

**Palladium-catalyzed allylic C–H oxidation under simple operation
and mild conditions**

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Supporting Information

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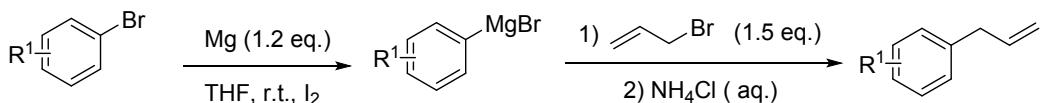
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1. General Information

All experiments were carried out under an air atmosphere unless otherwise noted. Commercial reagents were purchased from Aldrich or Adamas-beta unless otherwise stated. All solvents were dried and distilled before use according to the standard methods. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Visualization on TLC was achieved with UV light (254 nm) and potassium permanganate as visualization methods. ^1H NMR spectra were recorded on Mercury Plus-400 (400 MHz), BRUKER DRX-400 (400 MHz) and BRUKER DRX-500 (500 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. Data for ^1H NMR spectra are reported as follows: chemical shift (δ shift), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double of doublet, ddd = double of dd, dt = double of triplet, td = triple of doublet), integration, coupling constant (Hz), and assignment. ^{13}C NMR spectra were recorded on Mercury Plus-400 (100 MHz). Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. Infrared (IR) spectra were recorded on an AVATAR 370 Spectrometer with a thin film on the KBr plate. High resolution mass spectra were obtained with ACQUITYTM UPLC & Q-TOF MS Premier Spectrometer, and EI mass spectra were obtained with 7890B-5977B Spectrometer.

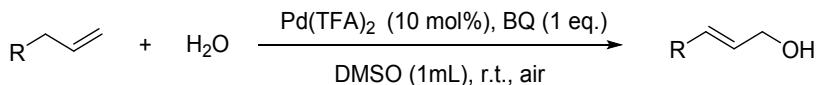
2. Experimental Section

2.1 General methods for the synthesis of allylic alkenes¹



In an oven-dried 50 mL round Schlenk tube containing a stirring bar, aryl bromide (5 mmol, 1 equiv.) and an iodide grain were dissolved in anhydrous THF (20 mL). Then Mg (6 mmol, 1.2 equiv.) was added into the Schlenk tube under a N₂ atmosphere. After the color of the mixture faded, allyl bromide (7.5 mmol, 1.5 equiv.) was carefully added under room temperature. Then the mixture was stirred at room temperature for 2h. After that, aqueous saturated NH₄Cl solution was added slowly to quench the reaction. The aqueous phase was separated and extracted with ethyl acetate (3 x 30 mL). The combined organic phases were dried with Na₂SO₄ and concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel to afford pure allylic alkenes (**1b**, **1d**, **1f-1i** and **1n-1s**).

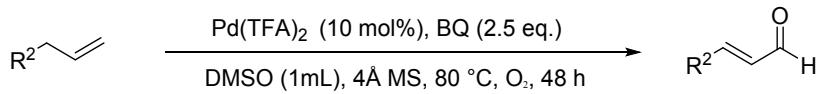
2.2 General procedure for the synthesis of allylic alcohols



Pd(TFA)₂ (0.03 mmol, 10.0 mg) and DMSO (1.0 mL) were added to an oven-dried 40 mL sample vial containing a stirring bar under air. The solution was stirred at room temperature for 5 minutes. Corresponding allylic alkenes (0.3 mmol), BQ (0.3 mmol, 32.4 mg) and H₂O (3 mmol, 54 mg) were added to the above mixture. The sample vial was sealed with a screw cap. The reaction mixture was stirred at room temperature for corresponding time. The resulting orange mixture was diluted with ethyl acetate, and

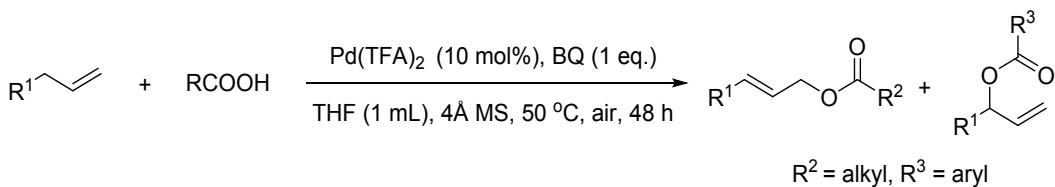
washed with brine. The aqueous layer was extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over Na_2SO_4 , and the filtrate was concentrated. The crude was purified by column chromatography with eluent (petroleum ether/ethyl acetate = 5:1 to 10:1) to afford the corresponding products.

2.3 General procedure for the synthesis of (*E*)–acrylaldehydes



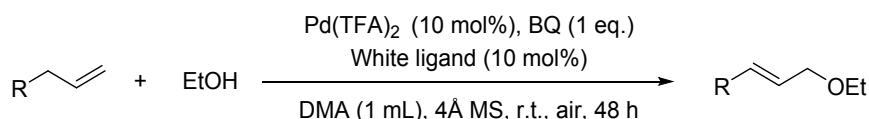
Pd(TFA)_2 (0.02 mmol, 6.7 mg) and DMSO (1.0 mL) were added to an oven-dried 25 mL Schlenk tube containing a stirring bar under oxygen. The solution was stirred at room temperature for 5 minutes. Corresponding allylic alkenes (0.2 mmol), BQ (0.5 mmol, 54.0 mg) and 4 \AA molecular sieves were added to the above mixture. The Schlenk tube was sealed with a Teflon-lined screw cap. Heating up to 80 °C for 48 h, the resulting mixture was allowed to cool to room temperature, diluted with ethyl acetate, and washed with brine. The aqueous layer was extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over Na_2SO_4 , and the filtrate was concentrated. The crude was purified by column chromatography with eluent (petroleum ether/ethyl acetate = 50:1 to 20:1) to afford the corresponding products.

2.4 General procedure for the synthesis of allylic esters



Pd(TFA)₂ (0.03 mmol, 10.0 mg) and THF (1.0 mL) were added to an oven-dried 25 mL Schlenk tube containing a stirring bar under air. The solution was stirred at room temperature for 5 minutes. Corresponding allylic alkenes (0.3 mmol), BQ (0.3 mmol, 32.4 mg), carboxylic acids (0.04 mmol, 2 equiv.) and 4Å molecular sieves were added to the above mixture. The Schlenk tube was sealed with a Teflon-lined screw cap. Heating up to 50 °C for 48 h, the resulting mixture was allowed to cool to room temperature, diluted with ethyl acetate and washed with brine. The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over Na₂SO₄, and the filtrate was concentrated. The crude was purified by column chromatography with eluent (petroleum ether/ethyl acetate = 50:1 to 30:1) to afford the corresponding products.

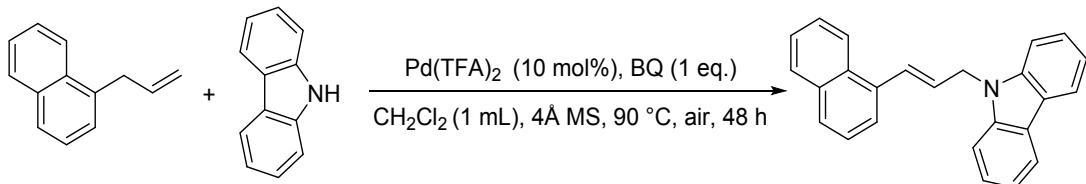
2.5 General procedure for the synthesis of allylic ethers



Pd(TFA)₂ (0.02 mmol, 6.7 mg), 1,2-bis(phenylsulfinyl)ethane (0.02 mmol, 5.6 mg) and DMA (1.0 mL) were added to an oven-dried 25 mL Schlenk tube containing a stirring bar under air. The solution was stirred at room temperature for 30 minutes. Corresponding allylic alkenes (0.2 mmol), ethanol (0.5 ml), BQ (0.2 mmol, 21.6 mg) and 4Å molecular sieves were added to the above mixture. The Schlenk tube was sealed with a Teflon-lined screw cap. The reaction mixture was stirred at room temperature for 48 h, the resulting mixture was diluted with ethyl acetate, and washed

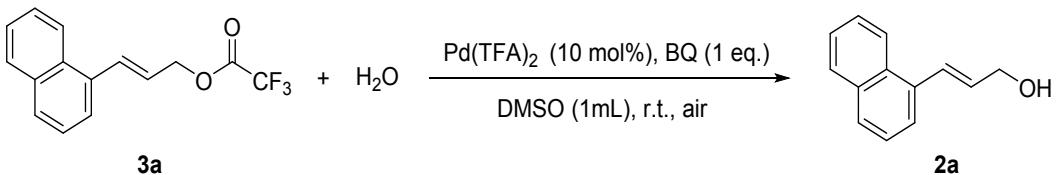
with brine. The aqueous layer was extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over Na_2SO_4 , and the filtrate was concentrated. The crude was purified by column chromatography with eluent (petroleum ether/ethyl acetate = 30:1 to 20:1) to afford the corresponding products.

2.6 General procedure for the synthesis of allylic carbazole



$\text{Pd}(\text{TFA})_2$ (0.02 mmol, 6.7 mg) and CH_2Cl_2 (1.0 mL) were added to an oven-dried 25 mL Schlenk tube containing a stirring bar under air. The solution was stirred at room temperature for 5 minutes. 1-Allylnaphthalene (0.2 mmol, 33.6 mg), carbazole (0.4 mmol, 66.8 mg), BQ (0.2 mmol, 21.6 mg) and 4 \AA molecular sieves were added to the above mixture. The Schlenk tube was sealed with a Teflon-lined screw cap. Heating up to 90 °C for 48 h, the resulting mixture was allowed to cool to room temperature, diluted with ethyl acetate, and washed with brine. The aqueous layer was extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over Na_2SO_4 , and the filtrate was concentrated. The crude was purified by column chromatography with eluent (petroleum ether/ethyl acetate = 30:1) to afford the corresponding product.

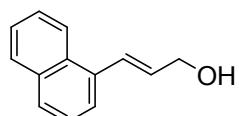
2.7 The procedure for the synthesis of 2a using 3a ((E)-3-(Naphthalen-1-yl)allyl 2,2,2-trifluoroacetate) as starting material



Pd(TFA)₂ (0.02 mmol, 6.6 mg) and DMSO (1.0 mL) were added to an oven-dried 25 mL Schlenk tube containing a stirring bar under air. The solution was stirred at room temperature for 5 minutes. **3a** (0.2 mmol, 56.0 mg), BQ (0.2 mmol, 21.6 mg) and H₂O (2 mmol, 36 mg) were added to the above mixture. The sample vial was sealed with a screw cap. The reaction mixture was stirred at room temperature for 39 hours. The resulting orange mixture was diluted with ethyl acetate, and washed with brine. The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over Na₂SO₄, and the filtrate was concentrated. The crude was purified by column chromatography with eluent (petroleum ether/ethyl acetate = 5:1) to afford **2a** in 79% yield.

3. Analytical data

(E)-3-(Naphthalen-1-yl)prop-2-en-1-ol (2a)^[2]: yield: 86% (47 mg); yellow oil; **IR**

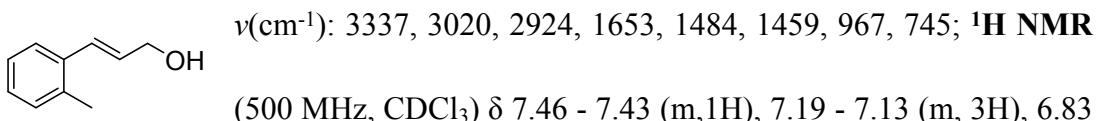


(KBr) ν (cm⁻¹): 3343, 3049, 2920, 2860, 1590, 1008, 967, 780; **¹H**

NMR (400 MHz, CDCl₃) δ 8.14 - 8.10 (m, 1H), 7.87 - 7.83 (m,

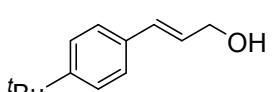
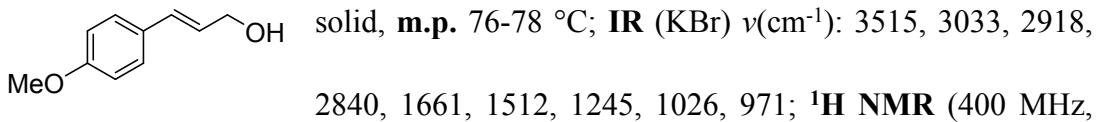
1H), 7.78 (d, $J = 8.2$ Hz, 1H), 7.59 (d, $J = 7.2$ Hz, 1H), 7.54 - 7.47 (m, 2H), 7.47 - 7.42 (m, 1H), 7.38 (d, $J = 15.6$ Hz, 1H), 6.40 (dt, $J = 15.6, 5.6$ Hz, 1H), 4.44 (dd, $J = 5.6, 1.6$ Hz, 2H), 1.65 (s, 1H); **MS** (ESI-TOF) m/z : [M+Na]⁺ calcd for C₁₃H₁₂O 207.08, found: 207.09.

(E)-3-(o-Tolyl)prop-2-en-1-ol (2b)^[2]: yield: 81% (36 mg); yellow oil; **IR** (KBr)



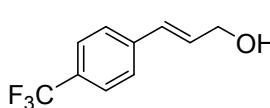
(d, $J = 15.8$ Hz, 1H), 6.26 (dt, $J = 15.8, 5.4$ Hz, 1H), 4.35 (d, $J = 5.4$ Hz, 2H), 2.35 (s, 3H), 1.52 (s, 1H); **MS** (ESI-TOF) m/z : [M+H]⁺ calcd for C₁₀H₁₂O 149.10, found: 148.99.

(E)-3-(4-Methoxyphenyl)prop-2-en-1-ol (2c)^[2]: yield: 77% (38 mg); pale yellow

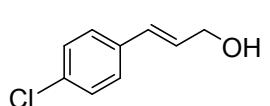


(E)-3-(4-(tert-Butyl)phenyl)prop-2-en-1-ol (2d)^[2]: yield: 45 mg (79%); pale yellow oil; **IR** (KBr) $\nu(\text{cm}^{-1})$: 3395, 2961, 2867, 1720, 1606, 1363, 1091, 969; **1H NMR** (500 MHz, CDCl₃) δ 7.36 - 7.31 (m, 4H), 6.60 (d, $J = 15.8$ Hz, 1H), 6.34 (dt, $J = 15.8, 5.8$ Hz, 1H), 4.32 (dd, $J = 5.8, 1.0$ Hz, 2H), 1.57 (s, 1H), 1.32 (s, 9H); **MS** (ESI-TOF) m/z : [M+H]⁺ calcd for C₁₃H₁₈O 191.14, found: 189.98.

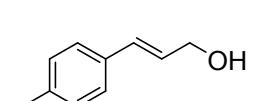
(E)-3-(4-(Trifluoromethyl)phenyl)prop-2-en-1-ol (2e)^[2]: yield: 83% (50 mg); white

 solid, **m.p.** 47-49 °C; **IR** (KBr) ν (cm⁻¹): 3342, 2926, 1614, 1329, 1124, 969; **¹H NMR** (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 16.0 Hz, 1H), 6.46 (dt, *J* = 16.0, 4.4 Hz, 1H), 4.37 (d, *J* = 4.4 Hz, 2H), 1.62 (s, 1H); **MS** (ESI-TOF) *m/z*: [M-H₂O+H]⁺ calcd for C₁₀H₉F₃O 185.06, found: 184.97.

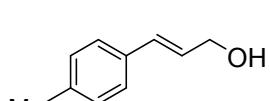
(E)-3-(4-Chlorophenyl)prop-2-en-1-ol (2f)^[2]: yield: 75% (38 mg); pale yellow oil;

 **IR** (KBr) ν (cm⁻¹): 3338, 2922, 2859, 1593, 1565, 1478, 1201, 964, 774, 681; **¹H NMR** (500 MHz, CDCl₃) δ 7.33 - 7.27 (m, 4H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.34 (dt, *J* = 16.0, 5.5 Hz, 1H), 4.33 (dd, *J* = 5.5, 1.5 Hz, 2H), 1.58 (s, 1H); **MS** (ESI-TOF) *m/z*: [M+Na]⁺ calcd for C₉H₉ClO 191.02, found: 190.90.

(E)-3-(4-Fluorophenyl)prop-2-en-1-ol. (2g)^[2]: yield: 81% (37 mg); yellow oil; **IR**

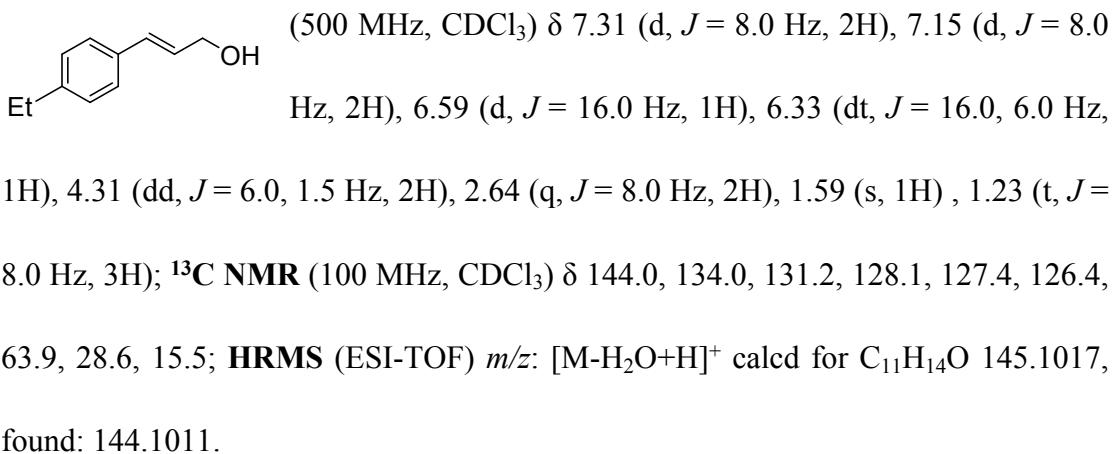
 **IR** (KBr) ν (cm⁻¹): 3426, 2921, 2851, 1600, 1227, 1158, 834; **¹H NMR** (500 MHz, CDCl₃) δ 7.38 - 7.32 (m, 2H), 7.01 (m, 2H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.28 (dt, *J* = 16.0, 5.5 Hz, 1H), 4.32 (dd, *J* = 5.5, 1.5 Hz, 2H), 1.62 (1H); **MS** (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₉H₉FO 153.07, found: 153.00.

(E)-3-(*p*-Tolyl)prop-2-en-1-ol (2h)^[2]: yield: 86% (38 mg); yellow oil; **IR** (KBr)

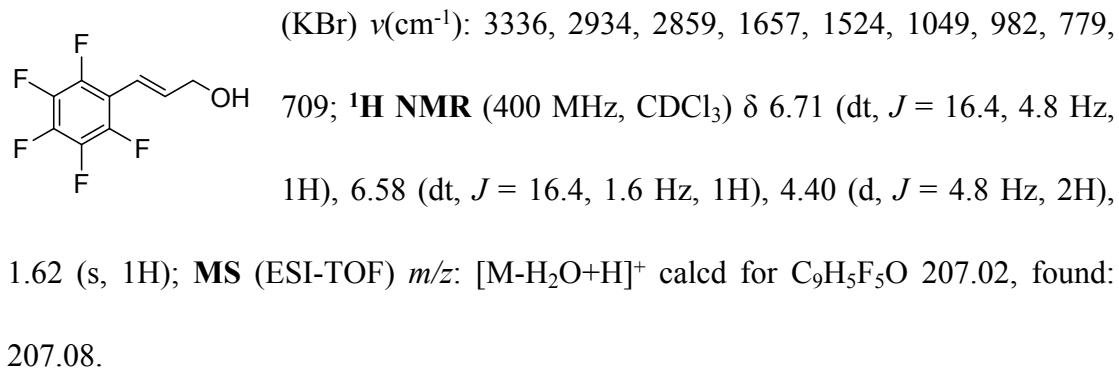
 **IR** ν (cm⁻¹): 3372, 2921, 2859, 1512, 1248, 1809, 968; **¹H NMR** (500 MHz, CDCl₃) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.32 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.31 (dd, *J* = 6.0,

1.5 Hz, 1H), 2.34 (s, 3H) , 1.59 (s, 1H); **MS** (ESI-TOF) *m/z*: [M-H₂O+H]⁺ calcd for C₁₀H₁₂O 131.09, found: 130.98.

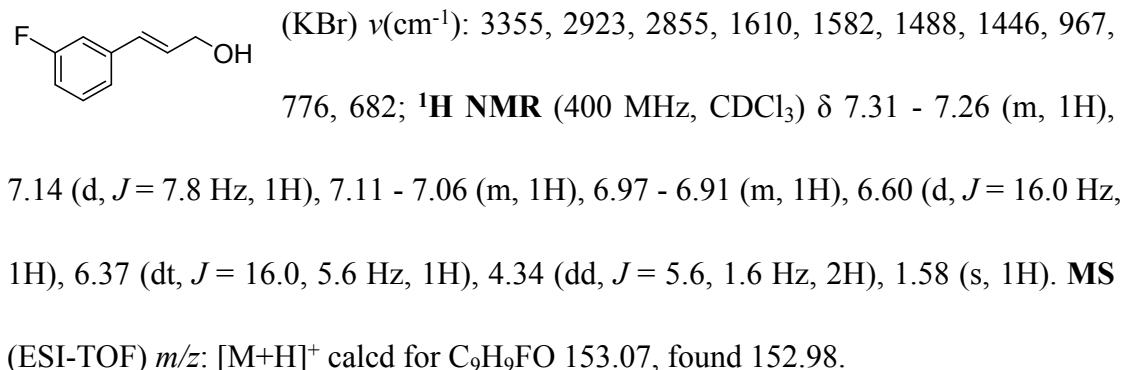
(E)-3-(4-Ethylphenyl)prop-2-en-1-ol (2i): yield: 80% (39 mg); yellow oil; **¹H NMR**



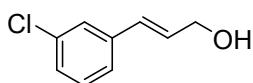
(E)-3-(Perfluorophenyl)prop-2-en-1-ol (2j)^[2]: yield: 82% (55 mg); yellow oil; **IR**



(E)-3-(3-Fluorophenyl)prop-2-en-1-ol (2k)^[3]: yield: 70% (32 mg); yellow oil; **IR**

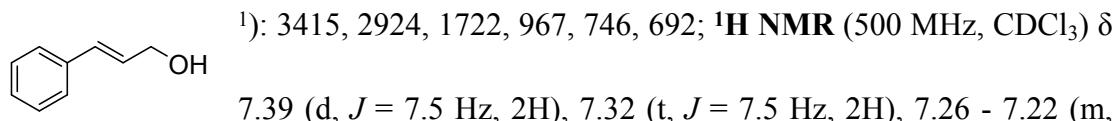


(E)-3-(3-Chlorophenyl)prop-2-en-1-ol (2l)^[2]: yield: 81% (41 mg); colorless oil; **IR**



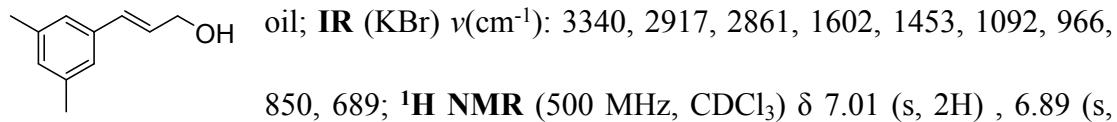
(KBr) ν (cm⁻¹): 3394, 2925, 2856, 1680, 1594, 1077, 966, 777, 682; **1H NMR** (400 MHz, CDCl₃) δ 7.37(s, 1H), 7.26 - 7.24 (m, 2H), 7.23 - 7.20 (m, 1H), 6.57 (dt, J = 16.0, 1.2 Hz, 1H), 6.37 (dt, J = 16.0, 5.6 Hz, 1H), 4.34 (d, J = 5.6 Hz, 2H), 1.61 (s, 1H); **MS** (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₉H₉ClO 169.04, found: 168.95.

(E)-3-Phenylprop-2-en-1-ol (2m)^[2]: yield: 85% (34 mg); yellow oil; **IR** (KBr) ν (cm⁻¹



7.39 (d, J = 7.5 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.26 - 7.22 (m, 1H), 6.62 (d, J = 15.0 Hz, 1H), 6.37 (dt, J = 15.0, 5.5 Hz, 1H), 4.33 (d, J = 5.5 Hz, 2H), 1.58 (s, 1H); **MS** (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₉H₁₀O 135.08, found: 135.01.

