Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

Visible-Light-Mediated Alkylation of 4-alkyl-1,4-dihydropyridines with Alkenyl Sulfone

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Supporting Information

1. General Information

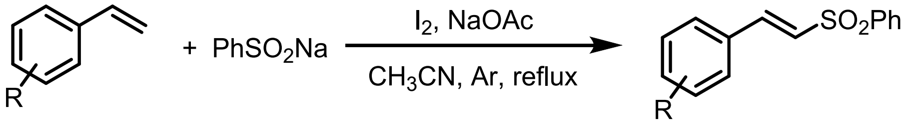
Reagents were purchased from commercial sources and were used as received. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. HRMS were made by means of ESI/EI-FTMS. The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh). 450 nm LED (26 W) purchased from JIADENG (LS) was used for light irradiation. A fan attached to the apparatus was used to maintain the reaction temperature at room temperature, the internal temperature is 30 ℃. When heating is needed for reaction, we use heating mantle as heat source.

Figure S1 Photograph of the Photocatalytic reactor used for reactions conducted under 450 nm LED irradiation.

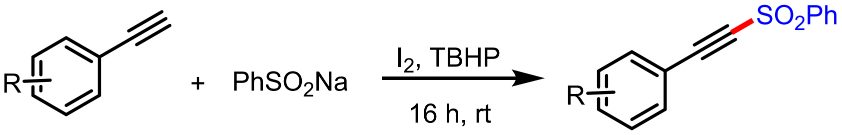
2. Preparation of photocatalyst

The photocatalyst Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ was synthesized according to literature report.[1] The spectral data of the photocatalyst is consistent with the literature data.[1] The other photocatalysts [Ir(dtbbpy)(ppy)$_2$][PF$_6$], fac-Ir(ppy)$_3$, [Ru(bpy)$_3$](PF$_6$)$_2$, [Ru(bpy)$_3$]6H$_2$O, Eosin-Y, Fluorescein, Mes-Acr are commercially available.

3. Preparation of alkenyl sulfones, alkynyl Sulfone.

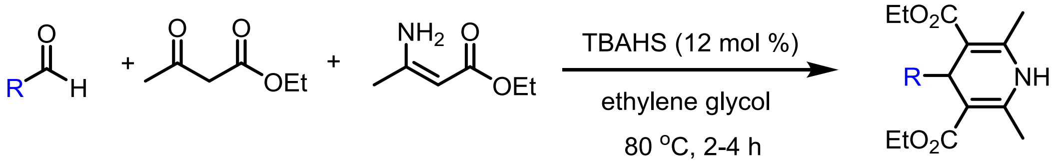


Alkenyl sulfones were synthesized according to literature report,[2] To a suspension of benzenesulfinic acid sodium salt (2.46 g, 15.0 mmol, 3.00 equiv.) and NaOAc (0.62 g, 7.5 mmol, 1.50 equiv.) in MeCN (20 mL) was added olefin (5.0 mmol, 1.00 equiv.) followed by iodine (1.9 g, 7.5 mmol, 1.50 equiv.). The mixture was heated to reflux for 1 h before being allowed to cool and the excess iodine quenched with 10% aq. sodium thiosulfate. Sat. aq. NaHCO$_3$ was added and the product extracted into DCM (3 x 20 mL). The combined organic phases were washed with H$_2$O (20 mL), brine (20 mL), dried (MgSO$_4$), filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography. The spectral data is consistent with the literature data.[2]



Alkenyl sulfones were synthesized according to literature report,[2] To a suspension of benzenesulfinic acid sodium salt (1.64 g, 10.0 mmol, 2.00 equiv.) in THF (25 mL) was added Alkynes (5.0 mmol, 1.00 equiv.) followed by iodine (0.2 g, 2.5 mmol, 0.50 equiv.), TBHP (15 mmol, 3 equiv). The mixture was stirred for 16 h at room temperature before the excess iodine quenched with 10% aq. sodium thiosulfate. Sat. aq. NaHCO$_3$ was added and the product extracted into DCM (3 x 20 mL). The combined organic phases were washed with H$_2$O (20 mL), brine (20 mL), dried (MgSO$_4$), filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography. The spectral data is consistent with the literature data.[2]

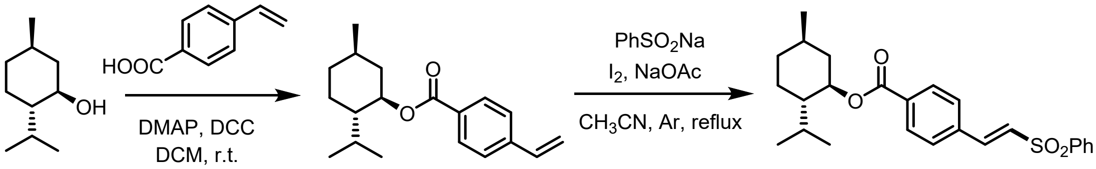
4. Preparation of 4-alkyl-1,4-dihydropyridines.



TBAHS = tetrabutylammonium

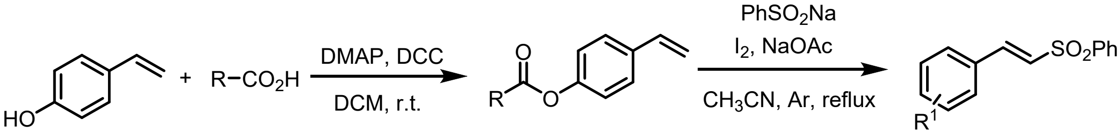
4-alkyl-1,4-dihydropyridines were synthesized according to literature report.[3] The spectral data is consistent with the literature data.

5. Preparation of 34a – 36a.



35a

35a was synthesized according to literature report,[2] 4-vinylbenzoic acid (20 mmol, 2.96 g) and alcohol (1 mmol, 1 equiv) and dry CH_2Cl_2 (250 mL) were added sequentially to a dry round-bottom flask at room temperature. The reaction was cooled to 0 °C and a catalytic amount of 4-Dimethylaminopyridine (DMAP, 0.08 mmol, 9.8 mg) and Dicyclohexylcarbodiimide (DCC, 40 mmol, 8.25 g) were added sequentially. The reaction was allowed to slowly warm to room temperature and further stirred for 8 hours. Upon completion, the solution was concentrated in vacuo and purified by column chromatography on silica to afford the desired product. Alkenyl sulfones were synthesized according to literature report.[2]

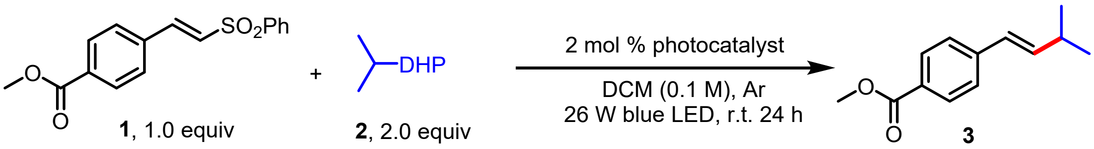


34a, 36a

34a and **36a** were synthesized according to literature report,[2] 4-vinylphenol (20 mmol, 2.4 g) and acid (20 mmol, 1 equiv) and dry CH_2Cl_2 (250 mL) were added sequentially to a dry round-bottom flask at room temperature. The reaction was cooled to 0 °C and a catalytic amount of 4-Dimethylaminopyridine (DMAP, 0.08 mmol, 9.8 mg) and Dicyclohexylcarbodiimide (DCC, 40 mmol, 8.25 g) were added sequentially. The reaction was allowed to slowly warm to room temperature and further stirred for 8 hours. Upon completion, the solution was concentrated in vacuo and purified by column chromatography on silica to afford the desired product. Alkenyl sulfones were synthesized according to literature report.[2,]

6. Reaction optimization

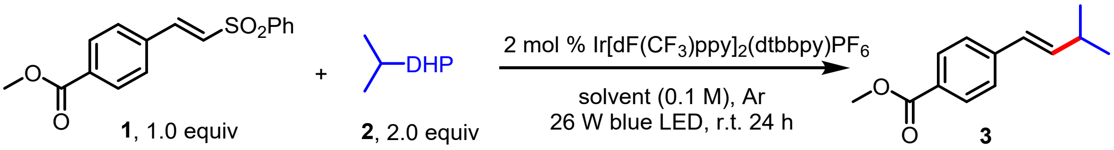
Table S1: Screening of different photocatalyst[a]



entry	photocatalyst	yield (%)[b]
1	Ir(dtbbpy)(ppy)$_2$PF$_6$	45
2	Ir(ppy)$_3$	<10
3	Ru(bpy)$_3$(PF$_6$)$_2$	trace
4	Ru(bpy)$_3$ 6H$_2$O	trace
5	Eosin-Y	trace
6	Fluorescein	NR
7	Mes-Acr-Ph$^+$	NR
8	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	60

[a]General conditions: **1** (0.2 mmol), **2** (0.4 mmol), photocatalyst (0.004 mmol) and solvent (2 mL) under Ar atmosphere. [b]Isolated yield. NR = no reaction.

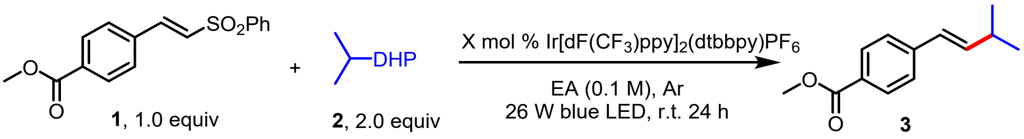
Table S2: Screening of different solvent[a]



entry	solvent	yield (%)[b]
1	DMF	38
2	DMSO	39
3	DMA	42
4	EA	85
5	acetone	32
6	MeOH	NR
7	EtOH	NR
8	DCE	47
9	MeCN	32
10	THF	27

[a]General conditions: **1** (0.2 mmol), **2** (0.4 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.004 mmol) and solvent (2 mL) under Ar atmosphere. [b]Isolated yield. NR = no reaction.

Table S3: Screening of the amount of photocatalyst[a]



entry	x mol % of photocatalyst	yield (%)[b]
1	0.5	75
4	1.0	84

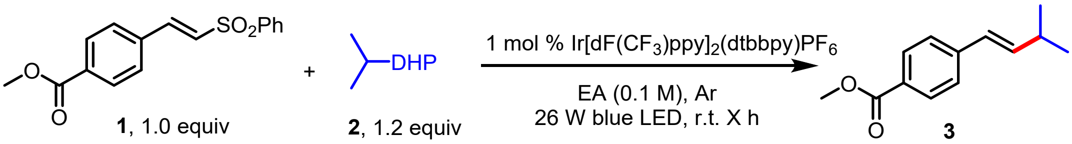
[a]General conditions: **1** (0.2 mmol), **2** (0.4 mmol) and solvent (2 mL) under Ar atmosphere. [b]Isolated yield.

Table S4: Screening of the amount of 2[a]

entry	x	yield (%)[b]
1	1.5	84
2	1.2	86

[a]General conditions: **1** (0.2 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.002 mmol) and solvent (2 mL) under Ar atmosphere. [b]Isolated yield.

Table S5: Screening of the time of reaction[a]



entry	x	yield (%)[b]
1	12	74
2	16	83

[a]General conditions: **1** (0.2 mmol), **2** (0.24 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.002 mmol) and solvent (2 mL) under Ar atmosphere. [b]Isolated yield.

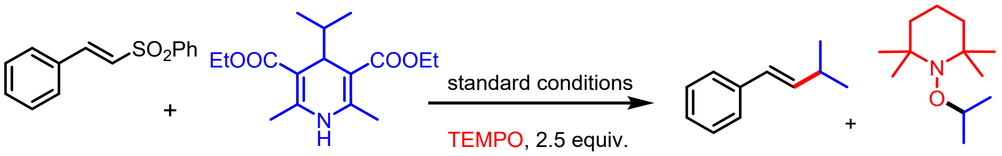
Table S6 Control experiments[a]

entry	control conditions	yield (%)[b]
1	air	60
2	w/o PC	NR
5	w/o light	NR

[a]General conditions: **1** (0.2 mmol), **2** (0.24 mmol), Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (0.002 mmol) and solvent (2 mL) under Ar atmosphere. [b]Isolated yield. NR = no reaction.

7. Investigation of the mechamism.

7.1 TEMPO was used as radical scavenger.



37, 1.0 equiv.

2, 1.2 equiv.

4, 0%

38, Detected by HRMS
$[M+H]^+$ Calc. 200.2009
Found: 200.2011

To a 10 mL glass vial was added Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2.24 mg, 0.004 mmol, 1 mol %), alkenyl sulfone (0.2 mmol, 1.0 equiv), **2** (0.24 mmol, 1.2 equiv), TEMPO (0.5 mmol, 2.5 equiv) and EA (2.0 mL). The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 26 W 450 nm LED (approximately 2 cm away from the light source) at room temperature for 16 hours. The reaction mixture was diluted with 10 mL of aqueous 1 M NaHCO$_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. that reaction was prevented and **38** was detected by HRMS

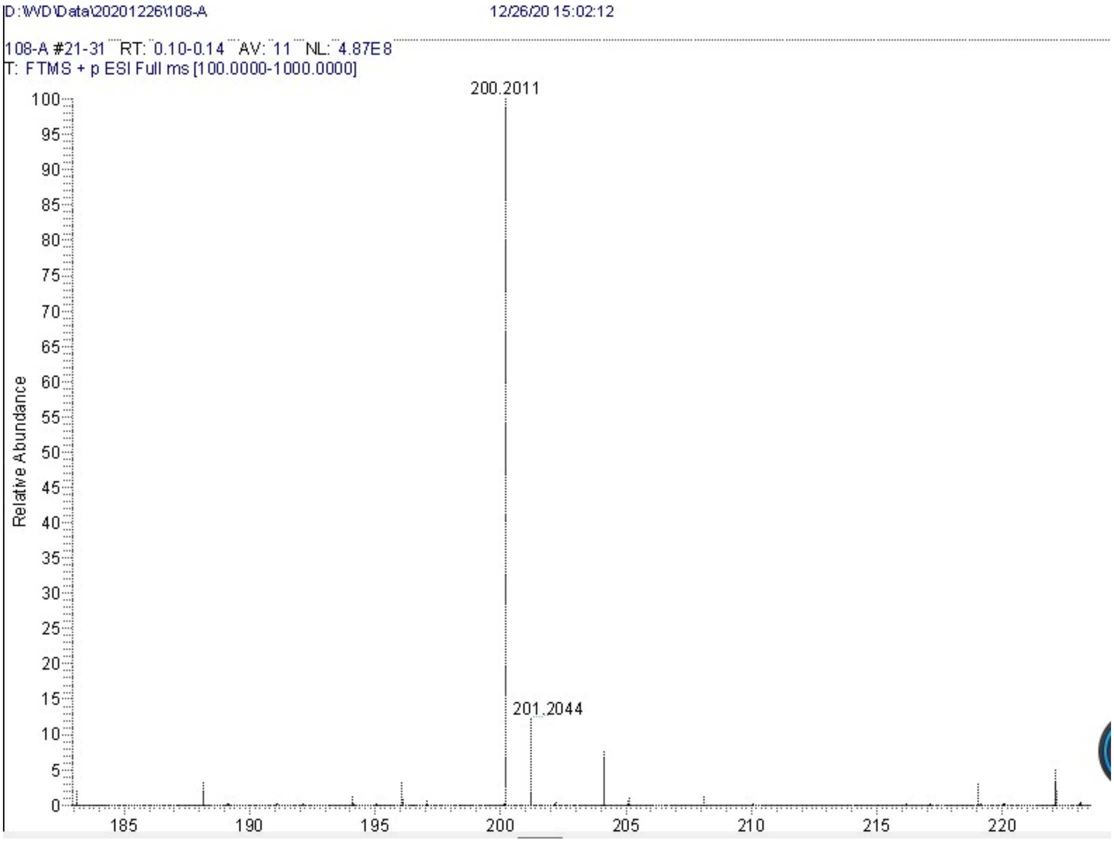
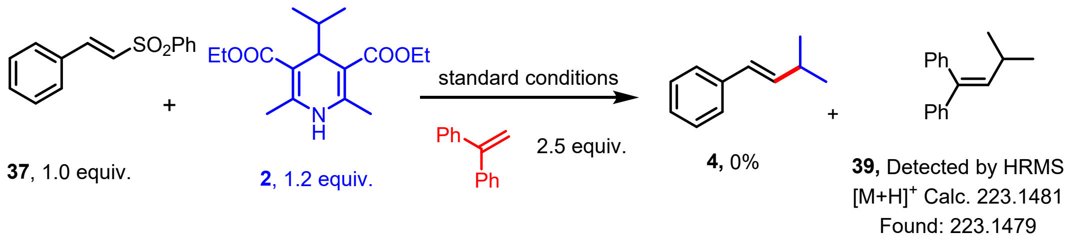


Figure S2 Species 38 was detected by HRMS

7.2 Ethene-1,1-diyldibenzene was used as radical scavenger.



To a 10 mL glass vial was added Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2.24 mg, 0.002 mmol, 1 mol %), alkenyl sulfone (0.2 mmol, 1.0 equiv), **2** (0.24 mmol, 1.2 equiv), ethene-1,1-diyldibenzene (0.5 mmol, 2.5 equiv.) and EA (2.0 mL). The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 26 W 450 nm LED (approximately 2 cm away from the light source) at room temperature for 16 hours. Yield were determined by ^{1}H NMR spectroscopy with dibromomethane as an internal standard. that reaction was prevented and **38** was detected by HRMS

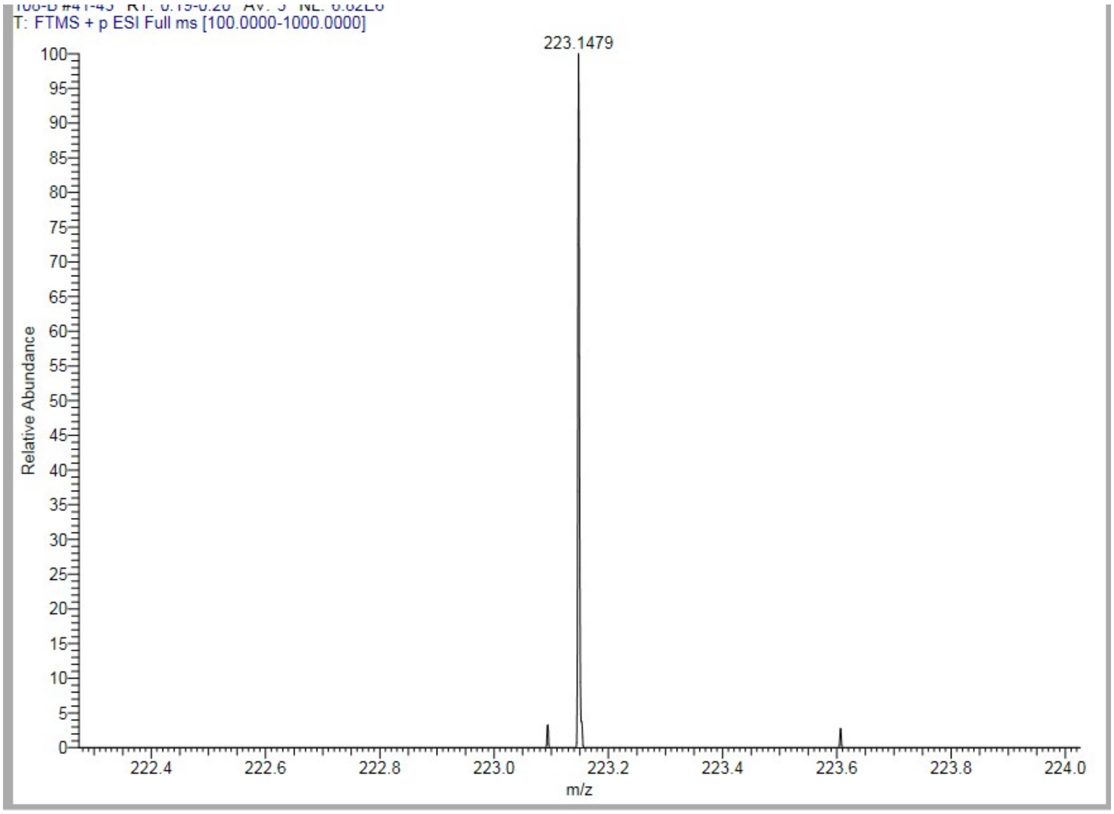
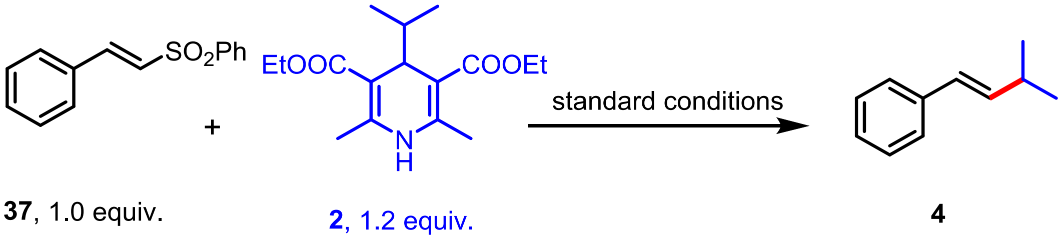


Figure S3 Species 39 was detected by HRMS

7.3 Light on/off experiments.



B) light/dark experiment

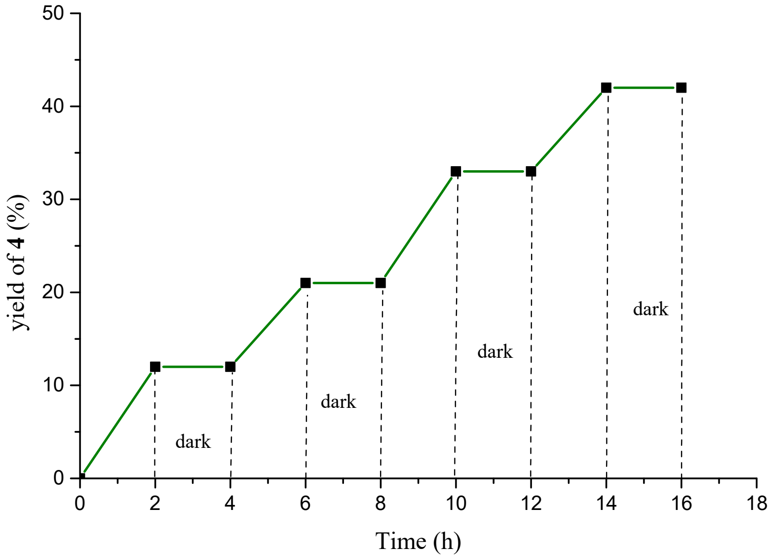
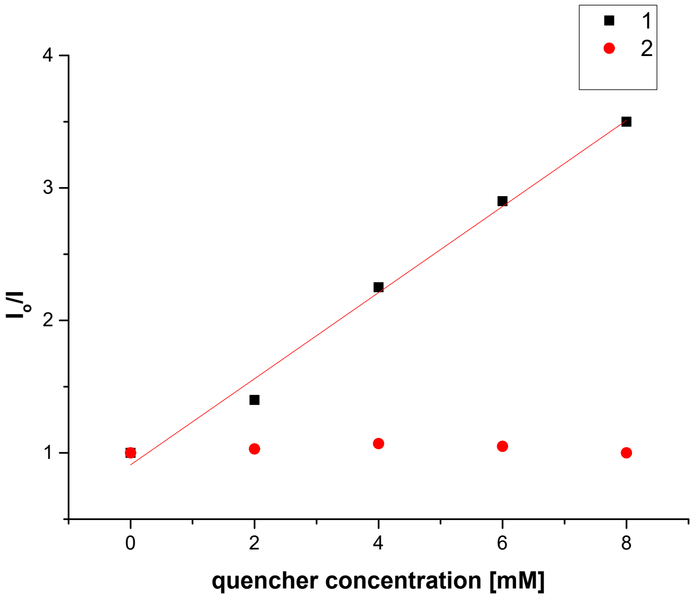


Figure S4 Light on-off experiments. Yields were determined by ^{1}H NMR spectroscopy with dibromomethane as an internal standard.

7.4 Emission Quenching Experiments (Stern–Volmer Studies)

Emission intensities were recorded using a CARY VARIAN luminescence spectrophotometer. All Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ solutions were excited at 380 nm and the emission intensity was collected at 470 nm. In a typical experiment, to a 3×10^{-6} M solution of Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ in EA was added the appropriate amount of a quencher in a screw-top quartz cuvette. After degassing the sample with a stream of argon for 10 minutes, the emission of the sample was collected.



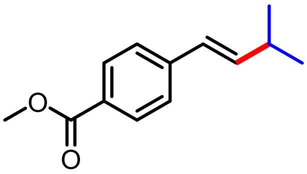
8. Experimental Procedures and Product Characterization

8.1 General Procedure.

To a 10 mL glass vial was added Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (2.24 mg, 0.002 mmol, 1 mol %), alkenyl sulfones (0.2 mmol, 1.0 equiv), 4-alkyl-DHPs (0.24 mmol, 1.2 equiv.) and EA (2.0 mL, 0.1 M). The reaction mixture was degassed by bubbling with Ar for 15 s with an outlet needle and the vial was sealed with PTFE cap. The mixture was then stirred rapidly and irradiated with a 26 W 450 nm LED (approximately 2 cm away from the light source) at room temperature for 16 hours. The reaction mixture was diluted with 10 mL of aqueous 1 M NaHCO$_3$ solution, and extracted with DCM (3 × 20 mL). The combined organic extracts were washed with brine (40 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

8.2. Product Characterization

methyl (E)-4-(3-methylbut-1-en-1-yl)benzoate (3).



E/Z = 2:3

According to the *general procedure*.

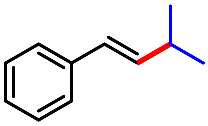
Yellow oil (33.8 mg, 83%).

R$_f$ 0.80 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.01 (dd, *J* = 12.7, 8.4 Hz, 2H), 7.38 (dd, *J* = 31.8, 8.0 Hz, 2H), 6.38 (dd, *J* = 24.2, 14.2 Hz, 1.40H), 5.60 (t, *J* = 11.0 Hz, 0.60H), 3.94 (d, *J* = 3.3 Hz, 3H), 2.97 – 2.83 (m, 0.56H), 2.53 (dt, *J* = 12.9, 6.5 Hz, 0.40H), 1.11 (dd, *J* = 20.6, 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 167.0, 142.6, 142.5, 142.4, 140.8, 129.8, 129.5, 128.5, 128.2, 128.0, 126.2, 125.8, 125.6, 52.0, 52.0, 31.6, 27.3, 23.0, 22.2.

HRMS (ESI) calcd for C$_{13}$H$_{17}$O$_2$ [M + H]$^+$ 205.1223, found 205.1222.

(E)-(3-methylbut-1-en-1-yl)benzene (4).



E/Z = 4:1

According to the *general procedure*.

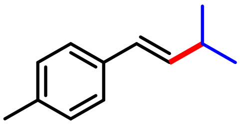
Yellow oil (22.5 mg, 77%).

R$_f$ 0.80 (Petroleum ether).

^{1}H NMR (400 MHz, CDCl$_3$) δ ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.44 – 7.18 (m, 5H), 6.34 (d, *J* = 16.1 Hz, 1H), 6.19 (dd, *J* = 15.9, 6.7 Hz, 0.80H), 5.53 – 5.34 (m, 0.20H), 3.01 – 2.82 (m, 0.20H), 2.53 – 2.39 (m, 0.82H), 1.08 (t, *J* = 9.5 Hz, 6H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 140.4, 138.0, 137.9, 128.6, 128.4, 128.1, 126.8, 126.7, 126.4, 125.9, 31.5, 27.1, 23.2, 22.4.

HRMS (EI) calcd for C$_{12}$H$_{14}$ [M$^+$] 146.1096, found 146.1089.

(E)-1-methyl-4-(3-methylbut-1-en-1-yl)benzene (5).



E/Z = 4:1

According to the *general procedure*.

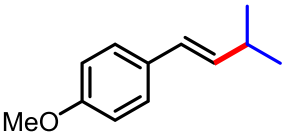
Colorless oil (20.8 mg, 64%).

*R*f 0.80 (Petroleum ether).

^{1}H NMR (400 MHz, CDCl$_3$) *δ* ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.24 (dd, *J* = 4.2, 3.6 Hz, 2H), 7.12 (dd, *J* = 22.1, 7.4 Hz, 2H), 6.28 (t, *J* = 15.1 Hz, 1H), 6.13 (dd, *J* = 15.9, 6.8 Hz, 0.8H), 5.42 (t, *J* = 10.9 Hz, 0.18H), 2.95 – 2.82 (m, 0.16H), 2.45 (dd, *J* = 13.4, 6.7 Hz, 0.81H), 2.33 (d, *J* = 8.7 Hz, 3H), 1.06 (dd, *J* = 16.8, 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, CDCl$_3$) *δ* 137.0, 136.4, 135.1, 129.1, 128.8, 128.5, 126.6, 125.8, 31.5, 23.2, 22.5, 21.1.

HRMS (EI) calcd for $C_{12}H_{16}$ [M]$^+$ 160.1252, found 160.1244.

(E)-1-methoxy-4-(3-methylbut-1-en-1-yl)benzene (6).



E/Z = 19:1

According to the *general procedure*.

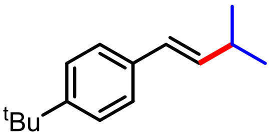
Yellow oil (15.1 mg, 43%).

*R*f 0.8 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, CDCl$_3$) *δ*7.28 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.28 (d, *J* = 15.9 Hz, 1H), 6.05 (dd, *J* = 15.9, 6.8 Hz, 0.94H), 5.42 – 5.34 (m, 0.05H), 3.79 (s, 3H), 2.44 (dq, *J* = 13.3, 6.6 Hz, 1H), 1.08 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (100 MHz, CDCl$_3$) *δ* 158.6, 135.9, 130.7, 127.0, 126.1, 113.9, 55.3, 31.5, 22.6.

HRMS (ESI) calcd for $C_{12}H_{17}O$ [M + H]$^+$ 177.1274, found 177.1273.

(E)-1-(tert-butyl)-4-(3-methylbut-1-en-1-yl)benzene (7).



E/Z = 9:1

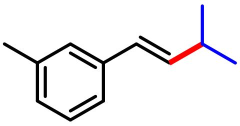
According to the *general procedure*.

Yellow oil (17.4 mg, 43%).

*R*f 0.80 (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 4H), 6.32 (d, J = 15.9 Hz, 1H), 6.15 (dd, J = 15.9, 6.8 Hz, 0.90H), 5.43 (t, J = 10.9 Hz, 0.09H), 2.92 (s, 0.08H), 2.45 (dq, J = 12.9, 6.5 Hz, 0.95H), 1.31 (d, J = 6.6 Hz, 9H), 1.08 (d, J = 6.7 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.7, 137.3, 135.2, 126.5, 125.6, 125.4, 34.5, 31.5, 31.3, 22.5.
HRMS (EI) calcd for $C_{15}H_{22}$ $[M]^+$ 202.1722, found 202.1714.

