Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Selective Cross-Coupling of α,β-Unsaturated Nitriles with Aldehydes or Alcohols by Hydrogen Transfer Catalysis towards β-Ketonitriles and Glutaronitriles

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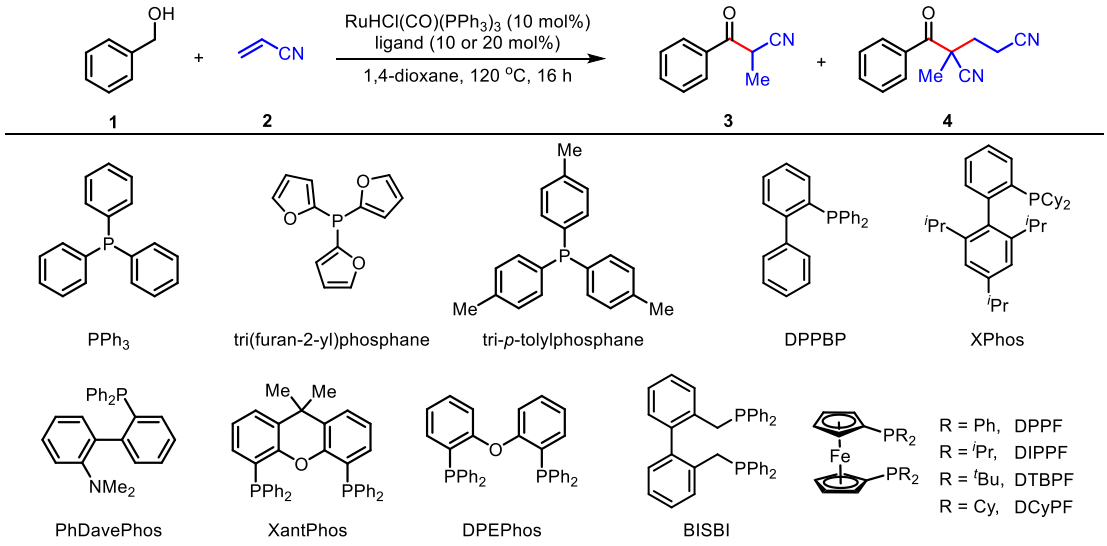
Table of Contents

I General Information

Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). The High Resolution MS analyses were performed on Thermo Fisher Scientific LTQ FT Ultra with DART Positive Mode or Agilent 6530 Accurate-Mass Q-TOF LC/MS with ESI mode. GC-MS spectra were recorded on a GCMS-QP2010 SE with helium gas as the carrier gas. NMR spectra were recorded on a 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR, using tetramethylsilane as an internal reference and $CDCl_3$ as solvent. Chemical shift values for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual proton of $CDCl_3$ (δ 7.26), benzene-d_6 (δ 7.16) and DMSO-d_6 (δ 2.50). Multiplicity is indicated by one or more of the following: s (singlet); d (doublet); t (triplet); q (quartet); ddd (doublet of doublet of doublets); m (multiplet); br (broad). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 MHz. Chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of $CDCl_3$ (δ 77.16), benzene-d_6 (δ 128.06), and DMSO-d_6 (δ 39.52). The acrylonitrile substrate of 3-phenylacrylonitrile, 3-(4-methoxyphenyl)acrylonitrile, 3-(4-fluorophenyl)acrylonitrile, 3-cyano-cinnamonitrile, 3-nitro-cinnamonitrile, and 2-(2-chlorobenzyl)-3-oxo-3-phenylpropanenitrile were prepared according to known procedures.[1] The other materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Adamas, Bidepharm or other commercial suppliers and used as received unless otherwise noted.

II Optimization of the Reaction Conditions for Cross-Coupling of Alcohol and Acrylonitrile.

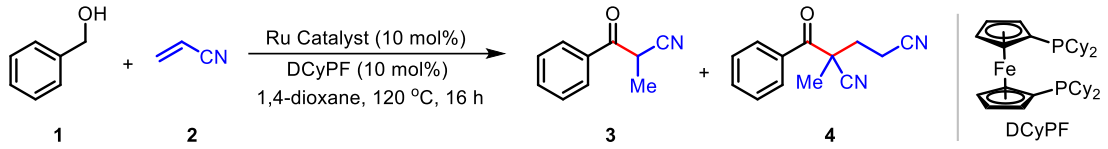
Table S1. The Effect of the Ligands[a]



Entry	Ligand (10 or 20 mol %)	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	-	18	11
2	PPh_3 (20)	26	18
3	tri(furan-2-yl)phosphane (20)	22	14
4	tri-*p*-tolylphosphane (20)	20	11
5	DPPBP (20)	16	11
6	XPhos (20)	16	8
7	PhDavePhos (20)	30	11
8	XantPhos (10)	22	17
9	DPEPhos (10)	32	28
10	BISBI (10)	48	21
11	DPPF (10)	14	6
12	DIPPF(10)	26	9
13	DTBPF (10)	0	0
14	**DCyPF (10)**	**50**	**35**

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.5 mmol), $RuHCl(CO)(PPh_3)_3$ (10 mol%), ligand (10 or 20 mol%), 1,4-dioxane (2 mL), 120 °C, 16 h, if otherwise noted. [b]The yield is determined by crude ^1H NMR analysis with 1,1,2,2-tetrachloroethane as internal standard.

Table S2. The Effect of the Ru Catalyst[a]

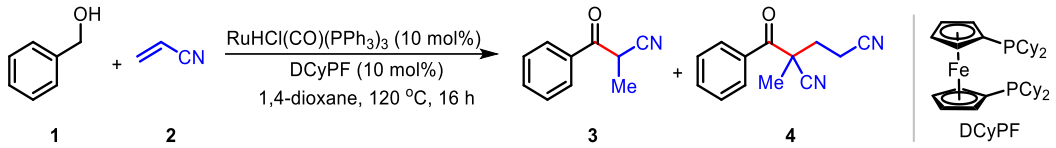


1 2 3 4

Entry	Ru catalyst	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	**$RuHCl(CO)(PPh_3)_3$**	**50**	**35**
2	$RuH_2(CO)(PPh_3)_3$	34	30
3	$RuH_2(PPh_3)_4$	0	0
4[c]	$Ru_3(CO)_{12}$	0	0
5[d]	$[RuH(Cp)(CO)_2]_2$	0	0
6	-	0	0

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.5 mmol), Ru catalyst (10 mol%), DCyPF (10 mol%), 1,4-dioxane (2 mL), 120 °C, 16 h, if otherwise noted. [b]The yield is determined by crude ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as internal standard. [c] with $Ru_3(CO)_{12}$ (3.3 mol%), [d] with $[RuH(Cp)(CO)_2]_2$ (5 mol%)

Table S3. The Effect of the Ratio of Substrates[a]

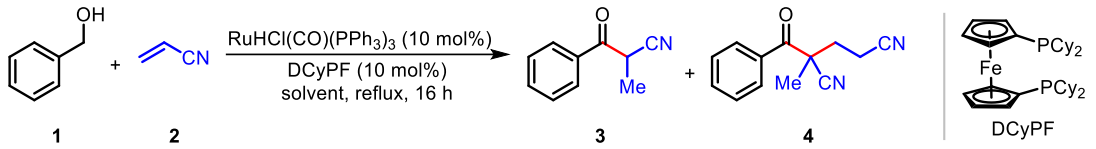


1 2 3 4

Entry	**2** (x equiv.)	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	1.0	38	0
2	1.5	60	3
3	**2.0**	**74**	**9**
4	2.5	50	35

[a]Reaction conditions: **1** (0.2 mmol), **2** (x equiv), $RuHCl(CO)(PPh_3)_3$ (10 mol%), DCyPF (10 mol%), 1,4-dioxane (2 mL), 120 °C, 16 h, if otherwise noted. [b]The yield is determined by crude ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as internal standard.

Table S4. The Effect of Solvent and Reaction Temperature[a]

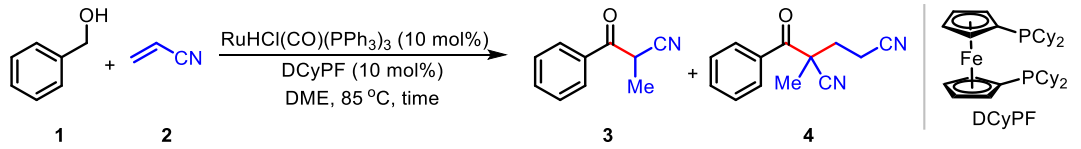


1 2 3 4

Entry	Solvent	Temperature (°C)	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	1,4-dioxane	120	74	9
2	**DME**	**85**	**72**	**27**
3	CH_3OH	85	0	0
4	CH_3O^tBu	85	42	38
5	DCE	85	trace	trace
6	benzene	85	46	38
7	CH_3CN	85	trace	trace
8	THF	85	50	30
9	toluene	120	58	24
10	NMP	120	trace	trace
11	DMF	120	trace	trace
12	DME	65	64	12

[a]Reaction conditions: **1** (0.2 mmol), **2** (2.0 equiv), $RuHCl(CO)(PPh_3)_3$ (10 mol%), DCyPF (10 mol%), solvent (2 mL), Temperature (°C), 16 h, if otherwise noted. [b]The yield is determined by crude ^1H NMR analysis with 1,1,2,2-tetrachloroethane as internal standard. DME: 1,2-dimethoxyethane.

Table S5. The Effect of Reaction Time[a]



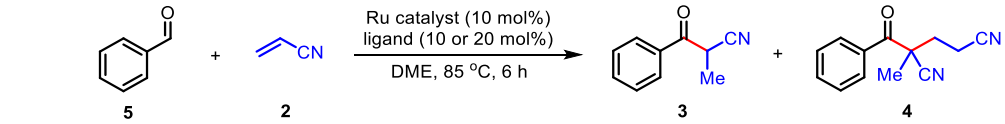
1 2 3 4

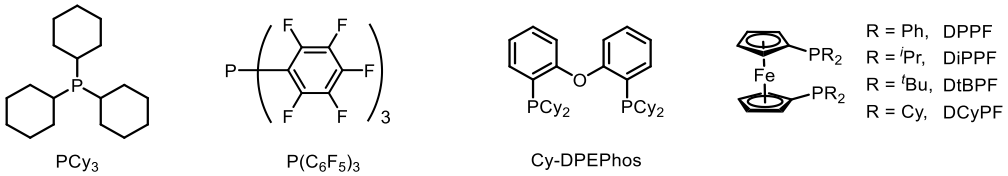
Entry	Time (h)	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	1	72	8
2	4	**82 (67)**	**4**
3	6	82	10
4	16	72	27
5[c]	**12**	**2**	**65 (62)**

[a]Reaction conditions: **1** (0.2 mmol), **2** (2.0 equiv), $RuHCl(CO)(PPh_3)_3$ (10 mol%), DCyPF (10 mol%), DME (2 mL), 85 °C, 16 h, if otherwise noted. [b]The yield is determined by crude ^1H NMR analysis with 1,1,2,2-tetrachloroethane as internal standard and isolated yield in the parenthesis. [c]With **2** (5.0 equiv)

III Optimization of the Reaction Conditions for Hydroacylation of Acrylonitrile with Aldehyde.

Table S6. The Effect of the Ru Catalyst and Ligands[a]

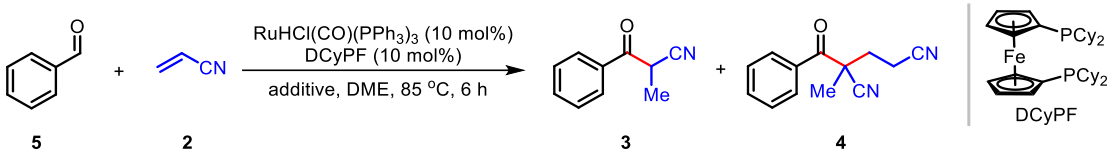




Entry	Ru catalyst	Ligand (10 or 20 mol %)	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	$RuHCl(CO)(PPh_3)_3$	-	0	0
2	$RuH_2(CO)(PPh_3)_3$	-	0	0
3	$RuHCl(CO)(PPh_3)_3$	PPh_3 (20)	0	0
4	$RuHCl(CO)(PPh_3)_3$	PCy_3 (20)	0	0
5	$RuHCl(CO)(PPh_3)_3$	tri-*p*-tolylphosphane (20)	5	12
6	$RuHCl(CO)(PPh_3)_3$	$P(C_6F_5)_3$ (20)	0	0
7	$RuHCl(CO)(PPh_3)_3$	XPhos (20)	0	0
8	$RuHCl(CO)(PPh_3)_3$	PhDavePhos (20)	0	0
9	$RuHCl(CO)(PPh_3)_3$	XantPhos (10)	0	0
10	$RuHCl(CO)(PPh_3)_3$	DPEPhos (10)	10	13
11	$RuHCl(CO)(PPh_3)_3$	Cy-DPEPhos (10)	0	0
12	$RuHCl(CO)(PPh_3)_3$	DPPF (10)	trace	trace
13	$RuHCl(CO)(PPh_3)_3$	DIPPF(10)	14	24
14	$RuHCl(CO)(PPh_3)_3$	DTBPF (10)	trace	trace
15	**$RuHCl(CO)(PPh_3)_3$**	**DCyPF (10)**	**25**	**17**

[a]Reaction conditions: **5** (0.2 mmol), **2** (0.2 mmol), Ru catalyst (10 mol%), ligand (10 mol% or 20 mol%), DME (2 mL), 85 °C, 6 h, if otherwise noted. [b]Determined by GC with dodecane as an internal standard.

Table S7. The Effect of the Additives[a]

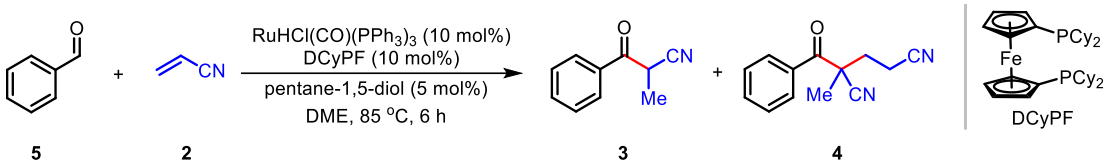


5 2 3 4

Entry	Additive (5 or 10 mol %)	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	-	25	17
2	$(EtO)_2PO_2H$ (10)	0	0
3	$(PhO)_2PO_2H$ (10)	10	9
4	CH_3SO_3H (10)	0	0
5	$PhCH_2OH$ (10)	42	10
6	ethane-1,2-diol (5)	33	16
7	propane-1,3-diol (5)	30	15
8	butane-1,4-diol (5)	37	13
9	**pentane-1,5-diol (5)**	**48**	**12**
10	hexane-1,6-diol (5)	46	12
11	heptane-1,7-diol (5)	40	12
12	octane-1,8-diol (5)	46	9
13	pentane-2,4-diol (5)	30	22
14	propane-1,2,3-triol (5)	35	11
15	3-methoxypropan-1-ol (5)	34	12

[a]Reaction conditions: 5 (0.2 mmol), **2** (0.2 mmol), $RuHCl(CO)(PPh_3)_3$ (10 mol%), DCyPF (10 mol%), additive (5 mol% or 10 mol%), DME (2 mL), 85 °C, 6 h. [b]Determined by GC with dodecane as an internal standard.

Table S8. The Effect of the Ratio of Substrates[a]

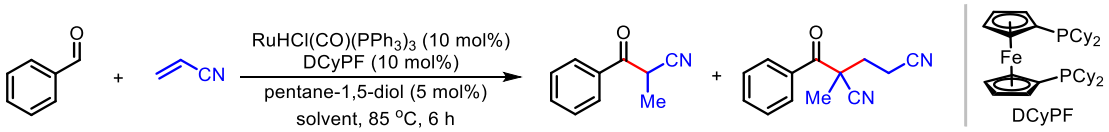


5 2 3 4

Entry	**5** (x equiv)	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	1.0	48	12
2	1.2	55	14
3	**1.5**	**70 (66)**[c]	**0**
4	2.0	71	0
5[d]	0.4	0	50 (47)[c]

[a]Reaction conditions: **5** (x equiv), **2** (0.2 mmol), $RuHCl(CO)(PPh_3)_3$ (10 mol%), DCyPF (10 mol%), pentane-1,5-diol (5 mol%), DME (2 mL), 85 °C, 6 h, if otherwise noted. [b]Determined by GC with dodecane as an internal standard. [c]Isolated yield in the parenthesis. [d]With **1** (0.2 mmol), **2** (0.5 mmol), 12 h.

Table S9. The Effect of Solvent[a]

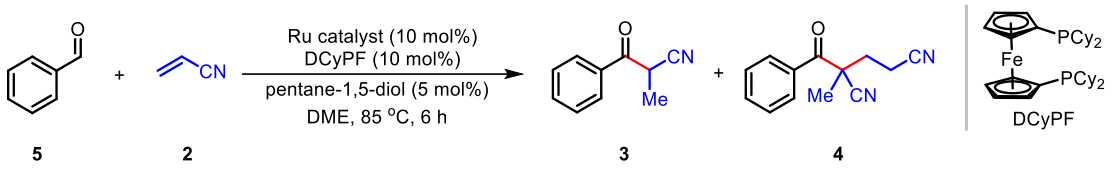


5 2 3 4

Entry	Solvent	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	**DME**	**70**	**0**
2	CH_3OH	trace	trace
3	CH_3O^tBu	61	0
4	DCE	26	6
5	benzene	53	18
6	CH_3CN	trace	trace
7[c]	toluene	51	6
8[c]	NMP	38	0
9[c]	DMF	16	11
10	THF	57	3
11	1,4-dioxane	64	3

[a]Reaction conditions: **5** (0.3 mmol), **2** (0.2 mmol), $RuHCl(CO)(PPh_3)_3$ (10 mol%), DCyPF (10 mol%), pentane-1,5-diol (5 mol%), solvent (2 mL), 85 °C, 6 h, if otherwise noted. [b]Determined by GC with dodecane as an internal standard. [c]At 110 °C.

Table S10. The Effect of Ru Catalyst and Control Experiments[a]

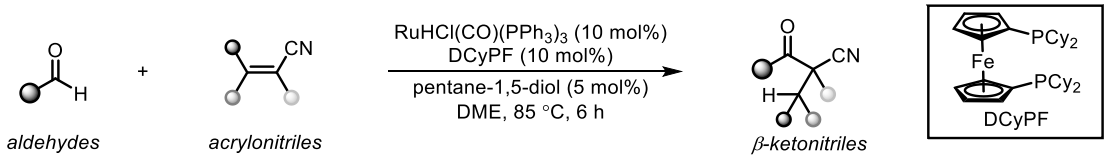


5 **2** **3** **4**

Entry	Ru catalyst	Yield of **3** (%)[b]	Yield of **4** (%)[b]
1	**$RuHCl(CO)(PPh_3)_3$**	**70**	**0**
2	$RuH_2(CO)(PPh_3)_3$	22	13
3	$RuCl_2(PPh_3)_3$	0	0
4	$(RuCpCO)_2$	0	0
5	$Ru_3(CO)_{12}$	0	0
6	$RuCl_2(COD)$	0	0
7	$RuHCl(CO)(PPh_3)_3$ (15 mol%)	70	0
8	$RuHCl(CO)(PPh_3)_3$ (5 mol%)	60	9
9[c]	-	0	0

[a]Reaction conditions: **5** (0.3 mmol), **2** (0.2 mmol), Ru catalyst (10 mol%), DME (2 mL), 85 °C, 6 h, if otherwise noted. [b]Determined by GC with dodecane as an internal standard. [c]Without Ru catalyst.

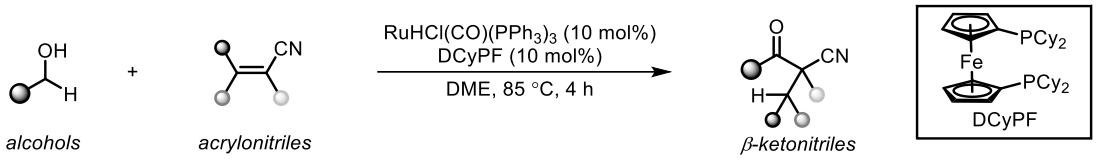
IV General Procedure and Characterization Data



aldehydes *acrylonitriles* *β-ketonitriles*

General Procedure A for Hydroacylation of Acrylonitriles with Aldehydes to *β*-Ketonitriles:

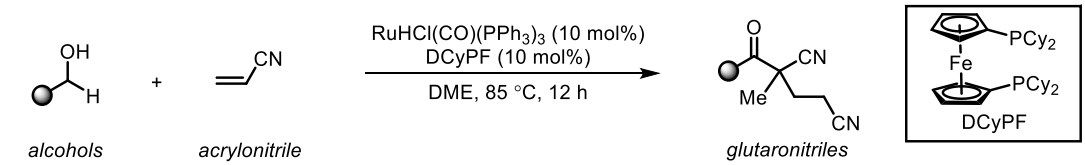
In a nitrogen-filled glovebox, a 25 mL Schlenk tube was charged with $RuHCl(CO)(PPh_3)_3$ (0.02 mmol, 19.2 mg), DCyPF (0.02 mmol, 11.4 mg), pentane-1,5-diol (0.01 mmol, 1 mg). Then, dry 1,2-dimethoxyethane (DME, 2 mL) was added, followed by aldehyde (0.3 mmol) and acrylonitrile (0.2 mmol). Then the Schlenk tube was removed from glovebox. The tube was stirred at 85 ºC for 6 h under N_2 atmosphere. The reaction mixture was concentrated under reduced pressure, which was purified by flash column chromatography on silica gel (PE:EA) to give to afford the desired product.



alcohols *acrylonitriles* *β-ketonitriles*

General Procedure B for Hydroacylation of Acrylonitriles with Alcohols to *β*-Ketonitriles:

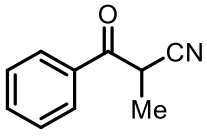
In a nitrogen-filled glovebox, a 25 mL Schlenk tube was charged with $RuHCl(CO)(PPh_3)_3$ (0.02 mmol, 19.2 mg), DCyPF (0.02 mmol, 11.4 mg). Then, dry 1,2-dimethoxyethane (DME, 2 mL) was added, followed by alcohol (0.2 mmol) and acrylonitriles (0.4 mmol). Then the Schlenk tube was removed from glovebox. The tube was stirred at 85 ºC for 4 h under N_2 atmosphere. The reaction mixture was concentrated under reduced pressure, which was purified by flash column chromatography on silica gel (PE:EA) to give to afford the desired product.



alcohols *acrylonitrile* *glutaronitriles*

General Procedure C for Cross-Coupling of Acrylonitrile with Alcohols to Glutaronitriles:

In a nitrogen-filled glovebox, a 25 mL Schlenk tube was charged with $RuHCl(CO)(PPh_3)_3$ (0.02 mmol, 19.2 mg) and DCyPF (0.02 mmol, 11.4 mg). Then, dry 1,2-dimethoxyethane (DME, 2 mL) was added, followed by alcohol (0.2 mmol) and acrylonitrile (1.0 mmol). Then the Schlenk tube was removed from glovebox. The tube was stirred at 85 ºC for 12 h under N_2 atmosphere. The reaction mixture was concentrated under reduced pressure, which was purified by flash column chromatography on silica gel (PE:EA) to give to afford the desired product.

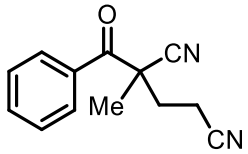


2-Methyl-3-oxo-3-phenylpropanenitrile (3). Synthesized according to the **General Procedure A** with benzaldehyde (0.3 mmol, 31.8 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **3** as a colorless oil (21.4 mg, 67%

yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.66 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.53 (dd, *J* = 7.6, 7.6 Hz, 2H), 4.38 (q, *J* = 7.2 Hz, 1H), 1.65 (d, *J* = 7.2 Hz, 3H). The data are consistent with the reported literature.[2]

Synthesized according to the **General Procedure B** with benzalcohol (0.2 mmol, 21.6 mg,) and acrylonitrile (0.4 mmol, 21.2 mg) at 85 °C for 4 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **3** as a colorless oil (21.0 mg, 66% yield).

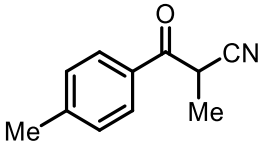


2-Benzoyl-2-methylpentanedinitrile (4). Synthesized according to the **General Procedure C** with benzalcohol (0.2 mmol, 21.6 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 °C for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **4** as a yellow oil (26.3 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.6 Hz, 2H), 7.66 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.53 (dd, *J* = 7.6, 7.2 Hz, 2H), 2.70 – 2.51 (m, 3H), 2.21 – 2.14 (m, 1H), 1.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 134.6 133.4, 129.5, 129.1, 120.4, 118.1, 45.1, 33.6, 24.8, 13.9.

HRMS (ESI): Calcd for $[C_{13}H_{12}N_2ONa]^+$ $[M+Na]^+$ 235.0842, Found 235.0850.



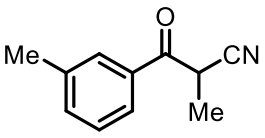
2-Methyl-3-oxo-3-(*p*-tolyl)propanenitrile (6). Synthesized according to the **General Procedure A** with 4-methylbenzaldehyde (0.3 mmol, 36.0 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **6** as a colorless oil (21.2 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.35 (q, *J* = 7.2 Hz, 1H), 2.44 (s, 3H), 1.64 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 145.9, 131.4, 129.9, 129.1, 118.4, 33.7, 21.9, 15.1.

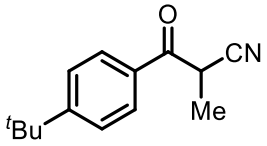
HRMS (ESI): Calcd for $[C_{11}H_{11}NO_2Na]^+$ $[M+Na]^+$ 196.0733, Found 196.0743.

Synthesized according to the **General Procedure B** with *p*-tolylmethanol (0.2 mmol, 24.4 mg,) and acrylonitrile (0.4 mmol, 21.2 mg) at 85 °C for 4 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **5** as a colorless oil (18.7 mg, 54% yield).

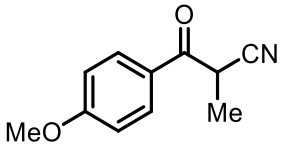


2-Methyl-3-oxo-3-(*m*-tolyl)propanenitrile (7). Synthesized according to the **General Procedure A** with 3-methylbenzaldehyde (0.3 mmol, 36.0 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **7** as a colorless oil (18.3 mg, 53% yield).

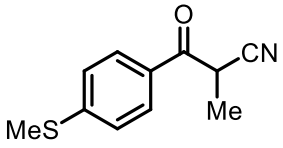
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.76 (m, 2H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.41 (dd, *J* = 7.6, 7.2 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 1H), 2.44 (s, 3H), 1.64 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 139.3, 135.5, 134.0, 129.4, 129.1, 126.1, 118.3, 33.8, 21.5, 15.2.
HRMS (ESI): Calcd for $[C_{11}H_{11}NO_2Na]^+$ $[M+Na]^+$ 196.0733, Found 196.0736.



3-(4-(*tert*-Butyl)phenyl)-2-methyl-3-oxopropanenitrile (8). Synthesized according to the **General Procedure A** with 4-(*tert*-butyl)benzaldehyde (0.3 mmol, 48.6 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **8** as a colorless oil (25.0 mg, 58% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 4.36 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H), 1.35 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 158.7, 131.3, 128.9, 126.2, 118.5, 35.4, 33.7, 31.1, 15.1.
HRMS (ESI): Calcd for $[C_{14}H_{17}NONa]^+$ $[M+Na]^+$ 238.1202, Found 238.1203.

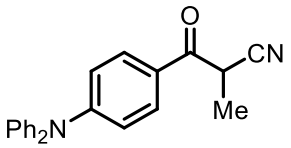


3-(4-Methoxyphenyl)-2-methyl-3-oxopropanenitrile (9). Synthesized according to the **General Procedure A** with 4-methoxybenzaldehyde (0.3 mmol, 40.8 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **9** as a colorless oil (22.0 mg, 58% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 4.31 (q, *J* = 7.2 Hz, 1H), 3.90 (s, 3H), 1.63 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 164.8, 131.4, 126.8, 118.6, 114.5, 55.8, 33.4, 15.2.
HRMS (ESI): Calcd for $[C_{11}H_{12}NO_2]^+$ $[M+H]^+$ 190.0863, Found 190.0861.
Synthesized according to the **General Procedure B** with (4-methoxyphenyl)methanol (0.2 mmol, 27.6 mg,) and acrylonitrile (0.4 mmol, 21.2 mg) at 85 °C for 4 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **9** as a colorless oil (23.4 mg, 62% yield).

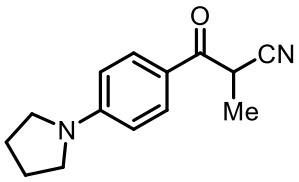


2-Methyl-3-(4-(methylthio)phenyl)-3-oxopropanenitrile (10). Synthesized according to the **General Procedure A** with 4-(methylthio)benzaldehyde (0.3 mmol, 45.6 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **10** as a colorless oil (23.0 mg, 56% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.31 (q, *J* = 7.2 Hz, 1H), 2.53 (s, 3H), 1.63 (d, *J* = 7.2 Hz, 3H).

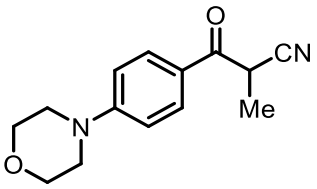
^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 148.5, 129.9, 129.2, 125.3, 118.4, 33.5, 15.1, 14.7.
HRMS (ESI): Calcd for $[C_{11}H_{11}NOSNa]^+$ $[M+Na]^+$ 228.0454, Found 228.0444.



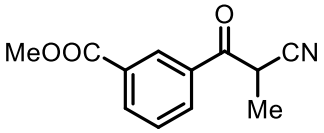
3-(4-(Diphenylamino)phenyl)-2-methyl-3-oxopropanenitrile (11). Synthesized according to the **General Procedure A** with 4-(diphenylamino)benzaldehyde (0.3 mmol, 81.9 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **11** as a yellow oil (40.4 mg, 62% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.34 (m, 4H), 7.20 – 7.17 (m, 6H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.27 (q, *J* = 7.2 Hz, 1H), 1.62 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 153.4, 146.0, 130.7, 129.9, 126.6, 125.5, 125.5, 118.9, 118.8, 33.1, 15.2.
HRMS (ESI): Calcd for $[C_{22}H_{18}N_2ONa]^+$ $[M+Na]^+$ 349.1311, Found 349.1319.



2-Methyl-3-oxo-3-(4-(pyrrolidin-1-yl)phenyl)propanenitrile (12). Synthesized according to the **General Procedure A** with 4-(pyrrolidin-1-yl)benzaldehyde (0.3 mmol, 52.5 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **12** as a white jelly (34.0 mg, 74% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 8.4 Hz, 2H), 4.29 (q, *J* = 7.2 Hz, 1H), 3.39 (s, 4H), 2.05 (s, 4H), 1.61 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 151.9, 131.4, 120.9, 119.4, 111.2, 47.8, 32.8, 25.5, 15.5.
HRMS (ESI): Calcd for $[C_{14}H_{17}N_2O]^+$ $[M+H]^+$ 229.1335, Found 229.1330.



2-Methyl-3-(4-morpholinophenyl)-3-oxopropanenitrile (13). Synthesized according to the **General Procedure A** with 4-morpholinobenzaldehyde (0.3 mmol, 57.3 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **13** as a white jelly (30.7 mg, 63% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 9.2 Hz, 2H), 6.86 (d, *J* = 9.2 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 1H), 3.83 (t, *J* = 4.8 Hz, 4H), 3.34 (t, *J* = 5.2 Hz, 4H), 1.59 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 155.0, 131.1, 123.8, 118.9, 113.2, 66.5, 47.1, 33.1, 15.3.
HRMS (ESI): Calcd for $[C_{14}H_{16}N_2O_2Na]^+$ $[M+ Na]^+$ 267.1104, Found 267.1104.

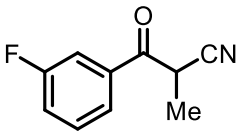


Methyl 3-(2-cyanopropanoyl)benzoate (14). Synthesized according to the **General Procedure A** with methyl 3-formylbenzoate (0.3 mmol, 49.2 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **14** as a colorless oil (25.2 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.30 (d, *J* = 7.6 Hz, 1H), 8.18 (d, *J* = 7.6 Hz, 1H), 7.62 (dd, *J* = 8.0, 7.6 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 1H), 3.95 (s, 3H), 1.65 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 165.8, 135.3, 134.1, 133.0, 131.3, 129.8, 129.6, 117.9, 52.7, 34.0, 15.0.

HRMS (ESI): Calcd for $[C_{12}H_{11}NO_3Na]^+$ $[M+Na]^+$ 240.0631, Found 240.0625.



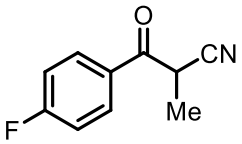
3-(3-Fluorophenyl)-2-methyl-3-oxopropanenitrile (15). Synthesized according to the **General Procedure A** with 3-fluorobenzaldehyde (0.3 mmol, 37.2 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **15** as a colorless oil (19.1 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.39 – 7.34 (m, 1H), 4.32 (q, *J* = 7.2 Hz, 1H), 1.65 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 163.1 (d, *J* = 248.4 Hz), 135.9 (d, *J* =6.5 Hz), 131.0 (d, *J* =7.5 Hz), 124.7 (d, *J* = 3.4 Hz), 121.8 (d, *J* = 21.1 Hz), 117.9, 115.8 (d, *J* = 22.5 Hz), 34.0, 15.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ –110.4.

HRMS (ESI): Calcd for $[C_{10}H_8NOFNa]^+$ $[M+Na]^+$ 200.0482, Found 200.0490.



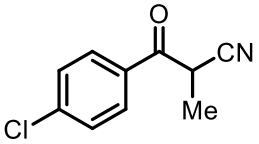
3-(4-Fluorophenyl)-2-methyl-3-oxopropanenitrile (16). Synthesized according to the **General Procedure A** with 4-fluorobenzaldehyde (0.3 mmol, 37.2 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **16** as a colorless oil (24.0 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.0, 6.0 Hz, 2H), 7.20 (dd, *J* = 8.4, 8.4 Hz, 2H), 4.33 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 166.6 (d, *J* = 256.3 Hz), 131.7 (d, *J* = 9.8 Hz), 130.3 (d, *J* = 3.2 Hz), 118.13, 116.5 (d, *J* = 21.9 Hz), 33.8, 15.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ –102.0.

HRMS (ESI): Calcd for$[C_{10}H_8NOFNa]^+$ $[M+Na]^+$ 200.0482, Found 200.0492.

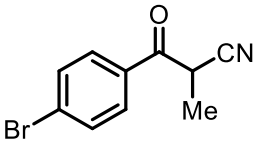


3-(4-Chlorophenyl)-2-methyl-3-oxopropanenitrile (17). Synthesized according to the **General Procedure A** with 4-chlorobenzaldehyde (0.3 mmol, 42.0 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **17** as a colorless oil (20.6 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 1H), 1.65 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 141.4, 132.2, 130.3, 129.7, 118.0, 33.8, 14.9.

HRMS (ESI): Calcd for $[C_{10}H_8NOClNa]^+$ $[M+Na]^+$ 216.0187, Found 216.0187.

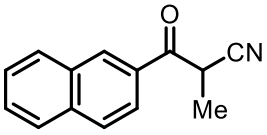


3-(4-Bromophenyl)-2-methyl-3-oxopropanenitrile (18). Synthesized according to the **General Procedure A** with 4-bromobenzaldehyde (0.3 mmol, 55.2 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **18** as a colorless oil (19.4 mg, 41% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 132.7, 132.6, 130.3, 130.2, 118.0, 33.8, 14.9.

HRMS (ESI): Calcd for $[C_{10}H_8NOBrNa]^+$ $[M+Na]^+$ 259.9681, Found 259.9779.

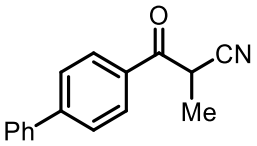


2-Methyl-3-(naphthalen-2-yl)-3-oxopropanenitrile (19). Synthesized according to the **General Procedure A** with 2-naphthaldehyde (0.3 mmol, 46.8 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **19** as a white jelly (31.4 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.00 (dd, *J* = 8.0, 7.6 Hz 2H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.66 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.60 (dd, *J* = 8.0, 6.8 Hz, 1H), 4.54 (q, *J* = 7.2 Hz, 1H), 1.71 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 136.2, 132.5, 131.2, 131.1, 129.9, 129.5, 129.3, 128.0, 127.4, 124.0, 118.4, 33.9, 15.3.

HRMS (ESI): Calcd for $[C_{14}H_{12}NO]^+$ $[M+H]^+$ 210.0913, Found 210.0913.



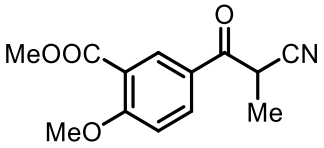
3-([1,1'-Biphenyl]-4-yl)-2-methyl-3-oxopropanenitrile (20). Synthesized according to the **General Procedure A** with [1,1'-biphenyl]-4-carbaldehyde (0.3 mmol, 54.6 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **20** as a white jelly (41.0 mg, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.46 (dd, *J* = 7.6, 7.2 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 1H), 4.40 (q, *J* = 7.2 Hz, 1H), 1.68 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 147.4, 139.4, 132.4, 129.6, 129.2, 128.8, 127.8, 127.4, 118.4, 33.8, 15.1.

HRMS (ESI): Calcd for $[C_{16}H_{13}NONa]^+$ $[M+Na]^+$ 258.0889, Found 258.0893.

Synthesized according to the **General Procedure B** with [1,1'-biphenyl]-4-ylmethanol (0.2 mmol, 36.8 mg,) and acrylonitrile (0.4 mmol, 21.2 mg) at 85 °C for 4 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **20** as a colorless oil (24.0 mg, 51% yield).

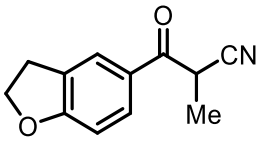


Methyl 5-(2-cyanopropanoyl)-2-methoxybenzoate (21). Synthesized according to the **General Procedure A** with methyl 5-formyl-2-methoxybenzoate (0.3 mmol, 58.2 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **21** as a colorless oil (29.6 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 2.0 Hz, 1H), 8.13 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 1H), 3.99 (s, 3H), 3.91 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.8, 165.5, 163.7, 134.6, 133.1, 126.0, 120.6, 118.2, 112.5, 56.6, 52.6, 33.5, 15.1.

HRMS (ESI): Calcd for $[C_{13}H_{13}NO_4Na]^+$ $[M+Na]^+$ 270.0737, Found 270.0746.

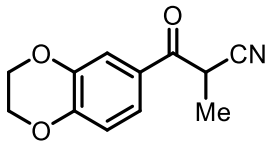


3-(2,3-Dihydrobenzofuran-5-yl)-2-methyl-3-oxopropanenitrile (22). Synthesized according to the **General Procedure A** with 2,3-dihydrobenzofuran-5-carbaldehyde (0.3 mmol, 44.4 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **22** as a colorless oil (18.8 mg, 47% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 4.69 (t, *J* = 8.8 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 1H), 3.27 (t, *J* = 8.8 Hz, 2H), 1.62 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 165.8, 131.2, 128.7, 127.1, 126.3, 118.7, 109.7, 72.7, 33.4, 29.0, 15.3.

HRMS (ESI): Calcd for $[C_{12}H_{12}NO_2]^+$ $[M+H]^+$ 202.0863, Found 202.0865.