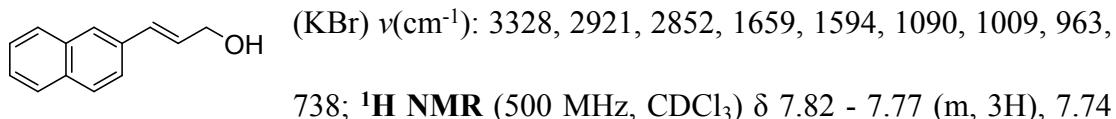
(E)-3-(3,5-Dimethylphenyl)prop-2-en-1-ol (2n)^[2]: yield: 80% (39 mg); pale yellow



(E)-3-(2,5-Dimethylphenyl)prop-2-en-1-ol (2o): yield: 76% (37 mg); yellow oil; **1H NMR** (500 MHz, CDCl₃) δ 7.27 (s, 1H), 7.04 (d, J = 7.5 Hz, 1H), 6.98 (d, J = 7.5 Hz, 1H), 6.81 (d, J = 16.0 Hz, 1H), 6.25 (dt, J = 16.0, 6.0 Hz, 1H), 4.34 (d, J = 6.0 Hz, 2H), 2.31 (s, 3H), 2.31 (s, 3H), 1.56 (s, 1H); **13C NMR** (125 MHz, CDCl₃) δ 135.9, 135.4, 132.6, 132.4, 130.2, 129.5, 129.1, 128.4, 126.4, 64.0, 21.0, 19.3; **HRMS** (ESI-TOF) *m/z*: [M-H₂O+H]⁺ calcd for

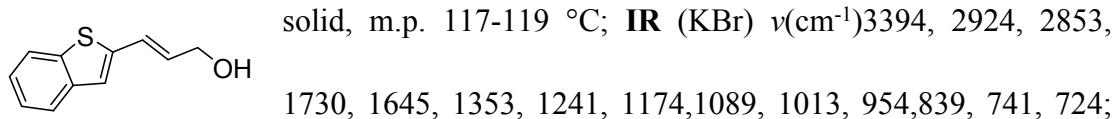
$C_{11}H_{14}O$ 145.1017, found: 145.1006.

(E)-3-(Naphthalen-2-yl)prop-2-en-1-ol (2p)^[2]: yield: 78% (43 mg); yellow oil; **IR**



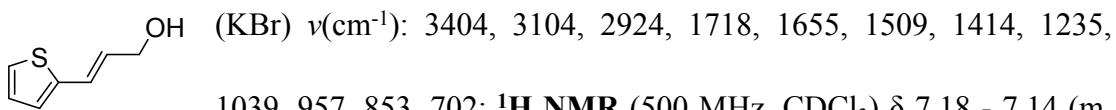
(s, 1H), 7.60 (dd, J = 8.5, 1.5 Hz, 1H), 7.49 - 7.42 (m, 2H), 6.78 (d, J = 16.0 Hz, 1H), 6.50 (dt, J = 16.0, 5.5 Hz, 1H), 4.39 (dd, J = 5.5, 1.5 Hz, 2H), 1.58 (1H); **MS** (ESI-TOF) m/z : [M-H₂O+H]⁺ calcd for $C_{13}H_{12}O$ 167.09, found: 166.90.

(E)-3-(Benzo[b]thiophen-2-yl)prop-2-en-1-ol (2q)^[4]: yield: 84% (48 mg); yellow



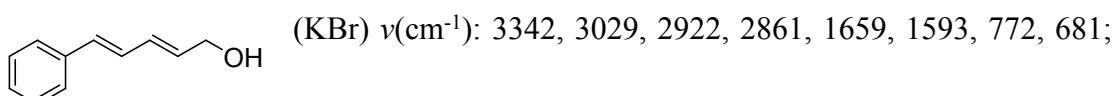
1H NMR (500 MHz, $CDCl_3$) δ 7.77 - 7.72 (m, 1H), 7.69 - 7.64 (m, 1H), 7.33 - 7.26 (m, 2H), 7.13 (s, 1H), 6.84 (d, J = 15.5 Hz, 1H), 6.28 (dt, J = 15.5, 5.5 Hz, 1H), 4.33 (dd, J = 5.5, 1.5 Hz, 2H), 1.65 (s, 1H); **MS** (ESI-TOF) m/z : [M-H₂O+H]⁺ calcd for $C_{11}H_{10}OS$ 173.04, found: 172.95.

(E)-3-(Thiophen-2-yl)prop-2-en-1-ol (2r)^[2]: yield: 86% (36 mg); yellow oil; **IR**



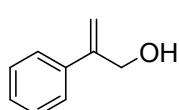
C_7H_8OS 123.03, found: 122.90.

(2E,4E)-5-Phenylpenta-2,4-dien-1-ol (2s)^[2]: yield: 56% (27 mg); yellow oil; **IR**



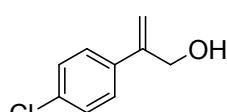
¹H NMR (500 MHz, CDCl₃) δ 7.42 - 7.38 (m, 2H), 7.32 (m, 2H), 7.25 - 7.21 (m, 1H), 6.79 (dd, *J* = 15.5, 10.5 Hz, 1H), 6.56 (d, *J* = 15.5 Hz, 1H), 6.43 (dd, *J* = 15.5, 10.5 Hz, 1H), 5.97 (dt, *J* = 15.5, 5.5 Hz, 1H), 4.26 (d, *J* = 5.5 Hz, 2H), 1.57 (s, 1H); **MS** (ESI-TOF) *m/z*: [M+Na]⁺ calcd for C₁₁H₁₂O 183.08, found: 183.01.

2-Phenylprop-2-en-1-ol (2t)^[2]: yield: 85% (34 mg); yellow oil; **IR** (KBr) ν (cm⁻¹):

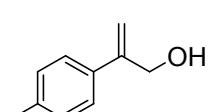


3354, 3056, 2922, 2857, 1631, 1495, 1291, 1025, 905, 779, 707; **¹H NMR** (400 MHz, CDCl₃) δ 7.45 (d, *J* = 7.2 Hz, 2H), 7.39 - 7.27 (m, 3H), 5.47 (s, 1H), 5.35 (s, 1H), 4.55 (s, 2H), 1.60 (s, 1H); **MS** (ESI-TOF) *m/z*: [M+Na]⁺ calcd for C₉H₁₀O 157.06, found: 156.94.

2-(4-Chlorophenyl)prop-2-en-1-ol (2u)^[2]: yield: 71% (36 mg); yellow oil; **IR** (KBr)

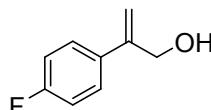


ν (cm⁻¹): 3368, 2918, 2857, 1630, 1493, 1298, 1043, 833, 765; **¹H NMR** (400 MHz, CDCl₃) δ 7.41 - 7.37 (m, 2H), 7.34 - 7.30 (m, 2H), 5.47 (d, *J* = 1.2 Hz, 1H), 5.38 - 5.36 (q, *J* = 1.2 Hz, 1H), 4.52 (s, 2H), 1.58 (s, 1H); **MS** (EI) *m/z*: 168.0, found: 168.0.



2-(*p*-Tolyl)prop-2-en-1-ol (2v)^[2]: yield: 83% (37 mg); yellow oil; **IR** (KBr) ν (cm⁻¹): 3411, 3026, 2921, 1682, 1607, 1514, 1181, 1108, 1043, 817, 722; **¹H NMR** (400 MHz, CDCl₃) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.43 (d, *J* = 1.2 Hz, 1H), 5.30 (d, *J* = 1.2 Hz, 1H), 4.52 (s, 2H), 2.35 (s, 3H), 1.61 (s, 1H); **MS** (ESI-TOF) *m/z*: [M+NH₄]⁺ calcd for C₁₀H₁₂O 166.12, found: 165.99.

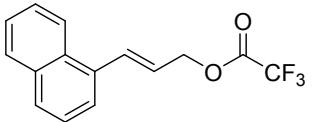
2-(4-Fluorophenyl)prop-2-en-1-ol (2w)^[2]: yield: 72% (33 mg); yellow solid, m.p.



143-145 °C; **IR** (KBr) ν (cm⁻¹): 2917, 2849, 1460, 1041, 893, 824;

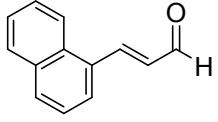
¹H NMR (500 MHz, CDCl₃) δ 7.45 - 7.41 (m, 2H), 7.06 - 7.02 (m, 2H), 5.42 (s, 1H), 5.33 (s, 1H), 4.52 (s, 2H), 1.56 (s, 1H); **MS** (EI) *m/z*: 152.1, found: 152.1.

(E)-3-(Naphthalen-1-yl)allyl 2,2,2-trifluoroacetate (3a): yield: 7% (11 mg); pale



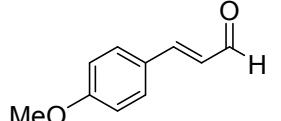
yellow oil; **¹H NMR** (500 MHz, CDCl₃) δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.89 - 7.82 (m, 2H), 7.62 (d, *J* = 7.0 Hz, 1H), 7.57 - 7.50 (m, 3H), 7.49 - 7.45 (m, 1H), 6.33 (dt, *J* = 15.5, 6.5 Hz, 1H), 5.10 (d, *J* = 6.5 Hz, 2H); **¹³C NMR** (125 MHz, CDCl₃) δ 157.9, 157.6, 157.2, 156.9 (q, *J* = 41.3 Hz), 134.3, 133.5, 133.1, 131.0, 129.0, 128.6, 126.5, 126.0, 125.5, 124.4, 123.4, 123.2, 117.9, 115.6, 113.4, 111.1 (q, *J* = 283.8 Hz), 68.6; **¹⁹F NMR** (471 MHz, CDCl₃) δ -74.9; **HRMS** (ESI-TOF) *m/z*: [M+NH₄]⁺ calcd for C₁₅H₁₁F₃O₂ 298.1055, found: 298.1046.

(E)-3-(Naphthalen-1-yl)acrylaldehyde (5a)^[2]: yield: 60% (22 mg); yellow oil; **IR**



(KBr) *v*(cm⁻¹): 3426, 3053, 2924, 2851, 1677, 1508, 1127, 970, 796, 773; **¹H NMR** (500 MHz, CDCl₃) δ 9.87 (d, *J* = 7.5 Hz, 1H), 8.35 (d, *J* = 15.5 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.65 - 7.61 (m, 1H), 7.60 - 7.52 (m, 2H), 6.86 (dd, *J* = 15.5, 7.5 Hz, 1H); **MS** (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₁₃H₁₀O 183.08, found: 182.99.

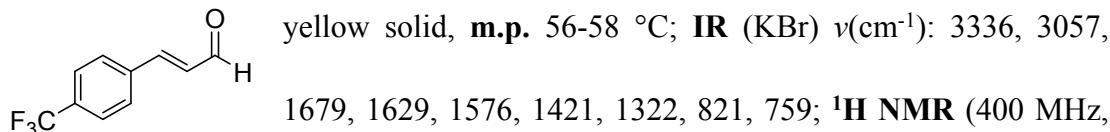
(E)-3-(4-Methoxyphenyl)acrylaldehyde (5b)^[2]: yield: 62% (20 mg); pale yellow oil;



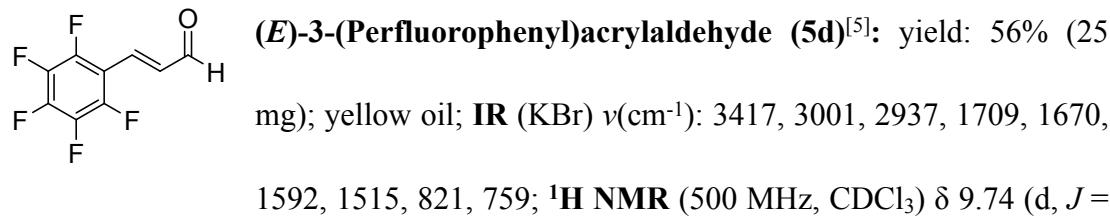
IR (KBr) *v*(cm⁻¹): 2958, 2925, 2853, 1677, 1602, 1512, 1254, 1177, 1125, 969, 817, 707; **¹H NMR** (500 MHz, CDCl₃) δ 9.66 (d, *J* = 8.5 Hz, 1H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 16.0 Hz, 1H), 6.95 (d, *J* =

8.5 Hz, 2H), 6.62 (dd, J = 16.0, 8.5 Hz, 1H), 3.86 (s, 3H); **MS** (ESI-TOF) m/z : [M+H]⁺ calcd for C₁₀H₁₀O₂ 163.08, found: 162.98.

(E)-3-(4-(Trifluoromethyl)phenyl)acrylaldehyde (5c)^[2]: yield: 73% (29 mg);

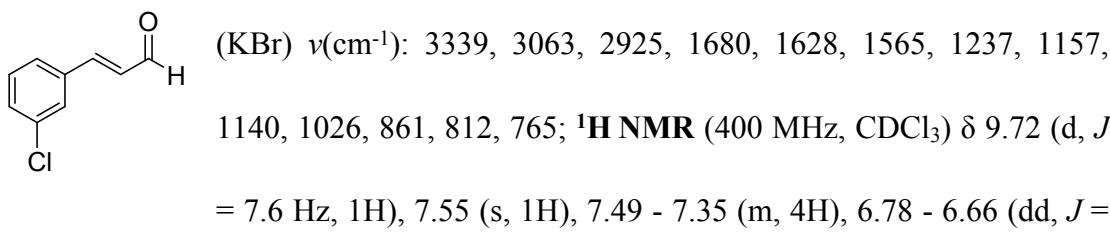


200.98.

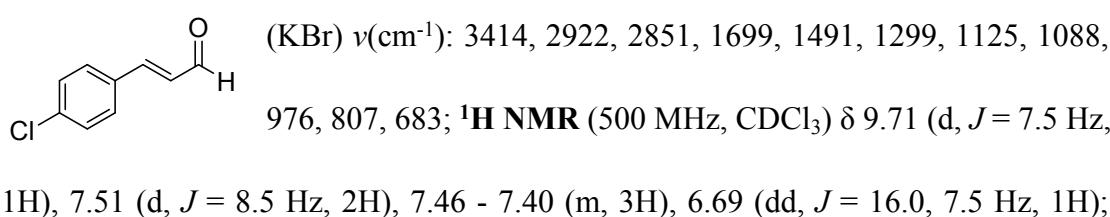


222.0, found: 222.0.

(E)-3-(3-Chlorophenyl)acrylaldehyde (5e)^[2] : yield: 76% (25 mg); yellow oil; **IR**

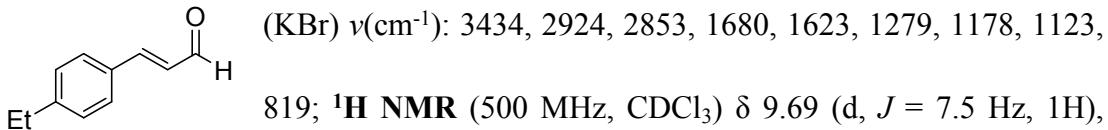


(E)-3-(4-Chlorophenyl)acrylaldehyde (5f)^[2]: yield: 69% (23 mg); yellow oil; **IR**

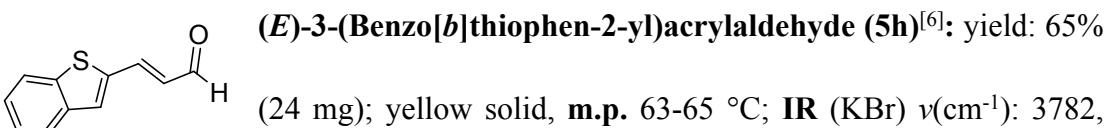


MS (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₉H₇ClO 167.03, found: 166.95.

(E)-3-(4-Ethylphenyl)acrylaldehyde (5g)^[2]: yield: 62% (20 mg); yellow oil; **IR**

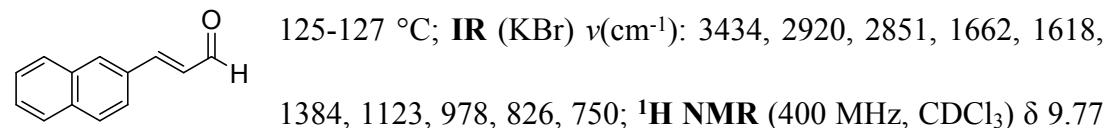


7.50 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 16.0 Hz, 1H), 7.28 (s, 2H), 6.70 (dd, *J* = 16.0, 7.5 Hz, 1H), 2.70 (q, *J* = 7.5 Hz, 2H), 1.27 (t, *J* = 7.5 Hz, 3H); **MS** (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₁₁H₁₂O 161.10, found: 161.05.



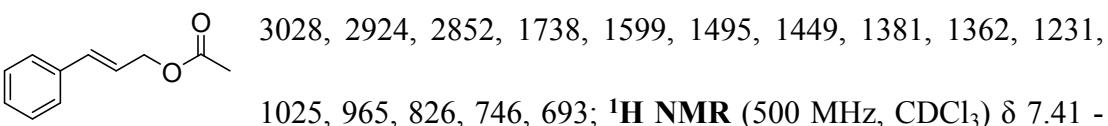
3326, 3056, 2923, 2799, 1667, 1612, 1236, 1113, 962, 821, 756, 724, 692; **¹H NMR** (500 MHz, CDCl₃) δ 9.70 (d, *J* = 7.5 Hz, 1H), 7.84 - 7.79 (m, 2H), 7.69 (d, *J* = 15.5 Hz, 1H), 7.58 (s, 1H), 7.45 - 7.36 (m, 2H), 6.57 (dd, *J* = 15.5, 7.5 Hz, 1H); **MS** (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₁₁H₈OS 189.04, found: 188.91.

(E)-3-(Naphthalen-2-yl)acrylaldehyde (5i)^[7]: yield: 66% (24 mg); white solid, **m.p.**



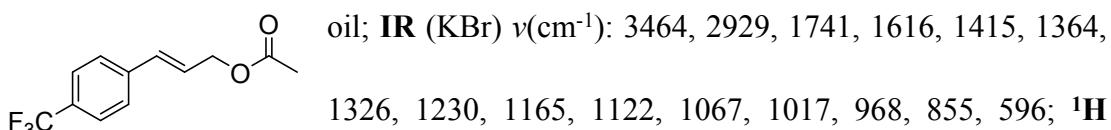
(d, *J* = 7.6 Hz), 8.00, 7.92 - 7.84 (m), 7.69 (dd, *J* = 8.4, 2.0 Hz), 7.65 (d, *J* = 16.0 Hz), 7.60 - 7.51 (m), 6.84 (dd, *J* = 16.0, 7.6 Hz); **MS** (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₁₃H₁₀O 183.08, found: 182.99.

Cinnamyl acetate (7a)^[8]: yield: 63% (33 mg); yellow oil; **IR** (KBr) $\nu(\text{cm}^{-1})$: 3460,

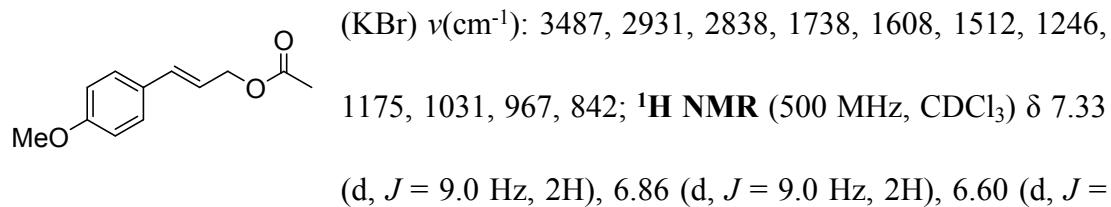


7.38 (m, 2H), 7.35 - 7.30 (m, 2H), 7.28 - 7.25(m, 1H), 6.66 (d, $J = 15.5$ Hz, 1H), 6.29 (dt, $J = 15.5, 6.5$ Hz, 1H), 4.73 (dd, $J = 6.5, 1.5$ Hz, 2H), 2.11 (s, 3H); **MS** (ESI-TOF) m/z : [M-AcOH+H]⁺ calcd for C₁₁H₁₂O₂ 117.07, found: 116.96.

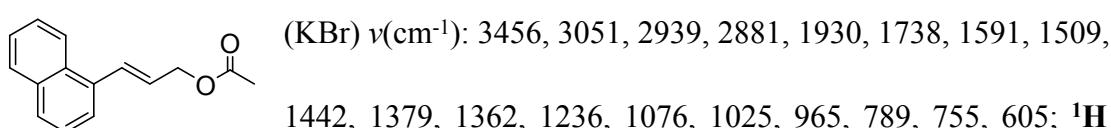
(E)-3-(4-(Trifluoromethyl)phenyl)allyl acetate (7b)^[8]: yield: 53% (39 mg); yellow



(E)-3-(4-Methoxyphenyl)allyl acetate (7c)^[8]: yield: 50% (31 mg); yellow oil; **IR**

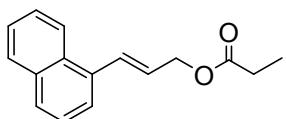


(E)-3-(Naphthalen-1-yl)allyl acetate (7d)^[9]: yield: 78% (53 mg); yellow oil; **IR**



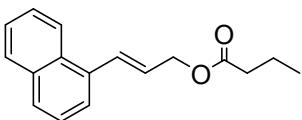
2H), 6.31 (dt, $J = 15.5, 6.5$ Hz, 1H), 4.83 (dd, $J = 6.5, 1.5$ Hz, 1H), 2.13 (s, 3H); **MS** (ESI-TOF) m/z : [M+NH₄]⁺ calcd for C₁₅H₁₄O₂ 244.13, found: 244.03.

(E)-3-(Naphthalen-1-yl)allyl propionate (7e): yield: 65% (47 mg); yellow oil; **¹H**



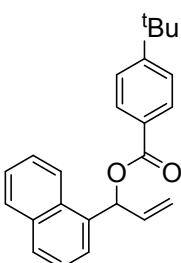
NMR (500 MHz, CDCl₃) δ 8.09 (d, $J = 8.5$ Hz, 1H), 7.84 (d, $J = 7.5$ Hz, 1H), 7.79 (d, $J = 8.5$ Hz, 1H), 7.60 (d, $J = 7.5$ Hz, 1H), 7.55 - 7.47 (m, 2H), 7.46 - 7.38 (m, 2H), 6.32 (dt, $J = 15.5, 6.0$ Hz, 1H), 4.85 (d, $J = 6.0$ Hz, 2H), 2.41 (q, $J = 7.5$ Hz, 2H), 1.19 (t, $J = 7.5$ Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 174.2, 134.0, 133.6, 131.1, 131.1, 128.5, 128.3, 126.6, 126.2, 125.8, 125.5, 124.1, 123.6, 65.0, 27.6, 9.1; **HRMS** (ESI-TOF) m/z : [M+NH₄]⁺ calcd for C₁₆H₁₆O₂ 258.1494, found: 258.1479.

(E)-3-(Naphthalen-1-yl)allyl butyrate (7f): yield: 60% (46 mg); yellow oil; **¹H**



NMR (500 MHz, CDCl₃) δ 8.09 (d, $J = 8.0$ Hz, 1H), 7.86 - 7.83 (d, $J = 7.5$ Hz, 1H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.59 (d, $J = 7.5$ Hz, 1H), 7.54 - 7.48 (m, 2H), 7.46 - 7.38 (m, 2H), 6.32 (dt, $J = 15.5, 6.5$ Hz, 1H), 4.85 (dd, $J = 6.5, 1.5$ Hz, 2H), 2.37 (t, $J = 7.5$ Hz, 2H), 1.75 - 1.67 (m, 2H), 0.98 (t, $J = 7.5$ Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 173.5, 134.0, 133.6, 131.1, 131.1, 128.5, 128.3, 126.6, 126.2, 125.8, 125.5, 124.1, 123.7, 64.9, 36.2, 18.5, 13.7; **HRMS** (ESI-TOF) m/z : [M+Na]⁺ calcd for C₁₇H₁₈O₂ 277.1204; found: 277.1270.

