Electronic Supplementary Material (ESI) for Chemical Communications.

Photoredox Catalysis Enabled Alkylation of Alkenyl Carboxylic Acids with *N*‐(Acyloxy)phthalimide *via* Dual Decarboxylation

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1. General Information

All reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity≥99.999%) unless otherwise mentioned. Commercial reagents were purchased from Energy Chemical and TCI. Redox active esters were prepared according to the previous reports (*J. Am. Chem. Soc.* 2016, ***138***, 2174–2177; *Green. Chem.* 2016, ***18***, 4743–4749; *J. Org. Chem.* 2015, ***80***, 6025–6030).^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Data for ^{1}H-NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Data for ^{13}CNMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). HRMS was recorded on a Waters™ Q-TOF Premier and a Thermo Scientific™ LTQ Orbitrap XL™ Hybrid Ion Trap Orbitrap Mass Spectrometer.

2. Experimental Procedures and Spectral Data

2.1 Experimental Procedures

General Procedure A

Cinnamic acid (1.0 equiv., 0.2 mmol), redox active ester (1.5 equiv., 0.3 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (1.0 mol %, 1.5 mg) and DABCO (0.5 equiv., 11.2 mg) were placed in a Schlenk tube (10 mL) equipped with a stirring bar. The tube was evacuated and filled with argon (three times). Then, anhydrous *N*,*N*-dimethylacetamide (DMA, 2.0 mL) was added via a syringe under argon atmosphere. The resulting reaction mixture was stirred under the irradiation of a 36 W Blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 12 h. After the reaction was completed, the mixture was quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (petroleum ether).

General Procedure B

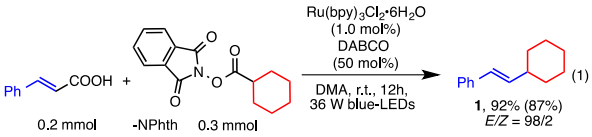
Cinnamic acid (1.0 equiv., 0.2 mmol), **redox active ester (2.0 equiv., 0.4 mmol)**, $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (1.0 mol %, 1.5 mg) and DABCO (0.5 equiv., 11.2 mg) were placed in a Schlenk tube (10 mL) equipped with a stirring bar. The tube was evacuated and filled with argon (three times). Then, anhydrous *N*,*N*-dimethylacetamide (DMA, 2.0 mL) was added via a syringe under argon atmosphere. The resulting reaction mixture was stirred under the irradiation of a 36 W Blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 12 h. After the reaction was completed, the mixture was quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (petroleum ether).

General Procedure C

Cinnamic acid (1.0 equiv., 0.2 mmol), redox active ester (1.5 equiv., 0.3 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (1.0 mol %, 1.5 mg) and **DABCO (1.0 equiv., 22.4 mg)** were placed in a Schlenk tube (10 mL) equipped with a stirring bar. The tube was evacuated and filled with argon (three times). Then, anhydrous *N*,*N*-dimethylacetamide (DMA, 2.0 mL) was added via a syringe under argon atmosphere. The resulting reaction mixture was stirred under the irradiation of a 36 W Blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 12 h. After the reaction was completed, the mixture was quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (petroleum ether).

2.2 Screen of Reaction Parameters

Table S1. Screen of reaction parameters



entry	variation from standard conditions	yield (%)
1	dioxane used instead of DMA	trace
2	DCE used instead of DMA	trace
3	without DABCO	< 5%
4	DIPEA (50 mol%) used instead of DABCO (50 mol%)	45%
5	Et_3N (50 mol%) used instead of DABCO (50 mol%)	70%
6	TMEDA (50 mol%) used instead of DABCO (50 mol%)	37%
7	DMAP (50 mol%) used instead of DABCO (50 mol%)	< 5%
8	DBU (50 mol%) used instead of DABCO (50 mol%)	25%
9	DABCO (25 mol%) was used	61%
10	without $Ru(bpy)_3Cl_2•6H_2O$	0%
11	without irradiation of blue-LEDs	0%

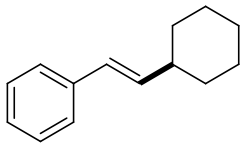
Reaction conditions: Cinnamic acid (0.2 mmol), redox active ester (0.3 mmol) and $Ru(bpy)_3Cl_2•6H_2O$ (0.002 mmol) in solvent (2 mL) irradiated by 36 W blue LEDs for 12 h under Ar. Yields reported are GC yields.

The alkylation product was obtained in 87% isolated yield upon a simple column chromatography. Although we also discovered that iridium based photoredox catalyst [$Ir(ppy)_3$] is effective for this transformation, while in albeit low yield (60%) and selectivity (*E*/*Z* = 16:1). Several reports revealed that iridium base photoredox catalyst can catalyze *E* to *Z* isomerization of styrene derivatives that may deteriorate the stereoselectivity of our desired product.[20] The relatively low cost of the ruthenium base photoredox catalyst and the high stereoselectivity making us to select $Ru(bpy)_3Cl_2•6H_2O$ as optimal catalyst to further develop this reaction. Some factors have significant influence on the reaction outcomes are demonstrates in Table 1. The reaction efficiency is highly solvent dependent. Amide solvent is the best choice while the reaction does not proceed in ether and chlorinated alkane solvent (entry 1 and entry 2). The reaction performed in the absence of DABCO cannot deliver the desired product, revealing the essential role of DABCO in the catalytic cycle (vide infra). Since amine additive plays a crucial role to determine the reaction

outcomes, we decided to test various amines instead of DABCO to find the correlation of amine structure with reactivity. Using acyclic tertiary amine such as triethyl amine (50 mol%), *N*-diisopropylethylamine (DIPEA, 50 mol%), and tetramethylethylenediamine (TMEDA) instead of DABCO all gave reduced yields. Using *N*,*N*-dimethyl-4-aminopyridine (DMAP, 50 mol%) instead of DABCO gave the desired product only in trace amount, revealing the effect of DABCO is not only a base to deprotonate carboxylic acids. When 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 50 mol%) was used, only a yield of 25% of desired product was detected. Reduction of the amount of DABCO to 25 mol% caused a decrease in product yield. From these results we realized that DABCO ($E_{1/2}$ = 0.6 V *vs* SCE) may acted as a single electron transfer catalyst in the catalytic cycle by oxidation by the photoredox catalyst [the redox potential of $Ru(bpy)_3Cl_2•6H_2O$ $E_{1/2}^{*II/I}$ = 0.77 V *vs* SCE, $E_{1/2}^{II/I}$ = –1.33 V *vs* SCE; $E_{1/2}^{III/II}$ = 1.29 V *vs* SCE, $E_{1/2}^{III/*II}$ = -0.81 V *vs* SCE] to generate nitrogen radical cation. The ineffectiveness of DMAP and DBU maybe attributed by its high oxidative potential. (eg. for DBU $E_{1/2}$ = 1.28 V *vs* SCE) Control experiments revealed that the reaction neither proceed in the absence of irradiation nor in the absence of photoredox catalyst (entry 10 and entry 11).

2.3 Spectral Data

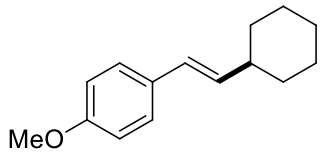
(*E*)-(2-cyclohexylvinyl) benzene (1)[1][CAS Number:18869-27-7]: Following general procedure A, The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 87 % yield as a colorless liquid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.9 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 6.9 Hz, 1H), 2.21 –

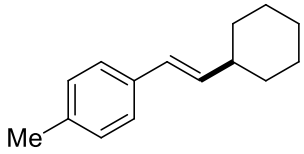
2.05 (m, 1H), 1.85 – 1.63 (m, 5H), 1.40 – 1.10 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.0, 128.6, 127.3, 126.8, 126.1, 41.3, 33.1, 26.3, 26.2.

(*E*)-1-(2-cyclohexylvinyl)-4-methoxybenzene (2)[1] [CAS Number:104151-26-0]: Following general procedure A, The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 88 % yield as a colorless liquid.



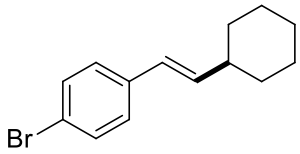
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.28 (d, *J* = 16.0 Hz, 1H), 6.03 (dd, *J* = 16.0, 7.0 Hz, 1H), 3.79 (s, 3H), 2.13 – 2.06 (m, 1H), 1.84 – 1.64 (m, 5H), 1.38 – 1.11 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 134.9, 131.0, 127.1, 126.6, 114.0, 55.4, 41.3, 33.2, 26.3, 26.2

(*E*)-1-(2-cyclohexylvinyl)-4-methylbenzene (3)[1][CAS Number: 61153-38-6]: Following general procedure A, The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 90 % yield as a colorless liquid.



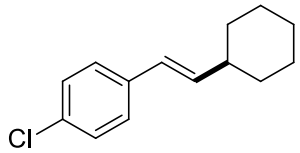
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8 Hz, 2H), 7.08 (d, *J* = 4 Hz, 2H), 6.30 (d, *J* = 16.0 Hz, 1H), 6.11 (dd, *J* = 16.0, 6.9 Hz, 1H), 2.31 (s, 3H), 2.13 – 2.07 (m, 1H), 1.81 – 1.66 (m, 5H), 1.36 – 1.12 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 136.0, 135.4, 129.3, 127.1, 125.9, 41.3, 33.2, 26.3, 26.2, 21.3.

(*E*)-1-bromo-4-(2-cyclohexylvinyl) benzene (4)[2][CAS Number:57438-80-9]: Following general procedure A, The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 78 % yield as a colorless liquid.



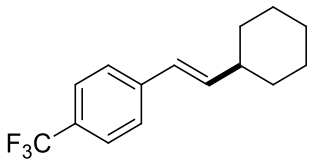
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.27 (d, *J* = 16.0 Hz, 1H), 6.16 (dd, *J* = 16.0, 6.7 Hz, 1H), 2.20 – 2.04 (m, 1H), 1.82 – 1.64 (m, 5H), 1.34 – 1.14 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.1, 131.6, 127.6, 126.2, 120.4, 41.3, 33.0, 26.3, 26.1.

(*E*)-1-chloro-4-(2-cyclohexylvinyl) benzene (5)[2][CAS Number:352226-75-6]: Following general procedure A, The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 79 % yield as a colorless liquid.



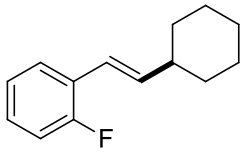
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.12 (m, 4H), 6.28 (d, *J* = 16.1 Hz, 1H), 6.14 (dd, *J* = 16.0, 6.8 Hz, 1H), 2.16 – 2.05 (m, 1H), 1.86 – 1.62 (m, 5H), 1.36 – 1.10 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 136.7, 132.3, 128.7, 127.3, 126.2, 41.3, 33.0, 26.3, 26.2.

(*E*)-1-(2-cyclohexylvinyl)-4-(trifluoromethyl) benzene (6)[1][CAS Number:1574277-10-3]: Following general procedure A, The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 68 % yield as a colorless liquid.



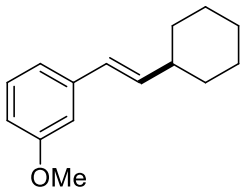
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.29 (d, *J* = 16.1 Hz, 1H), 6.19 (dd, *J* = 16.0, 6.6 Hz, 1H), 2.13 – 2.00 (m, 1H), 1.76 – 1.59 (m, 5H), 1.28 – 1.08 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7 (d, *J* = 1.1 Hz), 139.7, 128.7 (d, *J* = 32.3 Hz), 126.3, 126.2, 125.5 (q, *J* = 3.8 Hz), 124.5 (d, *J* = 270 Hz),41.4, 32.9, 26.2, 26.1.

(*E*)-1-(2-cyclohexylvinyl)-2-fluorobenzene (7)[2][CAS Number:1472064-46-2]: Following general procedure A, The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 73 % yield as a colorless liquid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 8 Hz, 1H), 7.17 – 7.12 (m, 1H), 7.07 – 6.97 (m, 2H), 6.51 (d, *J* = 16.2 Hz, 1H), 6.24 (dd, *J* = 16.1, 7.0 Hz, 1H), 2.14 (m, 1H), 1.85 – 1.64 (m, 5H), 1.37 – 1.13 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1 (d, *J* = 247 Hz), 139.5 (d, *J* = 4.0 Hz), 128.0 (d, *J* = 8.3 Hz), 127.0 (d, *J* = 4.1 Hz), 125.9 (d, *J* = 12.2 Hz), 124.1 (d, *J* = 3.5 Hz), 120.0 (d, *J* = 3.9 Hz), 115.7 (d, *J* = 22 Hz), 41.7, 33.0, 26.3, 26.2

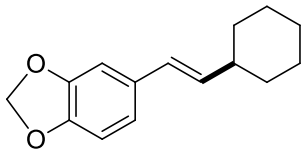
(*E*)-1-(2-cyclohexylvinyl)-3-methoxybenzene (8)[1][CAS Number:1472064-46-2]: Following general procedure A, The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 86 % yield as a colorless liquid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8 Hz, 1H), 6.96 (d, *J* = 8 Hz, 1H), 6.90 (s, 1H), 6.77 – 6.76 (m, 1H), 6.33 (d, *J* = 16 Hz, 1H), 6.22 – 6.16 (m, 1H), 3.82 (s, 1H), 2.16 – 2.09 (m, 1H), 1.83 – 1.68 (m, 5H), 1.38 – 1.15 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 139.7, 137.3, 129.5, 127.2, 118.8, 112.5, 111.3, 55.3, 41.3, 33.1,26.3, 26.2

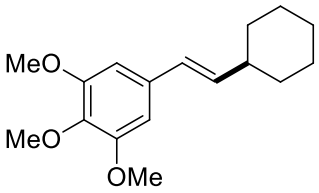
(*E*)-5-(2-cyclohexylvinyl) benzo[d] [1, 3] dioxole (9) [CAS Number:74131-63-8]: Following general procedure A, The product was purified by flash column

chromatography on silica gel (ethyl acetate: petroleum ether = 20: 1), obtained in 86 % yield as a colorless liquid.



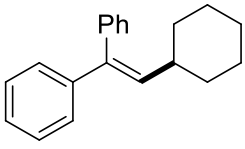
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 1H), 6.74 (q, *J* = 8.1 Hz, 2H), 6.25 (d, *J* = 15.9 Hz, 1H), 6.00 (dd, *J* = 15.9, 7.0 Hz, 1H), 5.92 (s, 2H), 2.12 – 2.05 (m, 1H), 1.79 – 1.65 (m, 5H), 1.35 – 1.10 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 146.6, 135.3, 132.7, 126.9, 120.4, 108.3, 105.5, 101.0, 41.2, 33.2, 26.3, 26.2. HRMS (ESI) Calcd for $C_{19}H_{15}O_2^+$ $[M+H]^+$: 231.1380, found: 231.1388.

(*E*)-5-(2-cyclohexylvinyl)-1, 2, 3-trimethoxybenzene (10)[3] [CAS Number:1831911-97-7]: Following general procedure A, The product was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 50: 1), obtained in 81 % yield as a white solid.



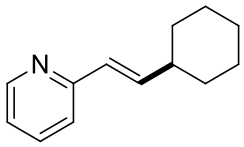
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (s, 2H), 6.27 (d, *J* = 15.9 Hz, 1H), 6.09 (dd, *J* = 15.9, 6.9 Hz, 1H), 3.87 (s, 6H), 3.83 (s, 3H), 2.15 – 2.08 (m, 1H), 1.84 – 1.66 (m, 5H), 1.36 – 1.14 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 137.2, 136.5, 133.9, 127.2, 103.0, 61.0, 56.1, 41.2, 33.1, 26.3, 26.2, 25.0.

(2-cyclohexylethene-1, 1-diyl) dibenzene (11)[3][CAS Number:91083-83-9]: Following general procedure A, The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 43 % yield as a white solid.



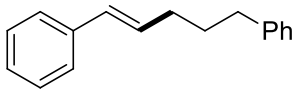
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 3H),7.25 – 7.17 (m, 7H), 5.90 (d, *J* = 10.1 Hz, 1H), 2.27 – 1.97 (m, 1H), 1.72 – 1.56 (m, 5H), 1.27 – 1.07 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 140.7, 139.7, 136.1, 129.9, 128.3, 128.2, 127.3, 126.9, 126.8, 38.4, 33.5, 26.1, 25.7.

(*E*)-2-(2-cyclohexylvinyl) pyridine (12)[1][CAS Number:1624610-64-5]: Following general procedure A, The product was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 20: 1), obtained in 61 % yield as a white solid.



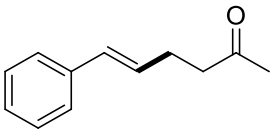
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.2 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.14 – 7.03 (m, 1H), 6.70 (dd, *J* = 15.9, 6.9 Hz, 1H), 6.45 (d, *J* = 16.9 Hz, 1H), 2.23 – 2.15 (m, 1H), 1.87 – 1.65 (m, 5H), 1.36 – 1.16 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 149.4, 141.4, 136.3, 127.4, 41.0, 32.6, 26.1, 26.0.

(*E*)-Pent-1-ene-1, 5-diyldibenzene (14)[4] [CAS Number:97455-11-3]: Following general procedure B, The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 73 % yield as a white solid.



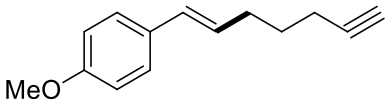
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 4H), 7.22 – 7.14 (m, 4H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.31 – 6.14 (m, 1H), 2.66 (t, *J* = 7.7 Hz, 2H), 2.25 (q, *J* = 7.1 Hz, 2H), 1.89 – 1.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 137.9, 130.7, 130.3, 128.61, 128.60, 128.4, 127.0, 126.1, 125.9, 35.5, 32.7, 31.2.

(*E*)-7-phenylhept-6-en-2-one (15)[5][CAS Number:33599-88-1]: Following general procedure B, The product was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 20: 1), obtained in 61 % yield as a colorless liquid.



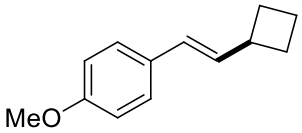
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 4H), 7.20 (t, *J* = 8 Hz, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.27 – 6.05 (m, 1H), 2.61 (t, *J* = 7.3 Hz, 2H), 2.48 (q, *J* = 7.1 Hz, 2H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 137.5, 130.9, 128.9, 128.6, 127.2, 126.1, 43.3, 30.2, 27.2.

(*E*)-1-(hept-1-en-6-yn-1-yl)-4-methoxybenzene (16) Following general procedure B, The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 67 % yield as a colorless liquid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.36 (d, *J* = 15.8 Hz, 1H), 6.15 – 5.90 (m, 1H), 3.80 (s, 3H), 2.37 – 2.18 (m, 4H), 1.98 (t, *J* = 2.6 Hz, 1H), 1.70 (q, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 130.6, 130.2, 127.5, 127.2, 114.0, 84.6, 68.6, 55.4, 32.0, 28.4, 18.0. HRMS (ESI) Calcd for $C_{14}H_{17}O^+$ $[M+H]^+$: 201.1274, found: 201.1271.

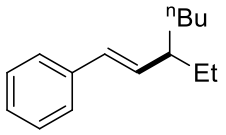
(*E*)-1-(2-cyclobutylvinyl)-4-methoxybenzene (17) Following general procedure A, The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 87 % yield as a colorless liquid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.2 Hz, 2H), 6.25 (d, *J* = 15.9 Hz, 1H), 6.18 (dd, *J* = 15.8, 6.4 Hz, 1H), 3.79 (s, 3H), 3.17 – 2.98 (m, 1H),

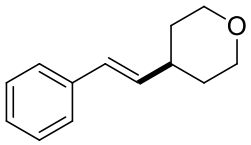
2.21 – 2.10 (m, 2H), 1.98 – 1.78 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 133.3, 130.7, 127.2, 127.1, 114.0, 55.4, 38.9, 29.0, 18.7. HRMS (ESI) Calcd for $C_{13}H_{17}O^+$ $[M+H]^+$: 189.1274, found: 189.1278.

(*E*)-(3-ethylhept-1-en-1-yl) benzene (18)[6][CAS Number:1580471-25-5]: Following general procedure A, The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 76 % yield as a colorless liquid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.11 (m, 5H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.95 (dd, *J* = 15.8, 9.0 Hz, 1H), 2.01 (m, 1H), 1.54 – 1.21 (m, 8H), 0.88 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 135.8, 129.7, 128.6, 126.8, 126.1, 45.3, 35.0, 29.8, 28.4, 23.0, 14.3, 12.0.

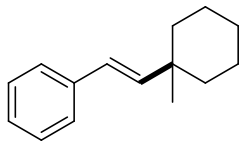
(*E*)-4-styryltetrahydro-2H-pyran (19)[6][CAS Number:592510-37-7]: Following general procedure A, The product was purified by flash column chromatography on silica gel(ethyl acetate: petroleum ether = 50: 1), obtained in 79 % yield as a colorless liquid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8 Hz, 2H), 7.31 – 7.28(m, 2H), 7.22 – 7.18(m, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.16 (dd, *J* = 16.0, 6.8 Hz, 1H), 4.11 – 3.91 (m, 2H), 3.46 (td, *J* = 11.7, 2.0 Hz, 2H), 2.38 (m, 1H), 1.75 – 1.48 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 134.7, 128.7, 128.4, 127.2, 126.2, 67.9, 38.5, 32.8.