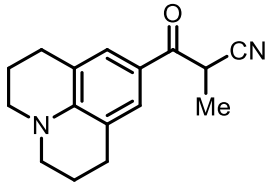


3-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-2-methyl-3-oxopropanenitrile (23). Synthesized according to the **General Procedure A** with 2,3-dihydrobenzo[*b*][1,4]dioxine-6-carbaldehyde (0.3 mmol, 49.2 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **23** as a colorless oil (27.2 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.50 (m, 2H), 6.94 (d, *J* = 9.2 Hz, 1H), 4.37 – 4.24 (m, 5H), 1.61 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 149.4, 143.9, 127.5, 123.1, 118.5, 118.4, 117.9, 64.9, 64.2, 33.5, 15.3.

HRMS (ESI): Calcd for $[C_{12}H_{11}NO_3Na]^+$ $[M+Na]^+$ 240.0631, Found 240.0630.

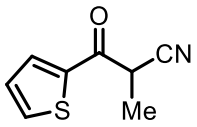


2-Methyl-3-oxo-3-(2,3,6,7-tetrahydro-*1H*,*5H*-pyrido[3,2,1-*ij*]quinolin-9-yl)propanenitrile (24). Synthesized according to the **General Procedure A** with 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline-9-carbaldehyde (0.3 mmol, 60.3 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **24** as a yellow oil (40.0 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 2H), 4.26 (q, *J* = 6.8 Hz, 1H), 3.28 (t, *J* = 5.6 Hz, 4H), 2.74 (t, *J* = 6.4 Hz, 4H), 2.06 – 1.85 (m, 4H), 1.58 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0, 147.9, 128.7, 120.3, 120.1, 119.5, 50.1, 32.5, 27.8, 21.3, 15.7.

HRMS (ESI): Calcd for $[C_{16}H_{19}N_2O]^+$ $[M+H]^+$ 255.1492, Found 255.1485.



2-Methyl-3-oxo-3-(thiophen-2-yl)propanenitrile (25). Synthesized according to the **General Procedure A** with thiophene-2-carbaldehyde (0.3 mmol, 33.6 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **25** as a pale yellow oil (24.7 mg, 75% yield).

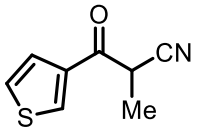
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 3.2 Hz, 1H), 7.78 (d, *J* = 4.4 Hz, 1H), 7.20 (dd, *J* = 4.0, 3.6 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 1H), 1.66 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 183.6, 140.6, 136.2, 133.8, 128.8, 118.2, 34.8, 15.4.

HRMS (ESI): Calcd for $[C_8H_7NOSNa]^+$ $[M+Na]^+$ 188.0141, Found 188.0146.

Synthesized according to the **General Procedure B** with thiophen-2-ylmethanol (0.2 mmol, 22.8 mg,)

and acrylonitrile (0.4 mmol, 21.2 mg) at 85 °C for 4 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **25** as a colorless oil (15.8 mg, 48% yield).

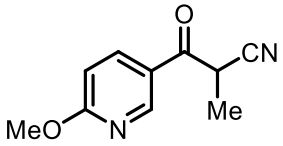


2-Methyl-3-oxo-3-(thiophen-3-yl)propanenitrile (26). Synthesized according to the **General Procedure A** with thiophene-3-carbaldehyde (0.3 mmol, 33.6 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **26** as a pale yellow oil (26.0 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.60 (d, *J* = 5.2 Hz, 1H), 7.44 – 7.34 (m, 1H), 4.17 (q, *J* = 7.2 Hz, 1H), 1.64 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 184.7, 138.7, 134.2, 127.4, 127.3, 118.4, 35.1, 15.1.

HRMS (ESI): Calcd for $[C_8H_7NOSNa]^+$ $[M+Na]^+$ 188.0141, Found 188.0132.



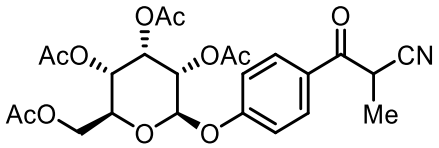
3-(6-Methoxypyridin-3-yl)-2-methyl-3-oxopropanenitrile (27). Synthesized according to the **General Procedure A** with 6-methoxynicotinaldehyde (0.3 mmol, 41.1 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **27** as a pale yellow oil (31.5 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 1H), 4.02 (s, 3H), 1.64 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 167.7, 150.0, 138.8, 123.8, 118.1, 112.0, 54.5, 33.7, 14.9.

HRMS (ESI): Calcd for $[C_{10}H_{11}N_2O_2]^+$ $[M+H]^+$ 191.0815, Found 191.0823.

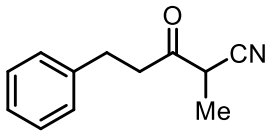
Synthesized according to the **General Procedure B** with (6-methoxypyridin-3-yl)methanol (0.2 mmol, 27.8 mg,) and acrylonitrile (0.4 mmol, 21.2 mg) at 85 °C for 4 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **27** as a colorless oil (14.1 mg, 37% yield).



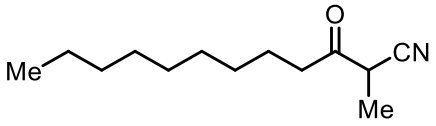
(2*S*,3*S*,4*S*,5*S*,6*R*)-2-(Acetoxymethyl)-6-(4-(2-cyanopropanoyl)phenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (28). Synthesized according to the **General Procedure A** with (2*S*,3*S*,4*S*,5*S*,6*R*)-2-(acetoxymethyl)-6-(4-formylphenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (0.3 mmol, 135.6 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 110 °C for 24 h. Purified by flash column chromatography on silica gel (PE:EA = 5:1) to give **28** as a yellow jelly (56.0 mg, 51% yield, 1:1 *regioisomer*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.2 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 5.75 (dd, *J* = 2.8 Hz, 2.8 Hz, 1H), 5.47 (d, *J* = 8.0 Hz, 1H), 5.18 (dd, *J* = 8.0, 4.0 Hz, 1H), 5.08 – 5.04 (m, 1H), 4.33 – 4.23 (m, 4H), 2.17 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.62 (d, *J* = 7.2 Hz, 3H).

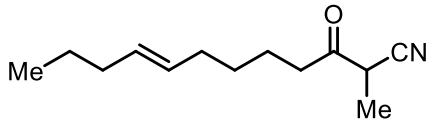
^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, (189.2), 170.7, 169.8, 169.2, (169.1), 161.7, (161.6), 131.2, 128.8, 118.4 (118.4), 116.9, 96.5, (96.5), 70.9, 68.8, 68.4, 66.2, (66.2), 62.4, (62.3), 33.6, (33.6), 20.8, (20.8), 20.7, (20.6), 14.9, (14.9).
HRMS (ESI): Calcd for $[C_{24}H_{27}NO_{11}Na]^+$ $[M+Na]^+$ 528.1476, Found 528.1469.



2-Methyl-3-oxo-5-phenylpentanenitrile (29). Synthesized according to the **General Procedure A** with 3-phenylpropanal (0.3 mmol, 40.2 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 15:1) to give **29** as a colorless oil (12.7 mg, 34% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 8.4, 7.6 Hz, 2H), 7.23 – 7.18 (m, 3H), 3.38 (q, *J* = 7.2 Hz, 1H), 3.13 – 3.07 (m, 1H), 3.05 – 2.99 (m, 1H), 2.97 – 2.93 (m, 2H), 1.45 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 140.1, 128.8, 128.5, 126.7, 118.3, 42.3, 38.1, 29.7, 14.1.
HRMS (ESI): Calcd for $[C_{12}H_{14}NO]^+$ $[M+H]^+$ 188.1070, Found 188.1077.
The data are consistent with the reported literature.[3]

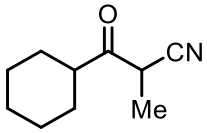


2-Methyl-3-oxododecanenitrile (29). Synthesized according to the **General Procedure A** with decanal (0.3 mmol, 46.8 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 15:1) to give **30** as a colorless oil (14.6 mg, 35% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.43 (q, *J* = 7.2 Hz, 1H), 2.81 – 2.59 (m, 2H), 1.67 – 1.56 (m, 2H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.28 – 1.26 (m, 12H), 0.87 (t, *J* = 6.4 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 118.5, 40.8, 37.8, 32.0, 29.5, 29.4, 29.4, 29.1, 23.6, 22.8, 14.2, 14.2.
HRMS (ESI): Calcd for$[C_{13}H_{23}NONa]^+$ $[M+Na]^+$ 232.1672, Found 232.1677.

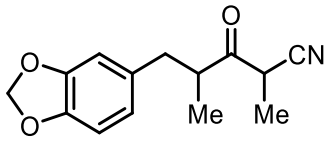


2-Methyl-3-oxododec-8-enenitrile (31) Synthesized according to the **General Procedure A** with dec-6-enal (0.3 mmol, 46.2 mg, *E*/*Z* isomers, major *E* isomer) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 15:1) to give **31** as a colorless oil (14.9 mg, 36% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 – 5.42 (m, 1H), 5.41 – 5.24 (m, 1H), 3.42 (q, *J* = 7.2 Hz, 1H), 2.85 – 2.68 (m, 2H), 2.42 – 2.24 (m, 2H), 2.05 – 1.93 (m, 2H), 1.48 (d, *J* = 7.2 Hz, 3H), 1.38 – 1.18 (m, 6H), 0.87 (t, *J* = 6.8 Hz, 3H).

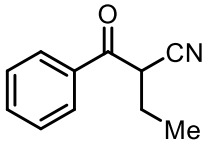
^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 132.8, (132.4), 127.2, (126.7), 118.4, 40.7, 37.9, 32.6, (31.6), 31.5, (29.4), 29.2, (27.3), 26.6, (22.7), 22.6, 21.5, 14.1.
HRMS (ESI): Calcd for $[C_{13}H_{21}NONa]^+$ $[M+Na]^+$ 230.1515, Found 230.1517.



3-Cyclohexyl-2-methyl-3-oxopropanenitrile (32). Synthesized according to the **General Procedure A** with cyclohexanecarbaldehyde (0.3 mmol, 33.6 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 15:1) to give **32** as a colorless oil (12.5 mg, 38% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54 (q, *J* = 7.2 Hz, 1H), 2.79 – 2.73 (m, 1H), 1.91– 1.88 (m, 2H), 1.85 – 1.74 (m, 2H), 1.74 – 1.62 (m, 1H), 1.46 (d, *J* = 7.2 Hz, 3H), 1.43 – 1.29 (m, 4H), 1.26 – 1.18 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 203.9, 118.5, 49.0, 36.0, 28.9, 28.5, 25.6, 25.5, 25.3, 14.2.
HRMS (ESI): Calcd for $[C_{10}H_{15}NONa]^+$ $[M+Na]^+$ 188.1046, Found 188.1042.



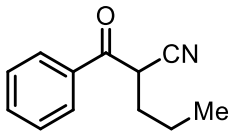
5-(Benzo[*d*][1,3]dioxol-5-yl)-2,4-dimethyl-3-oxopentanenitrile (33). Synthesized according to the **General Procedure A** with 3-(benzo[*d*][1,3]dioxol-5-yl)-2-methylpropanal (0.3 mmol, 57.6 mg) and acrylonitrile (0.2 mmol, 10.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **33** as a pale yellow oil (19.1 mg, 39% yield, d.r. = 1.2:1.).
^{1}H NMR (400 MHz, $CDCl_3$) *Major isomer:* δ 6.73 – 6.70 (m, 1H), 6.68 – 6.54 (m, 2H), 5.92 (s, 2H), 3.26 – 3.20 (m, 1H), 3.14 (q, *J* = 7.2 Hz, 1H), 2.98 – 2.85 (m, 1H), 2.61 – 2.52 (m, 1H), 1.32 (d, *J* = 7.2 Hz, 3H), 1.17 (d, *J* = 6.8 Hz, 3H). *Minor isomer:* 3.41 – 3.35 (m, 1H), 1.41 (d, *J* = 7.6 Hz, 3H), 1.20 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) *Major isomer:* δ 204.6, 148.0, 146.5, 132.5, 122.1, 118.2, 109.2, 108.5, 101.1, 47.3, 39.7, 38.0, 17.2, 13.6. *Minor isomer:* δ 204.5 147.9, 146.4, 132.5, 121.9, 118.2, 109.3, 108.5, 101.1, 46.7, 39.0, 37.4, 17.1, 14.0.
HRMS (ESI): Calcd for $[C_{14}H_{15}NO_3Na]^+$ $[M+Na]^+$ 268.0944, Found 268.0937.



2-Benzoylbutanenitrile (34). Synthesized according to the **General Procedure A** with benzaldehyde (0.3 mmol, 31.8 mg) and but-2-enenitrile (0.2 mmol, 13.4 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 15:1) to give **34** as a colorless oil (21.1 mg, 61% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.94 (m, 2H), 7.64 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.51 (dd, *J* = 8.0, 7.6 Hz, 2H), 4.32 (dd, *J* = 8.0, 5.6 Hz, 1H), 2.16 – 1.94 (m, 2H), 1.15 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 134.6, 134.1, 129.2, 128.8, 117.4, 41.6, 23.7, 11.6.

HRMS (ESI): Calcd for $[C_{11}H_{11}NONa]^+$ $[M+Na]^+$ 196.0733, Found 196.0734.

Synthesized according to the **General Procedure B** with benzalcohol (0.2 mmol, 21.6 mg) and but-2-enenitrile (0.4 mmol, 26.8 mg) at 85 °C for 4 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **34** as a colorless oil (20.1 mg, 58% yield).



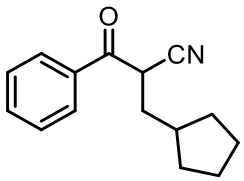
2-Benzoylpentanenitrile (35). Synthesized according to the **General Procedure A** with benzaldehyde (0.3 mmol, 31.8 mg) and pent-2-enenitrile (0.2 mmol, 16.2 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 15:1) to give **35** as a colorless oil (18.7 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.94 (m, 2H), 7.64 (dd, *J* = 7.6, 7.2 Hz,1H), 7.51 (dd, *J* = 8.0, 7.6 Hz, 2H), 4.37 (dd, *J* = 7.6, 15.2 Hz, 1H), 2.00 – 1.92 (m, 2H), 1.68 – 1.47 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 134.5, 134.1, 129.2, 128.8, 117.5, 40.0, 32.0, 20.5, 13.5.

HRMS (ESI): Calcd for $[C_{12}H_{13}NONa]^+$ $[M+Na]^+$ 210.0889, Found 210.0898.

Synthesized according to the **General Procedure B** with benzalcohol (0.2 mmol, 21.6 mg) and pent-2-enenitrile (0.4 mmol, 32.4 mg) at 85 °C for 4 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **35** as a colorless oil (16.8 mg, 45% yield).

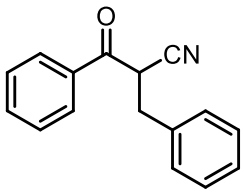


2-(Cyclopentylmethyl)-3-oxo-3-phenylpropanenitrile (36). Synthesized according to the **General Procedure A** with benzaldehyde (0.3 mmol, 31.8 mg) and 3-cyclopentylacrylonitrile (*Z*/*E*) (0.2 mmol, 24.2 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 15:1) to give **36** as a colorless oil (20.3 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6, 2H), 7.65 (dd, *J* = 7.6, 6.8 Hz, 1H), 7.53 (dd, *J* = 8.0, 7.6 Hz, 2H), 4.35 (dd, *J* = 9.6, 5.2 Hz, 1H), 2.15 – 2.02 (m, 2H), 2.02 – 1.78 (m, 3H), 1.74 – 1.49 (m, 5H), 1.17 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 134.6, 134.2, 129.3, 128.9, 117.7, 39.7, 38.2, 36.2, 32.8, 32.3, 25.2.

HRMS (ESI): Calcd for $[C_{15}H_{17}NONa]^+$ $[M+Na]^+$ 250.1202, Found 250.1209.



2-Benzyl-3-oxo-3-phenylpropanenitrile (37). Synthesized according to the **General Procedure A** with benzaldehyde (0.3 mmol, 31.8 mg) and 3-phenylacrylonitrile (0.2 mmol, 25.8 mg) at 85 °C for 6 h.

Purified by flash column chromatography on silica gel (PE:EA = 15:1) to give **37** as a colorless oil (28.7 mg, 62% yield).

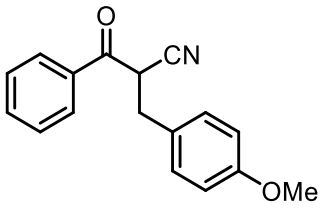
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.65 (m, 2H), 7.65 (dd, *J* = 7.6, 7.2 Hz,1H), 7.52 (dd, *J* = 8.0, 7.6 Hz, 2H), 7.41 – 7.28 (m, 5H), 4.52 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.37 (dd, *J* = 14.0, 5.6 Hz, 1H), 3.25 (dd, *J* = 14.0, 8.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 136.1, 134.7, 134.3, 129.3, 129.2, 129.1, 129.0, 127.8, 117.1, 41.9, 35.7.

HRMS (ESI): Calcd for $[C_{16}H_{13}NONa]^+$ $[M+Na]^+$ 258.0889, Found 258.0882.

The data are consistent with the reported literature.[2]

Synthesized according to the **General Procedure B** with benzalcohol (0.2 mmol, 21.6 mg) and 3-phenylacrylonitrile (0.4 mmol, 51.6 mg) at 85 °C for 4 h. Purified by flash column chromatography on silica gel (PE:EA = 15:1) to give **37** as a colorless oil (22.1 mg, 47% yield).



2-(4-Methoxybenzyl)-3-oxo-3-phenylpropanenitrile (38). Synthesized according to the **General Procedure A** with benzaldehyde (0.3 mmol, 31.8 mg) and 3-(4-methoxyphenyl)acrylonitrile (0.2 mmol, 31.8 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **38** as a colorless oil (28.0 mg, 53% yield).

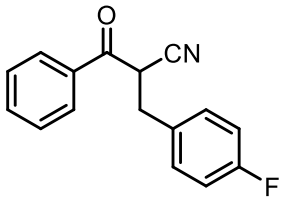
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.65 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.51 (dd, *J* = 8.0, 7.6 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.50 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.78 (s, 3H), 3.30 (dd, *J* = 14.4, 6.0 Hz, 1H), 3.19 (dd, *J* = 14.0, 8.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 159.3, 134.7, 134.3, 130.3, 129.3, 128.9, 128.0, 117.2, 114.5, 55.4, 42.3, 35.0.

HRMS (ESI): Calcd for $[C_{17}H_{15}NO_2Na]^+$ $[M+Na]^+$ 288.0995, Found 288.0986.

The data are consistent with the reported literature.[2]

Synthesized according to the **General Procedure B** with benzalcohol (0.2 mmol, 21.6 mg) and 3-(4-methoxyphenyl)acrylonitrile (0.4 mmol, 63.6 mg) at 85 °C for 4 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **38** as a colorless oil (8.5 mg, 16% yield).



2-(4-Fluorobenzyl)-3-oxo-3-phenylpropanenitrile (39). Synthesized according to the **General Procedure A** with benzaldehyde (0.3 mmol, 31.8 mg) and 3-(4-fluorophenyl)acrylonitrile (0.2 mmol, 29.4 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **39** as a colorless oil (32.0 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.94 (m, 2H), 7.66 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.52 (dd, *J* = 8.0, 7.6

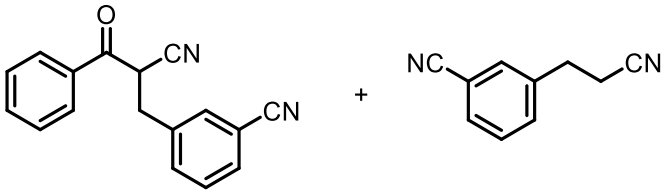
Hz, 2H), 7.27 – 7.24 (m, 2H), 7.02 (dd, *J* = 8.8, 8.4 Hz, 2H), 4.49 (dd, *J* = 8.4, 6.0 Hz, 1H), 3.34 (dd, *J* = 14.4, 6.0 Hz, 1H), 3.23 (dd, *J* = 14.4, 8.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 163.5 (d, *J* = 244.9 Hz), 134.8, 134.2, 131.8 (d, *J* = 3.1 Hz), 130.9 (d, *J* = 8.0 Hz), 129.3, 128.9, 116.9, 116.0 (d, *J* = 21.3 Hz), 41.9, 34.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ –114.6.

HRMS (ESI): Calcd for $[C_{16}H_{12}FNOK]^+$ $[M+K]^+$ 292.0535, Found 292.0535.

Synthesized according to the **General Procedure B** with benzalcohol (0.2 mmol, 21.6 mg) and 3-(4-fluorophenyl)acrylonitrile (0.4 mmol, 58.8 mg) at 85 °C for 4 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **39** as a colorless oil (17.7 mg, 35% yield).



3-(2-Cyano-3-oxo-3-phenylpropyl)benzonitrile (40). Synthesized according to the **General Procedure A** with benzaldehyde (0.3 mmol, 31.8 mg) and 3-cyano-cinnamonitrile (0.2 mmol, 30.8 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give a mixture (40.3 mg) of **40** (70% yield) and 3-(3-cyanophenyl)propanenitrile (13% yield, reductive product of 3-cyano-cinnamonitrile) as a colorless oil.

40: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.67 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.61 – 7.42 (m, 6H), 4.55 (dd, *J* = 8.4, 6.0 Hz, 1H), 3.40 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.29 (dd, *J* = 10.0, 4.4 Hz, 1H).

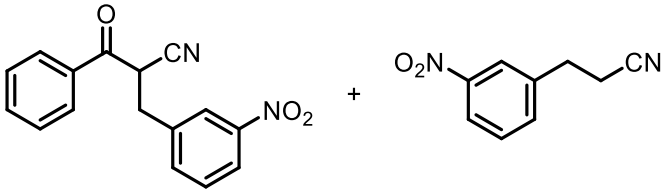
^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1, 137.4, 134.9, 133.8, 132.6, 131.4, 129.7, 129.2, 128.8, 118.5, 118.3, 116.3, 113.0, 40.9, 34.4.

HRMS (ESI): Calcd for $[C_{17}H_{12}N_2ONa]^+$ $[M+Na]^+$ 292.0535, Found 292.0535.

3-(3-Cyanophenyl)propanenitrile: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.42 (m, 4H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 133.0, 132.0, 131.2, 31.1, 19.1.

The data are consistent with the reported literature.[4]



2-(3-Nitrobenzyl)-3-oxo-3-phenylpropanenitrile (41). Synthesized according to the **General Procedure A** with benzaldehyde (0.3 mmol, 31.8 mg) and 3-nitro-cinnamonitrile (0.2 mmol, 34.8 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give a mixture (41.6 mg) of **41** (66% yield) and 3-(3-nitrophenyl)propanenitrile (13% yield, reductive product of 3-nitro-cinnamonitrile) as a colorless oil.

41: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.10 (m, 2H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.72 – 7.46 (m, 5H), 4.64 (dd, *J* = 8.4, 6.0 Hz, 1H), 3.47 (dd, *J* = 14.4, 6.0 Hz, 1H), 3.36 (dd, *J* = 14.0, 8.4 Hz, 1H).

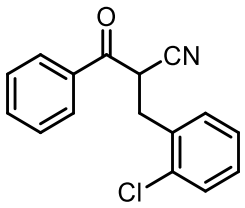
^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 148.6, 138.0, 135.7, 135.0, 133.9, 130.0, 129.4, 129.0, 124.1, 122.9, 116.5, 41.0, 34.6.

HRMS (ESI): Calcd for $[C_{16}H_{13}N_2O_3]^+$ $[M+H]^+$ 281.0921, Found 281.0916.

3-(3-Nitrophenyl)propanenitrile : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.46 (m, 4H), 3.07 (t, *J* = 7.2 Hz, 2H), 2.70 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 139.9, 134.8, 123.4, 122.6, 118.5, 31.1, 19.1.

The data are consistent with the reported literature.[5]

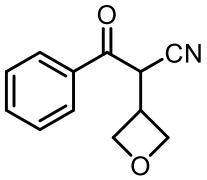


2-(2-Chlorobenzyl)-3-oxo-3-phenylpropanenitrile (42). Synthesized according to the **General Procedure A** with benzaldehyde (0.3 mmol, 31.8 mg) and 3-(2-chlorophenyl)acrylonitrile (0.2 mmol, 32.6 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **42** as a colorless oil (37.0 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.64 (dd, *J* = 7.6, 7.2 Hz,1H), 7.51 (dd, *J* = 8.0, 7.6 Hz, 2H), 7.40 – 7.38 (m, 2H), 7.26 – 7.24 (m, 2H), 4.78 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.55 (dd, *J* = 14.0, 6.0Hz, 1H), 3.24 (dd, *J* = 14.0, 9.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 134.8, 134.2, 134.0, 133.6, 132.3, 129.9, 129.5, 129.2, 129.0, 127.6, 116.7, 39.4, 33.9.

HRMS (ESI): Calcd for $[C_{16}H_{12}ClNONa]^+$ $[M+Na]^+$ 292.0500, Found 292.0508.

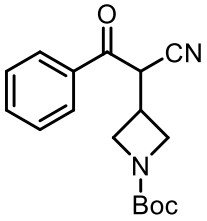


2-(Oxetan-3-yl)-3-oxo-3-phenylpropanenitrile (43). Synthesized according to the **General Procedure A** with benzaldehyde (0.3 mmol, 31.8 mg) and 2-(oxetan-3-ylidene)acetonitrile (0.2 mmol, 19.0 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **43** as a colorless oil (21.3 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.53 – 7.38 (m, 3H), 4.70 (dd, *J* = 10.0, 9.2 Hz, 1H), 4.62 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.90 – 3.73 (m, 2H), 3.57 – 3.50 (m, 1H), 2.35 – 2.07 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 131.7, 128.8, 127.9, 127.3, 117.5, 80.7, 74.0, 63.0, 46.8.

HRMS (ESI): Calcd for $[C_{12}H_{11}NO_2Na]^+$ $[M+Na]^+$ 224.0682, Found 292.0679.



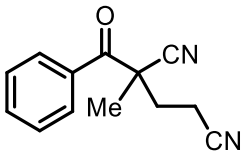
***tert*-Butyl 3-(1-cyano-2-oxo-2-phenylethyl)azetidine-1-carboxylate (44).** Synthesized according to

the **General Procedure A** with benzaldehyde (0.3 mmol, 31.8 mg) and *tert*-butyl 3-(cyanomethylene)azetidine-1-carboxylate (0.2 mmol, 19.0 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **44** as a yellow oil (44.0 mg, 73% yield).

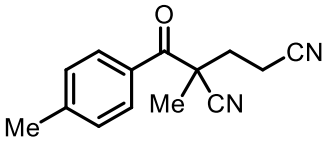
^{1}H NMR (400 MHz, Benzene-d_6) δ 7.68 (d, J = 7.6 Hz, 2H), 7.19 – 7.10 (m, 1H), 7.03 (dd, J = 7.6, 7.6 Hz, 2H), 4.00 – 3.80 (m, 3H), 3.72 (d, J = 7.6 Hz, 1H), 3.66 – 3.43 (m, 1H), 2.60 (d, J = 6.0 Hz, 1H), 1.43 (s, 9H).

^{13}C NMR (400 MHz, Benzene-d_6) δ 189.2, 156.0, 134.6, 134.2, 129.1, 129.1, 115.6, 79.4, 42.6, 28.4, 28.4.

HRMS (ESI): Calcd for $[C_{17}H_{20}N_2O_3Na]^+$ $[M+Na]^+$ 323.1366, Found 323.1365.



2-Benzoyl-2-methylpentanedinitrile (4). Synthesized according to the **General Procedure A** with benzaldehyde (0.3 mmol, 31.8 mg) and 2-methylenepentanedinitrile (0.2 mmol, 21.2 mg) at 85 °C for 6 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **4** as a yellow oil (10.6 mg, 25% yield).

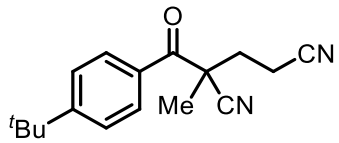


2-Methyl-2-(4-methylbenzoyl)pentanedinitrile (45). Synthesized according to the **General Procedure C** with *p*-tolylmethanol (0.2 mmol, 24.4 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 °C for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **45** as a colorless oil (29.4 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 2.67 – 2.53 (m, 3H), 2.44 (s, 3H), 2.16 (ddd, J =15.2, 10.8, 4.8 Hz, 1H), 1.77 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9, 145.9, 130.7, 129.7, 129.7, 120.6, 118.2, 44.9, 33.6, 24.9, 21.9, 13.9.

HRMS (ESI): Calcd for $[C_{14}H_{14}N_2ONa]^+$ $[M + Na]^+$ 249.0998, Found 249.0990.



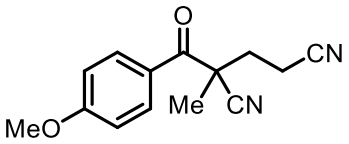
2-(4-(*tert*-Butyl)benzoyl)-2-methylpentanedinitrile (46). Synthesized according to the **General Procedure C** with (4-(*tert*-butyl)phenyl)methanol (0.2 mmol, 32.8 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 °C for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **46** as a colorless oil (24.7 mg, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 2.68 – 2.53 (m, 3H), 2.17 (ddd, J = 14.4, 10.4, 4.8 Hz, 1H), 1.78 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 158.8, 130.6, 129.7, 126.1, 120.6, 118.2, 44.9, 35.5, 33.6, 31.1,

24.8, 13.9.

HRMS (ESI): Calcd for $[C_{17}H_{20}N_2ONa]^+$ $[M + Na]^+$ 291.1468, Found 291.1459.

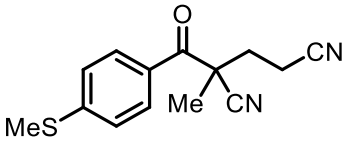


2-(4-Methoxybenzoyl)-2-methylpentanedinitrile (47). Synthesized according to the **General Procedure C** with (4-methoxyphenyl)methanol (0.2 mmol, 27.6 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 °C for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **47** as a colorless oil (30 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 6.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H), 2.67 – 2.48 (m, 3H), 2.15 (ddd, *J* =15.2, 10.4, 4.4 Hz, 1H), 1.76 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 164.6, 132.2, 125.9, 120.8, 118.3, 114.3, 55.8, 44.6, 33.6, 24.9, 13.8.

HRMS (ESI): Calcd for $[C_{14}H_{14}N_2O_2Na]^+$ $[M + Na]^+$ 265.0947, Found 265.0956.

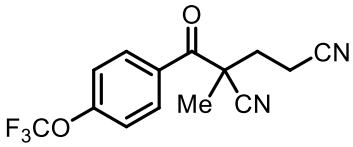


2-Methyl-2-(4-(methylthio)benzoyl)pentanedinitrile (48). Synthesized according to the **General Procedure C** with (4-(methylthio)phenyl)methanol (0.2 mmol, 30.8 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 °C for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **48** as a yellow oil (26.8 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 2.67 – 2.54 (m, 3H), 2.53 (s, 3H), 2.15 (ddd, *J* = 14.8, 10.4, 4.4 Hz, 1H), 1.77 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 148.7, 129.9, 129.1, 125.1, 120.6, 118.2, 44.8, 33.6, 24.9, 14.7, 13.9.

HRMS (ESI): Calcd for $[C_{14}H_{14}N_2OSNa]^+$ $[M + Na]^+$ 281.0719, Found 281.0722.



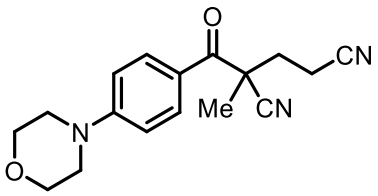
2-Methyl-2-(4-(trifluoromethoxy)benzoyl)pentanedinitrile (49). Synthesized according to the **General Procedure C** with (4-(trifluoromethoxy)phenyl)methanol (0.2 mmol, 38.4 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 °C for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **49** as a colorless oil (30.8 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 2.69 – 2.56 (m, 3H), 2.18 (ddd, *J* = 14.8, 10.0, 4.8 Hz, 1H), 1.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 153.7, 131.9, 131.4, 120.6, 120.4 (q, *J* = 258.2 Hz), 120.2, 118.0, 45.1, 33.4, 24.8, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ –57.58.

HRMS (ESI): Calcd for $[C_{14}H_{11}N_2O_2F_3Na]^+$ $[M + Na]^+$ 319.0665, Found 319.0661.

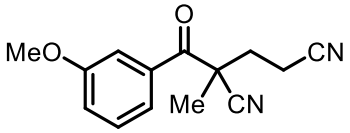


2-Methyl-2-(4-morpholinobenzoyl)pentanedinitrile (50). Synthesized according to the **General Procedure C** with (4-morpholinophenyl)methanol (0.2 mmol, 38.6 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 °C for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **50** as a brown oil (30.9 mg, 52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 9.2 Hz, 2H), 3.84 (t, J = 5.2 Hz, 4H), 3.36 (t, J = 5.2 Hz, 4H), 2.71 – 2.41 (m, 3H), 2.12 (ddd, J = 15.2, 10.8, 4.4 Hz, 1H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 154.8, 132.0, 122.8, 121.1, 118.4, 112.9, 66.5, 47.0, 44.2, 33.6, 24.9, 13.8.

HRMS (ESI): Calcd for $[C_{17}H_{20}N_3O_2]^+$ $[M+ H]^+$ 298.1550, Found 298.1546.

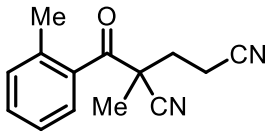


2-(3-Methoxybenzoyl)-2-methylpentanedinitrile (51). Synthesized according to the **General Procedure C** with 3-methoxybenzaldehyde (0.2 mmol, 27.2 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 °C for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **51** as a brown oil (24.2 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (ddd, J = 7.6, 1.6, 0.8 Hz, 1H), 7.59 (dd, J = 2.4, 2.0 Hz, 1H), 7.43 (dd, J = 8.0, 8.0 Hz, 1H), 7.19 (ddd, J = 8.0, 2.4, 0.8 Hz,, 1H), 3.87 (s, 3H), 2.68 – 2.55 (m, 3H), 2.17 (ddd, J = 15.2, 10.4, 6.4 Hz, 1H), 1.78 (s, 3H).

^{13}C NMR (100MHz, $CDCl_3$) δ 192.4, 160.1, 134.6, 130.0, 121.9, 121.0, 120.4, 118.1, 114.1, 55.7, 45.2, 33.6, 24.9, 13.9.

HRMS (ESI): Calcd for $[C_{14}H_{14}N_2O_2Na]^+$ $[M + Na]^+$ 265.0947, Found 265.0942.

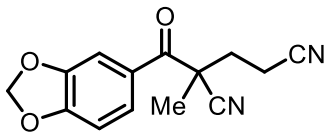


2-Methyl-2-(2-methylbenzoyl)pentanedinitrile (52). Synthesized according to the **General Procedure C** with *o*-tolylmethanol (0.2 mmol, 24.4 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 ℃ for 24 h. Purified by flash column chromatography on silica gel (PE:EA = 15:1) to give **52** as a colorless oil (22.6 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.73 (m, 1H), 7.46 – 7.42 (m, 1H), 7.33 – 7.30 (m, 2H), 2.63 – 2.54 (m, 3H), 2.38 (s, 3H), 2.23 – 2.13 (m, 1H), 1.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 137.7, 135.4, 132.2, 132.1, 127.3, 125.7, 119.9, 118.0, 47.6, 33.3, 24.2, 20.7, 14.0.

HRMS (ESI): Calcd for $[C_{14}H_{14}N_2ONa]^+$ $[M + Na]^+$ 249.0998, Found 249.0989.

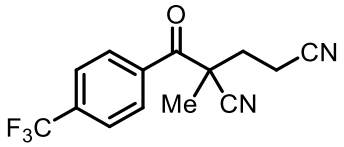


2-(Benzo[*d*][1,3]dioxole-5-carbonyl)-2-methylpentanedinitrile (53). Synthesized according to the **General Procedure C** with benzo[*d*][1,3]dioxol-5-ylmethanol (0.2 mmol, 30.4 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 °C for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **53** as a colorless oil (27.6 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.55 (d, *J* = 1.6 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.08 (s, 2H), 2.66 – 2.48 (m, 3H), 2.15 (ddd, *J* = 15.2, 10.4, 4.4 Hz, 1H), 1.76 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 153.1, 148.6, 127.6, 126.5, 120.7, 118.2, 109.4, 108.3, 102.5, 44.7, 33.7, 25.1, 13.9.

HRMS (ESI): Calcd for $[C_{14}H_{13}N_2O_3]^+$ $[M + H]^+$ 257.0921, Found 257.0929.



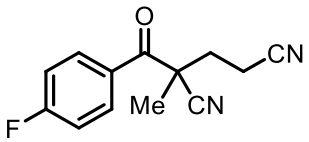
2-Methyl-2-(4-(trifluoromethoxy)benzoyl)pentanedinitrile (54). Synthesized according to the **General Procedure C** with (4-(trifluoromethoxy)phenyl)methanol (0.2 mmol, 35.2 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 °C for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **54** as a colorless oil (19.0 mg, 34% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 2.71 – 2.57 (m, 3H), 2.20 (ddd, *J* = 14.8, 10.0, 5.2 Hz, 1H), 1.81 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 136.2, 135.7 (q, *J* = 32.6 Hz), 129.9, 126.2 (q, *J* = 3.6 Hz), 123.3 (q, *J* = 271.4 Hz), 119.9, 117.9, 45.4, 33.3, 24.7, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ –63.45.

HRMS (ESI): Calcd for $[C_{14}H_{11}N_2OF_3Na]^+$ $[M + Na]^+$ 303.0716, Found 303.0716.



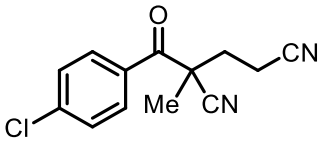
2-(4-Fluorobenzoyl)-2-methylpentanedinitrile (55). Synthesized according to the **General Procedure C** with (4-fluorophenyl)methanol (0.2 mmol, 25.2 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 ℃ for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **55** as a brown oil (25.8 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.19 (m, 2H), 7.23 – 7.18 (m, 2H), 2.68 – 2.51 (m, 3H), 2.17 (ddd, *J* = 14.8, 10.4, 4.8 Hz, 1H), 1.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 166.5 (d, *J* = 256.7 Hz), 132.5 (d, *J* = 9.5 Hz), 129.7 (d, *J* = 2.9 Hz), 120.4, 118.1, 116.4 (d, *J* = 21.8 Hz), 45.0, 33.5, 24.8, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ −101.66.

HRMS (ESI): Calcd for $[C_{13}H_{11}N_2OFNa]^+$ [M + Na]$^+$ 253.0748, Found 253.0747.

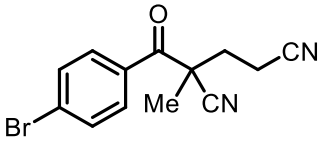


2-(4-Chlorobenzoyl)-2-methylpentanedinitrile (56). Synthesized according to the **General Procedure C** with (4-chlorophenyl)methanol (0.2 mmol, 28.4 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 °C for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **56** as a white jelly (22.6 mg, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 2.68 – 2.55 (m, 3H), 2.17 (ddd, *J* = 14.8, 10.4, 4.8 Hz, 1H), 1.78 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 141.4, 131.6, 131.0, 129.5, 120.2, 118.0, 45.1, 33.4, 24.8, 13.9.

HRMS (ESI): Calcd for $[C_{13}H_{11}N_2OClNa]^+$ [M + Na]$^+$ 269.0452, Found 269.0443.

