Supporting Information

Alkylamination of Styrenes with Alkyl *N*-Hydroxyphthalimide Esters and Amines by $B(C_6H_5)_3$-Facilitated Photoredox Catalysis

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(A) Typical experimental procedure

(a) Typical Experimental Procedure for the Decarboxylative Alkylamination of Styrenes with Alkyl *N*-Hydroxyphthalimide Esters and Amines using $B(C_6H_5)$ and Photoredox Cooperative Catalysis：

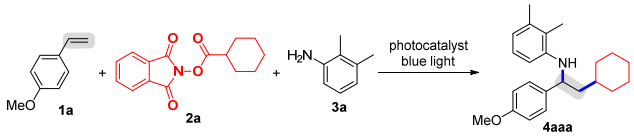
To a Schlenk tube were added alkenes **1** (0.2 mmol), alkyl *N*-Hydroxyphthalimide esters **2** (0.3 mol), amine **3** (0.3 mmol), $Ru(bpy)_3Cl_2$ (1 mol %; 0.002 mmol), $B(C_6F_5)_3$ (10 mol %) and DMSO (1 mL). Then the tube was charged with argon, and was stirred at room temperature under 5 W blue LED light for 24 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was concentrated in vacuum, diluted in diethyl ether, and washed with brine. The aqueous phase was re-extracted with diethyl ether. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **4**.

(b) Experimental Procedure for the 2 mmol Scale

To a Schlenk tube were added alkenes **1a** (2 mmol; 260 mg), alkyl *N*-Hydroxyphthalimide esters **2a** (3 mol; 798 mg), amine **3a** (3 mmol; 360 mg), $Ru(bpy)_3Cl_2$ (1 mol %; 13.1 mg), $B(C_6F_5)_3$ (10 mol %; 102.5 mg) and DMSO (5 mL). Then the tube was charged with argon, and was stirred at room temperature under 5 W blue LED light for 48 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the

saturated brine was washed three times. The resulting residue was purified by silica gel column chromatography (hexane/EtOAc = 100 : 1) to afford the desired product **4aaa** in 50% yield (337 mg).

(c) Table S1. Screening of Optimal Reaction Conditions[a]



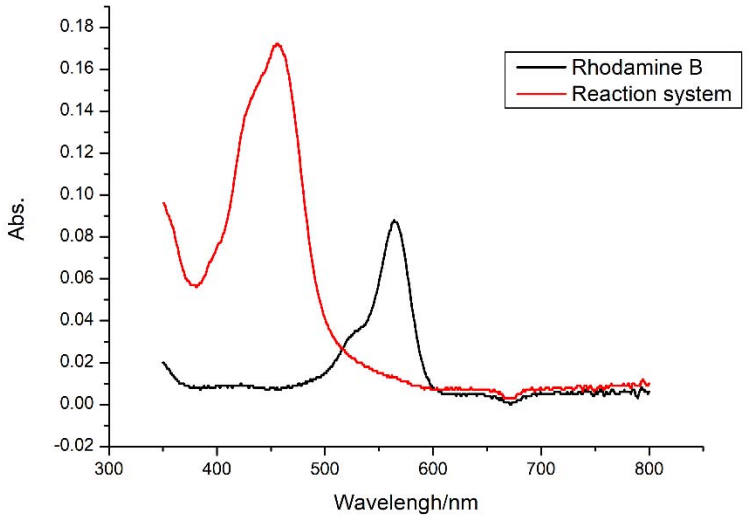
entry	photocatalyst	additive	solvent	yield (%)[b]
1	$Ru(bpy)_3Cl_2$	—	DMA	trace
2	$Ru(bpy)_3Cl_2$	—	DMF	trace
3	$Ru(bpy)_3Cl_2$	—	THF	trace
4	$Ru(bpy)_3Cl_2$	—	1,4-dioxane	trace
5	$Ru(bpy)_3Cl_2$	—	$PhCF_3$	11
6	$Ru(bpy)_3Cl_2$	—	DCM	trace
7[b]	$Mes[Acr^+]ClO_4^-$	—	DMSO	trace
8	$Ru(bpy)_3Cl_2$	HE (1equiv)	DMSO	trace
9	$Ru(bpy)_3Cl_2$	DIPEA (1equiv)	DMSO	trace
10	$Ru(bpy)_3Cl_2$	DIPEA (0.4 equiv)	DMSO	trace
11	$Ru(bpy)_3Cl_2$	Et_3N (1 equiv)	DMSO	trace
12	$Ru(bpy)_3Cl_2$	Cs_2CO_3 (1 equiv)	DMSO	trace
13	$Ru(bpy)_3Cl_2$	K_2CO_3 (1 equiv)	DMSO	trace
14	$Ru(bpy)_3Cl_2$	$Cu(MeCN)_4PF_6$ (10 mol %)	DMSO	trace
15	$Ru(bpy)_3Cl_2$	PTSA (10 mol %)	DMSO	31
16	$Ru(bpy)_3Cl_2$	$In(OTf)_3$ (10 mol %)	DMSO	49
17	$Ru(bpy)_3Cl_2$	TFA (10 mol %)	DMSO	46
18	$Ru(bpy)_3Cl_2$	$Sc(OTf)_3$ (10 mol %)	DMSO	36
19	$Ru(bpy)_3Cl_2$	PTSA (10 mol %)	DMSO	trace
20	$Ru(bpy)_3Cl_2$	dtbpy (10 mol %)	DMSO	24
21	$Ru(bpy)_3Cl_2$	phen (10 mol %)	DMSO	21
22	$Ru(bpy)_3Cl_2$	K_2SO_8 (1equiv)	DMSO	trace
23	$Ru(bpy)_3Cl_2$	$B(C_5F_6)_3$ (20 mol %)	DMSO	53
24	$Ru(bpy)_3Cl_2$	$B(C_5F_6)_3$ (5 mol %)	DMSO	35

25	$Ru(bpy)_3Cl_2$ (2 mol %)	$B(C_5F_6)_3$ (10 mol %)	DMSO	54
26[c]	$Ru(bpy)_3Cl_2$	$B(C_5F_6)_3$ (10 mol %)	DMSO	53

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), **3a** (1.5 equiv), photocatalyst (1 mol %), additive (10 mol %), solvent (1 mL), 5 W LED blue light, argon, room temperature and 24 h. [b] isolated yield. [c] 7 w blue LED

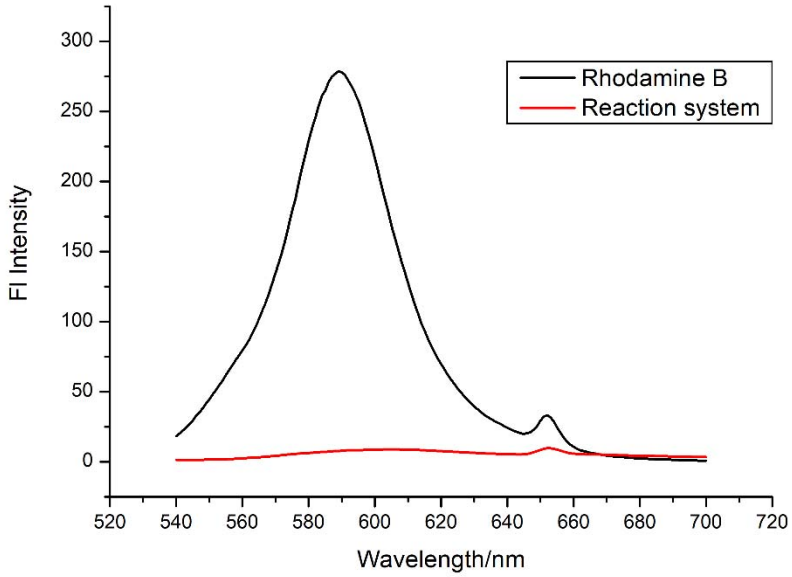
(d) Experiments for the Quantum Yield of the Catalytic Reaction

Figure S1. Information on the Quantum Yield of the Catalytic Reaction



As UV-Vis absorbtion of Rhodamine B at 565nm: 0.087 (black line)

Ax UV-Vis absorbtion of reaction system at 455nm: 0.172 (Red line)



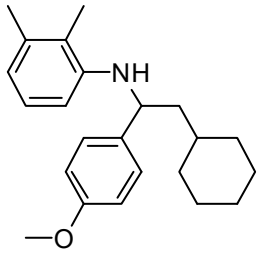
Fs Integrated area of fluorescence of Rhodamine B: 12404(black line)

Fx Integrated area of fluorescence of reaction system: 571(red line)

Φs quantum yield of Rhodamine B: 0.9

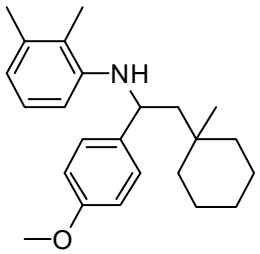
Φx = Φs (As/Ax)(Fx/Fs) = 0.9×(0.087/0.172)×(571/18467) = 0.014

(B) Analytical data



***N*-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-2,3-dimethylaniline (4aaa):**

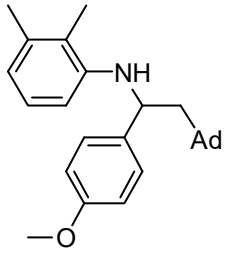
35.2 mg, 52% yield; Rf = 0.7 (PE/EA = 20 : 1); Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 (d, *J* = 9.2 Hz, 2H), 6.84-6.82 (m, 3H), 6.50 (d, *J* = 7.6 Hz, 1H), 6.27 (d, *J* = 8.0 Hz, 1H), 4.38 (t, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 2.27 (s, 3H), 2.12 (s, 3H), 1.81-1.57 (m, 7H), 1.26-1.13 (m, 4H), 1.00-0.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 145.3, 137.1, 136.2, 127.1, 126.0, 119.7, 118.9, 113.9, 109.1, 55.2, 54.8, 47.5, 34.7, 33.9, 33.0, 26.5, 26.2, 26.1, 20.7, 12.6; LRMS (EI, 70 eV) *m/z* (%): 337 (M^+, 7), 240 (52), 121 (100); HRMS *m/z* (ESI) calcd for $C_{23}H_{32}NO$ ($[M+H]^+$) 338.2478, found 338.2491.



***N*-(1-(4-methoxyphenyl)-2-(1-methylcyclohexyl)ethyl)-2,3-dimethylaniline (4aba):**

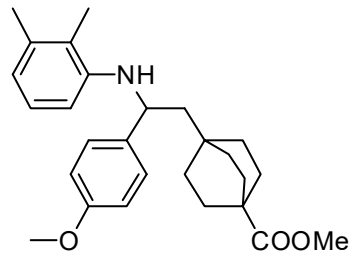
51.0 mg, 73% yield; Rf = 0.7 (PE/EA = 20 : 1); Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.22 (d, *J* = 7.5 Hz, 2H), 6.85-6.82 (m, 3H), 6.48 (d, *J* = 7.5 Hz, 1H), 6.23 (d, *J* = 8.0 Hz, 1H), 4.51-4.43 (m, 1H), 3.92 (s, 1H), 3.76 (s, 3H), 2.27 (s, 3H), 2.11 (s, 3H), 1.74-1.72 (m, 2H), 1.46-1.25 (m, 10H), 1.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.1, 144.9, 138.4,

136.2, 126.9, 126.0, 119.5, 118.7, 113.9, 108.9, 55.2, 53.9, 38.6, 38.3, 33.4, 26.3, 22.1, 22.0, 20.8, 12.6; LRMS (EI, 70 eV) *m/z* (%): 351 (M^+, 7), 240 (42), 97 (100); HRMS *m/z* (ESI) calcd for $C_{24}H_{34}NO$ ($[M+H]^+$) 352.2635, found 352.2641.



_N_-(2-adamant-1-yl-1-(4-methoxyphenyl)ethyl)-2,3 dimethylaniline (4aca):

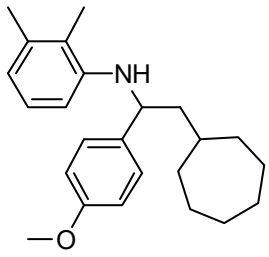
59.1 mg, 76% yield; Rf = 0.7 (PE/EA = 20 : 1); Light yellow solid, mp 109.3-110.8 ºC (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.20 (d, *J* = 8.5 Hz, 2H), 6.85-6.81 (m, 3H), 6.49 (d, *J* = 7.5 Hz, 1H), 6.22 (d, *J* = 8.5 Hz, 1H), 4.45-4.43 (m, 1H), 3.85 (s, 1H), 3.76 (s, 3H), 2.27 (s, 3H), 2.11 (s, 3H), 1.97-1.92 (m, 3H), 1.70-1.55 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.1, 144.9, 138.4, 136.1, 126.9, 126.0, 119.5, 118.7, 113.9, 109.0, 55.5, 55.2, 53.0, 43.1, 36.9, 33.0, 28.6, 20.8, 12.6; LRMS (EI, 70 eV) *m/z* (%): 389 (M^+, 10), 240 (100); HRMS *m/z* (ESI) calcd for $C_{27}H_{36}NO$ ($[M+H]^+$) 390.2791, found 390.2798.



Methyl 4-(2-(2,3-dimethylphenylamino)-2-(4-methoxyphenyl)ethyl)bicyclo[2.2.2]octane-1-carboxylate (4ada):

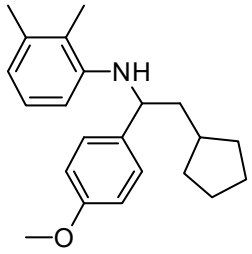
39.5 mg, 47% yield; Rf = 0.4 (PE/EA = 20 : 1); Light yellow solid, mp 131.3-133.0 ºC (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.18 (d, *J* = 8.5 Hz, 2H), 6.86-6.81 (m, 3H), 6.50 (d, *J* = 7.5 Hz, 1H), 6.23 (d, *J* = 8.0 Hz, 1H), 4.41-4.39 (m, 1H), 3.75 (s, 3H), 3.62 (s, 3H), 2.26 (s, 3H), 2.10 (s, 3H), 1.77-1.74 (m, 6H), 1.65-1.63 (m, 2H), 1.55-1.52 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:178.4, 158.2, 144.6, 137.8, 136.3, 126.9, 126.0, 119.6, 118.9, 113.9, 108.9, 55.2,

53.7, 51.9, 51.6, 38.7, 31.1, 31.0, 28.5, 20.8, 12.6; (EI, 70 eV) *m/z* (%): 421 (M^+, 7), 301 (56), 240 (100), 107 (77); HRMS *m/z* (ESI) calcd for $C_{27}H_{36}NO_3$ ($[M+H]^+$) 422.2690, found 422.2697.



_N_-(2-cycloheptyl-1-(4-methoxyphenyl)ethyl)-2,3-dimethylaniline (4aea)：

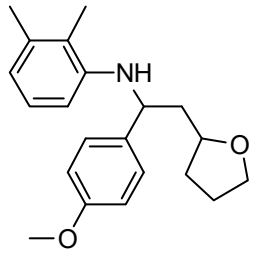
30.2 mg, 43% yield; Rf = 0.7 (PE/EA = 20 : 1); Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.26-7.21 (d, J = 9.0 Hz, 2H), 6.85-6.82 (m, 3H), 6.50 (d, J = 7.5 Hz, 1H), 6.27 (d, J = 8.0 Hz, 1H), 4.36-4.33 (m, 1H), 3.91 (s, 1H), 3.77 (s, 3H), 2.27 (s, 3H), 2.12 (s, 3H), 1.79-1.70 (m, 3H), 1.65-1.46 (m, 10H), 1.31-1.20 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.3, 145.3, 137.1, 136.2, 127.1, 126.0, 119.7, 118.9, 113.9, 109.1, 55.4, 55.2, 48.1, 36.0, 34.9, 34.3, 28.6, 28.4, 26.2, 26.1, 20.8, 12.6; (EI, 70 eV) *m/z* (%): 351 (M^+, 7), 240 (100), 121 (7); HRMS *m/z* (ESI) calcd for $C_{24}H_{34}NO$ ($[M+H]^+$) 352.2635, found 352.2644.



_N_-(2-cyclopentyl-1-(4-methoxyphenyl)ethyl)-2,3-dimethylaniline (4afa):

32.3 mg, 50% yield; Rf = 0.7 (PE/EA = 20 : 1); Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.25 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 7.5 Hz, 3H), 6.50 (d, *J* = 7.0 Hz, 1H), 6.28 (d, *J* = 7.5 Hz, 1H), 4.31 (t, *J* = 6.5 Hz, 1H), 3.91 (s, 1H), 3.77 (s, 3H), 2.26 (s, 3H), 2.12 (s, 3H), 1.84-1.75 (m, 5H), 1.60-1.48 (m, 4H), 1.18-1.16 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.3, 145.3, 136.8, 136.3, 127.2, 126.0, 119.7, 118.9, 113.9, 109.1, 57.0, 55.2, 46.0, 37.2, 32.9,

25.1, 24.0, 20.8, 12.6; LRMS (EI, 70 eV) *m/z* (%): 323 (M^+, 5), 240 (37), 121 (100); HRMS *m/z* (ESI) calcd for $C_{22}H_{30}NO$ ($[M+H]^+$) 324.2322, found 324.2335.



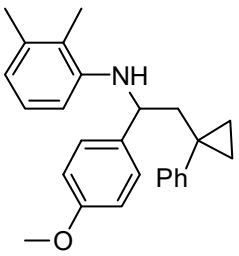
_N_-(1-(4-methoxyphenyl)-2-(tetrahydrofuran-2-yl)ethyl)-2,3-dimethylaniline (4aga):

dr = 1.1:1

29.5 mg, 46% yield; Rf = 0.6 (PE/EA = 10 : 1); Light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31 (d, *J* = 8.5 Hz, 2H), 6.85-6.78 (m, 3H), 6.49 (d, *J* = 7.5 Hz, 1H), 6.19 (d, *J* = 8.0 Hz, 1H), 5.22 (s, 1H), 4.37-4.31 (m, 1H), 3.97-3.87 (m, 2H), 3.79-3.74 (m, 4H), 2.27 (s, 3H), 2.16 (s, 3H), 2.01-1.81 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.4, 146.1, 137.0, 136.1, 127.1, 125.8, 120.7, 118.9, 114.0, 109.4, 78.5, 67.9, 58.2, 55.2, 45.2, 32.3, 25.2, 20.7, 12.6;

^{1}H NMR (500 MHz, $CDCl_3$) δ: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.5 Hz, 2H), 6.84-6.79 (m, 3H), 6.46 (d, *J* = 7.5 Hz, 1H), 6.15 (d, *J* = 8.0 Hz, 1H), 5.35 (s, 1H), 4.62-4.60 (m, 1H), 3.95-3.84 (m, 2H), 3.80-3.75 (m, 4H), 2.27 (s, 3H), 2.14-1.68 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ:158.3, 145.4, 136.2, 135.6, 127.4, 125.9, 119.7, 118.3, 113.8, 108.6, 76.2, 67.9, 55.4, 55.4, 43.0, 31.6, 29.7, 25.6, 20.8, 12.6;

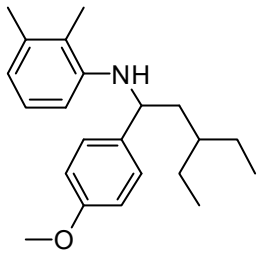
(EI, 70 eV) *m/z* (%): 325 (M^+, 8), 240 (28), 71 (100); HRMS *m/z* (ESI) calcd for $C_{21}H_{28}NO_2$ ($[M+H]^+$) 326.2115, found 326.2127.



_N_-(1-(4-methoxyphenyl)-2-(1-phenylcyclopropyl)ethyl)-2,3-dimethylaniline (4aha):

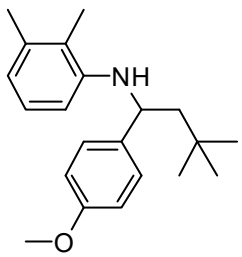
39.5 mg, 53% yield; Rf = 0.7 (PE/EA = 20 : 1); Brown oil; ^{1}H

NMR (400 MHz, $CDCl_3$) δ: 7.33-7.12 (m, 7H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.46 (d, *J* = 6.8 Hz, 1H), 6.00 (d, *J* = 7.6 Hz, 1H), 4.20-4.09 (m, 2H), 3.74 (s, 3H), 2.24 (s, 3H), 2.14-1.99 (m, 2H), 1.91 (s, 3H), 0.89-0.78 (m, 3H), 0.59-0.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 145.0, 144.2, 136.7, 135.9, 129.0, 128.5, 127.1, 126.4, 125.7, 119.9, 118.9, 113.8, 109.3, 56.7, 55.2, 50.1, 24.0, 20.7, 14.3, 12.3, 11.4; (EI, 70 eV) *m/z* (%): 371 (M^+, 6), 240 (100), 207 (12); HRMS *m/z* (ESI) calcd for $C_{26}H_{30}NO$ ($[M+H]^+$) 372.2322, found 372.2330.



_N_-(3-Ethyl-1-(4-methoxyphenyl)pentyl)-2,3-dimethylaniline (4aia):

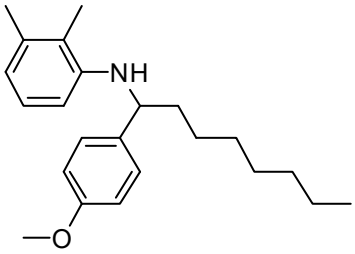
33.2 mg, 51% yield; Rf = 0.7 (PE/EA = 20 : 1); Light yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.24 (d, *J* = 8.0 Hz, 2H), 6.84-6.82 (m, 3H), 6.50 (d, *J* = 7.2 Hz, 1H), 6.27 (d, *J* = 8.0 Hz, 1H), 4.34 (t, *J* = 7.2 Hz, 1H), 3.76 (s, 3H), 2.26 (s, 3H), 2.11 (s, 3H), 1.76-1.61 (m, 2H), 1.41-1.26 (m, 5H), 0.90-0.80 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.3, 145.3, 137.1, 136.2, 127.1, 126.0, 119.7, 118.9, 113.9, 109.1, 55.5, 55.2, 43.5, 37.3, 25.6, 25.2, 20.7, 12.6, 10.9, 10.4; LRMS (EI, 70 eV) *m/z* (%): 325 (M^+, 7), 240 (37), 121 (100); HRMS *m/z* (ESI) calcd for $C_{22}H_{32}NO$ ($[M+H]^+$) 326.2478, found 326.2491.



_N_-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-2,3-dimethylaniline (4aja):

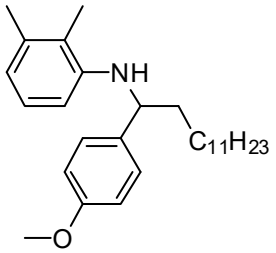
36.3 mg, 58% yield; Rf = 0.7 (PE/EA = 20 : 1); Light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.22 (d, *J* = 8.8 Hz, 2H), 6.86-6.81 (m, 3H), 6.49 (d, *J* = 7.6 Hz, 1H), 6.25 (d, *J* = 8.0 Hz, 1H), 4.41 (t, *J* = 6.0 Hz,

1H), 3.86 (s, 1H), 3.76 (s, 3H), 2.26 (s, 3H), 2.11 (s, 3H), 1.71 (d, *J* = 6.0 Hz, 2H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:158.3, 145.0, 138.2, 136.2, 127.0, 126.0, 119.6, 118.8, 114.0, 109.0, 55.3, 54.9, 54.2, 31.1, 30.3, 20.8, 12.6; LRMS (EI, 70 eV) *m/z* (%): 311 (M^+, 12), 240 (36), 121 (42), 57 (100); HRMS *m/z* (ESI) calcd for $C_{21}H_{30}NO$ ($[M+H]^+$) 312.2322, found 312.2329.



***N*-(1-(4-methoxyphenyl)octyl)-2,3-dimethylaniline(4aka):**

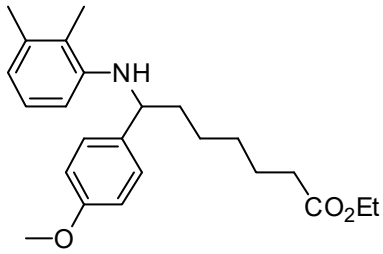
35.5 mg, 52% yield; Rf = 0.7 (PE/EA = 20 : 1); Light yellow oil, mp 163.2-164.7 (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.24 (d, *J* = 7.5 Hz, 2H), 6.86-6.83 (m, 3H), 6.50 (d, *J* = 7.5 Hz, 1H), 6.26 (d, *J* = 8.0 Hz, 1H), 4.26 (t, *J* = 6.0 Hz, 1H), 3.88 (s, 1H), 2.27 (s, 3H), 2.12 (s, 3H), 1.82-1.70 (m, 2H), 1.45-1.24 (m, 10H), 0.87 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.3, 145.3, 136.6, 136.3, 127.3, 126.0, 119.8, 118.9, 113.8, 109.1, 57.7, 55.2, 39.3, 31.8, 29.5, 29.2, 26.5, 22.6, 20.8, 14.1, 12.6; LRMS (EI, 70 eV) *m/z* (%): 339 (M^+, 9), 240 (52), 121 (100); HRMS *m/z* (ESI) calcd for $C_{23}H_{34}NO$ ($[M+H]^+$) 340.2635, found 340.2647.



