Supporting Information

Catalytic *Ortho* C-H Methylation and Trideuteromethylation of Arylthianthrenium Salts via the Catellani Strategy

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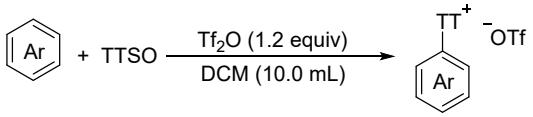
General Information:

The ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR were recorded with Bruker 400 MHz spectrometer instruments in $CDCl_3$. The chemical shifts (δ) of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR were measured in ppm, referenced to residual ^{1}H and ^{13}C signals of nondeuterated $CDCl_3$ (δ = 7.26 and 77.00) as internal standards. All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200~300 mesh). Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV-light (254 nm). Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. HRMS were recorded on Agilent 6520 Q-TOF mass spectrometer with ESI resource.

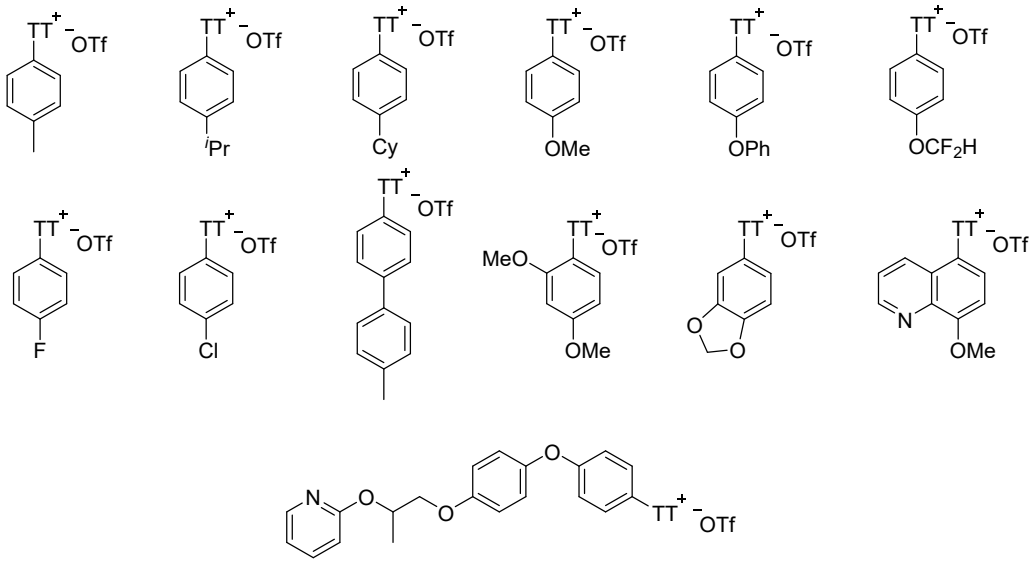
General Procedure for the Synthesis of Substrates:

1. General Procedure for the Synthesis of Aryl Thianthrenes

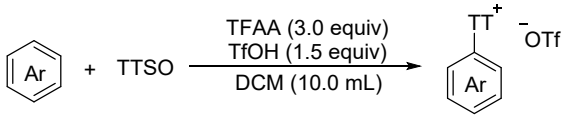
(1)



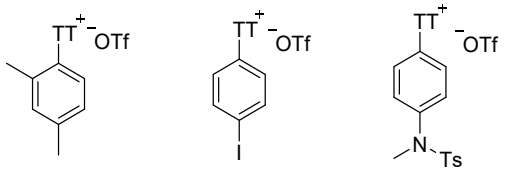
A 50 mL two-necked flask was charged with thianthrene S-oxide (TTSO, 5.0 mmol, 1.0 equiv), DCM (10.0 mL) and arenes (5.0 mmol, 1.0 equiv) under a nitrogen atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature. Tf_2O (6.0 mmol, 1.2 equiv) was added dropwise. The reaction mixture was stirred at -40 °C for 1 h, and then allowed to stir at room temperature for 12 h, neutralized by a saturated $NaHCO_3$ solution, and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM/MTBE system as a white solid.



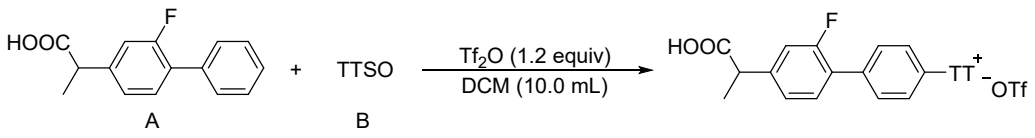
(2)



A 50 mL two-necked flask was charged with thianthrene S-oxide (TTSO, 5.0 mmol, 1.0 equiv), DCM (10.0 mL) and arenes (5.0 mmol, 1.0 equiv) under a nitrogen atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature, trifluoroacetic anhydride (TFAA, 15.0 mmol, 3.0 equiv) and trifluoromethanesulfonic acid (TfOH, 7.5 mmol, 1.5 equiv) were added dropwise. The reaction mixture was stirred at 40 °C for 1 h, and then allowed to stir at room temperature for 12 h, neutralized by a saturated aqueous $NaHCO_3$ solution, and extracted with DCM. Drying of organic phase with anhydrous Na_2SO_4, and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM/MTBE system as a white solid.

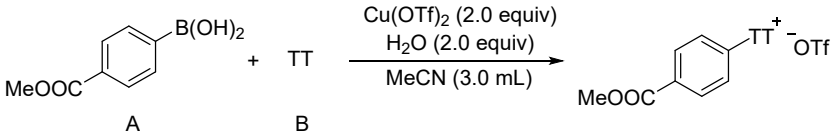


(3)



A 50 mL two-necked flask was charged with thianthrene S-oxide (TTSO, 5.0 mmol, 1.0 equiv), DCM (10.0 mL) and Flurbiprofen (5.0 mmol, 1.0 equiv) under a nitrogen atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature. Tf_2O (6.0 mmol, 1.2 equiv) was added dropwise. The reaction mixture was stirred at -40 °C for 1 h, and then allowed to stir at room temperature for 12 h, extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM/MTBE system as a white solid.

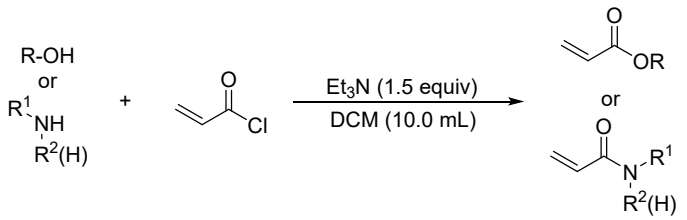
(4)



In a 38 mL sealed tube, the mixture of (4-(methoxycarbonyl)phenyl)boronic acid (3.0 mmol, 1.0 equiv), thianthrene (TT, 4.5 mmol, 1.5 equiv), $Cu(OTf)_2$ (6.0 mmol, 2.0 equiv), H_2O (6.0 mmol, 2.0 equiv) were added in 3.0 mL MeCN. Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was heated to 100 °C for 3 h. After cooling to room temperature, the reaction mixture was added into ammonia solution (50 mL, 25%–28% solution in water), and the water phase was extracted with DCM (3 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from DCM/Et_2O system as a white solid.

2. General Procedure for the Synthesis of Activated Olefins

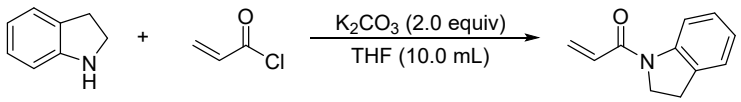
(1)



In a 50 mL round bottom flask, acryloyl chloride (6.0 mmol, 1.2 equiv) was added dropwise to a solution of corresponding alcohols and amines (5.0 mmol, 1.0 equiv) and Et_3N (7.5 mmol, 1.5 equiv) in DCM (10.0 mL) at 0 °C. After the addition was

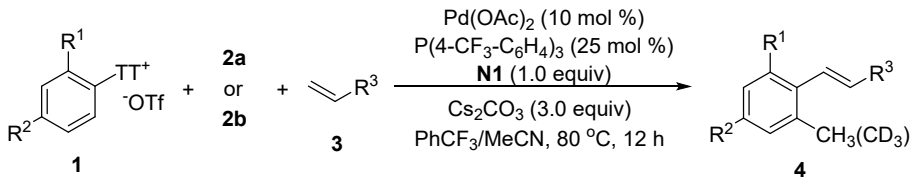
complete, the ice bath was removed, and the reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. Upon completion of the reaction, the reaction mixture was diluted with water and extracted with DCM. The combined organic layer was washed with saturated aqueous $NaHCO_3$. The organic extract was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by silica gel flash column chromatography using EtOAc and PE as the eluent to afford the activated olefins.

(2)



Indoline (5.0 mmol, 1.0 equiv) was dissolved in THF (10.0 mL) in a 50 mL two-necked flask, K_2CO_3 (10.0 mmol, 2.0 equiv) was added and the mixture was cooled to 0 °C under a nitrogen atmosphere. Acryloyl chloride (5.5 mmol, 1.1 equiv) was added dropwise via syringe with rapid stirring. The formation of a white precipitate was immediately observed. After the addition was complete, the mixture was stirred vigorously for 20 min, then poured into a large beaker of water (100.0 mL) cooled in an ice-water bath. The aqueous mixture was stirred slowly for 1 h under an open atmosphere and solid NaCl (approximately 2.0 g) was added to enhance precipitation. When a large amount of white precipitate was visible, the solid was collected by filtration, air dried for 2 h and dried under vacuum overnight to give 1-(indolin-1-yl)prop-2-en-1-one as an off-white solid.

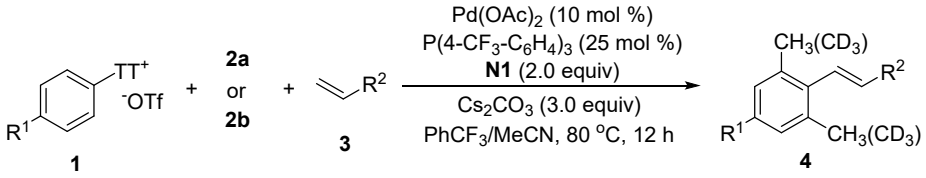
Experimental Procedure:



General procedure A: In a 38 mL sealed tube, the mixture of **1** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2.0 equiv), **3** (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), P(4-CF_3-$C_6H_4)_3$ (25 mol%), **N1** (0.2 mmol, 1.0 equiv), Cs_2CO_3 (0.6 mmol, 3.0 equiv) were added in 2.0 mL $PhCF_3$/MeCN (1:1). Then, the tube was purged with N_2 for

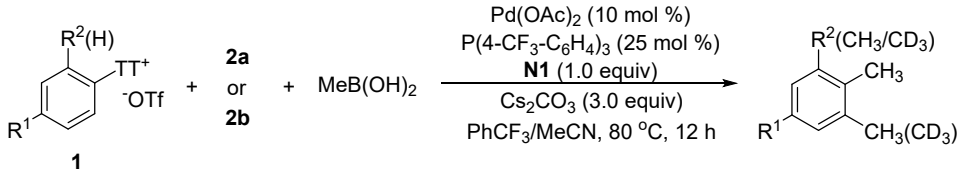
three times and sealed with PTEF cap. The reaction mixture was heated to 80 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the products **4a**-**4e**, **4g**-**4i**, **4o**, **4q**-**4r**, **4a**-d_3-**4c**-d_3.

The same procedure as General procedure A except changing the amount of **3** to 0.2 mmol (1.0 equiv) give the products **4f**, **4j**-**4n**, **4p**, **4s**, **4s**-d_3, **4af**-**4al**, **4an**-d_3, **4am**-d_3.



General procedure B: In a 38 mL sealed tube, the mixture of **1** (0.2 mmol, 1.0 equiv), **2** (0.8 mmol, 4.0 equiv), **3** (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), P(4-CF_3-C_6H_4)$_3$ (25 mol%), **N1** (0.4 mmol, 2.0 equiv), Cs_2CO_3 (0.6 mmol, 3.0 equiv) were added in 2.0 mL $PhCF_3$/MeCN (1:1). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was heated to 80 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the products **4a**, **4t**-**4z**, **4aa**-**4ae**, **4m**, **4n**, **4a**-d_6, **4t**-d_6, **4ac**-d_6, **4u**-d_6, **4w**-d_6, **4aa**-d_6, **4ad**-d_6, **4ae**-d_6, **4al**, **4ao**, **4ap**, **4as**.

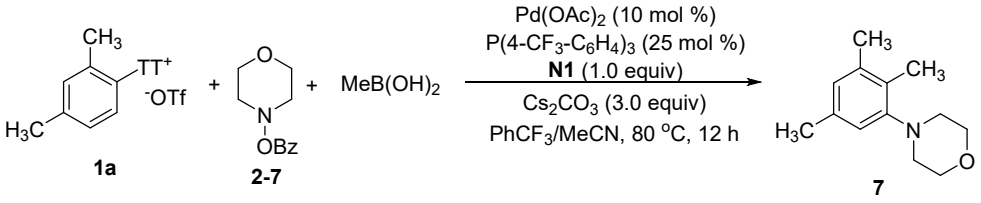
The same procedure as General procedure B except changing the amount of **3** to 0.2 mmol (1.0 equiv) give the products **4m**, **4n**, **4ag**-d_6, **4aq**, **4ar**-d_6.



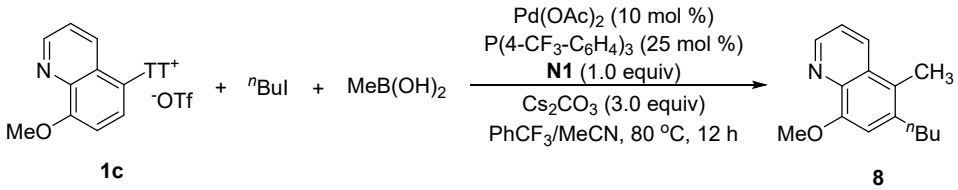
General procedure C: In a 38 mL sealed tube, the mixture of **1** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2.0 equiv), $MeB(OH)_2$ (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), P(4-CF_3-C_6H_4)$_3$ (25 mol%), **N1** (0.2 mmol, 1.0 equiv), Cs_2CO_3 (0.6 mmol, 3.0 equiv) were added in 2.0 mL $PhCF_3$/MeCN (1:1). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was heated to 80 °C

for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the product **5**.

The same procedure as General procedure C except changing the amount of **2** to 0.8 mmol (4.0 equiv) and **N1** to 0.4 equiv (2.0 equiv) give the products **6**, **4at**, **4at-*d*$_9$**.



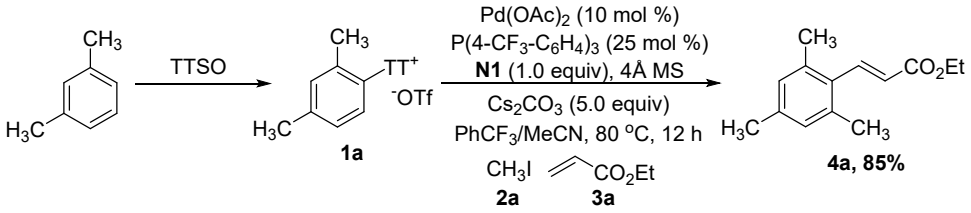
General procedure D: In a 38 mL sealed tube, the mixture of **1a** (0.2 mmol, 1.0 equiv), **2-7** (0.3 mmol, 1.5 equiv), $MeB(OH)_2$ (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (25 mol%), **N1** (0.2 mmol, 1.0 equiv), Cs_2CO_3 (0.6 mmol, 3.0 equiv) were added in 2.0 mL $PhCF_3$/MeCN (1:1). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was heated to 80 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the product **7**.



General procedure E: In a 38 mL sealed tube, the mixture of **1a** (0.2 mmol, 1.0 equiv), ^{n}BuI (0.4 mmol, 2.0 equiv), $MeB(OH)_2$ (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (25 mol%), **N1** (0.2 mmol, 1.0 equiv), Cs_2CO_3 (0.6 mmol, 3.0 equiv) were added in 2.0 mL $PhCF_3$/MeCN (1:1). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was heated to 80 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give the product **8**.

Control Experiments:

1. One-pot C-H methylation:

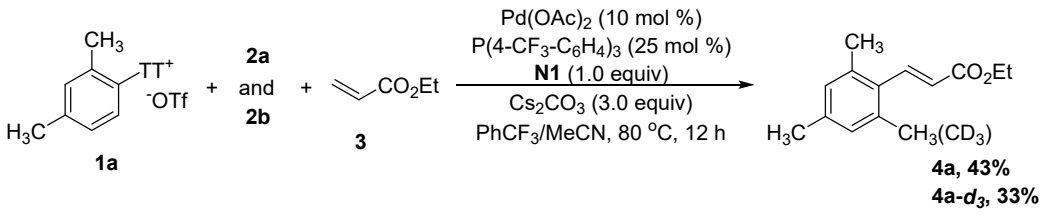


A 25 mL two-necked flask was charged with thianthrene S-oxide (TTSO, 0.2 mmol, 1.0 equiv), DCM (1.0 mL) and 1,3-dimethylbenzene (0.2 mmol, 1.0 equiv) under a nitrogen atmosphere. The reaction mixture was then cooled to -40 °C and stirred at this temperature, trifluoroacetic anhydride (TFAA, 0.6 mmol, 3.0 equiv) and trifluoromethanesulfonic acid (TfOH, 0.3 mmol, 1.5 equiv) were added dropwise. The reaction mixture was stirred at 40 °C for 0.5 h, and then allowed to stir at room temperature for 12 h. The mixture was concentrated to dryness under reduced pressure to give the crude product of **1a**.

In a 38 mL sealed tube, the mixture of the crude product of **1a**, **2a** (0.4 mmol, 2.0 equiv), **3a** (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol%), $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (25 mol%), **N1** (0.2 mmol, 1.0 equiv), Cs_2CO_3 (1.0 mmol, 5.0 equiv) were added in 2.0 mL $PhCF_3$/MeCN (1:1). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was heated to 80 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give product **4a** in 85% yield.

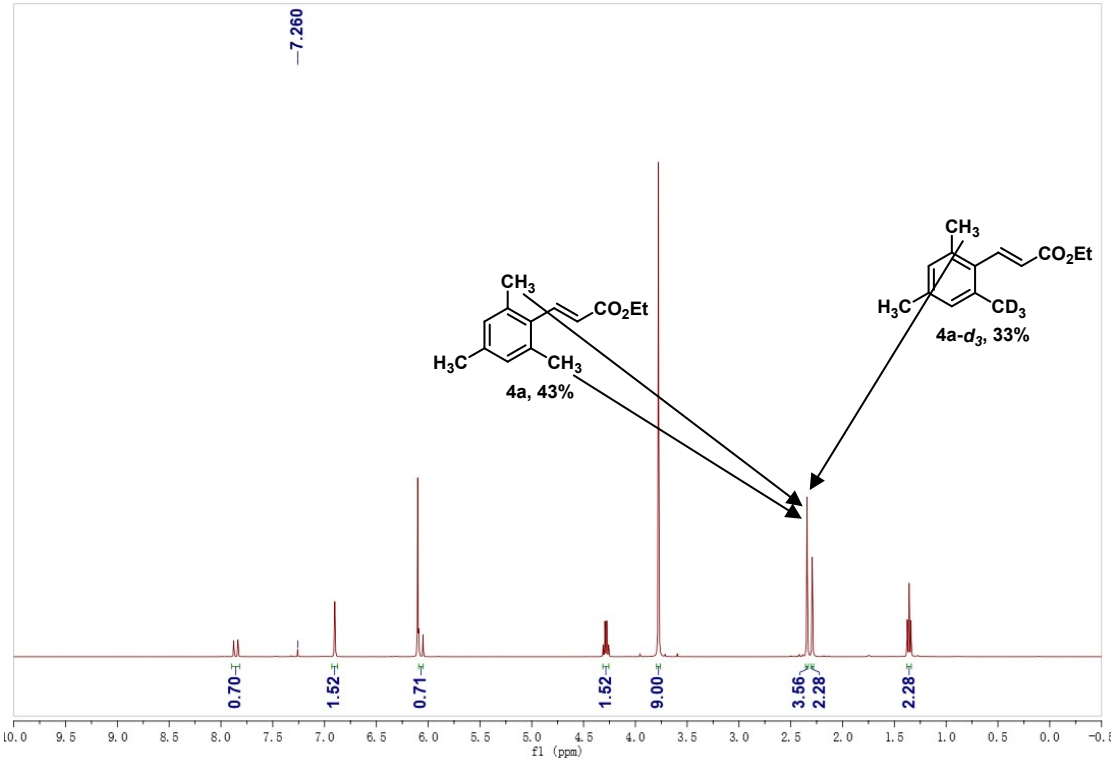
2. Competition experiments:

(1)

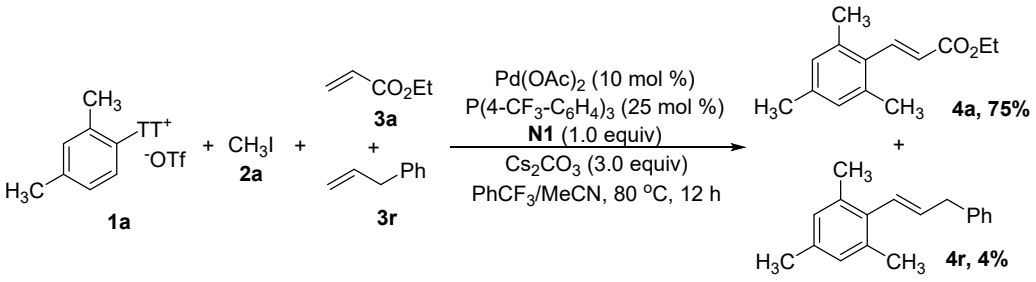


In a 38 mL sealed tube, the mixture of **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), **2b** (0.4 mmol, 2.0 equiv), ethyl acrylate (0.4 mmol, 0.2 equiv), $Pd(OAc)_2$

(10 mol%), P(4-CF_3-C_6H_4)$_3$ (25 mol%), **N1** (0.2 mmol, 1.0 equiv), Cs_2CO_3 (0.6 mmol, 3.0 equiv) were added in 2.0 mL $PhCF_3$/MeCN (1:1). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was heated to 80 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give a mixture of **4a** and **4a-*d*$_3$**. ^{1}H NMR was carried out by adding 1,3,5-trimethoxybenzene (0.2 mmol, 1.0 equiv) as an internal standard in a mixture of **4a** and **4a-*d*$_3$**. (the ^{1}H NMR spectrum of the crude product is shown below).

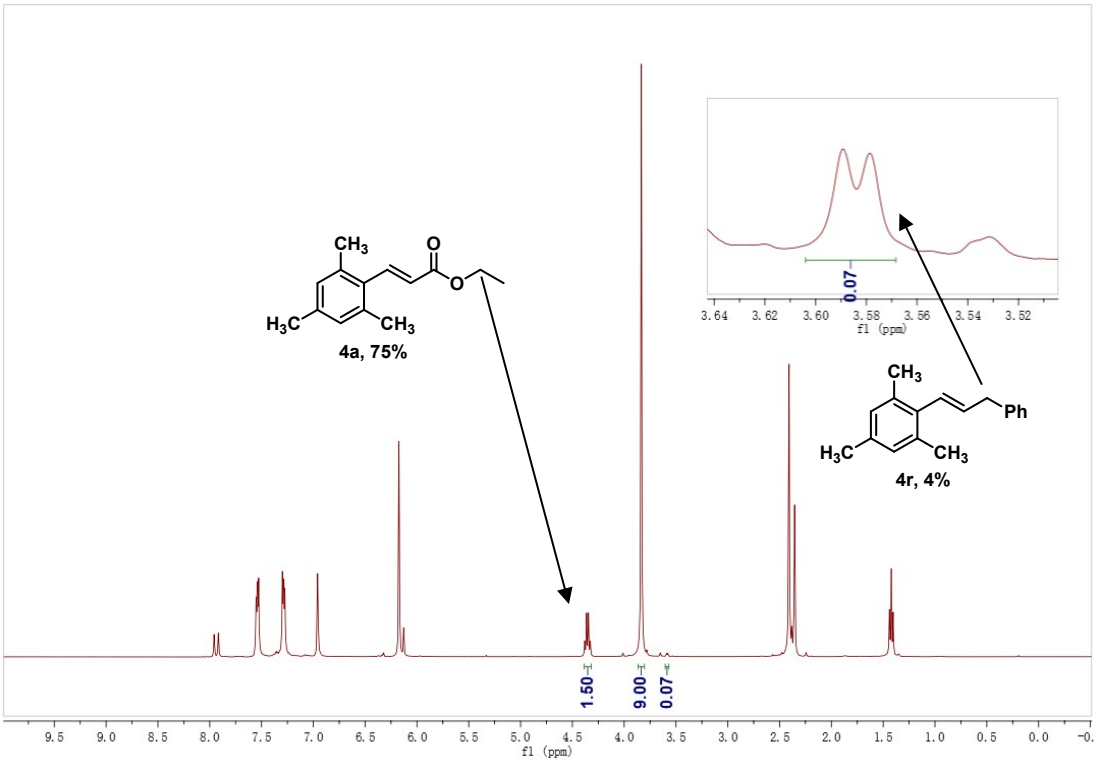


(2)



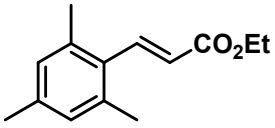
In a 38 mL sealed tube, the mixture of **1a** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), **3a** (0.4 mmol, 0.2 equiv), **3r** (0.4 mmol, 0.2 equiv), $Pd(OAc)_2$ (10 mol%),

P(4-CF_3-C_6H_4)$_3$ (25 mol%), **N1** (1.0 equiv), Cs_2CO_3 (0.6 mmol, 3.0 equiv) were added in 2.0 mL $PhCF_3$/MeCN (1:1). Then, the tube was purged with N_2 for three times and sealed with PTEF cap. The reaction mixture was heated to 80 °C for 12 h. When the reaction was finished, the mixture was cooled to room temperature and the solvents were removed under reduced pressure. The residue was purified by silica gel column chromatography to give a mixture of **4a** and **4r**. ^{1}H NMR was carried out by adding 1,3,5-trimethoxybenzene (0.2 mmol, 1.0 equiv) as an internal standard in a mixture of **4a** and **4r**. (the ^{1}H NMR spectrum of the crude product is shown below).



Characterization of Products:

(*E*)-3-(2,4,6-trimethylphenyl) ethyl acrylate(4a)[1]



4a

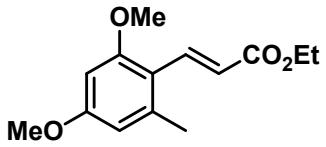
Yield: 96%, 41.9 mg; appearance: white solid, M.P.: 35-36 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 16.4 Hz, 1H), 6.90 (s, 2H), 6.06 (d, *J* = 16.4 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 6H), 2.29 (s, 3H), 1.35 (t, *J* = 6.8

Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.91, 143.07, 138.15, 136.71, 130.85, 129.05, 123.08, 60.35, 20.99, 20.93, 14.24.

(*E*)-3-(2,4-dimethoxy-6-methylphenyl) ethyl acrylate(4b)[2]



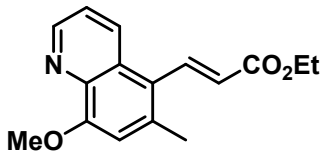
4b

Yield: 71%, 35.5 mg; appearance: white solid, M.P.: 68-70 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 16.0 Hz, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.36 – 6.32 (m, 2H), 4.24 (q, *J* = 6.8 Hz, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 2.43 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.51, 161.09, 160.93, 141.42, 138.25, 119.06, 115.18, 107.50, 96.17, 60.01, 55.29, 55.16, 21.45, 14.31.

(*E*)-3-(8-methoxy-6-methylquinolin-5-yl) ethyl acrylate(4c)



4c

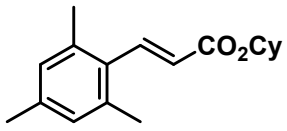
Yield: 75%, 40.7 mg; appearance: yellow solid, M.P.: 108-109 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 – 8.82 (m, 1H), 8.36 – 8.33 (m, 1H), 8.03 (d, *J* = 16.0 Hz, 1H), 7.40 – 7.36 (m, 1H), 6.85 (s, 1H), 6.11 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.04 (s, 3H), 2.49 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.54, 155.10, 148.28, 140.78, 138.94, 136.15, 132.82, 127.55, 124.67, 122.48, 121.90, 110.60, 60.58, 55.93, 21.46, 14.24.

ESI-MS: Calcd for $C_{16}H_{17}NO_3$: [M+H$^+$] 272.1281, found 272.1284.

(*E*)-3-(2,4,6-trimethylphenyl) cyclohexyl acrylate(4d)



4d

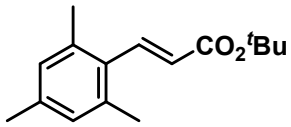
Yield: 83%, 45.2 mg; appearance: white solid, M.P.: 72-73 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 16.4 Hz, 1H), 6.89 (s, 2H), 6.05 (d, *J* = 16.4 Hz, 1H), 4.94 – 4.87 (m, 1H), 2.34 (s, 6H), 2.29 (s, 3H), 1.97 – 1.92 (m, 2H), 1.81 – 1.75 (m, 2H), 1.64 – 1.36 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.45, 142.79, 138.13, 136.78, 130.99, 129.09, 123.67, 72.68, 31.73, 25.43, 23.80, 21.07, 20.99.

ESI-MS: Calcd for $C_{18}H_{24}O_2$: [M+H$^+$] 273.1849, found 273.1848.

(*E*)-3-(2,4,6-trimethylphenyl) *tert* butyl acrylate(4e)[3]



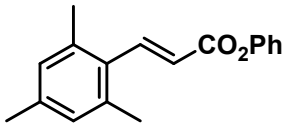
4e

Yield: 85%, 41.9 mg; appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 16.4 Hz, 1H), 6.89 (s, 2H), 5.98 (d, *J* = 16.0 Hz, 1H), 2.33 (s, 6H), 2.28 (s, 3H), 1.55 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.40, 142.00, 138.01, 136.79, 131.04, 129.05, 124.82, 80.41, 28.21, 21.13, 21.01.

(*E*)-3-(2,4,6-trimethylphenyl) phenyl acrylate(4f)[4]



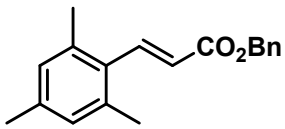
4f

Yield: 94%, 50.1 mg; appearance: white solid, M.P.: 60-62 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 16.4 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.18 – 7.08 (m, 3H), 6.83 (s, 2H), 6.19 (d, *J* = 16.4 Hz, 1H), 2.30 (s, 6H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.34, 150.83, 145.11, 138.73, 137.06, 130.53, 129.35, 129.29, 125.68, 122.02, 121.61, 21.16, 21.03.

(*E*)-3-(2,4,6-trimethylphenyl) Benzyl acrylate(4g)



4g

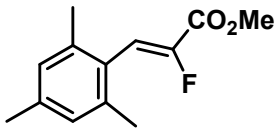
Yield: 66%, 37.0 mg; appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 16.4 Hz, 1H), 7.35 – 7.22 (m, 5H), 6.79 (s, 2H), 6.02 (d, *J* = 16.4 Hz, 1H), 5.17 (s, 2H), 2.24 (s, 6H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.18, 143.75, 138.38, 136.87, 136.05, 130.75, 129.16, 128.55, 128.26, 128.20, 122.64, 66.29, 21.10, 21.01.

ESI-MS: Calcd for $C_{19}H_{20}O_2$: [M+H$^+$] 281.1536, found 281.1537.

(*Z*)-2-fluoro-3-(2,4,6-trimethylphenyl) methyl acrylate(4h)



4h

Yield: 60%, 26.7 mg; appearance: yellow oil.

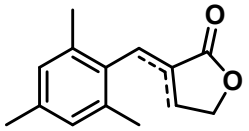
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 35.6 Hz, 1H), 6.91 (s, 2H), 3.91 (s, 3H), 2.29 (s, 3H), 2.24 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.46 (d, *J* = 35.0 Hz), 146.38 (d, *J* = 262.0 Hz), 138.33, 136.59, 128.35, 126.30, 116.98 (d, *J* = 11.0 Hz), 52.64, 21.02, 20.33 (d, *J* = 3.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -121.82 (s).

ESI-MS: Calcd for $C_{13}H_{15}FO_2$: [M+H$^+$] 223.1129, found 223.1128.

(*E*)-3-(2,4,6-trimethylbenzylidene)dihydrofuran-2(3H)-one/3-(2,4,6-trimethylbenzyl)furan-2(5H)-one(4i)



4i (1:0.8)

Yield: 53%, 22.9 mg; appearance: white solid, M.P.: 98-99 ºC.

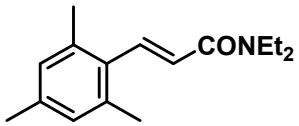
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 6.90 (s, 2H), 6.88 (s, 1.6H), 6.61 (s,

0.8H), 4.73 (s, 1.6H), 4.38 (t, *J* = 7.2 Hz, 2H), 3.55 (s, 1.6H), 2.68 (td, *J* = 7.2, 2.4 Hz, 2H), 2.29 (s, 3H), 2.28 (s, 2.4H), 2.20 (s, 4.8H), 2.18 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.07, 171.21, 144.73, 137.86, 137.19, 136.32, 136.19, 135.29, 133.04, 131.15, 131.04, 128.98, 128.36, 127.80, 70.33, 65.52, 26.52, 25.56, 20.96, 20.81, 20.00, 19.75.

ESI-MS: Calcd for $C_{14}H_{16}O_2$: [M+H$^+$] 217.1223, found 217.1224.

(*E*)-*N*,*N*-diethyl-3-(2,4,6-trimethylphenyl) acrylamide(4j)



4j

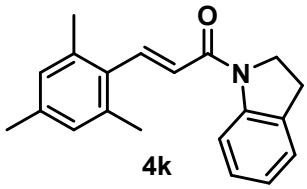
Yield: 92%, 45.1 mg; appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 16.0 Hz, 1H), 6.90 (s, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 3.49 – 3.42 (m, 4H), 2.33 (s, 6H), 2.28 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.61, 140.71, 137.53, 136.41, 132.41, 128.88, 123.13, 42.18, 41.09, 21.04, 20.97, 15.06, 13.28.

ESI-MS: Calcd for $C_{16}H_{23}NO$: [M+H$^+$] 246.1852, found 246.1852.

(*E*)-1-(indolin-1-yl)-3-mesitylprop-2-en-1-one(4k)



4k

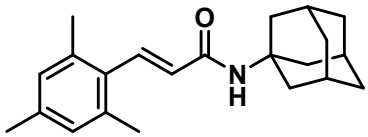
Yield: 84%, 49.0 mg; appearance: yellow solid, M.P.: 152-154 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 6.4 Hz, 1H), 8.02 (d, *J* = 16.0 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.98 (s, 2H), 6.53 (d, *J* = 15.6 Hz, 1H), 4.22 (t, *J* = 8.0 Hz, 2H), 3.25 (s, 2H), 2.44 (s, 6H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.16, 142.94, 141.51, 137.85, 136.52, 131.68, 129.00, 127.40, 124.39, 124.07, 123.69, 117.31, 47.88, 27.82, 21.04, 20.90.

ESI-MS: Calcd for $C_{20}H_{21}NO$: [M+H$^+$] 292.1696, found 292.1695.

(*E*)-N-((3s,5s,7s)-adamantan-1-yl)-3-mesitylacrylamide(4l)



4l

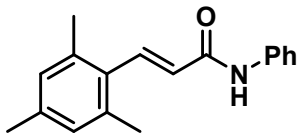
Yield: 71%, 45.9 mg; appearance: white solid, M.P.: 219-220 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 16.4 Hz, 1H), 6.86 (s, 2H), 5.94 (d, *J* = 16.0 Hz, 1H), 5.45 (s, 1H), 2.30 (s, 6H), 2.27 (s, 3H), 2.10 (s, 9H), 1.71 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.90, 138.53, 137.40, 136.52, 131.53, 128.85, 126.78, 52.12, 41.65, 36.32, 29.40, 21.04, 22.09.

ESI-MS: Calcd for $C_{22}H_{29}NO$: [M+H$^+$] 324.2322, found 324.2318.

(*E*)-3-mesityl-*N*-phenylacrylamide(4m)



4m

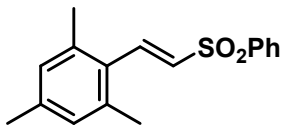
Yield: 77%, 40.9 mg; appearance: white solid, M.P.: 187-188 ºC.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.17 (s, 1H), 7.72 – 7.66 (m, 3H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.92 (s, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 2.31 (s, 6H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 163.62, 139.32, 138.06, 137.35, 136.32, 130.96, 129.11, 128.86, 126.67, 123.39, 119.20, 20.95, 20.67.

ESI-MS: Calcd for $C_{18}H_{19}NO$: [M+H$^+$] 266.1539, found 266.1540.

(*E*)-1,3,5-trimethyl-2-(2-(phenylsulfonyl)vinyl) benzene(4n)[5]



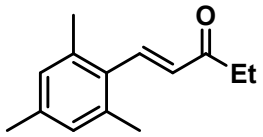
4n

Yield: 61%, 34.9 mg; appearance: white solid, M.P.: 116-118 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.94 (m, 2H), 7.87 (d, *J* = 16.0 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.58 – 7.54 (m, 2H), 6.88 (s, 2H), 6.54 (d, *J* = 15.6 Hz, 1H), 2.29 (s, 6H), 2.27 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.81, 140.76, 139.41, 137.06, 133.25, 131.51, 129.37, 129.28, 128.35, 127.47, 21.03, 20.99.

(*E*)-1-mesitylpent-1-en-3-one(4o)[2]



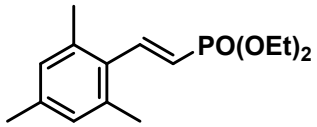
4o

Yield: 97%, 39.2 mg; appearance: white solid, M.P.: 43-45 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 16.8 Hz, 1H), 6.90 (s, 2H), 6.36 (d, *J* = 16.4 Hz, 1H), 2.70 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 6H), 2.29 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.97, 140.66, 138.29, 136.75, 131.12, 131.01, 129.13, 33.98, 21.04, 20.99, 8.18.

diethyl (*E*)-(2,4,6-trimethylstyryl) phosphonate(4p)[6]



4p

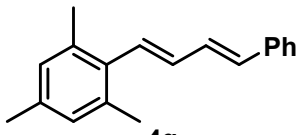
Yield: 63%, 35.6 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 23.6, 18.0 Hz, 1H), 6.88 (s, 2H), 5.86 (dd, *J* = 20.4, 18.0, Hz, 1H), 4.18 – 4.10 (m, 4H), 2.31 (s, 6H), 2.27 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.49 (d, *J* = 6.0 Hz), 138.08, 136.04, 131.98 (d, *J* = 22.0 Hz), 129.01, 119.96 (d, *J* = 184.0 Hz), 61.72 (d, *J* = 5.0 Hz), 20.95, 20.84, 16.38 (d, *J* = 6.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 18.77 (s).

1,3,5-trimethyl-2-((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl) benzene(4q)



4q

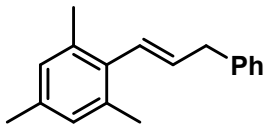
Yield: 62%, 30.8 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.18 (m, 1H), 7.00 (dd, *J* = 15.2, 10.4 Hz, 1H), 6.90 (s, 2H), 6.71 (d, *J* = 16.0 Hz, 1H), 6.60 (d, *J* = 15.6 Hz, 1H), 6.48 (dd, *J* = 15.6, 10.4 Hz, 1H), 2.35 (s, 6H), 2.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.38, 136.32, 136.05, 134.20, 133.62, 131.76, 131.06, 129.77, 128.80, 128.61, 127.39, 126.28, 21.17, 20.95.

ESI-MS: Calcd for $C_{19}H_{20}$: [M+H$^+$] 249.1638, found 249.1635.

(*E*)-1,3,5-trimethyl-2-(3-phenylprop-1-en-1-yl) benzene(4r)[7]



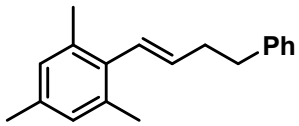
4r

Yield: 70%, 33.1 mg; appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.26 – 7.21 (m, 1H), 6.94 (s, 2H), 6.37 – 6.26 (m, 2H), 3.58 (d, *J* = 4.0 Hz, 2H), 2.37 (s, 6H), 2.34 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.60, 136.60, 135.51, 133.07, 129.81, 128.84, 128.39, 127.67, 126.85, 125.96, 32.55, 20.85, 19.88.

(*E*)-1,3,5-trimethyl-2-(4-phenylbut-1-en-1-yl)benzene(4s)



4s

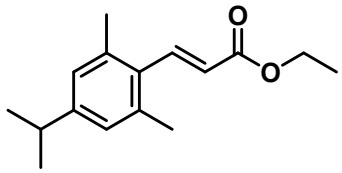
Yield: 53%, 26.5 mg; appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 2H), 7.34 – 7.29 (m, 2H), 7.24 – 7.20 (m, 1H), 6.87 (s, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.33 (dt, *J* = 15.6, 6.8 Hz, 1H), 2.80 – 2.75 (m, 2H), 2.41 – 2.36 (m, 2H), 2.34 (s, 6H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.65, 135.94, 135.42, 135.10, 130.34, 129.91, 128.90, 128.50, 126.92, 125.93, 32.62, 29.28, 20.80, 19.80.

ESI-MS: Calcd for $C_{19}H_{22}O$: [M+H$^+$] 251.1794, found 251.1788.

ethyl (*E*)-3-(4-isopropyl-2,6-dimethylphenyl)acrylate(4t)



4t

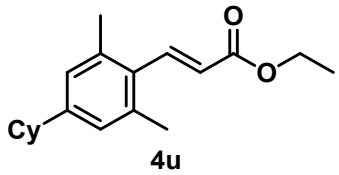
Yield: 71%, 35.0 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 16.4 Hz, 1H), 6.94 (s, 2H), 6.07 (d, *J* = 16.4 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.89 – 2.78 (m, 1H), 2.36 (s, 6H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.25 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.02, 149.21, 143.21, 136.87, 131.41, 126.49, 123.23, 60.44, 33.78, 23.81, 21.26, 14.31.

ESI-MS: Calcd for $C_{16}H_{22}O_2$: [M+H$^+$] 247.1693, found 247.1692.

ethyl (*E*)-3-(4-cyclohexyl-2,6-dimethylphenyl)acrylate(4u)



4u

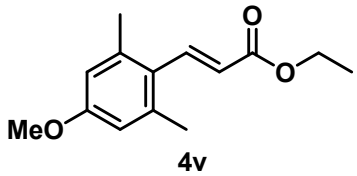
Yield: 80%, 45.8 mg; appearance: pink solid, M.P.: 58-59 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 16.0 Hz, 1H), 6.93 (s, 2H), 6.07 (d, *J* = 16.4 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.46 – 2.38 (m, 1H), 2.36 (s, 6H), 1.87 – 1.84 (m, 4H), 1.78 – 1.74 (m, 1H), 1.44 – 1.33 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.00, 148.44, 143.20, 136.80, 131.38, 126.90, 123.16, 60.40, 44.27, 34.25, 26.83, 26.11, 21.24, 14.29.

ESI-MS: Calcd for $C_{19}H_{26}O_2$: [M+H$^+$] 287.2006, found 287.2005.

ethyl (*E*)-3-(4-methoxy-2,6-dimethylphenyl)acrylate(4v)



4v

Yield: 55%, 25.8 mg; appearance: white solid, M.P.: 63-64 ºC.

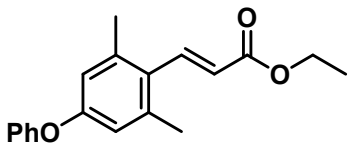
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 16.4 Hz, 1H), 6.62 (s, 2H), 6.03 (d, *J* = 16.4 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 2.37 (s, 6H), 1.34 (t, *J* = 6.8

Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.23, 159.25, 142.66, 139.02, 126.30, 122.08, 113.81, 60.38, 55.09, 21.66, 14.32.

ESI-MS: Calcd for $C_{14}H_{18}O_3$: [M+H$^+$] 235.1329, found 235.1325.

ethyl (*E*)-3-(2,6-dimethyl-4-phenoxyphenyl)acrylate(4w)



4w

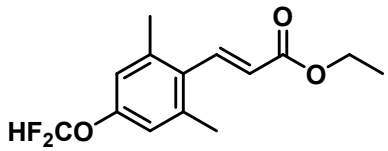
Yield: 61%, 36.2 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 16.4 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.16 – 7.11 (m, 1H), 7.05 – 7.01 (m, 2H), 6.70 (s, 2H), 6.06 (d, *J* = 16.4 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 6H), 1.35 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.98, 157.10, 156.53, 142.48, 139.07, 129.77, 128.68, 123.58, 123.09, 119.36, 118.00, 60.48, 21.41, 14.31.

ESI-MS: Calcd for $C_{19}H_{20}O_3$: [M+H$^+$] 297.1485, found 297.1485.

ethyl (*E*)-3-(4-(difluoromethoxy)-2,6-dimethylphenyl)acrylate(4x)



4x

Yield: 53%, 28.6 mg; appearance: yellow oil.

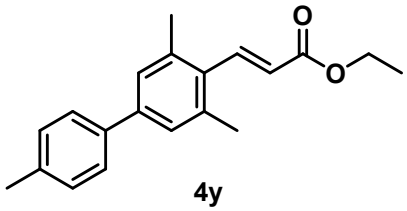
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 16.4 Hz, 1H), 6.82 (s, 2H), 6.50 (t, *J* = 73.6 Hz, 1H), 6.04 (d, *J* = 16.4 Hz, 1H), 4.28 (q, *J* = 6.8 Hz, 2H), 2.34 (s, 6H), 1.35 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.61, 150.59 (t, *J* = 3.0 Hz), 142.08, 138.87, 131.19, 124.25, 118.73, 115.78 (t, *J* = 258.0 Hz), 60.61, 21.20, 14.27.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.66.

ESI-MS: Calcd for $C_{14}H_{16}F_2O_3$: [M+H$^+$] 271.1140, found 271.1140.

ethyl (*E*)-3-(3,4',5-trimethyl-[1,1'-biphenyl]-4-yl)acrylate(4y)



4y

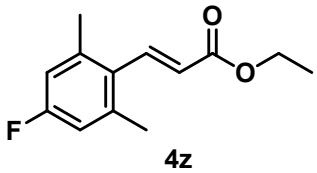
Yield: 60%, 35.3 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 16.4 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.21 (s, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 6.04 (d, *J* = 16.4 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.34 (s, 6H), 2.31 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.92, 142.88, 140.97, 137.56, 137.30, 132.59, 129.46, 126.84, 123.65, 60.54, 21.36, 21.11, 14.32.

ESI-MS: Calcd for $C_{20}H_{22}O_2$: [M+Na^+] 317.1512, found 317.1516.

ethyl (*E*)-3-(4-fluoro-2,6-dimethylphenyl)acrylate(4z)



4z

Yield: 62%, 27.6 mg; appearance: yellow oil.

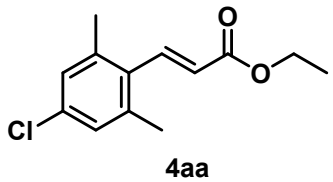
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 16.4 Hz, 1H), 6.77 (d, *J* = 9.6 Hz, 2H), 6.03 (d, *J* = 16.4 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.34 (s, 6H), 1.34 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.71, 161.98 (d, *J* = 246.0 Hz), 142.23, 139.25 (d, *J* = 8.0 Hz), 129.91, 123.98, 114.88 (d, *J* = 20.0 Hz), 60.58, 21.23 (d, *J* = 1.0 Hz), 14.29.

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.17.

ESI-MS: Calcd for $C_{13}H_{15}FO_2$: [M+H^+] 223.1129, found 223.1130.

ethyl (*E*)-3-(4-chloro-2,6-dimethylphenyl)acrylate(4aa)[1]



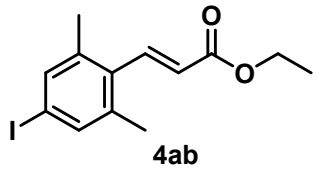
4aa

Yield: 70%, 33.4 mg; appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 16.0 Hz, 1H), 7.06 (s, 2H), 6.04 (d, *J* = 16.4 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.32 (s, 6H), 1.34 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.55, 142.06, 138.42, 133.59, 132.41, 128.00, 124.38, 60.64, 20.93, 14.26.

ethyl (*E*)-3-(4-iodo-2,6-dimethylphenyl)acrylate(4ab)



4ab

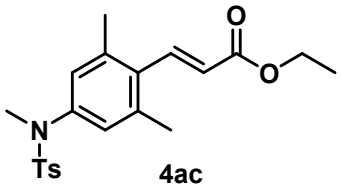
Yield: 68%, 44.9 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 16.0 Hz, 1H), 7.43 (s, 2H), 6.04 (d, *J* = 16.4 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.29 (s, 6H), 1.34 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.51, 142.18, 138.57, 136.90, 133.63, 124.50, 94.35, 60.66, 20.61, 14.27.

ESI-MS: Calcd for $C_{13}H_{15}IO_2$: [M+H$^+$] 331.0189, found 331.0190.

ethyl (*E*)-3-(4-((*N*,4-dimethylphenyl)sulfonamido)-2,6-dimethylphenyl)acrylate (4ac)



4ac

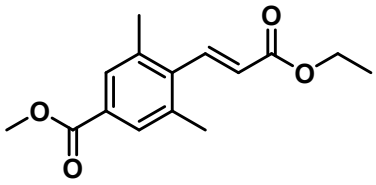
Yield: 70%, 54.2 mg; appearance: white solid, M.P.: 124-126 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.4 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 6.74 (s, 2H), 5.98 (d, *J* = 16.4 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.05 (s, 3H), 2.35 (s, 3H), 2.21 (s, 6H), 1.27 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.62, 143.57, 142.28, 141.12, 137.47, 133.63, 132.90, 129.29, 127.86, 125.95, 124.23, 60.59, 37.93, 21.53, 21.11, 14.26.

ESI-MS: Calcd for $C_{21}H_{25}NO_4S$: [M+H$^+$] 388.1577, found 388.1576.

methyl (*E*)-4-(3-ethoxy-3-oxoprop-1-en-1-yl)-3,5-dimethylbenzoate(4ad)



4ad

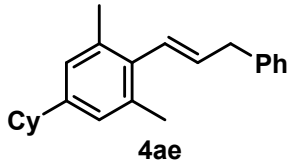
Yield: 83%, 43.5 mg; appearance: white solid, M.P.: 52-54 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 16.4 Hz, 1H), 7.70 (s, 2H), 6.06 (d, J = 16.8 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 3.88 (s, 3H), 2.35 (s, 6H), 1.33 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.79, 166.25, 142.25, 138.64, 136.63, 129.27, 128.96, 125.06, 60.63, 52.00, 20.85, 14.19.

ESI-MS: Calcd for $C_{15}H_{18}O_4$: [M+H$^+$] 263.1278, found 263.1274.

(*E*)-5-cyclohexyl-1,3-dimethyl-2-(3-phenylprop-1-en-1-yl)benzene(4ae)



4ae

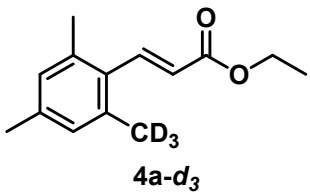
Yield: 63%, 38.4 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 4H), 7.24 (t, J = 7.2 Hz, 1H), 6.97 (s, 2H), 6.38 – 6.29 (m, 2H), 3.59 (d, J = 2.8 Hz, 2H), 2.53 – 2.46 (m, 1H), 2.40 (s, 6H), 1.96 – 1.89 (m, 4H), 1.84 – 1.80 (m, 1H), 1.55 – 1.44 (m, 4H), 1.37 – 1.34 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.86, 137.60, 136.49, 133.54, 129.88, 128.38, 127.70, 126.84, 126.59, 125.96, 44.12, 34.49, 32.79, 26.96, 26.20, 20.08.

ESI-MS: Calcd for $C_{23}H_{28}$: [M–H$^+$] 303.2118, found 303.2124.

ethyl (*E*)-3-(2,4-dimethyl-6-(methyl-*d*$_3$)phenyl)acrylate(4a-*d*$_3$)



4a-*d*$_3$

Yield: 88%, 39.0 mg; appearance: yellow solid, M.P.: 33-35 ºC.

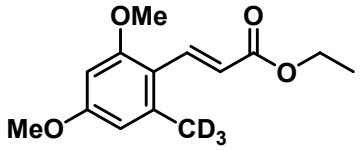
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 16.4 Hz, 1H), 6.90 (s, 2H), 6.06 (d, J =

16.4 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.34 (s, 3H), 2.29 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.00, 143.13, 138.24, 136.80, 136.69, 130.95, 129.11, 123.13, 60.43, 21.05, 21.00, 14.29.

ESI-MS: Calcd for $C_{14}H_{15}D_3O_2$: [M+H$^+$] 222.1568, found 222.1569.

ethyl (*E*)-3-(2,4-dimethoxy-6-(methyl-*d*$_3$)phenyl)acrylate(4b-*d*$_3$)



4b-*d*$_3$

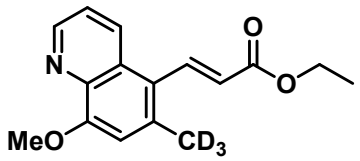
Yield: 65%, 32.9 mg; appearance: white solid, M.P.: 68-70 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 16.0 Hz, 1H), 6.61 (d, *J* = 16.4 Hz, 1H), 6.35 (dd, *J* = 12.0, 2.4 Hz, 2H), 4.25 (q, *J* = 6.8 Hz, 2H), 3.85 (s, 3H), 3.81 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.59, 161.15, 160.99, 141.41, 138.33, 119.15, 115.32, 107.53, 96.27, 60.09, 55.38, 55.25, 14.38.

ESI-MS: Calcd for $C_{14}H_{15}D_3O_4$: [M+H$^+$] 254.1466, found254.1465.

ethyl (*E*)-3-(8-methoxy-6-(methyl-*d*$_3$)quinolin-5-yl)acrylate(4c-*d*$_3$)



4c-*d*$_3$

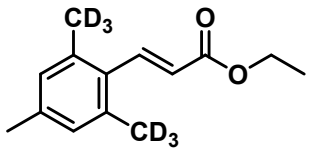
Yield: 70%, 38.4 mg; appearance: yellow solid, M.P.: 104-106 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 – 8.85 (m, 1H), 8.40 – 8.36 (m, 1H), 8.07 (d, *J* = 16.0 Hz, 1H), 7.43 – 7.39 (m, 1H), 6.89 (s, 1H), 6.14 (d, *J* = 16.4 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.08 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.58, 155.21, 148.35, 140.83, 139.06, 136.06, 132.82, 127.62, 124.71, 122.59, 121.93, 110.63, 60.60, 55.96, 14.28.

ESI-MS: Calcd for $C_{16}H_{14}D_3NO_3$: [M+H$^+$] 275.1470, found 275.1469.

ethyl (*E*)-3-(4-methyl-2,6-bis(methyl-*d*$_3$)phenyl)acrylate(4a-*d*$_6$)



4a-*d*$_6$

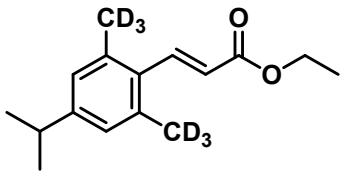
Yield: 71%, 31.9 mg; appearance: yellow solid, M.P.: 36-37 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84 (d, *J* = 16.0 Hz, 1H), 6.90 (s, 2H), 6.05 (d, *J* = 16.4 Hz, 1H), 4.28 (q, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 1.35 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 167.03, 143.14, 138.27, 136.72, 130.98, 129.13, 123.11, 60.45, 21.02, 14.31.

ESI-MS: Calcd for $C_{14}H_{12}D_6O_2$: [M+H$^+$] 225.1756, found 225.1753.

ethyl (*E*)-3-(4-isopropyl-2,6-bis(methyl-*d*$_3$)phenyl)acrylate(4t-*d*$_6$)



4t-*d*$_6$

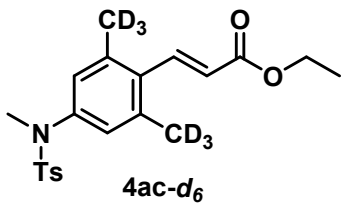
Yield: 69%, 34.8 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, *J* = 16.4 Hz, 1H), 6.94 (s, 2H), 6.07 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.88 – 2.80 (m, 1H), 1.35 (t, *J* = 6.8 Hz, 3H), 1.26 (s, 3H), 1.24 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 167.05, 149.22, 143.16, 136.79, 131.39, 126.49, 123.11, 60.45, 33.77, 23.81, 14.30.

ESI-MS: Calcd for $C_{16}H_{16}D_6O_2$: [M+H$^+$] 253.2069, found 253.2067.

ethyl (*E*)-3-(4-((*N*,4-dimethylphenyl)sulfonamido)-2,6-bis(methyl-*d*$_3$)phenyl) acrylate(4ac-*d*$_6$)



4ac-*d*$_6$

Yield: 68%, 53.5 mg; appearance: yellow solid, M.P.: 124-125 ºC.

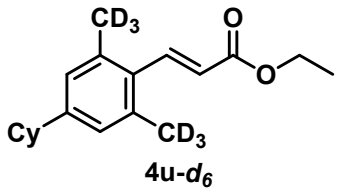
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.70 (d, *J* = 16.4 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H),

7.18 (d, J = 8.4 Hz, 2H), 6.74 (s, 2H), 5.98 (d, J = 16.4 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.05 (s, 3H), 2.35 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.58, 136.54, 135.21, 134.09, 130.34, 126.57, 125.87, 122.26, 120.81, 118.91, 117.14, 53.55, 30.89, 14.48, 7.22.

ESI-MS: Calcd for $C_{21}H_{19}D_6NO_4S$: [M+H$^+$] 394.1954, found 394.1954.

ethyl (*E*)-3-(4-cyclohexyl-2,6-bis(methyl-*d*$_3$)phenyl)acrylate(4u-*d*$_6$)



4u-*d*$_6$

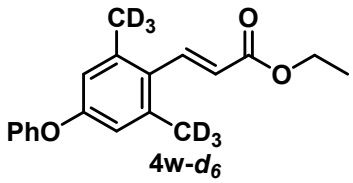
Yield: 76%, 44.5 mg; appearance: pink solid, M.P.: 56-58 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 16.0 Hz, 1H), 6.92 (s, 2H), 6.06 (d, J = 16.4 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 2.47 – 2.39 (m, 1H), 1.86 – 1.84 (m, 4H), 1.77 – 1.73 (m, 1H), 1.44 – 1.32 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.04, 148.47, 143.19, 136.74, 131.42, 126.92, 123.11, 60.42, 44.28, 34.26, 26.84, 26.12, 14.31.

ESI-MS: Calcd for $C_{19}H_{20}D_6O_2$: [M+H$^+$] 293.2382, found 293.2380.

ethyl (*E*)-3-(2,6-bis(methyl-*d*$_3$)-4-phenoxyphenyl)acrylate(4w-*d*$_3$)



4w-*d*$_6$

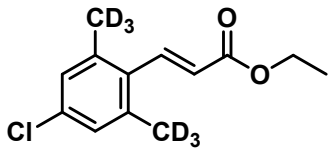
Yield: 62%, 37.5 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 15.6 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.50 – 7.45 (m, 1H), 7.40 – 7.36 (m, 2H), 7.05 (s, 2H), 6.41 (d, J = 16.4 Hz, 1H), 4.63 (q, J = 7.2 Hz, 2H), 1.70 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.93, 157.07, 156.45, 142.39, 138.94, 129.72, 128.62, 123.53, 122.92, 119.31, 117.96, 60.42, 14.26.

ESI-MS: Calcd for $C_{19}H_{14}D_6O_3$: [M+H$^+$] 303.1862, found 303.1858.

ethyl (*E*)-3-(4-chloro-2,6-bis(methyl-*d*$_3$)phenyl)acrylate(4aa-*d*$_6$)



4aa-d_6

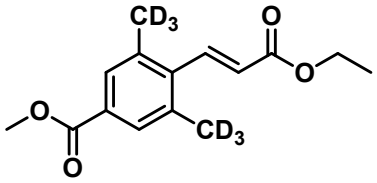
Yield: 66%, 32.3 mg; appearance: yellow solid, M.P.: 37-38 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 16.4 Hz, 1H), 7.05 (s, 2H), 6.04 (d, *J* = 16.4 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.50, 141.97, 138.28, 133.57, 132.38, 127.98, 124.27, 60.58, 14.23.

ESI-MS: Calcd for $C_{13}H_9D_6ClO_2$: [M+H$^+$] 245.1210, found 245.1209.

methyl (*E*)-4-(3-ethoxy-3-oxoprop-1-en-1-yl)-3,5-bis(methyl-d_3)benzoate (4ad-d_6)



4ad-d_6

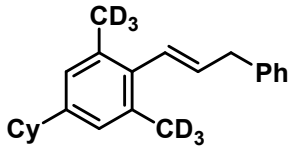
Yield: 81%, 43.5 mg; appearance: white solid, M.P.: 50-52 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 16.4 Hz, 1H), 7.70 (s, 2H), 6.06 (d, *J* = 16.4 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.79, 166.26, 142.23, 138.67, 136.54, 129.29, 128.99, 125.03, 60.63, 51.99, 14.19.

ESI-MS: Calcd for $C_{15}H_{12}D_6O_4$: [M+H$^+$] 269.1654, found 269.1656.

(*E*)-5-cyclohexyl-1,3- bis(methyl-d_3)-2-(3-phenylprop-1-en-1-yl)benzene(4ae-d_6)



4ae-d_6

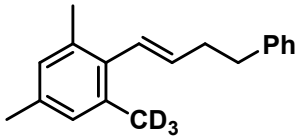
Yield: 57%, 35.4 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 4H), 7.22 – 7.17 (m, 1H), 6.92 (s, 2H), 6.34 – 6.26 (m, 2H), 3.55 – 3.53 (m, 2H), 2.48 – 2.41 (m, 1H), 1.92 – 1.85 (m, 4H), 1.80 – 1.75 (m, 1H), 1.53 – 1.42 (m, 4H), 1.40 – 1.35 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.86, 137.61, 136.38, 133.60, 129.87, 128.39, 127.74, 126.84, 126.59, 125.96, 44.13, 34.49, 32.78, 26.96, 26.21.

ESI-MS: Calcd for $C_{23}H_{22}D_6$: [M–H$^+$] 309.2495, found 309.2500.

(*E*)-1,5-dimethyl-3-(methyl-*d*$_3$)-2-(4-phenylbut-1-en-1-yl)benzene(4s-*d*$_3$)



4s-*d*$_3$

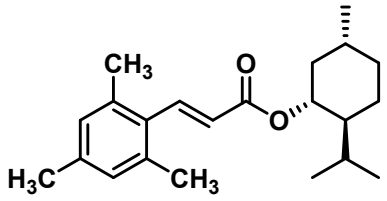
Yield: 47%, 23.8 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.87 (s, 2H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.37 – 6.29 (m, 1H), 2.80 – 2.75 (m, 2H), 2.40 – 2.35 (m, 2H), 2.33 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.66, 135.96, 135.45, 135.10, 130.35, 129.92, 128.90, 128.50, 126.92, 125.94, 32.64, 29.28, 20.80, 19.79.