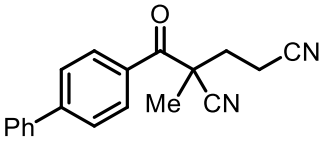


2-(4-Bromobenzoyl)-2-methylpentanedinitrile (57). Synthesized according to the **General Procedure C** with (4-bromophenyl)methanol (0.2 mmol, 37.2 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 °C for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **57** as a colorless oil (26.1 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 2.67 – 2.50 (m, 3H), 2.17 (ddd, *J* = 14.8, 10.4, 4.8 Hz, 1H), 1.77 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 132.5, 132.0, 131.0, 130.2, 120.2, 118.0, 45.1, 33.4, 24.8, 13.9.

HRMS (ESI): Calcd for $[C_{13}H_{11}N_2OBrNa]^+$ [M+Na]$^+$ 312.9947, Found 312.9943.

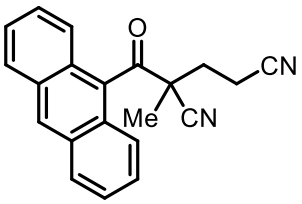


2-([1,1'-Biphenyl]-4-carbonyl)-2-methylpentanedinitrile (58). Synthesized according to the **General Procedure B** with [1,1'-biphenyl]-4-ylmethanol (0.2 mmol, 36.8 mg) and acrylonitrile (0.4 mmol, 21.2 mg). Then, another portion of acrylonitrile (0.6 mmol, 31.8 mg), was sequentially added into the Schlenk tube under N_2 atmosphere. The reaction mixture was stirred at 85 ℃ for another 8 h. The mixture was then concentrated in *vacuo*. The crude product was purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **58** as a white jelly (33.4 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.63 (m, 2H), 7.51 – 7.48(m, 2H), 7.46 – 7.42 (m, 1H), 2.72 – 2.53 (m, 3H), 2.20 (ddd, *J* = 15.2, 10.4, 4.8 Hz, 1H), 1.82 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.8, 147.3, 139.3, 131.9, 130.2, 129.2, 128.9, 127.6, 127.4, 120.5, 118.2, 45.1, 33.6, 24.9, 13.9.

HRMS (ESI): Calcd for $[C_{19}H_{16}N_2ONa]^+$ [M + Na]$^+$ 311.1155, Found 311.1157.

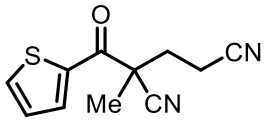


2-(Anthracene-9-carbonyl)-2-methylpentanedinitrile (59). Synthesized according to the **General Procedure C** with anthracene-9-carbaldehyde (0.2 mmol, 41.2 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 °C for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **59** as a brown jelly (31.2 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.69 – 7.52 (m, 6H), 2.79 – 2.59 (m, 3H), 2.38 – 2.30 (m, 1H), 1.74 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 131.4, 131.0, 130.3, 129.4, 127.9, 126.1, 126.1, 124.1, 119.3, 118.0, 50.2, 33.1, 23.1, 13.9.

HRMS (ESI): Calcd for $[C_{21}H_{16}N_2ONa]^+$ $[M + Na]^+$ 335.1155, Found 335.1154.

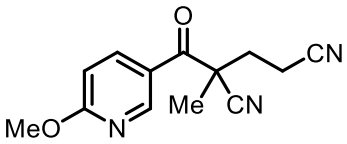


2-Methyl-2-(thiophene-2-carbonyl)pentanedinitrile (60). Synthesized according to the **General Procedure C** with thiophen-2-ylmethanol (0.2 mmol, 22.8 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 °C for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 6:1) to give **60** as a yellow oil (24.0 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 4.0, 0.8 Hz, 1H), 7.80 (dd, *J* = 4.8, 0.4 Hz, 1H), 7.21 (dd, *J* = 4.8, 4.0 Hz, 1H), 2.65 – 2.50 (m, 3H), 2.18 (ddd, *J* = 13.2, 7.2, 5.6 Hz, 1H), 1.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 184.9, 139.6, 136.9, 134.6, 129.0, 120.5, 118.1, 45.4, 33.3, 25.1, 13.8.

HRMS (ESI): Calcd for $[C_{11}H_{10}N_2OSNa]^+$ $[M + Na]^+$ 241.0406, Found 241.0405.

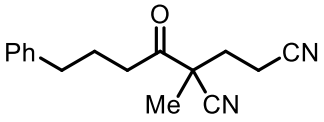


2-(6-Methoxynicotinoyl)-2-methylpentanedinitrile (61). Synthesized according to the **General Procedure C** with (6-methoxypyridin-3-yl)methanol (0.2 mmol, 27.8 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 ℃ for 12 h. Purified by flash column chromatography on silica gel (PE:EA = 10:1) to give **61** as a colorless oil (25.8 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, *J* = 2.4 Hz, 1H), 8.29 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 4.03 (s, 3H), 2.67 – 2.50 (m, 3H), 2.16 (ddd, *J* = 14.8, 10.4, 4.4 Hz, 1H), 1.77 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 167.4, 150.7, 139.4, 123.1, 120.3, 118.1, 111.7, 54.5, 44.9, 33.3, 24.7, 13.9.

HRMS (ESI): Calcd for $[C_{13}H_{13}N_3O_2Na]^+$ $[M + Na]^+$ 266.0900, Found 266.0909.

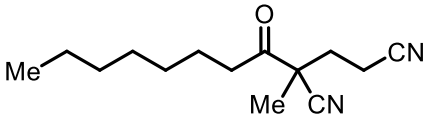


2-Methyl-2-(4-phenylbutanoyl)pentanedinitrile (62). Synthesized according to the **General Procedure C** with 4-phenylbutan-1-ol (0.2 mmol, 30.0 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 ℃ for 24 h. Purified by flash column chromatography on silica gel (PE:EA = 15:1) to give **62** as a colorless oil (31.0 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.23 – 7.21 (m, 1H), 7.19 – 7.16 (m, 2H), 2.82 (t, *J* = 6.4 Hz, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.50 – 2.31 (m, 3H), 2.05 – 1.94 (m, 3H), 1.50 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 140.9, 128.7, 128.6, 126.4, 119.8, 117.8, 47.9, 38.9, 34.8, 32.0, 24.8, 23.3, 13.8.

HRMS (ESI): Calcd for $[C_{16}H_{18}N_2ONa]^+$ [M+ Na]$^+$ 277.1311, Found 277.1305.

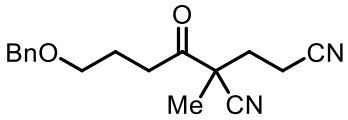


2-Methyl-2-octanoylpentanedinitrile (63). Synthesized according to the **General Procedure C** with octan-1-ol (0.2 mmol, 26 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 °C for 24 h. Purified by flash column chromatography on silica gel (PE:EA = 15:1) to give **63** as a brown oil (25.7 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (t, *J* = 7.2 Hz, 2H), 2.51 – 2.34 (m, 3H), 2.04 – 1.96 (m, 1H), 1.64 – 1.60 (m, 2H), 1.53 (s, 3H), 1.29 – 1.24 (m, 7H), 0.89 – 0.86 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 119.8, 117.9, 47.9, 39.9, 32.0, 31.7, 29.1, 29.0, 23.6, 23.2, 22.7, 14.1, 13.9.

HRMS (ESI): Calcd for $[C_{14}H_{22}N_2ONa]^+$ [M+ Na]$^+$ 257.1624, Found 257.1632.

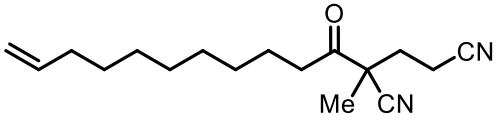


2-(4-(Benzyloxy)butanoyl)-2-methylpentanedinitrile (64). Synthesized according to the **General Procedure C** with 4-(benzyloxy)butan-1-ol (0.2 mmol, 36.0 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 ℃ for 24 h. Purified by flash column chromatography on silica gel (PE:EA = 15:1) to give **64** as a colorless oil (32.4 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 5H), 4.47 (s, 2H), 3.54 – 3.46 (m, 2H), 2.91 (t, *J* = 6.8 Hz, 2H), 2.40 – 2.26 (m, 3H), 2.04 – 1.91 (m, 3H), 1.49 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 138.2, 128.6, 128.0, 128.0, 119.8, 118.0, 73.2, 68.8, 48.0, 36.6, 31.9, 24.0, 23.2, 13.7.

HRMS (ESI): Calcd for $[C_{17}H_{21}N_2O_2]^+$ [M + H]$^+$ 285.1598, Found 285.1600.



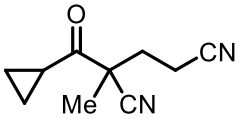
2-Methyl-2-(undec-10-enoyl)pentanedinitrile (65). Synthesized according to the **General Procedure C** with undec-10-en-1-ol (0.2 mmol, 34.0 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 ℃ for 24 h.

Purified by flash column chromatography on silica gel (PE:EA = 15:1) to give **65** as a colorless oil (37.3 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 – 5.75 (m, 1H), 5.01 – 4.91 (m, 2H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.55 – 2.34 (m, 3H), 2.06 – 1.96 (m, 3H), 1.63 – 1.58 (m, 2H), 1.53 (s, 3H), 1.35 – 1.25 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 139.2, 119.8, 117.8, 114.3, 47.9, 39.8, 33.9, 31.9, 29.3, 29.1, 29.0, 23.6, 23.2, 13.9.

HRMS (ESI): Calcd for $[C_{17}H_{26}N_2ONa]^+$ $[M + Na]^+$ 297.1937, Found 297.1946.



2-(Cyclopropanecarbonyl)-2-methylpentanedinitrile (66). Synthesized according to the **General Procedure C** with cyclopropylmethanol (0.2 mmol, 14.4 mg) and acrylonitrile (1.0 mmol, 53.0 mg) at 85 ℃ for 24 h. Purified by flash column chromatography on silica gel (PE:EA = 15:1) to give **66** as a colorless oil (25.7 mg, 73% yield).

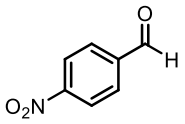
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 – 2.34 (m, 4H), 2.07 – 1.99 (m, 1H), 1.59 (s, 3H), 1.22 – 1.11 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 119.7, 117.9, 48.4, 31.6, 22.9, 18.0, 13.7, 13.6, 13.7.

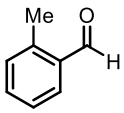
HRMS (ESI): Calcd for $[C_{10}H_{12}N_2ONa]^+$ $[M + Na]^+$ 199.0842, Found 199.0834.

Unsuccessful or less successful Substrates:

unsuccessful or less successful substrates for hydroacylation of acrylonitriles with aldehydes to β-ketonitriles:



N.R.



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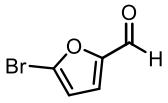

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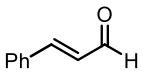

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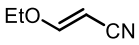
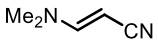


N.R.



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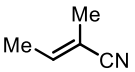

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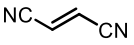
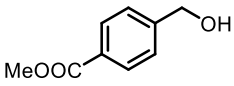
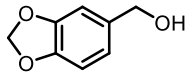


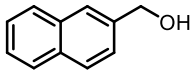
N.R.

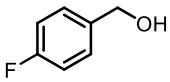
unsuccessful or less successful substrates for hydroacylation of acrylonitriles with alcohols to β-ketonitriles:

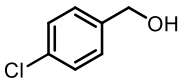
poor selectivity of β-ketonitrile and glutaronitrile

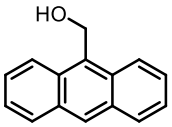




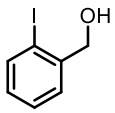




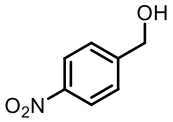




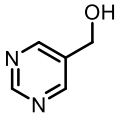
unsuccessful or less successful substrates for cross-coupling of acrylonitrile with alcohols to glutaronitriles:



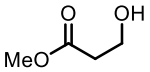
N.R.



N.R.

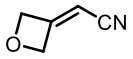


N.R.



N.R.

N.R.



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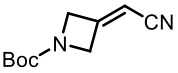
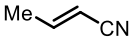
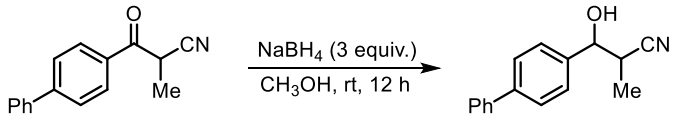


N.R.



β-ketonitrile product

V Synthetic Transformations of *β*-Ketonitrile and Glutaronitrile Derivatives



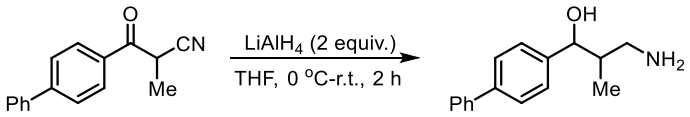
20 **67**, 87%

To a solution of *β*-ketonitrile **20** (0.2 mmol, 47.0 mg) in CH_3OH (5 mL) was added $NaBH_4$ (0.6 mmol, 22.7 mg), and the resulting mixture was stirred at room temperature for 12 h. Then the reaction was quenched with H_2O (2 mL). The resulting mixture was added DCM (10 mL), partitioned between H_2O and DCM, and then separated. The aqueous layer was extracted with DCM for three times (5 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (PE:EA) to give **67** as a white jelly (41.2 mg, 87% yield, d.r. = 1.2:1.).

^{1}H NMR (400 MHz, $CDCl_3$)*: Major isomer:* δ 7.64 – 7.58 (m, 4H), 7.50 – 7.44 (m, 4H), 7.36 (dd, *J* = 7.6, 7.6 Hz 1H), 4.78 (d, *J* = 6.4 Hz, 1H), 3.01 – 2.94 (m, 1H), 2.34 (s, 1H), 1.29 (d, *J* = 8.8 Hz, 3H); *Minor isomer:* 7.64 – 7.58 (m, 4H), 7.50 – 7.44 (m, 4H), 7.36 (dd, *J* = 7.6, 7.6 Hz 1H), 4.87 (d, *J* = 6.4 Hz, 1H), 3.10 – 3.03 (m, 1H), 2.34 (s, 1H), 1.29 (d, *J* = 8.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, (141.9), 140.6, (140.5), 139.1, (138.8), 129.0, 127.7, (127.7), 127.6, 127.5, 127.2, 127.0, 126.9, 121.1, (121.1), 75.1, (74.4), 34.7, (34.1), 14.9, 13.7.

HRMS (ESI): Calcd for $[C_{16}H_{16}NO]^+$ $[M+H]^+$ 238.1226, Found 238.1220.



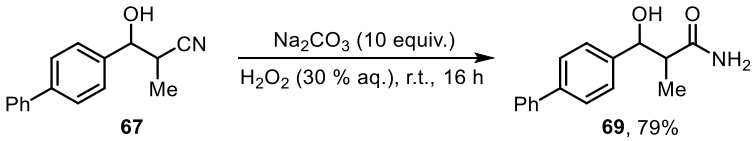
20 **68**, 52%

To a solution of *β*-ketonitrile **20** (0.2 mmol, 47.0 mg) in dry THF (10 mL) was added $LiAlH_4$ (0.4 mmol, 15.2 mg), and the resulting mixture was stirred for 2 h from 0 ºC to room temperature. Then the reaction was quenched with H_2O (2 mL). The resulting mixture was added DCM (10 mL). After separation, the aqueous layer was extracted with DCM for three times (5 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (PE:EA) to give **68** as a white jelly (25.0 mg, 52% yield, d.r. = 2:1.).

^{1}H NMR (400 MHz, $CDCl_3$) *Major isomer:* δ 7.62 – 7.52 (m, 4H), 7.47 – 7.37 (m, 4H), 7.33 (dd, *J* = 7.2, 7.2 Hz, 1H), 4.53 (d, *J* = 8.4 Hz, 1H), 4.37 (s, 3H), 3.14 – 2.73 (m, 2H), 1.91– 1.87 (m, 1H), 0.73 (d, *J* = 6.4 Hz, 3H). *Minor isomer:* 7.62 – 7.52 (m, 4H), 7.47 – 7.37 (m, 4H), 7.33 (dd, *J* = 7.2, 7.2 Hz, 1H), 5.00 (d, *J* = 2.8 Hz, 1H), 4.37 (s, 3H), 3.06 (d, *J* = 7.2 Hz, 2H), 1.91– 1.87 (m, 1H), 0.81 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.4, 141.1, 140.2, 139.7, 128.8, 127.4, 127.2, 127.2, 127.1, 127.1, 127.0, 126.8, 126.7, 81.2, 76.6, 47.3, 45.5, 40.4, 39.9, 15.5, 11.7.

HRMS (ESI): Calcd for $[C_{16}H_{18}NO]^+$ $[M+H]^+$ 240.1383, Found 240.1390.



67 **69**, 79%

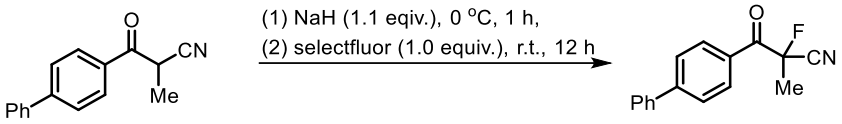
To a solution of **67** (0.2 mmol, 47.4 mg) in acetone (2 mL) were successively added 30% aqueous H_2O_2

solution (2 mL) and Na_2CO_3 (2.0 mmol, 212 mg), and the resulting suspension was stirred for 16 h at room temperature. After dilution with H_2O (5 mL), the resulting mixture was added DCM (10 mL), partitioned between H_2O and DCM. The aqueous layer was extracted with DCM for three times (5 mL × 3). The organic layers were collected, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (PE:EA) to give **69** as a white jelly (40.3 mg, 79% yield, d.r. = 2:1).[6]

^{1}H NMR (400 MHz, $CDCl_3$) *Major isomer:* δ 7.60 – 7.59 (m, 4H), 7.45 – 7.41 (m, 4H), 7.34 (dd, *J* = 7.6, 7.6 Hz, 1H), 5.81 (s, 1H), 5.52 (s, 1H), 5.15 (d, *J* = 3.2 Hz, 1H), 3.68 (s, 1H), 2.68 – 2.62 (m, 1H), 1.16 (d, *J* = 7.2 Hz, 3H). *Minor isomer:* δ 7.60 – 7.58 (m, 4H), 7.47 – 7.40 (m, 4H), 7.35 (dd, *J* = 7.6, 7.2 Hz, 1H), 5.73 (s, 1H), 5.40 (s, 1H), 4.80 (dd, *J* = 6.8, 4.4 Hz, 1H), 3.54 (d, *J* = 4.4 Hz, 1H), 2.66 (dq, *J* = 3.2, 6.8 Hz, 1H), 1.16 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) *Major isomer* δ 176.2, 143.5, 140.1, 138.5, 128.8, 127.2, 127.0, 126.5, 125.9, 73.5, 47.1, 13.5. *Minor isomer:* δ 176.6, 143.3, 134.0, 138.8, 128.8, 127.3, 127.2, 126.5, 126.2, 74.7, 47.0, 14.8.

HRMS (ESI): Calcd for $[C_{16}H_{17}NO_2]^+$ $[M+Na]^+$ 278.1151, Found 278.1152.



20 **70**, 87%

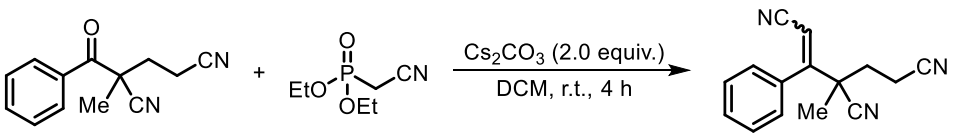
To a solution of **20** (0.2 mmol, 47.0 mg) in dry THF (2 mL) were added NaH (0.22 mmol, 8.8 mg, 60% in oil) under N_2 atmosphere, and the resulting suspension was stirred for 1 h at 0 ºC. Then the selectfluor (0.22 mmol, 80.0 mg,) was added to the resulting mixture, and the mixture was stirred for another 12 h from 0 ºC to room temperature. Then the reaction was quenched with H_2O (2 mL). The resulting mixture was added EA (10 mL). After separation, the aqueous layer was extracted with EA for three times (5 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (PE:EA) to give **70** as a white jelly (44.1 mg, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.8, 1.2 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.66 – 7.64 (m, 2H), 7.52 – 7.48 (m, 2H), 7.46 – 7.43 (m, 1H), 2.11 (d, *J* = 22.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 188.0 (d, *J* = 23.9 Hz), 147.81, 139.36, 131.0 (d, *J* = 5.5 Hz), 130.3 (d, *J* = 3.5 Hz), 129.2, 128.9, 127.7, 127.5, 115.9 (d, *J* = 23.1 Hz), 89.5 (d, *J* = 194.0 Hz), 23.9 (d, *J* = 24.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ −146.22.

HRMS (ESI): Calcd for $[C_{16}H_{12}NOFNa]^+$ $[M+Na]^+$ 276.0795, Found 276.0791.



4 **71**, 78% *E*/*Z* = 1.1:1

To a solution of Glutaronitrile **4** (0.2 mmol, 42.4 mg) in DCM (5 mL) was successively added diethyl (cyanomethyl)phosphonate (0.3 mmol, 53.1 mg) and Cs_2CO_3 (0.4 mmol, 130.3 mg), then the resulting

mixture was stirred at room temperature for 4 h. The reaction was quenched with H_2O (2 mL). The resulting mixture was added DCM (10 mL), partitioned between H_2O and DCM, and then separated. The aqueous layer was extracted with DCM for three times (5 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (PE:EA) to give **71** as a colorless jelly (36.7 mg, 78% yield, *E/Z* = 1.1:1).

Major isomer ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 3H), 7.28 – 7.22 (m, 2H), 5.62 (s, 1H), 2.78 – 2.67 (m, 1H), 2.66 – 2.56 (m, 2H), 2.38 (ddd, *J* = 15.2, 10.0, 6.4 Hz, 1H), 1.93 (s, 3H)

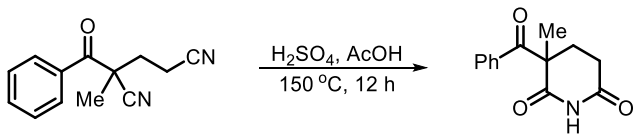
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 137.6, 130.3, 128.9, 127.4, 119.7, 117.7, 114.6, 101.7, 43.2, 34.8, 25.9, 14.1.

HRMS (ESI): Calcd for $[C_{15}H_{14}N_3]^+$ $[M+H]^+$ 236.1182, Found 236.1172.

Minor isomer ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.49 (m, 3H), 7.19 – 7.17 (m, 2H), 6.05 (s, 1H), 2.63 – 2.50 (m, 2H), 2.13 – 2.00 (m, 2H), 1.57 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 132.6, 130.3, 129.3, 128.2, 119.5, 117.6, 114.9, 103.4, 43.6, 33.5, 24.5, 13.8.

HRMS (ESI): Calcd for $[C_{15}H_{14}N_3]^+$ $[M+H]^+$ 236.1182, Found 236.1173.



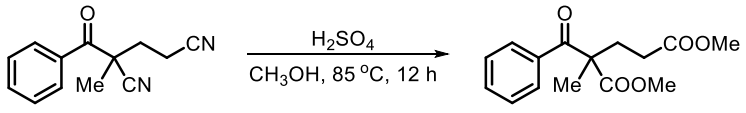
4 **72**, 36%

Glutaronitrile **4** (0.2 mmol, 42.4 mg), concentrated H_2SO_4 (0.6 mL) and AcOH (1.0 mL) were successively added into a Schlenk reaction tube under an air atmosphere. The mixture was heated at 150 ℃ for 12 h. after the reaction completed, the resulting dark-brown liquid was poured into crushed ice and extracted with DCM for three times (10 mL × 3). The organic layer was repeatedly washed with a saturated Na_2CO_3 solution, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (PE:EA) to give **72** as a colorless jelly (16.7 mg, 36% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.55 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.43 (dd, *J* = 8.0, 8.0 Hz, 2H), 2.74 – 2.68 (m, 3H), 1.95 – 1.86 (m, 1H), 1.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 173.8, 171.8, 135.2, 133.3, 129.0, 128.8, 54.8, 29.8, 29.2, 21.9.

HRMS (ESI): Calcd for $[C_{13}H_{14}NO_3]^+$ $[M+H]^+$ 232.0968, Found 232.0961.



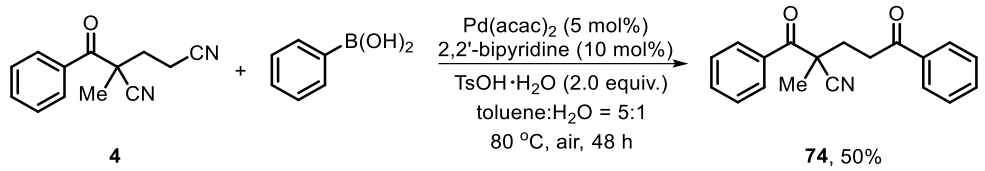
4 **73**, 44%

Glutaronitrile **4** (0.2 mmol, 42.4 mg), CH_3OH (2.0 mL) and concentrated H_2SO_4 (1.0 mL) were successively added into a Schlenk reaction tube under an air atmosphere. The mixture was heated at 85 ℃ for 12 h, Then the reaction was quenched with a saturated Na_2CO_3 solution and extracted with DCM for three times (5 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (PE:EA) to give **73** as a colorless oil (24.5 mg, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81– 7.79 (m, 2H), 7.55 – 7.51 (m, 1H), 7.44 – 7.40 (m, 2H), 3.65 (s, 3H), 3.64 (s, 3H), 2.44 – 2.24 (m, 4H), 1.53 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 174.4, 173.4, 135.3, 133.0, 128.8, 128.6, 56.2, 52.7, 51.9, 31.5, 29.3, 21.3.

HRMS (ESI): Calcd for $[C_{15}H_{18}O_5Na]^+$ $[M+ Na]^+$ 301.1046, Found 301.1056.



Glutaronitrile **4** (0.4 mmol, 84.8 mg), phenylboronic acid (0.2 mmol, 24.4 mg), $Pd(acac)_2$ (0.01 mmol, 3.1 mg), 2,2'-bipyridine (0.02 mmol, 3.1 mg), TsOH·H_2O (0.4 mmol, 76.1 mg), toluene (2 mL) and H_2O (0.4 mL) were successively added into a Schlenk reaction tube under an air atmosphere. and the resulting mixture was stirred at 85 ℃ for 12 h The resulting mixture was poured into ethyl acetate, which was washed with saturated $NaHCO_3$ solution (10 mL) and brine (10 mL). After the aqueous layer was extracted with ethyl acetate for three times (5 mL × 3), the combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel (PE:EA) to give **74** as a colorless oil (29.1 mg, 50% yield).

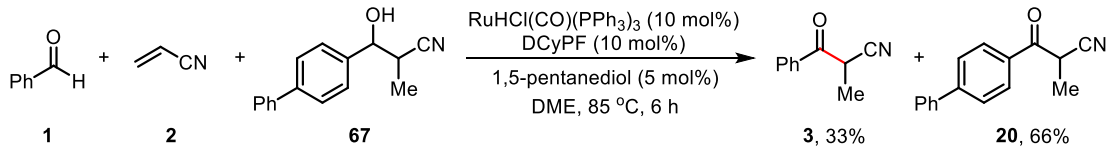
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.17 (m, 2H), 7.97 – 7.94 (m, 2H), 7.66 – 7.45 (m, 6H), 3.29 – 3.12 (m, 2H), 2.70 (ddd, *J* = 15.6, 10.4, 5.2 Hz, 1H), 2.32 (ddd, *J* = 16.0, 10.8, 5.2 Hz, 1H), 1.80 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 193.9, 136.6, 134.1, 134.1, 133.6, 129.5, 129.0, 128.8, 128.2, 121.8, 45.6, 34.5, 32.5, 24.6.

HRMS (ESI): Calcd for $[C_{19}H_{17}NO_2Na]^+$ $[M+Na]^+$ 314.1151, Found 314.1142.

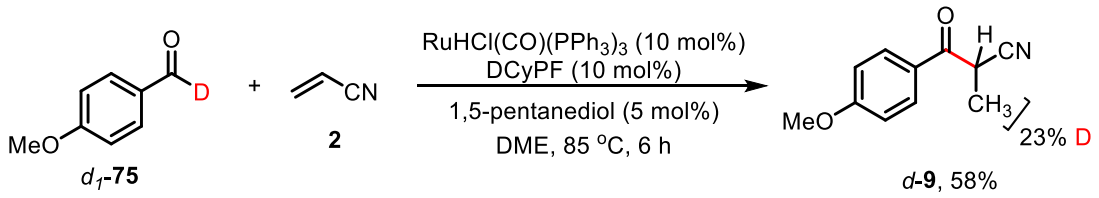
VI Control Experiments and Mechanistic Studies

(1) Control Experiment with *β*-Hydroxynitrile as an Additive

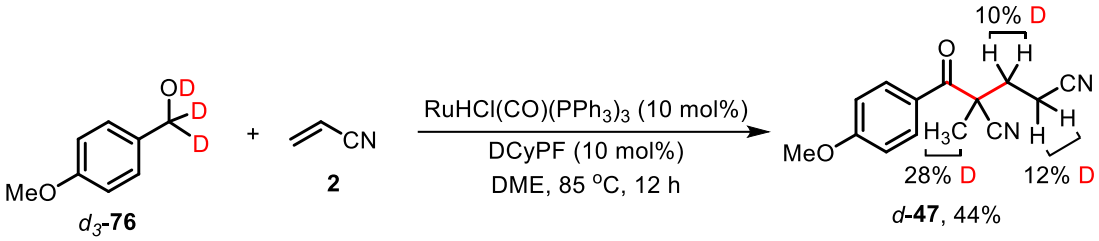


According to the **General Procedure A** with benzaldehyde **1** (0.3 mmol, 31.8 mg) and acrylonitrile **2** (10.6 mg, 0.2 mmol) as substrates. The *β*-hydroxynitrile **67** (47.4 mg, 0.2 mmol) was added as an additive. After reaction for 6 h, the *β*-ketonitrile **20** was obtained in 66% NMR yield and **3** was obtained in 33% NMR yield. The results might suggest a process of *β*-hydride elimination from alkoxy ruthenium species and *β*-hydroxynitrile should be the reaction intermediate in this hydroacylation reaction.

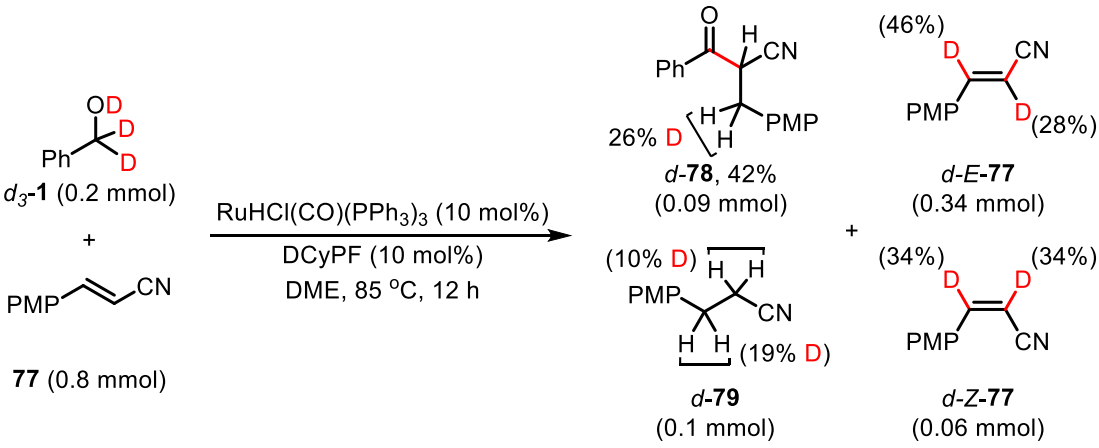
(2) Deuterium Labelling Experiment



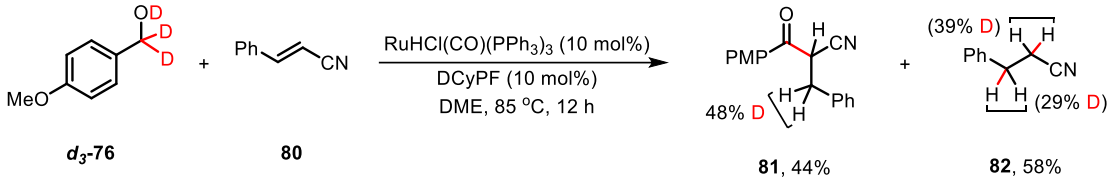
According to the **General Procedure A** with deuterated *para*-methoxybenzaldehyde (*d*$_1$-**75**) (0.3 mmol, 41.0 mg) and acrylonitrile **2** (10.6 mg, 0.2 mmol) as substrates. The reaction mixture was concentrated under reduced pressure, which was purified by flash column chromatography on silica gel (PE:EA) to give *d*-**9** in 58% isolated yield. ^{1}H NMR analysis revealed that deuterium was incorporated into only the *β*'-position of the resulting *β*-ketonitrile product.



According to the **General Procedure B** with deuterated *para*-methoxyphenylmethanol *d*$_3$-**76** (0.2 mmol, 22.2 mg) and acrylonitrile **2** (53.0 mg, 1.0 mmol) as substrates. The reaction mixture was concentrated under reduced pressure, which was purified by flash column chromatography on silica gel (PE:EA) to give *d*-**47** in 44% isolated yield. ^{1}H NMR analysis revealed that deuterium was incorporated into only the *β*'-position of the resulting *β*-ketonitrile product.



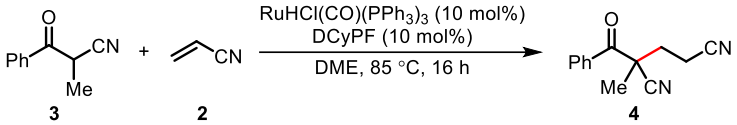
According to the **General Procedure B** with deuterated *para*-methoxyphenylmethanol *d*$_3$-**1** (0.2 mmol, 28.2 mg) and *para*-OMe-substituted cinnamonitrile **77** (103.2 mg, 0.8 mmol) as substrates. The reaction mixture was concentrated under reduced pressure, which was purified by flash column chromatography on silica gel (PE:EA) to give *d*-**78** in 42% isolated yield with deuterated 3-(4-methoxyphenyl)propanenitrile as alkene hydrogenation product. ^{1}H NMR analysis revealed that deuterium was incorporated into only the *β*'-position of the resulting *β*-ketonitrile product. Moreover, we recovered the deuterated cinnamonitrile *d*-*E*-**77** and *d*-*Z*-**77** after the cross-coupling reaction. These results clearly indicate the reversibility of hydrometallation of acrylonitrile with Ru–H complex.



d_3-**76** **80** **81**, 44% **82**, 58%

According to the **General Procedure B** with deuterated *para*-methoxyphenylmethanol d_3-**76** (0.2 mmol, 28.2 mg) and cinnamonitrile **80** (51.6 mg, 0.4 mmol) as substrates. The reaction mixture was concentrated under reduced pressure, which was purified by flash column chromatography on silica gel (PE:EA) to give **81** in 44% isolated yield with deuterated 3-phenylpropanenitrile as alkene hydrogenation product. ^{1}H NMR analysis revealed that deuterium was incorporated into only the *β*'-position of the resulting *β*-ketonitrile product, while deuterium was incorporated into both the α and *β* position of alkene hydrogenation product. These results clearly indicate the reversibility of hydrometallation of acrylonitrile with Ru–H complex.

(3) Control Experiments toward Pentanedinitrile Product 4



3 **2** **4**

Entry	Variations from above conditions	Yield (%)[b]
1	none	90
2	without Ru cat./DCyPF	0
3	without Ru cat.	0
4	without DCyPF	50
5	without Ru cat./DCyPF, with 20 mol% PPh_3	0
6	with 5 mol% pentane-1,5-diol	57
7	with 1 equiv pentane-1,5-diol	<5

[a]Reaction conditions: **3** (0.2 mmol), **2** (1.0 equiv), $RuHCl(CO)(PPh_3)_3$ (10 mol%), DCyPF (10 mol%), DME (2 mL), 85 ºC, 16 h, if otherwise noted. [b]Isolated yield.

