Supporting Information

Photocatalytic Dual Decarboxylative Alkenylation Mediated by Triphenylphosphine and Sodium Iodide

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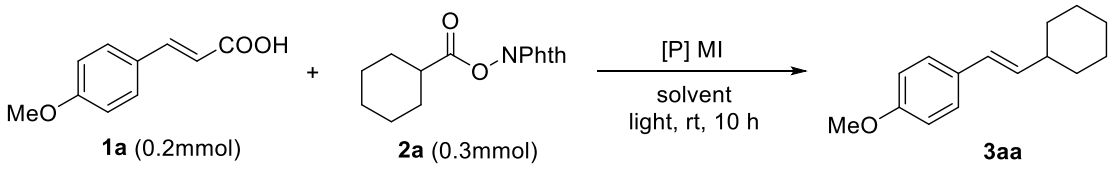
List of Contents

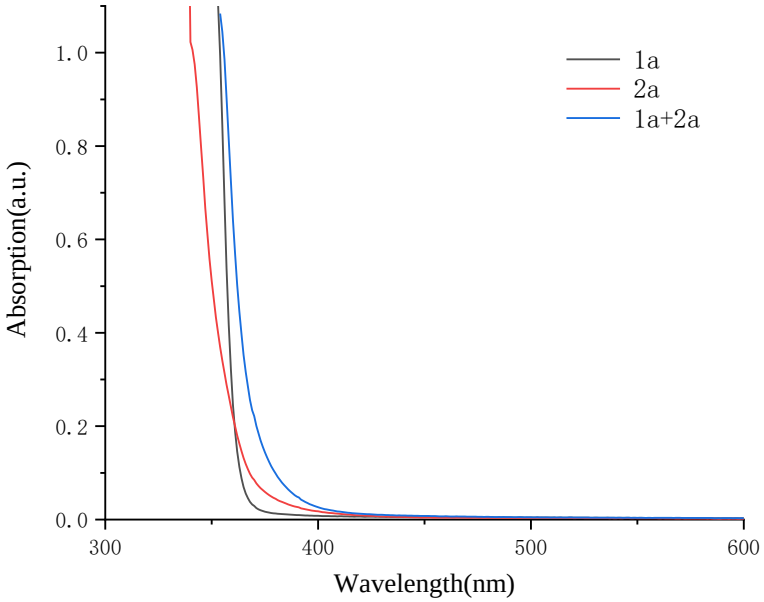
(A) Screening of optimal reaction conditions[a]

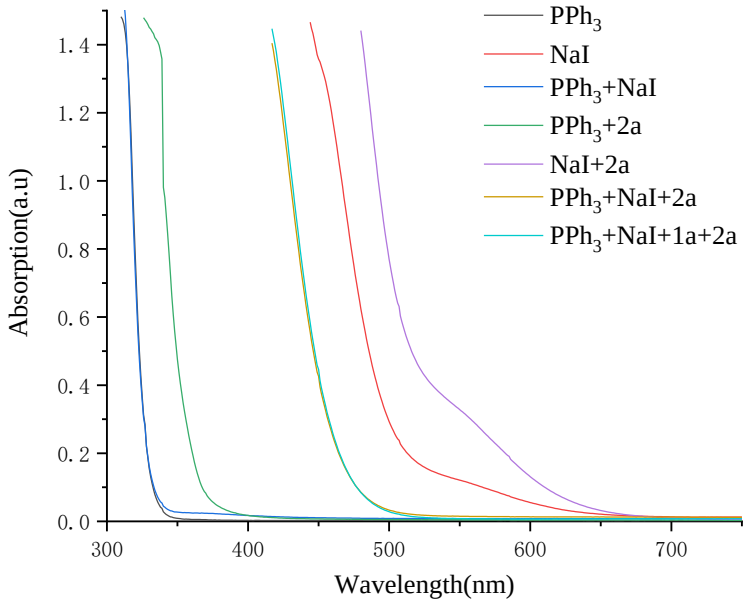


entry	MI	[P]	solvent	light(nm)	yield [%]
1	NaI	PPh_3	DMA	456	90
2	NaI	PPh_3	DMSO	456	62
3	NaI	PPh_3	DMF	456	60
4	NaI	PPh_3	1,4-dioxane	456	43
5	NaI	PPh_3	MeCN	456	35
6	LI	PPh_3	DMA	456	40
7	KI	PPh_3	DMA	456	57
8	*n*-Bu_4NI	PPh_3	DMA	456	60
9	NaI	$P(4\text{-}OMeC_6H_4)_3$	DMA	456	81
10	NaI	$P(4\text{-}FC_6H_4)_3$	DMA	456	84
11	NaI	PCy_3	DMA	456	33
12	NaI	PPh_3	DMA	395	34
13	--	PPh_3	DMA	456	0
14	NaI	--	DMA	456	0
15	NaI	PPh_3	DMA	--	0
16[b]	NaI	PPh_3	DMA	456	52
17[c]	NaI	PPh_3	DMA	456	85

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), NaI (1.5 equiv), PPh_3 (20 mol%), DMA (2 mL), room temperature, argon, and 10 h. *E/Z* was determined by ^{1}HNMR analysis of the crude mixture. [b] NaI (20 mol%). [c] **1a** (1.07 g) and 36 h.

(B) UV-Vis absorption spectra of reactant mixtures



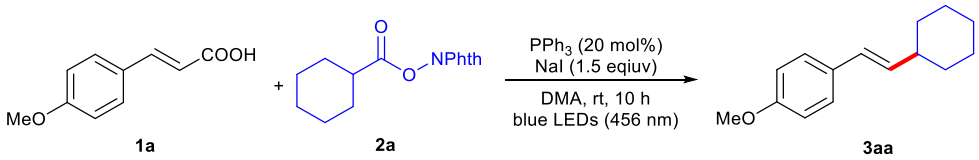


(C) Typical experimental procedure

(a) General

The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ solvents on a NMR spectrometer using TMS as the internal standard. LRMS was performed on a GC-MS instrument, and HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected.

(b) General procedure for synthesis of compound 3aa.



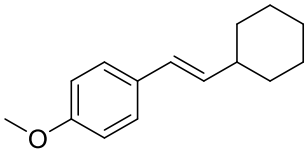
To a Schlenk tube were added substrates **1a** (0.2 mmol), **2a** (0.3 mmol), NaI (1.5 equiv), PPh_3 (20 mol%) and DMA (2 mL), the tube was then charged with argon. The mixture was stirred under blue light irradiation at a temperature of 25℃ until complete consumption of starting material as monitored by TLC and/or GC-MS analysis (about 10 h). After the reaction was finished, the reaction mixture was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford the desired product.

Substrate **1a** (0.2 mmol), **2a** (0.3 mmol), NaI (1.5 equiv), PPh_3 (20 mol%) and DMA (2 mL) were added to the Schlenk tube, and then the tube was filled with argon gas. Place the mixture at room temperature under 18W blue light irradiation and stir in an oil bath. In order to get enough blue light for the reaction, a layer of tin foil should be laid in the pot, and after fixing the reaction device, a circle of tin foil should also be wrapped on the outside. Until the complete consumption of raw materials is monitored by TLC and/or GC-MS analysis (about 10 hours).

Gram reaction： To a Schlenk tube were added substrates **1a** (1.07 g), **2a** (2.46 g), NaI (1.5 equiv), PPh_3 (20 mol%) and DMA (30 mL), the tube was then charged with argon. The mixture was stirred at room temperature until complete consumption of starting material as monitored by TLC and/or GC-MS analysis (about 36 h). After the reaction was finished, the reaction mixture was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (Petroleum ether/ethyl acetate) to afford the desired product **3aa** (85%, 1.10 g).

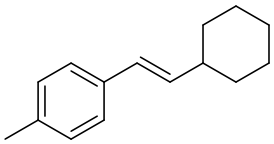
（D）Analytical data

(*E*)-1-(2-cyclohexylvinyl)-4-methoxybenzene (3aa):



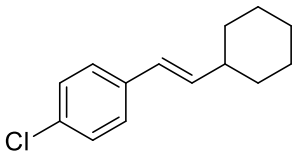
38.9 mg, 90% yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.28 (d, *J* = 16.0 Hz, 1H), 6.03 (dd, *J* = 16.0, 7.0 Hz, 1H), 3.79 (s, 3H), 2.14-2.06 (m, 1H), 1.82-1.73 (m, 4H), 1.70-1.63 (m, 1H), 1.33-1.27 (m, 2H), 1.20-1.13 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 134.8, 130.9, 127.0, 126.5, 113.9, 55.3, 41.1, 33.1, 26.1. LRMS (EI, 70eV) *m/z* (%): 216 (71), 159 (29), 121 (100), 91 (35); HRMS *m/z* (ESI) calcd for $C_{15}H_{21}O([M+H]^+)$ 217.1587, found 217.1576.

1-(2-Cyclohexylvinyl)-4-methylbenzene (3ba):



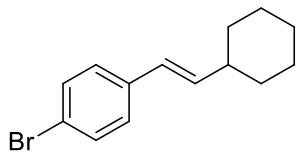
37.2 mg, 93% yield; Colorless liquid; *E*/*Z* = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.5Hz, 2.0H), 7.16 (d, *J* = 8.5 Hz, 0.2H), 7.13 (d, *J* = 8.0 Hz, 0.2H), 7.09 (d, *J* = 8.0 Hz, 2.0H), 6.29 (d, *J* = 16.0 Hz, 1.0H), 6.26 (s, 0.1H), 6.12 (dd, *J* = 16.0, 7.0 Hz, 1.0H), 5.44 (dd, *J* = 11.5, 10.0 Hz, 0.1H), 2.34 (s, 1.0H), 2.31 (s, 3.0H), 2.13-2.07 (m, 1.0H), 1.81-1.80 (m, 1.0H), 1.78-1.74 (m, 4.0H), 1.69-1.65 (m, 1.0H), 1.35-1.29 (m, , 2.0H), 1.21-1.15 (m, 3.0H).^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 136.4, 135.8 , 135.2 , 129.1 , 128.9 , 128.5, 127.0, 126.6, 125.8, 41.1, 36.9, 33.3, 33.0, 26.1,25.7, 21.1. LRMS (EI, 70eV) *m/z* (%): 200 (38), 143 (23), 118 (100), 105 (26); HRMS *m/z* (ESI) calcd. for $C_{15}H_{21}$ ($[M+H]^+$) 201.3325, found 201.3334.

1-chloro-4-(2-Cyclohexylvinyl)benzene (3ca):



35.7 mg, 81% yield; Colorless liquid; *E*/*Z* = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.5 Hz, 0.2H), 7.27-7.23 (m, 4.0H), 7.17 (d, *J* = 8.5 Hz, 0.2H), 6.28 (d, *J* = 16.0 Hz, 1.0H), 6.25 (d, *J* = 12.0 Hz, 0.1H), 6.15 (dd, *J* = 16.0, 7.0 Hz, 1.0H), 5.53- 5.47 (m, 0.1H), 2.52-2.46 (m, 0.1H), 2.15-2.08 (m, 1.0H), 1.81-1.74 (m, 4.0H), 1.68 (d, *J* = 13.0 Hz, 2.0H), 1.34-1.25 (m, 3.0H), 1.21-1.14 (m, 3.0H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5, 136.5, 132.2, 129.8, 128.5, 128.3, 127.1, 126.1, 41.1, 33.1, 32.8, 26.0, 25.6. LRMS (EI, 70eV) *m/z* (%): 220 (22), 138 (100), 185 (7), 129 (24); HRMS *m/z* (ESI) calcd. for $C_{14}H_{18}Cl$($[M+H]^+$) 221.7475, found 221.7453.

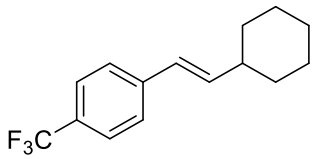
1-bromo-4-(2-Cyclohexylvinyl)benzene (3da):



40.3 mg, 76% yield; Colorless liquid; *E*/*Z* = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 0.4H), 7.39 (d, *J* = 8.5 Hz, 2.0H), 7.20 (d, *J* = 8.5 Hz, 2.0H), 7.11 (d, *J* = 8.5 Hz, 0.4H), 6.27 (d, *J* = 16.0 Hz, 1H), 6.23 (d, *J* = 12.0 Hz, 0.1H), 6.16 (dd, *J* = 16.0, 7.0 Hz, 1H), 5.51 (dd, *J* = 11.5, 10.5 Hz, 0.2H), 2.50-2.48 (m, 1.0H), 2.15-2.07 (m, 1.0H), 1.80-1.71 (m, 6.0H), 1.33-1.27 (m, 2.0H), 1.24-1.13 (m, 4.0H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7, 137.7, 137.0, 131.5, 131.2, 130.2, 127.5, 126.1, 125.7, 120.3, 41.1, 36.9, 33.1, 32.8 26.1, 25.6. LRMS (EI, 70eV) *m/z* (%): 265 (5), 182 (100), 142

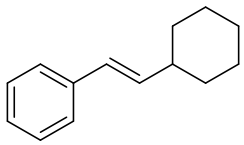
(26), 128 (48); HRMS *m/z* (ESI) calcd. for $C_{14}H_{18}Br$ ($[M+H]^+$) 266.2015, found 266.2006.

1-(2-Cyclohexylvinyl)-4-(trifluoromethyl)benzene (3ea):



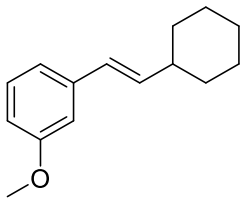
44.7 mg, 88% yield; Colorless liquid; *E*/*Z* = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 0.4H), 7.52 (d, *J* = 8.0 Hz, 2.0H), 7.42 (d, *J* = 8.0 Hz, 2.0H), 7.34 (d, *J* = 8.0 Hz, 0.4H), 6.36 (d, *J* = 16.0 Hz, 1.0H), 6.32 (d, *J* = 11.5 Hz, 0.2H), 6.27 (dd, *J* = 16.0, 6.5 Hz, 1.0H), 5.59 (dd, *J* = 11.5, 10.5 Hz, 0.2H), 2.53-2.49 (m, 0.2H), 2.19-2.11 (m, 1.0H), 1.83-1.75 (m, 4.0H), 1.74-1.66 (m, 2.0H), 1.34-1.25 (m, 3.0H), 1.22-1.16 (m, 3.0H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.5, 141.0, 139.6, 128.7, 128.4, 126.1, 125.4, 125.1, 41.2, 37.0, 33.1, 32.7, 29.7, 26.0, 25.6. ^{19}F NMR (500 MHz, $CDCl_3$) δ -62.34,-62.38. LRMS (EI, 70eV) *m/z* (%): 254 (27), 172 (100), 129 (39), 82 (73); HRMS *m/z* (ESI) calcd.for $C_{15}H_{18}F_3$ ($[M+H]^+$) 255.1355, found 255.1346.

(*E*)-(2-Cyclohexylvinyl)benzene (3fa):



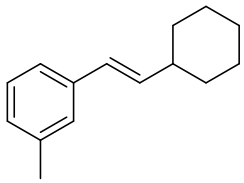
30.9 mg, 84% yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.0 Hz, 1H), 6.34 (d, J = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 7.0 Hz, 1H), 2.14-2.10 (m, 1H), 1.83-1.68 (m, 5H), 1.34-1.27 (m, 2H), 1.22-1.15 (m, 3H). ^{13}C NMR (125 MHz, CDCl3) δ 138.0, 136.9, 128.4, 127.2, 126.7, 125.9 , 41.1, 32.9, 26.1. LRMS (EI, 70eV) *m/z* (%): 186 (93), 143 (38), 104 (100), 95 (42); HRMS *m/z* (ESI) calcd. for $C_{14}H_{19}$ ($[M+H]^+$) 187.3655, found 187.3561.

(*E*)-1-(2-Cyclohexylvinyl)-3-methoxybenzene (3ga):



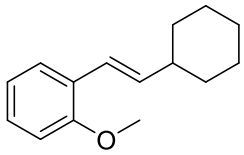
40.0 mg, 74% yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (t, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.87 (s, 1H), 6.72 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 6.15 (dd, *J* = 16.0, 7.0 Hz, 1H), 3.79 (s, 3H), 2.11-2.08 (m, 1H), 1.81-1.66 (m, 5H), 1.31-1.25 (m, 2H), 1.20-1.10 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 139.5, 137.2, 129.4, 127.1, 118.61 (s), 112.4, 111.2, 55.2, 41.1, 32.9, 26.1. LRMS (EI, 70eV) *m/z* (%): 216 (64), 159 (22), 134 (100), 91 (26); HRMS *m/z* (ESI) calcd for $C_{15}H_{21}O$($[M+H]^+$) 217.1587, found 217.1563.

(*E*)-1-(2-Cyclohexylvinyl)-3-methylbenzene (3ha):



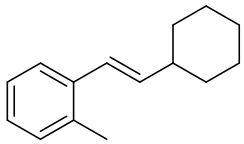
28.0 mg, 70% yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.0 Hz 2H), 7.15 (s, 1H)7.00 (d, *J* = 7.0 Hz, 1H), 6.31 (d, *J* = 16.0 Hz, 1H), 6.18-6.14 (1H), 2.33 (s, 3H), 2.15-2.08 (m, 1H), 1.81-1.74 (m, 4H), 1.69-1.66 (m, 1H), 1.33-1.27 (m, 2H), 1.21-1.16 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 136.7, 128.3, 127.5, 127.2, 126.6, 123.1, 41.2, 32.9, 26.1, 21.4. LRMS (EI, 70eV) *m/z* (%): 200 (30), 143 (19), 118 (100), 91 (24); HRMS *m/z* (ESI) calcd for $C_{15}H_{21}$([M+H]$^+$) 201.3325, found 201.3306.

(*E*)-1-(2-Cyclohexylvinyl)-2-methoxybenzene (3ia):



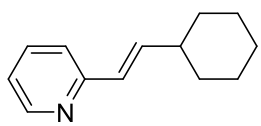
30.7 mg, 71% yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.16 (m, 1H), 6.89 (t, *J* = 7.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.15 (dd, *J* = 16.0, 7.0 Hz, 1H), 3.83 (s, 3H), 2.19-2.09 (m, 1H), 1.86-1.79 (m, 2H), 1.78-1.72 (m, 2H), 1.69-1.64 (m, 1H), 1.33-1.26 (m, 2H), 1.23-1.14 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.2, 137.5, 127.7, 127.0, 126.1, 121.6, 120.6, 110.7, 55.4, 41.6, 33.1, 26.1. LRMS (EI, 70eV) *m/z* (%): 216 (43), 159 (14), 121 (100), 91 (49); HRMS *m/z* (ESI) calcd for $C_{15}H_{21}O$([M+H]$^+$) 217.1587, found 217.1579.

(*E*)-1-(2-Cyclohexylvinyl)-2-methylbenzene (3ja):



26.8 mg, 67% yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 5.0 Hz, 2H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.04 (dd, *J* = 16.0, 7.0 Hz, 1H), 2.33 (s, 3H), 2.18-2.12 (m, 1H), 1.84-1.74 (m, 4H), 1.69-1.67 (m, 1H), 1.35-1.28 (m, 2H), 1.24-1.17 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 137.1, 134.9, 130.1, 126.7, 126.0, 125.3, 124.9, 41.5, 33.1, 26.1, 19.8. LRMS (EI, 70eV) *m/z* (%): 200 (43), 143 (26), 118 (100), 105 (34); HRMS *m/z* (ESI) calcd for $C_{15}H_{21}$([M+H]$^+$) 201.3325, found 201.3332.