ESI-MS: Calcd for $C_{19}H_{19}D_3$: [M+H$^+$] 254.1983, found 254.1979.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl (*E*)-3-mesitylacrylate(4af)



4af

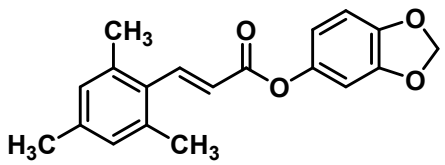
Yield: 94%, 61.8 mg; appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 16.4 Hz, 1H), 6.90 (s, 2H), 6.06 (d, *J* = 16.0 Hz, 1H), 4.88 – 4.80 (m, 1H), 2.35 (s, 6H), 2.29 (s, 3H), 2.14 – 2.10 (m, 1H), 1.99 – 1.89 (m, 1H), 1.74 – 1.70 (m, 2H), 1.61 – 1.44 (m, 2H), 1.15 – 1.02 (m, 2H), 0.96 – 0.92 (m, 7H), 0.83 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.58, 142.82, 138.16, 136.81, 130.89, 129.12, 123.41, 74.22, 47.12, 41.01, 34.28, 31.39, 26.49, 23.71, 22.02, 21.11, 21.00, 20.66, 16.63.

ESI-MS: Calcd for $C_{22}H_{32}O_2$: [M–H$^+$] 327.2330, found 327.2335.

benzo[*d*][1,3]dioxol-5-yl (*E*)-3-mesitylacrylate(4ag)



4ag

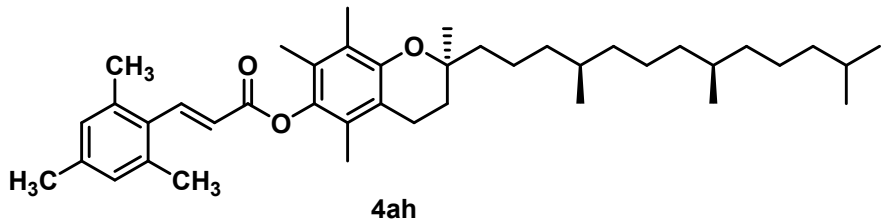
Yield: 81%, 50.3 mg; appearance: white solid, M.P.: 89-91 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 16.4 Hz, 1H), 6.95 (s, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.75 (d, *J* = 2.4 Hz, 1H), 6.66 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.27 (d, *J* = 16.4 Hz, 1H), 6.01 (s, 2H), 2.41 (s, 6H), 2.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.60, 147.93, 145.23, 145.12, 145.09, 138.73, 137.04, 130.46, 129.27, 121.81, 113.91, 107.87, 103.77, 101.61, 21.13, 21.00.

ESI-MS: Calcd for $C_{19}H_{18}O_4$: [M+H$^+$] 311.1278, found 311.1277.

(*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl (*E*)-3-mesitylacrylate(4ah)



4ah

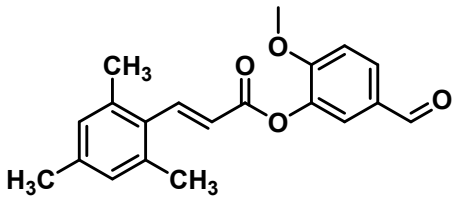
Yield: 75%, 90.4 mg; appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 16.4 Hz, 1H), 6.97 (s, 2H), 6.37 (d, *J* = 16.4 Hz, 1H), 2.66 (t, *J* = 6.4 Hz, 2H), 2.45 (s, 6H), 2.35 (s, 3H), 2.17 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H), 1.92 – 1.78 (m, 2H), 1.65 – 1.52 (m, 4H), 1.49 – 1.40 (m, 4H), 1.31 – 1.26 (m, 7H), 1.22 – 1.10 (m, 7H), 0.93 – 0.89 (m, 14H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.45, 149.32, 144.58, 140.48, 138.54, 136.92, 130.60, 129.26, 126.80, 125.01, 122.97, 121.96, 117.30, 74.94, 39.32, 37.40, 37.24, 32.74, 32.65, 31.07, 27.92, 24.77, 24.41, 22.68, 22.59, 21.16, 21.02, 20.98, 20.58, 19.71, 19.62, 12.97, 12.13, 11.80.

ESI-MS: Calcd for $C_{41}H_{62}O_3$: [M+H$^+$] 603.4772, found 603.4767.

5-formyl-2-methoxyphenyl (*E*)-3-mesitylacrylate(4ai)



4ai

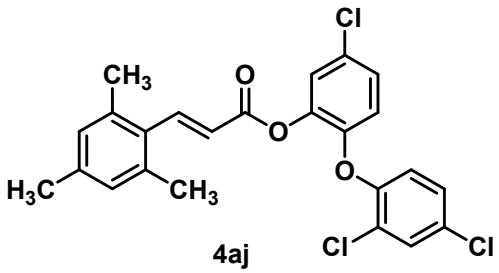
Yield: 73%, 47.4 mg; appearance: red solid, M.P.: 130-131 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (s, 1H), 8.08 (d, *J* = 16.4 Hz, 1H), 7.79 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.70 (d, *J* = 2.0 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.93 (s, 2H), 6.32 (d, *J* = 16.4 Hz, 1H), 3.94 (s, 3H), 2.41 (s, 6H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.97, 164.57, 156.44, 145.60, 140.22, 138.87, 137.14, 130.23, 129.93, 129.86, 129.30, 123.57, 120.89, 111.94, 56.17, 21.18, 20.99.

ESI-MS: Calcd for $C_{20}H_{20}O_4$: [M+H$^+$] 325.1434, found 325.1432.

5-chloro-2-(2,4-dichlorophenoxy)phenyl (*E*)-3-mesitylacrylate(4aj)



4aj

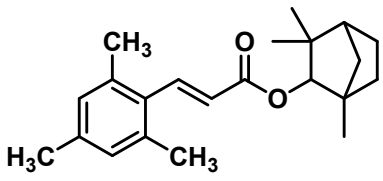
Yield: 83%, 76.7 mg; appearance: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 16.4 Hz, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.33 (d, *J* = 2.4 Hz, 1H), 7.22 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.16 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 6.91 (s, 2H), 6.87 (d, *J* = 8.8 Hz, 1H), 6.13 (d, *J* = 16.4 Hz, 1H), 2.32 (s, 6H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.04, 151.36, 146.42, 146.09, 142.07, 139.06, 137.20, 130.31, 130.24, 129.58, 129.35, 129.09, 128.00, 126.93, 125.47, 124.71, 120.94, 120.62, 119.65, 21.12, 21.08.

ESI-MS: Calcd for $C_{24}H_{19}Cl_3O_3$: [M–H$^+$] 459.0327, found 459.0337.

1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl (*E*)-3-mesitylacrylate(4ak)



4ak

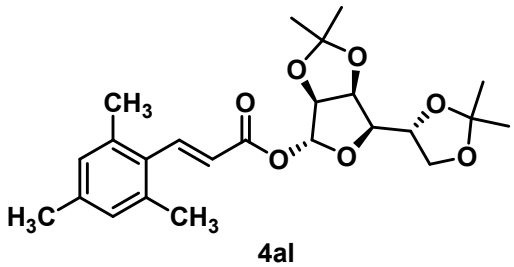
Yield: 89%, 58.1 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 16.4 Hz, 1H), 6.90 (s, 2H), 6.09 (d, *J* = 16.4 Hz, 1H), 4.52 (d, *J* = 1.6 Hz, 1H), 2.35 (s, 6H), 2.29 (s, 3H), 1.88 – 1.80 (m, 1H), 1.77 – 1.71 (m, 2H), 1.66 – 1.63 (m, 1H), 1.53 – 1.44 (m, 1H), 1.30 – 1.21 (m, 2H), 1.17 (s, 3H), 1.11 (s, 3H), 0.85 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.39, 142.80, 138.20, 136.76, 130.89, 129.13, 123.17, 86.12, 48.40, 48.38, 41.42, 39.70, 29.73, 26.70, 25.85, 21.07, 21.02, 20.14, 19.44.

ESI-MS: Calcd for $C_{22}H_{30}O_2$: [M–H$^+$] 325.2173, found 325.2179.

(3a*S*,4*R*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl (*E*)-3-mesitylacrylate(4al)



4al

Yield: 89%, 77.0 mg; appearance: white solid, M.P.: 114-116 ºC.

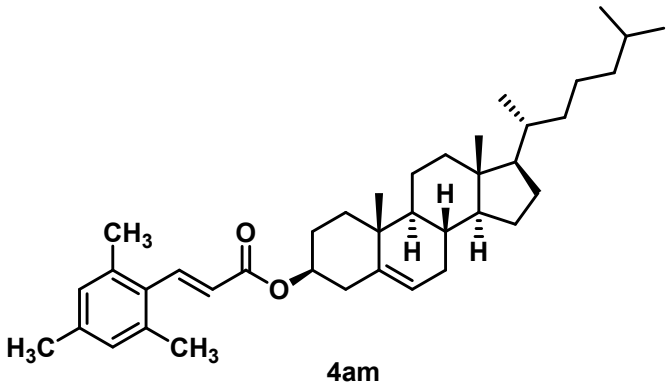
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 16.0 Hz, 1H), 6.90 (s, 2H), 6.27 (s, 1H), 6.02 (d, *J* = 16.0 Hz, 1H), 4.91 (dd, *J* = 6.4, 2.0 Hz, 1H), 4.81 (d, *J* = 6.4 Hz, 1H), 4.46 – 4.41 (m, 1H), 4.14 – 4.07 (m, 3H), 2.34 (s, 6H), 2.29 (s, 3H), 1.52 (s, 3H), 1.47 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.28, 144.83, 138.70, 137.04, 130.41, 129.24, 121.81, 113.19, 103.30, 101.00, 85.14, 82.27, 79.29, 72.90, 66.81, 26.97, 25.90, 25.08, 24.59, 21.16, 21.02.

ESI-MS: Calcd for $C_{24}H_{32}O_7$: [M+H$^+$] 433.2221, found 433.2220.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-

2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl (*E*)-3-mesitylacrylate(4am)



4am

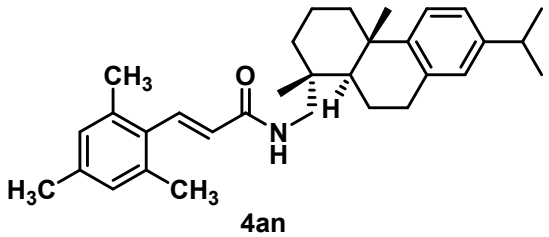
Yield: 95%, 106.2 mg; appearance: white solid, M.P.: 109-111 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 16.0 Hz, 1H), 6.89 (s, 2H), 6.05 (d, *J* = 16.4 Hz, 1H), 5.42 (d, *J* = 4.4 Hz, 1H), 4.82 – 4.73 (m, 1H), 2.44 – 2.41 (m, 2H), 2.35 (s, 6H), 2.29 (s, 3H), 2.06 – 1.87 (m, 5H), 1.71 – 1.47 (m, 8H), 1.41 – 1.29 (m, 4H), 1.21 – 1.10 (m, 7H), 1.07 (s, 3H), 1.04 – 0.97 (m, 2H), 0.94 (d, *J* = 6.4 Hz, 3H), 0.91 – 0.88 (m, 6H), 0.70 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.31, 142.86, 139.62, 138.08, 136.75, 130.86, 129.09, 123.37, 122.57, 73.97, 56.60, 56.06, 49.94, 42.22, 39.65, 39.46, 38.18, 36.97, 36.53, 36.13, 35.75, 31.84, 31.78, 28.18, 27.95, 27.83, 24.22, 23.80, 22.78, 22.53, 21.09, 20.98, 19.27, 18.66, 11.78.

ESI-MS: Calcd for $C_{39}H_{58}O_2$: [M+Na^+] 581.4329, found 581.4336.

(*E*)-*N*-(((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)-3-mesitylacrylamide(4an)



4an

Yield: 83%, 76.0 mg; appearance: yellow oil.

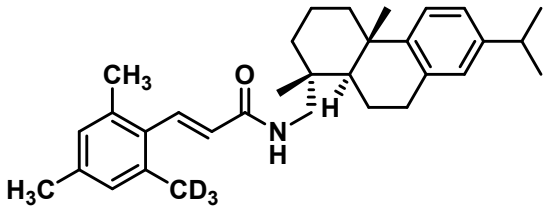
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 16.0 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.03 – 7.00 (m, 1H), 6.92 (s, 1H), 6.88 (s, 2H), 6.01 (d, *J* = 15.6 Hz, 1H), 5.72 (t, *J* = 6.0 Hz, 1H), 3.39 – 3.26 (m, 2H), 3.02 – 2.92 (m, 1H), 2.89 – 2.79 (m, 2H), 2.31

(s, 6H), 2.29 (s, 3H), 1.99 – 1.93 (m, 1H), 1.79 – 1.73 (m, 2H), 1.72 – 1.69 (m, 1H), 1.51 – 1.34 (m, 5H), 1.26 (s, 3H), 1.25 (s, 3H), 1.24 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.11, 147.10, 145.58, 139.55, 137.58, 136.55, 134.76, 131.33, 128.91, 126.86, 125.49, 124.11, 123.78, 49.94, 45.25, 38.24, 37.50, 37.39, 36.18, 33.36, 30.13, 26.85, 25.22, 23.92, 21.10, 20.95, 18.90, 18.74, 18.54.

ESI-MS: Calcd for $C_{32}H_{43}NO_3$: [M+H$^+$] 458.3417, found 458.3405.

(*E*)-3-(2,4-dimethyl-6-(methyl-*d*$_3$)phenyl)-*N*-(((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)acrylamide(4an-*d*$_3$)



4an-*d*$_3$

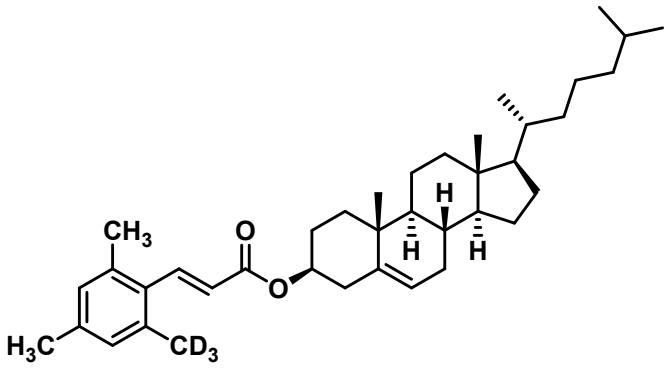
Yield: 79%, 72.8 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 16.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.07 – 7.04 (m, 1H), 6.95 (s, 1H), 6.90 (s, 2H), 6.13 – 6.05 (m, 2H), 3.42 – 3.27 (m, 2H), 3.01 – 2.84 (m, 3H), 2.34 (s, 3H), 2.31 (s, 3H), 2.01 – 1.95 (m, 1H), 1.84 – 1.68 (m, 3H), 1.56 – 1.49 (m, 2H), 1.48 – 1.38 (m, 2H), 1.30 – 1.27 (m, 10H), 1.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.18, 147.03, 145.40, 139.19, 137.38, 136.44, 136.32, 134.69, 131.28, 128.83, 126.76, 125.53, 124.02, 123.65, 49.90, 45.15, 38.14, 37.44, 37.29, 36.08, 33.28, 30.06, 25.16, 23.88, 21.02, 20.88, 18.82, 18.61, 18.48.

ESI-MS: Calcd for $C_{32}H_{40}D_3NO$: [M+Na$^+$] 483.3425, found 483.3430.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl (*E*)-3-(2,4-dimethyl-6-(methyl-*d*$_3$)phenyl)acrylate(4am-*d*$_3$)



4am-*d*$_3$

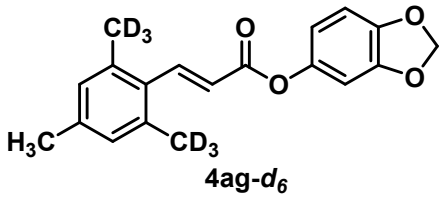
Yield: 87%, 97.8 mg; appearance: yellow solid, M.P.: 117-119 ºC.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, *J* = 16.0 Hz, 1H), 6.89 (s, 2H), 6.04 (d, *J* = 16.4 Hz, 1H), 5.41 (d, *J* = 3.6 Hz, 1H), 4.80 – 4.72 (m, 1H), 2.47 – 2.40 (m, 2H), 2.34 (s, 3H), 2.29 (s, 3H), 2.04 – 1.81 (m, 5H), 1.67 – 1.44 (m, 8H), 1.35 – 1.25 (m, 4H), 1.22 – 1.08 (m, 7H), 1.05 (s, 3H), 1.02 – 0.96 (m, 2H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.88 – 0.86 (m, 6H), 0.69 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 166.53, 143.02, 139.78, 138.28, 136.93, 136.81, 131.02, 129.19, 123.50, 122.70, 74.13, 56.72, 56.15, 50.05, 42.35, 39.76, 39.56, 38.28, 37.07, 36.22, 35.84, 31.97, 31.90, 28.29, 28.07, 27.93, 24.34, 23.87, 22.88, 22.62, 21.20, 21.10, 19.41, 18.76, 11.90.

ESI-MS: Calcd for $C_{39}H_{55}D_3O_2$: [M+H$^+$] 562.4698, found 562.4696.

benzo[*d*][1,3]dioxol-5-yl (*E*)-3-(4-methyl-2,6-bis(methyl-*d*$_3$)phenyl)acrylate (4ag-*d*$_6$)



4ag-*d*$_6$

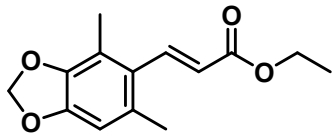
Yield: 76%, 48.1 mg; appearance: colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, *J* = 16.0 Hz, 1H), 6.94 (s, 2H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 2.4 Hz, 1H), 6.65 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.26 (d, *J* = 16.4 Hz, 1H), 6.01 (s, 2H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 165.67, 147.92, 145.23, 145.11, 145.04, 138.78, 136.99, 130.46, 129.29, 121.70, 113.92, 107.90, 103.78, 101.62, 21.03.

ESI-MS: Calcd for $C_{19}H_{12}D_6O_4$: [M+H$^+$] 317.1654, found 317.1657.

ethyl (E)-3-(4,6-dimethylbenzo[*d*][1,3]dioxol-5-yl)acrylate(4ao)



4ao

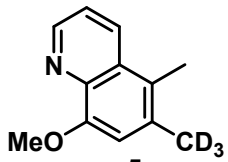
Yield: 76%, 37.7 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 16.4 Hz, 1H), 6.55 (s, 1H), 6.00 (d, *J* = 16.4 Hz, 1H), 5.92 (s, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 2.23 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.00, 146.72, 144.73, 142.30, 131.52, 127.17, 122.40, 117.99, 108.32, 100.73, 60.38, 21.22, 14.26, 13.23.

ESI-MS: Calcd for $C_{14}H_{16}O_4$: [M+H$^+$] 249.1121, found 249.1121.

8-methoxy-5-methyl-6-(methyl-*d*$_3$)quinoline(5)



5

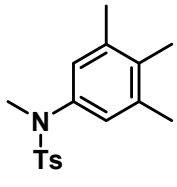
Yield: 78%, 29.7 mg; appearance: yellow solid, M.P.: 88-89 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 4.0, 1.2 Hz, 1H), 8.29 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.41 (dd, *J* = 8.4, 4.0 Hz, 1H), 6.86 (s, 1H), 4.05 (s, 3H), 2.47 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.91, 147.62, 139.15, 133.67, 132.01, 128.52, 122.47, 121.17, 110.68, 55.73, 13.51.

ESI-MS: Calcd for $C_{12}H_{10}D_3NO$: [M+H$^+$] 191.1258, found 191.1258.

***N*,4-dimethyl-*N*-(3,4,5-trimethylphenyl)benzenesulfonamide(6)**



6

Yield: 65%, 39.4 mg; appearance: red solid, M.P.: 93-95 ºC.

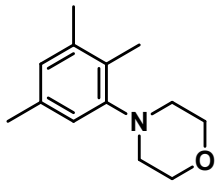
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H),

6.76 (s, 2H), 3.14 (s, 3H), 2.47 (s, 3H), 2.25 (s, 6H), 2.17 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.26, 138.50, 136.99, 134.51, 134.02, 129.17, 128.00, 125.77, 38.38, 21.52, 20.54, 15.14.

ESI-MS: Calcd for $C_{17}H_{21}NO_2S$: [M+Na^+] 326.1185, found 326.1189.

4-(2,3,5-trimethylphenyl)morpholine(7)



7

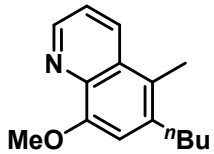
Yield: 52%, 21.4 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 1H), 6.75 (s, 1H), 3.89 – 3.87 (m, 4H), 2.89 (t, *J* = 4.0 Hz, 4H), 2.31 (s, 3H), 2.26 (s, 3H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.20, 137.85, 135.35, 127.89, 125.98, 117.23, 67.44, 52.61, 21.09, 20.53, 13.59.

ESI-MS: Calcd for $C_{13}H_{19}NO$: [M+H^+] 206.1539, found 206.1536.

6-butyl-8-methoxy-5-methylquinoline(8)



8

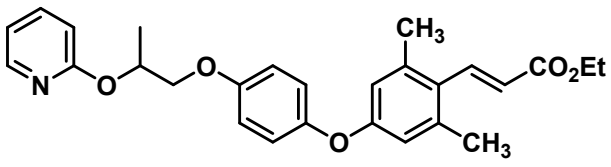
Yield: 86%, 39.4 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 – 8.83 (m, 1H), 8.29 – 8.23 (m, 1H), 7.41 – 7.36 (m, 1H), 6.83 (s, 1H), 4.04 (s, 3H), 2.76 (t, *J* = 8.0 Hz, 2H), 2.48 (s, 3H), 1.62 – 1.54 (m, 2H), 1.46 – 1.36 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.30, 147.58, 139.14, 138.64, 132.17, 128.71, 121.77, 121.07, 109.97, 55.67, 34.41, 33.16, 22.65, 13.93, 13.18.

ESI-MS: Calcd for $C_{15}H_{19}NO$: [M+H^+] 230.1539, found 230.1538.

ethyl (*E*)-3-(2,6-dimethyl-4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)acrylate(4ap)



4ap

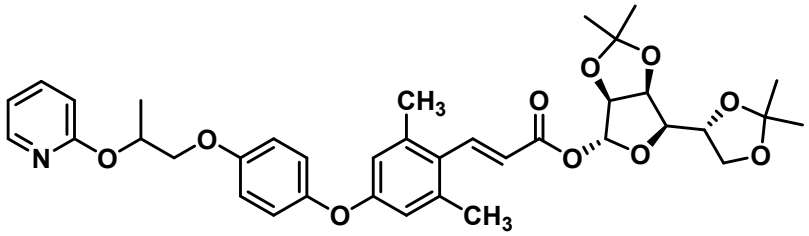
Yield: 50%, 44.8 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 5.2, 1.6 Hz, 1H), 7.82 (d, *J* = 16.4 Hz, 1H), 7.59 – 7.54 (m, 1H), 6.99 – 6.92 (m, 4H), 6.88 – 6.84 (m, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.63 (s, 2H), 6.05 (d, *J* = 16.4 Hz, 1H), 5.64 – 5.56 (m, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.20 (dd, *J* = 9.6, 5.2 Hz, 1H), 4.09 (dd, *J* = 10.0, 4.8 Hz, 1H), 2.32 (s, 6H), 1.49 (d, *J* = 6.4 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.00, 163.02, 158.29, 155.37, 149.40, 146.66, 142.45, 139.01, 138.66, 127.83, 122.69, 121.13, 116.79, 116.71, 115.68, 111.60, 70.87, 69.17, 60.40, 21.43, 16.93, 14.27.

ESI-MS: Calcd for $C_{27}H_{29}NO_5$: [M+H$^+$] 448.2118, found 448.2113.

(3a*S*,4*R*,6*R*,6a*S*)-6-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl (*E*)-3-(2,6-dimethyl-4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)acrylate(4aq)



4aq

Yield: 50%, 66.2 mg; appearance: yellow oil.

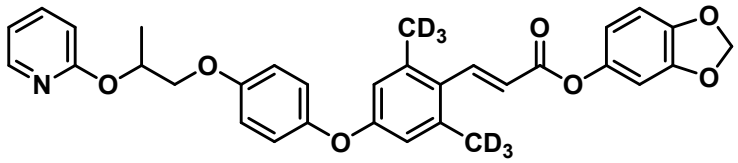
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.13 (m, 1H), 7.59 – 7.54 (m, 1H), 7.62 – 7.52 (m, 1H), 6.98 – 6.92 (m, 4H), 6.88 – 6.84 (m, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.62 (s, 2H), 6.27 (s, 1H), 6.01 (d, *J* = 16.4 Hz, 1H), 5.63 – 5.55 (m, 1H), 4.90 (dd, *J* = 6.4, 3.6 Hz, 1H), 4.80 (d, *J* = 6.4 Hz, 1H), 4.46 – 4.40 (m, 1H), 4.19 (dd, *J* = 9.6, 5.2 Hz, 1H), 4.14 – 4.06 (m, 4H), 2.33 (s, 6H), 1.51 (s, 3H), 1.48 (d, *J* = 6.4 Hz,

3H), 1.47 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.34, 163.02, 158.65, 155.45, 149.22, 146.66, 144.13, 139.40, 138.67, 127.28, 121.22, 116.84, 116.72, 115.70, 113.17, 111.61, 109.28, 100.95, 85.10, 82.22, 79.26, 72.87, 70.87, 69.16, 66.79, 26.96, 25.88, 25.06, 24.57, 21.58, 16.93.

ESI-MS: Calcd for $C_{37}H_{43}NO_{10}$: [M+H$^+$] 662.2960, found 662.2957.

benzo[*d*][1,3]dioxol-5-yl (*E*)-3-(2,6-bis(methyl-d3)-4-(4-(2-(pyridin-2-yloxy)propoxy)phenoxy)phenyl)acrylate(4ar-d_6)



4ar-d_6

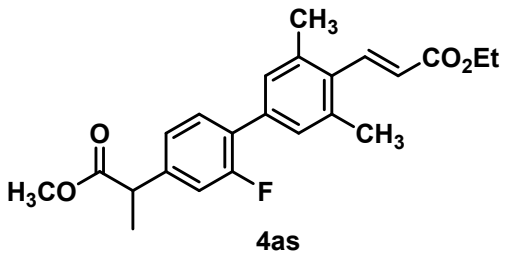
Yield: 48%, 52.4 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.01 (d, *J* = 16.0 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.01 – 6.94 (m, 4H), 6.89 – 6.85 (m, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 2.0 Hz, 1H), 6.66 (s, 2H), 6.63 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.23 (d, *J* = 16.4 Hz, 1H), 6.00 (s, 2H), 5.65 – 5.57 (m, 1H), 4.21 (dd, *J* = 10.0, 5.2 Hz, 1H), 4.10 (dd, *J* = 9.6, 4.8 Hz, 1H), 1.50 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.76, 163.03, 158.74, 155.47, 149.23, 147.92, 146.67, 145.23, 145.05, 144.45, 139.38, 138.68, 127.37, 121.25, 121.15, 116.90, 116.73, 115.72, 113.92, 111.61, 107.91, 103.79, 101.63, 70.87, 69.17, 16.94.

ESI-MS: Calcd for $C_{32}H_{23}D_6NO_7$: [M+H$^+$] 546.2393, found 546.2394.

ethyl (*E*)-3-(2'-fluoro-4'-(1-methoxy-1-oxopropan-2-yl)-3,5-dimethyl-[1,1'-biphenyl]-4-yl)acrylate(4as)



4as

Yield: 59%, 45.4 mg; appearance: colorless oil.

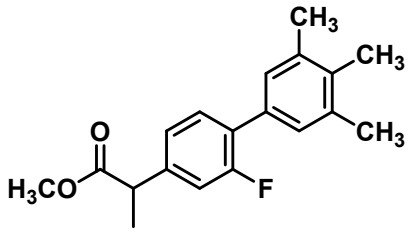
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 16.4 Hz, 1H), 7.38 (t, *J* = 8.4 Hz, 1H), 7.24 (s, 2H), 7.16 – 7.09 (m, 2H), 6.12 (d, *J* = 16.4 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 3.76 (q, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 2.41 (s, 6H), 1.53 (d, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.39, 166.80, 159.68 (d, *J* = 247.0 Hz), 142.77, 141.94 (d, *J* = 7.0 Hz), 136.92, 135.34, 133.38, 130.65 (d, *J* = 4.0 Hz), 128.72 (d, *J* = 2.0 Hz), 127.23 (d, *J* = 14.0 Hz), 124.05, 123.51 (d, *J* = 3.0 Hz), 115.23 (d, *J* = 23.0 Hz), 60.59, 52.22, 44.88, 21.25, 18.40, 14.30.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.11.

ESI-MS: Calcd for $C_{23}H_{25}FO_4$: [M+H$^+$] 385.1810, found 385.1807.

methyl 2-(2-fluoro-3',4',5'-trimethyl-[1,1'-biphenyl]-4-yl)propanoate(4at)



4at

Yield: 85%, 51.1 mg; appearance: yellow oil.

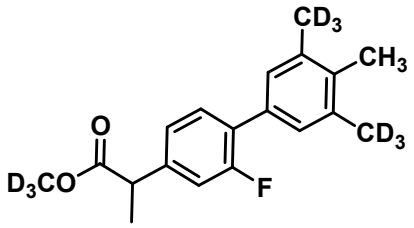
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 8.4 Hz, 1H), 7.20 (s, 2H), 7.15 – 7.09 (m, 2H), 3.77 (q, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 2.36 (s, 6H), 2.23 (s, 3H), 1.55 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.47, 159.67 (d, *J* = 246.0 Hz), 141.24 (d, *J* = 7.0 Hz), 136.51, 134.76, 132.32, 130.74 (d, *J* = 4.0 Hz), 128.04 (d, *J* = 3.0 Hz), 127.91, 123.32 (d, *J* = 3.0 Hz), 115.06 (d, *J* = 24.0 Hz), 52.15, 44.86, 20.64, 18.40, 15.22.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.35.

ESI-MS: Calcd for $C_{19}H_{21}FO_2$: [M–H$^+$] 299.1453, found 299.1455.

methyl-*d_3* 2-(2-fluoro-4'-methyl-3',5'-bis(methyl-*d_3*)-[1,1'-biphenyl]-4-yl)propanoate(4at-*d_9*)



4at-*d*$_9$

Yield: 80%, 49.5 mg; appearance: yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 8.4 Hz, 1H), 7.22 (s, 2H), 7.17 – 7.12 (m, 2H), 3.78 (q, *J* = 7.2 Hz, 1H), 2.25 (s, 3H), 1.57 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.46, 159.67 (d, *J* = 246.0 Hz), 141.24 (d, *J* = 8.0 Hz), 136.36, 134.76, 132.32, 130.72 (d, *J* = 4.0 Hz), 128.03 (d, *J* = 1.0 Hz), 127.92, 123.30 (d, *J* = 4.0 Hz), 115.05 (d, *J* = 24.0 Hz), 44.85, 18.37, 15.16.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.30.

ESI-MS: Calcd for $C_{19}H_{12}D_9FO_2$: [M+Na^+] 332.1983, found 332.1986.

References:

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[7] Sai, M. Direct Reduction of Allylic Alcohols Using Isopropanol as Reductant. *Adv. Synth. Catal.* **2018**, *360*, 3482-3487.

X-ray Date:

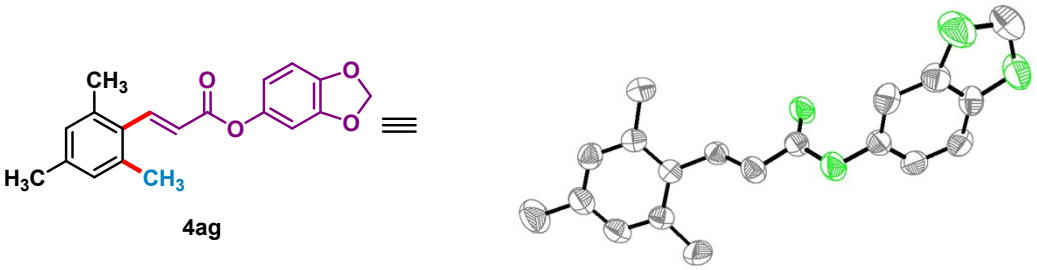


Figure S1. ORTEP drawing for the product **4ag**.

N240104A

Table 1 Crystal data and structure refinement for N240104A.

Identification code	N240104A
Empirical formula	C19H18O4
Formula weight	310.33
Temperature/K	296.15
Crystal system	monoclinic
Space group	P21/c
a/Å	13.6705(14)
b/Å	7.2456(7)
c/Å	16.9158(17)
α/°	90
β/°	105.335(2)
γ/°	90
Volume/Å3	1615.9(3)
Z	4
ρcalcg/cm3	1.276
μ/mm-1	0.089
F(000)	656.0
Crystal size/mm3	0.22 × 0.21 × 0.18

Radiation MoKα (λ = 0.71073)

2Θ range for data collection/° 4.994 to 50.016

Index ranges -15 ≤ h ≤ 16, -8 ≤ k ≤ 8, -20 ≤ l ≤ 20

Reflections collected 8941

Independent reflections 2836 [Rint = 0.0180, Rsigma = 0.0180]

Data/restraints/parameters 2836/0/208

Goodness-of-fit on F2 1.054

Final R indexes [I>=2σ (I)] R1 = 0.0399, wR2 = 0.1088

Final R indexes [all data] R1 = 0.0489, wR2 = 0.1172

Largest diff. peak/hole / e Å-3 0.16/-0.15

Table 2 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for N240104A. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
O1	7901.5(9)	1321.9(17)	4096.1(7)	68.2(4)
O2	9059.2(9)	3155.7(18)	4917.2(7)	68.5(4)
O3	10024.1(11)	4470(2)	2418.0(9)	97.1(5)
O4	11544.6(10)	2925.8(19)	2861.9(8)	78.5(4)
C1	10867.6(16)	3784(3)	2171.5(12)	80.0(6)
C2	10108.2(12)	3749(2)	3180.4(10)	57.1(4)
C3	11012.1(11)	2830(2)	3447.1(10)	53.2(4)
C4	11278.9(12)	1984(2)	4189.6(10)	58.1(4)
C5	10595.5(12)	2081(2)	4668.5(10)	57.4(4)
C6	9697.0(12)	3001(2)	4392.2(9)	52.5(4)
C7	9424.9(12)	3872(2)	3636.5(10)	58.3(4)
C8	8138.1(12)	2317(2)	4682.9(9)	51.9(4)
C9	7530.0(13)	2764(2)	5247.7(10)	57.9(4)
C10	6589.4(11)	2155(2)	5106.2(9)	49.9(4)
C11	5830.1(11)	2433.5(18)	5568.2(9)	45.2(3)
C12	6073.0(12)	2499(2)	6431.8(9)	52.8(4)

C13	5295.2(14)	2657(2)	6812.8(10)	61.1(4)
C14	4288.4(14)	2776(2)	6378.8(11)	63.9(4)
C15	4067.8(12)	2752(2)	5533.2(11)	59.5(4)
C16	4808.3(11)	2558.0(18)	5115.8(9)	48.8(4)
C17	4502.5(13)	2526(2)	4191.9(9)	61.3(4)
C18	7144.5(15)	2361(3)	6963.9(10)	80.2(6)
C19	3455.0(18)	2916(4)	6811.7(16)	104.2(8)

Table 3 Anisotropic Displacement Parameters (Å2×103) for N240104A. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U11	U22	U33	U23	U13	U12
O1	64.4(7)	83.1(8)	62.2(7)	-22.3(6)	25.7(6)	-20.3(6)
O2	61.4(7)	84.0(8)	67.5(7)	-27.3(6)	29.8(6)	-23.4(6)
O3	99.7(10)	117.0(12)	84.6(9)	53.1(9)	42.2(8)	32.5(9)
O4	69.8(8)	89.9(9)	89.4(9)	21.0(7)	45.2(7)	4.4(7)
C1	96.6(14)	79.9(12)	73.9(12)	15.7(10)	40.6(11)	-6.2(11)
C2	59.0(9)	53.5(9)	59.6(9)	13.7(7)	17.0(7)	2.4(7)
C3	48.3(8)	50.2(8)	64.6(10)	3.2(7)	20.9(7)	-6.2(7)
C4	43.9(8)	61.2(9)	65.8(10)	7.0(8)	8.7(7)	-0.3(7)
C5	55.3(9)	63.7(10)	49.3(8)	2.9(7)	7.0(7)	-9.2(7)
C6	52.0(9)	55.4(9)	53.1(8)	-10.8(7)	18.8(7)	-12.8(7)
C7	48.5(8)	56.4(9)	70.3(10)	3.1(8)	16.0(7)	4.8(7)
C8	53.6(9)	51.0(8)	53.0(9)	-3.8(7)	17.3(7)	-4.2(7)
C9	61.6(10)	57.1(9)	60.1(9)	-12.5(7)	25.0(8)	-8.2(7)
C10	55.1(9)	48.2(8)	47.5(8)	2.3(6)	15.3(7)	1.8(6)
C11	50.9(8)	38.8(7)	47.3(8)	0.9(6)	15.3(6)	-1.9(6)
C12	57.1(9)	53.9(8)	47.5(8)	0.4(7)	14.2(7)	-2.9(7)
C13	71.4(11)	67.2(10)	49.2(9)	-5.8(7)	24.0(8)	-5.7(8)
C14	63.8(10)	66.2(10)	68.5(10)	-13.5(8)	29.7(9)	-6.3(8)
C15	46.1(8)	60.4(9)	70.9(10)	-8.3(8)	13.8(8)	-4.1(7)

C16	53.5(9)	40.1(7)	51.9(8)	-1.8(6)	12.1(7)	-4.8(6)
C17	63.0(10)	61.6(10)	53.6(9)	-0.5(7)	5.6(8)	-3.5(8)
C18	67.2(11)	122.3(17)	47.2(9)	6.6(10)	8.2(8)	0.3(11)
C19	81.4(15)	142(2)	106.0(17)	-30.0(16)	54.4(13)	-8.8(14)

Table 4 Bond Lengths for N240104A.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C8	1.2001(18)	C8	C9	1.459(2)
O2	C6	1.4041(18)	C9	C10	1.320(2)
O2	C8	1.3592(19)	C10	C11	1.469(2)
O3	C1	1.416(2)	C11	C12	1.411(2)
O3	C2	1.3679(19)	C11	C16	1.407(2)
O4	C1	1.427(2)	C12	C13	1.386(2)
O4	C3	1.3769(18)	C12	C18	1.506(2)
C2	C3	1.371(2)	C13	C14	1.381(3)
C2	C7	1.363(2)	C14	C15	1.382(2)
C3	C4	1.358(2)	C14	C19	1.512(2)
C4	C5	1.391(2)	C15	C16	1.386(2)
C5	C6	1.367(2)	C16	C17	1.507(2)
C6	C7	1.385(2)			

Table 5 Bond Angles for N240104A.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	O2	C6	117.53(12)	O2	C8	C9	110.75(13)
C2	O3	C1	105.76(14)	C10	C9	C8	120.24(15)
C3	O4	C1	104.99(13)	C9	C10	C11	130.49(15)
O3	C1	O4	108.33(14)	C12	C11	C10	123.34(14)
O3	C2	C3	109.85(14)	C16	C11	C10	117.33(13)
C7	C2	O3	127.55(15)	C16	C11	C12	119.27(14)
C7	C2	C3	122.60(14)	C11	C12	C18	122.81(15)
C2	C3	O4	109.93(14)	C13	C12	C11	119.01(15)

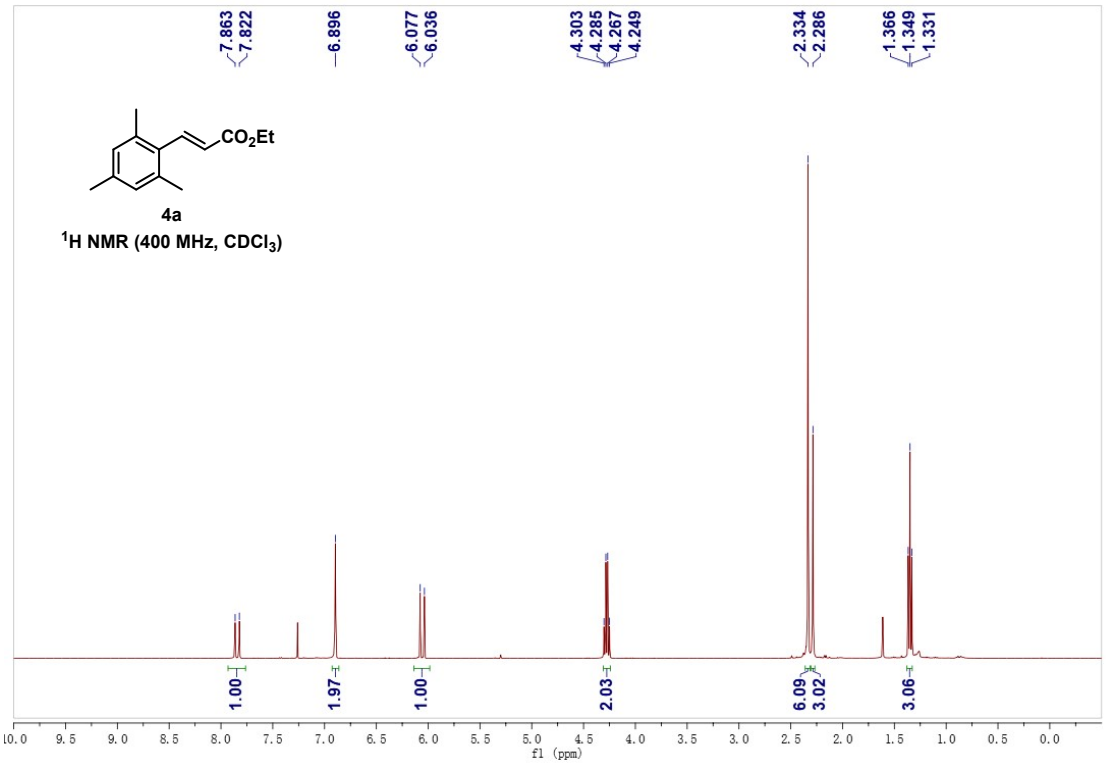
C4	C3	O4	128.61(15)	C13	C12	C18	118.16(15)
C4	C3	C2	121.46(15)	C14	C13	C12	122.50(15)
C3	C4	C5	117.29(14)	C13	C14	C15	117.62(15)
C6	C5	C4	120.45(14)	C13	C14	C19	121.30(17)
C5	C6	O2	118.35(14)	C15	C14	C19	121.08(18)
C5	C6	C7	122.38(14)	C14	C15	C16	122.67(15)
C7	C6	O2	119.16(14)	C11	C16	C17	121.74(14)
C2	C7	C6	115.82(14)	C15	C16	C11	118.90(14)
O1	C8	O2	122.42(14)	C15	C16	C17	119.35(14)
O1	C8	C9	126.81(14)				

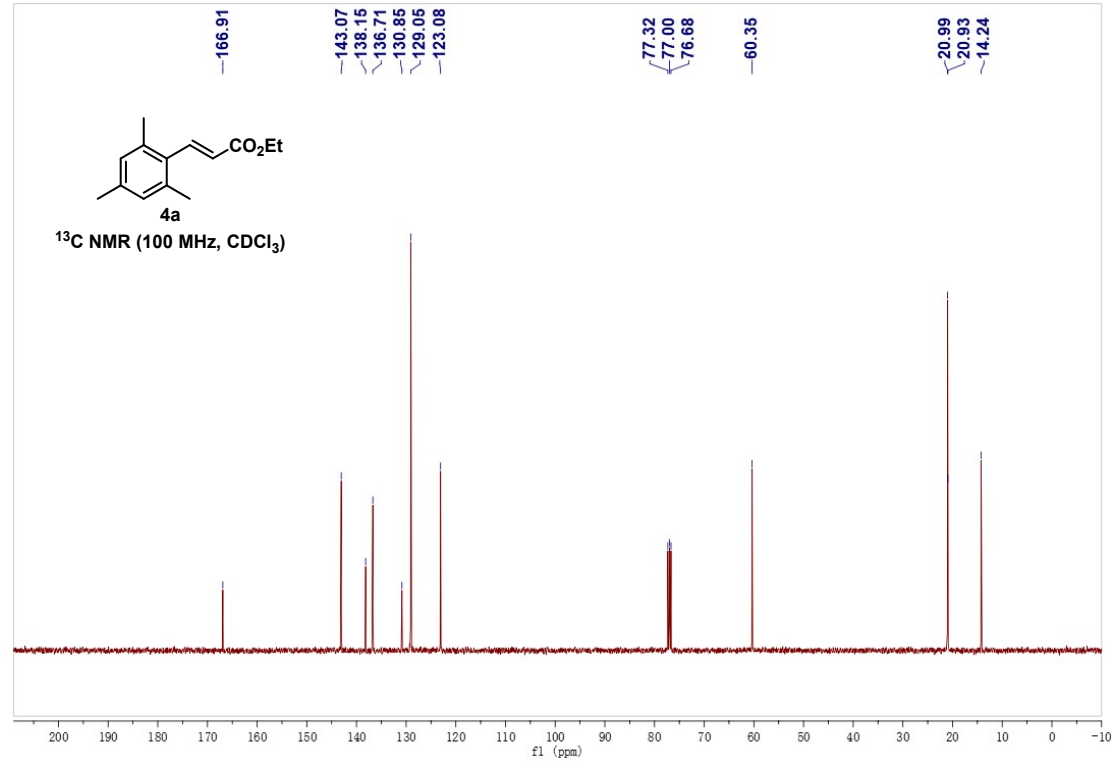
Table 6 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for N240104A.

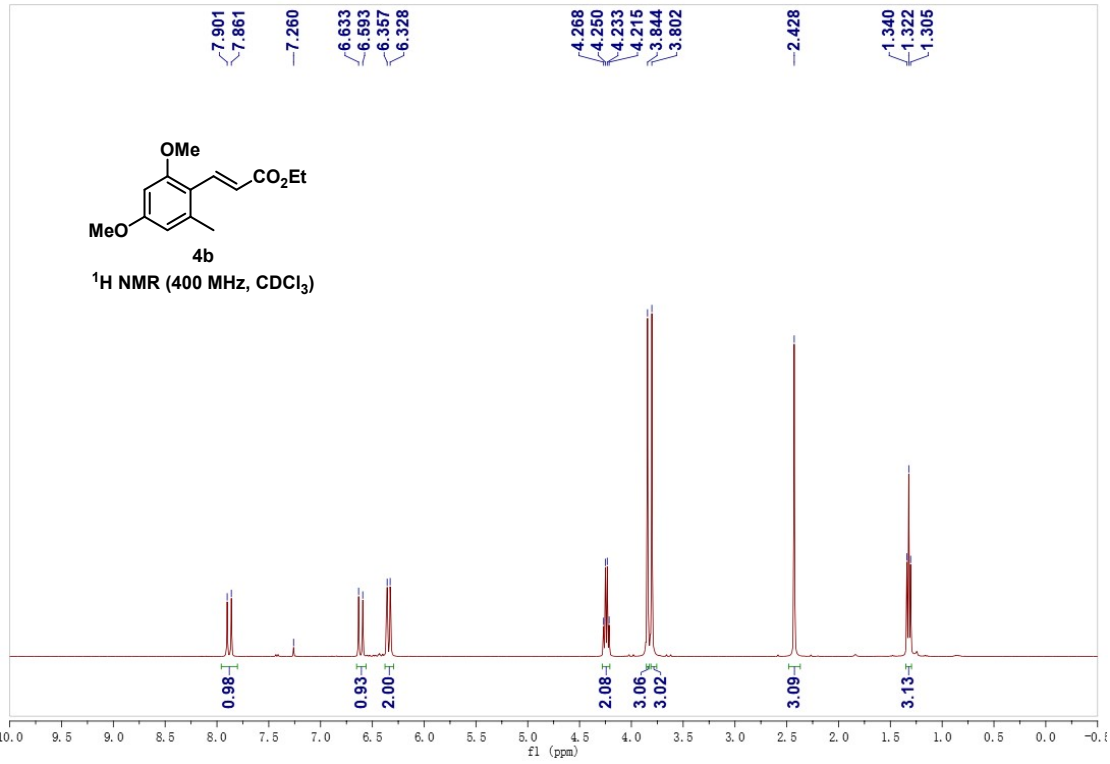
Atom	x	y	z	U(eq)
H1A	11208.85	4786.81	1973.13	96
H1B	10643.94	2894.8	1732.12	96
H4	11893.67	1365.24	4370.61	70
H5	10750.92	1515.61	5180.21	69
H7	8813.96	4501	3451.98	70
H9	7806.12	3479.57	5709.19	69
H10	6372.13	1433.48	4637.97	60
H13	5457.68	2682.8	7382.44	73
H15	3395.16	2870.29	5231.87	71
H17A	4842.12	3505.61	3988.98	92
H17B	3782.02	2689.91	3994.88	92
H17C	4690.32	1362.51	4003.38	92
H18A	7480.2	1341.06	6785.09	120
H18B	7134.3	2171.36	7523.29	120
H18C	7501.6	3481.96	6922.49	120
H19A	3351.22	1730.87	7029.77	156

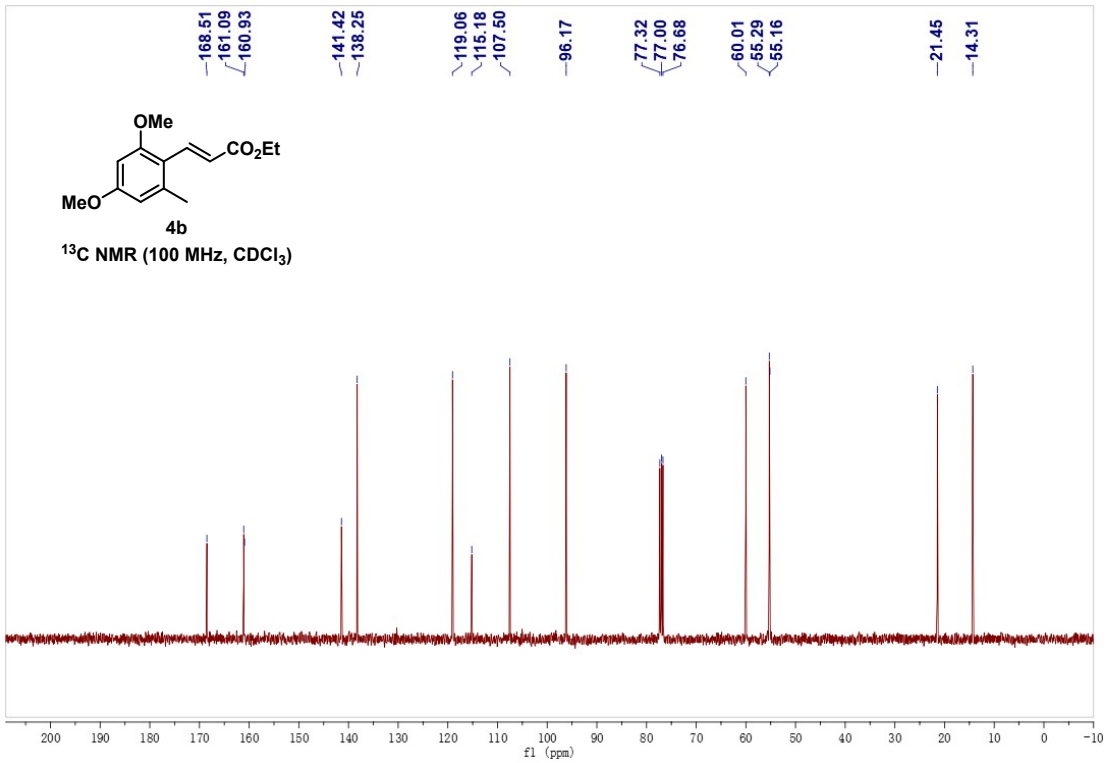
H19B	2838.72	3312.07	6429.67	156
H19C	3646.32	3794.17	7250.57	156

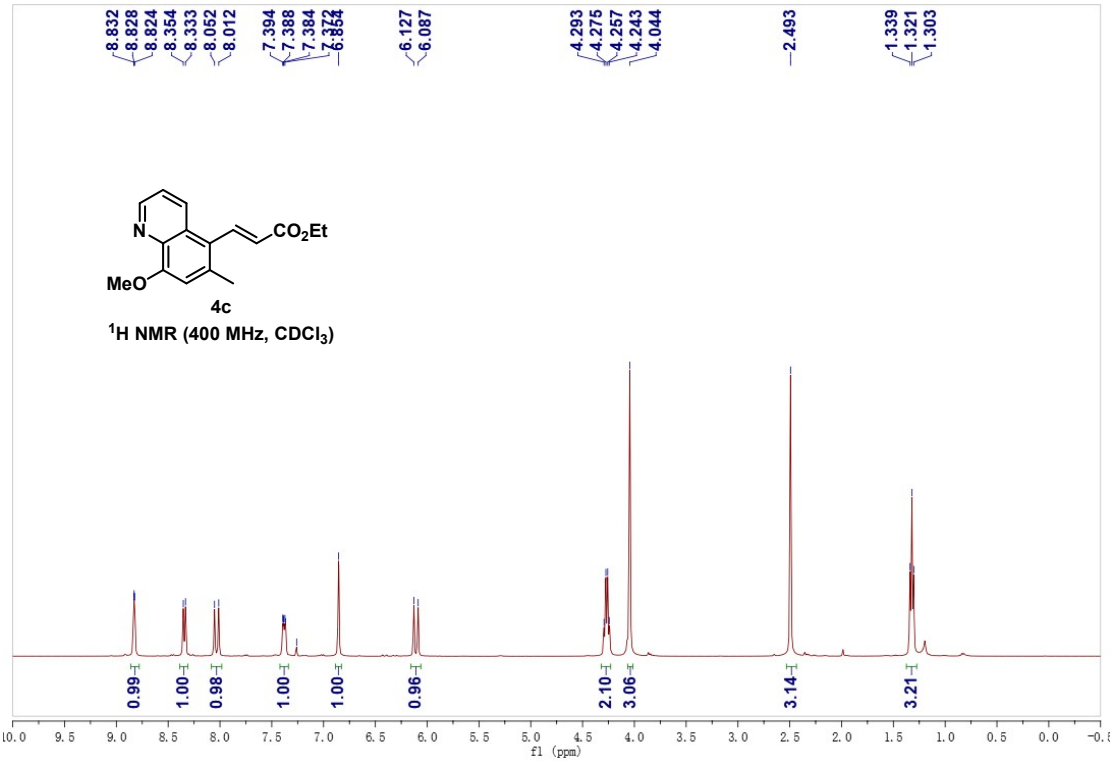
NMR Spectra:


7.863
7.822
6.896
6.077
6.036
4.303
4.285
4.267
4.249
2.334
2.286
1.366
1.349
1.331
CO2Et
4a
1H NMR (400 MHz, CDCl3)
1.00
1.97
1.00
2.03
6.09
3.02
3.06
f1 (ppm)


166.91
143.07
138.15
136.71
130.85
129.05
123.08
77.32
77.00
76.68
60.35
20.99
20.93
14.24
CO2Et
4a
13C NMR (100 MHz, CDCl3)
f1 (ppm)

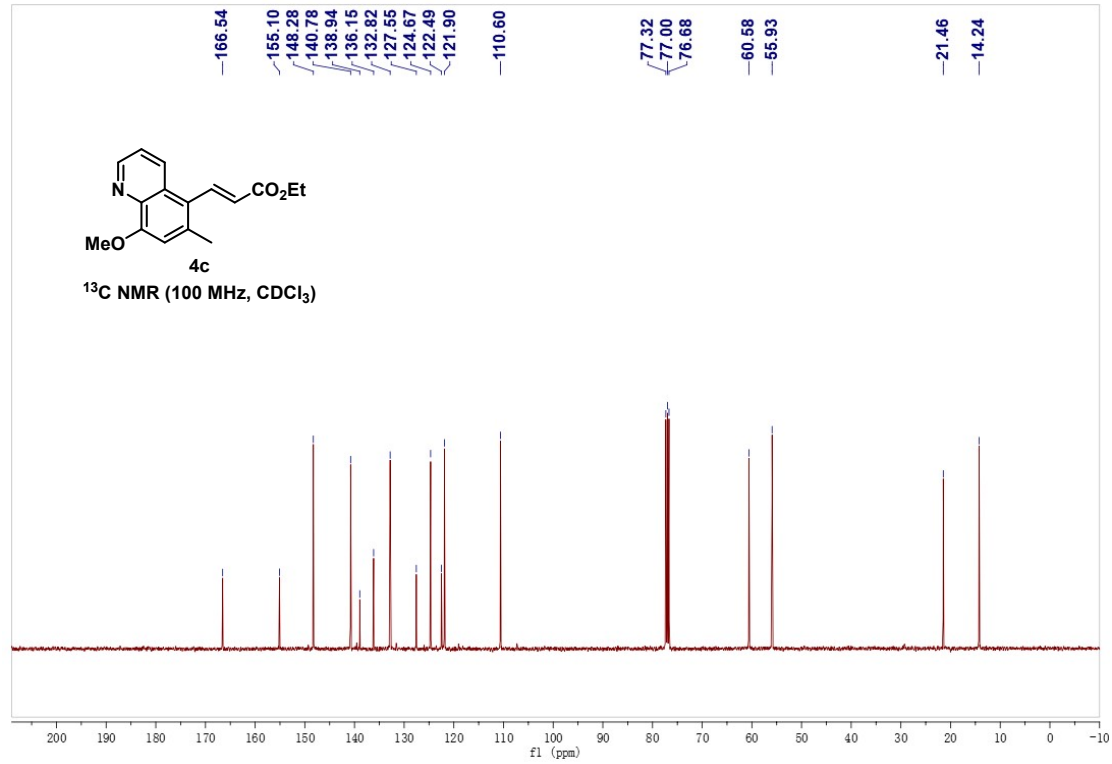

7.901
7.861
7.260
6.633
6.593
6.357
6.328
4.268
4.250
4.233
4.215
3.844
3.802
2.428
1.340
1.322
1.305
OMe
CO2Et
MeO
4b
1H NMR (400 MHz, CDCl3)
0.98
0.93
2.00
2.08
3.06
3.02
3.09
3.13
f1 (ppm)


168.51
161.09
160.93
141.42
138.25
119.06
115.18
107.50
96.17
77.32
77.00
76.68
60.01
55.29
55.16
21.45
14.31
OMe
CO2Et
MeO
4b
13C NMR (100 MHz, CDCl3)
f1 (ppm)



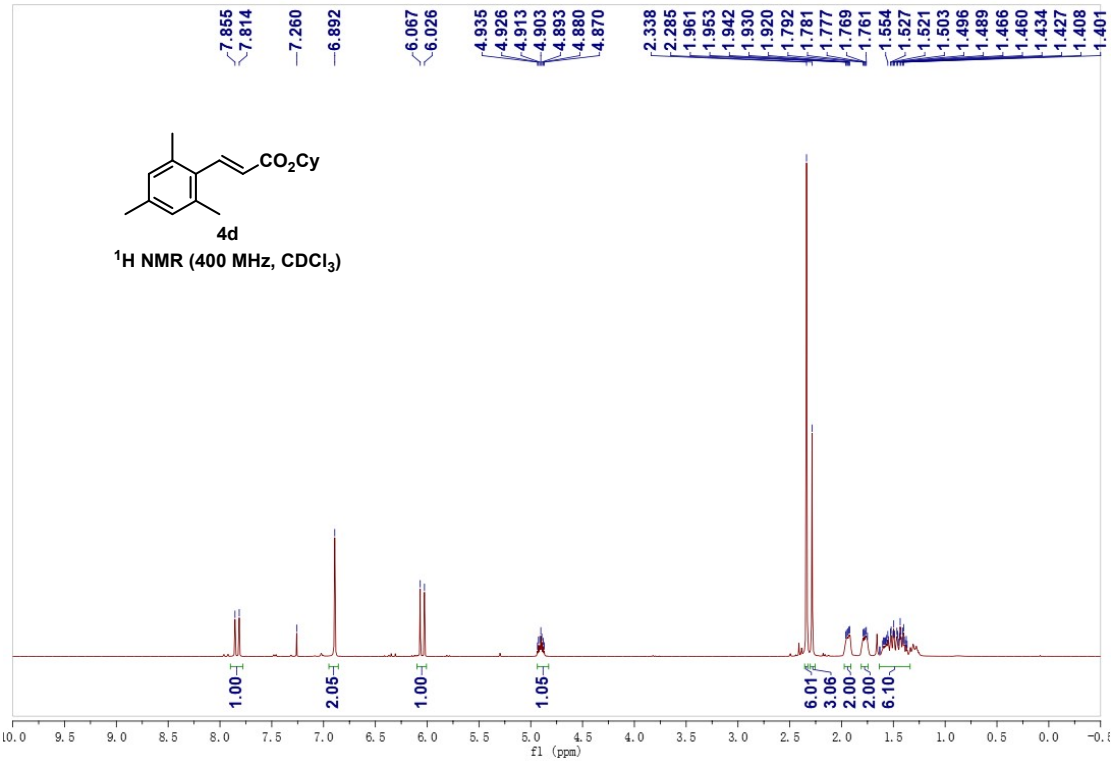
4c

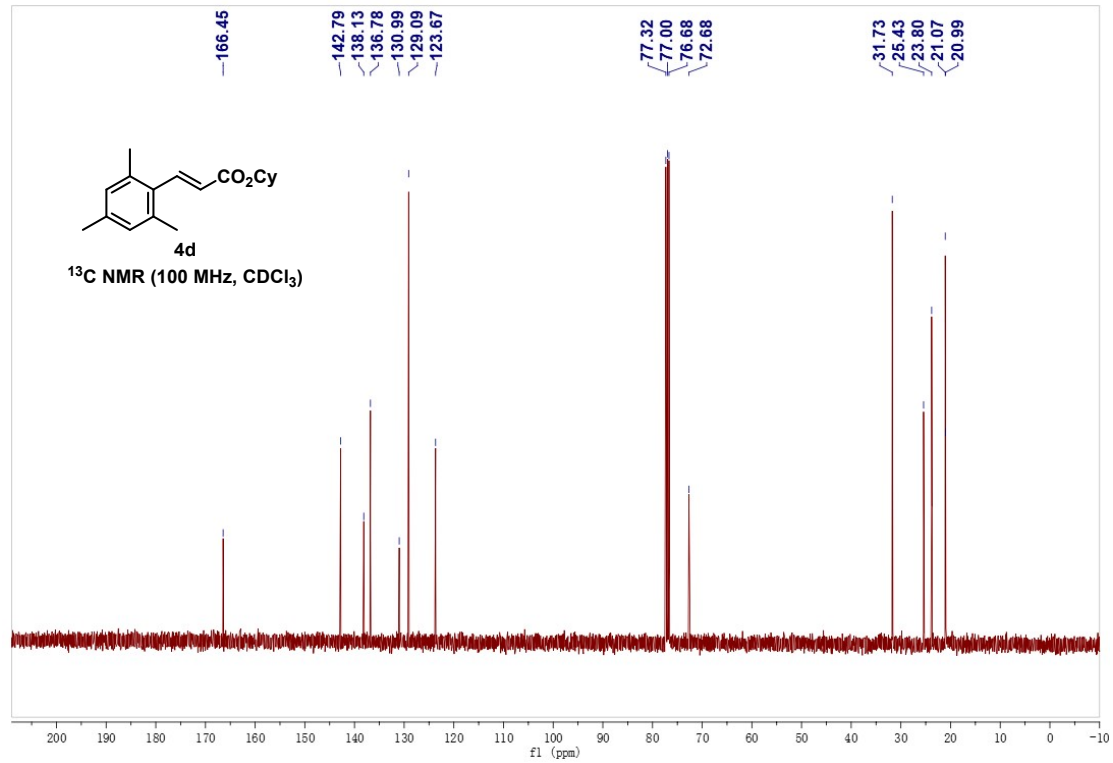
^{1}H NMR (400 MHz, $CDCl_3$)