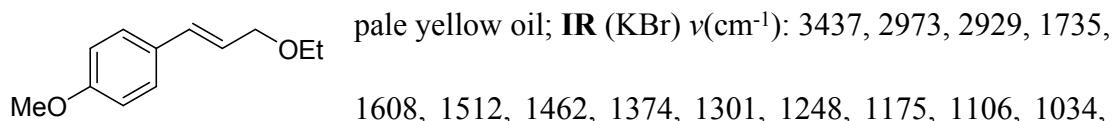
1-(1-(4-(tert-Butyl)phenyl)allyl)naphthalene (7g): yield: 26% (18mg); pale yellow



oil; **¹H NMR** (400 MHz, CDCl₃) δ 8.24 (d, $J = 8.0$ Hz, 1H), 8.05 (d, $J = 8.0$ Hz, 2H), 7.91 - 7.81 (m, 2H), 7.69 (d, $J = 6.8$ Hz, 1H), 7.55 - 7.43 (m, 5H), 7.21 (d, $J = 5.2$ Hz, 1H), 6.30 (ddd, $J = 17.2, 10.4, 5.2$ Hz, 1H).

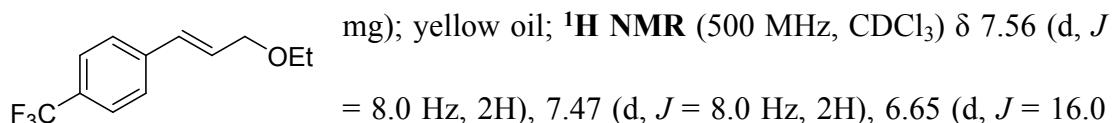
Hz, 1H), 5.42 (d, J = 17.2 Hz, 1H), 5.34 (d, J = 10.4 Hz, 1H) 1.33 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃) δ 165.6, 156.8, 136.1, 134.6, 133.9, 130.8, 129.6, 129.0, 128.8, 127.3, 126.3, 125.7, 125.5, 125.4, 125.3, 123.9, 117.2, 74.1, 35.1, 31.1; **HRMS** (ESI-TOF) *m/z*: [M+NH₄]⁺ calcd for C₂₄H₂₄O₂ 362.2120; found: 362.2144.

(E)-1-(3-Ethoxyprop-1-en-1-yl)-4-methoxybenzene (9a)^[10]: yield: 44% (17 mg);



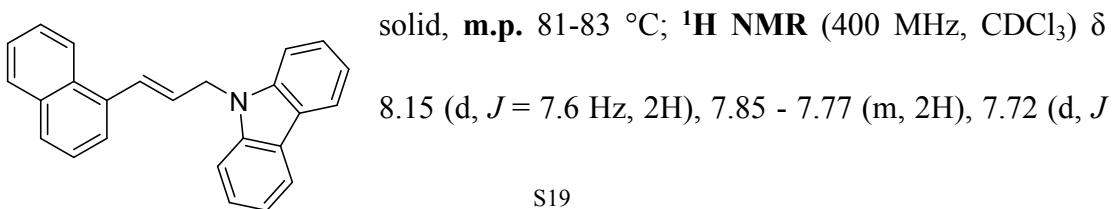
968, 836; **¹H NMR** (500 MHz, CDCl₃) δ 7.32 (d, J = 8.5 Hz, 2H), 6.85 (d, J = 8.5 Hz, 2H), 6.55 (d, J = 16.0 Hz, 1H), 6.17 (dt, J = 16.0, 6.0 Hz, 1H), 4.12 (dd, J = 6.0, 1.5 Hz, 2H), 3.81 (s, 3H), 3.54 (q, J = 7.0 Hz, 2H), 1.24 (t, J = 7.0 Hz, 3H); **MS** (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₁₂H₁₆O₂ 193.12; found: 193.01.

(E)-1-(3-Ethoxyprop-1-en-1-yl)-4-(trifluoromethyl)benzene (9b): yield: 48% (22



Hz, 1H), 6.40 (dt, J = 16.0, 5.5 Hz, 1H), 4.16 (dd, J = 5.5, 1.5 Hz, 2H), 3.57 (q, J = 7.0 Hz, 2H), 1.26 (t, J = 7.0 Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃) δ 140.3, 130.4, 129.20, 129.16, 128.7, 126.6, 125.5 (q, J = 3.8 Hz) 70.81, 66.02, 15.21.; **¹⁹F NMR** (471 MHz, CDCl₃) δ -62.5; **HRMS** (ESI-TOF) *m/z*: [M+H]⁺ calcd for C₁₂H₁₃F₃O 231.0997; found: 231.0991.

(E)-9-(3-(Naphthalen-1-yl)allyl)-9*H*-carbazole (10b): yield: 23% (15 mg); white



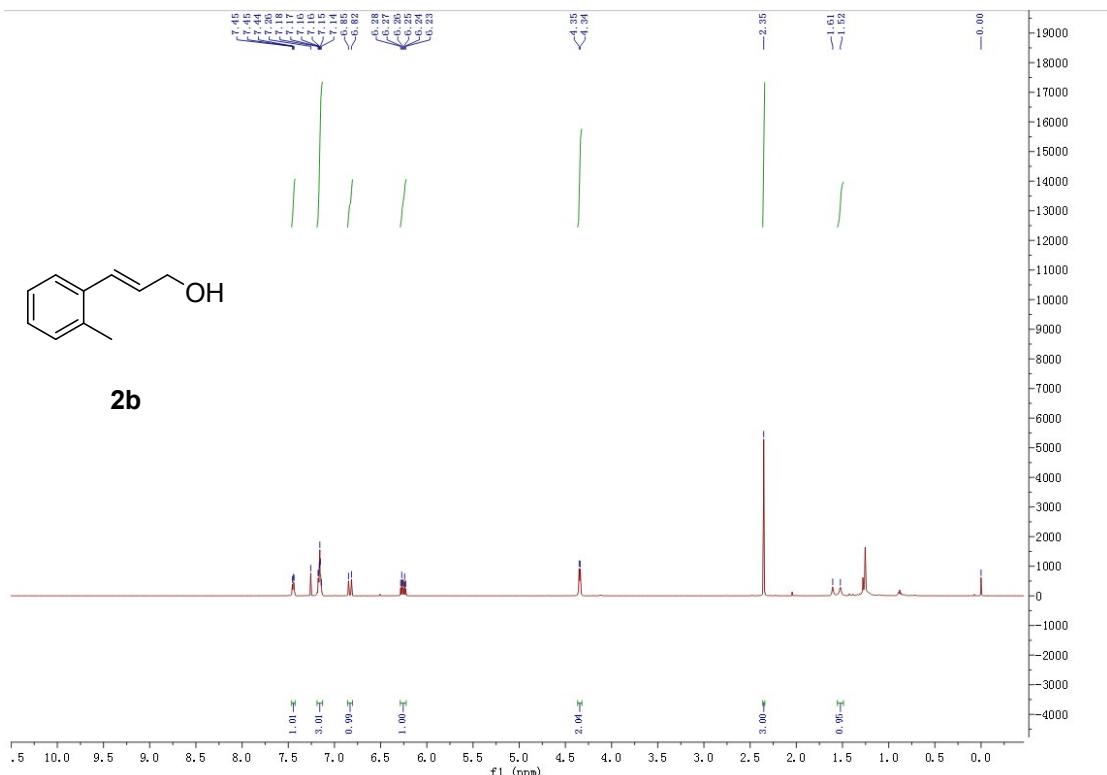
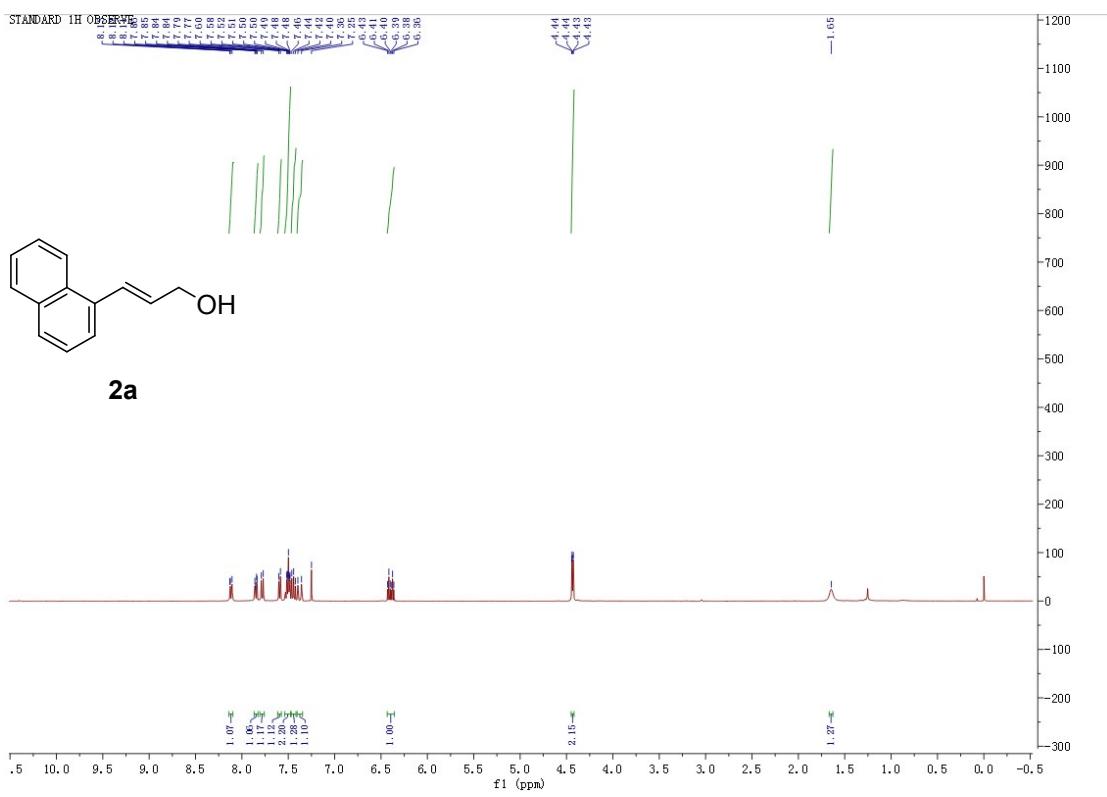
= 8.0 Hz, 1H), 7.52 - 7.46 (m, 5H), 7.45 - 7.40 (m, 2H), 7.39 - 7.34 (m, 1H), 7.29 - 7.25 (m, 2H), 7.18 (d, J = 15.6 Hz, 1H), 6.37 (dt, J = 15.6, 5.2 Hz, 1H), 5.19 (dd, J = 5.2, 2.0 Hz, 2H); **^{13}C NMR** (100 MHz, CDCl_3) δ 140.4, 134.1, 133.5, 130.9, 129.3, 128.4, 128.1, 127.1, 126.1, 125.8, 125.7, 125.5, 123.9, 123.6, 123.1, 120.4, 119.1, 108.9, 45.2; **HRMS** (ESI-TOF) m/z : [M+H]⁺ calcd for $\text{C}_{25}\text{H}_{19}\text{N}$ 334.1596.; found: 334.1592.

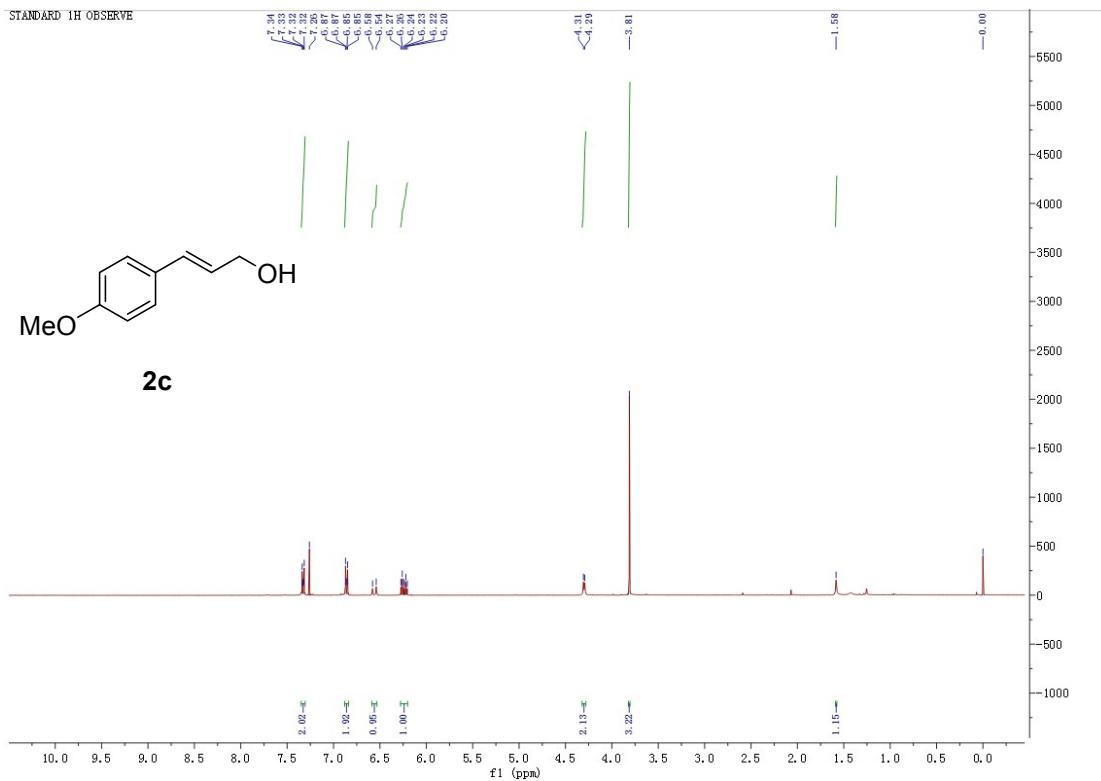
4. References

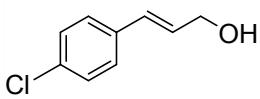
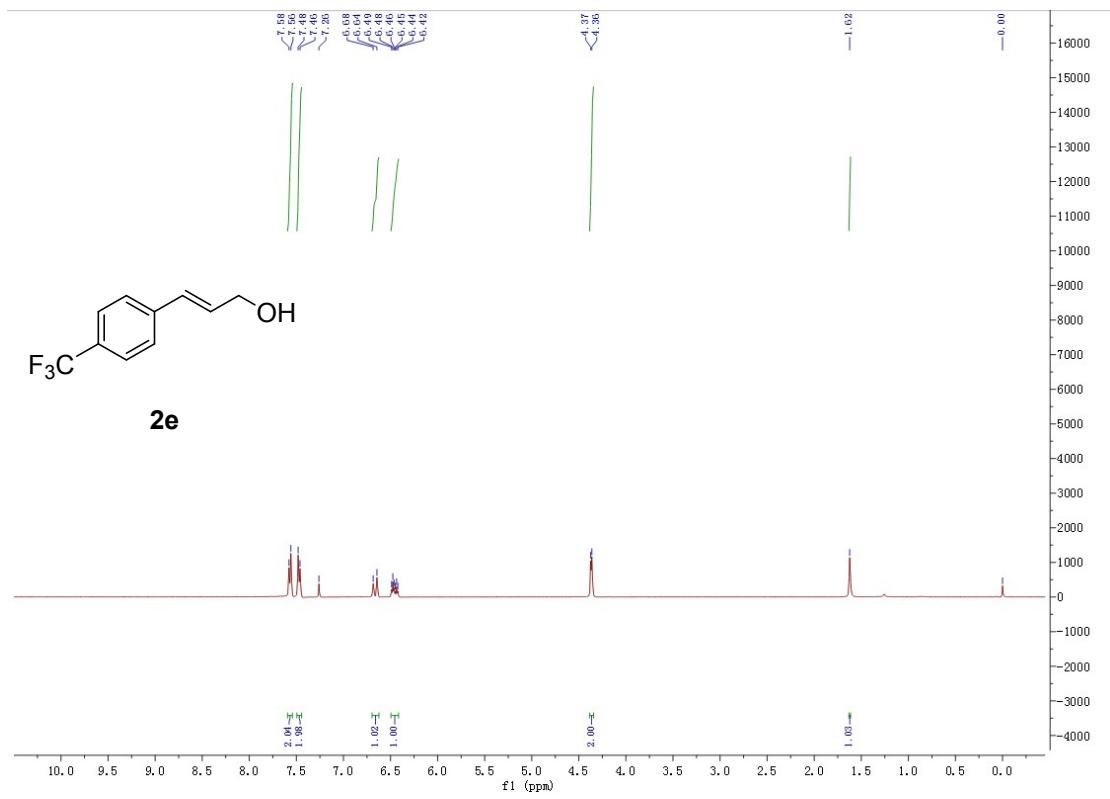
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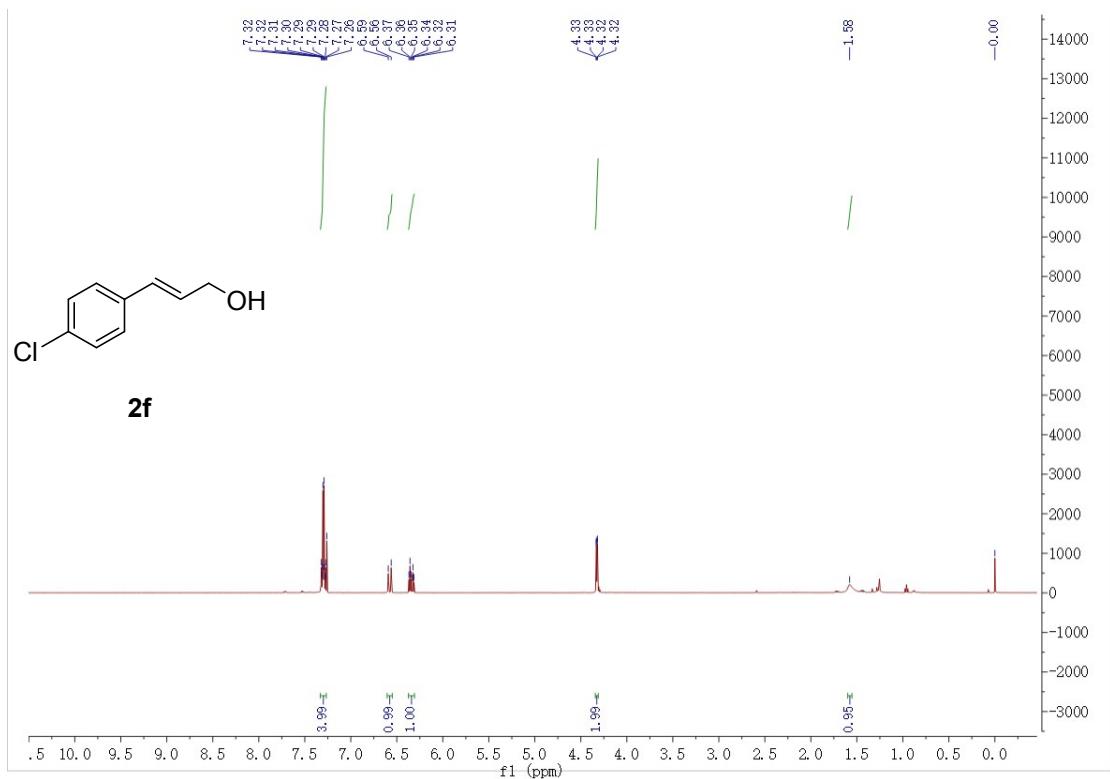
5. Spectra of ^1H and ^{13}C NMR

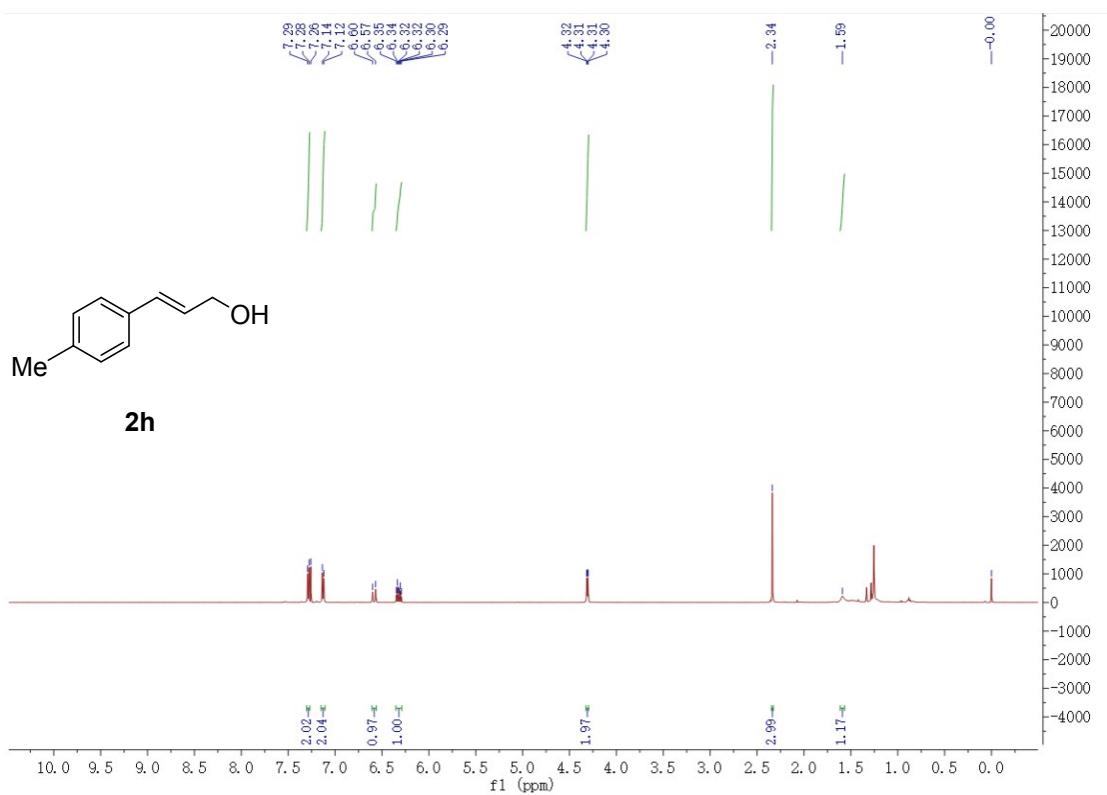
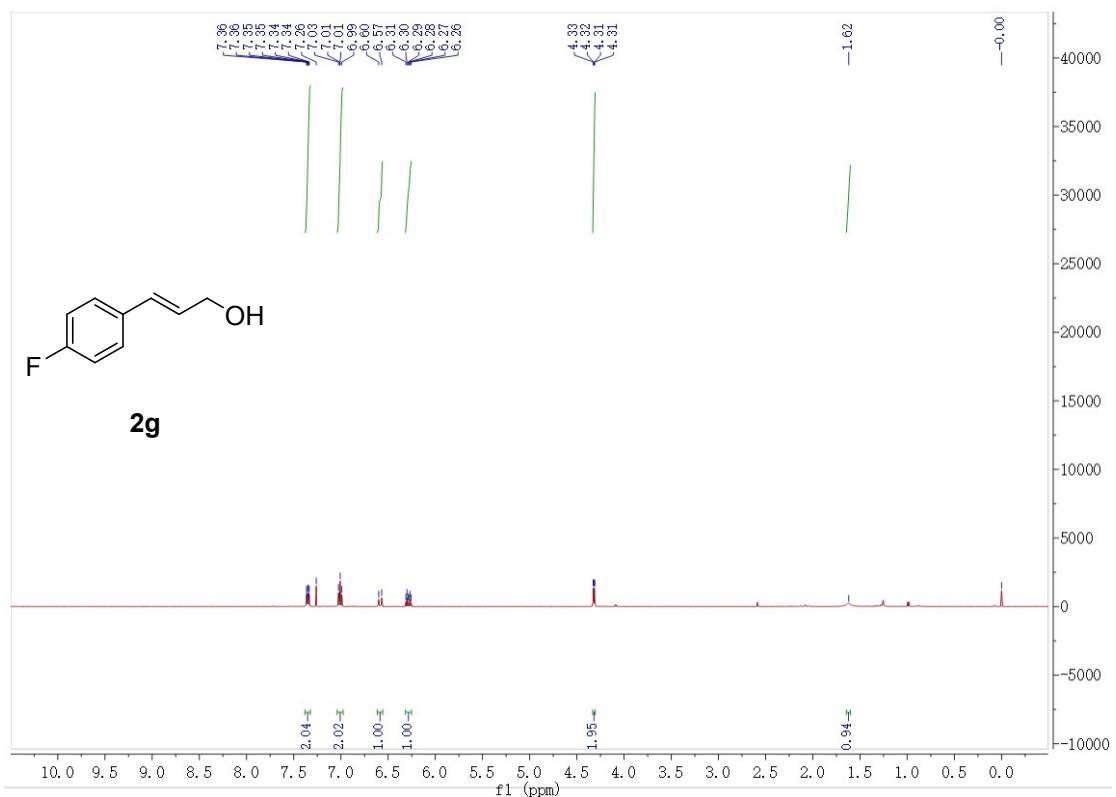


