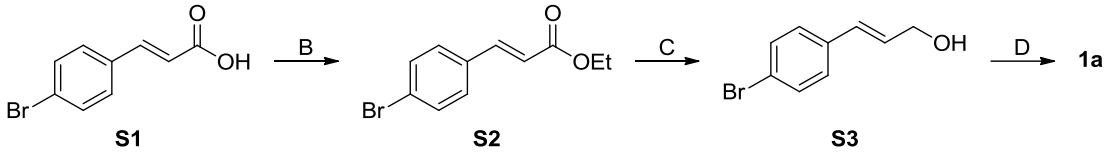
General Procedure D: Synthesis of allyl acetate
To a stirred solution of allylic alcohol in CH_2Cl_2 (1.1M) was added Ac_2O (2.0 equiv) and DMAP (0.05 equiv). The reaction was stirred at room temperature for 1h, and then CH_3OH (8.0 equiv) was added and stirring continued for a further 1h. The reaction was mixture was taken up in hexanes (2.5 equal volume DCM)， successively washed with H_2O and a sat. $NaHCO_3$ solution (2 x equal volume DCM), and dried over $MgSO_4$. The solution was removed under vacuum and the crude product was purified by

chromatography on SiO_2 with hexane/EtOAc to afford the product

(E)-3-(4-Bromophenyl)allyl acetate (1a) [1]



Route for **1a**

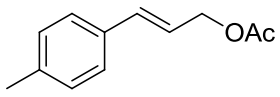


Following general procedure B, the reaction of (E)-3-(4-Bromophenyl)acrylic acid(**S1**) (5.0 g, 22.0 mmol, 1.0 equiv) with conc. H_2SO_4 (0.50 mL) in EtOH (50 mL) gave the title compound **S2** (5.15 g, 20.2 mmol, 92%) as a colorless oil that was used without further purification.

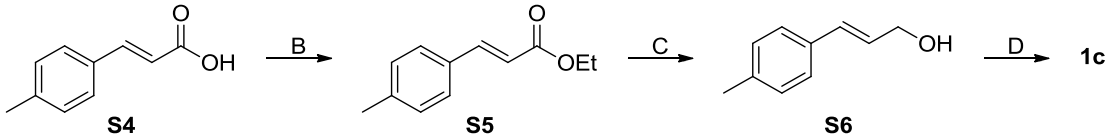
Following general procedure C, the reaction of (E)-ethyl 3-(4-Bromophenyl)acrylate (**S2**) (5.10 g, 20.0 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (100 mL) with DIBAL-H (1.2 M in toluene, 36.7 mL, 44.0 mmol, 2.2 equiv) gave the title compound **S3** (4.81 g, 17.5 mmol, 88%) as a white solid that was used without further purification.

Following general procedure D, the reaction of (E)-3-(4-Bromophenyl)prop-2-en-1-ol (**S3**) (5.00 g, 22.0 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) with Ac_2O (4.30 mL,44.0 mmol, 2.0 equiv) and DMAP (133.6 mg, 1.1 mmol, 0.05 equiv) gave the title compound **1a** (5.40 g, 21.2 mmol, 96%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.8 Hz, 2H), 7.23 (d, *J* = 6.8 Hz, 2H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.34–6.13 (m, 1H), 4.69 (d, *J* = 6.3 Hz, 2H), 2.08 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.48, 135.10, 132.54, 131.64, 128.08, 124.09, 121.77, 64.70, 20.89.

(E)-3-(p-Tolyl)allyl acetate (1c) [2]



Route for **1c**



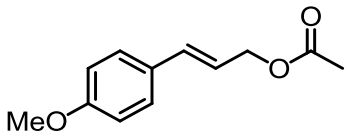
Following general procedure B, the reaction of (E)-3-(p-Tolyl)acrylic acid (**S4**) (5.0 g, 30.8 mmol, 1.0 equiv) with conc. H_2SO_4 (0.50 mL) in EtOH (50 mL) gave the title compound **S5** (5.74 g, 30.2 mmol, 98%) as a colorless oil that was used without further

purification.

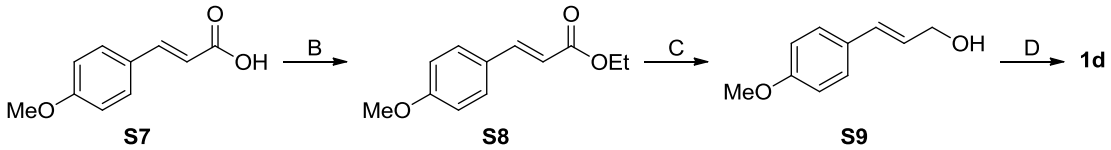
Following general procedure C, the reaction of (E)-ethyl 3-(p-Tolyl)acrylate (**S5**) (5.70 g, 30.0 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (150 mL) with DIBAL-H (1.0 M in toluene, 66.0 mL, 66.0 mmol, 2.2 equiv) gave the title compound **S6** (4.36 g, 29.4 mmol, 98%) as a white solid that was used without further purification.

Following general procedure D, the reaction of (E)-3-(p-Tolyl)prop-2-en-1-ol (**S6**) (4.3 g, 29.0 mmol, 1.0 equiv) in CH_2Cl_2 (25 mL) with Ac_2O (5.7 mL,58.0 mmol, 2.0 equiv) and DMAP (177.1 mg, 1.45 mmol, 0.05 equiv) gave the title compound **1c** (4.30 g, 22.6 mmol, 78%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.24 (dt, *J* = 15.9, 6.5 Hz, 1H), 4.72 (d, *J* = 6.6 Hz, 2H), 2.34 (s, 3H), 2.10 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.76, 137.91, 134.22, 133.43, 129.32, 126.56, 122.08, 65.22, 21.22, 20.97.

(E)-3-(4-Methoxyphenyl)allyl acetate (1d) [2]



Route for **1d**



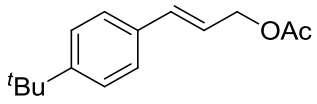
Following general procedure B, the reaction of (E)-3-(4-Methoxyphenyl)acrylic acid (**S7**) (5.0 g, 28.1 mmol, 1.0 equiv) with conc. H_2SO_4 (0.50 mL) in EtOH (50 mL) gave the title compound **S8** (5.03 g, 24.4 mmol, 87%) as a white solid that was used without further purification

Following general procedure C, the reaction of (E)-ethyl-3-(4-Methoxyphenyl)acrylate (**S8**) (3.3 g, 16.0 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (80 mL) with DIBAL-H (1.0 M in hexane, 35.2 mL, 35.2 mmol, 2.2 equiv) gave the title compound **S9** (2.2 g, 14.8 mmol, 93%) as a white solid that was used without further purification.

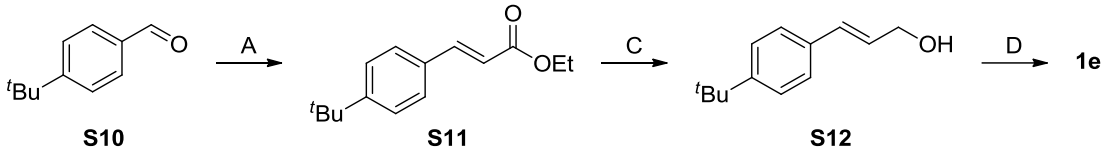
Following general procedure D, the reaction of (E)-3-(4-Methoxyphenyl)prop-2-en-1-ol (**S9**) (2.0 g, 13.5 mmol, 1.0 equiv) in CH_2Cl_2 (13 mL) with Ac_2O (2.60 mL,27.0 mmol, 2.0 equiv) and DMAP (83.1 mg, 0.68 mmol, 0.05 equiv) gave the title compound **1d** (1.8 g, 8.8 mmol, 65%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.59 (d, *J* = 15.8 Hz, 1H), 6.14 (dt, *J* = 15.8, 6.6 Hz, 1H), 4.69 (d, *J* = 6.6 Hz, 2H), 3.79 (s, 3H), 2.08 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.84, 159.56, 133.98, 128.89,

127.84, 120.79, 113.98, 77.50, 77.18, 76.86, 65.33, 55.20, 20.99.

(E)-3-(4-(tert-Butyl)phenyl)allyl acetate (1e)



Route for **1d**



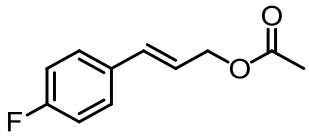
Following general procedure A, the reaction of 4-(tert-butyl)benzaldehyde (**S10)** (4.87 g, 30.0 mmol, 1.0 equiv) with the phosphorane (10.90 g, 31.5 mmol, 1.05 equiv) in CH_2Cl_2 (50 mL) gave the title compound **S11** (6.06 g, 26.1 mmol, 87%) as a white solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(4-(tert-Butyl)phenyl)acrylate (**S11**) (4.00 g, 17.2 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (86 mL) with DIBAL-H (1.0 M in hexane, 37.9 mL, 37.9 mmol, 2.2 equiv) gave the title compound **S12** (3.2 g, 16.8 mmol, 98%) as a white solid that was used without further purification.

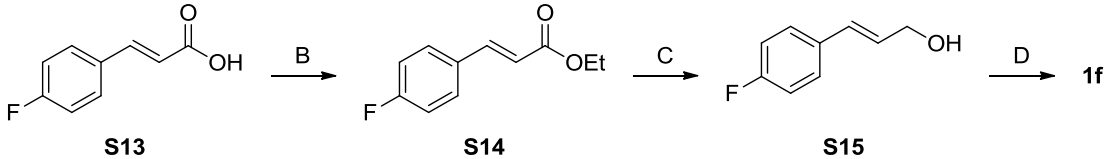
Following general procedure D, the reaction of (E)-3-(4-(tert-Butyl)phenyl)prop-2-en-1-ol (**S12**) (3.20 g, 16.8 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) with Ac_2O (3.20 mL,33.6 mmol, 2.0 equiv) and DMAP (102.6 mg, 0.84 mmol, 0.05 equiv) gave the title compound **1e** (3.79 g, 16.3 mmol, 97%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.33 (m, 4H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.28 (dt, *J* = 15.9, 6.5 Hz, 1H), 4.74 (d, *J* = 6.5 Hz, 2H), 2.11 (s, 3H), 1.34 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.77, 151.17, 134.13, 133.45, 126.40, 125.53, 122.36, 65.23, 34.61, 31.30, 21.00.

(E)-3-(4-Fluorophenyl)allyl acetate (1f) [1]



Route for **1f**

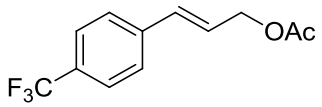


Following general procedure B, the reaction of (E)-3-(4-Fluorophenyl)acrylic acid (**S13**) (5.0 g, 30.1 mmol, 1.0 equiv) with conc. H_2SO_4 (0.50 mL) in EtOH (50 mL) gave the title compound **S14** (4.97 g, 25.6 mmol, 85%) as a colorless oil that was used without further purification.

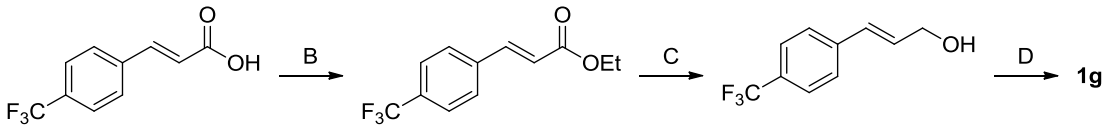
Following general procedure C, the reaction of (E)-ethyl-3-(4-Fluorophenyl)acrylate (**S14**) (4.90 g, 25.2 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (120 mL) with DIBAL-H (1.0 M in toluene, 56.0 mL, 55.4 mmol, 2.2 equiv) gave the title compound **S15** (3.79 g, 24.9 mmol, 99%) as a white solid that was used without further purification.

Following general procedure D, the reaction of (E)-3-(4-Fluorophenyl)prop-2-en-1-ol (**S15**) (2.0 g, 13.1 mmol, 1.0 equiv) in CH_2Cl_2 (12 mL) with Ac_2O (2.5 mL,26.2 mmol, 2.0 equiv) and DMAP (80.3 mg, 0.66 mmol, 0.05 equiv) gave the title compound **1f** (2.02 g, 10.4 mmol, 79%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.26 (m, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.18 (dt, *J* = 15.9, 6.5 Hz, 1H), 4.69 (d, *J* = 6.5 Hz, 2H), 2.08 (s, 3H). **^{13}C NMR** (101 MHz, cdcl$_3$) δ 170.71, 162.49 (d, *J* = 247.4 Hz), 132.87, 132.36 (d, *J* = 3.3 Hz), 128.13 (d, *J* = 8.1 Hz), 122.93 (d, *J* = 2.3 Hz), 115.46 (d, *J* = 21.6 Hz), 64.87, 20.81. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.68.

(E)-3-(4-(Trifluoromethyl)phenyl)allyl acetate (1g) [1]



Route for **1g**



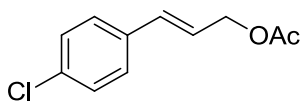
S16 **S17** **S18**

Following general procedure B, the reaction of (E)-3-(4-(Trifluoromethyl)phenyl)acrylic acid (**S16**) (2.0 g, 9.25 mmol, 1.0 equiv) with conc. H_2SO_4 (0.20 mL) in EtOH (20 mL) gave the title compound **S17** (2.20 g, 9.01 mmol, 97%) as a white solid that was used without further purification.

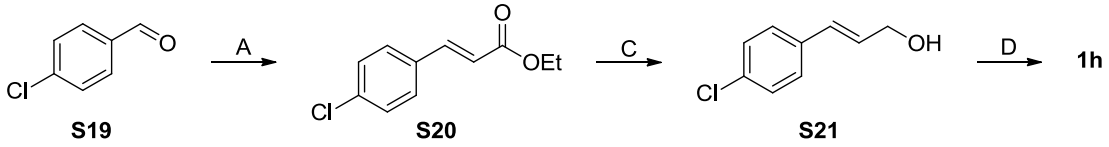
Following general procedure C, the reaction of (E)-ethyl 3-(4-(Trifluoromethyl)phenyl)acrylate (**S17**) (2.16 g, 8.84 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (45 mL) with DIBAL-H (1.2 M in toluene, 16.21 mL, 19.45 mmol, 2.2 equiv) gave the title compound **S18** (1.70 g, 8.40 mmol, 95%) as a white solid that was used without further purification.

Following general procedure D, the reaction of (E)-3-(4-(Trifluoromethyl)phenyl)prop-2-en-1-ol (**S18**) (1.65 g, 8.16 mmol, 1.0 equiv) in CH_2Cl_2 (8 mL) with Ac_2O (1.53 mL,16.32 mmol, 2.0 equiv) and DMAP (49.8 mg, 0.41 mmol, 0.05 equiv) gave the title compound **1g** (1.91 g, 7.83 mmol, 96%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.36 (dt, *J* = 15.9, 6.2 Hz, 1H), 4.74 (d, *J* = 6.2 Hz, 2H), 2.10 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.64.

(E)-3-(4-Chlorophenyl)allyl acetate (1h) [1]



Route for **1h**



S19 **S20** **S21**

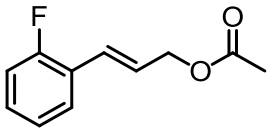
Following general procedure A, the reaction of 4-Chlorobenzaldehyde (**S19**) (2.81 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH_2Cl_2 (30 mL) gave the title compound **S20** (4.17 g, 19.8 mmol, 99%) as a colorless oil that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl 3-(4-Chlorophenyl)acrylate (**S20**) (4.10 g, 19.5 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (90 mL) with DIBAL-H (1.0 M in toluene, 43.0 mL, 42.9 mmol, 2.2 equiv) gave the title compound **S21** (3.22 g, 19.1 mmol, 98%) as a colorless oil that was used without further purification.

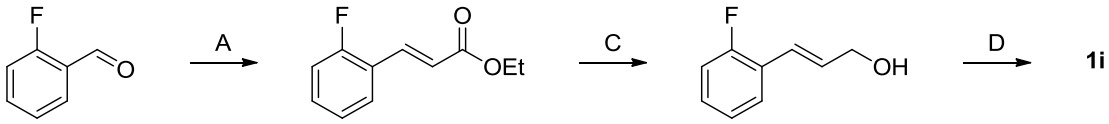
Following general procedure D, the reaction of (E)-3-(4-Chlorophenyl)prop-2-en-1-ol (**S21**) (3.00 g, 17.8 mmol, 1.0 equiv) in CH_2Cl_2 (16 mL) with Ac_2O (3.5 mL,35.6 mmol, 2.0 equiv) and DMAP (108.7 mg, 0.89 mmol, 0.05 equiv) gave the title compound **1h** (3.18 g, 15.1 mmol, 85%) as a colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.18 (m, 4H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.24 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.70 (d, *J* = 6.4 Hz, 2H), 2.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.69, 134.68, 133.63, 132.68, 128.73, 127.78, 123.90, 64.79, 20.92.

(E)-3-(2-Fluorophenyl)allyl acetate (1i) [2]



Route for **1i**



S22 **S23** **S24**

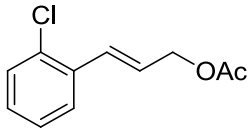
Following general procedure A, the reaction of 2-Fluorobenzaldehyde (**S22**) (2.5 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH_2Cl_2 (25 mL) gave the title compound **S23** (3.50 g, 18.0 mmol, 90%) as a colorless oil that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl 3-(2-Fluorophenyl)acrylate (**S23**) (3.50 g, 18.0 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (90 mL) with DIBAL-H (1.0

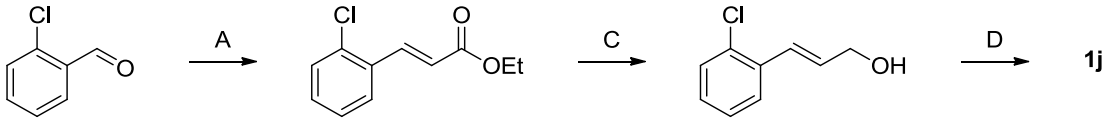
M in toluene, 39.6 mL, 39.6 mmol, 2.2 equiv) gave the title compound **S24** (2.50 g, 16.4 mmol, 91%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(2-Fluorophenyl)prop-2-en-1-ol (**S24**) (2.50 g, 16.4 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) with Ac_2O (3.1 mL,32.8 mmol, 2.0 equiv) and DMAP (100.1 mg, 0.82 mmol, 0.05 equiv) gave the title compound **1i** (2.84 g, 14.6 mmol, 89%) as a colorless oil. **mixture of *cis* and *trans* isomers**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.6 Hz, 1H), 7.20–7.11 (m, 1H), 7.06–6.93 (m, 2H), 6.74 (d, *J* = 16.1 Hz, 1H), 6.32 (dt, *J* = 16.0, 6.2 Hz, 1H), 4.68 (d, *J* = 6.2 Hz, 2H), 2.04 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.69, 160.26 (d, *J* = 249.7 Hz), 129.31 (d, *J* = 8.5 Hz), 127.54 (d, *J* = 3.6 Hz), 126.21 (d, *J* = 3.5 Hz), 125.84 (d, *J* = 5.1 Hz), 124.11 (d, *J* = 3.6 Hz), 123.95 (d, *J* = 12.1 Hz), 115.70 (d, *J* = 22.1 Hz), 65.00, 20.82. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.70 – -121.34 (m, 1F).

(E)-3-(2-Chlorophenyl)allyl acetate (1j) [3]



Route for **1j**



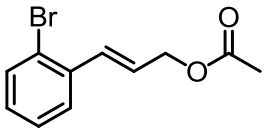
S25 **S26** **S27**

Following general procedure A, the reaction of 2-Chlorobenzaldehyde (**S25**) (2.81 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH_2Cl_2 (30 mL) gave the title compound **S26** (3.79 g, 18.0 mmol, 90%) as a colorless oil that was used without further purification.

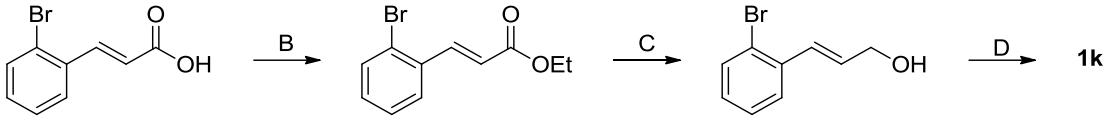
Following general procedure C, the reaction of (E)-ethyl 3-(2-Chlorophenyl)acrylate (**S26**) (3.70 g, 17.6 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (80 mL) with DIBAL-H (1.0 M in toluene, 39.0 mL, 38.7 mmol, 2.2 equiv) gave the title compound **S27** (2.82 g, 16.7 mmol, 95%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(2-Chlorophenyl)prop-2-en-1-ol (**S27**) (2.70 g, 16.0 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) with Ac_2O (3.2 mL,32.0 mmol, 2.0 equiv) and DMAP (97.7 mg, 0.80 mmol, 0.05 equiv) gave the title compound **1j** (3.03 g, 14.4 mmol, 90%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.26–7.18 (m, 1H), 7.13 – 7.01 (m, 2H), 6.93 (d, *J* = 15.9 Hz, 1H), 6.23–6.07 (m, 1H), 4.64 (d, *J* = 4.5, 1.6 Hz, 2H), 1.99 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.38, 134.24, 133.04, 129.59, 129.56, 128.94, 126.86, 126.83, 126.16, 64.64, 20.73.

(E)-3-(2-Bromophenyl)allyl acetate (1k) [3]



Route for **1k**



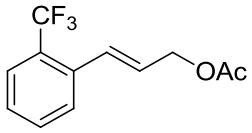
S28 **S29** **S30**

Following general procedure B, the reaction of (E)-3-(2-Bromophenyl)acrylic acid (**S28**) (5.0 g, 22.0 mmol, 1.0 equiv) with conc. H_2SO_4 (0.50 mL) in EtOH (50 mL) gave the title compound **S29** (5.0 g, 19.6 mmol, 89%) as a colorless oil that was used without further purification.

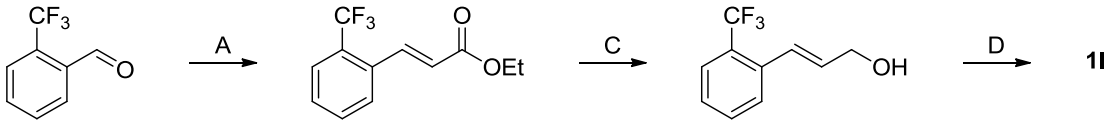
Following general procedure C, the reaction of (E)-ethyl 3-(2-Bromophenyl)acrylate (**S29**) (4.80 g, 18.8 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (95 mL) with DIBAL-H (1.0 M in hexane, 41.4 mL, 41.4 mmol, 2.2 equiv) gave the title compound **S30** (4.70 g, 18.4 mmol, 98%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(2-Bromophenyl)prop-2-en-1-ol (**S30**) (1.6 g, 7.0 mmol, 1.0 equiv) in CH_2Cl_2 (7 mL) with Ac_2O (1.3 mL,14.0 mmol, 2.0 equiv) and DMAP (43.0 mg, 0.35 mmol, 0.05 equiv) gave the title compound **1k** (1.7 g, 6.7 mmol, 95%) as a colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.46, (m, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 15.9 Hz, 1H), 6.21 (dt, *J* = 15.8, 6.2 Hz, 1H), 4.74 (d, *J* = 6.2 Hz, 2H), 2.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.60, 136.03, 132.92, 132.34, 129.26, 127.51, 127.13, 126.26, 123.69, 64.68, 20.93.

(E)-3-(2-(Trifluoromethyl)phenyl)allyl acetate (1l)



Route for **1l**



S31 **S32** **S33**

Following general procedure A, the reaction of 2-Trifluoromethyl)benzaldehyde (**S31**) (3.48 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH_2Cl_2 (35 mL) gave the title compound **S32** (4.20 g, 17.2 mmol, 86%) as a white solid that was used without further purification.

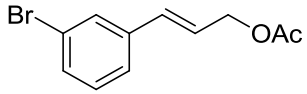
Following general procedure C, the reaction of (E)-ethyl-3-(2-(Trifluoromethyl)phen-

yl)acrylate (**S32**) (4.00 g, 16.4 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (80 mL) with DIBAL-H (1.0 M in toluene, 33.0 mL, 32.8 mmol, 2.2 equiv) gave the title compound **S33** (2.95 g, 14.6 mmol, 89%) as a white solid that was used without further purification.

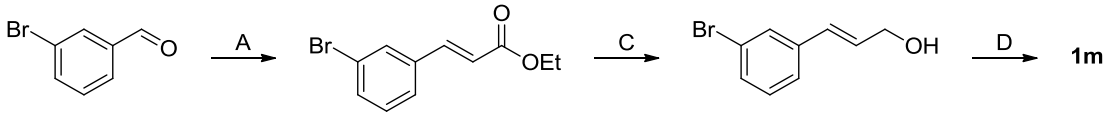
Following general procedure D, the reaction of (E)-3-(2-(Trifluoromethyl)phenyl)prop-2-en-1-ol (**S33**) (2.90 g, 14.3 mmol, 1.0 equiv) in CH_2Cl_2 (13 mL) with Ac_2O (2.80 mL,28.6 mmol, 2.0 equiv) and DMAP (88.0 mg, 0.72 mmol, 0.05 equiv) gave the title compound **1l** (3.00 g, 13.4 mmol, 94%) as a colorless oil. **mixture of *cis* and *trans* isomers**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.60 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 15.9 Hz, 1H), 6.34–6.03 (m, 1H), 4.76 (d, *J* = 5.9 Hz, 2H), 2.12 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -59.54. **HRMS** (ESI-TOF) calcd for $C_{12}H_{15}F_3NO_2$ $[M+NH_4]^+$: 262.1049, found: 262.105.

(E)-3-(3-Bromophenyl)allyl acetate (1m) [4]



Route for **1m**



S34 **S35** **S36**

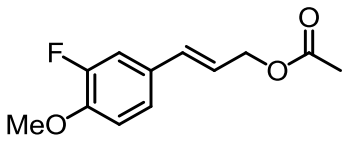
Following general procedure A, the reaction of 3-Bromobenzaldehyde (**S34**) (3.7 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH_2Cl_2 (40 mL) gave the title compound **S35** (4.80 g, 18.8 mmol, 94%) as a colorless oil that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(3-Bromophenyl)acrylate (**S35**) (4.80 g, 18.8 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (100 mL) with DIBAL-H (1.0 M in toluene, 41.4 mL, 41.4 mmol, 2.2 equiv) gave the title compound **S36** (3.2 g, 15.0 mmol, 80%) as a colorless oil that was used without further purification.

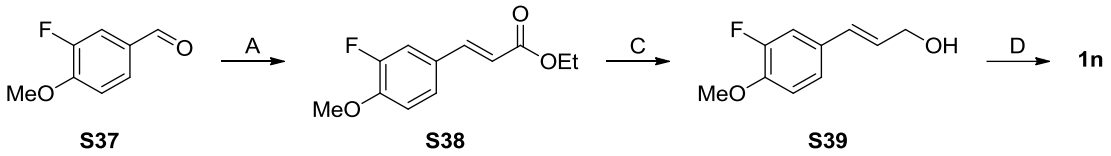
Following general procedure D, the reaction of (E)-3-(3-Bromophenyl)prop-2-en-1-ol (**S36**) (3.20 g, 15.0 mmol, 1.0 equiv) in CH_2Cl_2 (30 mL) with Ac_2O (2.80 mL,30.0 mmol, 2.0 equiv) and DMAP (84.0 mg, 0.75 mmol, 0.05 equiv) gave the title compound **1m** (3.67 g, 14.4 mmol, 96%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.46 (d, *J* = 15.9 Hz, 1H), 6.19 (dt, *J* = 12.8, 6.1 Hz, 1H), 4.64 (d, *J* = 6.2 Hz, 2H), 2.03 (s,3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.70, 138.32, 132.28, 130.84, 130.10, 129.40, 125.23, 124.84, 122.74, 64.64, 20.95.

(E)-3-(3-Fluoro-4-methoxyphenyl)allyl acetate (1n)



Route for **1n**

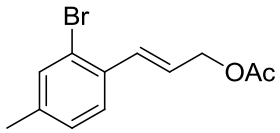


Following general procedure A, the reaction of 3-Fluoro-4-methoxybenzaldehyde (**S37**) (3.1 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH_2Cl_2 (30 mL) gave the title compound **S38** (4.00 g, 17.83 mmol, 89%) as a white solid that was used without further purification.

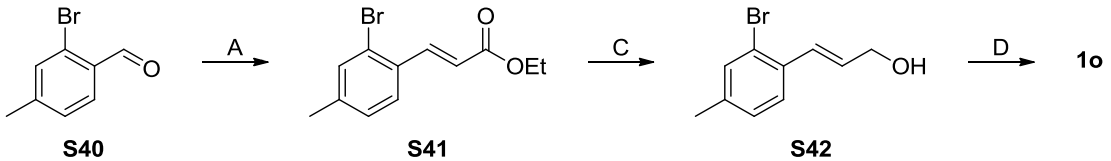
Following general procedure C, the reaction of (E)-ethyl-3-(3-Fluoro-4-methoxyphenyl)acrylate (**S38**) (3.95 g, 17.6 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (90 mL) with DIBAL-H (1.2 M in toluene, 32.3 mL, 38.72 mmol, 2.2 equiv) gave the title compound **S39** (3.06 g, 16.8 mmol, 95%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(3-Fluoro-4-methoxyphenyl)prop-2-en-1-ol (**S3**9) (3.06 g, 16.8 mmol, 1.0 equiv) in CH_2Cl_2 (30 mL) with Ac_2O (3.2 mL,33.6 mmol, 2.0 equiv) and DMAP (94.2 mg, 0.84 mmol, 0.05 equiv) gave the title compound **1n** (3.27 g, 14.6 mmol, 87%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 12.4 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.88 (t, *J* = 8.5 Hz, 1H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.19–6.05 (m, 1H), 4.68 (d, *J* = 6.4 Hz, 2H), 3.86 (s, 3H), 2.08 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.68, 152.26 (d, *J* = 245.5 Hz), 147.44 (d, *J* = 10.9 Hz), 132.64 (d, *J* = 2.2 Hz), 129.55 (d, *J* = 6.5 Hz), 123.00 (d, *J* = 3.3 Hz), 122.27, 113.44 (d, *J* = 18.7 Hz), 113.05 (d, *J* = 2.2 Hz), 64.83, 55.98, 20.79. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -135.24. **HRMS** (EI) calcd for $C_{12}H_1O_3F$: 224.0849, found: 224.0852.

(E)-3-(2-Bromo-4-methylphenyl)allyl acetate (1o)



Route for **1o**



Following general procedure A, the reaction of 2-Bromo-4-methylbenzaldehyde (**S40**) (3.98 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv)

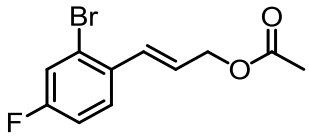
in CH_2Cl_2 (40 mL) gave the title compound **S41** (5.22 g, 19.4 mmol, 97%) as a white solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(2-Bromo-4-methylphenyl)acrylate (**S41**) (5.00 g, 18.6 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (90 mL) with DIBAL-H (1.0 M in toluene, 41.0 mL, 40.9 mmol, 2.2 equiv) gave the title compound **S42** (4.14 g, 18.2 mmol, 98%) as a colorless oil that was used without further purification.

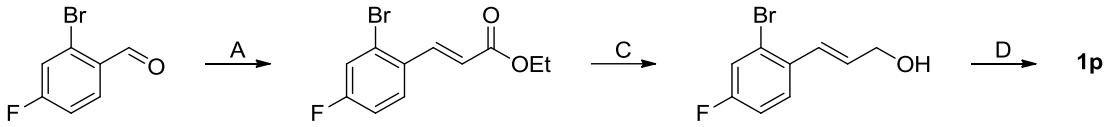
Following general procedure D, the reaction of (E)-3-(2-Bromo-4-methoxyphenyl)prop-2-en-1-ol (**S42**) (4.10 g, 18.1 mmol, 1.0 equiv) in CH_2Cl_2 (16 mL) with Ac_2O (3.5 mL, 36.2 mmol, 2.0 equiv) and DMAP (110.5 mg, 0.91 mmol, 0.05 equiv) gave the title compound **1o** (3.88 g, 14.4 mmol, 80%) as a colorless oil. **mixture of *cis* and *trans* isomers**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.1 Hz, 1H), 7.37 (s, 1H), 7.11–7.04 (m, 1H), 6.95 (d, *J* = 15.7 Hz, 1H), 6.18 (dt, *J* = 15.8, 6.4 Hz, 1H), 4.74 (d, *J* = 6.3 Hz, 2H), 2.30 (s, 3H), 2.10 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.67, 139.58, 133.28, 133.07, 132.39, 128.41, 126.76, 125.13, 123.51, 64.86, 20.95, 20.75. **HRMS** (ESI-TOF) calcd for $C_{12}H_{17}BrNO_2$ $[M+NH_4]^+$: 286.0437, found: 284.0436.

(E)-3-(2-Bromo-4-fluorophenyl)allyl acetate (1p)



Route for **1p**



S43 **S44** **S45**

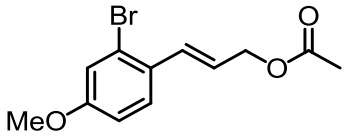
Following general procedure A, the reaction of 2-Bromo-4-fluorobenzaldehyde (**S43**) (4.06 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH_2Cl_2 (40 mL) gave the title compound **S44** (5.30 g, 19.4 mmol, 97%) as a white solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(2-Bromo-4-fluorophenyl)acrylate (**S44**) (5.00 g, 18.3 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (90 mL) with DIBAL-H (1.0 M in toluene, 41.0 mL, 40.3 mmol, 2.2 equiv) gave the title compound **S45** (2.80 g, 12.1 mmol, 66%) as a colorless oil that was used without further purification.

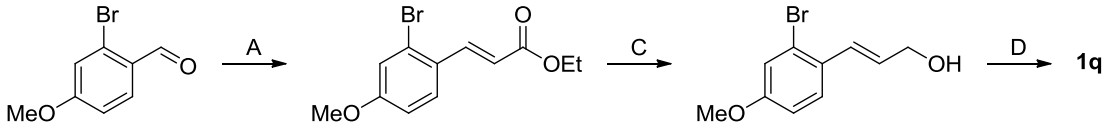
Following general procedure D, the reaction of (E)-3-(2-Bromo-4-fluorophenyl)prop-2-en-1-ol (**S45**) (2.70 g, 11.7 mmol, 1.0 equiv) in CH_2Cl_2 (11 mL) with Ac_2O (2.3 mL, 23.4 mmol, 2.0 equiv) and DMAP (71.5 mg, 0.59 mmol, 0.05 equiv) gave the title

compound **1p** (2.70 g, 9.9 mmol, 85%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.43 (m, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.01 (t, *J* = 8.3 Hz, 1H), 6.92 (d, *J* = 15.8 Hz, 1H), 6.25–6.10 (m, 1H), 4.75 (d, *J* = 6.2 Hz, 2H), 2.12 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.74, 161.85 (d, *J* = 251.9 Hz), 132.43, 131.46, 128.10 (d, *J* = 8.4 Hz), 126.05, 123.60 (d, *J* = 9.3 Hz), 120.00 (d, *J* = 24.4 Hz), 114.94 (d, *J* = 21.3 Hz), 64.64, 20.96. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.02. **HRMS** (EI) calcd for $C_{11}H_{10}O_2FBr$: 271.9848, found: 271.9853.