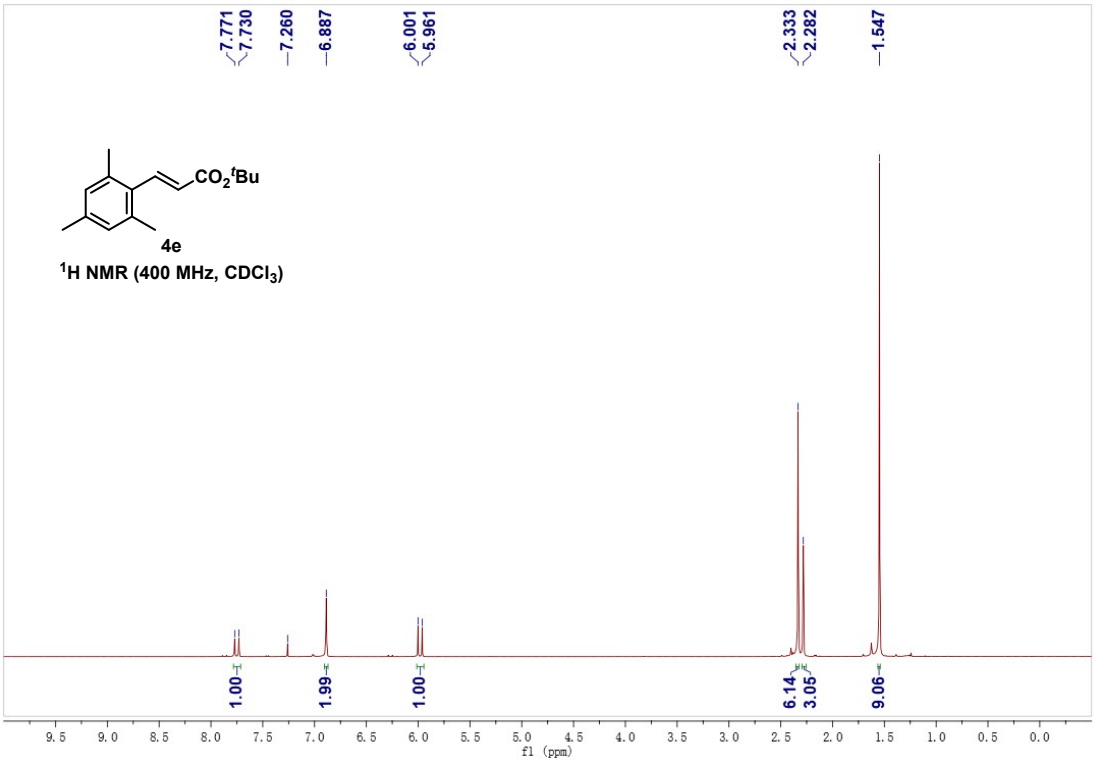


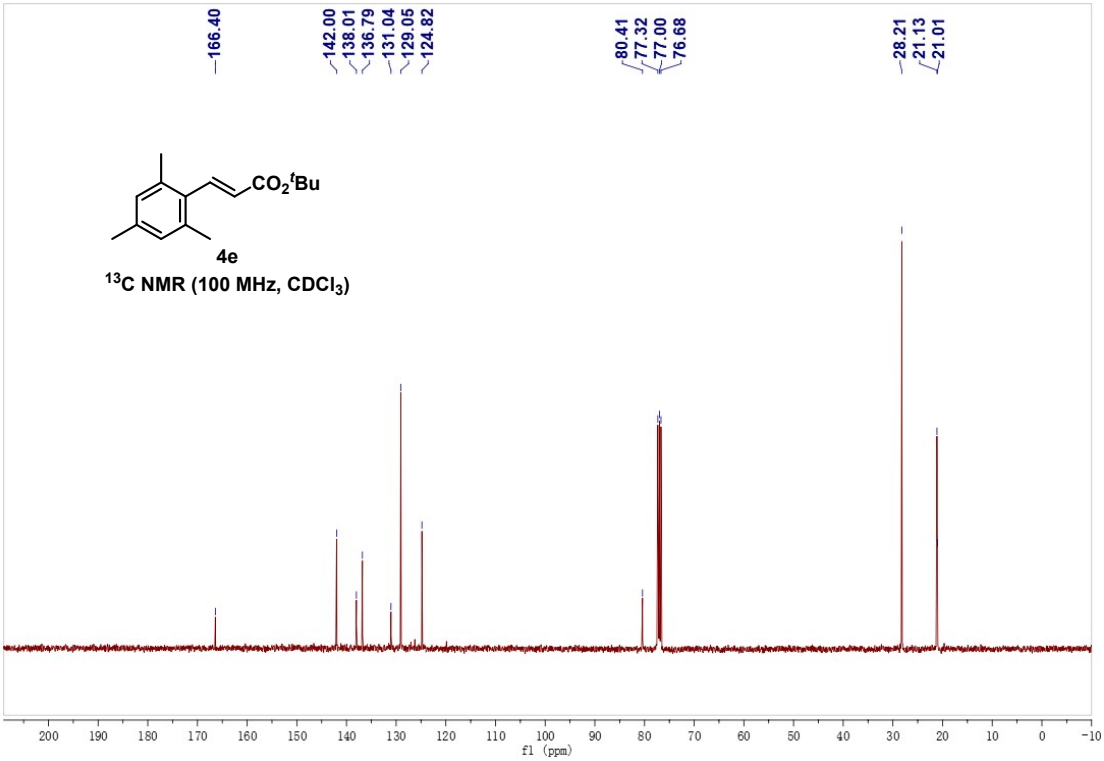
4c

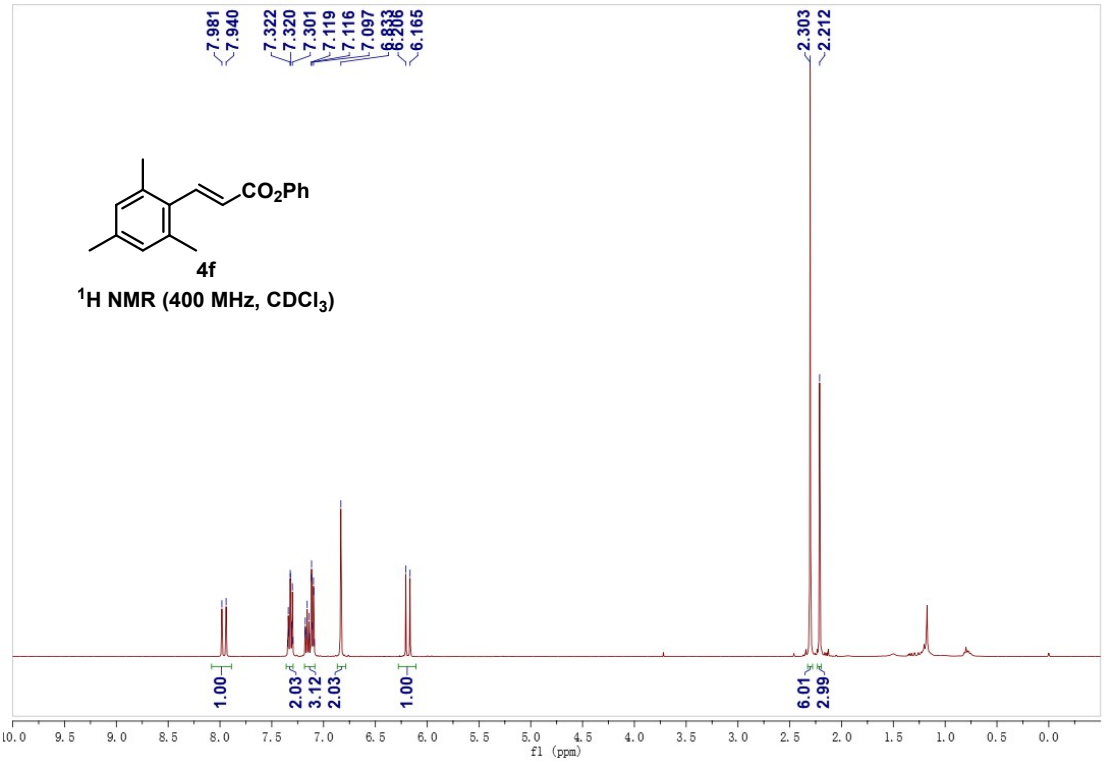
^{13}C NMR (100 MHz, $CDCl_3$)


7.855
7.814
7.260
6.892
6.067
6.026
4.935
4.926
4.913
4.903
4.893
4.880
4.870
2.338
2.285
1.961
1.953
1.942
1.930
1.920
1.792
1.781
1.777
1.769
1.761
1.554
1.527
1.521
1.503
1.496
1.489
1.466
1.460
1.434
1.427
1.408
1.401
CO2Cy
4d
1H NMR (400 MHz, CDCl3)
1.00
2.05
1.00
1.05
6.01
3.06
2.00
2.00
6.10
f1 (ppm)


166.45
142.79
138.13
136.78
130.99
129.09
123.67
77.32
77.00
76.68
72.68
31.73
25.43
23.80
21.07
20.99
CO2Cy
4d
13C NMR (100 MHz, CDCl3)
f1 (ppm)

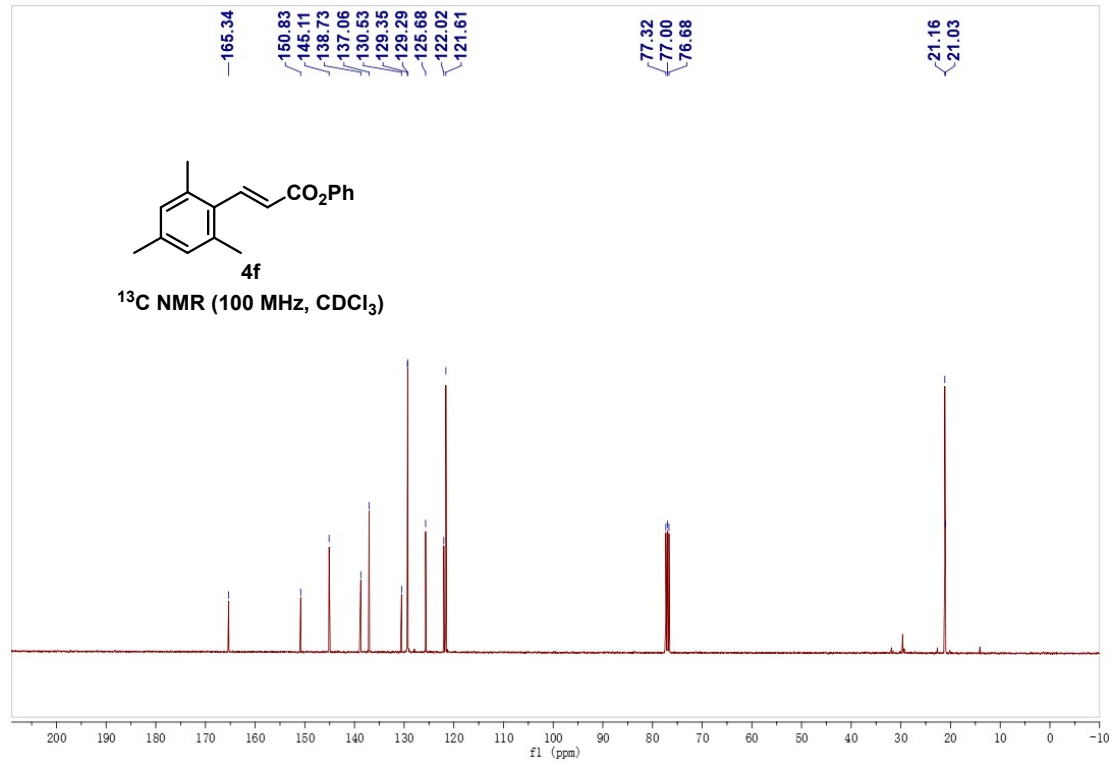

7.771
7.730
7.260
6.887
6.001
5.961
2.333
2.282
1.547
CO2tBu
4e
1H NMR (400 MHz, CDCl3)
1.00
1.99
1.00
6.14
3.05
9.06
f1 (ppm)


166.40
142.00
138.01
136.79
131.04
129.05
124.82
80.41
77.32
77.00
76.68
28.21
21.13
21.01
CO2tBu
4e
13C NMR (100 MHz, CDCl3)
f1 (ppm)



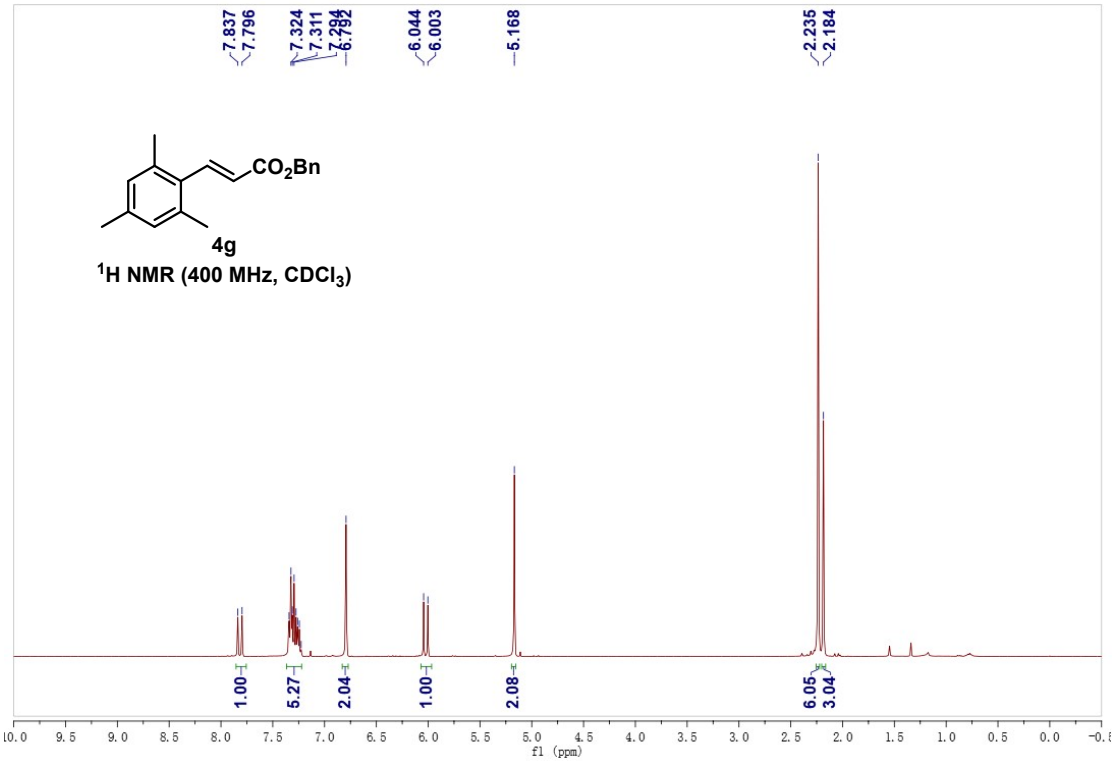
4f

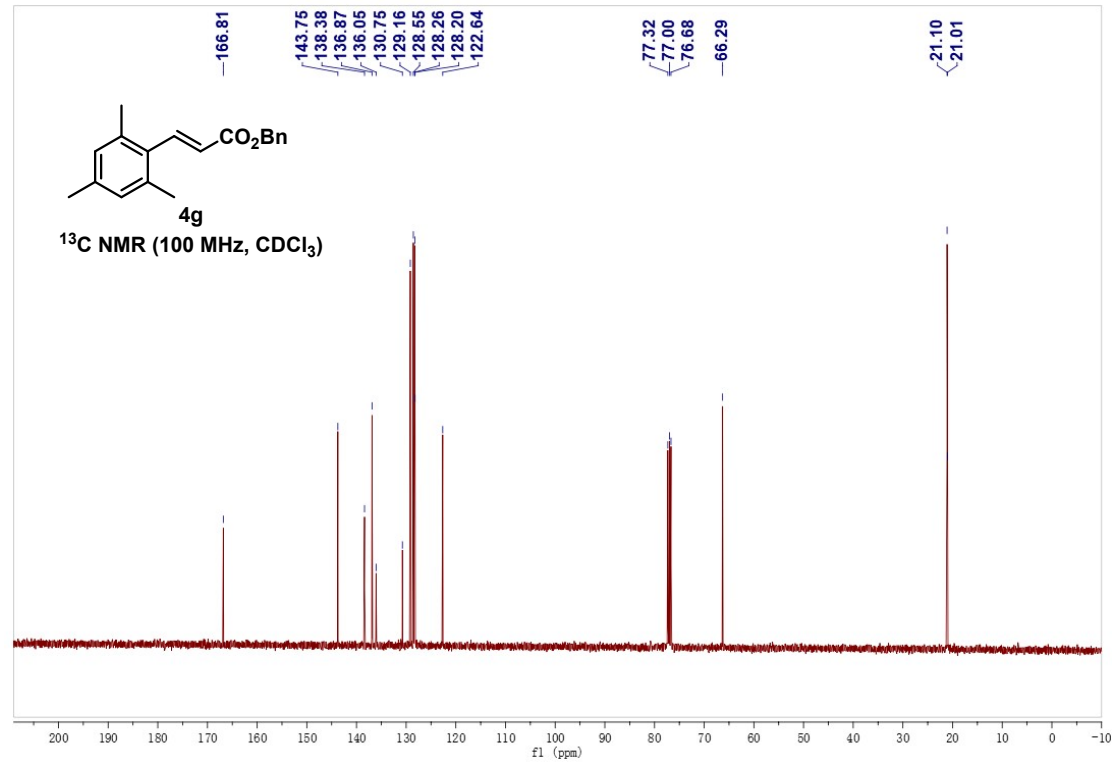
^{1}H NMR (400 MHz, $CDCl_3$)

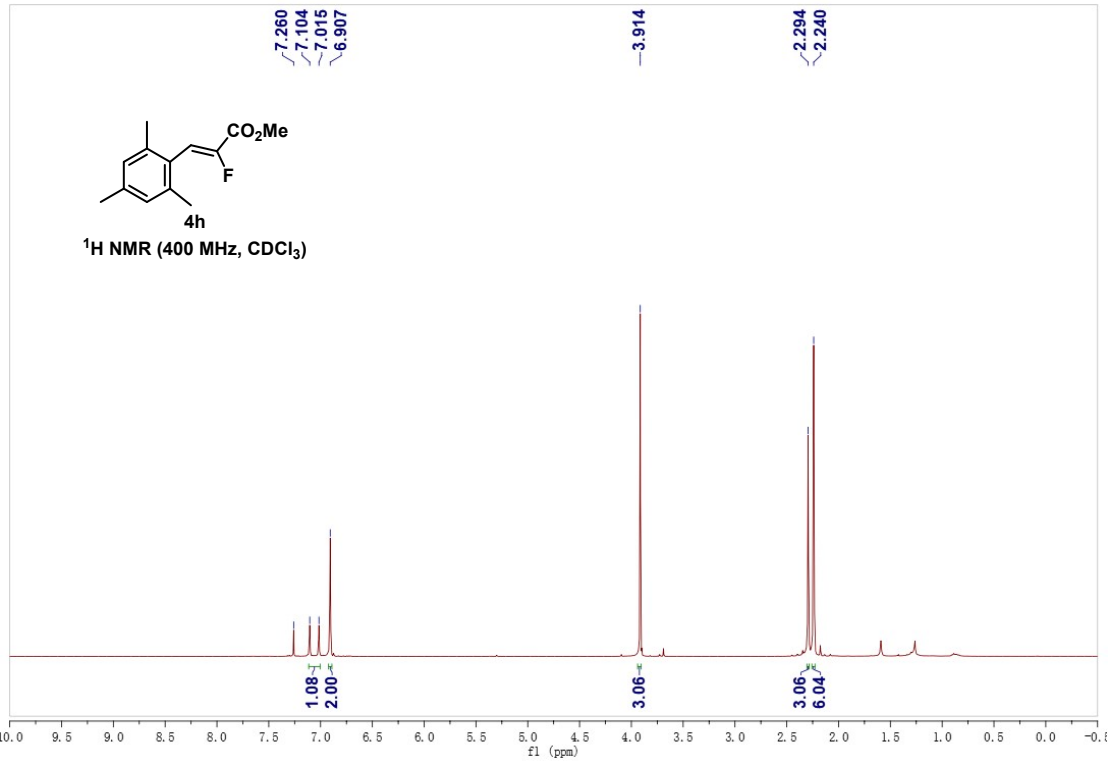


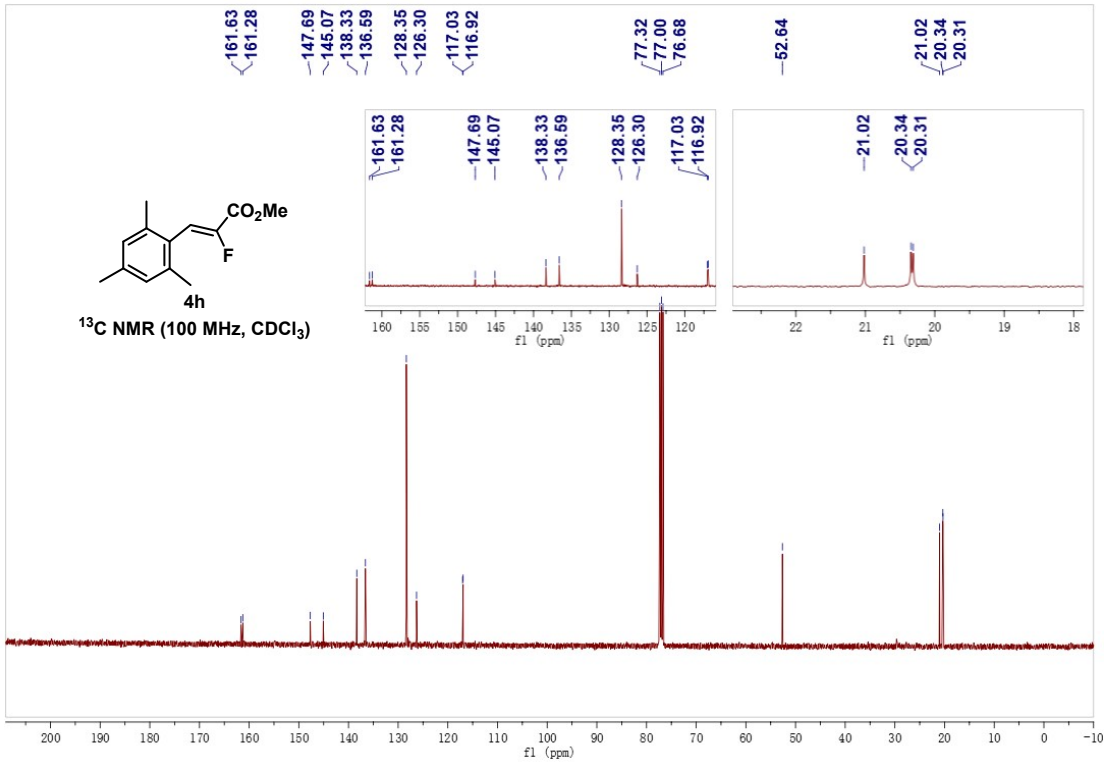
4f

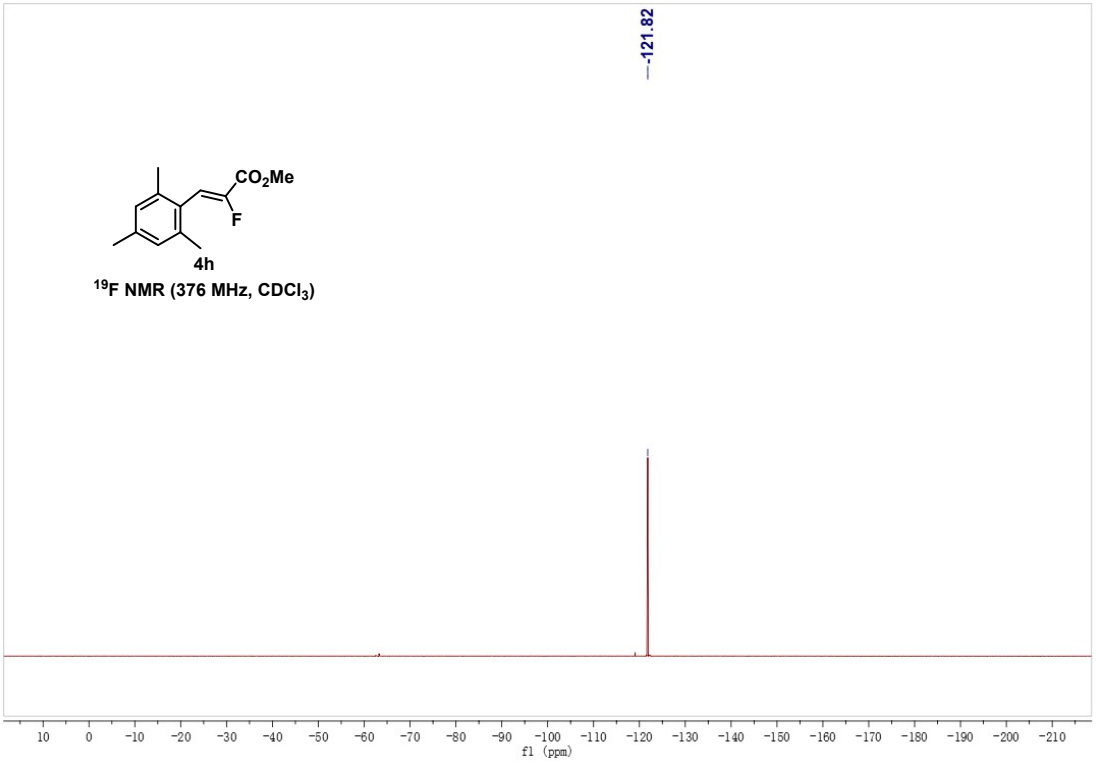
^{13}C NMR (100 MHz, $CDCl_3$)


7.837
7.796
7.324
7.311
7.294
6.792
6.044
6.003
5.168
2.235
2.184
CO2Bn
4g
1H NMR (400 MHz, CDCl3)
1.00
5.27
2.04
1.00
2.08
6.05
3.04
f1 (ppm)


166.81
143.75
138.38
136.87
136.05
130.75
129.16
128.55
128.26
128.20
122.64
77.32
77.00
76.68
66.29
21.10
21.01
CO2Bn
4g
13C NMR (100 MHz, CDCl3)
f1 (ppm)

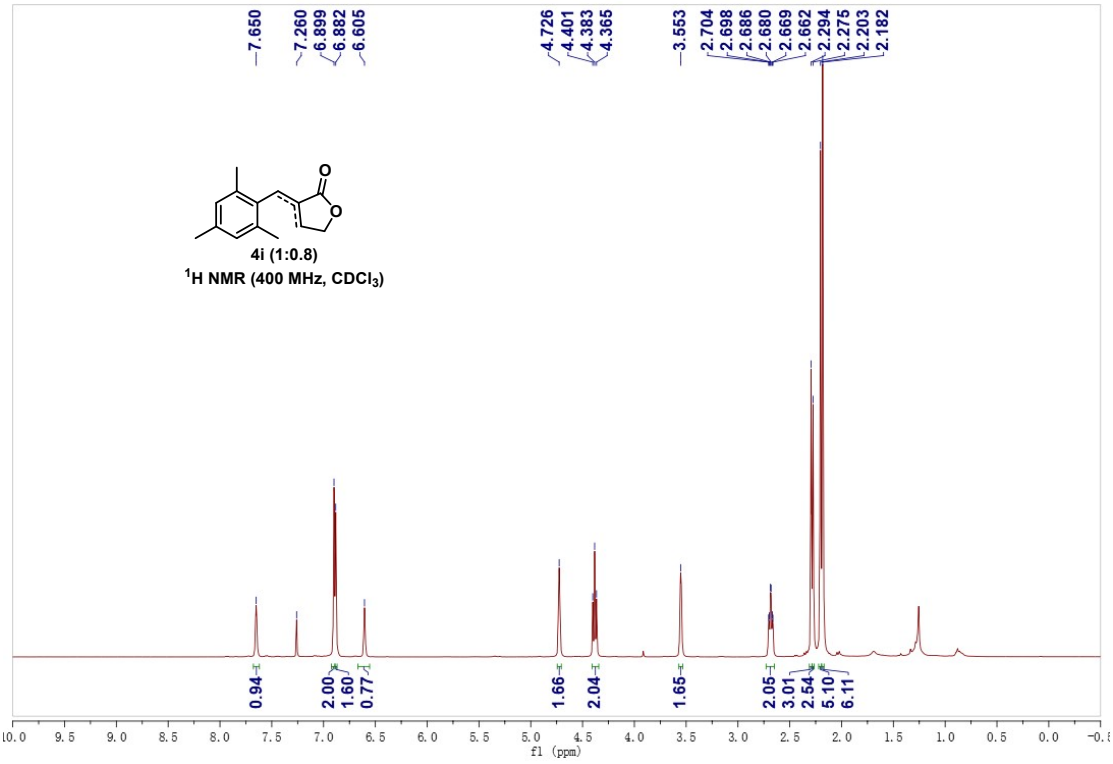

7.260
7.104
7.015
6.907
3.914
2.294
2.240
CO2Me
F
4h
1H NMR (400 MHz, CDCl3)
1.08
2.00
3.06
3.06
6.04
f1 (ppm)


161.63
161.28
147.69
145.07
138.33
136.59
128.35
126.30
117.03
116.92
77.32
77.00
76.68
52.64
21.02
20.34
20.31
CO2Me
F
4h
13C NMR (100 MHz, CDCl3)
f1 (ppm)



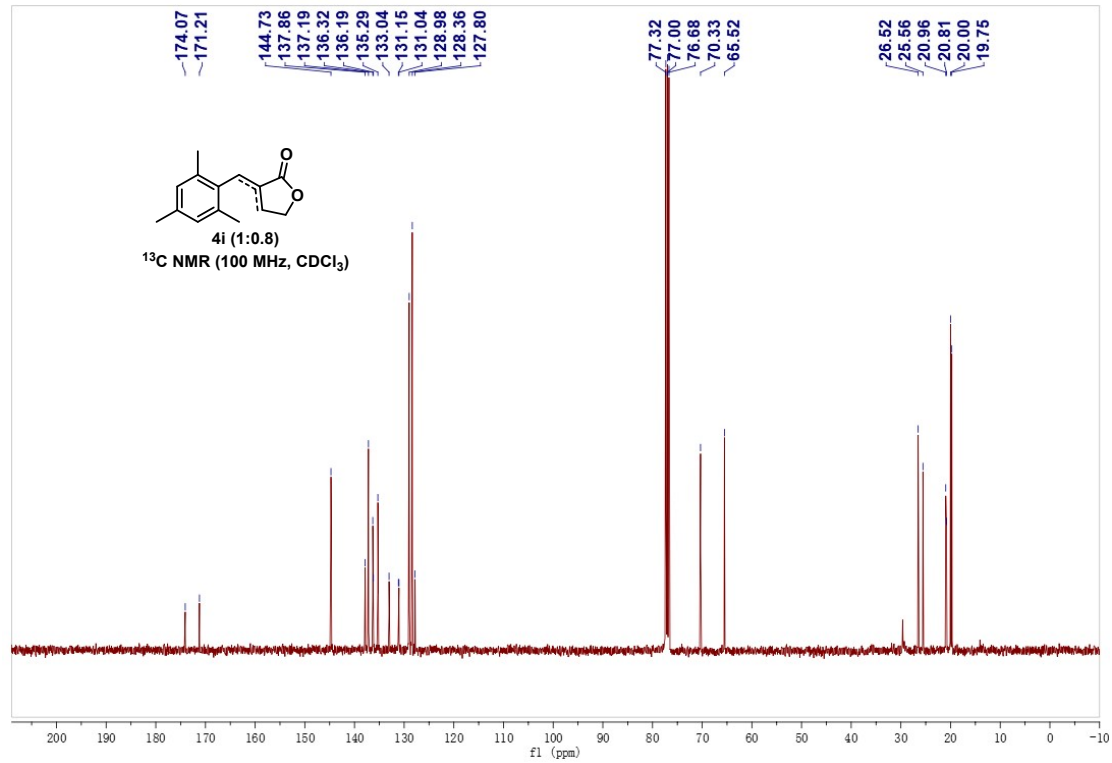
4h

^{19}F NMR (376 MHz, $CDCl_3$)



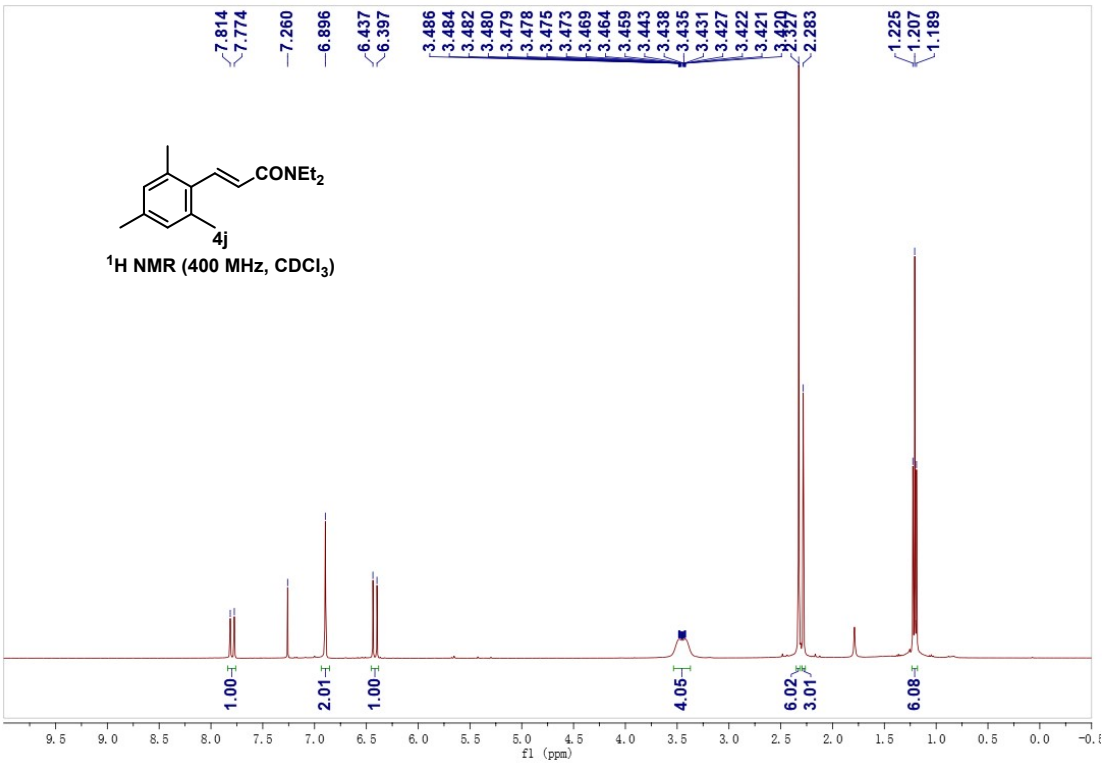
4i (1:0.8)

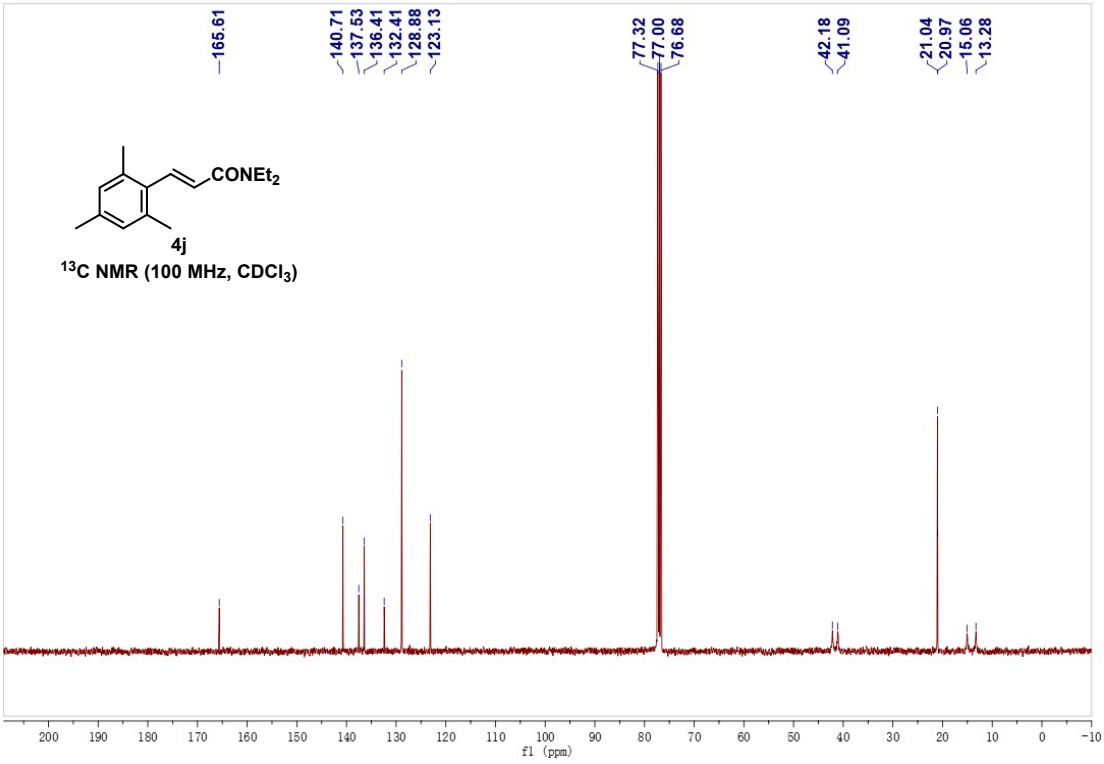
^{1}H NMR (400 MHz, $CDCl_3$)

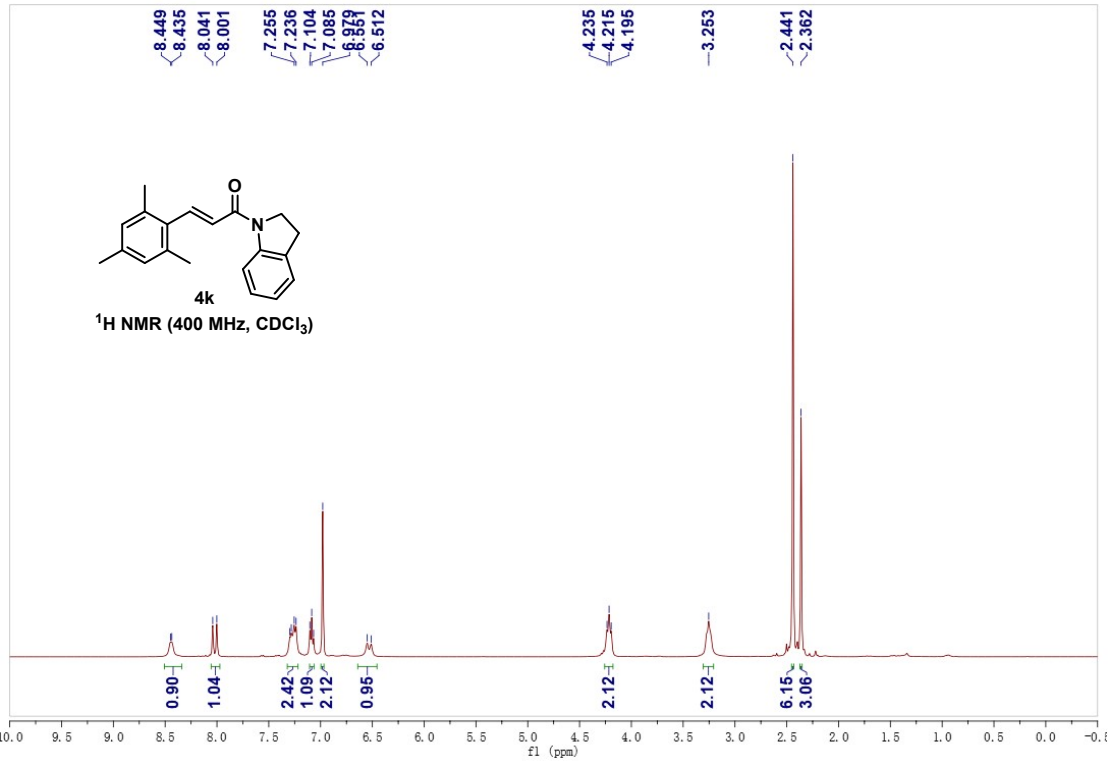


4i (1:0.8)

^{13}C NMR (100 MHz, $CDCl_3$)

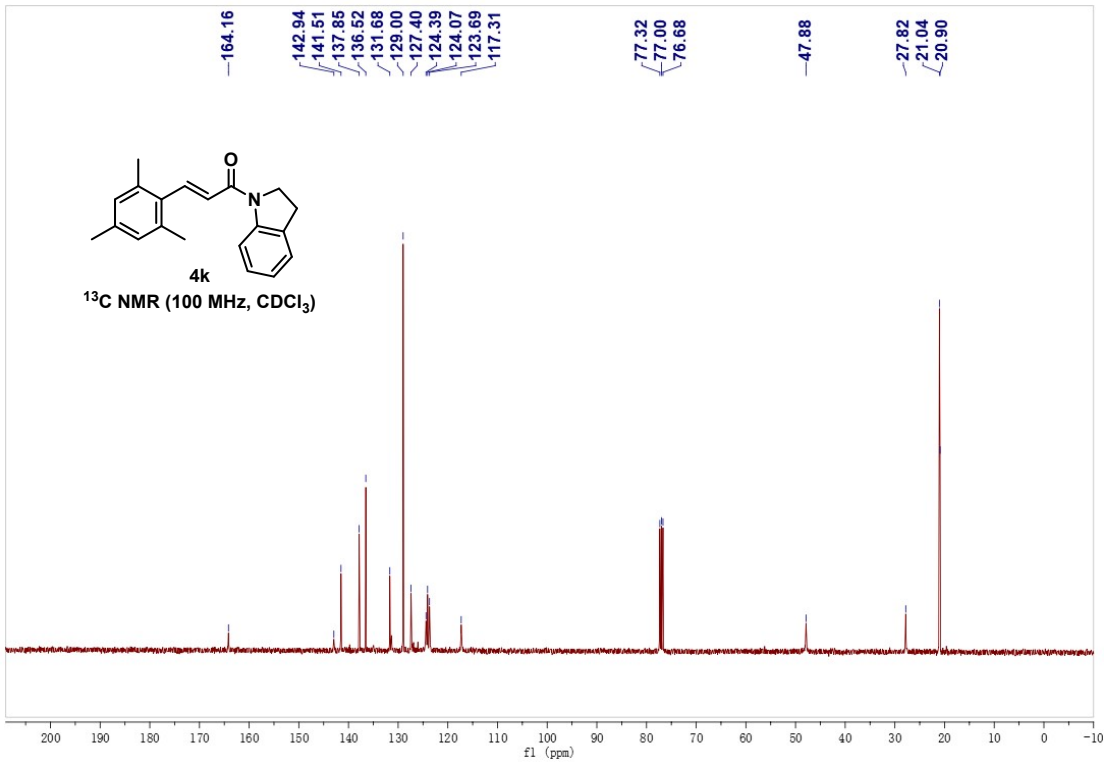

7.814
7.774
7.260
6.896
6.437
6.397
3.486
3.484
3.482
3.480
3.479
3.478
3.475
3.473
3.469
3.464
3.459
3.443
3.438
3.435
3.431
3.427
3.422
3.421
3.420
3.327
2.283
1.225
1.207
1.189
CONEt2
4j
1H NMR (400 MHz, CDCl3)
1.00
2.01
1.00
4.05
6.02
3.01
6.08
f1 (ppm)


165.61
140.71
137.53
136.41
132.41
128.88
123.13
77.32
77.00
76.68
42.18
41.09
21.04
20.97
15.06
13.28
CONEt2
4j
13C NMR (100 MHz, CDCl3)
f1 (ppm)



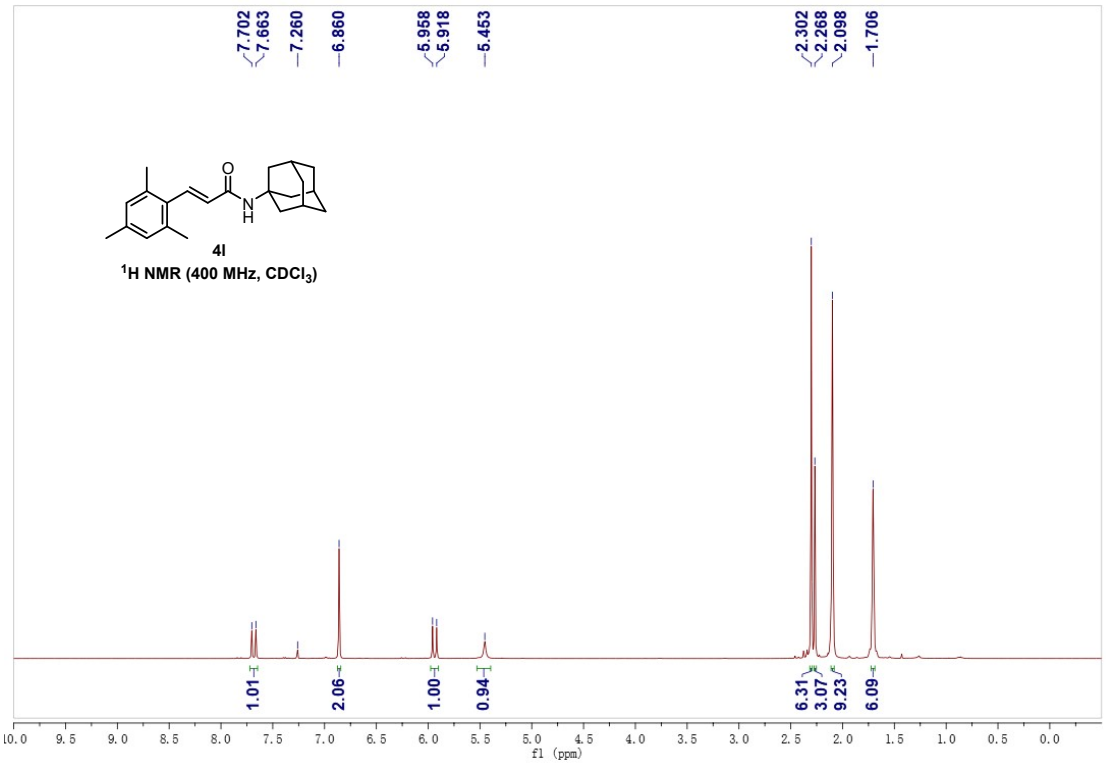
4k

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



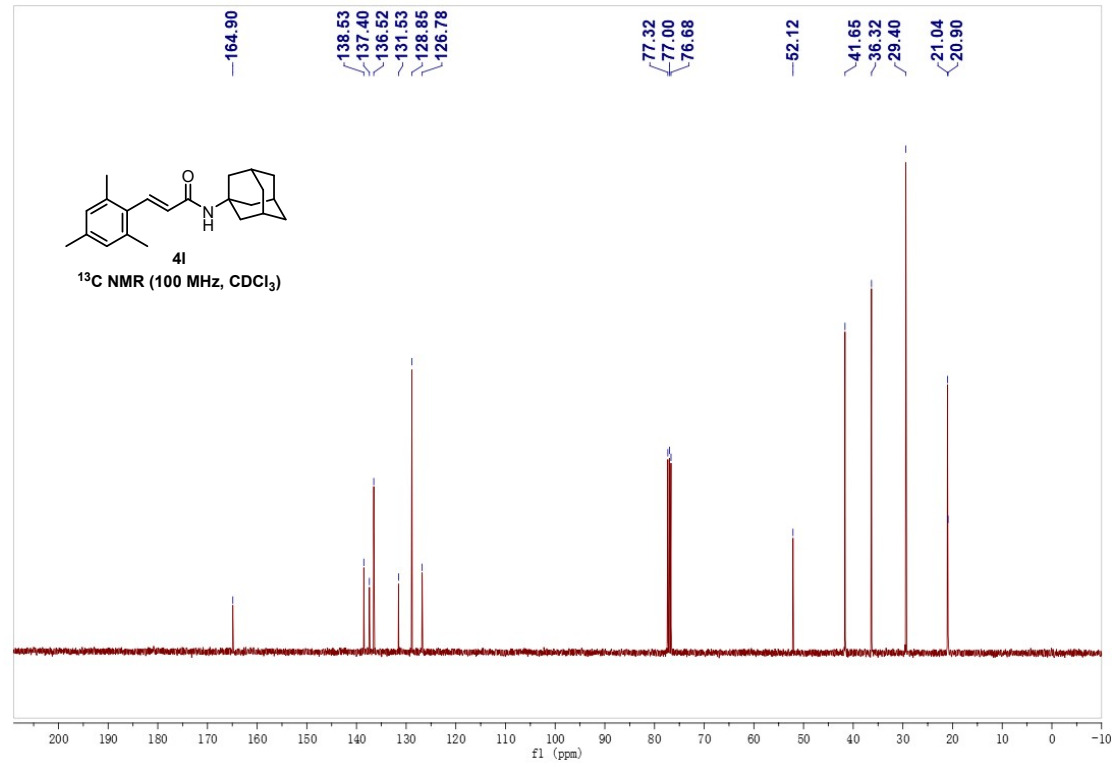
4k

^{13}C NMR (100 MHz, $CDCl_3$)



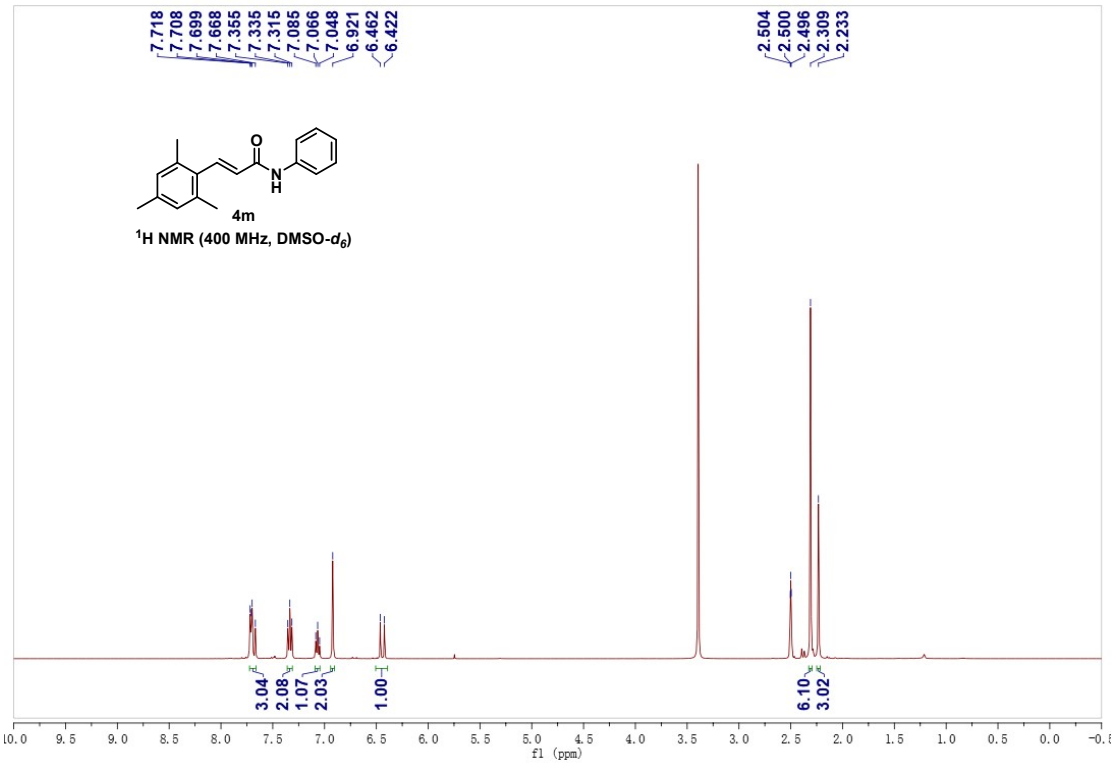
4l

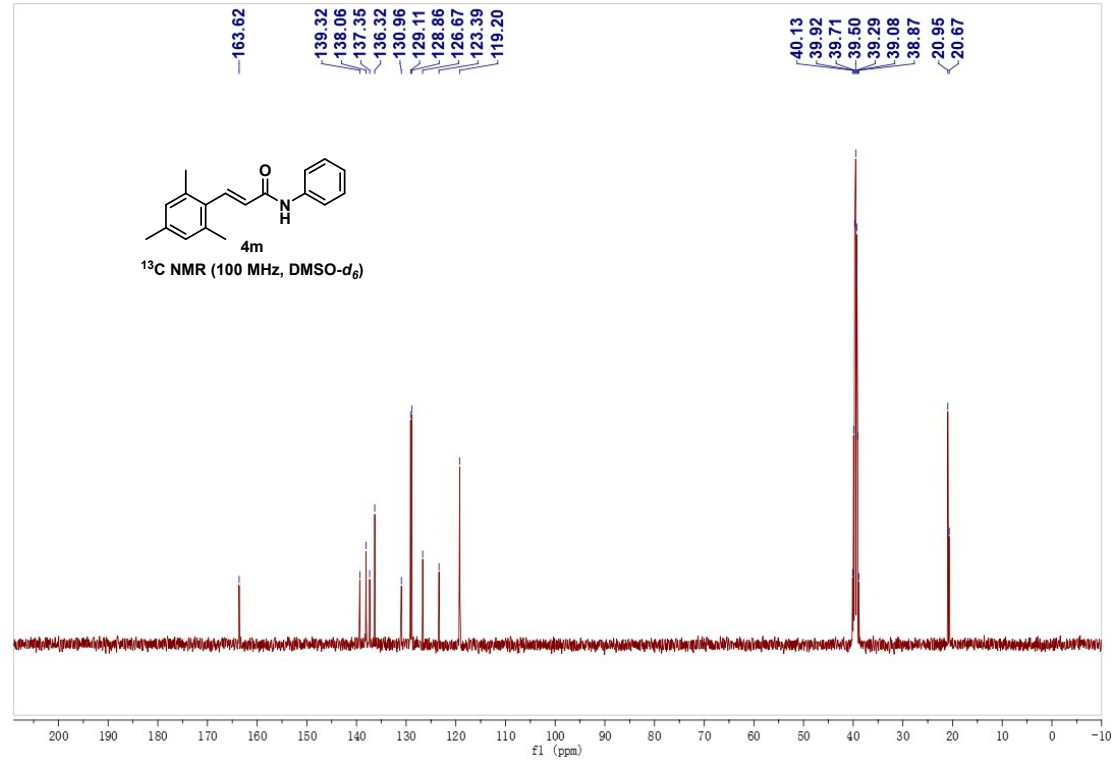
^{1}H NMR (400 MHz, $CDCl_3$)

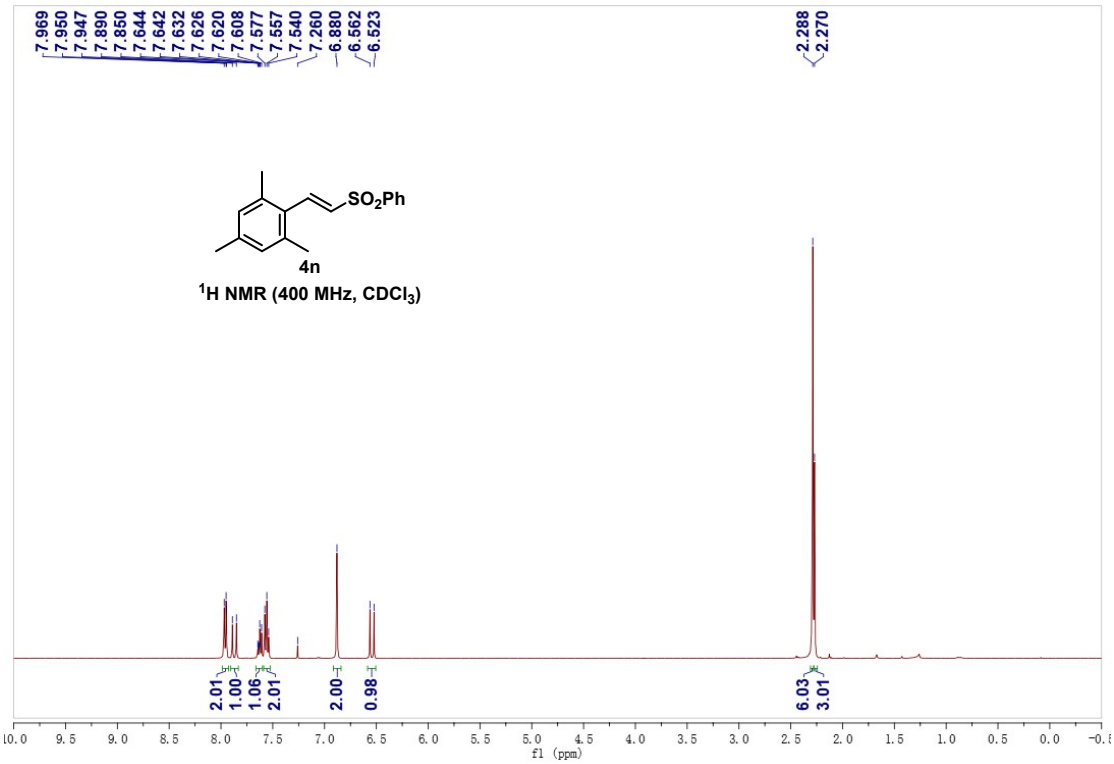


4l

^{13}C NMR (100 MHz, $CDCl_3$)

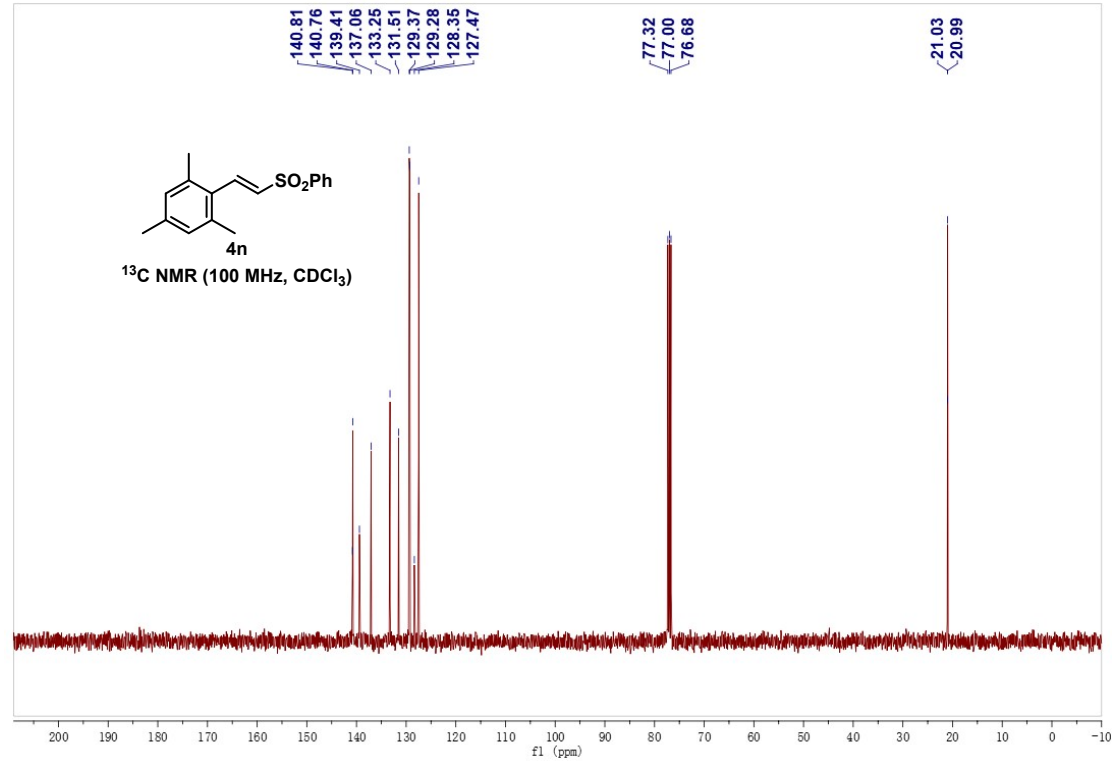

7.718
7.708
7.699
7.668
7.355
7.335
7.315
7.085
7.066
7.048
6.921
6.462
6.422
2.504
2.500
2.496
2.309
2.233
O
N
H
4m
3.04
2.08
1.07
2.03
1.00
6.10
3.02
f1 (ppm)


163.62
139.32
138.06
137.35
136.32
130.96
129.11
128.86
126.67
123.39
119.20
40.13
39.92
39.71
39.50
39.29
39.08
38.87
20.95
20.67
O
N
H
4m
f1 (ppm)