VII References

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4. Amatore, M.; Gosmini, C.; Périchon, J. *J. Org. Chem.* **2006**, *71*, 6130 – 6134.
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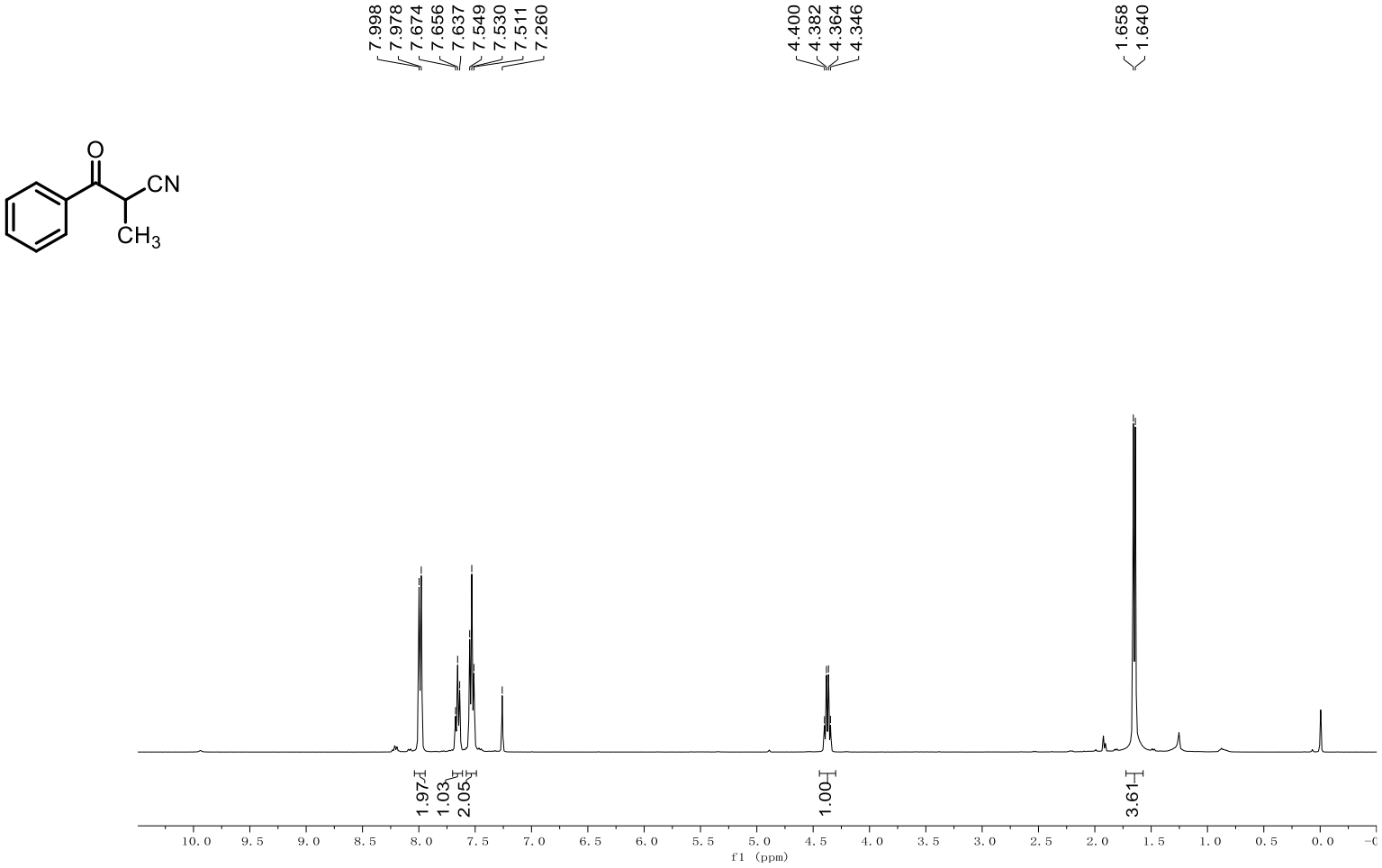
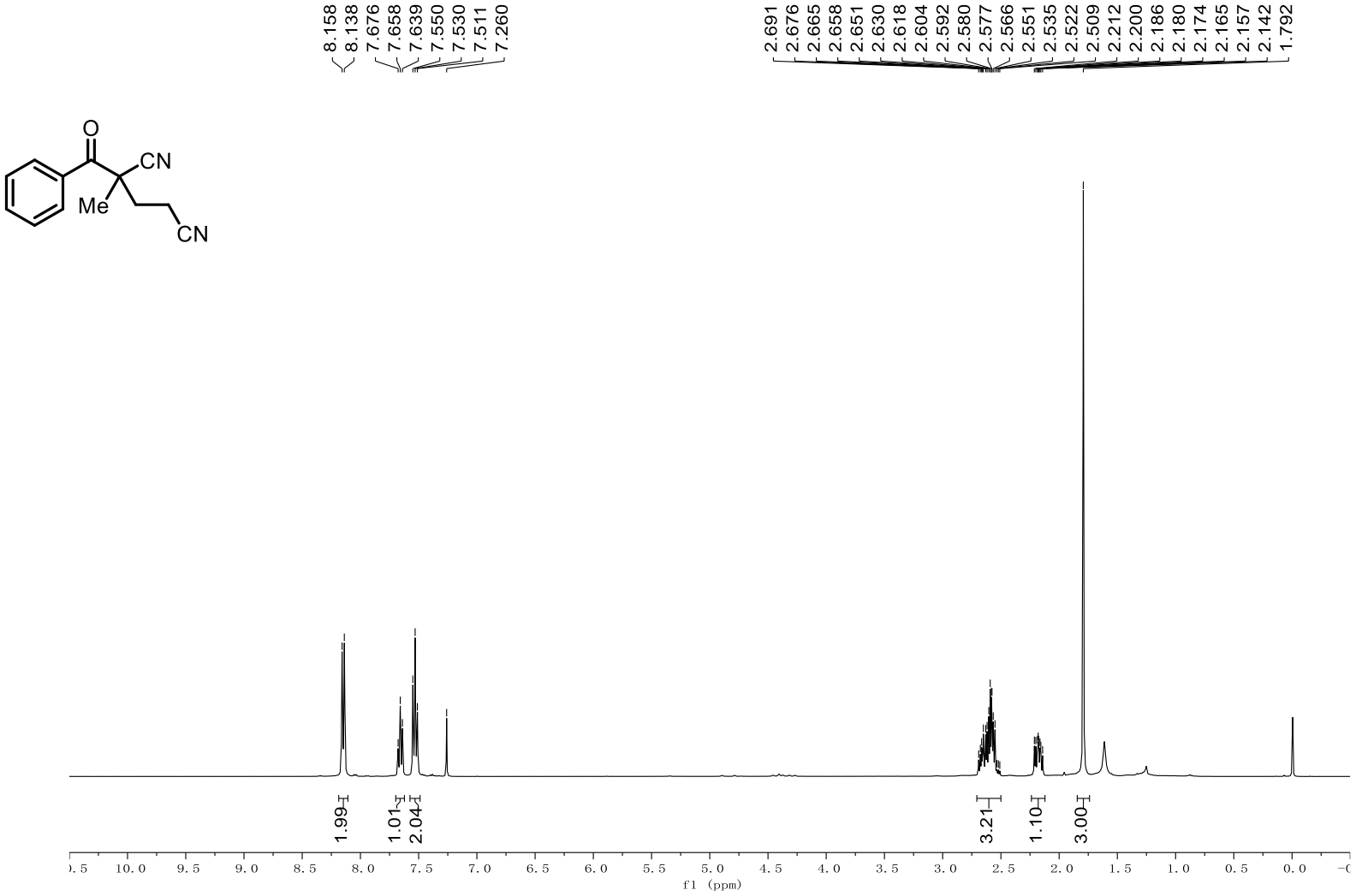
VII NMR Spectra

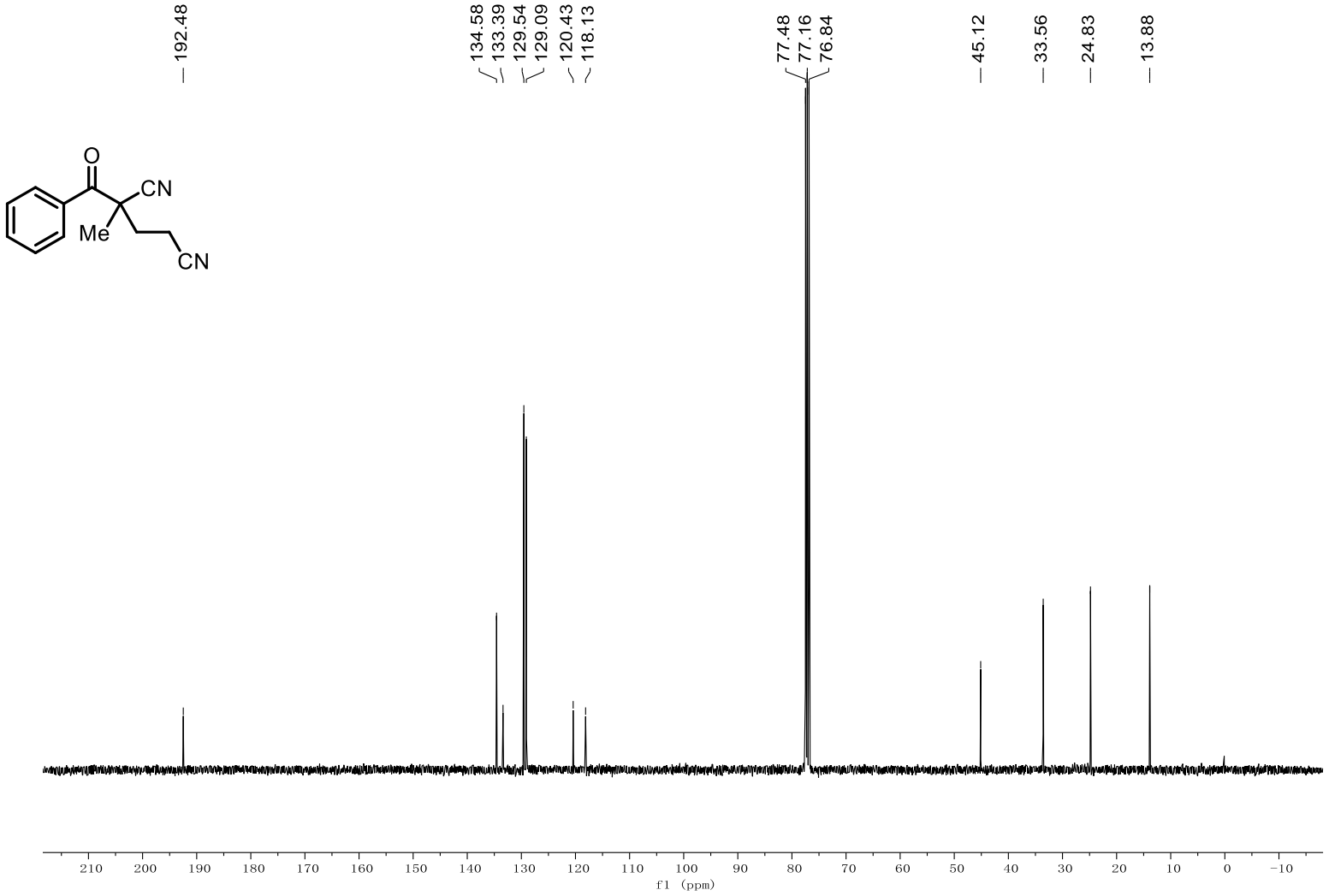
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxo-3-phenylpropanenitrile (3)



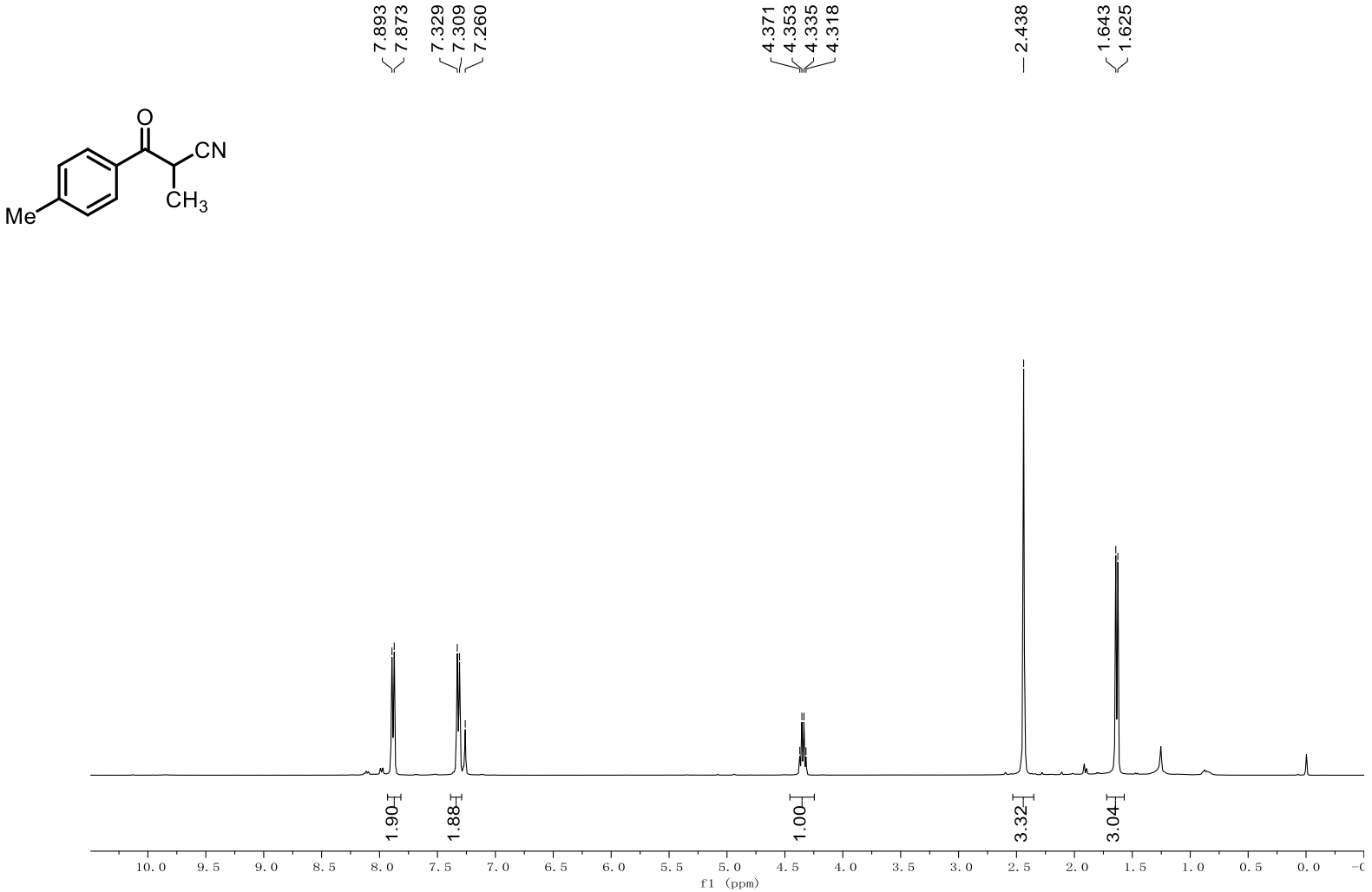
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Benzoyl-2-methylpentanedinitrile (4)



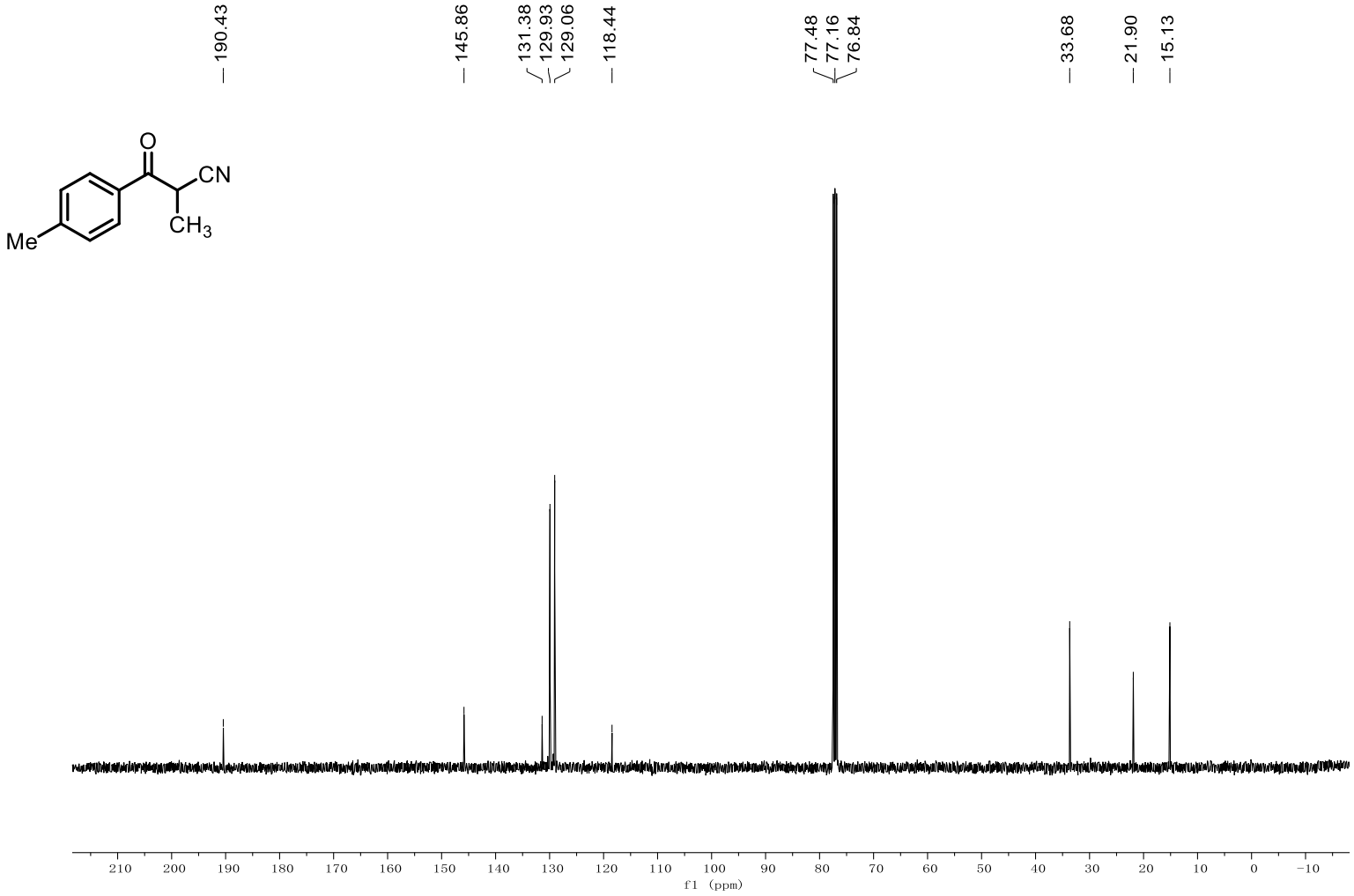
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Benzoyl-2-methylpentanedinitrile (4)



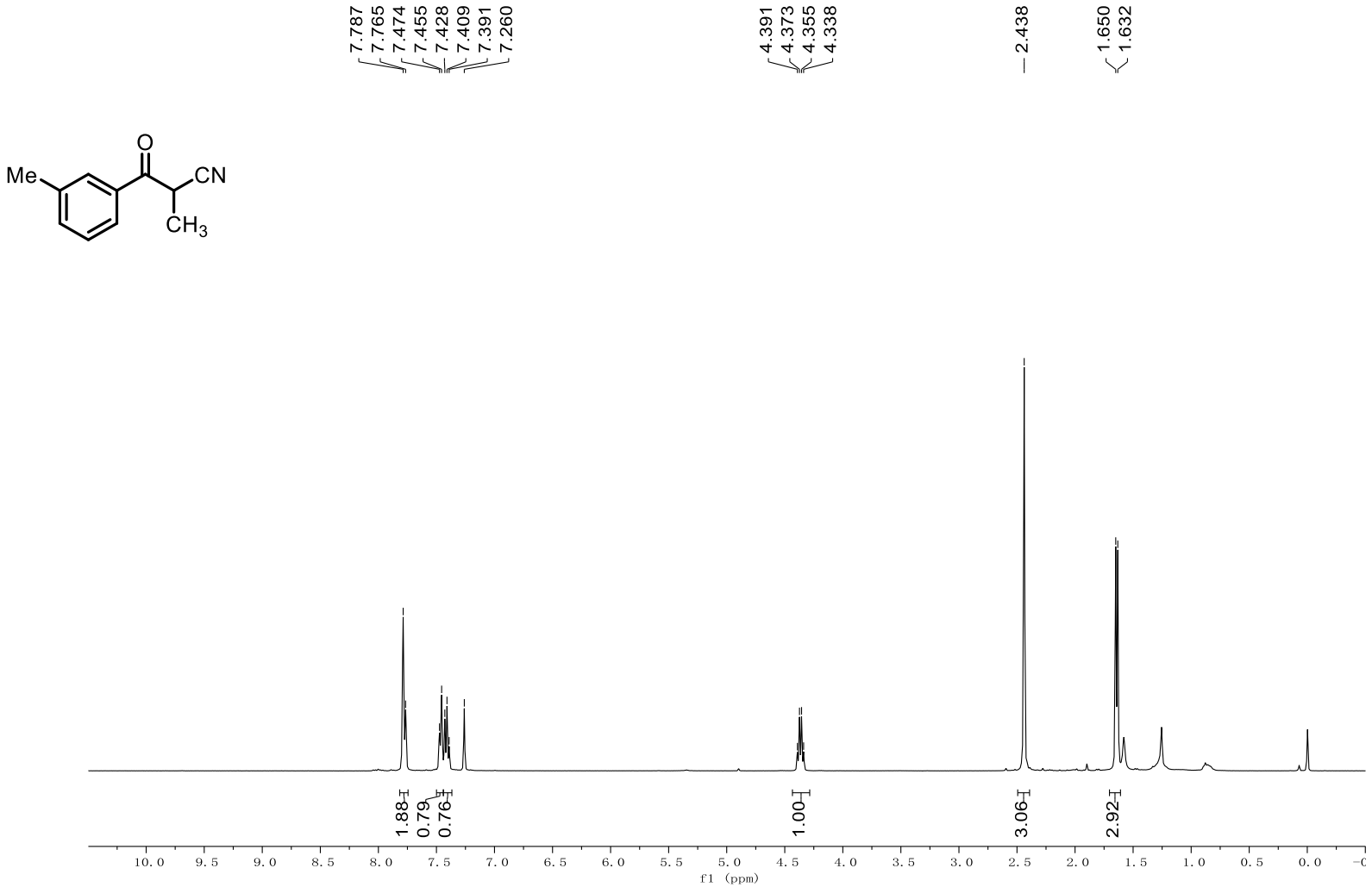
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxo-3-(*p*-tolyl)propanenitrile (6)



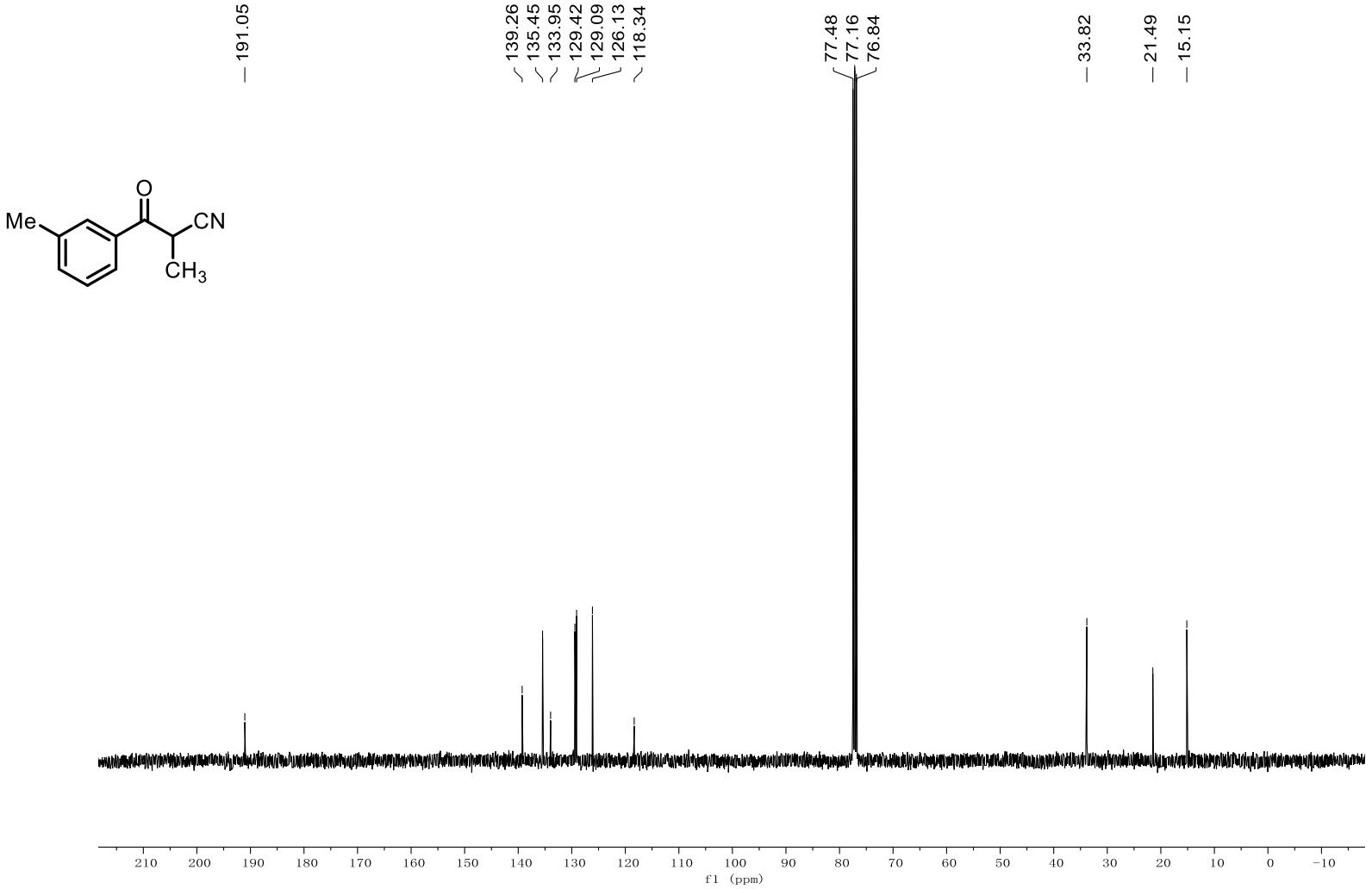
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxo-3-(*p*-tolyl)propanenitrile (6)



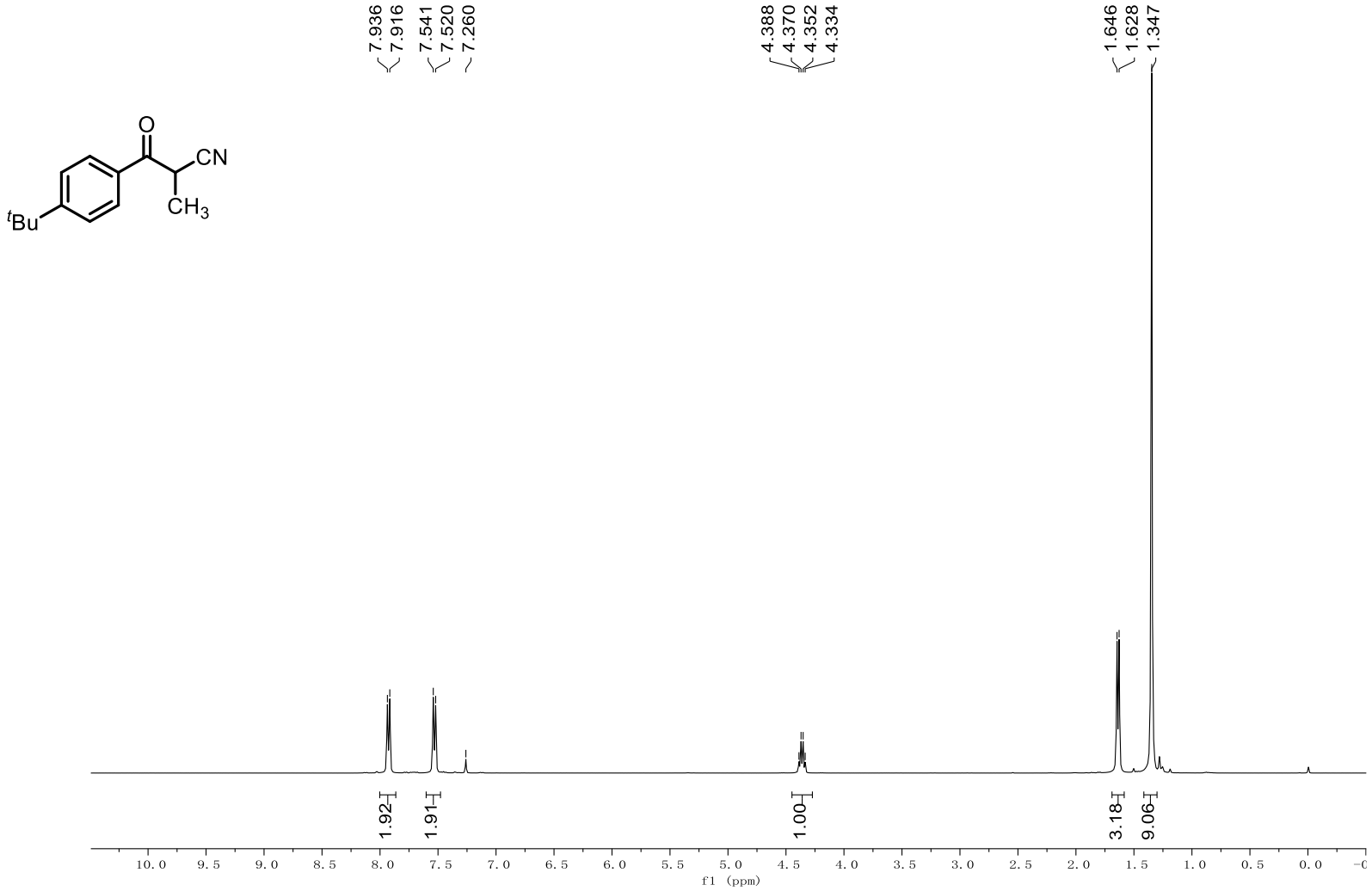
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxo-3-(*m*-tolyl)propanenitrile (7)



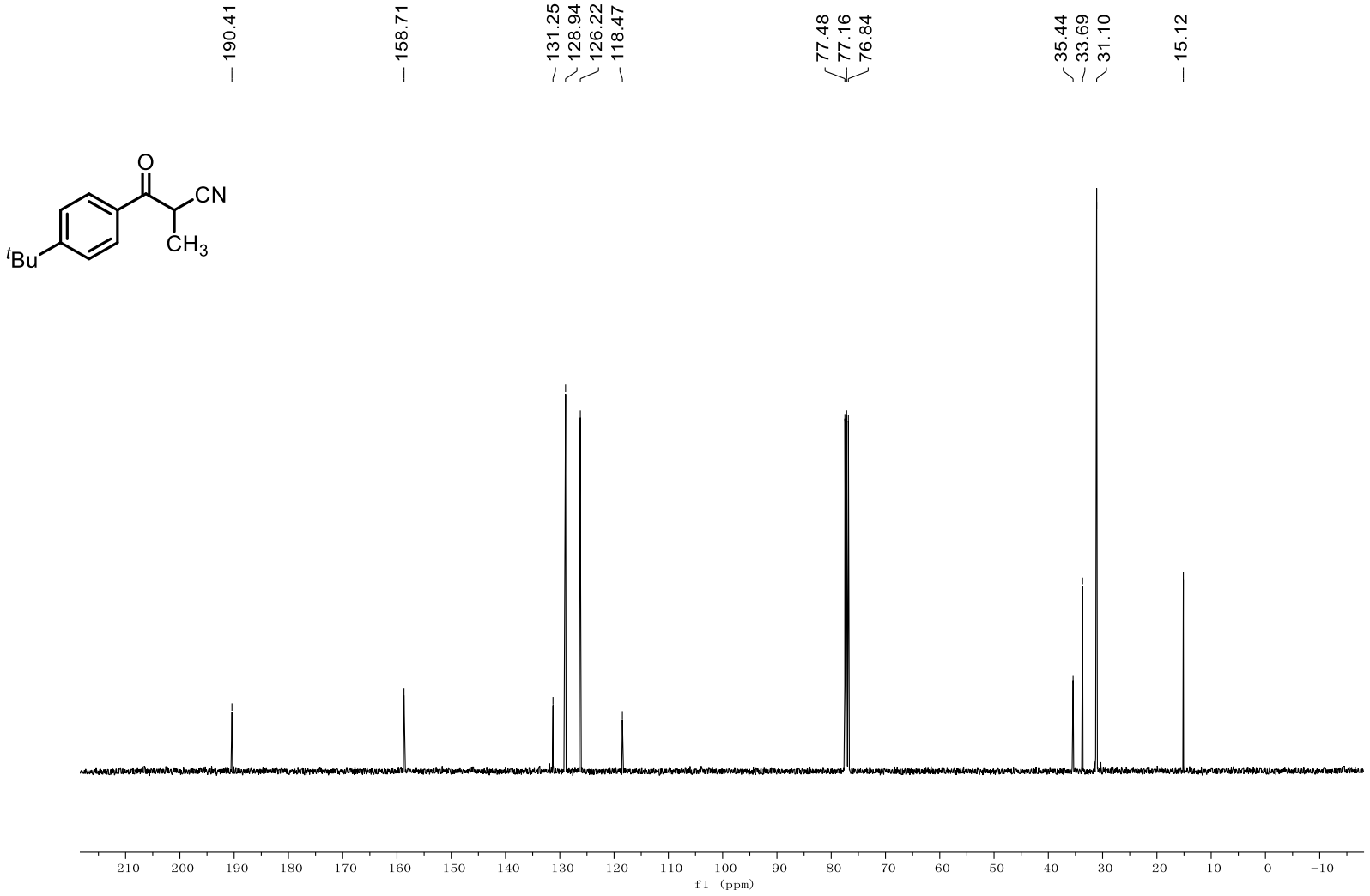
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxo-3-(*m*-tolyl)propanenitrile (7)



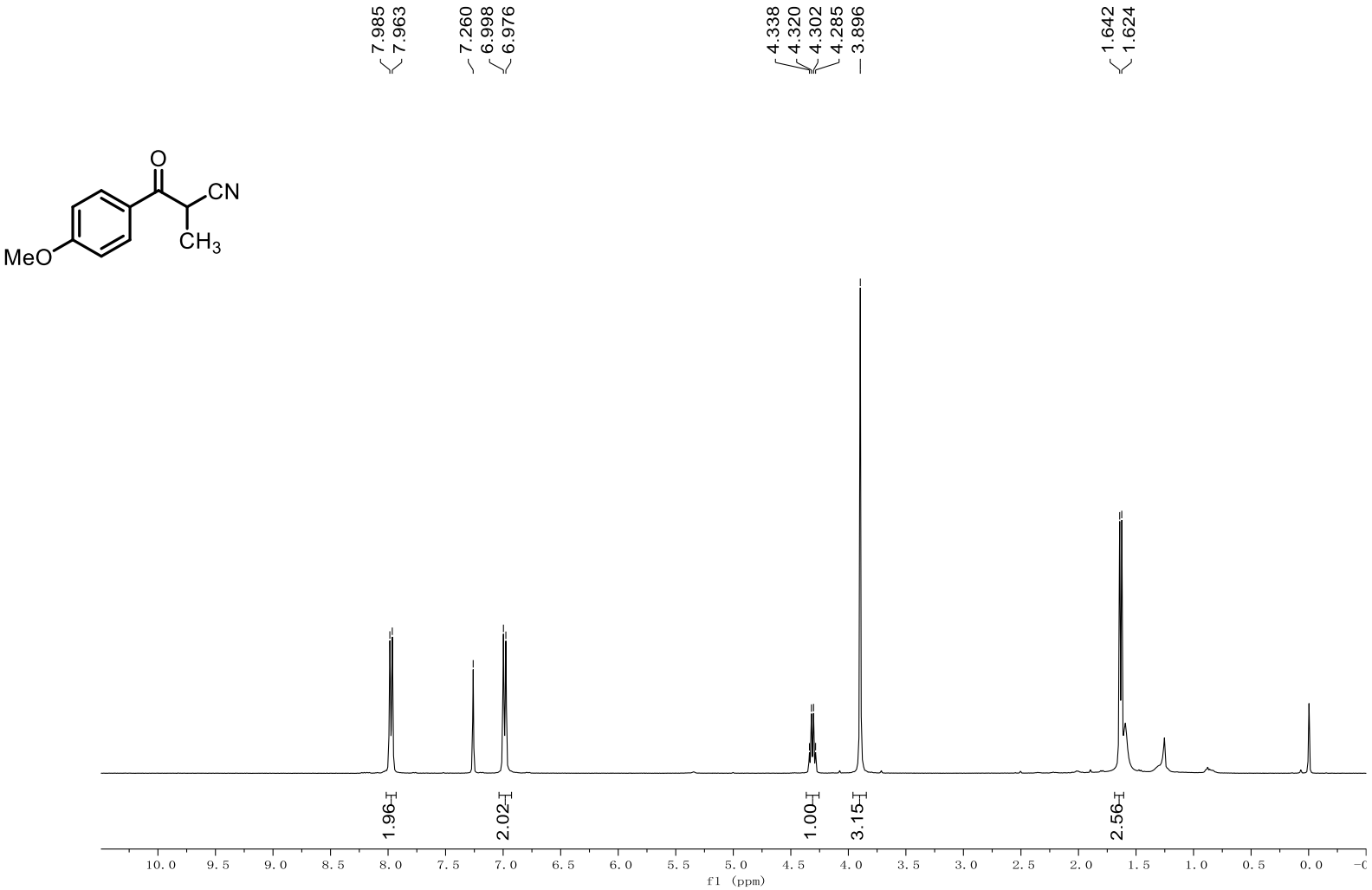
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(4-(*tert*-Butyl)phenyl)-2-methyl-3-oxopropanenitrile (8)



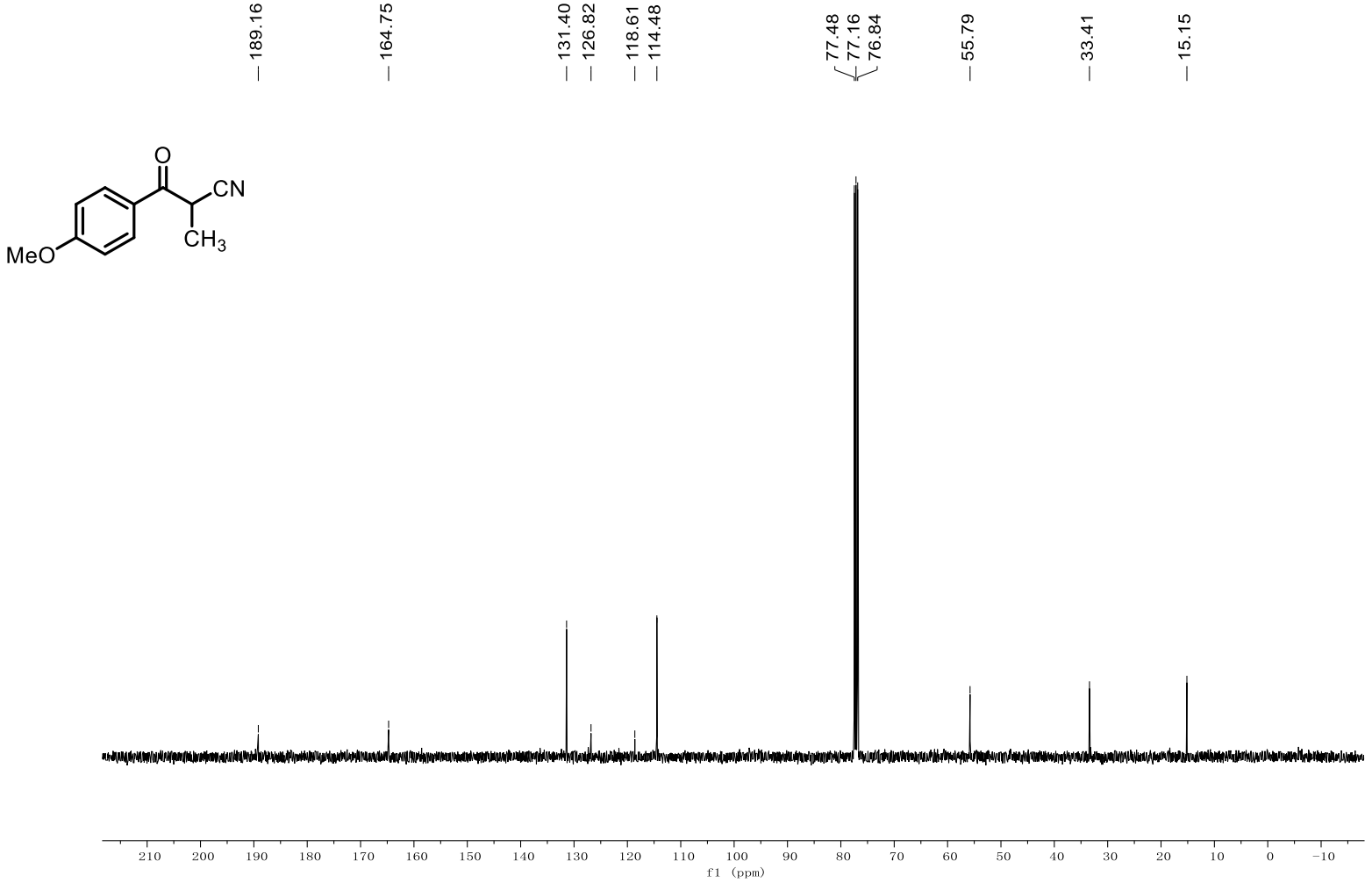
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(4-(*tert*-Butyl)phenyl)-2-methyl-3-oxopropanenitrile (8)