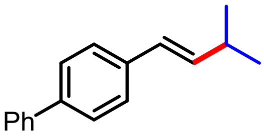
(E)-1-methyl-3-(3-methylbut-1-en-1-yl)benzene (8).



E/Z = 9:1

According to the *general procedure*.
Yellow oil (23.04 mg, 72%).
R_f 0.80 (Petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.00 (m, 4H), 6.36 (d, J = 16.0 Hz, 1H), 6.23 (dd, J = 15.9, 6.7 Hz, 0.90H), 5.50 (t, J = 11.0 Hz, 0.08H), 2.94 (s, 0.07H), 2.49 (dt, J = 13.3, 6.7 Hz, 0.96H), 2.39 (d, J = 6.7 Hz, 3H), 1.11 (dd, J = 17.3, 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.9, 137.8, 128.4, 127.5, 126.8, 126.6, 123.1, 31.5, 22.5, 21.4.
HRMS (EI) calcd for $C_{12}H_{16}$ $[M]^+$ 160.1252, found 160.1245.

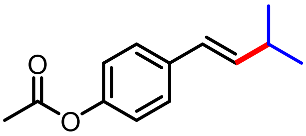
(E)-4-(3-methylbut-1-en-1-yl)-1,1'-biphenyl (9).



E/Z = 3:1

According to the *general procedure*.
White solid (21.7 mg, 49%). Mp: 37 - 39 °C.
R_f 0.80 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 13.3, 8.2 Hz, 5H), 7.42 (s, 2H), 7.36 – 7.28 (m, 2H), 6.35 (t, J = 16.8 Hz, 1H), 6.28 – 6.18 (m, 0.75H), 5.50 (t, J = 11.0 Hz, 0.24H), 2.96 (dd, J = 6.5, 3.3 Hz, 0.24H), 2.48 (dd, J = 13.3, 6.7 Hz, 0.26H), 1.08 (ddd, J = 12.4, 6.6, 2.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.9, 140.7, 139.5, 138.2, 137.0, 130.3, 129.1, 128.7, 127.7, 127.2, 127.1, 127.0, 126.9, 126.4, 126.0, 31.6, 27.3, 23.2, 22.5.
HRMS (EI) calcd for $C_{17}H_{18}$ $[M]^+$ 222.1409, found 222.1400.

(E)-4-(3-methylbut-1-en-1-yl)phenyl acetate (10).



E/Z = 93:7

According to the *general procedure*.

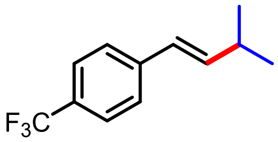
Yellow oil (22.0 mg, 54%).

R$_f$ 0.60 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.02 (t, *J* = 9.6 Hz, 2H), 6.29 (t, *J* = 17.3 Hz, 1H), 6.14 (dd, *J* = 15.9, 6.7 Hz, 0.93H), 5.47 (t, *J* = 10.8 Hz, 0.07H), 2.87 (s, 0.07H), 2.45 (td, *J* = 13.2, 6.5 Hz, 0.94H), 2.29 (s, 3H), 1.06 (dd, *J* = 17.8, 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.5, 149.4, 138.3, 135.8, 126.8, 125.9, 121.5, 31.5, 23.1, 22.4, 21.1.

HRMS (ESI) calcd for $C_{13}H_{16}O_2Na$ $[M + Na]^+$ 227.1043, found 227. 1039.

(E)-1-(3-methylbut-1-en-1-yl)-4-(trifluoromethyl)benzene (11).



E/Z = 7:3

According to the *general procedure*.

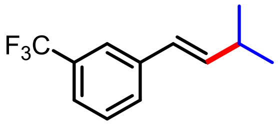
Yellow oil (23.1 mg, 54%).

R$_f$ 0.80 (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 15.9, 8.2 Hz, 2H), 7.38 (dd, *J* = 31.3, 8.1 Hz, 2H), 6.40 – 6.22 (m, 1.71H), 5.63 – 5.49 (m, 0.30H), 2.84 (qd, *J* = 13.0, 6.5 Hz, 0.30H), 2.49 (dq, *J* = 13.3, 6.6 Hz, 0.69H), 1.07 (dd, *J* = 22.6, 6.7 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.4, 141.4, 140.7, 128.8 (q, J_{CF} = 29.7 Hz), 126.0, 125.7, 125.4, 125.2 (q, J_{CF} = 3.5 Hz), 125.1 (q, *J* = 3.7 Hz), 31.6, 27.2, 23.0, 22.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.33 – -62.43 (m, 3F).

HRMS (EI) calcd for $C_{12}H_{13}F_3$ $[M]^+$ 214.0969, found 214.0962.

(E)-1-(3-methylbut-1-en-1-yl)-3-(trifluoromethyl)benzene (12).



E/Z = 9:1

According to the *general procedure*.

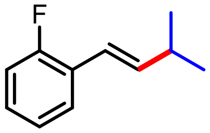
Colorless oil (25.6 mg, 60%).

R$_f$ 0.80 (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (ddd, *J* = 26.9, 21.3, 19.4 Hz, 4H), 6.51 – 6.16 (m, 1.90H), 5.60 (t, *J* = 11.0 Hz, 0.09H), 2.85 (d, *J* = 4.1 Hz, 0.09H), 2.53 (dq, *J* = 13.4, 6.7 Hz, 0.91H), 1.12 (dd, *J* = 20.4, 6.7 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$ δ 139.9, 138.7, 129.1, 128.8, 125.6, 123.3(q, J_{CF} = 2.9 Hz), 122.5(q, *J* = 3.5 Hz), 31.5, 23.0, 22.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.69 – -62.79 (m, 3F).

HRMS (EI) calcd for $C_{12}H_{13}F_3$ $[M]^+$ 214.0969, found 214.0961.

(E)-1-fluoro-2-(3-methylbut-1-en-1-yl)benzene (13).



E/Z > 20:1

According to the *general procedure*.

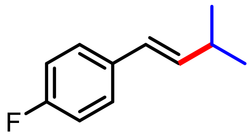
Colorless oil (22.0 mg, 67%).

R_f 0.80 (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (td, *J* = 7.7, 1.7 Hz, 1H), 7.22 – 7.14 (m, 1H), 7.14 – 7.00 (m, 2H), 6.54 (d, *J* = 16.1 Hz, 1H), 6.35 – 6.25 (m, 1H), 2.61 – 2.43 (m, 1H), 1.13 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.0 (d, *J* = 248.0 Hz), 140.5 (d, *J* = 4.1 Hz), 127.9, 126.9 (d, *J* = 4.0 Hz), 125.5 (d, *J* = 12.3 Hz), 123.9 (d, *J* = 3.6 Hz), 119.2 (d, *J* = 3.8 Hz), 115.5 (d, *J* = 22.3 Hz), 31.9, 22.9, 22.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.67 – -119.34 (m, 1F).

HRMS (EI) calcd for $C_{11}H_{13}F$ $[M]^+$ 164.1001, found 164.0995.

(E)-1-fluoro-4-(3-methylbut-1-en-1-yl)benzene (14).



E/Z = 93:7

According to the *general procedure*.

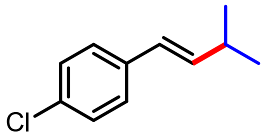
Colorless oil (21.5 mg, 65%).

R_f 0.80 (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.31 (t, *J* = 16.9 Hz, 1H), 6.14 (dd, *J* = 15.9, 6.8 Hz, 0.93H), 5.49 (t, *J* = 11.1 Hz, 0.07H), 2.87 (s, 0.07H), 2.48 (dt, *J* = 13.3, 6.7 Hz, 0.93H), 1.09 (dd, *J* = 18.7, 6.7 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.0, 137.7 (d, *J* = 1.9 Hz), 134.0 (q, *J* = 5.6 Hz), 127.3 (d, *J* = 7.7 Hz), 125.6, 115.3 (d, *J* = 21.3 Hz), 31.5, 22.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.91 – -116.08 (m, 1F).

HRMS (EI) calcd for $C_{11}H_{13}F$ $[M]^+$ 164.1001, found 164.0995.

(E)-1-chloro-4-(3-methylbut-1-en-1-yl)benzene (15).



E/Z = 4:6

According to the *general procedure*.

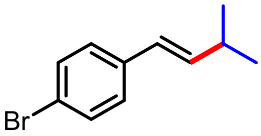
Yellow oil (21.0 mg, 59%).

R_f 0.90 (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 42.3, 8.2 Hz, 4H), 6.26 (dd, *J* = 19.8, 13.9 Hz, 1H), 6.17 (dd, *J* = 15.9, 6.6 Hz, 0.39H), 5.49 (t, *J* = 10.9 Hz, 0.58H), 2.83 (tt, *J* = 13.3, 6.6 Hz, 0.60H), 2.45 (dt, J = 13.1, 6.5 Hz, 0.40H), 1.06 (dd, J = 19.7, 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.1, 138.7, 136.3, 132.1, 129.9, 128.5, 128.3, 127.1, 125.7, 125.2, 31.5, 27.1, 23.1, 22.3.

HRMS (EI) calcd for $C_{11}H_{13}Cl$ $[M]^+$ 180.0706, found 180.0697.

(E)-1-bromo-4-(3-methylbut-1-en-1-yl)benzene (16).



E/Z = 9:1

According to the *general procedure*.

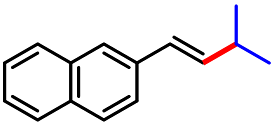
Yellow oil (29.9 mg, 67%).

R_f 0.90 (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 12.1, 5.3 Hz, 2H), 7.23 – 7.13 (m, 2H), 6.27 (d, J = 16.0 Hz, 1H), 6.18 (dd, J = 15.9, 6.4 Hz, 0.93H), 5.53 – 5.46 (m, 0.10H), 2.84 – 2.77 (m, 0.11H), 2.45 (dq, J = 13.2, 6.7 Hz, 0.90H), 1.08 (d, J = 6.7 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.8, 136.9, 132.4, 131.5, 131.5, 131.2, 127.5, 127.1, 125.7, 120.3, 31.5, 22.3.

HRMS (EI) calcd for $C_{11}H_{13}Br$ $[M]^+$ 224.0201, found 224.0195.

(E)-2-(3-methylbut-1-en-1-yl)naphthalene (17).



E/Z = 93:7

According to the *general procedure*.

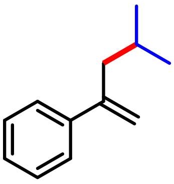
Yellow solid (29.4 mg, 75%). Mp: 40 - 43 °C.

R_f 0.80 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 24.8, 16.6 Hz, 4H), 7.57 (d, J = 8.2 Hz, 1H), 7.40 (dd, J = 9.4, 5.4 Hz, 2H), 6.47 (t, J = 16.9 Hz, 1H), 6.31 (ddd, J = 15.8, 6.6, 3.8 Hz, 1H), 5.55 (t, J = 10.9 Hz, 1H), 3.00 (s, 1H), 2.60 – 2.31 (m, 1H), 1.18 – 1.03 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.5, 135.4, 133.7, 132.7, 128.0, 127.8, 127.6, 127.0, 126.1, 125.4, 123.6, 31.7, 22.5.

HRMS (ESI) calcd for $C_{15}H_{17}$ $[M + H]^+$ 197.1325, found 197.1324.

(4-methylpent-1-en-2-yl)benzene (18).



According to the *general procedure*.

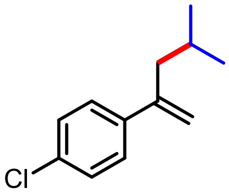
Yellow oil (21.2 mg, 66%).

R_f 0.80 (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 5H), 5.26 (d, J = 1.5 Hz, 1H), 5.02 (s, 1H), 2.38 (d, J = 7.2 Hz, 2H), 1.65 (td, J = 13.5, 6.8 Hz, 1H), 0.87 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.8, 141.4, 128.2, 127.2, 126.3, 113.4, 45.1, 26.3, 22.4.

HRMS (EI) calcd for $C_{12}H_{16}$ $[M]^+$ 160.1252, found 160.1245.

1-chloro-4-(4-methylpent-1-en-2-yl)benzene (19).



According to the *general procedure*.

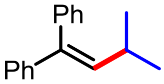
Yellow oil (25.2 mg, 65%).

R_f 0.80 (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (q, J = 8.6 Hz, 4H), 5.24 (s, 1H), 5.03 (s, 1H), 2.35 (d, J = 7.1 Hz, 2H), 1.63 (dt, J = 13.4, 6.7 Hz, 1H), 0.86 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.7, 139.8, 132.9, 128.3, 127.6, 114.0, 45.0, 26.3, 22.3.

HRMS (EI) calcd for $C_{12}H_{15}Cl$ $[M]^+$ 194.0862, found 194.0855.

(3-methylbut-1-ene-1,1-diyl)dibenzene (20).



According to the *general procedure*.

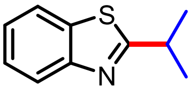
Yellow oil (37.5 mg, 84%).

R_f 0.80 (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.24 (m, 10H), 5.98 (d, J = 10.1 Hz, 1H), 2.53 (qd, J = 13.1, 6.5 Hz, 1H), 1.10 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.7, 140.5, 139.1, 137.3, 129.8, 128.2, 128.1, 127.2, 126.8, 126.8, 28.8, 23.3.

HRMS (ESI) calcd for $C_{17}H_{19}$ $[M + H]^+$ 223.1481, found 223.1481.

2-isopropylbenzo[*d*]thiazole (21).



According to the *general procedure*.

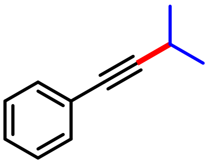
Yellow oil (21.2 mg, 60%).

R_f 0.80 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 8.4, 1.2 Hz, 2H), 7.97 (d, J = 8.2 Hz, 1H), 7.83 (d, J = 7.9 Hz, 1H), 7.48 – 7.39 (m, 1H), 7.36 – 7.28 (m, 1H), 3.48 – 3.36 (m, 1H), 1.46 (d, J = 6.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.8, 152.9, 134.6, 125.9, 124.6, 122.5, 121.5, 34.0, 22.9.

HRMS (ESI) calcd for $C_{10}H_{12}NS$ $[M + H]^+$ 178.0685, found 178.0686.

(3-methylbut-1-yn-1-yl)benzene (22).



According to the *general procedure*.

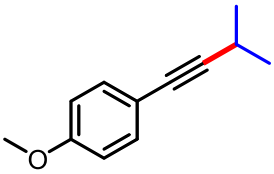
Yellow oil (19.5 mg, 68%).

R_f 0.80 (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 5H), 2.77 (dt, J = 13.7, 6.9 Hz, 1H), 1.26 (d, J = 6.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 131.5, 129.8, 128.1, 128.0, 127.4, 127.1, 126.8, 126.7, 95.7, 79.7, 23.0, 21.1.

HRMS (EI) calcd for $C_{11}H_{12}$ $[M]^+$ 144.0939, found 144.0932.

1-methoxy-4-(3-methylbut-1-yn-1-yl)benzene (23).



According to the *general procedure*.

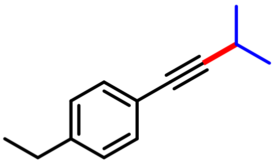
Yellow oil (18.4 mg, 53%).

R_f 0.80 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, J = 8.9 Hz, 2H), 6.83 (t, J = 7.1 Hz, 2H), 3.82 (s, 3H), 2.79 (dt, J = 13.7, 6.9 Hz, 1H), 1.29 (d, J = 6.9 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.9, 132.8, 116.1, 113.7, 113.5, 113.4, 94.1, 79.4, 55.2, 23.2, 23.1, 21.1.

HRMS (ESI) calcd for $C_{12}H_{15}O$ $[M + H]^+$ 175.1117, found 175.1119.

1-ethyl-4-(3-methylbut-1-yn-1-yl)benzene (24).



According to the *general procedure*.

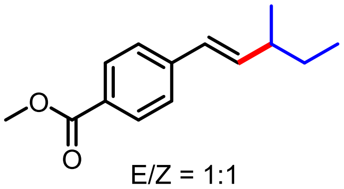
Yellow oil (18.3 mg, 55%).

R_f 0.80 (Petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.77 (m, 1H), 7.52 – 7.14 (m, 1H), 3.17 – 3.02 (m, 1H), 2.30 – 1.23 (m, 6H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.6, 153.1, 134.5, 125.8, 124.5, 122.5, 121.5, 43.4, 33.4, 26.0, 25.8.

HRMS (ESI) calcd for $C_{13}H_{17}$ $[M + H]^+$ 173.1325, found 173.1326.

methyl (E)-4-(but-1-en-1-yl)benzoate (27).



E/Z = 1:1

According to the *general procedure*.

Yellow oil (32.7 mg, 75%).

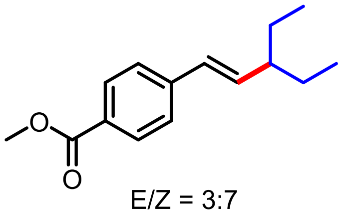
R_f 0.70 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 11.3, 8.4 Hz, 2H), 7.39 (dd, J = 32.7, 8.2 Hz, 2H), 6.42 (dd, J = 13.8, 9.2 Hz, 1H), 6.26 (dd, J = 15.9, 7.8 Hz, 0.51H), 5.55 (t, J = 11.1 Hz, 0.51H), 3.93 (d, J = 3.3 Hz, 3H), 2.66 (dt, J = 17.0, 6.7 Hz, 0.55H), 2.26 (dt, J = 13.7, 6.8 Hz, 0.51H), 1.42 (ddt, J = 14.7, 11.4, 7.3 Hz, 2H), 1.09 (dd, J = 17.6, 6.7 Hz, 3H), 0.91 (dt, J = 25.9, 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 142.7, 142.5, 141.3, 139.7, 129.8, 129.5, 128.5, 128.2, 128.0, 127.4, 126.8, 125.8, 52.0, 39.0, 34.0, 30.2, 29.6, 20.5, 20.0, 11.8.

HRMS (ESI) calcd for $C_{14}H_{19}O_2$ $[M + H]^+$ 219.1380, found 219.1379.

methyl (E)-4-(pent-1-en-1-yl)benzoate (28).



E/Z = 3:7

According to the *general procedure*.

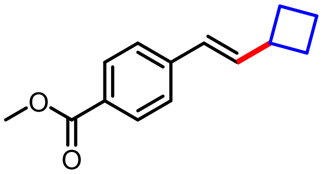
Yellow oil (32.4 mg, 70%).

R_f 0.60 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (t, J = 8.0 Hz, 2H), 7.39 (dd, J = 32.1, 8.2 Hz, 2H), 6.47 (dd, J = 55.2, 13.8 Hz, 1H), 6.13 (dd, J = 15.8, 9.0 Hz, 0.31H), 5.49 (t, J = 11.3 Hz, 0.68H), 3.94 (d, J = 2.1 Hz, 3H), 2.48 (qd, J = 13.3, 5.2 Hz, 0.72H), 2.05 – 1.97 (m, 0.31H), 1.57 – 1.29 (m, 4H), 0.90 (dt, J = 15.0, 7.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 143.0, 142.4, 139.9, 138.3, 129.8, 129.4, 129.1, 128.5, 128.4, 127.9, 125.8, 52.0, 46.9, 40.8, 28.0, 27.6, 11.8, 11.7.

HRMS (ESI) calcd for $C_{15}H_{21}O_2$ $[M + H]^+$ 233.1536, found 233.1536.

methyl (E)-4-(2-cyclobutylvinyl)benzoate (29).



E/Z = 1:1

According to the *general procedure*.

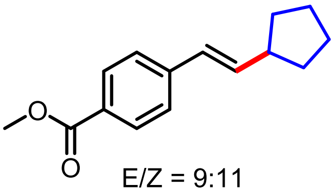
Colorless oil (17.1 mg, 40%).

R_f 0.60 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.90 (m, 2H), 7.48 – 7.28 (m, 2H), 6.49 (dd, J = 15.1, 6.1 Hz, 0.50H), 6.42 – 6.28 (m, 1H), 5.92 (t, J = 10.3 Hz, 0.51H), 3.96 (d, J = 20.4 Hz, 3H), 3.50 – 3.40 (m, 0.52H), 3.24 – 3.03 (m, 0.50H), 2.24 (dd, J = 5.5, 3.0 Hz, 2H), 2.02 – 1.84 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 142.3, 140.2, 138.1, 129.9, 129.4, 128.5, 126.9, 126.5, 125.8, 52.0, 52.0, 38.7, 34.6, 29.8, 28.6, 18.7, 18.6.

HRMS (ESI) calcd for $C_{14}H_{17}O_2$ $[M + H]^+$ 217.1223, found 217.1223.

methyl (E)-4-(2-cyclopentylvinyl)benzoate (30).



E/Z = 9:11

According to the *general procedure*.

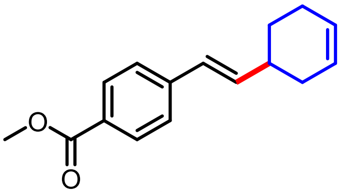
Colorless oil (28.5 mg, 62%).

R_f 0.60 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 15.2, 8.1 Hz, 2H), 7.36 (dd, J = 25.0, 8.0 Hz, 2H), 6.45 – 6.28 (m, 1.45H), 5.68 (t, J = 10.9 Hz, 0.55H), 3.91 (d, J = 4.3 Hz, 3H), 2.93 (dd, J = 17.1, 8.5 Hz, 0.48H), 2.63 (dp, J = 15.7, 7.9 Hz, 0.59H), 1.87 (d, J = 6.5 Hz, 2H), 1.72 – 1.57 (m, 4H), 1.47 – 1.30 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 142.6, 142.5, 140.4, 138.7, 129.8, 129.4, 128.5, 128.1, 127.1, 126.5, 125.7, 52.0, 52.0, 43.9, 38.9, 34.1, 33.1, 25.5, 25.2.

HRMS (ESI) calcd for $C_{15}H_{19}O_2$ $[M + H]^+$ 231.1380, found 231.1378.

methyl (S,E)-4-(2-(cyclohex-3-en-1-yl)vinyl)benzoate (31).



E/Z = 11:9

According to the *general procedure*.

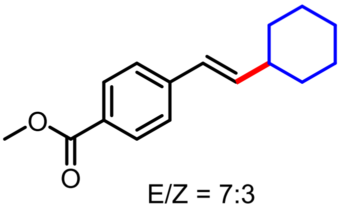
Yellow oil (31.0 mg, 64%).

R_f 0.60 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.91 (m, 2H), 7.34 (dd, J = 34.9, 8.3 Hz, 2H), 6.49 – 6.30 (m, 1.55H), 5.79 – 5.57 (m, 2.44H), 3.89 (d, J = 2.9 Hz, 3H), 2.89 – 2.74 (m, 0.45H), 2.52 – 2.37 (m, 0.56H), 2.24 – 1.77 (m, 5H), 1.55 – 1.39 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 142.4, 139.9, 138.6, 129.8, 129.5, 128.5, 128.3, 127.3, 127.0, 126.9, 126.9, 125.8, 125.8, 125.7, 52.0, 52.0, 37.2, 32.8, 31.5, 31.1, 28.8, 28.5, 24.7, 24.3.

HRMS (ESI) calcd for $C_{16}H_{19}O_2$ $[M + H]^+$ 243.1380, found 243.1379.

methyl (E)-4-(2-cyclohexylvinyl)benzoate (32).



E/Z = 7:3

According to the *general procedure*.

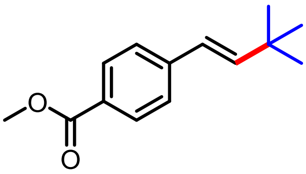
Yellow oil (38.5 mg, 79%).

R$_f$ 0.60 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 17.6, 8.1 Hz, 2H), 7.35 (dd, J = 31.6, 8.2 Hz, 2H), 6.41 – 6.24 (m, 1.70H), 5.60 (d, J = 11.1 Hz, 0.29H), 3.89 (s, 3H), 2.54 (d, J = 10.5 Hz, 0.31H), 2.14 (dd, J = 10.3, 7.0 Hz, 0.69H), 1.83 – 1.64 (m, 5H), 1.33 – 1.14 (m, 5H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 142.6, 141.0, 139.7, 129.8, 129.5, 128.5, 128.2, 126.5, 126.1, 125.8, 52.0, 51.9, 41.3, 37.1, 33.1, 32.7, 26.1, 25.9, 25.6.

HRMS (ESI) calcd for $C_{16}H_{21}O_2$ $[M + H]^+$ 245.1536, found 245.1537.

methyl (E)-4-(3,3-dimethylbut-1-en-1-yl)benzoate (33).



E/Z > 20:1

According to the *general procedure*.

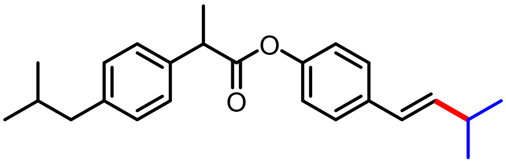
Yellow oil (18.7 mg, 43%).

R$_f$ 0.60 (Petroleum ether/EtOAc, 20/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.25 (d, J = 7.6 Hz, 2H), 6.43 – 6.33 (m, 1H), 5.66 (d, J = 12.8 Hz, 1H), 3.91 (s, 3H), 0.97 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.1, 144.6, 143.6, 129.8, 129.0, 128.9, 126.0, 52.0, 31.1, 29.4.

HRMS (ESI) calcd for $C_{14}H_{19}O_2$ $[M + H]^+$ 219.1380, found 219.1380.

(E)-4-(3-methylbut-1-en-1-yl)phenyl 2-(4-isobutylphenyl)propanoate (34).



E/Z = 7:3

According to the *general procedure*.

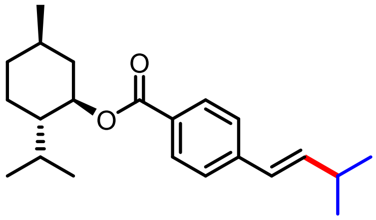
Yellow oil (46.5 mg, 63%).

R$_f$ 0.40 (Petroleum ether/EtOAc, 7/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (ddd, J = 17.7, 15.9, 5.1 Hz, 4H), 7.14 (d, J = 6.1 Hz, 2H), 6.98 – 6.88 (m, 2H), 6.33 – 6.20 (m, 1H), 6.12 (ddd, J = 15.9, 6.8, 2.6 Hz, 0.34H), 5.52 – 5.40 (m, 0.64H), 3.93 (dd, J = 9.4, 4.7 Hz, 1H), 2.92 – 2.76 (m, 0.65H), 2.50 – 2.42 (m, 2.36H), 1.94 – 1.79 (m, 1H), 1.62 – 1.57 (m, 3H), 1.04 (ddd, J = 22.9, 6.6, 2.7 Hz, 6H), 0.91 (dd, J = 6.6, 2.5 Hz, 6H).

^{13}C NMR (100 MHz, CDCl$_3$) δ 173.3, 149.6, 149.2, 140.8, 140.6, 138.1, 137.2, 135.6, 135.5, 129.5, 127.2, 126.7, 125.9, 125.5, 121.3, 121.0, 45.2, 45.0, 31.5, 30.2, 27.0, 23.1, 22.4, 18.6, 18.5..
HRMS (ESI) calcd for $C_{24}H_{31}O_2$ [M + H]$^+$ 351.2319, found 351.2319.

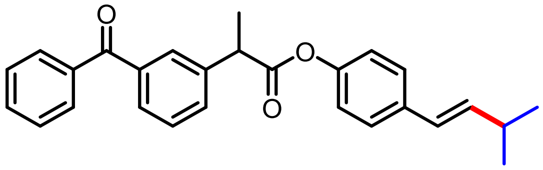
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-((E)-3-methylbut-1-en-1-yl)benzoate (35).



E/Z = 4:1

According to the *general procedure*.
Yellow oil (44.0 mg, 67%).
R_f 0.40 (Petroleum ether/EtOAc, 20/1).
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (dd, J = 16.1, 8.0 Hz, 2H), 7.35 (dd, J = 30.3, 8.2 Hz, 2H), 6.44 – 6.26 (m, 1.79H), 5.56 (t, J = 11.0 Hz, 0.21H), 4.92 (td, J = 10.8, 4.1 Hz, 1H), 2.93 – 2.81 (m, 0.20H), 2.49 (dq, J = 13.2, 6.6 Hz, 0.79H), 2.13 (d, J = 12.0 Hz, 1H), 2.02 – 1.88 (m, 1H), 1.72 (d, J = 11.4 Hz, 2H), 1.62 – 1.48 (m, 2H), 1.12 – 1.05 (m, 6H), 0.96 – 0.90 (m, 6H), 0.79 (d, J = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 166.0, 142.3, 142.2, 140.6, 129.8, 129.5, 128.9, 128.5, 126.2, 125.7, 125.7, 74.6, 47.2, 41.0, 34.3, 31.6, 31.4, 27.3, 26.3, 23.6, 23.6, 23.0, 22.2, 22.0, 20.7, 16.5, 16.5.
HRMS (ESI) calcd for $C_{22}H_{32}O_2Na$ [M + Na]$^+$ 351.2295, found 351.2293.

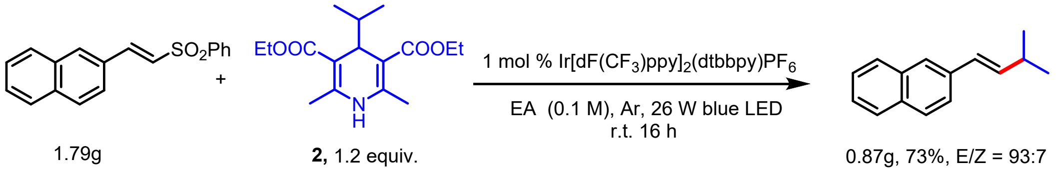
(E)-4-(3-methylbut-1-en-1-yl)phenyl 2-(3-benzoylphenyl)propanoate (36).