(E)-3-(2-Bromo-4-methoxyphenyl)allyl acetate (1q)



Route for **1q**



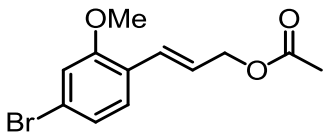
S46 **S47** **S48**

Following general procedure A, the reaction of 2-Bromo-4-methoxybenzaldehyde (**S46**) (4.30 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH_2Cl_2 (45 mL) gave the title compound **S47** (4.73 g, 16.6 mmol, 83%) as a white solid that was used without further purification.

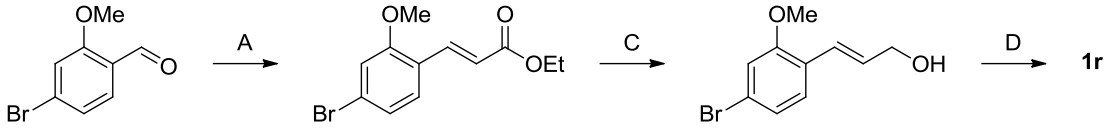
Following general procedure C, the reaction of (E)-ethyl-3-(4-Bromo-2-methoxyphenyl)acrylate (**S47**) (4.70 g, 16.5 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (80 mL) with DIBAL-H (1.0 M in toluene, 36.3 mL, 36.3 mmol, 2.2 equiv) gave the title compound **S48** (3.93 g, 16.2 mmol, 98%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(2-Bromo-4-methoxyphenyl)prop-2-en-1-ol (**S48**) (3.90 g, 16.0 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) with Ac_2O (3.1 mL, 32.0 mmol, 2.0 equiv) and DMAP (97.7 mg, 0.80 mmol, 0.05 equiv) gave the title compound **1q** (3.97 g, 13.9 mmol, 87%) as a colorless oil. **mixture of *cis* and *trans* isomers**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.7 Hz, 1H), 7.07 (s, 1H), 6.91 (d, *J* = 15.7 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 1H), 6.11 (dt, *J* = 15.5, 6.5 Hz, 1H), 4.72 (d, *J* = 6.4 Hz, 1H), 3.78 (s, 3H), 2.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.59, 159.65, 132.05, 128.38, 127.54, 124.08, 123.94, 117.57, 114.03, 64.91, 55.40, 20.88. **HRMS** (EI) calcd for $C_{12}H1_3O_3Br$: 284.0048, found: 284.0045.

(E)-3-(4-Bromo-2-methoxyphenyl)allyl acetate (1r)



Route for **1r**



S49 **S50** **S51**

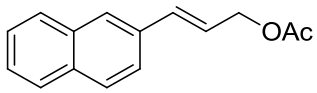
Following general procedure A, the reaction of 4-Bromo-2-methoxybenzaldehyde (**S49**) (4.3 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH_2Cl_2 (45 mL) gave the title compound **S50** (5.53 g, 19.4 mmol, 97%) as a white solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(4-Bromo-2-methoxyphenyl)acrylate (**S50)** (5.40 g, 18.9 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (95 mL) with DIBAL-H (1.0 M in toluene, 41.6 mL, 41.6 mmol, 2.2 equiv) gave the title compound **S51** (3.08 g, 12.7 mmol, 67%) as a colorless oil that was used without further purification.

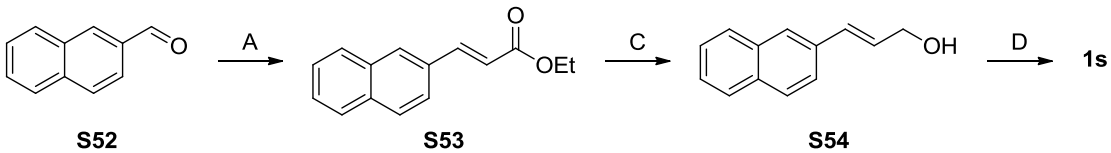
Following general procedure D, the reaction of (E)-3-(4-Bromo-2-methoxyphenyl)prop-2-en-1-ol (**S51**) (3.00 g, 12.3 mmol, 1.0 equiv) in CH_2Cl_2 (12 mL) with Ac_2O (2.3 mL, 24.6 mmol, 2.0 equiv) and DMAP (75.1 mg, 0.62 mmol, 0.05 equiv) gave the title compound **1r** (3.25 g, 11.4 mmol, 93%) as a white solid. **mixture of *cis* and *trans* isomers**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.1 Hz, 1H), 6.90 (s, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 6.59 (d, *J* = 15.8 Hz, 1H), 6.39–6.18 (m, 1H), 4.72 (d, *J* = 6.2 Hz, 2H), 3.91 (s, 3H), 2.11 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.80, 155.88, 136.90, 133.30, 133.18, 124.08, 120.18, 111.30, 109.69, 64.79, 56.14, 20.99. **HRMS** (EI) calcd for $C_{12}H_{13}O_3Br$: 284.0048, found: 284.0056.

(E)-3-(Naphthalen-2-yl)allyl acetate (1s) [5]



Route for **1s**



S52 **S53** **S54**

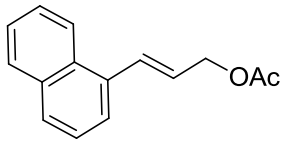
Following general procedure A, the reaction of 2-Naphthaldehyde (**S52**) (3.12 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH_2Cl_2 (30 mL) gave the title compound **S53** (4.16 g, 18.4 mmol, 92%) as a white solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(Naphthalen-2-yl)acrylate

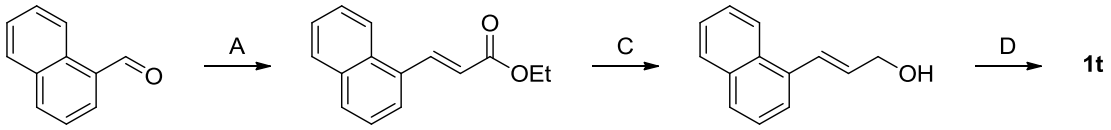
(**S53**) (4.00 g, 17.7 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (90 mL) with DIBAL-H (1.0 M in toluene, 40.0 mL, 38.9 mmol, 2.2 equiv) gave the title compound **S54** (2.90 g, 15.8 mmol, 89%) as a white solid that was used without further purification.

Following general procedure D, the reaction of (E)-3-(Naphthalen-2-yl)prop-2-en-1-ol (**S54**) (2.80 g, 15.2 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) with Ac_2O (3.0 mL, 30.4 mmol, 2.0 equiv) and DMAP (92.8 mg, 0.76 mmol, 0.05 equiv) gave the title compound **1s** (2.92 g, 12.9 mmol, 85%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.77 (m, 3H), 7.75 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.50–7.40 (m, 2H), 6.81 (d, *J* = 15.9 Hz, 1H), 6.49–6.31 (m, 1H), 4.78 (d, *J* = 6.5 Hz, 2H), 2.12 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.89, 134.28, 133.64, 133.48, 133.18, 128.30, 128.06, 127.68, 126.88, 126.36, 126.12, 123.49, 123.46, 65.17, 21.06.

(E)-3-(Naphthalen-1-yl)allyl acetate (1t)



Route for **1t**



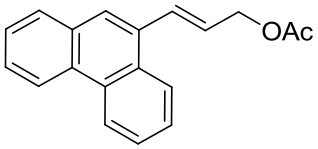
S55 **S56** **S57**

Following general procedure A, the reaction of 2-Naphthaldehyde (**S55**) (3.12 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH_2Cl_2 (30 mL) gave the title compound **S56** (4.07 g, 18.0 mmol, 90%) as a colorless oil that was used without further purification.

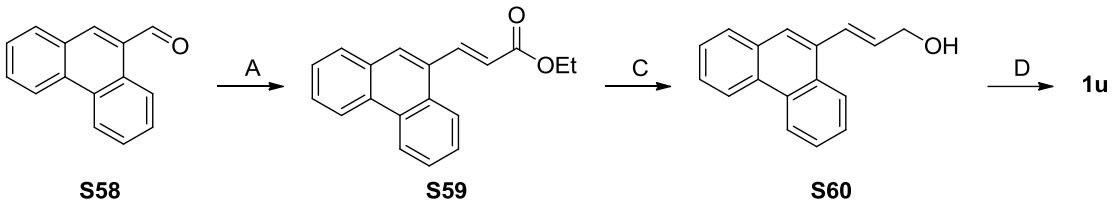
Following general procedure C, the reaction of (E)-ethyl-3-(Naphthalen-2-yl)acrylate (**S56**) (4.00 g, 17.7 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (90 mL) with DIBAL-H (1.0 M in toluene, 40.0 mL, 38.9 mmol, 2.2 equiv) gave the title compound **S57** (3.10 g, 16.8 mmol, 95%) as a colorless oil that was used without further purification.

Following general procedure D, the reaction of (E)-3-(Naphthalen-2-yl)prop-2-en-1-ol (**S57**) (3.00 g, 16.3 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) with Ac_2O (3.2 mL, 32.6 mmol, 2.0 equiv) and DMAP (99.5 mg, 0.82 mmol, 0.05 equiv) gave the title compound **1t** (3.53 g, 15.6 mmol, 96%) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 7.1 Hz, 1H), 7.56–7.48 (m, 2H), 7.48–7.38 (m, 2H), 6.33 (dt, *J* = 15.5, 6.4 Hz, 1H), 4.85 (d, *J* = 6.3 Hz, 2H), 2.15 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.75, 133.97, 133.68, 131.25, 131.19, 128.65, 128.47, 126.46, 126.27, 125.93, 125.66, 124.14, 123.73, 65.23, 21.02.

(E)-3-(Phenanthren-9-yl)allyl acetate (1u)



Route for **1u**

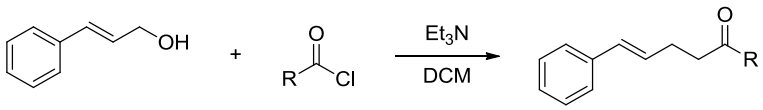


Following general procedure A, the reaction of Phenanthrene-9-carbaldehyde (**S58**) (4.12 g, 20.0 mmol, 1.0 equiv) with the phosphorane (7.32 g, 21.0 mmol, 1.05 equiv) in CH_2Cl_2 (40 mL) gave the title compound **S59** (3.98 g, 14.4 mmol, 72%) as a yellow solid that was used without further purification.

Following general procedure C, the reaction of (E)-ethyl-3-(Phenanthren-9-yl)acrylate (**S59**) (3.80 g, 13.7 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (70 mL) with DIBAL-H (1.0 M in toluene, 31.0 mL, 30.1 mmol, 2.2 equiv) gave the title compound **S60** (2.47 g, 10.5 mmol, 77%) as a yellow solid that was used without further purification.

Following general procedure D, the reaction of (E)-3-(Phenanthren-9-yl)prop-2-en-1-ol (**S60**) (2.40 g, 10.2 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) with Ac_2O (2.0 mL, 20.4 mmol, 2.0 equiv) and DMAP (62.3 mg, 0.51 mmol, 0.05 equiv) gave the title compound **1u** (2.21 g, 8.0 mmol, 78%) as a yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 7.6 Hz, 1H), 8.64 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 7.4 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.83 (s, 1H), 7.72–7.56 (m, 4H), 7.40 (d, *J* = 15.5 Hz, 1H), 6.40 (dt, *J* = 15.5, 6.3 Hz, 1H), 4.89 (d, *J* = 6.3 Hz, 1H), 2.19 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.92, 132.97, 131.87, 131.65, 130.41, 130.33, 128.73, 126.83, 126.73, 126.61, 125.18, 124.56, 123.12, 122.55, 65.19, 21.13. **HRMS** (EI) calcd for $C_{19}H_{16}O_2$: 276.1150, found: 276.1156.

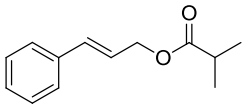
General scheme 2 for the synthesis of 3a-3e [6]



General procedure E:
To a stirred solution of cinnamyl alcohol (1.0 equiv) in anhydrous CH_2Cl_2 (3 mL/mmol) was added triethylamine (3.0 equiv) and acetyl chloride derivative (1.1 equiv) at 0 °C. The mixture was stirred for 30 min and then allowed to warm to room temperature and stirred overnight. The mixture was quenched with NH_4Cl (aq) and extracted with CH_2Cl_2 (3 equal volume). The combine organic layers was washed with brine, dried

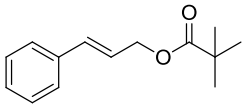
over $MgSO_4$, and the solution was removed under vacuum and the crude residue was purified by chromatography on SiO_2 with hexane/EtOAc to afford corresponging product **3a**[7], **3b**[6], **3c**[8] , **3d**[9], **3e**[10].

Cinnamyl isobutyrate (**3a**)



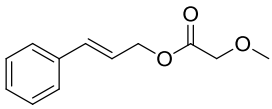
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.1 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.29 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.73 (d, *J* = 7.6 Hz, 2H), 2.78–2.34 (m, 1H), 1.22 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.78, 136.28, 133.88, 128.60, 128.02, 126.61, 123.43, 64.86, 34.03, 19.03.

Cinnamyl pivalate (**3b**)



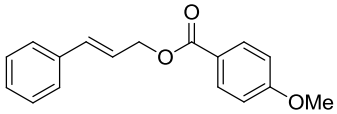
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, 7.0 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.26 – 7.20 (m, 1H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.39 – 6.17 (m, 1H), 4.72 (d, *J* = 6.2 Hz, 2H), 1.27 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.00, 136.33, 133.6 (s), 128.60, 127.99, 126.62, 123.55, 64.89, 38.78, 27.26.

Cinnamyl 2-methoxyacetate (**3c**)



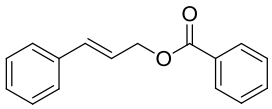
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.1 Hz, 2H), 7.20 (t, *J* = 6.7 Hz, 2H), 7.16 – 7.11 (m, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.25 – 6.10 (m, 1H), 4.68 (d, *J* = 6.1 Hz, 2H), 3.93 (s, 2H), 3.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.97, 135.98, 134.54, 128.56, 128.11, 126.59, 122.61, 69.56, 65.19, 59.11.

Cinnamyl 4-methoxybenzoate (**3d**)



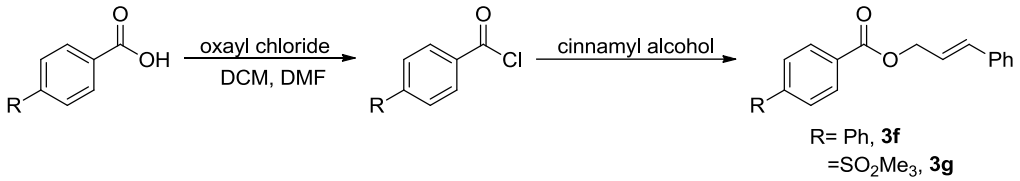
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 7.1 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 6.6 Hz, 1H), 7.02 – 6.88 (m, 2H), 6.74 (d, *J* = 15.9 Hz, 1H), 6.42 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.97 (d, *J* = 6.3 Hz, 2H), 3.84 (s, 3H). **^{13}C NMR** (101 MHz,$CDCl_3$) δ 166.12, 163.42, 136.30, 134.00, 131.72, 128.64, 128.06, 126.66, 123.56, 122.60, 113.65, 65.27, 55.41.

Cinnamyl benzoate (**3e**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.51 – 7.42 (m, 4H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 6.77 (d, *J* = 15.9 Hz, 1H), 6.44 (dt, *J* = 15.9, 6.4 Hz, 1H), 5.02 (d, *J* = 6.4 Hz, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.40, 136.25, 134.29, 133.05, 130.24, 129.71, 128.67, 128.43, 128.14, 126.70, 123.29, 65.58.

General scheme 3 for the synthesis of 3f, 3g [6,11]

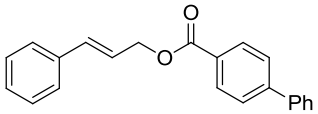


General procedure F:

To a stirred solution of benzoic acid derivative (1.0 equiv) in anhydrous CH_2Cl_2 (3 mL/mmol) was added dropwise oxalyl chloride (1.5 equiv) and drops of DMF at 0 ^{o}C for 30 min. Then the mixture was stirred at room temperature until no gas releasing and evaporated to afford the crude product without further purification.

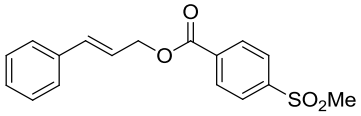
To a stirred solution of acetyl chloride derivative (1.0 equiv) in anhydrous CH_2Cl_2 (3 mL/mmol) was added triethylamine (3.0 equiv) cinnamyl alcohol (0.9 equiv) at 0 ^{o}C. The mixture was stirred for 30 min and then allowed to warm to room temperature and stirred overnight. The mixture was quenched with NH_4Cl (aq) and extracted with CH_2Cl_2 (3 equal volume). The combine organic layers was washed with brine, dried over $MgSO_4$, and the solution was removed under vacuum and the crude residue was purified by chromatography on SiO_2 with hexane/EtOAc to afford corresponging product **3f-3g** [12].

Cinnamyl [1,1'-biphenyl]-4-carboxylate (**3f**)



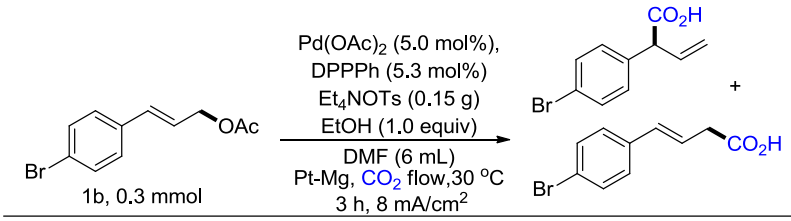
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.52 – 7.38 (m,5H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.31 – 7.25 (m, 1H), 6.77 (d, *J* = 15.9 Hz, 1H), 6.44 (dt, *J* = 15.9, 6.4 Hz, 1H), 5.02 (d, *J* = 6.4 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.29, 145.72, 139.98, 136.22, 134.29, 130.20, 128.93, 128.63, 128.16, 128.11, 127.29, 127.07, 126.66, 123.28, 65.58.

Cinnamyl 4-(methylsulfonyl)benzoate (**3g**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.3 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 6.75 (d, *J* = 15.9 Hz, 1H), 6.39 (dt, *J* = 15.8, 6.5 Hz, 1H), 5.01 (d, *J* = 6.4 Hz, 2H), 3.07 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.73, 144.31, 135.94, 135.11, 134.95, 130.60, 128.67, 128.31, 127.50, 126.69, 122.45, 66.36, 44.28.

4 Conditions Screening of the Reaction



	Entry[a]	deviation from above conditions	Yield%[b]	B:L[c]
Catalysts	1	none	85(81)[d]	20:1
	2	no $Pd(OAc)_2$	19	2:1
	3	$Pd(PPh_3)_2Cl_2$ as catalyst	20	3:1
	4	$Pd_2(dba)_3$ as catalyst	19	3:1
	5	$Pd(COCF_3)_2$ as catalyst	24	5:1
	6	$[Pd(allyl)Cl]_2$ as catalyst	22	4:1
EtOH	7	no EtOH	21	2:1
	8	0.5 eq. EtOH	56	14;1
	9	2 eq. EtOH	40	14:1
	10	5 eq. EtOH	60	11:1
	11	10 eq. EtOH	28	3:1
	12	30 eq. EtOH	50	3:1
Alcohols	13	1.0 eq. CH_3OH	37	19:1
	14	1.0 eq. $^{n}PrOH$	40	14:1
	15	1.0 eq. $^{i}PrOH$	57	13:1
	16	1.0 eq. $^{t}BuOH$	45	11:1
	17	1.0 eq. $C_8H_{17}OH$	38	9:1
Ligands	18	no DPPPh	38	3:1
	19	PPh_3 as ligand	35	2:1
	20	DPPE as ligand	70	15:1
	21	DPPP as ligand	65	18:1
	22	DPPB as ligand	50	6:1
	23	DPPcyE as ligand	75	8:1
Temperature	24	0 °C	29	6:1
	25	10 °C	80	20:1
	26	rt. (22 °C)	86	12:1
	27	40 °C	45	8:1
	28	50 °C	43	4:1
Other	29	no electric current	-	NP
	30	Mn or Zn in lieu of electric current	-	NP
	31	$^{n}Bu_4NBF_4$ as electrolyte	58	3:1
	32	$^{n}Bu_4PF_6$ as electrolyte	18	-

[a] Reaction conditions:1b (0.3 mmol), $Pd(OAc)_2$ (5 mol%), DPPPh (5.3 mol%), Et_4NOTs (0.15 g) and EtOH (1.0 equiv), DMF (6 mL) in an undevided cell with a paltinum electrode and magnesium rod as sarifical anode. [b] The yield was determined by H^1-NMR with CH_2Br_2 as the internal standard. [c] The ratio of BL products was determined by H^1-NMR. [d] Isolated yield.

Note: 1) The reason for choosing alcohol as additive is that the alcohol may be useful for the activation of CO_2.[13] When the additive was ethanol, the crude ^1H NMR was

much cleaner and the yield was significantly increased.

2) When no ligand or simple PPh_3 was employed as the ligand, after the electrolysis, the platinum cathode was covered by a black precipitation. This may arise from the palladium catalyst deactivation.

5 Photographic Guide for Electrochemical Carboxylation

1 Easily hand-made electrochemical cell

Step 0. Overview of materials used.

From left to right: 1) The magnesium rod attached to a copper wire. 2) The platinum cathode 3) The rubber stopper pierced with two hypodermic needles. 4) A 10 mL hydrogenation tube.

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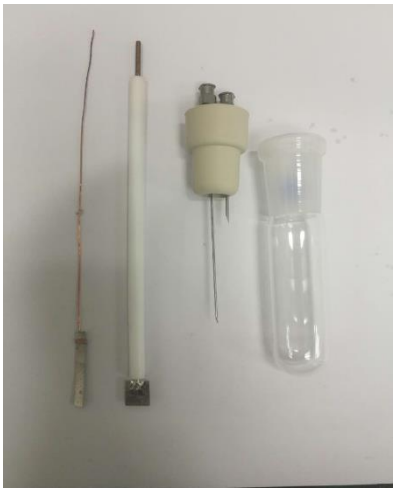
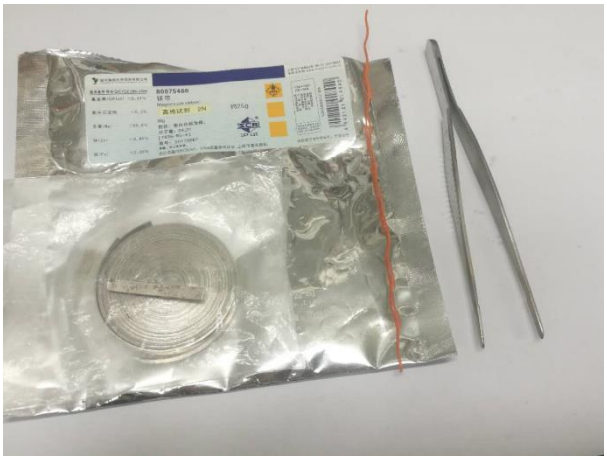


Step 1. Preparation of the sacrificial magnesium rod anode

Cut a magnesium rod about 3 cm with a scissors.

Strip the protective skin of the copper wire with a tweezer.

Wrap the magnesium with copper wire.

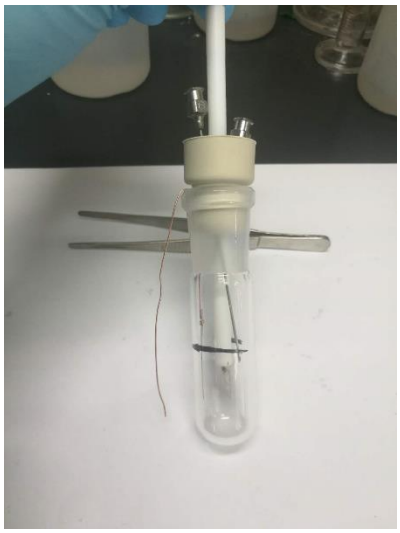


Step 2. Assembly of the cell

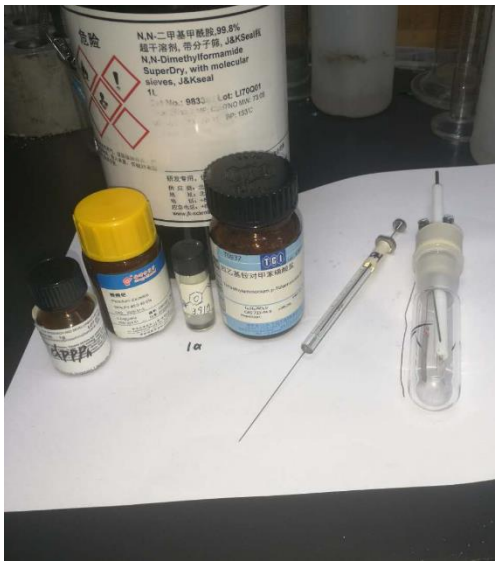
Pierce the rubber stopper with the platinum cthode.

The magneium rod and stopper were fitted into the tube.

Note: the copper wire is not supposed to be immersed the reaction. (the black line on the tube, 6 mL)



2 Graphical Guide for Electrochemical carboxylation



Left materials used in the reaction.
Right the electrolyte weighted in glovebox was dissolved in DMF (SuperDry) and injected into the tube charged with a stir bar with a 10.0mL disposable syringe.

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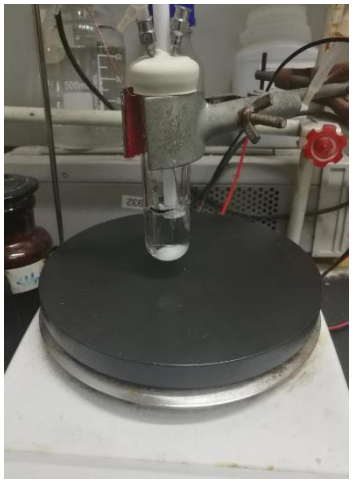
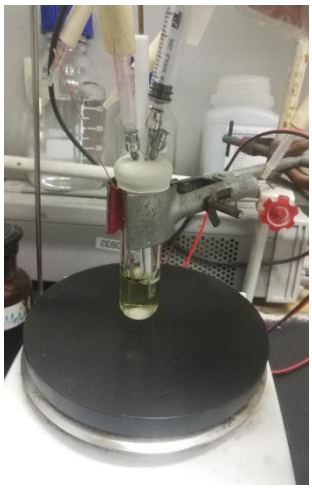
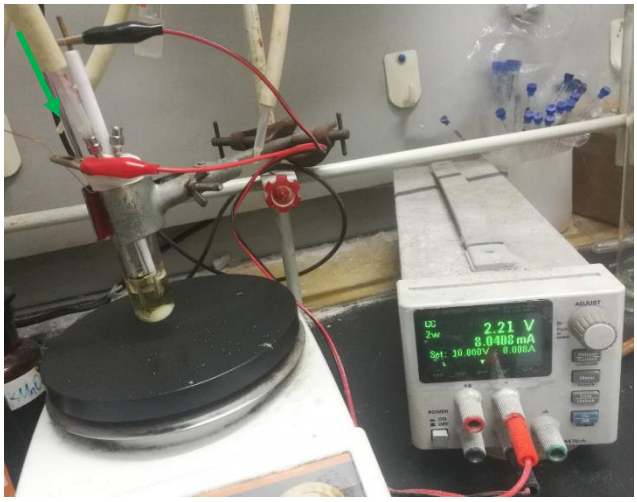




Left Bubbling CO_2 for 30 mins. **Right** injected the catalysts, EtOH, SM.



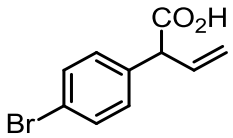
Attached to electrode (the red (+) to the magnesium, the black (-) to the platinum). Conducted constant current electrolysis (I = 8.0 mA) using an potentiostat.(E36105A, KEYSIGHT) under continuous bubbling CO_2.(**green line**)

6 General Procedure for the Electrolysis

A 10 mL hydrogenation tube charged with a stir bar was installed a platinum electrode (1.0 x 1.0 cm^2) as cathode and magnesium rod as sacrificial anode. The electrolyte was dissolved in DMF (6.0 mL, superDry) and was injected into the tube with a 10 mL syringe. After bubbling of CO_2 gas (dried over conc. H_2SO_4) into the electrolytes for 30 min, $Pd(OAc)_2$ (0.015 mmol, 3.4 mg, 5 mol%), DPPPh (0.016 mmol, 7.2 mg, 5.3 mol%), allyl eater (0.3 mmol, 1.0 equiv), and EtOH (0.3 mmol, 17.5 uL, 1.0 equiv) were added to the tube. Under continuous bubbling of CO_2 gas, the reaction mixture was electrolyzed under a constant current of 8 mA until the complete consumption of the starting materials as judged by TLC (about 3 hours). After that, the reaction mixture was transferred to a 50 mL erlenmeyer flask and acidized with HCl (1 N). The aqueous layer extracted with EtOAc (3 x equal volume) and the combined organics were washed with sat. NH_4Cl (4 x equal volume), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography to furnish the desired product.

Characterization Data for the Products

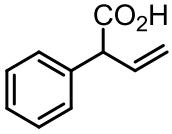
2-(4-Bromophenyl)but-3-enoic acid (2a) [14]



According to the procedure, (E)-3-(4-Bromophenyl)allyl acetate (**1a**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2a** (58.6 mg, 81% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.25 –6.07 (m, 1H), 5.28 (t, *J* = 7.9 Hz, 1H), 5.19 (d, *J* = 17.1 Hz, 1H), 4.29 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.17, 136.22, 134.31, 131.89, 129.87, 121.73, 118.61, 54.84. **HRMS** (EI) calcd for $C_{10}H_9O_2Br$: 239.9786, found: 239.9794.

2-Phenylbut-3-enoic acid (2b) [15]

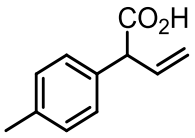


According to the procedure, cinnamyl acetate (**1b**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2b** (28.2 mg, 58% yield) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.27 (m, 5H), 6.38–6.17 (m, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 5.23 (d, *J* = 17.1 Hz, 1H), 4.37 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR** (101 MHz,

$CDCl_3$) δ 178.80, 137.37, 134.97, 128.83, 128.12, 127.65, 118.13, 55.59. **HRMS** (ESI-TOF) calcd for $C_{10}H_{11}O_2$ $[M+H]^+$: 163.0754, found: 163.0754.

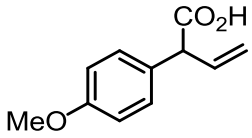
2-(p-Tolyl)but-3-enoic acid (2c) [14]



According to the procedure, (E)-3-(p-Tolyl)allyl acetate (**1c**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2c** (35.0 mg, 65% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 6.28 –6.12 (m, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 5.17 (d, *J* = 17.7 Hz, 1H), 4.29 (d, *J* = 8.0 Hz, 1H), 2.33 (s, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.79, 137.33, 135.10, 134.38, 129.47, 127.92, 117.85, 55.11, 21.05.**HRMS** (ESI-TOF) calcd for $C_{11}H_{113}O_2$ $[M+H]^+$: 177.0910, found: 177.0910.

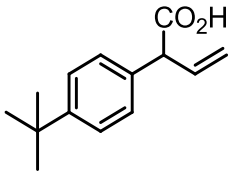
2-(4-Methoxyphenyl)but-3-enoic acid (2d) [14]



According to the procedure, (E)-3-(4-Methoxyphenyl)allyl acetate (**1d**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2d** (36.0 mg, 62% yield) as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.7 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.31 –6.09 (m, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 5.17 (d, *J* = 17.1 Hz, 1H), 4.28 (d, *J* = 7.9 Hz, 1H), 3.80 (s, 1H). **^{13}C NMR** (101 MHz,$CDCl_3$) δ 178.71, 158.99, 135.16, 129.43, 129.16, 117.79, 114.17, 55.28, 54.63. **HRMS** (ESI-TOF) calcd for $C_{11}H_{13}O_3$ $[M+H]^+$: 193.0859, found: 193.0860.

2-(4-(tert-Butyl)phenyl)but-3-enoic acid (2e)

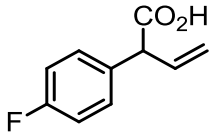


According to the procedure, (E)-3-(4-Methoxyphenyl)allyl acetate (**1d**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2d** (52.4 mg, 80% yield) as a yellowish solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.31 –6.15 (m, 1H), 5.31–5.18 (m, 2H), 4.33 (d, *J* = 8.2 Hz, 1H), 1.34 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.00, 150.51, 135.10, 134.32, 127.67, 125.75, 117.88, 55.18,

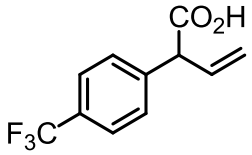
34.50, 31.33. **HRMS** (ESI-TOF) calcd for $C_{14}H_{19}O_2$ $[M+H]^+$: 219.1380, found: 219.1381.
IR (neat): 3084, 2963, 2929, 2869, 1698, 1639, 1287, 929, 822, 711 cm^{-1}.

2-(4-Fluorophenyl)but-3-enoic acid (2f) [14]



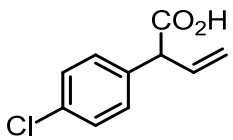
According to the procedure, (E)-3-(4-Fluorophenyl)allyl acetate (**1f**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2f** (42.8 mg, 78% yield) as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.28 (m, 2H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.30–6.09 (m, 1H), 5.27 (d, *J* = 10.1 Hz, 1H), 5.19 (d, *J* = 17.1 Hz, 1H), 4.32 (d, *J* = 7.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.56, 162.21 (d, *J* = 246.4 Hz), 134.69, 132.98 (d, *J* = 3.3 Hz), 129.76 (d, *J* = 8.1 Hz), 118.31, 115.66 (d, *J* = 21.5 Hz), 54.65. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.77. **HRMS** (EI) calcd for $C_{10}H_9O_2F$: 180.0587, found: 180.0588.

2-(4-(Trifluoromethyl)phenyl)but-3-enoic acid (2g)



According to the procedure, (E)-3-(4-(Trifluoromethyl)phenyl)allyl acetate (**1g**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2f** (43.0 mg, 62% yield) as a yellowish oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 6.24 –6.14 (m, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 5.21 (d, *J* = 17.1 Hz, 1H), 4.40 (d, *J* = 7.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.75, 141.09, 134.01, 129.95 (q, *J* = 32.5 Hz), 128.56, 125.70 (q, *J* = 7.3, 3.6 Hz), 123.95(q, *J* = 272.7 Hz), 118.95, 55.17. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.67. **HRMS** (EI) calcd for $C_{11}H_9O_2F_3$: 230.0555, found: 230.0557.
IR (neat): 3088, 3021, 2925, 1708, 1640, 1322, 1164, 1121, 1067, 834 cm^{-1}.

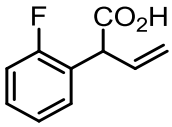
2-(4-Chlorophenyl)but-3-enoic acid (2h) [14]



According to the procedure, (E)-3-(4-Chlorophenyl)allyl acetate (**1h**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2h** (51.0 mg, 87% yield) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.23 – 6.12 (m, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 5.19 (d, *J* = 17.1 Hz, 1H), 4.31 (d, *J* = 7.9

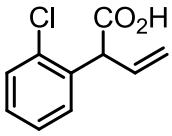
Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.39, 135.70, 134.40, 133.61, 129.52, 128.94, 118.56, 54.80. **HRMS** (EI) calcd for $C_{10}H_9O_2Cl$: 196.0291, found: 196.0289.