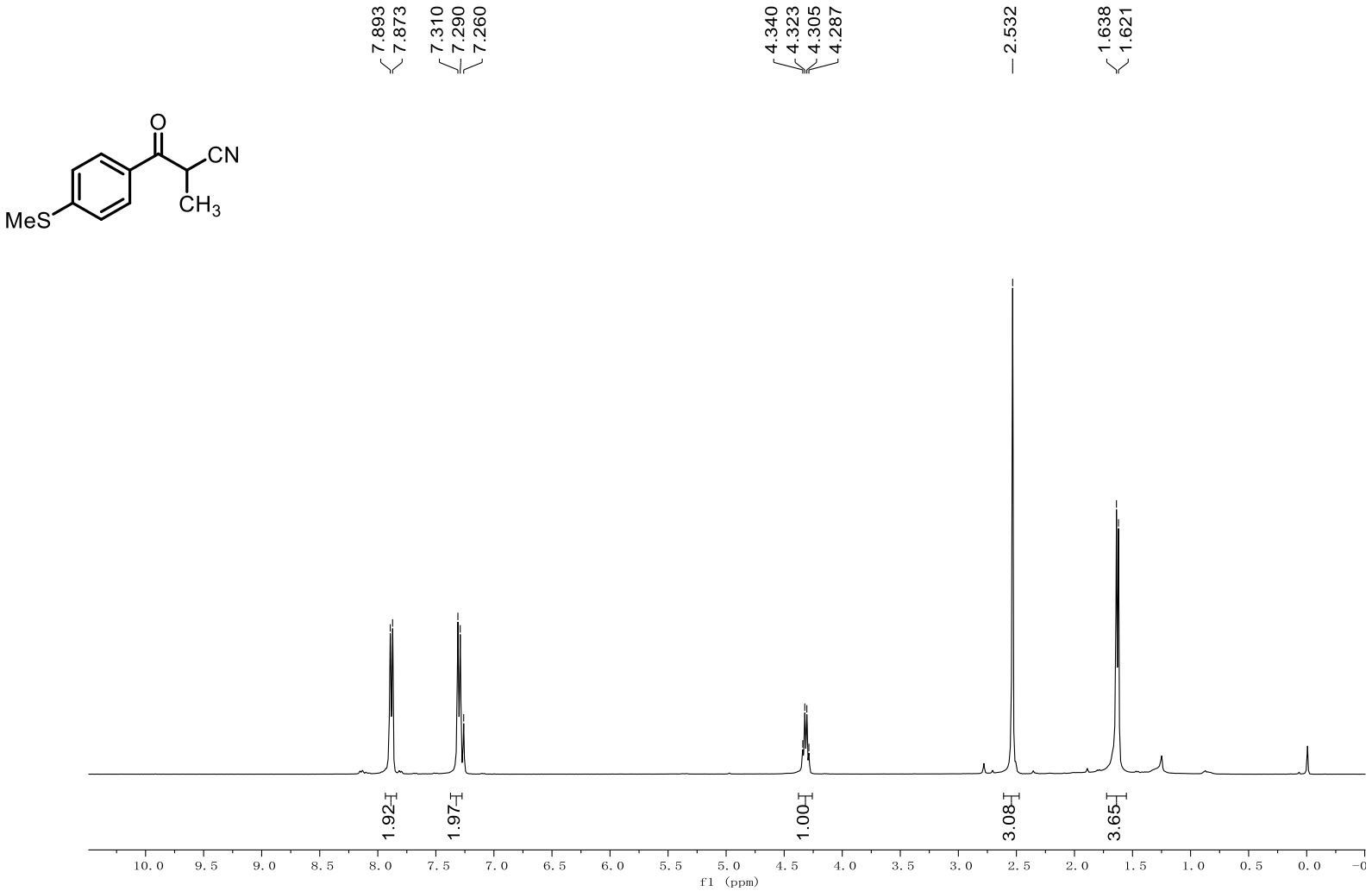
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(4-Methoxyphenyl)-2-methyl-3-oxopropanenitrile (9)



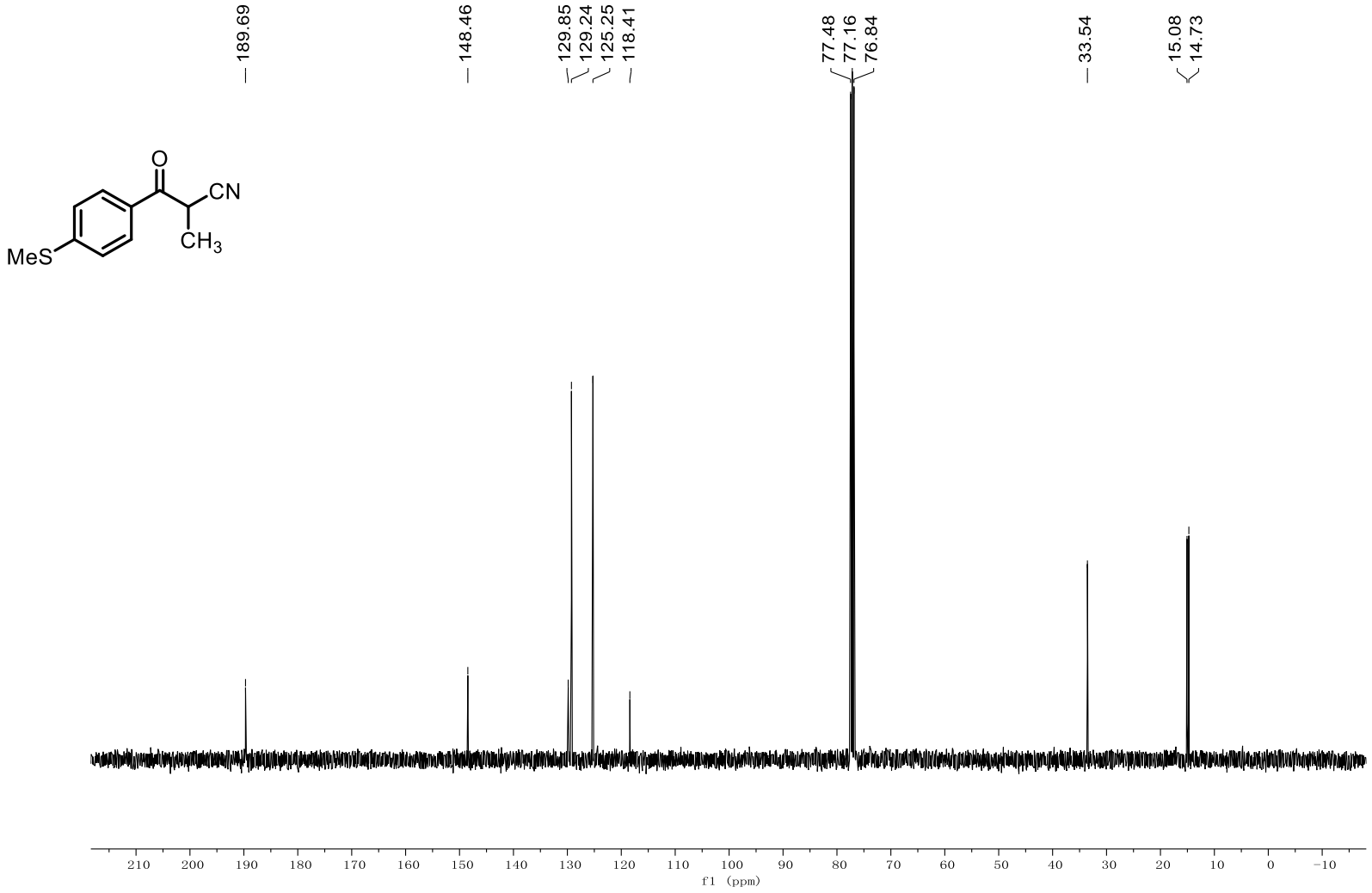
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(4-Methoxyphenyl)-2-methyl-3-oxopropanenitrile (9)



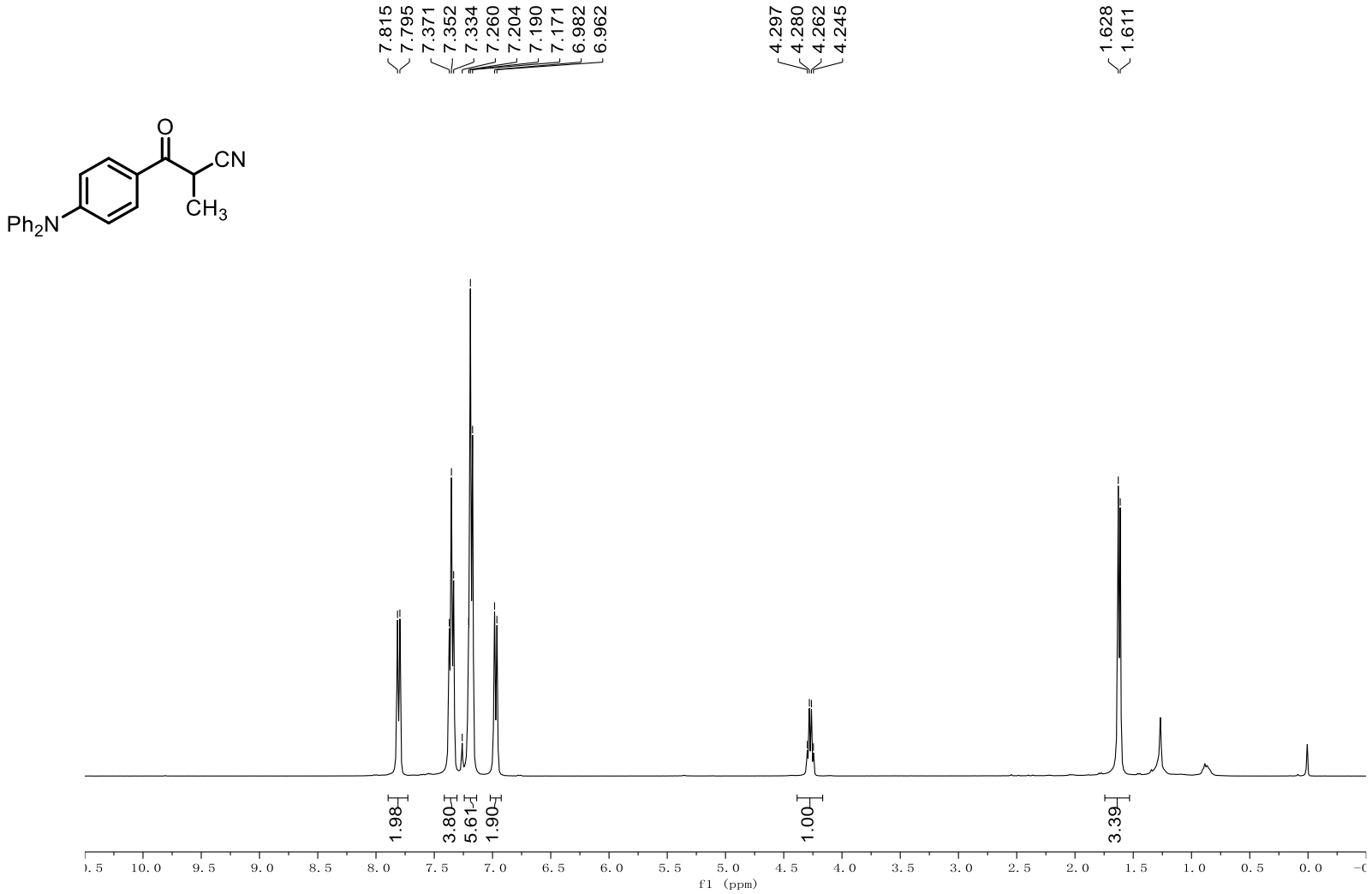
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-3-(4-(methylthio)phenyl)-3-oxopropanenitrile (10)



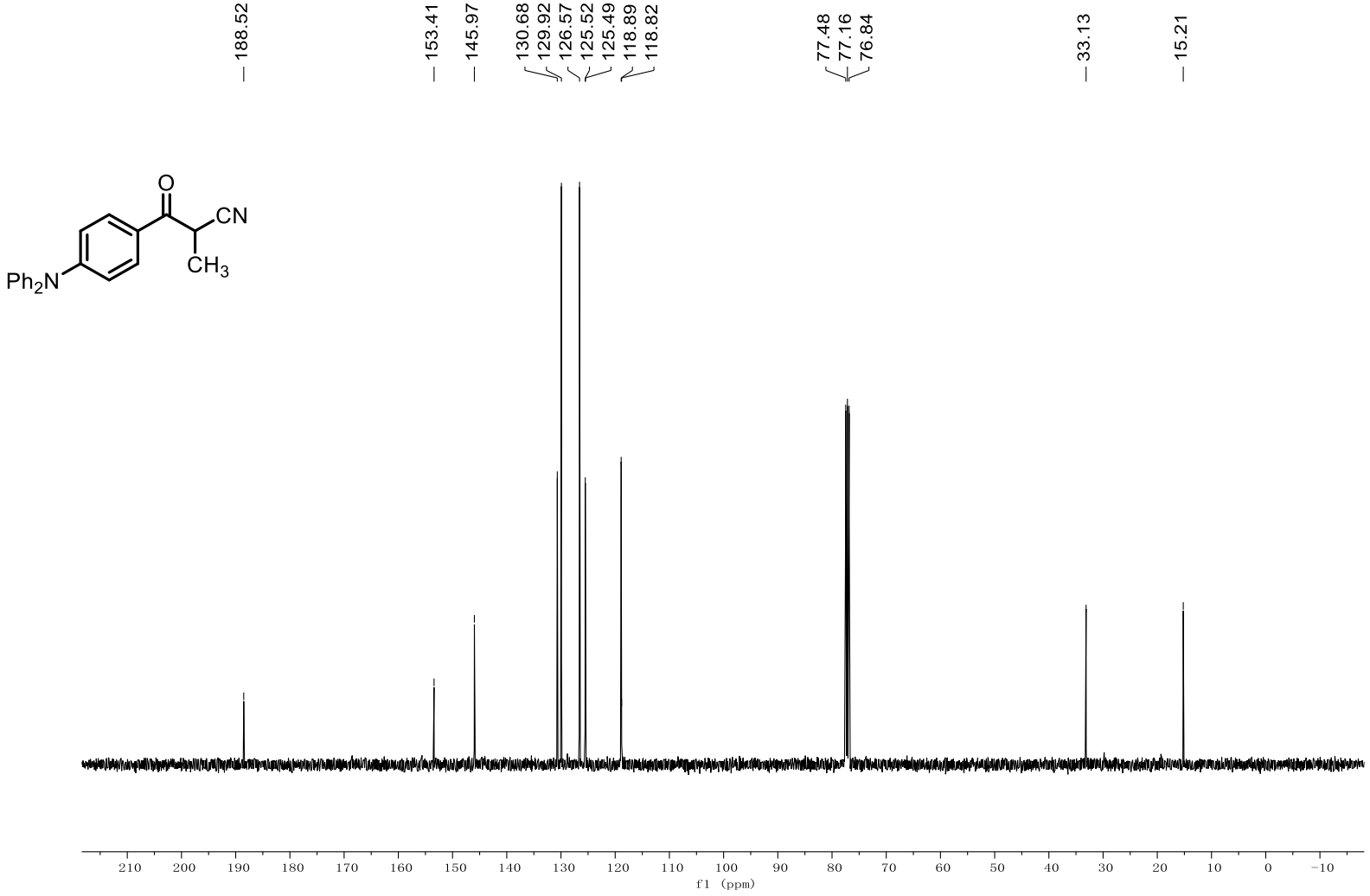
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-3-(4-(methylthio)phenyl)-3-oxopropanenitrile (10)



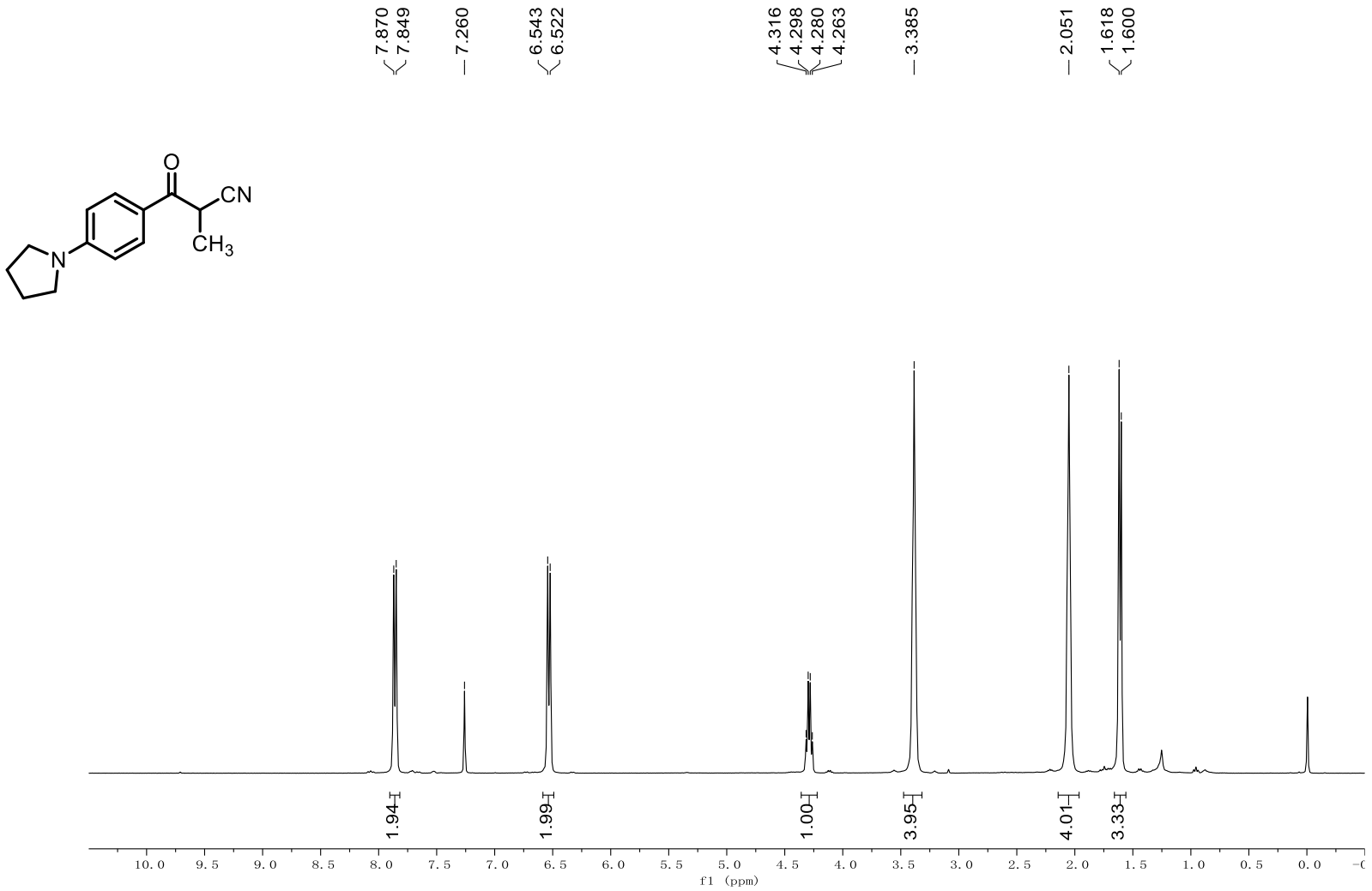
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(4-(Diphenylamino)phenyl)-2-methyl-3-oxopropanenitrile (11)



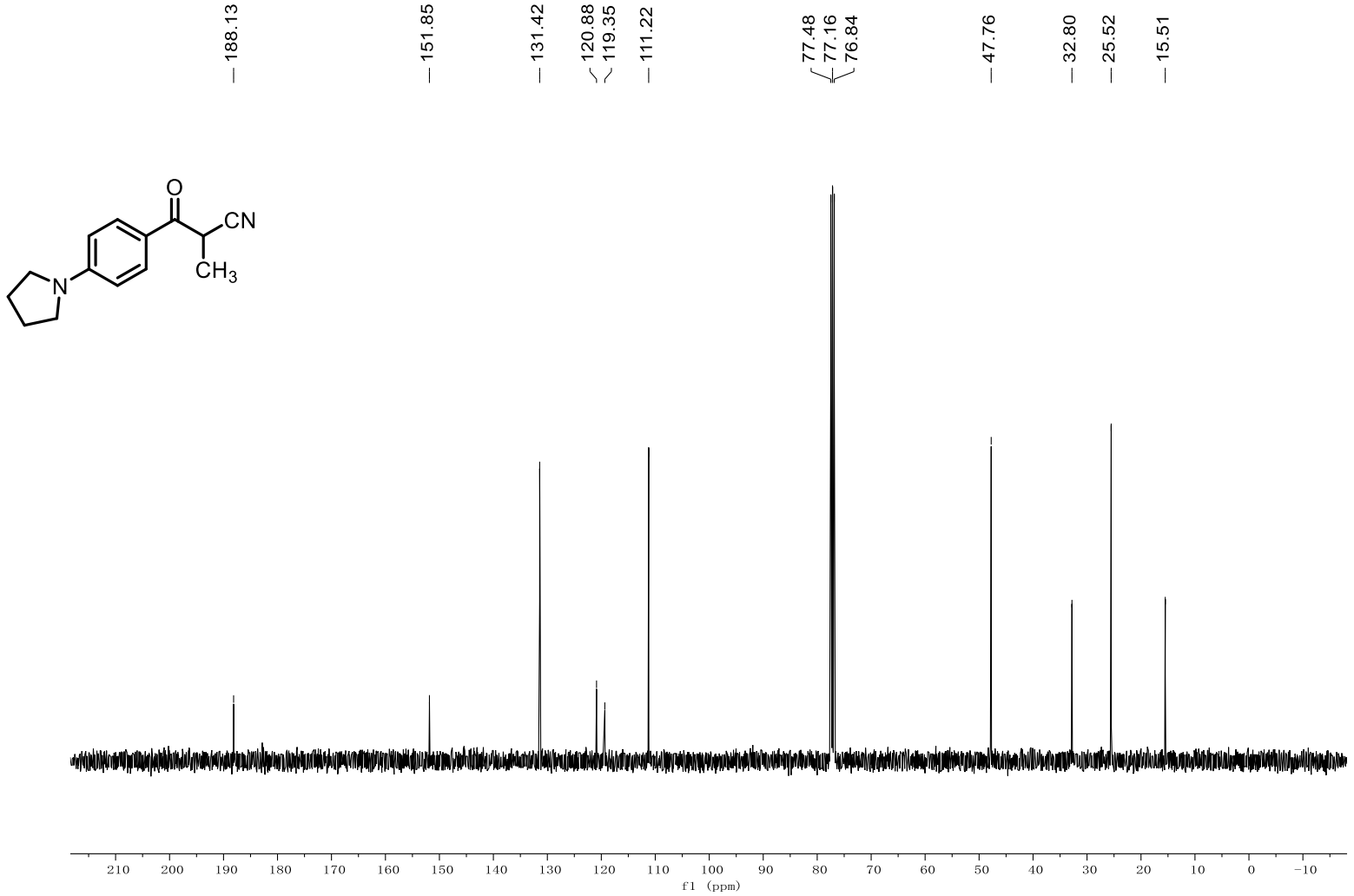
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(4-(Diphenylamino)phenyl)-2-methyl-3-oxopropanenitrile (11)



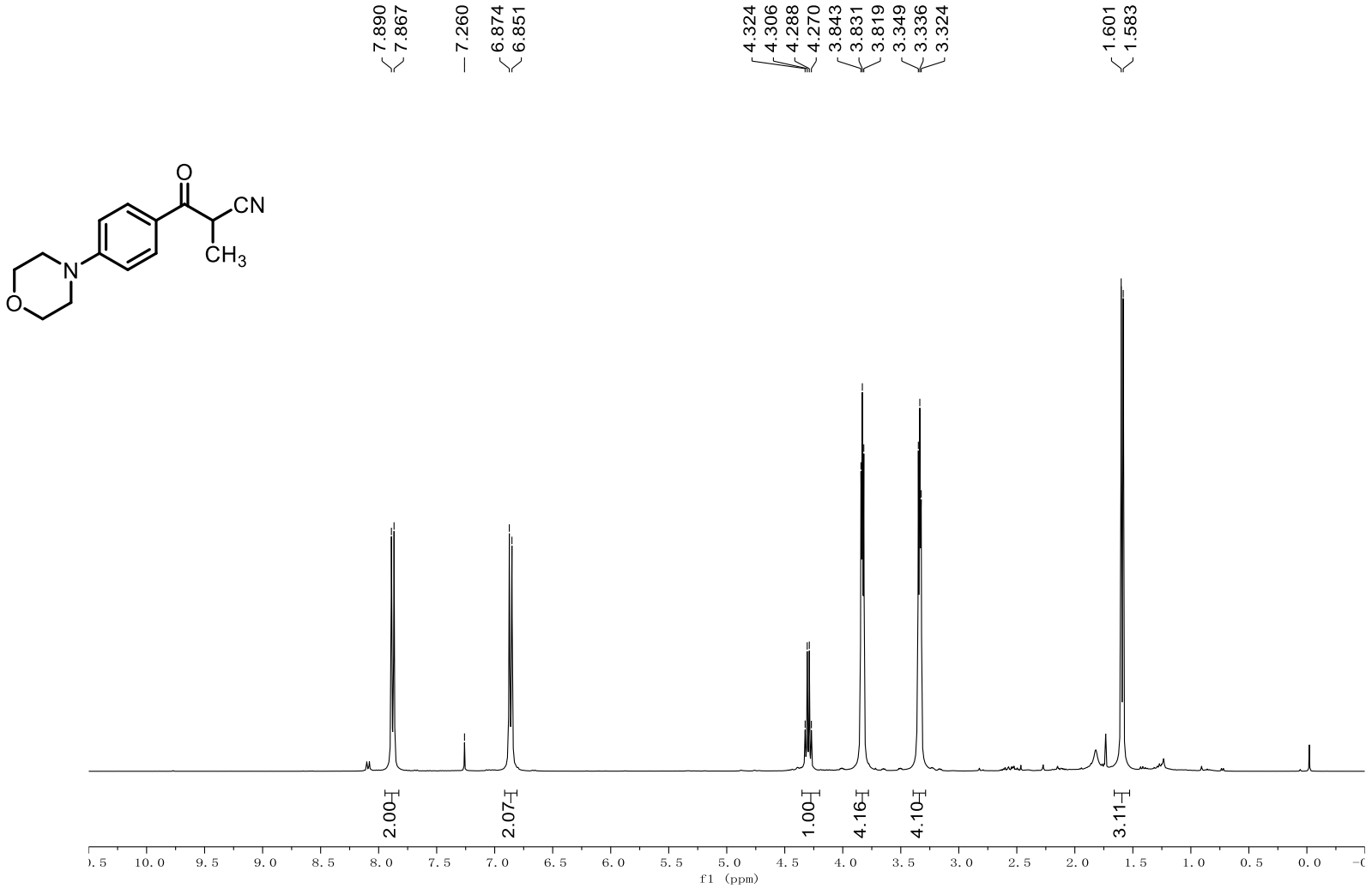
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxo-3-(4-(pyrrolidin-1-yl)phenyl)propanenitrile (12)



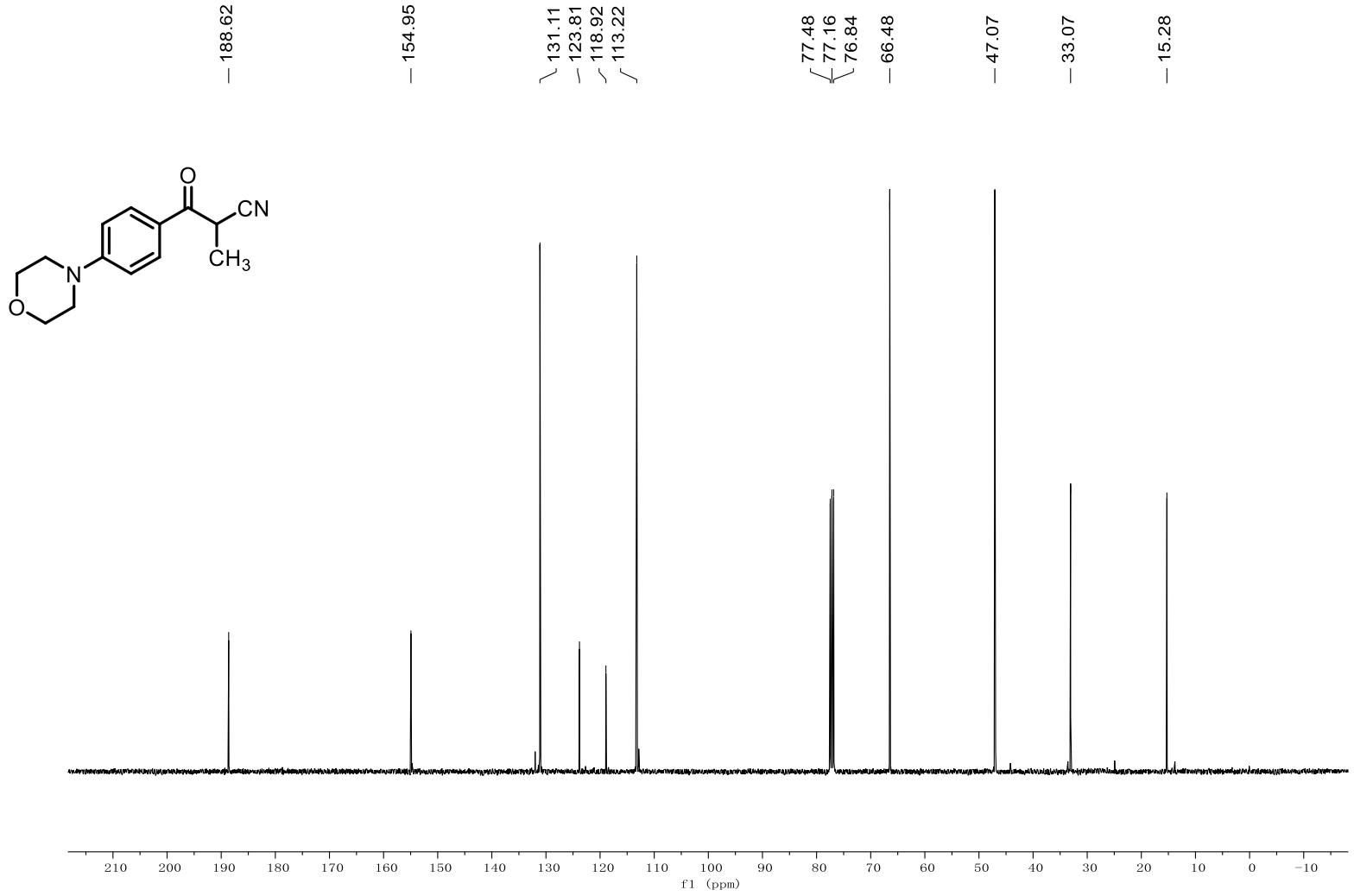
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxo-3-(4-(pyrrolidin-1-yl)phenyl)propanenitrile (12)



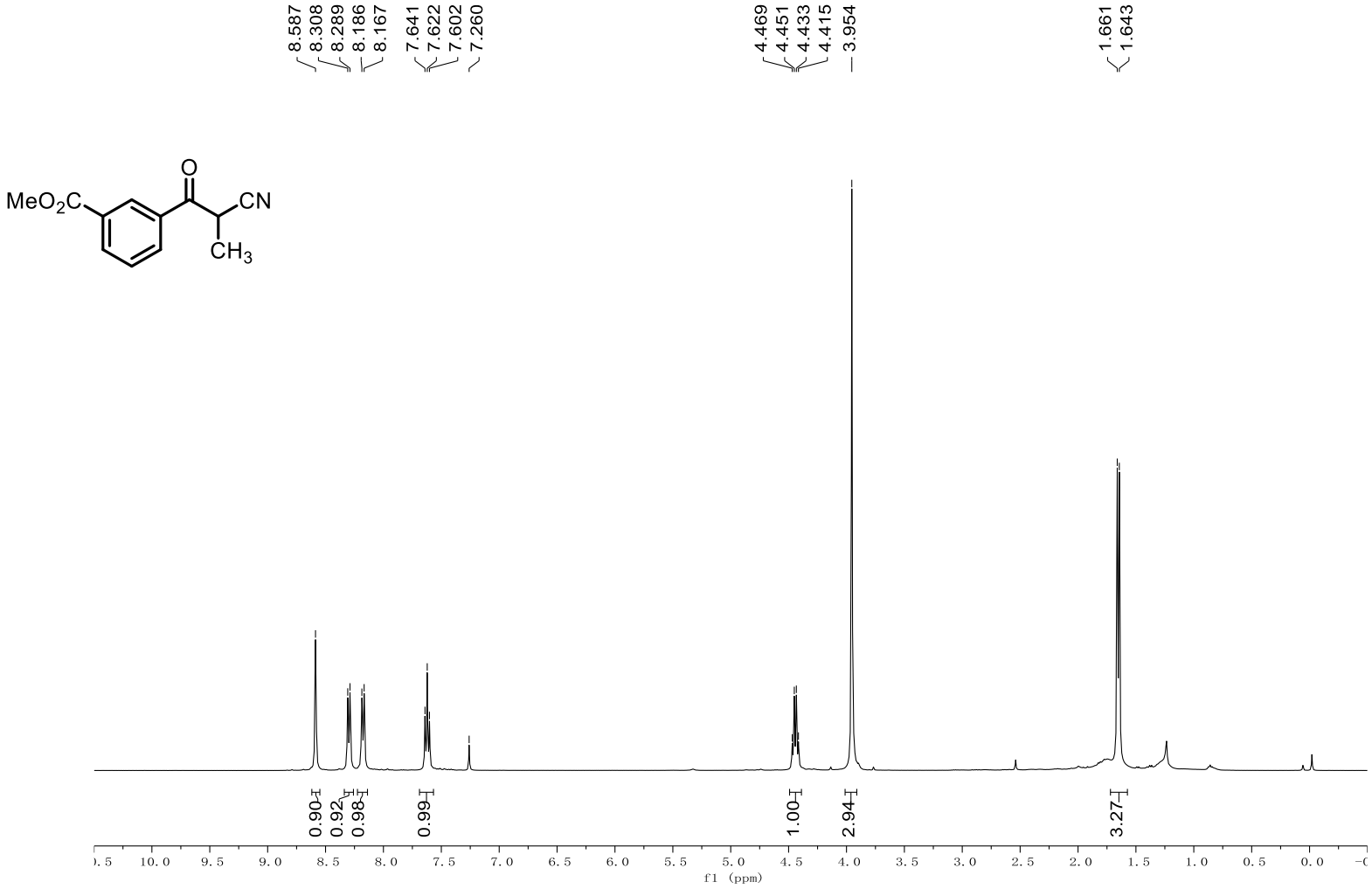
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-3-(4-morpholinophenyl)-3-oxopropanenitrile (13)



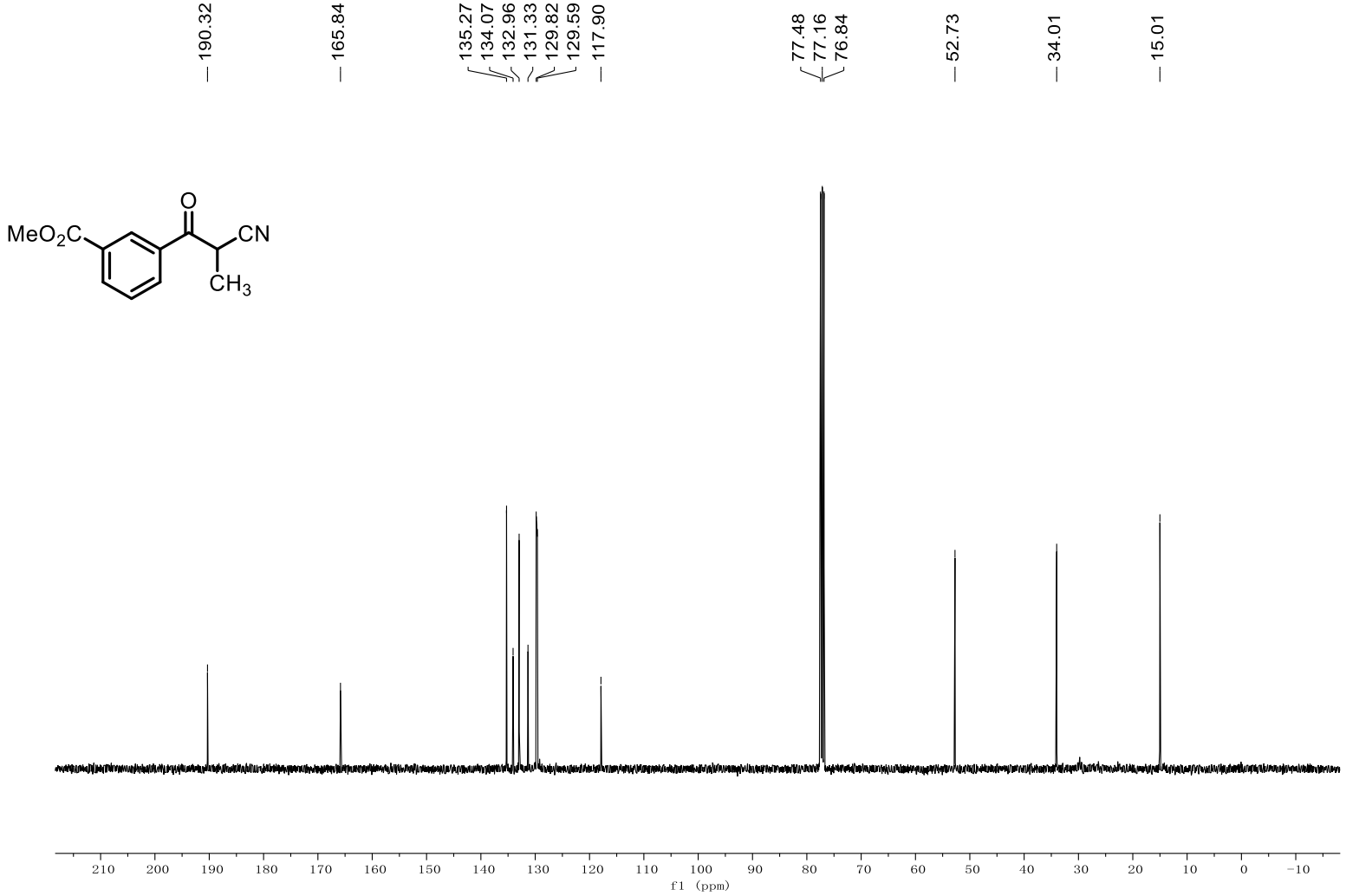
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-3-(4-morpholinophenyl)-3-oxopropanenitrile (13)