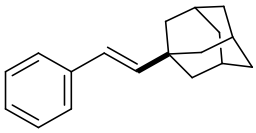
(*E*)-(2-(1-methylcyclohexyl) vinyl) benzene (20)[7][CAS Number:1788861-73-3]: Following general procedure A, The product was purified by flash column

chromatography on silica gel (petroleum ether), obtained in 76 % yield as a white solid.



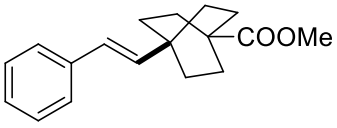
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8 Hz, 2H),7.31 – 7.27 (m, 2H), 7.18 (t, *J* = 8 Hz, 1H), 6.25 (d, *J* = 16.3 Hz, 1H), 6.14 (d, *J* = 16.4 Hz, 1H), 1.56 – 1.26 (m, 10H), 0.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 138.4, 128.6, 126.8, 126.07, 126.05, 38.1, 36.3, 27.7, 26.5, 22.6.

(3r, 5r, 7r)-1-((*E*)-styryl) adamantane (21)[6][CAS Number:70624-80-5]: Following general procedure A, The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 81 % yield as a white solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.1 Hz, 1H), 6.24 (d, *J* = 16.3 Hz, 1H), 6.11 (d, *J* = 22.5 Hz, 1H), 2.02 (s, 3H), 1.78 – 1.66 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 138.3, 128.6, 126.8, 126.1, 124.6, 42.4, 37.0, 35.3, 28.6.

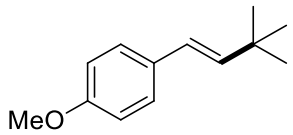
(*E*)-methyl 4-styrylbicyclo [2.2.2] octane-1-carboxylate (22) Following general procedure A, The product was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 20: 1), obtained in 72 % yield as a white solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.6 Hz, 2H), 7.27 (dd, *J* = 13.1, 4.7 Hz, 2H), 7.18 (t, *J* = 7.1 Hz, 1H), 6.24 (d, *J* = 16.3 Hz, 1H), 6.12 (d, *J* = 16.3 Hz, 1H), 3.66 (s, 3H), 1.90 – 1.80 (m, 6H), 1.67 – 1.59 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

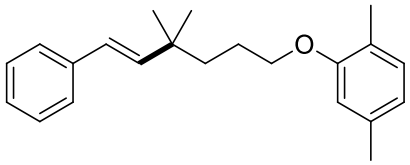
178.5, 139.3, 137.9, 128.6, 127.0, 126.1, 126.0, 51.8, 39.2, 33.4, 30.9, 28.5. HRMS (ESI) Calcd for $C_{18}H_{23}O_2^+$ $[M+H]^+$: 271.1693, found: 271.1687. M.p. 107-108 ºC.

(*E*)-1-(3,3-dimethylbut-1-en-1-yl)-4-methoxybenzene(23)[8] [CAS Number:79958-53-5]: Following general procedure A, The product was purified by flash column chromatography on silica gel (petroleum ether), obtained in 84 % yield as a colorless liquid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8 Hz, 2H), 6.84 (d, *J* = 8 Hz, 2H), 6.25 (d, *J* = 16.2 Hz, 1H), 6.12 (d, *J* = 16.1 Hz, 1H), 3.80 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 140.0, 131.0, 127.2, 124.0, 114.0, 55.4, 33.4, 29.8.

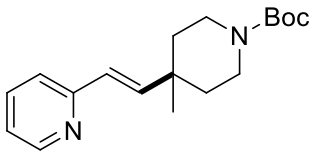
(*E*)-2-((4, 4-dimethyl-6-phenylhex-5-en-1-yl) oxy)-1, 4-dimethylbenzene (24) Following general procedure A, The product was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 50: 1), obtained in 71 % yield as a white solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8 Hz, 2H), 7.29 (t, *J* = 8 Hz, 2H), 7.21 – 7.18 (m, 1H), 6.98 (d, *J* = 8 Hz, 1H), 6.65 – 6.60 (m, 2H), 6.31 (d, *J* = 14.9 Hz, 1H), 6.19 (d, *J* = 16.2 Hz, 1H), 3.90 (t, *J* = 8 Hz, 2H), 2.28 (s, 3H), 2.18 (s, 3H), 1.80 – 1.73 (m, 2H), 1.58 – 1.54 (m, 2H), 1.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 140.4, 138.1, 136.6, 130.4, 128.6, 127.0, 126.23, 126.16, 123.7, 120.7, 112.1, 68.5, 39.5, 36.2, 27.4, 25.1, 21.6, 16.0. HRMS (ESI) Calcd for $C_{22}H_{29}O^+$ $[M+H]^+$: 309.2213, found: 309.2216. M.p. 101-103 ºC.

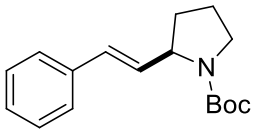
(*E*)-*tert*-butyl-4-methyl-4-(2-(pyridin-2-yl)vinyl)piperidine-1-carboxylate(25)

Following general procedure A, The product was purified by flash column chromatography on silica gel(ethyl acetate: petroleum ether = 20: 1), obtained in 52 % yield as a white solid.



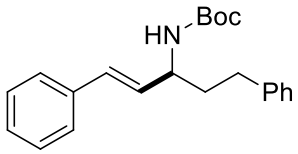
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.5 Hz, 1H), 7.63 (td, *J* = 7.7, 1.5 Hz, 1H), 7.31 – 7.22 (m, 1H), 7.12 (dd, *J* = 7.1, 5.1 Hz, 1H), 6.73 (d, *J* = 16.2 Hz, 1H), 6.46 (d, *J* = 16.2 Hz, 1H), 3.58 – 3.47 (m, 2H), 3.39 (m, 2H), 1.78 – 1.70 (m, 2H), 1.46 (m, 11H), 1.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 155.1, 149.4, 143.3, 136.8, 127.4, 122.0, 121.5, 79.4, 36.8, 35.2, 28.6, 26.7. HRMS (ESI) Calcd for $C_{18}H_{27}N_2O_2^+$ $[M+H]^+$: 303.2067, found: 303.2069. M.p. 55-56 °C.

(*E*)-*tert*-butyl 2-styrylpyrrolidine-1-carboxylate (26)[9][CAS Number:84193-86-2]: Following general procedure C, The product was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 20: 1), obtained in 68 % yield as a white solid.



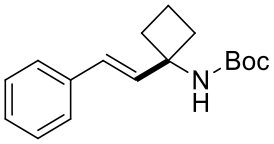
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H), 7.21 (t, *J* = 7.1 Hz, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.09 (dd, *J* = 15.7, 6.4 Hz, 1H), 4.43 (s, 1H), 3.54 – 3.32 (m, 2H), 2.12 – 2.04 (m, 4H), 1.96 – 1.75 (m, 3H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 137.1, 130.8, 129.5, 128.6, 127.3, 126.3, 79.3, 59.1, 46.3, 32.6, 28.6, 23.1.

(*E*)-*tert*-butyl (1, 5-diphenylpent-1-en-3-yl) carbamate (27) Following general procedure A, The product was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 20: 1), obtained in 62 % yield as a white solid.



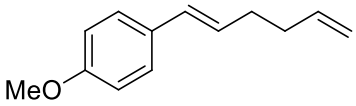
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.19 (m, 10H), 6.52 (d, J = 15.7 Hz, 1H), 6.13 – 6.08 (m, 1H), 4.62 (s, 1H), 4.32 (s, 1H), 2.70 (t, *J* = 7.7 Hz, 2H), 1.91 – 1.90 (m, 2H) (d, *J* = 7.1 Hz, 2H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 141.7, 136.9, 130.5, 130.4, 128.7, 128.6, 128.5, 127.7, 126.5, 126.1, 79.6, 52.5, 37.4, 32.4, 28.6. HRMS (ESI) Calcd for $C_{22}H_{28}NO_2^+$ $[M+H]^+$: 338.2115, found: 338.2118. M.p. 91-93 ºC.

(*E*)-*tert*-butyl (1-styrylcyclobutyl) carbamate (28) Following general procedure A, The product was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 20: 1), obtained in 51 % yield as a white solid.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.48 (t, 2H), 2.43 – 2.24 (m, 4H), 2.04 – 1.83 (m, 2H), 1.44 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 137.1, 133.5, 128.5, 127.3, 126.8, 126.4, 79.4, 57.1, 33.5, 28.4, 15.0. HRMS (ESI) Calcd for $C_{17}H_{24}NO_2^+$$[M+H]^+$: 274.1802, found: 274.1886. M.p. 89-91 ºC.

(*E*)-1-(hexa-1, 5-dien-1-yl)-4-methoxybenzene (29)[10][CAS Number: 270901-64-9]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 6.88 – 6.83 (m, 2H), 6.35 (d, *J* = 16.1 Hz, 1H), 6.12 – 6.05 (m, 1H), 5.90 – 5.82 (m, 1H), 5.02 (dd, *J* = 27.2, 14.0 Hz, 2H), 3.80 (s, 3H), 2.32 – 2.21 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 138.4, 130.7, 129.6, 128.1, 127.2, 115.0, 114.0, 55.4, 33.9, 32.6.

3. Mechanism Studies

3.1 Determination of quantum yield:

The photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at λ = 436 nm with an emission slit width at 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq 1.

$$\text{mol } Fe^{2+} = \frac{V \bullet \Delta A}{l \bullet \varepsilon} \qquad \text{eq 1}$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}). The photon flux can be calculated using eq 2.

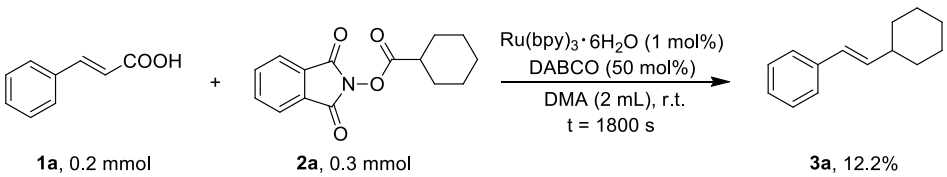
$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi \bullet t \bullet f} \qquad \text{eq 2}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at λ = 436 nm), t is the time (90.0 s), and f is the fraction of light absorbed at λ = 465 nm (0.99833, *vide infra*).

Sample calculation:

$$\text{mol } Fe^{2+} = \frac{0.00235 \text{ L} \bullet (0.532-0.102)}{1.000 \text{ cm} \bullet 11{,}100 \text{ L mol}^{-1} \text{ cm}^{-1}} = 9.1\times10^{-8}$$

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{1.01 \bullet 90.0 \text{ s} \bullet 0.99833} = 1.002\times10^{-9} \text{ einstein s}^{-1}$$



1a, 0.2 mmol + **2a**, 0.3 mmol → **3a**, 12.2%

A cuvette was charged with **1a** (0.2 mmol), **2a** (0.3 mmol), DABCO (0.1 mmol) and $Ru(bpy)_3Cl_2 \bullet 6H_2O$ (0.002 mmol) in DMA (2 mL). The cuvette was then capped with a PTFE stopper. The sample was stirred and irradiated (λ = 436 nm, slit width = 5 nm) for 1800 s (30 min). After irradiation, the solution was passed through a silica plug. The yield of product formed was determined by ^1H NMR based on a diphenylmethane standard (**3a**, yield = 12.2%). The quantum yield was determined using eq 3.

$$\Phi = \frac{\text{mol product}}{\text{flux} \bullet t \bullet f} \qquad \text{eq 3}$$

$$\Phi = \frac{0.2 \bullet 0.122 \bullet 10^{-3}}{1.002 \times 10^{-9}\ \text{einsteins}^{-1} \bullet 1800\ \text{s} \bullet 1.00} = 13.5$$

3.2 Stern–Volmer quenching rate data:

Rates of quenching (k_q) were determined using Stern–Volmer kinetics (eq 4).

$$\frac{I_0}{I} = K_q \tau_0 [\text{quencher}] \qquad \text{eq 4}$$

here I_0 is the luminescence intensity without the quencher, I is the intensity with the quencher, and τ_0 is the lifetime of the photocatalyst. Samples were prepared by adding solutions of photocatalyst, quencher, and MeCN to obtain a total volume of 2.0 mL. The cuvette was sealed with a septum and parafilm, and then sparged for 15 min with N_2. The concentration of $Ru(bpy)_3Cl_2$ was 5.0×10^{-5} M. Samples were irradiated at 451 nm, and emission was detected at 600 nm. The lifetime measurement for $Ru(bpy)_3Cl_2$ in MeCN (855 ns) was previously reported.

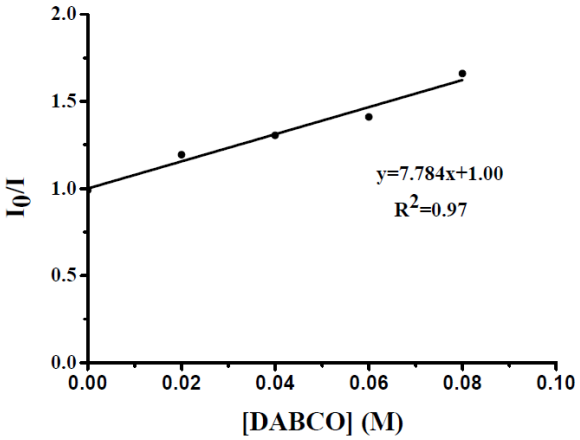
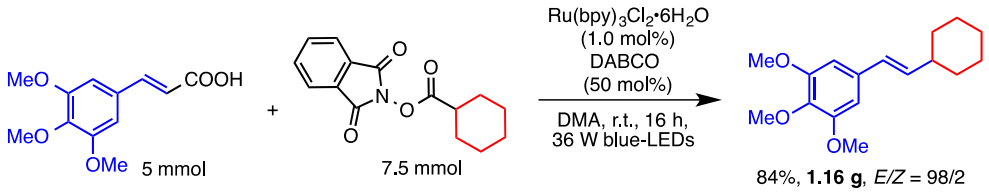


Figure S1 Stern–Volmer quenching of $Ru(bpy)_3Cl_2$ and DABCO. For the amine, $k_q = 9.1 \times 10^6$ $M^{-1}S^{-1}$

4. Gram-scale Reaction



(*E*)-3-(3,4,5-trimethoxyphenyl)acrylic acid (1.0 equiv., 5 mmol, 1.2 g), redox active ester (1.5 equiv., 7.5 mmol, 2.05g), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (1.0 mol %, 38 mg) and DABCO (0.5 equiv., 280 mg) were placed in a Schlenk tube (100 mL) equipped with a stirring bar. The tube was evacuated and filled with argon (three times). Then, anhydrous *N*, *N*-dimethylacetamide (DMA, 40 mL) was added via a syringe under argon atmosphere. The resulting reaction mixture was stirred under the irradiation of a 36 W Blue LEDs (distance app. 3.0 cm from the bulb) at room temperature for 16 h. After the reaction was completed, the mixture was quenched with water and extracted with ethyl acetate (3 x 40 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 50: 1) to give the product in 84 % yield as a white solid (1.16g).

5. References

[1] C. M. McMahon, E. J. Alexanian, *Angew. Chem. Int. Ed.* **2014**, *53*, 5974–5977.

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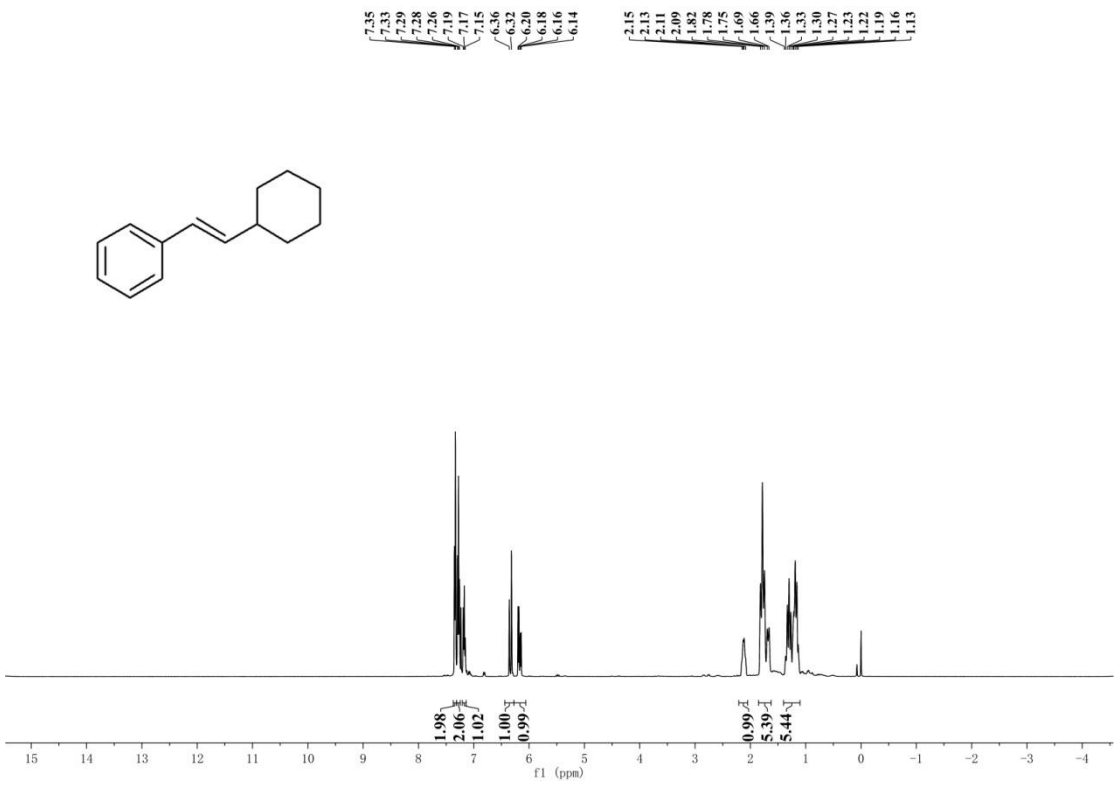
6. NMR Spectra