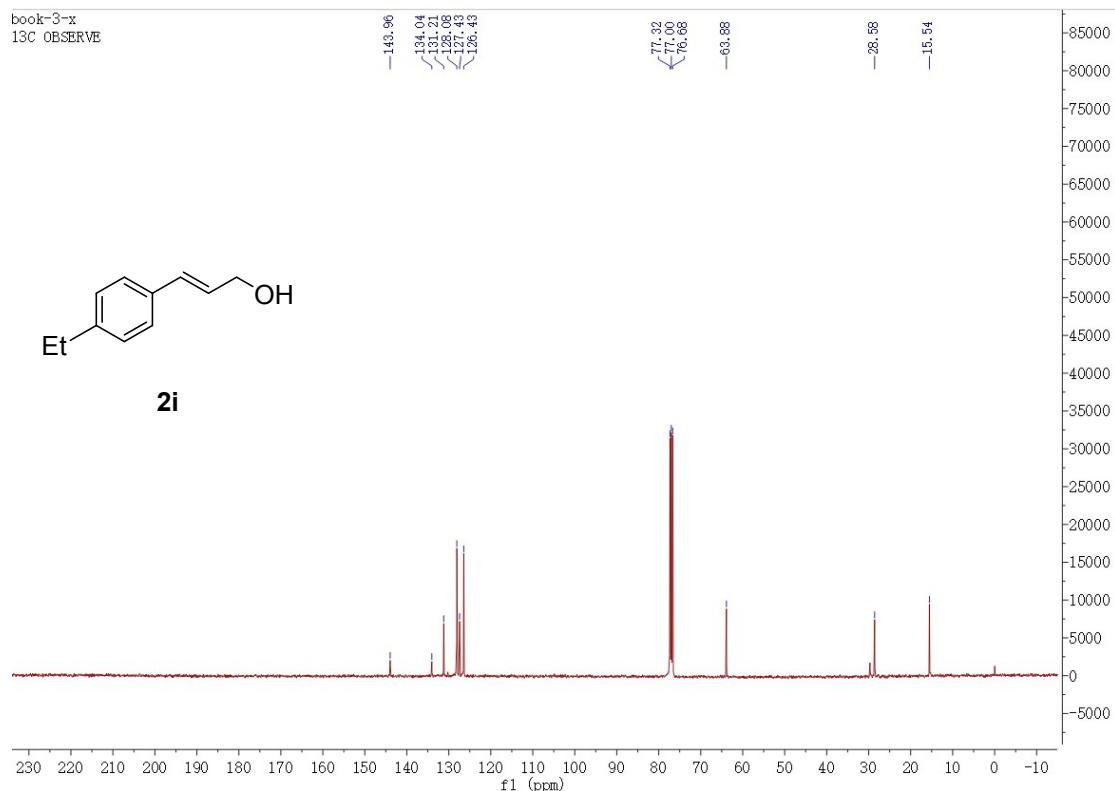
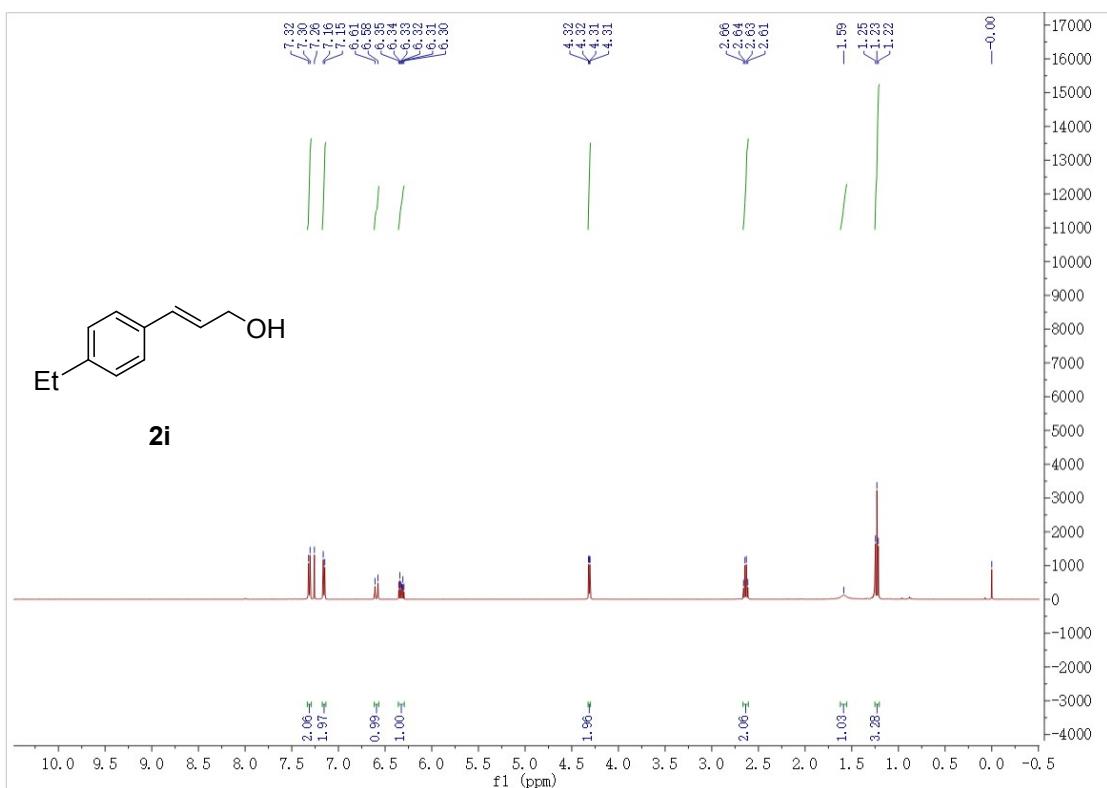


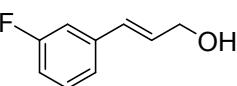
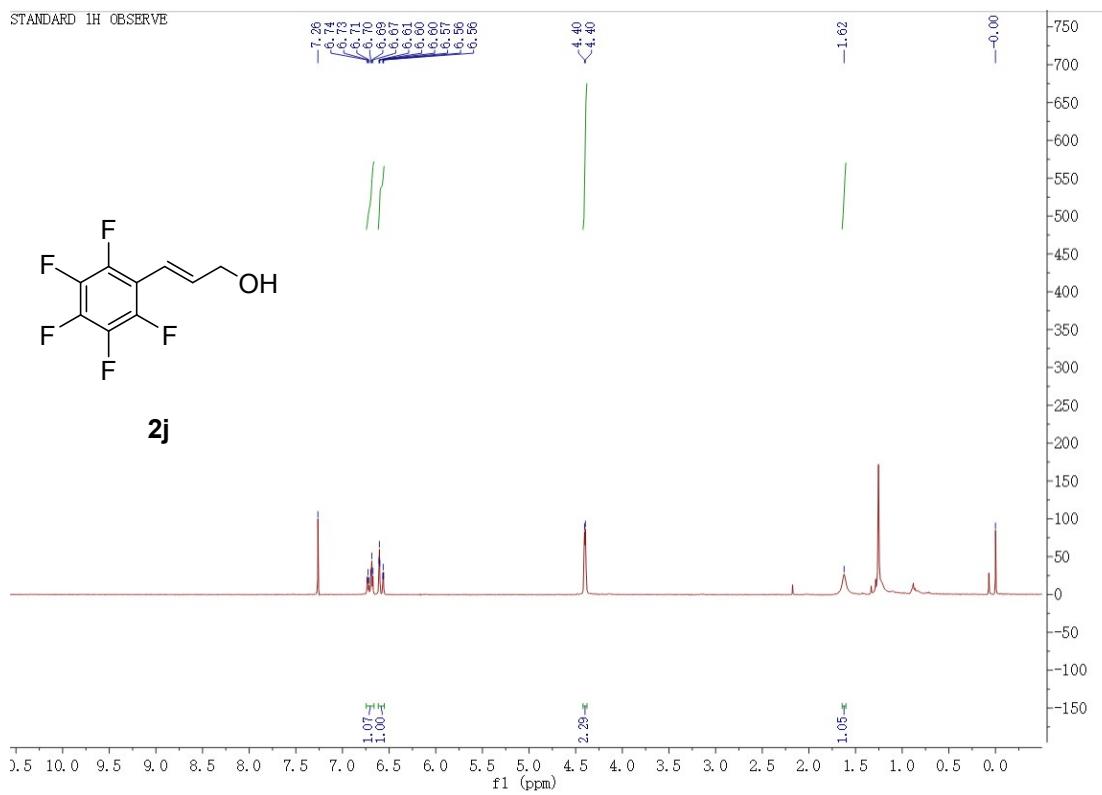


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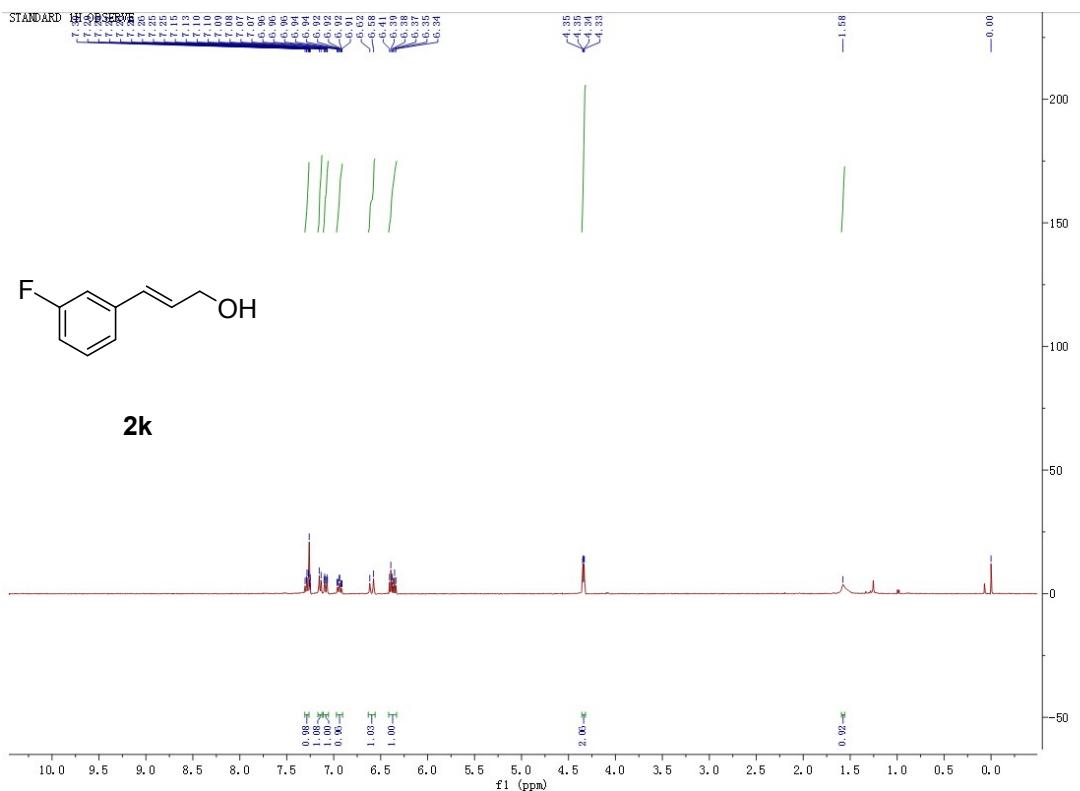


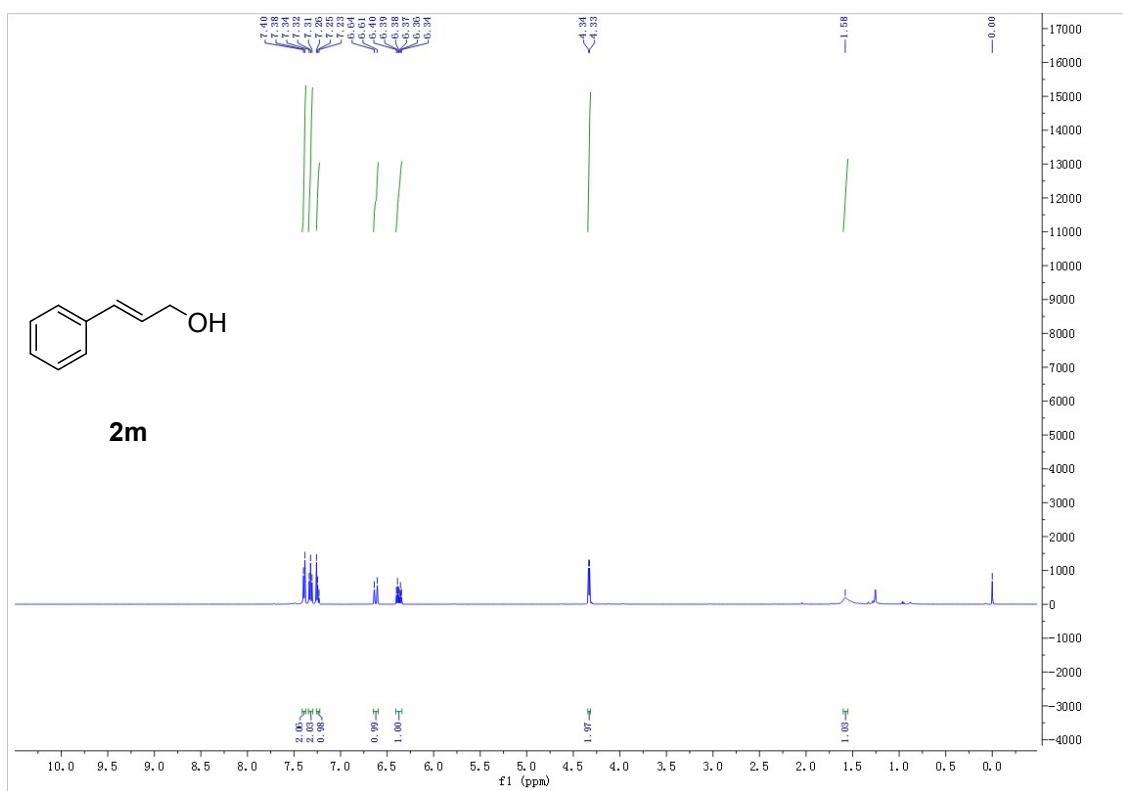
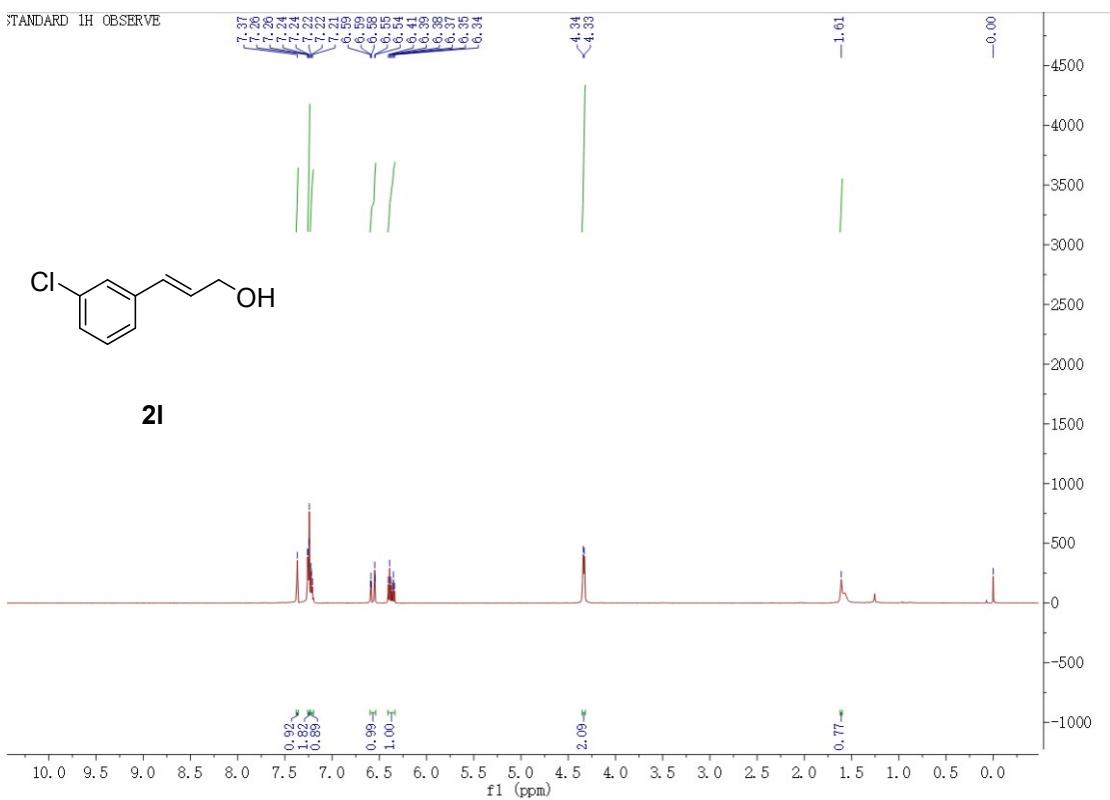


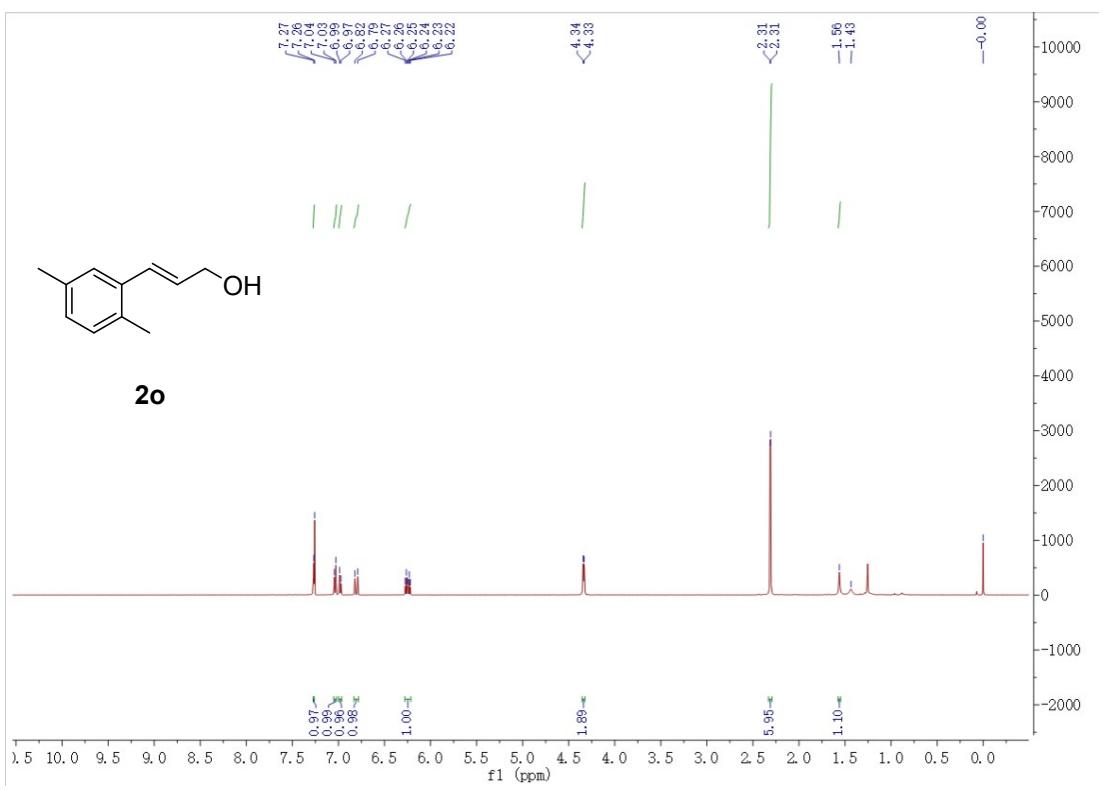
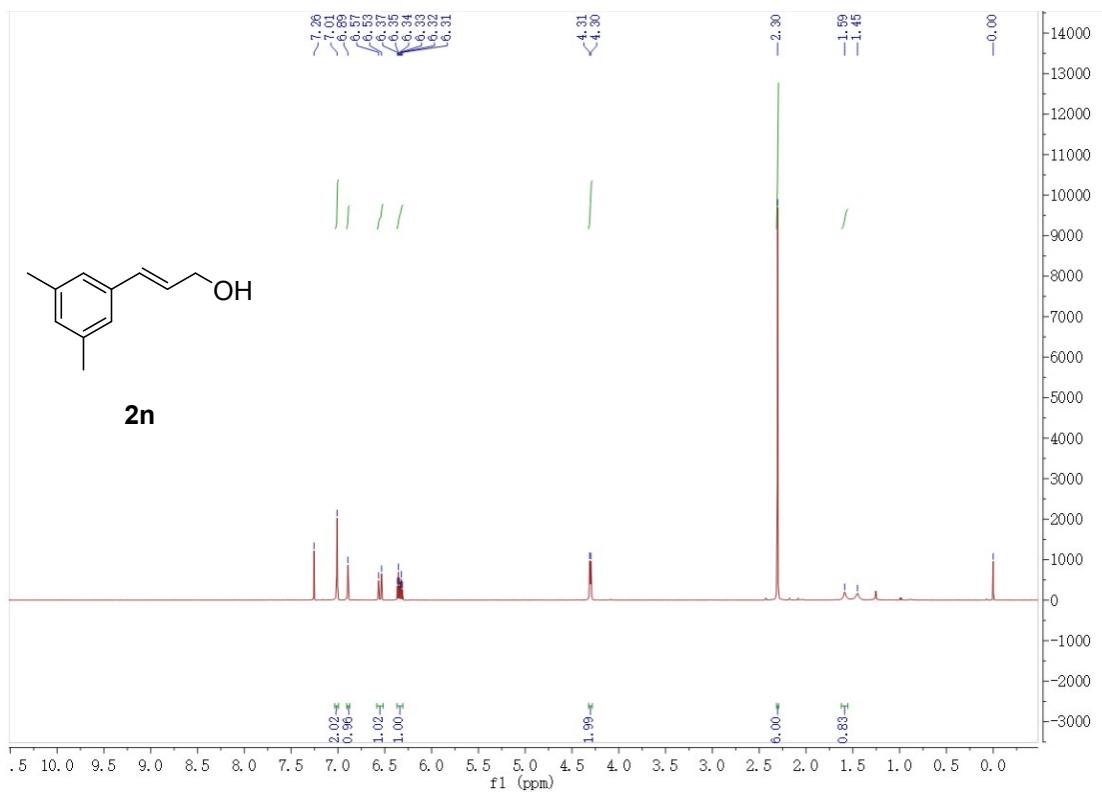


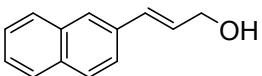
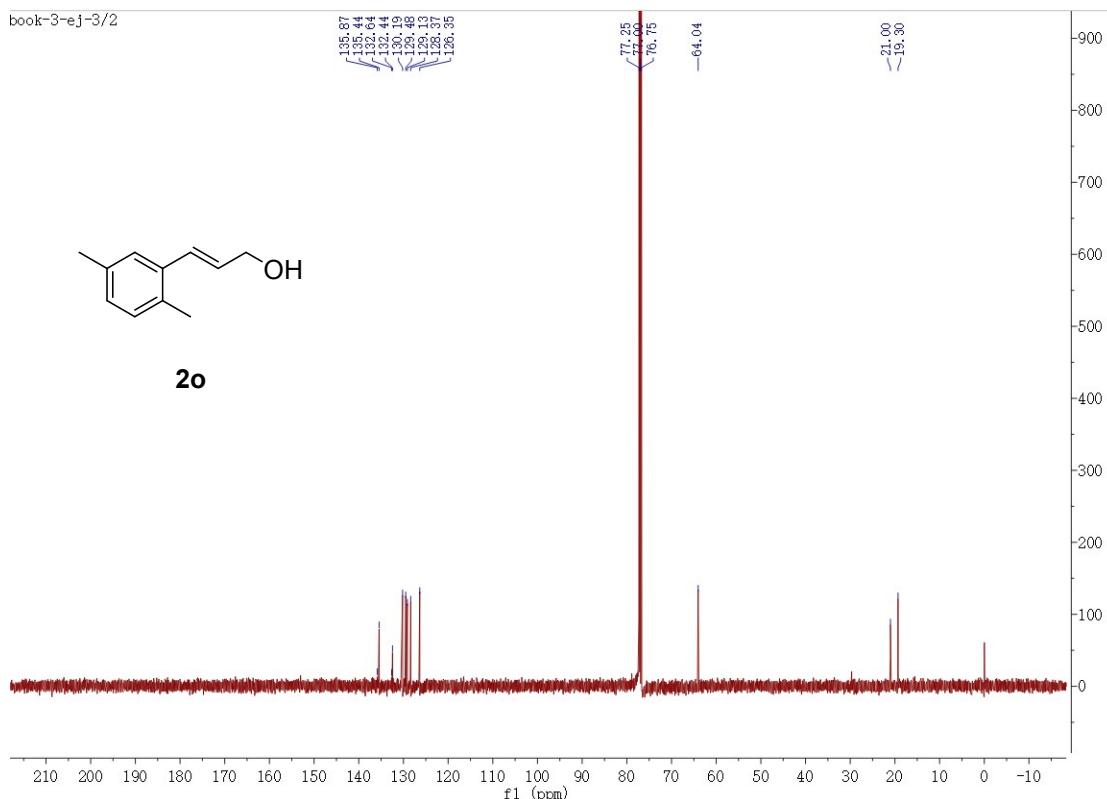