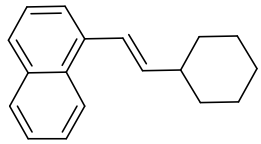
(*E*)-2-(2-Cyclohexylvinyl)pyridine (3ka):



35.5 mg, 95% yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.25

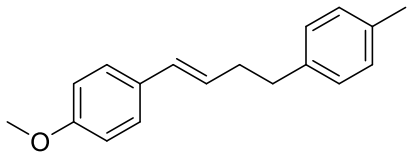
(d, *J* = 8.0 Hz, 1H), 7.09-7.06 (m, 1H), 6.69 (dd, *J* = 16.0, 7.0 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 2.22-2.15 (m, 1H), 1.84-1.66 (m, , 5H), 1.36-1.31 (m, 2H), 1.25-1.21 (m, *3*H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3, 149.3, 141.4, 136.4, 127.3, 121.5, 121.0, 40.9, 32.6, 26.0. LRMS (EI, 70eV) *m/z* (%): 187(75), 186(80), 130(100), 93(75); HRMS *m/z* (ESI) calcd. for $C_{13}H_{18}N([M+H]^+)$ 188.2935, found 188.2927.

(*E*)-1-(2-Cyclohexylvinyl)naphthalene (3la):



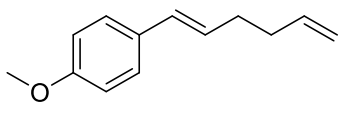
33.5 mg, 71% yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 7.0 Hz, 1H), 7.51-7.38 (m, 3H), 7.07 (d, *J* = 15.5 Hz, 1H), 6.19 (dd, *J* = 15.5, 7.0 Hz, 1H), 2.30-2.20 (m, 1H), 1.89-1.91 (m, Hz, 2H), 1.84-1.77 (m, 2H), 1.72-169 (m, 1H), 1.40-1.33 (m,2H), 1.31-1.22 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 135.9, 133.6, 131.2, 128.4, 127.1, 125.8, 124.3, 123.9, 123.4, 41.5, 33.0, 26.1. LRMS (EI, 70eV) *m/z* (%): 236(75), 186(80), 130(100), 93(75); HRMS *m/z* (ESI) calcd. for $C_{18}H_{21}([M+H]^+)$ 237.3655, found 237.3632.

(*E*)-1-methoxy-4-(4-(*p*-tolyl)but-1-en-1-yl)benzene (3ab):



56.3 mg, 80% yield; White solid; mp 92.3-95.1 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2H), 7.11 (s, 4H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 6.17-6.07 (m, 1H), 3.80 (s, 3H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.48 (dd, *J* = 14.5, 7.0 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 138.8, 135.2, 130.6, 129.6, 129.0, 128.3, 128.0, 127.0, 113.9, 55.3, 35.6, 35.0, 21.0. LRMS (EI, 70eV) *m/z* (%): 252 (12), 147 (100), 115 (16), 91 (24); HRMS *m/z* (ESI) calcd. for $C_{18}H_{21}O([M+H]^+)$353.3645, found 353.3651.

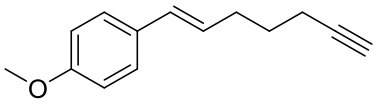
(*E*)-1-(hexa-1,5-dien-1-yl)-4-methoxybenzene (3ac):



30.8mg, 82% yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.11-6.06 (m, 1H), 5.90-5.82 (m, 1H), 5.06 (dd, *J* = 17.0, 1.5 Hz, 1H), 4.99 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 2.31-2.27 (m, 2H), 2.24-2.20 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 138.2, 130.6, 129.5, 128.0,

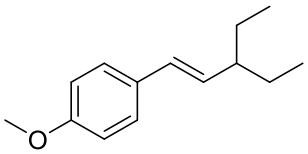
127.0, 114.8, 113.9, 55.3, 33.7, 32.4. LRMS (EI, 70eV) *m/z* (%): 188 (20), 147 (100), 115 (25), 91 (36); HRMS *m/z* (ESI) calcd. for $C_{13}H_{17}O([M+H]^+)$189.2775, found 189.2761.

(*E*)-1-(hept-1-en-6-yn-1-yl)-4-methoxybenzene (3ad):



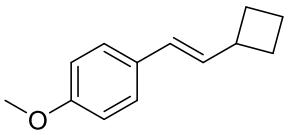
29.2 mg, 73% yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (s, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 6.08-6.02 (m, 1H), 3.80 (s, 3H), 2.33-2.28 (m, 2H), 2.26-2.23 (m, 2H), 1.97 (t, *J* = 2.5 Hz, 1H), 1.70 (dd, *J* = 14.5, 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 130.1, 127.4, 127.1, 113.9, 68.5, 55.3, 31.9, 28.2, 17.8. LRMS (EI, 70eV) *m/z* (%): 200 (50), 172 (75), 115 (70), 91 (100); HRMS *m/z* (ESI) calcd. for $C_{14}H_{17}O([M+H]^+)$201.2885, found 201.2872.

(*E*)-1-(3-Ethylpent-1-en-1-yl)-4-methoxybenzene (3ae):



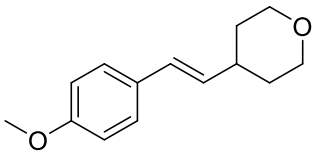
27.7 mg, 68% yield; White solid; mp 108.3-109.6 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.28 (d, *J* = 16.0 Hz, 1H), 5.80 (dd, *J* = 16.0, 9.0 Hz, 1H), 3.80 (s, 3H), 1.94-1.87 (m, 1H), 1.52-1.47 (m, 2H), 1.35-1.29 (m, 2H), 0.88 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 133.1, 130.8, 129.1, 127.0, 113.8, 55.3, 46.8, 27.9, 11.9. LRMS (EI, 70eV) *m/z* (%): 204 (21), 175 (100), 147 (14), 121 (13); HRMS *m/z* (ESI) calcd. for $C_{15}H_{21}O([M+H]^+)$ 205.1587, found 205.1568.

(*E*)-1-(2-Cyclobutylvinyl)-4-methoxybenzene (3af):



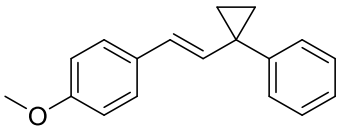
29.3 mg, 78% yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.25 (d, *J* = 16.0 Hz, 1H), 6.18 (dd, *J* = 15.5, 6.5 Hz, 1H), 3.80 (s, 3H), 3.07 (d, *J* = 7.0 Hz, 1H), 2.16 (s, 2H), 1.93 (s, 3H), 1.81 (s, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 133.2, 130.6, 127.0, 113.9, 55.3, 38.8, 28.9, 18.6. LRMS (EI, 70eV) *m/z* (%): 188 (96), 144 (100), 102 (58), 80 (25); HRMS *m/z* (ESI) calcd. for $C_{13}H_{17}O([M+H]^+)$189.2775, found 189.2763.

(*E*)-4-(4-Methoxystyryl)tetrahydro-2H-pyran (3ag):



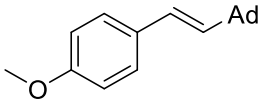
31.8 mg, 73% yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.01 (dd, *J* = 16.0, 7.0 Hz, 1H), 4.01-3.98 (m, 2H), 3.80 (s, 3H), 3.48-3.42 (m, 2H), 2.38-2.31 (m, 1H), 1.70-1.67 (m, 2H), 1.58-1.52 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 132.5, 130.3, 127.6, 127.1, 113.9, 67.7, 55.3, 38.3, 32.7. LRMS (EI, 70eV) *m/z* (%): 218 (85), 173 (85), 121 (100), 110 (81); HRMS *m/z* (ESI) calcd. for $C_{14}H_{19}O_2$([M+H]$^+$) 219.3035, found 219.3025

(*E*)-1-methoxy-4-(2-(1-Phenylcyclopropyl)vinyl)benzene (3ah):



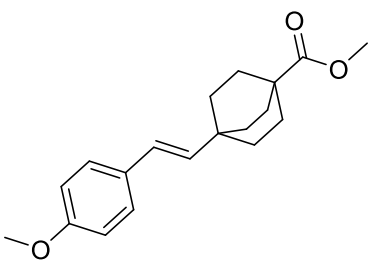
31.0 mg, 62% yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.31 (m, 4H), 7.25 (m, 1H), 7.18 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 6.00 (d, *J* = 16.0 Hz, 1H), 5.89 (d, *J* = 16.0 Hz, 1H), 3.78 (s, 3H), 1.17 (dd, *J* = 6.5, 4.5 Hz, 2H), 1.08 (dd, *J* = 6.5, 4.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.6, 143.5, 135.6, 130.4, 129.9, 128.3, 127.3, 126.9, 126.4, 113.9, 55.3, 28.4, 15.2 . LRMS (EI, 70eV) *m/z* (%): 250 (84), 219 (100), 178 (29), 91 (46); HRMS *m/z* (ESI) calcd. for $C_{18}H_{19}O$([M+H]$^+$) 251.1430, found 251.1459.

(3r,5r,7r)-1-((*E*)-4-Methoxystyryl)adamantine (3ai):



34.8 mg, 65% yield; White solid; mp 102.6-103.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.18 (d, *J* = 16.0 Hz, 1H), 5.97 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 2.02 (s, 3H), 1.76-1.67 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 140.1, 131.0, 127.0, 123.7, 113.9, 55.3, 42.3, 36.9, 35.0, 28.5. LRMS (EI, 70eV) *m/z* (%): 268 (100), 211 (36), 121 (21), 91 (19); HRMS *m/z* (ESI) calcd. for $C_{19}H_{25}O$([M+H]$^+$) 269.4075, found 269.4063.

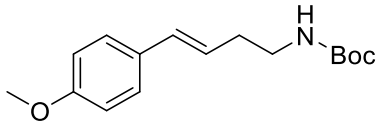
Methyl (*E*)-4-(4-Methoxystyryl)bicyclo[2.2.2]octane-1-carboxylate (3aj):



52.8 mg, 88% yield; White solid; mp 117.0-121.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 7.0, 2.0 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 6.18 (d, *J* = 16.5 Hz,

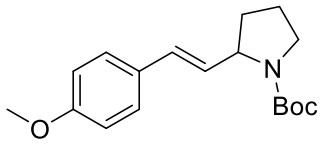
1H), 5.98 (d, *J* = 16.5 Hz, 1H), 3.79 (s, 3H), 3.65 (s, 3H), 1.85-1.82 (m, 6H), 1.63-1.60 (m, 6H).^{13}C NMR (125MHz, $CDCl_3$) δ 178.5, 158.7, 137.1, 130.6, 127.1, 125.1, 113.9, 55.3, 51.7, 39.1, 33.2, 30.8, 28.4. LRMS (EI, 70eV) *m/z* (%): 300 (100), 240 (81), 211 (38), 171 (49); HRMS *m/z* (ESI) calcd. for $C_{19}H_{25}O_3$([M+H]$^+$) 301.4055, found 301.4036.

Tert-butyl (4-(4-Methoxyphenyl)but-3-en-1-yl)carbamate (3ak):



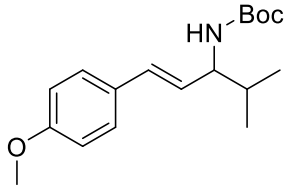
39.9 mg, 72% yield; White solid; mp 90.4-94.5 °C; *E*/*Z* = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.5 Hz, 2.0H), 7.21 (d, *J* = 8.5 Hz, 0.4H), 6.87 (d, *J* = 9.0 Hz, 0.4H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.47 (d, *J* = 11.5 Hz, 0.2H), 6.39 (d, *J* = 16 Hz, 1.0H), 6.03-5.97 (m, 1.0H), 5.55-5.49 (m, 0.2H), 4.61 (s, 1.0H), 3.81 (s, 0.6H), 3.80 (s, 3.0H), 3.27-3.22 (m, 2.0H), 2.54-2.50 (m, 0.4H), 2.40-2.36 (m, 2.0H), 1.44 (s, 2.0H), 1.43 (s, 9.0H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 158.4, 155.9, 131.6, 130.6, 129.9, 127.2, 124.7, 113.9, 113.6, 79.2, 55.3, 40.5, 40.1, 33.5, 28.4. HRMS *m/z* (ESI) calcd. for $C_{16}H_{24}NO_3$([M+H]$^+$)278.3715, found 278.3731.

Tert-butyl (*E*)-2-(4-Methoxystyryl)pyrrolidine-1-carboxylate (3al):



56.1 mg, 93% yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 6.84 (d, *J* = 7.5 Hz, 2H), 6.33 (d, *J* = 15.0 Hz, 1H), 5.94 (s, 1H), 4.51 (s, 1H), 3.80 (s, 3H), 3.45 (s, 2H), 2.06 (d, *J* = 14.5 Hz, 1H), 1.90-1.75 (m, 3H), 1.41 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 154.8, 129.8, 128.9, 128.5, 127.3, 113.9, 79.1, 59.1, 55.2, 46.2, 32.6, 28.5, 23.0. LRMS (EI, 70eV) *m/z* (%): 303 (2), 202 (100), 174 (60), 121 (38); HRMS *m/z* (ESI) calcd. for $C_{18}H_{26}NO_3$([M+H]$^+$) 304.4095, found 304.4089.

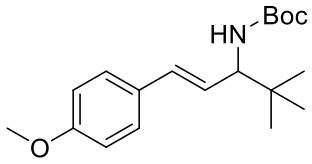
Tert-butyl (*E*)-(1-(4-Methoxyphenyl)-4-methylpent-1-en-3-yl)carbamate (3am):



42.9 mg, 74% yield; White solid; mp 75.0-77.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 5.94 (dd, *J* = 16.0, 6.5 Hz, 1H), 4.60 (s, 1H), 4.11 (s, 1H), 3.80 (s, 3H), 1.86-1.83 (m, 1H), 1.46 (s, 9H), 0.95-0.93 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 155.5, 130.1), 129.7, 127.5, 126.8, 113.9, 79.2, 57.8, 55.3, 32.8, 28.4, 18.8, 18.3. HRMS *m/z*

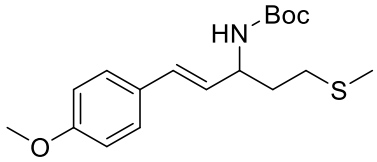
(ESI) calcd. for $C_{18}H_{28}NO_3$([M+H]$^+$)291.3905, found 291.3914.

Tert-butyl (*E*)-(1-(4-Methoxyphenyl)-4,4-dimethylpent-1-en-3-yl)carbamate (3an):



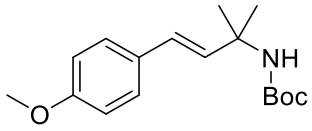
47.9 mg, 75% yield; White solid; mp 115.6-118.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.45 (d, *J* = 15.5 Hz, 1H), 6.00 (dd, *J* = 16.0, 7.0 Hz, 1H), 4.63 (d, *J* = 8.5 Hz, 1H), 4.05 (s, 1H), 3.81 (s, 3H), 1.45 (s, 9H), 0.95 (s, 9H).^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 155.5, 130.8, 129.8, 127.5, 125.4, 113.9, 79.2, 61.1, 55.3, 34.9, 28.4, 26.4. HRMS *m/z* (ESI) calcd. for $C_{19}H_{30}NO_3$([M+H]$^+$) 320.2220, found 320.2232.

Tert-butyl(*E*)-(1-(4-methoxyphenyl)-5-(methylthio)pent-1-en-3-yl)carbamate (3ao):



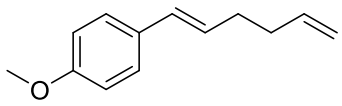
53.9 mg, 80% yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 5.94 (dd, *J* = 16.0, 6.5 Hz, 1H), 4.62 (s, 1H), 4.35 (s, 1H), 3.80 (s, 3H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.12 (s, 3H), 1.93-1.82 (m, 2H), 1.45 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 155.3, 130.2, 129.4, 127.6, 127.4, 114.0, 79.5, 55.3, 52.2, 35.2, 30.6, 28.4, 15.6; HRMS *m/z* (ESI) calcd. for $C_{15}H_{28}NO_3S$([M+H]$^+$)338.4855, found 338.4836.

Tert-butyl (*E*)-(4-(4-Methoxyphenyl)-2-methylbut-3-en-2-yl)carbamate (3ap):



40.7 mg, 70%. yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.22 (d, *J* = 15.5 Hz, 1H), 4.65 (s, 1H), 3.80 (s, 3H), 1.47 (s, 6H), 1.43 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 154.3, 134.0, 129.8, 127.5, 126.1, 113.9, 79.0, 55.2, 53.2, 28.5, 28.1. HRMS *m/z* (ESI) calcd. for $C_{17}H_{26}NO_3$([M+H]$^+$)292.3985, found 292.3973.