E/Z = 3:1

According to the *general procedure*.
Yellow oil (54.1 mg, 68%).
R_f 0.40 (Petroleum ether/EtOAc, 7/1).
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 – 7.77 (m, 3H), 7.73 (d, J = 7.6 Hz, 1H), 7.60 (dt, J = 25.2, 9.0 Hz, 2H), 7.49 (q, J = 7.6 Hz, 3H), 7.31 (dd, J = 22.3, 13.8 Hz, 2H), 6.95 (dd, J = 12.1, 8.6 Hz, 2H), 6.35 – 6.21 (m, 1H), 6.13 (dd, J = 15.9, 6.8 Hz, 0.76H), 5.46 (t, J = 10.9 Hz, 0.24H), 4.09 – 3.99 (m, 1H), 2.84 (qd, J = 13.1, 6.6 Hz, 0.21H), 2.45 (dq, J = 13.4, 6.7 Hz, 0.74H), 1.65 (dd, J = 7.1, 3.2 Hz, 3H), 1.05 (dd, J = 22.0, 6.7 Hz, 6H). **^{13}C NMR** (100 MHz, CDCl$_3$) δ 196.5, 172.6, 149.4, 140.7, 140.3, 138.3, 138.1, 137.4, 135.8, 132.6, 131.5, 130.1, 129.6, 129.3, 129.2, 128.8, 128.3, 126.8, 125.8, 125.4, 121.3, 120.9, 45.5, 31.5, 27.0, 23.1, 22.4, 18.5.
HRMS (ESI) calcd for $C_{27}H_{27}O_3$ [M + H]$^+$ 399.1955, found 399.1954.

9. Gram-scale Reaction



To an oven dried Schlenk tube was added was added Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ (68 mg, 0.06 mmol, 1 mol %), alkenyl sulfones (6 mmol, 1.0 equiv), **2** (2.15 g, 7.2 mmol, 1.2 equiv), and EA (60 mL). The tube was evacuated and backfilled with Ar (this process was repeated three times). The mixture was then stirred rapidly and irradiated with a 26 W 450 nm LED (approximately 2 cm away from the light source) at room temperature for 36 hours. The reaction mixture was diluted with 30 mL of aqueous 1 M NaHCO$_3$ solution, and extracted with DCM (3 × 25 mL). The combined organic extracts were washed with brine (75 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product **17** in 73% yield

References

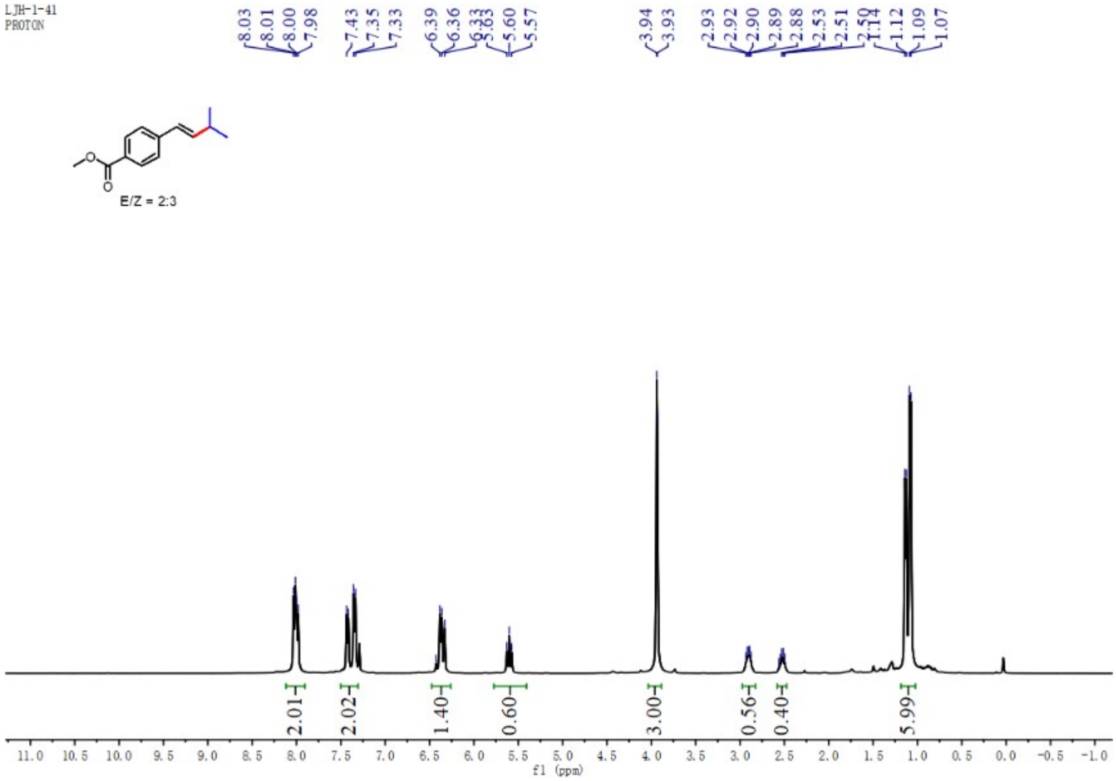
(1) M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, G. G. Malliaras, S. Bernhard, *Chem. Mater.*2005, **17**, 5712.

(2) F. Yue J., Dong, H. Song, Y. Liu and Q. Wang, V *Org. Lett.*, 2021, **23**, 2477.

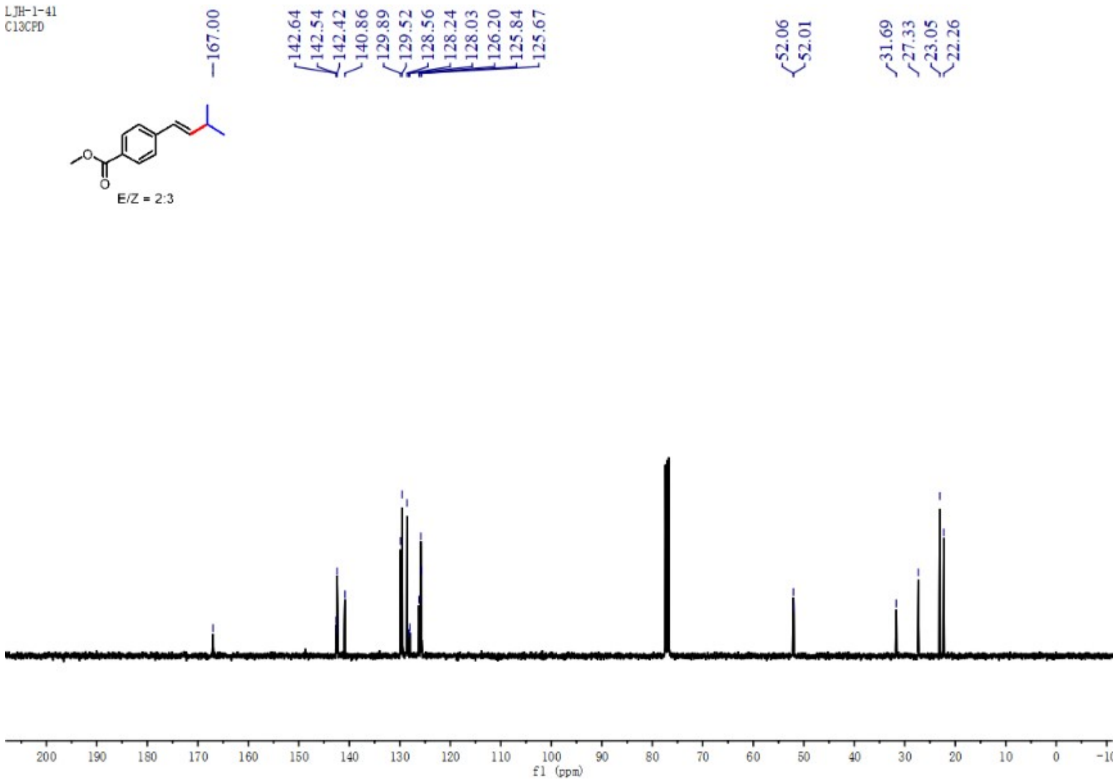
(3) J. Dong, F. Yue, W. Xu, H. Song, Y. Liu and Q. Wang, *Green Chem.*, 2020, **22**, 5599.