2-(2-Fluorophenyl)but-3-enoic acid (2i)



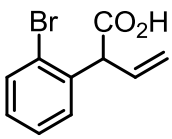
According to the procedure, (E)-3-(2-Fluorophenyl)allyl acetate (**1i**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2i** (49.0 mg, 91% yield) as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.26 (m, 2H), 7.19–7.01 (m, 2H), 6.25–6.17 (m, 1H), 5.29 (d, *J* = 10.2 Hz, 1H), 5.20 (d, *J* = 17.1 Hz, 1H), 4.65 (d, *J* = 7.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.03, 160.31 (d, *J* = 247.1 Hz), 133.43, 129.72 (d, *J* = 3.7 Hz), 129.32 (d, *J* = 8.3 Hz), 124.62 (d, *J* = 14.8 Hz), 124.36 (d, *J* = 3.6 Hz), 118.73, 115.63 (d, *J* = 22.0 Hz), 48.46. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.05–-117.13 (m, 3F). **HRMS** (ESI-TOF) calcd for $C_{10}H_{10}FO_2$ $[M+H]^+$: 180.0659, found: 180.0661.
IR (neat): 3086, 3024, 2987, 2907, 1705, 1490, 1407, 1284, 1229, 925, 751 cm^{-1}.

2-(2-Chlorophenyl)but-3-enoic acid (2j)



According to the procedure, (E)-3-(2-Chlorophenyl)allyl acetate (**1h**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2h** (52.0 mg, 87% yield) as a yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 8.3 Hz, 2H), 7.29–7.19 (m, 2H), 6.22–6.13 (m, 1H), 5.29 (d, *J* = 10.2 Hz, 1H), 5.18 (d, *J* = 17.2 Hz, 1H), 4.87 (d, *J* = 7.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.15, 135.11, 133.95, 133.40, 129.79, 129.74, 128.85, 127.13, 118.89, 51.82. **HRMS** (ESI-TOF) calcd for $C_{10}H_{10}ClO_2$ $[M+H]^+$: 197.0364, found: 197.0366
IR (neat): 3067, 2961, 2919, 2853, 1693, 1293, 928, 747, 648 cm^{-1}.

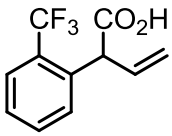
2-(2-Bromophenyl)but-3-enoic acid (2k)



According to the procedure, with DPPE as the ligand, (E)-3-(2-Bromophenyl)allyl acetate (**1k**) was electrolyzed for 4h. The product was purified by flash column chromatography on silica to afford **2k** (61.5 mg, 85% yield) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.25–6.07 (m, 1H), 5.29 (d, *J* = 10.2 Hz,

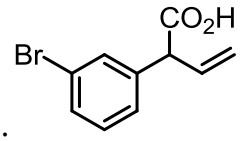
1H), 5.18 (d, *J* = 17.1 Hz, 1H), 4.89 (d, *J* = 7.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.72, 136.81, 133.36, 133.11, 129.82, 129.06, 127.74, 124.63, 118.82, 54.19. **HRMS** (EI) calcd for $C_{10}H_9O_2Br$: 239.9786, found: 239.9792.
IR (neat): 3061, 3001, 2983, 2826, 1692, 1636, 1422, 1292, 1024, 926, 744, 643 cm^{-1}

2-(2-(Trifluoromethyl)phenyl)but-3-enoic acid (2l)



According to the procedure, (E)-3-(2-(Trifluoromethyl)phenyl)allyl acetate (**1l**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2l** (50.0 mg, 72% yield) as a yellowish oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.59–7.49 (m, 2H), 7.37 (t, *J* = 7.1 Hz, 1H), 6.19 – 6.10 (m, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 5.14 (d, *J* = 17.1 Hz, 1H), 4.79 (d, *J* = 7.1 Hz, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.81, 135.81, 134.36, 132.07, 130.26, 128.51(q, *J* = 59.8, 29.9 Hz), 127.57, 126.05(q, *J* = 5.7 Hz), 124.15(q, *J* = 273 Hz), 118.74, 50.40. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.60. **HRMS** (EI) calcd for $C_{11}H_9O_2F_3$: 230.0555, found: 230.0566.
IR (neat): 3088, 3023, 2989, 2920, 1709, 1310, 1114, 1035, 926, 766 cm^{-1}.

2-(3-Bromophenyl)but-3-enoic acid (2m) [14]



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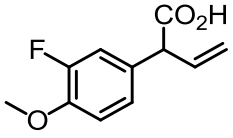
According to the procedure, (E)-3-(3-Bromophenyl)allyl acetate (**1m**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2m** (58.0 mg, 80% yield) as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 6.24–6.08 (m, 1H), 5.27 (d, *J* = 10.2 Hz, 1H), 5.19 (d, *J* = 17.1 Hz, 1H), 4.28 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.18, 139.34, 134.15, 131.21, 130.79, 130.29, 126.80, 122.75, 118.82, 55.02. **HRMS** (EI) calcd for $C_{10}H_9O_2Br$: 239.9786, found: 239.9782.

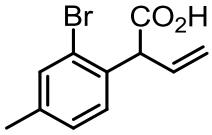
2-(3-Fluoro-4-methoxyphenyl)but-3-enoic acid (2n)



According to the procedure, (E)-3-(3-Fluoro-4-methoxyphenyl)allyl acetate (**1n**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2n** (53.0 mg, 83% yield) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 12.1, 2.0 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 1H),

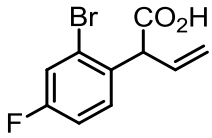
6.92 (t, *J* = 8.5 Hz, 1H), 6.28–6.06 (m, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 5.18 (d, *J* = 17.1 Hz, 1H), 4.26 (d, *J* = 7.9 Hz, 1H), 3.87 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.32, 152.25 (d, *J* = 246.4 Hz), 147.08 (d, *J* = 10.7 Hz), 134.5, 130.06 (d, *J* = 6.3 Hz), 123.89 (d, *J* = 3.6 Hz), 118.3, 115.93 (d, *J* = 19.2 Hz), 113.44 (d, *J* = 2.1 Hz), 56.25, 54.40. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -134.35. **HRMS** (EI) calcd for $C_{11}H_{11}O_3F$: 210.0692, found: 210.0687.
IR (neat): 3083, 3010, 2936, 2841, 1704, 1513, 1270, 1150,1026, 925, 759, 731, 638 cm^{-1}.

2-(2-Bromo-4-methylphenyl)but-3-enoic acid (2o)



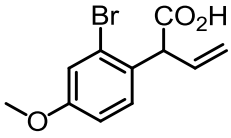
According to the procedure, (E)-3-(2-Bromo-4-methylphenyl)allyl acetate (**1o**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2o** (73.3 mg, 95% yield) as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.26 (d, *J* = 7.9 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 1H), 6.26–6.06 (m, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 4.87 (d, *J* = 7.2 Hz, 1H), 2.32 (s, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.28, 139.32, 133.78, 133.75, 133.54, 129.47, 128.62, 124.37, 118.64, 53.85, 20.70. **HRMS** (EI) calcd for $C_{11}H_{11}O_2Br$: 253.9942, found: 253.9953.
IR (neat): 3084, 3022, 2983, 2921, 1703, 1406, 1283, 1214, 1037, 922, 742, 673 cm^{-1}.

2-(2-Bromo-4-fluorophenyl)but-3-enoic acid (2p)



According to the procedure, (E)-3-(2-Bromo-4-fluorophenyl)allyl acetate (**1p**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2p** (73.0 mg, 93% yield) as a yellowish oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.31 (m, 2H), 7.05 (td, *J* = 8.2, 2.6 Hz, 1H), 6.21 –6.05 (m, 1H), 5.32 (d, *J* = 10.2 Hz, 1H), 5.19 (d, *J* = 17.2 Hz, 1H), 4.86 (d, *J* = 7.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.74, 161.53 (d, *J* = 251.3 Hz), 133.42, 132.78 (d, *J* = 3.6 Hz), 130.80 (d, *J* = 8.5 Hz), 124.63 (d, *J* = 9.4 Hz), 120.26 (d, *J* = 24.5 Hz), 119.02, 114.98 (d, *J* = 21.1 Hz), 53.42. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.40. **HRMS** (EI) calcd for $C_{10}H_8O_2FBr$: 257.9692, found: 257.9700.
IR (neat): 3085, 3017,2985, 2919, 1705, 1596, 1484, 1221, 1167, 875, 673 cm^{-1}.

2-(2-Bromo-4-methoxyphenyl)but-3-enoic acid (2q)

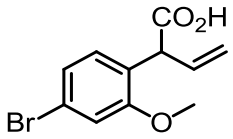


According to the procedure, (E)-3-(2-Bromo-4-methoxyphenyl)allyl acetate (**1q**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2q** (59.0 mg, 72% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.7 Hz, 1H), 7.12 (s, 1H), 6.85 (d, *J* = 8.6, 1H), 6.21–6.00 (m, 1H), 5.26 (d, *J* = 10.2 Hz, 1H), 5.15 (d, *J* = 17.2 Hz, 1H), 4.81 (d, *J* = 7.0 Hz, 1H), 3.77 (s, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.88, 159.26, 133.91, 130.19, 128.80, 124.82, 118.44, 118.16, 113.93, 55.53, 53.33.**HRMS** (EI) calcd for $C_{11}H_{11}O_3Br$: 269.9892, found: 269.9902.

IR (neat): 3084, 3005, 2939, 1907, 2836, 1703, 1601, 1490, 1283, 1228, 1180, 1026, 923, 862, 741, 676 cm^{-1}.

2-(4-Bromo-2-methoxyphenyl)but-3-enoic acid (2r)

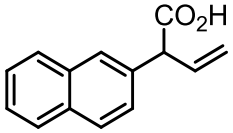


According to the procedure, (E)-3-(4-Bromo-2-methoxyphenyl)allyl acetate (**1r**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2r** (61.0 mg, 75% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 1H), 6.85 (s, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 6.23–6.11 (m, 1H), 5.27 (d, *J* = 10.2 Hz, 1H), 5.20 (d, *J* = 17.1 Hz, 1H), 4.29 (d, *J* = 7.8 Hz, 1H), 3.89 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.90, 156.00, 138.00 , 134.32, 133.44, 121.47, 118.60, 111.85, 111.03 , 56.22, 55.19. **HRMS** (EI) calcd for $C_{11}H_{11}O_3Br$: 269.9892, found: 269.9901.

IR (neat): 3082, 3007, 2939, 1703, 1581, 1484, 1403, 1280, 1164, 1045, 1024, 725, 670 cm^{-1}.

2-(Naphthalen-2-yl)but-3-enoic acid (2s)

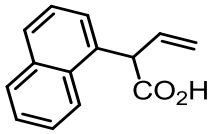


According to the procedure, with DPPE as the ligand, (E)-3-(Naphthalen-2-yl)allyl acetate (**1s**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2s** (52.5 mg, 82% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.77 (m, 4H), 7.54–7.44 (m, 3H), 6.42–6.26 (m, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 4.53 (d, *J* = 7.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.70, 134.86, 134.73, 133.44, 132.74, 128.54, 127.89, 127.65, 127.08, 126.30, 126.12, 126.00, 118.36, 55.60. **HRMS** (ESI-TOF) calcd for $C_{14}H_{16}NO_2$ $[M+NH_4]^+$: 230.1176, found: 230.1176

IR (neat): 3067, 2985, 2923, 2853, 1693, 1405, 1210, 929, 825, 748 cm^{-1}.

2-(Naphthalen-1-yl)but-3-enoic acid (2t)

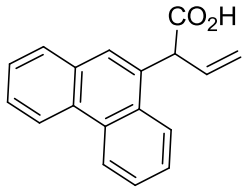


According to the procedure, with DPPE as the ligand, (E)-3-(Naphthalen-1-yl)allyl acetate (**1t**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2t** (51.5 mg, 81% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.60–7.40 (m, 4H), 6.50–6.30 (m, 1H), 5.33 (d, *J* = 10.3 Hz, 1H), 5.23 (d, *J* = 17.2 Hz, 1H), 5.12 (d, *J* = 7.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.99, 134.44, 134.06, 133.51, 131.29, 129.02, 128.43, 126.56, 126.32, 125.82, 125.53, 123.34, 118.60, 51.61. **HRMS** (ESI-TOF) calcd for $C_{14}H_{16}NO_2$ $[M+NH_4]^+$: 230.1176, found: 230.1176.

IR (neat): 3042, 2890, 2822, 2659, 2565, 1689, 1596, 1417, 1289, 946,775 cm^{-1}.

2-(Phenanthren-9-yl)but-3-enoic acid (2u)



According to the procedure, (E)-3-(Phenanthren-9-yl)allyl acetate (**1u**) was electrolyzed for 3h. The product was purified by flash column chromatography on silica to afford **2u** (72.4 mg, 92% yield) as a white solid.

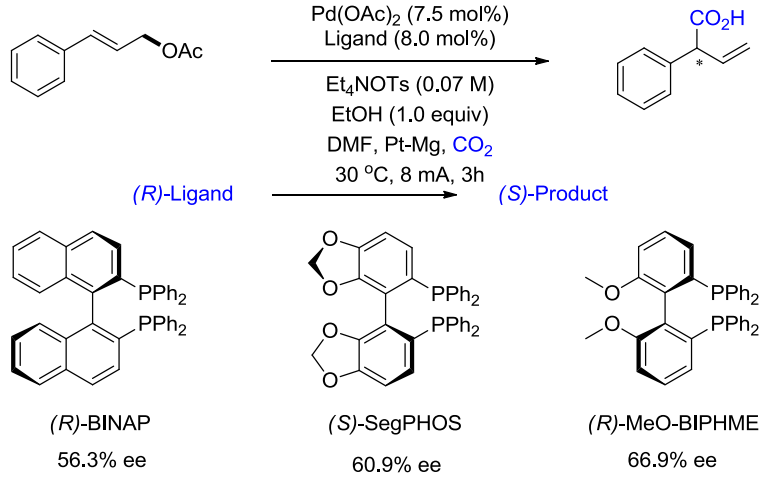
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.0 Hz, 1H), 8.67 (d, *J* = 8.2 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.77 (s, 1H), 7.72–7.54 (m, 4H), 6.46 (ddd, *J* = 17.2, 10.3, 7.0 Hz, 1H), 5.37 (d, *J* = 10.3 Hz, 1H), 5.27 (d, *J* = 17.3 Hz, 1H), 5.10 (d, *J* = 6.9 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.45, 134.13, 131.85, 131.33, 130.95, 130.17, 130.14, 128.75, 127.57, 126.97, 126.93, 126.83, 126.55, 124.14, 123.40, 122.46, 118.97, 51.99. **HRMS** (ESI-TOF) calcd for $C_{18}H_{18}NO_2$ $[M+NH_4]^+$: 280.1332, found: 280.1333.

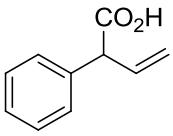
IR (neat): 2952, 2919, 2852, 1689, 1635, 1404, 1200, 926, 764, 742, 615 cm^{-1}.

.

7 Enantioselective Carboxylation

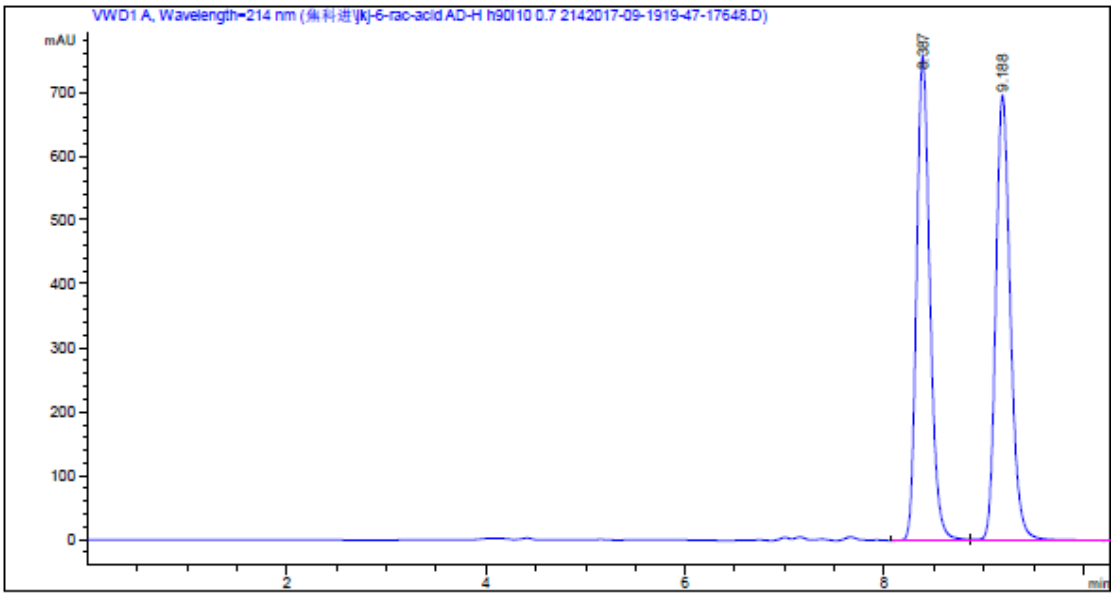
Ligands results





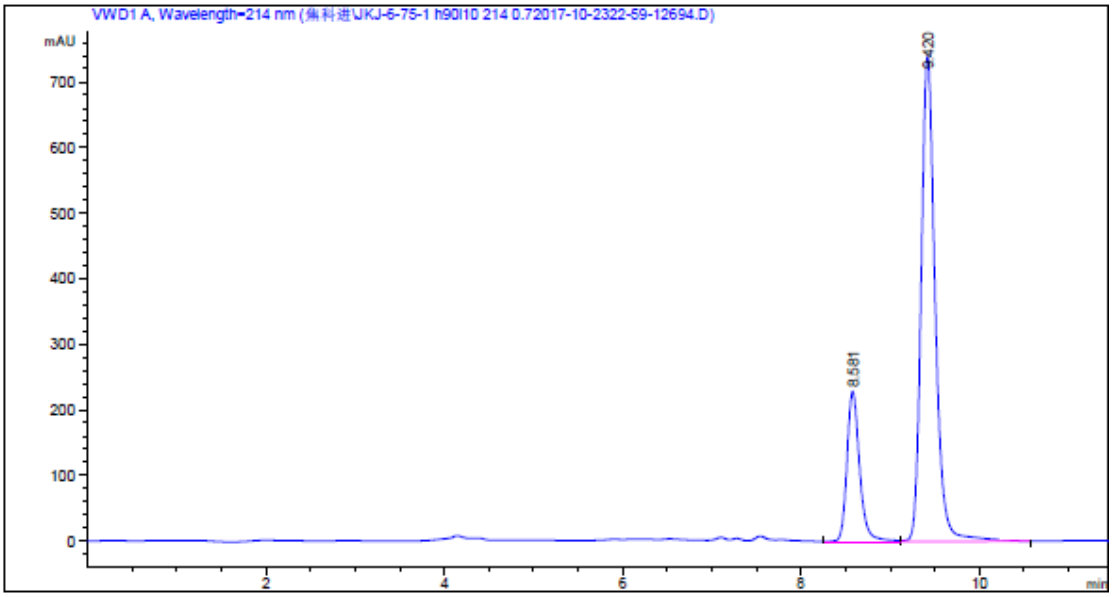
2b (±)- 2-phenylbut-3-enoic acid (**2b**)

HPLC: Chiralpak AD-H (10% IPA:hexane, flow rate 0.7 ml min^{-1}, 214 nm, 40 ℃) t_R minor: 8.4 min, tR major: 9.2 min, *0% ee*



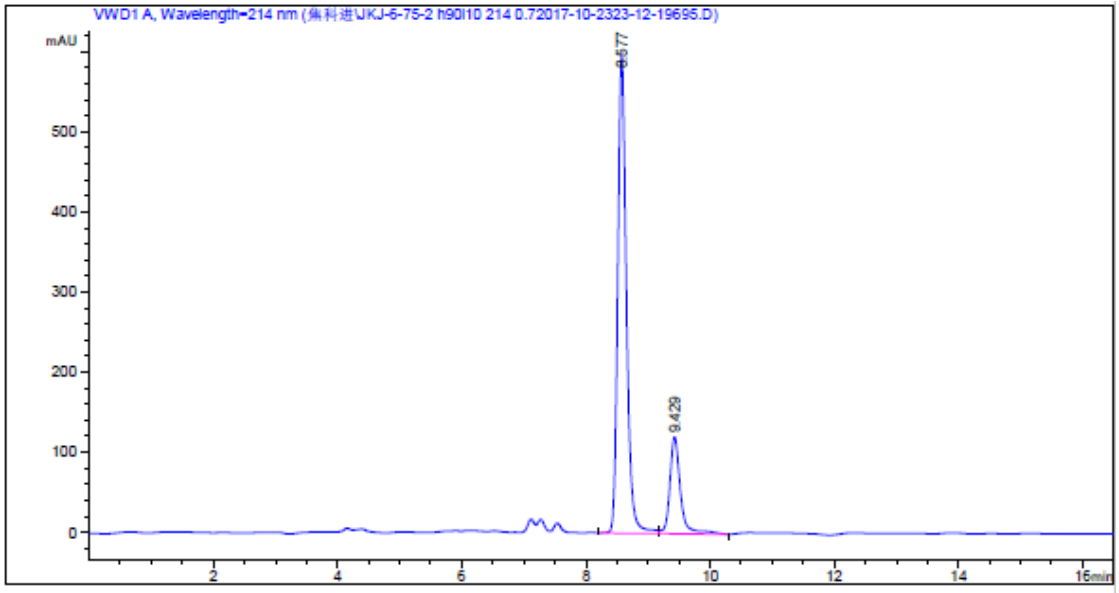
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.387	BV	0.1449	7062.05176	756.50781	49.7387
2	9.188	VBA	0.1596	7136.26123	696.29437	50.2613

(R)-BINAP as the ligand. t_R minor: 8.6 min, tR major: 9.4 min, *56% ee*



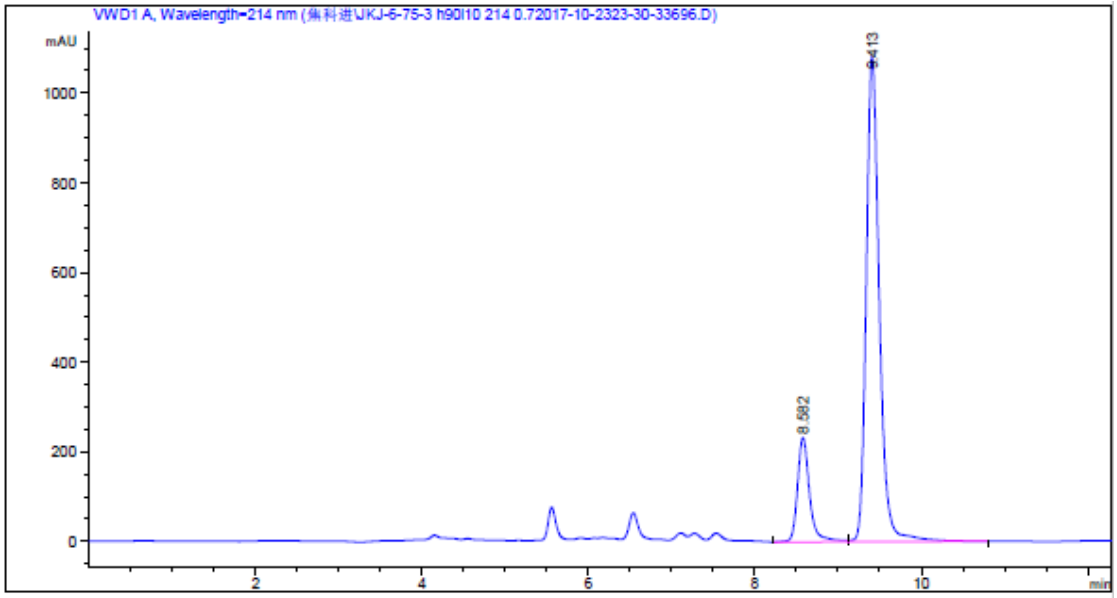
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.581	BV	0.1511	2252.30811	228.38083	21.8008
2	9.420	VB	0.1717	8079.02002	738.16583	78.1992

(S)-SegPhos as the ligand. t_R minor: 8.6 min, tR major: 9.4 min, *60% ee*



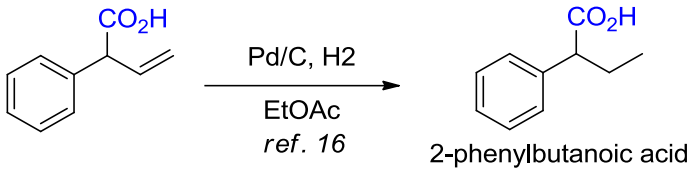
#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.577	BV	0.1548	5842.46777	593.68561	80.4273
2	9.429	VB	0.1779	1421.81433	120.27148	19.5727

(R)-MeO-BIPHME as the ligand. t_R minor: 8.6 min, tR major: 9.4 min, *67% ee*

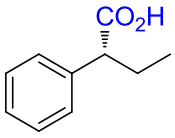


#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.582	BV	0.1540	2353.63257	232.66830	16.5495
2	9.413	VB	0.1683	1.18681e4	1078.84717	83.4505

Absolute Configuration of the Product

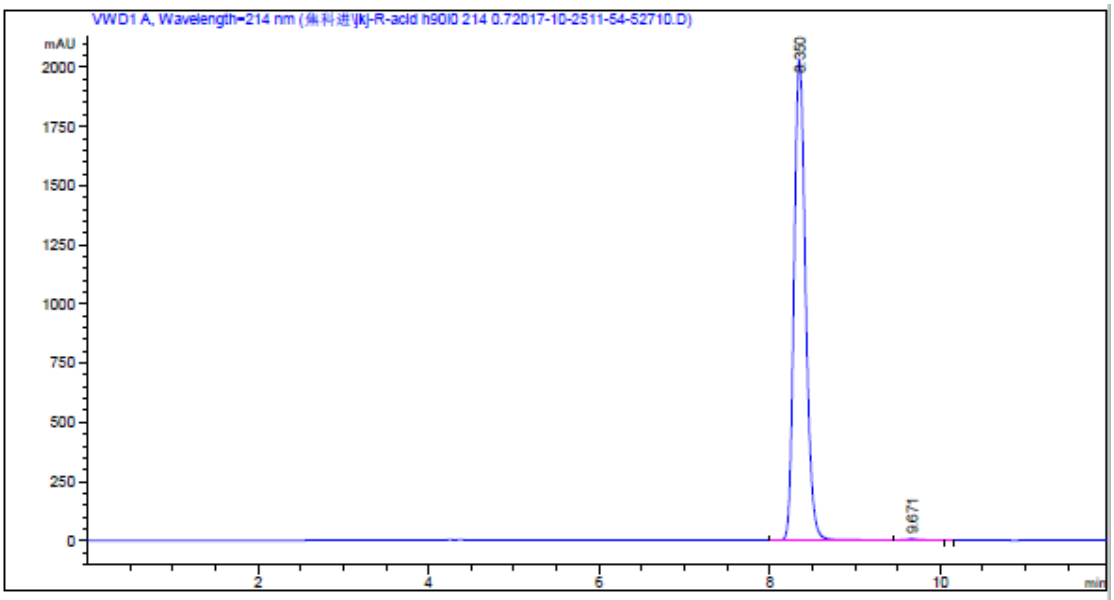


The *(R)*-2-phenylbutanoic acid was purchased for a contrast.



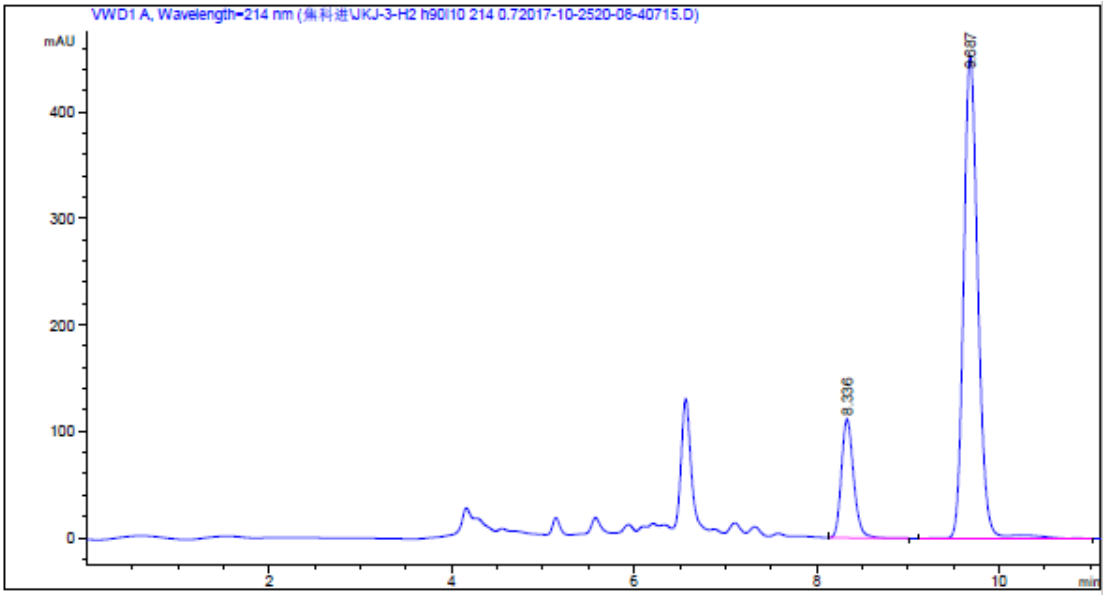
(*R*)-2-phenylbutanoic acid

HPLC: Chiralpak AD-H (10% IPA:hexane, flow rate 0.7 ml min^{-1}, 214 nm, 40 ℃) t_R minor: 8.3 min, tR major: 9.7 min, *99% ee*



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.350	BV R	0.1465	1.91614e4	2022.82556	99.6208
2	9.671	VB E	0.1647	72.94473	7.05273	0.3792

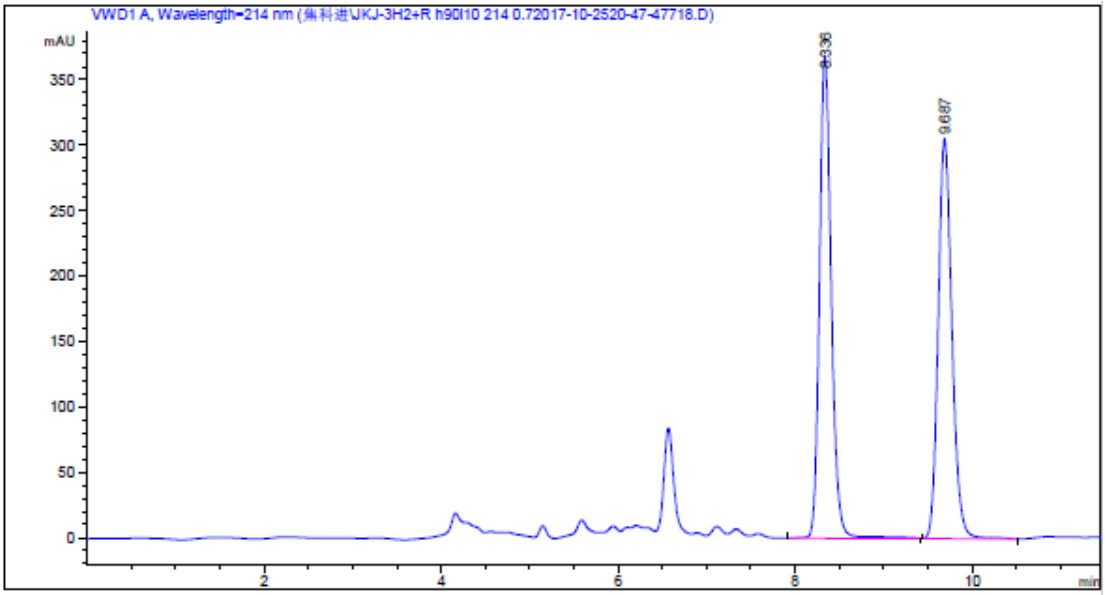
The product of *(R)*-MeO-BIPHME as ligand hydrogenated according to *ref. 10*
HPLC: Chiralpak AD-H (10% IPA:hexane, flow rate 0.7 ml min^{-1}, 214 nm, 40 ℃) t_R minor: 8.3 min, tR major: 9.7 min, *65% ee*



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.336	BB	0.1489	1039.26294	111.29173	17.3562
2	9.687	BV R	0.1692	4948.59912	452.99640	82.6438

A mixture of *(R)*-2-phenylbutanoic acid and the hydrogenated product.

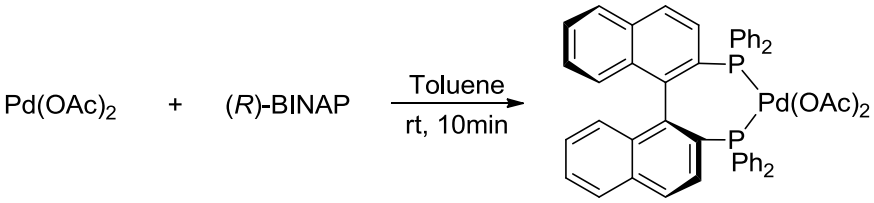
HPLC: Chiralpak AD-H (10% IPA:hexane, flow rate 0.7 ml min^{-1}, 214 nm, 40 ℃) t_R minor: 8.3 min, tR major: 9.7 min, *0.7% ee*



#	[min]		[min]	[mAU*s]	[mAU]	%
1	8.336	BB	0.1487	3417.62622	366.72635	50.8171
2	9.687	BB	0.1704	3307.71729	305.22974	49.1829

8 Electrochemical Set-up and Cyclic Voltammetry

1) Preparation of [*(R)*-BINAP]Pd(OAc)$_2$ [17]



Procedure: A 25 mL Schlenk tube charged with stir bar was added Pd(OAc)$_2$ (0.45 mmol Pd, 100 mg) and (*R*)-BINAP (0.45 mmol, 280 mg). Capped vial and evacuated / backfilled with nitrogen three times. To the vial added 2 mL anhydrous toluene and stirred at room temperature for 5 – 10 minutes resulting in a red homogeneous solution. Added 5 mL pentane to reaction in air over 5 minutes resulting in a thick yellow slurry. The suspension was filtered, washed with 2x 5 mL pentane and dried under vacuum at room temperature for 1 hour. Collected 350 mg yellow solids for 92% yield.
^{1}H NMR (400 MHz, CDCl3) δ 7.89 (br, 5H), 7.80–7.66, (m, 5H), 7.55 (d, *J* = 8.3 Hz, 5H), 7.49 (br, 7H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.24 (t, 2H), 7.19–7.11 (m, 2H), 7.01 (t, *J* = 7.7 Hz, 2H), 6.80–6.72 (m, 3H), 6.68 (br, 3H), 6.53 (d, *J* = 8.6 Hz, 2H). 2.34 (s, 3H), 1.34 (s, 6H). **^{31}P NMR** (400 MHz, CDCl3) δ: 25.4 ppm. (The signal of δ 2.34(s, 3H) belongs to toluene)

2) Cyclic Voltammetry

Cyclic voltammograms were recorded with a CHI660E potentiostat at room temperature in DMF. Bu_4NPF_6 (0.07 M) was used as the supporting electrolyte, and a Pt electrode (0.03 cm^2) was used as the working electrode. The auxiliary electrode was a platinum sheet. All potentials are referenced against the Ag/AgI redox couple.

