Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Visible Light-Induced Palladium-Catalyzed Ring Opening β-H Elimination and Addition of Cyclobutanone Oxime Esters

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Table of Contents

1. General Information

All reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity≥99.999%) unless otherwise mentioned. Commercial reagents were purchased from Adamas-beta, TCI and Aldrich. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Data for ^{1}H-NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. ESI-mass data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software. UV-Vis spectrum was measured by UV-3600. The LED light sources we used were all purchased from Kessil company (PR160L 440 nm, 456 nm).

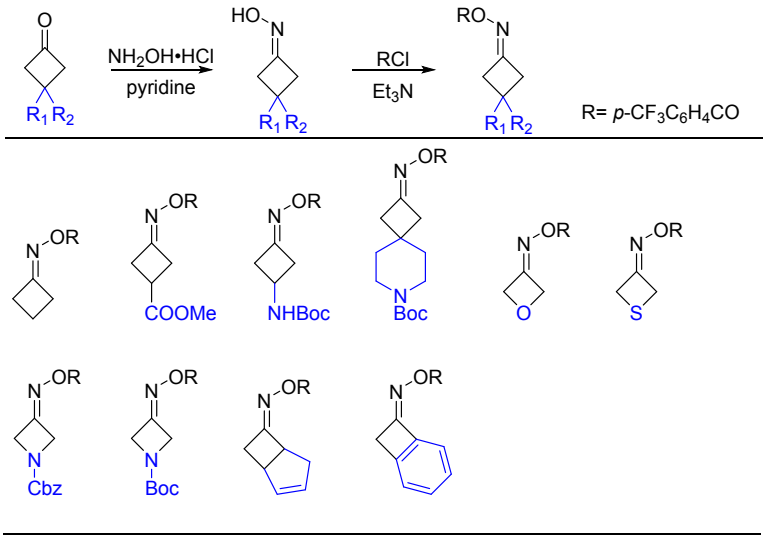
2. Preparation of Substrates

2.1 Preparation of Enol Silyl Ether

A mixture of ketone (2.5 mmol) (when solid) and sodium iodide (450 mg, 3 mmol) were placed in a Schlenk (10 mL) tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To these solids, ketone (2.5 mmol) (when liquid) and dry acetonitrile (3 mL) were added. The resulting solution was stirred for 5 min at room temperature, and triethylamine (420 μL, 3 mmol) was added, followed by addition of chlorotrimethylsilane (382 μL, 3 mmol). The reaction mixture was then stirred at 40 ^{o}C overnight and quenched with cold pentane (5 mL) and ice water (5 mL). The organic phase was separated, and the aqueous layer was extracted with pentane (20 mL × 2). The combined organics were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced atmospheric pressure. Finally, The residue was distilled under reduced pressure to provide pure silyl enol ether.

The silyl enol ethers used here are known compounds.[1]

2.2 Preparation of Cyclobutanone Oxime Esters

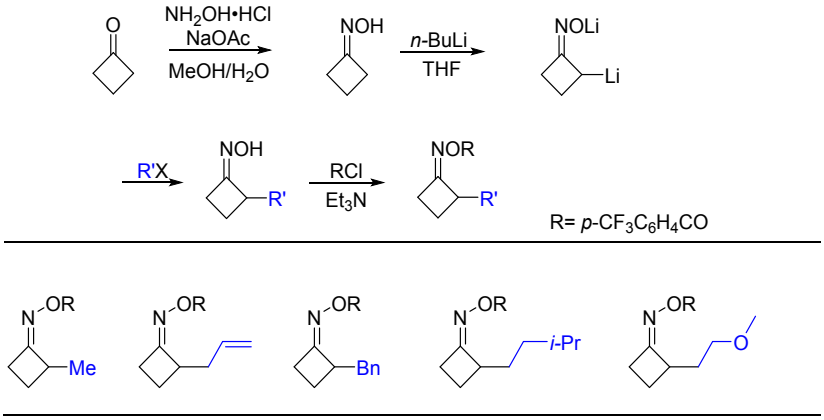


To a stirred solution of cyclobutanones (1.0 equiv) in pyridine (0.5 M) was added hydroxylamine hydrochloride (2.0 equiv) at room temperature. After stirring for 2 h, pyridine was removed under reduced pressure. The residue was diluted with water and extracted with ethyl acetate. The organic layers were combined, washed with brine, dried over Na_2SO_4 and concentrated under reduced atmospheric pressure to give the crude material (cyclobutanone oxime), which were used in the next step without further purification.

To a mixture of cyclobutanone oxime (1.0 equiv), triethylamine (2.0 equiv) and DCM (0.5 M) in a two-necked flask (30 mL) was added 4-(Trifluoromethyl)benzoyl chloride (1.5 equiv) at 0 °C. After 6 h, the mixture was then quenched with saturated NaCl solution and extracted with diethyl ether. The organic layers were combined and concentrated under reduced atmospheric pressure. The product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give cyclobutanone oxime esters.

The final products shown above are known compounds.[2]

2.3 Preparation of *a*-alkyl Substituted Cyclobutanone Oxime Esters



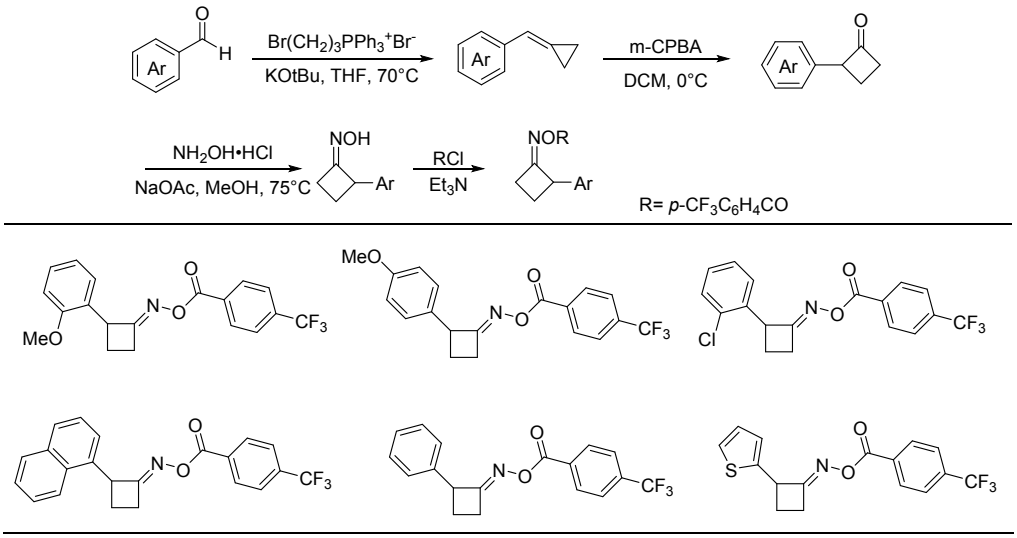
To a mixture of hydroxylamine hydrochloride (18.0 mmol), sodium acetate (22.5 mmol), ethanol (10.5 mL) and water (4.5 mL) in a two-necked flask (30 mL) was added cyclobutanone (15 mmol) and the mixture was stirred at 100 °C for 12 h. The reaction mixture was cooled to room temperature and then ethanol was removed under reduced pressure. The resulting mixture was extracted with diethyl ether. The organic layers were combined and concentrated under reduced atmospheric pressure. The product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give cyclobutanone oxime as a white solid.

Cyclobutanone oxime (1.0 equiv) in absolute THF (0.5 M) was added *n*-BuLi (2.0 equiv) slowly at 0 °C, then continue to stirring for another 15 min at this temperature for the formation of syn dianion. Then RX (1.0 equiv) was added dropwise at 0 °C, then the mixture was warmed to room temperature and stirred for 2 h. Subsequently, the reaction was quenched by cold water, extracted with ethyl acetate. The organic layers were combined and concentrated under reduced atmospheric pressure. The product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give *a*-substituted oximes in quantively yield.

To a mixture of cyclobutanone oxime (1.0 equiv), triethylamine (2.0 equiv) and DCM (0.5 M) in a 30 mL two-necked flask was added 4-(Trifluoromethyl)benzoyl chloride (1.5 equiv) at 0 °C. After 6 h, the mixture was then quenched with saturated NaCl solution and extracted with diethyl ether. The organic layers were combined and concentrated under reduced atmospheric pressure. The product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give cyclobutanone oxime esters.

The final product showed above are known compounds.[2]

2.4 Preparation of *a*-aryl Substituted Cyclobutanone Oxime Esters



α-Aryl substituted cyclobutanone o-(4-(trifluoromethyl)benzoyl) oximes were prepared from the correspounding cyclobutanones, which were produced by the oxidation of (arylmethylene)cyclopropanes synthesized from the corresponding benzaldehydes through a Wittig reaction.

A solution of KO*t*-Bu (6.74 g, 60 mmol, 3.0 equiv) in THF (46 mL, 1.3 M) was slowly added to a solution of (3-bromopropyl) triphenylphosphonium bromide (13.92 g, 30 mmol, 1.5 equiv) in dry THF (60 mL, 0.5 M) and stirred at 70 °C for 1 h. Then a THF solution of benzaldehyde (2.04 mL, 20 mmol, 2.0 M in THF, 1.0 equiv) was added dropwise and the mixture was refluxed for 3 h. After cooling, the suspension was filtered and the solvent of the filtrate was removed under vacuum, the products were purified by column chromatography on silica gel, eluting with petroleum ether to afford (phenylmethylene)cyclopropanes.

To the solution of (phenylmethylene)cyclopropanes (2.47 g, 19 mmol, 1.0 equiv) in DCM (127 mL, 0.15 M) was added a solution of *m*-CPBA (4.37 g, 19 mmol, 1.0 equiv) in DCM (50 mL, 0.38 M) dropwise at 0 °C and stirred for 1 h. Then, the solution was diluted with a saturated solution of aqueous Na_2SO_3 (30 mL) and extracted with DCM (3*20 mL). The organic phase was washed successively with a saturated solution of aqueous $NaHCO_3$ (3*30 mL), and brine (30 mL), then dried over Na_2SO_4 and concentrated in vacuum. The product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent (20:1) to give various cyclobutanones.

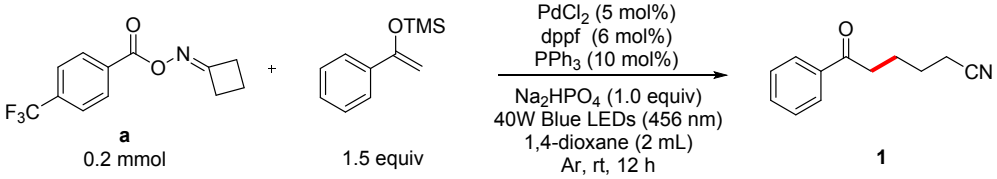
To a mixture of hydroxylamine hydrochloride (1.41 g, 20.3 mmol, 1.2 equiv), sodium acetate (2.08 g, 25.4 mmol, 1.5 equiv), methanol (30 mL, 0.56 M) in a 100-mL two-necked flask was added cyclobutanone (2.47 g, 16.9 mmol, 1.0 equiv) and the mixture was stirred at 75 °C for 12 h. The reaction mixture was cooled to room temperature and then methanol was removed under reduced pressure. The resulting mixture was extracted with diethyl ether. The organic layers were combined and concentrated under reduced atmospheric pressure. The product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to give cyclobutanone oximes.

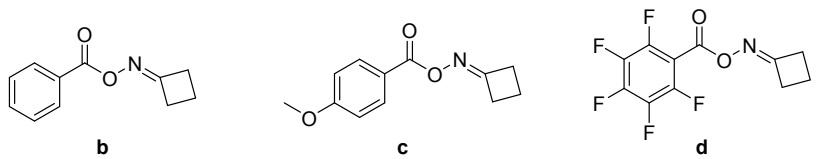
To a mixture of cyclobutanone oxime (865.8 mg, 5.37 mmol, 1.0 equiv), triethylamine (1.12 mL, 8.06 mmol, 1.5 equiv) and DCM (10.7 mL, 0.5 M) in a 30-mL two-necked flask was added 4-(trifluoromethyl)benzoyl chlorides (0.88 mL, 5,91 mmol, 1.1 equiv) at 0 °C. After 1 h, a saturated solution of aqueous $NaHCO_3$ (30 mL) was added to the above solution, and the mixture was diluted with DCM. The organic layer was washed with brine (30 mL) and dried over Na_2SO_4. The solvent was removed under vacuum and the residue was subjected to column chromatography on silica gel with petroleum ether/ethyl acetate as eluent to give cyclobutanone O-(4-(trifluoromethyl)benzoyl) oximes.

The final product showed above are known compounds.[3]

3. Investigation of the Key Reaction Parameters

Table S1: Parameters affecting ring opening addition of cyclobutanone oxime ester.





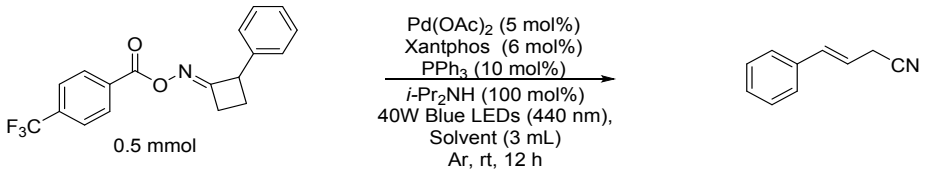
entry	variations from above conditions	yield[b] (%)
1	none	85(83[c])
2	w/o irradiation	trace

3	w/o PPh_3	60
4	w/o dppf	trace
5	w/o irradiation and PPh_3	trace
6	w/o Na_2HPO_4	60
7	$Pd(dppf)Cl_2$ instead of $PdCl_2$/dppf	76
8	$Pd(PPh_3)_4$ instead of $PdCl_2$/PPh_3	80
9	$Pd(PPh_3)_2Cl_2$ instead of $PdCl_2$/PPh_3	77
10	$Pd(TFA)_2$ instead of $PdCl_2$	66
11	$Pd(OAc)_2$ instead of $PdCl_2$	56
12	PCy_3 instead of PPh_3	57
13	Tris(pentafluorophenyl)phosphine instead of PPh_3	51
15	Tri(*p*-methoxyphenyl)phosphine instead of PPh_3	59
16	dppp instead of dppf	34
17	DPEphos instead of dppf	30
18	Xantphos instead of dppf	trace
19	(±) BINAP instead of dppf	37
20	Bphen instead of dppf	trace
21	1,10-phen instead of dppf	19
22	MeCN instead of 1,4-dioxane	62
23	THF instead of 1,4-dioxane	57
24	DMA instead of 1,4-dioxane	41
25	DCM instead of 1,4-dioxane	58
26	DCE instead of 1,4-dioxane	64
27	**b** instead of **a**	71
28	**c** instead of **a**	59
29	**d** instead of **a**	64

[a] Reaction conditions: oxime ester (0.2 mmol), silyl enol ether (0.3 mmol), $PdCl_2$ (5 mol%), dppf (6 mol%), PPh_3 (10 mol%) and Na_2HPO_4 (0.2 mmol) in dioxane (2 mL) at room temperature under irradiation using 40 W blue LEDs (456 nm) for 12 h. [b] Yield determined by GC with diphenylmethane as an internal standard. [c] Isolated yield. OAc = Acetate. Xantphos = 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene. TMS = trimethylsilyl. dppf = 1,1'-Bis(diphenylphosphino)ferrocene. Cy = Cyclohexyl. dppp = 1,3-Bis(diphenylphosphino)propane. DPEphos = Bis(2-diphenylphosphinophenl)ether. (±)

BINAP = (+/-)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl. Bphen = Bathophenanthroline. 1,10-phen = o-Phenanthroline. THF = Tetrahydrofuran. DMA = N,N-Dimethylacetamide. DCE = 1,2-Dichloroethane.

Table S2: Parameters affecting ring opening β-H Elimination of Cyclobutane Oximes.



entry	variations from above conditions	yield[b] (%)
1	none	89
2	390 nm purple LEDs	73
3	427 nm purple LEDs	74
4	456nm blue LEDs	70
5	w/o irradiation	<5
6	w/o $Pd(OAc)_2$	<5
7	w/o Xantphos	<5
8	w/o PPh_3	10
9	dppf instead of Xantphos	20
10	(±) BINAP instead of Xantphos	18
11	DPEphos instead of Xantphos	67
12	Ni-Xantphos instead of Xantphos	63
13	Tris(4-methoxyphenyl)phosphine instead of PPh_3	59
14	Tris(4-fluorophenyl)phosphine instead of PPh_3	65
15	Cy-Johnphos instead of PPh_3	54
16	X-phos instead of PPh_3	37
17	Ruphos instead of PPh_3	40
18	Et_3N instead of *i*-Pr_2NH	42
19	DIPEA instead of *i*-Pr_2NH	50
20	NaOAc instead of *i*-Pr_2NH	36
21	DMA instead of 1,4-dioxane	48
22	MeCN instead of 1,4-dioxane	30

23	$PhCF_3$ instead of 1,4-dioxane	56

[a] Reaction conditions: oxime ester (0.5 mmol), $Pd(OAc)_2$ (5 mol%), Xantphos (6 mol%), PPh_3 (10 mol%) and *i*-Pr_2NH (0.5 mmol) in dioxane (3 mL) at room temperature under irradiation using 40 W blue LEDs (440 nm) for 12 h. [b] Yield determined by GC with diphenylmethane as an internal standard. Ni-Xantphos = 4,6-Bis(diphenylphosphino)phenoxazine. Cy-Johnphos = (2-biphenyl)dicyclohexylphosphine. X-phos = (2-(2,4,6-triisopropylphenethyl)phenyl)dicyclohexylphosphine. Ruphos = 2-dicyclohexylphosphino-2',6'-di-i-propoxy-1,1'-biphenyl. DIPEA = N,N-Diisopropyl-ethylamin.

4. Experimental procedures and spectral data

4.1 General Procedure A

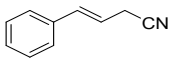
Oxime esters (1.0 equiv, 0.5 mmol) (when solid), $PdCl_2$ (5 mol %, 4.4 mg), PPh_3 (10 mol %, 13.1 mg), 1,1'-Bis(diphenylphosphino)ferrocene (dppf, 6 mol%, 16.6 mg) and Na_2HPO_4 (100 mol%, 71.0 mg) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To these solids, oxime esters (1.0 equiv, 0.5 mmol) (when liquid), enol silyl ether (1.5 equiv, 1.0 mmol) and anhydrous 1,4-dioxane (4.0 mL) were added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with 40W blue LEDs (456 nm, distance app. 3.0 cm from the bulb), maintained at approximately room temperature by a desk fan in the air-conditioned room of 25 ^oC for 12 h. The mixture was then quenched with saturated NaCl solution and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and concentrated under reduced atmospheric pressure. The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10:1~2:1).

4.2 General Procedure B

Oxime esters (1.0 equiv, 0.5 mmol) (when solid), $Pd(OAc)_2$ (5 mol %, 5.6 mg), PPh_3 (10 mol %, 13 mg) and 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos, 6 mol%, 17 mg) were placed in a transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To these solids, oxime esters (1.0 equiv, 0.5 mmol) (when liquid), Diisopropylamine (*i*-Pr_2NH, 100

mol%, 51 mg) and anhydrous 1,4-dioxane (3.0 mL) were added via a gastight syringe under argon atmosphere. The reaction mixture was stirred under irradiation with 40W blue LEDs (440 nm, distance app. 3.0 cm from the bulb), maintained at approximately room temperature by a desk fan in the air-conditioned room of 25 °C for 12 h. The mixture was then quenched with saturated NaCl solution and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and concentrated under reduced atmospheric pressure. The product was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1~2:1).

4.3 Spectral Data

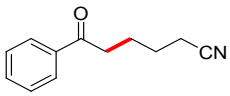


***(E)*-4-phenylbut-3-enenitrile (1):** Following the general procedure B, obtained in 89% yield as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 6.74 (dt, *J* = 15.8, 1.7 Hz, 1H), 6.05 (dt, *J* = 15.8, 5.7 Hz, 1H), 3.29 (dd, *J* = 5.7, 1.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6, 133.5, 127.7, 127.2, 125.4, 116.3, 115.7, 19.7.

HRMS (ESI) Calcd for $C_{10}H_{10}N^+$ $[M+H]^+$: 144.0375, found: 144.0379.

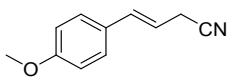


6-oxo-6-phenylhexanenitrile (2): Following the general procedure A, obtained in 81% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.88 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 3.05 (t, *J* = 6.9 Hz, 2H), 2.41 (t, *J* = 7.1 Hz, 2H), 1.97 – 1.86 (m, 2H), 1.82 – 1.66 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 136.7, 133.2, 128.7, 128.0, 119.6, 37.3, 25.0, 23.1, 17.2.

HRMS (ESI) Calcd for $C_{12}H_{14}NO^+$ $[M+H]^+$: 187.0997, found: 188.1004.



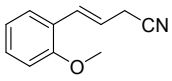
***(E)*-4-(4-methoxyphenyl)but-3-enenitrile (3):** Following the general procedure B,

obtained in 87% yield as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 15.8 Hz, 1H), 5.90 (dt, *J* = 15.8, 5.7 Hz, 1H), 3.81 (s, 3H), 3.26 (dd, *J* = 5.7, 1.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 134.0, 128.5, 127.7, 117.5, 114.4, 114.1, 55.3, 20.7.

HRMS (ESI) Calcd for $C_{11}H_{12}NO^+$ $[M+H]^+$: 174.0841, found: 174.0851.

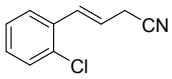


***(E)*-4-(2-methoxyphenyl)but-3-enenitrile (4):** Following the general procedure B, obtained in 68% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.06 – 6.87 (m, 3H), 6.10 (dt, *J* = 15.9, 5.8 Hz, 1H), 3.85 (s, 3H), 3.29 (dd, *J* = 5.7, 1.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.8, 130.0, 129.3, 127.3, 124.7, 120.7, 117.6, 117.5, 110.9, 55.4, 21.2.

HRMS (ESI) Calcd for $C_{11}H_{12}NO^+$ $[M+H]^+$: 174.0841, found: 174.0850.

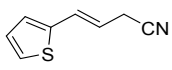


***(E)*-4-(2-chlorophenyl)but-3-enenitrile (5):** Following the general procedure B, obtained in 60% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.46 (m, 1H), 7.39 – 7.36 (m, 1H), 7.26 – 7.17 (m, 2H), 7.11 (dt, *J* = 15.8, 1.7 Hz, 1H), 6.05 (dt, *J* = 15.8, 5.9 Hz, 1H), 3.34 (dd, *J* = 5.9, 1.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.9, 133.2, 131.3, 129.8, 129.3, 127.1, 127.0, 119.8, 117.0, 21.0.

HRMS (ESI) Calcd for $C_{10}H_9ClN^+$ $[M+H]^+$: 178.0345, found: 178.0361.

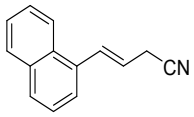


***(E)*-4-(thiophen-2-yl)but-3-enenitrile (6):** Following the general procedure B, obtained in 42% yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 4.7 Hz, 1H), 7.03 – 6.94 (m, 2H), 6.87 (d, *J* = 15.6 Hz, 1H), 5.89 (dt, *J* = 15.6, 5.7 Hz, 1H), 3.27 (dd, *J* = 5.6, 1.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 129.3, 127.7, 127.5, 126.6, 125.0, 115.9, 20.5.

HRMS (ESI) Calcd for $C_8H_8NS^+$ $[M+H]^+$: 150.0299, found: 150.0312.

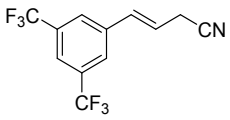


***(E)*-4-(naphthalen-1-yl)but-3-enenitrile (7):** Following the general procedure B, obtained in 40% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.88 – 7.80 (m, 2H), 7.57 – 7.48 (m, 4H), 7.43 – 7.47 (m, 1H), 6.09 (dt, *J* = 15.5, 5.5 Hz, 1H), 3.41 (dd, *J* = 5.5, 1.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.6, 133.5, 132.2, 130.9, 128.7, 128.6, 126.4, 126.0, 125.5, 124.1, 123.6, 119.9, 117.3, 21.1.

HRMS (ESI) Calcd for $C_{14}H_{12}N^+$ $[M+H]^+$: 194.0891, found: 194.0902.

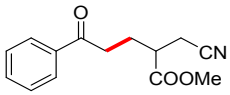


***(E)*-4-(3,5-bis(trifluoromethyl)phenyl)but-3-enenitrile (8):** Following the general procedure B, obtained in 54% yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.75 (m, 3H), 6.86 (dt, *J* = 15.9, 1.6 Hz, 1H), 6.27 (dt, *J* = 15.9, 5.5 Hz, 1H), 3.38 (dd, *J* = 5.5, 1.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 132.2 (q, *J* = 33.4 Hz), 131.9, 126.5 – 126.2 (m), 123.2 (q, *J* = 271.0 Hz)., 121.9 – 121.6 (m), 121.2, 116.4, 20.8.

HRMS (ESI) Calcd for $C_{12}H_8F_6N^+$ $[M+H]^+$: 280.0561, found: 280.0562.



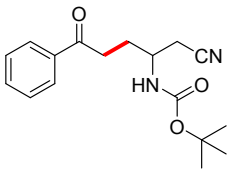
Methyl 2-(cyanomethyl)-5-oxo-5-phenylpentanoate (9): Following the general procedure A, obtained in 92% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t,

J = 7.6 Hz, 2H), 3.73 (s, 3H), 3.11 (t, *J* = 7.1 Hz, 2H), 2.91 (dt, *J* = 13.7, 6.7 Hz, 1H), 2.77 – 2.62 (m, 2H), 2.24 – 2.11 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 172.8, 136.4, 133.4, 128.7, 127.9, 117.6, 52.5, 40.7, 35.2, 25.5, 19.8.

HRMS (ESI) Calcd for $C_{14}H_{16}NO_3^+$ $[M+H]^+$: 246.1130, found: 246.1128.

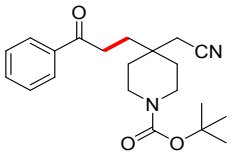


***tert*-butyl (1-cyano-5-oxo-5-phenylpentan-2-yl)carbamate (10)：** Following the general procedure A, obtained in 84% yield as a light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.3 Hz, 2H), 7.61 – 7.55 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 4.90 (d, *J* = 8.2 Hz, 1H), 4.02 – 3.82 (m, 1H), 3.24 – 3.02 (m, 2H), 2.87 – 2.52 (m, 2H), 2.10 (d, *J* = 6.5 Hz, 2H), 1.40 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 155.2, 136.5, 133.4, 128.6, 128.0, 125.4, 80.2, 47.4, 34.8, 28.2, 27.6, 24.2.

HRMS (ESI) Calcd for $C_{17}H_{23}N_2O_3^+$ $[M+H]^+$: 303.1709, found: 303.1709.

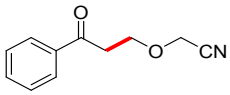


***tert*-butyl 4-(cyanomethyl)-4-(3-oxo-3-phenylpropyl)piperidine-1-carboxylate (11)：** Following the general procedure A, obtained in 87% yield as a light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.92 (m, 2H), 7.64 – 7.55 (m, 1H), 7.49 (t, J = 7.6 Hz, 2H), 3.62 – 3.27 (m, 4H), 3.05 – 2.92 (m, 2H), 2.44 (s, 2H), 2.09 – 1.91 (m, 2H), 1.59 (t, J = 5.5 Hz, 4H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 154.8, 136.5, 133.4, 128.8, 128.0, 117.4, 80.0, 34.1, 34.0, 32.2, 31.0, 28.4, 26.1. (one carbon signal is overlapped)

HRMS (ESI) Calcd for $C_{21}H_{29}N_2O_3^+$ $[M+H]^+$: 357.2178, found: 357.2175.

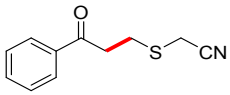


2-(3-oxo-3-phenylpropoxy)acetonitrile (12)： Following the general procedure A, obtained in 75% yield as a light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.88 (m, 2H), 7.64 – 7.55 (m, 1H), 7.51 – 7.45 (m, 2H), 4.31 (s, 2H), 4.05 (t, J = 6.1 Hz, 2H), 3.30 (t, J = 6.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 136.5, 133.5, 128.7, 128.1, 116.0, 66.8, 56.6, 38.1.

HRMS (ESI) Calcd for $C_{11}H_{12}NO_2^+$ $[M+H]^+$: 190.0868, found: 190.0862.

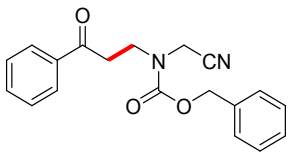


2-((3-oxo-3-phenylpropyl)thio)acetonitrile (13)： Following the general procedure A, obtained in 45% yield as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.61 (m, 2H), 7.44 – 7.32 (m, 1H), 7.29 – 7.23 (m, 2H), 3.16 – 3.22 (m, 4H), 2.94 (t, J = 6.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 136.2, 133.6, 128.8, 128.0, 116.9, 38.3, 26.9, 17.9.

HRMS (ESI) Calcd for $C_{11}H_{12}NOS^+$ $[M+H]^+$: 206.0640, found: 206.0641.