(*E*)-1-(hexa-1,5-dien-1-yl)-4-methoxybenzene (3aq):

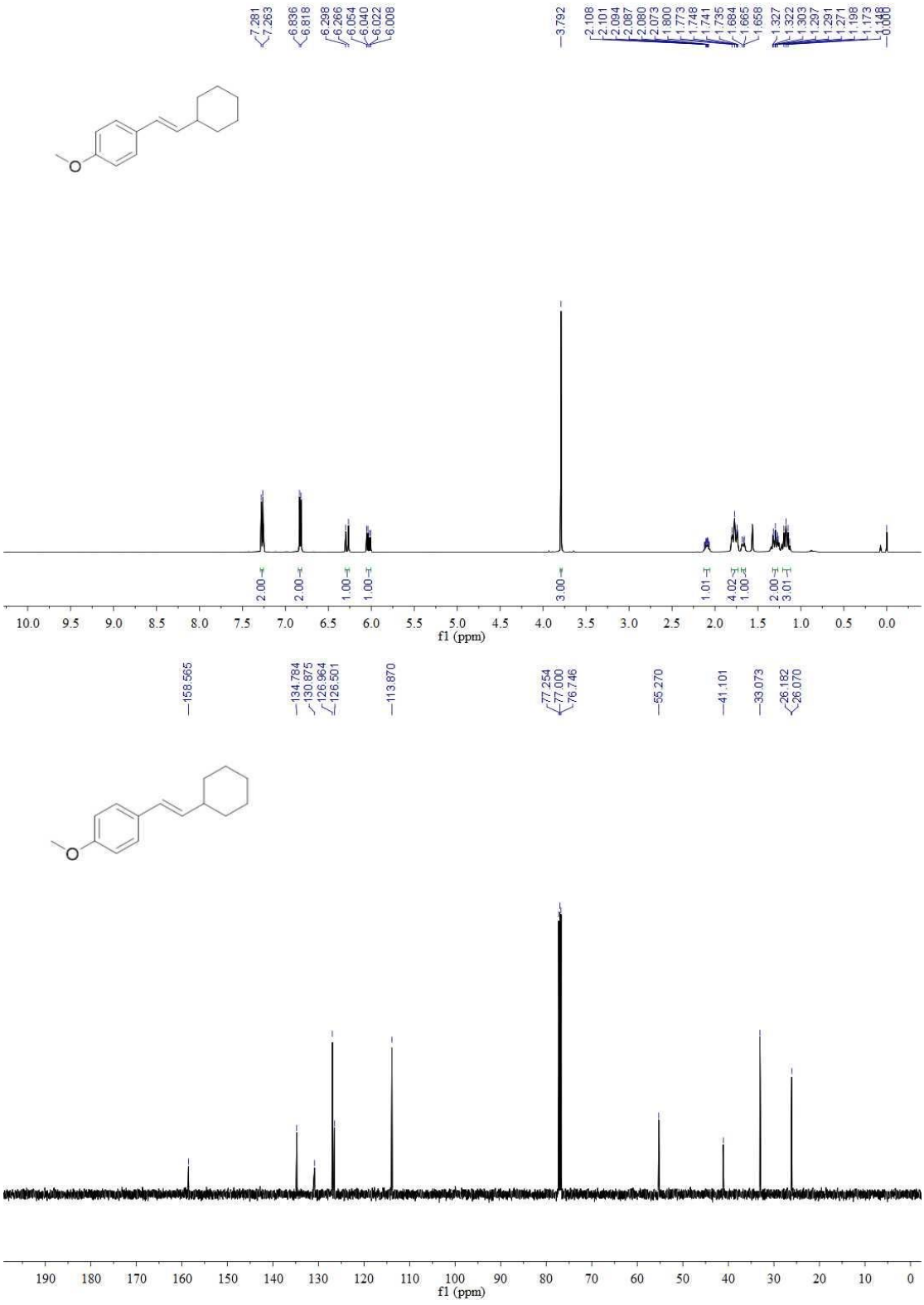


26.3 mg, 70%. yield; Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 5.06 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.91-5.82 (m, 1H),

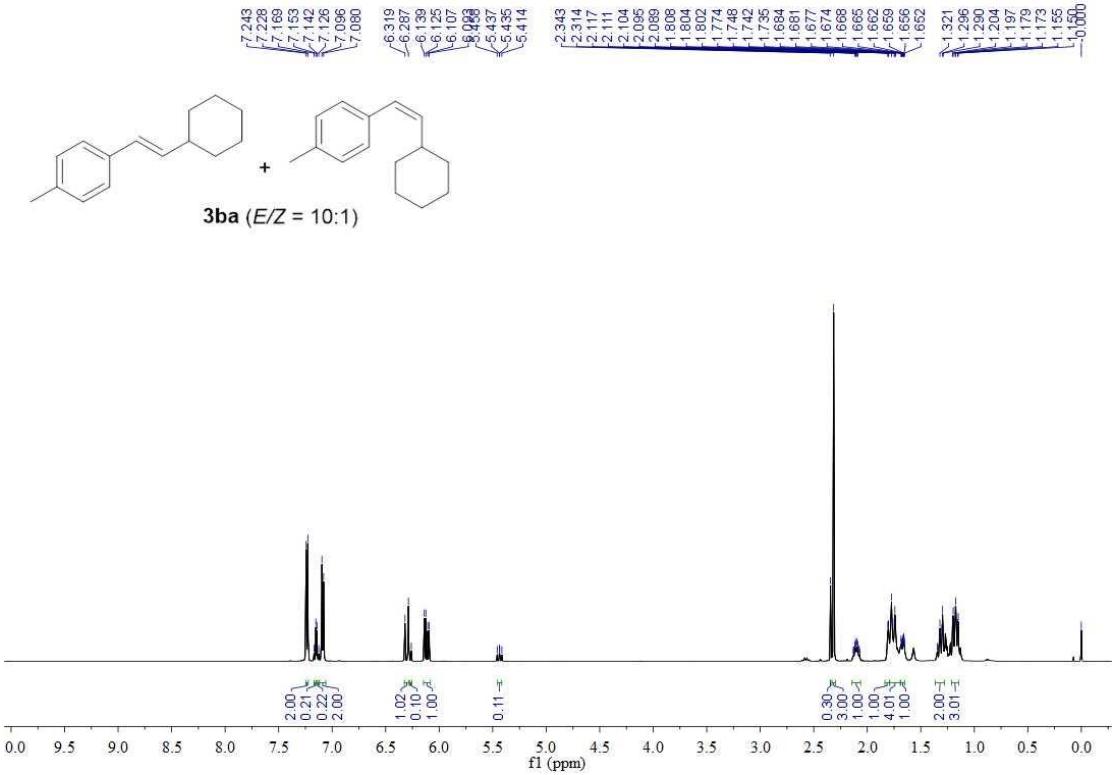
5.08-5.04 (m, 1H), 4.99 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 2.31-2.29 (m, 2H), 2.24-2.20 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 138.3, 130.6, 129.5, 128.0, 127.0, 114.8, 113.9, 55.3 33.7, 32.4. LRMS (EI, 70eV) *m/z* (%): 188 (90), 148 (100), 115 (95), 91 (99); HRMS *m/z* (ESI) calcd. for $C_{13}H_{17}O([M+H]^+)$ 189.2775, found 189.2762.

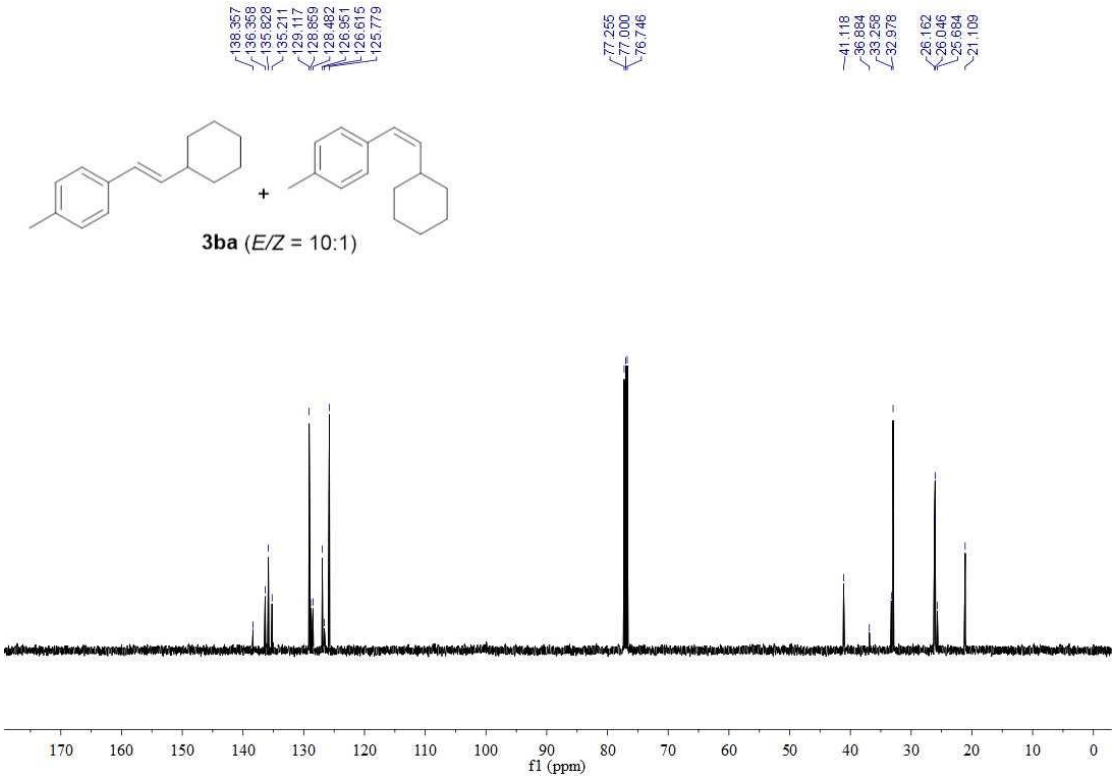
(E) Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra

(*E*)-1-(2-cyclohexylvinyl)-4-methoxybenzene (3aa):

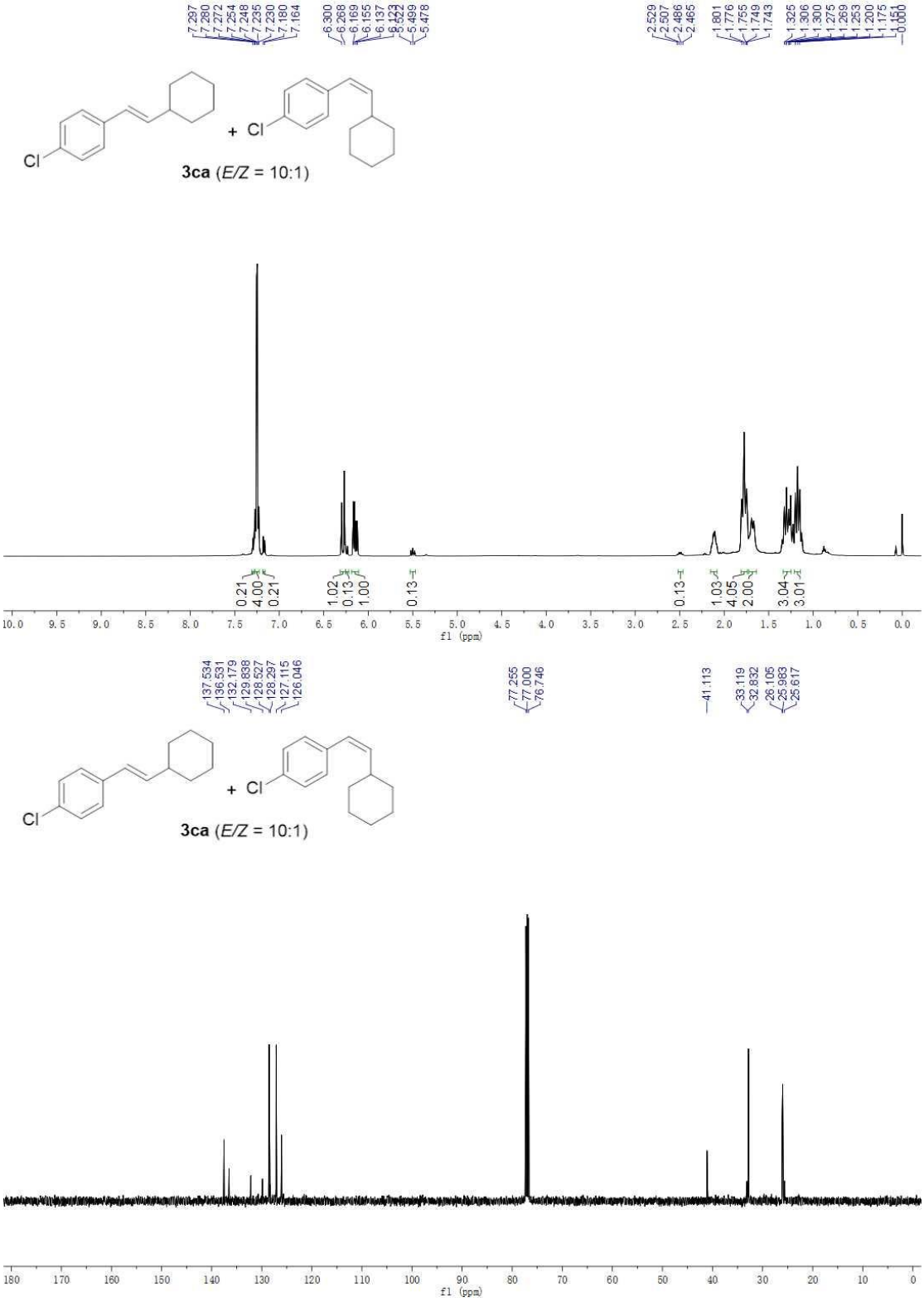


1-(2-Cyclohexylvinyl)-4-methylbenzene (3ba):

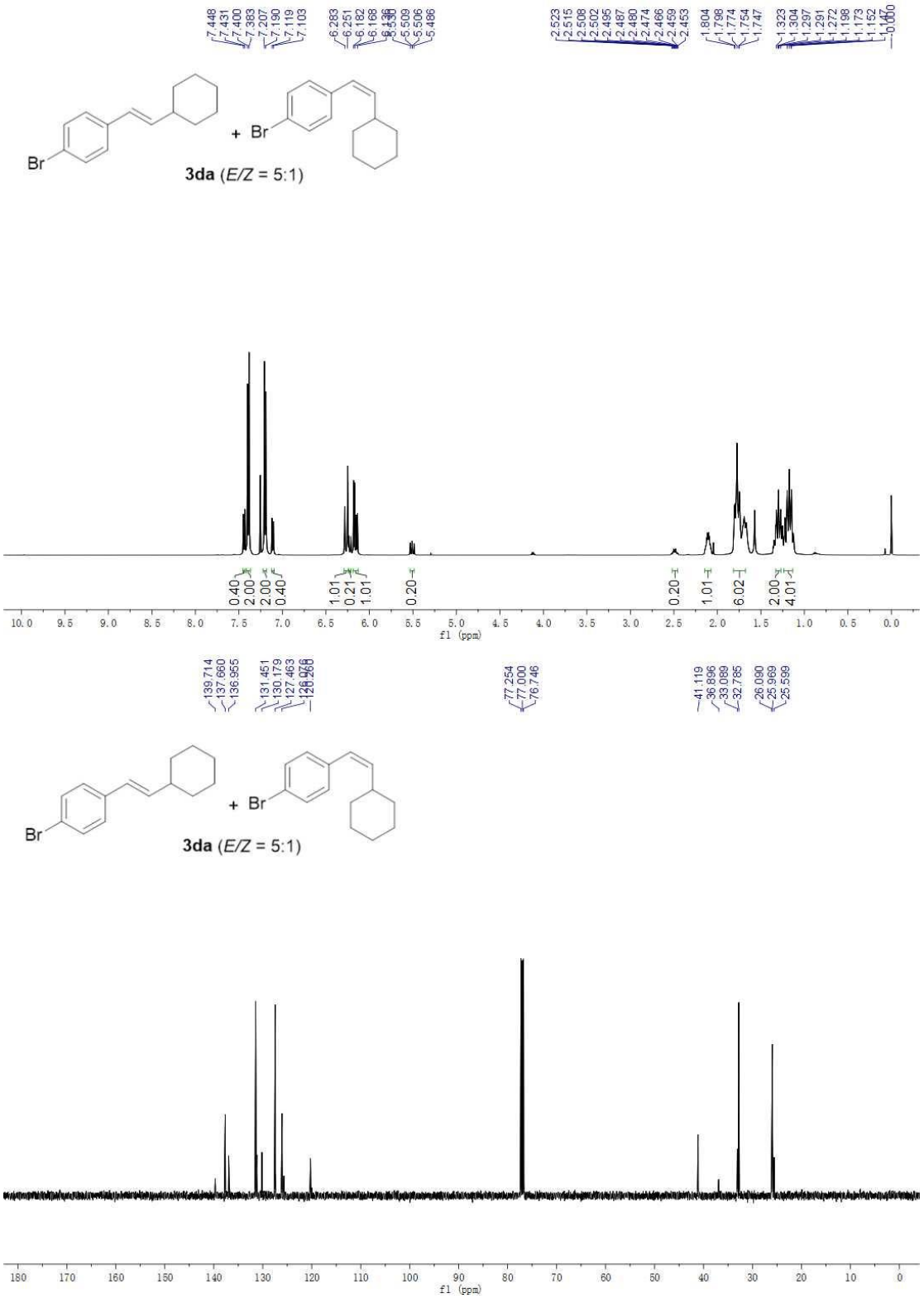




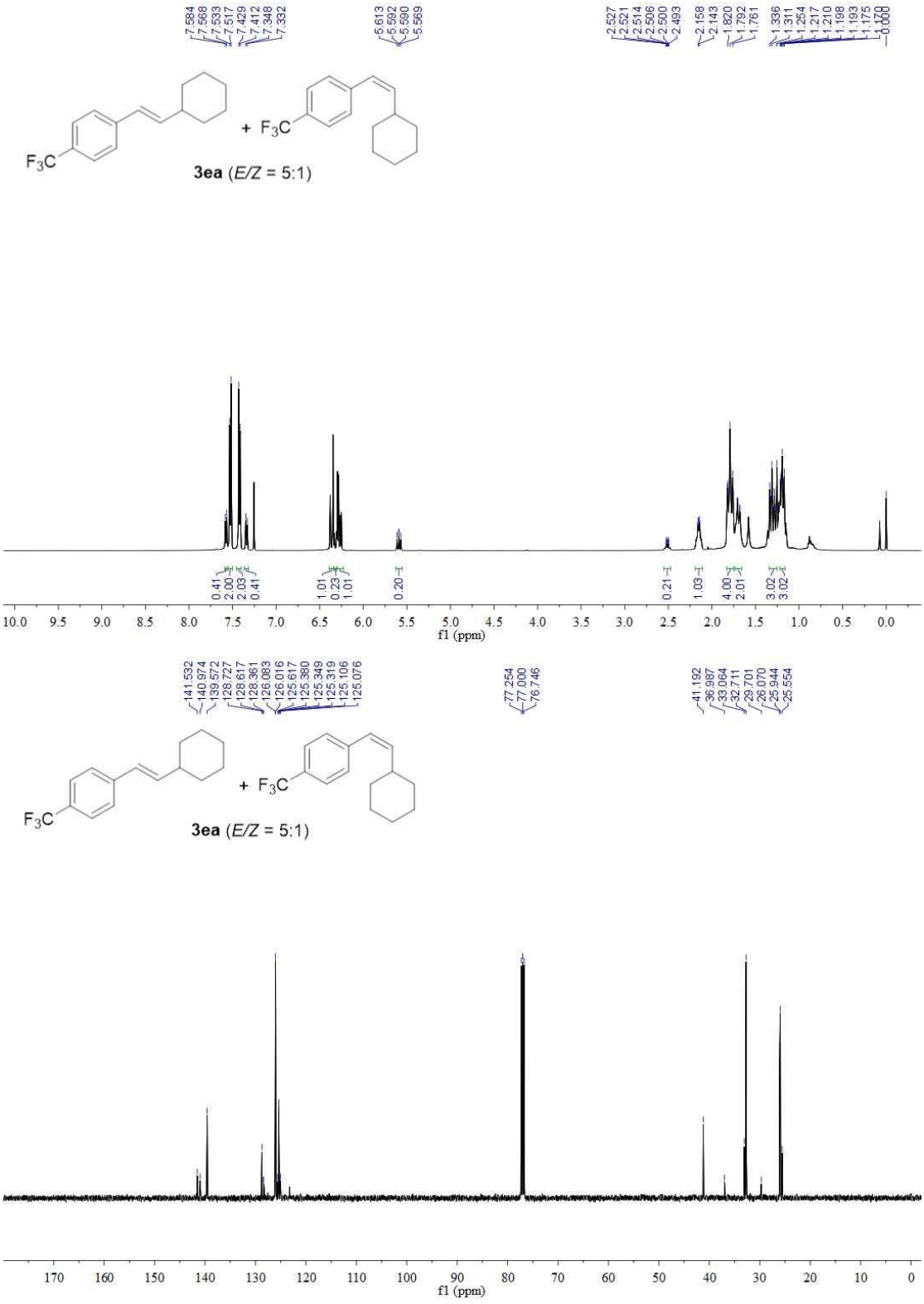
1-chloro-4-(2-Cyclohexylvinyl)benzene (3ca):

