Supporting Information

Iron-Catalyzed Reductive Vinylation of Tertiary Alkyl Oxalates with Activated Vinyl Halides

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I. Experimental Section

Part 1. General Information

1. Chemicals and Reagents

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk or glove box techniques. CH_3CN (99.9%, extra dry, Acros) was purchased and used directly. Deuterated solvents were used as received ($CDCl_3$ from Maclin Co., China). $Fe(acac)_3$ (Alfa Aesar), $Fe(acac)_2$ (Alfa Aesar), $FeCl_3$ (Alfa Aesar), $Fe(OTf)_3$ (Strem), $Fe(Ac)_2$ (Alfa Aesar), $Co(acac)_2$ (Alfa Aesar), CuI (Alfa Aesar) were used as received. Zinc powder (Aladdin) was activated with hydrochloric acid before use. Anhydrous $MgCl_2$ (Alfa Aesar) and anhydrous LiCl (Alfa Aesar) were purchased and used directly. PBI (2-(2-pyridyl)benzimidazole (>98%, Alfa Aesar) was purchased and used directly. Procedures for the synthesis of the ligands, tertiary alkyl oxalates and vinyl bromides used in this study have been reported in our previous publications,[1] or purchased and used directly. Unless otherwise noted, starting materials, and other reagents were purchased from commercial sources and used without further purification.

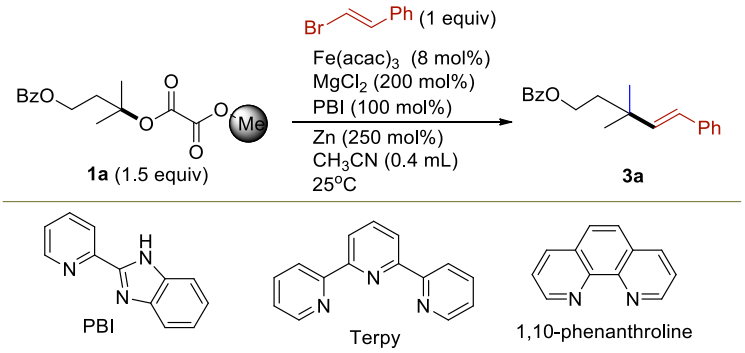
2. Physical Method

Column chromatography was performed using silica gel 200-300 mesh (purchased from Qingdao-Haiyang Co., China) as the solid support. All NMR spectra were recorded on a Bruker Avance 600 MHz spectrometer, or a JEOL 400 MHz at STP, unless otherwise indicated. ^1H NMR and ^{13}C NMR chemical shifts are reported in δ units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in ^1H NMR and ^{13}C NMR spectra were set at 7.26 ppm and 77.16 ppm, respectively. High-resolution mass spectra (HRMS) were obtained using a Bruker APEXIII 7.0 Tesla Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) and IonSpec 4.7 Tesla FT-MS instruments. Melting points were recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China). GC chromatograms were recorded on a GCMS-QP2010 SE (SHIMADZU) using an Agilent column CP7502 and Rxi-5 ms (Restek).

Part 2. Details of Optimization and Control Experiments

1. Typical procedure for optimization of the vinylation reaction conditions: Alkyl oxalate, Zn, the chosen ligand, the Fe catalyst, and $MgCl_2$ were added to a flame-dried Schlenk tube equipped with a stir bar under air. The tube was capped with a rubber septum, and it was evacuated and refilled with nitrogen (N_2) three times. Vinyl bromide (the limiting reagent, 0.15 mmol) and a solvent were then added via syringes. After the reaction mixture was allowed to stir in an oil bath overnight under an N_2 atmosphere at 25 °C, it was directly loaded onto a silica column without work-up. The residue in the reaction vessel was rinsed with small amount of CH_2Cl_2 or eluent. A quick flash column offered a mixture of the product with other impurities. The yield was determined by ^1H NMR spectroscopy using 2,5-dimethyl furan as the internal standard, unless otherwise noted.

Table S1. Optimization for the reaction of **1a** with vinyl bromide.

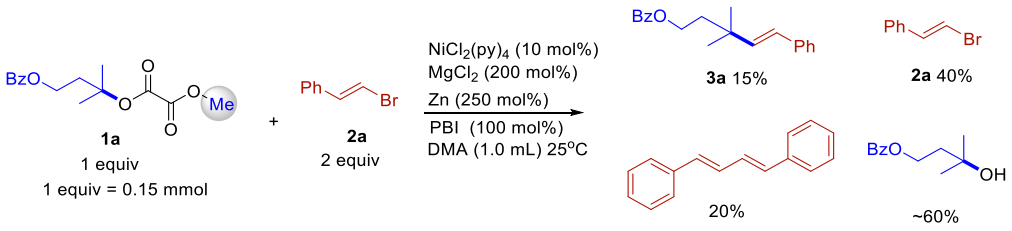


entry	variation from the standard conditions	yield%[a]
1	PPh_3 instead of PBI	21
2	Terpy instead of PBI	ND[b]
3	1,10-Phenanthroline instead of PBI	ND[b]
4	DMA	34
5	$Fe(OTf)_3$	65
6	$FeCl_2$	46
7	$Fe(Ac)_2$	41
8	$FeCl_3$	34
9	$Co(acac)_2$	ND[b]
10	CuI	trace
11	$NiCl_2(py)_4$	35
12	CH_3CN (1 mL)	45
13	Zn (150%)	53

14	$MgCl_2$ (100%)	21
15	PBI (50%)	67
16	$Fe(acac)_3$ (5%)	61
17	LiCl instead of $MgCl_2$	ND[b]
18	$Mg(OTf)_2$ instead of $MgCl_2$	ND[b]

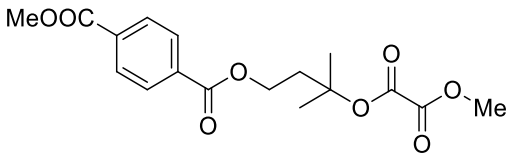
[a] NMR yield using 2,5-dimethyl furan as the internal standard from a mixture containing other impurities after a quick flash column chromatography; [b] Not detected.

2. Vinylation of **1a** with **2a** using the previously developed Ni-catalyzed conditions using DMA as the solvent.



Part 3. Preparation of Alkyl Oxalates

A general procedure for the preparation of tertiary alkyl oxalates: The *tertiary* alkyl oxalates were prepared according to a literature procedure from the corresponding *tertiary* alcohols.[1f,2] To a solution of alcohol (10.0 mmol, 100 mol%) in CH_2Cl_2 (50 mL) was added Et_3N (1.81 mL, 12.0 mmol, 120 mol%), DMAP (0.12 g, 1.0 mmol, 10 mol%) at 0 ºC in an ice bath. Following this, ethyl oxalyl chloride (1.10 mL, 12.0 mmol, 120 mol%) was added dropwise. The reaction mixture was allowed to warm to r.t. and stirred overnight. The reaction mixture was diluted with Et_2O, washed with water, saturated $NaHCO_3$, and brine. The organic phase was collected, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatograph to afford the product as a solid or oil.



3-(2-Methoxy-2-oxoacetoxy)-3-methylbutyl methyl terephthalate (4a).

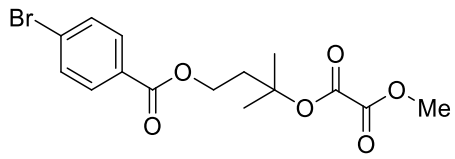
The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 80% yield (2.8 g, 8.0 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 (q, J = 8.4 Hz, 4H), 4.49 (t, J = 6.6 Hz, 2H), 3.94 (s, 3H), 3.78 (s, 3H), 2.36 (t, J = 6.7 Hz, 2H), 1.64 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.4, 165.8, 158.7, 156.7, 134.1, 133.9, 129.7, 129.7, 85.4, 61.3, 53.4, 52.6, 38.9, 26.2.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{17}H_{21}O_8$: 353.1231. Found: 353.1225.

M.p.: 56-57 ºC.



4-((4-Bromobenzoyl)oxy)-2-methylbutan-2-yl methyl oxalate (5a).

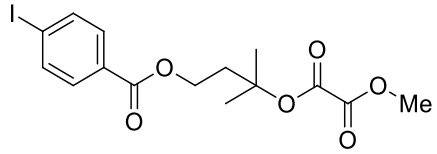
The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 70% yield (2.6 g, 7.0 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 4.43 (t, J = 6.6 Hz,

2H), 3.76 (s, 3H), 2.32 (t, *J* = 6.6 Hz, 2H), 1.60 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 165.7, 158.6, 156.6, 131.7, 131.1, 128.9, 128.1, 85.3, 61.1, 53.3, 38.8, 26.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{15}H_{18}BrO_6$: 373.0281. Found: 373.0284.



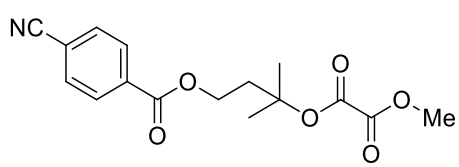
4-((4-Iodobenzoyl)oxy)-2-methylbutan-2-yl methyl oxalate (6a).

The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 76% yield (3.2 g, 7.6 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 4.45 (t, *J* = 6.6 Hz, 2H), 3.78 (s, 3H), 2.34 (t, *J* = 6.6 Hz, 2H), 1.62 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.0, 158.7, 156.7, 137.9, 131.1, 129.6, 100.9, 85.4, 61.1, 53.4, 38.9, 26.2.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{15}H_{18}IO_6$: 421.0143. Found: 421.0144.



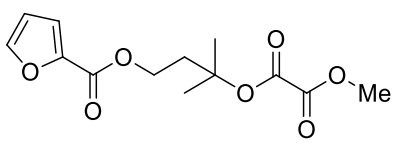
4-((4-Cyanobenzoyl)oxy)-2-methylbutan-2-yl methyl oxalate (7a).

The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 5% ethyl acetate in petroleum ether), the title compound was isolated in 88% yield (2.8 g, 8.8 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 4.48 (t, *J* = 6.7 Hz, 2H), 3.77 (s, 3H), 2.34 (t, *J* = 6.7 Hz, 2H), 1.62 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 164.9, 158.6, 156.6, 133.9, 132.3, 130.1, 117.9, 116.5, 85.2, 61.6, 53.4, 38.9, 26.1.

HRMS (ESI) m/z ($[M+Na]^+$) calcd for $C_{16}H_{17}NNaO_6$: 342.0948. Found: 342.0954.



4-((Furan-2-carbonyl)oxy)-2-methylbutan-2-yl methyl oxalate (8a).

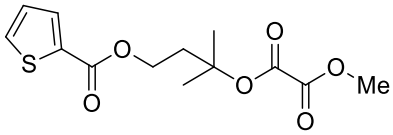
The title compound was prepared according the general

procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 81% yield (2.3 g, 8.1 mmol) as a yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 (d, J = 3.6 Hz, 1H), 7.13 (d, J = 3.6 Hz, 1H), 6.48 (t, J = 3.5 Hz, 1H), 4.42 (t, J = 6.6 Hz, 2H), 3.79 (s, 3H), 2.30 (t, J = 6.6 Hz, 2H), 1.60 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 158.7, 158.5, 156.6, 146.5, 144.6, 118.1, 111.9, 85.3, 60.7, 53.4, 38.9, 26.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{13}H_{17}O_7$: 285.0969. Found: 285.0971.



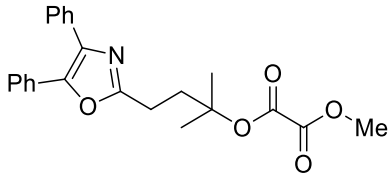
Methyl (2-methyl-4-((thiophene-2-carbonyl)oxy)butan-2-yl) oxalate (9a).

The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 78% yield (2.3 g, 7.8 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.71 (d, J = 3.6 Hz, 1H), 7.50 (d, J = 5.0 Hz, 1H), 7.03 (t, J = 4.3 Hz, 1H), 4.37 (t, J = 6.6 Hz, 2H), 3.73 (s, 3H), 2.26 (t, J = 6.6 Hz, 2H), 1.57 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 161.9, 158.5, 156.5, 133.5, 133.4, 132.5, 127.7, 85.2, 60.8, 53.2, 38.8, 25.9.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{13}H_{17}O_6S$: 301.0740. Found: 301.0746.



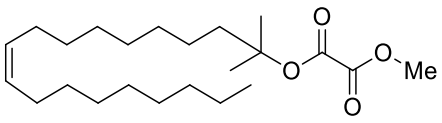
4-(4,5-Diphenyloxazol-2-yl)-2-methylbutan-2-yl methyl oxalate (14a).

The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 83% yield (3.3 g, 8.3 mmol) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 (d, J = 7.8 Hz, 2H), 7.58 (d, J = 7.8 Hz, 2H), 7.39–7.30 (m, 6H), 3.83 (s, 3H), 2.99 (t, J = 8.9 Hz, 2H), 2.41 (t, J = 8.9 Hz, 2H), 1.64 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 162.6, 158.8, 156.7, 145.5, 135.2, 132.6, 129.1, 128.8, 128.7, 128.6, 128.2, 128.1, 126.6, 85.9, 53.4, 37.9, 25.6, 23.1.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{23}H_{24}NO_5$: 394.1649. Found: 394.1648.



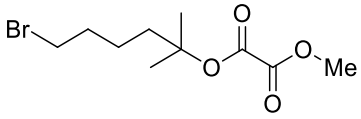
Methyl (2-methylnonadec-10-en-2-yl) oxalate (15a).

The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 80% yield (3.2 g, 8.0 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.38–5.31 (m, 2H), 3.85 (s, 3H), 2.00 (dd, J = 12.9, 6.6 Hz, 4H), 1.85–1.78 (m, 2H), 1.52 (s, 6H), 1.32–1.26 (m, 22H), 0.87 (t, J = 6.9 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.2, 156.9, 130.1, 129.9, 87.6, 53.3, 40.6, 32.0, 29.9, 29.8, 29.7, 29.5, 29.5, 29.4, 27.4, 27.3, 25.8, 23.9, 22.8, 14.2.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{23}H_{43}O_4$: 383.3156. Found: 383.3155.



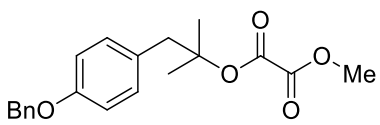
6-Bromo-2-methylhexan-2-yl methyl oxalate (16a).

The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 78% yield (2.2 g, 7.8 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.85 (s, 3H), 3.40 (t, J = 6.7 Hz, 2H), 1.89–1.80 (m, 4H), 1.56–1.47 (m, 8H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.0, 156.8, 87.0, 53.4, 39.6, 35.5, 32.7, 25.7, 22.5.

HRMS (ESI) m/z ([M+K]$^+$) calcd for $C_{10}H_{17}BrKO_4$: 320.9922. Found: 320.9935.



1-(4-(Benzyloxy)phenyl)-2-methylpropan-2-yl methyl oxalate (18a).

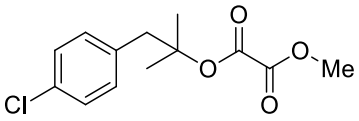
The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 93% yield (3.2 g, 9.3 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.15 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.3 Hz, 2H), 5.05 (s, 2H), 3.87 (s, 3H), 3.05 (s, 2H), 1.53 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.0, 157.9, 156.9, 137.2, 131.8, 128.8, 128.7, 128.1, 127.6, 114.6, 87.1, 70.2, 53.4, 45.9, 25.4.

HRMS (ESI) m/z ($[M+K]^+$) calcd for $C_{20}H_{22}KO_5$: 381.1099. Found: 381.1117.

M.p.: 66-67 ºC.

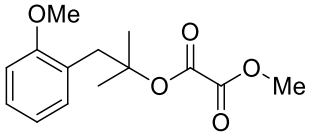


1-(4-Chlorophenyl)-2-methylpropan-2-yl methyl oxalate (19a). The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 90% yield (2.4 g, 9.0 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 3.87 (s, 3H), 3.07 (s, 2H), 1.53 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 158.8, 156.7, 134.8, 132.9, 132.0, 128.4, 86.3, 53.4, 46.2, 25.4.

HRMS (ESI) m/z ($[M+Na]^+$) calcd for $C_{13}H_{15}ClNaO_4$: 293.0551. Found: 253.0565.

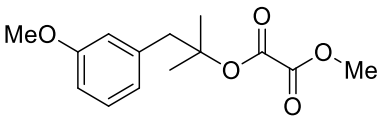


1-(2-Methoxyphenyl)-2-methylpropan-2-yl methyl oxalate (23a). The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 89% yield (2.4 g, 8.9 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.21 (dd, J = 15.1, 7.6 Hz, 2H), 6.89 (t, J = 7.4 Hz, 1H), 6.86 (d, J = 8.2 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.20 (s, 2H), 1.54 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.0, 157.9, 156.7, 132.6, 128.2, 125.0, 120.2, 110.5, 87.5, 55.1, 53.2, 39.2, 25.6.

HRMS (ESI) m/z ($[M+K]^+$) calcd for $C_{14}H_{18}KO_5$: 305.0786. Found: 305.0796.



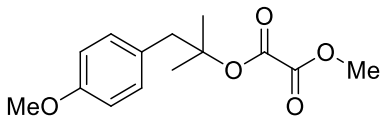
1-(3-Methoxyphenyl)-2-methylpropan-2-yl methyl oxalate (24a). The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in

petroleum ether), the title compound was isolated in 82% yield (2.2 g, 8.2 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20 (t, J = 7.8 Hz, 1H), 6.83–6.78 (m, 3H), 3.86 (s, 3H), 3.80 (s, 3H), 3.08 (s, 2H), 1.55 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.5, 158.9, 156.8, 137.9, 128.1, 123.2, 116.3, 112.5, 86.8, 55.2, 53.4, 46.9, 25.5.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{14}H_{19}O_5$: 267.1227. Found: 267.1228.



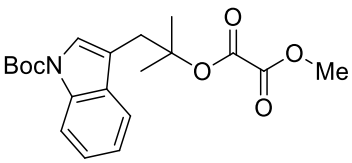
1-(4-Methoxyphenyl)-2-methylpropan-2-yl methyl oxalate (25a).

The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 73% yield (1.9 g, 7.3 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.14 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 3.87 (s, 3H), 3.79 (s, 3H), 3.04 (s, 2H), 1.52 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 158.9, 158.6, 156.8, 131.7, 128.4, 113.6, 87.0, 55.3, 53.4, 45.9, 25.4.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{14}H_{19}O_5$: 267.1227. Found: 267.1228.



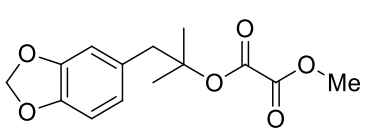
1-(1-(Tert-butoxycarbonyl)-1H-indol-3-yl)-2-methylpropan-2-yl methyl oxalate (28a).

The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 78% yield (2.9 g, 7.8 mmol) as a pale yellow liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.53 (s, 1H), 7.31 (t, J = 7.7 Hz, 1H), 7.25 (dd, J = 12.8, 5.1 Hz, 1H), 3.87 (s, 3H), 3.20 (s, 2H), 1.68 (s, 9H), 1.62 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 158.9, 156.9, 149.8, 131.4, 125.3, 124.3, 122.5, 119.6, 115.3, 115.2, 100.1, 86.9, 83.7, 53.4, 36.1, 28.3, 25.6.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{20}H_{26}NO_6$: 376.1755. Found: 376.1757.



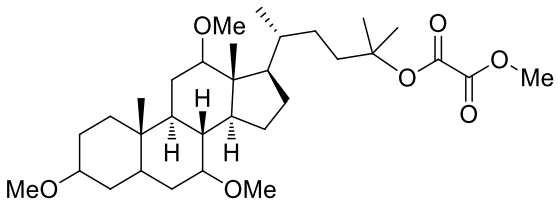
1-(Benzo[d][1,3]dioxol-5-yl)-2-methylpropan-2-yl methyl oxalate (31a).

The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 80% yield (2.2 g, 8.0 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.74 (s, 1H), 6.71 (d, J = 7.9 Hz, 1H), 6.64 (d, J = 7.9 Hz, 1H), 5.91 (s, 2H), 3.85 (s, 3H), 2.99 (s, 2H), 1.51 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 158.8, 156.7, 147.4, 146.5, 129.9, 123.7, 110.9, 107.9, 100.9, 86.7, 53.3, 46.5, 25.3.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{14}H_{17}O_6$: 281.1019. Found: 281.1012.



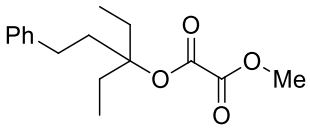
Methyl-((5*R*)-2-methyl-5-((8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3,7,12-trimethoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)hexan-2-yl) oxalate (38a).

The title compound was prepared from cholic acid and according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 73% yield (4.0 g, 7.3 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.85 (s, 3H), 3.35 (s, 1H), 3.32 (s, 3H), 3.25 (s, 3H), 3.20 (s, 3H), 3.13 (d, J = 2.1 Hz, 1H), 3.02–2.95 (m, 1H), 2.18 (dd, J = 24.9, 12.8 Hz, 1H), 2.12–1.99 (m, 2H), 1.93 (q, J = 9.8 Hz, 1H), 1.88–1.70 (m, 8H), 1.67 (d, J = 12.9 Hz, 1H), 1.60 (s, 1H), 1.50 (d, J = 8.6 Hz, 6H), 1.43–1.23 (m, 5H), 0.89 (s, 6H), 0.64 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.9, 156.9, 87.9, 82.1, 80.9, 55.9, 55.8, 55.5, 53.3, 46.2, 46.2, 42.8, 42.1, 39.8, 36.7, 35.5, 35.4, 35.0, 34.6, 29.6, 28.1, 27.9, 27.5, 26.8, 25.9, 25.7, 23.3, 22.9, 17.9, 12.6.

HRMS (ESI) m/z ($[M+Na]^+$) calcd for $C_{32}H_{54}NaO_7$: 573.3761. Found: 573.3758.



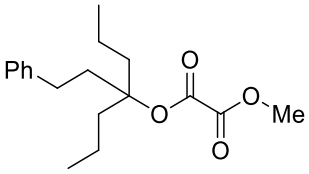
3-Ethyl-1-phenylpentan-3-yl methyl oxalate (41a).

The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 69% yield (1.9 g, 6.9 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 (t, J = 7.6 Hz, 2H), 7.21–7.17 (m, 3H), 3.87 (s, 3H), 2.60 (t, J = 14.5 Hz, 2H), 2.20 (t, J = 14.5 Hz, 2H), 2.00 (q, J = 7.5 Hz, 4H), 0.93 (t, J = 7.5 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.1, 156.7, 141.7, 128.6, 128.4, 126.1, 92.8, 53.3, 36.4, 29.8, 27.2, 7.8.

HRMS (ESI) m/z ($[M+K]^+$) calcd for $C_{16}H_{22}KO_4$: 317.1150. Found: 317.1164.



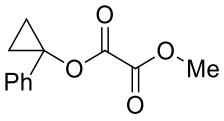
Methyl (4-phenethylheptan-4-yl) oxalate (42a).

The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 65% yield (2.0 g, 6.5 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 (t, J = 7.5 Hz, 2H), 7.19 (t, J = 5.7 Hz, 3H), 3.87 (s, 3H), 2.60 (t, J = 14.5 Hz, 2H), 2.21 (t, J = 14.5 Hz, 2H), 1.95 (q, J = 7.5 Hz, 4H), 1.42–1.30 (m, 4H), 0.93 (t, J = 7.3 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.1, 156.7, 141.6, 128.5, 128.4, 126.1, 92.2, 53.3, 37.4, 37.3, 29.9, 16.8, 14.4.

HRMS (ESI) m/z ($[M+K]^+$) calcd for $C_{18}H_{26}KO_4$: 345.1463. Found: 345.1468.



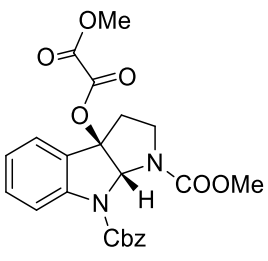
Methyl (1-phenylcyclopropyl) oxalate (43a).

The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 68% yield (1.5 g, 6.8 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (t, J = 9.2 Hz, 3H), 7.33 (t, J = 7.6 Hz, 2H), 3.87 (s, 3H), 1.67–1.66 (m, 1H), 1.43–1.41 (m, 2H), 1.31–1.29 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 158.2, 157.3, 138.0, 128.8, 128.5, 128.1, 127.3, 126.4, 63.2, 53.6, 21.9, 14.2.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{12}H_{13}O_4$: 221.0808. Found: 221.0817.



(3a*R*,8a*R*)-8-Benzyl-1-methyl-3a-(2-methoxy-2-oxoacetoxy)-3,3a-dihydropyrrolo[2,3-b]indole-1,8(2H,8aH)-dicarboxylate (47a).

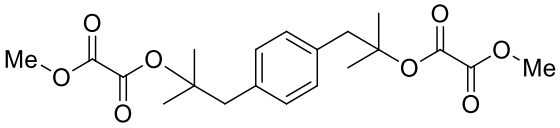
The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 76% yield (3.5 g, 7.6 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 (s, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 7.4 Hz, 2H), 7.37 (dt, J = 20.8, 7.2 Hz, 4H), 7.10 (t, J = 7.5 Hz, 1H), 6.53 (s, 1H), 5.30 (s, 2H), 4.04 (s, 1H), 3.86 (s, 3H), 3.52 (s, 3H), 2.93 (td, J = 12.0, 5.0 Hz, 1H), 2.79 (dd, J = 12.3, 4.9 Hz, 1H), 2.54 (td, J = 12.3, 8.3 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.6, 156.2, 153.2, 144.2, 135.9, 131.7, 128.7, 128.5, 128.4, 126.9, 125.3, 124.3, 116.8, 100.1, 79.9, 68.1, 53.8, 53.6, 52.9, 45.3, 0.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{23}H_{23}N_2O_8$: 455.1449. Found: 455.1455.

M.p.: 145-146 ºC.



_O,O'_-(1,4-Phenylenebis(2-methylpropane-2, 1-diyl)) dimethyl dioxalate (48a).

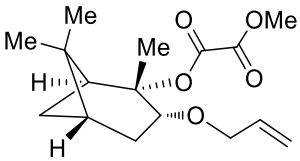
The title compound was prepared according the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 63% yield (2.5 g, 6.3 mmol) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.16 (s, 4H), 3.87 (s, 6H), 3.08 (s, 4H), 1.53 (s, 12H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 158.9, 156.9, 134.9, 130.5, 86.9, 53.4, 46.4, 25.5.

HRMS (ESI) m/z ($[M+Na]^+$) calcd for $C_{20}H_{26}NaO_8$: 417.1520. Found: 417.1537.

M.p.: 134-135 ºC.



(1*S*,2*S*,3*R*,5*S*)-3-(Allyloxy)-2,5,6,6-tetramethylbicyclo[3.1.1]hepta n-2-yl methyl oxalate (49d).

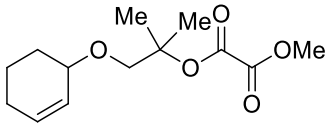
The title compound was prepared from (1*S*,2*S*,3*R*,5*S*)-(+)-2,3-pinanediol and according the literature[3a] and the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 46% yield (1.4 g, 4.6 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.91 (dq, J = 10.7, 5.6 Hz, 1H), 5.27 (d, J = 17.1 Hz, 1H), 5.15 (d, J = 10.4 Hz, 1H), 4.07 (d, J = 5.5 Hz, 2H), 3.85–3.83 (m, 1H), 3.82 (s, 3H), 2.62 (t, J = 5.7 Hz, 1H), 2.39–2.32

(m, 1H), 2.23–2.15 (m, 1H), 1.96 (s, 1H), 1.86–1.80 (m, 1H), 1.74 (s, 3H), 1.47 (d, *J* = 10.5 Hz, 1H), 1.27 (s, 3H), 0.94 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.3, 156.6, 135.1, 117.0, 90.1, 76.3, 71.5, 53.3, 52.1, 39.9, 38.7, 34.9, 28.0, 27.4, 26.2, 23.9.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{16}H_{25}O_5$: 297.1696. Found: 297.1696.



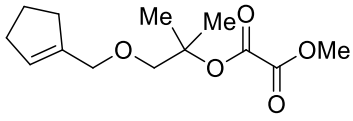
1-(Cyclohex-2-en-1-yloxy)-2-methylpropan-2-yl methyl oxalate (49e).

The title compound was prepared according the literature[3a] and the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 37% yield (0.9 g, 3.7 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.78 (d, *J* = 10.0 Hz, 1H), 5.67 (d, *J* = 9.9 Hz, 1H), 3.83 (s, 1H), 3.79 (s, 3H), 3.61 (dd, *J* = 35.7, 9.9 Hz, 2H), 1.92 (dd, *J* = 54.9, 16.9 Hz, 2H), 1.82–1.52 (m, 4H), 1.48 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 158.7, 156.6, 130.9, 127.6, 85.8, 73.6, 72.8, 53.2, 28.1, 25.1, 23.1, 19.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{13}H_{21}O_5$: 257.1383. Found: 257.1383.



1-(Cyclopent-1-en-1-ylmethoxy)-2-methylpropan-2-yl methyl oxalate (49g).

The title compound was prepared according the literature[3] and the general procedure. After purification by a flash column chromatography (SiO_2: 10% ethyl acetate in petroleum ether), the title compound was isolated in 62% yield (1.6 g, 6.2 mmol) as a colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.61 (s, 1H), 4.07 (s, 2H), 3.85 (s, 3H), 3.56 (s, 2H), 2.29 (dd, *J* = 22.3, 15.5 Hz, 4H), 1.95–1.83 (m, 2H), 1.54 (s, 6H).

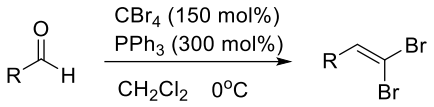
^{13}C NMR (150 MHz, $CDCl_3$): δ 158.9, 156.7, 141.3, 127.9, 85.9, 74.8, 70.4, 53.4, 32.9, 32.5, 23.4, 23.2.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{13}H_{21}O_5$: 257.1384. Found: 257.1388.

Part 4. Preparation of Vinyl Bromides

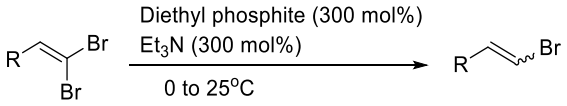
A general procedure for the preparation of vinyl bromides:

Step 1: The Ramirez protocol for the Wittig-type dibromoolefination.[4]



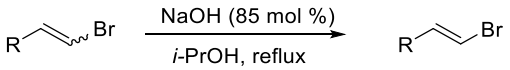
To a flame-dried flask was added aldehyde (20 mmol, 100 mol%), CBr_4 (30 mmol, 150 mol%), and CH_2Cl_2 (80 mL). The flask was cooled to 0 °C in an ice bath, at which point a solution of PPh_3 (60 mmol, 300 mol%) in CH_2Cl_2 (70 mL) was added dropwise via addition funnel over 30 min. The solution was stirred at 0 °C under N_2 for 1 h. About half of the volume of CH_2Cl_2 was removed under reduced pressure. Pentane (100 mL) was added, and triphenylphosphine oxide (TPPO) precipitated out. After filtration and evaporation of the solvent, the residue was dissolved in pentane (50 mL) which led to further precipitation of TPPO. Filtration and evaporation of the solvent afforded the crud dibromide which was directly used for the next step.

Step 2: Hayes protocol of the Hirao reaction.[5]

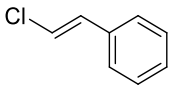


To a solution of the crude dibromide (~ 20.0 mmol, 100 mol%) and NEt_3 (60 mmol, 300 mol%) in DMF (20 mL) was added dimethyl phosphonate (60.0 mmol, 300 mol%). The solution was stirred over night at room temperature. Water (60 mL) was added to the mixture, which was extracted with pentane (2 × 100 mL). The combined organic phases were washed with an aqueous solution of HCl (1 M, 55 mL) and dried over Na_2SO_4, filtered, and concentrated. The crude material was purified by flash chromatography.

Step 3: Selective destruction of the (*Z*)-isomer as reported by Dolby.[6]



The crude product (~20.0 mmol, 100 mol %) from the previous step was dissolved in *i*-PrOH (30 mL). Solid NaOH (17.0 mmol, 85 mol%) was added and the mixture was heated to reflux for 1.5 hours. The reaction mixture was cooled to room temperature, diluted with pentane (100 mL), and partitioned with distillated H_2O (2 × 100 mL). The organic phase was collected, and washed with an aqueous solution of HCl (1 M, 75 mL), dried over Na_2SO_4. The solvent was removed under reduced pressure. The crude material was purified by flash chromatography.



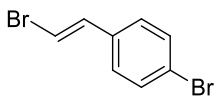
(*E*)-(2-Chlorovinyl)benzene (2a-Cl).

This compound was prepared from cinnamic acid (2.96 g, 20.0 mmol) according to the literature.[7] The crude residue was purified by silicagel chromatography (hexanes) to give the title compound in 52% yield (0.7 g, 5.2 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.27 (m, 5H), 6.85 (d, J = 13.7 Hz, 1H), 6.66 (d, J = 13.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3, 136.1, 128.9, 128.4, 126.2, 106.2.

HRMS (ESI) m/z ($[M+H]^+$) calcd for C_8H_8Cl: 139.0309. Found: 139.0310.



(*E*)-1-Bromo-4-(2-bromovinyl)benzene (2h).

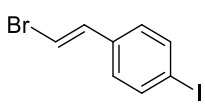
This compound was prepared according to general procedure. The crude residue was purified by silicagel chromatography (hexanes) to give the title compound in 83% yield (2.2 g, 8.3 mmol) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 14.1 Hz, 1H), 6.78 (d, J = 14.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2, 134.9, 132.1, 127.7, 122.3, 107.5.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_8H_7Br_2$: 260.8909. Found: 260.8910.

M.p.: 69-70 ºC.



(*E*)-1-(2-Bromovinyl)-4-iodobenzene (2i).

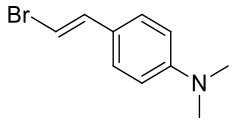
This compound was prepared according to general procedure. The crude residue was purified by silicagel chromatography (hexanes) to give the title compound in 73% yield (2.2 g, 7.3 mmol) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.5 Hz, 2H), 7.06–6.99 (m, 3H), 6.80 (d, J = 14.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 136.3, 127.9, 107.6, 93.9, 88.8.

HRMS (ESI) m/z ($[M+H]^+$) calcd for C_8H_7BrI: 308.8770. Found: 308.8765.

M.p.: 92-93 ºC.



(*E*)-4-(2-Bromovinyl)-N,N-dimethylaniline (2j).

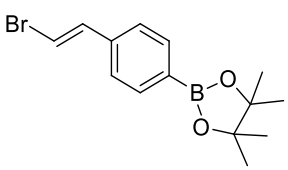
This compound was prepared from according to general procedure. The crude residue was purified by silica gel chromatography (hexanes) to give the title compound in 84% yield (1.9 g, 8.4 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.18 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 13.9 Hz, 1H), 6.65 (d, J = 8.7 Hz, 2H), 6.51 (d, J = 13.9 Hz, 1H), 2.96 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 150.5, 137.1, 127.3, 124.4, 112.4, 101.6, 40.5.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{10}H_{13}BrN$: 226.0226. Found: 226.0227.

M.p.: 118-119 ºC.



(*E*)-2-(4-(2-Bromovinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaboro lane (2k).

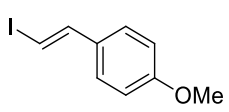
This compound was prepared according to general procedure. The crude residue was purified by silicagel chromatography (hexanes) to give the title compound in 65% yield (2.0 g, 6.5 mmol) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 14.0 Hz, 1H), 6.85 (d, J = 14.0 Hz, 1H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 137.3, 135.4, 125.5, 107.9, 84.0, 25.0.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{14}H_{19}BBrO_2$: 309.0656. Found: 309.0651.

M.p.: 36-37 ºC.



(*E*)-1-(2-Iodovinyl)-4-methoxybenzene (2n-I).

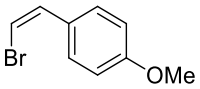
This compound was prepared according to the literature[9]. The crude residue was purified by silicagel chromatography (hexanes) to give the title compound in 62% yield (1.6 g, 6.2 mmol) as a pale yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, J = 14.9 Hz, 1H), 7.23 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 6.63 (d, J = 14.9 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.9, 144.4, 130.9, 127.4, 114.2, 73.7, 55.5.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_9H_{10}IO$: 260.9771. Found: 260.9773.

M.p.: 95-96 ºC.



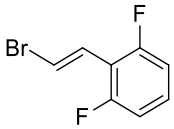
(*Z*)-1-(2-Bromovinyl)-4-methoxybenzene (*Z*-2n).

This compound was prepared according to the literature[9]. The crude residue was purified by silicagel chromatography (hexanes) to give the title compound in 62% yield (1.3 g, 6.2 mmol) as a pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.1 Hz, 1H), 6.89 (d, J = 8.7 Hz, 2H), 6.29 (d, J = 8.1 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.6, 131.7, 130.6, 127.7, 113.7, 104.3, 55.4.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_9H_{10}BrO$: 212.9909. Found: 212.9913.



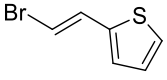
(*E*)-2-(2-Bromovinyl)-1,3-difluorobenzene (2o).

This compound was prepared according to general grocedure. The crude residue was purified by silicagel chromatography (hexanes) to give the title compound in 77% yield (1.7 g, 7.7 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.17 (m, 3H), 6.90–6.86 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7 (d, J = 7.3 Hz), 159.2 (d, J = 7.3 Hz), 129.1 (t, J = 10.7 Hz), 123.9 (t, J = 2.3 Hz), 113.8 (t, J = 9.3 Hz), 112.0–111.6 (m).

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_8H_6BrF_2$: 218.9616. Found: 218.9613.



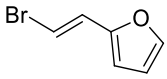
(*E*)-2-(2-Bromovinyl)thiophene (2r).

This compound was prepared according to general procedure. The crude residue was purified by silicagel chromatography (hexanes) to give the title compound in 53% yield (1.0 g, 5.3 mmol) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.16 (m, 2H), 7.00–6.95 (m, 2H), 6.63 (d, J = 13.9 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 130.4, 127.6, 126.2, 125.2, 105.3.

HRMS (ESI) m/z ([M+H]$^+$) calcd for C_6H_6BrS: 188.9368. Found: 188.9370.



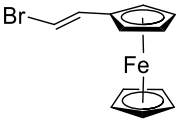
(*E*)-2-(2-Bromovinyl)furane (2s).

This compound was prepared according to general procedure. The crude residue was purified by silicagel chromatography (hexanes) to give the title compound in 60% yield (1.0 g, 6.0 mmol) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.34 (m, 1H), 6.89 (d, J = 13.9 Hz, 1H), 6.72 (d, J = 13.9 Hz, 1H), 6.41–6.34 (m, 1H), 6.26 (d, J = 3.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 142.7, 125.5, 111.5, 108.8, 105.4.

HRMS (ESI) m/z ([M+H]$^+$) calcd for C_6H_6BrO: 172.9596. Found: 2175.9594.



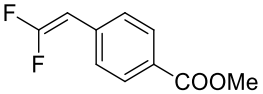
(*E*)-(2-Bromovinyl) ferrocene (2t).

This compound was prepared according to general procedure. The crude residue was purified by silicagel chromatography (hexanes) to give the title compound in 50% yield (1.5 g, 5.0 mmol) as a red brown oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.81 (d, J = 13.8 Hz, 1H), 6.27 (d, J = 13.8 Hz, 1H), 4.29 (s, 2H), 4.24 (s, 2H), 4.15 (s, 5H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 135.0, 101.3, 69.4, 69.2, 66.6.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{12}H_{12}BrFe$: 290.9466. Found: 290.9468.



Methyl 4-(2,2-difluorovinyl)benzoate (2u).

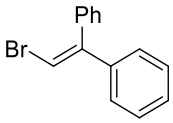
This compound was prepared according to the literature.[8] The crude residue was purified by silicagel chromatography (hexanes) to give the title compound in 62% yield (1.2 g, 6.2 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 5.33 (dd, J = 25.9, 3.5 Hz, 1H), 3.91 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8, 158.9–154.9 (m), 135.3, 130.1, 128.7, 127.6 (dd, J = 6.7, 3.5 Hz), 82.2 (dd, J = 29.8, 13.1 Hz), 52.3.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{10}H_9F_2O_2$: 199.0565. Found: 199.0564.

2-Bromoethene-1,1-diyl)dibenzene (2x).



This compound was prepared according to general procedure. The crude residue was purified by silicagel chromatography (hexanes) to give the title compound in 73% yield (1.9 g, 7.3 mmol) as a white solid.

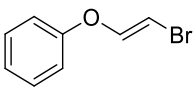
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43 (t, J = 7.2 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 7.35–7.30 (m, 5H), 7.24 (dd, J = 6.5, 3.2 Hz, 2H), 6.80 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 146.9, 140.9, 139.2, 129.8, 128.6, 128.4, 128.3, 128.1, 127.8, 105.3.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{14}H_{12}Br$: 259.0117. Found: 259.0118.

M.p.: 51-52 ºC.

(*E*)-((2-Bromovinyl)oxy)benzene (2y).



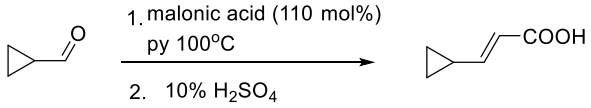
This compound was prepared according to general procedure. The crude residue was purified by silicagel chromatography (hexanes) to give the title compound in 53% yield (1.1 g, 5.3 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39–7.32 (m, 2H), 7.14 (t, J = 7.4 Hz, 1H), 7.06 (t, J = 5.6 Hz, 2H), 7.05 (d, J = 4.2 Hz, 1H), 5.56 (d, J = 4.2 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 156.7, 144.1, 129.9, 123.9, 116.9, 88.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{13}H_{16}NaO_4$: 198.9753. Found: 198.9753.

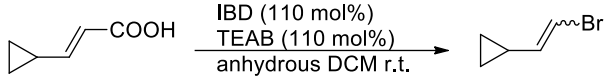
Preparation of (2-bromovinyl)cyclopropane.[10]



Cyclopropanecarboxaldehyde (10 g, 0.14 mol), malonic acid (16 g, 0.15 mol) and pyridine (20 mL,) were heated for 6 hours at 100 °C in an oil bath under N_2. The cooled mixture was acidified with 10% of H_2SO_4 (500 mL) and cooled in an ice-bath. The precipitate was collected and washed with water to give the acid as colorless needles (6.1 g, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.72 (s, 1H), 6.52 (dd, J = 15.3, 10.3 Hz, 1H)), 5.89 (d, J = 15.4 Hz, 1H)), 1.68–1.54 (m, 1H)), 1.05–0.93 (m, 2H)), 0.73– 0.63 (m, 2H)).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 157.4, 117.6, 14.8, 9.2.



To a stirred suspension of diacetoxyiodobenzene (IBD) (18 g, 55 mmol) in anhydrous CH_2Cl_2 (50 ml) was added tertraethylammonium bromide (TEAB) (12 g, 55 mmol) in one portion. The resultant mixture was stirred at room temperature for 5 min followed by addition of 3-cyclopropylacrylic acid (5.6 g, 50 mmol). The reaction mixture was stirred over night at room temperature until the starting material was completely consumed (monitored by TLC). The reaction mixture was distilled at atmospheric pressure to remove CH_2Cl_2 in an oil bath. Distillation of the crude mixture at 60^{o}C in an oil bath afforded the desired vinyl bromide as a colorless oil (1.1 g, 15% yield, *Z*: *E*= 1:1.1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.06–5.99 (m, 2H), 5.69 (dd, *J* = 13.5, 9.0 Hz, 1H), 5.47 (dd, *J* = 9.4, 7.0 Hz, 1H), 1.89–1.77 (m, 1H), 1.48–1.37 (m, 1H), 0.88–0.82 (m, 2H), 0.78–0.71 (m, 2H), 0.51–0.46 (m, 2H), 0.46–0.42 (m, 2H).

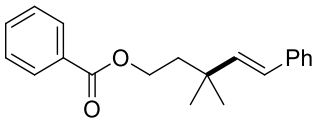
^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6 (d, *J* = 1.5 Hz), 138.9 (d, *J* = 1.7 Hz), 104.8 (d, *J* = 1.4 Hz), 101.4 (d, *J* = 1.7 Hz), 14.5 (s), 12.58 (s), 6.9 (d, *J* = 1.7 Hz), 6.5 (d, *J* = 1.5 Hz).

Part 5. Coupling of Tertiary Alkyl Oxalates with Vinyl Bromides

1. General Procedure (GP):

A flame-dried Schlenk tube was charged with a *tertiary* alkyl oxalate if it is a solid (0.225 mmol, 150 mol%), Zn (24.5 mg, 0.38 mmol, 250 mol%), $Fe(acac)_3$ (4.2 mg, 0.012 mmol, 8 mol%), $MgCl_2$ (28.5 mg, 0.30 mmol, 200 mol%), and PBI (29.3 mg, 0.45 mmol, 100 mol%). The tube was capped with a rubber septum. After being evacuated and backfilled with nitrogen three times, vinyl bromide (20.0 μL, 0.15 mmol, 100 mol%) and a *tertiary* alkyl oxalate if it is a liquid (0.225 mmol, 150 mol%) were added via syringes followed by addition of CH_3CN (0.4 mL), again via a syringe. The reaction mixture was allowed to stir in an oil bath overnight under a N_2 atmosphere at 25 °C, and was directly loaded onto a silica gel column without work-up. The residue was rinsed with small amount of CH_2Cl_2 or the eluent and was transferred to a silica gel column. Flash column chromatography offered the product.

2. Details of the Experimental Data



(*E*)-3,3-Dimethyl-5-phenylpent-4-en-1-yl benzoate (3a).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in <83% yield (36.6 mg, 0.125 mmol, contaminated with ~3% of the *tert*-alkyl chloride derived from the oxalate) as a pale yellow oil.

This compound was also prepared according to the GP using (*E*)-(2-chlorovinyl)benzene (20.8 mg, 0.15 mmol, 100 mol%). After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 77% yield (34.0 mg, 0.116 mmol) as a pale yellow oil.

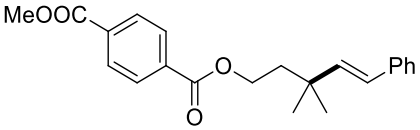
Following the *GP*, a gram scale reaction was preformed using *tertiary* alkyl oxalate **1a** (1.32 g, 4.5 mmol, 150 mol%), Zn (490 mg, 7.6 mmol, 250 mol%), $Fe(acac)_3$ (84 mg, 0.24 mmol, 8 mol%), $MgCl_2$ (570 mg, 6.0 mmol, 200 mol%), PBI (586 mg, 9.0 mmol, 100 mol%), vinyl bromide (0.4 mL, 3.0 mmol, 100 mol%) and CH_3CN (10.0 mL). The title compound **3a** was isolated in 88% yield (0.8 g,

2.64 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (d, J = 7.1 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.42–7.36 (m, 4H), 7.31 (t, J = 7.7 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H), 6.37 (d, J = 16.4 Hz, 1H), 6.30 (d, J = 16.4 Hz, 1H), 4.40 (t, J = 7.1 Hz, 2H), 1.94 (t, J = 7.1 Hz, 2H), 1.24 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 139.5, 137.7, 132.9, 130.5, 129.6, 128.6, 128.4, 127.1, 126.5, 126.2, 62.6, 41.3, 35.6, 27.6.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{20}H_{23}O_2$: 295.1693. Found: 295.1692.



(*E*)-3,3-Dimethyl-5-phenylpent-4-en-1-yl methyl terephthalate (4).

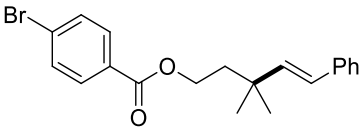
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in <65% yield (34.4 mg, 0.098 mmol, contaminated with ~4% of the *tert*-alkyl chloride derived from the oxalate) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (q, J = 8.6 Hz, 4H), 7.34 (d, J = 7.4 Hz, 2H), 7.28 (t, J = 7.7 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 6.35 (d, J = 16.2 Hz, 1H), 6.24 (d, J = 16.2 Hz, 1H), 4.39 (t, J = 7.1 Hz, 2H), 3.94 (s, 3H), 1.92 (t, J = 7.1 Hz, 2H), 1.22 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.4, 165.9, 139.3, 137.7, 134.3, 133.9, 129.6, 129.6, 128.6, 127.2, 126.6, 126.2, 63.1, 52.5, 41.3, 35.6, 27.7.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{22}H_{25}O_4$: 353.1747. Found: 353.1748.

M.p.: 64-65 ºC.



(*E*)-3,3-Dimethyl-5-phenylpent-4-en-1-yl 4-bromobenzoate (5).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 70% yield (39.2 mg, 0.105 mmol) as a white solid.

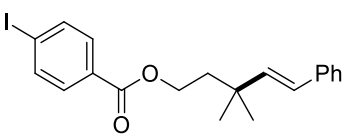
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 7.3 Hz, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 6.34 (d, J = 16.2 Hz, 1H), 6.23 (d, J = 16.2 Hz, 1H),

4.37 (t, *J* = 7.0 Hz, 2H), 1.90 (t, *J* = 7.0 Hz, 2H), 1.21 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.0, 139.4, 137.7, 131.7, 131.2, 129.3, 128.6, 127.9, 127.1, 126.5, 126.2, 62.8, 41.3, 35.6, 27.6.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{20}H_{22}BrO_2$: 373.0797. Found: 373.0791.

M.p.: 51-52 ºC.



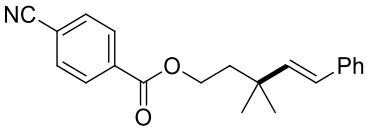
(*E*)-3,3-Dimethyl-5-phenylpent-4-en-1-yl 4-iodobenzoate (6).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in <65% yield (40.9 mg, 0.098 mmol, contaminated with ~4% of the *tert*-alkyl chloride derived from the oxalate) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.34 (d, *J* = 16.2 Hz, 1H), 6.23 (d, *J* = 16.2 Hz, 1H), 4.37 (t, *J* = 7.0 Hz, 2H), 1.90 (t, *J* = 7.0 Hz, 2H), 1.21 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.0, 139.4, 137.7, 131.7, 131.2, 129.4, 128.6, 128.0, 127.2, 126.5, 126.2, 62.8, 41.4, 35.6, 27.7.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{20}H_{22}IO_2$: 421.0659. Found: 421.0651.



(*E*)-3,3-Dimethyl-5-phenylpent-4-en-1-yl-4-cyano benzoate (7).

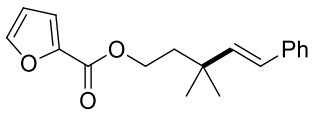
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 46% yield (44.1 mg, 0.069 mmol) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.29–7.26 (m, 2H), 7.23–7.18 (m, 1H), 6.33 (d, *J* = 16.3 Hz, 1H), 6.22 (d, *J* = 16.2 Hz, 1H), 4.40 (t, *J* = 6.9 Hz, 2H), 1.91 (t, *J* = 6.9 Hz, 2H), 1.21 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 139.3, 137.6, 134.2, 132.2, 130.2, 128.7, 127.2, 126.5, 126.2, 118.2, 116.3, 63.4, 41.4, 35.6, 27.6.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{21}H_{22}NO_2$: 320.1645. Found: 320.1642.

M.p.: 56-57 ºC.



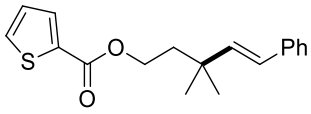
(*E*)-3,3-Dimethyl-5-phenylpent-4-en-1-yl-furan-2-carboxylate (8).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 41% yield (17.5 mg, 0.062 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (s, 1H), 7.35 (d, J = 7.4 Hz, 2H), 7.28 (t, J = 7.7 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 3.1 Hz, 1H), 6.45 (dd, J = 3.5, 1.7 Hz, 1H), 6.34 (d, J = 16.2 Hz, 1H), 6.22 (d, J = 16.2 Hz, 1H), 4.35 (t, J = 7.3 Hz, 2H), 1.89 (t, J = 7.3 Hz, 2H), 1.19 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 158.9, 146.3, 144.9, 139.3, 137.7, 128.6, 127.1, 126.6, 126.3, 117.9, 118.9, 62.6, 41.3, 35.6, 27.6.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{18}H_{21}O_3$: 285.1485. Found: 285.1475.



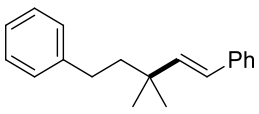
(*E*)-3,3-Dimethyl-5-phenylpent-4-en-1-yl thiophene-2-carboxylate (9).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 60% yield (27.0 mg, 0.090 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, J = 2.8 Hz, 1H), 7.51 (d, J = 4.0 Hz, 1H), 7.35 (d, J = 7.5 Hz, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.19 (d, J = 7.3 Hz, 1H), 7.06–7.03 (m, 1H), 6.35 (d, J = 16.2 Hz, 1H), 6.23 (d, J = 16.2 Hz, 1H), 4.34 (t, J = 7.2 Hz, 2H), 1.89 (t, J = 7.2 Hz, 2H), 1.21 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 162.4, 139.4, 137.7, 134.2, 133.4, 132.3, 128.6, 127.8, 127.1, 126.7, 126.3, 62.8, 41.3, 35.6, 27.7.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{18}H_{21}O_2S$: 301.1257. Found: 301.1258.



(*E*)-(3,3-Dimethylpent-1-ene-1,5-diyl)dibenzene (10).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 61% yield (22.9 mg, 0.092 mmol) as a colorless solid.

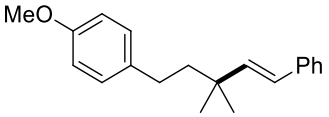
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.29–7.24 (m, 3H),

7.21 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 6.35 (d, *J* = 16.2 Hz, 1H), 6.25 (d, *J* = 16.2 Hz, 1H), 2.58 (t, *J* = 7.4 Hz, 2H), 1.71 (t, *J* = 7.4 Hz, 2H), 1.18 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 143.3, 140.3, 138.1, 128.6, 128.5, 128.5, 127.0, 126.4, 126.2, 125.7, 45.4, 36.6, 31.5, 27.4.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{19}H_{23}$: 251.1794. Found: 251.1793.

M.p.: 50-51 ºC.



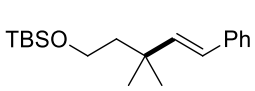
(*E*)-1-(3,3-Dimethyl-5-phenylpent-4-en-1-yl)-4-methoxy benzene (11).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 81% yield (34.1 mg, 0.122 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 6.34 (d, *J* = 16.2 Hz, 1H), 6.23 (d, *J* = 16.2 Hz, 1H), 3.78 (s, 3H), 2.52 (t, *J* = 7.4 Hz, 2H), 1.66 (t, *J* = 7.4 Hz, 2H), 1.17 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.8, 140.4, 138.1, 135.4, 129.3, 128.6, 126.9, 126.3, 126.2, 113.9, 55.4, 45.7, 36.6, 30.5, 27.4.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{20}H_{25}O$: 281.1900. Found: 281.1900.



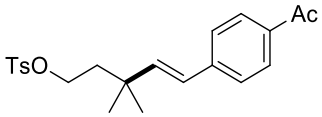
(*E*)-Tert-butyl((3,3-dimethyl-5-phenylpent-4-en-1-yl)oxy)dimethylsilane (12).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 67% yield (30.6 mg, 0.101 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.28 (d, *J* = 16.2 Hz, 1H), 6.20 (d, *J* = 16.2 Hz, 1H), 3.65 (t, *J* = 7.4 Hz, 2H), 1.68 (t, *J* = 7.4 Hz, 2H), 1.13 (s, 6H), 0.88 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 140.4, 138.1, 128.6, 126.9, 126.2, 125.9, 60.5, 45.7, 35.5, 27.8, 26.1, 18.4, -5.1.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{19}H_{33}OSi$: 305.2295. Found: 305.2295.



(*E*)-Tert-butyl((3,3-dimethyl-5-phenylpent-4-en-1-yl)oxy)dimethylsilane (13).

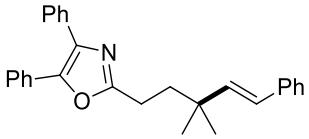
This compound was prepared according to the GP using (*E*)-1-(4-(2-bromovinyl)phenyl)ethanone (33.8 mg, 0.15 mmol, 100 mol%). After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 81% yield (46.9 mg, 0.122 mmol) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.24 (d, *J* = 16.3 Hz, 1H), 6.17 (d, *J* = 16.2 Hz, 1H), 4.05 (t, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 2.40 (s, 3H), 1.80 (t, *J* = 7.1 Hz, 2H), 1.10 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 144.8, 141.9, 141.4, 133.1, 129.9, 129.9, 128.7, 127.9, 126.2, 126.1, 67.9, 52.2, 41.1, 35.7, 27.4, 21.7.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{22}H_{27}O_4S$: 387.1625. Found: 387.1624.

M.p.: 60-61 ºC.



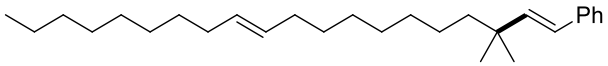
(*E*)-2-(3,3-Dimethyl-5-phenylpent-4-en-1-yl)-4,5-diphenyloxazole (14).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in <74% yield (43.7 mg, 0.111 mmol, contaminated with ~6% of the *tert*-alkyl chloride derived from the oxalate) as a pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.32 (ddd, *J* = 22.7, 11.5, 6.4 Hz, 8H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 6.34 (d, *J* = 16.2 Hz, 1H), 6.20 (d, *J* = 16.2 Hz, 1H), 2.83 (t, *J* = 7.4 Hz, 2H), 1.99 (t, *J* = 7.4 Hz, 2H), 1.20 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 163.9, 145.1, 139.1, 137.7, 135.2, 132.8, 129.3, 128.7, 128.6, 128.6, 128.4, 128.1, 128.0, 127.1, 126.9, 126.5, 126.2, 40.0, 36.4, 27.2, 24.3.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{28}H_{28}NO$: 394.2165. Found: 394.2161.



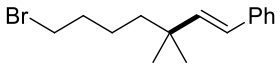
(1*E*,11*E*)-3,3-Dimethylicosa-1,11-dien-1-yl benzene (15).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 62% yield (35.6 mg, 0.093 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (d, J = 7.4 Hz, 2H), 7.30 (t, J = 7.7 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 6.28 (d, J = 16.2 Hz, 1H), 6.20 (d, J = 16.2 Hz, 1H), 5.38–5.36 (m, 2H), 2.08–1.93 (m, 10H), 1.74 (dd, J = 10.4, 6.5 Hz, 2H), 1.34 (d, J = 14.2 Hz, 16H), 1.10 (s, 6H), 0.90 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 141.1, 138.3, 130.5 (dd, J = 16.4, 11.8 Hz), 130.0 (dd, J = 16.6, 11.2 Hz), 128.6, 126.8, 126.1, 125.7, 71.4, 46.3, 43.5, 36.4, 32.6, 32.1, 30.6, 29.9, 29.7, 29.5, 29.4, 27.4, 25.3, 24.9, 22.9, 17.8, 14.3.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{28}H_{47}$: 383.3672. Found: 383.3673



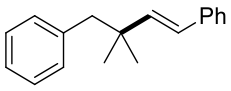
(*E*)-(7-Bromo-3,3-dimethylhept-1-en-1-yl)benzene (16).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 58% yield (24.5 mg, 0.087 mmol) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (d, J = 7.4 Hz, 2H), 7.30 (t, J = 7.7 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 6.29 (d, J = 16.2 Hz, 1H), 6.17 (d, J = 16.2 Hz, 1H), 3.40 (t, J = 6.9 Hz, 2H), 1.88–1.81 (m, 2H), 1.44–1.37 (m, 4H), 1.11 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 140.4, 138.1, 128.6, 127.3, 126.9, 126.2, 42.4, 36.4, 33.9, 33.6, 27.3, 23.6.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{15}H_{22}Br$: 281.0899. Found: 281.0895



(*E*)-(3,3-Dimethylbut-1-ene-1,4-diyl)dibenzene (17).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 80% yield (28.4 mg, 0.120 mmol) as a colorless solid.

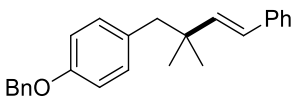
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, J = 7.5 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.29–7.26 (m, 2H),

7.22 (t, *J* = 7.1 Hz, 2H), 7.15 (d, *J* = 7.2 Hz, 2H), 6.25 (d, *J* = 16.2 Hz, 1H), 6.23 (d, *J* = 16.2 Hz, 1H), 2.70 (s, 2H), 1.14 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 140.3, 138.9, 138.2, 130.8, 128.6, 127.8, 126.9, 126.2, 126.1, 49.8, 37.5, 27.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{18}H_{21}$: 237.1638. Found: 237.1638.

M.p.: 47-48 ºC.



(*E*)-1-(Benzyloxy)-4-(2,2-dimethyl-4-phenylbut-3-en-1-yl) benzene (18).

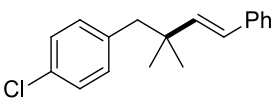
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 67% yield (34.4 mg, 0.101 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.1 Hz, 3H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.24 (d, *J* = 16.2 Hz, 1H), 6.20 (d, *J* = 16.2 Hz, 1H), 5.04 (s, 2H), 2.62 (s, 2H), 1.10 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.4, 140.4, 138.2, 137.4, 131.6, 131.3, 128.7, 128.6, 128.0, 127.7, 126.9, 126.2, 126.1, 114.2, 70.1, 48.9, 37.5, 27.0.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{25}H_{27}O$: 343.2056. Found: 343.2049.

M.p.: 72-73 ºC.



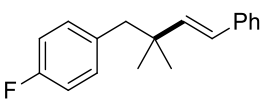
(*E*)-1-Chloro-4-(2,2-dimethyl-4-phenylbut-3-en-1-yl)benzene (19).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 71% yield (28.8 mg, 0.107 mmol) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34–7.29 (m, 4H), 7.23–7.21 (m, 3H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.20 (s, 2H), 2.65 (s, 2H), 1.11 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 139.7, 137.9, 137.3, 131.9, 128.7, 128.2, 127.9, 127.1, 126.5, 126.2, 49.1, 37.4, 27.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{18}H_{20}Cl$: 271.1248. Found: 271.1246.



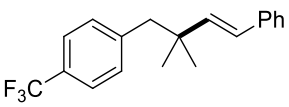
(*E*)-1-(2,2-Dimethyl-4-phenylbut-3-en-1-yl)-4-fluorobenzene (20).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 74% yield (28.2 mg, 0.111 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (dt, J = 15.3, 7.5 Hz, 4H), 7.22 (t, J = 6.4 Hz, 1H), 7.11–7.05 (m, 2H), 6.94 (t, J = 8.7 Hz, 2H), 6.23 (d, J = 16.2 Hz, 1H), 6.20 (d, J = 16.3 Hz, 1H), 2.66 (s, 2H), 1.11 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 139.9, 138.0, 137.5, 131.9 (d, J = 7.7 Hz), 128.7, 127.1, 126.4, 126.2, 114.6, 114.5, 48.9, 37.4, 27.0.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{18}H_{20}F$: 255.1544. Found: 255.1543.



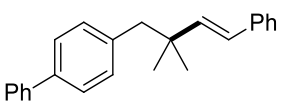
(*E*)-1-(2,2-Dimethyl-4-phenylbut-3-en-1-yl)-4-(trifluoromethyl)benzene (21).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 60% yield (27.4 mg, 0.090 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, J = 8.0 Hz, 2H), 7.35–7.28 (m, 4H), 7.25–7.17 (m, 3H), 6.20 (s, 2H), 2.73 (s, 2H), 1.12 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 143.0, 139.4, 137.8, 131.3, 130.9, 128.7, 127.2, 126.7, 126.2, 125.5, 124.7 (q, J = 3.7 Hz), 49.5, 37.5, 27.1.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{19}H_{20}F_3$: 305.1511. Found: 305.1505.



(*E*)-4-(2,2-Dimethyl-4-phenylbut-3-en-1-yl)-1,1'-biphenyl (22).

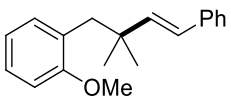
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 70% yield (32.8 mg, 0.105 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, J = 7.1 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.43 (t, J = 7.7 Hz, 2H), 7.33 (dt, J = 25.5, 7.5 Hz, 5H), 7.21 (t, J = 6.2 Hz, 3H), 6.29 (d, J = 16.2 Hz, 1H), 6.24 (d, J = 16.2 Hz, 1H), 2.73 (s, 2H), 1.16 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 141.1, 140.1, 138.8, 137.9, 138.9, 131.0, 128.7, 128.5, 127.0, 126.9, 126.9, 126.4, 126.1, 126.1, 49.3, 37.4, 27.0.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{24}H_{25}$: 313.1951. Found: 313.1953.

M.p.: 58-59 ºC.



(*E*)-1-(2,2-Dimethyl-4-phenylbut-3-en-1-yl)-2-methoxybenzene (23).

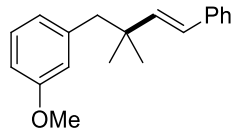
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 46% yield (18.4 mg, 0.069 mmol) as a pale yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (d, J = 7.4 Hz, 2H), 7.28 (dd, J = 14.0, 6.0 Hz, 2H), 7.18 (t, J = 7.2 Hz, 2H), 7.08 (d, J = 7.2 Hz, 1H), 6.84 (dd, J = 18.3, 7.6 Hz, 2H), 6.32 (d, J = 16.2 Hz, 1H), 6.15 (d, J = 16.2 Hz, 1H), 3.74 (s, 3H), 2.74 (s, 2H), 1.12 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 158.2, 141.1, 138.4, 132.6, 128.5, 127.5, 127.4, 126.7, 126.1, 125.1, 119.8, 110.4, 55.3, 42.3, 38.1, 27.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{19}H_{23}O$: 267.1743. Found: 267.1746.

M.p.: 52-53 ºC.



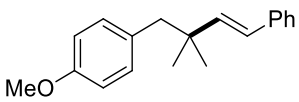
(*E*)-1-(2,2-Dimethyl-4-phenylbut-3-en-1-yl)-3-methoxybenzene (24).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in <69% yield (27.6 mg, 0.104 mmol, contaminated with 8% of the *tert*-alkyl chloride derived from the oxalate) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (d, J = 7.3 Hz, 2H), 7.30 (t, J = 7.7 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 7.17 (t, J = 7.9 Hz, 1H), 6.78–6.72 (m, 2H), 6.69 (d, J = 1.8 Hz, 1H), 6.27 (d, J = 16.2 Hz, 1H), 6.22 (d, J = 16.3 Hz, 1H), 3.74 (s, 3H), 2.67 (s, 2H), 1.13 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 159.1, 140.5, 140.4, 138.1, 128.7, 128.6, 126.9, 126.2, 126.1, 123.3, 116.3, 111.6, 55.2, 49.9, 37.5, 27.2.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{19}H_{23}O$: 267.1743. Found: 267.1746.



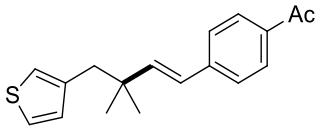
(*E*)-1-(2,2-Dimethyl-4-phenylbut-3-en-1-yl)-4-methoxy benzene (25).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 75% yield (29.9 mg, 0.113 mmol) as a pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (d, J = 7.2 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.22 (d, J = 7.2 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 7.06 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 6.26 (d, J = 16.2 Hz, 1H), 6.22 (d, J = 16.2 Hz, 1H), 3.80 (s, 3H), 2.63 (s, 2H), 1.11 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 158.1, 140.4, 138.2, 131.6, 130.9, 128.6, 126.9, 126.2, 126.1, 113.2, 55.3, 48.9, 37.5, 27.0.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{19}H_{23}O$: 267.1743. Found: 267.1747.



(*E*)-1-(4-(3,3-Dimethyl-4-(thiophen-3-yl)but-1-en-1-yl)phenyl)ethanone (26).

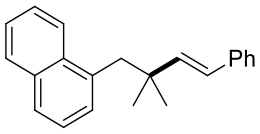
This compound was prepared according to the GP using (*E*)-1-(4-(2-bromovinyl)phenyl)ethanone (33.8 mg, 0.15 mmol, 100 mol%). After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 52% yield (22.2 mg, 0.078 mmol) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.11 (dd, J = 5.2, 1.2 Hz, 1H), 6.92 (dd, J = 5.1, 3.4 Hz, 1H), 6.77 (d, J = 4.3 Hz, 1H), 6.41 (d, J = 16.2 Hz, 1H), 6.31 (d, J = 16.2 Hz, 1H), 3.91 (s, 3H), 2.91 (s, 2H), 1.17 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 142.6, 142.5, 140.7, 130.1, 128.5, 126.9, 126.6, 126.3, 126.1, 123.9, 52.2, 43.6, 37.7, 27.0.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{18}H_{21}OS$: 285.1306. Found: 285.1301.

M.p.: 57-58 ºC.



(*E*)-1-(2,2-Dimethyl-4-phenylbut-3-en-1-yl)naphthalene (27).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 59% yield (25.3 mg, 0.089 mmol) as a colorless solid.

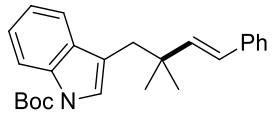
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 (d, J = 9.1 Hz, 1H), 7.86–7.81 (m, 1H), 7.73 (d, J = 8.1 Hz, 1H),

7.46–7.37 (m, 3H), 7.31 (d, *J* = 7.0 Hz, 1H), 7.23 (dt, *J* = 17.6, 7.4 Hz, 4H), 7.16 (t, *J* = 7.0 Hz, 1H), 6.25 (d, *J* = 16.2 Hz, 1H), 6.19 (d, *J* = 16.2 Hz, 1H), 3.19 (s, 2H), 1.19 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 140.7, 138.1, 135.3, 134.0, 133.3, 129.3, 128.7, 128.5, 127.0, 126.9, 126.3, 125.6, 125.5, 125.3, 125.3, 125.1, 44.9, 38.4, 27.8.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{22}H_{23}$: 287.1794. Found: 287.1795.

M.p.: 47-48 ºC.



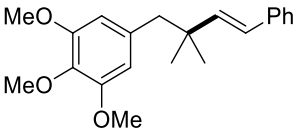
(*E*)-Tert-butyl-3-(2,2-dimethyl-4-phenylbut-3-en-1-yl)-1H-indole-1-carboxylate (28).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 61% yield (34.4 mg, 0.092 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.38–7.27 (m, 6H), 7.23–7.16 (m, 2H), 6.32 (d, *J* = 16.3 Hz, 1H), 6.27 (d, *J* = 16.2 Hz, 1H), 2.76 (s, 2H), 1.69 (s, 3H), 1.63 (s, 6H), 1.19 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 137.9, 128.6, 126.9, 126.2, 126.1, 124.7, 124.3, 124.1, 122.6, 122.4, 119.9, 117.7, 115.3, 115.1, 38.3, 37.6, 32.6, 28.3, 27.4.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{25}H_{30}NO_2$: 376.2271. Found: 376.2271.



(*E*)-5-(2,2-Dimethyl-4-phenylbut-3-en-1-yl)-1,2,3-trimethoxybenzene (29).

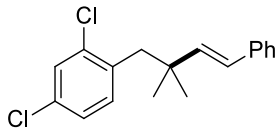
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 67% yield (32.8 mg, 0.101 mmol) as a colorless solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.33 (s, 2H), 6.26 (d, *J* = 16.4 Hz, 1H), 6.21 (d, *J* = 16.4 Hz, 1H), 3.83 (s, 3H), 3.74 (s, 6H), 2.62 (s, 2H), 1.13 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 152.5, 140.2, 138.0, 136.5, 134.6, 128.7, 127.1, 126.3, 126.1, 107.8, 61.0, 56.1, 50.3, 37.6, 27.2.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{21}H_{27}O_3$: 327.1955. Found: 327.1956.

M.p.: 42-43 ºC.

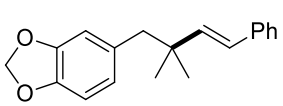


(*E*)-2,4-Dichloro-1-(2,2-dimethyl-4-phenylbut-3-en-1-yl)benzene (30). This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 55% yield (25.2 mg, 0.083 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.29 (m, 5H), 7.22 (t, J = 7.0 Hz, 1H), 7.14–7.09 (m, 2H), 6.27 (d, J = 16.2 Hz, 1H), 6.17 (d, J = 16.2 Hz, 1H), 2.86 (s, 2H), 1.17 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.4, 137.8, 135.8, 135.3, 133.4, 132.5, 129.4, 128.7, 127.1, 126.4, 126.3, 126.2, 44.8, 38.6, 27.1.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{18}H_{19}Cl_2$: 305.0858. Found: 305.0859



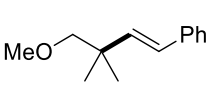
(*E*)-5-(2,2-Dimethyl-4-phenylbut-3-en-1-yl)benzo[d][1,3]dioxole (31). This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 71% yield (29.9 mg, 0.107 mmol) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (dt, J = 15.2, 7.4 Hz, 4H), 7.20 (t, J = 7.1 Hz, 1H), 6.71 (d, J = 7.9 Hz, 1H), 6.63 (d, J = 1.6 Hz, 1H), 6.58 (dd, J = 7.9, 1.5 Hz, 1H), 6.23 (s, 2H), 5.92 (s, 2H), 2.60 (s, 2H), 1.10 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 145.9, 140.3, 138.1, 132.6, 128.6, 126.9, 126.2, 126.1, 123.6, 111.1, 107.7, 100.8, 49.4, 37.5, 27.1.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{19}H_{21}O_2$: 281.1536. Found: 281.1536.

M.p.: 47-48 ºC.



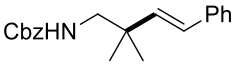
(*E*)-(4-Methoxy-3,3-dimethylbut-1-en-1-yl)benzene (32). This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 60% yield (17.1 mg, 0.090 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (d, J = 7.7 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.3 Hz,

1H), 6.38 (d, *J* = 16.3 Hz, 1H), 6.29 (d, *J* = 16.3 Hz, 1H), 3.37 (s, 3H), 3.23 (s, 2H), 1.14 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 138.0, 137.9, 128.6, 127.0, 126.9, 126.3, 82.4, 59.6, 37.9, 24.7.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{13}H_{19}O$: 191.1430. Found: 191.1431.



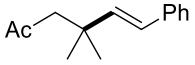
(*E*)-Benzyl (2,2-dimethyl-4-phenylbut-3-en-1-yl)carbamate (33).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 70% yield (32.5 mg, 0.105 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 10.0, 6.2 Hz, 4H), 7.32 (t, *J* = 6.1 Hz, 5H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.35 (d, *J* = 16.3 Hz, 1H), 6.13 (d, *J* = 16.3 Hz, 1H), 5.08 (s, 2H), 4.77 (s, 1H), 3.19 (d, *J* = 6.2 Hz, 2H), 1.13 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 156.8, 137.3, 137.1, 136.7, 128.7, 128.6, 128.4, 128.3, 128.2, 127.4, 126.3, 66.8, 51.4, 29.9, 25.0.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{20}H_{24}NO_2$: 310.1802. Found: 310.1805.



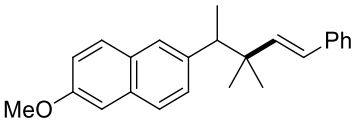
(*E*)-4,4-Dimethyl-6-phenylhex-5-en-2-one (34).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 73% yield (22.1 mg, 0.110 mmol) as a pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.0 Hz, 1H), 6.33 (s, 2H), 2.52 (s, 2H), 2.11 (s, 3H), 1.23 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 208.2, 139.1, 137.7, 128.7, 127.2, 126.4, 126.3, 55.8, 36.2, 32.3, 27.6.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{14}H_{19}O$: 203.1431. Found: 203.1433.



(*E*)-2-(3,3-Dimethyl-5-phenylpent-4-en-2-yl)-6-methoxy-naphthalene (35).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 42% yield (20.8 mg, 0.063 mmol) as a white solid.

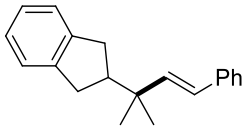
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74–7.63 (m, 3H), 7.55 (s, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* =

7.6 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.13 (s, 2H), 6.28 (s, 2H), 3.93 (s, 3H), 2.87 (q, *J* = 7.1 Hz, 1H), 1.37 (d, *J* = 7.1 Hz, 3H), 1.11 (d, *J* = 30.8 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.4, 139.7, 139.2, 138.3, 133.3, 129.5, 129.3, 128.7, 128.7, 127.5, 127.0, 126.9, 126.2, 125.8, 118.7, 105.6, 55.5, 50.2, 40.0, 26.8, 24.9, 16.6.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{24}H_{27}O$: 331.2056. Found: 331.2055.

M.p.: 70-71 ºC.



(*E*)-2-(2-Methyl-4-phenylbut-3-en-2-yl)-2,3-dihydro-1H-indene (36).

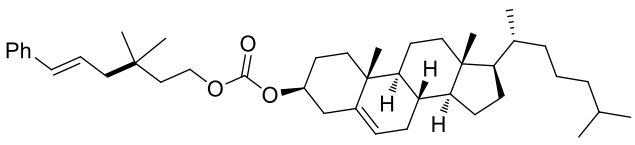
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 57% yield (22.4 mg, 0.086 mmol) as a pale yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.18 (ddd, *J* = 14.6, 12.9, 5.9 Hz, 3H), 7.12 (dd, *J* = 5.3, 3.4 Hz, 2H), 6.39 (d, *J* = 16.2 Hz, 1H), 6.31 (d, *J* = 16.3 Hz, 1H), 2.92 (dd, *J* = 15.6, 8.5 Hz, 2H), 2.85 (dd, *J* = 15.6, 9.9 Hz, 2H), 2.60–2.48 (m, 1H), 1.19 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 143.5, 138.9, 138.1, 128.6, 127.0, 126.9, 126.2, 126.2, 124.5, 50.8, 38.3, 34.6, 25.8.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{20}H_{23}$: 263.1794. Found: 263.1792.

M.p.: 48-49 ºC.



(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*)-3,3-dimethyl-6-phenylhex-5-en-1-yl) carbonate (37).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 65% yield (60.2 mg, 0.098 mmol) as a white solid.

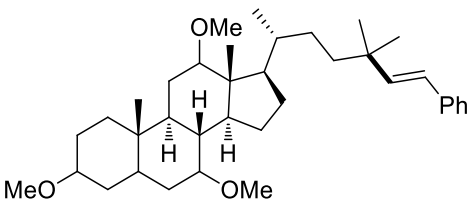
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.31 (d, *J* = 16.2 Hz, 1H), 6.18 (d, *J* = 16.2 Hz, 1H), 5.37 (d, *J* = 4.6 Hz, 1H), 4.48–4.39 (m, 1H), 4.15

(t, *J* = 7.4 Hz, 2H), 2.37 (ddd, *J* = 28.0, 14.4, 9.3 Hz, 3H), 1.99 (dd, *J* = 21.0, 18.0 Hz, 4H), 1.84 (ddd, *J* = 19.6, 17.6, 11.0 Hz, 7H), 1.61–1.42 (m, 12H), 1.27 (dd, *J* = 13.6, 8.8 Hz, 4H), 1.16 (s, 6H), 0.99 (s, 3H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.87–0.86 (m, 6H), 0.68 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 154.7, 139.6, 139.2, 137.7, 128.6, 127.1, 126.6, 126.3, 122.9, 65.3, 56.8, 56.3, 50.1, 50.1, 42.5, 41.1, 39.9, 39.7, 38.1, 36.9, 36.7, 36.3, 35.9, 35.4, 32.9, 32.0, 31.9, 28.4, 28.2, 27.8, 27.6, 27.6, 24.4, 23.9, 22.9, 22.7, 21.2, 19.4, 18.9, 12.0.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{42}H_{65}O_3$: 617.4928. Found: 617.4931.

M.p.: 50-51 ºC.



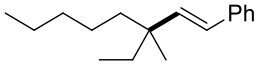
(8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*,*E*)-5,5-Dimethyl-7-phenylhept-6-en-2-yl)-3,7,12-trimethoxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene (38).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 56% yield (46.3 mg, 0.084 mmol) as a pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 6.26 (d, *J* = 16.2 Hz, 1H), 6.17 (d, *J* = 16.2 Hz, 1H), 3.36 (d, *J* = 10.8 Hz, 1H), 3.33 (s, 3H), 3.26 (s, 3H), 3.20 (s, 3H), 3.16–3.11 (m, 1H), 2.99 (dd, *J* = 13.2, 8.9 Hz, 1H), 2.23–2.16 (m, 1H), 2.13–2.00 (m, 3H), 1.94 (dd, *J* = 12.6, 7.0 Hz, 1H), 1.84–1.67 (m, 10H), 1.51–1.43 (m, 3H), 1.34–1.24 (m, 6H), 1.07 (s, 6H), 0.89 (d, *J* = 2.8 Hz, 6H), 0.63 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 141.3, 138.4, 128.6, 126.7, 126.1, 125.6, 82.2, 80.9, 55.9, 55.8, 55.5, 46.3, 46.2, 42.8, 42.1, 39.8, 39.1, 36.3, 35.9, 35.4, 35.1, 34.6, 30.5, 28.1, 27.9, 27.5, 27.2, 26.9, 23.3, 23.0, 22.1, 18.1, 12.6.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{37}H_{59}O_3$: 551.4458. Found: 551.4459.



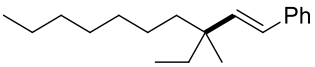
(*E*)-(3-Ethyl-3-methyloct-1-en-1-yl)benzene (39).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 46% yield (15.9 mg, 0.069 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (d, J = 7.6 Hz, 2H), 7.30 (t, J = 7.1 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 6.25 (d, J = 16.3 Hz, 1H), 6.11 (d, J = 16.3 Hz, 1H), 1.42 (dt, J = 13.9, 6.8 Hz, 2H), 1.39–1.25 (m, 8H), 1.05 (s, 3H), 0.88 (t, J = 7.3 Hz, 3H), 0.83 (t, J = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 140.1, 138.4, 128.9, 128.6, 126.8, 126.1, 41.2, 39.5, 33.8, 32.9, 24.0, 22.8, 22.8, 14.3, 8.7.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{17}H_{27}$: 231.2107. Found: 231.2109.



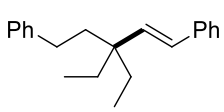
(*E*)-(3Ethyl-3-methyldec-1-en-1-yl)benzene (40).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 47% yield (18.3 mg, 0.071 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (d, J = 7.7 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 6.25 (d, J = 16.3 Hz, 1H), 6.11 (d, J = 16.3 Hz, 1H), 1.42 (dt, J = 14.0, 6.8 Hz, 2H), 1.39–1.25 (m, 12H), 1.04 (s, 3H), 0.88 (t, J = 6.9 Hz, 3H), 0.83 (t, J = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 140.1, 138.4, 128.6, 126.9, 126.8, 126.1, 41.2, 39.5, 33.8, 32.1, 30.7, 29.5, 24.4, 22.8, 22.8, 14.3, 8.7.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{19}H_{31}$: 259.2420. Found: 259.2423.



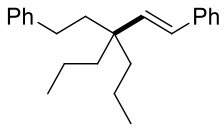
(*E*)-(3,3-Diethylpent-1-ene-1,5-diyl)dibenzene (41).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 40% yield (16.7 mg, 0.060 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 (d, J = 7.7 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.23–7.17 (m, 4H), 6.32 (d, J = 16.4 Hz, 1H), 6.09 (d, J = 16.4 Hz, 1H), 2.52 (t, J = 7.5 Hz, 2H), 1.54 (t, J = 7.5 Hz, 2H), 1.54 (q, J = 13.3, Hz, 4H), 0.86 (t, J = 7.4 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 143.5, 139.1, 138.3, 128.6, 128.5, 128.5, 128.3, 126.9, 126.1, 125.8, 42.3, 38.5, 30.4, 28.8, 8.7.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{21}H_{27}$: 279.2107. Found: 279.2109.



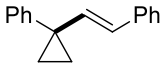
(*E*)-(3,3-Dipropylpent-1-ene-1,5-diyl)dibenzene (42).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 28% yield (12.9 mg, 0.042 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 (d, J = 7.8 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 7.4 Hz, 2H), 7.20 (t, J = 8.1 Hz, 4H), 6.30 (d, J = 16.4 Hz, 1H), 6.12 (d, J = 16.4 Hz, 1H), 2.52 (t, J = 7.5 Hz, 2H), 1.70 (t, J = 7.5 Hz, 2H), 1.47–1.44 (m, 4H), 1.31–1.27 (m, 4H), 0.93 (t, J = 7.2 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 143.5, 139.7, 138.3, 128.7, 128.5, 128.4, 127.7, 126.9, 126.1, 125.8, 42.1, 39.6, 39.4, 30.5, 16.9, 15.1.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{23}H_{31}$: 307.2420. Found: 307.2417.



(*E*)-(2-(1-Phenylcyclopropyl)vinyl)benzene (43).

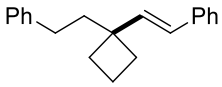
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 35% yield (11.6 mg, 0.053 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (dt, J = 15.1, 7.4 Hz, 4H), 7.26–7.23 (m, 5H), 7.18–7.13 (m, 1H), 6.13 (d, J = 15.8 Hz, 1H), 5.95 (d, J = 15.8 Hz, 1H), 1.19 (t, J = 5.4 Hz, 2H), 1.11 (t, J = 5.4 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 143.4, 137.9, 137.7, 130.1, 128.6, 128.4, 128.0, 126.9, 126.6, 125.9, 28.6, 15.4.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{17}H_{17}$: 221.1325. Found: 221.1326.

M.p.: 54-55 ºC.



(*E*)-(2-(1-Phenethylcyclobutyl)vinyl)benzene (44).

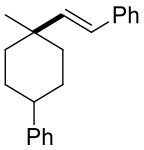
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 30% yield (11.8 mg, 0.045 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, J = 7.4 Hz, 2H), 7.33 (t, J = 7.7 Hz, 2H), 7.28–7.26 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.17 (dd, J = 14.0, 7.2 Hz, 3H), 6.40 (d, J = 16.1 Hz, 1H), 6.32 (d, J = 16.1 Hz, 1H), 2.52 (t, J = 7.5 Hz, 2H), 2.19–2.12 (m, 2H), 1.98–1.87 (m, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 143.1, 137.9, 137.8, 128.7, 128.5, 128.4, 127.1, 127.0, 126.2, 125.7, 44.9, 43.3, 31.9, 31.4, 15.8.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{20}H_{23}$: 263.1794. Found: 263.1794.

M.p.: 49-50 ºC.



(*E*)-(2-(1-Methyl-4-phenylcyclohexyl)vinyl)benzene (45).

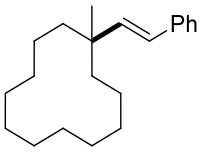
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 50% yield (20.7 mg, 0.075 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 (d, J = 7.3 Hz, 2H), 7.35–7.27 (m, 5H), 7.21 (t, J = 7.3 Hz, 3H), 6.37 (d, J = 16.3 Hz, 1H), 6.27 (d, J = 16.3 Hz, 1H), 2.50 (tt, J = 12.0, 4.0 Hz, 1H), 1.85–1.56 (m, 8H), 1.22 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 147.6, 143.3, 138.3, 128.7, 128.5, 127.0, 126.9, 126.2, 126.1, 124.8, 44.5, 37.6, 35.4, 29.8, 22.3.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{21}H_{25}$: 277.1951. Found: 277.1950.

M.p.: 60-61 ºC.



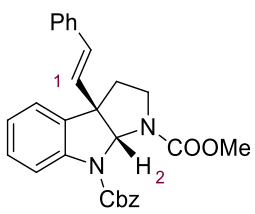
(*E*)-1-Methyl-1-styrylcyclododecane (46).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 37% yield (15.8 mg, 0.055 mmol) as a colorlss oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, J = 7.5 Hz, 2H), 7.29 (t, J = 7.5 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 6.29 (d, J = 16.3 Hz, 1H), 6.24 (d, J = 16.3 Hz, 1H), 1.47–1.33 (m, 22H), 1.04 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 141.6, 138.4, 128.6, 126.8, 126.1, 125.4, 38.7, 34.3, 26.9, 26.8, 26.3, 22.9, 22.4, 19.8.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{21}H_{33}$: 285.2576. Found: 285.2572.



(3a*R*,8a*R*)-8-Benzyl-1-methyl-3a-((*E*)-styryl)-3,3a-dihydropyrrolo[2, 3-b]indole-1,8(2H,8aH)-dicarboxylate (47).

This compound was prepared according to the GP. After purification by

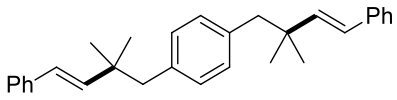
column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 41% yield (28.0 mg, 0.062 mmol) as a colorless solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (s, 1H), 7.41 (d, J = 7.2 Hz, 2H), 7.35–7.25 (m, 8H), 7.21 (dd, J = 8.7, 4.6 Hz, 1H), 7.18 (d, J = 7.4 Hz, 1H), 7.10 (t, J = 7.4 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 6.21 (d, J = 16.0 Hz, 1H), 6.18 (s, 1H), 5.23–5.24 (m, 2H), 3.90 (s, 1H), 3.54 (s, 3H), 3.02–2.93 (m, 1H), 2.3–2.26 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 153.5, 136.4, 133.3, 130.8, 130.7, 129.7, 129.4, 129.0, 128.7, 128.7, 128.3, 127.9, 127.4, 126.6, 125.5, 124.2, 121.9, 117.0, 67.8, 53.6, 52.6, 46.3, 29.5, 0.1.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{28}H_{27}N_2O_4$: 455.1965. Found: 455.1964.

M.p.: 44-45 ºC.



1,4-Bis((*E*)-2,2-dimethyl-4-phenylbut-3-en-1-yl)-benzene (48).

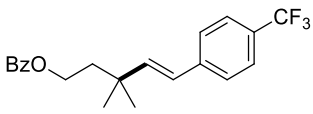
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 63% yield (37.3 mg, 0.095 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36–7.25 (m, 10H), 7.22–7.18 (m, 2H), 7.11 (dd, J = 39.6, 7.9 Hz, 2H), 6.24 (d, J = 16.2 Hz, 2H), 6.20 (d, J = 16.2 Hz, 2H), 2.65 (s, 4H), 1.10 (s, 12H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 140.5, 138.2, 136.4, 130.0, 128.6, 126.9, 126.2, 125.9, 49.4, 37.4, 27.1.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{30}H_{35}$: 395.2733. Found: 395.2729.

M.p.: 72-73 ºC.



(*E*)-3,3-Dimethyl-5-(4-(trifluoromethyl)phenyl)pent-4-en-1-yl-benzoate (3b).

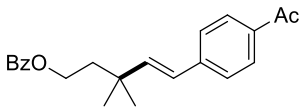
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 65% yield (35.3 mg, 0.098 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (d, J = 7.1 Hz, 2H), 7.51 (dd, J = 10.4, 4.4 Hz, 3H), 7.41 (d, J =

8.1 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 6.37 (d, *J* = 16.3 Hz, 1H), 6.34 (d, *J* = 16.3 Hz, 1H), 4.37 (t, *J* = 6.9 Hz, 2H), 1.93 (t, *J* = 6.9 Hz, 2H), 1.23 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.6, 142.2, 141.2, 132.9, 130.2, 129.6, 129.5, 128.4, 128.3, 126.2, 125.4 (q, *J* = 3.2 Hz), 125.2, 62.2, 41.2, 35.8, 27.4.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{21}H_{22}F_3O_2$: 363.1566. Found: 363.1567.



(*E*)-5-(4-Acetylphenyl)-3,3-dimethylpent-4-en-1-yl benzoate (3c).

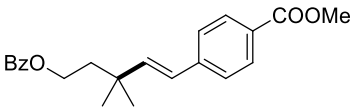
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 95% yield (47.9 mg, 0.143 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 6.38 (s, 2H), 4.37 (t, *J* = 7.0 Hz, 2H), 3.91 (s, 3H), 1.93 (t, *J* = 7.0 Hz, 2H), 1.22 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 167.1, 166.7, 142.4, 142.3, 132.9, 130.4, 129.9, 129.6, 128.6, 128.4, 126.1, 125.8, 62.4, 52.1, 41.3, 35.9, 27.5.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{22}H_{25}O_3$: 337.1798. Found: 337.1799.

M.p.: 80-81 ºC.



(*E*)-Methyl-4-(5-(benzoyloxy)-3,3-dimethylpent-1-en-1-yl)benzoate (3d).

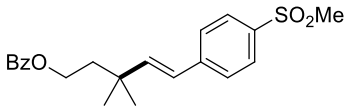
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 86% yield (45.4 mg, 0.129 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.5 Hz, 2H), 7.94 (d, *J* = 8.3 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 6.38 (s, 2H), 4.37 (t, *J* = 7.0 Hz, 2H), 3.91 (s, 3H), 1.93 (t, *J* = 7.0 Hz, 2H), 1.22 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 167.1, 166.7, 142.4, 142.3, 132.9, 130.4, 129.9, 129.6, 128.6, 128.4, 126.1, 125.8, 62.4, 52.1, 41.3, 35.9, 27.5.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{22}H_{25}O_4$: 353.1747. Found: 353.1756.

M.p.: 81-82 ºC.



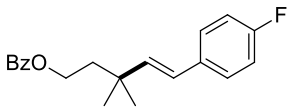
(*E*)-3,3-Dimethyl-5-(4-(methylsulfonyl)phenyl)pent-4-en-1-yl-benzoate (3e).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 70% yield (39.1 mg, 0.105 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 7.0 Hz, 2H), 7.80 (d, J = 8.5 Hz, 2H), 7.50 (t, J = 7.0 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.34 (t, J = 7.8 Hz, 2H), 6.42 (d, J = 16.2 Hz, 1H), 6.37 (d, J = 16.3 Hz, 1H), 4.36 (t, J = 6.9 Hz, 2H), 3.03 (s, 3H), 1.93 (t, J = 6.9 Hz, 2H), 1.22 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 143.9, 143.3, 138.4, 135.6, 133.0, 129.6, 128.4, 127.7, 126.9, 124.9, 62.3, 44.7, 41.2, 36.0, 27.4.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{21}H_{25}O_4S$: 373.1468. Found: 373.1464.



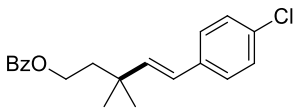
(*E*)-5-(4-Fluorophenyl)-3,3-dimethylpent-4-en-1-yl benzoate (3f).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 72% yield (33.7 mg, 0.108 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, J = 7.7 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.7 Hz, 2H), 7.30 (dd, J = 8.4, 5.6 Hz, 2H), 6.96 (t, J = 8.6 Hz, 2H), 6.31 (d, J = 16.2 Hz, 1H), 6.16 (d, J = 16.2 Hz, 1H), 4.37 (t, J = 7.0 Hz, 2H), 1.91 (t, J = 7.0 Hz, 2H), 1.21 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8, 139.3, 132.9, 130.5, 129.7, 128.4, 127.7, 127.6, 125.4, 115.5, 115.4, 62.6, 41.4, 35.6, 27.7.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{20}H_{22}FO_2$: 313.1598. Found: 313.1601.



(*E*)-5-(4-Chlorophenyl)-3,3-dimethylpent-4-en-1-yl benzoate (3g).

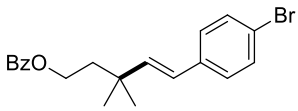
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 84% yield (41.4 mg, 0.126 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, J = 7.1 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.8 Hz,

2H), 7.25–7.22 (m, 4H), 6.30 (d, *J* = 16.2 Hz, 1H), 6.22 (d, *J* = 16.2 Hz, 1H), 4.37 (t, *J* = 7.0 Hz, 2H), 1.91 (t, *J* = 7.0 Hz, 2H), 1.21 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 140.3, 136.3, 132.9, 132.6, 130.4, 129.6, 128.7, 128.4, 127.4, 125.4, 62.5, 41.3, 35.7, 27.6.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{20}H_{22}ClO_2$: 329.1302. Found: 329.1303.



(*E*)-5-(4-Bromophenyl)-3,3-dimethylpent-4-en-1-yl benzoate (3h).

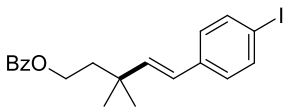
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 84% yield (47.0 mg, 0.126 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.37 (dd, *J* = 13.0, 8.1 Hz, 4H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.28 (d, *J* = 16.2 Hz, 1H), 6.23 (d, *J* = 16.2 Hz, 1H), 4.36 (t, *J* = 7.0 Hz, 2H), 1.90 (t, *J* = 7.0 Hz, 2H), 1.20 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8, 140.4, 136.7, 132.9, 131.7, 130.4, 129.7, 128.4, 127.8, 125.4, 120.7, 62.5, 41.3, 35.8, 27.6.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{20}H_{22}BrO_2$: 373.0798. Found: 373.0799.

M.p.: 48-49 ºC.



(*E*)-5-(4-Iodophenyl)-3,3-dimethylpent-4-en-1-yl benzoate (3i).

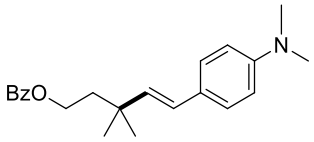
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 64% yield (40.3 mg, 0.096 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.25 (s, 2H), 4.36 (t, *J* = 7.0 Hz, 2H), 1.90 (t, *J* = 7.0 Hz, 2H), 1.20 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 140.6, 137.6, 137.3, 132.9, 130.4, 129.7, 128.4, 128.1, 125.5, 92.1, 62.5, 41.3, 35.7, 27.6.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{20}H_{22}IO_2$: 421.0659. Found: 421.0658.

M.p.: 51-52 ºC.



(*E*)-5-(4-(Dimethylamino)phenyl)-3,3-dimethylpent-4-en-1-yl-ben zoate (3j).

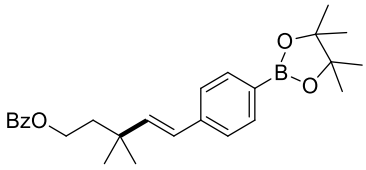
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 65% yield (32.9 mg, 0.098 mmol) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (d, J = 7.5 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.7 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 6.68 (d, J = 8.6 Hz, 2H), 6.27 (d, J = 16.2 Hz, 1H), 6.04 (d, J = 16.2 Hz, 1H), 4.37 (t, J = 7.2 Hz, 2H), 2.94 (s, 6H), 1.89 (t, J = 7.2 Hz, 2H), 1.20 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8, 149.9, 135.4, 132.9, 130.6, 129.7, 128.4, 127.1, 126.5, 126.3, 112.8, 62.8, 41.5, 40.8, 35.4, 27.9.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{22}H_{28}NO_2$: 338.2115. Found: 338.2113.