NMR Spectra and IR Spectra

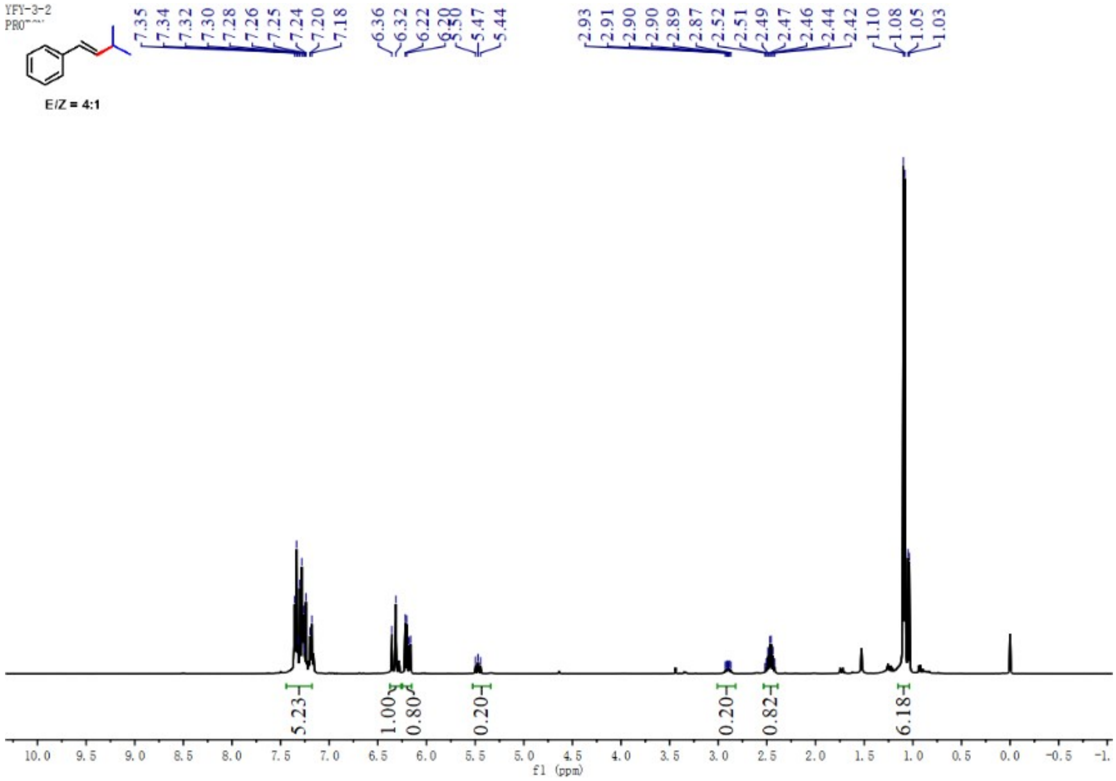
^{1}H NMR spectrum of compound **3**



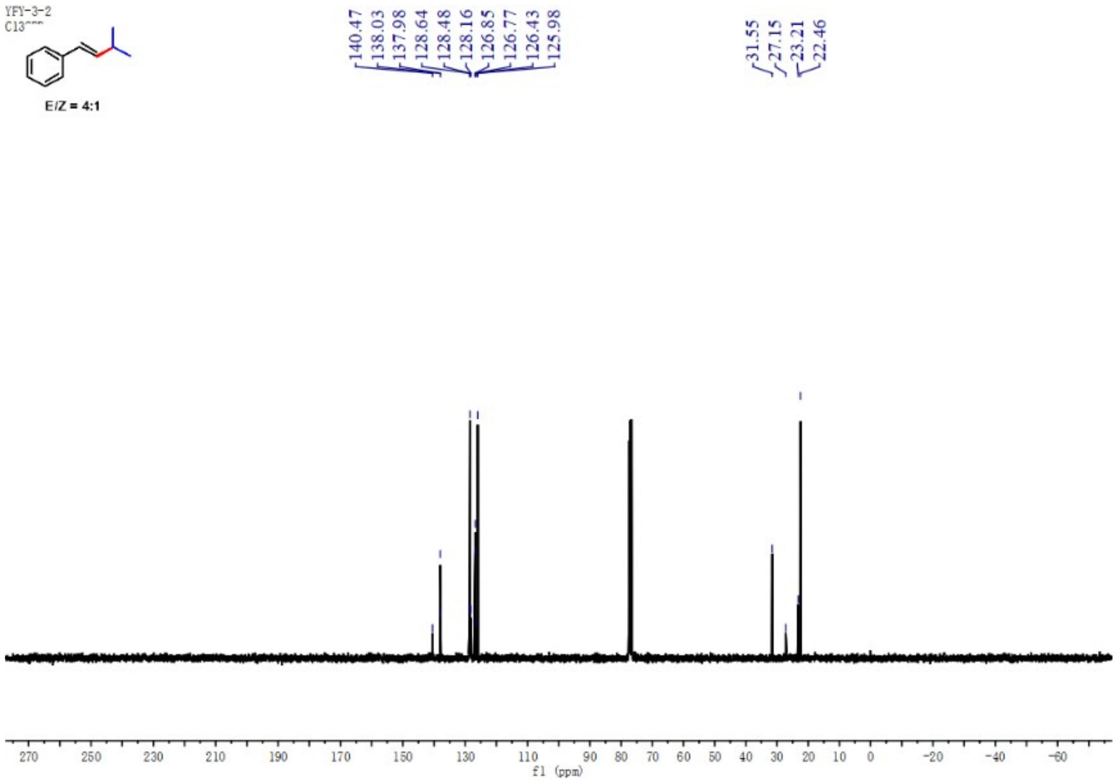
^{13}C NMR spectrum of compound **3**



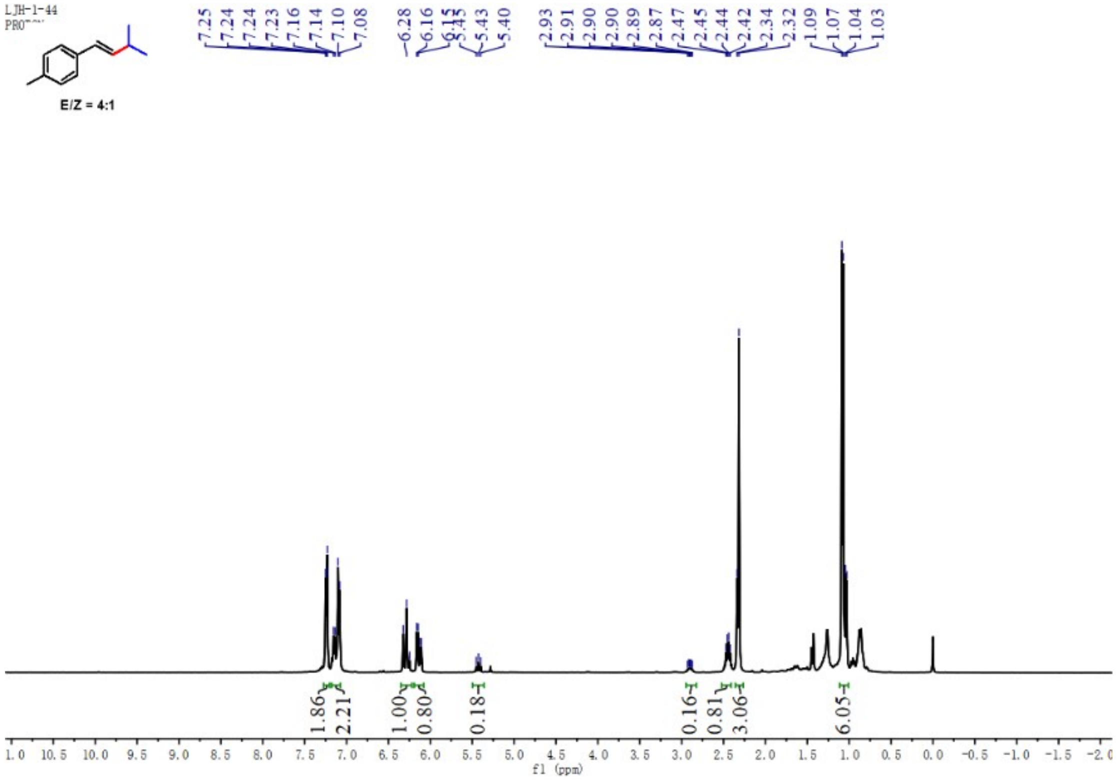
^{1}H NMR spectrum of compound **4**



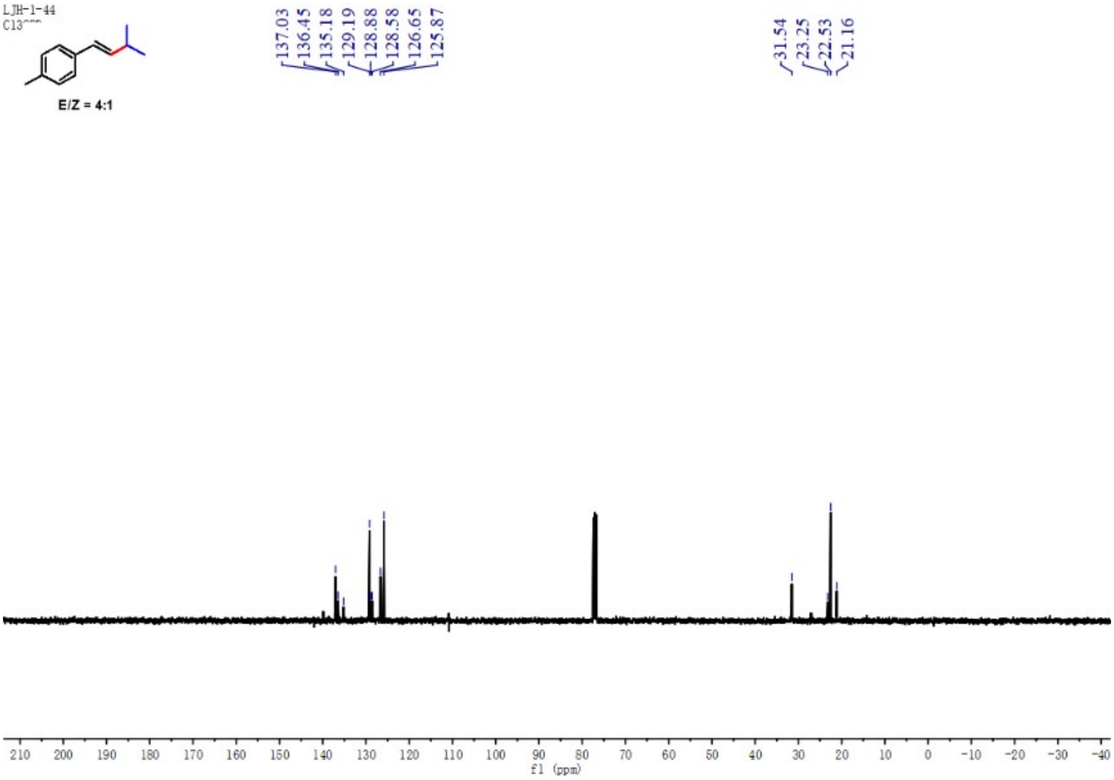
^{13}C NMR spectrum of compound **4**



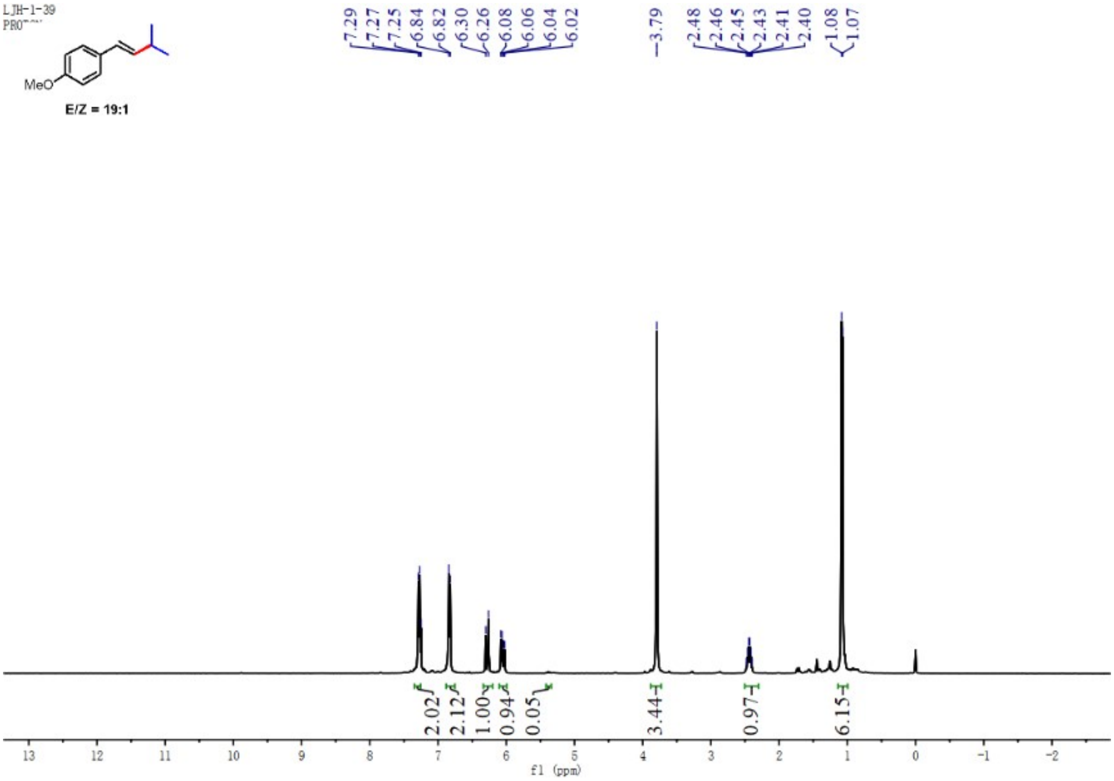
^{1}H NMR spectrum of compound **5**



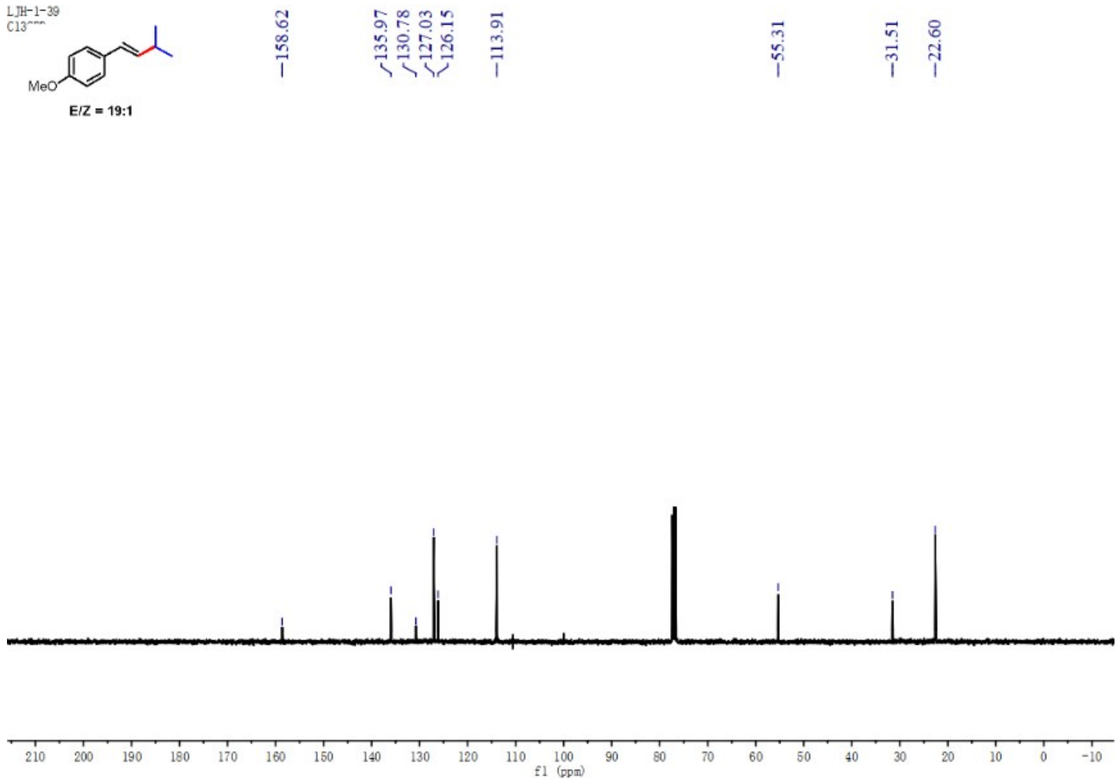
^{13}C NMR spectrum of compound **5**



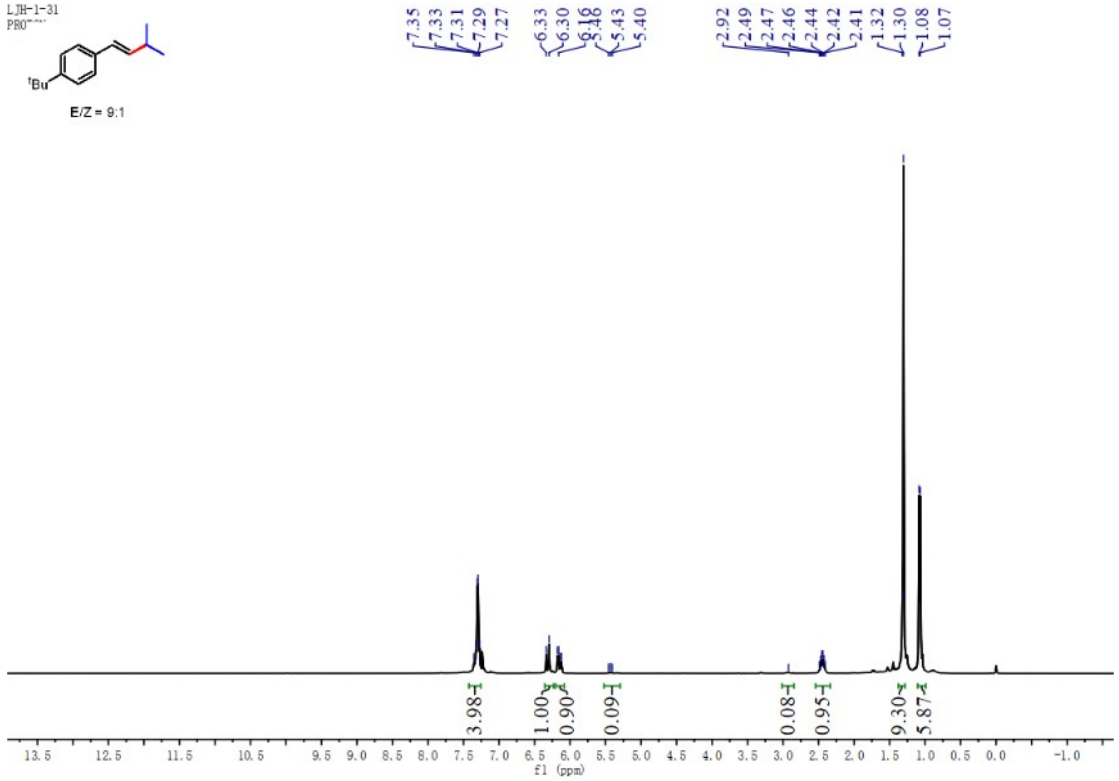
^{1}H NMR spectrum of compound **6**



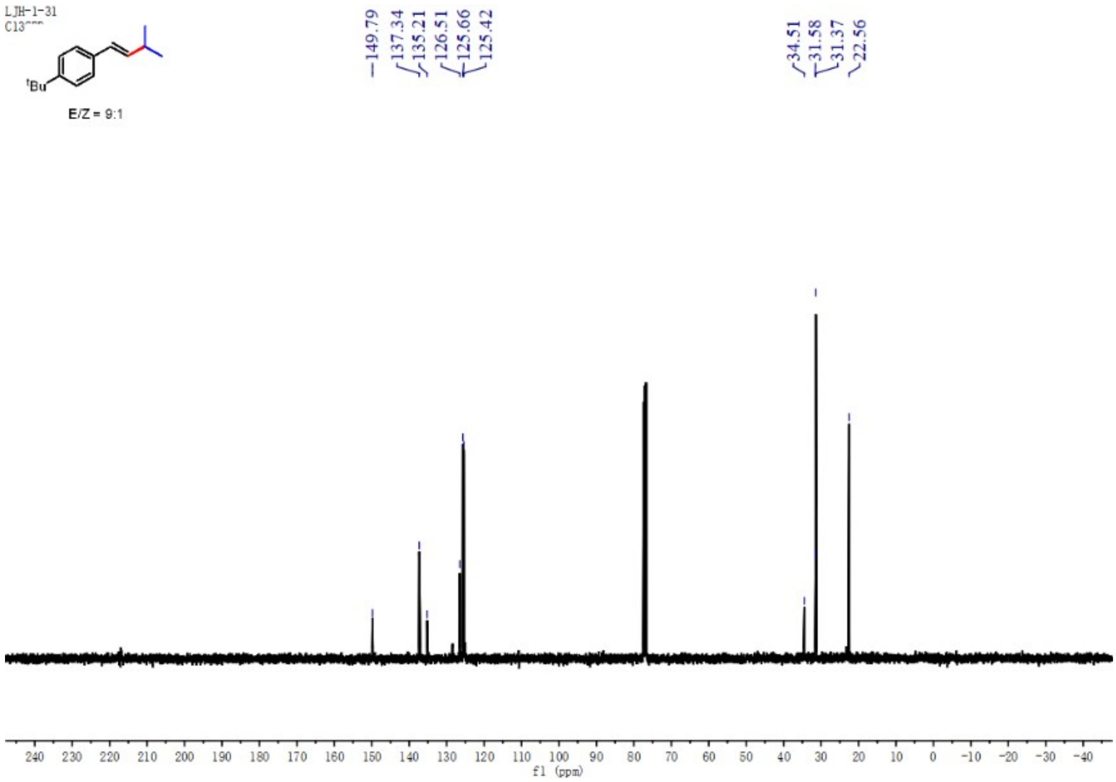
^{13}C NMR spectrum of compound **6**



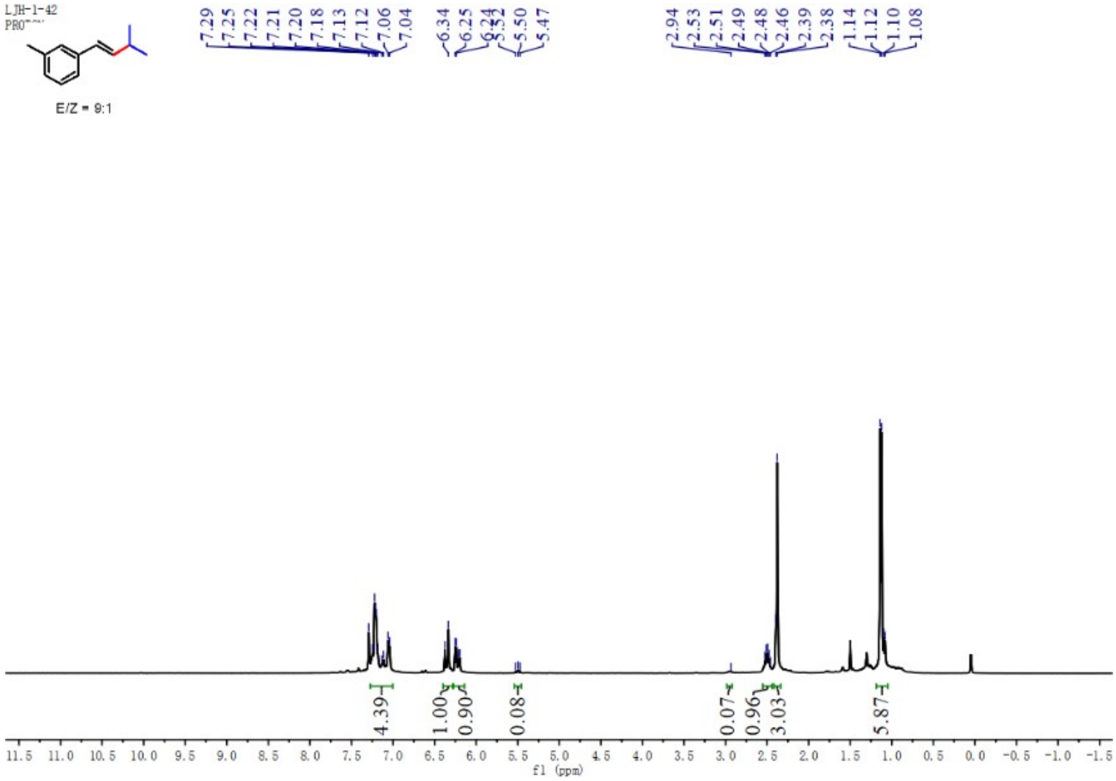
^{1}H NMR spectrum of compound **7**



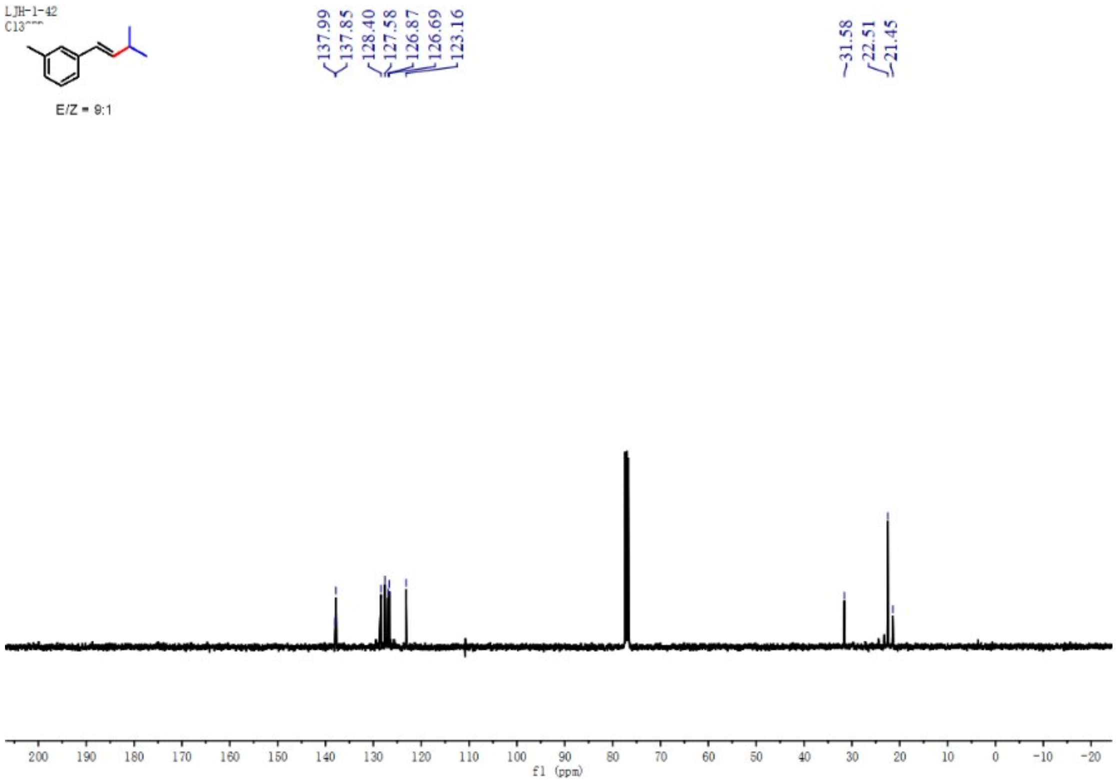
^{13}C NMR spectrum of compound **7**



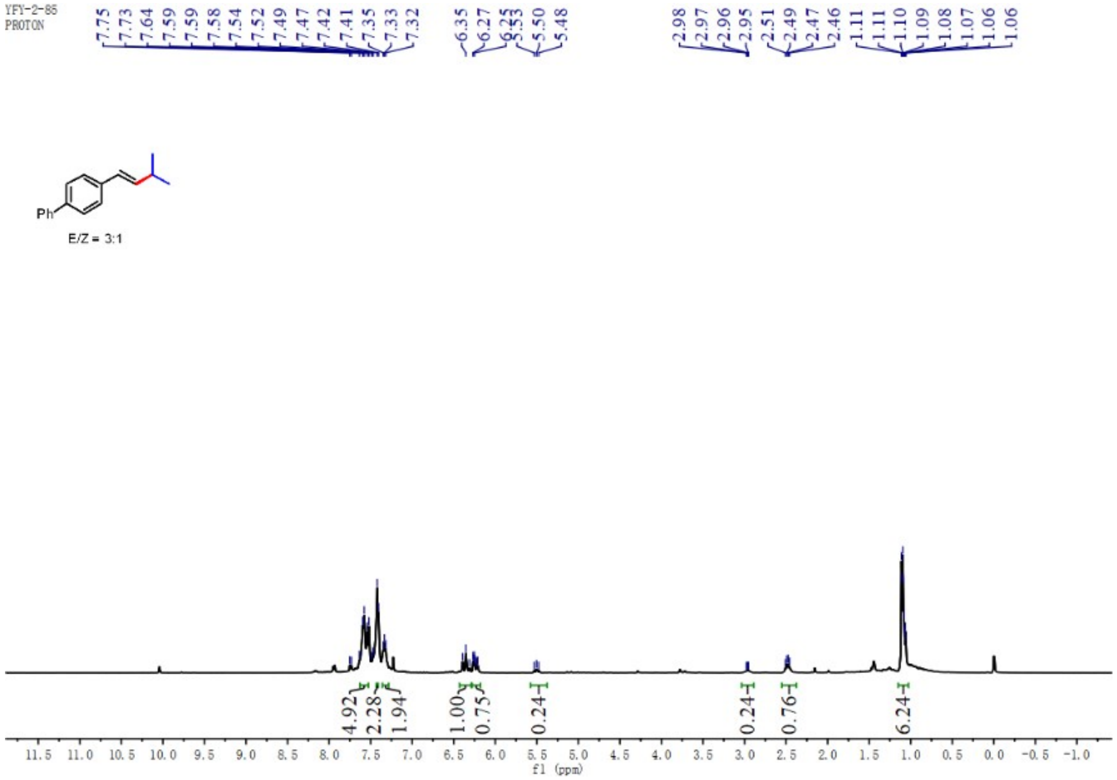
^{1}H NMR spectrum of compound **8**



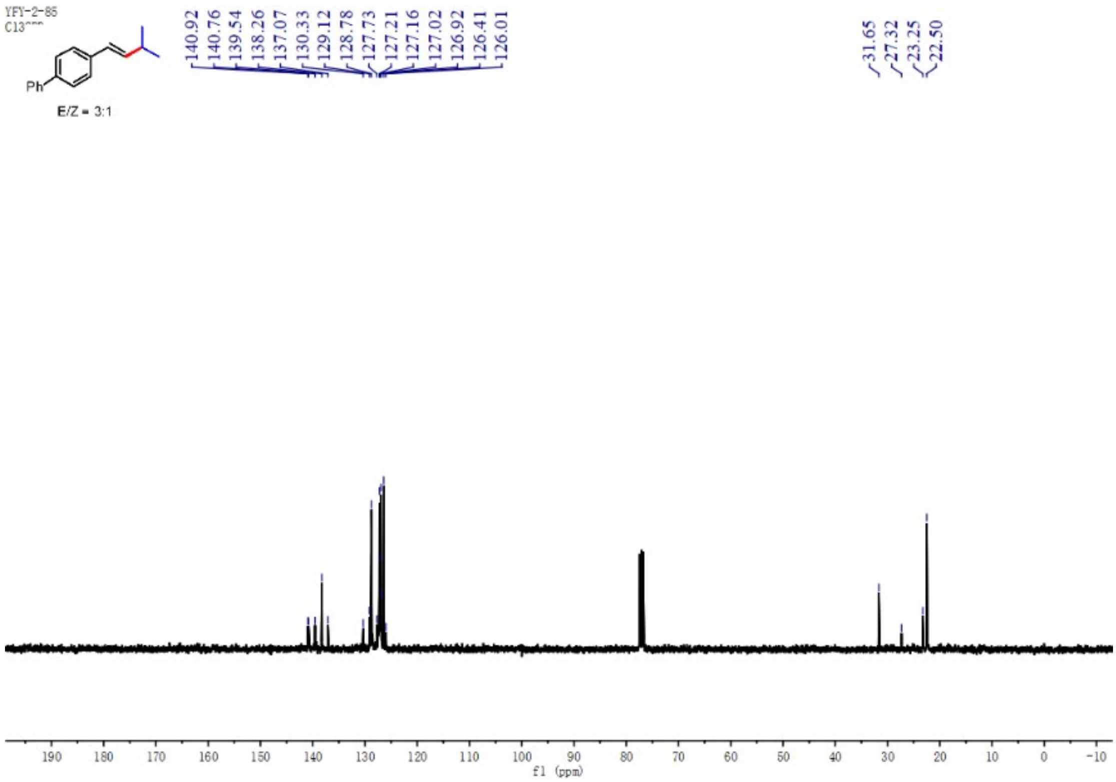
^{13}C NMR spectrum of compound **8**



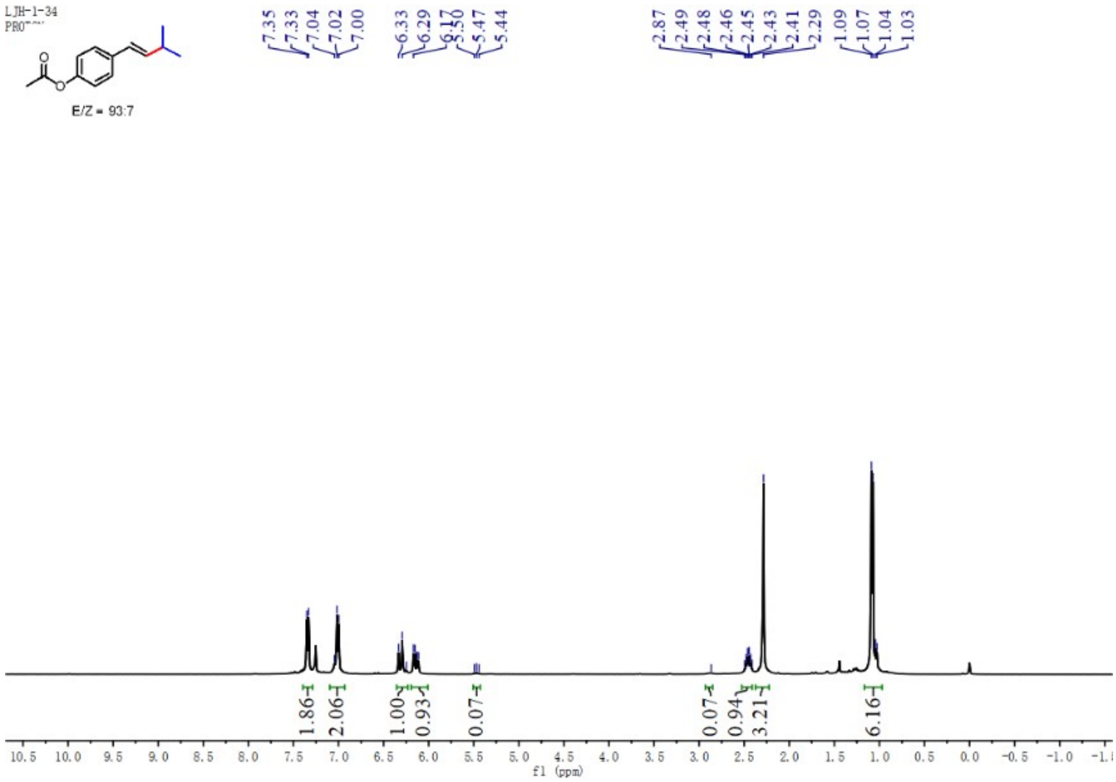
¹H NMR spectrum of compound **9**