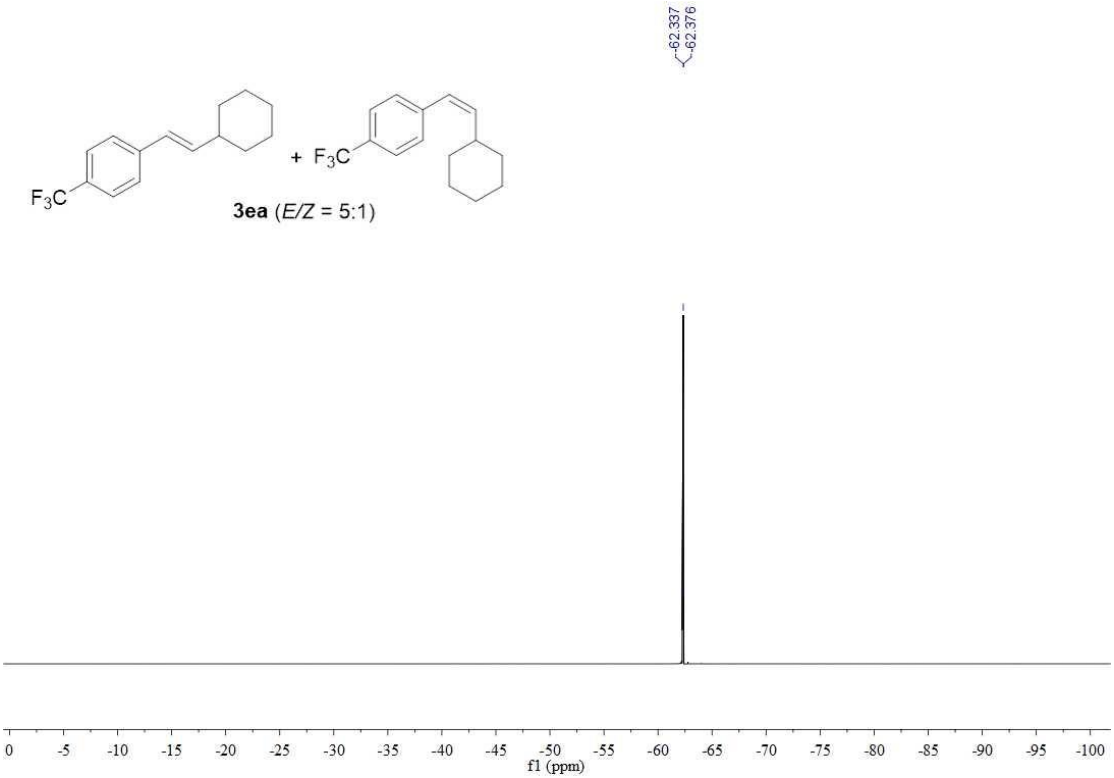


1-bromo-4-(2-Cyclohexylvinyl)benzene (3da):

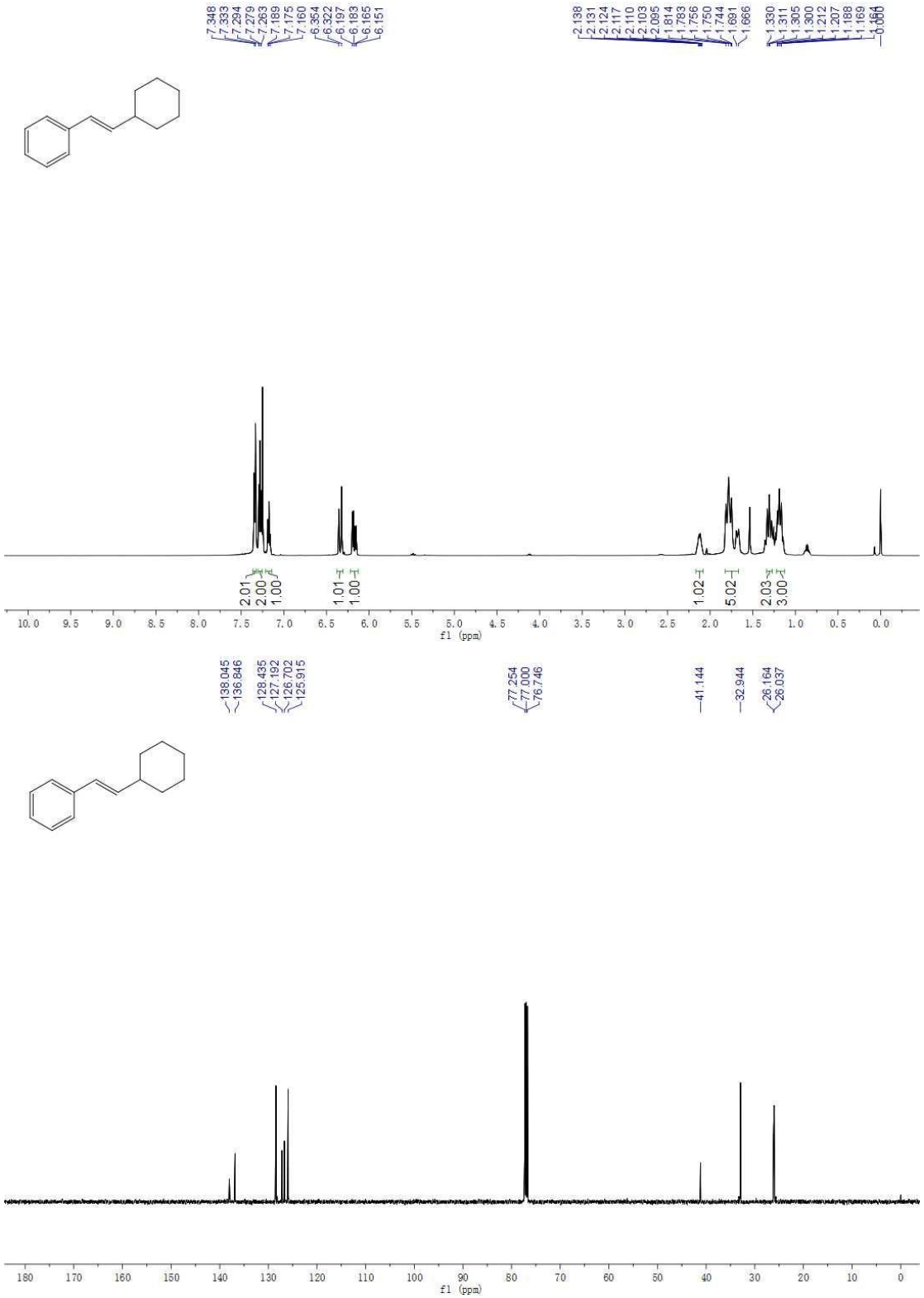


1-(2-Cyclohexylvinyl)-4-(trifluoromethyl)benzene (3ea):

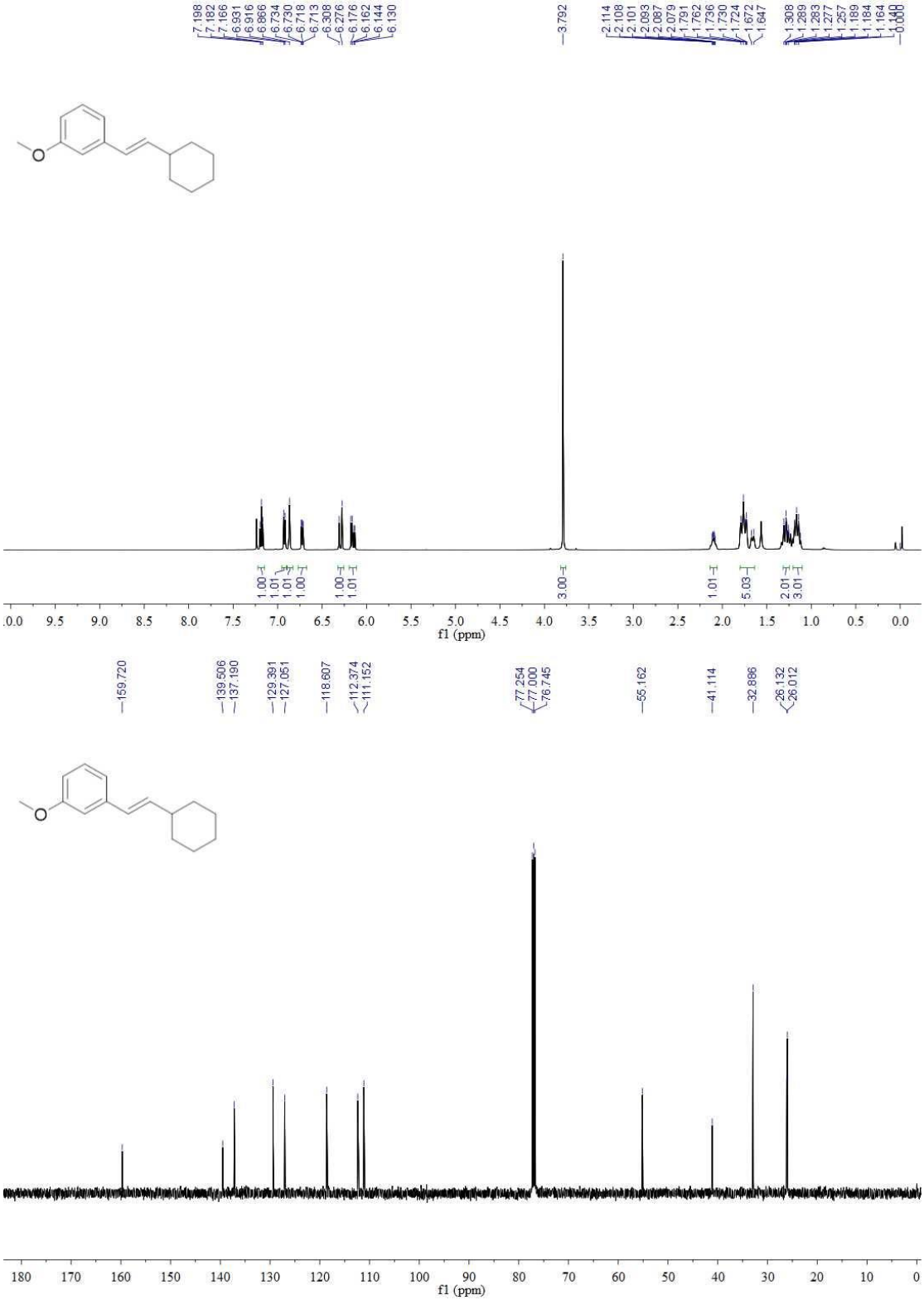



-62.337
-62.376
F3C
+ F3C
3ea (E/Z = 5:1)
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100
f1 (ppm)

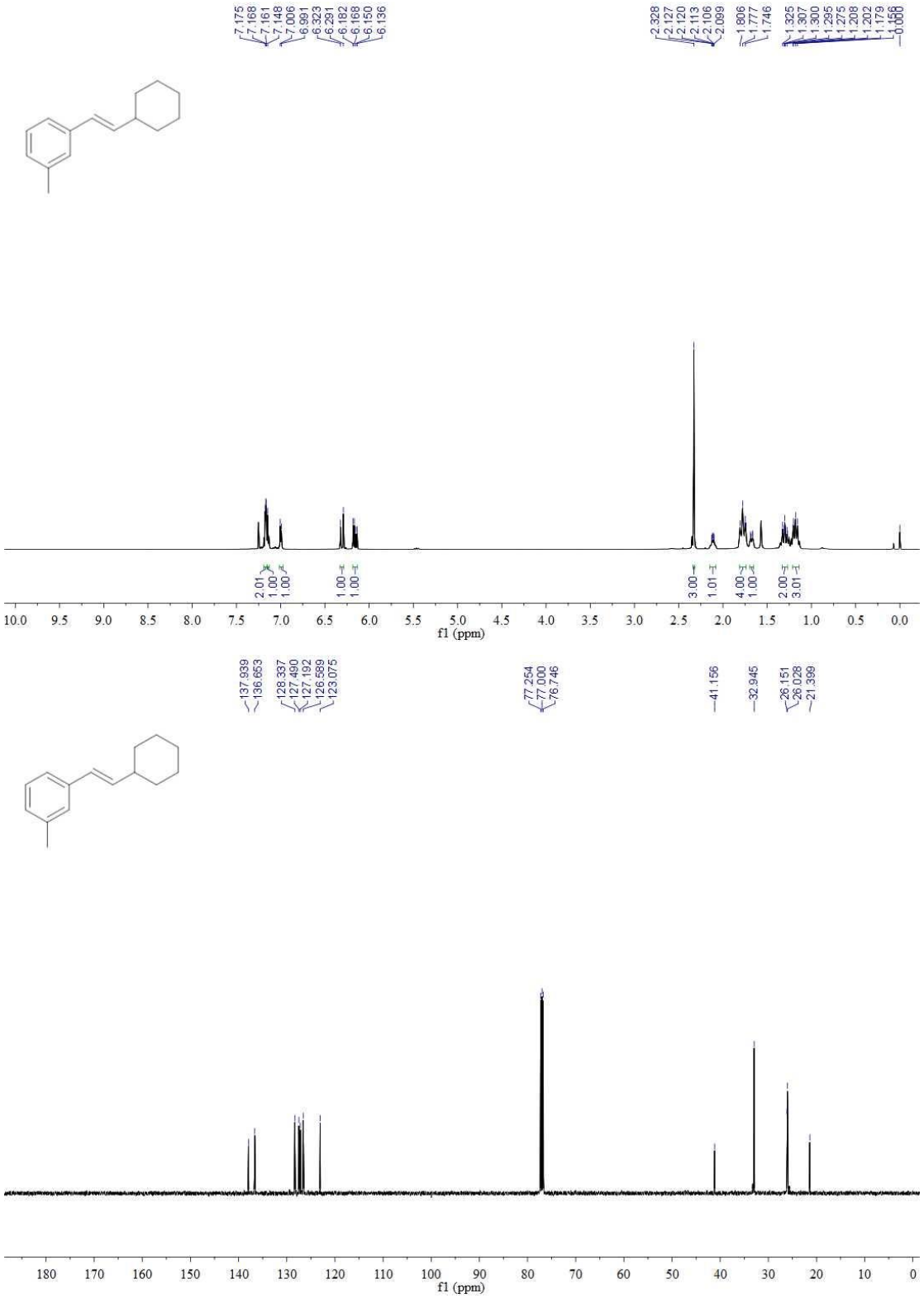
(*E*)-(2-Cyclohexylvinyl)benzene (3fa):



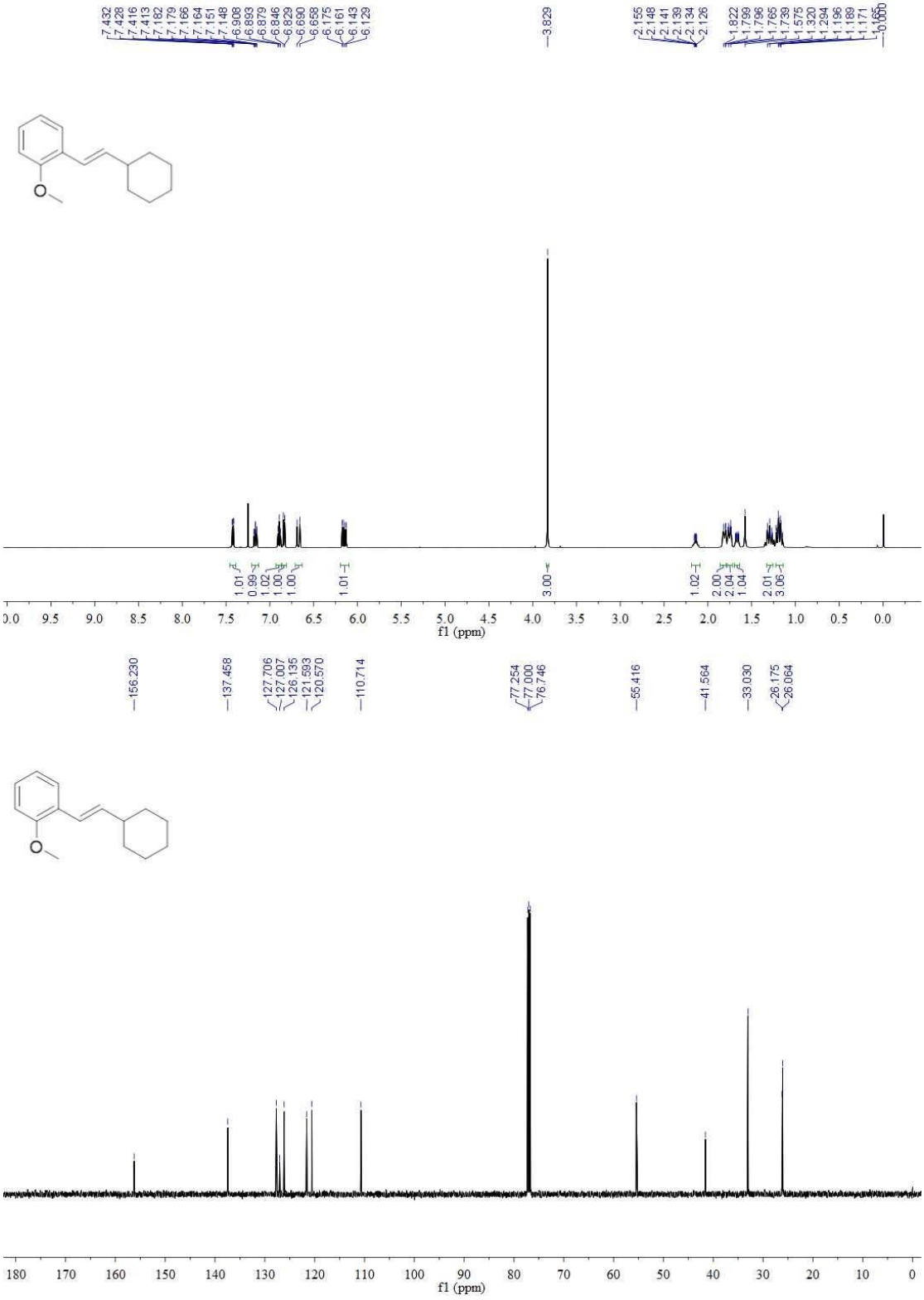
(*E*)-1-(2-Cyclohexylvinyl)-3-methoxybenzene (3ga):



