Supplementary Information

Ruthenium(II)-catalyzed olefination *via* carbonyl reductive cross-coupling

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1. General information

Chemicals: All catalysts, ligands, bases and additives that are commercially available (Aldrich), were used without further purification: hydrazine hydrate (reagent grade, 64-65% wt), mesitylene, anhydrous sodium sulfate. All liquid carbonyls were distilled and solid ones were recrystallized prior to use.

Solvents: Tetrahydrofuran (THF), dimethyl sulfoxide (DMSO) and toluene were taken directly from the *Pure Solvent MD-7* purification system (Innovative Technology). Reaction solvent *tert*-butanol (*t*-BuOH) (ACS grade) was distilled over CaH_2 prior to use. Solvents for filtration, transfers, chromatography and recrystallization were hexane (Fisher, ACS grade), pentane (ACS grade) and dichloromethane (CH_2Cl_2)(ACS grade, amylene stabilized).

NMR Spectroscopy: Nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were recorded on a Bruker AV500 equipped with a 60-position SampleXpress sample changer (^{1}H, 500 MHz; ^{13}C, 125 MHz), or Bruker AV400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz). Chemical shifts for both ^{1}H NMR and ^{13}C NMR spectra are expressed in parts per million (ppm) units downfield from TMS, with the solvent residue peak as the reference ($CDCl_3$: δ 7.26 ppm in ^{1}H NMR; δ 77.0 ppm in ^{13}C NMR). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, dt = doublet of triplets, q = quartet, quin = quintet, sep = septet, m = multiplet, br = broad singlet), coupling constants *J* (Hz), and integration.

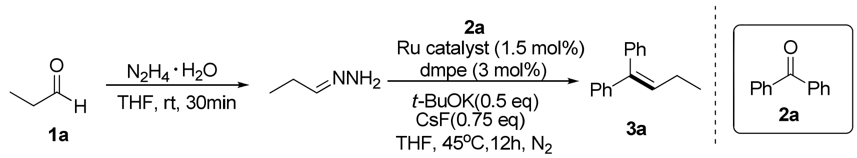
Mass Spectrometry: Mass spectrometry (MS) was performed by the McGill Chemistry Department Mass Spectrometry Facility. High Resolution Mass spectra were recorded using electrospray ionization (ESI+) and/or atmospheric pressure chemical ionization APCI (+/-), performed either on an "Exactive Plus Orbitrap" Thermo Scientific high resolution accurate mass (HR/AM) FT mass spectrometer, or a Bruker Daltonics Maxis Impact quadrupole-time of flight (QTOF) mass spectrometer.

Reaction Setup: All reactions were carried out in flamed-dried V-shaped microwave reaction vials, covered by aluminum seals with PTFE-faced silicone septa, under an atmosphere of nitrogen unless otherwise stated. All reported reaction temperatures correspond to oil bath temperatures. All air and moisture sensitive catalysts, ligands, and reagents were stored and charged in MBRAUN UNIlab Pro Glove Box Workstation.

Purifications: All work-up and purification procedures were carried out with reagent grade solvents. Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Flash column chromatography was performed with E. Merck silica gel P60 (40-63 µm particle size, 230–00 mesh) (SiO_2). Unless otherwise specified, "SiO_2" refers to P60 grade silica gel. Automated flash column chromatography was performed on Biotage Isolera™Spektra Systems with ACI™.

2. Optimization of the reaction conditions

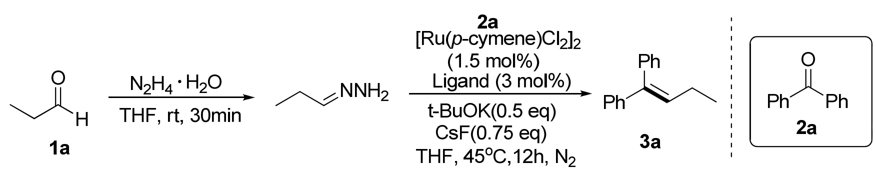
Table S1. The effect of catalysts[a]



Entry	Catalyst	Yield(%)[b]	Entry	Catalyst	Yield(%)[b]
1	---	0	8	Chlorocyclopentadienyl-bis(triphenylphosphine)-ruthenium(II)	22
2	$[(C_5H_5)Ru(CH_3CN)_3]PF_6$	2	9	dichloro(pentamethylcyclopentadienyl)ruthenium(III) polymer	2
3	$[(C_6H_5)_3P]_3Ru(CO)(Cl)H$	3	10	$Ru_3(CO)_{12}$	0
4	[Ru(*p*-cymene)Cl_2]$_2$	84	11	bis(cyclopentadienyl)-ruthenium(II)	0
5	$RuCl_2(PPh_3)_3$	74	12	$Ru_2(C_6H_6)_2Cl_4$	68
6	$[Ru(COD)Cl_2]_n$	78	13	$[Ru(CO)_3Cl_2]_2$	16
7	$RuCl_3$	2			

[a] **1a** (0.28 mmol, 1.4 equiv.), $N_2H_4{\cdot}H_2O$ (0.3 mmol, 1.5 equiv.), THF (0.14 mL), r.t., 30 min; **2a** (0.20 mmol, 1.0 equiv.), Ru catalyst (0.003 mmol, 1.5 mol%), dmpe (0.006 mmol, 3.0 mol%), *t*-BuOK (0.1 mmol, 50 mol%), CsF (0.15 mmol, 75 mol%), 45°C, 12 h, under N_2. [b] Yields were determined by crude ^{1}H NMR using mesitylene as an internal standard.

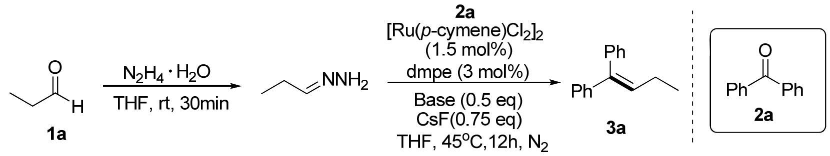
Table S2. The effect of ligands[a]



Entry	Ligand	Yield(%)[b]	Entry	Ligand	Yield(%)[b]
1	---	0	8	P(*p*-tolyl)$_3$	4
2	dppe	10	9	$Ph_4P^+BF_4$	2
3	dppb	11	10	trimesitylphosphine	0
4	dppp	15	11	1,4-bis(dicyclohexyl-phosphino)butane	10
5	dppm	4	12	dicyclohexylphenyl-phosphine	8
6	dmpe	84	13	DavePhos	2
7	*trans*-$PPh_2CH{=}CHPPh_2$	3	14	BrettPhos	0

[a] **1a** (0.28 mmol, 1.4 equiv.), $N_2H_4{\cdot}H_2O$ (0.3 mmol, 1.5 equiv.), THF (0.14 mL), r.t., 30 min; **2a** (0.20 mmol, 1.0 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (0.003 mmol, 1.5 mol%), ligand (0.006 mmol, 3.0 mol%), *t*-BuOK (0.1 mmol, 50 mol%), CsF (0.15 mmol, 75 mol%), 45°C, 12 h, under N_2. [b] Yields were determined by crude ^{1}H NMR using mesitylene as an internal standard.

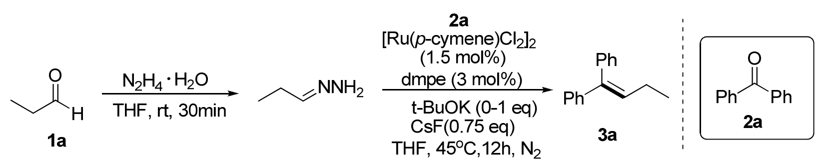
Table S3. The effect of bases[a]



Entry	Base	Yield(%)[b]	Entry	Base	Yield(%)[b]
1	---	0	7	NaOH	78
2	K_3PO_4	51	8	*t*-BuOK	84
3	K_2CO_3	4	9	*t*-BuONa	80
4	Na_2CO_3	0	10	CsOH	82
5	Cs_2CO_3	21	11	DBU	0
6	KOH	78	12	Et_3N	0

[a] **1a** (0.28 mmol, 1.4 equiv.), $N_2H_4 \cdot H_2O$ (0.3 mmol, 1.5 equiv.), THF (0.14 mL), r.t., 30 min; **2a** (0.20 mmol, 1.0 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (0.003 mmol, 1.5 mol%), dmpe (0.006 mmol, 3.0 mol%), base (0.1 mmol, 50 mol%), additive: CsF (0.15 mmol, 75 mol%), 45°C, 12 h, under N_2. [b] Yields were determined by crude ^{1}H NMR using mesitylene as an internal standard.

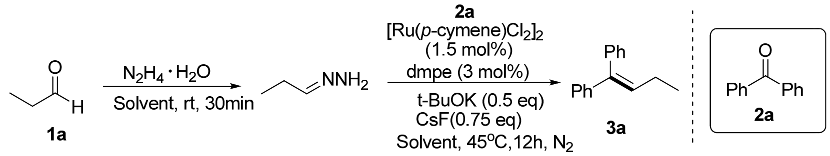
Table S4. The effect of loading of base[a]



Entry	*t*-BuOK(equiv)	Yield(%)[b]	Entry	*t*-BuOK(equiv)	Yield(%)[b]
1	0	0	4	0.5	84
2	0.125	41	5	0.75	84
3	0.25	74	6	1	58

[a] **1a** (0.28 mmol, 1.4 equiv.), $N_2H_4 \cdot H_2O$ (0.3 mmol, 1.5 equiv.), THF (0.14 mL), r.t., 30 min; **2a** (0.20 mmol, 1.0 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (0.003 mmol, 1.5 mol%), dmpe (0.006 mmol, 3.0 mol%), *t*-BuOK (0-1eq), additive: CsF (0.15 mmol, 75 mol%), 45°C, 12 h, under N_2. [b] Yields were determined by crude ^{1}H NMR using mesitylene as an internal standard.

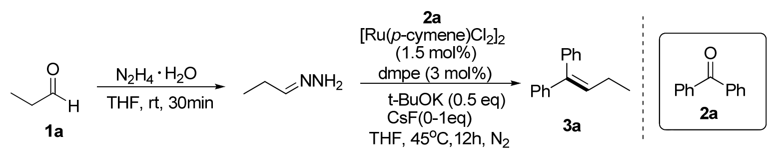
Table S5. The effect of solvents[a]



Entry	Solvent	Yield(%)[b]	Entry	Solvent	Yield(%)[b]
1	THF	84	6	DMSO	0
2	1,4-dioxane	67	7	CH_3CN	0
3	DME	76	8	DCE	0
4	toluene	7	9	DMF	0
5	*t*-BuOH	12	10	EtOH	0

[a] **1a** (0.28 mmol, 1.4 equiv.), $N_2H_4 \cdot H_2O$ (0.3 mmol, 1.5 equiv.), solvent (0.14 mL), r.t., 30 min; **2a** (0.20 mmol, 1.0 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (0.003 mmol, 1.5 mol%), dmpe (0.006 mmol, 3.0 mol%), *t*-BuOK (0.1 mmol, 50 mol%), additive: CsF (0.15 mmol, 75 mol%), 45ºC, 12 h, under N_2. [b] Yields were determined by crude ^{1}H NMR using mesitylene as an internal standard.

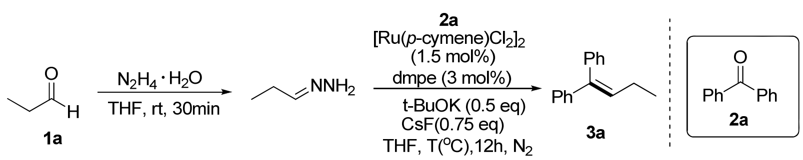
Table S6. The effect of loading of CsF[a]



Entry	CsF(equiv)	Yield(%)[b]	Entry	CsF(equiv)	Yield(%)[b]
1	0	52	4	0.75	84
2	0.25	60	5	1	76
3	0.5	69			

[a] **1a** (0.28 mmol, 1.4 equiv.), $N_2H_4 \cdot H_2O$ (0.3 mmol, 1.5 equiv.), THF (0.14 mL), r.t., 30 min; **2a** (0.20 mmol, 1.0 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (0.003 mmol, 1.5 mol%), dmpe (0.006 mmol, 3.0 mol%), KO^{t}Bu (0.1 mmol, 50 mol%), additive: CsF (0-1 equiv.), 45ºC, 12 h, under N_2. [b] Yields were determined by crude ^{1}H NMR using mesitylene as an internal standard.

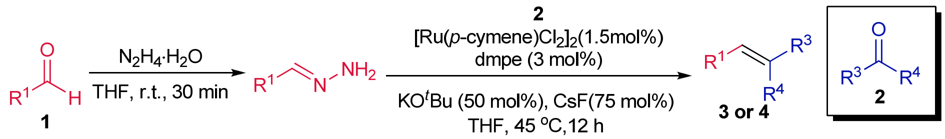
Table S7. The effect of temperature[a]

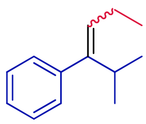


Entry	T(ºC)	Yield(%)[b]	Entry	T(ºC)	Yield(%)[b]
1	25	48	4	55	70
2	35	80	5	65	77
3	45	84			

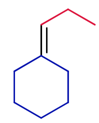
[a] **1a** (0.28 mmol, 1.4 equiv.), $N_2H_4 \cdot H_2O$ (0.3 mmol, 1.5 equiv.), THF (0.14 mL), r.t., 30 min; **2a** (0.20 mmol, 1.0 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (0.003 mmol, 1.5 mol%), dmpe (0.006 mmol, 3.0 mol%), *t*-BuOK (0.1 mmol, 50 mol%), additive: CsF (0.15 mmol, 75 mol%), 25-65ºC, 12 h, under N_2. [b] Yields were determined by crude ^{1}H NMR using mesitylene as an internal standard.

Table S8. The scope of other substrates [a,b]

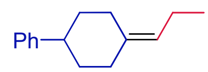




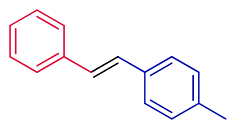
3p 30% (*E*/*Z*: 57/43)



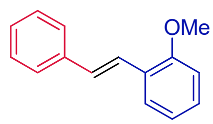
3q 25% (41%)[c]



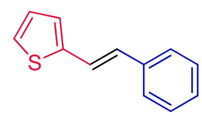
3r 25% (56%)[c]



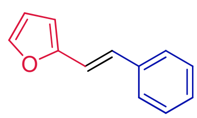
4o 50% (*E*/*Z*: 98/2)[d]



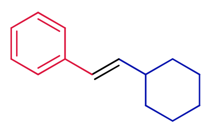
4p 49% (*E*/*Z*: 98/2)[d]



4q 38% (*E*/*Z*> 99/1)[d]



4r 36% (*E*/*Z*> 99/1)[d]



4s 23%(*E*/*Z*> 99/1)[e]

[a] **1** (0.28 mmol, 1.4 equiv.), $N_2H_4 \cdot H_2O$ (0.3 mmol, 1.5 equiv.), THF (0.14 mL), r.t., 30 min; **2** (0.20 mmol, 1.0 equiv.), $[Ru(p\text{-cymene})Cl_2]_2$ (0.003 mmol, 1.5 mol%), dmpe (0.006 mmol, 3.0 mol%), *t*-BuOK (0.1 mmol, 50 mol%); additive: CsF (0.15 mmol, 75 mol%), 45°C, 12 h, under N_2. [b] Isolated yields and the ratio of *E/Z* isomers were determined by crude ^1H NMR analysis. [c] Yields were determined by crude ^1H NMR using mesitylene as an internal standard. [d] K_2CO_3 (0.1 mmol, 50 mol%), 120 °C, 24 h. [e] K_3PO_4 (0.1 mmol, 50 mol%), 12h.

3. General reaction procedure

3.1 The general procedure for intermolecular olefination via carbonyl cross-coupling

A flamed-dried V-shape microwave reaction vial (10 cm^3) equipped with a magnetic stir bar was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (1.8 mg, 0.003 mmol, 1.5 mol%) and KO^{t}Bu (11.2 mg, 0.1 mmol, 50 mol%). The reaction vial was then transferred into the glovebox and charged with dmpe (1.0 µL, 0.006 mmol, 3 mol%) and CsF (22.8 mg, 0.15 mmol, 75 mol%), before being sealed with a rubber septum. The reaction vial was then moved out of the glovebox and sequentially charged with ketones or aldehydes (0.2 mmol, 1.0 equiv) and the **hydrazone solution** (0.28 mmol). The reaction mixture was then heated to 45 °C in an oil bath. Upon stirring for 12 h, the reaction mixture was filtered through a plug of silica gel with CH_2Cl_2 (10 mL) as eluent, concentrated and purified by flash chromatography (hexane as eluent) to give the corresponding alkenes.

Hydrazone solution: A mixture of carbonyls (0.28 mmol, 1.4 equiv) and hydrazine monohydrate (17.5 µL, 0.3 mmol, 64-65 wt%, 1.5 equiv) in THF (0.14 mL) solution was stirred at room temperature for 30 min. Prior to the injection of this hydrazone solution into reaction mixture, a small amount of anhydrous Na_2SO_4 was added.

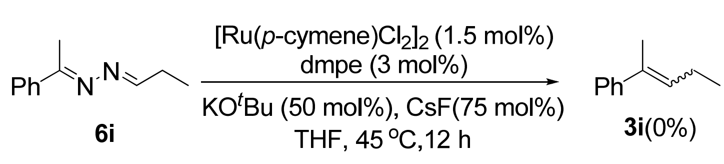
3.2 The general procedure for intramolecular olefination via carbonyl cross-coupling

A flamed-dried V-shape microwave reaction vial (10 cm^3) equipped with a magnetic stir bar was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (1.8 mg, 0.003 mmol, 1.5 mol%) and KO^tBu (11.2 mg, 0.1 mmol, 50 mol%). The reaction vial was then transferred into the glovebox and charged with dmpe (1.0 µL, 0.006 mmol, 3 mol%) and CsF (22.8 mg, 0.15 mmol, 75 mol%), before being sealed with a rubber septum. The reaction vial was then moved out of the glovebox and charged with the **hydrazone solution** (0.2 mmol). The reaction mixture was then heated to 45 °C in an oil bath. Upon stirring for 12 h, the reaction mixture was filtered through a plug of silica gel with CH_2Cl_2 (10 mL) as eluent, concentrated and purified by flash chromatography (hexane as eluent) to give the corresponding cyclic alkenes.

Hydrazone solution: A mixture of carbonyls (0.2 mmol, 1 equiv) and hydrazine monohydrate (15 µL, 0.26 mmol, 64-65 wt%, 1.3 equiv) in THF (0.15 mL) solution was stirred at room temperature for 30 min. Prior to the injection of this hydrazone solution into reaction mixture, a small amount of anhydrous Na_2SO_4 was added.

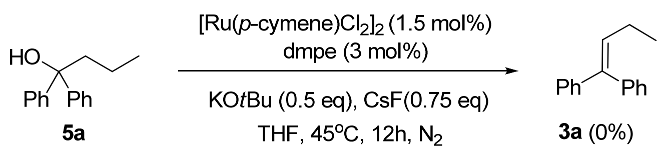
4. Mechanism investigation

4.1 Olefin production from asymmetric azine



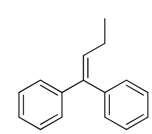
A flamed-dried V-shape microwave reaction vial (10 cm^3) equipped with a magnetic stir bar was charged with [Ru(*p*-cymene)Cl_2]$_2$ (1.8 mg, 0.003 mmol, 1.5 mol%) and KO^{t}Bu (11.2 mg, 0.1 mmol, 50 mol%). The reaction vial was then transferred into the glovebox and charged with dmpe (1.0 µL, 0.006 mmol, 3 mol%) and CsF (22.8 mg, 0.15 mmol, 75 mol%), before being sealed with a rubber septum. The reaction vial was then moved out of the glovebox and sequentially charged with presynthesized azine **6i** (0.2 mmol, 1.0 equiv) and THF (140 µL). The reaction mixture was then heated to 45 °C in an oil bath. Upon stirring for 12 h, the reaction mixture was analyzed by ^{1}H NMR using mesitylene as an internal standard. No desired alkene **3i** was detected.

4.2 Olefin production from alcohol



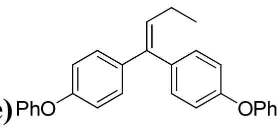
A flamed-dried V-shape microwave reaction vial (10 cm^3) equipped with a magnetic stir bar was charged with [Ru(*p*-cymene)Cl_2]$_2$ (1.8 mg, 0.003 mmol, 1.5 mol%) and KO^{t}Bu (11.2 mg, 0.1 mmol, 50 mol%). The reaction vial was then transferred into the glovebox and charged with dmpe (1.0 µL, 0.006 mmol, 3 mol%) and CsF (22.8 mg, 0.15 mmol, 75 mol%), before being sealed with a rubber septum. The reaction vial was then moved out of the glovebox and sequentially charged with 1,1-diphenylbutan-1-ol **5a** (0.2 mmol, 1.0 equiv) and THF (140 µL). The reaction mixture was then heated to 45 °C in an oil bath. Upon stirring for 12 h, the reaction mixture was analyzed by ^{1}H NMR using mesitylene as an internal standard. No desired alkene **3a** was detected.

5. Characterization data of products 3a-4s

but-1-ene-1,1-diyldibenzene  **(3a)**

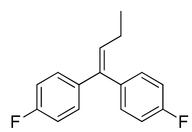
Colorless oil; The spectroscopic data correspond to those previously reported in the literature.[1] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.43-7.40 (m, 2H), 7.34 (tt, J_1 = 1.4

Hz, J_2 = 7.5 Hz, 1H), 7.32-7.22 (m, 7H), 6.12 (t, J = 7.5 Hz, 1H), 2.17 (quint, J = 7.5 Hz, 2H), 1.09 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 142.9, 141.0, 140.3, 131.8, 129.9, 128.1, 128.0, 127.2, 126.9, 126.8, 23.2, 14.6; MS (EI) m/z: 208.1, 193.1, 178.1, 165.1, 129.1.

4,4'-(but-1-ene-1,1-diyl)bis(phenoxybenzene) 

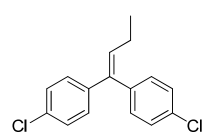
(3b)

Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.41-7.34 (m, 4H), 7.23 (d, J = 8.7 Hz, 2H), 7.18-7.09 (m, 6H), 7.06-7.03 (m, 4H), 6.94 (d, J = 8.7 Hz, 2H), 6.04 (t, J = 7.5 Hz, 1H), 2.18 (quint, J = 7.5 Hz, 2H), 1.08 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 157.3, 157.1, 156.3, 156.2, 139.6, 138.1, 135.1, 131.2, 131.2, 129.8, 129.7, 128.5, 123.4, 123.2, 119.1, 118.8, 118.5, 118.3, 23.3, 14.6; HRMS calc. for $C_{28}H_{25}O_2$ $(M+H)^+$, 393.18491; found, 393.18478.

4,4'-(but-1-ene-1,1-diyl)bis(fluorobenzene) 

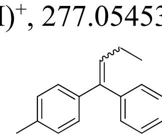
(3c)

Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.20-7.14 (m, 4H), 7.09 (tt, J_1 = 2.7 Hz, J_2 = 8.8 Hz, 2H), 6.98 (tt, J_1 = 3.1 Hz, J_2 = 8.7 Hz, 2H), 6.03 (t, J = 7.5 Hz, 1H), 2.13 (quint, J = 7.5 Hz, 2H), 1.07 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 162.9 (d, J = 15.2 Hz), 160.9 (d, J = 15.0 Hz), 139.0, 138.8 (d, J = 3.2 Hz), 135.9 (d, J = 3.3 Hz), 131.9, 131.4 (d, J = 7.9 Hz), 128.7 (d, J = 7.8 Hz), 115.1 (d, J = 21.2 Hz), 114.9 (d, J = 21.2 Hz), 23.2, 14.5; HRMS calc. for $C_{16}H_{15}F_2$ $(M+H)^+$, 245.11363; found, 245.11323.

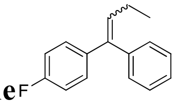
4,4'-(but-1-ene-1,1-diyl)bis(chlorobenzene) 

(3d)

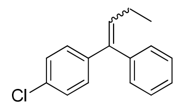
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.37 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.08 (t, J = 7.5 Hz, 1H), 2.13 (quint, J = 7.5 Hz, 2H), 1.06 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 140.9, 138.9, 138.2, 133.0, 132.8, 132.7, 131.2, 128.5, 128.4, 128.3, 23.2, 14.4; HRMS calc. for $C_{16}H_{15}Cl_2$ $(M+H)^+$, 277.05453; found, 277.05431.

1-methyl-4-(1-phenylbut-1-enyl)benzene  (***E/Z***) **(3e)**

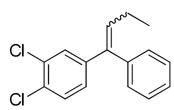
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.41-7.38 (m, 2H), 7.34-7.20 (m, 10H), 7.16-7.14 (m, 2H), 7.11-7.09 (m, 4H), 6.09-6.06 (m, 2H), 2.42 (s, 3H), 2.36 (s, 3H), 2.20-2.11 (m, 4H), 1.08-1.05 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 143.1, 140.9, 140.8, 140.5, 140.1, 137.3, 136.5, 136.4, 131.6, 130.9, 129.9, 129.8, 128.8, 128.8, 128.1, 128.0, 127.3, 127.1, 126.8, 126.7, 23.3, 23.2, 21.3, 21.1, 14.6, 14.6; HRMS calc. for $C_{17}H_{19}$ $(M+H)^+$, 223.14813; found, 223.14783.

1-fluoro-4-(1-phenylbut-1-enyl)benzene  **(*E/Z*)(3f)**

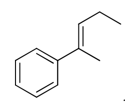
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.41-7.38 (m, 1.83H), 7.35-7.27 (m, 3.49H), 7.26-7.16 (m, 8.65H), 7.08 (tt, J_1 = 2.2 Hz, J_2 = 6.6 Hz, 2H), 6.97 (tt, J_1 = 2.2 Hz, J_2 = 6.6 Hz, 1.84H), 6.10 (t, J = 7.5 Hz, 1H), 6.03 (t, J = 7.5 Hz, 0.92H), 2.17-2.11 (m, 3.88H), 1.08-1.05 (m, 5.76H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 161.9 (d, J = 244.2 Hz), 161.8 (d, J = 244.2 Hz), 142.7, 140.1, 140.0, 140.0, 139.0 (d, J = 3.2 Hz), 136.1 (d, J = 3.4 Hz), 132.1, 131.6, 131.6, 131.5 (d, J = 7.8 Hz), 129.8, 128.7 (d, J = 7.8 Hz), 128.2 (d, J = 10.3 Hz), 127.2, 126.9 (d, J = 10.6 Hz), 115.0 (d, J = 21.1 Hz), 114.8 (d, J = 21.1 Hz), 23.2, 14.5, 14.5; HRMS calc. for $C_{16}H_{16}F$ $(M+H)^+$, 227.12306; found, 227.12267.

1-chloro-4-(1-phenylbut-1-enyl)benzene  **(*E/Z*)(3g)**

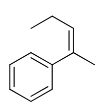
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.41-7.33 (m, 5H), 7.29-7.21 (m, 7H), 7.19-7.13 (m, 6H), 6.10 (t, J = 7.5 Hz, 1H), 6.08 (t, J = 7.5 Hz, 1H), 2.17-2.10 (m, 4H), 1.08-1.04 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 142.4, 141.3, 140.0, 139.9, 139.8, 138.7, 132.8, 132.6, 132.3, 132.2, 131.3, 129.8, 128.5, 128.4, 128.3, 128.2, 128.2, 127.2, 127.1, 127.0, 23.2, 23.2, 14.5; HRMS calc. for $C_{16}H_{16}Cl$ $(M+H)^+$, 243.09350; found, 243.09303.

1,2-dichloro-4-(1-phenylbut-1-enyl)benzene  **(*E/Z*)(3h)**

Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.46 (d, J = 8.2 Hz, 0.56H), 7.41 (d, J = 7.0 Hz, 0.9H), 7.37-7.26 (m, 3.68H), 7.22-7.20 (m, 1.12H), 7.17-7.16 (m, 0.9H), 7.05(dd, J_1 = 2.0 Hz, J_2 = 8.2 Hz, 1H), 6.13-6.08 (m, 1H), 2.14 (quint, J = 7.5 Hz, 2H), 1.09-1.05 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 143.0, 141.8, 140.3, 139.1, 138.9, 133.4, 133.0, 132.3, 132.2, 131.7, 131.0, 130.6, 130.2, 129.9, 129.8, 129.4, 129.0, 128.4, 128.3, 127.3, 127.2, 127.2, 126.6, 23.3, 23.2, 14.4, 14.4; HRMS calc. for $C_{16}H_{15}Cl_2$ $(M+H)^+$, 277.05453; found, 277.05406.

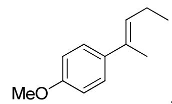
(*E*)-pent-2-en-2-ylbenzene  ***E*-(3i)**

Colorless oil; The spectroscopical data correspond to those previously reported in the literature.[1a] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.44-7.42 (m, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.26 (tt, J_1 = 1.3 Hz, J_2 = 7.3 Hz, 1H), 5.83 (tq, J_1 = 1.3 Hz, J_2 = 7.5 Hz, 1H), 2.26 (quint, J = 7.5 Hz, 2H), 2.08 (d, J = 1.2 Hz, 3H), 1.11 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 144.0, 134.1, 130.3, 128.2, 126.4, 125.6, 22.1, 15.6, 14.1; MS (EI) m/z: 146.1, 131.1, 115.0, 91.1.

(*Z*)-pent-2-en-2-ylbenzene  ***Z*-(3i)**

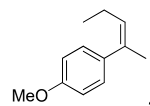
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.35 (t, J = 7.4 Hz, 2H), 7.25 (tt, J_1

= 1.3 Hz, J_2 = 7.5 Hz, 1H), 7.22-7.20 (m, 2H), 5.48 (td, J_1 = 1.3 Hz, J_2 = 7.4 Hz, 1H), 2.05 (d, J = 1.7 Hz, 3H), 2.01 (quintd, J_1 = 1.1 Hz, J_2 = 7.4 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 142.2, 135.4, 129.5, 128.0, 127.9, 126.4, 25.5, 22.4, 14.7; HRMS calc. for $C_{11}H_{15}$ $(M+H)^+$, 147.11683; found, 147.11686.

(*E*)-1-methoxy-4-(pent-2-en-2-yl)benzene 

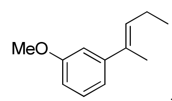
***E*-(3ia)**

Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.34 (dt, J_1 = 3.1 Hz, J_2 = 8.9 Hz, 2H), 6.87 (dt, J_1 = 3.1 Hz, J_2 = 8.9 Hz, 2H), 5.72 (td, J_1 = 1.3 Hz, J_2 = 7.5 Hz, 1H), 3.83 (s, 3H), 2.22 (quint, J = 7.5 Hz, 2H), 2.03 (d, J = 1.0 Hz, 3H), 1.08 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 158.3, 136.6, 133.3, 128.7, 126.6, 113.5, 55.3, 22.0, 15.7, 14.2; HRMS calc. for $C_{12}H_{17}O$ $(M+H)^+$, 177.12739; found, 177.12710.

(*Z*)-1-methoxy-4-(pent-2-en-2-yl)benzene 

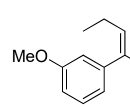
***Z*-(3ia)**

Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.15 (dt, J_1 = 2.9 Hz, J_2 = 8.8 Hz, 2H), 6.89 (dt, J_1 = 2.9 Hz, J_2 = 8.8 Hz, 2H), 5.44 (tq, J_1 = 1.4 Hz, J_2 = 7.5 Hz, 1H), 3.84 (s, 3H), 2.05-1.99 (m, 5H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 158.1, 134.8, 134.5, 129.2, 129.0, 113.4, 55.2, 25.6, 22.5, 14.8; HRMS calc. for $C_{12}H_{17}O$ $(M+H)^+$, 177.12739; found, 177.12712.

(*E*)-1-methoxy-3-(pent-2-en-2-yl)benzene 

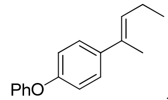
***E*-(3ib)**

Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.25 (t, J = 8.0 Hz, 1H), 7.03-7.00 (m, 1H), 6.95 (t, J = 2.4 Hz, 1H), 6.81-6.79 (m, 1H), 5.72 (td, J_1 = 1.3 Hz, J_2 = 7.1 Hz, 1H), 3.85 (s, 3H), 2.24 (quint, J = 7.5 Hz, 2H), 2.05 (d, J = 1.1 Hz, 3H), 1.09 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 159.5, 145.6, 133.9, 130.5, 129.0, 118.2, 111.7, 111.6, 55.2, 22.0, 15.7, 14.1; HRMS calc. for $C_{12}H_{17}O$ $(M+H)^+$, 177.12739; found, 177.12717.

(*Z*)-1-methoxy-3-(pent-2-en-2-yl)benzene 

***Z*-(3ib)**

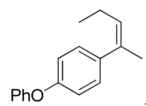
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.27 (t, J = 7.9 Hz, 1H), 6.82-6.79 (m, 2H), 6.76 (t, J = 1.7 Hz, 1H), 5.44 (td, J_1 = 1.4 Hz, J_2 = 7.5 Hz, 1H), 3.84 (s, 3H), 2.04-1.98 (m, 5H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 159.3, 143.7, 135.3, 129.6, 129.0, 120.5, 113.7, 111.7, 55.2, 25.5, 22.5, 14.7; HRMS calc. for $C_{12}H_{17}O$ $(M+H)^+$, 177.12739; found, 177.12706.

(*E*)-1-(pent-2-en-2-yl)-4-phenoxybenzene 

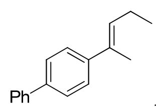
***E*-(3ic)**

Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.40-7.34 (m, 4H), 7.18 (tt, J_1 = 2.8 Hz, J_2 = 7.4 Hz, 1H), 7.05-7.03 (m, 2H), 6.99 (d, J = 8.8Hz, 2H), 5.78 (tq, J_1 = 1.2

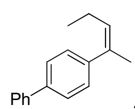
Hz, J_2 = 7.2 Hz, 1H), 2.24 (quint, J = 7.5 Hz, 2H), 2.05 (d, J = 1.2 Hz, 3H), 1.09 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 157.5, 155.7, 139.2, 133.3, 129.7, 129.7, 126.8, 123.0, 118.7, 118.6, 22.1, 15.7, 14.2; HRMS calc. $C_{17}H_{19}O$ $(M+H)^+$, 239.14304; found, 239.14258.

(*Z*)-1-(pent-2-en-2-yl)-4-phenoxybenzene  ***E*-(3ic)**

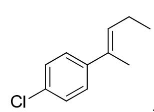
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.38-7.35 (m, 2H), 7.18 (dt, J_1 = 2.8 Hz, J_2 = 8.7 Hz, 2H), 7.14-7.11 (m, 1H), 7.07-7.05 (m, 2H), 6.99 (dt, J_1 = 2.8 Hz, J_2 = 8.7 Hz, 2H), 5.47 (td, J_1 = 1.5 Hz, J_2 = 7.4 Hz, 1H), 2.07-2.01 (m, 5H), 0.98 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 157.3, 155.7, 137.1, 134.6, 129.7, 129.6, 129.3, 123.2, 118.9, 118.3, 25.5, 22.5, 14.7; HRMS calc. $C_{17}H_{19}O$ $(M+H)^+$, 239.14304; found, 239.14264.

(*E*)-4-(pent-2-en-2-yl)biphenyl  ***E*-(3id)**

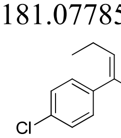
White solid; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.63 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.51-7.45 (m, 4H), 7.36 (t, J = 7.4 Hz, 1H), 5.89 (td, J_1 = 1.2 Hz, J_2 = 7.1 Hz, 1H), 2.28 (quint, J = 7.1 Hz, 2H), 2.10 (s, 3H), 1.12 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 142.9, 140.9, 139.2, 133.6, 130.4, 128.7, 127.1, 127.0, 126.9, 125.9, 22.1, 15.6, 14.1; HRMS calc. $C_{17}H_{19}$ $(M+H)^+$, 223.14813; found, 223.14774.

(*Z*)-4-(pent-2-en-2-yl)biphenyl  ***Z*-(3id)**

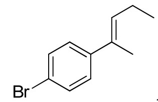
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.64 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.30 (d, J = 8.3 Hz, 2H), 5.52 (td, J_1 = 1.4 Hz, J_2 = 7.4 Hz, 1H), 2.11-2.06 (m, 5H), 1.00 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 141.1, 141.0, 139.2, 134.9, 129.9, 128.7, 128.4, 127.1, 127.0, 126.7, 25.4, 22.6, 14.8; HRMS calc. $C_{17}H_{19}$ $(M+H)^+$, 223.14813; found, 223.14760.

(*E*)-1-chloro-4-(pent-2-en-2-yl)benzene  ***E*-(3ie)**

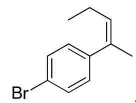
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.33 (dt, J_1 = 2.3 Hz, J_2 = 8.8 Hz, 2H), 7.29 (dt, J_1 = 2.3 Hz, J_2 = 8.8 Hz, 2H), 5.79 (tq, J_1 = 1.3 Hz, J_2 = 7.1 Hz, 1H), 2.23 (quint, J = 7.5 Hz, 2H), 2.03 (d, J = 1.3 Hz, 3H), 1.09 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 142.4, 133.0, 132.1, 130.8, 128.2, 126.9, 22.1, 15.6, 14.0; HRMS calc. for $C_{11}H_{14}Cl$ $(M+H)^+$, 181.07785; found, 181.07753.

(*Z*)-1-chloro-4-(pent-2-en-2-yl)benzene  ***Z*-(3ie)**

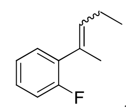
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.31 (dt, J_1 = 2.5 Hz, J_2 = 8.5 Hz, 2H), 7.13 (dt, J_1 = 2.5 Hz, J_2 = 8.5 Hz, 2H), 5.49 (td, J_1 = 1.3 Hz, J_2 = 7.4 Hz, 1H), 2.02 (d, *J* = 1.3 Hz, 3H), 1.98 (quint, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 140.5, 134.2, 132.1, 130.2, 129.3, 128.2, 25.3, 22.4, 14.6; HRMS calc. for $C_{11}H_{14}Cl$ $(M+H)^+$, 181.07785; found, 181.07769.

(*E*)-1-bromo-4-(pent-2-en-2-yl)benzene  ***E*-(3if)**

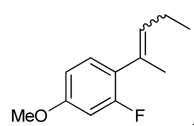
Colorless oil; ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.44 (dt, J_1 = 2.6 Hz, J_2 = 8.7 Hz, 2H), 7.27 (dt, J_1 = 2.6 Hz, J_2 = 8.7 Hz, 2H), 5.79 (tq, J_1 = 1.3 Hz, J_2 = 7.1 Hz, 1H), 2.22 (quint, *J* = 7.6 Hz, 2H), 2.02 (d, *J* = 1.2 Hz, 3H), 1.08 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 142.8, 133.1, 131.1, 130.9, 127.2, 120.2, 22.1, 15.5, 14.0; HRMS calc. for $C_{11}H_{14}Br$ $(M+H)^+$, 225.02734; found, 225.02725.

(*Z*)-1-bromo-4-(pent-2-en-2-yl)benzene  ***Z*-(3if)**

Colorless oil; ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.47 (dt, J_1 = 2.5 Hz, J_2 = 8.5 Hz, 2H), 7.08 (dt, J_1 = 2.5 Hz, J_2 = 8.4 Hz, 2H), 5.49 (td, J_1 = 1.4 Hz, J_2 = 7.4 Hz, 1H), 2.01 (d, *J* = 1.4 Hz, 3H), 2.00-1.94 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 141.0, 134.3, 131.1, 130.2, 129.7, 120.2, 25.3, 22.4, 14.6; HRMS calc. for $C_{11}H_{14}Br$ $(M+H)^+$, 225.02734; found, 225.02727.

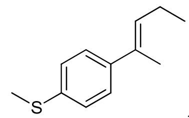
1-fluoro-2-(pent-2-en-2-yl)benzene  ***E/Z*-(3ig)**

Colorless oil; ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.28-7.19 (m, 2.41H), 7.17-7.01 (m, 3.37H), 5.63-5.58 (m, 1.45H), 2.23 (quint, *J* = 7.4 Hz, 2.04H), 2.03 (s, 4.39H), 1.89 (quint, *J* = 7.4 Hz, 0.9H), 1.09 (t, *J* = 7.5 Hz, 3H), 0.95 (t, *J* = 7.5 Hz, 1.37H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 159.9 (d, *J* = 244.8 Hz), 159.5 (d, *J* = 243.4 Hz), 133.5 (d, *J* = 2.0 Hz), 132.8 (d, *J* = 14.1 Hz), 131.7, 130.7, 130.4 (d, *J* = 4.6 Hz), 129.9, 129.7 (d, *J* = 4.7 Hz), 129.5 (d, *J* = 16.9 Hz), 128.2 (d, *J* = 8.0 Hz), 127.9 (d, *J* = 8.2 Hz), 123.8 (d, *J* = 3.5 Hz), 123.7 (d, *J* = 3.5 Hz), 115.6 (d, *J* = 22.7 Hz), 115.5 (d, *J* = 22.6 Hz), 24.7 (d, *J* = 1.6 Hz), 22.7, 21.7, 16.7(d, *J* = 3.7 Hz), 14.2, 13.9; HRMS calc. $C_{11}H_{14}F$ $(M+H)^+$, 165.10741; found, 165.10719.

2-fluoro-4-methoxy-1-(pent-2-en-2-yl)benzene  ***E/Z*-(3ih)**

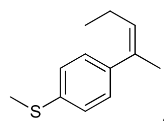
Colorless oil; ^1H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.15 (t, *J*= 8.7 Hz, 0.66H), 7.04 (t, *J* = 8.4 Hz, 0.34H), 6.71-6.59 (m, 2H), 5.56 (t, *J*= 7.4 Hz, 1H), 3.82 (s, 1.02H), 3.81 (s, 1.98H), 2.21 (quint, *J*= 7.5 Hz, 1.32H), 2.00 (s, 3H), 1.88(quint, *J*= 7.5 Hz, 0.68H), 1.07 (t, *J* = 7.5 Hz, 1.98H), 0.94 (t, *J* = 7.5 Hz, 1.02H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 160.4 (d, *J*= 244.9 Hz), 159.9 (d, *J*= 243.9 Hz), 159.5 (d, *J*= 10.6 Hz), 159.4 (d, *J*= 10.8 Hz), 132.6 (d, *J*= 2.2 Hz), 131.6, 130.6 (d, *J*= 6.6 Hz), 130.2 (d, *J*= 1.1 Hz), 130.0 (d, *J*= 6.6 Hz), 129.6, 125.1 (d, *J*= 14.5 Hz), 121.5 (d, *J*= 17.5 Hz), 109.6 (d, *J*= 3.1 Hz), 109.5 (d, *J*= 2.8 Hz), 101.7 (d, *J*= 26.7 Hz), 101.6 (d, *J*= 26.4 Hz), 55.53, 55.50, 24.8 (d, *J*= 1.7 Hz), 22.7, 21.7, 16.8 (d, *J*= 3.6 Hz), 14.2, 14.0;

HRMS calc. $C_{12}H_{16}OF$ $(M+H)^+$, 195.11797, found, 195.11792.

(*E*)-methyl(4-(pent-2-en-2-yl)phenyl)sulfane 

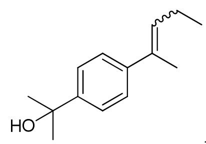
***E*-(3ii)**

Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.34 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 5.79 (dt, J_1 = 1.4 Hz, J_2 = 7.2 Hz, 1H), 2.51 (s, 3H), 2.23 (quint, J = 7.5 Hz, 2H), 2.03 (d, J = 1.2 Hz, 3H), 1.08 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 141.0, 136.1, 133.4, 130.0, 126.7, 126.0, 22.1, 16.2, 15.5, 14.1; HRMS calc. $C_{12}H_{16}S$ $(M+H)^+$, 193.10455, found, 193.10444.

(*Z*)-methyl(4-(pent-2-en-2-yl)phenyl)sulfane 

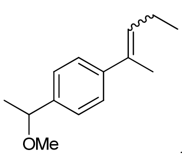
***Z*-(3ii)**

Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.25 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 5.47 (dt, J_1 = 1.8 Hz, J_2 = 7.5 Hz, 1H), 2.52 (s, 3H), 2.04-1.98 (m, 5H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 139.1, 136.1, 134.7, 129.8, 128.5, 126.4, 25.3, 22.5, 16.0, 14.7; HRMS calc. $C_{12}H_{16}S$ $(M+H)^+$, 193.10455, found, 193.10449.

2-(4-(pent-2-en-2-yl)phenyl)propan-2-ol 

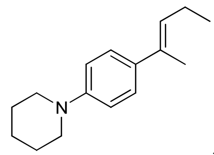
***E*/*Z*-(3ij)**

Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.48-7.44 (m, 3.14H), 7.39 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 8.3 Hz, 1.14H), 5.82 (t, J_1 = 1.4 Hz, J_2 = 7.2 Hz, 1H), 5.48 (t, J_1 = 1.4 Hz, J_2 = 7.4 Hz, 0.57H), 2.24 (quint, J = 7.5 Hz, 2H), 2.06-2.00 (m, 5.75H), 1.77 (brs, 1.58H), 1.63 (s, 3.42H), 1.61 (s, 6H), 1.08 (t, J = 7.5 Hz, 3H), 0.97 (t, J = 7.5 Hz, 1.71H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 147.3, 147.1, 142.4, 140.5, 135.0, 133.6, 130.2, 129.7, 127.8, 125.4, 124.2, 124.1, 72.4, 72.4, 31.7, 25.4, 22.5, 22.1, 15.6, 14.7, 14.1; HRMS calc. $C_{14}H_{20}ONa$$(M+Na)^+$, 227.14064, found, 227.14064.

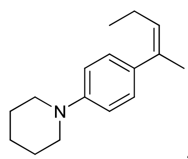
1-(1-methoxyethyl)-4-(pent-2-en-2-yl)benzene 

***E*/*Z*-(3ik)**

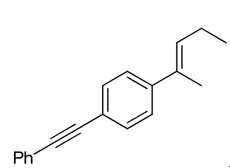
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.39 (d, J = 8.3 Hz, 2H), 7.29-7.26 (m, 2.88H), 7.19 (d, J = 8.1 Hz, 0.88H), 5.82 (t, J_1 = 1.4 Hz, J_1 = 7.2 Hz, 1H), 5.47 (t, J_1 = 1.4 Hz, J_1 = 7.4 Hz, 0.44H), 4.34-4.29 (m, 1.44H), 3.27 (s, 1.32H), 3.25 (s, 3H), 2.24 (quint, J = 7.5 Hz, 2H), 2.06-2.01 (m, 5.07H), 1.48-1.45(m, 4.34H), 1.08 (t, J = 7.5 Hz, 3H), 0.97 (t, J = 7.5 Hz, 1.32H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 143.2, 141.6, 141.5, 141.3, 135.1, 133.7, 130.2, 129.6, 128.0, 126.0, 125.8, 125.6, 79.5, 79.4, 56.5, 56.4, 25.5, 23.8, 23.7, 22.5, 22.1, 15.6, 14.7, 14.1; HRMS calc. $C_{14}H_{20}ONa$$(M+Na)^+$, 227.14064, found, 227.14060.

(*E*)1-(4-(pent-2-en-2-yl)phenyl)piperidine  ***E*-(3il)**

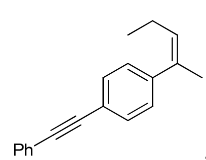
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.32 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 5.73 (dt, J_1 = 1.4 Hz, J_2 = 7.2 Hz, 1H), 3.17 (t, J = 5.5 Hz, 4H), 2.22 (quint, J = 7.5 Hz, 2H), 2.06 (d, J= 1.2 Hz, 3H), 1.76-1.72 (m, 4H), 1.62-1.58 (m, 2H), 1.08 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 150.9, 134.7, 133.4, 127.9, 126.1, 116.2, 50.7, 25.9, 24.3, 22.0, 15.5, 14.3; HRMS calc. $C_{16}H_{24}N$ $(M+H)^+$, 230.19033, found, 230.19014.

(*Z*)1-(4-(pent-2-en-2-yl)phenyl)piperidine  ***Z*-(3il)**

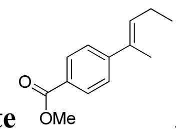
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.12 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 5.41 (dt, J_1 = 1.4 Hz, J_2 = 7.2 Hz, 1H), 3.18 (t, J = 5.5 Hz, 4H), 2.08-2.04 (m, 2H), 2.03 (d, J= 1.4 Hz, 3H), 1.76-1.72 (m, 4H), 1.62-1.59 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 150.6, 134.9, 132.7, 128.8, 128.6, 115.8, 50.6, 25.9, 25.4, 24.3, 22.5, 14.8; HRMS calc. $C_{16}H_{24}N$ $(M+H)^+$, 230.19033, found, 230.19012.

(*E*)-1-(pent-2-en-2-yl)-4-(phenylethynyl)benzene  ***E*-(3im)**

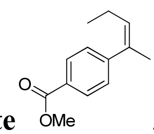
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.57-7.55 (m, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.42-7.35 (m, 5H), 5.88 (dt, J_1 = 1.4 Hz, J_2 = 7.2 Hz, 1H), 2.26 (quint, J = 7.5 Hz, 2H), 2.06 (d, J= 1.2 Hz, 3H), 1.10 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 143.7, 133.5, 131.6, 131.4, 131.2, 128.3, 128.1, 125.4, 123.5, 121.1, 89.6, 89.5, 22.2, 15.4, 14.0; HRMS calc. $C_{19}H_{19}$ $(M+H)^+$, 247.14813, found, 247.14718.

(*Z*)-1-(pent-2-en-2-yl)-4-(phenylethynyl)benzene  ***Z*-(3im)**

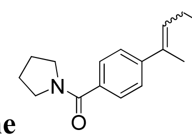
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.57-7.55 (m, 2H), 7.52 (d, J = 8.3 Hz, 2H), 7.39-7.35 (m, 3H), 7.20 (d, J = 8.3 Hz, 2H), 5.51 (dt, J_1 = 1.5 Hz, J_2 = 7.4 Hz, 1H), 2.05 (d, J = 1.4 Hz, 3H), 2.04-1.99 (m, 2H), 0.97 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 142.3, 134.8, 131.6, 131.3, 130.3, 128.3, 128.2, 128.0, 123.4, 121.2, 89.5, 89.2, 25.2, 22.5, 14.7; HRMS calc. $C_{19}H_{19}$ $(M+H)^+$, 247.14813, found, 247.14729.

(*E*)-methyl 4-(pent-2-en-2-yl)benzoate  ***E*-(3in)**

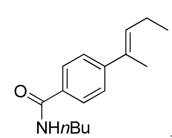
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.99 (d, J = 8.7 Hz, 2H), 7.46 (d, J J = 8.7 Hz, 2H), 5.92 (td, J_1 = 1.4 Hz, J_2 = 7.2 Hz, 1H), 3.93 (s, 3H), 2.26 (quint, J = 7.5 Hz, 2H), 2.06 (d, J = 1.2 Hz, 3H), 1.10 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 167.1, 148.4, 133.4, 132.5, 129.5, 128.0, 125.4, 52.0, 22.2, 15.4, 13.9; HRMS calc. for $C_{13}H_{16}O_2Na$ $(M+Na)^+$, 227.1043; found, 227.1047.

(*Z*)-methyl 4-(pent-2-en-2-yl)benzoate  ***Z*-(3in)**

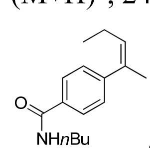
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 8.02 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 5.53 (td, J_1 = 1.3 Hz, J_2 = 7.4 Hz, 1H), 3.94 (s, 3H), 2.05 (d, J = 1.1 Hz, 3H), 1.99 (quint, J = 7.5 Hz, 2H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 167.1, 147.2, 134.6, 130.8, 129.4, 128.2, 128.0, 52.0, 25.1, 22.5, 14.6; HRMS calc. for $C_{13}H_{16}O_2Na$ $(M+Na)^+$, 227.1043; found, 227.1045.

(4-(pent-2-en-2-yl)phenyl)(pyrrolidin-1-yl)methanone  ***Z/E*-(3io)**

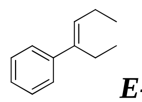
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.51-7.48 (m, 2.75H), 7.41 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 7.4 Hz, 0.82H), 5.84 (t, J = 7.4 Hz, 1H), 5.50 (t, J = 7.4 Hz, 0.41H), 3.69-3.65 (m, 2.82H), 3.51-3.46 (m, 2.82H), 2.24 (quint, J = 7.5 Hz, 2H), 2.04 (s, 3H), 2.03 (s, 1.22H), 2.00-1.95 (m, 3.45H), 1.92-1.86 (m, 2.89H), 1.08 (t, J = 7.5 Hz, 1H), 0.95 (t, J = 7.4 Hz, 1.24H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 169.67, 169.66, 145.39, 143.85, 135.21, 135.08, 134.75, 133.47, 131.36, 130.28, 127.80, 127.16, 126.95, 125.27, 49.65, 46.21, 26.45, 25.26, 24.48, 22.42, 22.12, 15.50, 14.64, 14.02; HRMS calc. for $C_{16}H_{22}ON$ $(M+H)^+$, 244.16959; found, 244.17014.

(*E*)-N-butyl-4-(pent-2-en-2-yl)benzamide  ***E*-(3ip)**

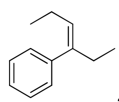
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.72 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 6.14 (s, 1H), 5.87 (td, J_1 = 1.4 Hz, J_2 = 7.5 Hz, 1H), 3.50-3.46 (m, 2H), 2.25 (quint, J = 7.5 Hz, 2H), 2.05 (d, J = 1.2 Hz, 2H), 1.65-1.59 (m, 2H), 1.47-1.40 (m, 2H), 1.09 (t, J = 7.5 Hz, 3H), 0.98 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 167.3, 146.9, 133.3, 132.6, 131.9, 126.7, 125.6, 39.8, 31.8, 22.2, 20.2, 15.5, 14.0, 13.8; HRMS calc. for $C_{16}H_{24}ON$ $(M+H)^+$, 246.18524; found, 246.18564.

(*Z*)-N-butyl-4-(pent-2-en-2-yl)benzamide  ***Z*-(3ip)**

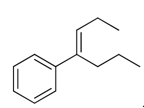
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.74 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 8.3 Hz, 2H), 6.12 (s, 1H), 5.52 (td, J_1 = 1.4 Hz, J_2 = 7.5 Hz, 1H), 3.51-3.47 (m, 2H), 2.04 (d, J = 1.4 Hz, 2H), 1.97 (quintd, J_1 = 1.3 Hz, J_2 = 7.5 Hz, 2H), 1.66-1.60 (m, 2H), 1.48-1.41 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 167.4, 145.5, 134.6, 132.9, 130.5, 128.2, 126.6, 39.8, 31.8, 25.2, 22.4, 20.2, 14.6, 13.8; HRMS calc. for $C_{16}H_{24}ON$ $(M+H)^+$, 246.18524; found, 246.18578.

(*E*)-hex-3-en-3-ylbenzene  ***E*-(3j)**

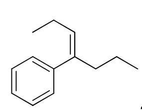
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.39 (d, J = 7.7 Hz, 2H), 7.33 (t, J = 7.4 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H), 5.67 (t, J = 7.2 Hz, 1H), 2.55 (quint, J = 7.5 Hz, 2H), 2.25 (quint, J = 7.5 Hz, 2H), 1.10 (t, J = 7.5 Hz, 3H), 1.02 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 143.1, 140.9, 130.0, 128.1, 126.4, 126.3, 22.9, 21.7, 14.5, 13.7; HRMS calc. for $C_{12}H_{17}$ $(M+H)^+$, 161.13248; found, 161.13263.