***N*-(1-(4-methoxyphenyl)tridecyl)-2,3-dimethylaniline (4ala):**

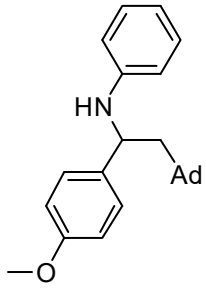
35.9 mg, 44% yield; Rf = 0.7 (PE/EA = 20 : 1); Yellow solid, mp 134.2-135.6 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 3H), 6.50 (d, *J* = 7.2 Hz, 1H), 6.26 (d, *J* = 7.6 Hz, 1H), 4.26 (t, *J* = 6.4 Hz, 1H), 3.76 (s, 3H), 2.26 (s, 3H), 2.11 (s, 3H), 1.90-1.70 (m, 2H), 1.41-1.19 (m, 20H), 0.91-0.86 (m, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ:158.3, 145.3, 136.6, 136.2, 127.2, 126.0, 119.8, 118.9, 113.8, 109.1, 57.7, 55.2, 39.3, 31.9, 29.6, 29.6, 29.6, 29.5, 29.5, 29.3, 26.4, 22.7, 20.7, 14.1, 12.6; LRMS (EI, 70 eV) *m/z* (%): 409 (M^+, 14), 240 (100); HRMS *m/z* (ESI) calcd for $C_{28}H_{44}NO$ ($[M+H]^+$) 410.3417, found 410.3431.



Ethyl 7-(2,3-dimethylphenylamino)-7-(4-methoxyphenyl)heptanoate (4ama):

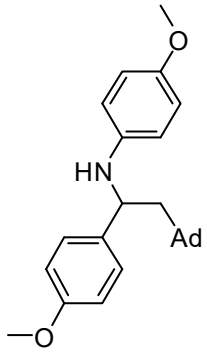
38.5 mg, 50% yield; Rf = 0.4 (PE/EA = 20 : 1); Light yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ: 7.23 (d, *J* = 8.0 Hz, 2H), 6.86-6.82 (m, 3H), 6.50 (d, *J* = 7.2 Hz, 1H), 6.27 (d, *J* = 8.0 Hz, 1H), 4.26 (t, *J* = 6.8 Hz, 1H), 4.13-4.08 (m, 2H), 3.76 (s, 3H), 2.30-2.24 (m, 5H), 2.11 (s, 3H), 1.82-1.75 (m, 2H), 1.62-1.59 (m, 2H), 1.44-1.35 (m, 4H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl3) δ: 173.7, 158.4, 145.2, 136.3, 136.2, 127.2, 125.9, 119.8, 119.0, 113.9, 109.1, 60.2, 57.5, 55.2, 39.0, 34.2, 29.0, 26.1, 24.8, 20.7, 14.2, 12.6; LRMS (EI, 70 eV) m/z (%): 383 (M^+, 9), 240 (85), 121 (100); HRMS m/z (ESI) calcd for $C_{24}H_{34}NO_3$ ($[M+H]^+$) 384.2533, found 384.2541.



***N*-(2-adamant-1-yl-1-(4-methoxyphenyl)ethyl)aniline (4acb):**

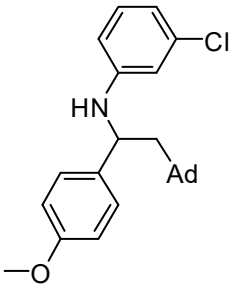
44.5 mg, 62% yield; Rf = 0.7 (PE/EA = 20 : 1); Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.22 (d, *J* = 7.2 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 2H), 6.83 (d, *J* = 7.2 Hz, 2H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 2H), 4.44-4.37 (m, 1H), 3.93 (s, 1H), 3.75 (s, 3H), 1.94 (s, 3H), 1.71-1.52 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 147.1, 138.2, 129.0, 127.0, 116.8, 113.9, 113.1, 55.2, 55.0, 53.1, 43.0, 36.9, 32.9, 28.6; (EI, 70 eV) *m/z* (%): 361 (M^+, 7),

269 (9), 212 (73), 135 (100); HRMS *m/z* (ESI) calcd for $C_{25}H_{32}NO$ ($[M+H]^+$) 362.2478, found 362.2485.



***N*-(2-adamant-1-yl-1-(4-methoxyphenyl)ethyl)-4-methoxyaniline (4acc):**

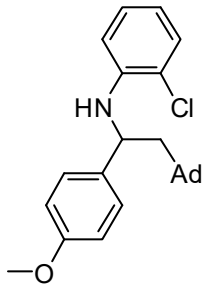
31.5 mg, 40% yield; Rf = 0.8 (PE/EA = 20 : 1); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 7.6 Hz, 2H), 4.37-4.28 (m, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 1.99-1.90 (m, 3H), 1.70-1.51 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.1, 151.6, 141.6, 138.5, 127.1, 114.7, 114.2, 113.9, 55.7, 55.2, 55.0, 54.0, 43.0, 36.9, 33.0, 28.6; LRMS (EI, 70 eV) *m/z* (%): 391 (M^+, 3), 242 (18), 135 (100); HRMS *m/z* (ESI) calcd for $C_{26}H_{34}NO_2$ ($[M+H]^+$) 392.2584, found 392.2595.



3-Chloro-*N*-(2-adamant-1-yl-1-(4-methoxyphenyl)ethyl)-aniline (4acd):

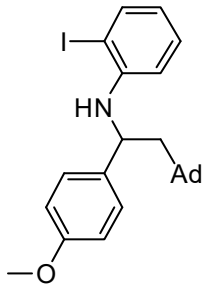
40.5 mg, 51% yield; Rf = 0.7 (PE/EA = 20 : 1); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 (d, *J* = 7.6 Hz, 2H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 1H), 6.46 (s, 1H), 6.33 (d, *J* = 8.4 Hz, 1H), 4.37 (t, *J* = 5.6 Hz, 1H), 4.00 (s, 1H), 3.77 (s, 3H), 1.99-1.92 (m, 3H), 1.72-1.48 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 148.2, 137.4, 134.7, 130.0, 127.0, 116.8, 114.0, 112.8, 111.3, 55.2, 54.9, 53.1, 43.0, 36.9, 33.0, 28.6; LRMS (EI, 70 eV) *m/z* (%): 397 (M^++2, 1), 395 (M^+, 3), 246 (39),

135 (100); HRMS *m/z* (ESI) calcd for $C_{25}H_{31}{}^{35}ClNO$ ($[M+H]^+$) 396.2089, found 396.2103.



2-Chloro-*N*-(2- adamant-1-yl -1-(4-methoxyphenyl)ethyl)aniline (4ace):

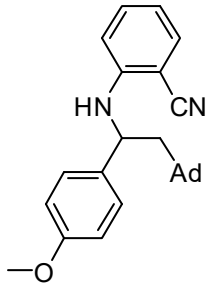
42.0 mg, 53% yield; Rf = 0.7 (PE/EA = 20 : 1); White solid, mp 102.6-103.6 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23-7.19 (m, 3H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 2H), 6.53 (t, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 8.4 Hz, 1H), 4.65 (s, 1H), 4.42-4.38 (m, 1H), 3.76 (s, 3H), 2.02-1.90 (m, 3H), 1.71-1.52 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 142.8, 137.5, 128.8, 127.6, 126.9, 118.8, 116.7, 114.0, 112.2, 55.2, 53.0, 43.0, 36.9, 32.9, 28.6; LRMS (EI, 70 eV) *m/z* (%): 397 (M^++2, 1), 395 (M^+, 3), 246 (38), 135 (100); HRMS *m/z* (ESI) calcd for $C_{25}H_{31}{}^{35}ClNO$ ($[M+H]^+$) 396.2089, found 396.2097.



***N*-(2- adamant-1-yl -1-(4-methoxyphenyl)ethyl)-2-iodoaniline (4acf):**

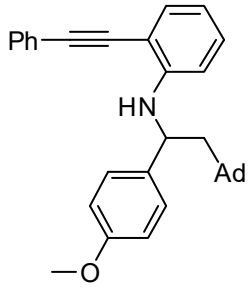
35.1 mg, 36% yield; Rf = 0.7 (PE/EA = 20 : 1); Lihgt yellow solid, mp 111.6-112.7 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 2H), 6.35 (t, *J* = 7.2 Hz, 1H), 6.27 (d, *J* = 8.0 Hz, 1H), 4.56 (s, 1H), 4.45-4.43 (m, 1H), 3.77 (s, 3H), 2.00-1.92 (s, 3H), 1.71-1.53 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 146.0, 138.8, 137.3, 129.2, 126.9, 118.1, 114.0, 111.7, 85.2, 55.3, 55.2, 53.3, 43.1, 36.9, 32.9, 28.6; LRMS (EI, 70 eV) *m/z* (%): 487 (M^+, 4), 338 (35),

135 (100); HRMS *m/z* (ESI) calcd for $C_{25}H_{31}INO$ ($[M+H]^+$) 488.1445, found 488.1453.



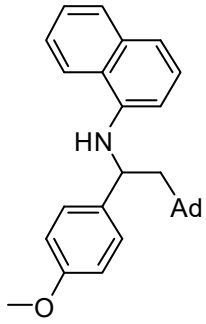
2-(2-adamant-1-yl-1-(4-methoxyphenyl)ethylamino)benzonitrile (4acg):

29.3 mg, 38% yield; Rf = 0.5 (PE/EA = 10 : 1); Lihgt yellow solid, mp 115.6-116.7 ºC (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (d, *J* = 7.6 Hz, 1H), 7.23-7.19 (m, 3H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.60 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 8.4 Hz, 1H), 4.85-4.84 (m, 1H), 4.48 (s, 1H), 3.77 (s, 3H), 2.00-1.93 (s, 3H), 1.71-1.54 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.5, 149.1, 136.5, 134.1, 132.5, 126.8, 118.0, 116.3, 114.1, 111.8, 95.6, 55.2, 54.9, 52.9, 42.9, 36.8, 32.9, 28.5; LRMS (EI, 70 eV) *m/z* (%): 386 (M^+, 2), 269 (13), 237 (57), 135 (100); HRMS *m/z* (ESI) calcd for $C_{26}H_{31}N_2O$ ($[M+H]^+$) 387.2431, found 387.2439.



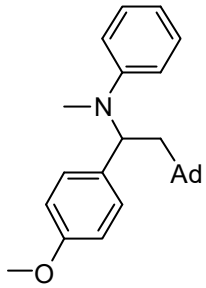
***N*-(2-adamant-1-yl-1-(4-methoxyphenyl)ethyl)-2-(phenylethynyl)aniline (4ach):**

50.8 mg, 55% yield; Rf = 0.6 (PE/EA = 20 : 1); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (d, *J* = 7.2 Hz, 2H), 7.38-7.32 (m, 4H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 2H), 6.57 (t, *J* = 7.2 Hz, 1H), 6.32 (d, *J* = 8.0 Hz, 1H), 5.08 (s, 1H), 4.51-4.43 (m, 1H), 3.75 (s, 3H), 1.97-1.90 (m, 3H), 1.69-1.54 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 147.8, 137.7, 131.8, 131.3, 129.8, 128.4, 128.1, 126.9, 123.4, 116.0, 114.0, 110.7, 107.3, 94.9, 86.4, 55.3, 55.2, 53.2, 43.1, 36.9, 32.9, 28.6; HRMS *m/z* (ESI) calcd for $C_{33}H_{36}NO$ ($[M+H]^+$) 462.2791, found 462.2798.



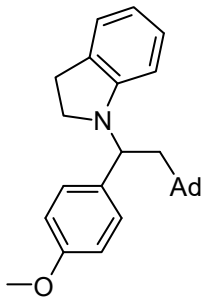
***N*-(2- adamant-1-yl -1-(4-methoxyphenyl)ethyl)naphthalen-1-amine (4aci):**

43.6 mg, 53% yield; Rf = 0.6 (PE/EA = 20 : 1); Yellow solid, mp 145.6-146.9 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 6.8Hz, 1H), 7.45-7.43 (m, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.20-7.12 (m, 2H), 6.81 (d, *J* = 7.6 Hz, 2H), 6.33 (d, *J* = 7.2 Hz, 1H), 4.70 (s, 1H), 4.63-4.59 (m, 1H), 3.73 (m, 3H), 1.97-1.88 (s, 3H), 1.75-1.61 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 141.9, 137.7, 134.2, 128.7, 126.9, 126.7, 125.5, 124.6, 123.1, 119.6, 116.6, 114.0, 105.5, 55.4, 55.2, 53.2, 43.1, 36.9, 33.0, 28.6; (EI, 70 eV) *m/z* (%): 411 (M^+, 20), 262 (100), 230 (12); HRMS *m/z* (ESI) calcd for $C_{29}H_{34}NO$ ($[M+H]^+$) 412.2635, found 412.2647.



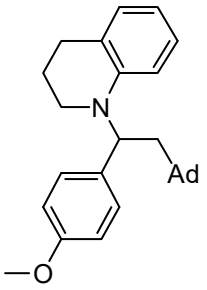
***N*-(2-adamant-1-yl -1-(4-methoxyphenyl)ethyl)-*N*-methylaniline (4acj):**

42.8 mg, 57% yield; Rf = 0.8 (PE/EA = 20 : 1); Brown oil, mp 88.3-89.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22 (t, *J* = 7.2 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.80 (t, *J* = 7.2 Hz, 4H), 6.69 (t, *J* = 7.2 Hz, 1H), 5.10 (t, *J* = 6.0 Hz, 1H), 3.76 (s, 3H), 2.65 (s, 3H), 1.90 (s, 3H), 1.85-1.75 (m, 2H), 1.67-1.49 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 149.9, 134.5, 129.1, 128.3, 116.3, 113.4, 113.3, 56.2, 55.1, 46.0, 42.9, 37.0, 32.6, 32.1, 28.7; (EI, 70 eV) *m/z* (%): 375 (M^+, 7), 226 (100); HRMS *m/z* (ESI) calcd for $C_{26}H_{34}NO$ ($[M+H]^+$) 376.2635, found 376.2648.



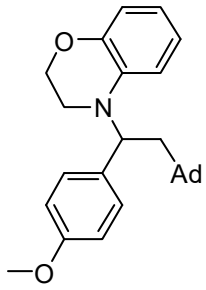
1-(2-Adamant-1-yl-1-(4-methoxyphenyl)ethyl)indoline (4ack)：

49.5 mg, 64% yield; Rf = 0.6 (PE/EA = 20 : 1); Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 6.8 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 2H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.53 (t, *J* = 7.2 Hz, 1H), 4.82 (t, *J* = 6.0 Hz, 1H), 3.75 (s, 3H), 3.49-3.42 (m, 1H), 3.14-3.07 (m, 1H), 2.89-2.77 (m, 2H), 1.94-1.86 (m, 3H), 1.78 (d, *J* = 6.4 Hz, 2H), 1.67-1.48 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.4, 150.8, 133.4, 129.8, 129.1, 127.1, 124.4, 116.2, 113.4, 106.4, 55.1, 53.2, 46.3, 44.7, 43.0, 37.0, 32.6, 28.7, 27.9; (EI, 70 eV) *m/z* (%): 387 (M^+, 4), 238 (12), 135 (100); HRMS *m/z* (ESI) calcd for $C_{27}H_{34}NO$ ($[M+H]^+$) 388.2635, found 388.2644.



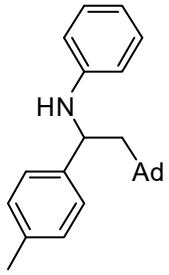
1-(2-Adamant-1-yl-1-(4-methoxyphenyl)ethyl)-1,2,3,4-tetrahydroquinoline (4acl):

54.5 mg, 68% yield; Rf = 0.6 (PE/EA = 20 : 1); Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.53 (t, *J* = 7.2 Hz, 1H), 5.13 (t, *J* = 6.0 Hz, 1H), 3.75 (s, 3H), 3.27-3.22 (m, 1H), 3.00-2.96 (m, 1H), 2.70-2.60 (m, 2H), 1.91-1.80 (m, 6H), 1.68-1.52 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 145.1, 134.4, 129.3, 128.5, 127.0, 122.9, 115.0, 113.4, 111.2, 55.1, 54.2, 45.1, 43.0, 37.0, 32.8, 28.7, 21.9; LRMS (EI, 70 eV) *m/z* (%): 401 (M^+, 9), 252 (100); HRMS *m/z* (ESI) calcd for $C_{28}H_{36}NO$ ($[M+H]^+$) 402.2791, found 402.2799.



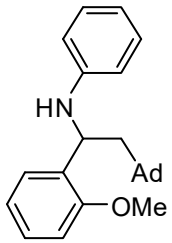
4-(2-adamant-1-yl-1-(4-methoxyphenyl)ethyl)-3,4-dihydro-2H-benzo[*b*][1,4]oxazine (4acm):

51.6 mg, 64% yield; Rf = 0.6 (PE/EA = 20 : 1); Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22 (d, *J* = 7.2 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.89-6.70 (m, 4H), 6.59 (d, *J* = 7.6 Hz, 1H), 5.13 (t, *J* = 6.0 Hz, 1H), 4.11-4.08 (m, 1H), 3.84-3.76 (m, 1H), 3.76 (s, 3H), 3.26-3.24 (m, 1H), 3.05-3.04 (m, 1H), 1.95-1.89 (s, 3H), 1.78 (d, *J* = 6.0 Hz, 2H), 1.69-1.50 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.5, 144.1, 134.7, 133.2, 128.8, 121.5, 116.7, 116.6, 113.4, 112.6, 64.2, 55.1, 54.2, 44.1, 43.0, 40.5, 36.9, 32.7, 28.6; LRMS (EI, 70 eV) m/z (%): 403 (M^+, 15), 254 (100); HRMS *m/z* (ESI) calcd for $C_{27}H_{34}NO_2$ ($[M+H]^+$) 404.2584, found 404.2591.



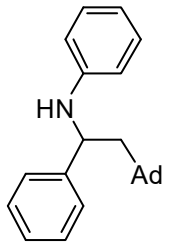
***N*-(2- adamant-1-yl -1-p-tolylethyl)aniline (4bcb):**

34.5 mg, 50% yield; Rf = 0.8 (PE/EA = 20 : 1); Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 (d, *J* = 7.6 Hz, 2H), 7.11-7.06 (m, 4H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 2H), 4.42 (t, *J* = 5.2 Hz, 1H), 3.97 (s, 1H), 2.30 (s, 3H), 1.98-1.91 (s, 3H), 1.71-1.53 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.1, 143.2, 136.0, 129.3, 129.0, 125.9, 116.8, 113.1, 55.1, 53.5, 43.0, 36.9, 33.0, 28.7, 21.0; LRMS (EI, 70 eV) *m/z* (%): 345 (M^+, 3), 196 (100), 135 (30); HRMS *m/z* (ESI) calcd for $C_{25}H_{32}N$ ($[M+H]^+$) 346.2529, found 346.2543.



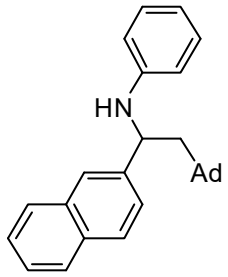
***N*-(2-adamant-1-yl -1-(2-methoxyphenyl)ethyl)aniline (4dcb):**

36.5 mg, 51% yield; Rf = 0.7 (PE/EA = 20 : 1); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (d, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.2 Hz, 2H), 6.87-6.83 (m, 2H), 6.59 (t, *J* = 7.2 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 2H), 4.87-4.80 (m, 1H), 3.89 (s, 3H), 1.97-1.91 (m, 3H), 1.70-1.52 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.3, 147.2, 133.7, 129.0, 127.4, 126.5, 120.6, 116.6, 113.0, 110.3, 55.2, 52.9, 48.2, 43.0, 37.0, 33.2, 28.7; LRMS (EI, 70 eV) m/z (%): 361 (M^+, 3), 212 (100), 135 (23); HRMS *m/z* (ESI) calcd for $C_{27}H_{38}NO$ ($[M+H]^+$) 392.2948, found 392.2955.



***N*-(2-adamant-1-yl-1-phenylethyl)aniline (4ecb):**

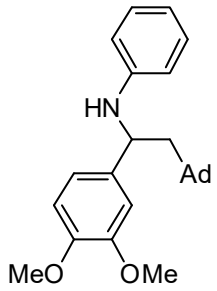
31.7 mg, 48% yield; Rf = 0.8 (PE/EA = 20 : 1); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31-7.25 (m, 4H), 7.19 (t, *J* = 6.8 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 2H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.47 (d, *J* = 7.6 Hz, 2H), 4.44 (t, *J* = 5.6 Hz, 1H), 2.00-1.91 (s, 3H), 1.71-1.55 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.1, 146.2, 129.1, 128.6, 126.5, 126.0, 116.9, 113.1, 55.1, 53.8, 43.0, 36.9, 33.1, 28.6; LRMS (EI, 70 eV) *m/z* (%): 331 (M^+, 3), 182 (100), 135 (10); HRMS *m/z* (ESI) calcd for $C_{24}H_{30}N$ ($[M+H]^+$) 332.2373, found 332.2388.



***N*-(2- adamant-1-yl -1-(naphthalen-2-yl)ethyl)aniline (4fcb):**

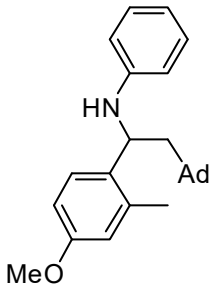
26.7 mg, 35% yield; Rf = 0.6 (PE/EA = 20 : 1); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82-7.75 (m, 4H), 7.47-7.41 (m, 3H), 7.06 (t, *J* = 7.6 Hz, 2H), 6.61 (t, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 2H), 4.59 (t, *J* = 5.2 Hz, 1H), 2.00-1.94 (s, 3H), 1.71-1.55 (m, 14H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ: 147.1, 143.7, 133.6, 132.6, 129.1, 128.4, 127.8, 127.6, 125.9, 125.3, 124.7, 124.3, 117.0, 113.2, 55.0, 54.1, 43.1, 36.9, 33.2, 28.7; LRMS (EI, 70 eV) *m/z* (%): 381 (M^+, 3), 232 (100), 135 (45); HRMS *m/z* (ESI) calcd for $C_{28}H_{32}N$ ($[M+H]^+$) 382.2529, found 382.2541.



***N*-(2- adamant-1-yl-1-(3,4-dimethoxyphenyl)ethyl)aniline (4gcb):**

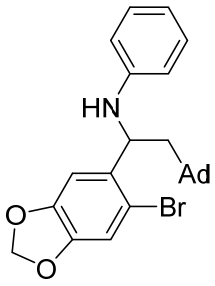
44.5 mg, 57% yield; Rf = 0.8 (PE/EA = 10 : 1); Light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.08 (t, *J* = 7.2 Hz, 2H), 6.88-6.77 (m, 3H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 2H), 4.41-4.32 (m, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 1.99-1.91 (m, 3H), 1.70-1.54 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.1, 158.2, 135.7, 132.9, 132.9, 128.1, 127.3, 122.1, 119.5, 117.5, 116.1, 114.0, 55.2, 45.8, 38.6, 31.5, 29.0, 15.6, 12.6, 12.1; LRMS (EI, 70 eV) *m/z* (%): 391 (M^+, 4), 242 (65), 135 (100); HRMS *m/z* (ESI) calcd for $C_{26}H_{34}NO_2$ ($[M+H]^+$) 392.2584, found 392.2591.