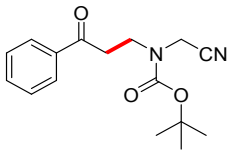


Benzyl (cyanomethyl)(3-oxo-3-phenylpropyl)carbamate (14)： Following the general procedure A, obtained in 65% yield as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.82 (m, 2H), 7.61 – 7.53 (m, J = 7.3 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.38 – 7.31 (m, 5H), 5.17 (s, 2H), 4.40 (s, 2H), 3.78 (t, J = 5.9 Hz, 2H), 3.40 – 3.28 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 155.5, 136.2, 135.5, 133.6, 128.7, 128.6, 128.4, 128.1, 128.0, 116.2, 68.2, 44.1, 37.6, 37.2.

HRMS (ESI) Calcd for $C_{19}H_{19}N_2O_3^+$ $[M+H]^+$: 323.1396, found: 323.1398.

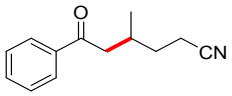


***tert*-butyl (cyanomethyl)(3-oxo-3-phenylpropyl)carbamate (15):** Following the general procedure A, obtained in 77% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 4.36 – 4.31 (m, 2H), 3.73 (t, J = 5.7 Hz, 2H), 3.38 – 3.28 (m, 2H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 154.1, 136.3, 133.5, 128.7, 128.0, 116.5, 82.0, 43.7, 37.8, 36.3, 28.2.

HRMS (ESI) Calcd for $C_{16}H_{21}N_2O_3^+$ $[M+H]^+$: 289.1552, found: 289.1552.

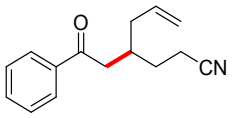


4-methyl-6-oxo-6-phenylhexanenitrile (16): Following the general procedure A, obtained in 79% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.86 (m, 2H), 7.64 – 7.53 (m, 1H), 7.51 – 7.42 (m, 2H), 3.00 – 2.86 (m, 2H), 2.53 – 2.25 (m, 3H), 1.92 – 1.79 (m, 1H), 1.70 – 1.50 (m, 1H), 1.04 (d, J = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 136.9, 133.2, 128.7, 128.0, 119.7, 45.0, 32.2, 28.8, 19.3, 15.0.

HRMS (ESI) Calcd for $C_{13}H_{16}NO^+$ $[M+H]^+$: 202.1232, found: 202.1236.

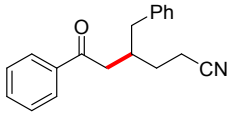


4-(2-oxo-2-phenylethyl)hept-6-enenitrile (17): Following the general procedure A, using 200 mol% enol silyl ether, obtained in 75% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.5 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 5.81 – 5.55 (m, 1H), 5.14 – 4.88 (m, 2H), 2.96 – 2.82 (m, 2H), 2.40 – 2.23 (m, 3H), 2.17 – 2.04 (m, 2H), 1.69 (dd, J = 14.4, 7.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 136.9, 135.2, 133.2, 128.6, 128.0, 119.6, 117.9, 41.9, 37.7, 32.9, 29.5, 15.0.

HRMS (ESI) Calcd for $C_{15}H_{18}NO^+$ $[M+H]^+$: 228.1388, found: 228.1387.

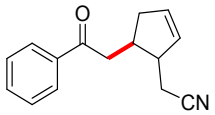


4-benzyl-6-oxo-6-phenylhexanenitrile (18): Following the general procedure A, obtained in 85% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.1 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.26 – 7.10 (m, 3H), 3.00 – 2.88 (m, 2H), 2.79 – 2.61 (m, 2H), 2.53 (dt, *J* = 12.7, 6.3 Hz, 1H), 2.35 (t, *J* = 7.5 Hz, 2H), 1.78 (dd, *J* = 14.0, 7.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 139.2, 136.8, 133.3, 129.2, 128.7, 128.6, 128.0, 126.5, 119.7, 41.7, 40.1, 35.5, 29.6, 15.1.

HRMS (ESI) Calcd for $C_{19}H_{20}NO^+$ $[M+H]^+$: 278.1545, found: 278.1539.

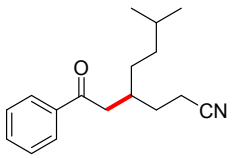


2-(5-(2-oxo-2-phenylethyl)cyclopent-2-en-1-yl)acetonitrile (19): Following the general procedure A, obtained in 71% yield as a white solid, d.r. > 20:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 7.90 (m, 2H), 7.64 – 7.52 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 5.87 (dd, *J* = 5.7, 2.0 Hz, 1H), 5.67 (dd, *J* = 5.7, 2.2 Hz, 1H), 3.25 – 3.13 (m, 2H), 2.92 – 2.78 (m, 1H), 2.78 – 2.68 (m, 1H), 2.64 – 2.46 (m, 3H), 2.15 – 2.04 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 136.8, 133.2, 132.5, 130.5, 128.6, 127.9, 118.9, 48.6, 44.7, 39.0, 38.3, 22.9.

HRMS (ESI) Calcd for $C_{15}H_{16}NO^+$ $[M+H]^+$: 226.1232, found: 226.1228.



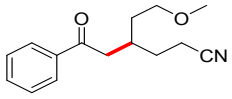
7-methyl-4-(2-oxo-2-phenylethyl)octanenitrile (20): Following the general procedure A, obtained in 89% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 7.60 – 7.54 (m, 1H), 7.51 – 7.43 (m,

2H), 3.02 – 2.89 (m, 2H), 2.38 (td, J = 7.3, 2.7 Hz, 2H), 2.26 – 2.16 (m, 1H), 1.81 – 1.68 (m, 2H), 1.56 – 1.46 (m, 1H), 1.43 – 1.31 (m, 2H), 1.25 – 1.15 (m, 2H), 0.91 – 0.83 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 137.0, 133.1, 128.6, 128.0, 119.8, 42.5, 35.6, 33.5, 31.2, 29.8, 28.1, 22.5, 14.9.

HRMS (ESI) Calcd for $C_{17}H_{24}NO^+$ $[M+H]^+$: 258.1858, found: 258.1866.

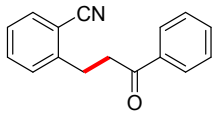


4-(2-methoxyethyl)-6-oxo-6-phenylhexanenitrile (21): Following the general procedure A, obtained in 85% yield as a light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 5.2, 3.3 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 3.44 (t, J = 6.2 Hz, 2H), 3.27 (s, 3H), 3.08 – 2.95 (m, 2H), 2.48 – 2.33 (m, 3H), 1.86 – 1.75 (m, 2H), 1.73 – 1.59 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 136.9, 133.2, 128.7, 128.0, 119.8, 70.5, 58.6, 42.5, 33.3, 31.4, 30.2, 14.9.

HRMS (ESI) Calcd for $C_{15}H_{20}NO_2^+$ $[M+H]^+$: 246.1494, found: 246.1502.

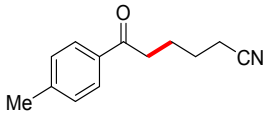


2-(3-oxo-3-phenylpropyl)benzonitrile (22): Following the general procedure A, obtained in 78% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.89 (m, 2H), 7.66 – 7.65 (m, 1H), 7.59 – 7.54 (m, 1H), 7.54 – 7.50 (m, 1H), 7.49 – 7.38 (m, 3H), 7.34 – 7.28 (m, 1H), 3.44 – 3.36 (m, 2H), 3.36 – 3.22 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 145.3, 136.4, 133.3, 132.9, 130.1, 128.7, 128.0, 126.8, 118.0, 112.3, 39.1, 28.8. (one carbon signal is overlapped)

HRMS (ESI) Calcd for $C_{16}H_{14}NO^+$ $[M+H]^+$: 236.1075, found: 236.1074.

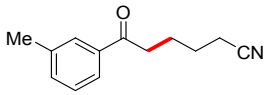


6-oxo-6-(p-tolyl)hexanenitrile (23): Following the general procedure A, obtained in 85% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 3.01 (t, *J* = 6.9 Hz, 2H), 2.50 – 2.34 (m, 5H), 1.96 – 1.84 (m, 2H), 1.82 – 1.69 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 144.0, 134.2, 129.3, 128.1, 119.6, 37.2, 25.0, 23.2, 21.6, 17.2.

HRMS (ESI) Calcd for $C_{13}H_{16}NO^+$ $[M+H]^+$: 202.1232, found: 202.1226.

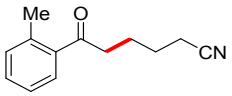


6-oxo-6-(m-tolyl)hexanenitrile (24): Following the general procedure A, obtained in 87% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.69 (m, 2H), 7.46 – 7.31 (m, 2H), 3.03 (t, *J* = 6.9 Hz, 2H), 2.47 – 2.37 (m, 5H), 1.97 – 1.85 (m, 2H), 1.82 – 1.70 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 138.5, 136.7, 134.0, 128.5, 128.5, 125.2, 119.5, 37.4, 25.0, 23.1, 21.3, 17.2.

HRMS (ESI) Calcd for $C_{13}H_{16}NO^+$ $[M+H]^+$: 202.1232, found: 202.1226.

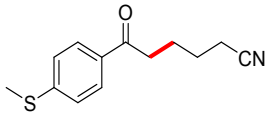


6-oxo-6-(o-tolyl)hexanenitrile (25): Following the general procedure A, obtained in 55% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.7 Hz, 1H), 7.38 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29 – 7.23 (m, 2H), 2.96 (t, *J* = 6.9 Hz, 2H), 2.49 (s, 3H), 2.40 (t, *J* = 7.0 Hz, 2H), 1.94 – 1.82 (m, 2H), 1.81 – 1.68 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1, 138.1, 137.5, 132.1, 131.4, 128.4, 125.7, 119.5, 40.2, 25.0, 23.3, 21.3, 17.2.

HRMS (ESI) Calcd for $C_{13}H_{16}NO^+$ $[M+H]^+$: 202.1232, found: 202.1229.



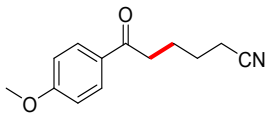
6-(4-(methylthio)phenyl)-6-oxohexanenitrile (26): Following the general procedure A,

obtained in 84% yield as a light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.28 – 7.26 (m, 2H), 3.00 (t, J = 6.9 Hz, 2H), 2.53 (s, 3H), 2.41 (t, J = 7.1 Hz, 2H), 1.93 – 1.86 (m, 2H), 1.80 – 1.72 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 146.1, 132.9, 128.4, 125.0, 119.5, 37.1, 25.0, 23.2, 17.2, 14.7.

HRMS (ESI) Calcd for $C_{13}H_{16}NOS^+$ $[M+H]^+$: 234.0953, found: 234.0948.

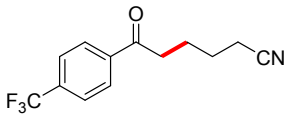


6-(4-methoxyphenyl)-6-oxohexanenitrile (27): Following the general procedure A, obtained in 82% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 3.87 (s, 3H), 2.99 (t, J = 6.9 Hz, 2H), 2.40 (t, J = 7.0 Hz, 2H), 1.99 – 1.82 (m, 2H), 1.83 – 1.58 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 163.5, 130.3, 129.7, 119.6, 113.8, 55.5, 37.0, 25.0, 23.3, 17.2.

HRMS (ESI) Calcd for $C_{13}H_{16}NO_2^+$ $[M+H]^+$: 218.1181, found: 218.1182.

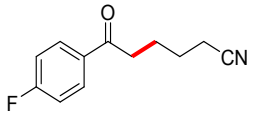


6-oxo-6-(4-(trifluoromethyl)phenyl)hexanenitrile (28): Following the general procedure A, obtained in 82% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 3.08 (t, J = 6.9 Hz, 2H), 2.43 (t, J = 7.0 Hz, 2H), 1.97 – 1.89 (m, 2H), 1.83 – 1.74 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 139.2, 134.4 (q, J = 32.7 Hz), 128.3, 125.7 (q, J = 3.7 Hz), 123.6 (q, J = 272.8 Hz), 119.4, 37.7, 24.9, 22.8, 17.2.

HRMS (ESI) Calcd for $C_{13}H_{13}F_3NO^+$ $[M+H]^+$: 256.0949, found: 256.0948.

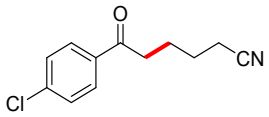


6-(4-fluorophenyl)-6-oxohexanenitrile (29): Following the general procedure A, obtained in 60% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.94 (m, 2H), 7.19 – 7.12 (m, 2H), 3.02 (t, *J* = 6.9 Hz, 2H), 2.42 (t, *J* = 7.1 Hz, 2H), 1.95 – 1.87 (m, 2H), 1.73 – 1.81 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 165.8 (d, *J* = 254.9 Hz), 133.1 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 9.3 Hz), 119.5, 115.8 (d, *J* = 21.9 Hz), 37.3, 24.9, 23.0, 17.2.

HRMS (ESI) Calcd for $C_{12}H_{13}FNO^+$ $[M+H]^+$: 206.0981, found: 206.0982.

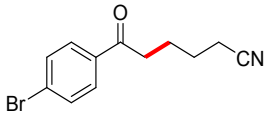


6-(4-chlorophenyl)-6-oxohexanenitrile (30): Following the general procedure A, obtained in 96% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.83 (m, 2H), 7.55 – 7.36 (m, 2H), 3.02 (t, *J* = 6.9 Hz, 2H), 2.42 (t, *J* = 7.1 Hz, 2H), 2.17 – 1.83 (m, 2H), 1.83 – 1.55 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 139.6, 134.9, 129.4, 129.0, 119.5, 37.3, 24.9, 23.0, 17.2.

HRMS (ESI) Calcd for $C_{12}H_{13}ClNO^+$ $[M+H]^+$: 222.0686, found: 222.0688.

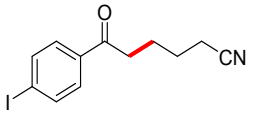


6-(4-bromophenyl)-6-oxohexanenitrile (31): Following the general procedure A, obtained in 70% yield as a light yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 3.01 (t, *J* = 6.9 Hz, 2H), 2.41 (t, *J* = 7.1 Hz, 2H), 1.95 – 1.87 (m, 2H), 1.80 – 1.72 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 135.3, 132.0, 129.5, 128.4, 119.5, 37.3, 24.9, 23.0, 17.2.

HRMS (ESI) Calcd for $C_{12}H_{13}BrNO^+$ $[M+H]^+$: 266.0181, found: 266.0181.

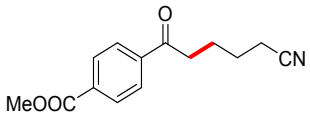


6-(4-iodophenyl)-6-oxohexanenitrile (32): Following the general procedure A, obtained in 84% yield as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 3.00 (t, *J* = 6.8 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.97 – 1.82 (m, 2H), 1.81 – 1.68 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 137.9, 135.91, 129.4, 119.5, 101.2, 37.3, 24.9, 22.9, 17.2.

HRMS (ESI) Calcd for $C_{12}H_{13}INO^+$ $[M+H]^+$: 314.0042, found: 314.0042.

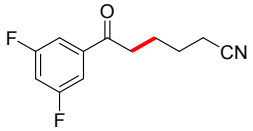


Methyl 4-(5-cyanopentanoyl)benzoate (33): Following the general procedure A, obtained in 90% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 2H), 3.96 (s, 3H), 3.08 (t, *J* = 6.9 Hz, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.03 – 1.85 (m, 2H), 1.84 – 1.67 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 166.1, 139.8, 133.9, 129.9, 127.9, 119.4, 52.5, 37.7, 24.9, 22.9, 17.2.

HRMS (ESI) Calcd for $C_{14}H_{16}NO_3^+$ $[M+H]^+$: 246.1130, found: 246.1129.

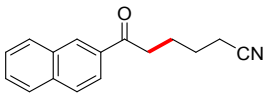


6-(3,5-difluorophenyl)-6-oxohexanenitrile (34): Following the general procedure A, obtained in 67% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 7.8, 2.2 Hz, 2H), 7.03 (tt, *J* = 8.4, 2.3 Hz, 1H), 3.00 (t, *J* = 6.9 Hz, 2H), 2.43 (t, *J* = 7.0 Hz, 2H), 1.95 – 1.87 (m, 2H), 1.80 – 1.73 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 163.0 (dd, *J* = 251.2, 11.7 Hz), 139.5 (t, *J* = 7.4 Hz), 119.3, 111.1 – 110.7 (m), 108.5 (t, *J* = 25.4 Hz), 37.6, 24.8, 22.8, 17.2.

HRMS (ESI) Calcd for $C_{12}H_{12}F_2NO^+$ $[M+H]^+$: 224.0887, found: 224.0885.

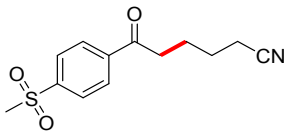


6-(naphthalen-2-yl)-6-oxohexanenitrile (35): Following the general procedure A, obtained in 74% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.04 – 7.94 (m, 2H), 7.94 – 7.85 (m, 2H), 7.63 – 7.54 (m, 2H), 3.17 (t, *J* = 7.0 Hz, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.13 – 1.87 (m, 2H), 1.86 – 1.65 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 135.6, 134.0, 132.5, 130.5, 129.7, 129.5, 128.5, 127.8, 126.9, 123.7, 119.6, 37.4, 25.0, 23.2, 17.2.

HRMS (ESI) Calcd for $C_{16}H_{16}NO^+$ $[M+H]^+$: 238.1232, found: 238.1233.

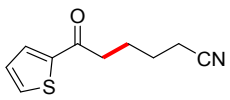


6-(4-(methylsulfonyl)phenyl)-6-oxohexanenitrile (36): Following the general procedure A, obtained in 75% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.11 (m, 2H), 8.05 (d, *J* = 8.5 Hz, 2H), 3.14 – 3.08 (m, 5H), 2.45 (t, *J* = 7.0 Hz, 2H), 1.98 – 1.89 (m, 2H), 1.84 – 1.74 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 144.2, 140.5, 128.8, 127.8, 119.5, 44.3, 37.9, 24.8, 22.7, 17.2.

HRMS (ESI) Calcd for $C_{13}H_{16}NO_3S^+$ $[M+H]^+$: 266.0851, found: 266.0848.

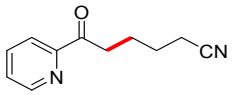


6-oxo-6-(thiophen-2-yl)hexanenitrile (37): Following the general procedure A, obtained in 73% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 2.6 Hz, 1H), 7.65 (d, *J* = 4.9 Hz, 1H), 7.18 – 7.11 (m, 1H), 2.98 (t, *J* = 7.0 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 2.01 – 1.83 (m, 2H), 1.79 – 1.71 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 143.9, 133.8, 131.9, 128.2, 119.5, 38.0, 24.9, 23.3, 17.1.

HRMS (ESI) Calcd for $C_{10}H_{12}NOS^+$ $[M+H]^+$: 194.0640, found: 194.0642.

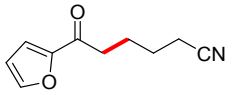


6-oxo-6-(pyridin-2-yl)hexanenitrile (38): Following the general procedure A, obtained in 68% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 – 8.64 (m, 1H), 8.05 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.86 (td, *J* = 7.7, 1.7 Hz, 1H), 7.53 – 7.45 (m, 1H), 3.29 (t, *J* = 7.1 Hz, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 1.96 – 1.86 (m, 2H), 1.83 – 1.74 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9, 153.1, 148.9, 136.9, 127.2, 121.7, 119.5, 36.5, 25.0, 22.9, 17.1.

HRMS (ESI) Calcd for $C_{11}H_{13}N_2O^+$ $[M+H]^+$: 189.1028, found: 189.1022.



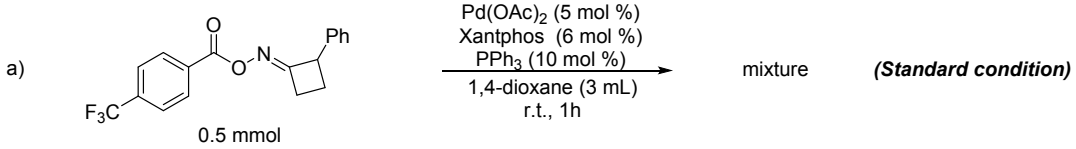
6-(furan-2-yl)-6-oxohexanenitrile (39): Following the general procedure A, obtained in 81% yield as a white solid.

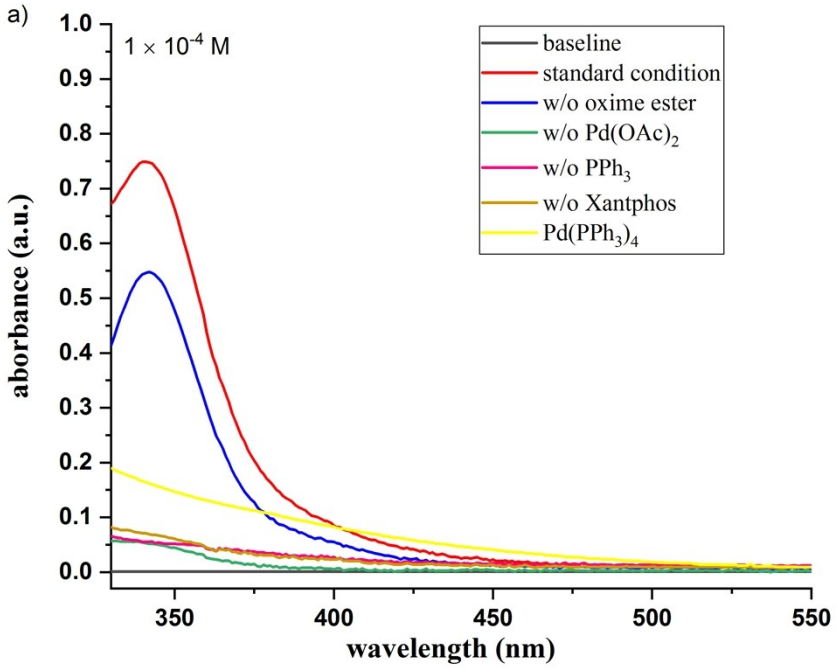
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 1H), 7.16 – 7.11 (m, 1H), 6.48 (dd, *J* = 3.6, 1.7 Hz, 1H), 2.83 (t, *J* = 7.0 Hz, 2H), 2.33 (t, *J* = 7.1 Hz, 2H), 1.89 – 1.76 (m, 2H), 1.76 – 1.51 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.4, 152.5, 146.4, 119.4, 117.1, 112.3, 37.2, 24.9, 22.9, 17.1.

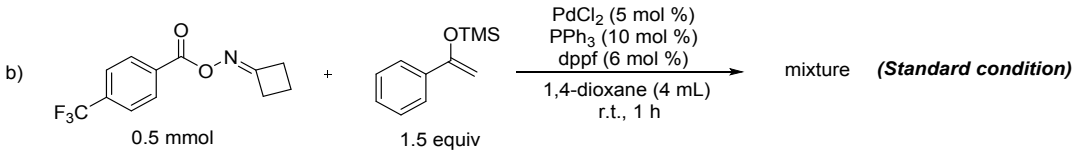
HRMS (ESI) Calcd for $C_{10}H_{12}NO_2^+$ $[M+H]^+$: 178.0868, found: 178.0866.

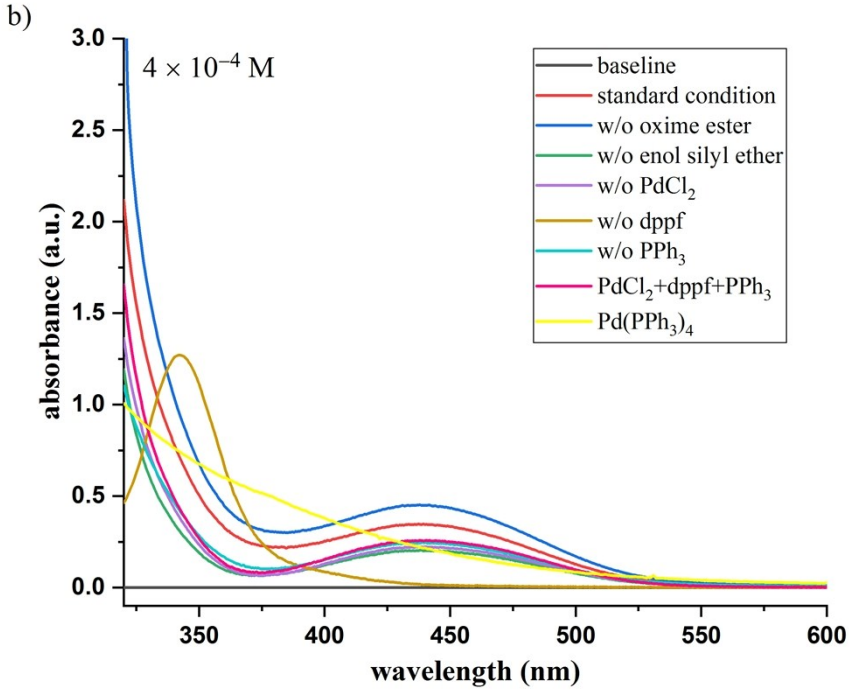
5. UV-vis. Spectrum





The UV-vis absorption spectrum was measured using a spectrophotometer and standard sample was prepared by the following procedure: Oxime esters (0.5 mmol), $Pd(OAc)_2$ (5 mol %), PPh_3 (10 mol %) and 1,1'-Bis(diphenylphosphino)ferrocene (dppf, 6 mol %) were placed in a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To these solids, anhydrous 1,4-dioxane (4.0 mL) were added under argon atmosphere. The reaction mixture was stirred under room temperature for 1 h. After completed, 20 μL of the mixture was diluted to 3 mL anhydrous 1,4-dioxane and transferred to a cuvette pending test. (Note: other samples were prepared in the same way in the absence of specific component)





The UV-vis absorption spectrum was measured using a spectrophotometer and standard sample was prepared by the following procedure: Oxime esters (0.5 mmol), $PdCl_2$ (5 mol %), PPh_3 (10 mol %) and 1,1'-Bis(diphenylphosphino)ferrocene (dppf, 6 mol %) were placed in a 10 mL transparent Schlenk tube equipped with a stirring bar. The tube was evacuated and filled with argon (repeated for three times). To these solids, enol silyl ether (0.75 mmol) and anhydrous 1,4-dioxane (4.0 mL) were added under argon atmosphere. The reaction mixture was stirred under room temperature for 1 h. After completed, 100 μL of the mixture was diluted to 3 mL anhydrous 1,4-dioxane and transferred to a cuvette pending test. (Note: other samples were prepared in the same way in the absence of specific component)

6. References

[1] (a) Kamigata, N.; Udodaira, K.; Shimizu T. *Phorphomr, Sulphur. and Silicon*, **1997**, *129*. 155. (b) Shen, H.; Liu, J.; Liu, Q.; Huang, R.; Xiong, Y. *J. Org. Chem.* **2015**, *80*,

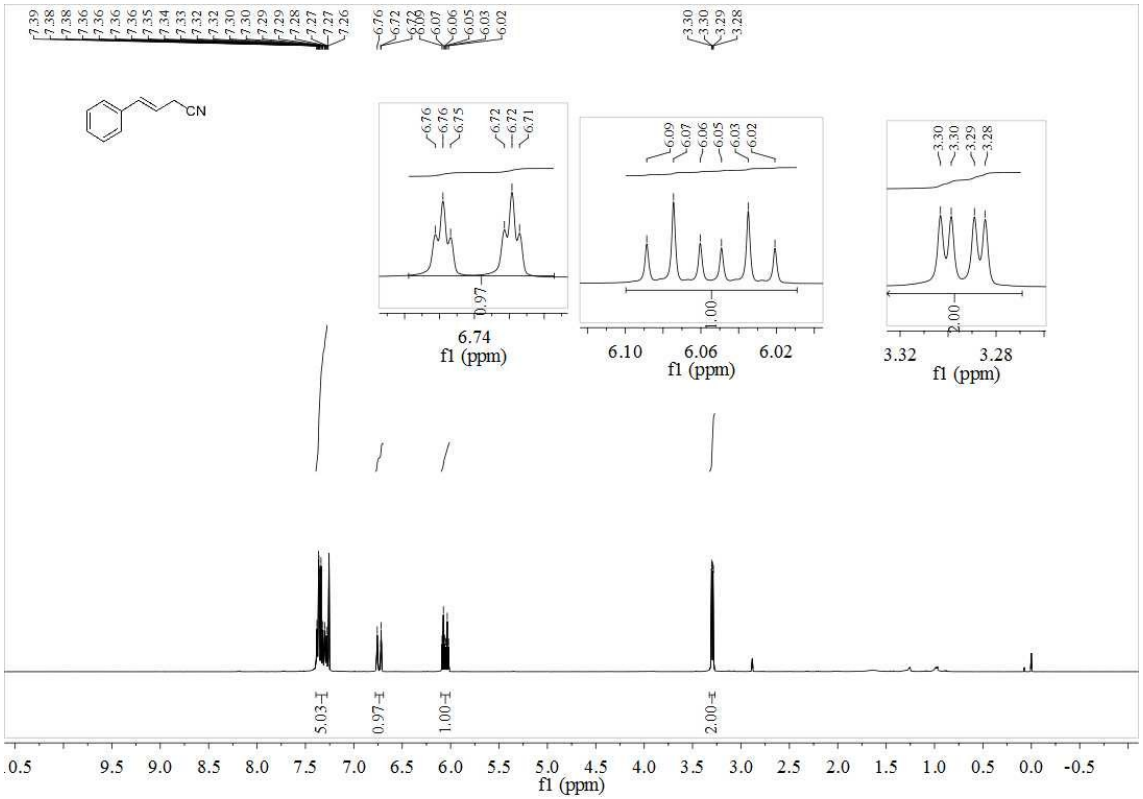
7212. (c) Fuglseth, E.; Thvedt, T. H. K.; Møll, M. F.; Hoff, B. H. *Tetrahedron* **2008**, *64*, 7318. (d) Biswas, S.; Page, J. P.; Dewese, K. R.; RajanBabu, T. V. *J. Am. Chem. Soc.* **2015**, *137*, 14268.