(*Z*)-hex-3-en-3-ylbenzene  ***Z*-(3j)**

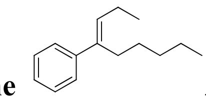
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.35 (t, J = 7.4 Hz, 2H), 7.26 (tt, J_1 = 1.3 Hz, J_2 = 7.5 Hz, 1H), 7.18-7.16 (m, 2H), 5.45 (t, J = 7.4 Hz, 1H), 2.36 (q, J = 7.5 Hz, 2H), 1.96 (quint, J = 7.5 Hz, 2H), 0.99 (t, J = 7.5 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 142.0, 141.6, 128.4, 127.9, 127.7, 126.3, 32.0, 22.2, 14.8, 13.1; HRMS calc. for $C_{12}H_{17}$ $(M+H)^+$, 161.13248; found, 161.13280.

(*E*)-hept-3-en-4-ylbenzene  ***E*-(3k)**

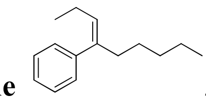
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.39-7.37 (m, 2H), 7.34-7.31 (m, 2H), 7.24 (tt, J_1 = 1.3 Hz, J_2 = 7.2 Hz, 1H), 5.69 (t, J = 7.2 Hz, 1H), 2.51 (t, J = 7.5 Hz, 2H), 2.25 (quint, J = 7.5 Hz, 2H), 1.44-1.37 (m, 2H), 1.09 (t, J = 7.5 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 143.4, 139.4, 130.9, 128.1, 126.4, 126.3, 31.6, 21.9, 21.8, 14.5, 13.9; HRMS calc. for $C_{13}H_{19}$ $(M+H)^+$, 175.14813; found, 175.14864.

(*Z*)-hept-3-en-4-ylbenzene  ***Z*-(3k)**

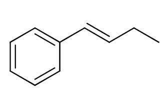
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.36-7.32 (m, 2H), 7.25 (tt, J_1 = 1.3 Hz, J_2 = 7.4 Hz, 1H), 7.17-7.15 (m, 2H), 5.45 (t, J = 7.4 Hz, 1H), 2.32 (t, J = 7.5 Hz, 2H), 1.96 (quint, J = 7.5 Hz, 2H), 1.37-1.31 (m, 2H), 0.95 (t, J = 7.5 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 141.5, 140.2, 129.1, 128.4, 127.9, 126.2, 41.3, 22.2, 21.2, 14.8, 13.6; HRMS calc. for $C_{13}H_{19}$ $(M+H)^+$, 175.14813; found, 175.14834.

(*E*)-non-3-en-4-ylbenzene  ***E*-(3l)**

Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.38-7.36 (m, 2H), 7.34-7.30 (m, 2H), 7.24 (tt, J_1 = 1.3 Hz, J_2 = 7.2 Hz, 1H), 5.67 (t, J = 7.2 Hz, 1H), 2.51 (t, J = 7.2 Hz, 2H), 2.24 (quint, J = 7.5 Hz, 2H), 1.39-1.34 (m, 2H), 1.31-1.29 (m, 4H), 1.08 (t, J = 7.5 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 143.4, 139.6, 130.6, 128.1, 126.4, 126.3, 31.8, 29.7, 28.5, 22.5, 21.9, 14.5, 14.1; HRMS calc. for $C_{15}H_{23}$ $(M+H)^+$, 203.17943; found, 203.17949.

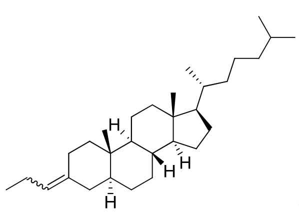
(*Z*)-non-3-en-4-ylbenzene  ***Z*-(3l)**

Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.36-7.33 (m, 2H), 7.26 (tt, J_1 = 1.3 Hz, J_2 = 7.4 Hz, 1H), 7.17-7.16 (m, 2H), 5.45 (t, J = 7.4 Hz, 1H), 2.34 (t, J = 7.4 Hz, 2H), 1.96 (quint, J = 7.5 Hz, 2H), 1.34-1.31 (m, 2H), 1.29-1.27 (m, 4H), 0.95 (t, J = 7.5 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 141.6, 140.5, 128.8, 128.4, 127.9, 126.2, 39.2, 31.4, 27.9, 22.5, 22.2, 14.8, 14.1; HRMS calc. for $C_{15}H_{23}$ $(M+H)^+$, 203.17943; found, 203.17951.

(*E*)-but-1-enylbenzene  **(3m)**

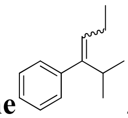
Colorless oil; The spectroscopic data correspond to those previously reported in the literature.[4] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.38-7.36 (m, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 6.41(d, J = 15.9 Hz, 1H), 6.31 (dt, J_1 = 6.4 Hz, J_2 = 15.9 Hz, 1H), 2.26 (quint, J = 7.5 Hz, 2H), 1.12 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 137.9, 132.7, 128.8, 128.5, 126.7, 125.9, 26.1, 13.7; MS (EI) m/z: 132.1, 117.1, 91.1.

(5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-3-propylidenehexadecahydro-1H-cyclopenta[a]phenanthrene

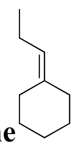


(3o)

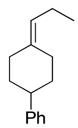
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 5.08 (t, J = 7.0 Hz, 1H), 2.22-2.16 (m, 1H), 2.03-1.96 (m, 4H), 1.87-1.65 (m, 5H), 1.59-1.49 (m, 3H), 1.38-1.24 (m, 9H), 1.17-0.98 (m, 10H), 0.95 (t, J = 7.5 Hz, 3H), 0.92 (d, J = 6.5 Hz, 3H), 0.91-0.88 (m 10H), 0.68 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 138.8, 138.7, 122.9, 122.7, 56.6, 56.3, 54.53, 54.49, 48.4, 47.6, 42.62, 42.61, 40.13, 40.11, 39.54, 39.50, 39.46, 36.53, 36.49, 36.2, 35.8, 35.5, 32.5, 32.1, 32.0, 31.2, 29.2, 28.9, 28.3, 28.0, 24.2, 24.1, 23.8, 22.8, 22.6, 21.1, 21.0, 20.3, 18.7, 14.90, 14.87, 12.1, 11.82, 11.80; HRMS calc. for $C_{30}H_{53}$ $(M+H)^+$, 413.41418; found, 413.41460.

(2-methylhex-3-en-3-yl)benzene  ***Z/E*-(3p)**

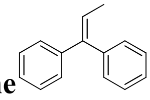
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.36-7.32 (m, 2H), 7.30-7.23 (m, 3.5H), 7.20-7.18 (m, 1.5H), 7.11-7.09 (m, 2H), 5.42 (t, J_1 =1.2 Hz, J_2 =7.3 Hz, 1H), 5.28 (t, J =7.3 Hz, 0.75H), 3.10-3.02 (m, 0.75H), 2.58-2.53 (m, 1H), 2.23 (quint, J = 7.4 Hz, 1.5H), 1.84 (quint, J = 7.2Hz, 2H), 1.08-1.05 (m, 6.75H), 1.02 (d, J = 6.8 Hz, 6H), 0.91 (d, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 146.7, 146.2, 143.5, 141.5, 130.7, 128.9, 128.6, 127.7, 127.4, 126.3, 126.1, 126.0, 35.7, 29.2, 22.1, 21.9, 21.8, 21.0, 14.7, 14.6; HRMS calc. for $C_{13}H_{19}$ $(M+H)^+$, 175.14813; found, 175.14786.

propylidenecyclohexane  **(3q)**

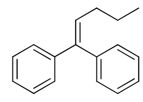
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 5.09 (t, J = 7.2 Hz, 1H), 2.14 (t, J = 6.2 Hz, 2H), 2.08 (t, J = 6.0 Hz, 2H), 2.01 (quint, J = 7.5 Hz, 2H), 1.57-1.50 (m, 6H), 0.95 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 139.0, 123.1, 37.1, 28.7, 28.6, 27.9, 27.0, 20.3, 14.9; HRMS calc. for C_9H_{17} $(M+H)^+$, 125.13248; found, 125.13276.

(4-propylidenecyclohexyl)benzene  **(3r)**

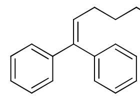
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.32 (t, J = 8.0 Hz, 2H), 7.25-7.19 (m, 3H), 5.19 (t, J = 7.3 Hz, 1H), 2.78-2.68 (m, 2H), 2.34-2.29 (m, 1H), 2.25-2.19 (m, 1H), 2.10-2.03 (m, 2H), 2.02-1.96 (m, 2H), 1.93-1.86 (m, 1H), 1.59-1.43 (m, 2H), 1.00 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 147.2, 137.6, 128.3, 126.9, 125.9, 124.0, 44.9, 36.8, 35.9, 35.2, 28.3, 20.5, 14.9; HRMS calc. for $C_{15}H_{21}$ $(M+H)^+$, 201.16378; found, 201.16400.

prop-1-ene-1,1-diyldibenzene  **(4a)**

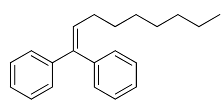
White solid, mp. 50-50.8^{o}C, The spectroscopic data correspond to those previously reported in the literature.[5] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.42 (t, J = 7.2 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.31-7.22 (m, 7H), 6.22 (q, J = 7.0 Hz, 1H), 1.80 (d, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 143.0, 142.4, 140.0, 130.1, 128.2, 128.1, 127.2, 126.8, 126.7, 124.2, 15.7; MS (EI) m/z: 194.1, 178.1, 165.1, 115.0.

pent-1-ene-1,1-diyldibenzene  **(4b)**

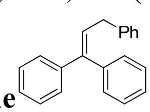
Colorless oil; The spectroscopic data correspond to those previously reported in the literature.[6] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.41 (t, J = 7.1 Hz, 2H), 7.35 (tt, J_1 = 1.4 Hz, J_2 = 7.4 Hz, 1H), 7.31-7.22 (m, 7H), 6.14 (t, J = 7.5 Hz, 1H), 2.14 (q, J = 7.5 Hz, 2H), 1.55-1.48 (m, 2H), 0.95 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 142.9, 141.6, 140.4, 130.1, 130.0, 128.1, 128.0, 127.2, 126.8, 126.7, 31.9, 23.2, 13.9; MS (EI) m/z: 222.2, 193.2, 165.2, 115.2, 91.2.

hex-1-ene-1,1-diyldibenzene  **(4c)**

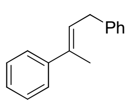
Colorless oil; The spectroscopic data correspond to those previously reported in the literature.[7] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.42 (tt, J_1 = 1.1 Hz, J_2 = 7.1 Hz, 2H), 7.34 (tt, J_1 = 2.7 Hz, J_2 = 7.4 Hz, 1H), 7.31-7.21 (m, 7H), 6.13 (t, J = 7.5 Hz, 1H), 2.15 (q, J = 7.5 Hz, 2H), 1.49-1.43 (m, 2H), 1.39-1.32 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 142.9, 141.4, 140.4, 130.3, 130.0, 128.1, 128.0, 127.2, 126.8, 126.7, 32.2, 29.5, 22.4, 14.0; MS (EI) m/z: 236.2, 193.2, 178.2, 165.1, 115.1.

non-1-ene-1,1-diyldibenzene  **(4d)**

Colorless oil; The spectroscopic data correspond to those previously reported in the literature.[8] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.40 (t, J = 7.2 Hz, 2H), 7.34 (t, J = 7.5 Hz, 1H), 7.31-7.21 (m, 7H), 6.12 (t, J = 7.5 Hz, 1H), 2.15 (q, J = 7.5 Hz, 2H), 1.50-1.44 (m, 2H), 1.33-1.28 (m, 8H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 142.9, 141.4, 140.4, 130.4, 130.0, 128.1, 128.0, 127.2, 126.8, 126.7, 31.8, 30.0, 29.8, 29.3, 29.2, 22.7, 14.1; MS (EI) m/z: 278.1, 193.1, 165.1, 115.1.

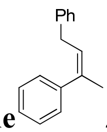
prop-1-ene-1,1,3-triyltribenzene  **(4e)**

Colorless oil; The spectroscopic data correspond to those previously reported in the literature.[9] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.43 (t, J = 7.1 Hz, 2H), 7.38-7.32 (m, 3H), 7.31-7.28 (m, 6H), 7.27-7.22 (m, 4H), 6.32 (t, J = 7.6 Hz, 1H), 3.52 (d, J = 7.6Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 142.5, 142.4, 141.0, 139.8, 129.9, 128.5, 128.4, 128.3, 128.1, 127.8, 127.4, 127.2, 127.1, 126.0, 35.9; MS (EI) m/z: 270.1, 255.2, 192.1, 178.1, 115.1.

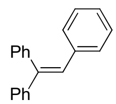
(*E*)-but-2-ene-1,3-diyldibenzene  ***E*-(4f)**

Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.46-7.44 (m, 2H), 7.36-7.32 (m, 4H), 7.29-7.23 (m, 4H), 6.01 (tq, J_1 = 1.3 Hz, J_2 = 7.4 Hz, 1H), 3.61 (d, J = 7.4 Hz, 2H), 2.19 (d, J = 0.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 143.6, 141.0, 135.7, 128.5, 128.4, 128.2, 126.8, 126.7, 125.9, 125.7, 35.0, 16.0; HRMS calc. for

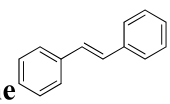
$C_{16}H_{16}$ (M)$^+$, 208.12465; found, 208.12451.

(*Z*)-but-2-ene-1,3-diyldibenzene  ***Z*-(4f)**

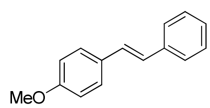
Colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.38 (t, J = 7.4 Hz, 2H), 7.32-7.27 (m, 5H), 7.22-7.18 (m, 3H), 5.69 (td, J_1 = 1.4 Hz, J_2 = 7.5 Hz, 1H), 3.36 (d, J = 7.5 Hz, 2H), 2.11(d, J = 1.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 141.8, 141.5, 137.4, 128.4, 128.3, 128.2, 127.9, 126.7, 125.8, 125.7, 35.3, 25.7; HRMS calc. for $C_{16}H_{16}$ (M)$^+$, 208.12465; found, 208.12390.

ethene-1,1,2-triyltribenzene  **(4g)**

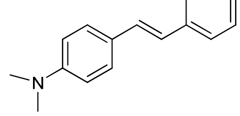
Colorless oil; The spectroscopic data correspond to those previously reported in the literature.[10] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.38-7.31 (m, 8H), 7.26-7.23 (m, 2H), 7.18-7.13 (m, 3H), 7.07-7.06 (m, 2H), 7.00 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 143.4, 142.6, 140.4, 137.4, 130.4, 129.6, 128.6, 128.2, 128.1, 127.9, 127.6, 127.5, 127.4, 126.8; MS (EI) m/z: 256.1, 239.1, 178.1, 165.1.

(*E*)-1,2-diphenylethene  **(4h)**

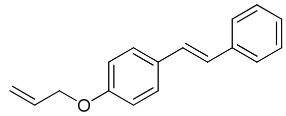
White solid; mp. 124.6-126.1^{o}C. The spectroscopic data correspond to those previously reported in the literature.[11] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.56 (d, J = 7.7 Hz, 4H), 7.40 (t, J = 7.6 Hz, 4H), 7.30 (t, J = 7.4 Hz, 2H), 7.16 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 137.3, 128.7, 127.6, 126.5; MS (EI) m/z: 236.2, 193.2, 178.2, 165.1, 115.1.

(*E*)-1-methoxy-4-styrylbenzene  **(4i)**

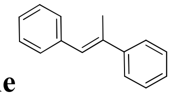
White solid, mp 108.4-108.6^{o}C; The spectroscopic data correspond to those previously reported in the literature.[11a] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.52 (d, J = 7.6 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.27 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 16.3 Hz, 1H), 7.01 (d, J = 16.3 Hz, 1H), 6.93 (d, J = 8.7 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 159.3, 137.7, 130.2, 128.7, 128.2, 127.7, 127.2, 126.6, 126.3, 114.1, 55.3; MS (EI) m/z: 210.1, 165.1, 152.1, 104.1.

(*E*)-N,N-dimethyl-4-styrylaniline  **(4j)**

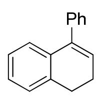
White solid, mp 144.2-145.6^{o}C. The spectroscopic data correspond to those previously reported in the literature.[13] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.51 (d, J = 6.9 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 16.4 Hz, 1H), 6.95 (d, J = 16.4 Hz, 1H), 6.76 (d, J = 8.8 Hz, 2H), 3.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 150.1, 138.2, 128.8, 128.6, 127.6, 126.7, 126.0, 125.8, 124.4, 112.5, 40.5; MS (EI) m/z: 223.1, 165.1, 114.1.

(*E*)-1-(allyloxy)-4-styrylbenzene  **(4k)**

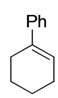
White solid, mp 124.4-126.2°C. The spectroscopic data correspond to those previously reported in the literature[14]. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.52 (d, J = 6.9 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.26 (t, J = 7.3 Hz, 1H), 7.08 (d, J = 16.3 Hz, 1H), 7.01 (d, J = 16.3 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 6.13-6.06 (m, 1H), 5.47(dq, J_1 = 1.6 Hz, J_2 = 17.3 Hz, 1H), 5.33(dq, J_1 = 1.5 Hz, J_2 = 10.4 Hz, 1H), 4.59(dt, J_1 = 1.6 Hz, J_2 = 5.3 Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ 158.3, 137.6, 133.2, 130.3, 128.6, 128.2, 127.7, 127.2, 126.7, 126.3, 117.8, 115.0, 68.9; MS (EI) m/z: 236.1, 195.1, 165.1, 115.1

(*E*)-prop-1-ene-1,2-diyldibenzene  **(4l)**

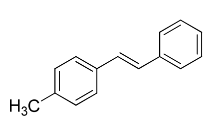
White solid, mp. 78.2-80.5; The spectroscopic data correspond to those previously reported in the literature.[16] ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.58-7.56 (m, 2H), 7.43-7.40 (m, 6H), 7.35-7.32 (m, 1H), 7.29-7.27(m, 1H), 6.88 (d, J = 1.1 Hz, 1H), 2.33 (d, J = 1.4 Hz, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ 144.0, 138.4, 137.4, 129.2, 128.4, 128.2, 127.7, 127.2, 126.5, 126.0, 17.5; MS (EI) m/z: 194.1, 179.1, 165.1, 115.0.

4-phenyl-1,2-dihydronaphthalene  **(4m)**

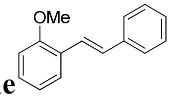
Colorless oil; The spectroscopic data correspond to those previously reported in the literature[17] .^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.44-7.35 (m, 5H), 7.24 (d, J = 7.3 Hz, 1H), 7.20 (t, J = 7.3 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 6.13 (t, J = 4.7 Hz, 1H), 2.90 (t, J = 7.9 Hz, 2H), 2.47-2.43 (m, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ 140.8, 139.9, 136.8, 135.1, 128.8, 128.2, 127.7, 127.6, 127.1, 127.0, 126.2, 125.4, 28.3, 23.6; MS (EI) m/z: 206.1, 191.1, 178.1, 152.0, 128.1.

cyclohexenylbenzene  **(4n)**

Colorless oil; The spectroscopic data correspond to those previously reported in the literature[6]. ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): δ 7.42-7.40 (m, 2H), 7.33 (t, J = 7.4 Hz, 2H), 7.24 (tt, J_1 = 1.2 Hz, J_2 = 7.4 Hz, 1H), 6.16-6.14 (m, 1H), 2.46-2.43 (m, 2H), 2.26-2.22 (m, 2H), 1.84-1.79 (m, 2H), 1.72-1.67 (m, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz, ppm): δ 142.7, 136.6, 128.2, 126.5, 124.9, 124.8, 27.4, 25.9, 23.1, 22.2; MS (EI) m/z: 158.1, 143.1, 129.1, 115.1.

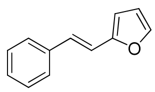
(*E*)-1-methyl-4-styrylbenzene  **(4o)**

White solid; mp 119.4-121.3^{o}C. The spectroscopic data correspond to those previously reported in the literature.[11] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.54 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 7.5 Hz, 2H), 7.30-7.26 (m, 1H), 7.20 (d, J = 7.9 Hz, 2H), 7.11(d, J = 3.8 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 137.5, 134.6, 129.4, 128.7, 128.6, 127.7, 127.4, 126.4, 126.4, 21.3; MS (EI) m/z: 194.1, 179.1, 165.1, 152.1, 115.1.

(*E*)-1-methoxy-2-styrylbenzene 

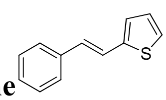
(4p)

White solid, mp 59.1-59.7^{o}C. The spectroscopic data correspond to those previously reported in the literature.[12] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.63 (dd, J_1 = 1.6 Hz, J_2 = 7.7 Hz, 1H), 7.57 (d, J = 7.4 Hz, 2H), 7.52 (d, J = 16.5 Hz, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.30-7.26 (m, 2H), 7.15 (d, J = 16.5 Hz, 1H), 7.00 (t, J = 7.4 Hz, 1H), 6.94 (d, J = 8.3 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 156.9, 138.0, 129.1, 128.7, 128.6, 127.4, 126.6, 126.5, 126.4, 123.5, 120.8, 111.0, 55.5; MS (EI) m/z: 210.1, 165.1, 152.1, 104.1.

(*E*)-2-styrylfuran 

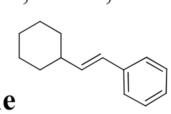
(4q)

White solid, mp. 51.4-53.2^{o}C; The spectroscopic data correspond to those previously reported in the literature[15]. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.50 (d, J = 7.4 Hz, 2H), 7.43 (d, J = 1.8 Hz, 1H), 7.39-7.36 (m, 2H), 7.29-7.26 (m, 1H), 7.07 (d, J = 16.3 Hz, 1H), 6.93 (d, J = 16.3 Hz, 1H); 6.46 (dd, J_1 = 1.8, J_2 =3.3 Hz, 1H), 6.38 (d, J = 3.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 153.3, 142.1, 137.0, 128.7, 127.6, 127.1, 126.3, 116.5, 111.6, 108.6; MS (EI) m/z: 170.1, 141.1, 115.1.

(*E*)-2-styrylthiophene 

(4r)

White solid, mp. 110.2-111.6^{o}C; The spectroscopic data correspond to those previously reported in the literature.[11a] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.49 (d, J = 7.4 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.29-7.24 (m, 2H), 7.22 (d, J = 5.0 Hz, 1H), 7.10 (d, J = 3.1 Hz, 1H), 7.04-7.03 (m, 1H), 6.96 (d, J = 16.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 142.9, 137.0, 128.7, 128.3, 127.6, 126.3, 126.1, 124.3, 121.8; MS (EI) m/z: 186.1, 171.1, 152.1, 115.1.

***(E)*-(2-cyclohexylvinyl)benzene**  **(4s)**

Colorless oil; The spectroscopic data correspond to those previously reported in the literature.[6] ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ 7.37 (d, J = 7.3 Hz, 2H), 7.31 (d, J = 7.5 Hz, 2H), 7.21 (tt, J_1 = 1.4 Hz, J_2 = 7.4 Hz, 1H), 6.36 (d, J = 16.0 Hz, 1H), 6.20 (dd, J_1 = 6.9 Hz, J_2 = 16.0 Hz, 1H), 2.19-2.12 (m, 1H), 1.85-1.77 (m, 4H), 1.73-1.69 (m, 1H), 1.39-1.30 (m, 2H), 1.27-1.17 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, ppm): δ 138.1, 136.9, 128.5, 127.2, 126.7, 125.9, 41.2, 33.0, 26.2, 26.1; MS (EI) m/z: 186.2, 171.2, 129.2, 104.2, 91.2.

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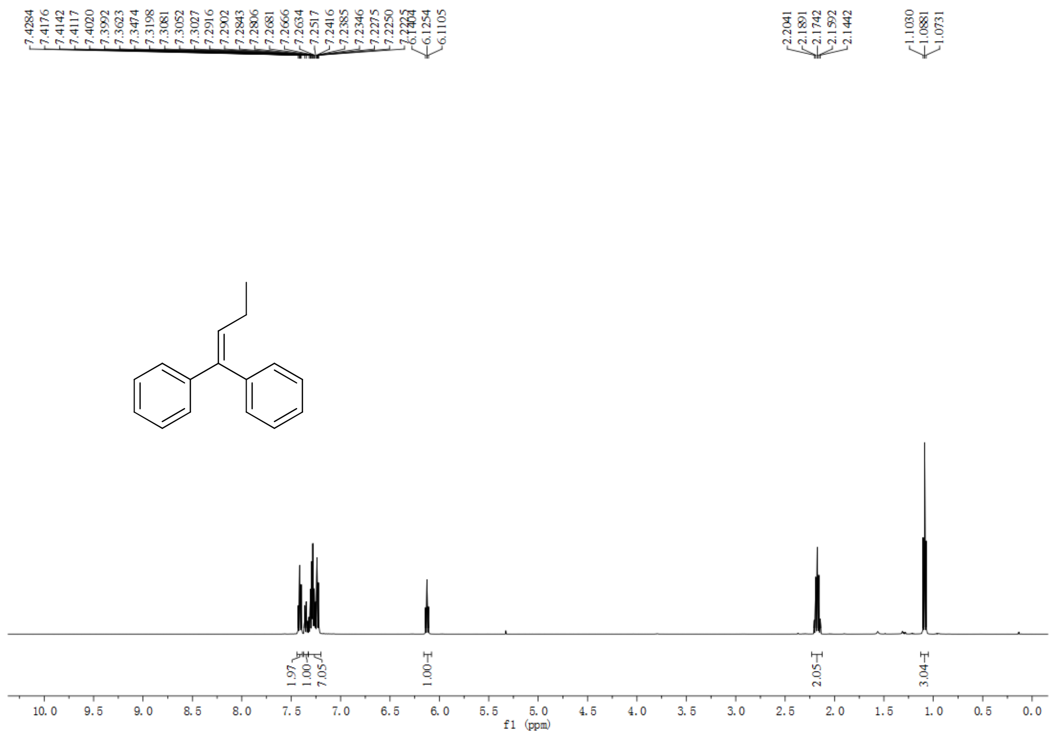
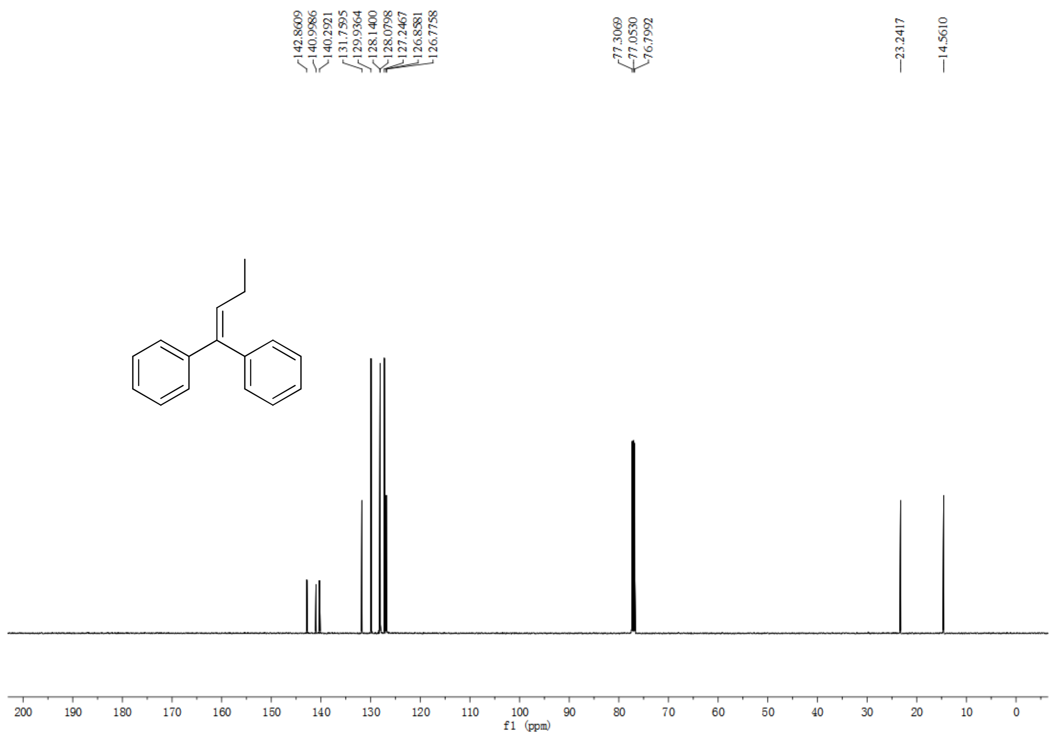
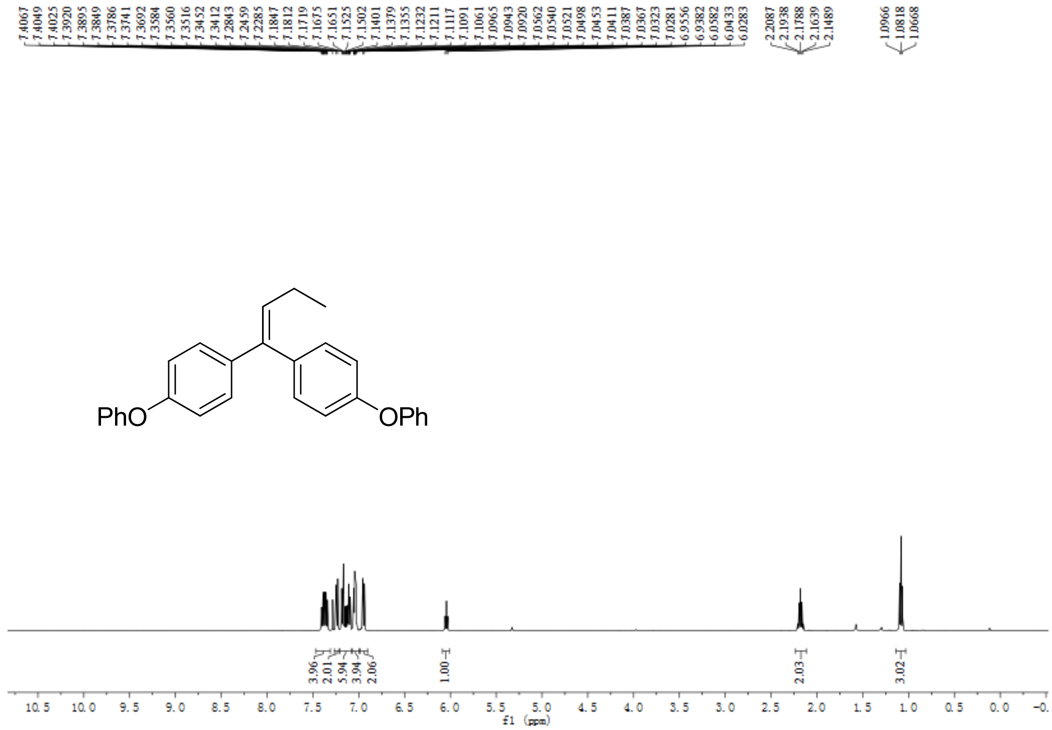
7. Copies of NMR Spectra for 3a-4s

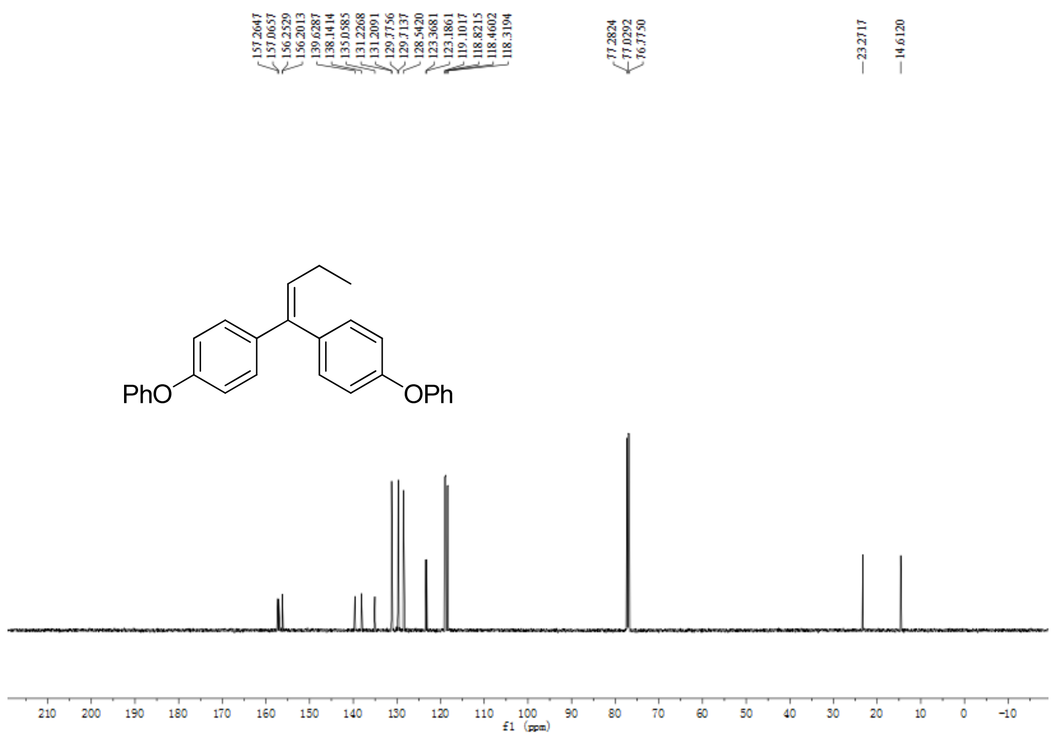
3a



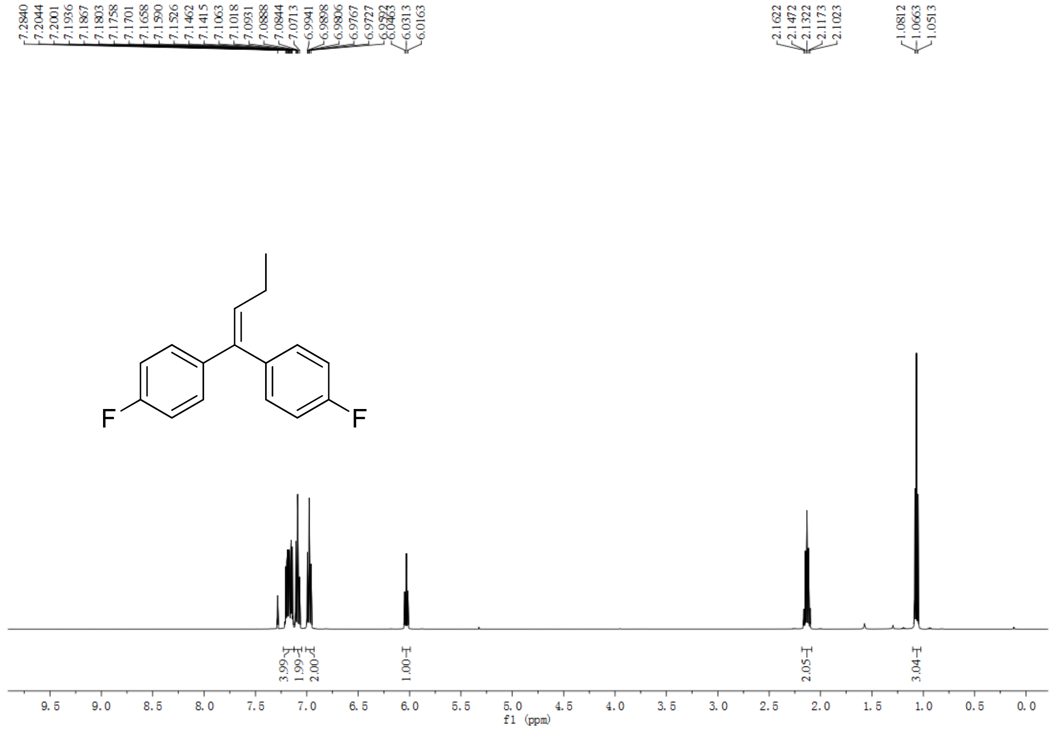


3b





3c



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7.1415
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7.0931
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6.9941
6.9898
6.9806
6.9767
6.9727
6.0313
6.0163
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2.1472
2.1322
2.1173
2.1023
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F
F
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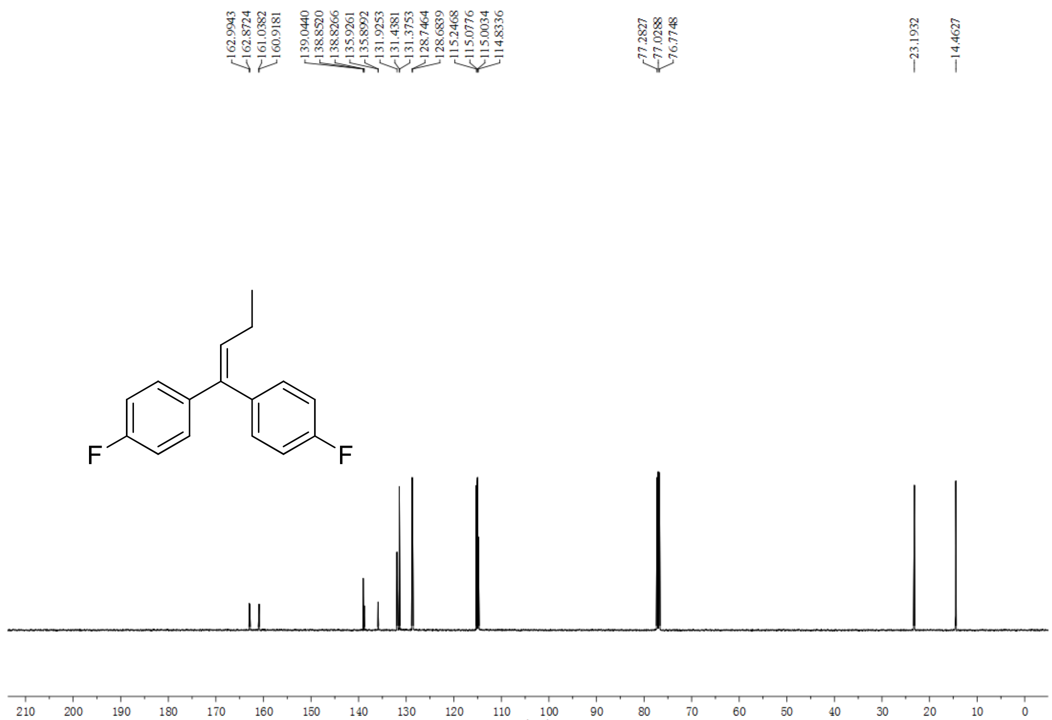
3.04
f1 (ppm)



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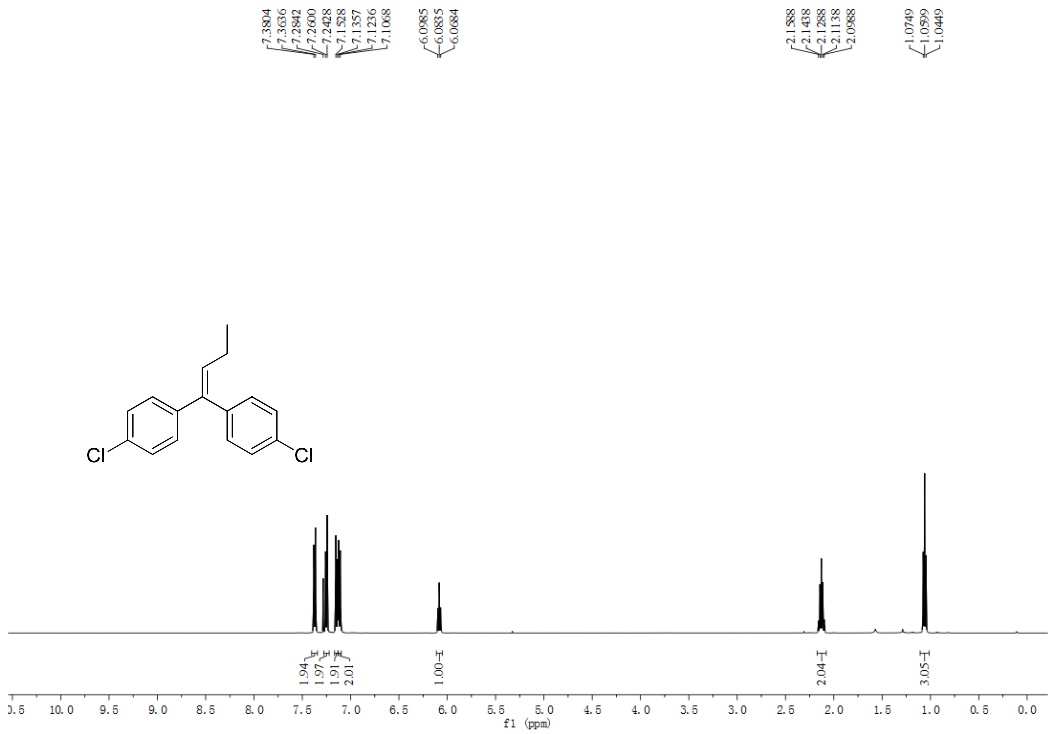
F
F
f1 (ppm)

3d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6.0835
6.0684
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2.1438
2.1288
2.1138
2.0988
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Cl
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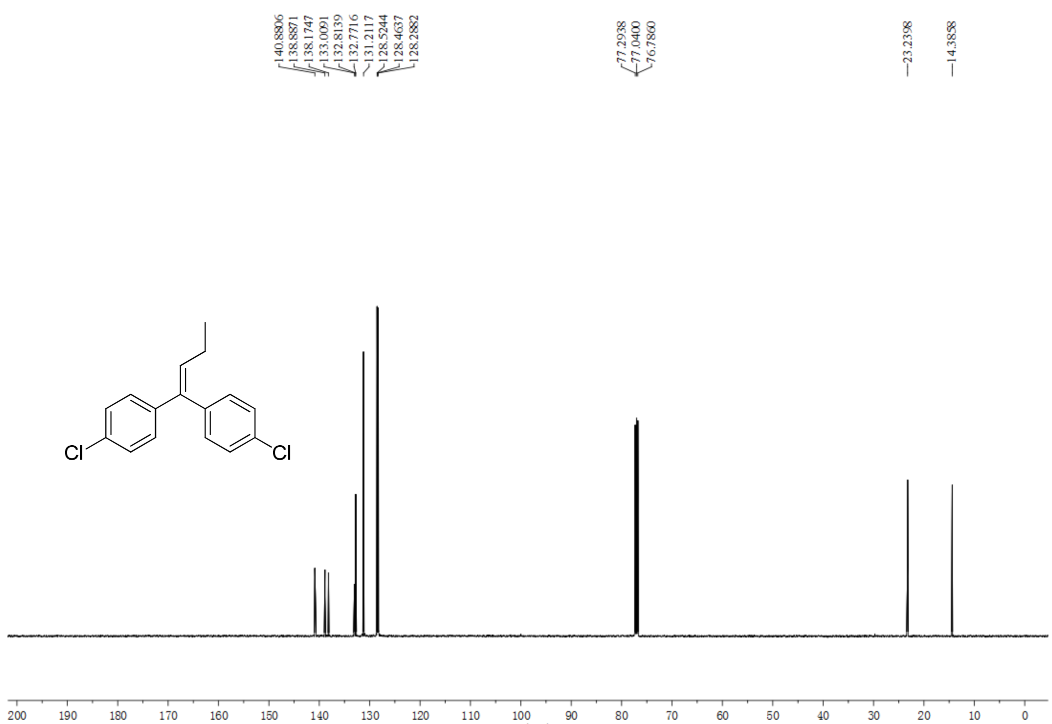
3.05
f1 (ppm)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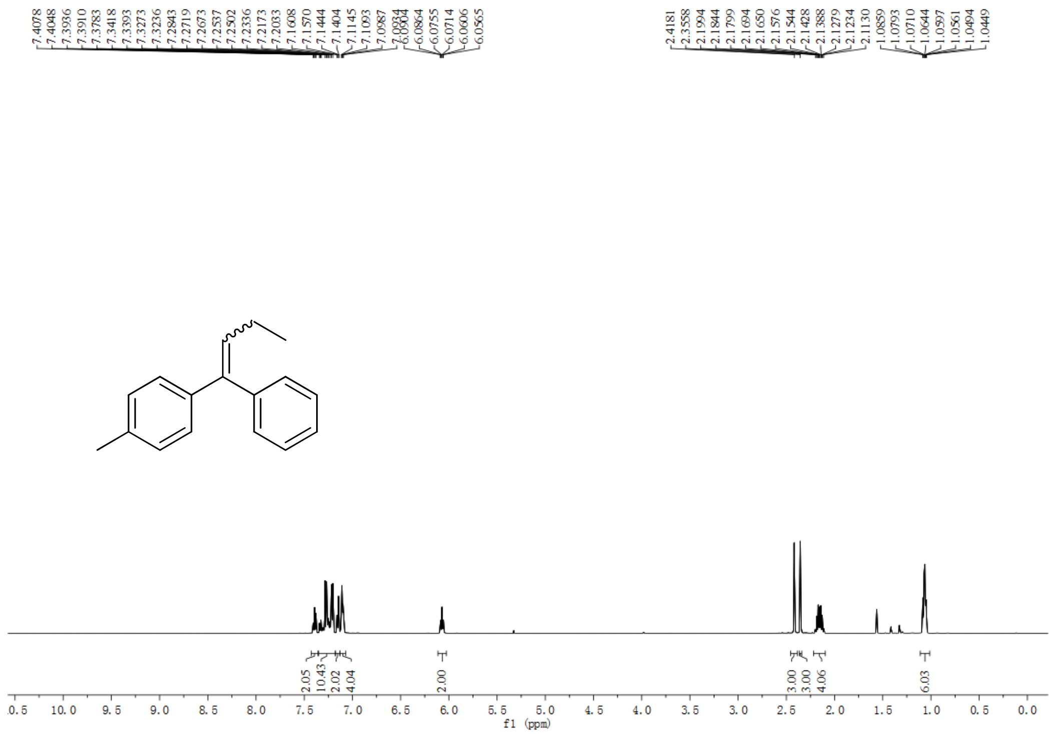
Cl
Cl
f1 (ppm)

3e (*Z*/*E*)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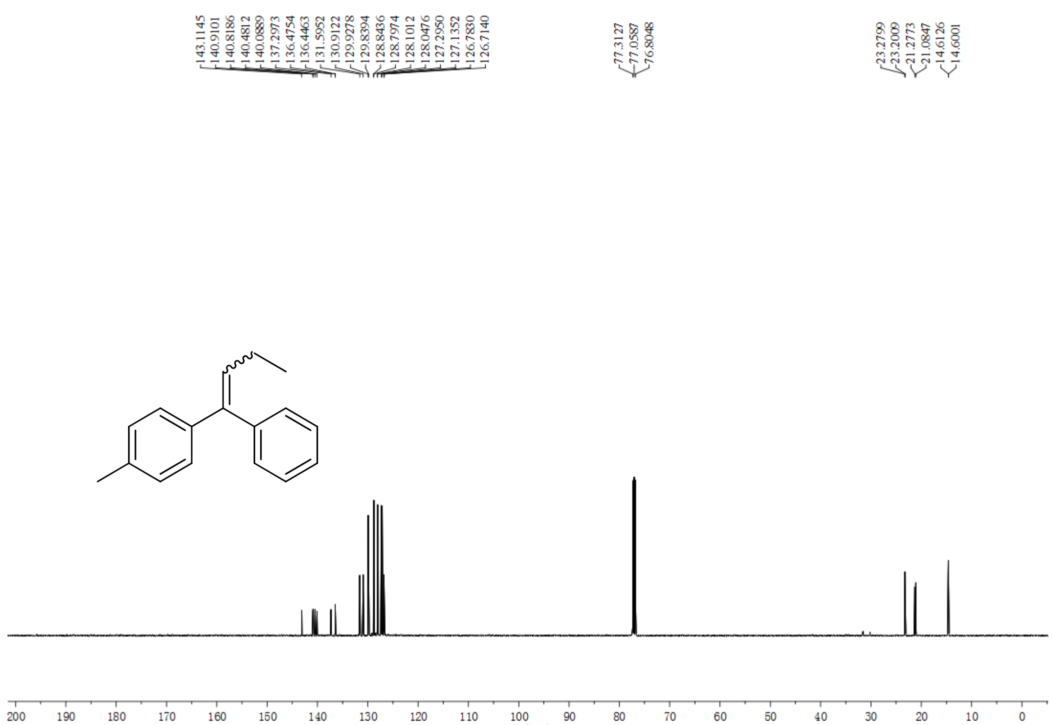
f1 (ppm)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126.7140
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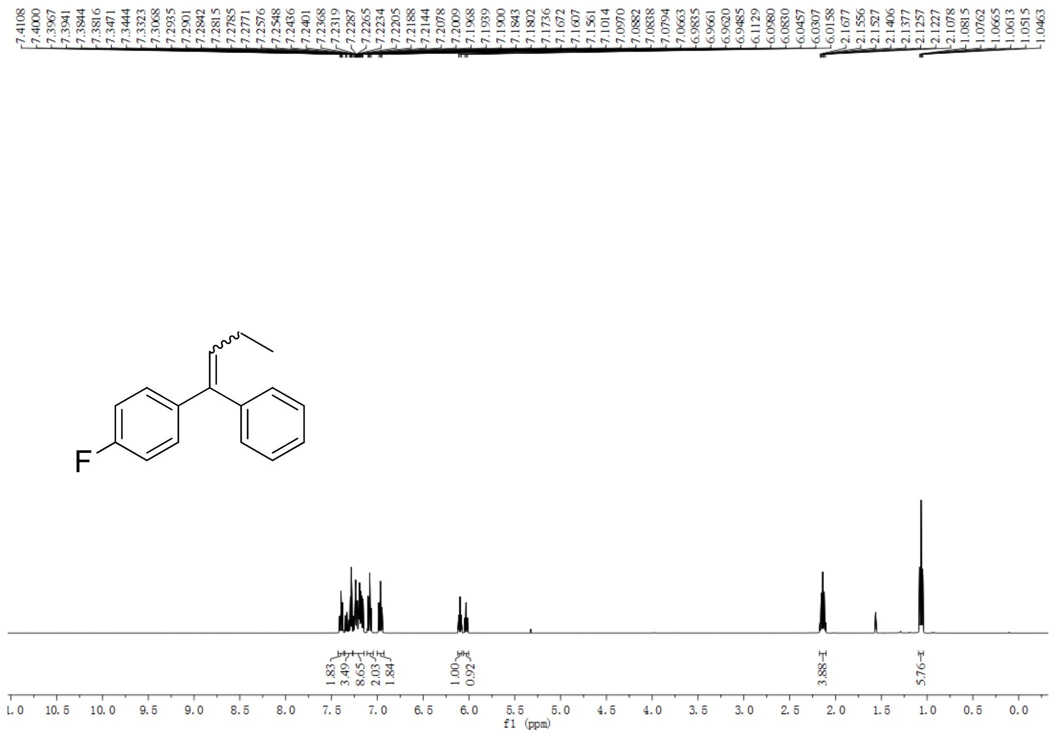
14.6001
f1 (ppm)

3f (*Z*/*E*)



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F
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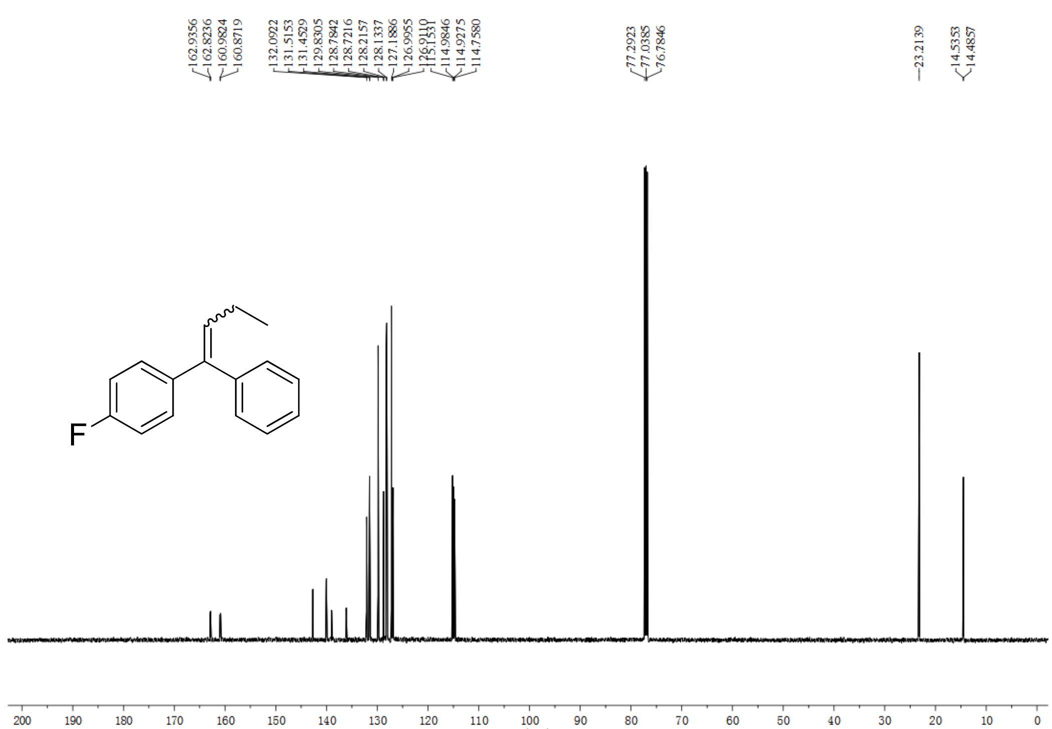
f1 (ppm)



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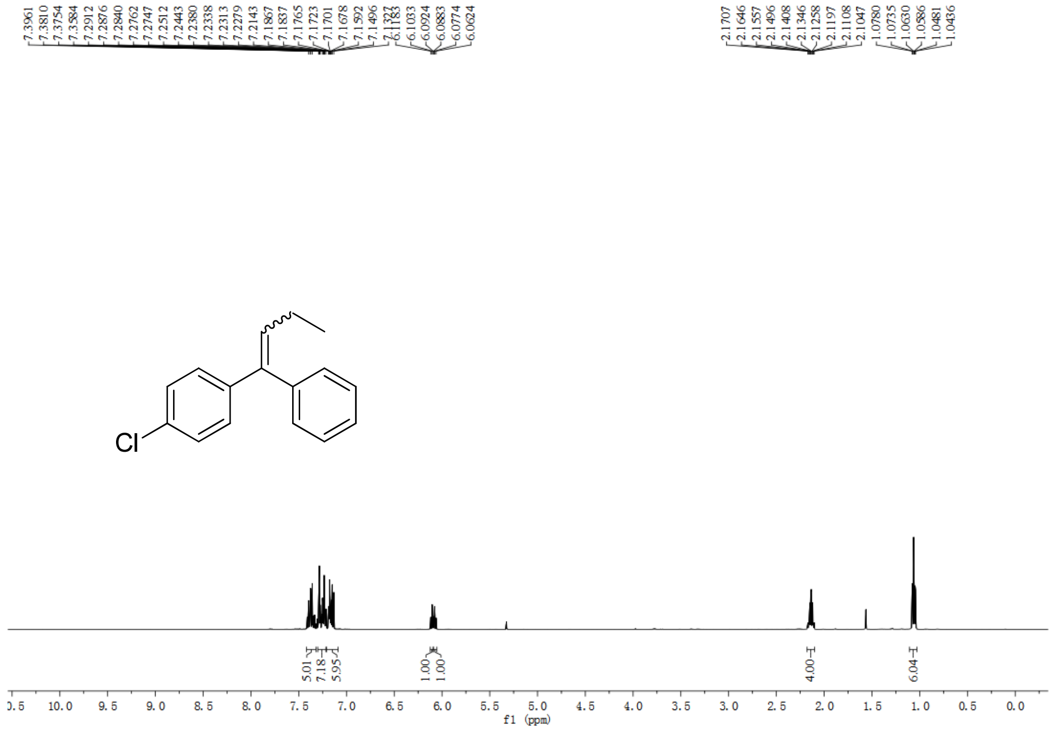
F
f1 (ppm)