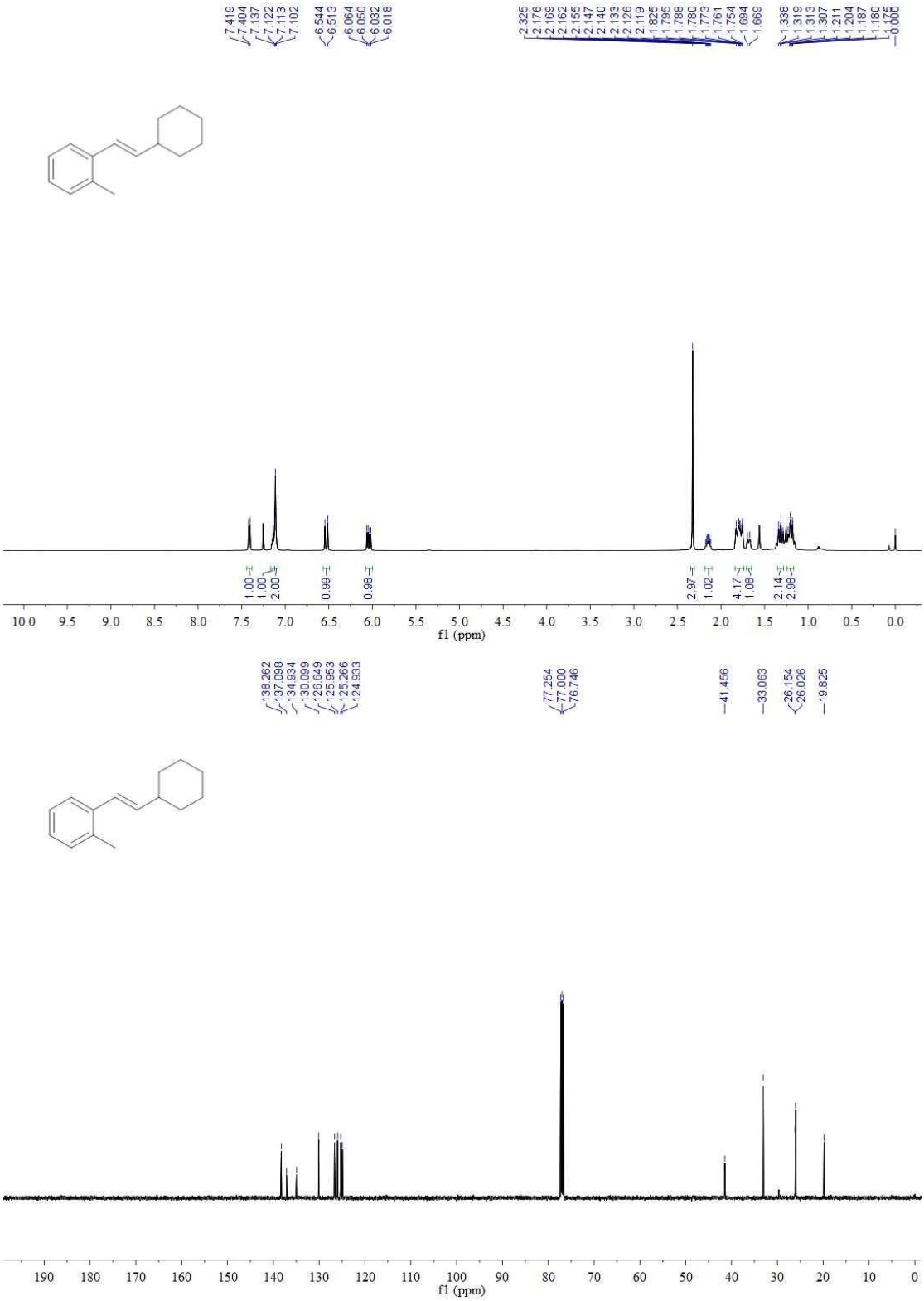
(*E*)-1-(2-Cyclohexylvinyl)-3-methylbenzene (3ha):



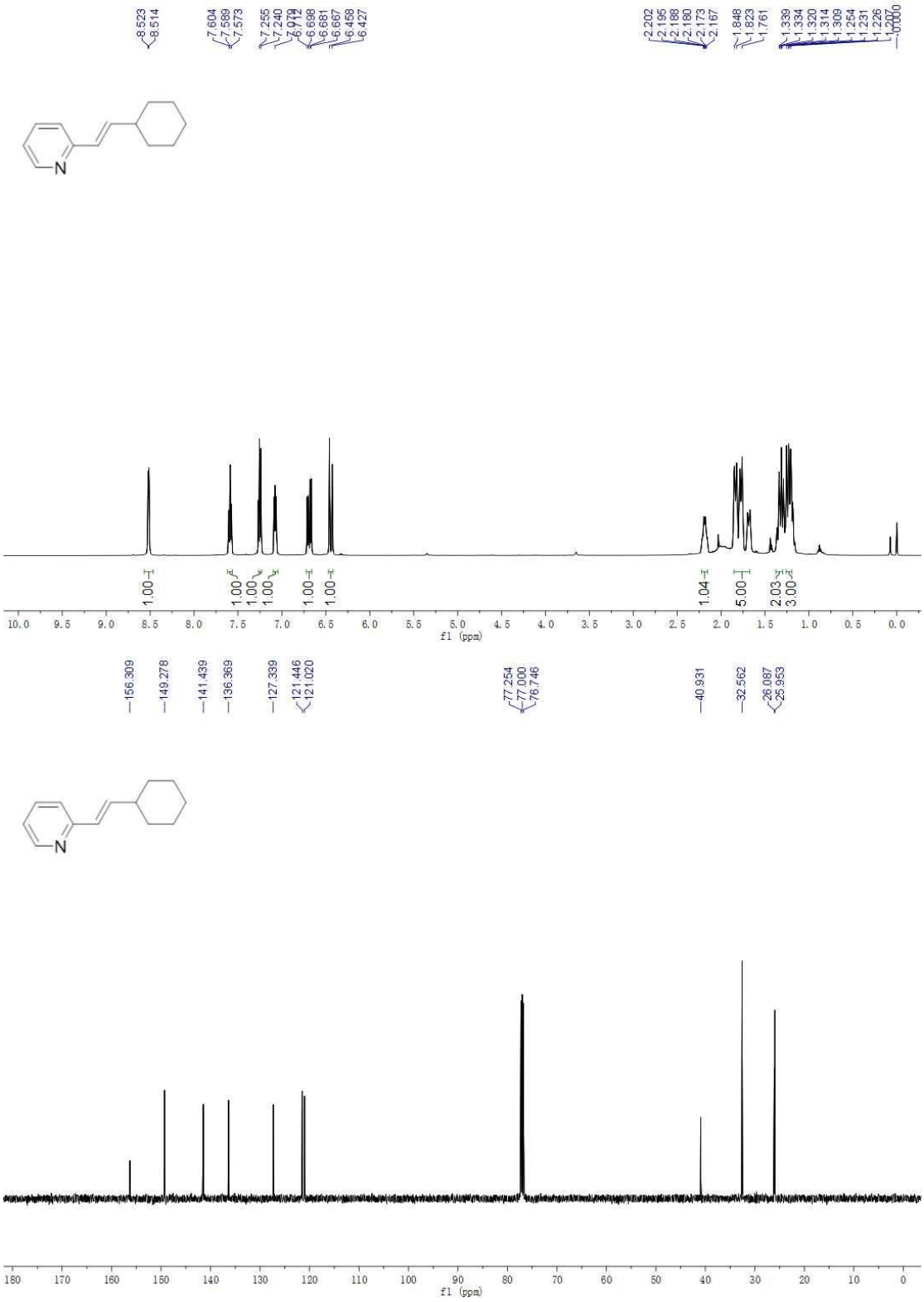
(*E*)-1-(2-Cyclohexylvinyl)-2-methoxybenzene (3ia):



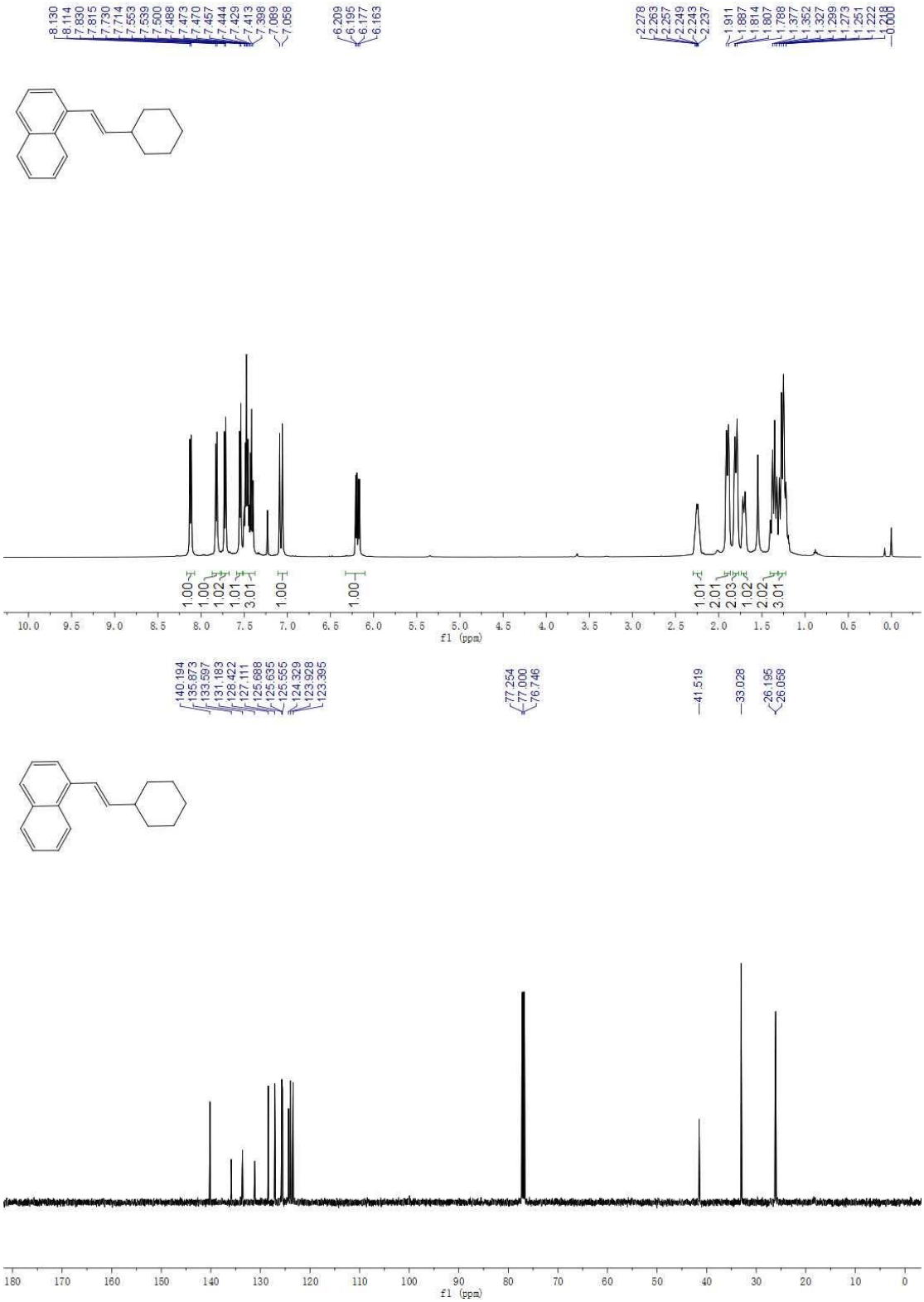
(*E*)-1-(2-Cyclohexylvinyl)-2-methylbenzene (3ja):



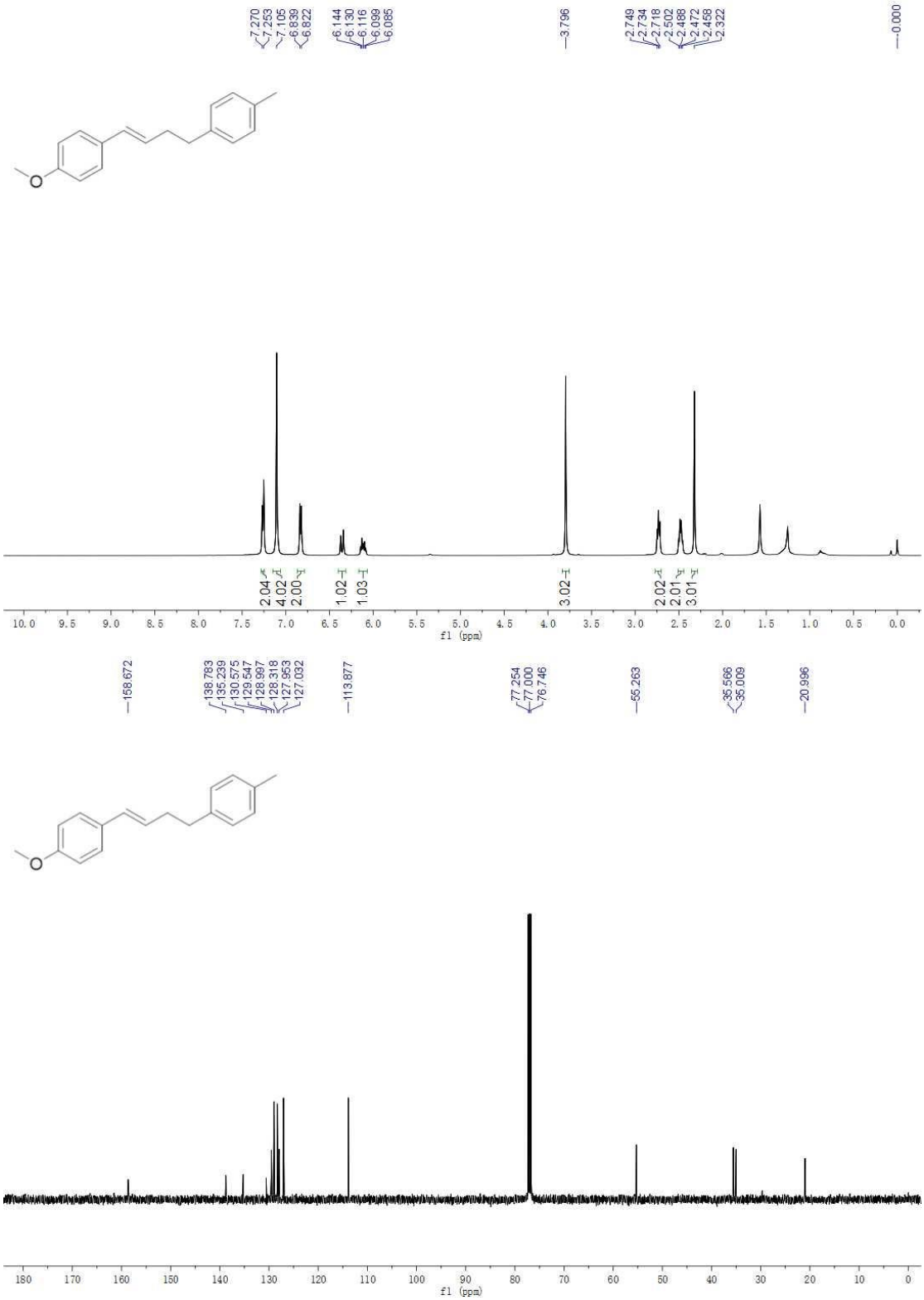
(*E*)-2-(2-Cyclohexylvinyl)pyridine (3ka):



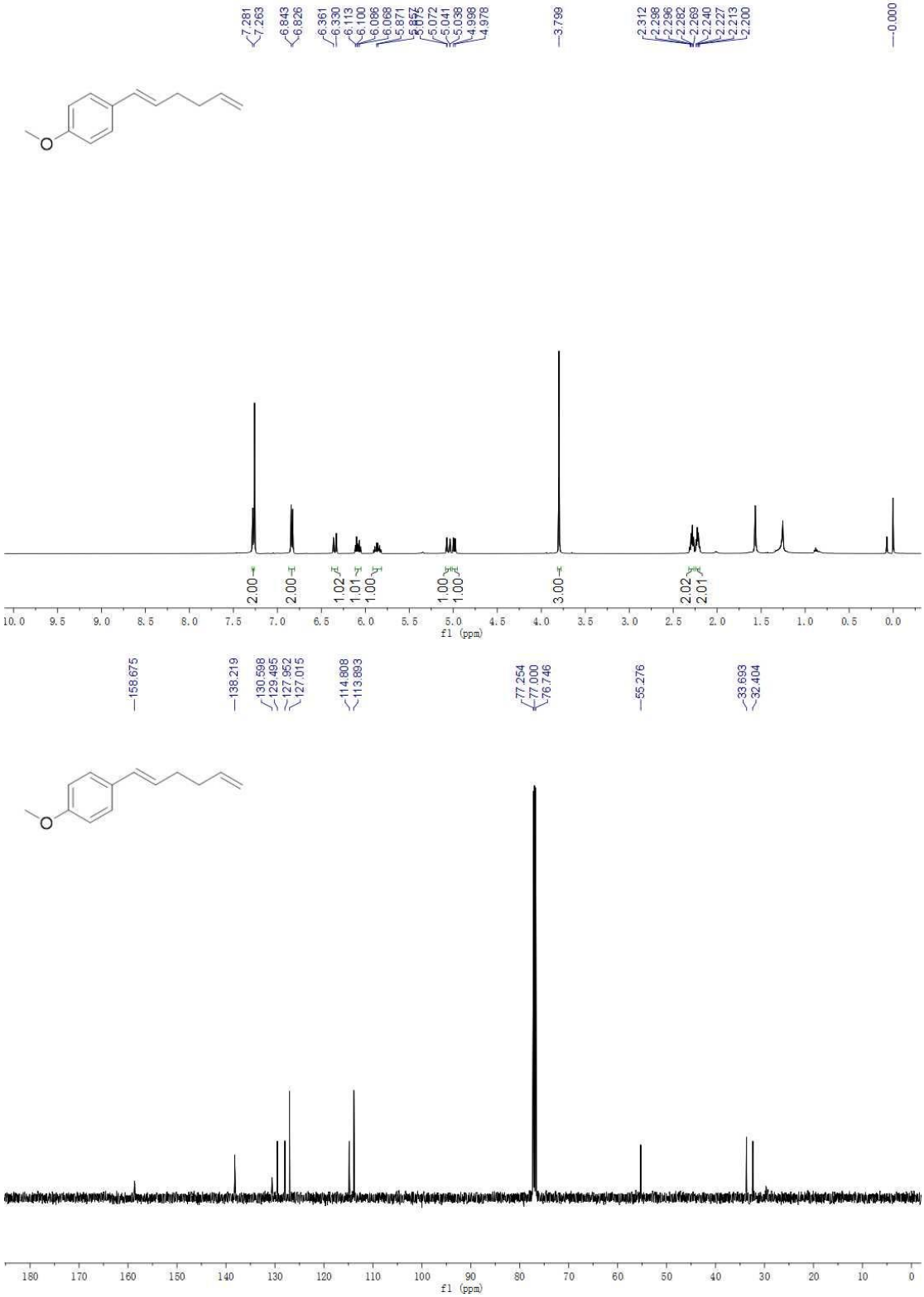
(*E*)-1-(2-Cyclohexylvinyl)naphthalene (3la):