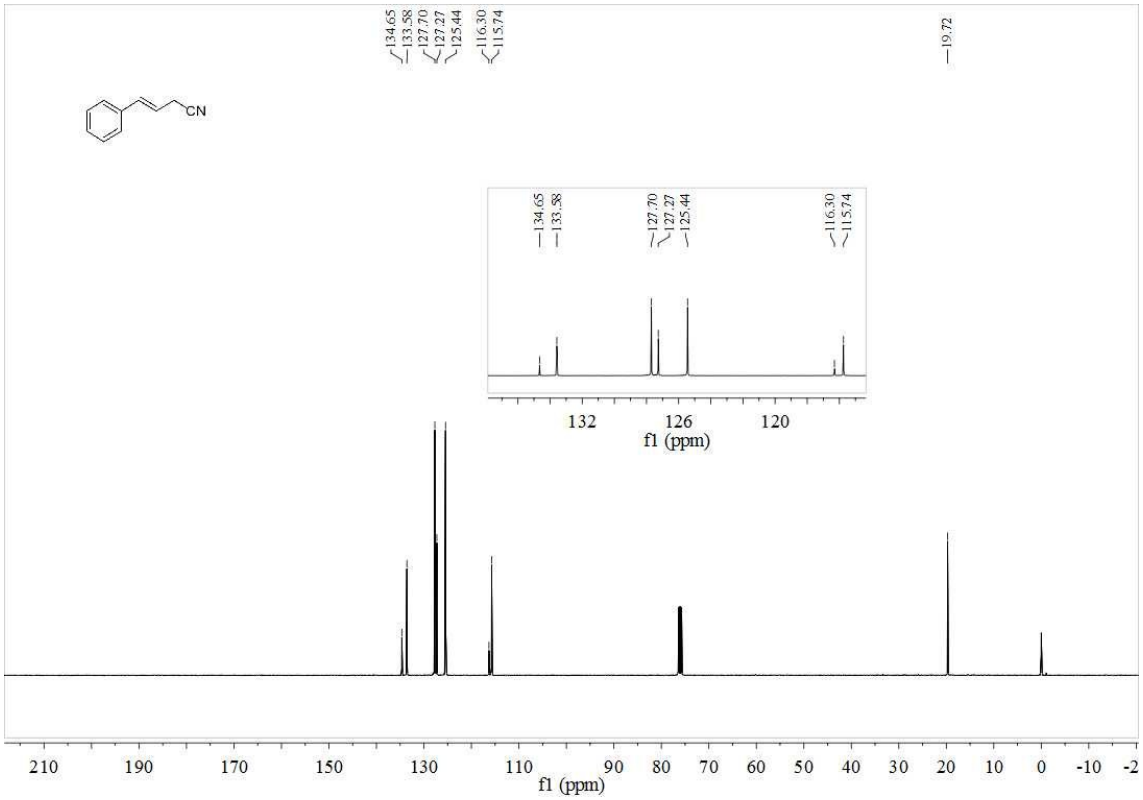
[2] (a) Ramnauth, J.; Lee-Ruff, E. *Can. J. Chem*. **2001**, *79*, 114. (b) Vesna, Š. M.; Zlatko, M.; Hrvoj, V. *Chem. Soc. Perkin Trans. 2*, **2002**, 2154–2158. (c) Yang, H.; Selander, N. *Chem. Eur. J.* **2017**, *23*, 1779. (d) Li, L.; Chen, H.; Mei, M.; Zhou, L. *Chem. Commun*. **2017**, *53*, 11544. (e) Gu, Y.; Duan, X.; Yang, L.; Guo, L. *Org. Lett*. **2017**, *19*, 5908.

[3] Ai, W.; Liu, Y.; Wang, Q.; Liu, Z.; Liu, Q. *Org. Lett.* **2018**, *20*, 409.

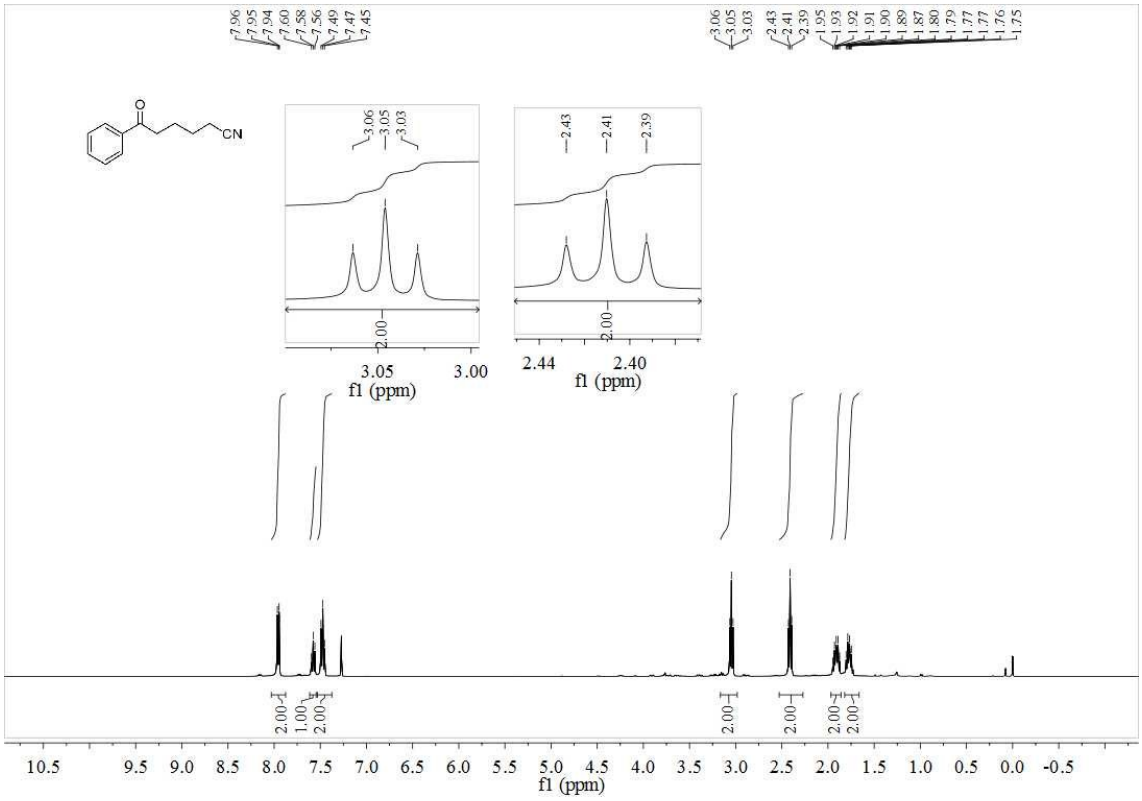
6. ^{1}H NMR and ^{13}C NMR Spectra

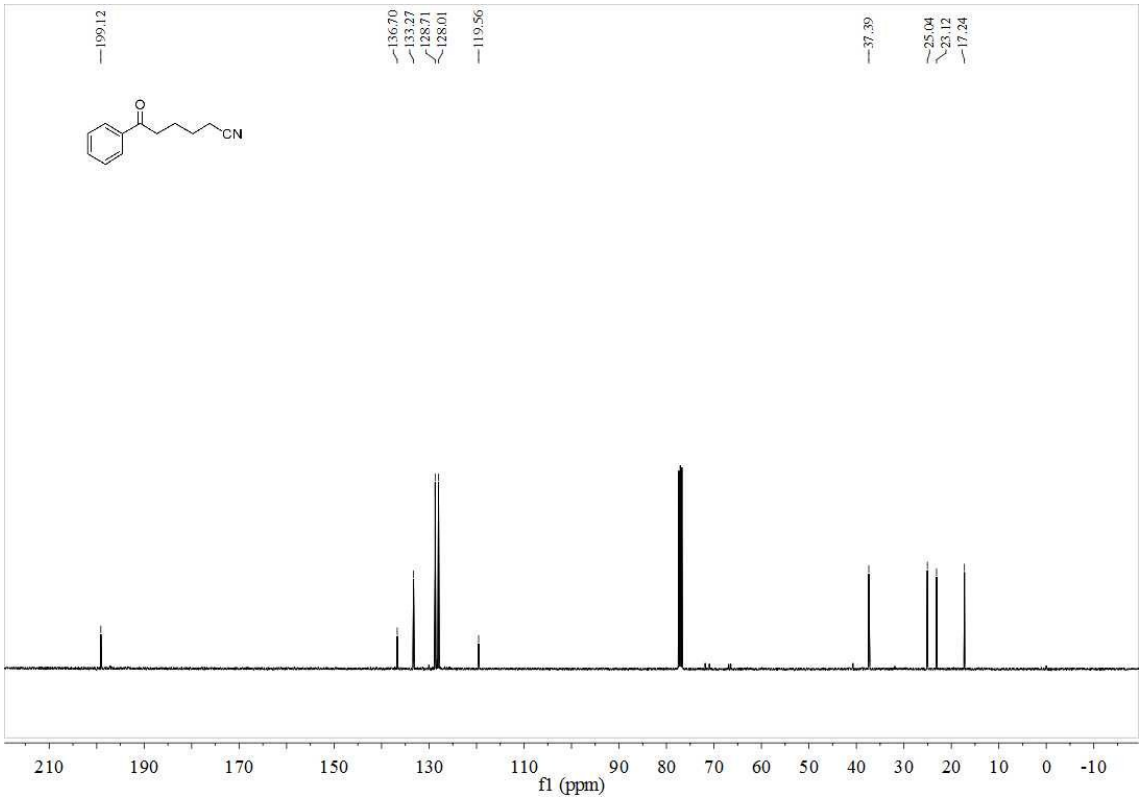
***(E)*-4-phenylbut-3-enenitrile (1)**



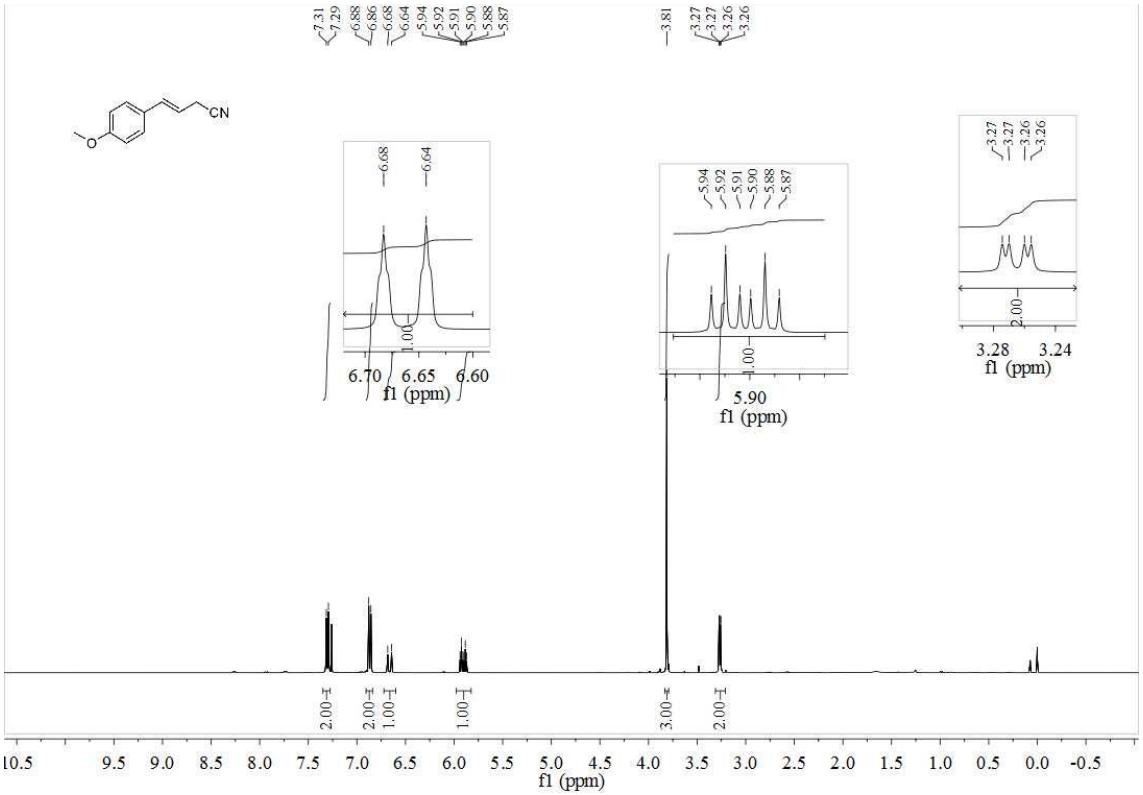


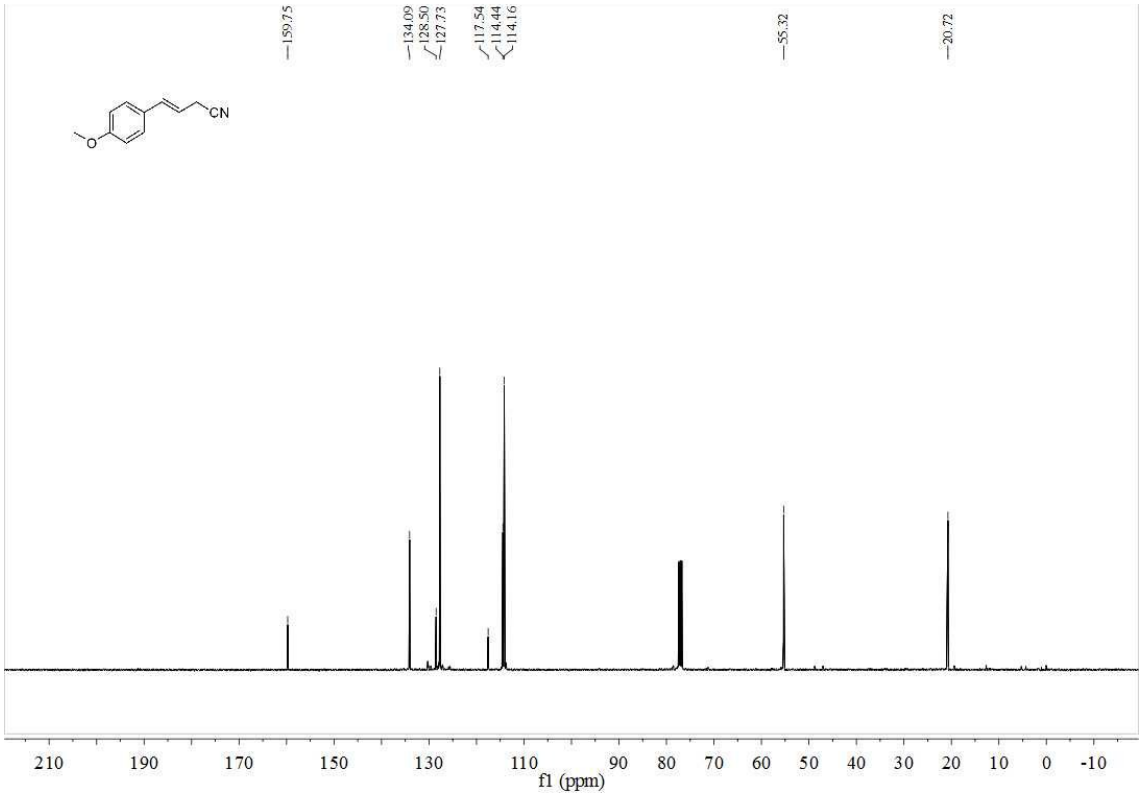
6-oxo-6-phenylhexanenitrile (2)



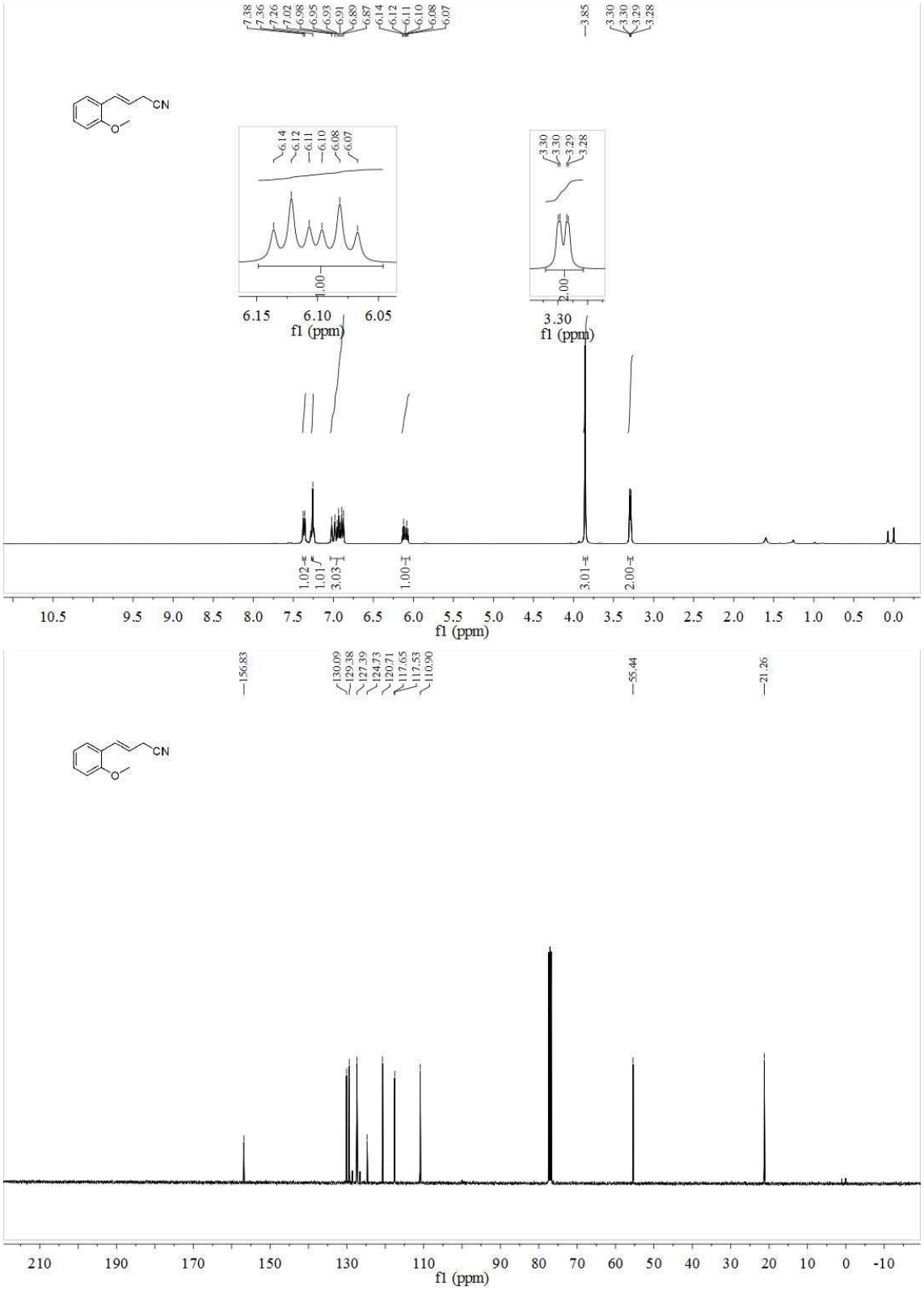


***(E)*-4-(4-methoxyphenyl)but-3-enenitrile (3)**

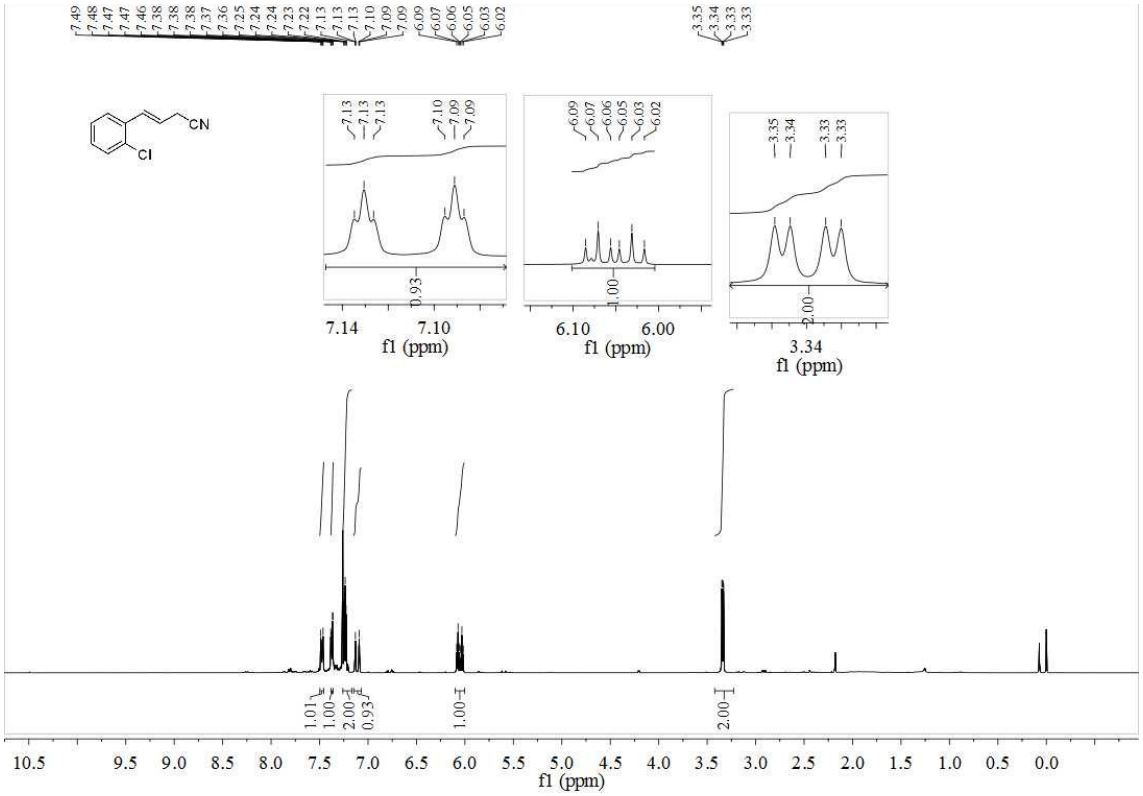


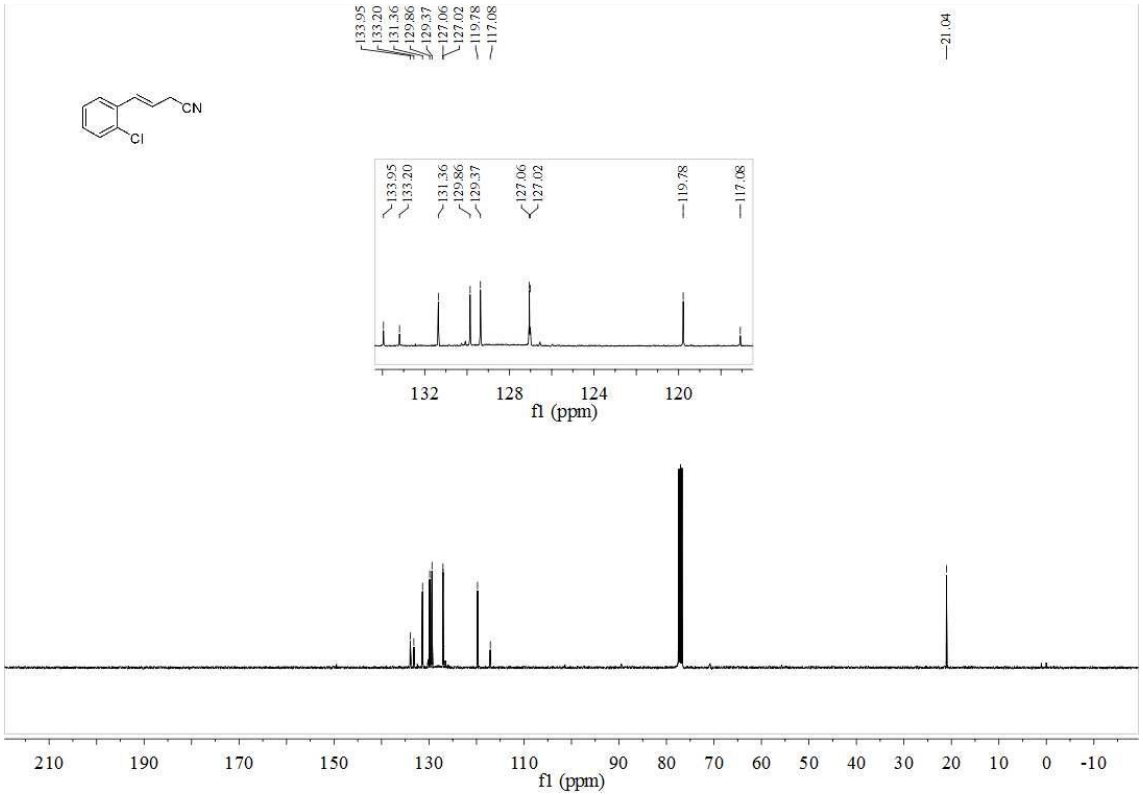


***(E)*-4-(2-methoxyphenyl)but-3-enenitrile (4)**

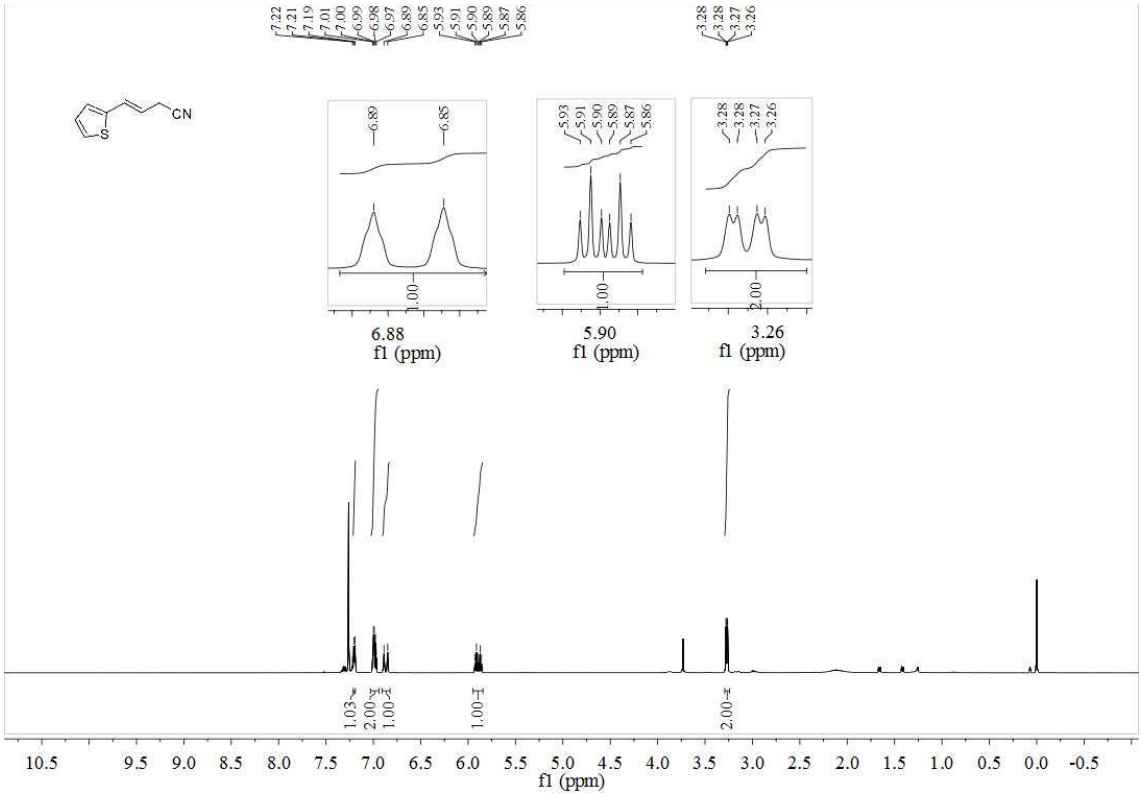


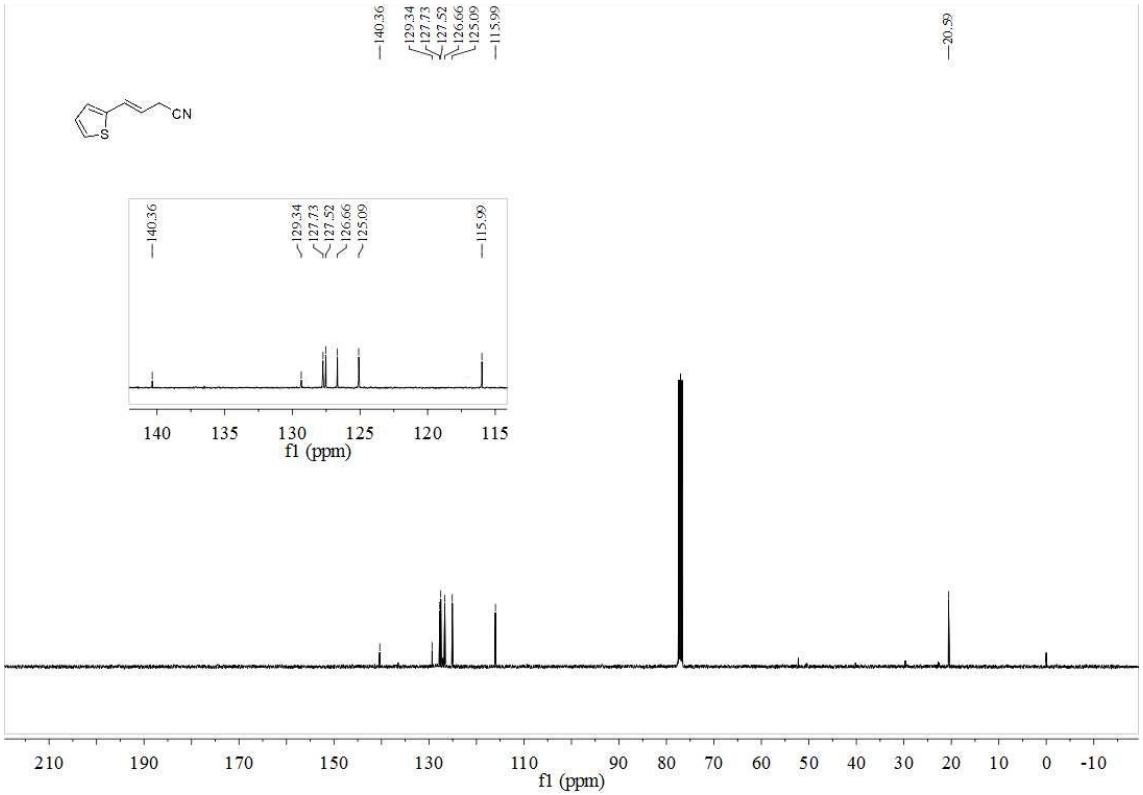
***(E)*-4-(2-chlorophenyl)but-3-enenitrile (5)**