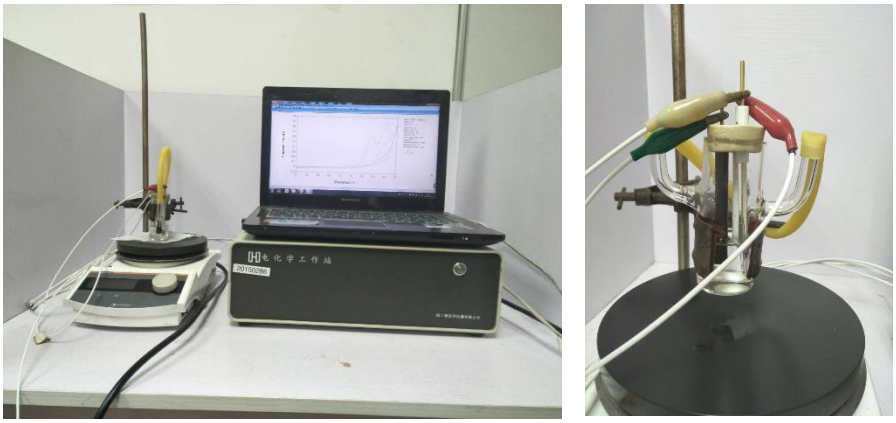


Figure 1 Photograph of setup used for cyclic voltammetry.

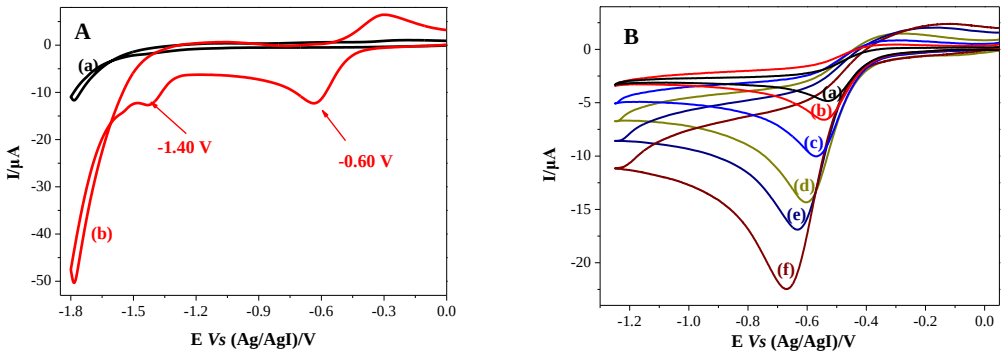


Figure 2. Cyclic voltammograms recorded on a Pt electrode (area = 0.031 cm^2), A: (a) DMF containing 0.07 M Bu_4NPF_6 ; (b) solution (a) after addition of 2 mM [(*R*)-BINAP]Pd$(OAc)_2$ (v = 100 mV s^{-1}); B: CVs of [(*R*)-BINAP]Pd$(OAc)_2$ (2 mM) eletroreduction at different scanning speed, (a) 0.01 V s^{-1} (b) 0.02 V s^{-1} (c) 0.05 V s^{-1} (d) 0.1 V s^{-1} (e) 0.2 V s^{-1} (f) 0.3 V s^{-1}.

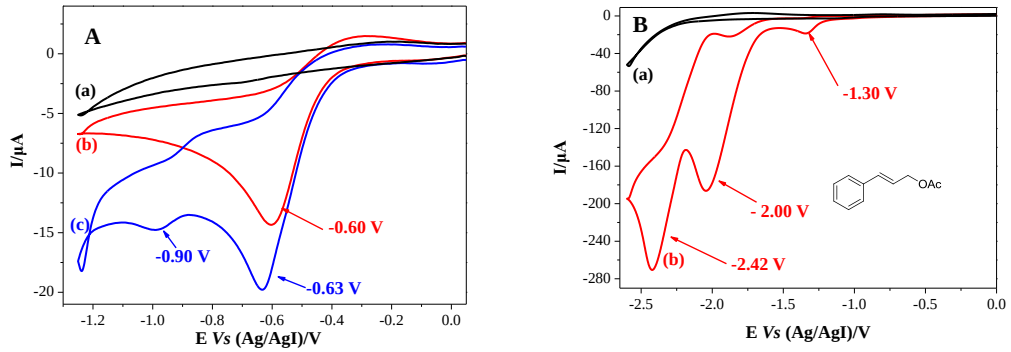


Figure 3. Cyclic voltammograms recorded on a Pt electrode (area = 0.031 cm^2) at 100 mV s^{-1}, A: (a) DMF containing 0.07 M Bu_4NPF_6; (b) solution (a) after addition of 2 mM [(*R*)-BINAP]Pd$(OAc)_2$; (c) solution (b) after addition of 20 mM **1b**; B: DMF containing 0.07 M Bu_4NPF_6 ; (b) solution (a) after addition of 20 mM **1b**.

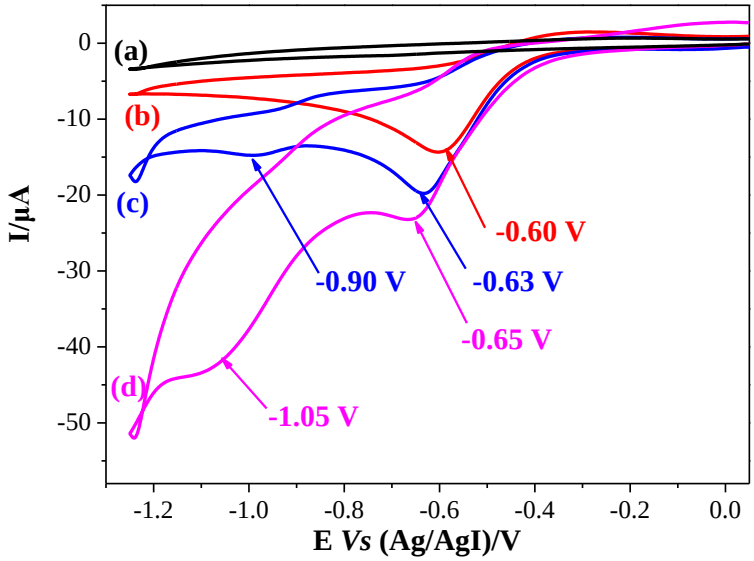


Figure 4. Cyclic voltammograms recorded on a Pt electrode (area = 0.031 cm^2) at 100 mVs^{-1} in: (a) DMF containing 0.07 M Bu_4NPF_6; (b) solution (a) after addition of 2 mM [(*R*)-BINAP]Pd$(OAc)_2$; (c) solution (b) after addition of 20 mM **1b**; (d) solution (c) saturated with CO_2.

9 Reference

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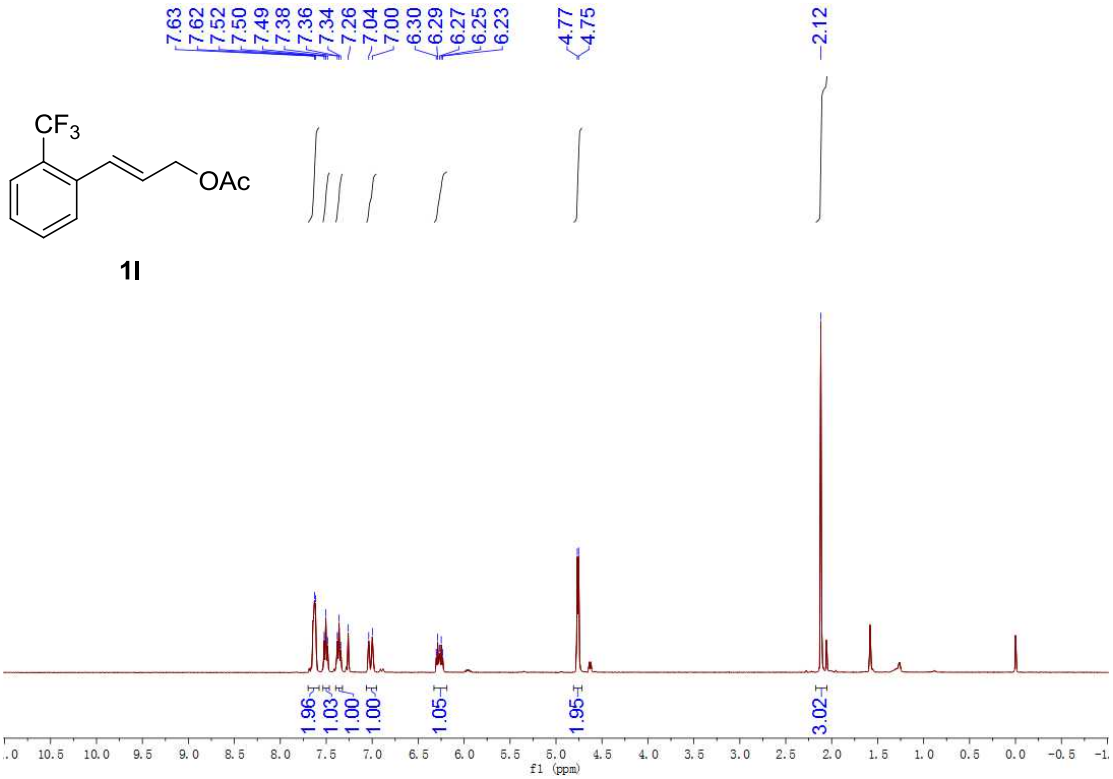
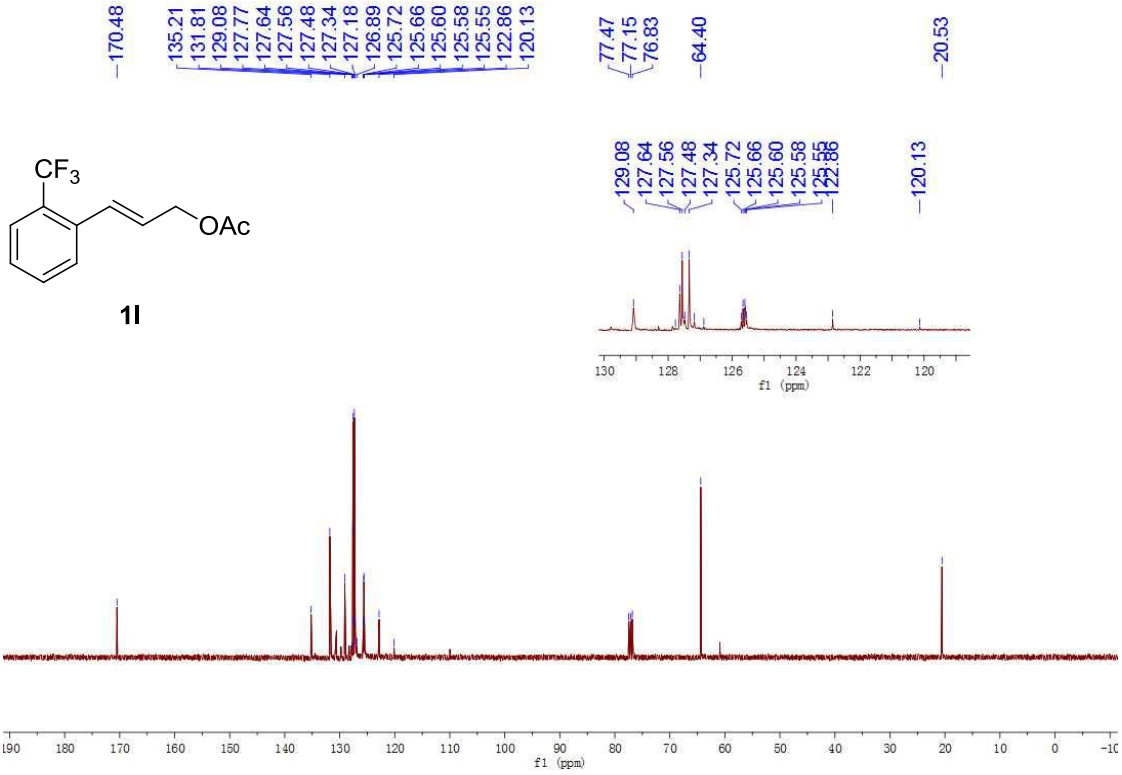
10 Spectra of Compounds

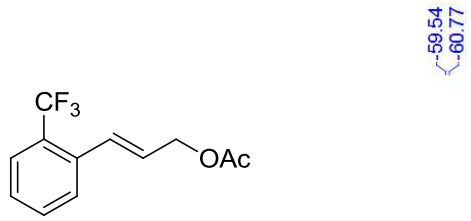
^{1}H NMR Spectrum of 1l ($CDCl_3$)



^{13}C NMR Spectrum of 1l ($CDCl_3$)

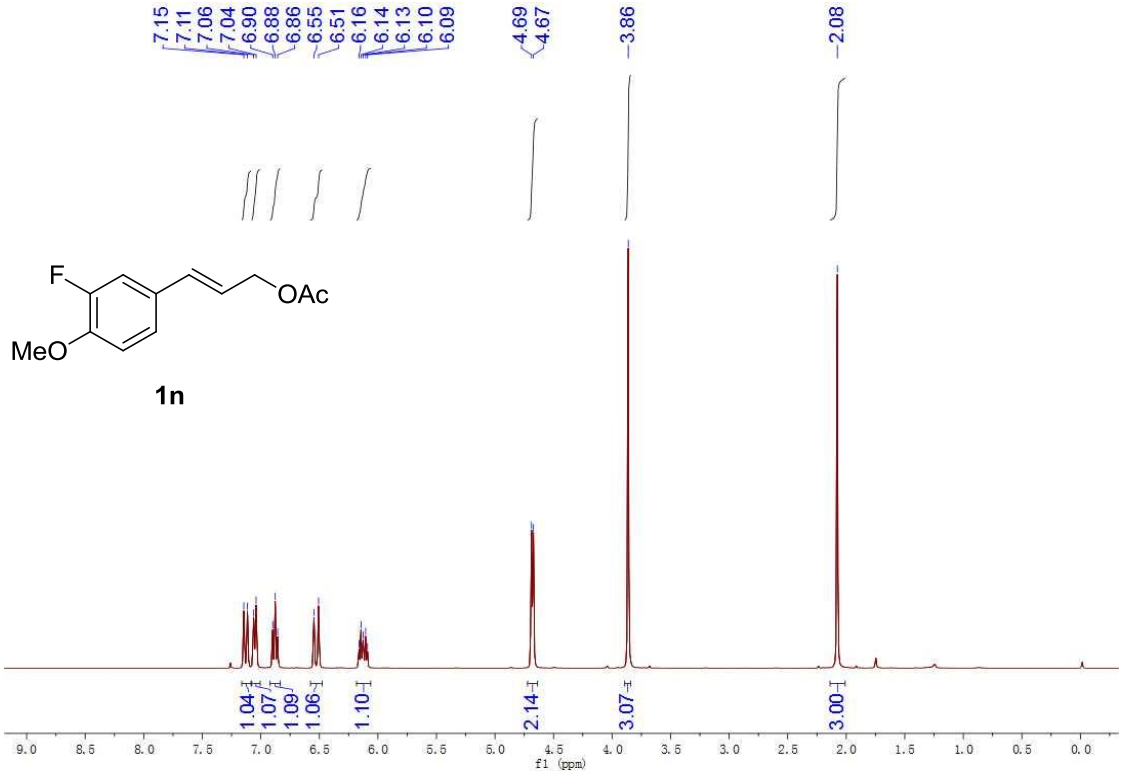


^{19}F NMR Spectrum of 1l ($CDCl_3$)



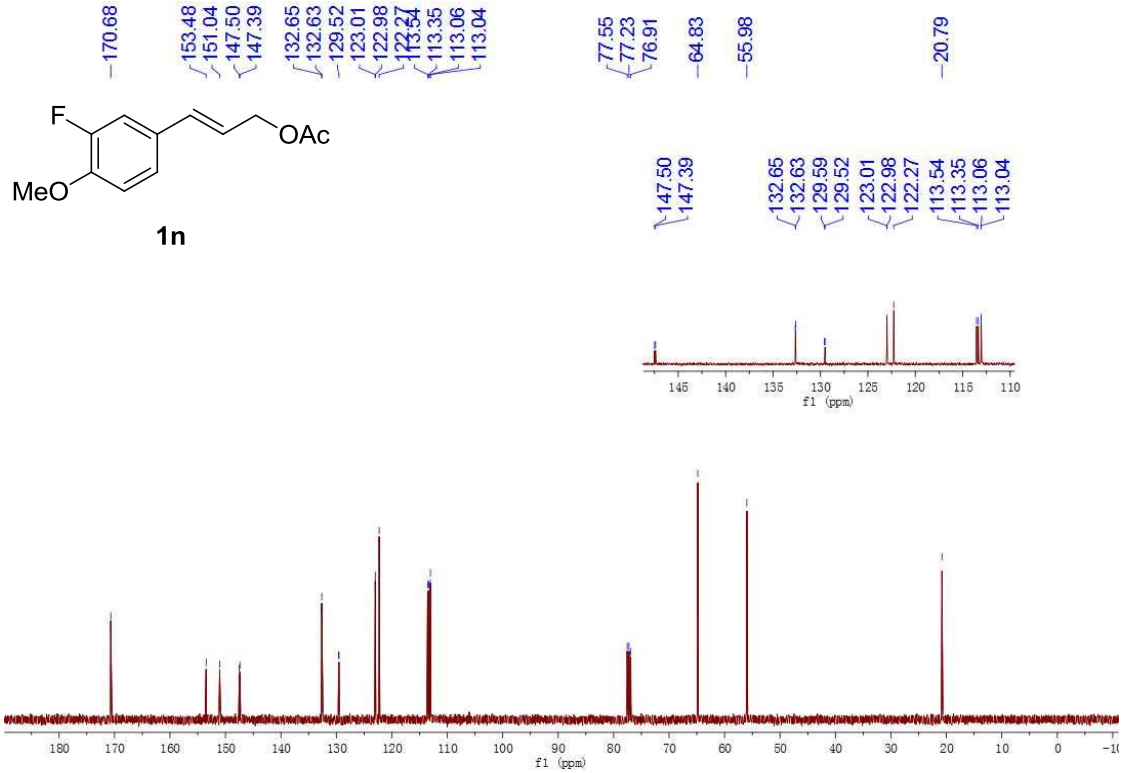
1l

^{1}H NMR Spectrum of 1n ($CDCl_3$)

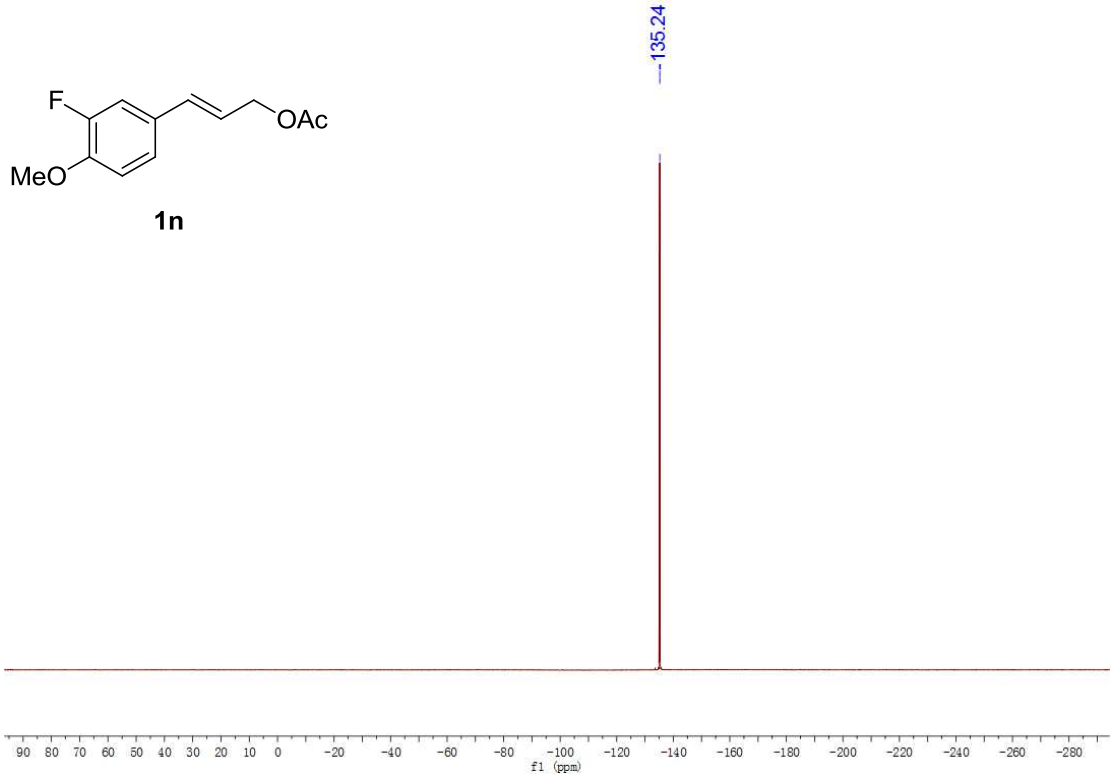


1n

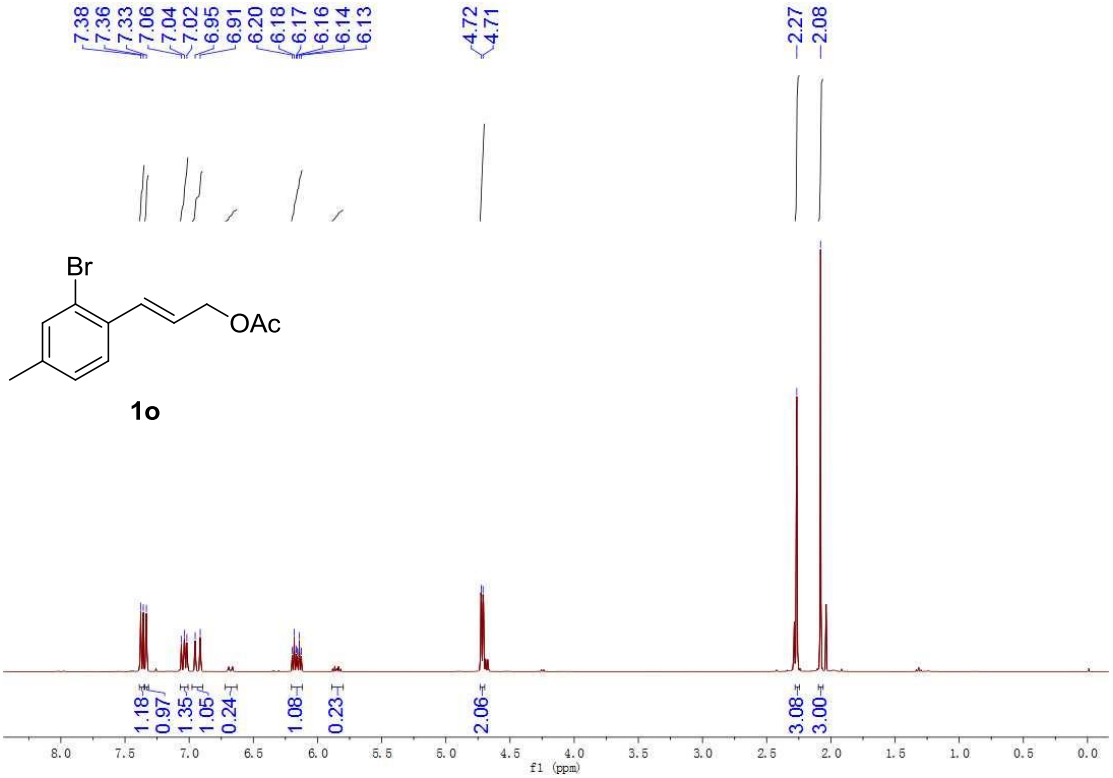
^{13}C NMR Spectrum of 1n ($CDCl_3$)



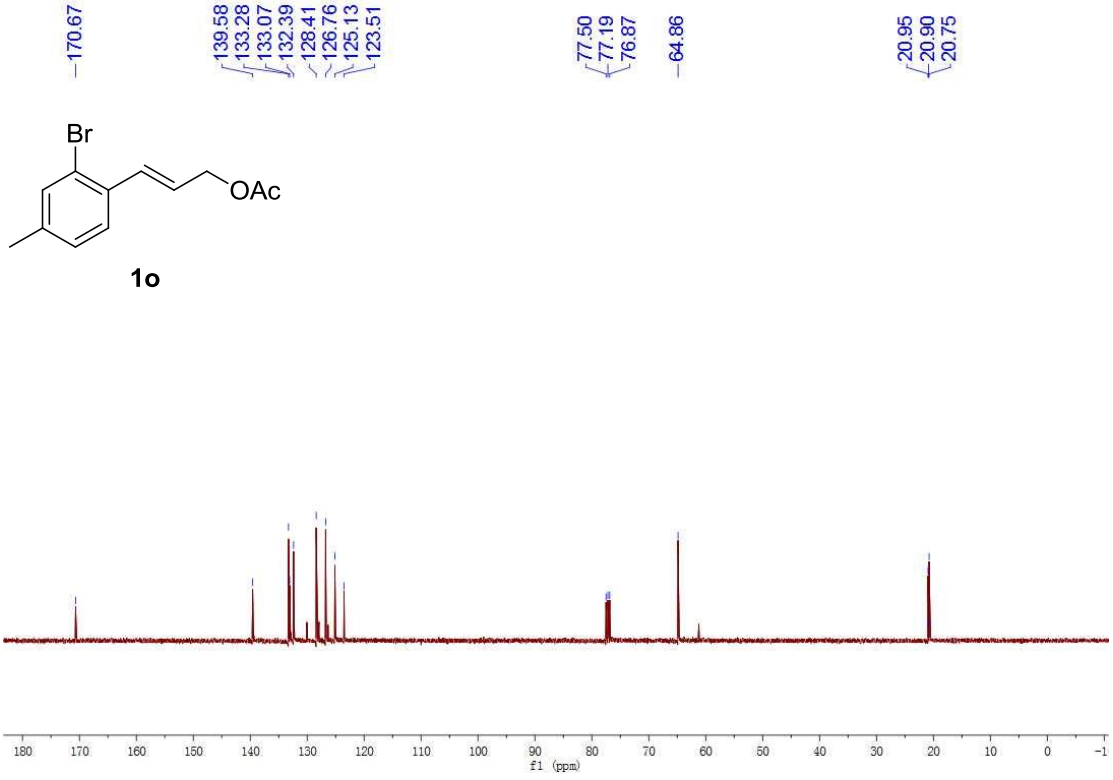
^{19}F NMR Spectrum of 1n ($CDCl_3$)



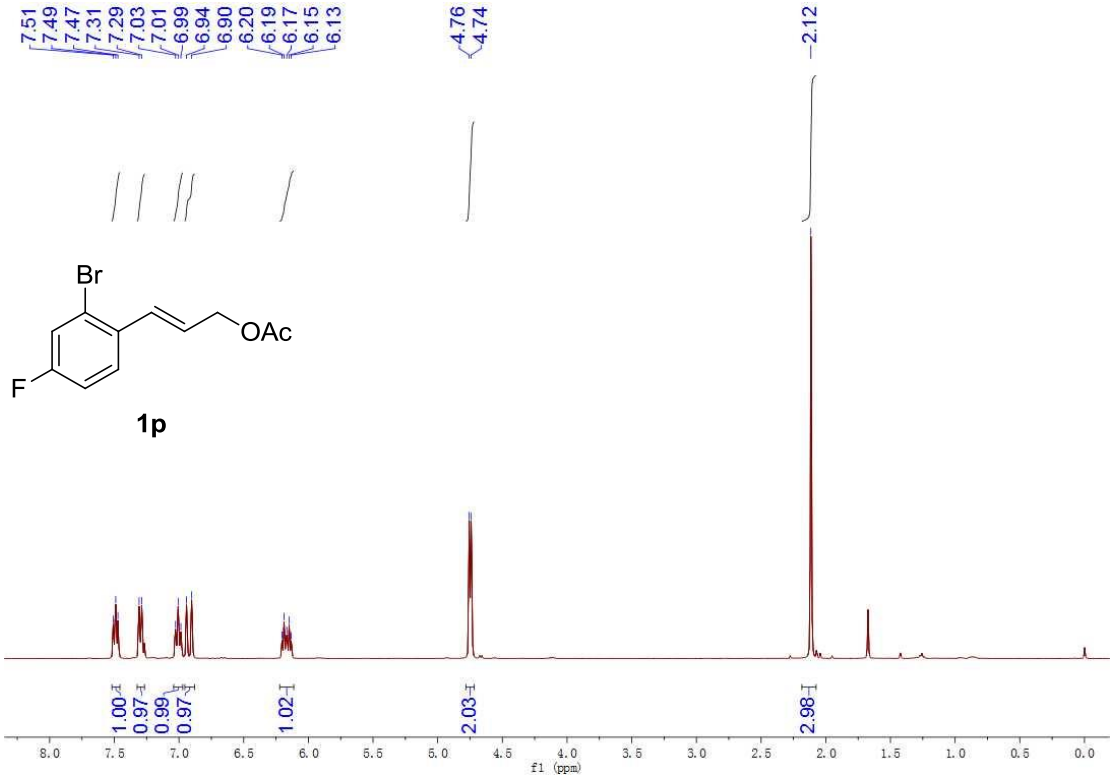
^{1}H NMR Spectrum of 1o ($CDCl_3$)



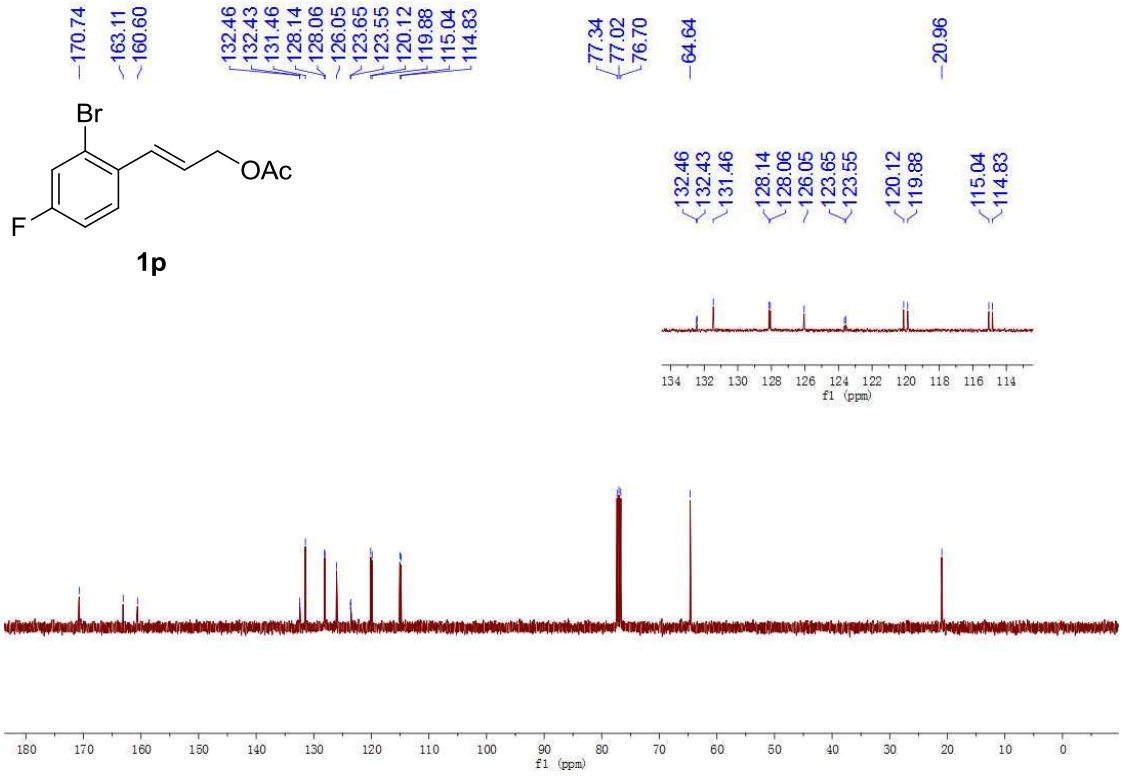
^{13}C NMR Spectrum of 1o ($CDCl_3$)



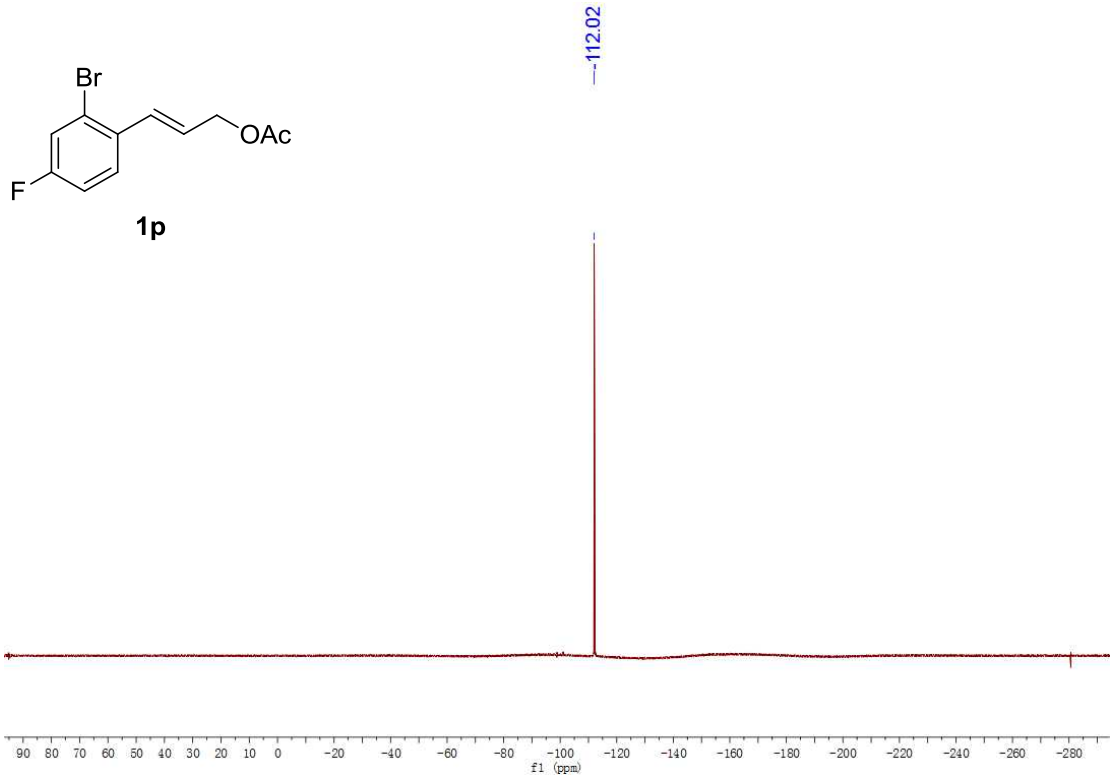
^{1}H NMR Spectrum of 1p ($CDCl_3$)