***N*-(2-adamant-1-yl-1-(4-methoxy-2-methylphenyl)ethyl)aniline (4hcb):**

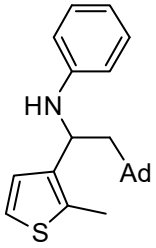
62.5 mg, 83% yield; Rf = 0.6 (PE/EA = 20 : 1); Light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.12-7.04 (m, 4H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.48 (m, 2H), 4.40-4.33 (s, 1H), 3.90 (s, 1H), 3.77 (s, 3H), 2.19 (s, 3H), 1.98-1.91 (s, 3H), 1.70-1.51 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.3, 147.2, 137.7, 129.0, 128.3, 126.6, 124.0, 116.7, 113.0, 109.8, 55.2, 55.0, 53.2, 43.0, 36.9, 33.0, 28.6, 16.4; LRMS (EI, 70 eV) *m/z* (%): 375 (M^+, 4), 226

(100), 135 (6); HRMS *m/z* (ESI) calcd for $C_{26}H_{34}NO$ ($[M+H]^+$) 376.2635, found 376.2642.



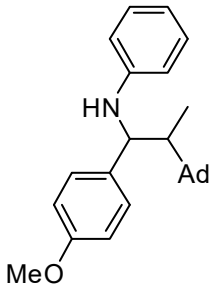
_N_-(1-(6-bromobenzo[*d*][1,3]dioxol-5-yl)-2-adamant-1-ylethyl)aniline (4icb):

68.9 mg, 76% yield; Rf = 0.5 (PE/EA = 10 : 1); Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.15-7.07 (m, 2H), 6.97-6.92 (m, 2H), 6.69-6.61 (m, 1H), 6.48-6.40 (m, 2H), 5.88 (d, *J* = 11.2 Hz, 2H), 4.81-4.73 (m, 1H), 2.00-1.92 (m, 3H), 1.76-1.40 (s, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.8, 147.1, 146.4, 138.0, 129.2, 117.2, 112.9, 112.6, 112.0, 107.3, 101.5, 53.3, 52.9, 43.2, 36.9, 33.3, 28.7; LRMS (EI, 70 eV) m/z (%): 455 (M^++2, 3), 453 (M^+, 3), 306 (49), 135 (100); HRMS *m/z* (ESI) calcd for $C_{25}H_{29}{}^{79}BrNO_2$ ($[M+H]^+$) 454.1376, found 454.1385.



***N*-(2- adamant-1-yl -1-(2-methylthiophen-3-yl)ethyl)aniline (4jcb):**

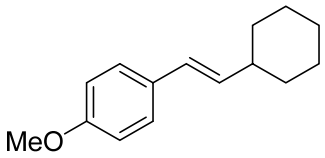
40.7 mg, 58% yield; Rf = 0.7 (PE/EA = 20 : 1); Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.11 (t, *J* = 6.8 Hz, 2H), 7.03-6.98 (m, 1H), 6.80-6.74 (s, 1H), 6.67 (t, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 2H), 4.74-4.67 (m, 1H), 3.93 (s, 1H), 2.27 (s, 3H), 2.00-1.91 (s, 3H), 1.71-1.57 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.9, 145.6, 130.4, 130.2, 129.1, 121.8, 117.5, 113.1, 54.1, 48.6, 43.0, 36.8, 32.9, 28.6, 13.9; LRMS (EI, 70 eV) *m/z* (%): 351 (M^+, 4), 202 (31), 135 (100); HRMS *m/z* (ESI) calcd for $C_{23}H_{30}NS$ ($[M+H]^+$) 352.2093 found 352.2101.



***N*-(2- adamant-1-yl -1-(4-methoxyphenyl)propyl)aniline (4lcb):**

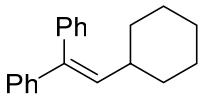
dr >20:1

32.3 mg, 43% yield; Rf = 0.7 (PE/EA = 20 : 1); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (d, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 2H), 6.83 (d, *J* = 7.6 Hz, 2H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.42 (d, *J* = 7.6 Hz, 2H), 4.66 (s, 1H), 4.06 (s, 1H), 3.77 (s, 3H), 2.04-1.94 (m, 3H), 1.67-1.56 (m, 13H), 0.83 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.0, 147.0, 136.8, 129.0, 127.5, 116.6, 113.6, 113.1, 55.4, 55.2, 51.4, 40.6, 37.1, 35.3, 28.8, 6.1; LRMS (EI, 70 eV) *m/z* (%): 375 (M^+, 3), 212 (100), 135 (10); HRMS *m/z* (ESI) calcd for $C_{26}H_{34}NO$ ($[M+H]^+$) 376.2635, found 376.2646.



(*E*)-1-(2-cyclohexylvinyl)-4-methoxybenzene (5aa) [1]**:**

12.3 mg, 29% yield; Rf = 0.8 (PE/EA = 30 : 1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.27 (d, J = 9.2 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 6.26 (d, J = 16.0 Hz, 1H), 6.10-6.05 (m, 1H), 3.80 (s, 3H), 2.31-2.27 (m, 1H), 1.83-1.79 (m, 2H)1.71-1.62 (m, 4H), 1.54-1.40 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.5, 135.7, 130.9, 127.0, 125.9, 113.9, 55.3, 43.2, 34.8, 29.7, 28.4, 26.2; LRMS (EI, 70 eV) *m/z* (%): 216 (M^+, 59), 165 (47), 134 (100), 121 (41).



(2-Cyclohexylethene-1,1-diyl)dibenzene (5n)[1]**:**

46.6 mg, 88% yield; Rf = 0.5 (PE/EA = 50 : 1); Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1H NMR (500 MHz, CDCl3) δ 7.37-7.17 (m, 10H), 5.90 (d, J = 10.0 Hz, 1H), 2.15-2.09 (m, 1H), 1.69-1.59 (m, 5H), 1.26-1.15 (m, 5H); ^{13}C

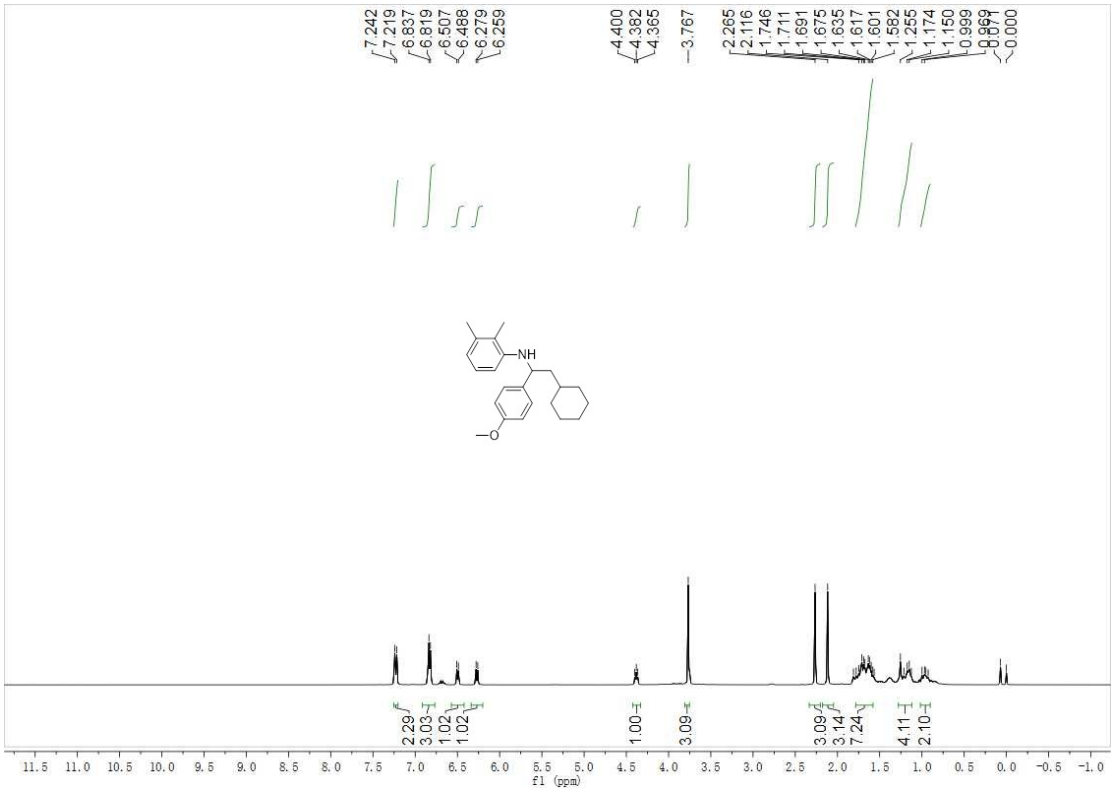
NMR (125 MHz, $CDCl_3$) δ: 142.9, 140.6, 139.6, 136.0, 129.8, 128.1, 128.0, 127.2, 126.7, 126.7, 38.3, 33.3, 26.0, 25.6.

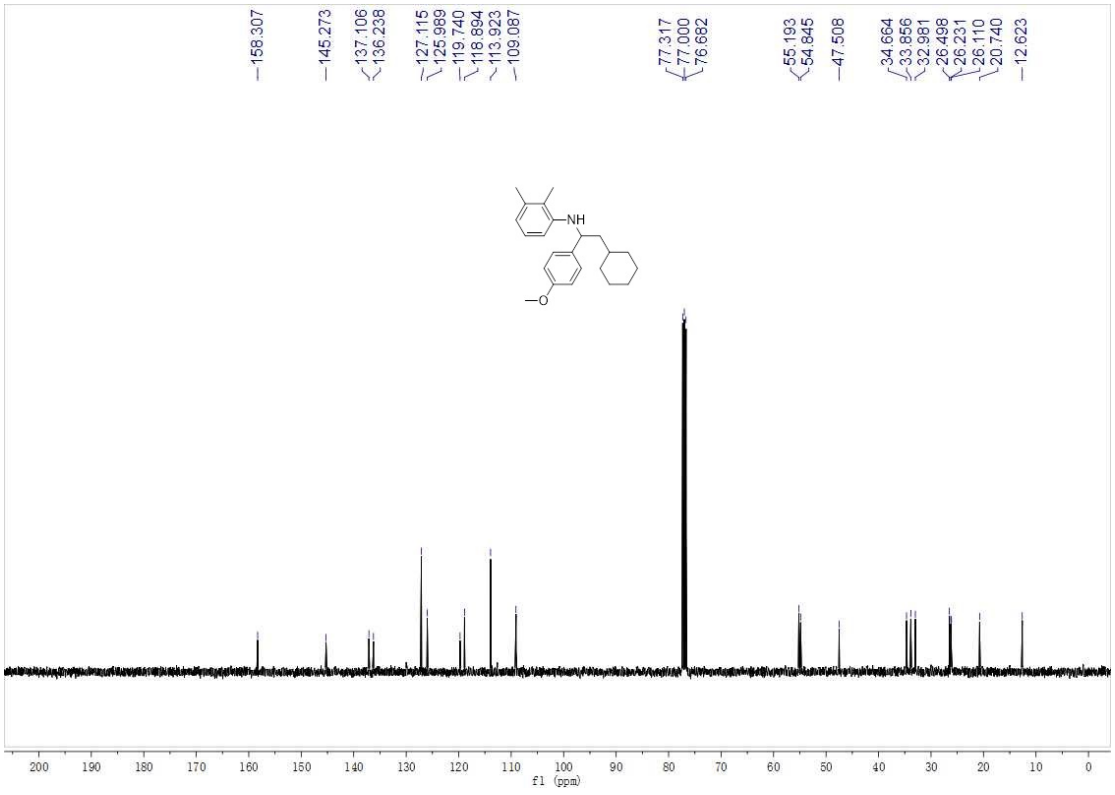
(C) References

(1) Xia, Z.-H.; Zhang, C.-L.; Gao, Z.-H.; Ye, S. *Org. Lett.* **2018**, *20*, 3496.

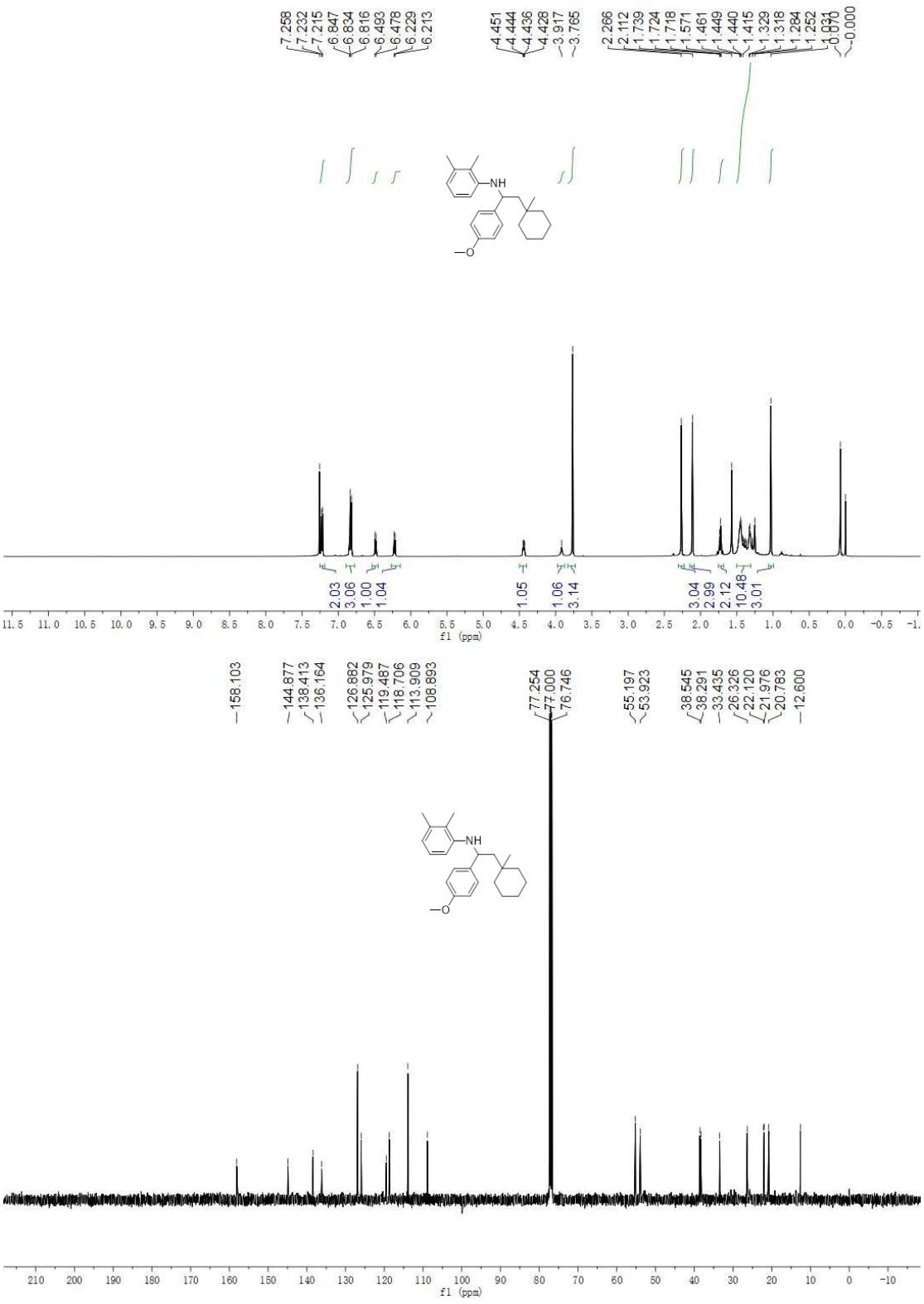
(D) Spectra

N-(2-cyclohexyl-1-(4-methoxyphenyl)ethyl)-2,3-dimethylaniline (4aaa)





_N_-(1-(4-methoxyphenyl)-2-(1-methylcyclohexyl)ethyl)-2,3-dimethylaniline (4aba)



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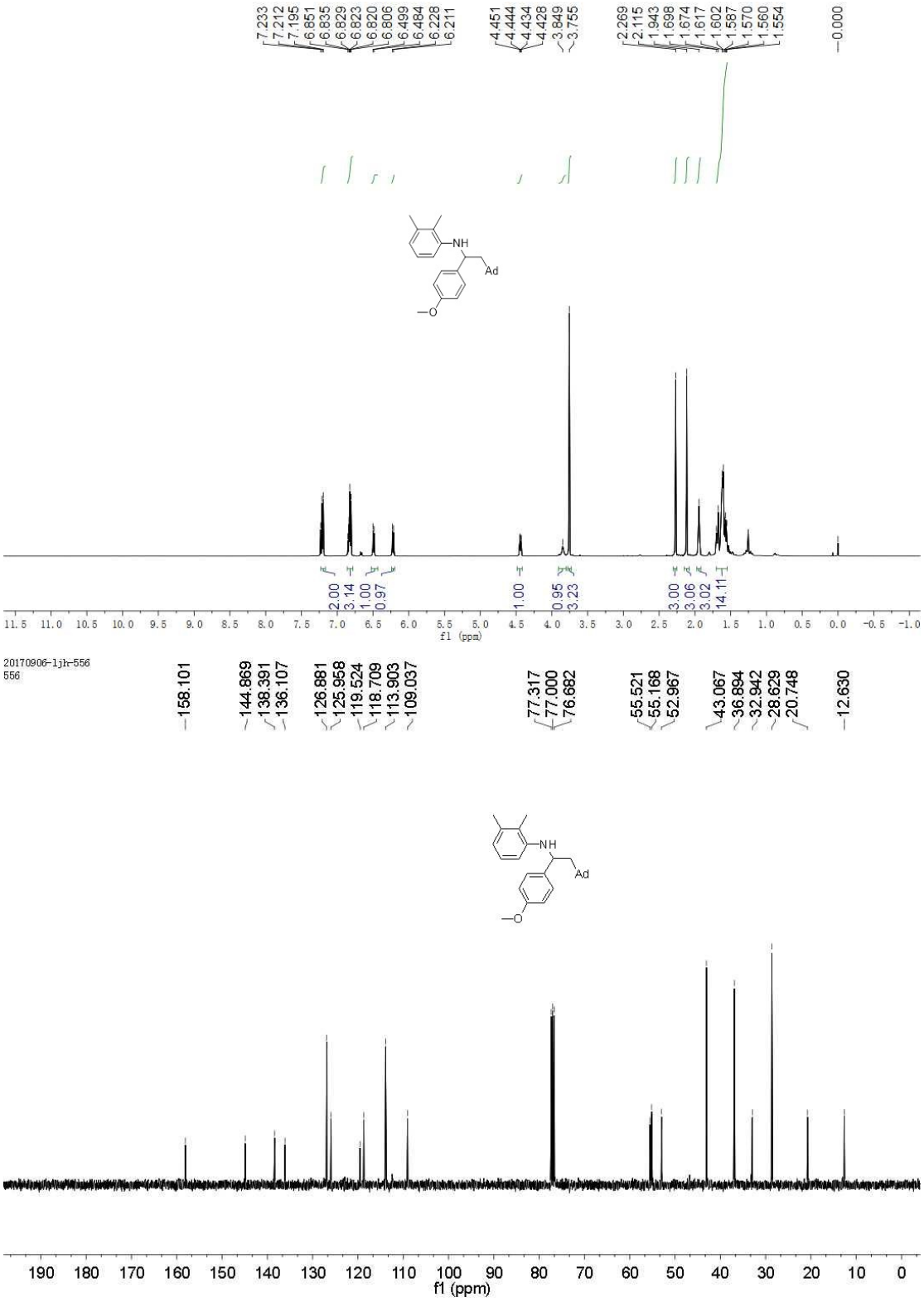
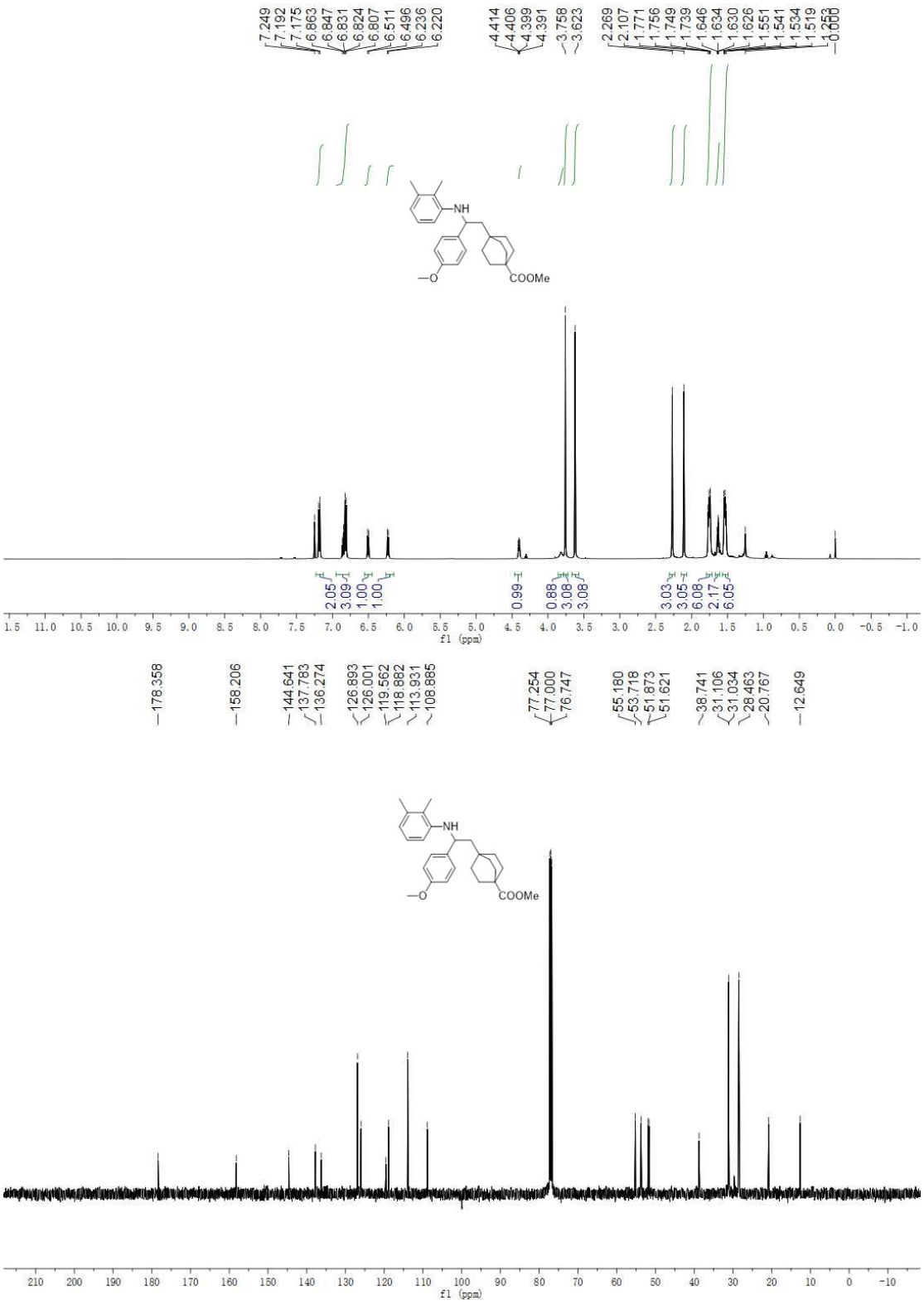


Methyl 4-(2-(2,3-dimethylphenylamino)-2-(4-methoxyphenyl)ethyl)bicyclo[2.2.2]octane-1-carboxylate (4ada)