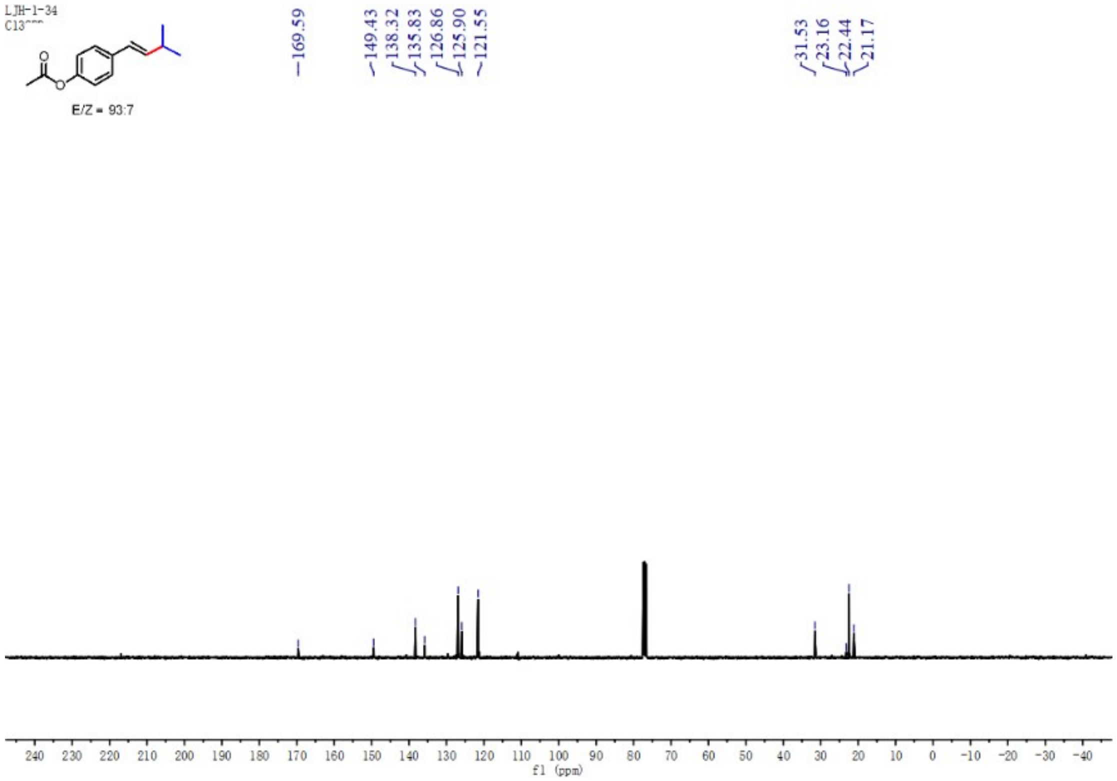
^{13}C NMR spectrum of compound **9**



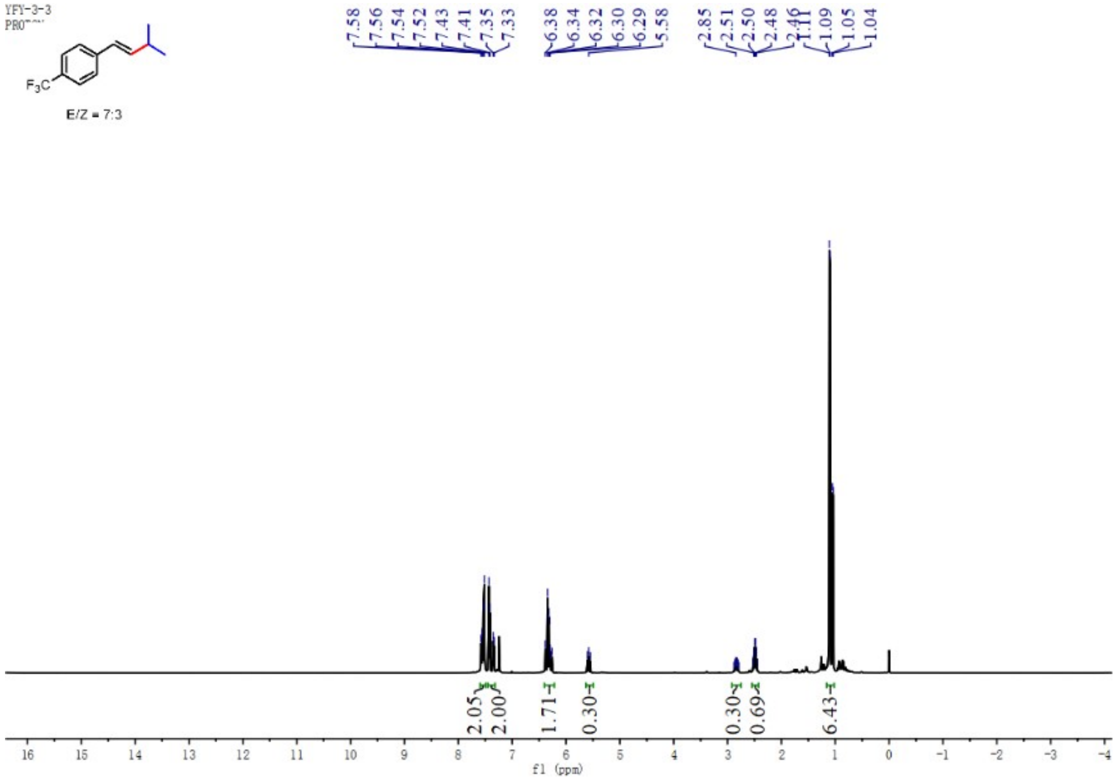
^{1}H NMR spectrum of compound **10**



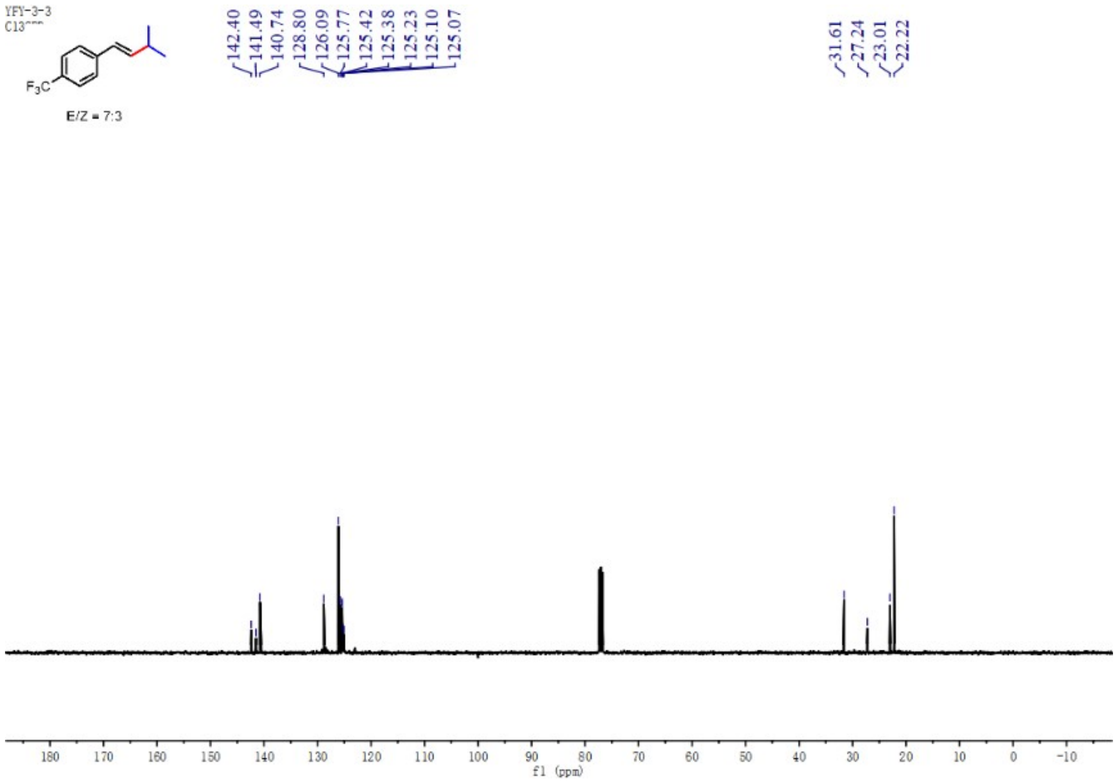
^{13}C NMR spectrum of compound **10**



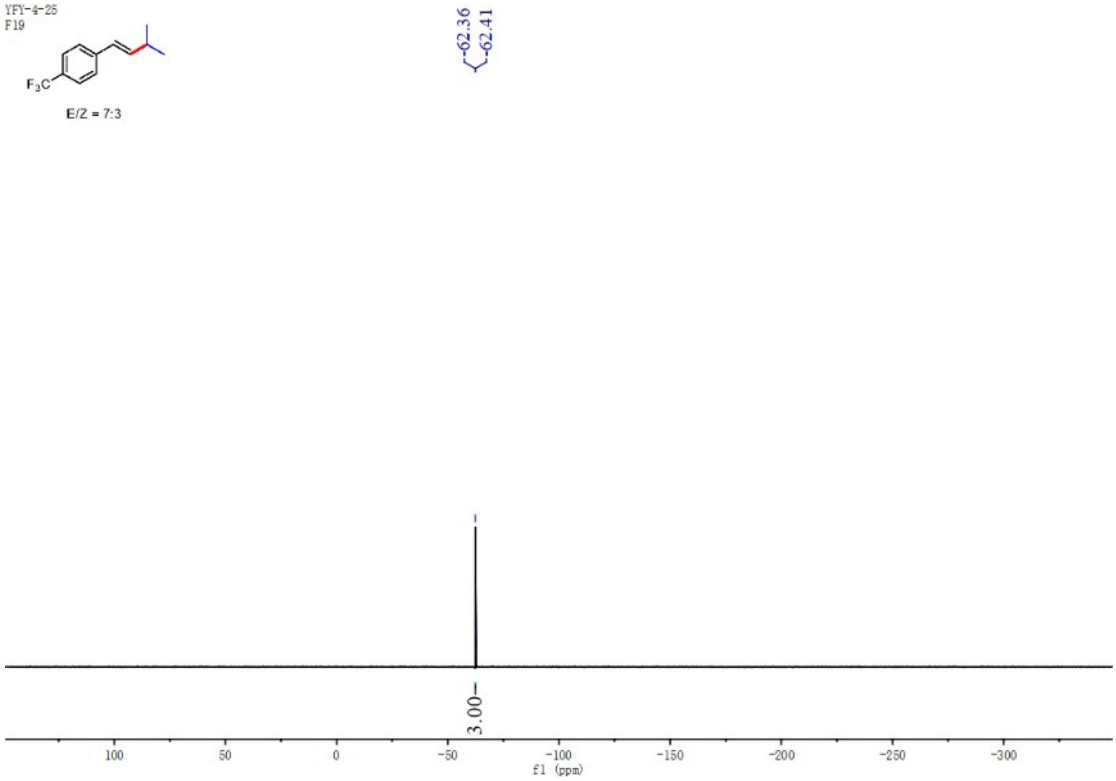
^{1}H NMR spectrum of compound **11**



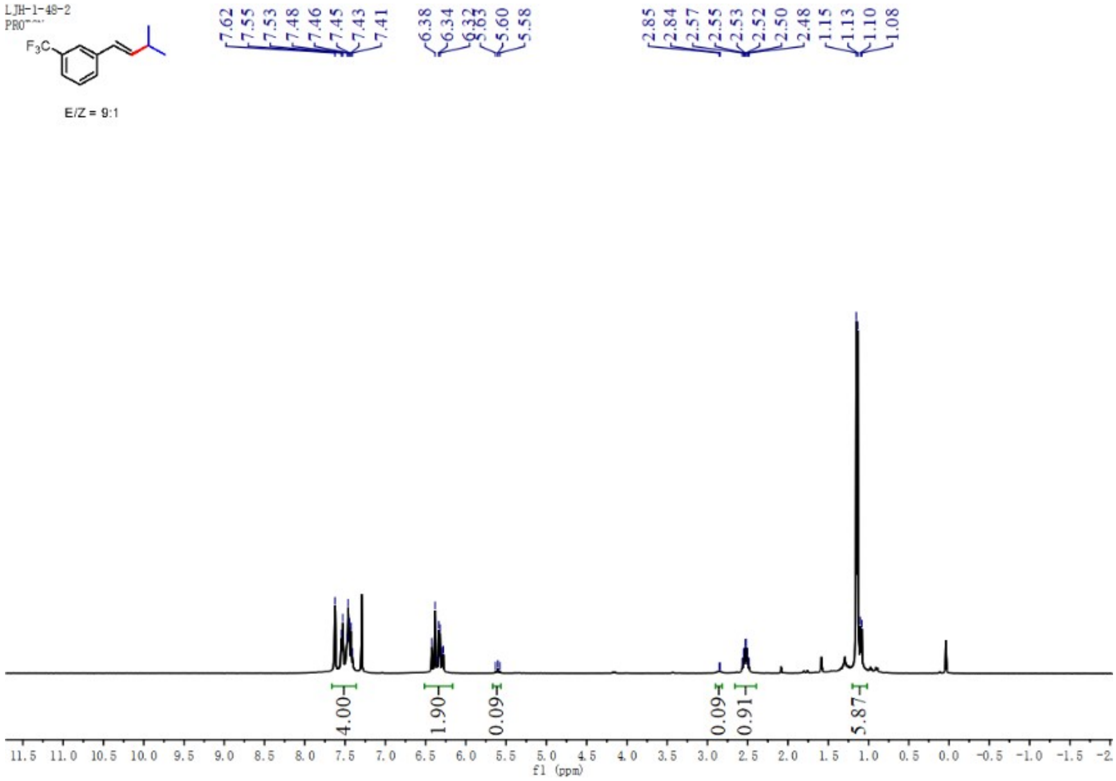
^{13}C NMR spectrum of compound **11**



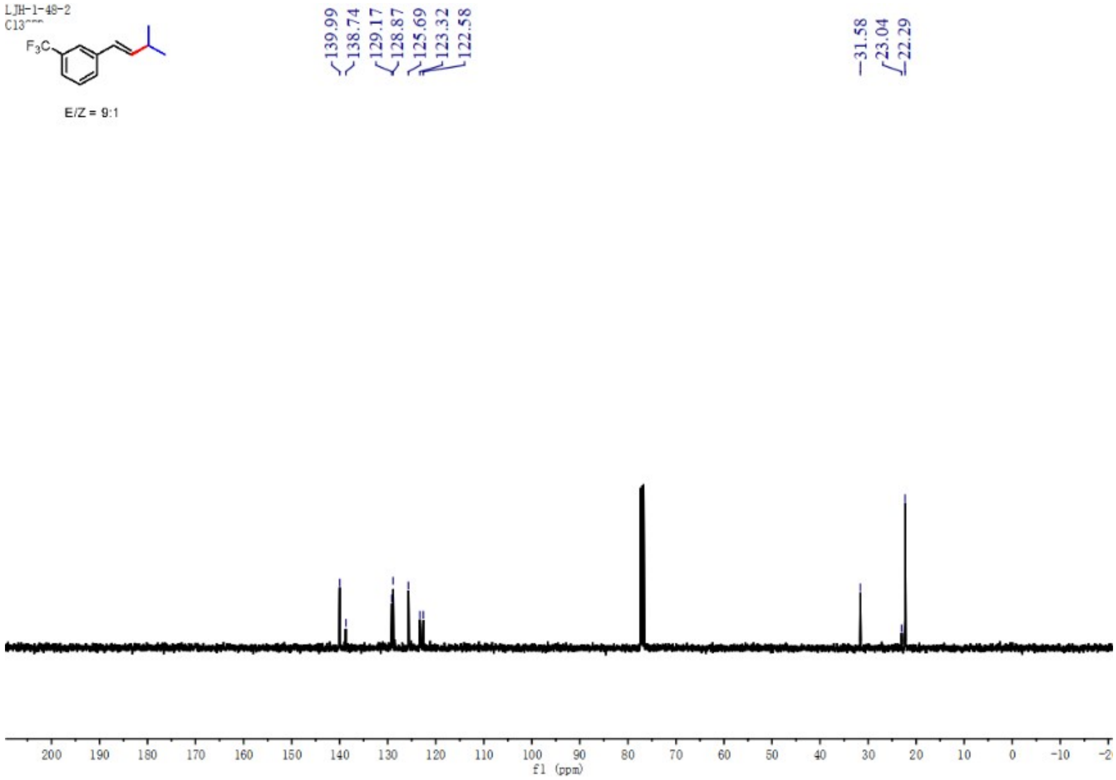
^{19}F NMR spectrum of compound **11**



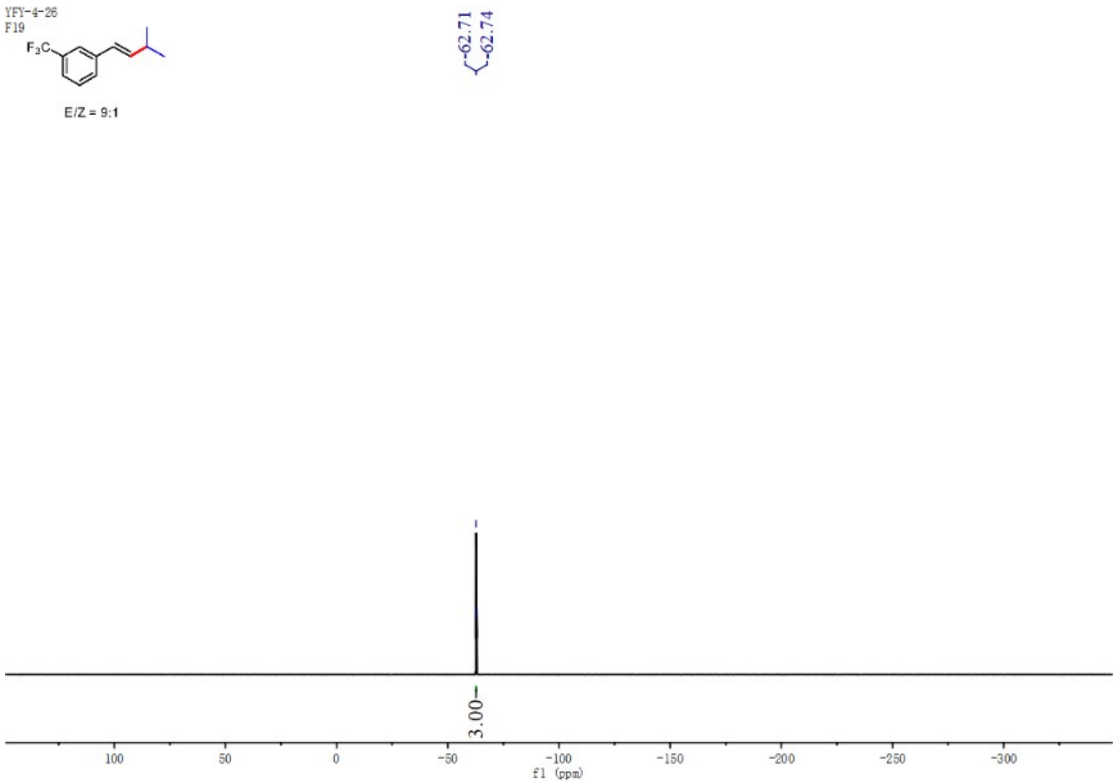
^{1}H NMR spectrum of compound **12**



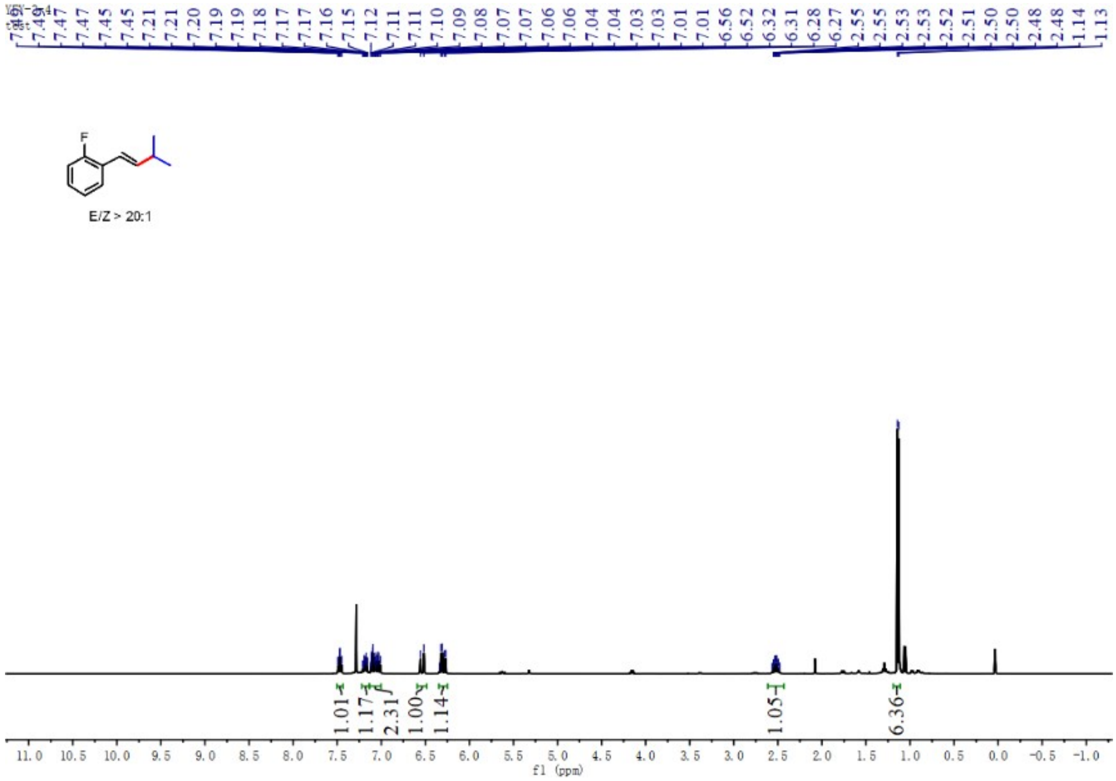
^{13}C NMR spectrum of compound **12**



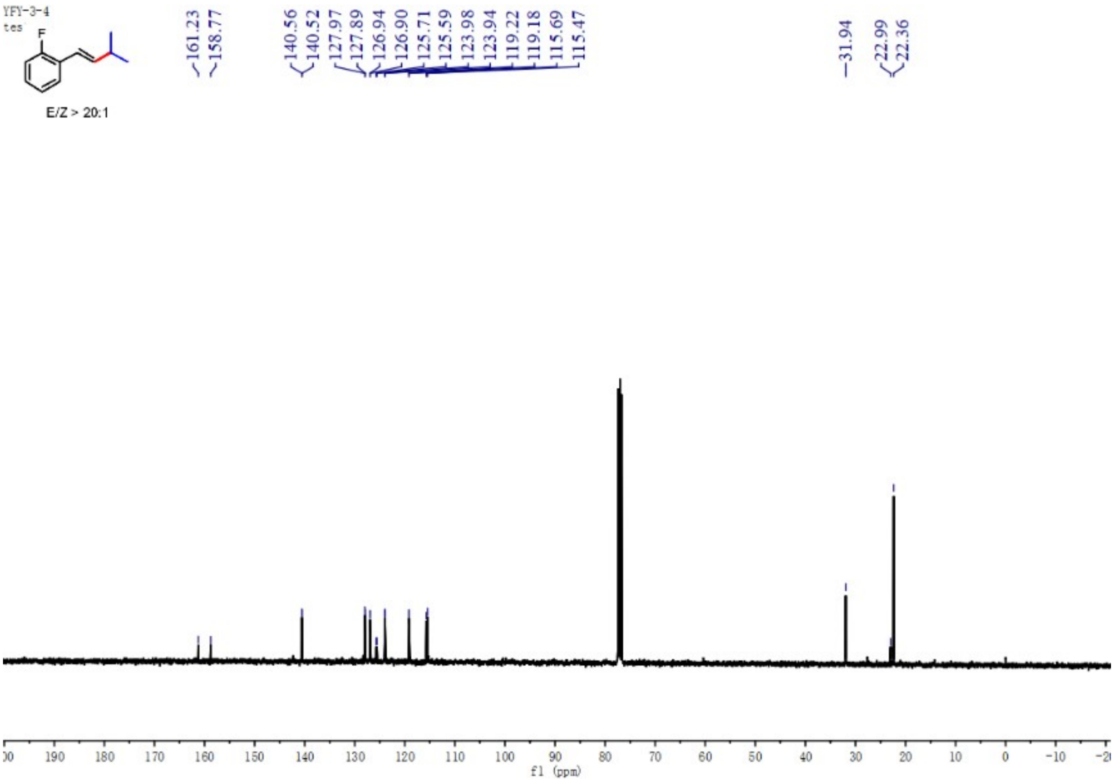
^{19}F NMR spectrum of compound **12**



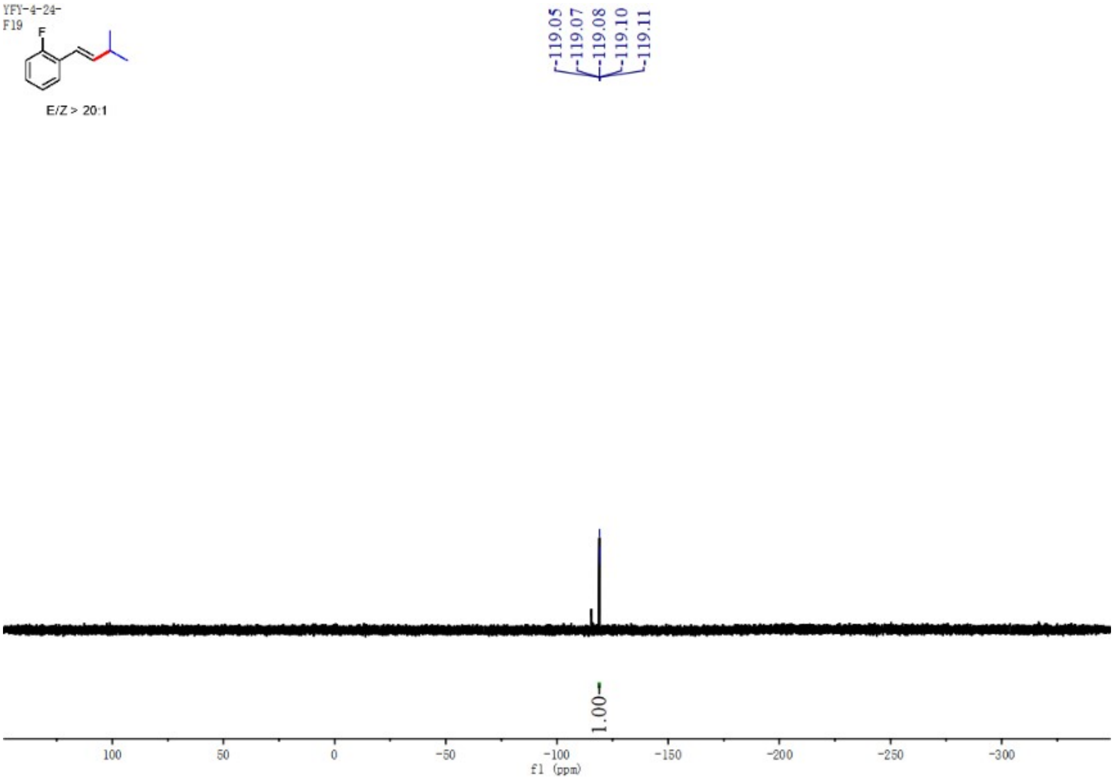
^{1}H NMR spectrum of compound **13**



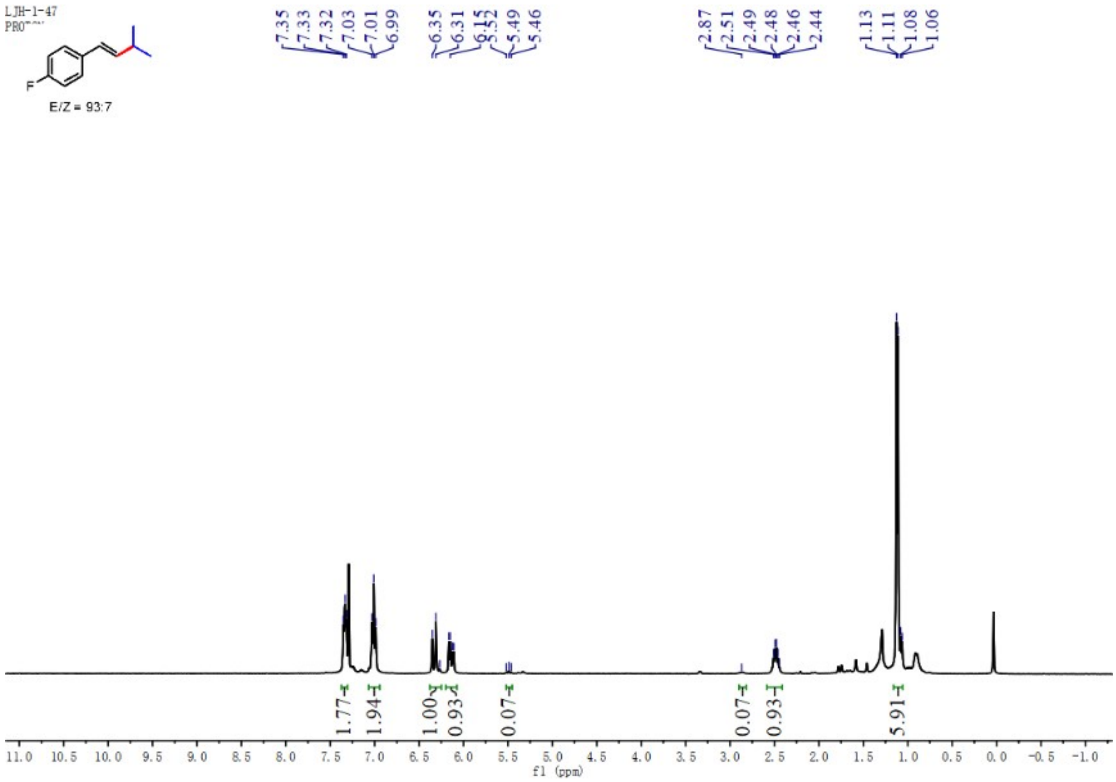
^{13}C NMR spectrum of compound **13**



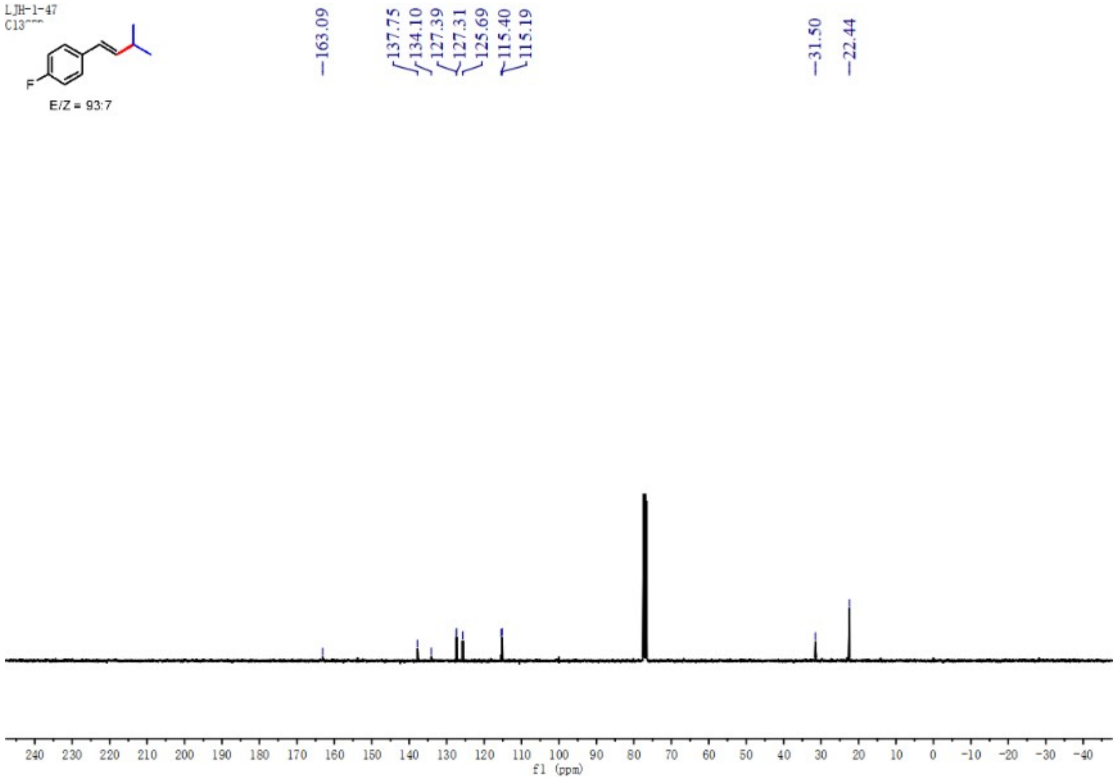
^{19}F NMR spectrum of compound **13**



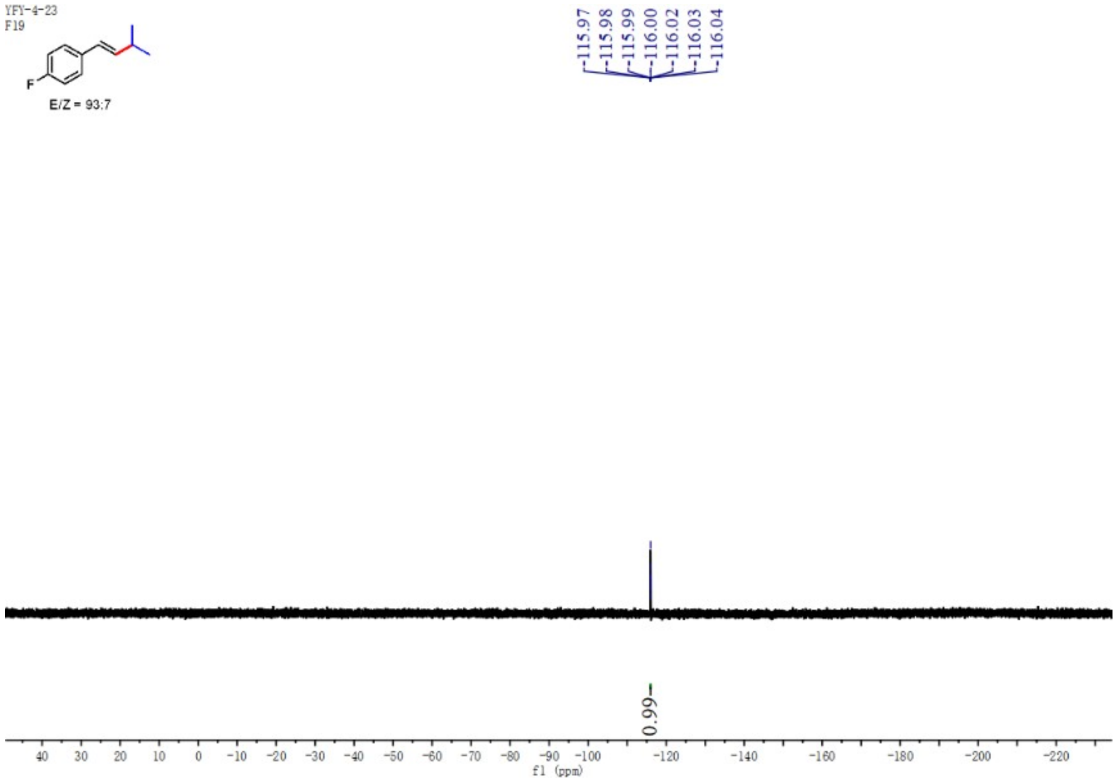
^{1}H NMR spectrum of compound **14**



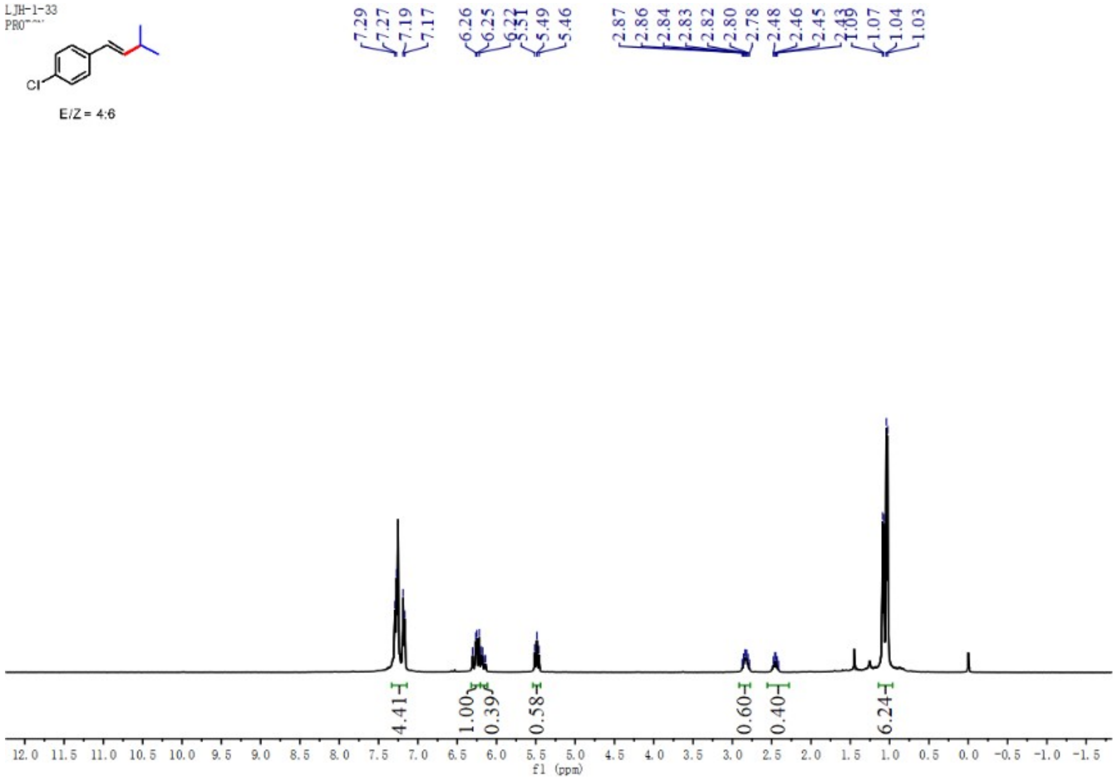