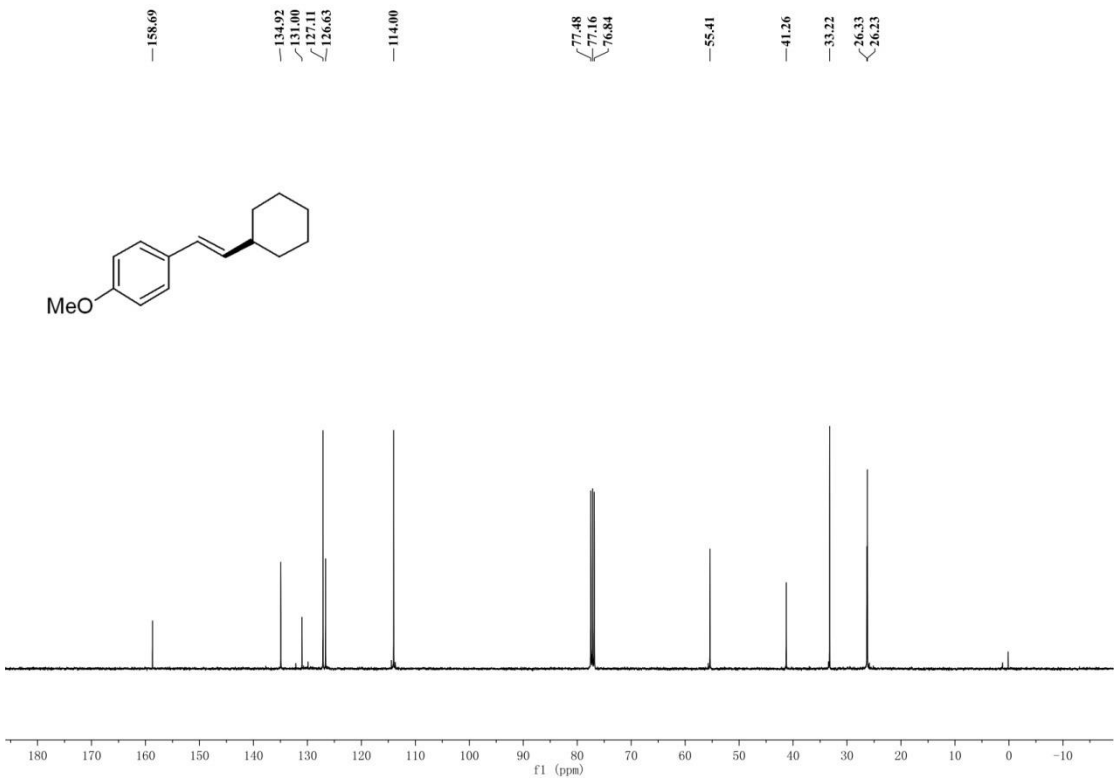
^{1}HNMR of **1**



^{13}CNMR of **1**

^{1}HNMR of **2**

^{13}CNMR of **2**



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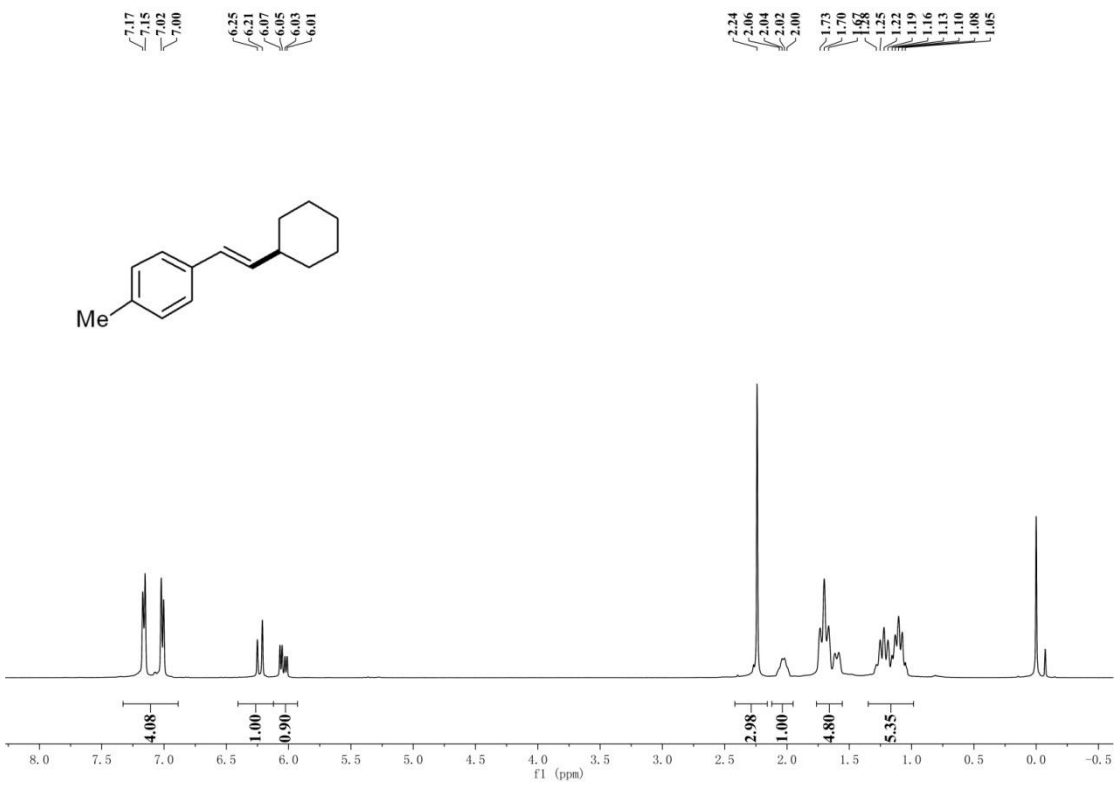
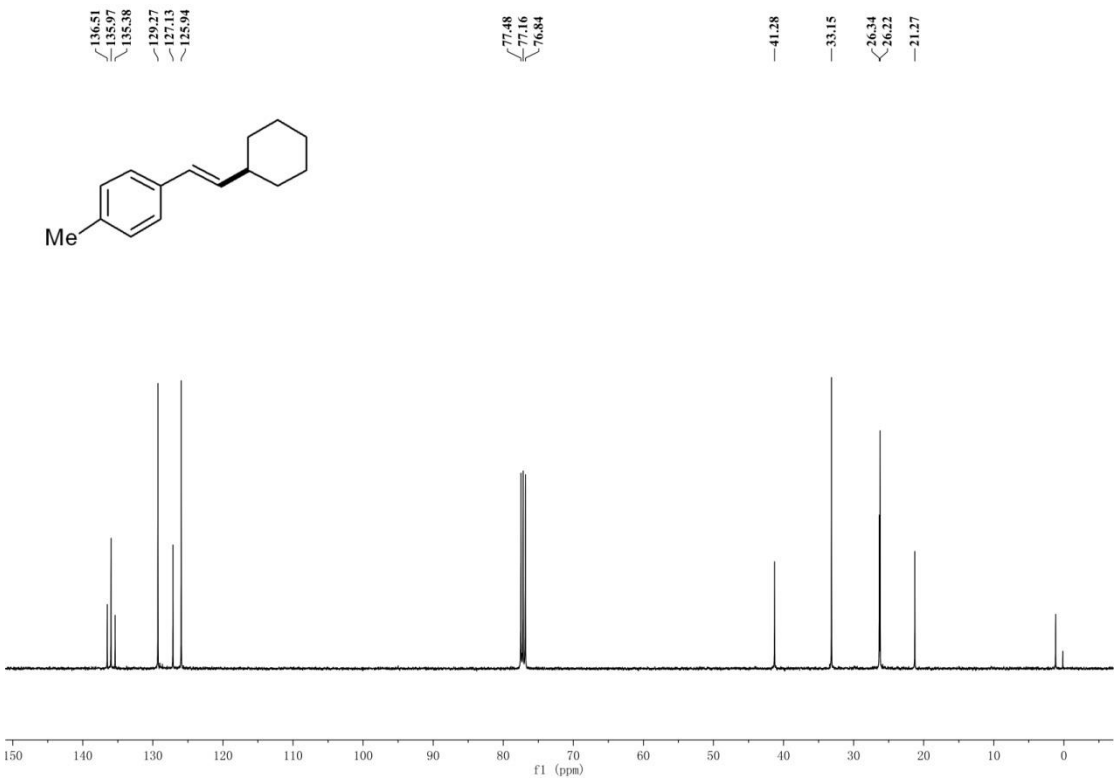


^{13}CNMR of **3**



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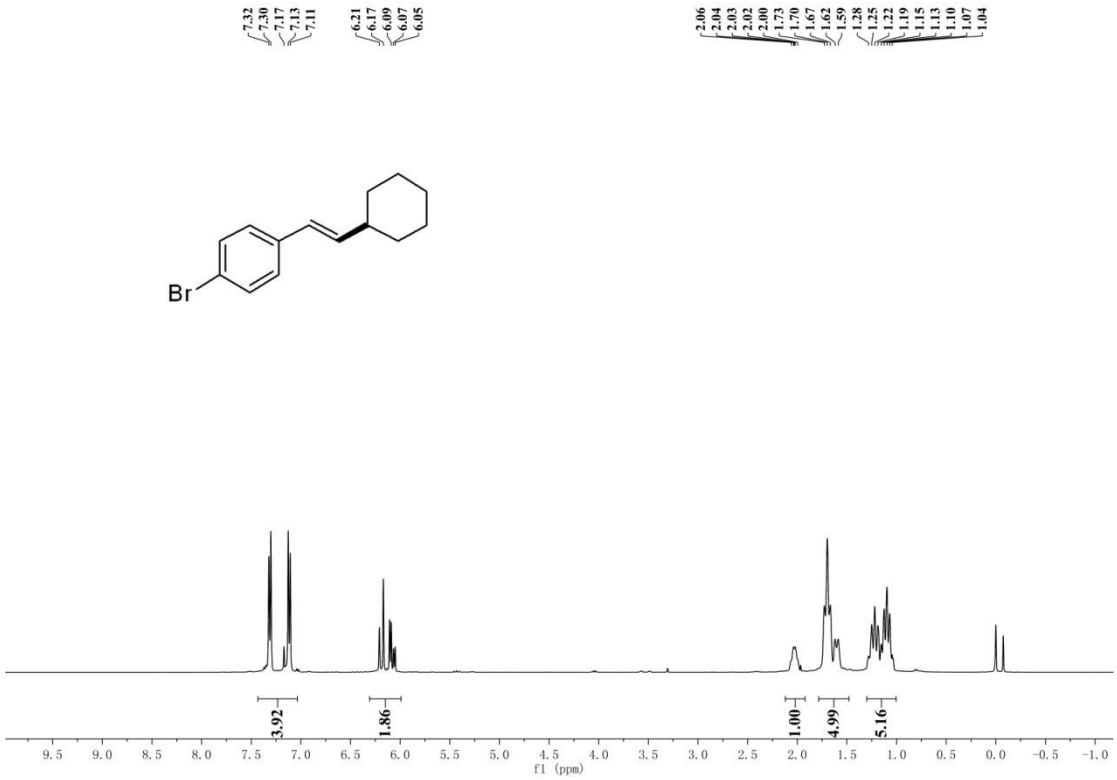
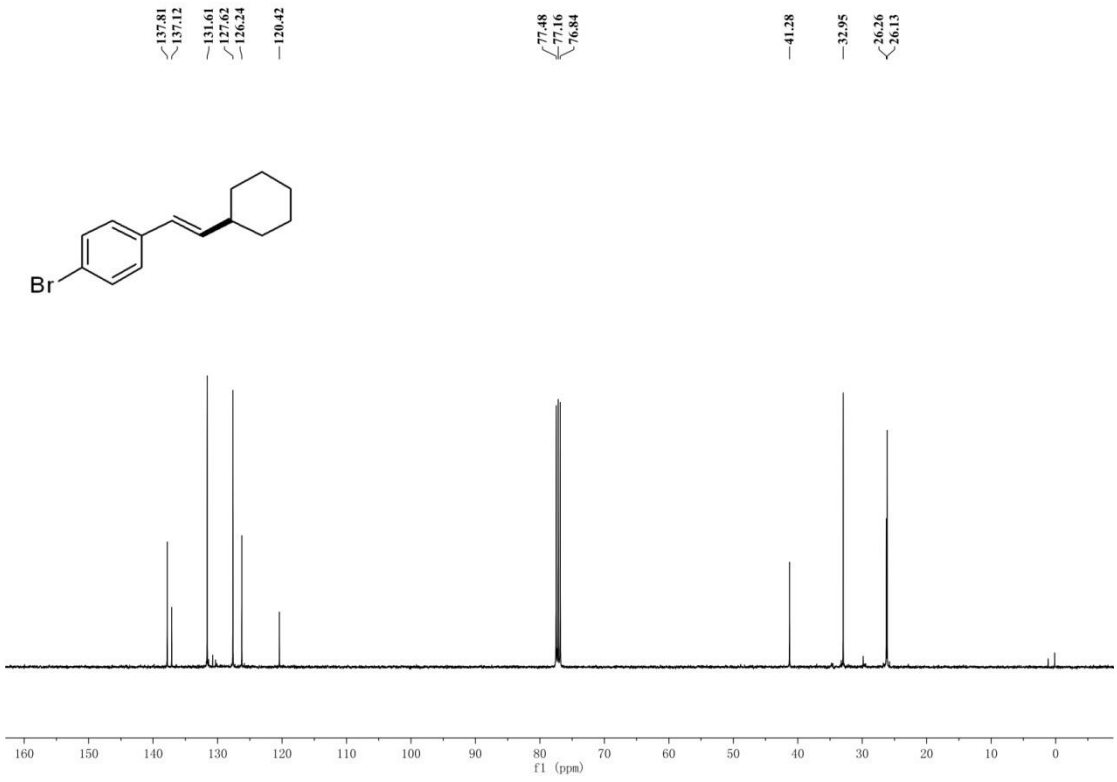


^{13}CNMR of **4**



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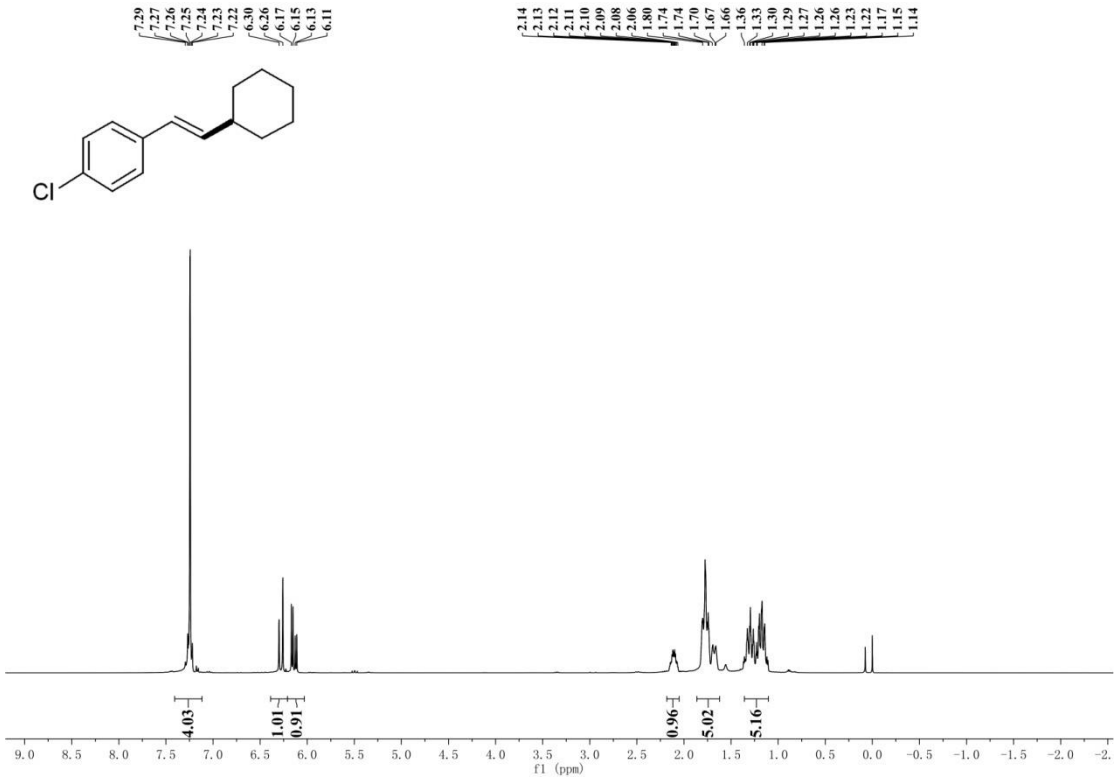

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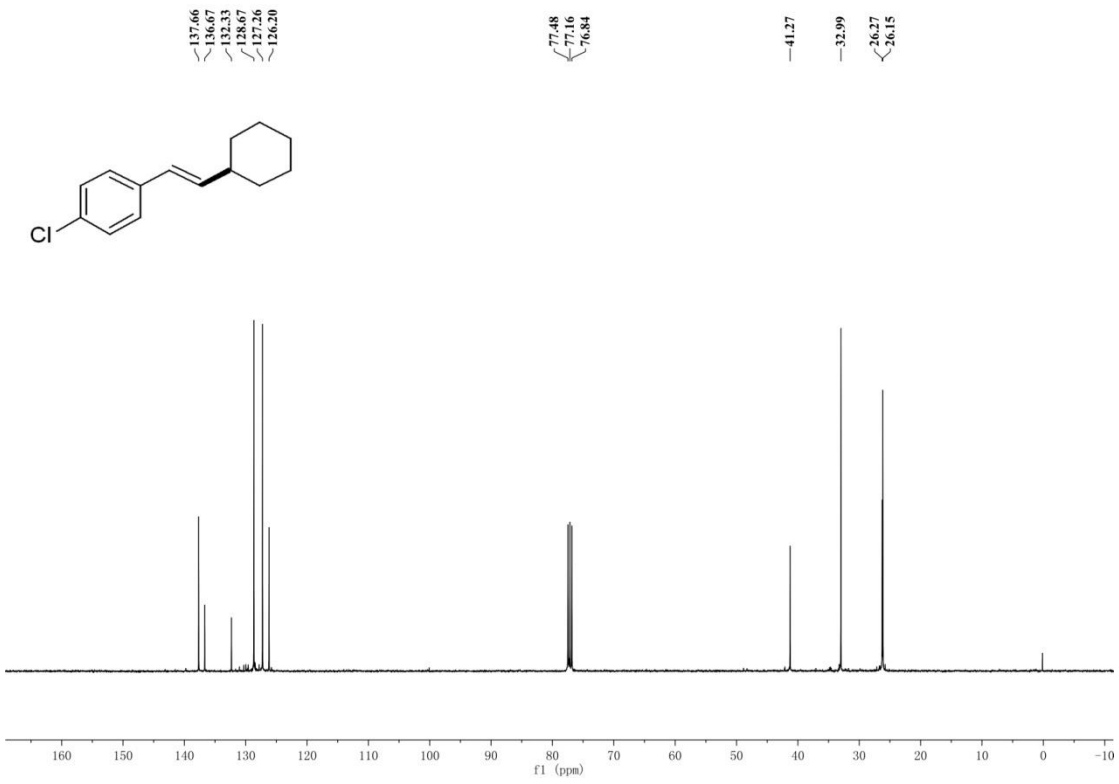

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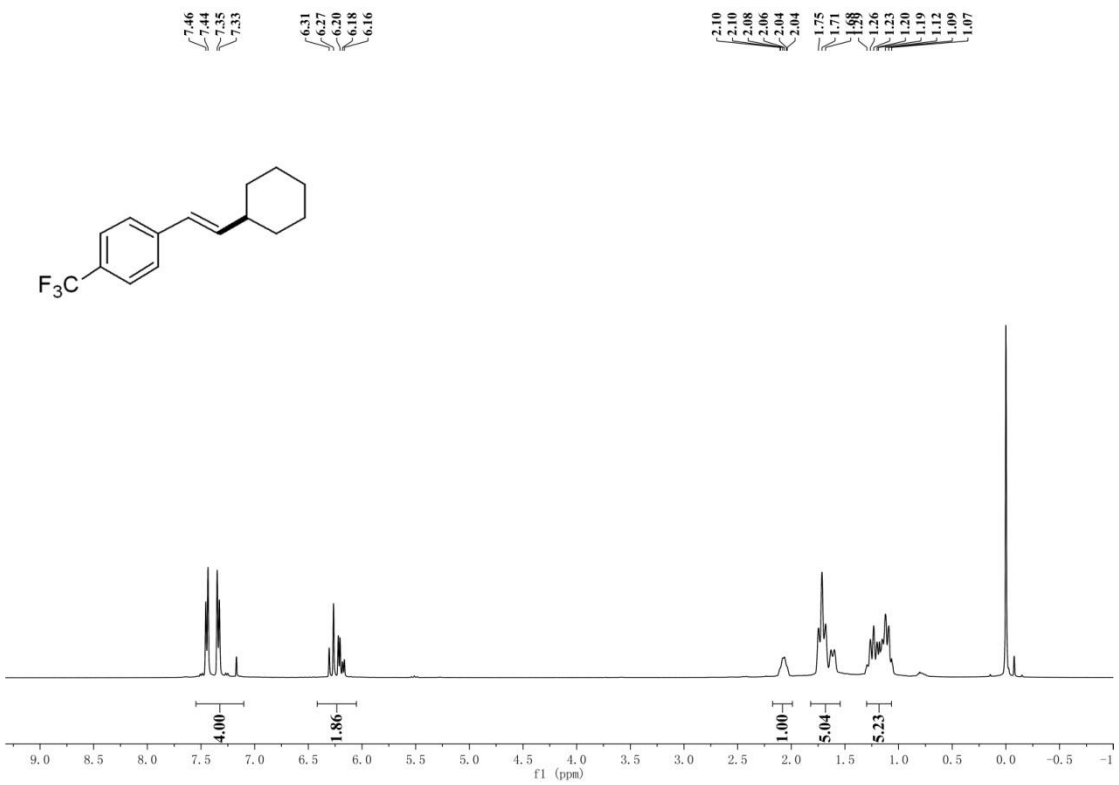

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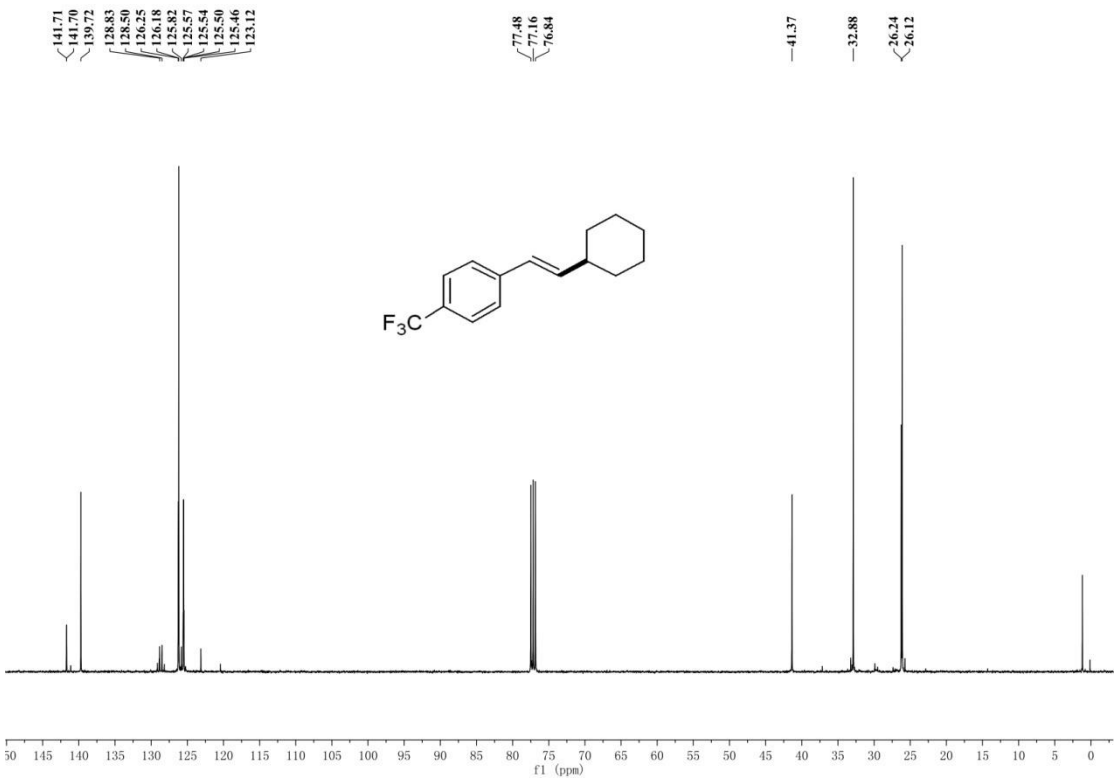