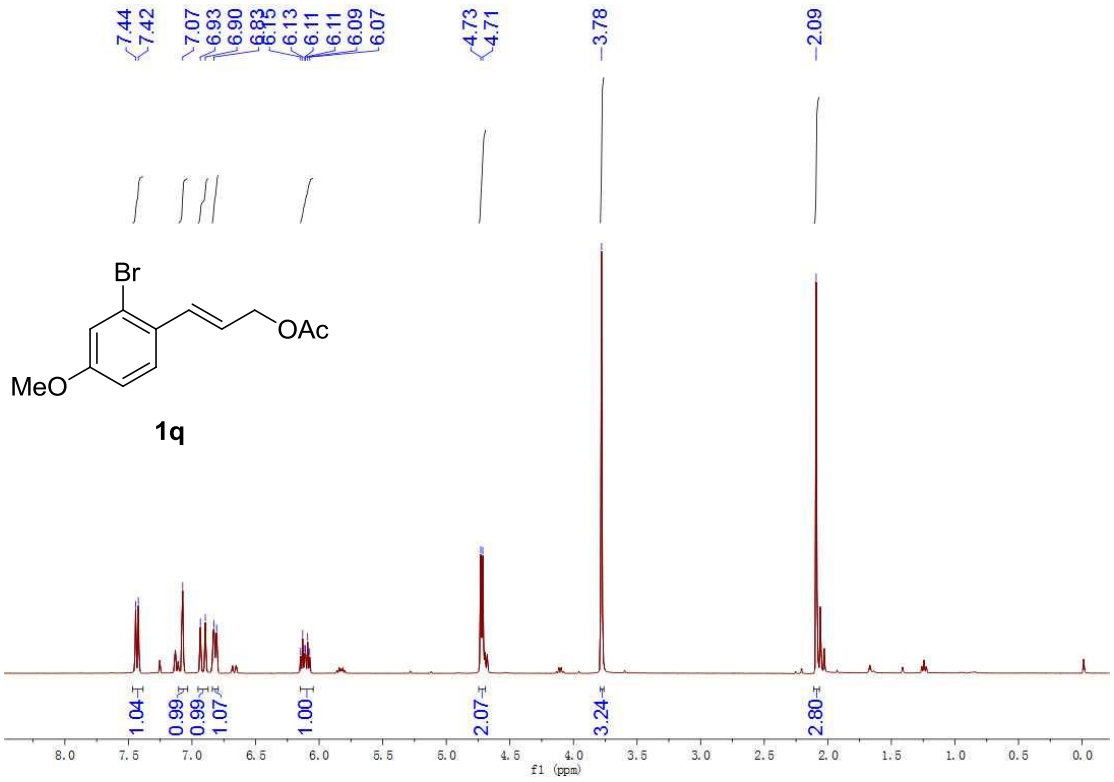
^{13}C NMR Spectrum of 1p ($CDCl_3$)



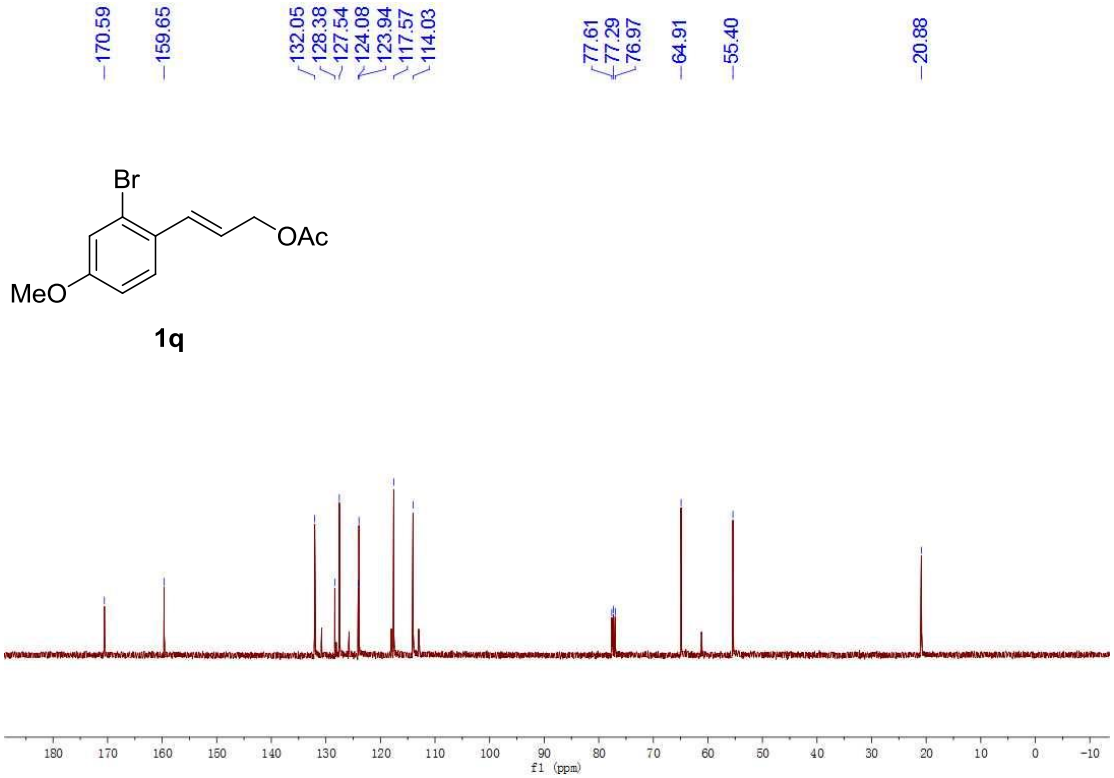
^{19}F NMR Spectrum of 1p ($CDCl_3$)



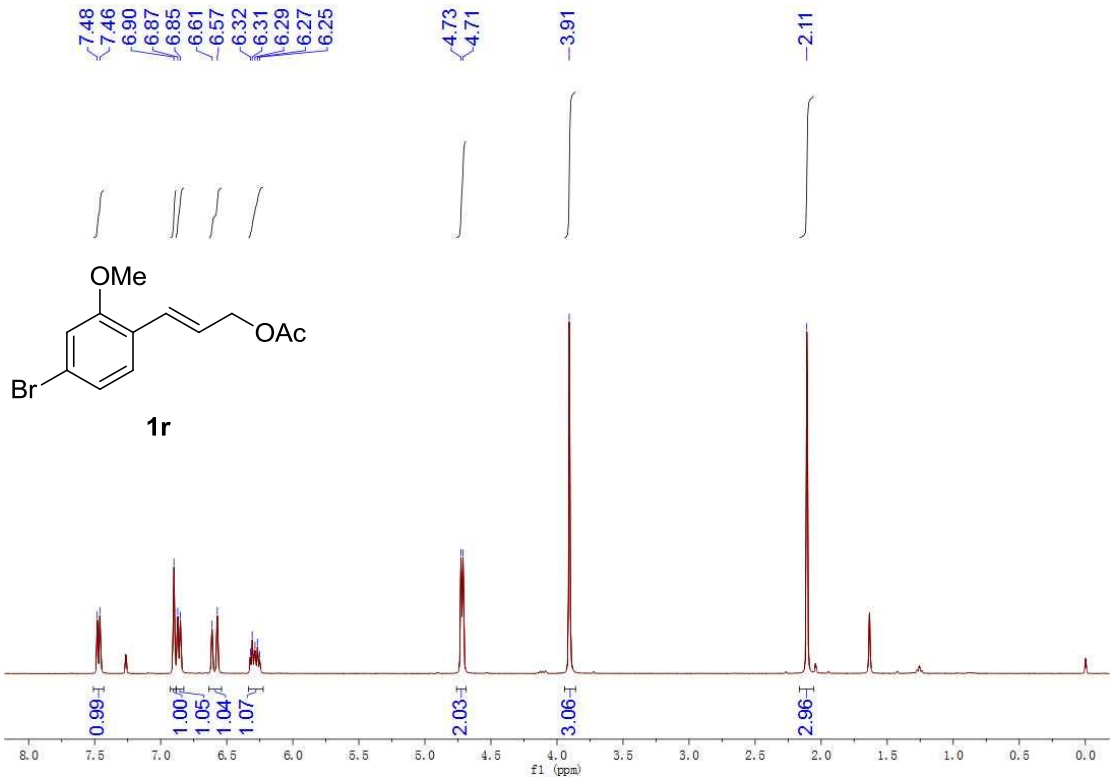
^{1}H NMR Spectrum of 1q ($CDCl_3$)



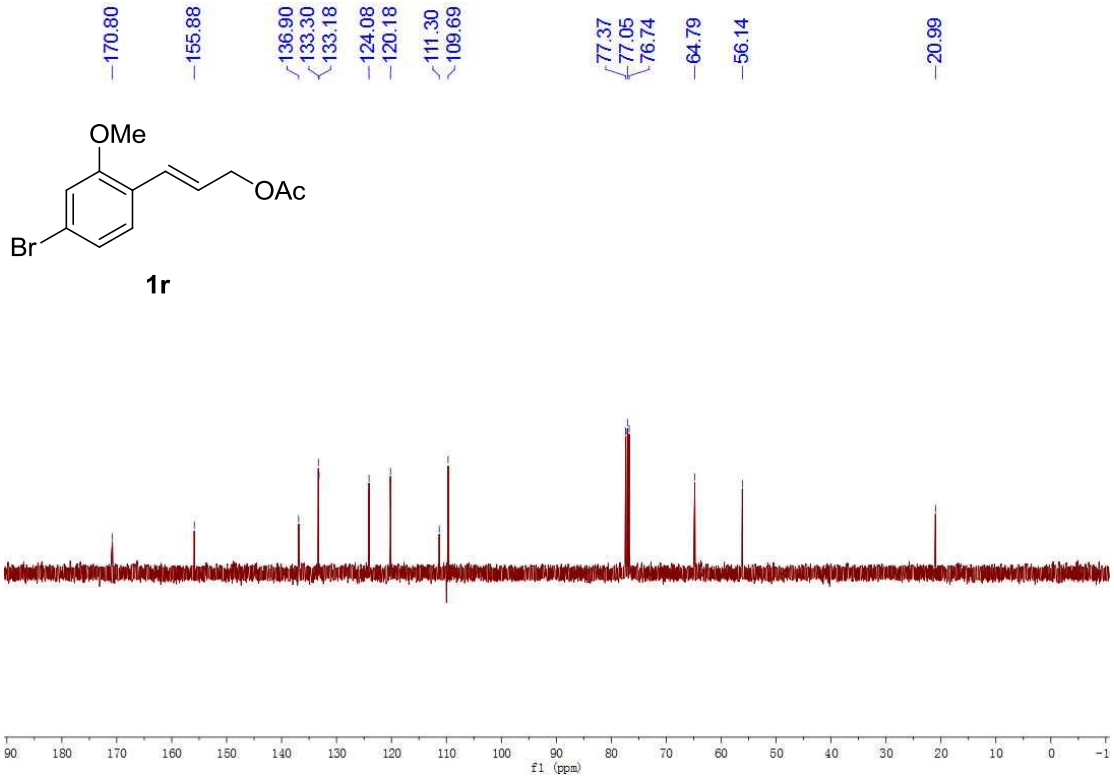
^{13}C NMR Spectrum of 1q ($CDCl_3$)



^{1}H NMR Spectrum of 1r ($CDCl_3$)

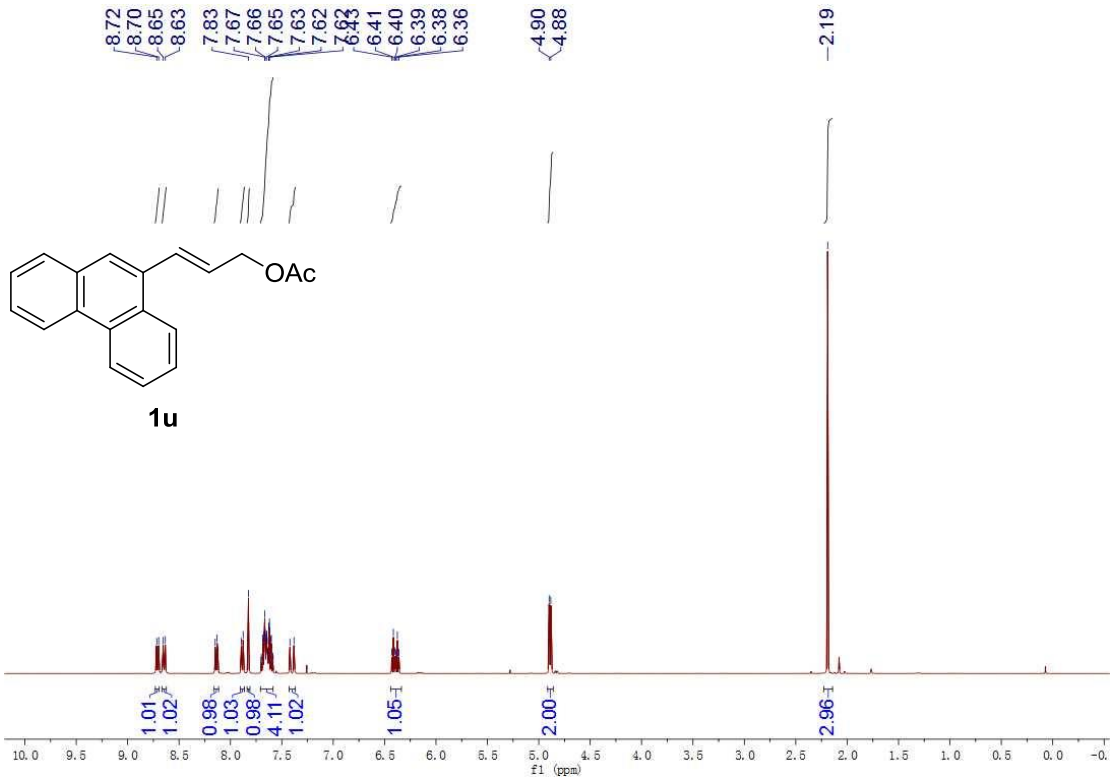


^{13}C NMR Spectrum of 1r ($CDCl_3$)



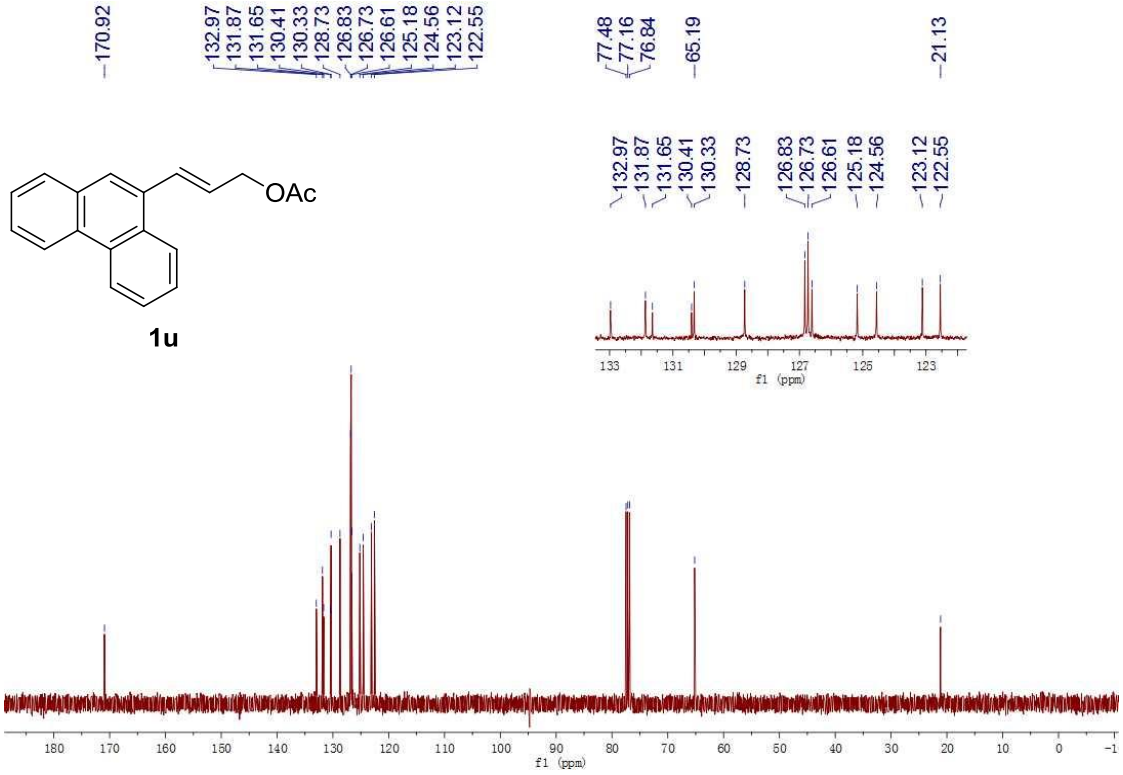
1r

^{1}H NMR Spectrum of 1u ($CDCl_3$)

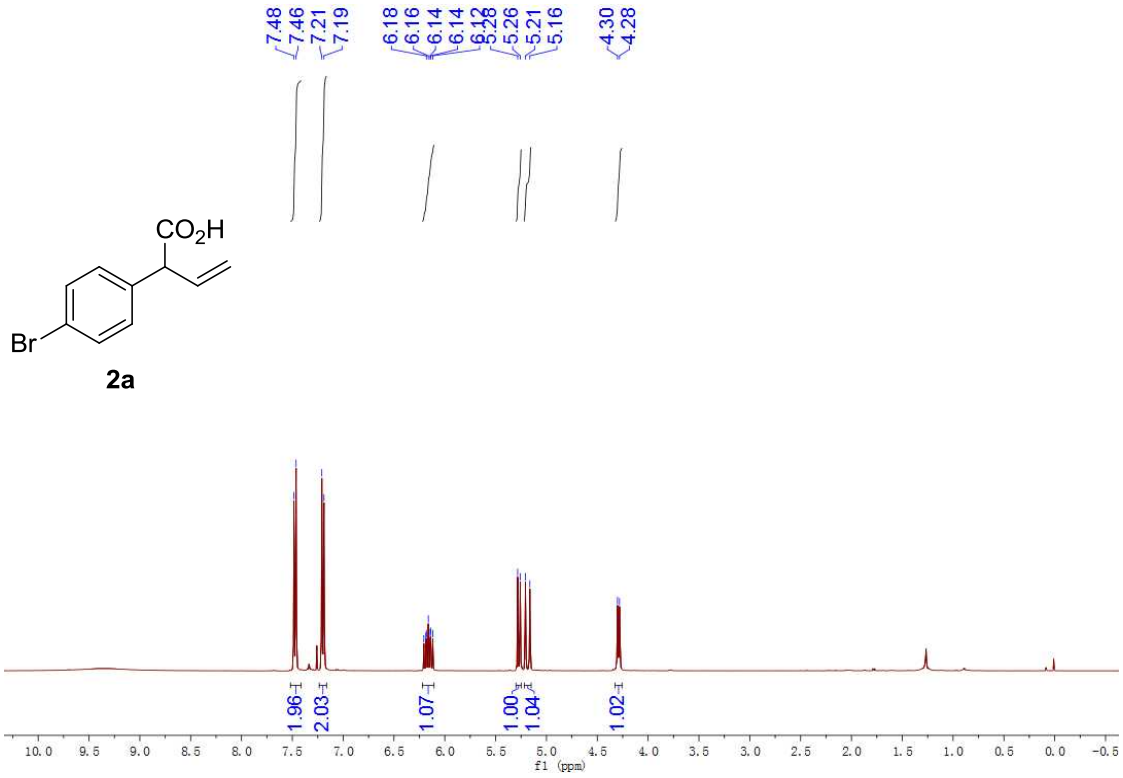


1u

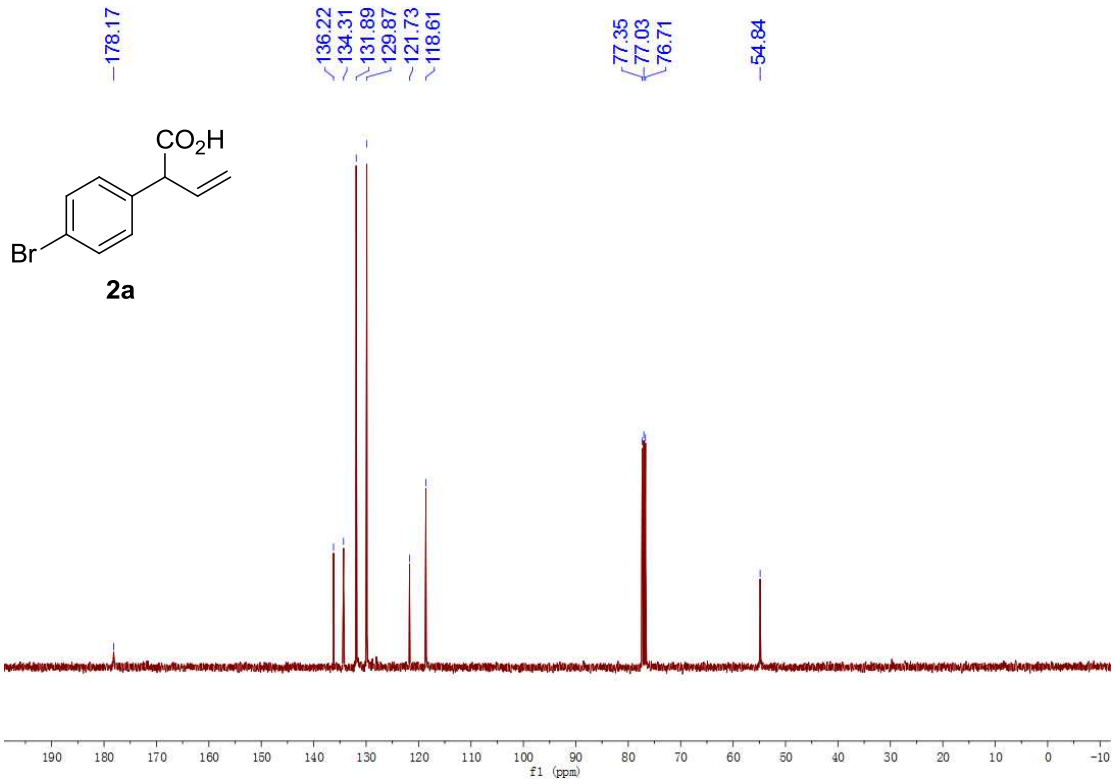
^{13}C NMR Spectrum of 1u ($CDCl_3$)



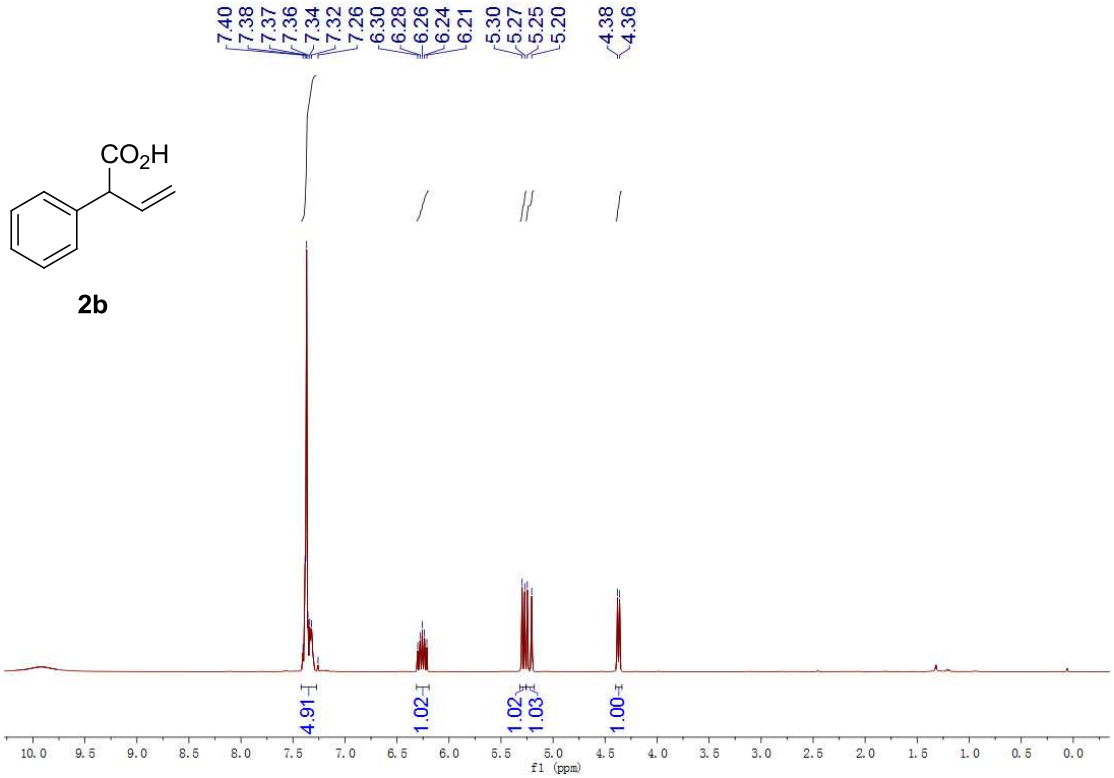
^{1}H NMR Spectrum of 2a ($CDCl_3$)



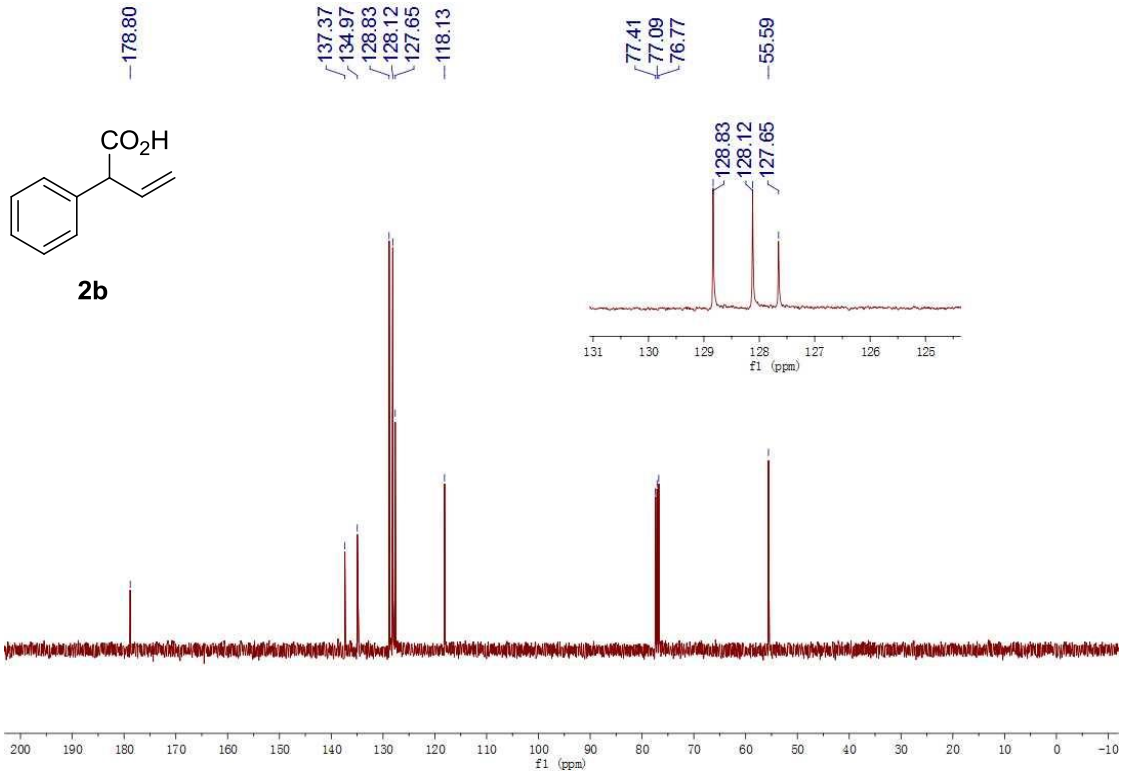
^{13}C NMR Spectrum of 2a ($CDCl_3$)



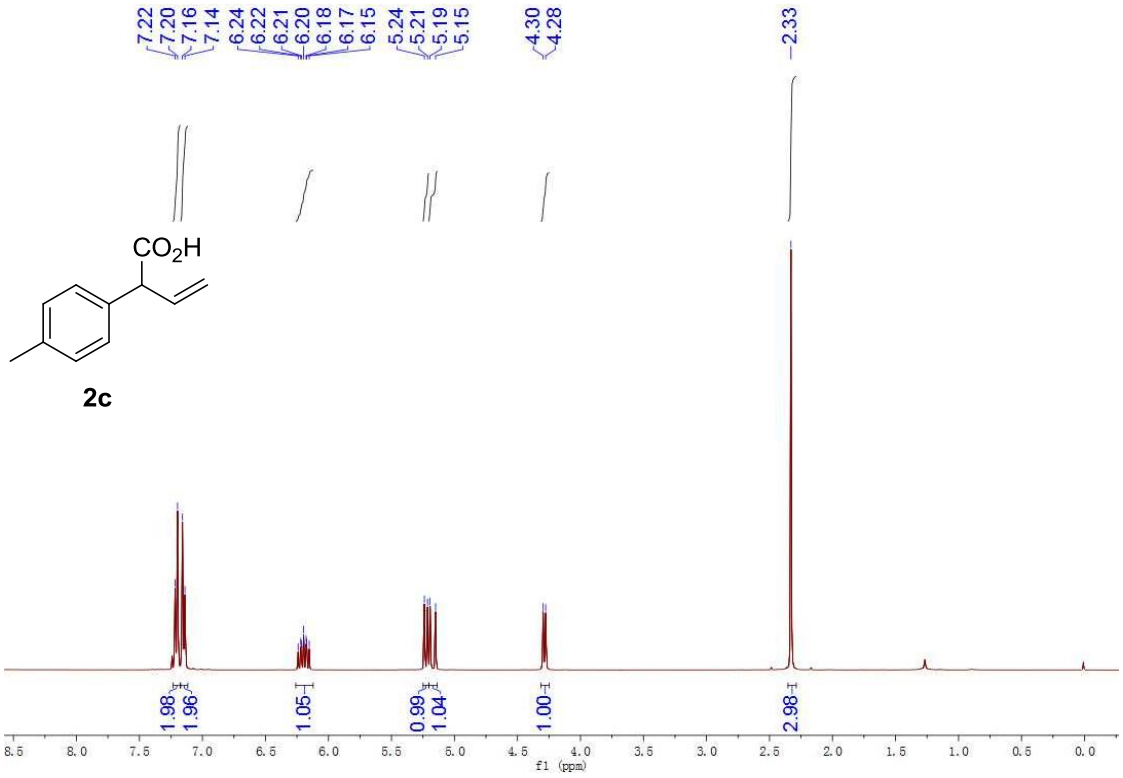
^{1}H NMR Spectrum of 2b ($CDCl_3$)



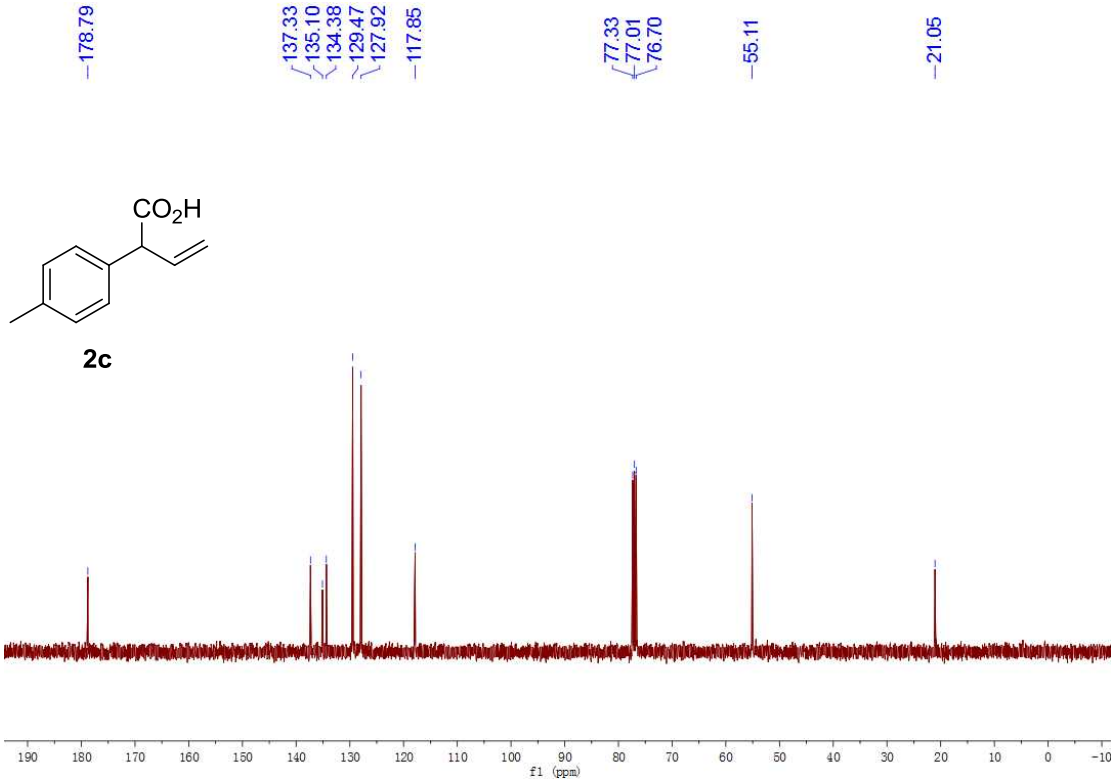
^{13}C NMR Spectrum of 2b ($CDCl_3$)



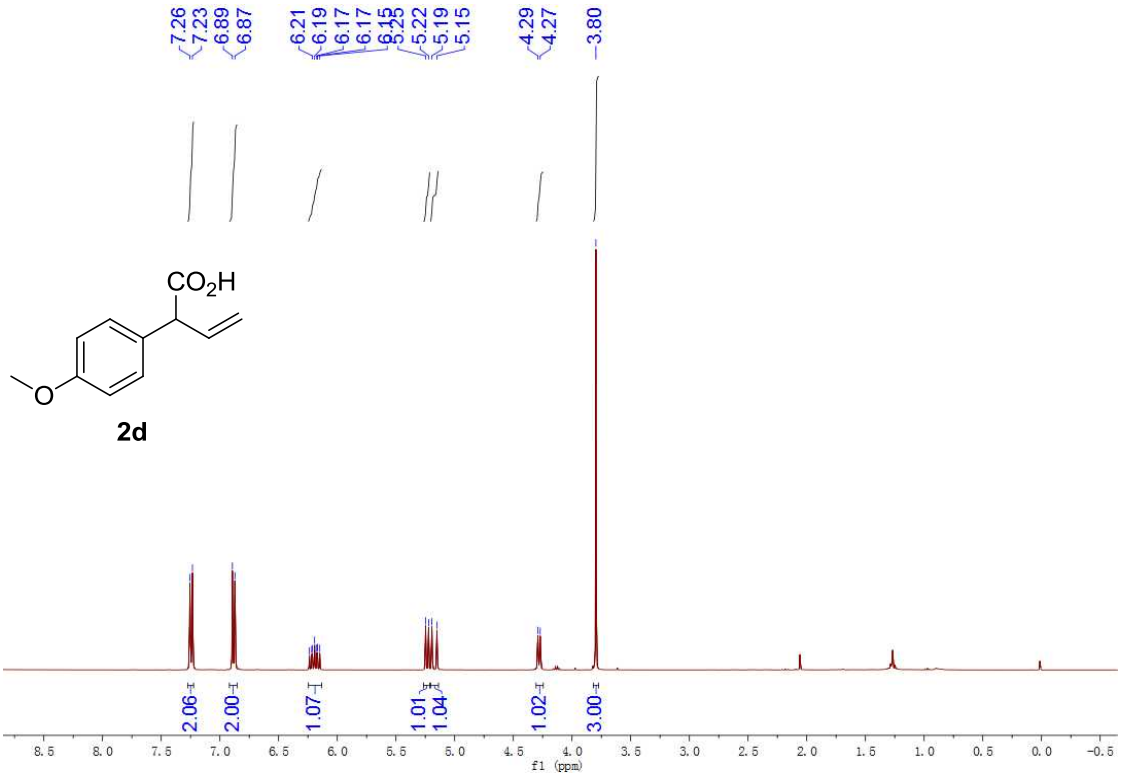
^{1}H NMR Spectrum of 2c ($CDCl_3$)