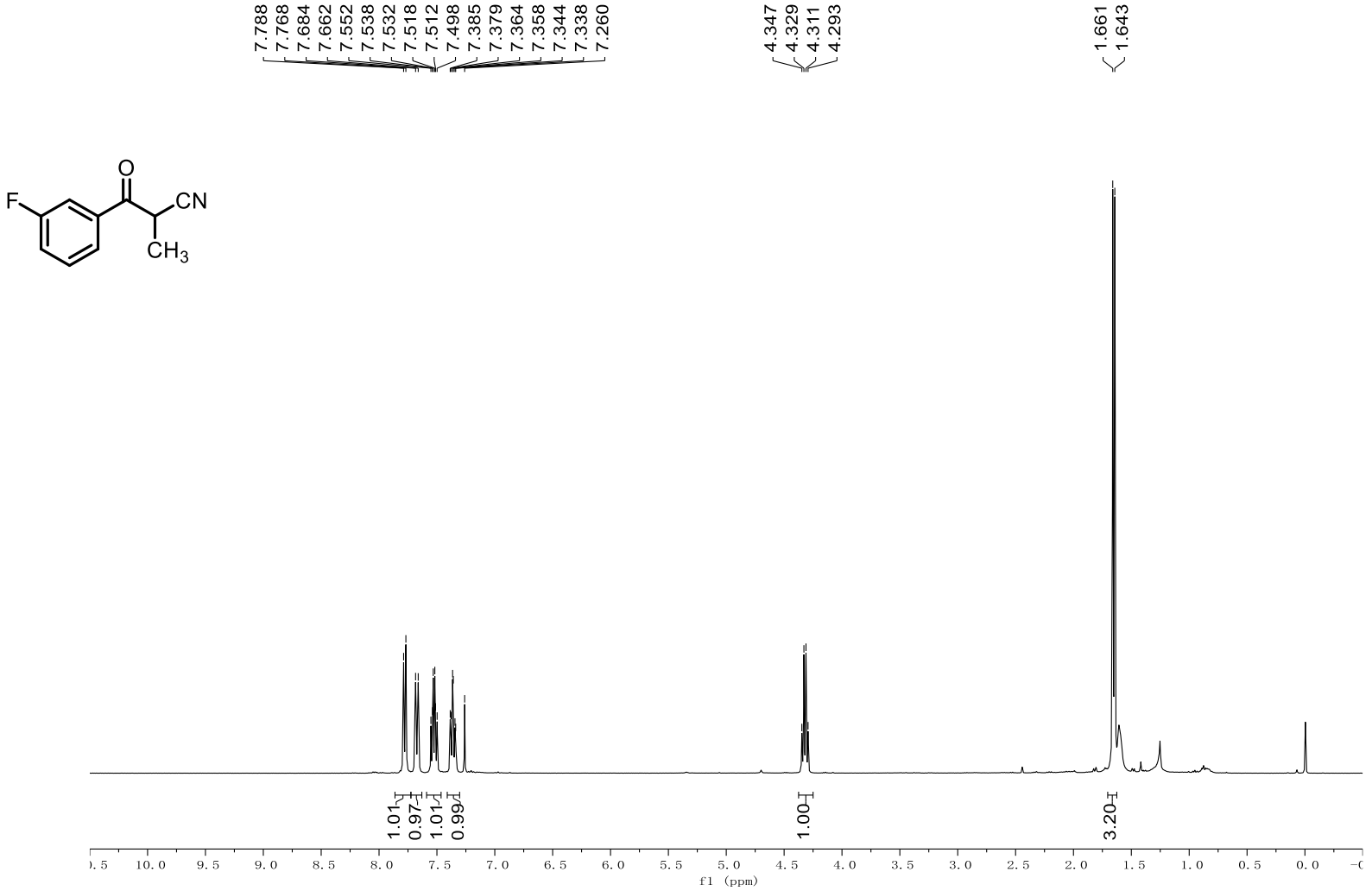
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Methyl 3-(2-cyanopropanoyl)benzoate (14)



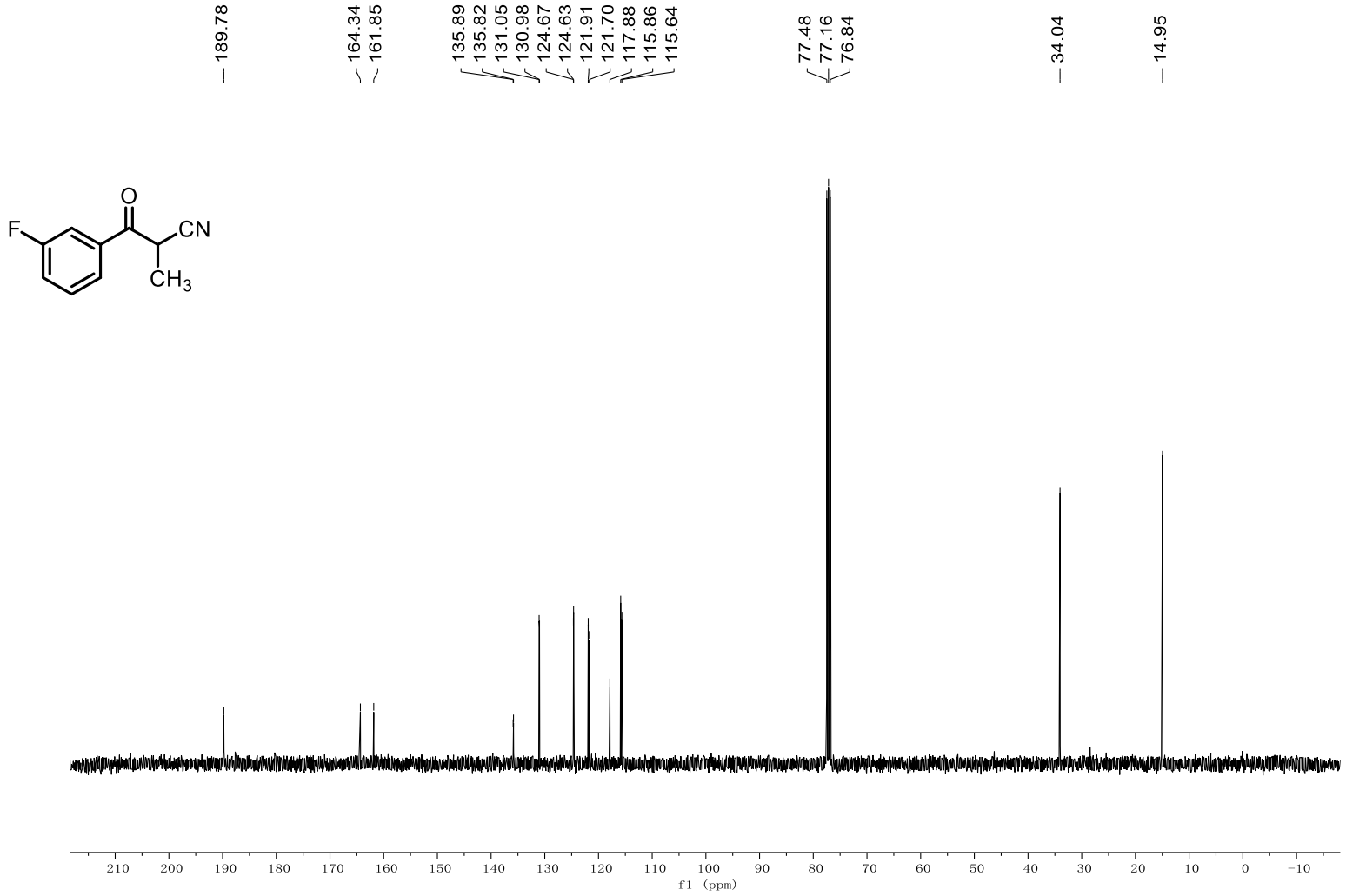
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of Methyl 3-(2-cyanopropanoyl)benzoate (14)



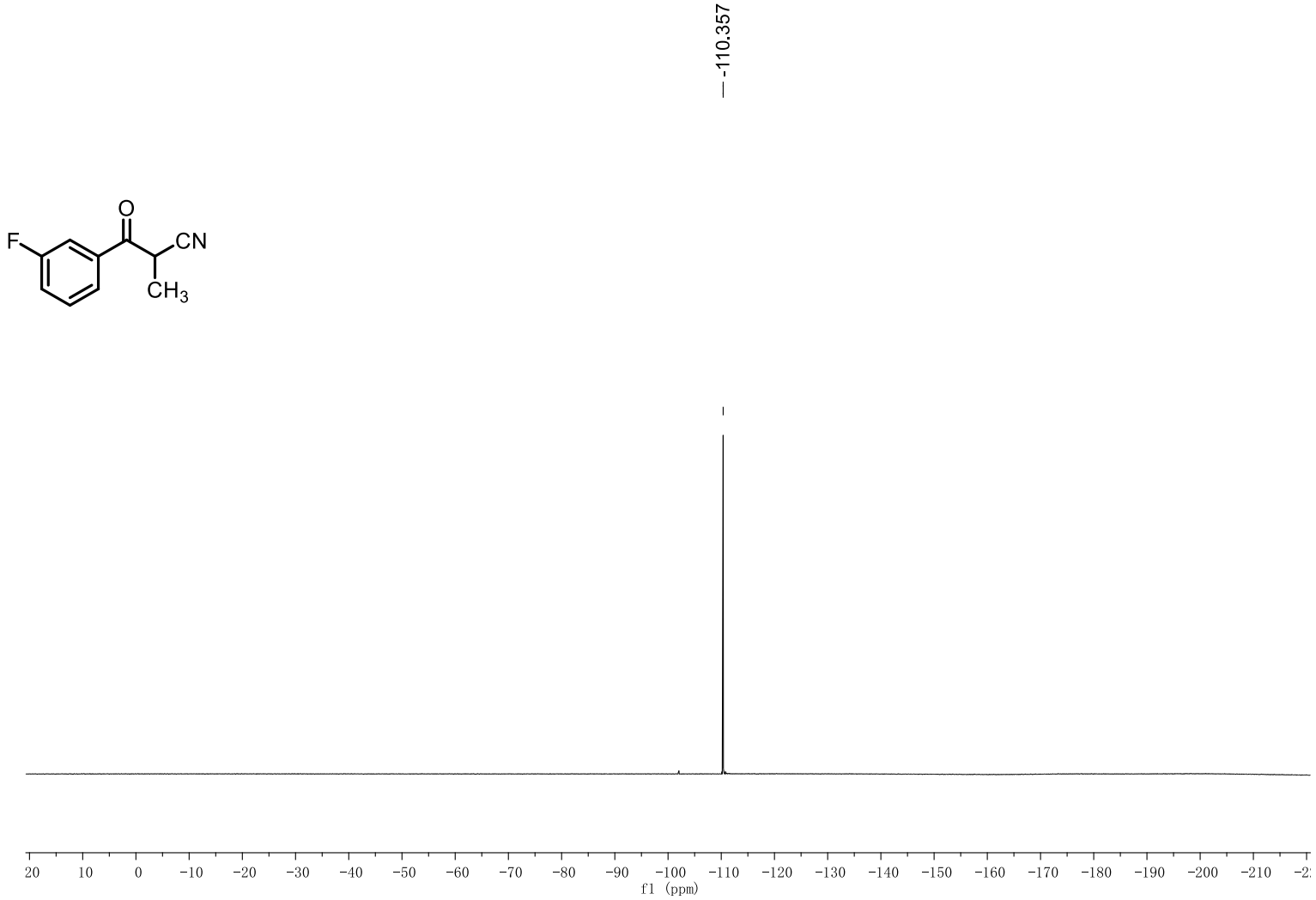
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(3-Fluorophenyl)-2-methyl-3-oxopropanenitrile (15)



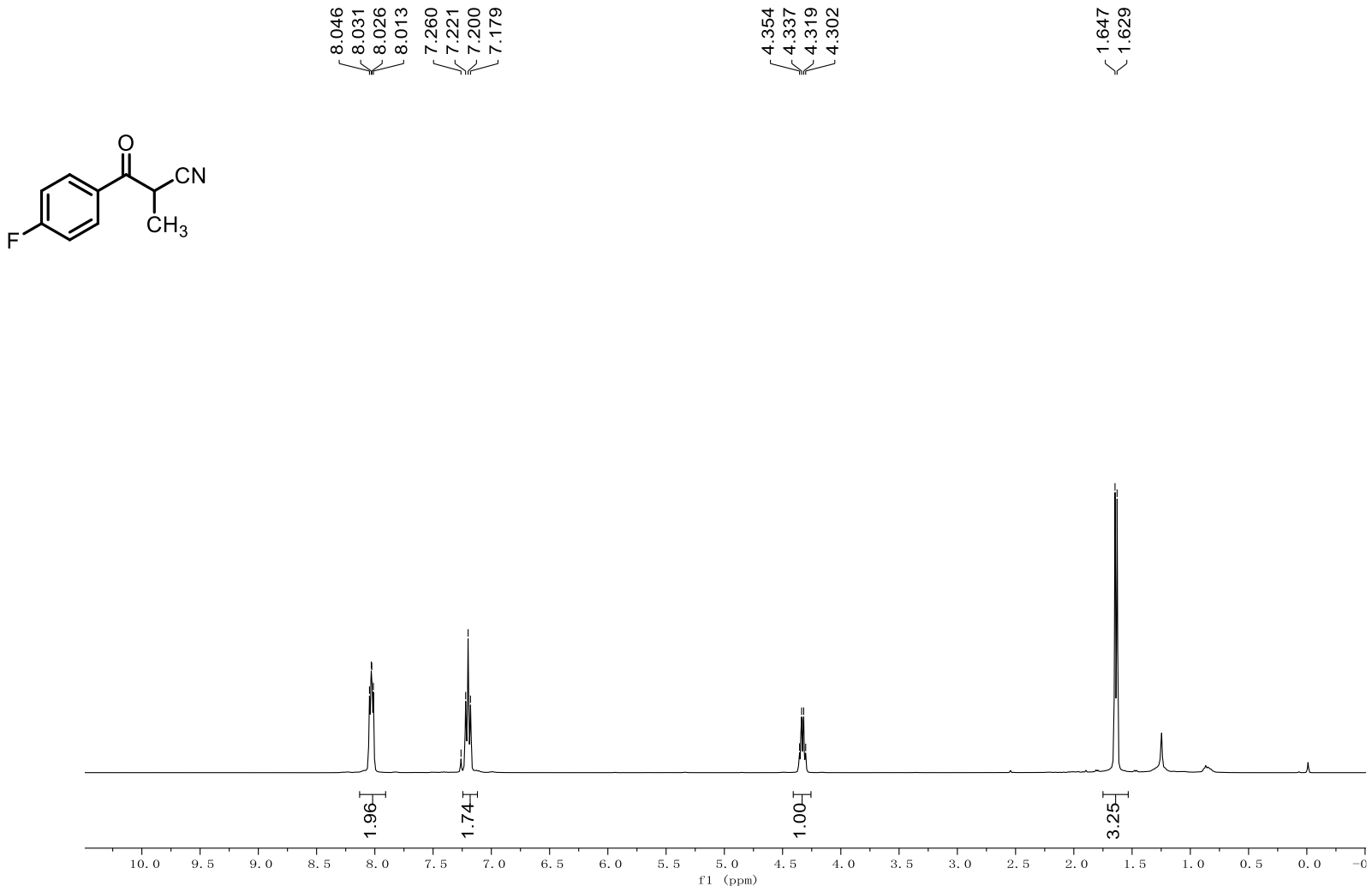
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(3-Fluorophenyl)-2-methyl-3-oxopropanenitrile (15)



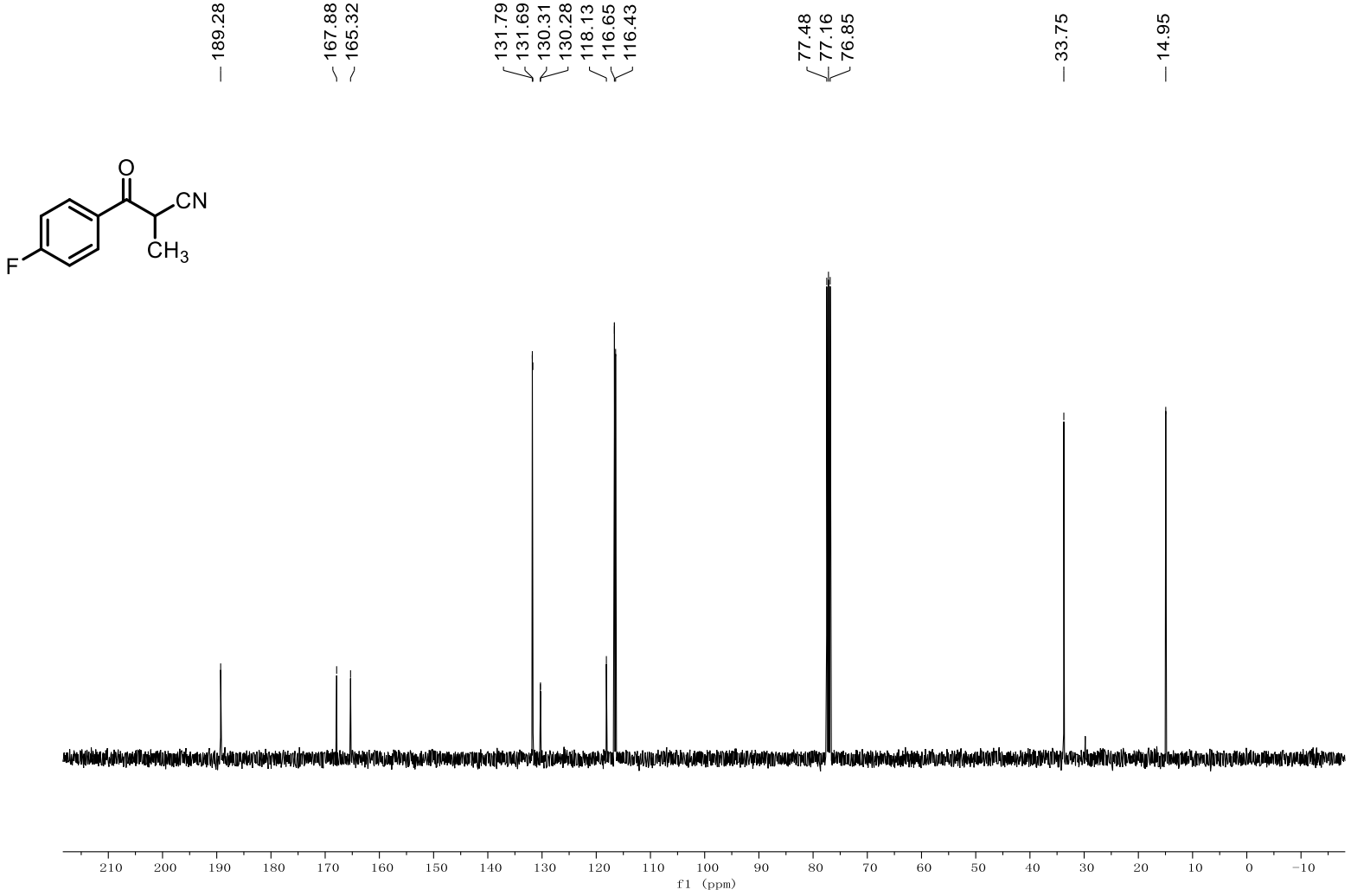
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3-(3-Fluorophenyl)-2-methyl-3-oxopropanenitrile (15)



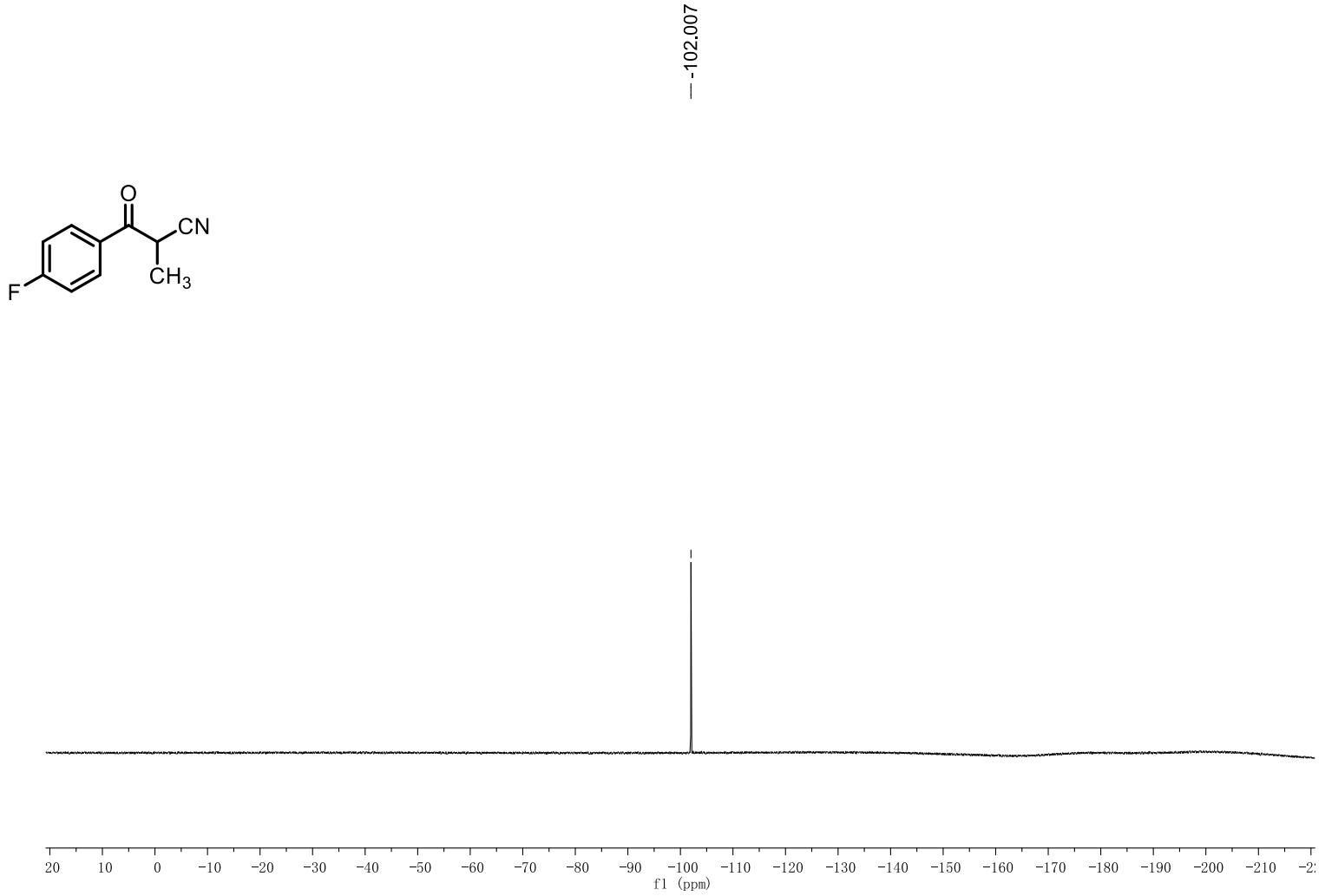
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(4-Fluorophenyl)-2-methyl-3-oxopropanenitrile (16)



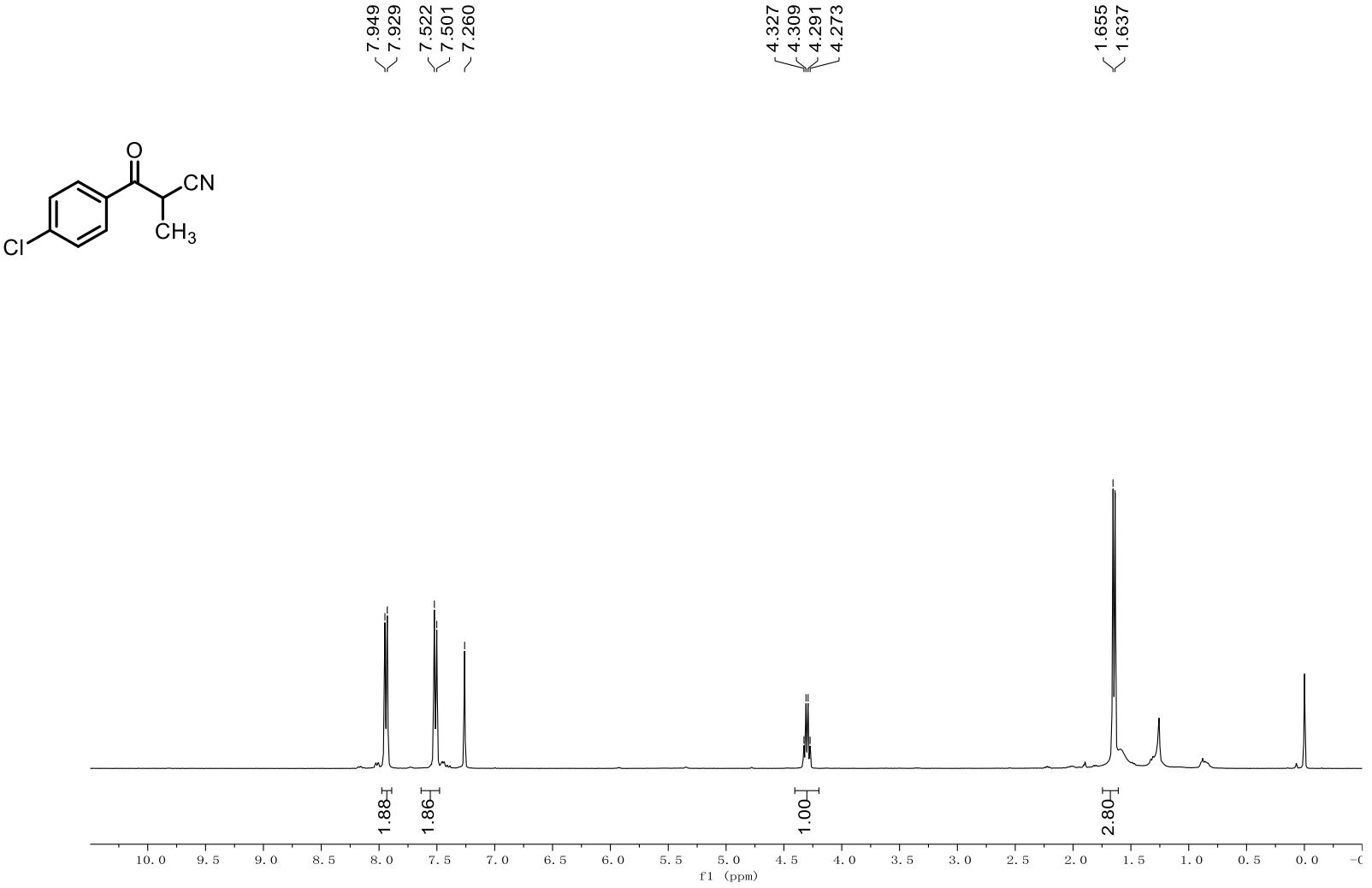
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(4-Fluorophenyl)-2-methyl-3-oxopropanenitrile (16)



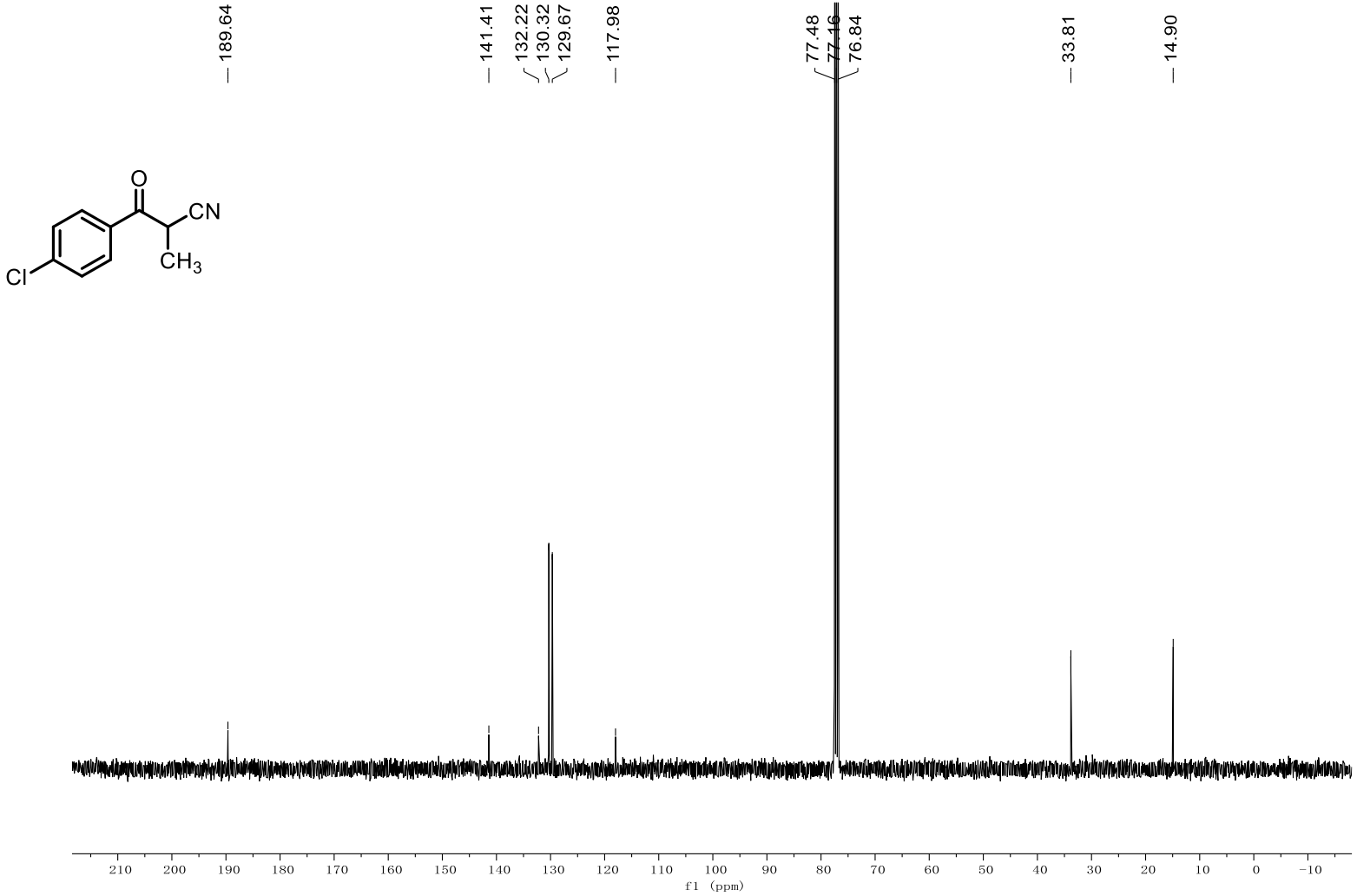
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3-(4-Fluorophenyl)-2-methyl-3-oxopropanenitrile (16)



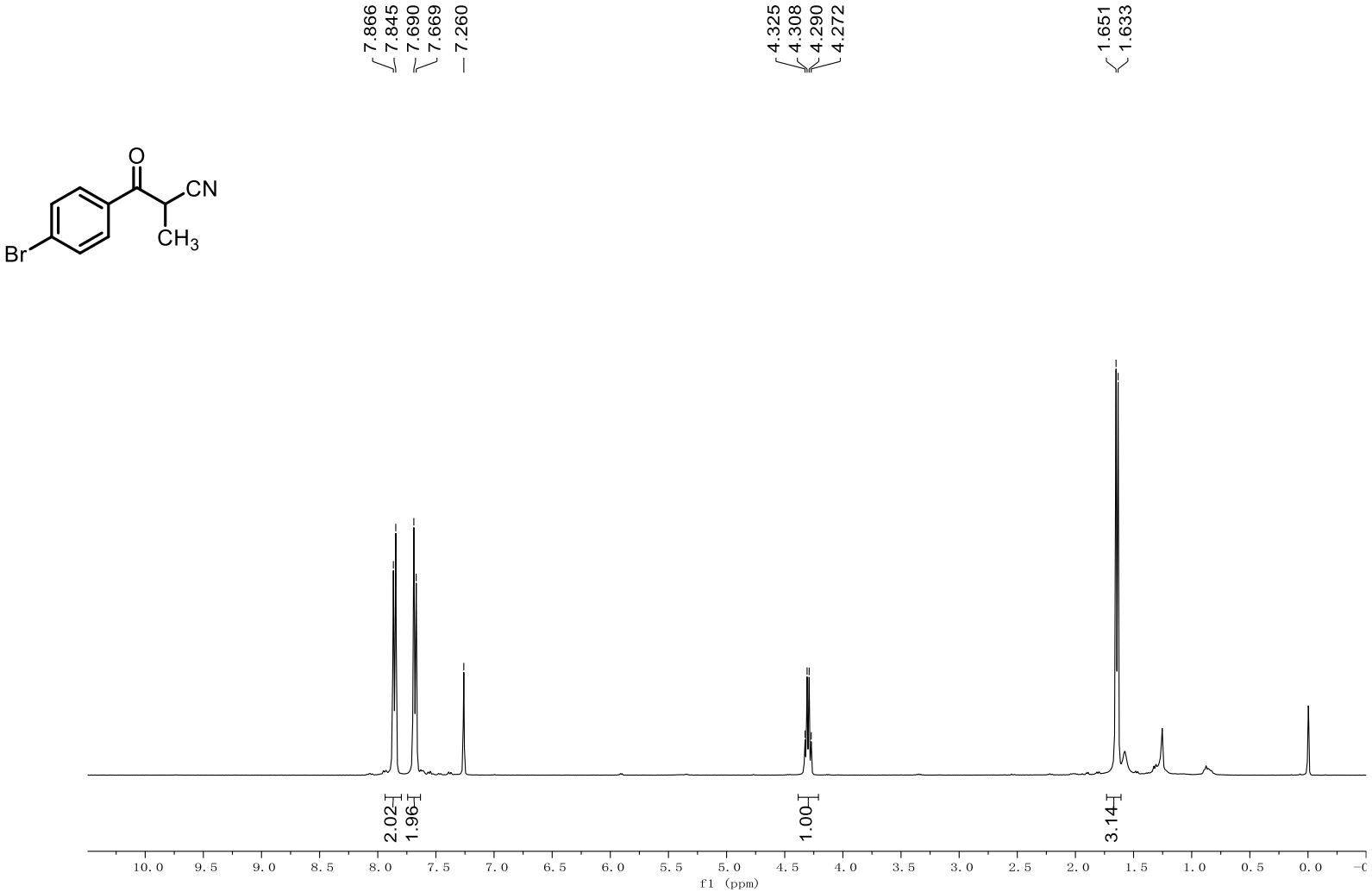
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(4-Chlorophenyl)-2-methyl-3-oxopropanenitrile (17)



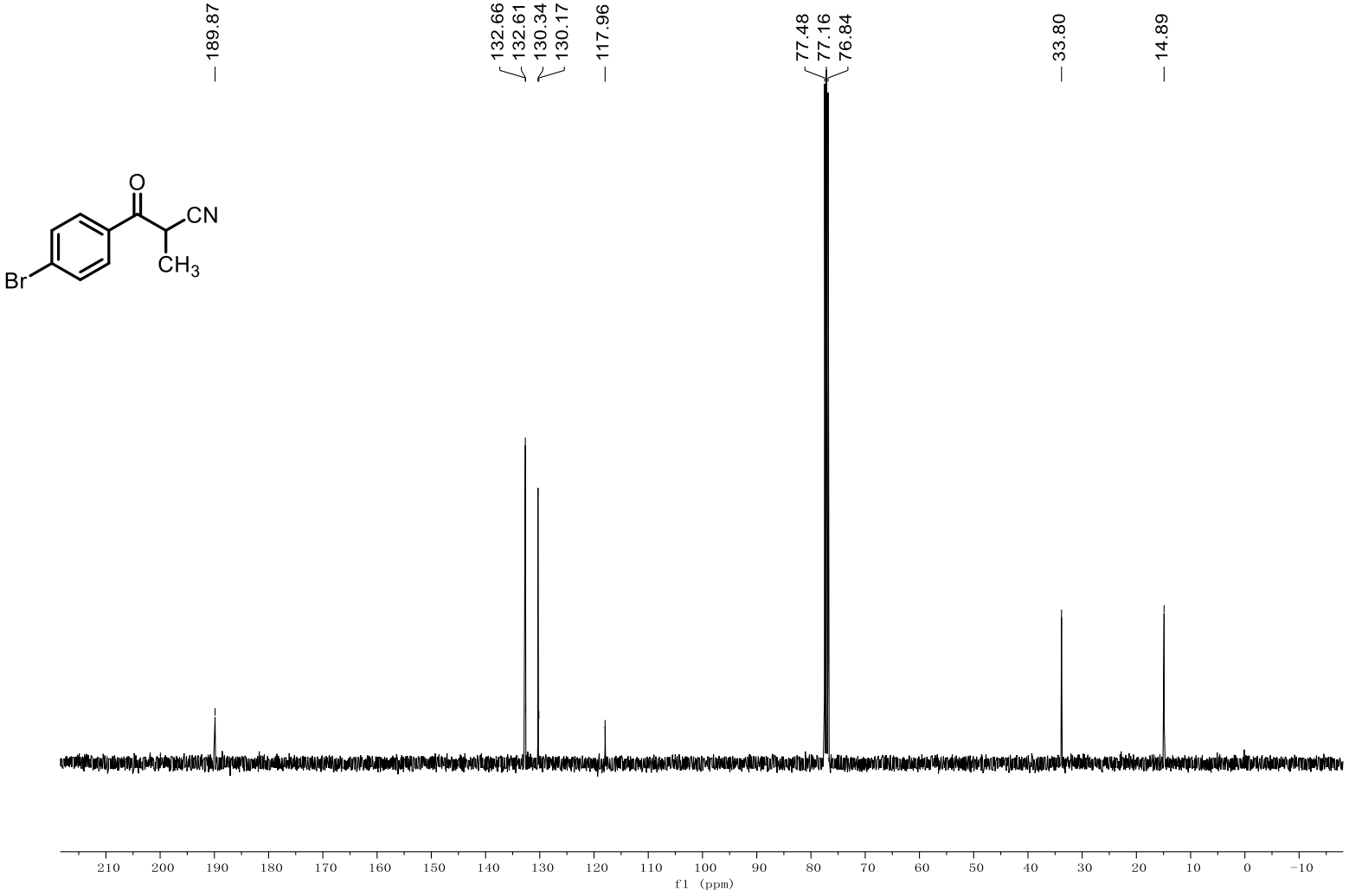
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(4-Chlorophenyl)-2-methyl-3-oxopropanenitrile (17)



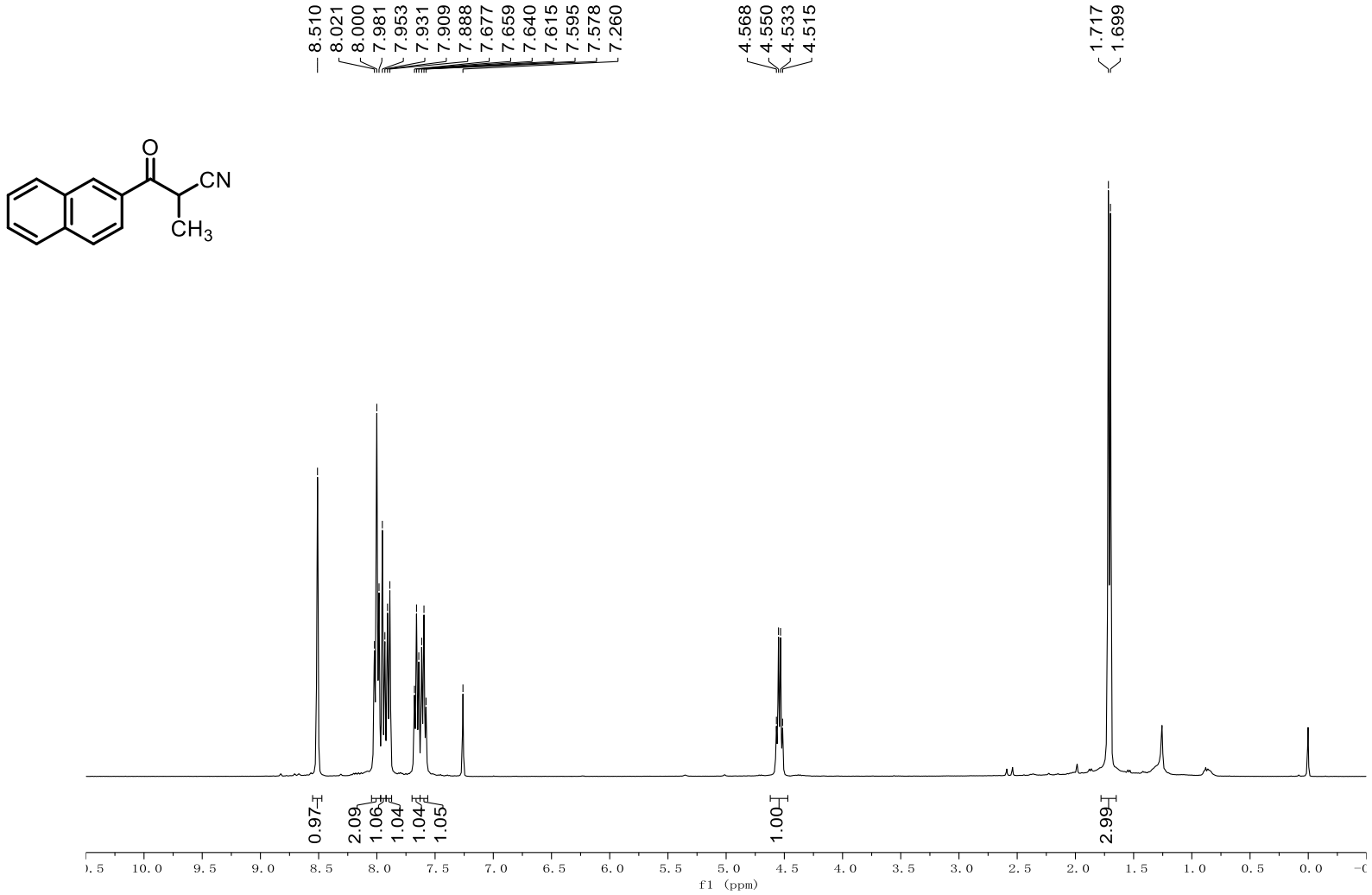
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(4-Bromophenyl)-2-methyl-3-oxopropanenitrile (18)