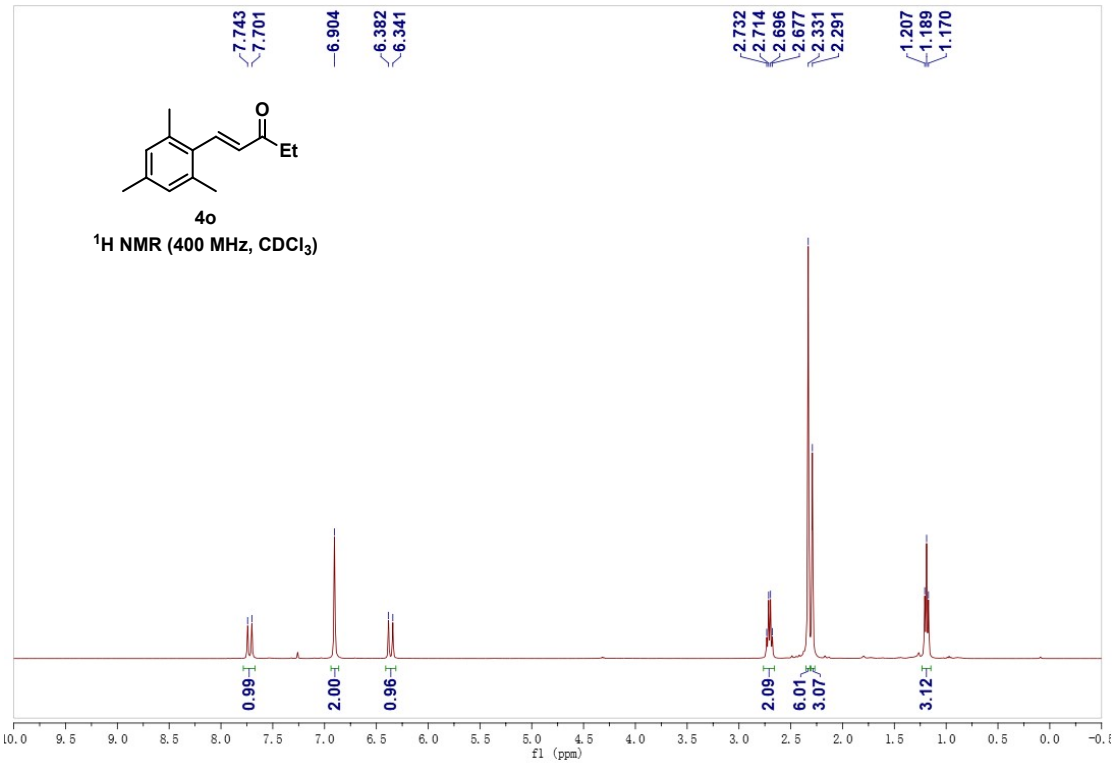
4n

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



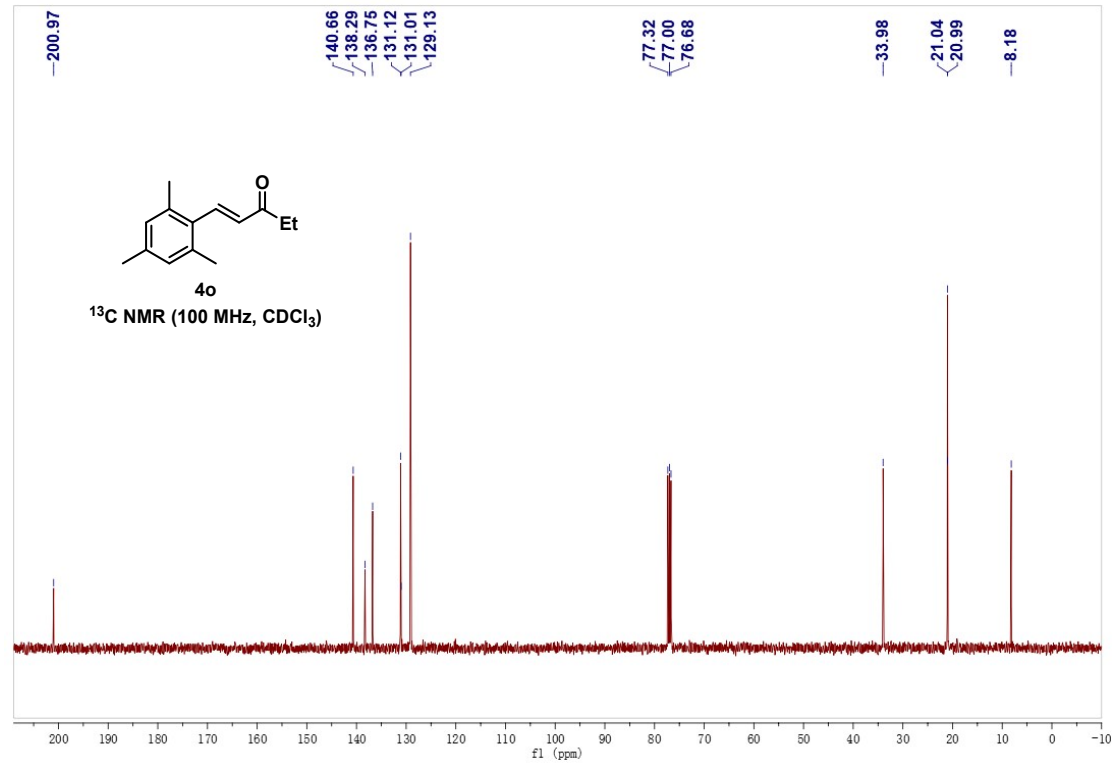
4n

^{13}C NMR (100 MHz, $CDCl_3$)



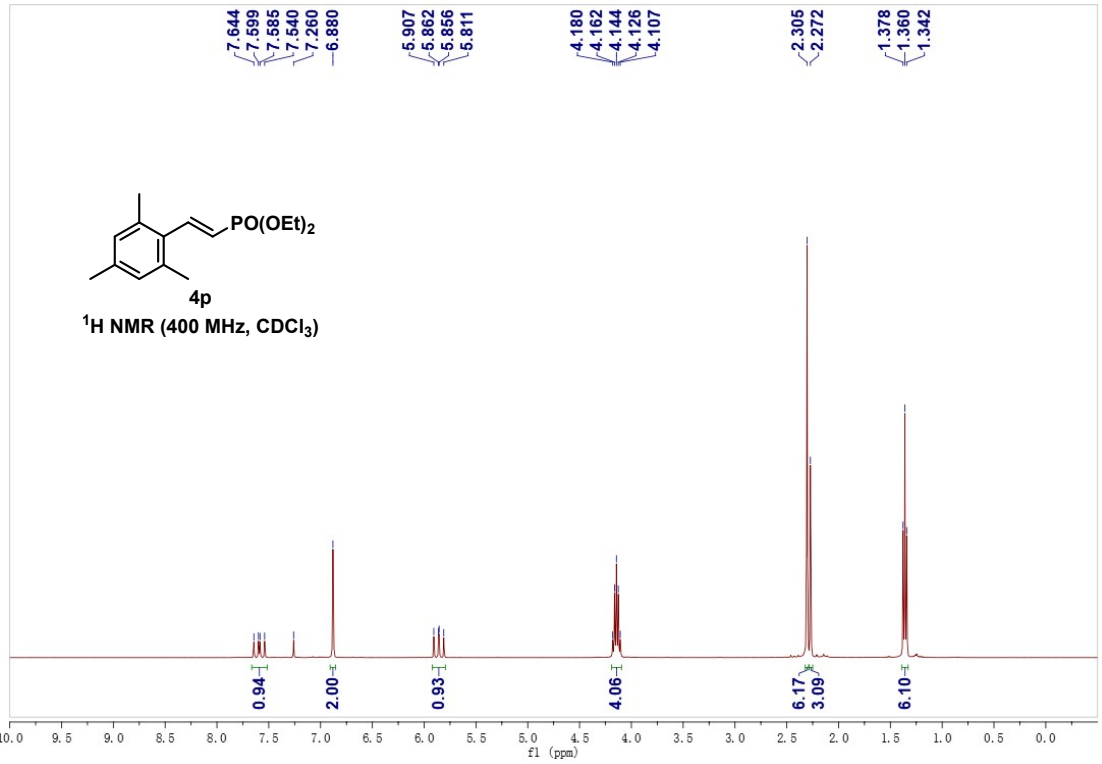
4o

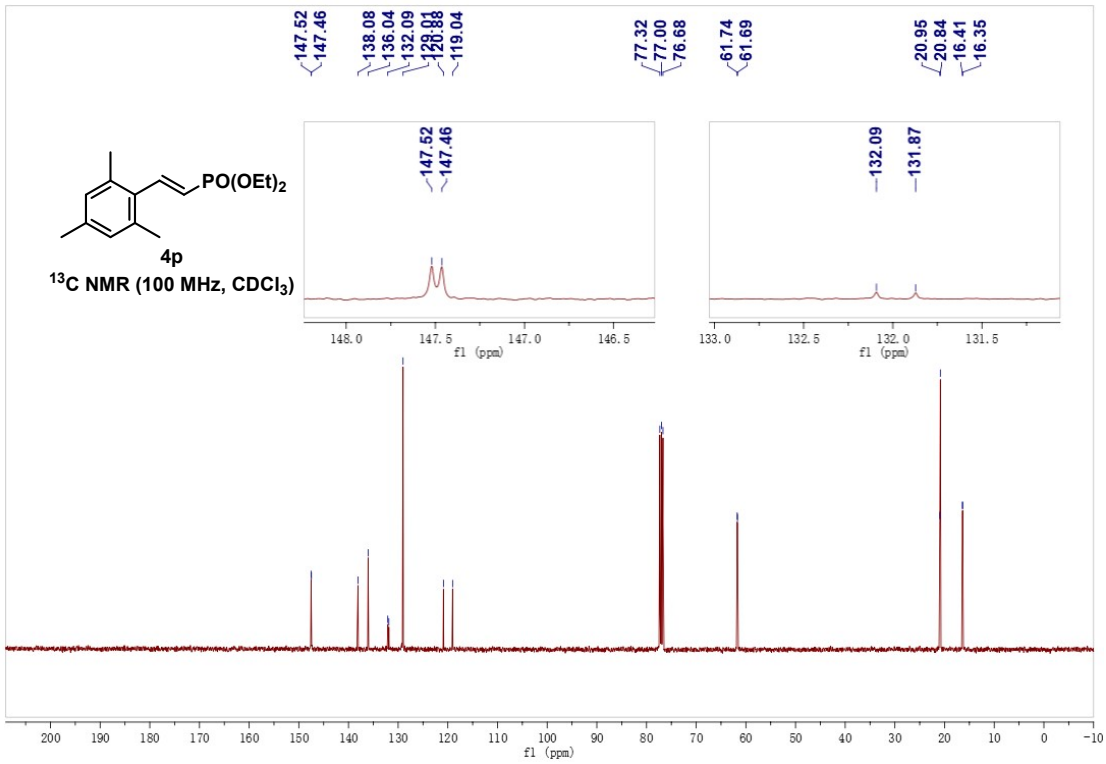
^{1}H NMR (400 MHz, $CDCl_3$)

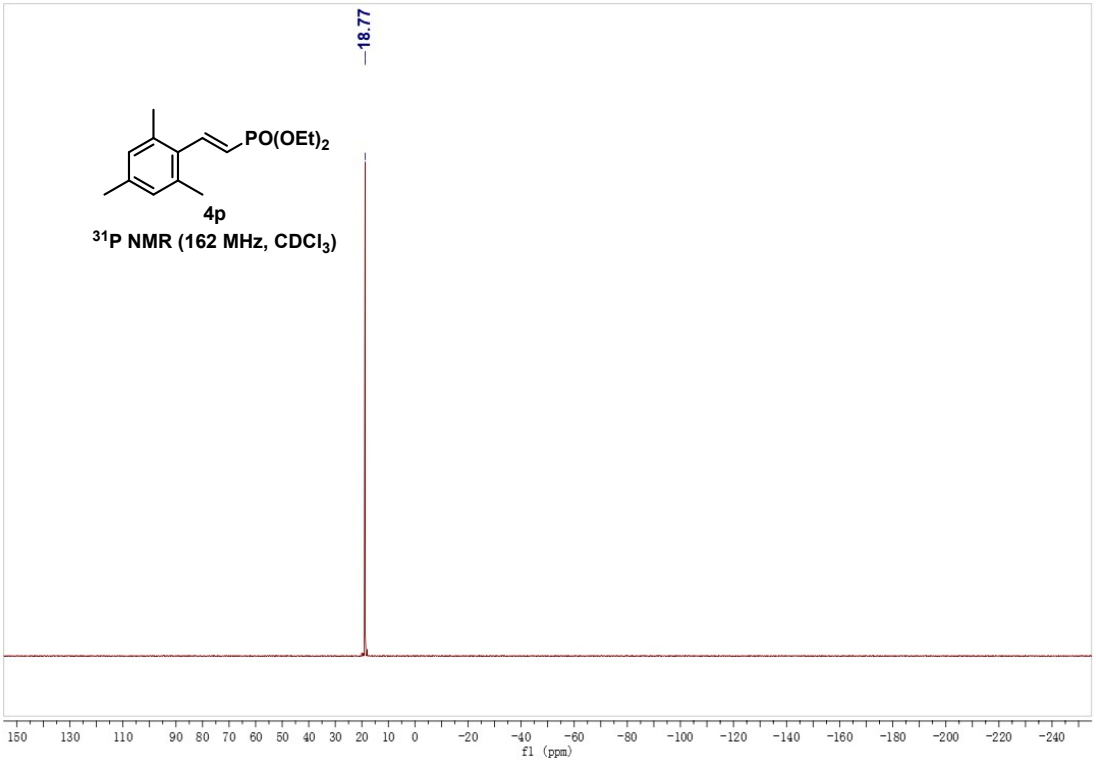


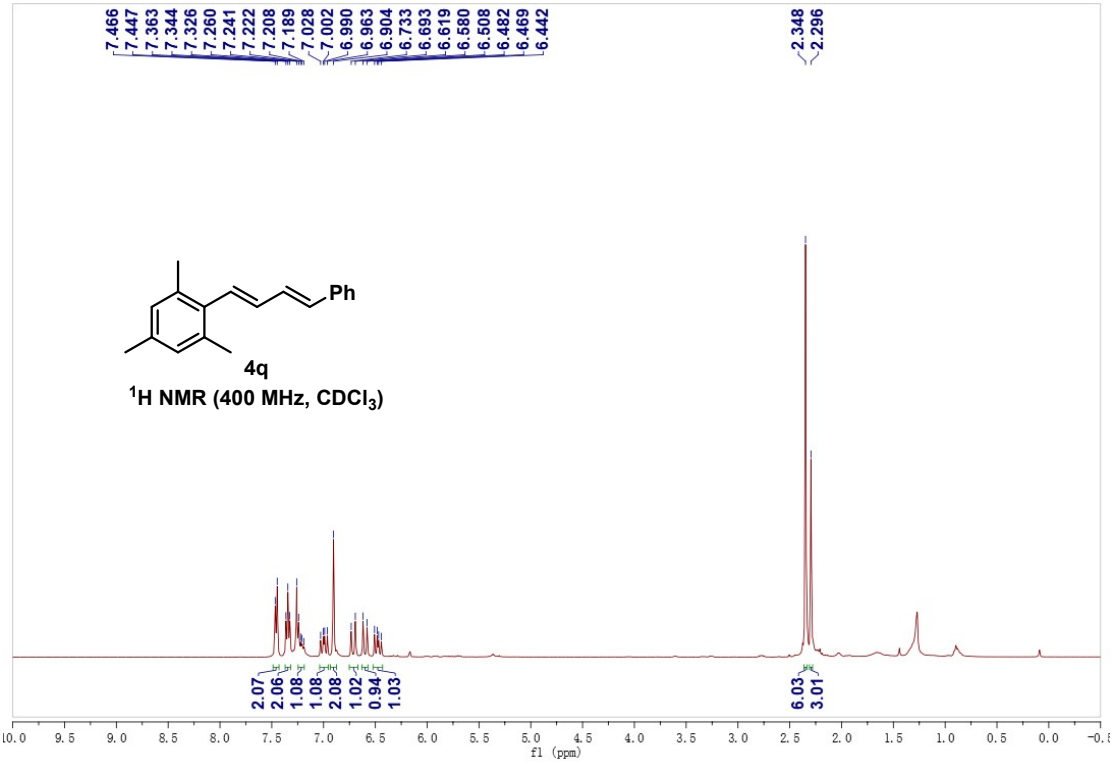
4o

^{13}C NMR (100 MHz, $CDCl_3$)


7.644
7.599
7.585
7.540
7.260
6.880
5.907
5.862
5.856
5.811
4.180
4.162
4.144
4.126
4.107
2.305
2.272
1.378
1.360
1.342
PO(OEt)2
4p
1H NMR (400 MHz, CDCl3)
0.94
2.00
0.93
4.06
6.17
3.09
6.10
f1 (ppm)

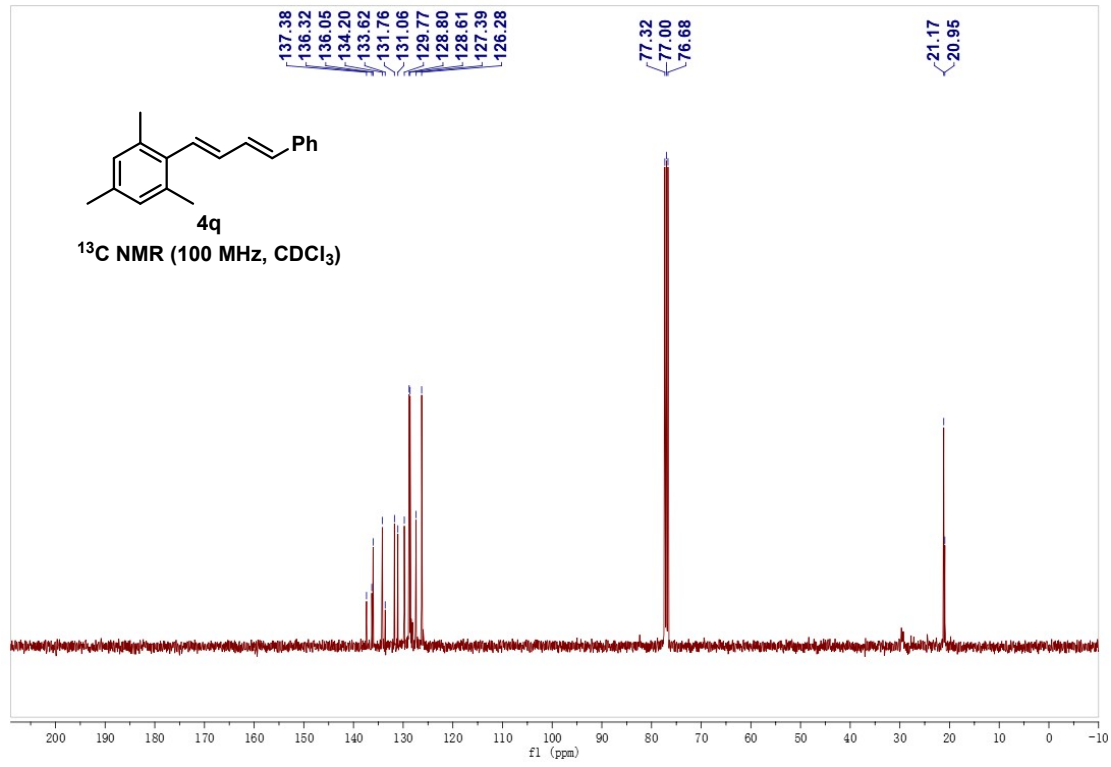

147.52
147.46
138.08
136.04
132.09
119.04
77.32
77.00
76.68
61.74
61.69
20.95
20.84
16.41
16.35
PO(OEt)2
4p
13C NMR (100 MHz, CDCl3)
f1 (ppm)


18.77
PO(OEt)2
4p
31P NMR (162 MHz, CDCl3)
150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)



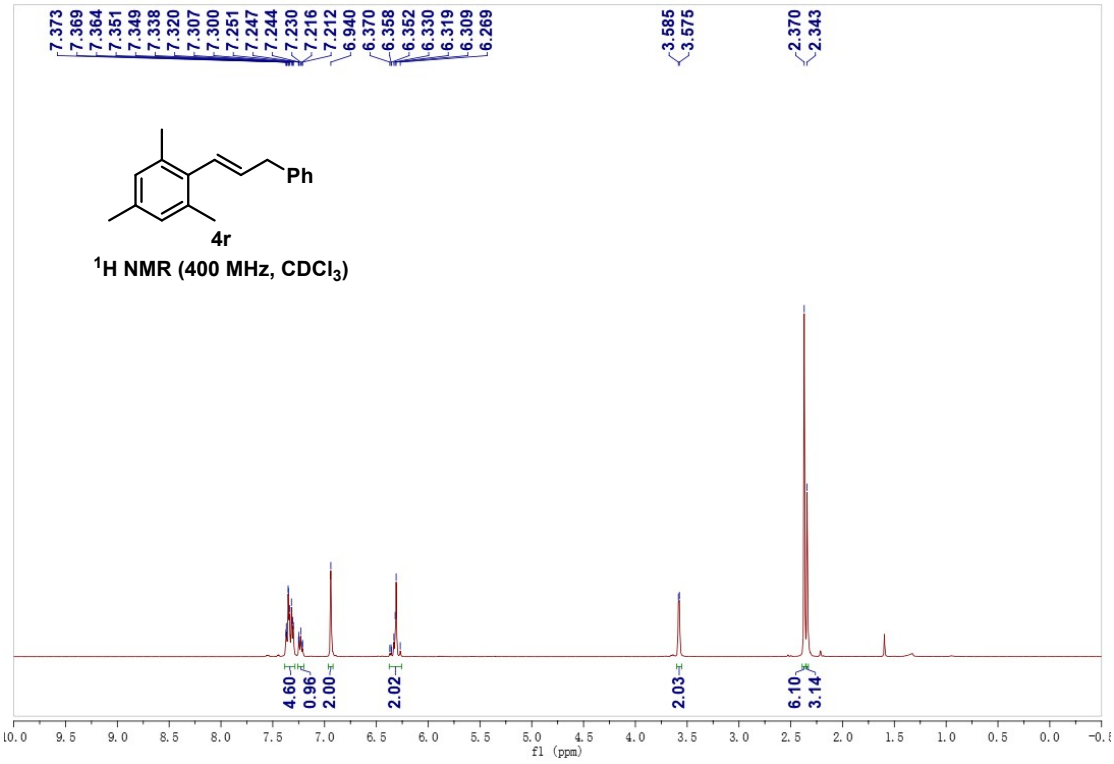
4q

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

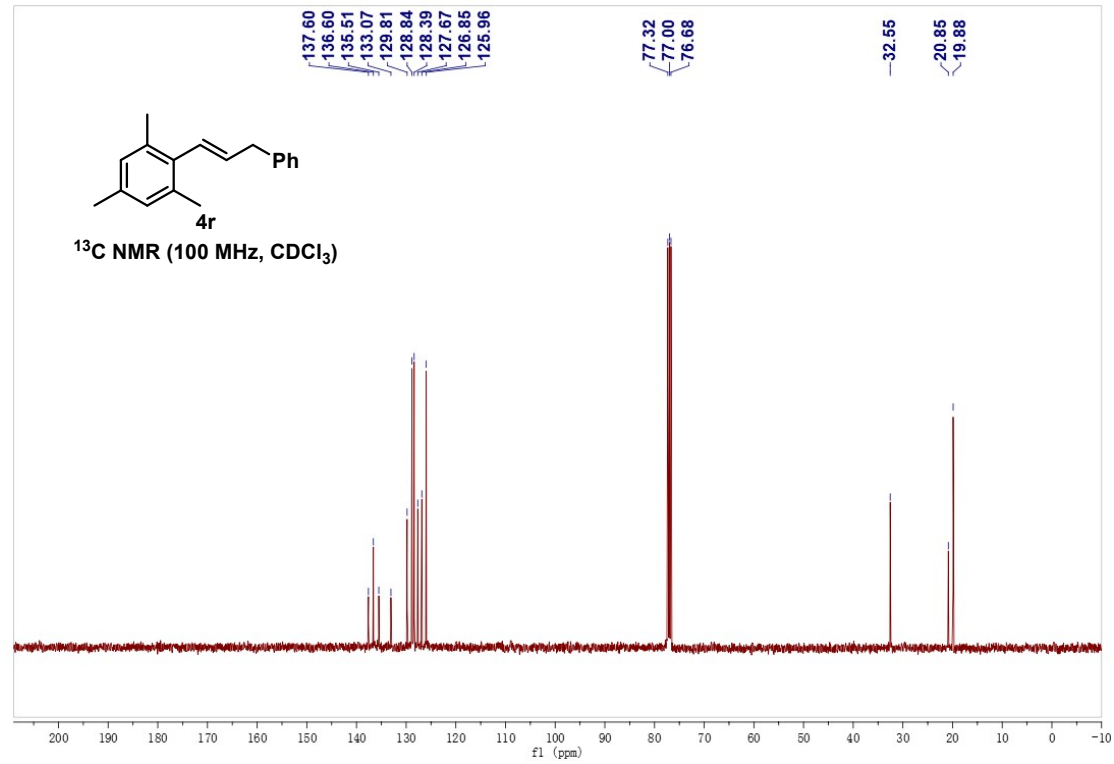


4q

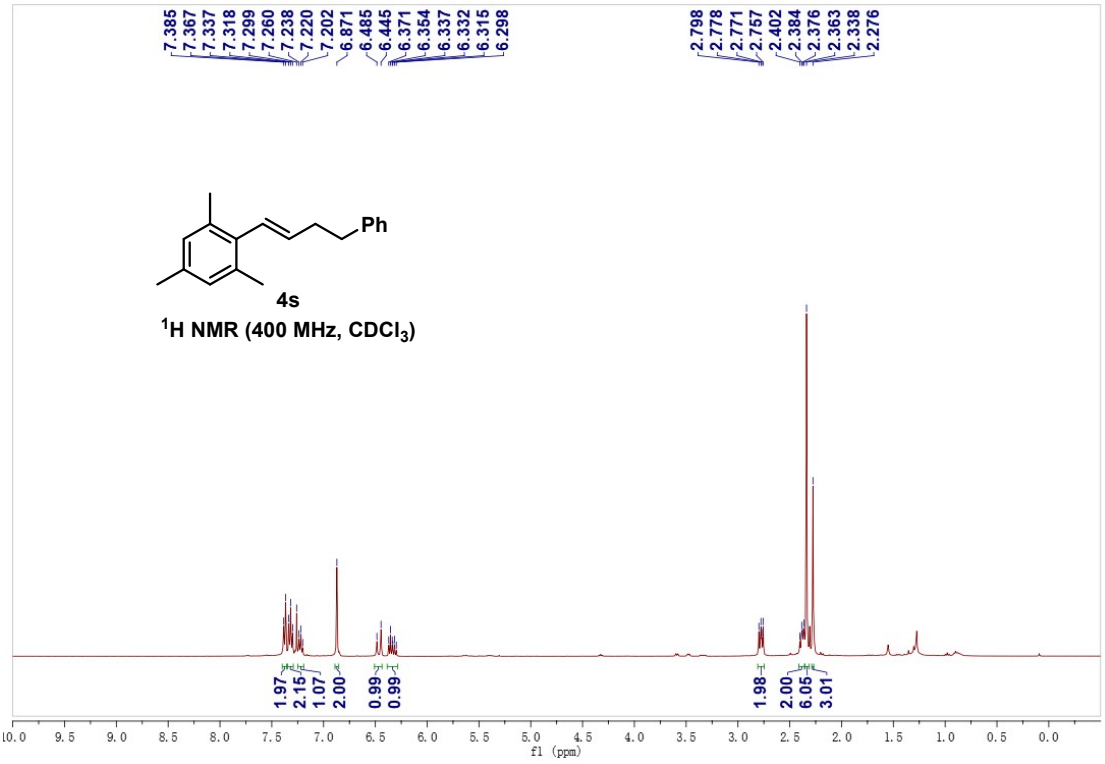
^{13}C NMR (100 MHz, $CDCl_3$)



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

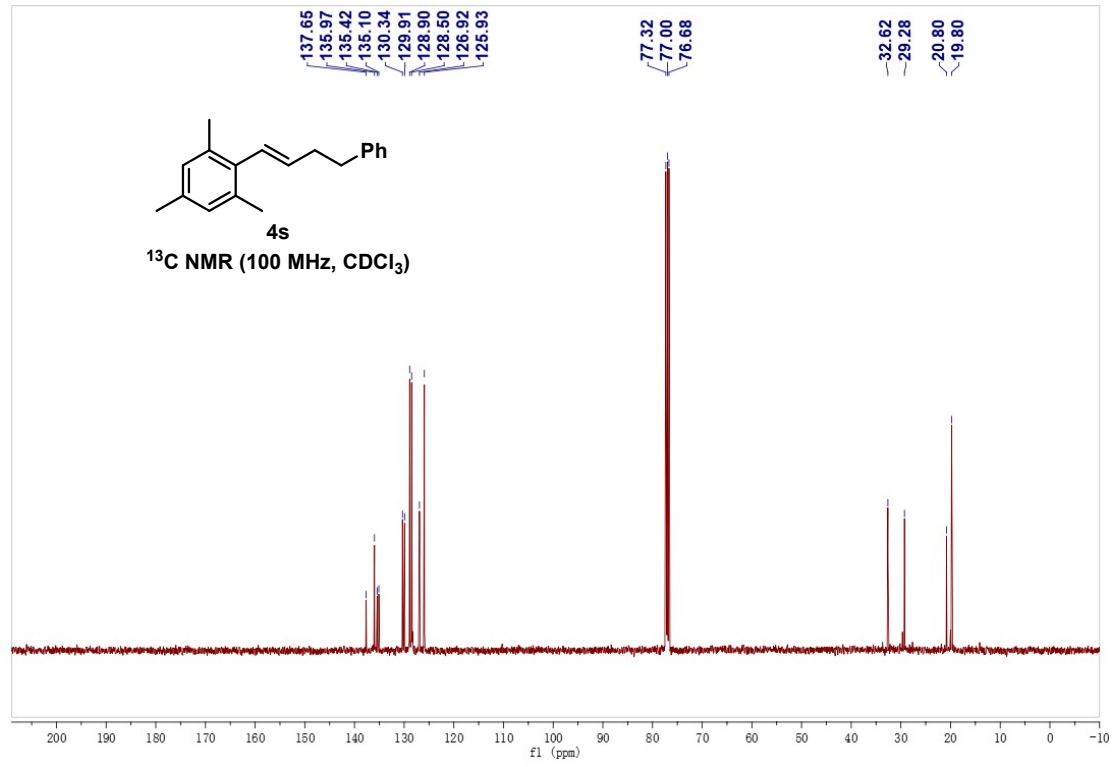


^{13}C NMR (100 MHz, $CDCl_3$)



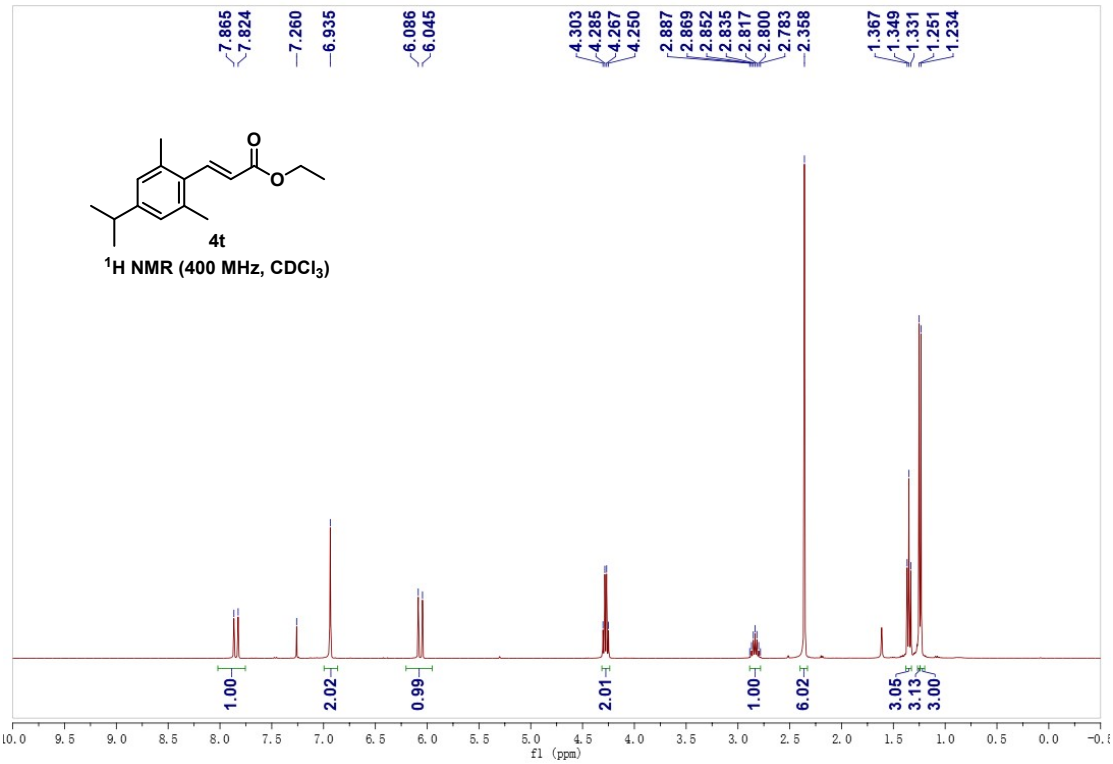
4s

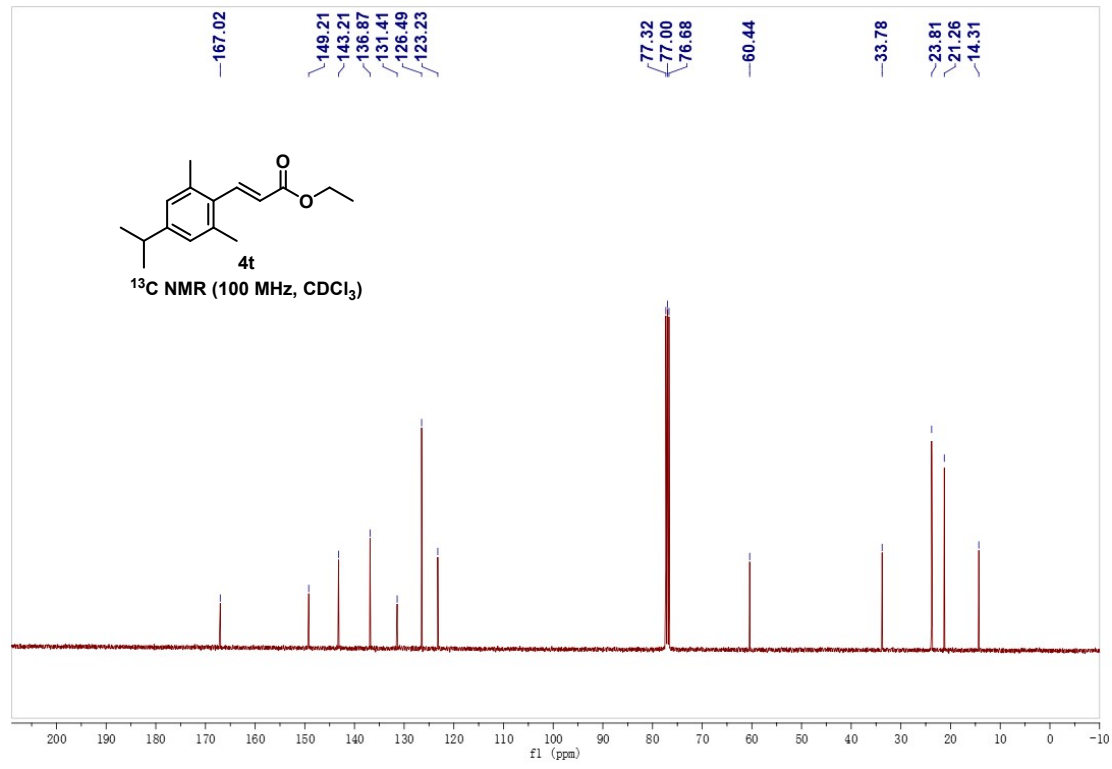
^{1}H NMR (400 MHz, $CDCl_3$)

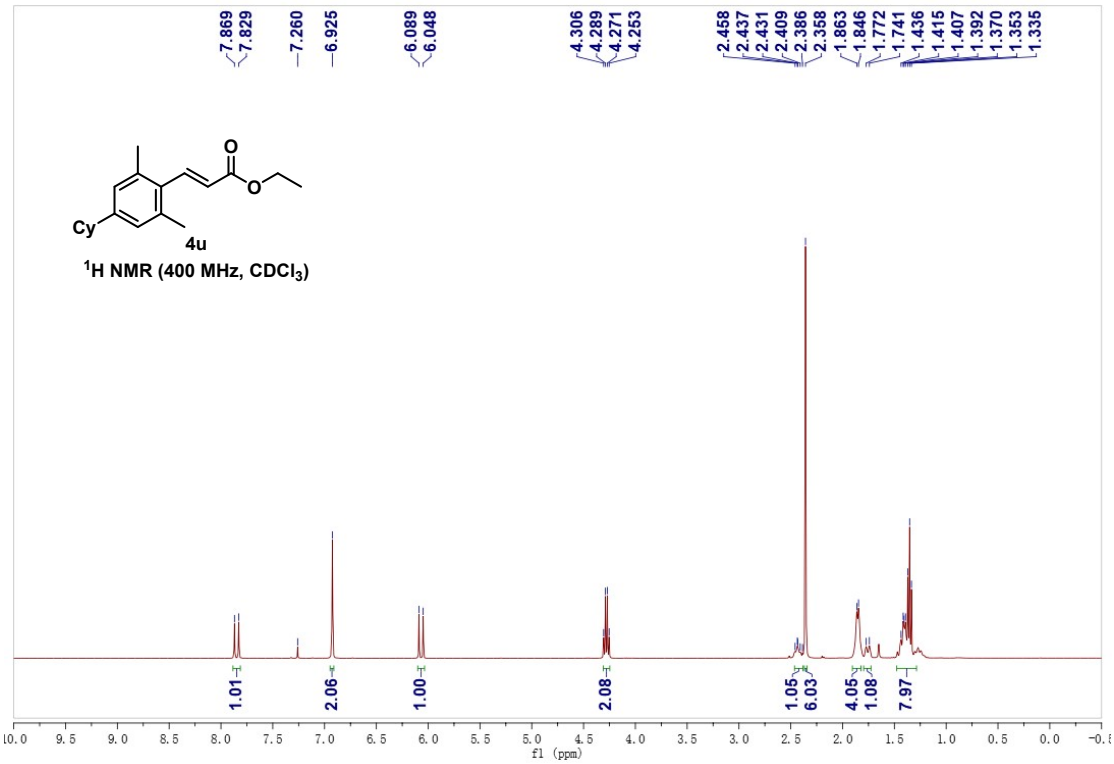


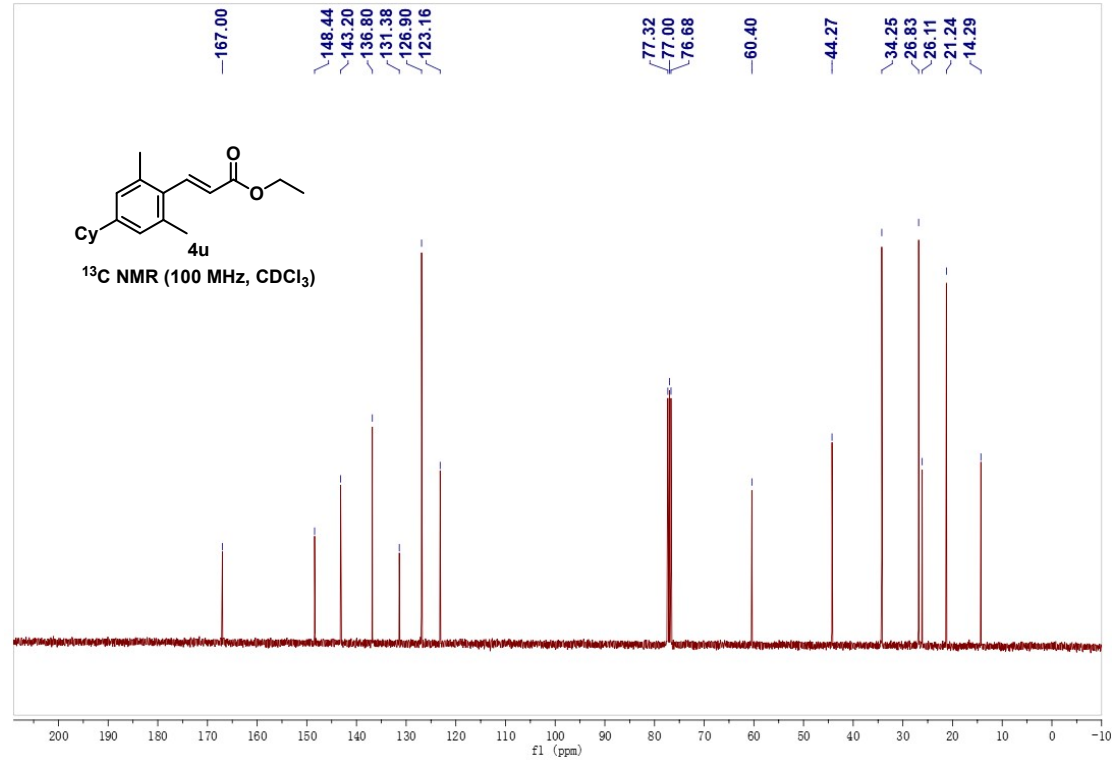
4s

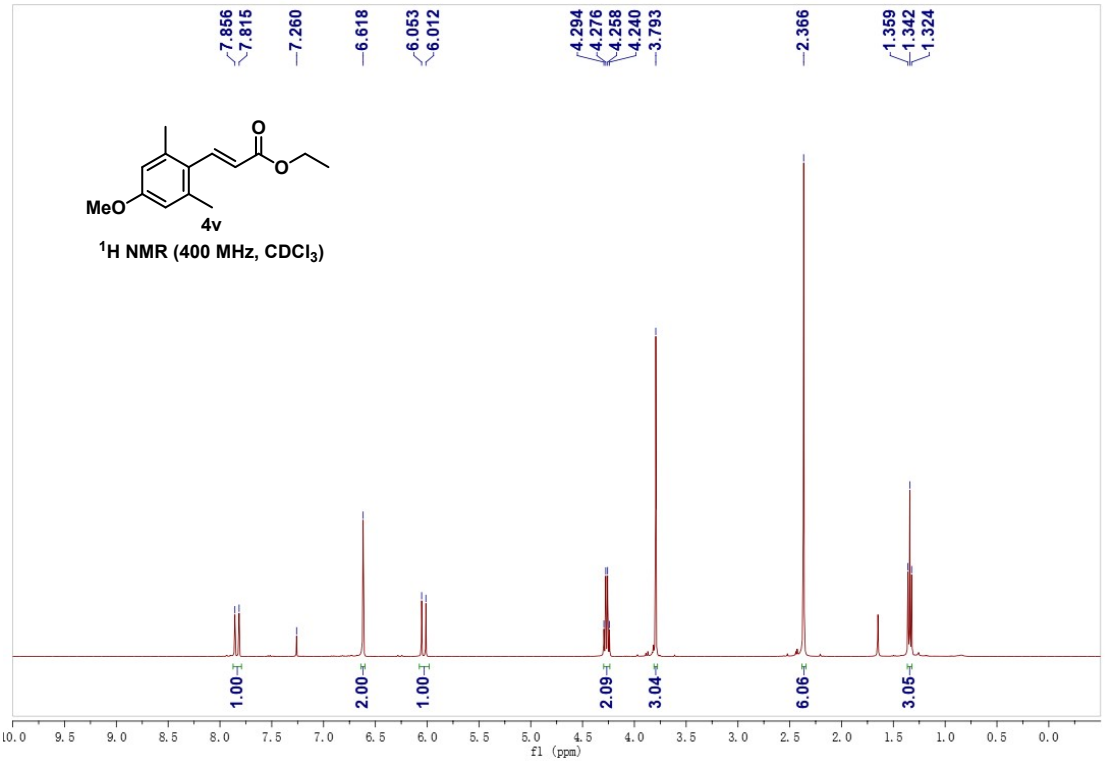
^{13}C NMR (100 MHz, $CDCl_3$)


7.865
7.824
7.260
6.935
6.086
6.045
4.303
4.285
4.267
4.250
2.887
2.869
2.852
2.835
2.817
2.800
2.783
2.358
1.367
1.349
1.331
1.251
1.234
O
O
4t
1H NMR (400 MHz, CDCl3)
1.00
2.02
0.99
2.01
1.00
6.02
3.05
3.13
3.00
f1 (ppm)

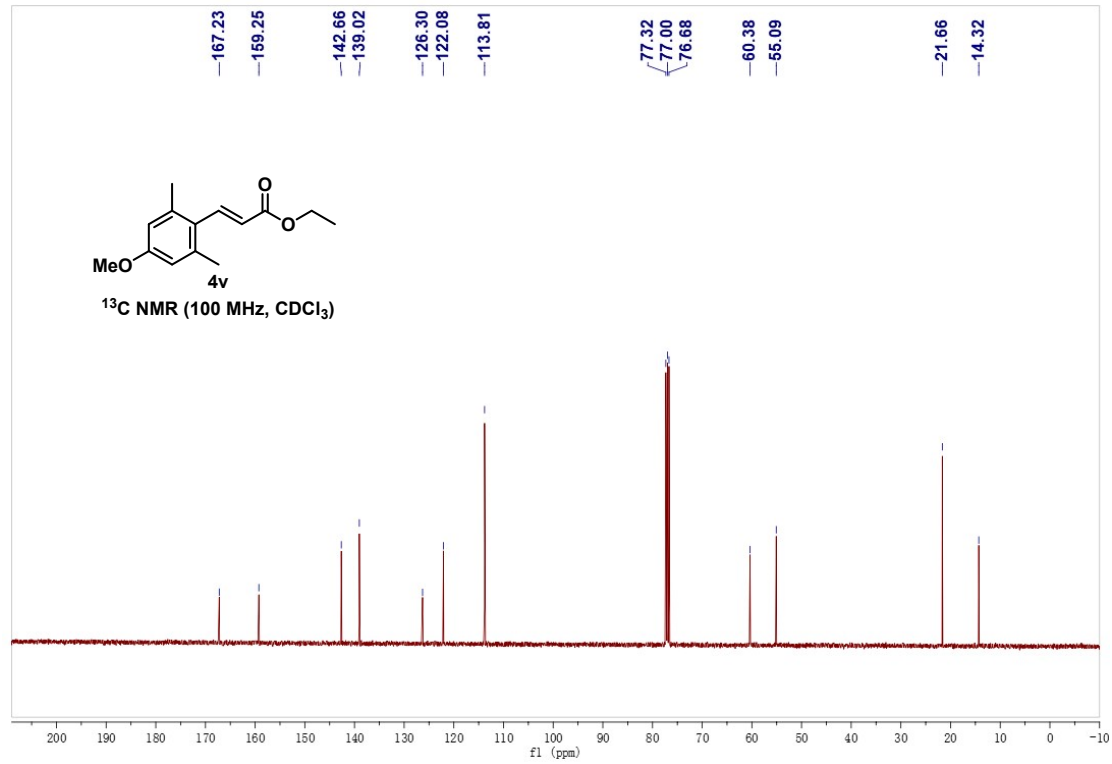

167.02
149.21
143.21
136.87
131.41
126.49
123.23
77.32
77.00
76.68
60.44
33.78
23.81
21.26
14.31
O
O
4t
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.869
7.829
7.260
6.925
6.089
6.048
4.306
4.289
4.271
4.253
2.458
2.437
2.431
2.409
2.386
2.358
1.863
1.846
1.772
1.741
1.436
1.415
1.407
1.392
1.370
1.353
1.335
Cy
4u
1H NMR (400 MHz, CDCl3)
1.01
2.06
1.00
2.08
1.05
6.03
4.05
1.08
7.97
f1 (ppm)

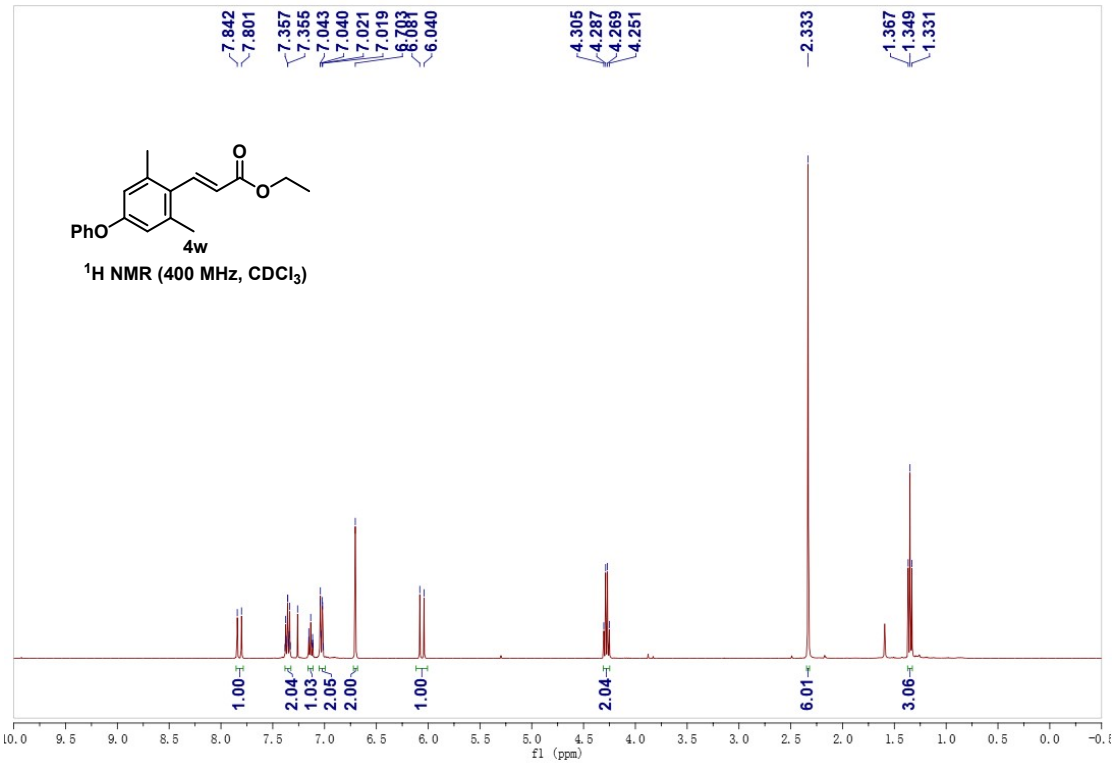

167.00
148.44
143.20
136.80
131.38
126.90
123.16
77.32
77.00
76.68
60.40
44.27
34.25
26.83
26.11
21.24
14.29
Cy
4u
13C NMR (100 MHz, CDCl3)
f1 (ppm)

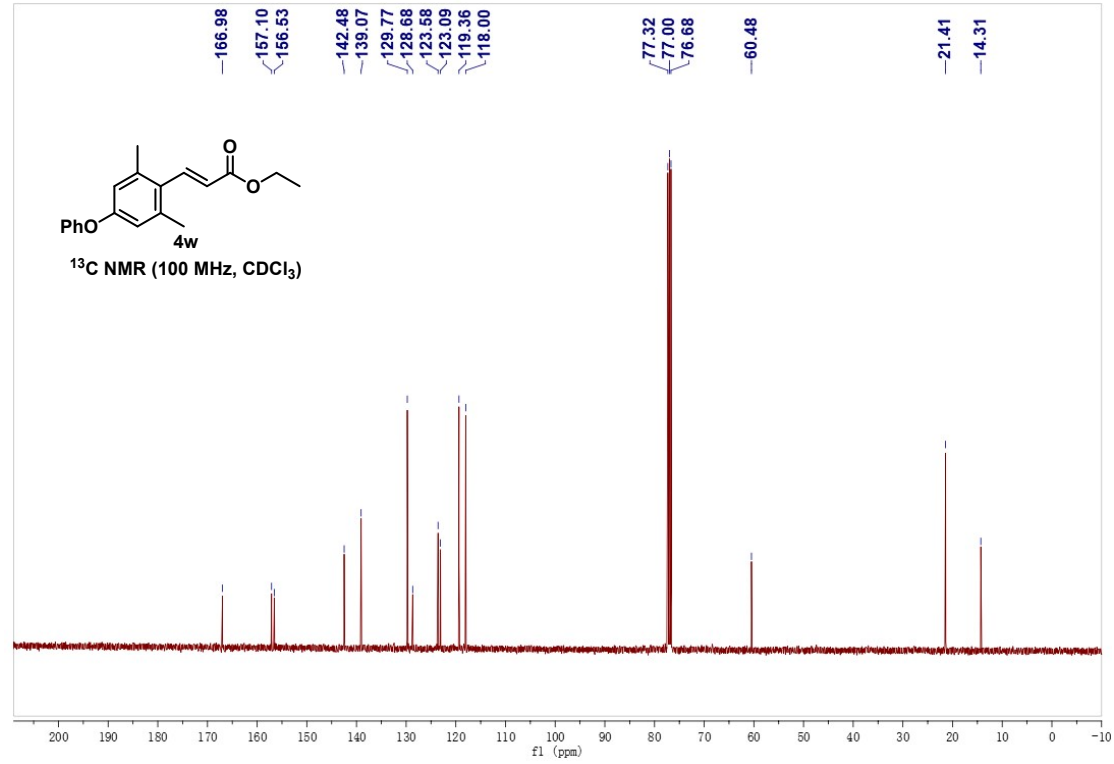


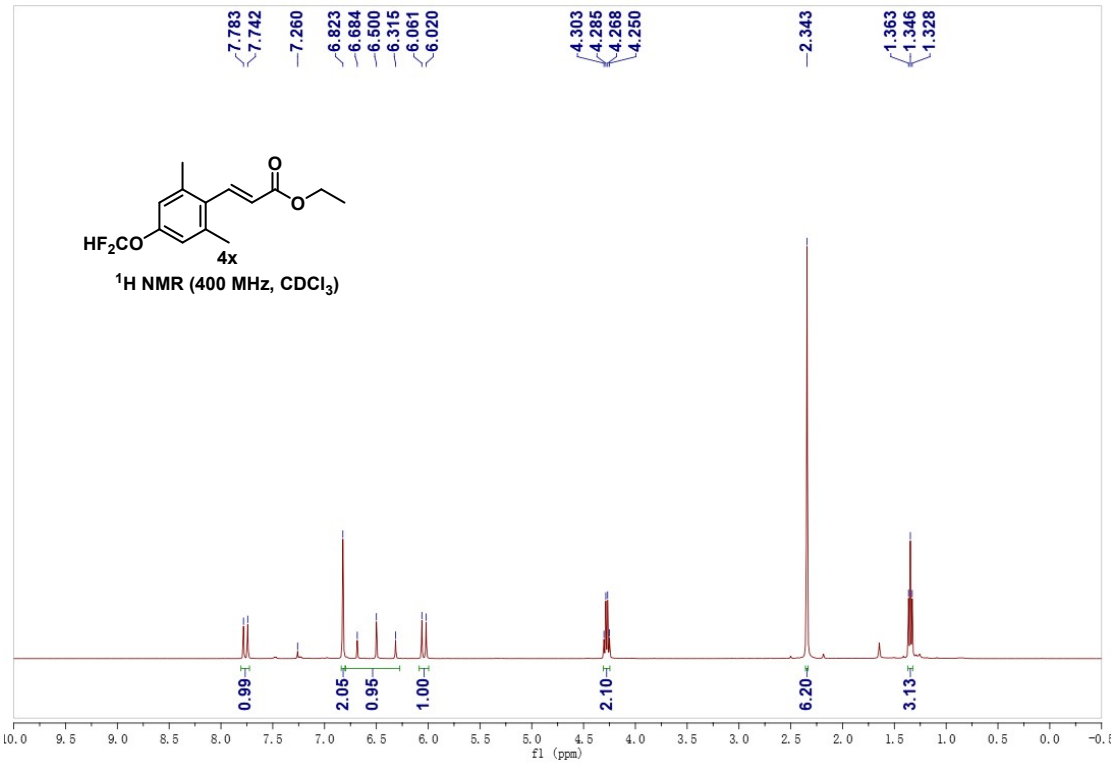
^{1}H NMR (400 MHz, $CDCl_3$)

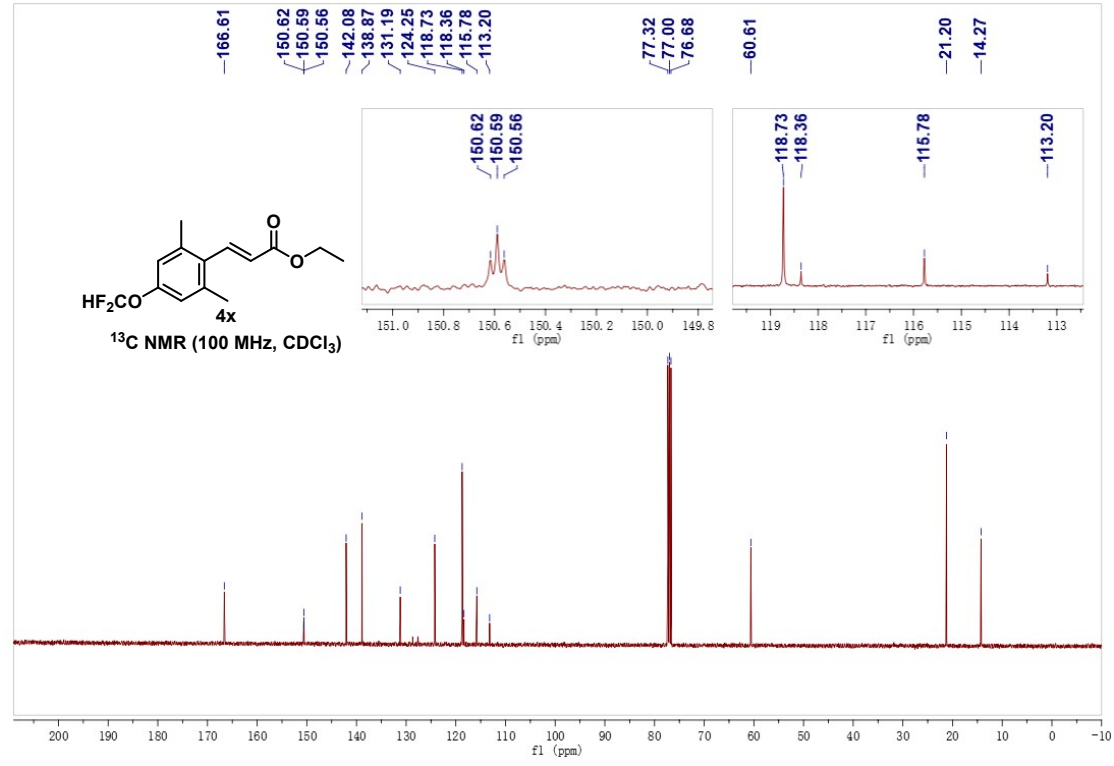


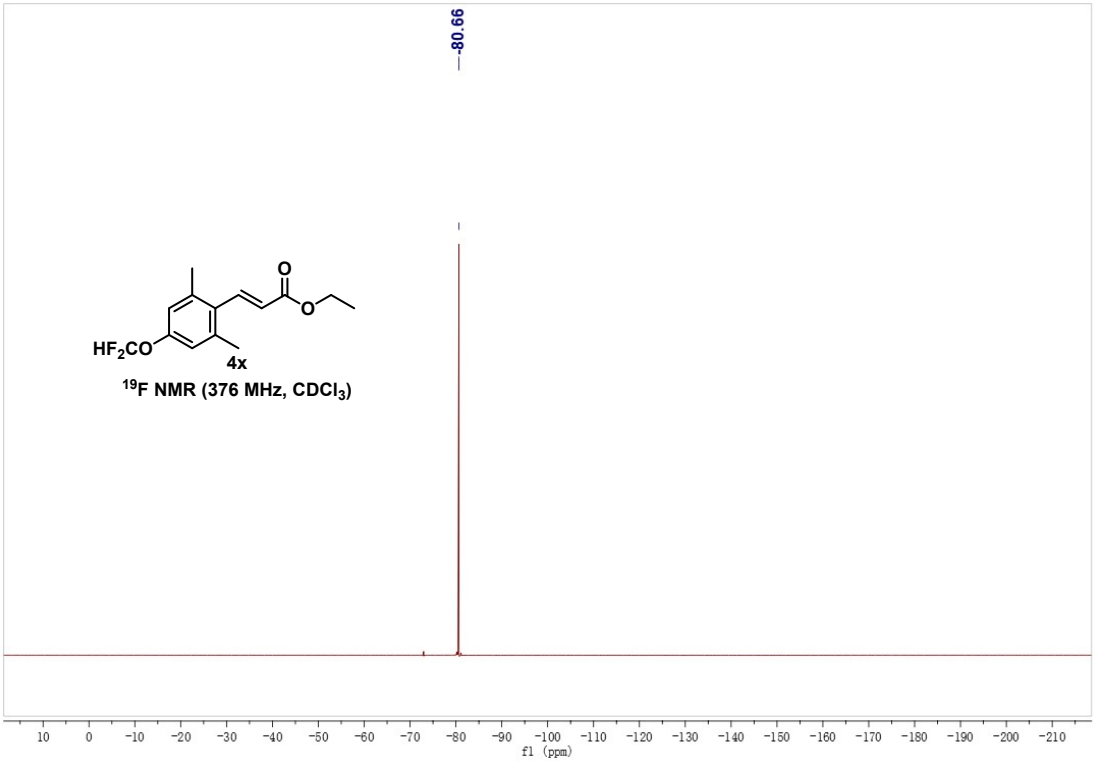
^{13}C NMR (100 MHz, $CDCl_3$)


7.842
7.801
7.357
7.355
7.043
7.040
7.021
7.019
6.081
6.040
4.305
4.287
4.269
4.251
2.333
1.367
1.349
1.331
PhO
O
O
4w
1H NMR (400 MHz, CDCl3)
1.00
2.04
1.03
2.05
2.00
1.00
2.04
6.01
3.06
f1 (ppm)


166.98
157.10
156.53
142.48
139.07
129.77
128.68
123.58
123.09
119.36
118.00
77.32
77.00
76.68
60.48
21.41
14.31
PhO
O
O
4w
13C NMR (100 MHz, CDCl3)
f1 (ppm)