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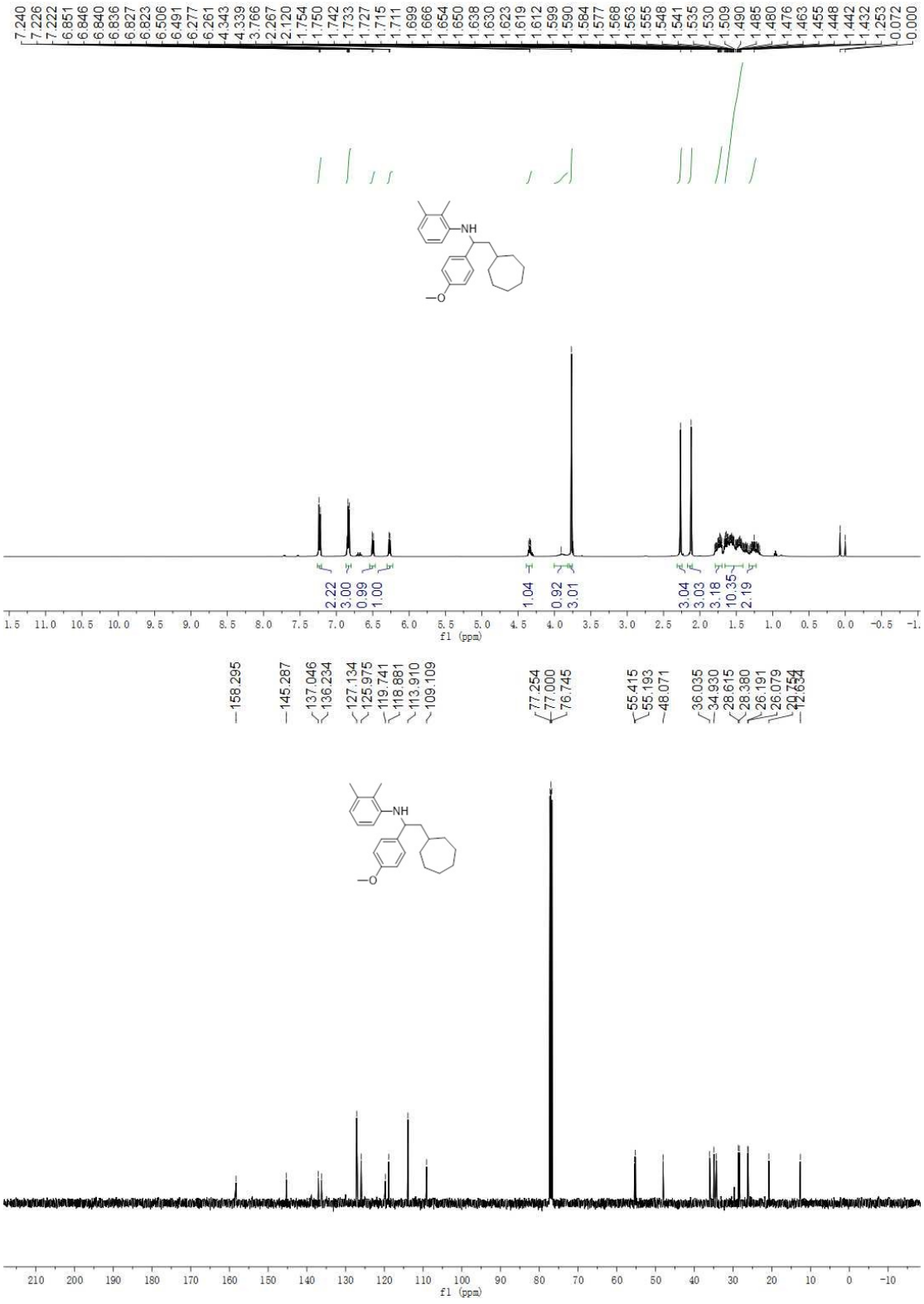
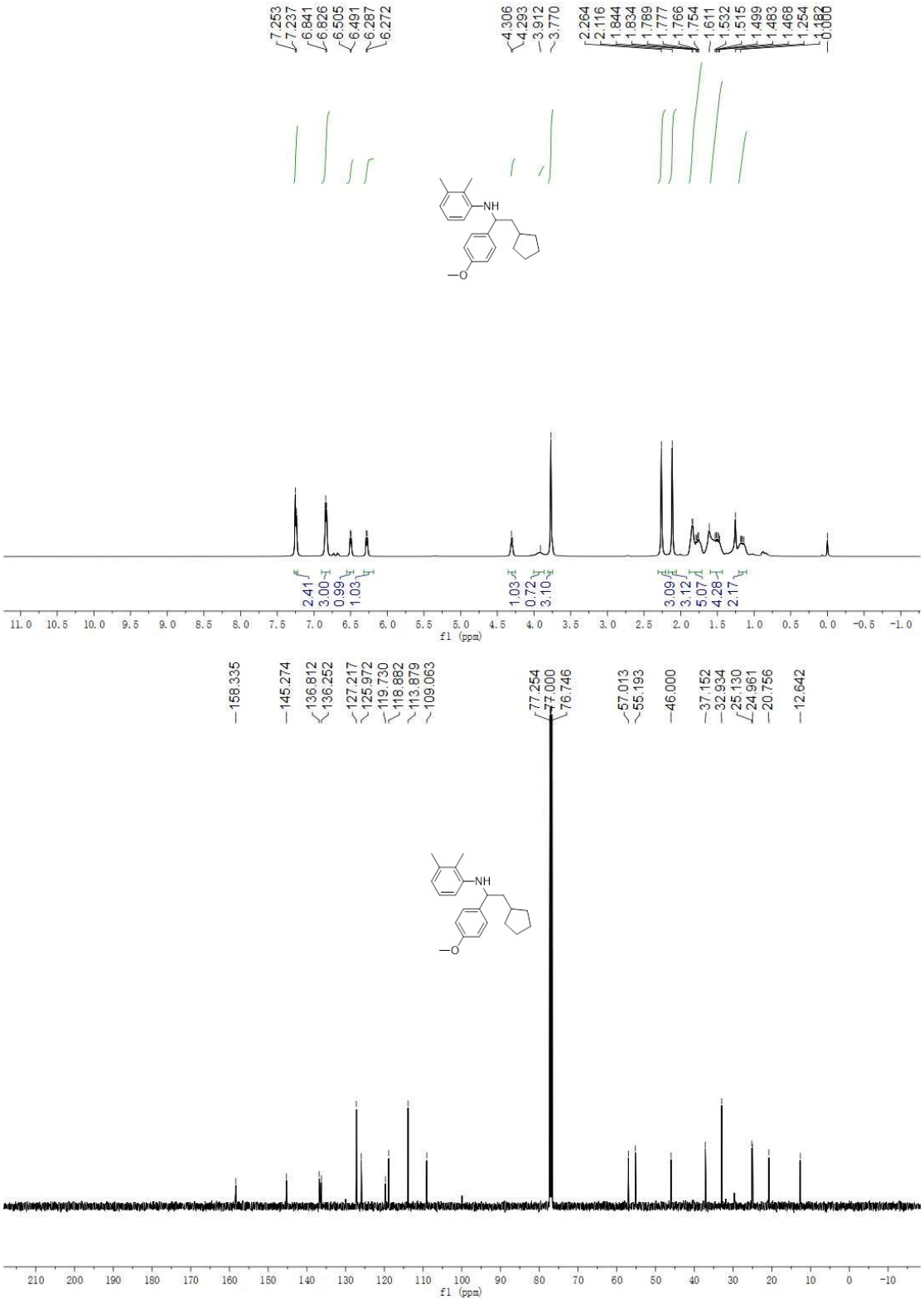
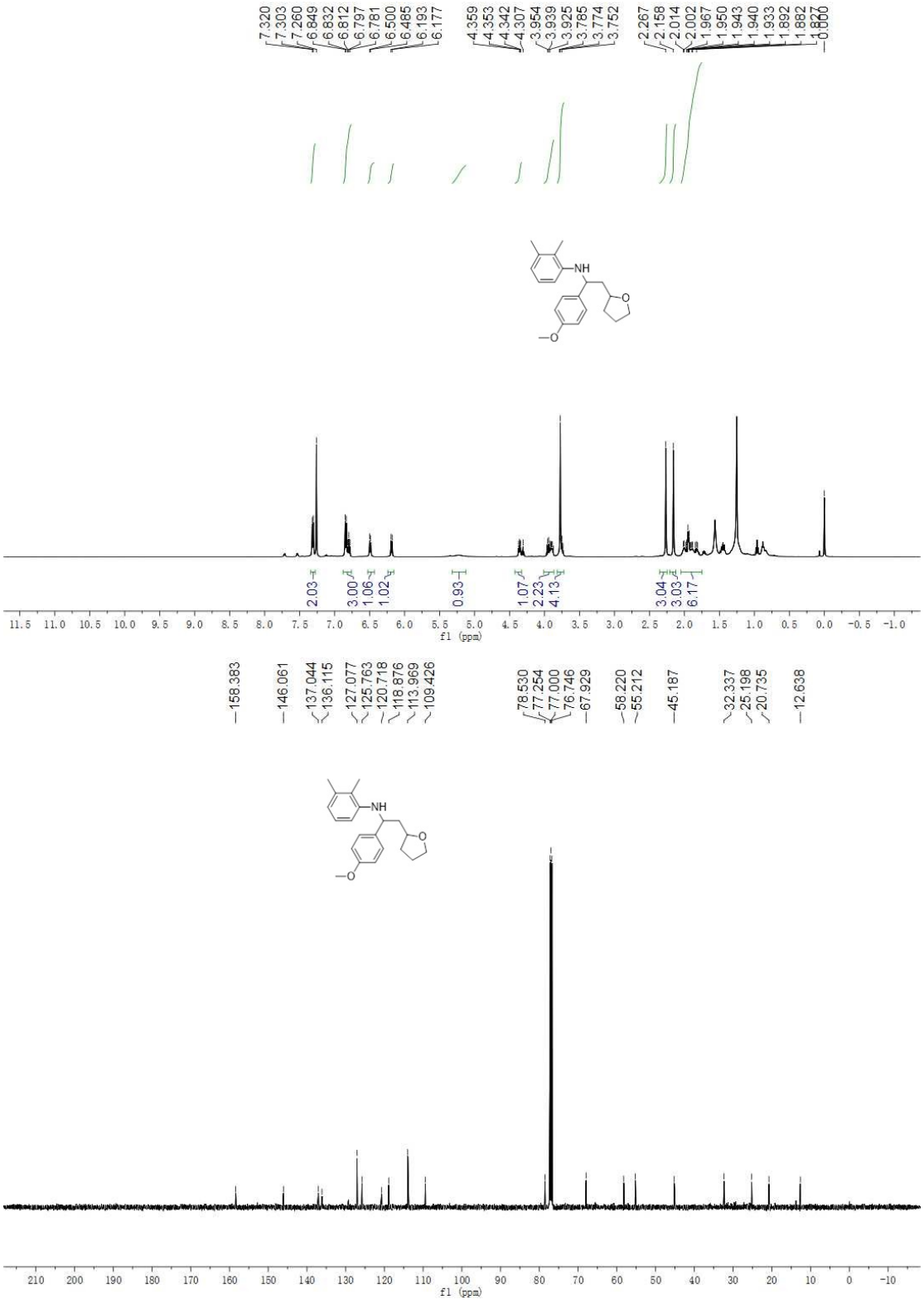
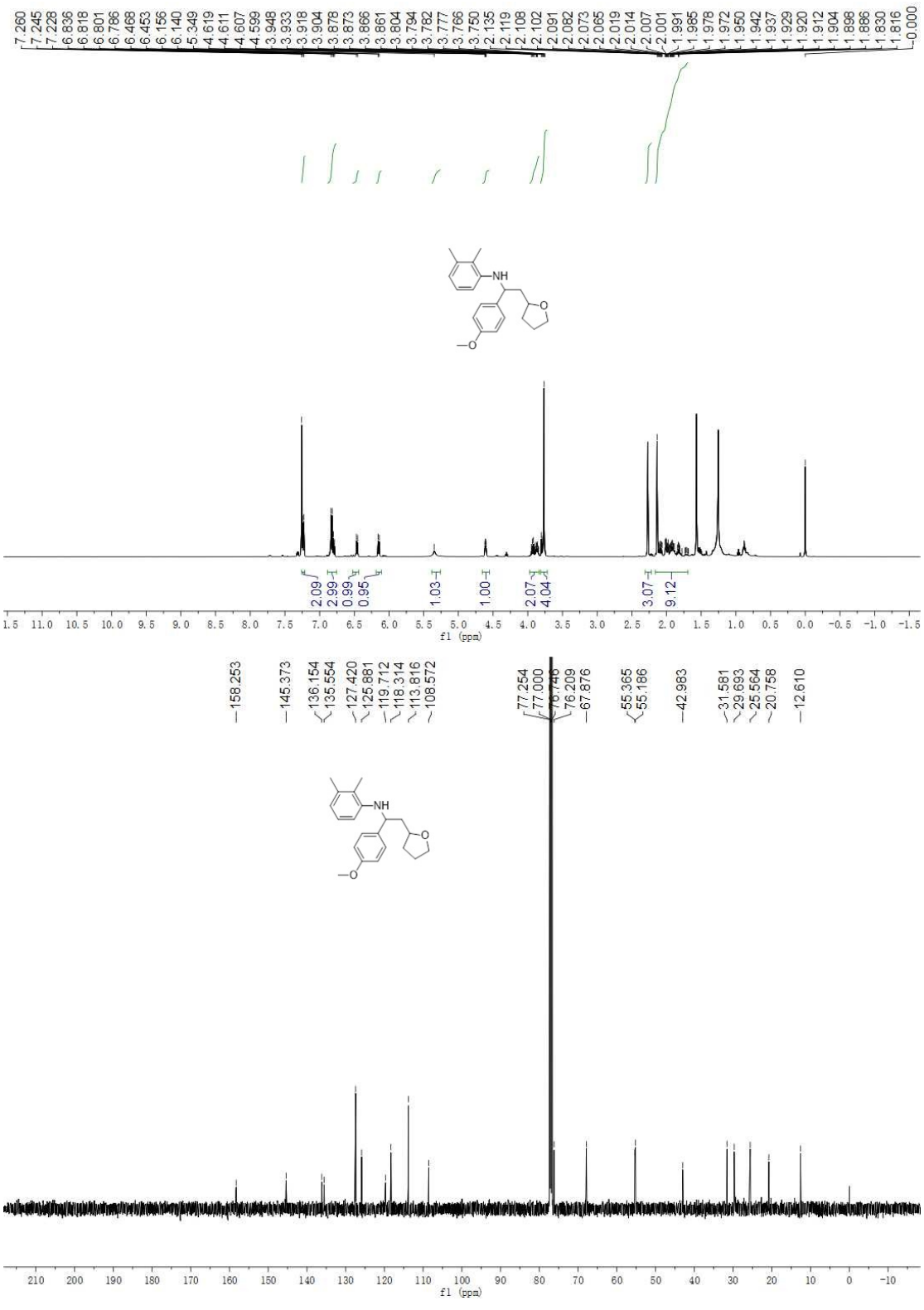


N-(2-cyclopentyl-1-(4-methoxyphenyl)ethyl)-2,3-dimethylaniline (4afa)



_N_-(1-(4-methoxyphenyl)-2-(tetrahydrofuran-2-yl)ethyl)-2,3-dimethylaniline (4aga)

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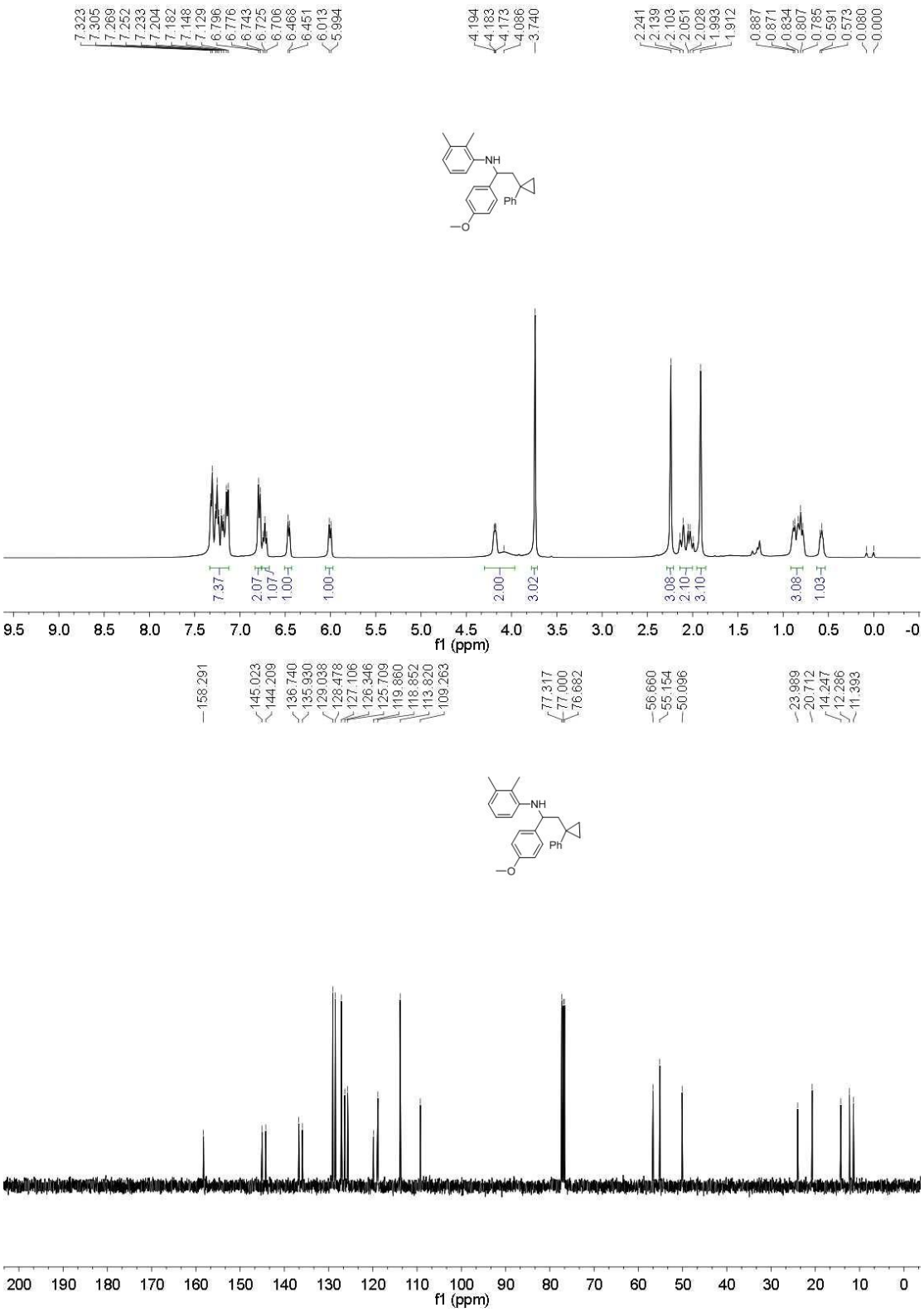
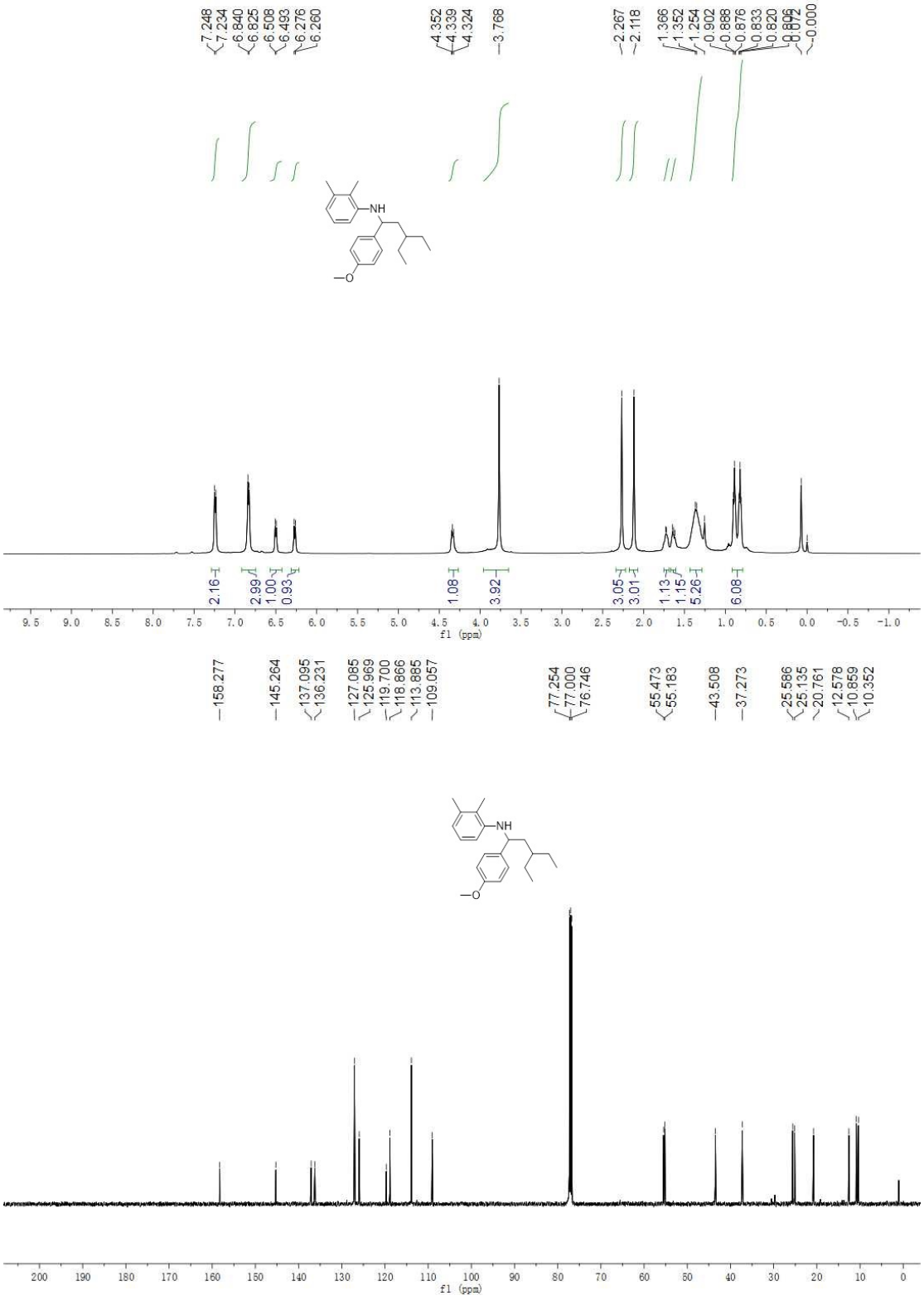
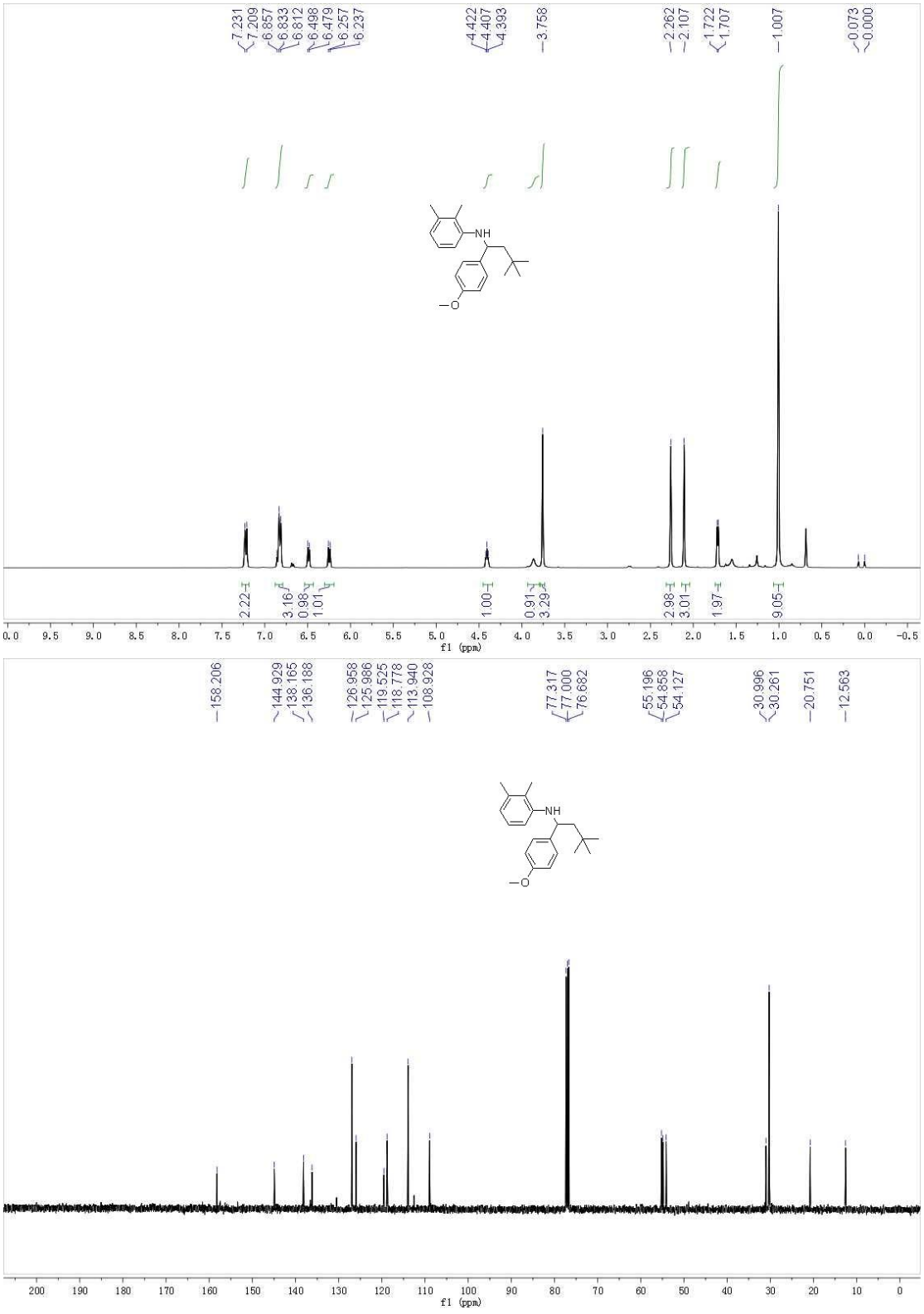