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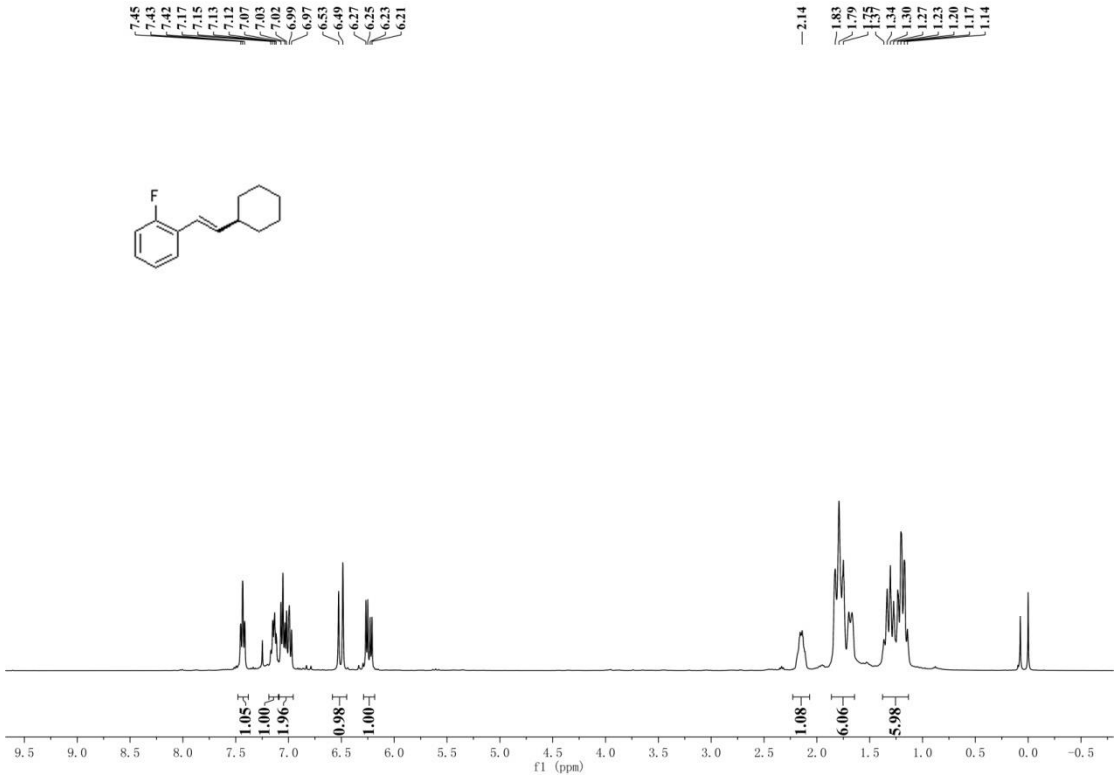
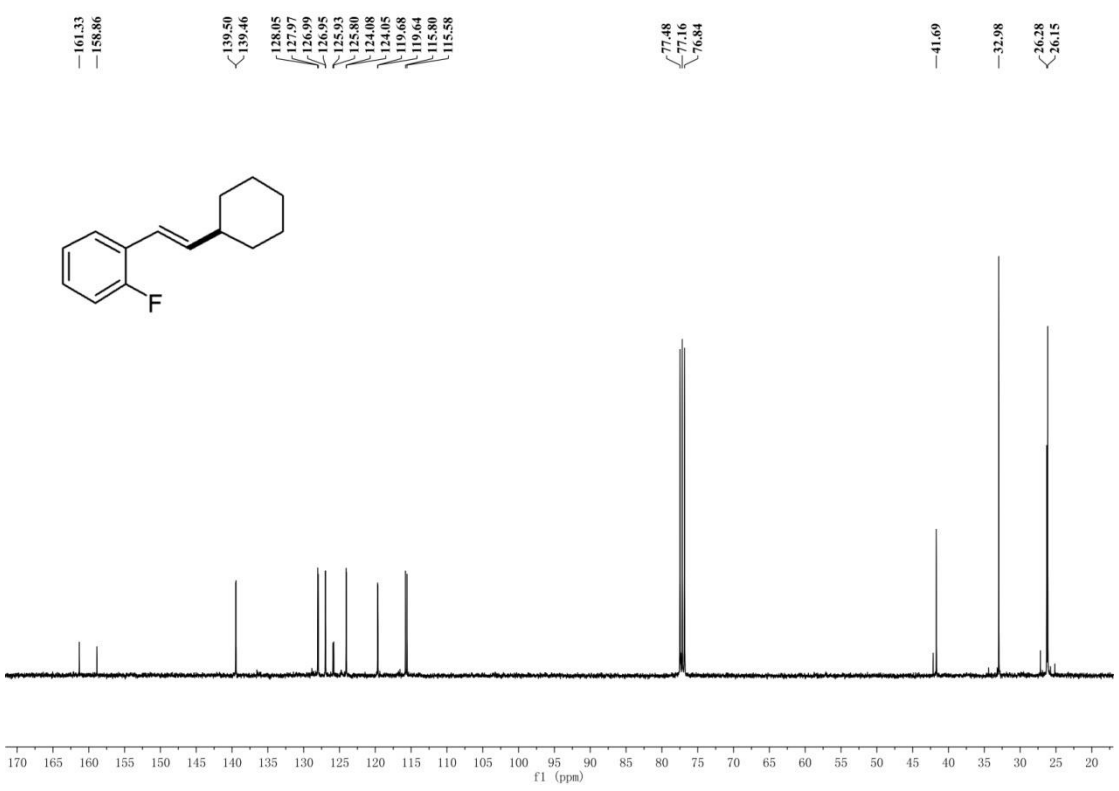


^{13}CNMR of **7**



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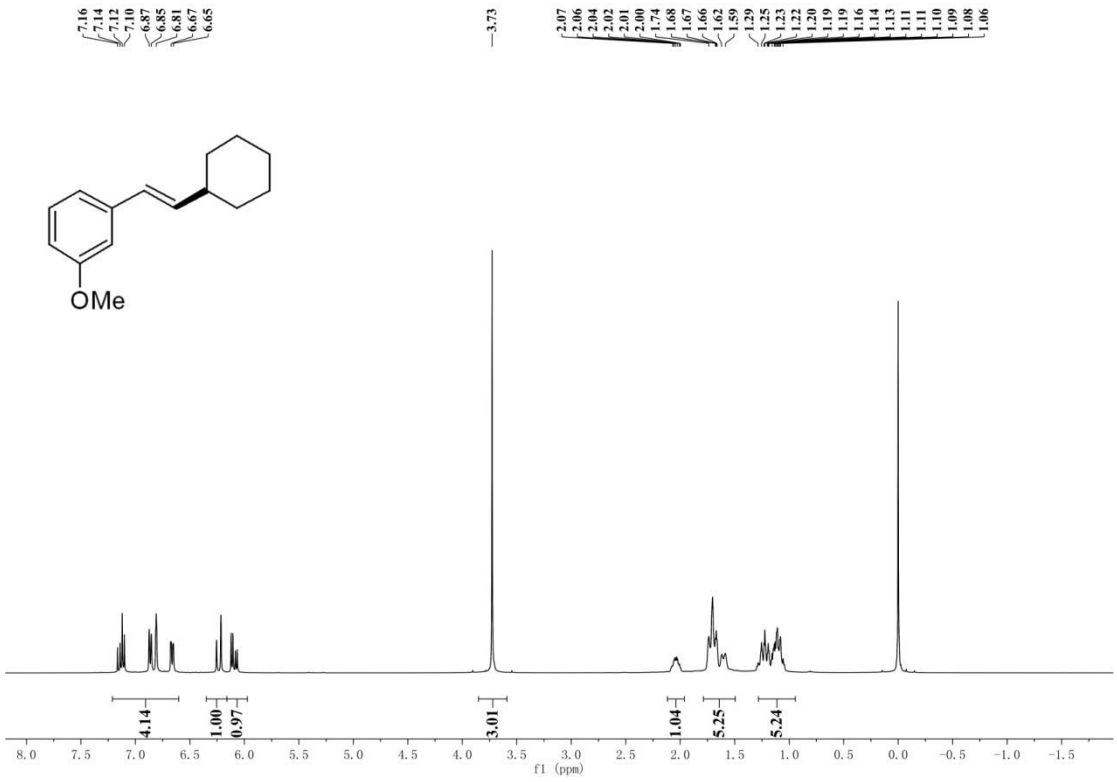
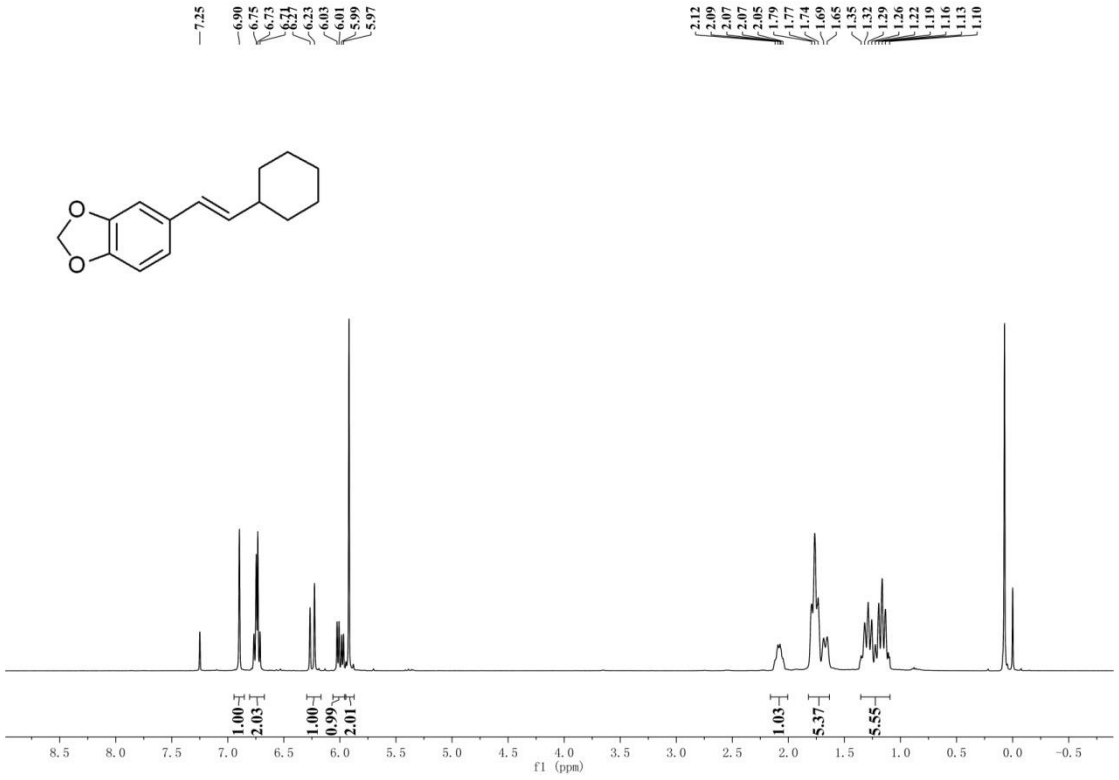
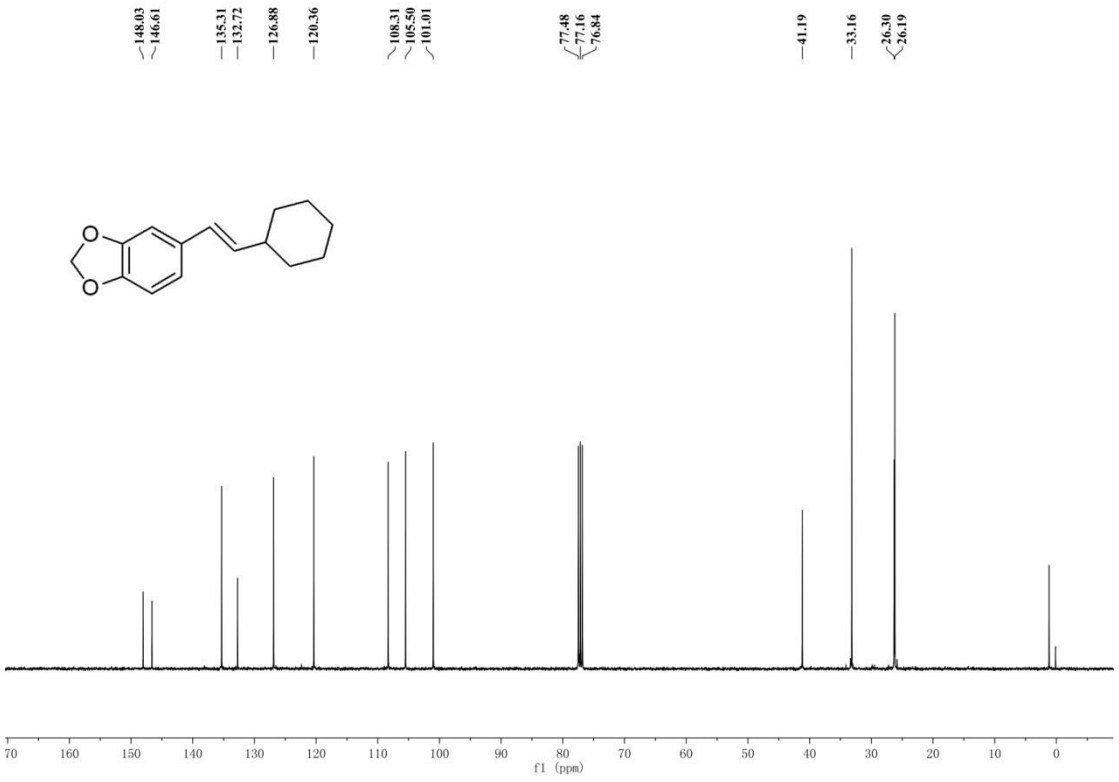