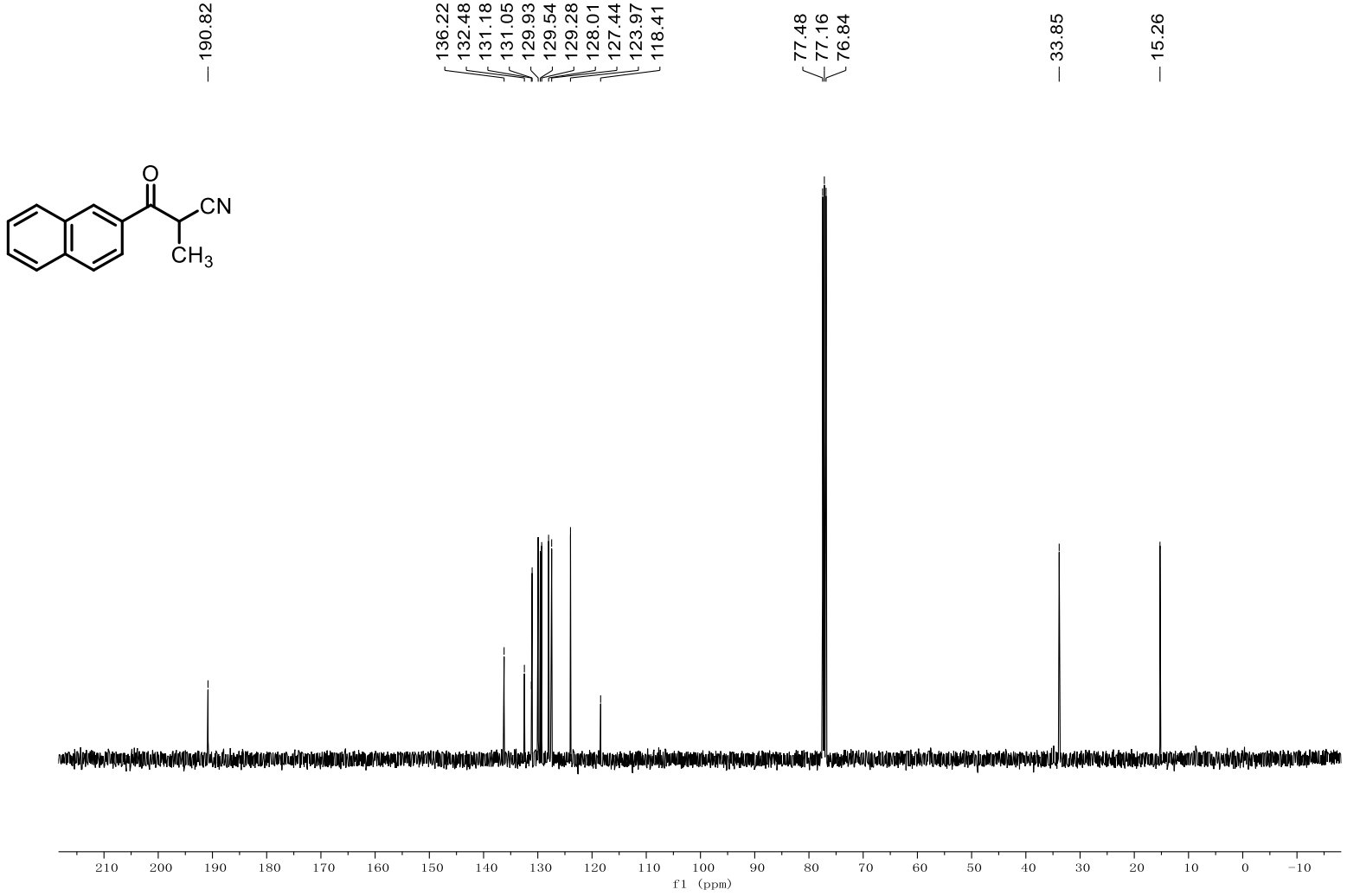
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(4-Bromophenyl)-2-methyl-3-oxopropanenitrile (18)



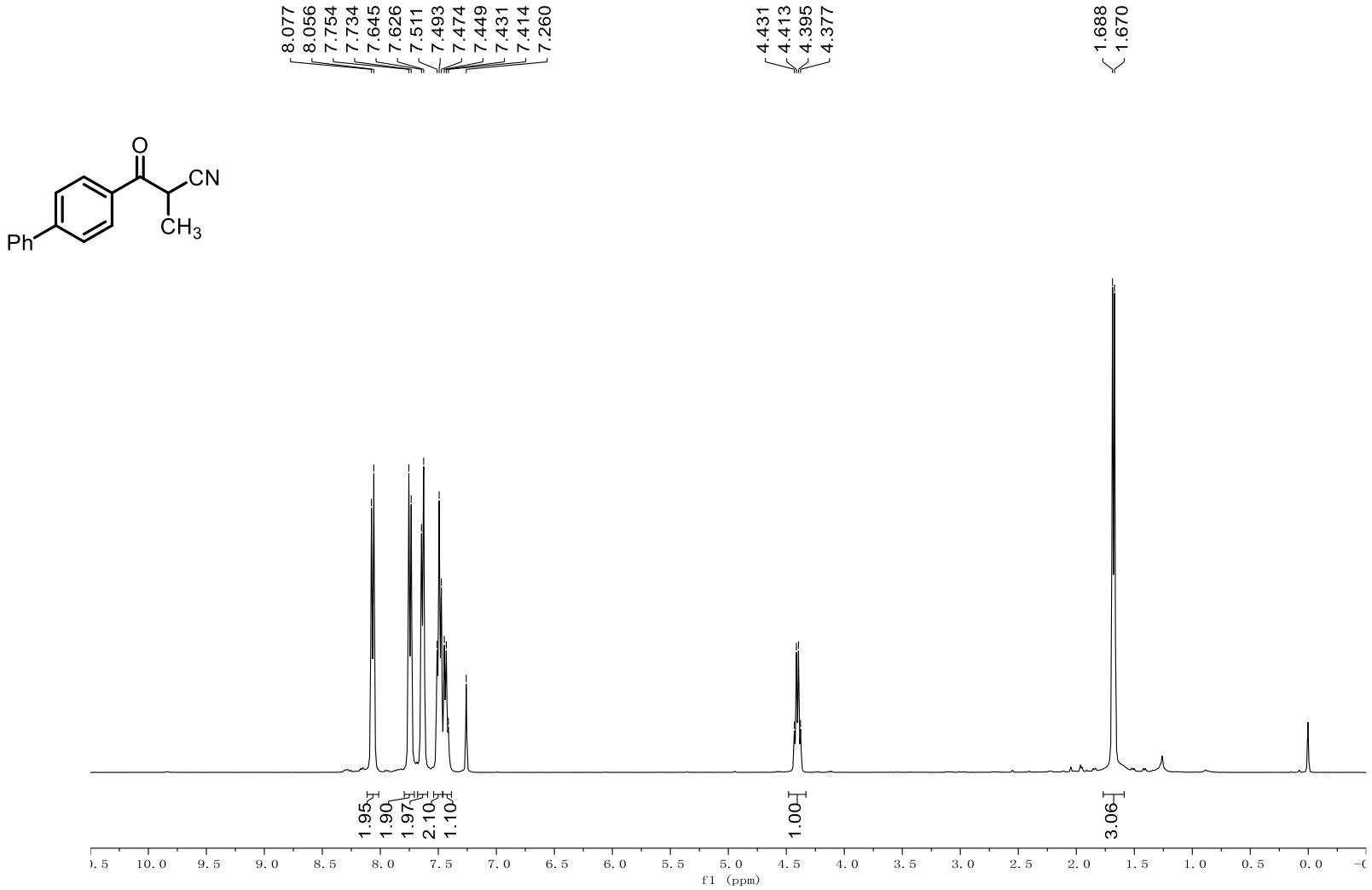
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-3-(naphthalen-2-yl)-3-oxopropanenitrile (19)



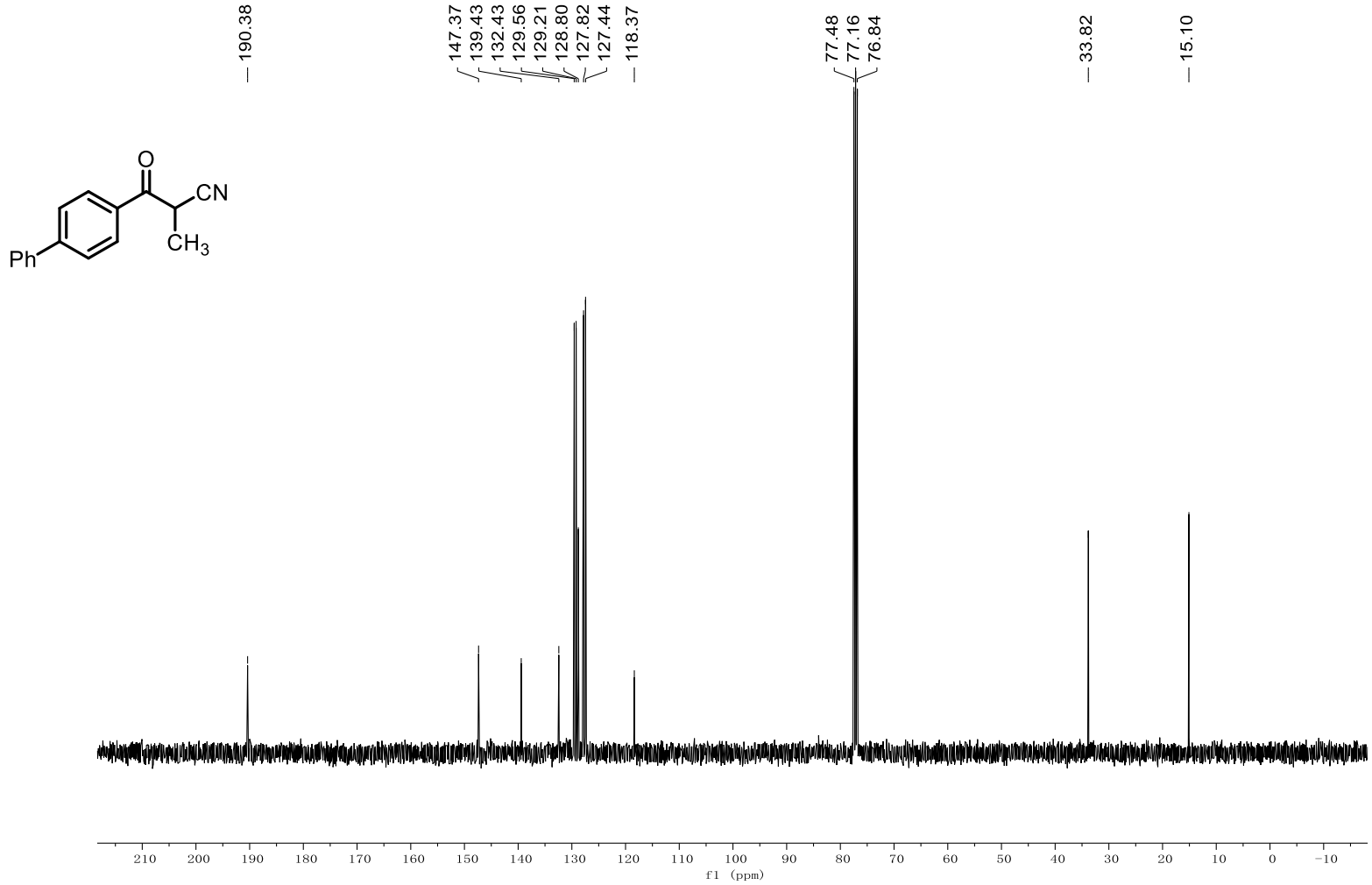
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-3-(naphthalen-2-yl)-3-oxopropanenitrile (19)



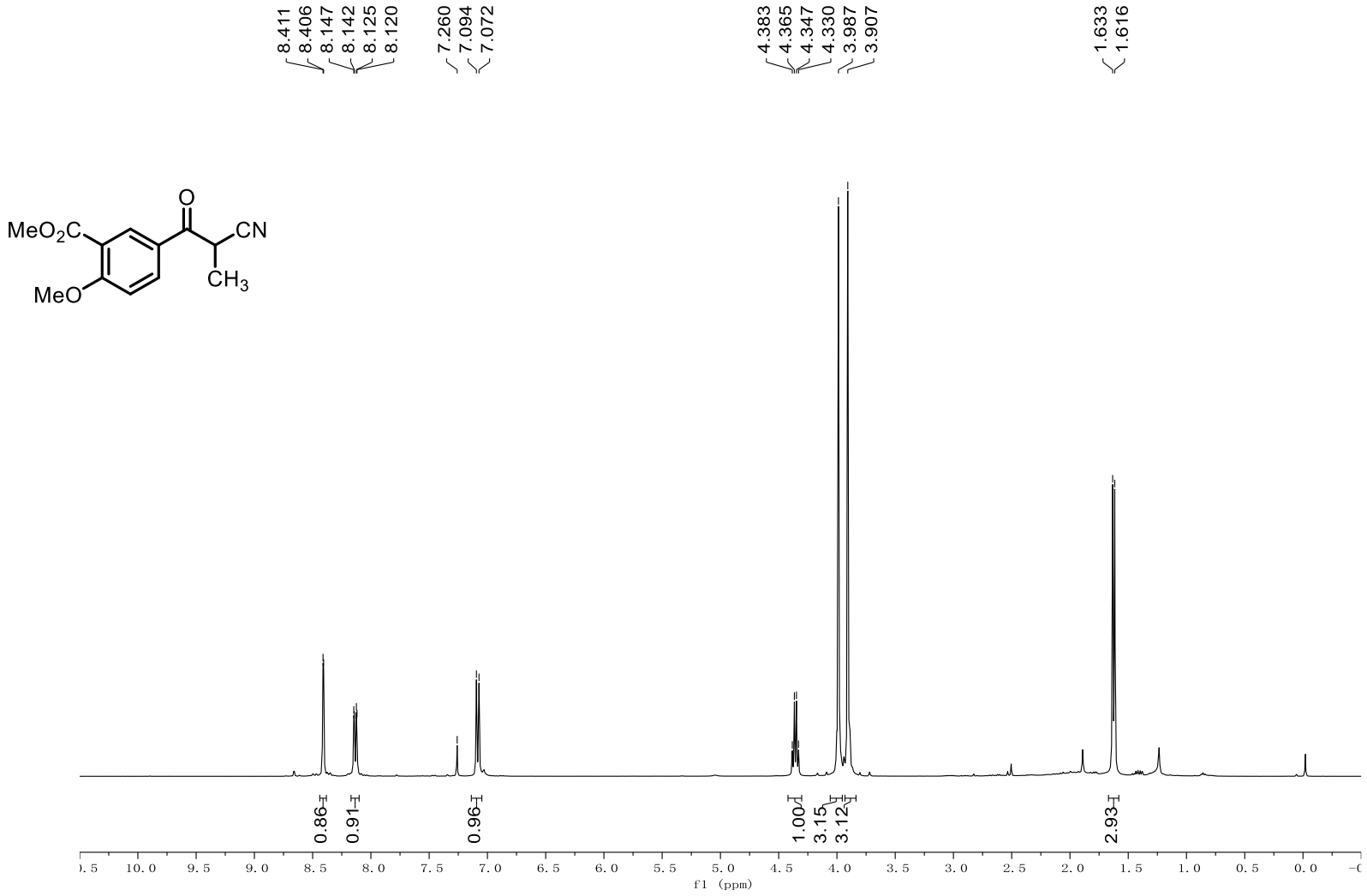
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-([1,1'-Biphenyl]-4-yl)-2-methyl-3-oxopropanenitrile (20)



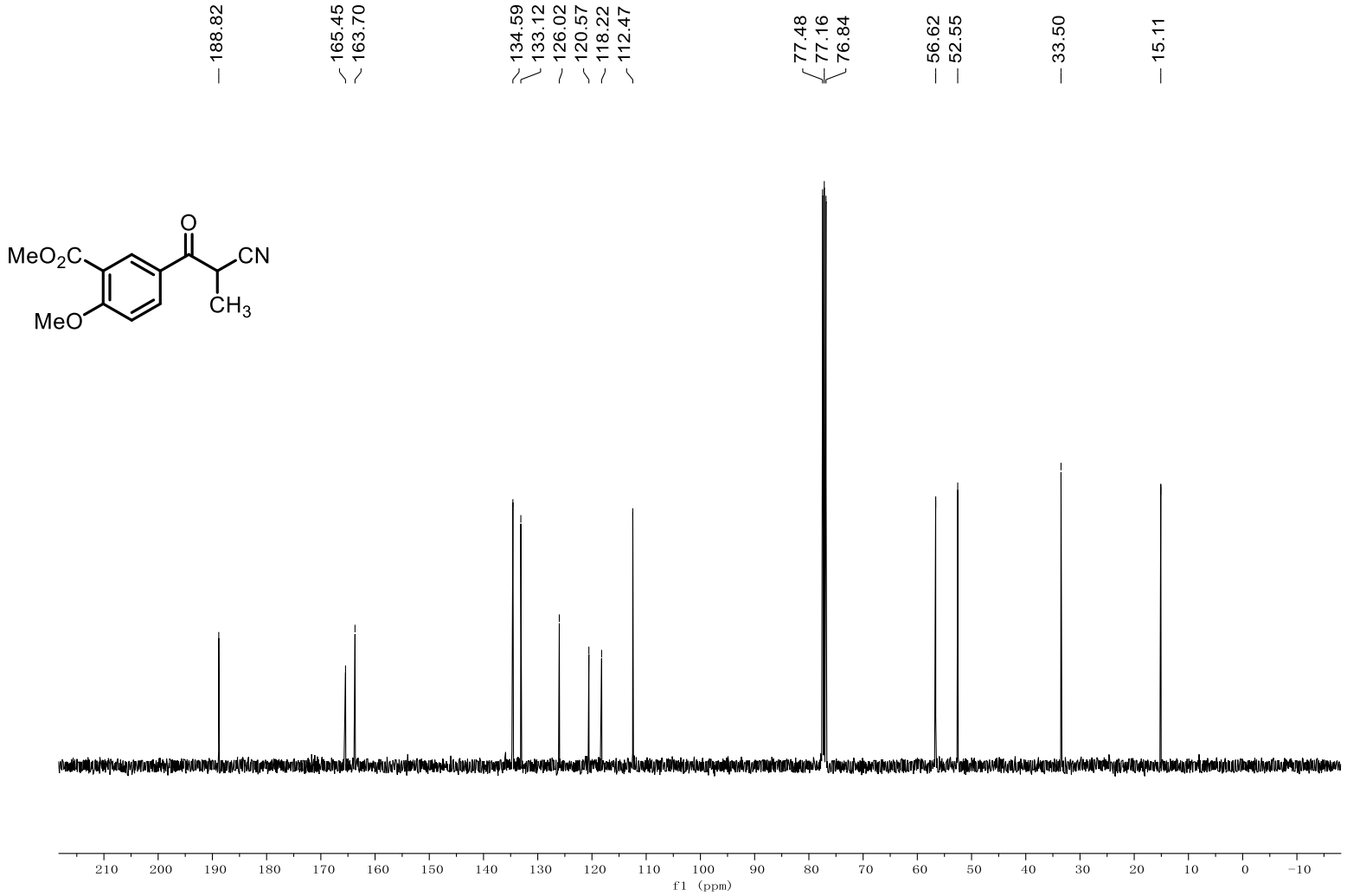
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-([1,1'-Biphenyl]-4-yl)-2-methyl-3-oxopropanenitrile (20)



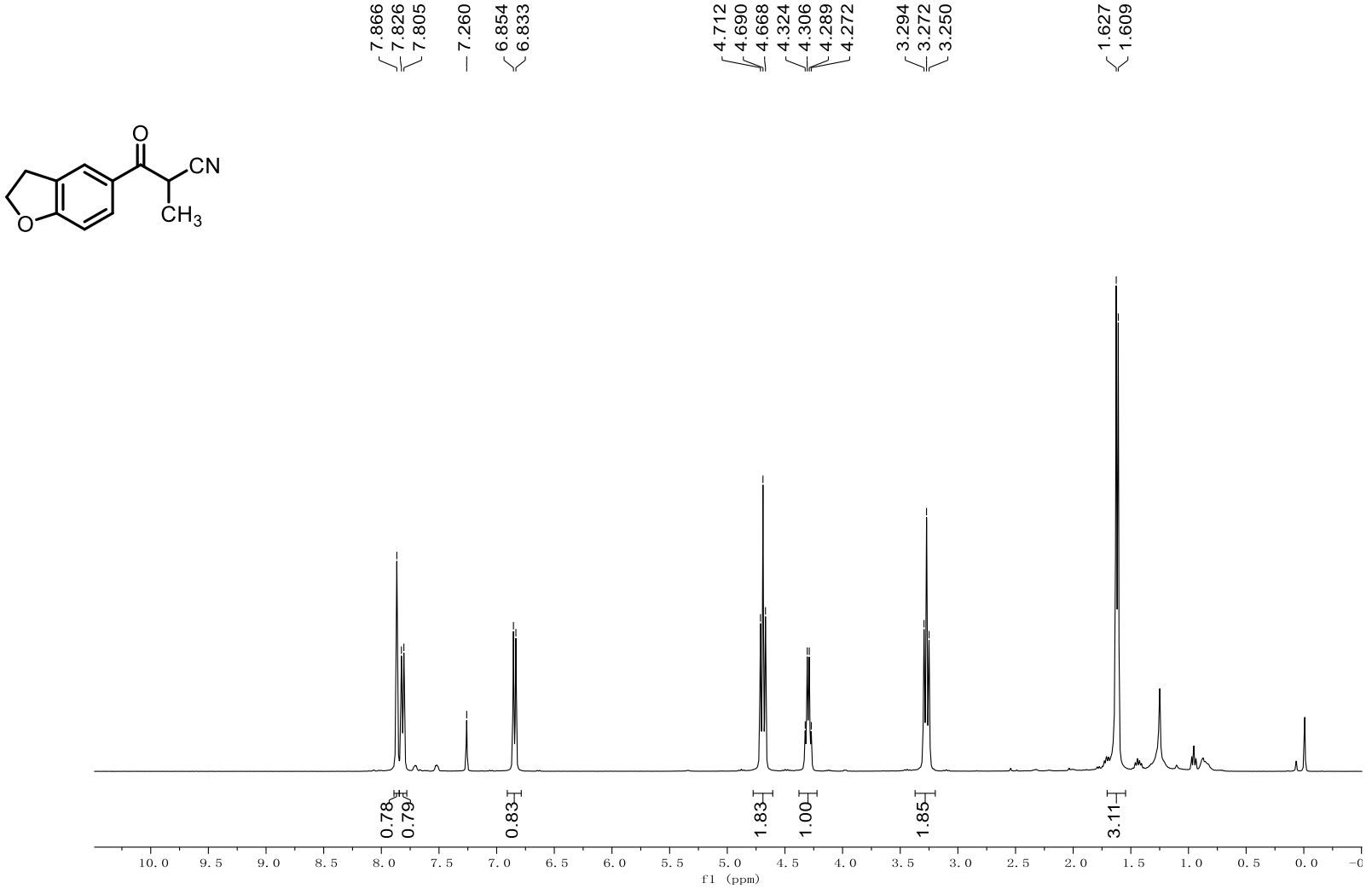
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of methyl 5-(2-Cyanopropanoyl)-2-methoxybenzoate (21)



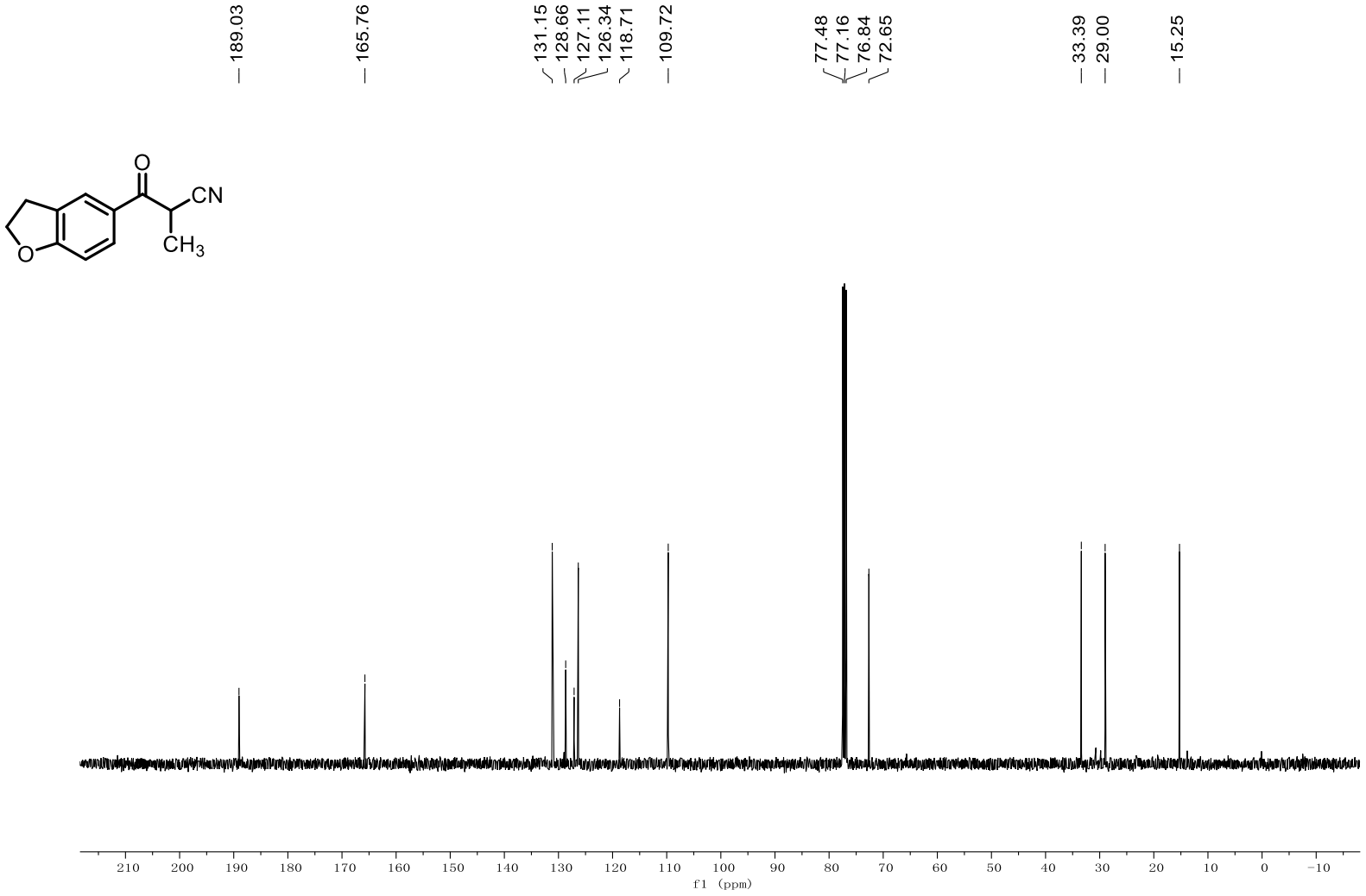
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of methyl 5-(2-Cyanopropanoyl)-2-methoxybenzoate (21)



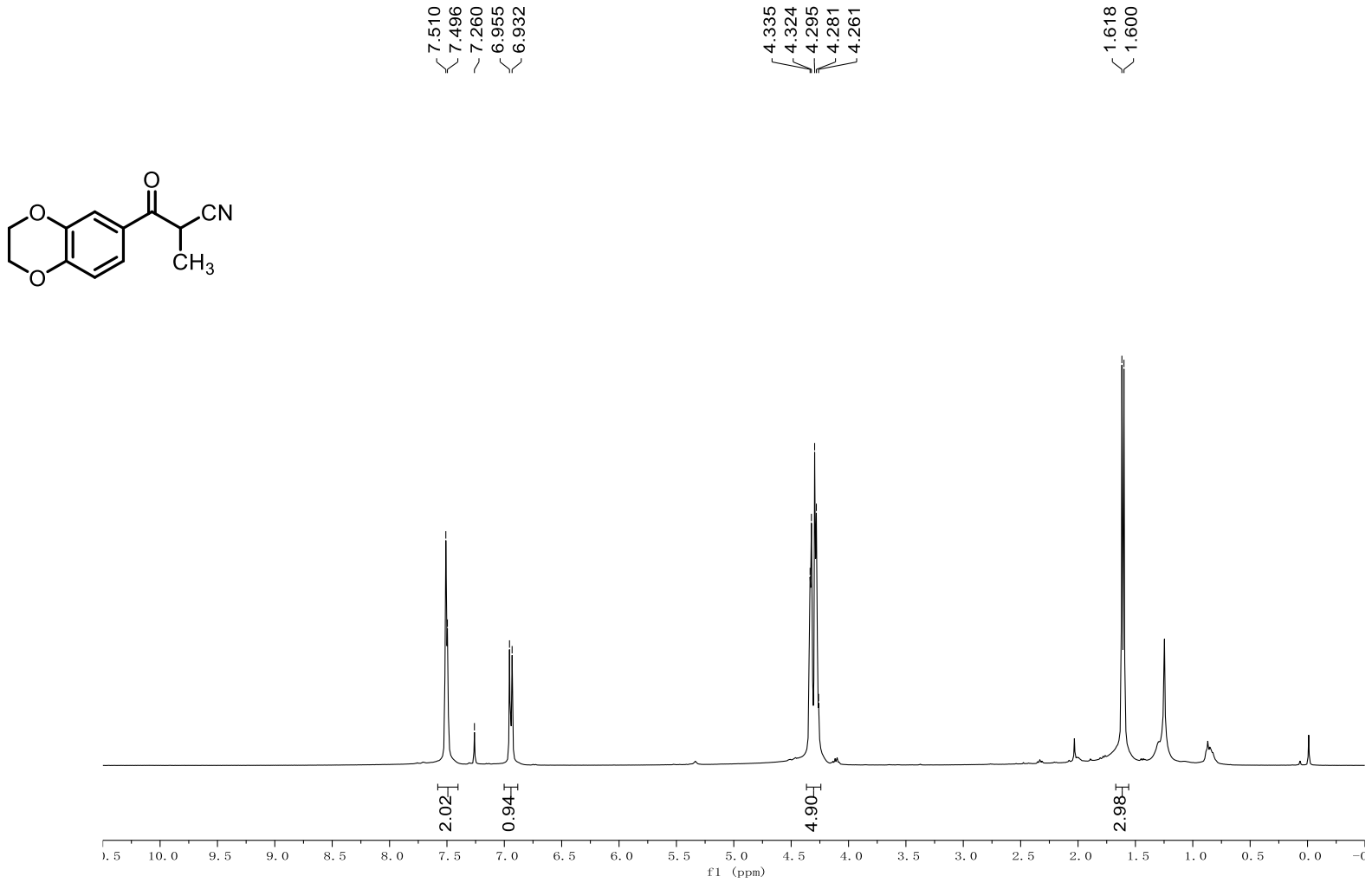
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(2,3-Dihydrobenzofuran-5-yl)-2-methyl-3-oxopropanenitrile (22)



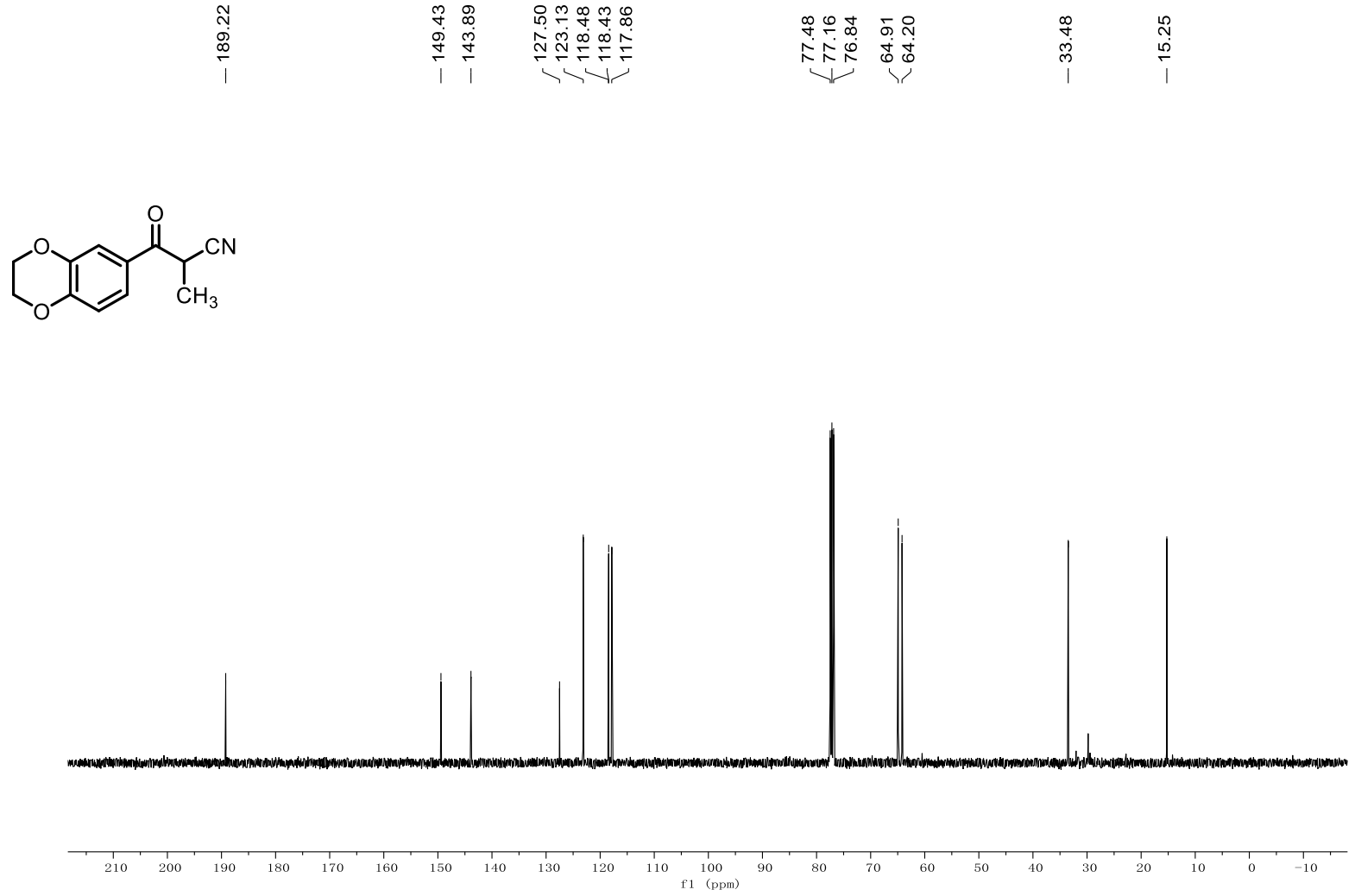
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(2,3-Dihydrobenzofuran-5-yl)-2-methyl-3-oxopropanenitrile (22)



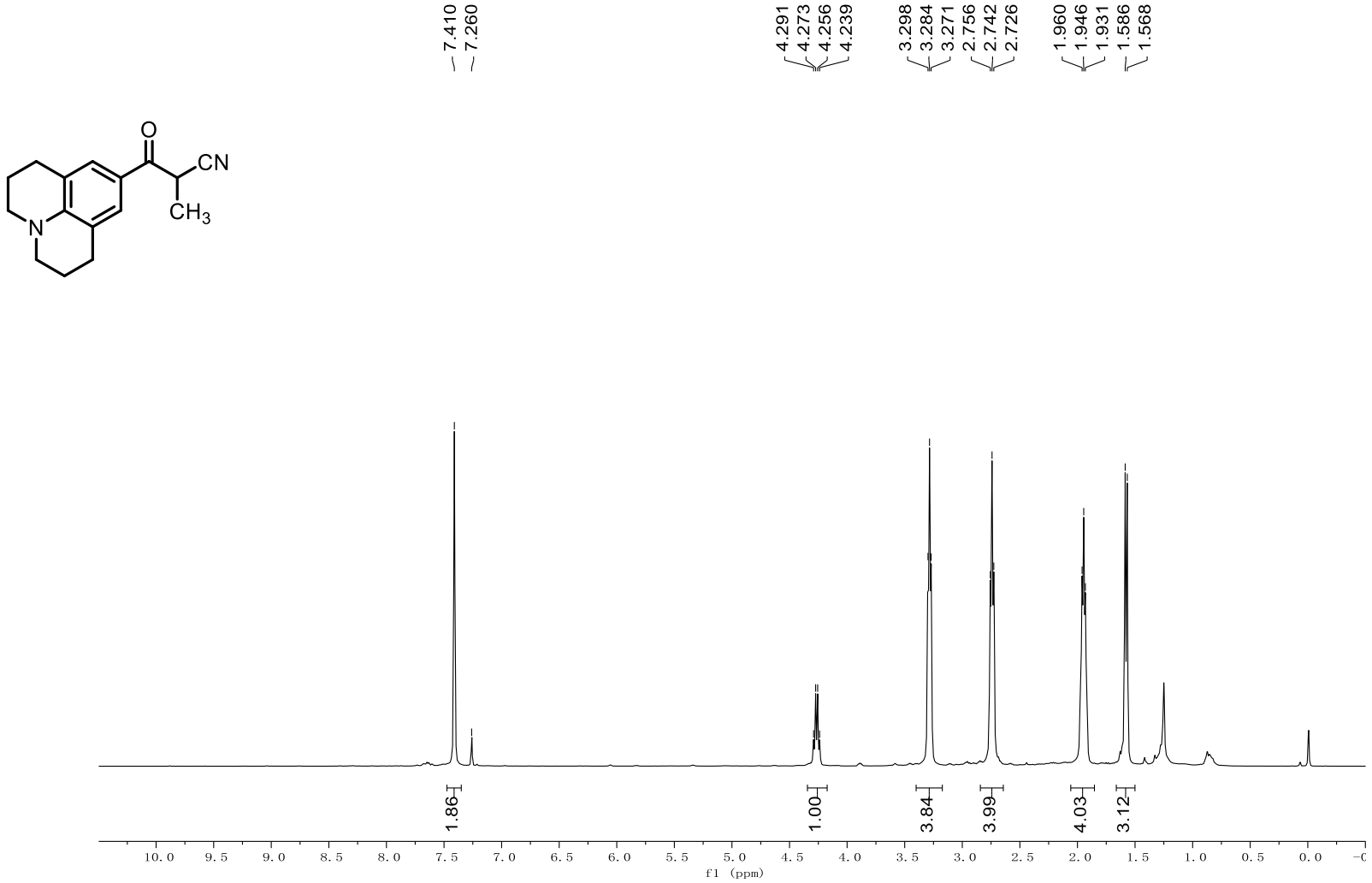
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-2-methyl-3-oxopropanenitrile (23)