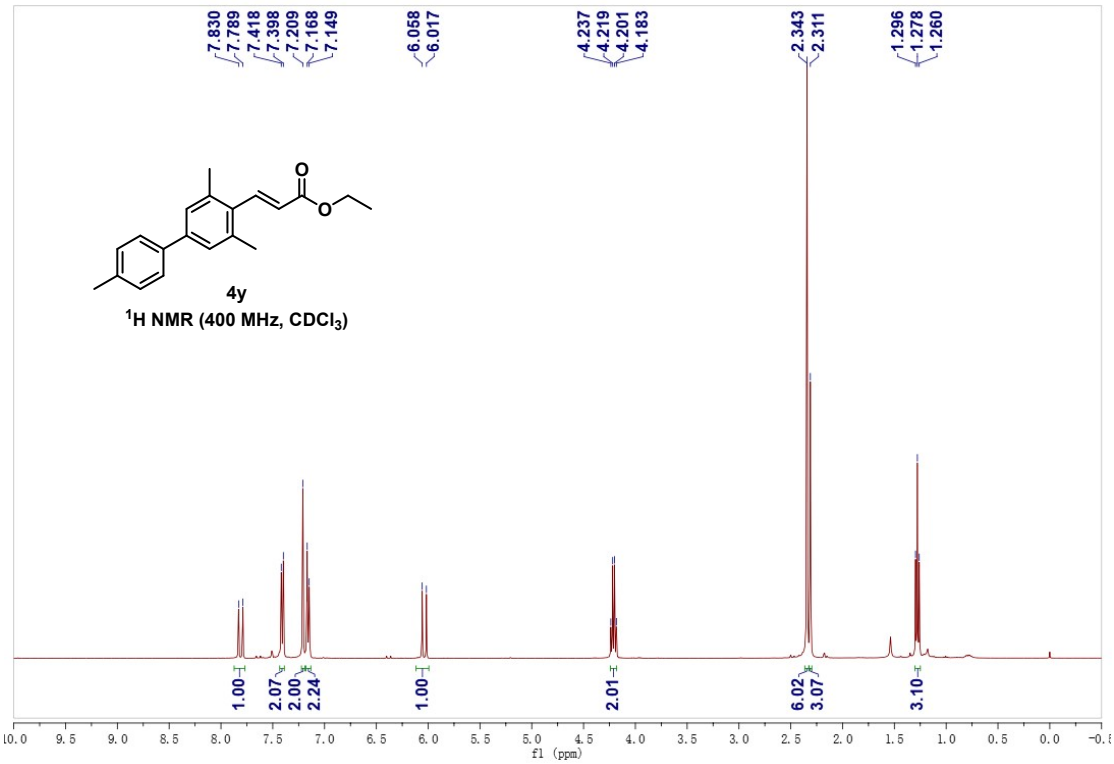

7.783
7.742
7.260
6.823
6.684
6.500
6.315
6.061
6.020
4.303
4.285
4.268
4.250
2.343
1.363
1.346
1.328
O
O
HF2CO
4x
1H NMR (400 MHz, CDCl3)
0.99
2.05
0.95
1.00
2.10
6.20
3.13
f1 (ppm)

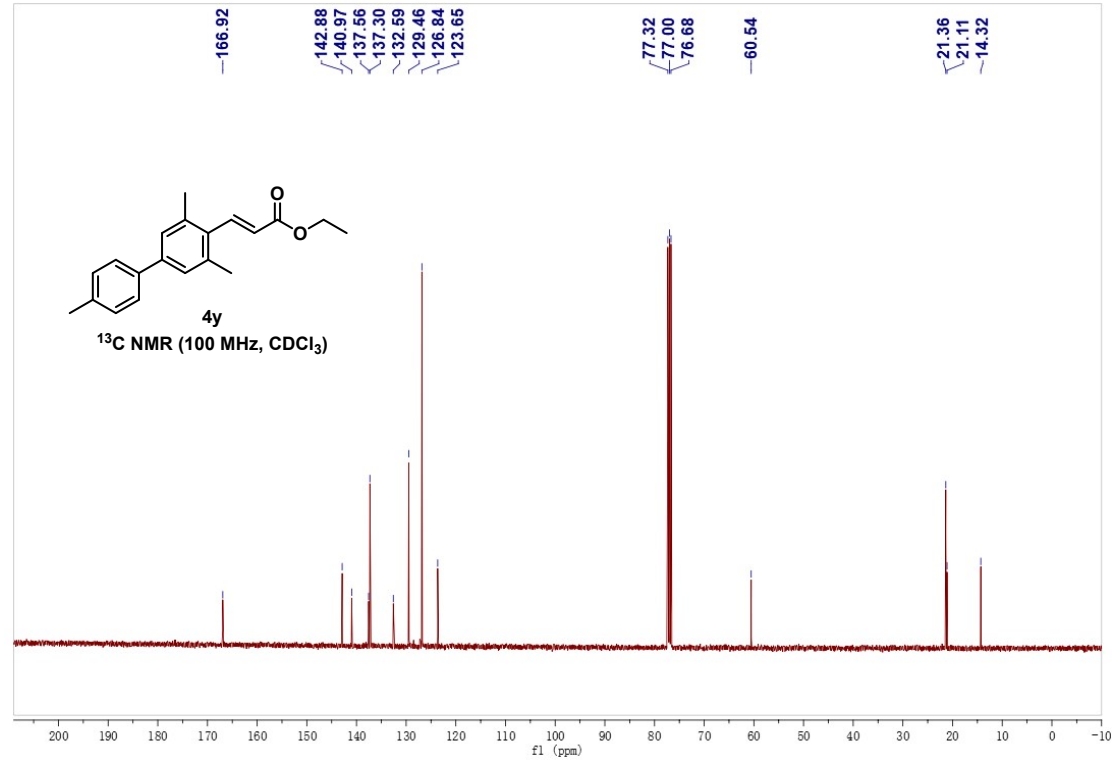

166.61
150.62
150.59
150.56
142.08
138.87
131.19
124.25
118.73
118.36
115.78
113.20
77.32
77.00
76.68
60.61
21.20
14.27
O
O
HF2CO
4x
13C NMR (100 MHz, CDCl3)
f1 (ppm)

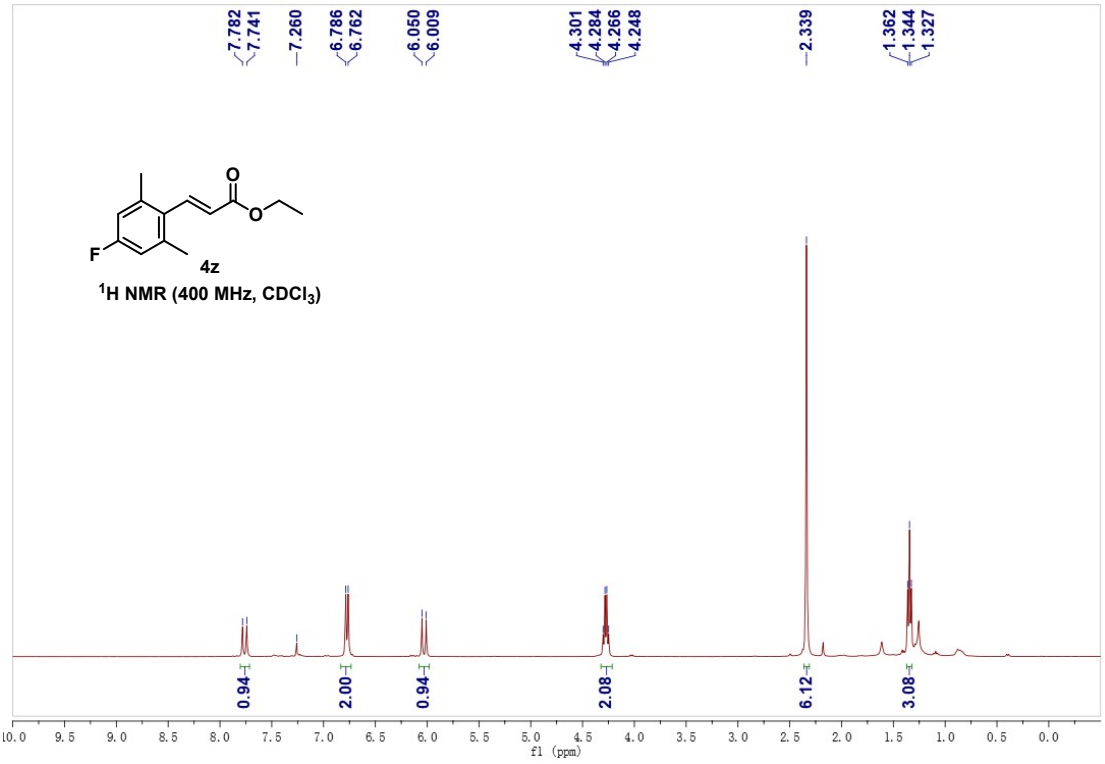


4x

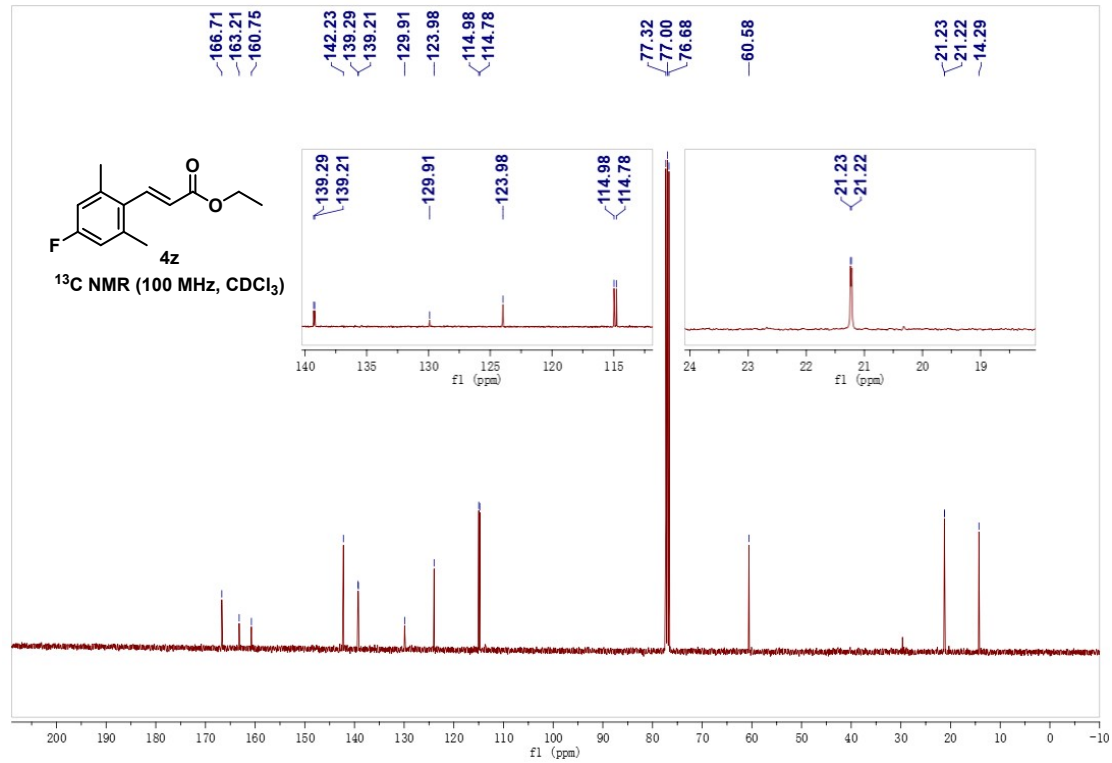
^{19}F NMR (376 MHz, $CDCl_3$)


7.830
7.789
7.418
7.398
7.209
7.168
7.149
6.058
6.017
4.237
4.219
4.201
4.183
2.343
2.311
1.296
1.278
1.260
O
O
4y
1H NMR (400 MHz, CDCl3)
1.00
2.07
2.00
2.24
1.00
2.01
6.02
3.07
3.10
f1 (ppm)

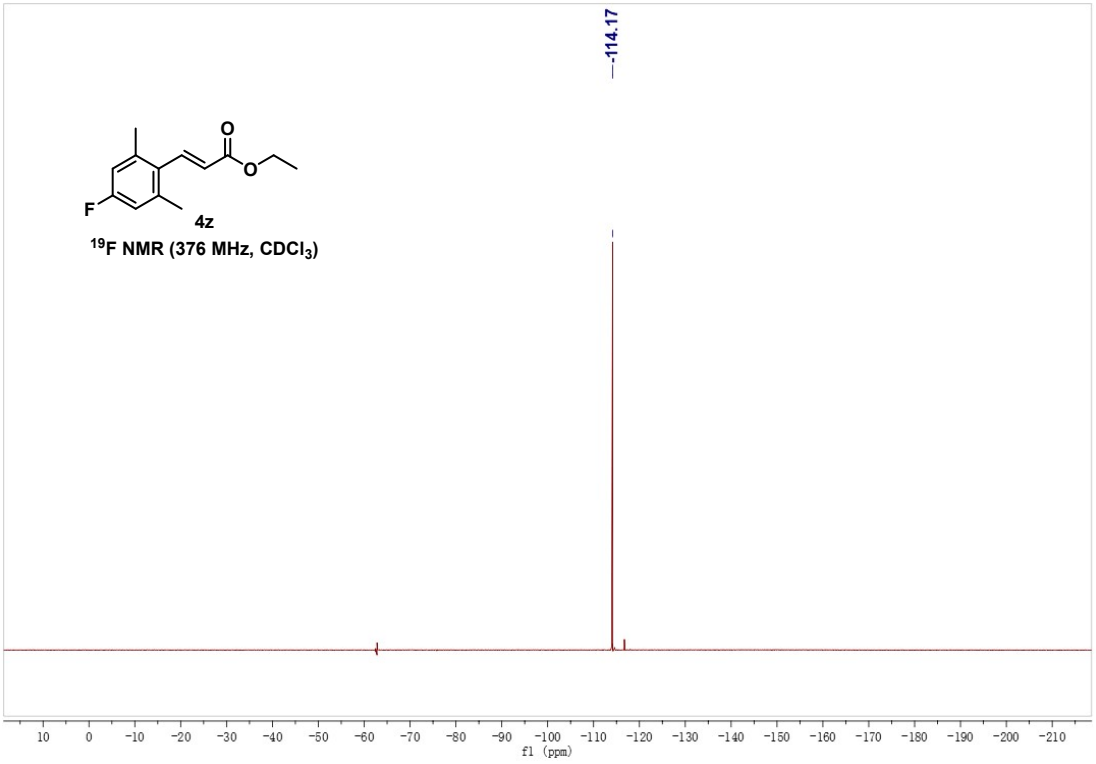

166.92
142.88
140.97
137.56
137.30
132.59
129.46
126.84
123.65
77.32
77.00
76.68
60.54
21.36
21.11
14.32
O
O
4y
13C NMR (100 MHz, CDCl3)
f1 (ppm)



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

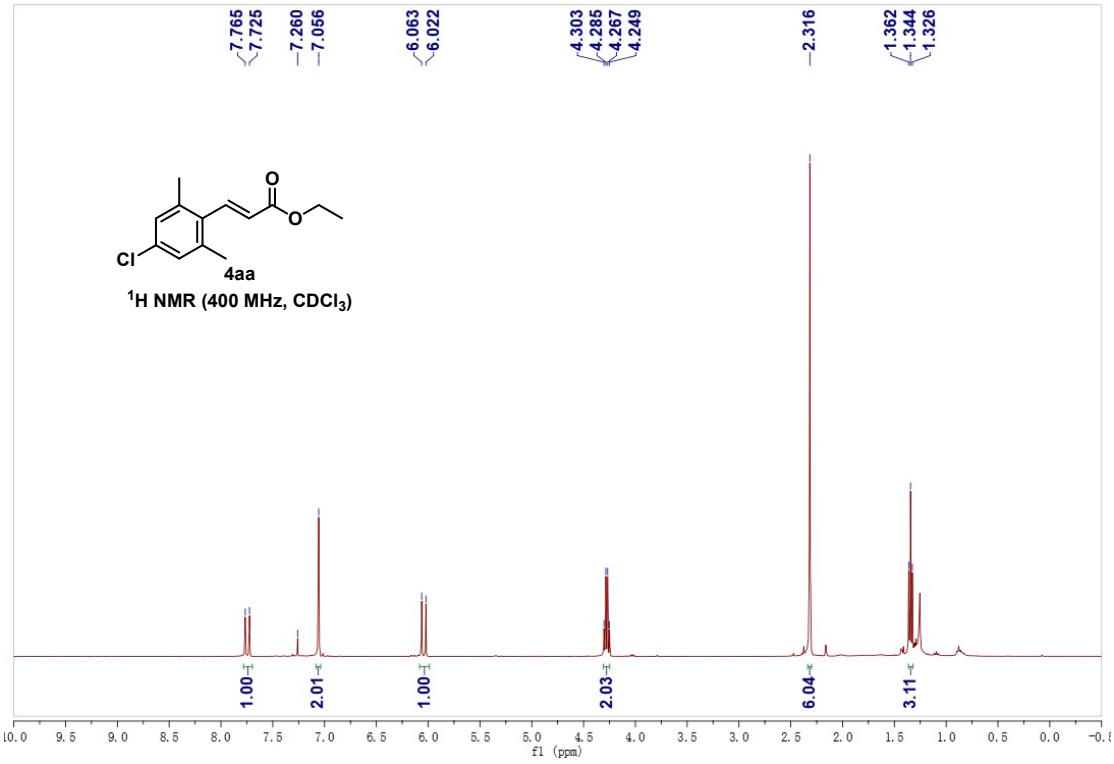


^{13}C NMR (100 MHz, $CDCl_3$)

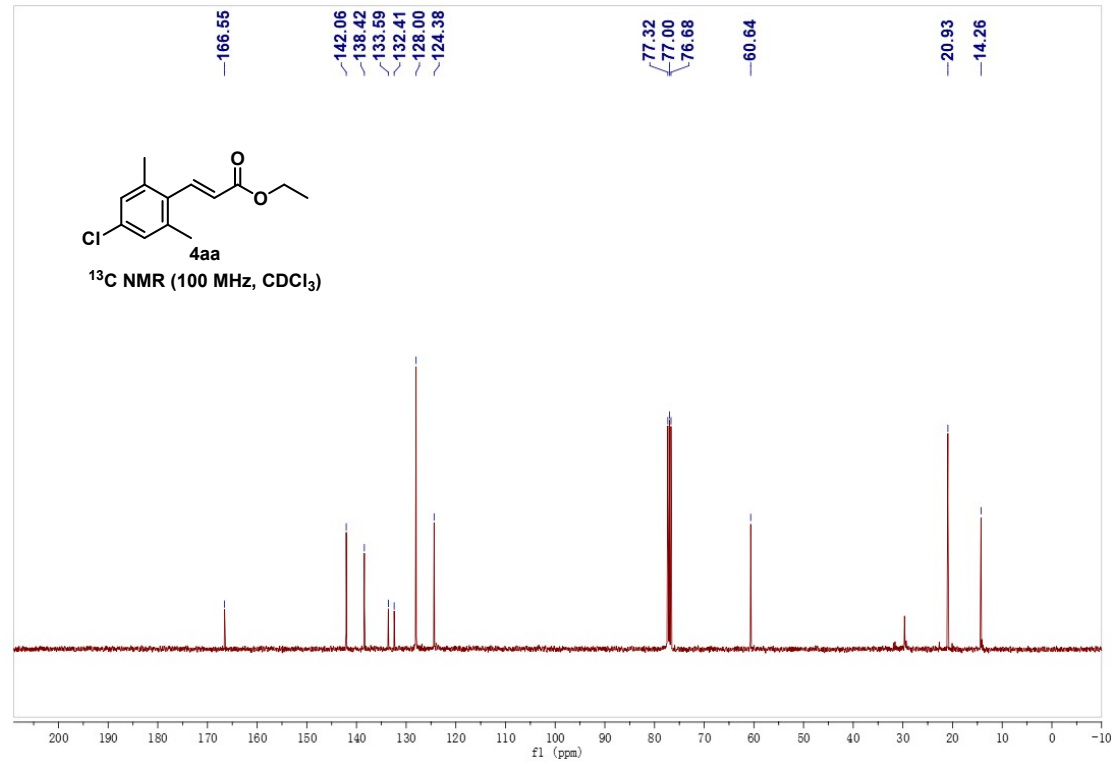


4z

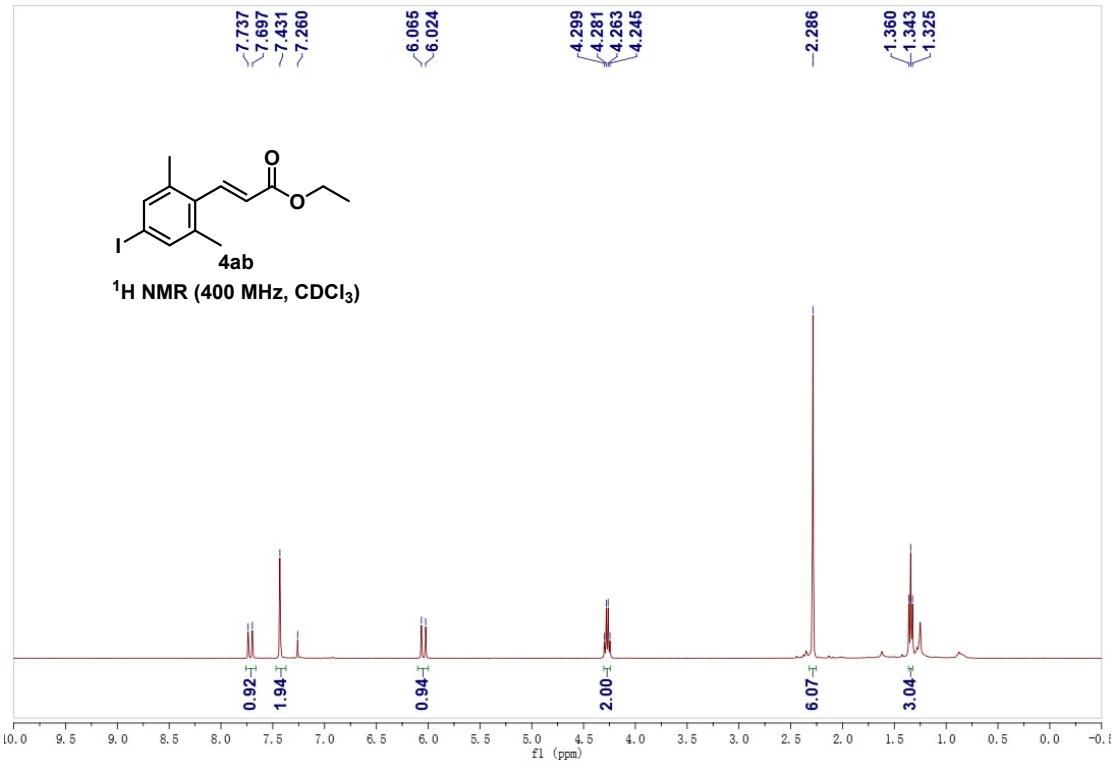
^{19}F NMR (376 MHz, $CDCl_3$)



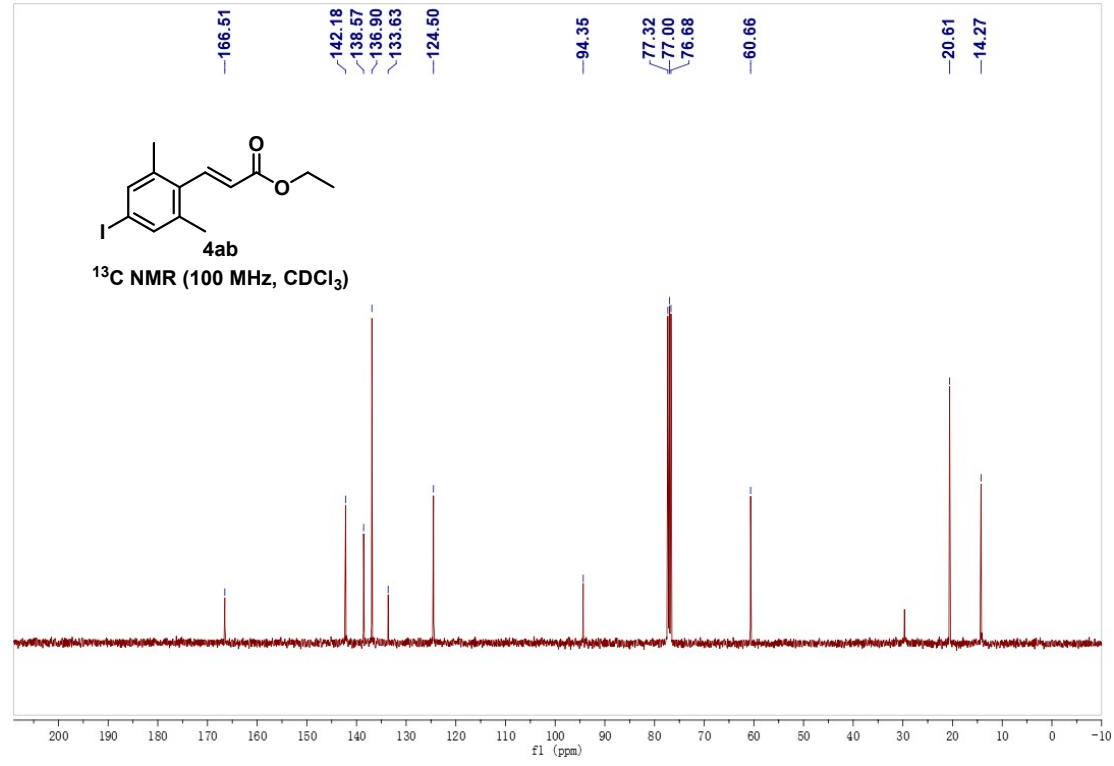
^{1}H NMR (400 MHz, $CDCl_3$)



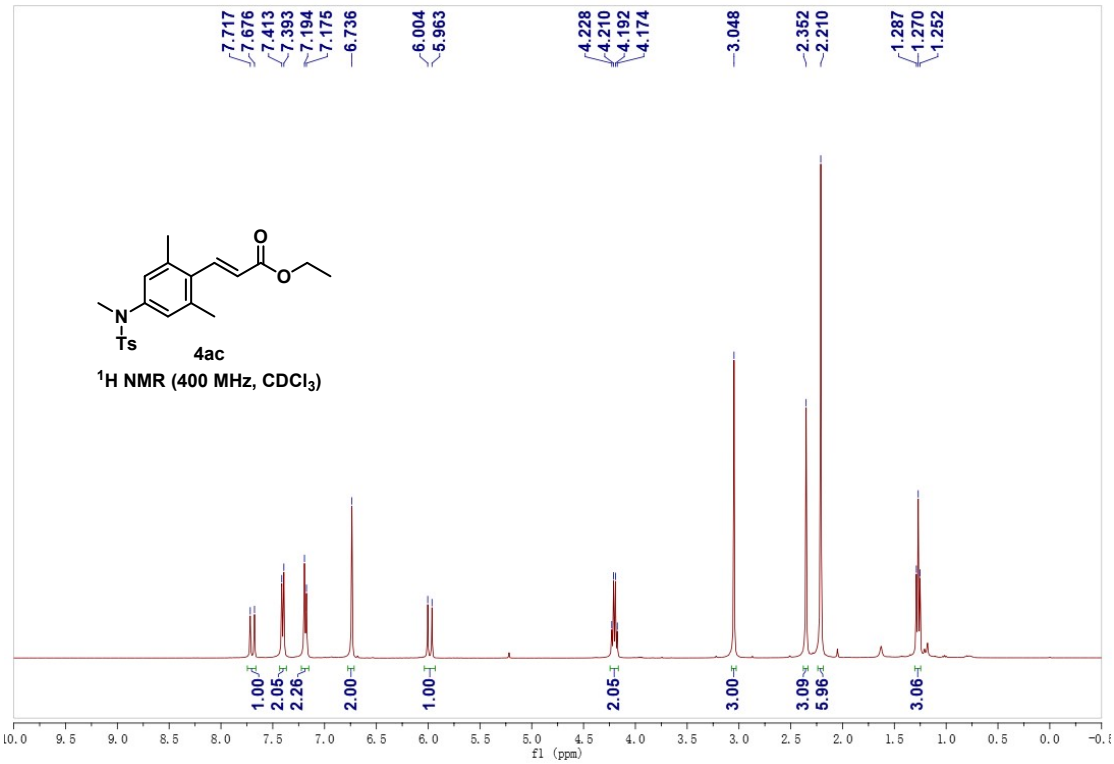
^{13}C NMR (100 MHz, $CDCl_3$)



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

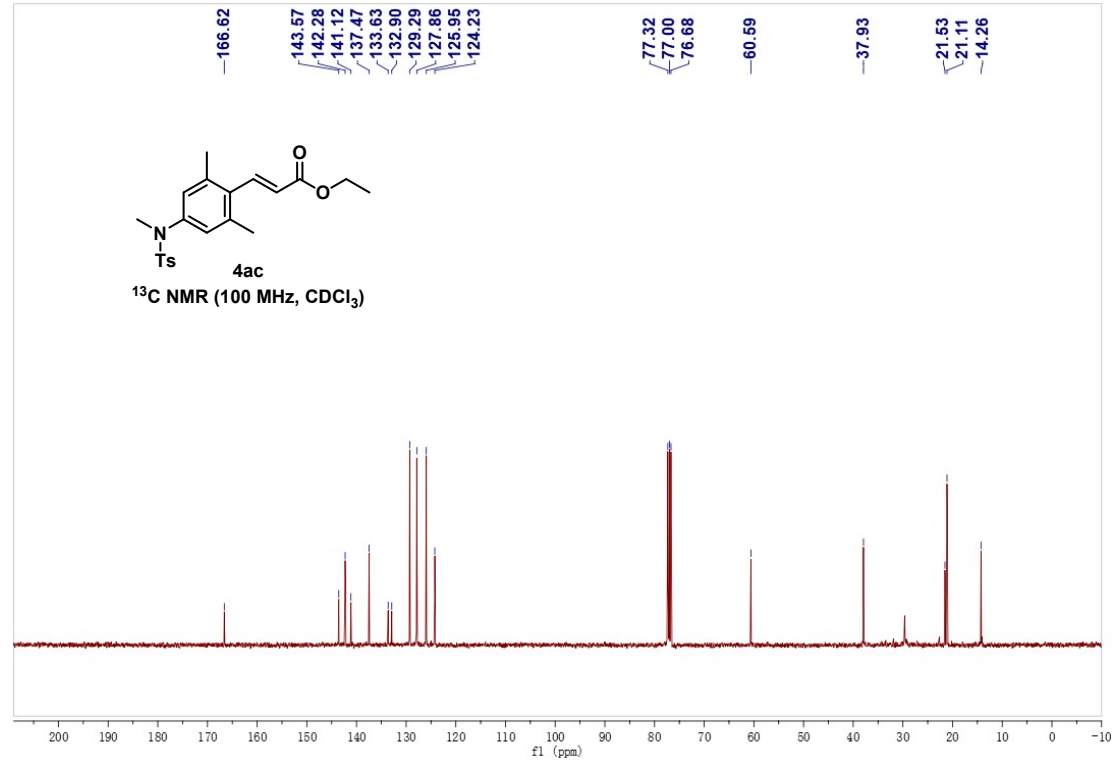


^{13}C NMR (100 MHz, $CDCl_3$)



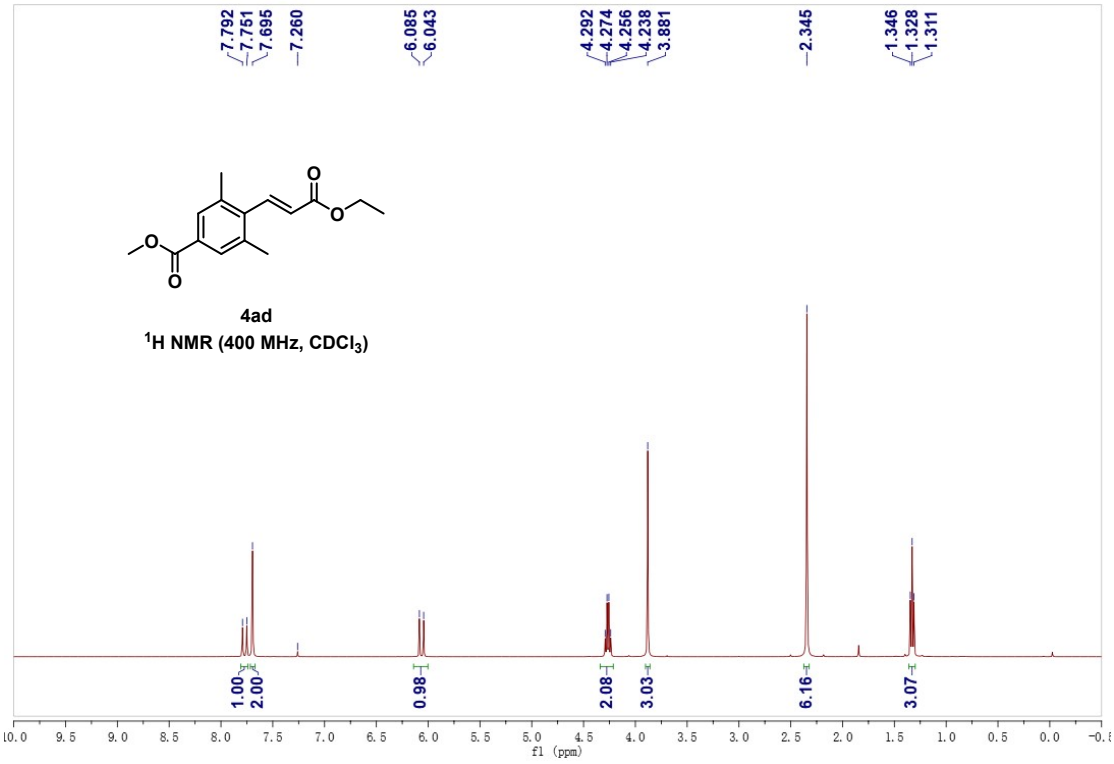
4ac

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



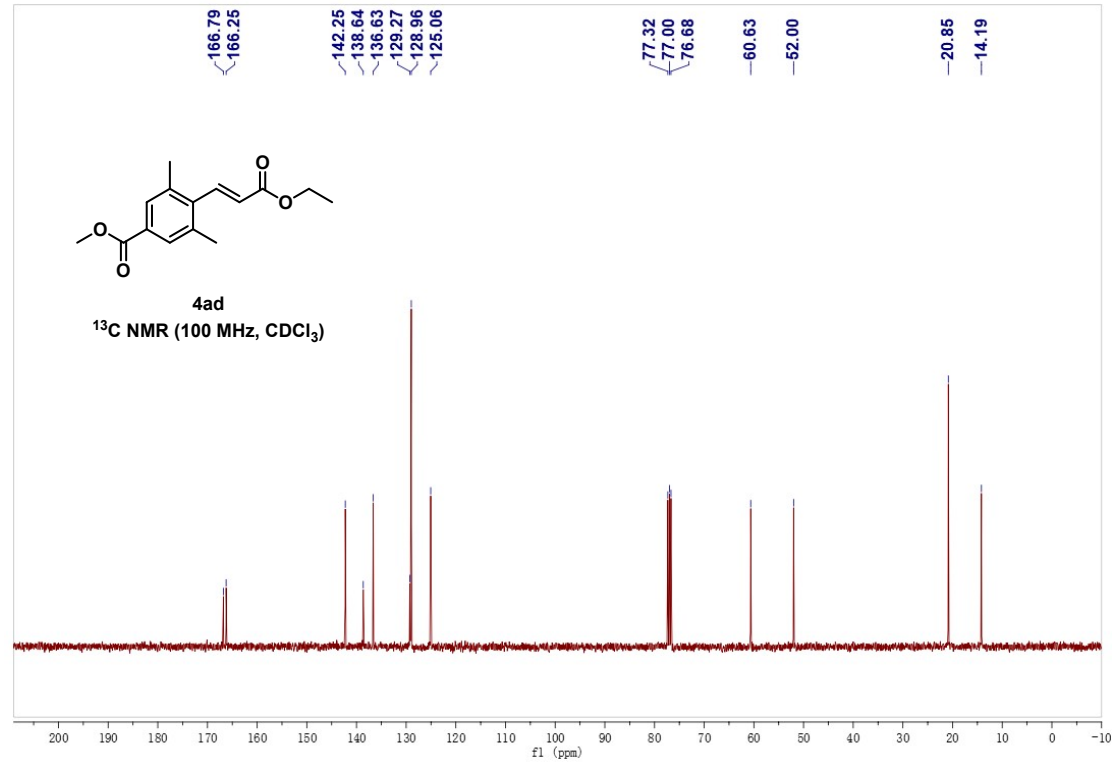
4ac

^{13}C NMR (100 MHz, $CDCl_3$)



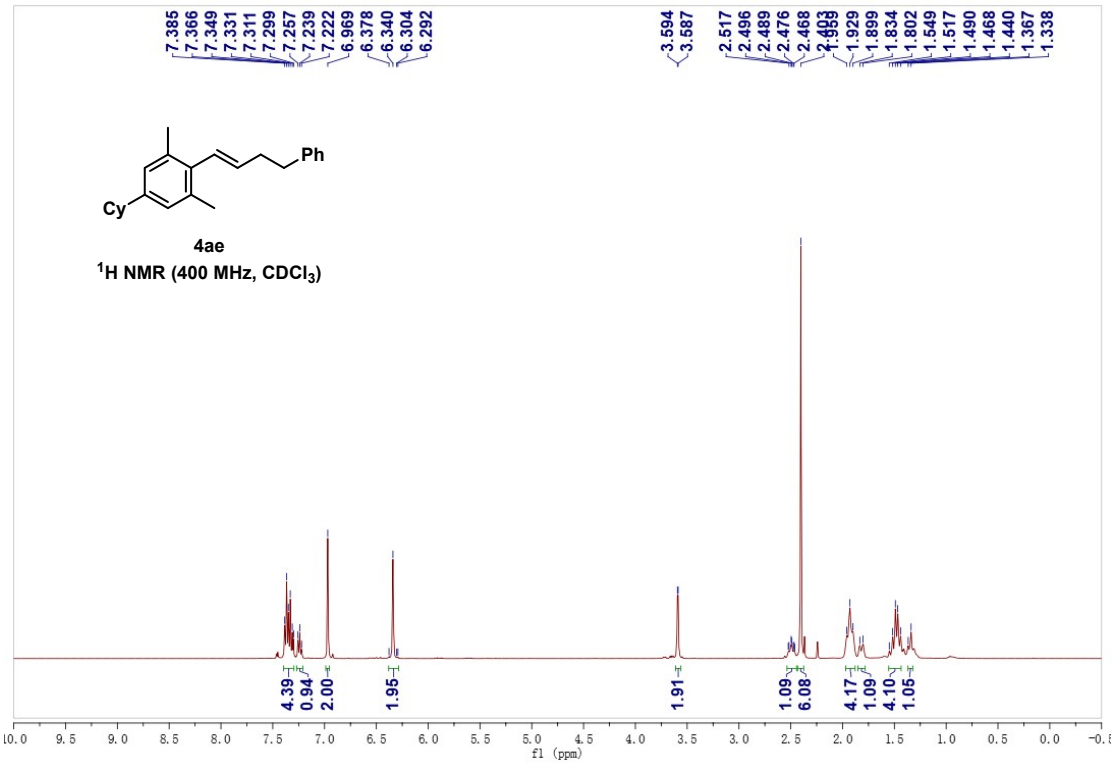
4ad

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



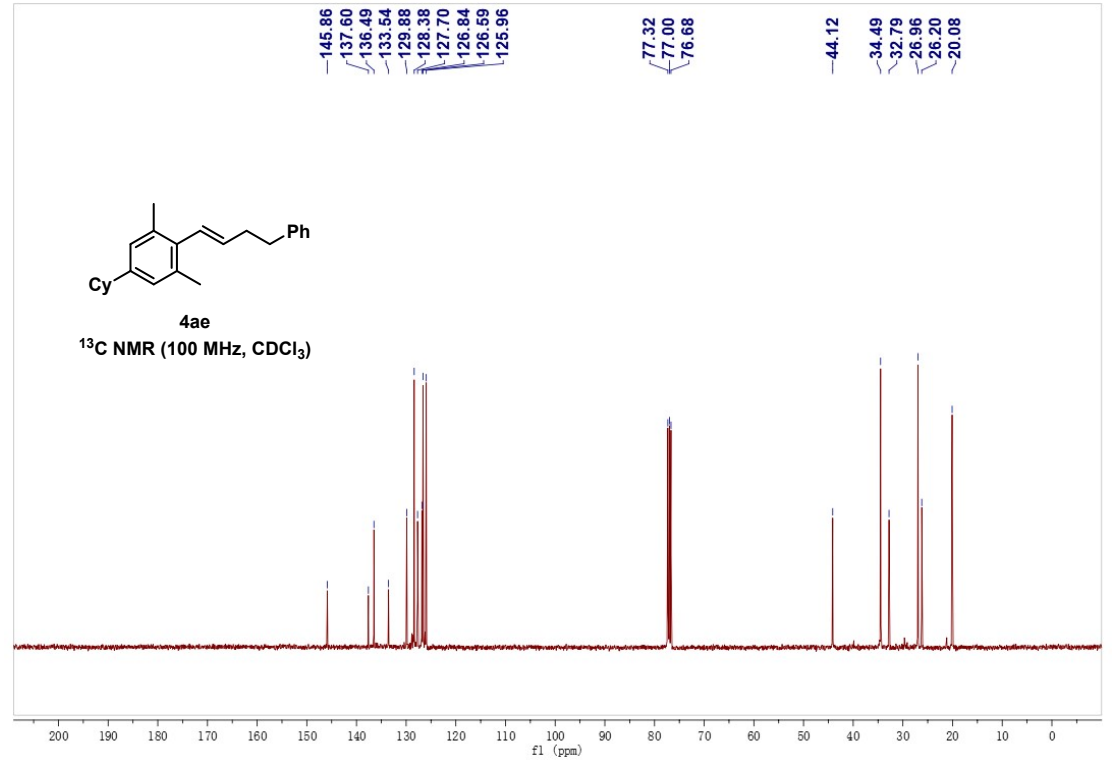
4ad

^{13}C NMR (100 MHz, $CDCl_3$)



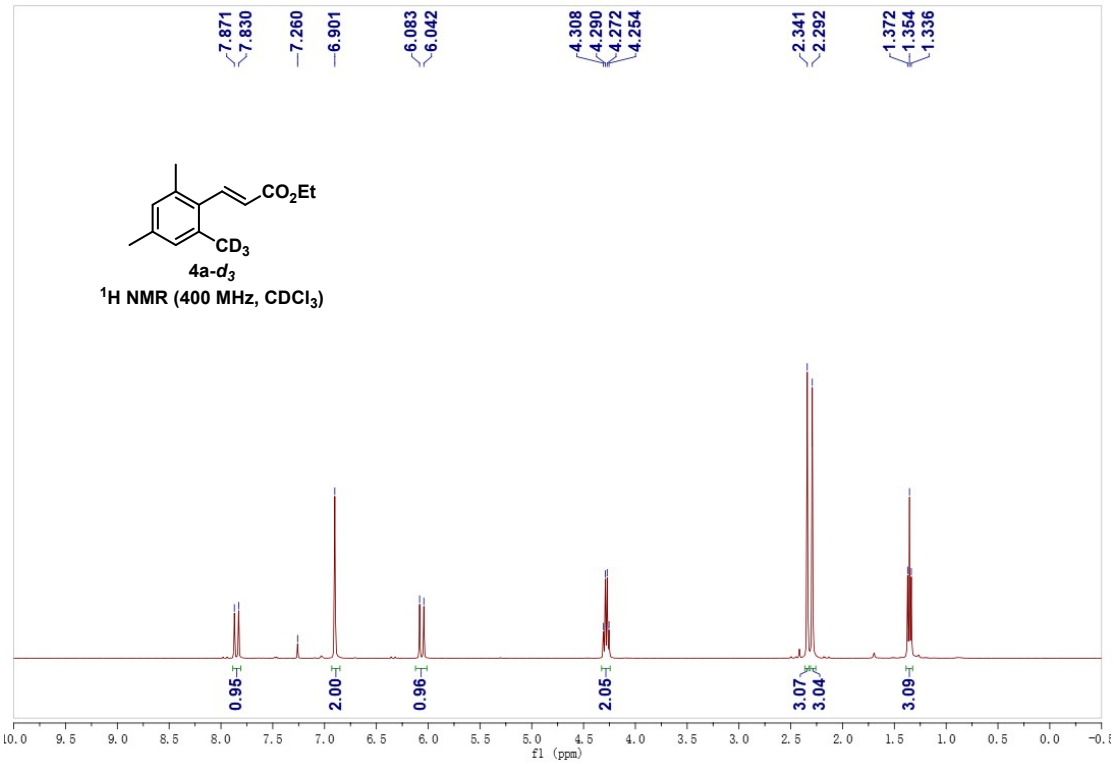
4ae

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



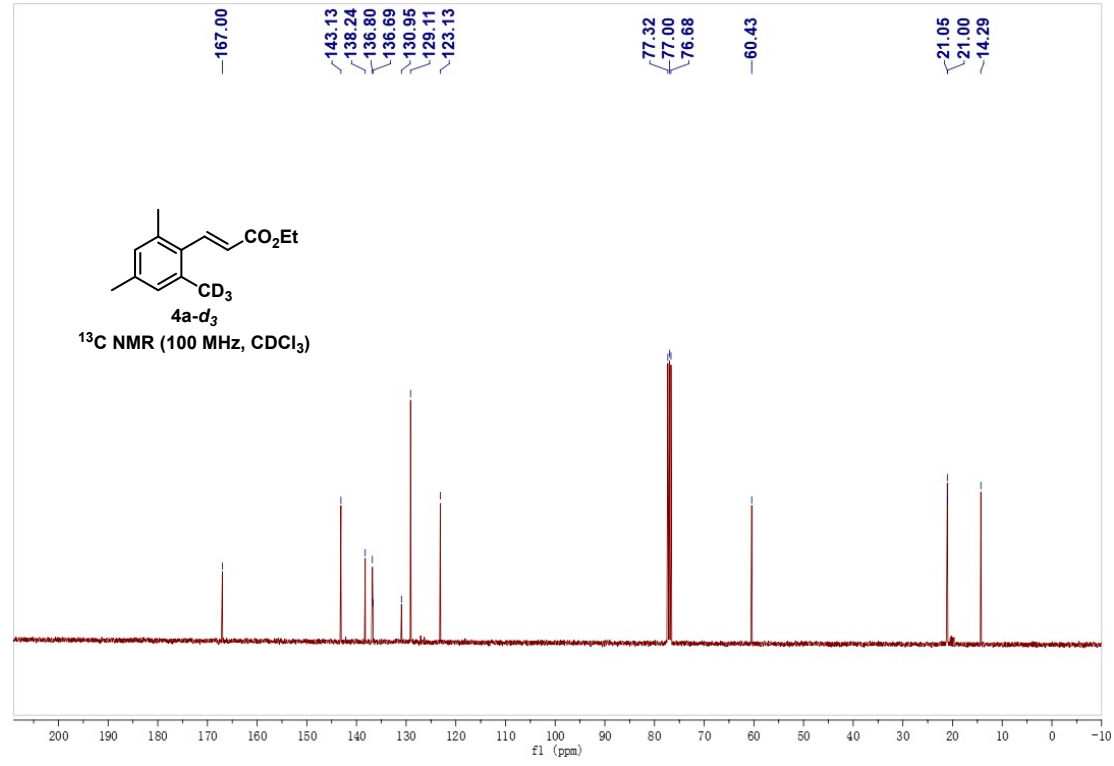
4ae

^{13}C NMR (100 MHz, $CDCl_3$)



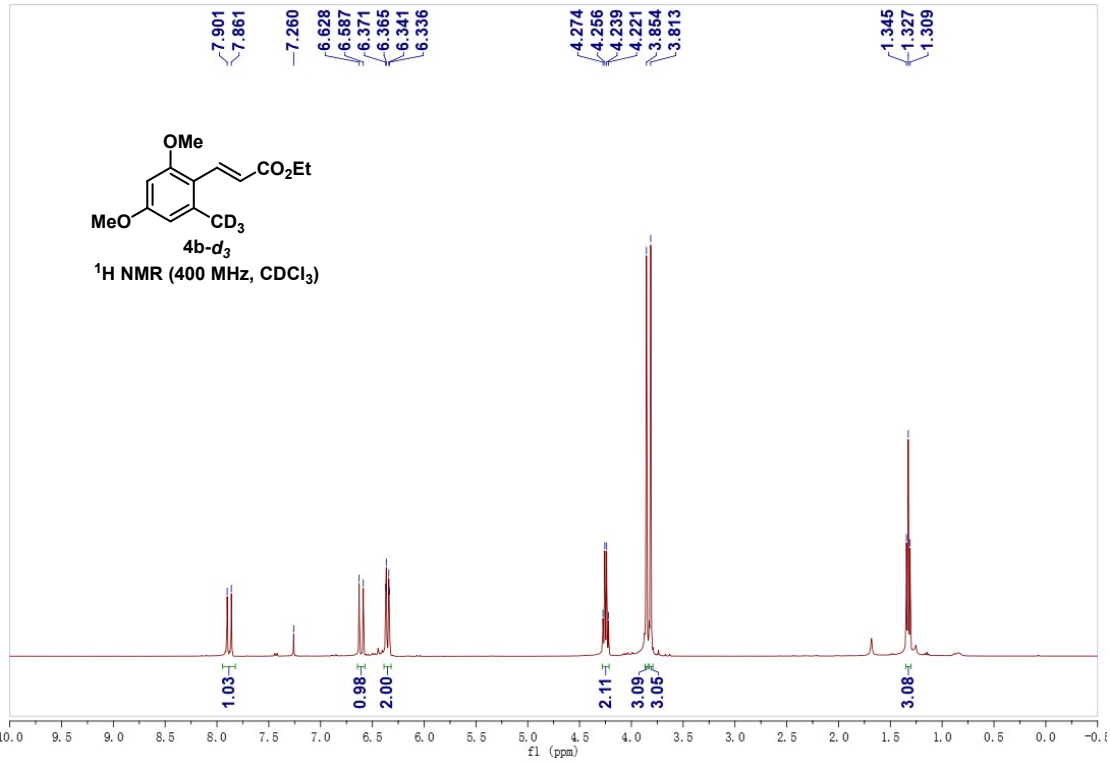
4a-d_3

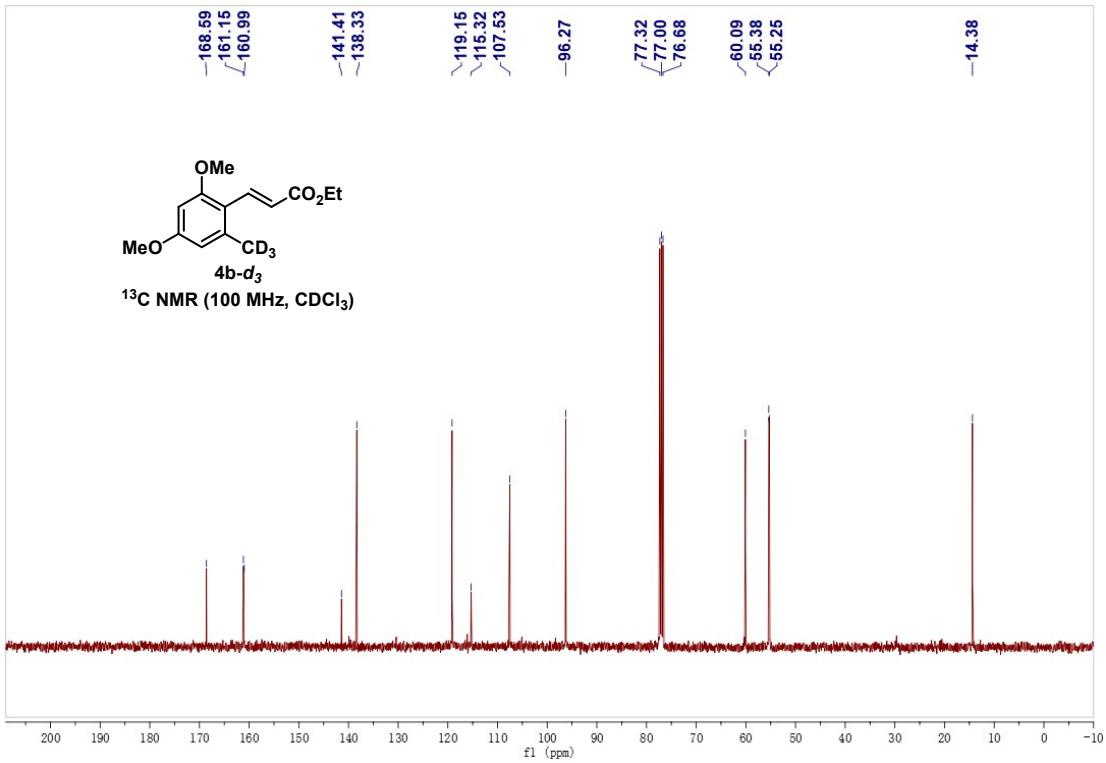
^{1}H NMR (400 MHz, $CDCl_3$)

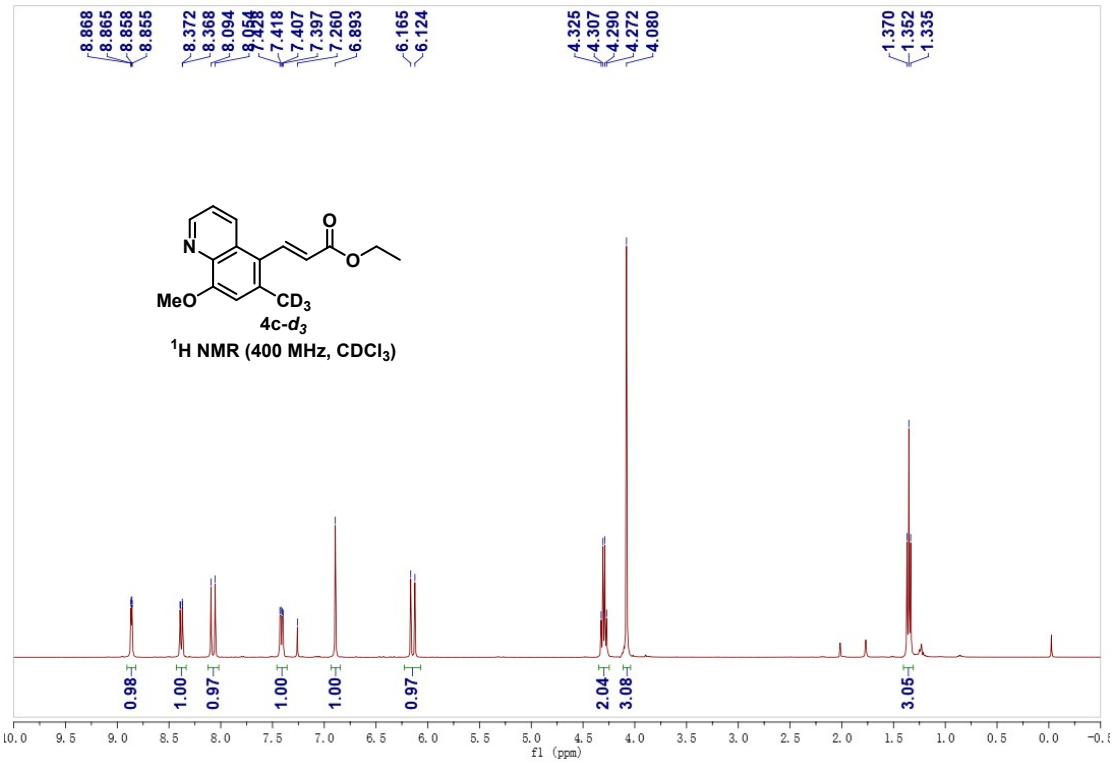


4a-d_3

^{13}C NMR (100 MHz, $CDCl_3$)

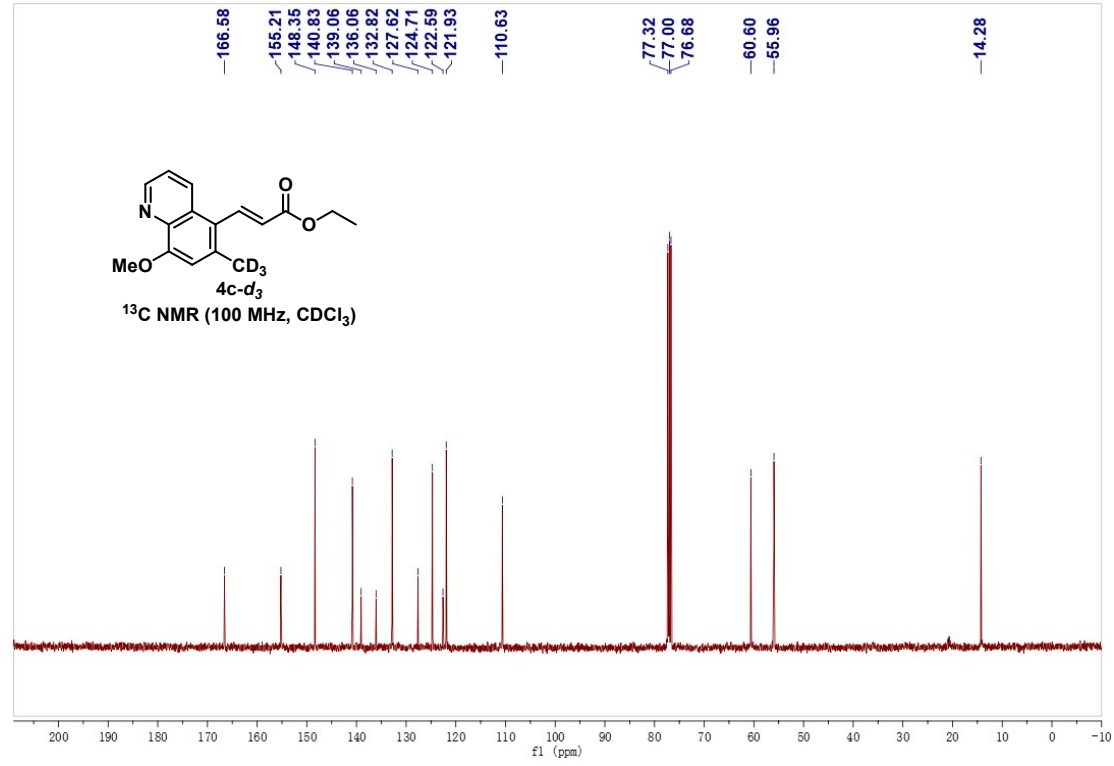

7.901
7.861
7.260
6.628
6.587
6.371
6.365
6.341
6.336
4.274
4.256
4.239
4.221
3.854
3.813
1.345
1.327
1.309
OMe
CO2Et
MeO
CD3
4b-d3
1H NMR (400 MHz, CDCl3)
1.03
0.98
2.00
2.11
3.09
3.05
3.08
f1 (ppm)


168.59
161.15
160.99
141.41
138.33
119.15
115.32
107.53
96.27
77.32
77.00
76.68
60.09
55.38
55.25
14.38
OMe
CO2Et
MeO
CD3
4b-d3
13C NMR (100 MHz, CDCl3)
f1 (ppm)