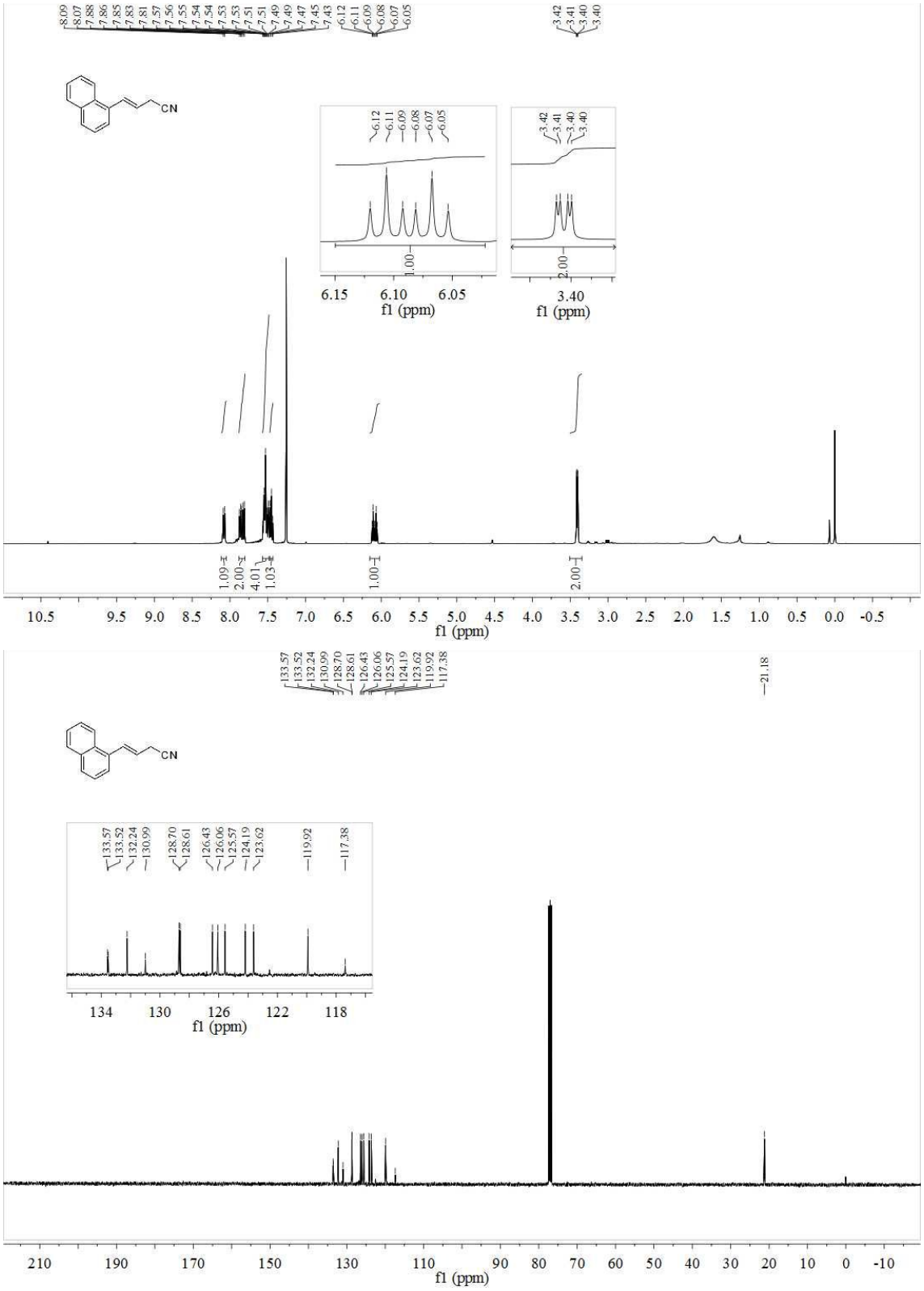


***(E)*-4-(thiophen-2-yl)but-3-enenitrile (6)**

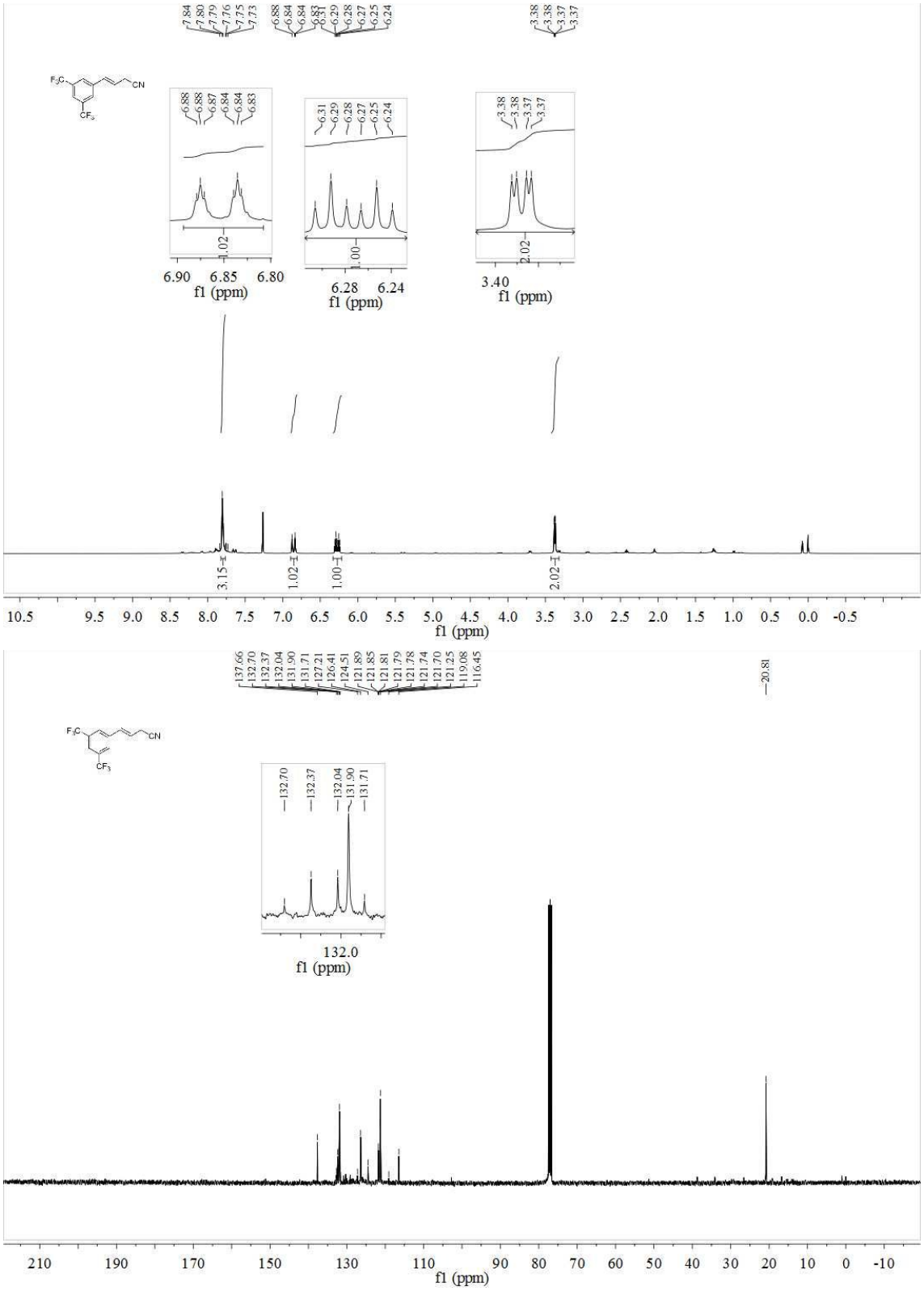




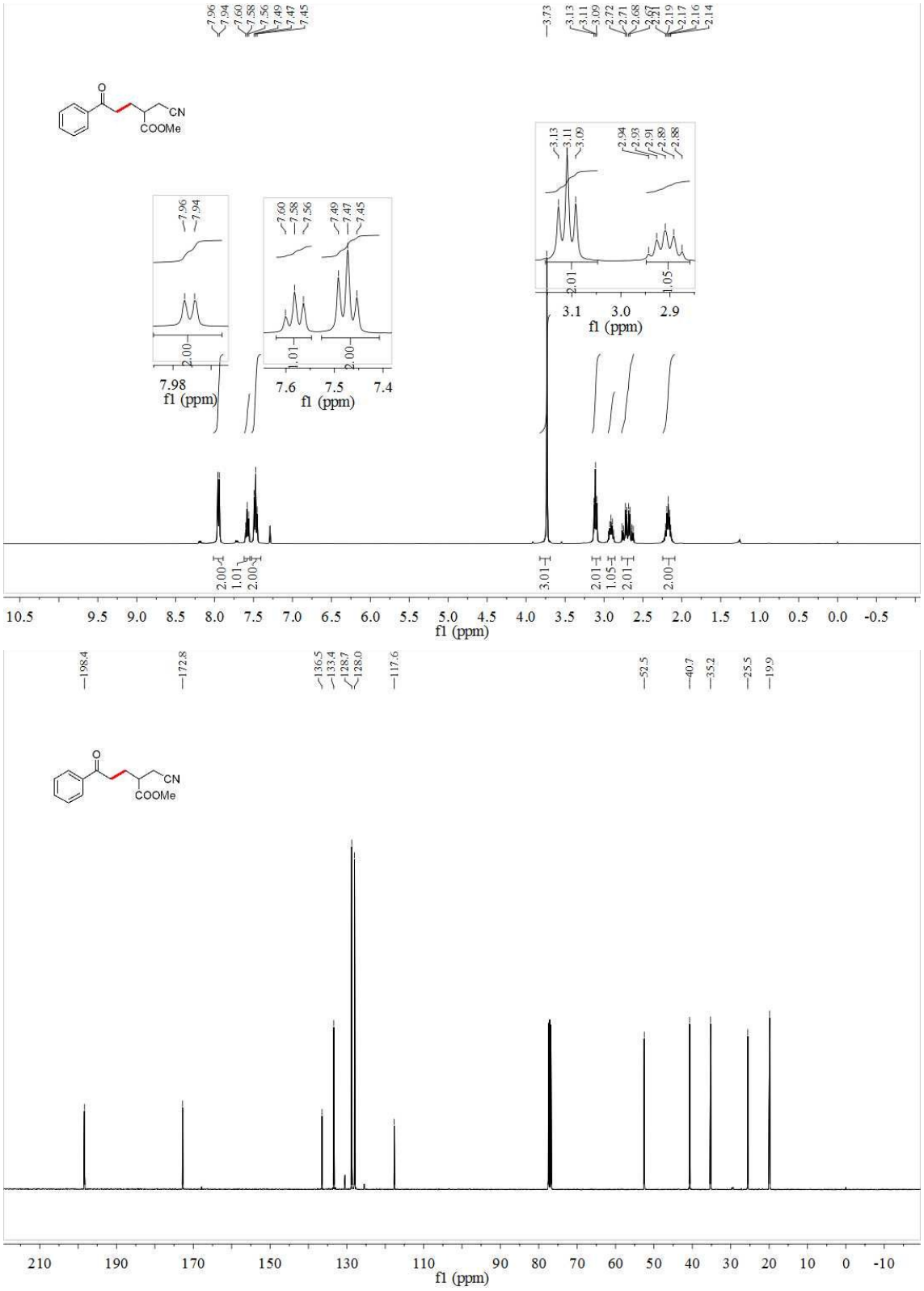
***(E)*-4-(naphthalen-1-yl)but-3-enenitrile (7)**



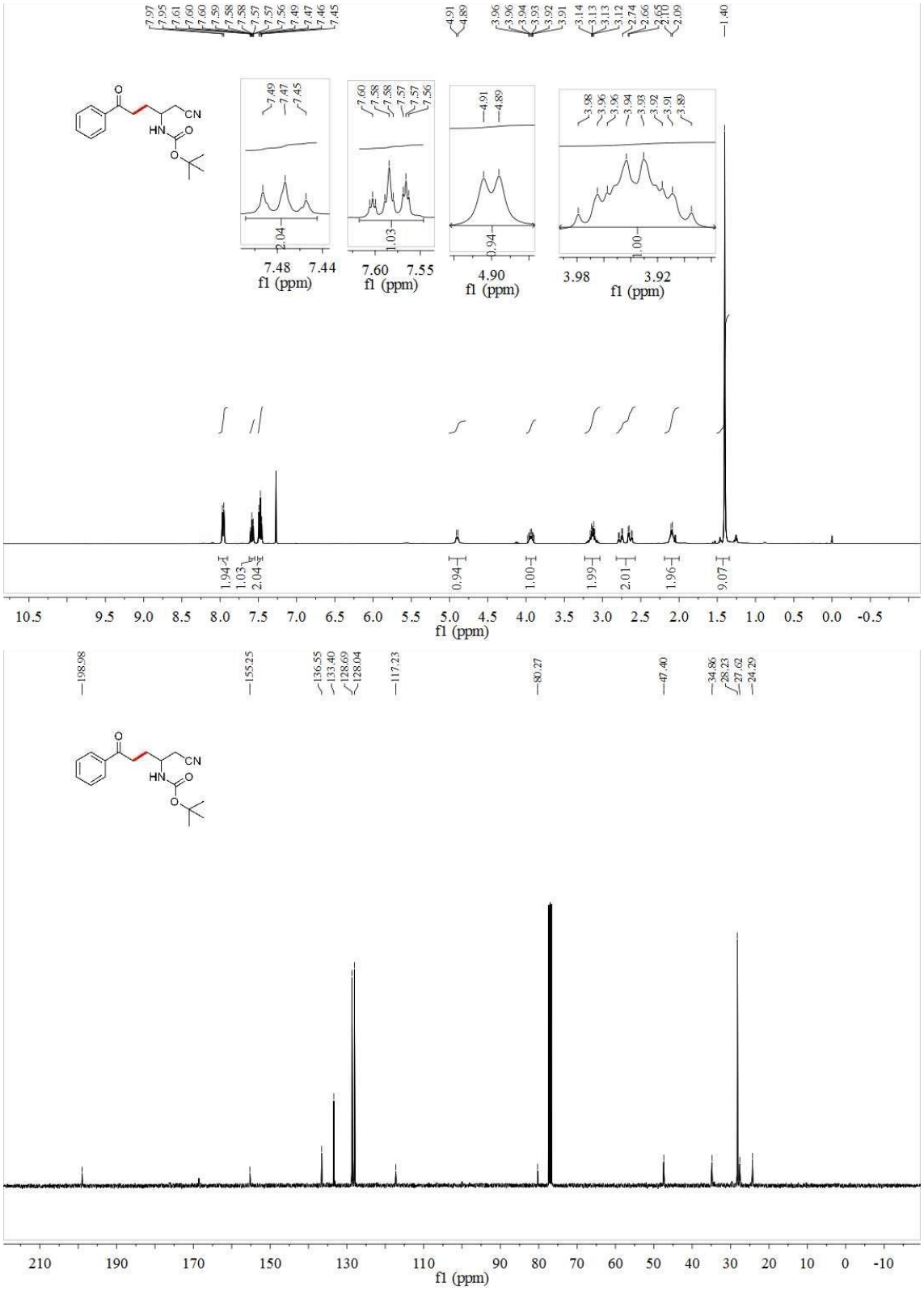
***(E)*-4-(3,5-bis(trifluoromethyl)phenyl)but-3-enenitrile (8)**



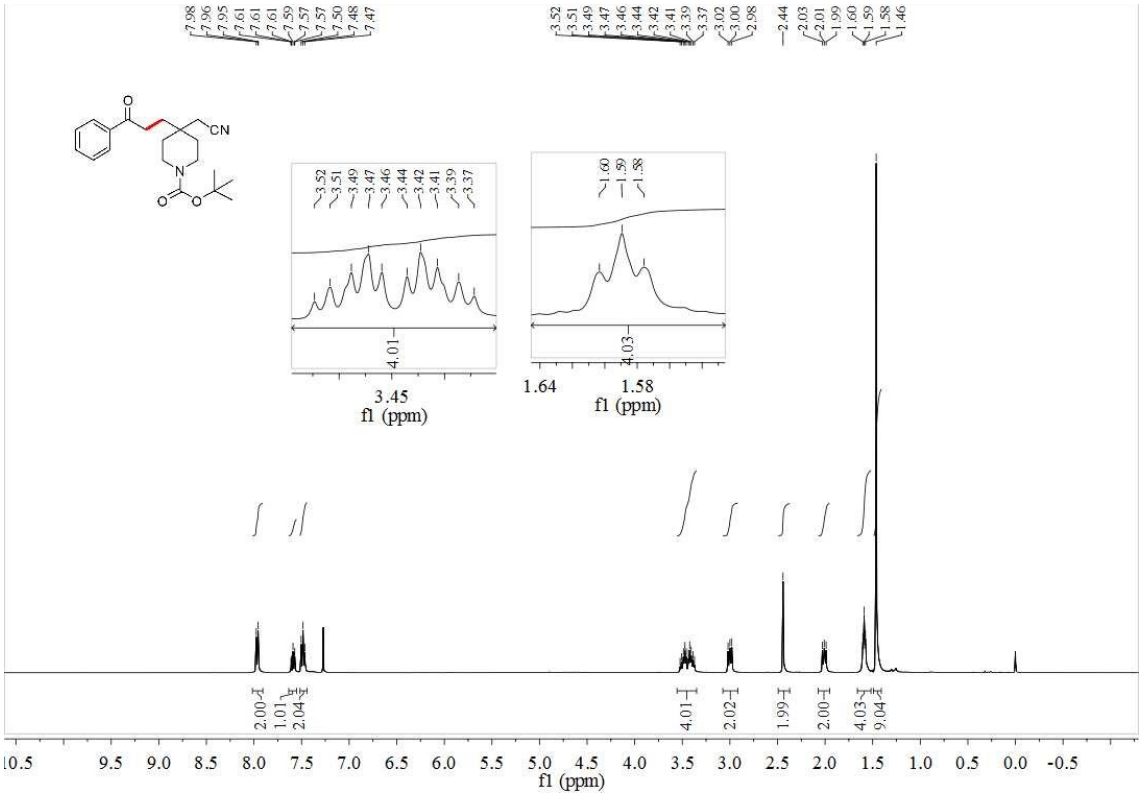
Methyl 2-(cyanomethyl)-5-oxo-5-phenylpentanoate (9)