3g (*Z*/*E*)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7.1701
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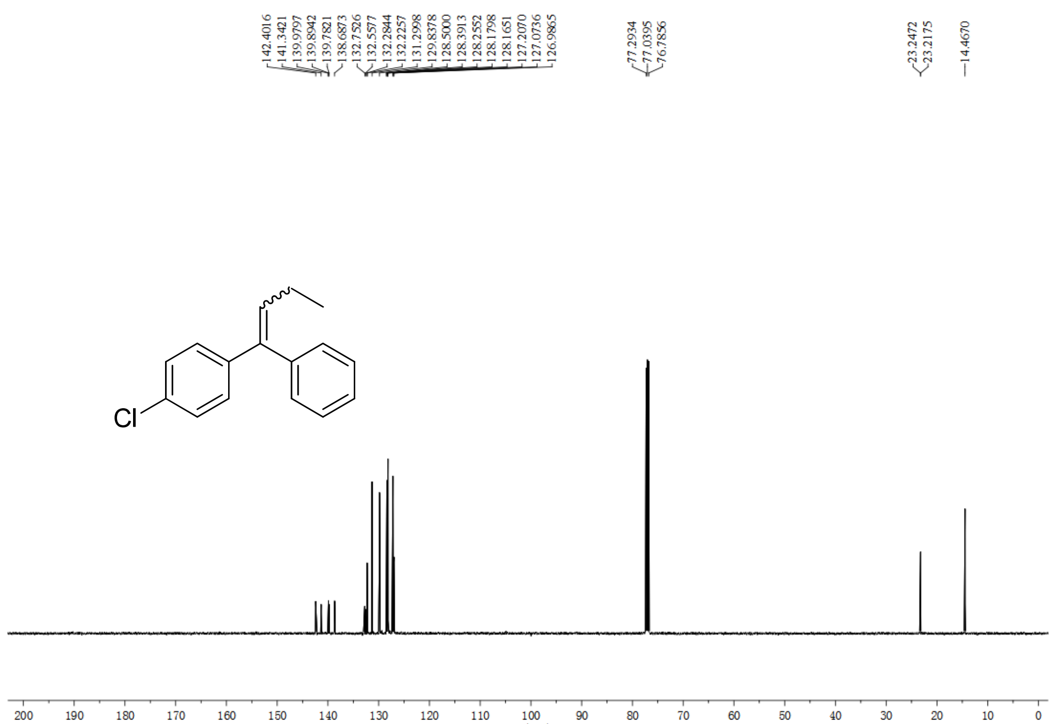
f1 (ppm)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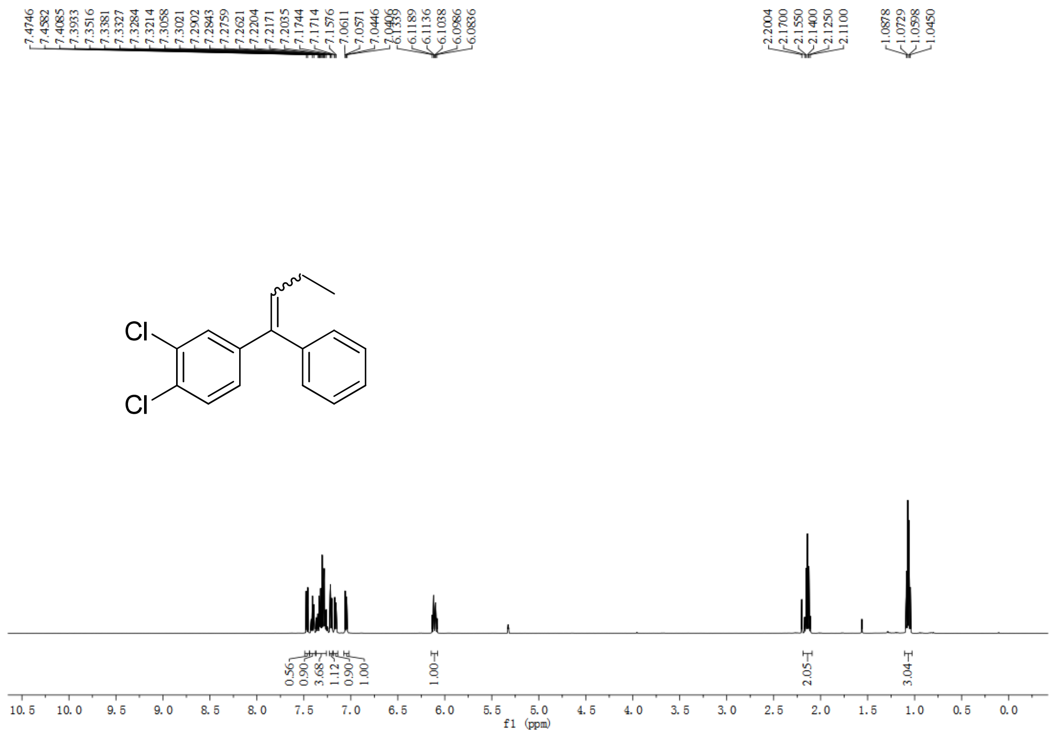
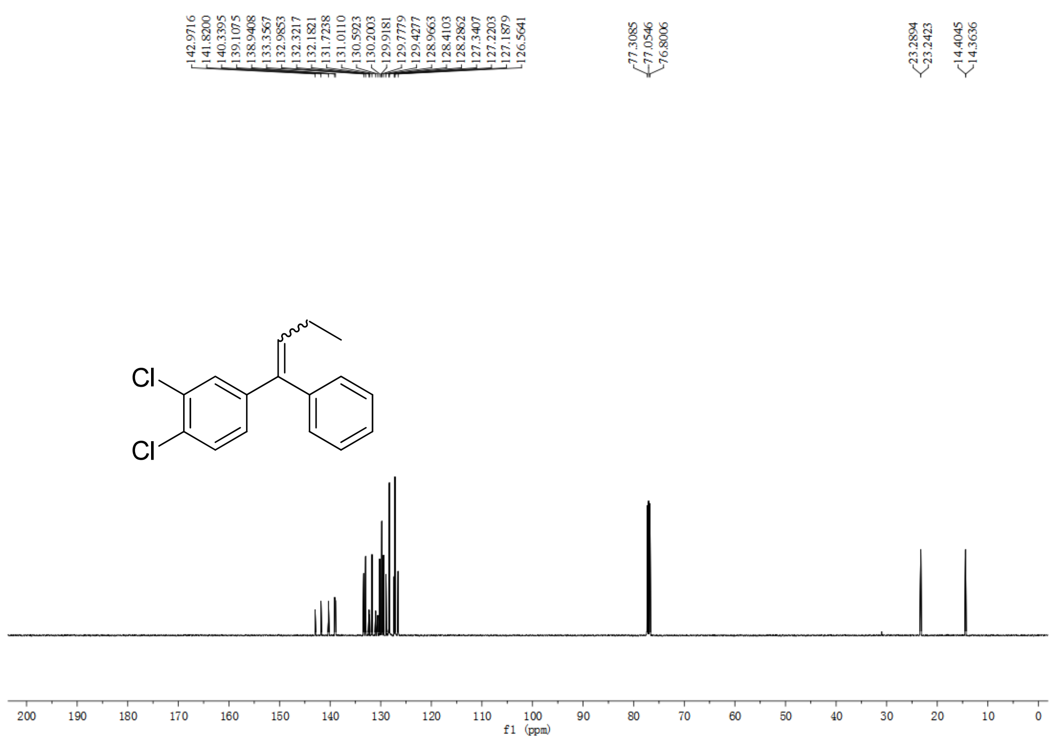
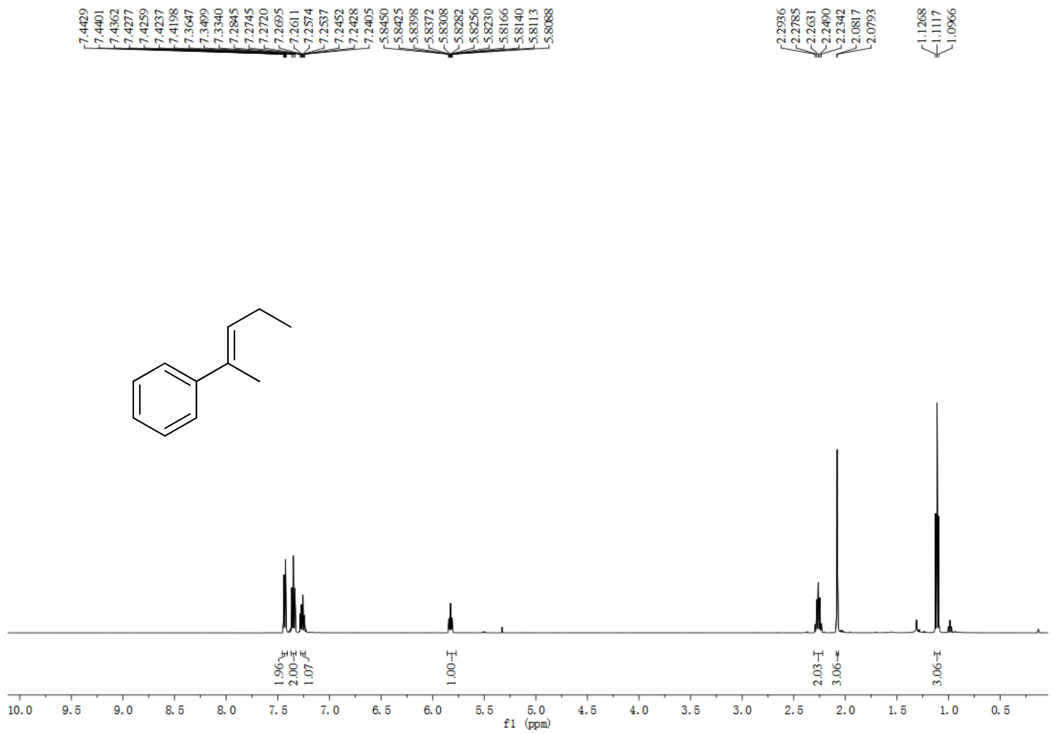
Cl
f1 (ppm)

3h (*Z*/*E*)





3i(*E*)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7.2537
7.2452
7.2428
7.2405
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5.8425
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2.2490
2.2342
2.0817
2.0793
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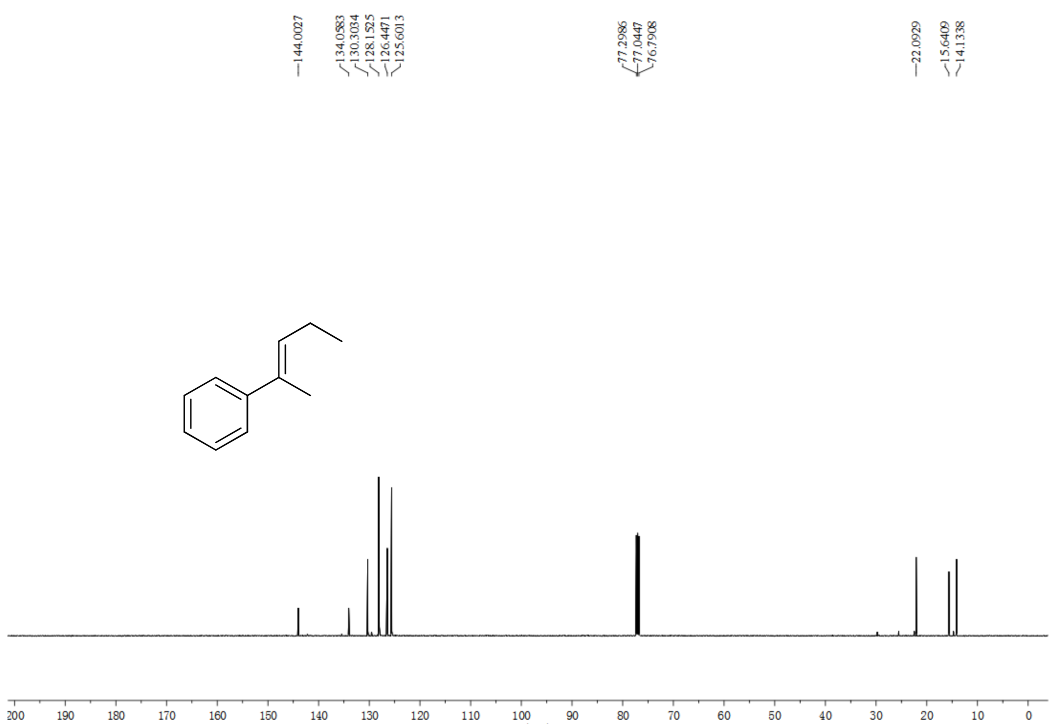
1.07
1.00
2.03
3.06
3.06
f1 (ppm)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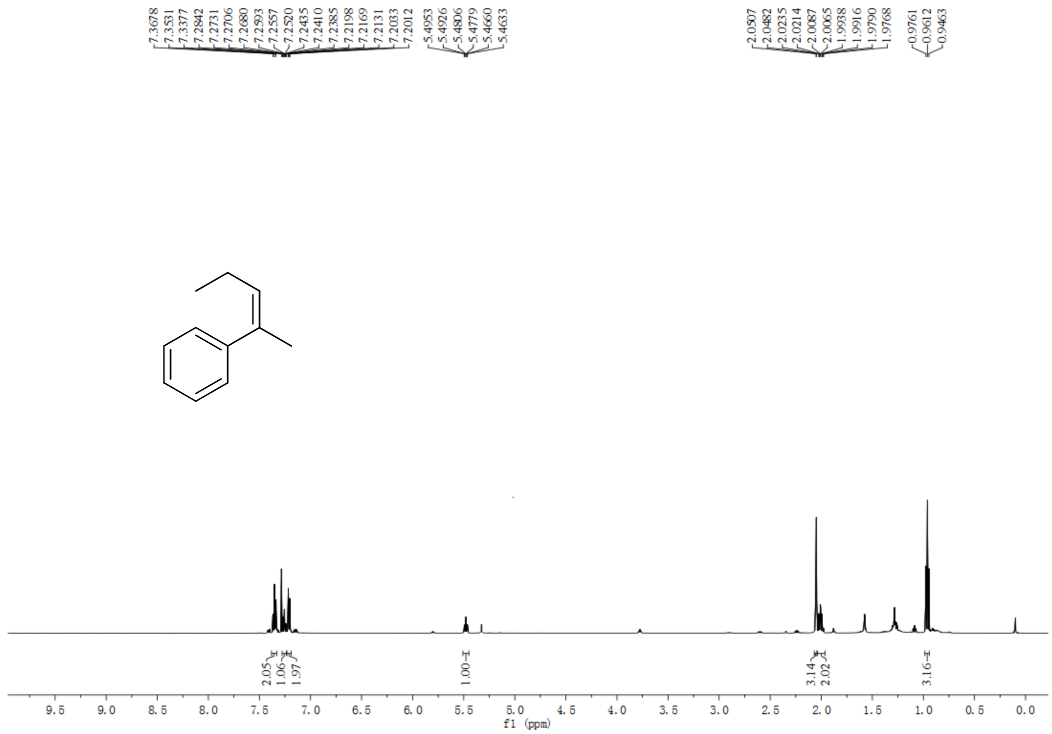
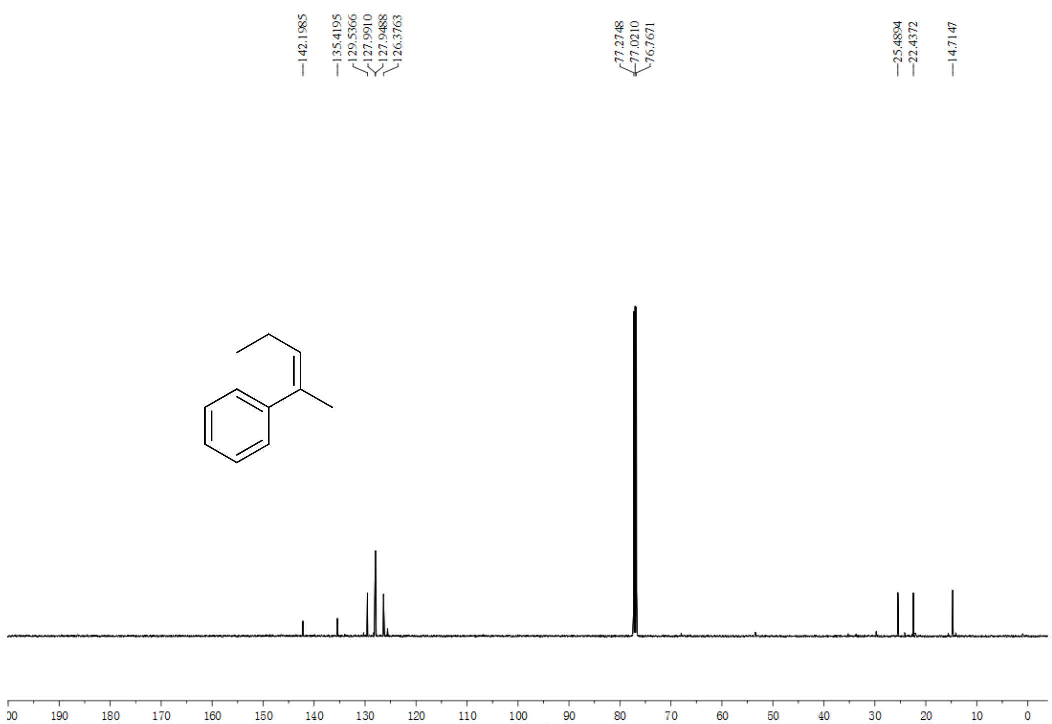
f1 (ppm)

3i(*Z*)





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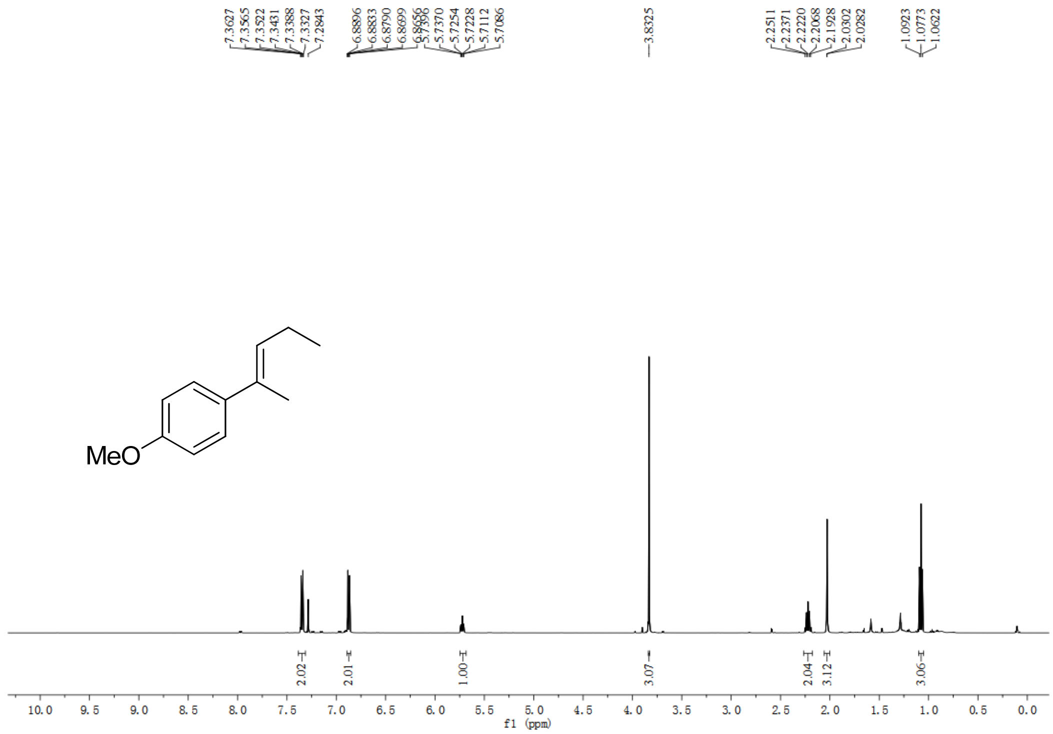

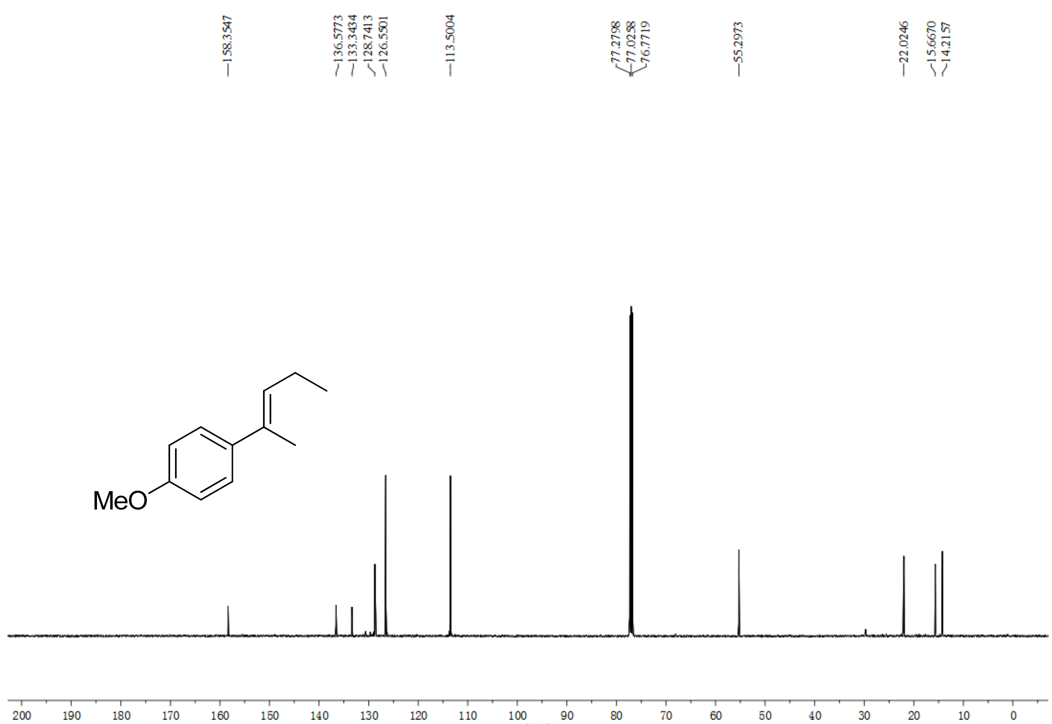

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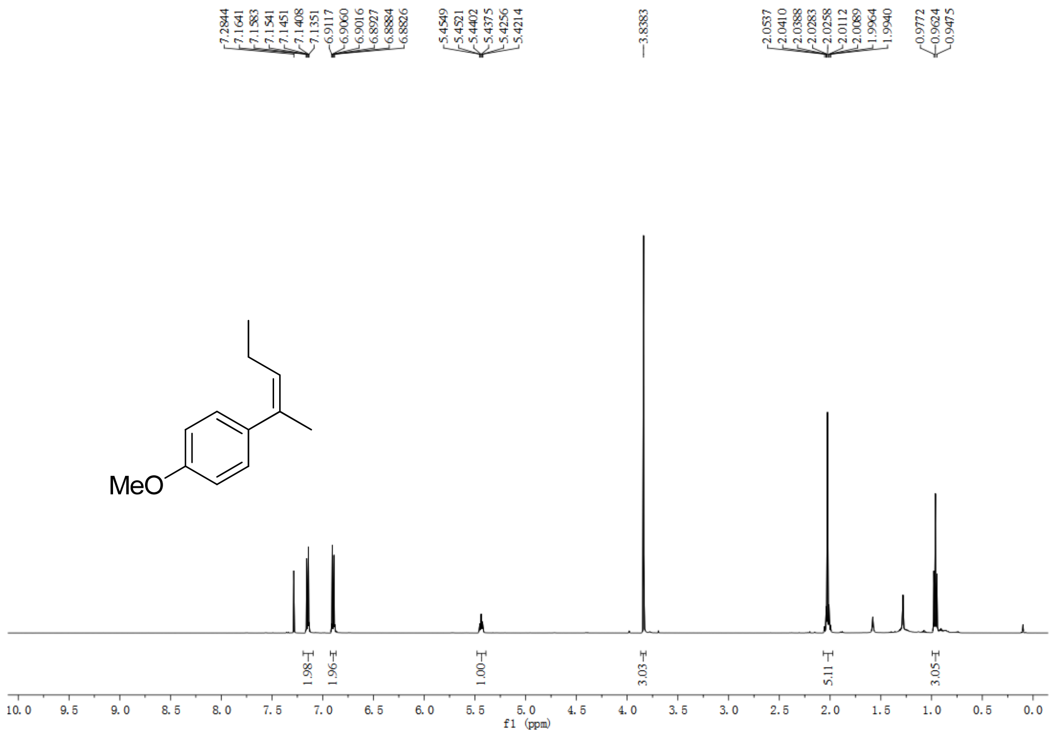
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5.4521
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5.4256
5.4214
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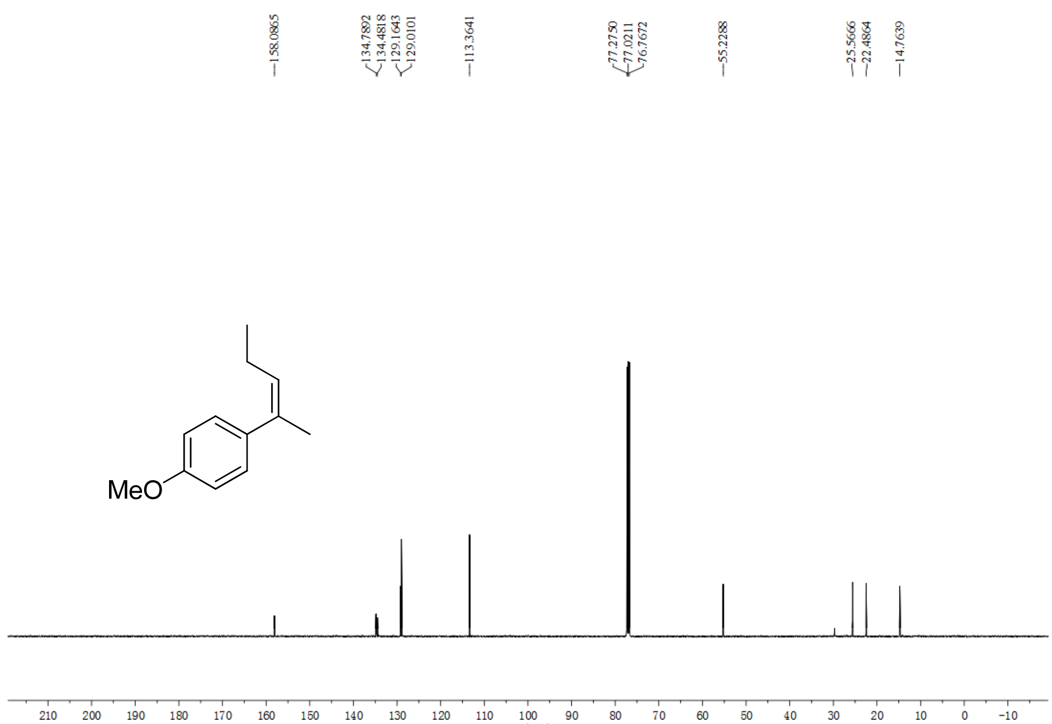
2.0410
2.0388
2.0283
2.0258
2.0112
2.0089
1.9964
1.9940
0.9772
0.9624
0.9475
MeO
1.98
1.96
1.00
3.03
5.11
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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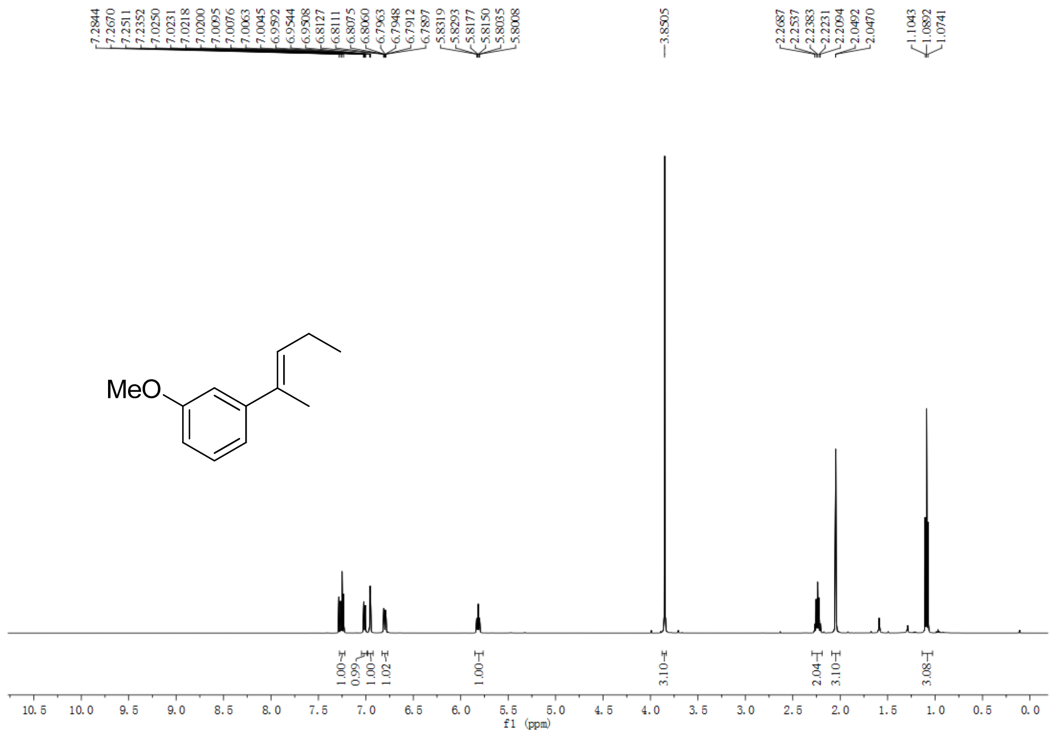
MeO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3ib(*E*)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6.7912
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5.8293
5.8177
5.8150
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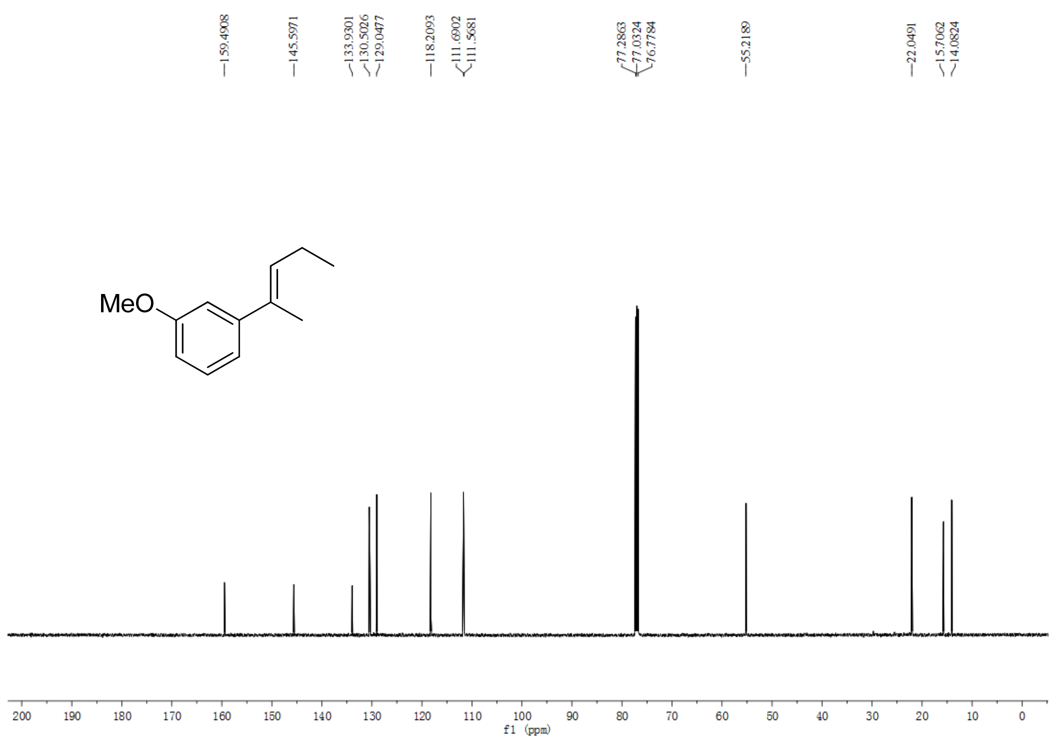
2.2383
2.2231
2.2094
2.0492
2.0470
1.1043
1.0892
1.0741
MeO
1.00
0.99
1.00
1.02
1.00
3.10
2.04
3.10
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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55.2189
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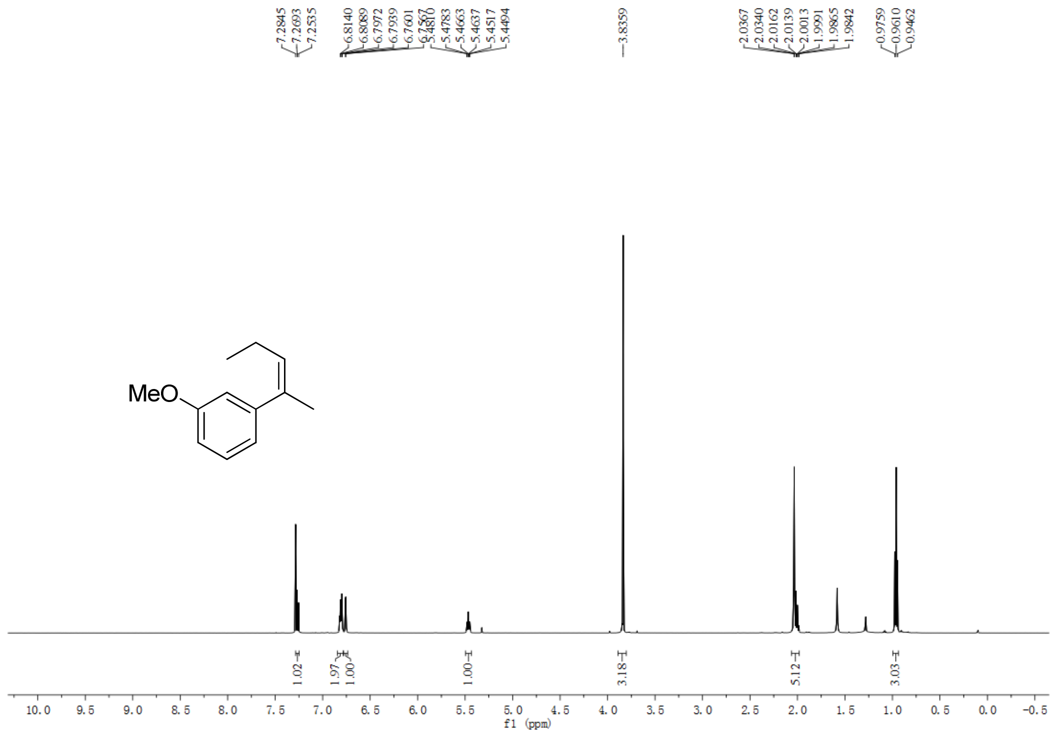
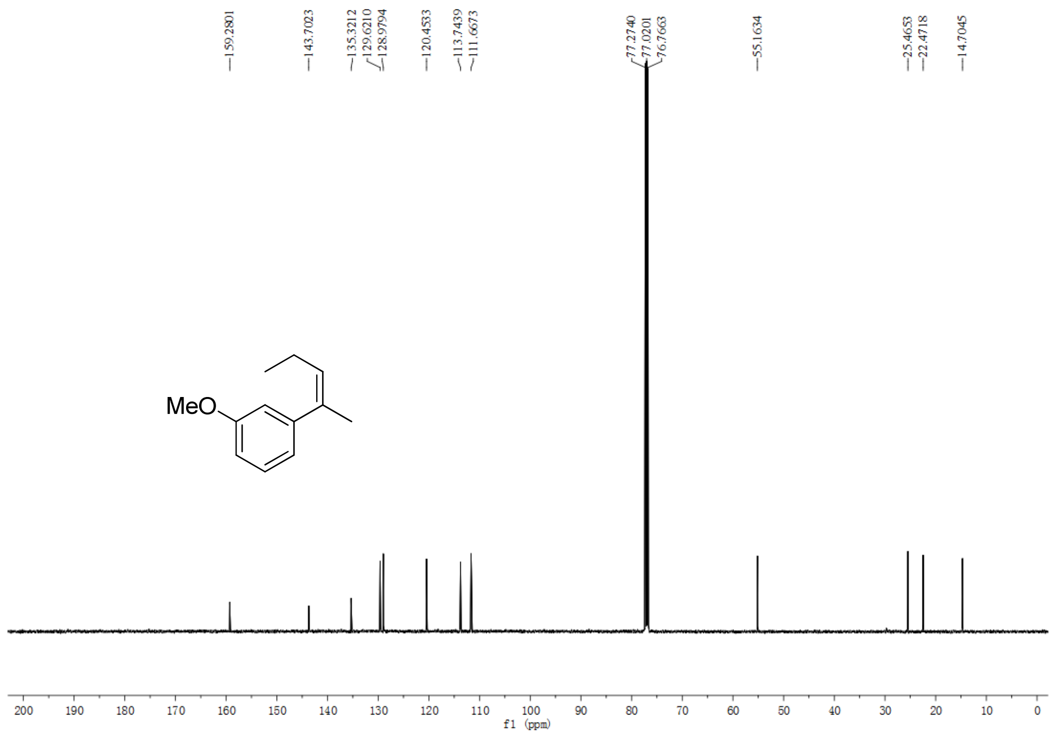
MeO
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3ib(*Z*)





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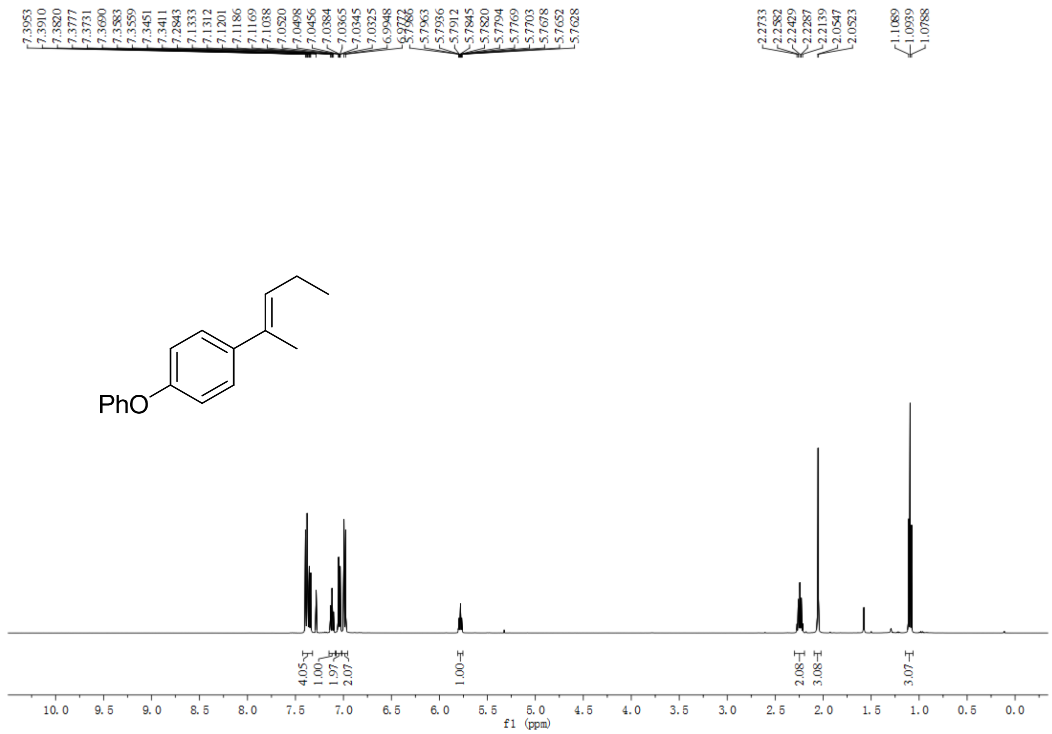
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7.2843
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7.1201
7.1186
7.1169
7.1038
7.0520
7.0498
7.0456
7.0384
7.0365
7.0345
7.0325
6.9948
5.7963
5.7936
5.7912
5.7845
5.7820
5.7794
5.7769
5.7703
5.7678
5.7652
5.7628
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2.2582
2.2429
2.2287
2.2139
2.0547
2.0523
1.1089
1.0939
1.0788
PhO
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1.97
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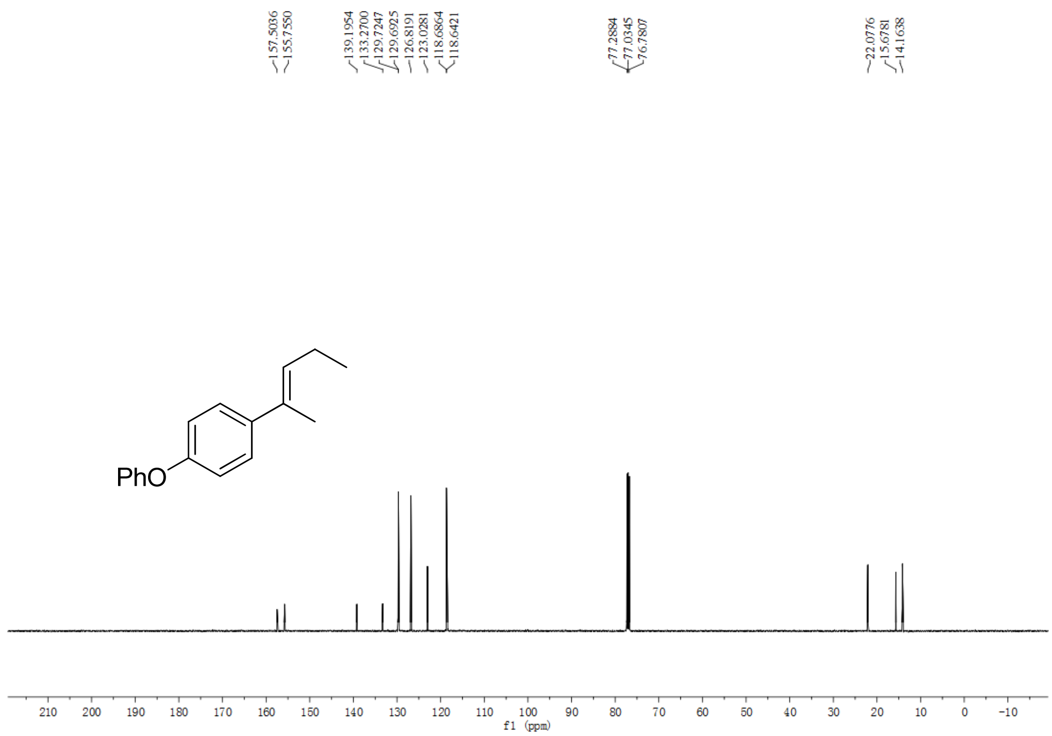
1.00
2.08
3.08
3.07
f1 (ppm)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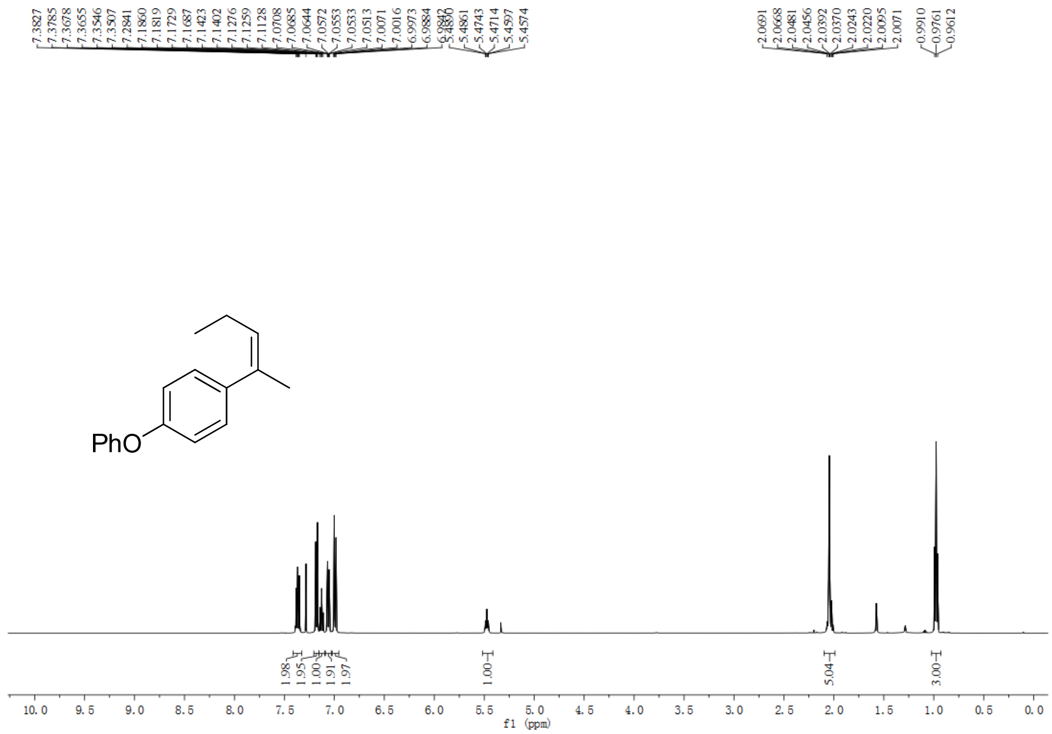
PhO
f1 (ppm)

3ic(*Z*)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7.1423
7.1402
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7.0685
7.0644
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7.0553
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7.0016
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5.4497
5.4574
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2.0668
2.0481
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2.0392
2.0370
2.0243
2.0220
2.0095
2.0071
0.9910
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1.95
1.00
1.91
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1.00
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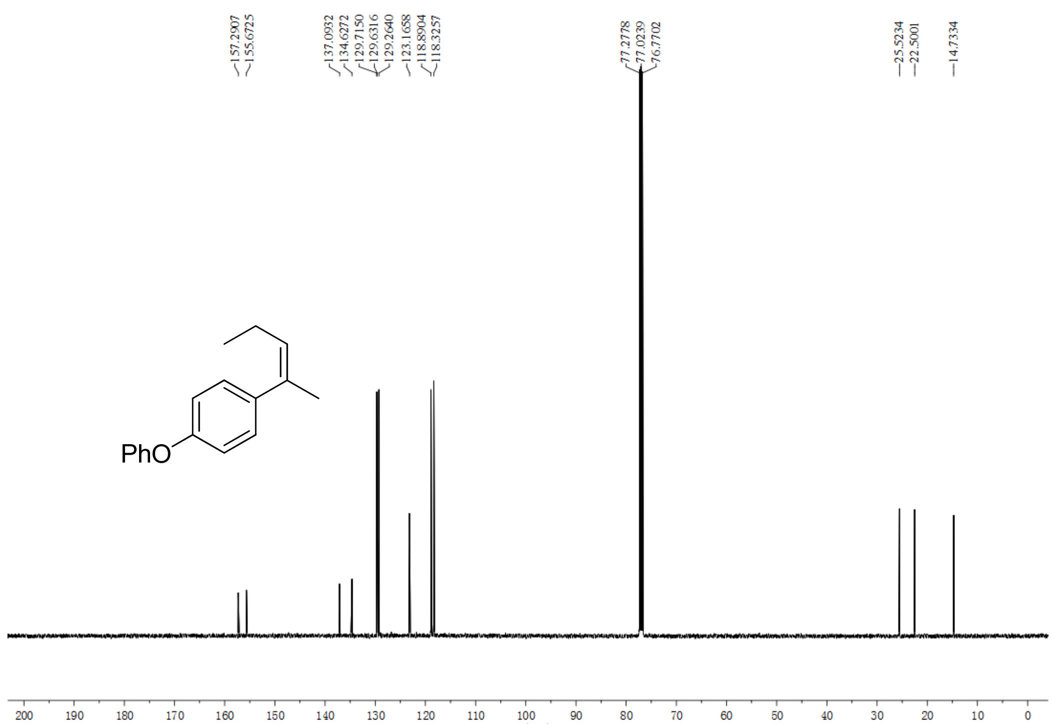
3.00
f1 (ppm)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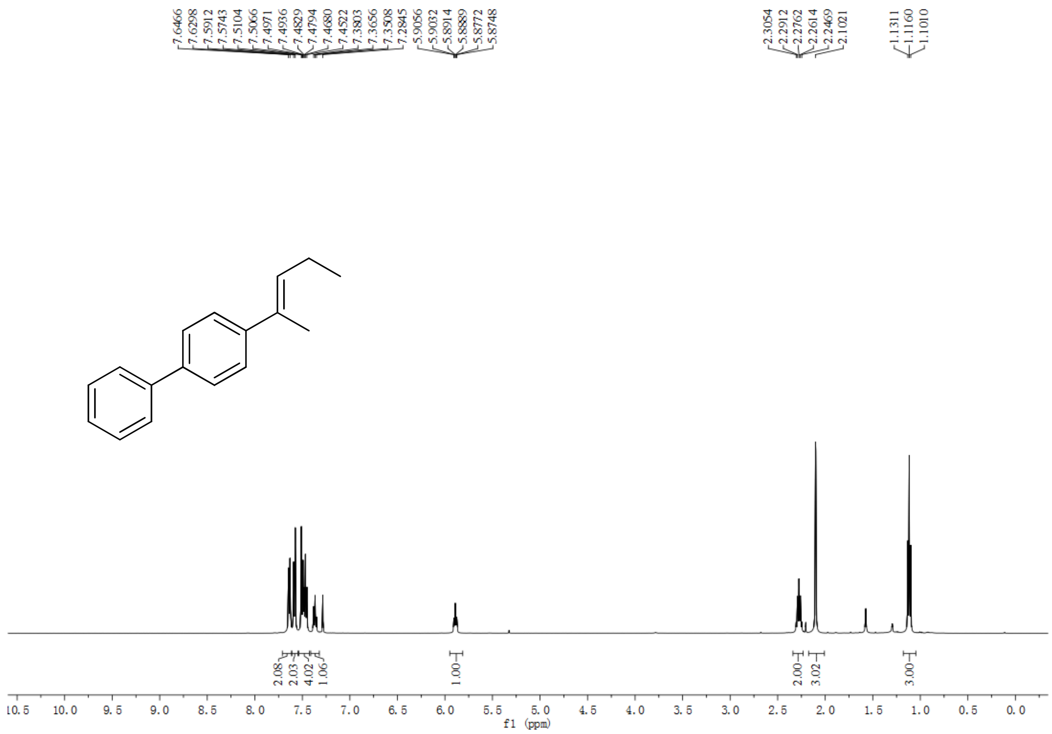
PhO
f1 (ppm)

3id(*E*)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4.02
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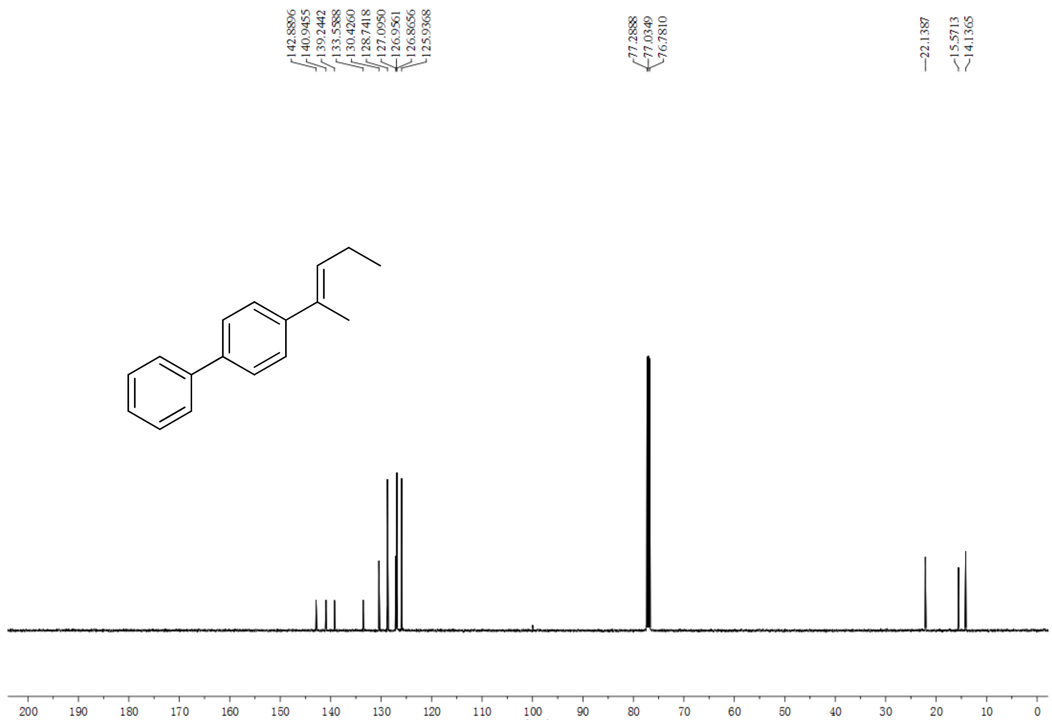
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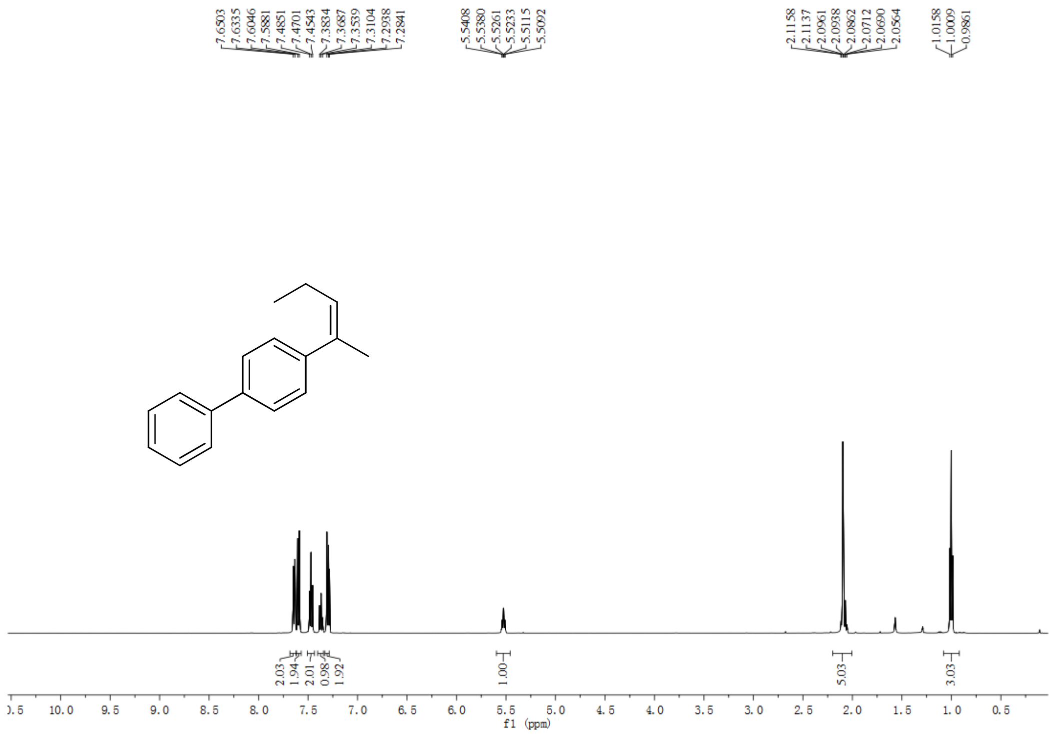
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1.0158
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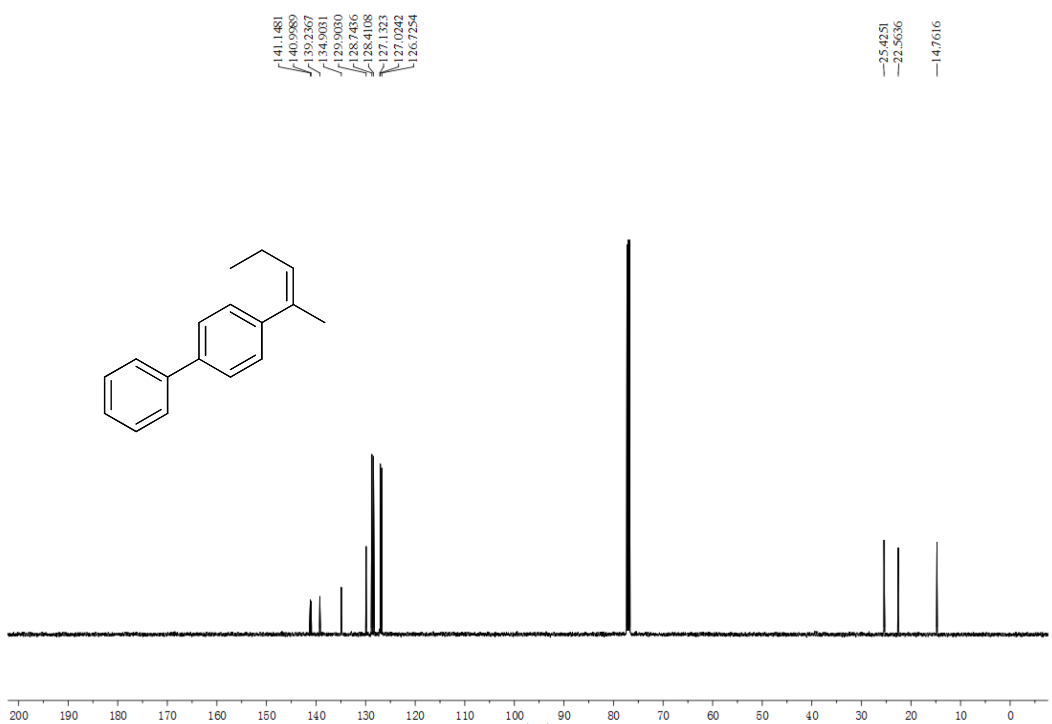
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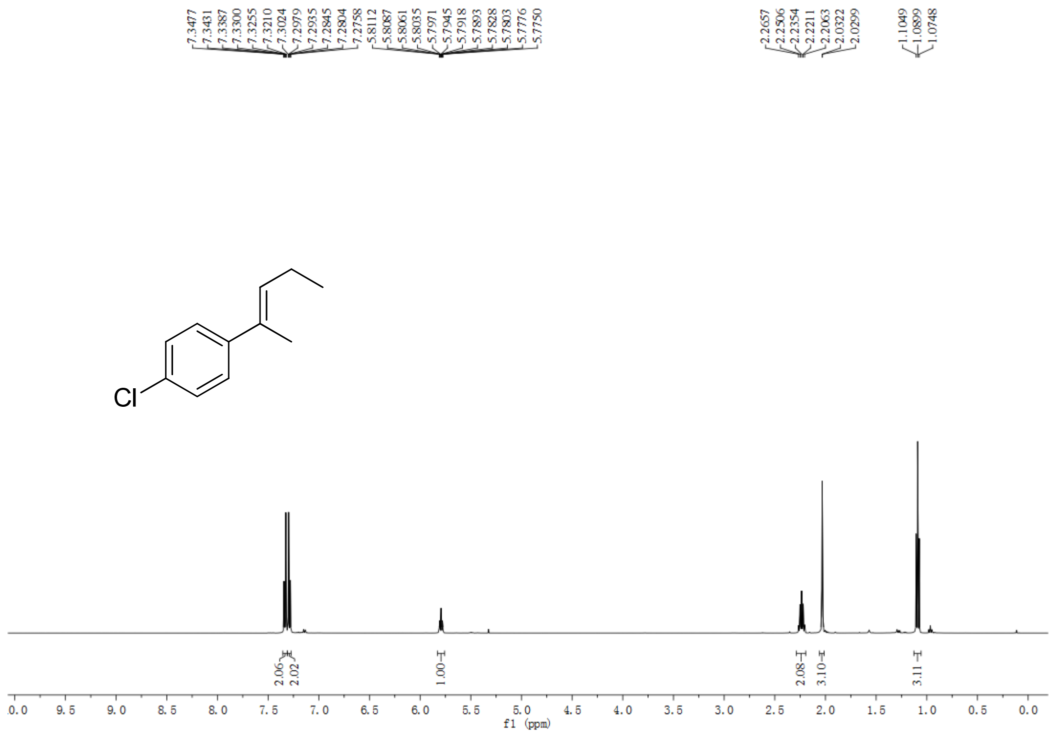
f1 (ppm)