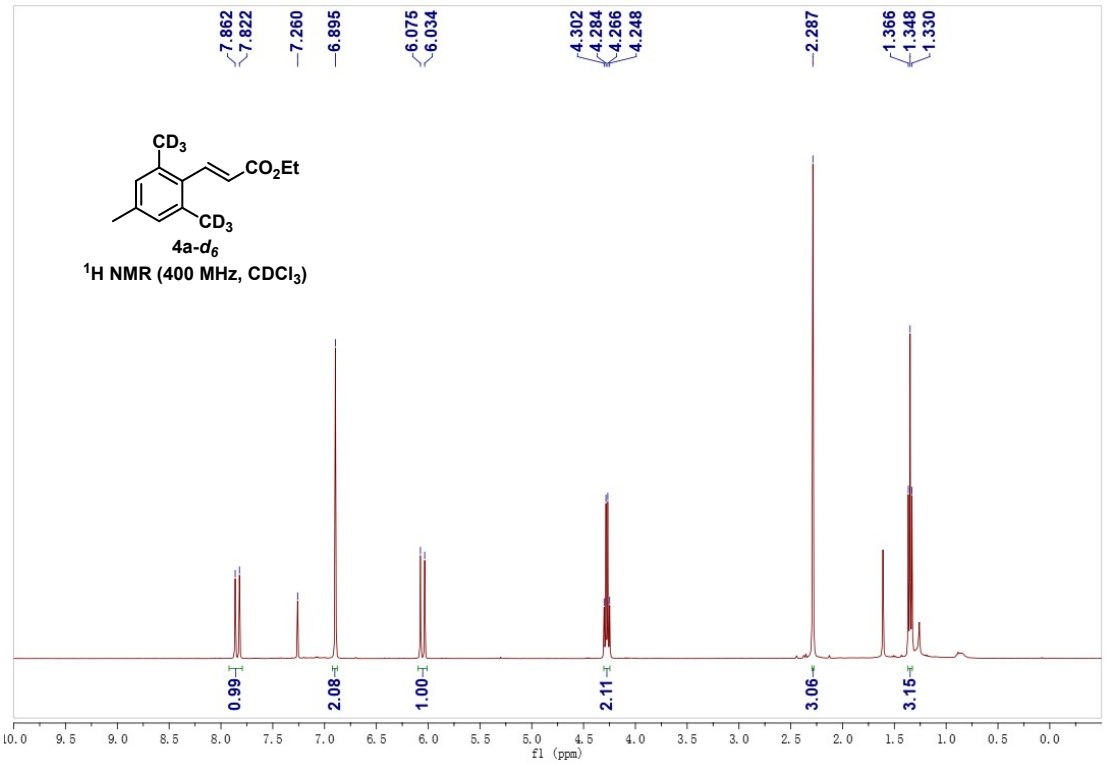
4c-d_3

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



4c-d_3

^{13}C NMR (100 MHz, $CDCl_3$)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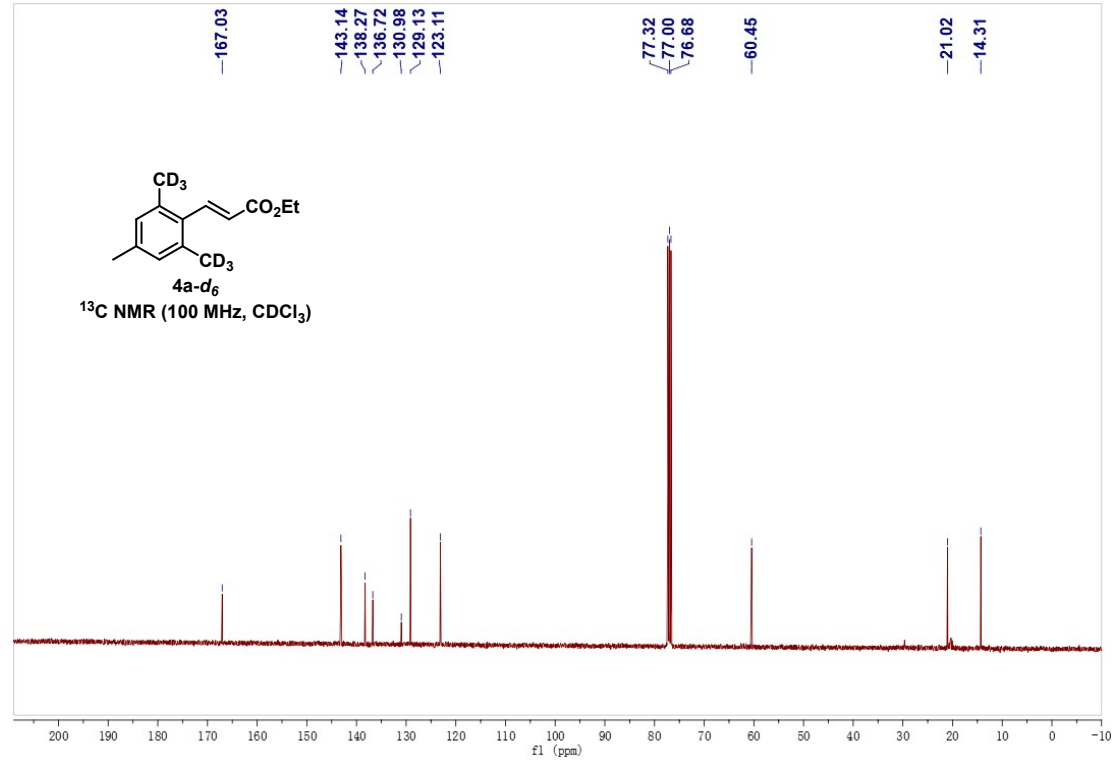
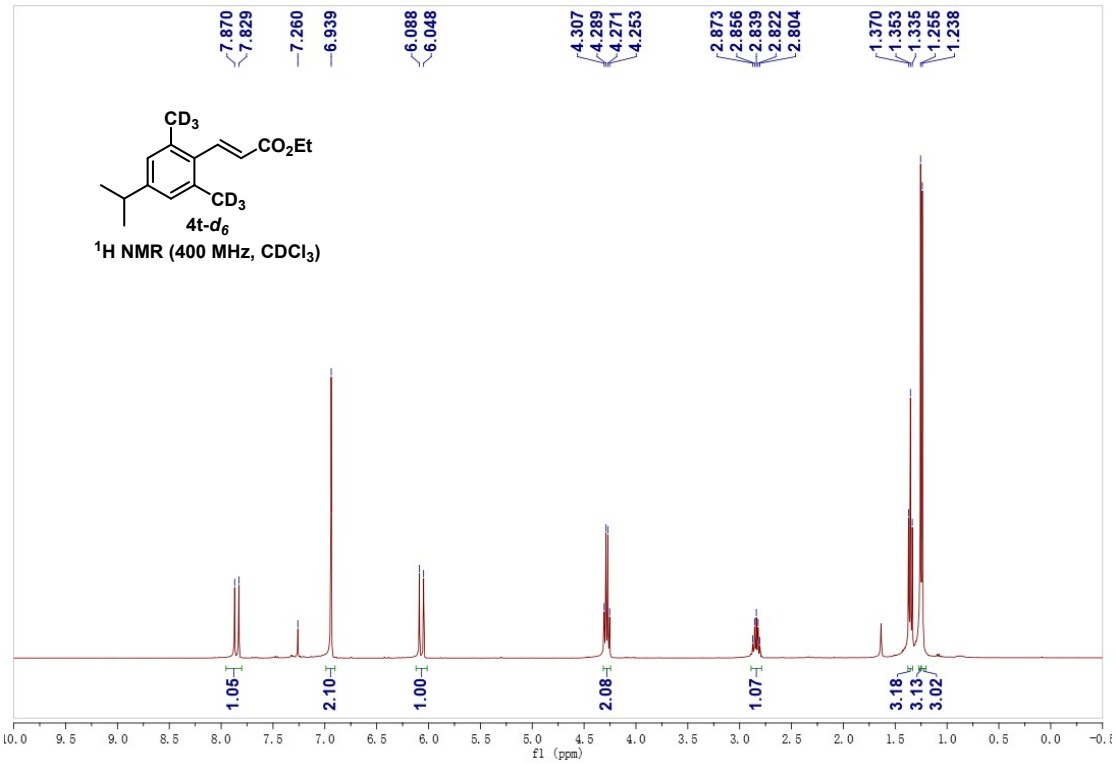
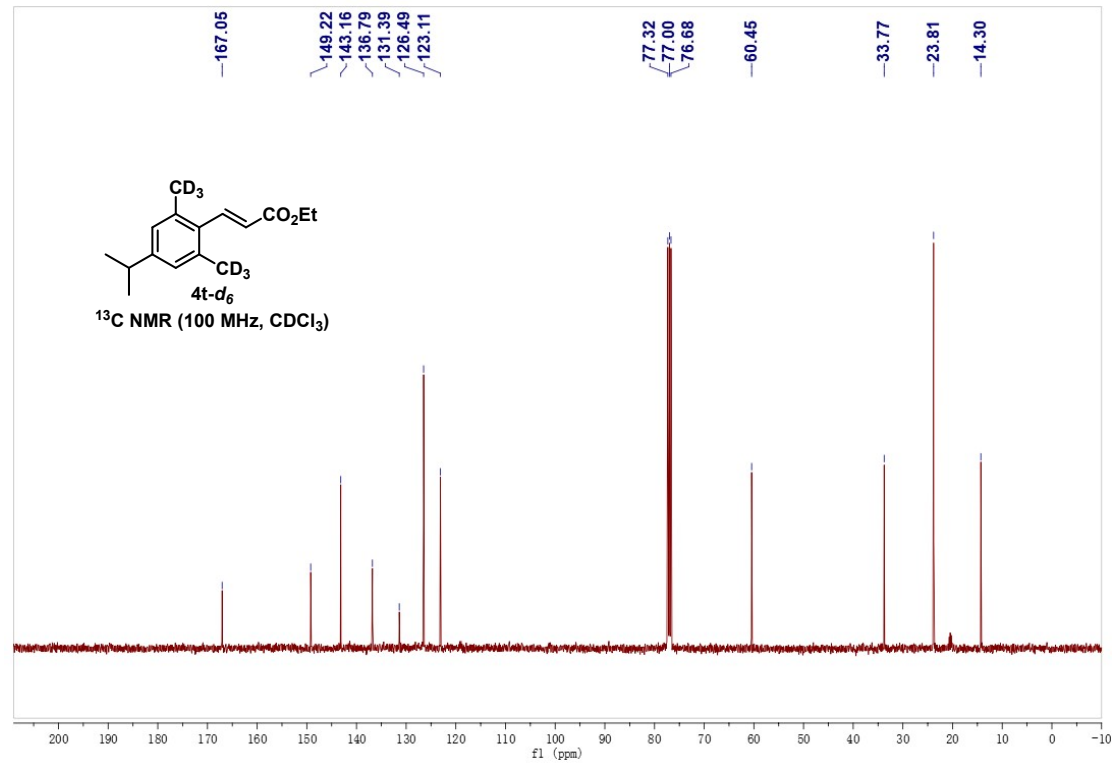
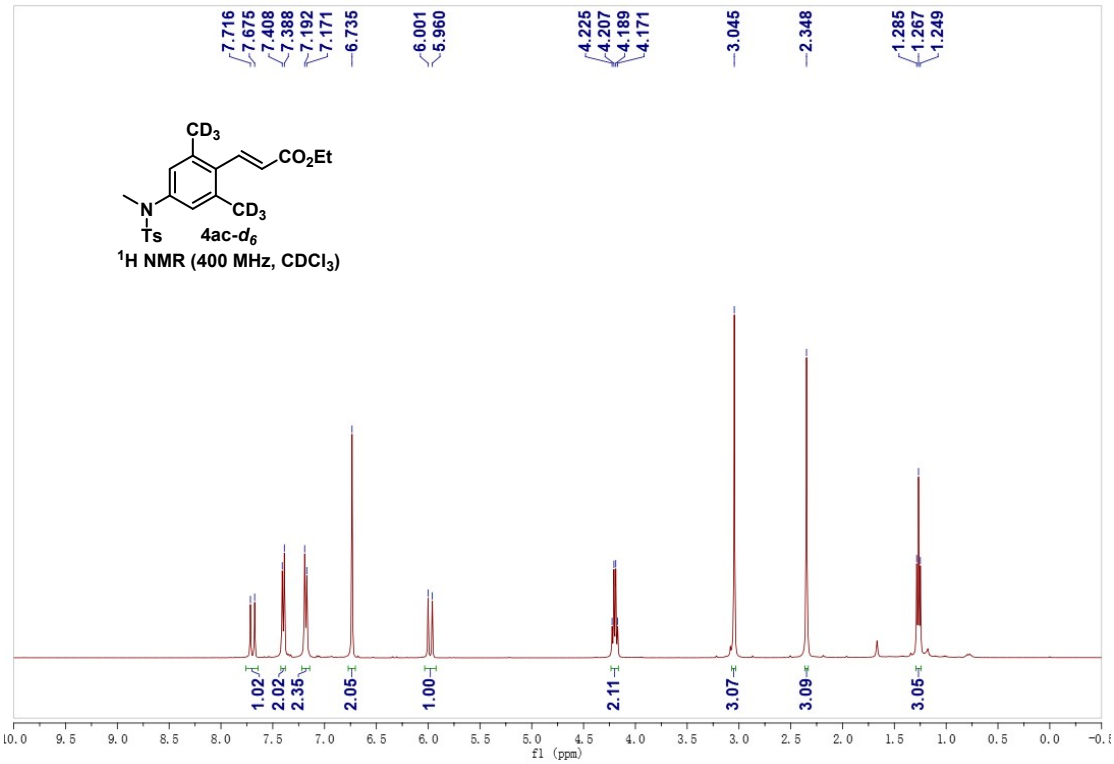
7.822
7.260
6.895
6.075
6.034
4.302
4.284
4.266
4.248
2.287
1.366
1.348
1.330
CD3
CO2Et
CD3
4a-d6
1H NMR (400 MHz, CDCl3)
0.99
2.08
1.00
2.11
3.06
3.15
f1 (ppm)


167.03
143.14
138.27
136.72
130.98
129.13
123.11
77.32
77.00
76.68
60.45
21.02
14.31
CD3
CO2Et
CD3
4a-d6
13C NMR (100 MHz, CDCl3)
f1 (ppm)


7.870
7.829
7.260
6.939
6.088
6.048
4.307
4.289
4.271
4.253
2.873
2.856
2.839
2.822
2.804
1.370
1.353
1.335
1.255
1.238
CD3
CO2Et
CD3
4t-d6
1H NMR (400 MHz, CDCl3)
1.05
2.10
1.00
2.08
1.07
3.18
3.13
3.02
f1 (ppm)


167.05
149.22
143.16
136.79
131.39
126.49
123.11
77.32
77.00
76.68
60.45
33.77
23.81
14.30
CD3
CO2Et
CD3
4t-d6
13C NMR (100 MHz, CDCl3)
f1 (ppm)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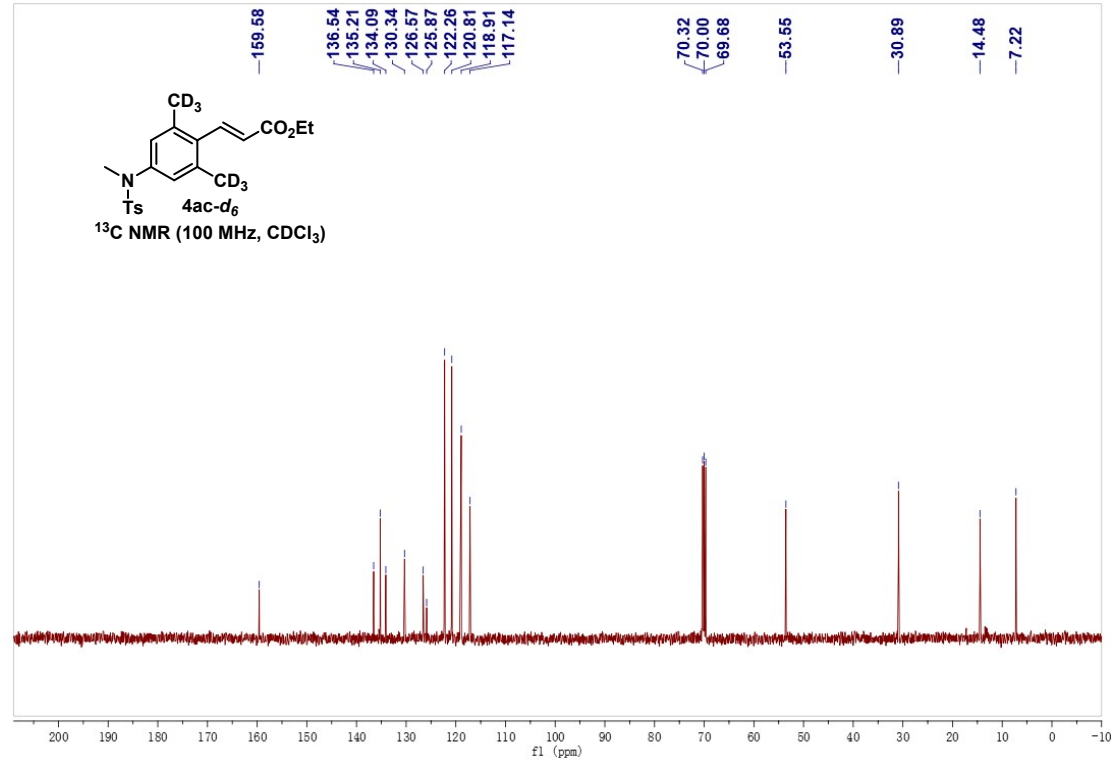
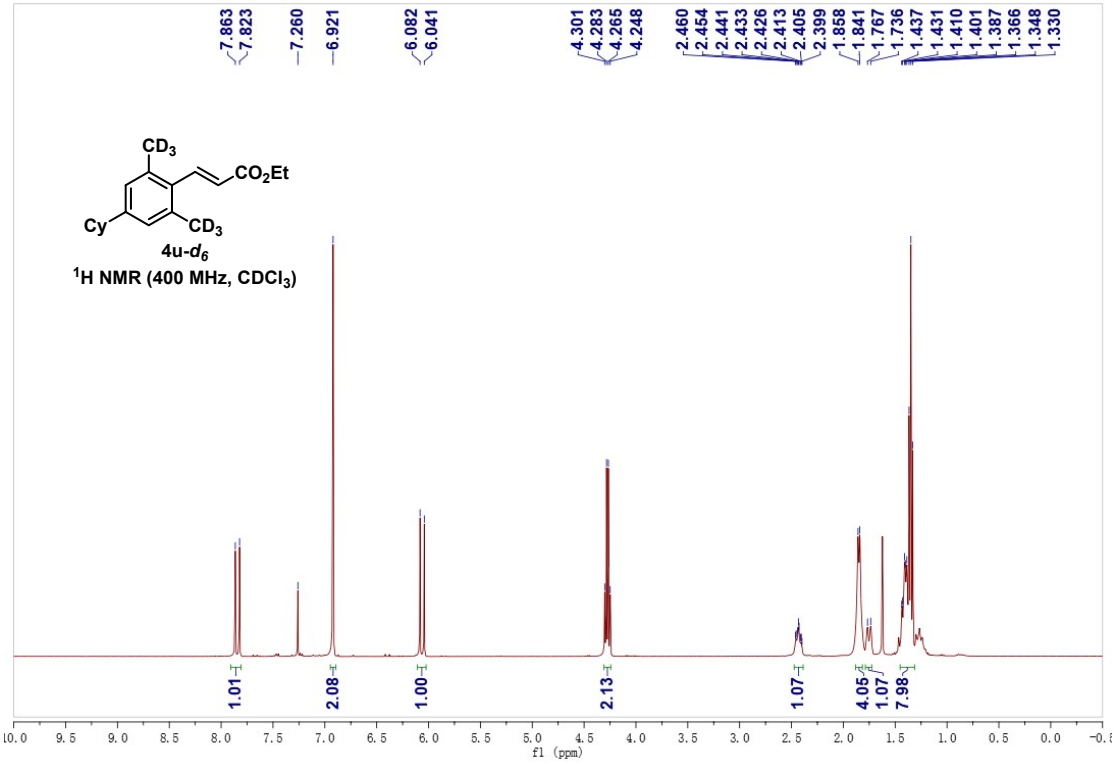
7.675
7.408
7.388
7.192
7.171
6.735
6.001
5.960
4.225
4.207
4.189
4.171
3.045
2.348
1.285
1.267
1.249
CD3
CO2Et
N
Ts
CD3
4ac-d6
1H NMR (400 MHz, CDCl3)
1.02
2.02
2.35
2.05
1.00
2.11
3.07
3.09
3.05
f1 (ppm)


159.58
136.54
135.21
134.09
130.34
126.57
125.87
122.26
120.81
118.91
117.14
70.32
70.00
69.68
53.55
30.89
14.48
7.22
CD3
CO2Et
N
Ts
CD3
4ac-d6
13C NMR (100 MHz, CDCl3)
f1 (ppm)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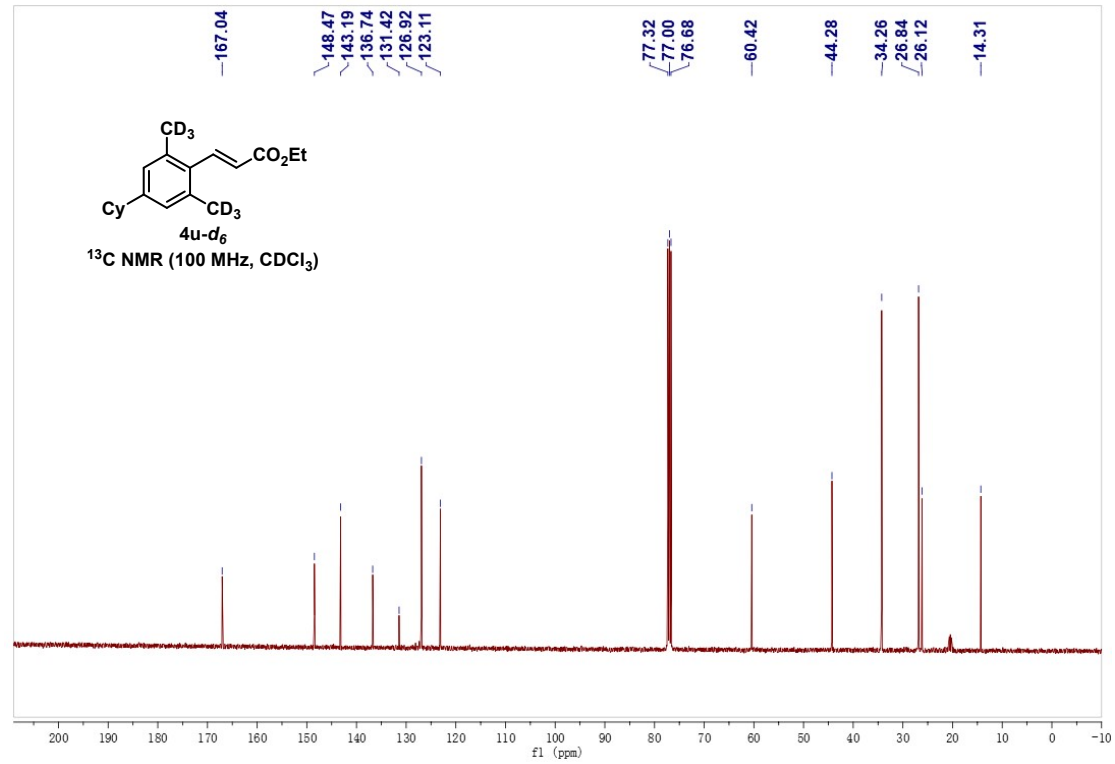
7.823
7.260
6.921
6.082
6.041
4.301
4.283
4.265
4.248
2.460
2.454
2.441
2.433
2.426
2.413
2.405
2.399
1.858
1.841
1.767
1.736
1.437
1.431
1.410
1.401
1.387
1.366
1.348
1.330
CD3
CO2Et
Cy
CD3
4u-d6
1H NMR (400 MHz, CDCl3)
1.01
2.08
1.00
2.13
1.07
4.05
1.07
7.98
f1 (ppm)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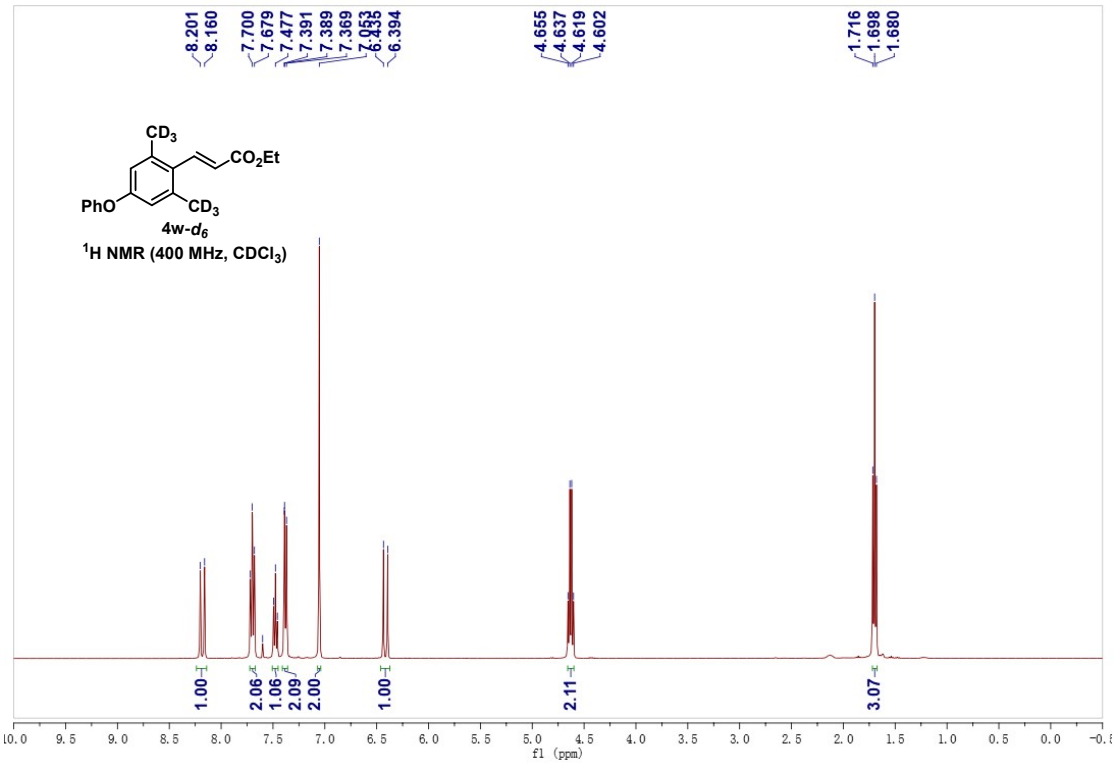
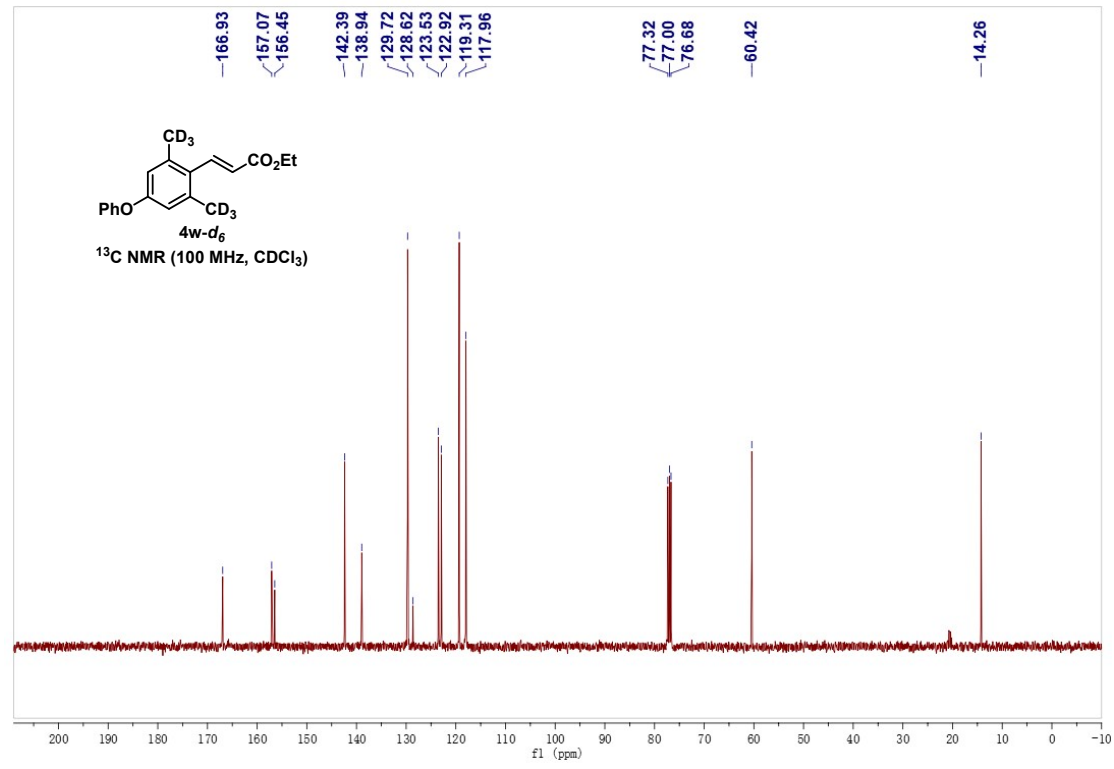
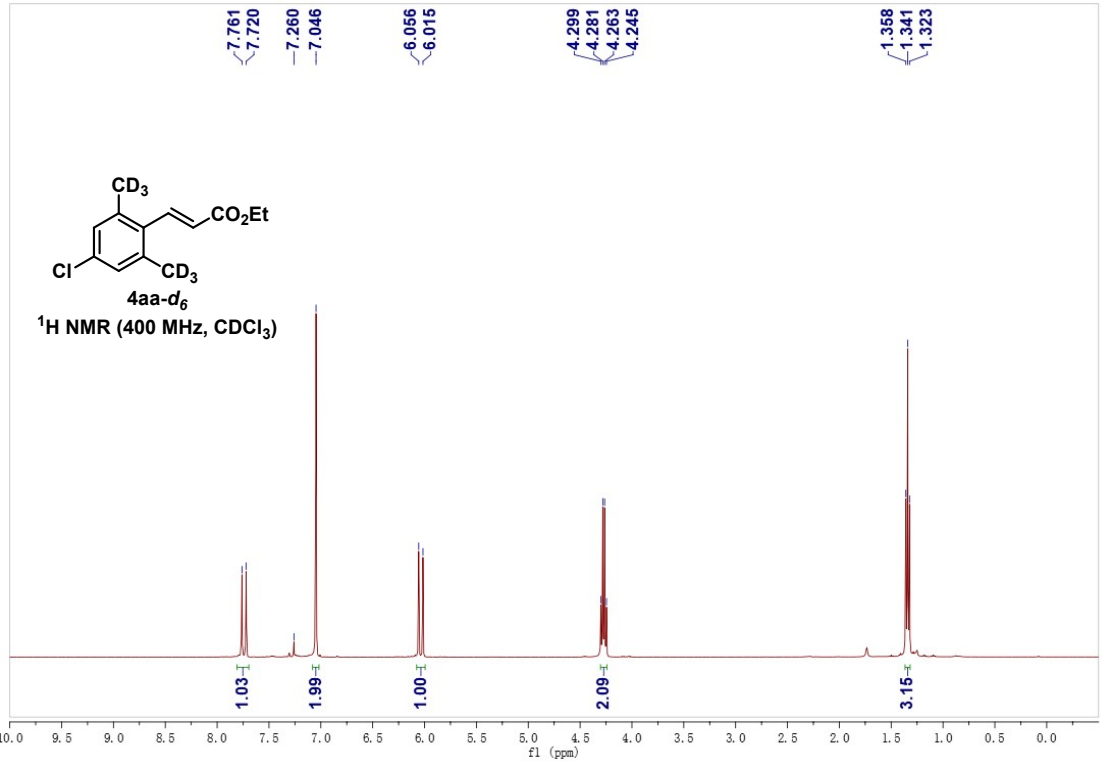
148.47
143.19
136.74
131.42
126.92
123.11
77.32
77.00
76.68
60.42
44.28
34.26
26.84
26.12
14.31
CD3
CO2Et
Cy
CD3
4u-d6
13C NMR (100 MHz, CDCl3)
f1 (ppm)


8.201
8.160
7.700
7.679
7.477
7.391
7.389
7.369
7.053
6.433
6.394
4.655
4.637
4.619
4.602
1.716
1.698
1.680
CD3
CO2Et
PhO
CD3
4w-d6
1H NMR (400 MHz, CDCl3)
1.00
2.06
1.06
2.09
2.00
1.00
2.11
3.07
f1 (ppm)


166.93
157.07
156.45
142.39
138.94
129.72
128.62
123.53
122.92
119.31
117.96
77.32
77.00
76.68
60.42
14.26
CD3
CO2Et
PhO
CD3
4w-d6
13C NMR (100 MHz, CDCl3)
f1 (ppm)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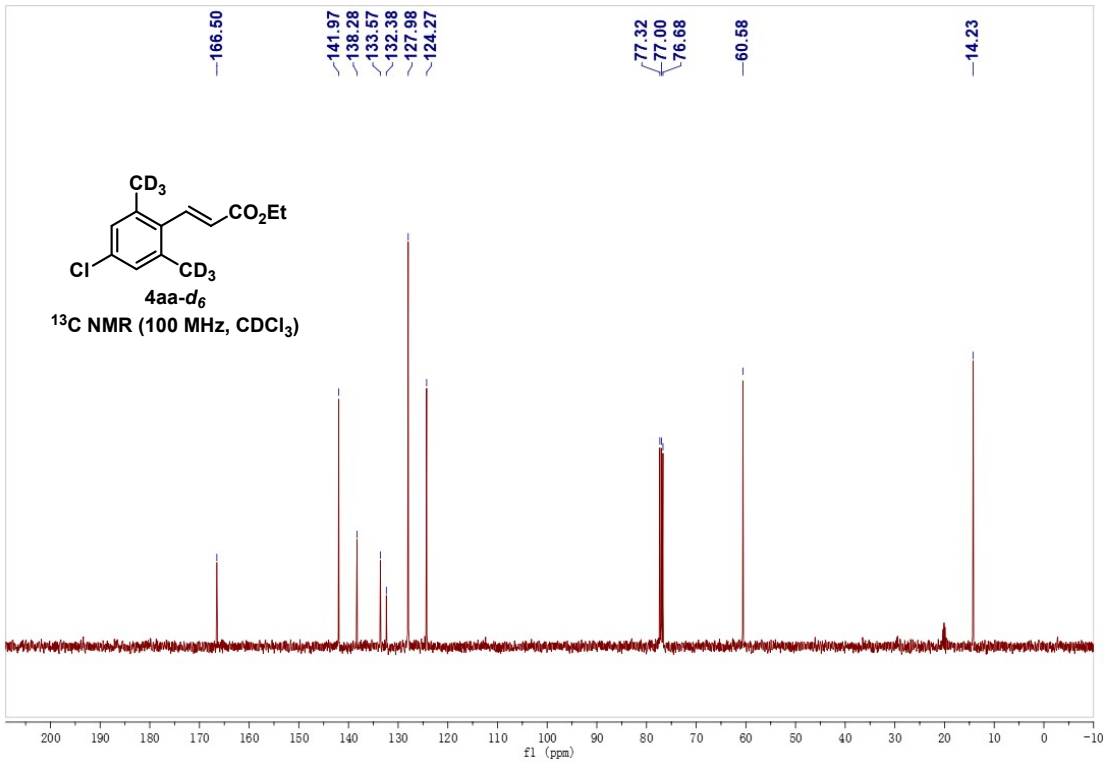
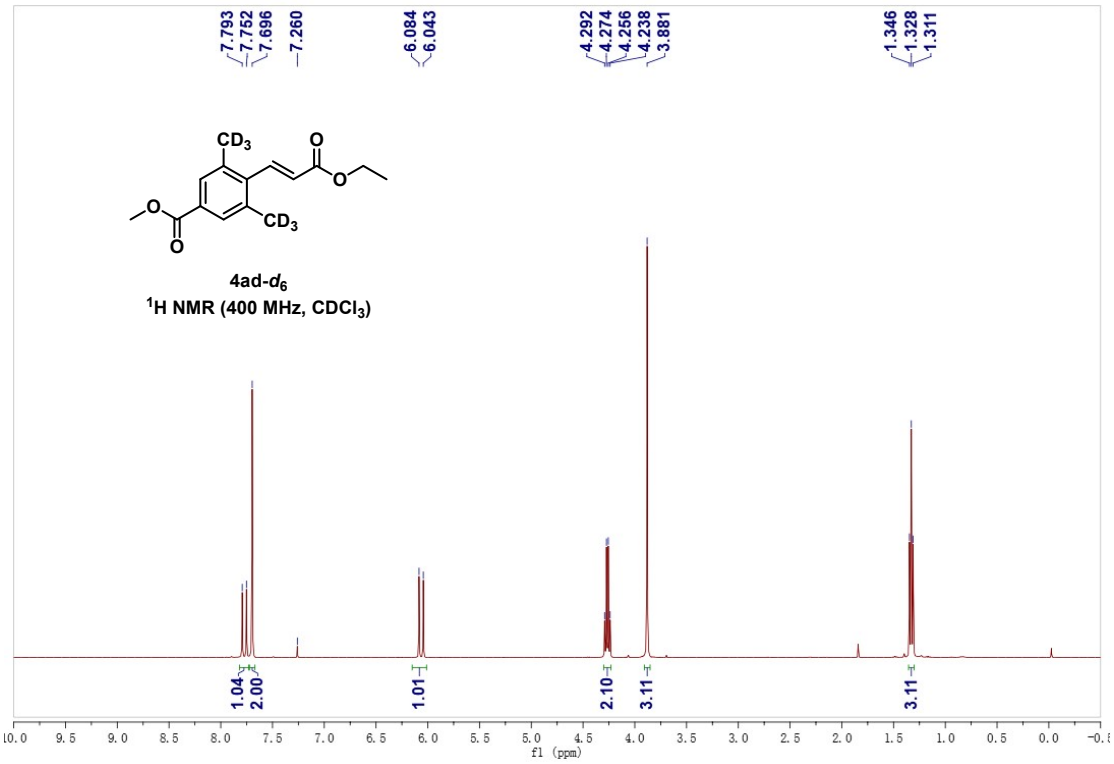
7.720
7.260
7.046
6.056
6.015
4.299
4.281
4.263
4.245
1.358
1.341
1.323
CD3
CO2Et
Cl
CD3
4aa-d6
1H NMR (400 MHz, CDCl3)
1.03
1.99
1.00
2.09
3.15
f1 (ppm)


166.50
141.97
138.28
133.57
132.38
127.98
124.27
77.32
77.00
76.68
60.58
14.23
CD3
CO2Et
Cl
CD3
4aa-d6
13C NMR (100 MHz, CDCl3)
f1 (ppm)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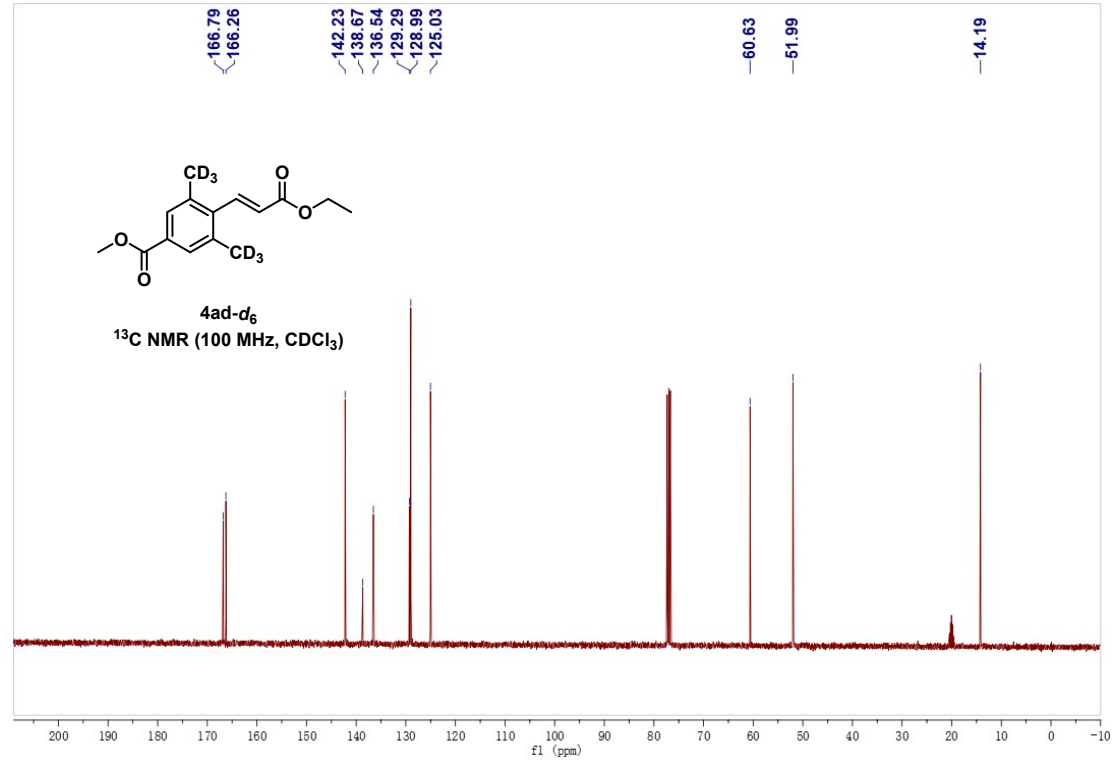
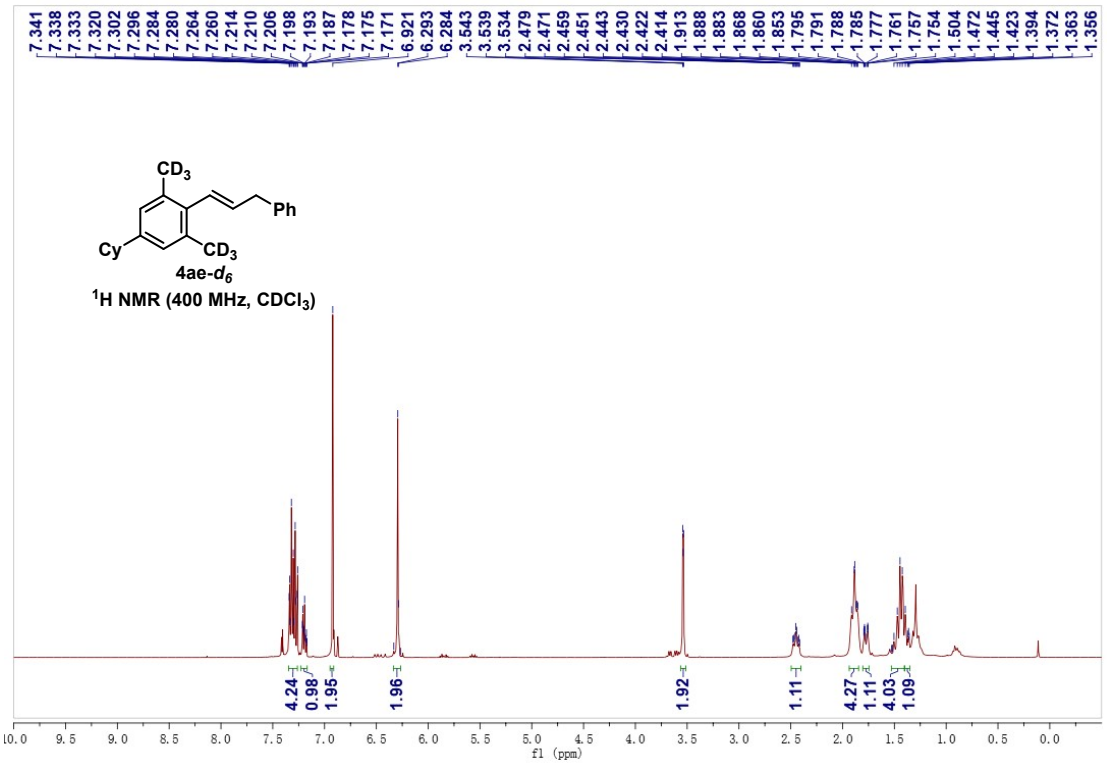
7.762
7.696
7.260
6.084
6.043
4.292
4.274
4.256
4.238
3.881
1.346
1.328
1.311
CD3
O
O
O
CD3
O
4ad-d6
1H NMR (400 MHz, CDCl3)
1.04
2.00
1.01
2.10
3.11
3.11
f1 (ppm)


166.79
166.26
142.23
138.67
136.54
129.29
128.99
125.03
60.63
51.99
14.19
CD3
O
O
O
CD3
O
4ad-d6
13C NMR (100 MHz, CDCl3)
f1 (ppm)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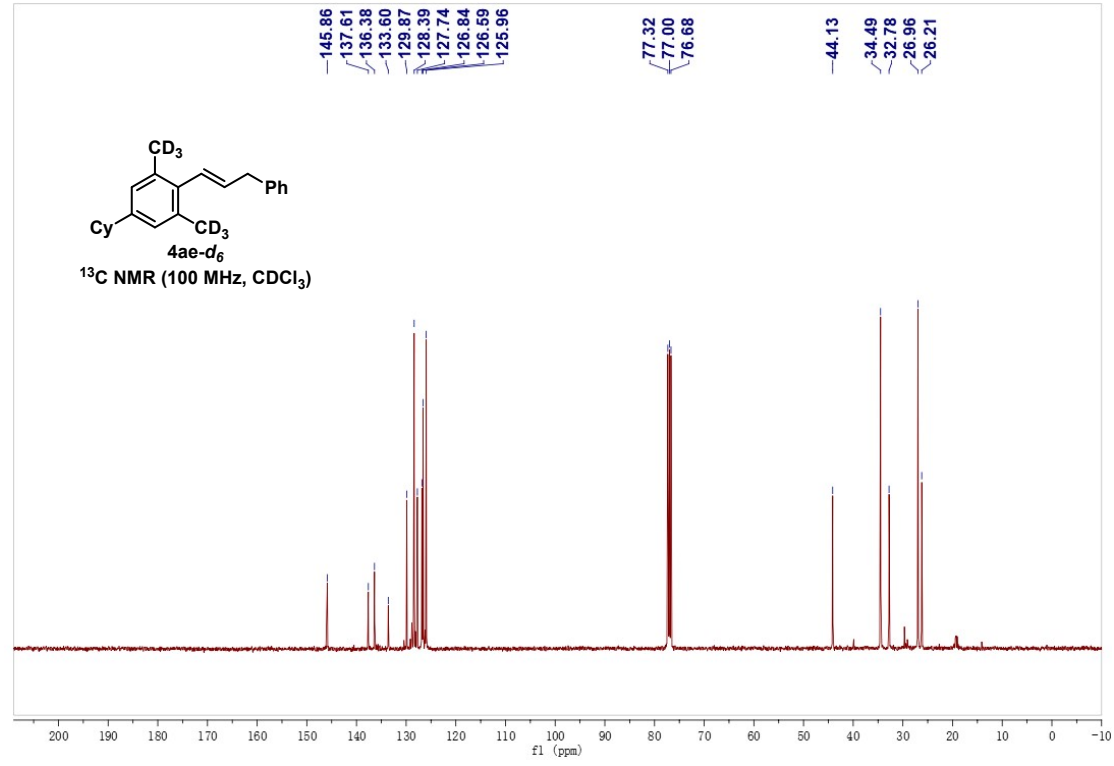
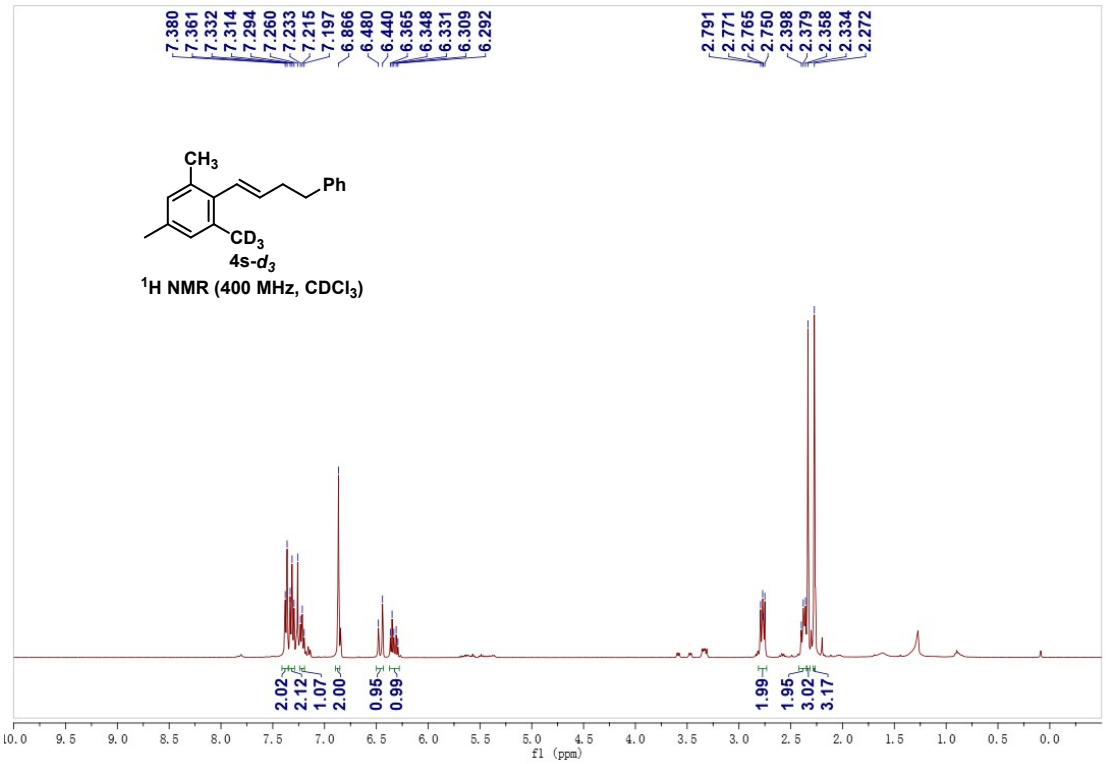
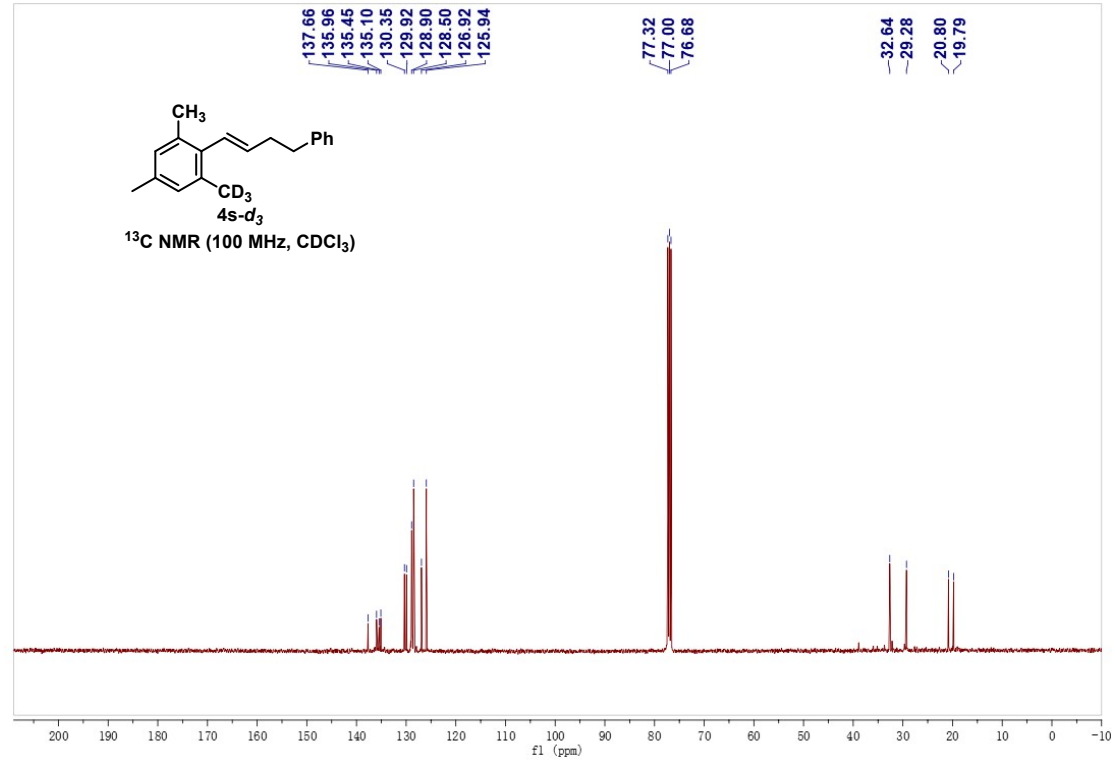
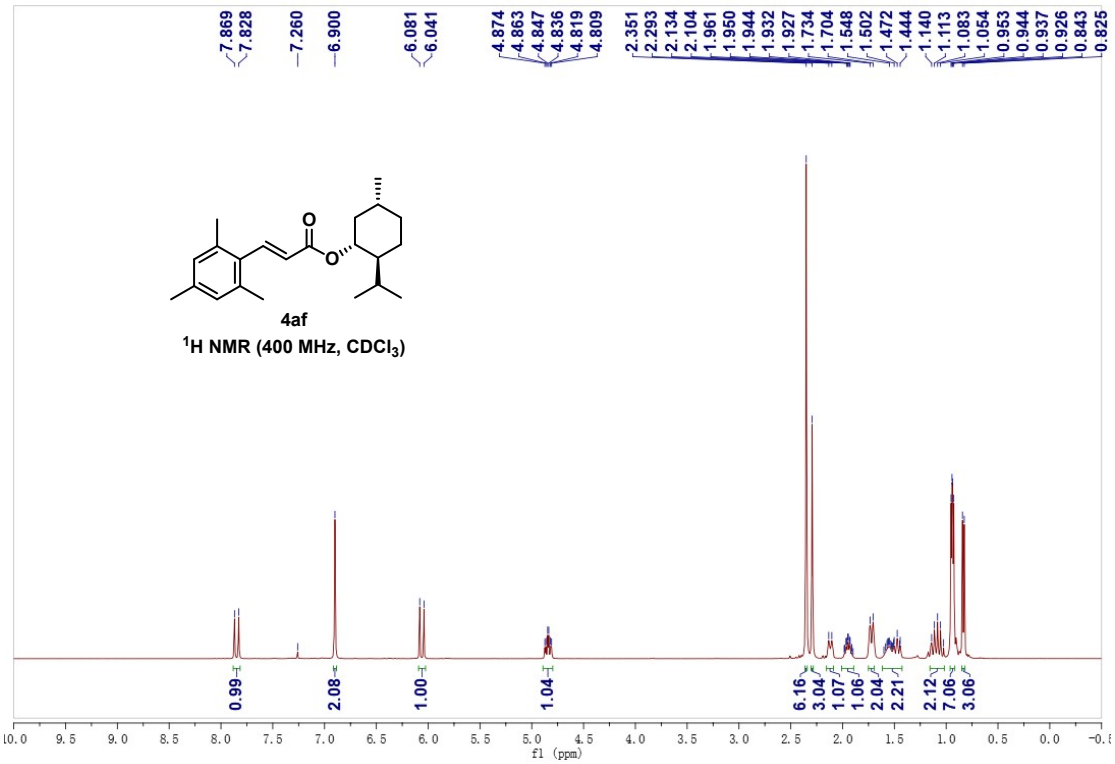
7.338
7.333
7.320
7.302
7.296
7.284
7.280
7.264
7.260
7.214
7.210
7.206
7.198
7.193
7.187
7.178
7.175
7.171
6.921
6.293
6.284
3.543
3.539
3.534
2.479
2.471
2.459
2.451
2.443
2.430
2.422
2.414
1.913
1.888
1.883
1.868
1.860
1.853
1.795
1.791
1.788
1.785
1.777
1.761
1.757
1.754
1.504
1.472
1.445
1.423
1.394
1.372
1.363
1.356
CD3
Ph
Cy
CD3
4ae-d6
1H NMR (400 MHz, CDCl3)
4.24
0.98
1.95
1.96
1.92
1.11
4.27
1.11
4.03
1.09
f1 (ppm)


145.86
137.61
136.38
133.60
129.87
128.39
127.74
126.84
126.59
125.96
77.32
77.00
76.68
44.13
34.49
32.78
26.96
26.21
CD3
Ph
Cy
CD3
4ae-d6
13C NMR (100 MHz, CDCl3)
f1 (ppm)

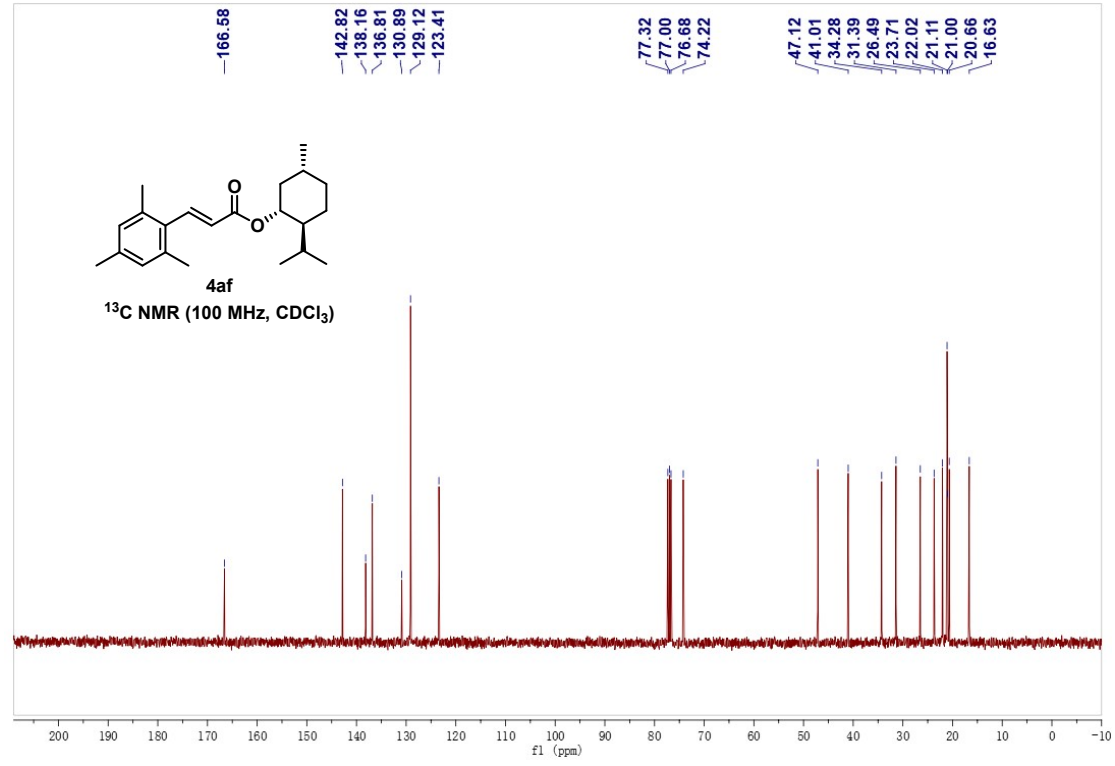

7.380
7.361
7.332
7.314
7.294
7.260
7.233
7.215
7.197
6.866
6.480
6.440
6.365
6.348
6.331
6.309
6.292
2.791
2.771
2.765
2.750
2.398
2.379
2.358
2.334
2.272
CH3
Ph
CD3
4s-d3
1H NMR (400 MHz, CDCl3)
2.02
2.12
1.07
2.00
0.95
0.99
1.99
1.95
3.02
3.17
f1 (ppm)


137.66
135.96
135.45
135.10
130.35
129.92
128.90
128.50
126.92
125.94
77.32
77.00
76.68
32.64
29.28
20.80
19.79
CH3
Ph
CD3
4s-d3
13C NMR (100 MHz, CDCl3)
f1 (ppm)



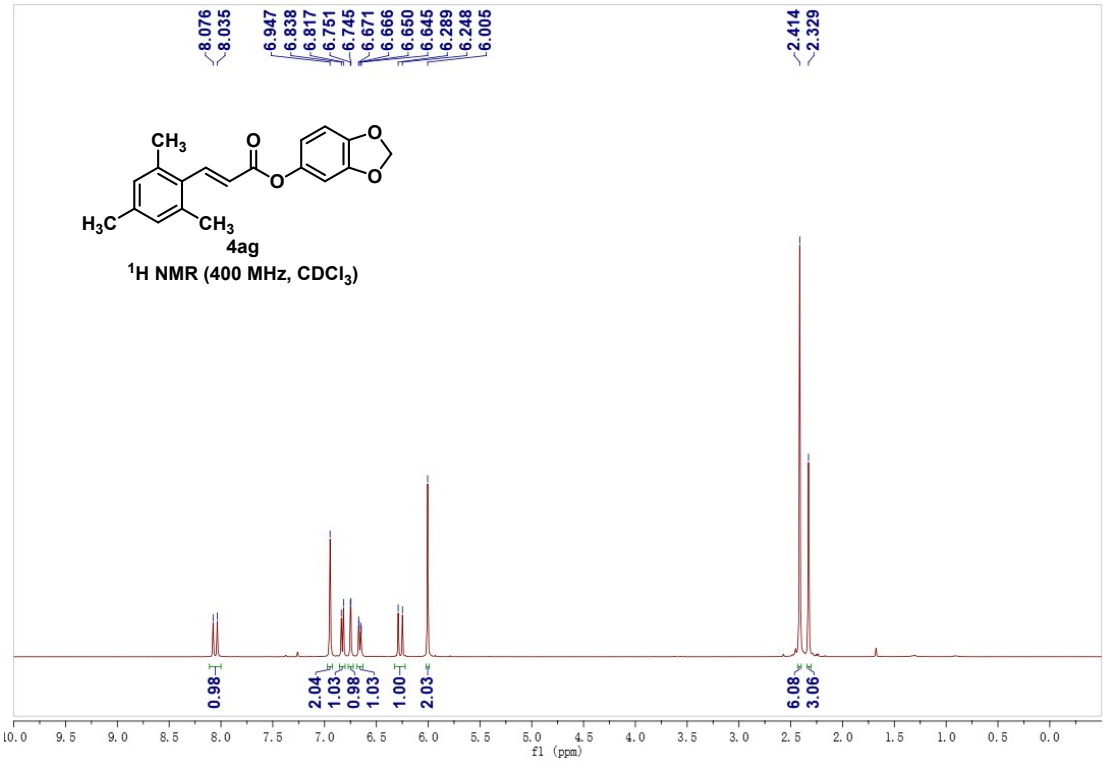
4af

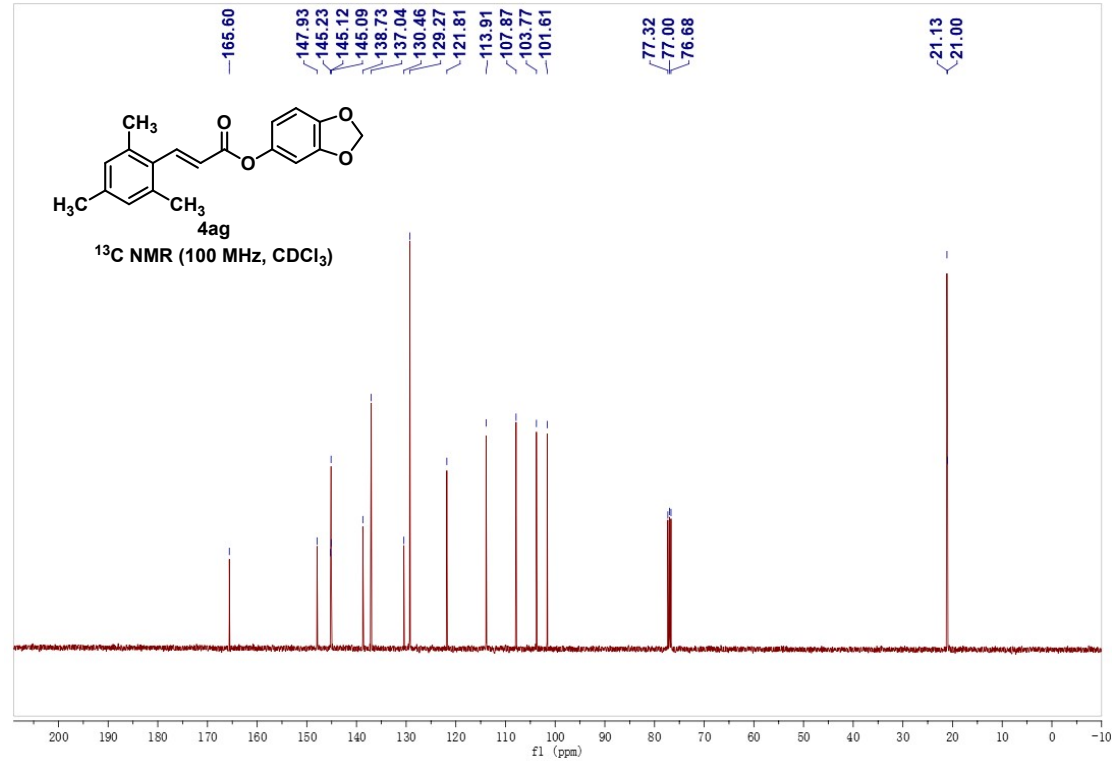
^{1}H NMR (400 MHz, $CDCl_3$)