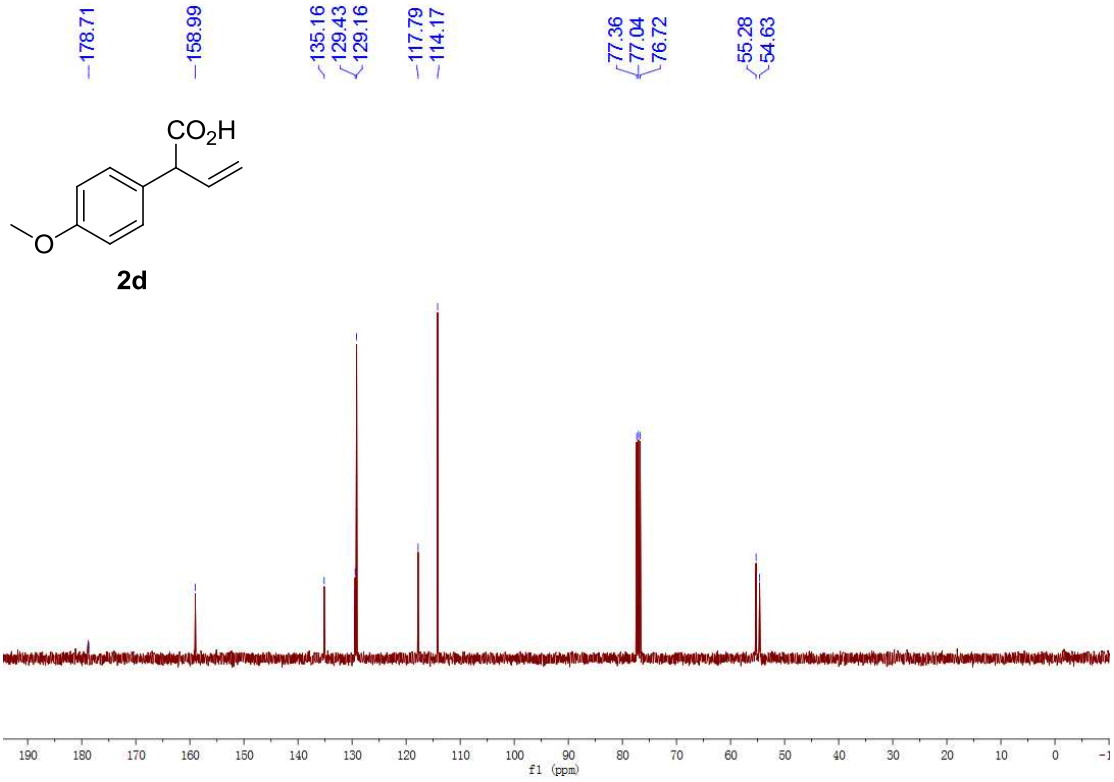
^{13}C NMR Spectrum of 2c ($CDCl_3$)



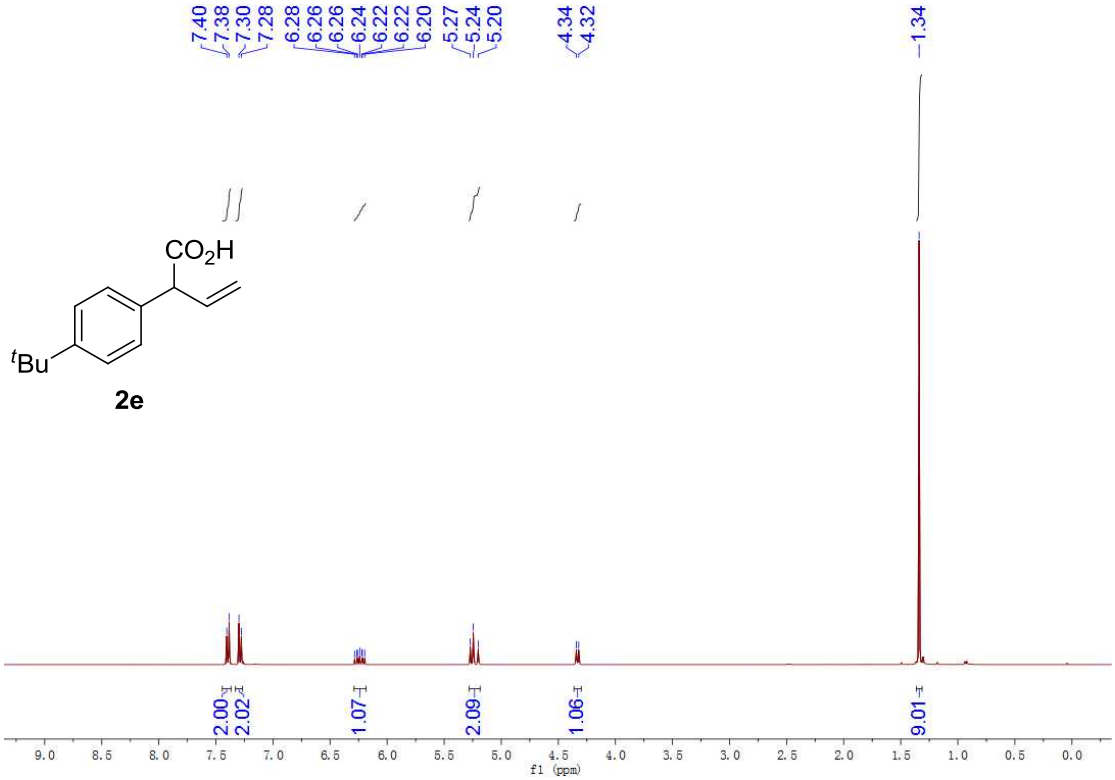
^{1}H NMR Spectrum of 2d ($CDCl_3$)



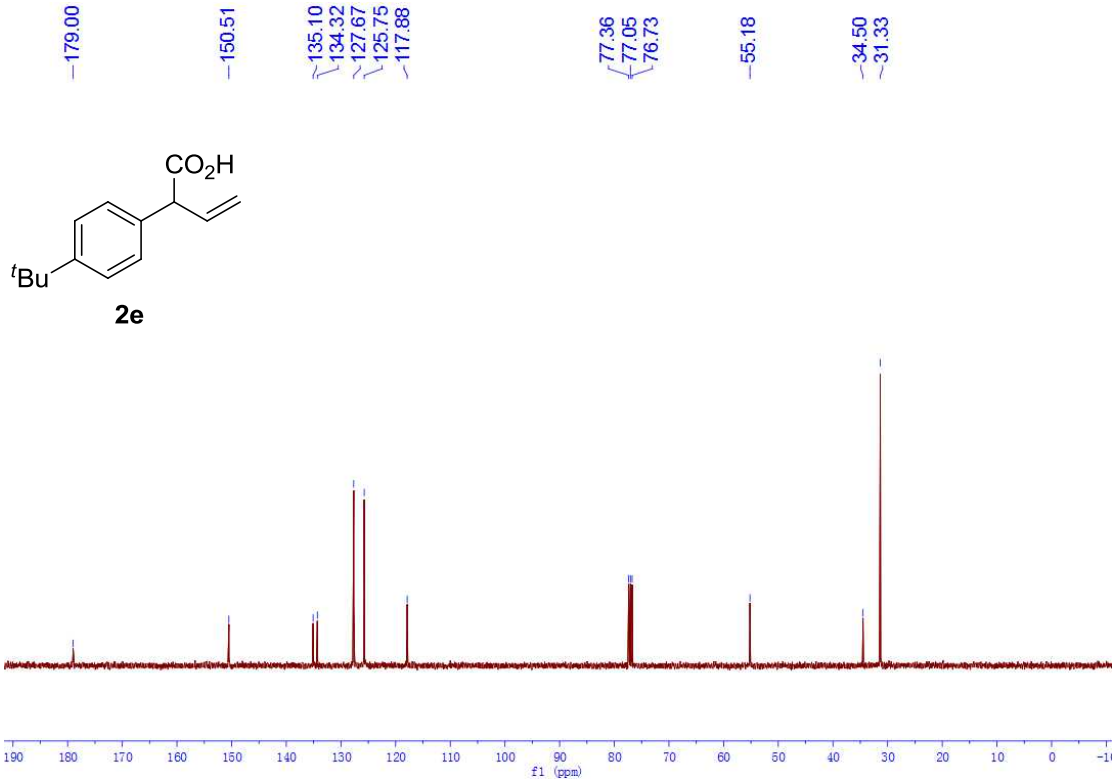
^{13}C NMR Spectrum of 2d ($CDCl_3$)



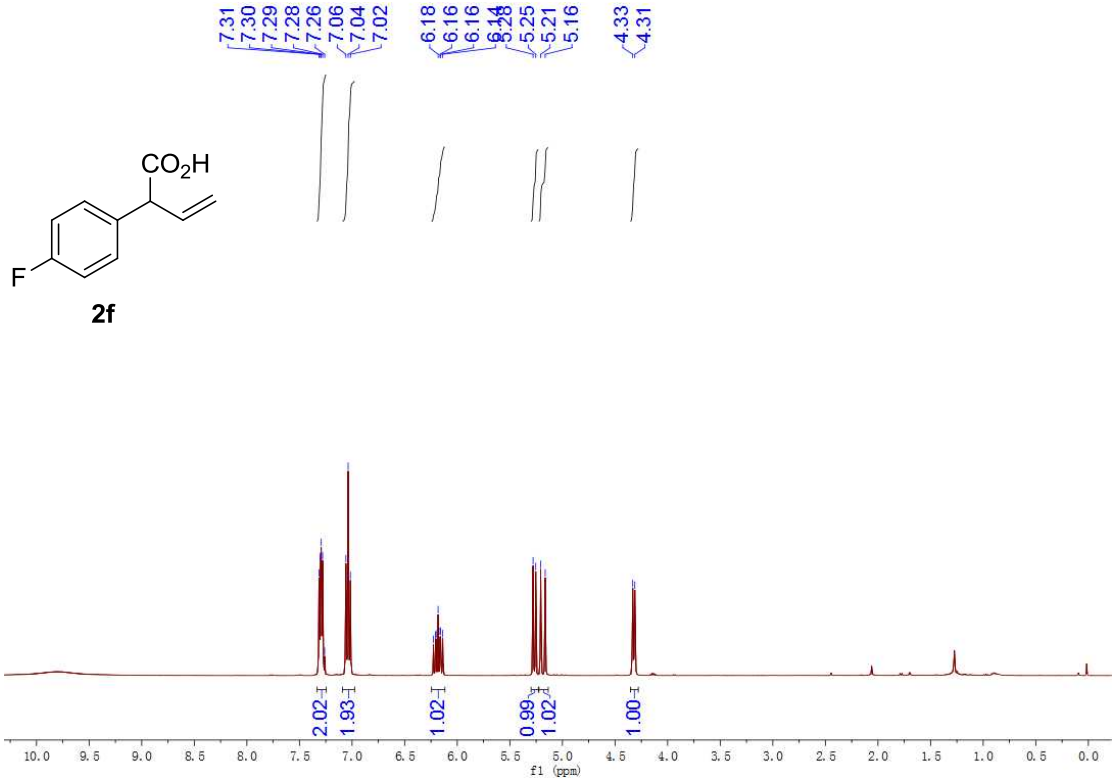
^{1}H NMR Spectrum of 2e ($CDCl_3$)



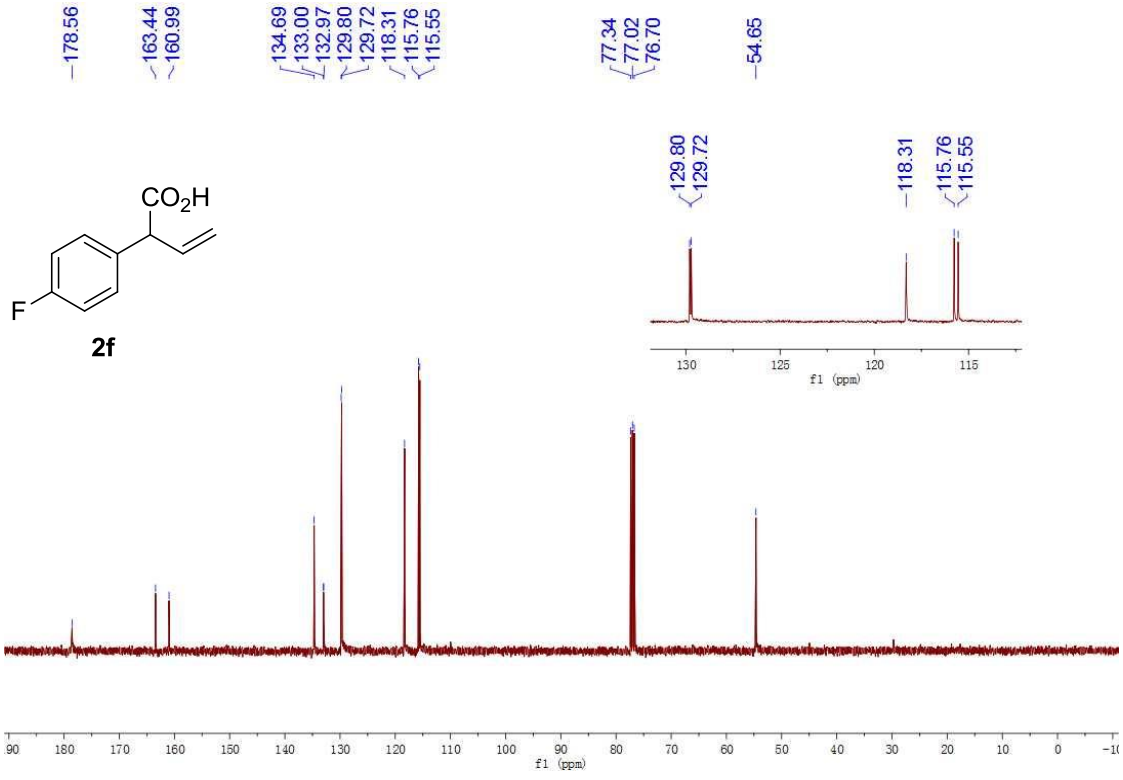
^{13}C NMR Spectrum of 2e ($CDCl_3$)



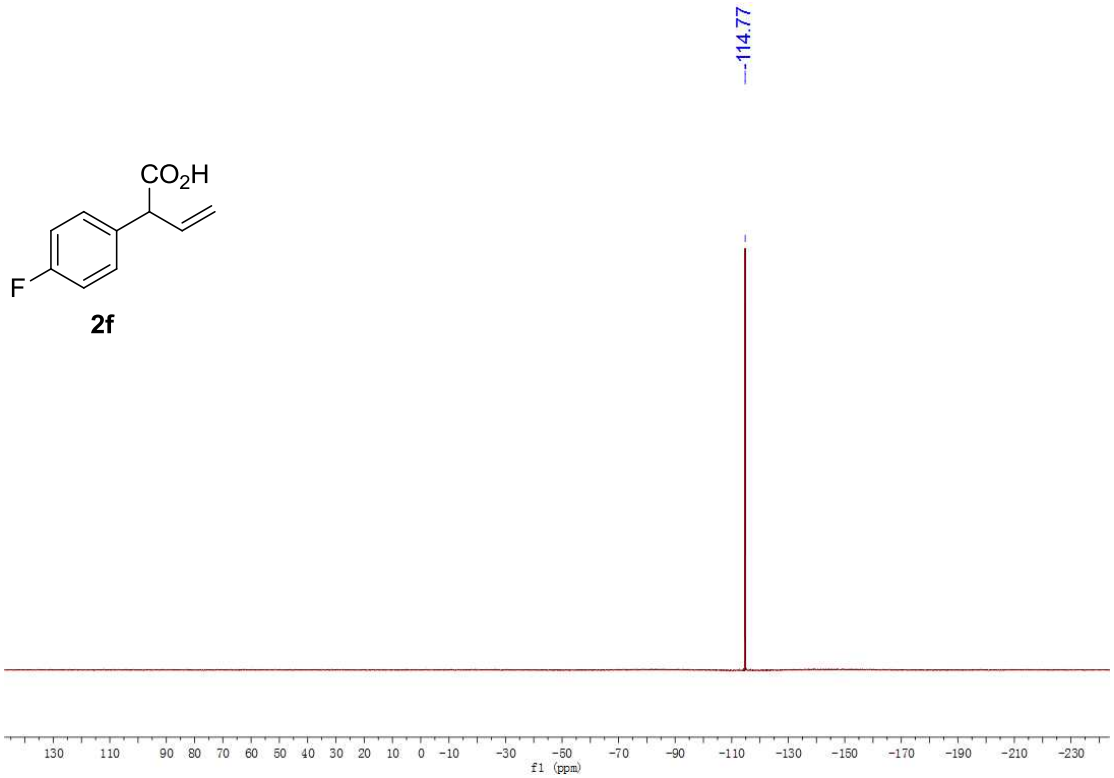
^{1}H NMR Spectrum of 2f ($CDCl_3$)



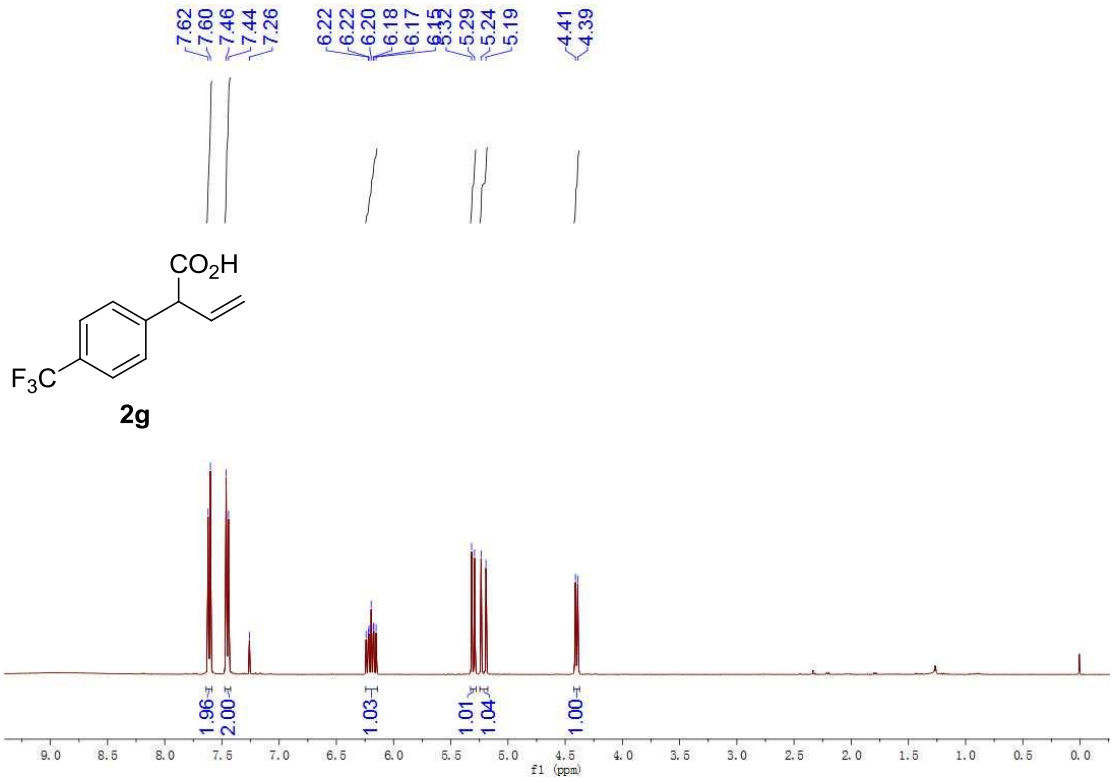
^{13}C NMR Spectrum of 2f ($CDCl_3$)



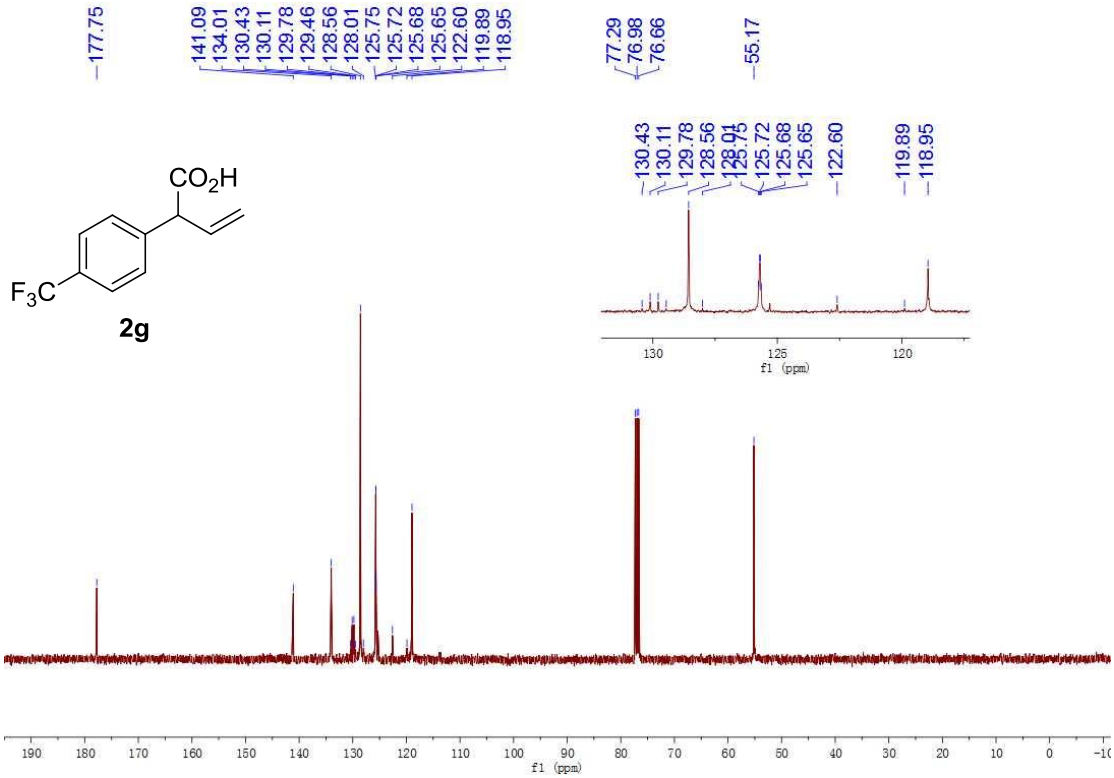
^{19}F NMR Spectrum of 2f ($CDCl_3$)



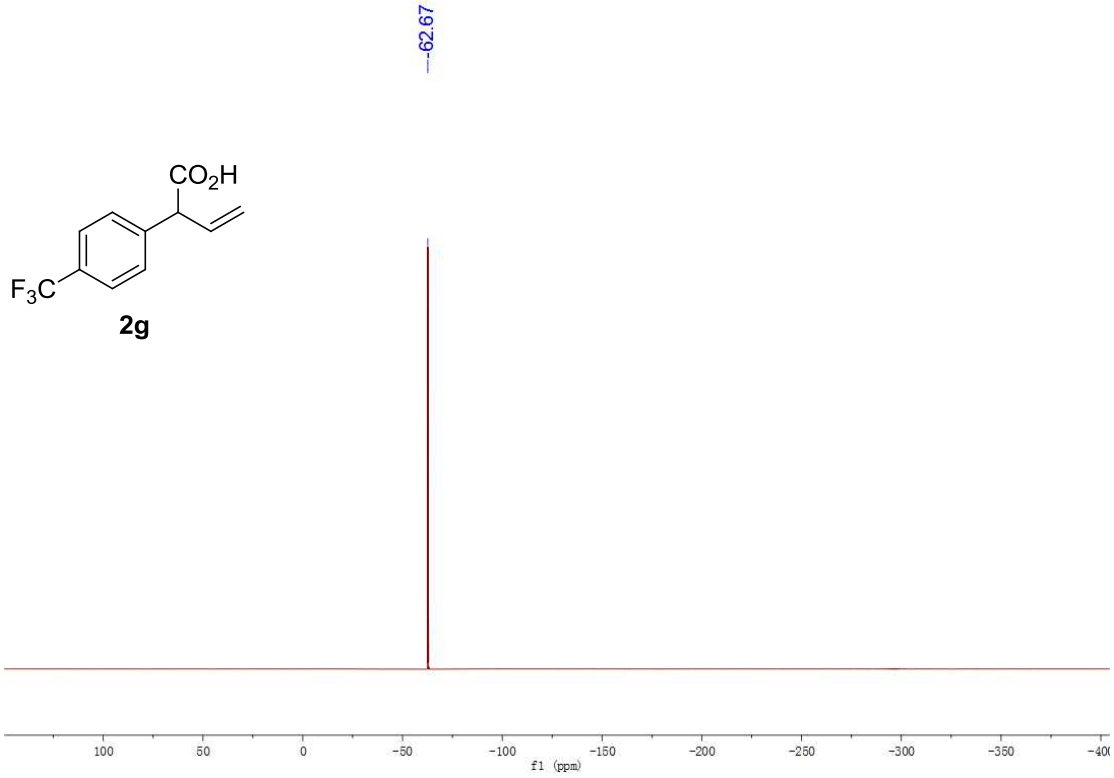
^{1}H NMR Spectrum of 2g ($CDCl_3$)



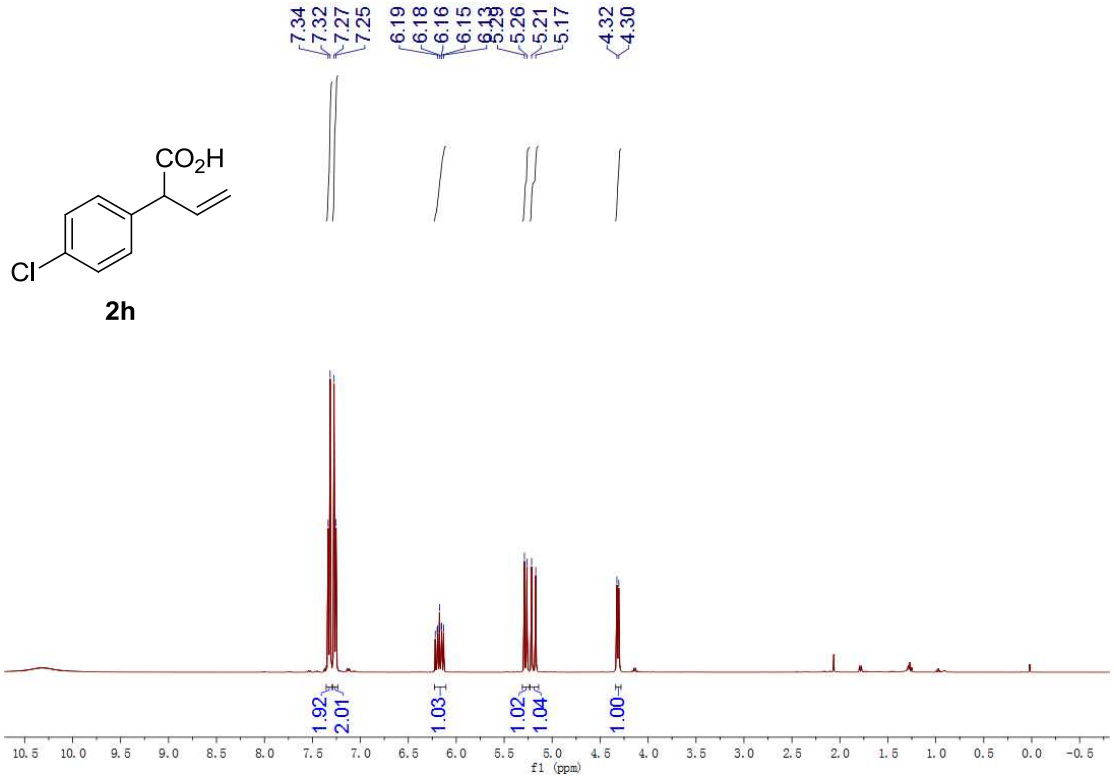
^{13}C NMR Spectrum of 2g ($CDCl_3$)



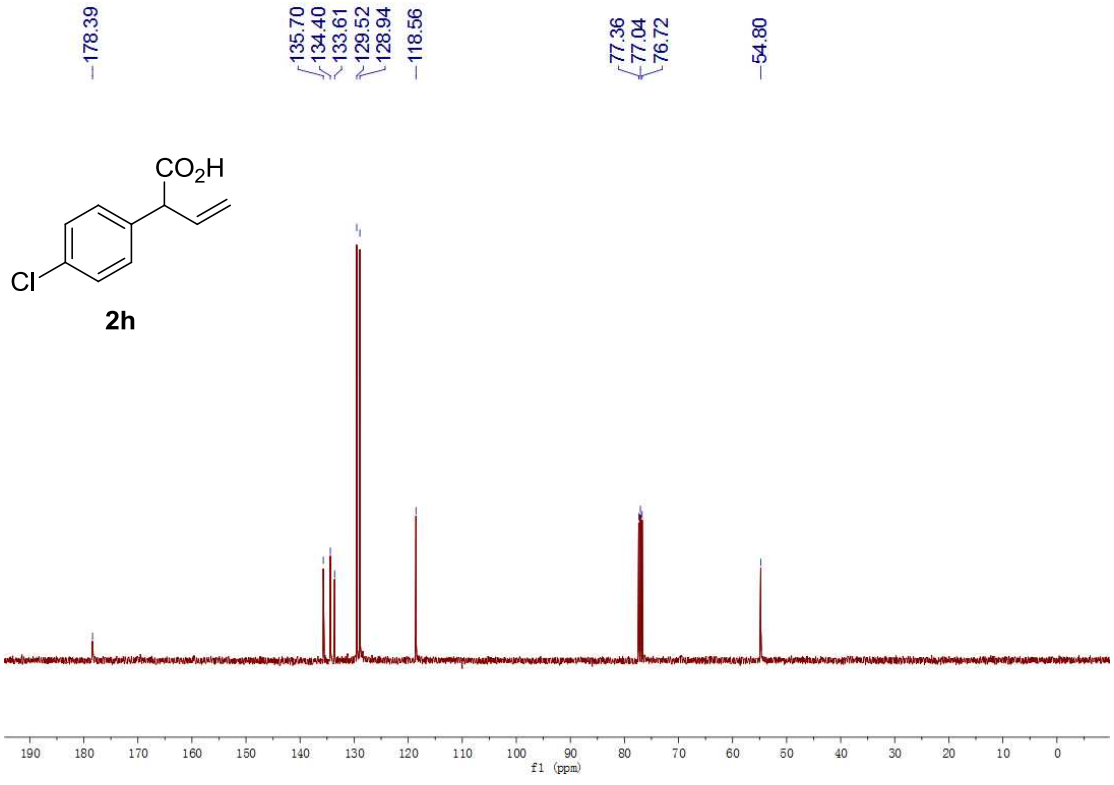
^{19}F NMR Spectrum of 2g ($CDCl_3$)



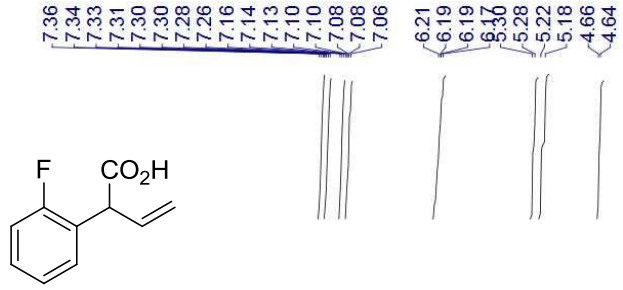
^{1}H NMR Spectrum of 2h ($CDCl_3$)



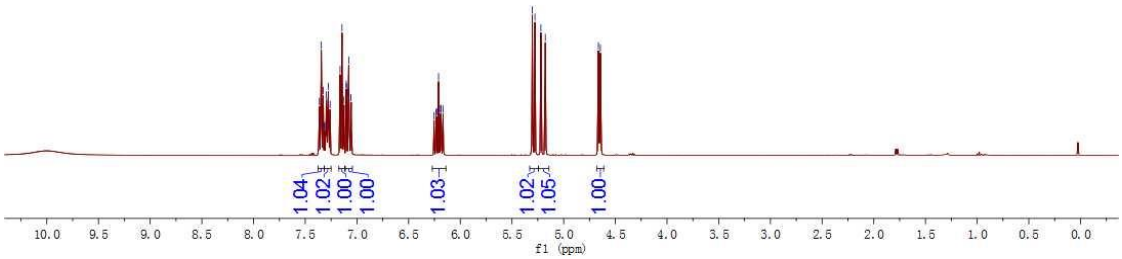
^{13}C NMR Spectrum of 2h ($CDCl_3$)



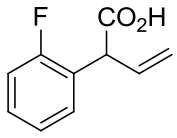
^{1}H NMR Spectrum of 2i ($CDCl_3$)



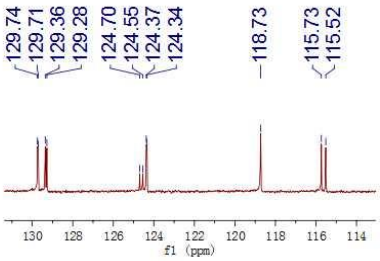
2i

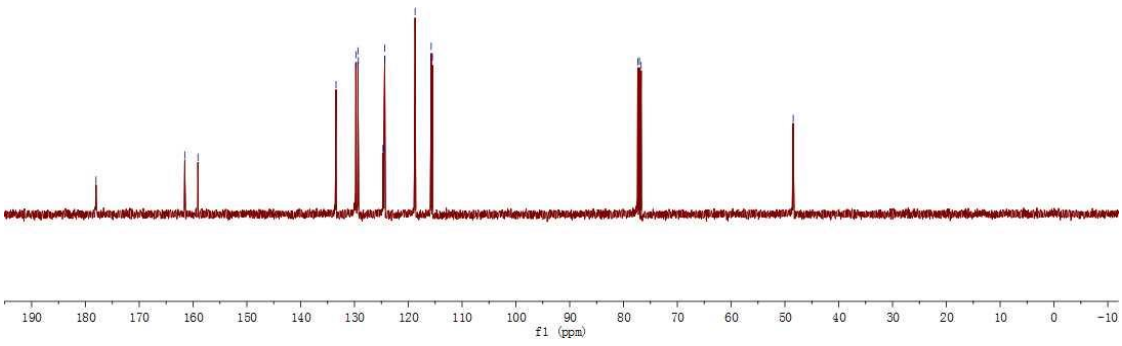


^{13}C NMR Spectrum of 2i ($CDCl_3$)