3ie(*E*)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5.7918
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5.7803
5.7776
5.7750
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2.2354
2.2211
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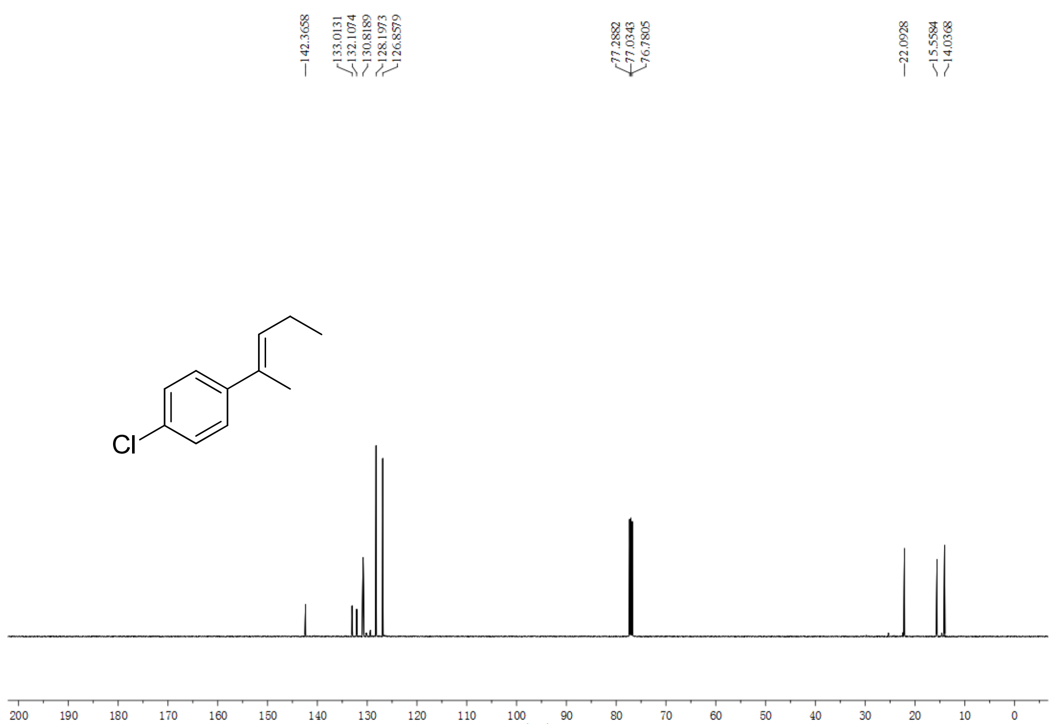
3.11
f1 (ppm)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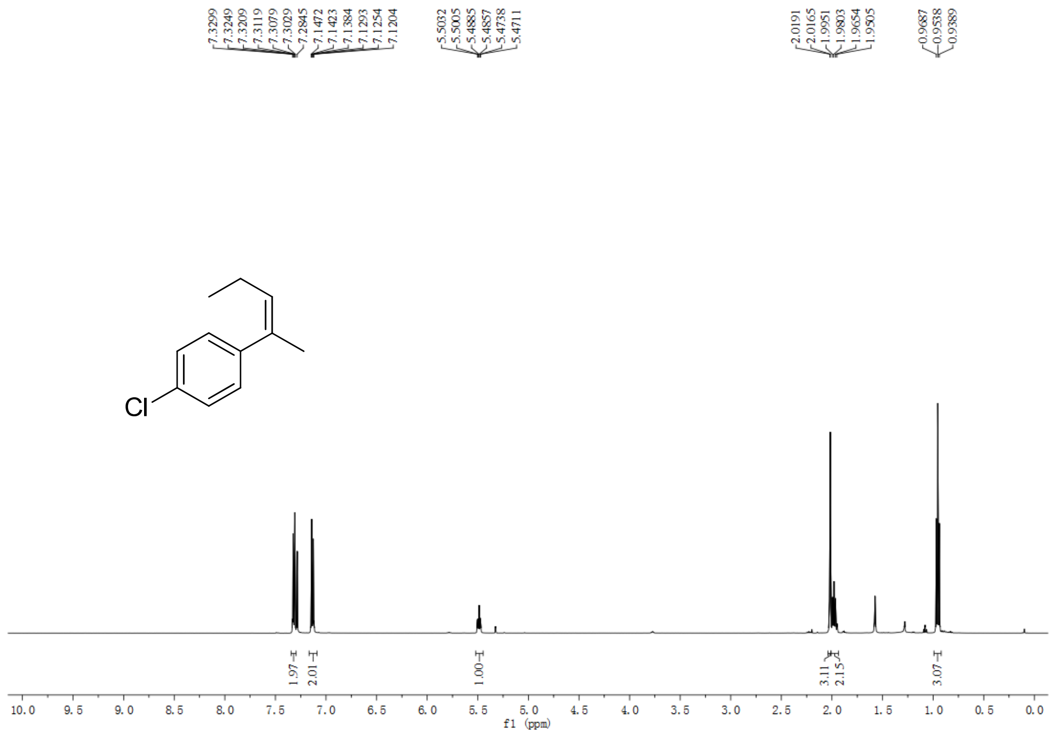
3ie(*E*)



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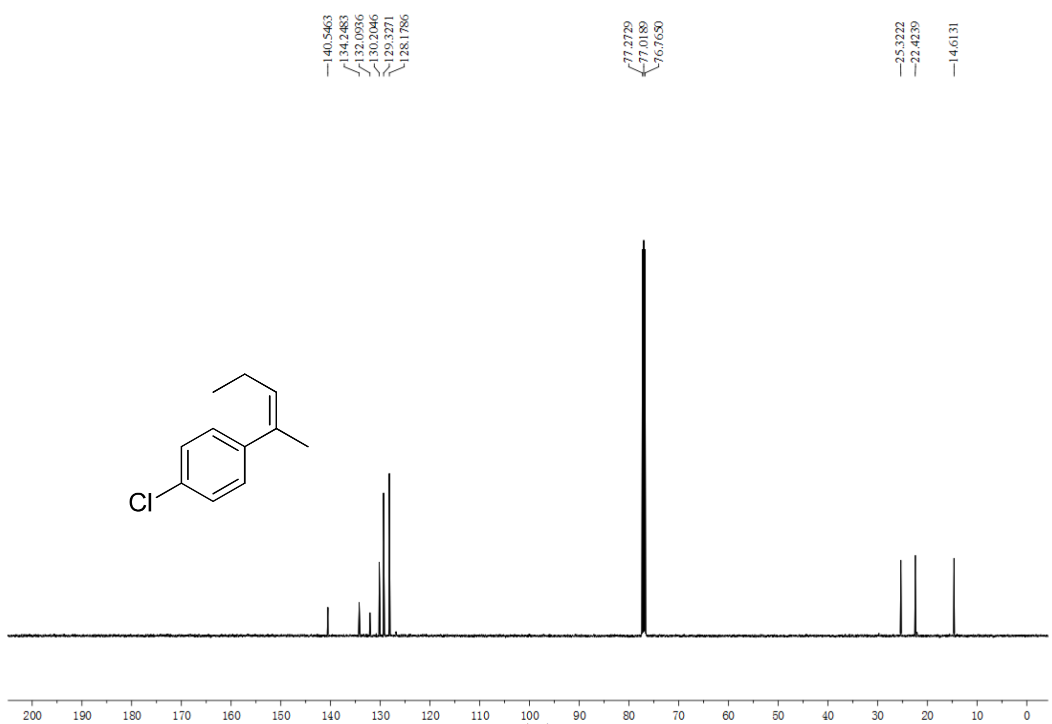
f1 (ppm)



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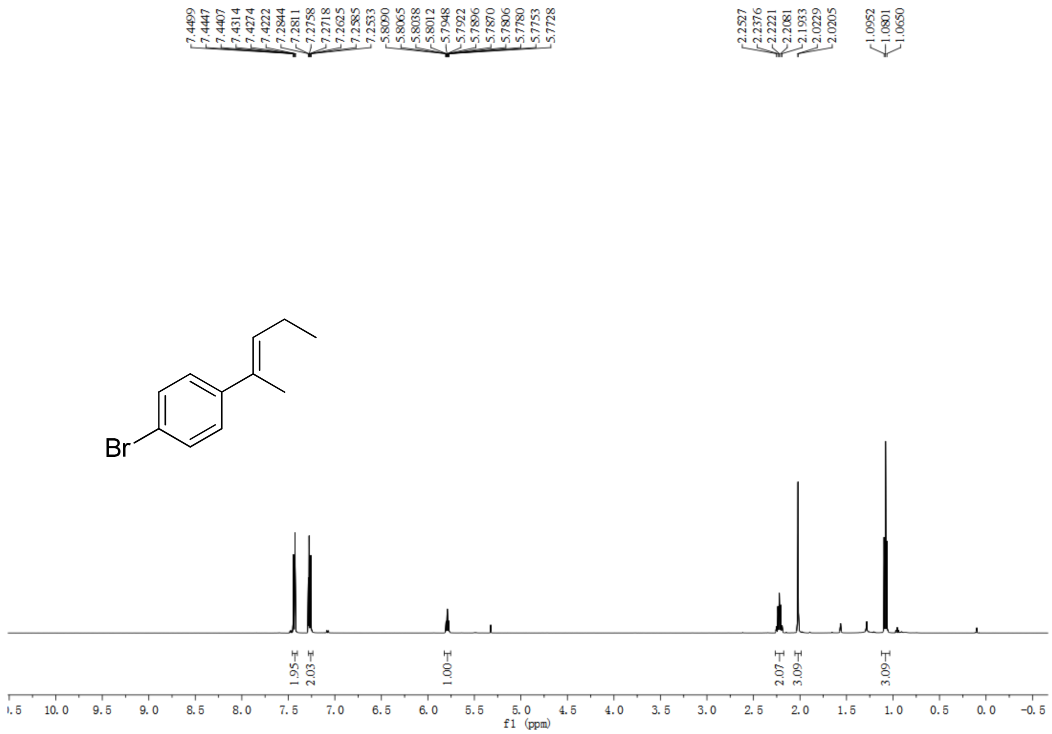
Cl
f1 (ppm)

3if(*E*)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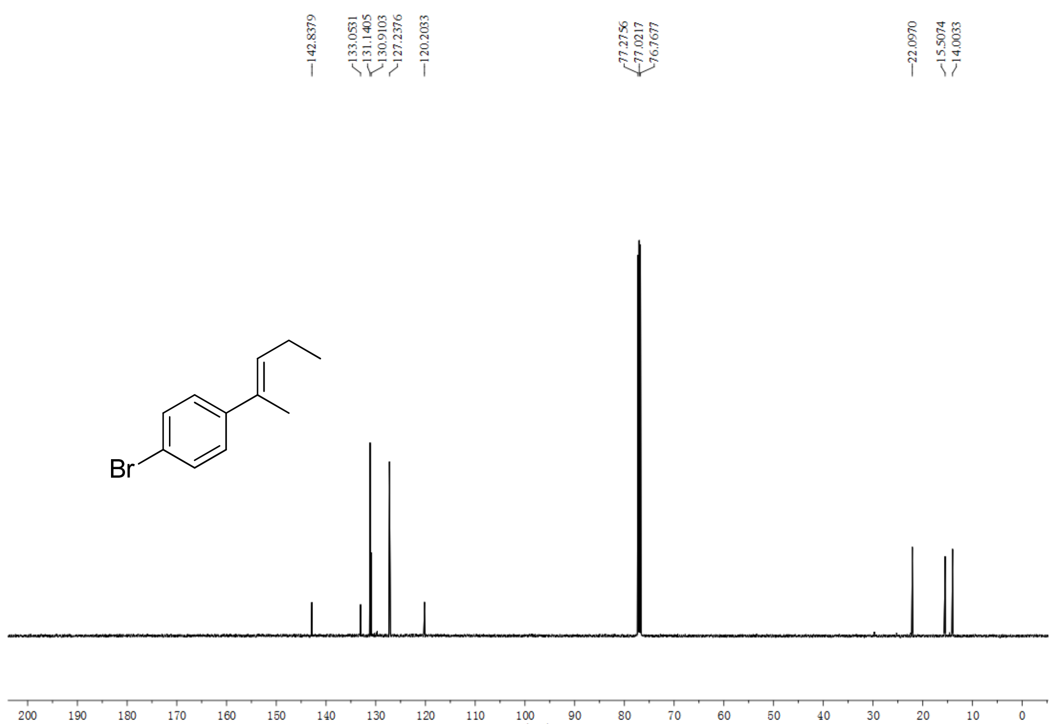
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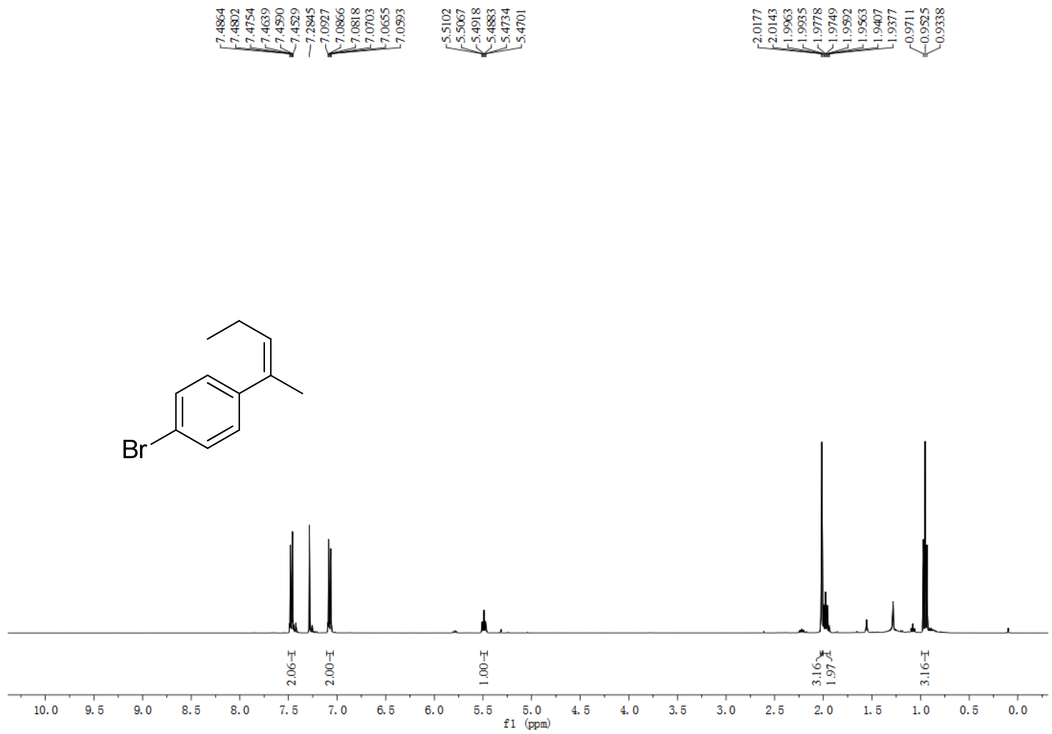
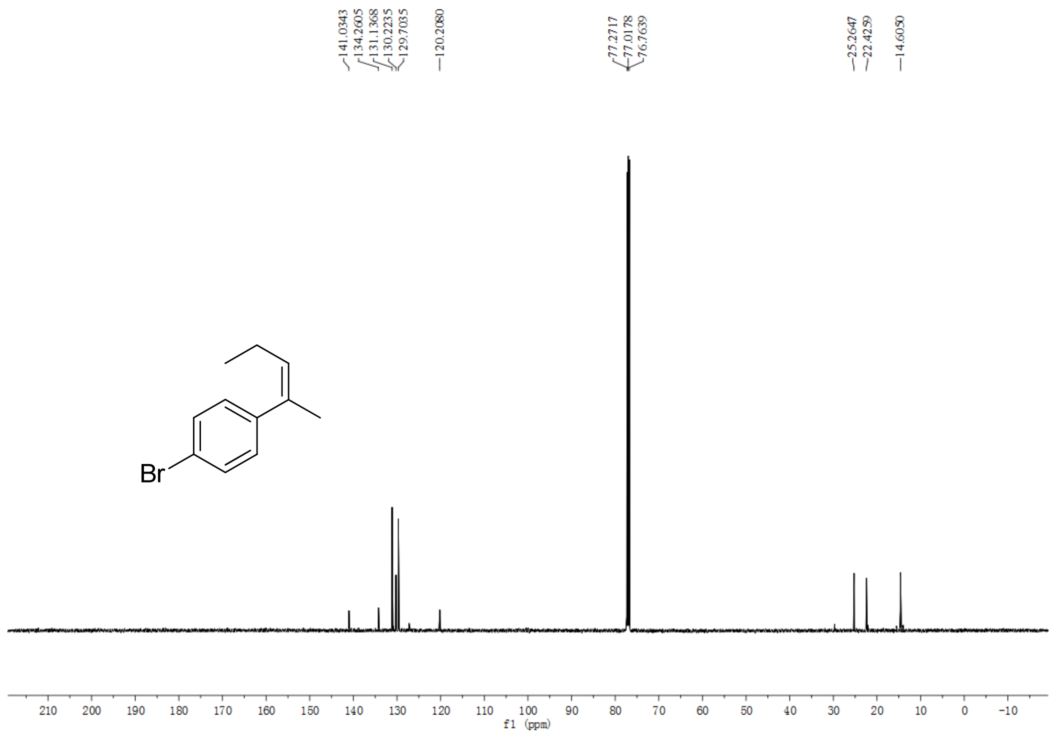
Br
f1 (ppm)

3if(*Z*)





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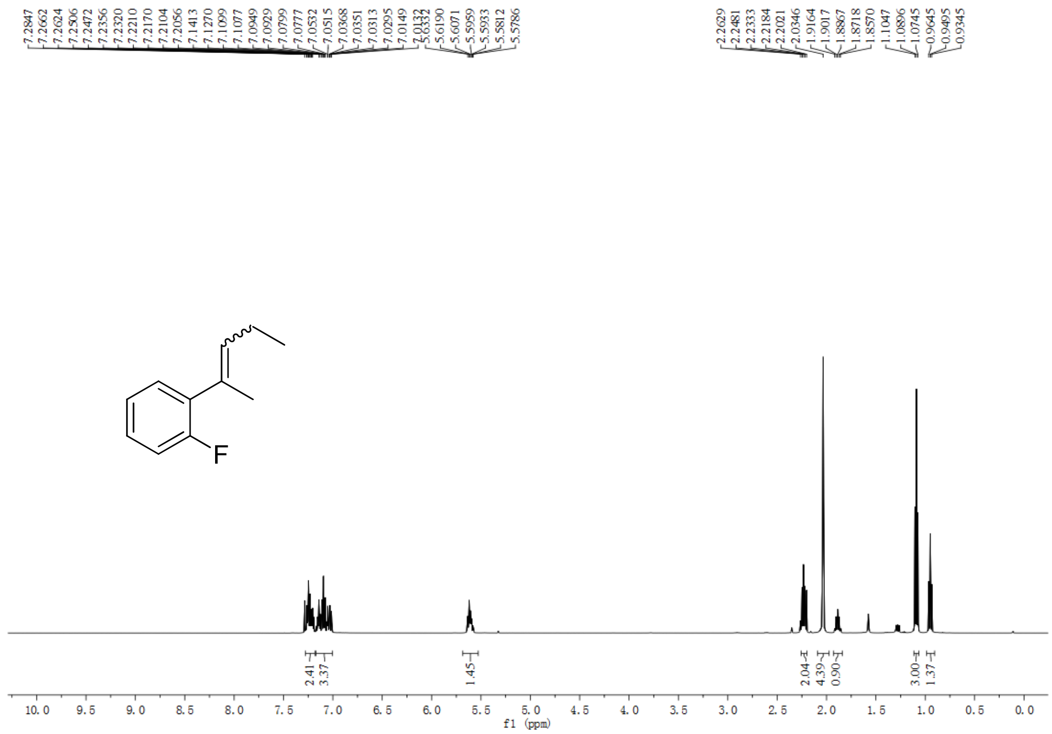

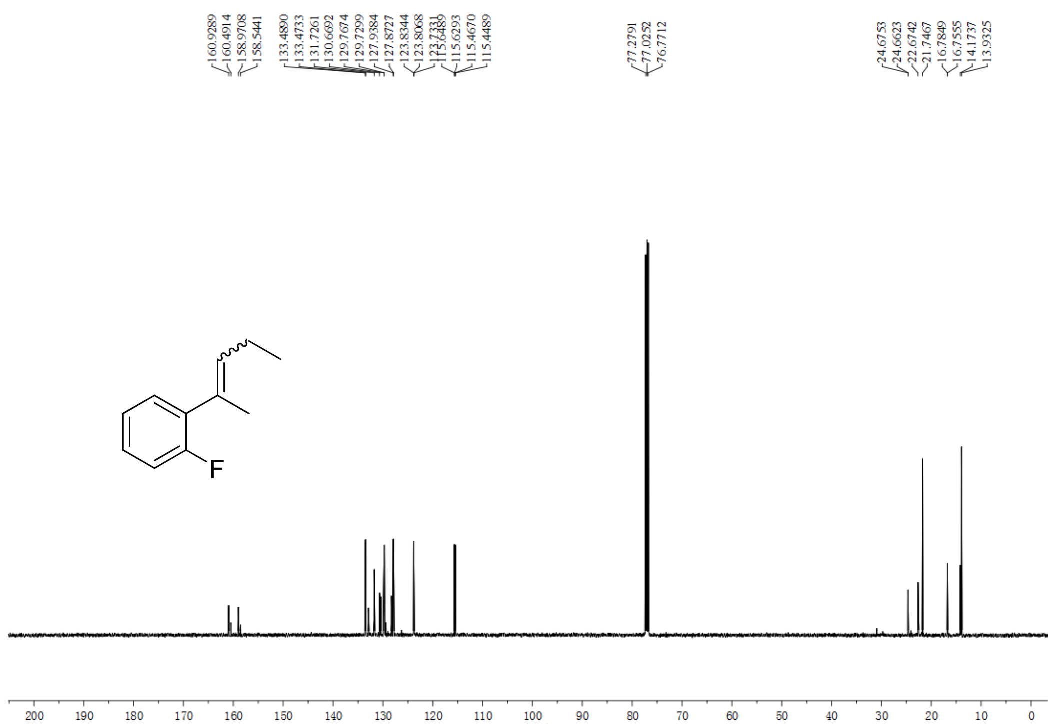

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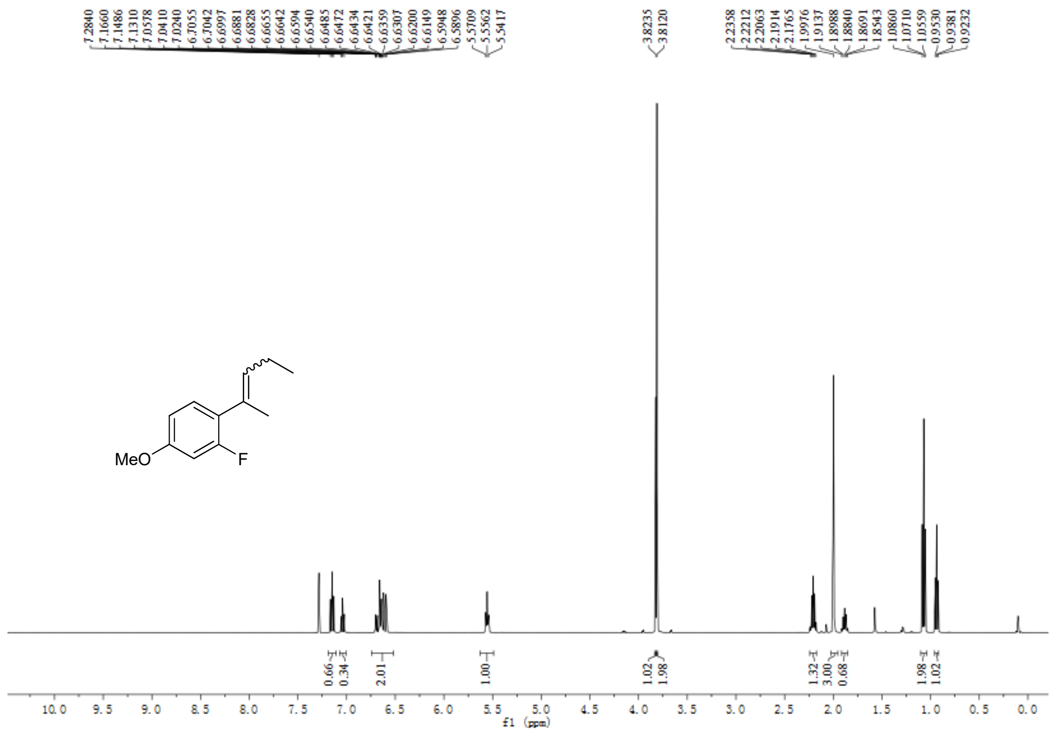
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MeO
F
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1.02
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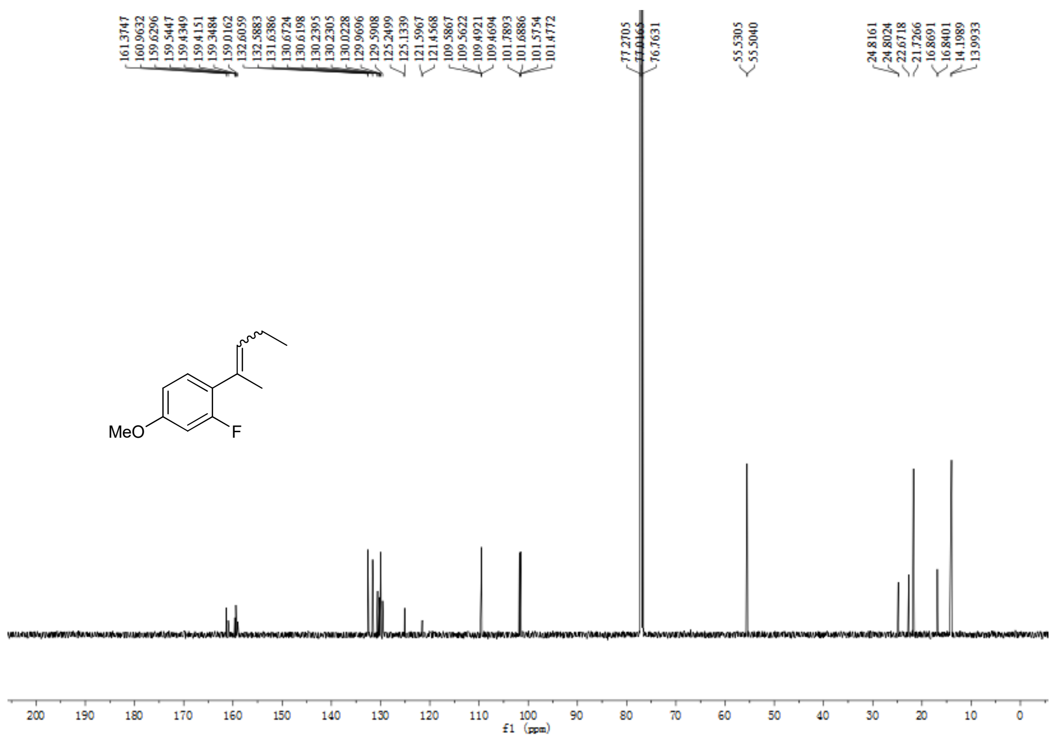
f1 (ppm)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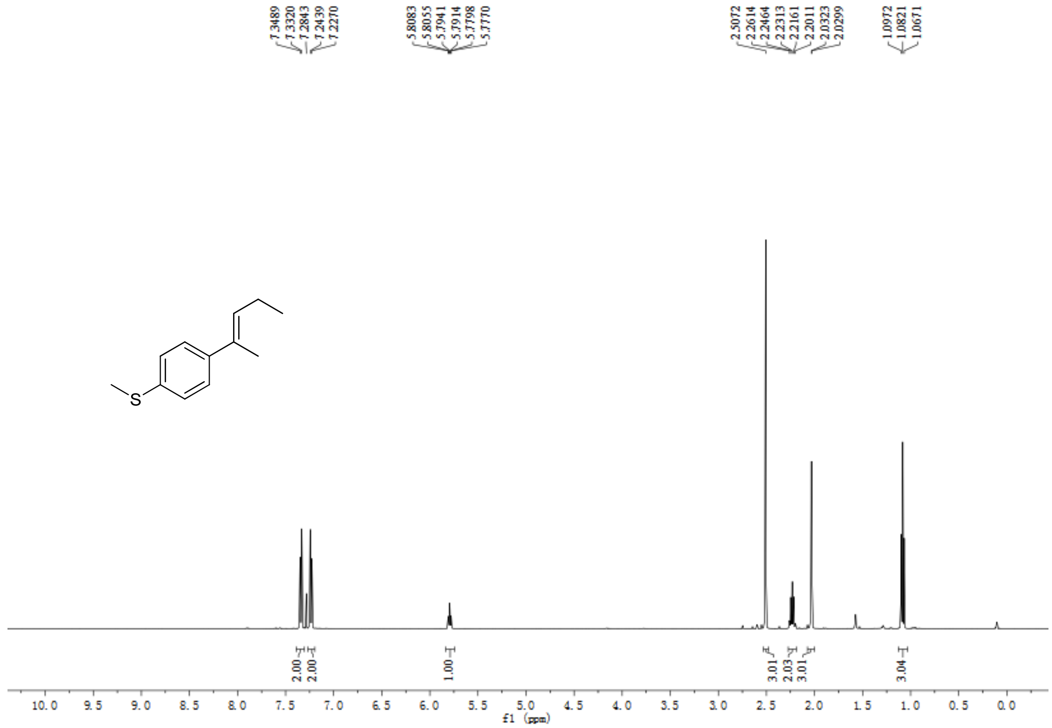
MeO
F
f1 (ppm)

3ii(*E*)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2.2011
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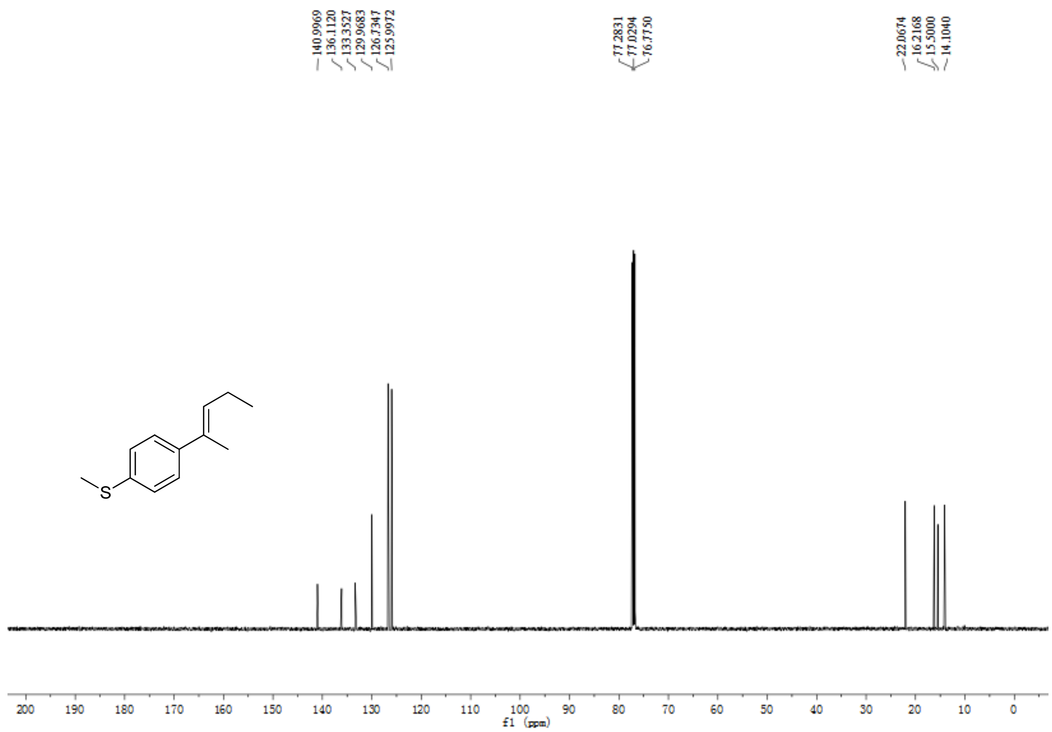
2.0299
1.0972
1.0821
1.0671
S
2.00
2.00
1.00
3.01
2.03
3.01
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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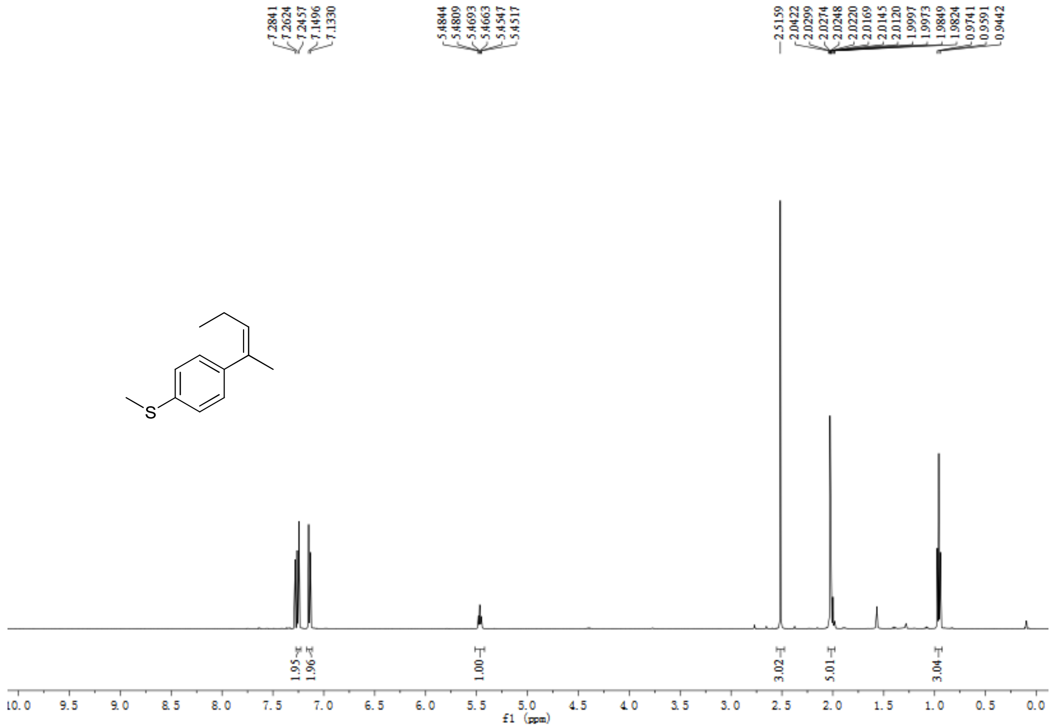
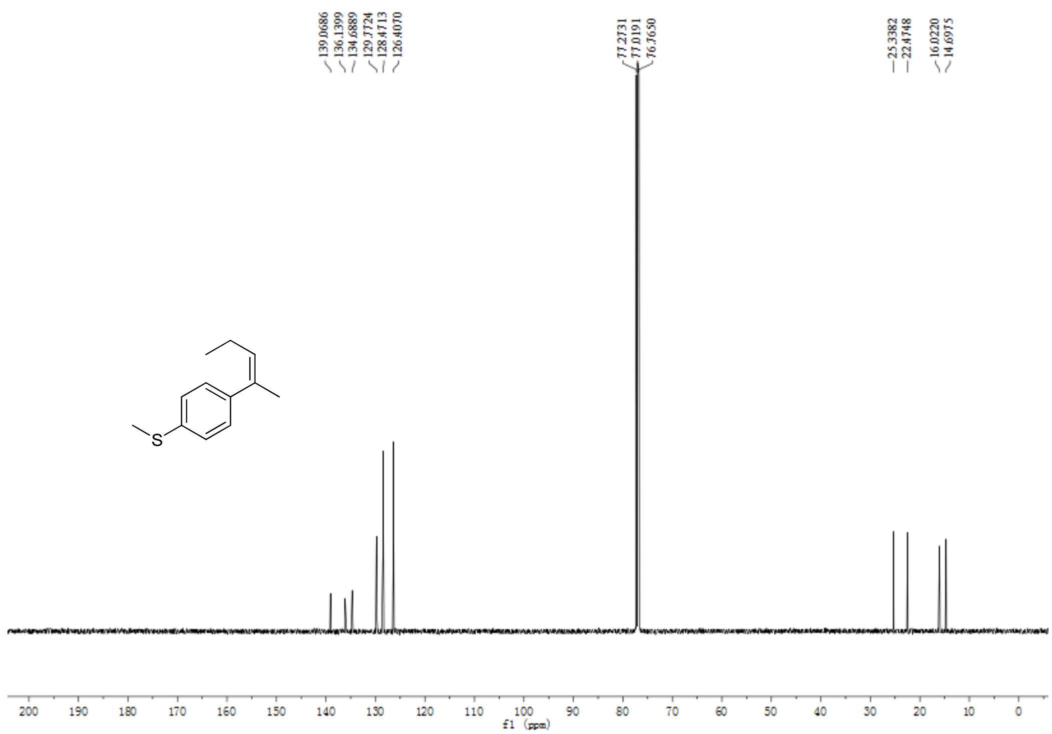
f1 (ppm)

3ii(Z)





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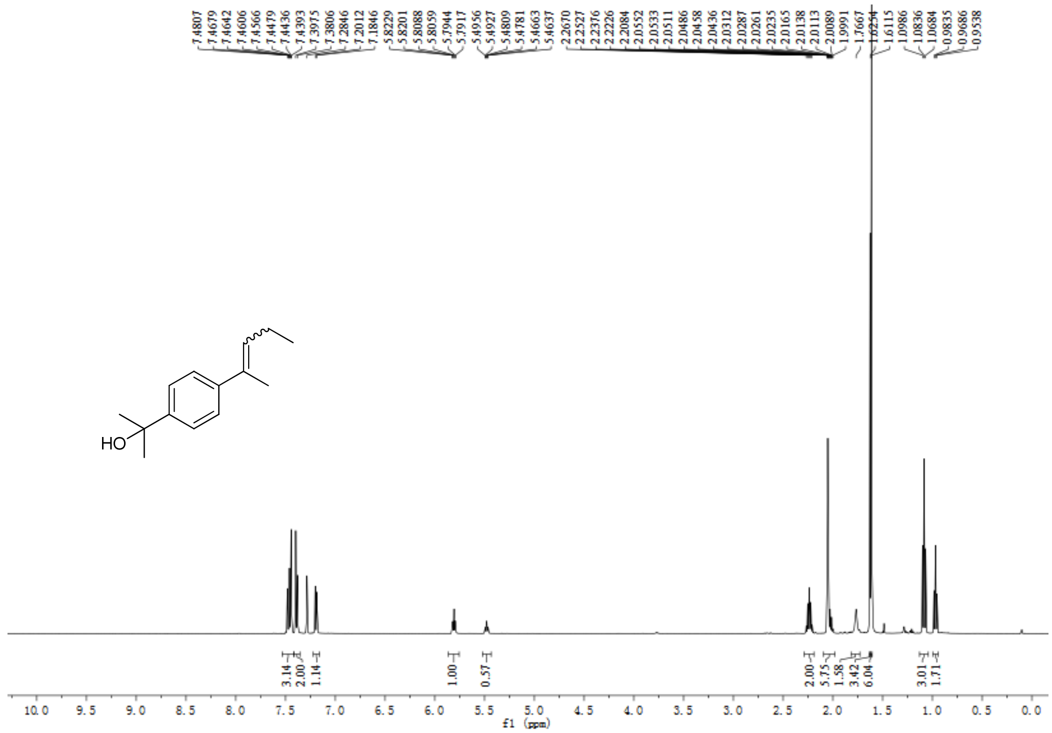

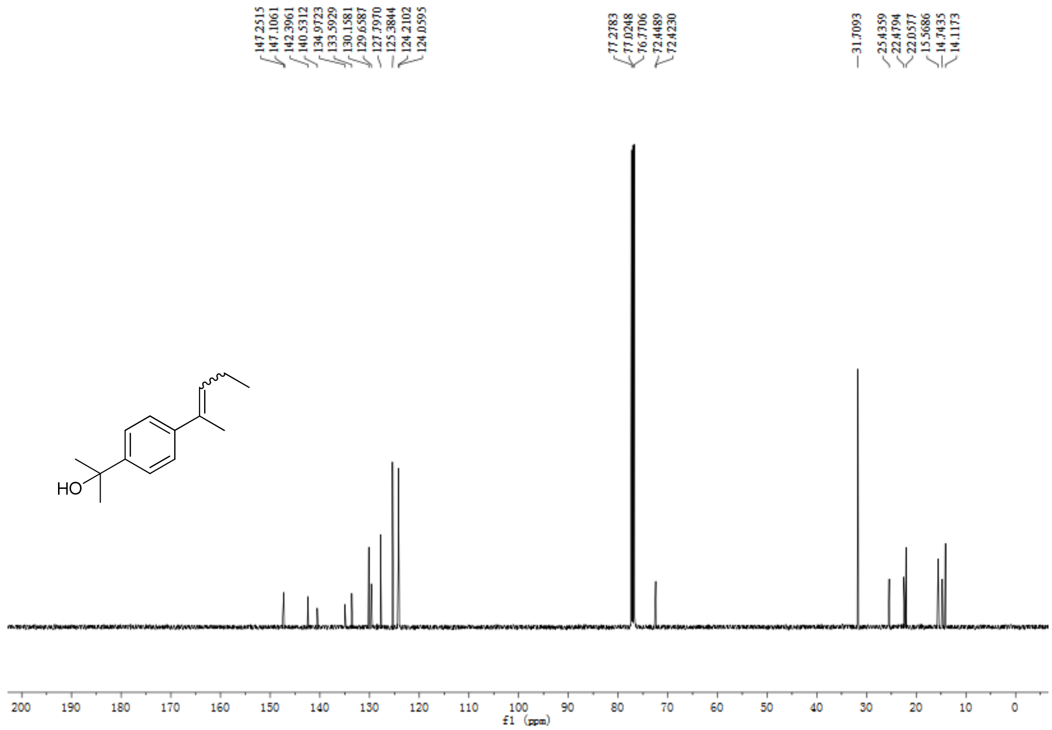

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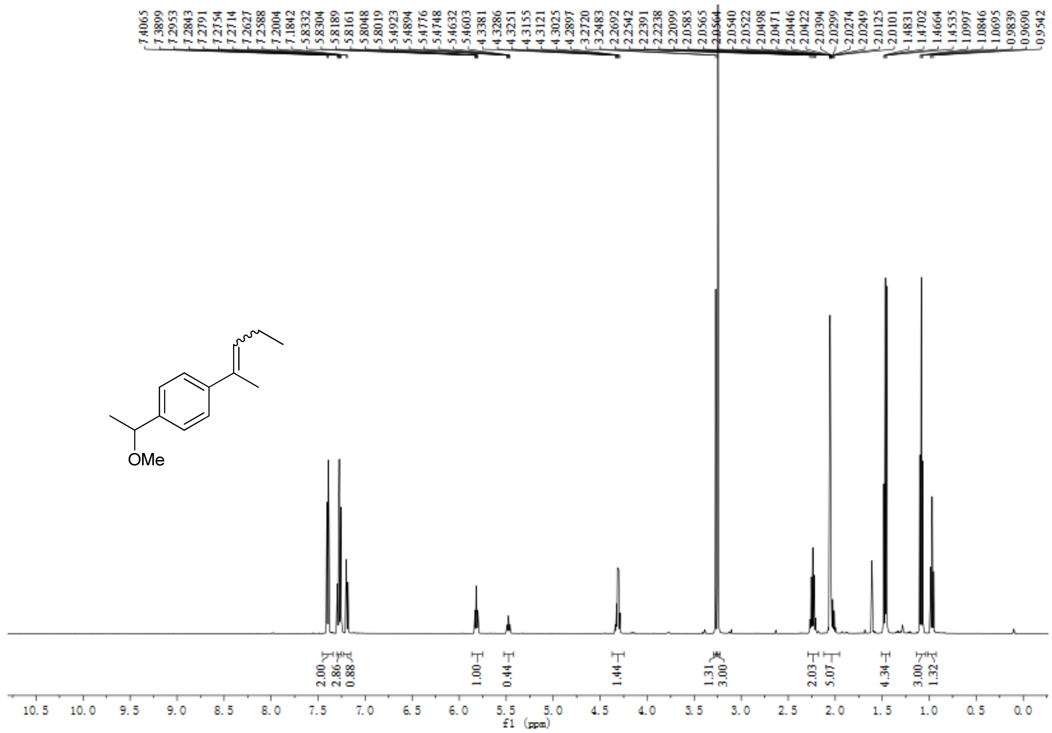
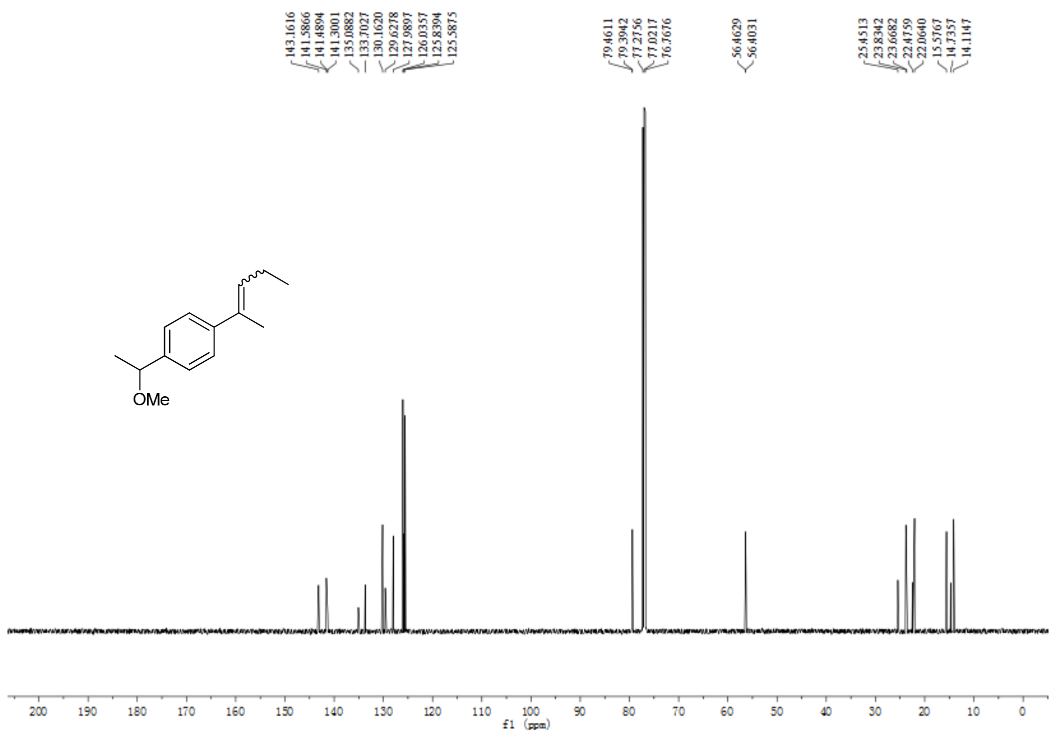
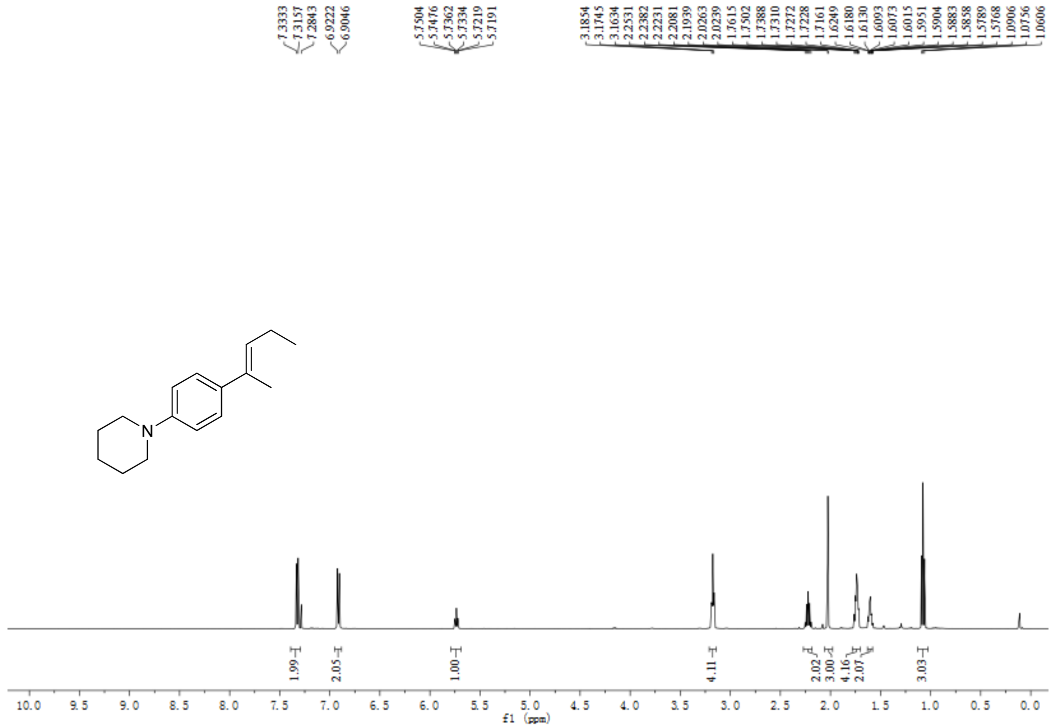