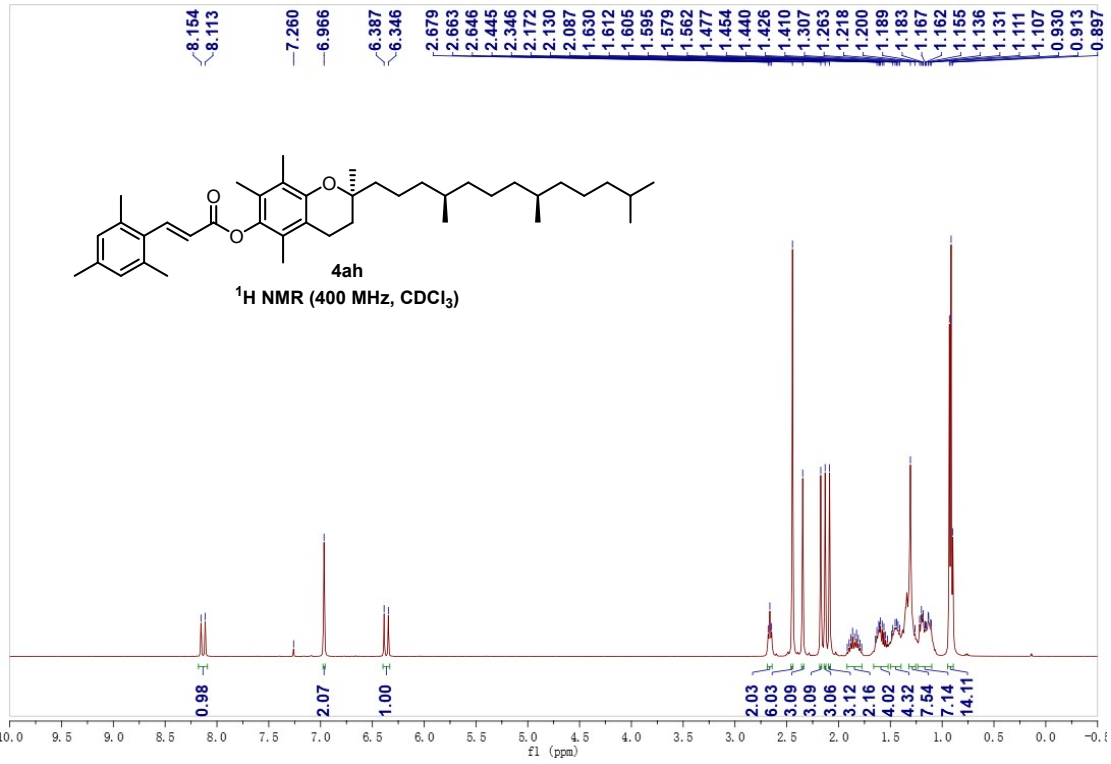


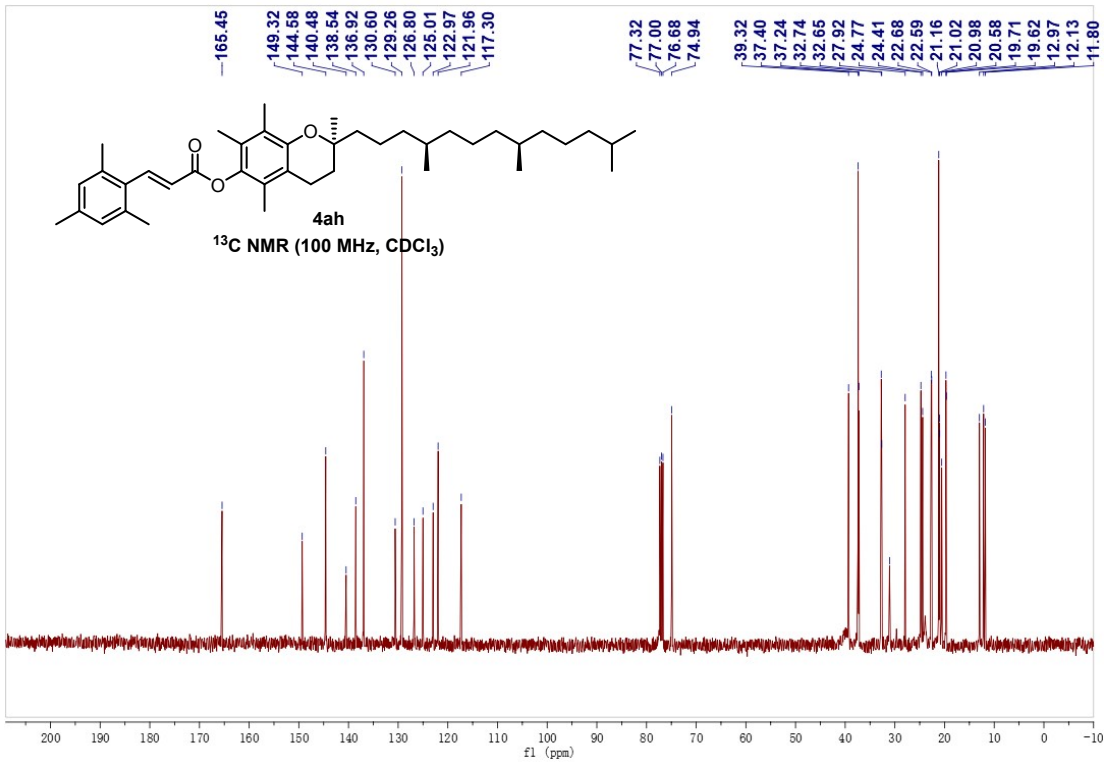
4af

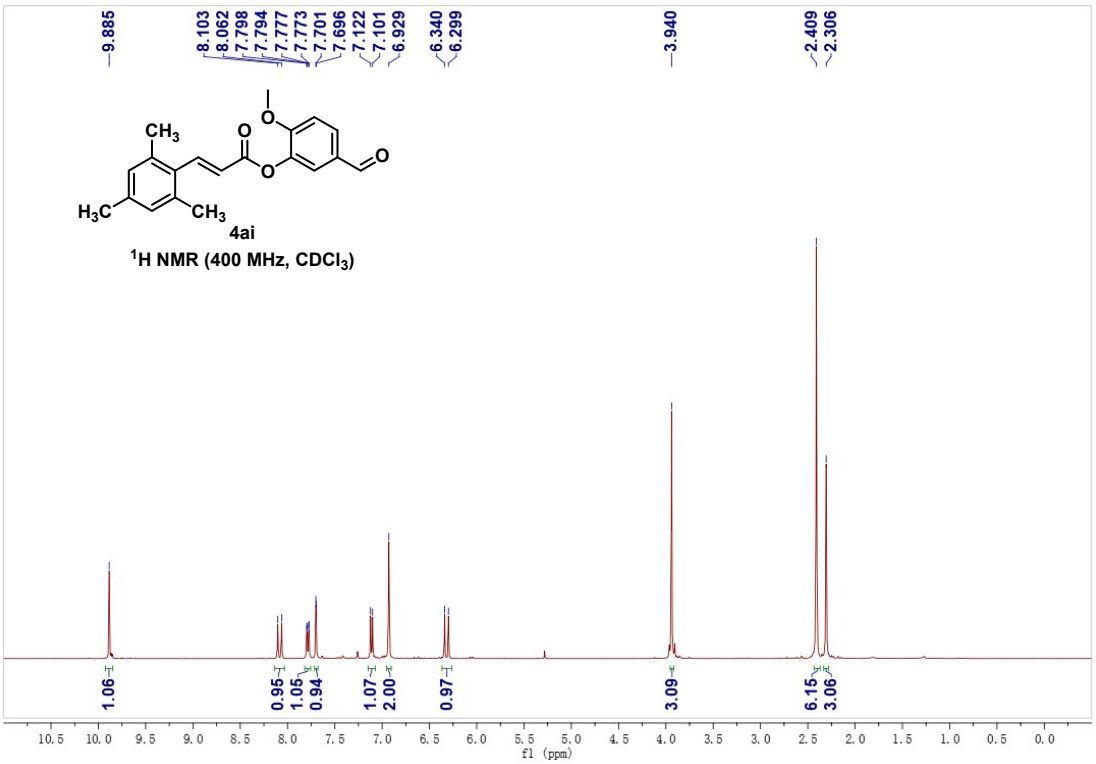
^{13}C NMR (100 MHz, $CDCl_3$)


8.076
8.035
6.947
6.838
6.817
6.751
6.745
6.671
6.666
6.650
6.645
6.289
6.248
6.005
2.414
2.329
CH3
O
O
O
H3C
CH3
4ag
1H NMR (400 MHz, CDCl3)
0.98
2.04
1.03
0.98
1.03
1.00
2.03
6.08
3.06
f1 (ppm)


165.60
147.93
145.23
145.12
145.09
138.73
137.04
130.46
129.27
121.81
113.91
107.87
103.77
101.61
77.32
77.00
76.68
21.13
21.00
CH3
O
O
O
H3C
CH3
4ag
13C NMR (100 MHz, CDCl3)
f1 (ppm)

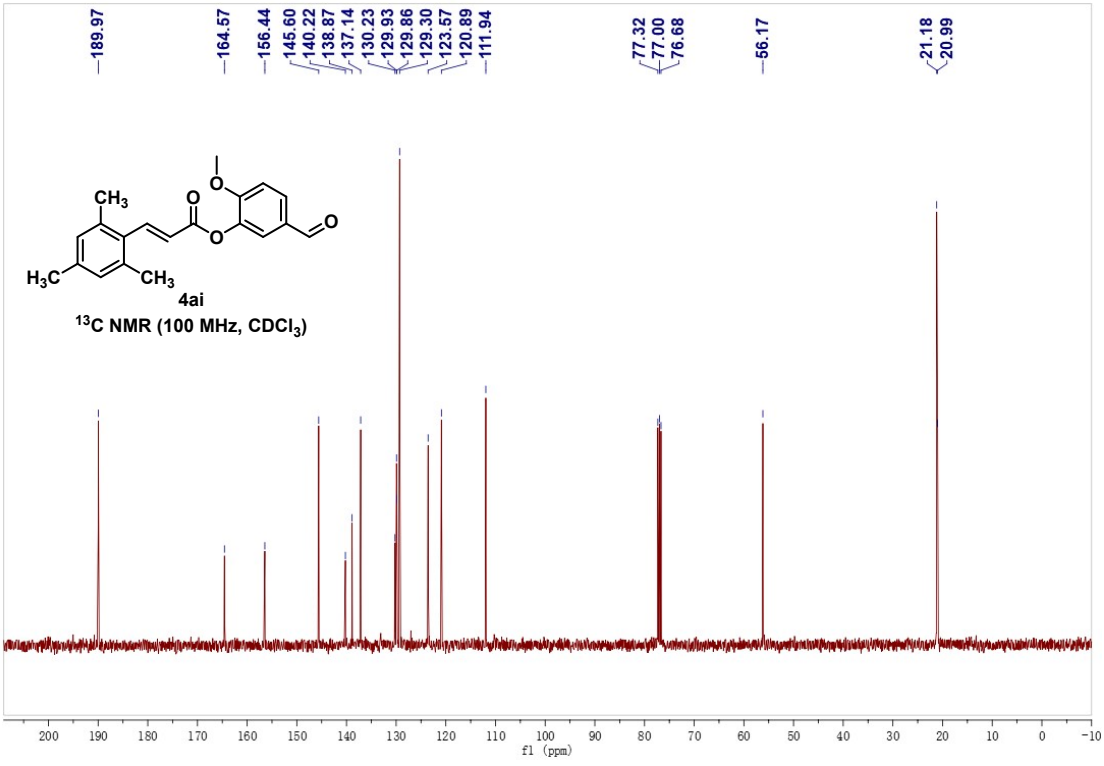

8.154
8.113
7.260
6.966
6.387
6.346
2.679
2.663
2.646
2.445
2.346
2.172
2.130
2.087
1.630
1.612
1.605
1.595
1.579
1.562
1.477
1.454
1.440
1.426
1.410
1.307
1.263
1.218
1.200
1.189
1.183
1.167
1.162
1.155
1.136
1.131
1.111
1.107
0.930
0.913
0.897
4ah
^{1}H NMR (400 MHz, CDCl$_3$)
0.98
2.07
1.00
2.03
6.03
3.09
3.09
3.06
3.12
2.16
4.02
4.32
7.54
7.14
14.11
f1 (ppm)


165.45
149.32
144.58
140.48
138.54
136.92
130.60
129.26
126.80
125.01
122.97
121.96
117.30
77.32
77.00
76.68
74.94
39.32
37.40
37.24
32.74
32.65
27.92
24.77
24.41
22.68
22.59
21.16
21.02
20.98
20.58
19.71
19.62
12.97
12.13
11.80
4ah
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



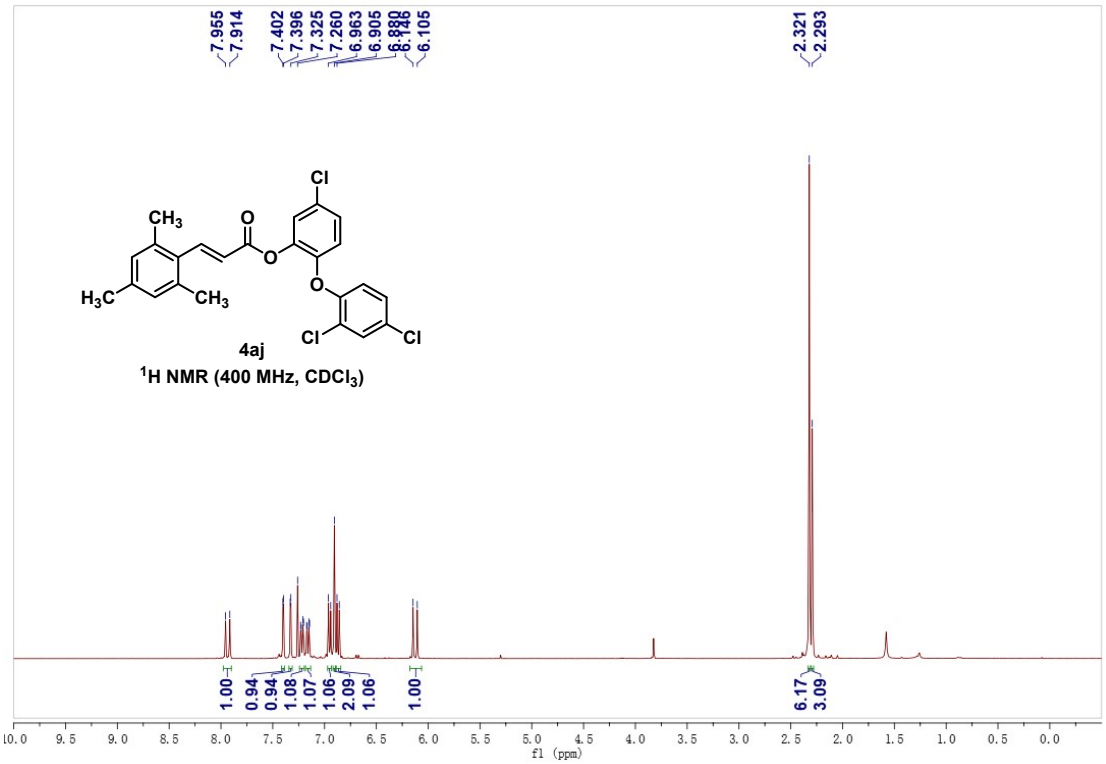
4ai

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



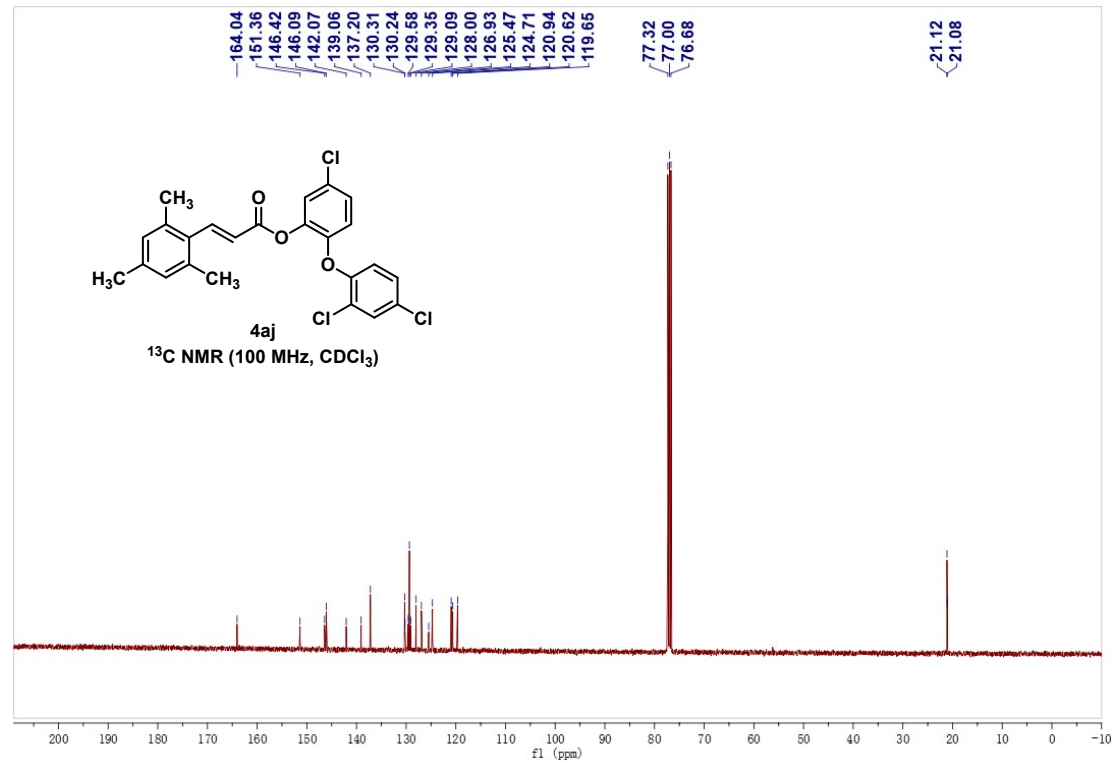
4ai

^{13}C NMR (100 MHz, $CDCl_3$)



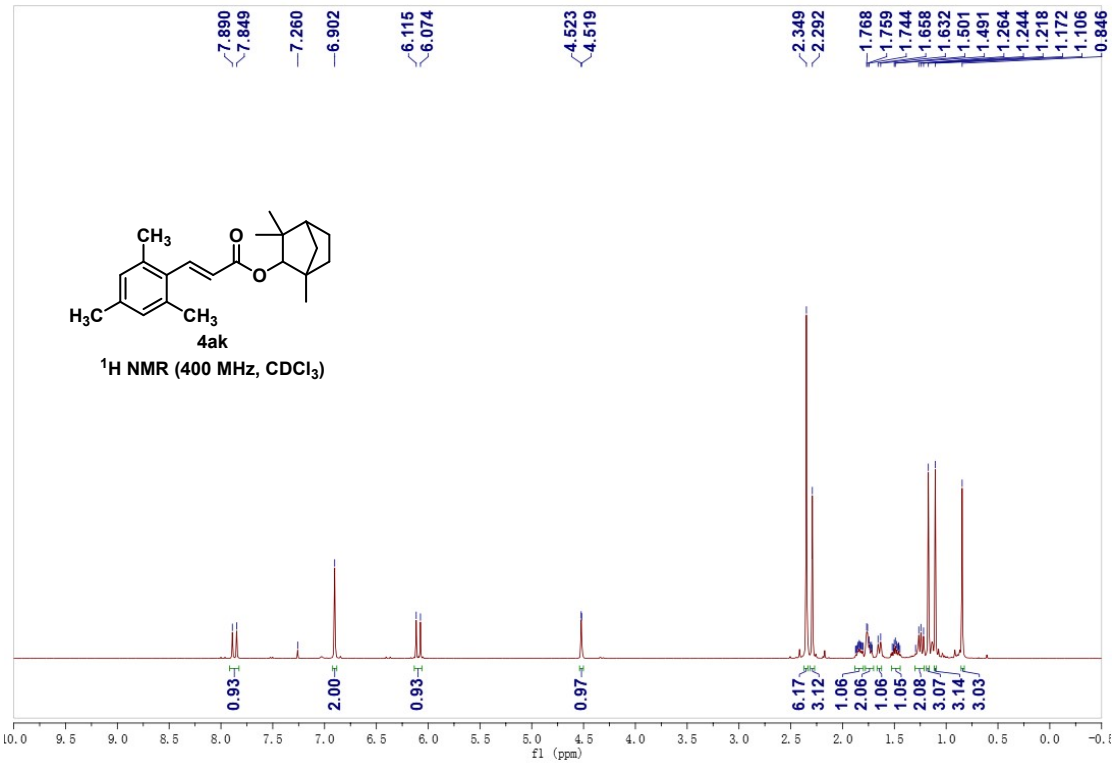
4aj

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



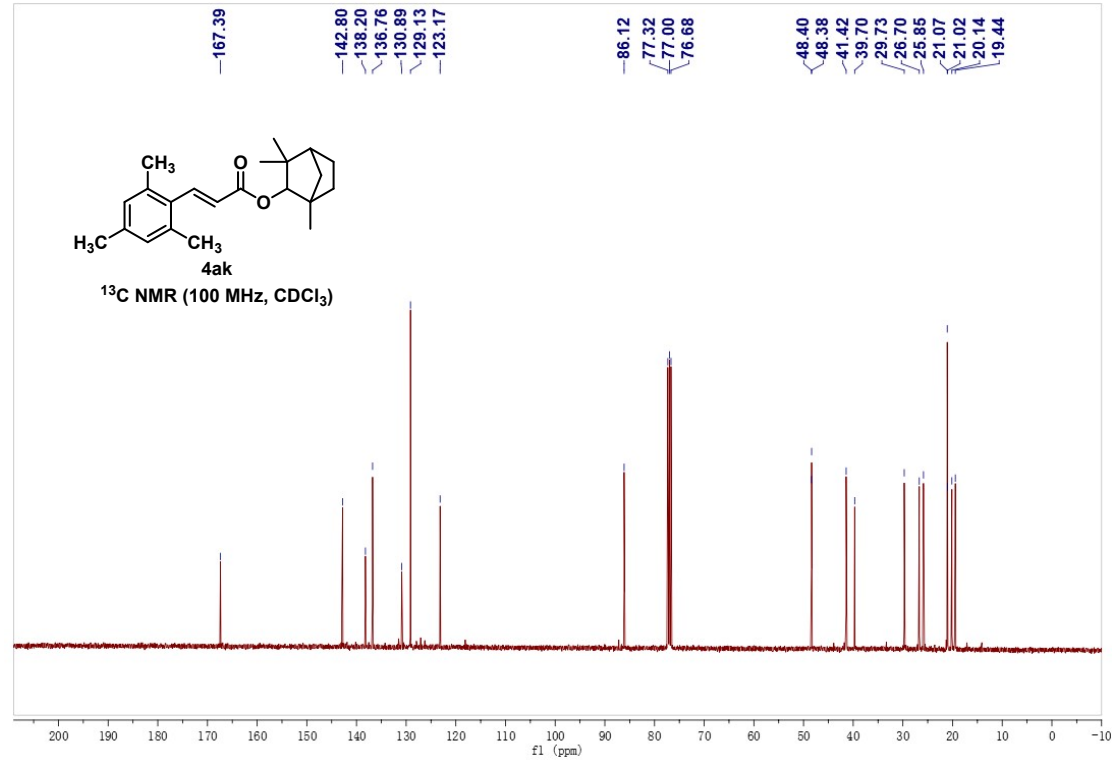
4aj

^{13}C NMR (100 MHz, $CDCl_3$)



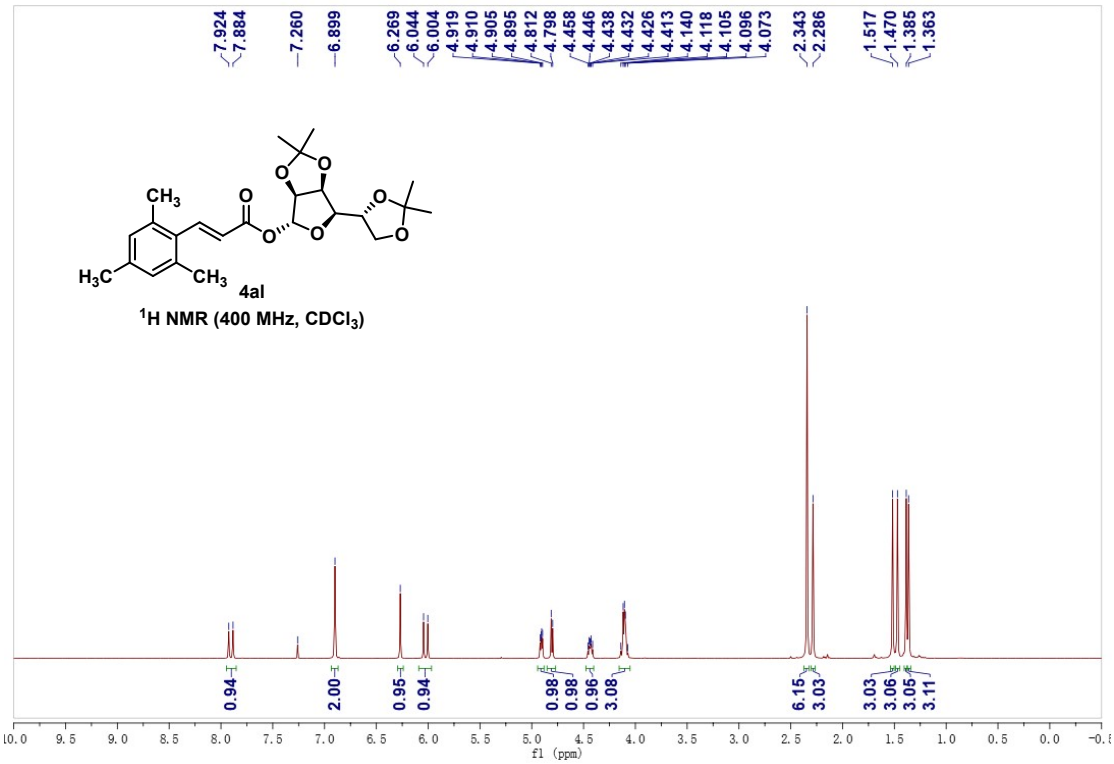
4ak

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

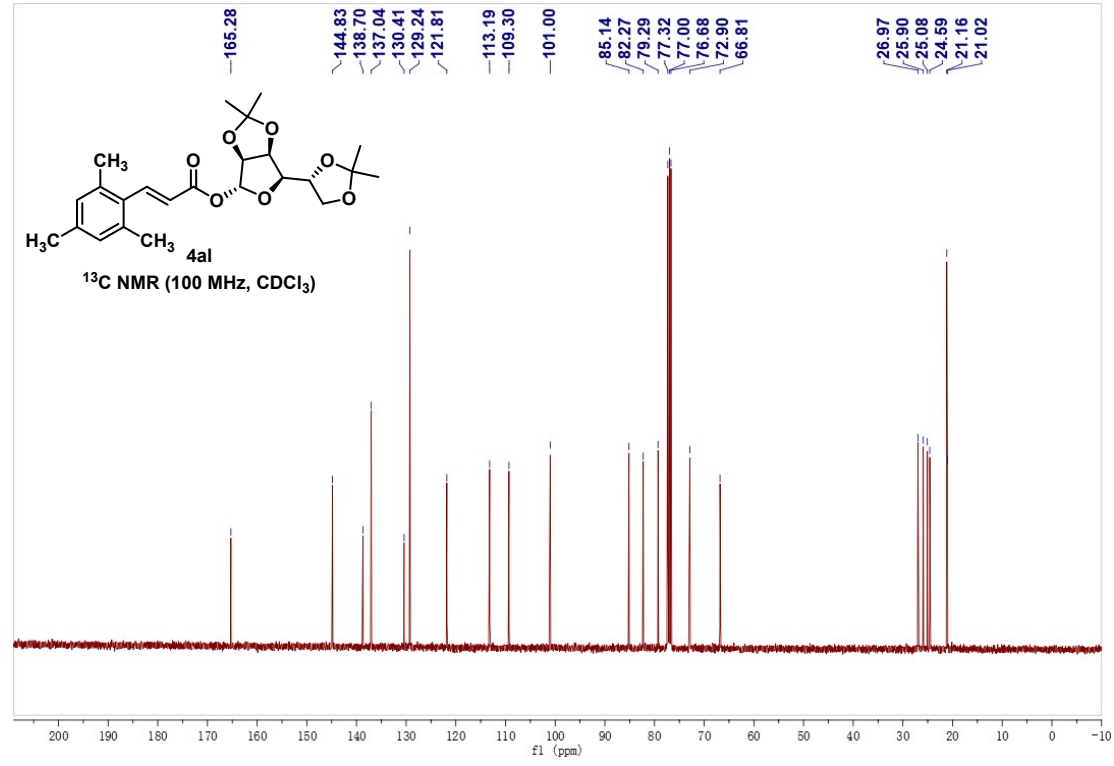


4ak

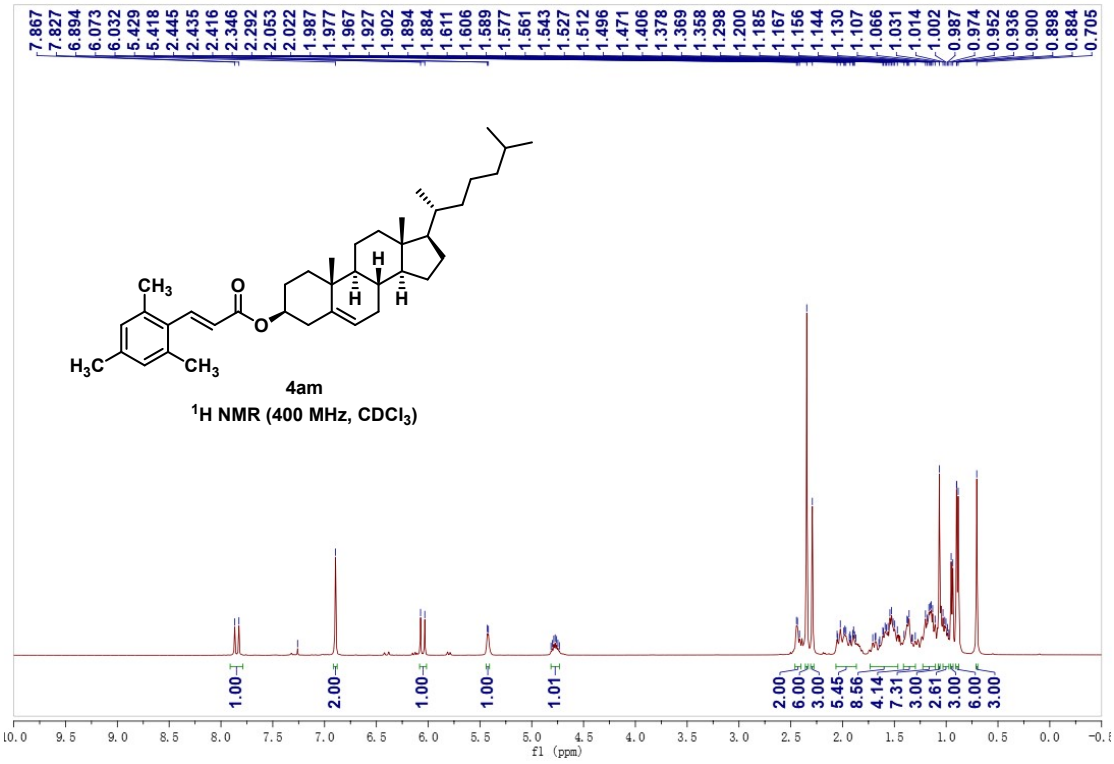
^{13}C NMR (100 MHz, $CDCl_3$)

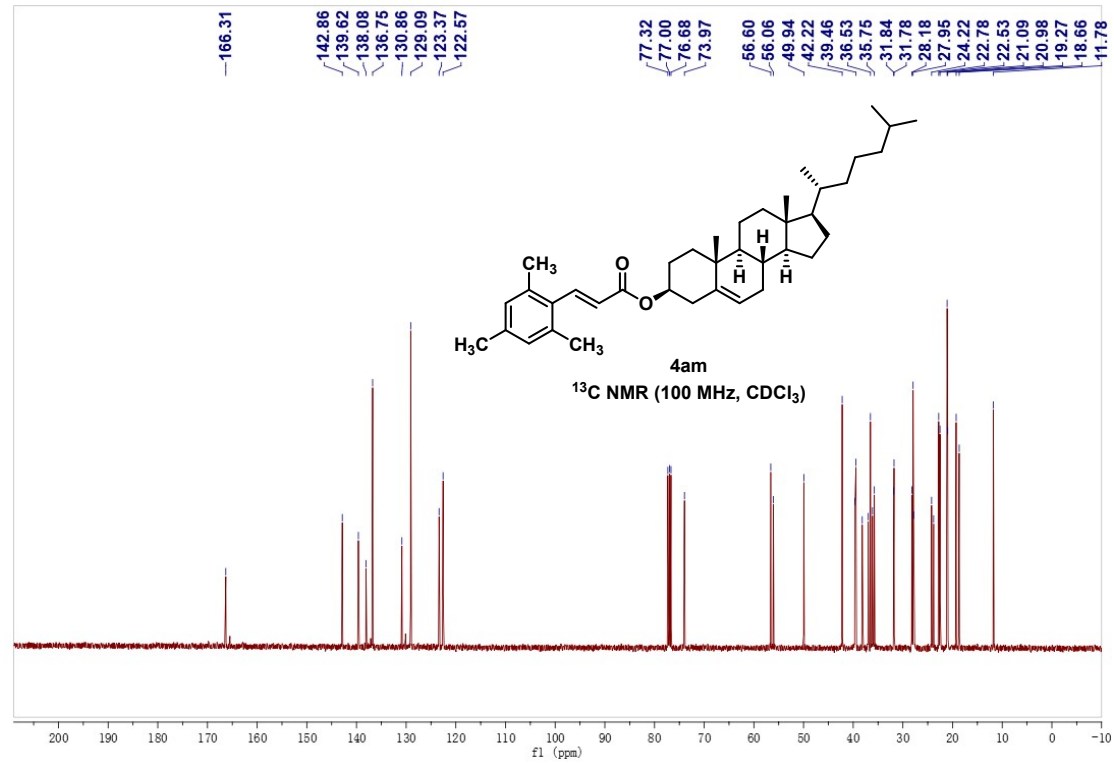


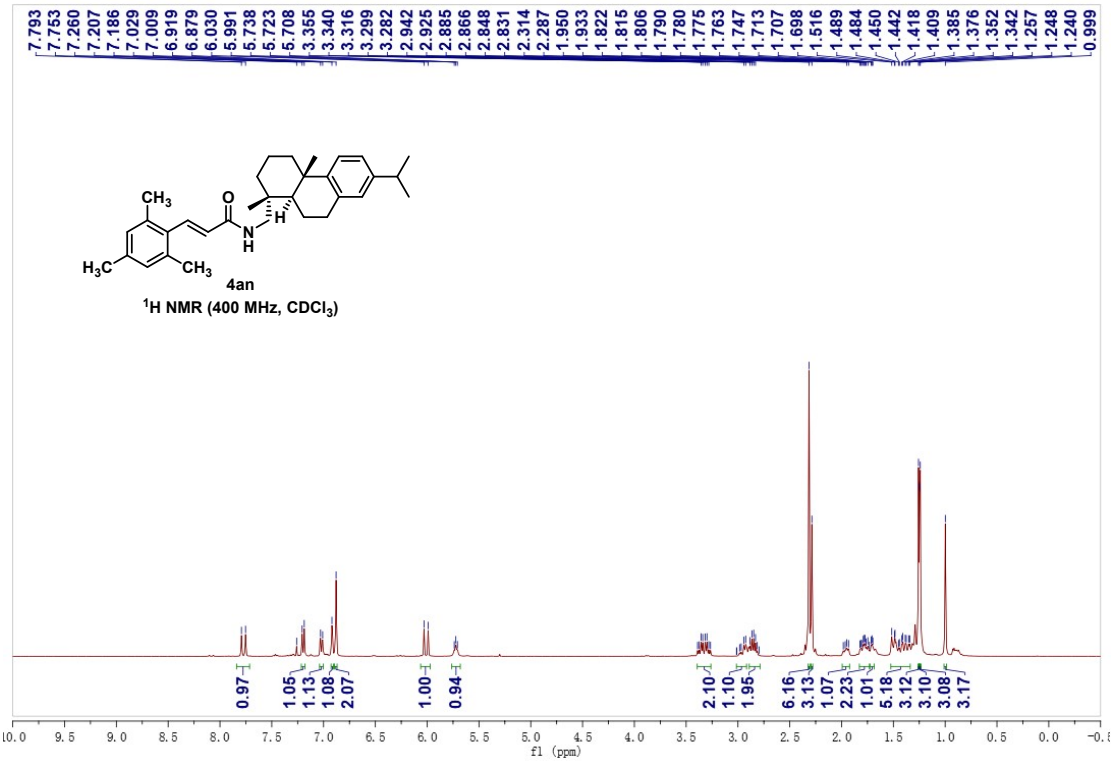
^{1}H NMR (400 MHz, $CDCl_3$)

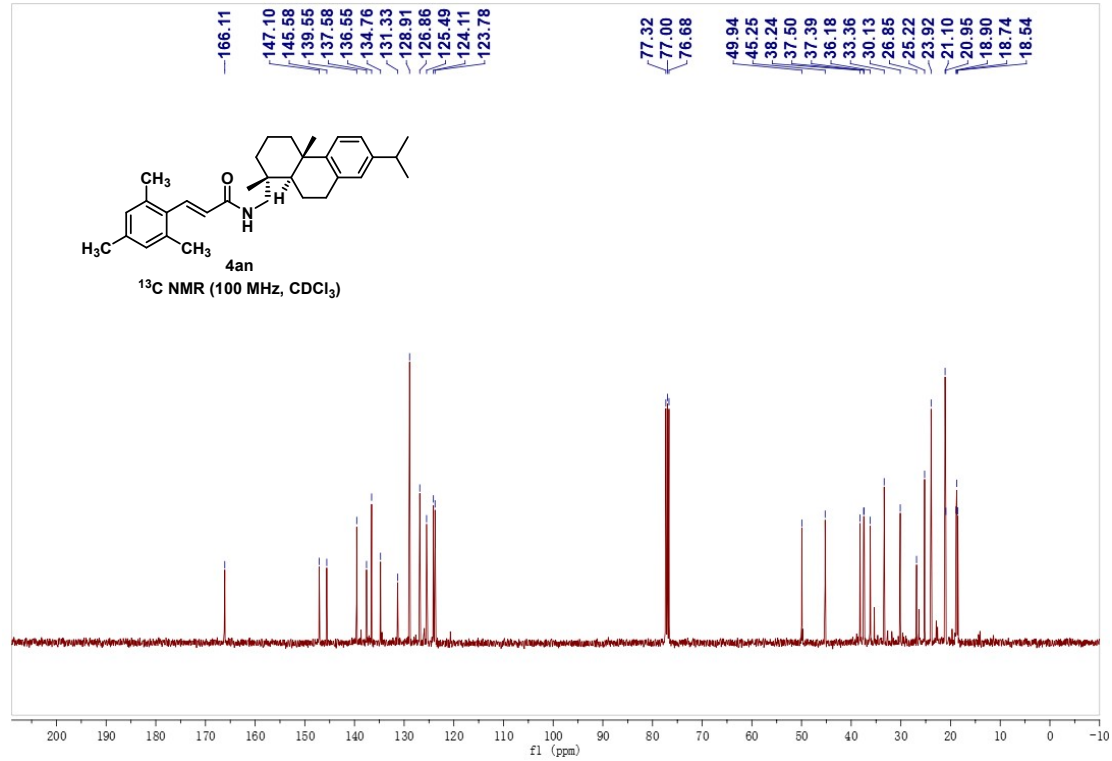


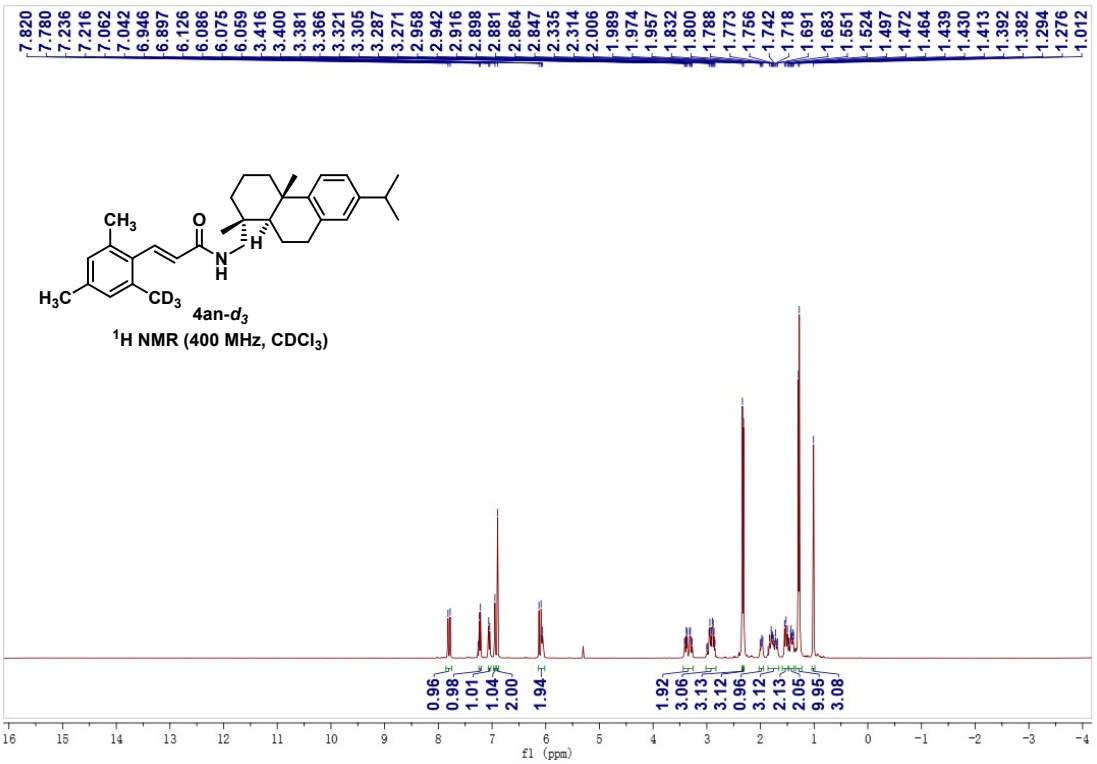
^{13}C NMR (100 MHz, $CDCl_3$)


7.867
7.827
6.894
6.073
6.032
5.429
5.418
2.445
2.435
2.416
2.346
2.292
2.053
2.022
1.987
1.977
1.967
1.927
1.902
1.894
1.884
1.611
1.606
1.589
1.577
1.561
1.543
1.527
1.512
1.496
1.471
1.406
1.378
1.369
1.358
1.298
1.200
1.185
1.167
1.156
1.144
1.130
1.107
1.066
1.031
1.014
1.002
0.987
0.974
0.952
0.936
0.900
0.898
0.884
0.705
CH3
O
O
H
H
H
H3C
CH3
4am
1H NMR (400 MHz, CDCl3)
1.00
2.00
1.00
1.00
1.01
2.00
6.00
3.00
5.45
8.56
4.14
7.31
3.00
2.61
3.00
6.00
3.00
f1 (ppm)


166.31
142.86
139.62
138.08
136.75
130.86
129.09
123.37
122.57
77.32
77.00
76.68
73.97
56.60
56.06
49.94
42.22
39.46
36.53
35.75
31.84
31.78
28.18
27.95
24.22
22.78
22.53
21.09
20.98
19.27
18.66
11.78
CH3
O
O
H
H
H
H3C
CH3
4am
13C NMR (100 MHz, CDCl3)
f1 (ppm)

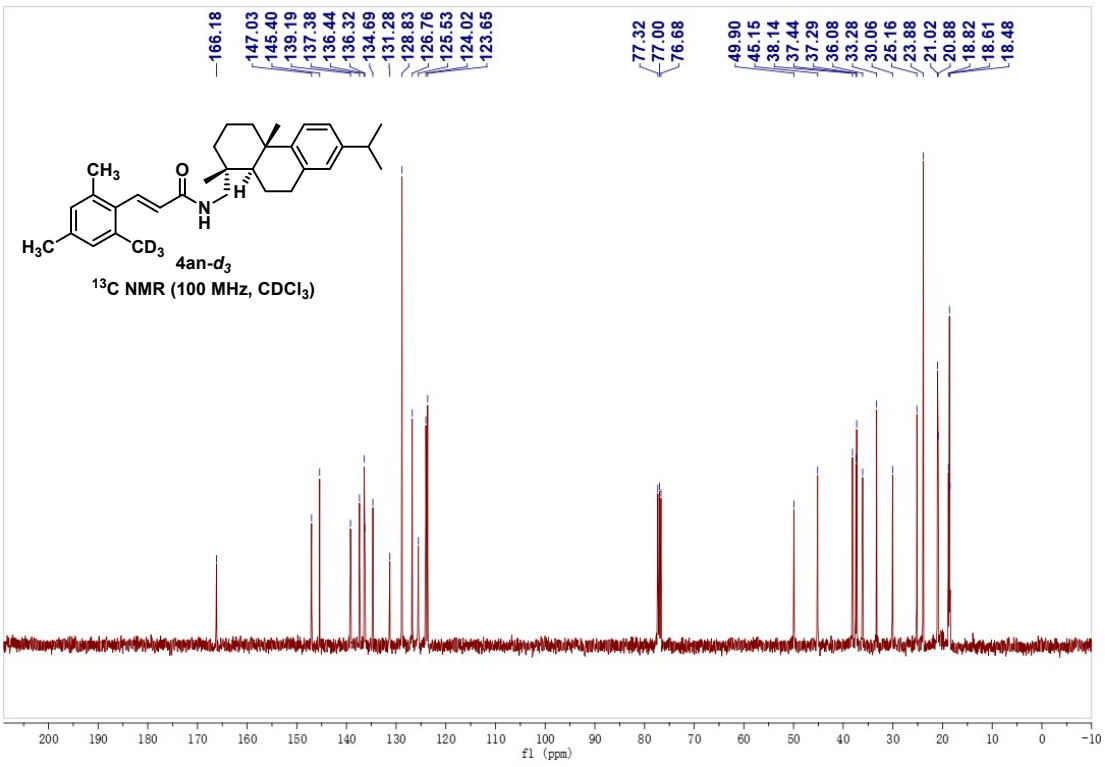

7.793
7.753
7.260
7.207
7.186
7.029
7.009
6.919
6.879
6.030
5.991
5.738
5.723
5.708
3.355
3.340
3.316
3.299
3.282
2.942
2.925
2.885
2.866
2.848
2.831
2.314
2.287
1.950
1.933
1.822
1.815
1.806
1.790
1.780
1.775
1.763
1.747
1.713
1.707
1.698
1.516
1.489
1.484
1.450
1.442
1.418
1.409
1.385
1.376
1.352
1.342
1.257
1.248
1.240
0.999
CH3
O
H
N
H
H3C
CH3
4an
1H NMR (400 MHz, CDCl3)
0.97
1.05
1.13
1.08
2.07
1.00
0.94
2.10
1.10
1.95
6.16
3.13
1.07
2.23
1.01
5.18
3.12
3.10
3.08
3.17
f1 (ppm)


166.11
147.10
145.58
139.55
137.58
136.55
134.76
131.33
128.91
126.86
125.49
124.11
123.78
77.32
77.00
76.68
49.94
45.25
38.24
37.50
37.39
36.18
33.36
30.13
26.85
25.22
23.92
21.10
20.95
18.90
18.74
18.54
CH3
O
H
N
H
H3C
CH3
4an
13C NMR (100 MHz, CDCl3)
f1 (ppm)



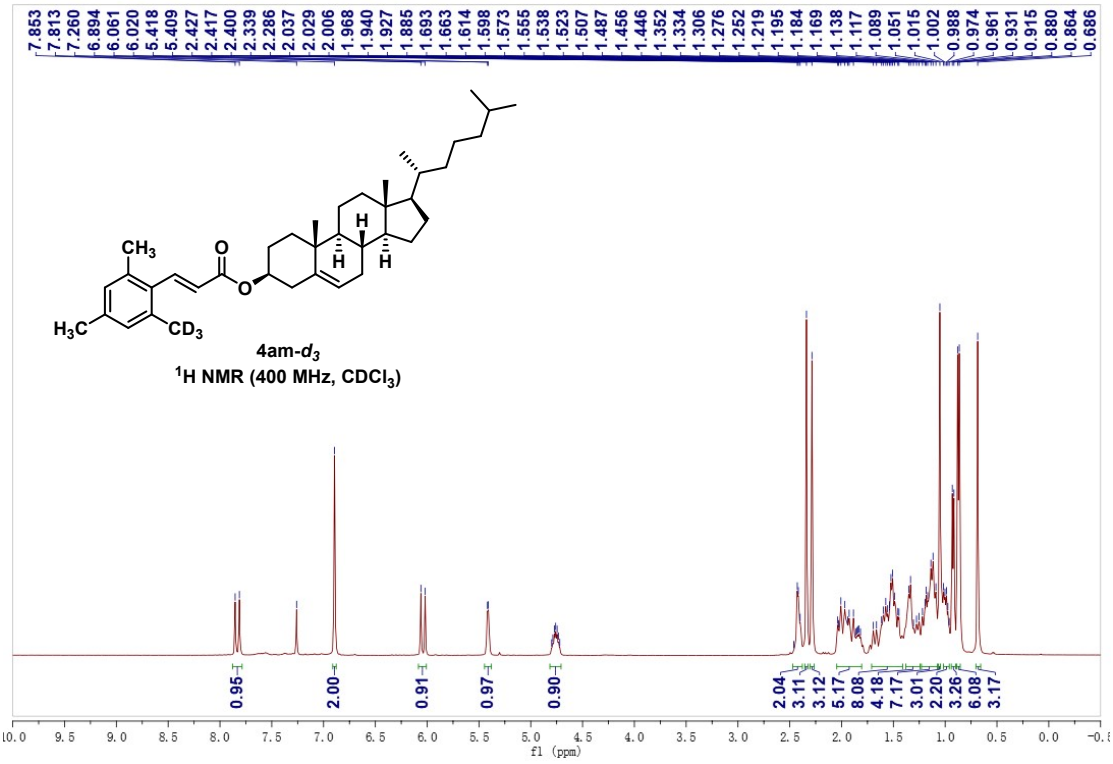
4an-d_3

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



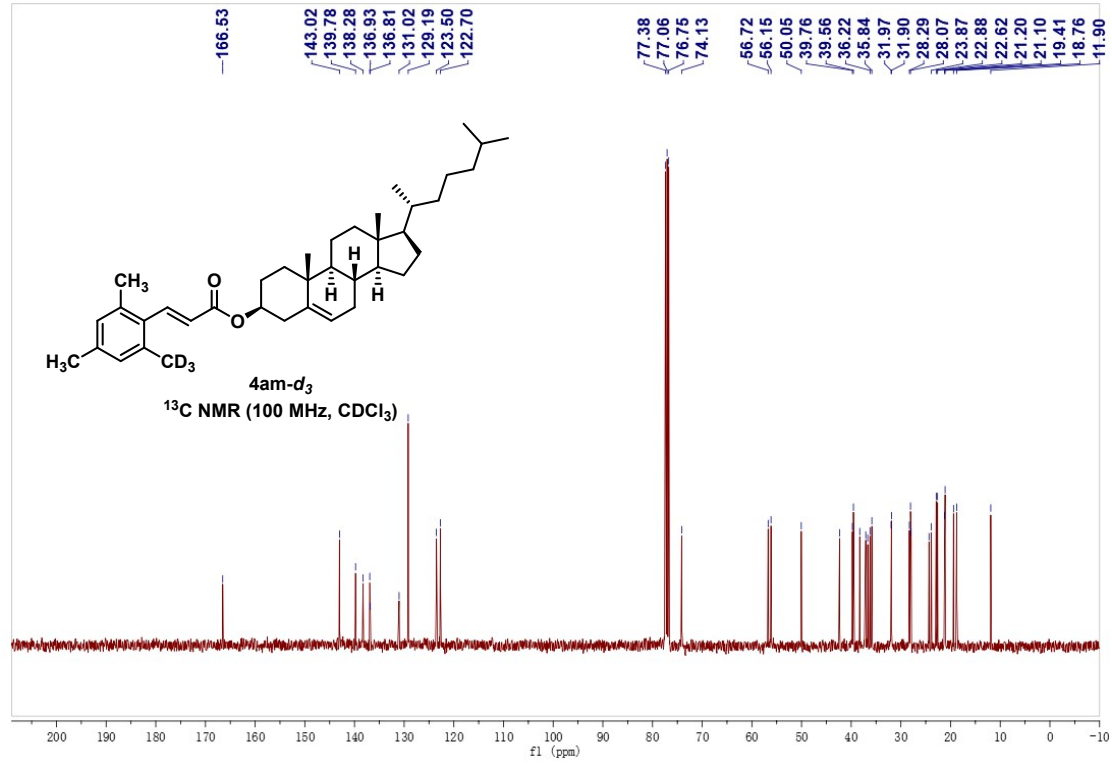
4an-d_3

^{13}C NMR (100 MHz, $CDCl_3$)



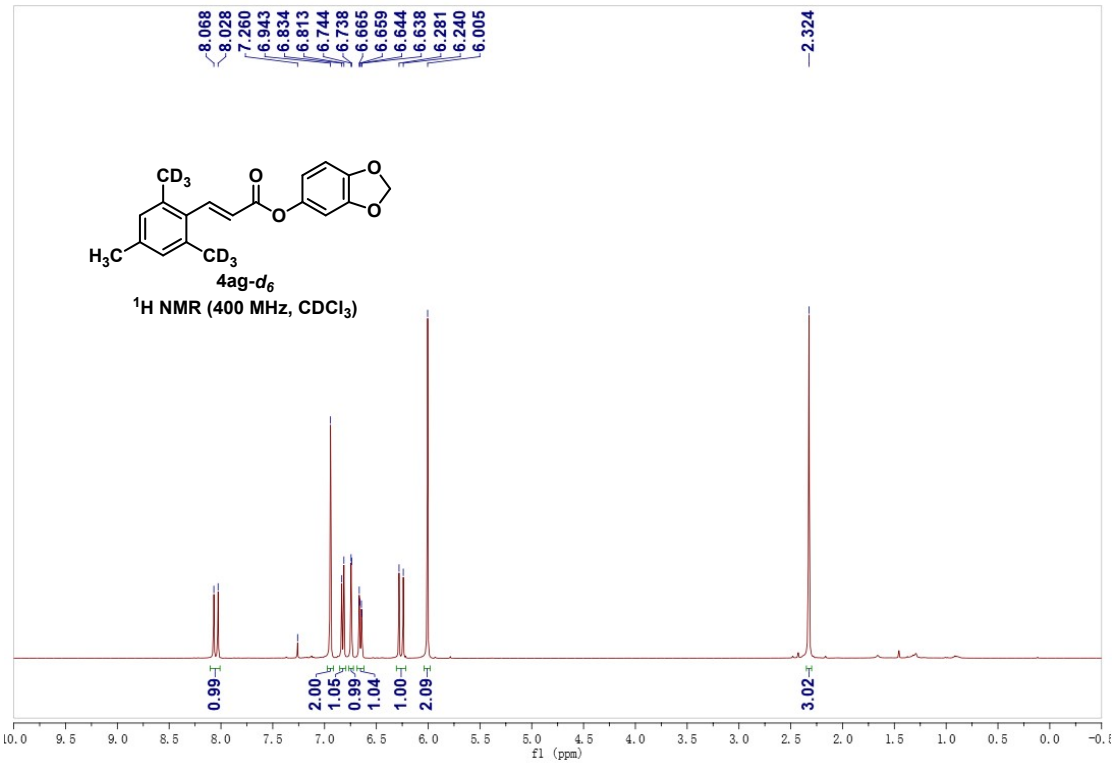
4am-d_3

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



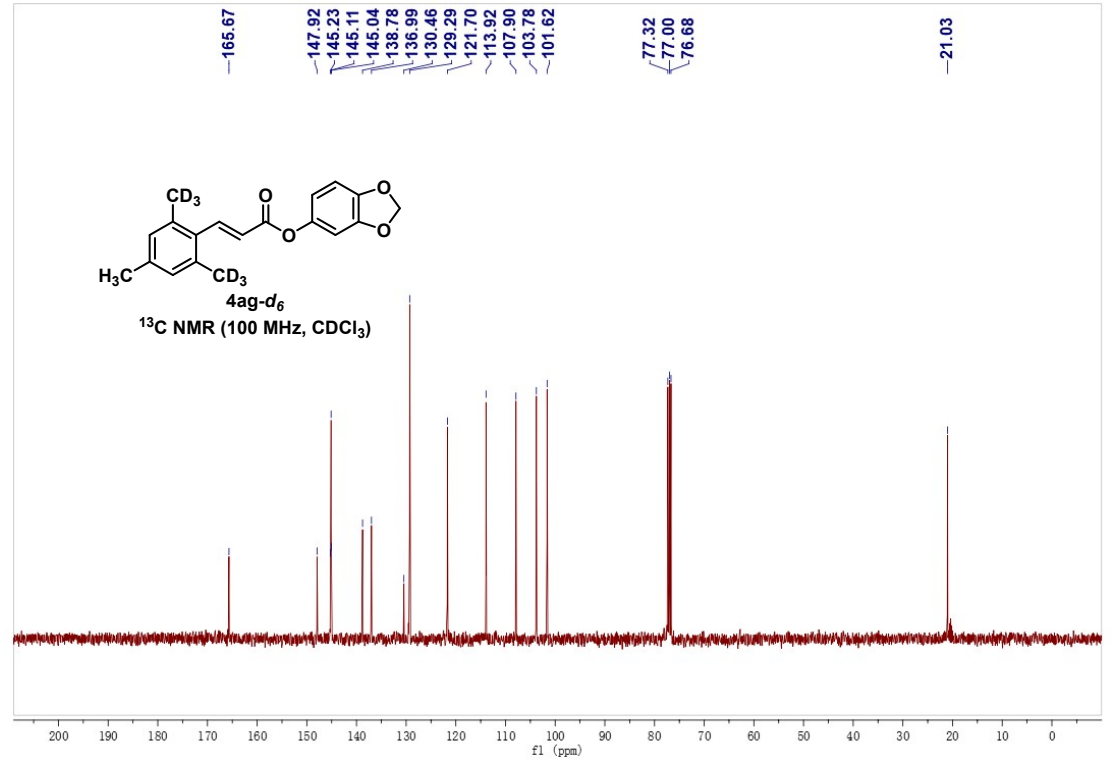
4am-d_3

^{13}C NMR (100 MHz, $CDCl_3$)



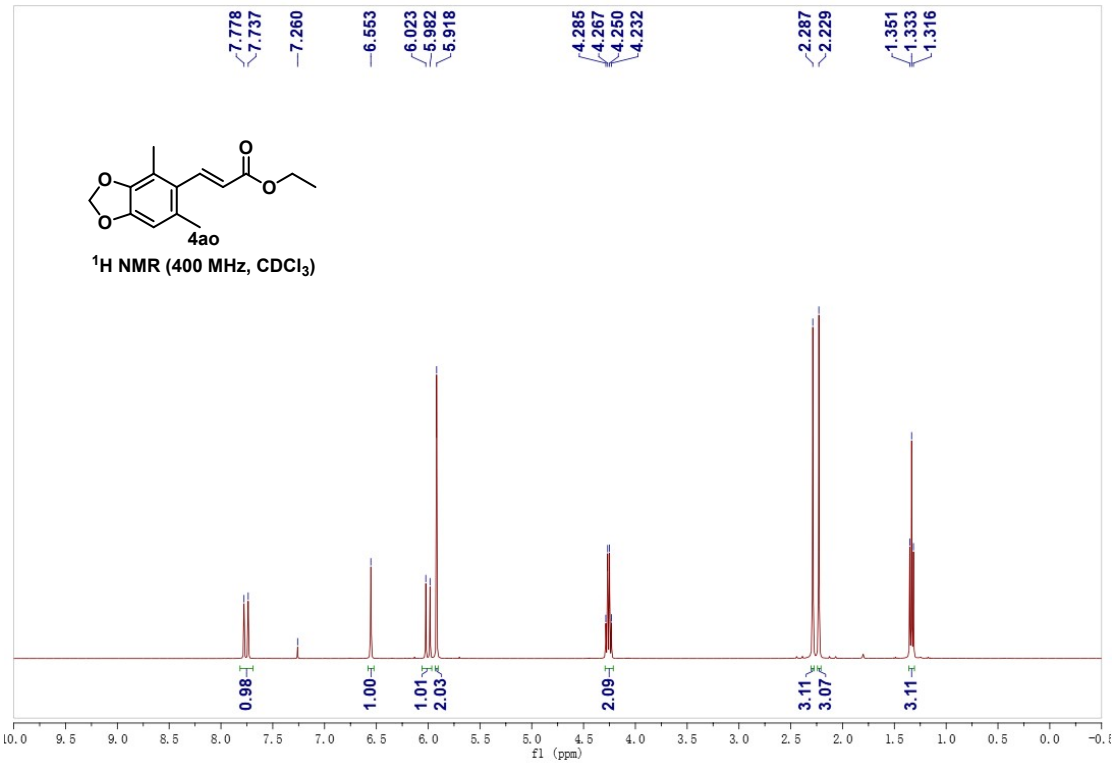
4ag-*d*$_6$

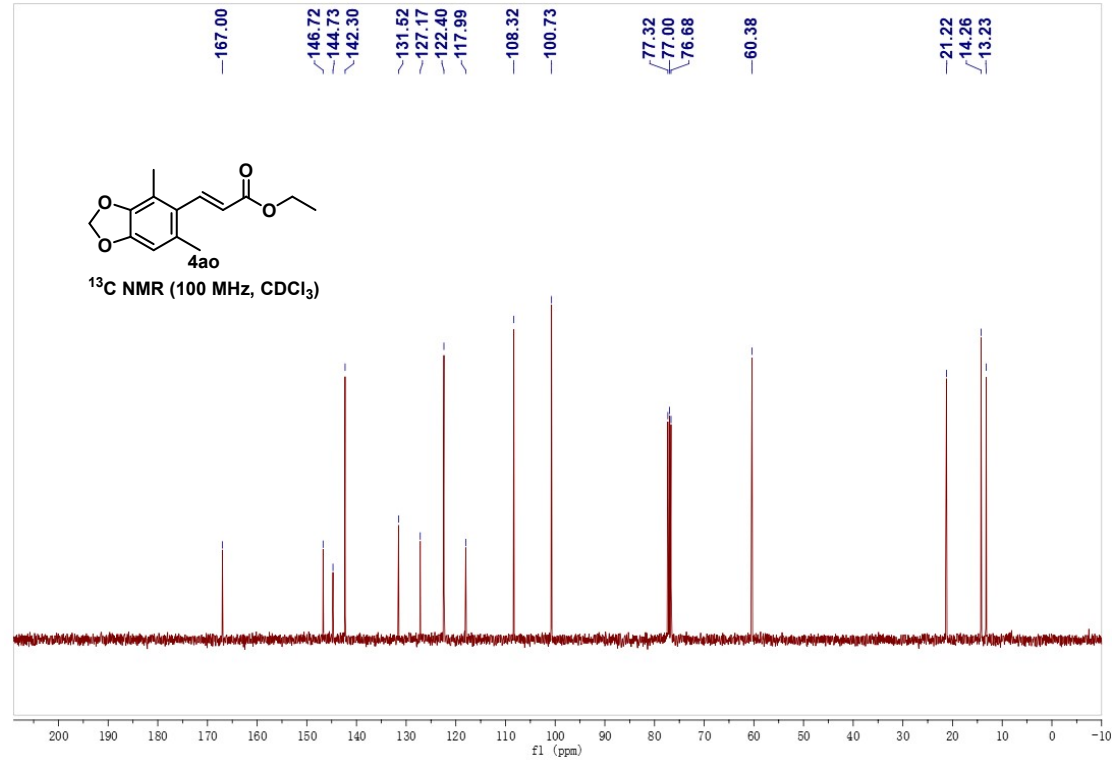
^{1}H NMR (400 MHz, $CDCl_3$)