^{13}C NMR spectrum of compound **14**



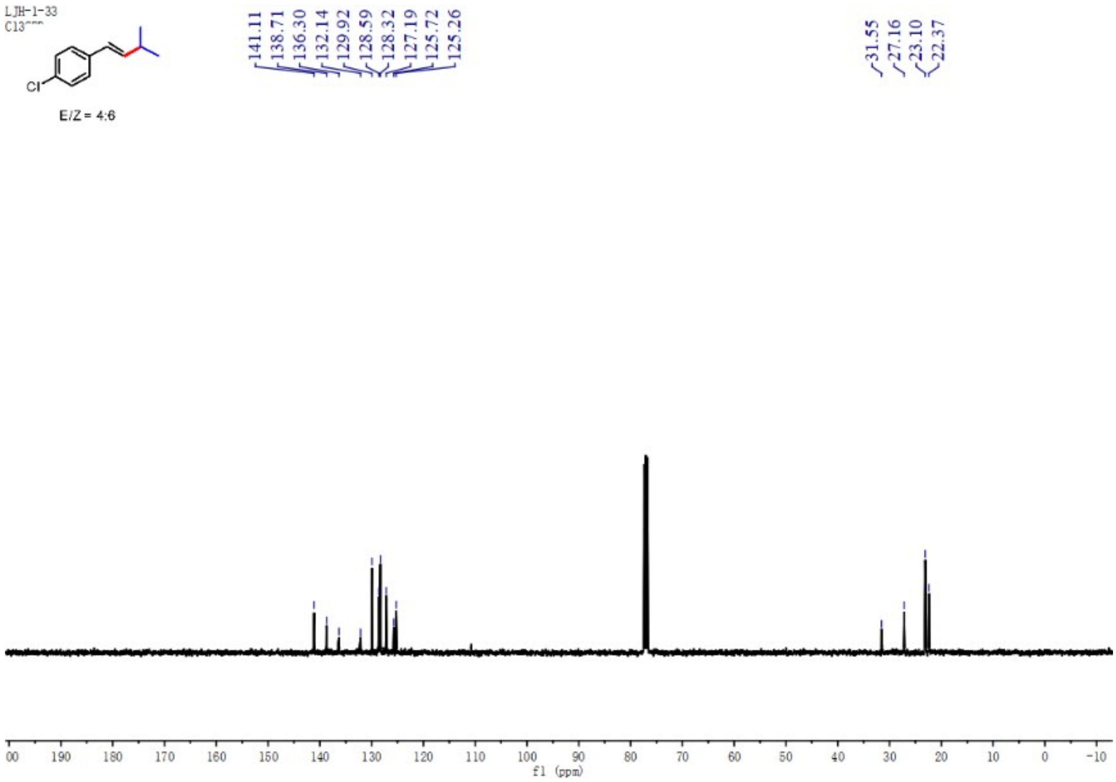
^{19}F NMR spectrum of compound **14**



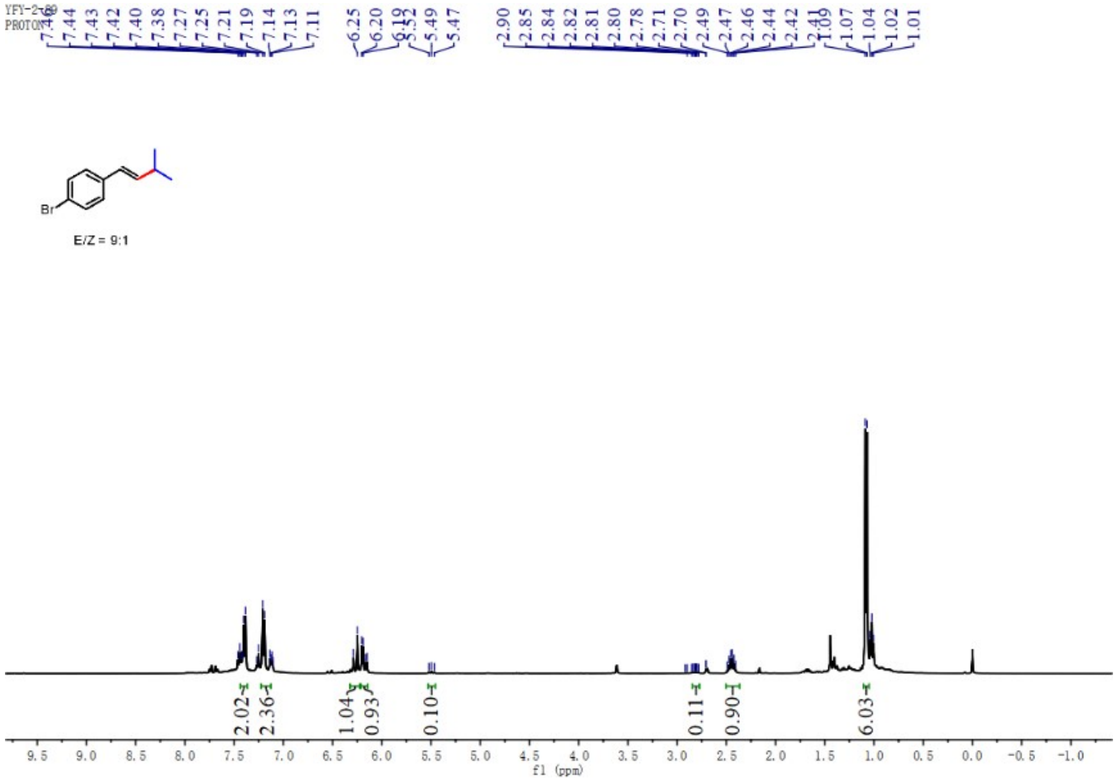
^{1}H NMR spectrum of compound **15**



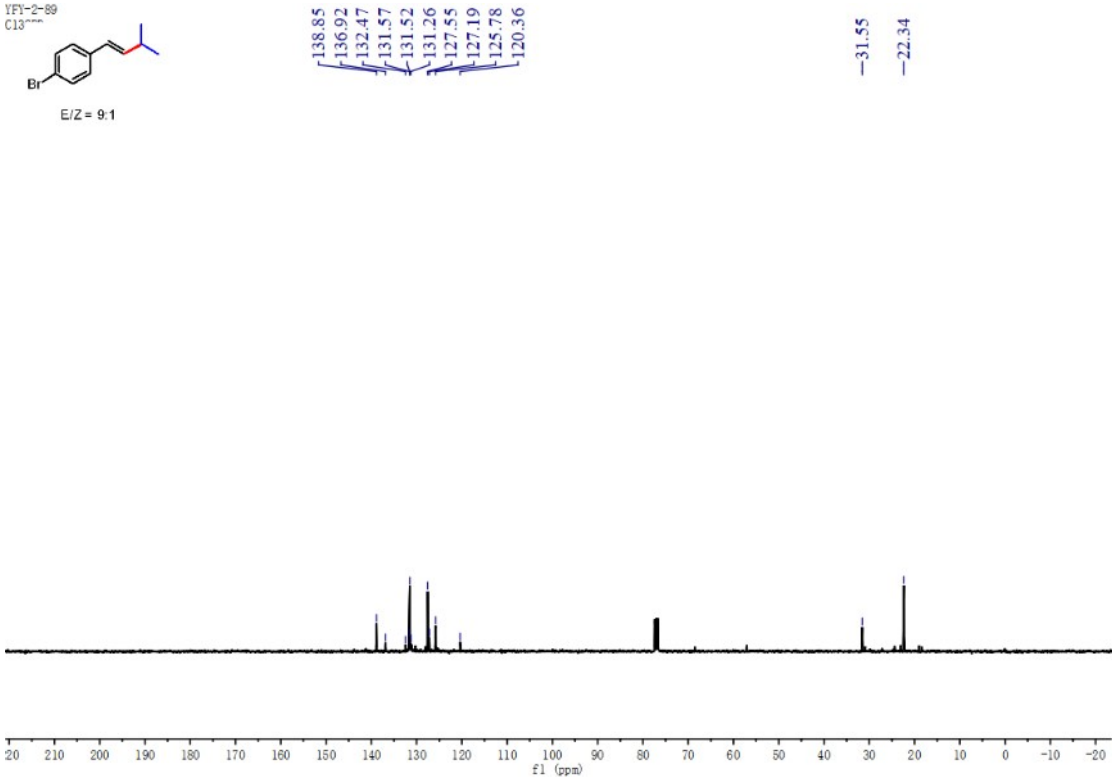
^{13}C NMR spectrum of compound **15**



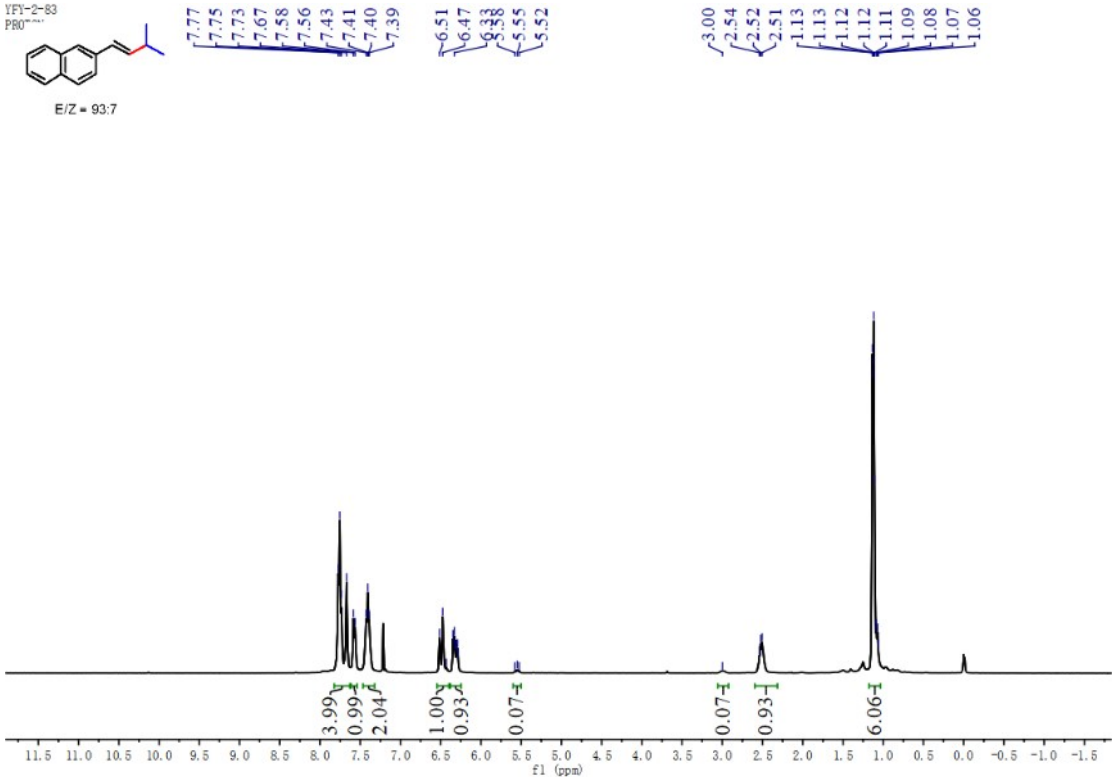
^{1}H NMR spectrum of compound **16**



^{13}C NMR spectrum of compound **16**

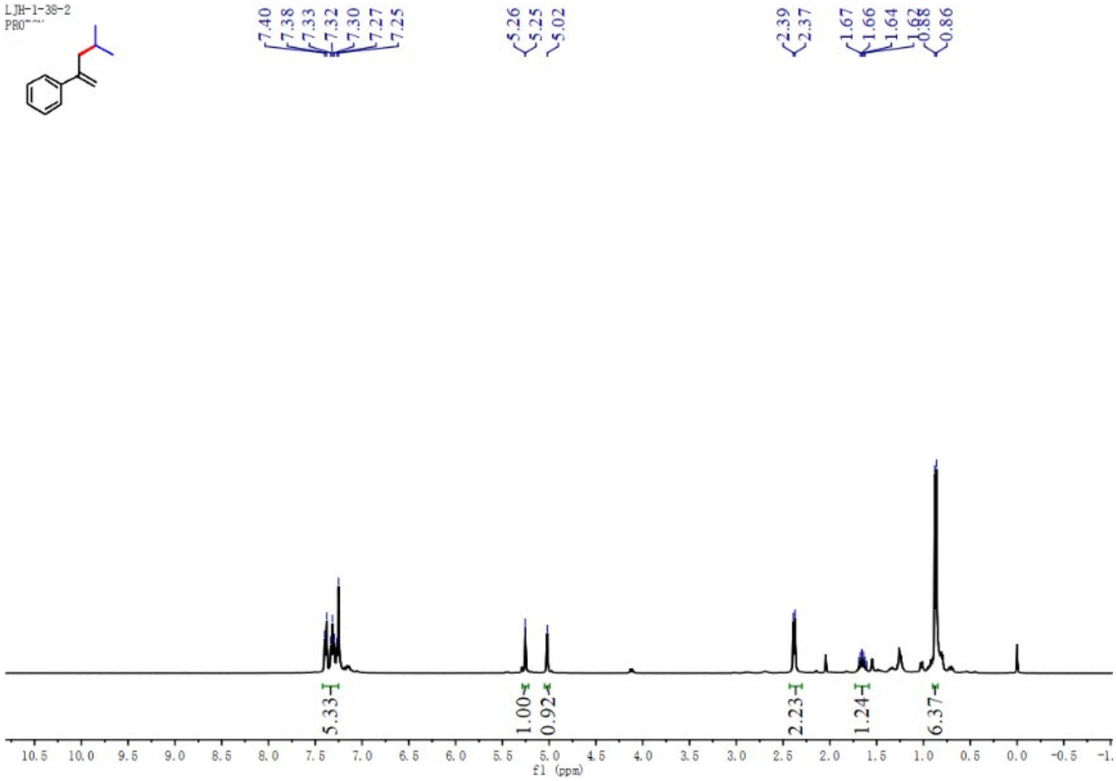


^{1}H NMR spectrum of compound **17**

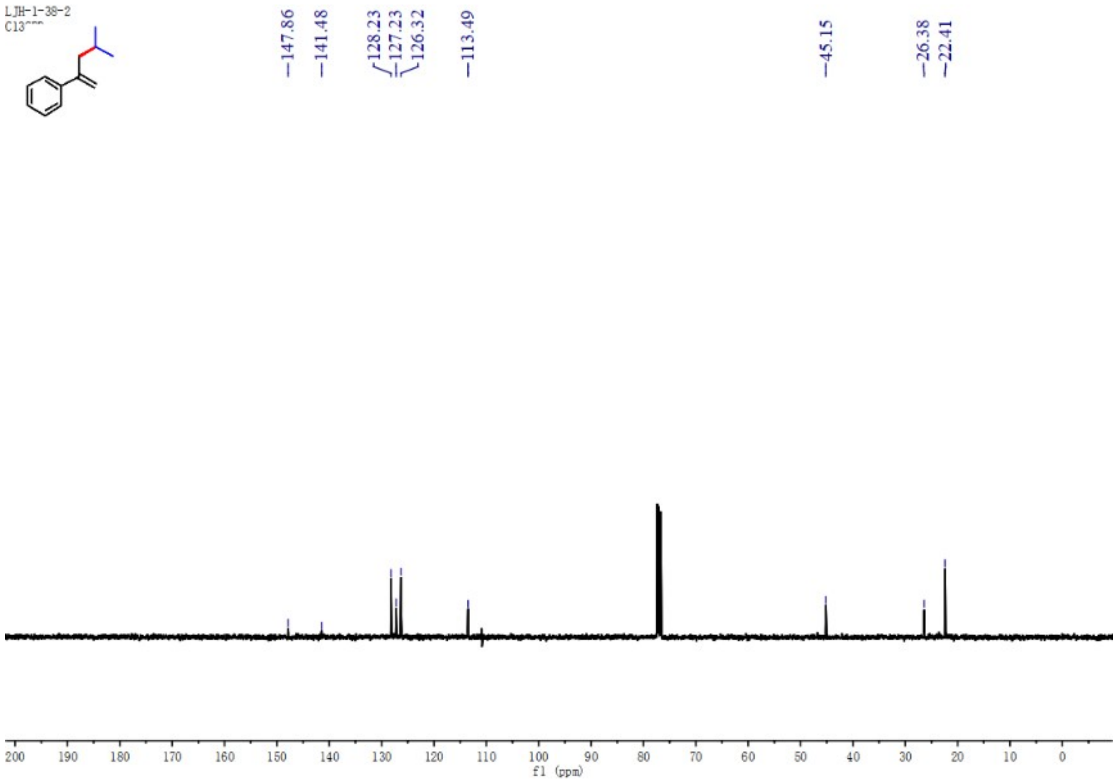


^{13}C NMR spectrum of compound **17**

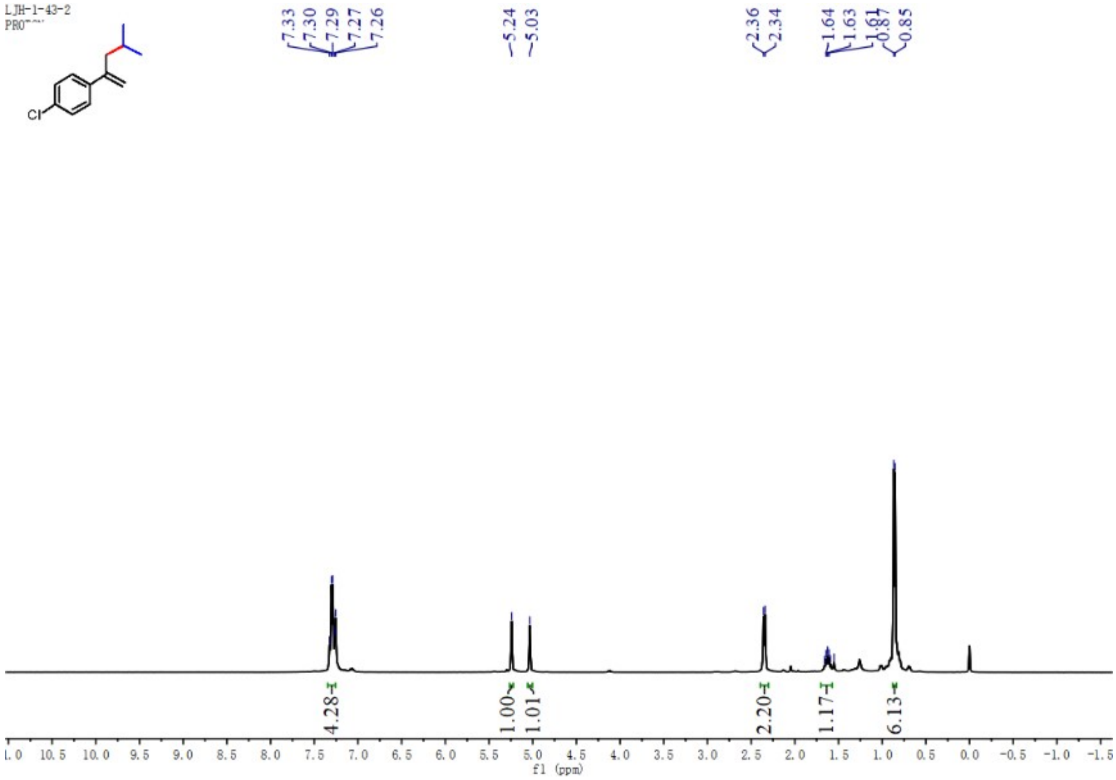
^{1}H NMR spectrum of compound **18**



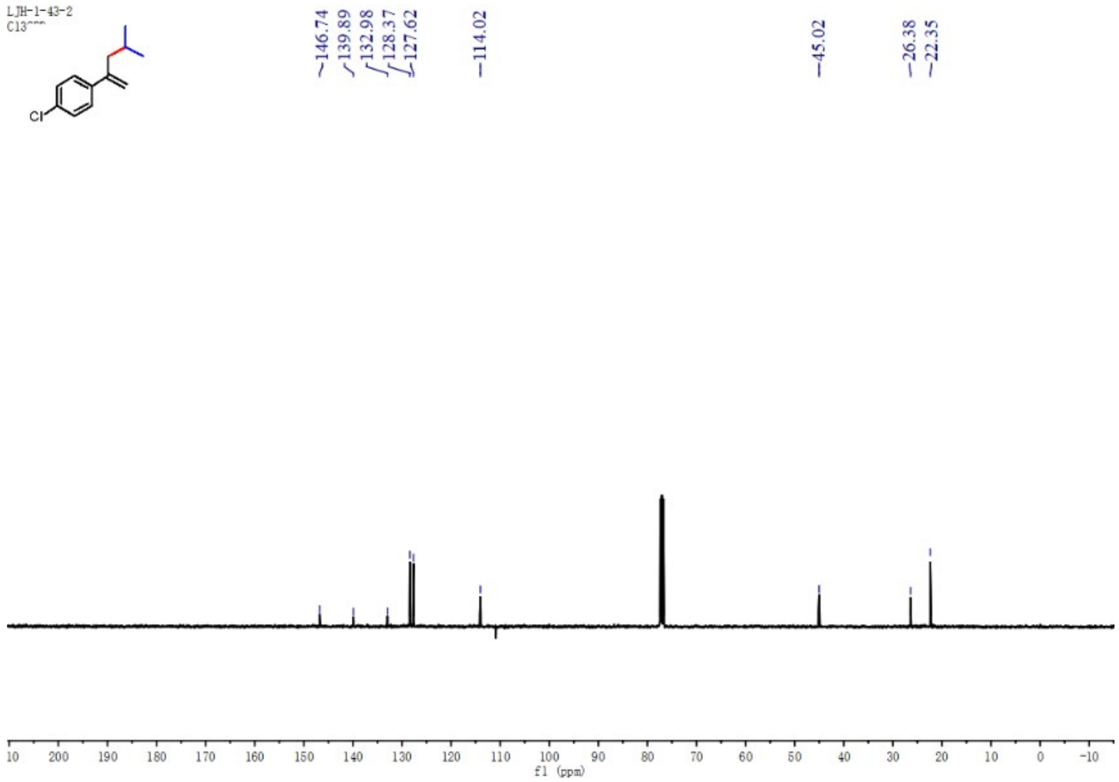
^{13}C NMR spectrum of compound **18**



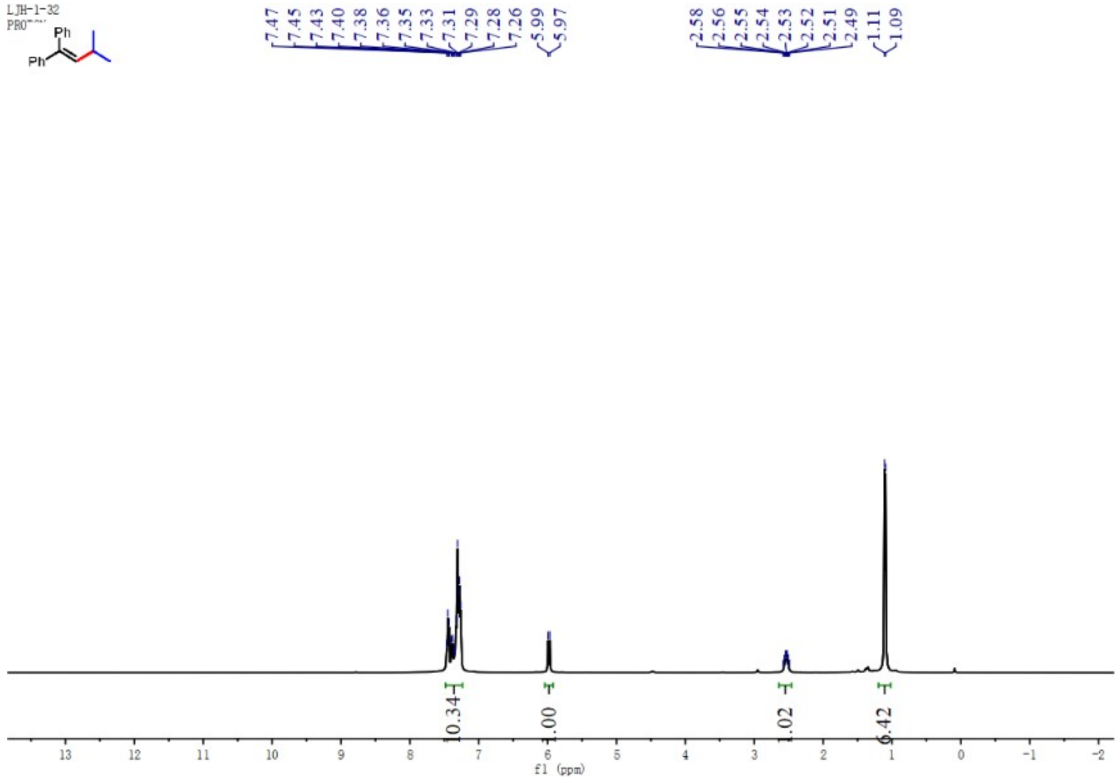
^{1}H NMR spectrum of compound **19**



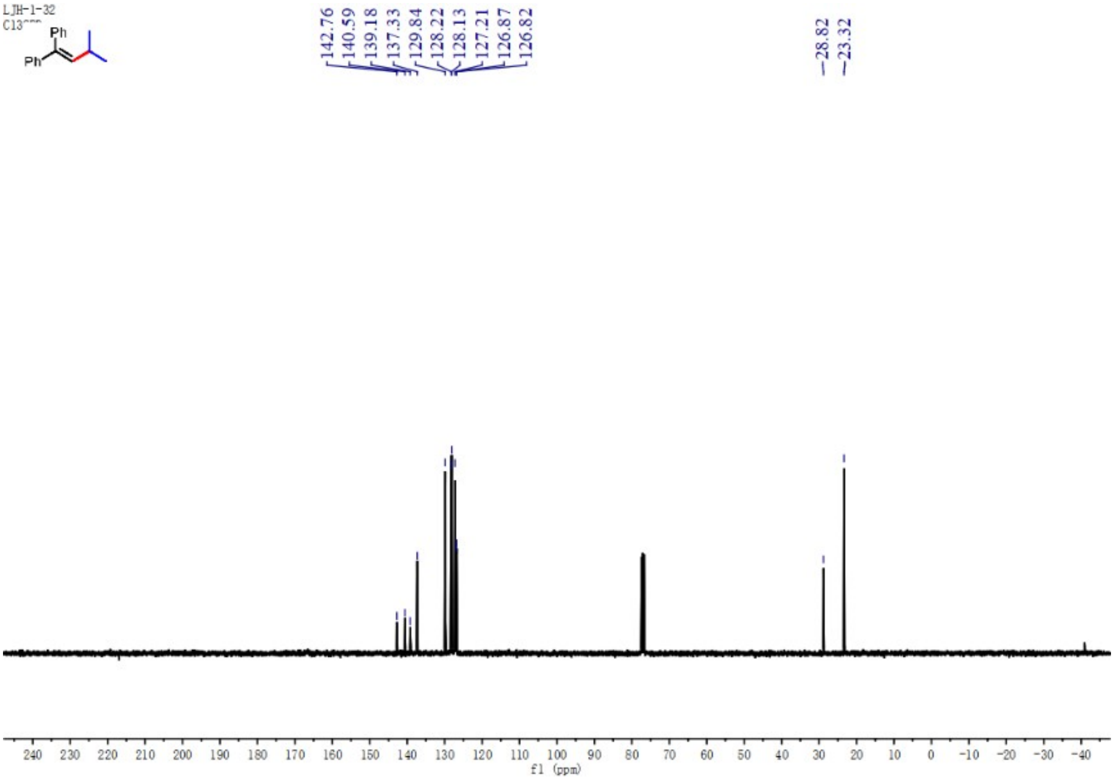
^{13}C NMR spectrum of compound **19**



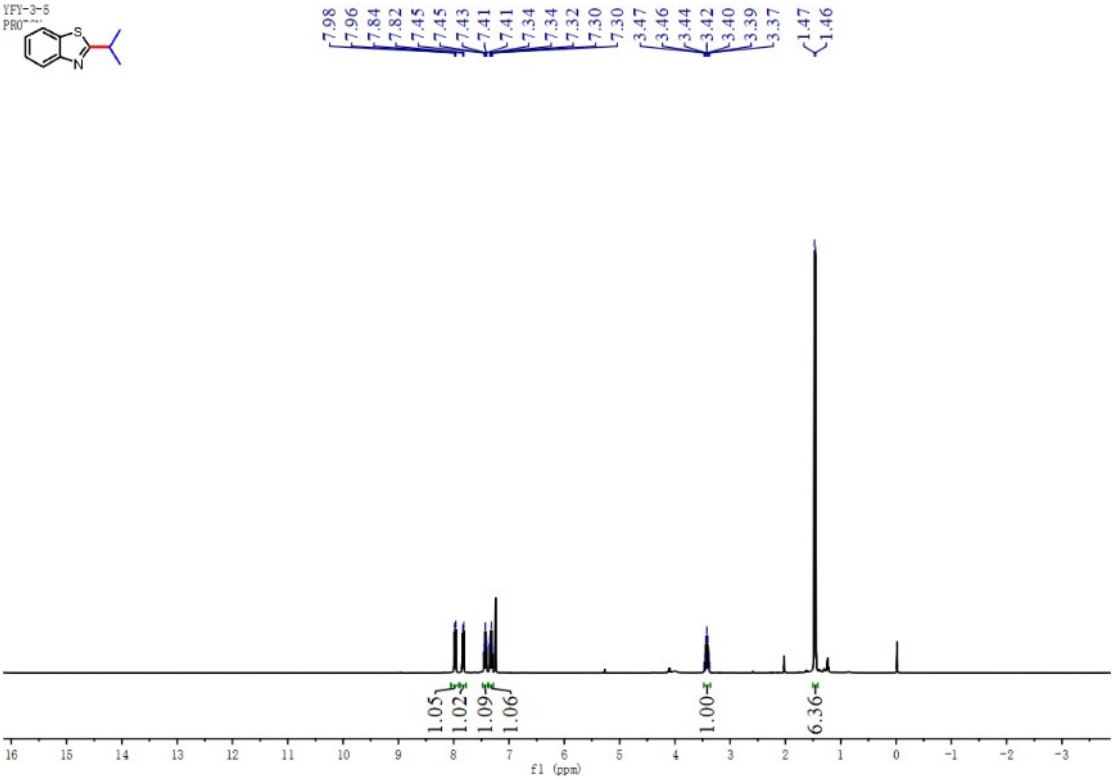
^{1}H NMR spectrum of compound **20**



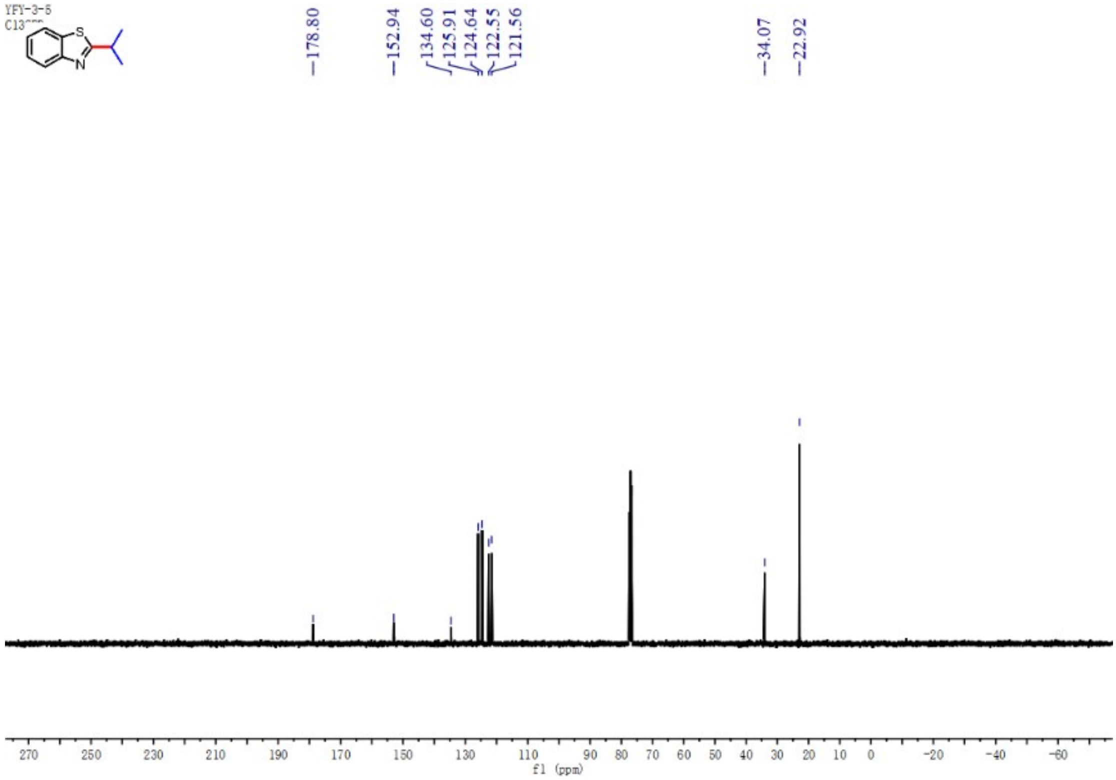
^{13}C NMR spectrum of compound **20**