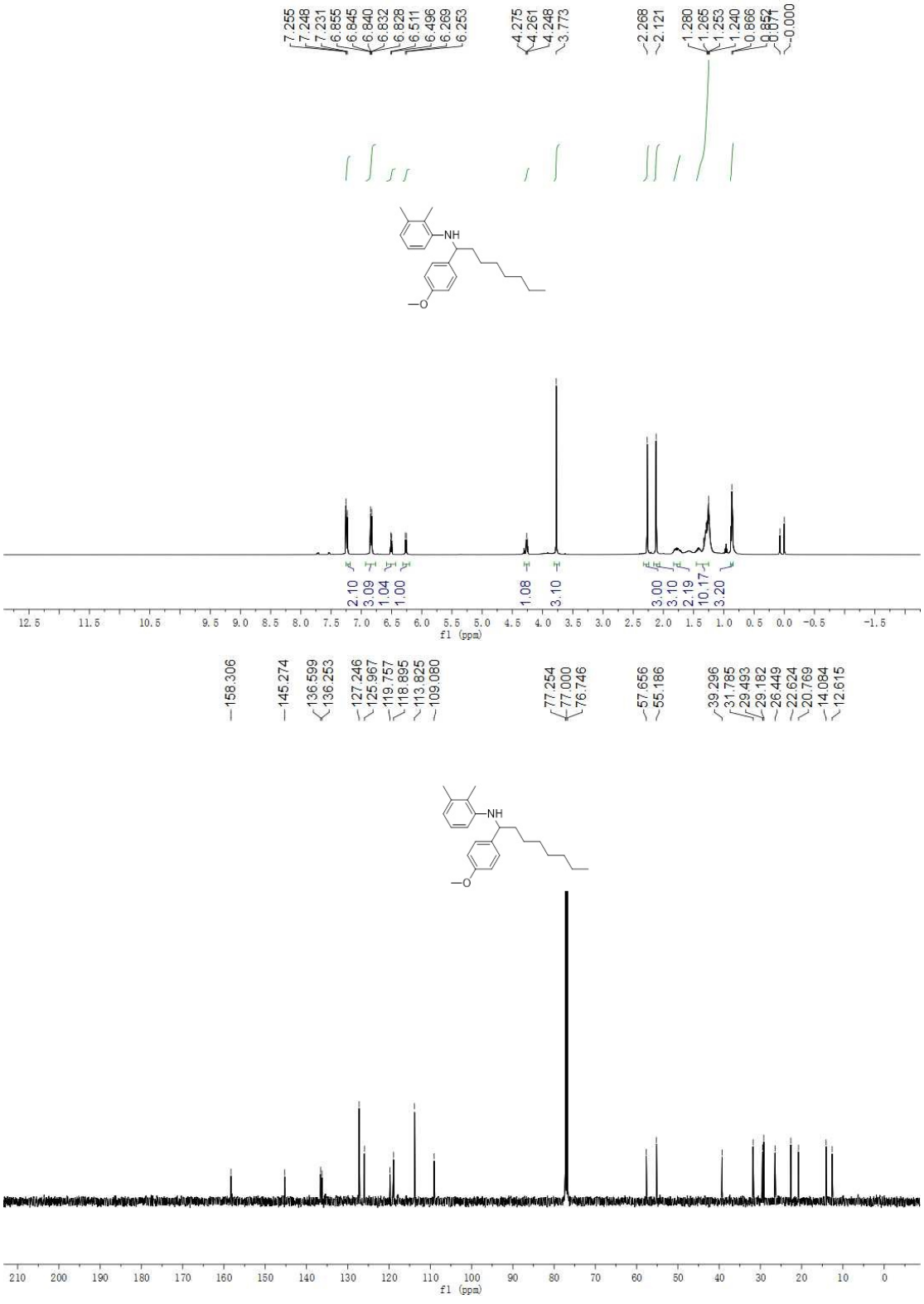
***N*-(3-Ethyl-1-(4-methoxyphenyl)pentyl)-2,3-dimethylaniline (4aia)**



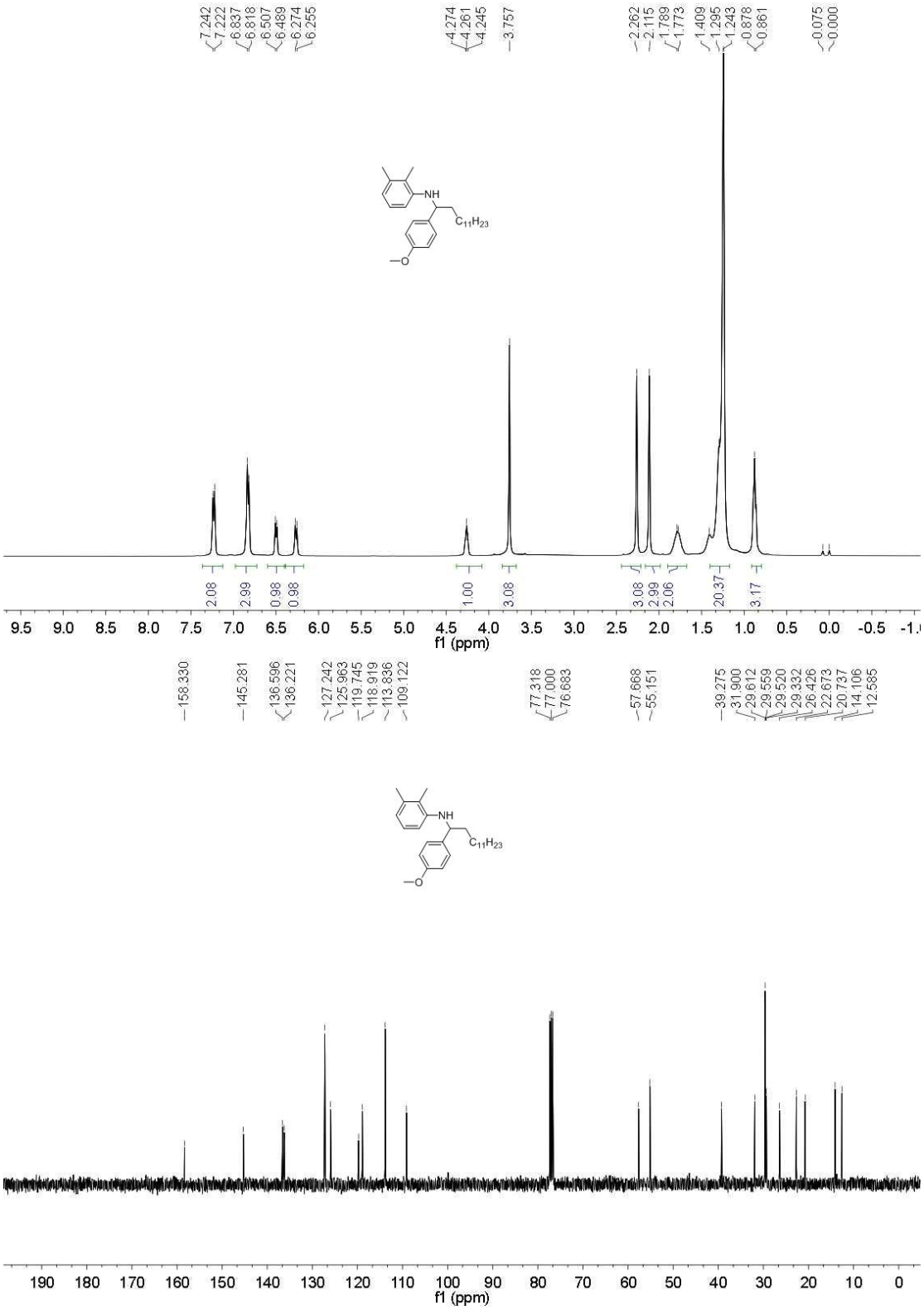
***N*-(1-(4-methoxyphenyl)-3,3-dimethylbutyl)-2,3-dimethylaniline (4aja)**



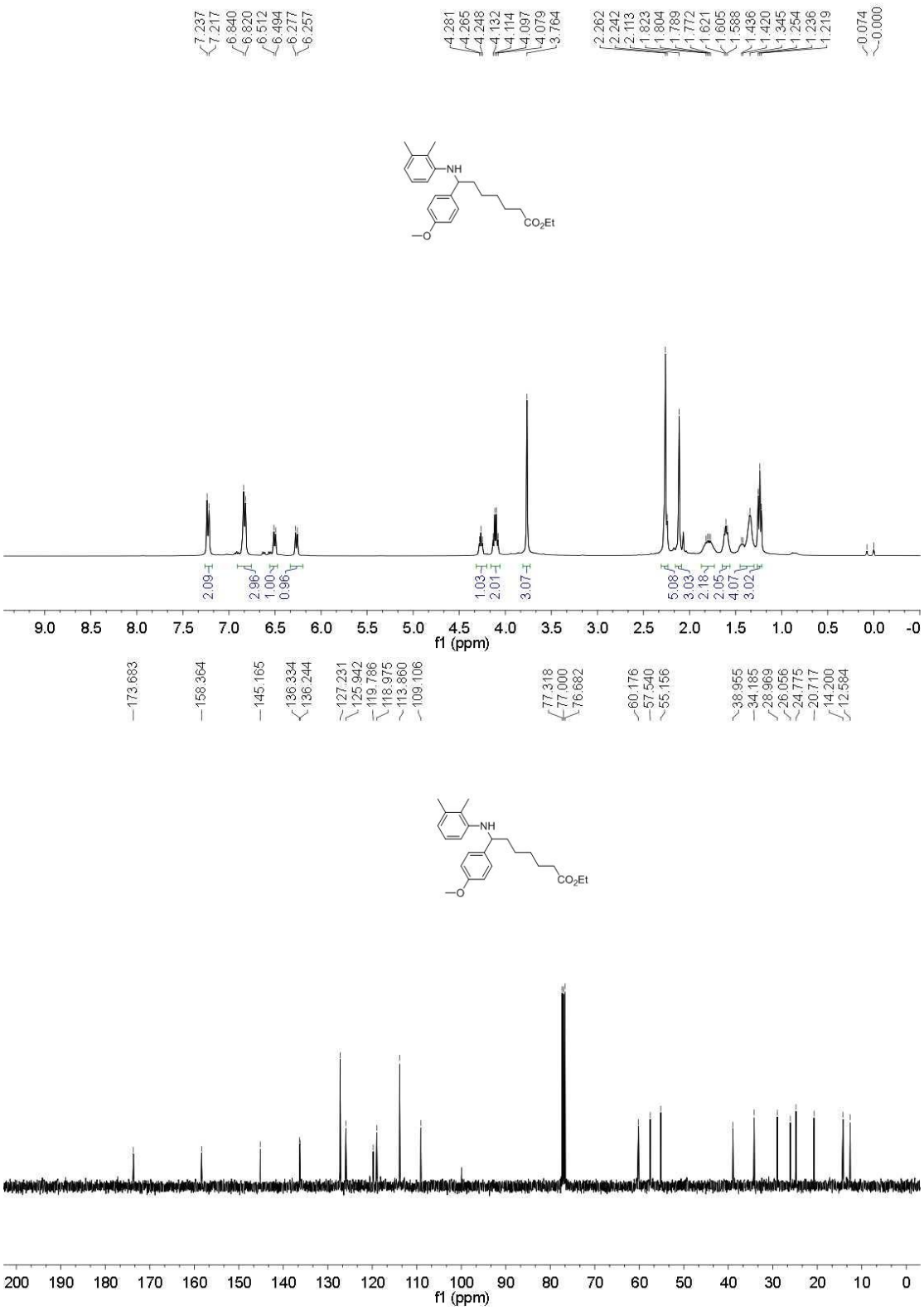
N-(1-(4-methoxyphenyl)octyl)-2,3-dimethylaniline(4aka)



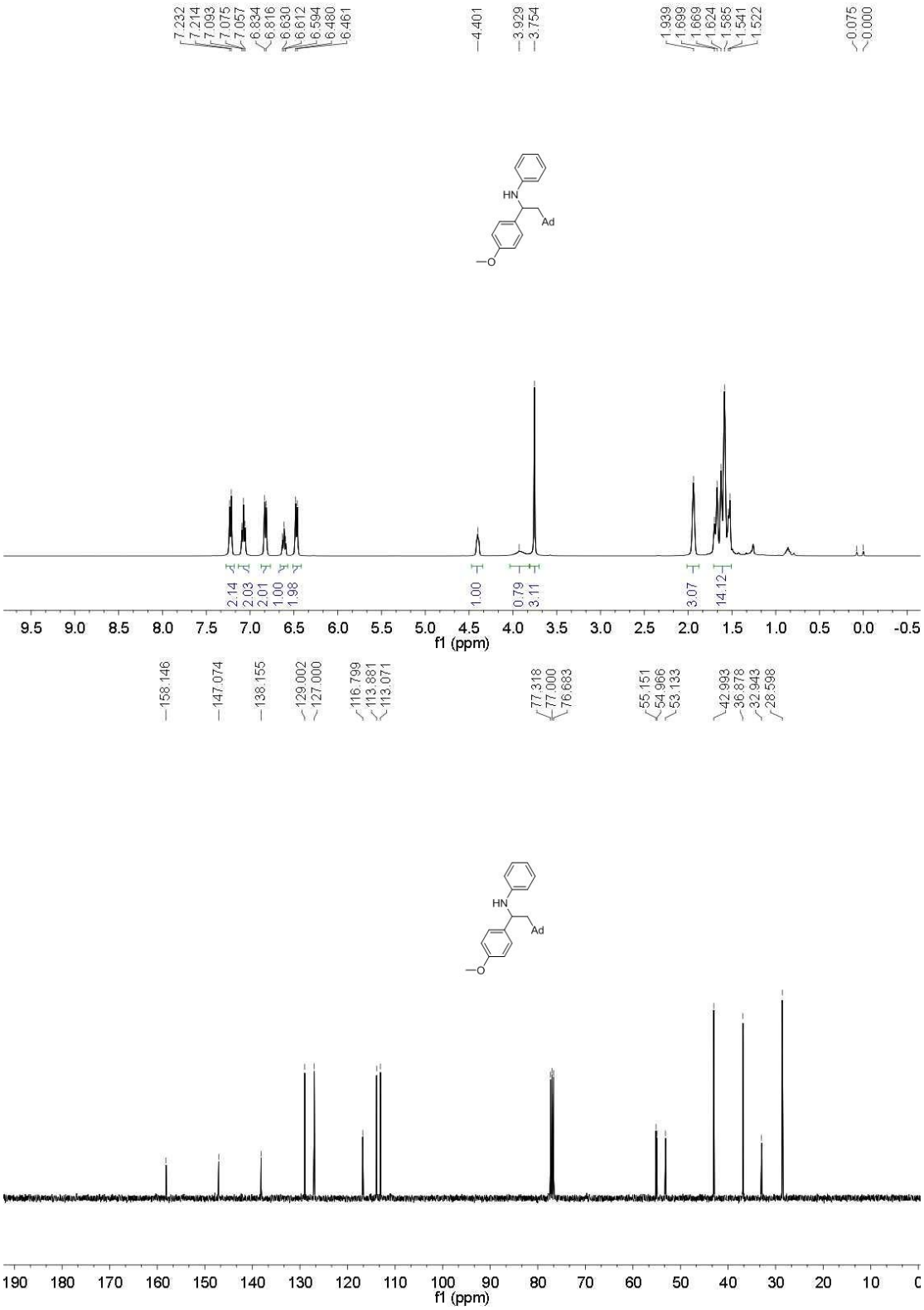
_N_-(1-(4-methoxyphenyl)tridecyl)-2,3-dimethylaniline (4ala)



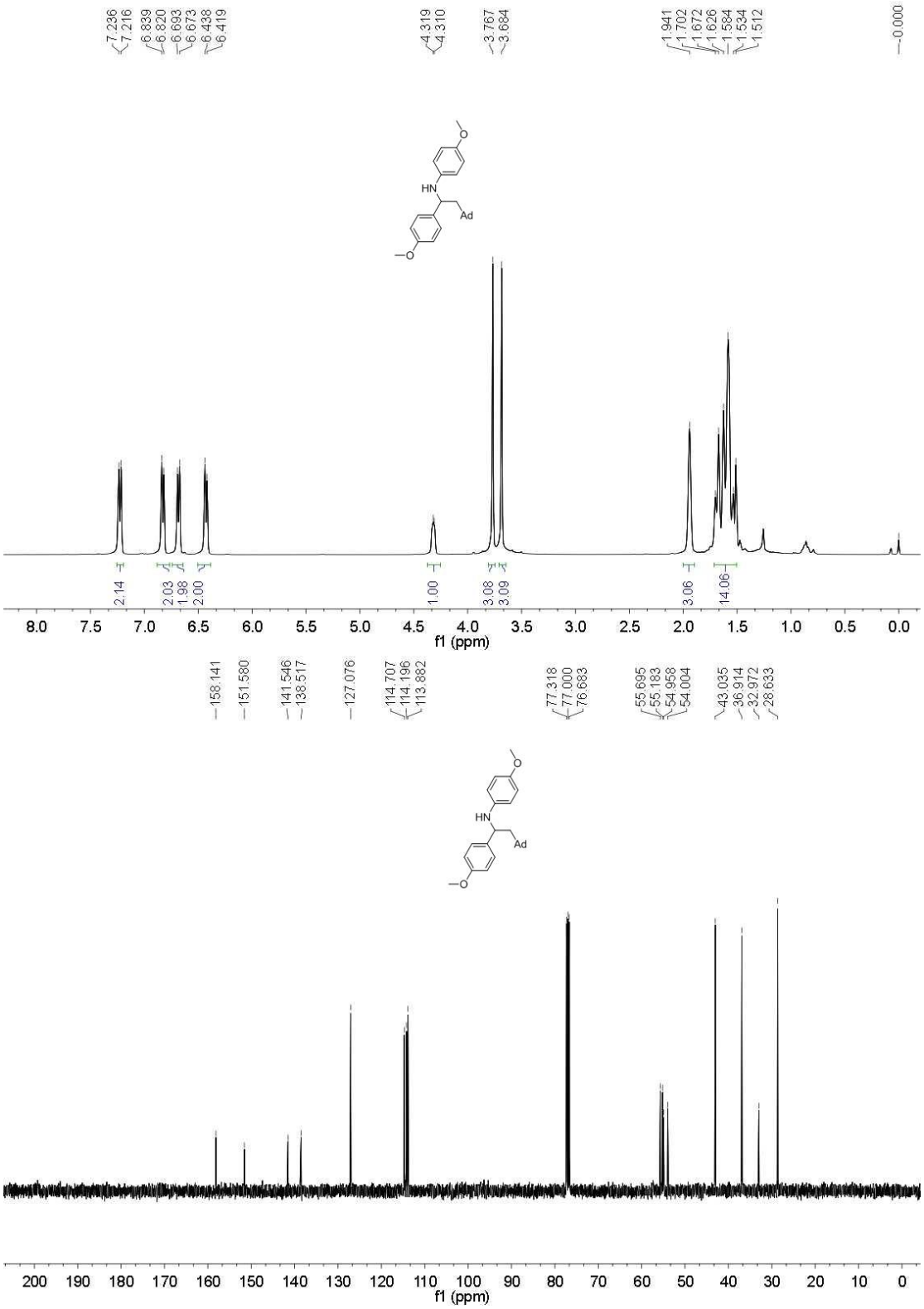
Ethyl 7-(2,3-dimethylphenylamino)-7-(4-methoxyphenyl)heptanoate (4ama)



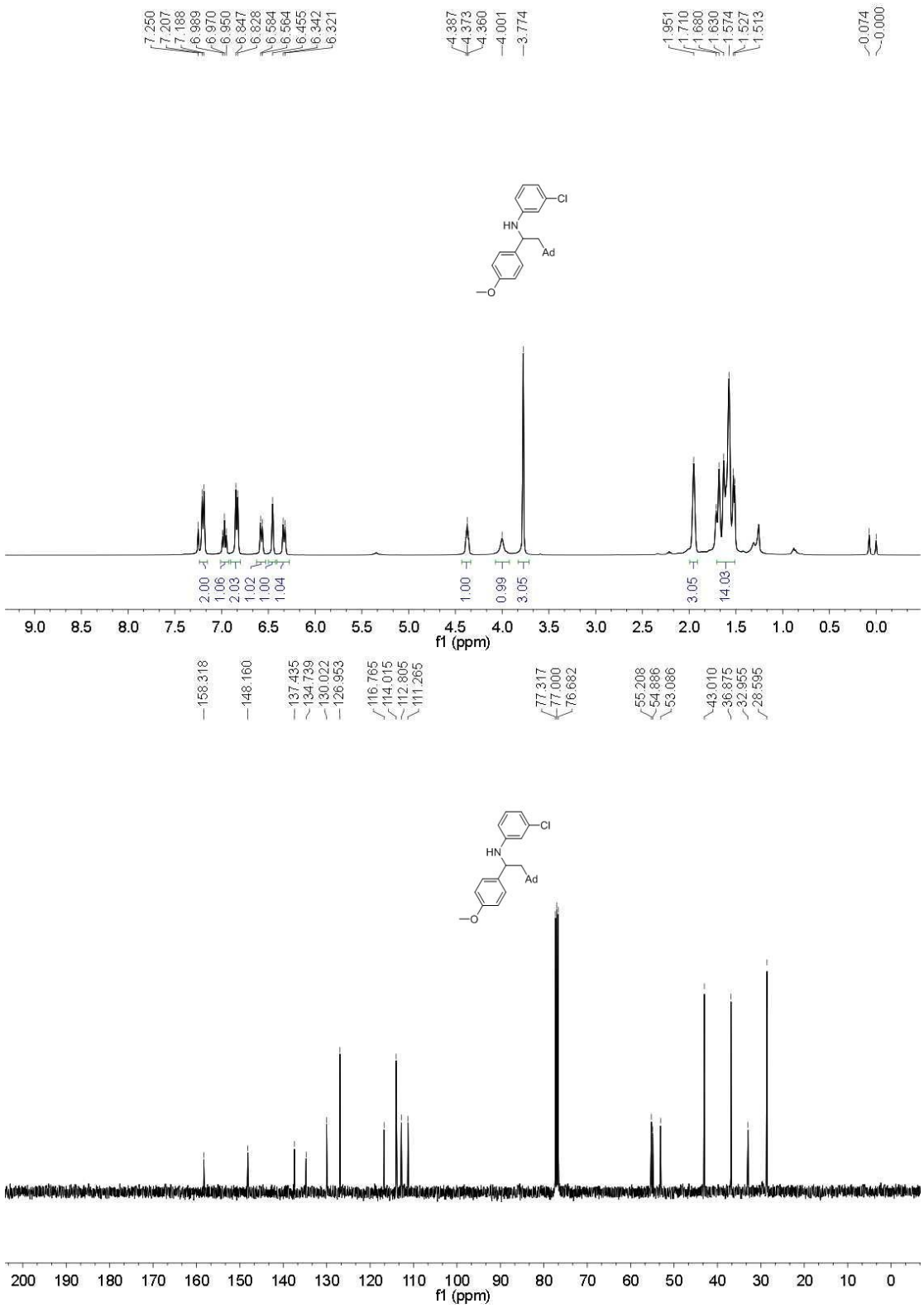
N-(2-adamant-1-yl-1-(4-methoxyphenyl)ethyl)aniline (4acb)