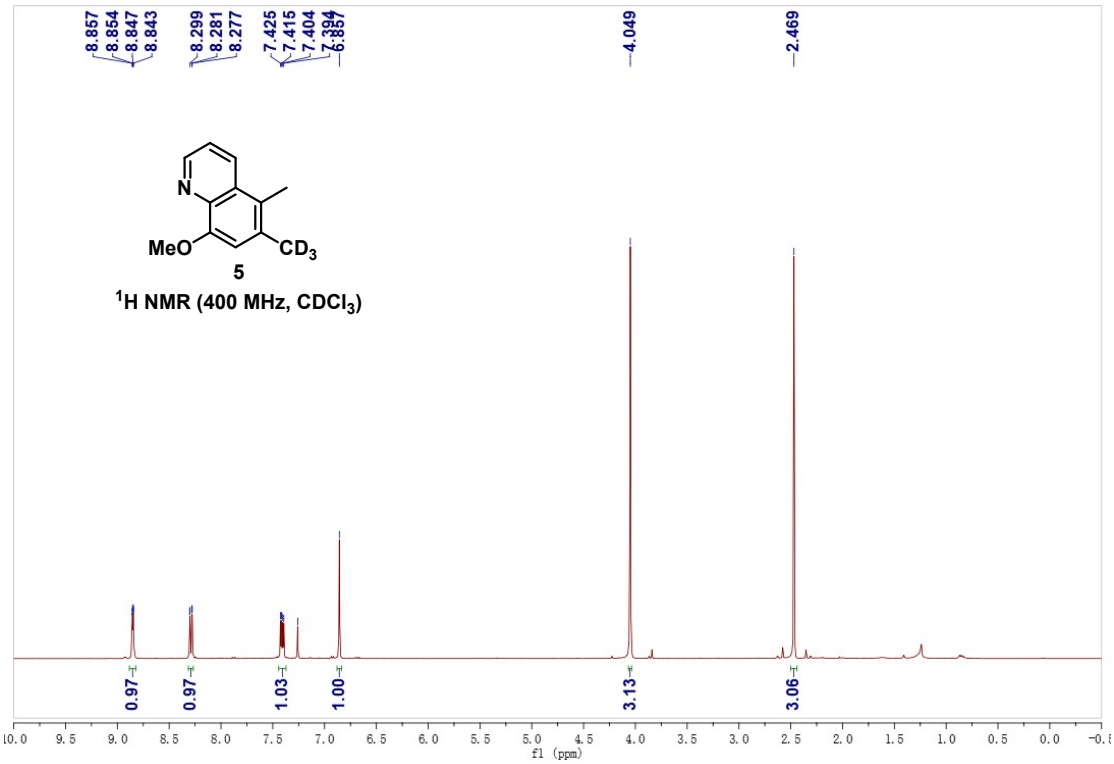


4ag-*d*$_6$

^{13}C NMR (100 MHz, $CDCl_3$)

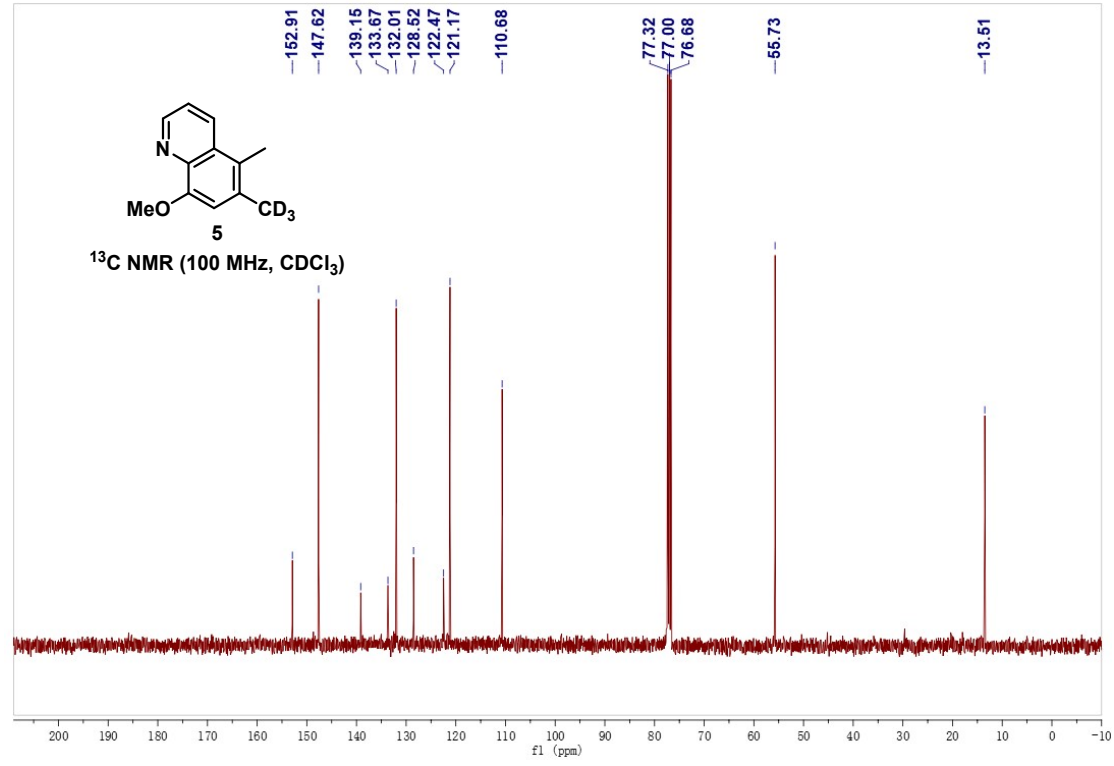

7.778
7.737
7.260
6.553
6.023
5.982
5.918
4.285
4.267
4.250
4.232
2.287
2.229
1.351
1.333
1.316
4ao
^{1}H NMR (400 MHz, CDCl$_3$)
0.98
1.00
1.01
2.03
2.09
3.11
3.07
3.11
f1 (ppm)


167.00
146.72
144.73
142.30
131.52
127.17
122.40
117.99
108.32
100.73
77.32
77.00
76.68
60.38
21.22
14.26
13.23
4ao
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



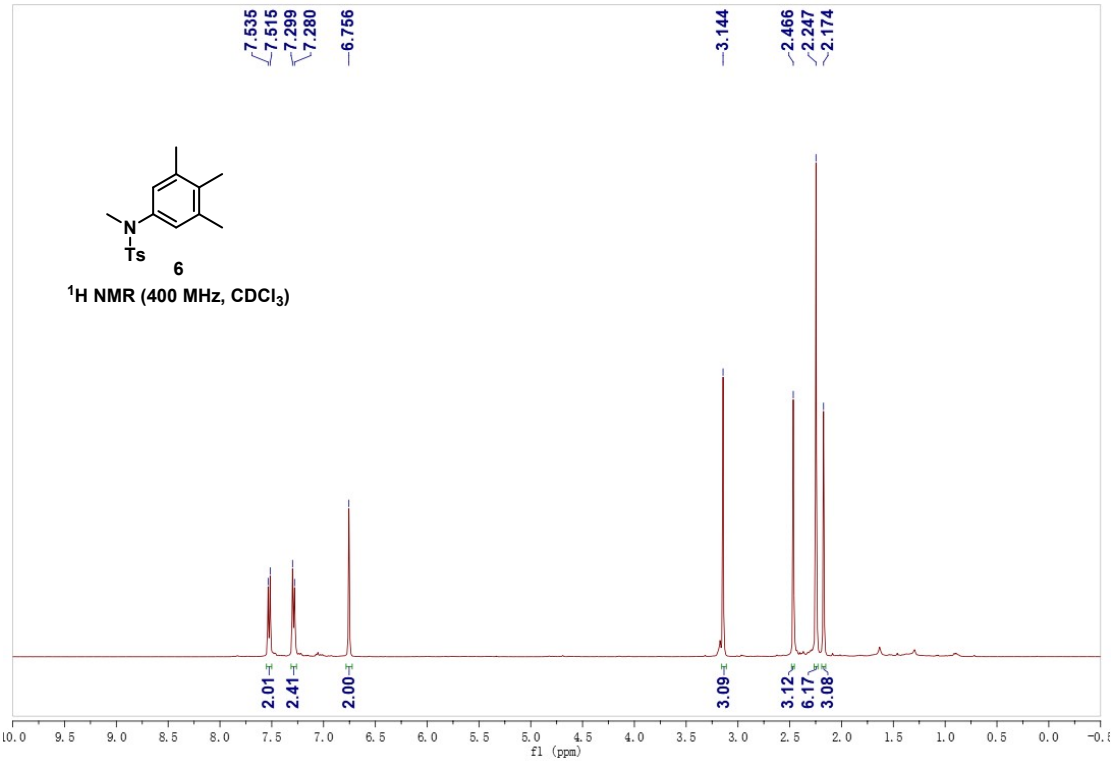
5

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



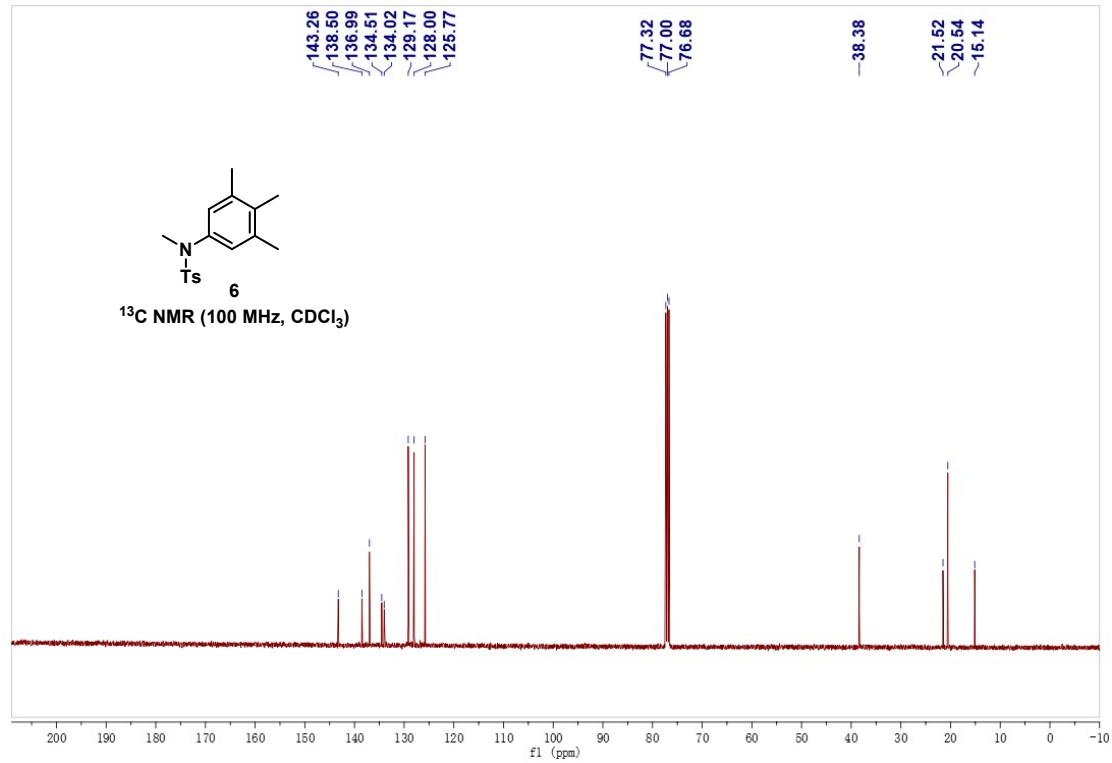
5

^{13}C NMR (100 MHz, $CDCl_3$)



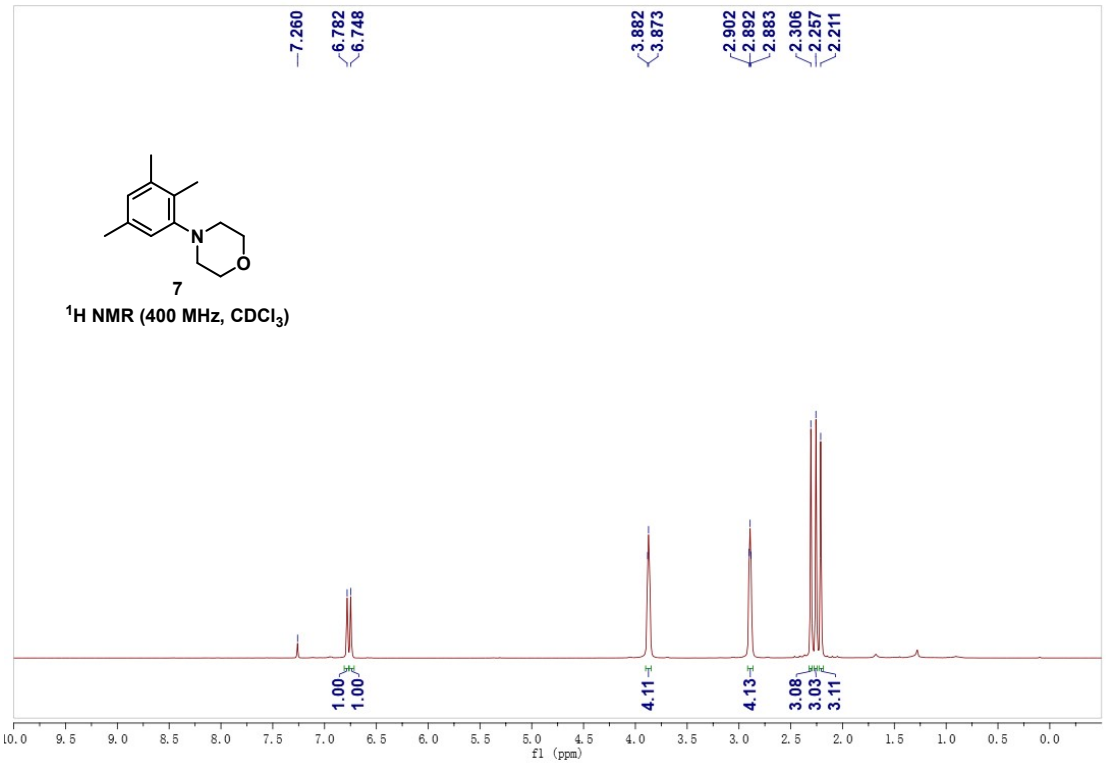
N
Ts
6

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



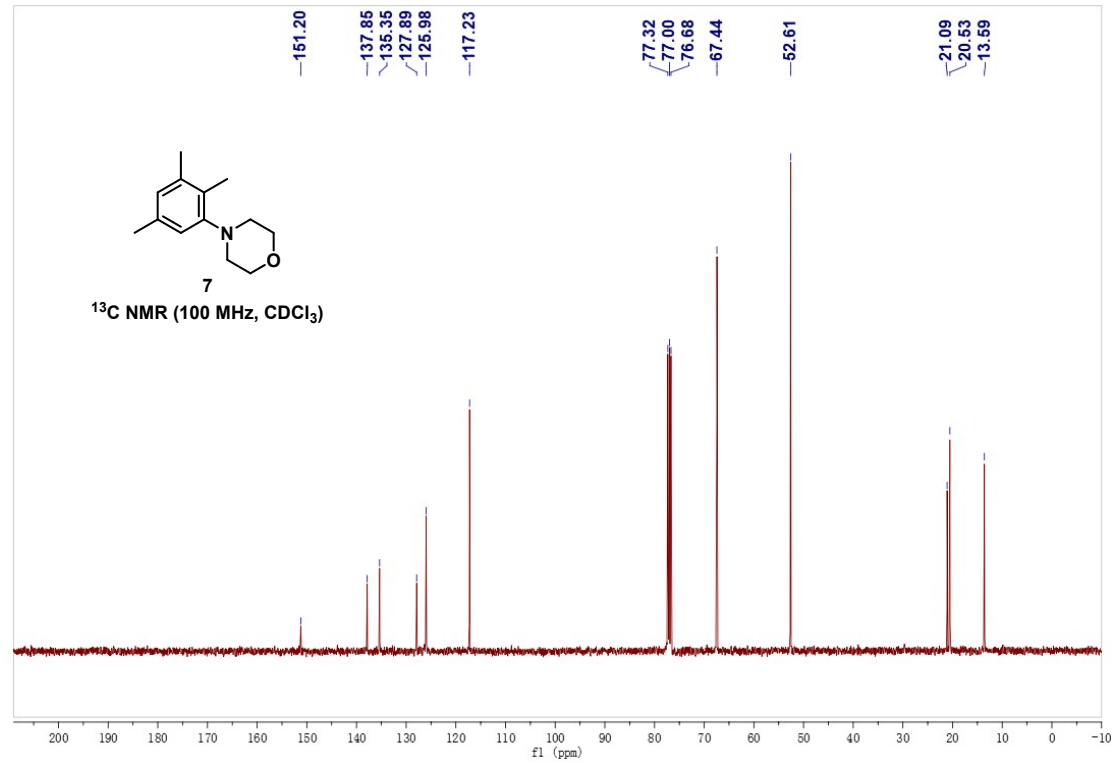
N
Ts
6

^{13}C NMR (100 MHz, $CDCl_3$)



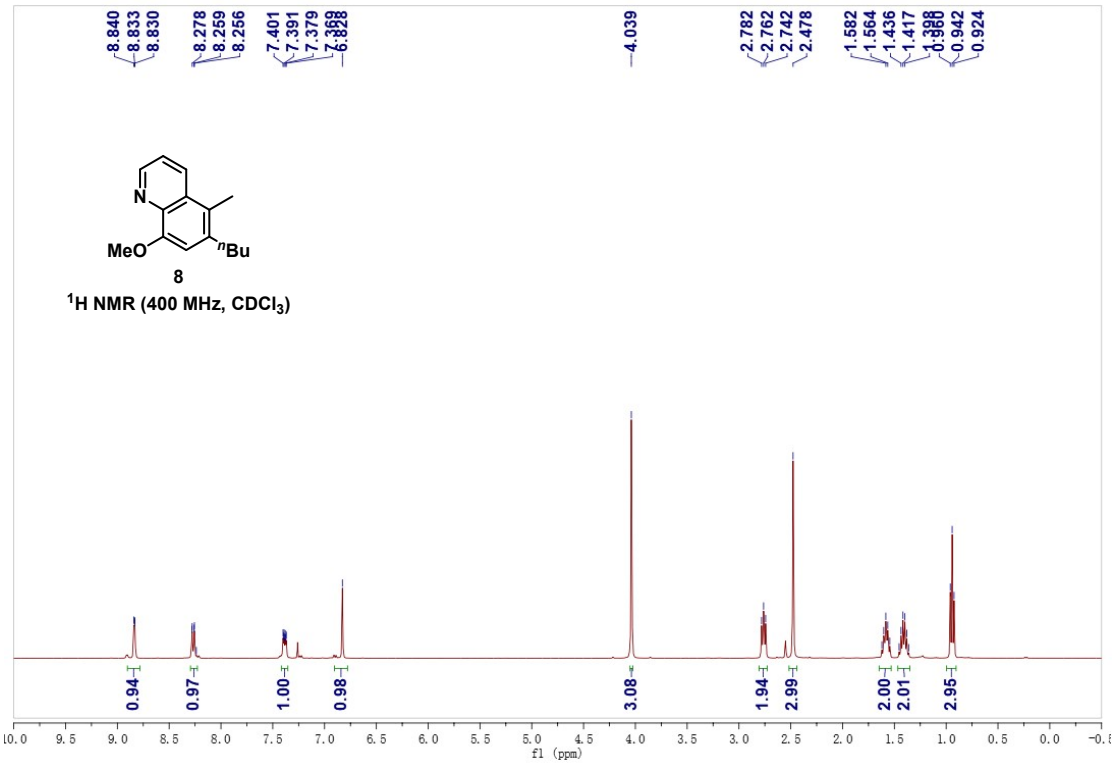
7

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



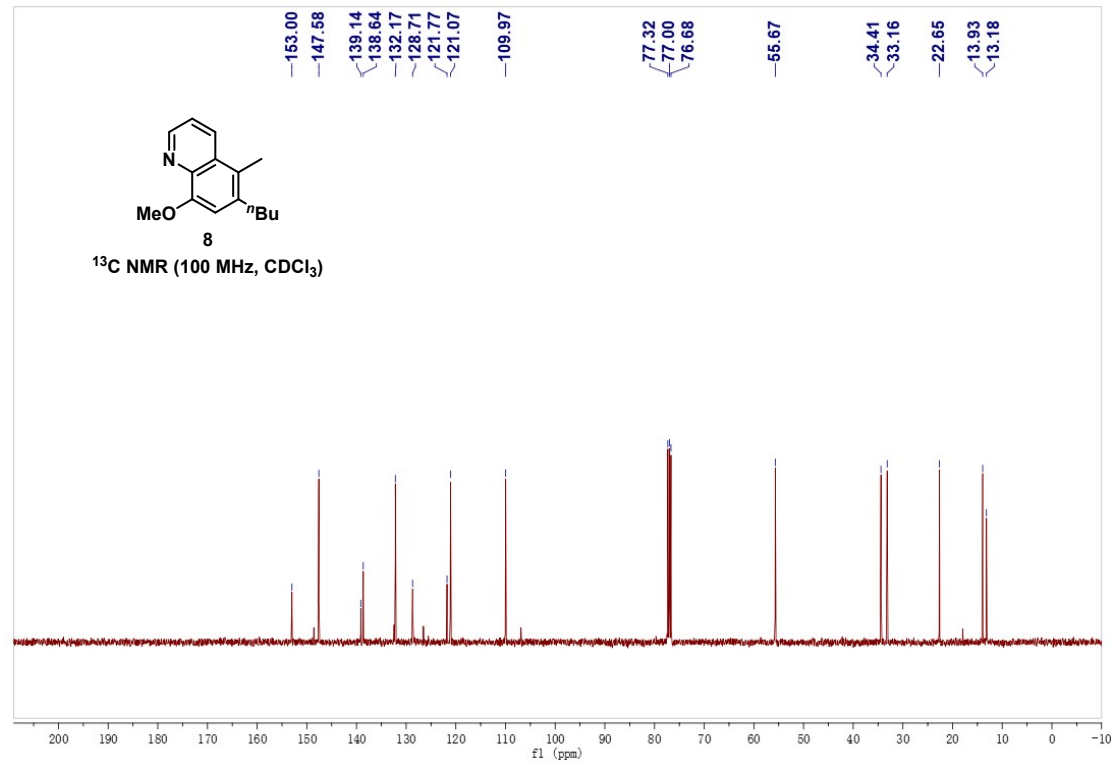
7

^{13}C NMR (100 MHz, $CDCl_3$)



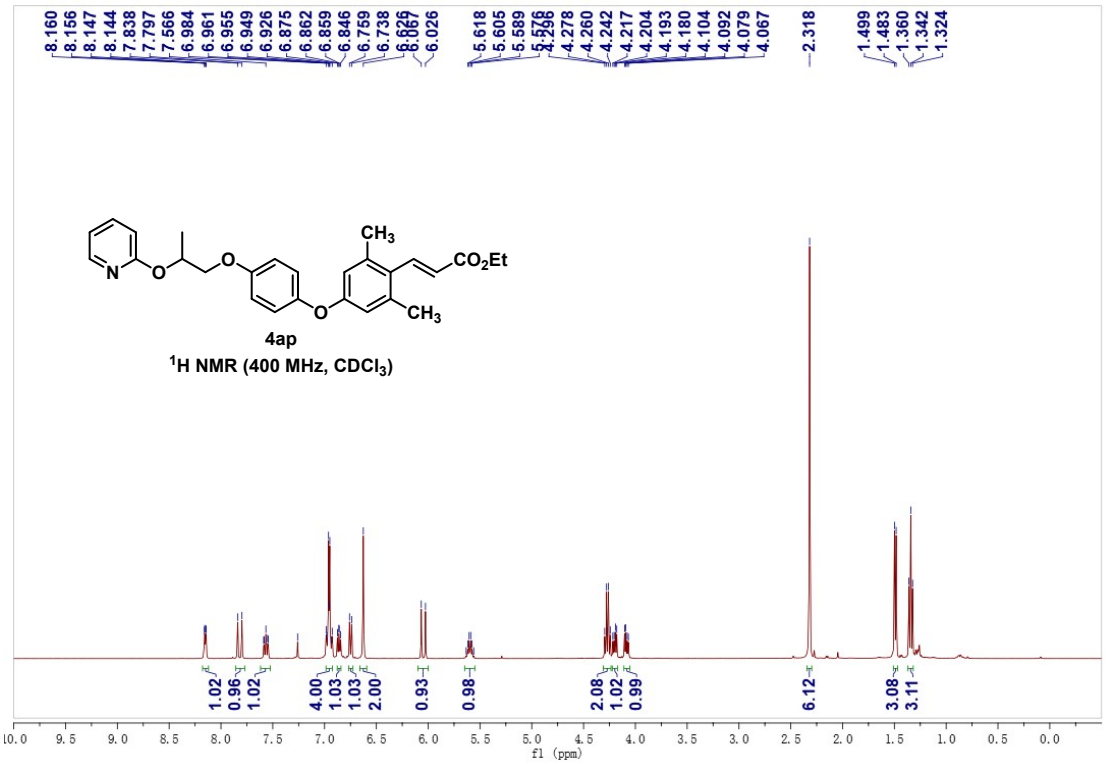
8

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



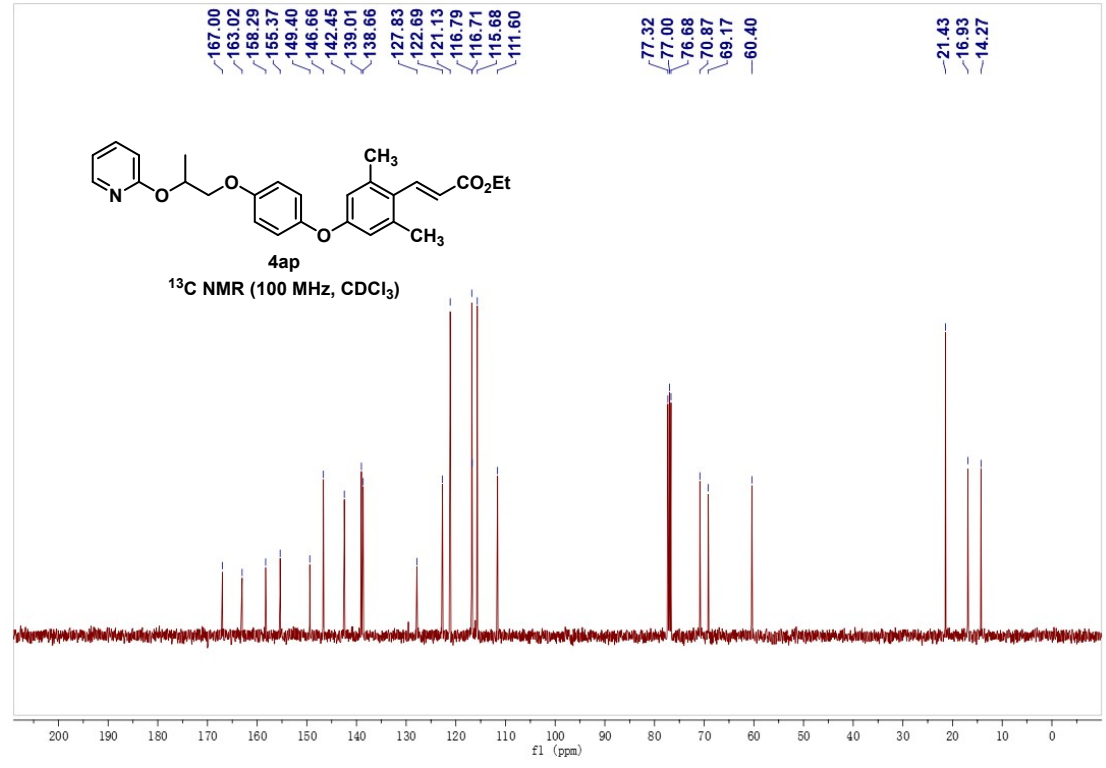
8

^{13}C NMR (100 MHz, $CDCl_3$)



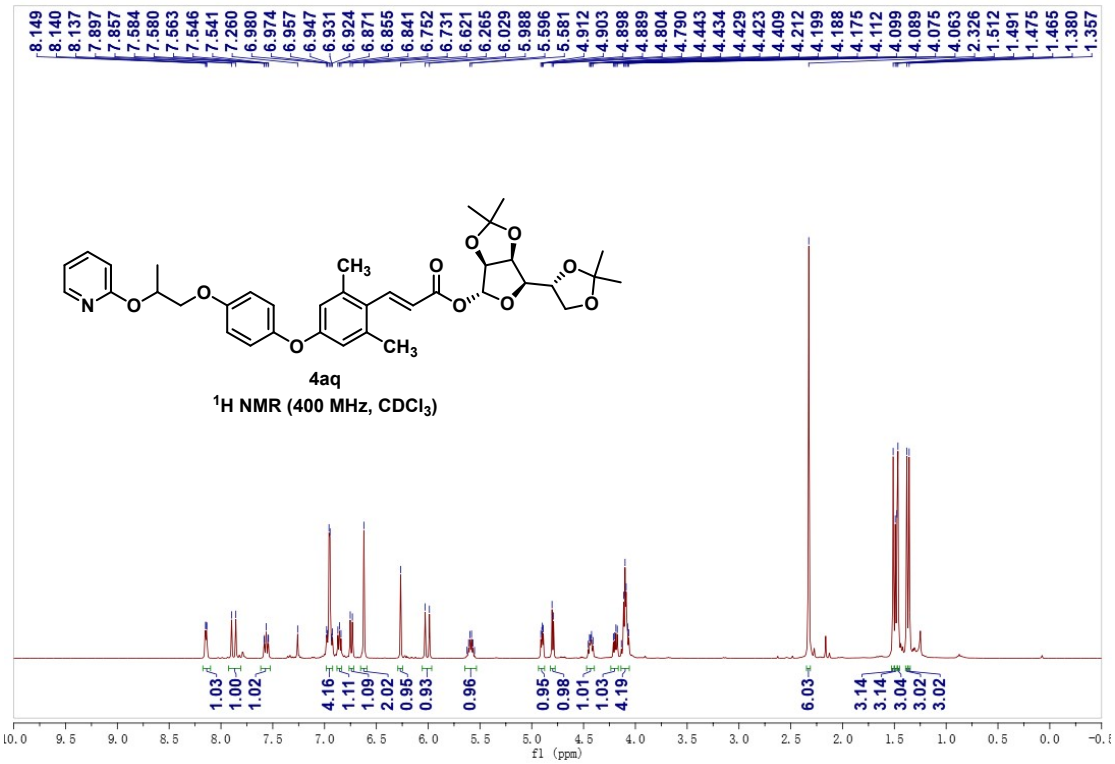
4ap

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



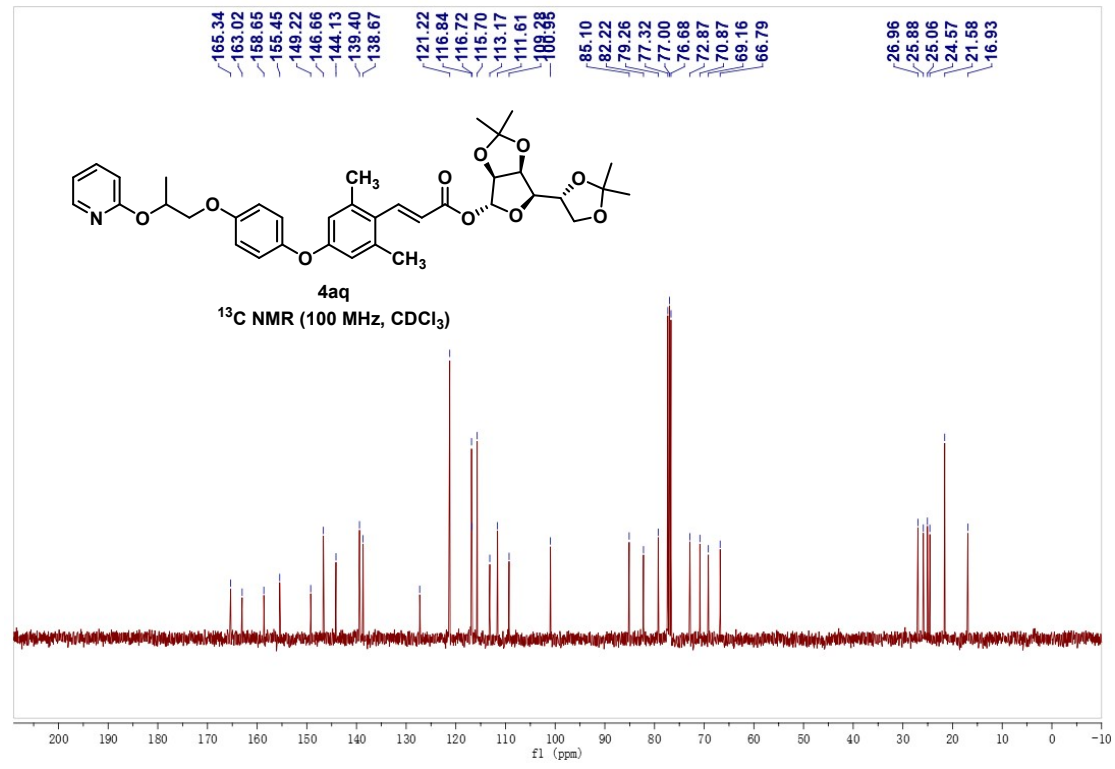
4ap

^{13}C NMR (100 MHz, $CDCl_3$)



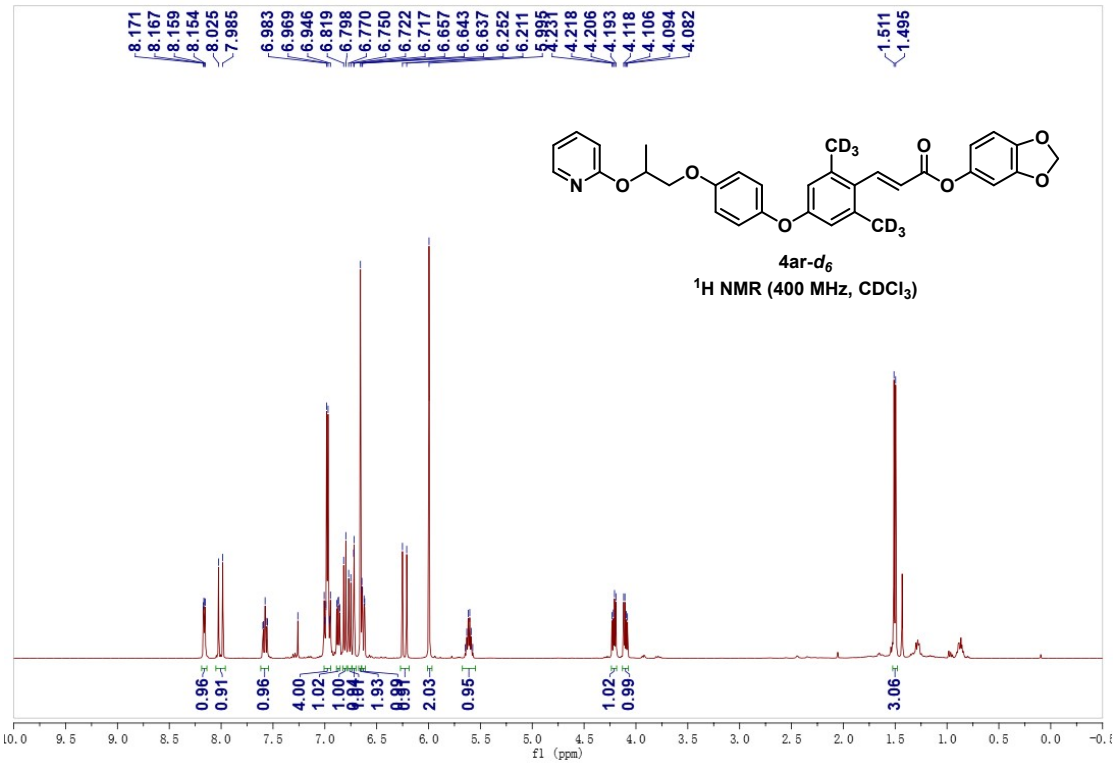
4aq

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



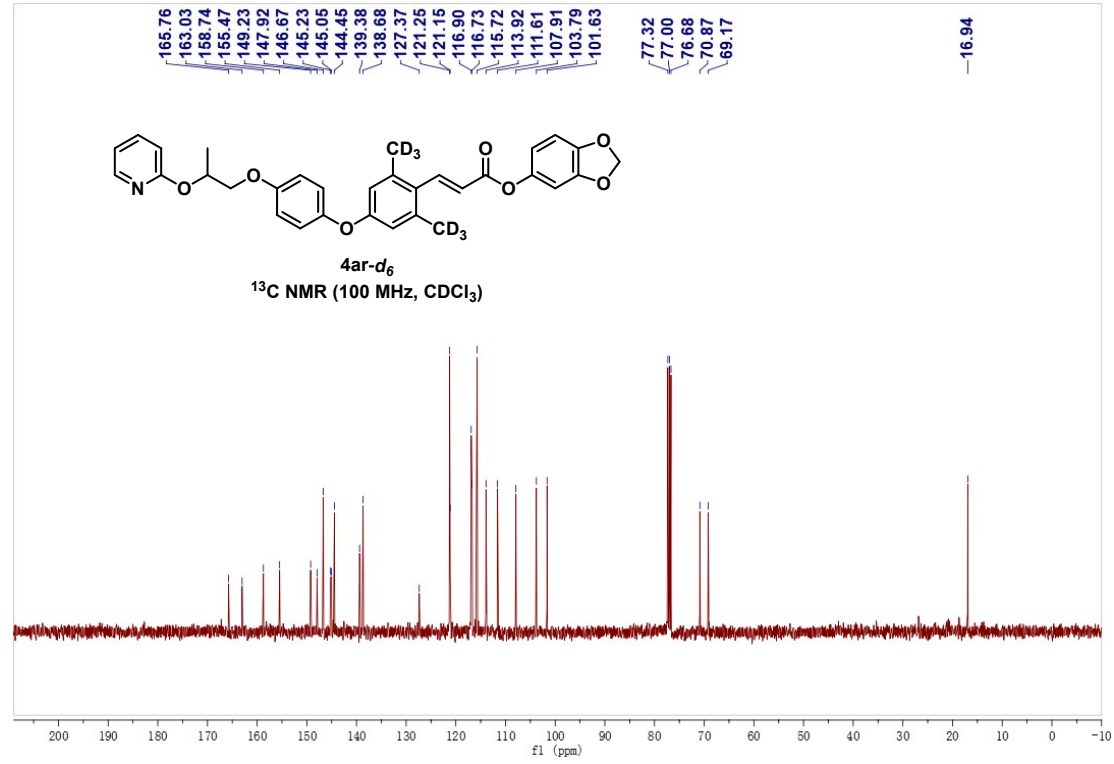
4aq

^{13}C NMR (100 MHz, $CDCl_3$)



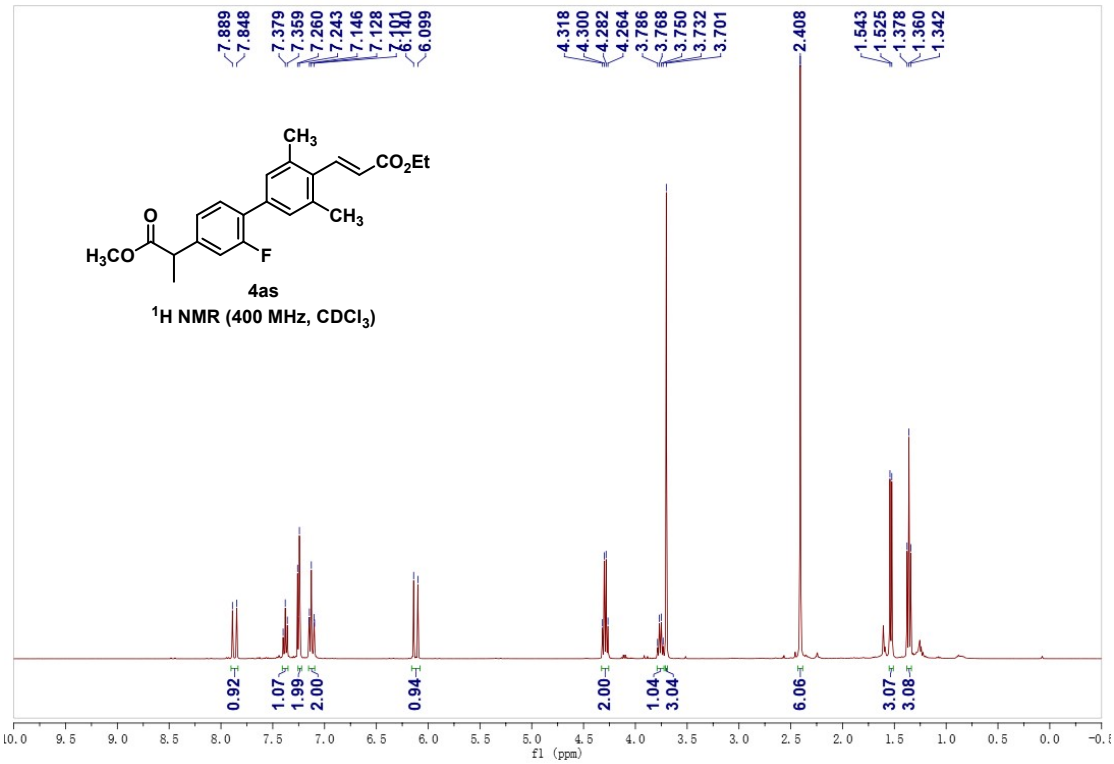
4ar-d_6

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



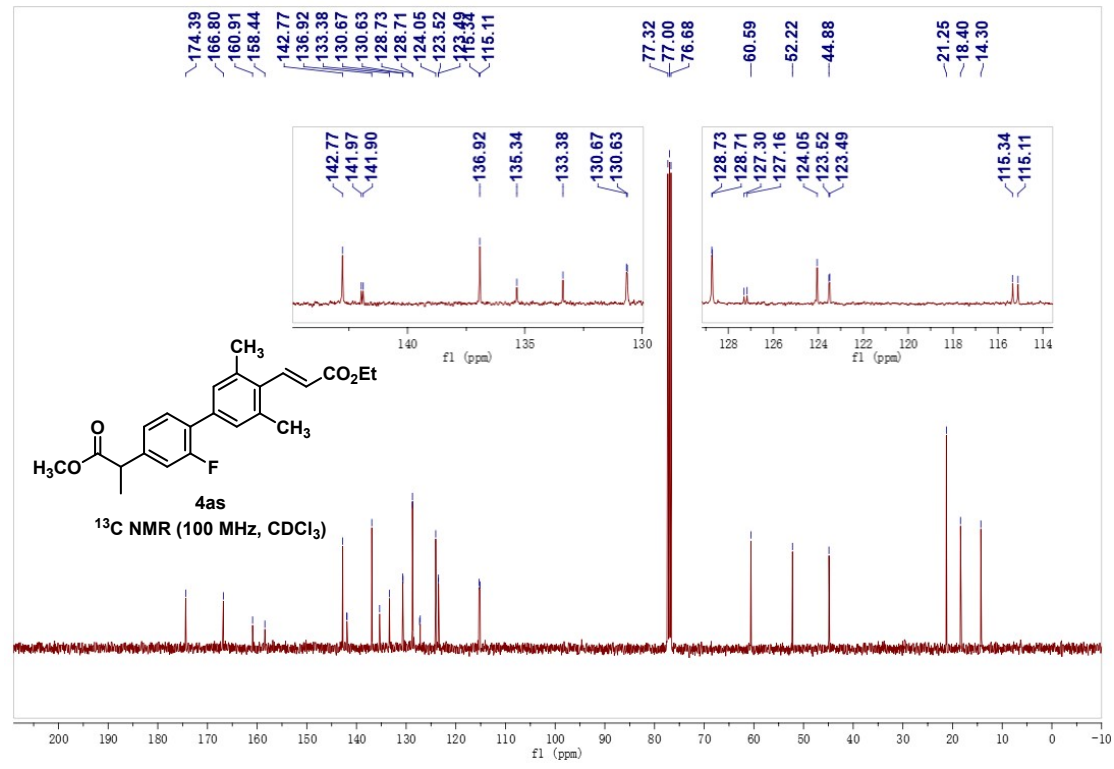
4ar-d_6

^{13}C NMR (100 MHz, $CDCl_3$)



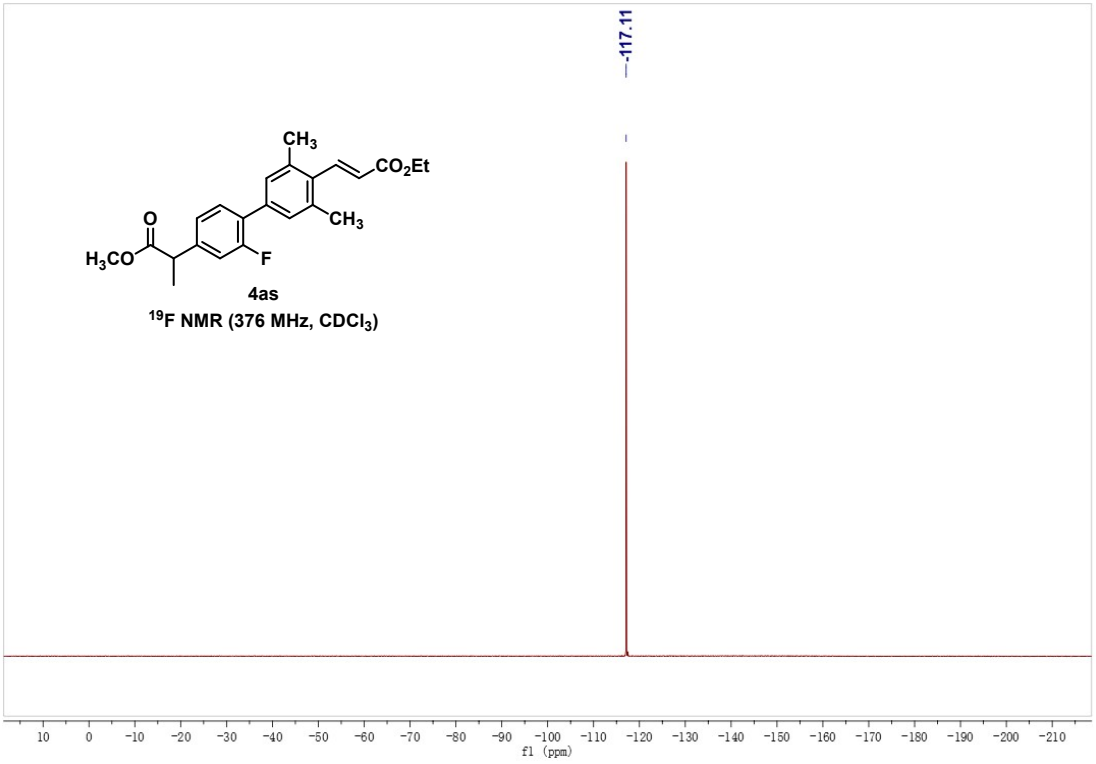
4as

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



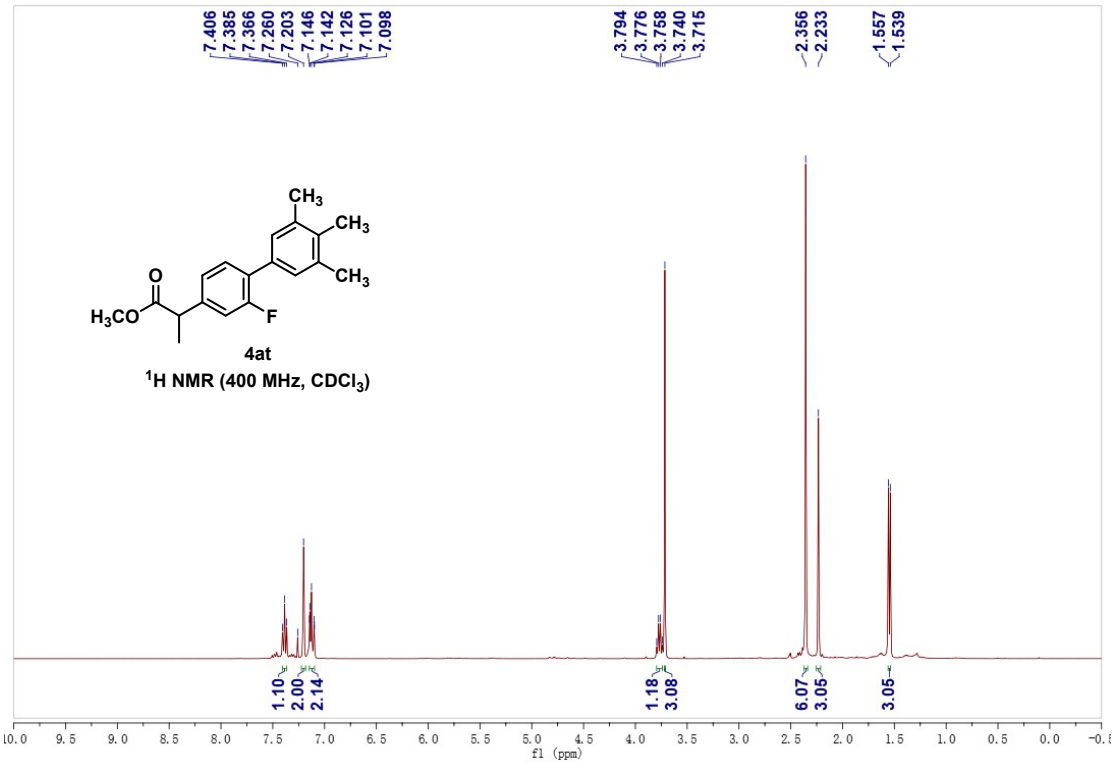
4as

^{13}C NMR (100 MHz, $CDCl_3$)



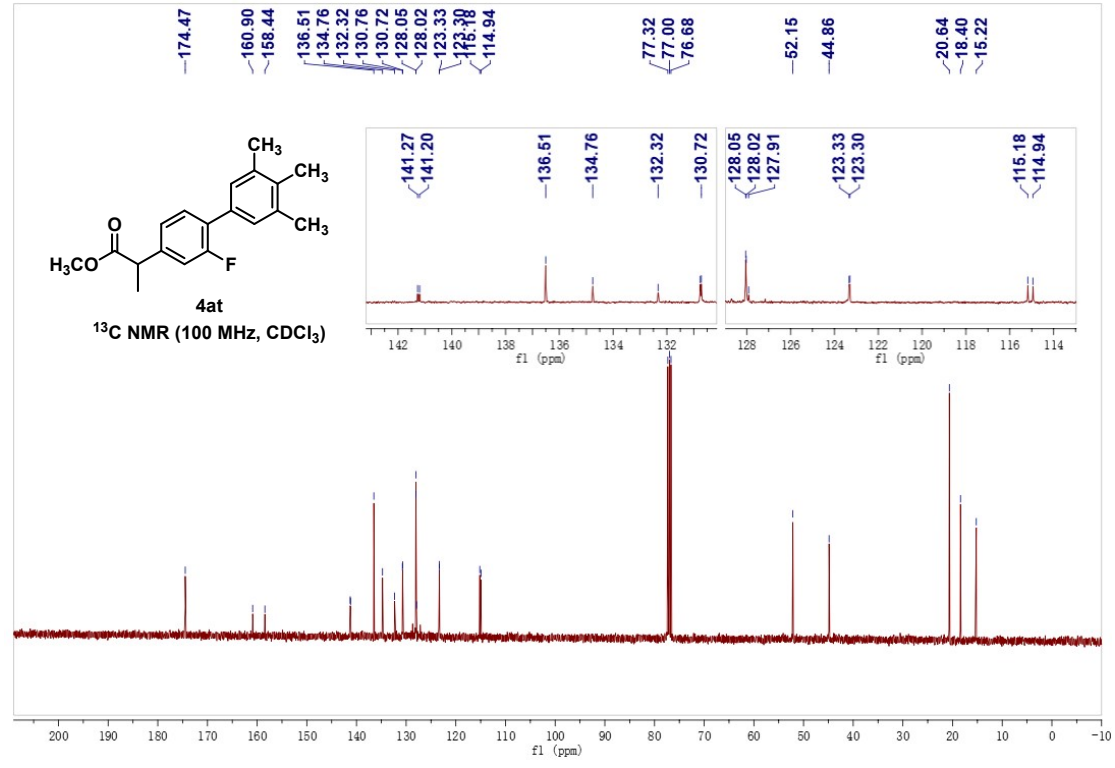
4as

^{19}F NMR (376 MHz, $CDCl_3$)



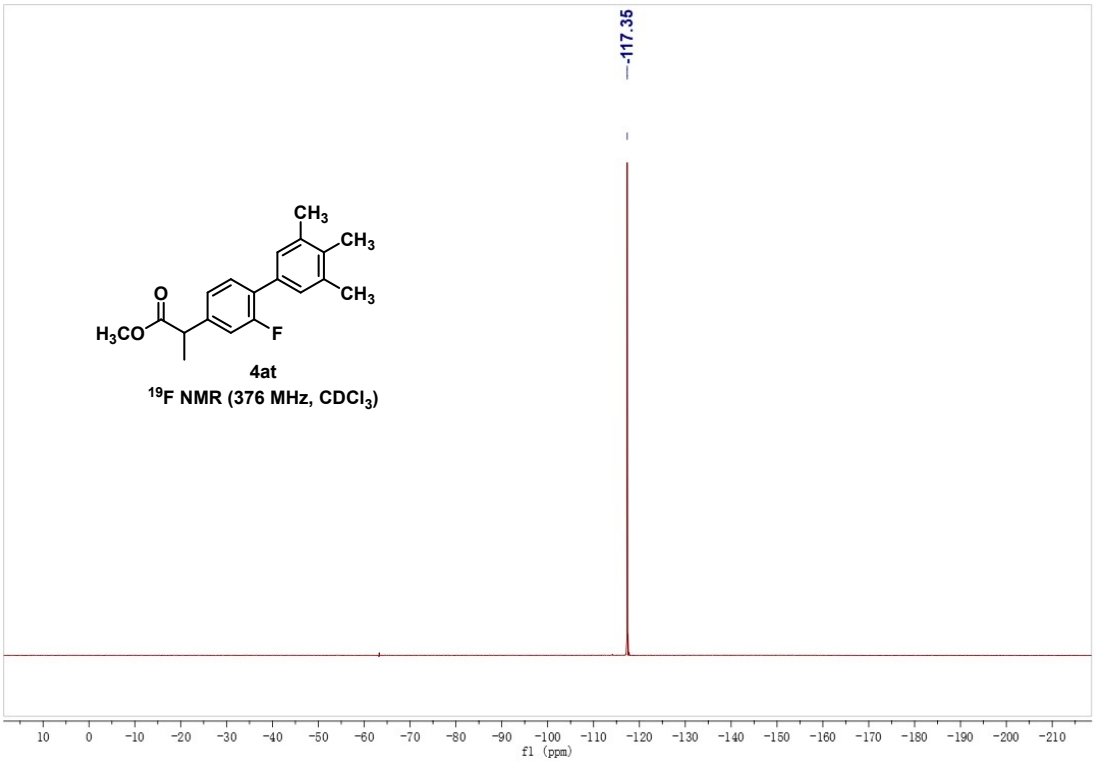
4at

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



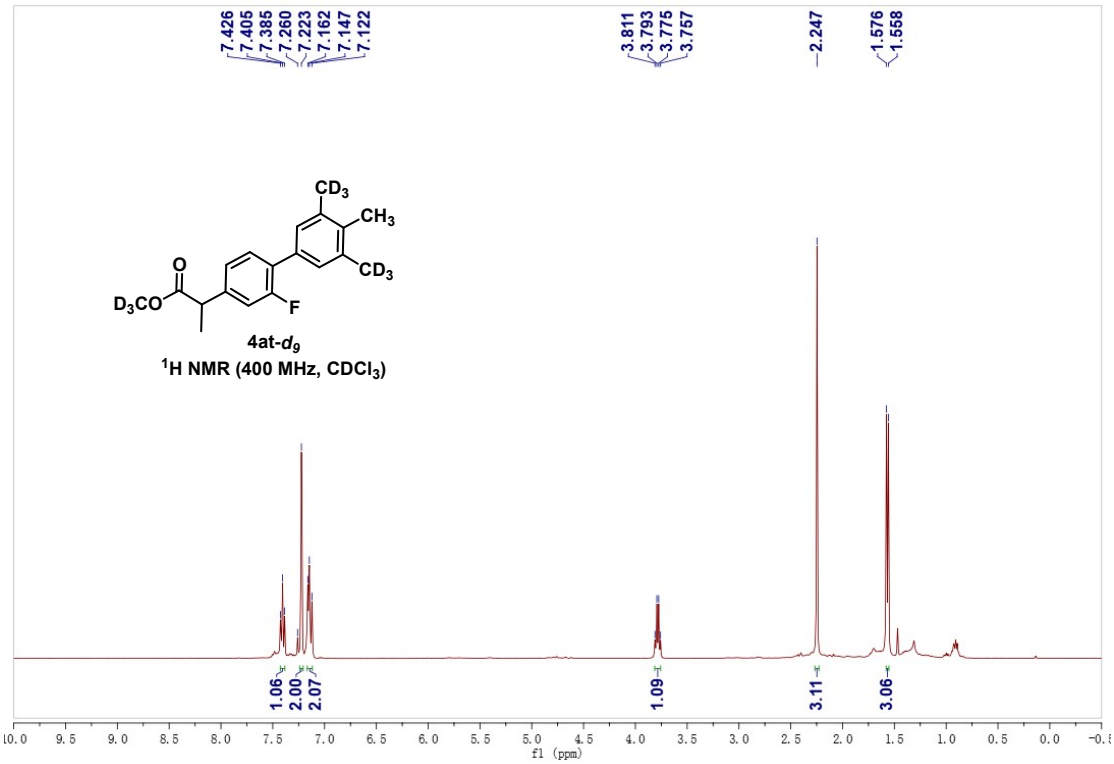
4at

^{13}C NMR (100 MHz, $CDCl_3$)



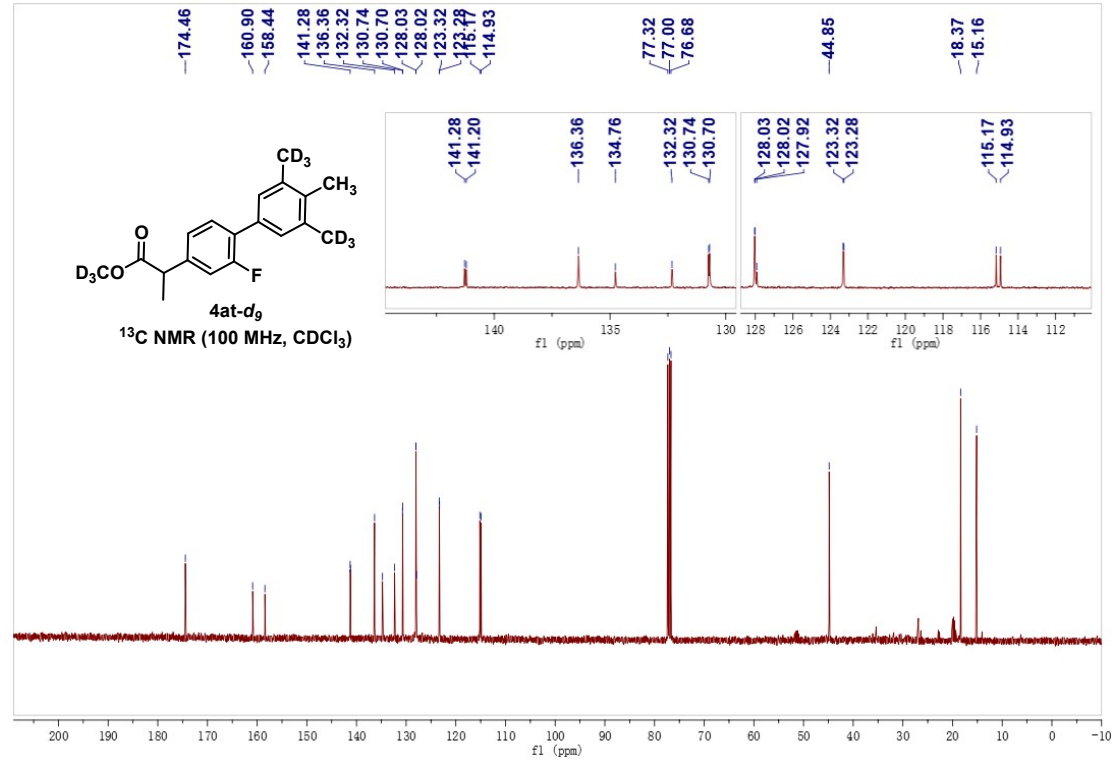
4at

^{19}F NMR (376 MHz, $CDCl_3$)



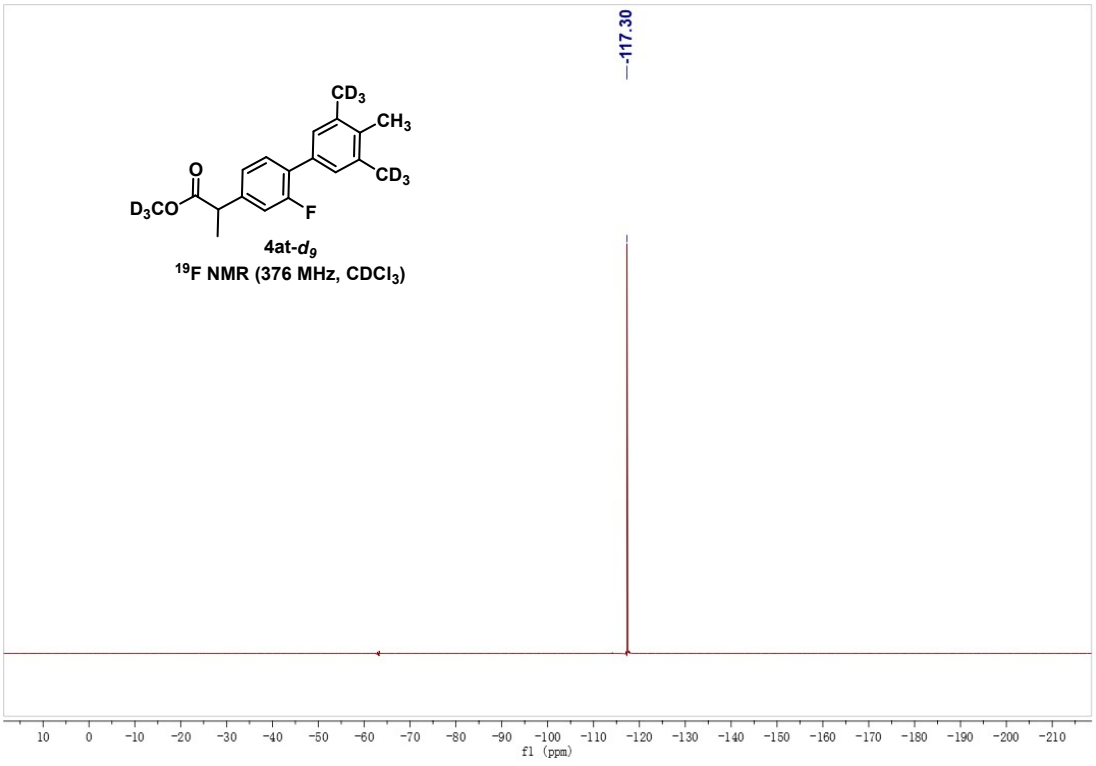
4at-d_9

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



4at-d_9

^{13}C NMR (100 MHz, $CDCl_3$)



4at-d_9

^{19}F NMR (376 MHz, $CDCl_3$)