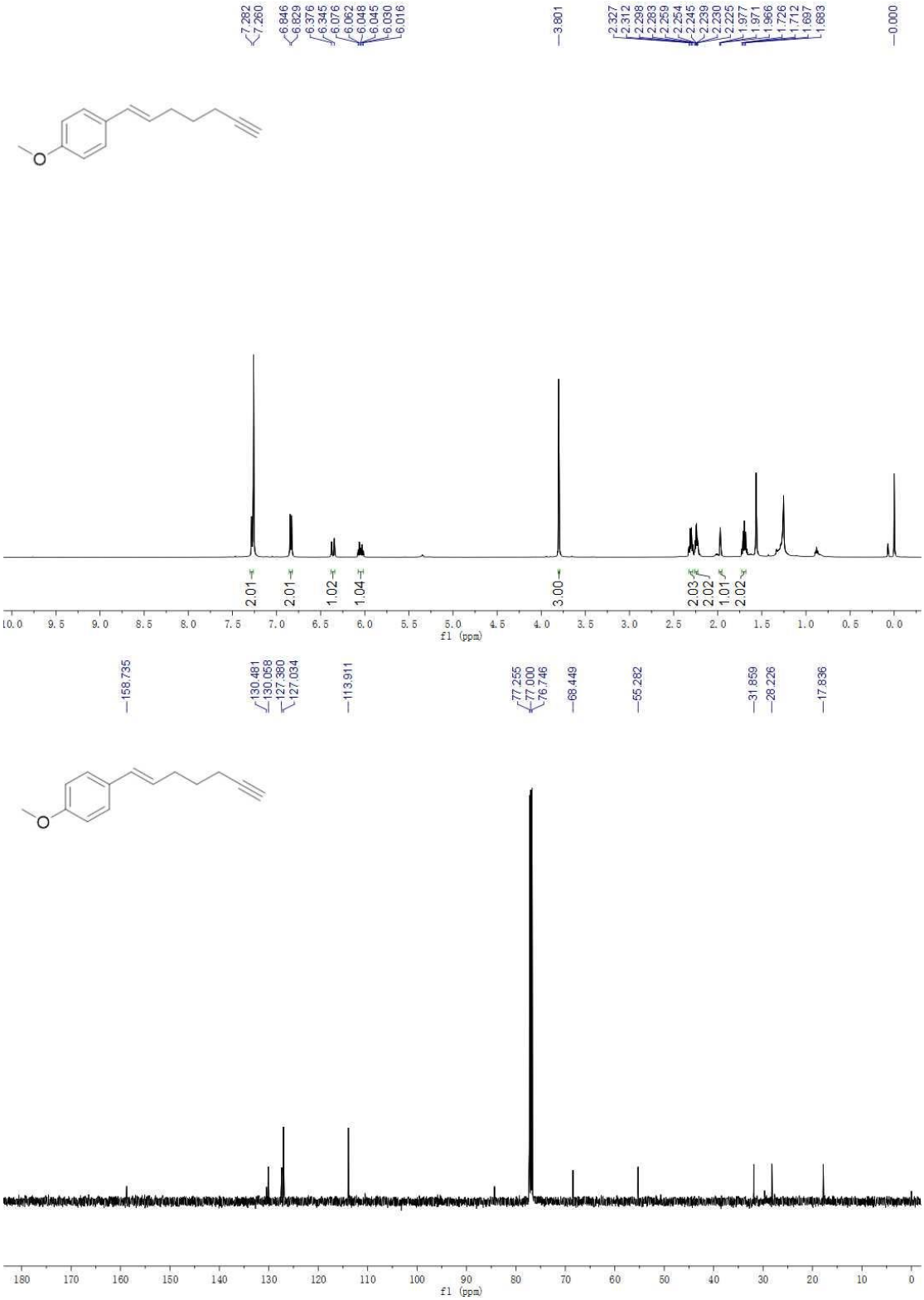
(*E*)-1-methoxy-4-(4-(p-tolyl)but-1-en-1-yl)benzene (3ab):



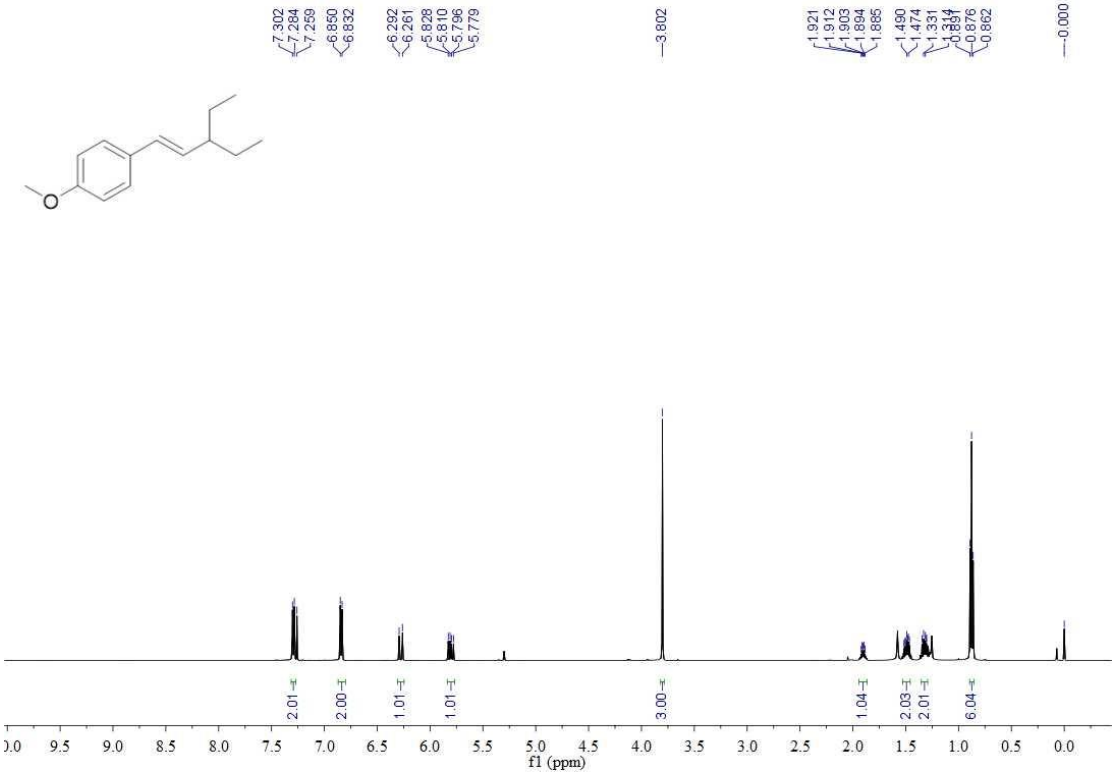
(*E*)-1-(hexa-1,5-dien-1-yl)-4-methoxybenzene (3ac):

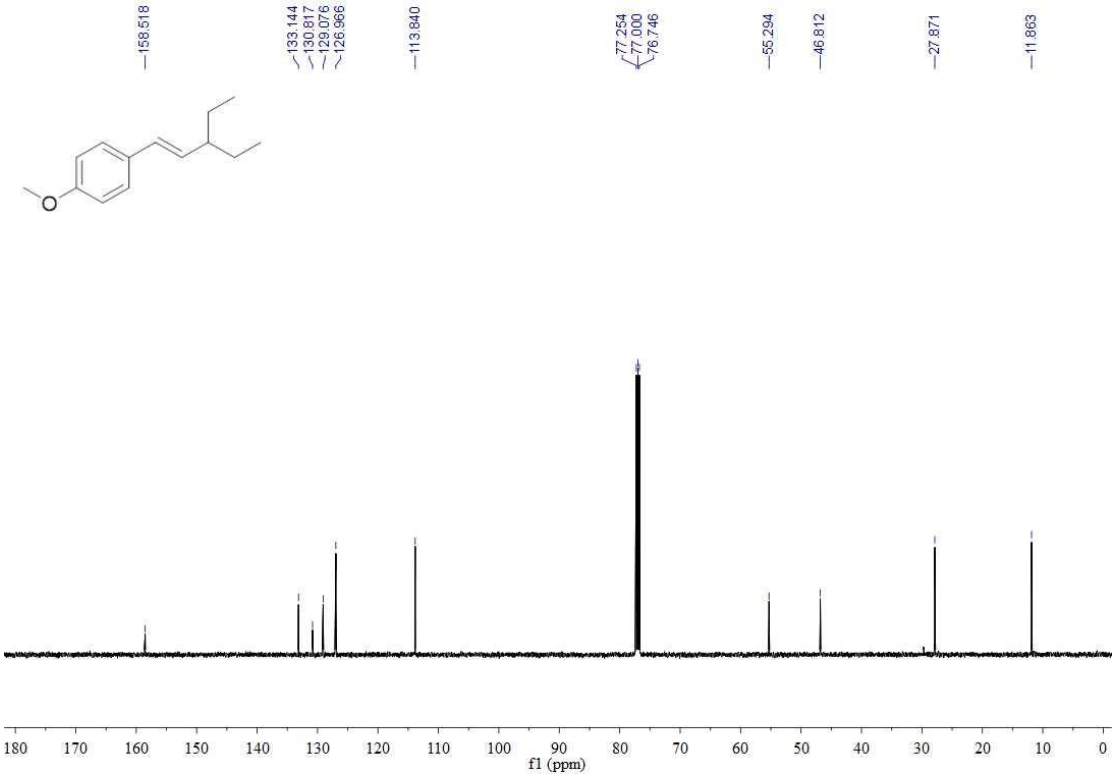


(*E*)-1-(hept-1-en-6-yn-1-yl)-4-methoxybenzene (3ad):

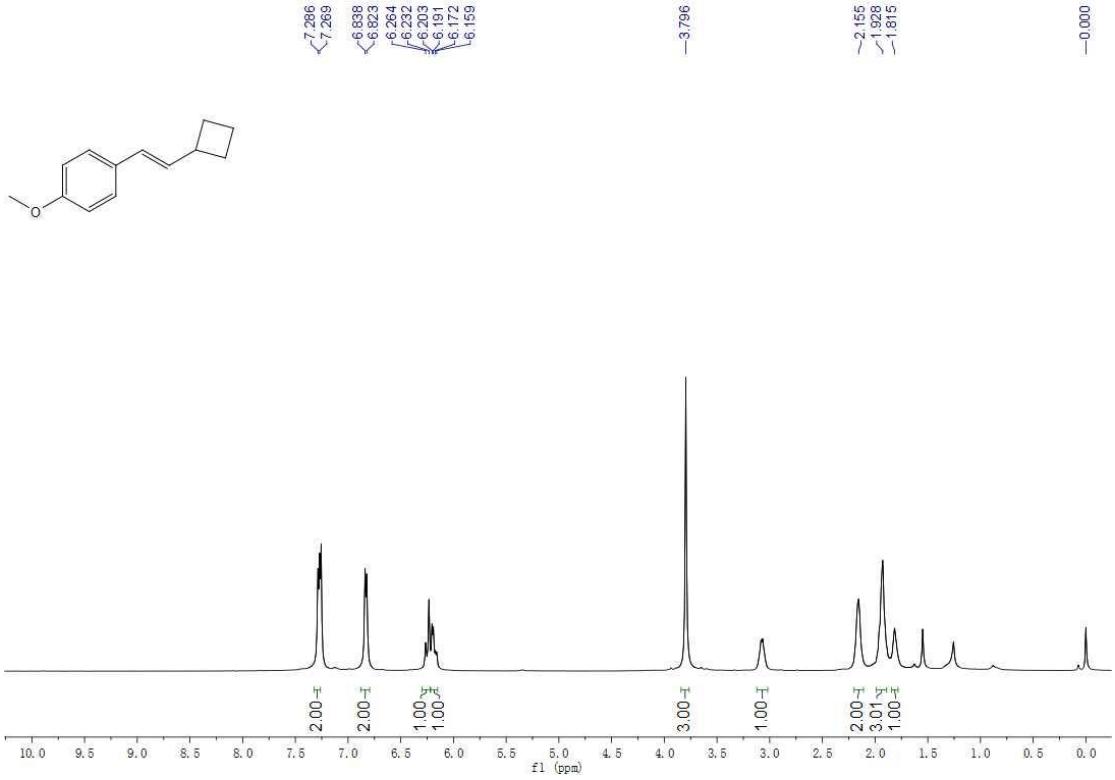


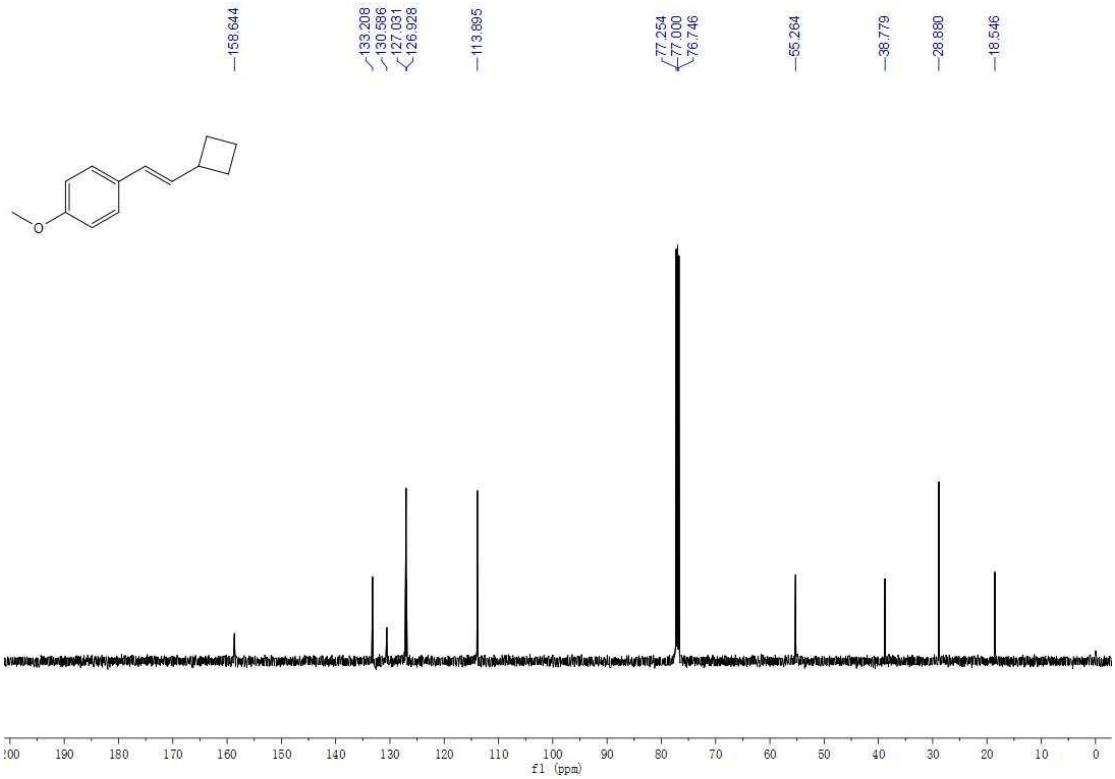
(*E*)-1-(3-Ethylpent-1-en-1-yl)-4-methoxybenzene (3ae):





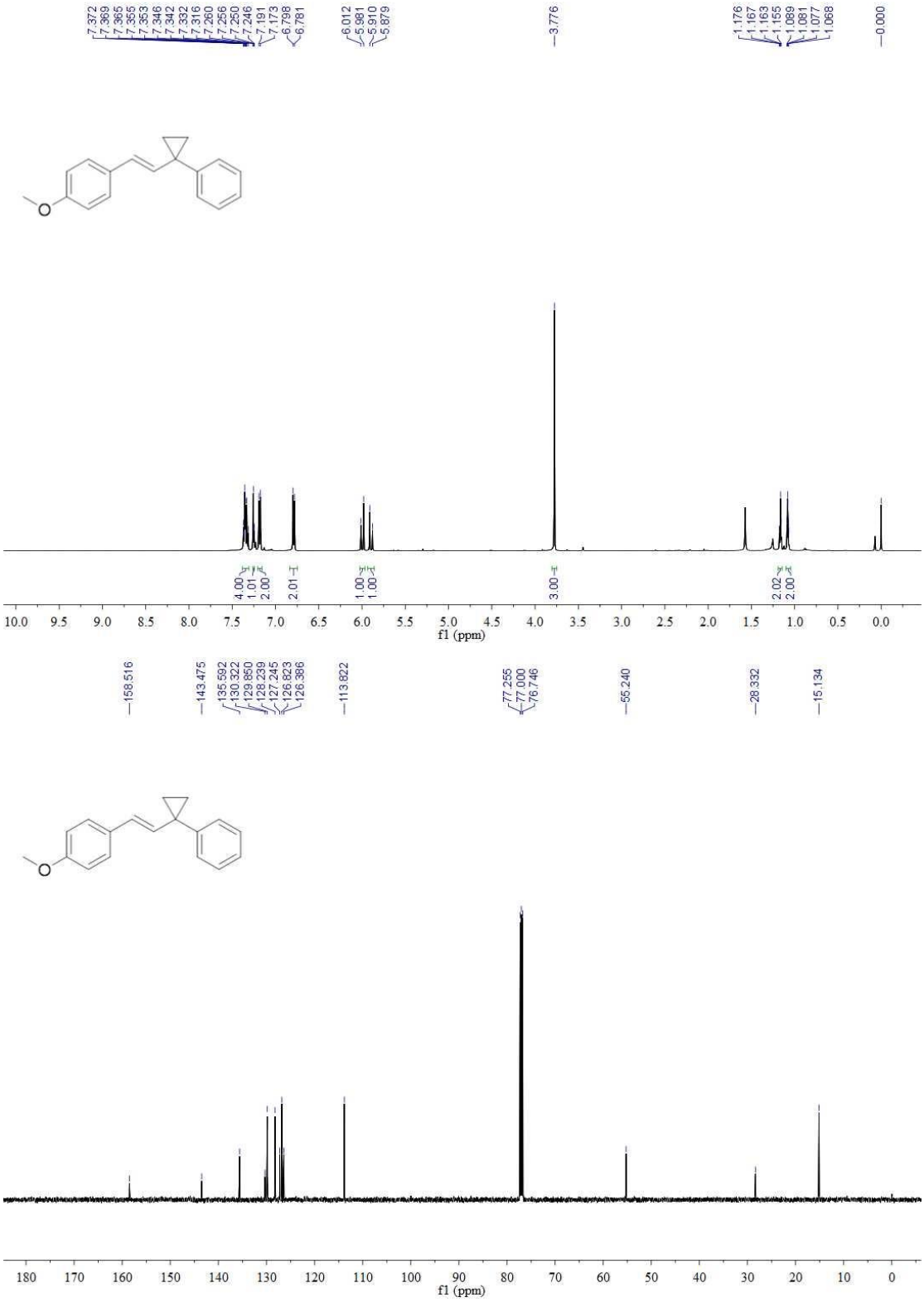
(*E*)-1-(2-Cyclobutylvinyl)-4-methoxybenzene (3af):