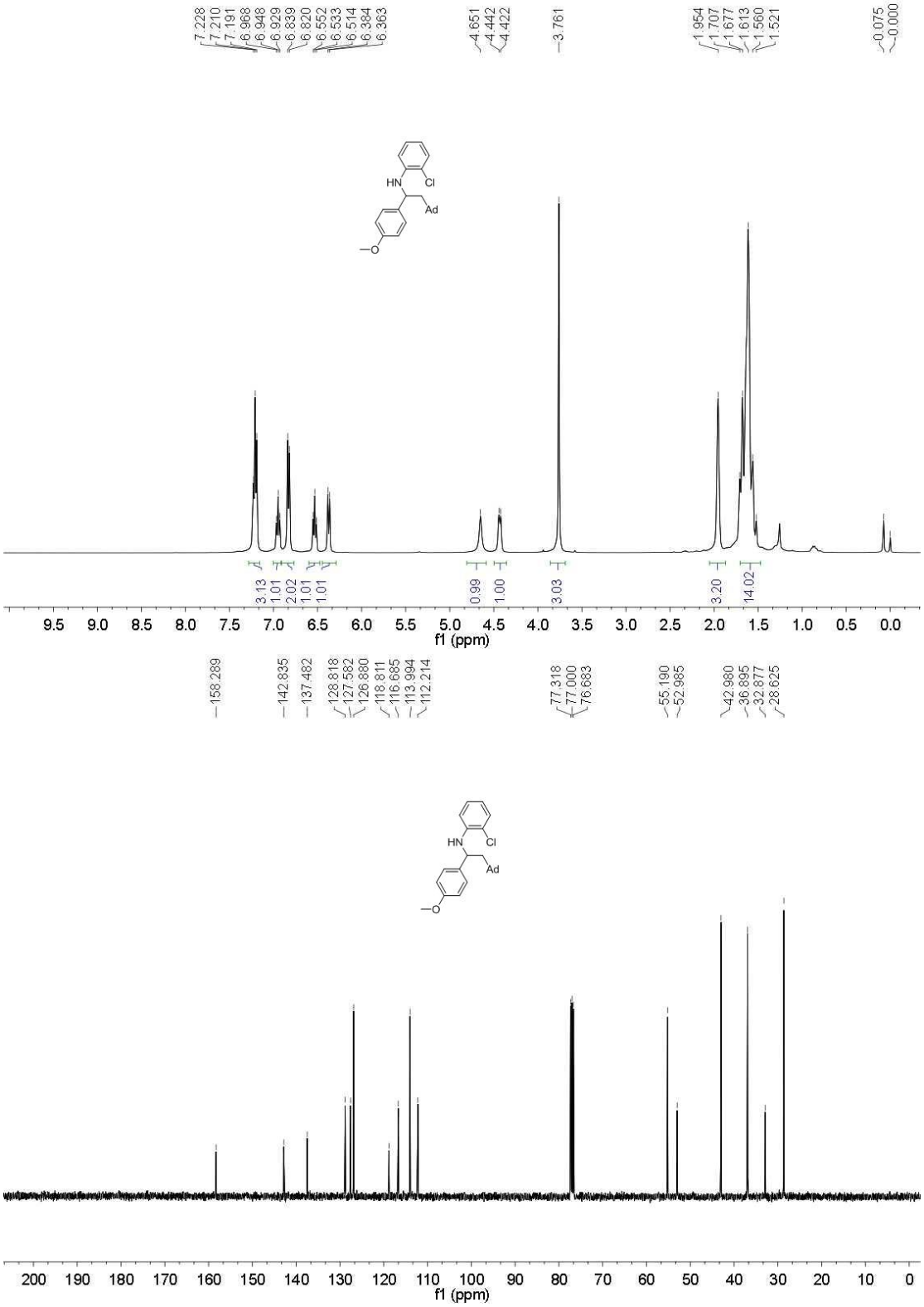
_N_-(2-adamant-1-yl-1-(4-methoxyphenyl)ethyl)-4-methoxyaniline (4acc)



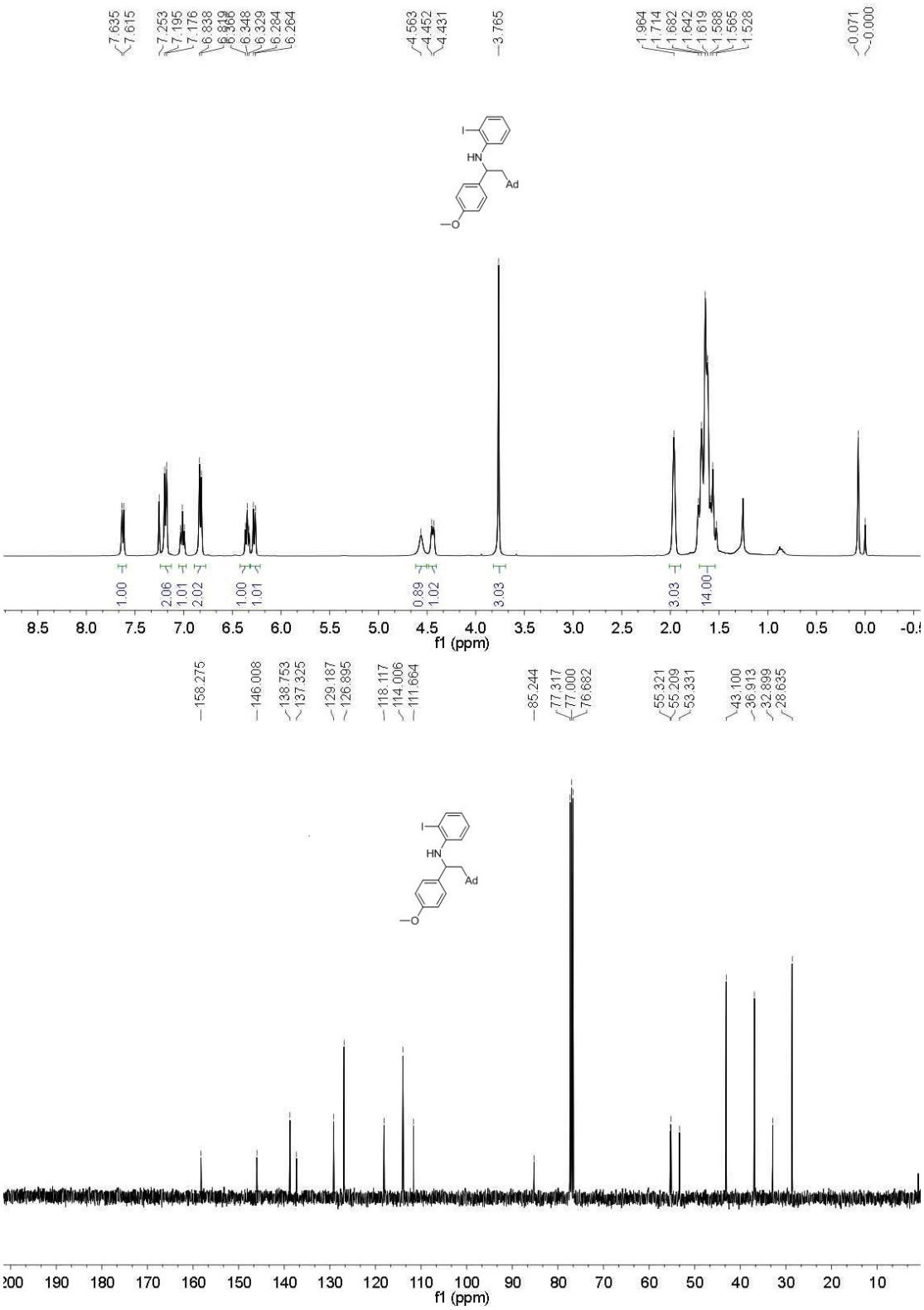
3-Chloro-*N*-(2-adamant-1-yl-1-(4-methoxyphenyl)ethyl)-aniline (4acd)



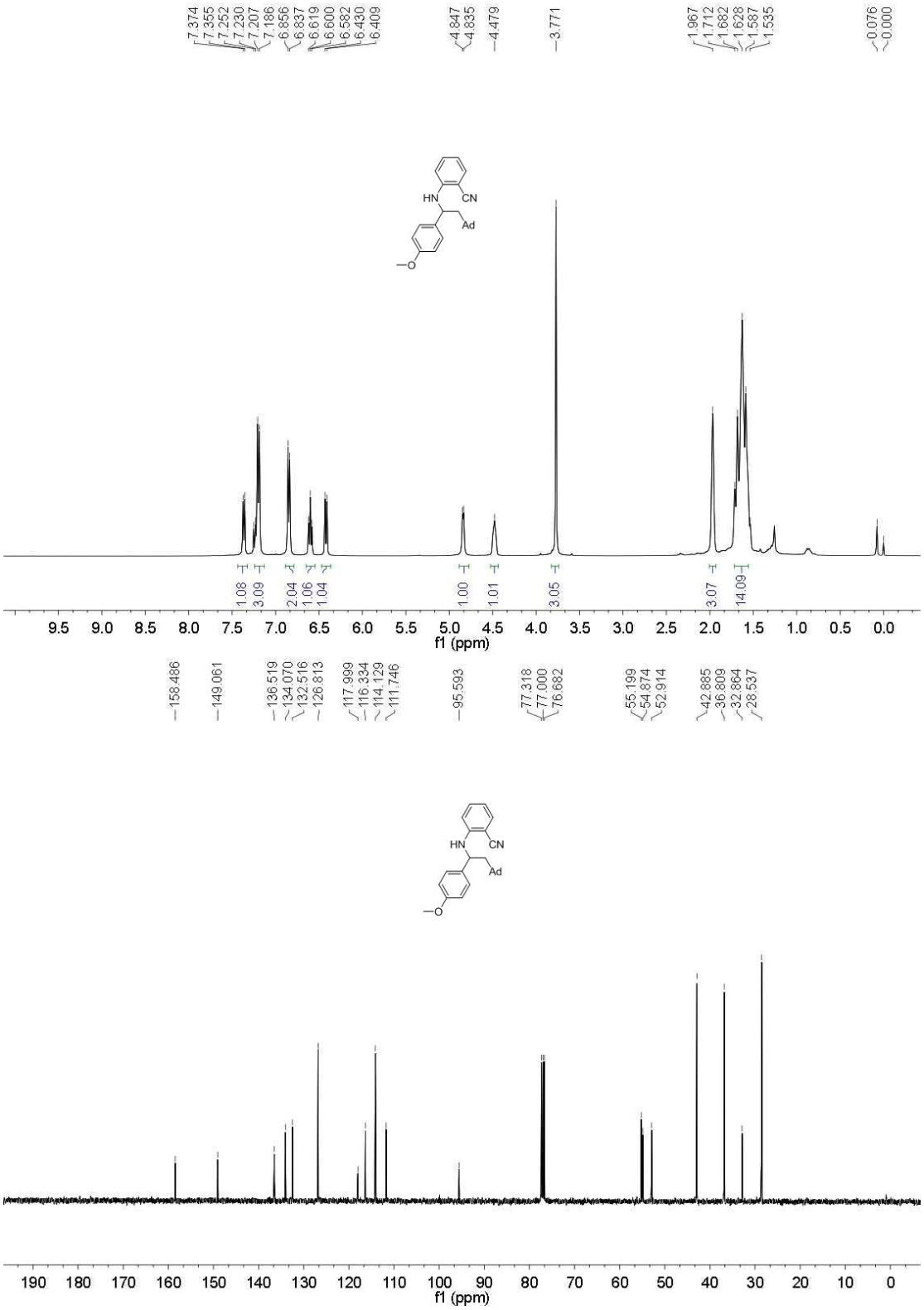
2-Chloro-*N*-(2- adamant-1-yl -1-(4-methoxyphenyl)ethyl)aniline (4ace)



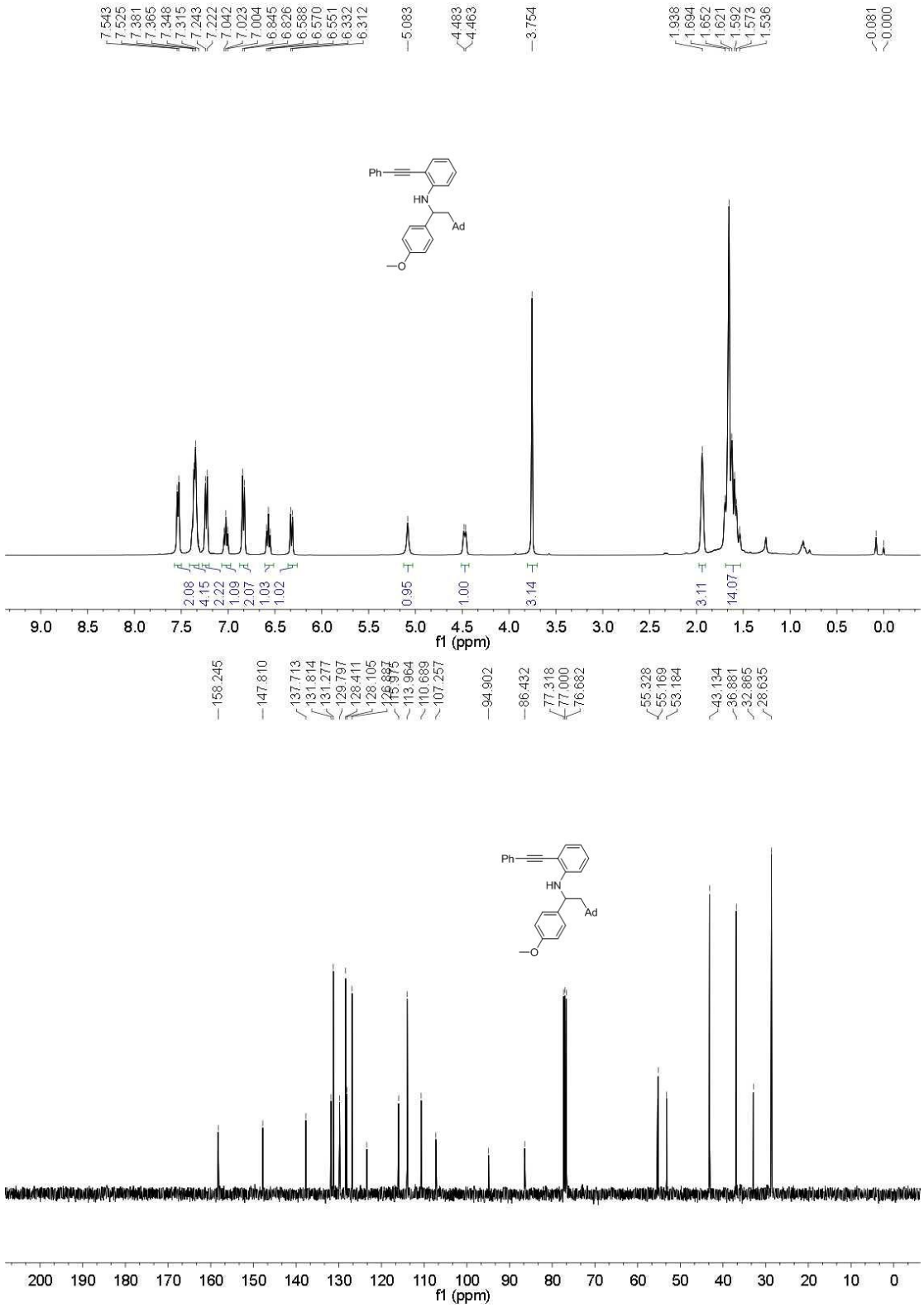
N-(2- adamant-1-yl -1-(4-methoxyphenyl)ethyl)-2-iodoaniline (4acf)



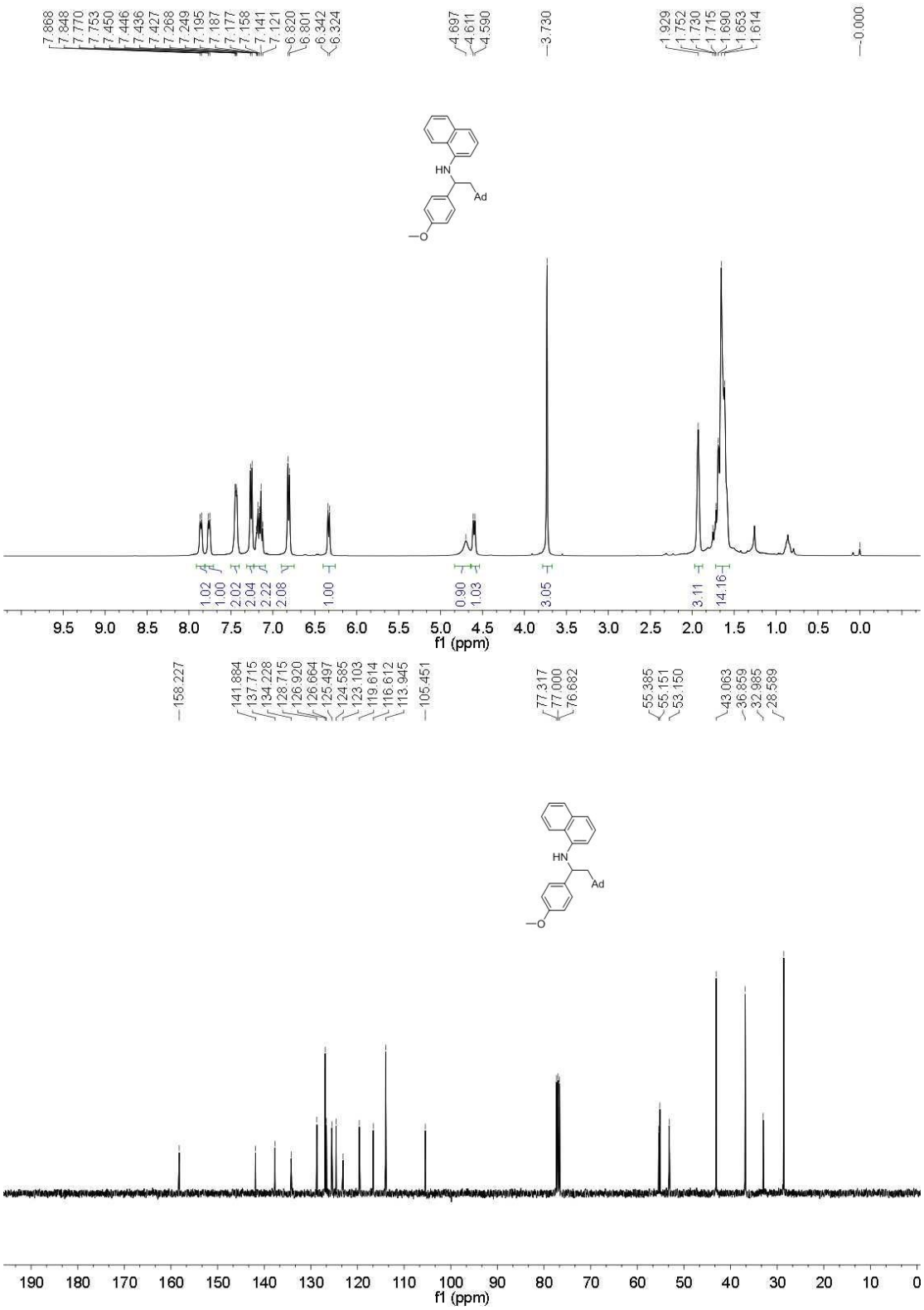
2-(2-adamant-1-yl-1-(4-methoxyphenyl)ethylamino)benzonitrile (4acg)



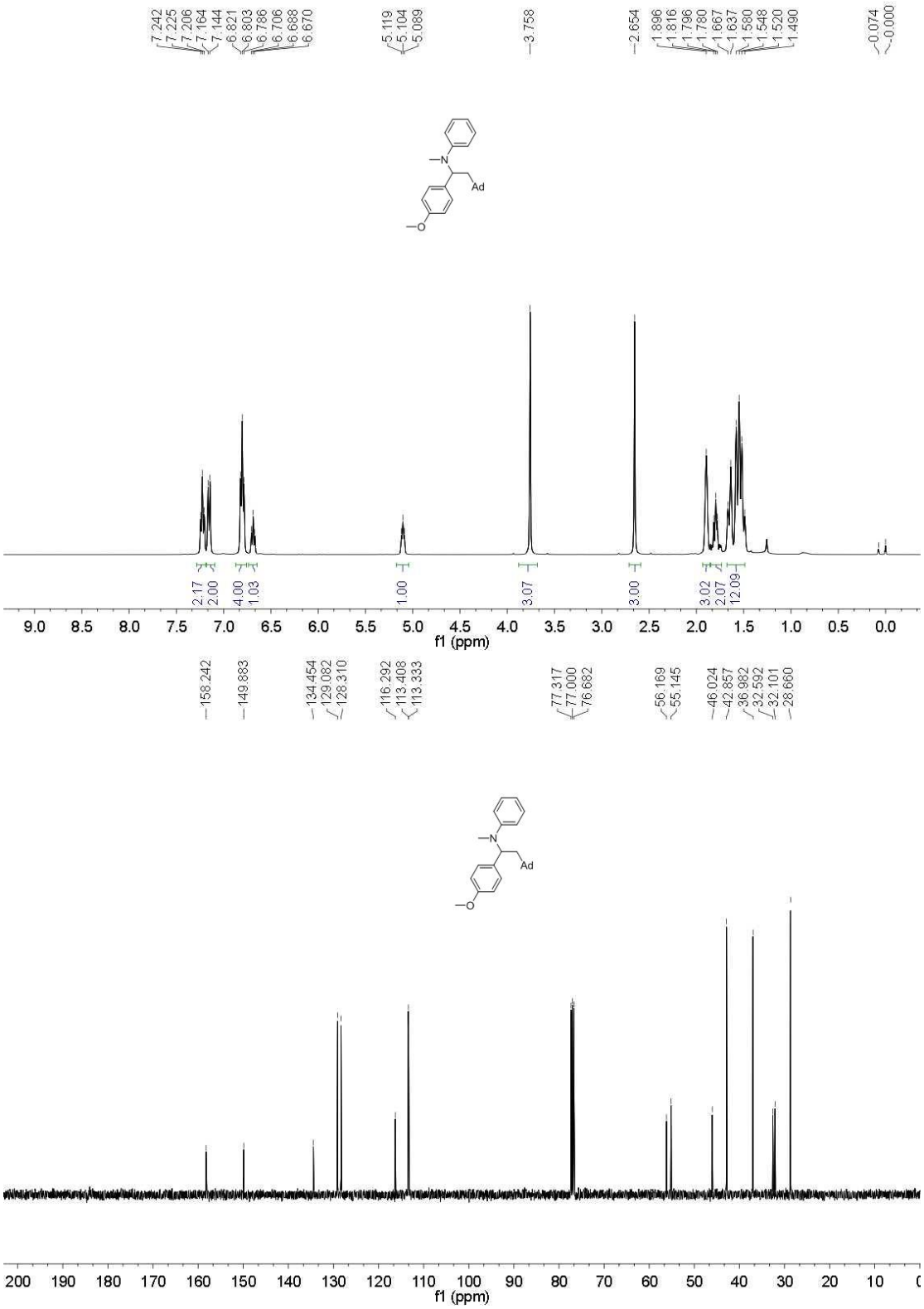
N-(2-adamant-1-yl-1-(4-methoxyphenyl)ethyl)-2-(phenylethynyl)aniline (4ach)