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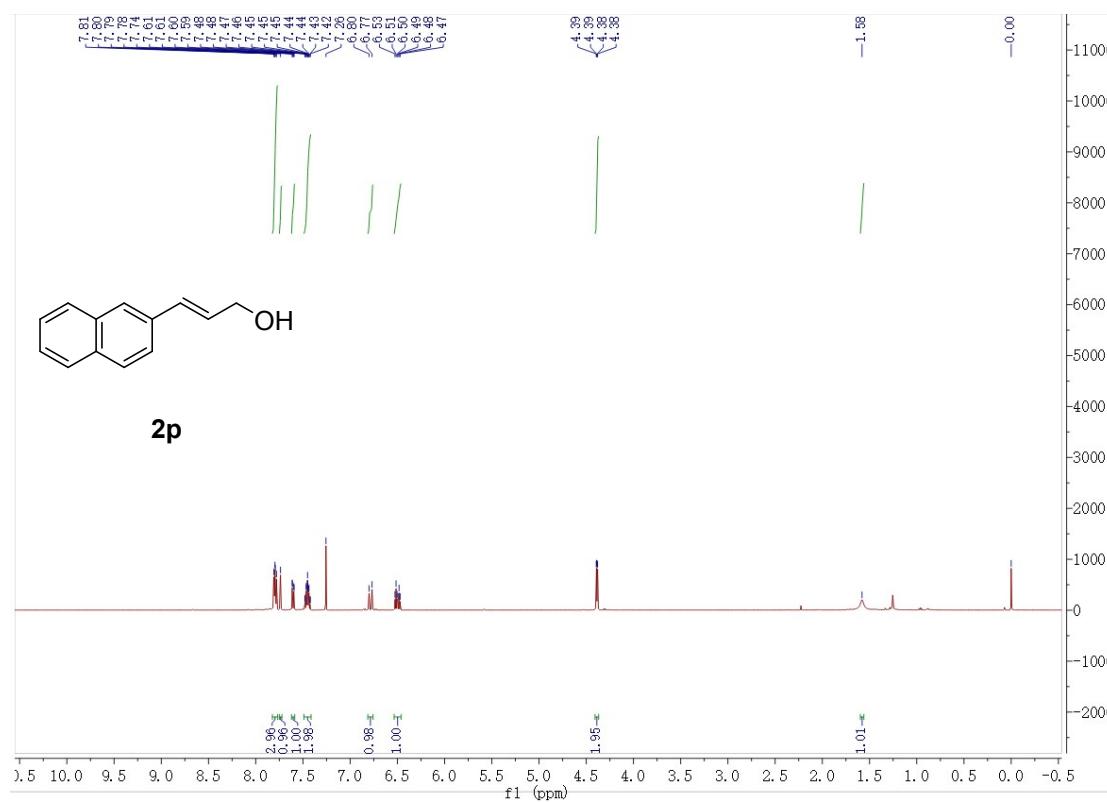


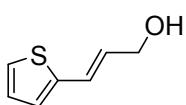
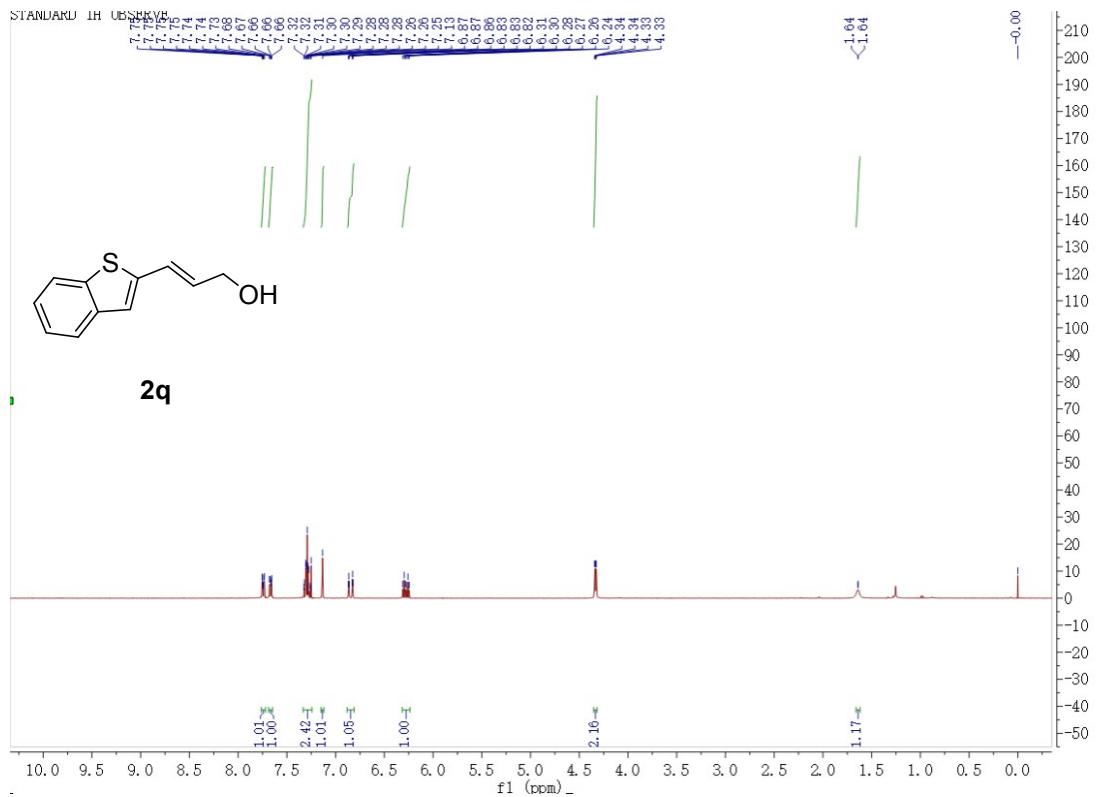




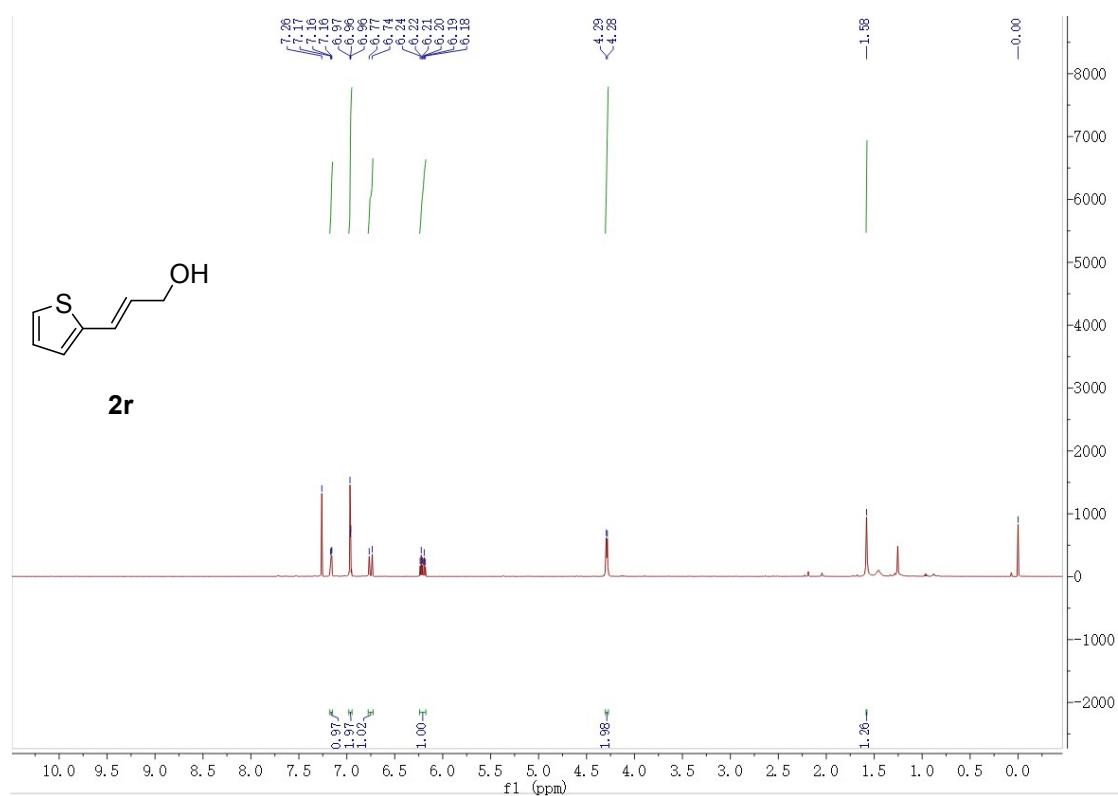


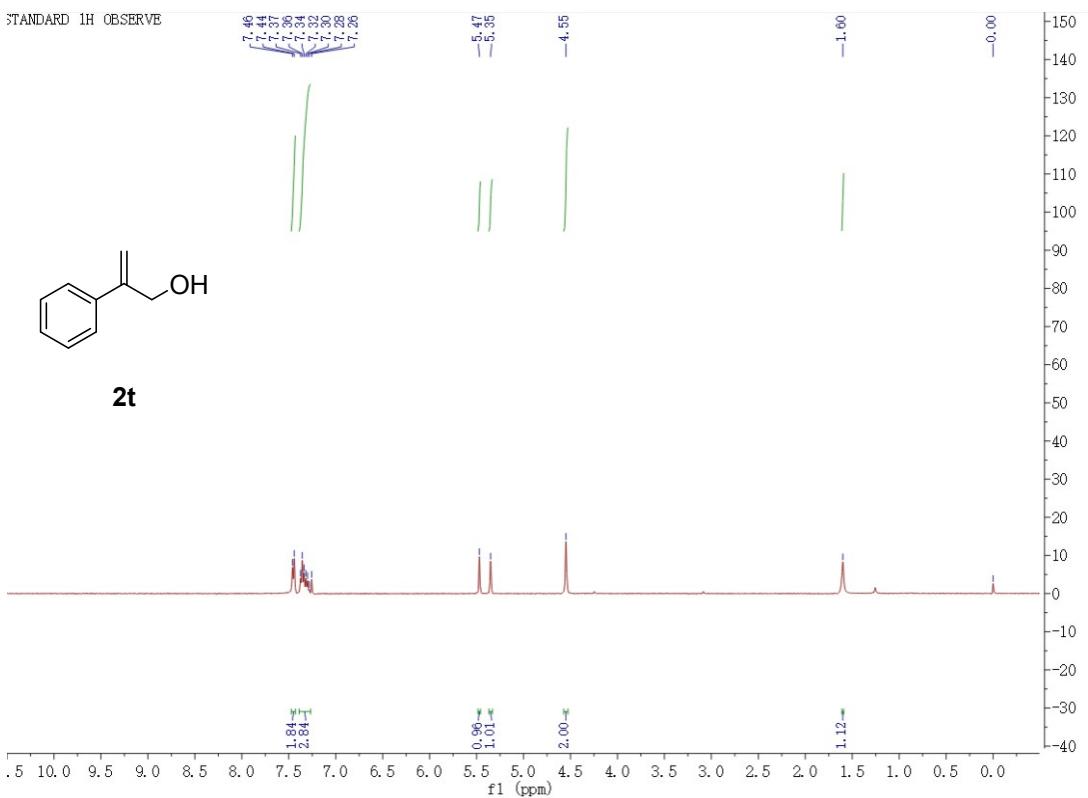
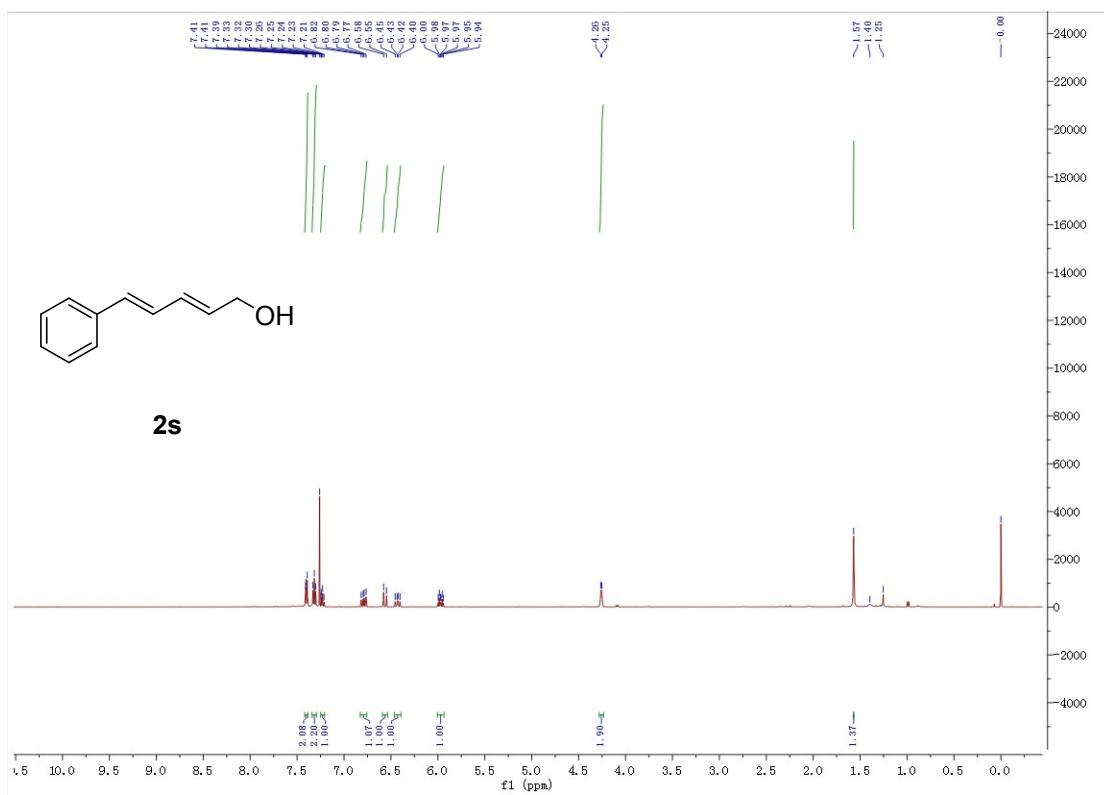
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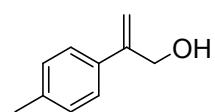
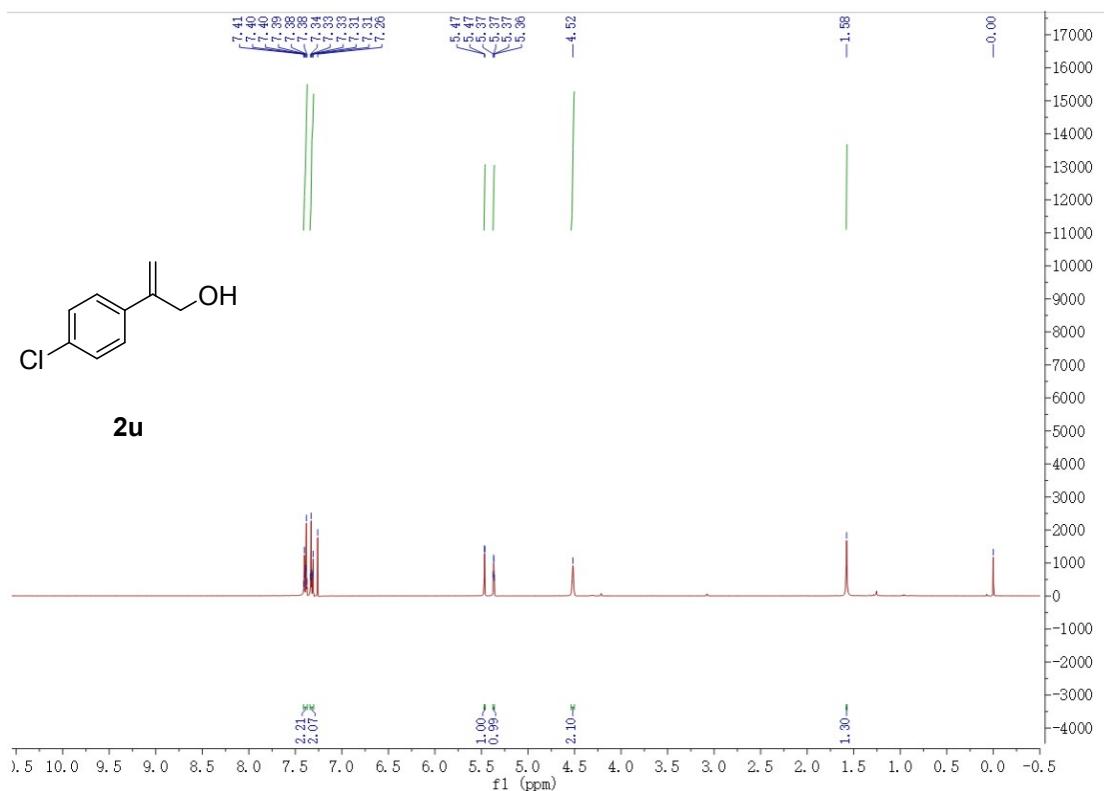




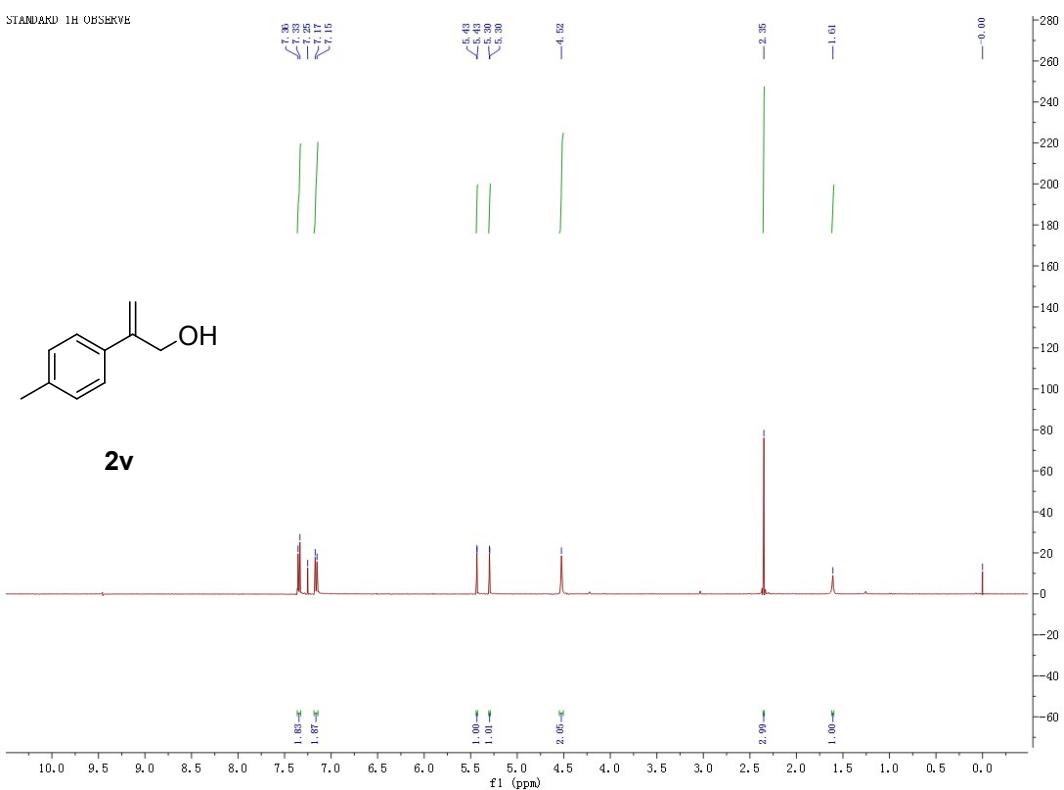
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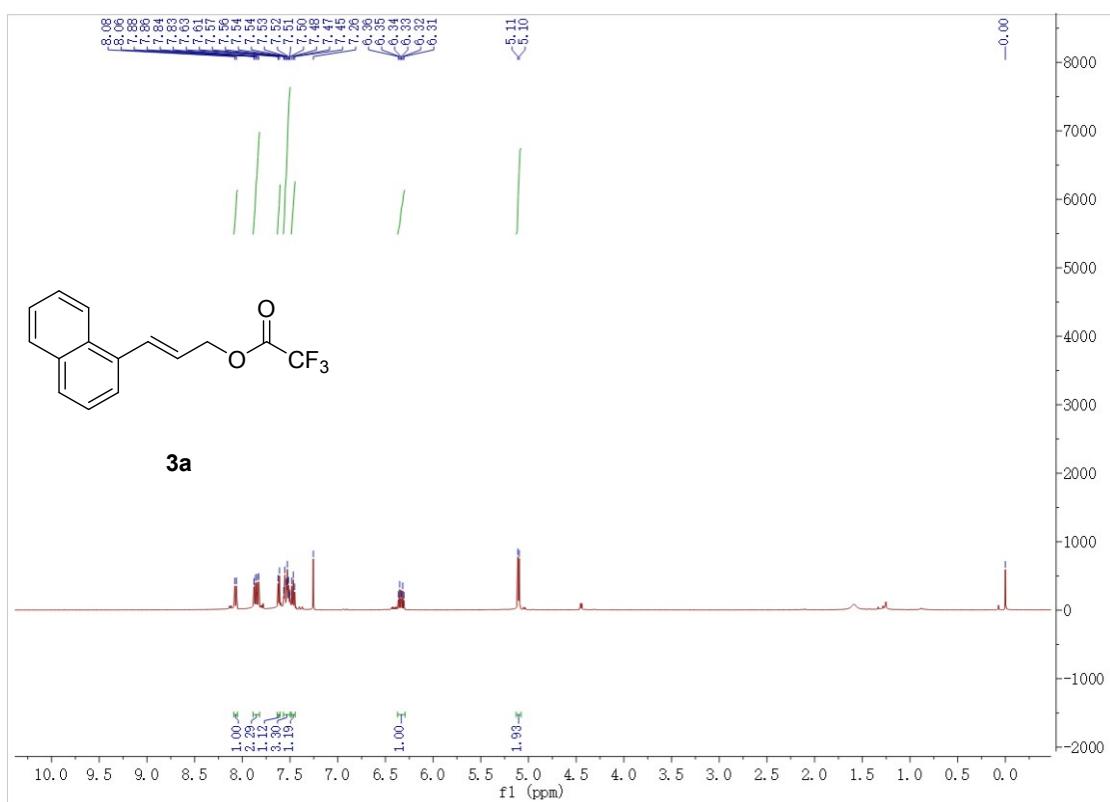
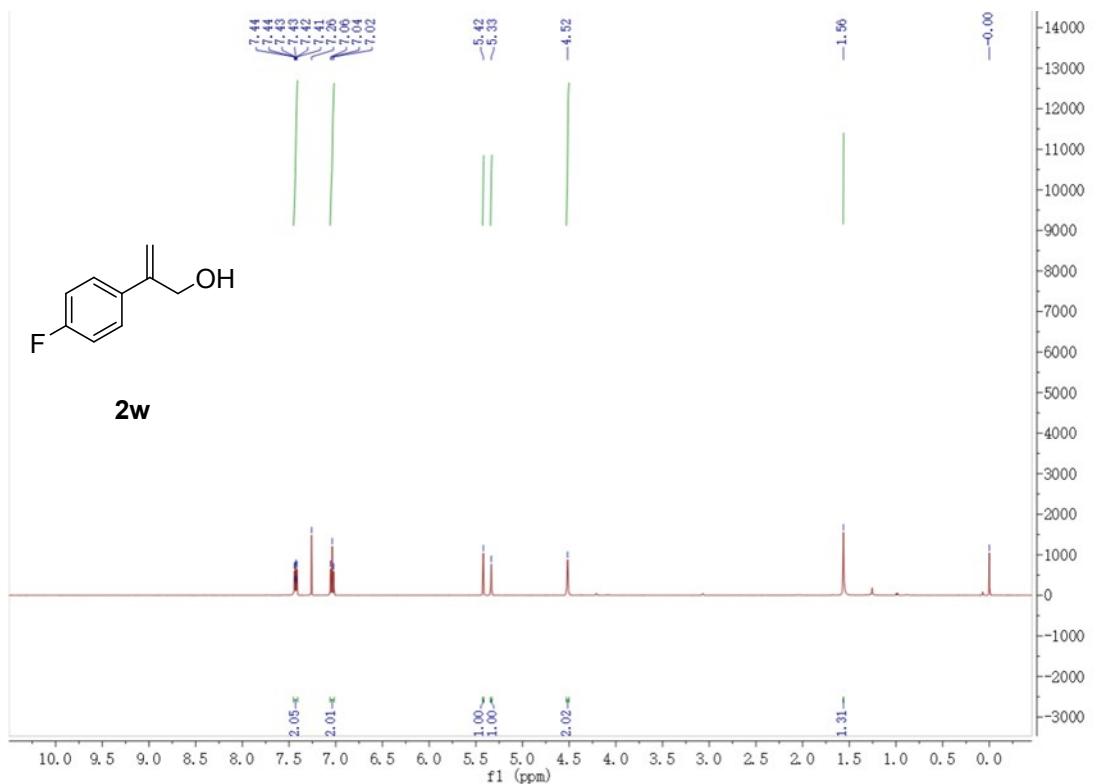