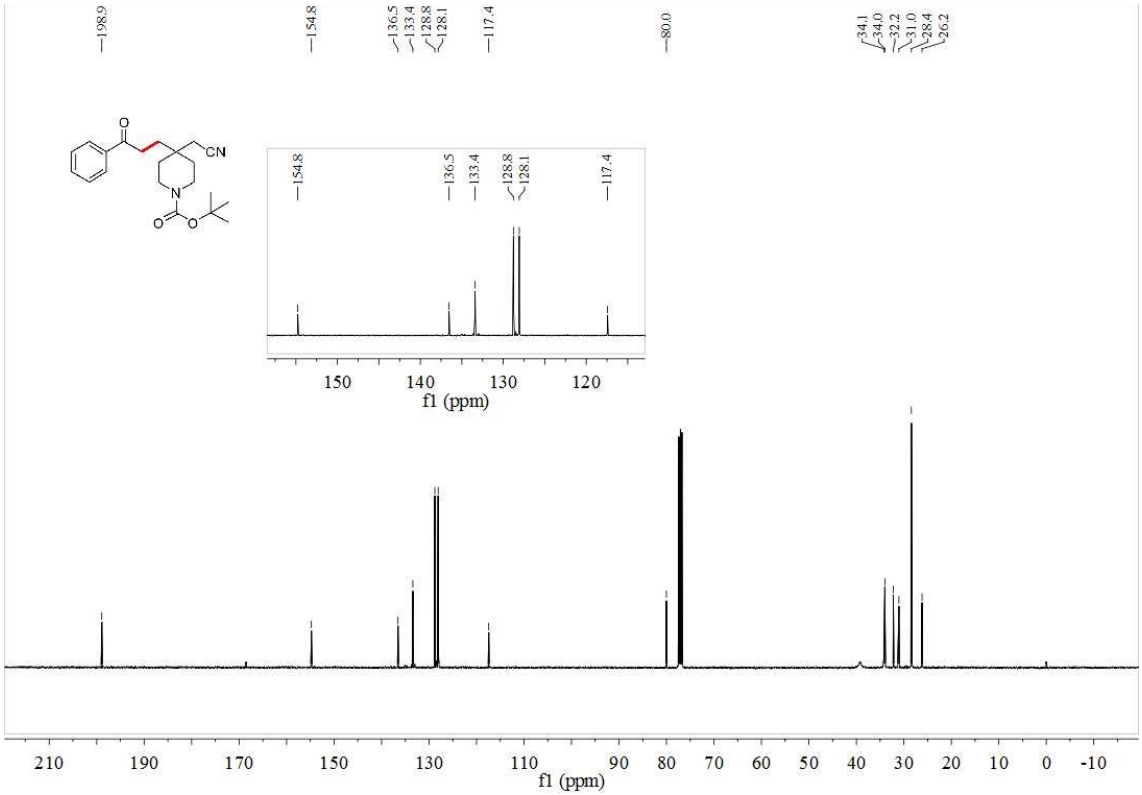


***tert*-butyl (1-cyano-5-oxo-5-phenylpentan-2-yl)carbamate (10)**

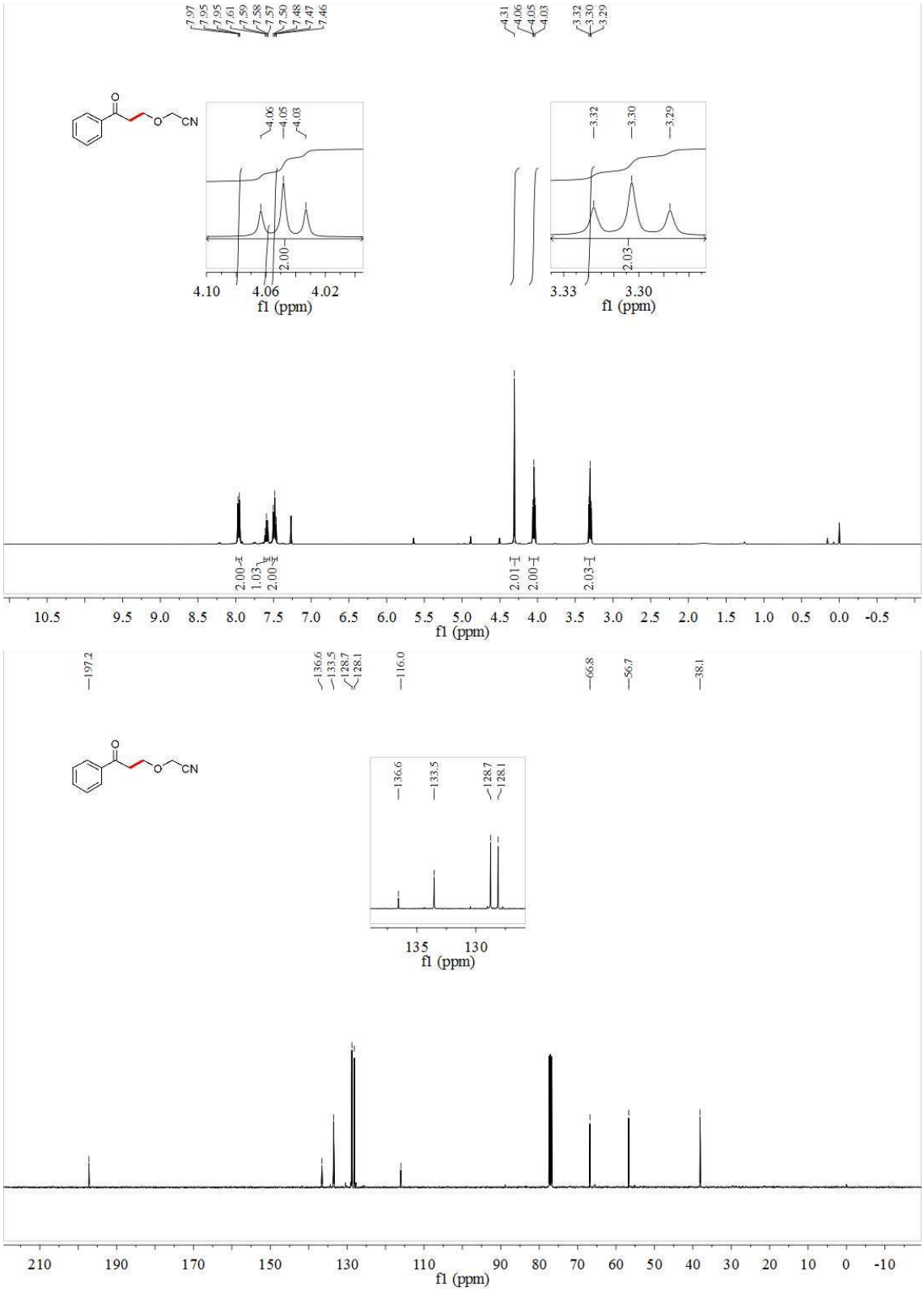


***tert*-butyl 4-(cyanomethyl)-4-(3-oxo-3-phenylpropyl)piperidine-1-carboxylate (11)**

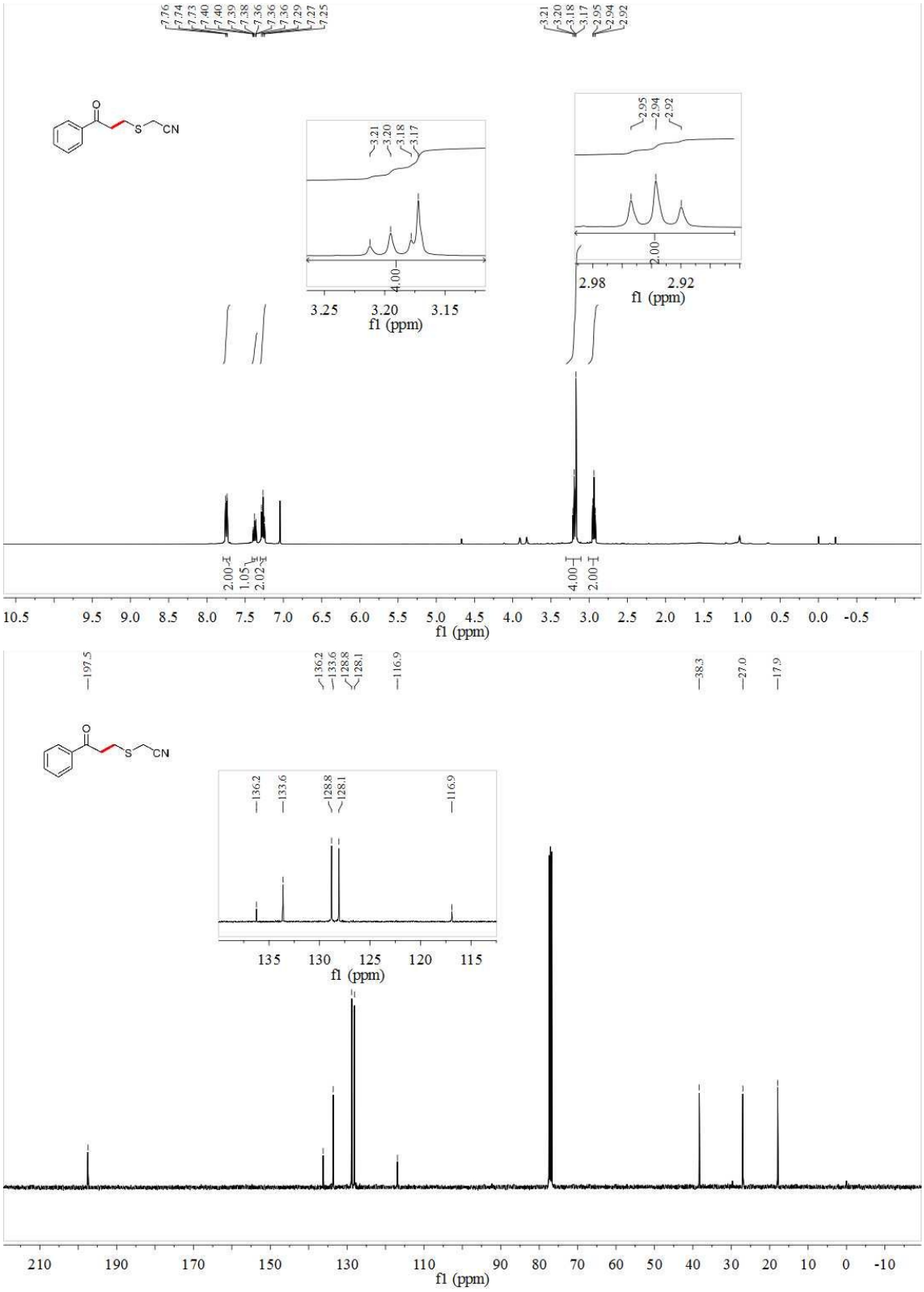




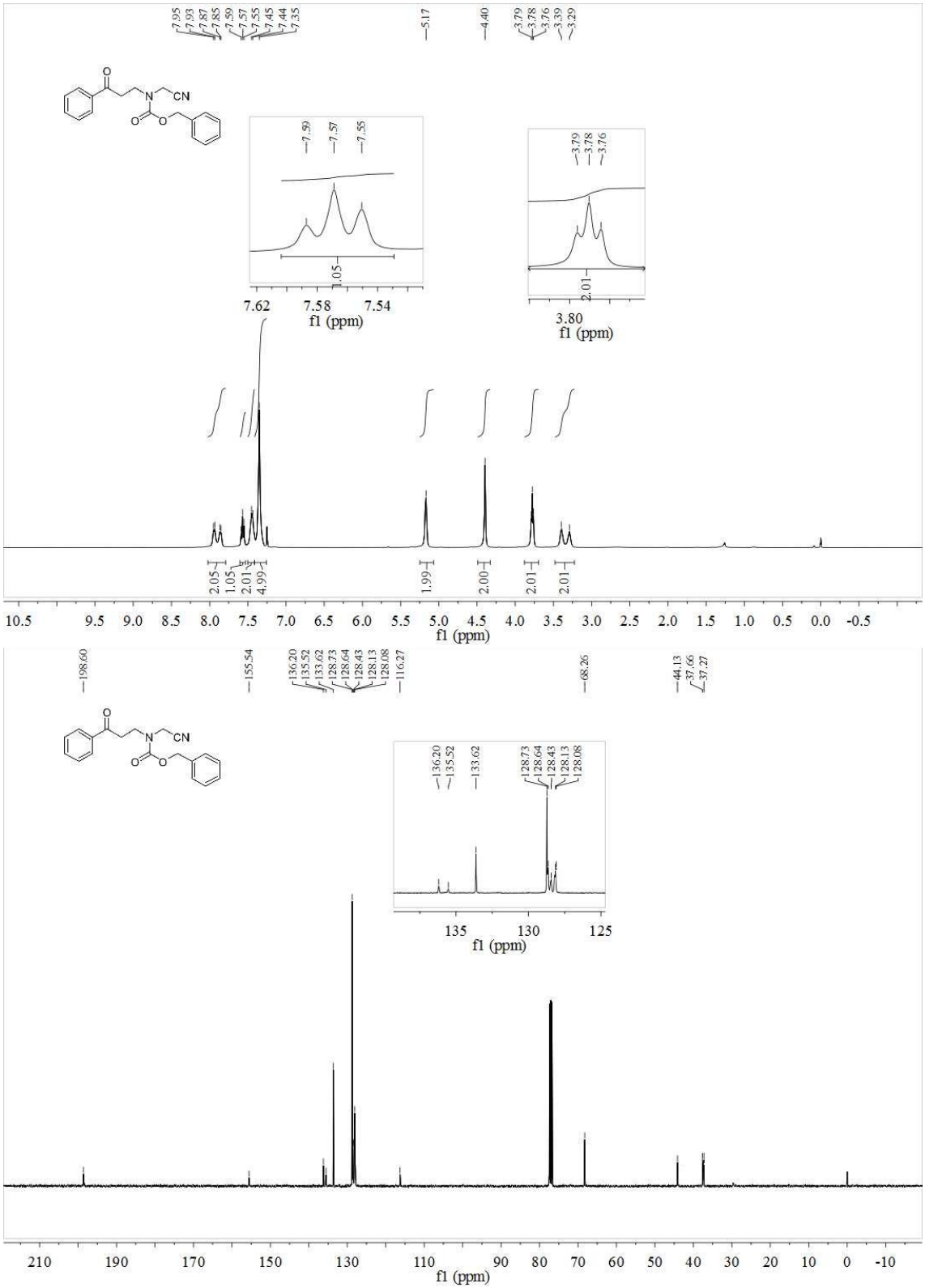
2-(3-oxo-3-phenylpropoxy)acetonitrile (12)



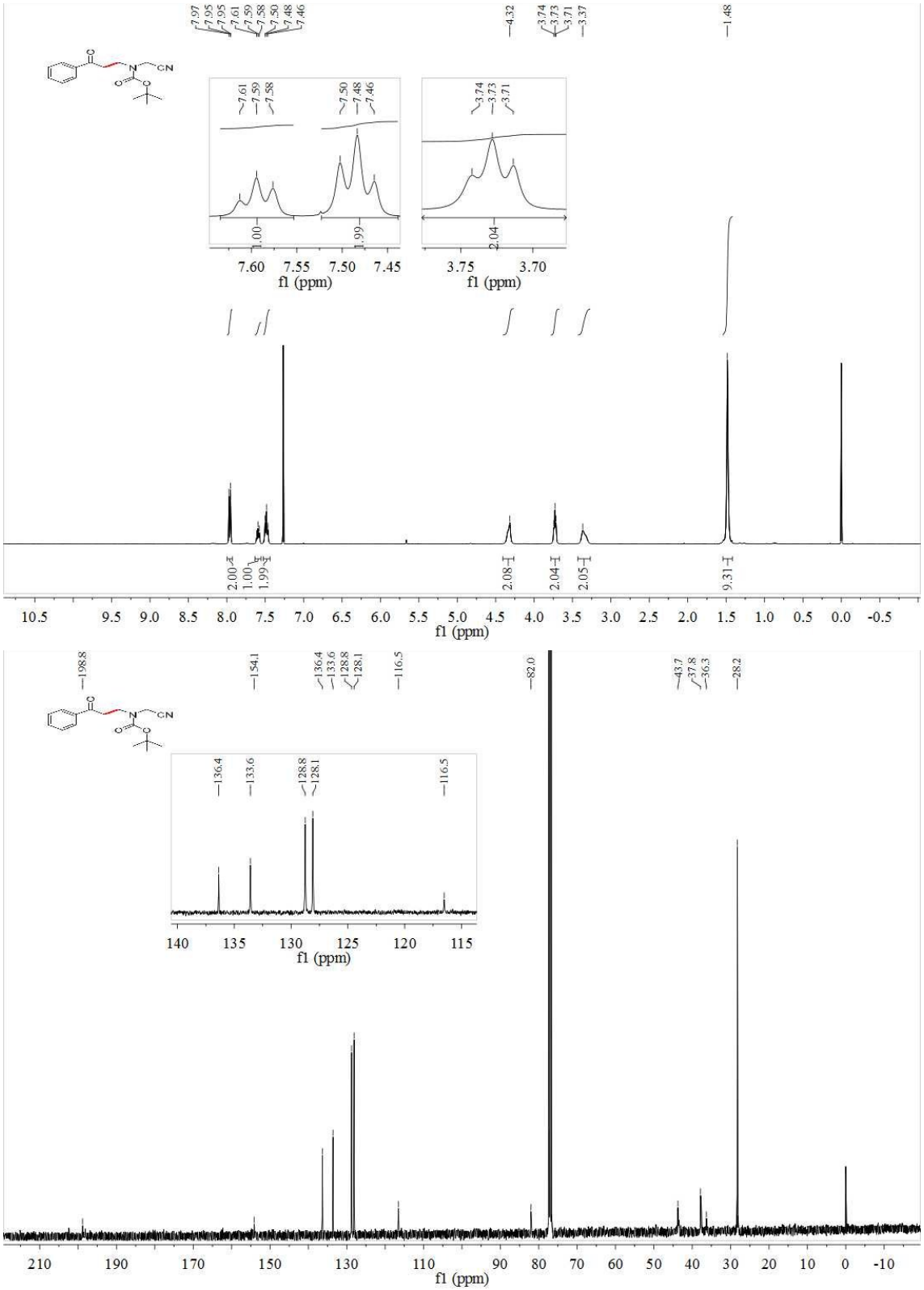
2-((3-oxo-3-phenylpropyl)thio)acetonitrile (13)



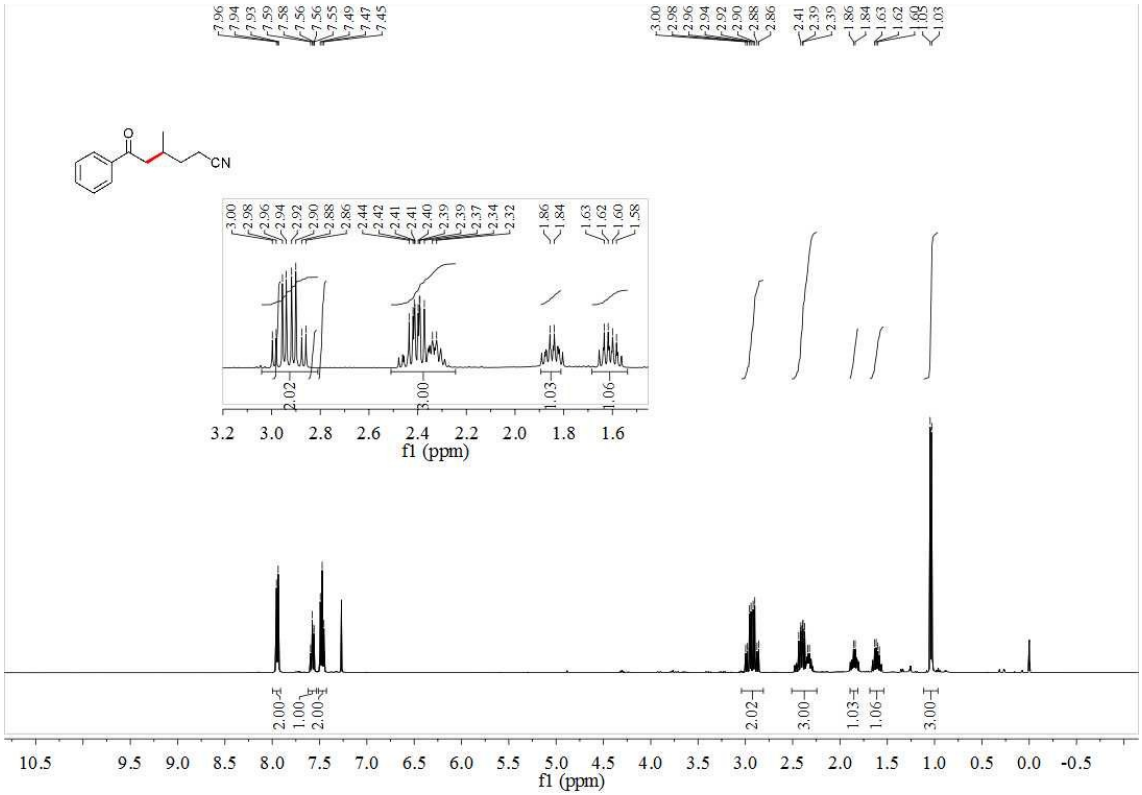
Benzyl (cyanomethyl)(3-oxo-3-phenylpropyl)carbamate (14)

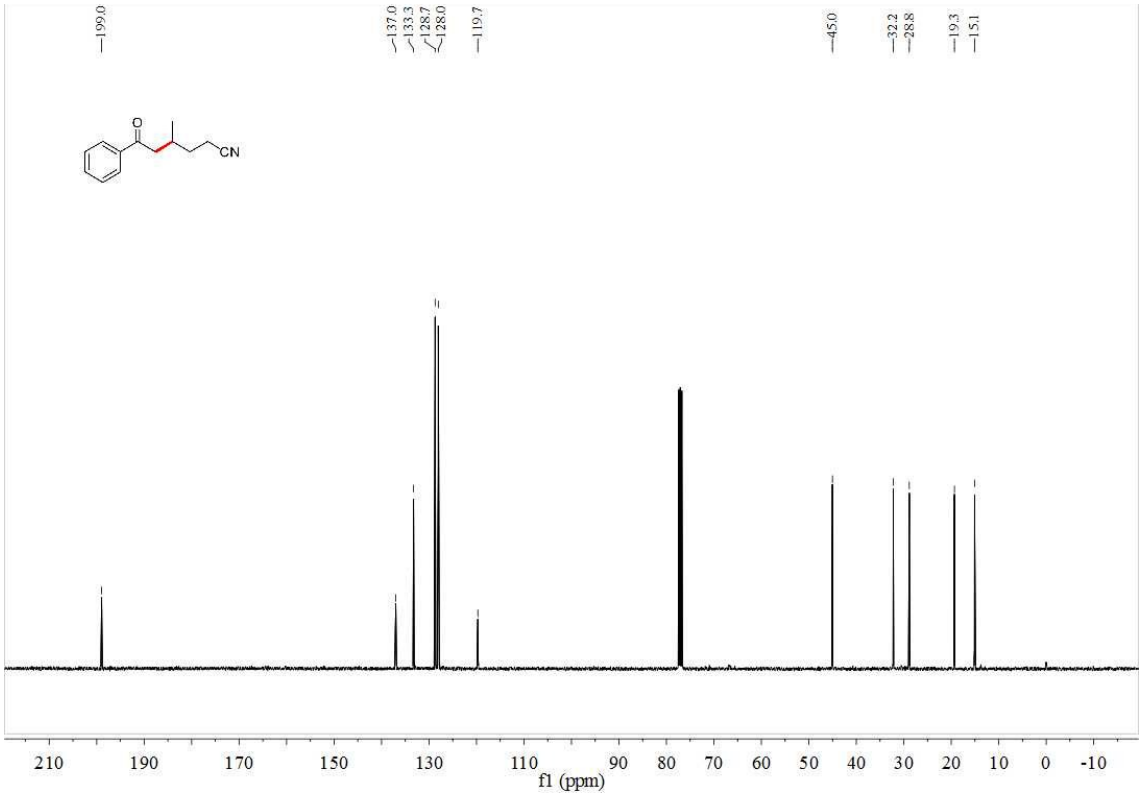


***tert*-butyl (cyanomethyl)(3-oxo-3-phenylpropyl)carbamate (15)**

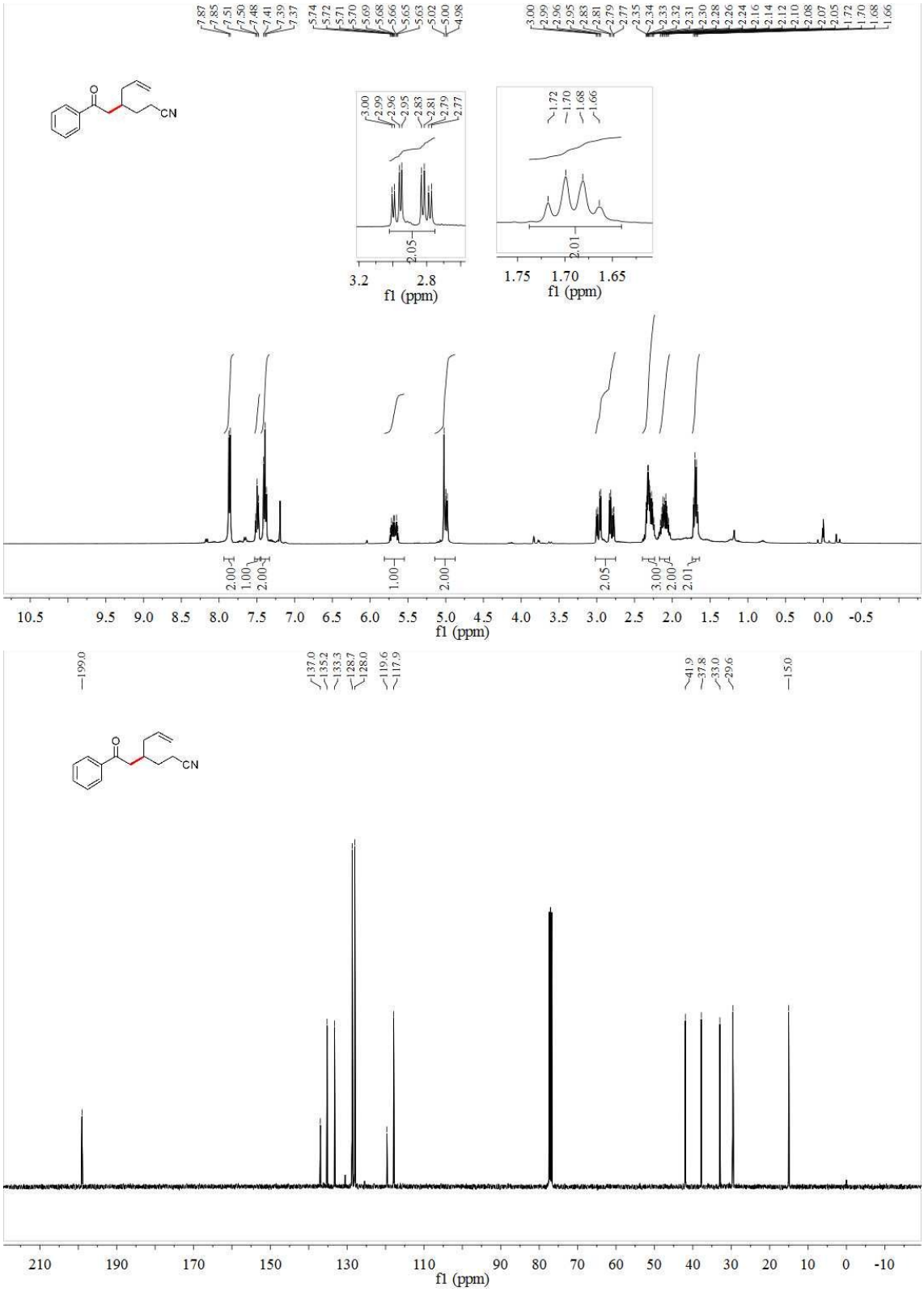


4-methyl-6-oxo-6-phenylhexanenitrile (16)

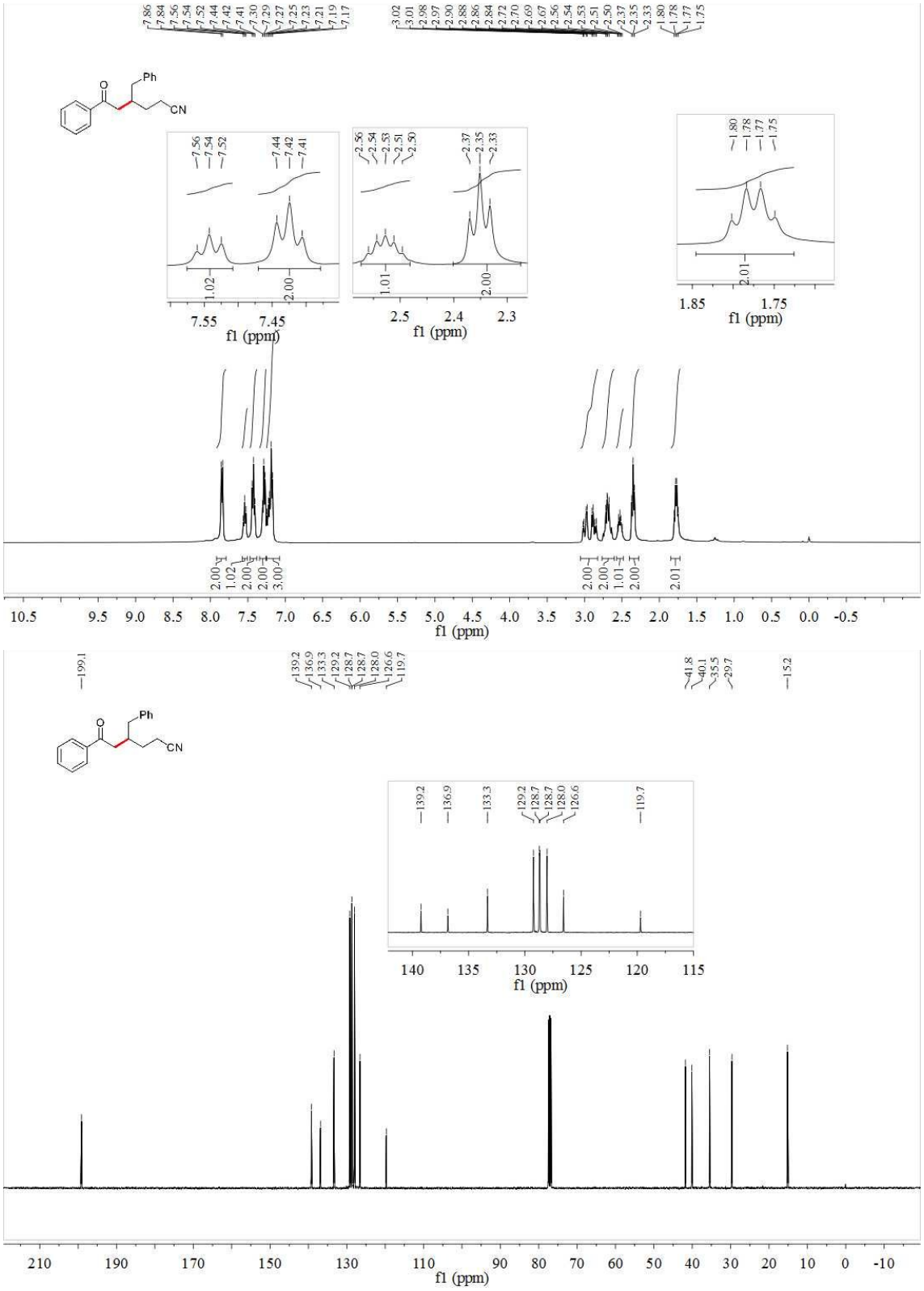




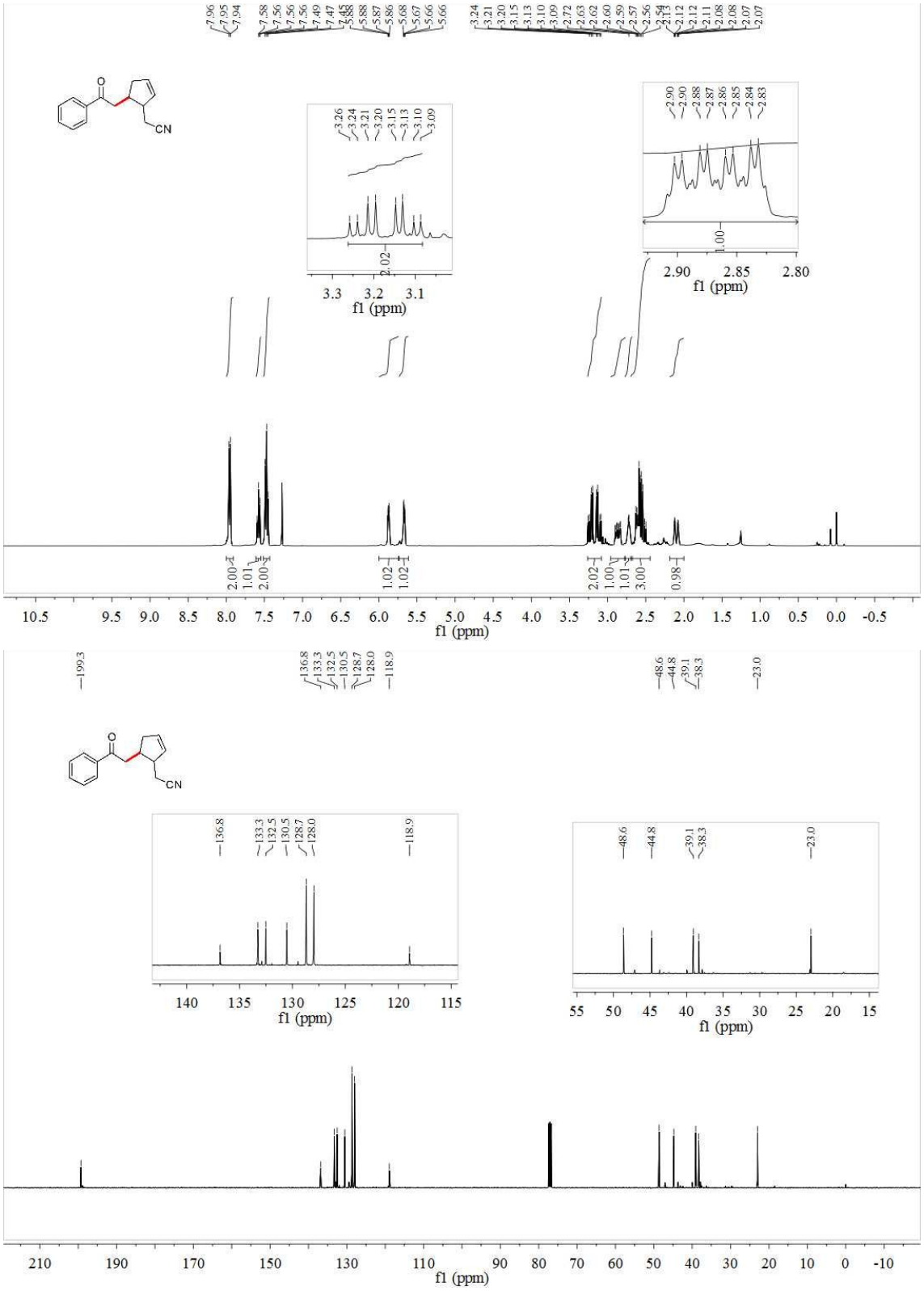
4-(2-oxo-2-phenylethyl)hept-6-enenitrile (17)



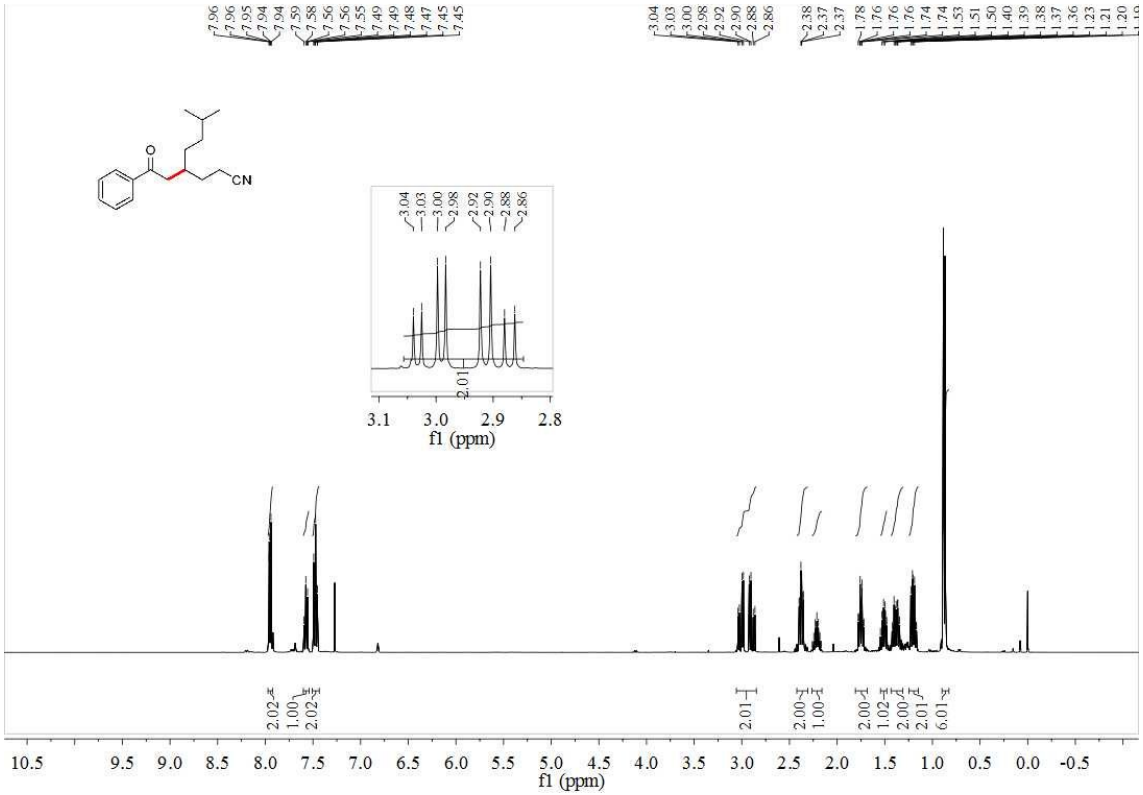
4-benzyl-6-oxo-6-phenylhexanenitrile (18)