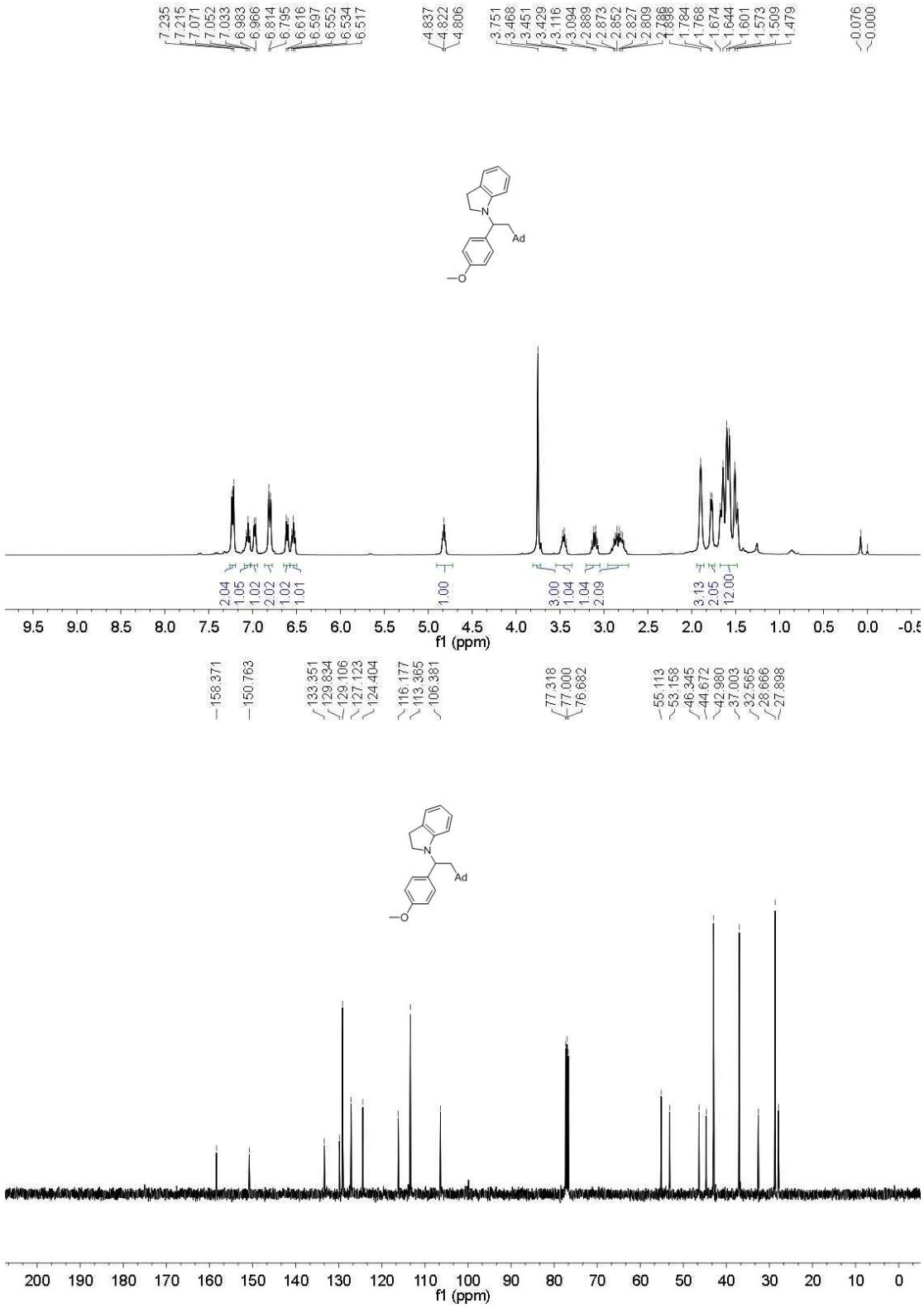
_N_-(2- adamant-1-yl -1-(4-methoxyphenyl)ethyl)naphthalen-1-amine (4aci)



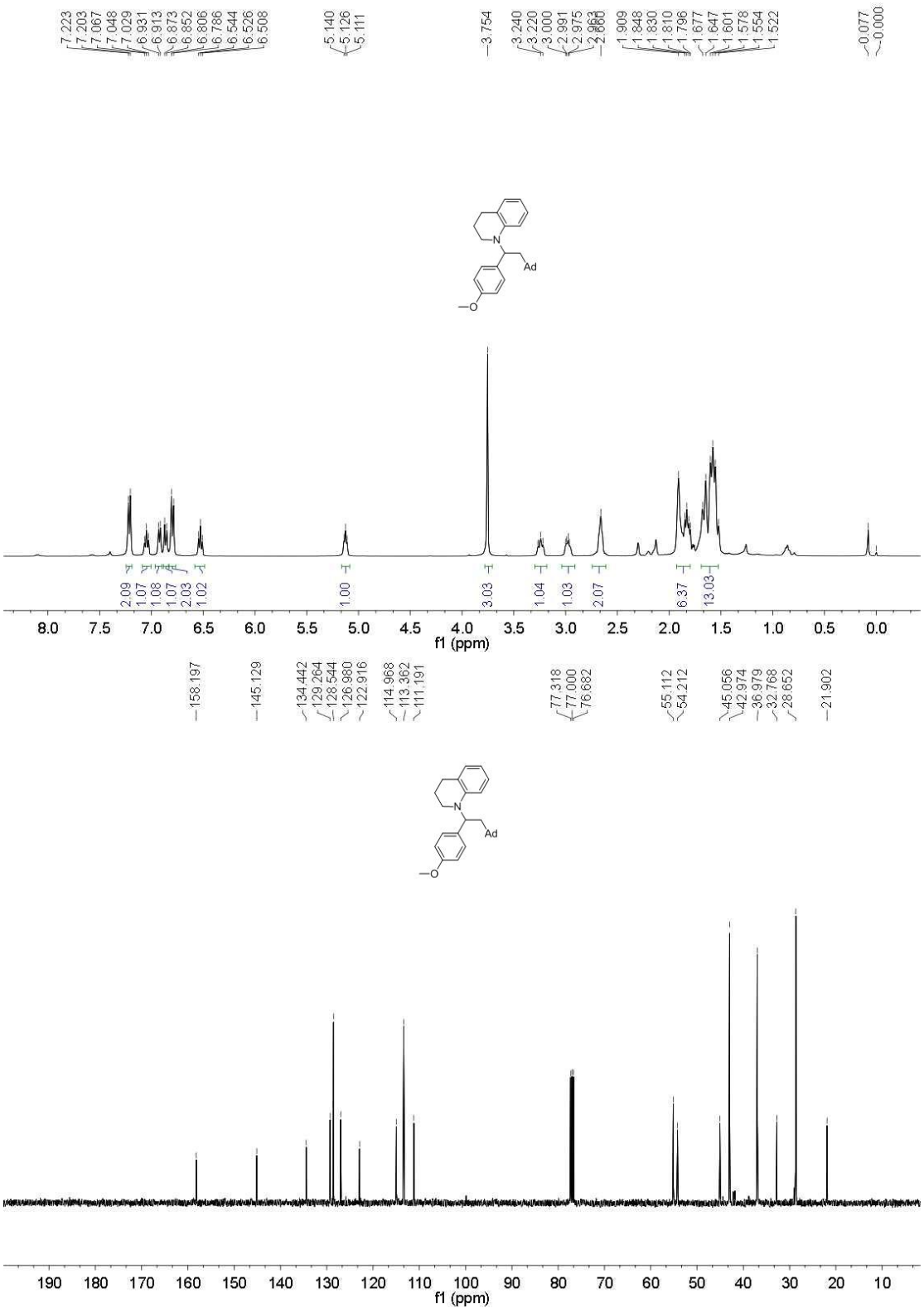
N-(2-adamant-1-yl -1-(4-methoxyphenyl)ethyl)-N-methylaniline (4acj)



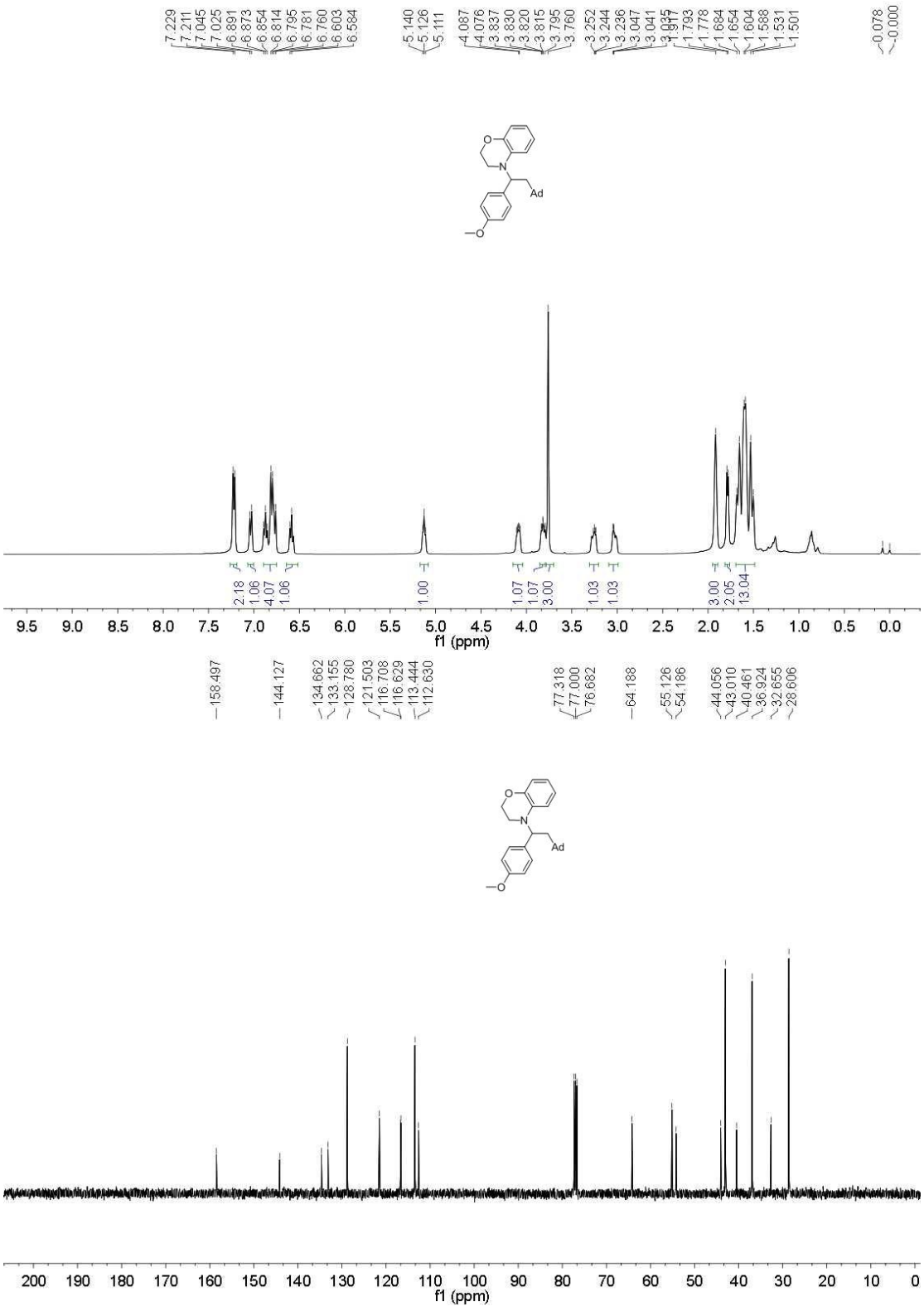
1-(2-Adamant-1-yl-1-(4-methoxyphenyl)ethyl)indoline (4ack)



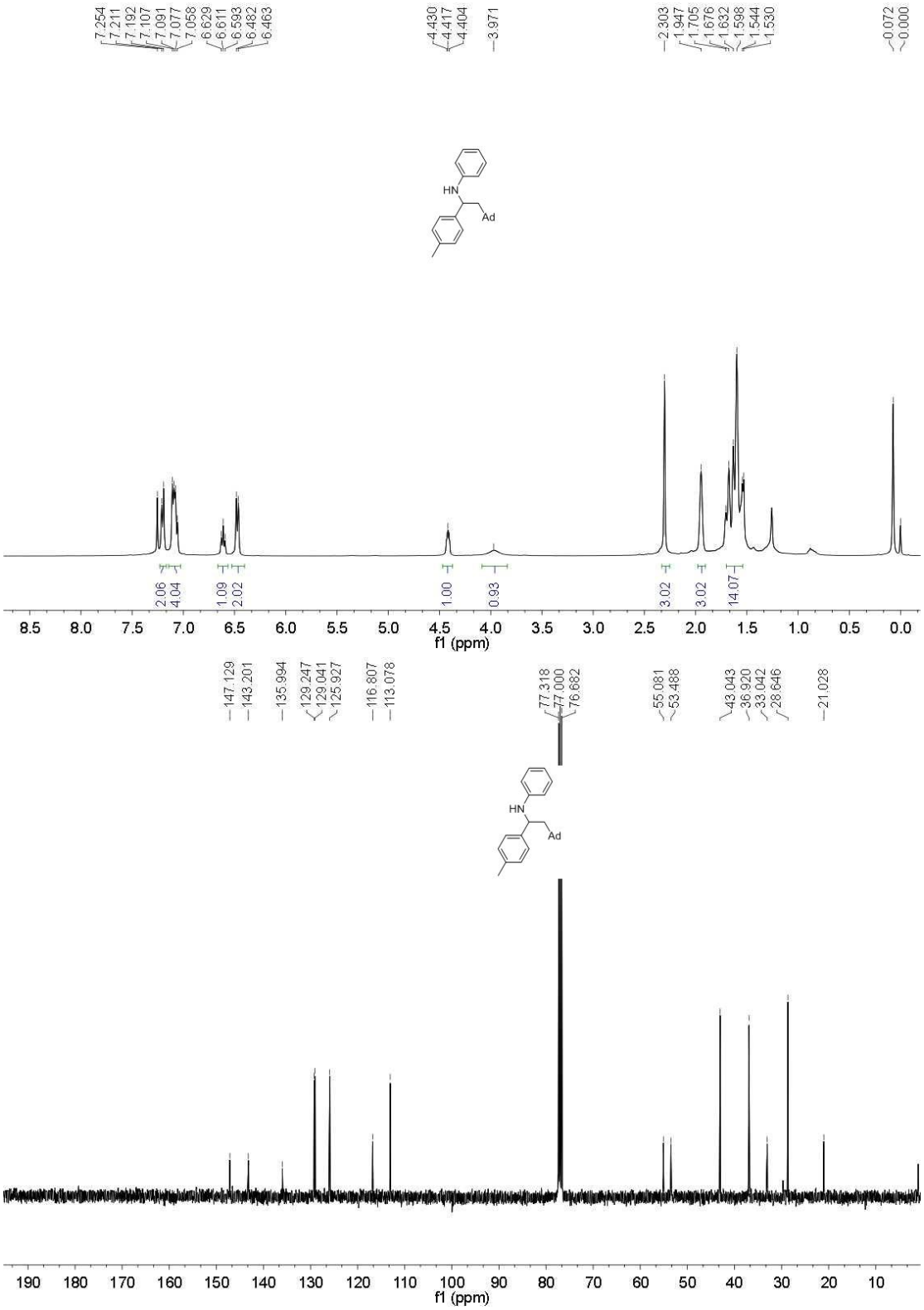
1-(2-Adamant-1-yl-1-(4-methoxyphenyl)ethyl)-1,2,3,4-tetrahydroquinoline (4acl)



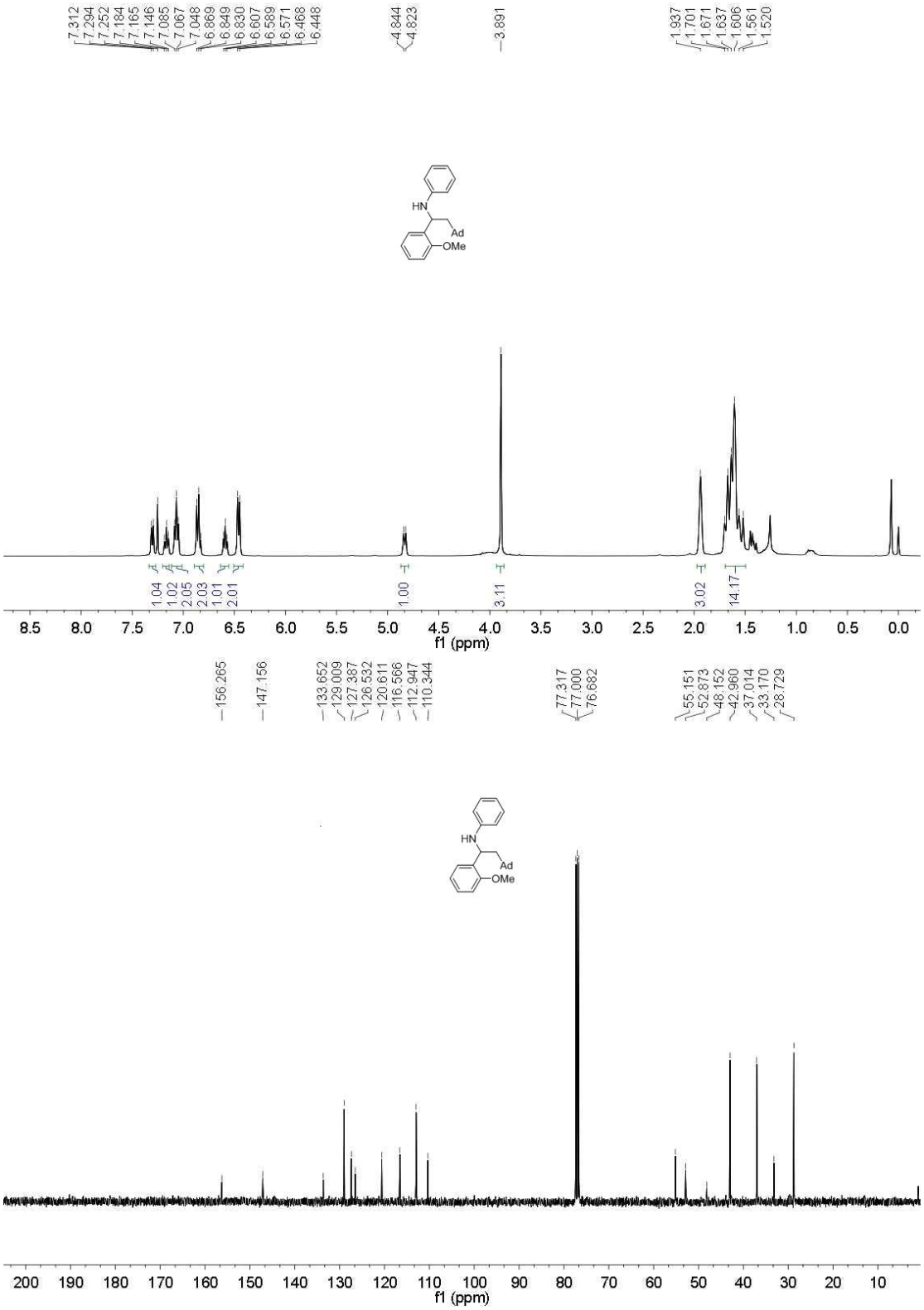
4-(2-adamant-1-yl-1-(4-methoxyphenyl)ethyl)-3,4-dihydro-2H-benzo[*b*][1,4]oxazine (4acm)



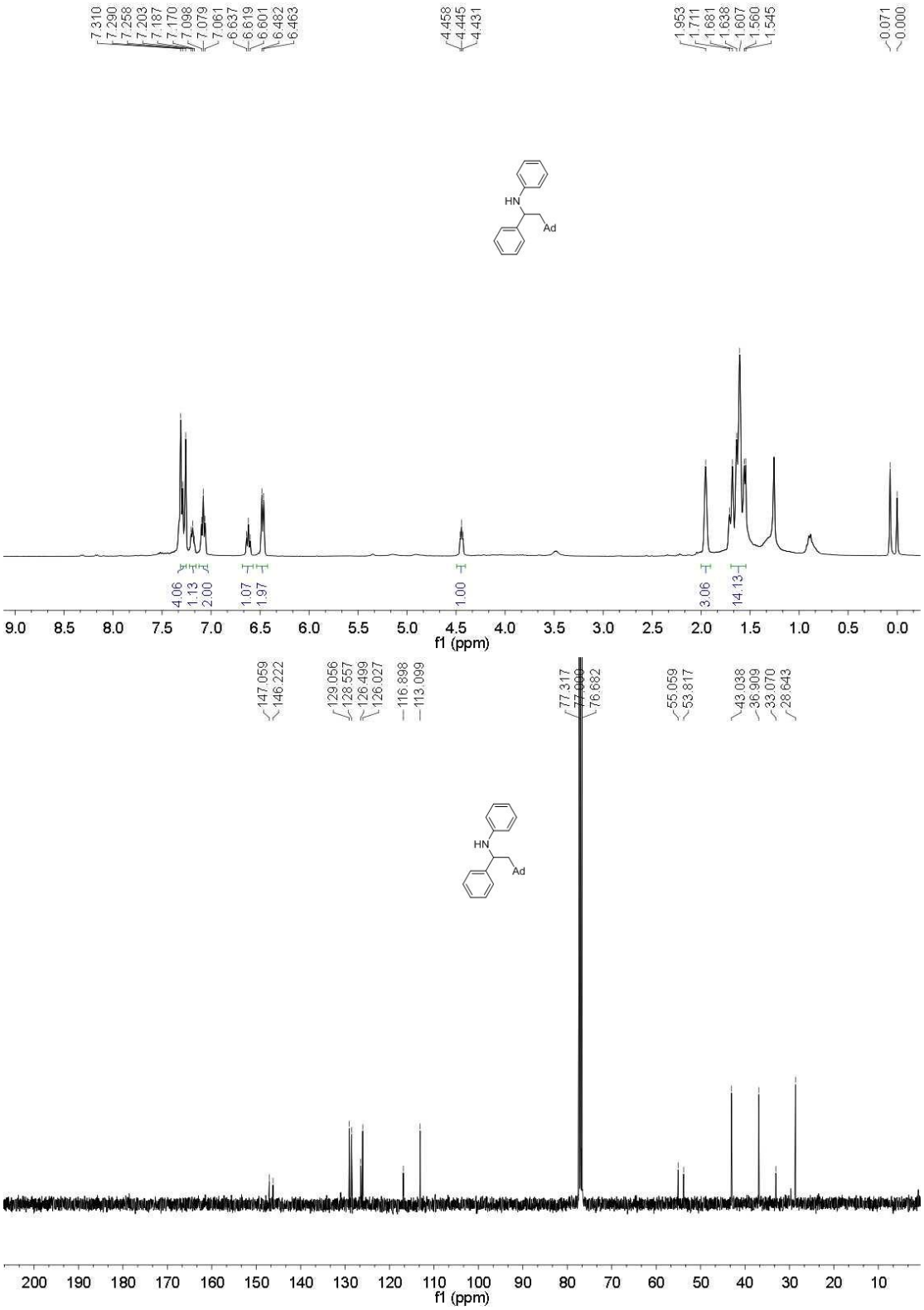
N-(2- adamant-1-yl -1-p-tolylethyl)aniline (4bcb)



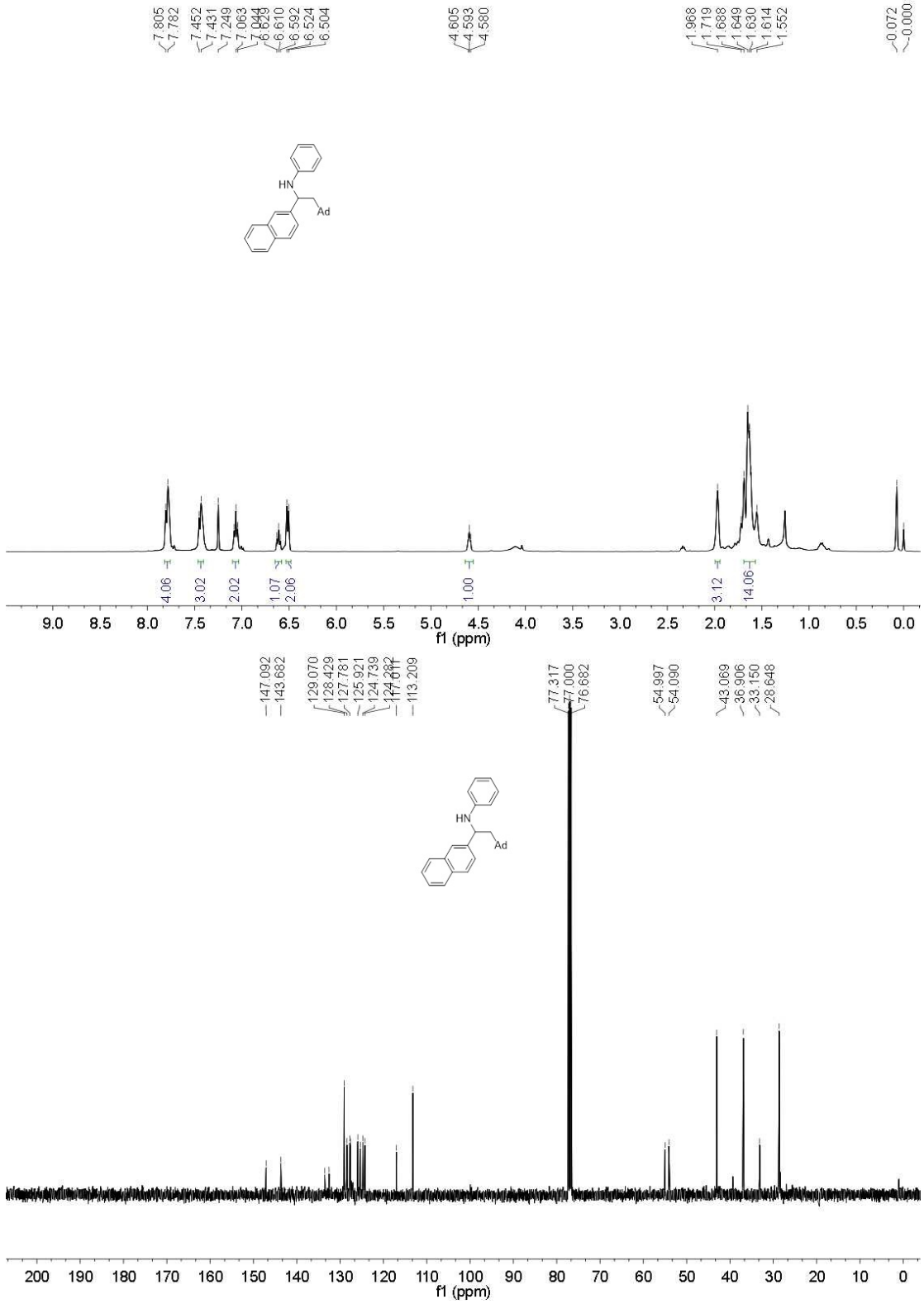
N-(2-adamant-1-yl -1-(2-methoxyphenyl)ethyl)aniline (4dcb)