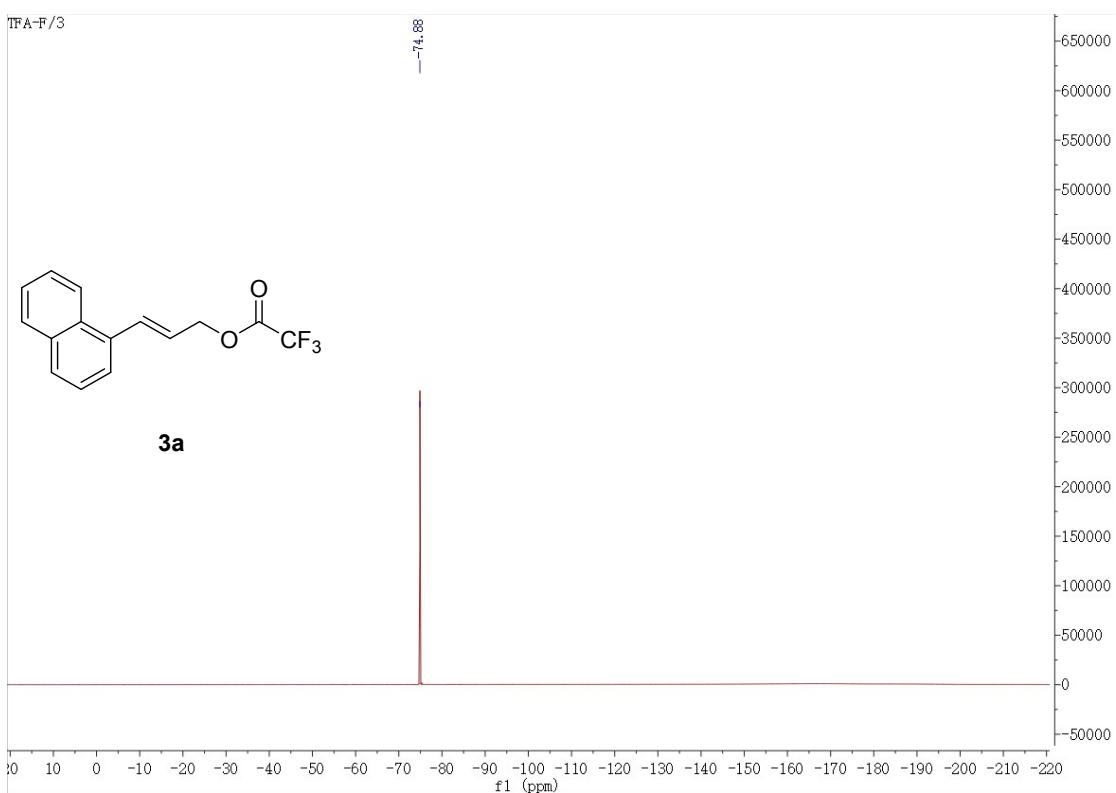
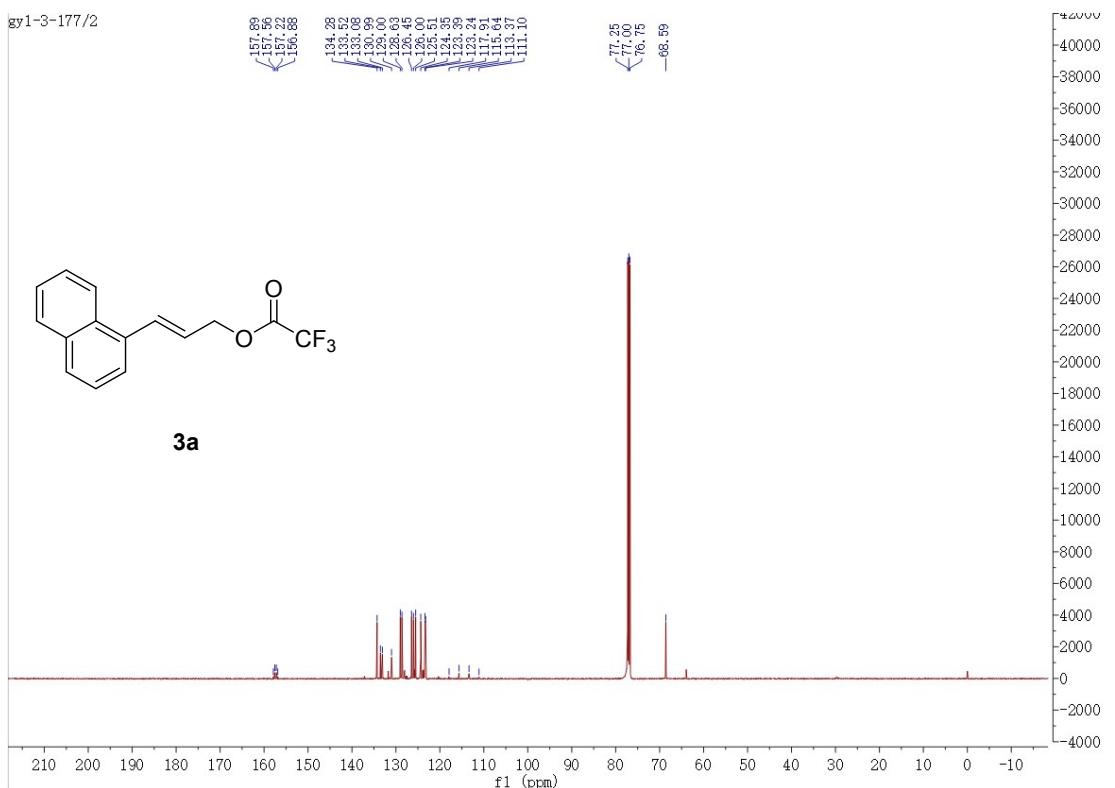


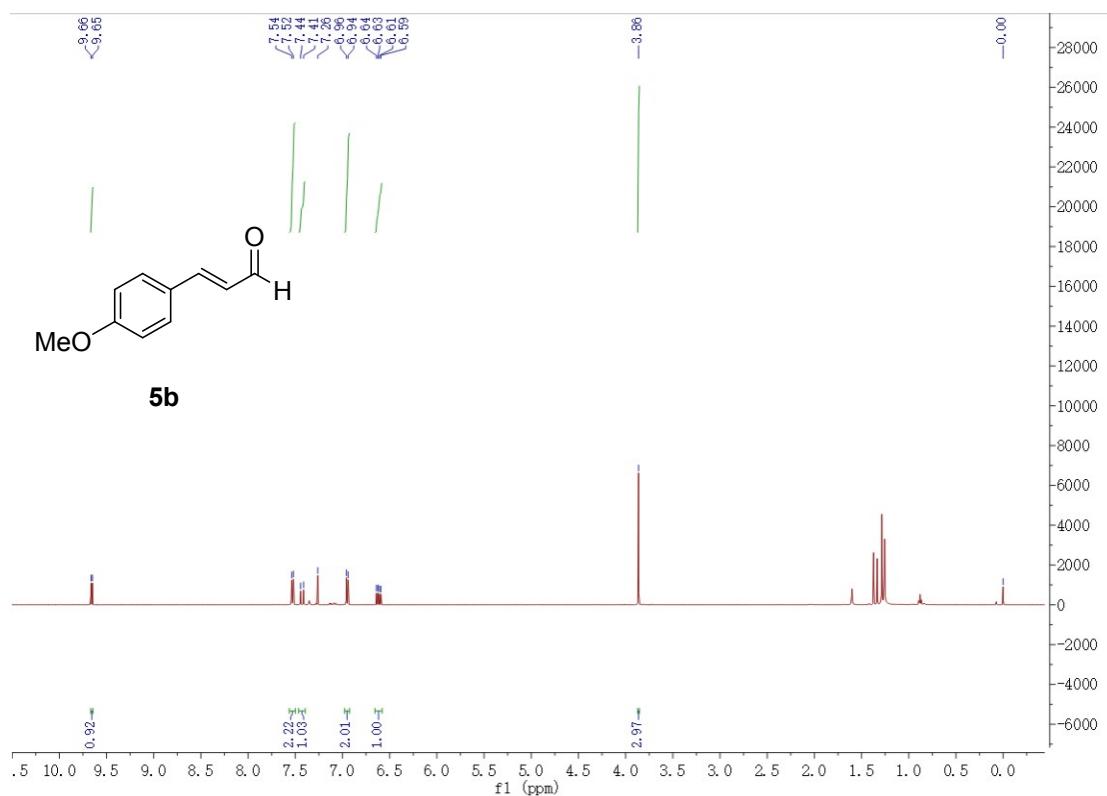
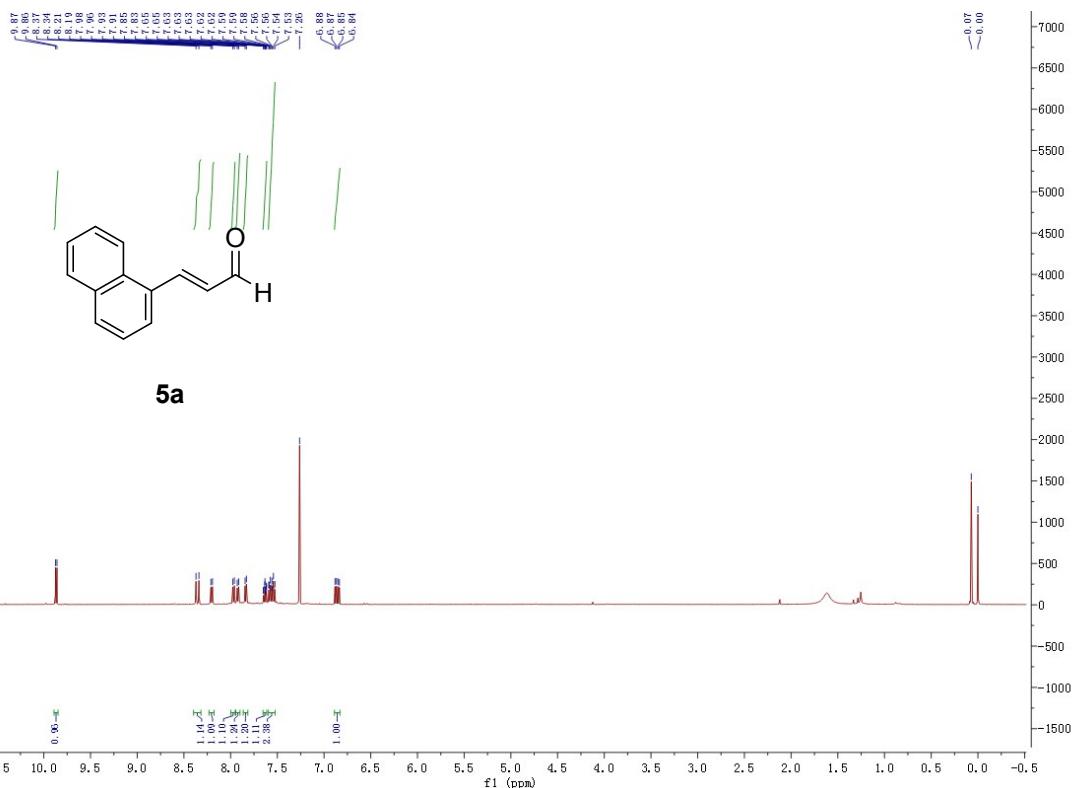


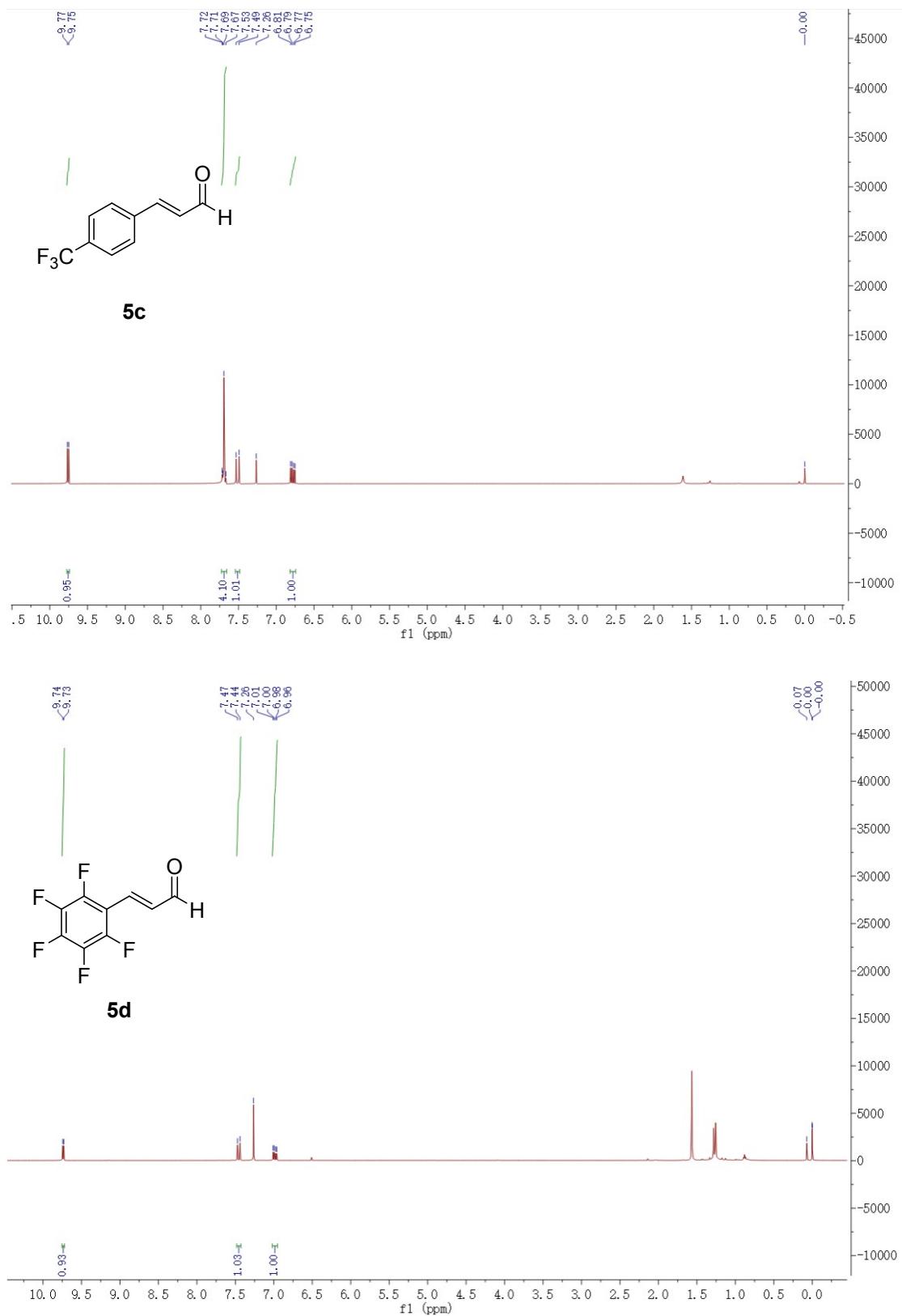
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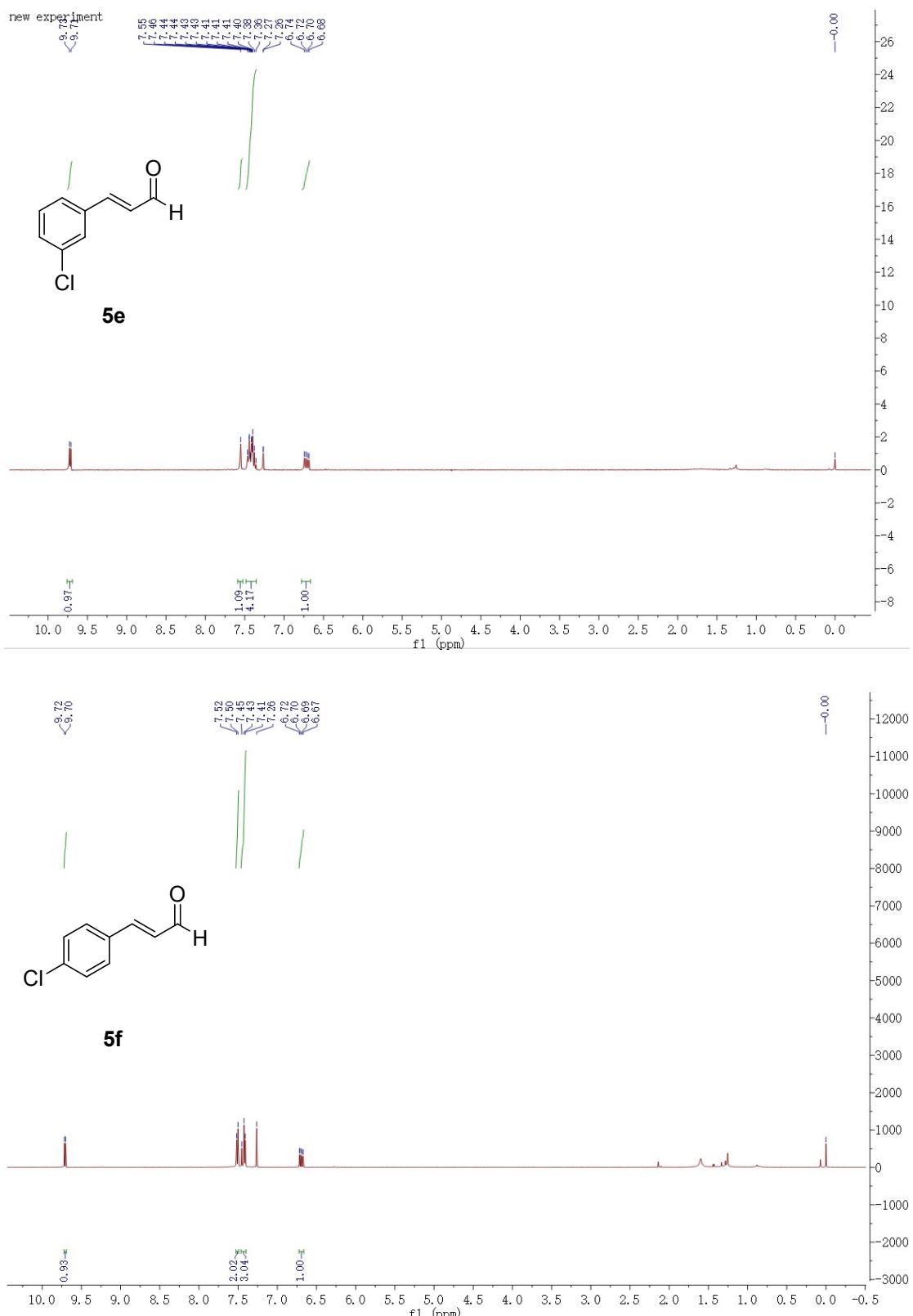


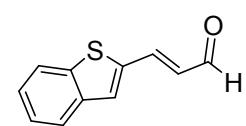
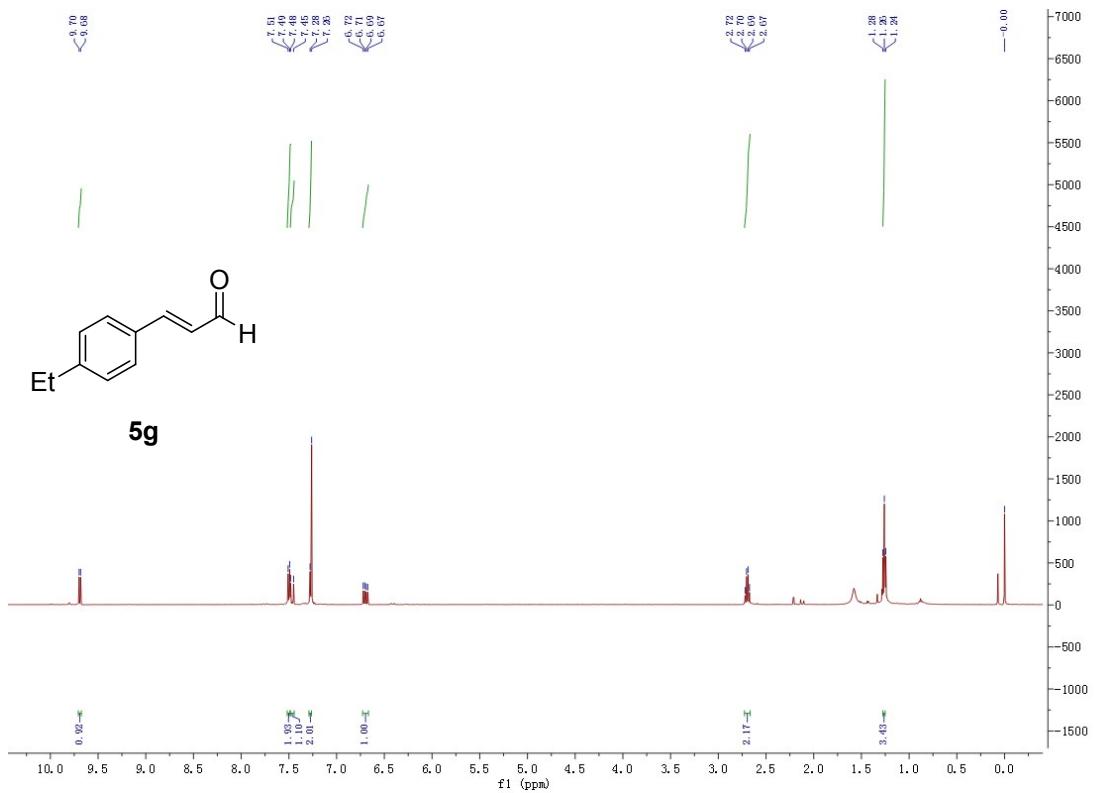