M.p.: 44-45 ºC.



(*E*)-3,3-Dimethyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborola n-2-yl)phenyl)pent-4-en-1-yl benzoate (3k).

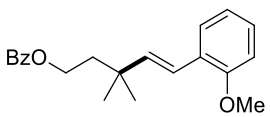
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 64% yield (40.3 mg, 0.096 mmol) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 7.3 Hz, 2H), 7.73 (d, J = 7.8 Hz, 2H), 7.52 (t, J = 7.2 Hz, 2H), 7.39–7.34 (m, 4H), 6.37 (d, J = 16.3 Hz, 1H), 6.31 (d, J = 16.3 Hz, 1H), 4.36 (t, J = 7.1 Hz, 2H), 1.91 (t, J = 7.2 Hz, 2H), 1.35 (s, 12H), 1.21 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 140.6, 140.5, 135.2, 132.9, 130.5, 129.7, 128.4, 126.6, 125.6, 83.8, 62.6, 41.3, 35.7, 29.9, 27.6, 25.0.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{26}H_{34}BO_4$: 421.2544. Found: 421.2542.

M.p.: 52-53 ºC.



(*E*)-5-(2-Methoxyphenyl)-3,3-dimethylpent-4-en-1-yl benzoate (3l).

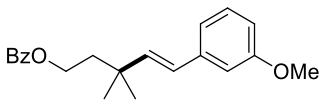
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated

in 78% yield (37.9 mg, 0.117 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.44 (d, J = 7.5 Hz, 1H), 7.38 (t, J = 7.7 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H), 6.72 (d, J = 16.4 Hz, 1H), 6.25 (d, J = 16.4 Hz, 1H), 4.39 (t, J = 7.1 Hz, 2H), 3.83 (s, 3H), 1.93 (t, J = 7.1 Hz, 2H), 1.24 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8, 156.5, 139.9, 132.9, 130.6, 129.7, 128.4, 128.1, 126.8, 126.3, 121.0, 120.7, 110.9, 62.7, 55.6, 41.4, 35.9, 27.8.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{21}H_{25}O_3$: 325.1798. Found: 325.1797.



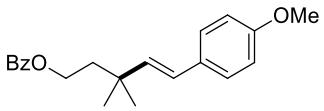
(*E*)-5-(3-Methoxyphenyl)-3,3-dimethylpent-4-en-1-yl benzoate (3m).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 67% yield (32.6 mg, 0.101 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, J = 7.1 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.8 Hz, 2H), 7.20 (t, J = 7.9 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 6.89 (s, 1H), 6.76 (d, J = 10.0 Hz, 1H), 6.33 (d, J = 16.2 Hz, 1H), 6.25 (d, J = 16.2 Hz, 1H), 4.37 (t, J = 7.1 Hz, 2H), 3.80 (s, 3H), 1.92 (t, J = 7.1 Hz, 2H), 1.22 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8, 159.9, 139.8, 139.3, 132.9, 130.5, 129.7, 129.6, 128.4, 126.5, 118.9, 112.9, 111.5, 62.6, 55.3, 41.4, 35.6, 27.7.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{21}H_{25}O_3$: 325.1798. Found: 325.1797.



(*E*)-5-(4-Methoxyphenyl)-3,3-dimethylpent-4-en-1-yl benzoate (3n).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 52% yield (25.3 mg, 0.078 mmol) as a colorless oil.

This compound was also prepared according to the GP using (*E*)-1-(2-iodovinyl)-4-methoxybenzene (39.0 mg, 0.15 mmol, 100 mol%). After purification by column chromatography (SiO_2: 2% ethyl

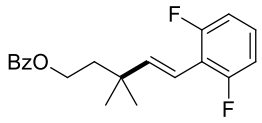
acetate in petroleum ether), the title compound was isolated in 63% yield (30.6 mg, 0.095 mmol) as a colorless oil.

This compound was also prepared according to the GP using (*Z*)-1-(2-bromovinyl)-4-methoxybenzene (31.9 mg, 0.15 mmol, 100 mol%). After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 67% yield (32.6 mg, 0.101 mmol) as a pale colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (d, J = 7.1 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.8 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 6.30 (d, J = 16.2 Hz, 1H), 6.11 (d, J = 16.2 Hz, 1H), 4.37 (t, J = 7.1 Hz, 2H), 3.81 (s, 3H), 1.21 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8, 158.9, 137.4, 132.9, 130.6, 130.5, 129.7, 128.4, 127.3, 125.9, 114.0, 62.7, 55.4, 41.4, 35.5, 27.8.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{21}H_{25}O_3$: 325.1798. Found: 325.1798.



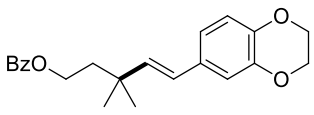
(*E*)-5-(2,6-Difluorophenyl)-3,3-dimethylpent-4-en-1-yl benzoate (3o).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 84% yield (41.6 mg, 0.126 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, J = 7.7 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.7 Hz, 2H), 7.12–7.05 (m, 1H), 6.84 (t, J = 8.3 Hz, 2H), 6.58 (d, J = 16.7 Hz, 1H), 6.34 (d, J = 16.7 Hz, 1H), 4.38 (t, J = 7.1 Hz, 2H), 1.93 (t, J = 7.1 Hz, 2H), 1.23 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 161.8 (d, J = 7.5 Hz), 160.1 (d, J = 9.0 Hz), 146.7 (t, J = 7.5 Hz), 132.9, 130.5, 129.6, 128.4, 127.4, 113.2, 111.6 (d, J = 10.5 Hz), 62.5, 41.2, 36.5, 27.3.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{20}H_{21}F_2O_2$: 331.1504. Found: 331.1509.



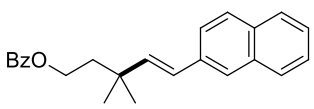
(*E*)-5-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-3,3-dimethylpent-4-en-1-yl benzoate (3p).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 73% yield (38.6 mg, 0.110 mmol) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, J = 7.4 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.7 Hz, 2H), 6.88 (s, 1H), 6.84 (d, J = 8.3 Hz, 1H), 6.78 (d, J = 8.3 Hz, 1H), 6.23 (d, J = 16.2 Hz, 1H), 6.09 (d, J = 16.2 Hz, 1H), 4.36 (t, J = 7.1 Hz, 2H), 4.24 (s, 4H), 1.89 (t, J = 7.1 Hz, 2H), 1.19 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8, 143.6, 142.9, 138.0, 132.9, 131.6, 130.6, 129.7, 128.4, 125.8, 119.6, 117.3, 114.7, 64.6, 64.5, 62.6, 41.4, 35.5, 27.7.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{22}H_{25}O_4$: 353.1747. Found: 353.1749.



(*E*)-3,3-Dimethyl-5-(naphthalen-2-yl)pent-4-en-1-yl benzoate (3q).

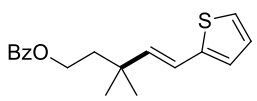
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 85% yield (43.9 mg, 0.128 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (d, J = 7.4 Hz, 2H), 7.78 (t, J = 9.1 Hz, 2H), 7.76 (d, J = 8.6 Hz, 1H), 7.71 (s, 1H), 7.59 (d, J = 8.5 Hz, 1H), 7.52–7.40 (m, 3H), 7.34 (t, J = 7.7 Hz, 2H), 6.54 (d, J = 16.2 Hz, 1H), 6.40 (d, J = 16.2 Hz, 1H), 4.42 (t, J = 7.0 Hz, 2H), 1.97 (t, J = 7.0 Hz, 2H), 1.27 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8, 140.0, 135.2, 133.8, 132.9, 132.8, 130.5, 129.7, 128.4, 128.2, 127.9, 127.7, 126.6, 126.3, 125.8, 125.6, 123.8, 62.6, 41.4, 35.8, 27.7.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{24}H_{25}O_2$: 345.1849. Found: 345.1849.

M.p.: 56-57 ºC.



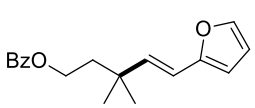
(*E*)-3,3-Dimethyl-5-(thiophen-3-yl)pent-4-en-1-yl benzoate (3r).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 50% yield (22.5 mg, 0.075 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 7.9 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.7 Hz, 2H), 7.09 (d, J = 5.1 Hz, 1H), 6.95–6.90 (m, 1H), 6.89 (d, J = 3.5 Hz, 1H), 6.48 (d, J = 16.0 Hz, 1H), 6.10 (d, J = 16.0 Hz, 1H), 4.36 (t, J = 7.1 Hz, 2H), 1.89 (t, J = 7.1 Hz, 2H), 1.19 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 143.1, 139.4, 132.9, 130.5, 129.7, 128.4, 127.4, 124.9, 123.4, 120.1, 62.6, 41.2, 35.7, 27.6.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{18}H_{21}O_2S$: 301.1257. Found: 301.1259.



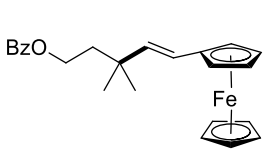
(*E*)-5-(Furan-3-yl)-3,3-dimethylpent-4-en-1-yl benzoate (3s).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 69% yield (29.4 mg, 0.104 mmol) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 7.1 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.7 Hz, 2H), 7.29 (s, 1H), 6.34 (dd, J = 3.2, 1.8 Hz, 1H), 6.23 (d, J = 16.3 Hz, 1H), 6.17 (d, J = 16.3 Hz, 1H), 6.15 (s, 1H), 4.36 (t, J = 7.0 Hz, 2H), 1.89 (t, J = 7.0 Hz, 2H), 1.19 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 141.5, 138.4, 132.9, 130.5, 129.7, 128.5, 128.4, 115.5, 111.3, 106.8, 62.6, 41.3, 35.5, 27.5.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{18}H_{21}O_3$: 285.1485. Found: 285.1489.



(*E*)-3,3-Dimethyl-5-(ferrocene)pent-4-en-1-yl benzoate (3t).

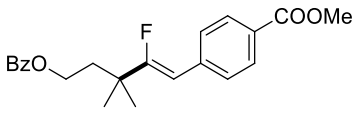
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 52% yield (31.4 mg, 0.078 mmol) as a red brown solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 6.07 (d, J = 16.1 Hz, 1H), 5.83 (d, J = 16.1 Hz, 1H), 4.37 (t, J = 7.3 Hz, 2H), 4.31 (s, 2H), 4.17 (s, 2H), 4.08 (s, 5H), 1.86 (t, J = 7.3 Hz, 2H), 1.16 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8, 136.6, 132.9, 130.6, 129.7, 128.5, 123.7, 84.1, 69.2, 68.5, 66.6, 62.8, 41.2, 35.5, 27.9.

HRMS (ESI) m/z ([M]) calcd for $C_{24}H_{26}FeO_2$: 402.1282. Found: 402.1283.

M.p.: 61-62 ºC.



(*Z*)-Methyl-4-(5-(benzoyloxy)-2-fluoro-3,3-dimethylpent-1-en-1-yl) benzoate (3u).

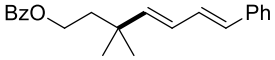
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 58% yield (32.2 mg, 0.087 mmol) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.94 (d, J = 7.6 Hz, 4H), 7.49 (dd, J = 17.2, 7.8 Hz, 3H), 7.30 (t, J = 7.6 Hz, 2H), 5.63 (d, J = 40.3 Hz, 1H), 4.40 (t, J = 6.6 Hz, 2H), 3.91 (s, 3H), 2.05 (t, J = 6.6 Hz, 2H), 1.32 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 167.0, 166.7, 138.5, 132.9, 130.1, 129.8, 129.7, 128.6, 128.5, 128.4, 128.2, 103.9 (d, J = 9.0 Hz), 61.9, 52.2, 38.2, 38.0 (d, J =22.5 Hz), 26.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{22}H_{24}FO_4$: 371.1653. Found: 371.1662.

M.p.: 102-103 ºC.



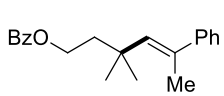
(4*E*,6*E*)-3,3-Dimethyl-7-phenylhepta-4,6-dien-1-yl benzoate (3v).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 78% yield (37.5 mg, 0.117 mmol) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.04 (d, J = 7.6 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.37 (d, J = 7.6 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 6.74 (dd, J = 15.6, 10.3 Hz, 1H), 6.50 (d, J = 15.7 Hz, 1H), 6.20 (dd, J = 15.5, 10.3 Hz, 1H), 5.85 (d, J = 15.6 Hz, 1H), 4.37 (t, J = 7.1 Hz, 2H), 1.88 (t, J = 7.1 Hz, 2H), 1.18 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.7, 144.2, 137.7, 132.9, 130.9, 130.5, 129.7, 129.6, 128.7, 128.4, 127.3, 127.2, 126.3, 62.6, 41.3, 35.7, 27.7.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{22}H_{25}O_2$: 321.1849. Found: 321.1844.



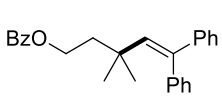
(*E*)-3,3-Dimethyl-5-phenylhex-4-en-1-yl benzoate (3w).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 58% yield (26.8 mg, 0.087 mmol) as a pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.40 (t, J = 7.7 Hz, 2H), 7.33 (d, J = 7.4 Hz, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 5.71 (s, 1H), 4.43 (t, J = 7.3 Hz, 2H), 2.18 (s, 3H), 2.03 (t, J = 7.3 Hz, 2H), 1.31 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.9, 146.1, 137.0, 135.9, 132.9, 130.6, 129.7, 128.4, 128.2, 126.7, 126.2, 63.0, 41.9, 35.1, 29.5, 17.6.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{21}H_{25}O_2$: 309.1849. Found: 309.1849.



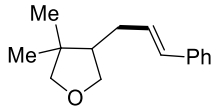
3,3-Dimethyl-5,5-diphenylpent-4-en-1-yl benzoate (3x).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 32% yield (17.8 mg, 0.048 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.99 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.31 (dt, J = 23.2, 7.0 Hz, 3H), 7.24–7.17 (m, 7H), 6.10 (s, 1H), 4.42 (t, J = 7.1 Hz, 2H), 1.82 (t, J = 7.1 Hz, 2H), 1.01 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.8, 143.9, 140.6, 140.6, 137.9, 132.9, 130.2, 129.7, 128.4, 128.2, 128.0, 127.0, 62.9, 42.7, 36.4, 29.6.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{26}H_{27}O_2$: 371.2006. Found: 371.2007.



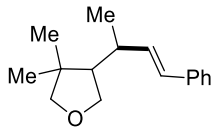
(*E*)-4-Cinnamyl-3,3-dimethyltetrahydrofuran (50a).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 49% yield (15.9 mg, 0.074 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.28 (m, 4H), 7.23–7.19 (m, 1H), 6.41 (d, J = 15.8 Hz, 1H), 6.14 (dt, J = 15.8, 7.0 Hz, 1H), 4.11–4.03 (t, J = 8.0 Hz,, 1H), 3.57 (t, J = 8.0 Hz,, 2H), 3.51 (d, J = 8.0 Hz, 1H), 2.42–2.32 (m, 1H), 2.15–1.95 (m, 2H), 1.07 (s, 3H), 0.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 130.9, 129.3, 128.7, 127.2, 126.1, 81.5, 73.2, 48.7, 40.8, 31.6, 24.9, 20.8.

HRMS (ESI) m/z ([M+H]$^+$) calcd for $C_{15}H_{21}O$: 217.1587. Found: 217.1588.



(*E*)-3,3-Dimethyl-4-(4-phenylbut-3-en-2-yl)tetrahydrofuran (50b).

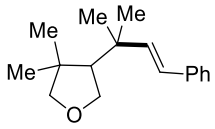
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in <41% yield (dr = 4:1, 14.3 mg, 0.062 mmol, contaminated with substantial amount of petroleum ether) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 (dt, J = 15.2, 7.5 Hz, 4H), 7.20 (t, J = 7.0 Hz, 1H), 6.35 (d, J =

15.8 Hz, 1H), 6.02 (dd, *J* = 15.7, 8.9 Hz, 1H), 3.94 (t, *J* = 8.6 Hz, 1H), 3.60 (t, *J* = 9.3 Hz, 1H), 3.52 (q, *J* = 8.0 Hz, 2H), 2.41–2.33 (m, 1H), 1.82 (dd, *J* = 18.0, 9.5 Hz, 1H), 1.17 (d, *J* = 6.6 Hz, 3H), 1.14 (s, 3H), 1.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 135.1, 128.6, 128.4, 127.2, 126.1, 82.8, 73.2, 53.7, 38.1, 26.2, 20.6, 20.5.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{16}H_{23}O$: 231.1743. Found: 231.1745.



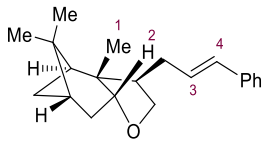
(*E*)-3,3-dimethyl-4-(2-methyl-4-phenylbut-3-en-2-yl)tetrahydrofuran (50c).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 38% yield (13.9 mg, 0.057 mmol) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.1 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.37 (d, *J* = 16.2 Hz, 1H), 6.31 (d, *J* = 16.3 Hz, 1H), 4.04 (t, *J* = 8.7 Hz, 1H), 3.95 (dd, *J* = 9.9, 8.6 Hz, 1H), 3.44 (t, *J* = 8.5 Hz, 2H), 2.00 (dd, *J* = 9.8, 8.9 Hz, 1H), 1.23 (s, 3H), 1.17 (s, 3H), 1.11 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 138.9, 128.7, 127.1, 126.7, 126.2, 126.1, 83.4, 70.2, 58.2, 41.9, 38.4, 28.7, 27.1, 23.1.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{17}H_{25}O$: 245.1900. Found: 245.1900.



(3*R*,3a*R*,4*S*,6*S*,7a*R*)-3-Cinnamyl-3a,5,5-trimethyloctahydro-4,6-methanobenzofuran (50d).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 41% yield (18.2 mg, 0.062 mmol) as a colorless oil.

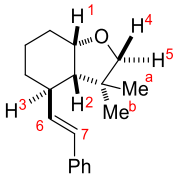
The stereochemistry is assigned based on the correlation of H1 and H3 (vinyl) in the NOESY spectra.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.0 Hz, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 6.15–6.07 (m, 1H), 4.09–3.99 (m, 1H), 3.79 (d, *J* = 8.3 Hz, 1H), 3.27 (t, *J* =

9.7 Hz, 1H), 2.38 –1.97 (m, 6H), 1.91–1.79 (m, 3H), 1.26 (s, 3H), 1.08 (s, 3H), 0.95 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 137.7, 130.7, 129.8, 128.7, 127.2, 126.1, 82.2, 72.1, 51.1, 48.5, 47.3, 40.2, 38.6, 34.7, 30.8, 28.0, 27.3, 25.1, 21.8.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{21}H_{29}O$: 297.2213. Found: 297.2213.



(*E*)-3,3-Dimethyl-4-styryloctahydrobenzofuran (50e).

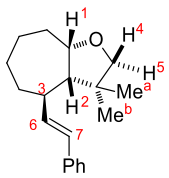
This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 52% yield (20.0 mg, 0.078 mmol) as a colorless oil.

The relative stereochemistry was determined based on the following correlations found in NOESY spectra: No correlation was found between H1 and H3, suggesting a *trans* geometry of H1 with respect to H3. The trans geometry of H2 with respect to H3 was supported by the correlation of H5 and H3, whereas H4 correlates H1 and H2. Finally, the cis geometry of H1 and H2 was determined based on the following correlations: Me(a) with H1 and H2, Me(b) with H2 and H3, respectively, and more importantly, H4 and H1 and H2, respectively.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (d, J = 7.7 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 7.1 Hz, 1H), 6.37 (d, J = 16.0 Hz, 1H), 6.13 (dd, J = 16.0, 8.1 Hz, 1H), 4.31–4.18 (m, 1H), 3.65 (d, J = 8.1 Hz, 1H), 3.49 (d, J = 8.1 Hz, 1H), 2.32–2.19 (m, 1H), 1.96–1.89 (m, 1H), 1.73–1.66 (m, 1H), 1.64–1.45 (m, 5H), 1.14 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 138.1, 137.4, 129.0, 128.7, 127.0, 126.0, 79.6, 77.3, 52.1, 43.3, 38.8, 32.9, 28.9, 23.9, 19.4.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{18}H_{25}O$: 257.1900. Found: 257.1905.



(*E*)-3,3-Dimethyl-4-styryloctahydro-2H-cyclohepta[b]furan (50f).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in <46% yield (18.6 mg, 0.069 mmol, contaminated with substantial amount of inseparable petroleum ether) as a colorless oil.

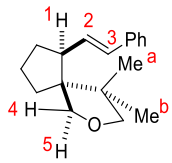
The relative stereochemistry for **50f** was assigned based on the characterisic correlations in the

NOESY spectra. The cis geometry of H2 with respect to H1 was evidencded by the corrleations of H2-H1, H4-H1, and H4-H2. The trans geometry of H2 with respect to H3 was manifested by Me(a)-H2, Me(b)-H3, Me(b)-H5. The trans geometry of H3 with respect to H1 is supported by no correlation between H1 and H3, and no correlation between H5 and H1, and H5 and H2.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (d, J = 7.7 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H), 7.20 (t, J = 7.0 Hz, 1H), 6.36 (d, J = 15.8 Hz, 1H), 6.08 (dd, J = 15.8, 9.7 Hz, 1H), 4.17 (t, J = 10.5 Hz, 1H), 3.48 (d, J = 8.2 Hz, 1H), 3.37 (d, J = 8.2 Hz, 1H), 2.42 (dd, J = 19.9, 9.7 Hz, 1H), 2.04 (t, J = 10.5 Hz, 1H), 1.84 (d, J = 7.5 Hz, 4H), 1.44 (ddd, J = 34.8, 15.5, 8.3 Hz, 4H), 1.08 (s, 3H), 0.94 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 137.9, 137.4, 128.7, 127.3, 127.0, 126.1, 85.1, 81.2, 57.2, 43.3, 42.3, 37.4, 33.8, 30.6, 27.0, 25.3, 21.9.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{19}H_{27}O$: 271.2056. Found: 271.2058.



(*E*)-4,4-Dimethyl-6-styryl-2-oxaspiro[4.4]nonane (50g).

This compound was prepared according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the title compound was isolated in 41% yield (15.8 mg, 0.062 mmol) as a colorless oil.

The relative stereochemistry was determined based on the following correlations found in the NOESY spectra: no correlation was found between H1 and H4 suggesting that H1 is away from H4; the correlations of H2-H4 and H3-H4, Me(a)-H2, Me(a)-H3 and Me(a)-H4; the correlations of H1-H5 and H1-Me(b).

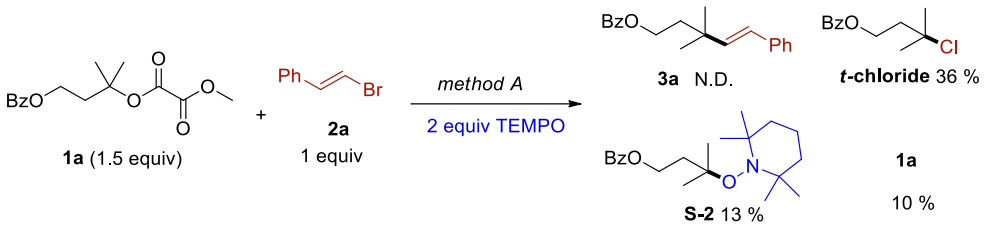
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 7.1 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 6.41 (d, J = 15.7 Hz, 1H), 6.24 (dd, J = 15.7, 9.5 Hz, 1H), 4.11 (d, J = 8.6 Hz, 1H), 3.69 (d, J = 8.6 Hz, 1H), 3.64 (d, J = 7.8 Hz, 1H), 3.54 (d, J = 7.7 Hz, 1H), 2.69–2.56 (m, 1H), 2.05–1.62 (m, 3H), 1.57–1.41 (m, 3H), 1.01 (d, J = 7.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137. 9, 132.4, 130.3, 128.6, 127.1, 126.2, 80.8, 75.0, 58.4, 47.8, 42.9, 32.5, 32.3, 25.6, 21.8, 19.2.

HRMS (ESI) m/z ($[M+H]^+$) calcd for $C_{18}H_{25}O$: 257.1900. Found: 257.1900.

Part 6. Mechanistic Consideration

1. Capture of Tertiary Alkyl Radical with TEMPO



This reaction was carried out according to the GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), the cross-coupling compound **3a** was not detected. However, the radical captured compound **S-2** was produced and detected by NMR in 13% yield, and ~36% of the tertiary chloride ***t*-chloride** was detected along with ~10% of **1a** was recovered.

2. Complexation of $Fe(acac)_n$ with Vinyl Bromide

A mixture of 0.15 mmol of $Fe(acac)_3$ with 0.15 mmol of vinyl bromide **2a** in 0.4 mL of CD_3CN was stirred overnight. ^1H NMR spectra of the resultant mixture showed two new peaks at ~4.0 ppm and ~5.5 ppm as compared to the individual spectra of **2a** and $Fe(acac)_3$ in CD_3CN (Figure S1). This result is supportive of the complexation of Fe^{3+} with **2a**.

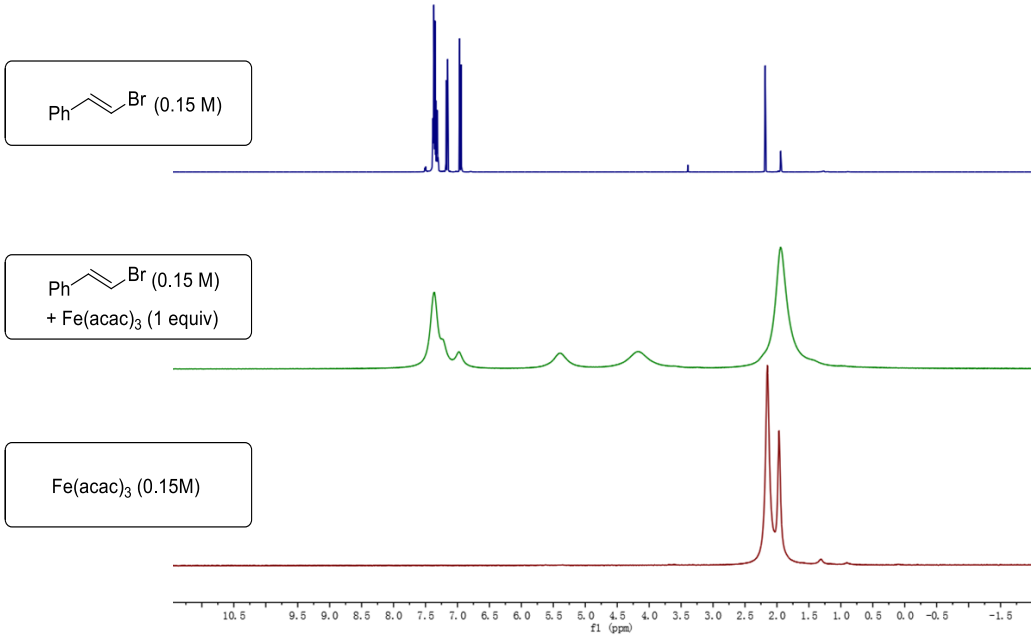


Figure S1. ^1H NMR spectra of the complexation of **2a** with $Fe(acac)_3$.

A mixture of 0.015 mmol of $Fe(acac)_2$ with 0.15 mmol of vinyl bromide **2a** in 0.4 mL of CD_3CN was stirred overnight. ^1H NMR spectra of the resultant mixture showed two new peaks at ~3.6 ppm and ~5.3 ppm as compared to the individual spectra of **2a** and $Fe(acac)_2$ in CD_3CN (Figure S2). This result is supportive of the complexation of Fe^{2+} with **2a**.

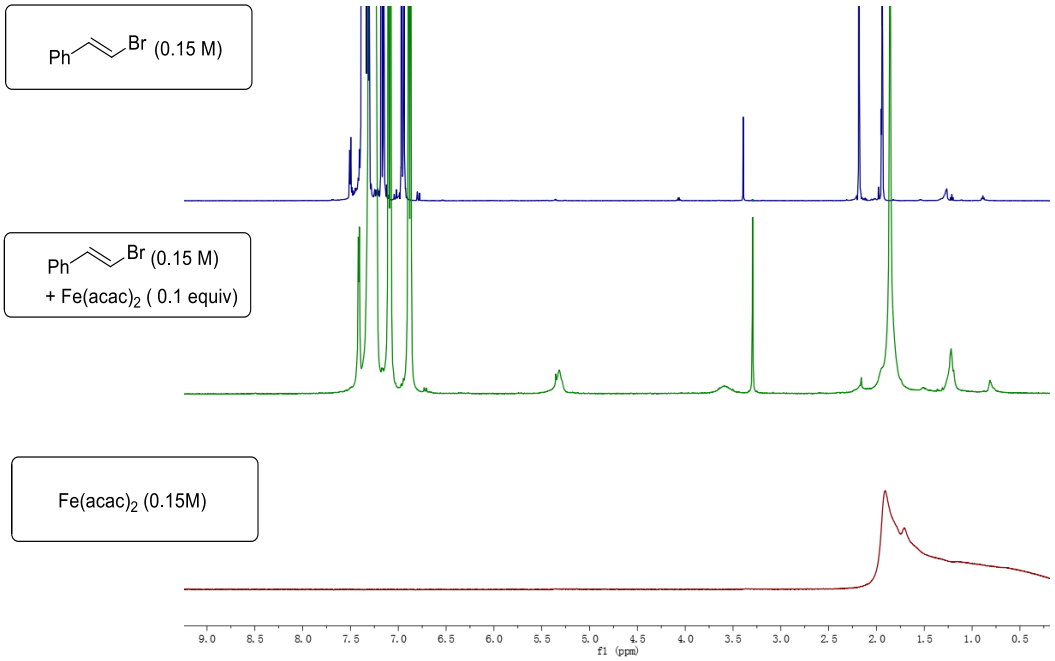


Figure S2. ^1H NMR spectra of the complexation of **2a** with $Fe(acac)_2$.

3. Role of Fe in reduction of oxalates

The roles of Fe are sophisticated in addition to activate the vinyl halides by complexation. In a control experiment by exposing **1a** to the reductive conditions, ~50% of oxalate **1a** was recovered (see blow and Figure S3). The lack of Fe resulted in ~62% of recovered **1a**, suggesting that Fe may indeed promote the reduction of **1a**.

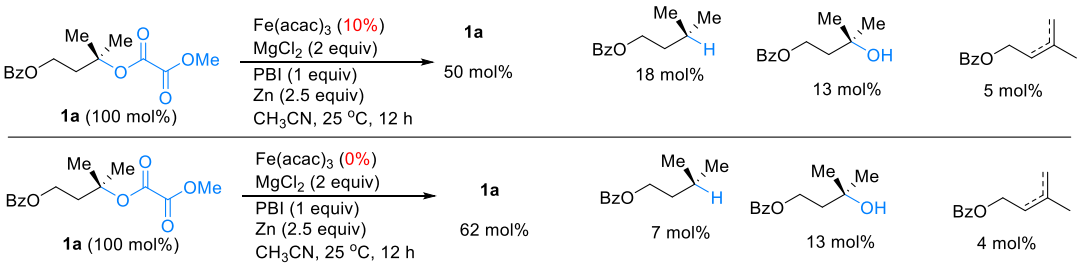
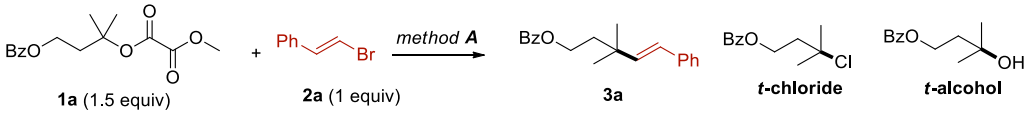


Figure S3. Reaction profiles for oxalate **1a** alone under the reduction conditions

4. Tracking the Reaction Progress

Following the general *GP*, a series of separate reactions were run in parallel, and stopped at the indicated time shown in the table below. The reaction mixture was collected by passing a short pad of silica column, affording a crude mixture without PBI and solvent. The amount of each individual compound in the mixture was estimated using an 2,5-dimehylfuran as an internal standard.

Table S2. Tracking the reaction progress of the reaction of **1a** with vinyl bromide.



Time (h)	**1a** (mmol)	**2a** (mmol)	**3a** (mmol)	***t*-chloride** (mmol)	***t*-alcohol** (mmol)
0	0.225	0.150	0	0	0
0.5	0.089	0.036	0.060	0.024	0.075
1.0	0.096	0.033	0.054	0.023	0.074
3.0	0.104	0.030	0.045	0.011	0.072
5.0	0.114	0.029	0.032	0.011	0.068
7.0	0.131	0.026	0.015	0.012	0.057

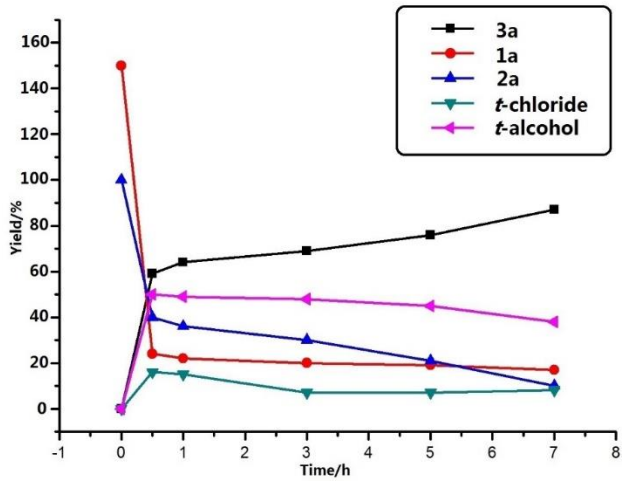
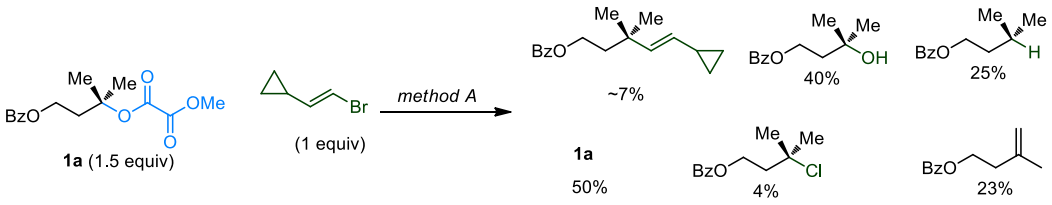


Figure S4. Monitoring the reaction progress for the reaction of **1a** with vinyl bromide. Yield% was referred to as the initial molar number of the alkyl oxalate.

5. The Radical Clock Reaction



This reaction was carried out according to GP. After purification by column chromatography (SiO_2: 2% ethyl acetate in petroleum ether), ~7% of the no cyclopropane ring-opened product was detected by NMR, and the ESI-MS results also support the produce for this product (**HRMS** (ESI) exact mass calculated for $[M+H^+]$ ($C_{17}H_{23}O_2^+$): m/z 259.1693; found: 259.1692). In addition, the hydrogenated and eliminated products were produced and detected by NMR in 25% and 23% yield, respectively. Finally, ~40% of the tertiary alcohol and ~4% of the tertiary chloride were detected along with ~50% of **1a** was recovered.

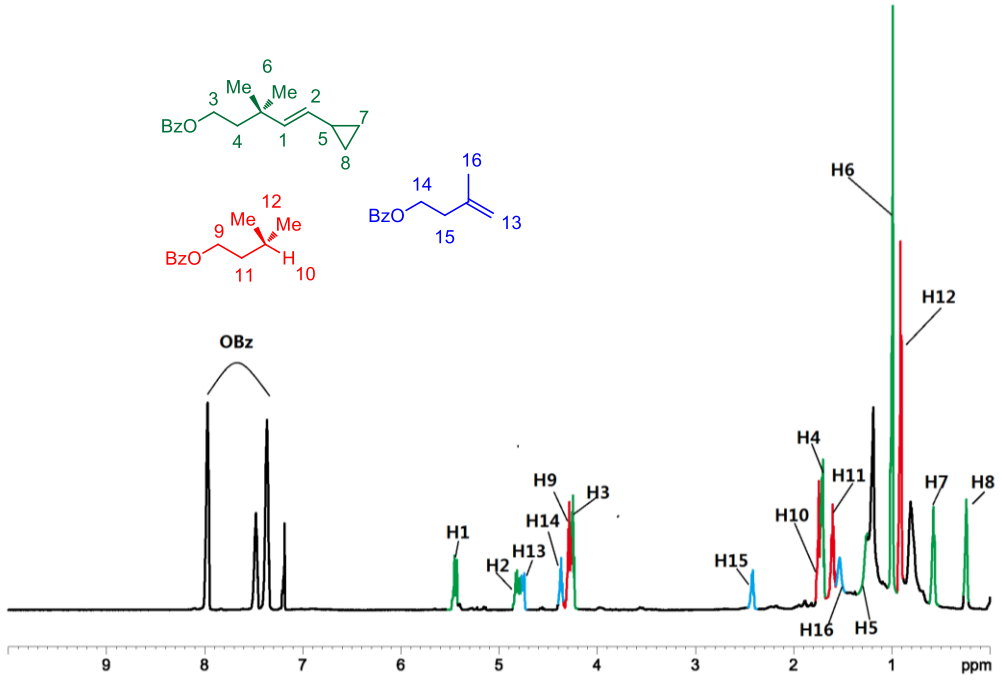


Figure S5. ^{1}H NMR spectra of the no cyclopropane ring-opened product (green) mixed with the hydrogenated (red) and eliminated (blue) products.

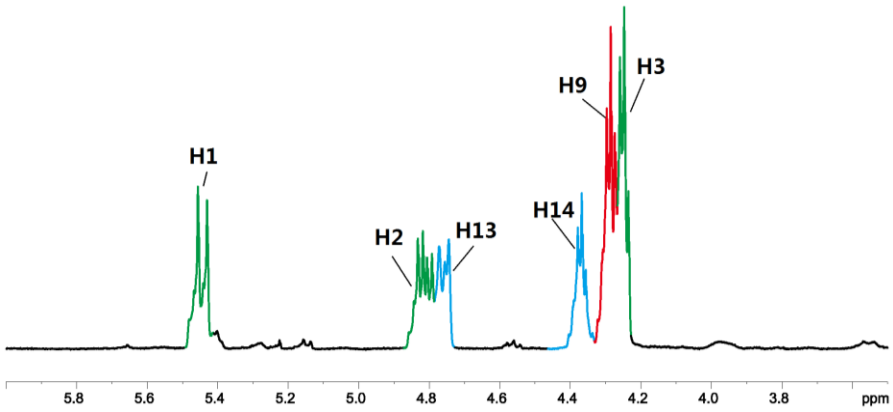


Figure S6. ^{1}H NMR part spectra of the no cyclopropane ring-opened product (green) mixed with the hydrogenated (red) and eliminated (blue) products.

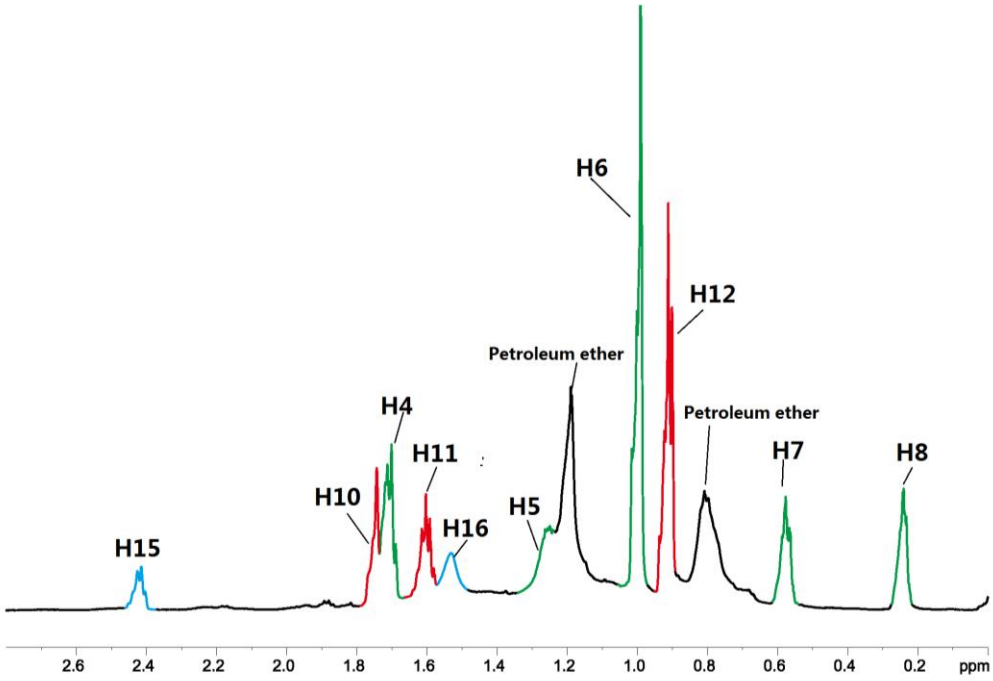
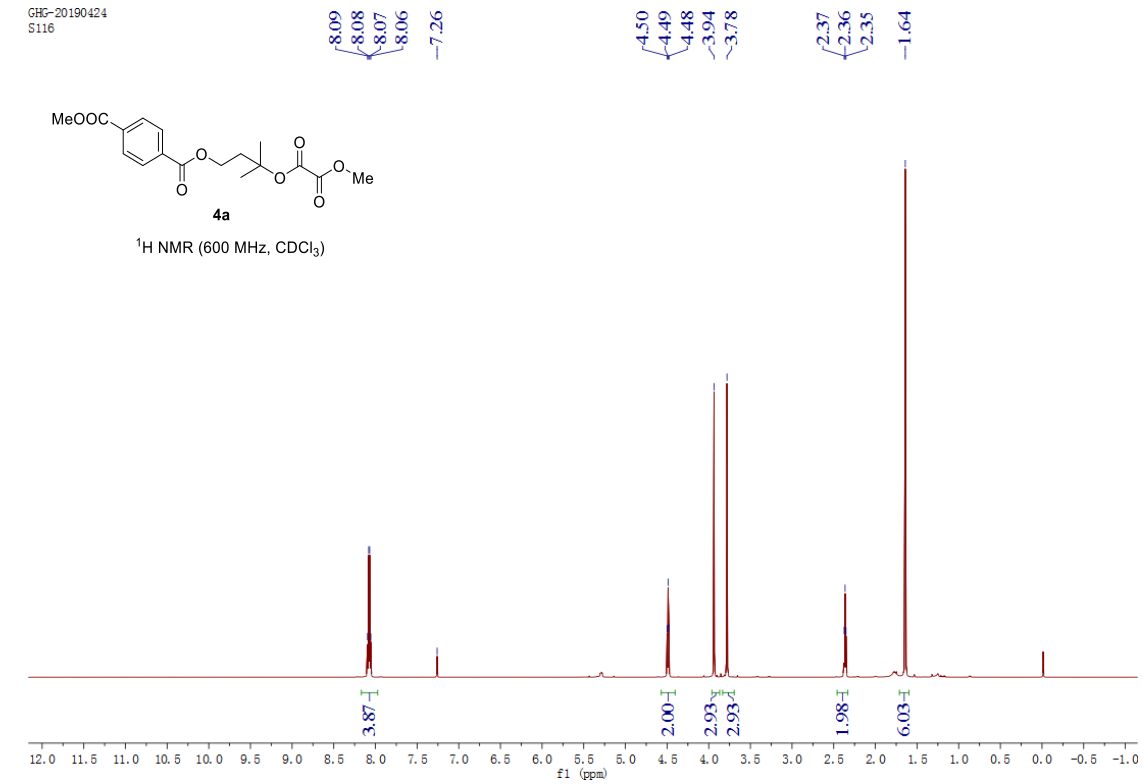


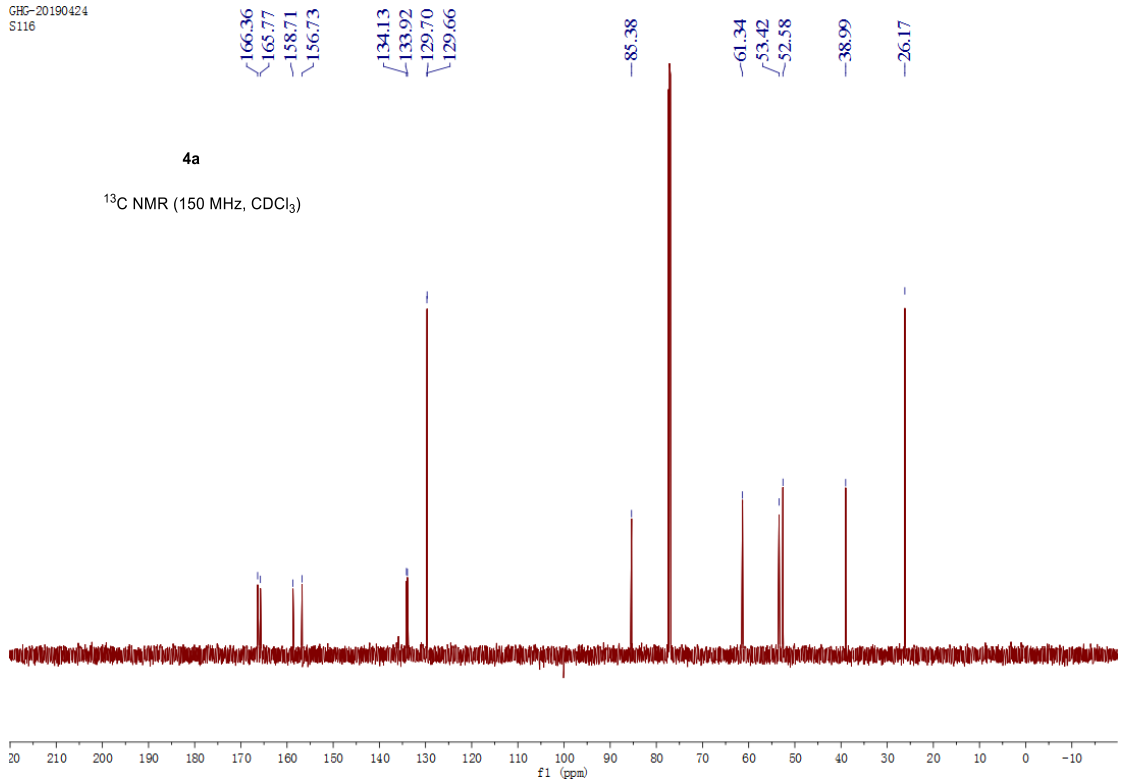
Figure S7. ^{1}H NMR part spectra of the no cyclopropane ring-opened product (green) mixed with the hydrogenated (red) and eliminated (blue) products.

II. Spectral Data for Reported Compounds



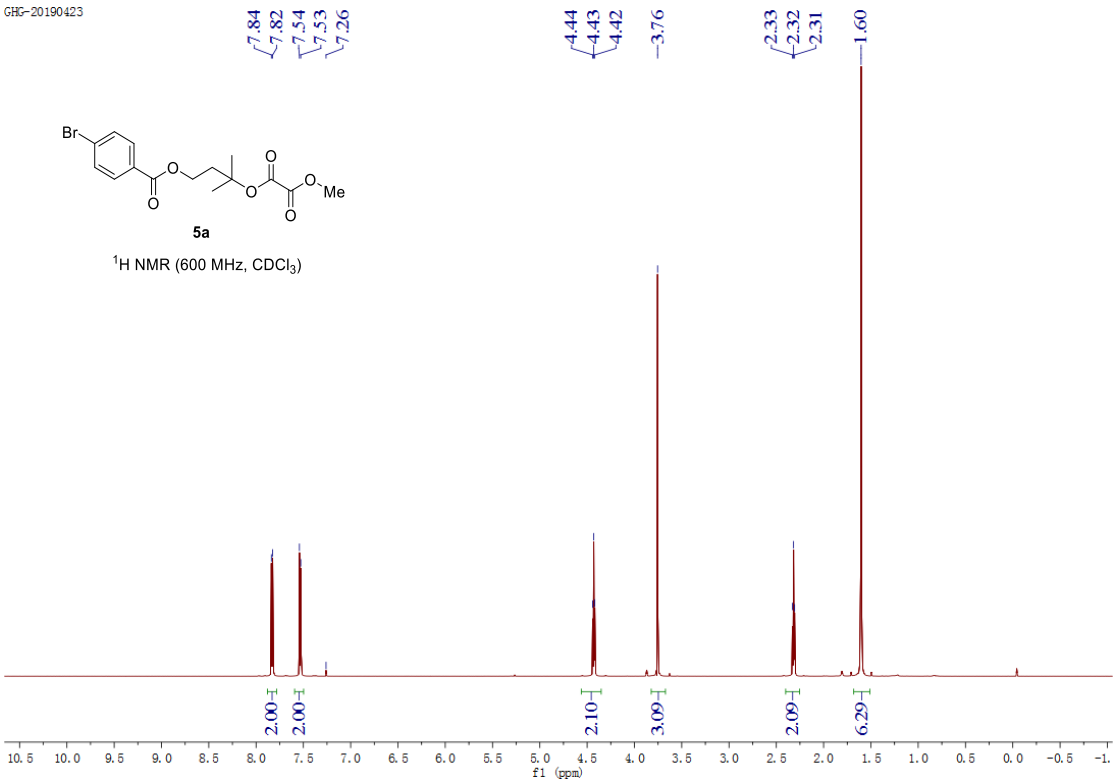
4a

^{1}H NMR (600 MHz, $CDCl_3$)



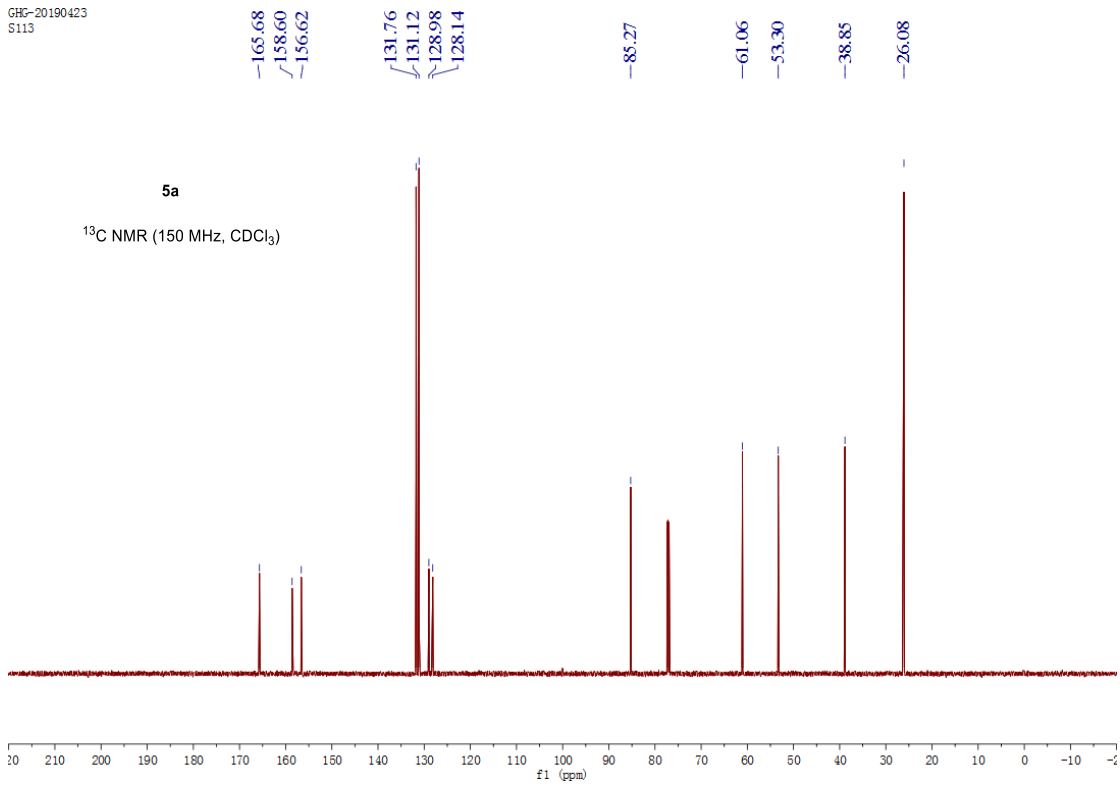
4a

^{13}C NMR (150 MHz, $CDCl_3$)



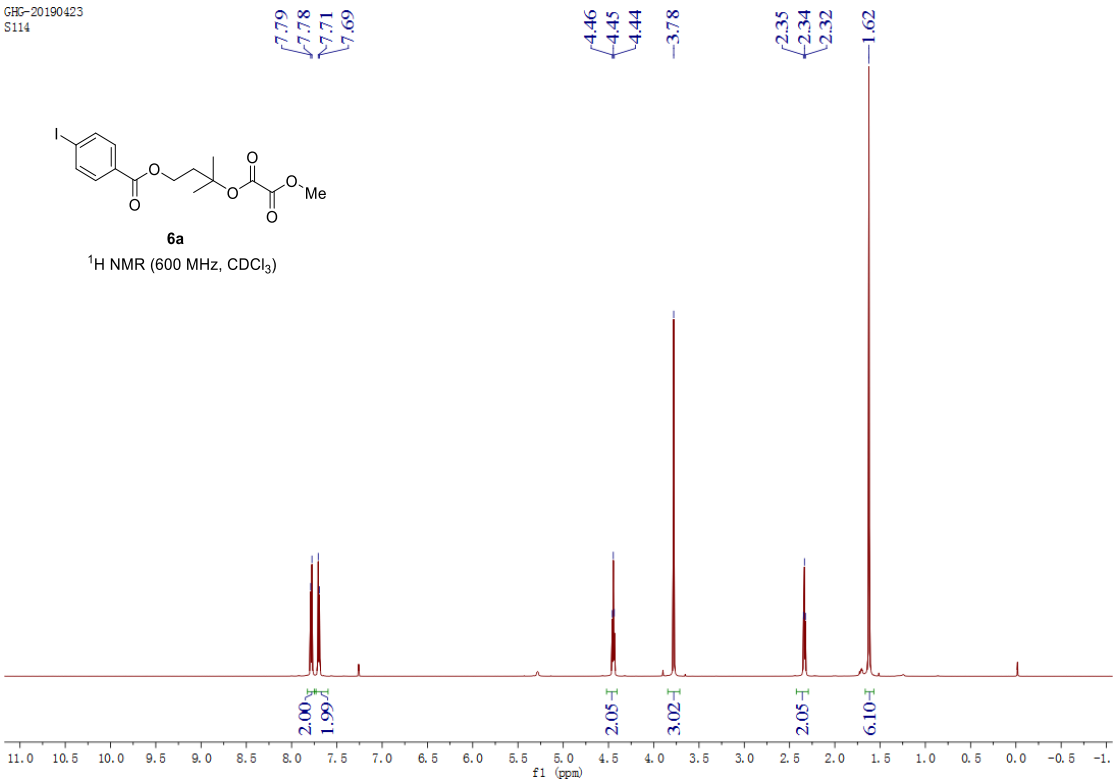
5a

^{1}H NMR (600 MHz, $CDCl_3$)



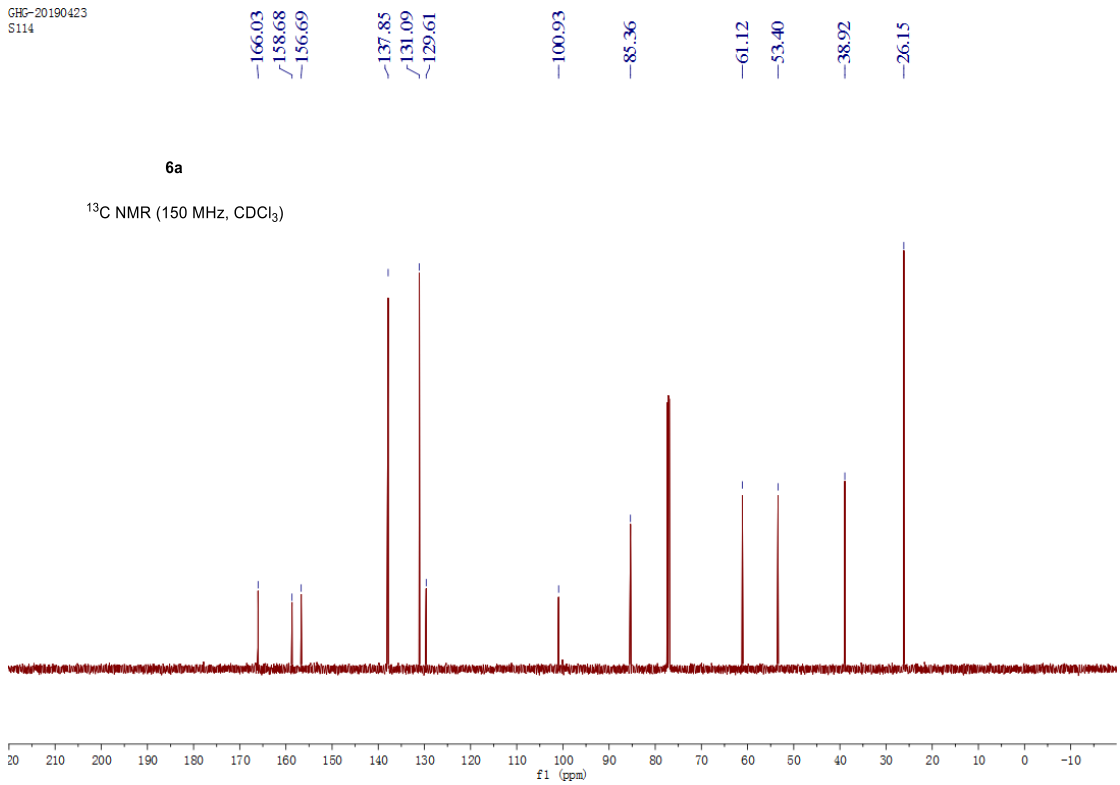
5a

^{13}C NMR (150 MHz, $CDCl_3$)



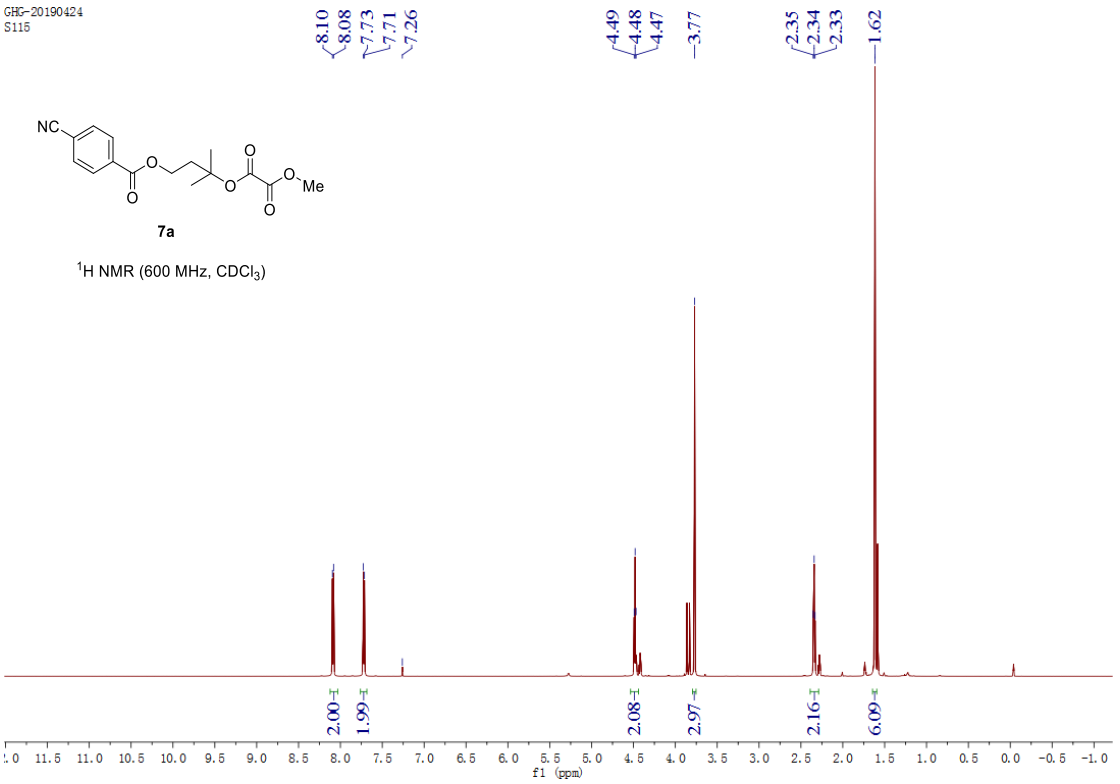
6a

^{1}H NMR (600 MHz, $CDCl_3$)



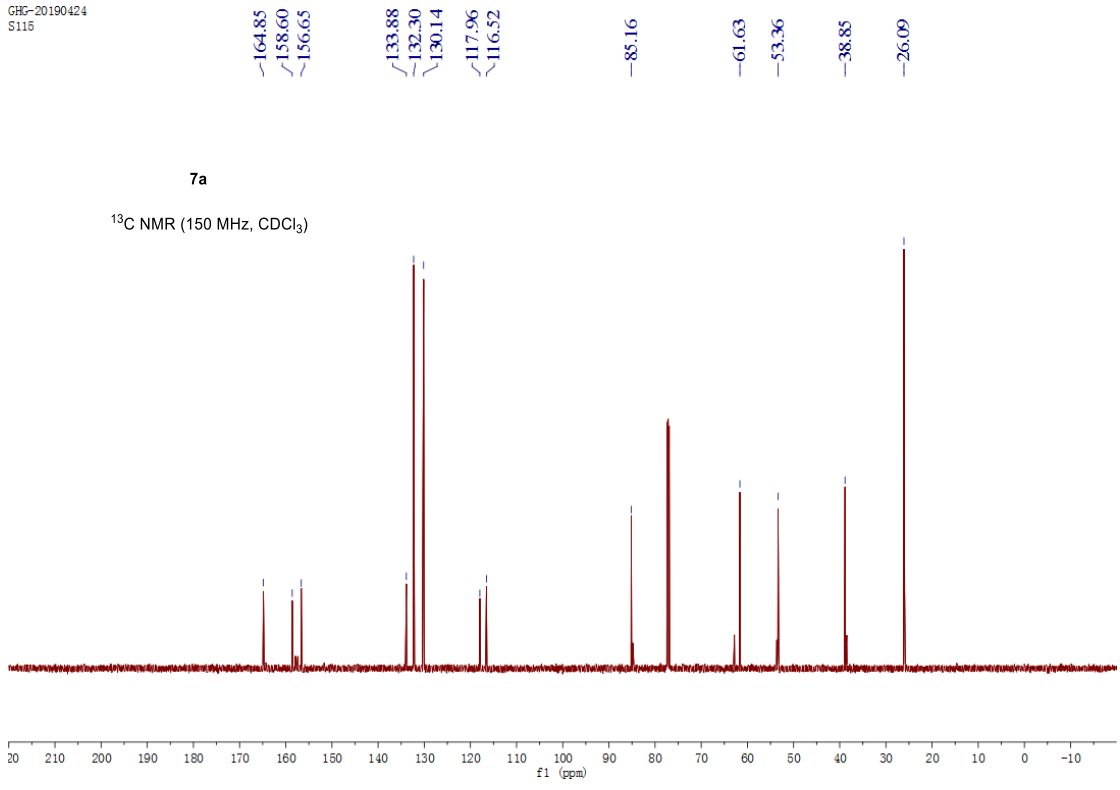
6a

^{13}C NMR (150 MHz, $CDCl_3$)



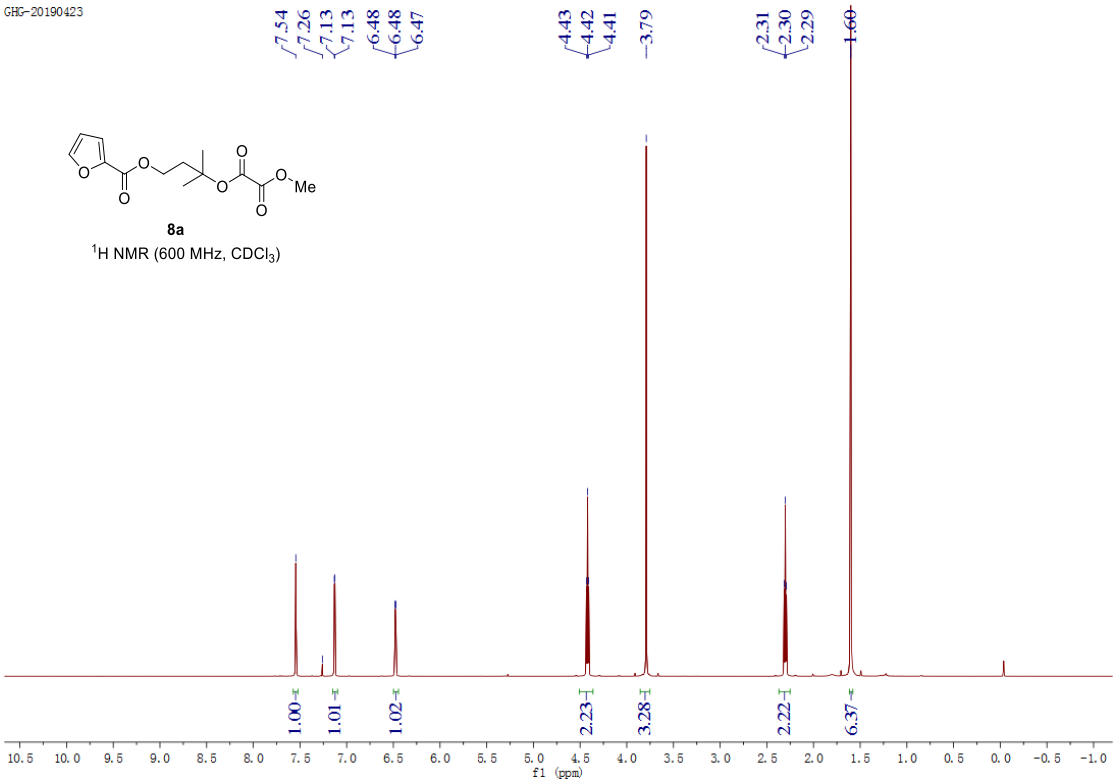
7a

^{1}H NMR (600 MHz, $CDCl_3$)



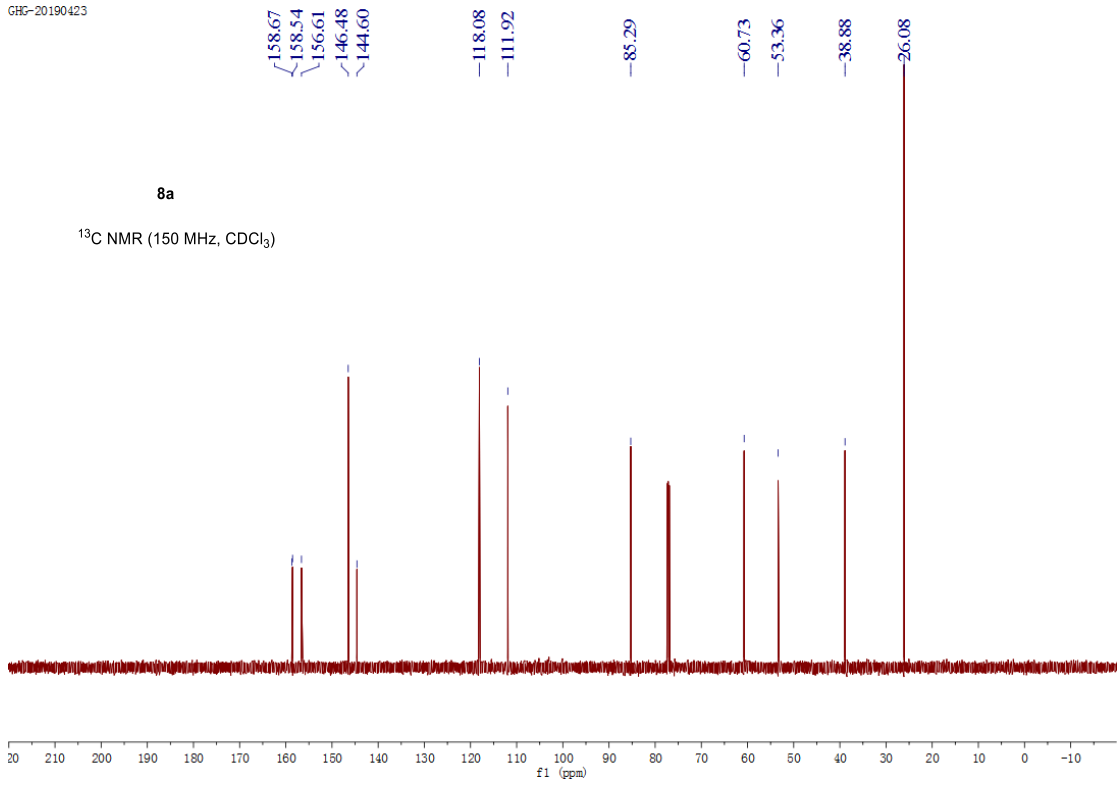
7a

^{13}C NMR (150 MHz, $CDCl_3$)



8a

^{1}H NMR (600 MHz, $CDCl_3$)



8a

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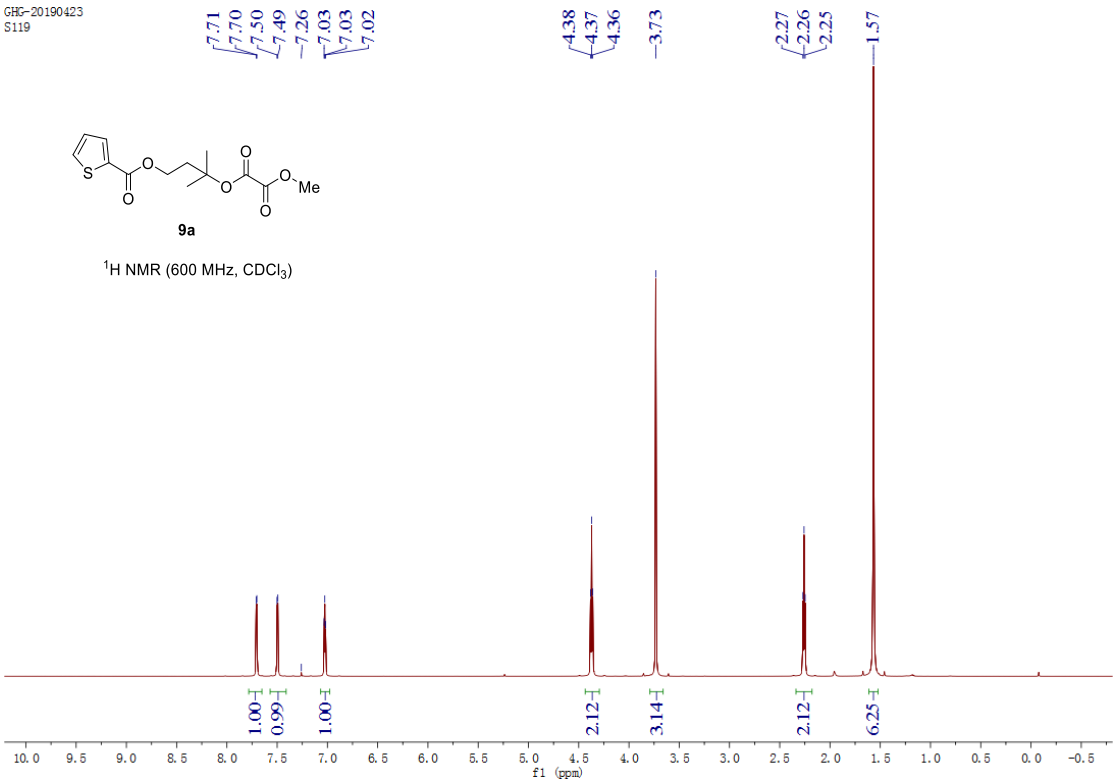
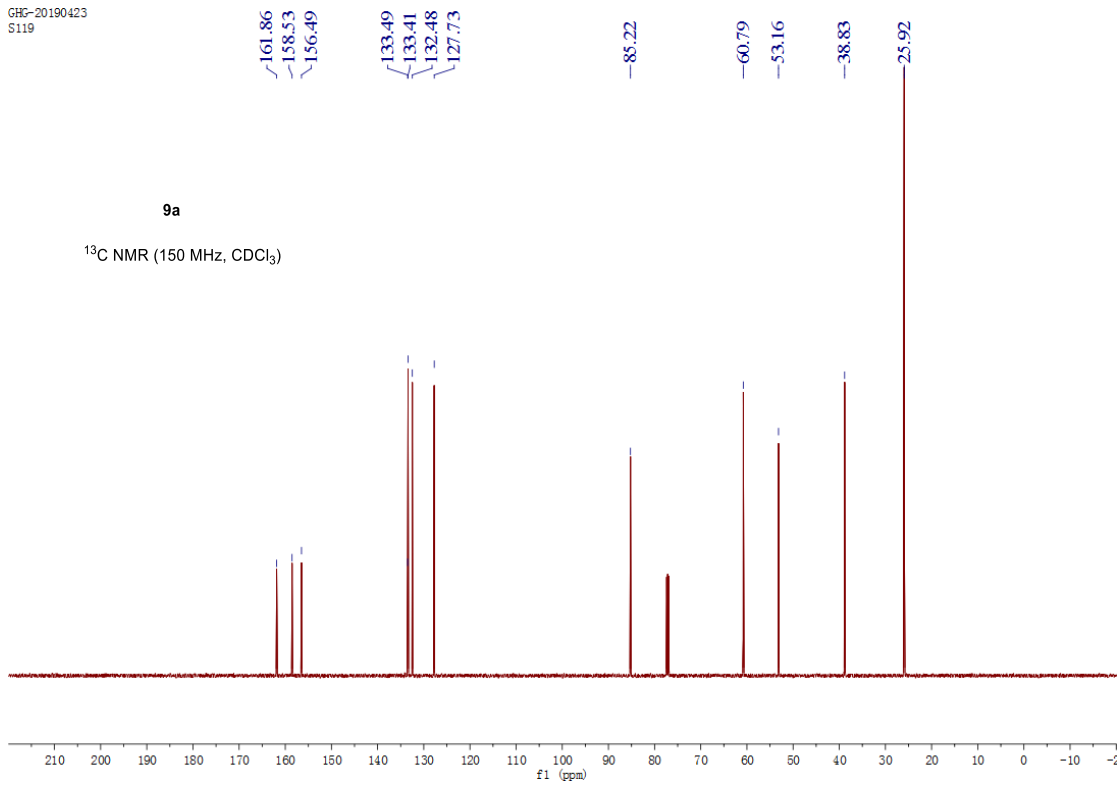


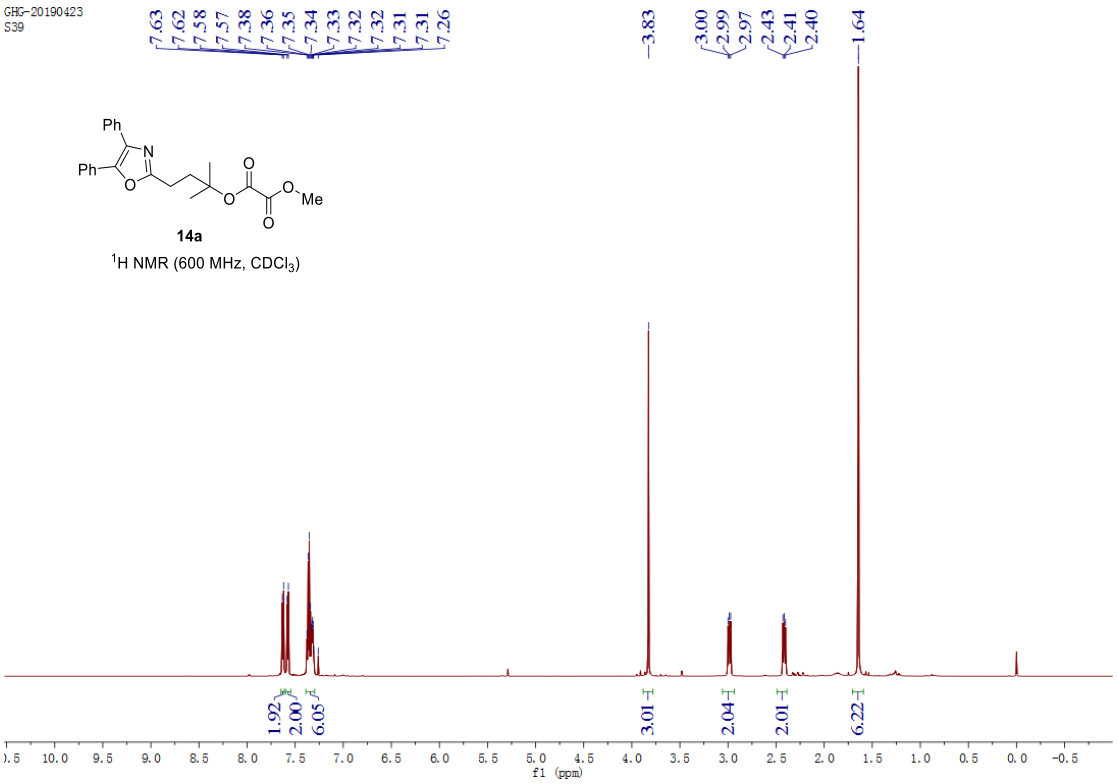
9a

^{1}H NMR (600 MHz, $CDCl_3$)



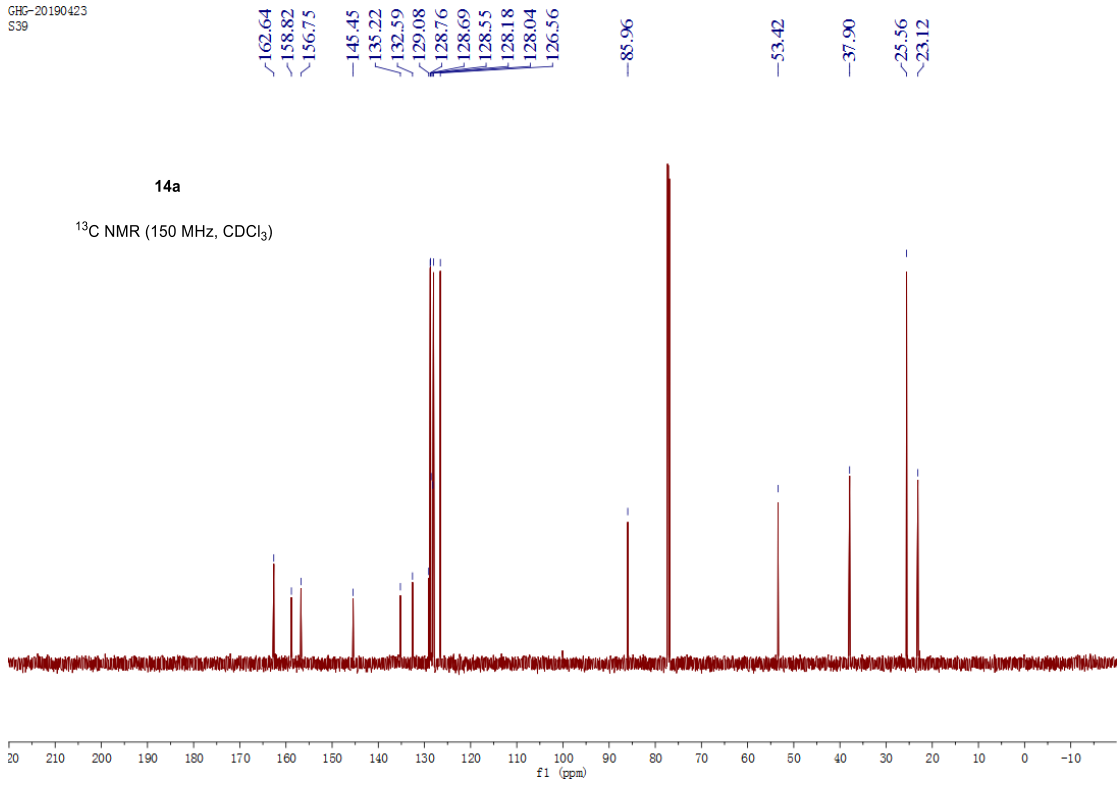
9a

^{13}C NMR (150 MHz, $CDCl_3$)



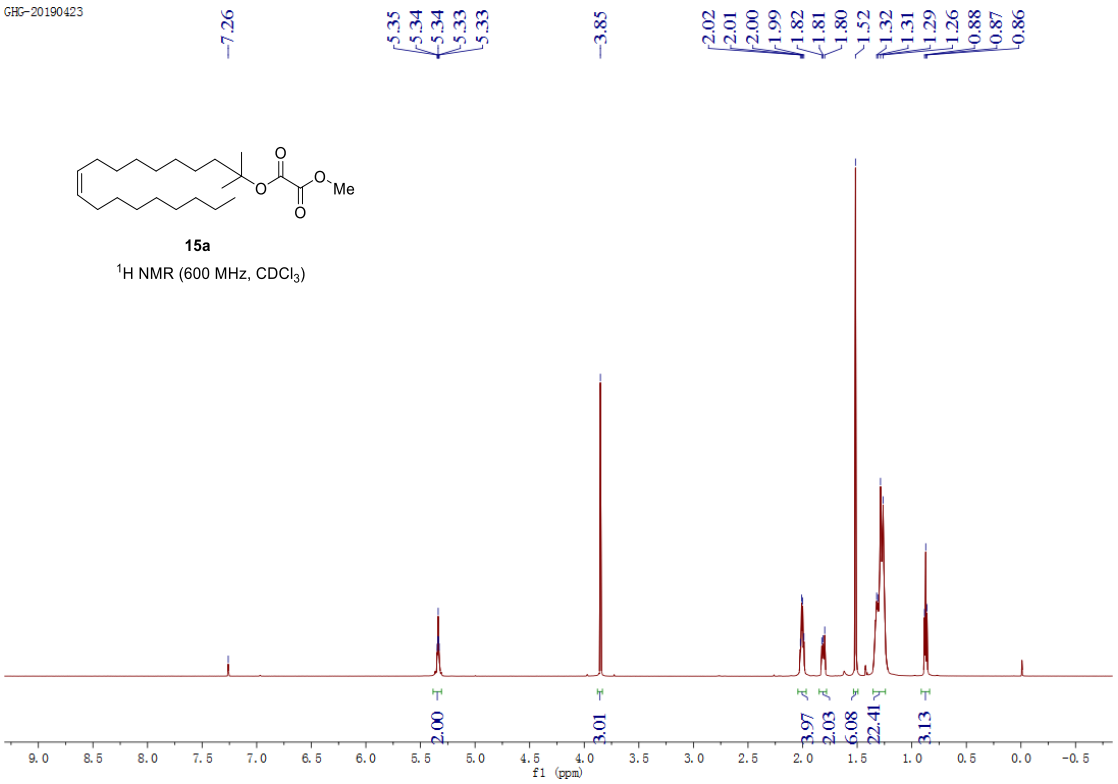
14a

^{1}H NMR (600 MHz, $CDCl_3$)



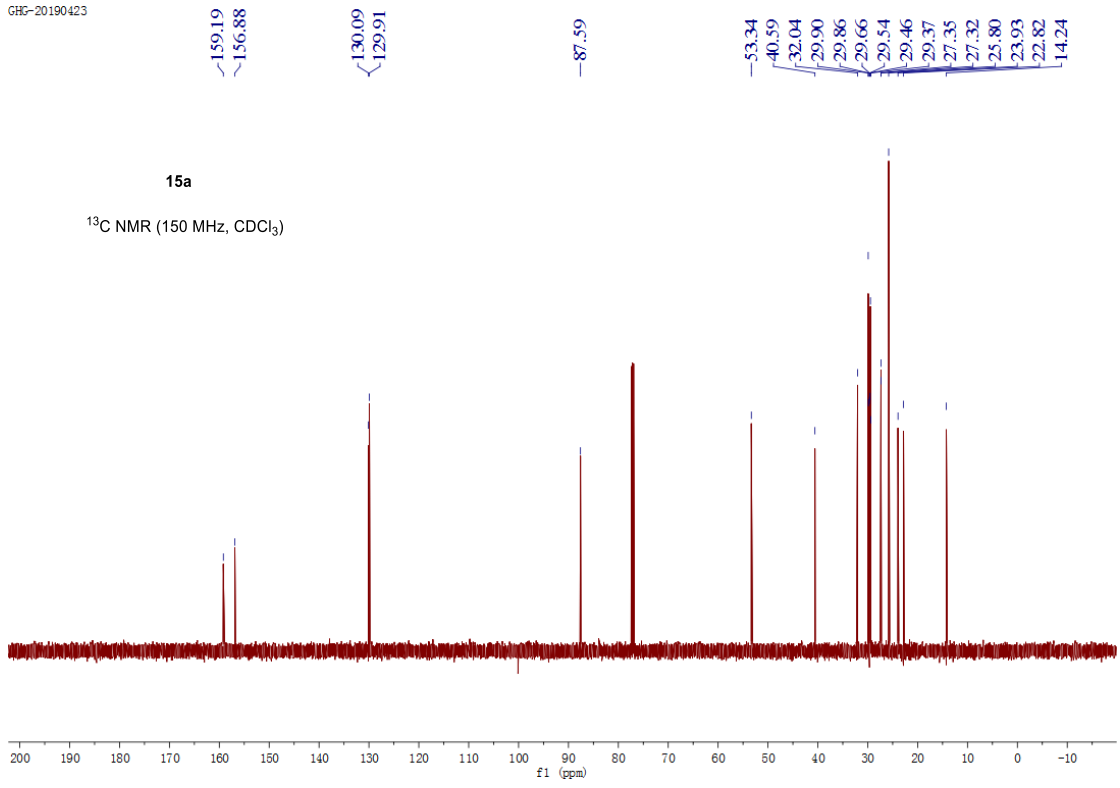
14a

^{13}C NMR (150 MHz, $CDCl_3$)



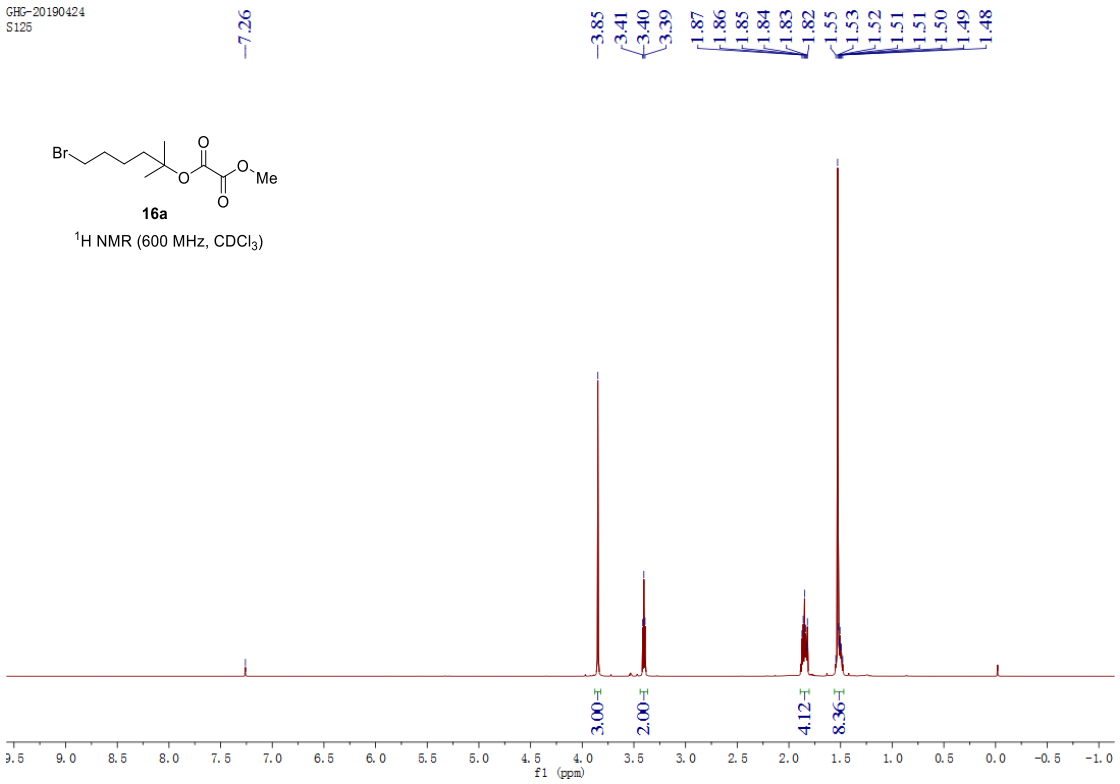
15a

^{1}H NMR (600 MHz, $CDCl_3$)



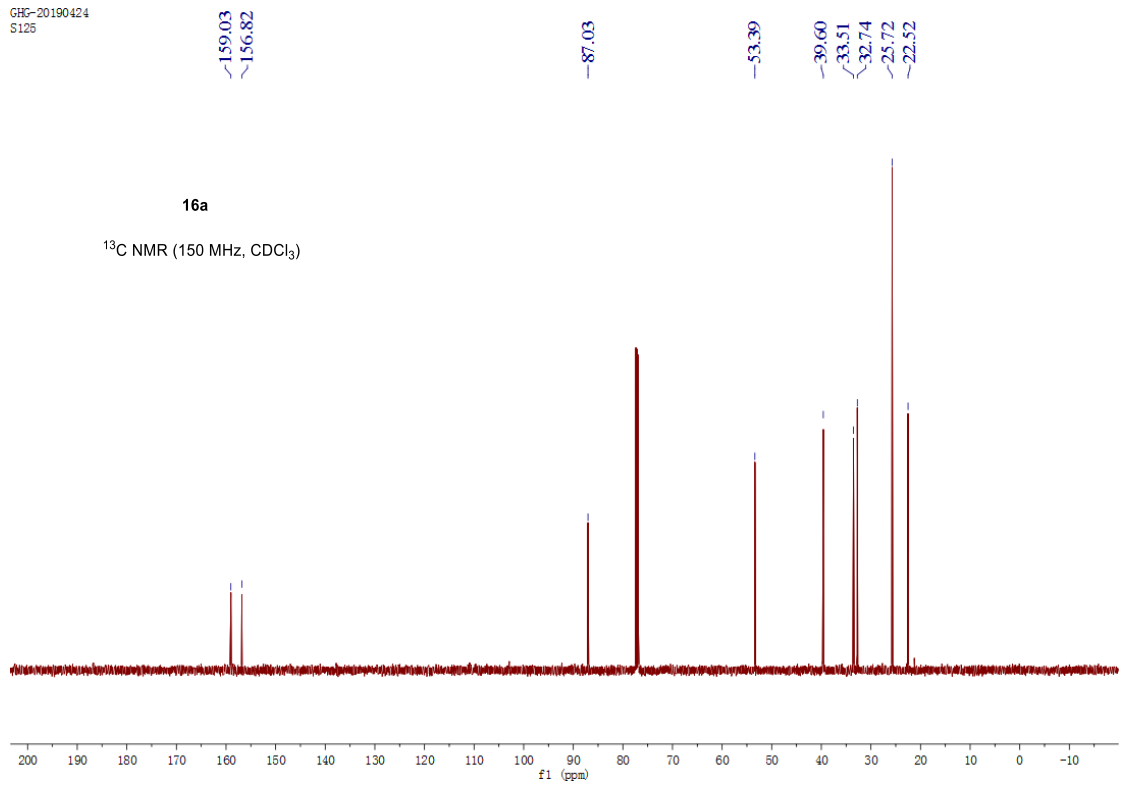
15a

^{13}C NMR (150 MHz, $CDCl_3$)



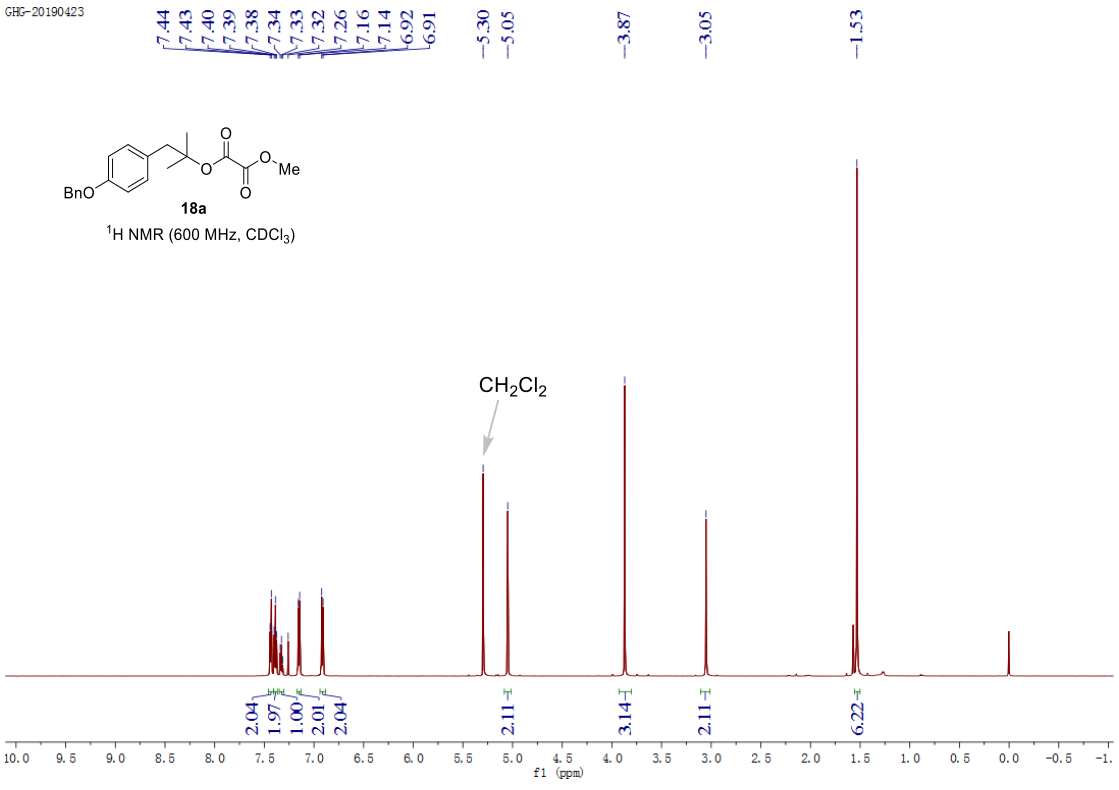
16a

^{1}H NMR (600 MHz, $CDCl_3$)



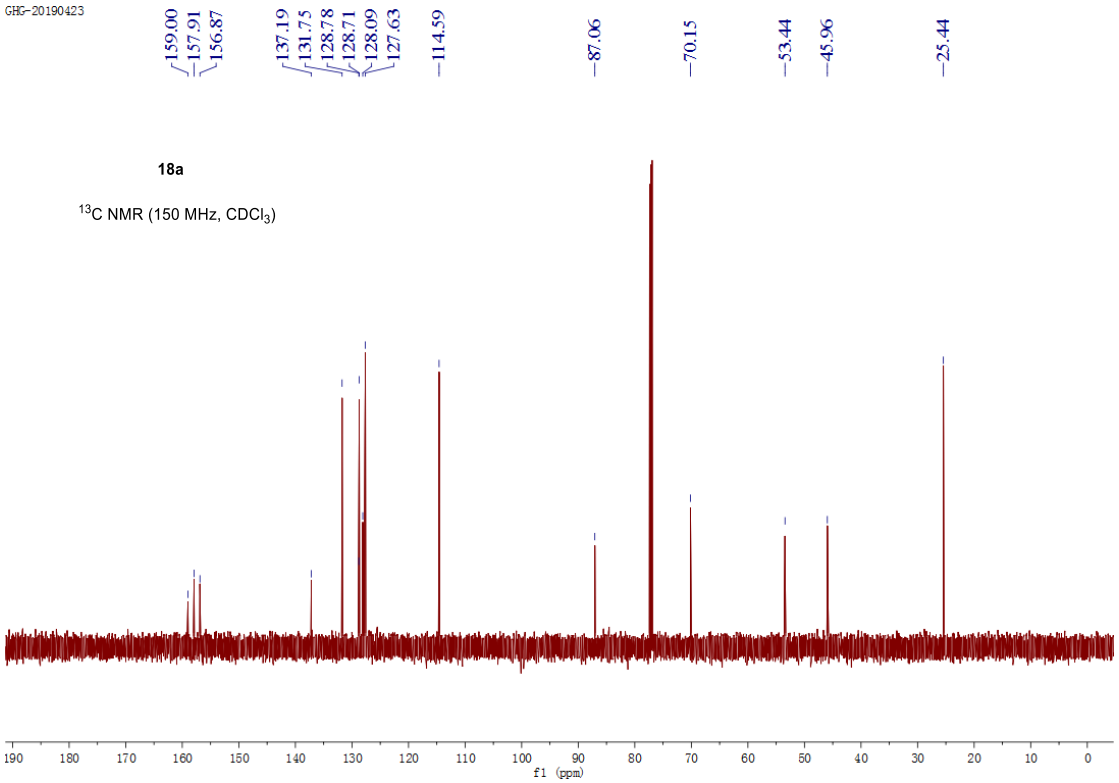
16a

^{13}C NMR (150 MHz, $CDCl_3$)



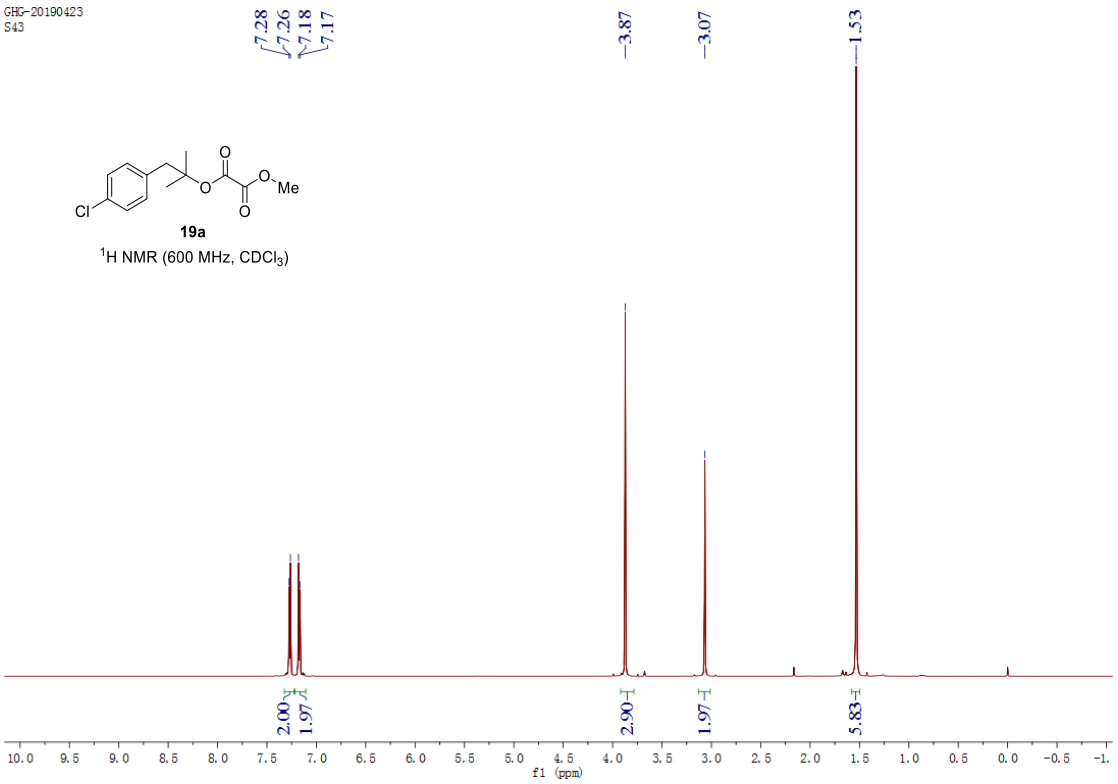
18a

^{1}H NMR (600 MHz, $CDCl_3$)