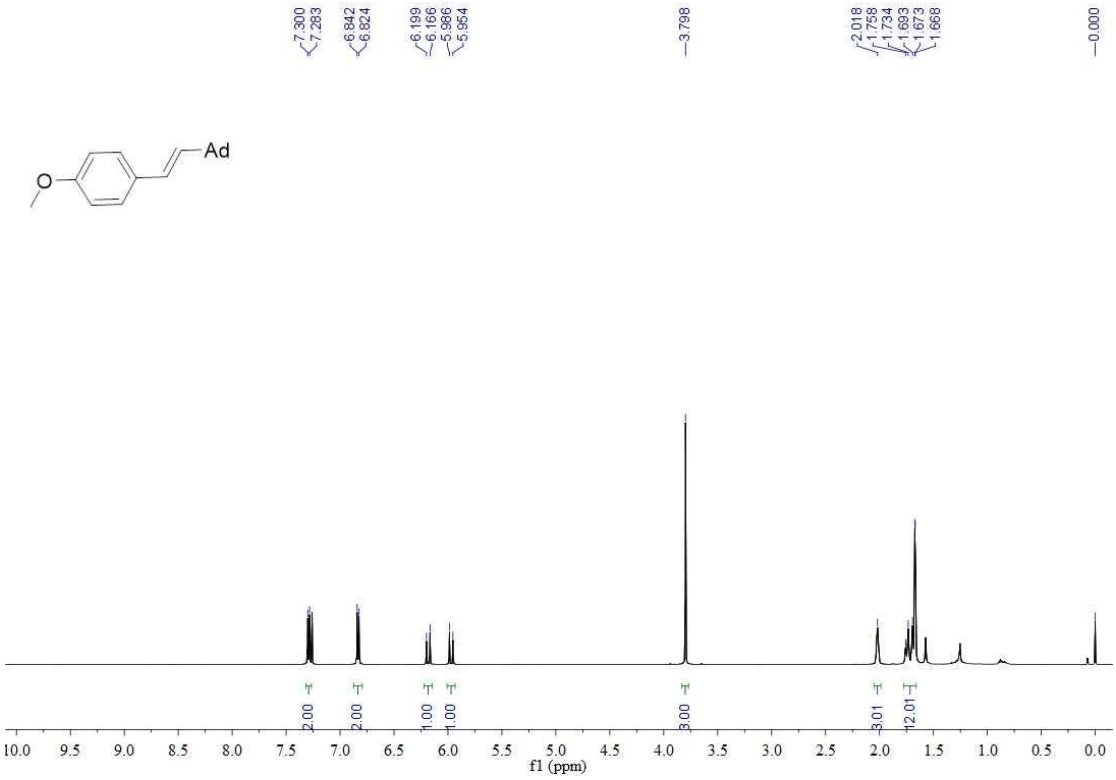


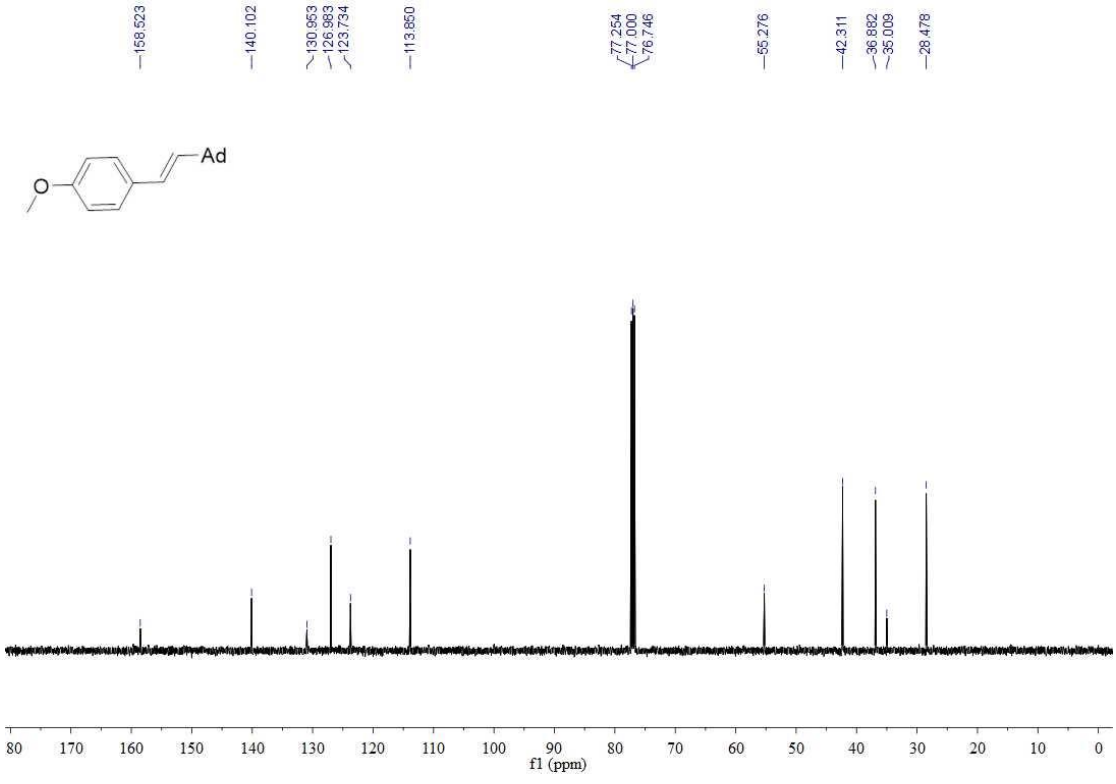
(*E*)-4-(4-Methoxystyryl)tetrahydro-2H-pyran (3ag):

(*E*)-1-methoxy-4-(2-(1-Phenylcyclopropyl)vinyl)benzene (3ah):

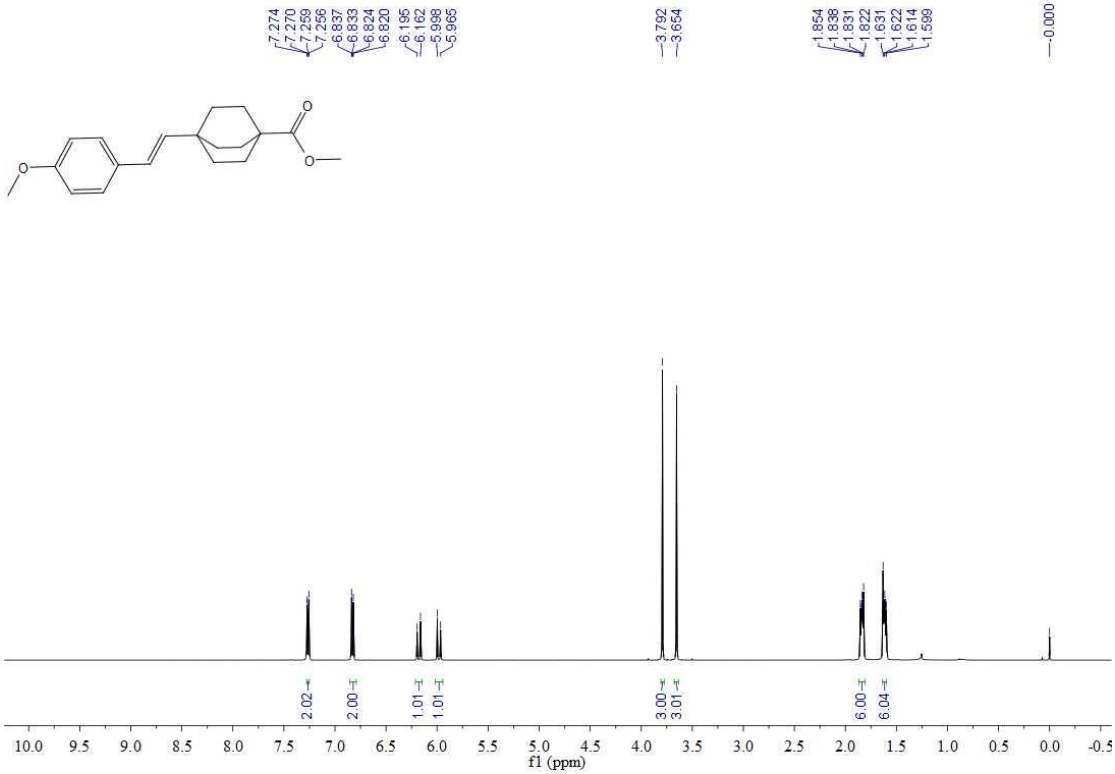


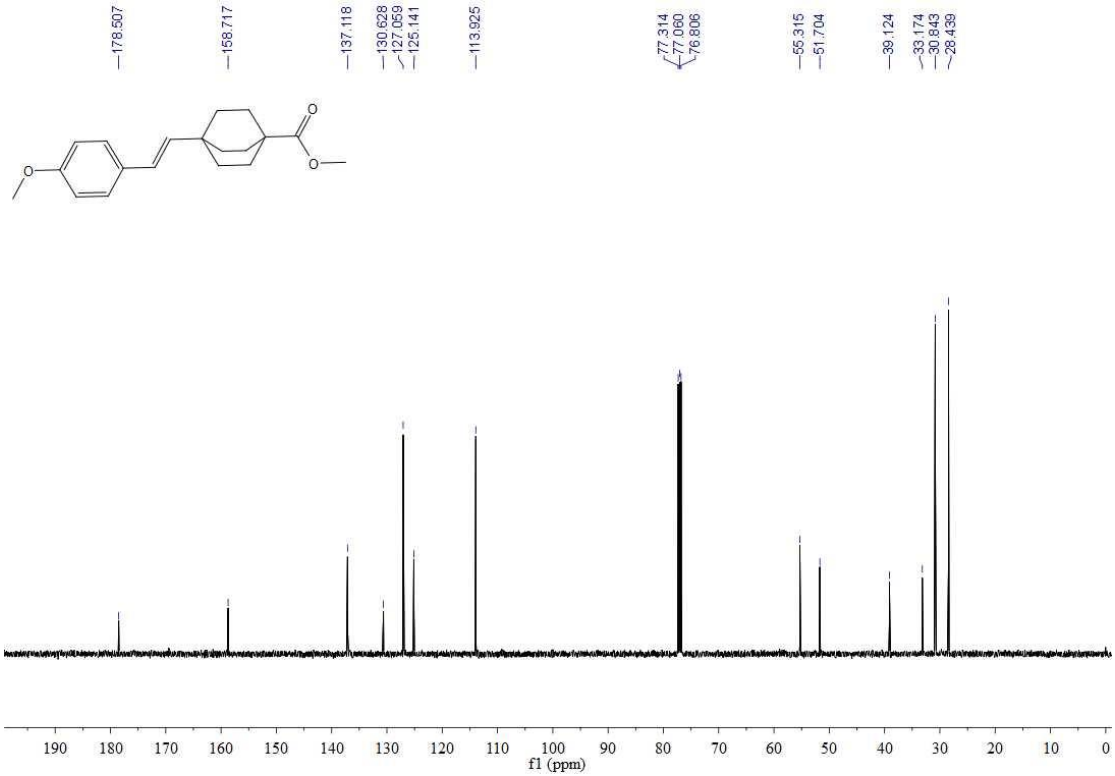
(3r,5r,7r)-1-((*E*)-4-Methoxystyryl)adamantane (3ai):



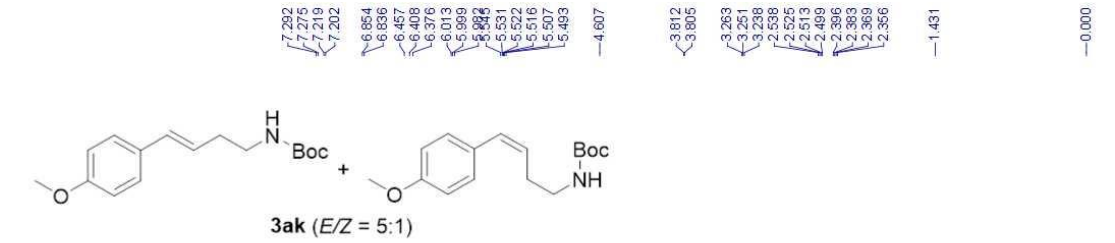


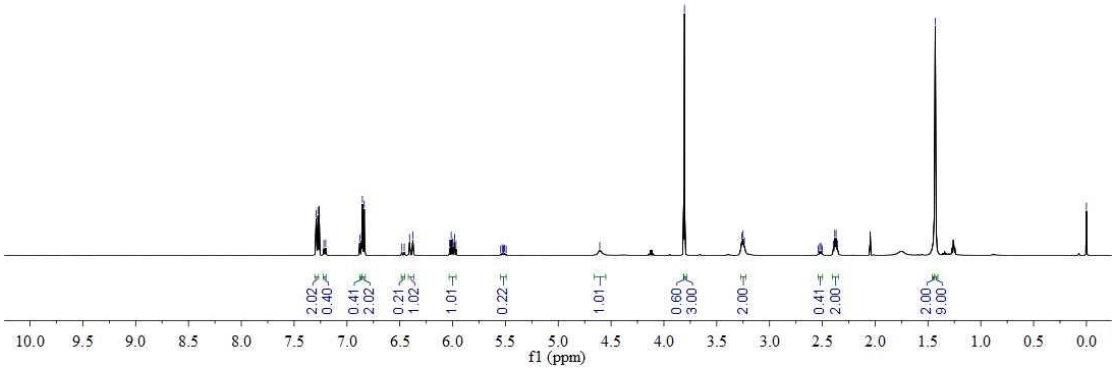
Methyl (*E*)-4-(4-Methoxystyryl)bicyclo[2.2.2]octane-1-carboxylate (3aj):

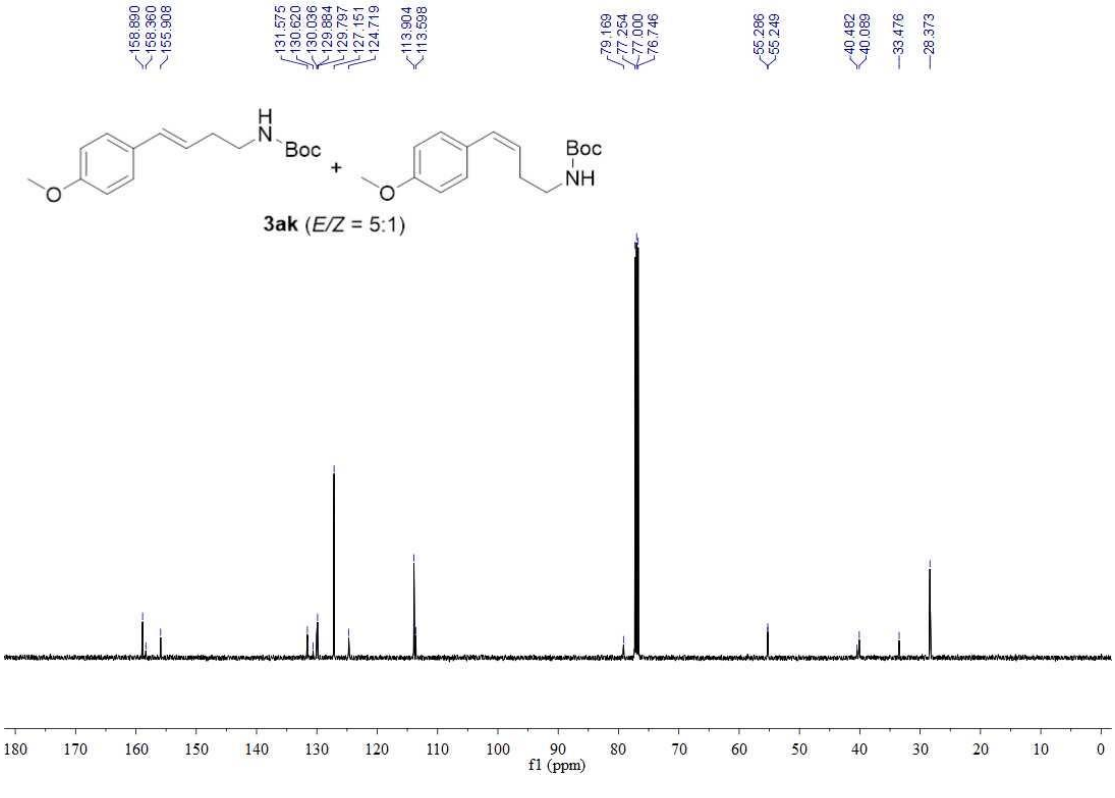




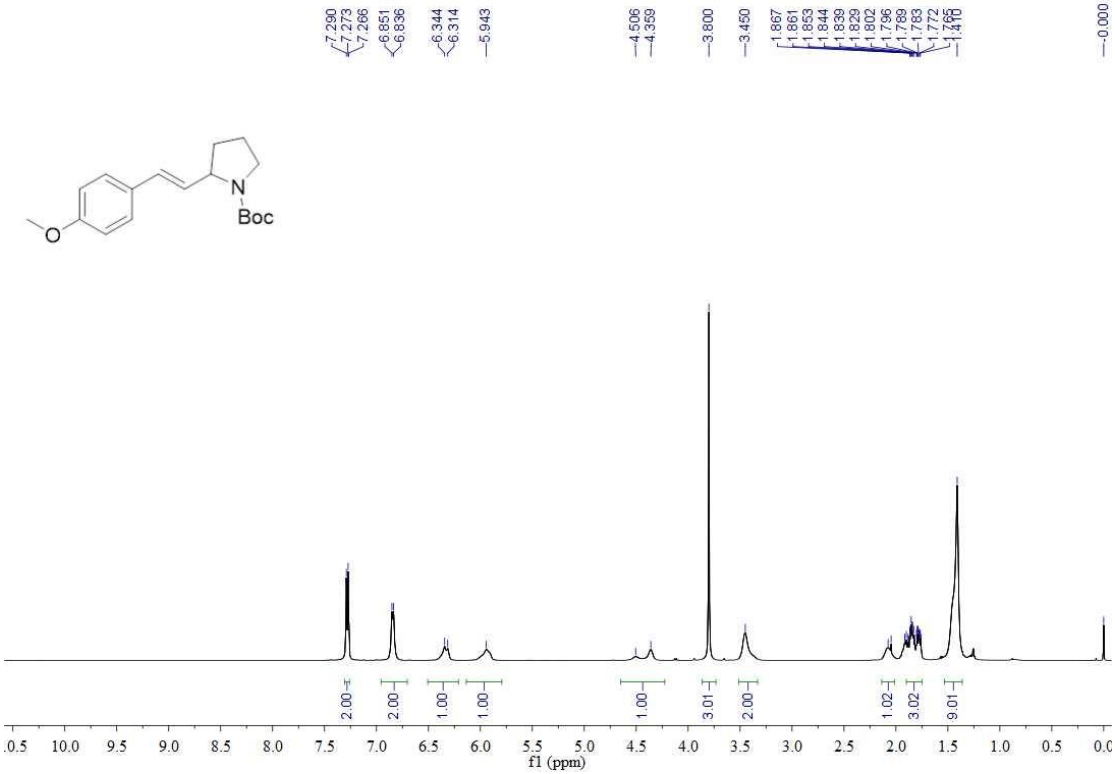
Tert-butyl (4-(4-Methoxyphenyl)but-3-en-1-yl)carbamate (3ak):