3il(*E*)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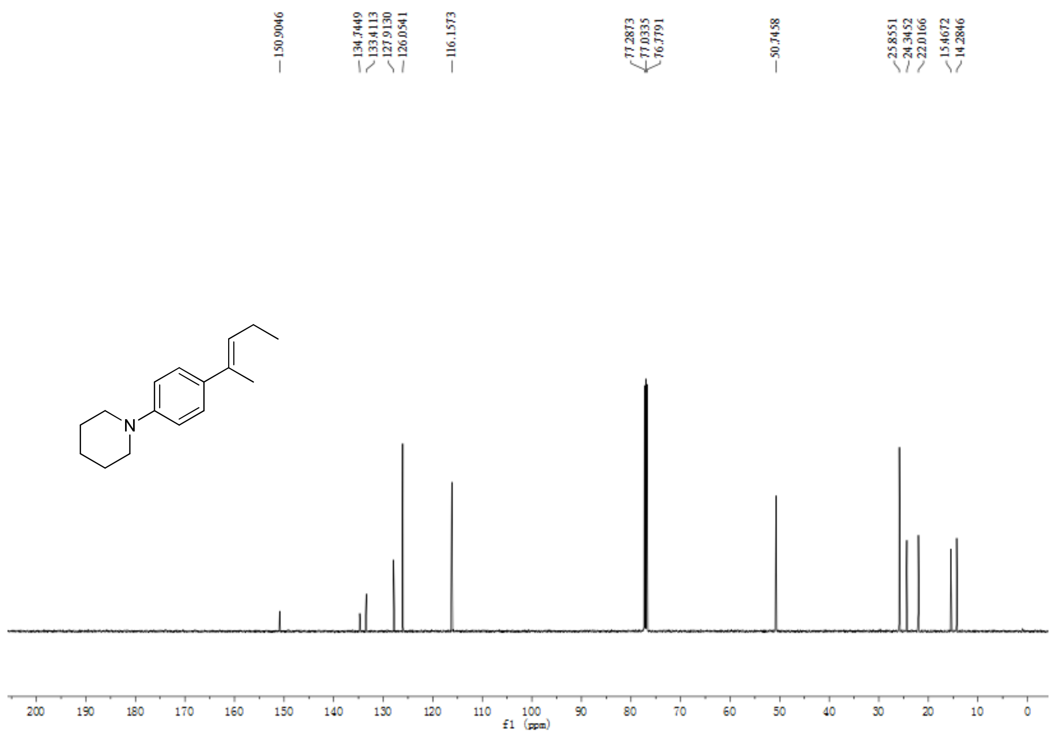
3.03
f1 (ppm)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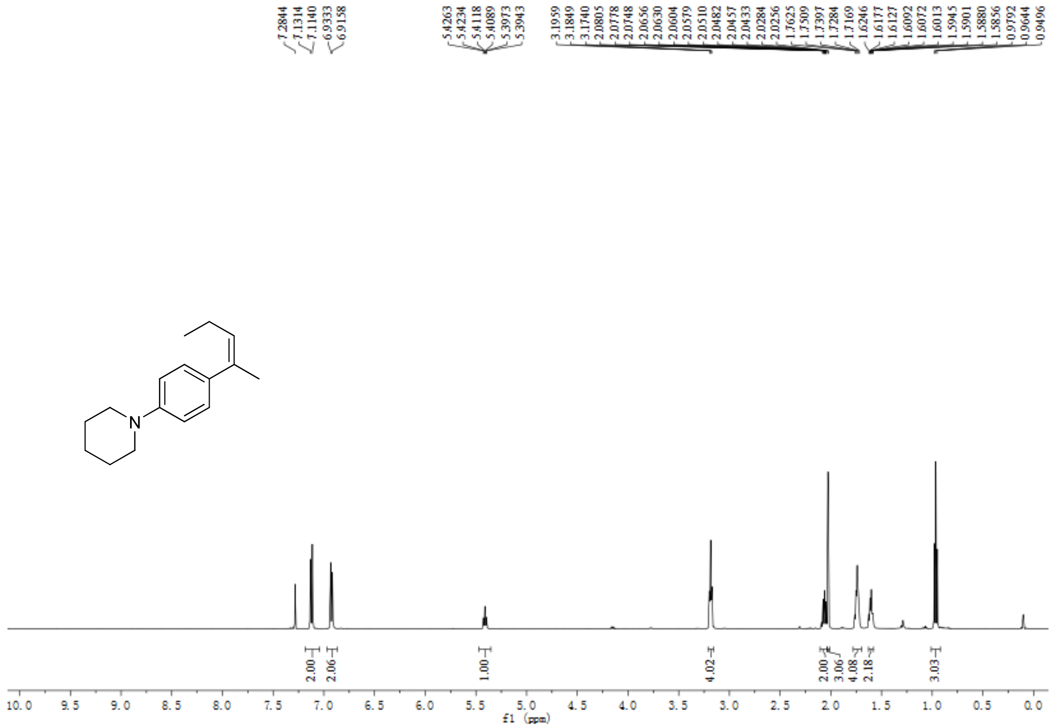
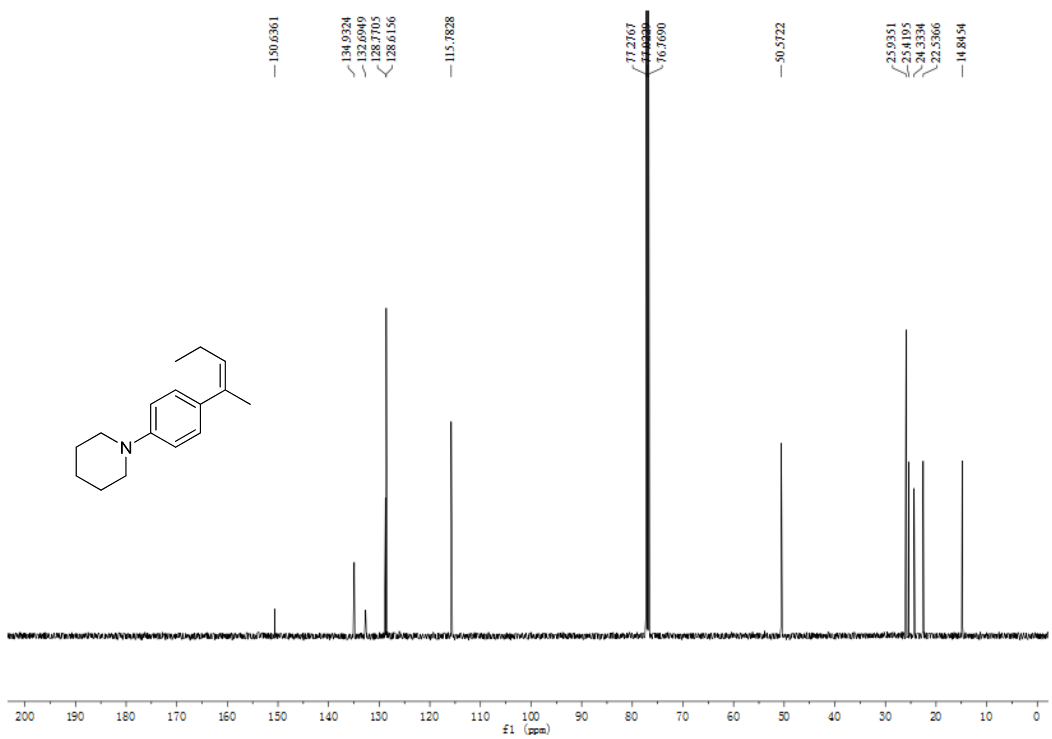
N
f1 (ppm)

3il(*Z*)





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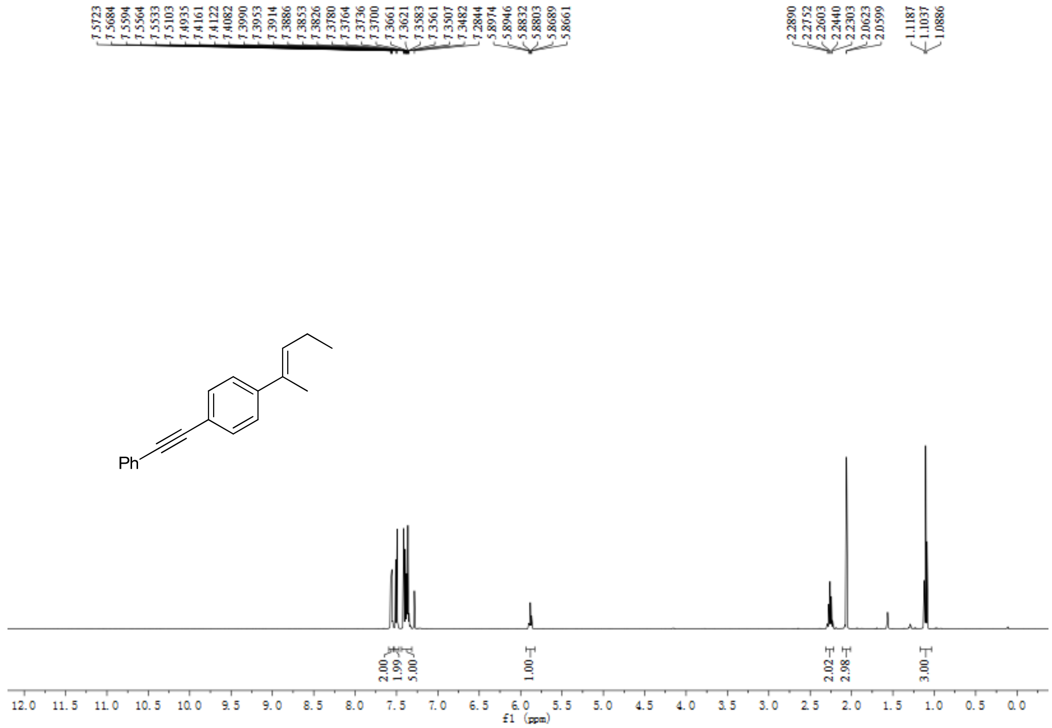

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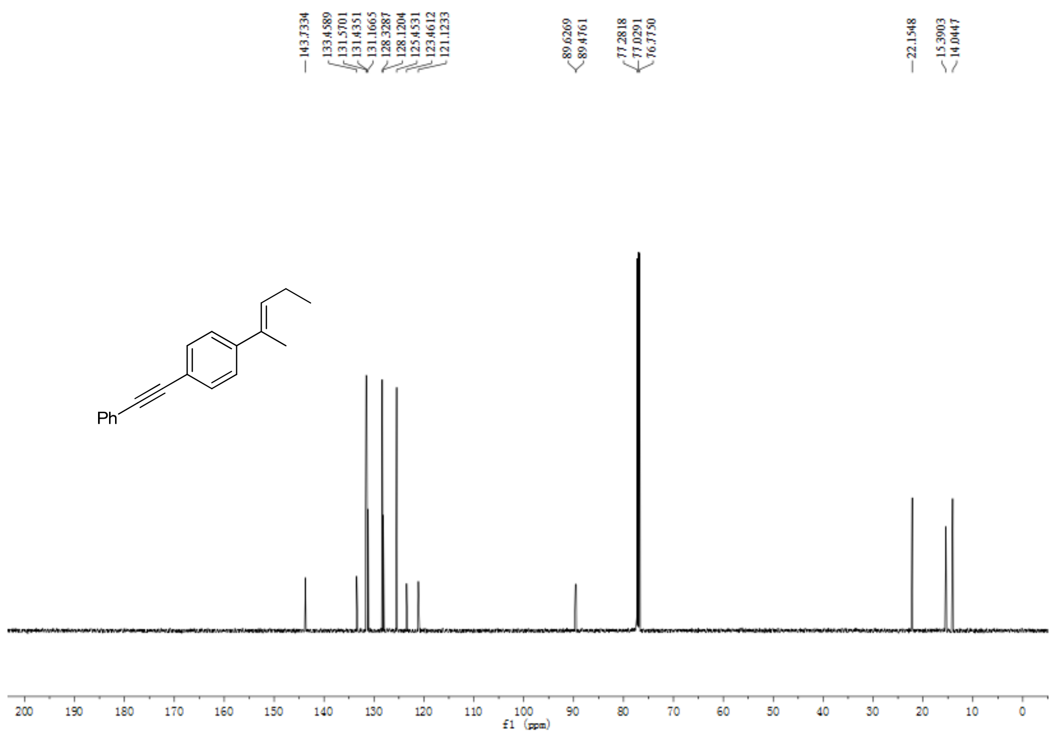
f1 (ppm)



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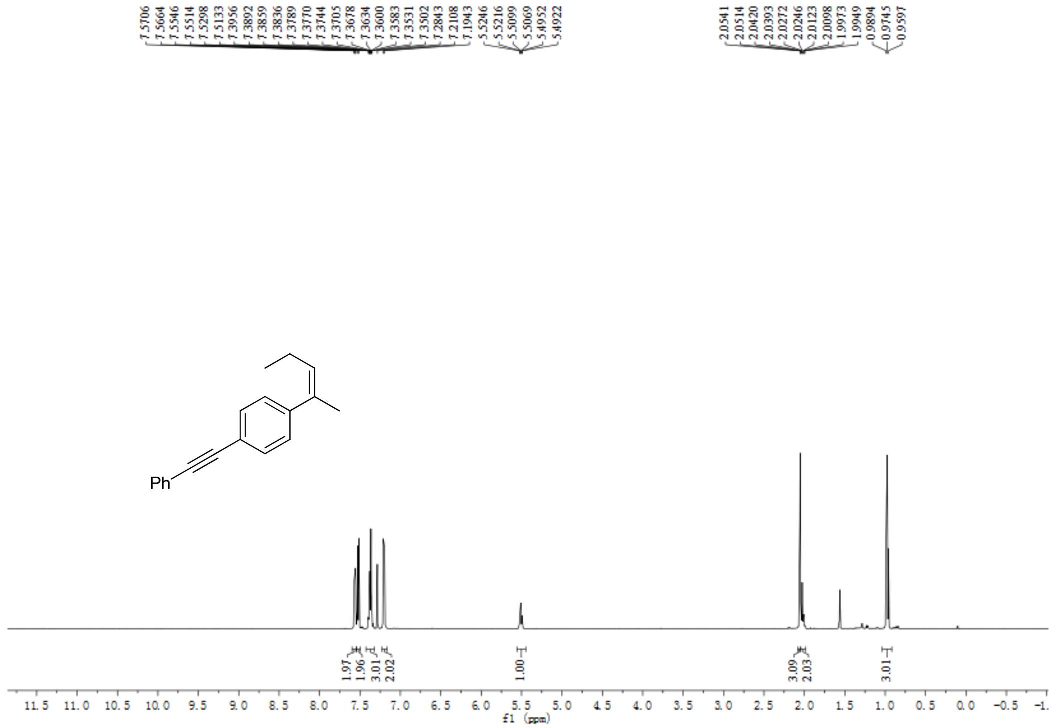
Ph
f1 (ppm)

3im(Z)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7.3744
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7.3600
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Ph
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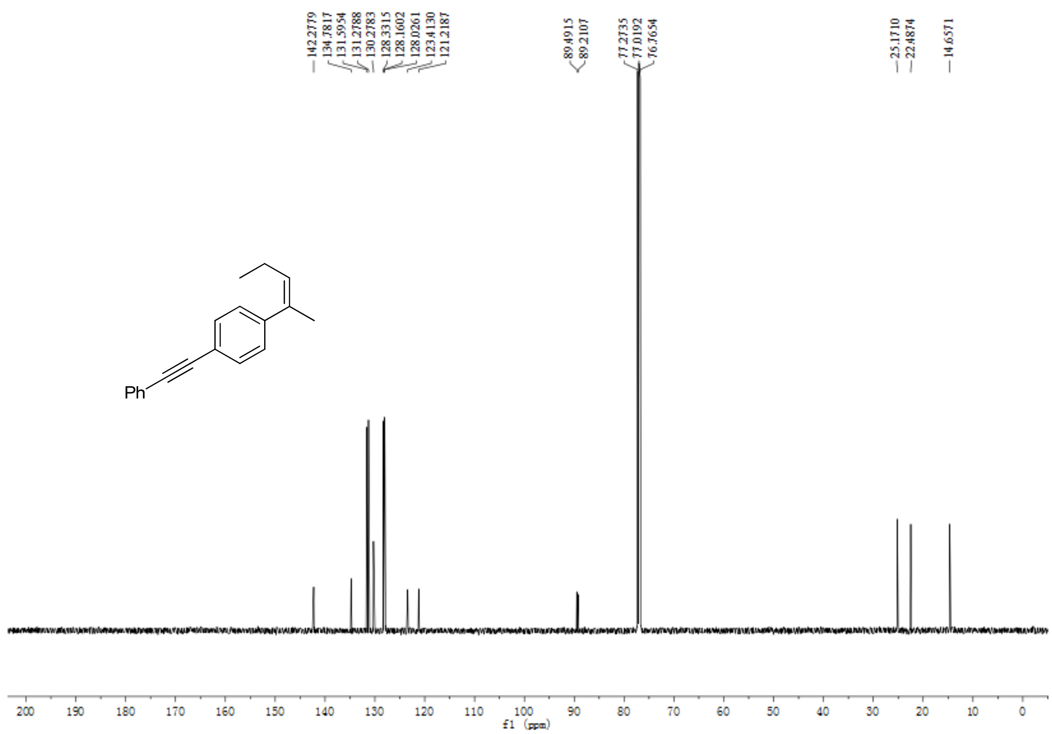
1.00
3.09
2.03
3.01
f1 (ppm)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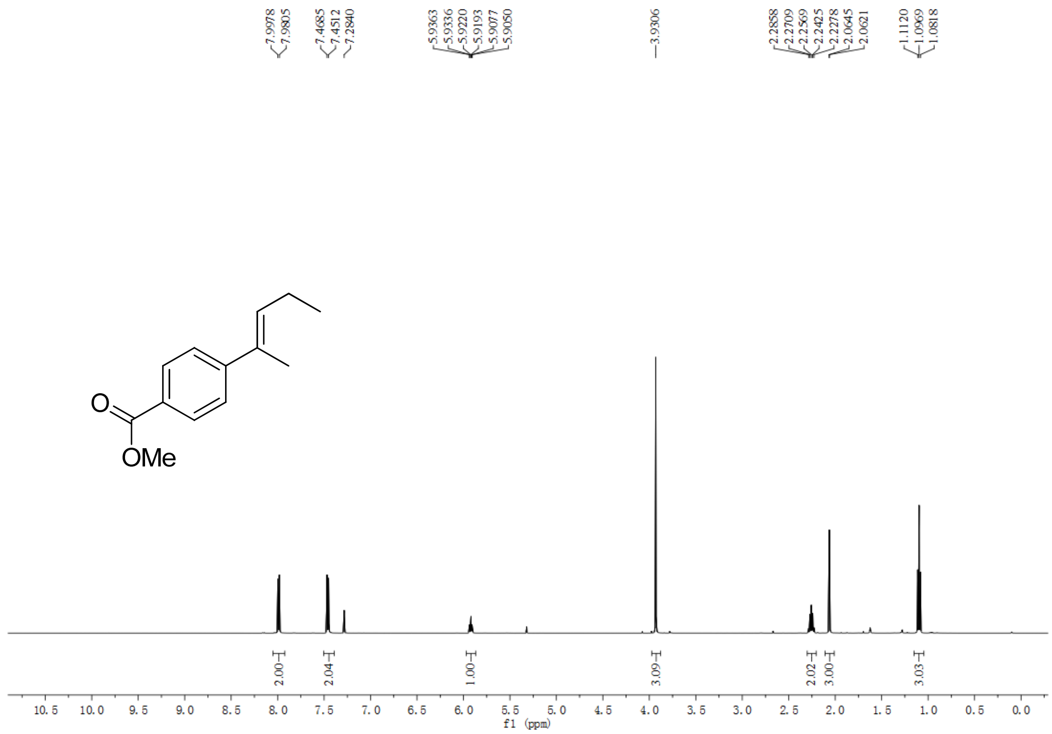
Ph
f1 (ppm)

3in(*E*)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2.2425
2.2278
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O
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2.04
1.00
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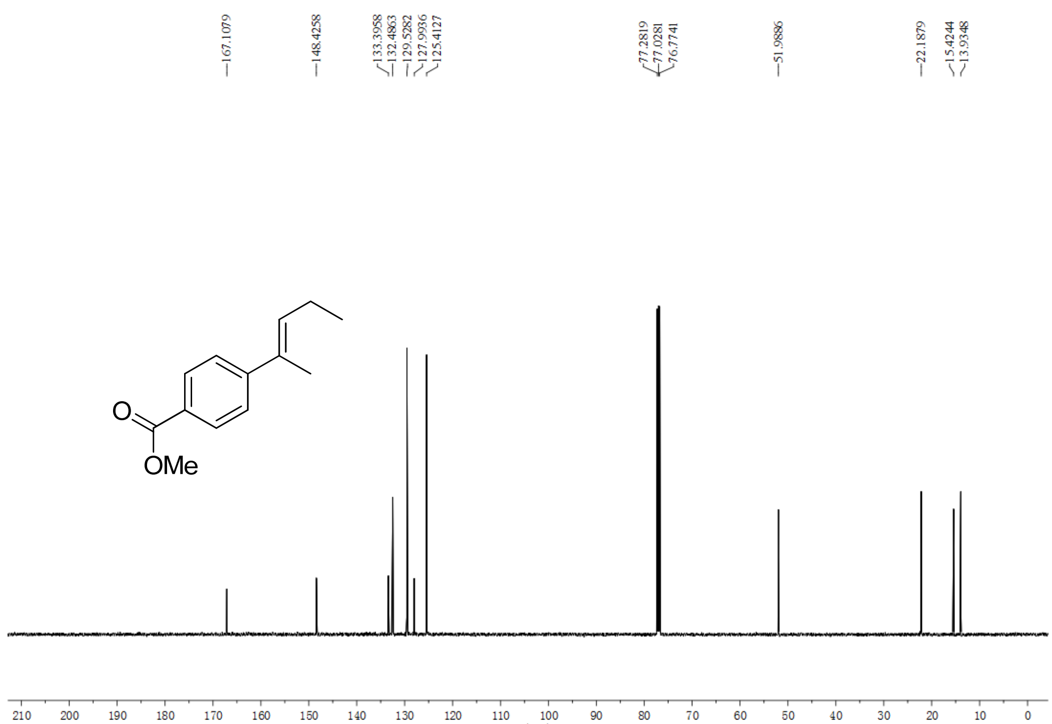
2.02
3.00
3.03
f1 (ppm)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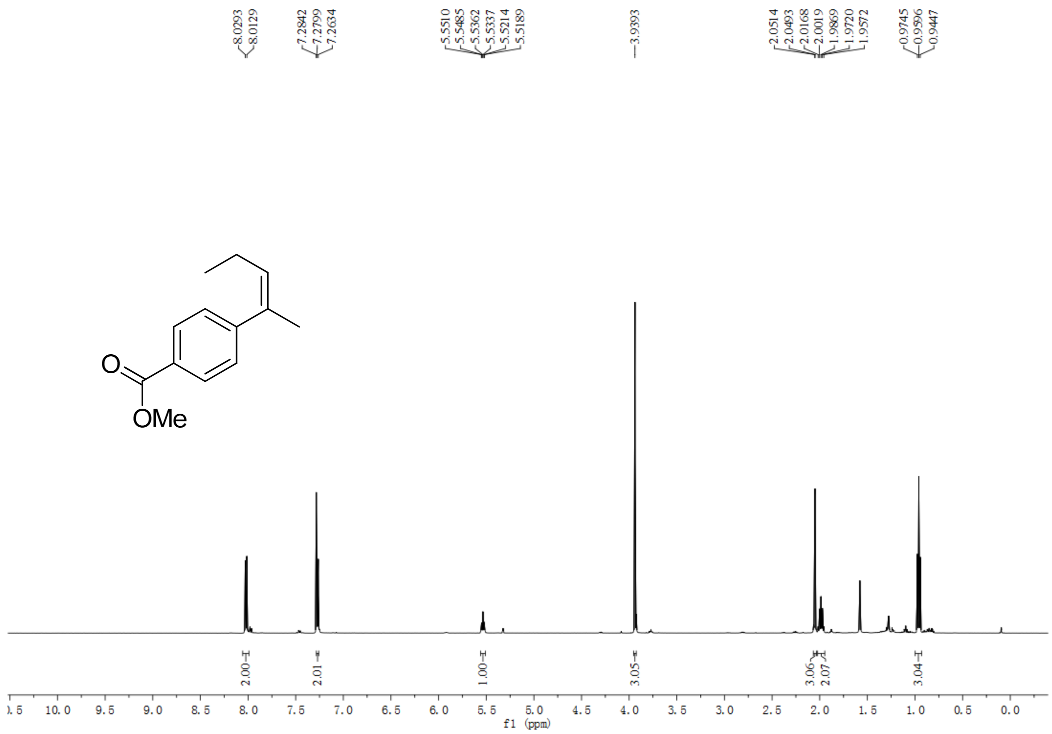
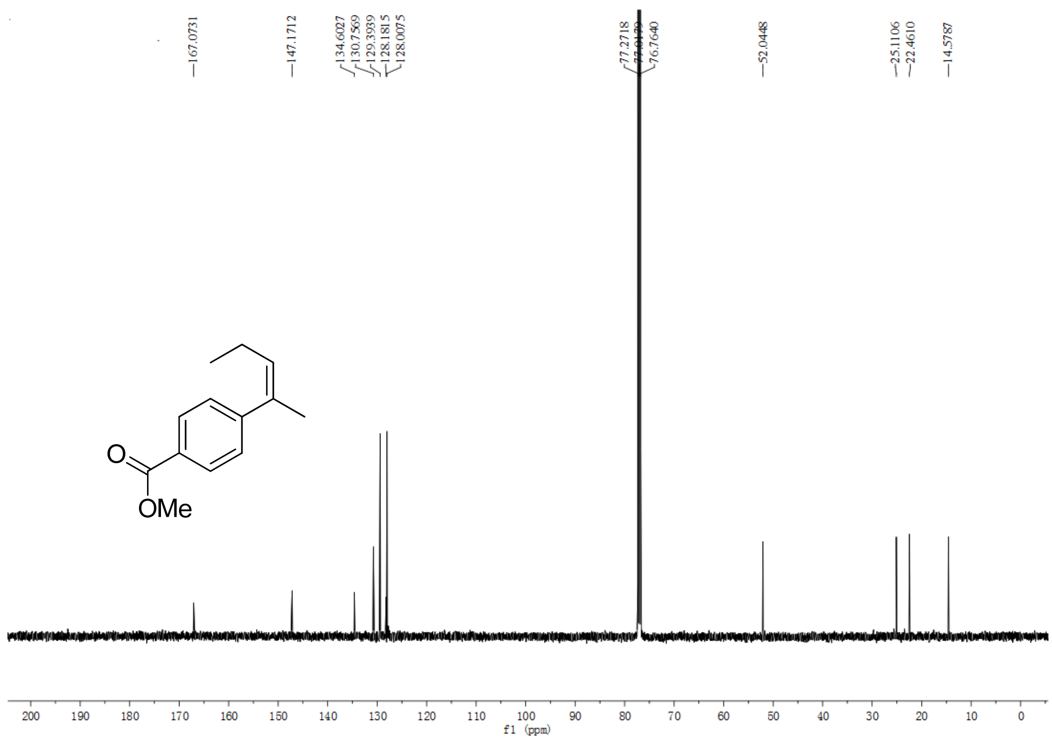
O
OMe
f1 (ppm)

3in(*Z*)





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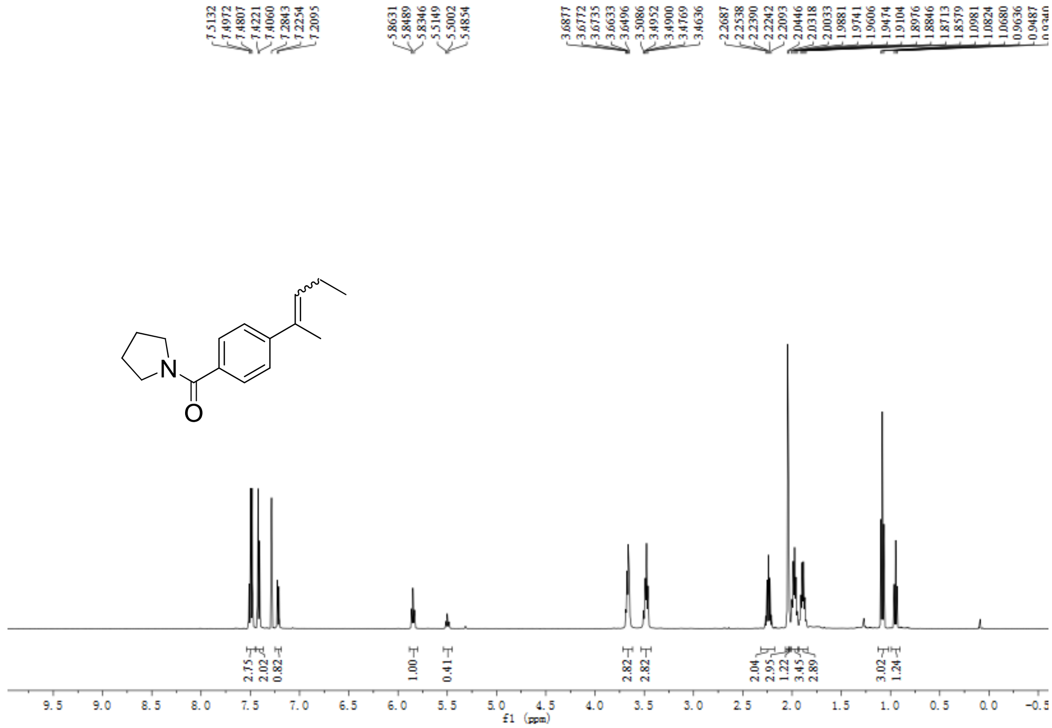

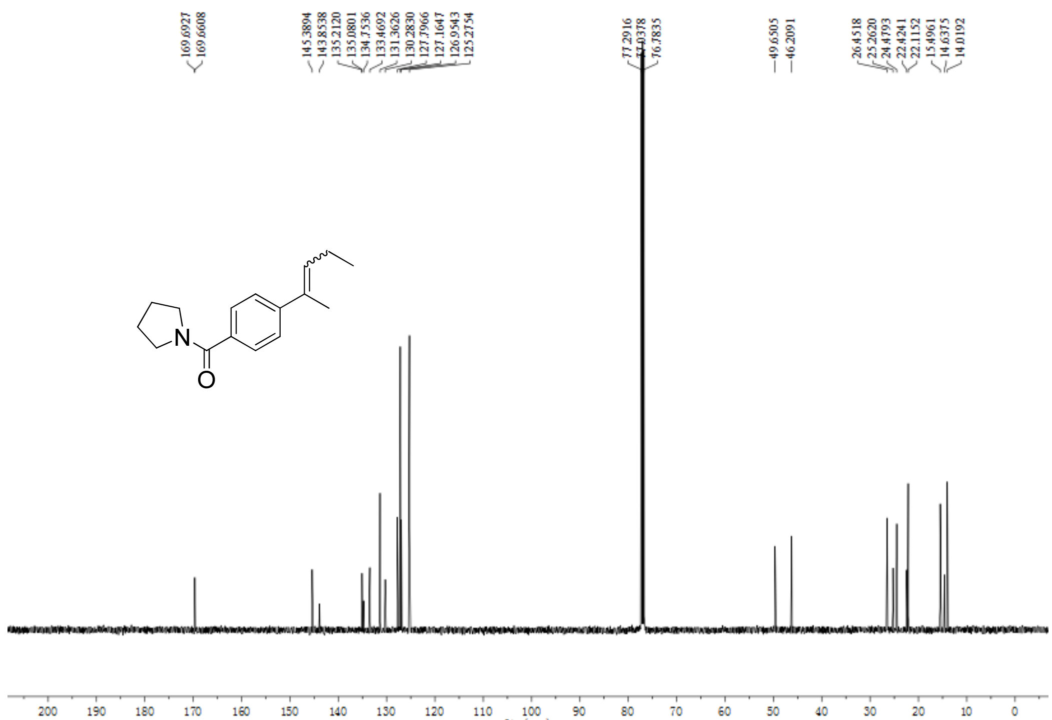

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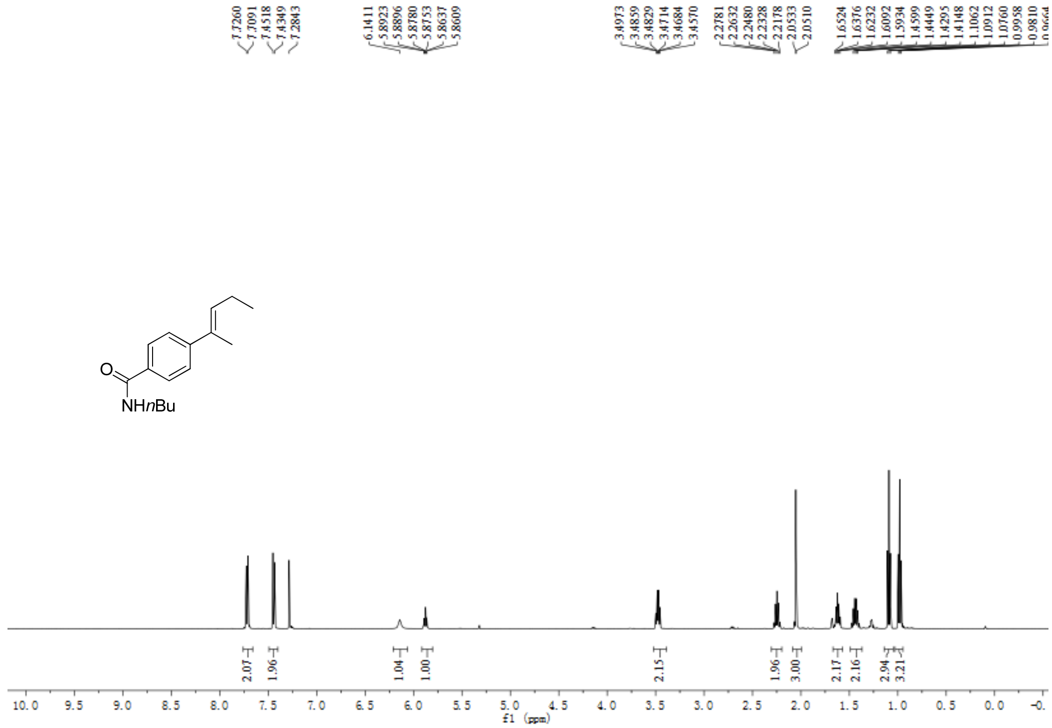

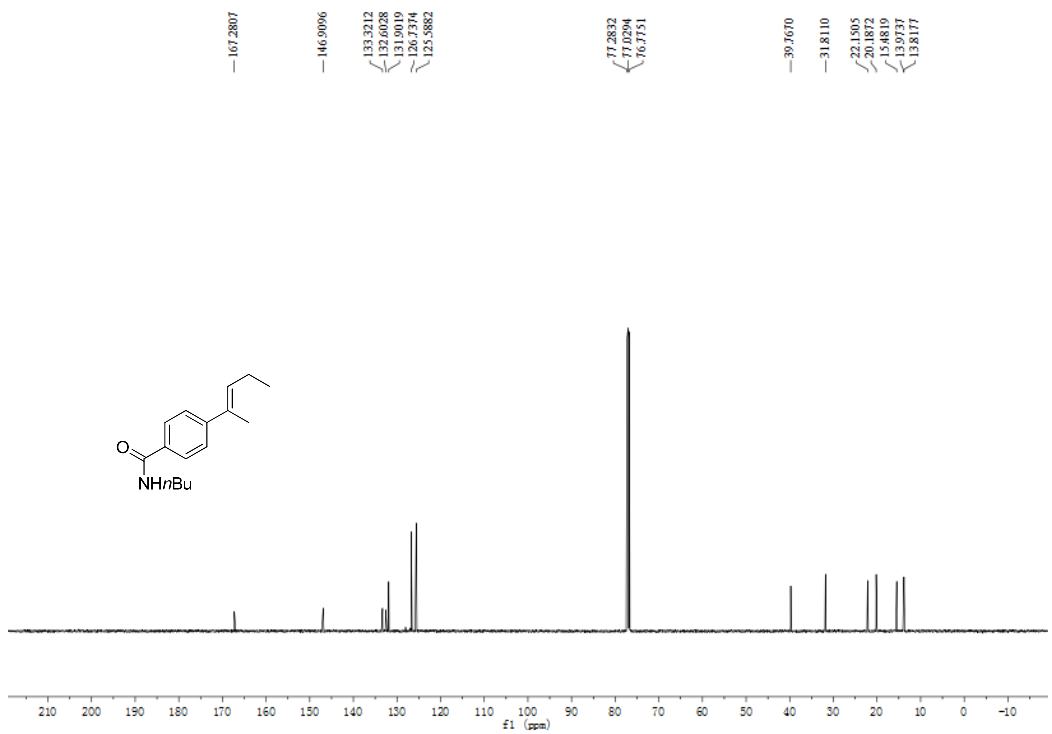

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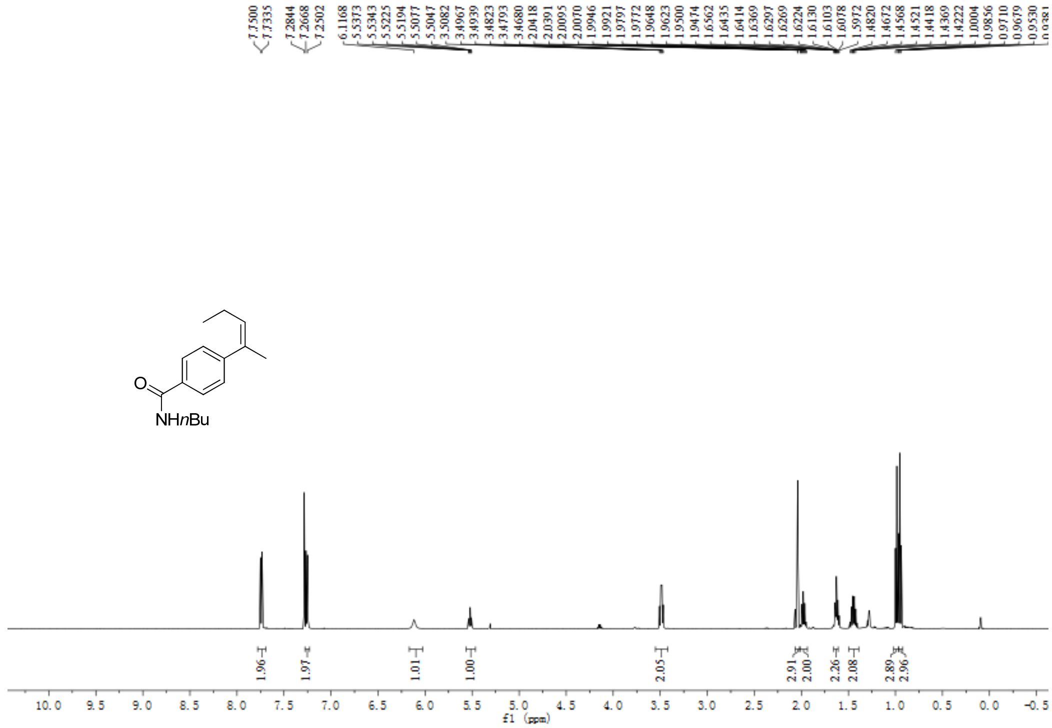

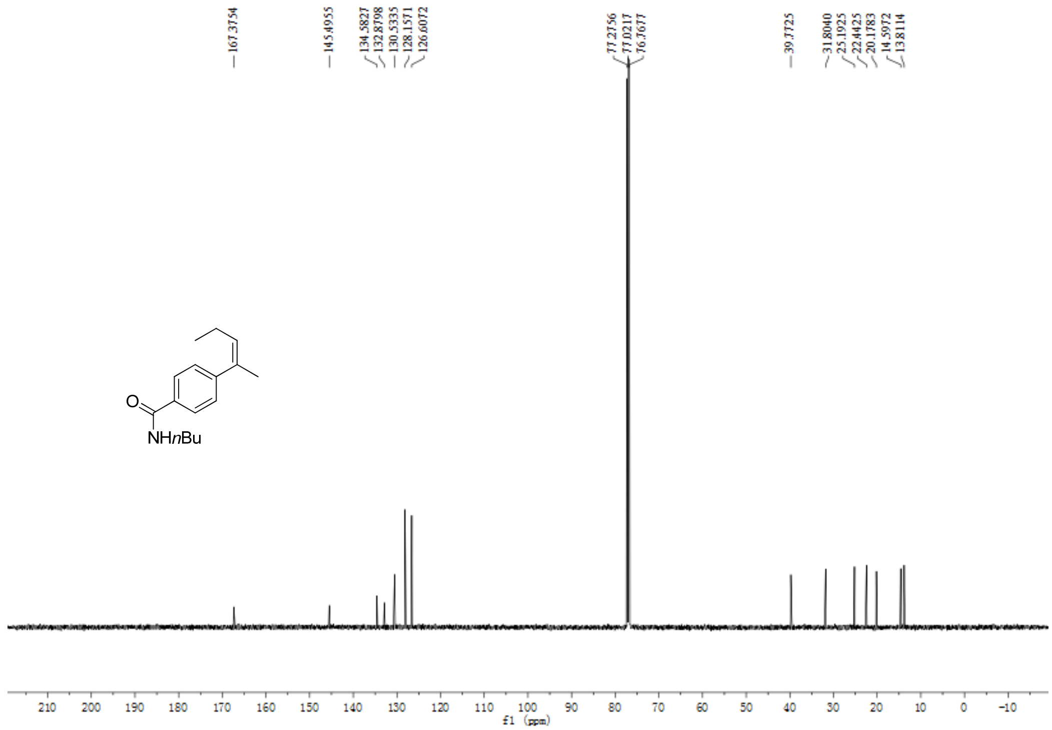

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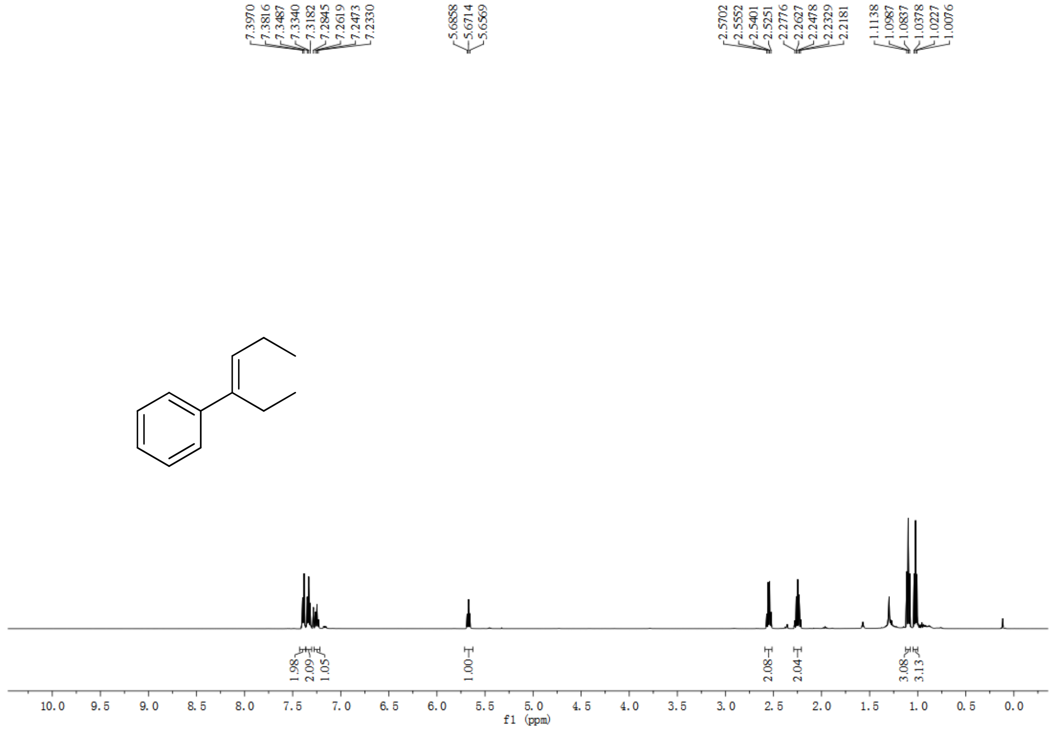

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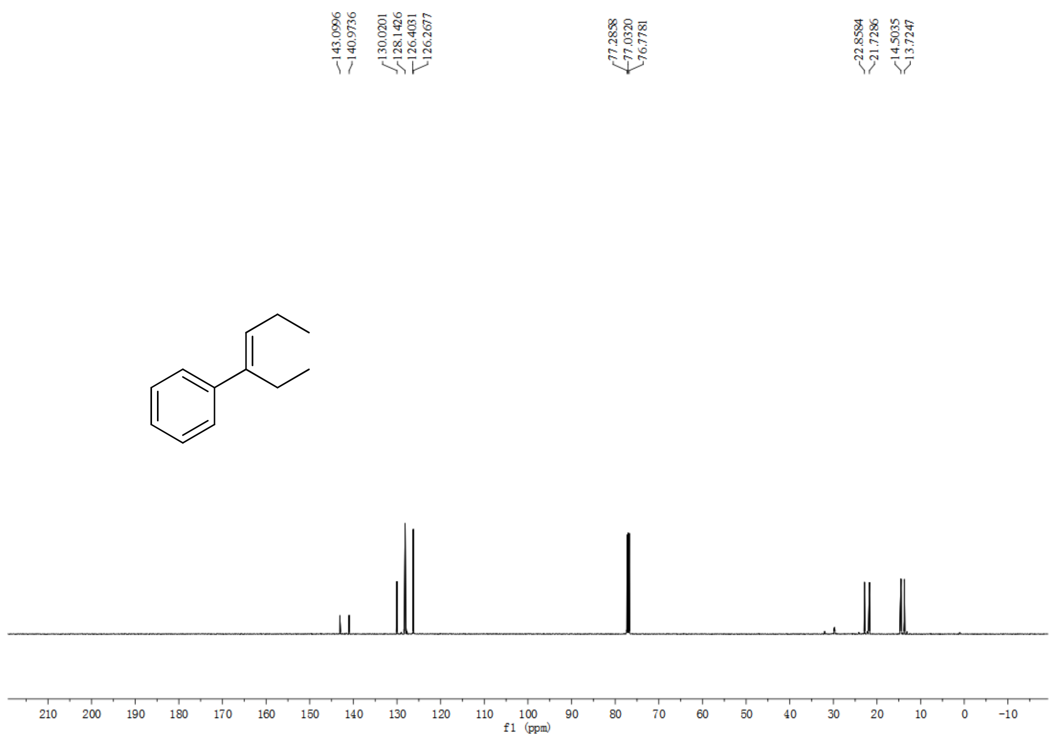
f1 (ppm)



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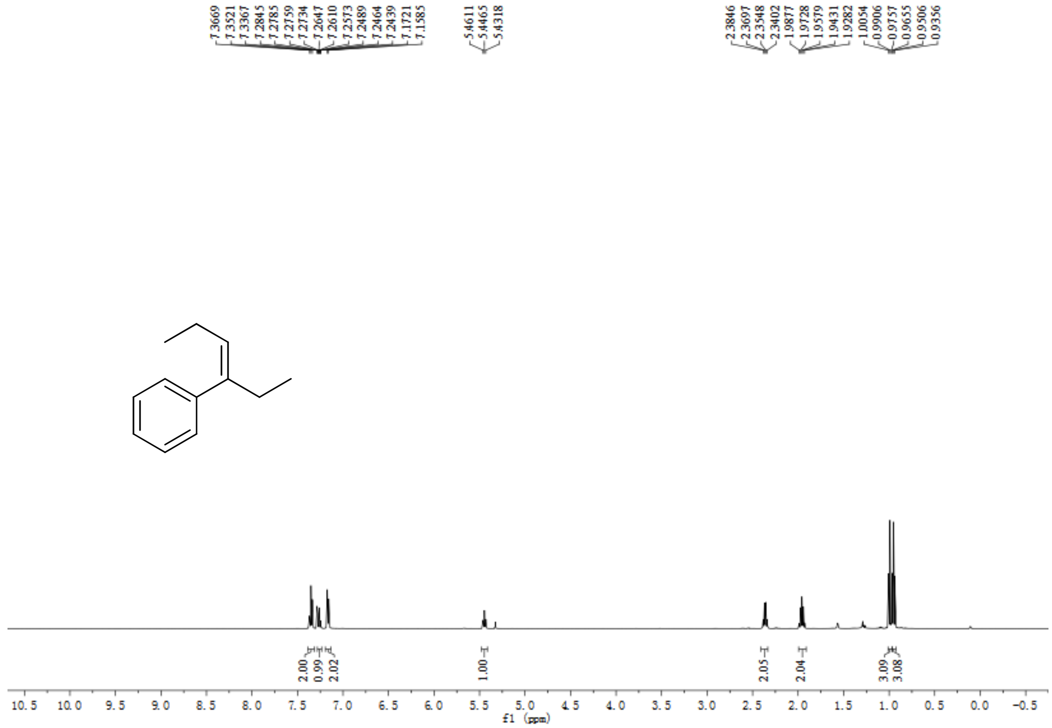
3j(*Z*)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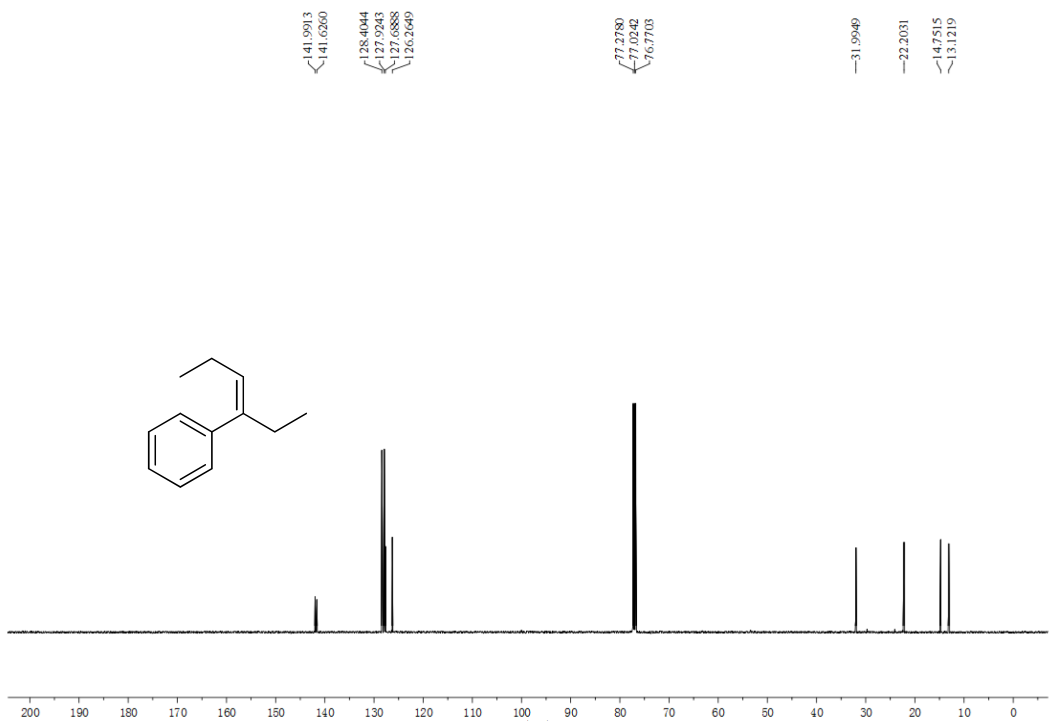
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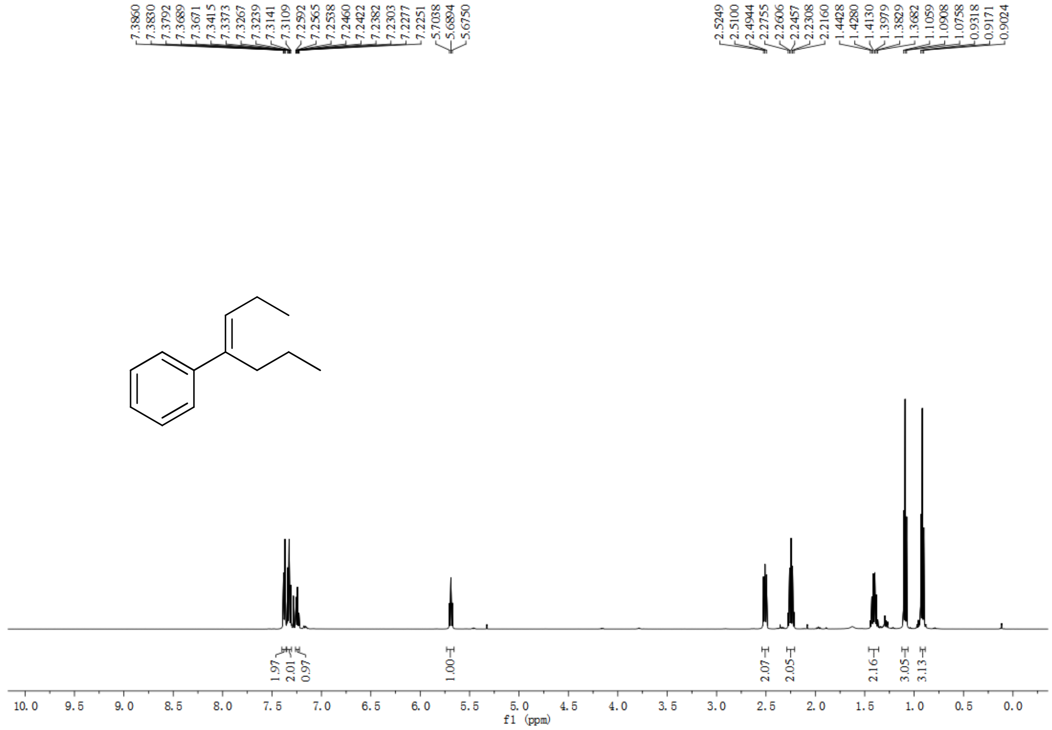
3k(*E*)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3.05
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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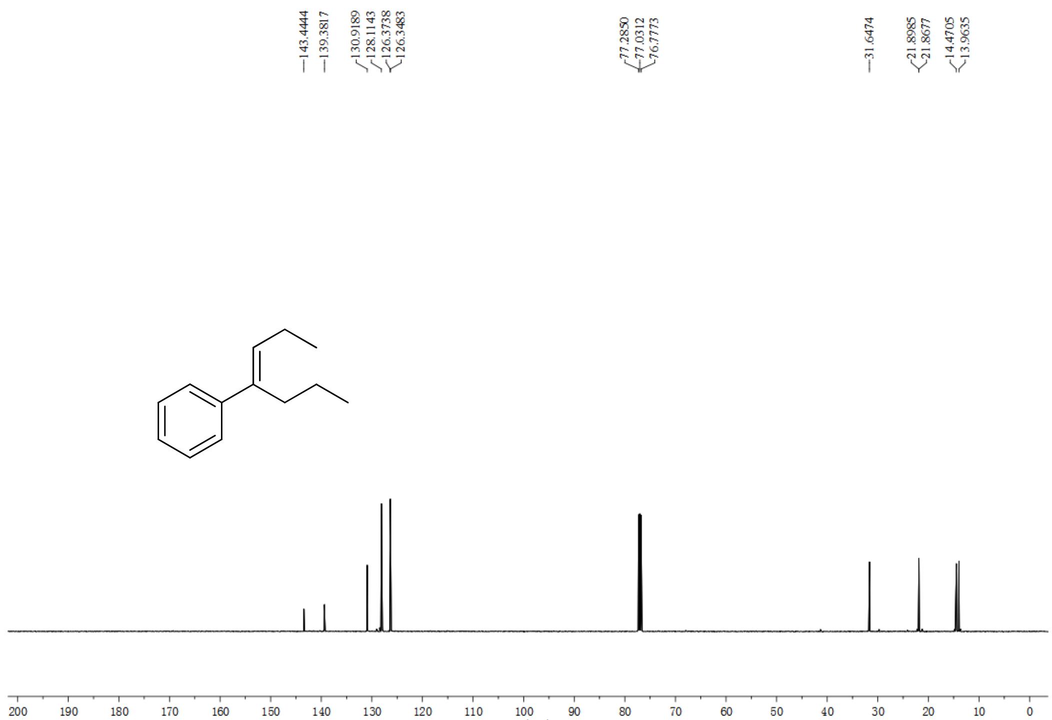
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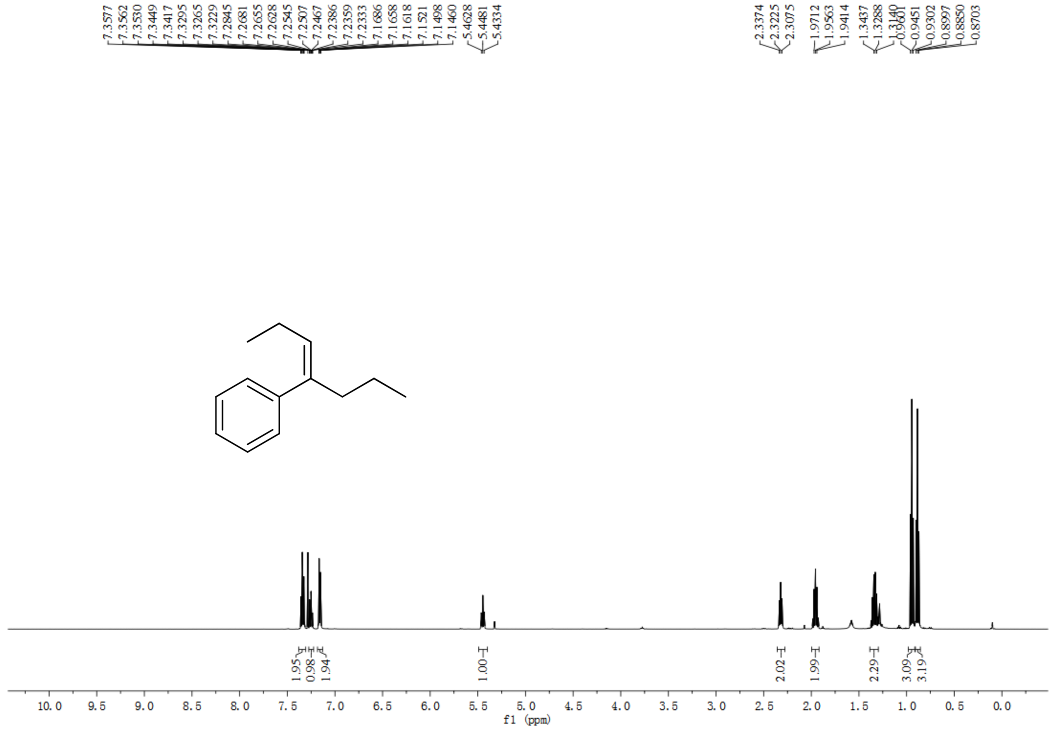
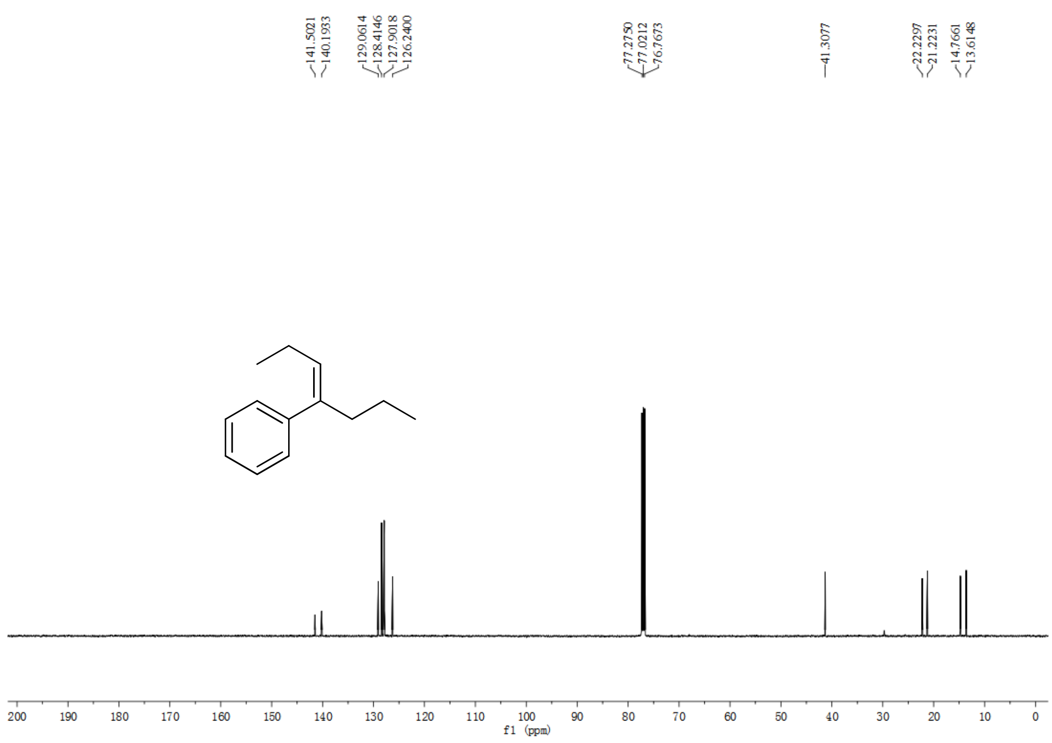
f1 (ppm)