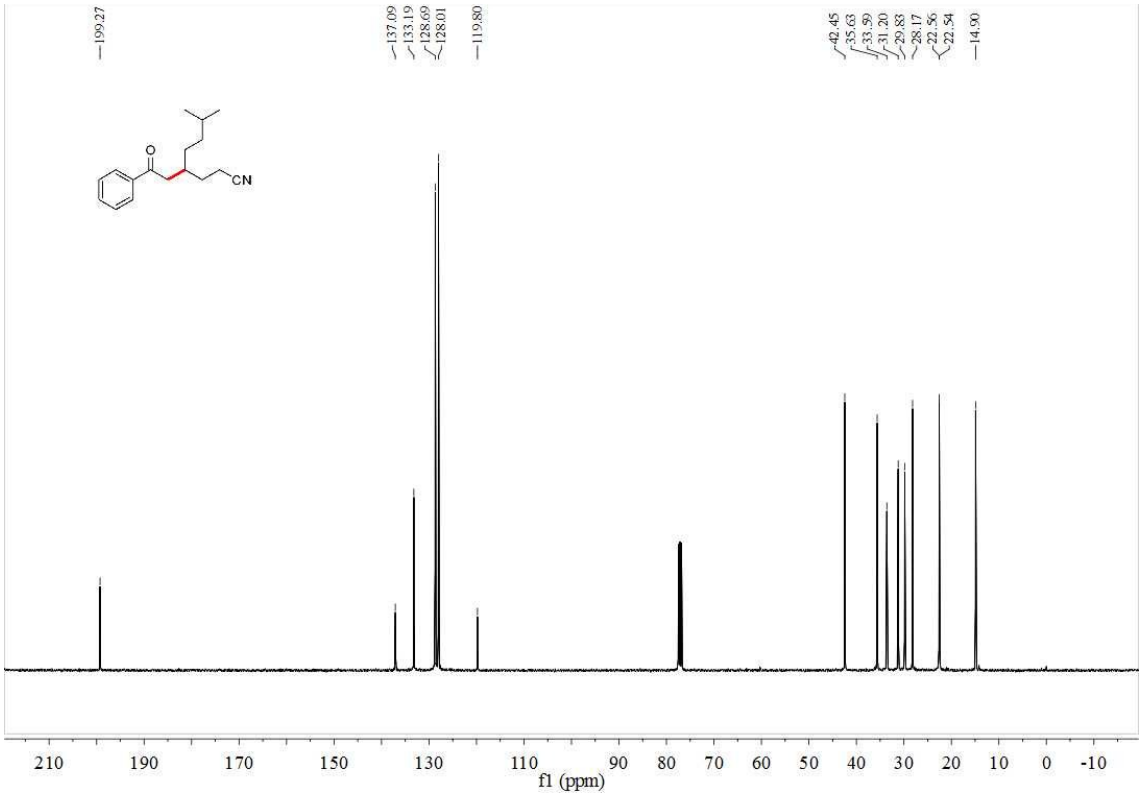


2-(5-(2-oxo-2-phenylethyl)cyclopent-2-en-1-yl)acetonitrile (19)

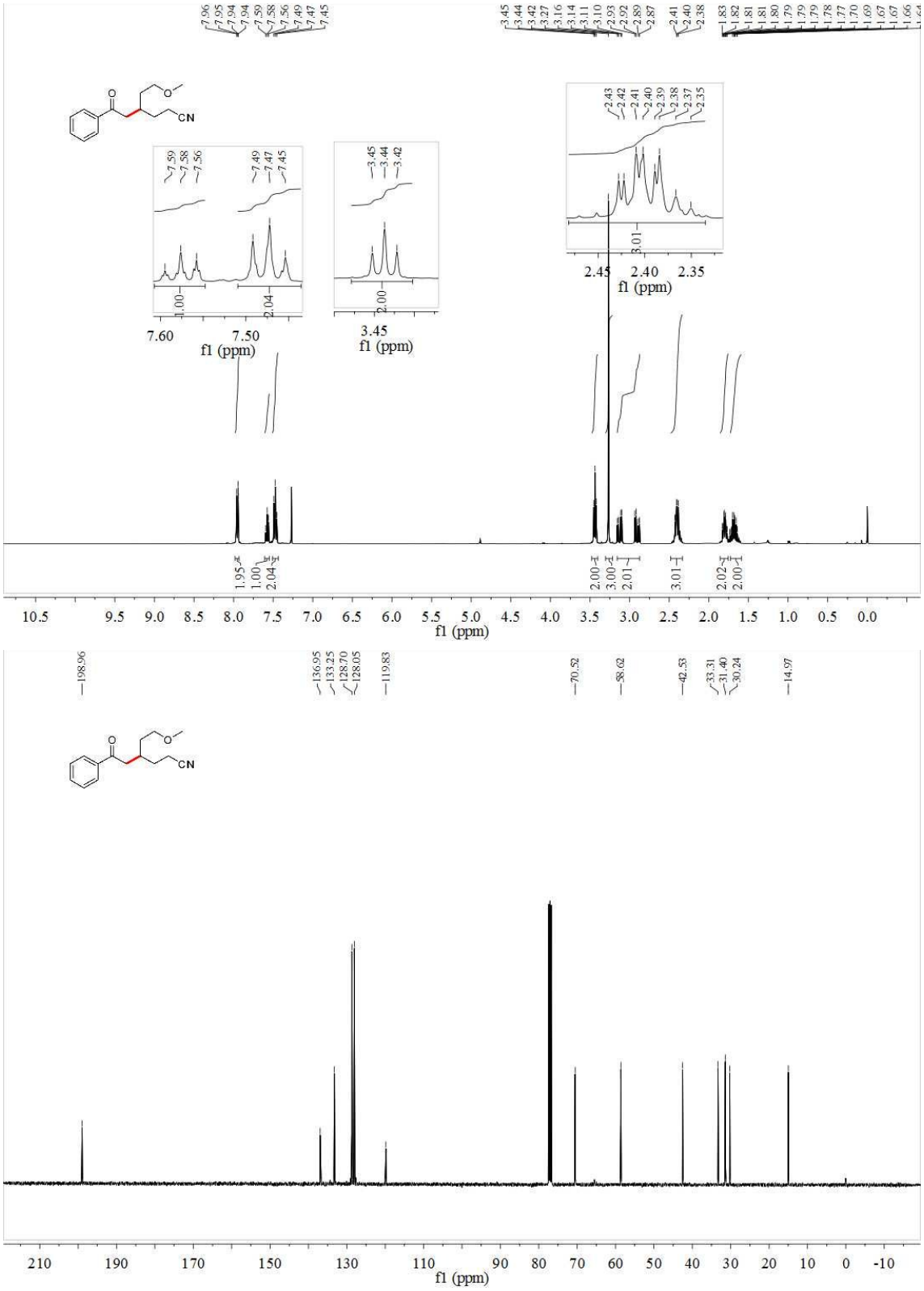


7-methyl-4-(2-oxo-2-phenylethyl)octanenitrile (20)

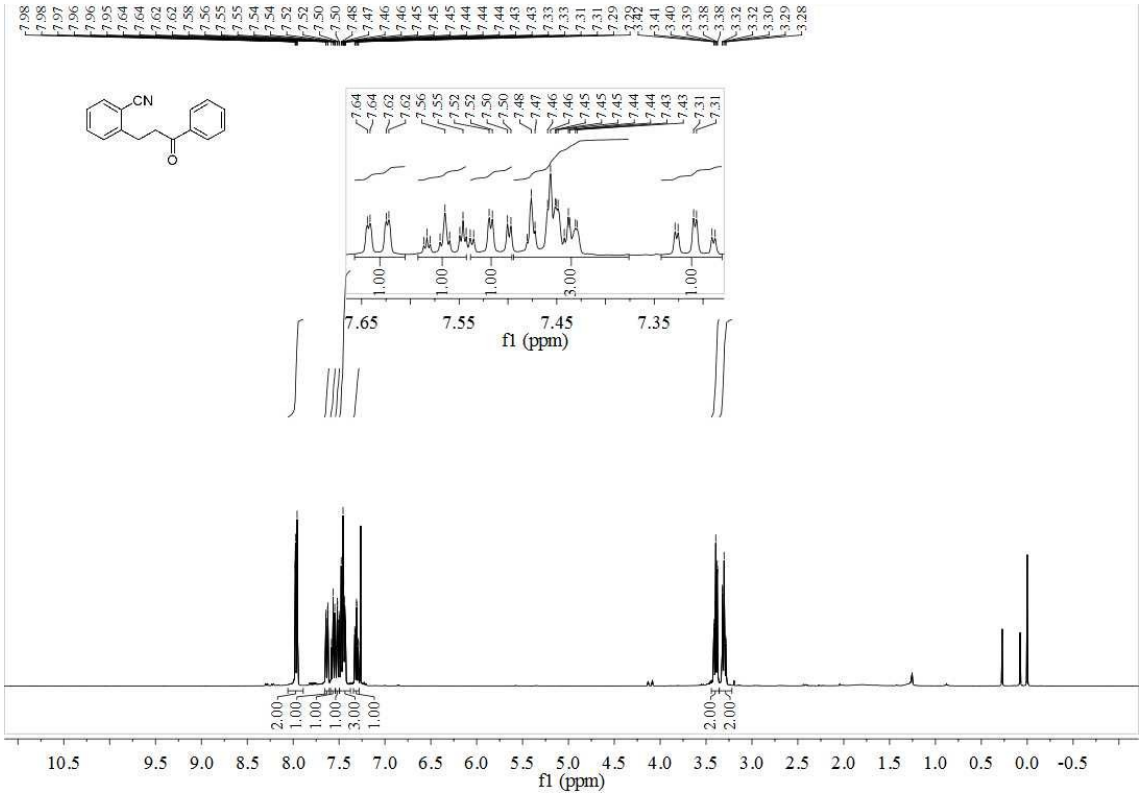


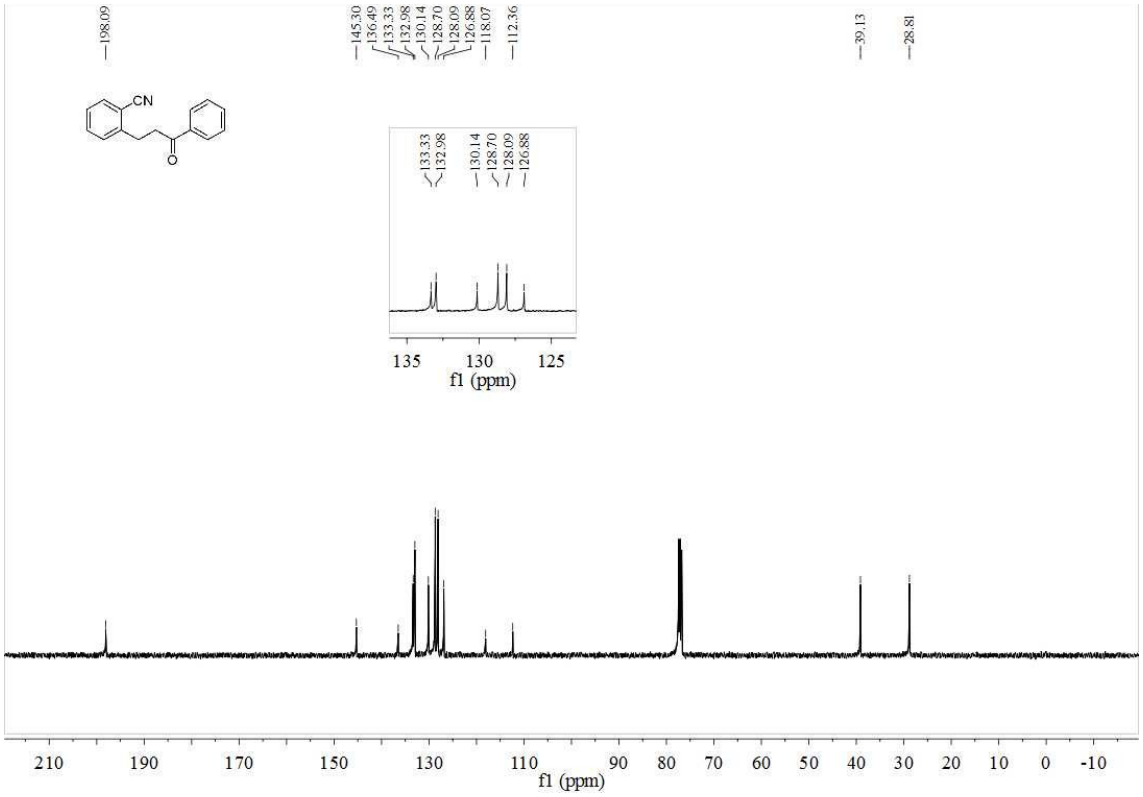


4-(2-methoxyethyl)-6-oxo-6-phenylhexanenitrile (21)

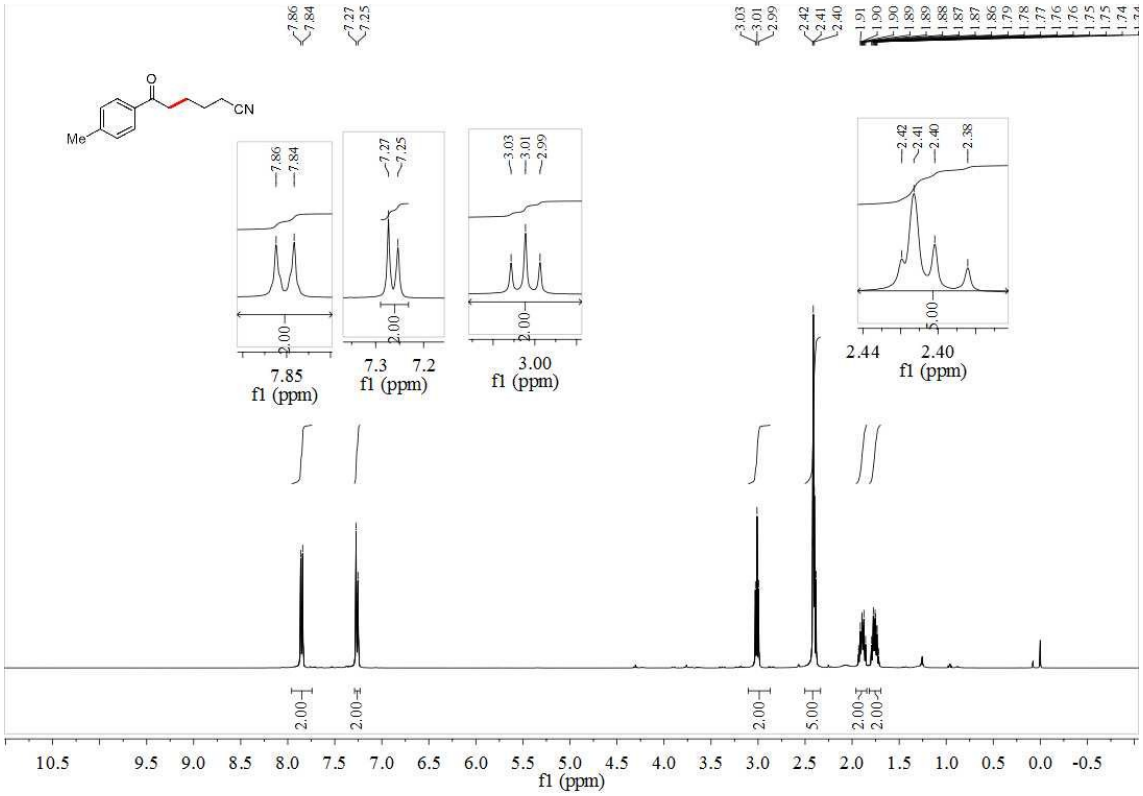


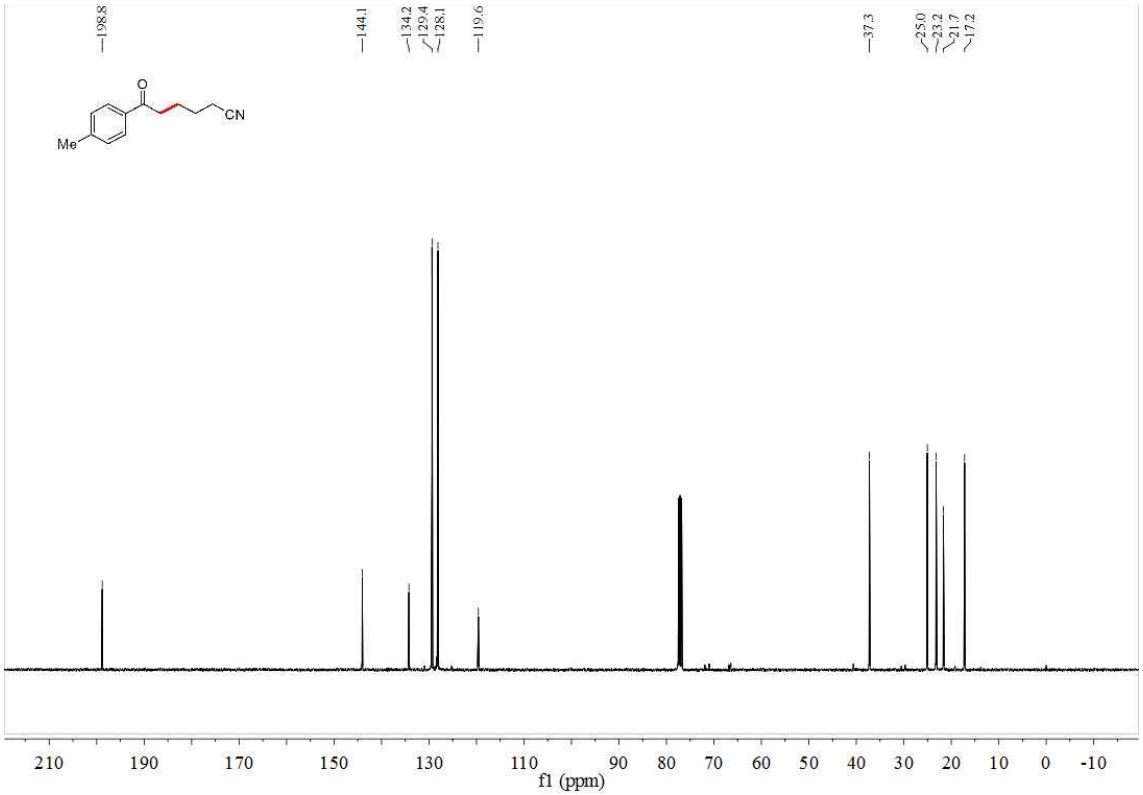
2-(3-oxo-3-phenylpropyl)benzonitrile (22)



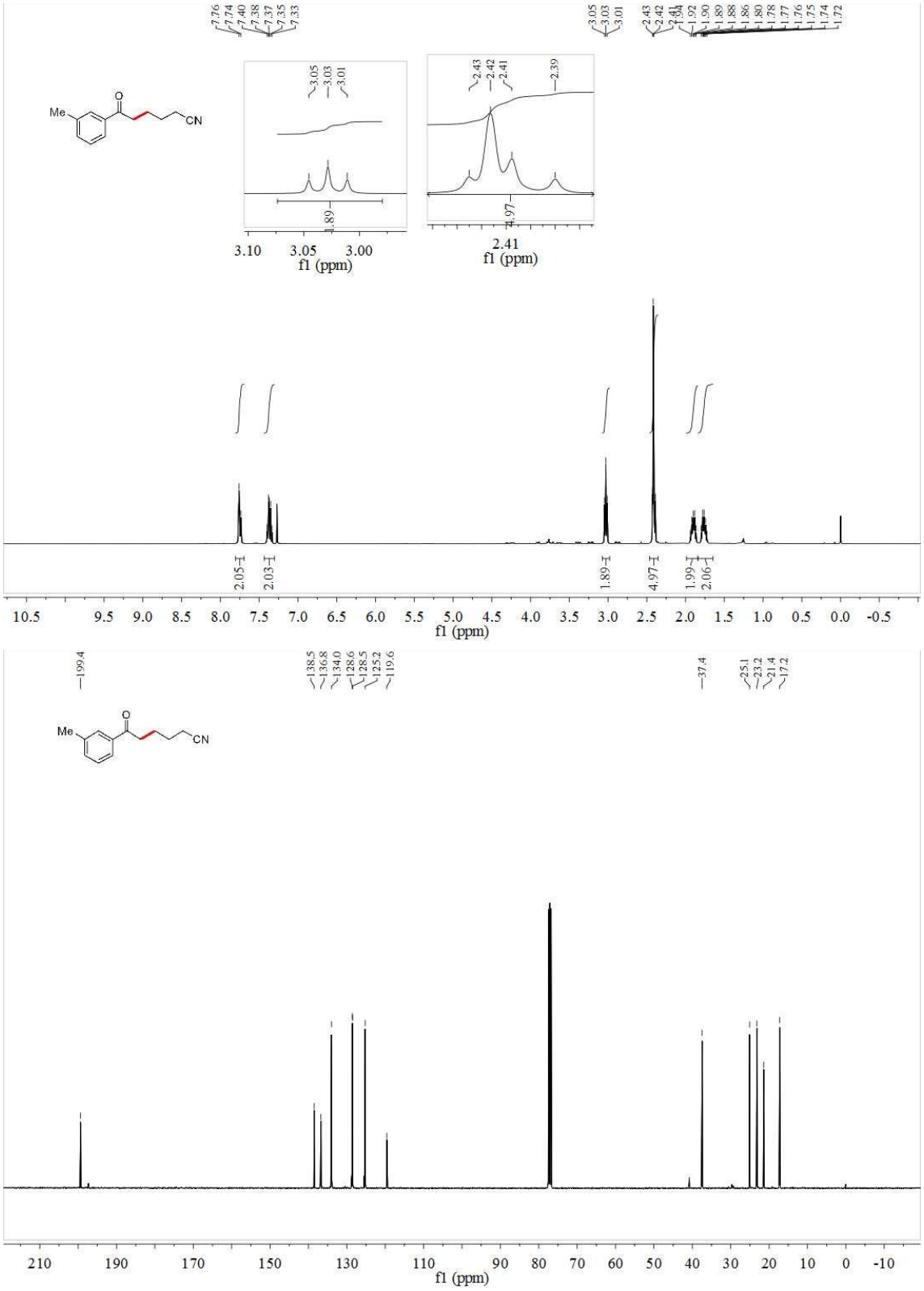


6-oxo-6-(p-tolyl)hexanenitrile (23)

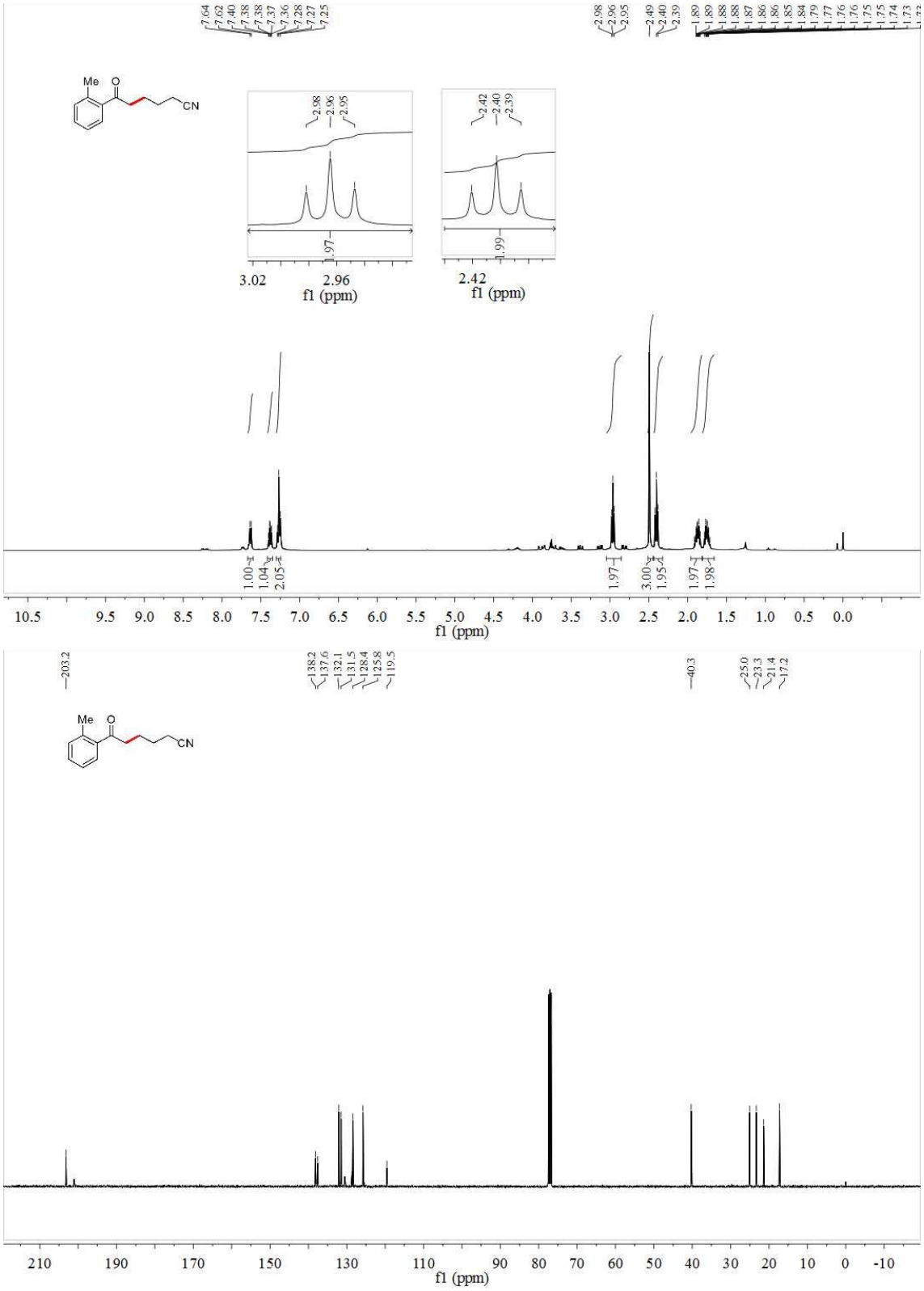




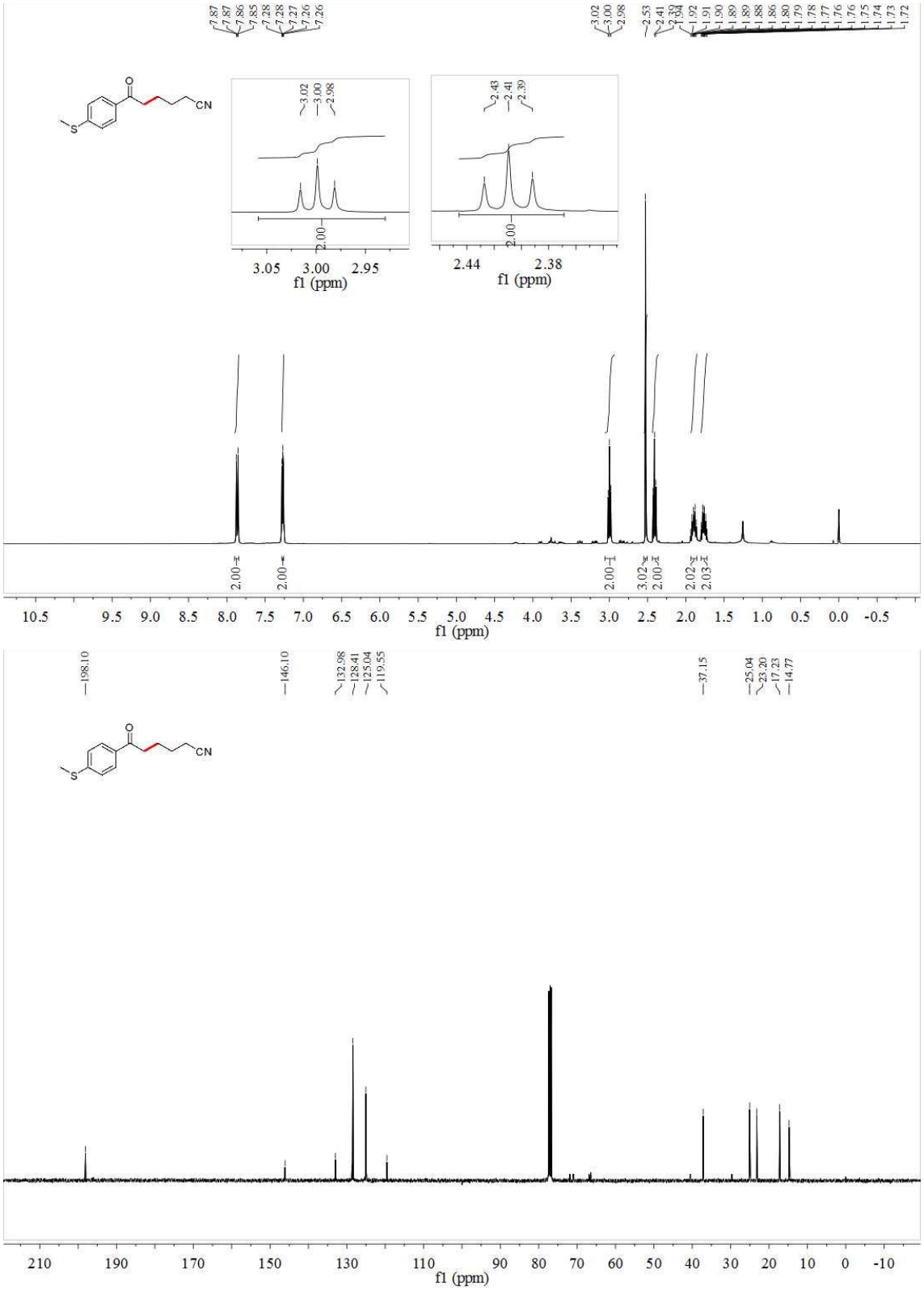
6-oxo-6-(m-tolyl)hexanenitrile (24)