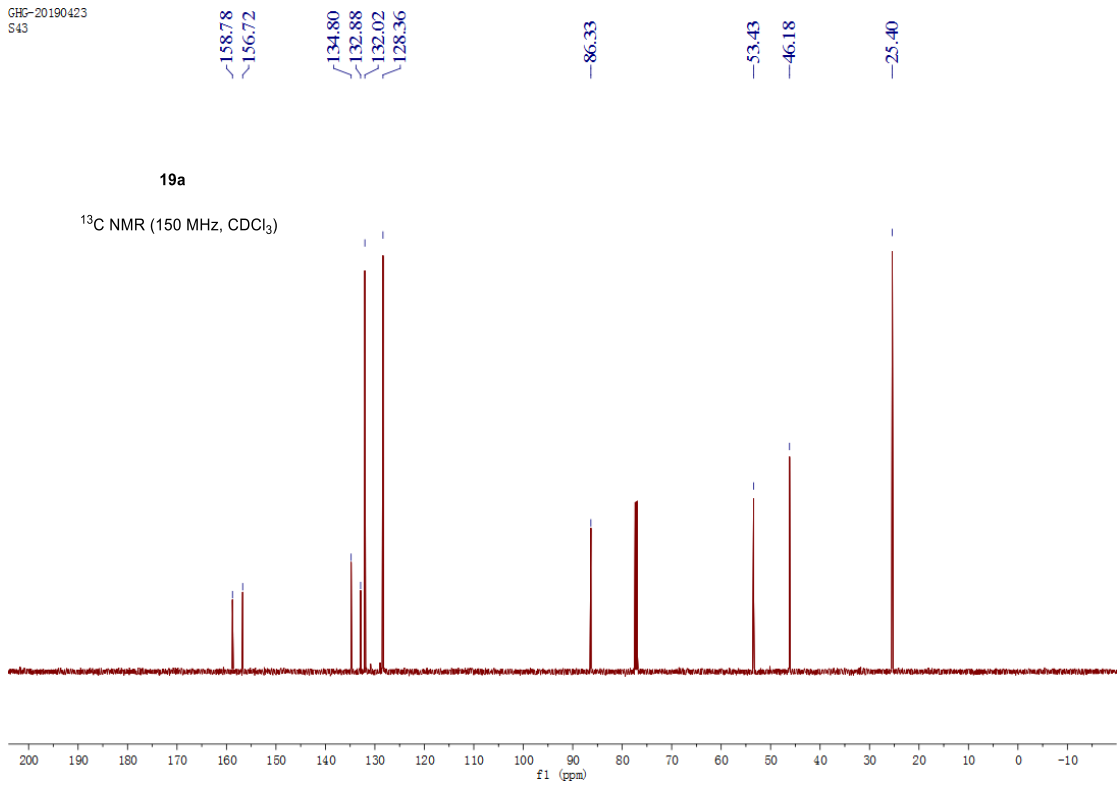
18a

^{13}C NMR (150 MHz, $CDCl_3$)



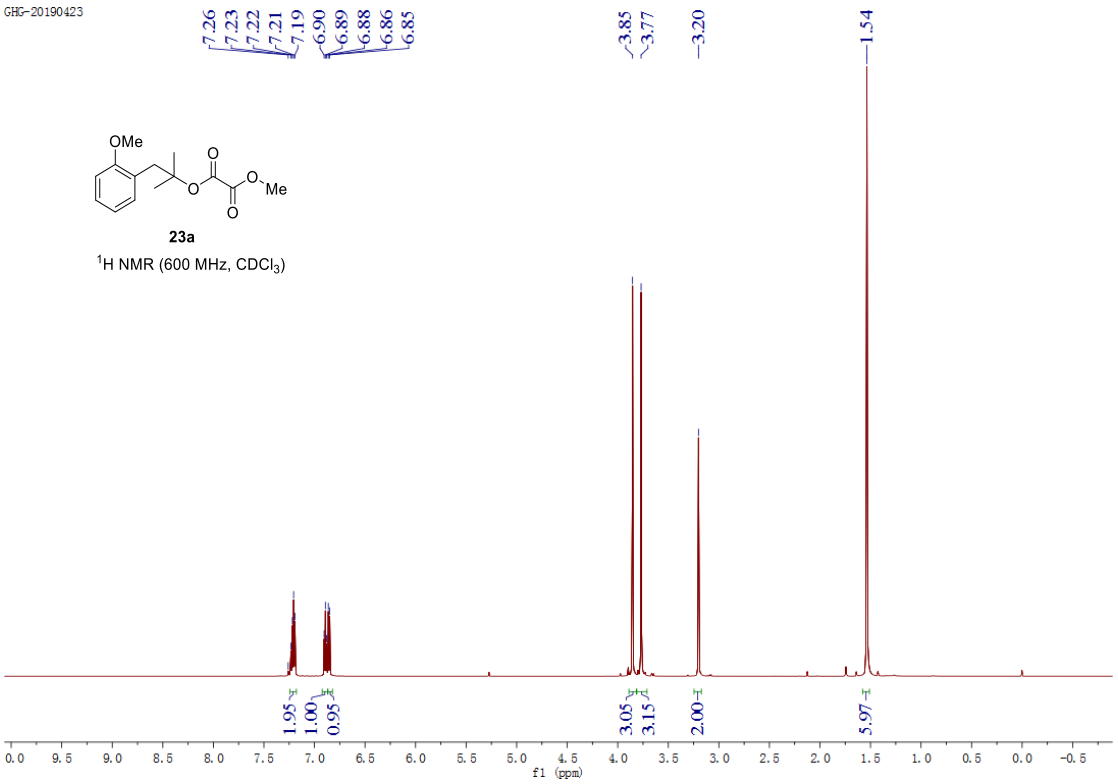
19a

^{1}H NMR (600 MHz, $CDCl_3$)



19a

^{13}C NMR (150 MHz, $CDCl_3$)



23a

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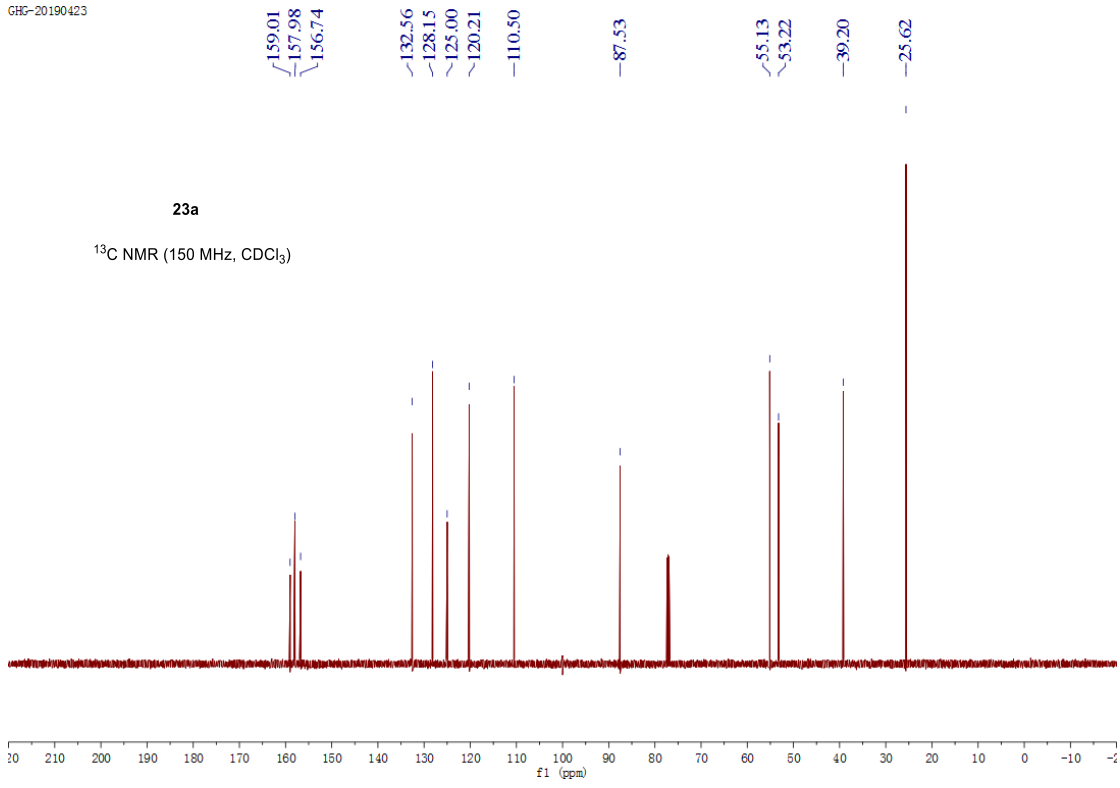
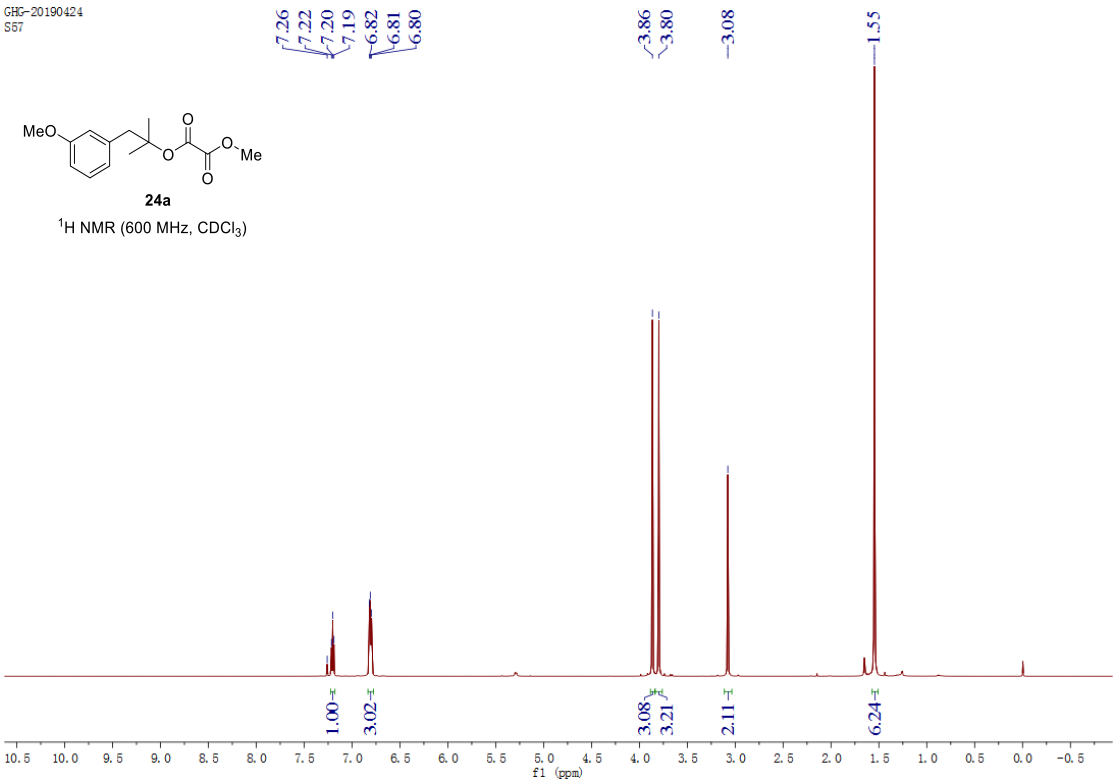


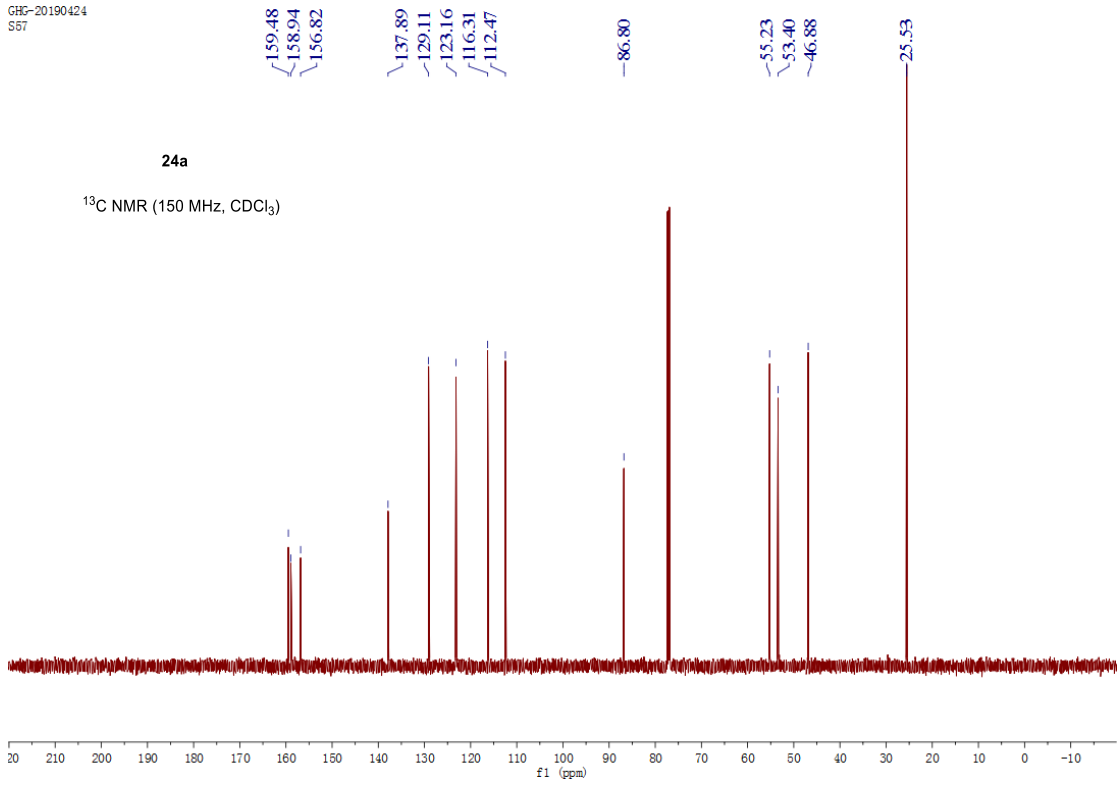
23a

^{13}C NMR (150 MHz, $CDCl_3$)



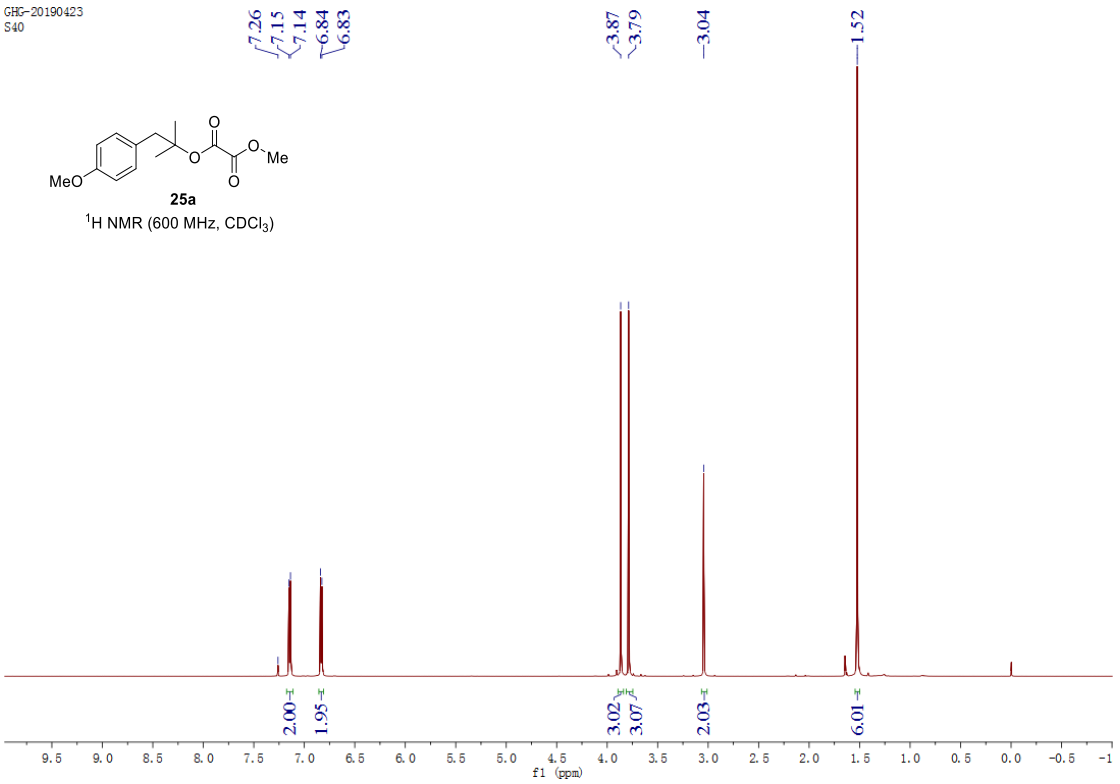
24a

^{1}H NMR (600 MHz, $CDCl_3$)



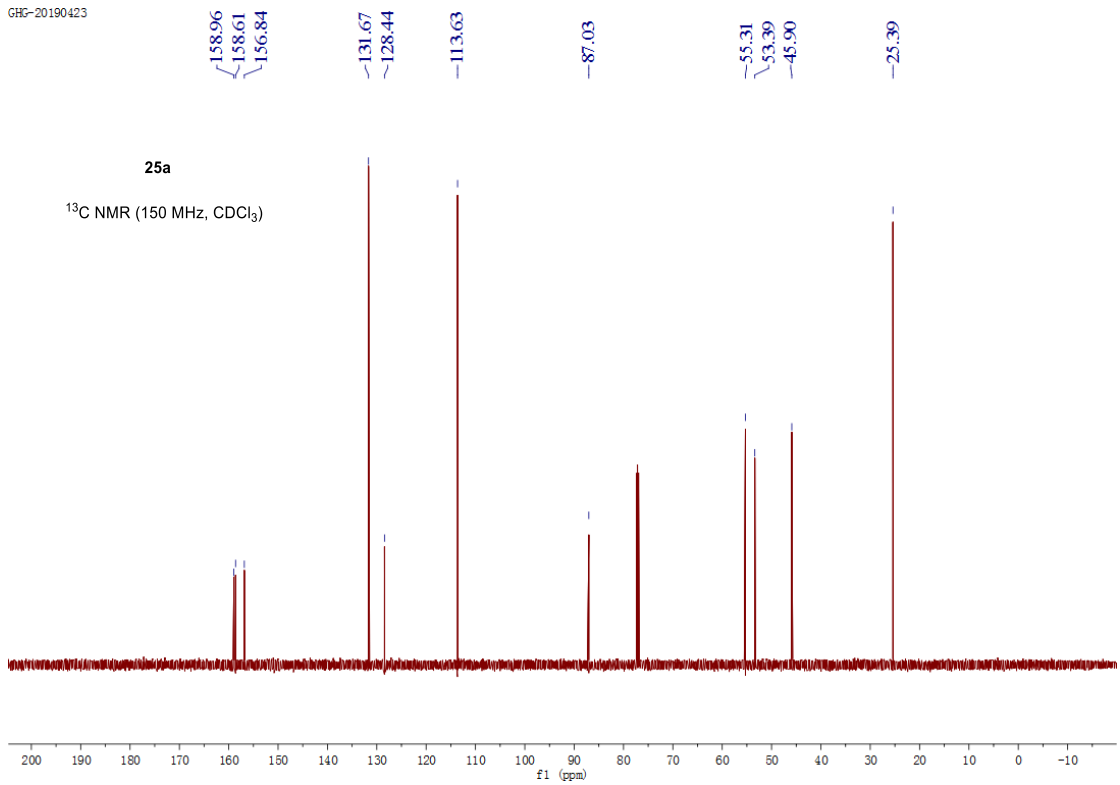
24a

^{13}C NMR (150 MHz, $CDCl_3$)



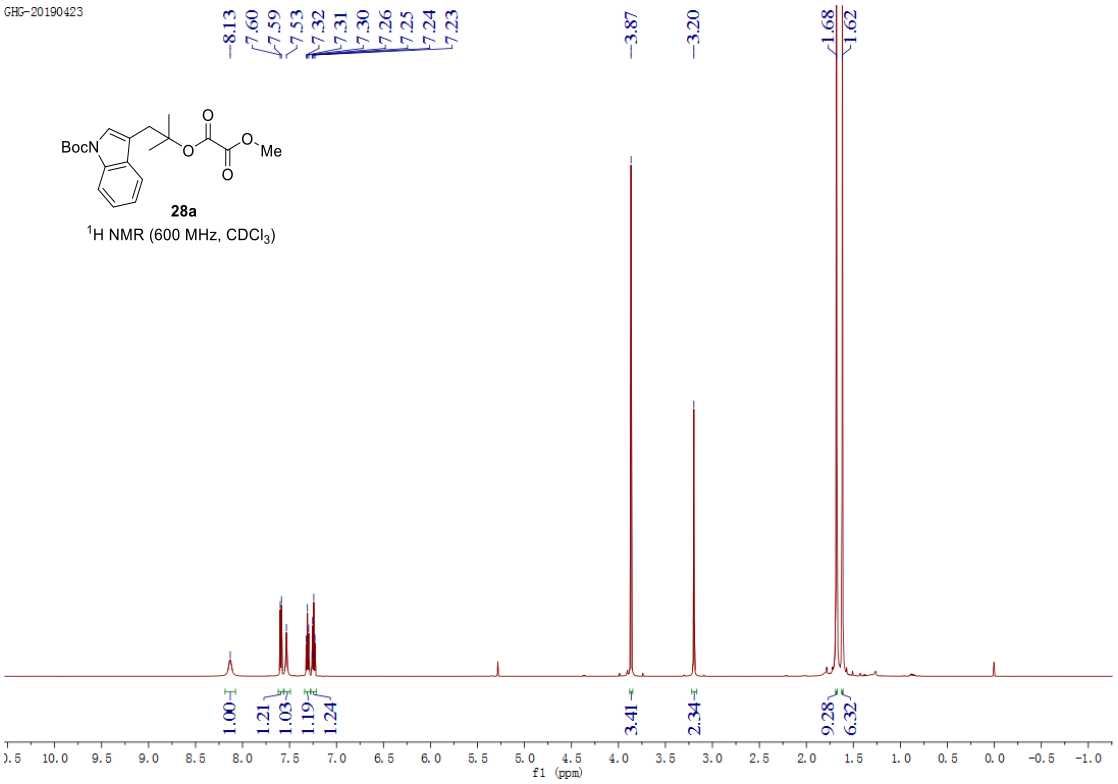
25a

^{1}H NMR (600 MHz, $CDCl_3$)



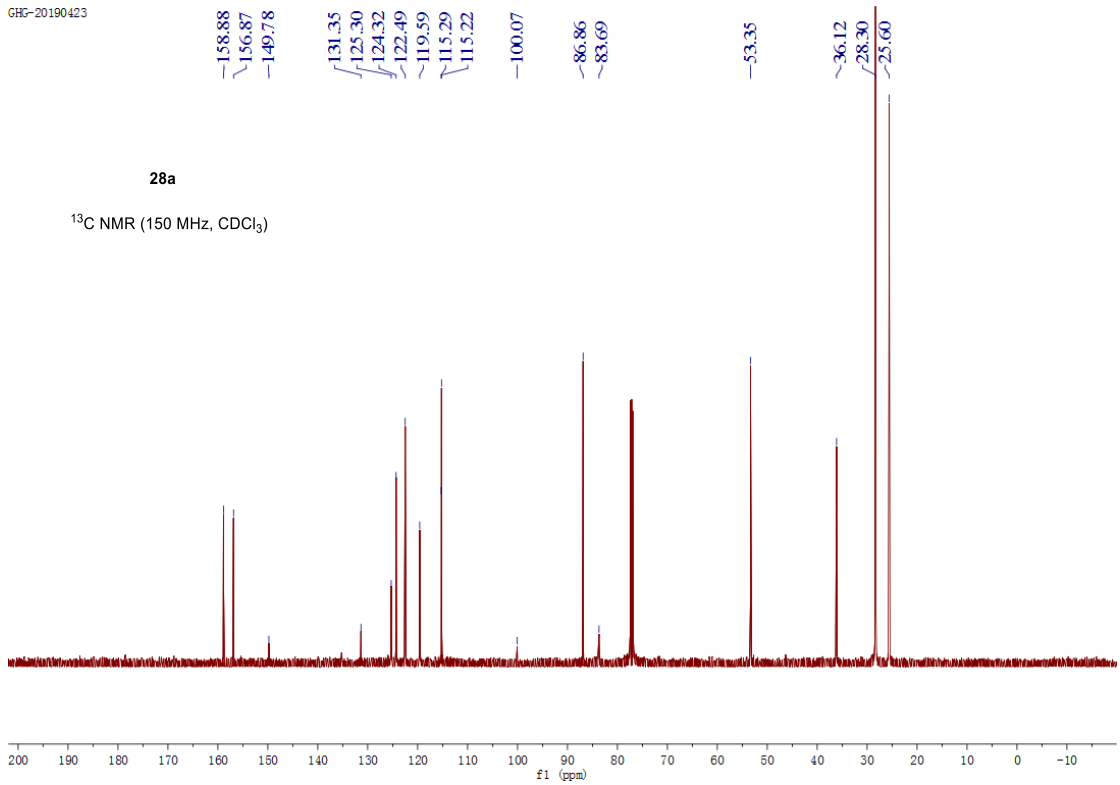
25a

^{13}C NMR (150 MHz, $CDCl_3$)



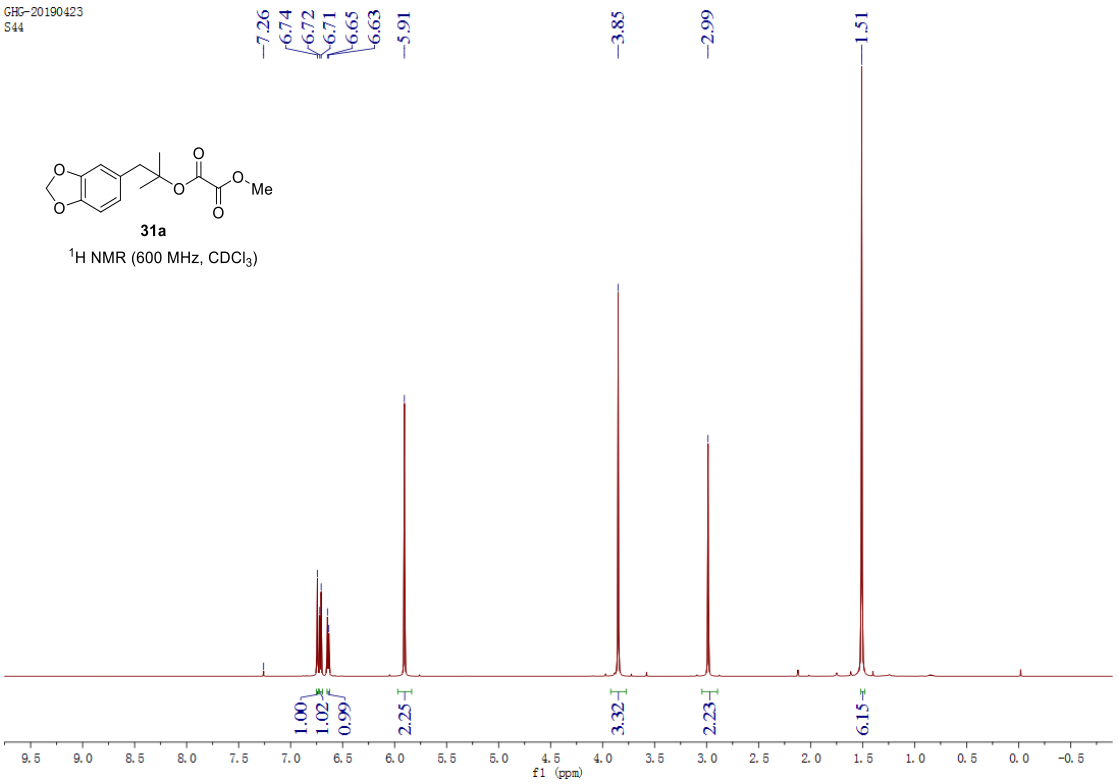
28a

^{1}H NMR (600 MHz, $CDCl_3$)



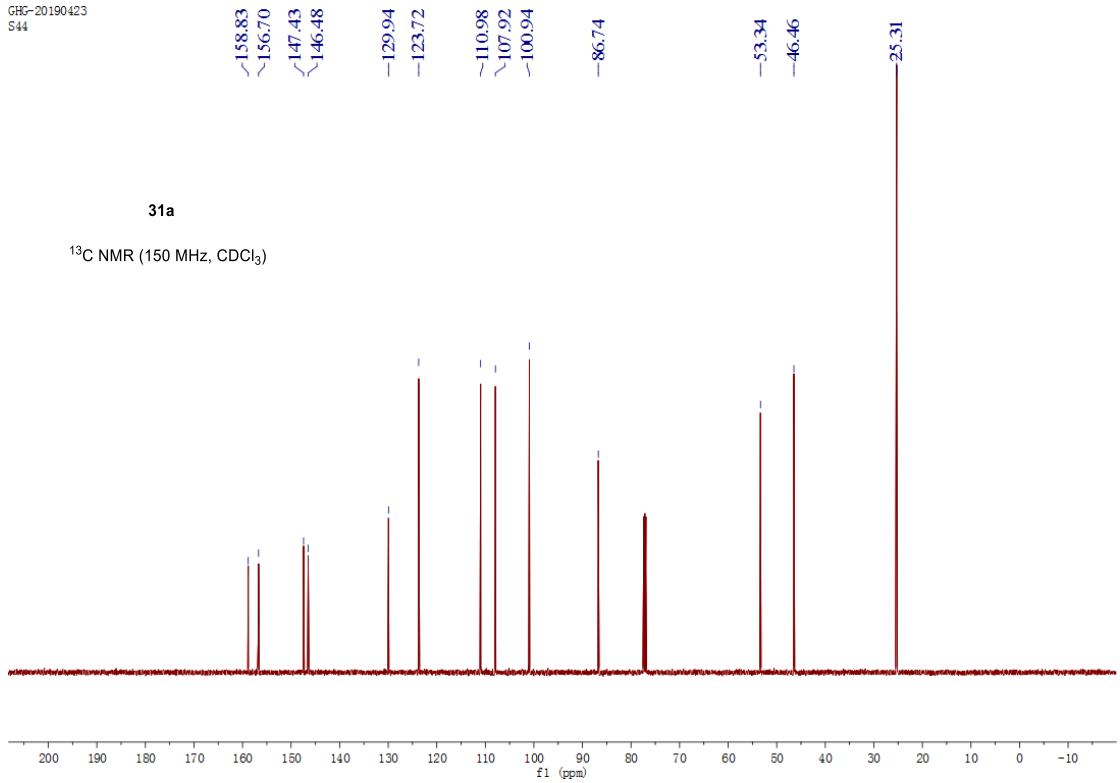
28a

^{13}C NMR (150 MHz, $CDCl_3$)



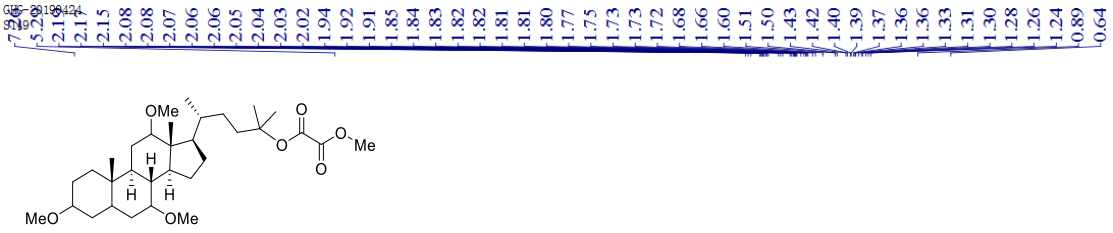
31a

^{1}H NMR (600 MHz, $CDCl_3$)



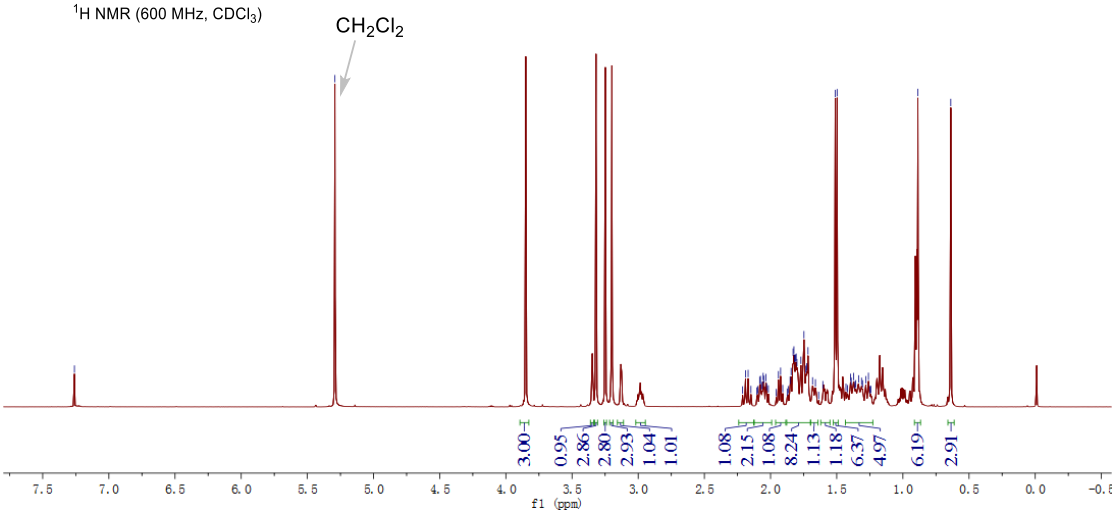
31a

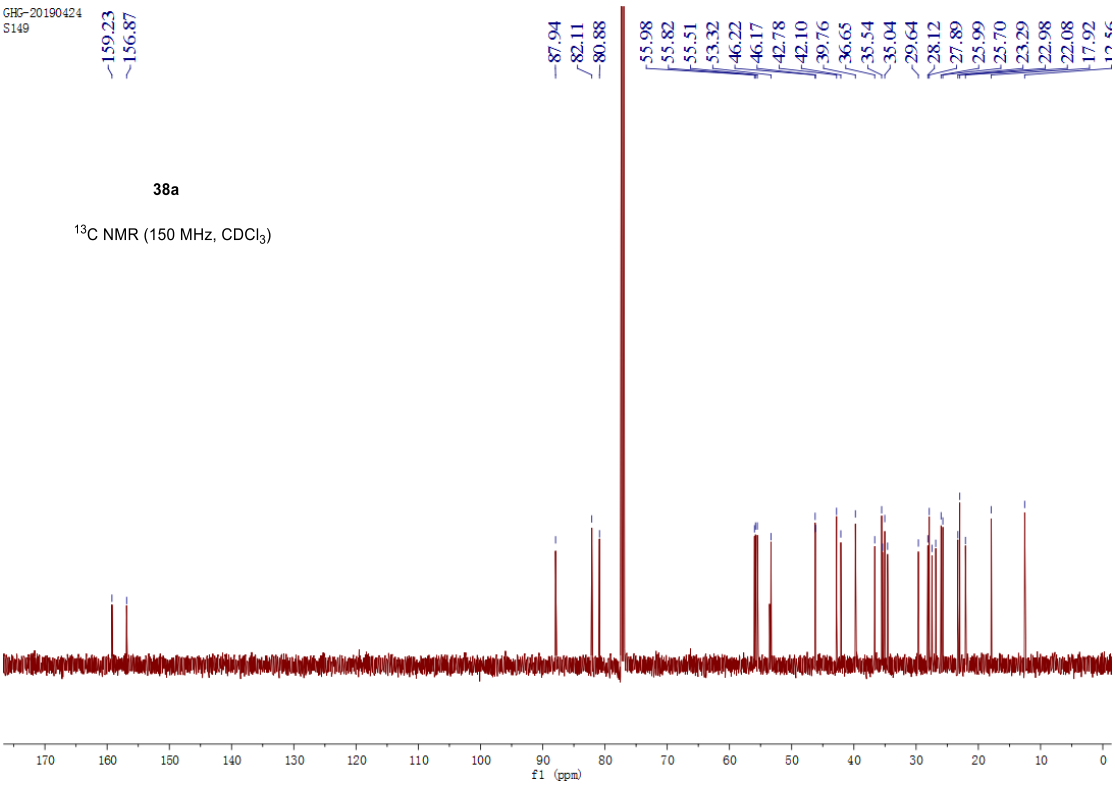
^{13}C NMR (150 MHz, $CDCl_3$)



38a

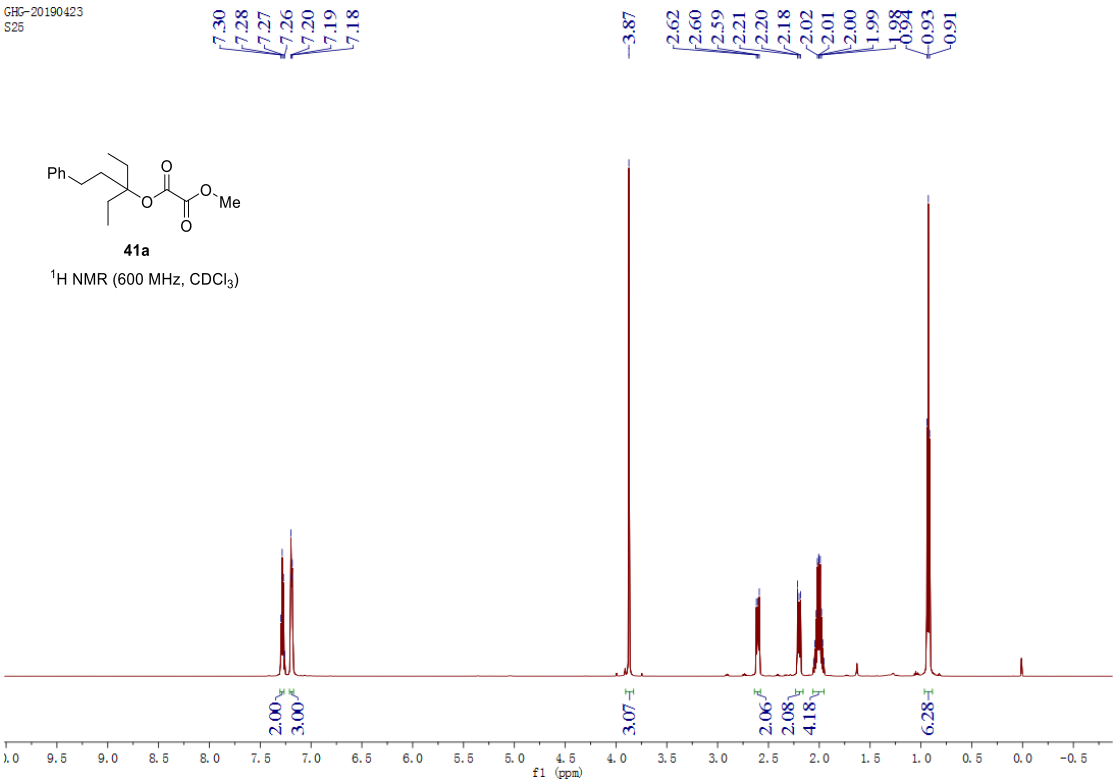
^{1}H NMR (600 MHz, $CDCl_3$)





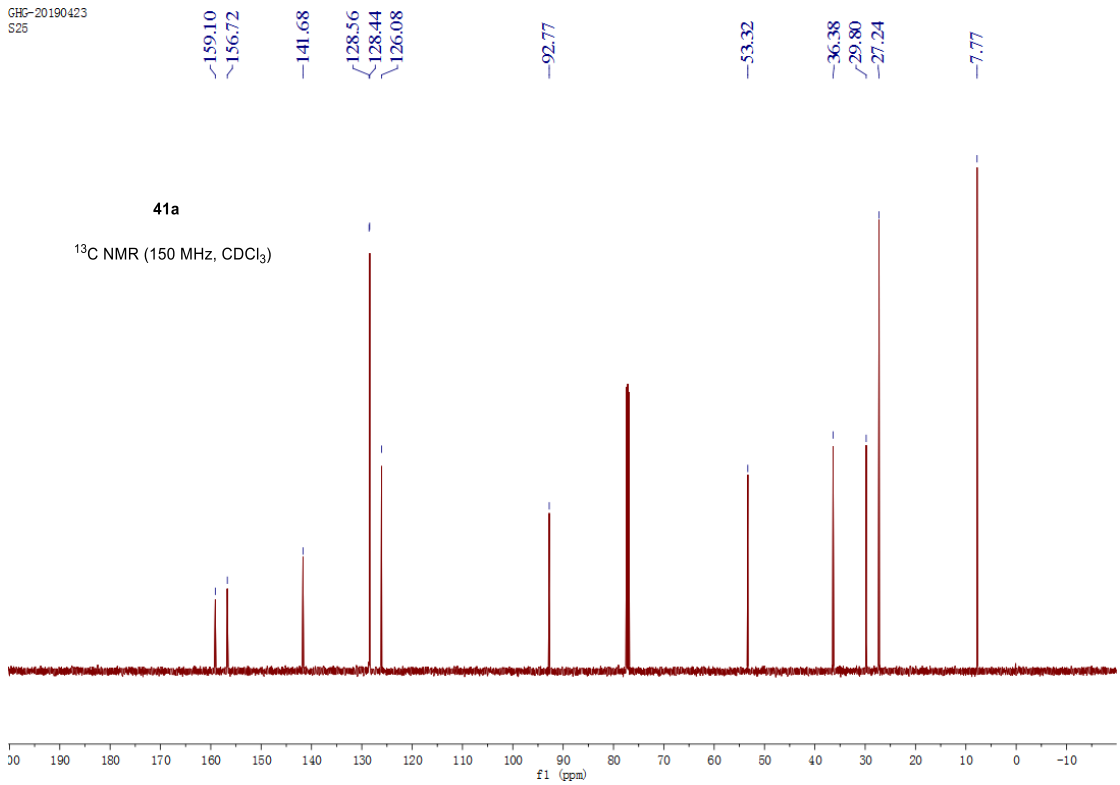
38a

^{13}C NMR (150 MHz, $CDCl_3$)



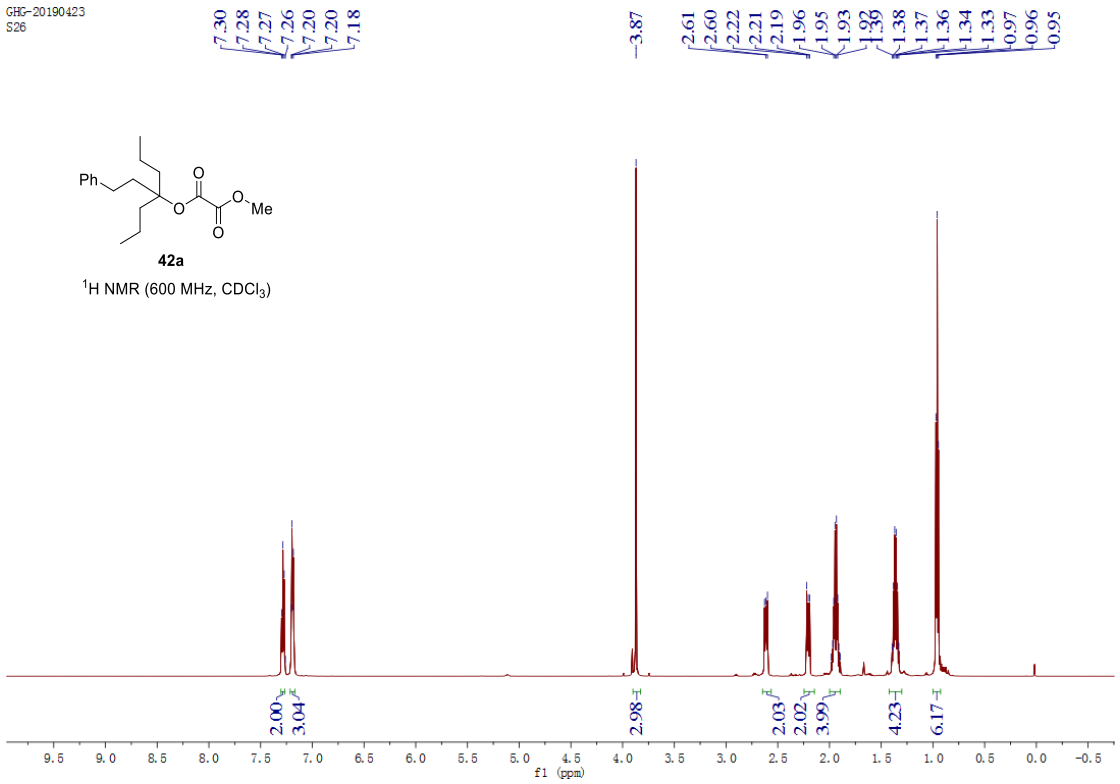
41a

^{1}H NMR (600 MHz, $CDCl_3$)



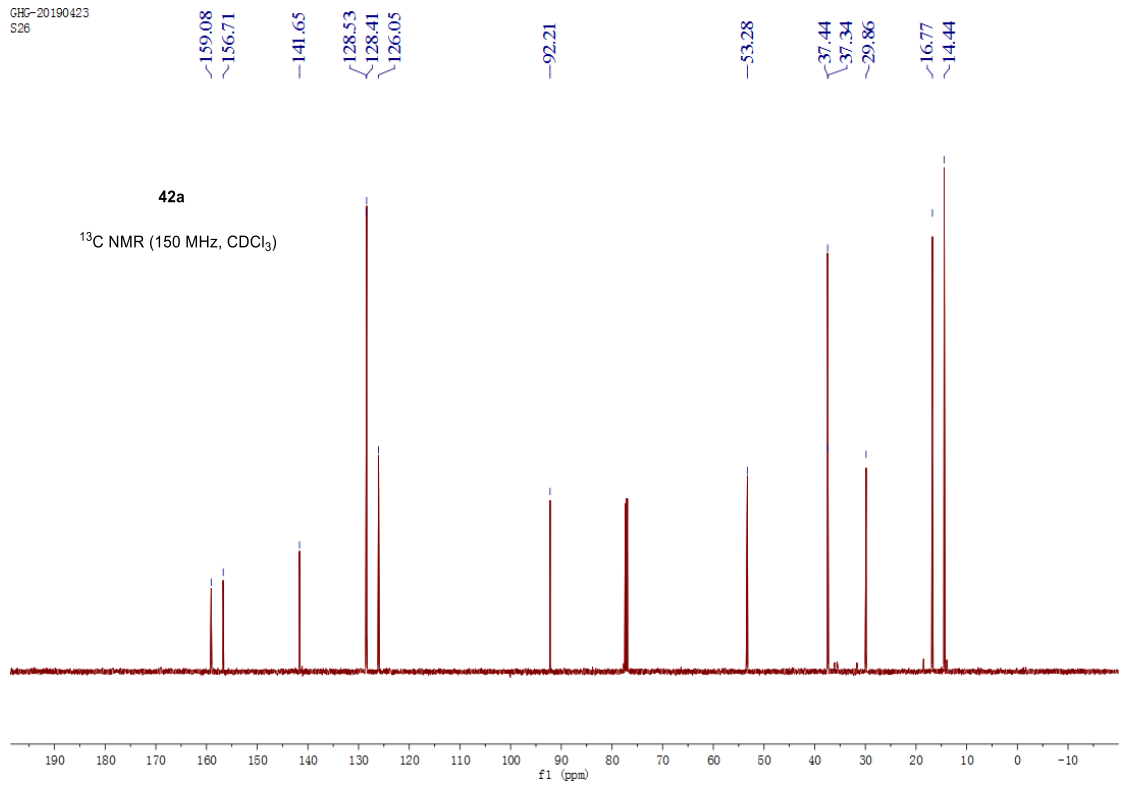
41a

^{13}C NMR (150 MHz, $CDCl_3$)



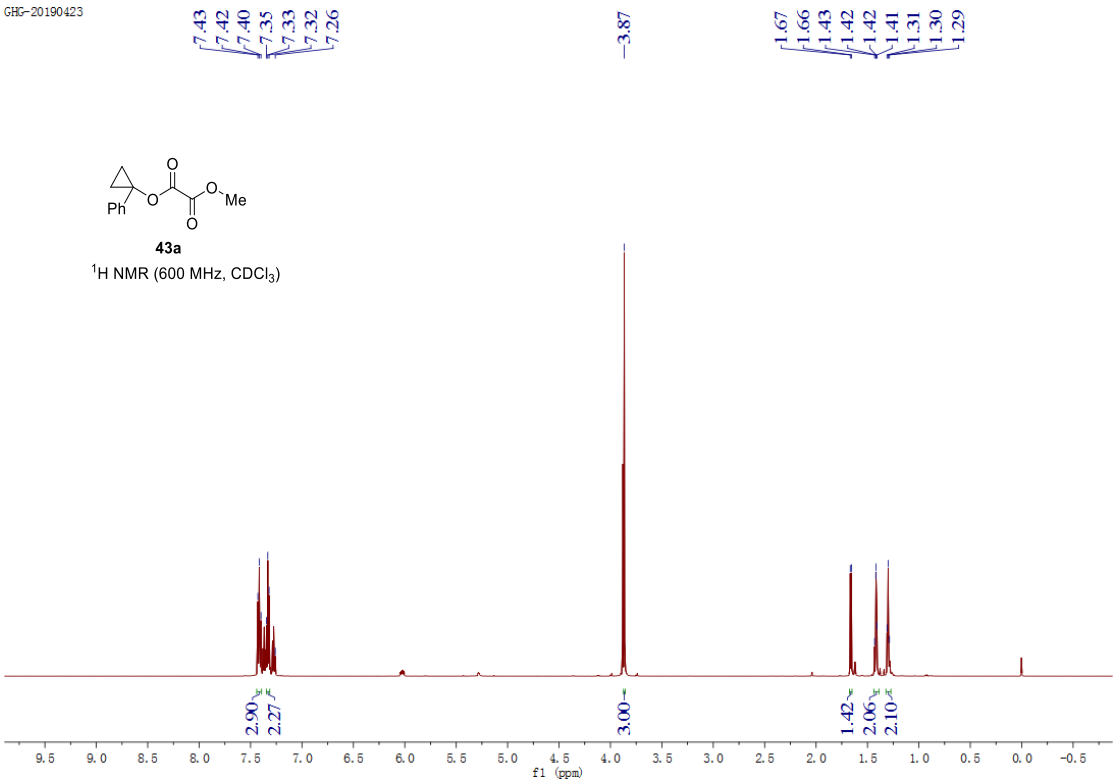
42a

^{1}H NMR (600 MHz, $CDCl_3$)



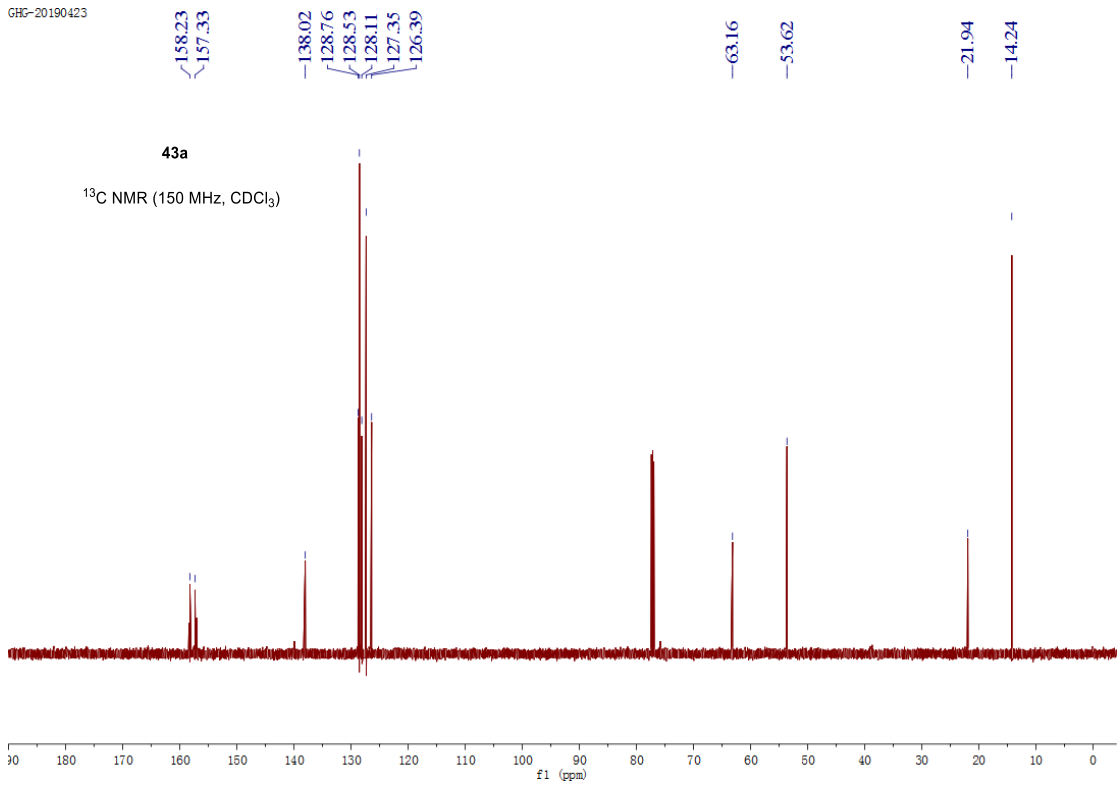
42a

^{13}C NMR (150 MHz, $CDCl_3$)



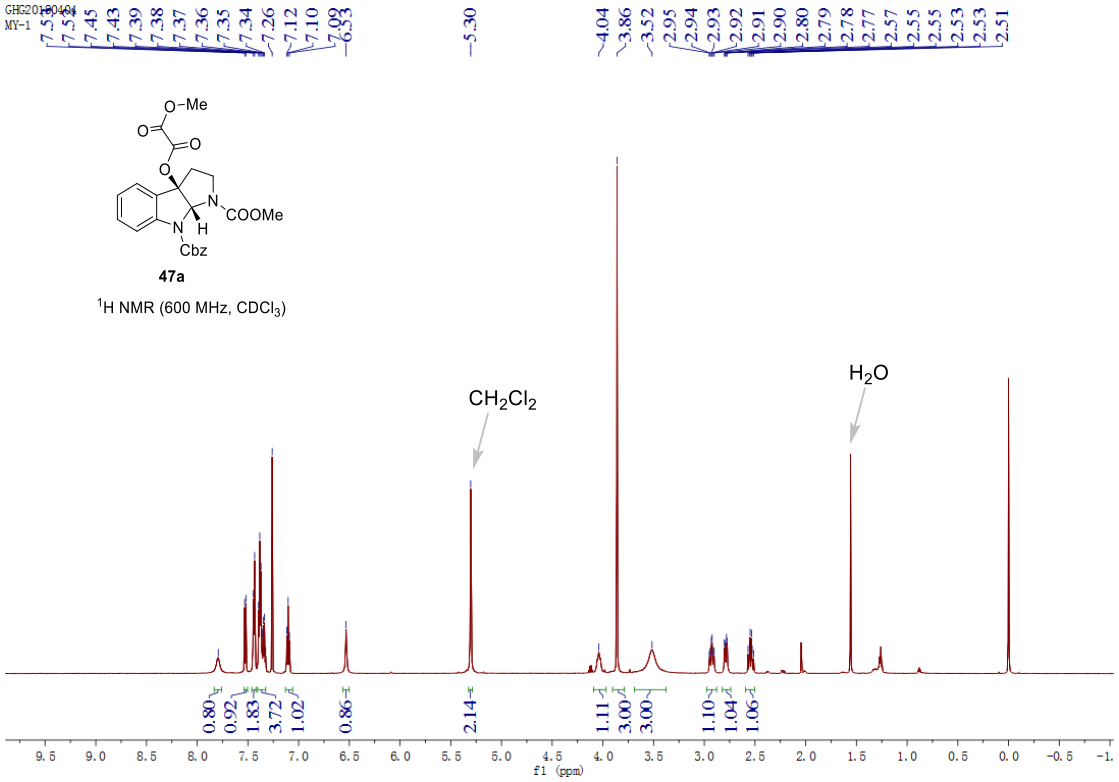
43a

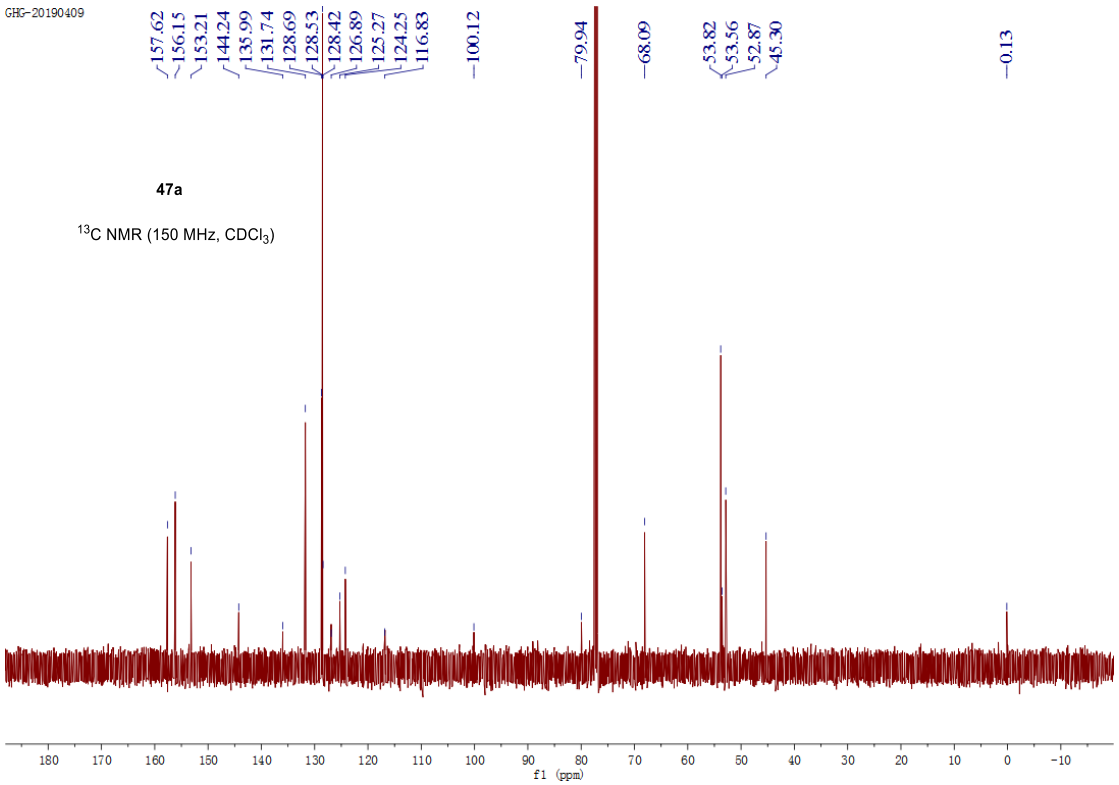
^{1}H NMR (600 MHz, $CDCl_3$)

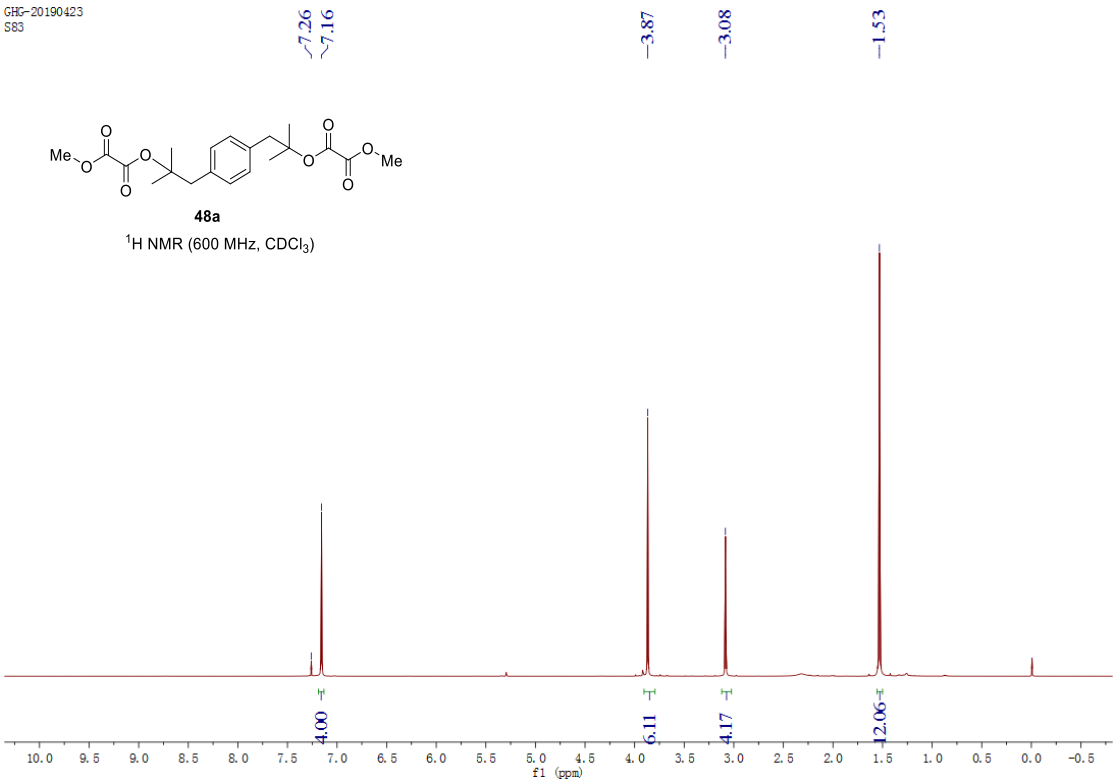


43a

^{13}C NMR (150 MHz, $CDCl_3$)

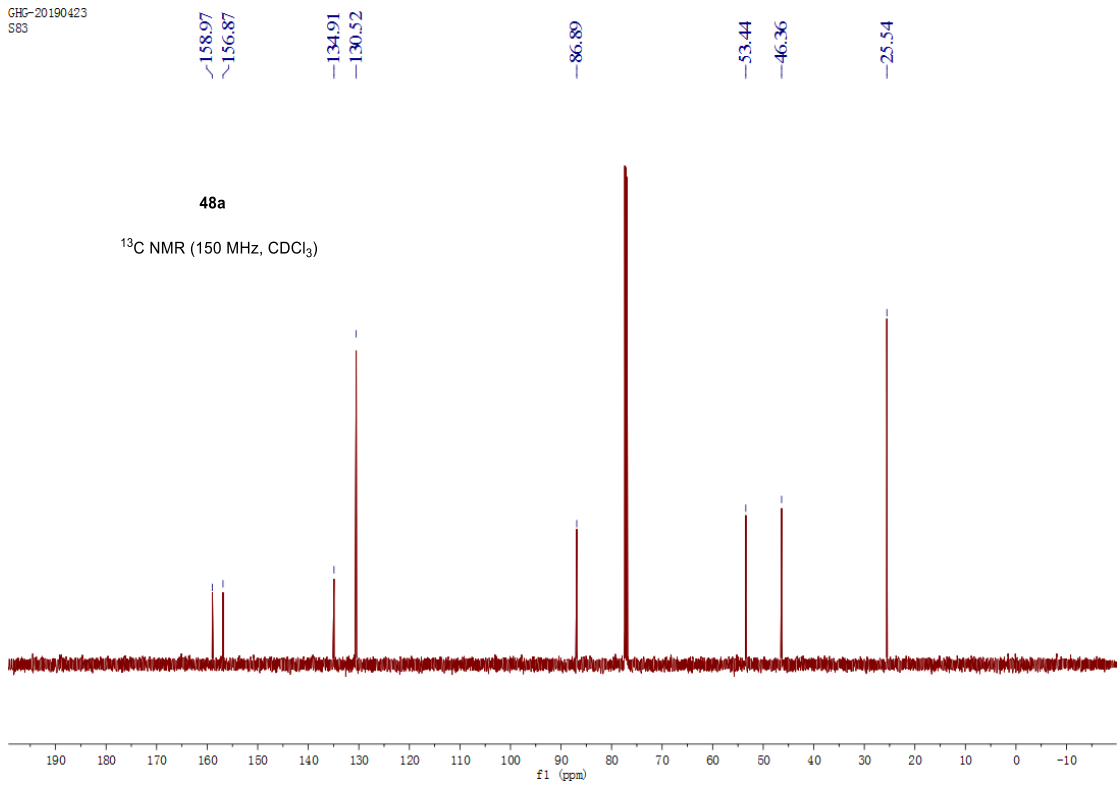

O-Me
O
O
O
N
COOMe
N
H
Cbz
47a
^{1}H NMR (600 MHz, $CDCl_3$)
CH_2Cl_2
H_2O
f1 (ppm)


GHG-20190409
47a
^{13}C NMR (150 MHz, $CDCl_3$)
f1 (ppm)



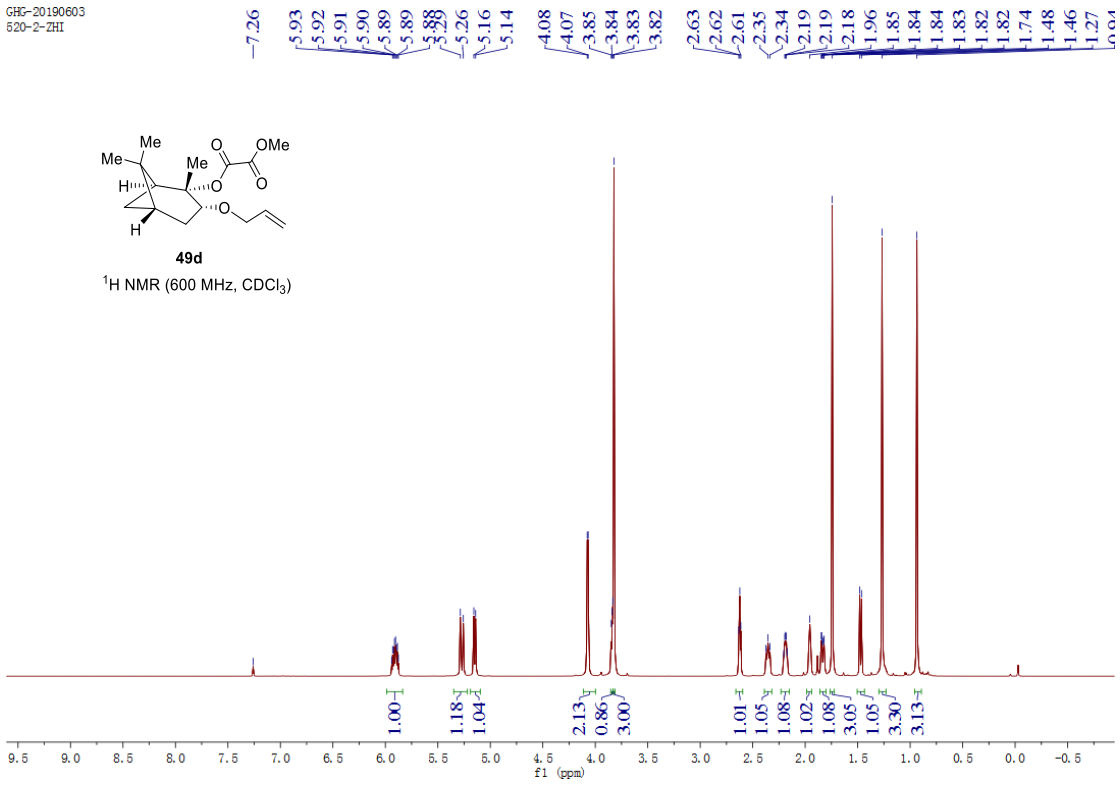
48a

^{1}H NMR (600 MHz, $CDCl_3$)



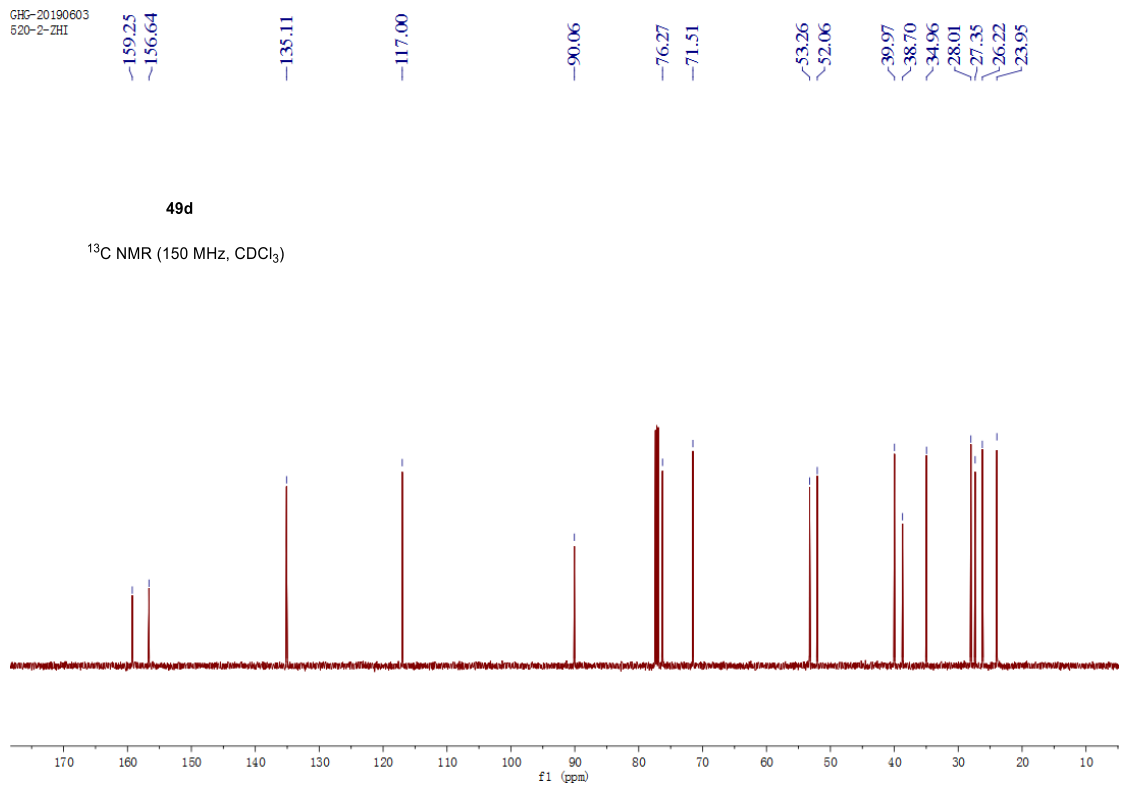
48a

^{13}C NMR (150 MHz, $CDCl_3$)



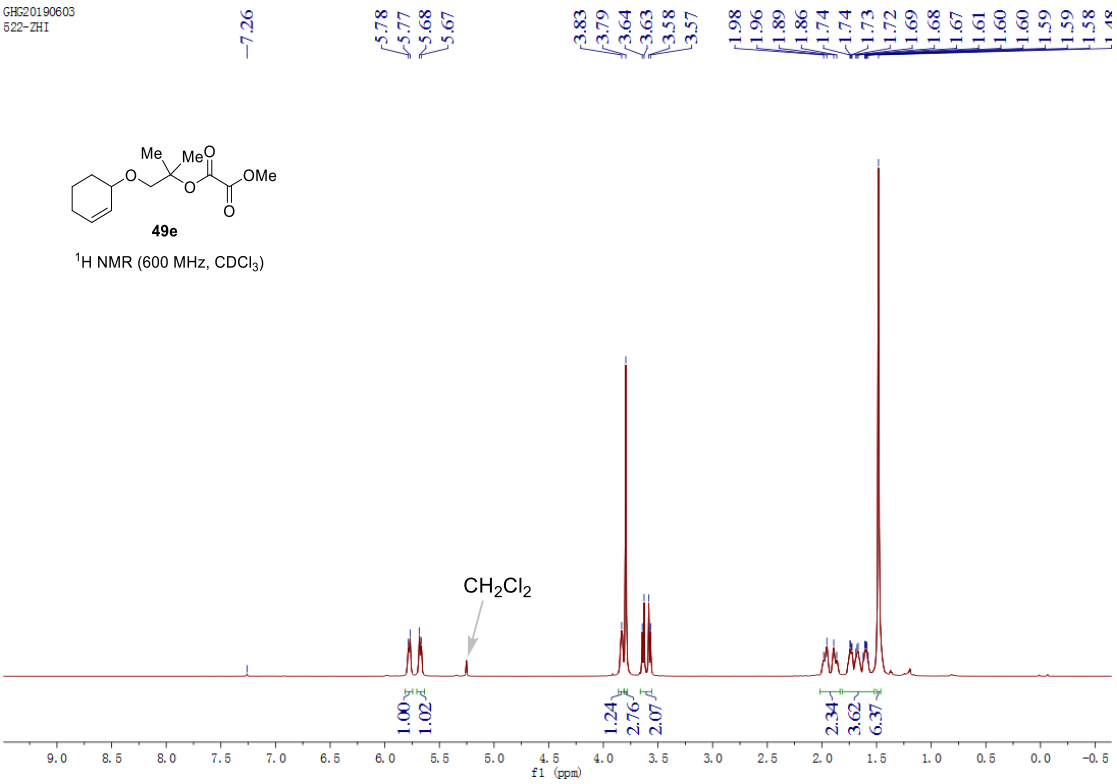
49d

^{1}H NMR (600 MHz, $CDCl_3$)



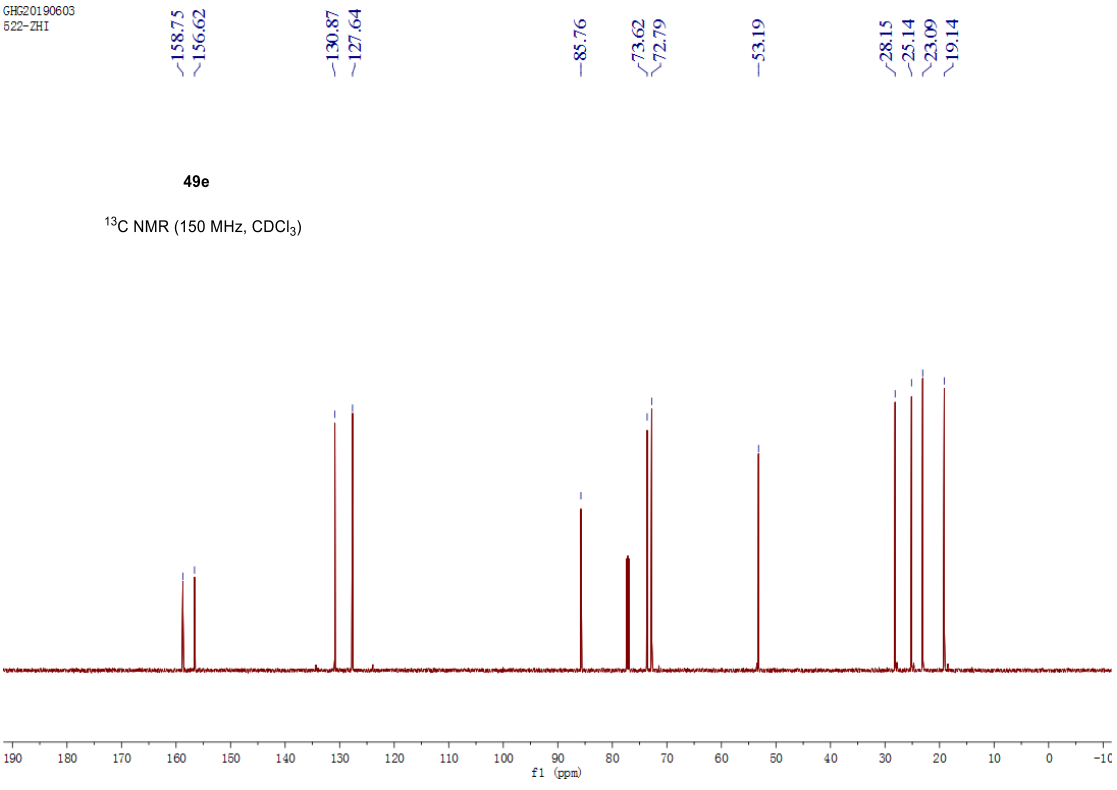
49d

^{13}C NMR (150 MHz, $CDCl_3$)



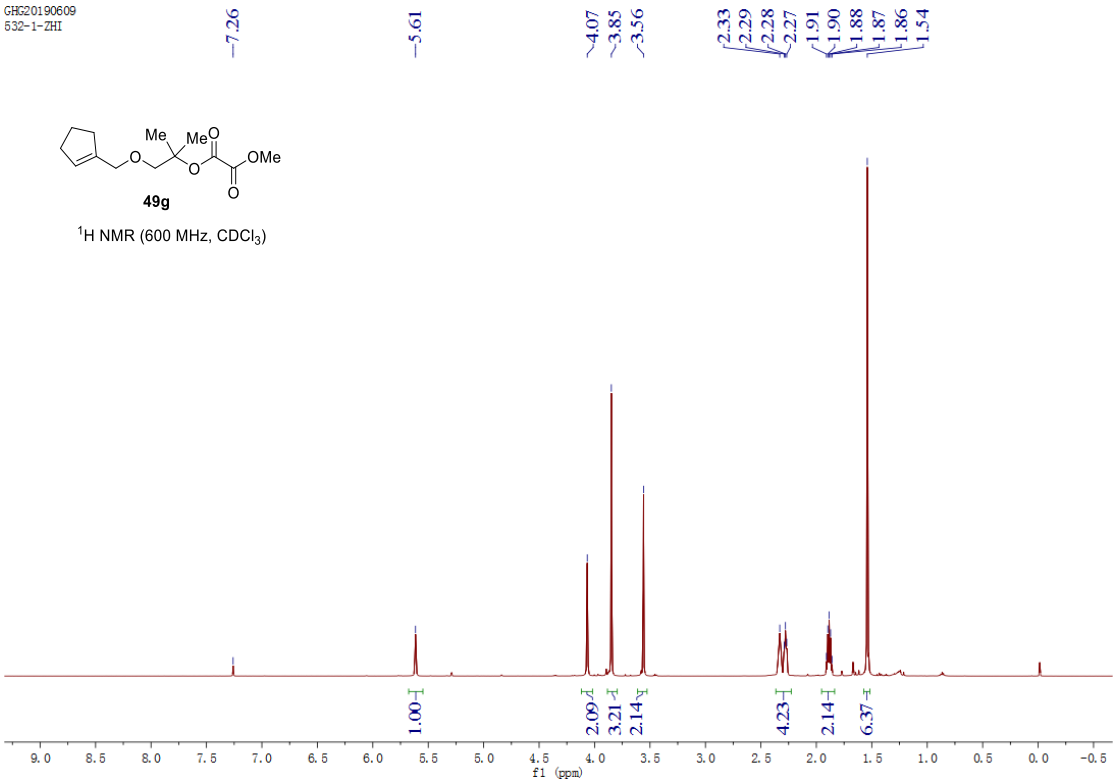
49e

^{1}H NMR (600 MHz, $CDCl_3$)



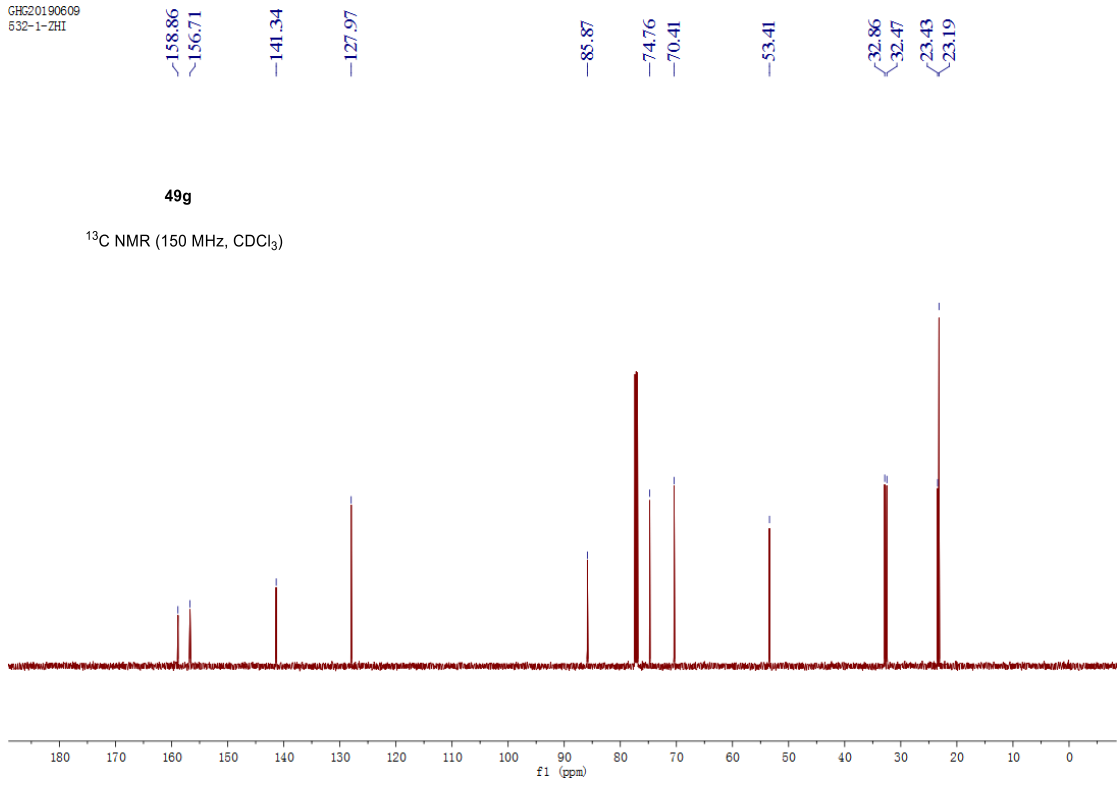
49e

^{13}C NMR (150 MHz, $CDCl_3$)



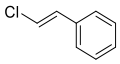
49g

^{1}H NMR (600 MHz, $CDCl_3$)



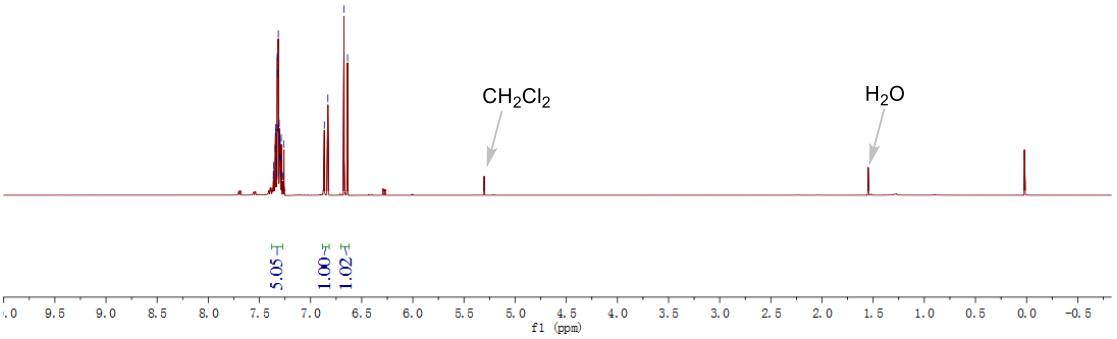
49g

^{13}C NMR (150 MHz, $CDCl_3$)



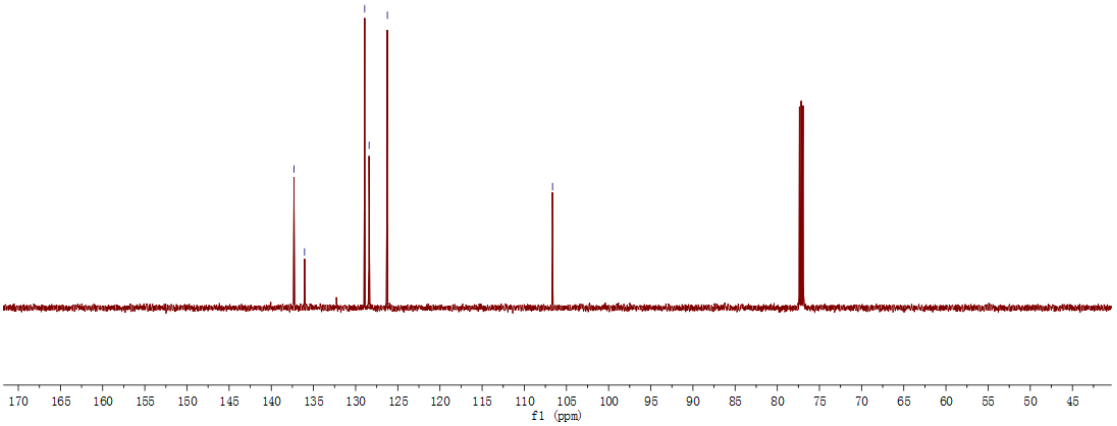
2a-Cl

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



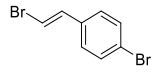
2a-Cl

^{13}C NMR (150 MHz, $CDCl_3$)



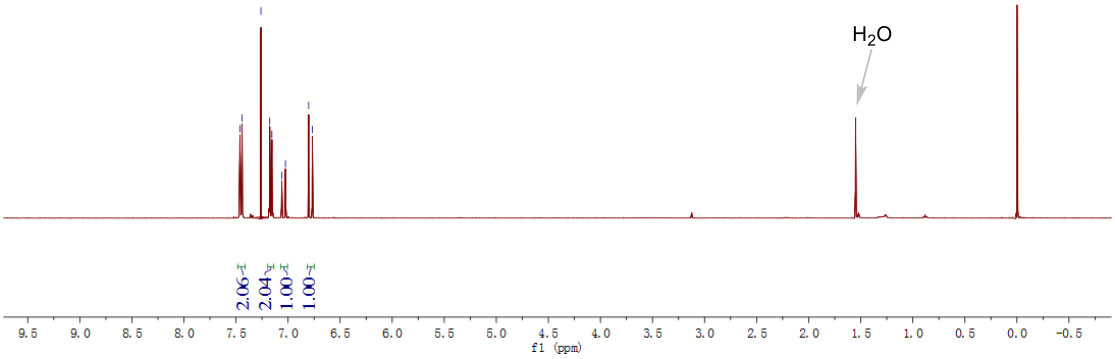
430-6
single_pulse

7.46
7.44
7.26
7.18
7.16
7.06
7.03
6.80
6.77



2h

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

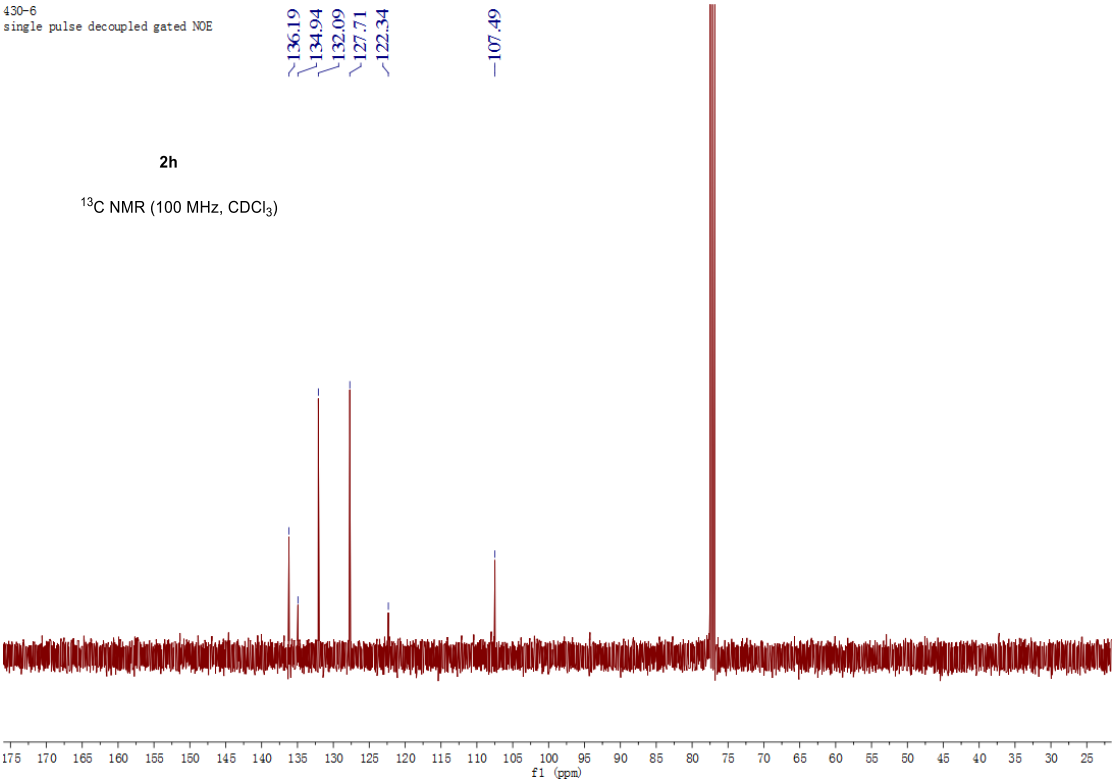


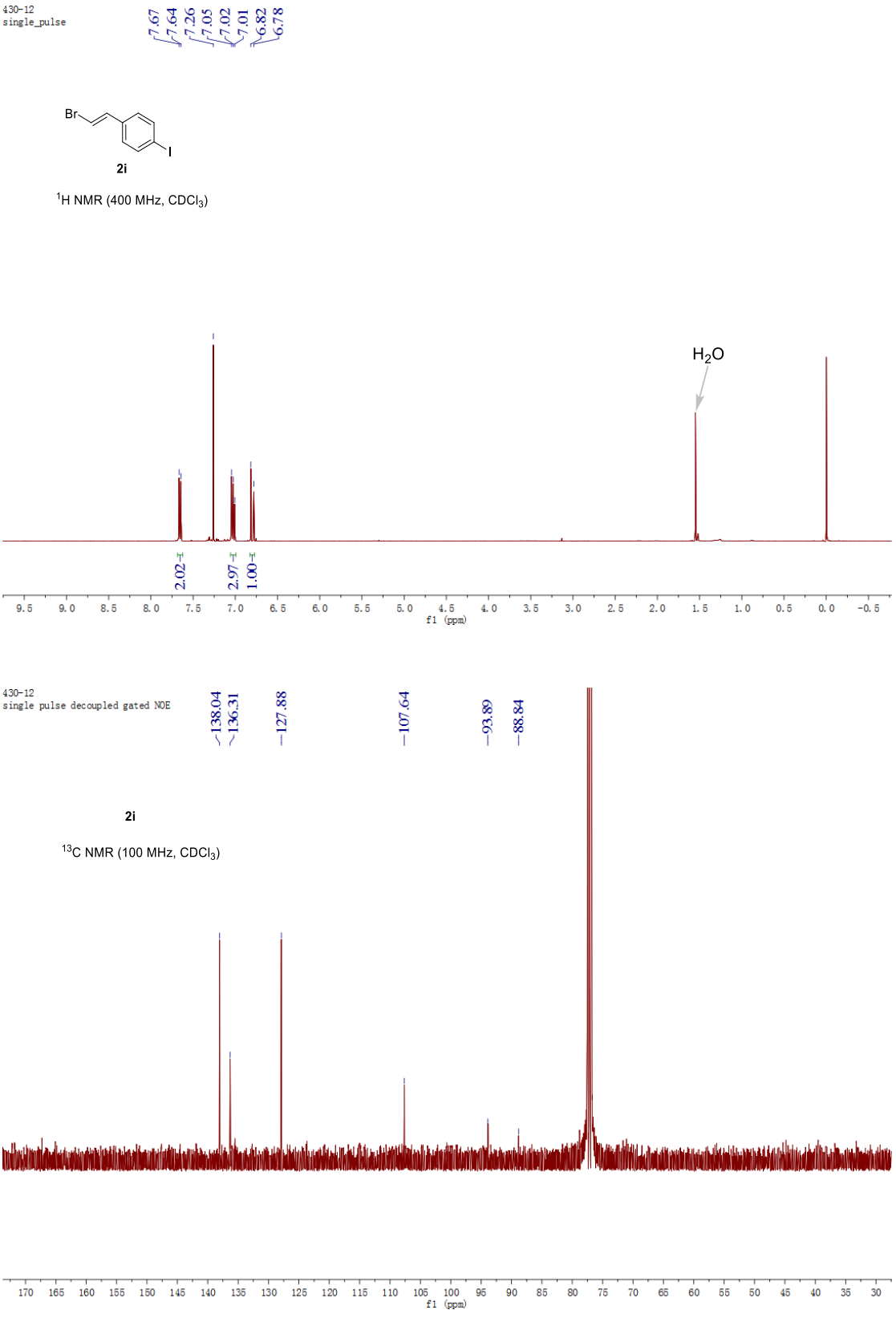
430-6
single pulse decoupled gated NOE

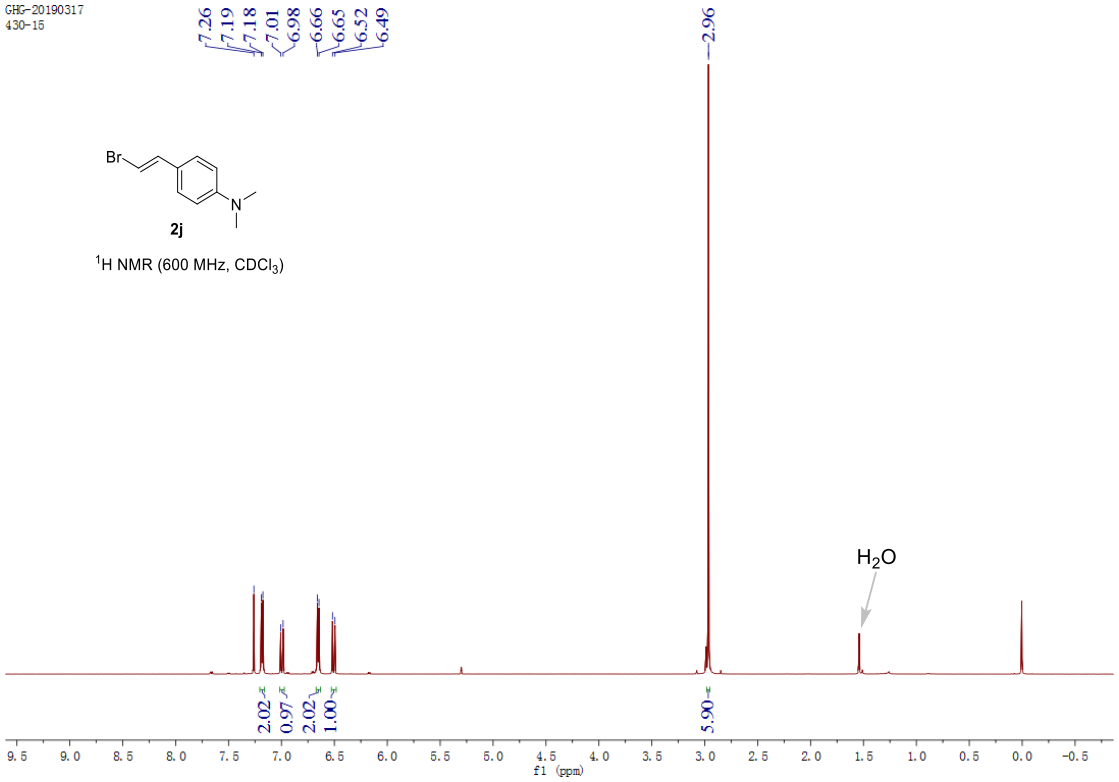
136.19
134.94
132.09
127.71
122.34
107.49

2h

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

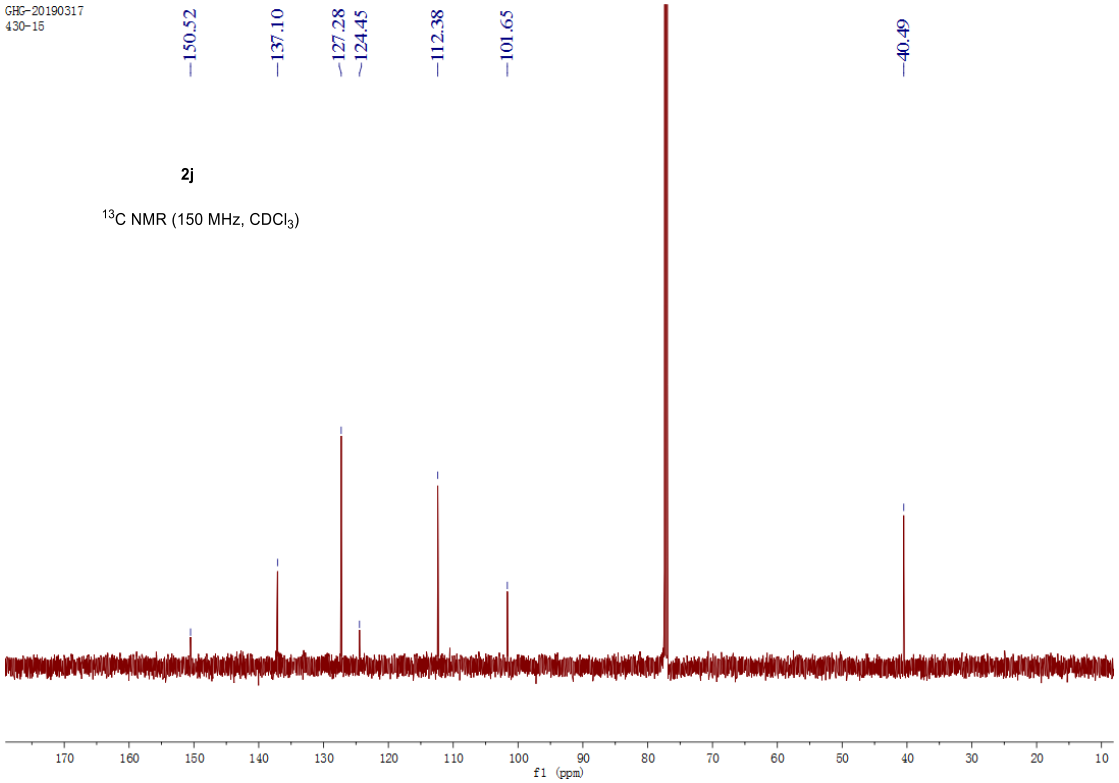



430-12
single_pulse
7.67
7.64
7.26
7.05
7.02
7.01
6.82
6.78
Br
I
2i
^{1}H NMR (400 MHz, CDCl$_3$)
H$_2$O
2.02
2.97
1.00
f1 (ppm)
430-12
single pulse decoupled gated NOE
138.04
136.31
127.88
107.64
93.89
88.84
2i
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