3k(*Z*)





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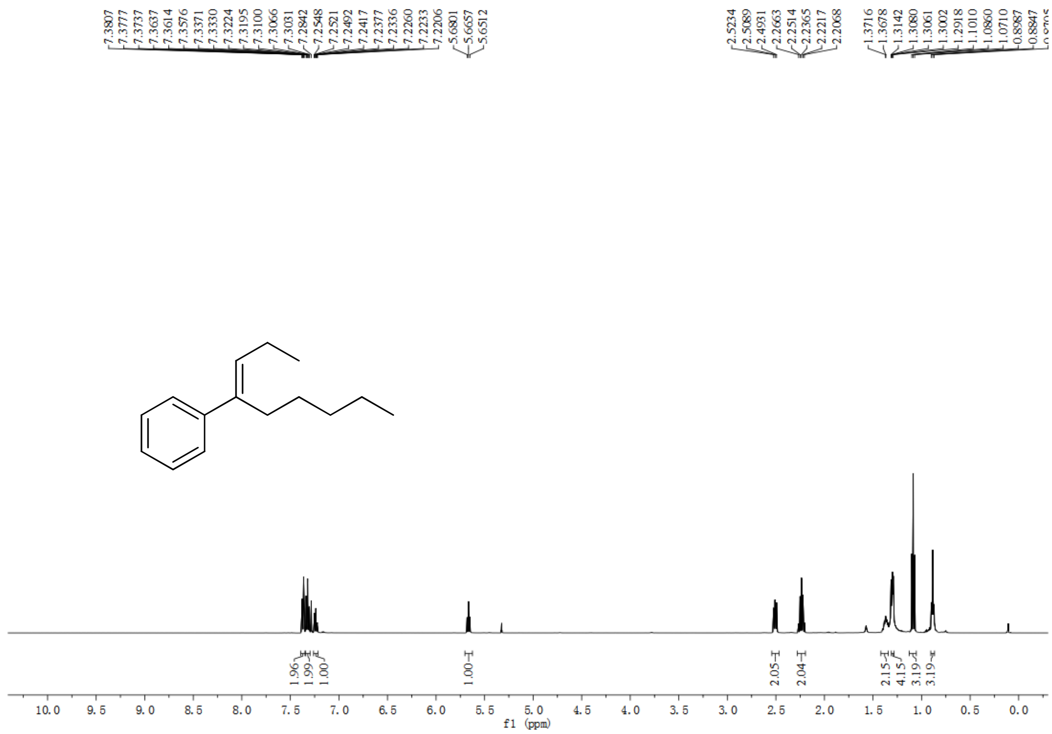
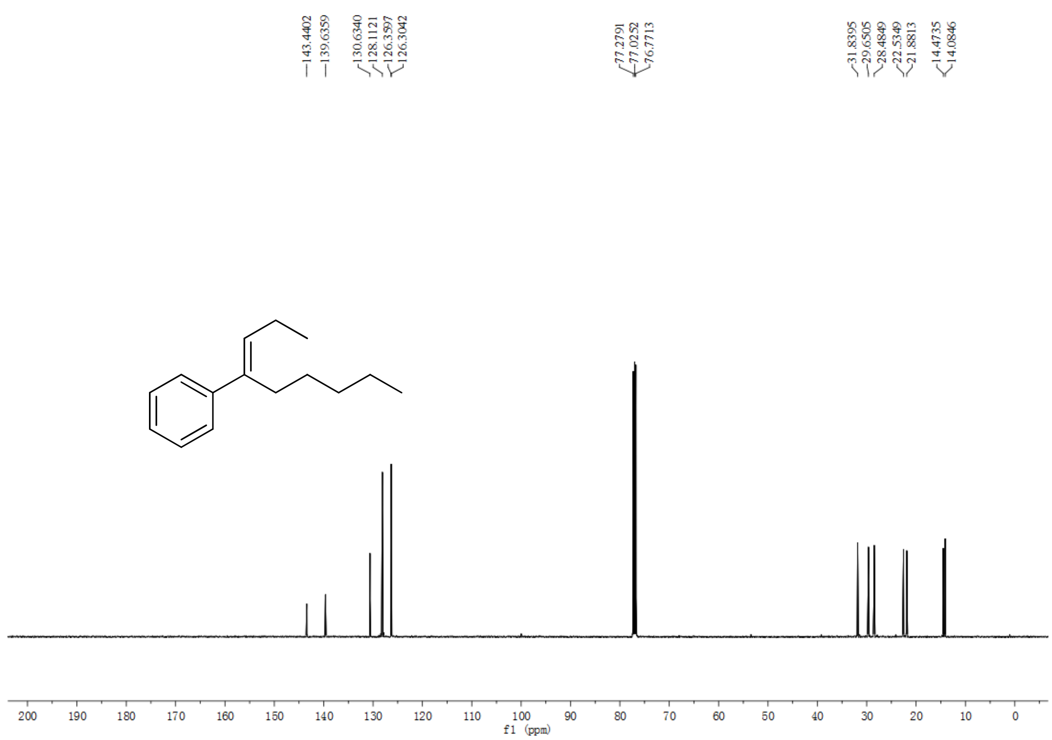
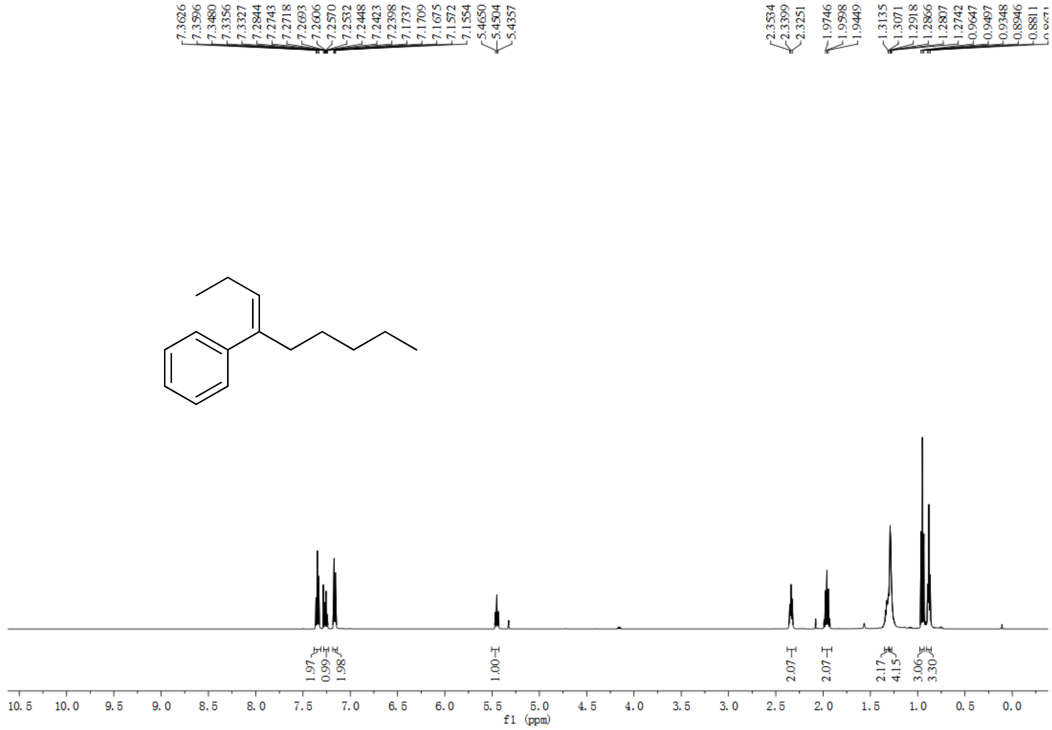




3l(Z)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3.06
3.30
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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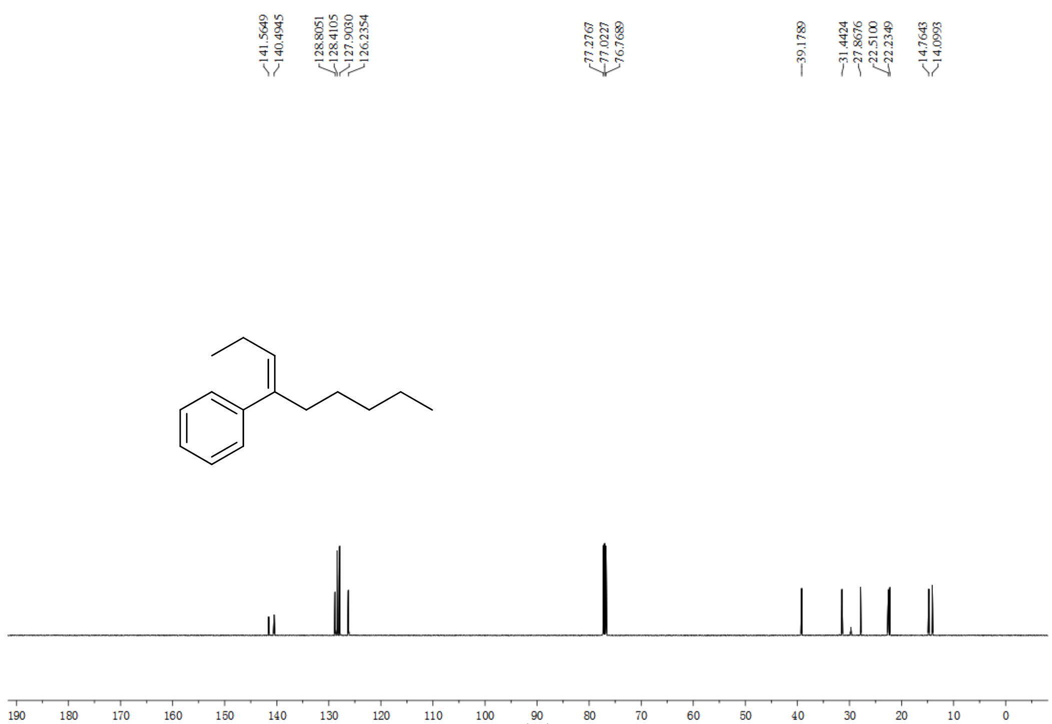
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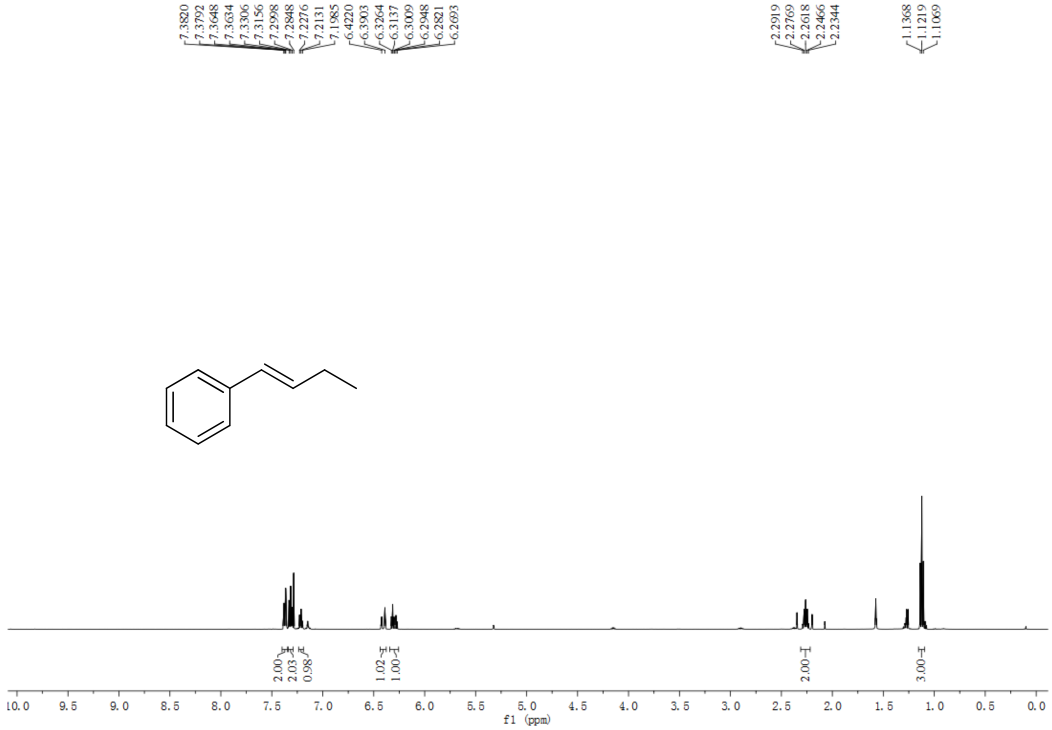
3m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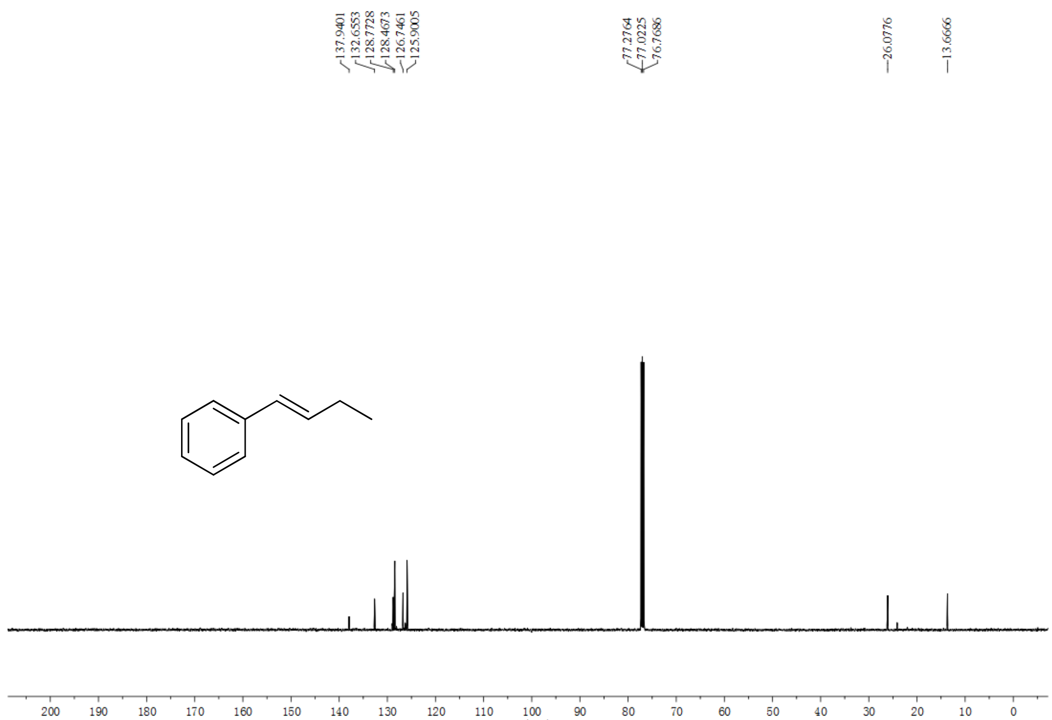
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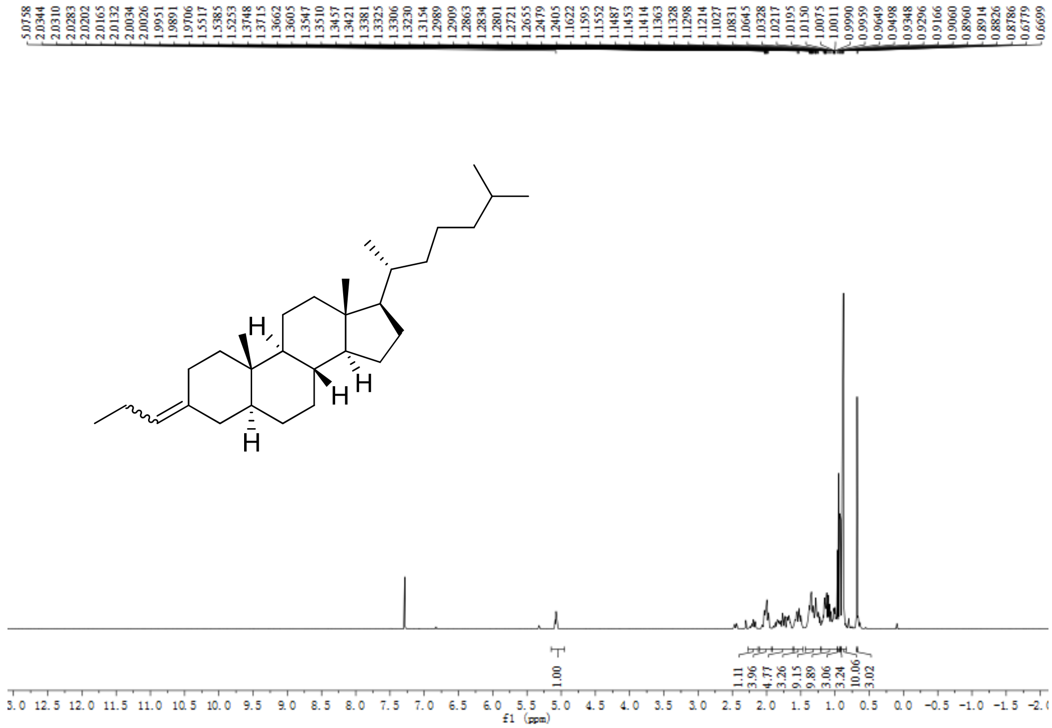
3o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1.1622
1.1595
1.1552
1.1487
1.1453
1.1414
1.1363
1.1328
1.1298
1.1214
1.1027
1.0831
1.0645
1.0328
1.0217
1.0195
1.0150
1.0075
1.0011
0.9990
0.9959
0.9649
0.9498
0.9348
0.9296
0.9166
0.9060
0.8960
0.8914
0.8826
0.8786
0.6779
0.6699
H
H
H
H
1.00
1.11
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4.17
3.26
9.15
9.89
3.06
3.24
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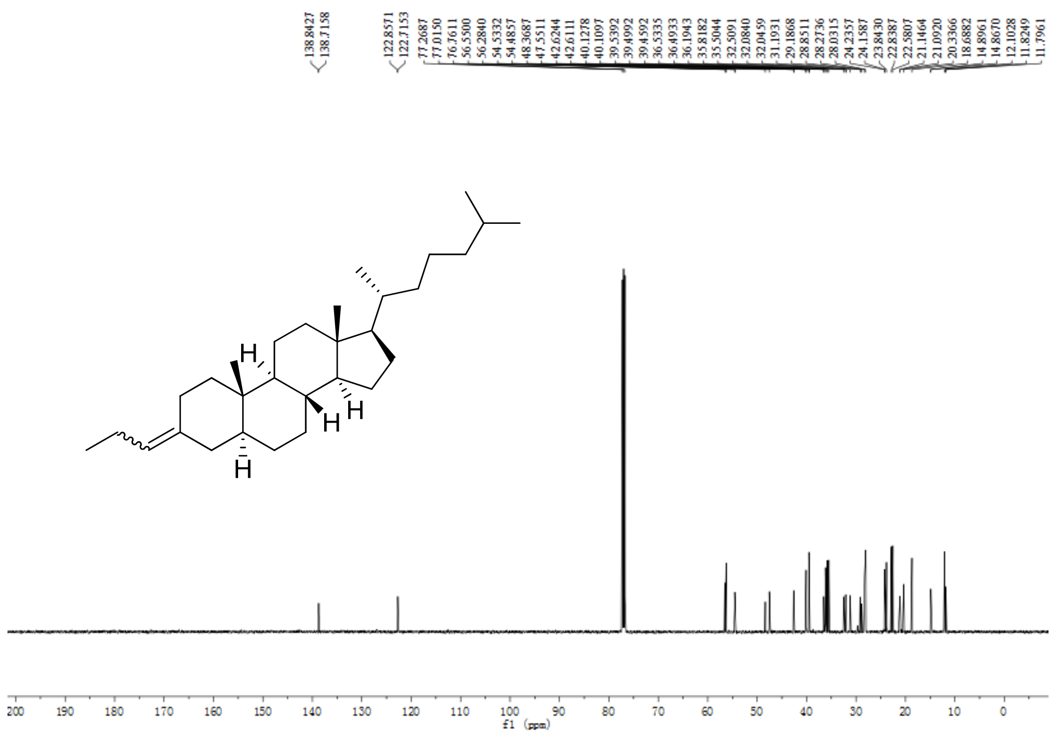
3.02
f1 (ppm)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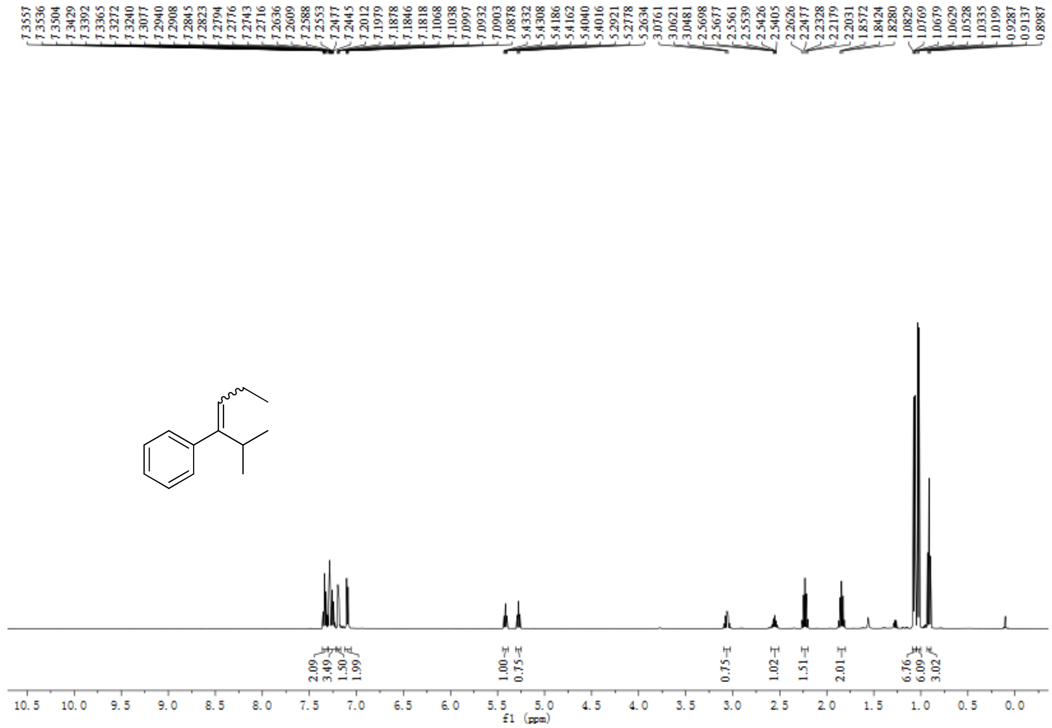
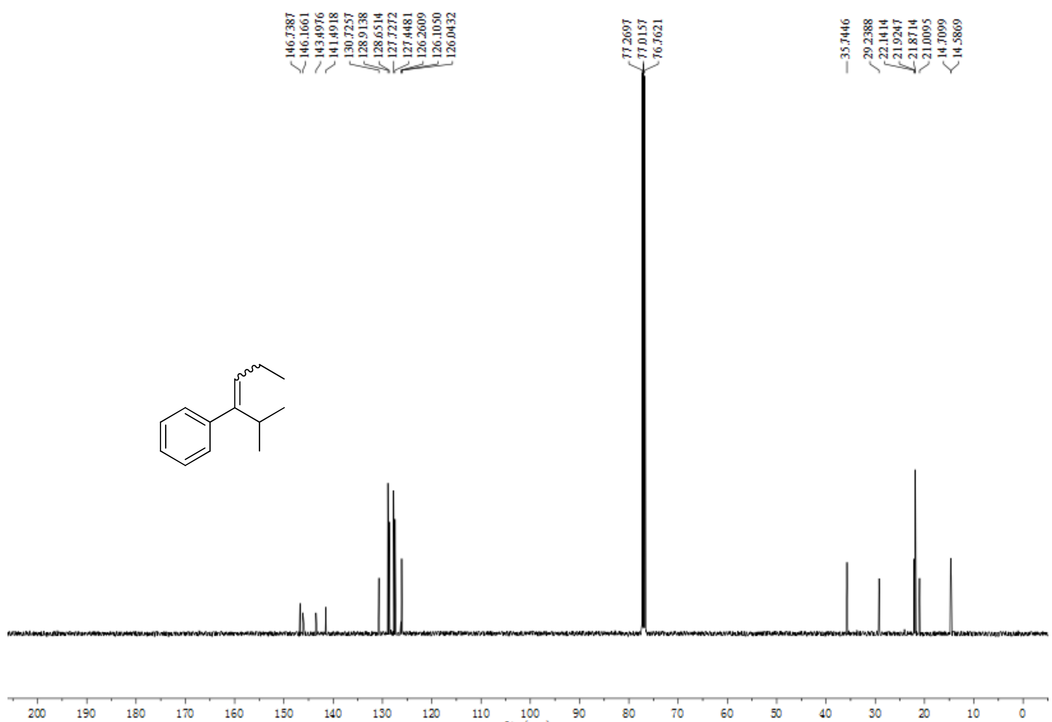
54.5332
54.4857
48.3687
47.5511
42.6244
42.6111
40.1278
40.1097
39.5392
39.4992
39.4592
36.5335
36.4933
36.1943
35.8182
35.5044
32.5091
32.0840
32.0459
31.1931
29.1868
28.8511
28.2736
28.0315
24.2357
24.1587
23.8430
22.8387
22.5807
21.1464
21.0920
20.3366
18.6882
14.8961
14.8670
12.1028
11.8249
11.7961
H
H
H
H
f1 (ppm)

3p





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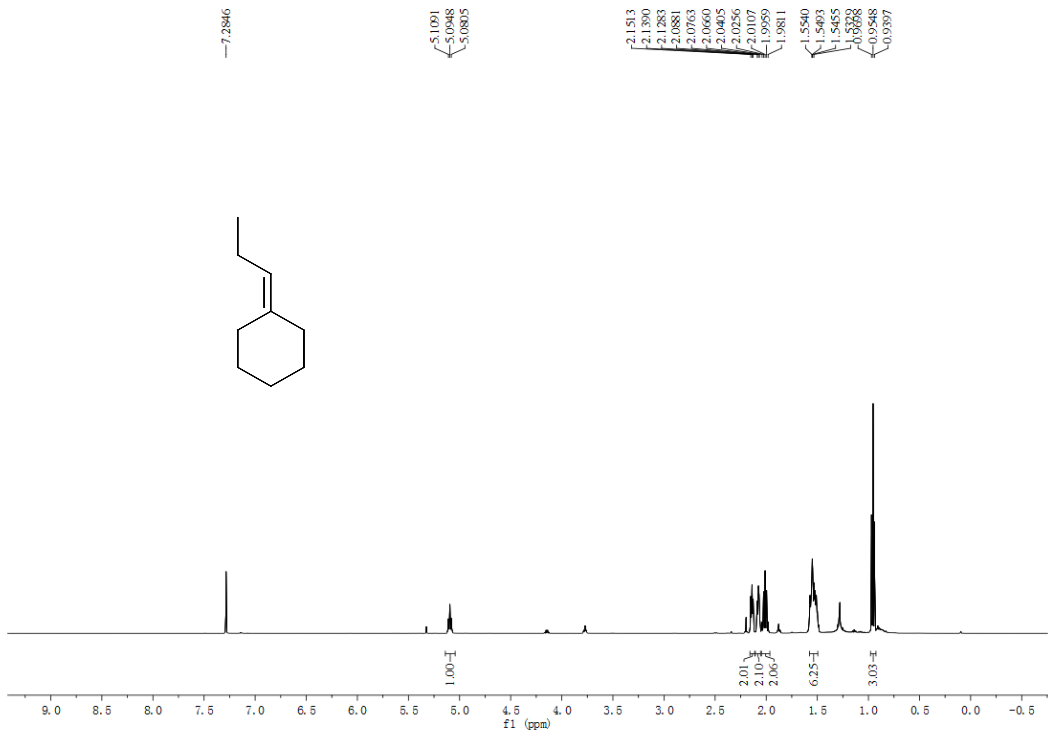
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5.0948
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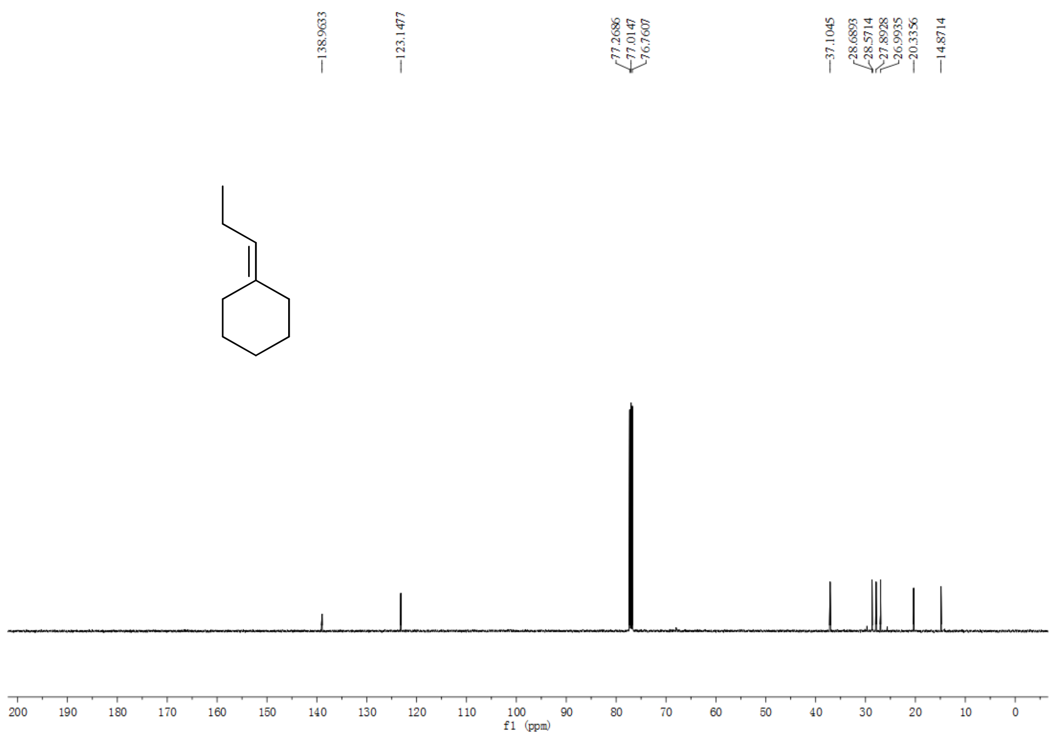
2.1283
2.0881
2.0763
2.0660
2.0405
2.0256
2.0107
1.9959
1.9811
1.5540
1.5493
1.5455
0.9548
0.9397
1.00
2.01
2.10
2.06
6.25
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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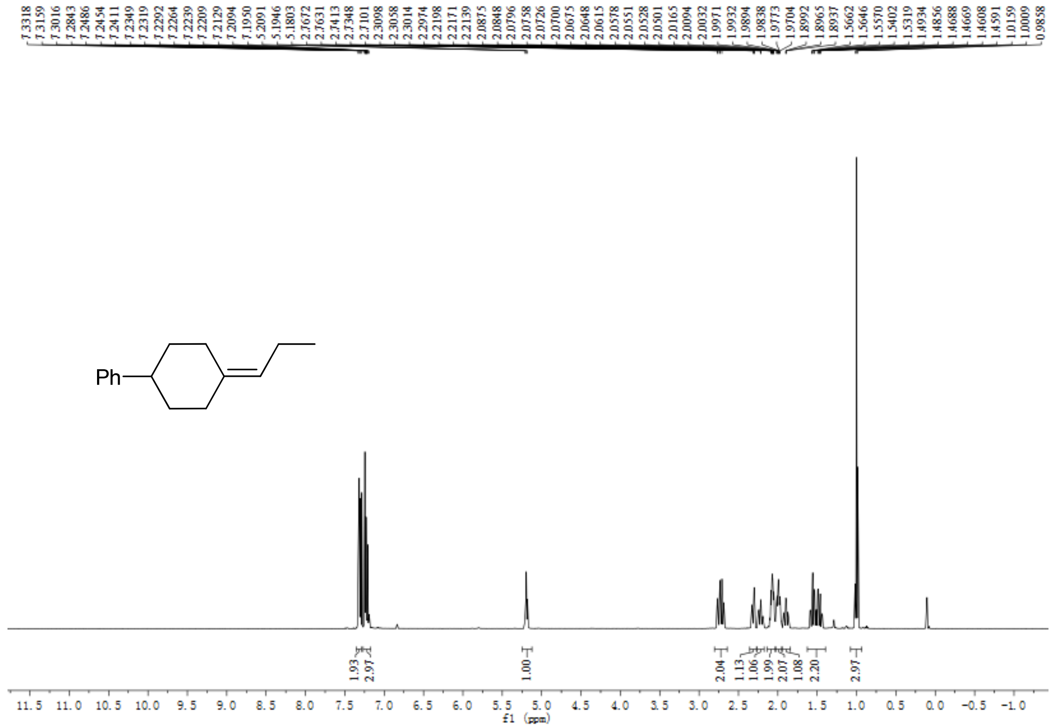
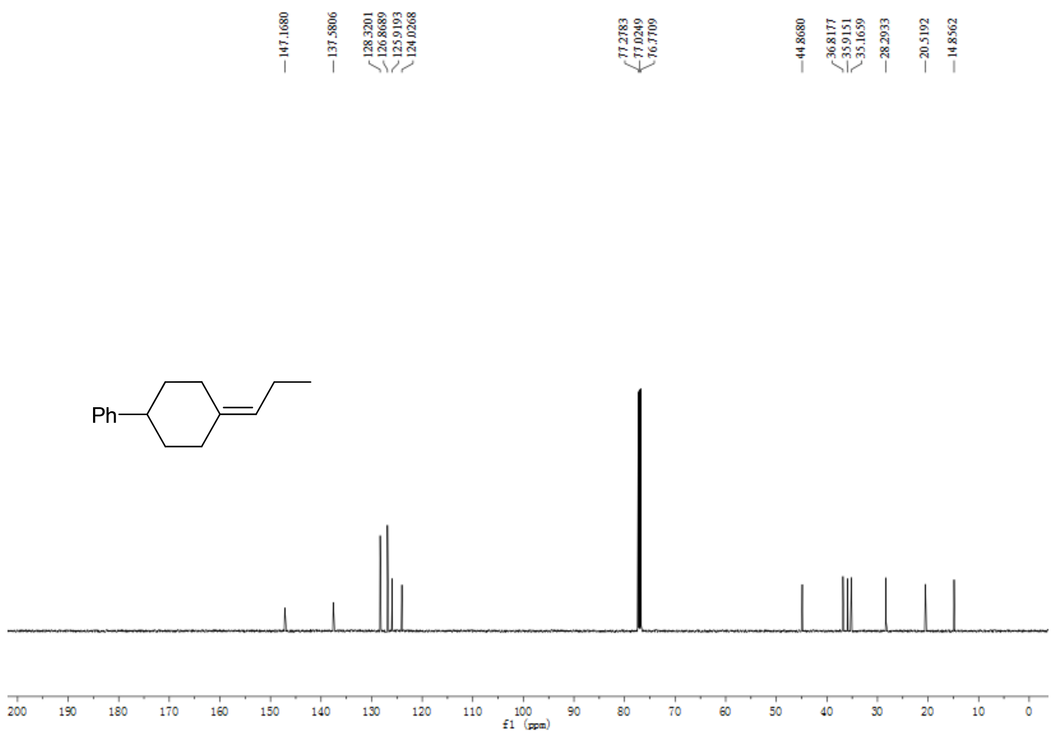
77.0147
76.7607
37.1045
28.6893
28.5714
27.8928
26.9935
20.3356
14.8714
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3r





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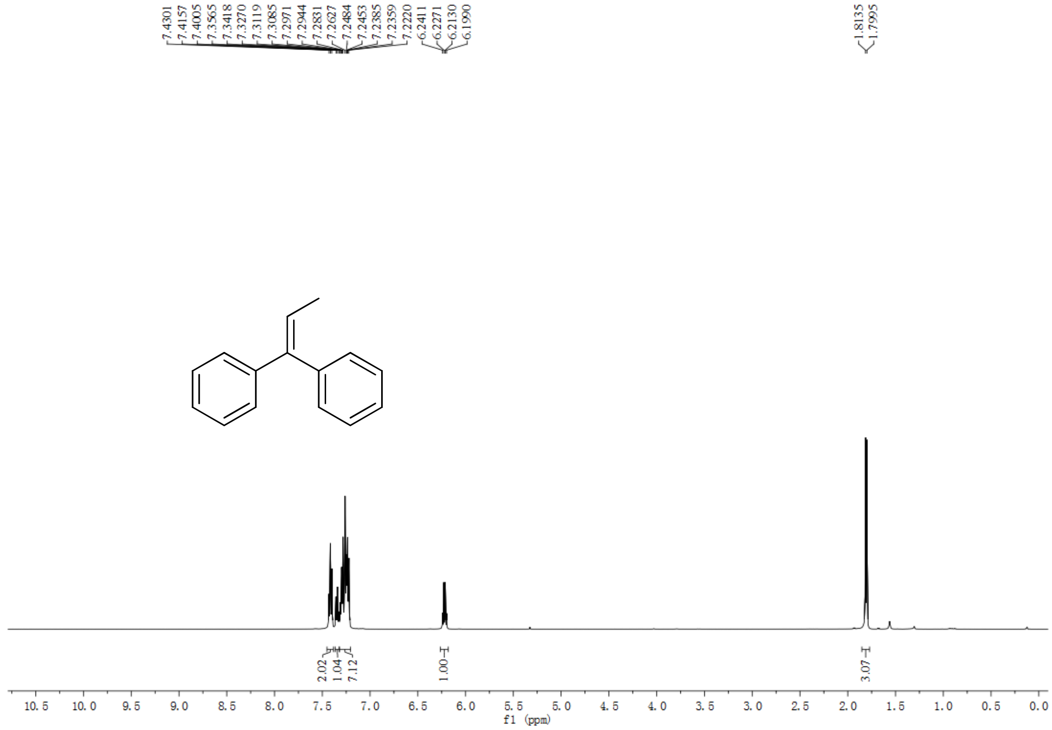
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7.4005
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7.3418
7.3270
7.3119
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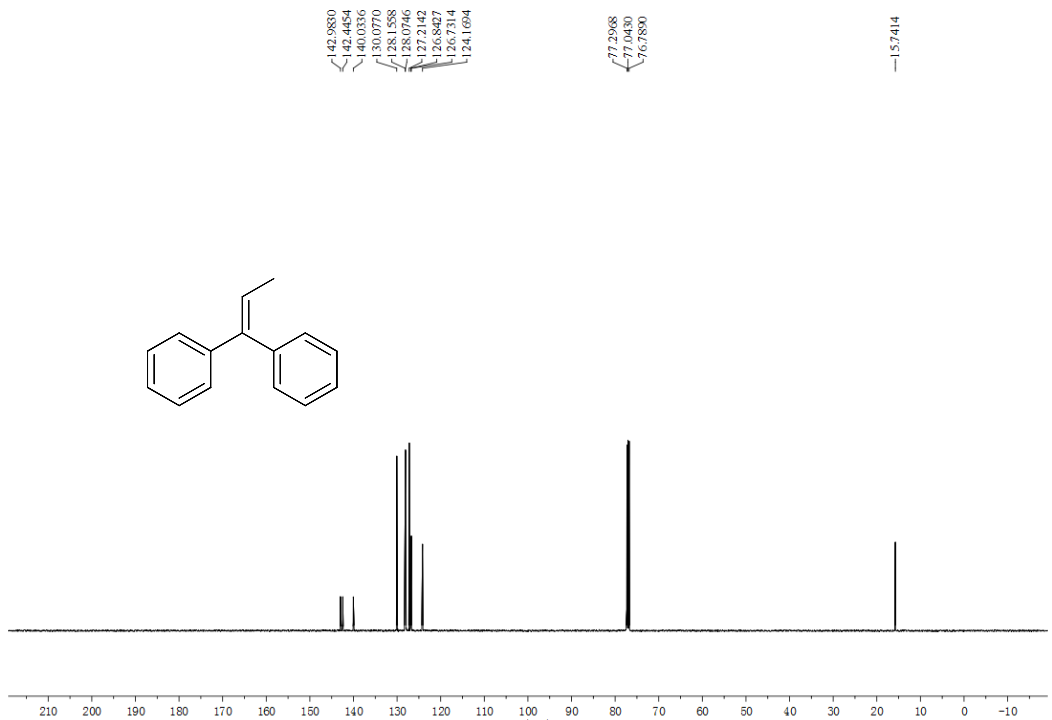
7.2971
7.2944
7.2831
7.2627
7.2484
7.2453
7.2385
7.2359
7.2220
6.2411
6.2271
6.2130
6.1990
1.8135
1.7995
2.02
1.04
7.12
1.00
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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142.4454
140.0336
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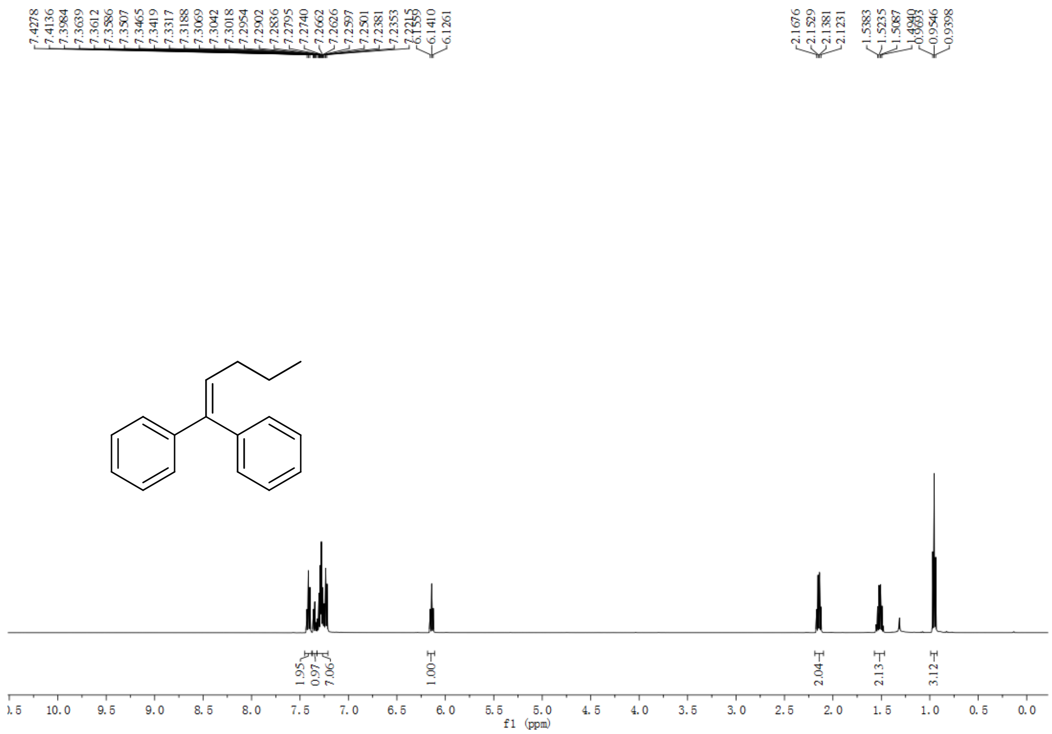
128.1558
128.0746
127.2142
126.8427
126.7314
124.1694
77.2968
77.0430
76.7890
15.7414
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4b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7.3984
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7.3507
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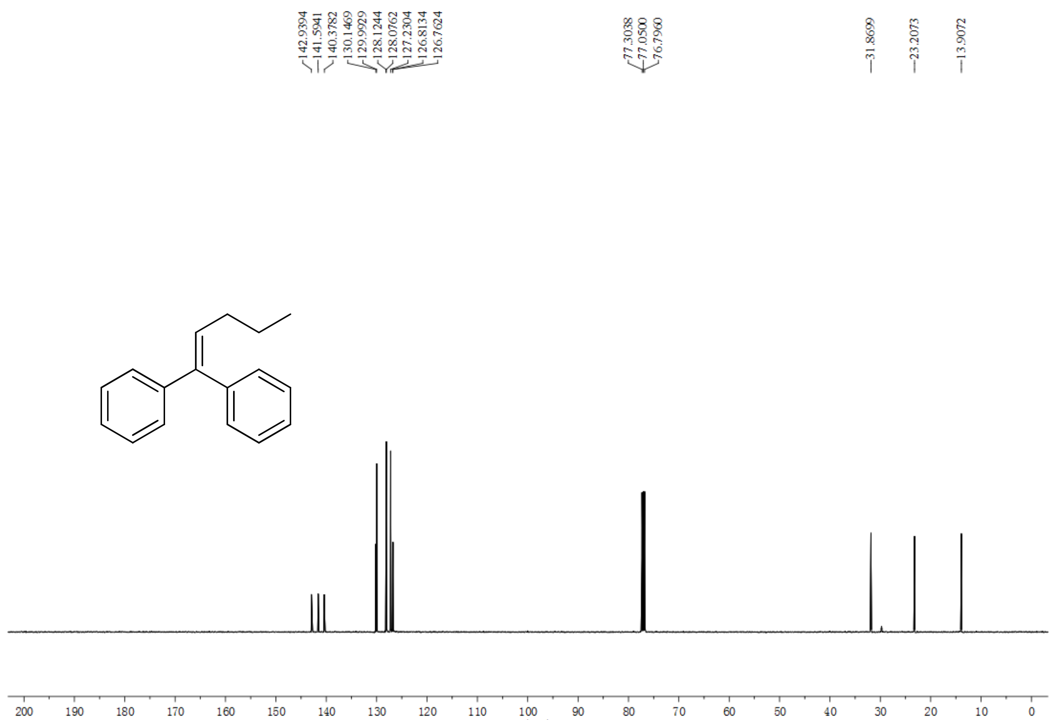
7.3419
7.3317
7.3188
7.3069
7.3042
7.3018
7.2954
7.2902
7.2836
7.2795
7.2740
7.2662
7.2626
7.2597
7.2501
7.2381
7.2353
6.1410
6.1261
2.1676
2.1529
2.1381
2.1231
1.5383
1.5235
1.5087
0.9546
0.9398
1.95
0.97
7.06
1.00
2.04
2.13
3.12
f1 (ppm)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140.3782
130.1469
129.9929
128.1244
128.0762
127.2304
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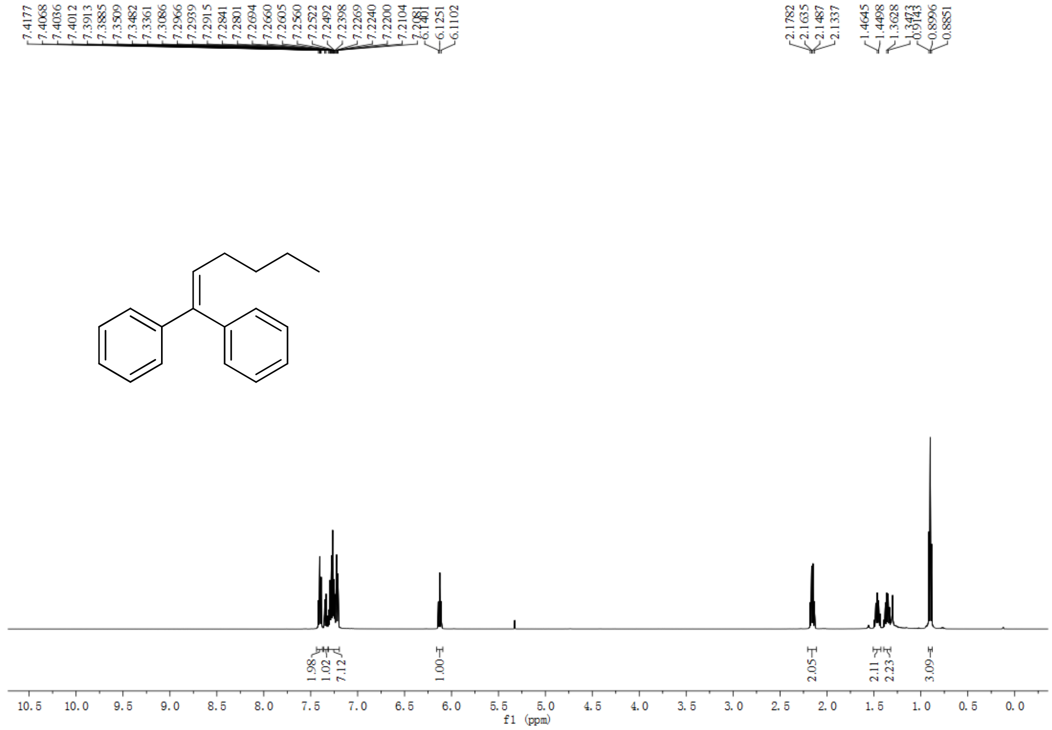
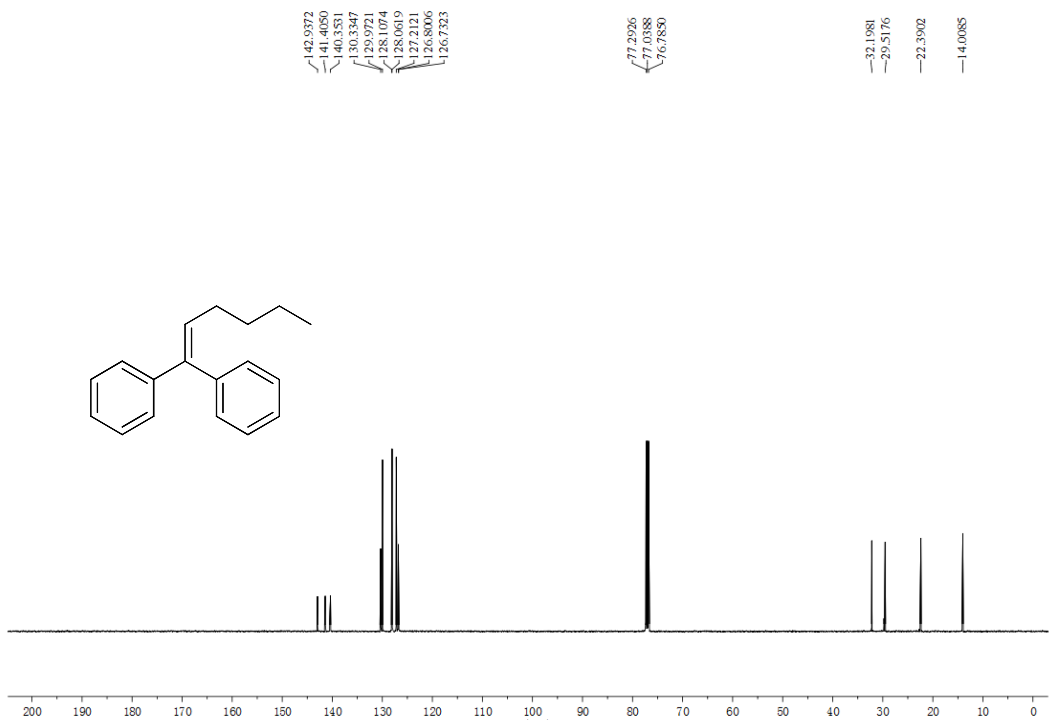
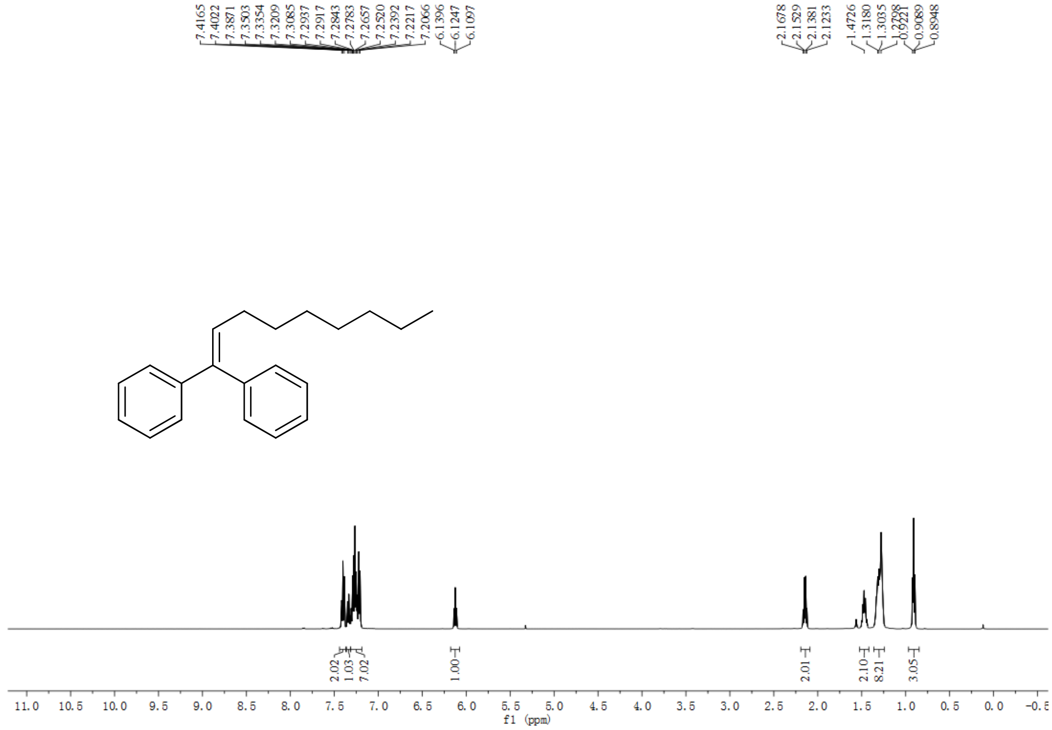
126.7624
77.3038
77.0500
76.7960
31.8699
23.2073
13.9072
f1 (ppm)