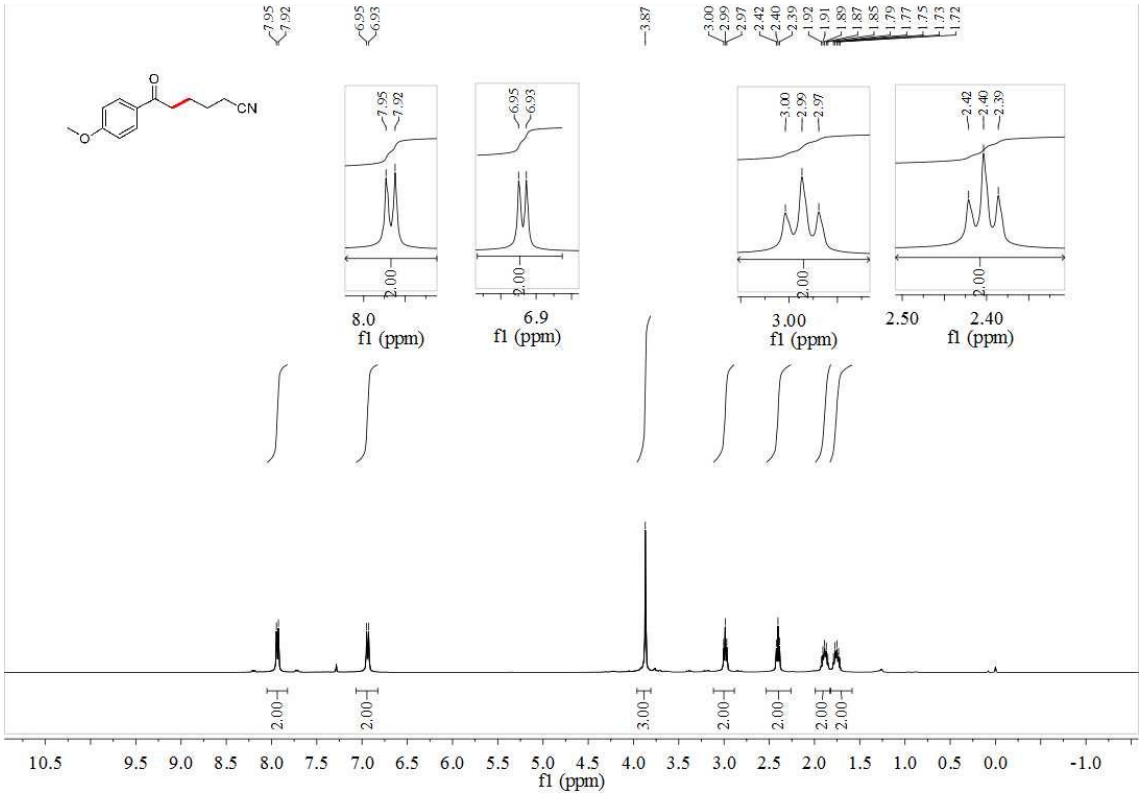
6-oxo-6-(o-tolyl)hexanenitrile (25)

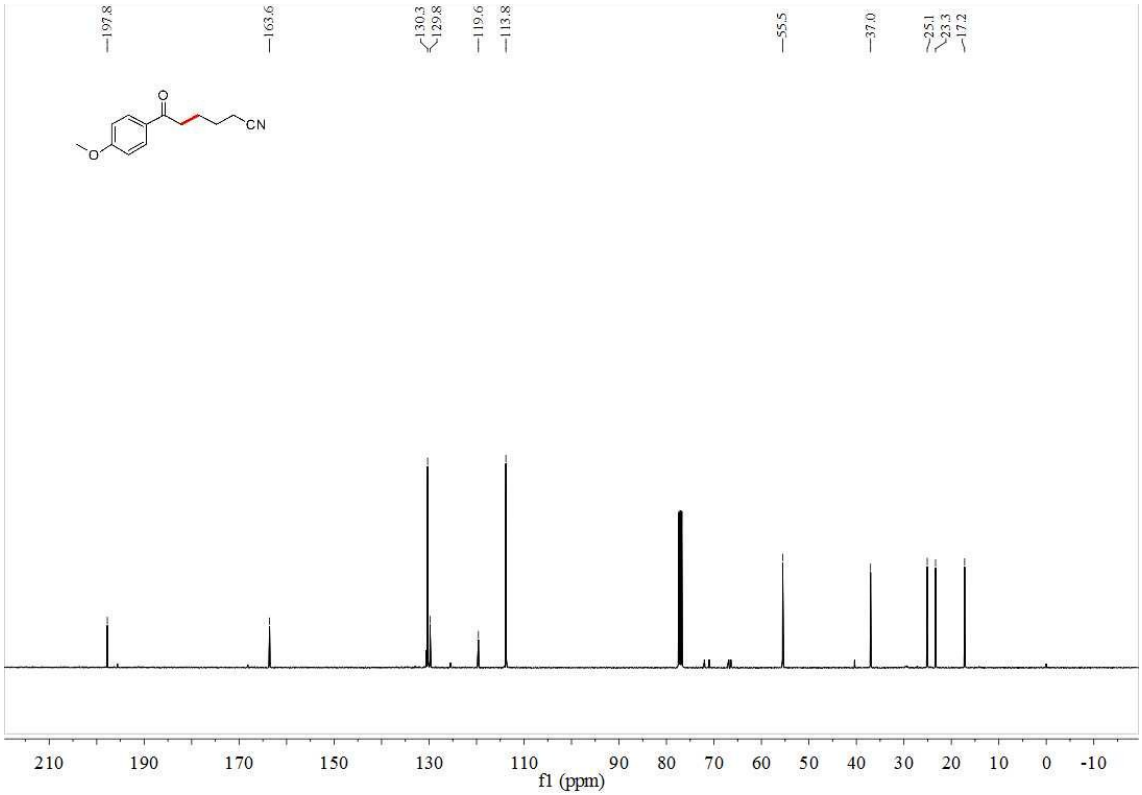


6-(4-(methylthio)phenyl)-6-oxohexanenitrile (26)

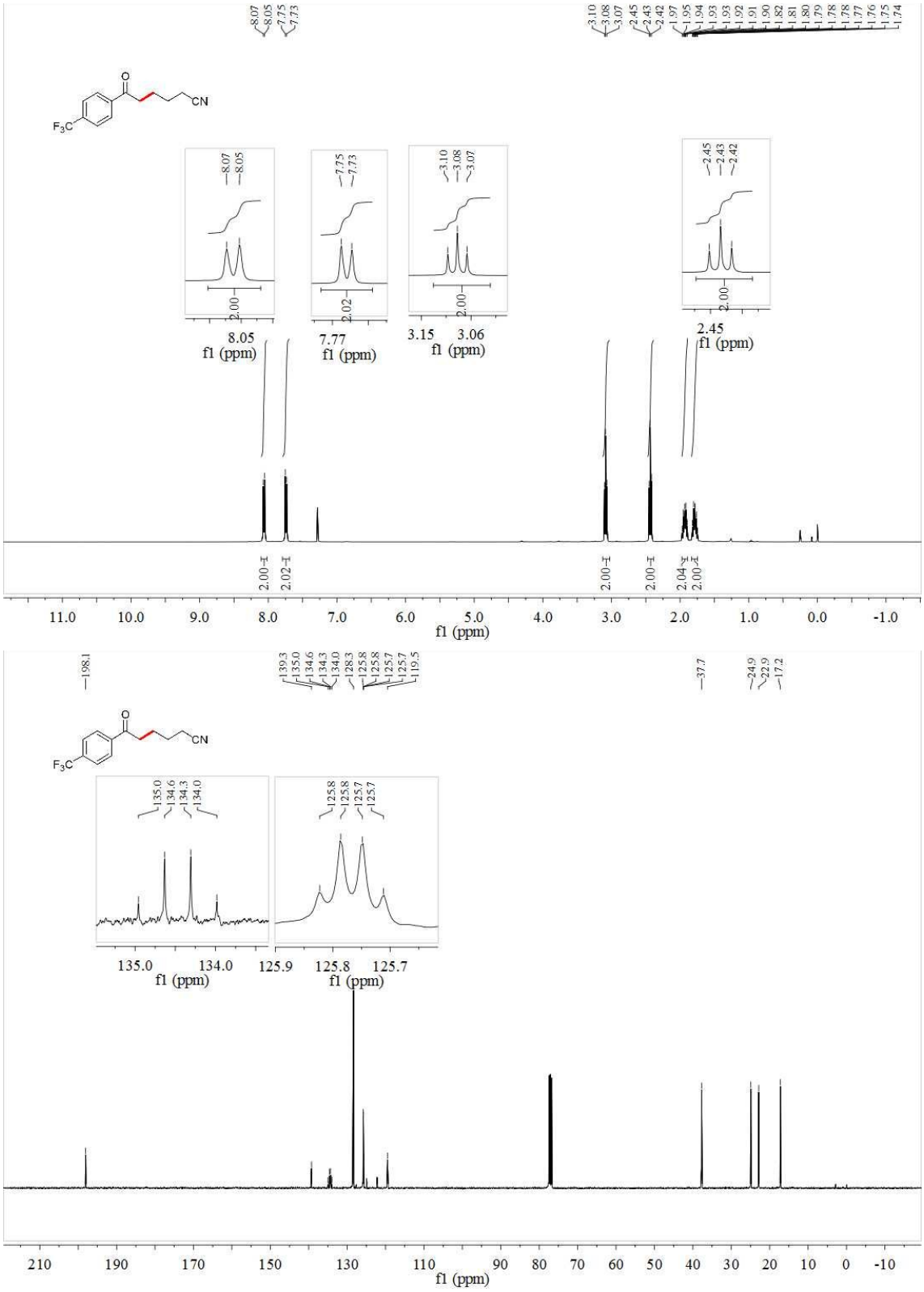


6-(4-methoxyphenyl)-6-oxohexanenitrile (27)

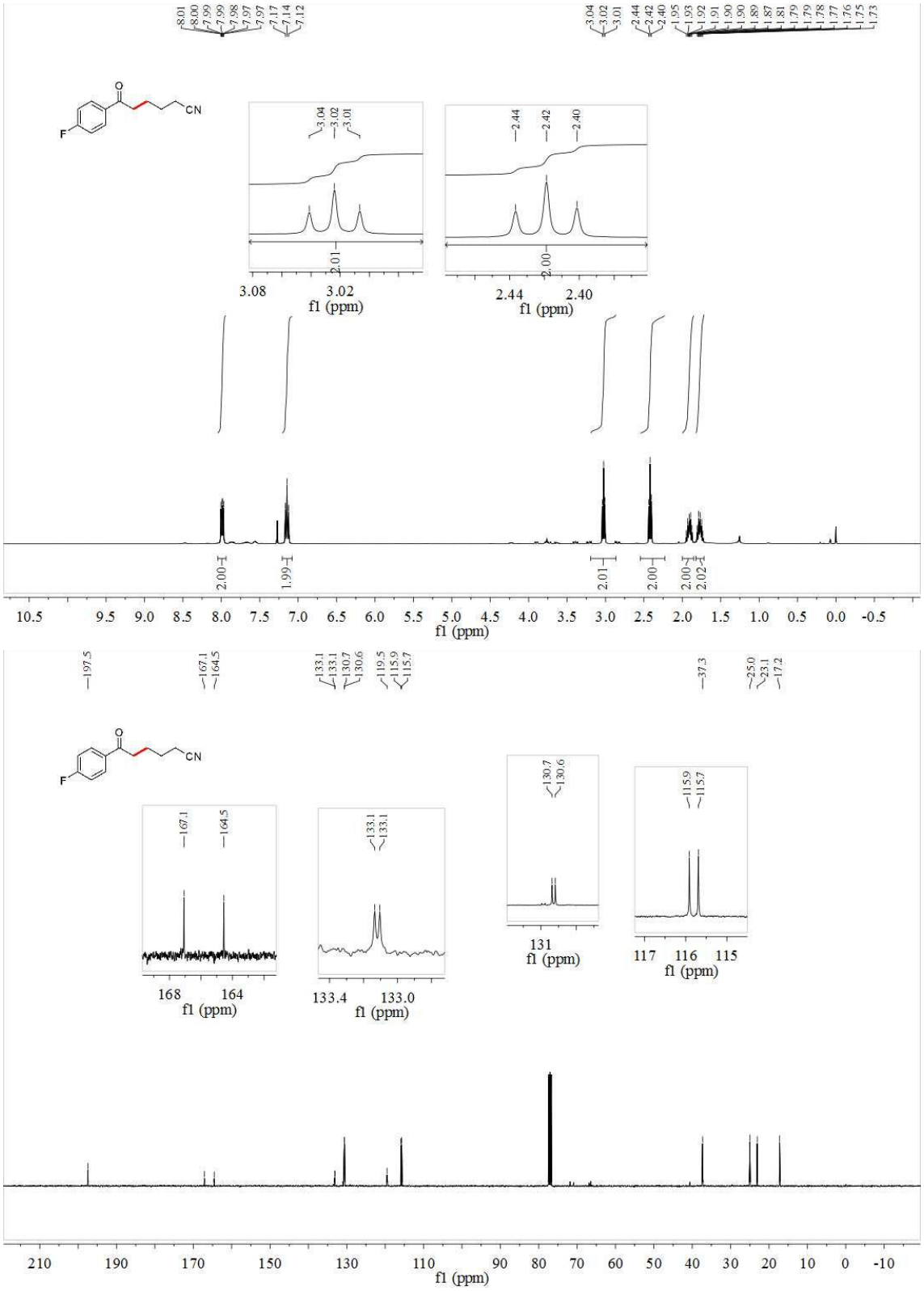




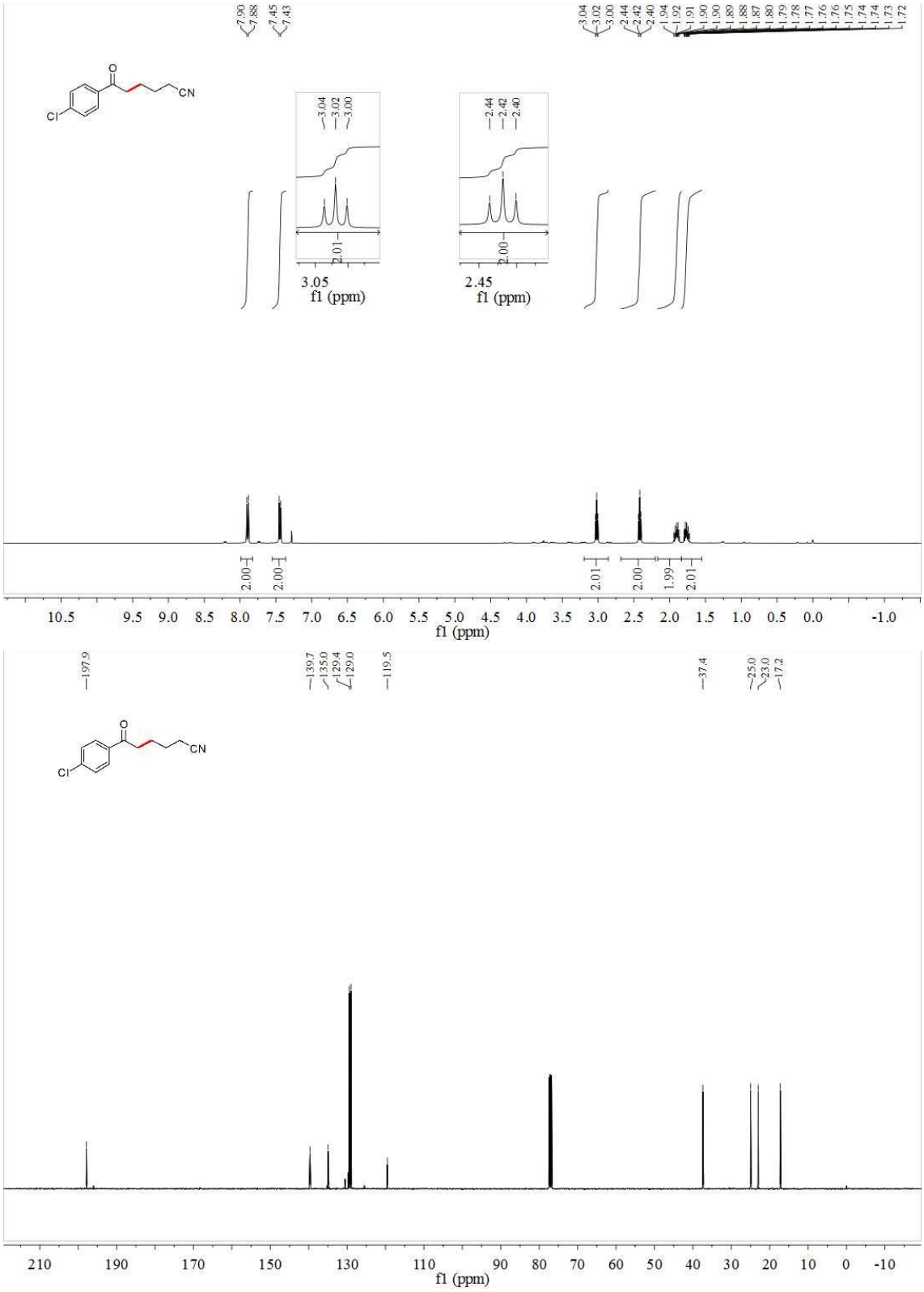
6-oxo-6-(4-(trifluoromethyl)phenyl)hexanenitrile (28)



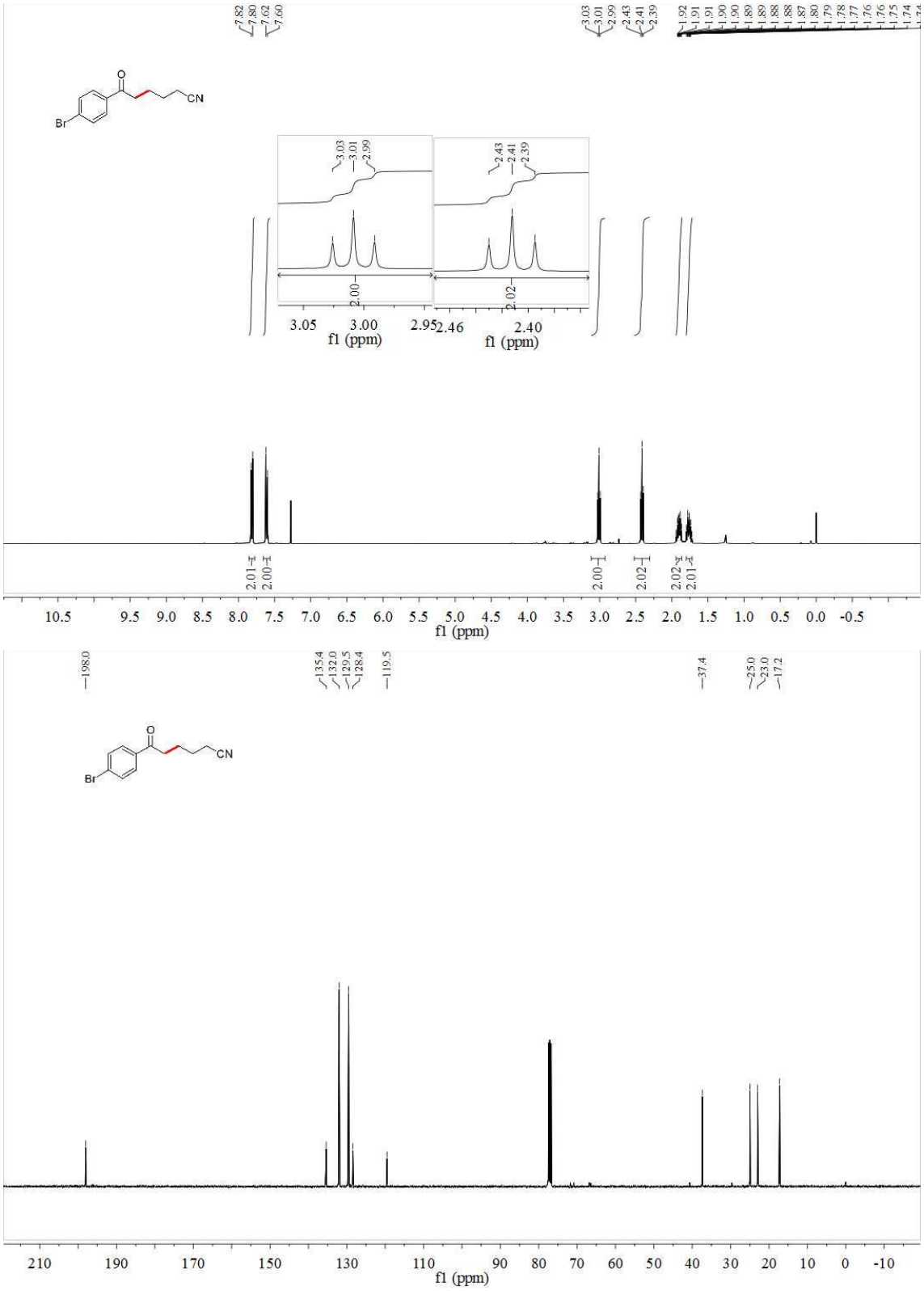
6-(4-fluorophenyl)-6-oxohexanenitrile (29)



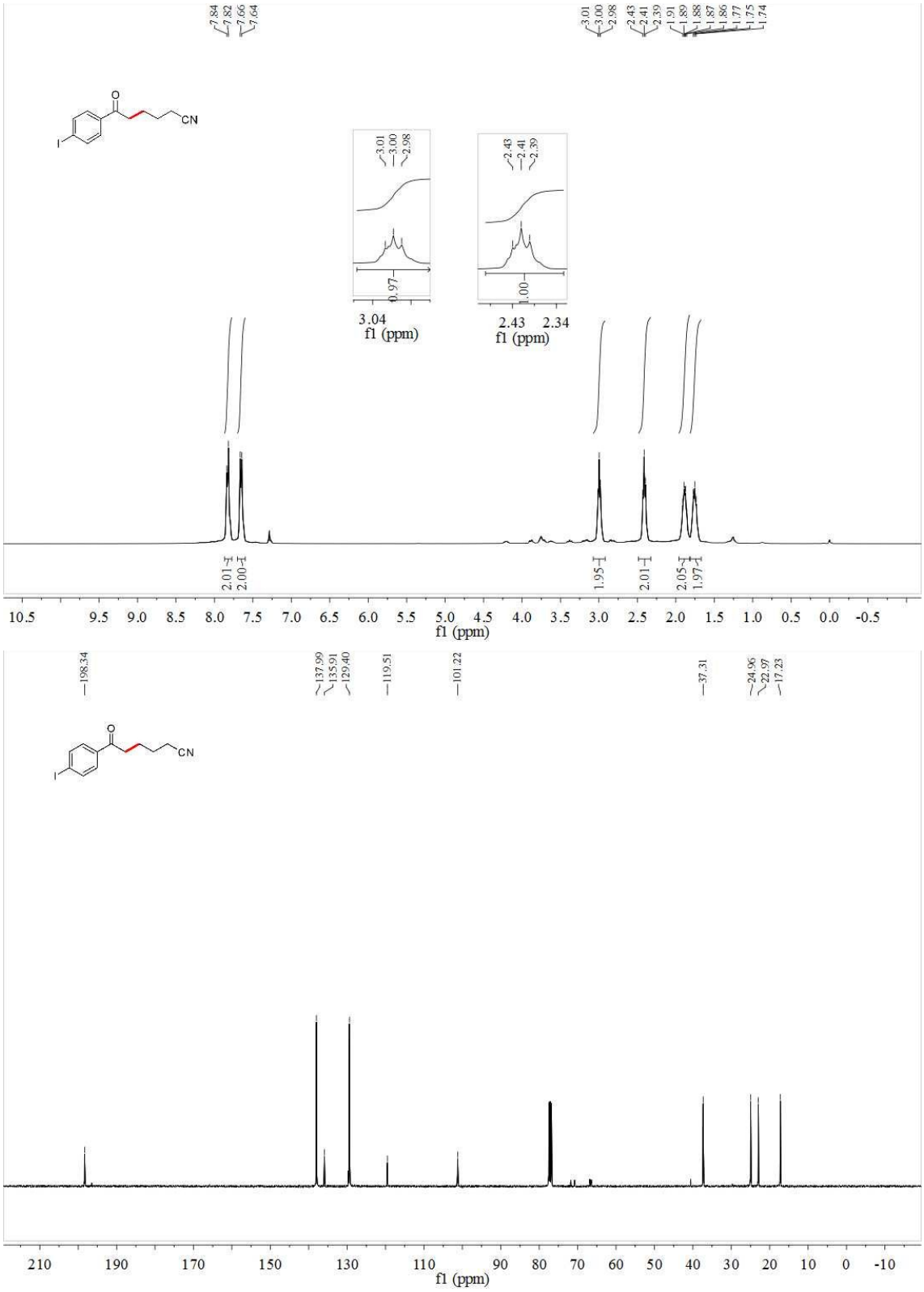
6-(4-chlorophenyl)-6-oxohexanenitrile (30)



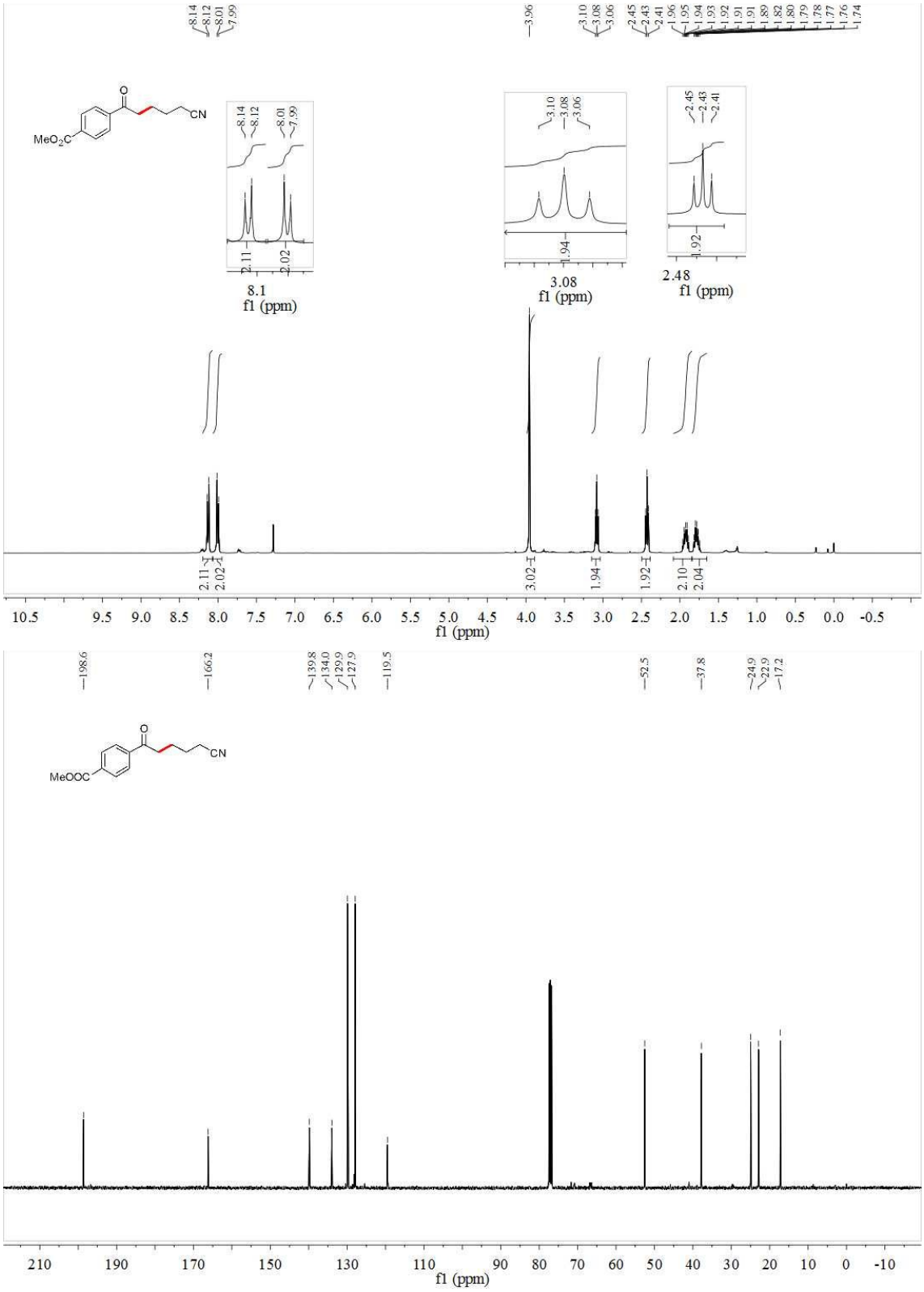
6-(4-bromophenyl)-6-oxohexanenitrile (31)