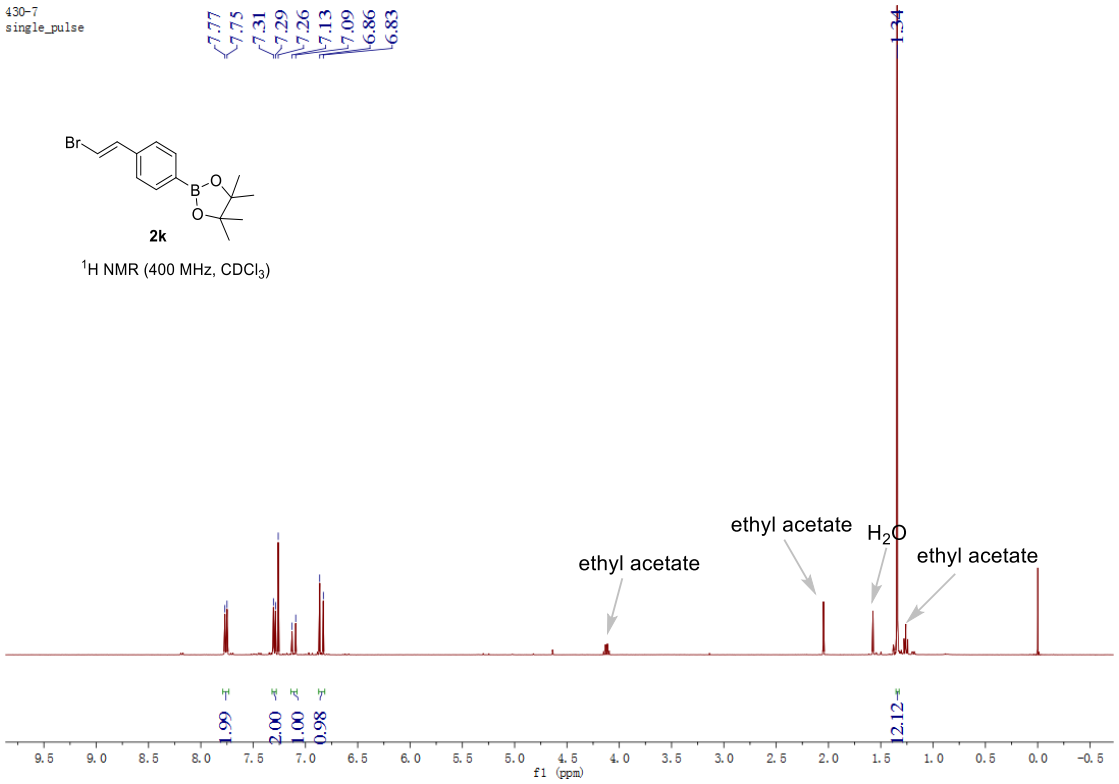
2j

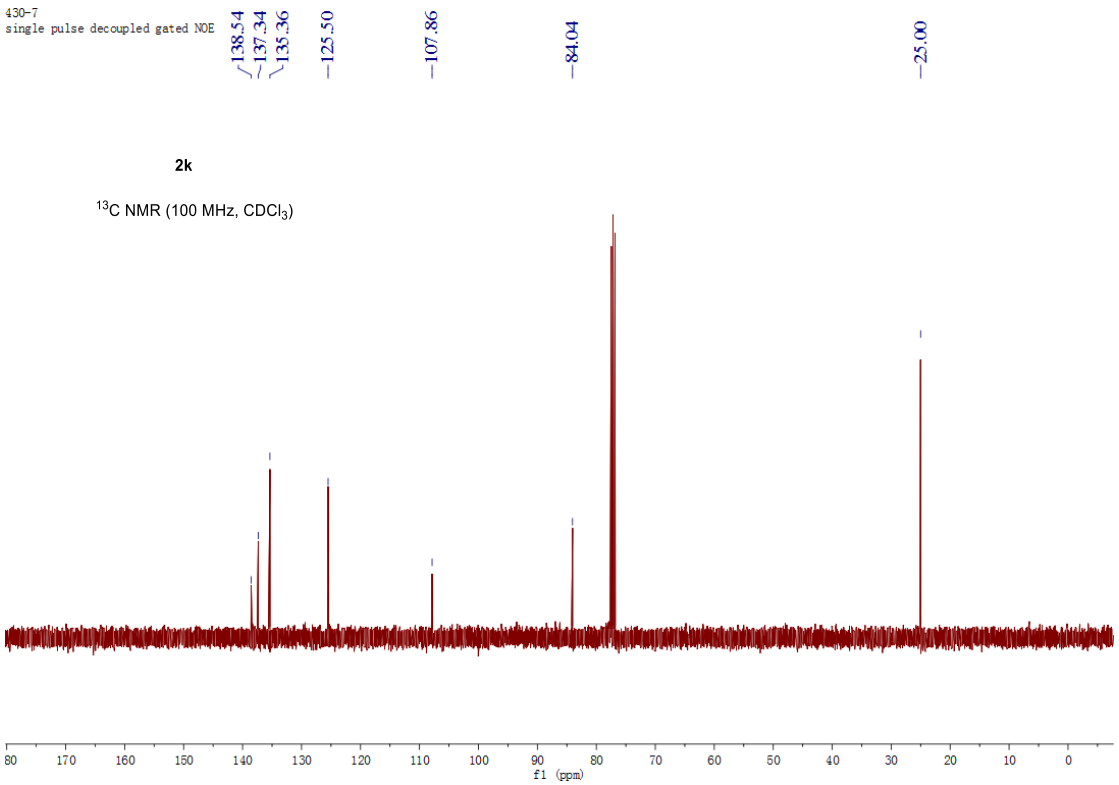
^{1}H NMR (600 MHz, $CDCl_3$)

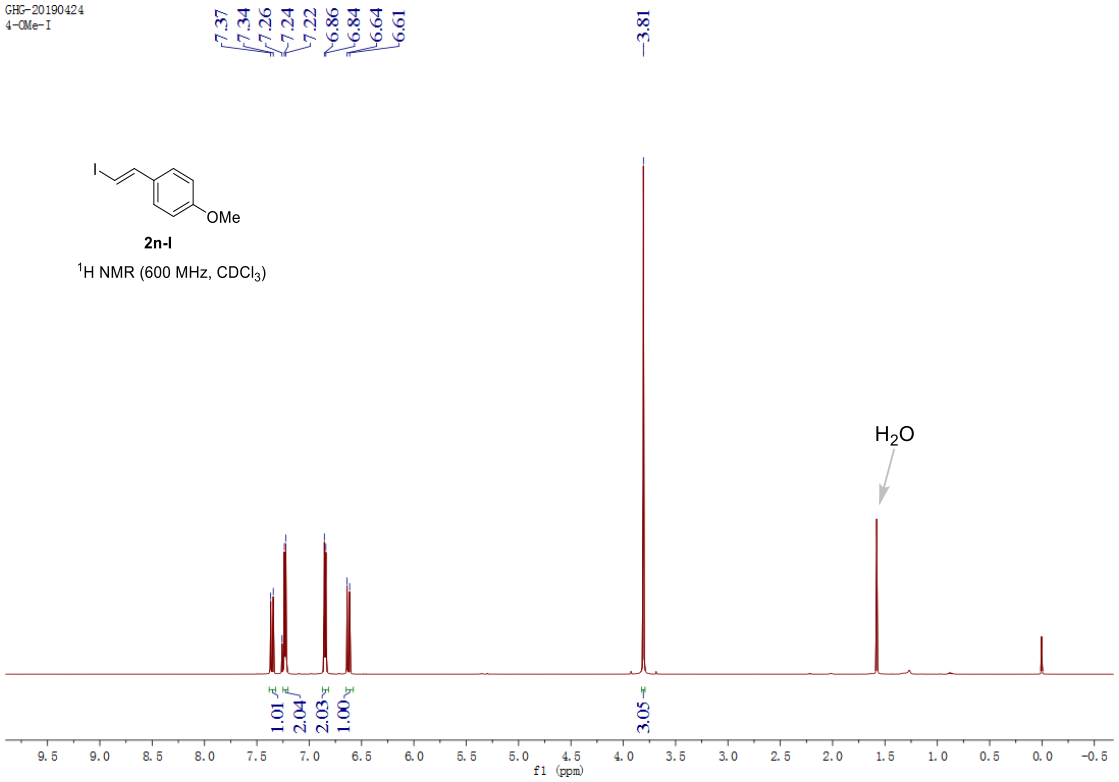


2j

^{13}C NMR (150 MHz, $CDCl_3$)

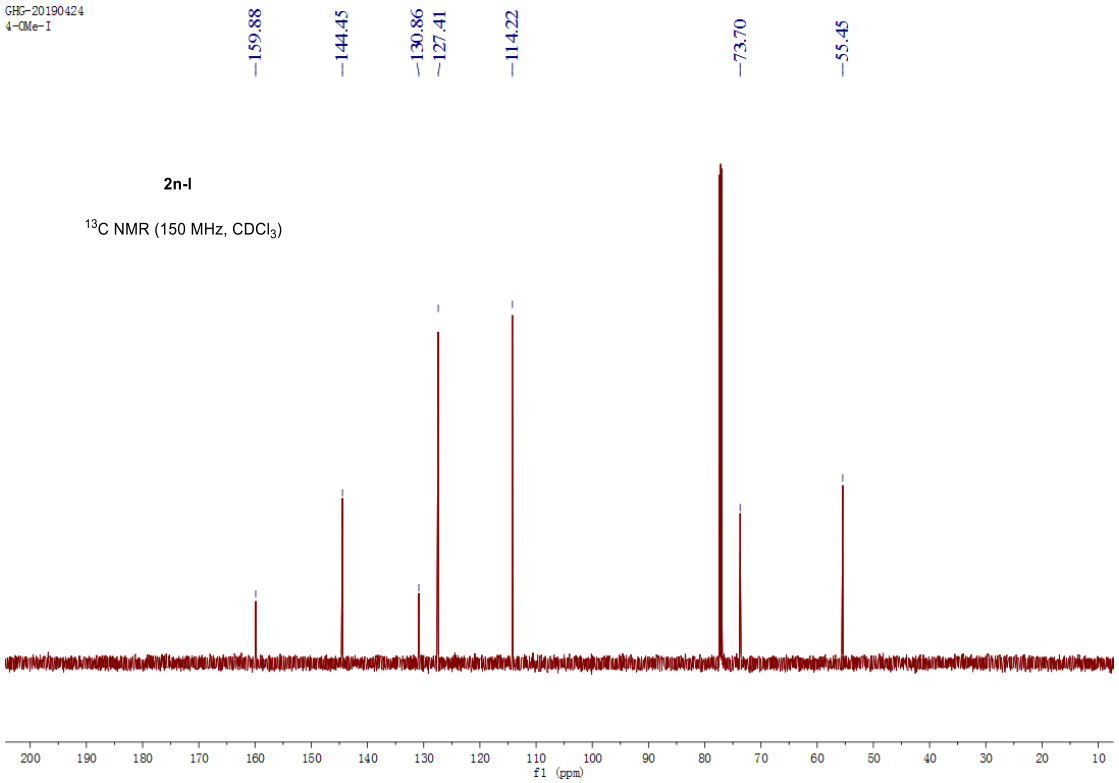

430-7
single_pulse
7.77
7.75
7.31
7.29
7.26
7.13
7.09
6.86
6.83
1.34
Br
B
O
O
2k
^{1}H NMR (400 MHz, CDCl$_3$)
ethyl acetate
ethyl acetate
H$_2$O
ethyl acetate
1.99
2.00
1.00
0.98
12.12
f1 (ppm)


430-7
single pulse decoupled gated NOE
138.54
137.34
135.36
125.50
107.86
84.04
25.00
2k
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)



2n-l

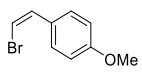
^{1}H NMR (600 MHz, $CDCl_3$)



2n-l

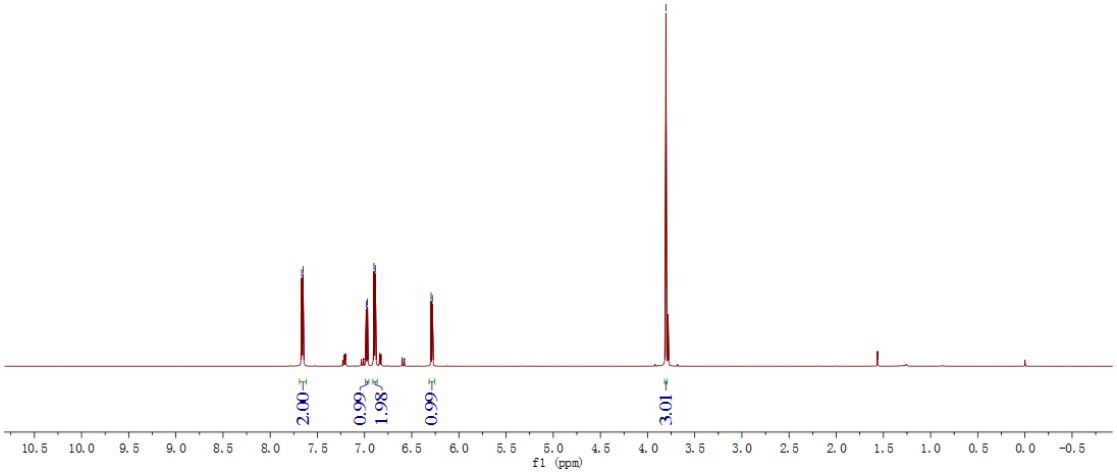
^{13}C NMR (150 MHz, $CDCl_3$)

GHG-20190424
4-OMe-Z



Z-2n

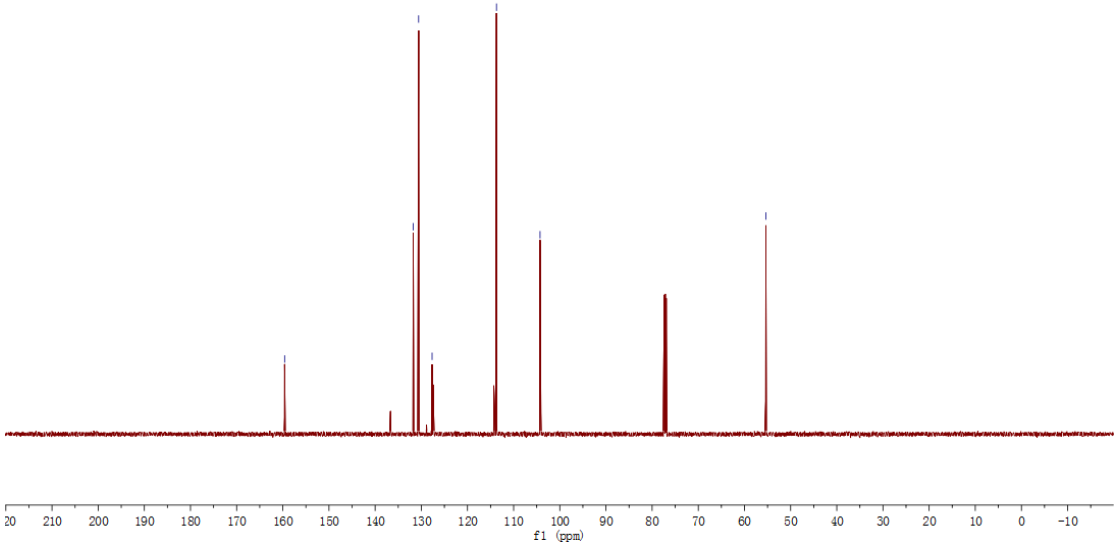
^{1}H NMR (600 MHz, $CDCl_3$)

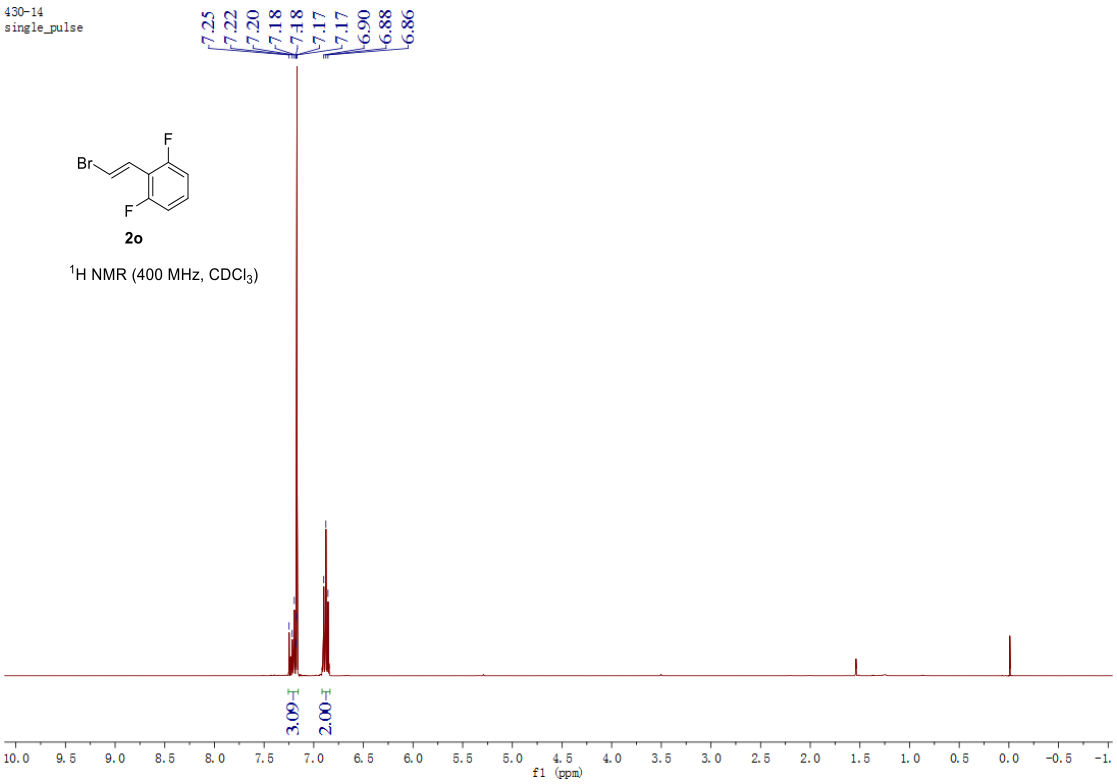


GHG-20190424
4-OMe-Z

Z-2n

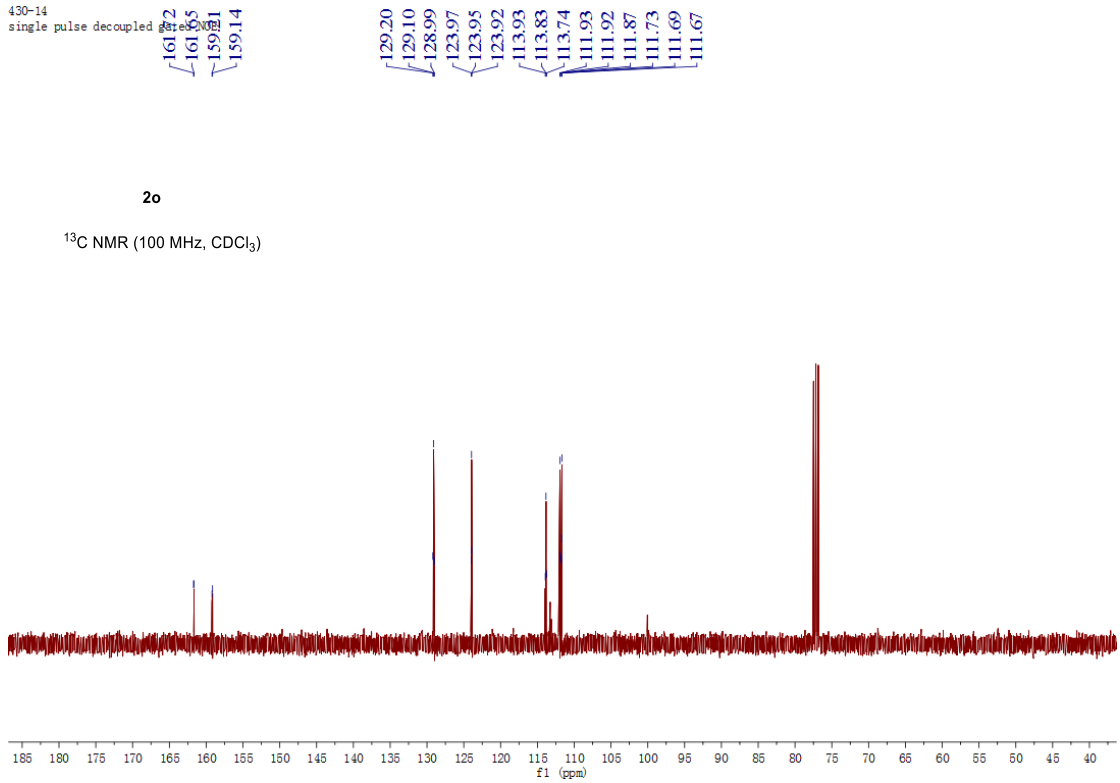
^{13}C NMR (150 MHz, $CDCl_3$)





2o

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

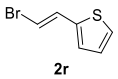


2o

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

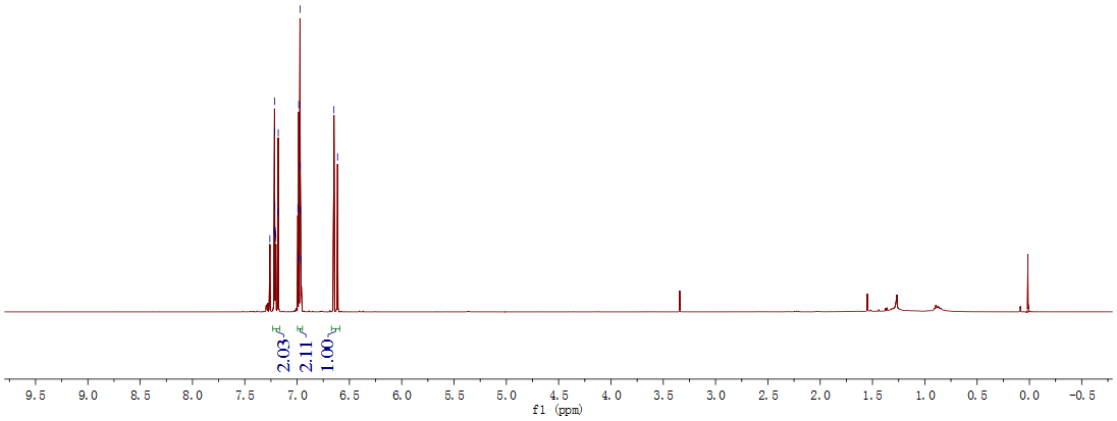
426-S-Br
single_pulse

7.26 7.22 7.22 7.22 7.21 7.21 7.20 7.20 7.18 7.18 6.99 6.98 6.98 6.97 6.97 6.97 6.96 6.65 6.61



2r

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

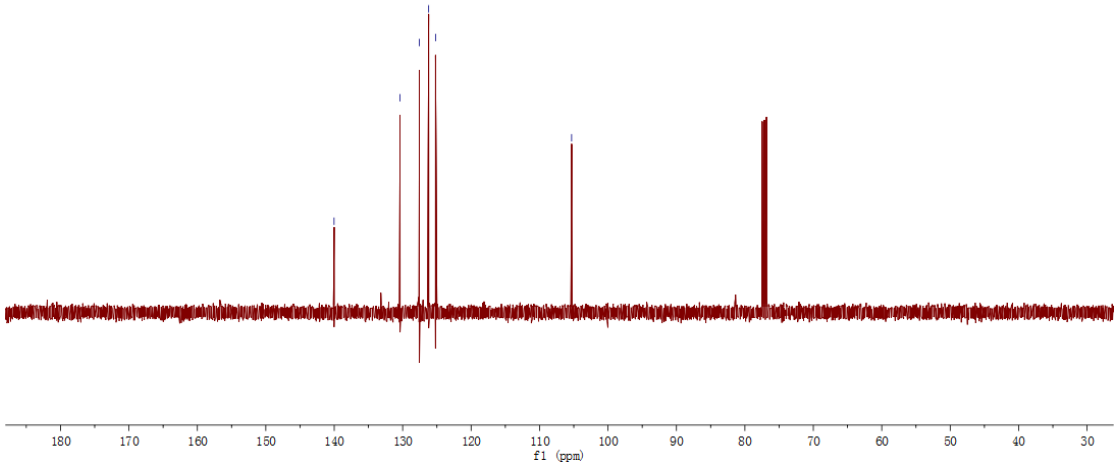


426-S-Br
single pulse decoupled gated NOE

140.02 130.38 127.56 126.20 125.20 105.32

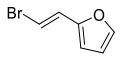
2r

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



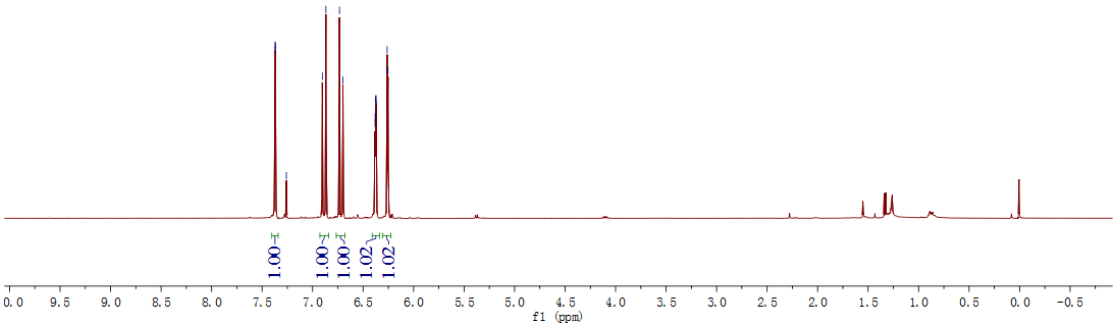
426-O-Br
single_pulse

7.37
7.37
7.37
7.26
6.90
6.87
6.73
6.70
6.38
6.38
6.38
6.38
6.37
6.37
6.37
6.26
6.25



2s

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

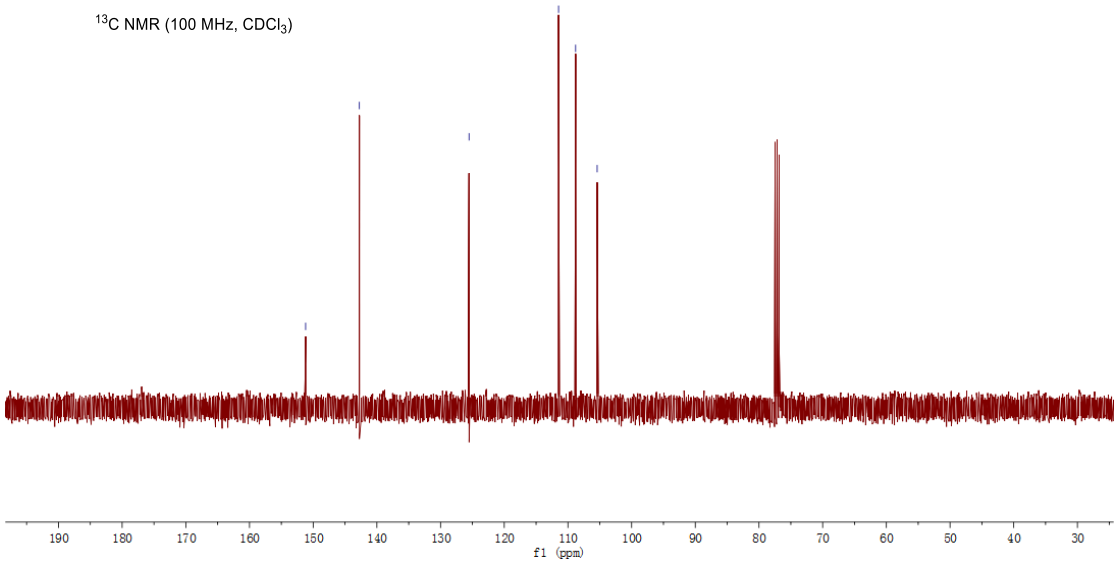


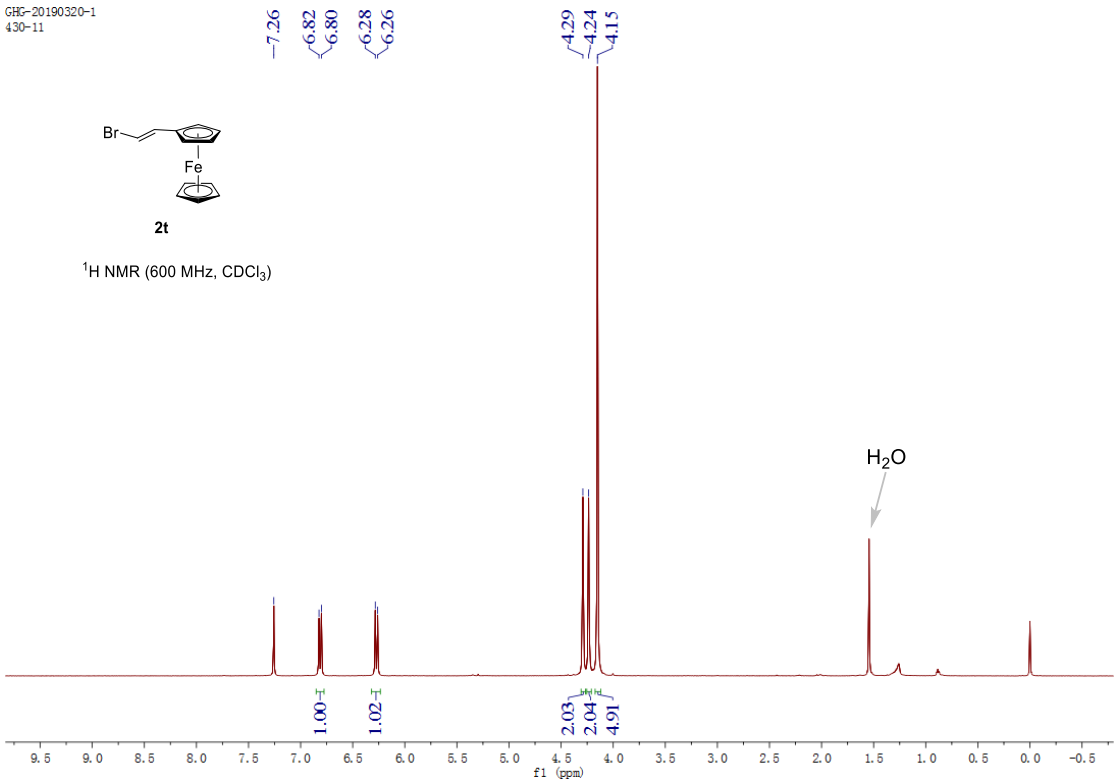
426-O-Br
single pulse decoupled gated NOE

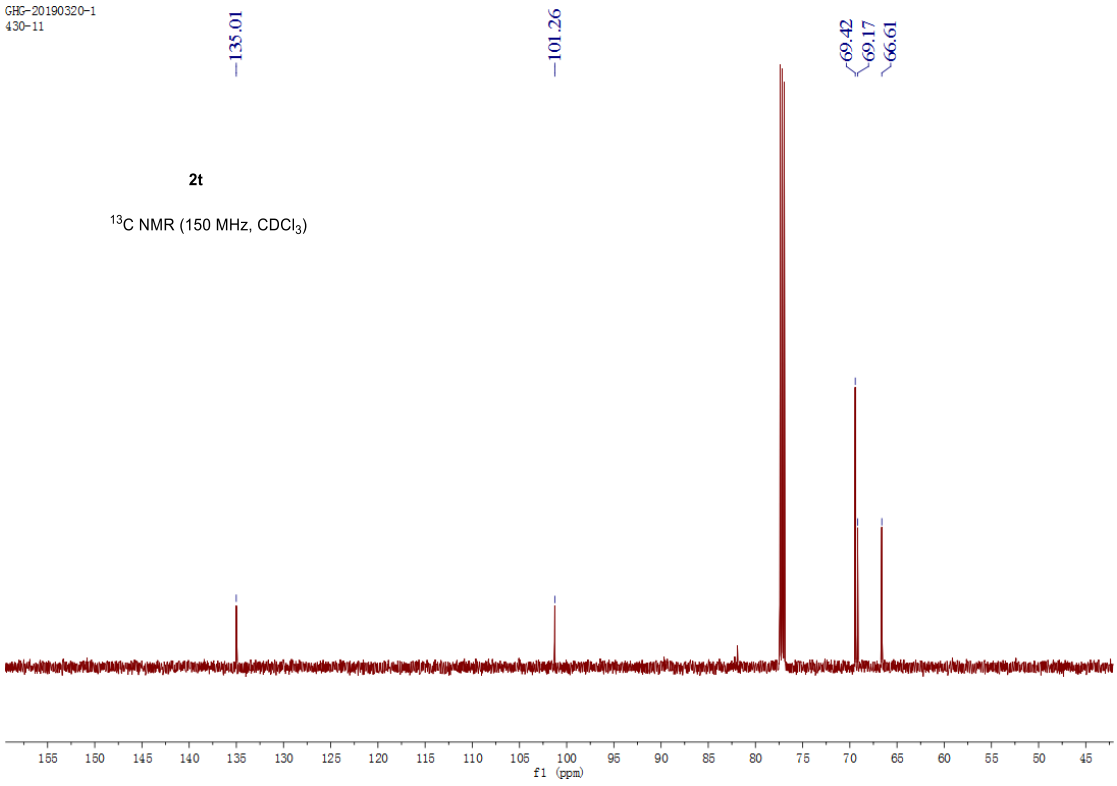
151.19
142.75
125.53
111.47
108.79
105.41

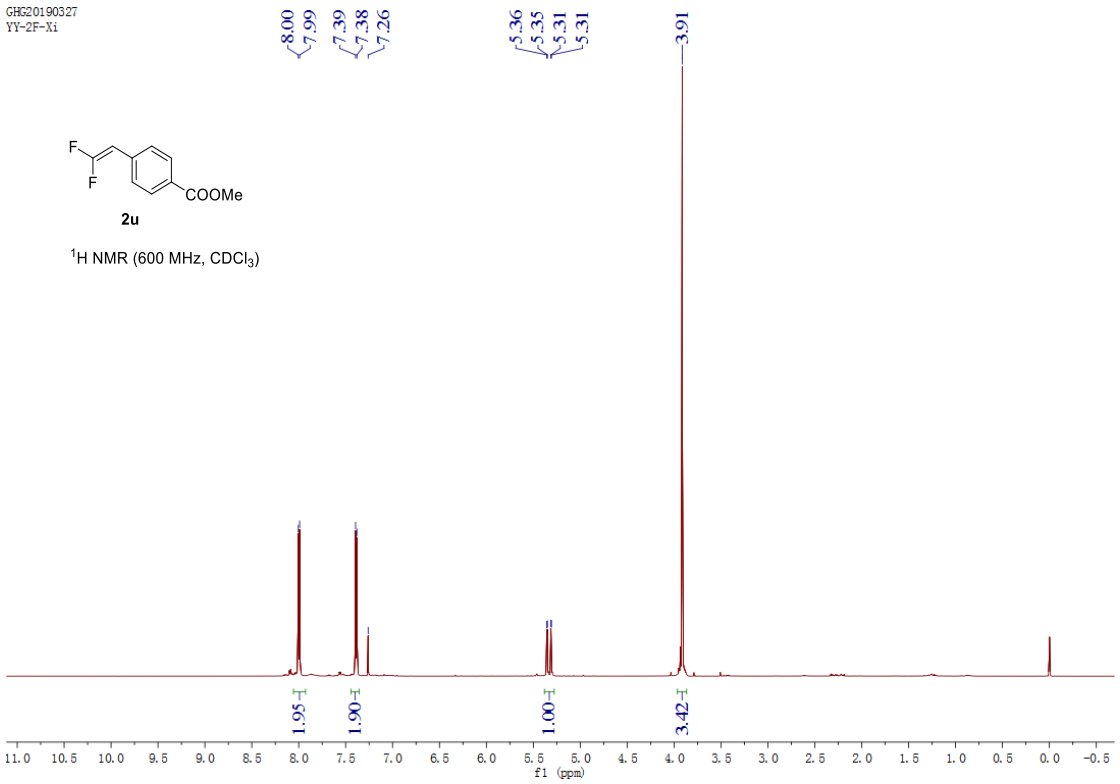
2s

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



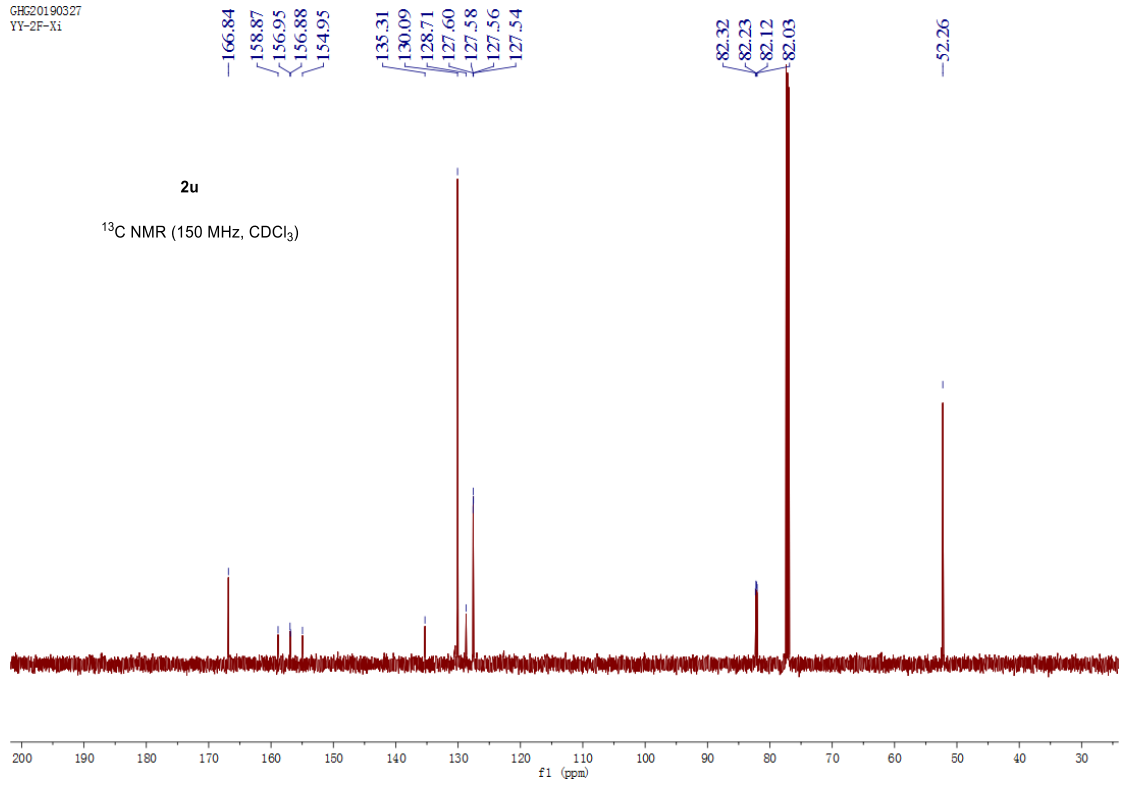

GHG-20190320-1
430-11
7.26
6.82
6.80
6.28
6.26
4.29
4.24
4.15
Br
Fe
2t
1H NMR (600 MHz, CDCl3)
H2O
1.00
1.02
2.03
2.04
4.91
f1 (ppm)


GHG-20190320-1
430-11
135.01
101.26
69.42
69.17
66.61
2t
13C NMR (150 MHz, CDCl3)
f1 (ppm)



2u

^{1}H NMR (600 MHz, $CDCl_3$)

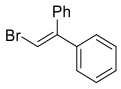


2u

^{13}C NMR (150 MHz, $CDCl_3$)

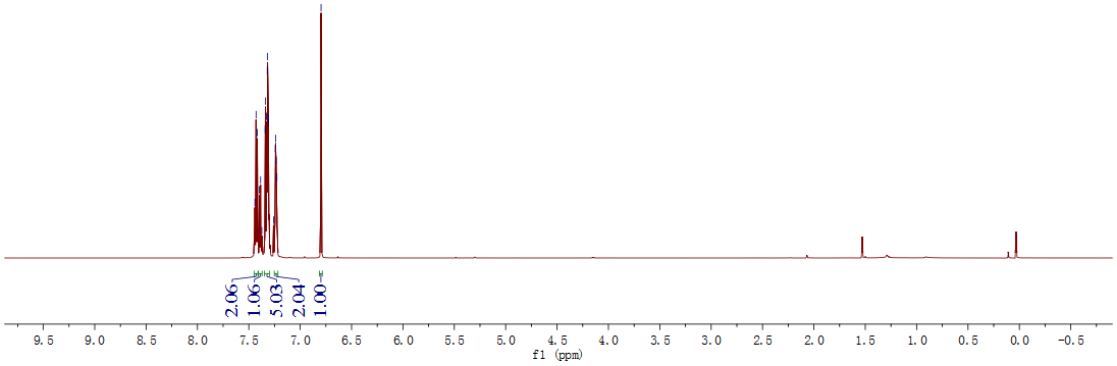
GHG-20190322
423-36-B

7.44 7.43 7.42 7.40 7.39 7.37 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.26 7.24 7.24 7.23 7.23 6.80



2x

^{1}H NMR (600 MHz, $CDCl_3$)

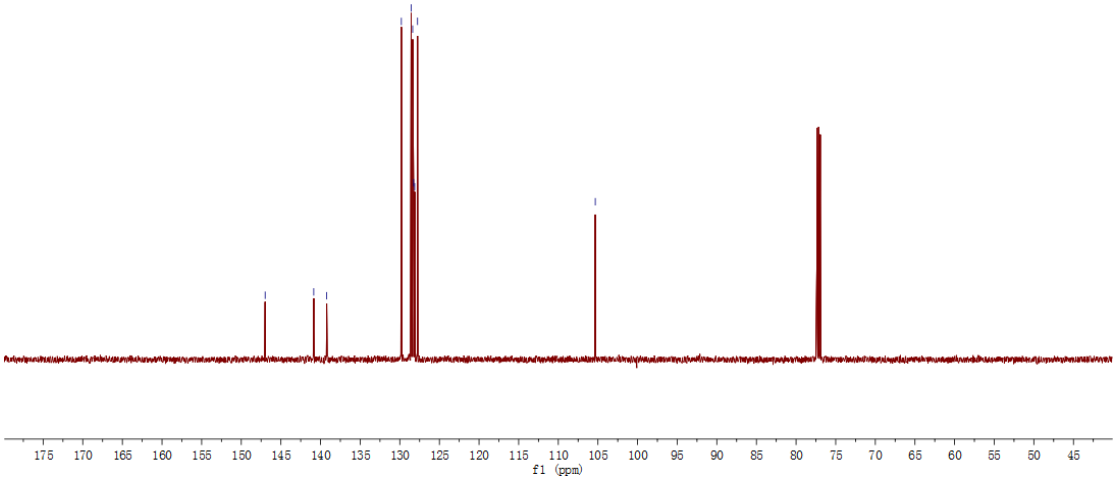


GHG-20190322
423-36-B

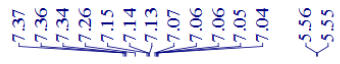
146.99 140.86 139.22 129.80 128.57 128.37 128.26 128.12 127.76 105.33

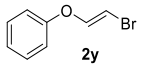
2x

^{13}C NMR (150 MHz, $CDCl_3$)



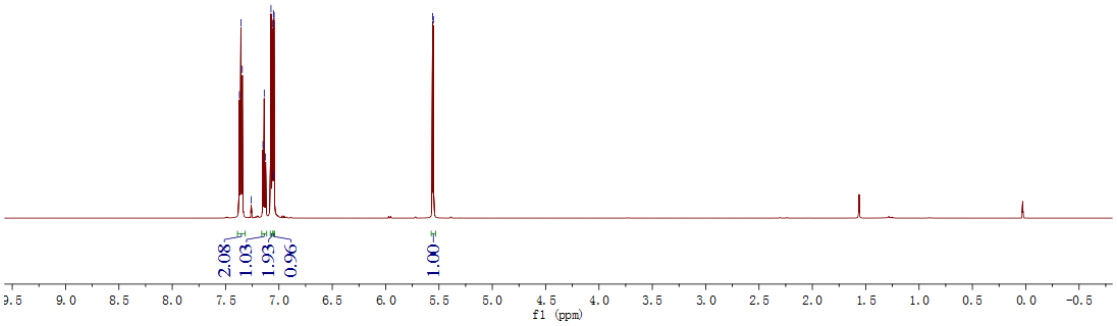
GHG-20190530
PhO-xixiu



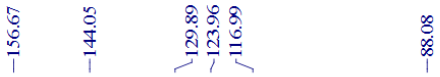


2y

^{1}H NMR (600 MHz, $CDCl_3$)

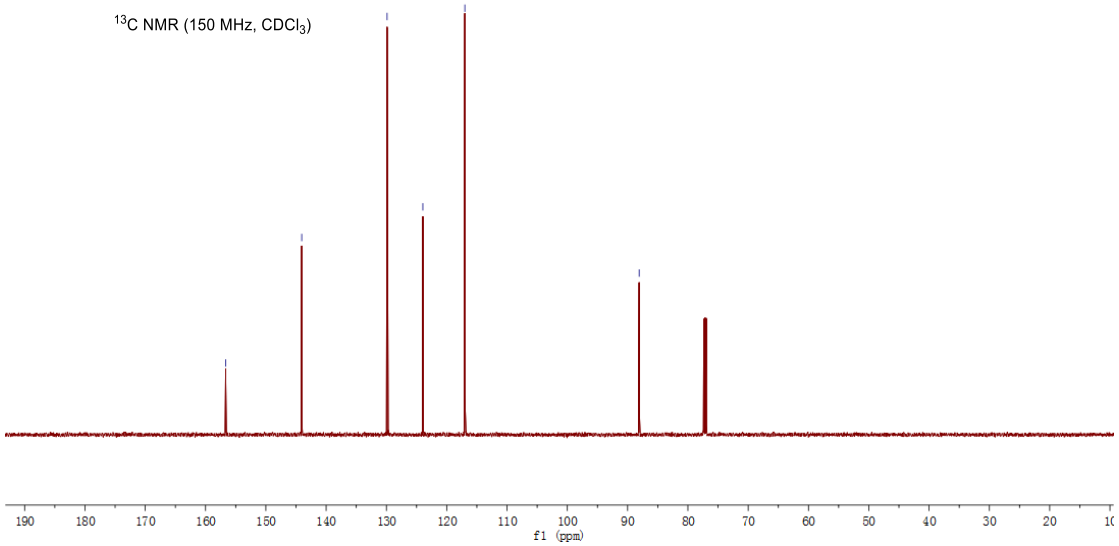


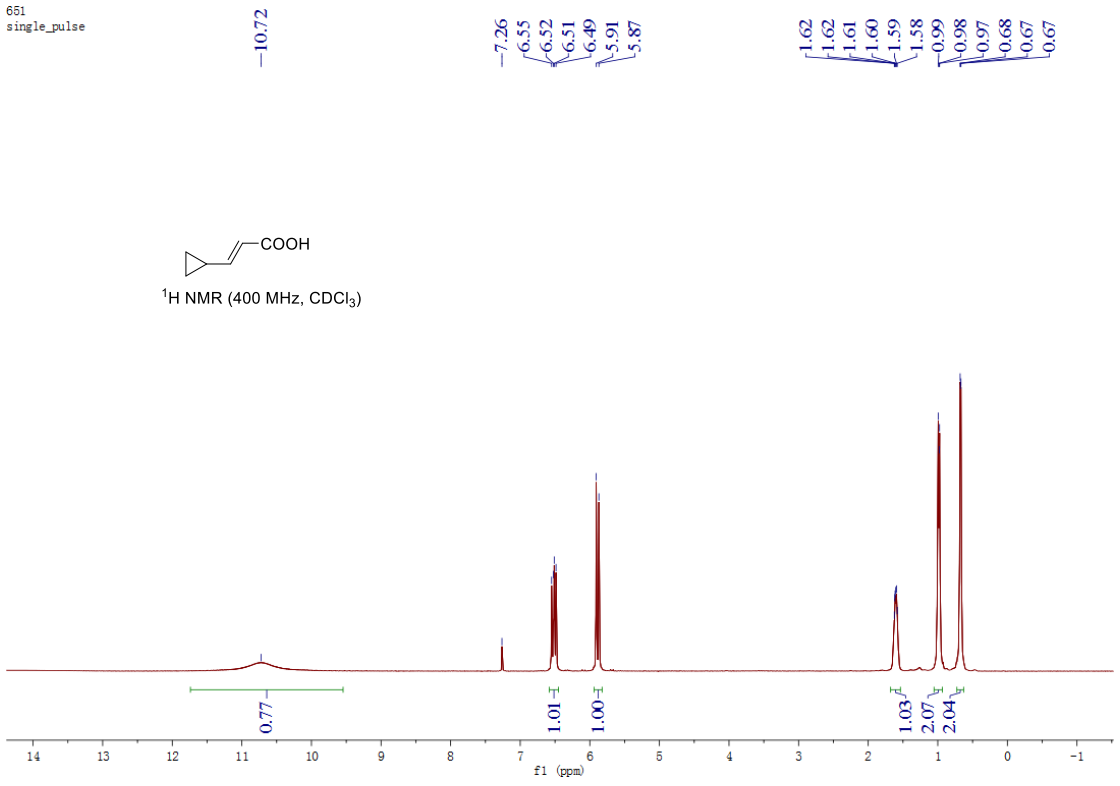
GHG-20190530
PhO-xixiu



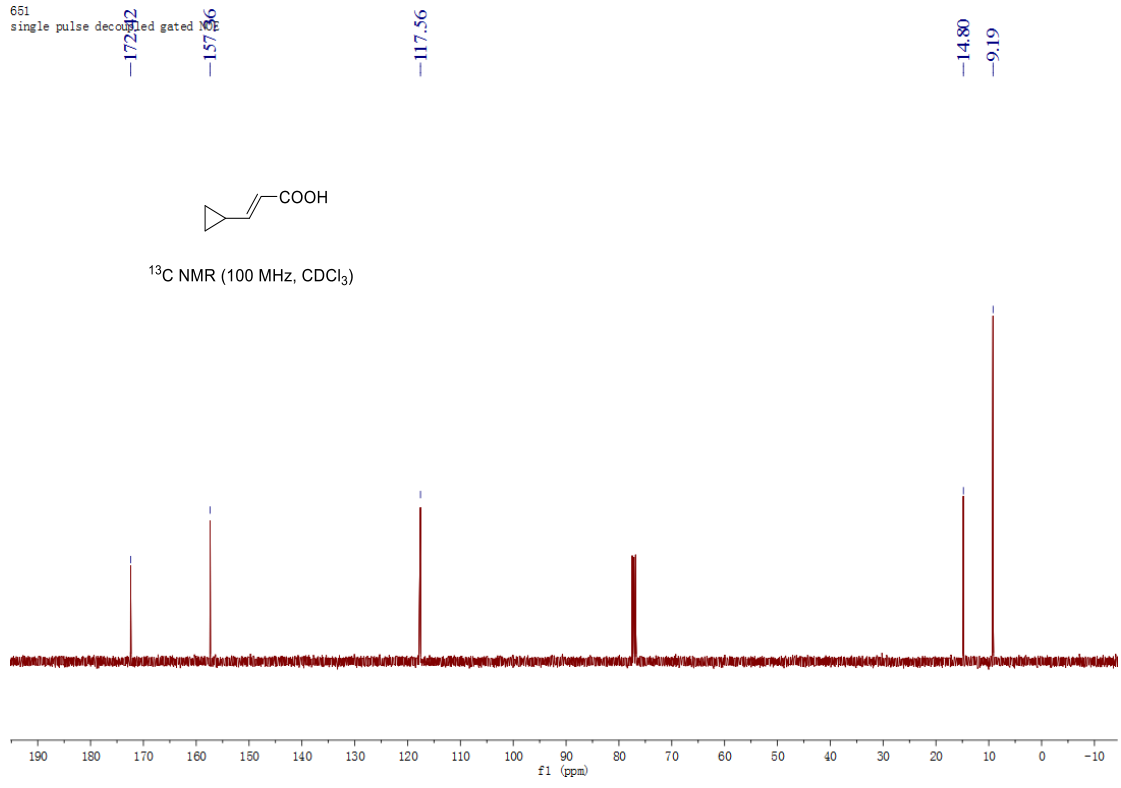
2y

^{13}C NMR (150 MHz, $CDCl_3$)

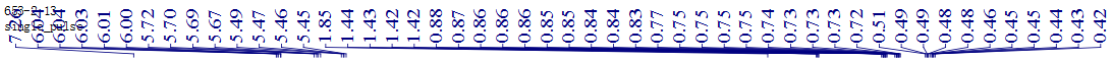


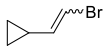


^{1}H NMR (400 MHz, $CDCl_3$)

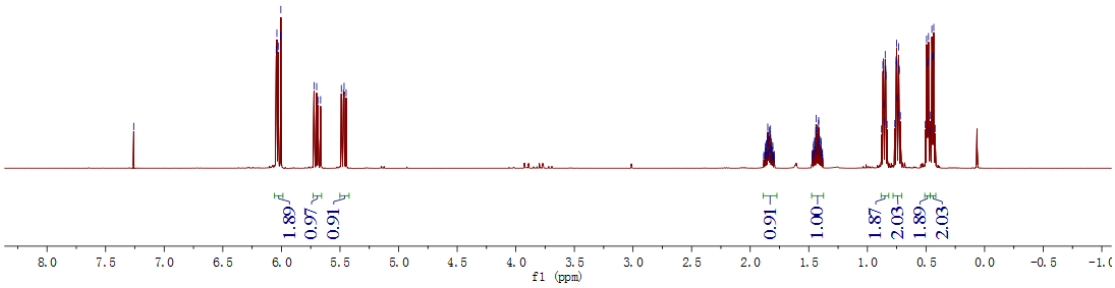


^{13}C NMR (100 MHz, $CDCl_3$)

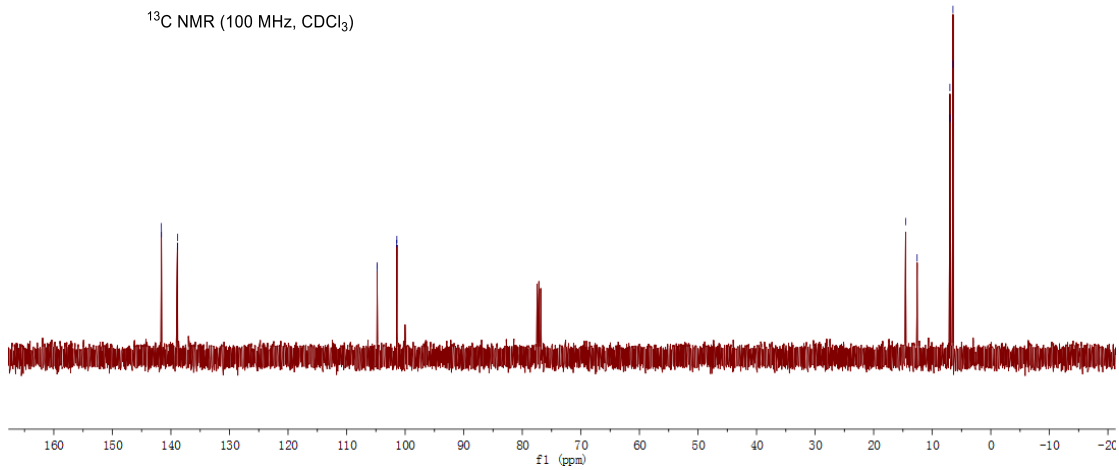


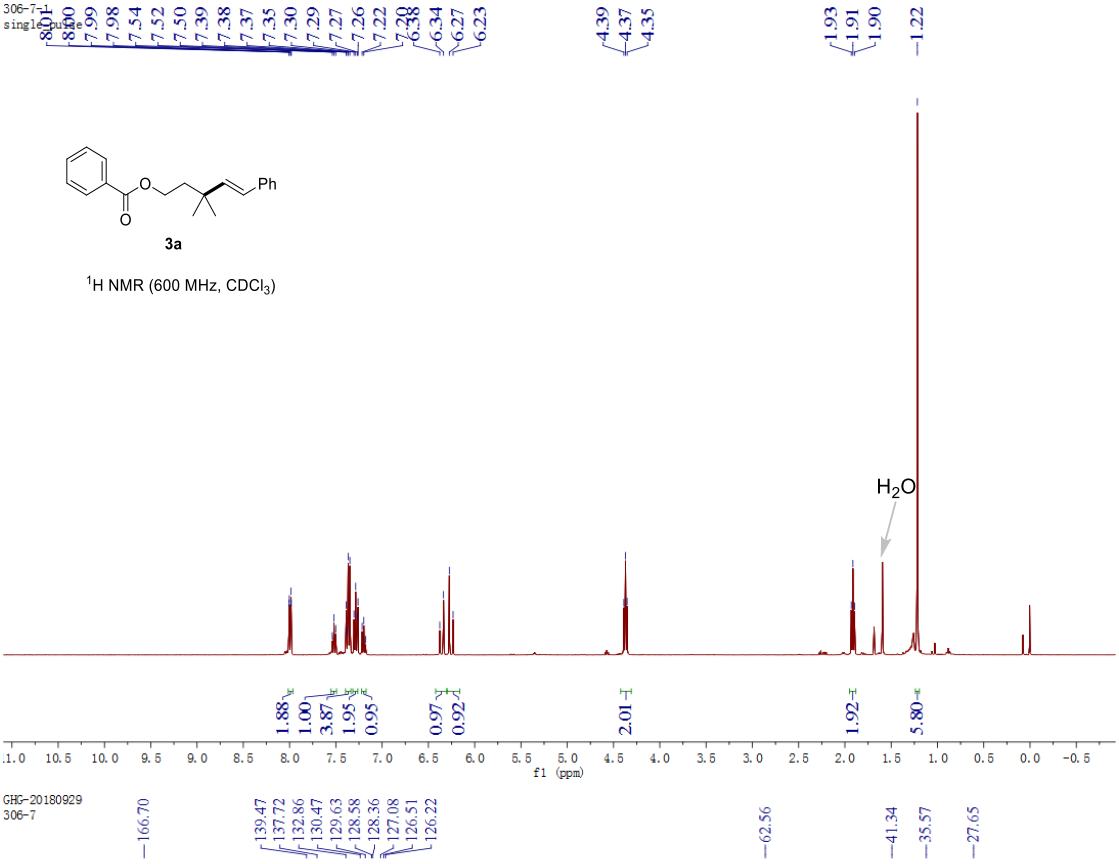


^{1}H NMR (400 MHz, $CDCl_3$)



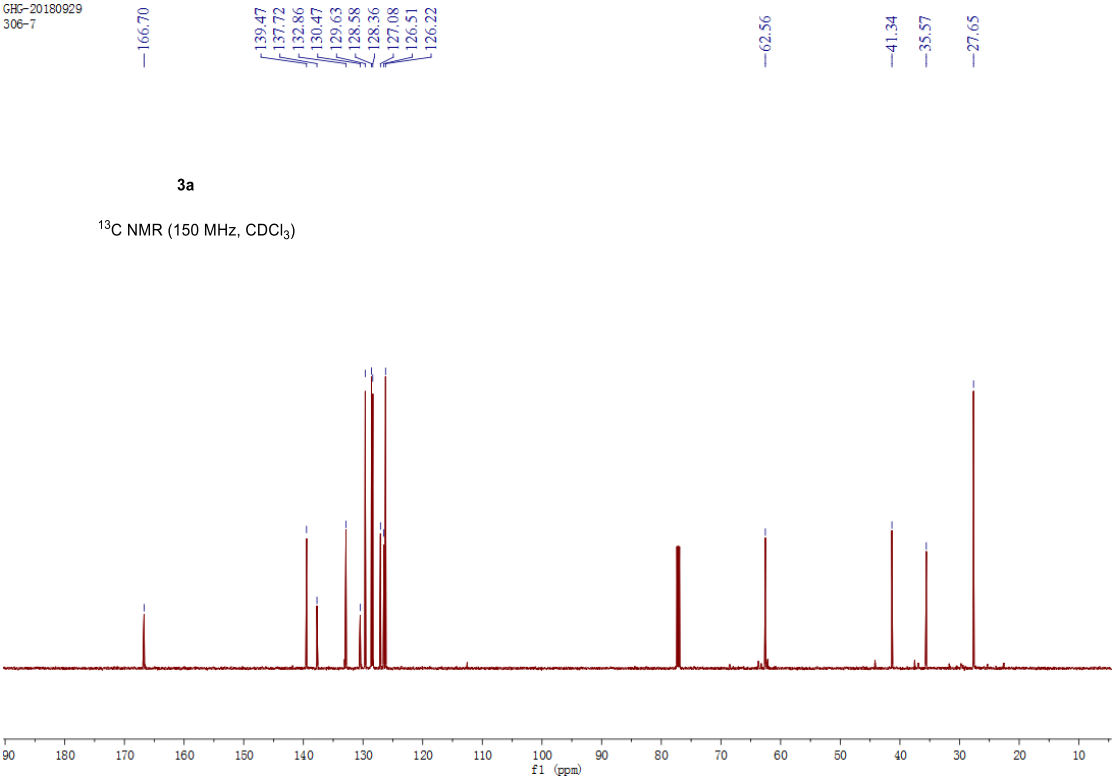
^{13}C NMR (100 MHz, $CDCl_3$)





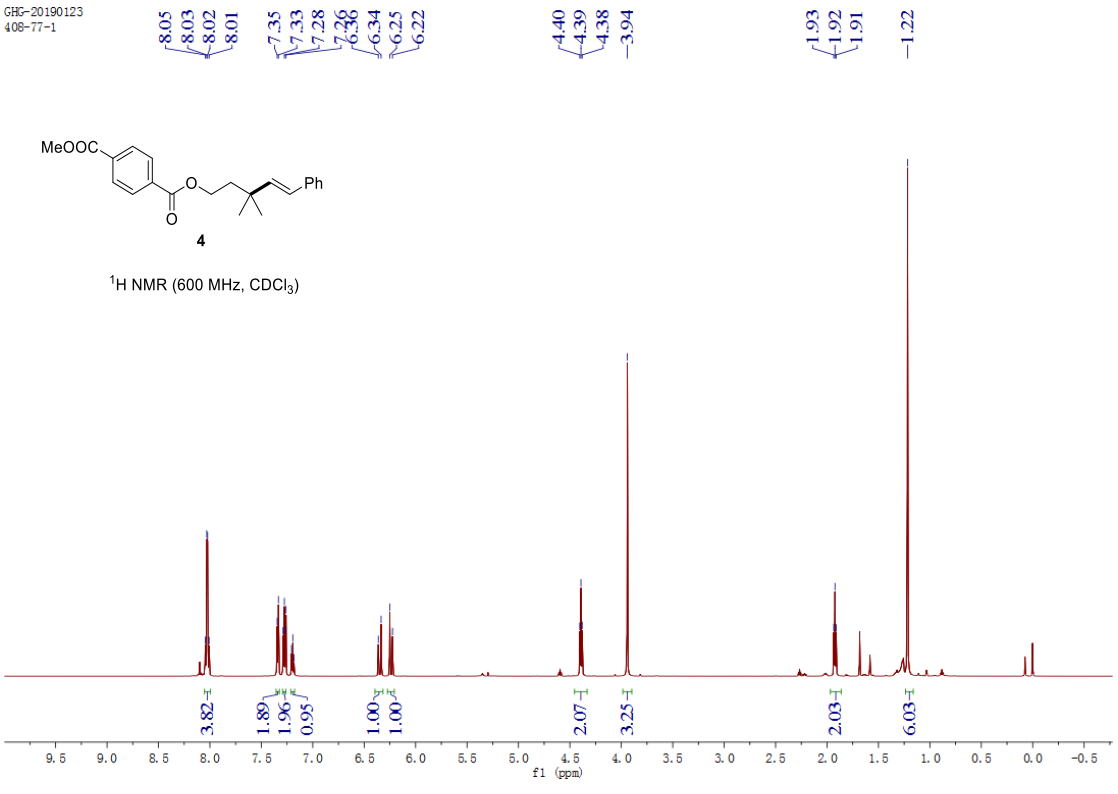
3a

^{1}H NMR (600 MHz, $CDCl_3$)



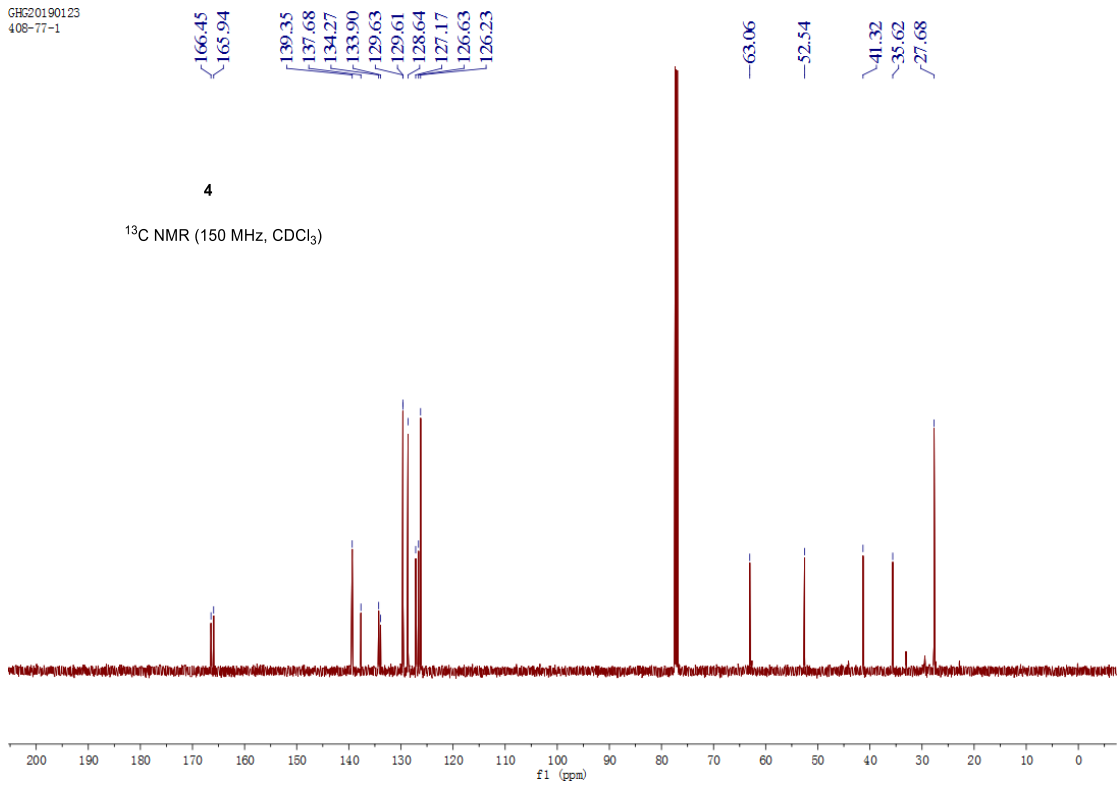
3a

^{13}C NMR (150 MHz, $CDCl_3$)



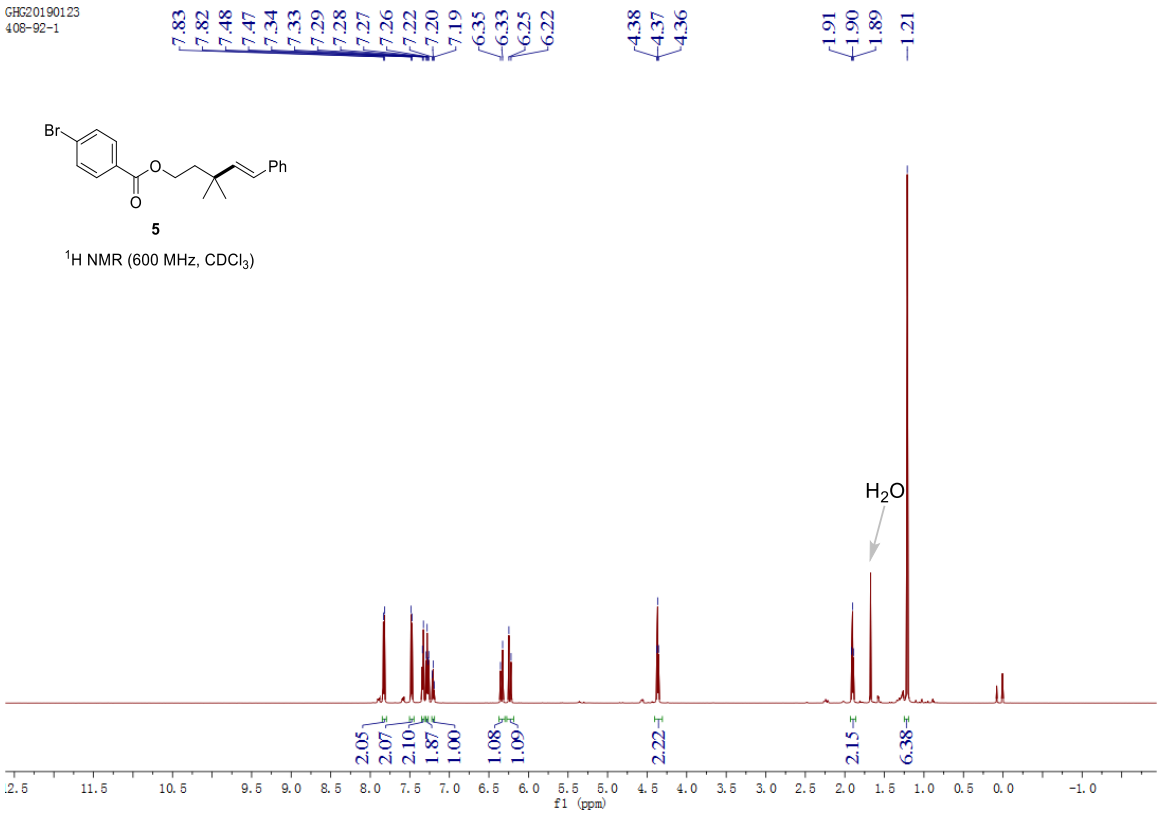
4

^{1}H NMR (600 MHz, $CDCl_3$)



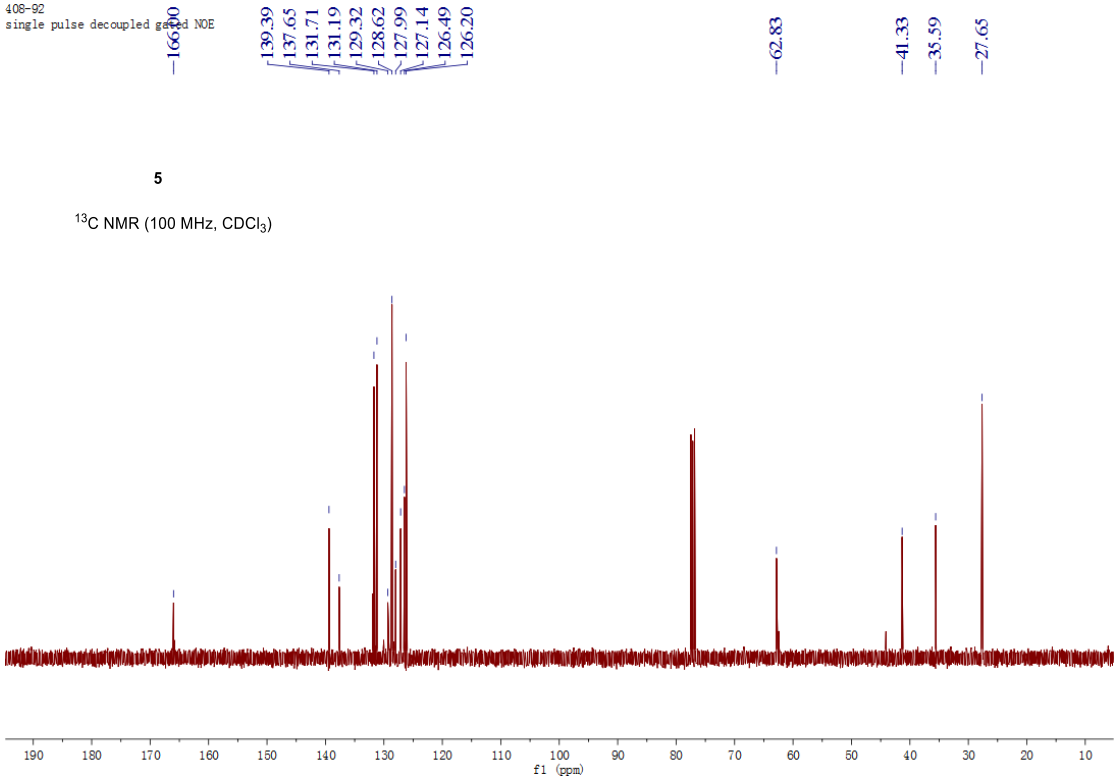
4

^{13}C NMR (150 MHz, $CDCl_3$)



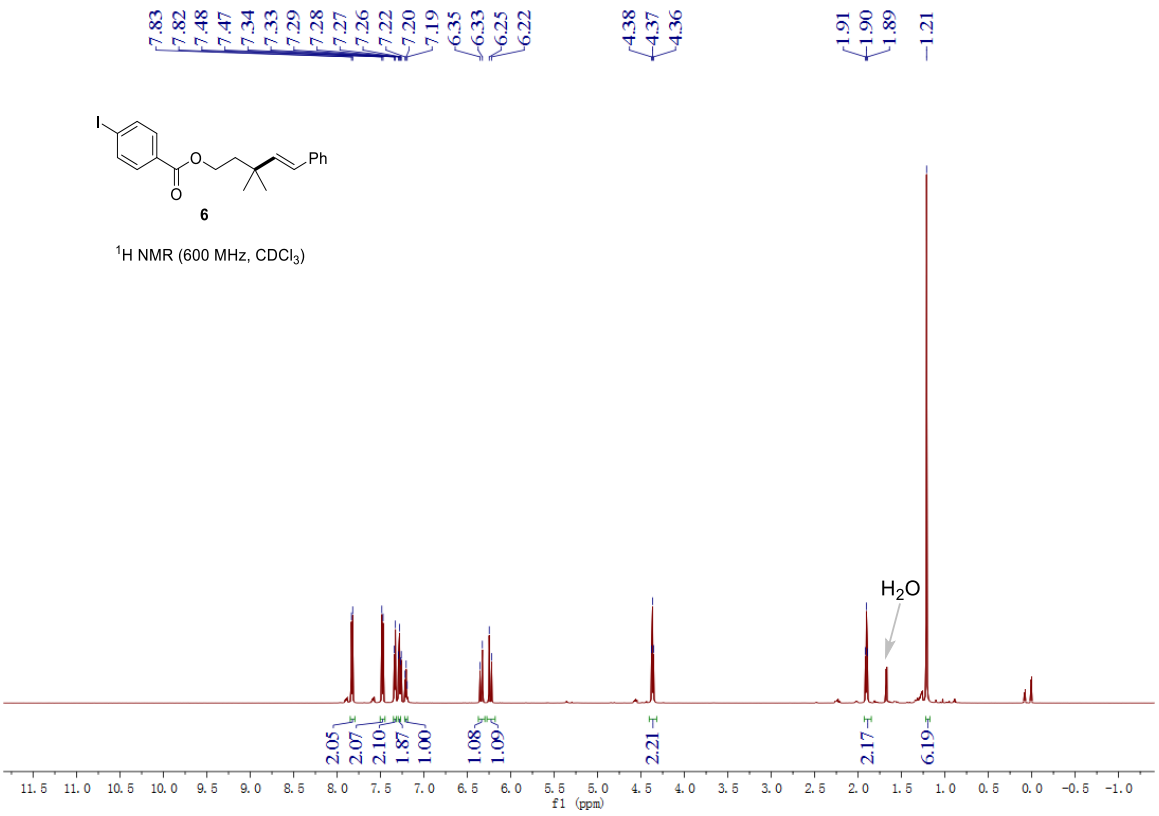
5

^{1}H NMR (600 MHz, $CDCl_3$)

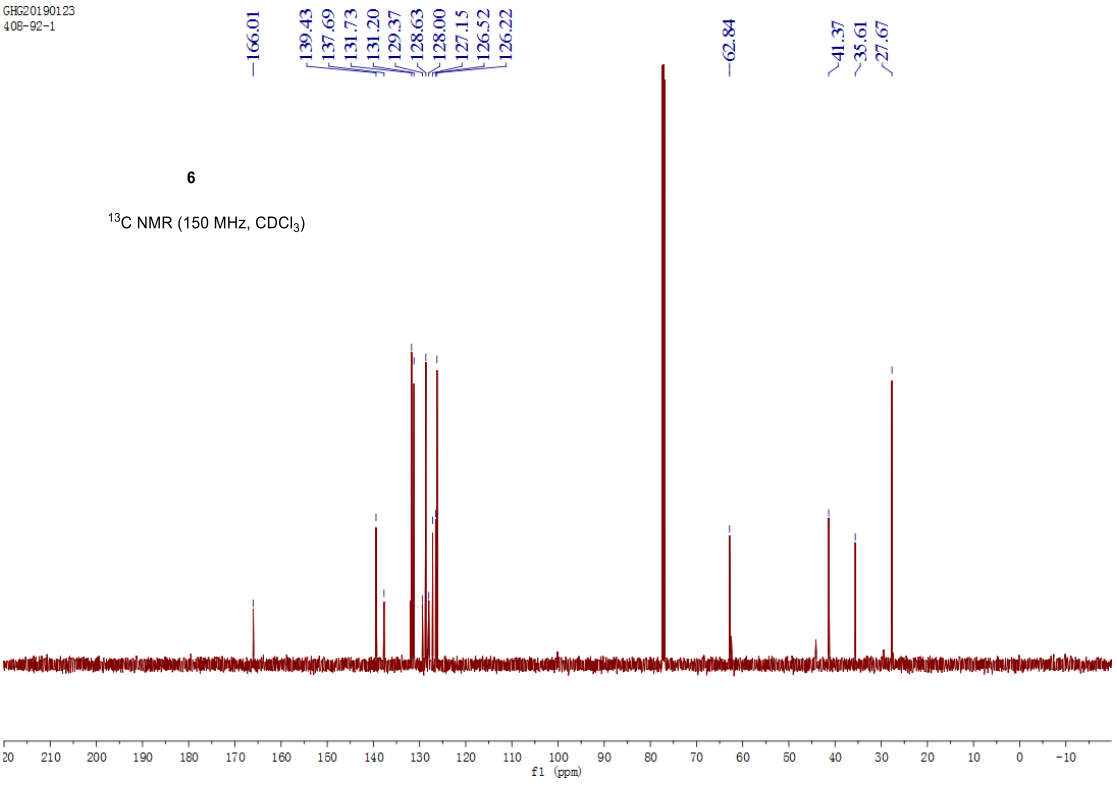


5

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

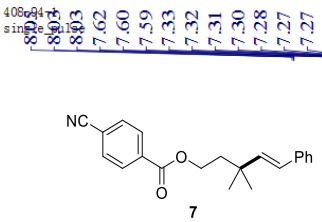


^{1}H NMR (600 MHz, $CDCl_3$)



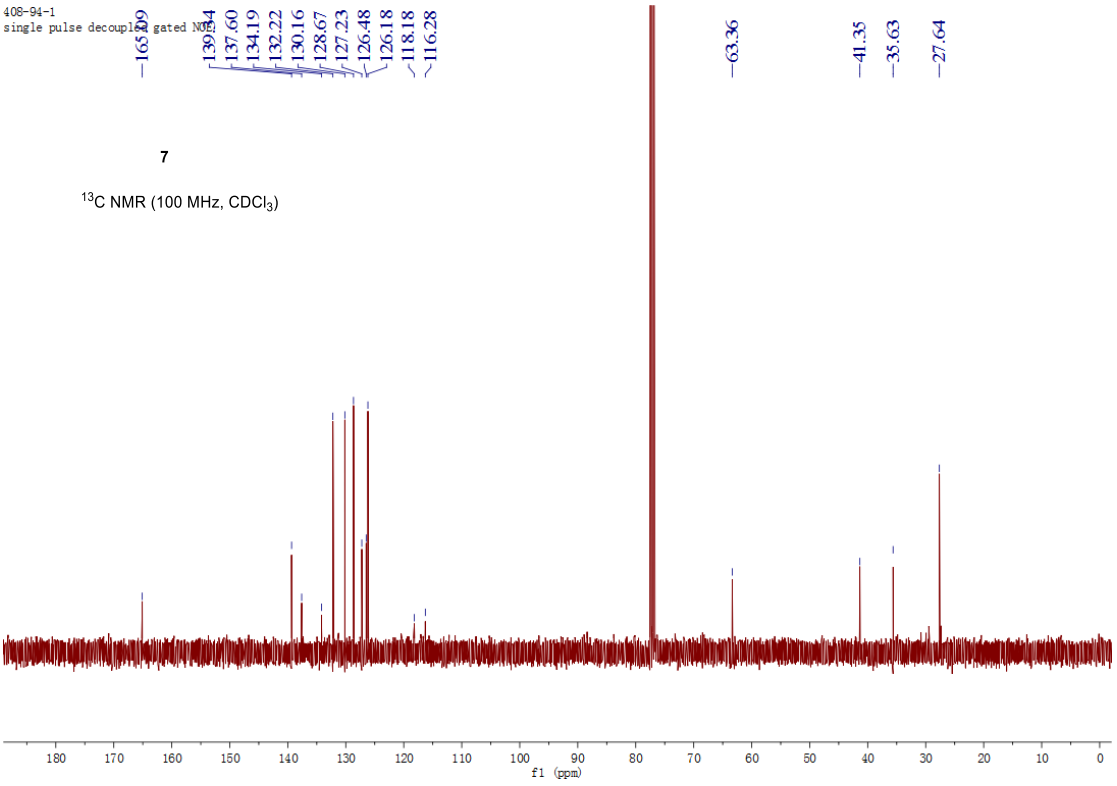
6

^{13}C NMR (150 MHz, $CDCl_3$)



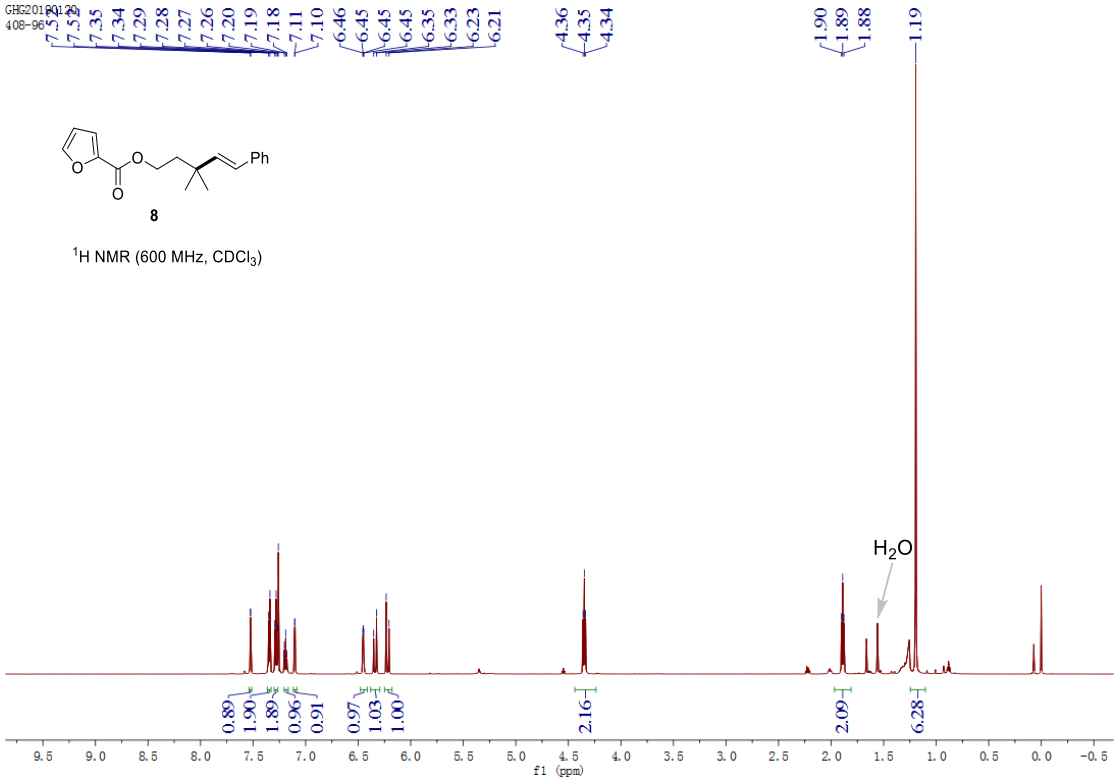
7

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



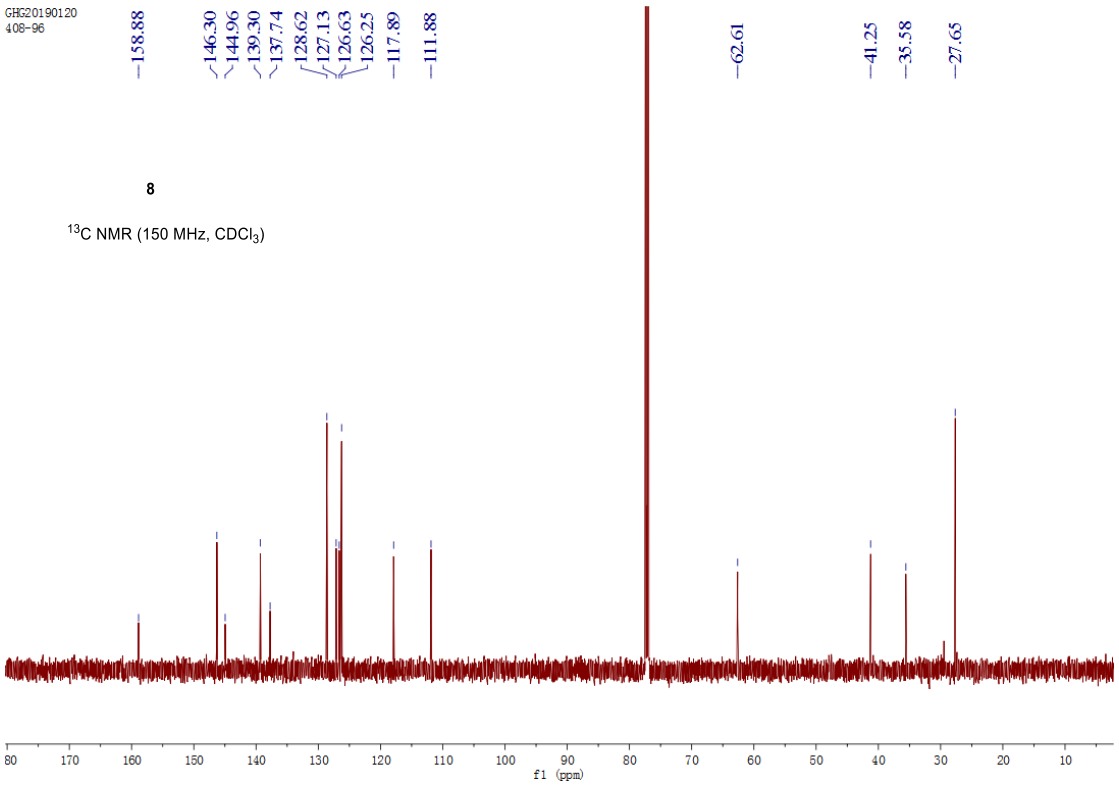
7

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



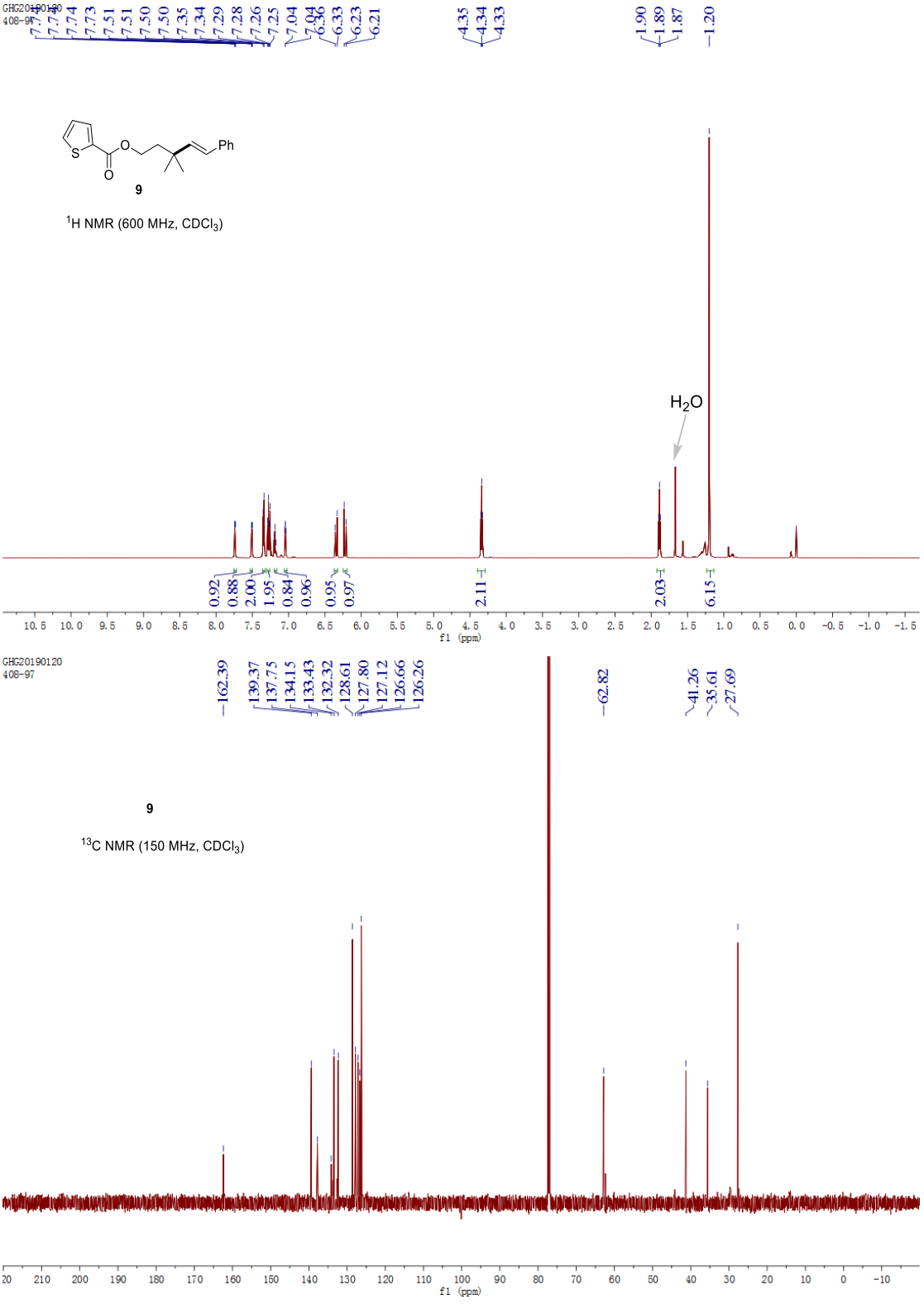
8

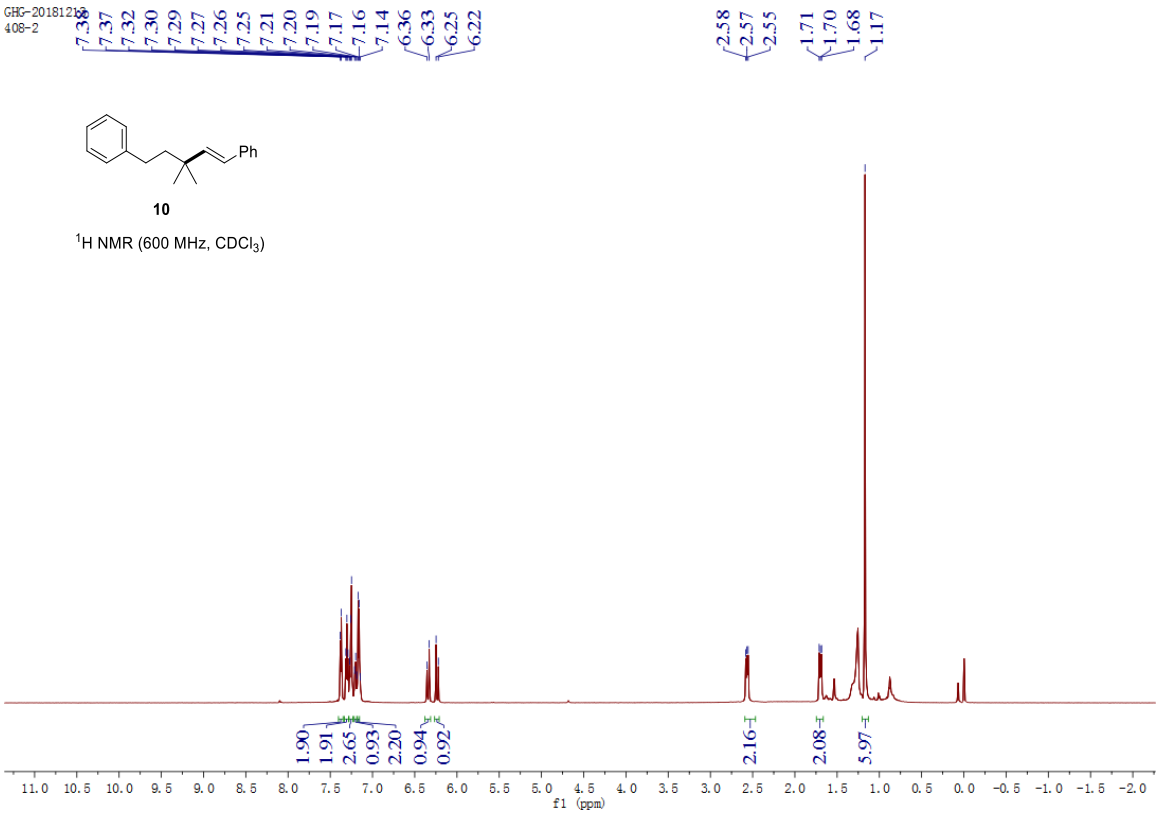
^{1}H NMR (600 MHz, $CDCl_3$)



8

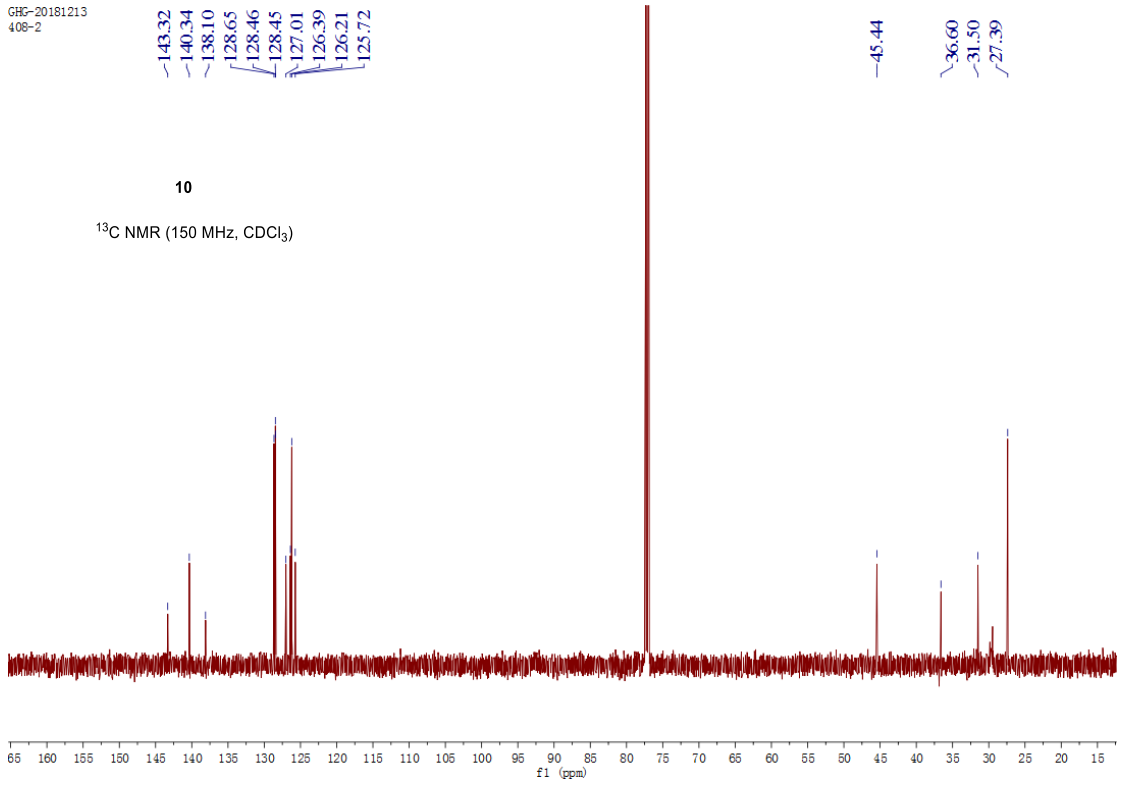
^{13}C NMR (150 MHz, $CDCl_3$)