^{13}CNMR of **8**

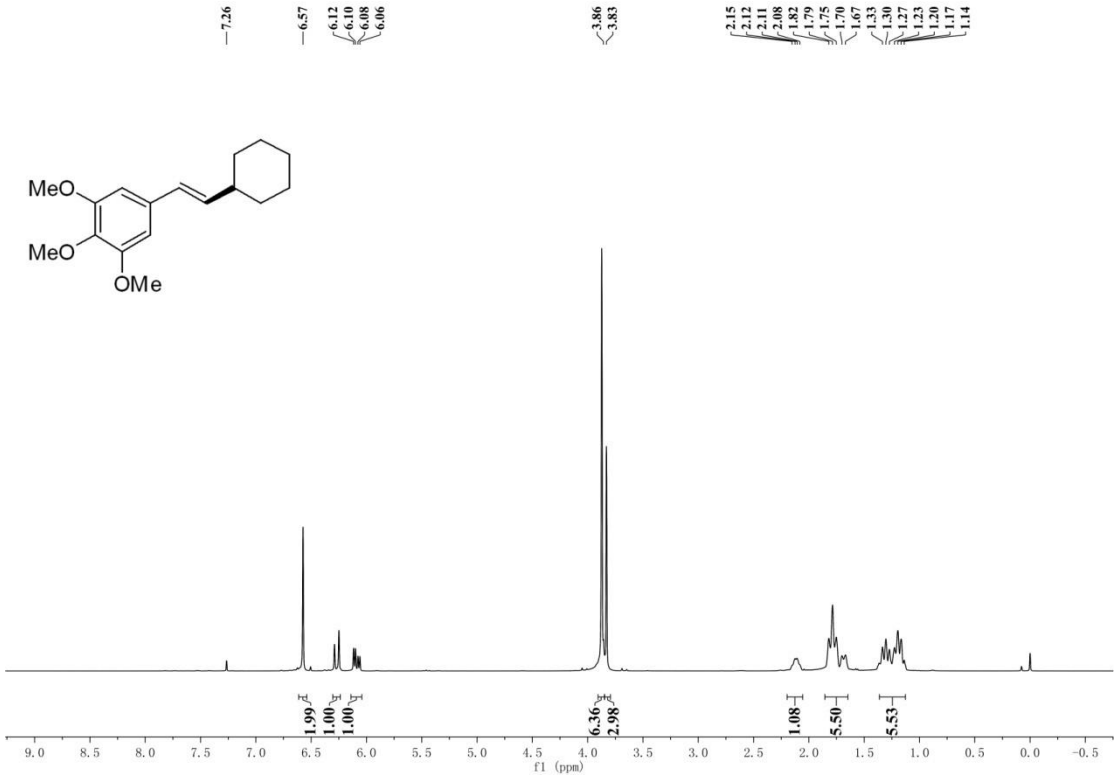
^{1}HNMR of **9**



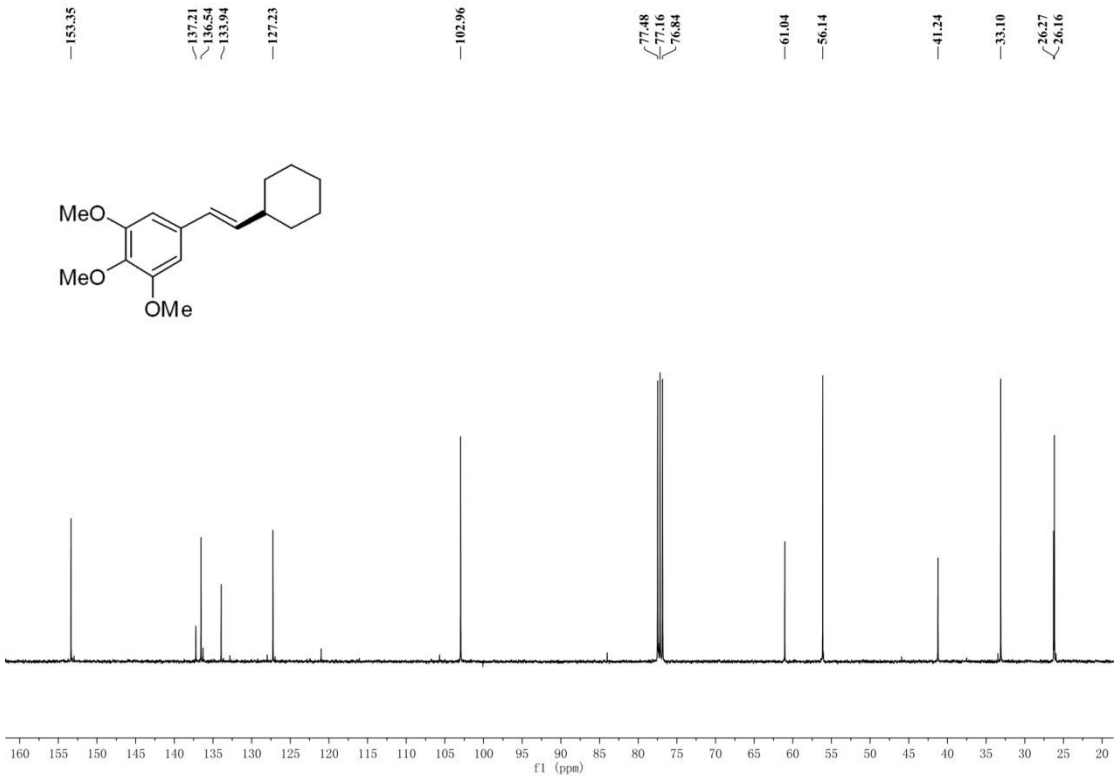
^{13}CNMR of **9**



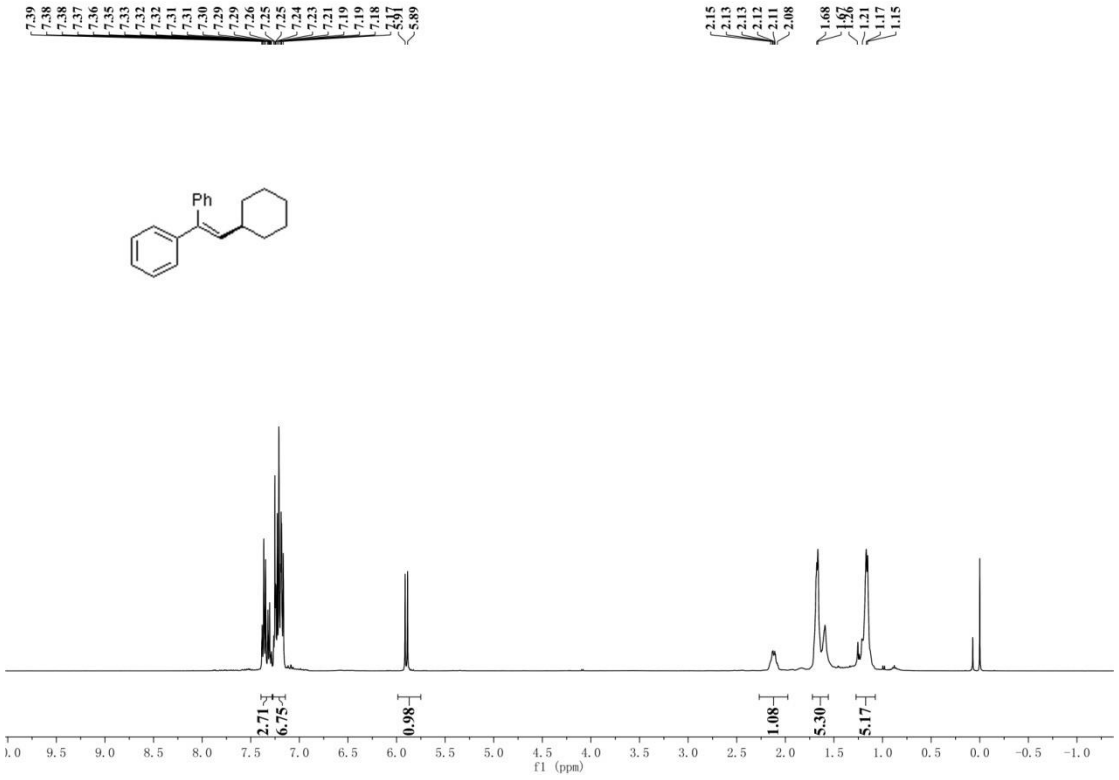
^{1}HNMR of **10**



^{13}CNMR of **10**



[1]HNMR of **11**



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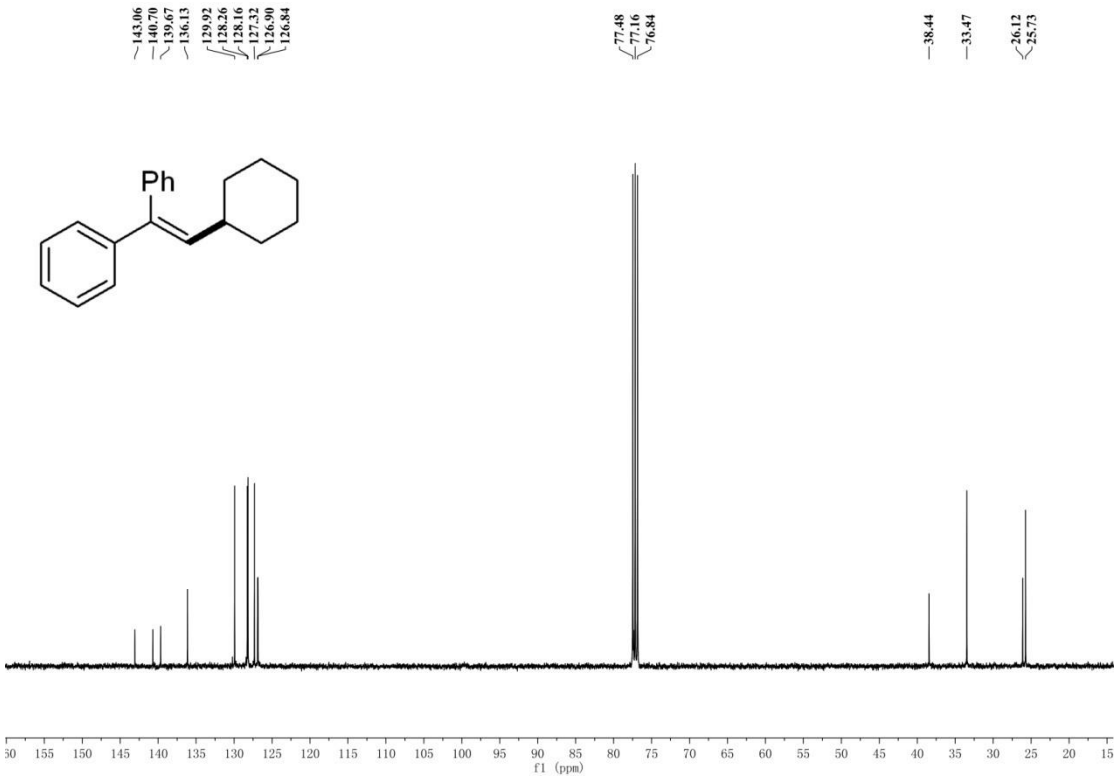

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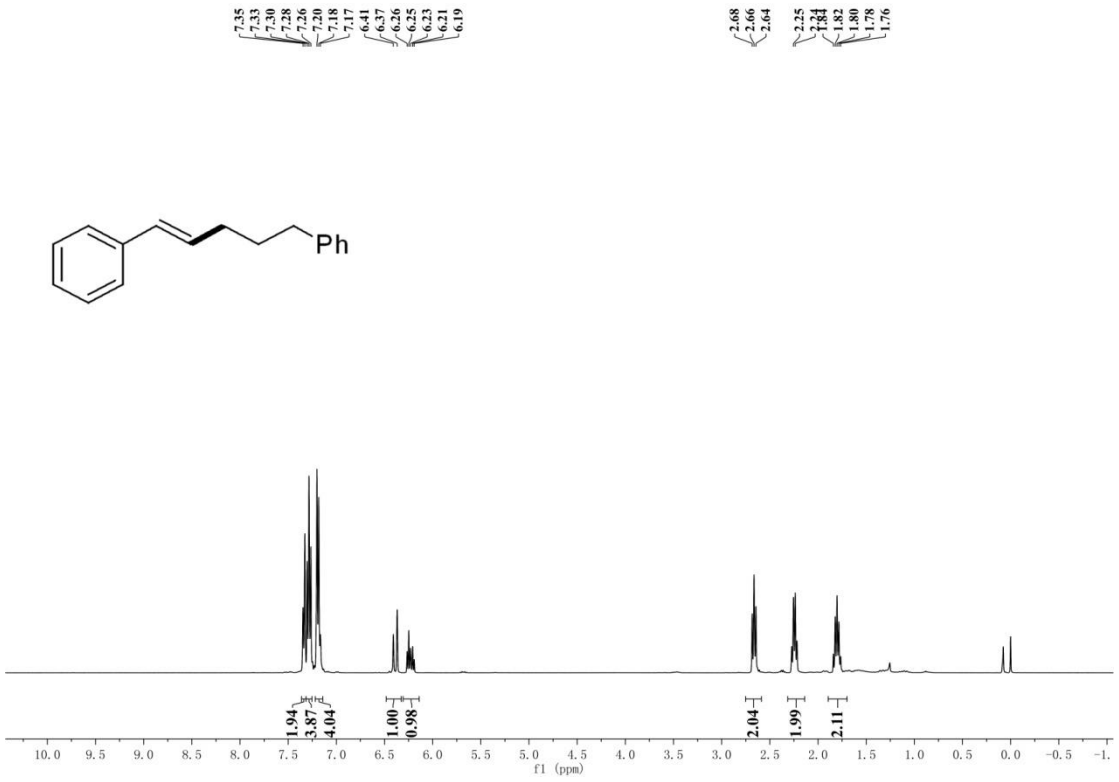

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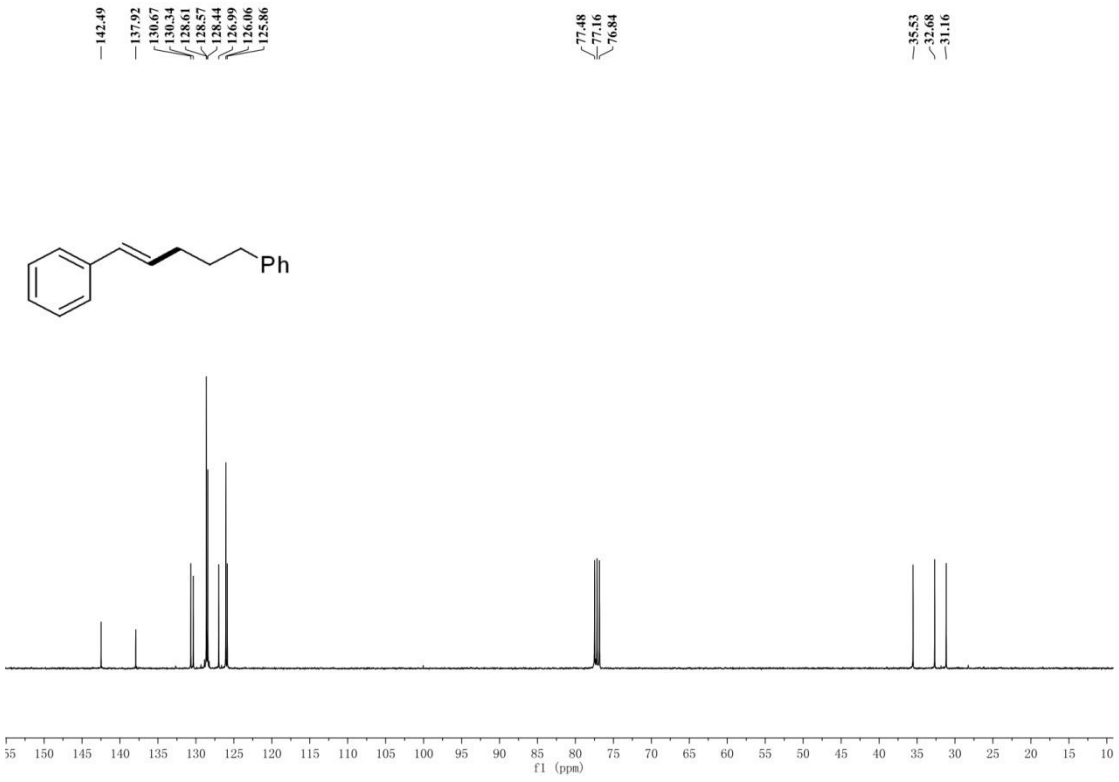

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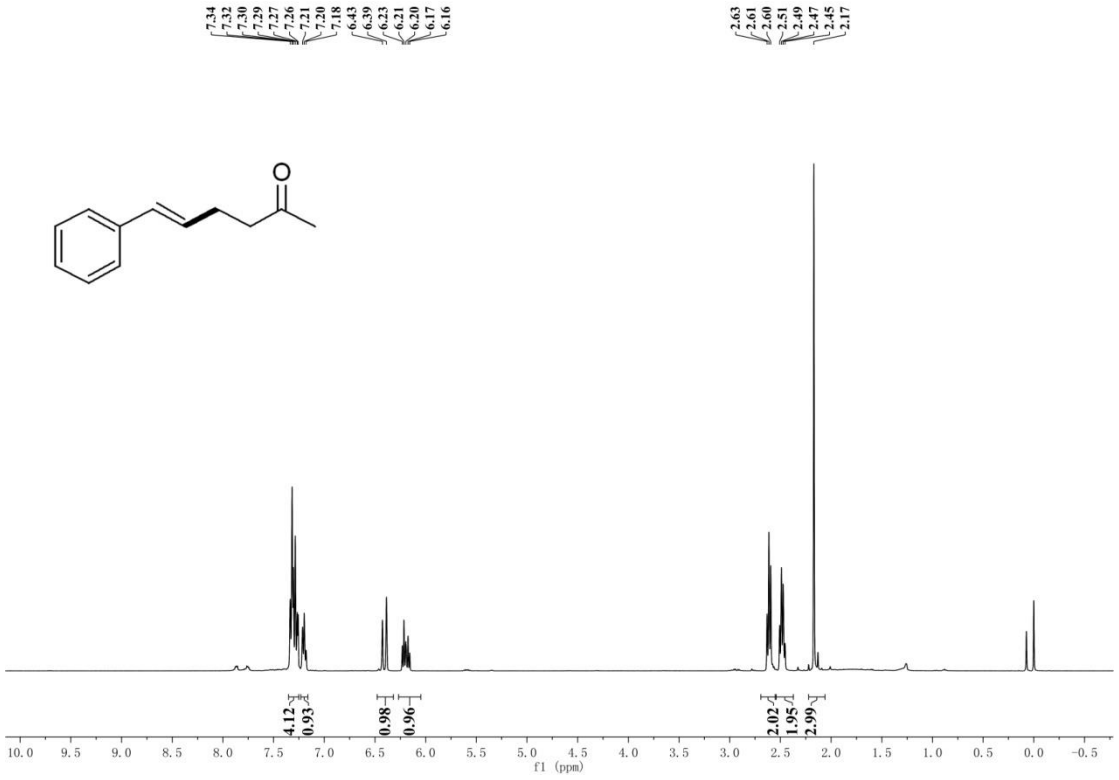

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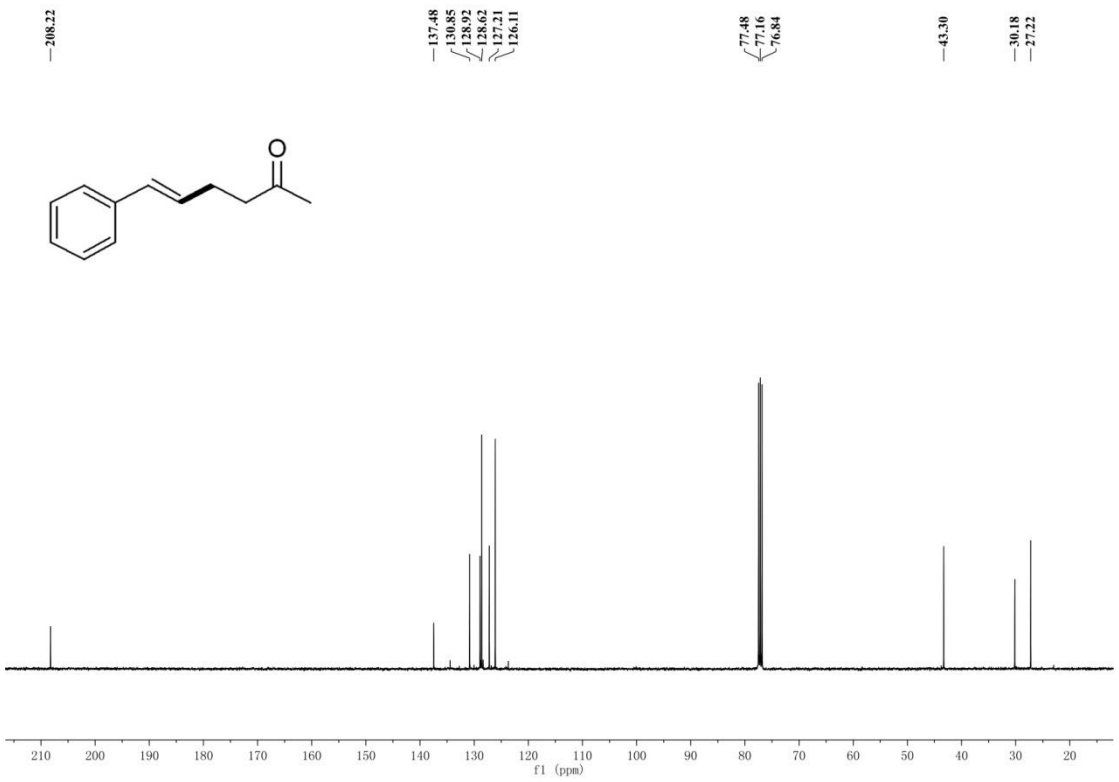

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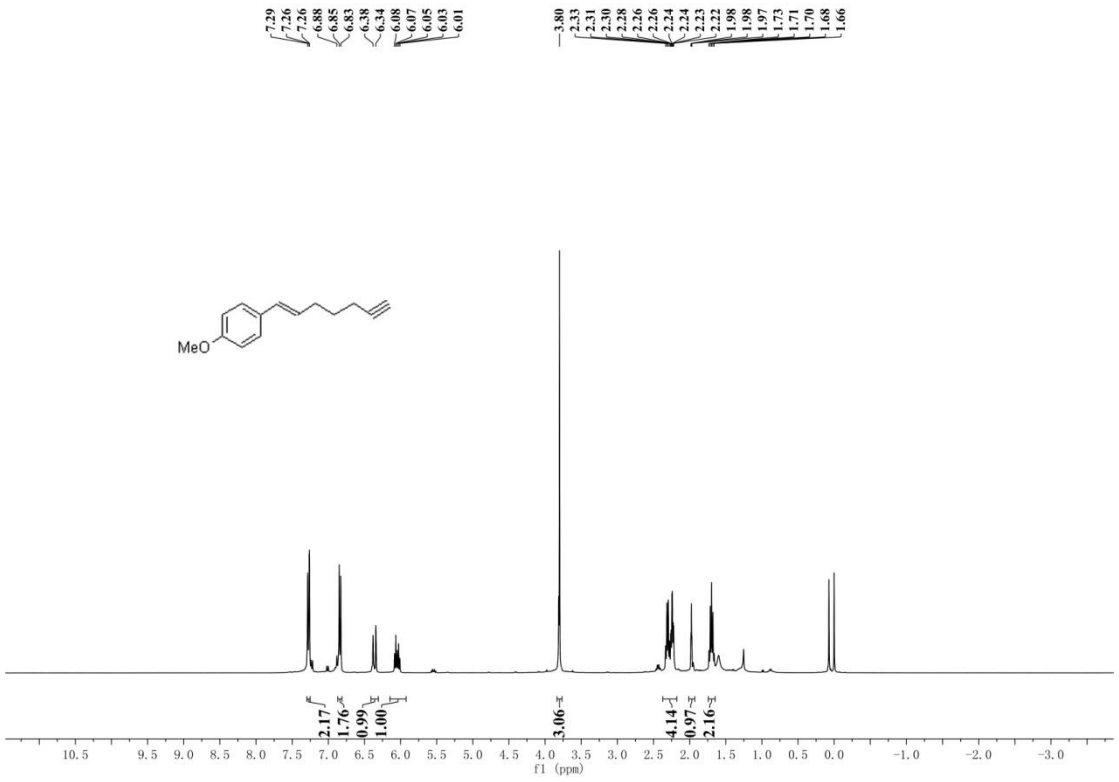

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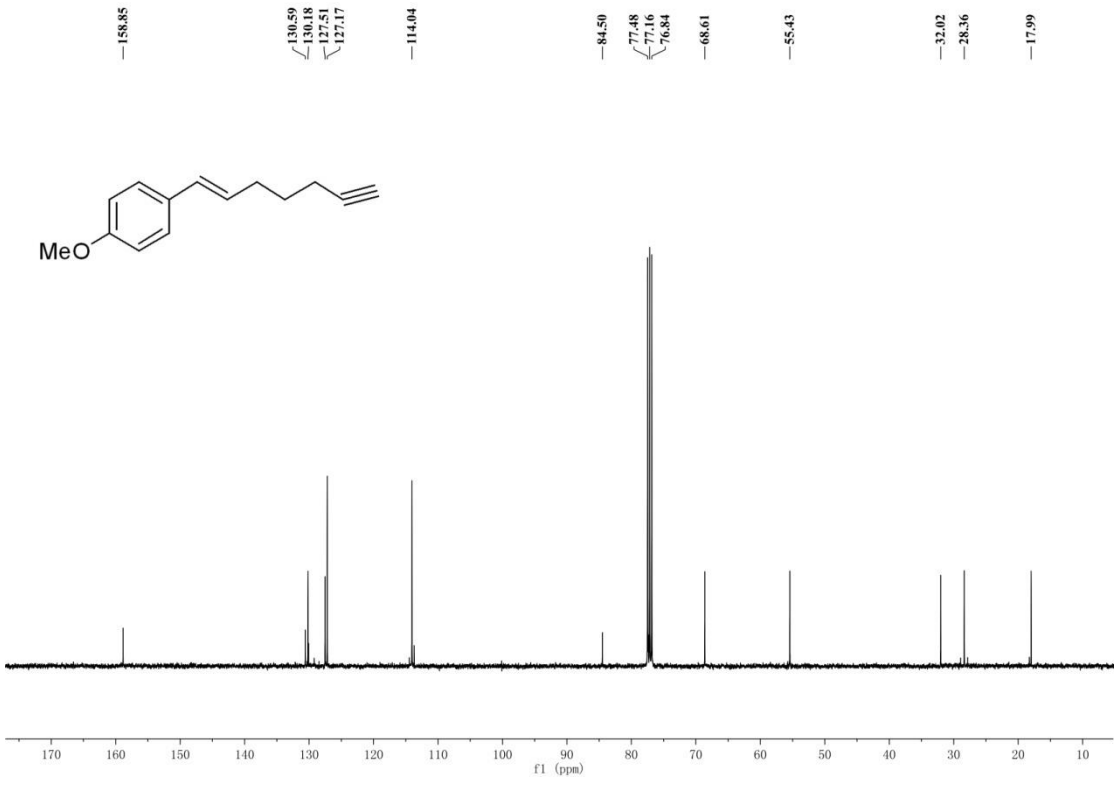

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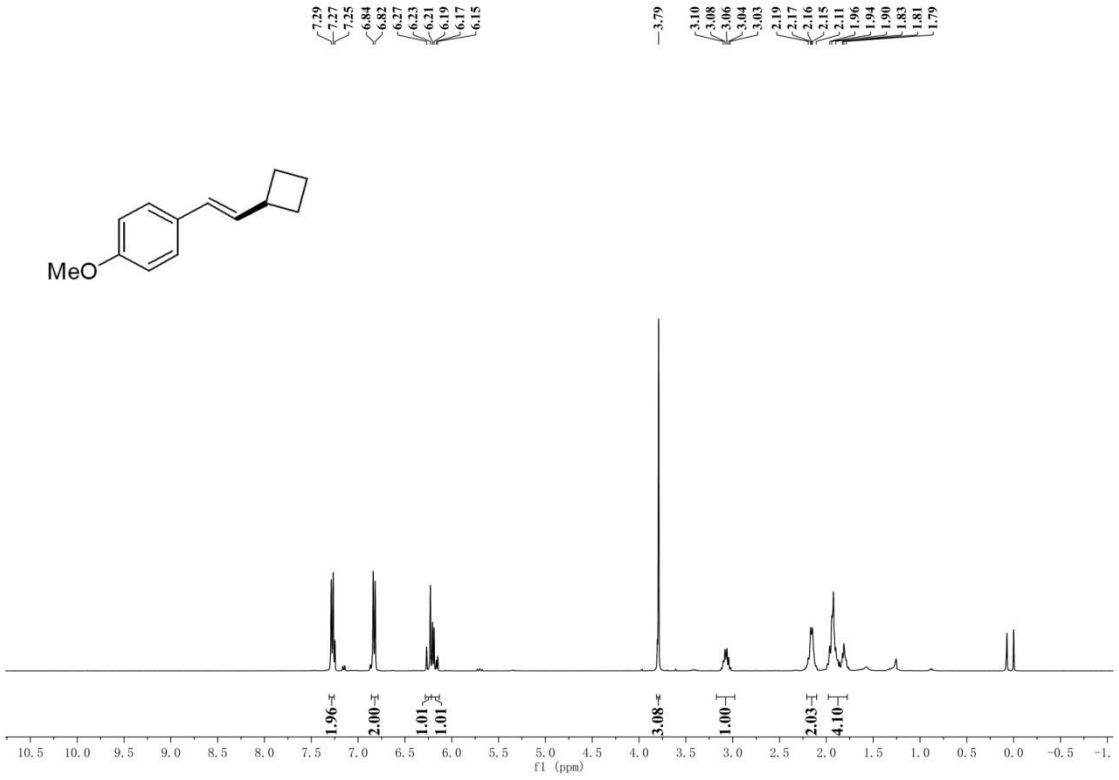