4c





4d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7.3871
7.3503
7.3354
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7.3085
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7.2917
7.2843
7.2783
7.2657
7.2520
7.2392
7.2217
7.2066
6.1396
6.1247
6.1097
2.1678
2.1529
2.1381
2.1233
1.4726
1.3180
1.3035
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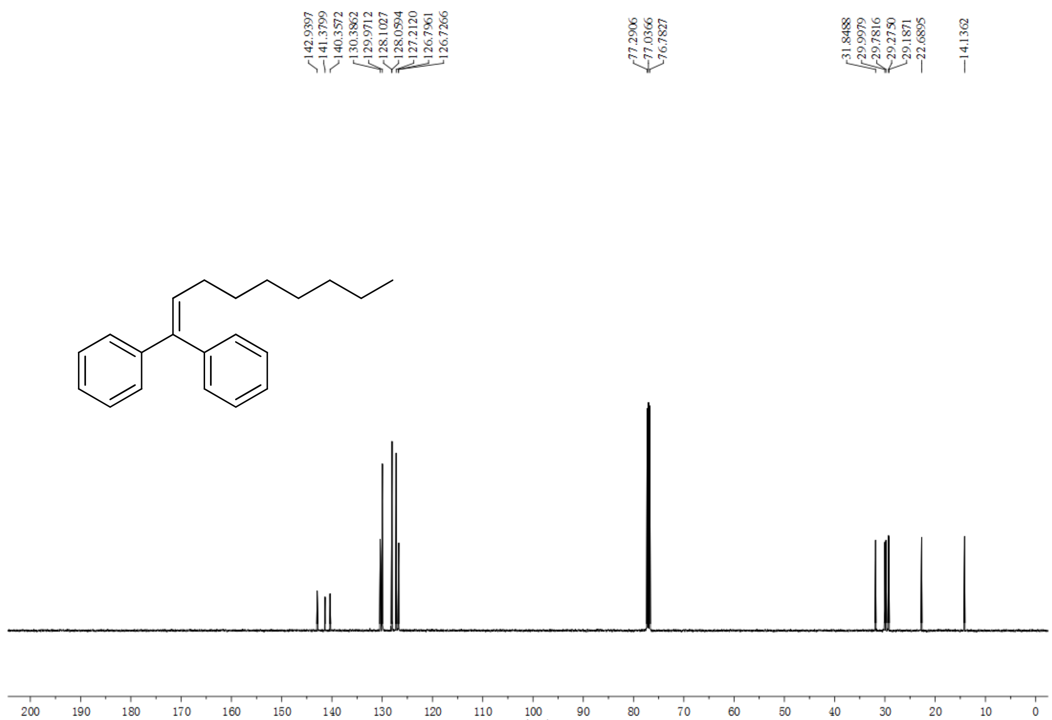
1.03
7.02
1.00
2.01
2.10
8.21
3.05
f1 (ppm)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127.2120
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77.2906
77.0366
76.7827
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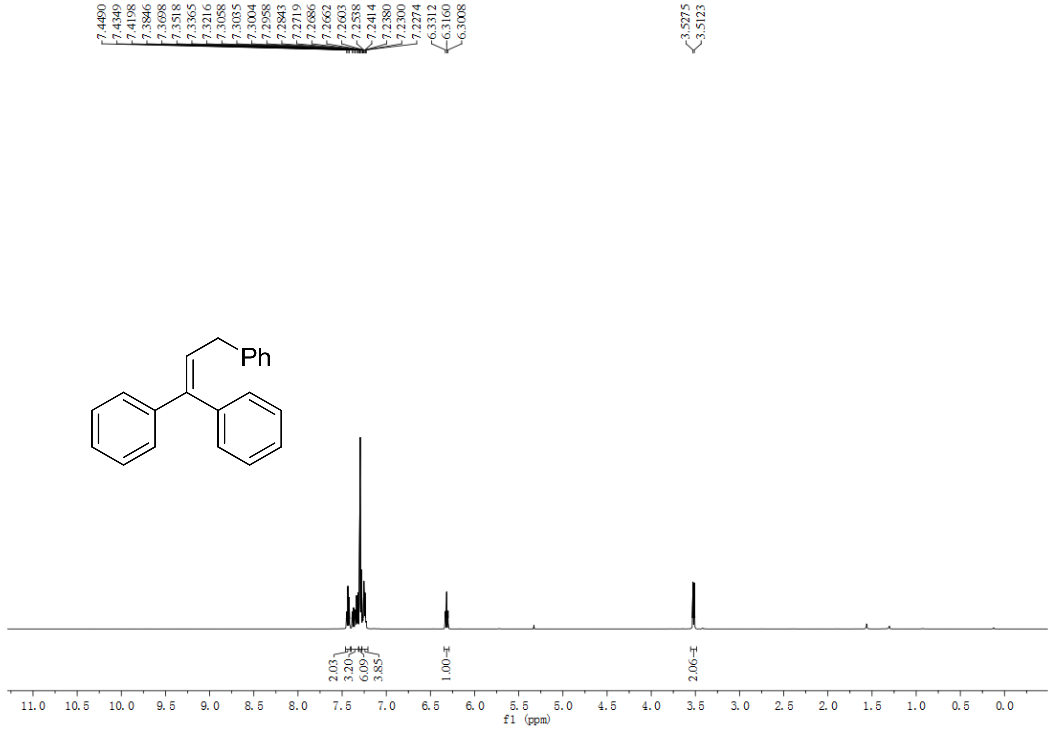
29.9979
29.7816
29.2750
29.1871
22.6895
14.1362
f1 (ppm)

4e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7.3365
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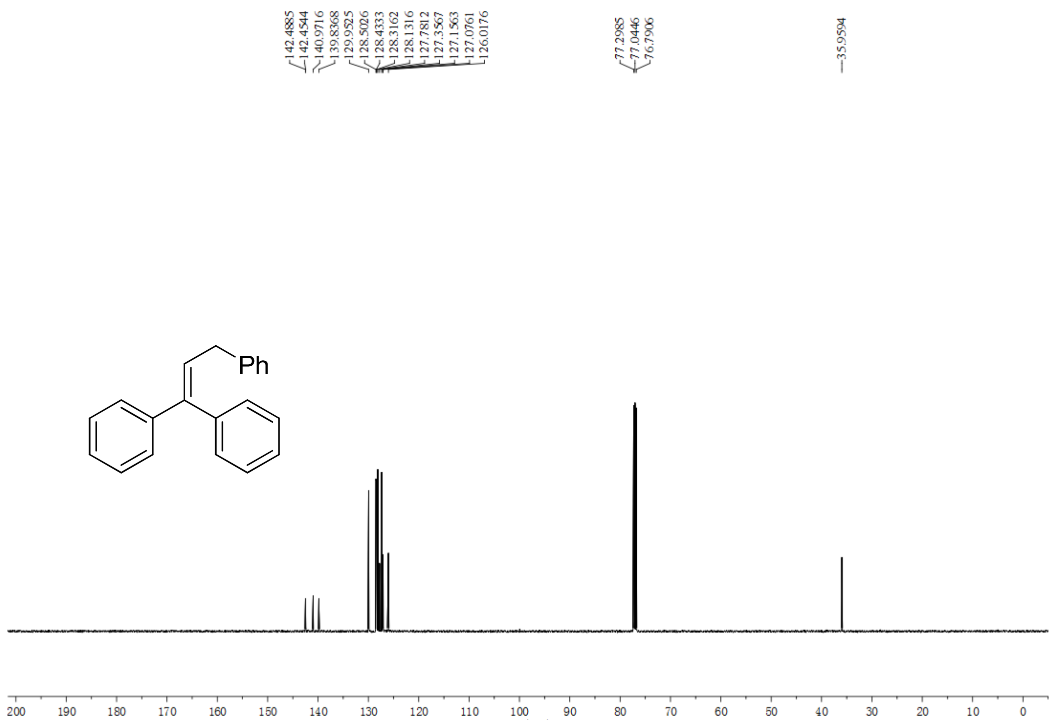
7.3058
7.3035
7.3004
7.2958
7.2843
7.2719
7.2686
7.2662
7.2603
7.2538
7.2414
7.2380
7.2300
7.2274
6.3312
6.3160
6.3008
3.5275
3.5123
Ph
2.03
3.20
6.09
3.85
1.00
2.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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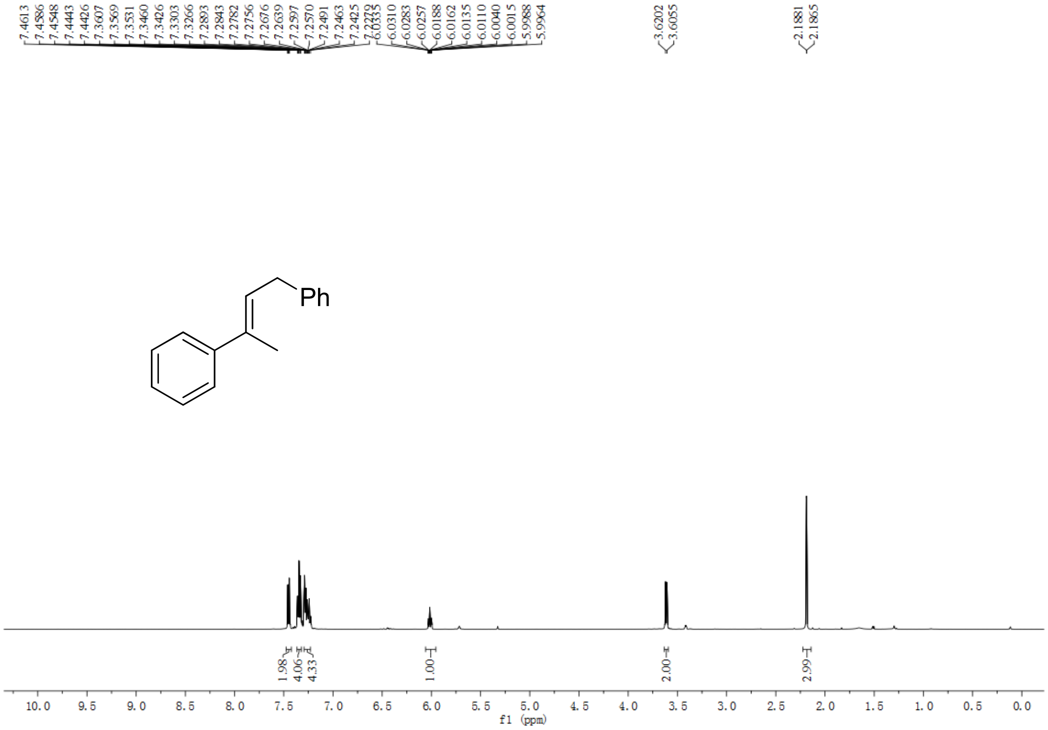
128.4333
128.3162
128.1316
127.7812
127.3567
127.1563
127.0761
126.0176
77.2985
77.0446
76.7906
35.9594
Ph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4f(*E*)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7.3569
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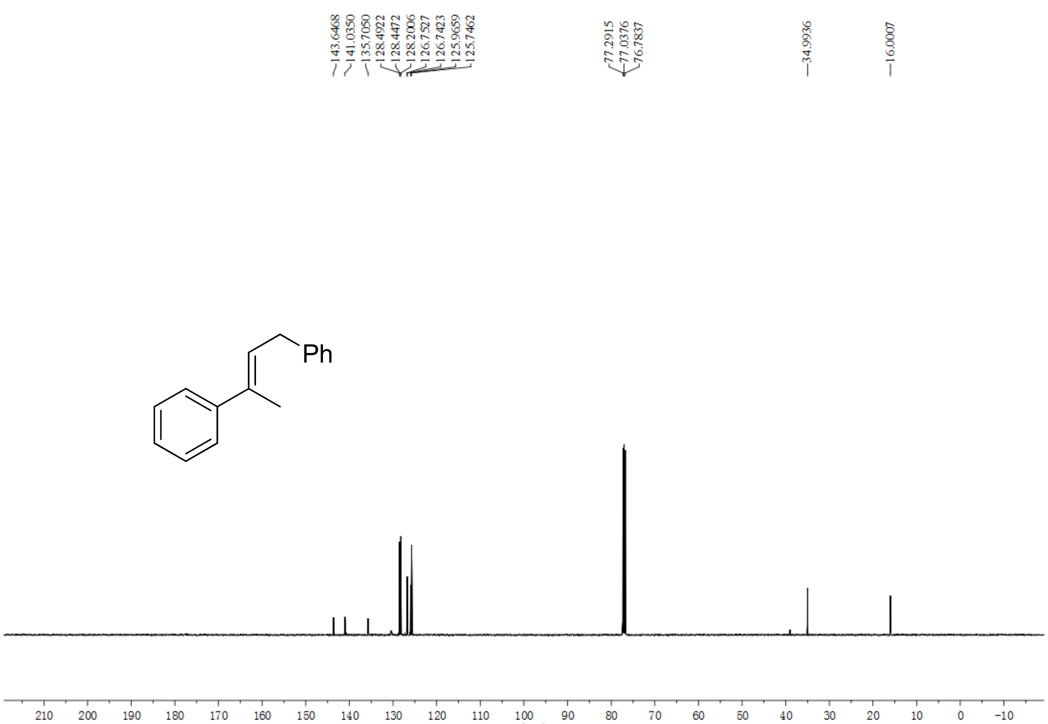
7.3460
7.3426
7.3303
7.3266
7.2893
7.2843
7.2782
7.2756
7.2676
7.2639
7.2597
7.2570
7.2491
7.2463
7.2425
7.2279
6.0335
6.0310
6.0283
6.0257
6.0188
6.0162
6.0135
6.0110
6.0040
6.0015
5.9988
5.9964
3.6202
3.6055
2.1881
2.1865
Ph
1.98
4.06
4.33
1.00
2.00
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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135.7050
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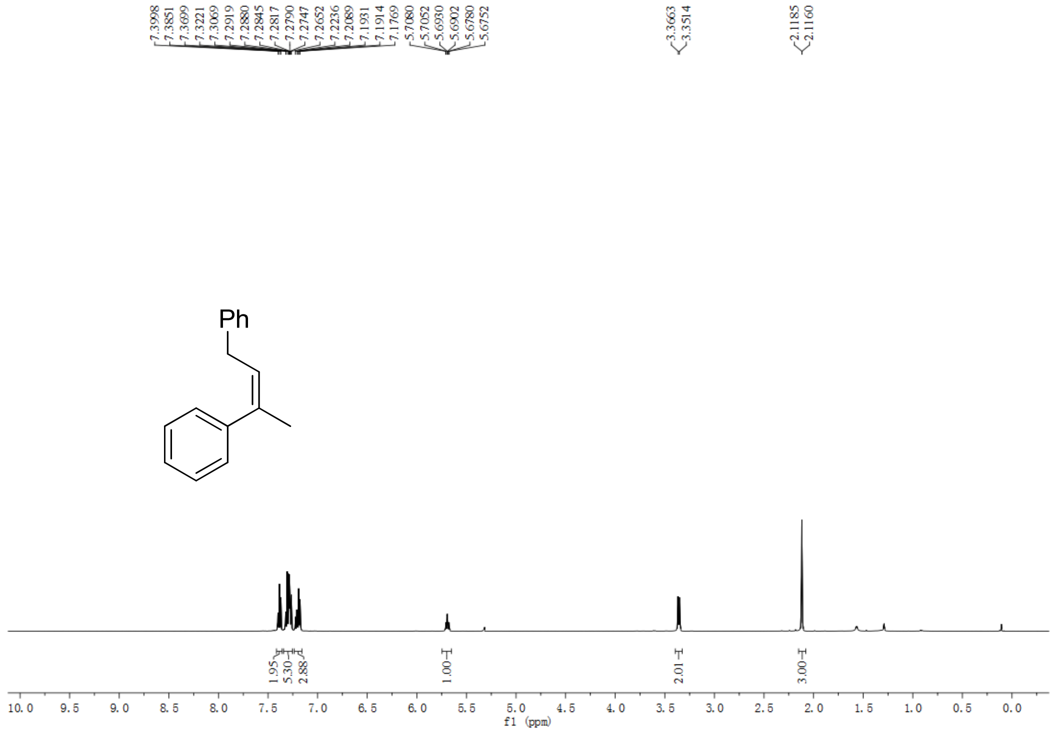
126.7527
126.7423
125.9659
125.7462
77.2915
77.0376
76.7837
34.9936
16.0007
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4f(*Z*)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7.2817
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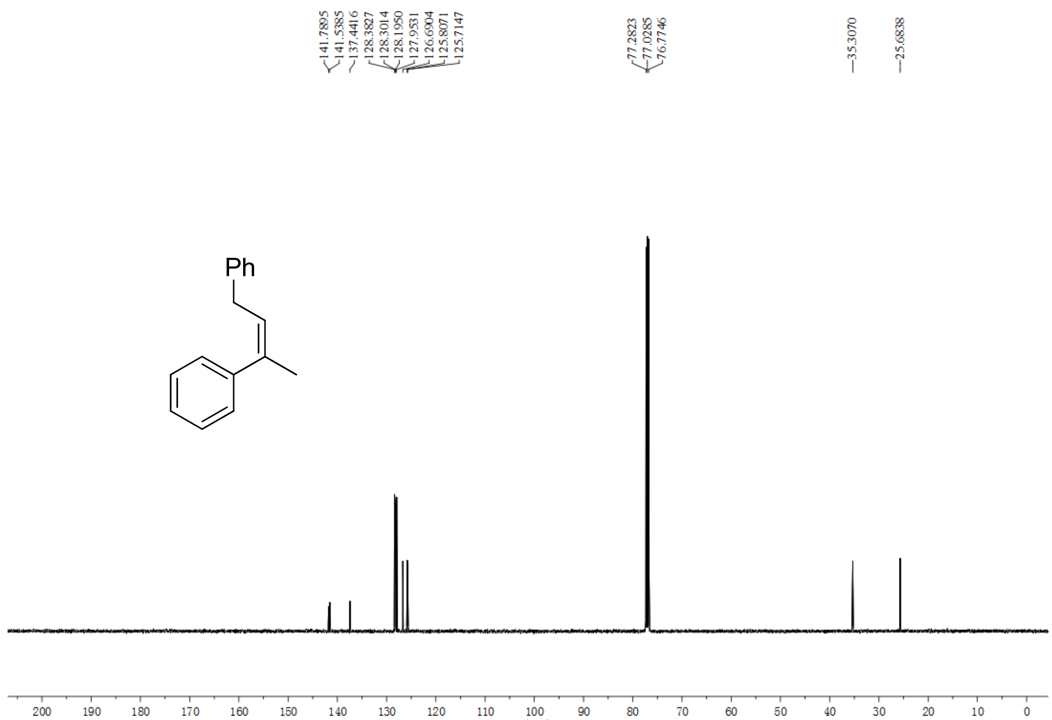
7.2747
7.2652
7.2236
7.2089
7.1931
7.1914
7.1769
5.7080
5.7052
5.6930
5.6902
5.6780
5.6752
3.3663
3.3514
2.1185
2.1160
Ph
1.95
5.30
2.88
1.00
2.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.9531
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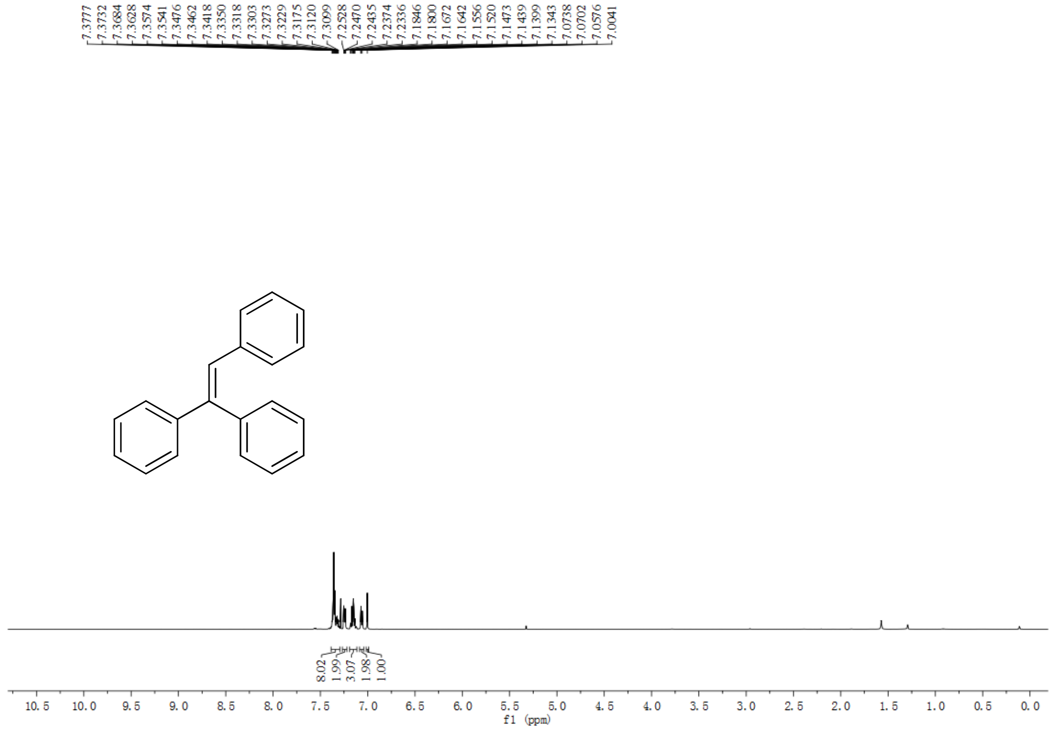
125.8071
125.7147
77.2823
77.0285
76.7746
35.3070
25.6838
Ph
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4g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7.3476
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7.3418
7.3350
7.3318
7.3303
7.3273
7.3229
7.3175
7.3120
7.3099
7.2528
7.2470
7.2435
7.2374
7.2336
7.1846
7.1800
7.1672
7.1642
7.1556
7.1520
7.1473
7.1439
7.1399
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7.0576
7.0041
8.02
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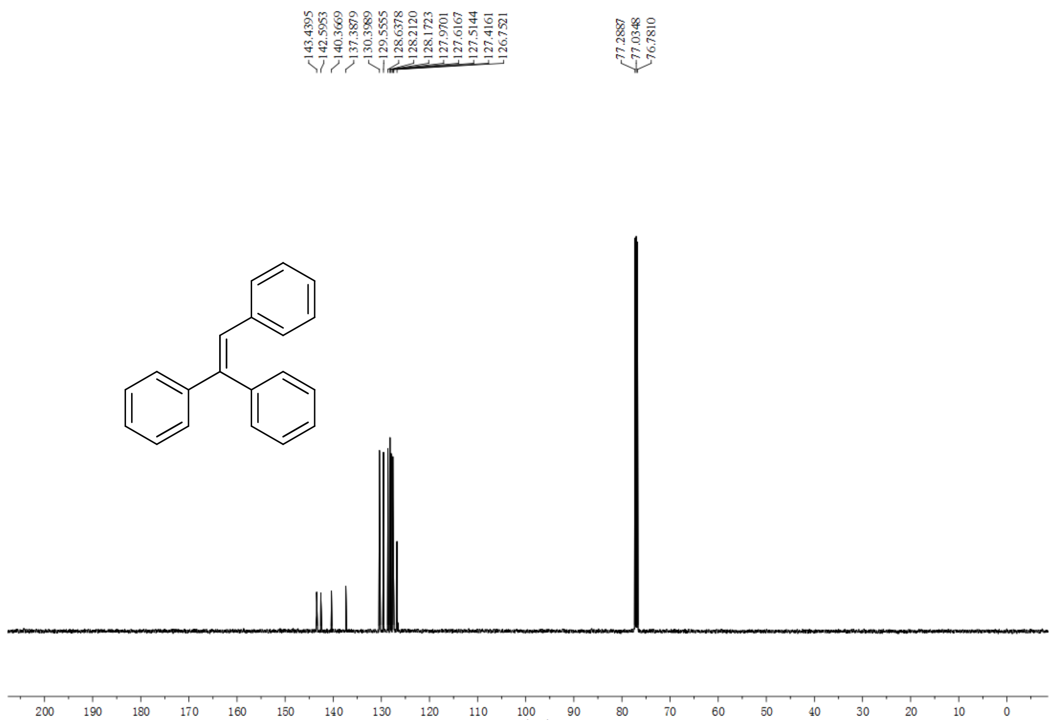
1.98
1.00
f1 (ppm)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127.5144
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126.7521
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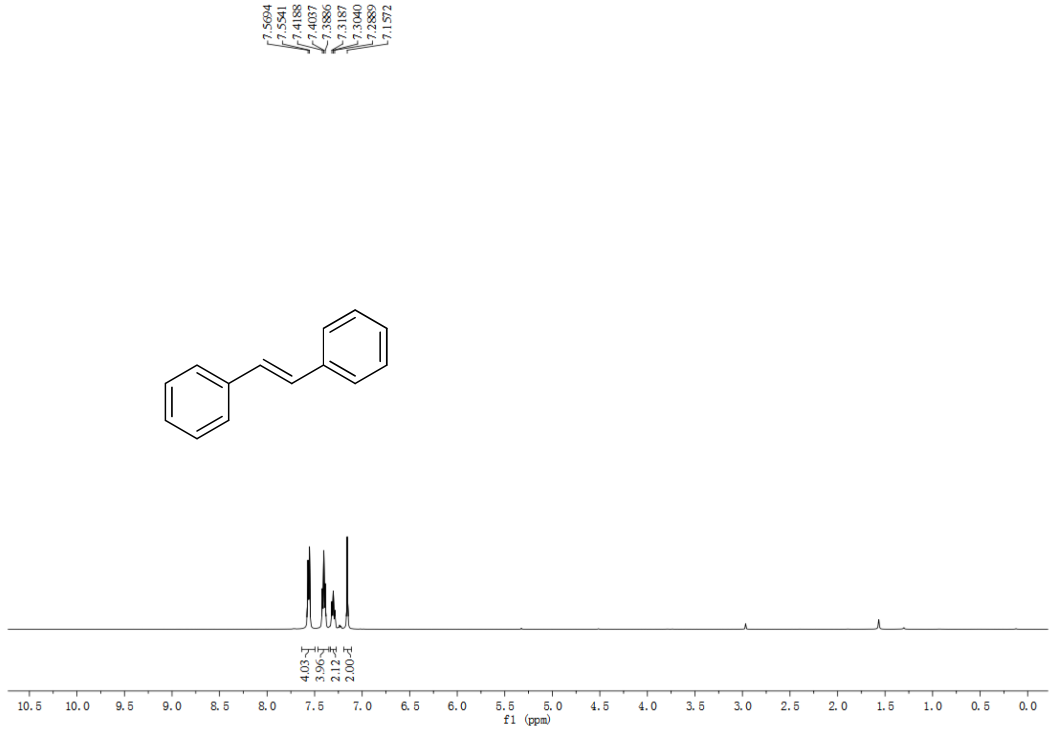
77.0348
76.7810
f1 (ppm)

4h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7.3886
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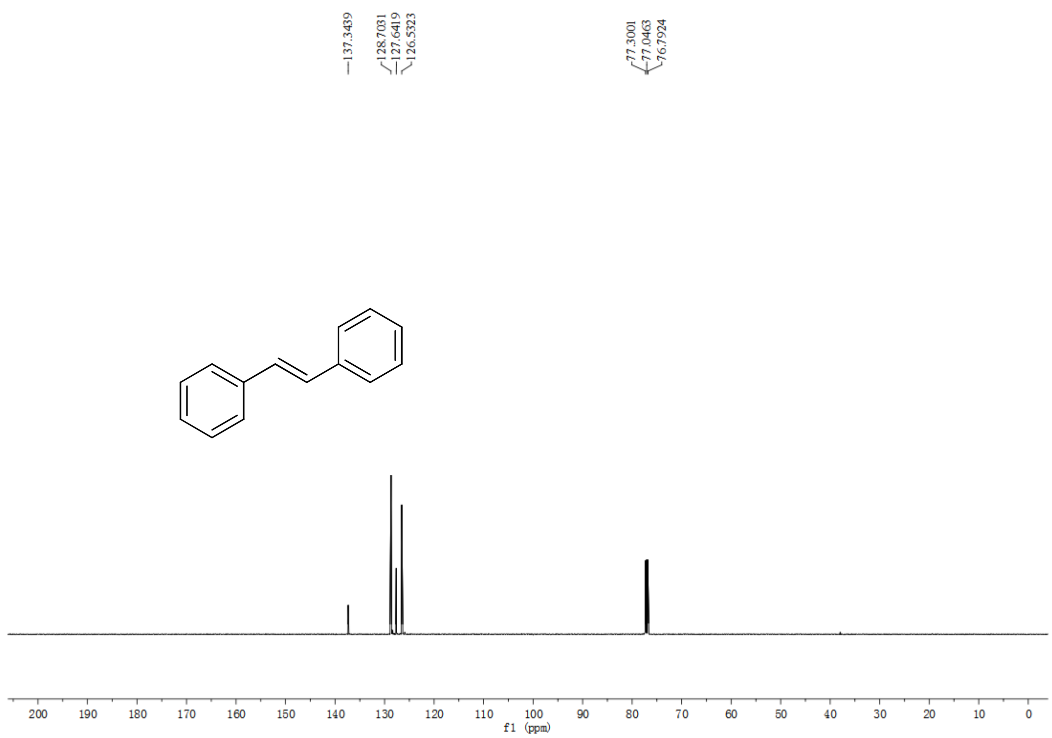
7.3040
7.2889
7.1572
4.03
3.96
2.12
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.0463
76.7924
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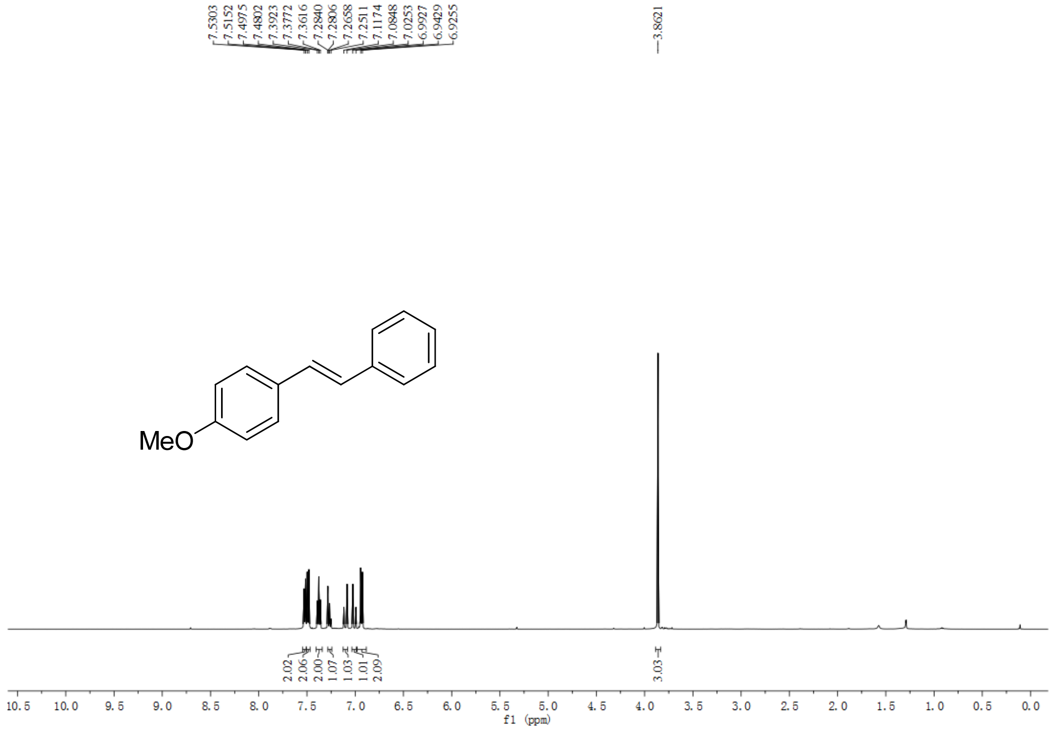
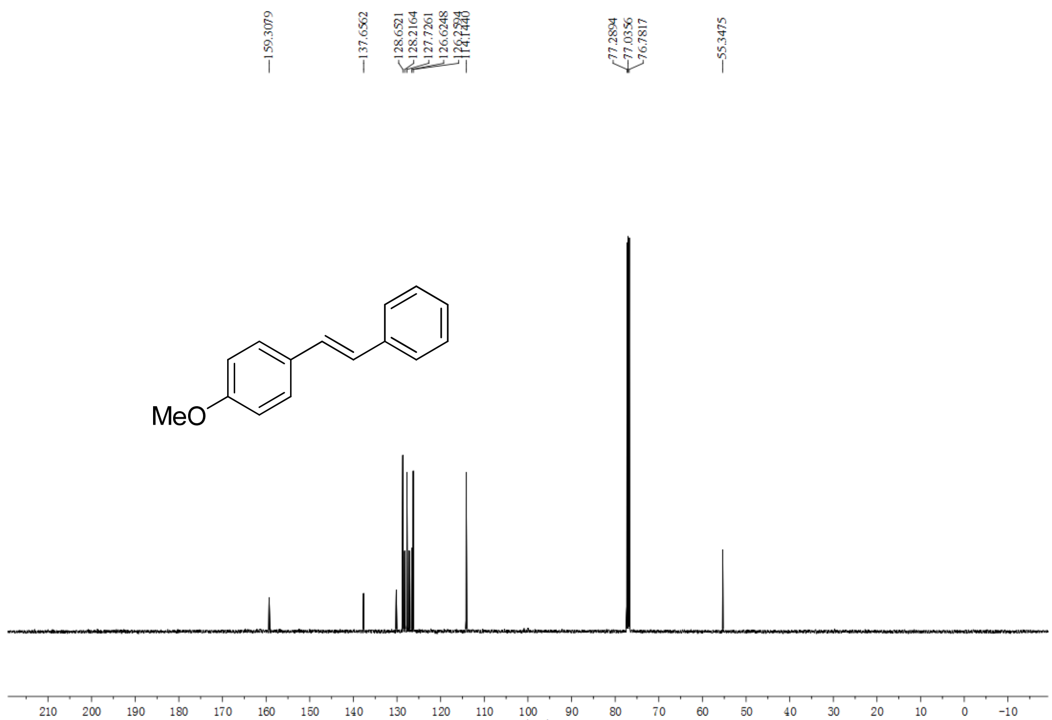
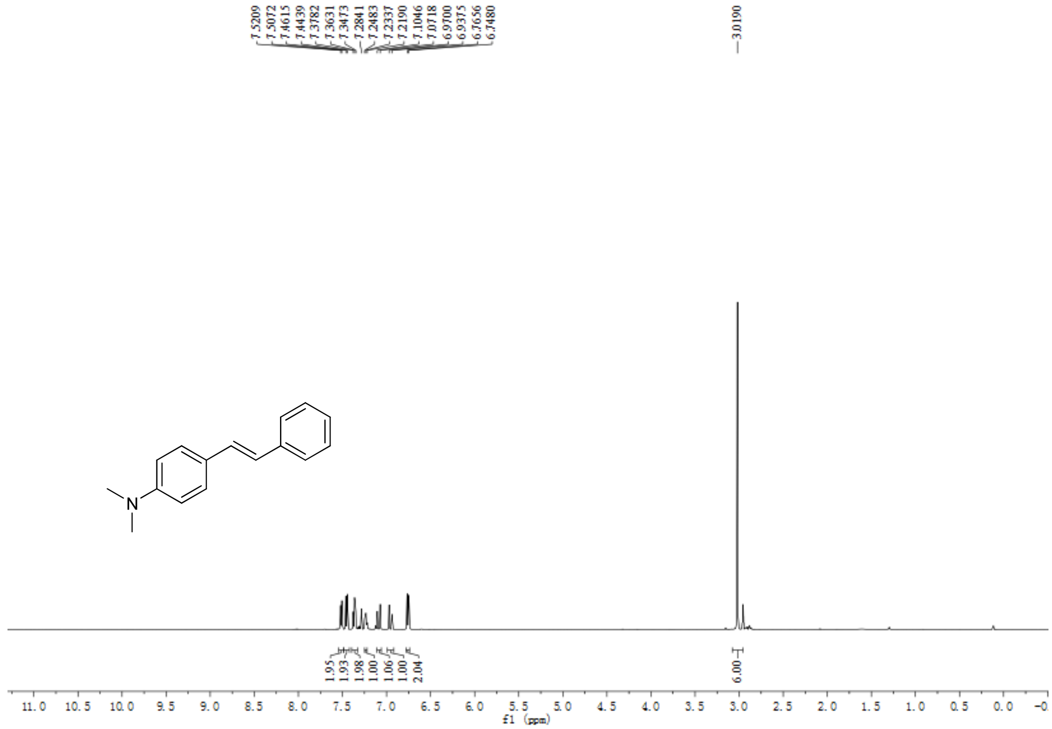
f1 (ppm)

4i





4j



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7.3631
7.3473
7.2841
7.2483
7.2337
7.2190
7.1046
7.0718
6.9700
6.9375
6.7656
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3.0190
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1.93
1.98
1.00
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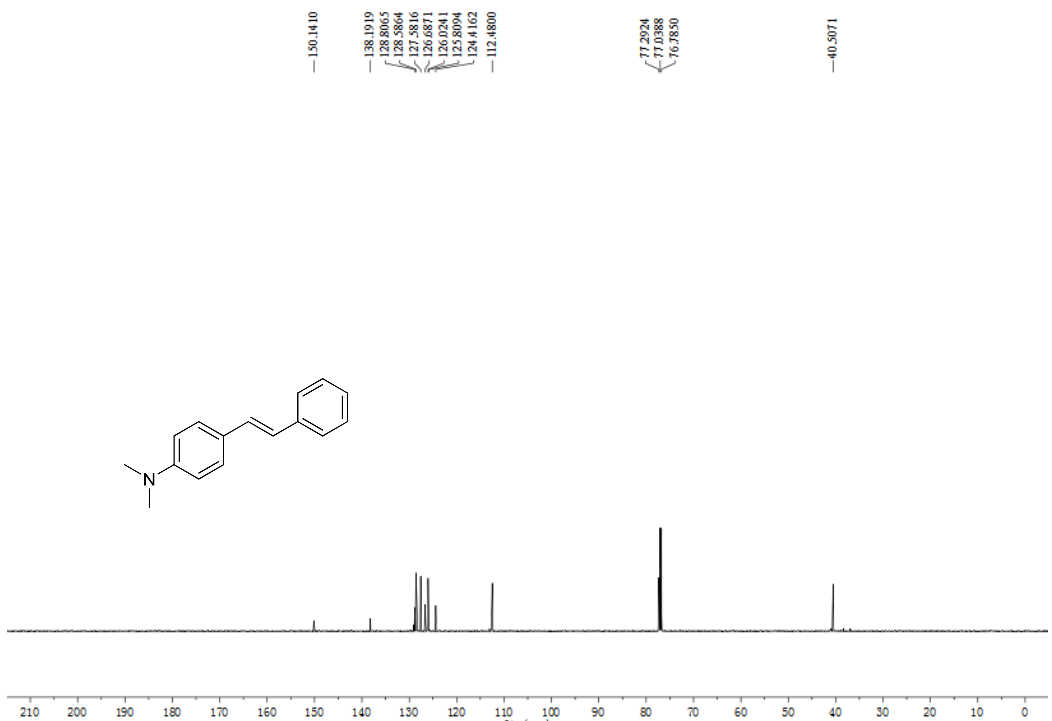
1.00
2.04
6.00
f1 (ppm)



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77.0388
76.7850
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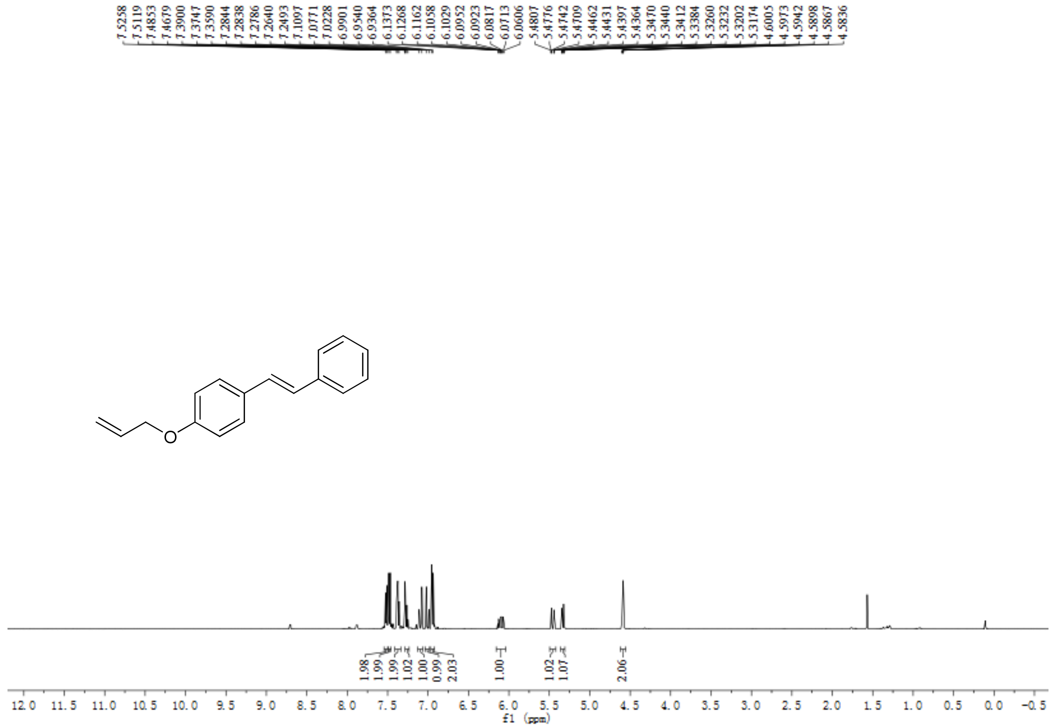
N
f1 (ppm)

4k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7.1097
7.0771
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6.9364
6.1373
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6.1162
6.1058
6.1029
6.0952
6.0923
6.0817
6.0713
6.0606
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5.3260
5.3232
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5.3174
4.6005
4.5973
4.5942
4.5898
4.5867
4.5836
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1.99
1.99
1.02
1.00
0.99
2.03
1.00
1.02
1.07
2.06
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
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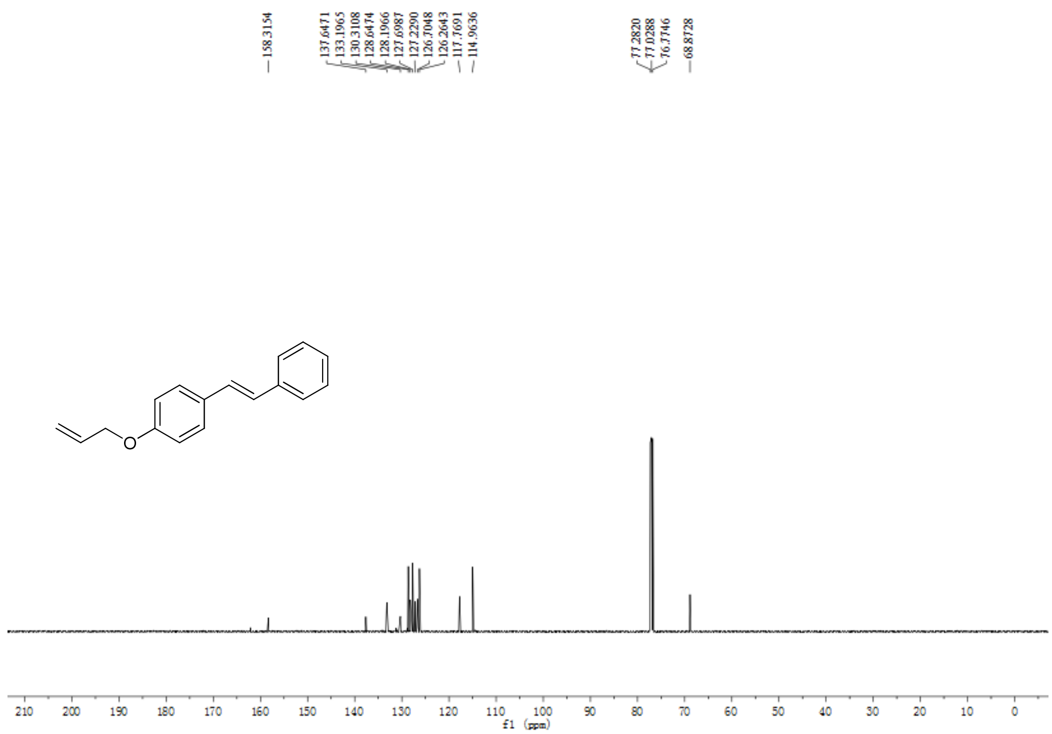
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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117.7691
114.9636
77.2820
77.0288
76.7746
68.8728
210
200
190
180
170
160
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140
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110
100
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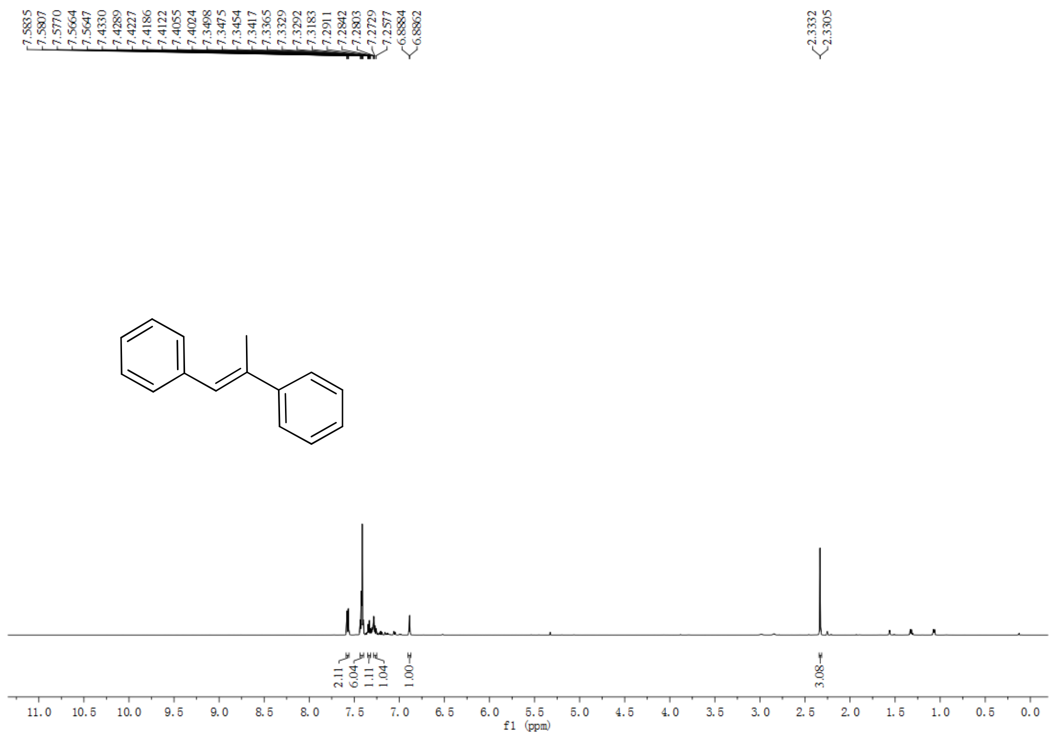
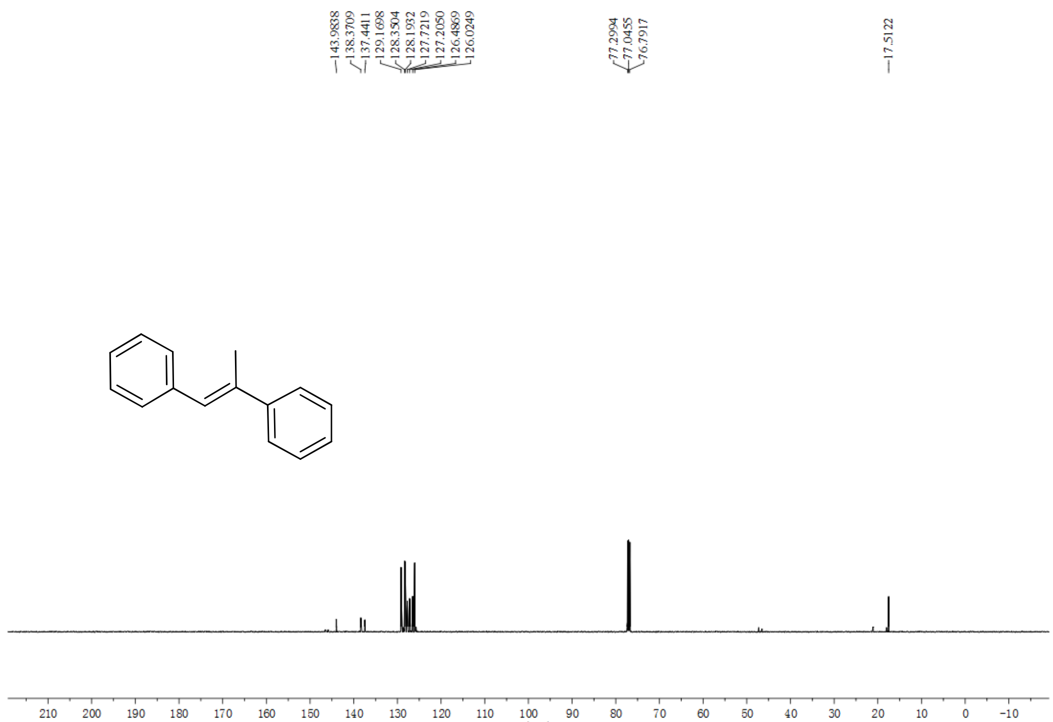
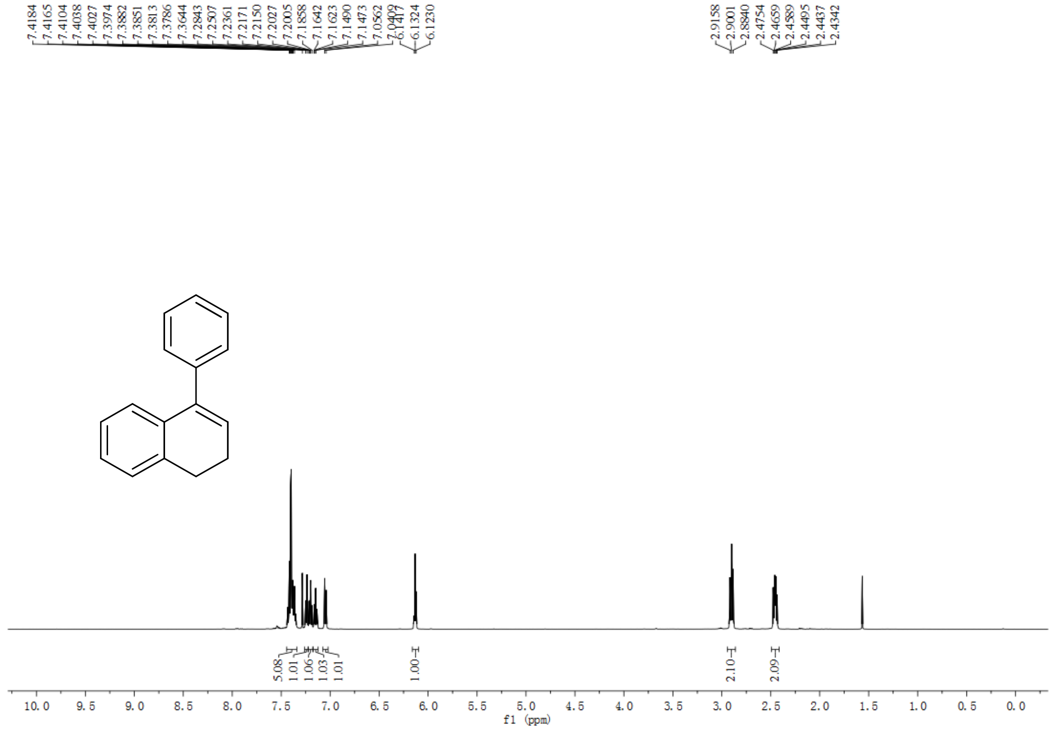
80
70
60
50
40
30
20
10
0
f1 (ppm)

4l

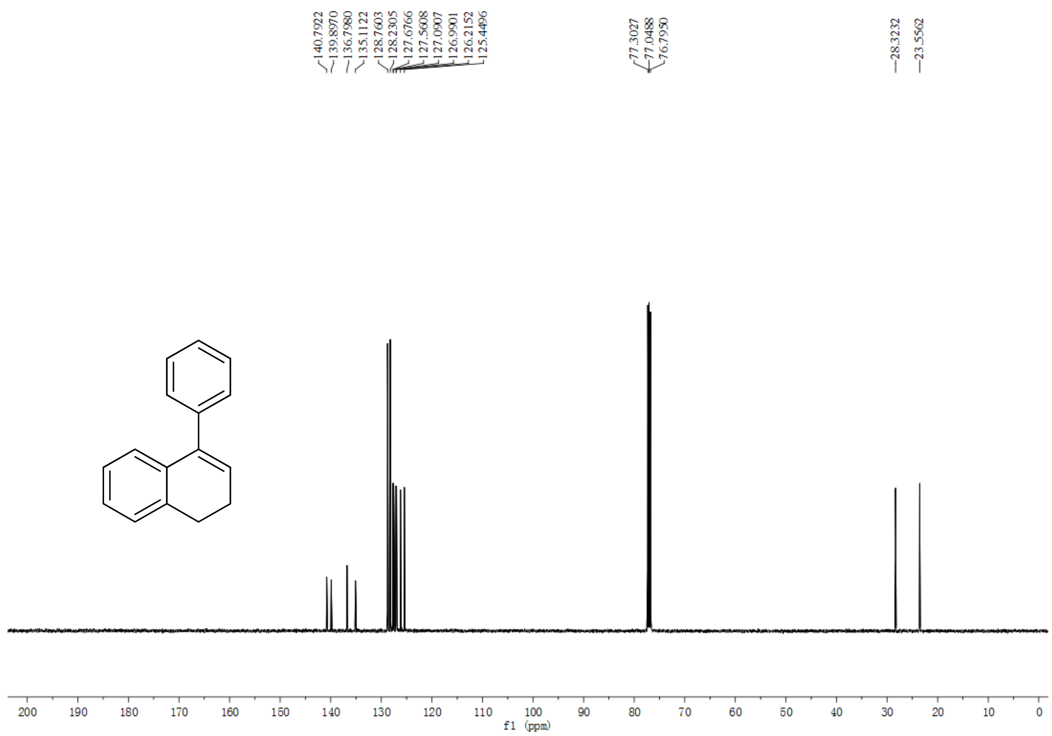

7.5835
7.5807
7.5770
7.5664
7.5647
7.4330
7.4289
7.4227
7.4186
7.4122
7.4055
7.4024
7.3498
7.3475
7.3454
7.3417
7.3365
7.3329
7.3292
7.3183
7.2911
7.2842
7.2803
7.2729
7.2577
6.8884
6.8862
2.3332
2.3305
2.11
6.04
1.11
1.04
1.00
3.08
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