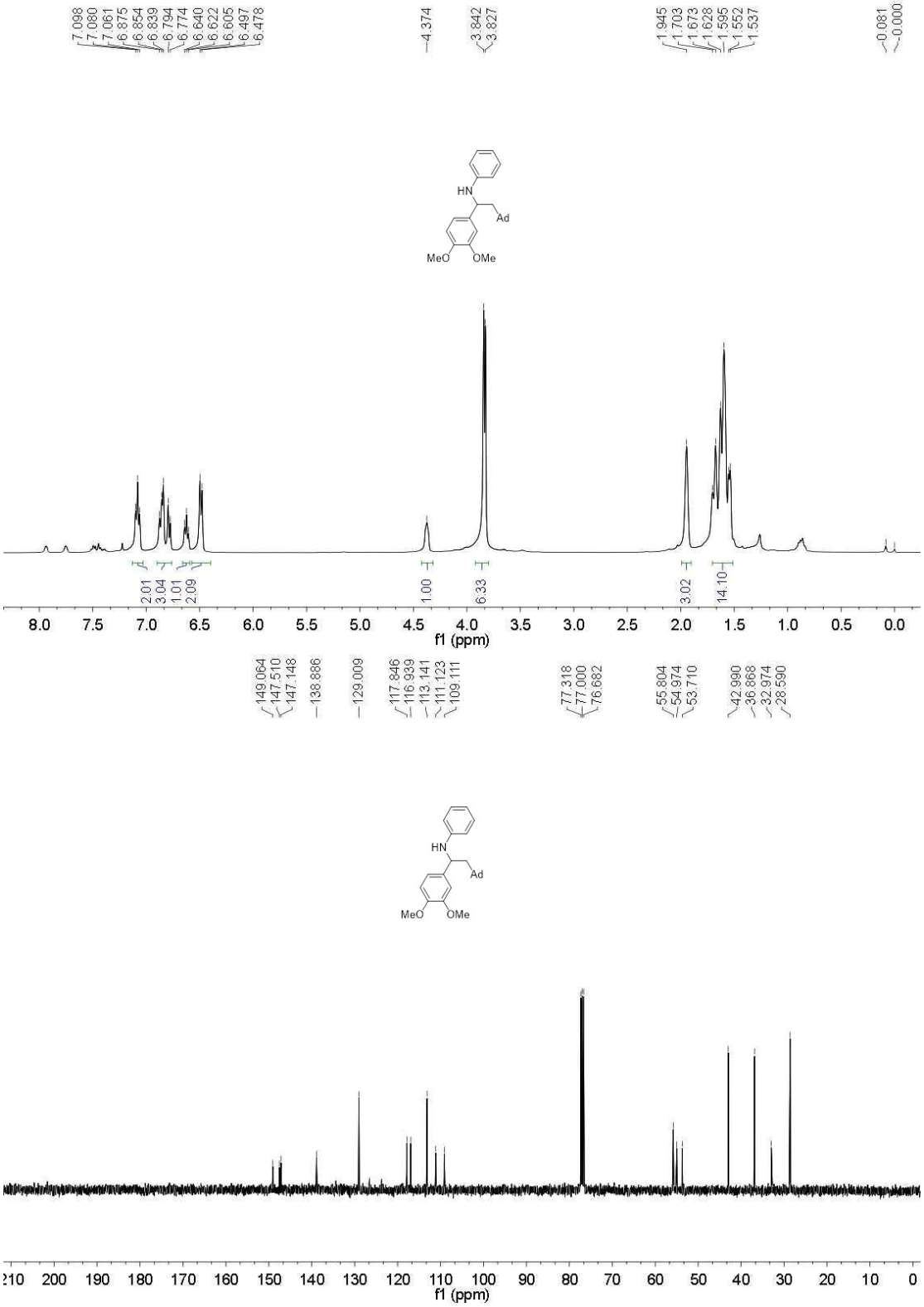
N-(2-adamant-1-yl-1-phenylethyl)aniline (4ecb)



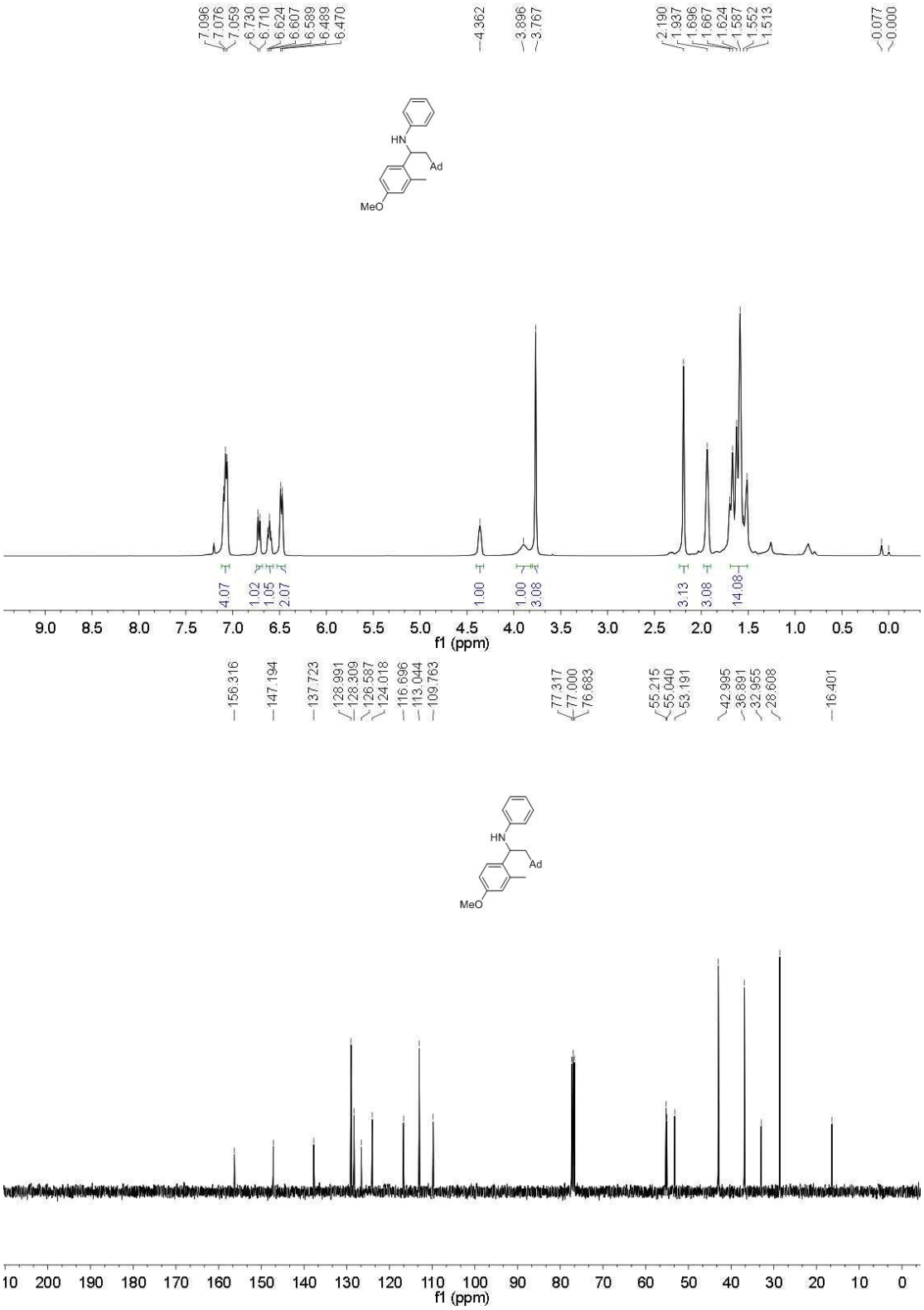
N-(2- adamant-1-yl -1-(naphthalen-2-yl)ethyl)aniline (4fcb)



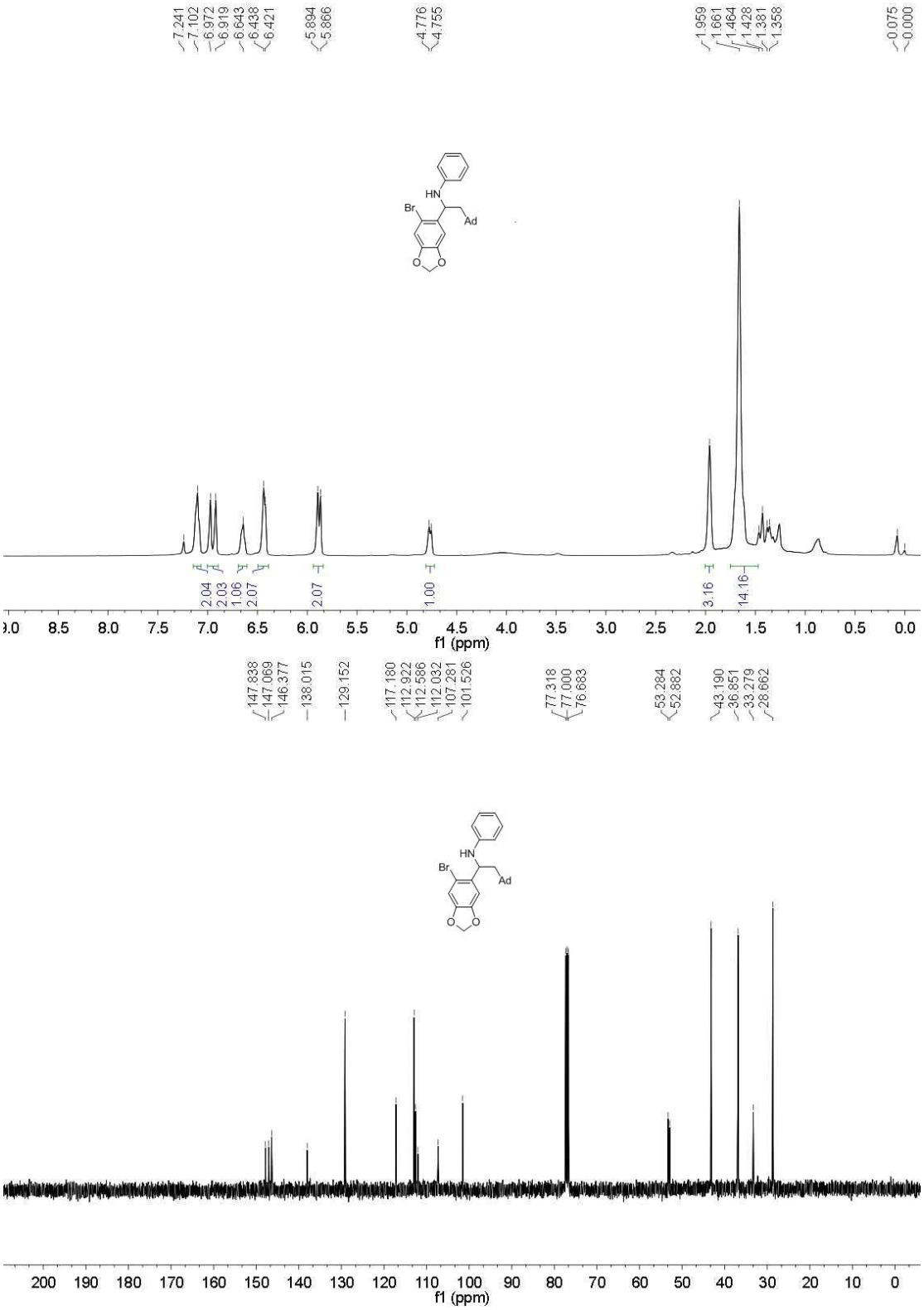
N-(2- adamant-1-yl-1-(3,4-dimethoxyphenyl)ethyl)aniline (4gcb)



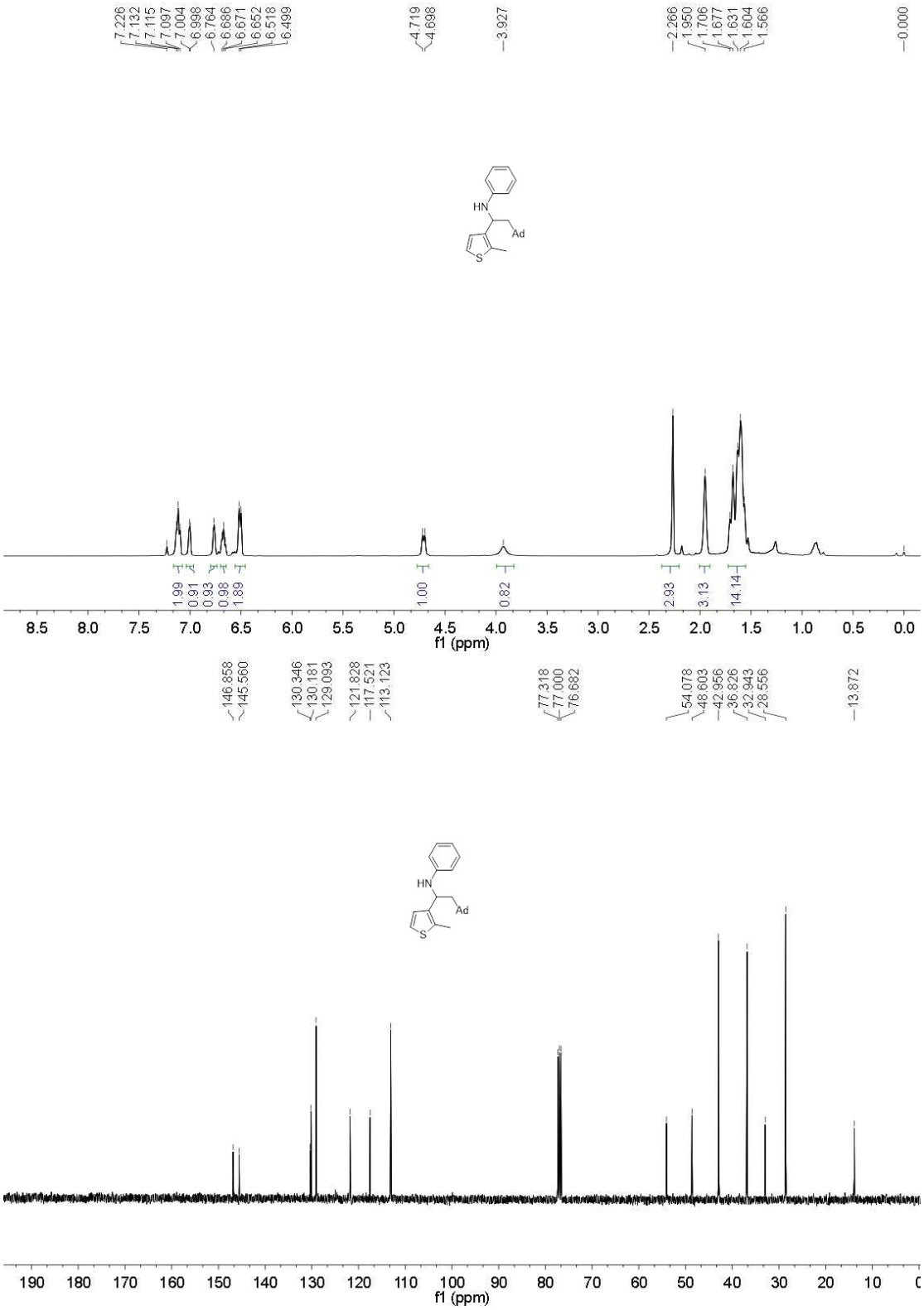
_N_-(2-adamant-1-yl-1-(4-methoxy-2-methylphenyl)ethyl)aniline (4hcb)



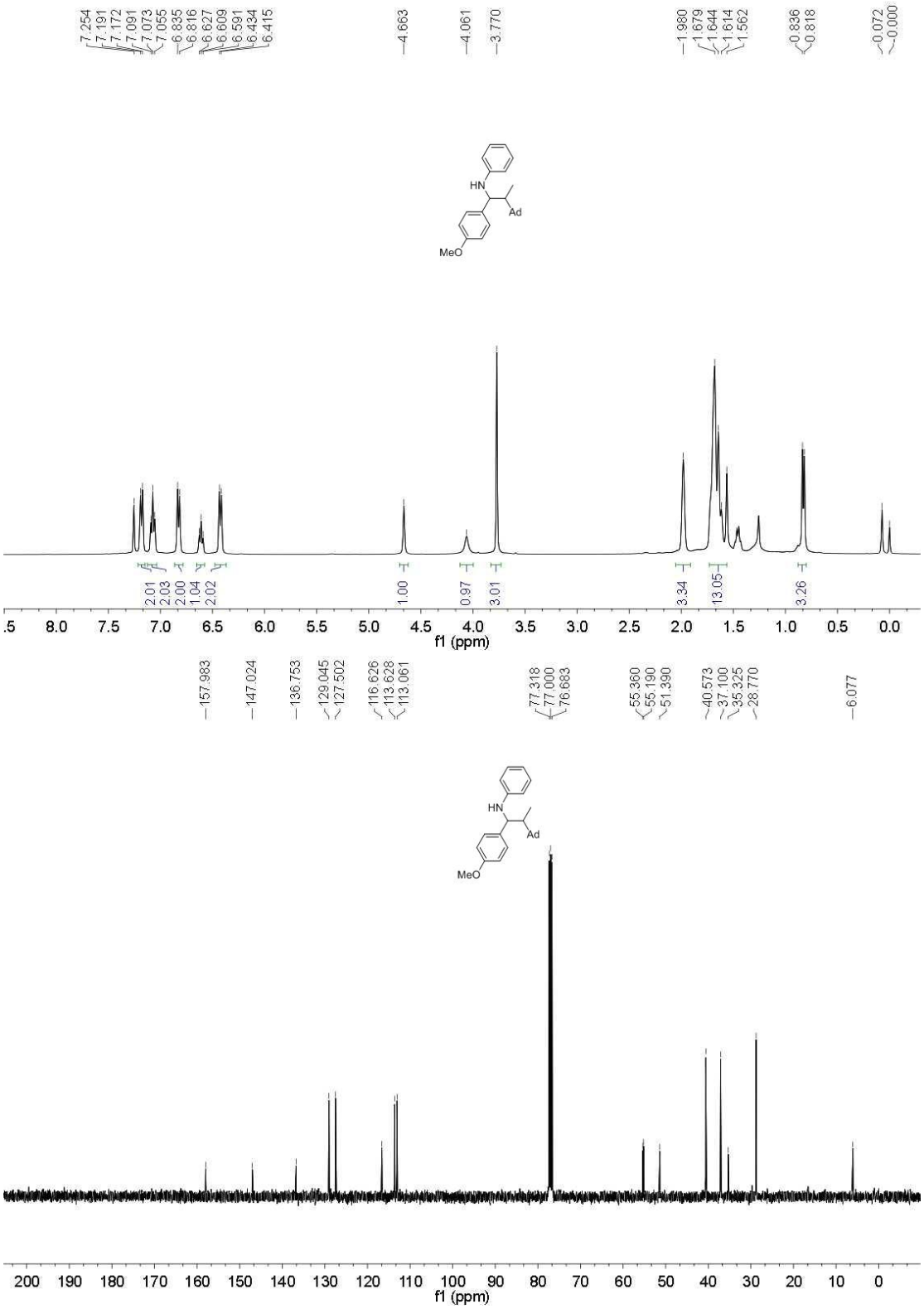
_N_-(1-(6-bromobenzo[_d_][1,3]dioxol-5-yl)-2-adamant-1-ylethyl)aniline (4icb)



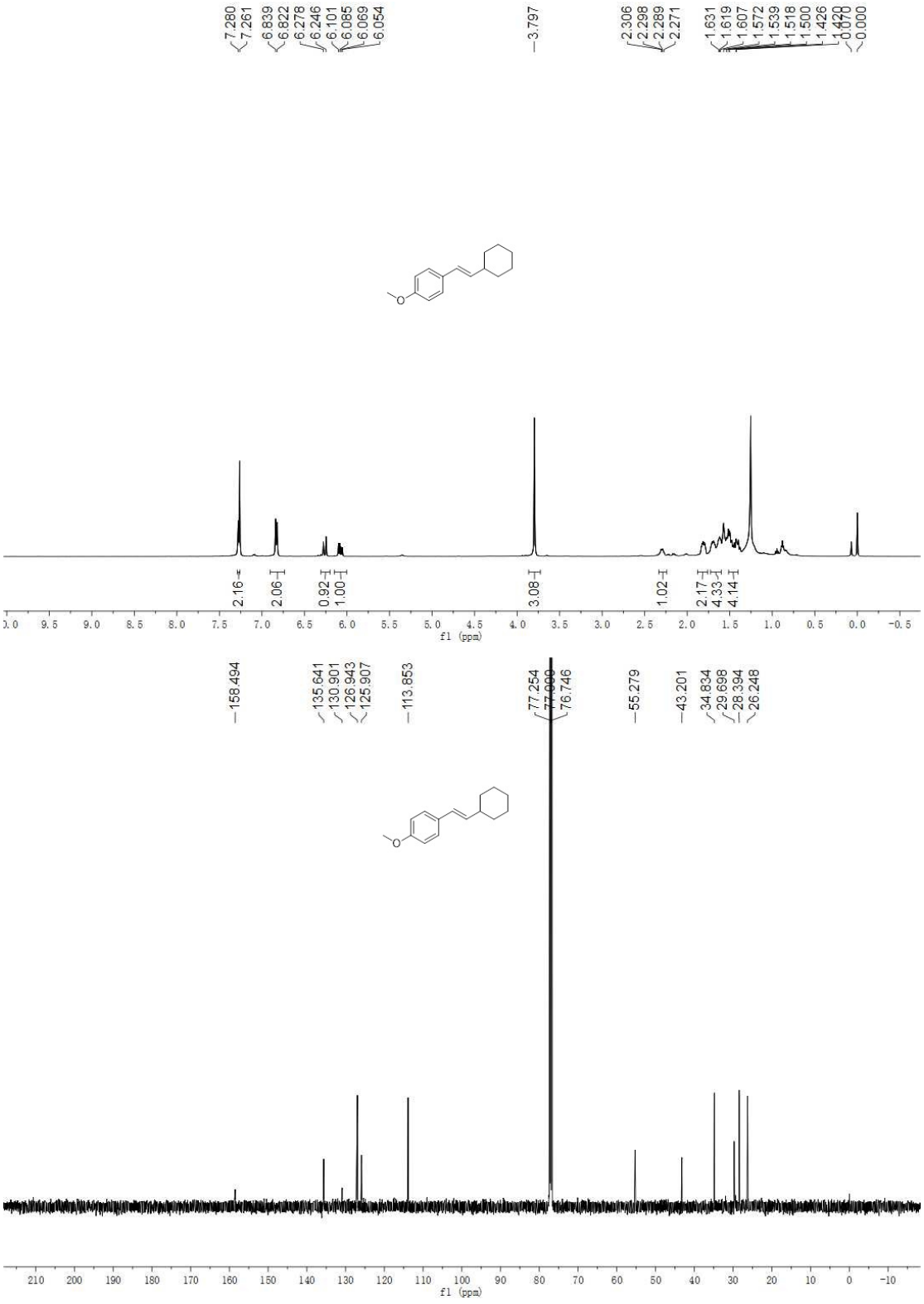
N-(2- adamant-1-yl -1-(2-methylthiophen-3-yl)ethyl)aniline (4jcb)



N-(2- adamant-1-yl -1-(4-methoxyphenyl)propyl)aniline (4lcb)



(*E*)-1-(2-cyclohexylvinyl)-4-methoxybenzene (5aa)



(2-Cyclohexylethene-1,1-diyl)dibenzene (5n)