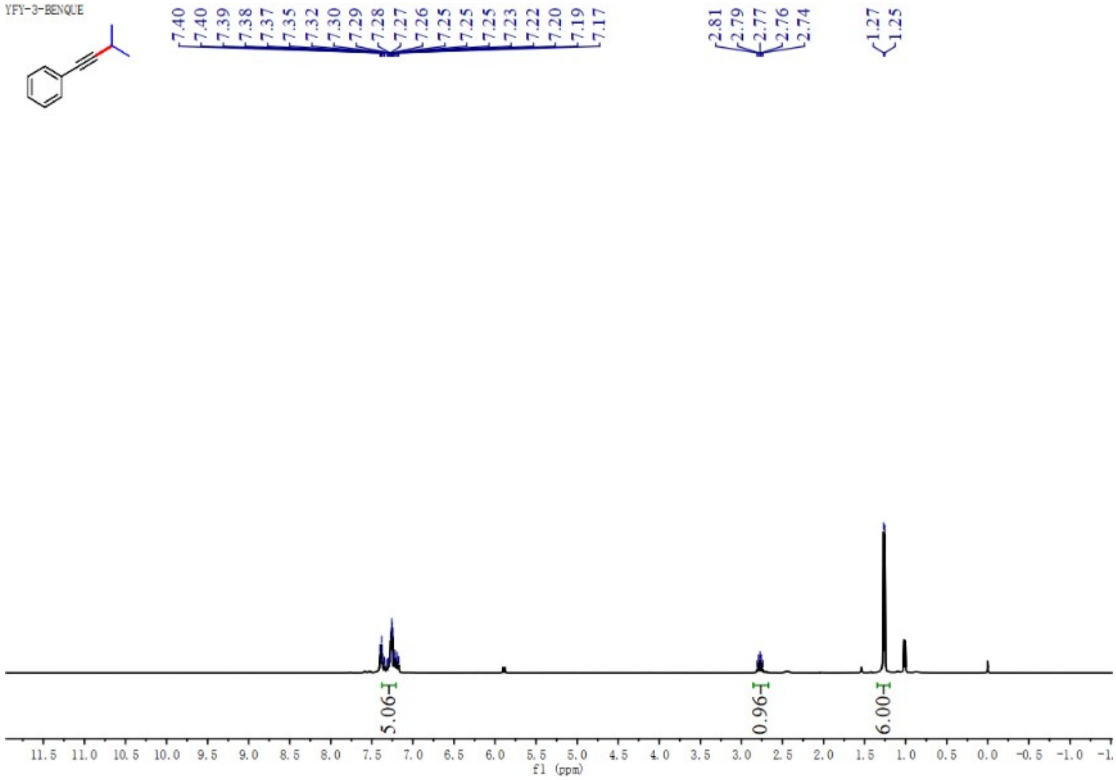
^{1}H NMR spectrum of compound **21**



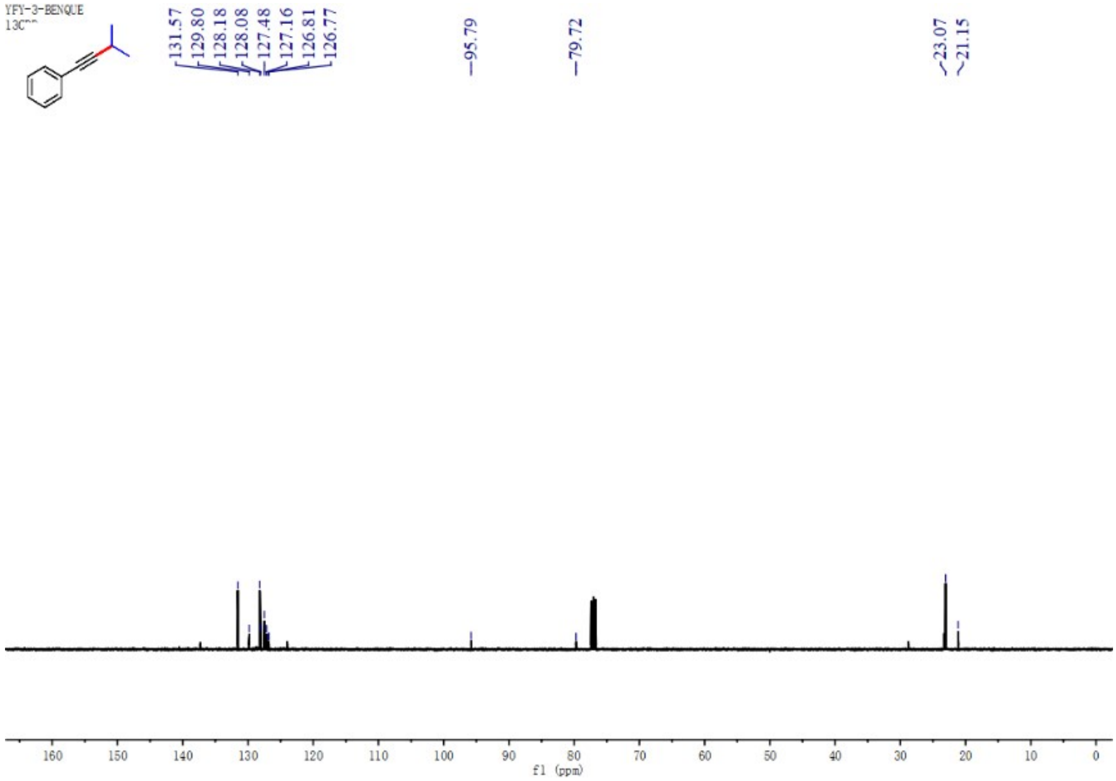
^{13}C NMR spectrum of compound **21**



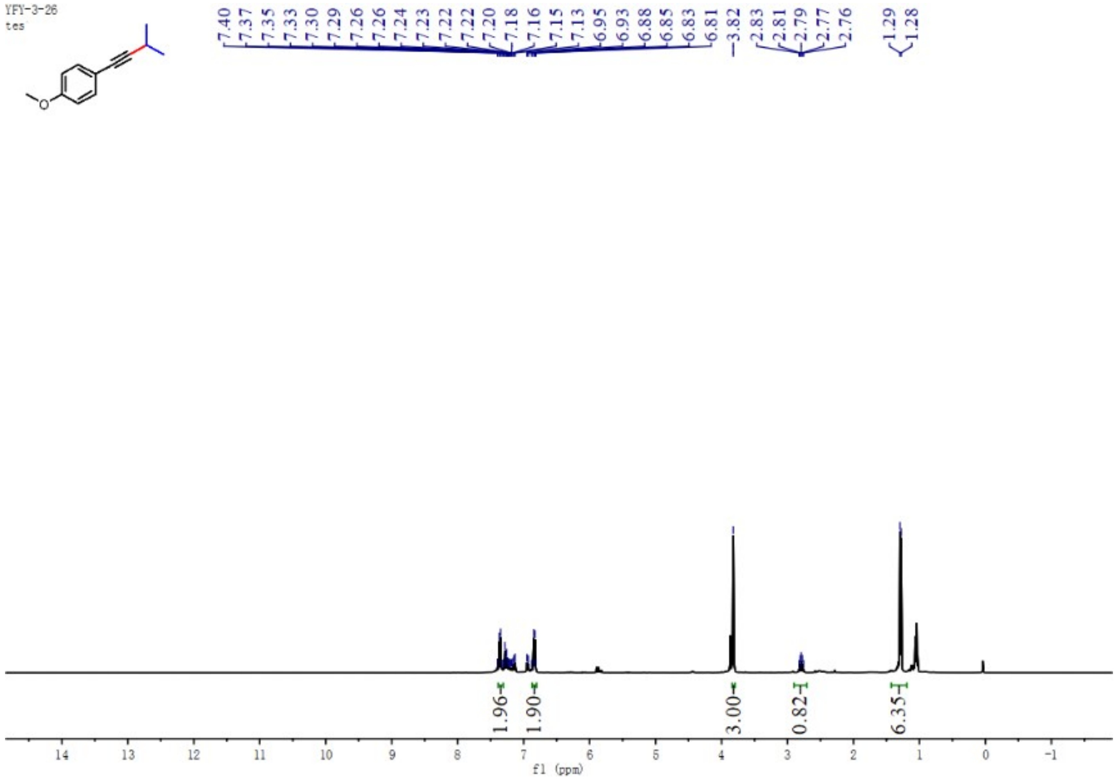
^{1}H NMR spectrum of compound **22**



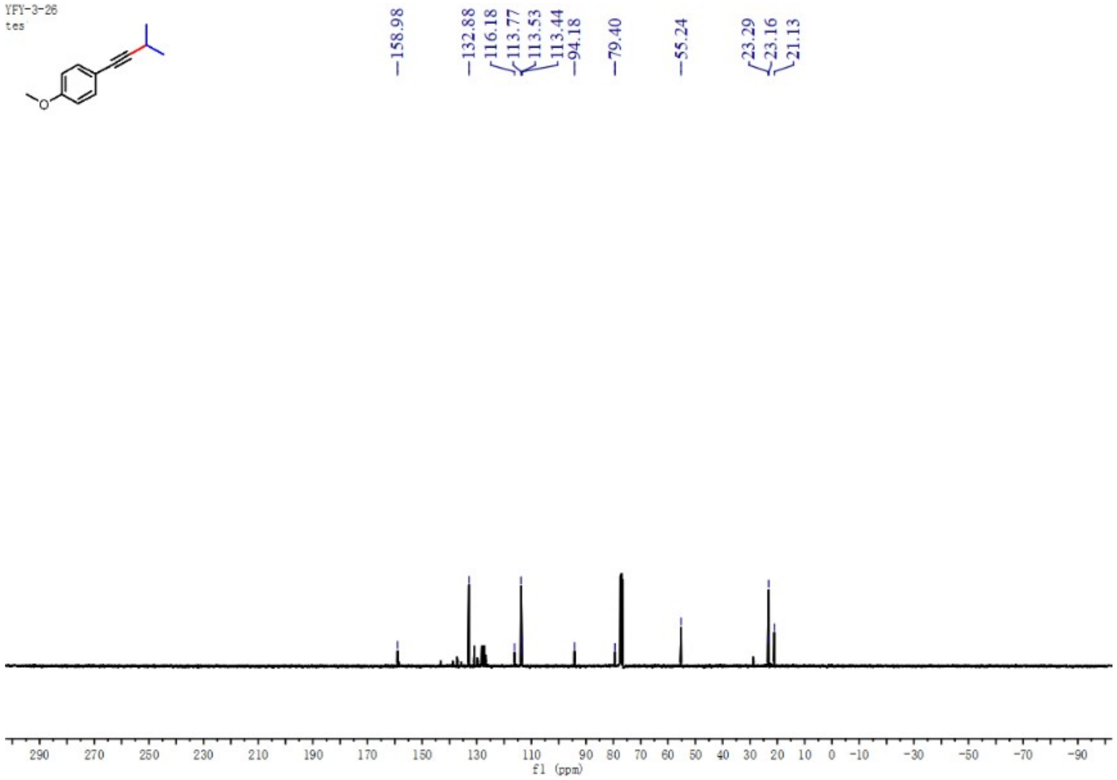
^{13}C NMR spectrum of compound **22**



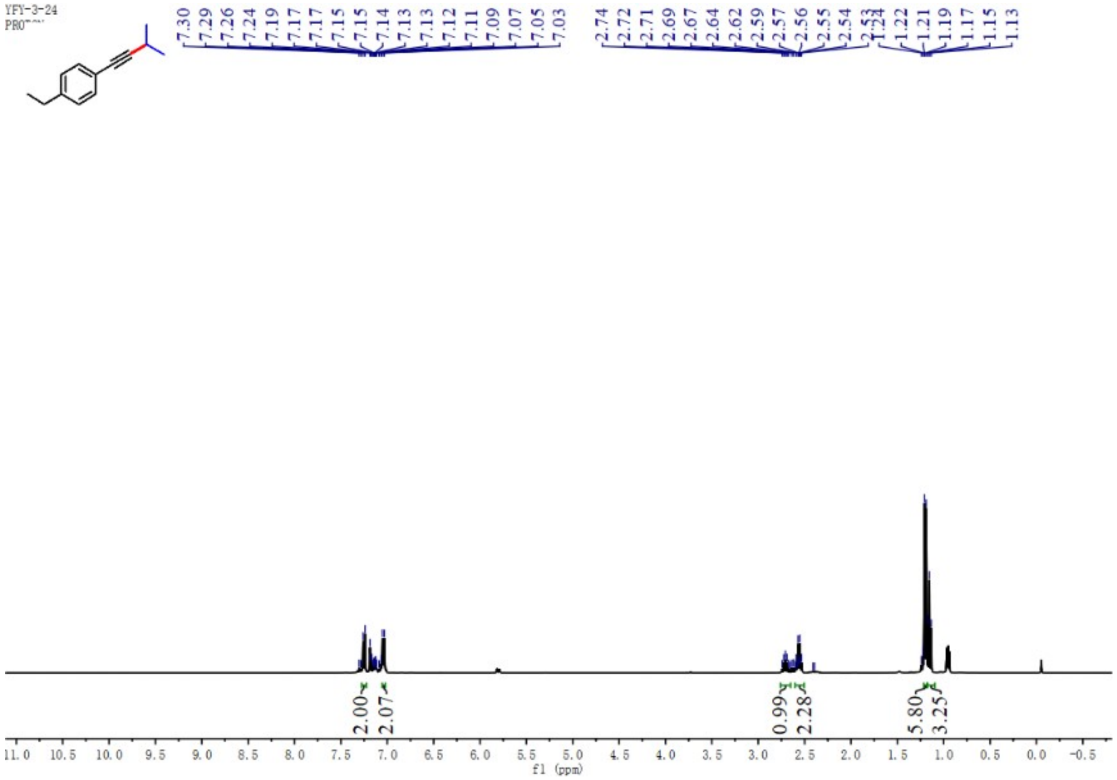
^{1}H NMR spectrum of compound **23**



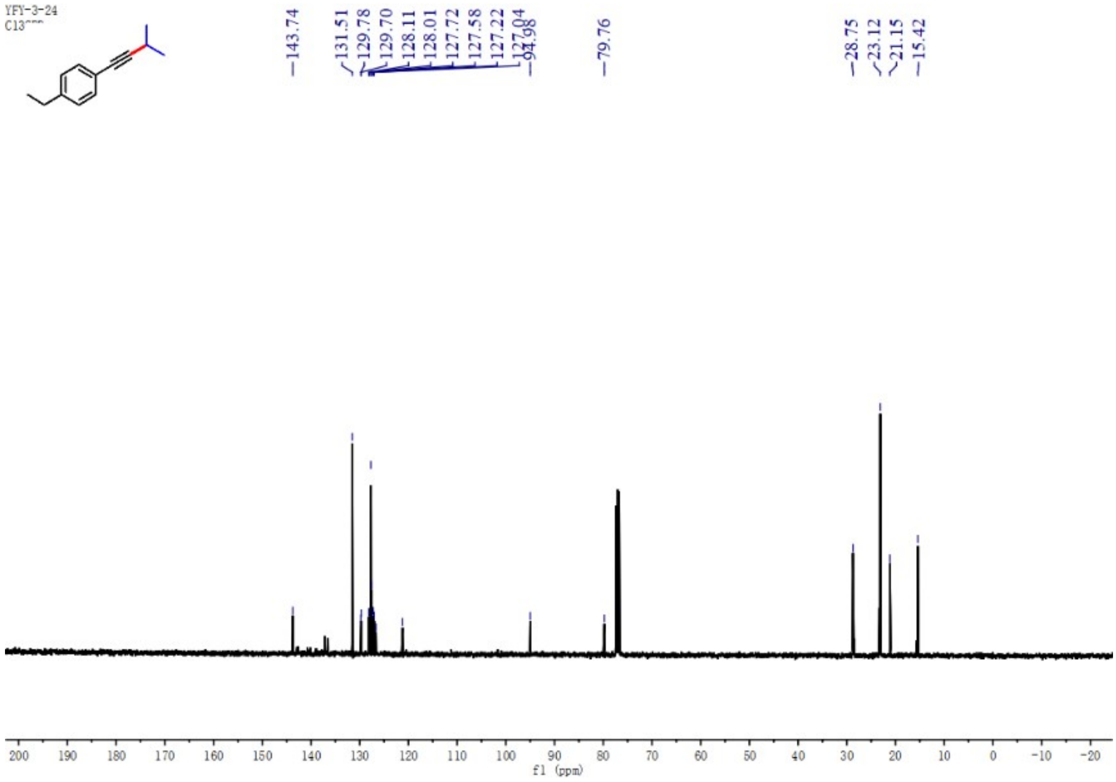
^{13}C NMR spectrum of compound **23**



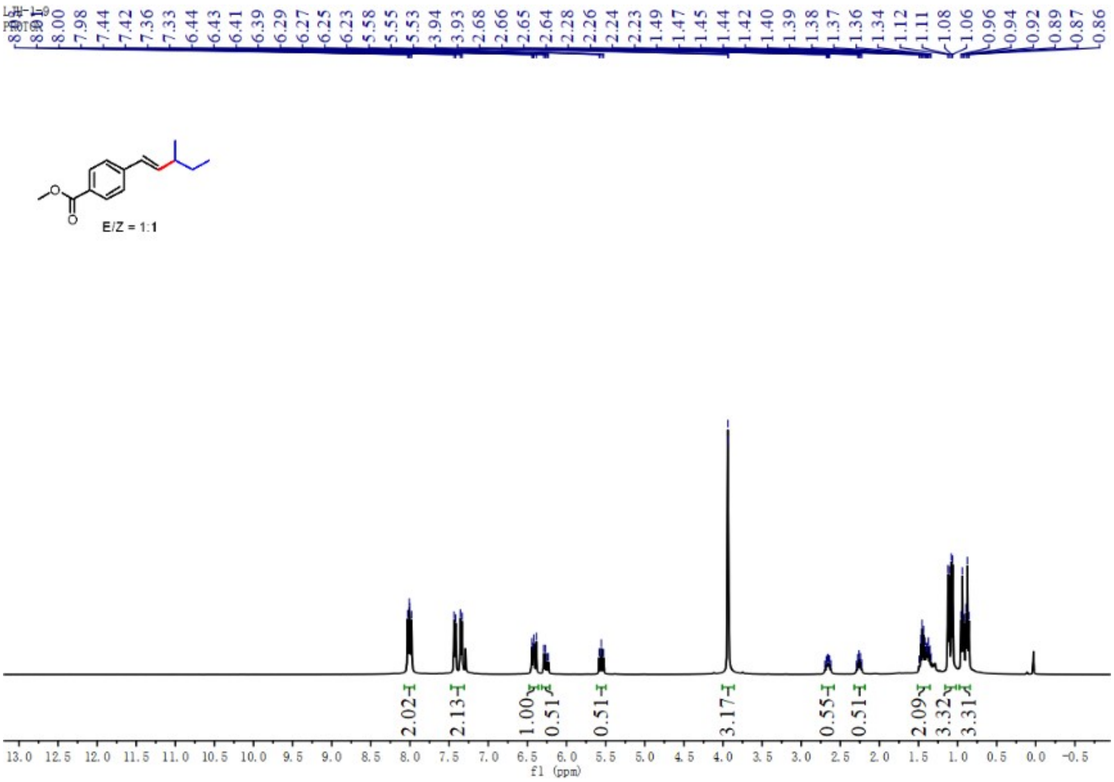
^{1}H NMR spectrum of compound **24**



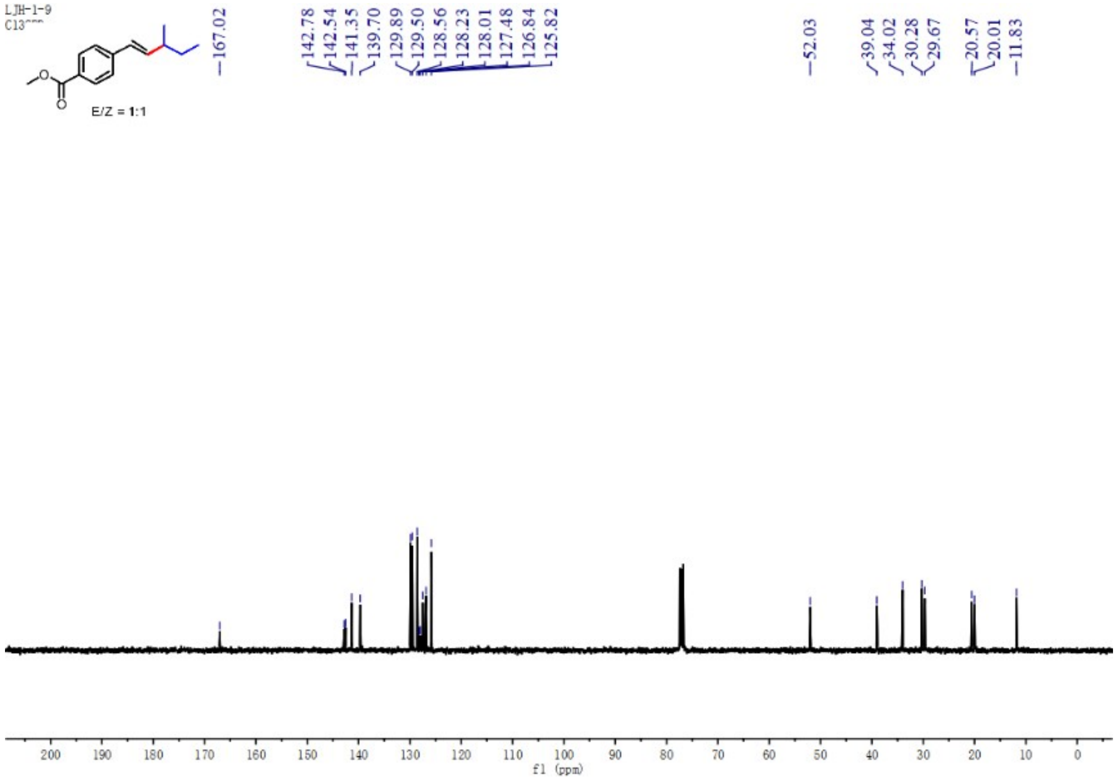
^{13}C NMR spectrum of compound **24**



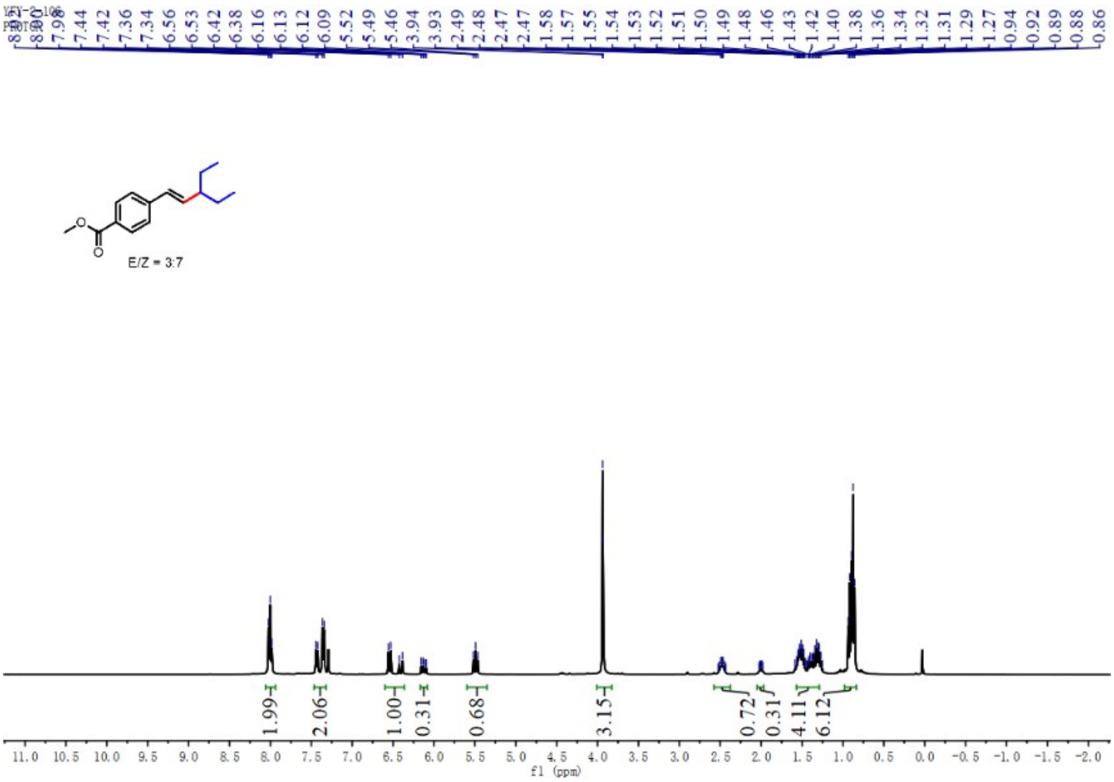
^{1}H NMR spectrum of compound **27**



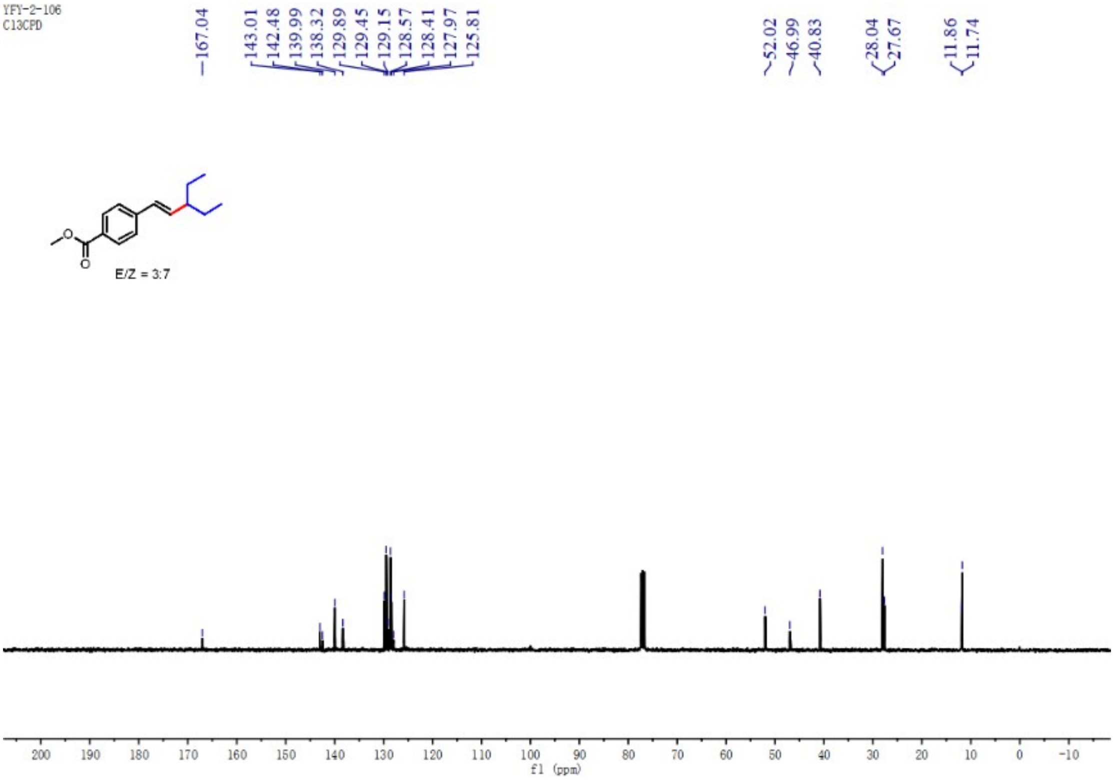
^{13}C NMR spectrum of compound **27**



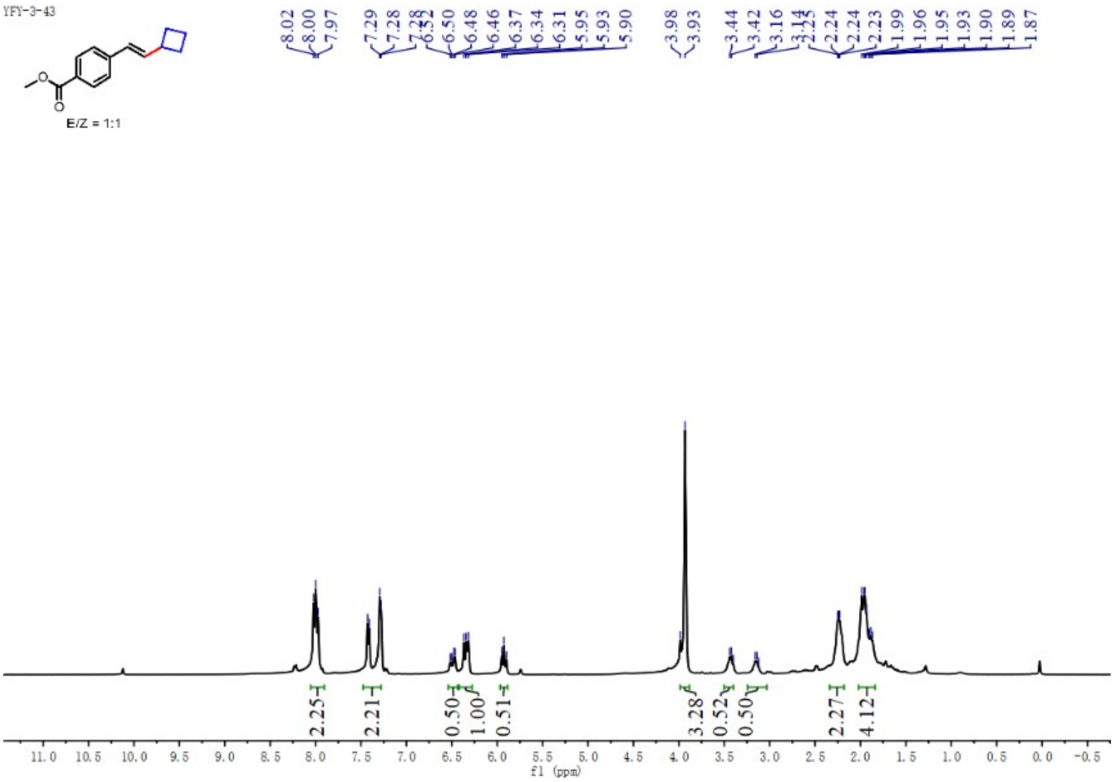
^{1}H NMR spectrum of compound **28**



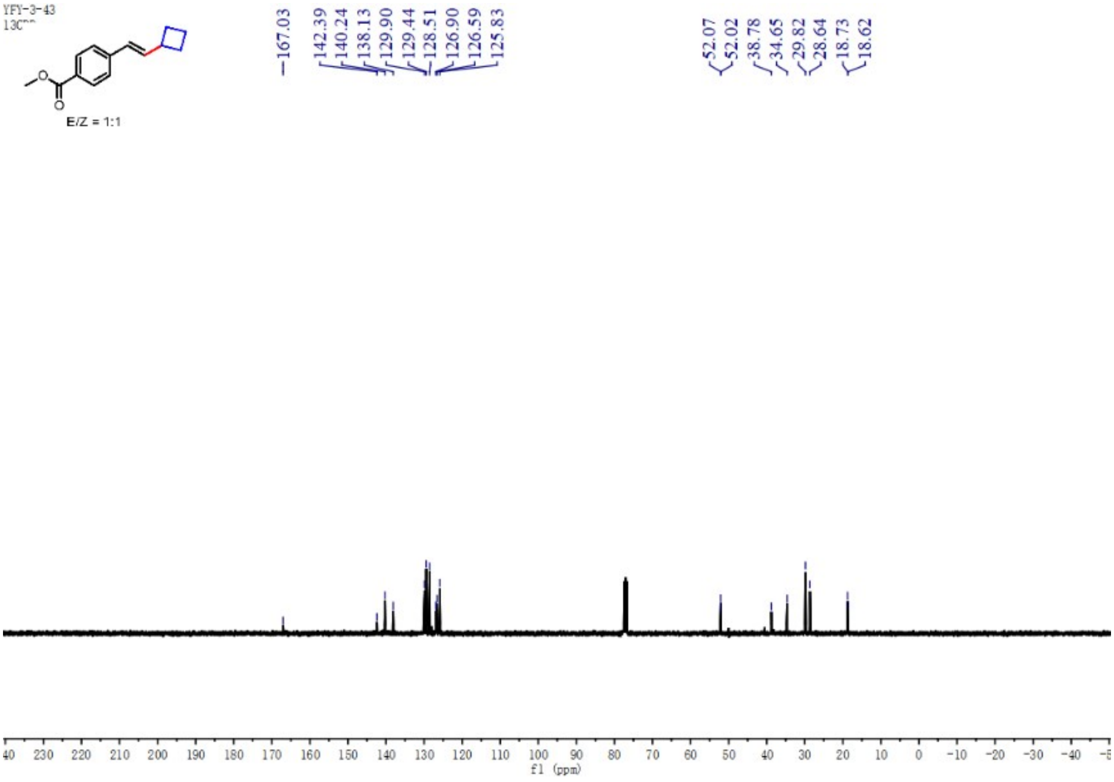
^{13}C NMR spectrum of compound **28**



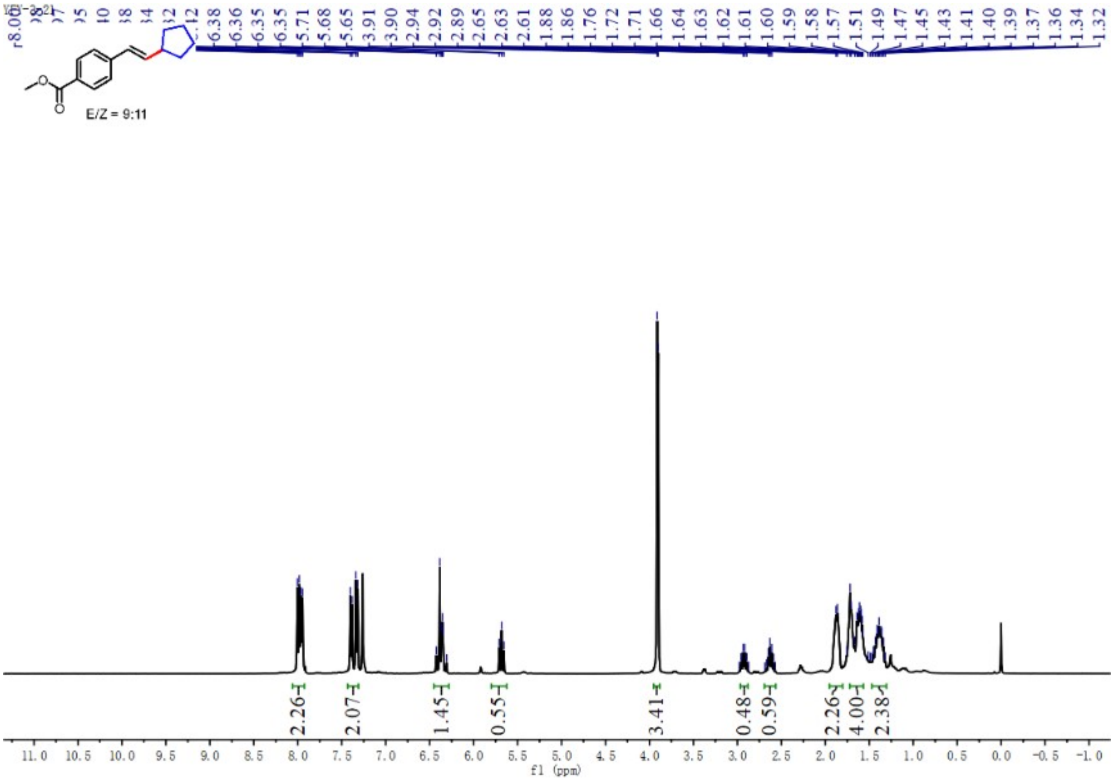
^1H NMR spectrum of compound **29**



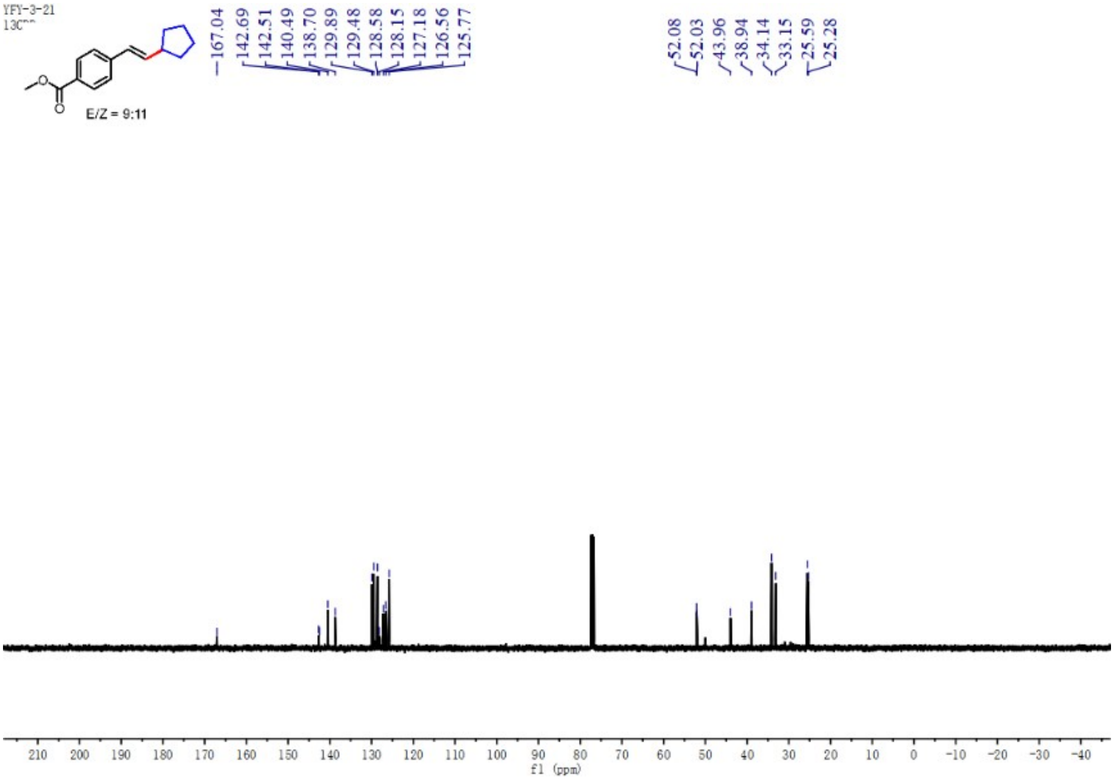