143.9838
138.3709
137.4411
129.1698
128.3504
128.1932
127.7219
127.2050
126.4869
126.0249
77.2994
77.0455
76.7917
17.5122
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4m

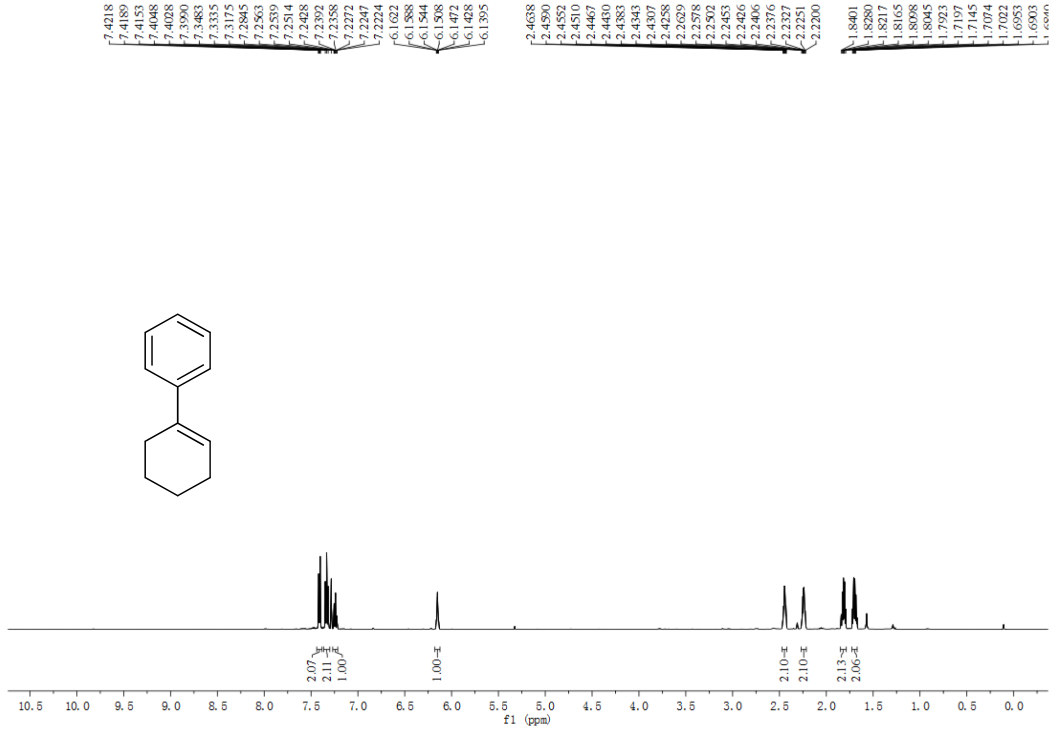


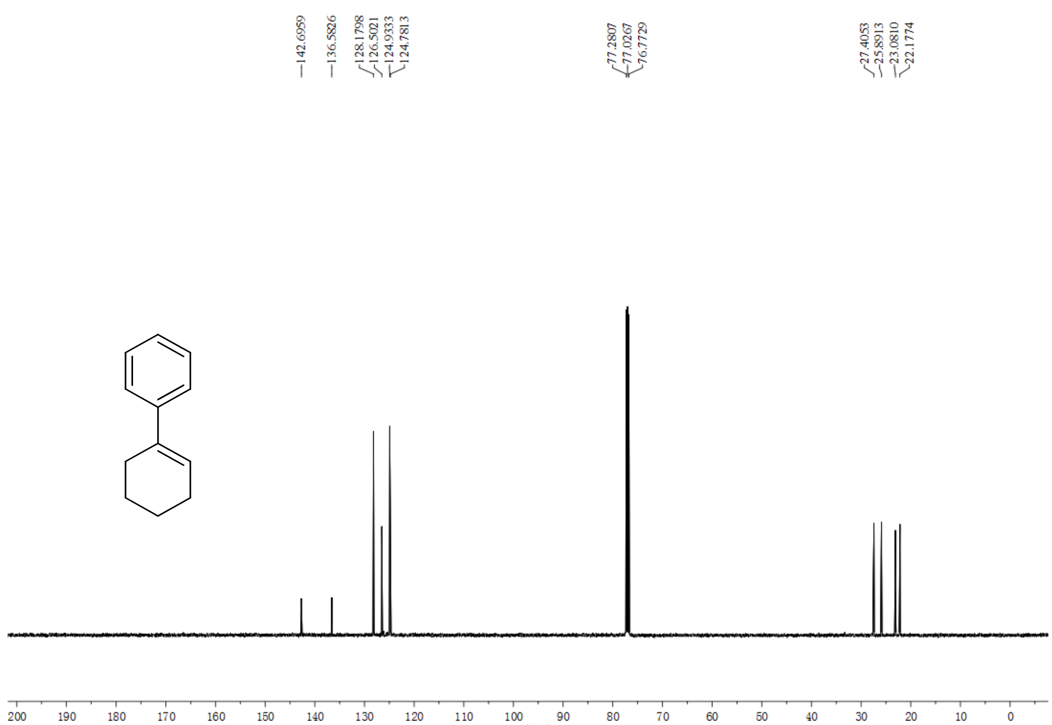
7.4184
7.4165
7.4104
7.4038
7.4027
7.3974
7.3882
7.3851
7.3813
7.3786
7.3644
7.2843
7.2507
7.2361
7.2171
7.2150
7.2027
7.2005
7.1858
7.1642
7.1623
7.1490
7.1473
7.0562
7.0409
6.1417
6.1324
6.1230
2.9158
2.9001
2.8840
2.4754
2.4659
2.4589
2.4495
2.4437
2.4342
5.08
1.01
1.06
1.03
1.01
1.00
2.10
2.09
f1 (ppm)



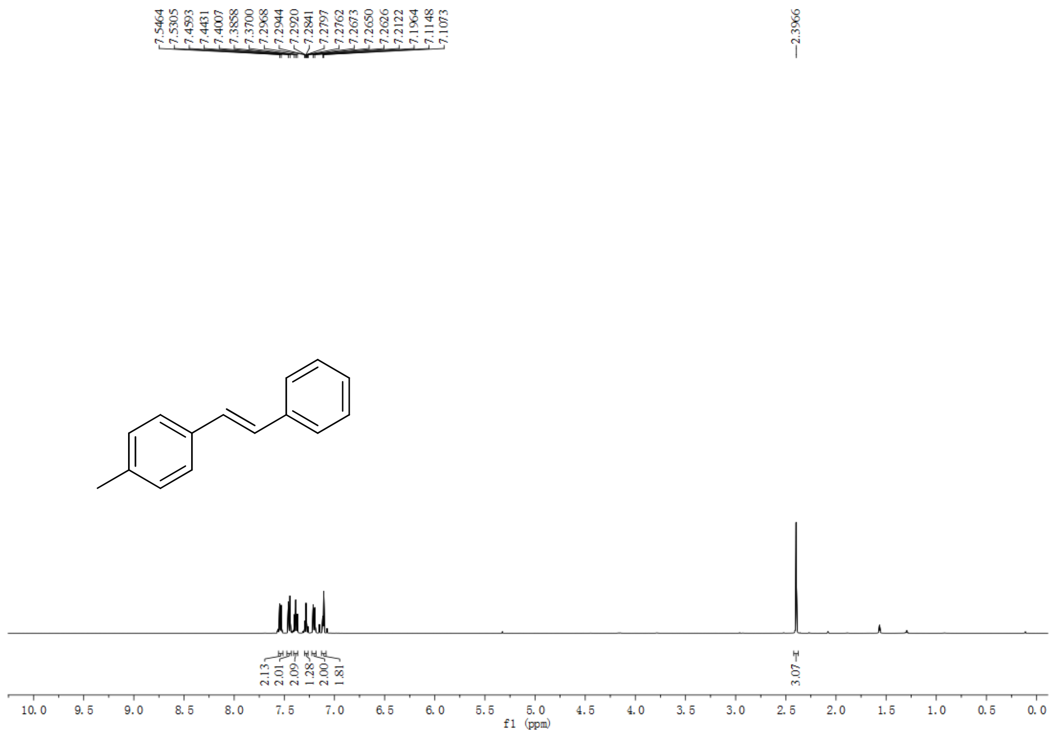
140.7922
139.8970
136.7980
135.1122
128.7603
128.2305
127.6766
127.5608
127.0907
126.9901
126.2152
125.4496
77.3027
77.0488
76.7950
28.3232
23.5562
f1 (ppm)

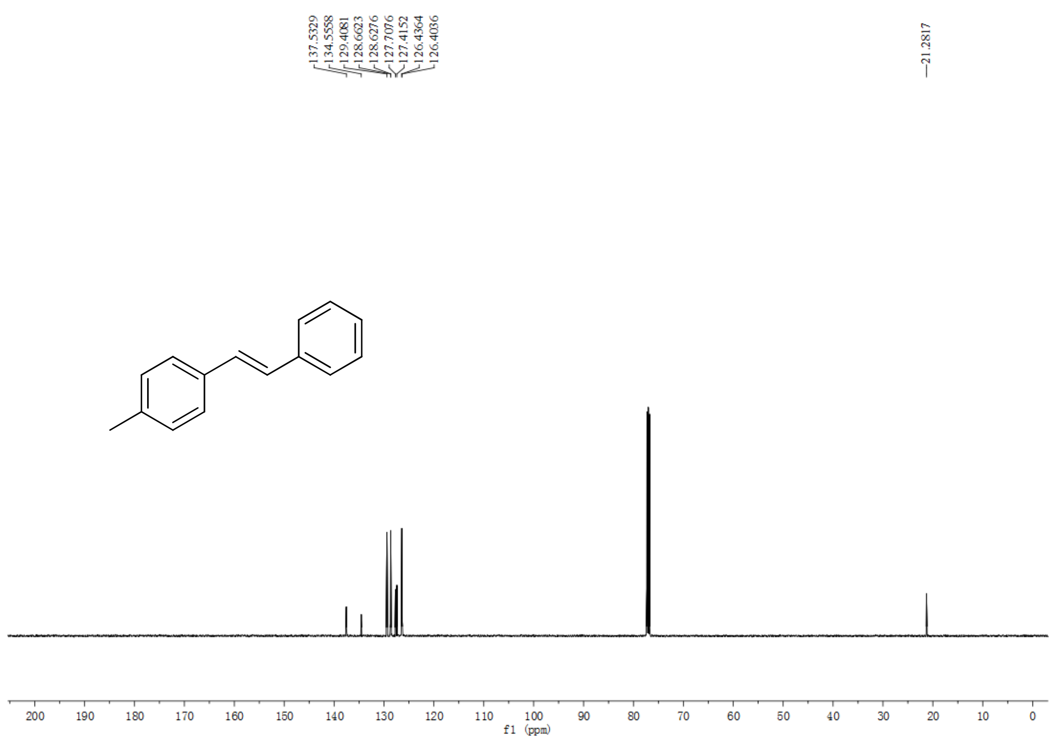
4n


7.4218
7.4189
7.4153
7.4048
7.4028
7.3990
7.3483
7.3335
7.3175
7.2845
7.2563
7.2539
7.2514
7.2428
7.2392
7.2358
7.2272
7.2247
7.2224
6.1622
6.1588
6.1544
6.1508
6.1472
6.1428
6.1395
2.4638
2.4590
2.4552
2.4510
2.4467
2.4430
2.4383
2.4343
2.4307
2.4258
2.2629
2.2578
2.2502
2.2453
2.2426
2.2406
2.2376
2.2327
2.2251
2.2200
1.8401
1.8280
1.8217
1.8165
1.8098
1.8045
1.7923
1.7197
1.7145
1.7074
1.7022
1.6953
1.6903
2.07
2.11
1.00
1.00
2.10
2.10
2.13
2.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

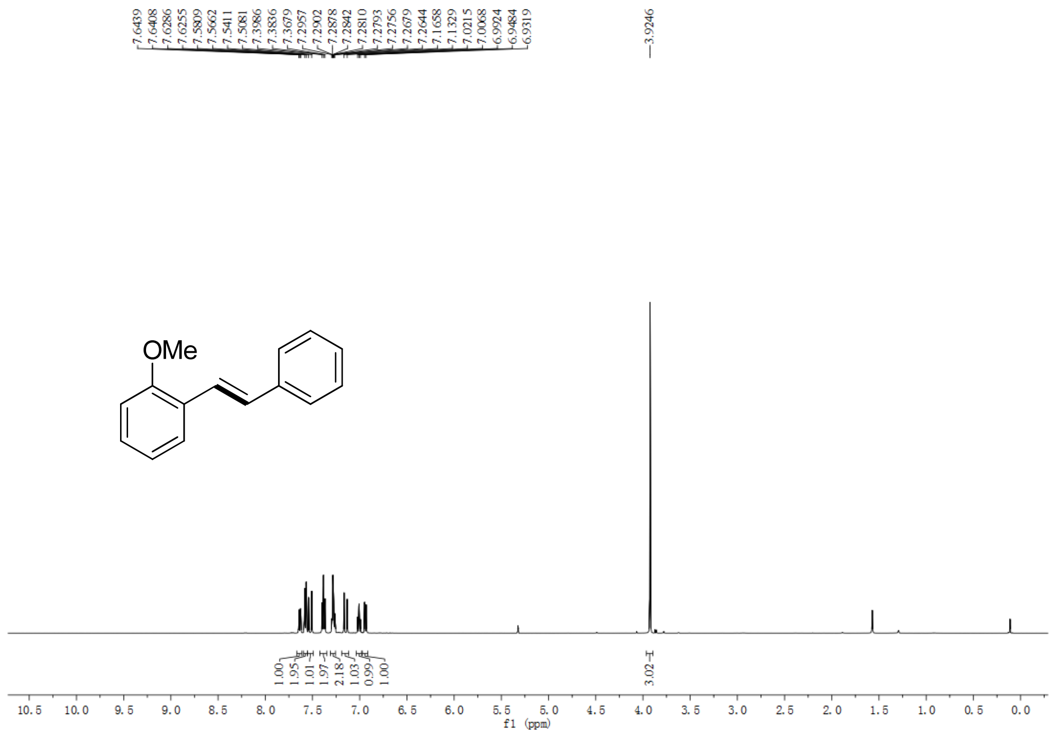

142.6959
136.5826
128.1798
126.5021
124.9333
124.7813
77.2807
77.0267
76.7729
27.4053
25.8913
23.0810
22.1774
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

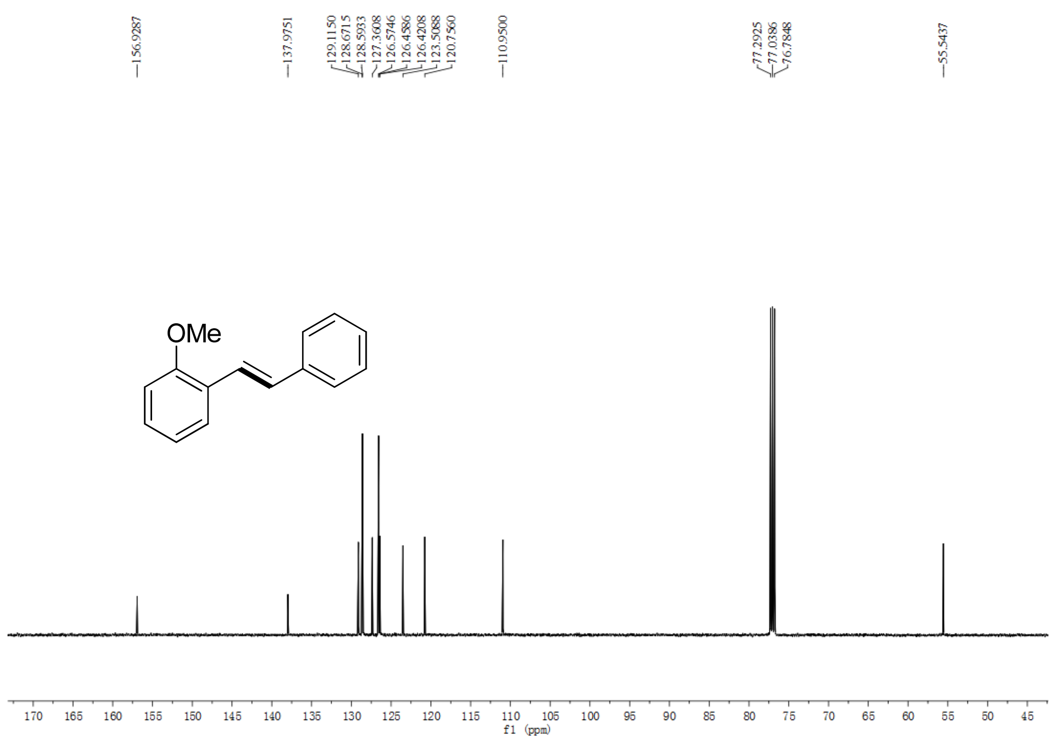
4o



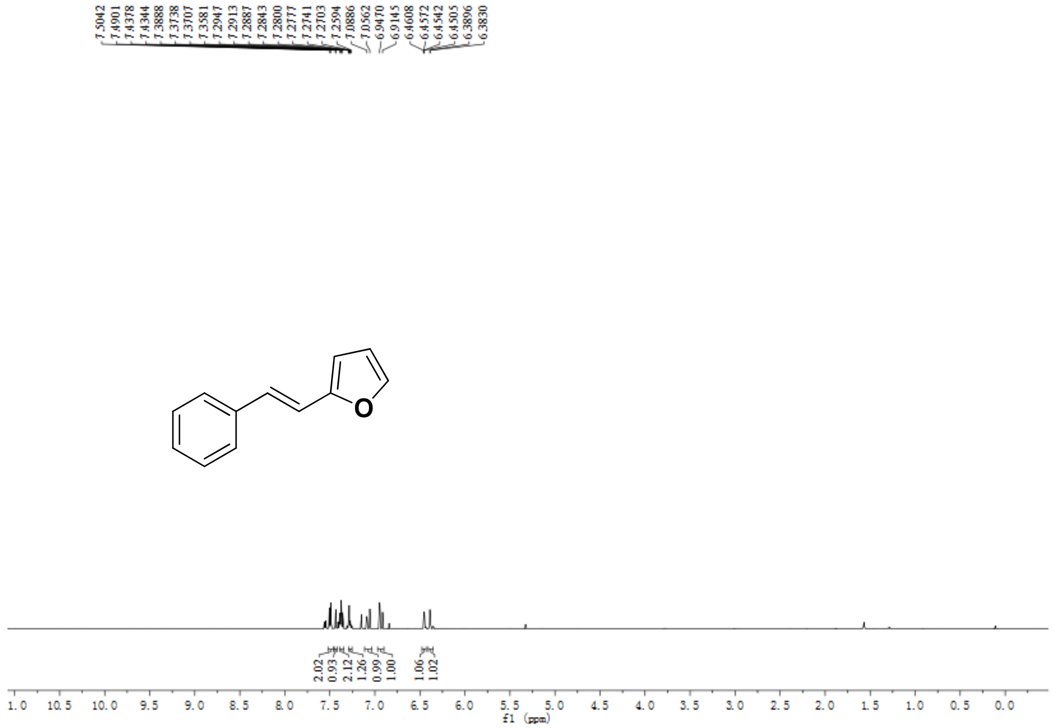


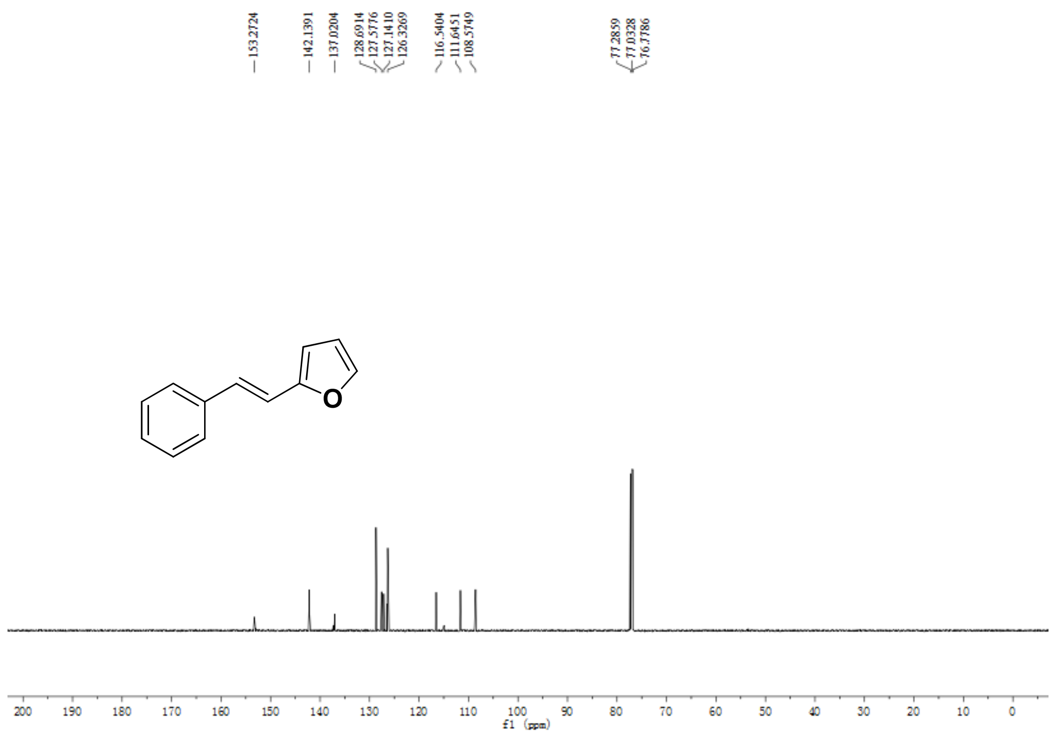
4p



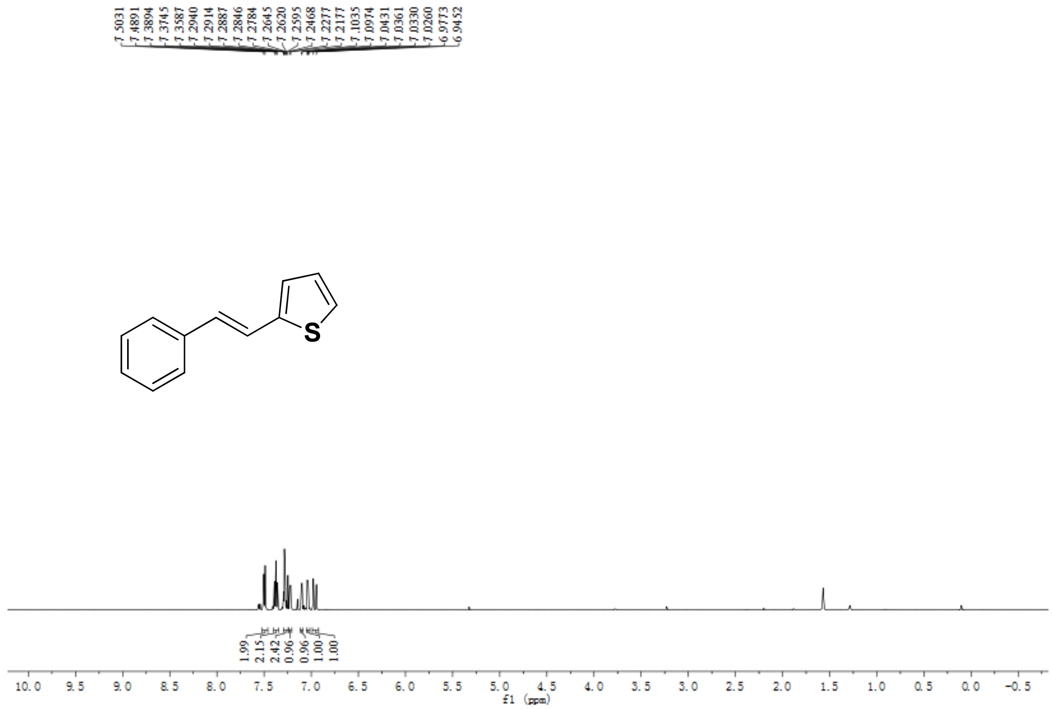


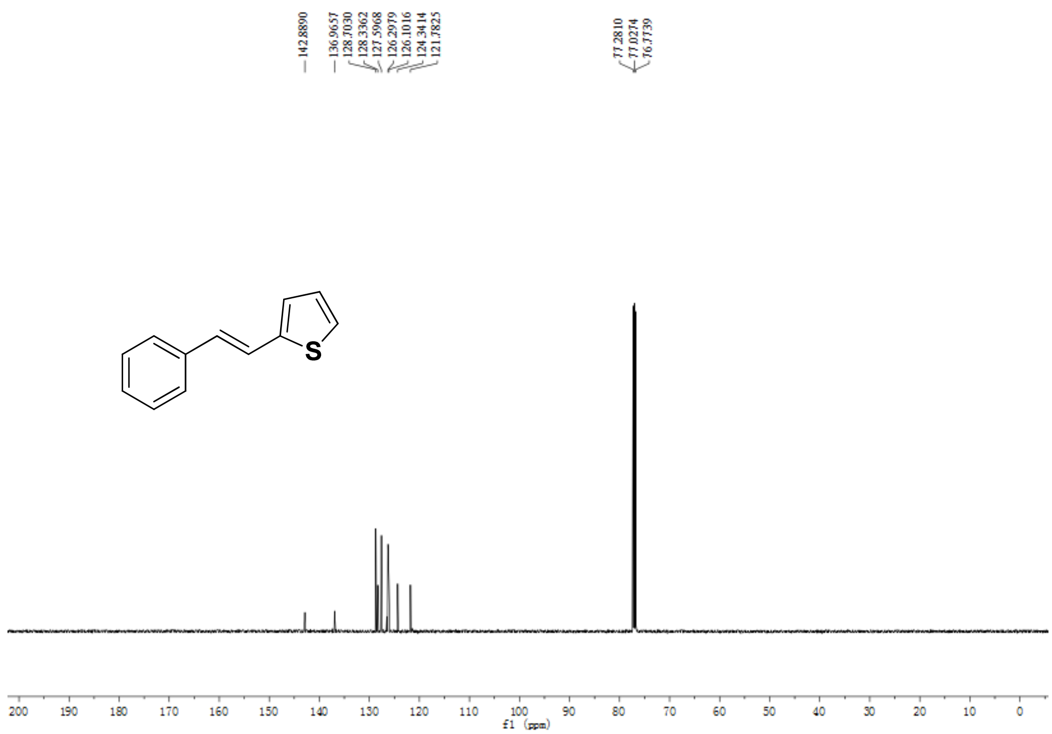
4q


7.5042
7.4901
7.4378
7.4344
7.3888
7.3738
7.3707
7.3581
7.2947
7.2913
7.2887
7.2843
7.2800
7.2777
7.2741
7.2703
7.2594
7.0886
7.0562
6.9470
6.9145
6.4608
6.4572
6.4542
6.4505
6.3896
6.3830
O
2.02
0.93
2.12
1.26
0.99
1.00
1.06
1.02
f1 (ppm)

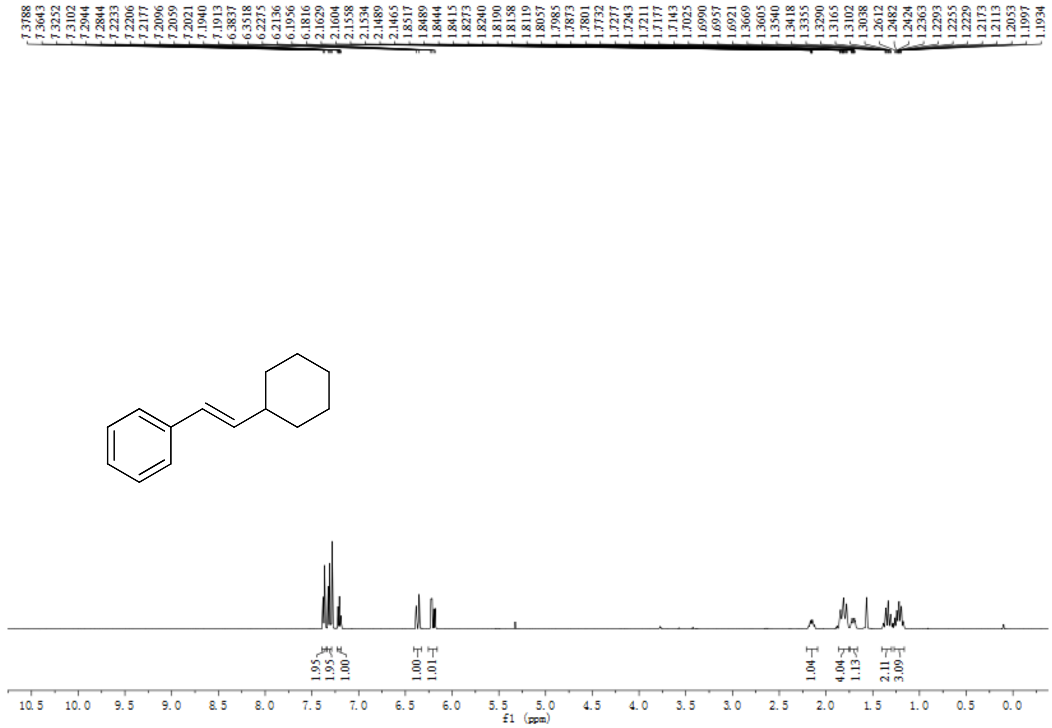

153.2724
142.1391
137.0204
128.6914
127.5776
127.1410
126.3269
116.5404
111.6451
108.5749
77.2859
77.0328
76.7786
O
f1 (ppm)

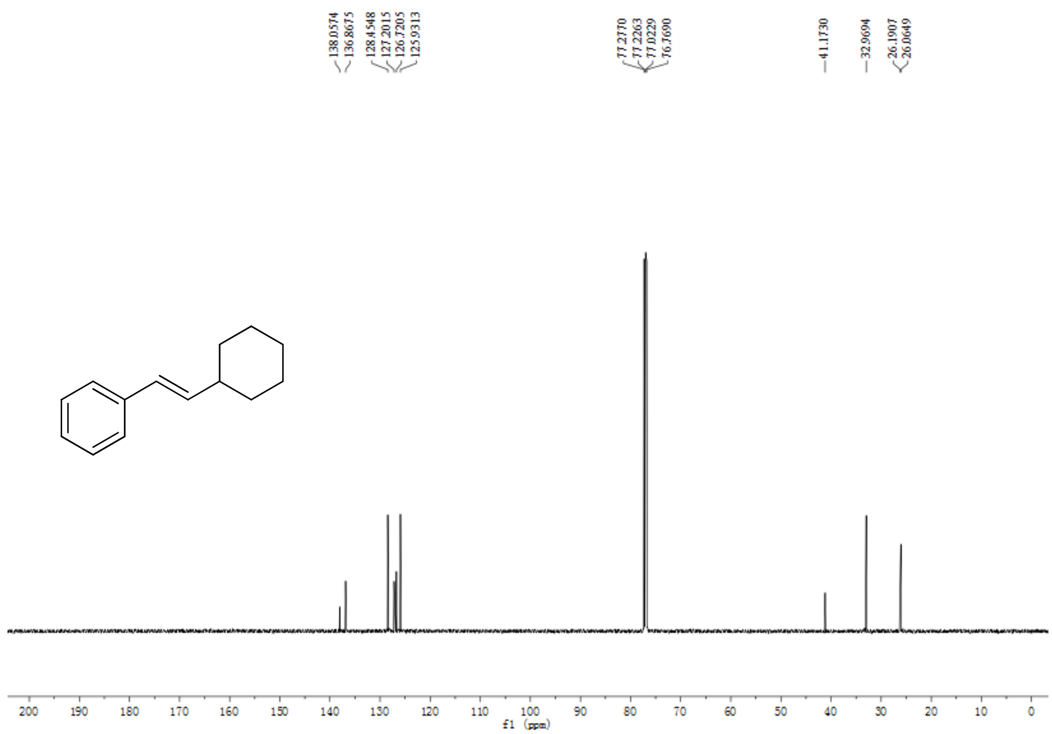
4r


7.5031
7.4891
7.3894
7.3745
7.3587
7.2940
7.2914
7.2887
7.2846
7.2784
7.2645
7.2620
7.2595
7.2468
7.2277
7.2177
7.1035
7.0974
7.0431
7.0361
7.0330
7.0260
6.9773
6.9452
S
1.99
2.15
2.42
0.96
0.96
1.00
1.00
f1 (ppm)

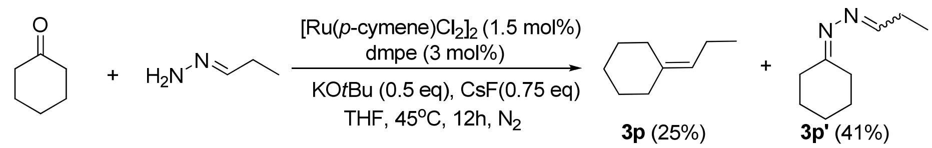

142.8890
136.9657
128.7030
128.3362
127.5968
126.2979
126.1016
124.3414
121.7825
77.2810
77.0274
76.7739
S
f1 (ppm)

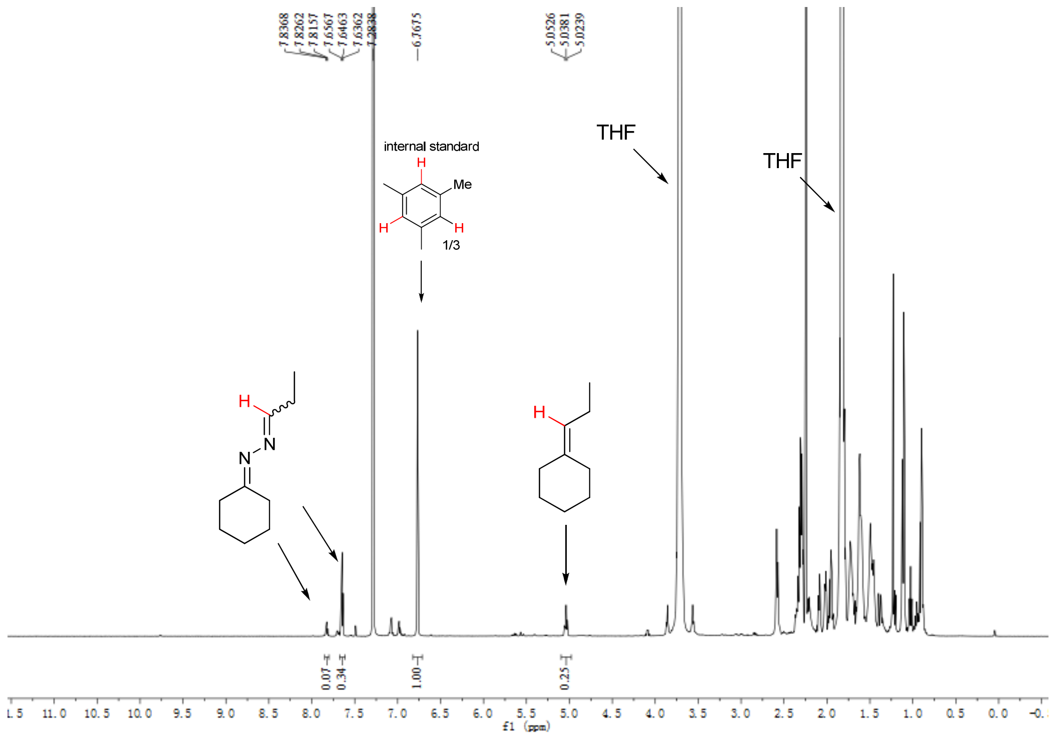
4s



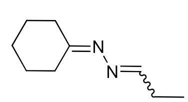


7. Crude ¹H NMR and HRMS copies of cross azines.

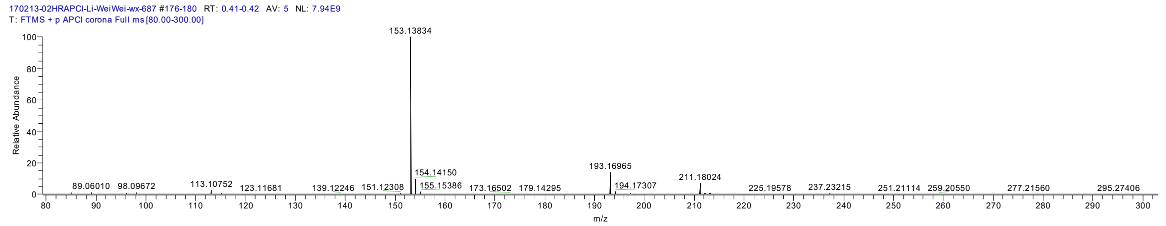


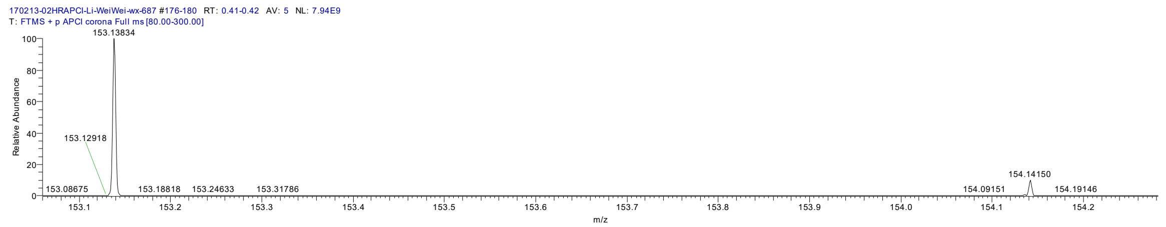


Crude NMR

1-cyclohexylidene-2-propylidenehydrazine  (41%yield), HRMS calc. for $C_9H_{17}N_2$ $(M+H)^+$, 153.13863; found, 153.13834.

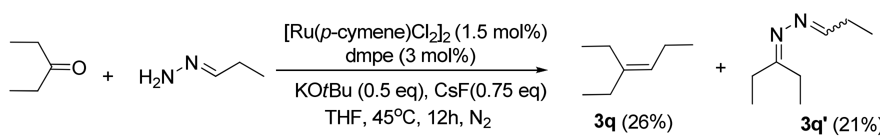
170213-02HRAPCI-Li-WeiWei-wx-687 2/13/2017 11:19:41 AM

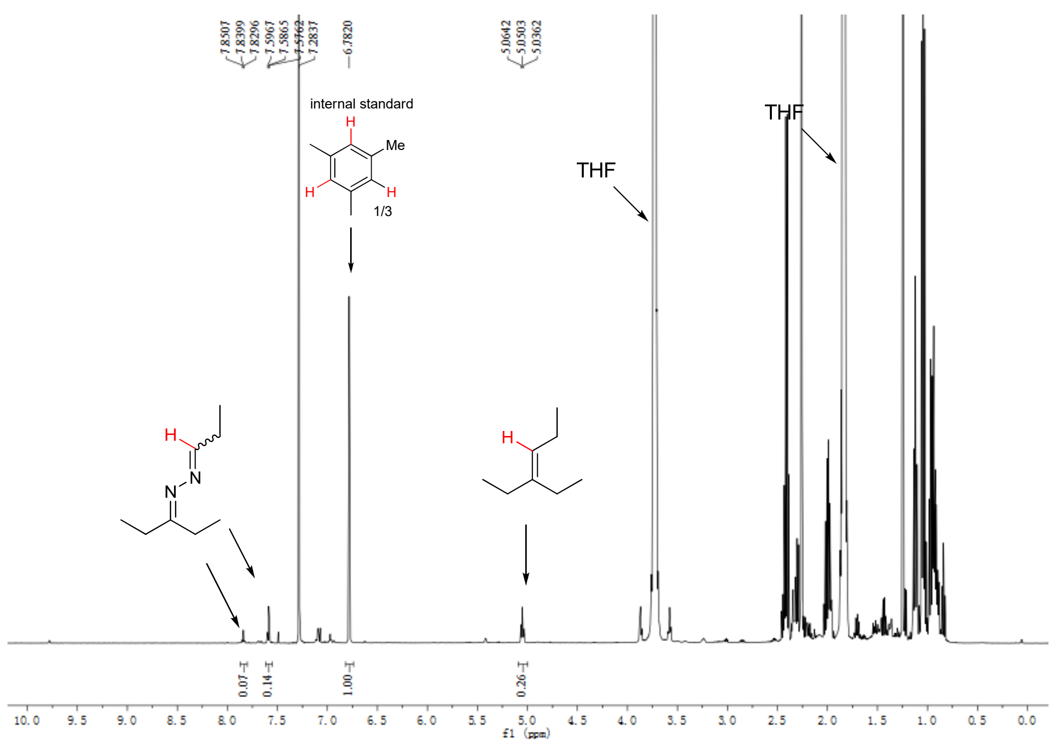


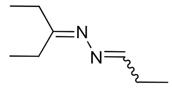


170213-02HRAPCI-Li-WeiWei-wx-687#176-180 RT: 0.41-0.42 AV: 5
T: FTMS + p APCI corona Full ms [80.00-300.00]
m/z= 153.13489-153.14501

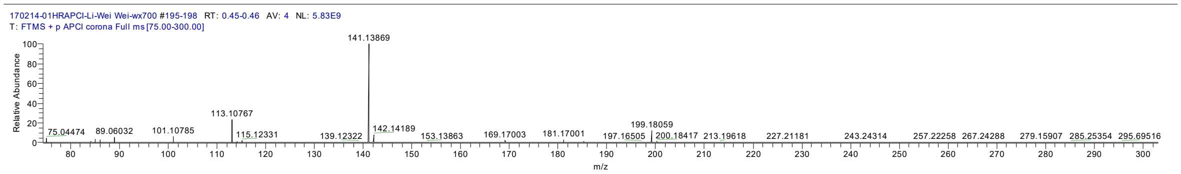
m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
153.13834	7991873024.0	100.00	43108.14	1.00	153.13863	-1.85	2.5	$C_9H_{17}N_2$

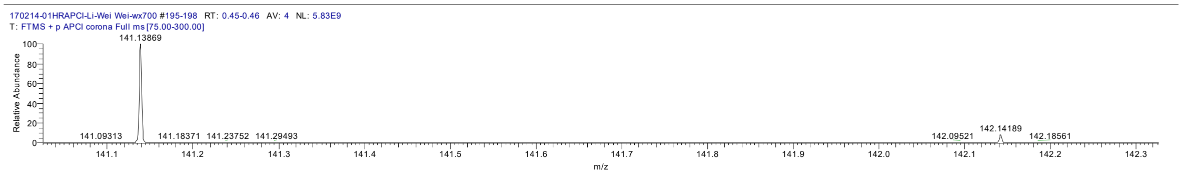




1-(pentan-3-ylidene)-2-propylidenehydrazine  (21%yield), HRMS calc. for $C_8H_{17}N_2$ $(M+H)^+$, 141.13863; found, 141.13869.

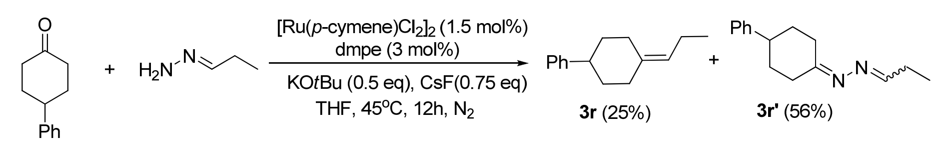
170214-01HRAPCI-Li-Wei Wei-wx700 2/14/2017 10:22:57 AM

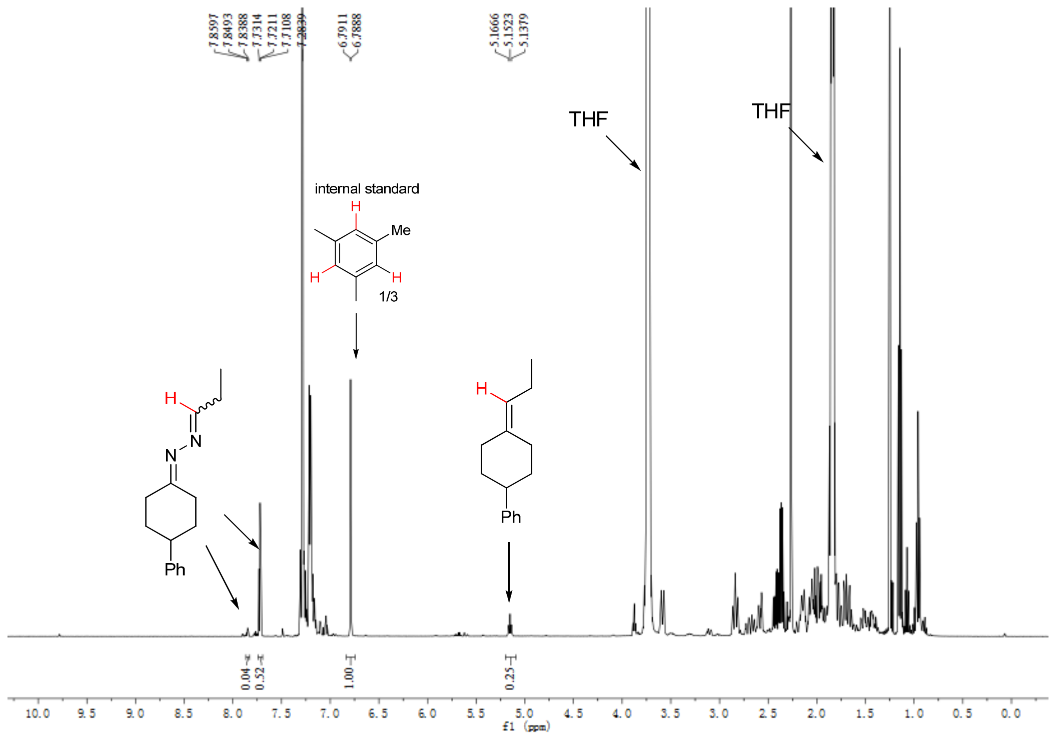


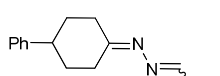


m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
141.13869	5951567360.0	100.00	46054.66	1.00	141.13863	0.45	1.5	C 8 H 17 N 2

m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
113.10767	1356701824.0	100.00	50451.31	1.00	113.10732	3.09	1.5	C 6 H 13 N 2

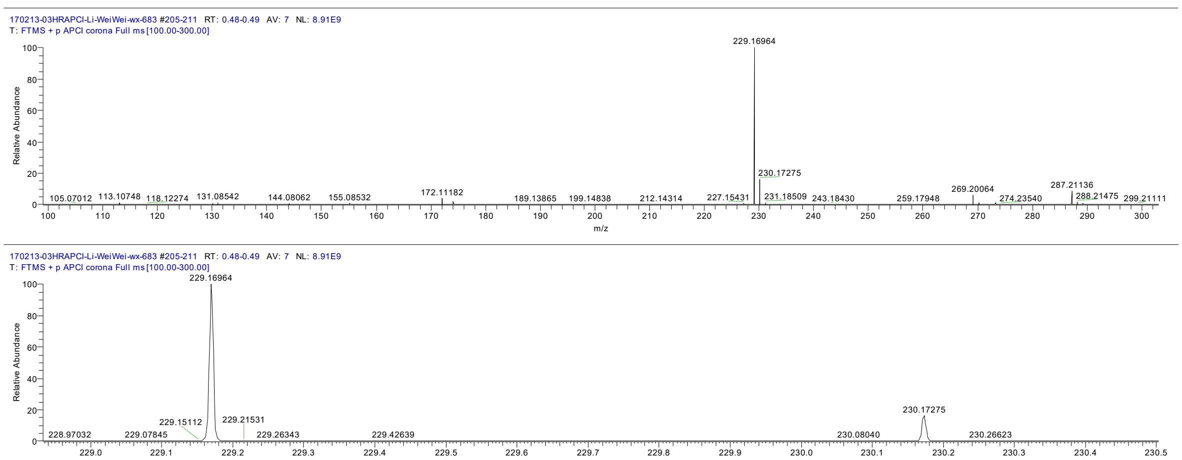




1-(4-phenylcyclohexylidene)-2-propylidenehydrazin  (56%yield),

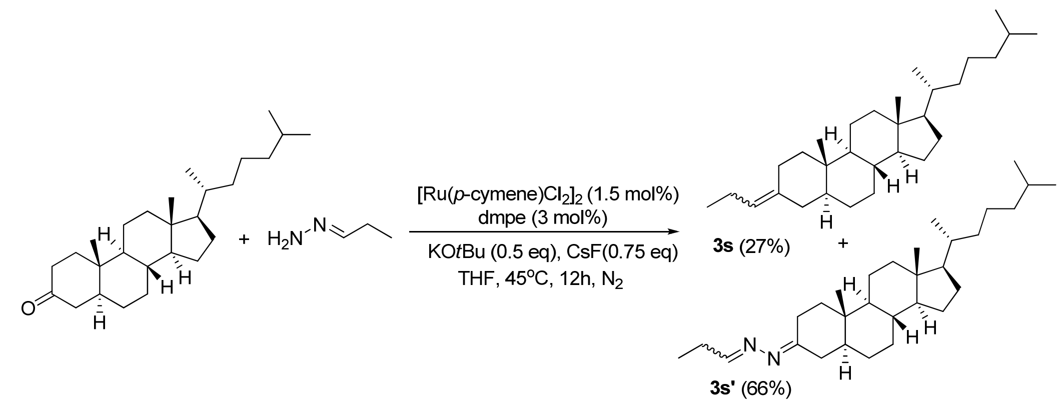
HRMS calc. for $C_{15}H_{21}N_2$ $(M+H)^+$, 229.16993; found, 229.16964.

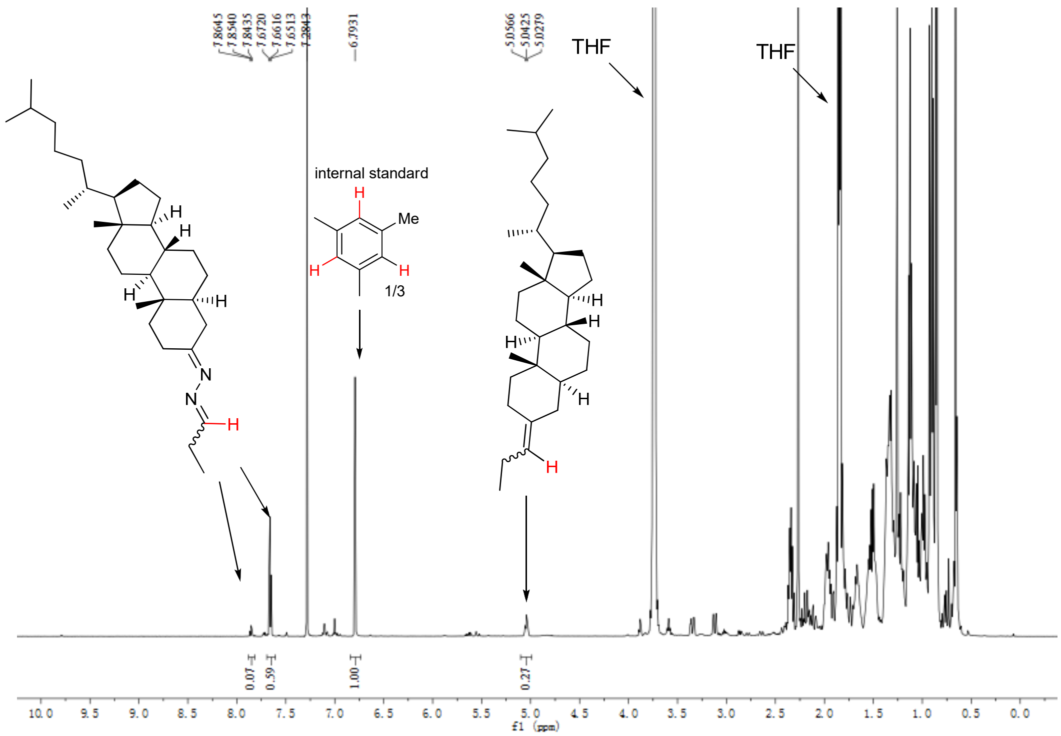
170213-03HRAPCI-Li-WeiWei-wx-683 2/13/2017 11:22:35 AM



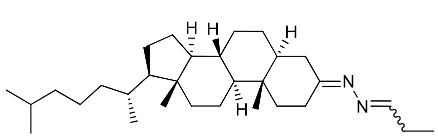
170213-03HRAPCI-Li-WeiWei-wx-683#205-211 RT: 0.48-0.49 AV: 7
T: FTMS + p APCI corona Full ms [100.00-300.00]
m/z= 229.15931-229.18177

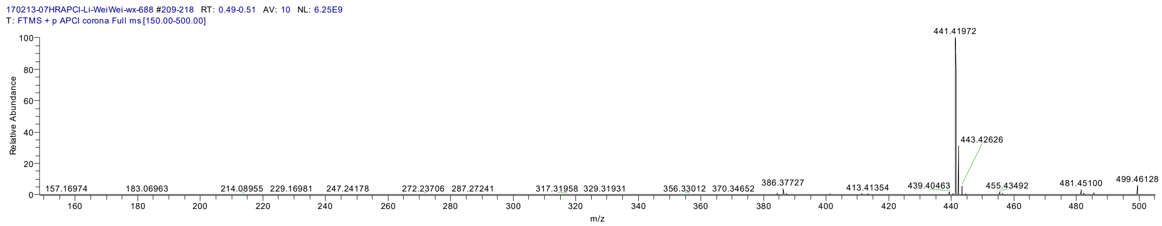
m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
229.16964	8991578112.0	100.00	35657.69	1.00	229.16993	-1.23	6.5	$C_{15}H_{21}N_2$

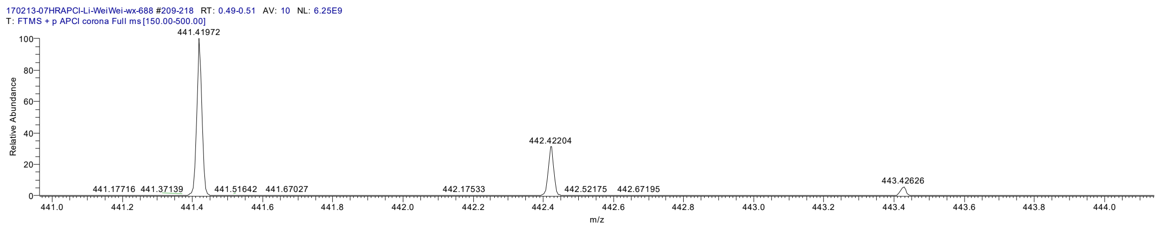




1-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexahydro-1H-cyclopenta[a]phenanthren-3(2H,4H,10H,12H,13H,14H,15H,16H,17H)-ylidene)-2-propylidenehydrazine

 (66%yield), HRMS calc. for $C_{30}H_{53}N_2$ $(M+H)^+$, 441.42033; found, 441.41972.





170213-07HRAPCI-Li-WeiWei-wx-688#209-218 RT: 0.49-0.51 AV: 10
T: FTMS + p APCI corona Full ms [150.00-500.00]
m/z= 441.39345-441.45088

m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
441.41972	6253150720.0	100.00	26389.25	1.00	441.42033	-1.36	5.5	$C_{30}H_{53}N_2$
					441.41765	4.71	1.0	$C_{27}H_{55}O_3N$