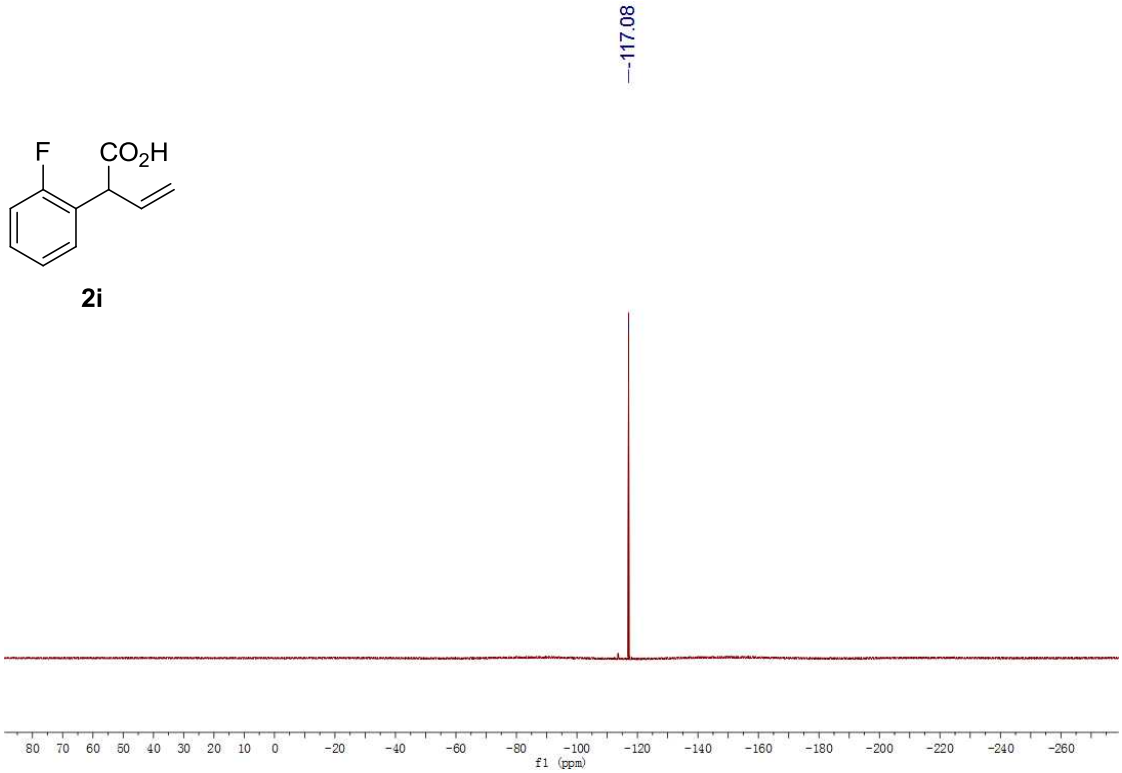


2i

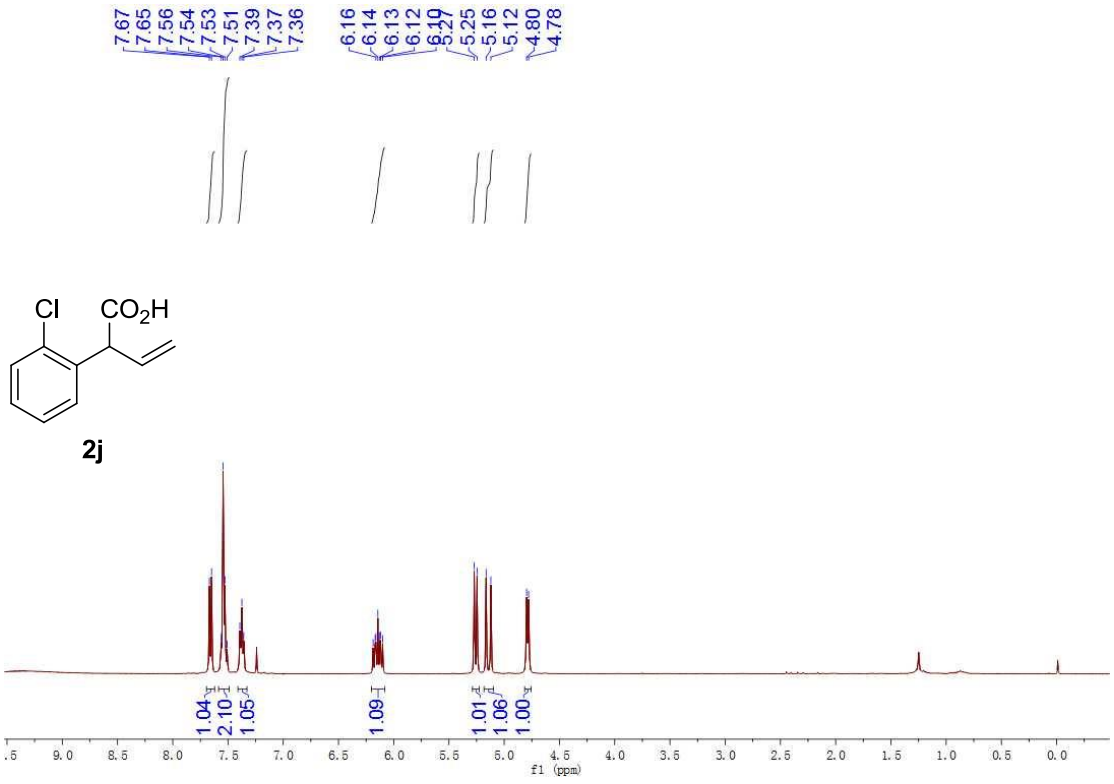




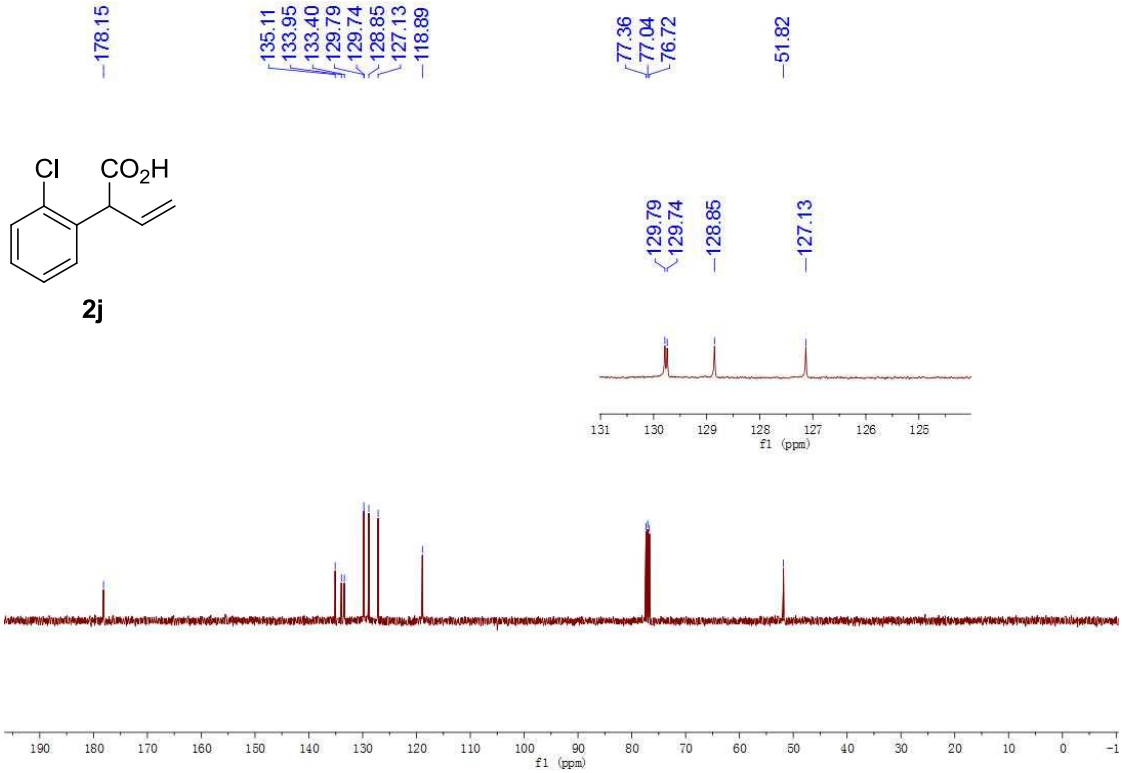
^{19}F NMR Spectrum of 2i ($CDCl_3$)



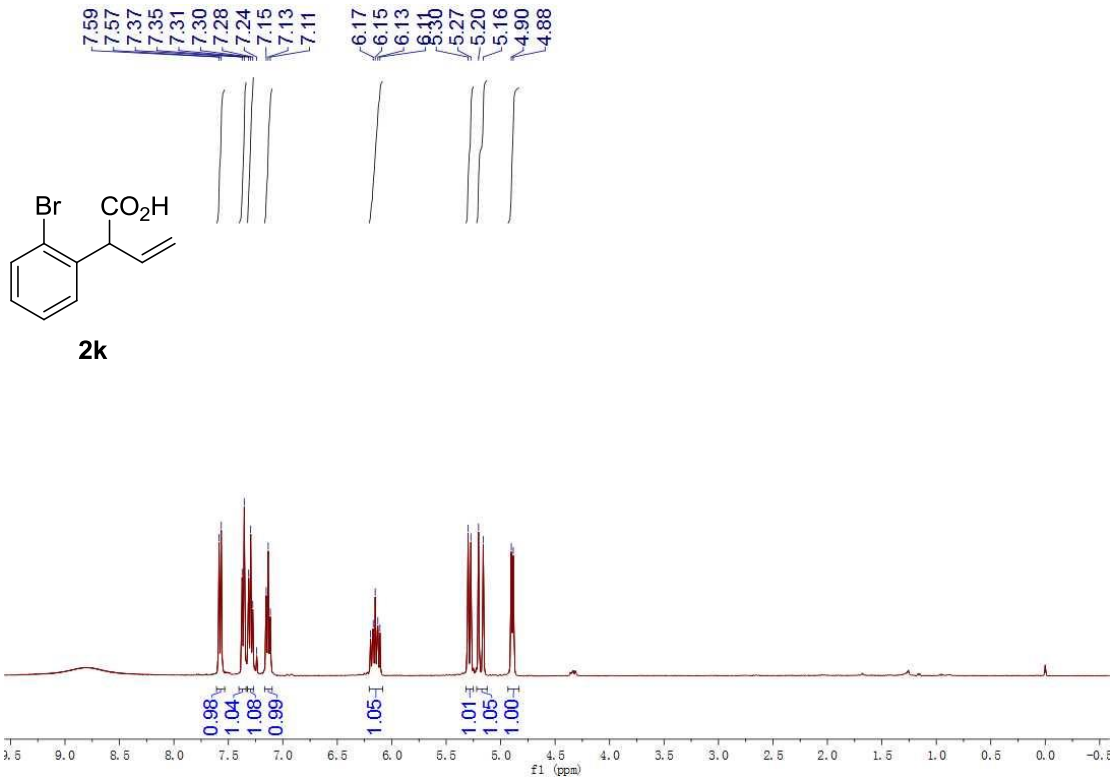
^{1}H NMR Spectrum of 2j ($CDCl_3$)



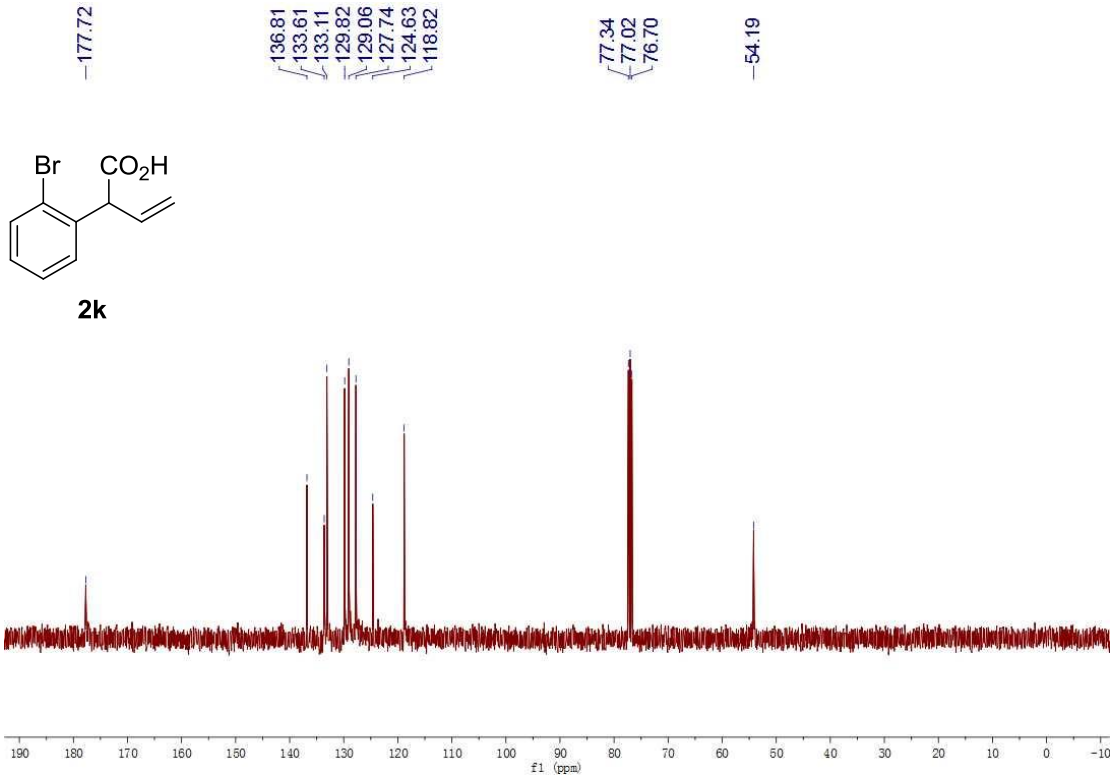
^{13}C NMR Spectrum of 2j ($CDCl_3$)



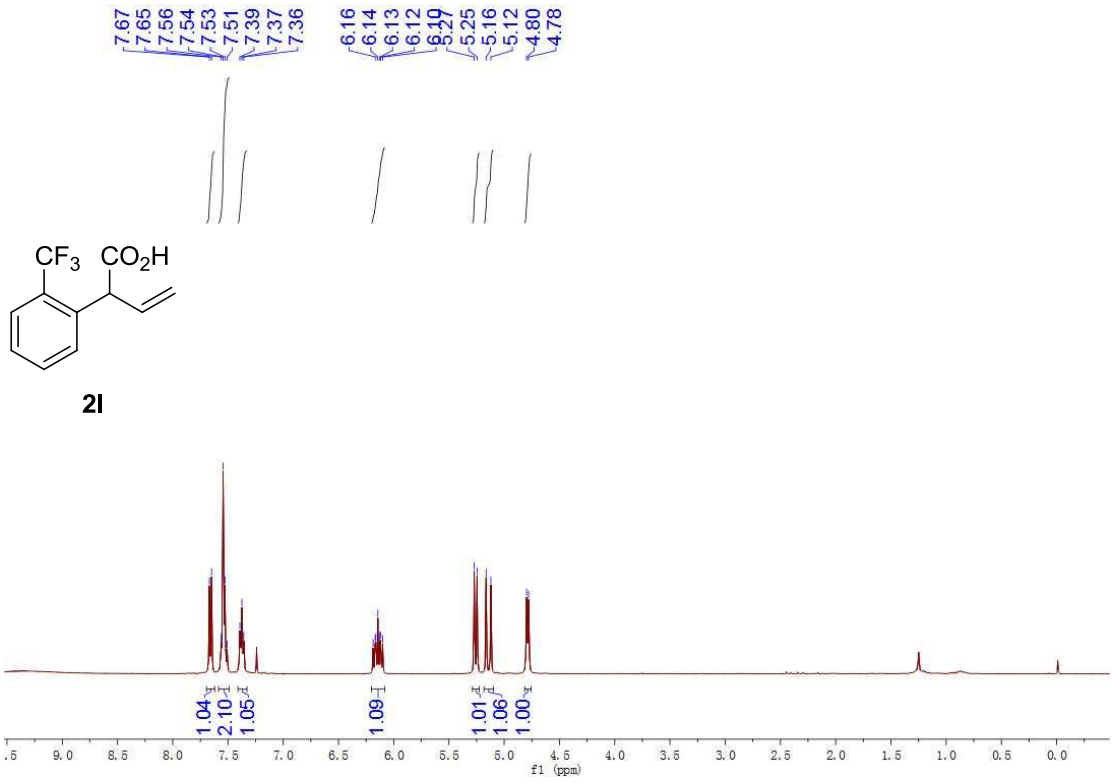
^{1}H NMR Spectrum of 2k ($CDCl_3$)



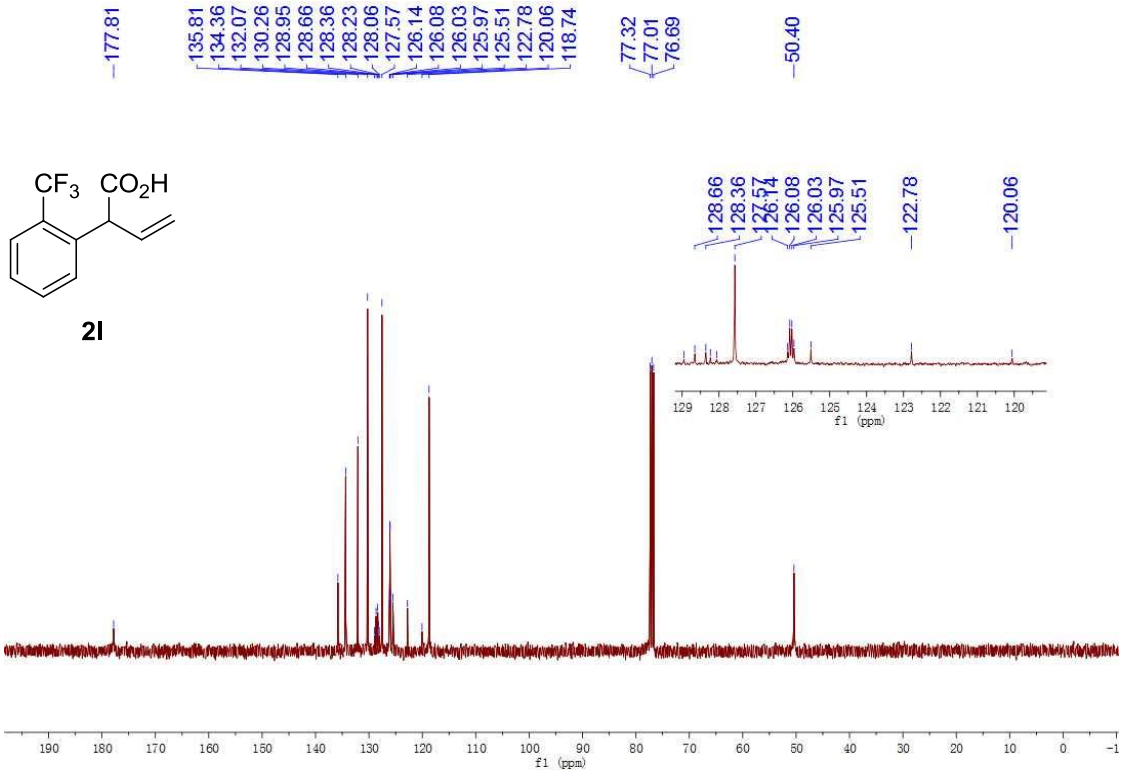
^{13}C NMR Spectrum of 2k ($CDCl_3$)



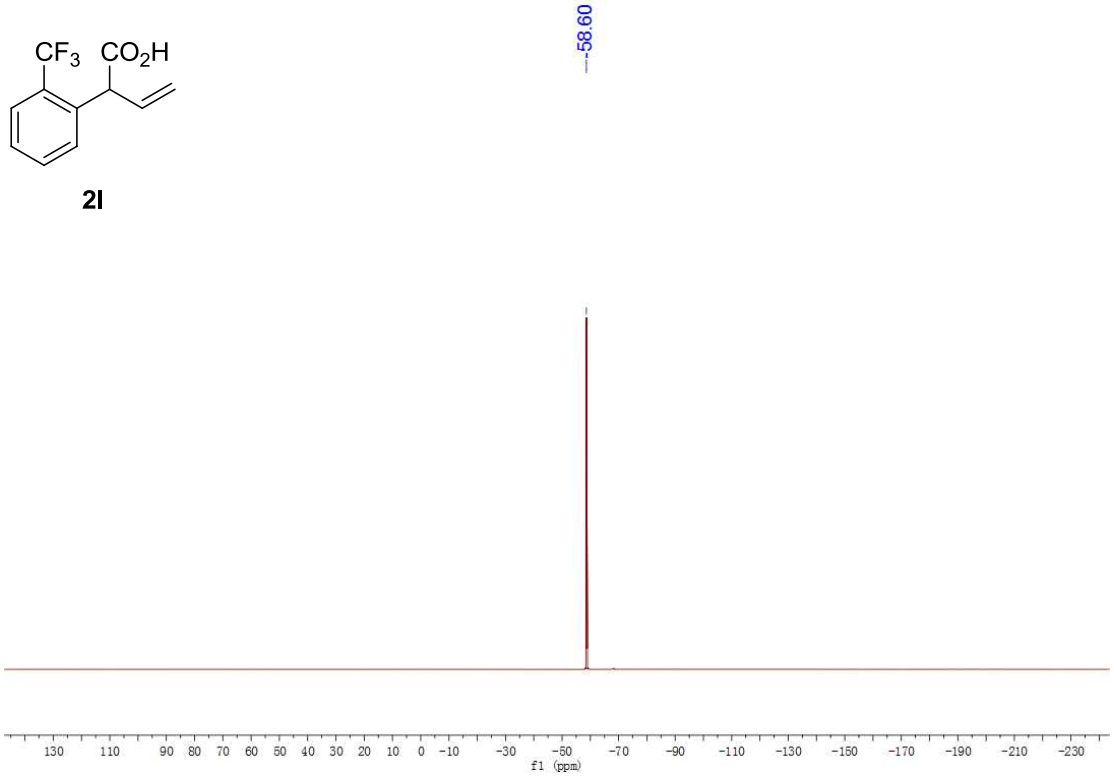
^{1}H NMR Spectrum of 2l ($CDCl_3$)



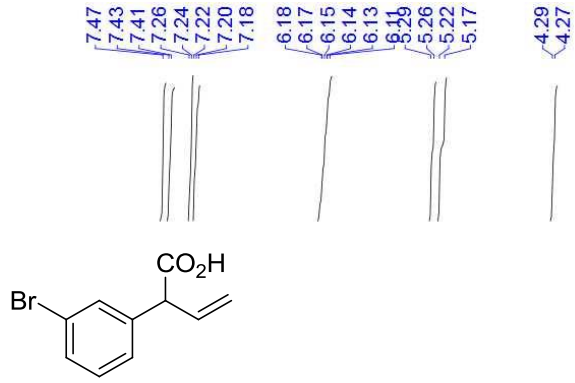
^{13}C NMR Spectrum of 2l ($CDCl_3$)



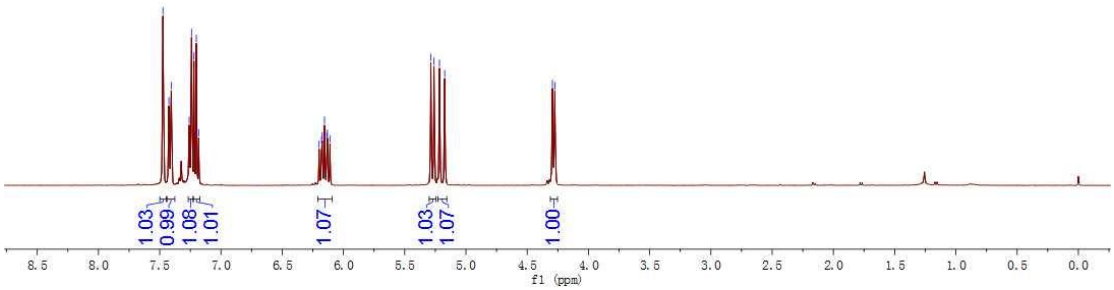
^{19}F NMR Spectrum of 2l ($CDCl_3$)



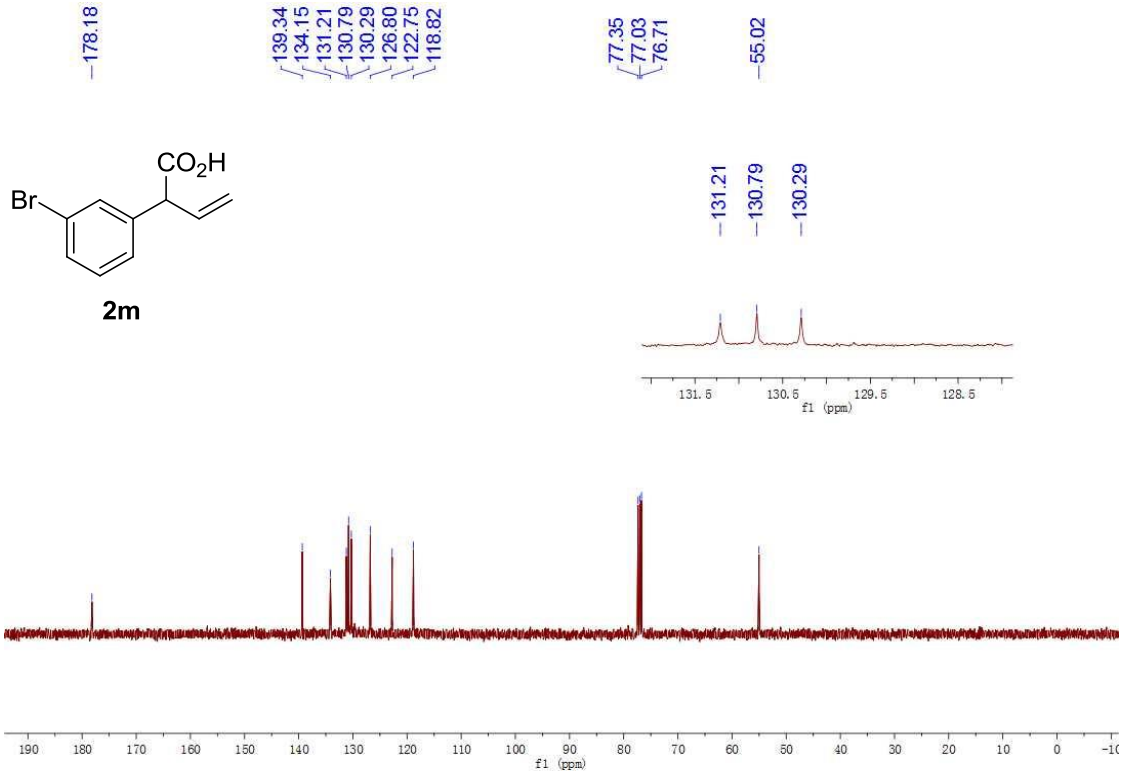
^{1}H NMR Spectrum of 2m ($CDCl_3$)



2m

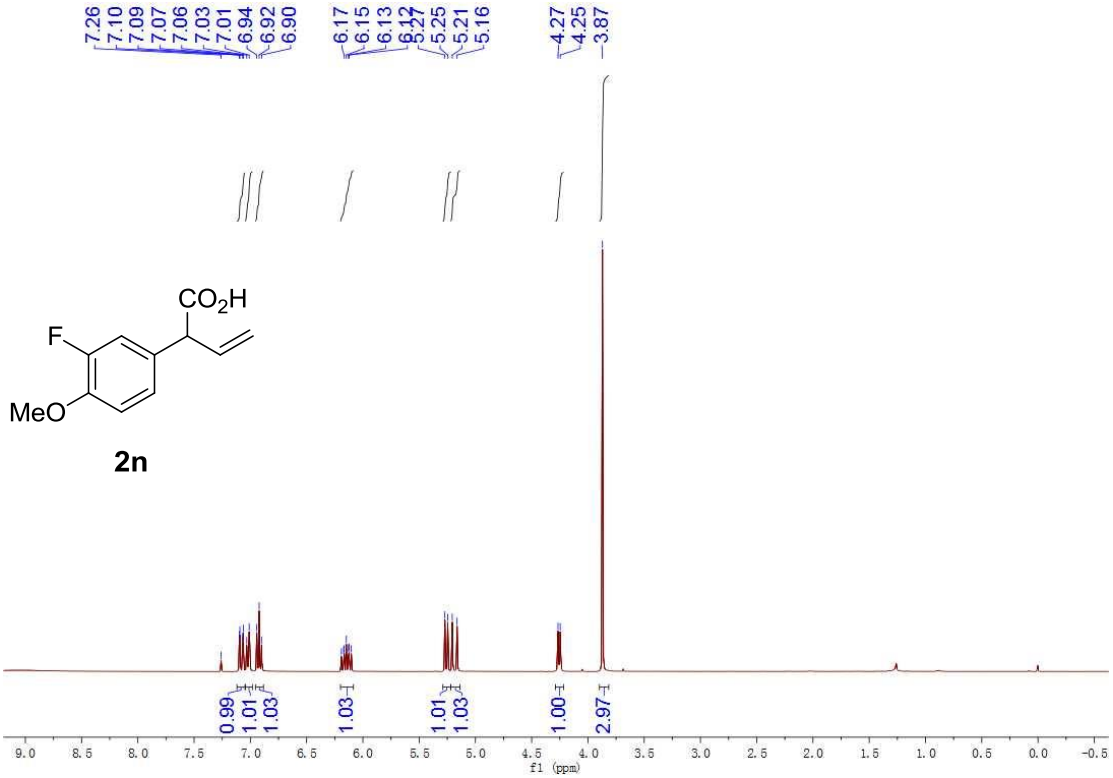


^{13}C NMR Spectrum of 2m ($CDCl_3$)

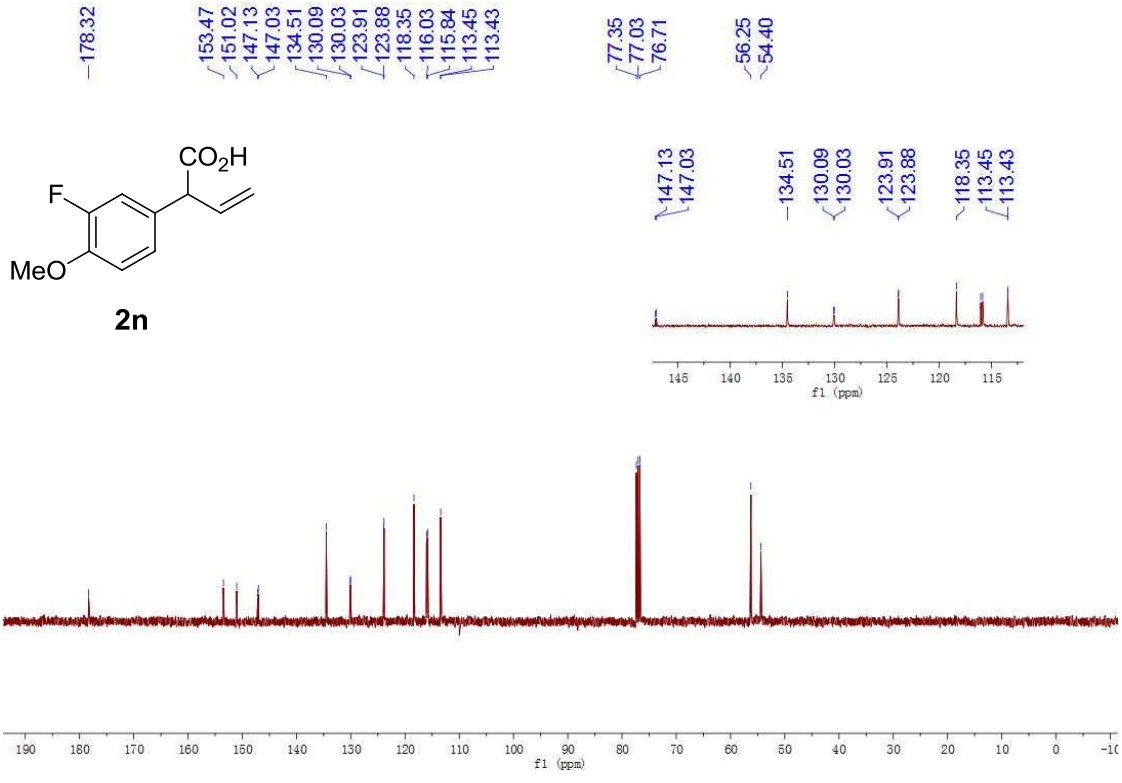


2m

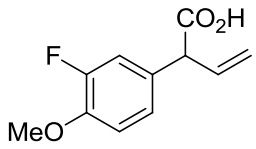
^{1}H NMR Spectrum of 2n ($CDCl_3$)



^{13}C NMR Spectrum of 2n ($CDCl_3$)

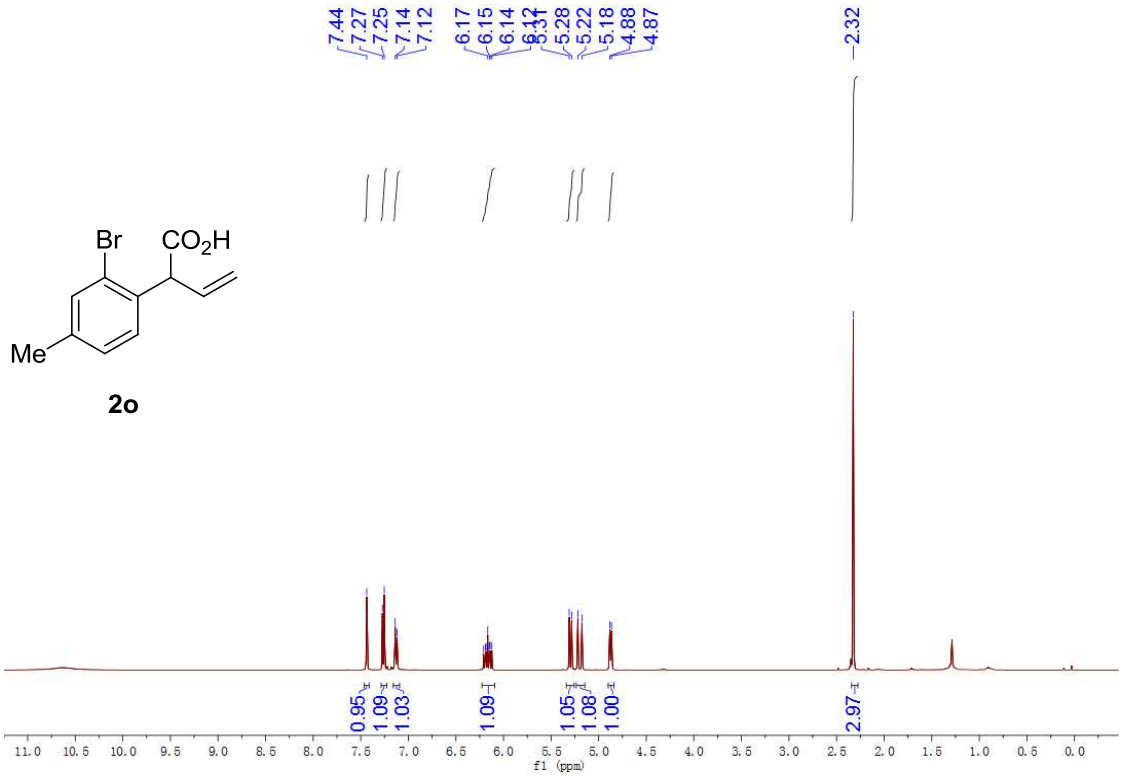


^{19}F NMR Spectrum of 2n ($CDCl_3$)