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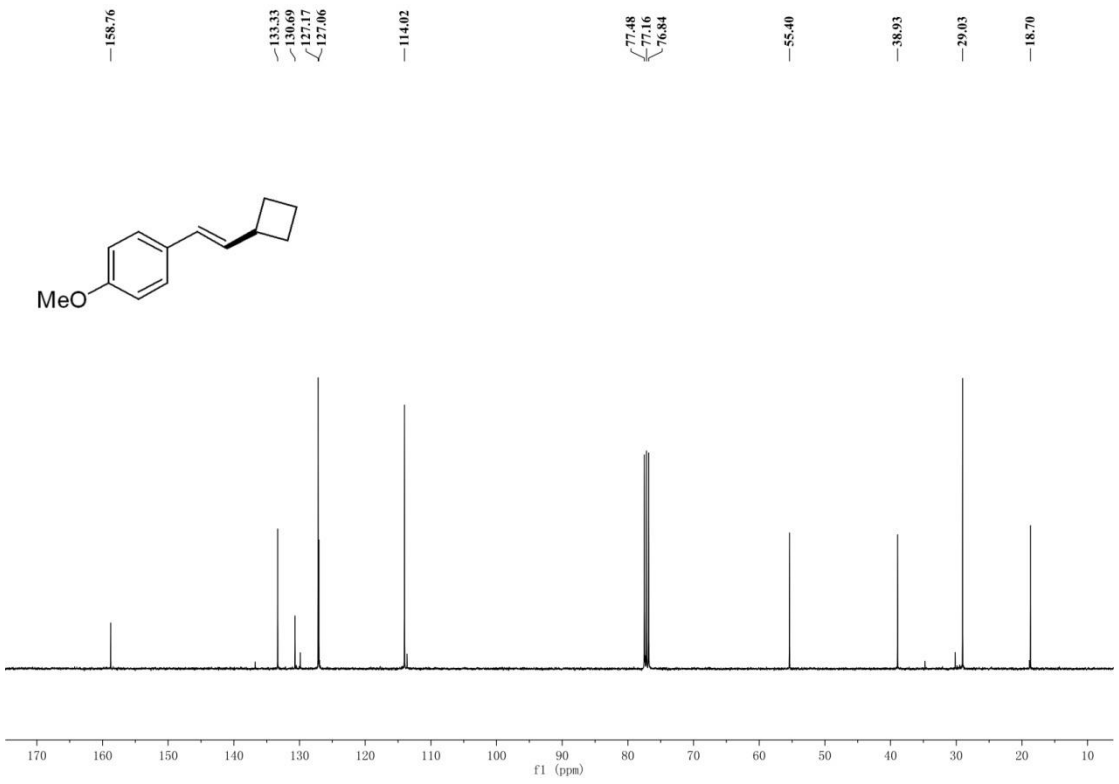

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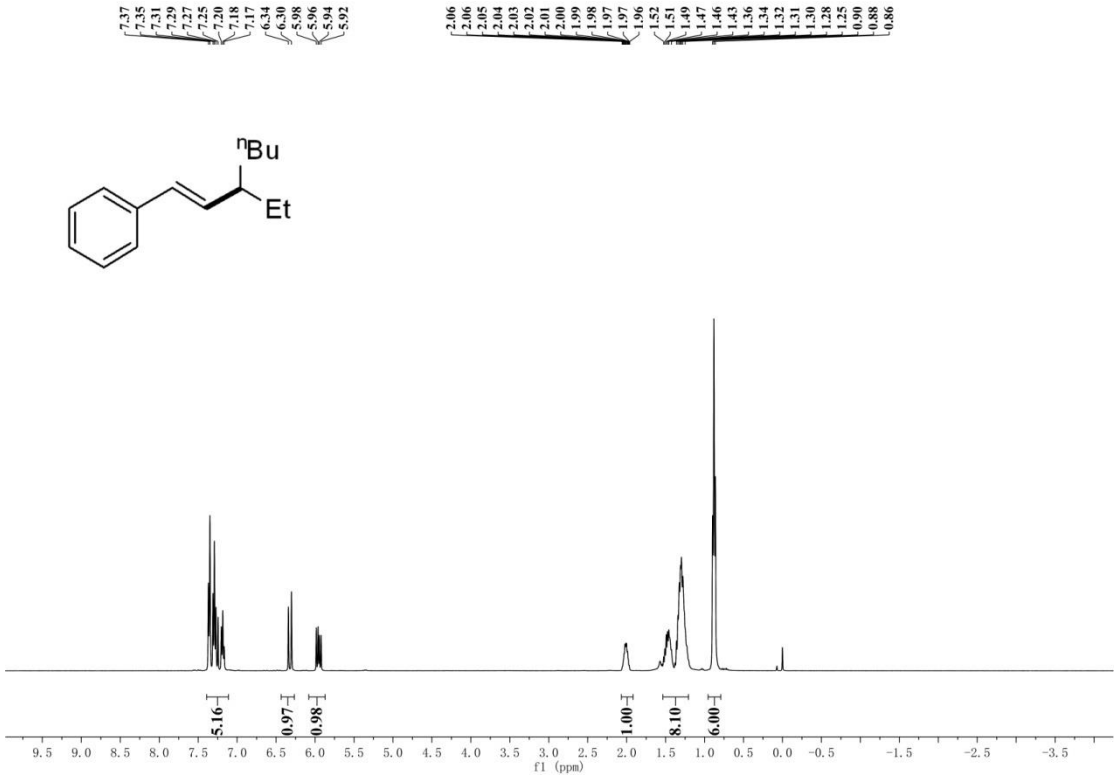

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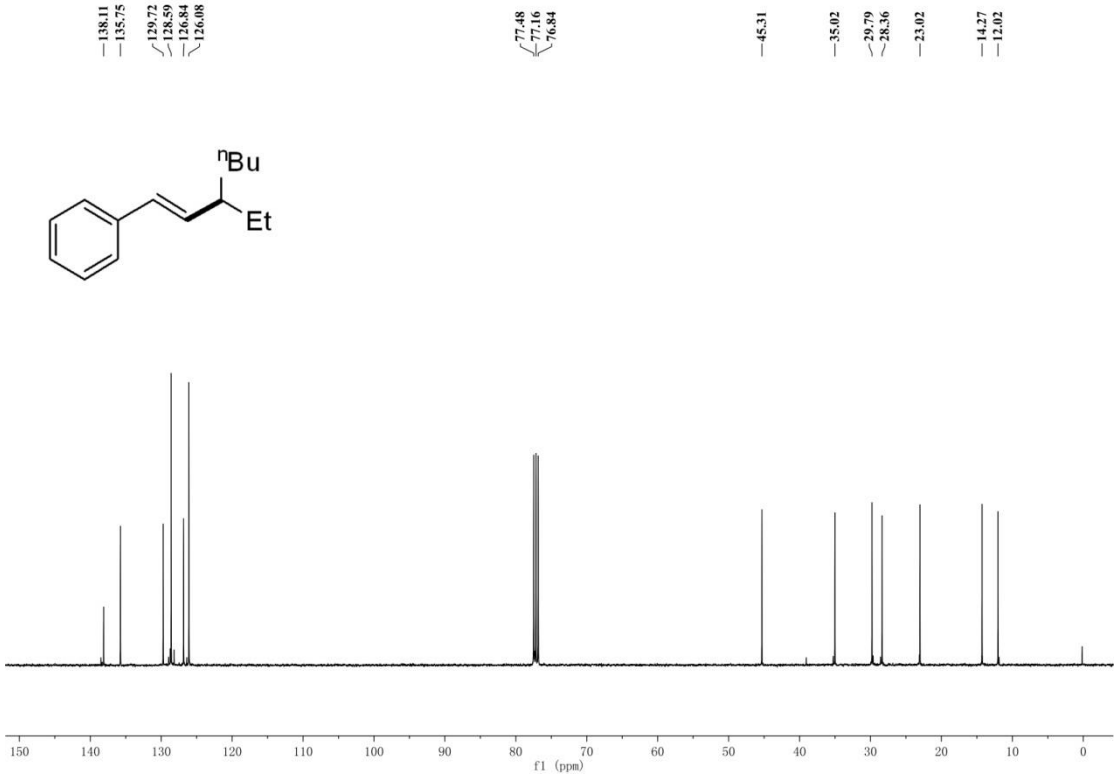

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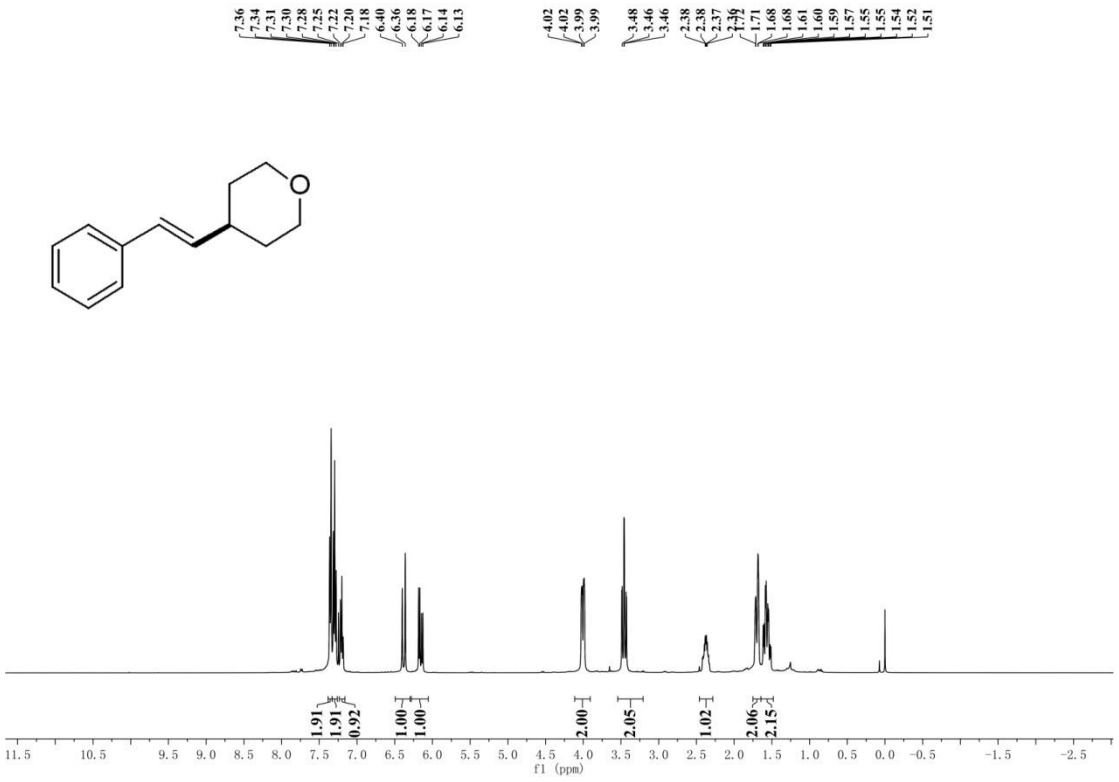

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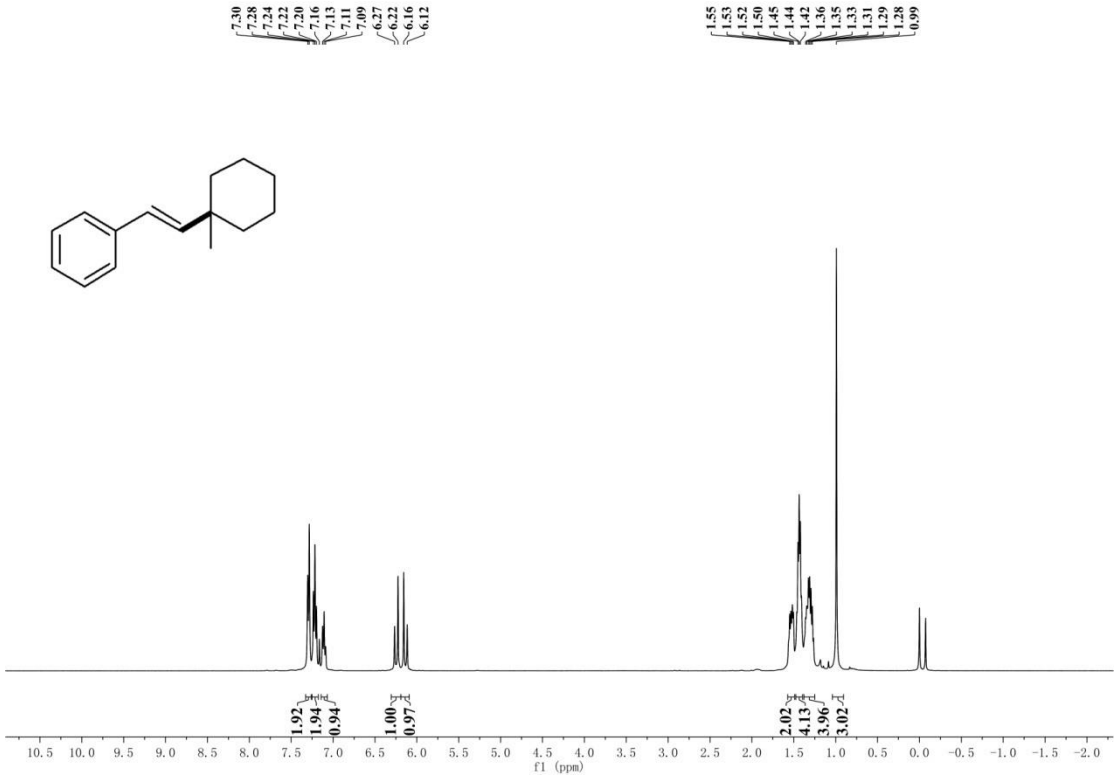
^{1}HNMR of **20**



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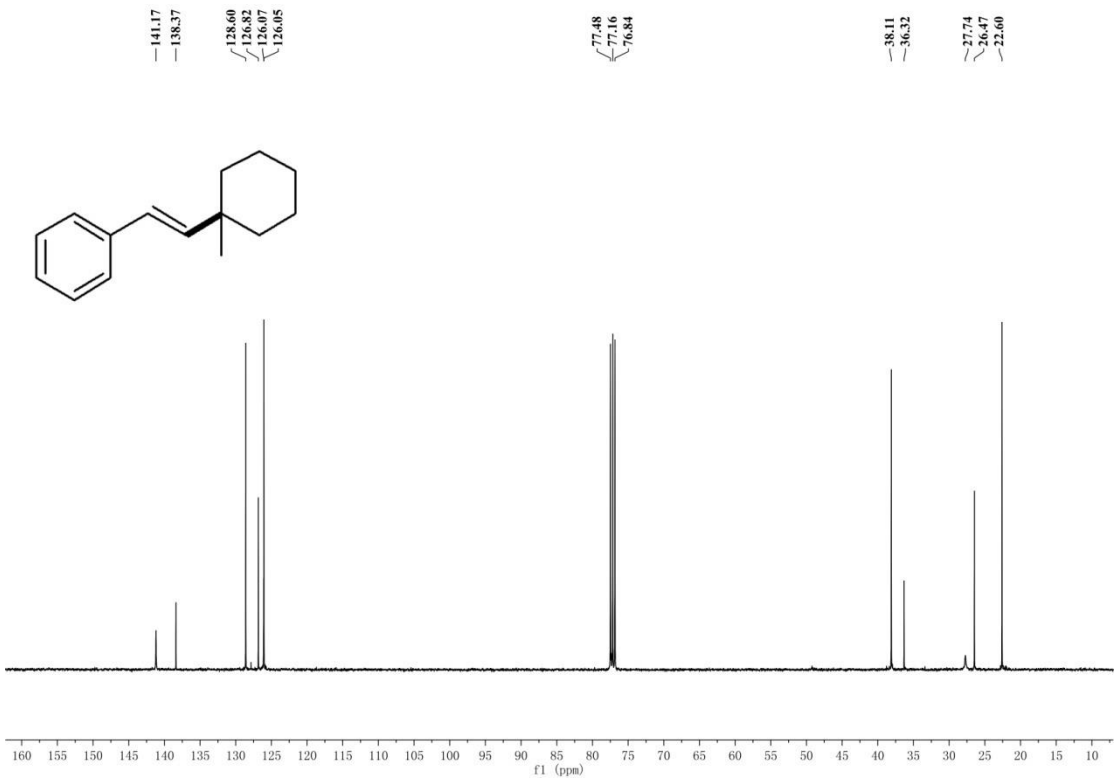

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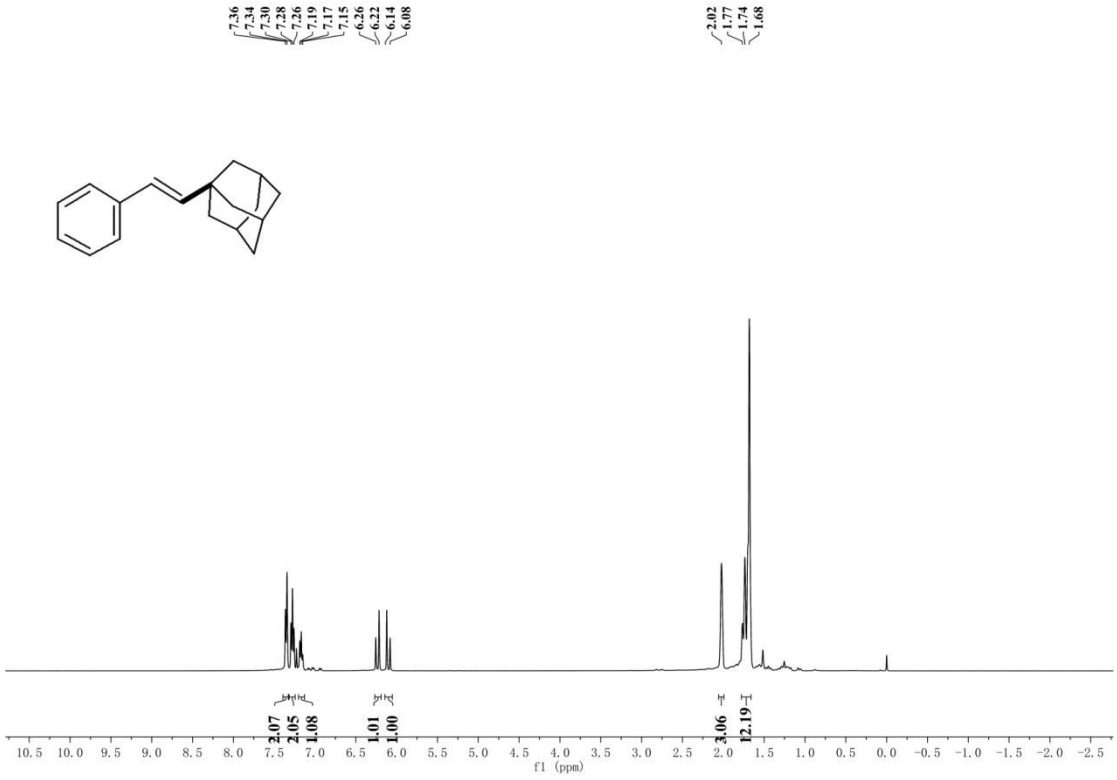