GHG20190120
408-97
7.75
7.74
7.73
7.51
7.50
7.35
7.34
7.29
7.28
7.26
7.25
7.04
6.36
6.33
6.23
6.21
4.35
4.34
4.33
1.90
1.89
1.87
1.20
S
O
O
Ph
9
1H NMR (600 MHz, CDCl3)
H2O
0.92
0.88
2.00
1.95
0.84
0.96
0.95
0.97
2.11
2.03
6.15
f1 (ppm)
GHG20190120
408-97
162.39
139.37
137.75
134.15
133.43
132.32
128.61
127.80
127.12
126.66
126.26
62.82
41.26
35.61
27.69
9
13C NMR (150 MHz, CDCl3)
f1 (ppm)



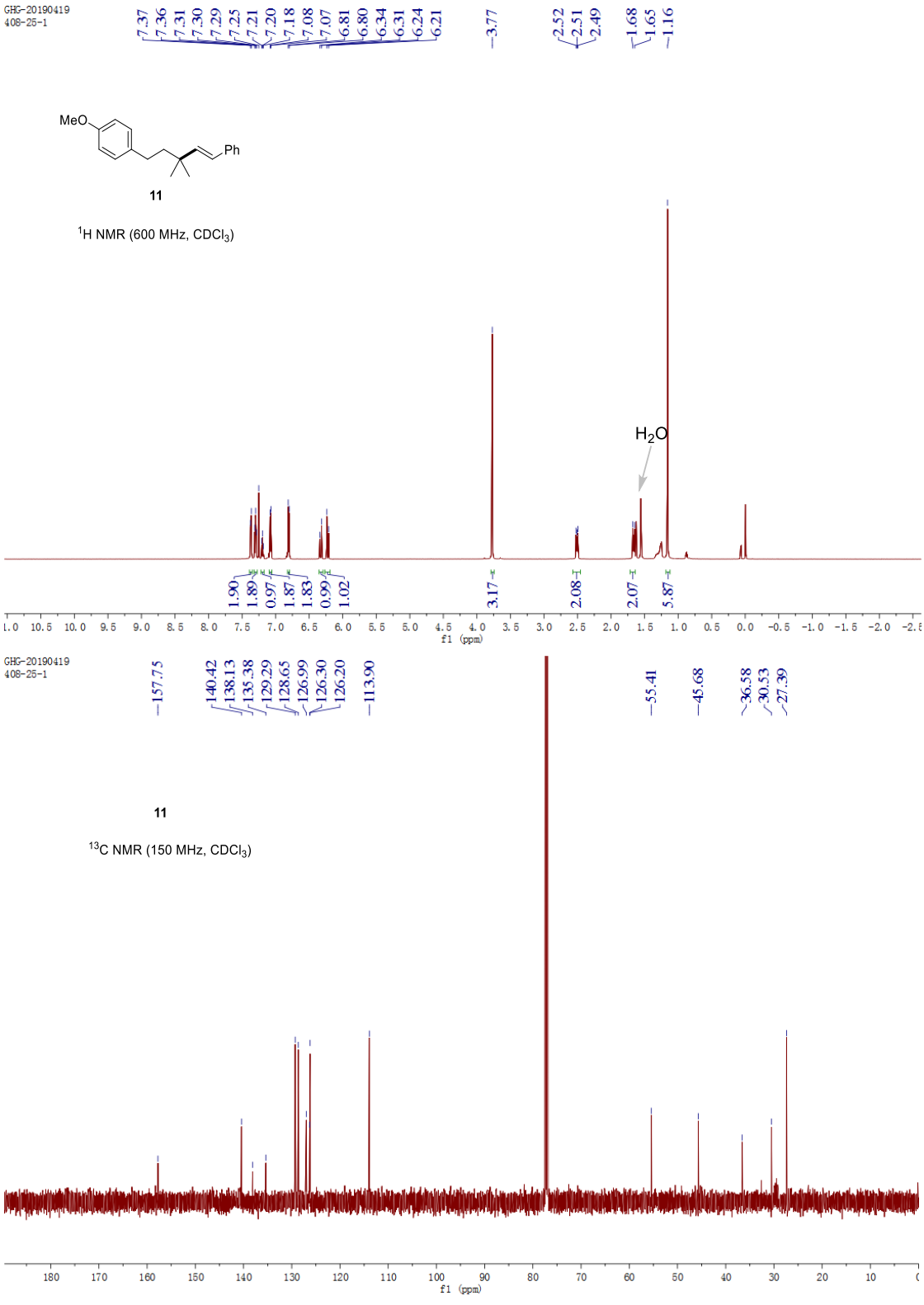
10

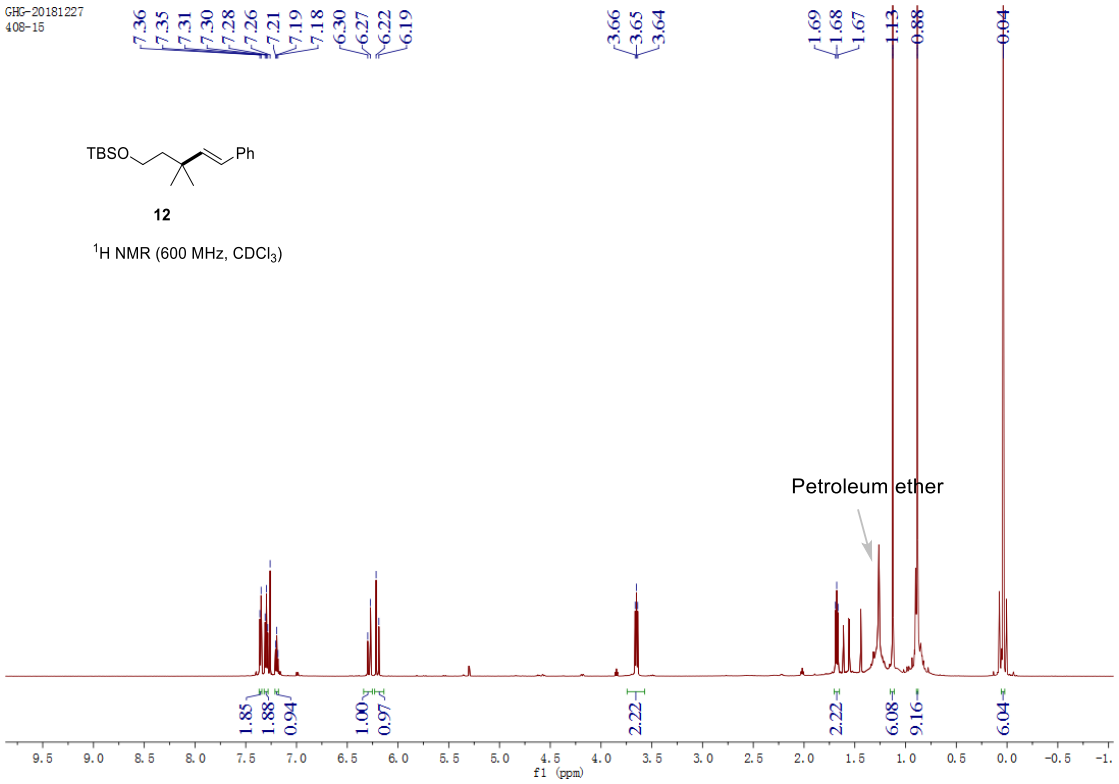
^{1}H NMR (600 MHz, $CDCl_3$)

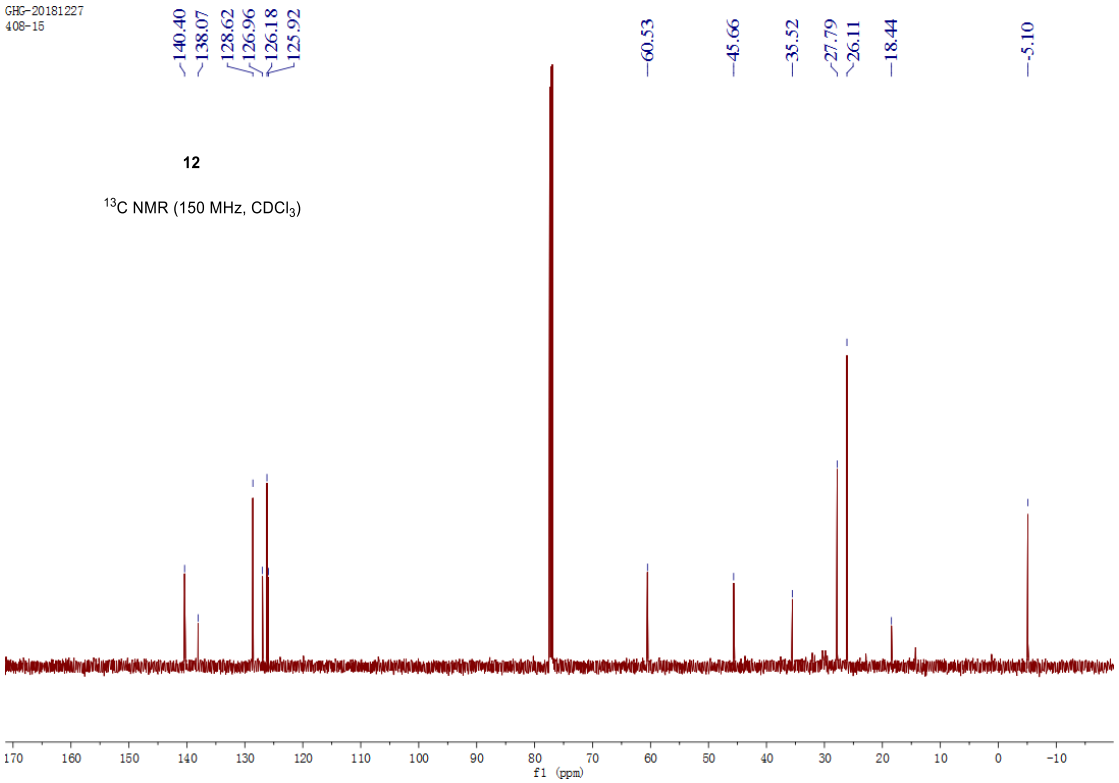


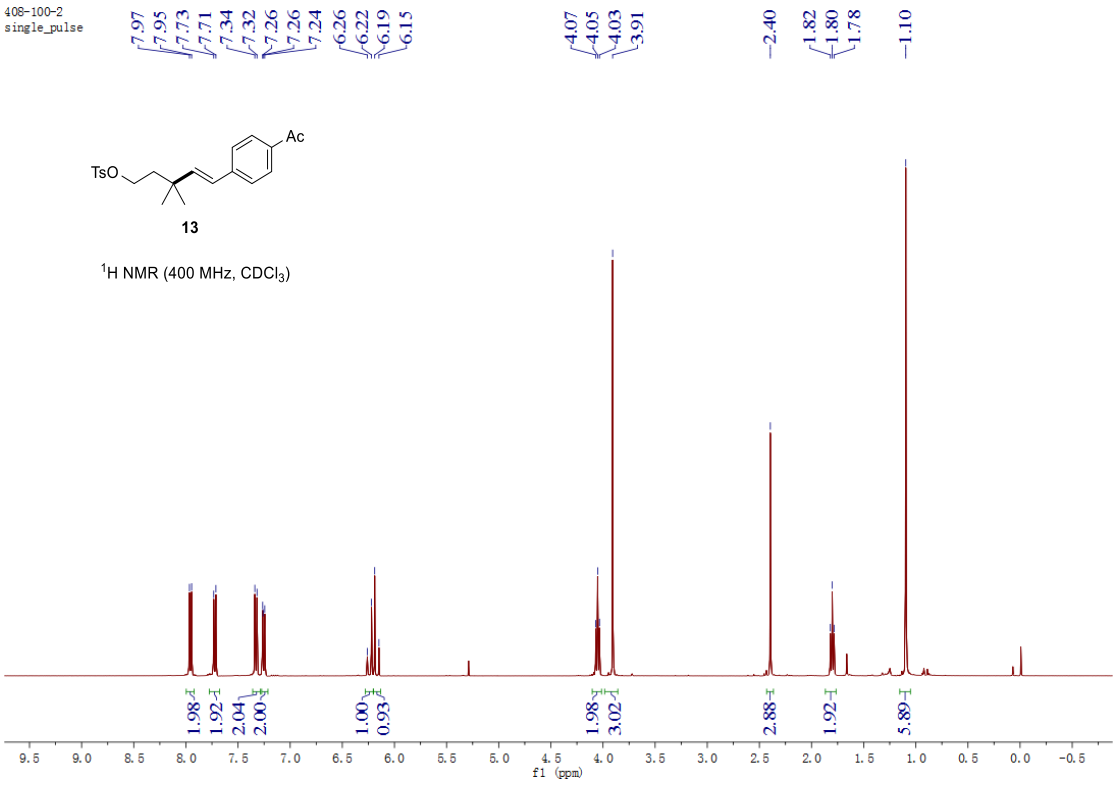
10

^{13}C NMR (150 MHz, $CDCl_3$)


GHG-20190419
408-25-1
7.37
7.36
7.31
7.30
7.29
7.25
7.21
7.20
7.18
7.08
7.07
6.81
6.80
6.34
6.31
6.24
6.21
3.77
2.52
2.51
2.49
1.68
1.65
1.16
MeO
Ph
11
1H NMR (600 MHz, CDCl3)
H2O
1.90
1.89
0.97
1.87
1.83
0.99
1.02
3.17
2.08
2.07
5.87
f1 (ppm)
GHG-20190419
408-25-1
157.75
140.42
138.13
135.38
129.29
128.65
126.99
126.30
126.20
113.90
55.41
45.68
36.58
30.53
27.39
11
13C NMR (150 MHz, CDCl3)
f1 (ppm)

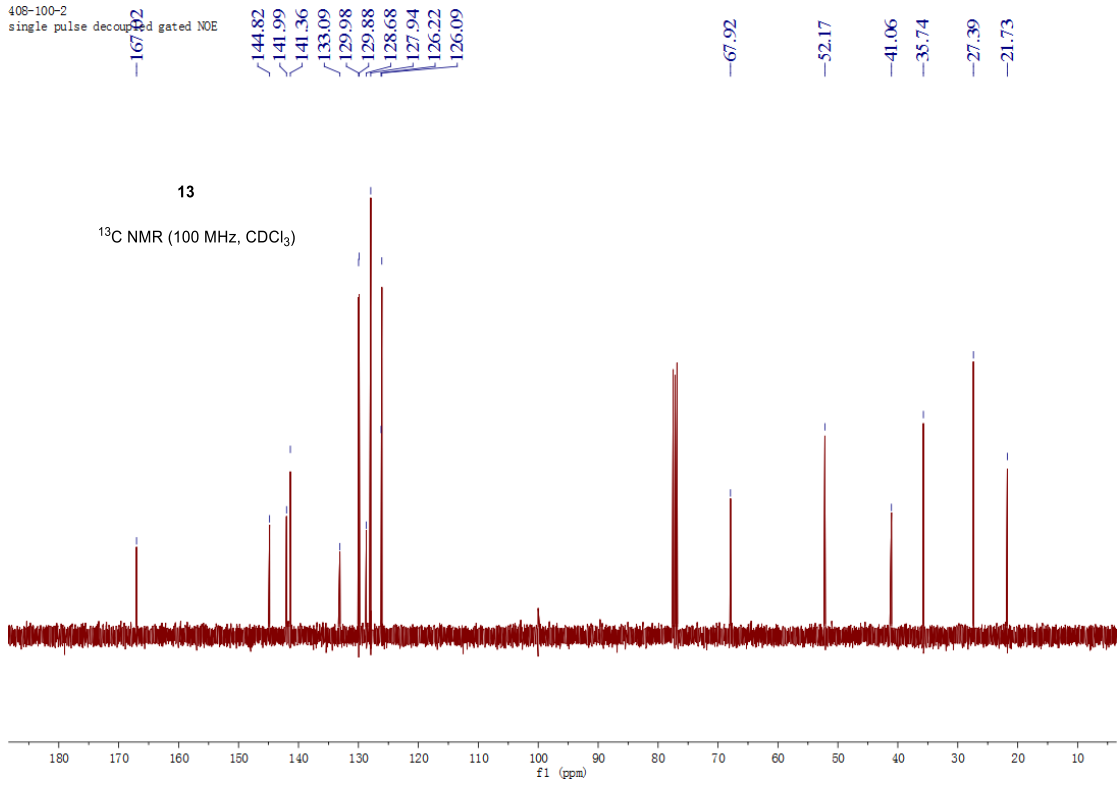

GHG-20181227
408-15
7.36
7.35
7.31
7.30
7.28
7.26
7.21
7.19
7.18
6.30
6.27
6.22
6.19
3.66
3.65
3.64
1.69
1.68
1.67
1.13
0.88
0.04
TBSO
Ph
12
^{1}H NMR (600 MHz, $CDCl_3$)
Petroleum ether
1.85
1.88
0.94
1.00
0.97
2.22
2.22
6.08
9.16
6.04
f1 (ppm)


GHG-20181227
408-15
140.40
138.07
128.62
126.96
126.18
125.92
60.53
45.66
35.52
27.79
26.11
18.44
-5.10
12
^{13}C NMR (150 MHz, $CDCl_3$)
f1 (ppm)



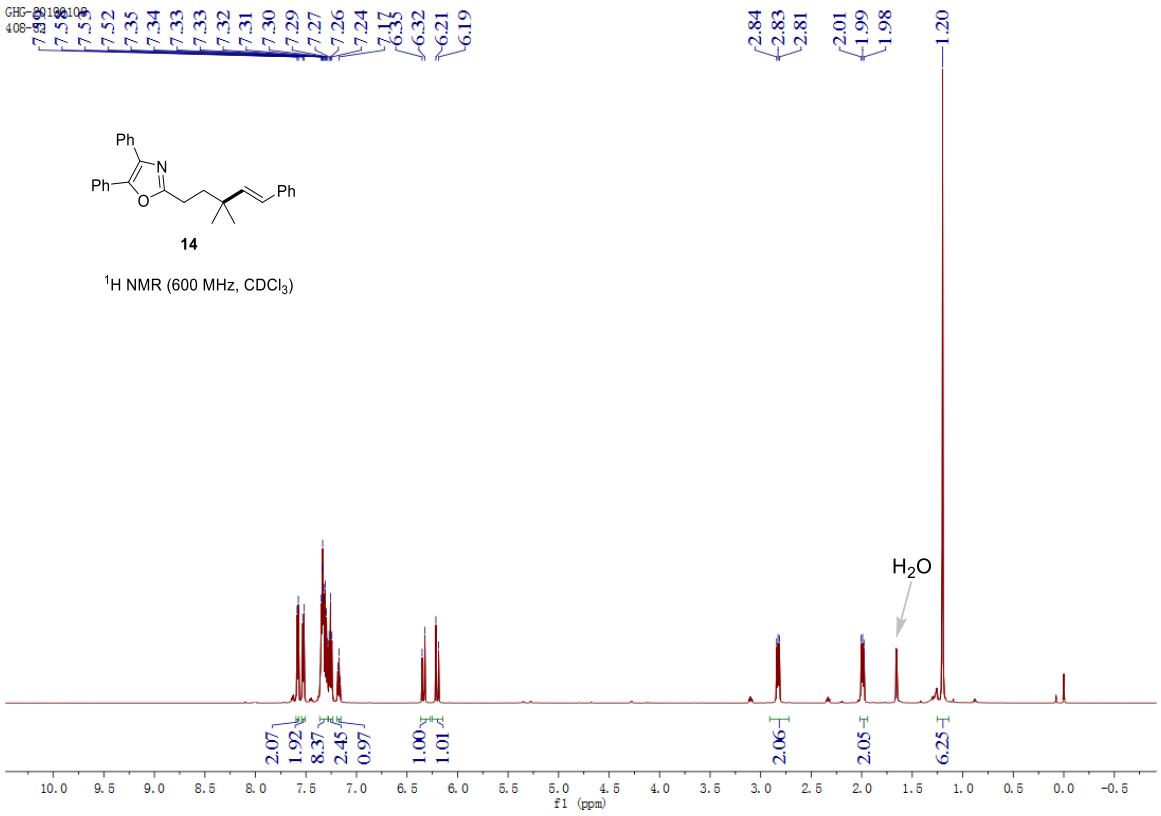
13

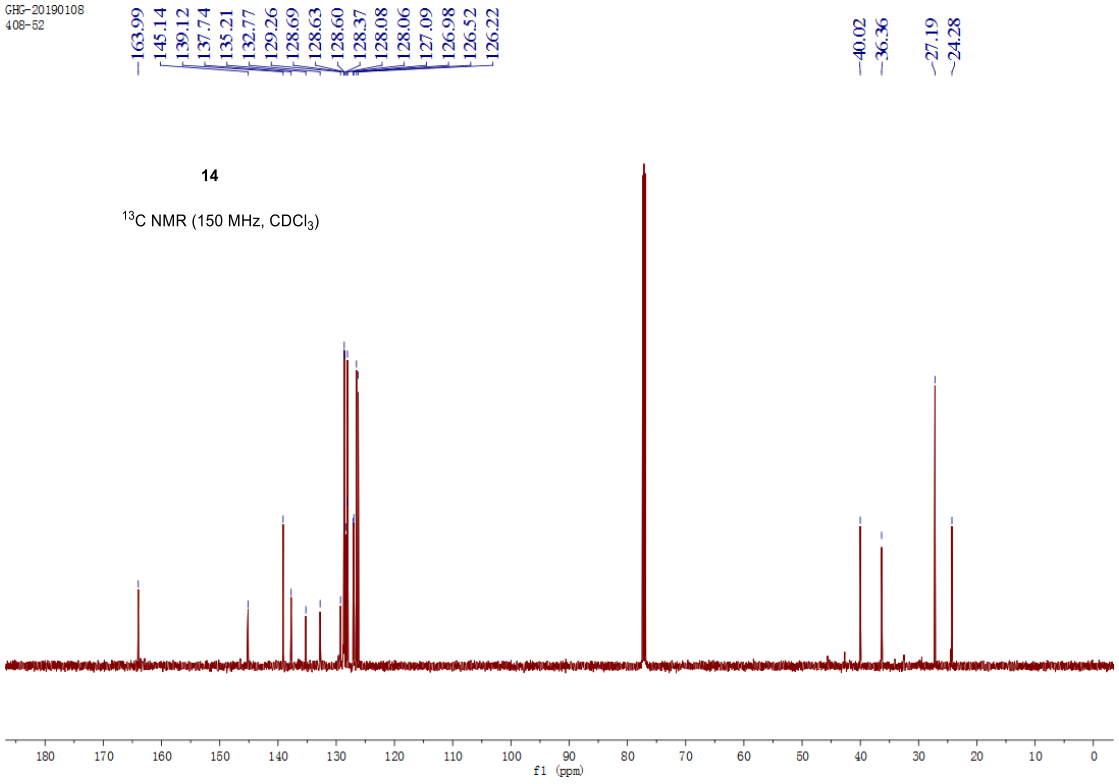
^{1}H NMR (400 MHz, $CDCl_3$)



13

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

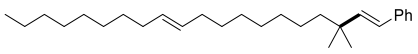

GHG-20190108
408-52
7.55
7.53
7.52
7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.29
7.27
7.26
7.24
7.17
6.35
6.32
6.21
6.19
2.84
2.83
2.81
2.01
1.99
1.98
1.20
Ph
N
Ph
O
Ph
14
^{1}H NMR (600 MHz, CDCl$_3$)
H$_2$O
2.07
1.92
8.37
2.45
0.97
1.00
1.01
2.06
2.05
6.25
f1 (ppm)


GHG-20190108
408-52
163.99
145.14
139.12
137.74
135.21
132.77
129.26
128.69
128.63
128.60
128.37
128.08
128.06
127.09
126.98
126.52
126.22
40.02
36.36
27.19
24.28
14
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)

GHG-20190118
408-90

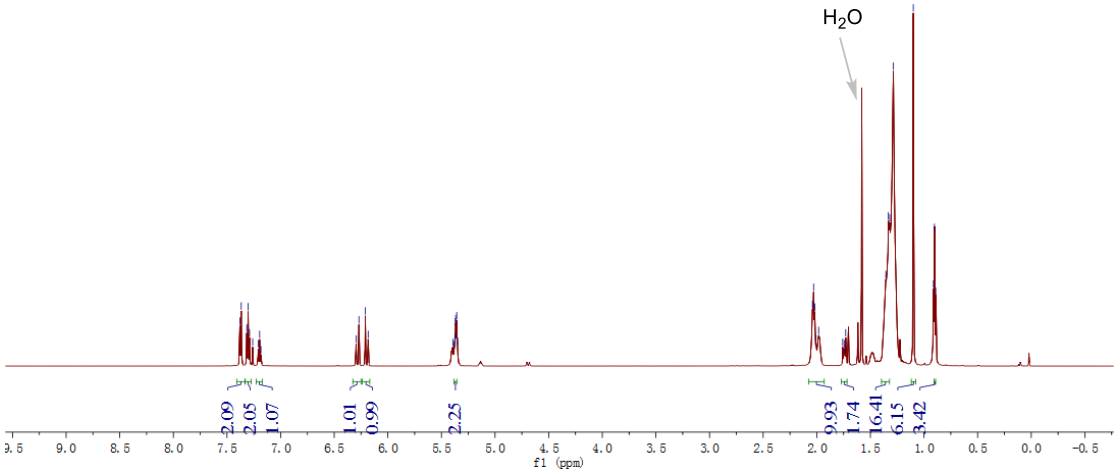
7.38 7.37 7.32 7.30 7.29 7.26 7.21 7.20 7.18 6.30 6.27 6.21 6.18 5.39 5.38 5.38 5.37 5.37 5.36 5.35

2.04 2.03 2.02 2.01 1.98 1.76 1.74 1.74 1.73 1.36 1.33 1.32 1.29 1.10 0.91 0.90 0.89



15

^{1}H NMR (600 MHz, $CDCl_3$)



GHG-20190118
408-90

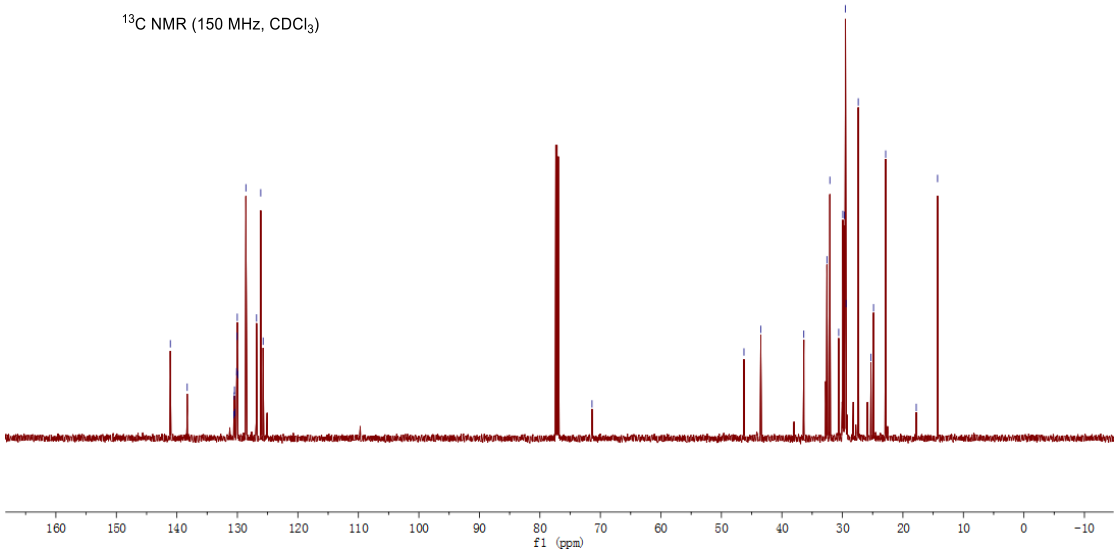
141.08 138.29 130.60 130.51 130.48 130.41 130.13 130.05 130.02 129.94 128.59 126.83 126.14 125.74

71.38

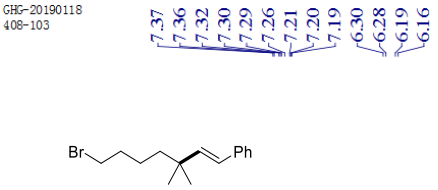
46.27 43.49 36.38 32.56 32.07 30.61 29.93 29.69 29.49 29.39 27.38 25.28 24.86 22.85 17.80 14.27

15

^{13}C NMR (150 MHz, $CDCl_3$)

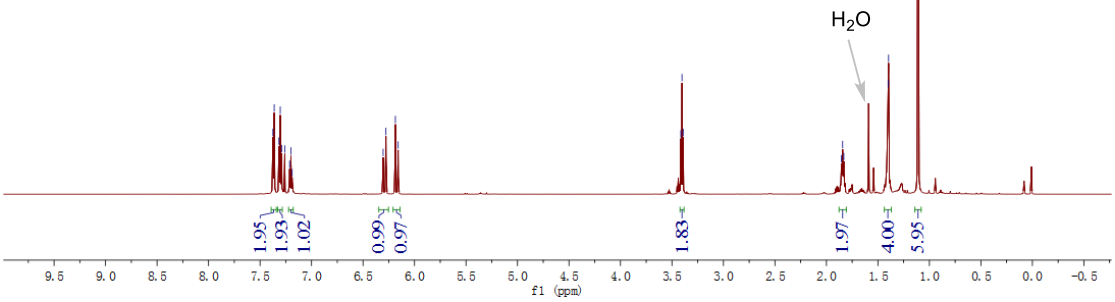


GHG-20190118
408-103



16

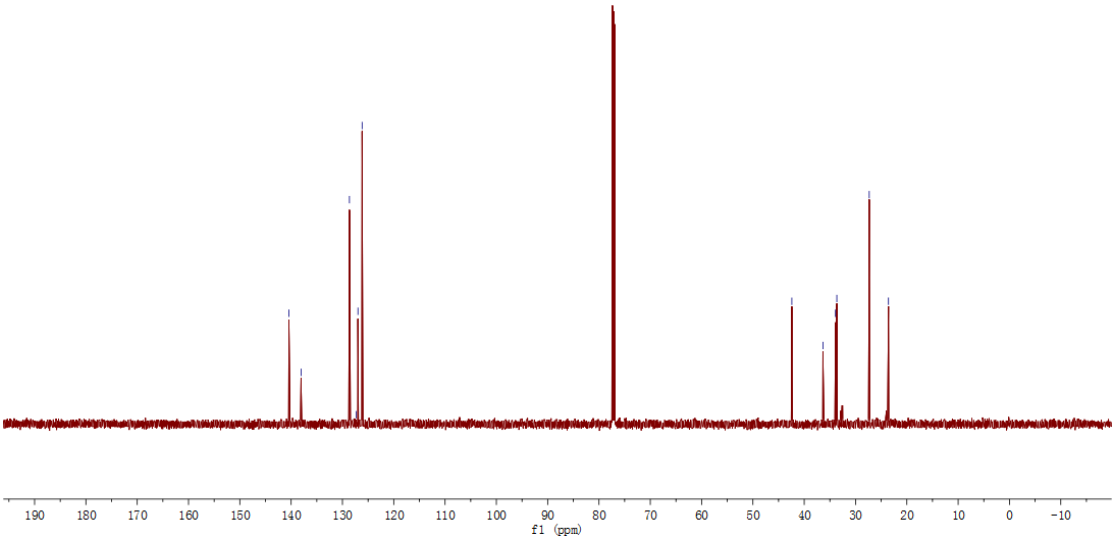
^{1}H NMR (600 MHz, $CDCl_3$)

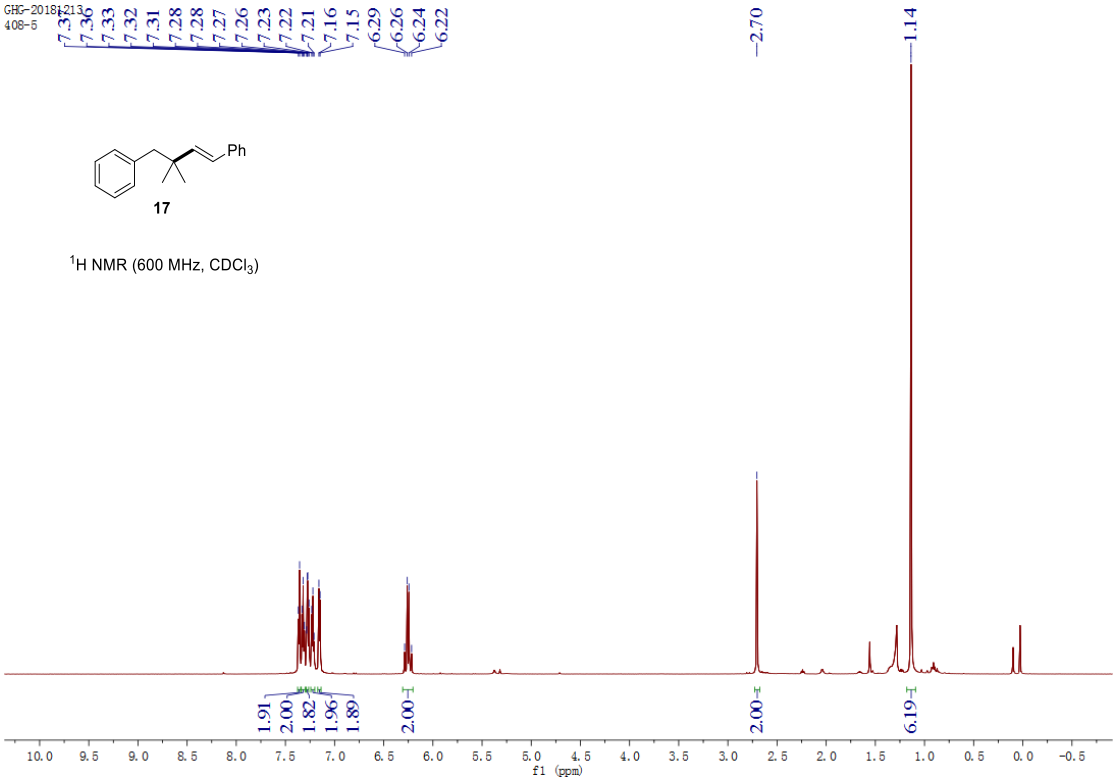


GHG-20190118
408-103

16

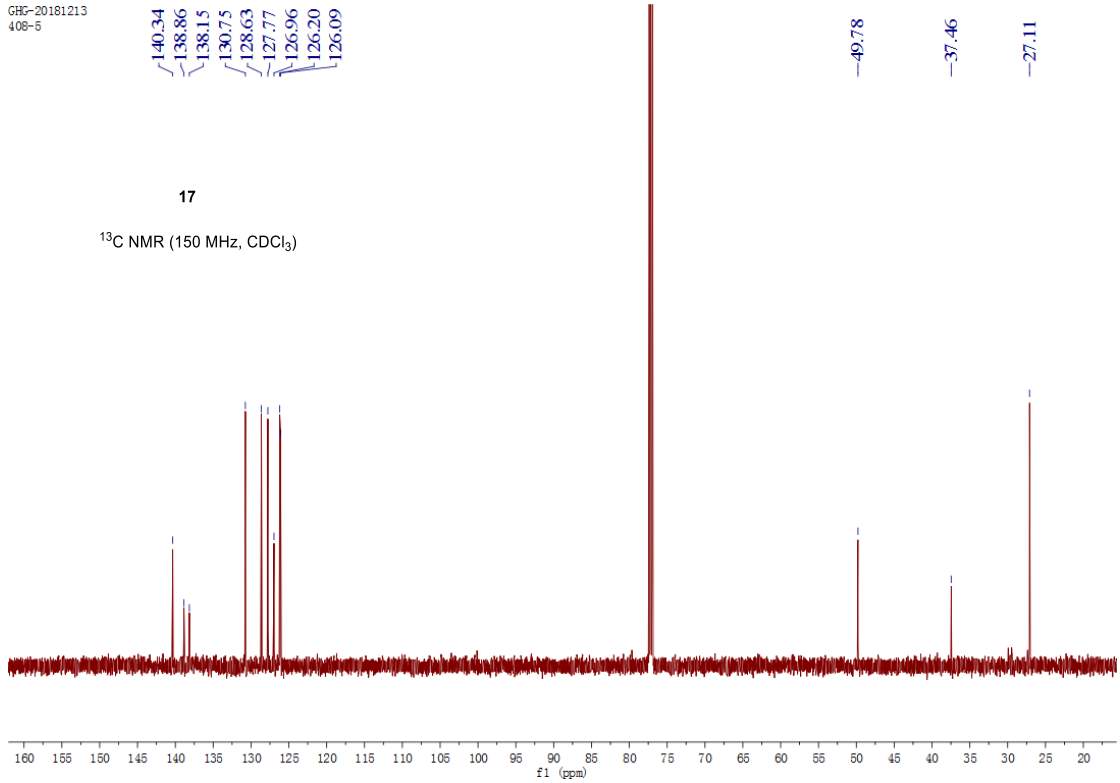
^{13}C NMR (150 MHz, $CDCl_3$)





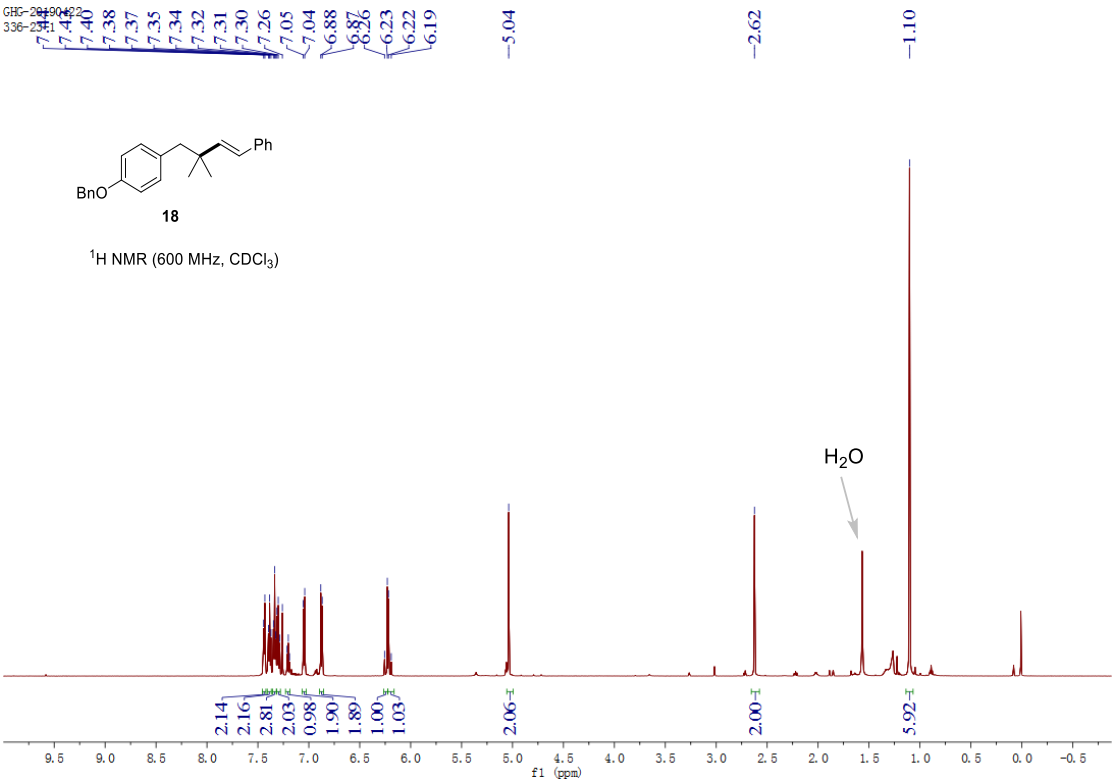
17

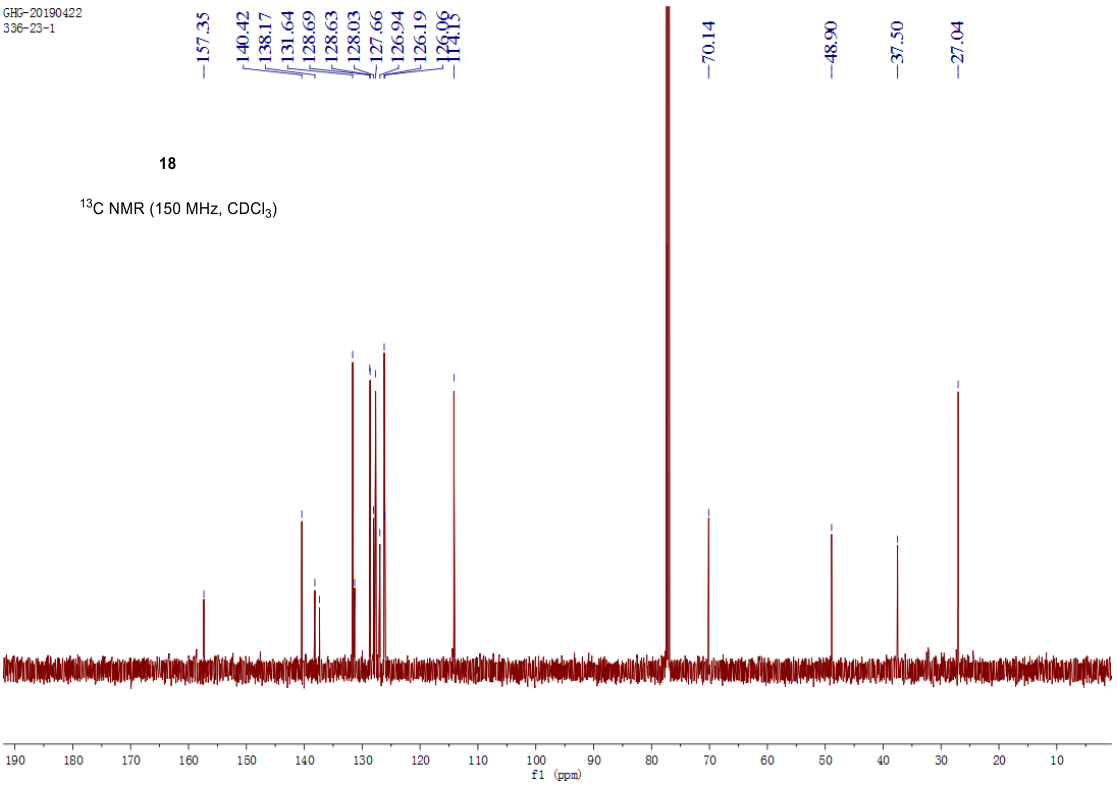
^{1}H NMR (600 MHz, $CDCl_3$)

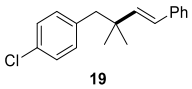


17

^{13}C NMR (150 MHz, $CDCl_3$)

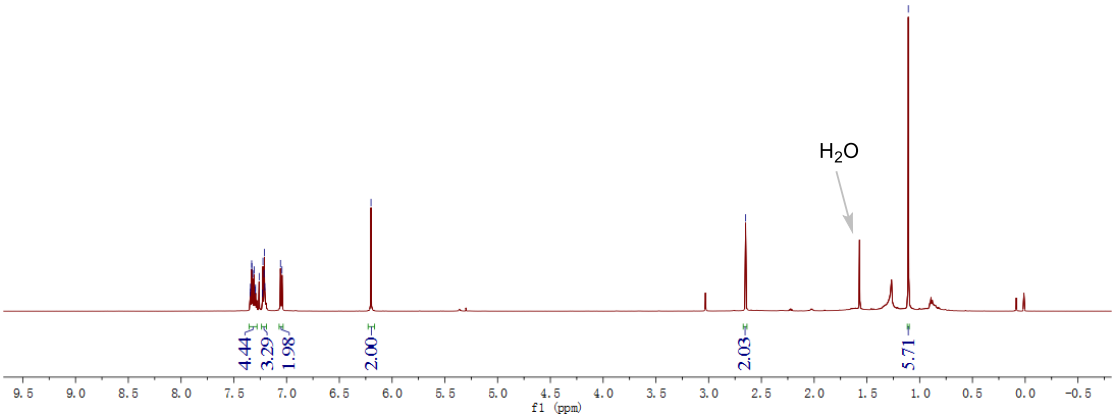

Ph
BnO
18
^{1}H NMR (600 MHz, CDCl$_3$)
H$_2$O


GHG-20190422
336-23-1
18
^{13}C NMR (150 MHz, CDCl$_3$)



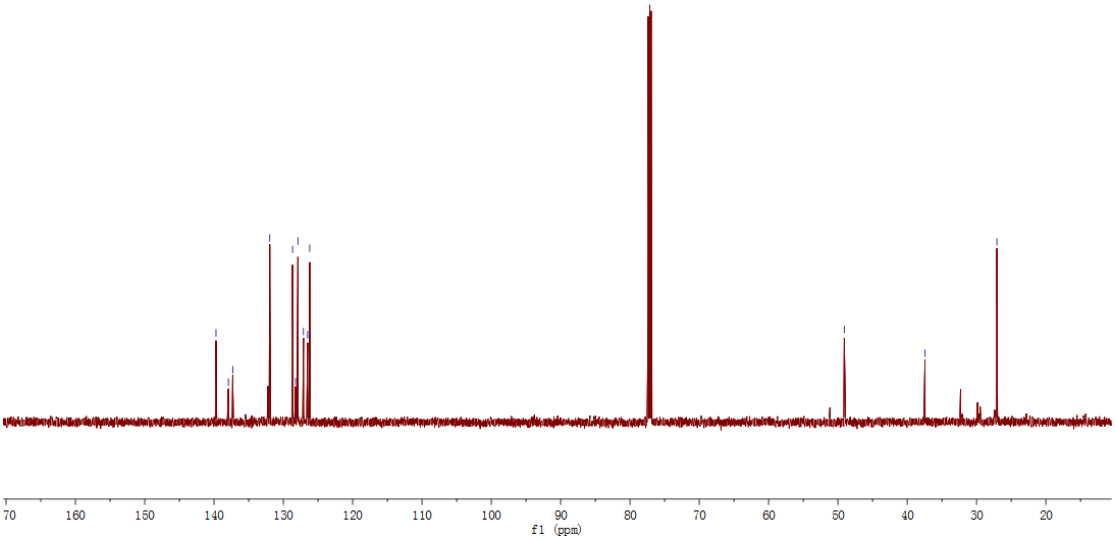
19

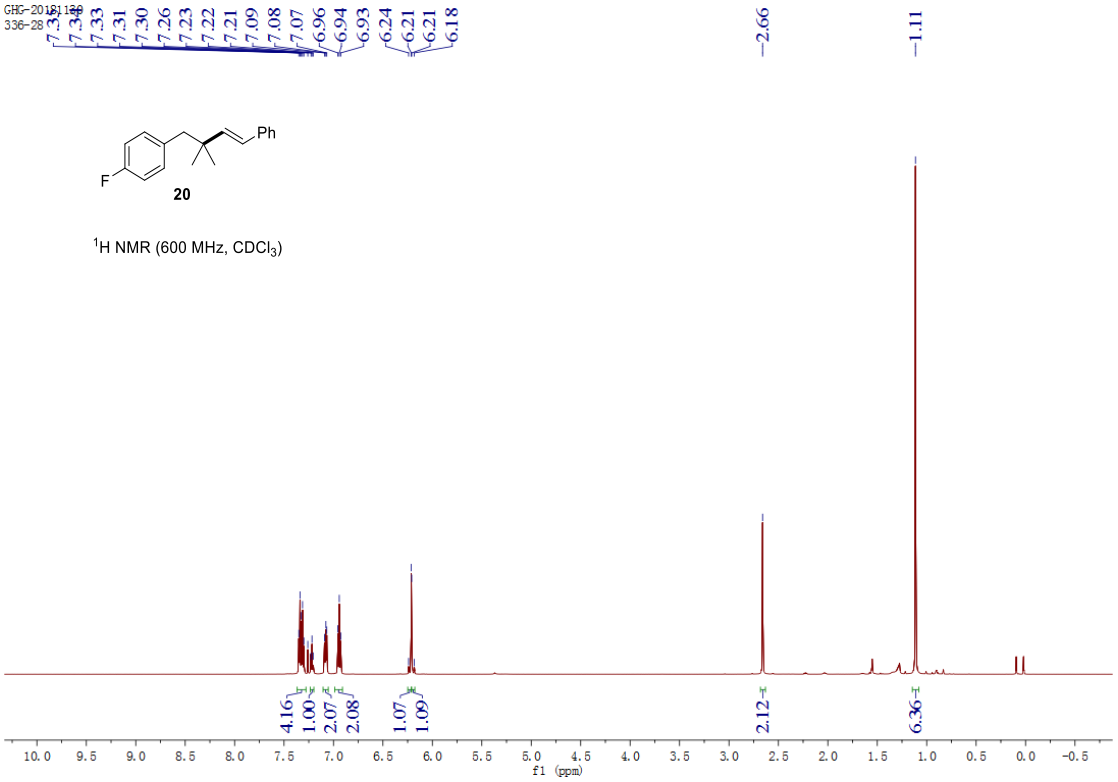
^{1}H NMR (600 MHz, $CDCl_3$)



19

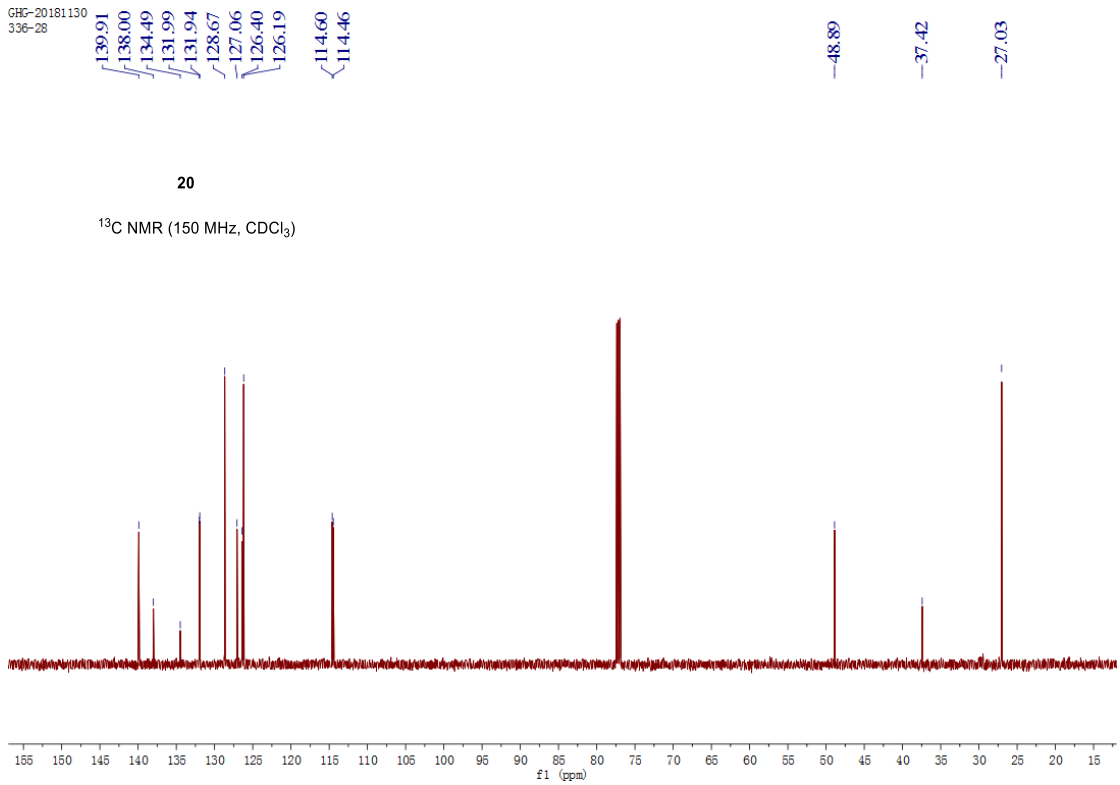
^{13}C NMR (150 MHz, $CDCl_3$)





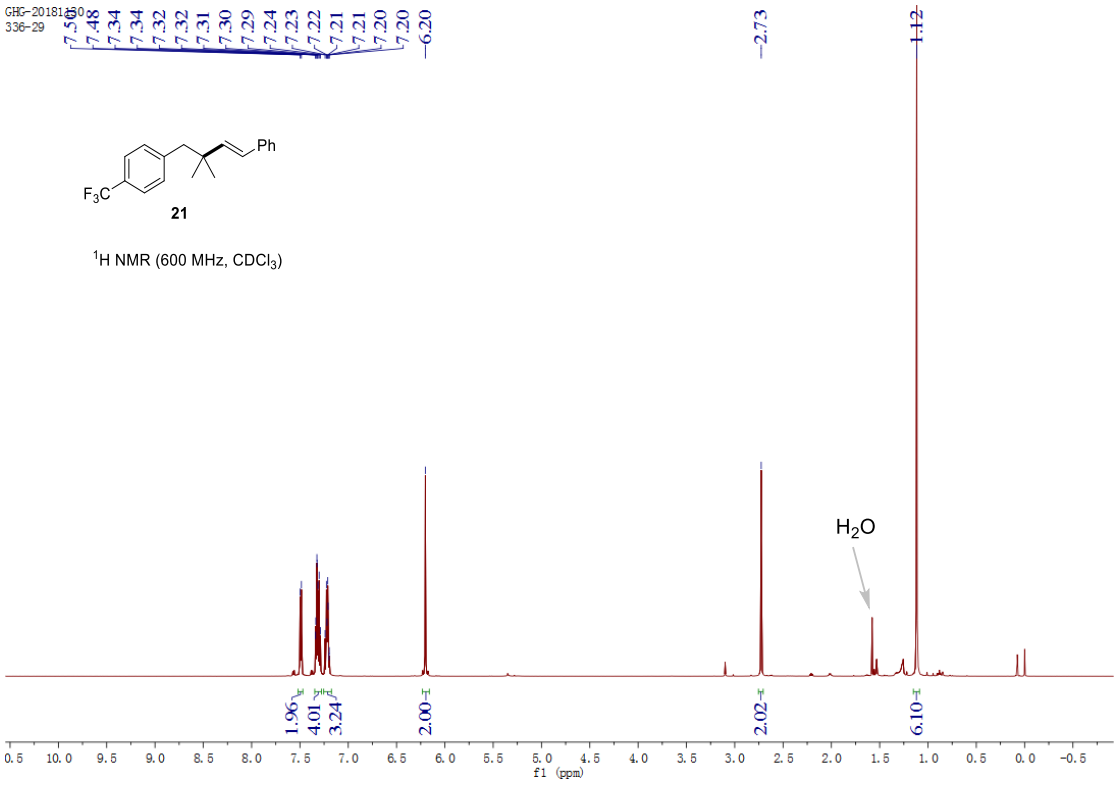
20

^{1}H NMR (600 MHz, $CDCl_3$)



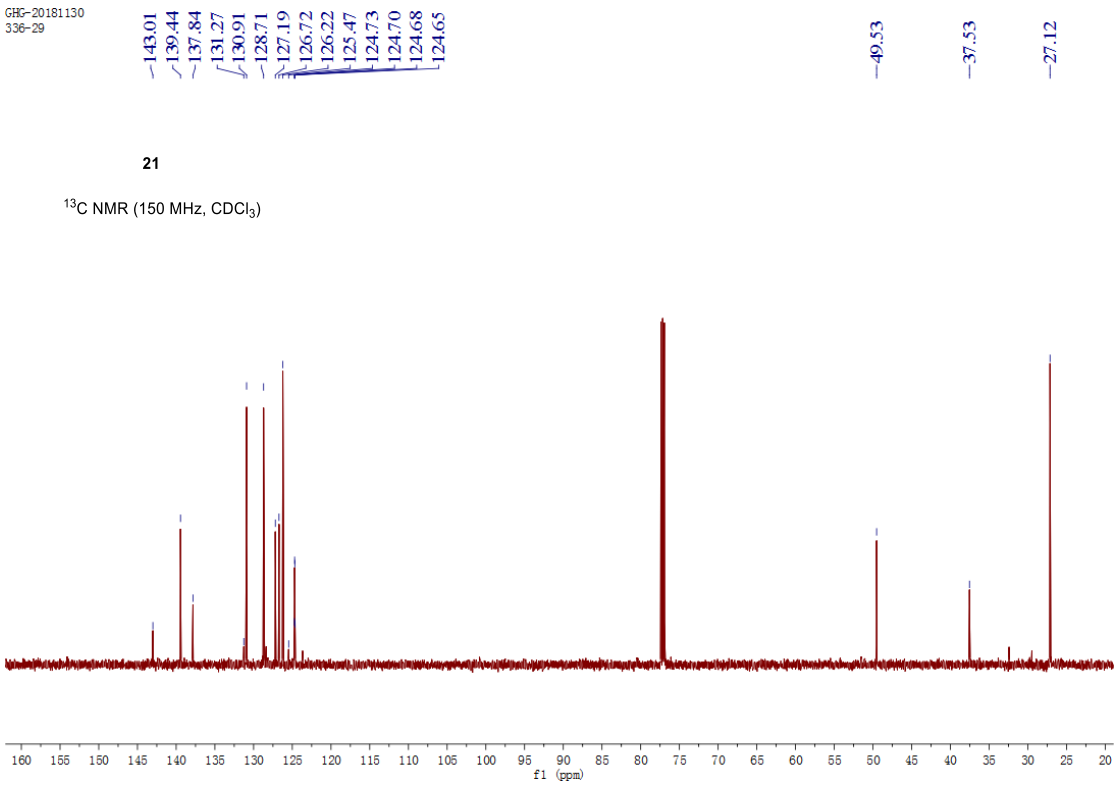
20

^{13}C NMR (150 MHz, $CDCl_3$)



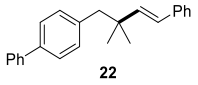
21

^{1}H NMR (600 MHz, $CDCl_3$)



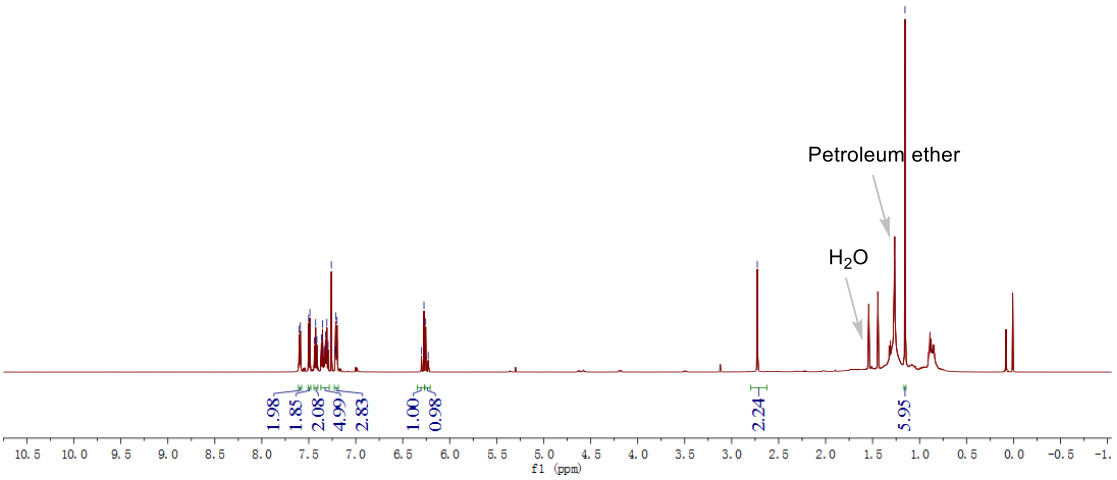
21

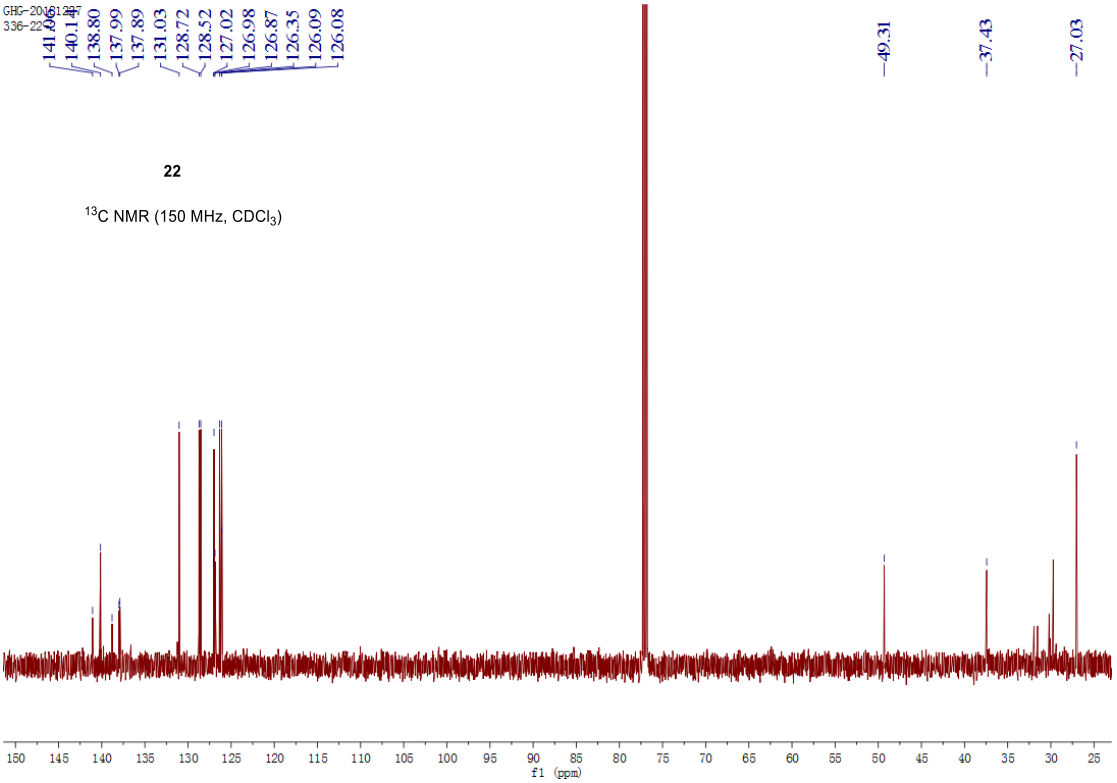
^{13}C NMR (150 MHz, $CDCl_3$)



22

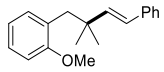
^{1}H NMR (600 MHz, $CDCl_3$)





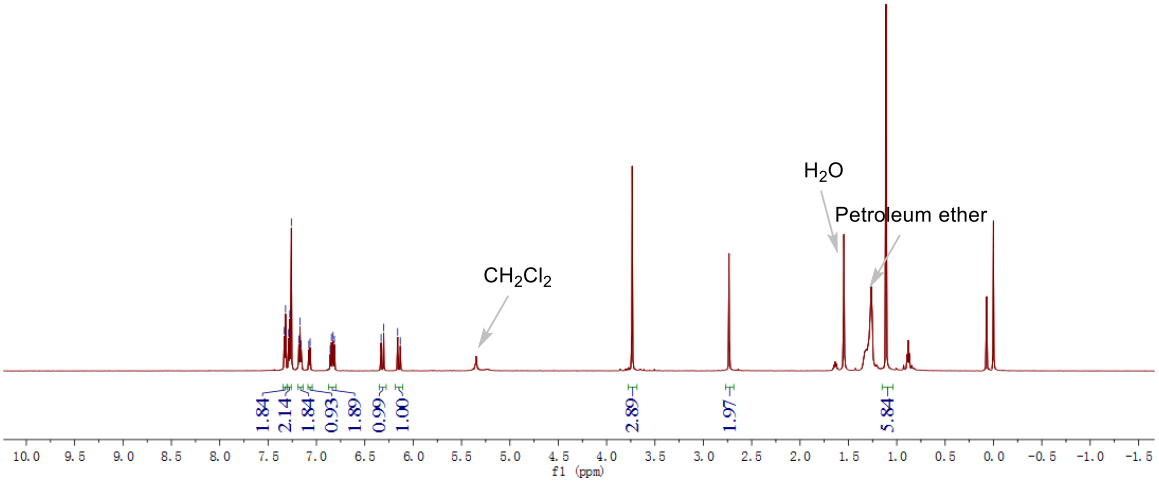
22

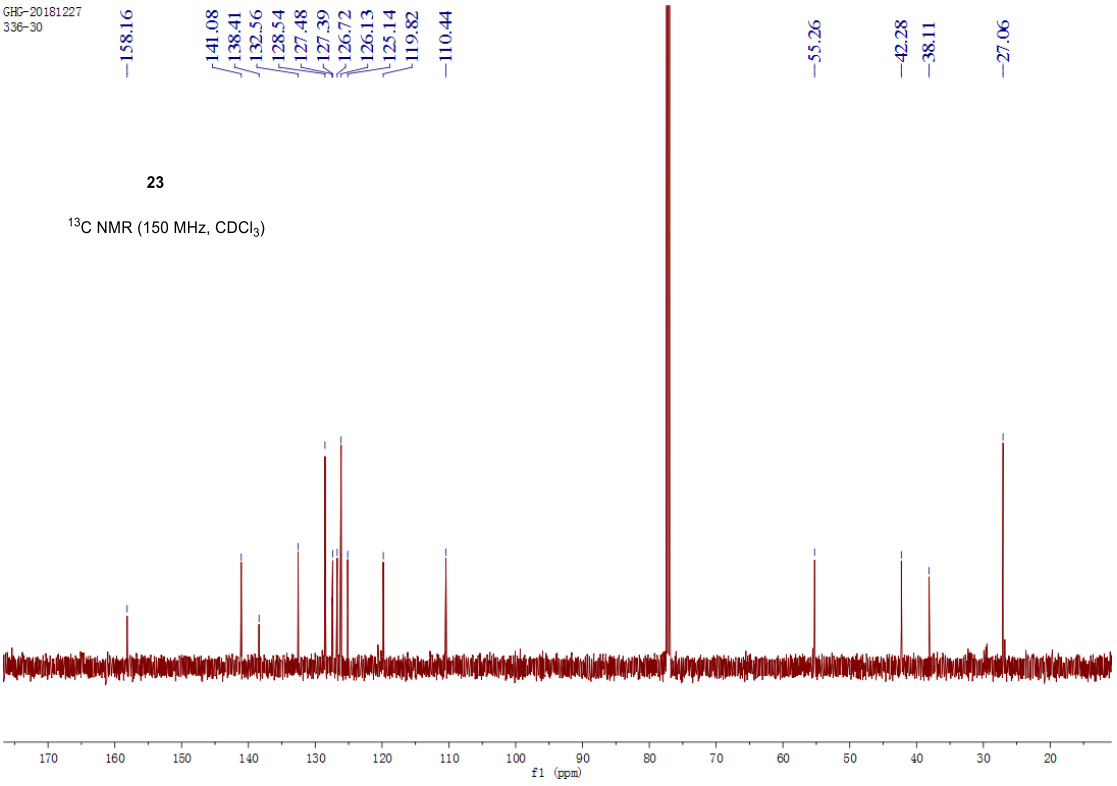
^{13}C NMR (150 MHz, $CDCl_3$)



23

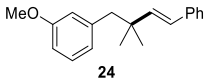
^{1}H NMR (600 MHz, $CDCl_3$)





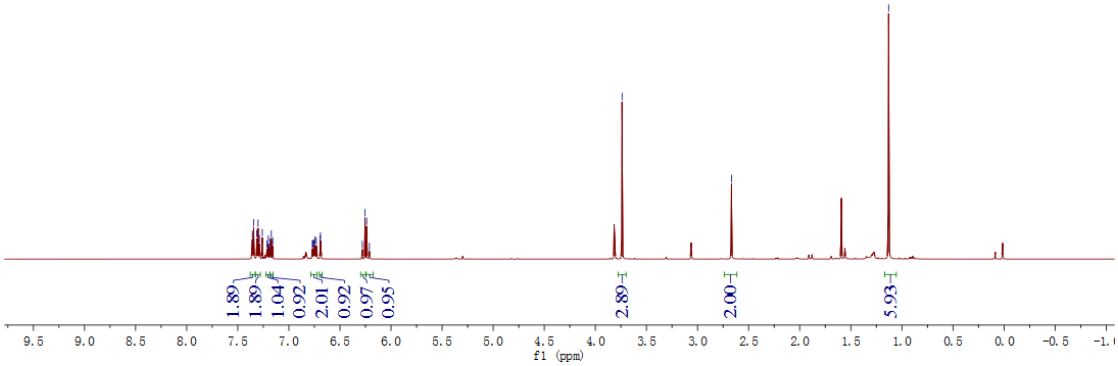
23

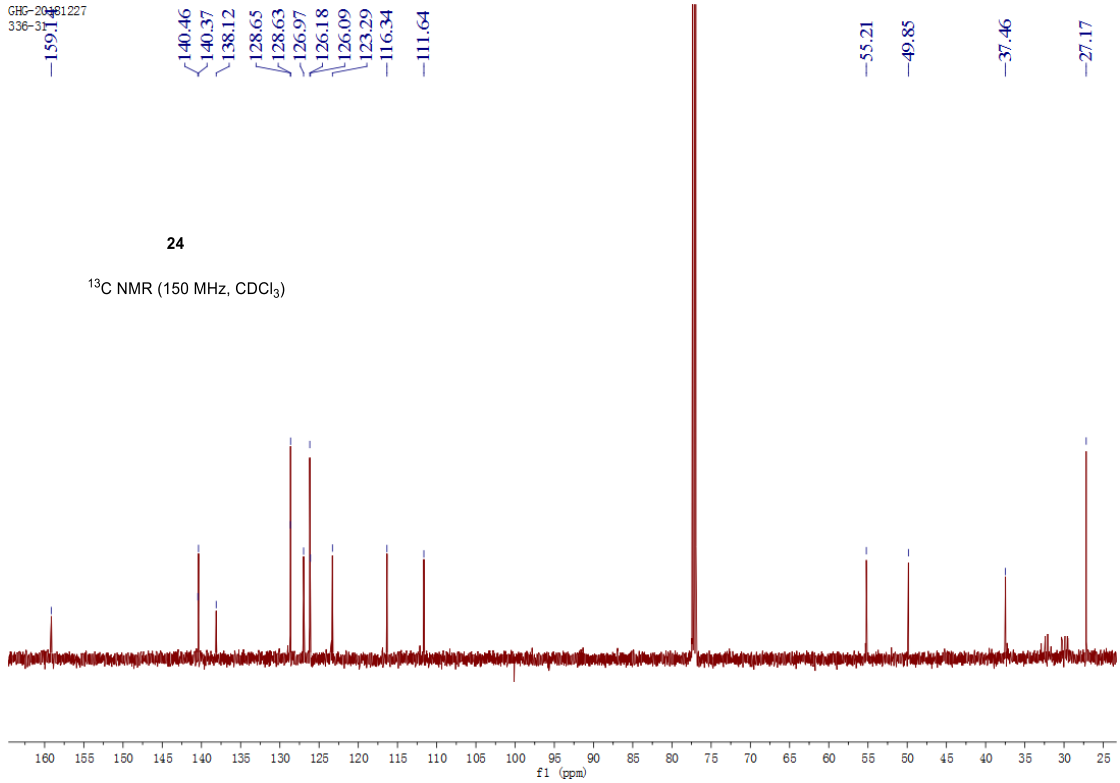
^{13}C NMR (150 MHz, $CDCl_3$)



24

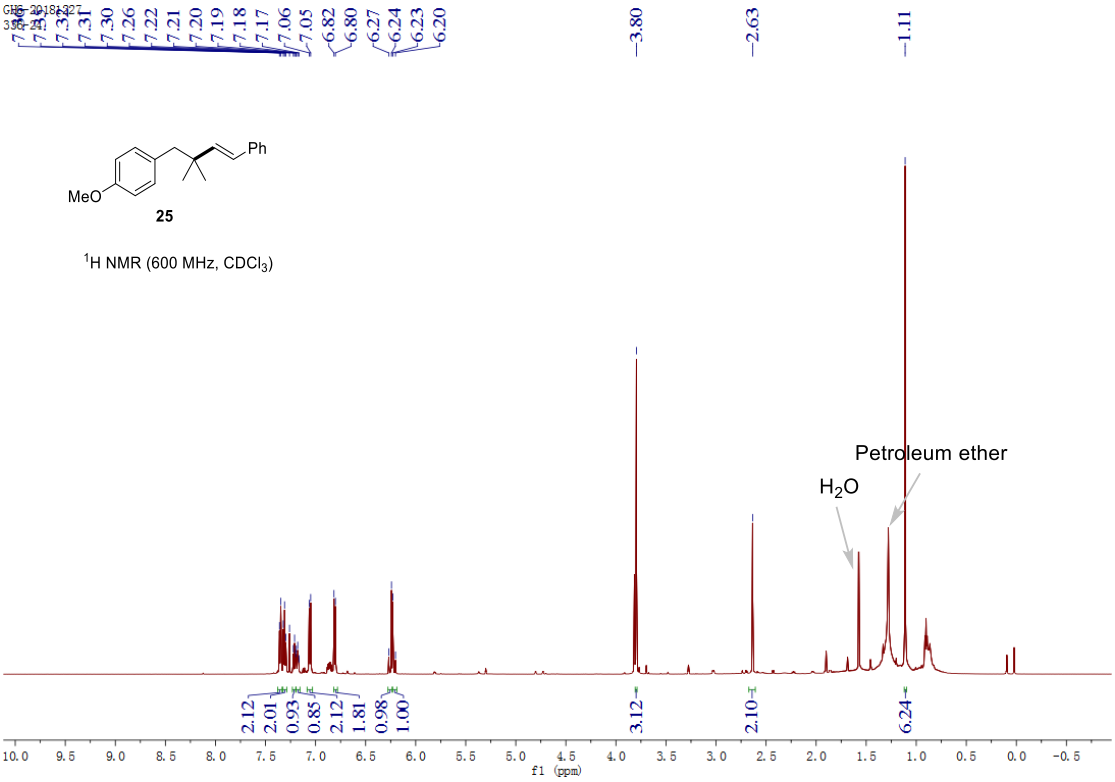
^{1}H NMR (600 MHz, $CDCl_3$)

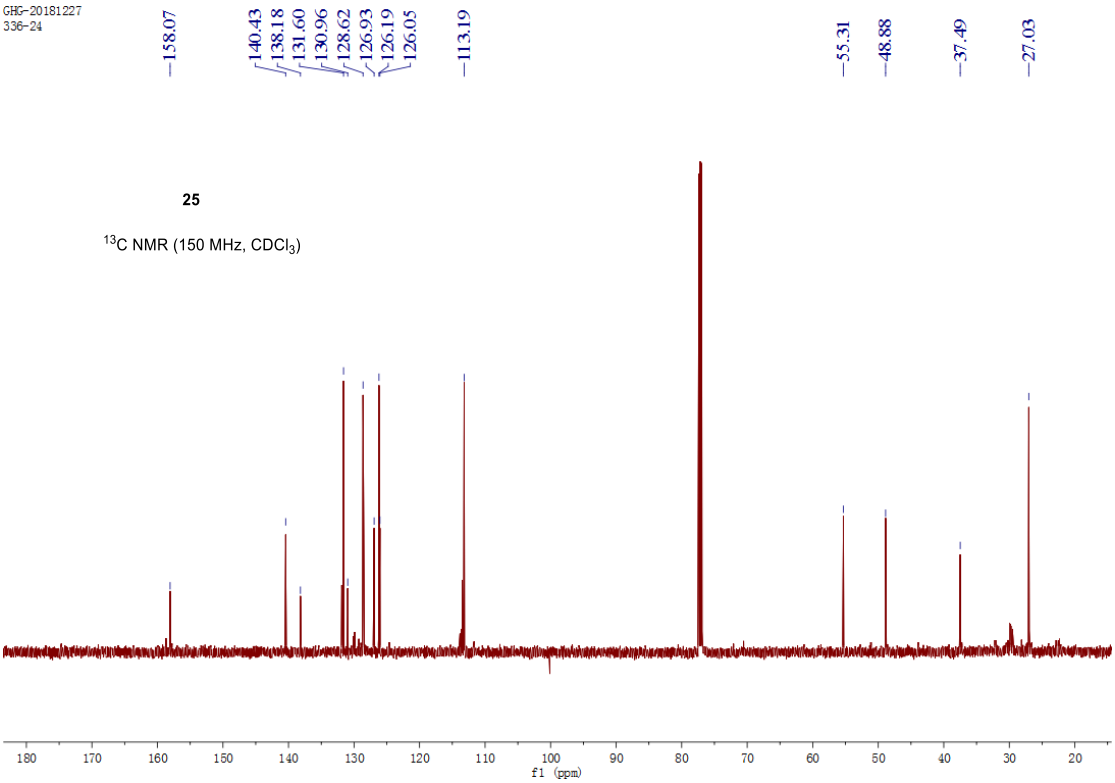


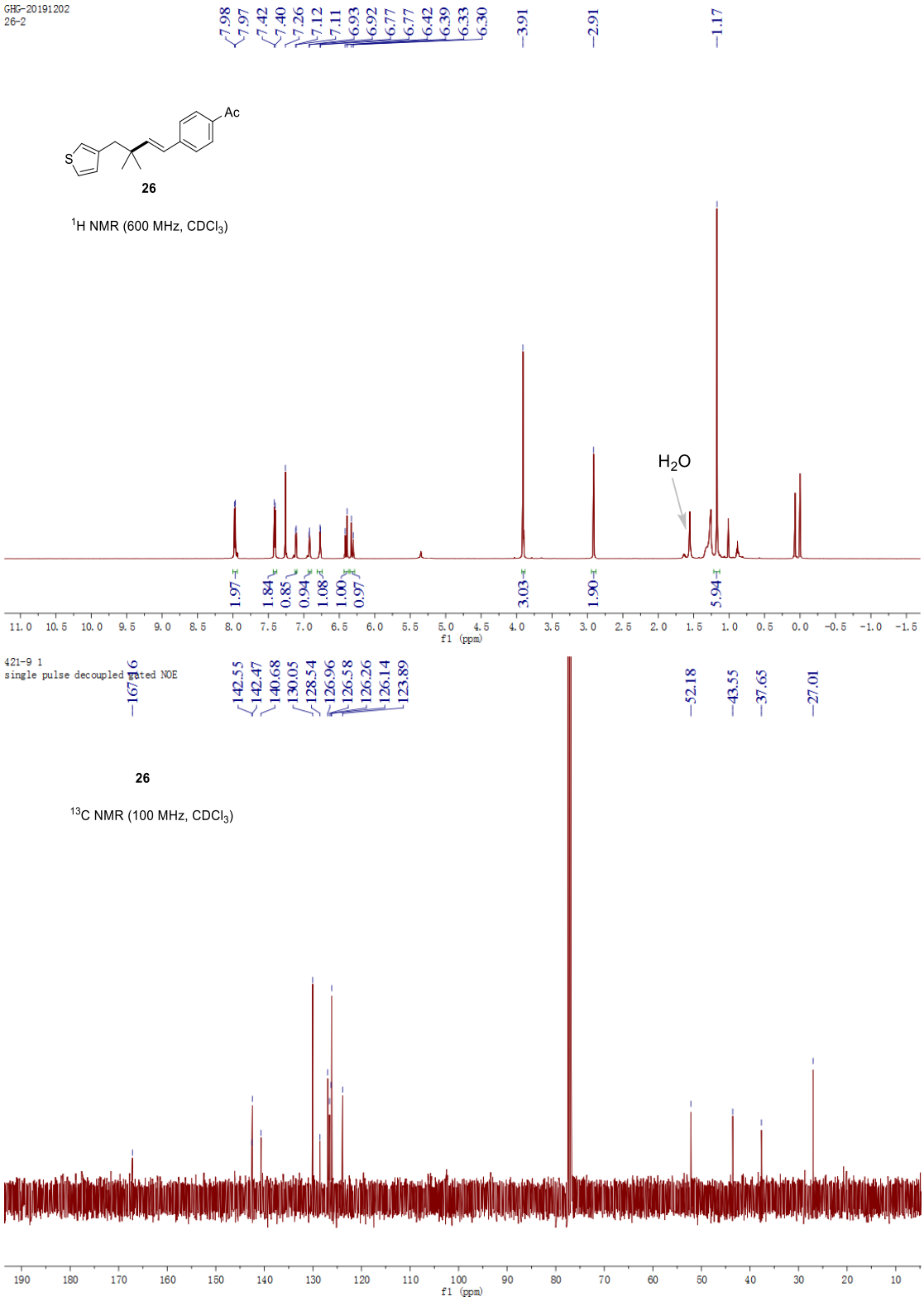


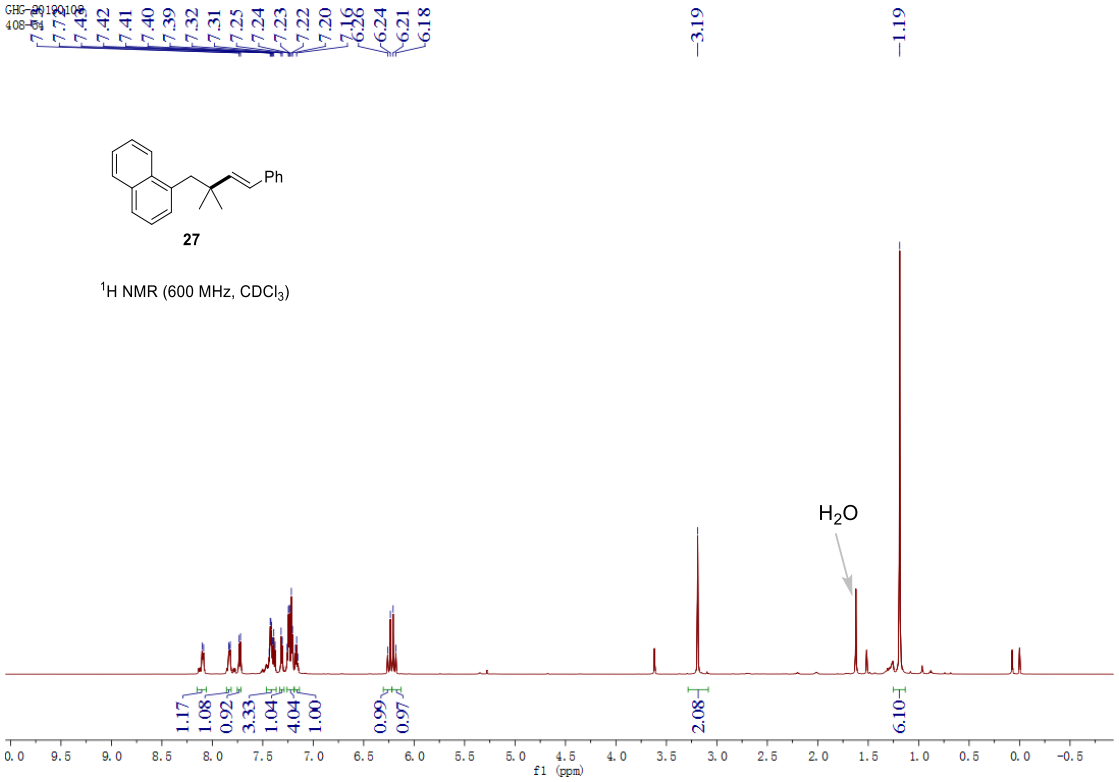
24

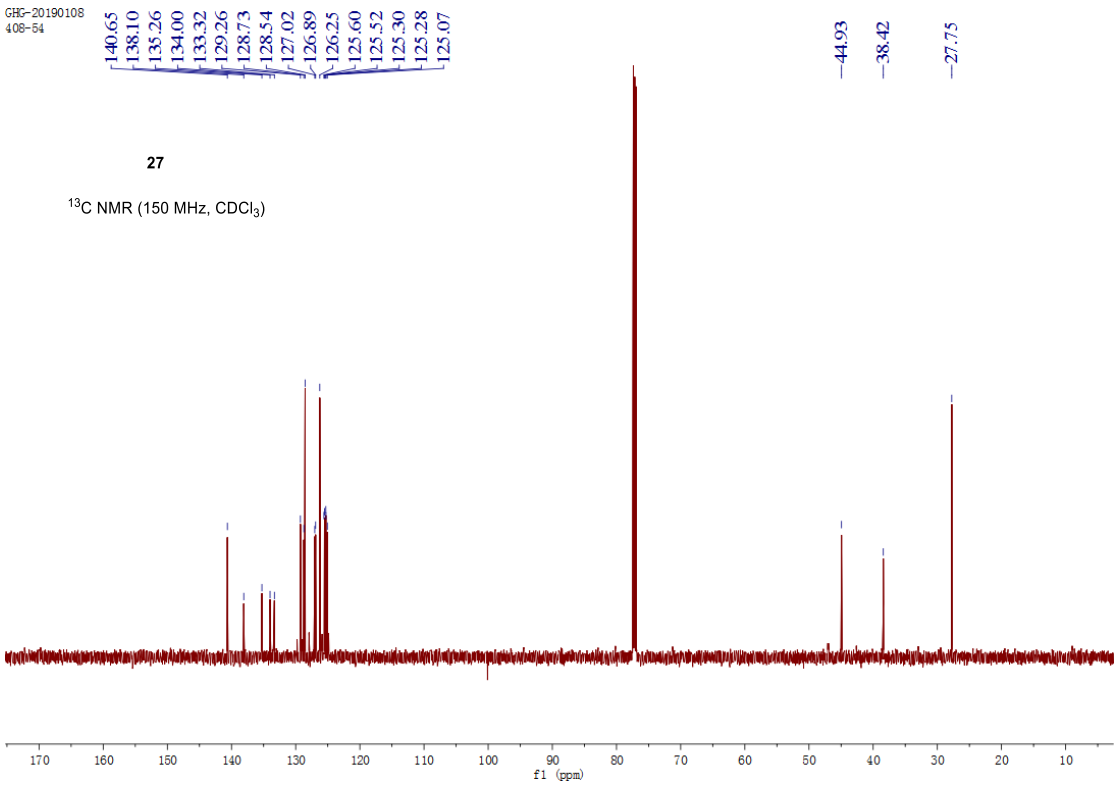
^{13}C NMR (150 MHz, $CDCl_3$)

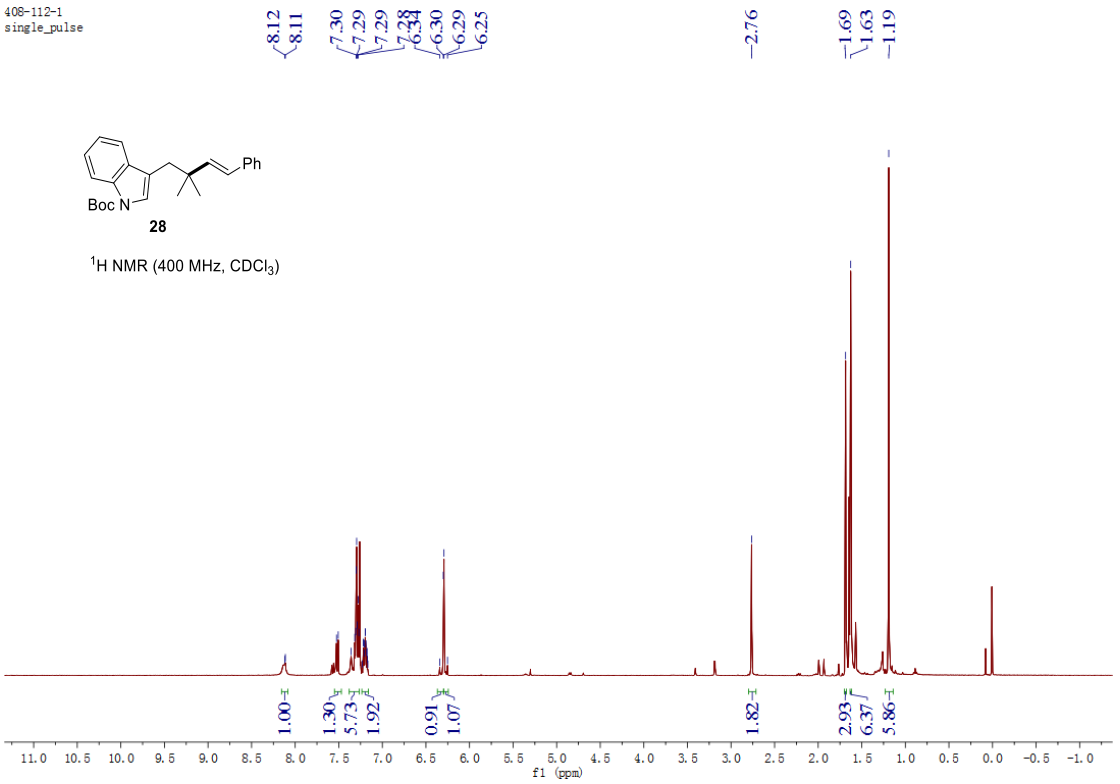

Ph
MeO
25
1H NMR (600 MHz, CDCl3)
Petroleum ether
H2O
f1 (ppm)


GHG-20181227
336-24
25
13C NMR (150 MHz, CDCl3)
f1 (ppm)


GHG-20191202
26-2
7.98
7.97
7.42
7.40
7.26
7.12
7.11
6.93
6.92
6.77
6.77
6.42
6.39
6.33
6.30
3.91
2.91
1.17
Ac
S
26
1H NMR (600 MHz, CDCl3)
H2O
1.97
1.84
0.85
0.94
1.08
1.00
0.97
3.03
1.90
5.94
f1 (ppm)
421-9 1
single pulse decoupled gated NOE
167.6
142.55
142.47
140.68
130.05
128.54
126.96
126.58
126.26
126.14
123.89
52.18
43.55
37.65
27.01
26
13C NMR (100 MHz, CDCl3)
f1 (ppm)

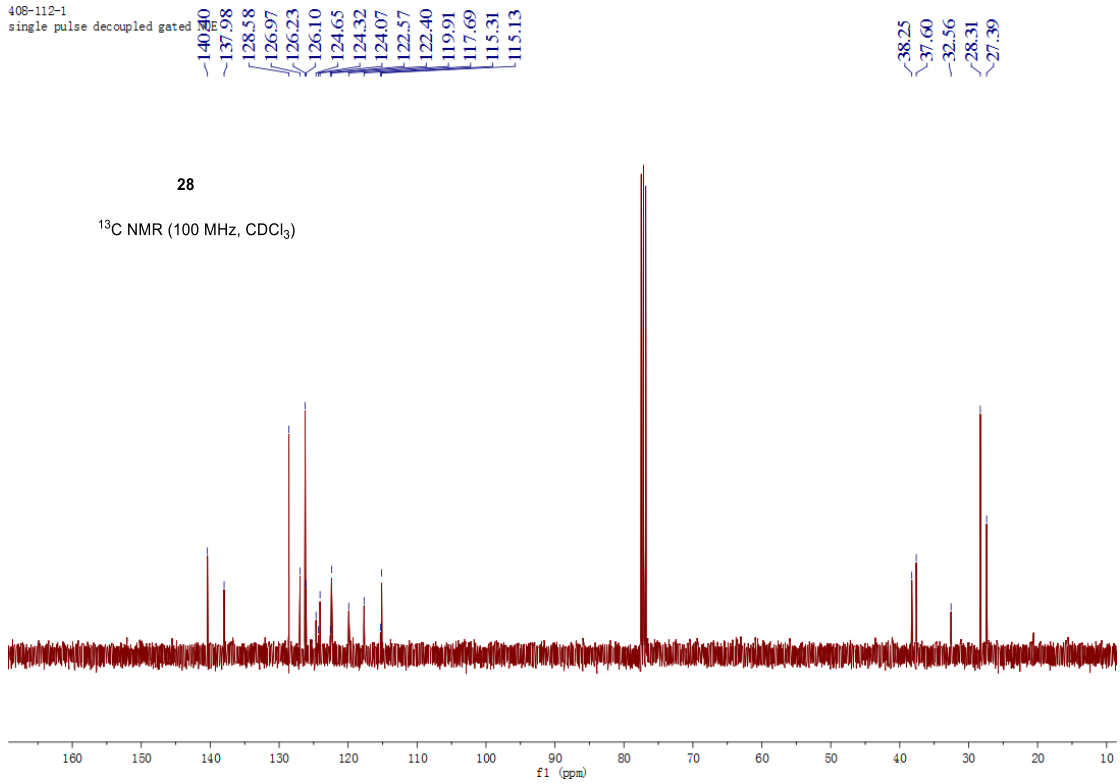

7.43
7.42
7.41
7.40
7.39
7.32
7.31
7.25
7.24
7.23
7.22
7.20
7.16
6.28
6.24
6.21
6.18
3.19
1.19
Ph
27
1H NMR (600 MHz, CDCl3)
H2O
1.17
1.08
0.92
3.33
1.04
4.04
1.00
0.99
0.97
2.08
6.10
f1 (ppm)


GHG-20190108
408-54
140.65
138.10
135.26
134.00
133.32
129.26
128.73
128.54
127.02
126.89
126.25
125.60
125.52
125.30
125.28
125.07
44.93
38.42
27.75
27
13C NMR (150 MHz, CDCl3)
f1 (ppm)



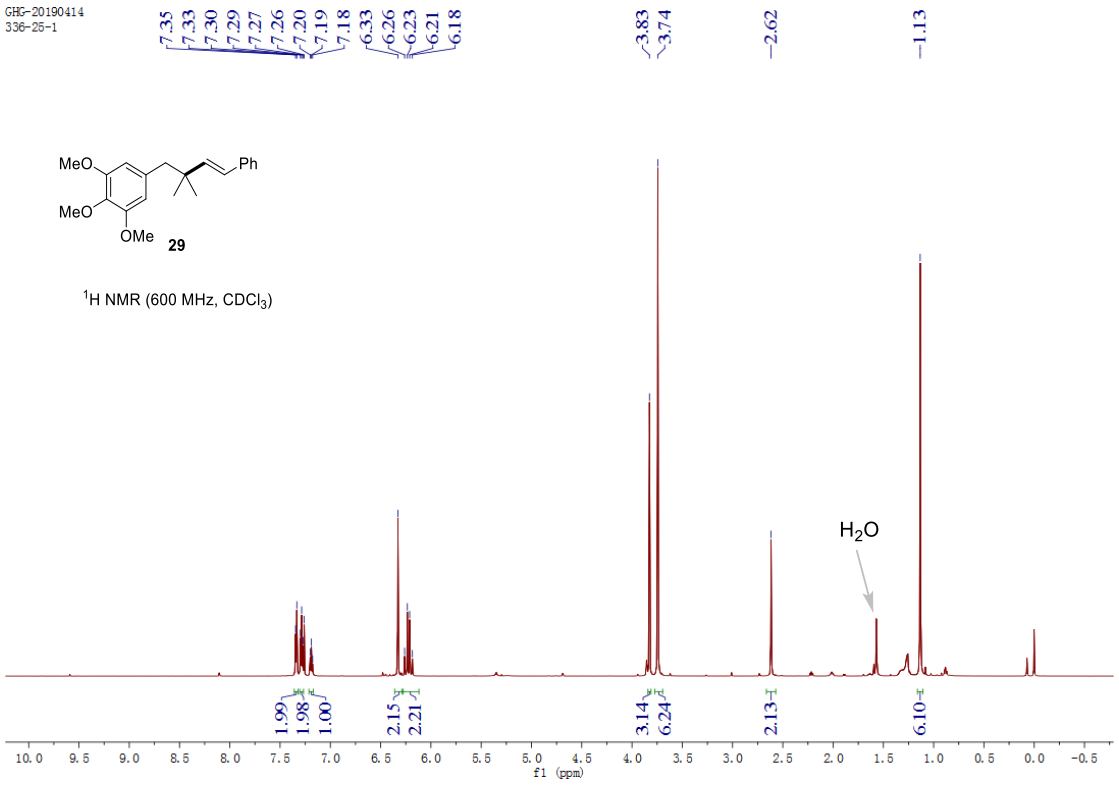
28

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



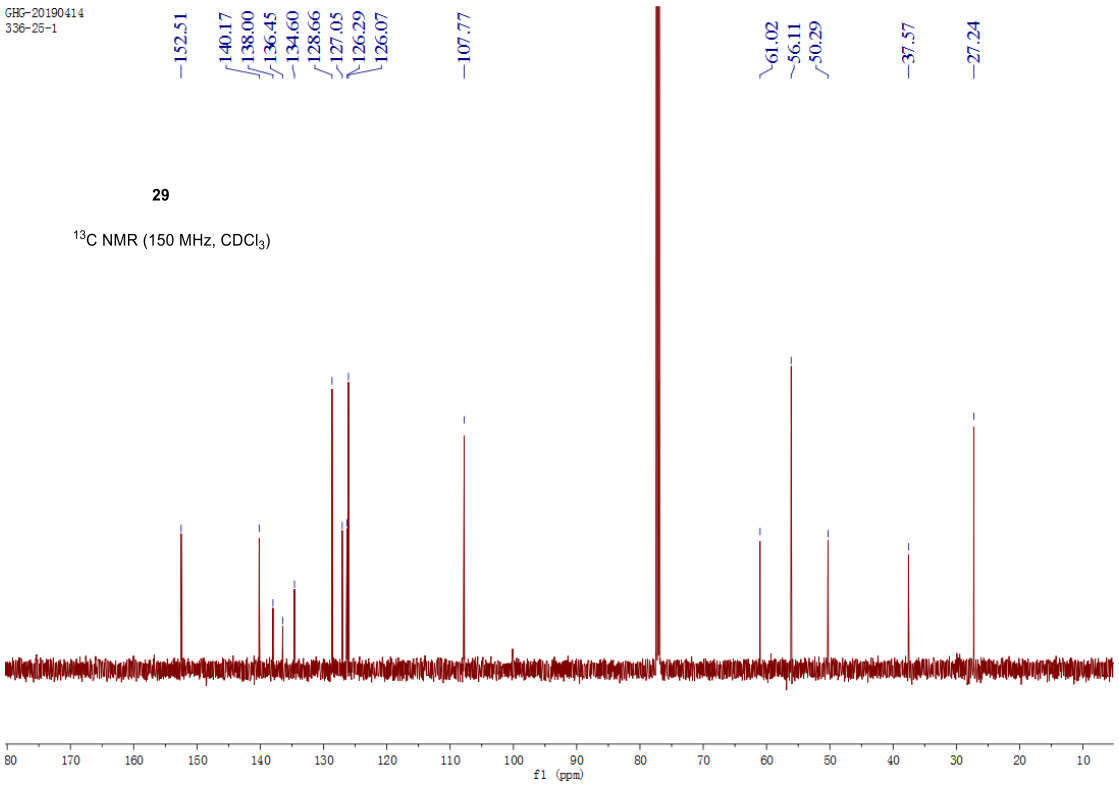
28

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



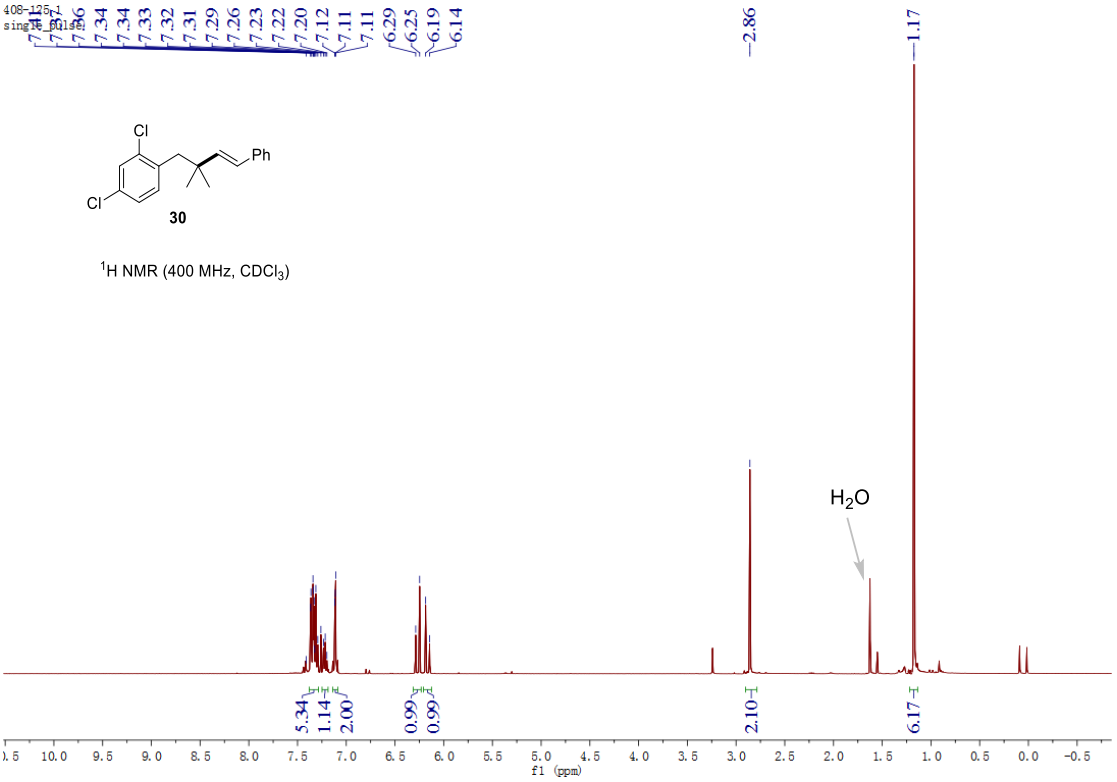
29

^{1}H NMR (600 MHz, $CDCl_3$)