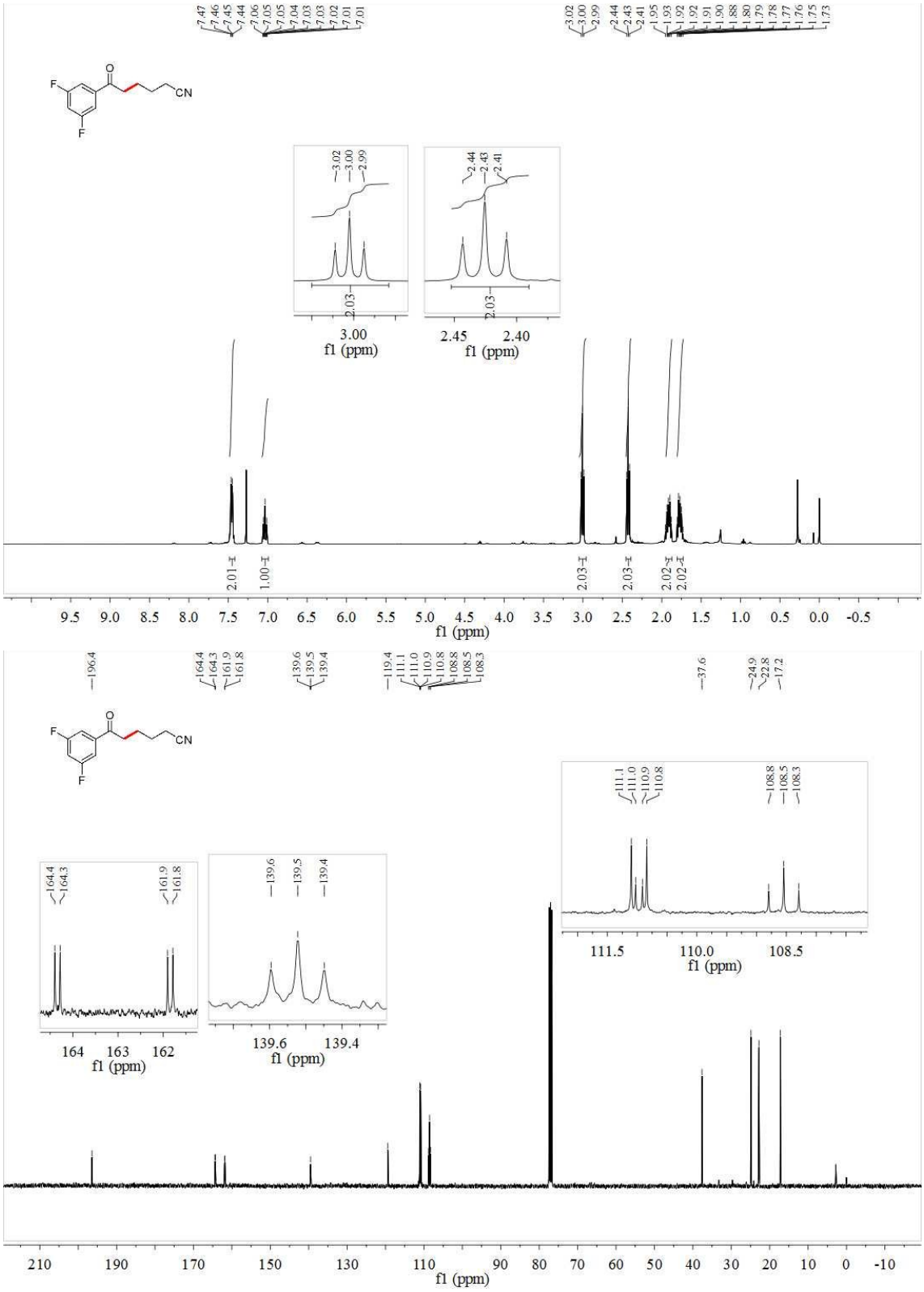
6-(4-iodophenyl)-6-oxohexanenitrile (32)



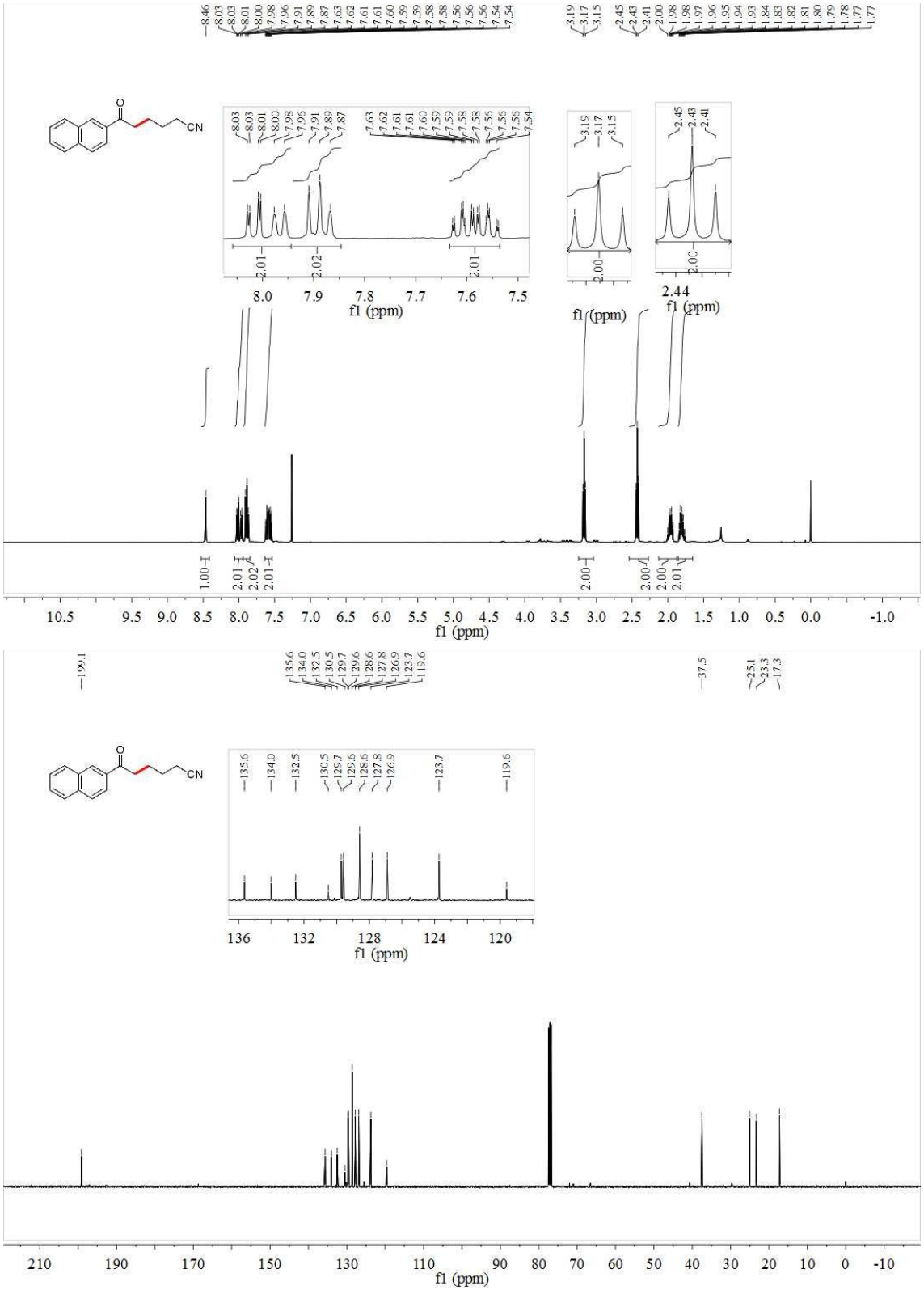
Methyl 4-(5-cyanopentanoyl)benzoate (33)



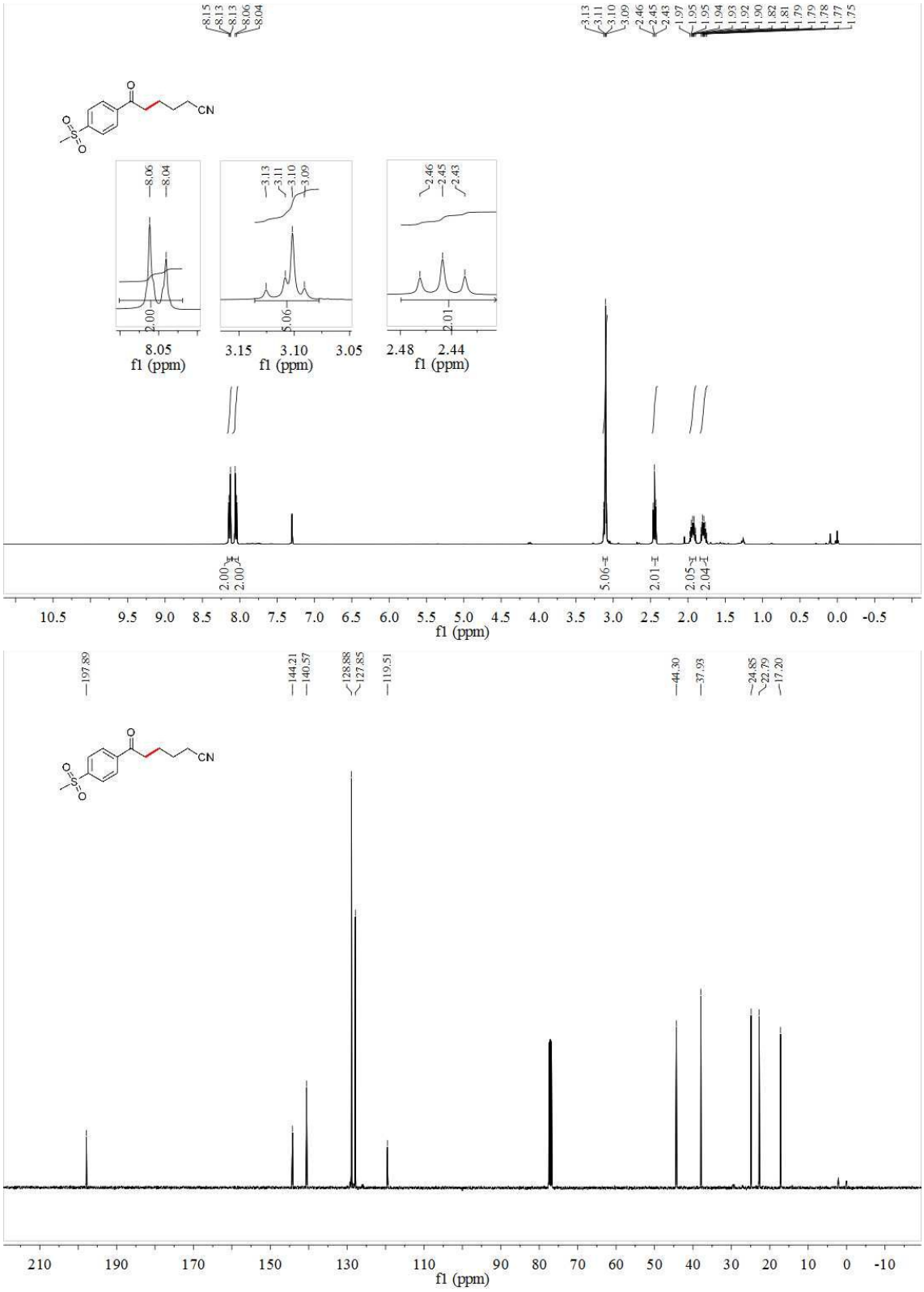
6-(3,5-difluorophenyl)-6-oxohexanenitrile (34)



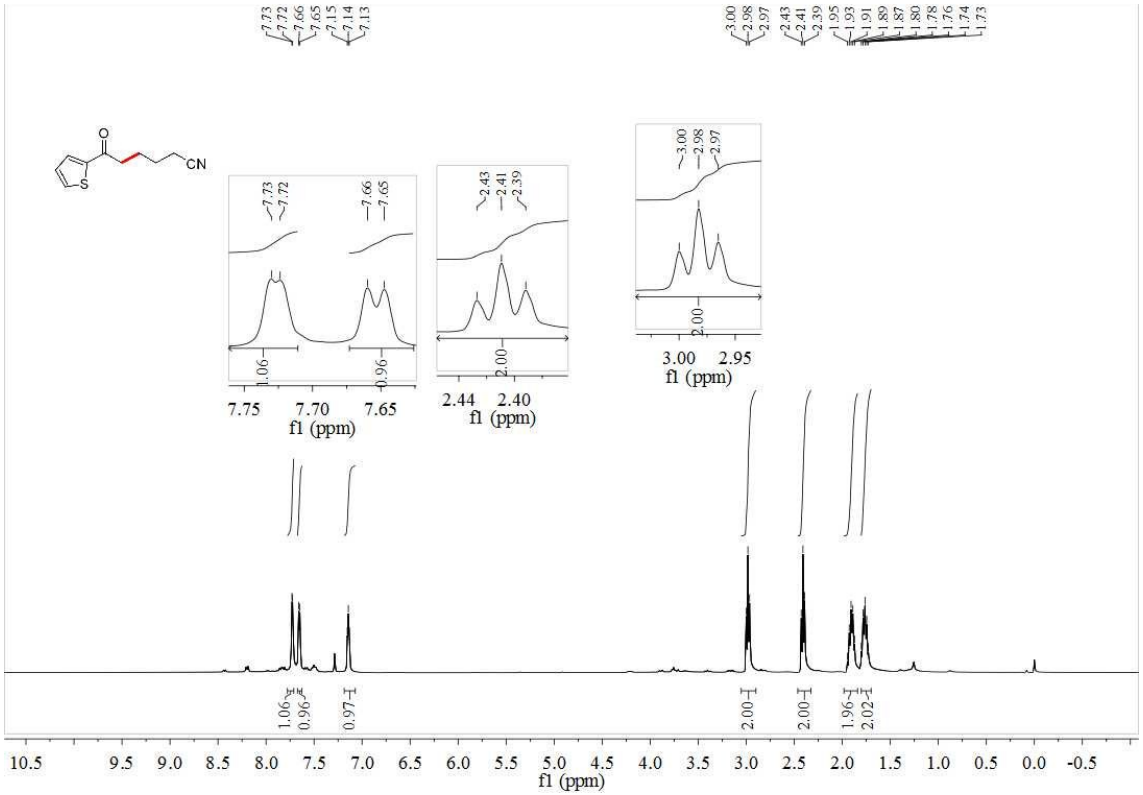
6-(naphthalen-2-yl)-6-oxohexanenitrile (35)

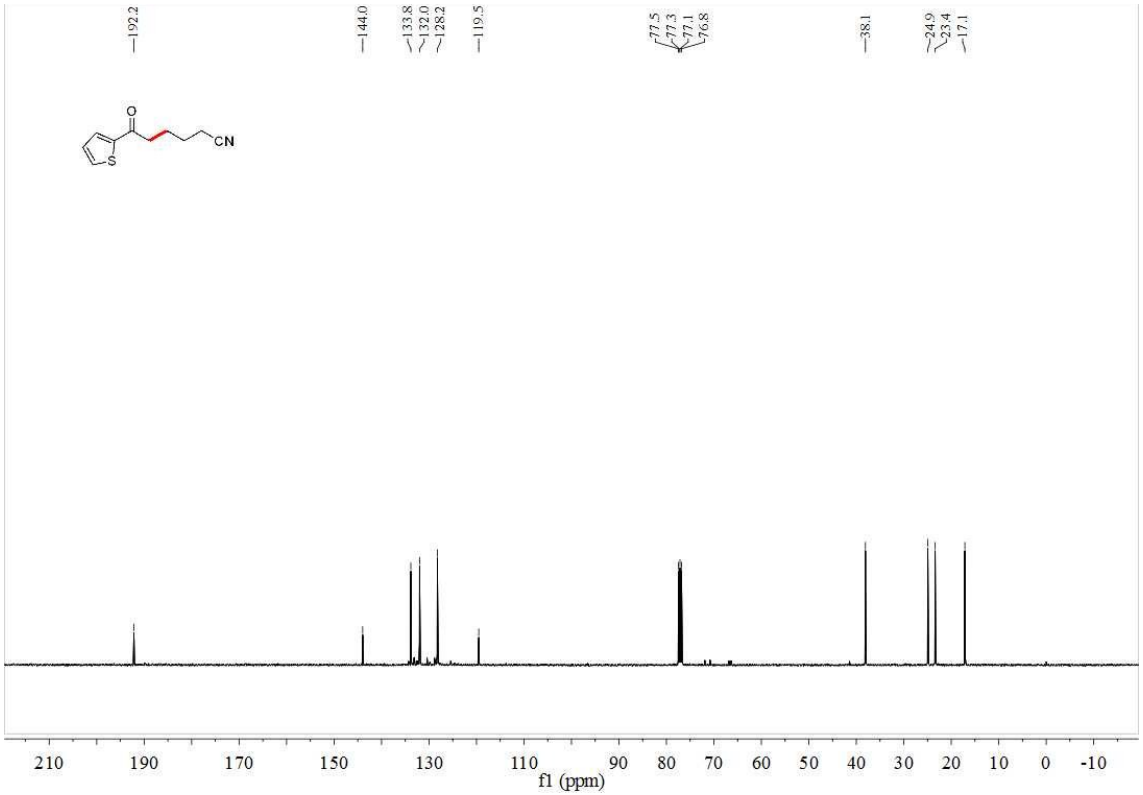


6-(4-(methylsulfonyl)phenyl)-6-oxohexanenitrile (36)

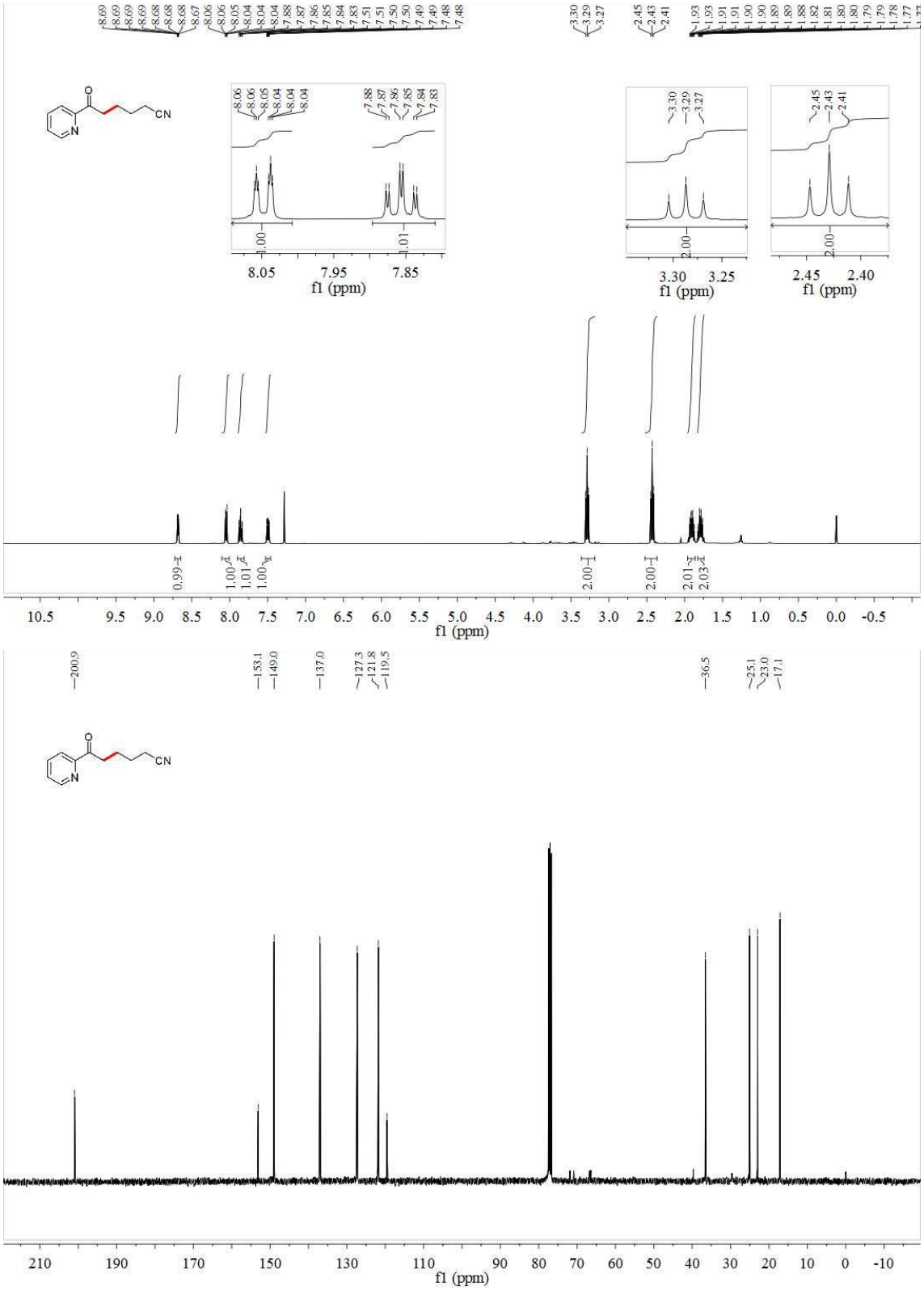


6-oxo-6-(thiophen-2-yl)hexanenitrile (37)

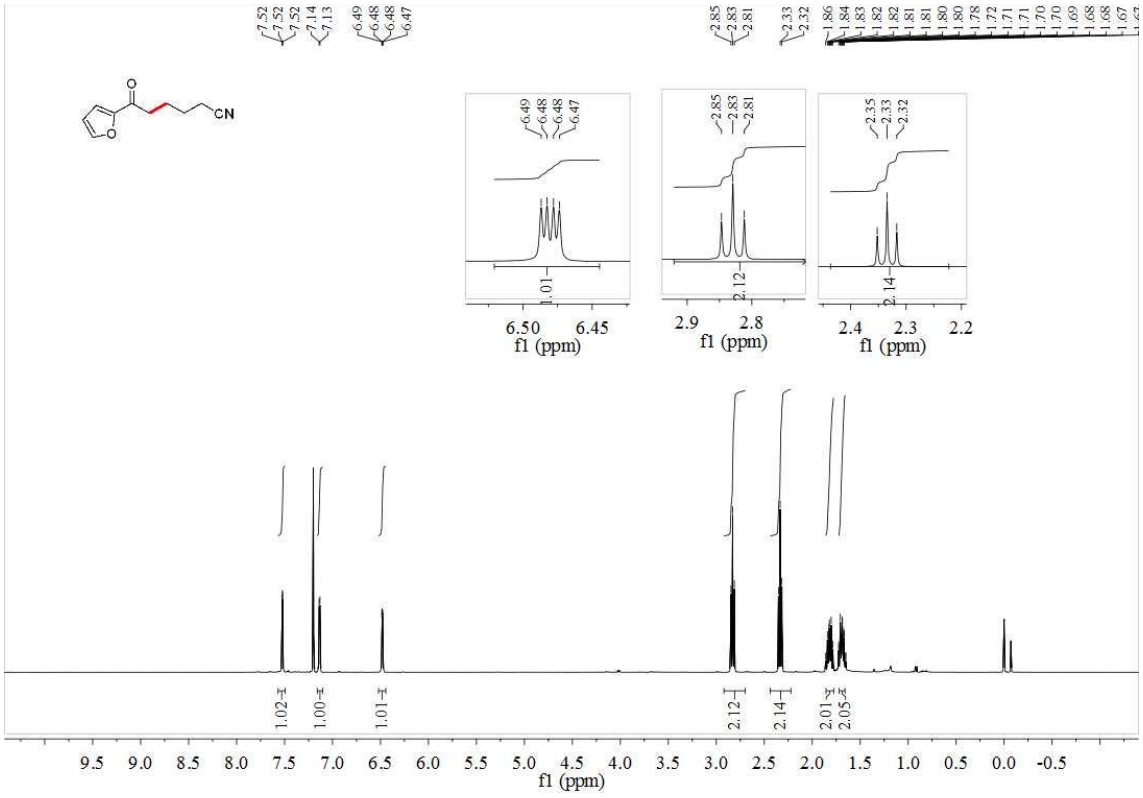




6-oxo-6-(pyridin-2-yl)hexanenitrile (38)



6-(furan-2-yl)-6-oxohexanenitrile (39)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1.70
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1.69
1.68
1.68
1.67
O
CN
1.01
2.12
2.14
6.50
6.45
f1 (ppm)
2.9
2.8
f1 (ppm)
2.4
2.3
2.2
f1 (ppm)
1.02
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1.01
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2.14
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2.05
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9.0
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8.0
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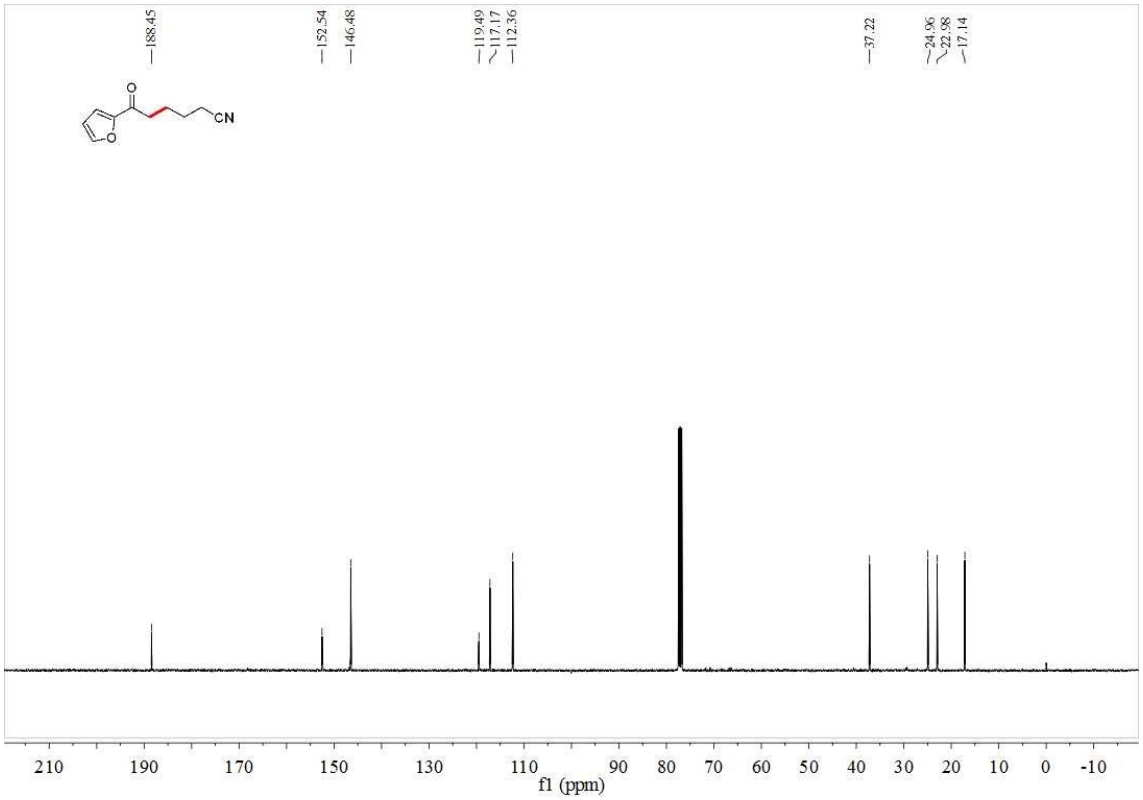
-0.5
f1 (ppm)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O
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90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)