^{13}C NMR spectrum of compound **29**



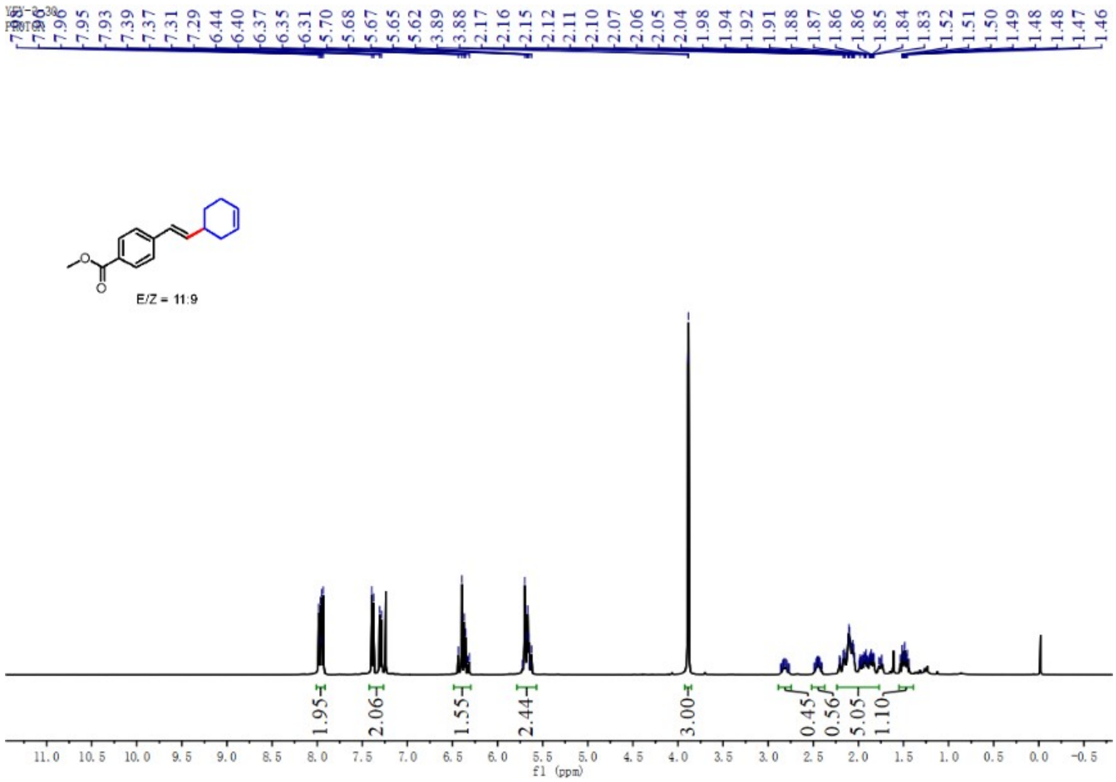
^{1}H NMR spectrum of compound **30**



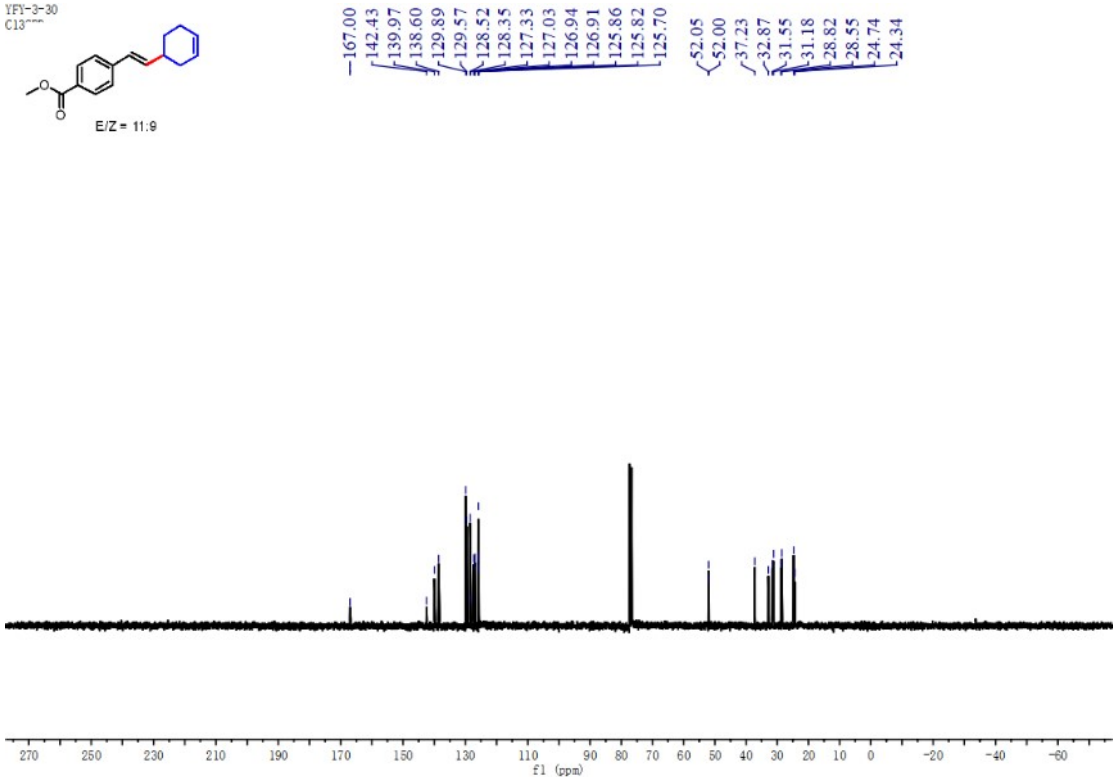
^{13}C NMR spectrum of compound **30**



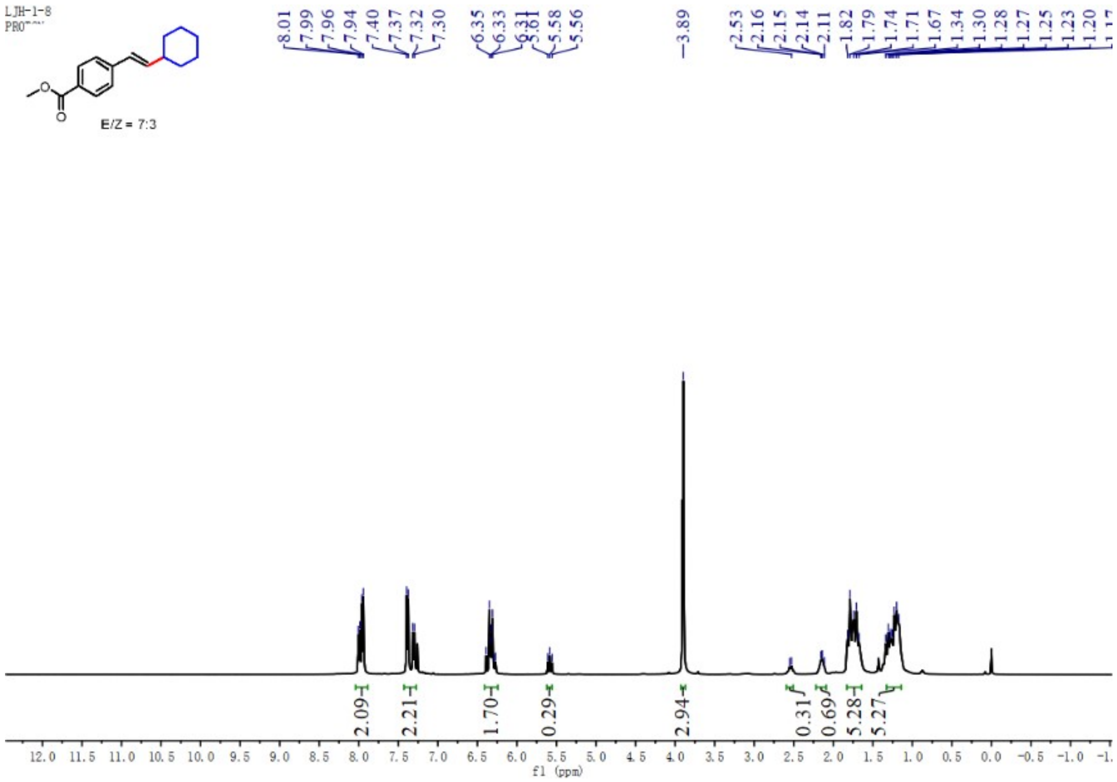
^{1}H NMR spectrum of compound **31**



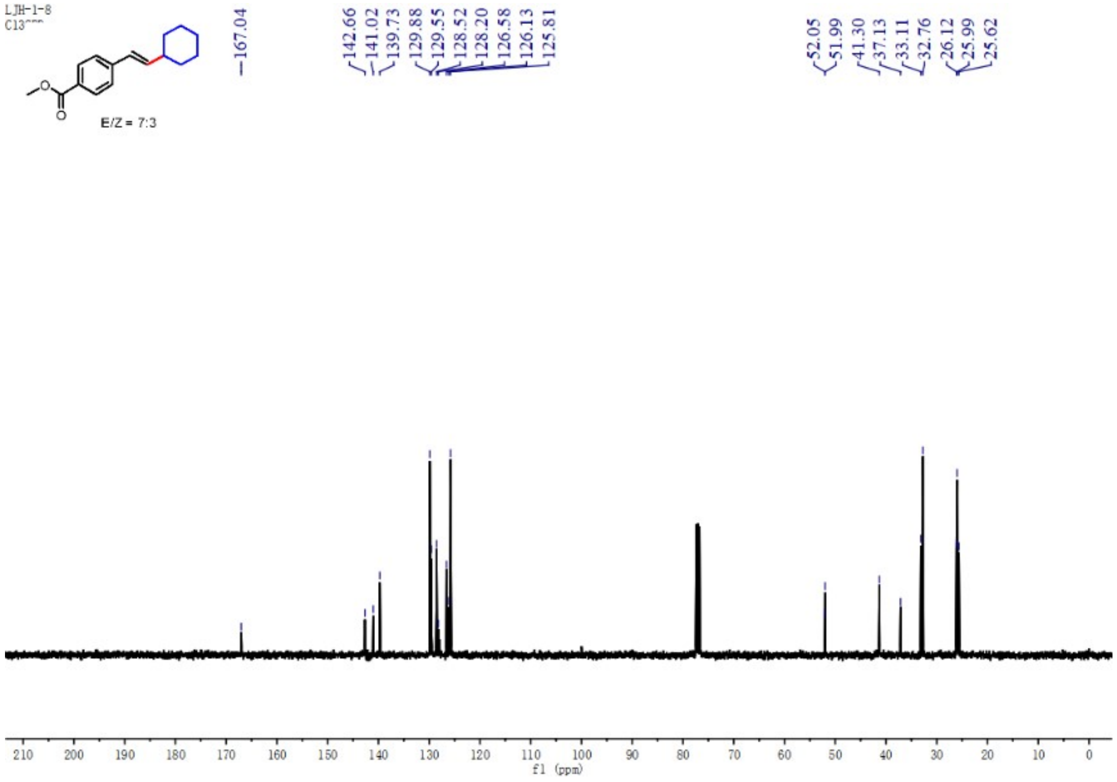
^{13}C NMR spectrum of compound **31**



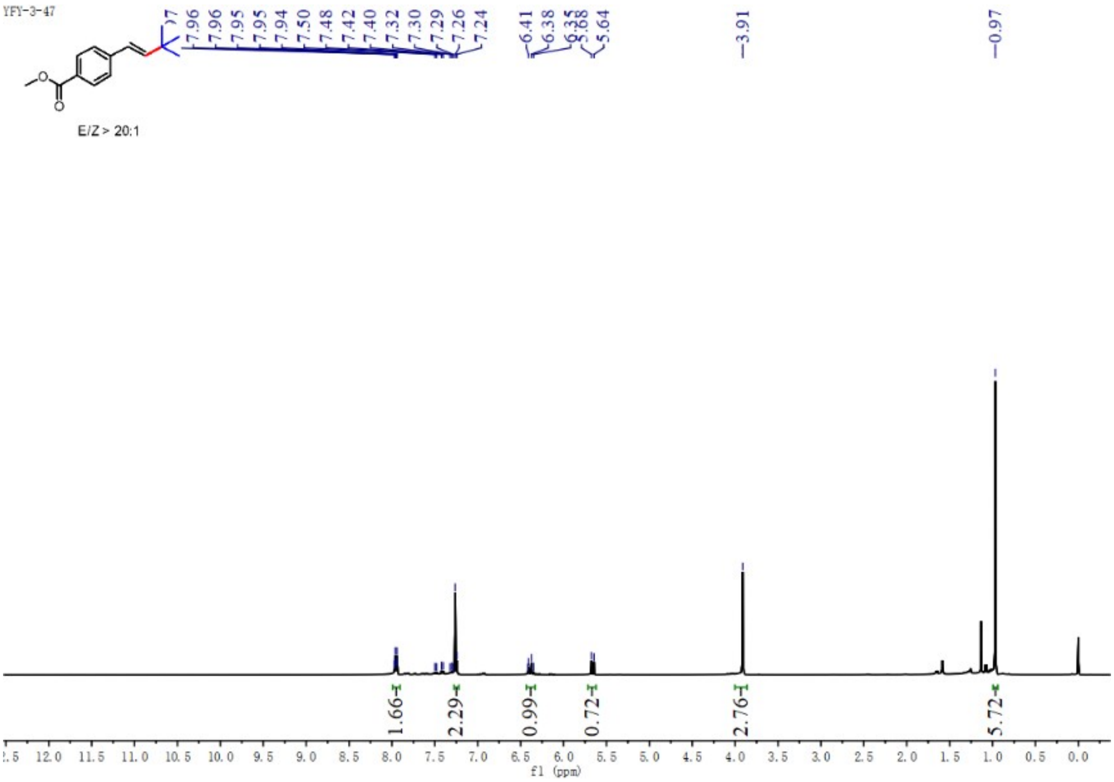
^{1}H NMR spectrum of compound **32**



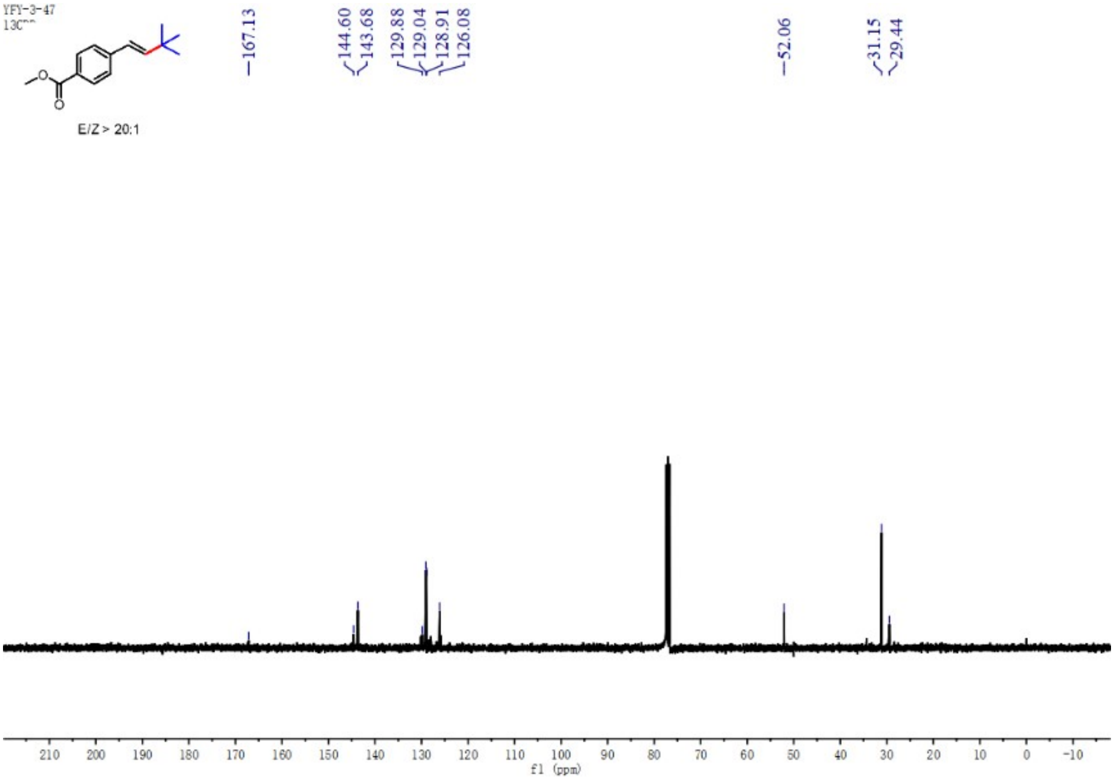
^{13}C NMR spectrum of compound **32**



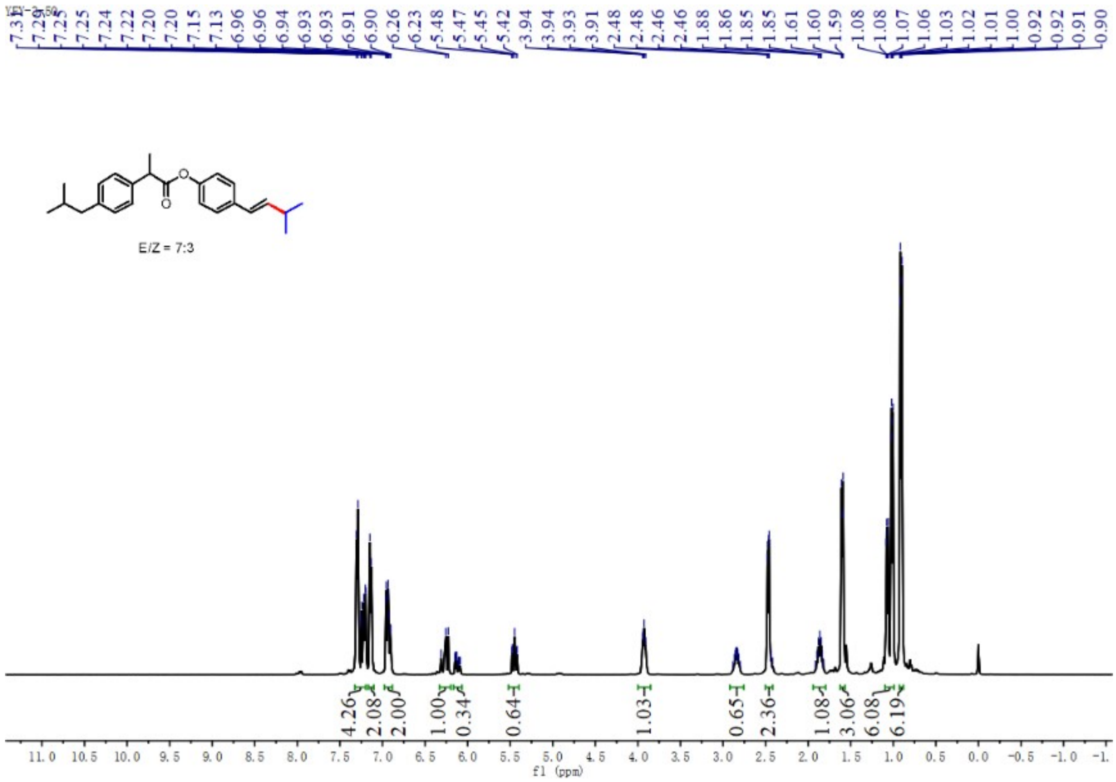
^{1}H NMR spectrum of compound **33**



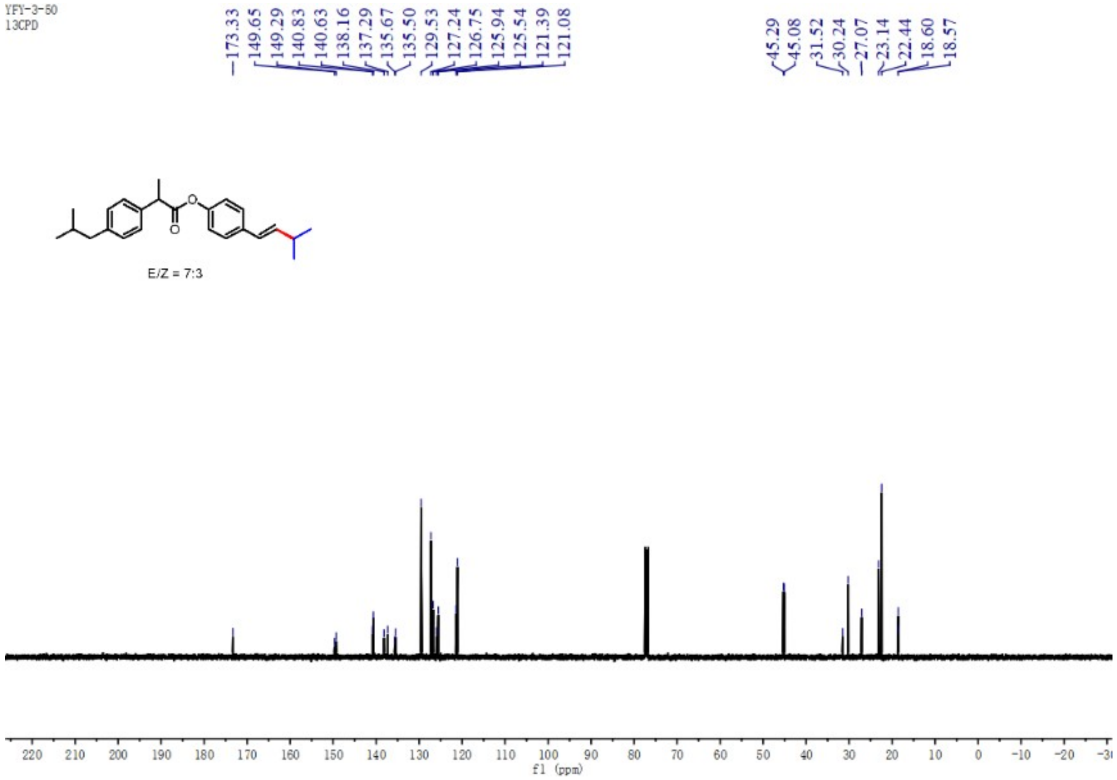
^{13}C NMR spectrum of compound **33**



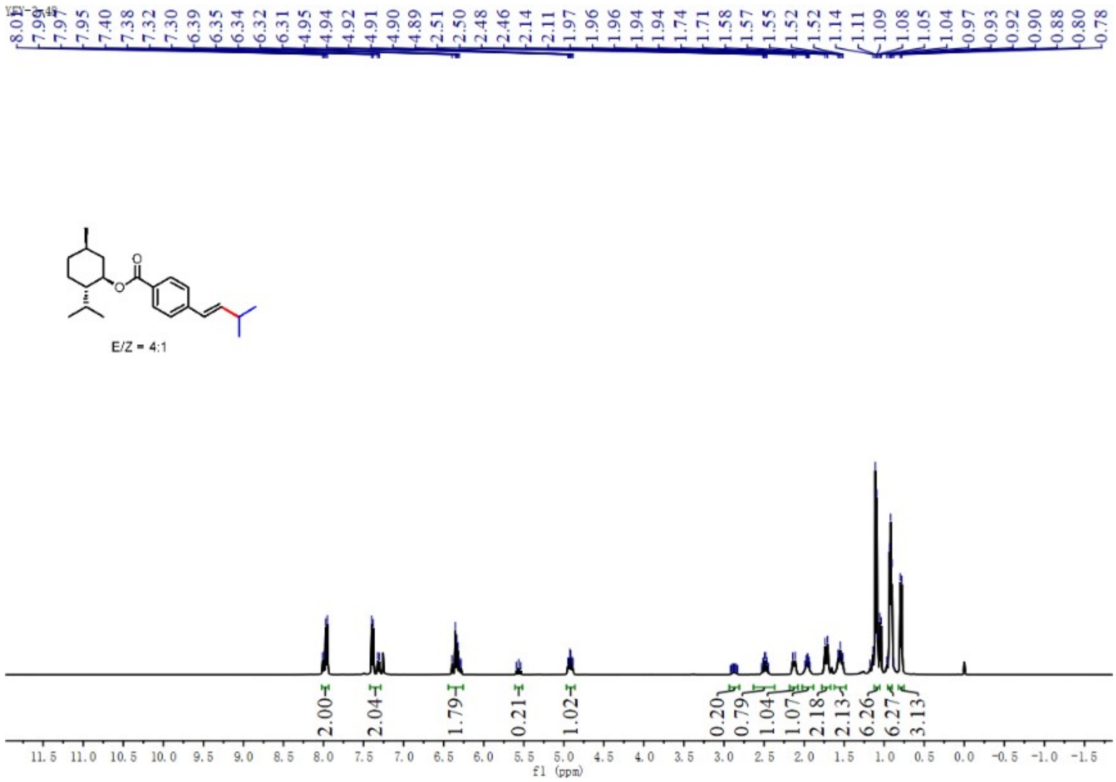
^{1}H NMR spectrum of compound **34**



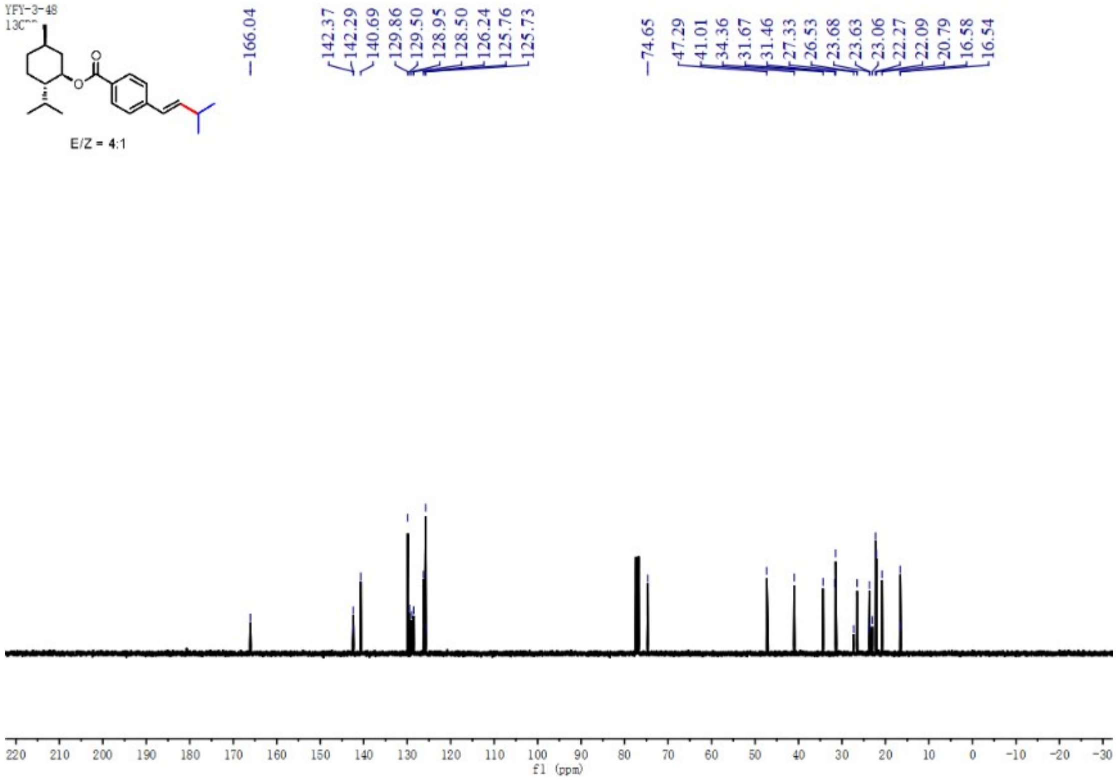
^{13}C NMR spectrum of compound **34**



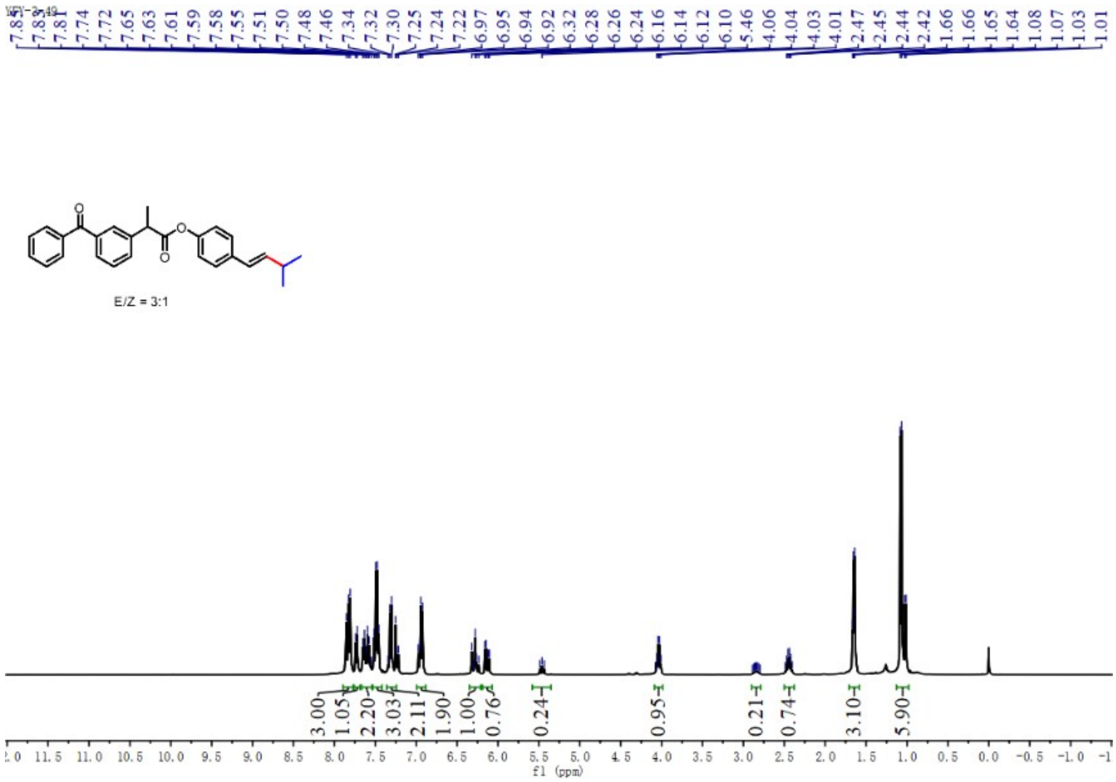
^{1}H NMR spectrum of compound **35**



^{13}C NMR spectrum of compound **35**



^{1}H NMR spectrum of compound **36**



^{13}C NMR spectrum of compound **36**