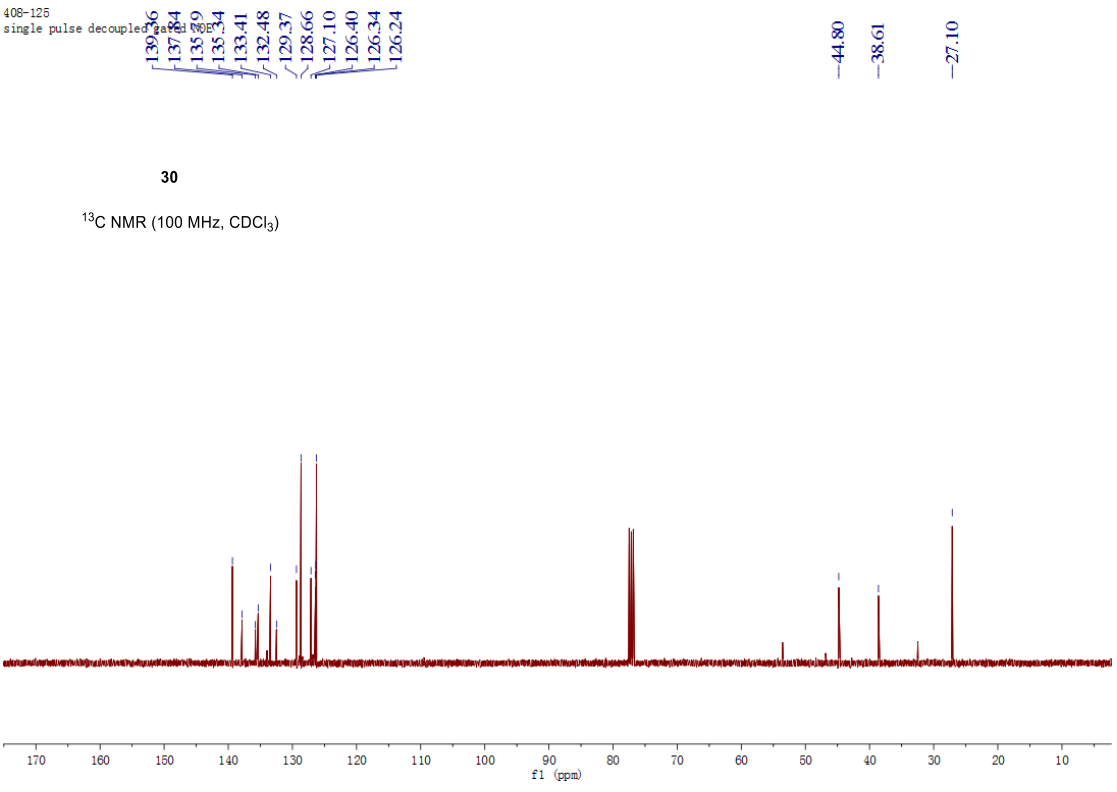
29

^{13}C NMR (150 MHz, $CDCl_3$)



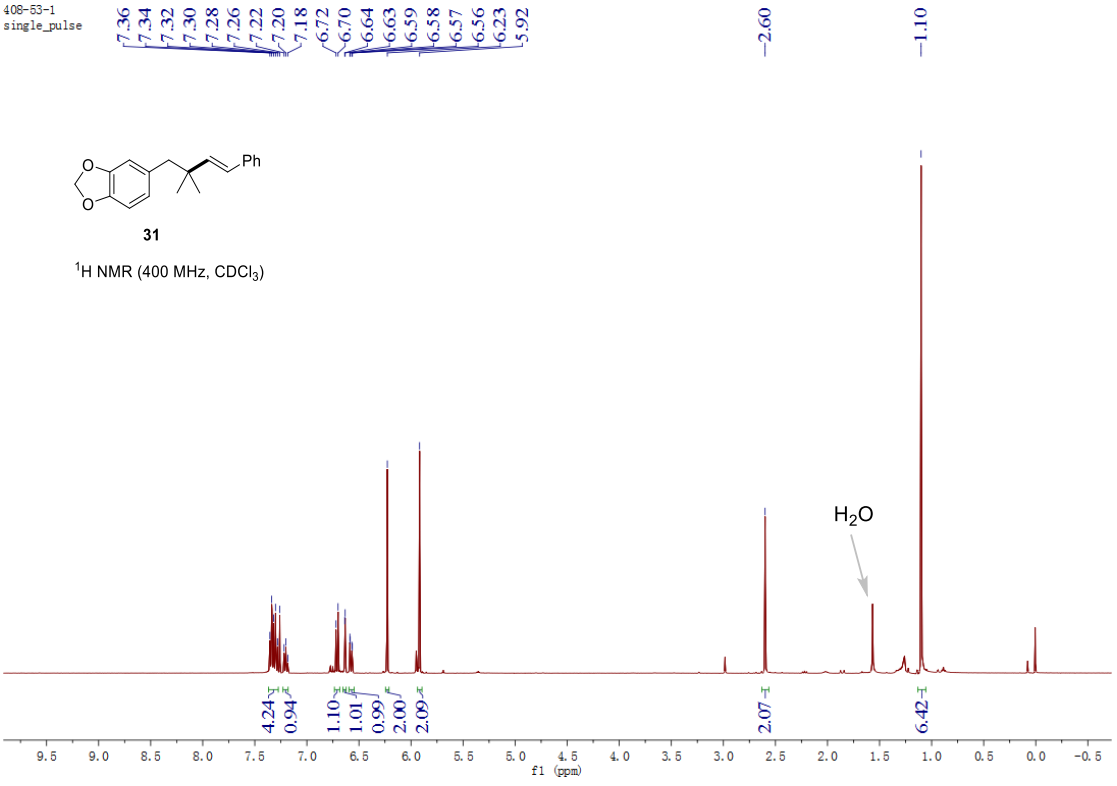
30

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



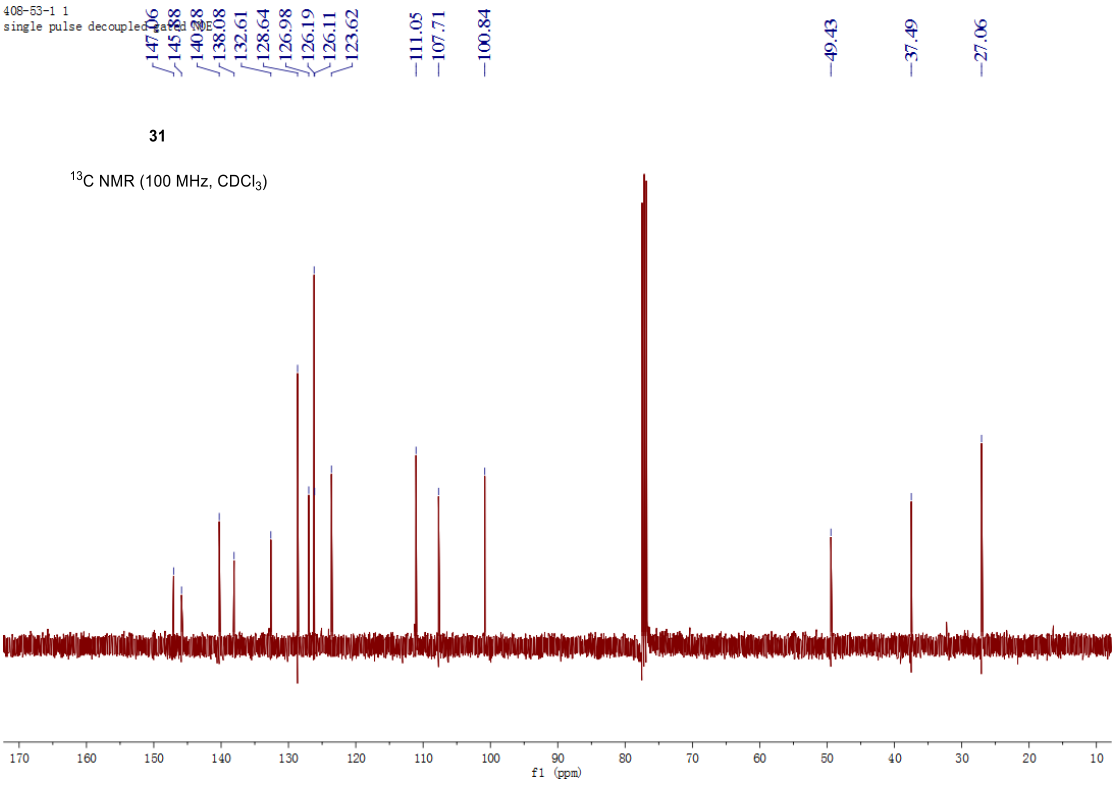
30

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



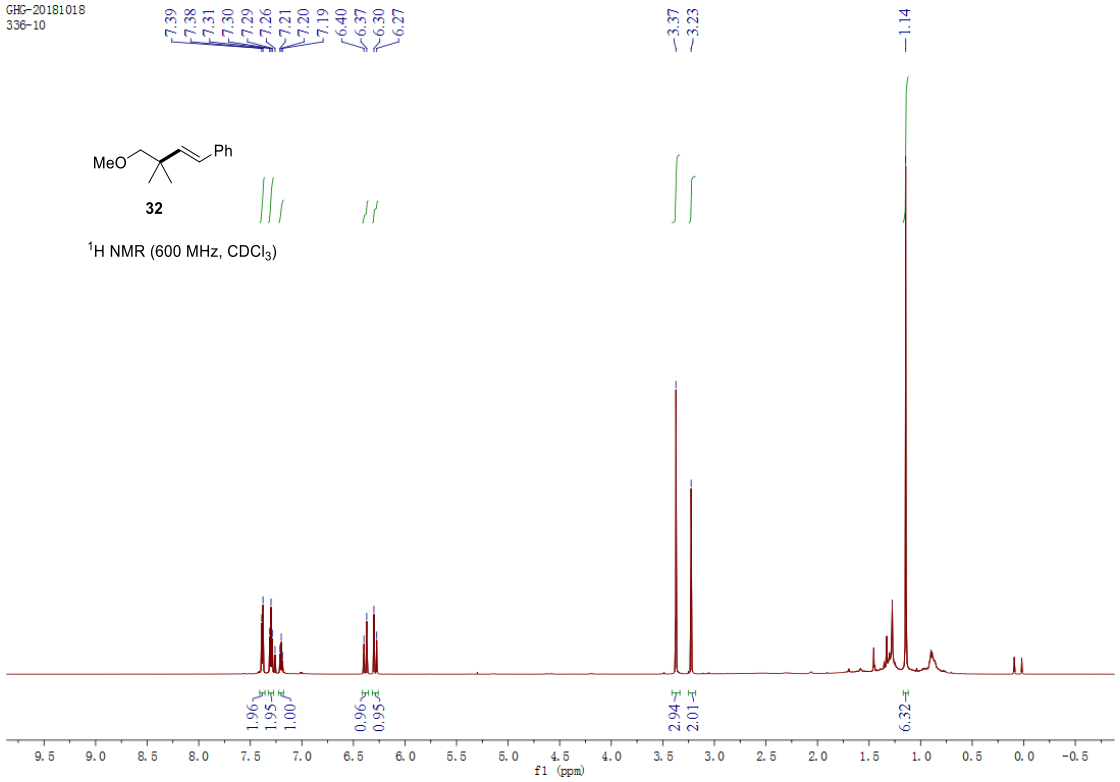
31

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



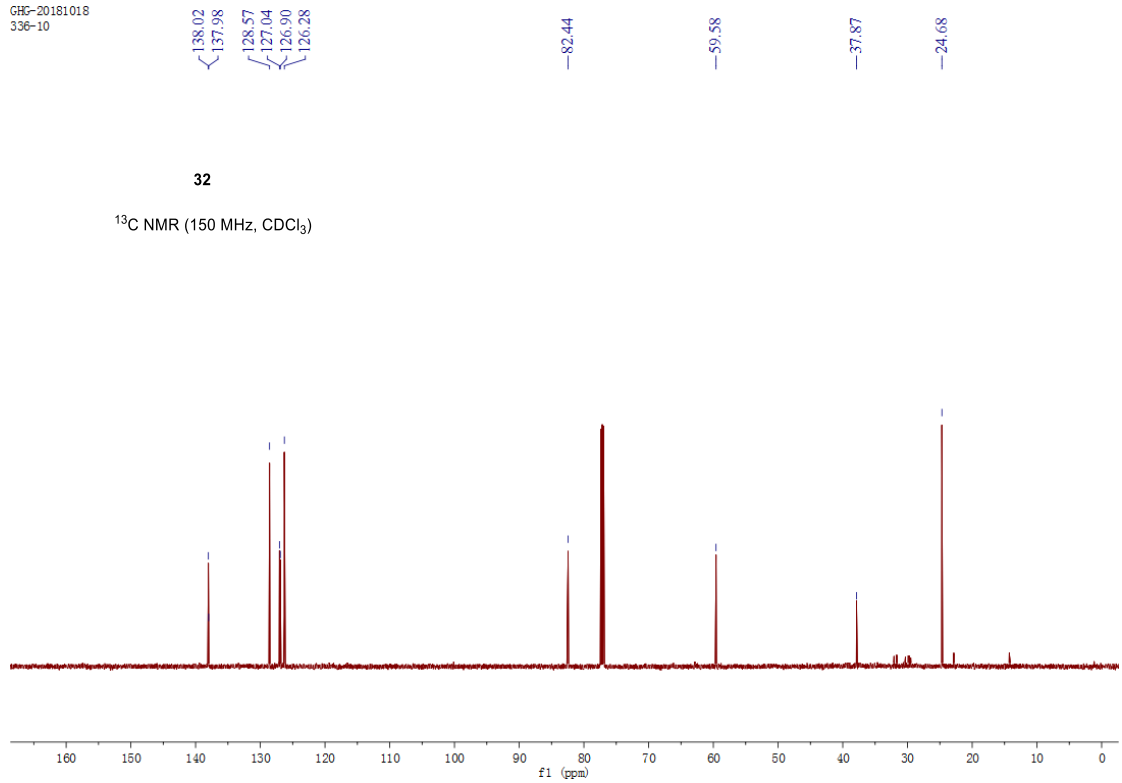
31

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



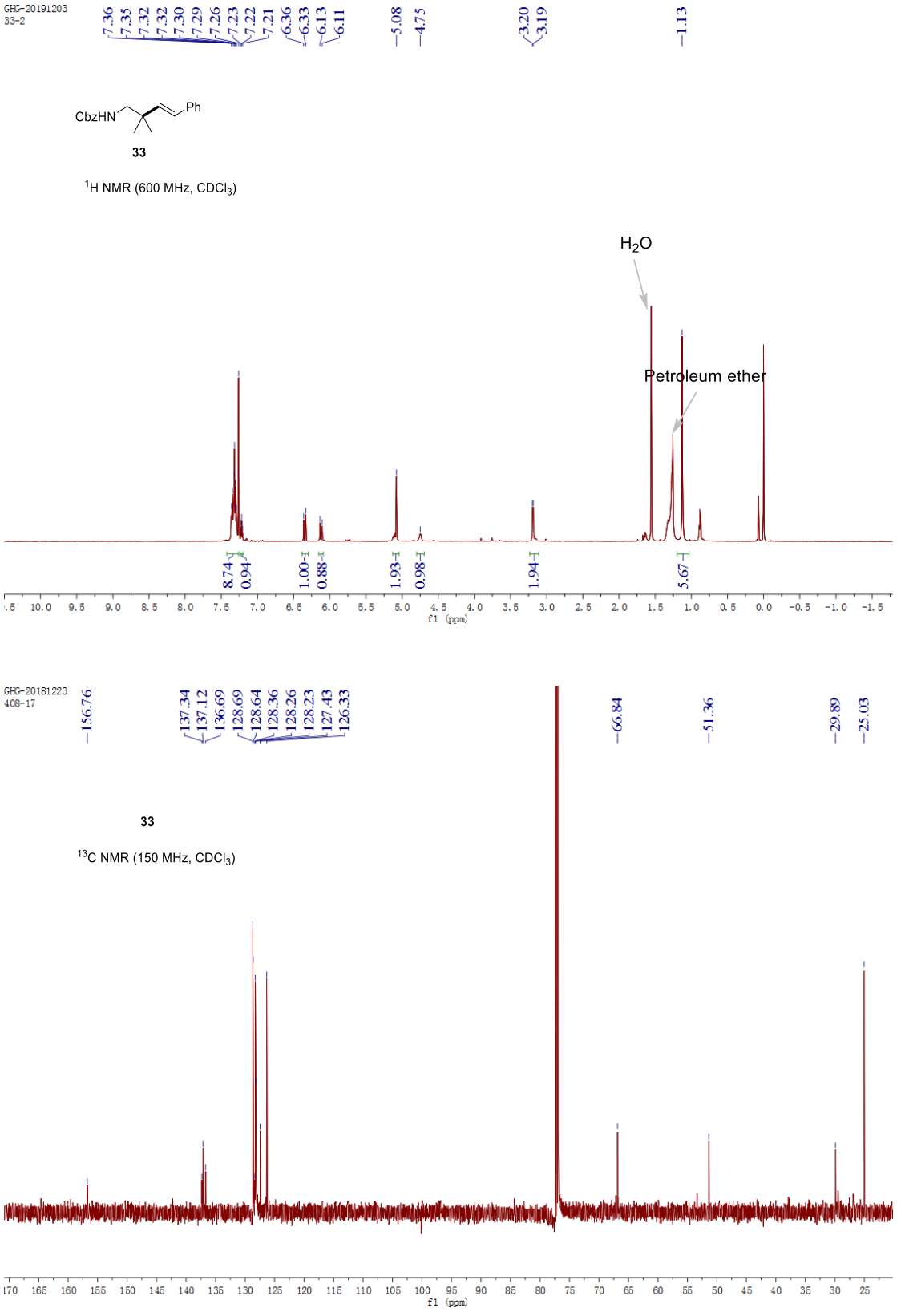
32

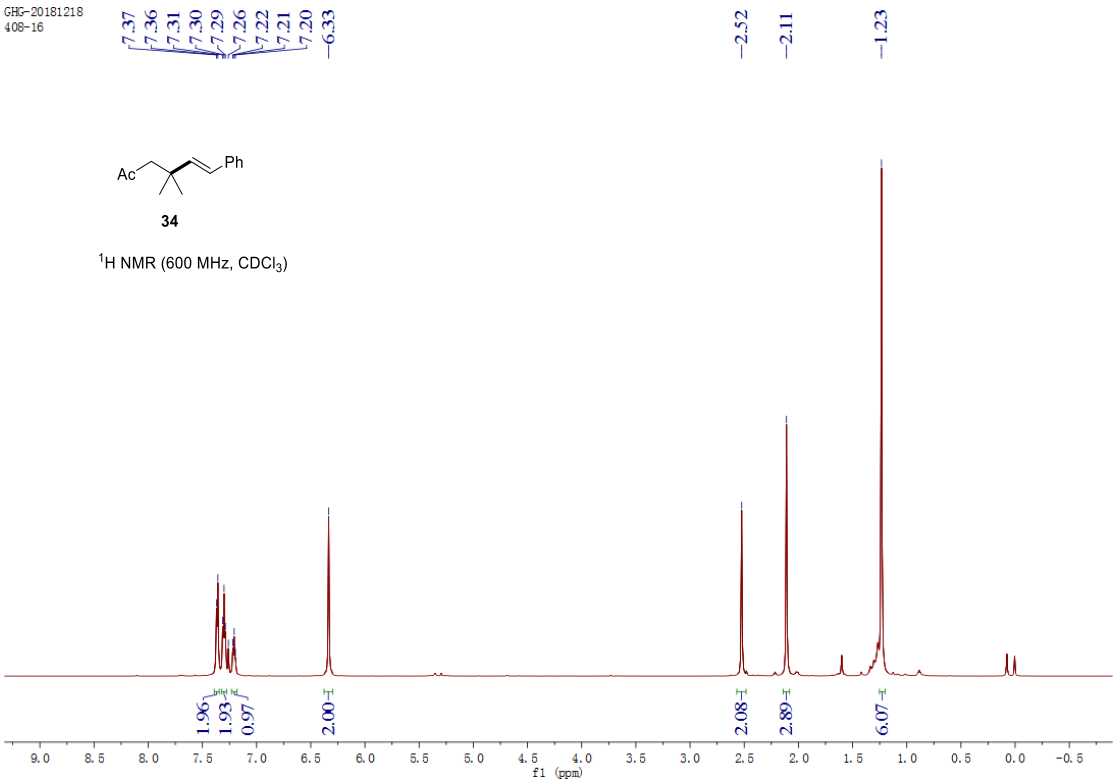
^{1}H NMR (600 MHz, $CDCl_3$)



32

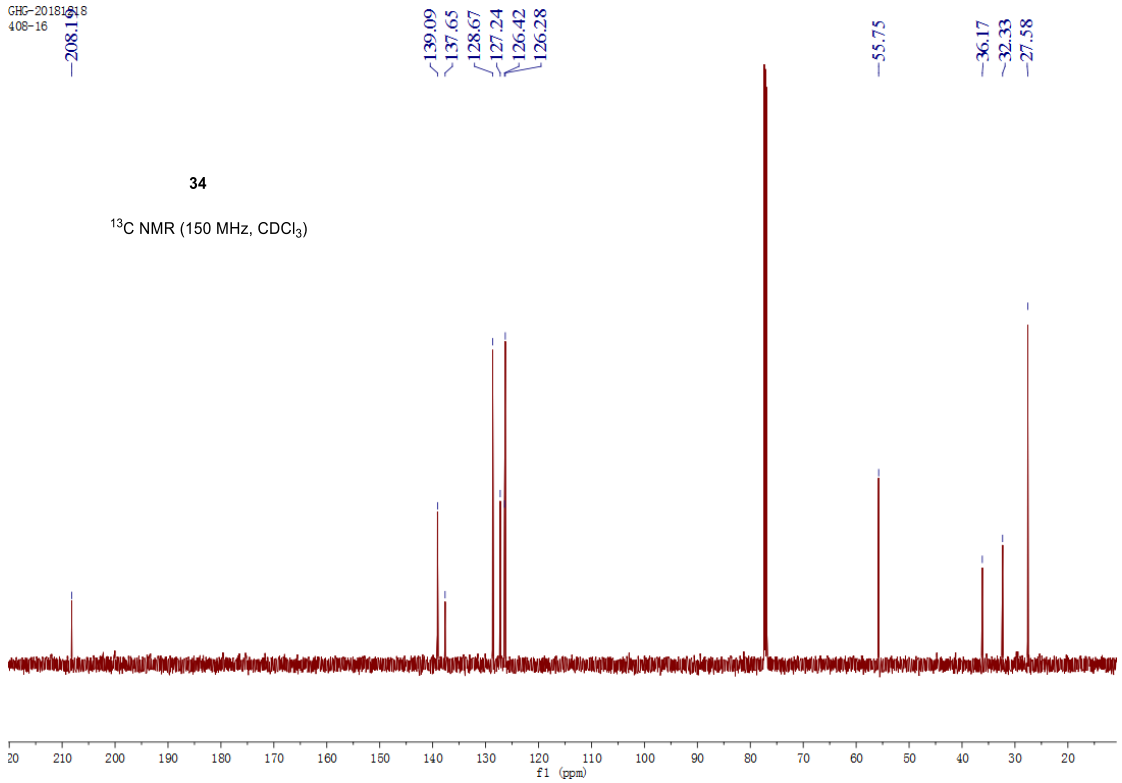
^{13}C NMR (150 MHz, $CDCl_3$)


GHG-20191203
33-2
7.36
7.35
7.32
7.32
7.30
7.29
7.26
7.23
7.22
7.21
6.36
6.33
6.13
6.11
5.08
4.75
3.20
3.19
1.13
CbzHN
Ph
33
1H NMR (600 MHz, CDCl3)
H2O
Petroleum ether
8.74
0.94
1.00
0.88
1.93
0.98
1.94
5.67
f1 (ppm)
GHG-20181223
408-17
156.76
137.34
137.12
136.69
128.69
128.64
128.36
128.26
128.23
127.43
126.33
66.84
51.36
29.89
25.03
33
13C NMR (150 MHz, CDCl3)
f1 (ppm)



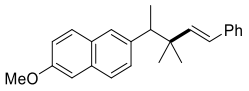
34

^{1}H NMR (600 MHz, $CDCl_3$)



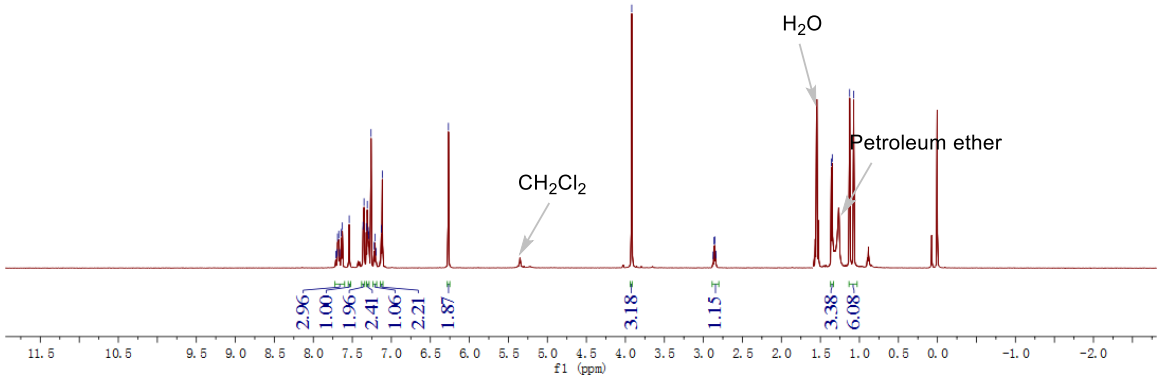
34

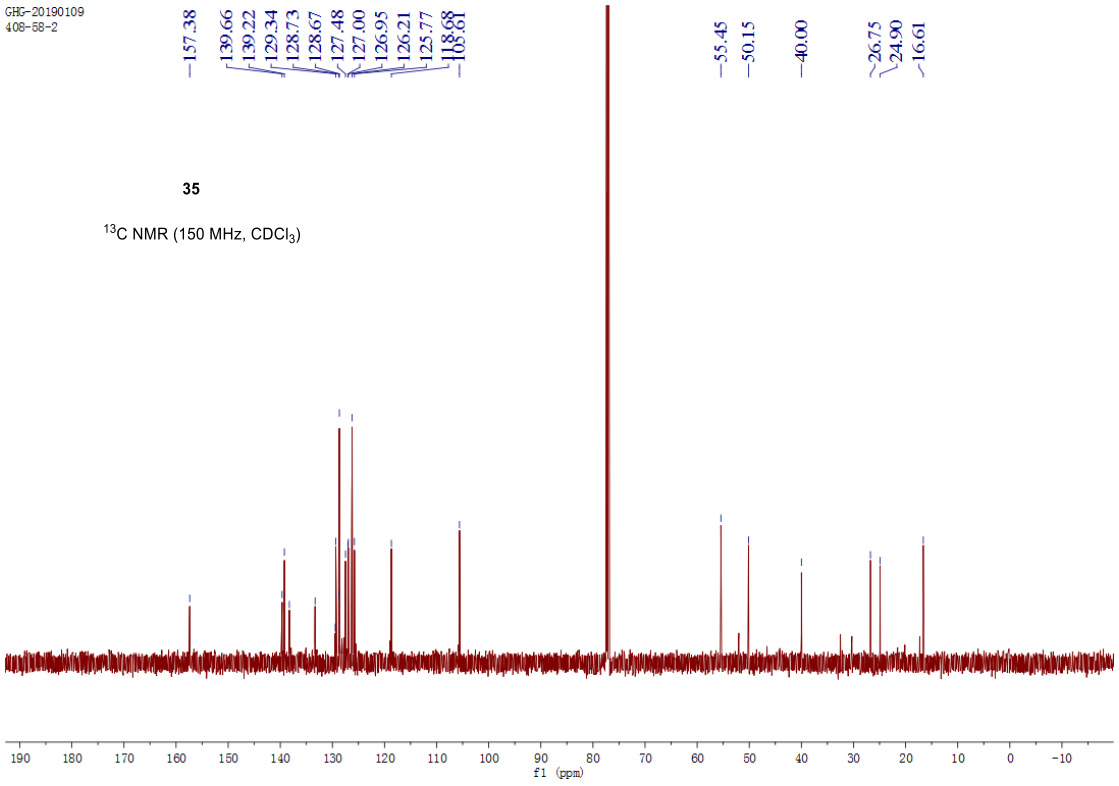
^{13}C NMR (150 MHz, $CDCl_3$)



35

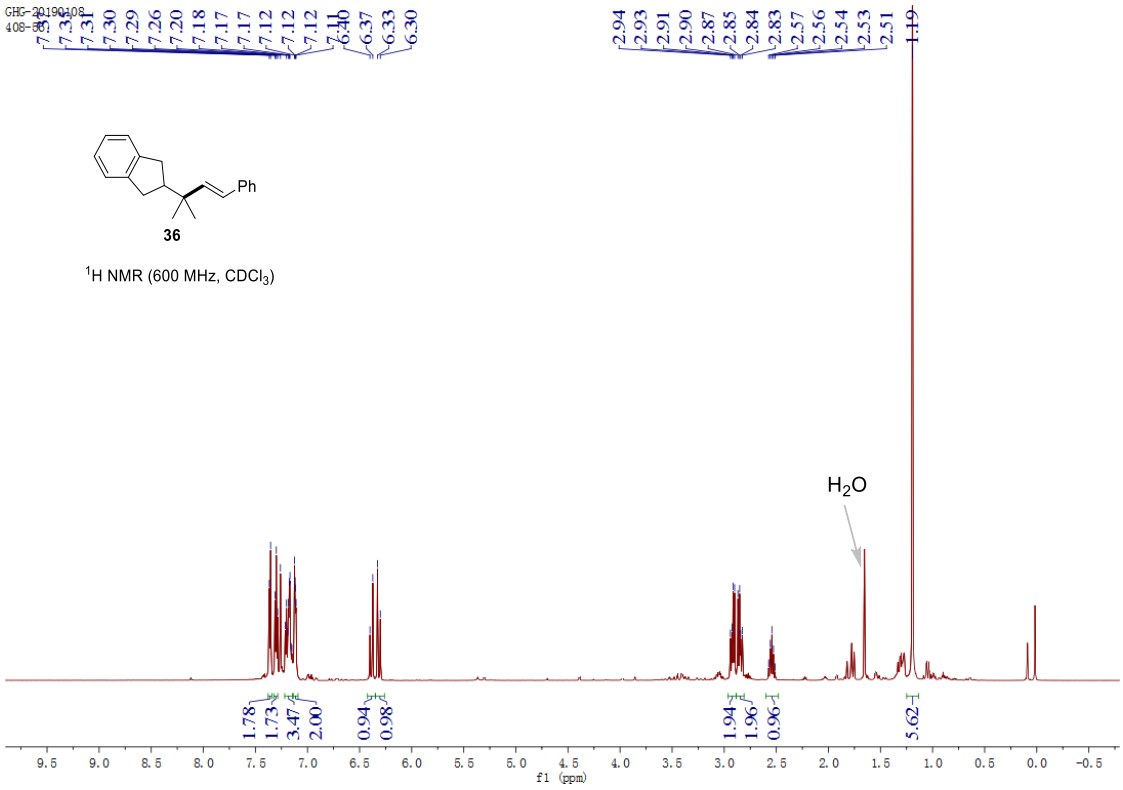
^{1}H NMR (600 MHz, $CDCl_3$)

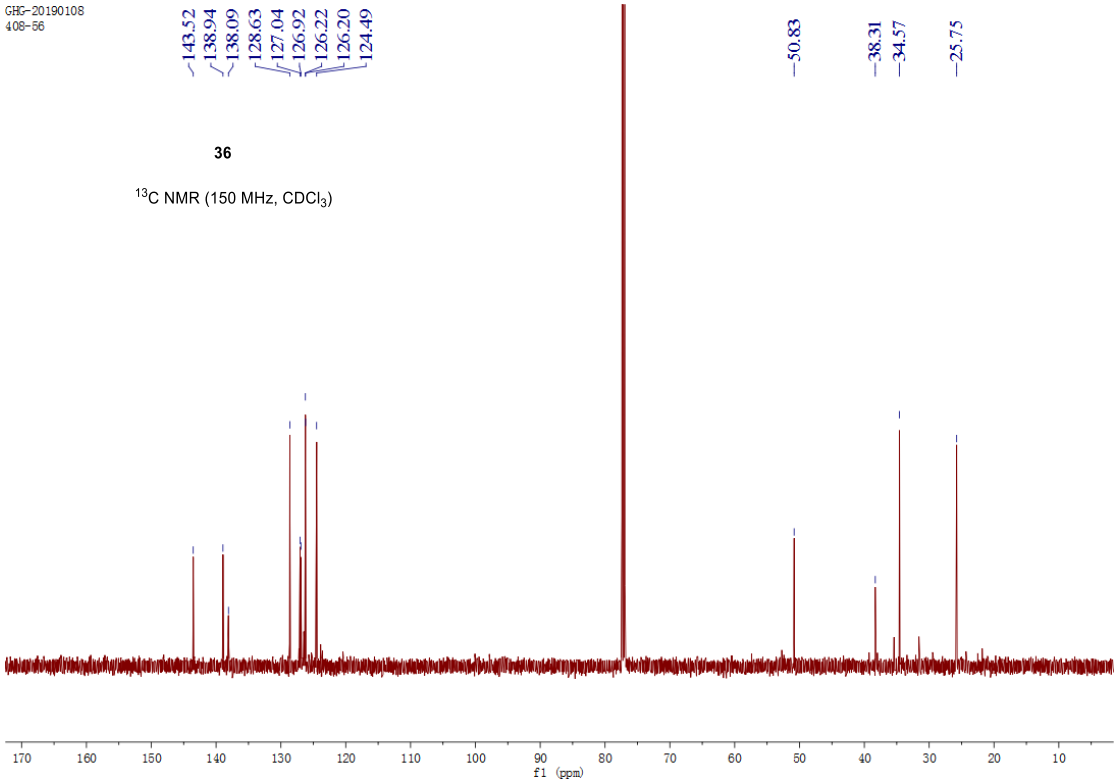


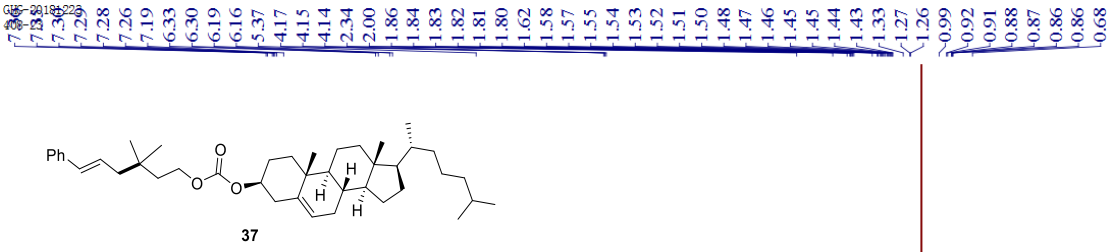


35

^{13}C NMR (150 MHz, $CDCl_3$)

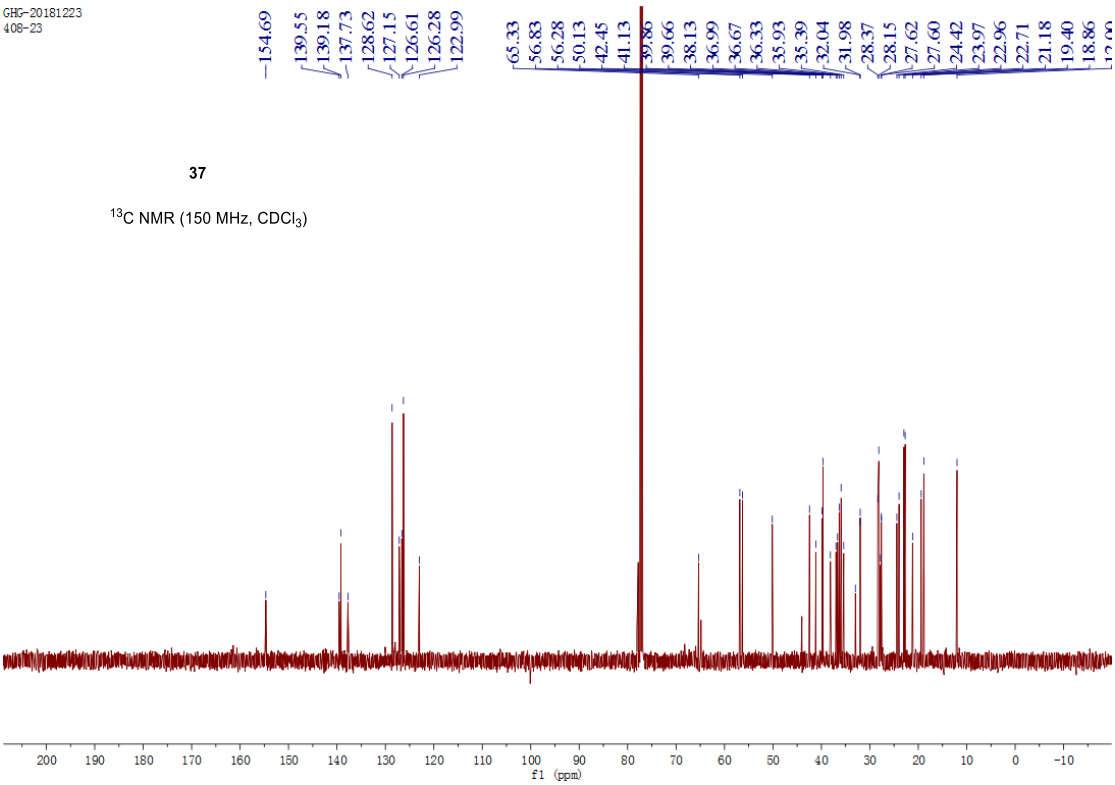

GHG-20190108
408-56
Ph
36
^{1}H NMR (600 MHz, CDCl$_3$)
H$_2$O
f1 (ppm)


GHG-20190108
408-56
36
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)



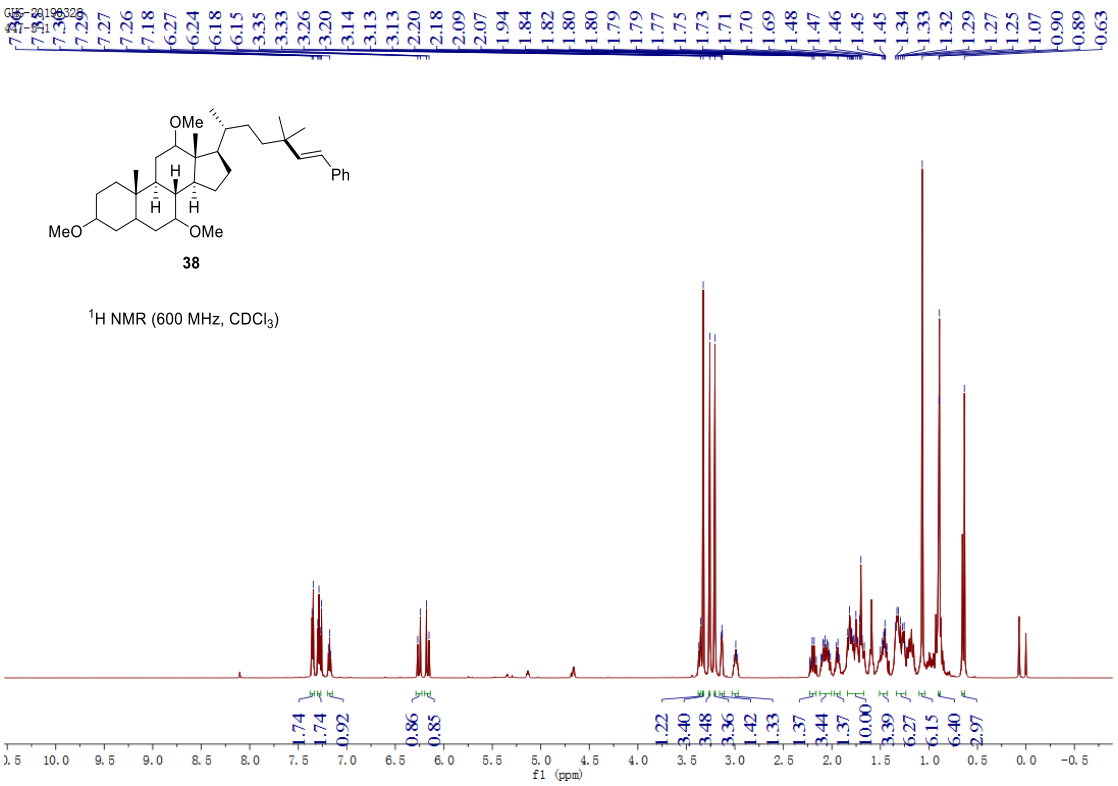
37

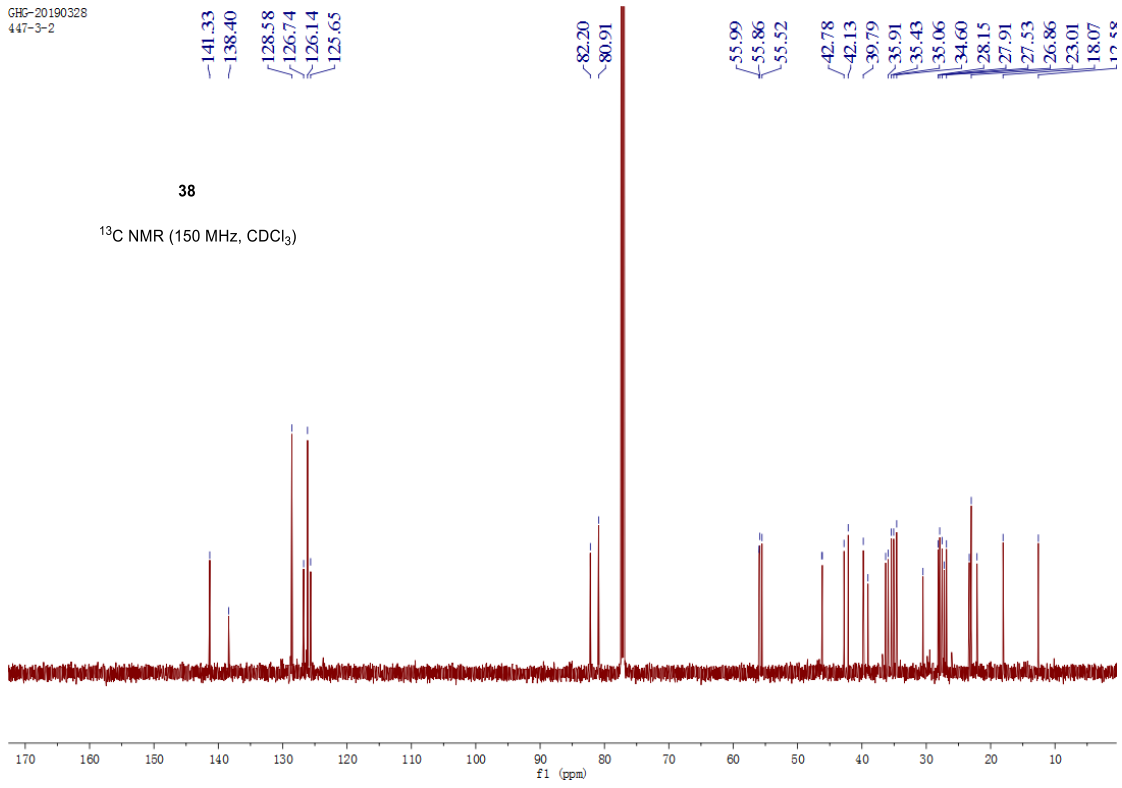
^{1}H NMR (600 MHz, $CDCl_3$)



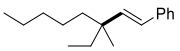
37

^{13}C NMR (150 MHz, $CDCl_3$)


OMe
H
H
H
MeO
OMe
Ph
38
1H NMR (600 MHz, CDCl3)
f1 (ppm)

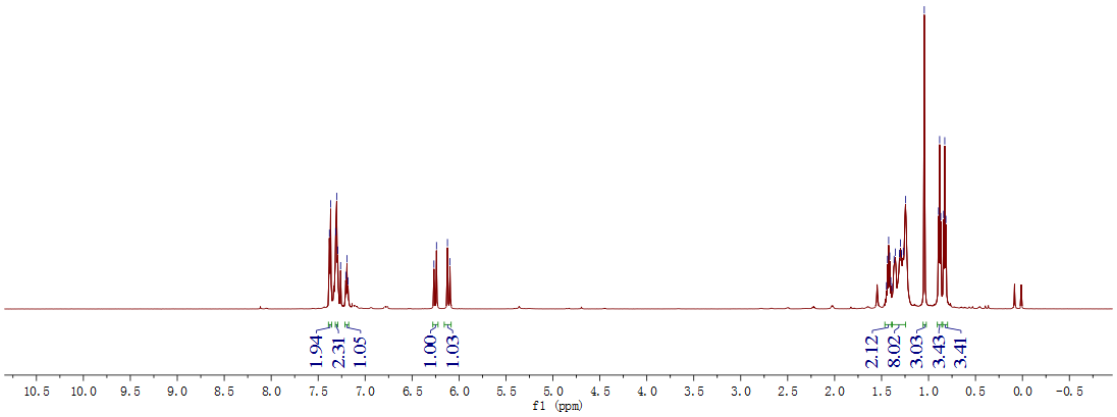

GHG-20190328
447-3-2
38
13C NMR (150 MHz, CDCl3)
f1 (ppm)

GHG-20190326
441-1

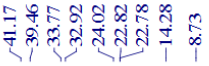


39

^{1}H NMR (600 MHz, $CDCl_3$)

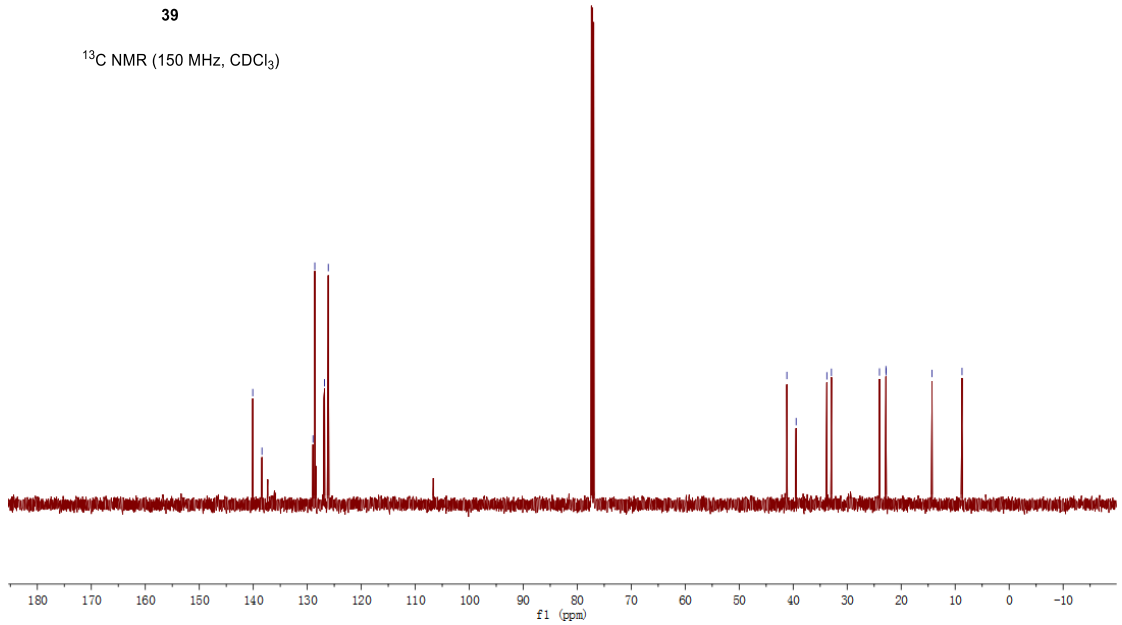


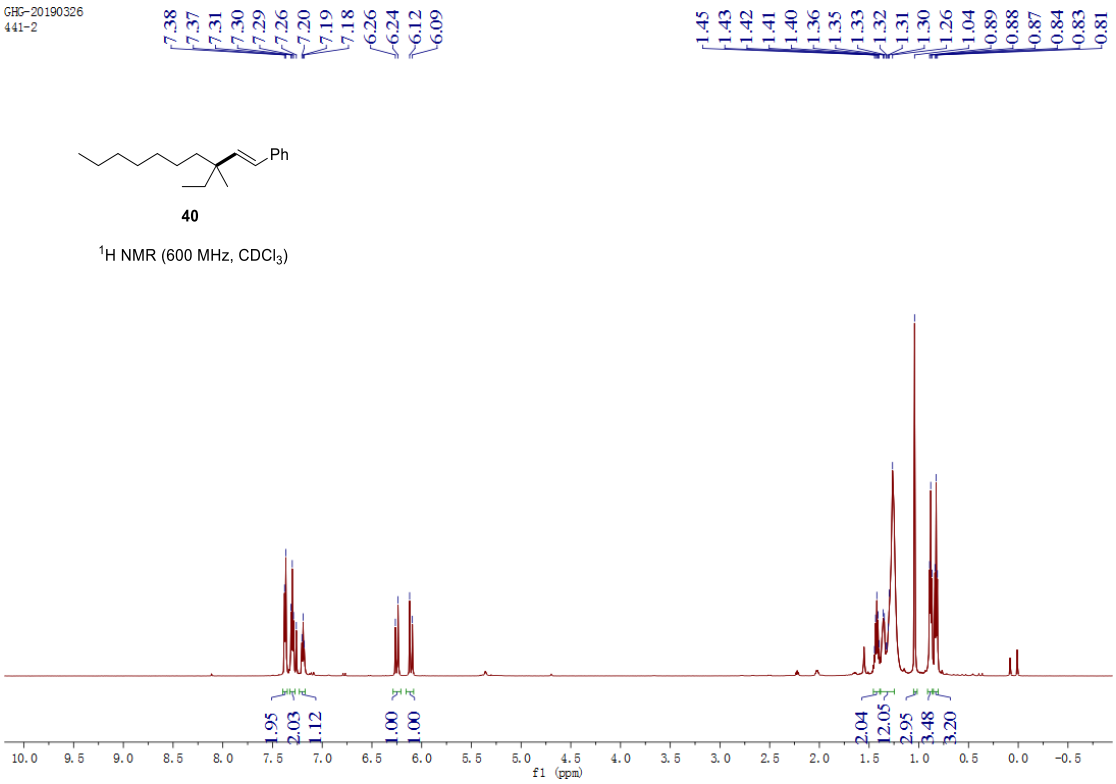
GHG-20190326
441-1

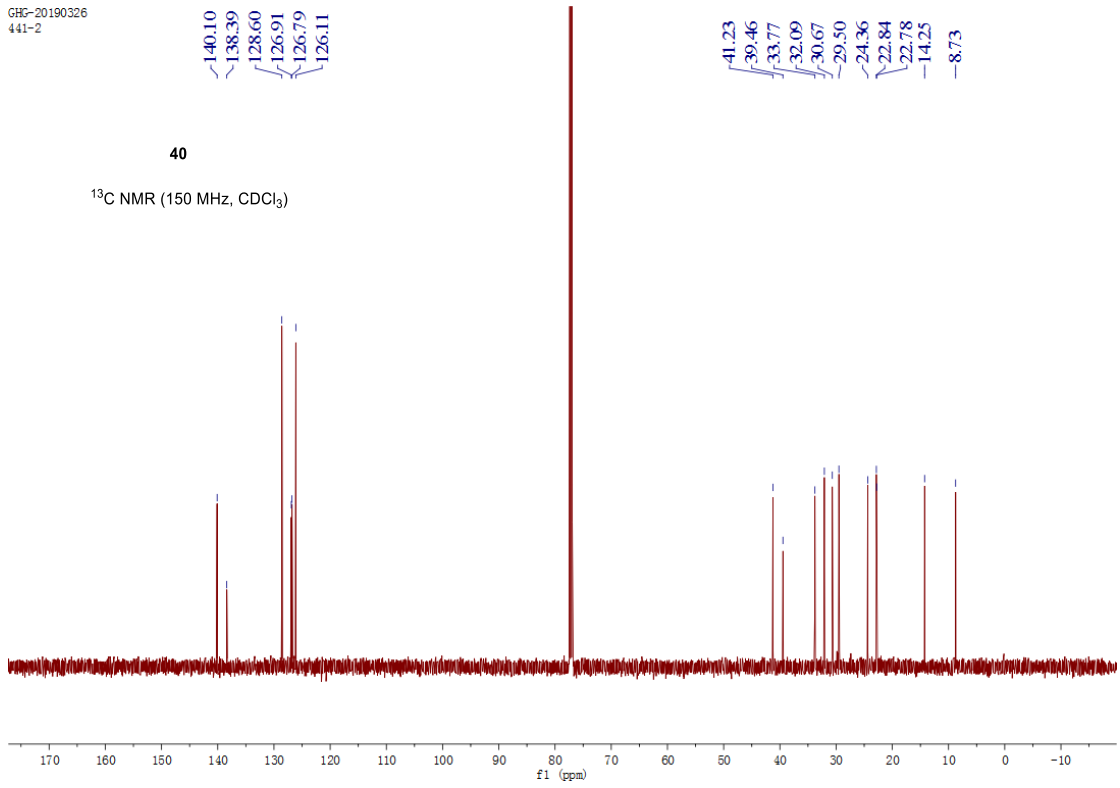


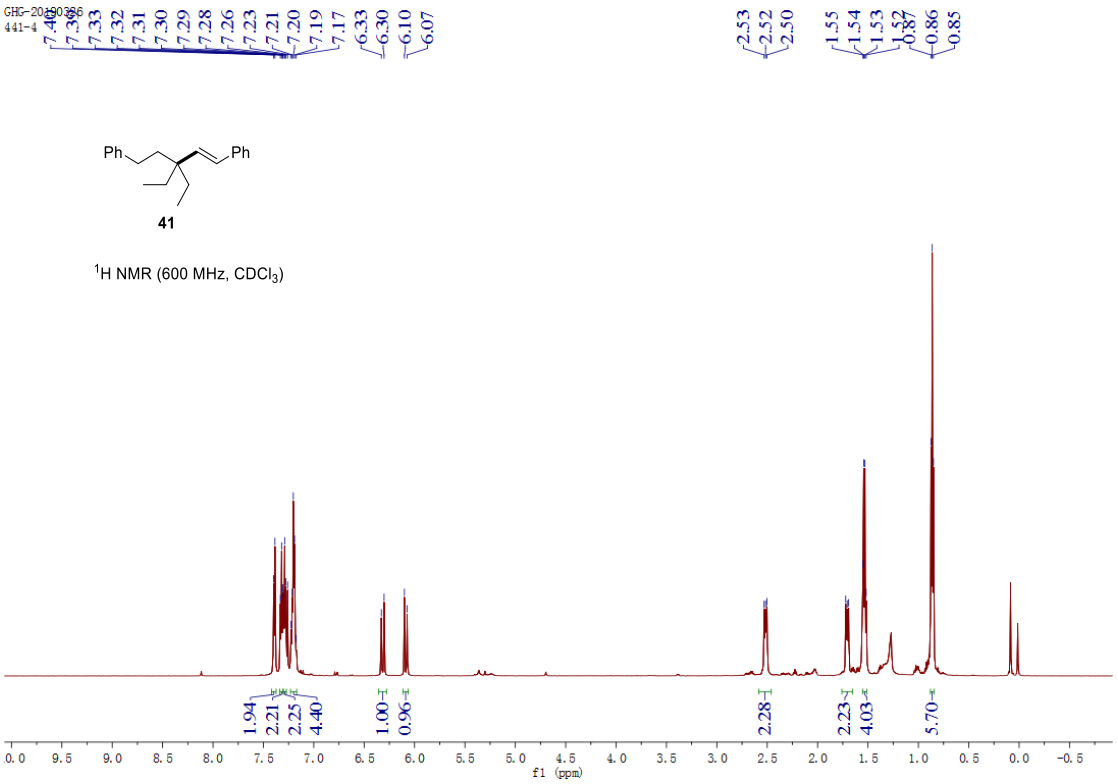
39

^{13}C NMR (150 MHz, $CDCl_3$)



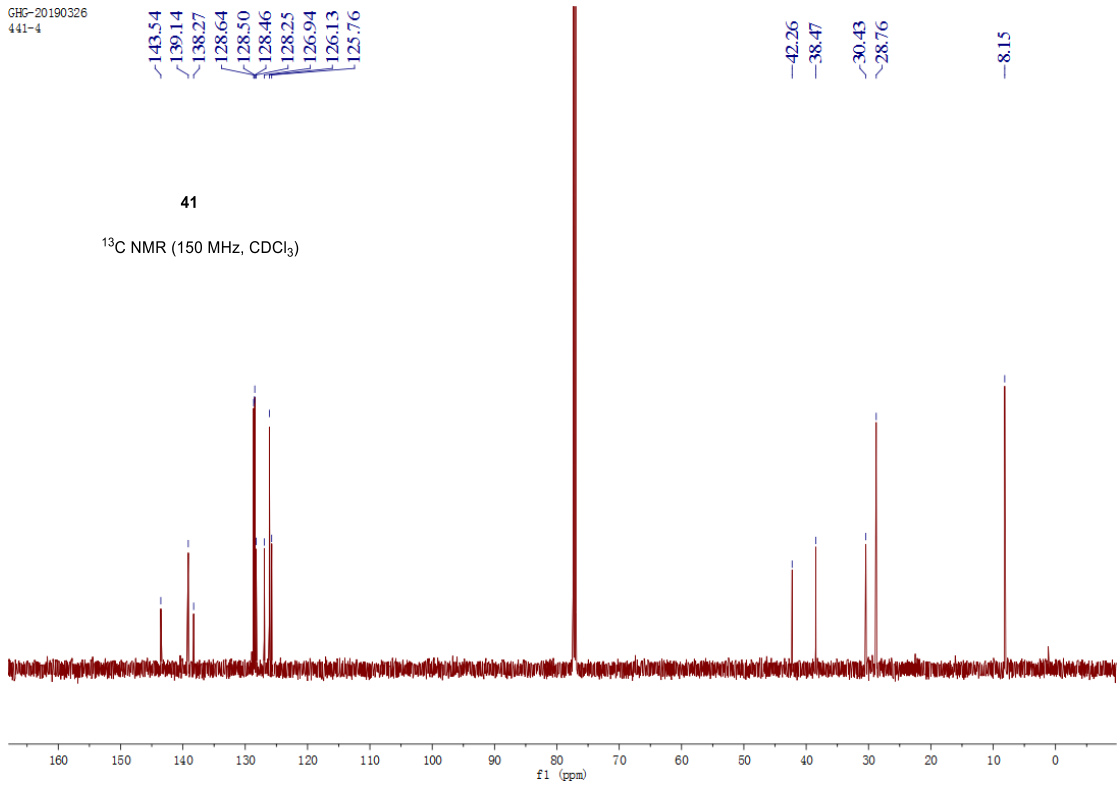

GHG-20190326
441-2
7.38
7.37
7.31
7.30
7.29
7.26
7.20
7.19
7.18
6.26
6.24
6.12
6.09
1.45
1.43
1.42
1.41
1.40
1.36
1.35
1.33
1.32
1.31
1.30
1.26
1.04
0.89
0.88
0.87
0.84
0.83
0.81
Ph
40
1H NMR (600 MHz, CDCl3)
1.95
2.03
1.12
1.00
1.00
2.04
12.05
2.95
3.48
3.20
f1 (ppm)


GHG-20190326
441-2
140.10
138.39
128.60
126.91
126.79
126.11
41.23
39.46
33.77
32.09
30.67
29.50
24.36
22.84
22.78
14.25
8.73
40
13C NMR (150 MHz, CDCl3)
f1 (ppm)



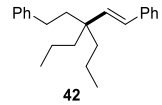
41

^{1}H NMR (600 MHz, $CDCl_3$)



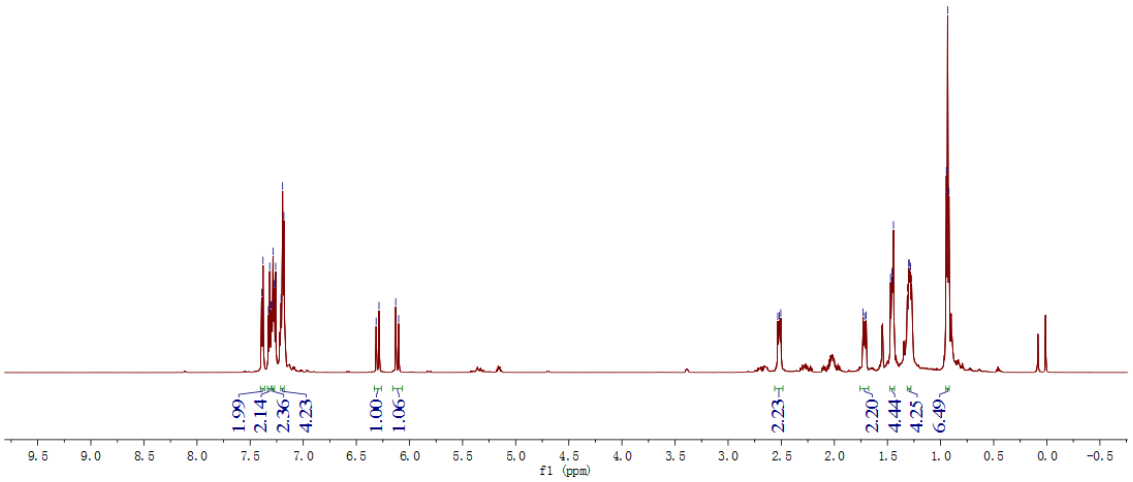
41

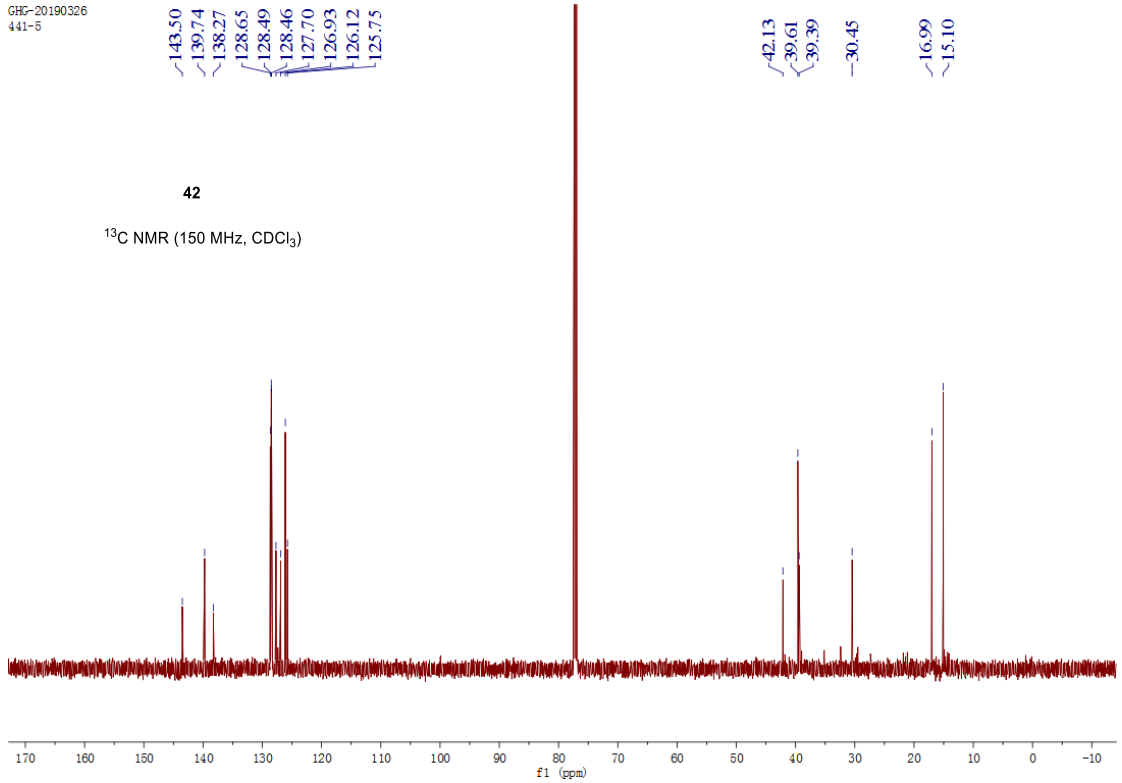
^{13}C NMR (150 MHz, $CDCl_3$)



42

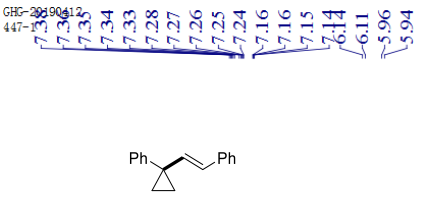
^{1}H NMR (600 MHz, $CDCl_3$)





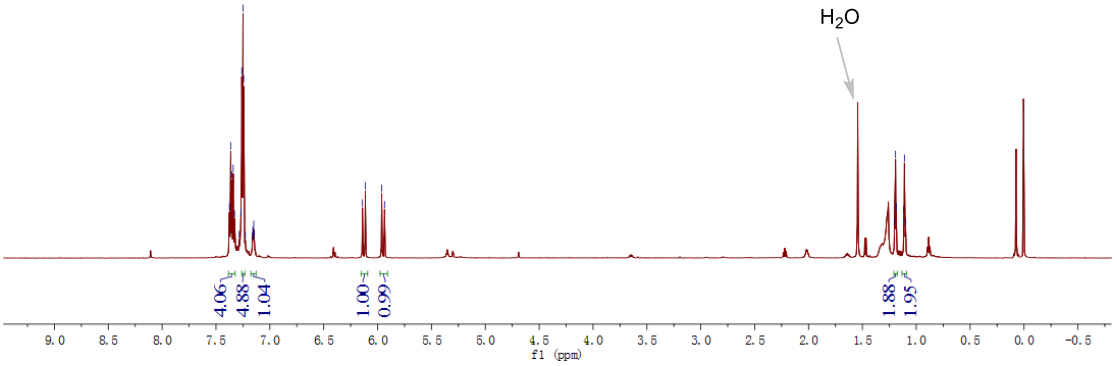
42

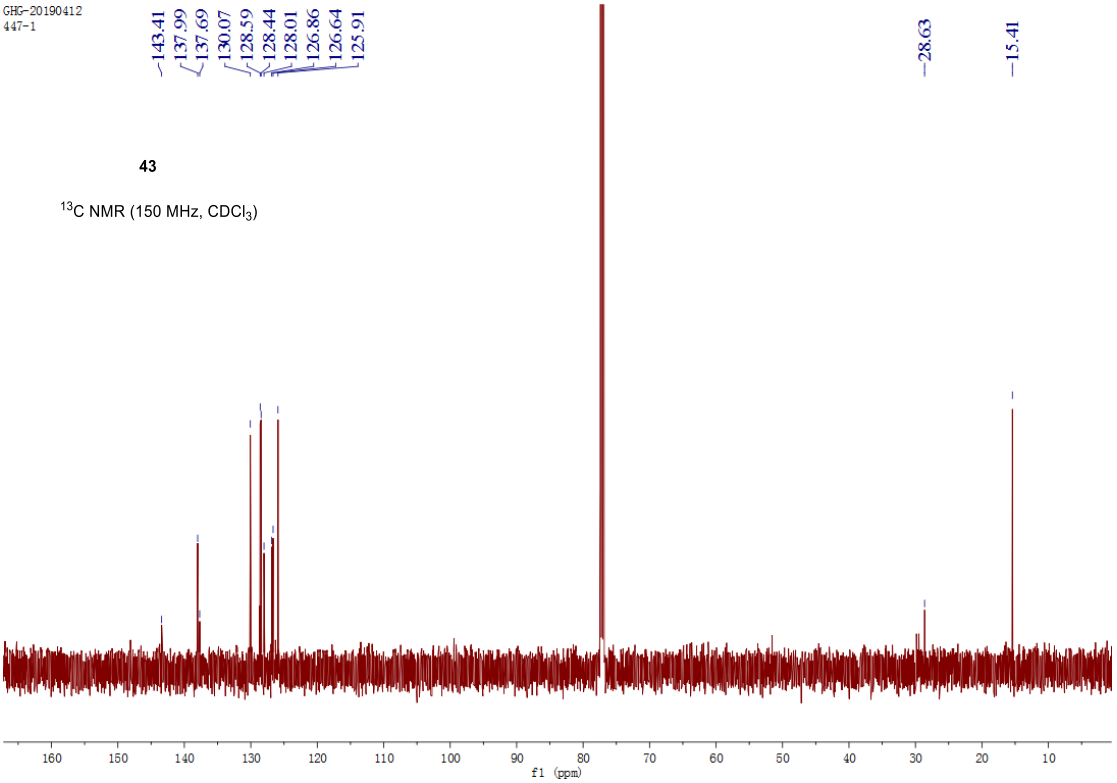
^{13}C NMR (150 MHz, $CDCl_3$)



43

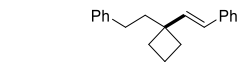
^{1}H NMR (600 MHz, $CDCl_3$)





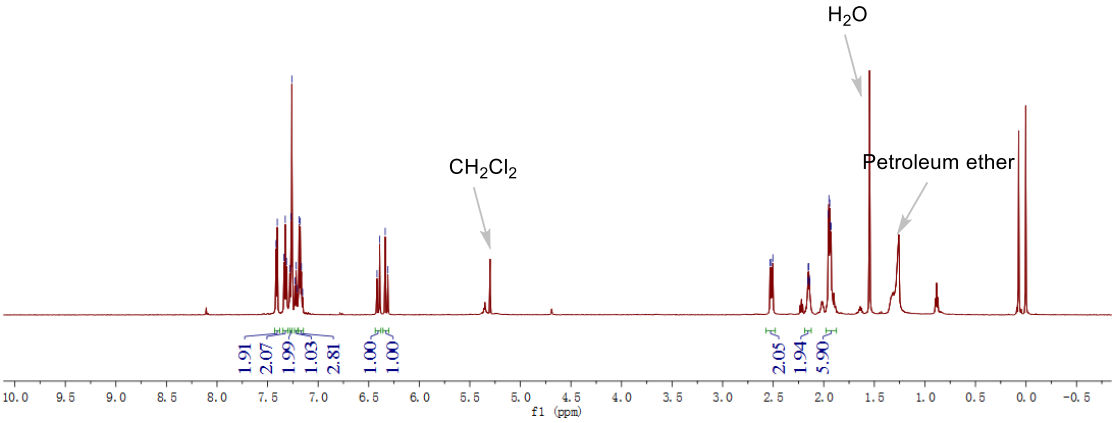
43

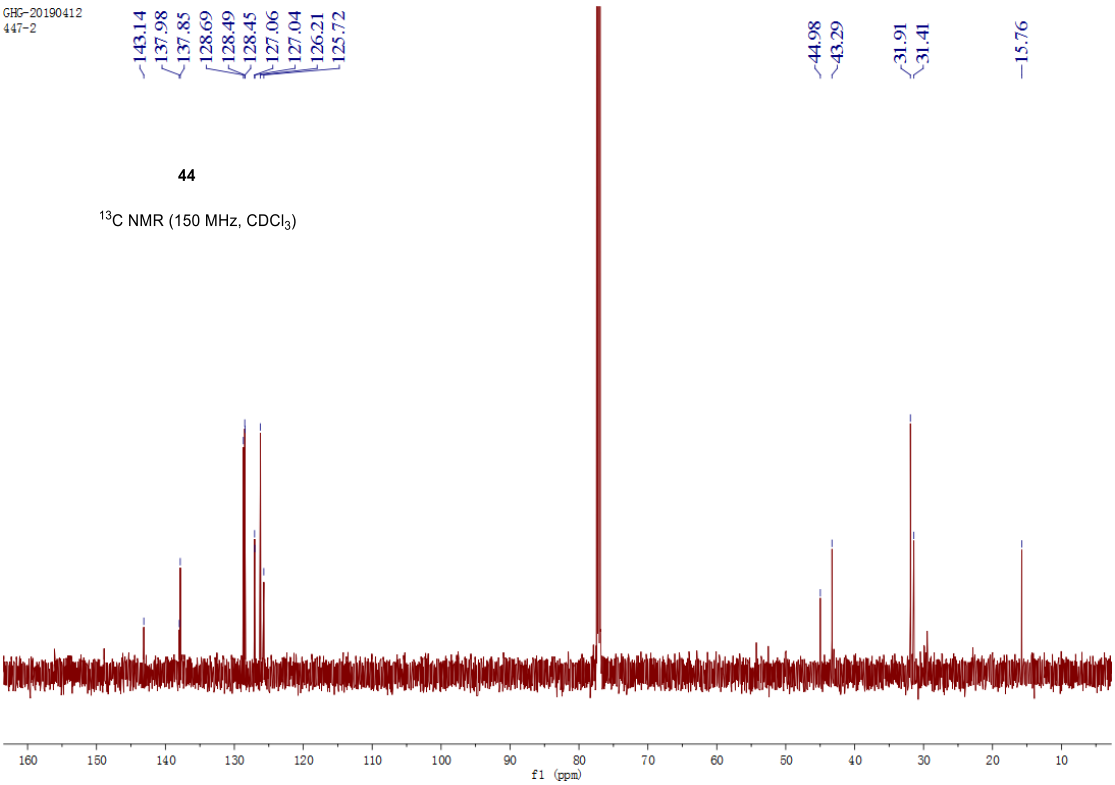
^{13}C NMR (150 MHz, $CDCl_3$)



44

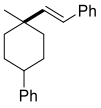
^{1}H NMR (600 MHz, $CDCl_3$)





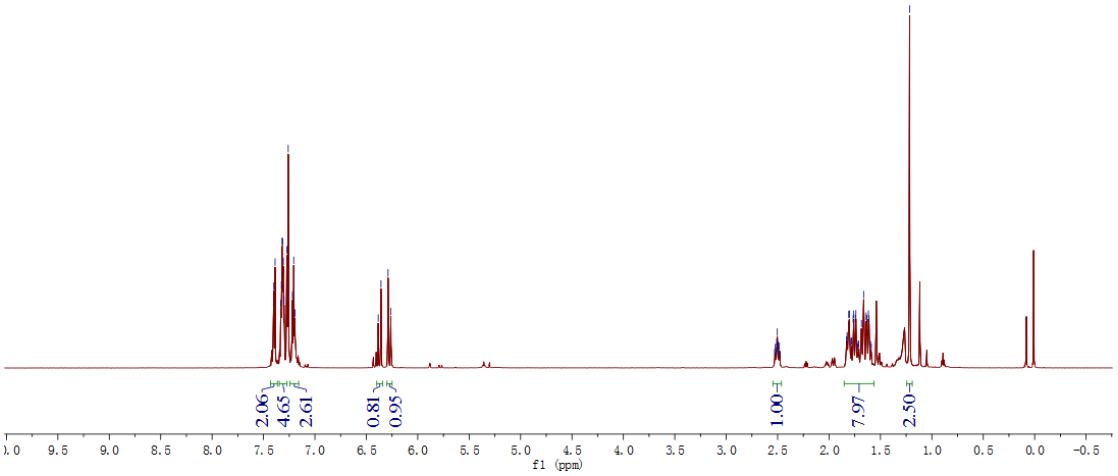
44

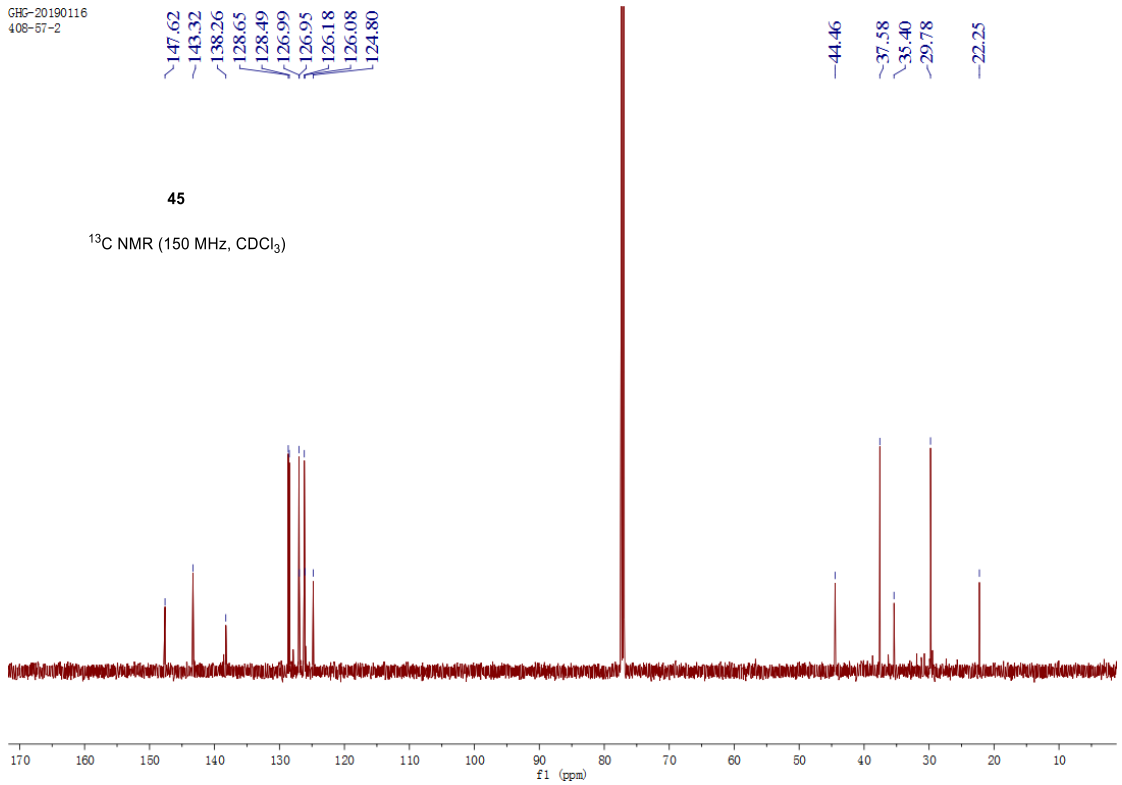
^{13}C NMR (150 MHz, $CDCl_3$)



45

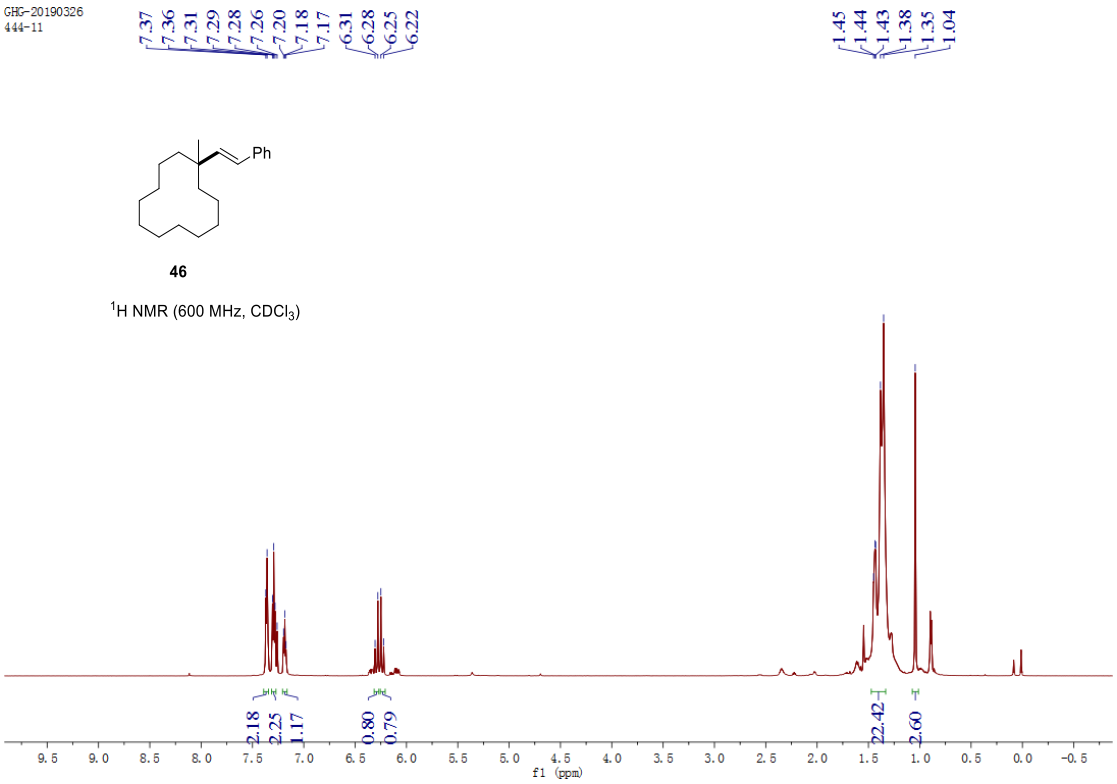
^{1}H NMR (600 MHz, $CDCl_3$)

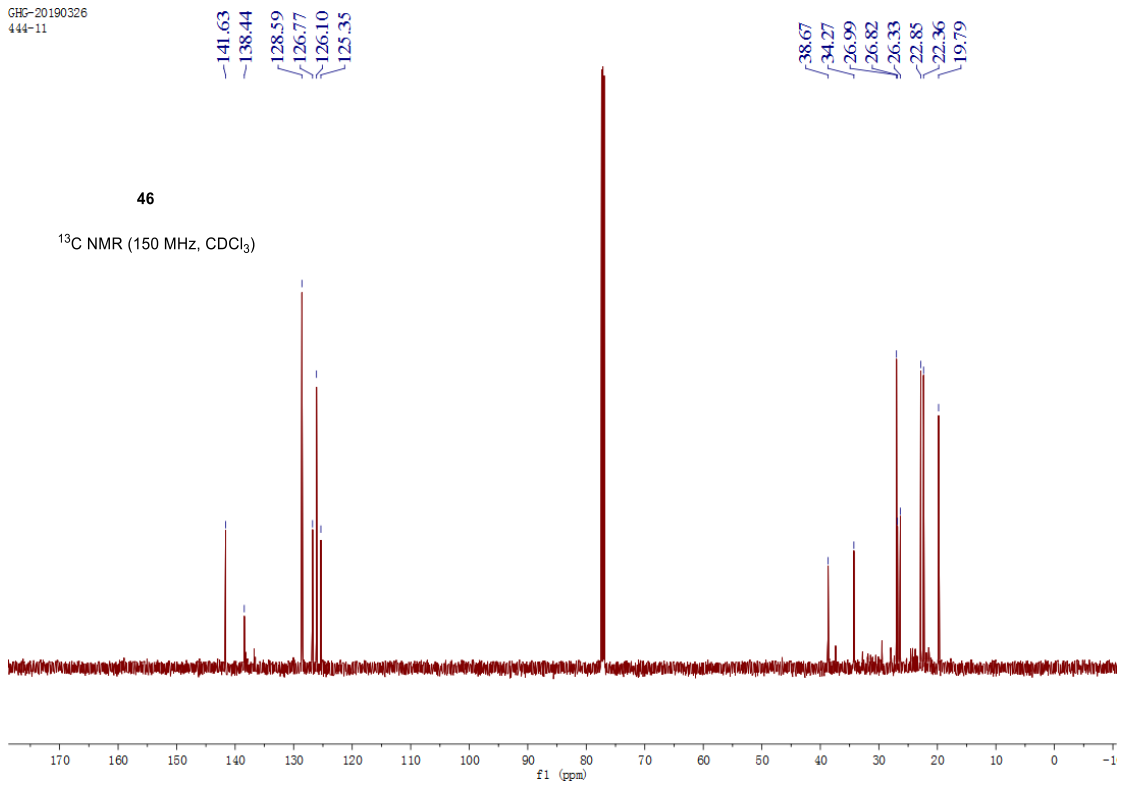


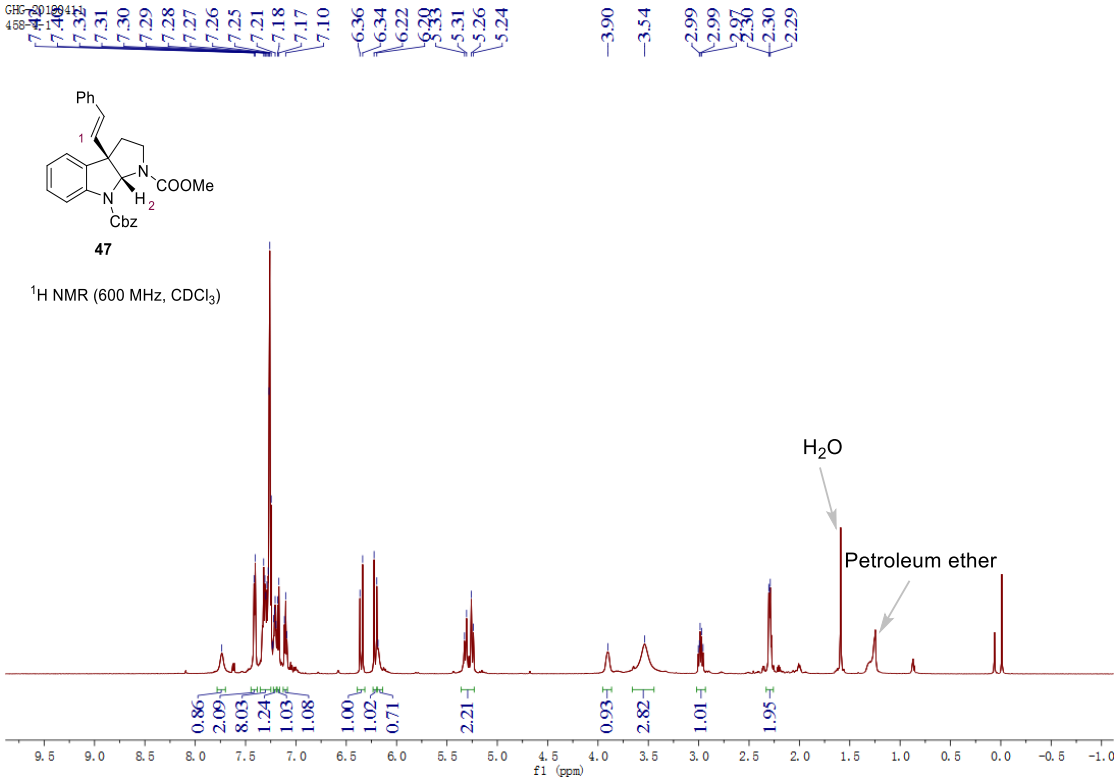


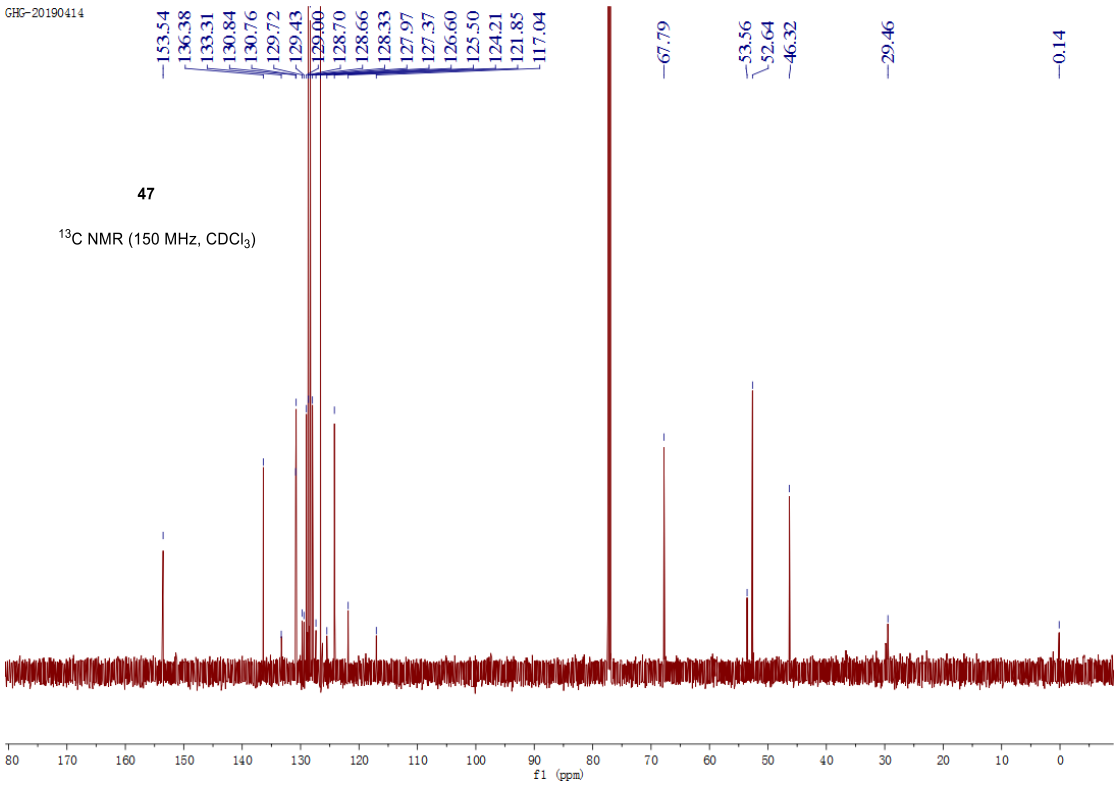
45

^{13}C NMR (150 MHz, $CDCl_3$)

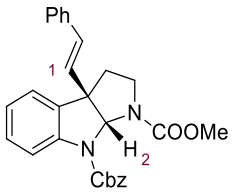

GHG-20190326
444-11
7.37
7.36
7.31
7.29
7.28
7.26
7.20
7.18
7.17
6.31
6.28
6.25
6.22
1.45
1.44
1.43
1.38
1.35
1.04
Ph
46
1H NMR (600 MHz, CDCl3)
2.18
2.25
1.17
0.80
0.79
22.42
2.60
f1 (ppm)


GHG-20190326
444-11
141.63
138.44
128.59
126.77
126.10
125.35
38.67
34.27
26.99
26.82
26.33
22.85
22.36
19.79
46
13C NMR (150 MHz, CDCl3)
f1 (ppm)

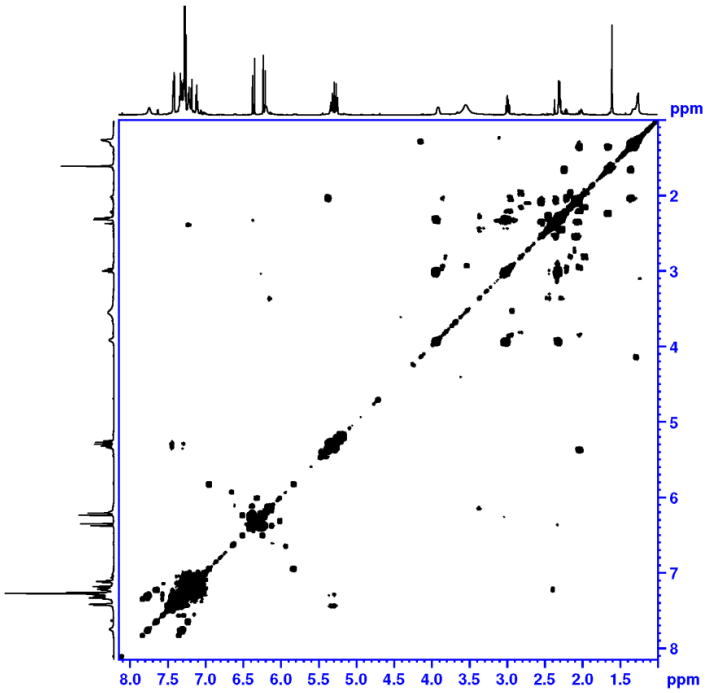

Ph
COOMe
Cbz
47
1H NMR (600 MHz, CDCl3)
H2O
Petroleum ether
f1 (ppm)


GHG-20190414
47
13C NMR (150 MHz, CDCl3)
f1 (ppm)

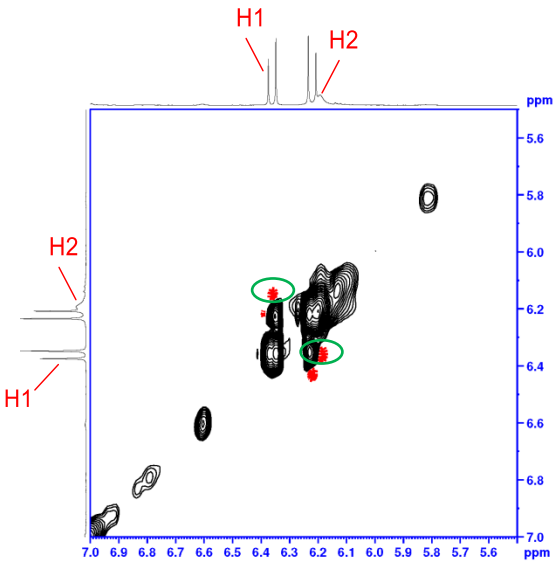
^{1}H-^{1}H COSY of **47**:

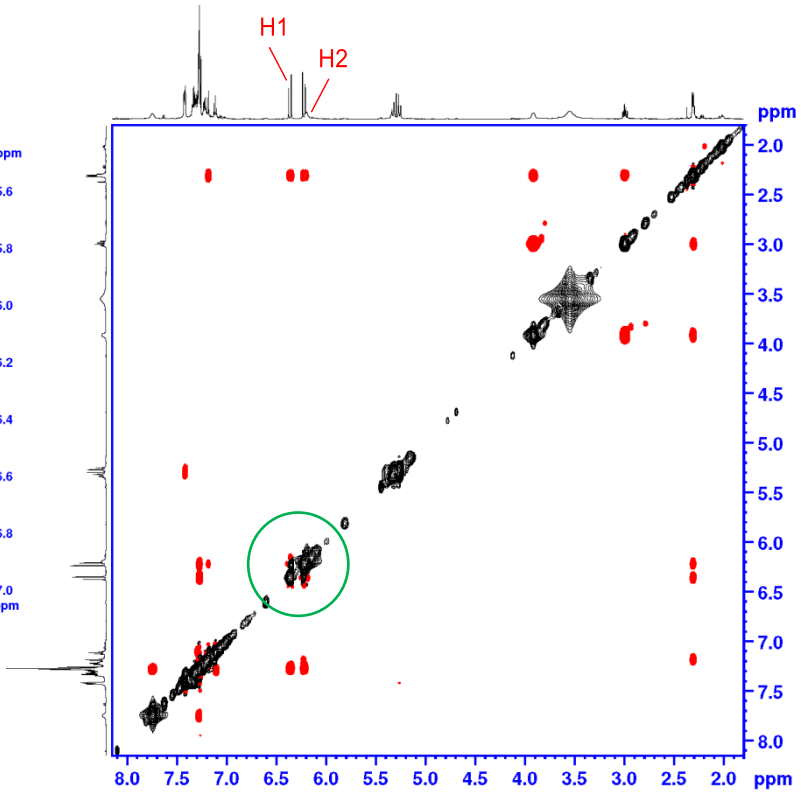


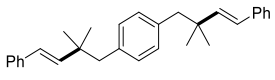
47



2D NOESY of **47**:

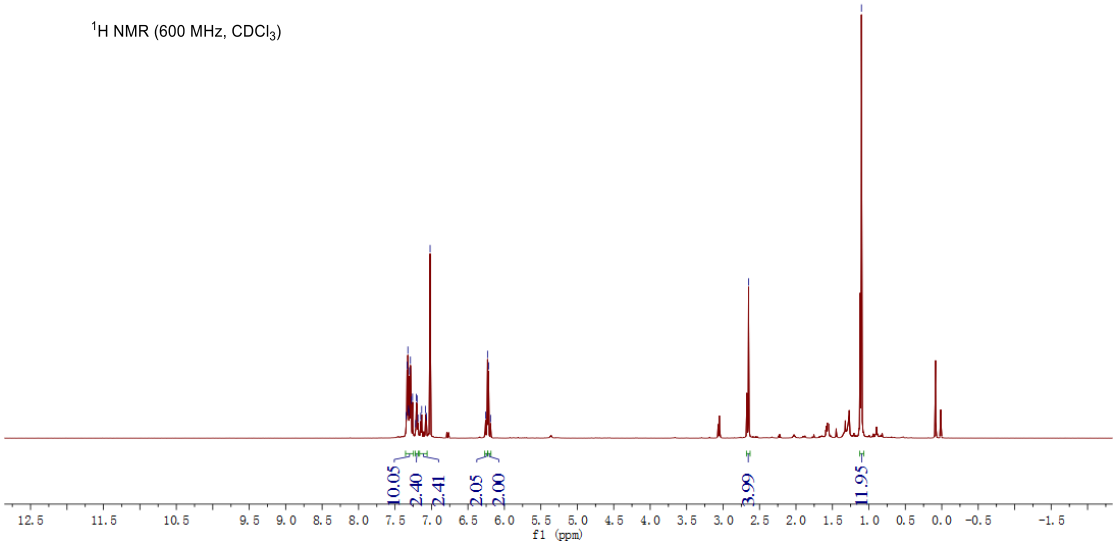


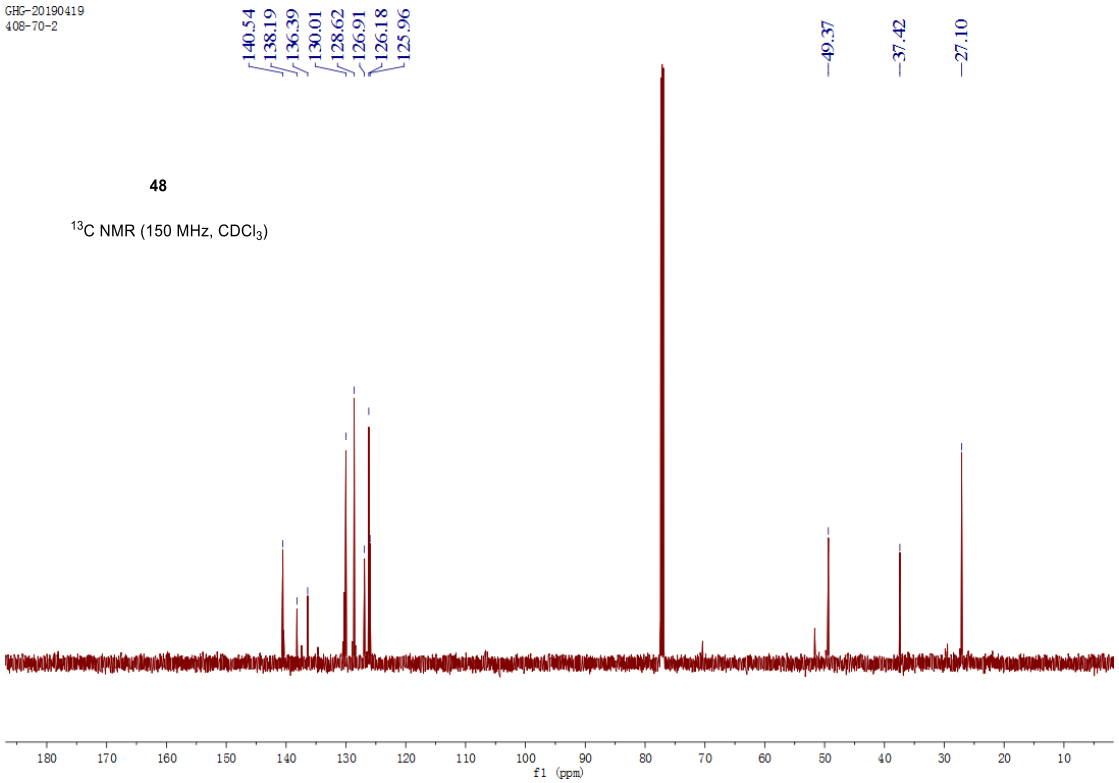




48

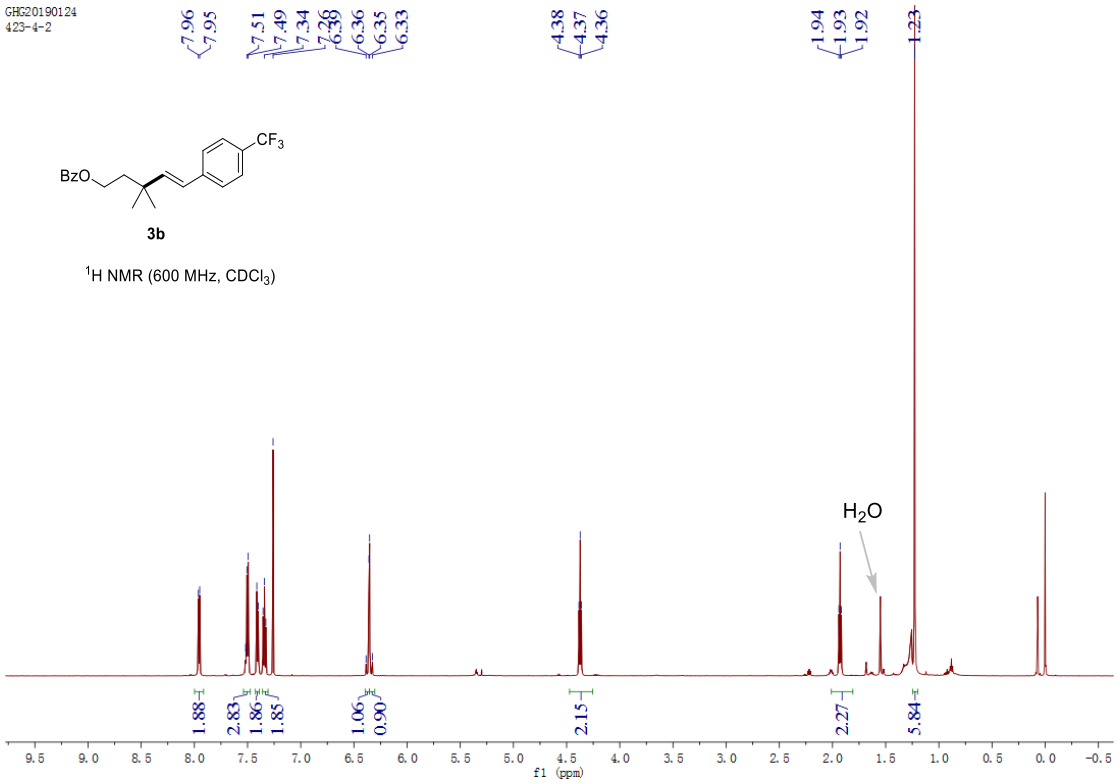
^{1}H NMR (600 MHz, $CDCl_3$)





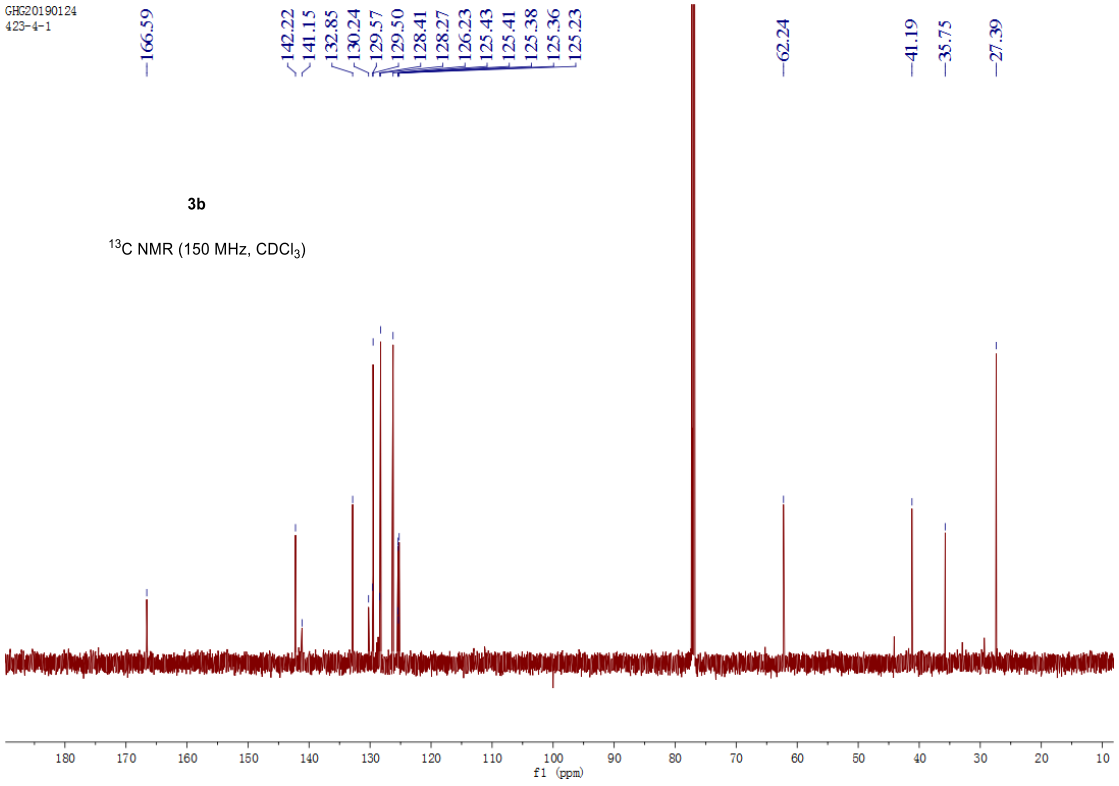
48

^{13}C NMR (150 MHz, $CDCl_3$)



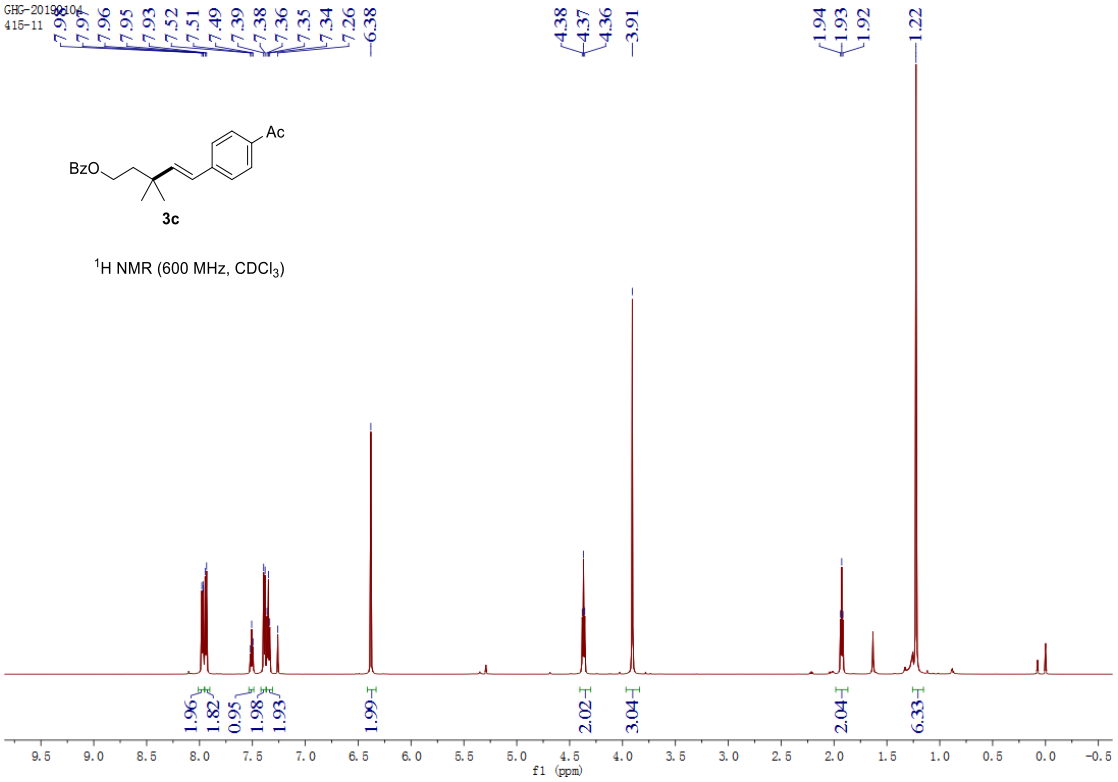
3b

^{1}H NMR (600 MHz, $CDCl_3$)



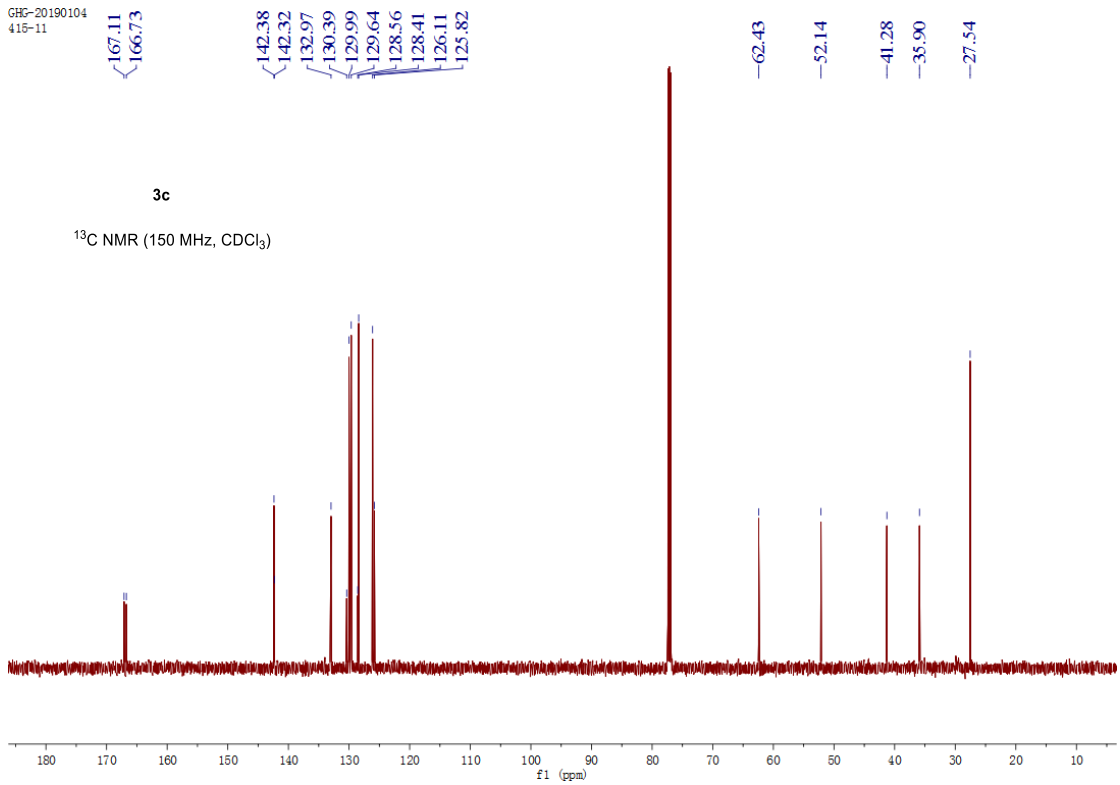
3b

^{13}C NMR (150 MHz, $CDCl_3$)



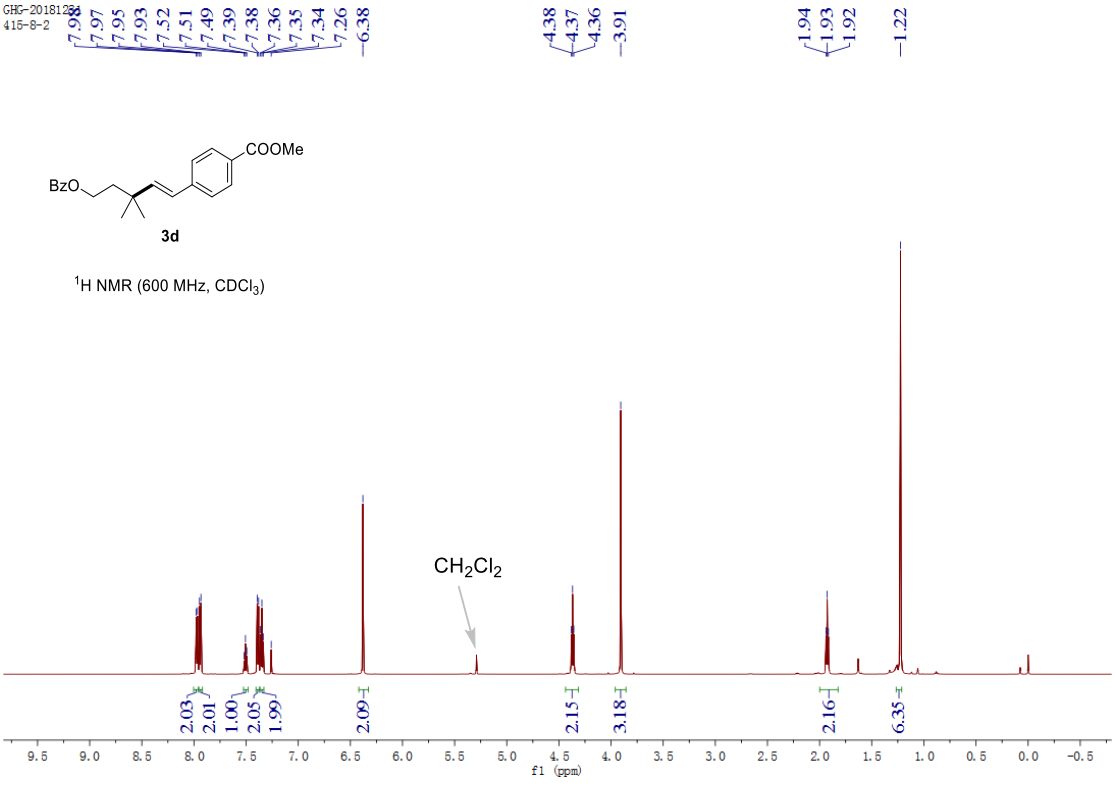
3c

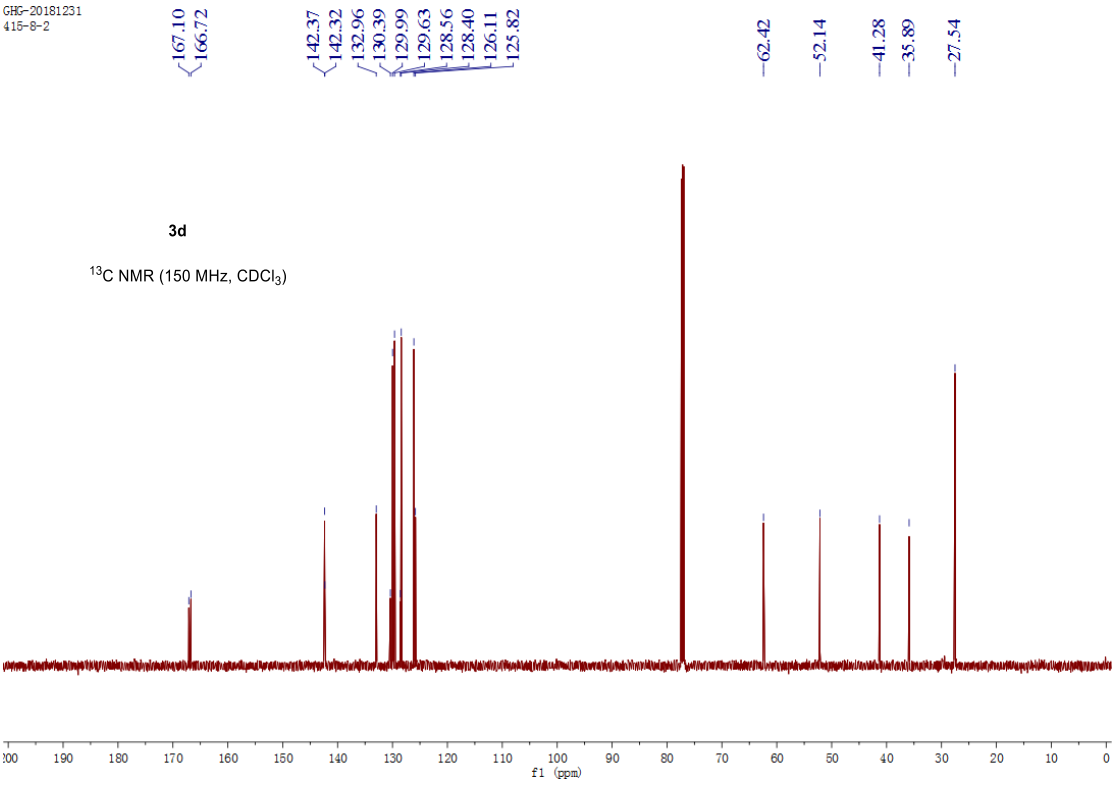
^{1}H NMR (600 MHz, $CDCl_3$)

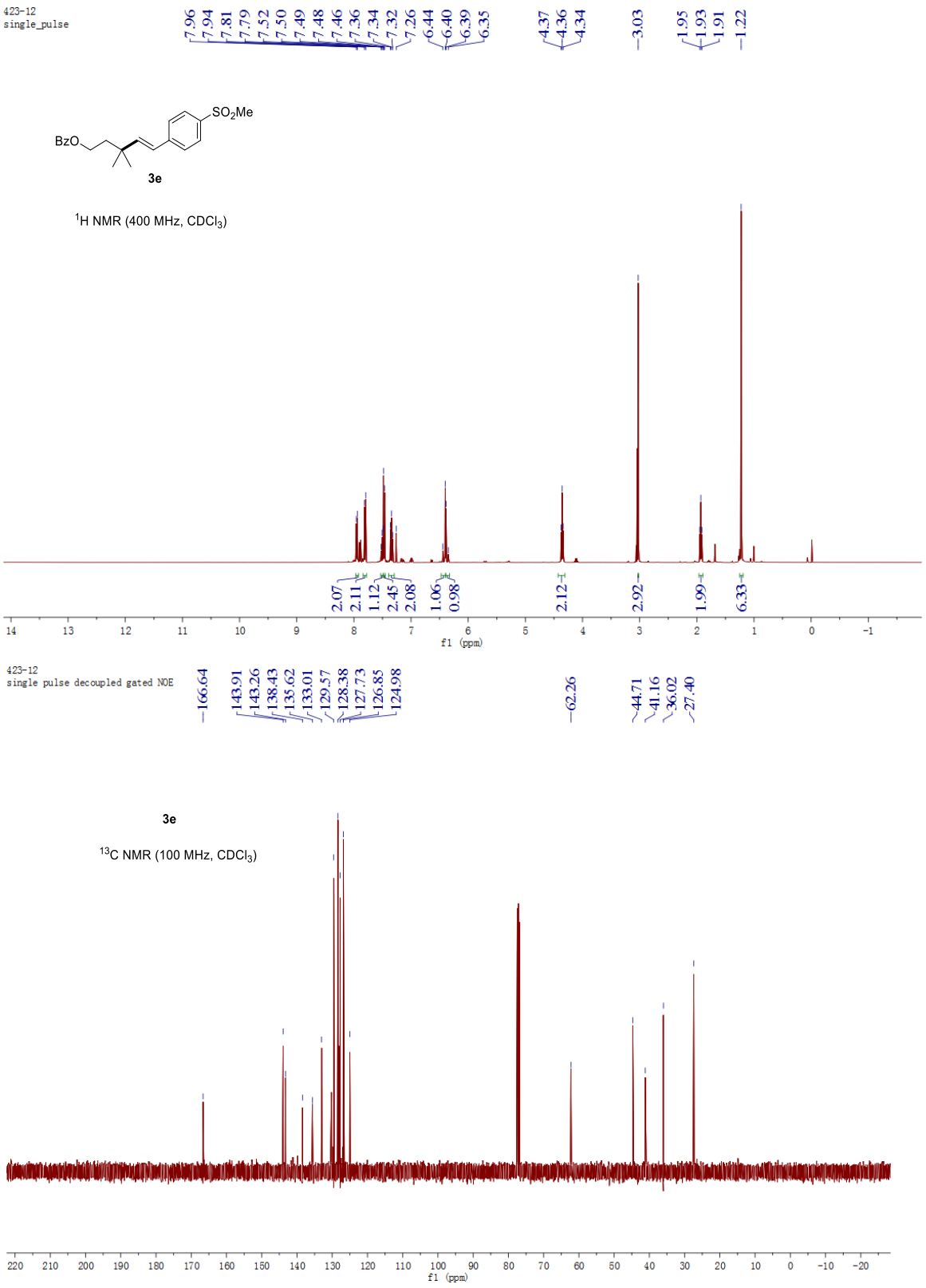


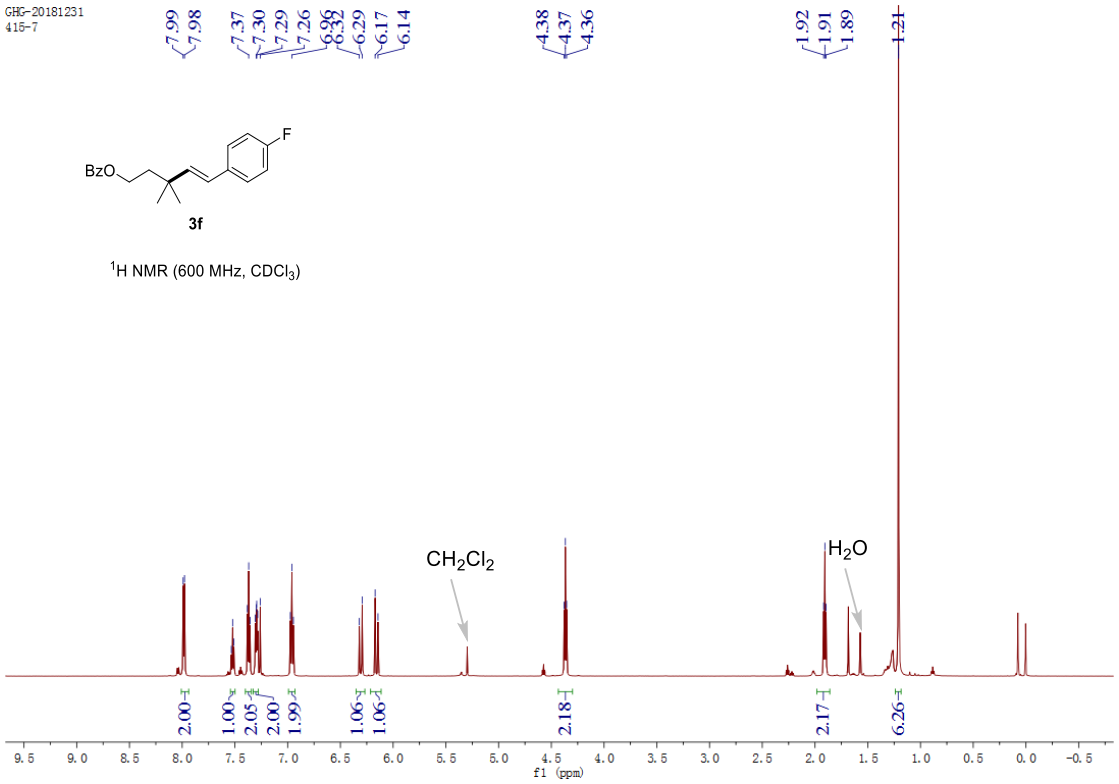
3c

^{13}C NMR (150 MHz, $CDCl_3$)


GHG-20181230
415-8-2
7.98
7.97
7.95
7.93
7.52
7.51
7.49
7.39
7.38
7.36
7.35
7.34
7.26
6.38
4.38
4.37
4.36
3.91
1.94
1.93
1.92
1.22
COOMe
BzO
3d
1H NMR (600 MHz, CDCl3)
CH2Cl2
2.03
2.01
1.00
2.05
1.99
2.09
2.15
3.18
2.16
6.35
f1 (ppm)

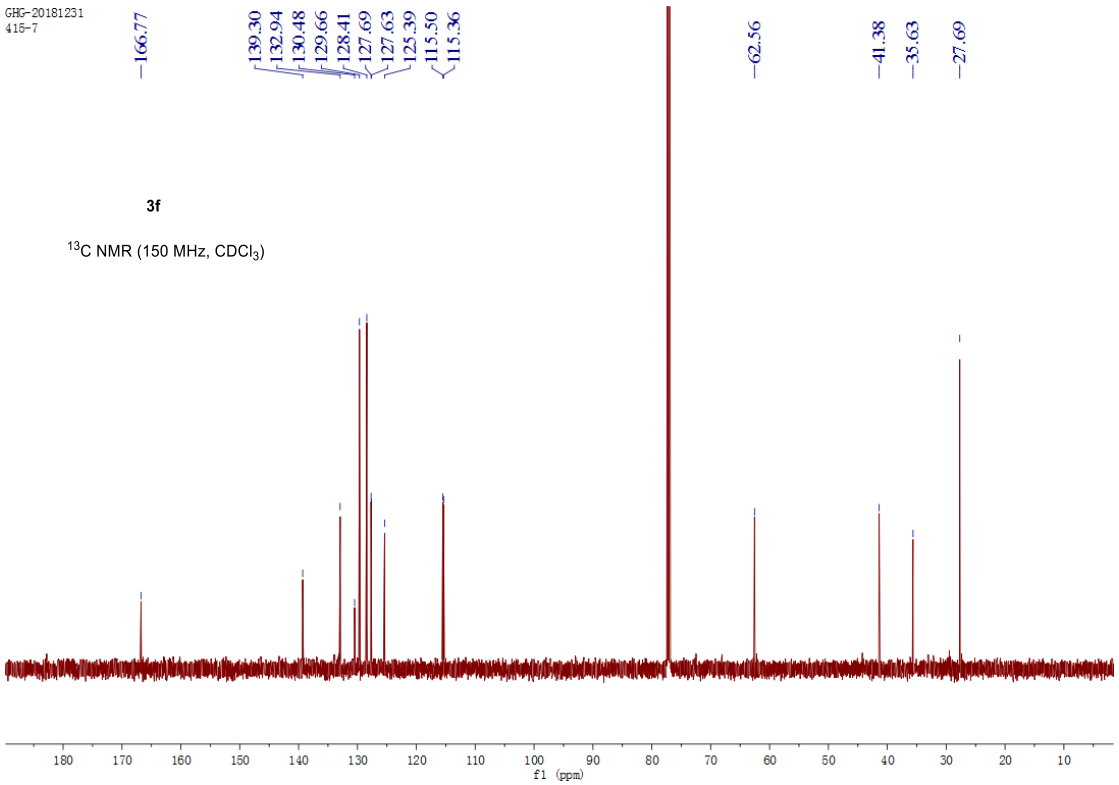

GHG-20181231
415-8-2
167.10
166.72
142.37
142.32
132.96
130.39
129.99
129.63
128.56
128.40
126.11
125.82
62.42
52.14
41.28
35.89
27.54
3d
13C NMR (150 MHz, CDCl3)
f1 (ppm)


423-12
single_pulse
7.96
7.94
7.81
7.79
7.52
7.50
7.49
7.48
7.46
7.36
7.34
7.32
7.26
6.44
6.40
6.39
6.35
4.37
4.36
4.34
3.03
1.95
1.93
1.91
1.22
SO2Me
BzO
3e
1H NMR (400 MHz, CDCl3)
2.07
2.11
1.12
2.45
2.08
1.06
0.98
2.12
2.92
1.99
6.33
f1 (ppm)
423-12
single pulse decoupled gated NOE
166.64
143.91
143.26
138.43
135.62
133.01
129.57
128.38
127.73
126.85
124.98
62.26
44.71
41.16
36.02
27.40
3e
13C NMR (100 MHz, CDCl3)
f1 (ppm)



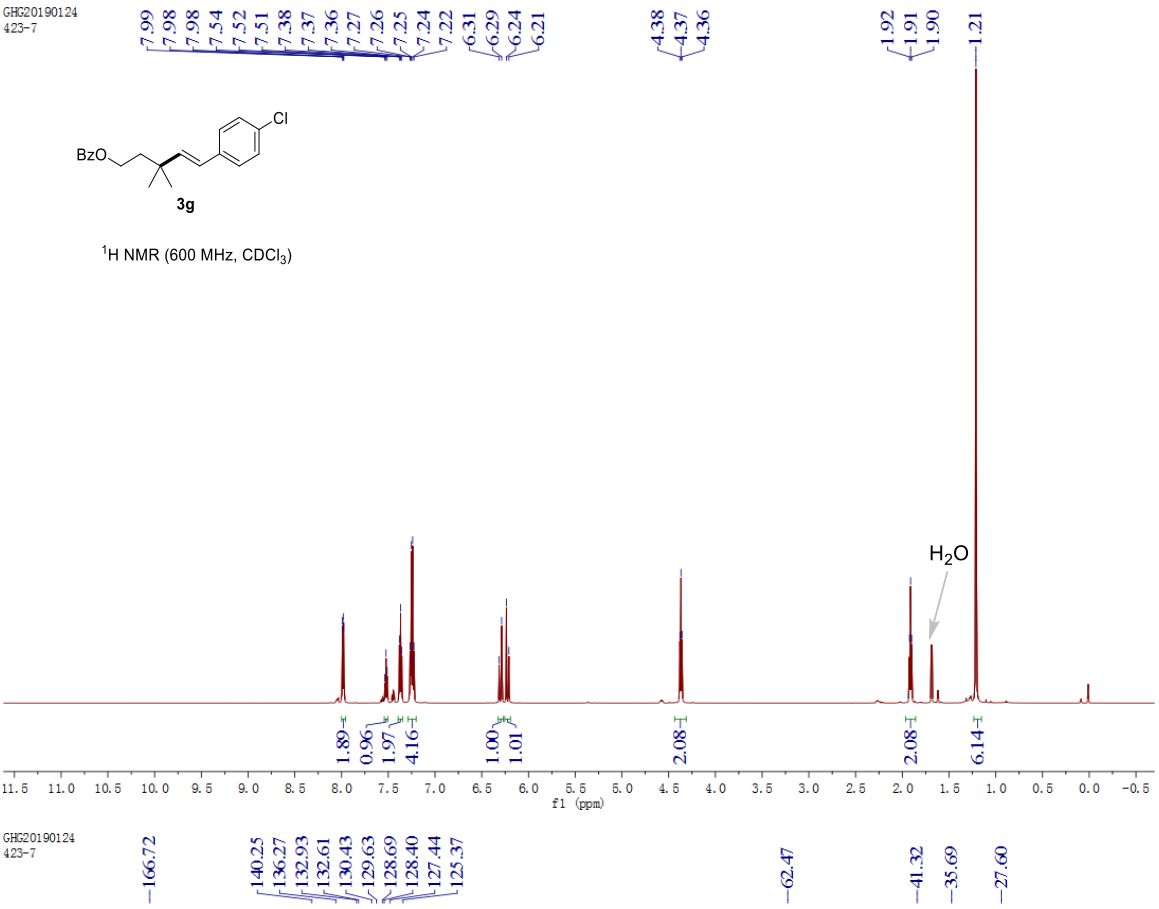
3f

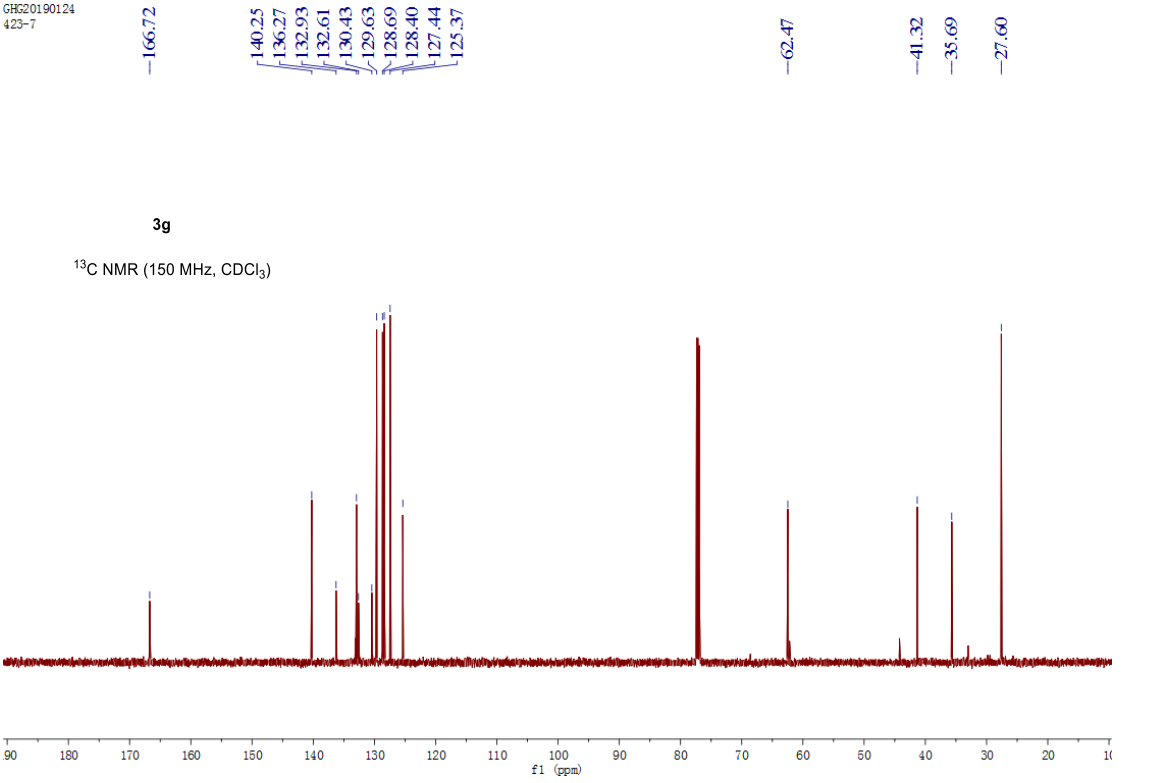
^{1}H NMR (600 MHz, $CDCl_3$)

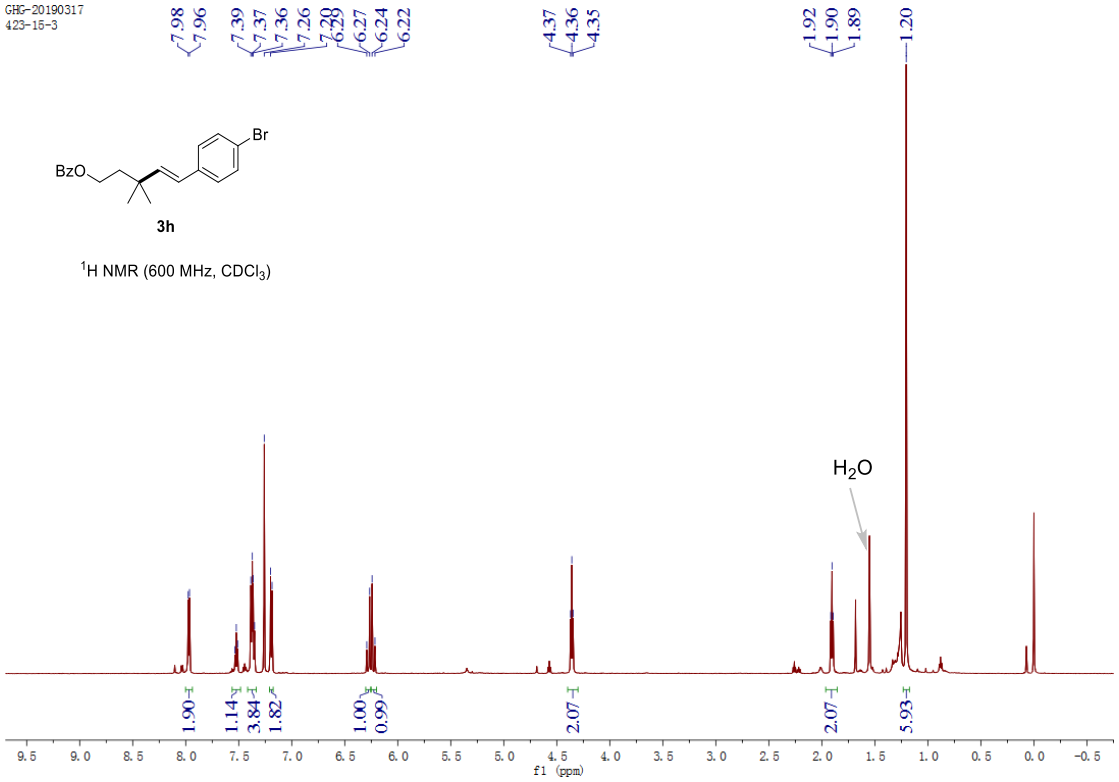


3f

^{13}C NMR (150 MHz, $CDCl_3$)

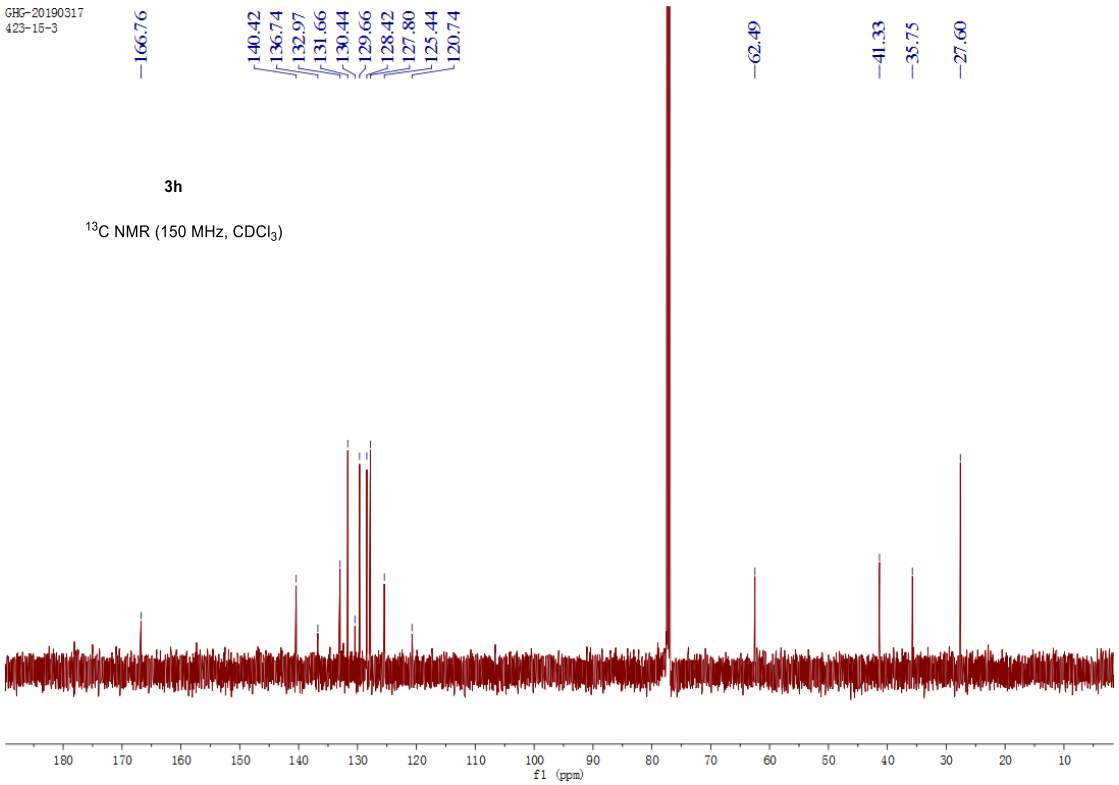

GHG20190124
423-7
7.99
7.98
7.98
7.54
7.52
7.51
7.38
7.37
7.36
7.27
7.26
7.25
7.24
7.22
6.31
6.29
6.24
6.21
4.38
4.37
4.36
1.92
1.91
1.90
1.21
Cl
BzO
3g
^{1}H NMR (600 MHz, CDCl$_3$)
H$_2$O
1.89
0.96
1.97
4.16
1.00
1.01
2.08
2.08
6.14
f1 (ppm)


GHG20190124
423-7
166.72
140.25
136.27
132.93
132.61
130.43
129.63
128.69
128.40
127.44
125.37
62.47
41.32
35.69
27.60
3g
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)



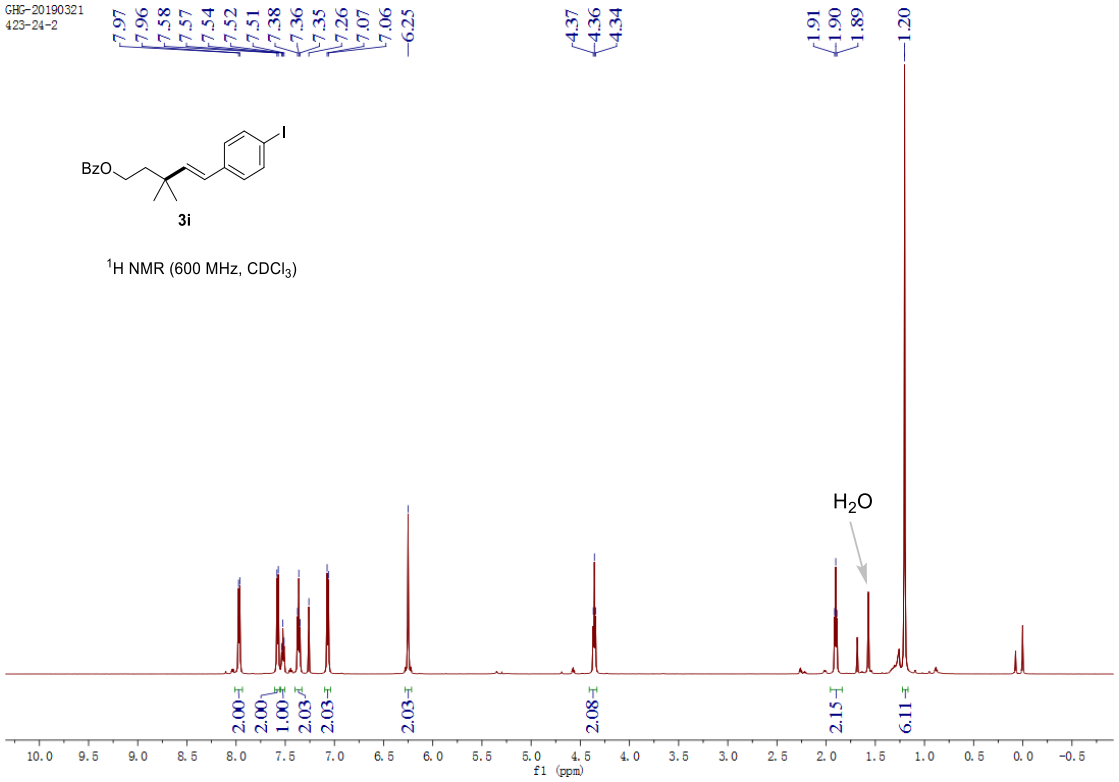
3h

^{1}H NMR (600 MHz, $CDCl_3$)



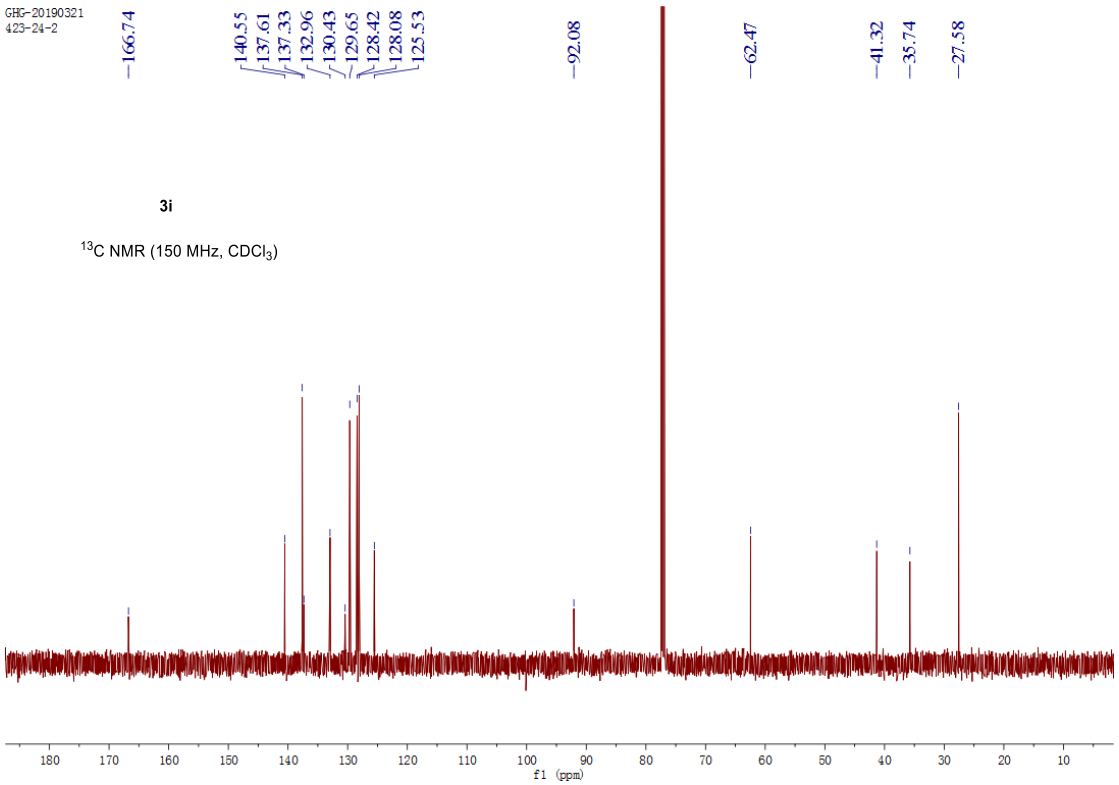
3h

^{13}C NMR (150 MHz, $CDCl_3$)



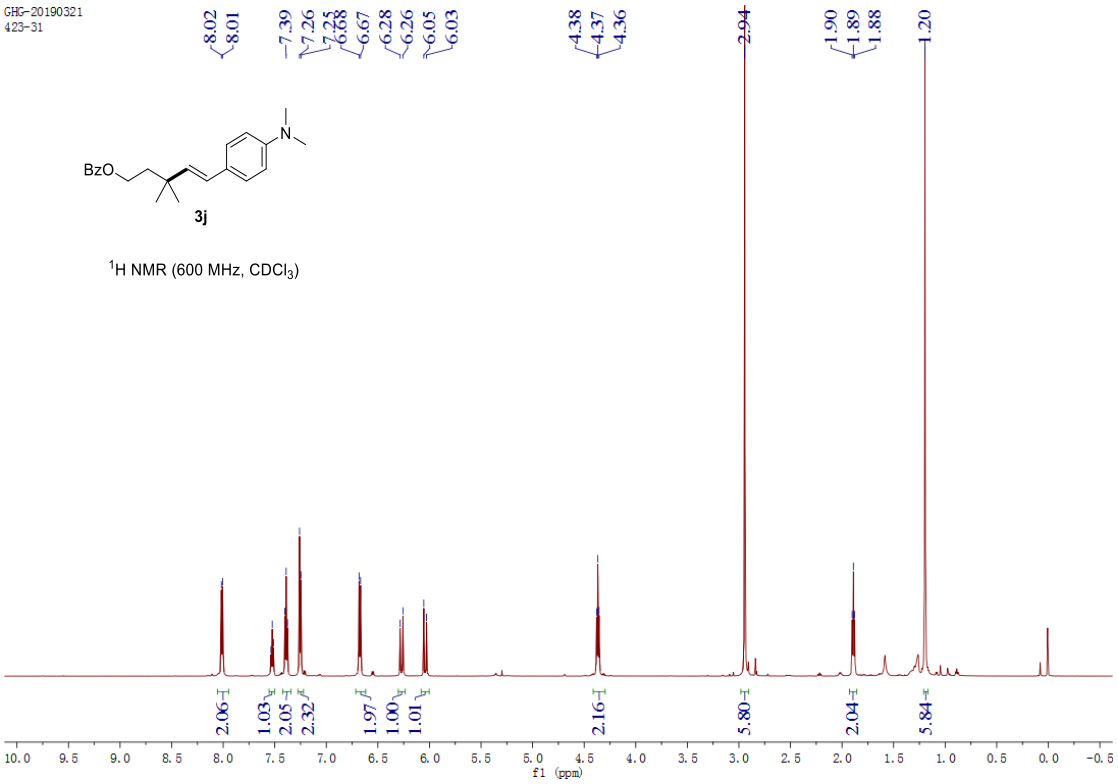
3i

^{1}H NMR (600 MHz, $CDCl_3$)



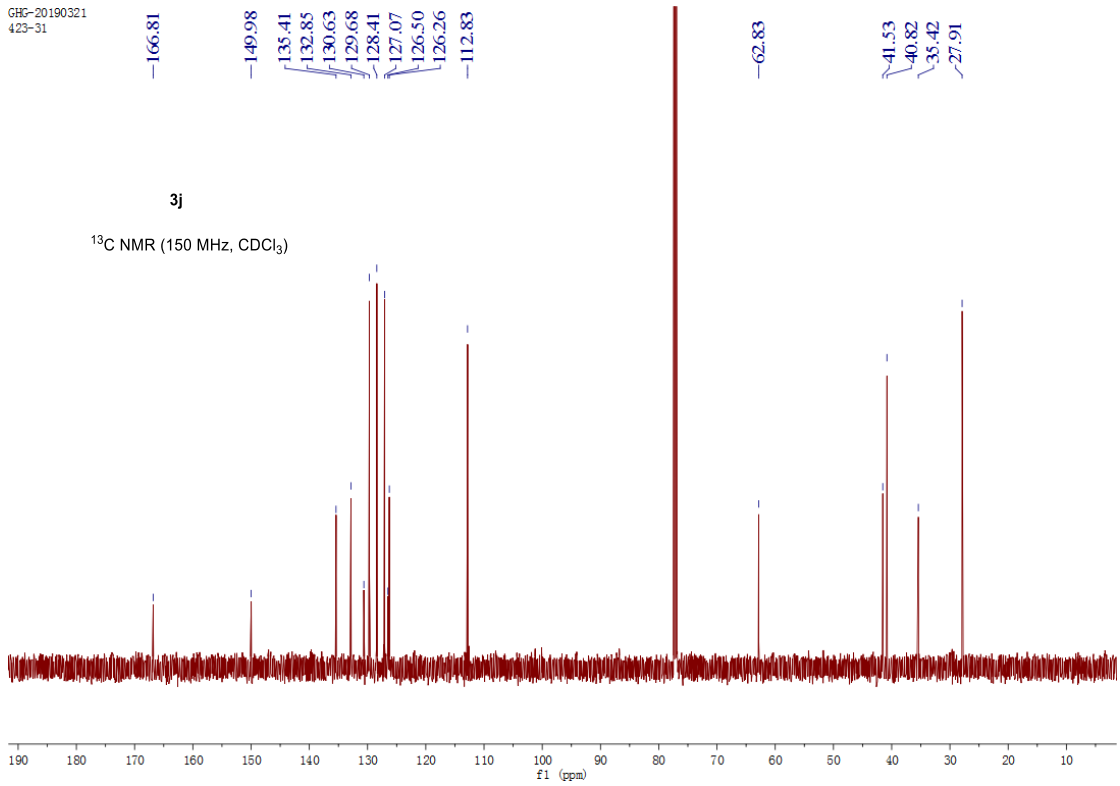
3i

^{13}C NMR (150 MHz, $CDCl_3$)



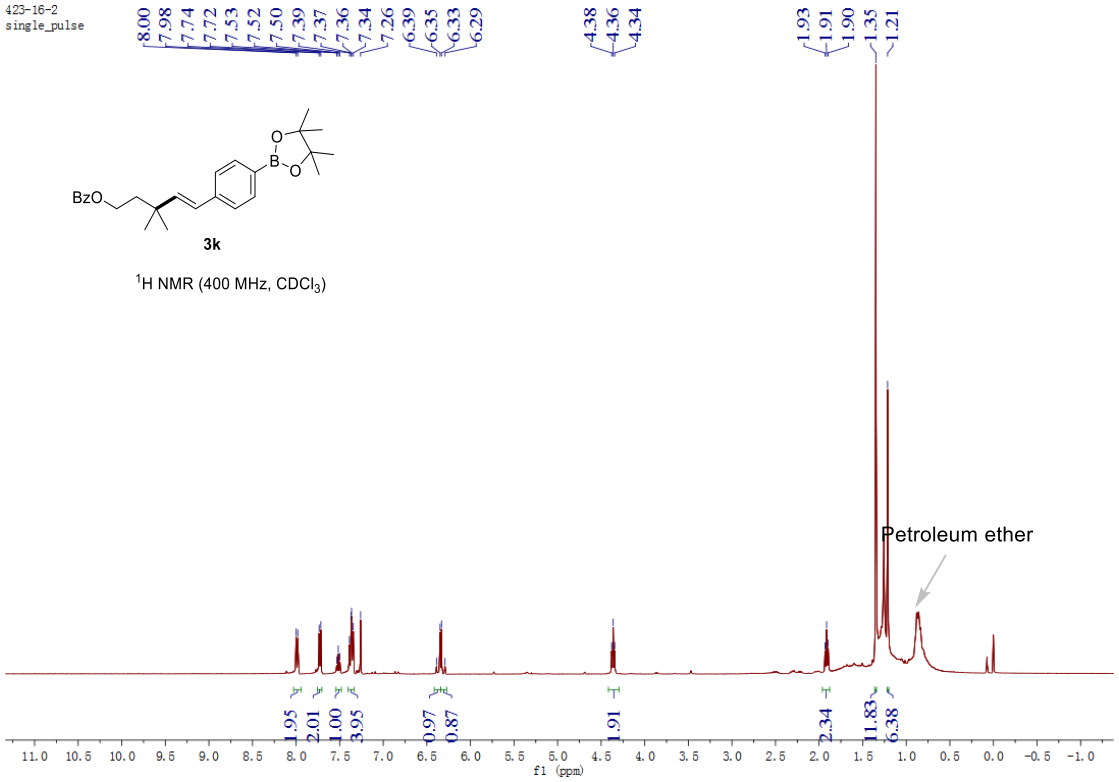
3j

^{1}H NMR (600 MHz, $CDCl_3$)



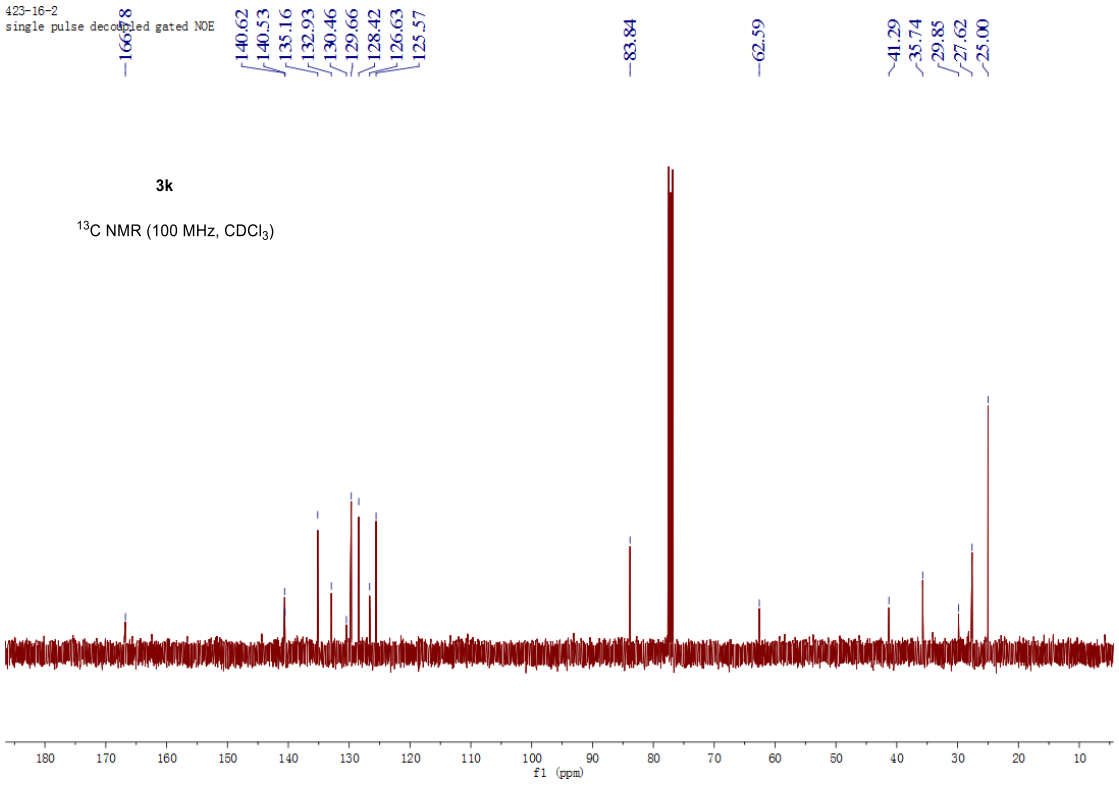
3j

^{13}C NMR (150 MHz, $CDCl_3$)



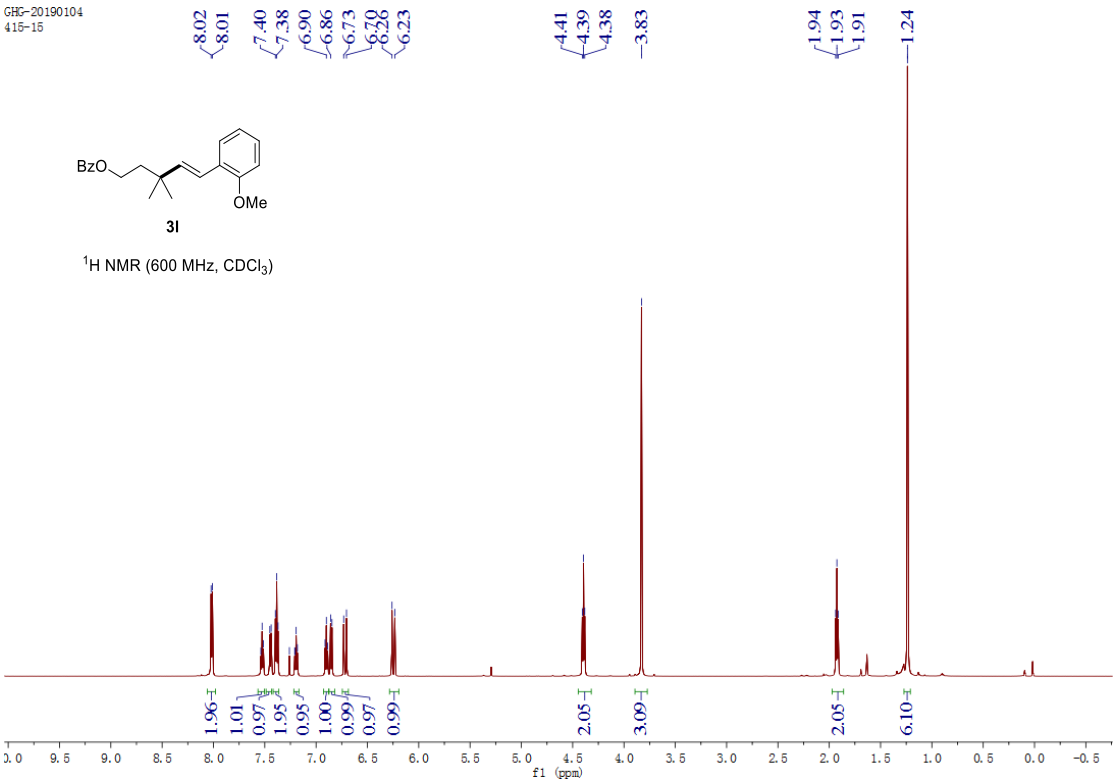
3k

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



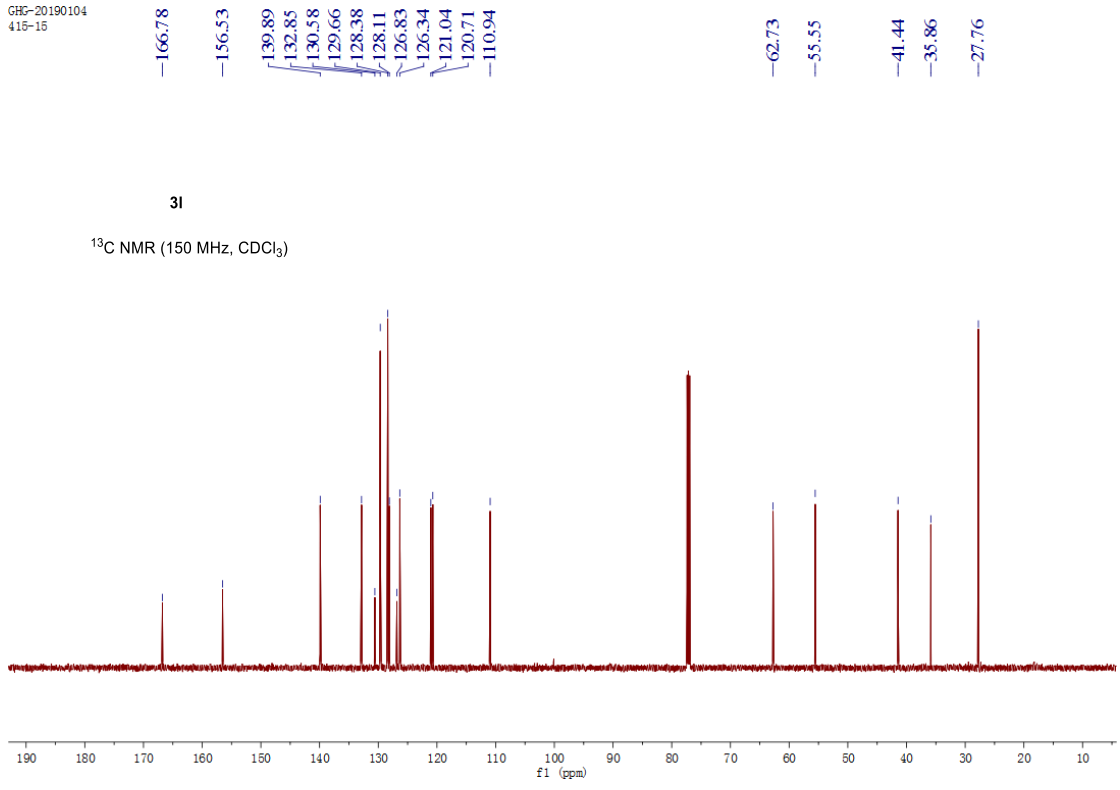
3k

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



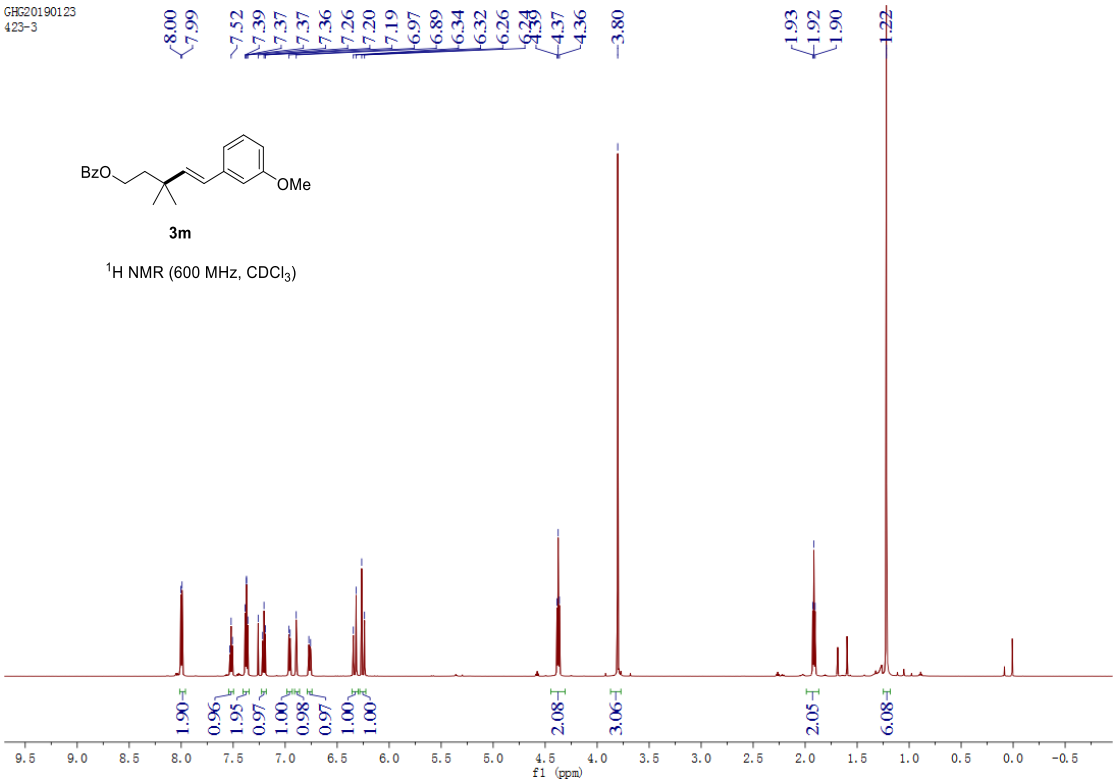
3l

^{1}H NMR (600 MHz, $CDCl_3$)



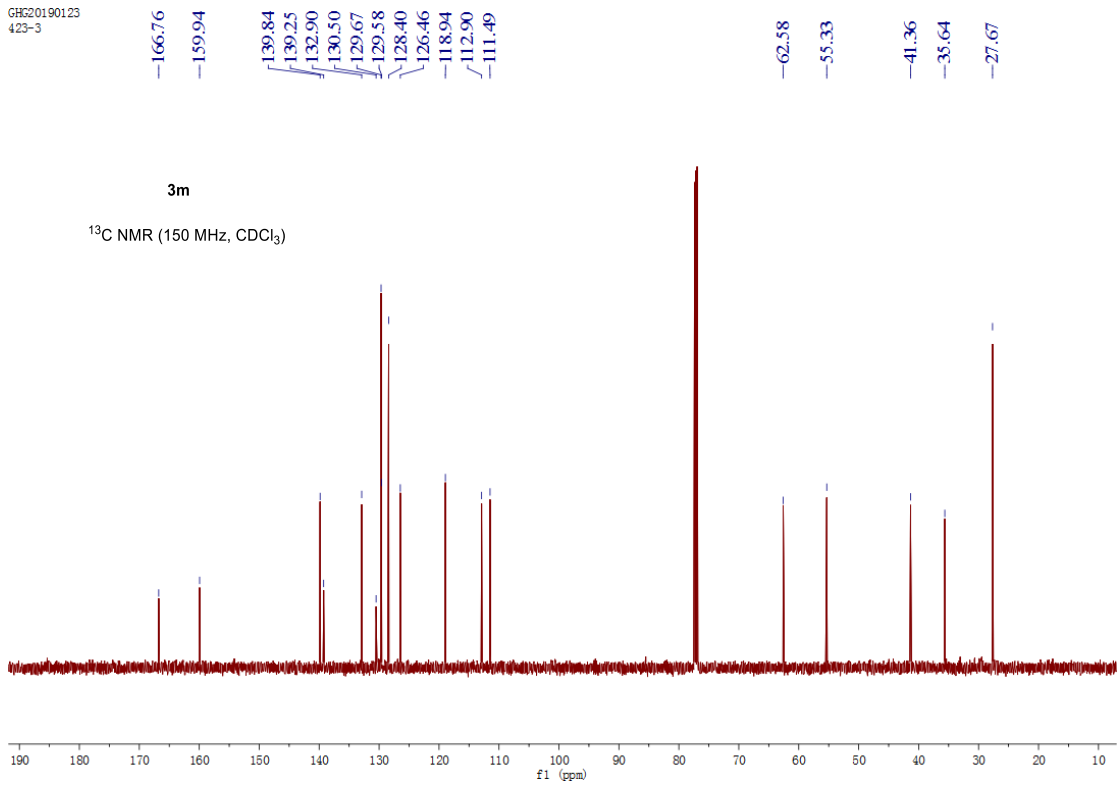
3l

^{13}C NMR (150 MHz, $CDCl_3$)



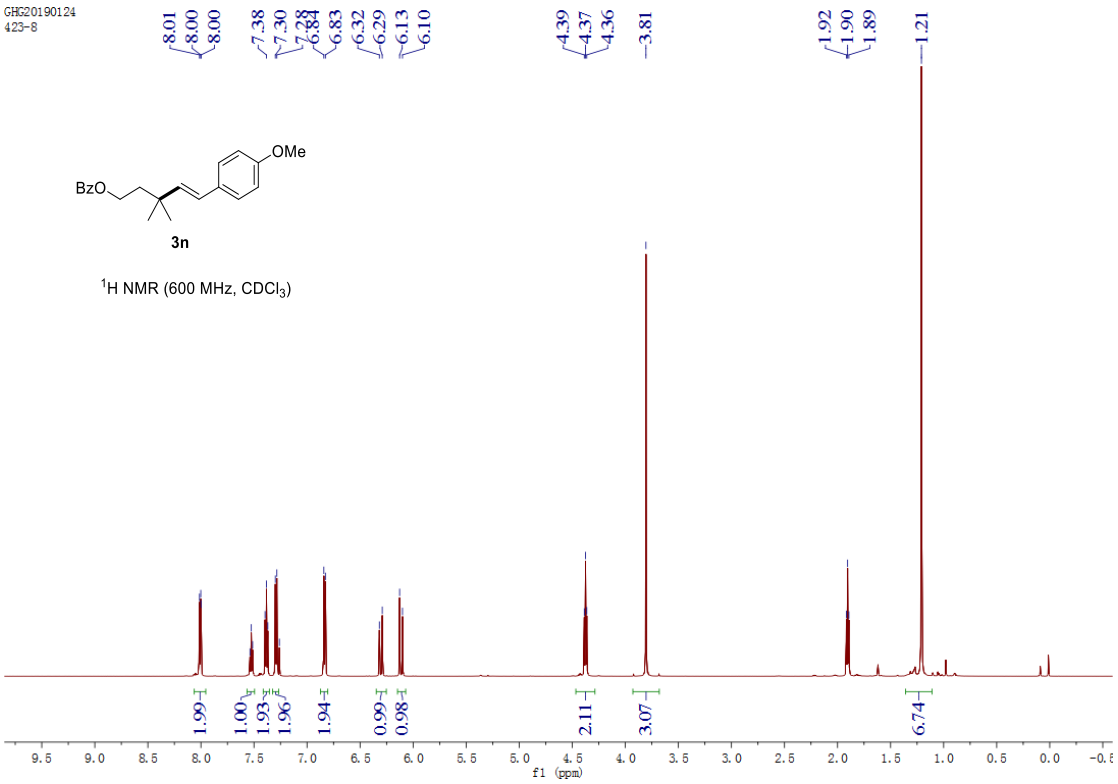
3m

^{1}H NMR (600 MHz, $CDCl_3$)



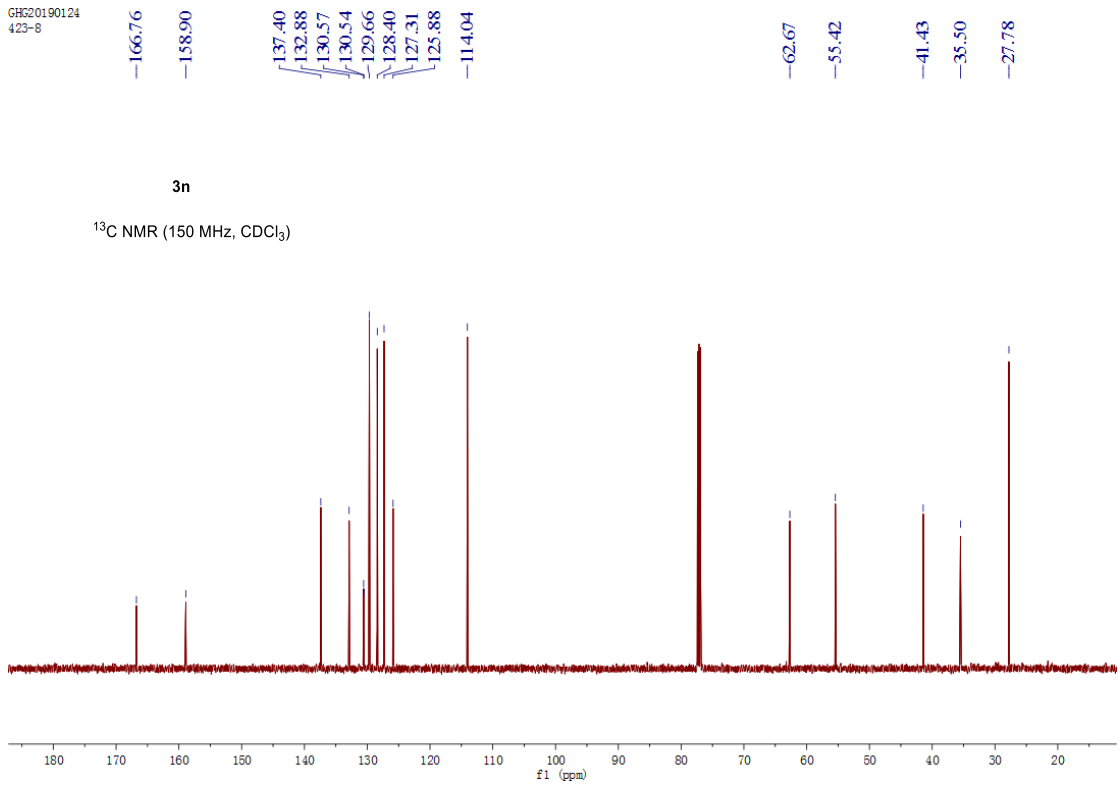
3m

^{13}C NMR (150 MHz, $CDCl_3$)



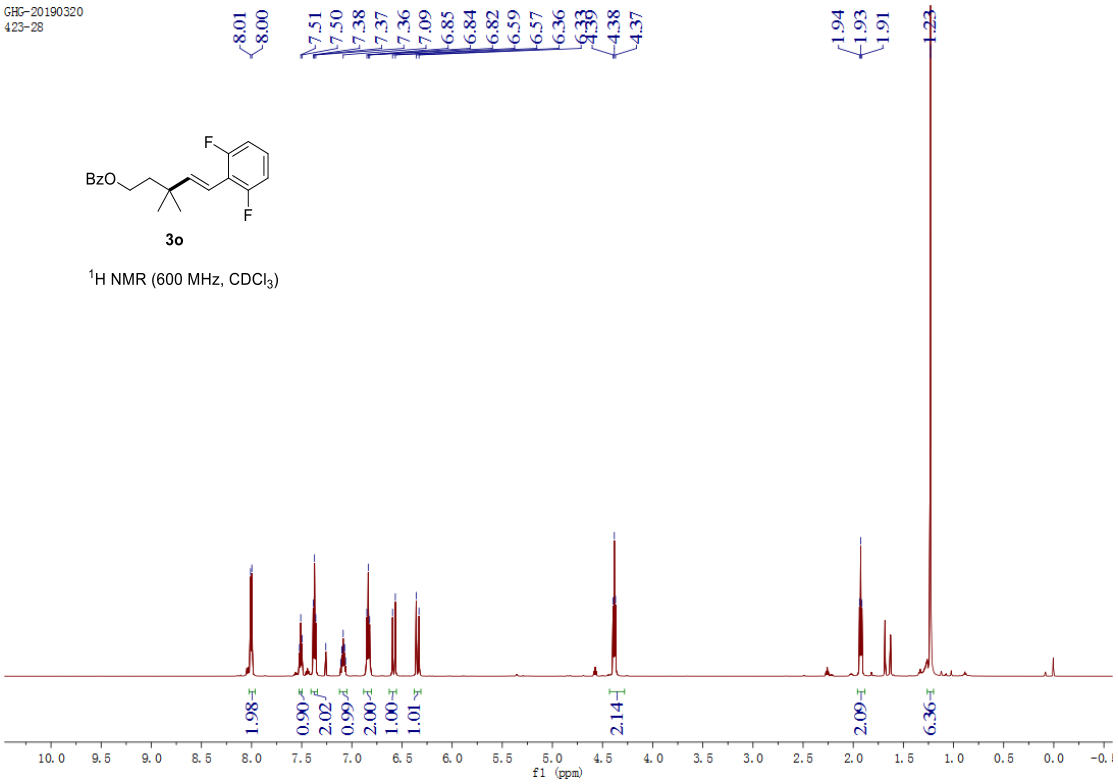
3n

^{1}H NMR (600 MHz, $CDCl_3$)



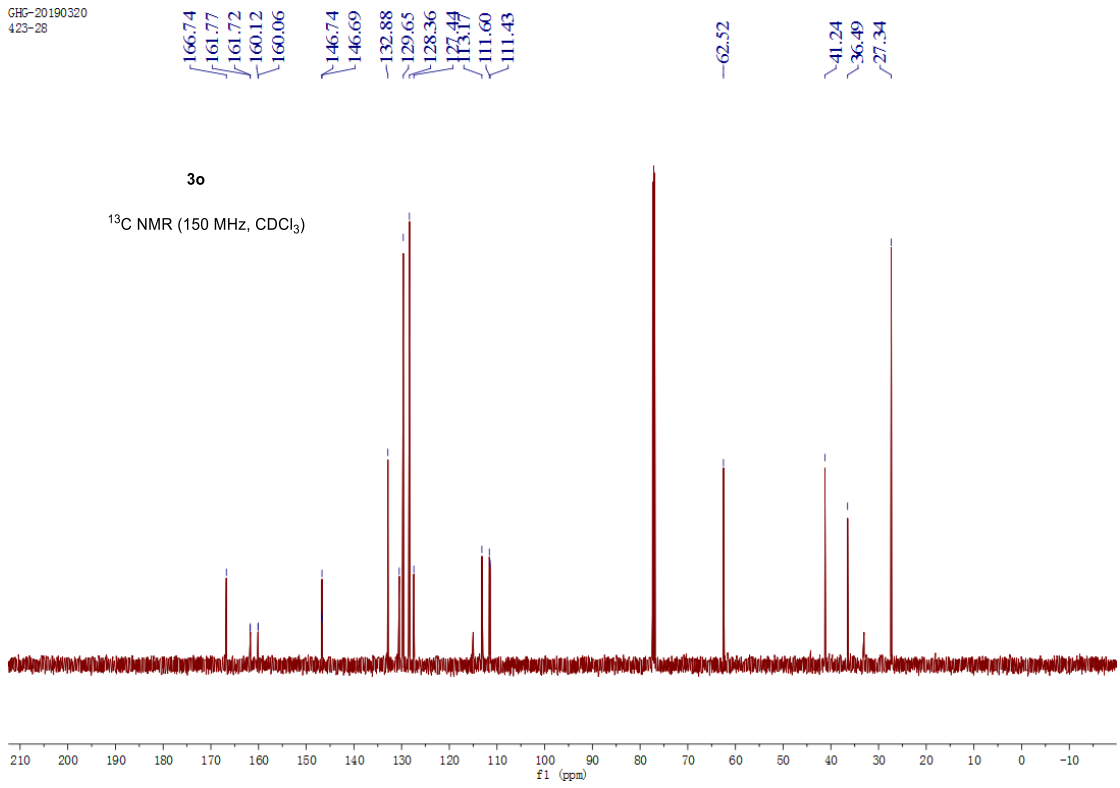
3n

^{13}C NMR (150 MHz, $CDCl_3$)



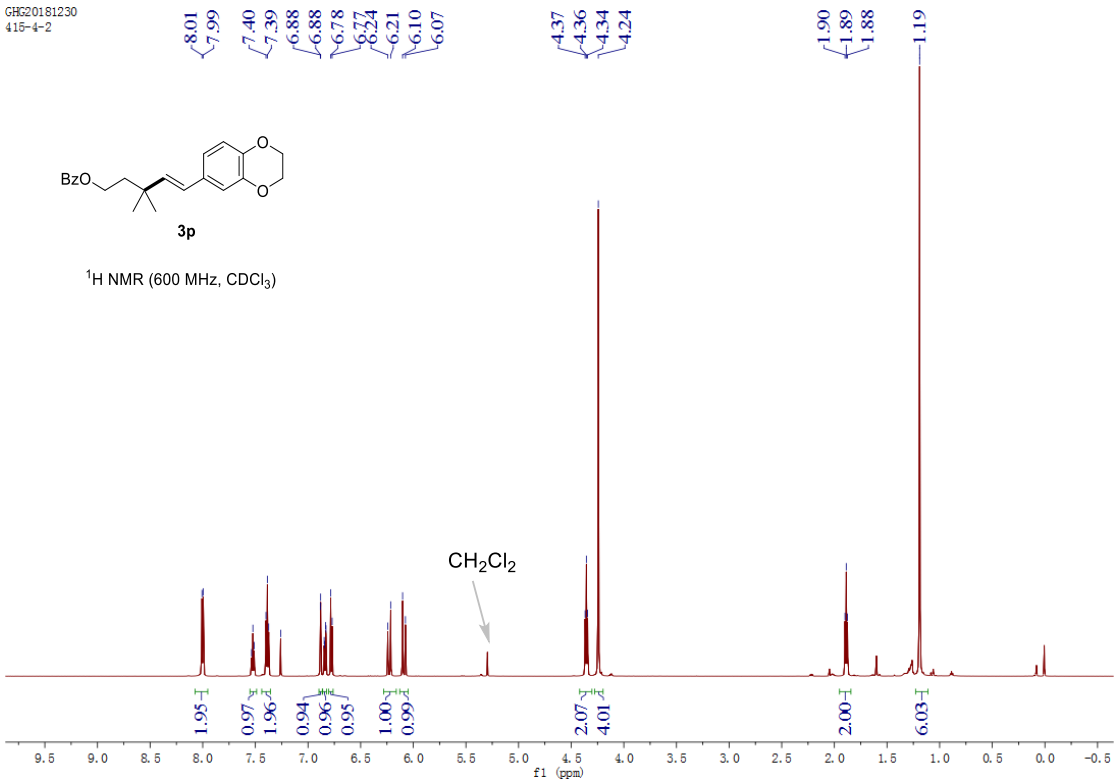
3o

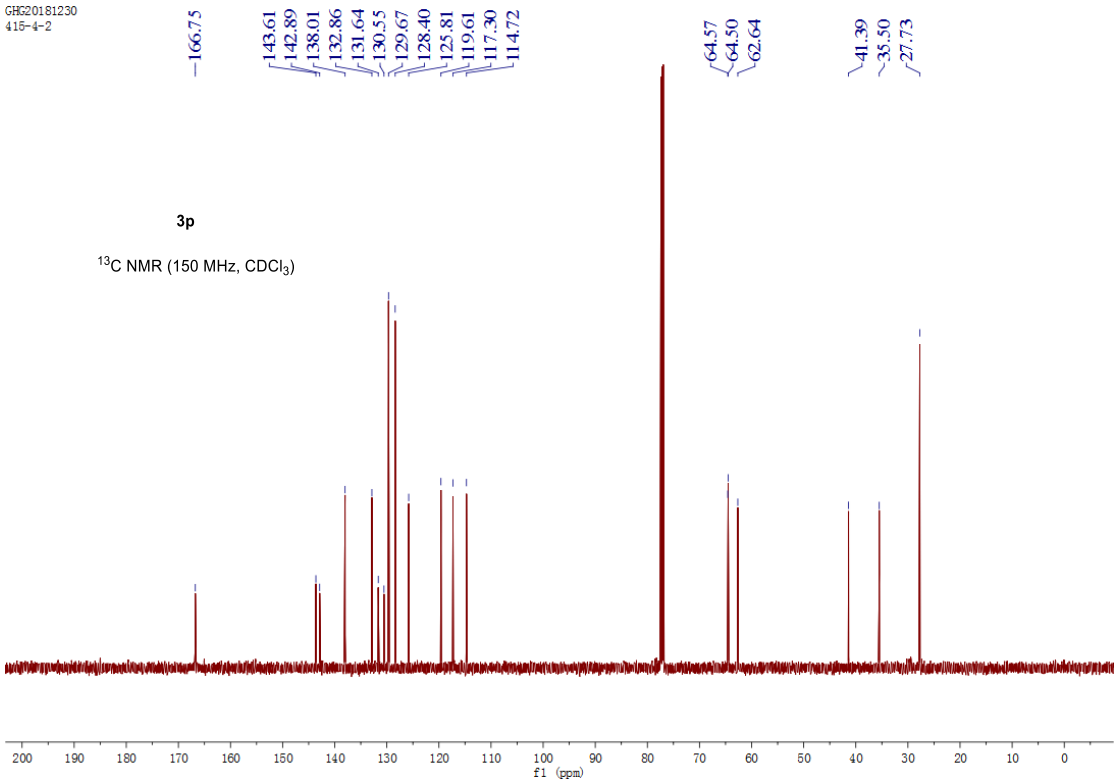
^{1}H NMR (600 MHz, $CDCl_3$)

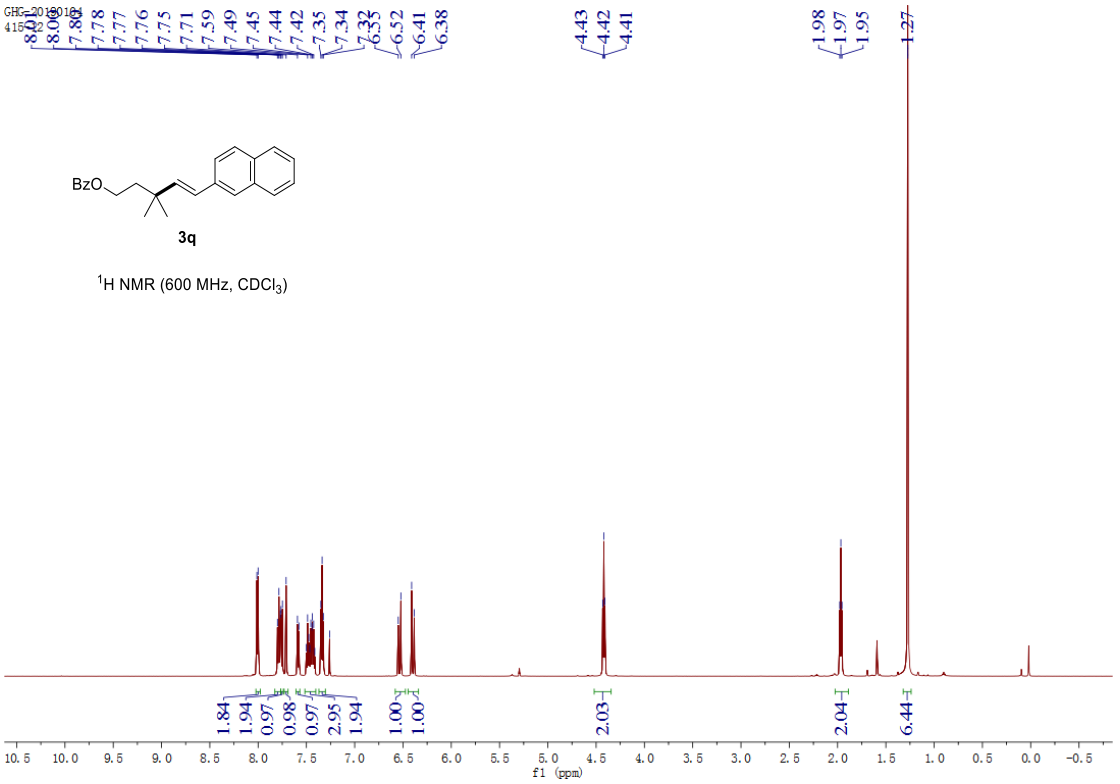


3o

^{13}C NMR (150 MHz, $CDCl_3$)

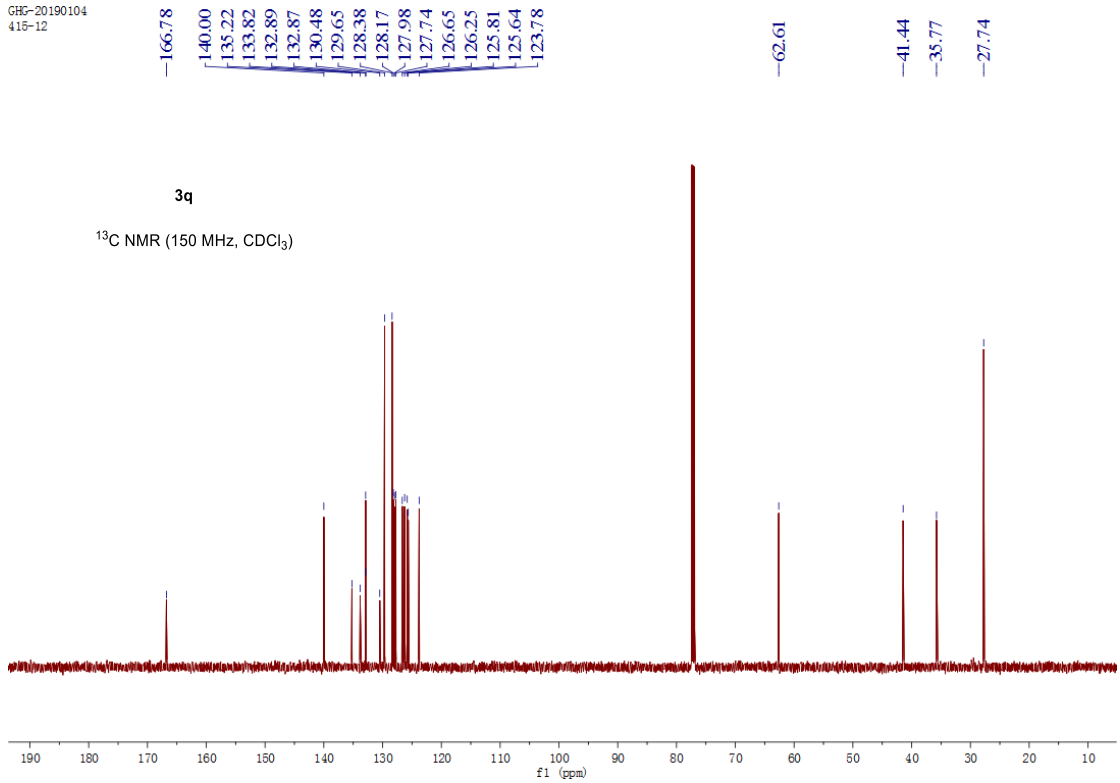

GHG20181230
415-4-2
8.01
7.99
7.40
7.39
6.88
6.88
6.78
6.77
6.24
6.21
6.10
6.07
4.37
4.36
4.34
4.24
1.90
1.89
1.88
1.19
BzO
O
O
3p
^{1}H NMR (600 MHz, $CDCl_3$)
CH_2Cl_2
1.95
0.97
1.96
0.94
0.96
0.95
1.00
0.99
2.07
4.01
2.00
6.03
f1 (ppm)


GHG20181230
415-4-2
166.75
143.61
142.89
138.01
132.86
131.64
130.55
129.67
128.40
125.81
119.61
117.30
114.72
64.57
64.50
62.64
41.39
35.50
27.73
3p
^{13}C NMR (150 MHz, $CDCl_3$)
f1 (ppm)



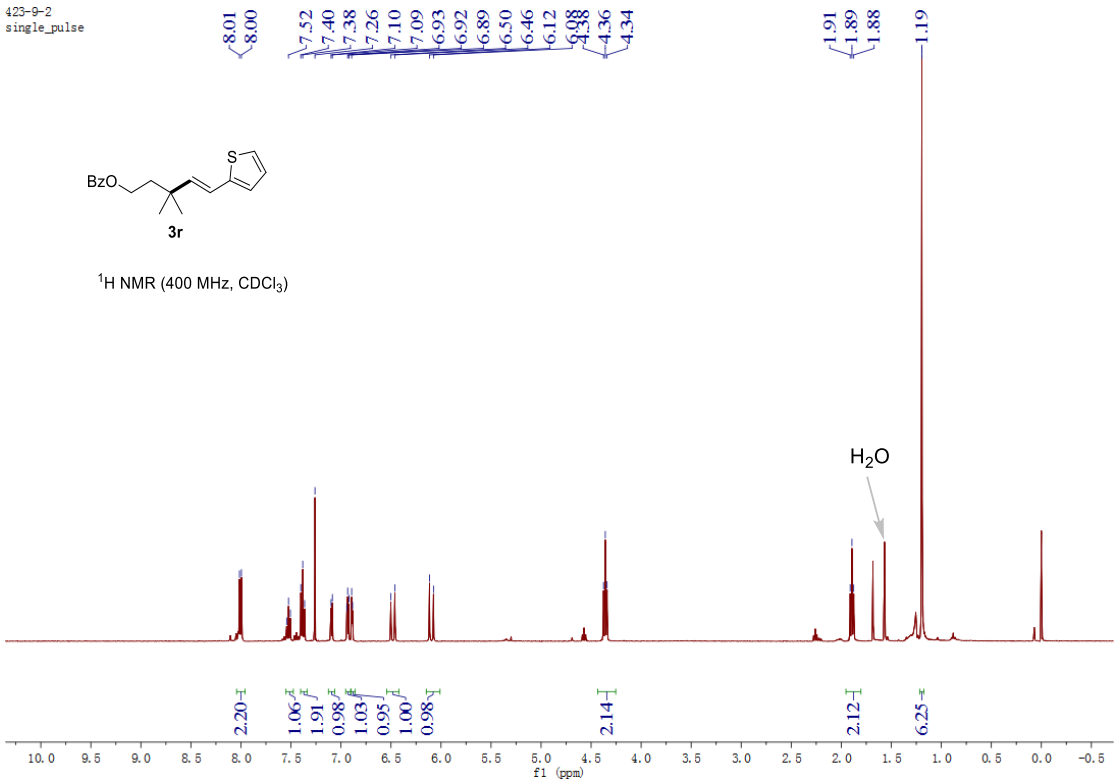
3q

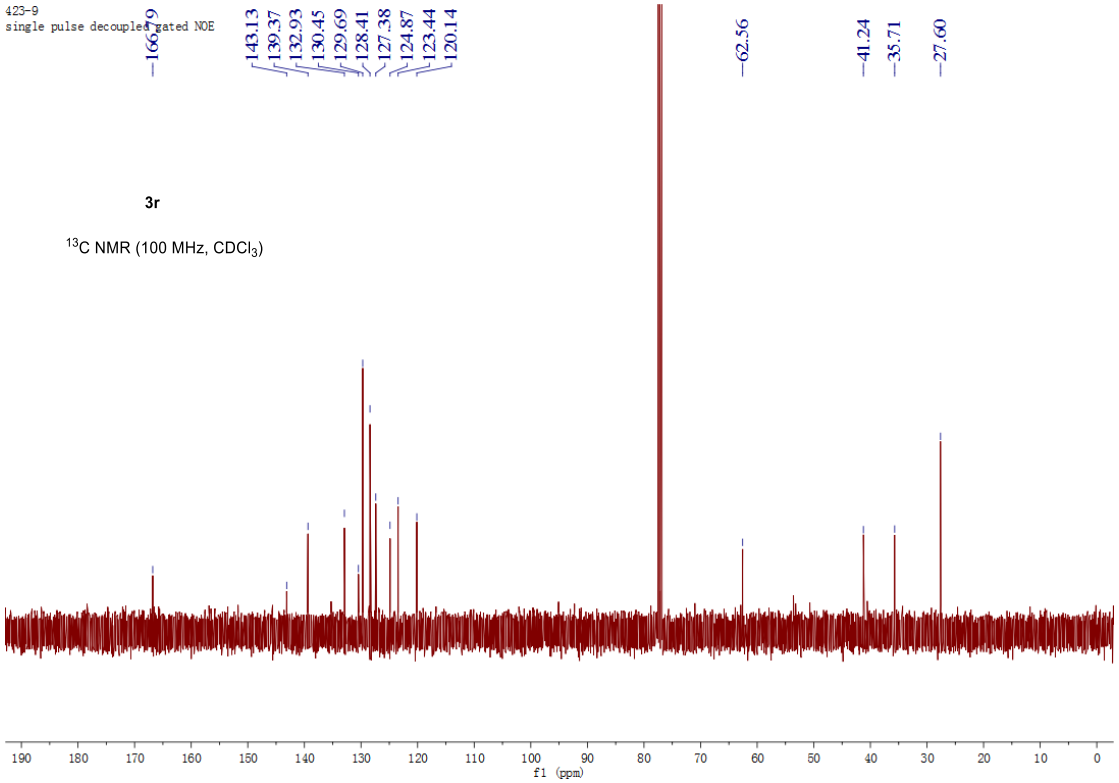
^{1}H NMR (600 MHz, $CDCl_3$)