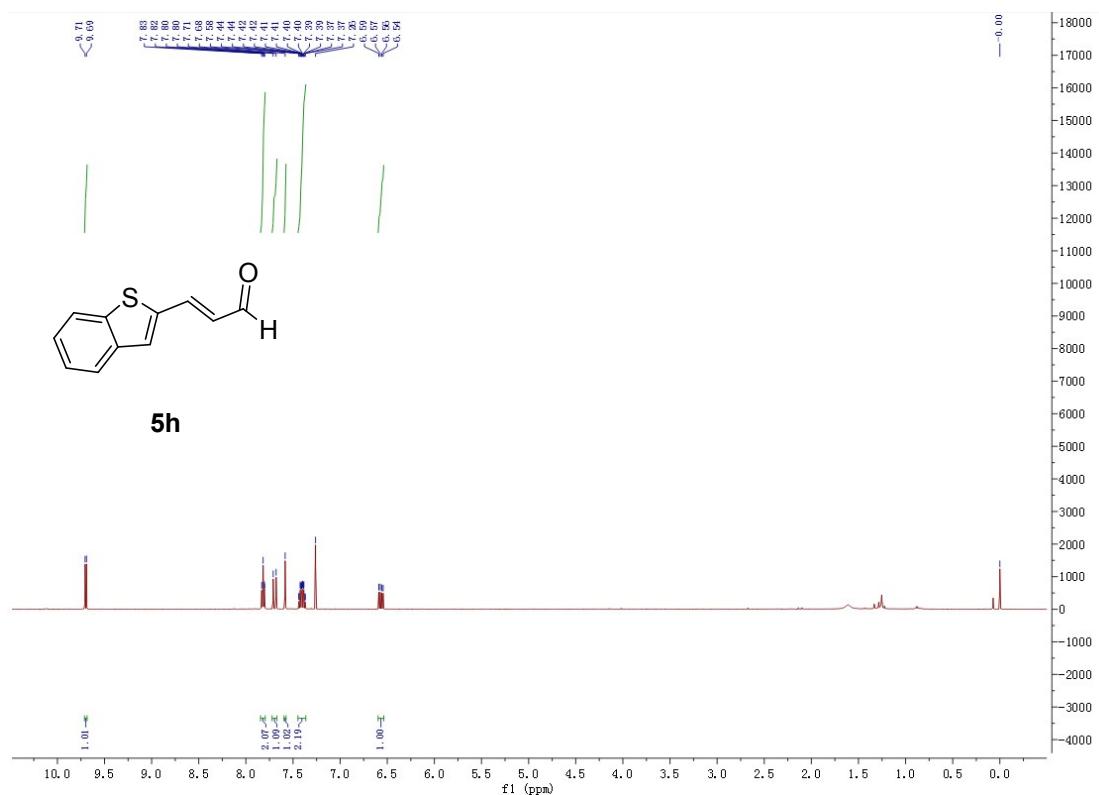


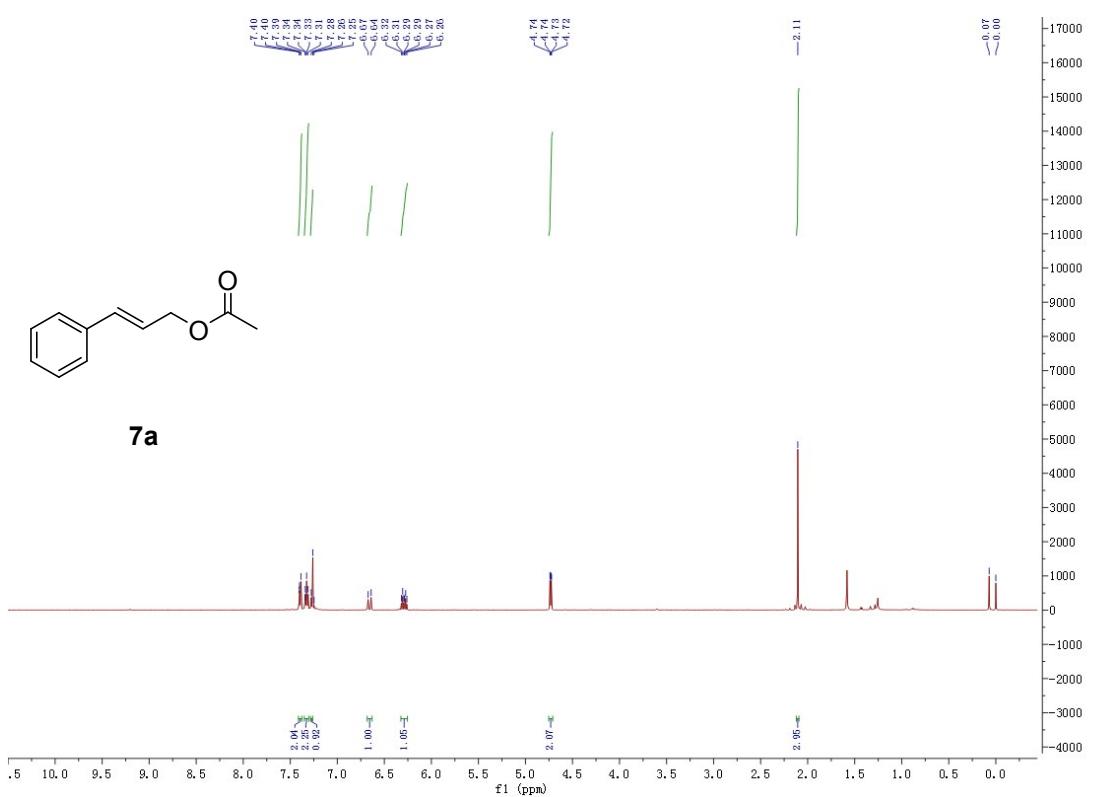
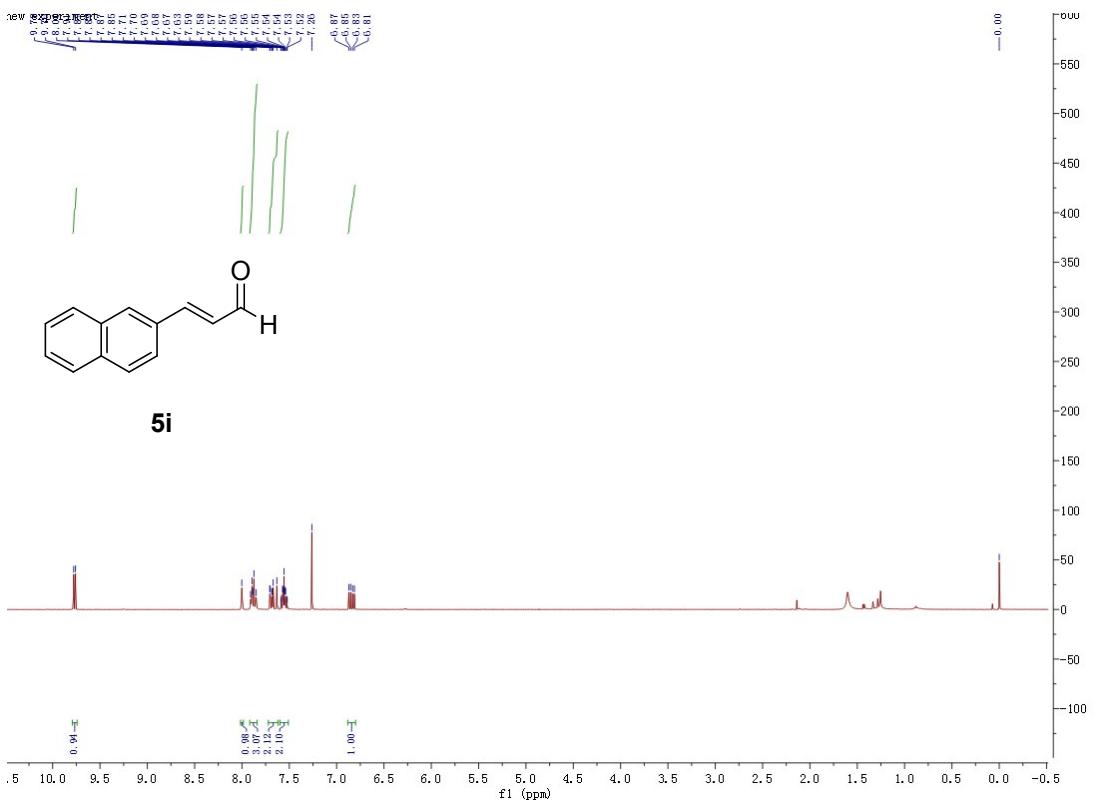


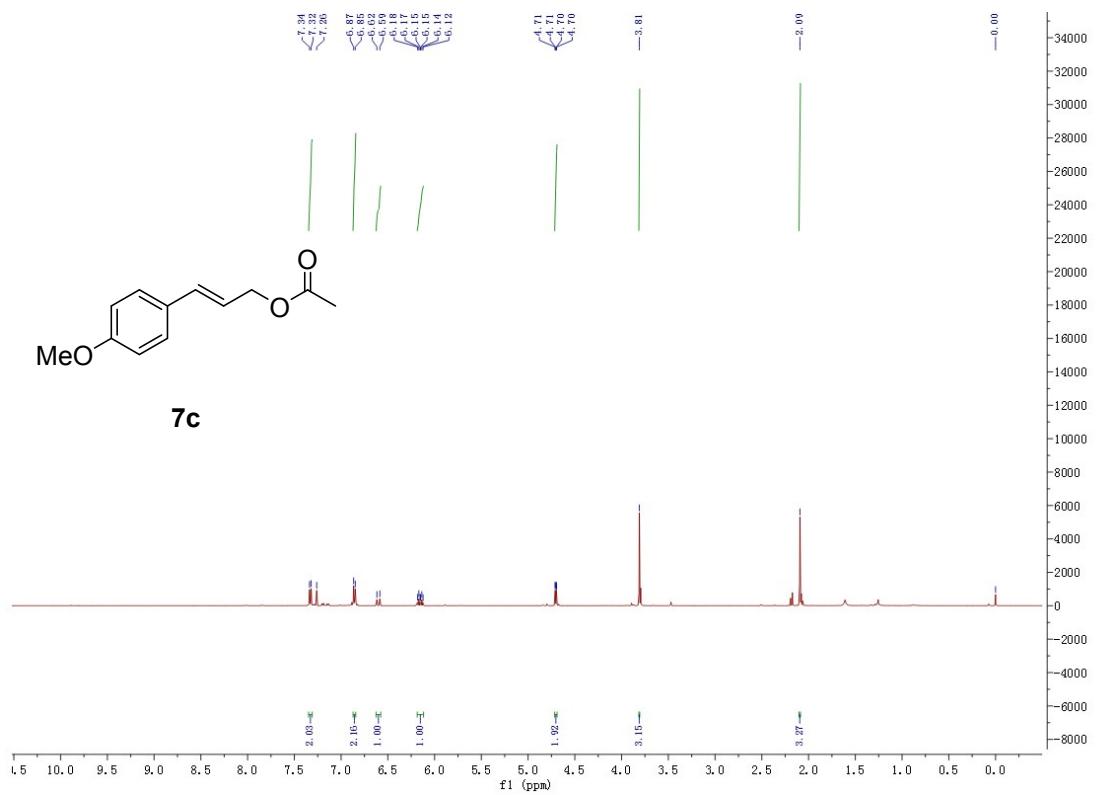
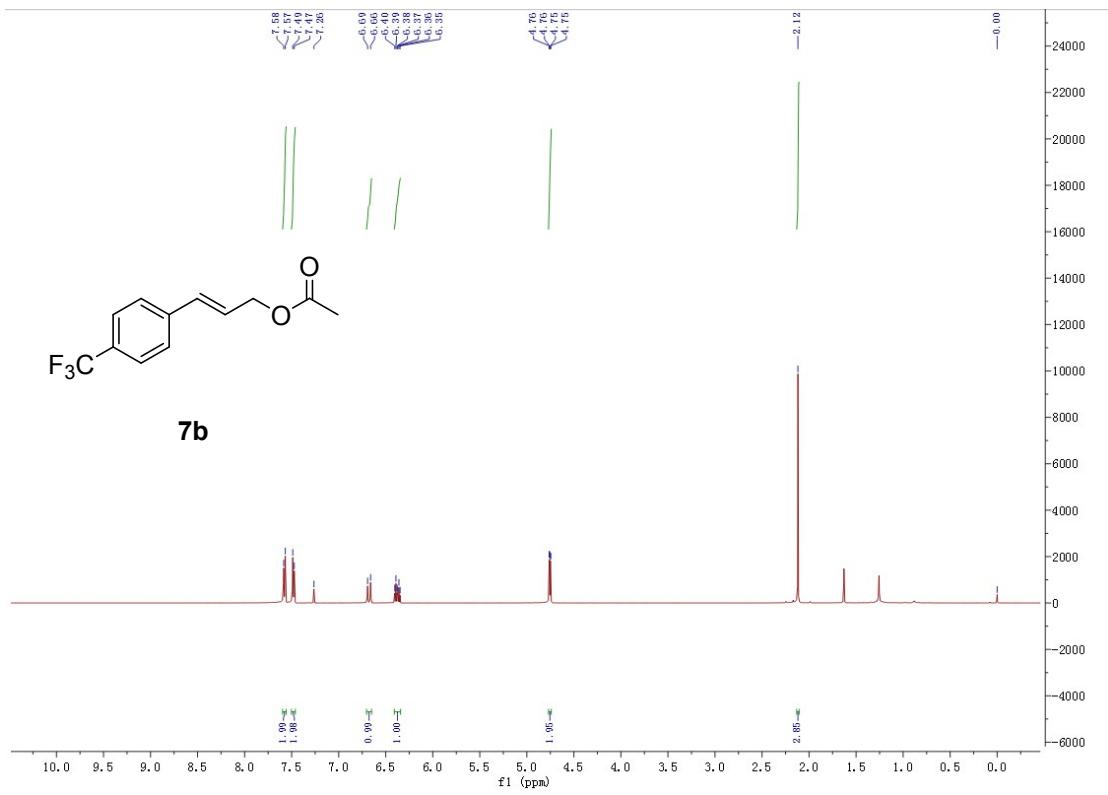


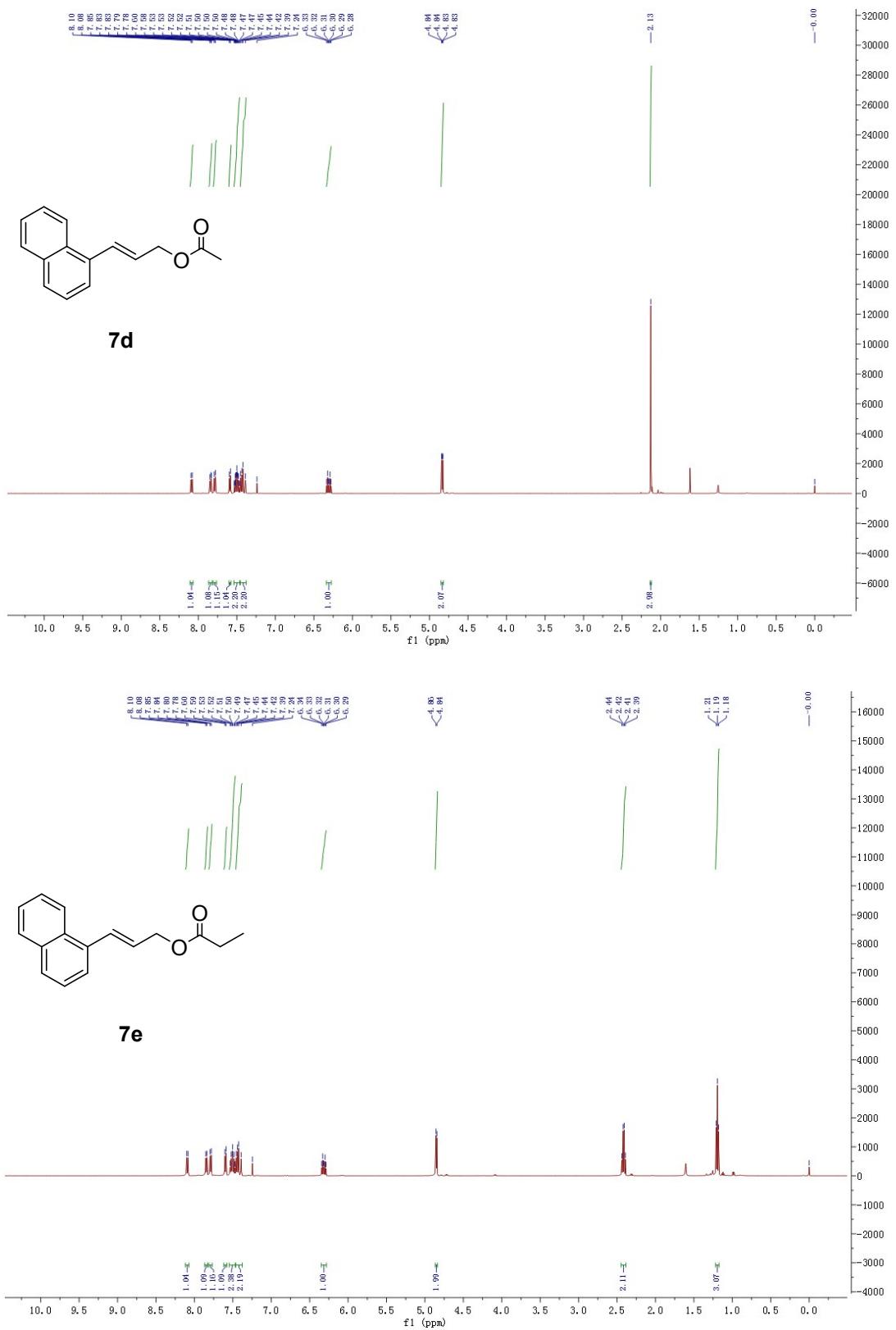


5h









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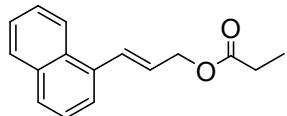
-174.29

134.03
133.60
131.18
131.13
128.59
128.37
126.61
126.19
125.88
124.11
123.68

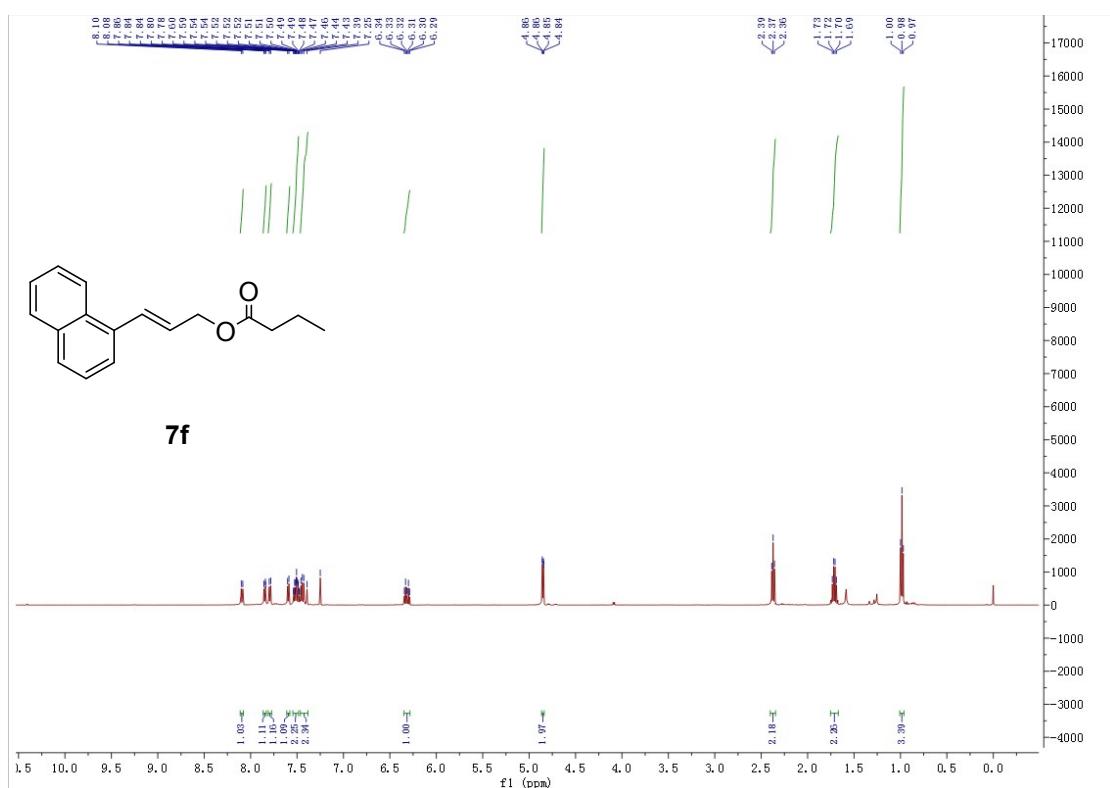
77.30
77.04
76.73

-65.06

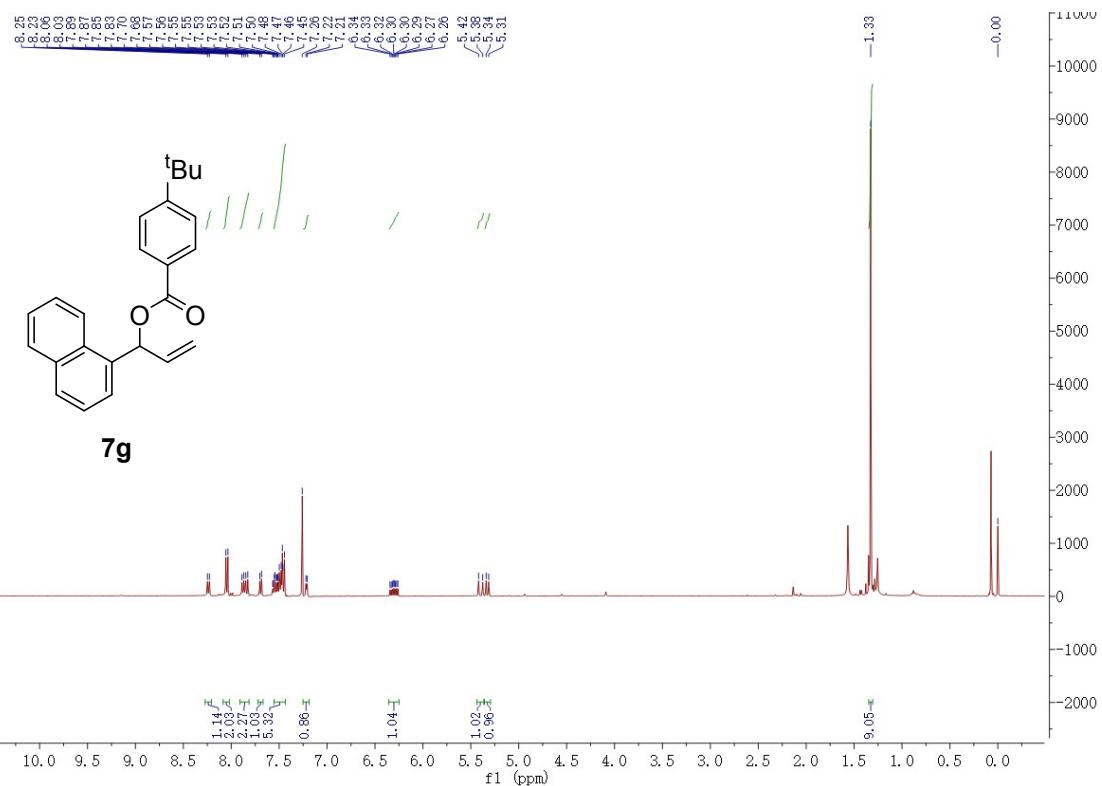
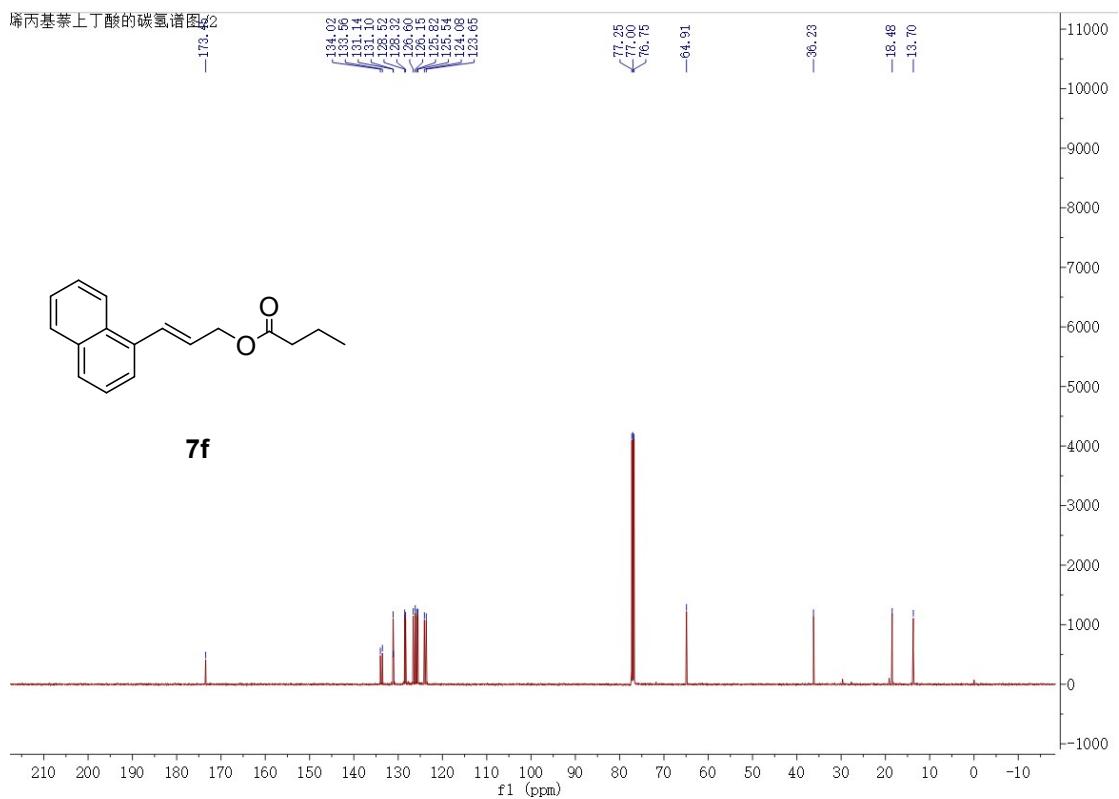
-27.67
-9.19