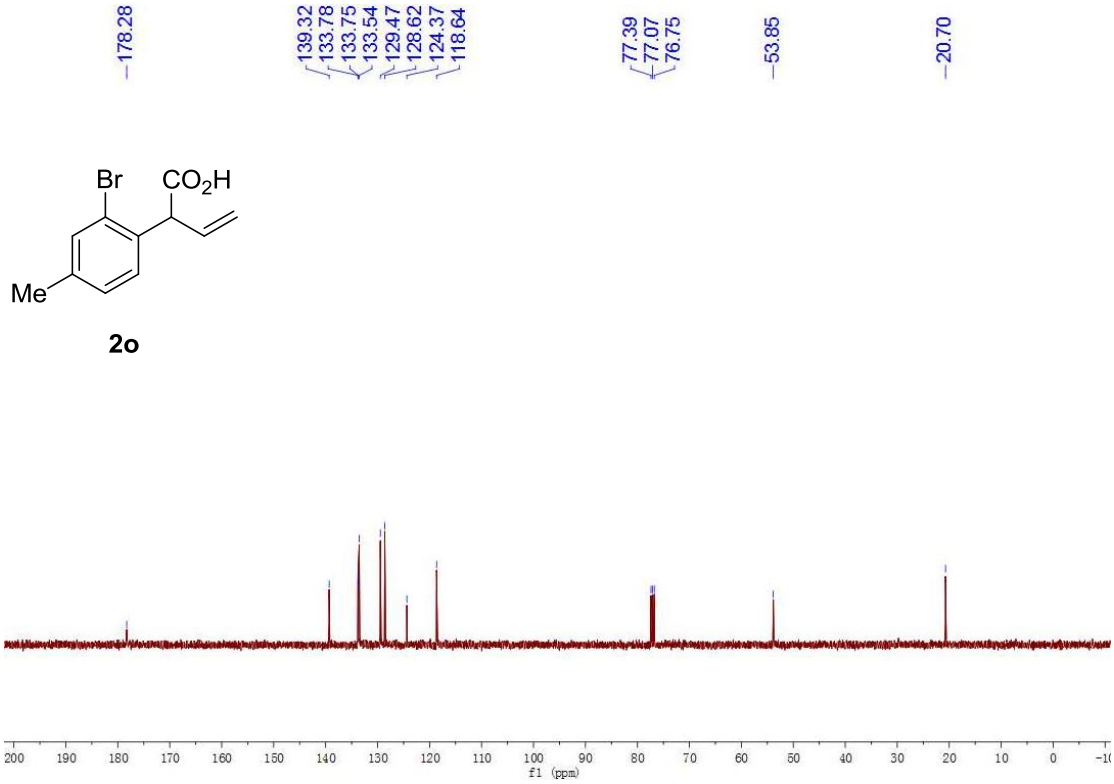
2n

^{1}H NMR Spectrum of 2o ($CDCl_3$)

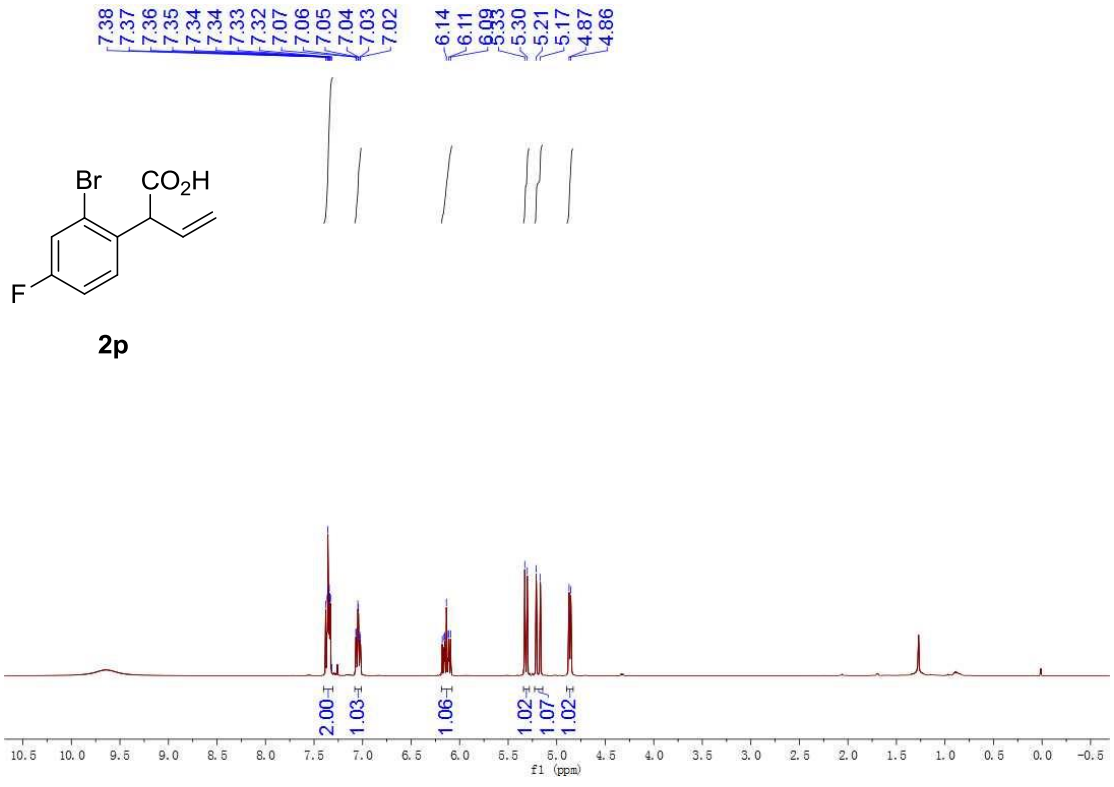


2o

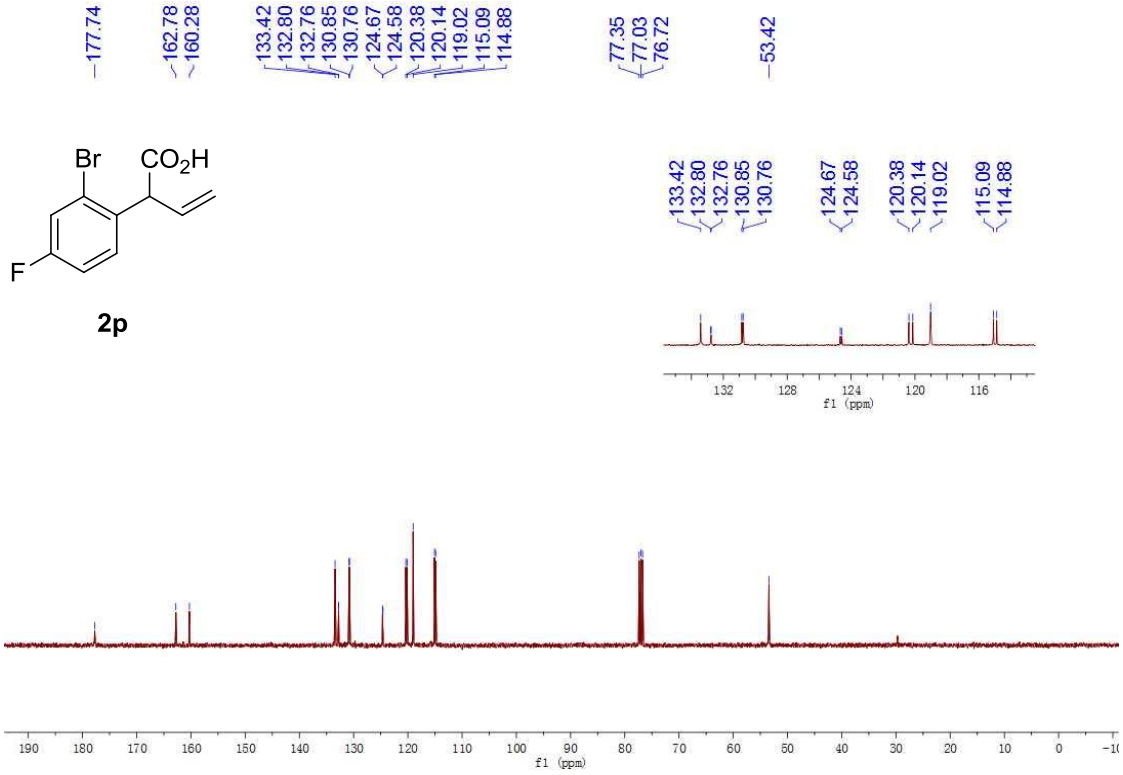
^{13}C NMR Spectrum of 2o ($CDCl_3$)



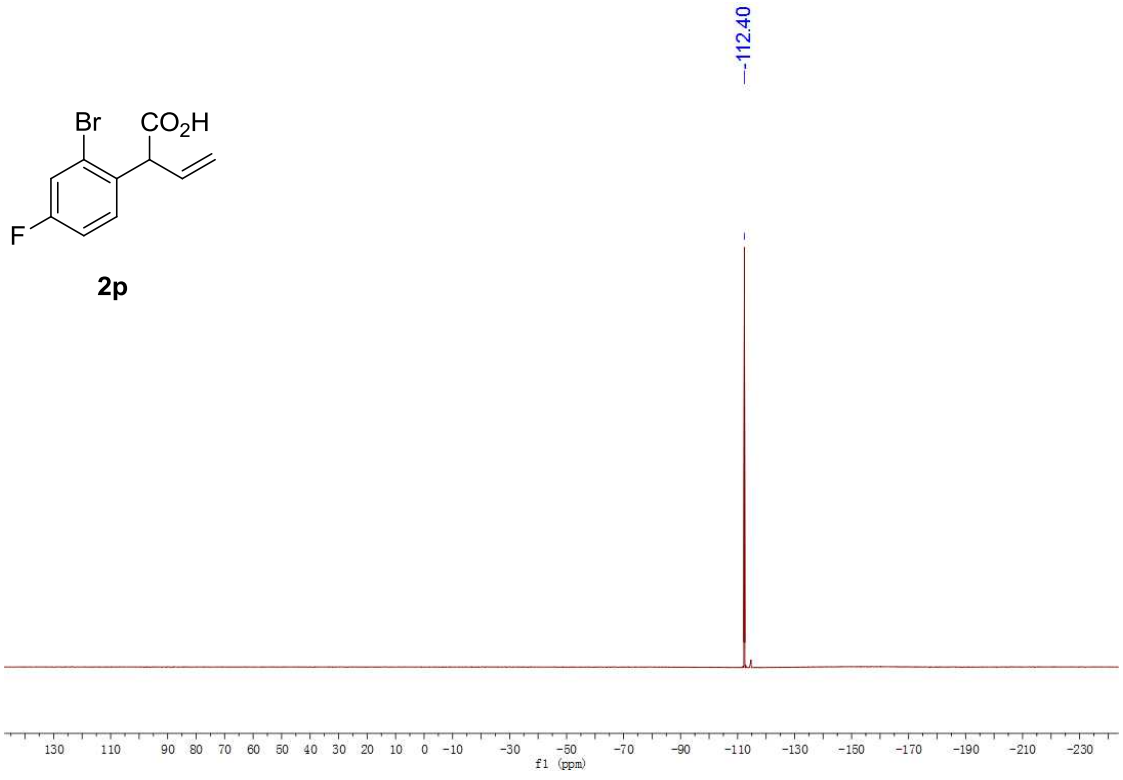
^{1}H NMR Spectrum of 2p ($CDCl_3$)



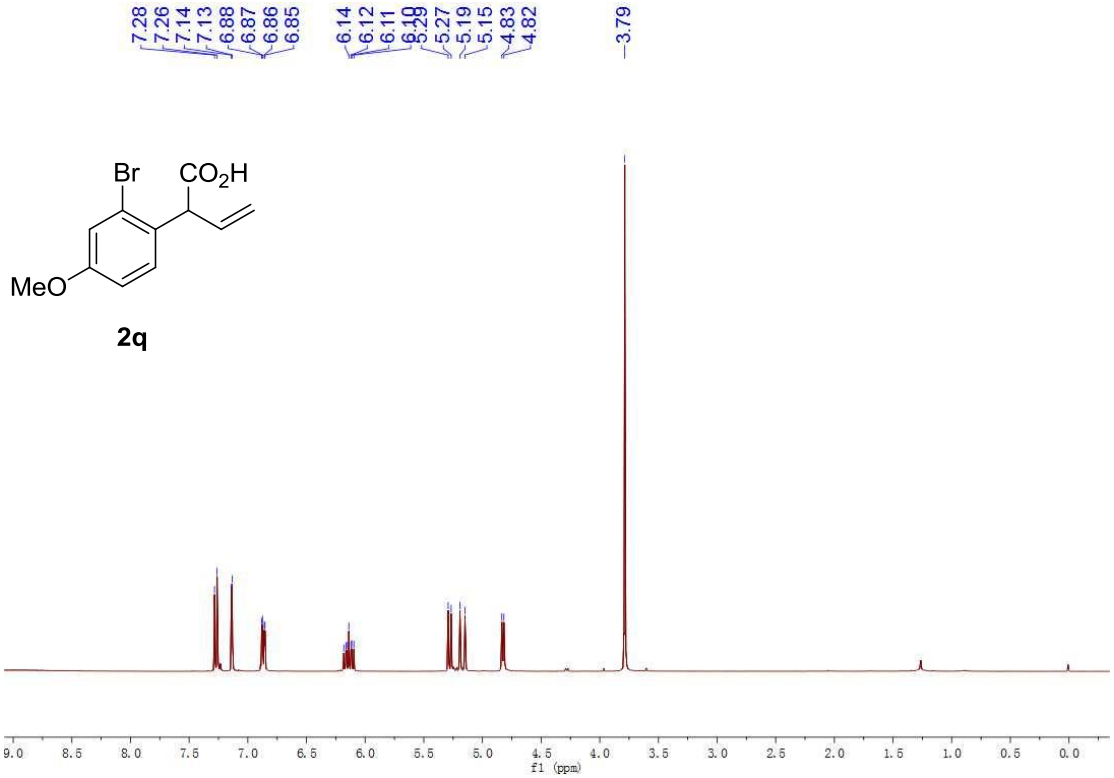
^{13}C NMR Spectrum of 2p ($CDCl_3$)



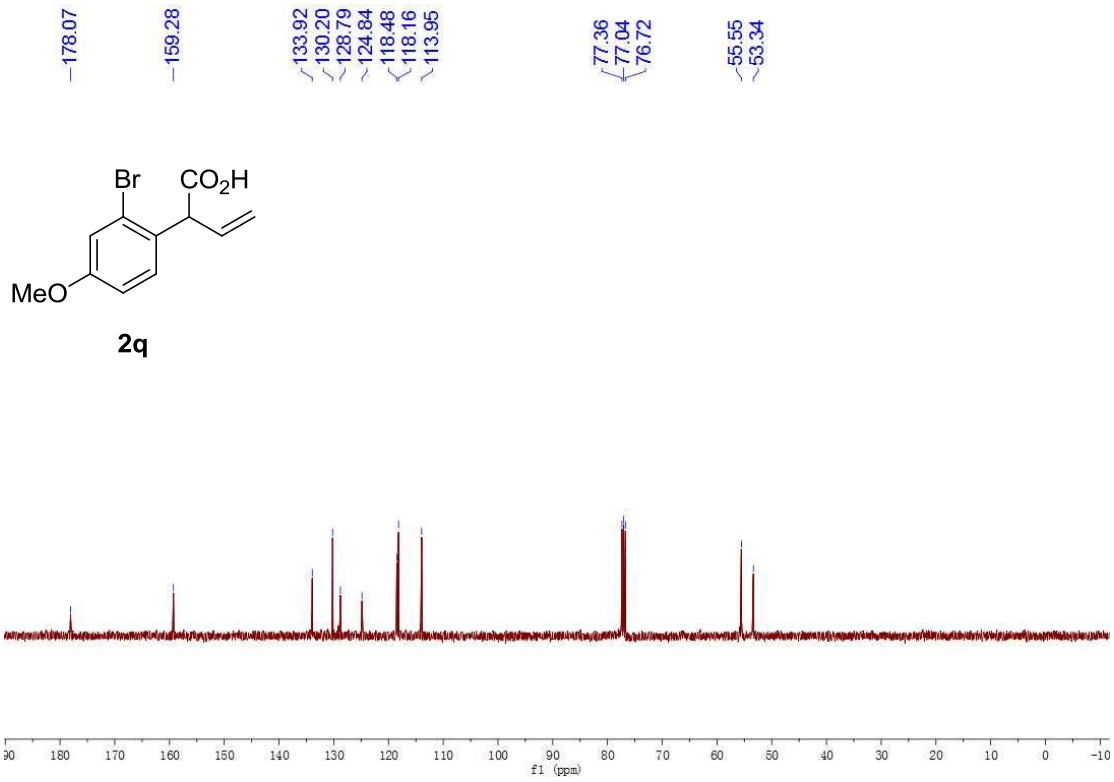
^{19}F NMR Spectrum of 2p ($CDCl_3$)



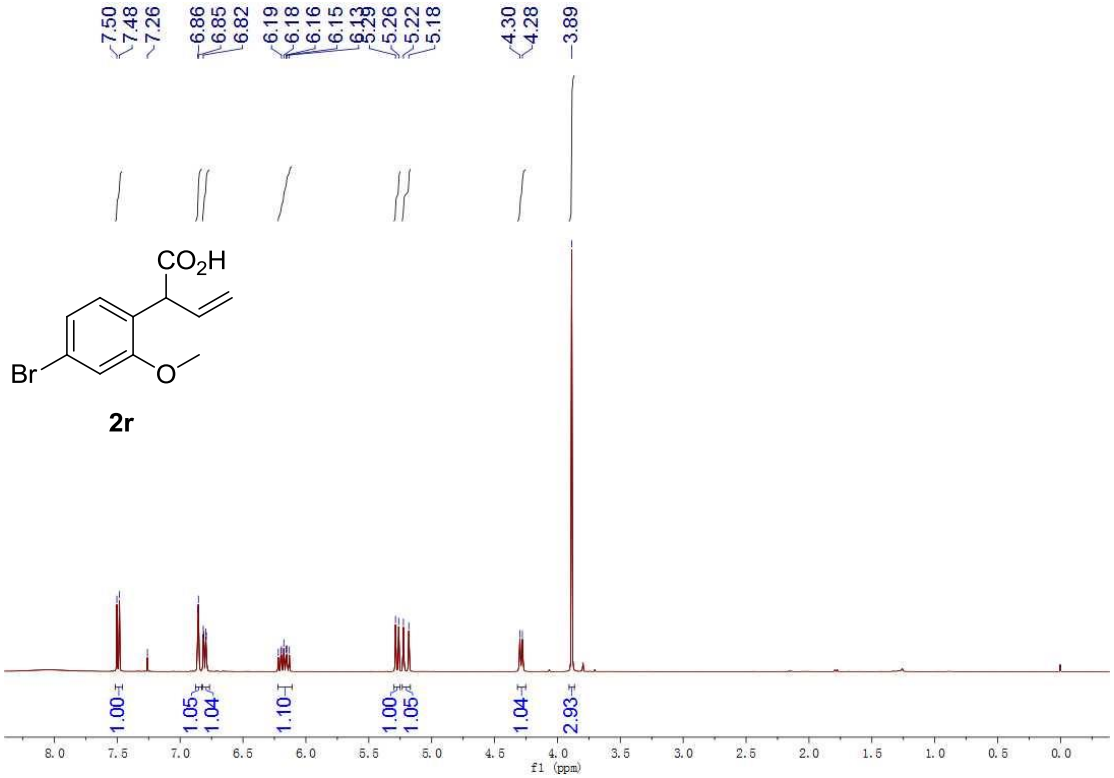
^{1}H NMR Spectrum of 2q ($CDCl_3$)



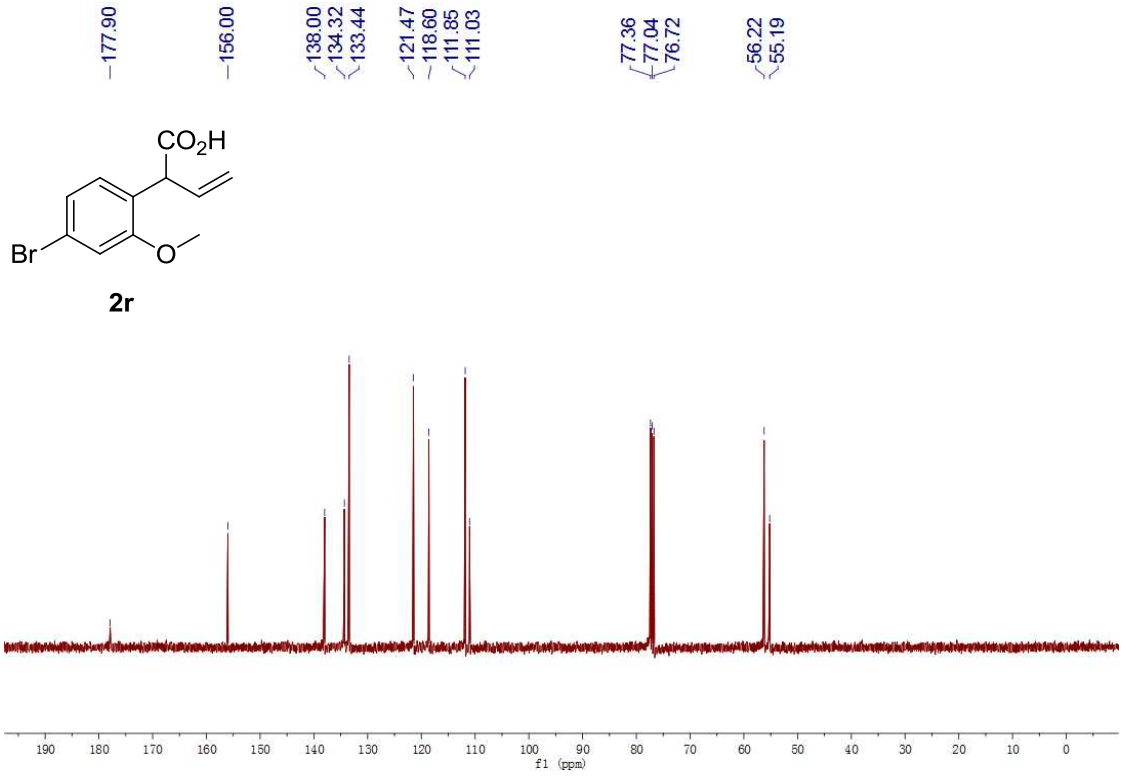
^{13}C NMR Spectrum of 2q ($CDCl_3$)



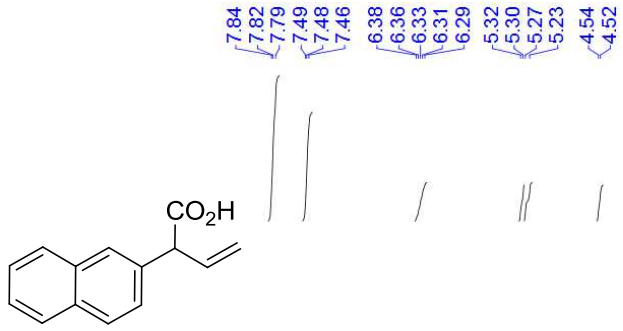
^{1}H NMR Spectrum of 2r ($CDCl_3$)



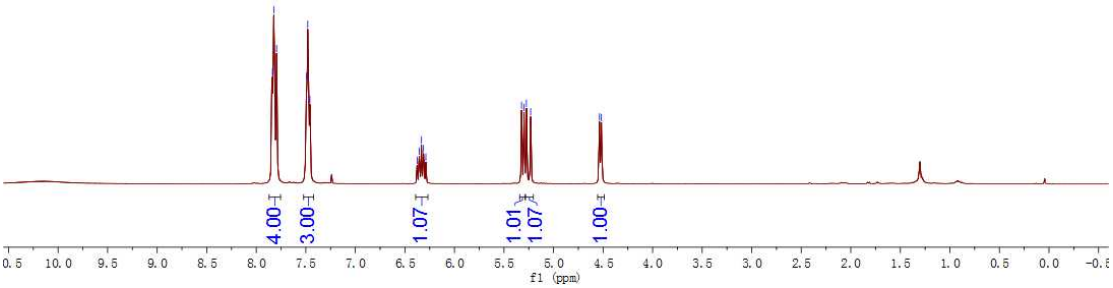
^{13}C NMR Spectrum of 2r ($CDCl_3$)



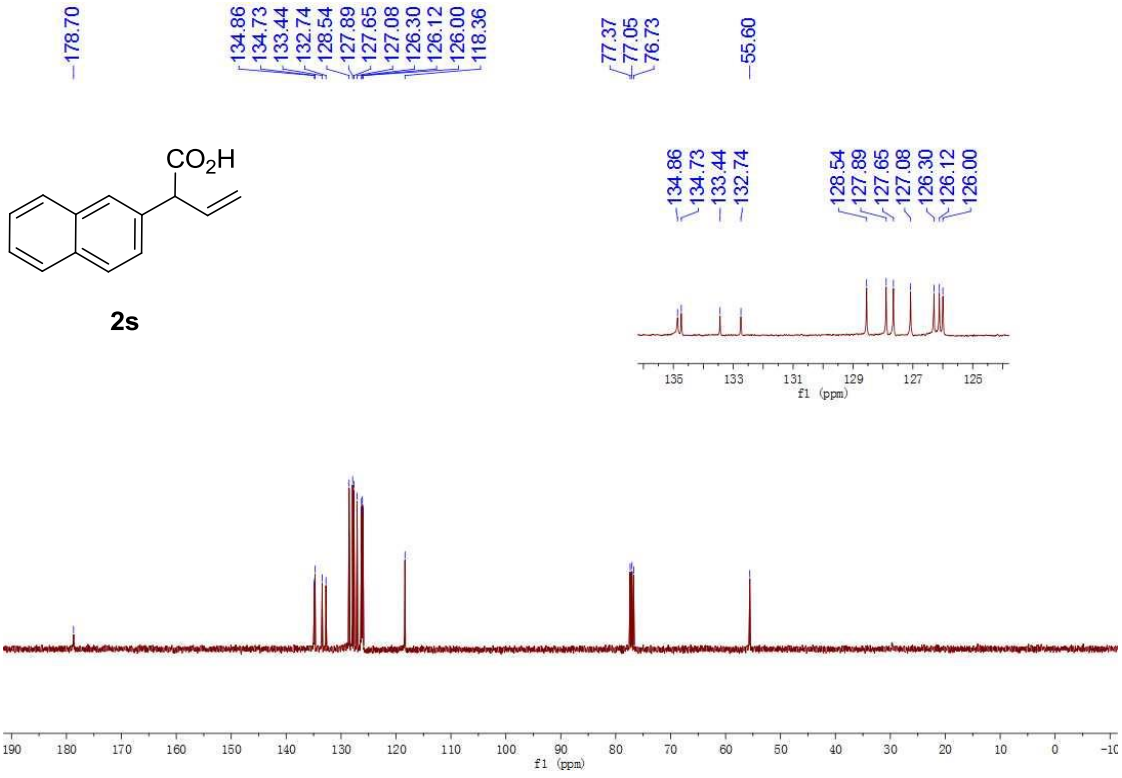
^{1}H NMR Spectrum of 2s ($CDCl_3$)



2s

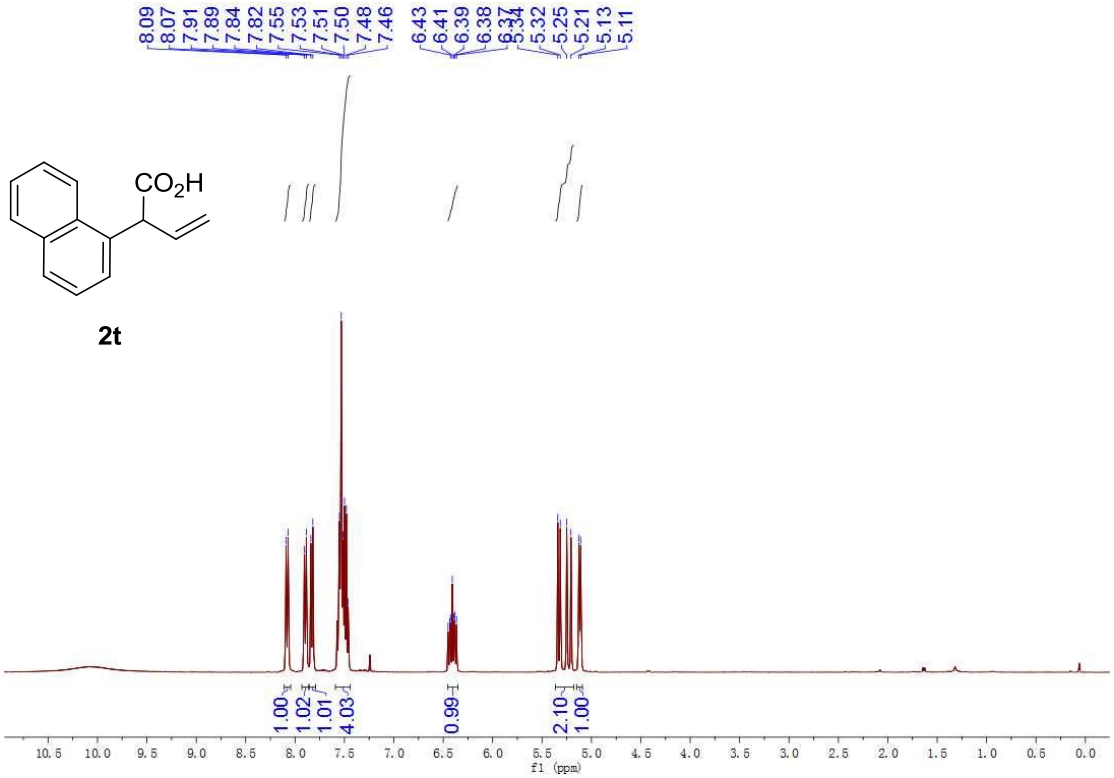


^{13}C NMR Spectrum of 2s ($CDCl_3$)

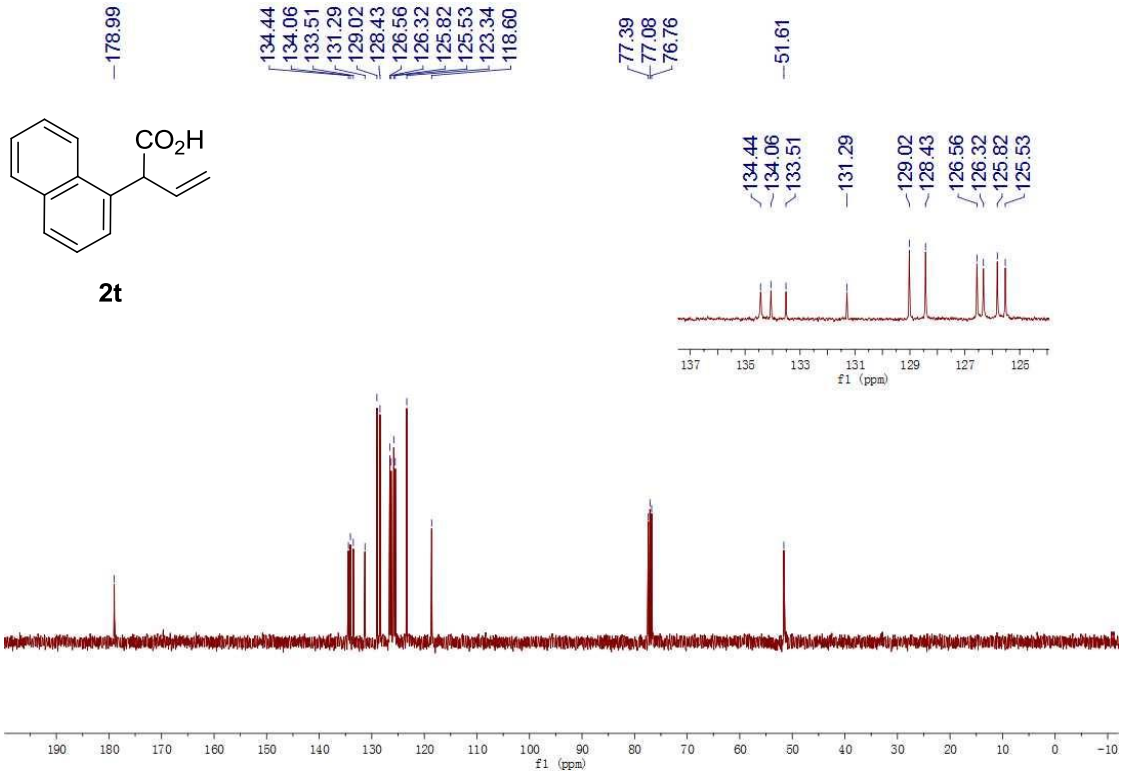


2s

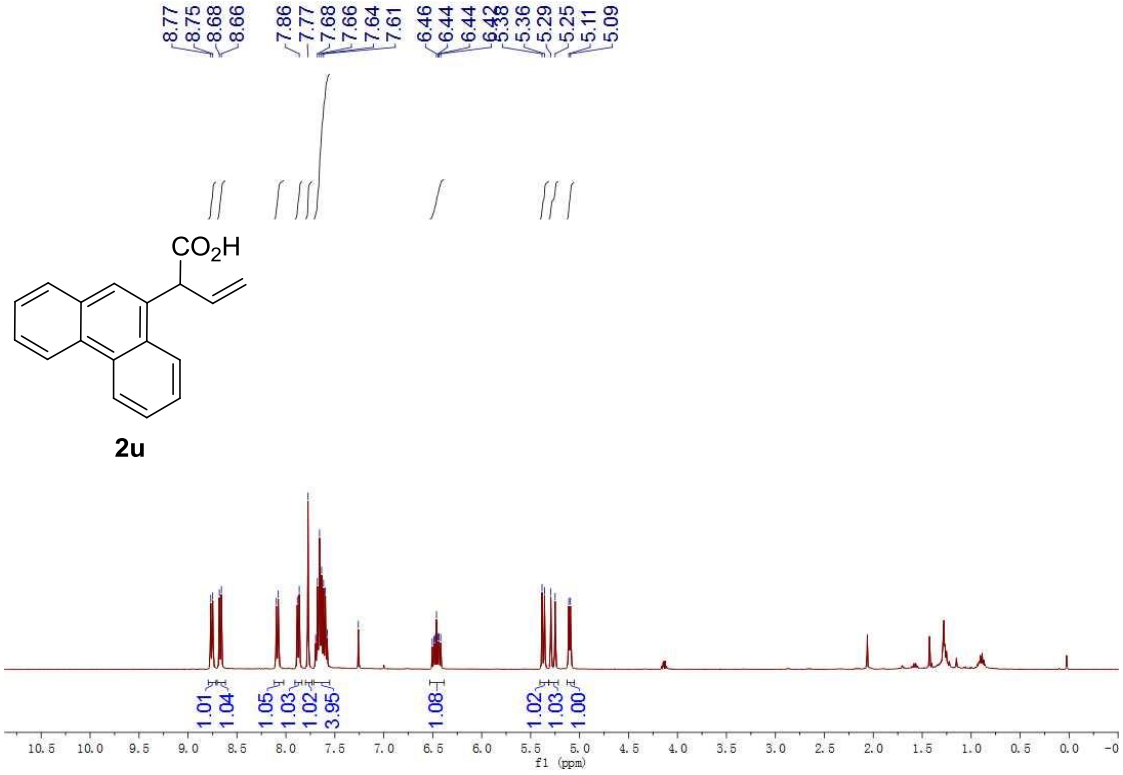
^{1}H NMR Spectrum of 2t ($CDCl_3$)



^{13}C NMR Spectrum of 2t ($CDCl_3$)



^{1}H NMR Spectrum of 2u ($CDCl_3$)



^{13}C NMR Spectrum of 2u ($CDCl_3$)