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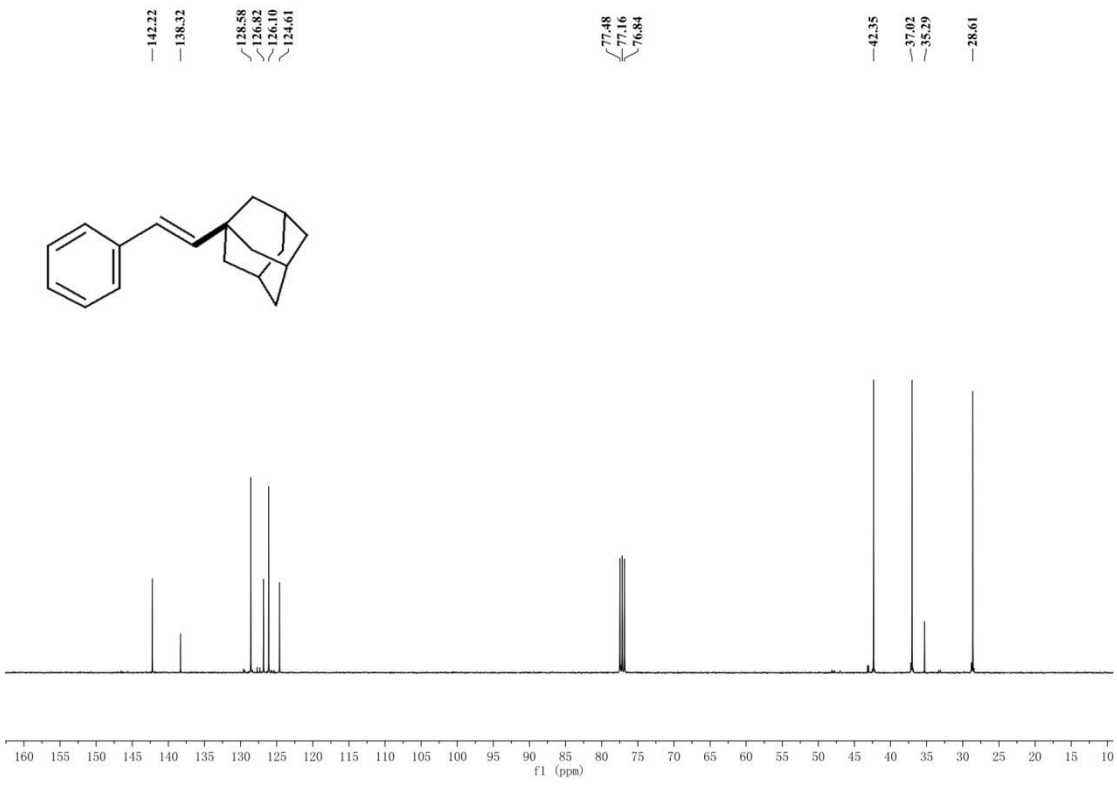

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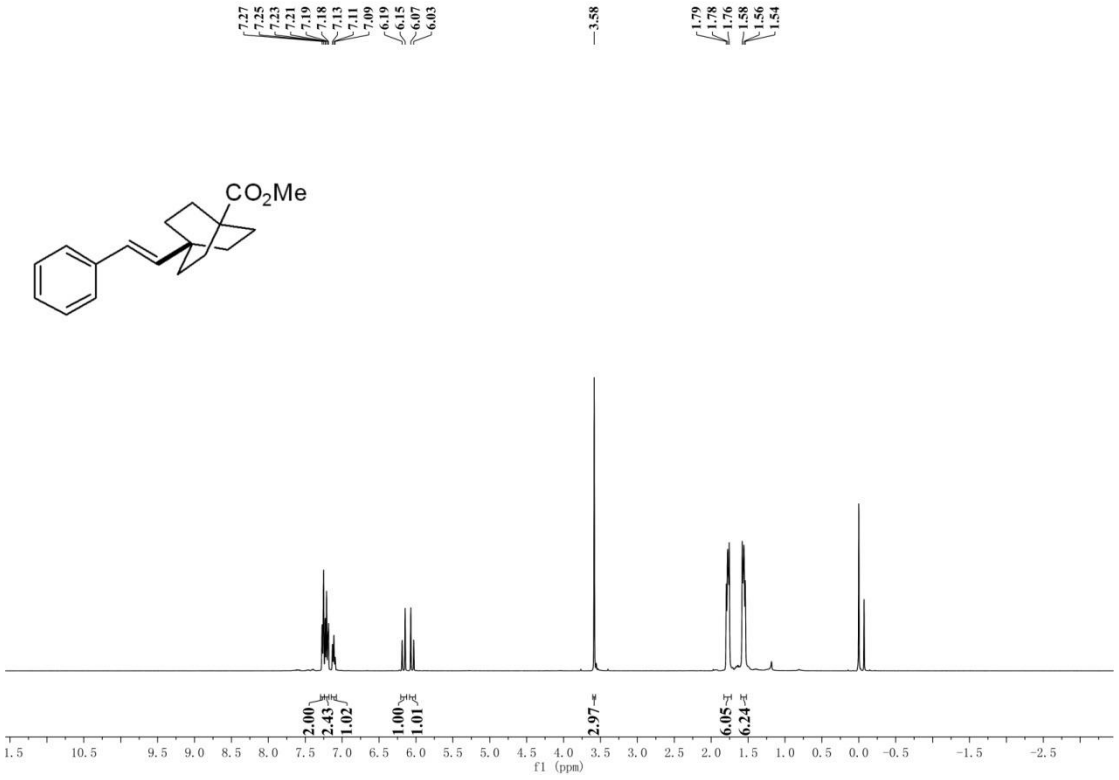

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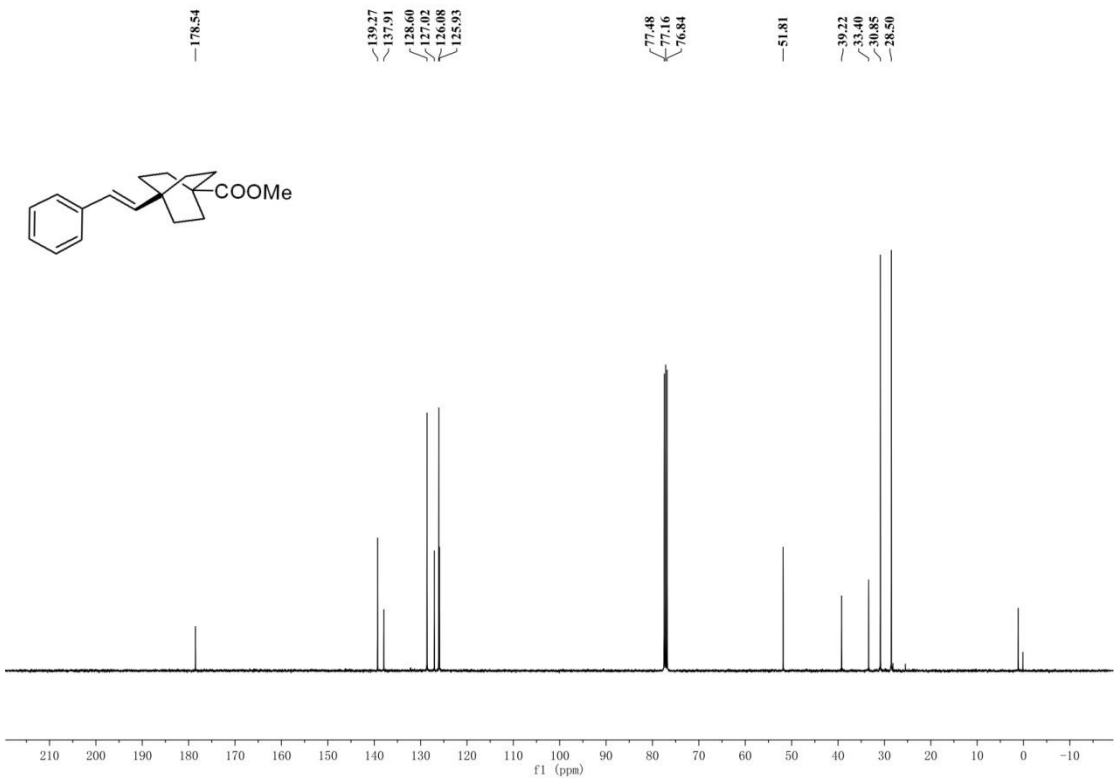

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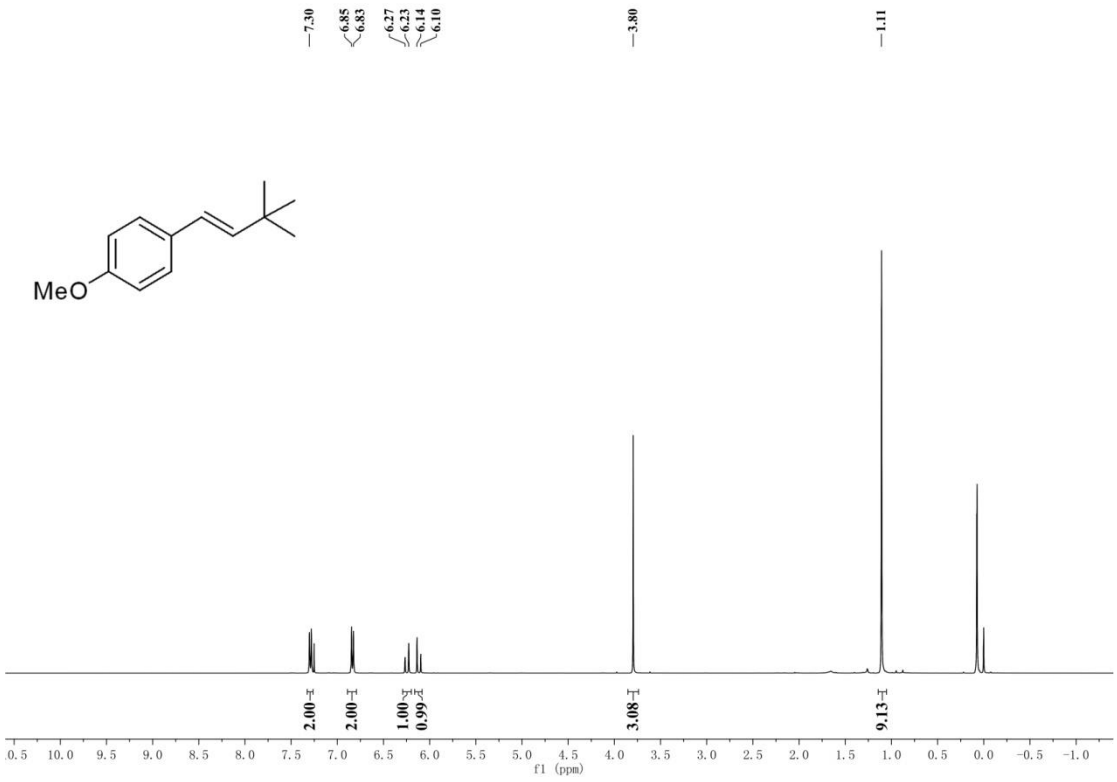

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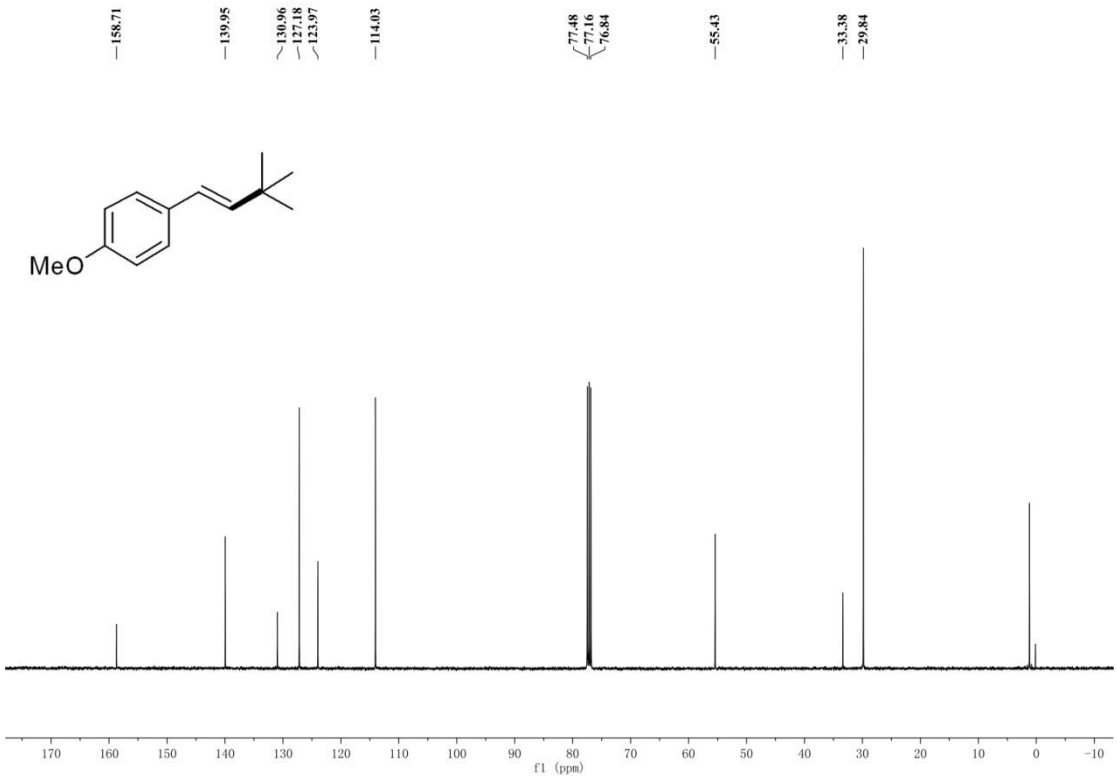

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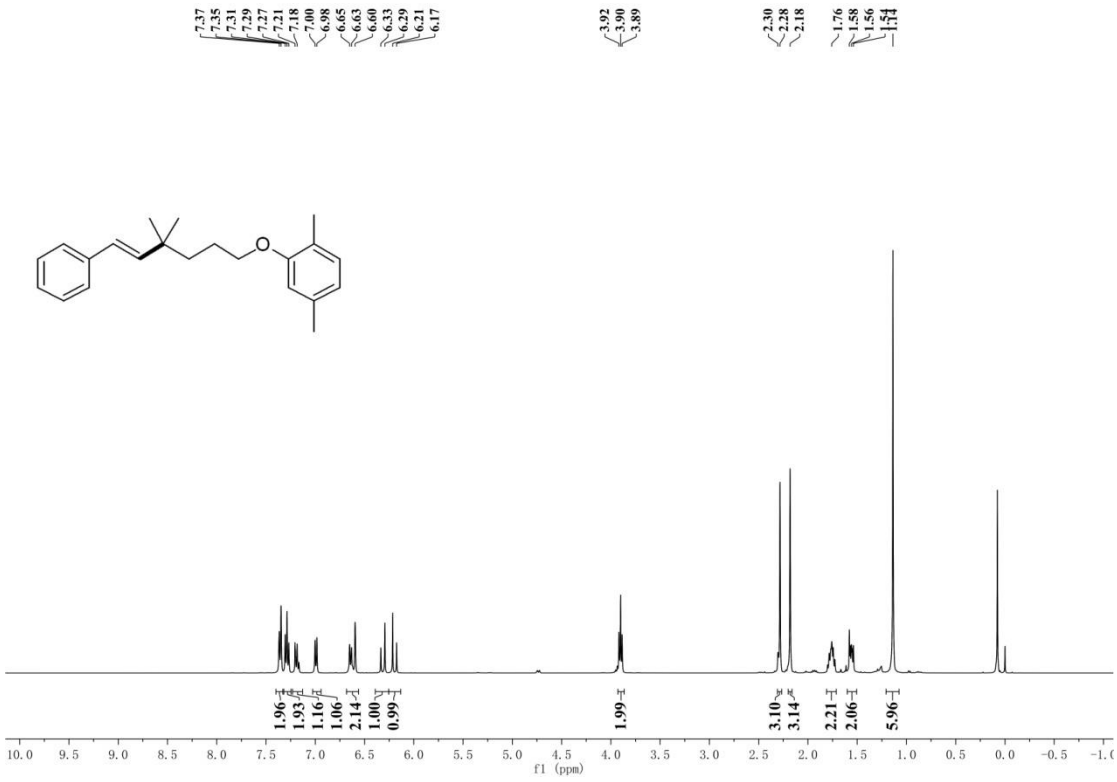

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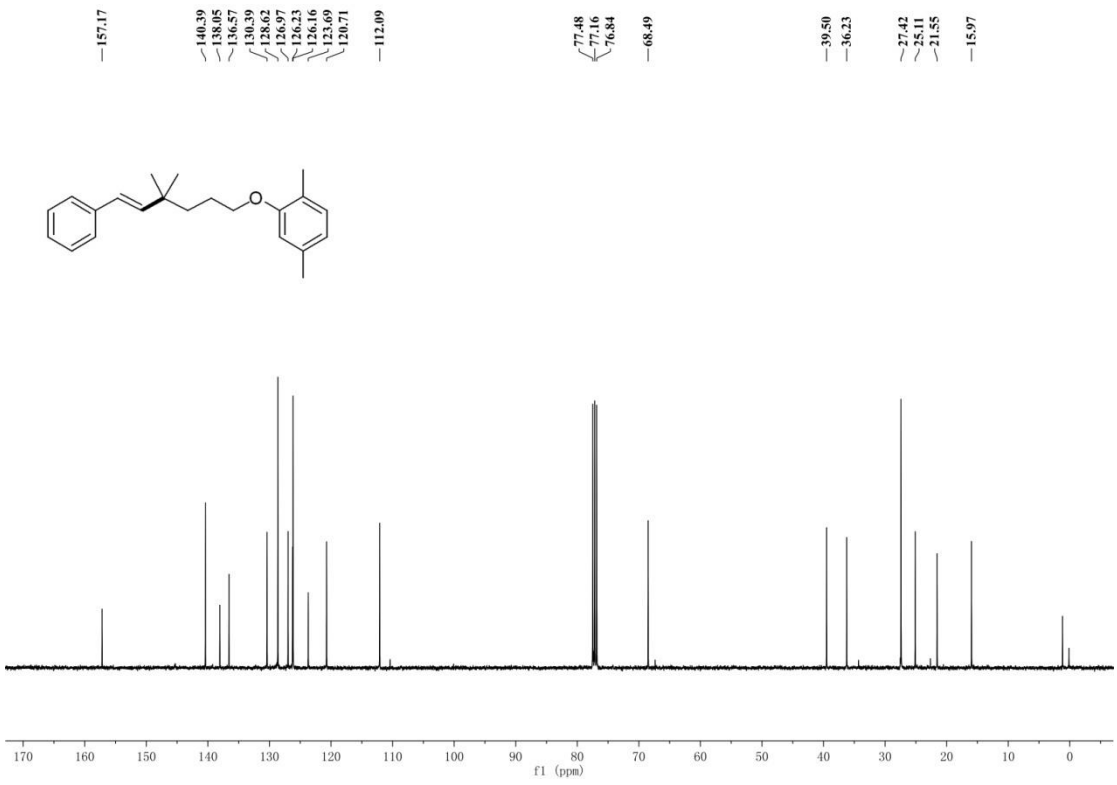

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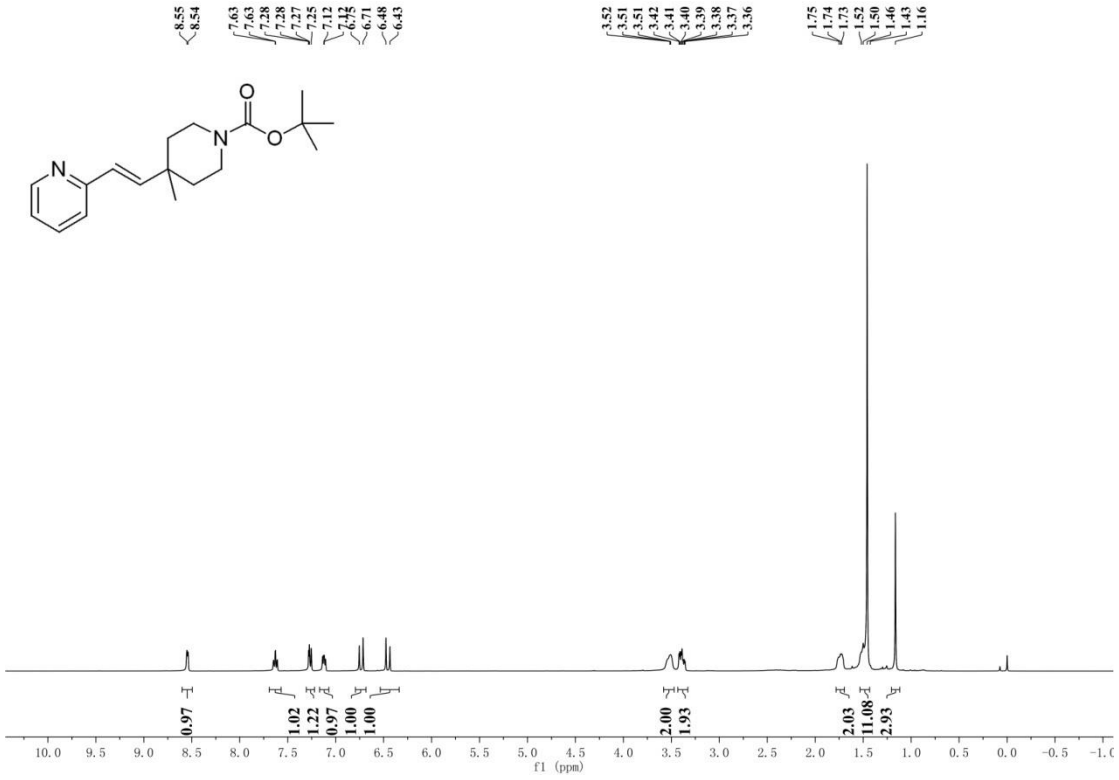