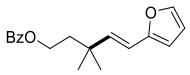
3q

^{13}C NMR (150 MHz, $CDCl_3$)


423-9-2
single_pulse
8.01
8.00
7.52
7.40
7.38
7.26
7.10
7.09
6.93
6.92
6.89
6.50
6.46
6.12
6.08
4.38
4.36
4.34
1.91
1.89
1.88
1.19
BzO
S
3r
1H NMR (400 MHz, CDCl3)
H2O
2.20
1.06
1.91
0.98
1.03
0.95
1.00
0.98
2.14
2.12
6.25
f1 (ppm)

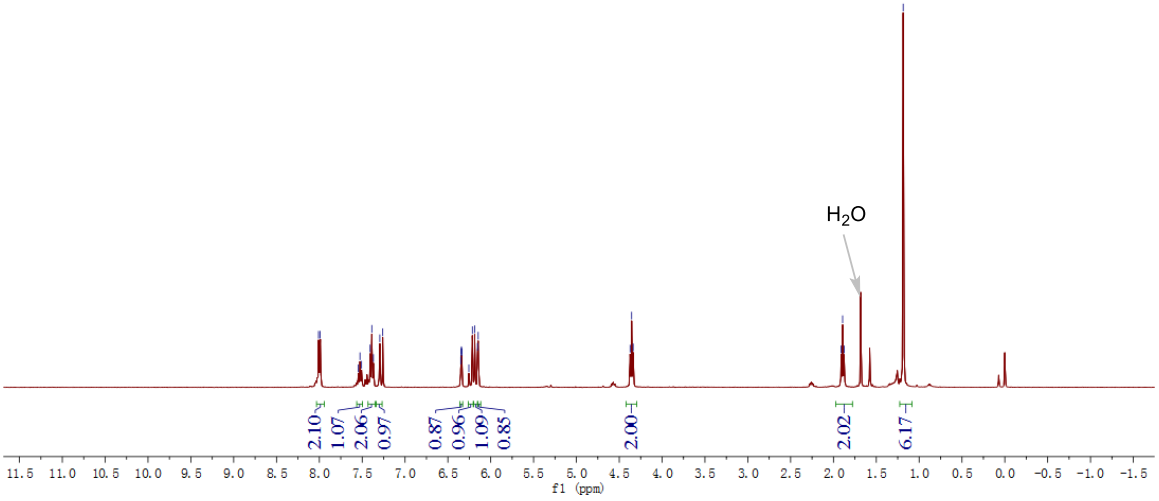

423-9
single pulse decoupled gated NOE
166.9
143.13
139.37
132.93
130.45
129.69
128.41
127.38
124.87
123.44
120.14
62.56
41.24
35.71
27.60
3r
13C NMR (100 MHz, CDCl3)
f1 (ppm)

423-10-2
single_pulse



3s

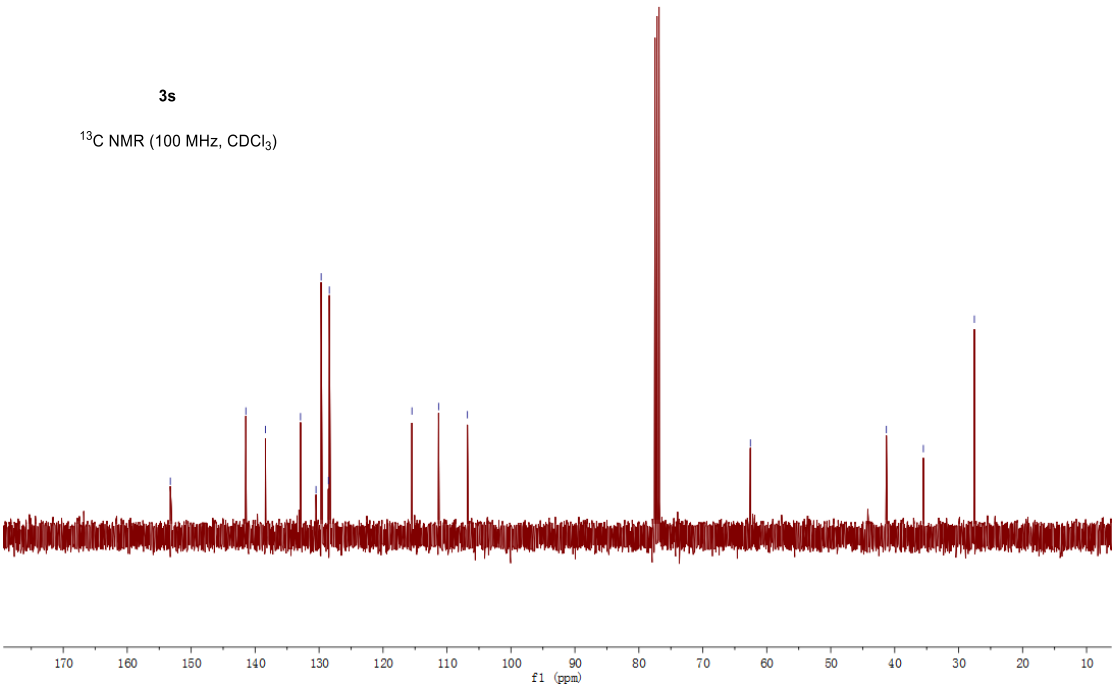
^{1}H NMR (400 MHz, $CDCl_3$)

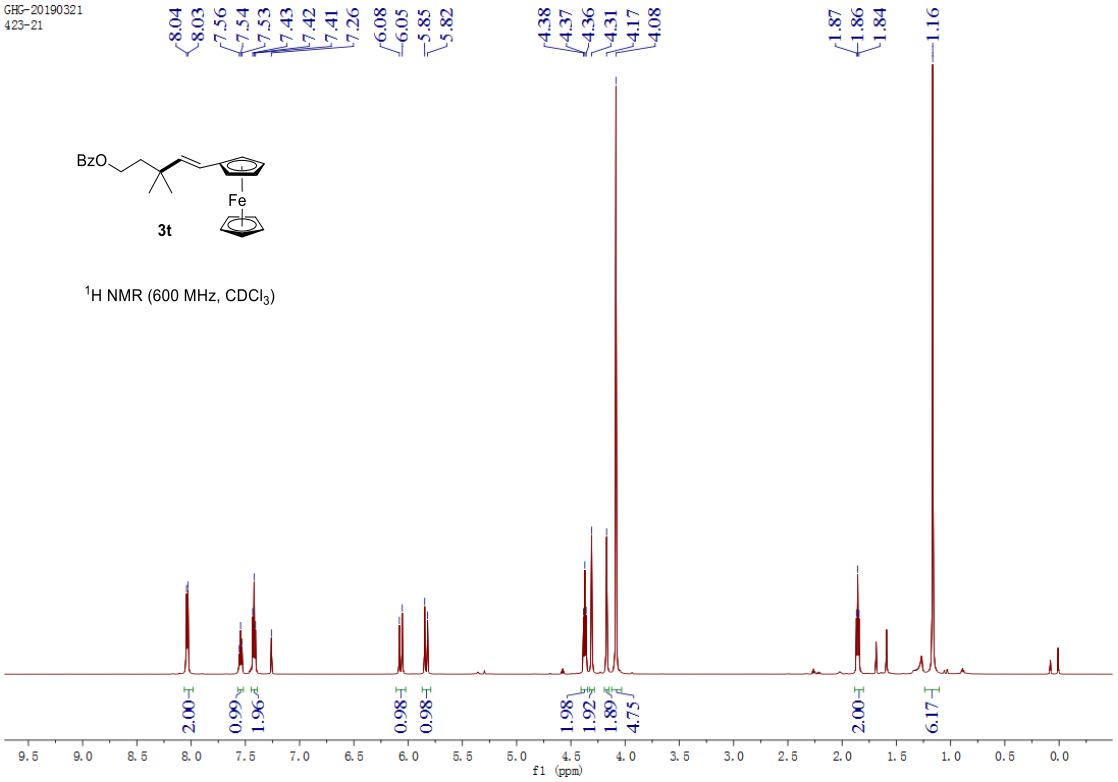


423-10 1
single pulse decoupled gated NOE

3s

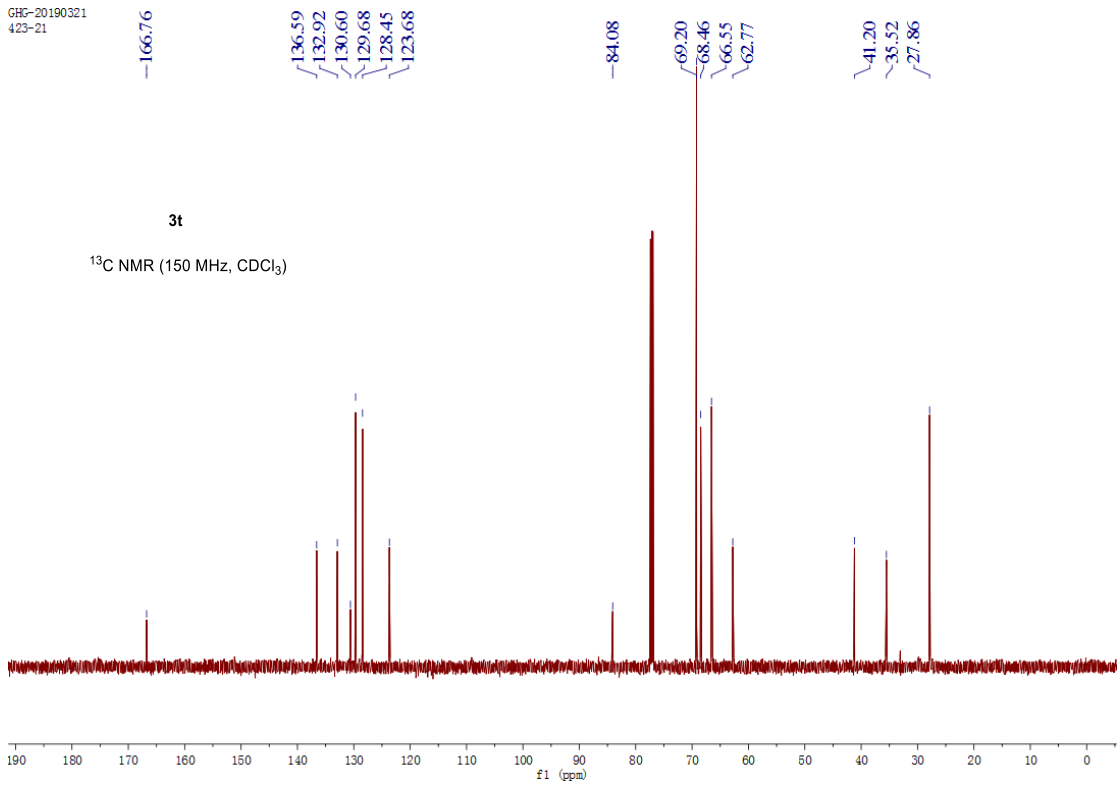
^{13}C NMR (100 MHz, $CDCl_3$)





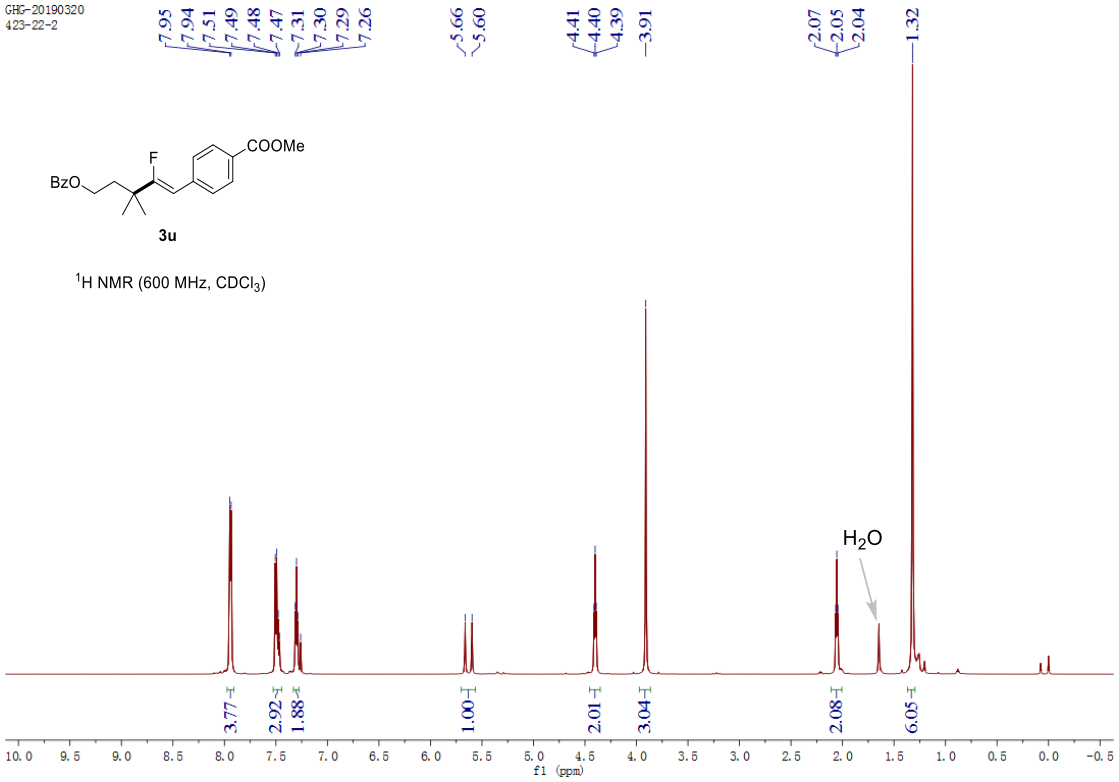
3t

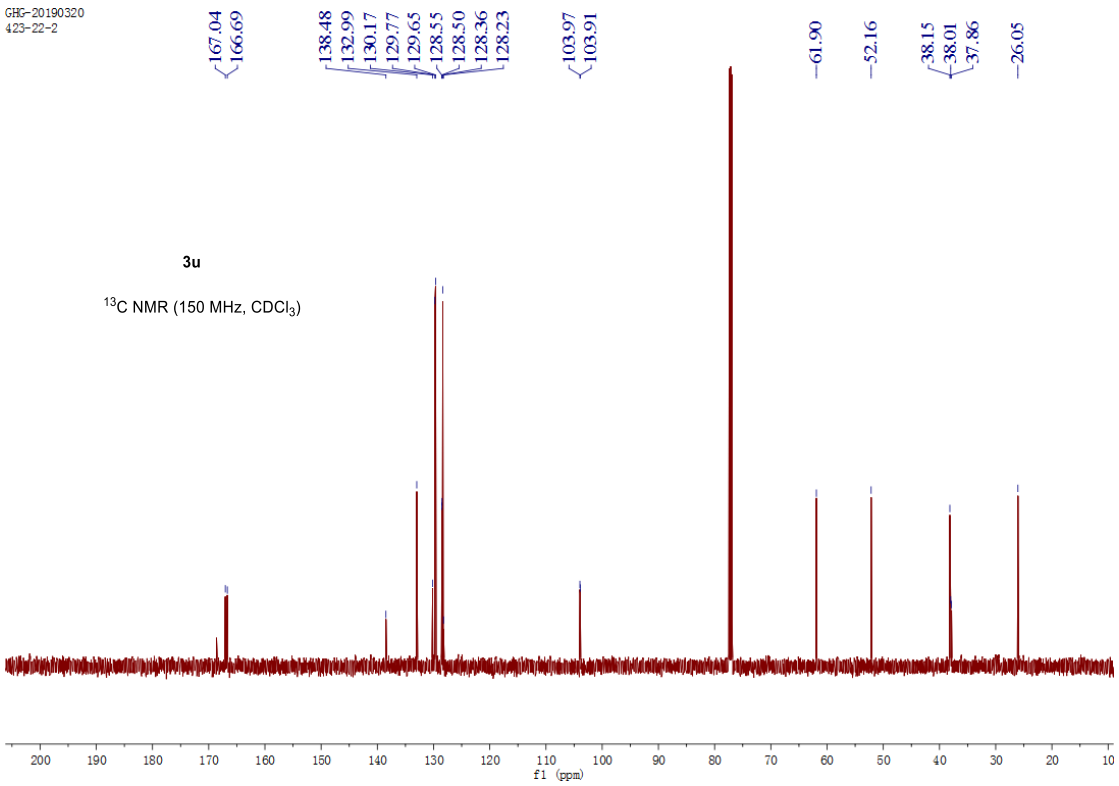
^{1}H NMR (600 MHz, $CDCl_3$)

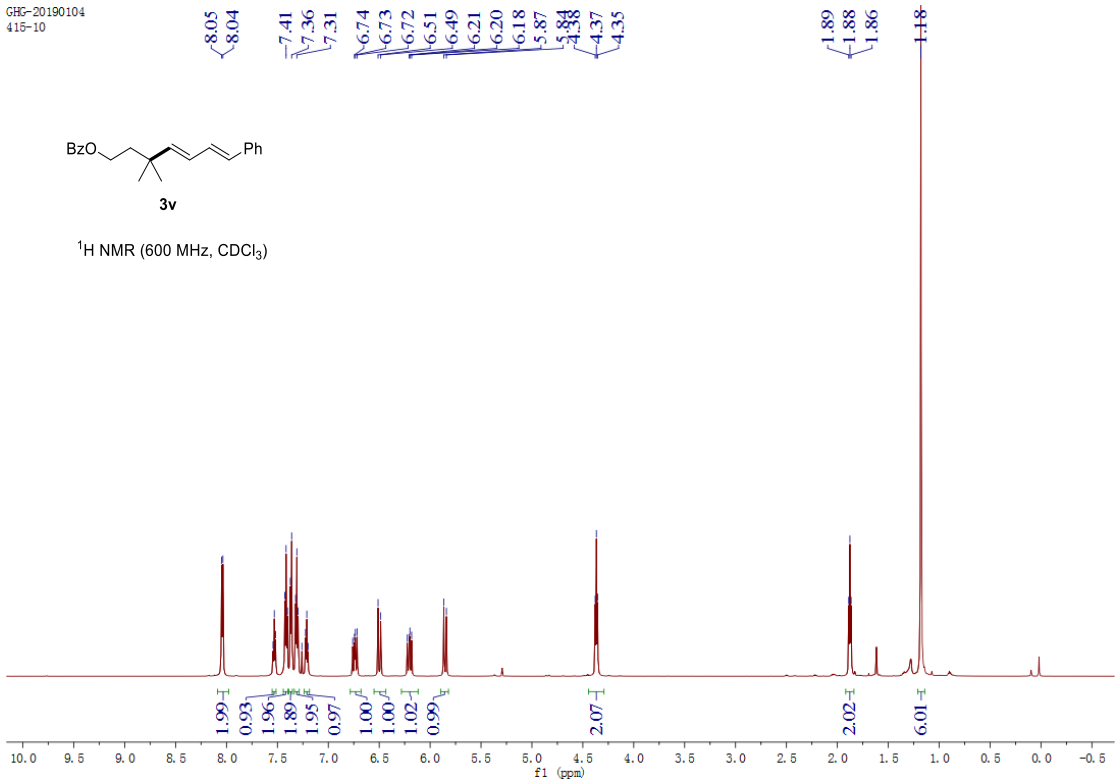


3t

^{13}C NMR (150 MHz, $CDCl_3$)


GHG-20190320
423-22-2
7.95
7.94
7.51
7.49
7.48
7.47
7.31
7.30
7.29
7.26
5.66
5.60
4.41
4.40
4.39
3.91
2.07
2.05
2.04
1.32
F
COOMe
BzO
3u
^{1}H NMR (600 MHz, $CDCl_3$)
H_2O
3.77
2.92
1.88
1.00
2.01
3.04
2.08
6.05
f1 (ppm)


GHG-20190320
423-22-2
167.04
166.69
138.48
132.99
130.17
129.77
129.65
128.55
128.50
128.36
128.23
103.97
103.91
61.90
52.16
38.15
38.01
37.86
26.05
3u
^{13}C NMR (150 MHz, $CDCl_3$)
f1 (ppm)

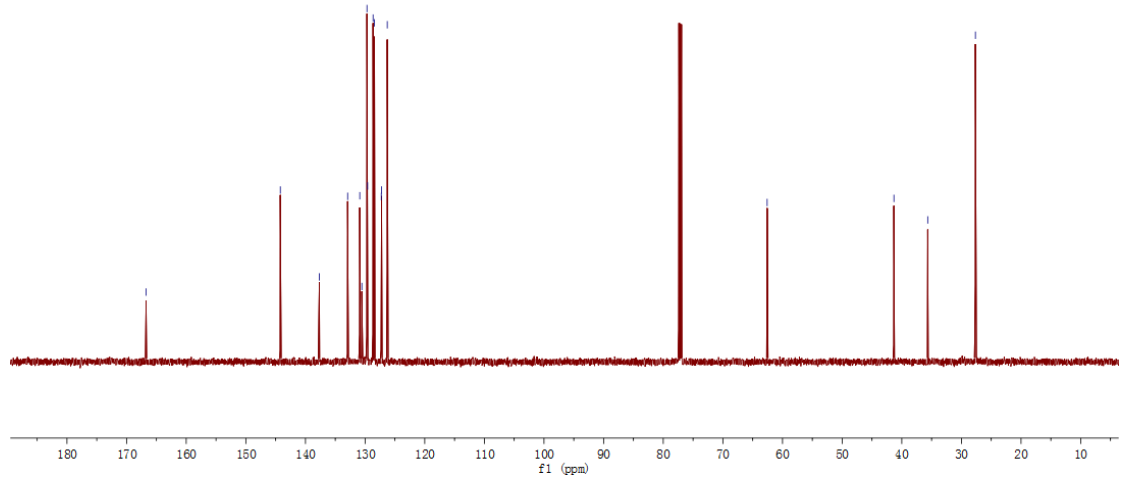


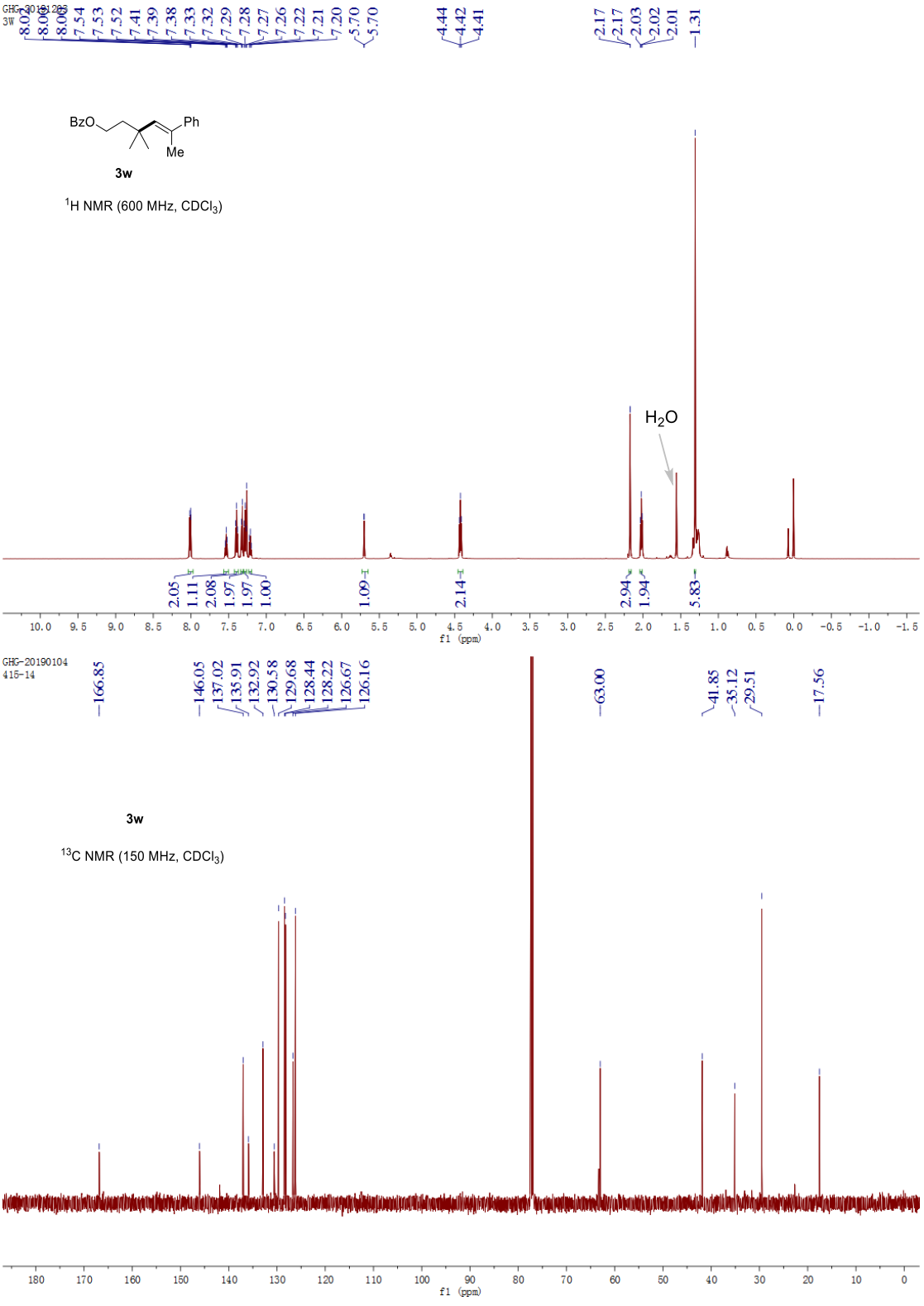
3v

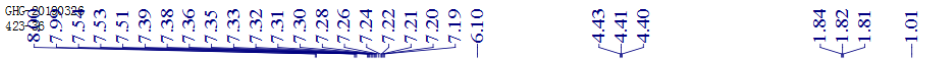
^{1}H NMR (600 MHz, $CDCl_3$)

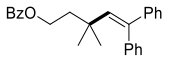
3v

^{13}C NMR (150 MHz, $CDCl_3$)



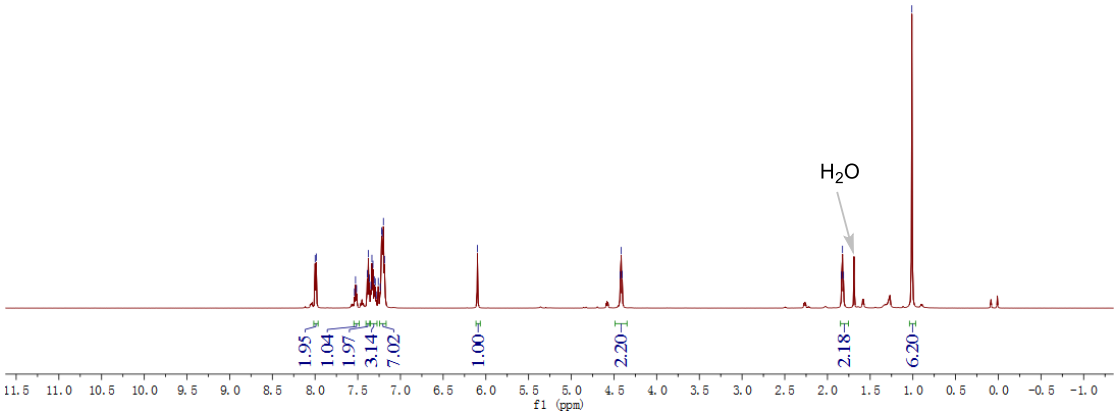

8.02
8.00
8.00
7.54
7.53
7.52
7.41
7.39
7.38
7.33
7.32
7.29
7.28
7.27
7.26
7.22
7.21
7.20
5.70
5.70
4.44
4.42
4.41
2.17
2.17
2.03
2.02
2.01
1.31
BzO
Ph
Me
3w
1H NMR (600 MHz, CDCl3)
H2O
2.05
1.11
2.08
1.97
1.97
1.00
1.09
2.14
2.94
1.94
5.83
f1 (ppm)
GHG-20190104
415-14
166.85
146.05
137.02
135.91
132.92
130.58
129.68
128.44
128.22
126.67
126.16
63.00
41.85
35.12
29.51
17.56
3w
13C NMR (150 MHz, CDCl3)
f1 (ppm)

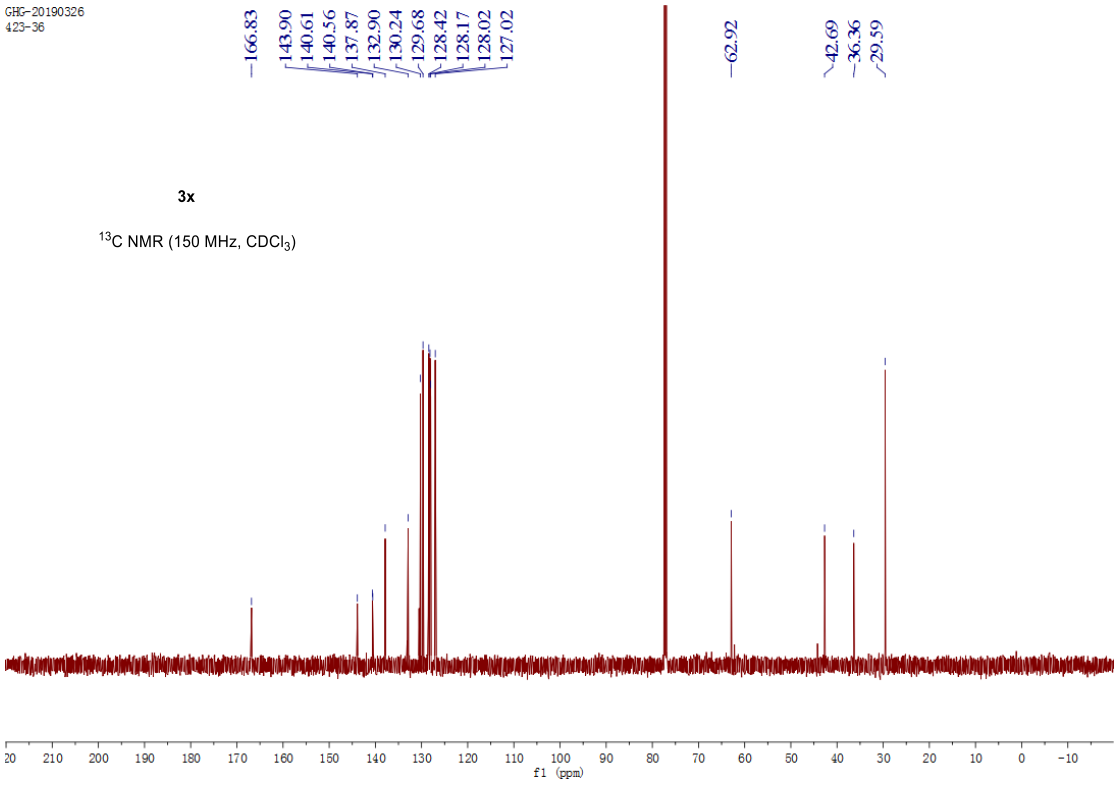




3x

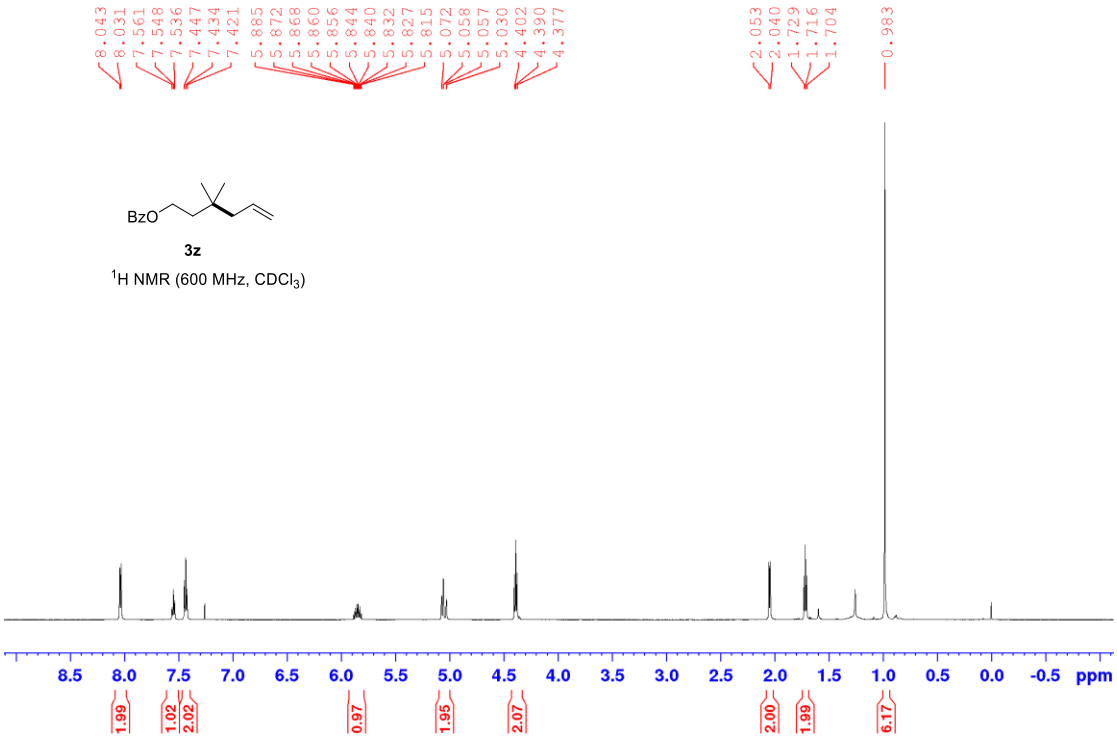
^{1}H NMR (600 MHz, $CDCl_3$)

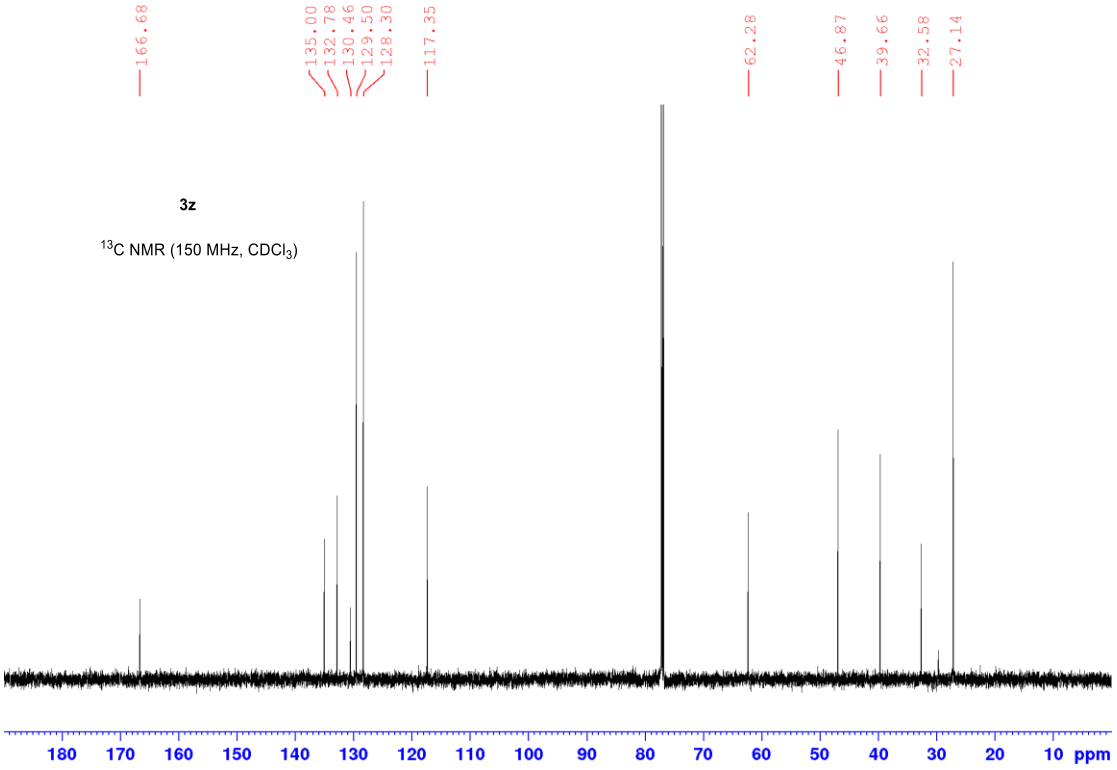


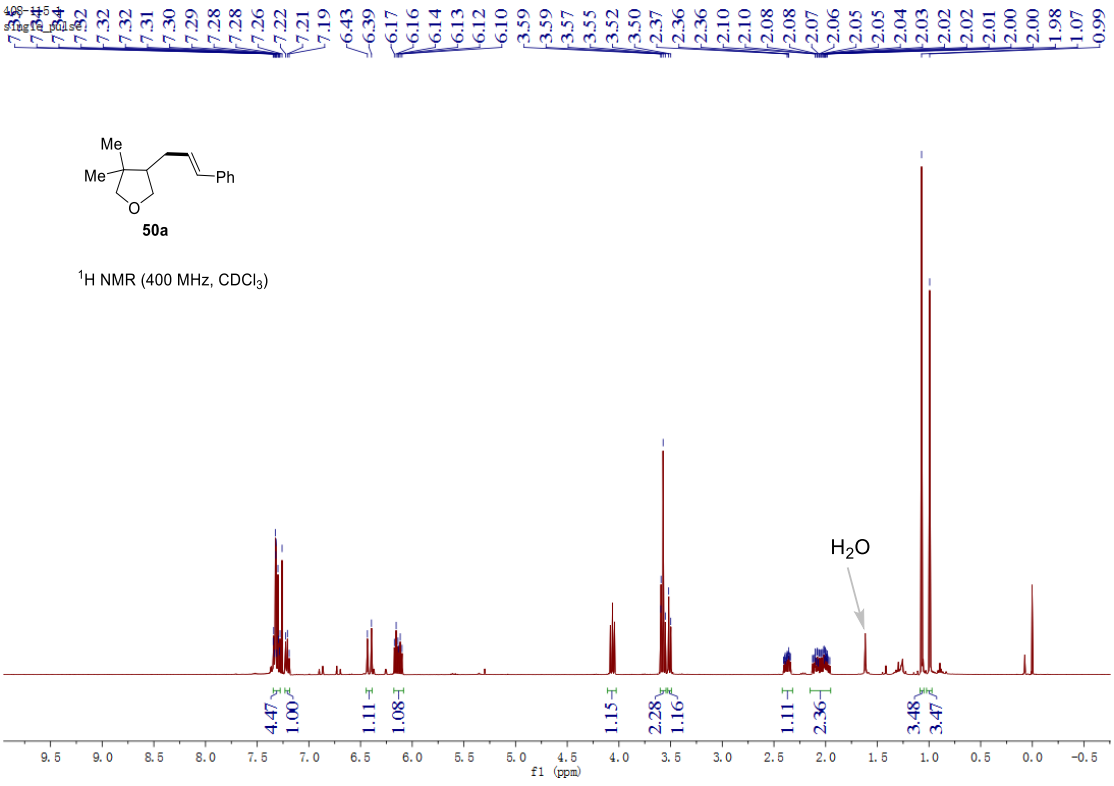


3x

^{13}C NMR (150 MHz, $CDCl_3$)

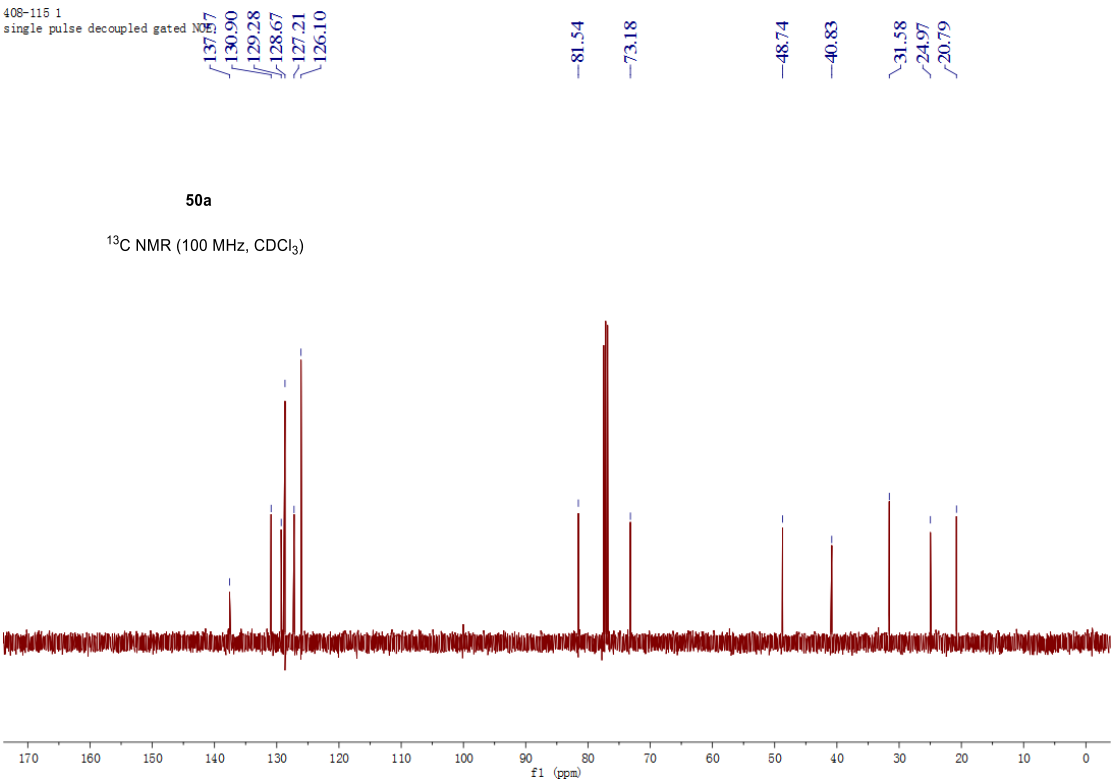

8.043
8.031
7.561
7.548
7.536
7.447
7.434
7.421
5.885
5.872
5.868
5.860
5.856
5.844
5.840
5.832
5.827
5.815
5.072
5.058
5.057
5.030
4.402
4.390
4.377
2.053
2.040
1.729
1.716
1.704
0.983
BzO
3z
1H NMR (600 MHz, CDCl3)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.99
1.02
2.02
0.97
1.95
2.07
2.00
1.99
6.17


166.68
135.00
132.78
130.46
129.50
128.30
117.35
62.28
46.87
39.66
32.58
27.14
3z
13C NMR (150 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



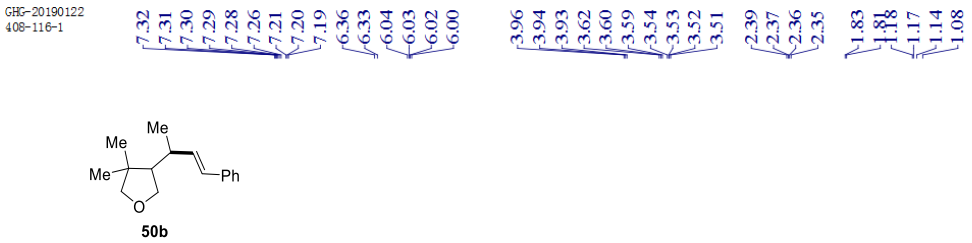
50a

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



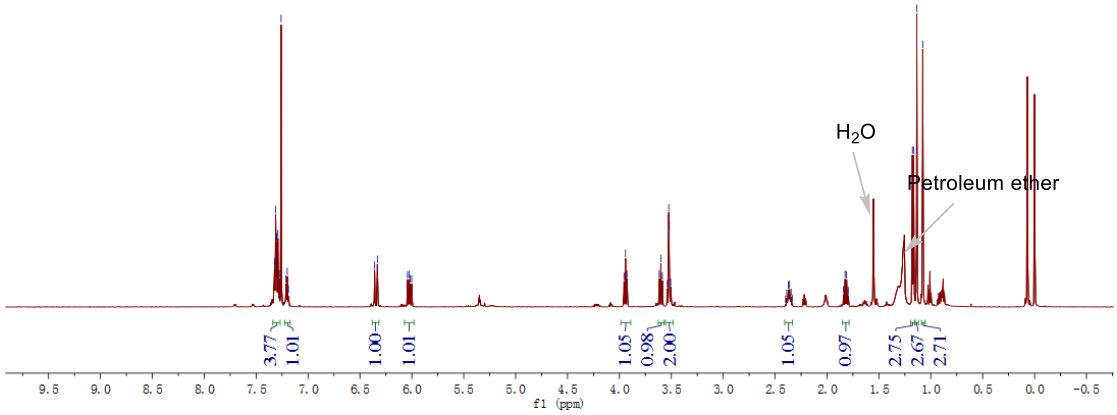
50a

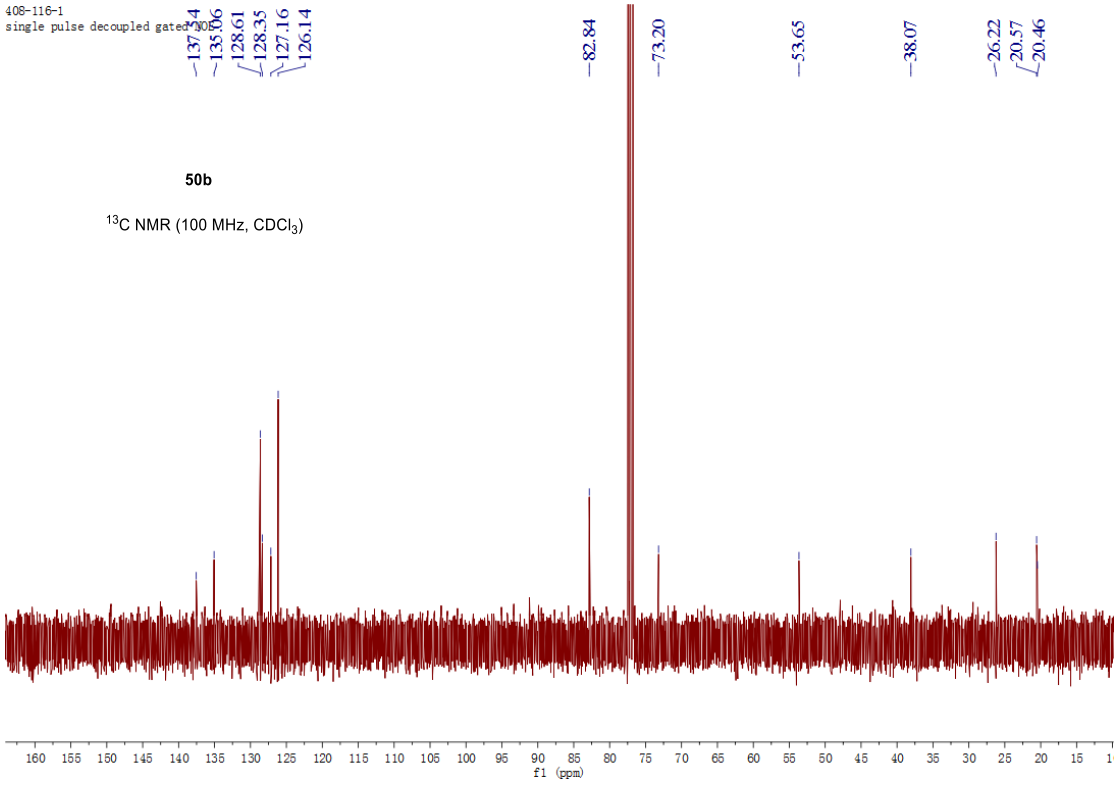
^{13}C NMR (100 MHz, $CDCl_3$)



50b

^{1}H NMR (600 MHz, $CDCl_3$)

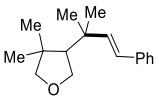




50b

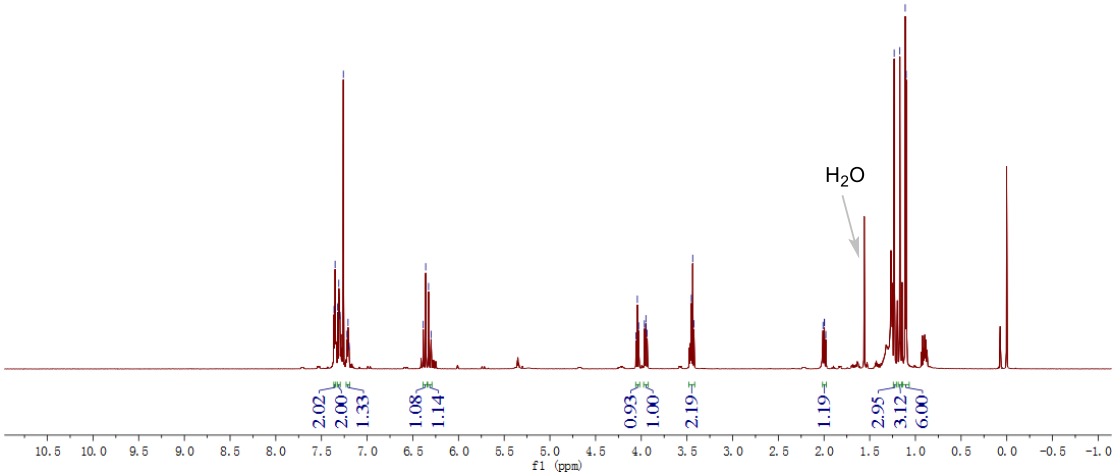
^{13}C NMR (100 MHz, $CDCl_3$)

GHG-20190116
408-67-2

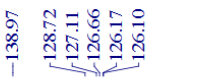


50c

^{1}H NMR (600 MHz, $CDCl_3$)

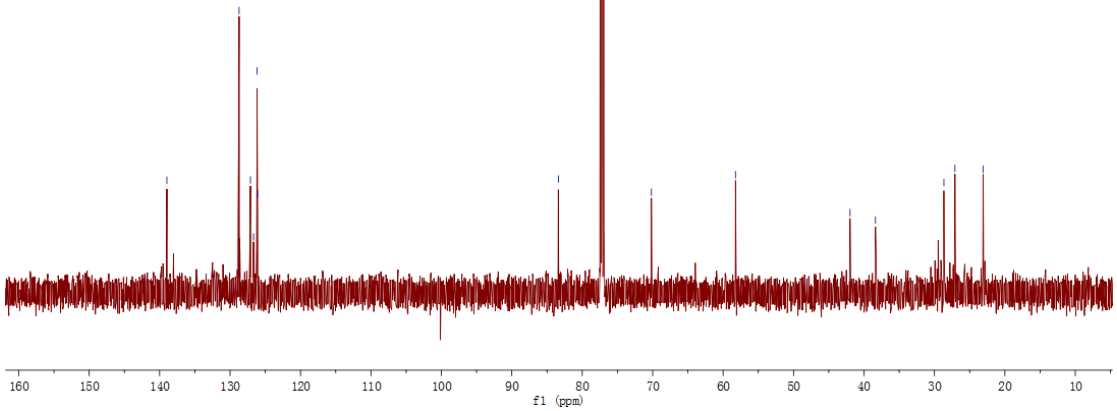


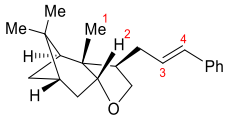
GHG-20190116
408-67-2



50c

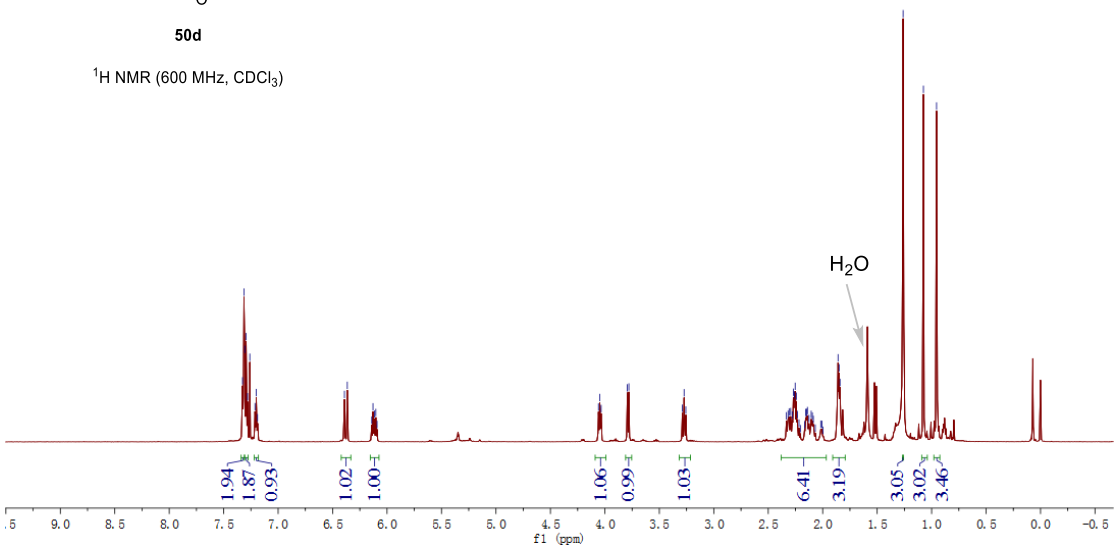
^{13}C NMR (150 MHz, $CDCl_3$)

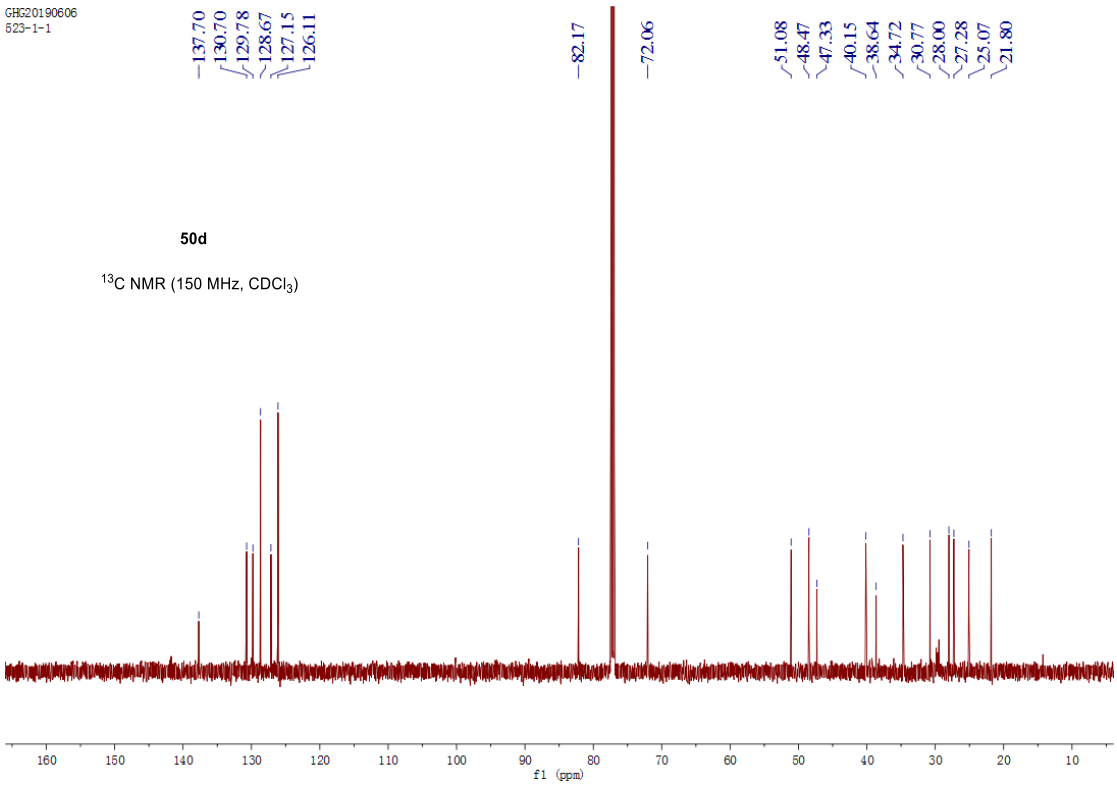




50d

^{1}H NMR (600 MHz, $CDCl_3$)

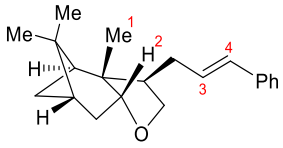




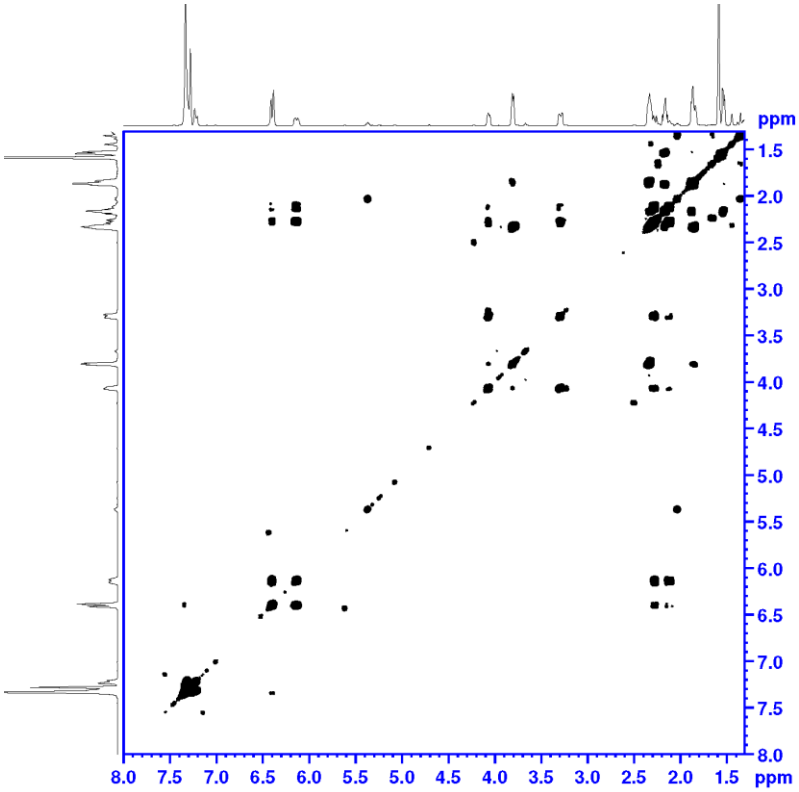
50d

^{13}C NMR (150 MHz, $CDCl_3$)

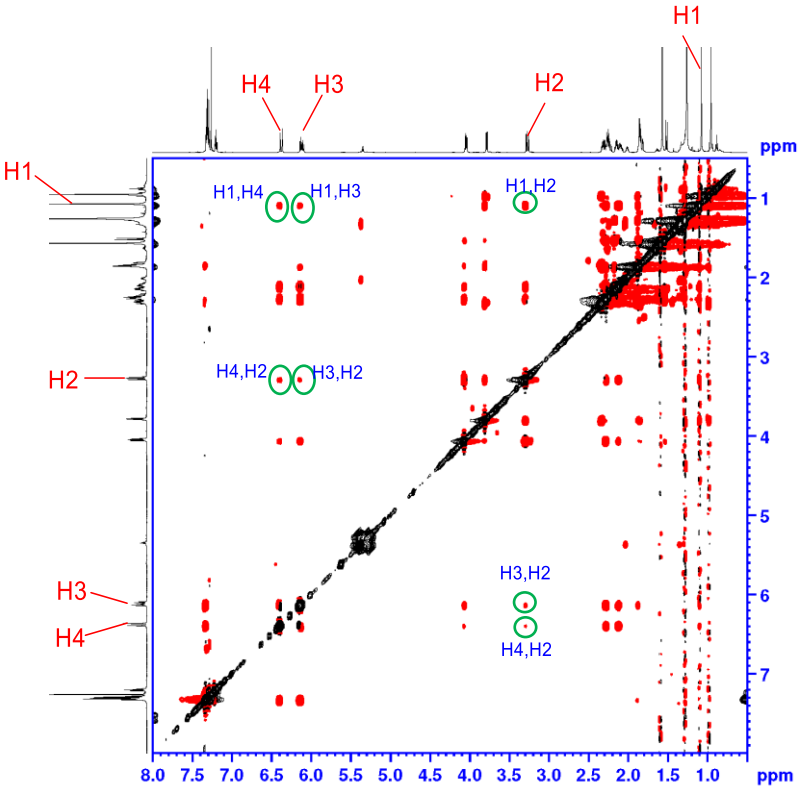
^{1}H-^{1}H COSY of **50d**:

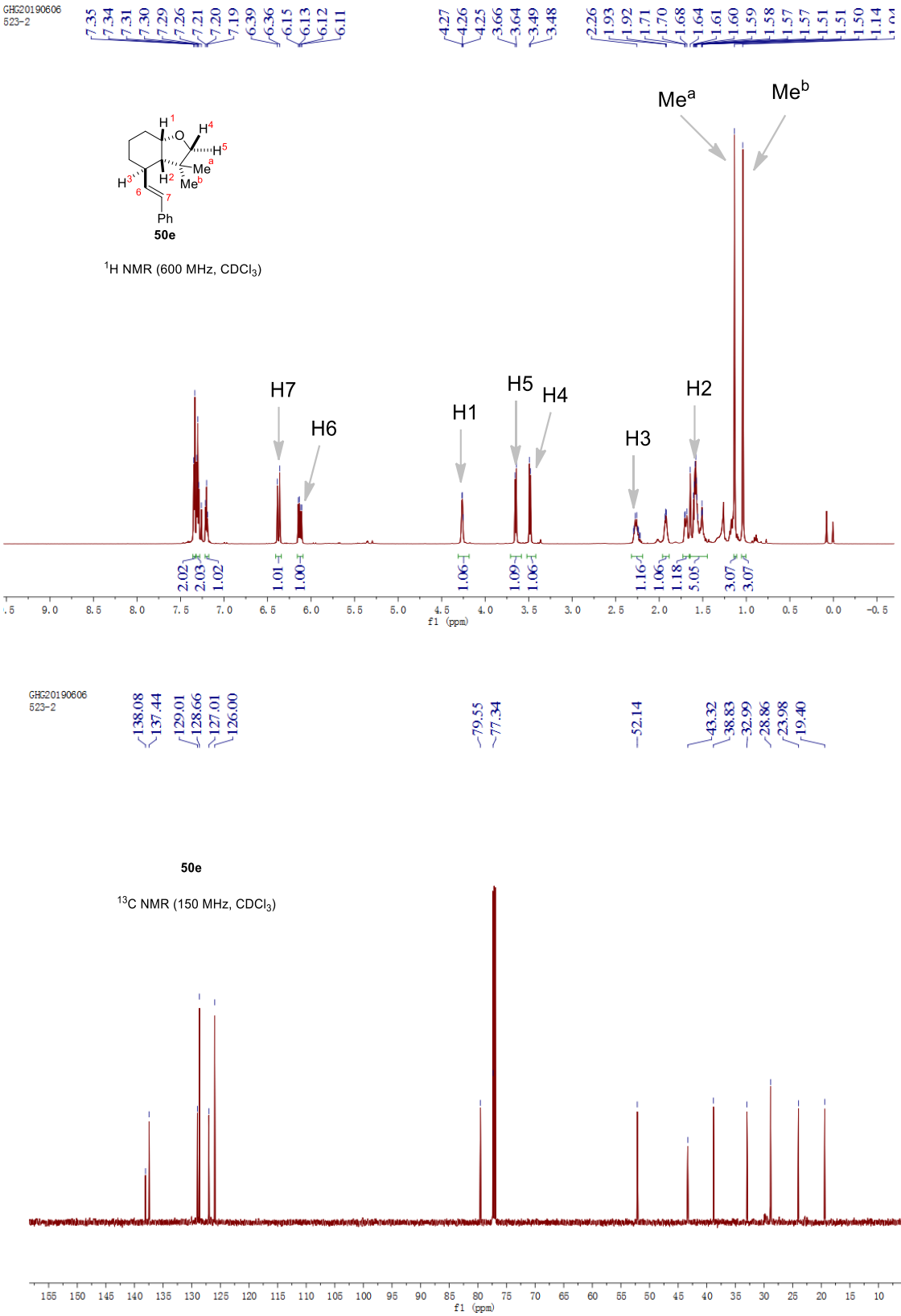


50d



2D NOESY of **50d**:





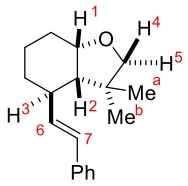
50e

^{1}H NMR (600 MHz, $CDCl_3$)

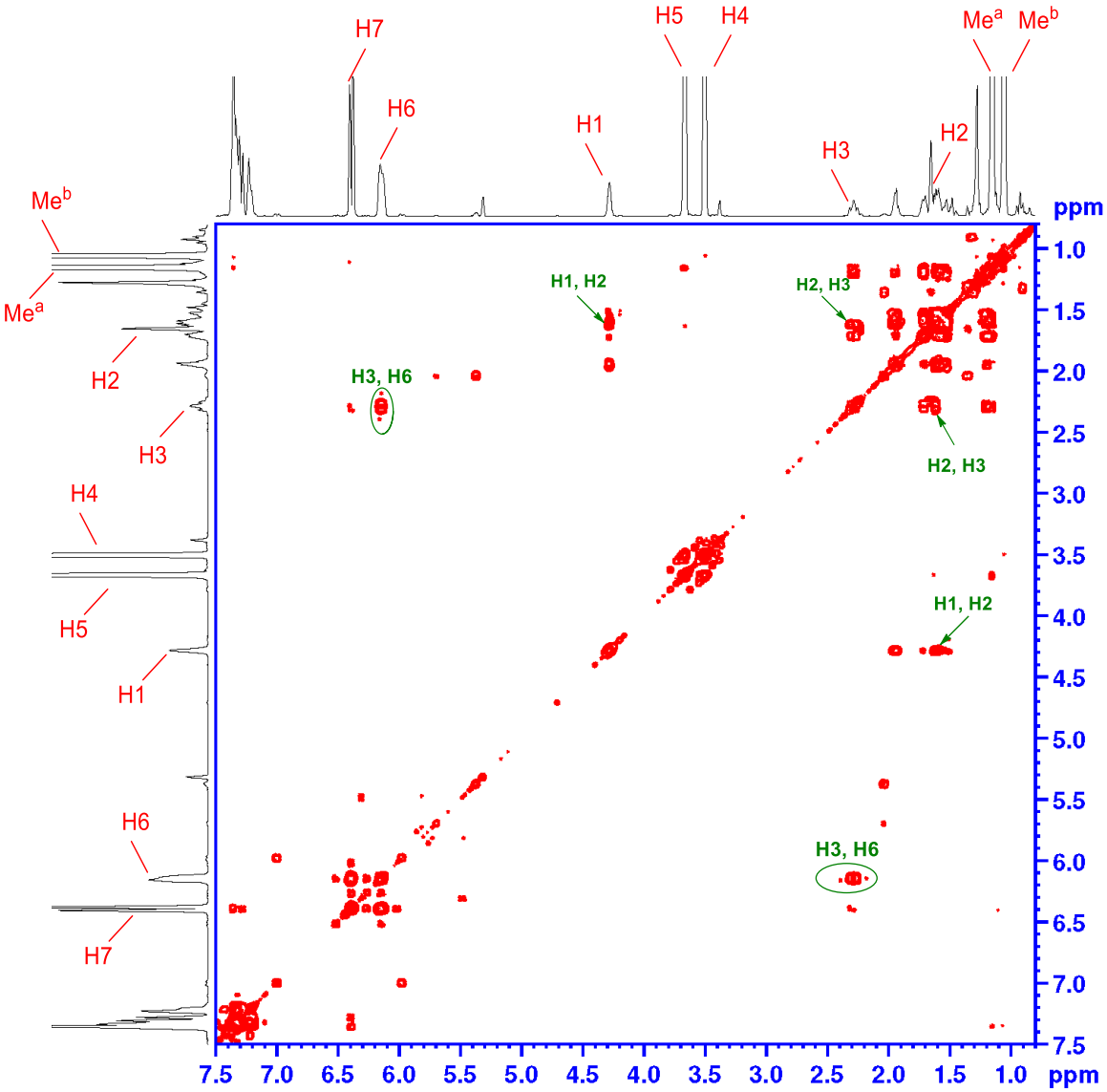
50e

^{13}C NMR (150 MHz, $CDCl_3$)

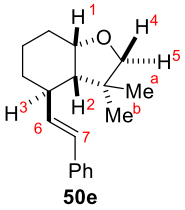
^{1}H-^{1}H COSY of **50e**:



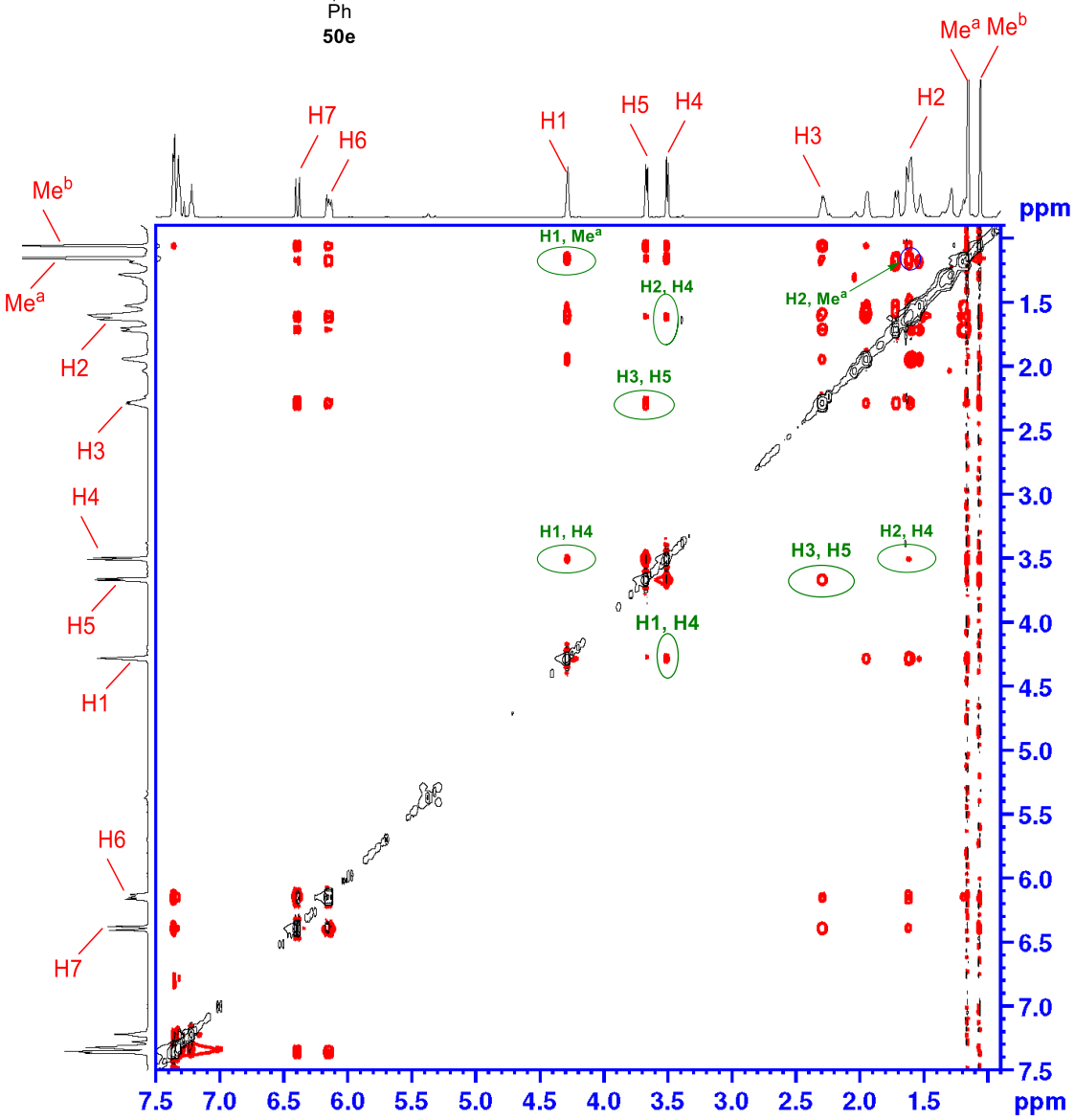
50e



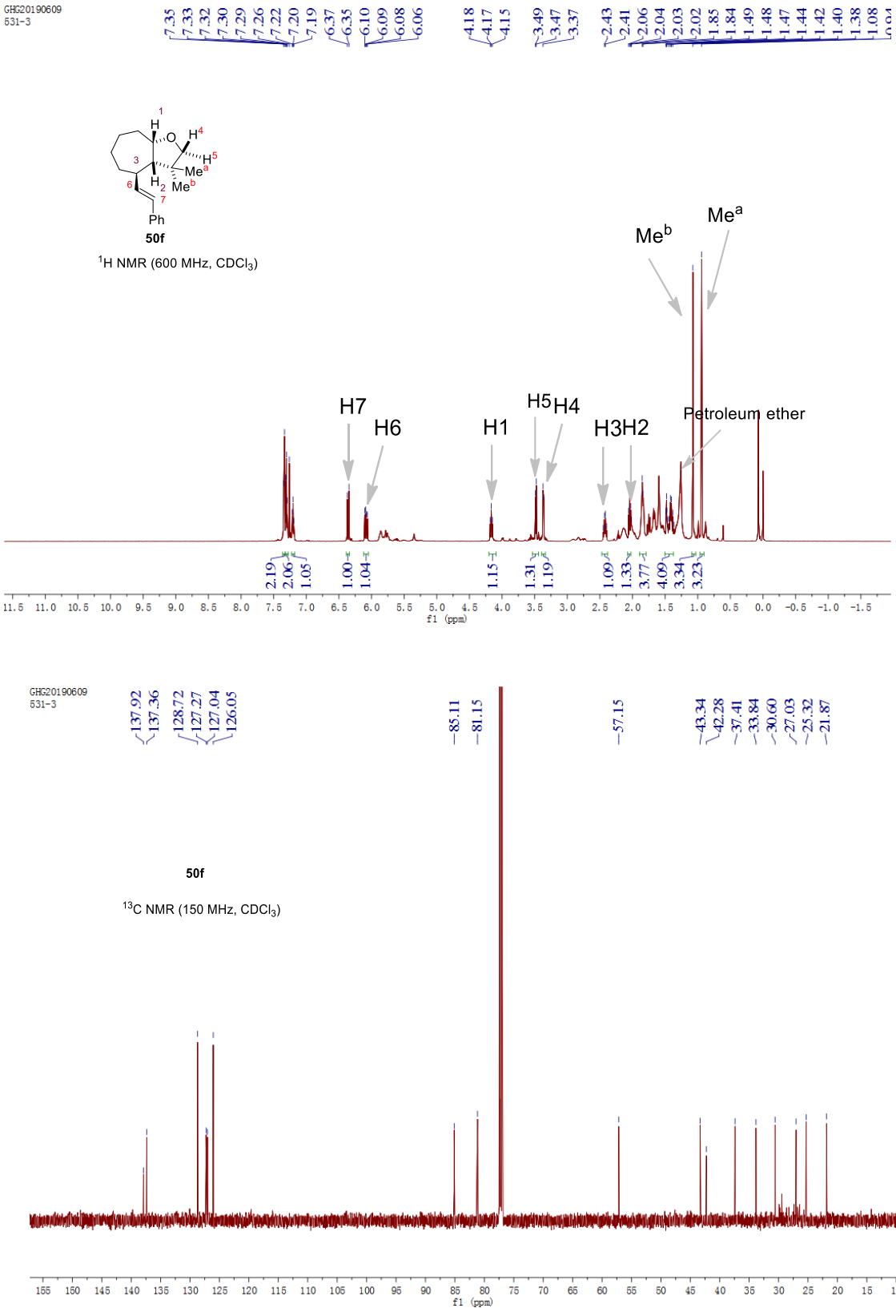
2D NOESY of **50e**:



50e



The relative stereochemistry was determined based on the following correlations found in NOESY spectra: No correlation was found between H1 and H3, suggesting a *trans* geometry of H1 with respect to H3. The trans geometry of H2 with respect to H3 was supported by the correlation of H5 and H3, whereas H4 correlates H1 and H2. Finally, the cis geometry of H1 and H2 was determined based on the following correlations: Me(a) with H1 and H2, Me(b) with H2 and H3, respectively, and more importantly, H4 and H1 and H2, respectively.



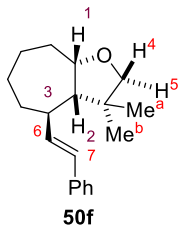
50f

^{1}H NMR (600 MHz, $CDCl_3$)

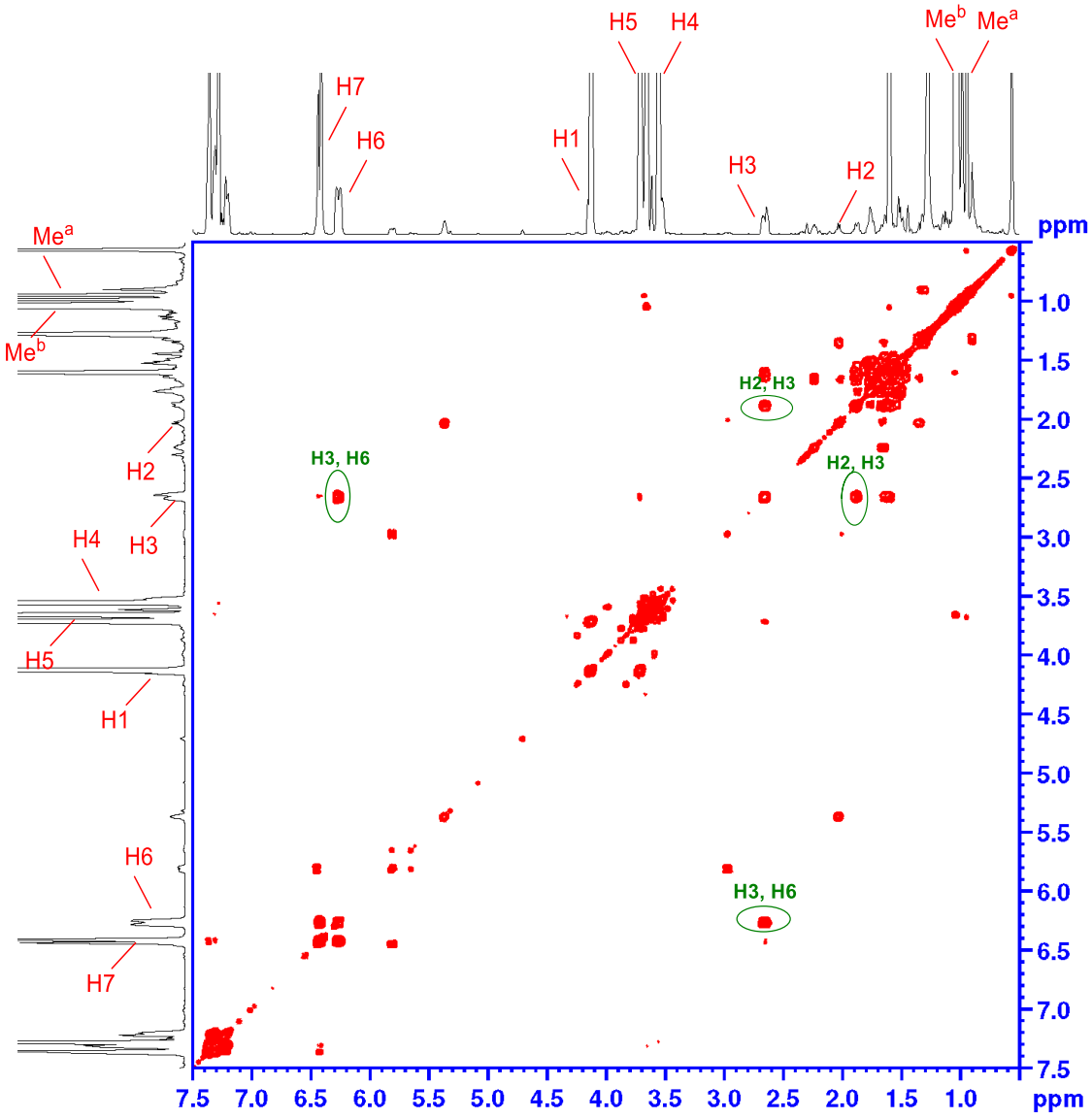
50f

^{13}C NMR (150 MHz, $CDCl_3$)

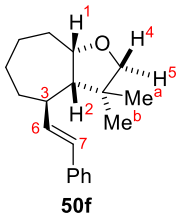
^{1}H-^{1}H COSY of **50f**:



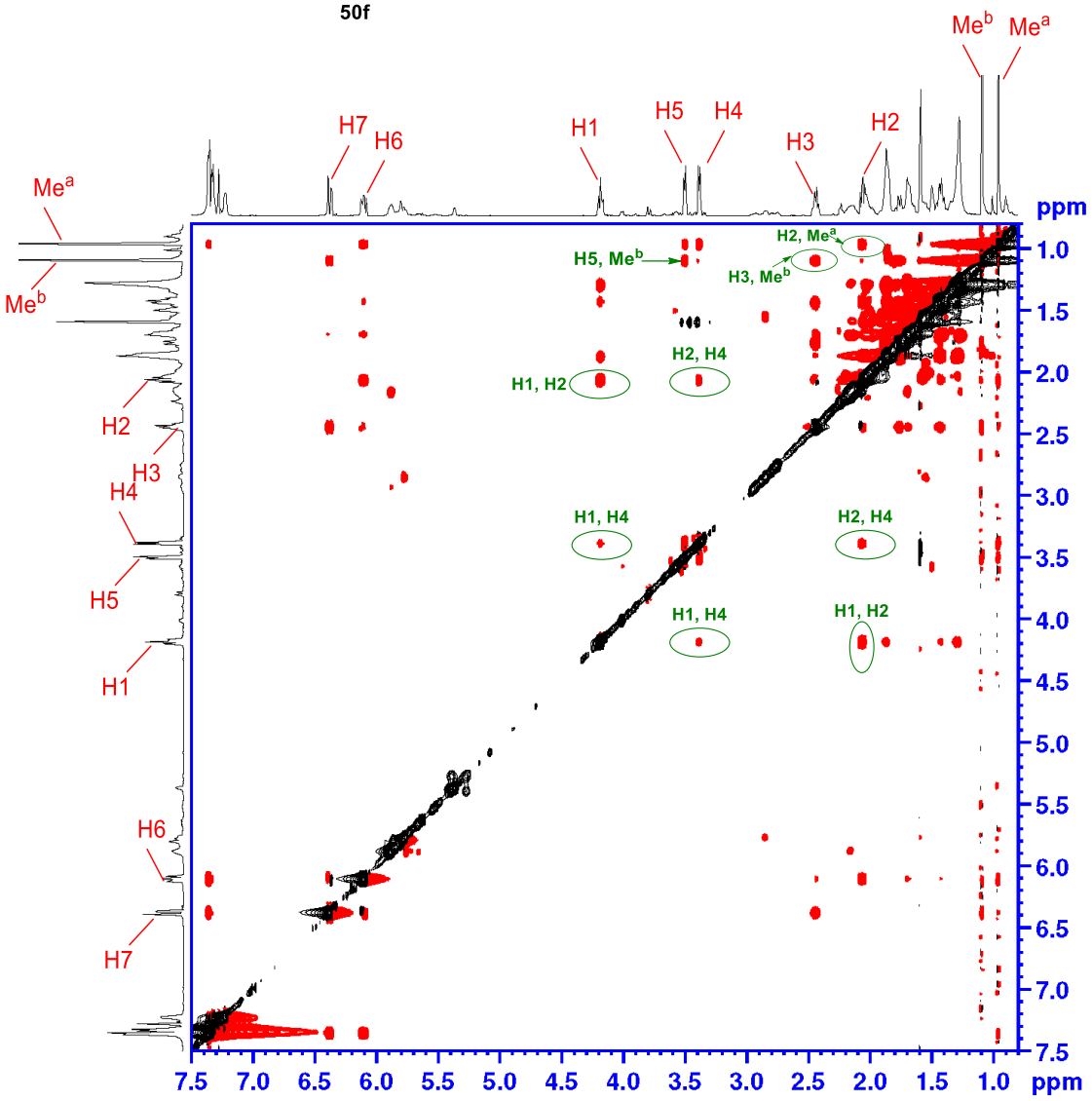
50f



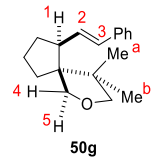
2D NOESY of **50f**:



50f

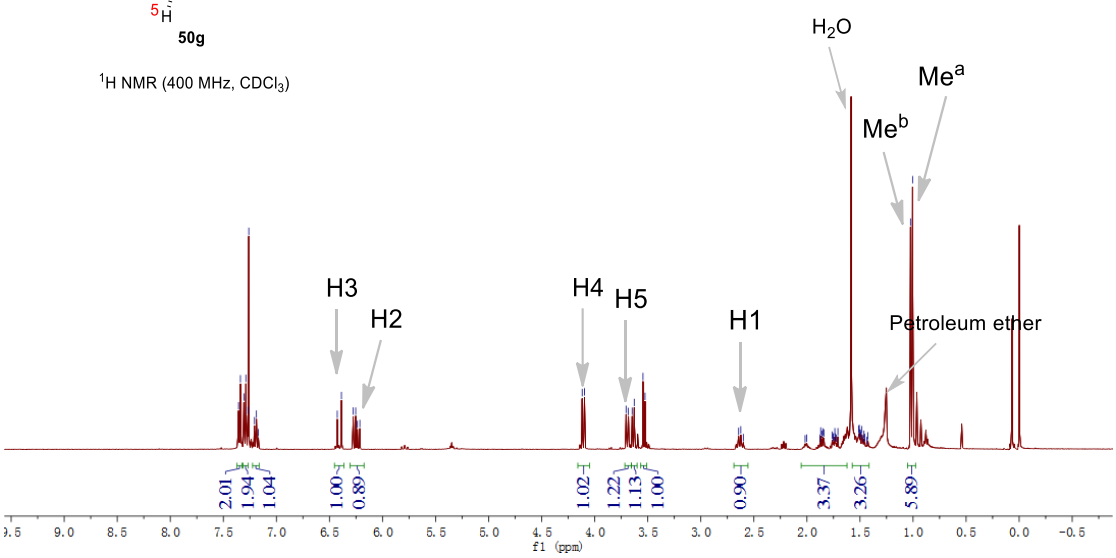


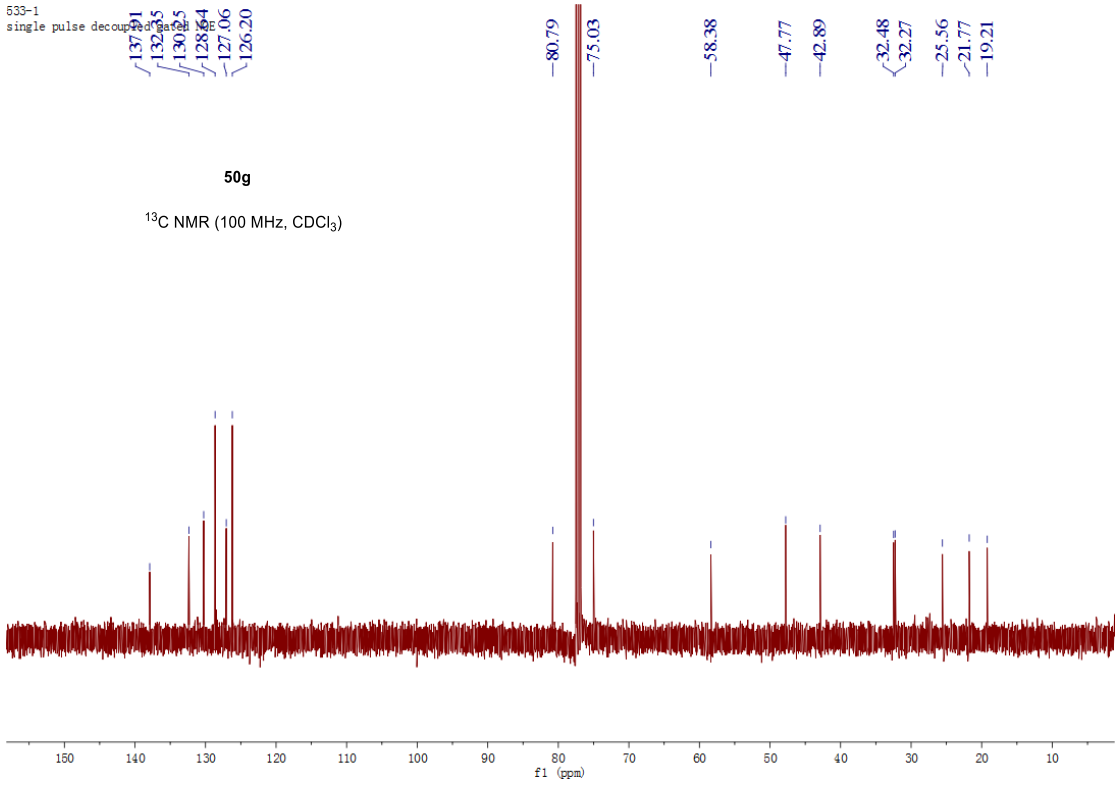
Similar to the case of **50e**, the relative stereochemistry for **50f** was assigned based on the characterisic correlations in the NOESY spectra. The cis geometry of H2 with respect to H1 was evidencded by the corrleations of H2-H1, H4-H1, and H4-H2. The trans geometry of H2 with respect to H3 was manifested by Me(a)-H2, Me(b)-H3, Me(b)-H5. The trans geometry of H3 with respect to H1 is supported by no correlation between H1 and H3, and no correlation between H5 and H1, and H5 and H2.



50g

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

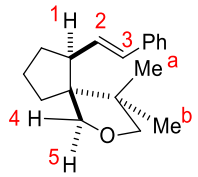




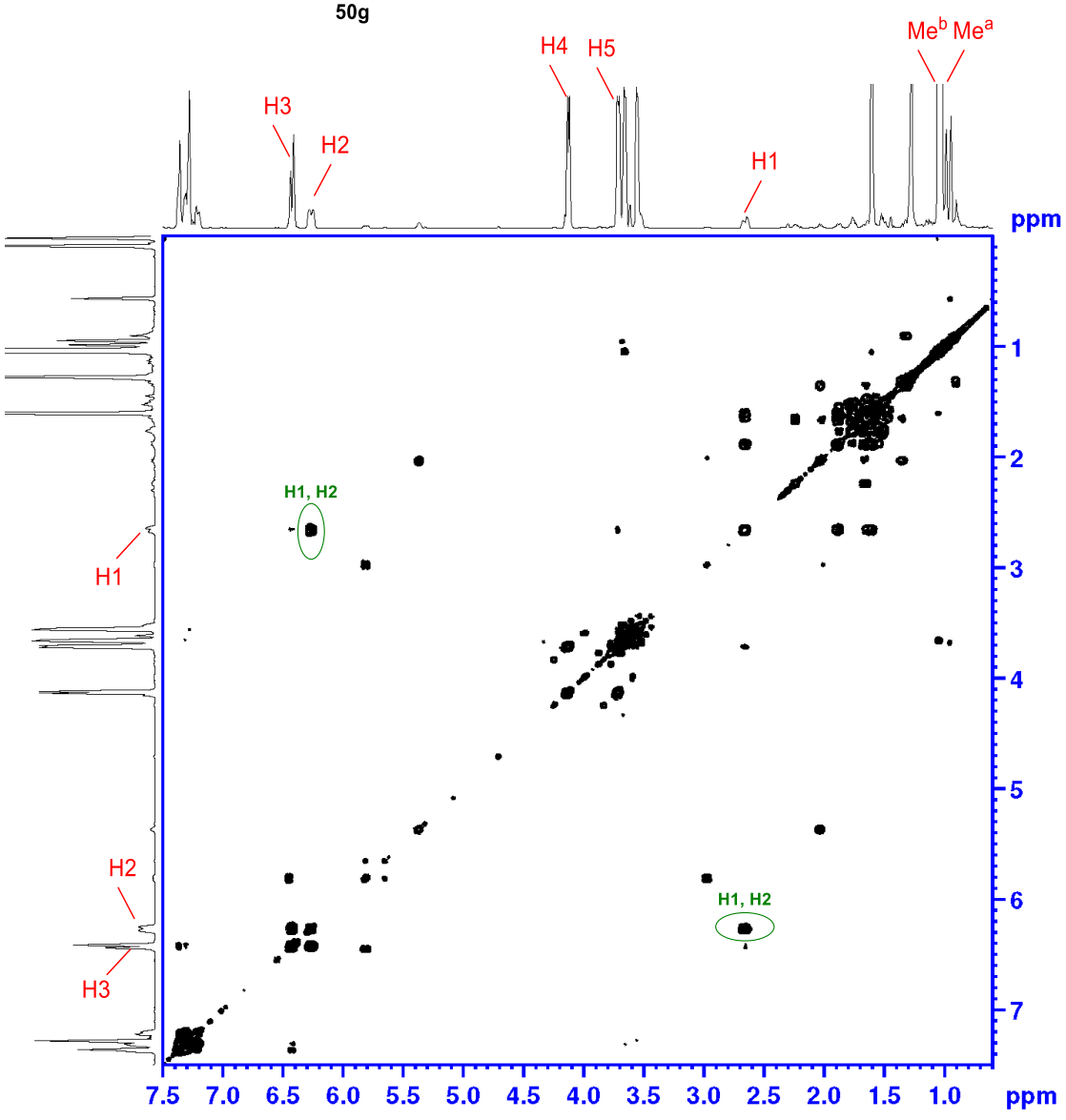
50g

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

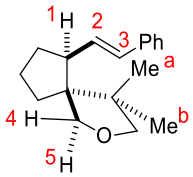
^{1}H-^{1}H COSY of **50g**:



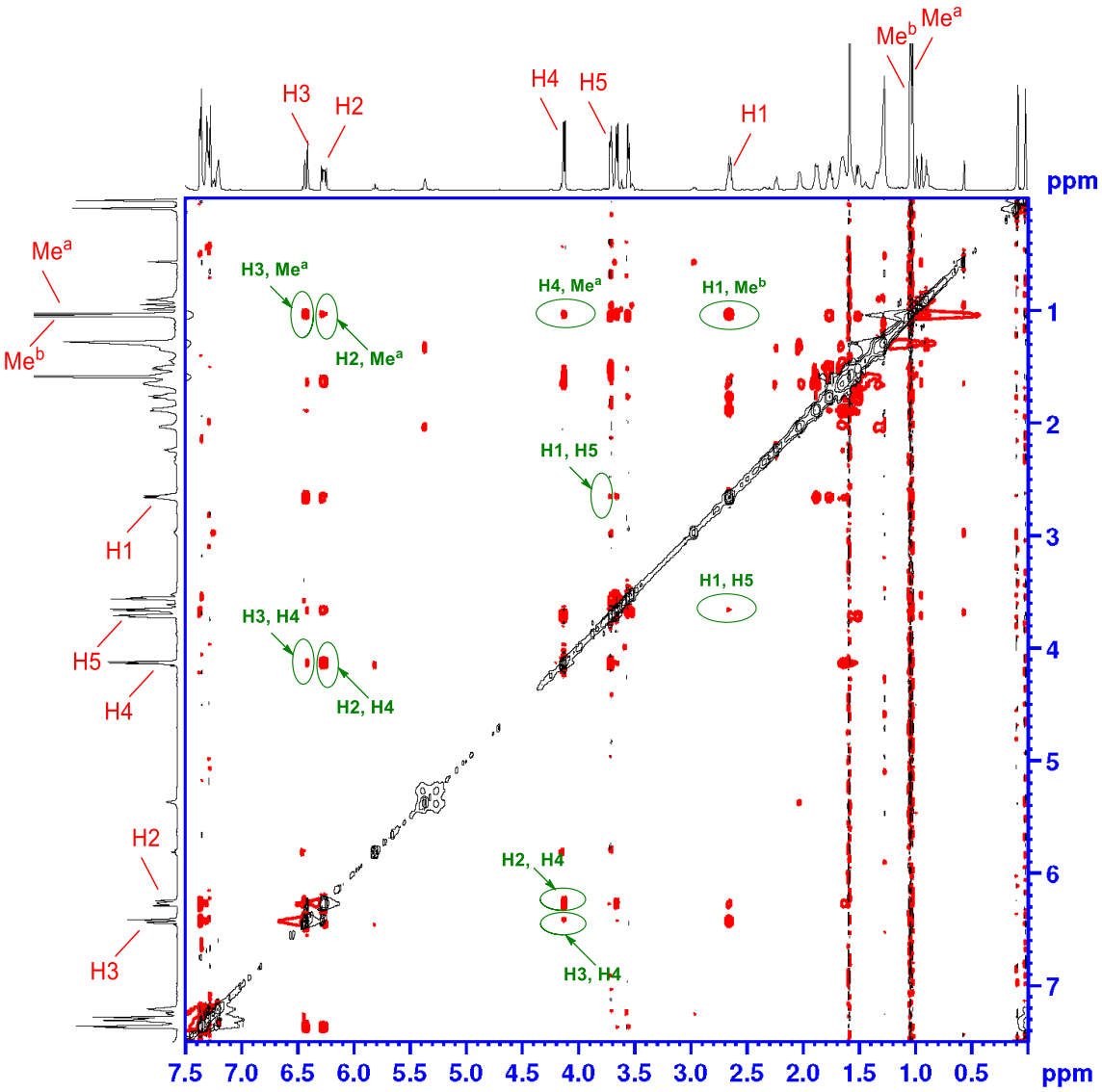
50g



2D NOESY of **50g**:



50g



The relative stereochemistry was determined based on the following correlations found in the NOESY spectra: no correlation was found between H1 and H4 suggesting that H1 is away from H4; the correlations of H2-H4 and H3-H4, Me(a)-H2, Me(a)-H3 and Me(a)-H4; the correlations of H1-H5 and H1-Me(b).

III. References

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