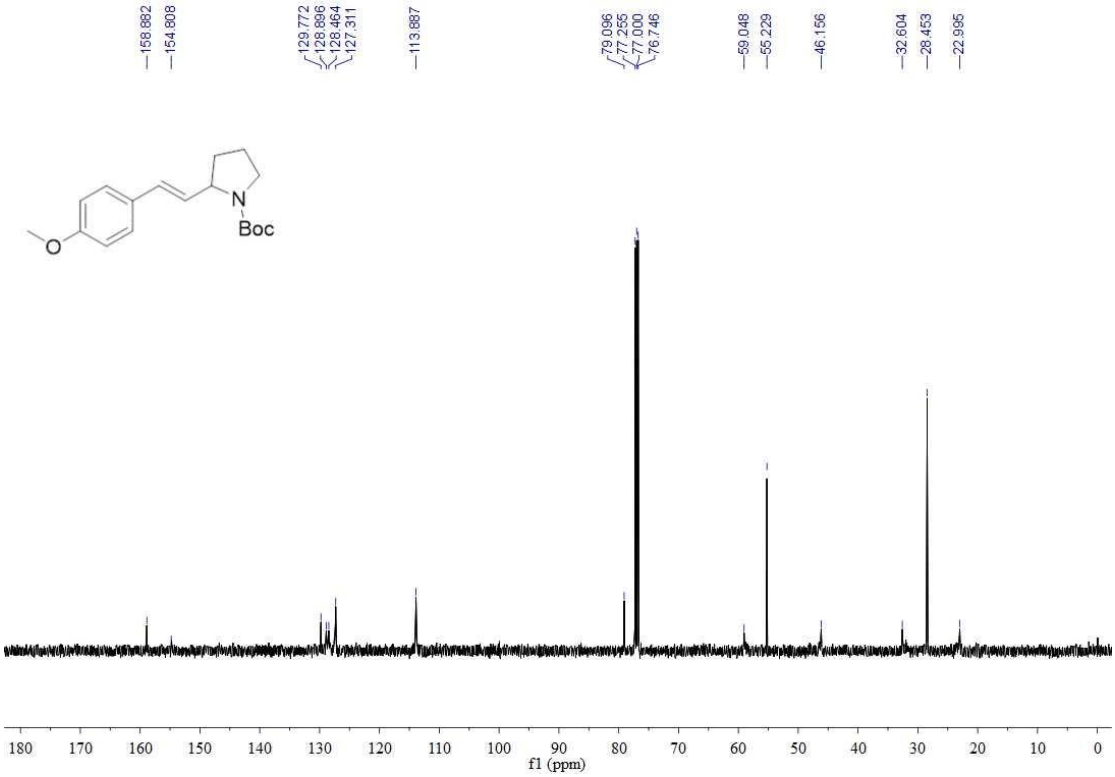




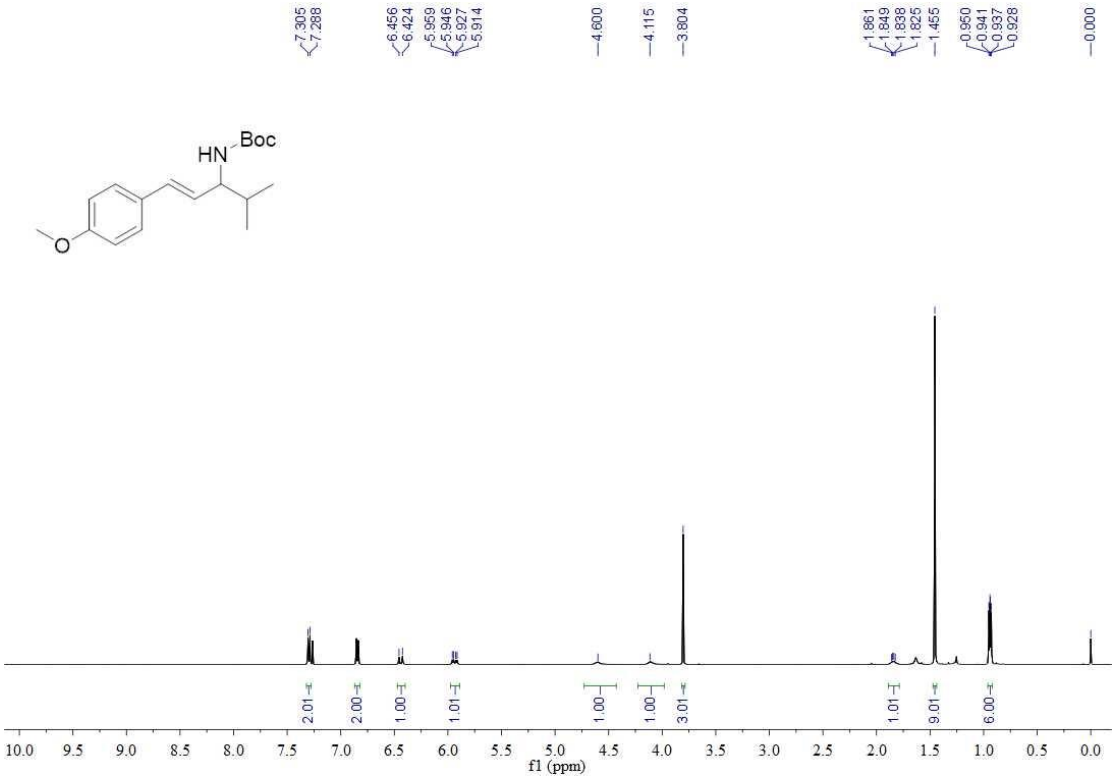


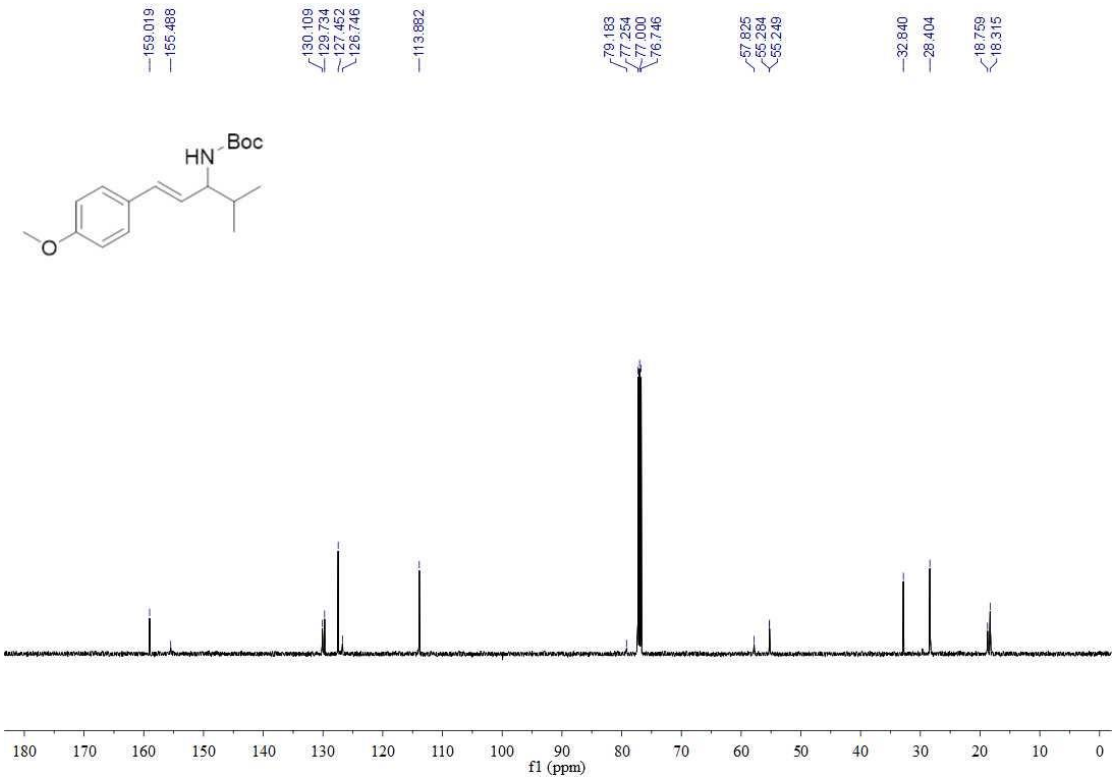
Tert-butyl (*E*)-2-(4-Methoxystyryl)pyrrolidine-1-carboxylate (3al):



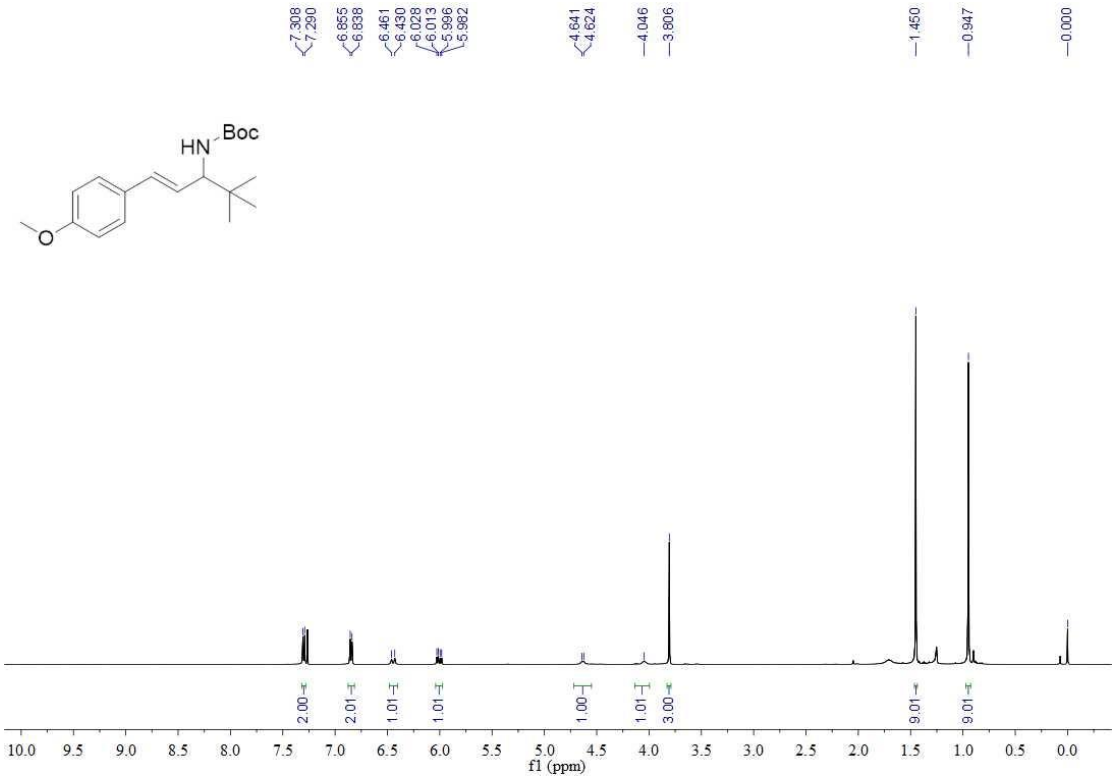


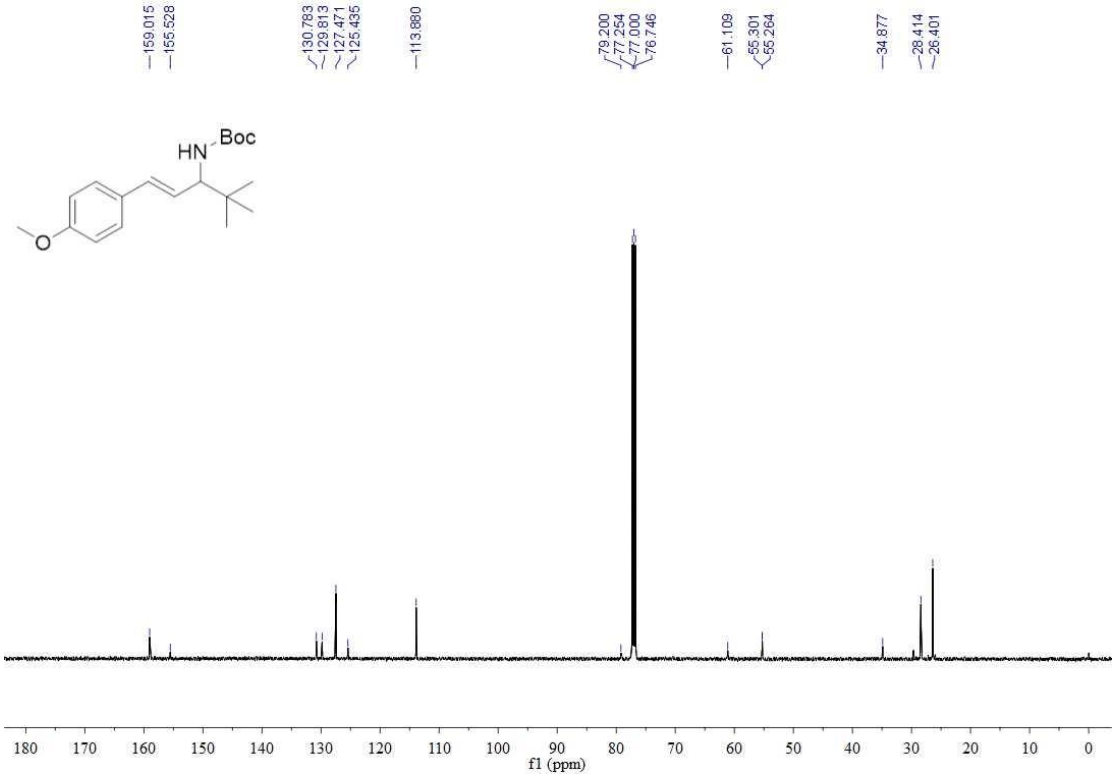
Tert-butyl (*E*)-(1-(4-Methoxyphenyl)-4-methylpent-1-en-3-yl)carbamate (3am):



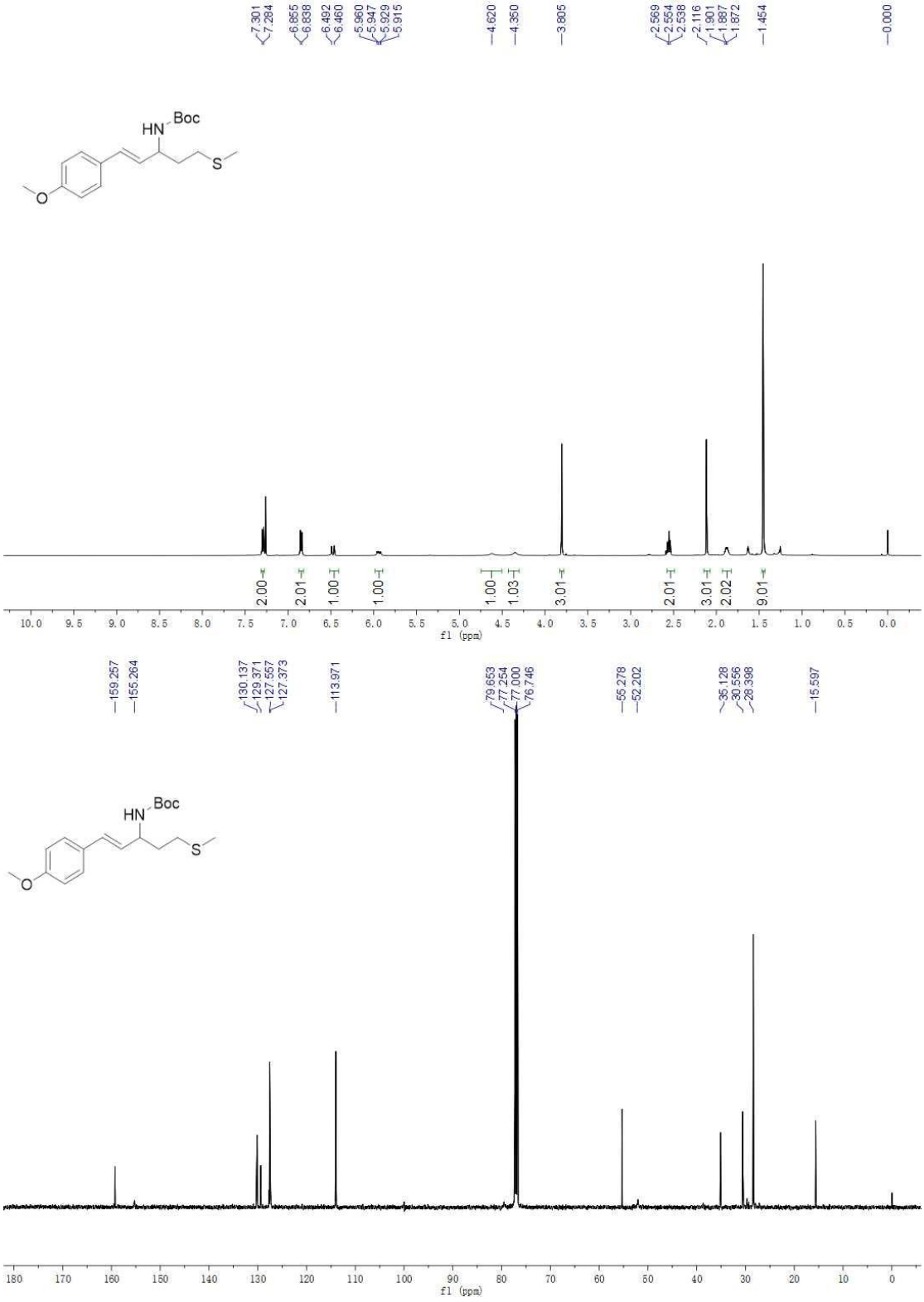


Tert-butyl (*E*)-(1-(4-Methoxyphenyl)-4,4-dimethylpent-1-en-3-yl)carbamate (3an):

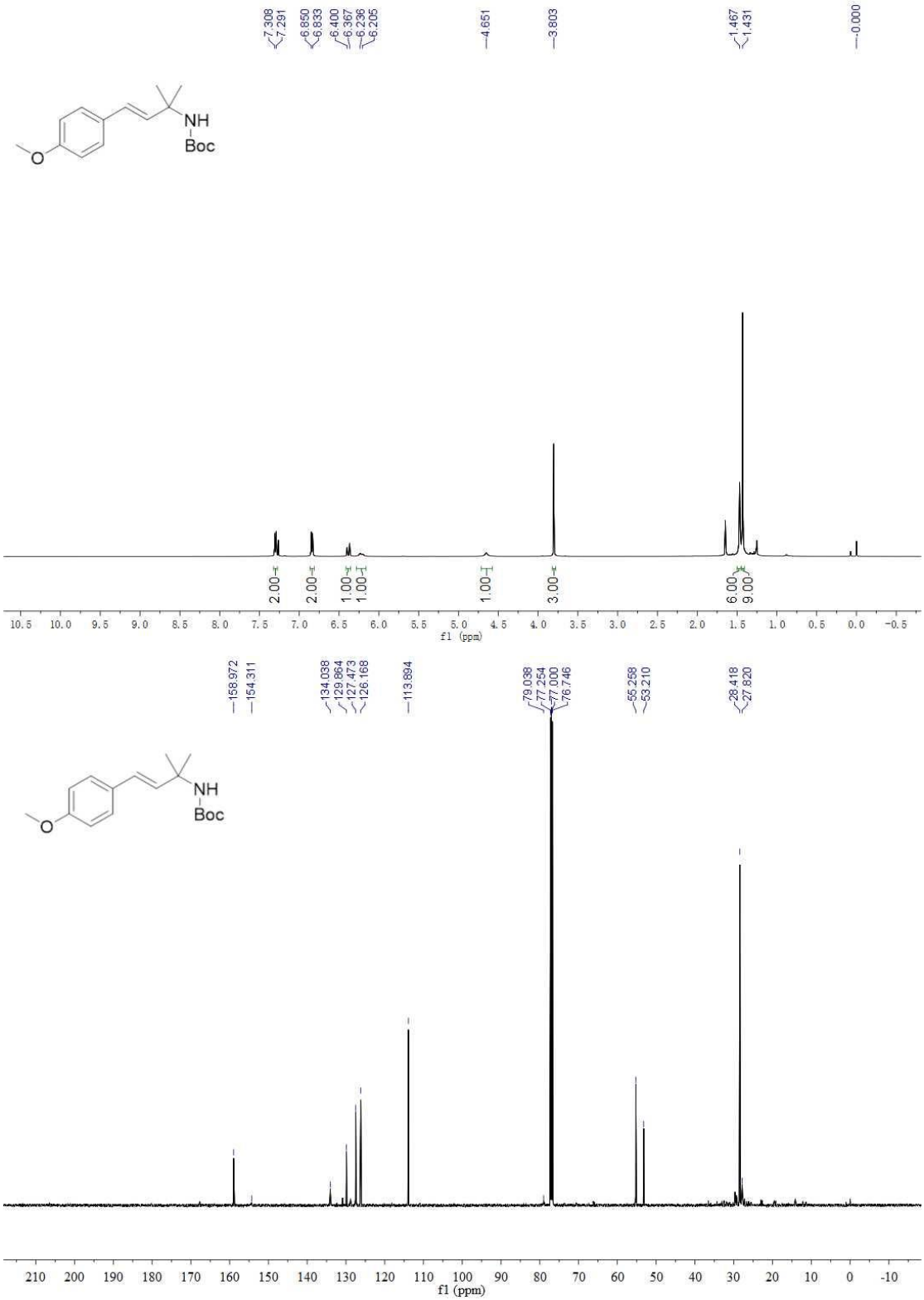




Tert-butyl (*E*)-(1-(4-methoxyphenyl)-5-(methylthio)pent-1-en-3-yl)carbamate (3ao):



Tert-butyl (*E*)-(4-(4-Methoxyphenyl)-2-methylbut-3-en-2-yl)carbamate (3ap):



(*E*)-1-(hexa-1,5-dien-1-yl)-4-methoxybenzene (3aq):