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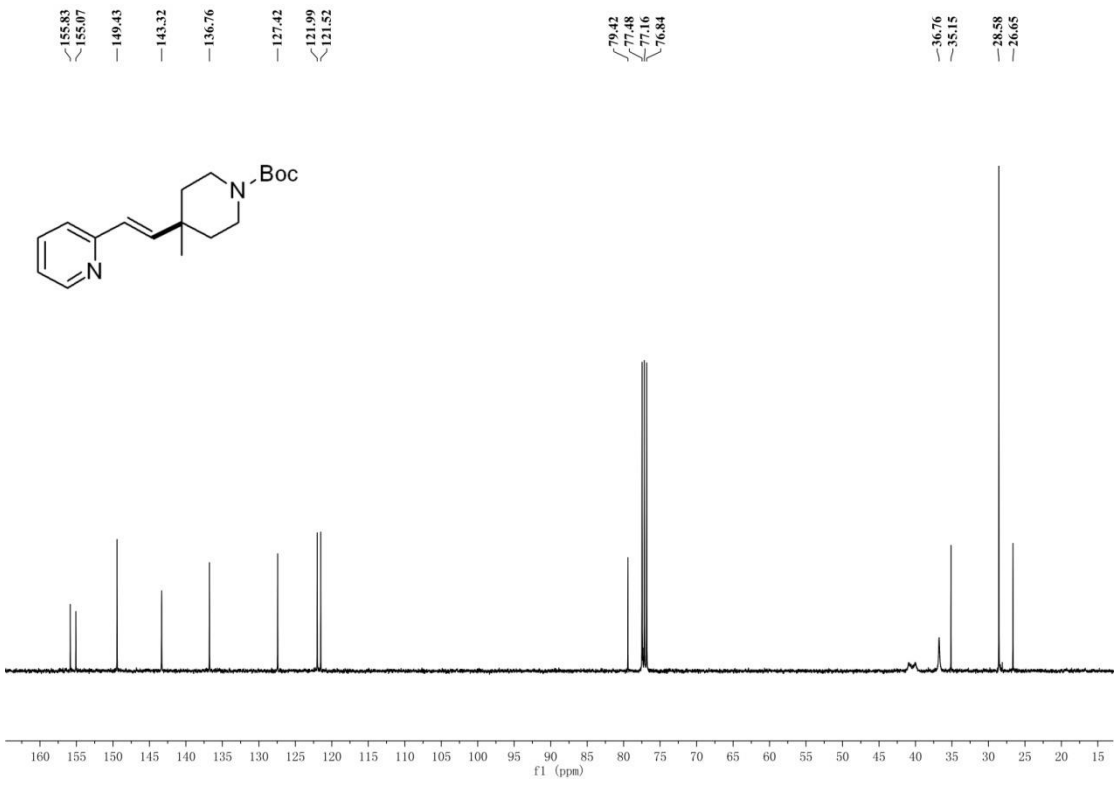

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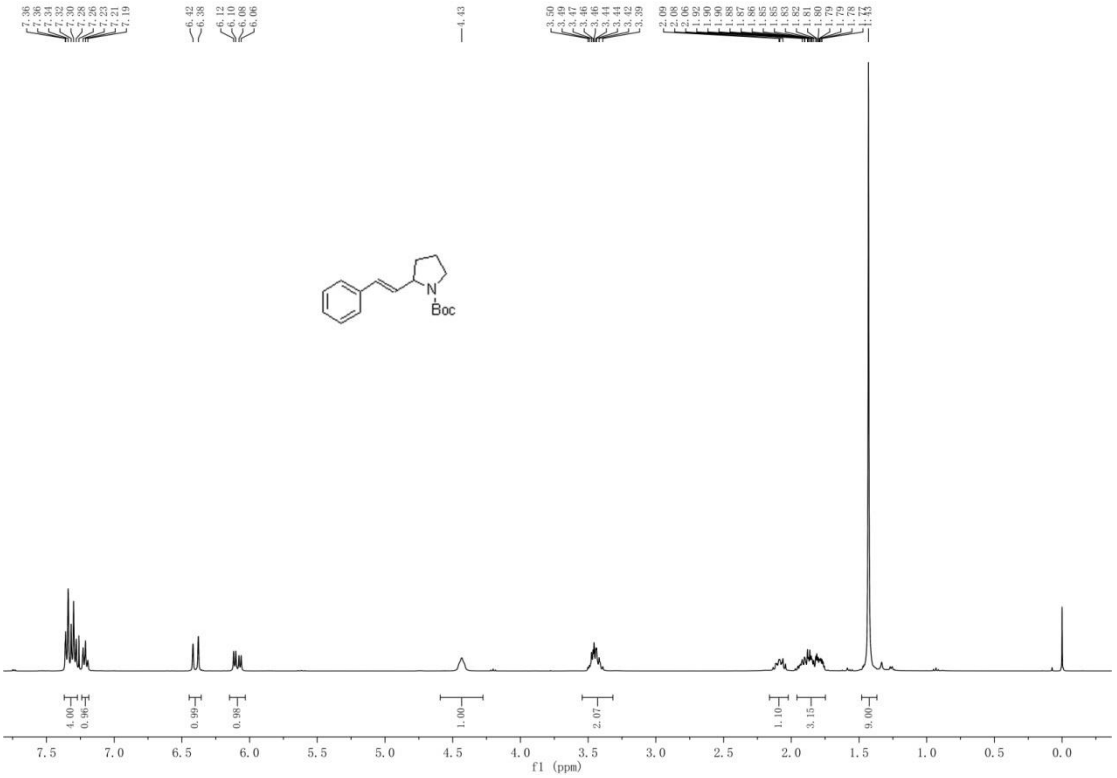

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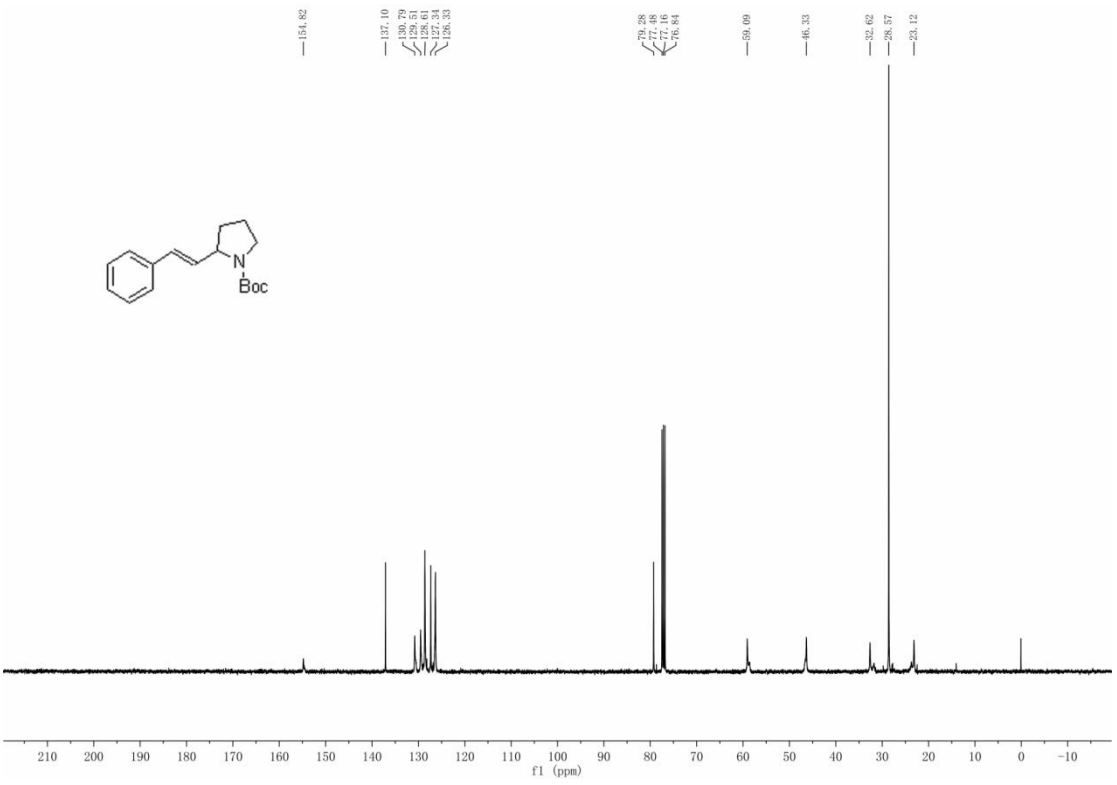

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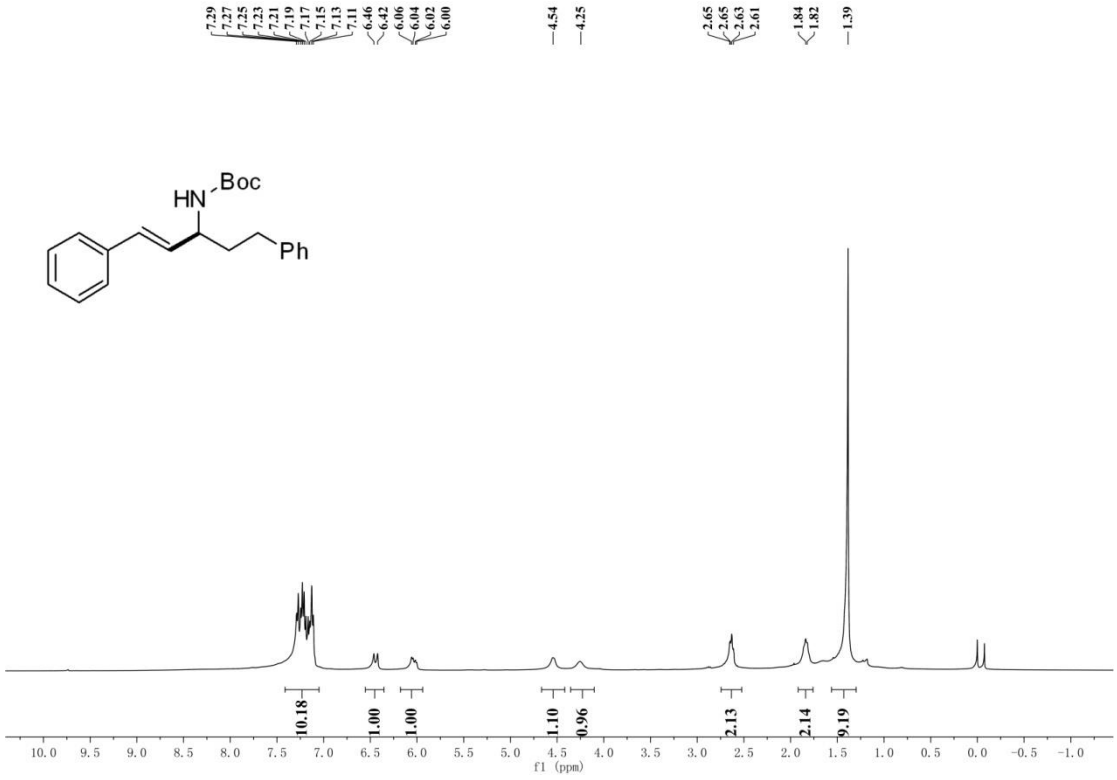

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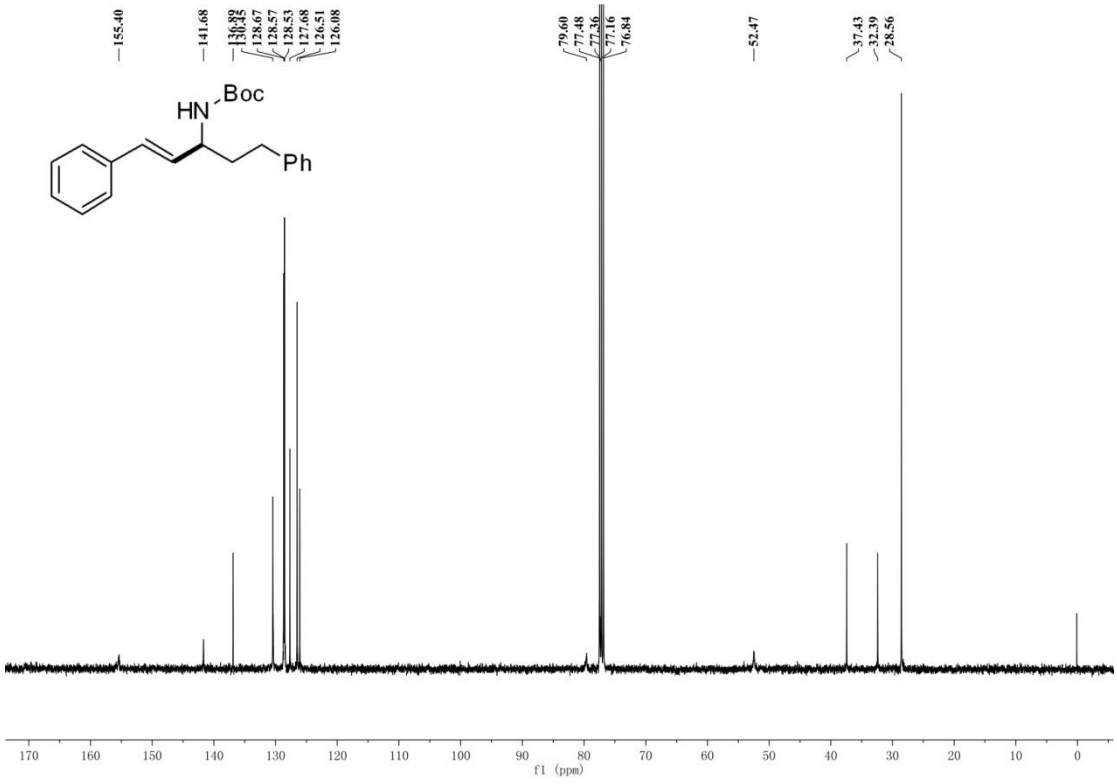

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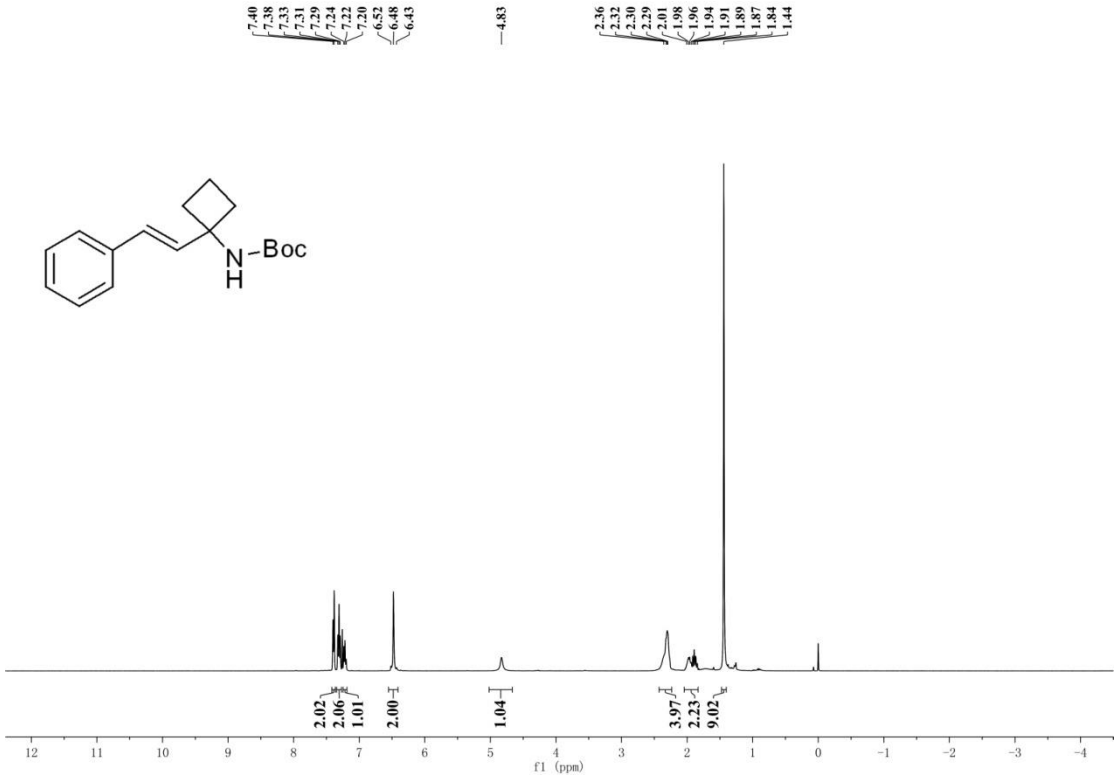

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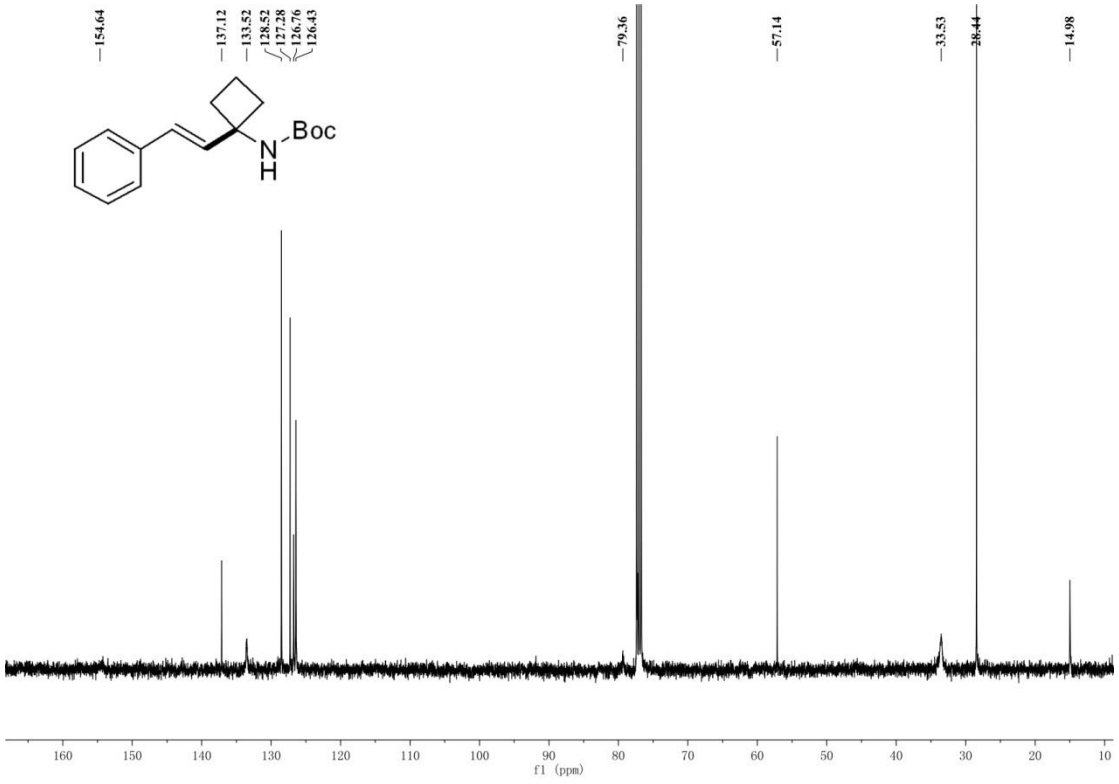

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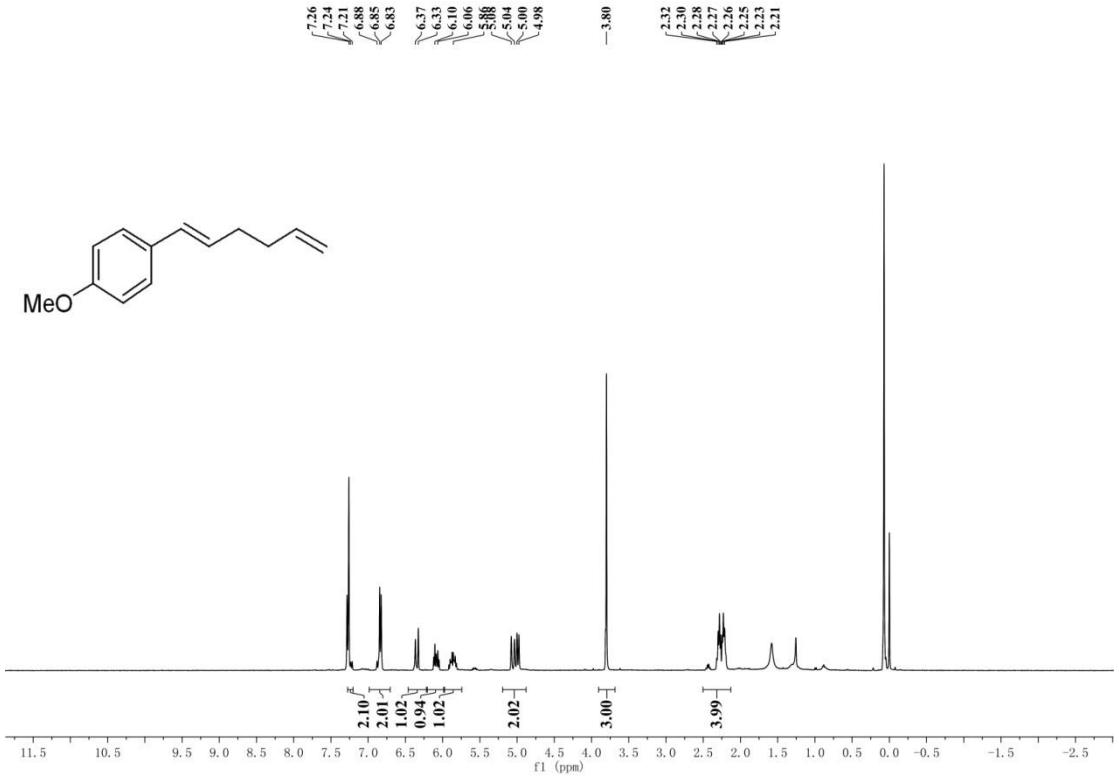

^{13}CNMR of **29**