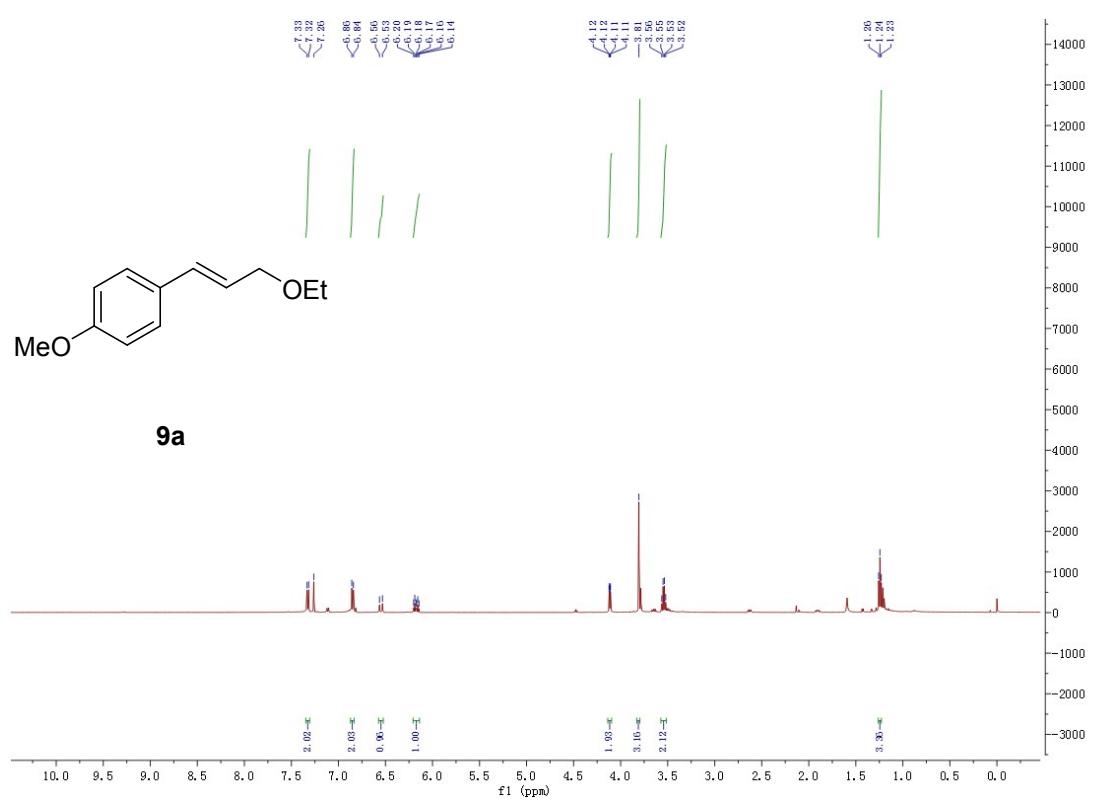
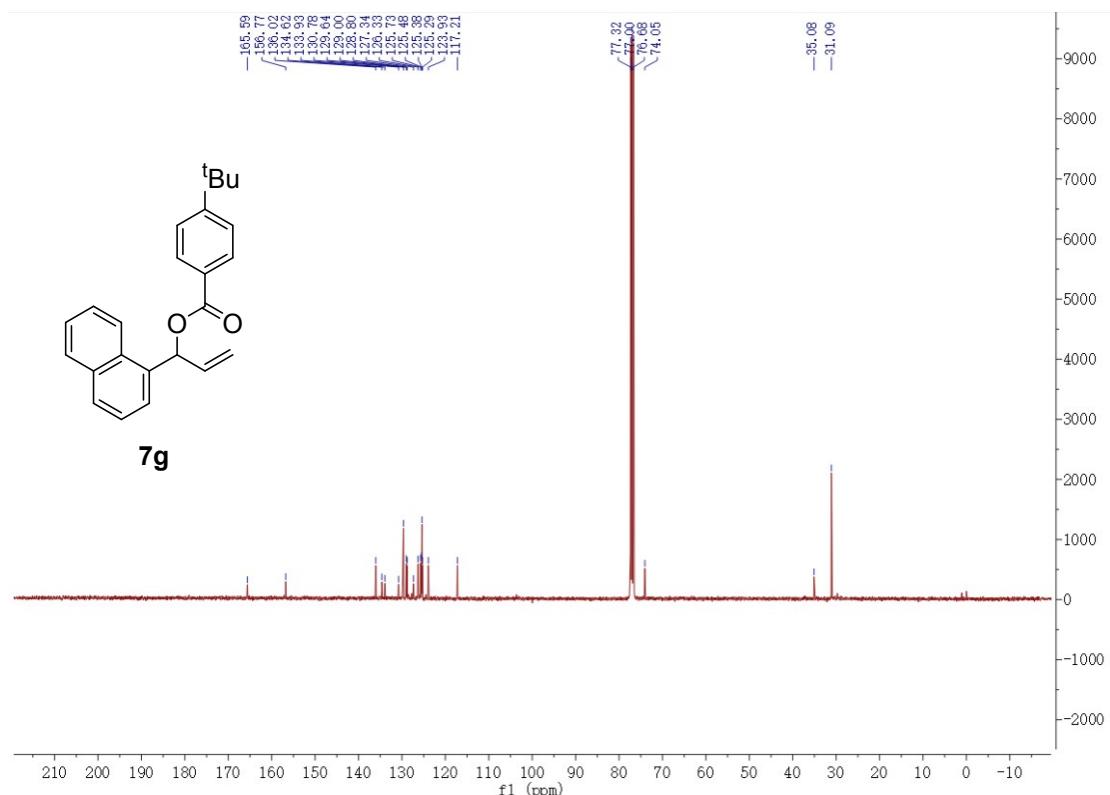


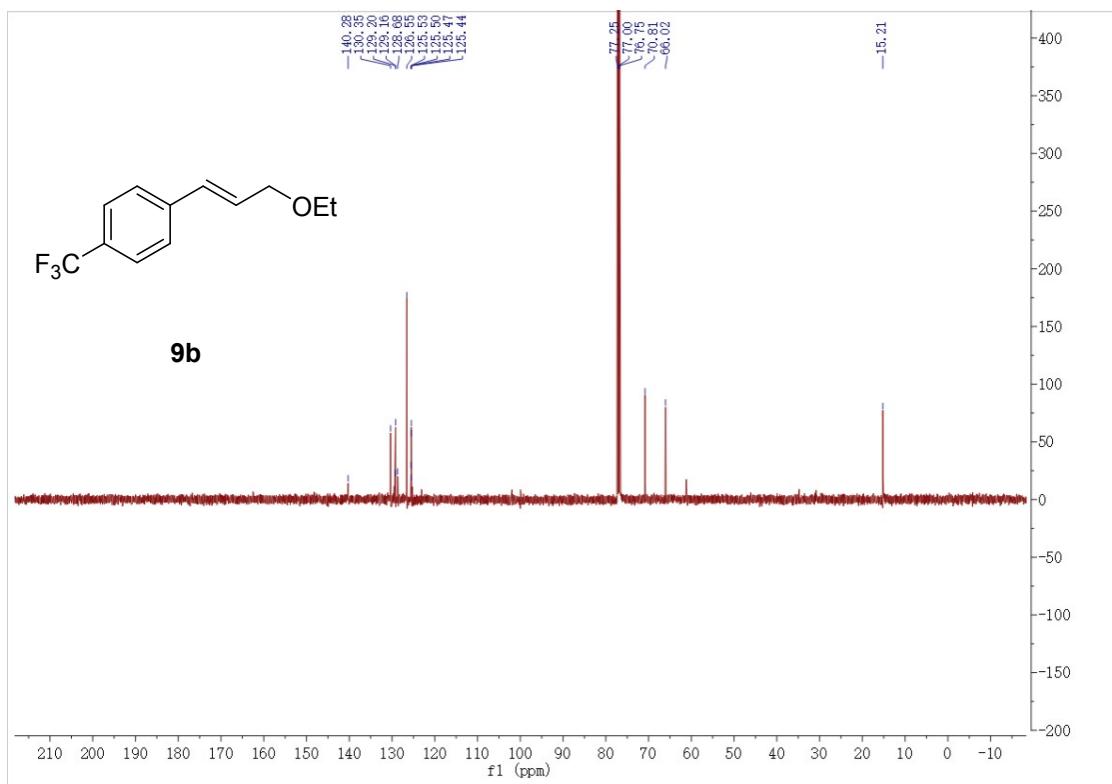
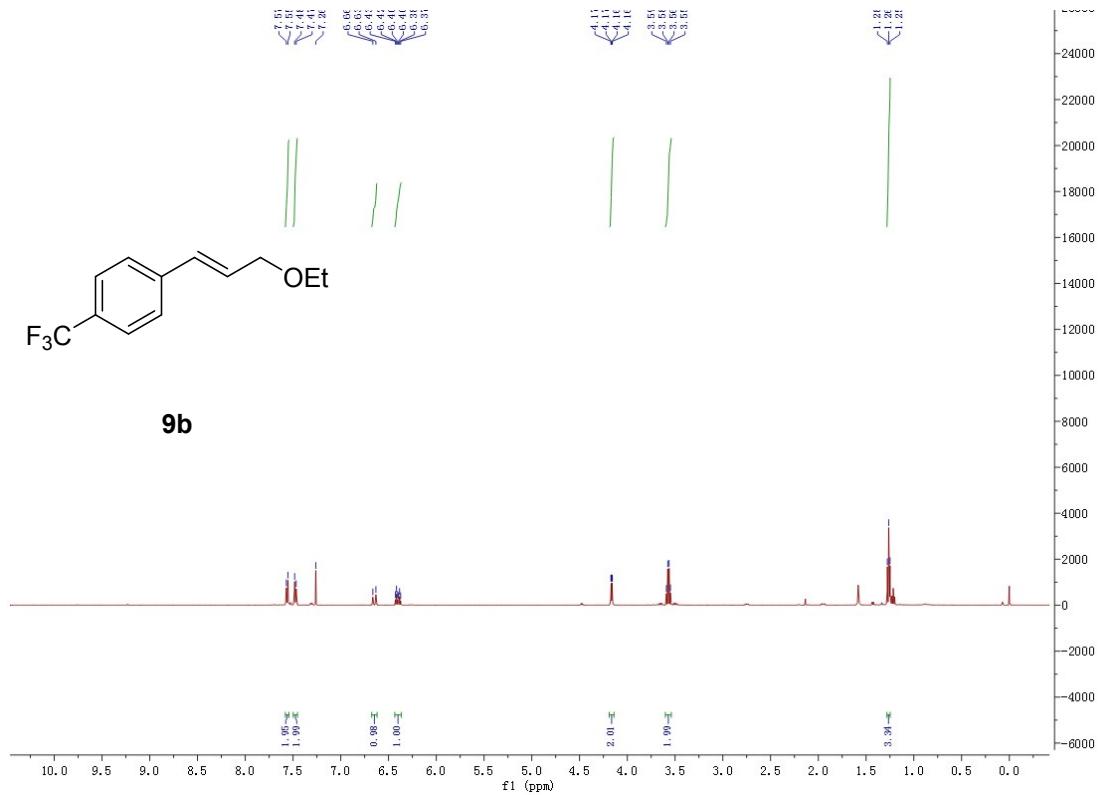
7e



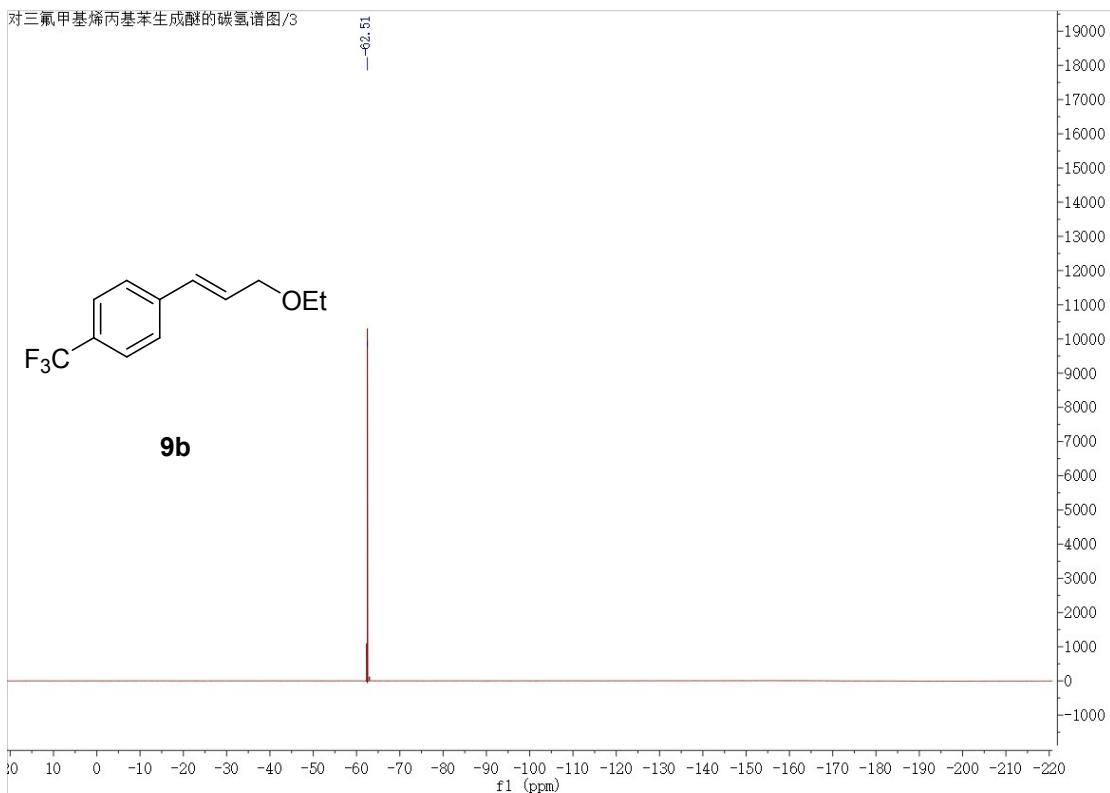
烯丙基苯上丁酸的碳氢谱图¹³C NMR



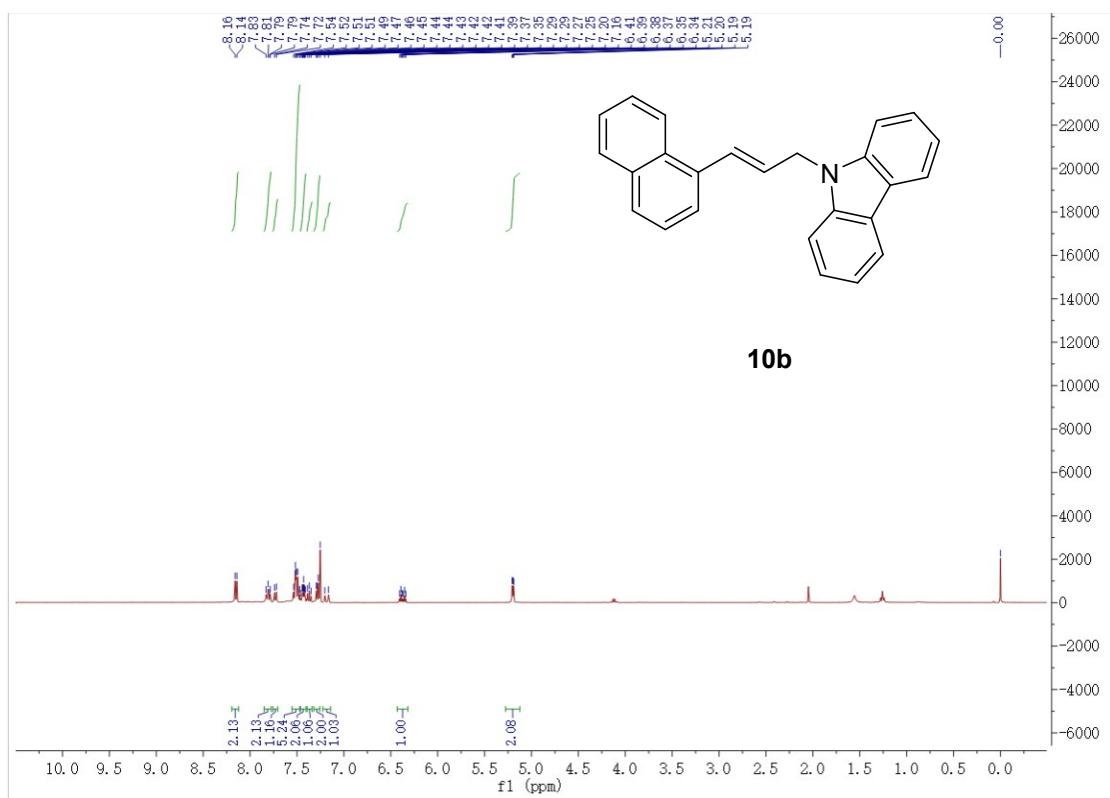




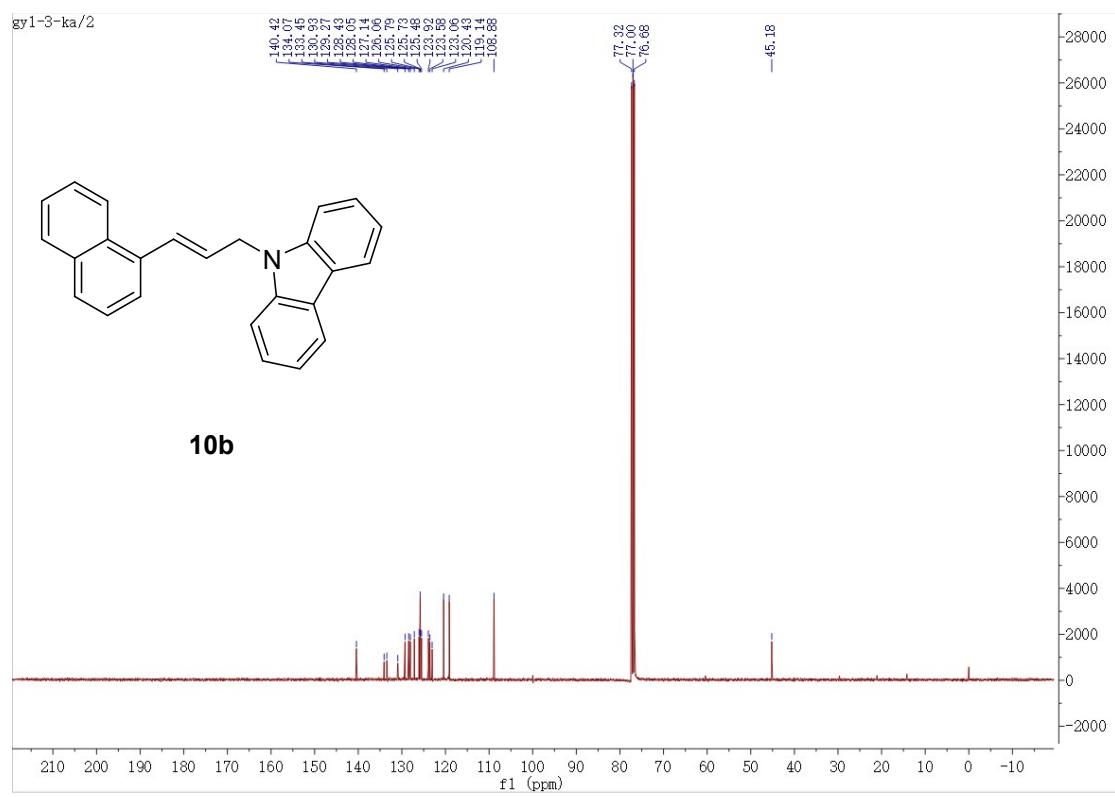
对三氟甲基烯丙基苯生成醚的碳氢谱图/3



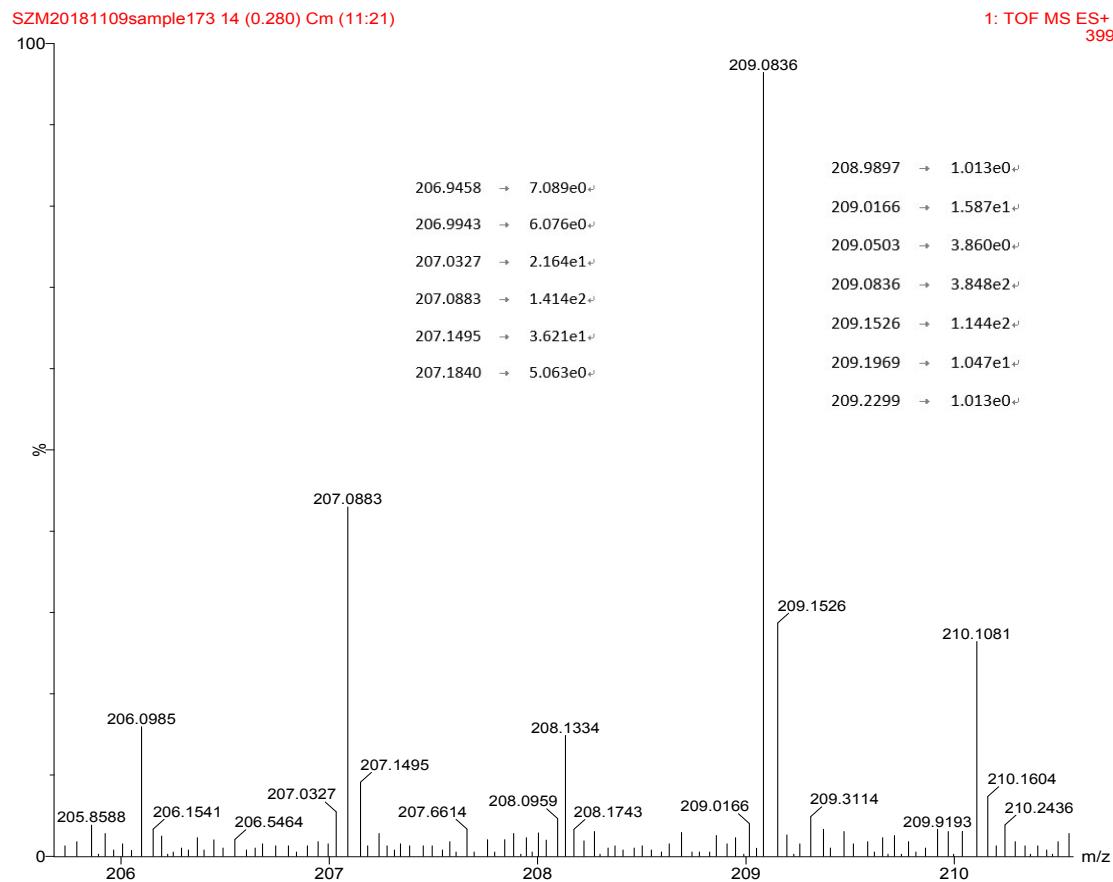
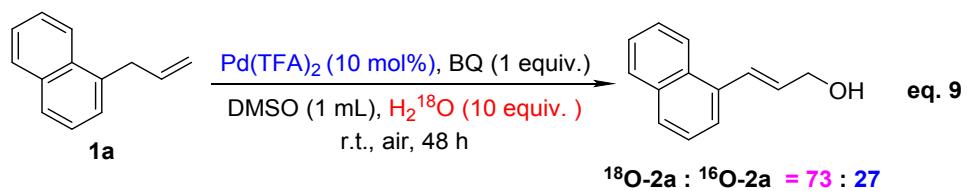
9b



10b



HRMS for eqn (9)



HRMS for eqn (10)