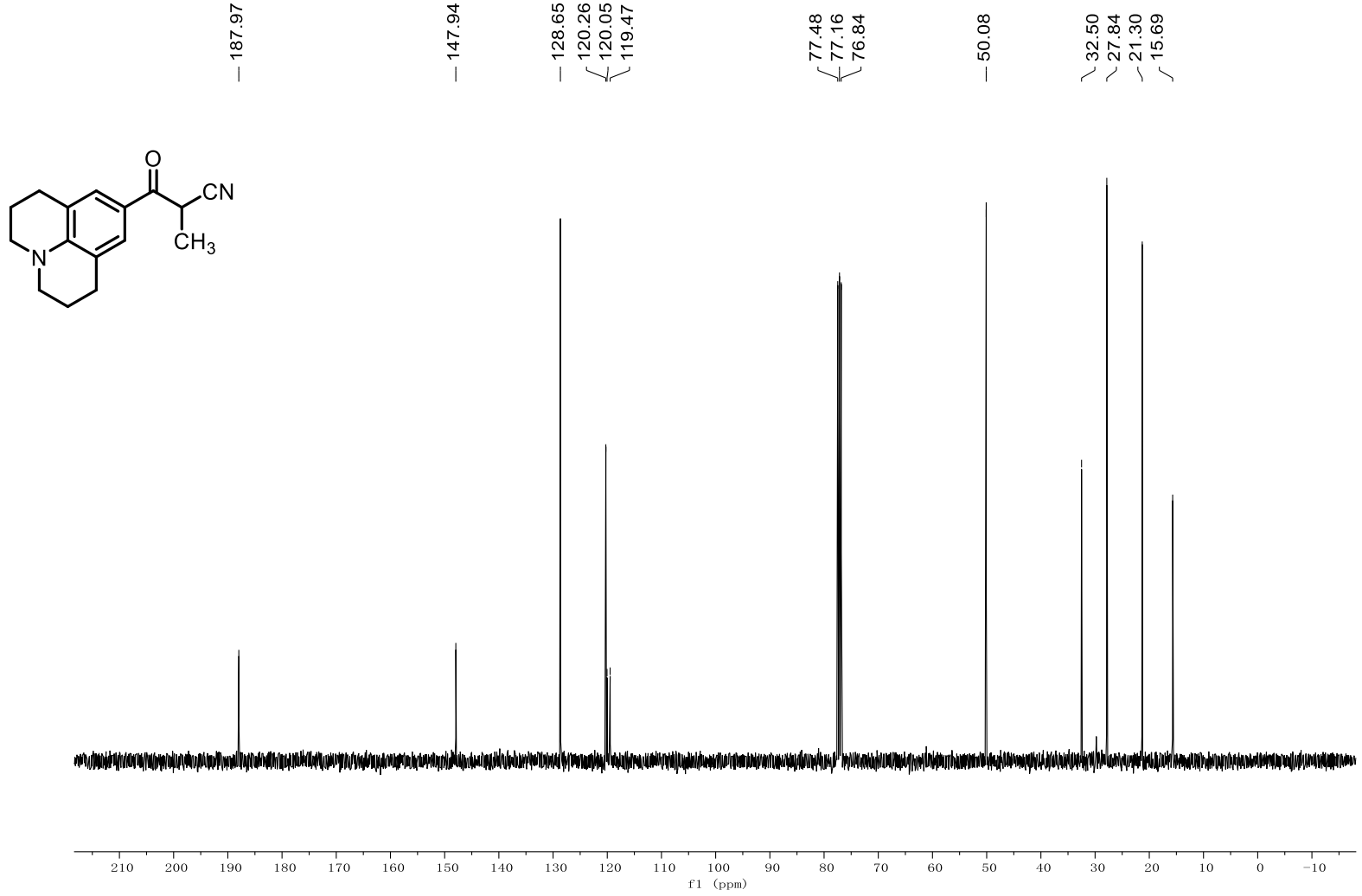
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(2,3-Dihydrobenzo[*b*][1,4]dioxin-6-yl)-2-methyl-3-oxopropanenitrile (23)



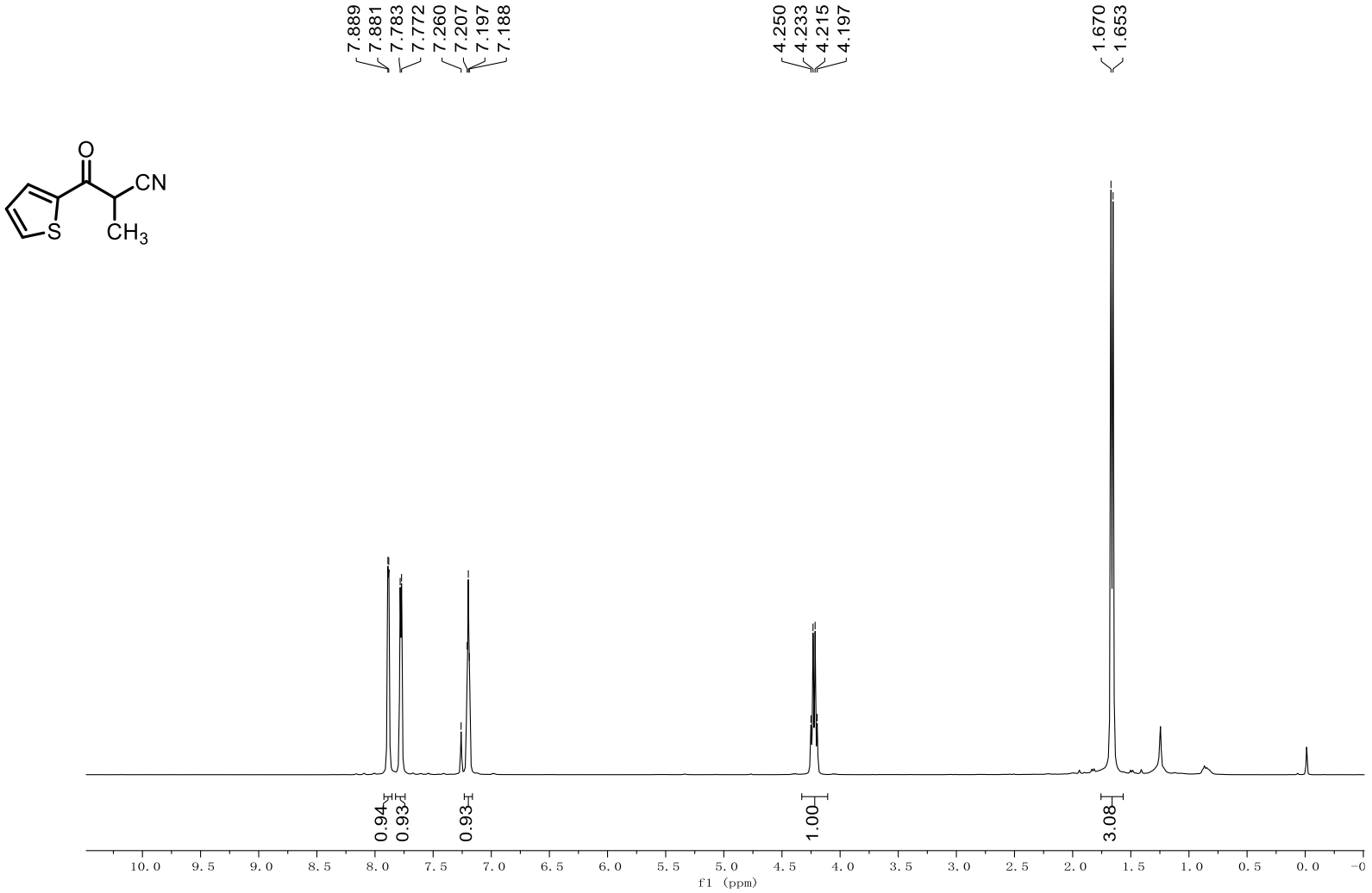
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxo-3-(2,3,6,7-tetrahydro-*1H*,*5H*-pyrido[3,2,1-*ij*]quinolin-9-yl)propanenitrile (24)



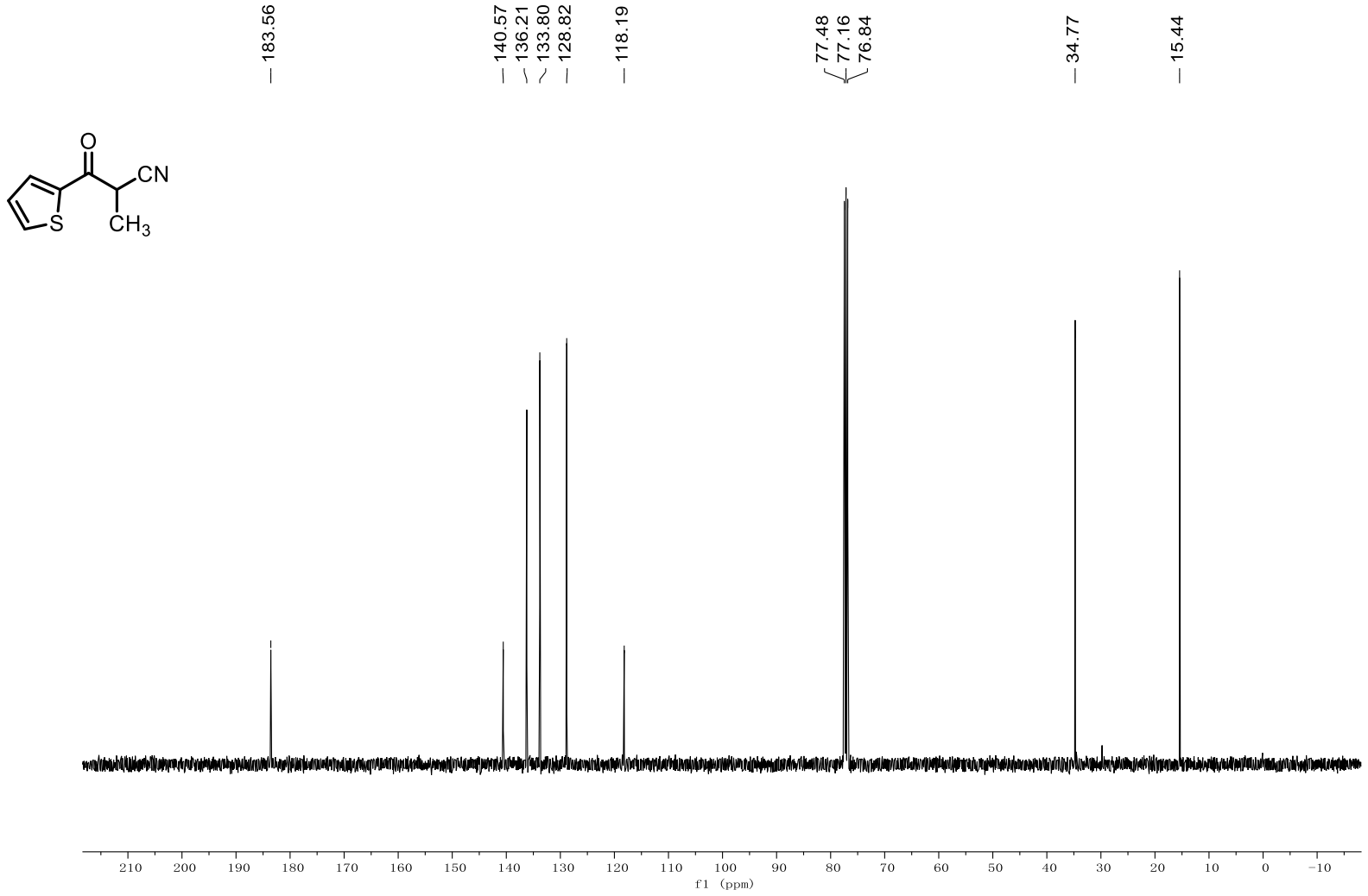
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxo-3-(2,3,6,7-tetrahydro-*1H*,*5H*-pyrido[3,2,1-*ij*]quinolin-9-yl)propanenitrile (24)



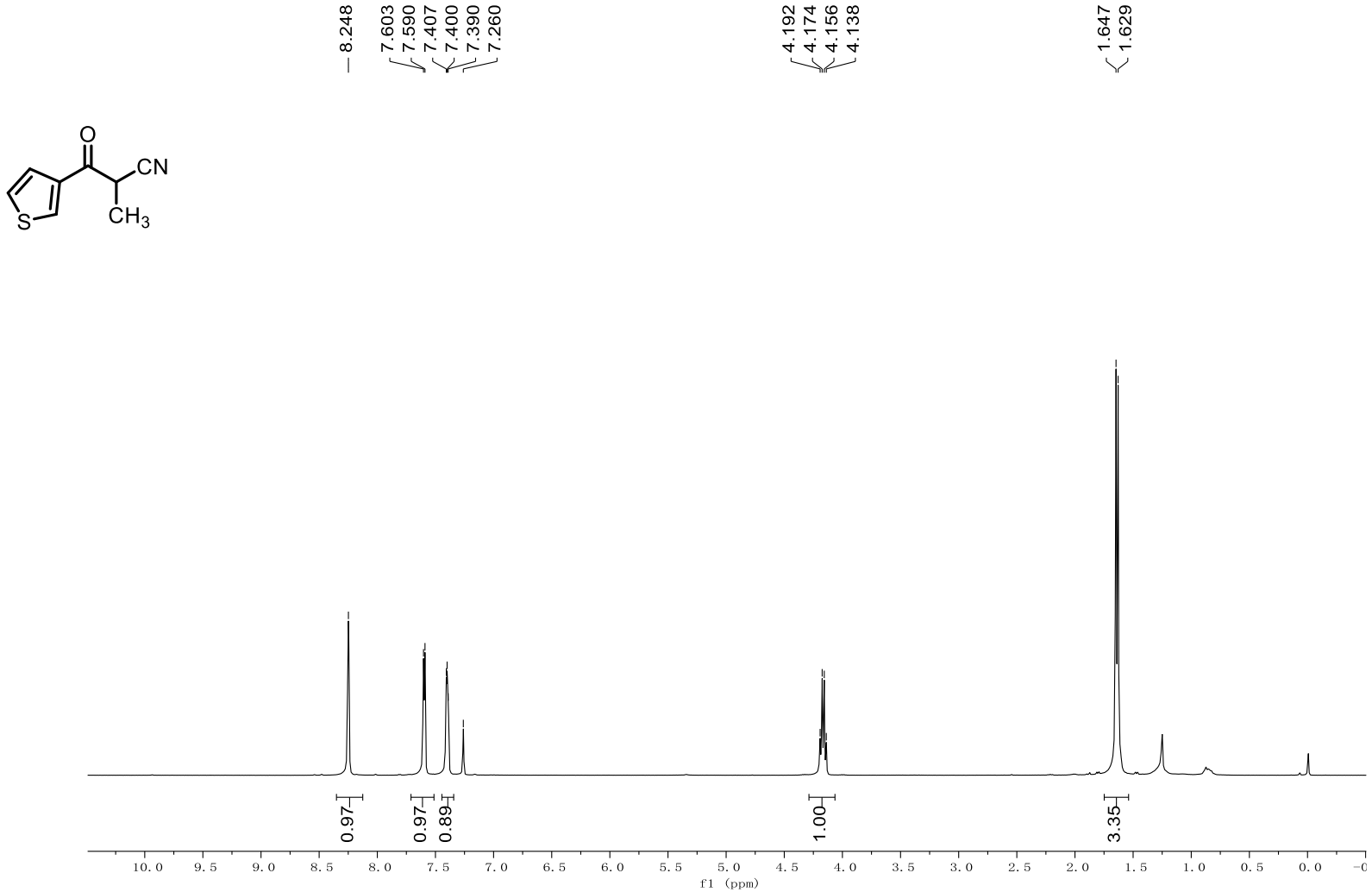
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxo-3-(thiophen-2-yl)propanenitrile (25)



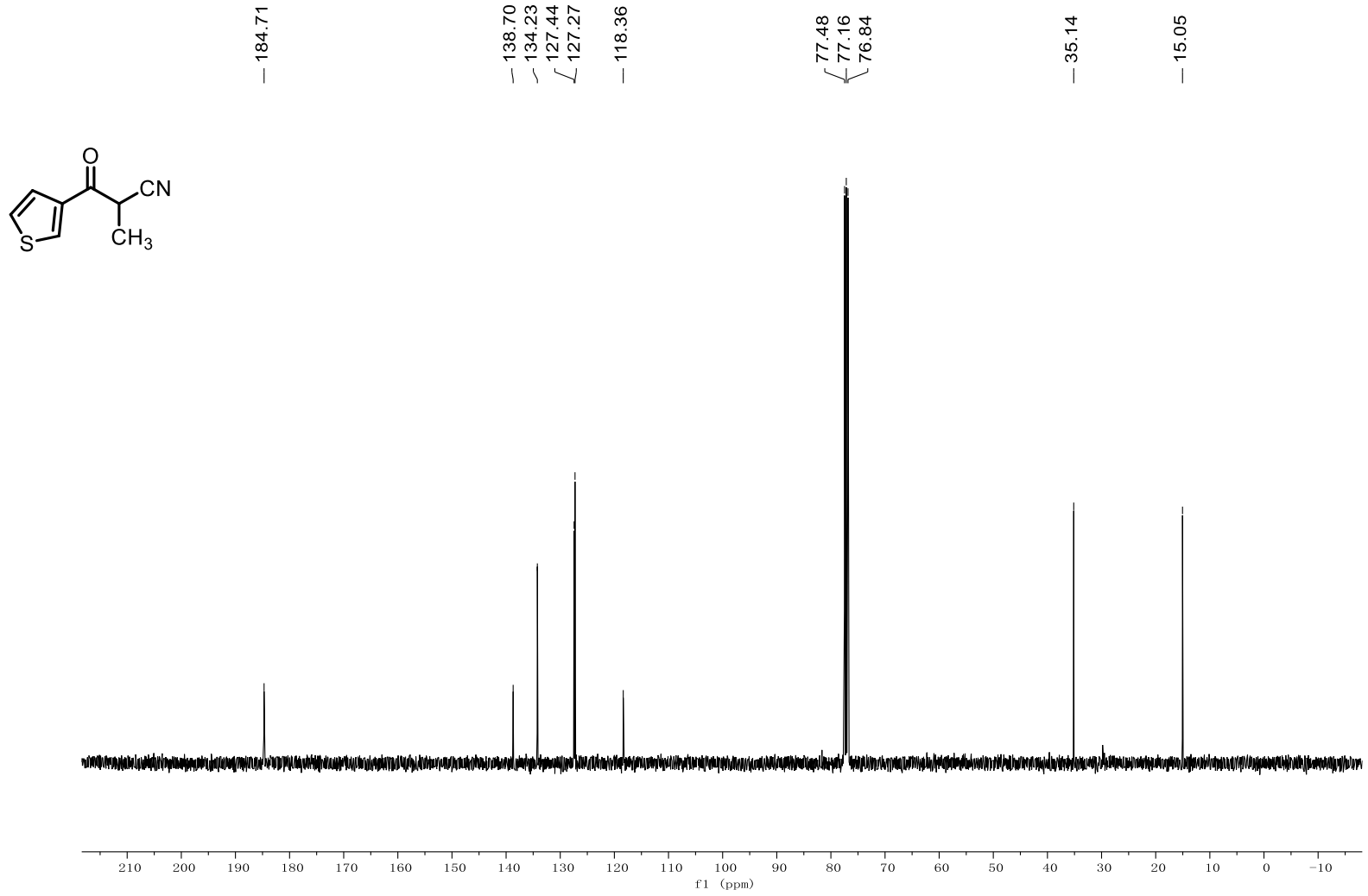
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxo-3-(thiophen-2-yl)propanenitrile (25)



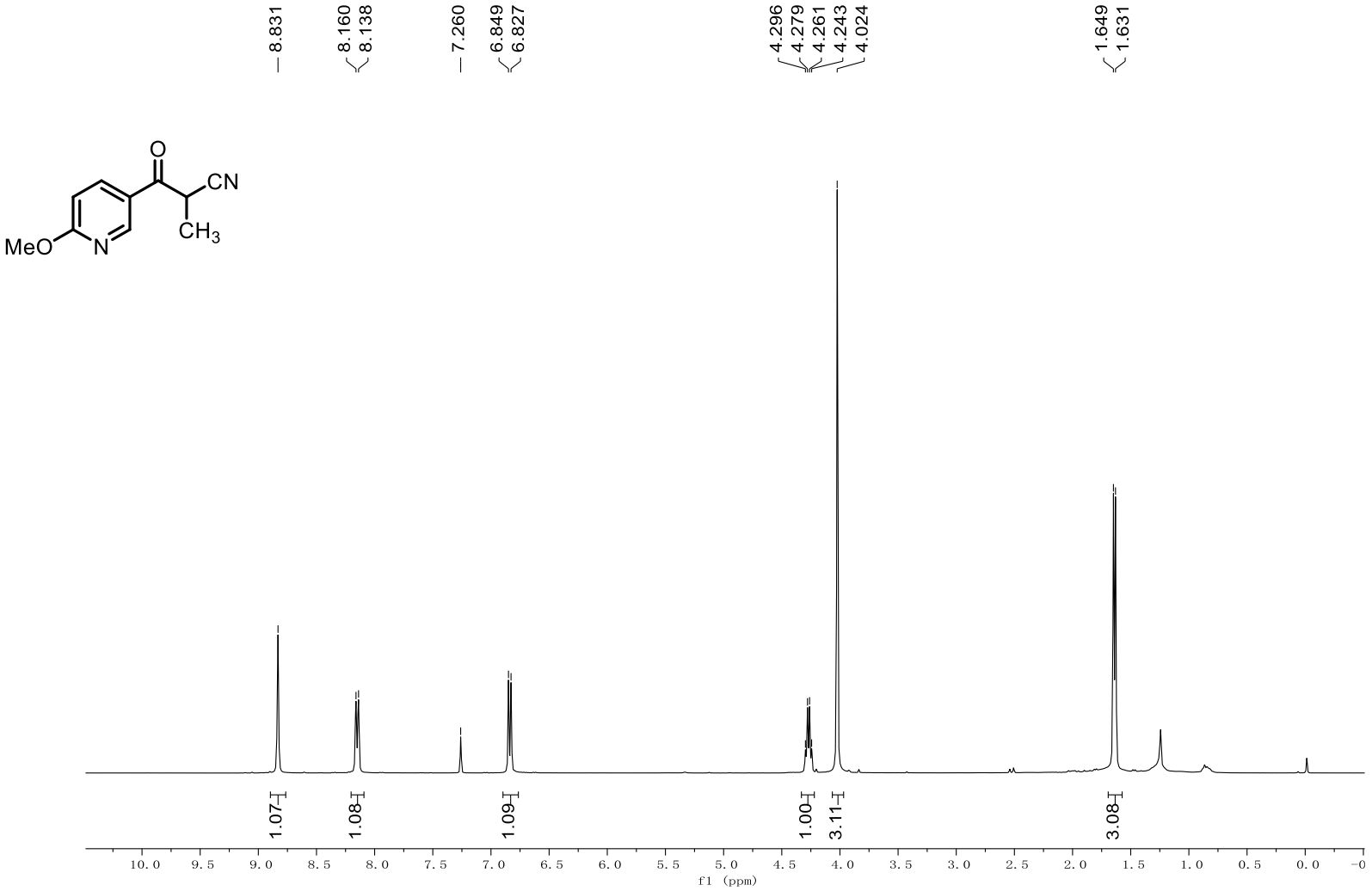
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxo-3-(thiophen-3-yl)propanenitrile (26)



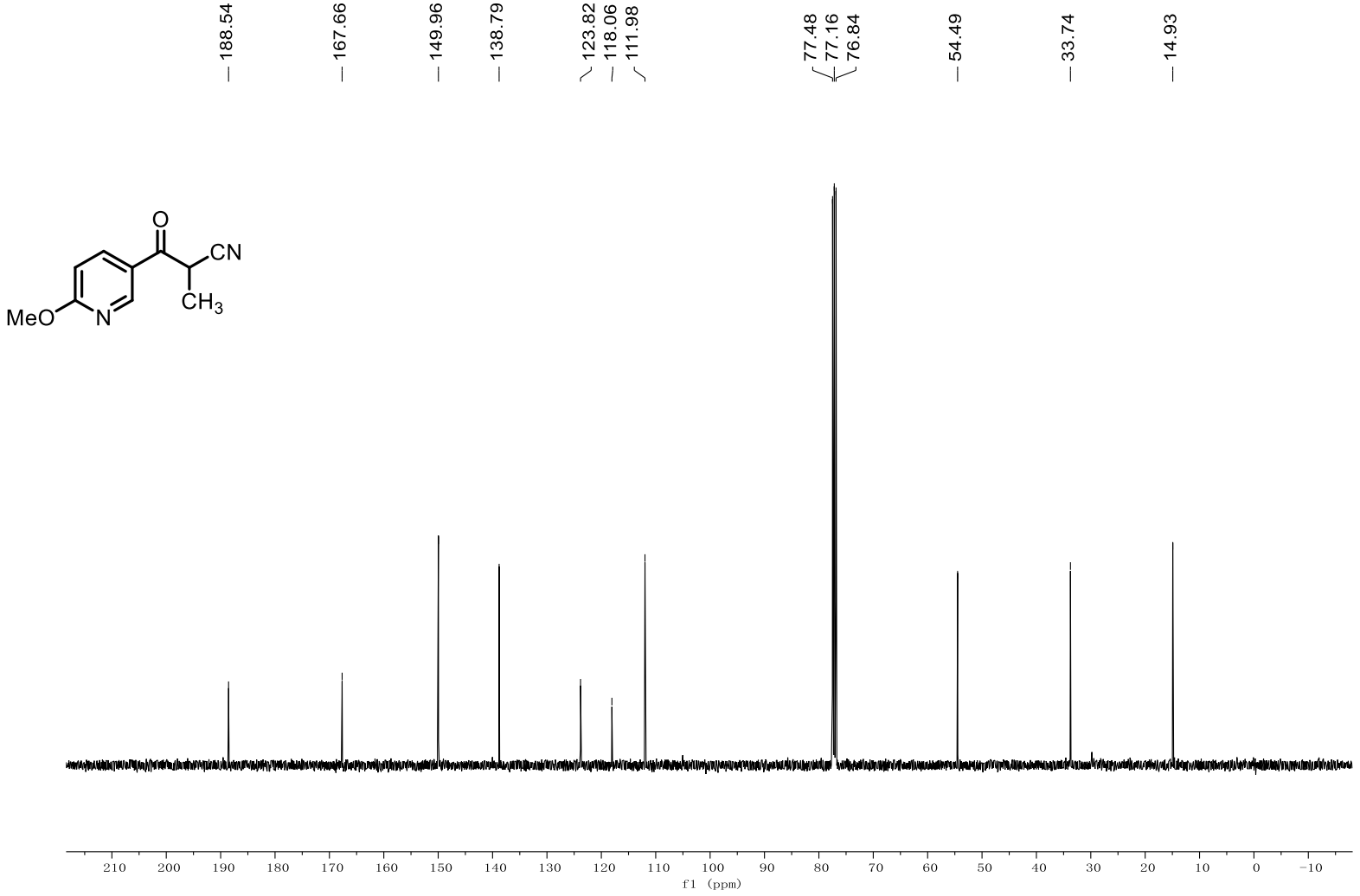
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxo-3-(thiophen-3-yl)propanenitrile (26)



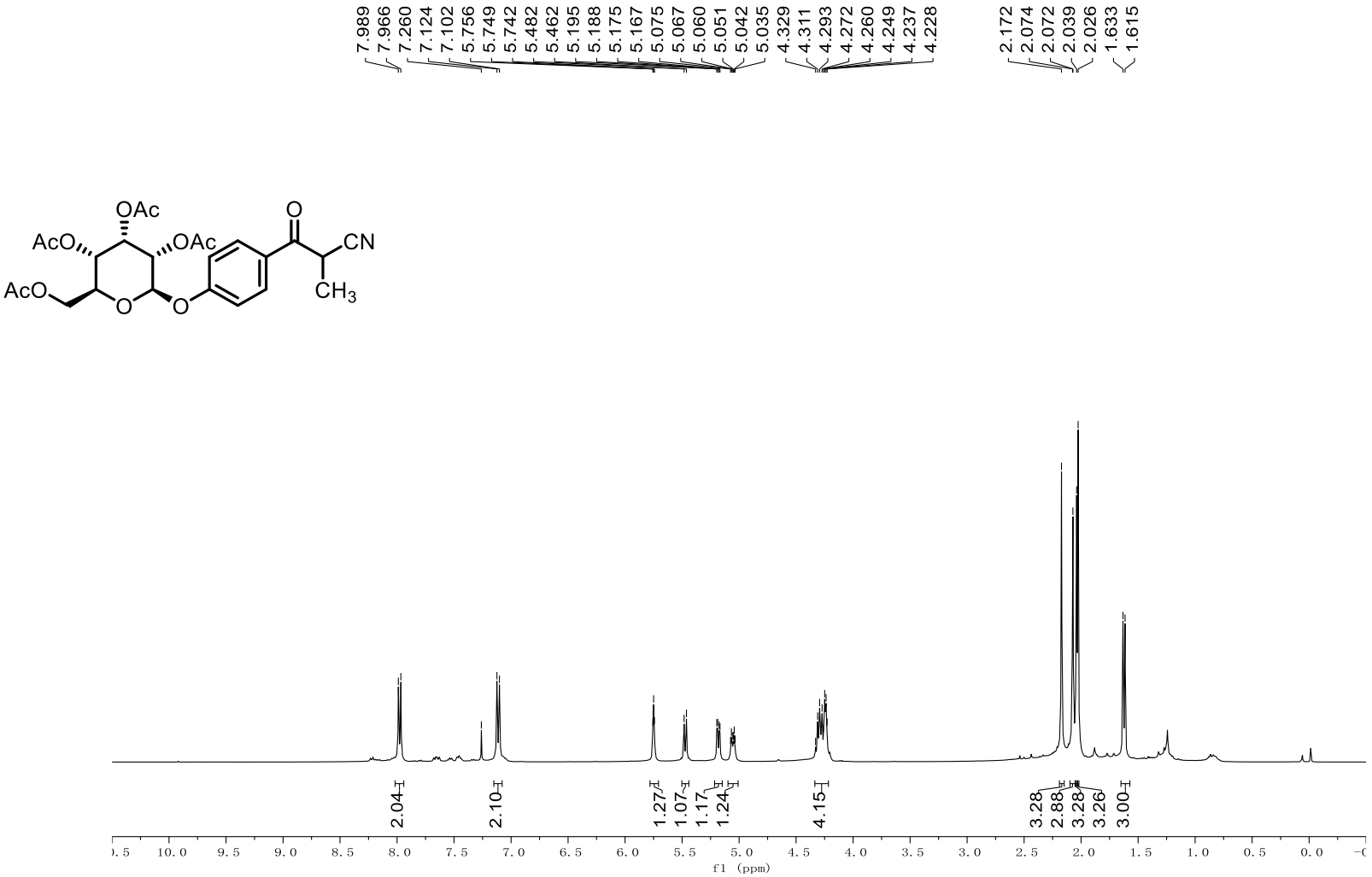
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(6-Methoxypyridin-3-yl)-2-methyl-3-oxopropanenitrile (27)



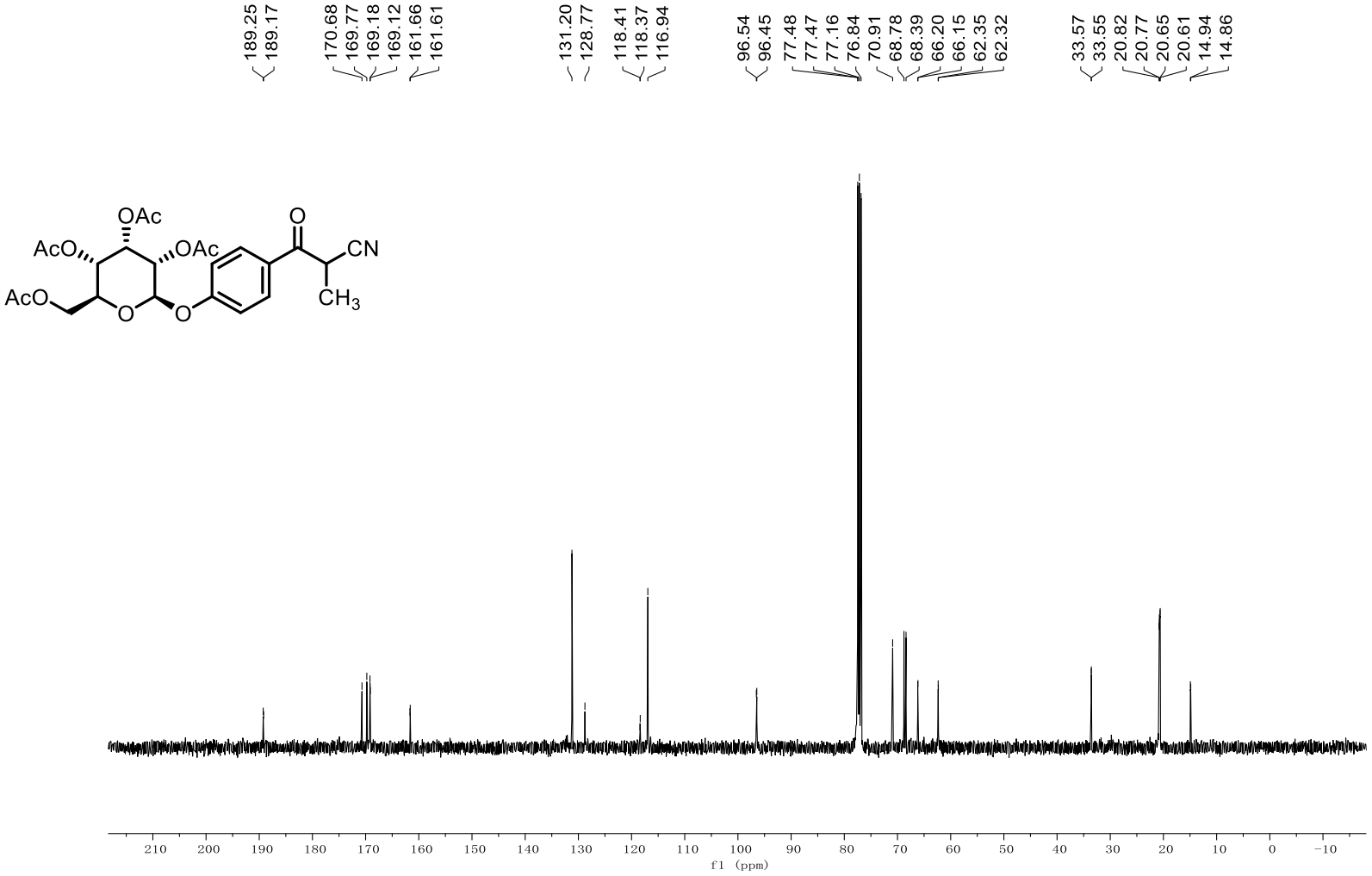
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(6-Methoxypyridin-3-yl)-2-methyl-3-oxopropanenitrile (27)



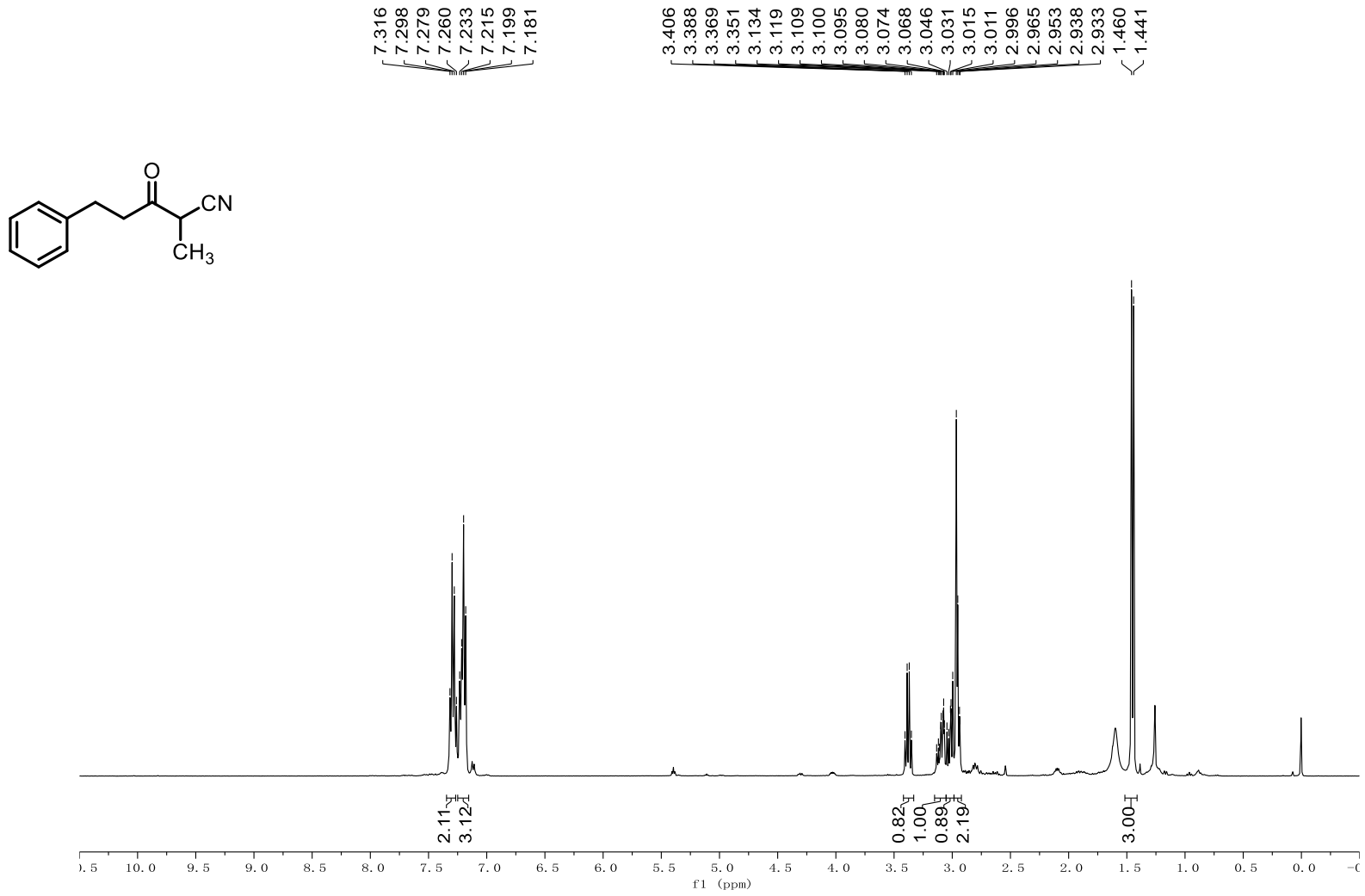
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (2*S*,3*S*,4*S*,5*S*,6*R*)-2-(Acetoxymethyl)-6-(4-(2-cyanopropanoyl)phenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (28)



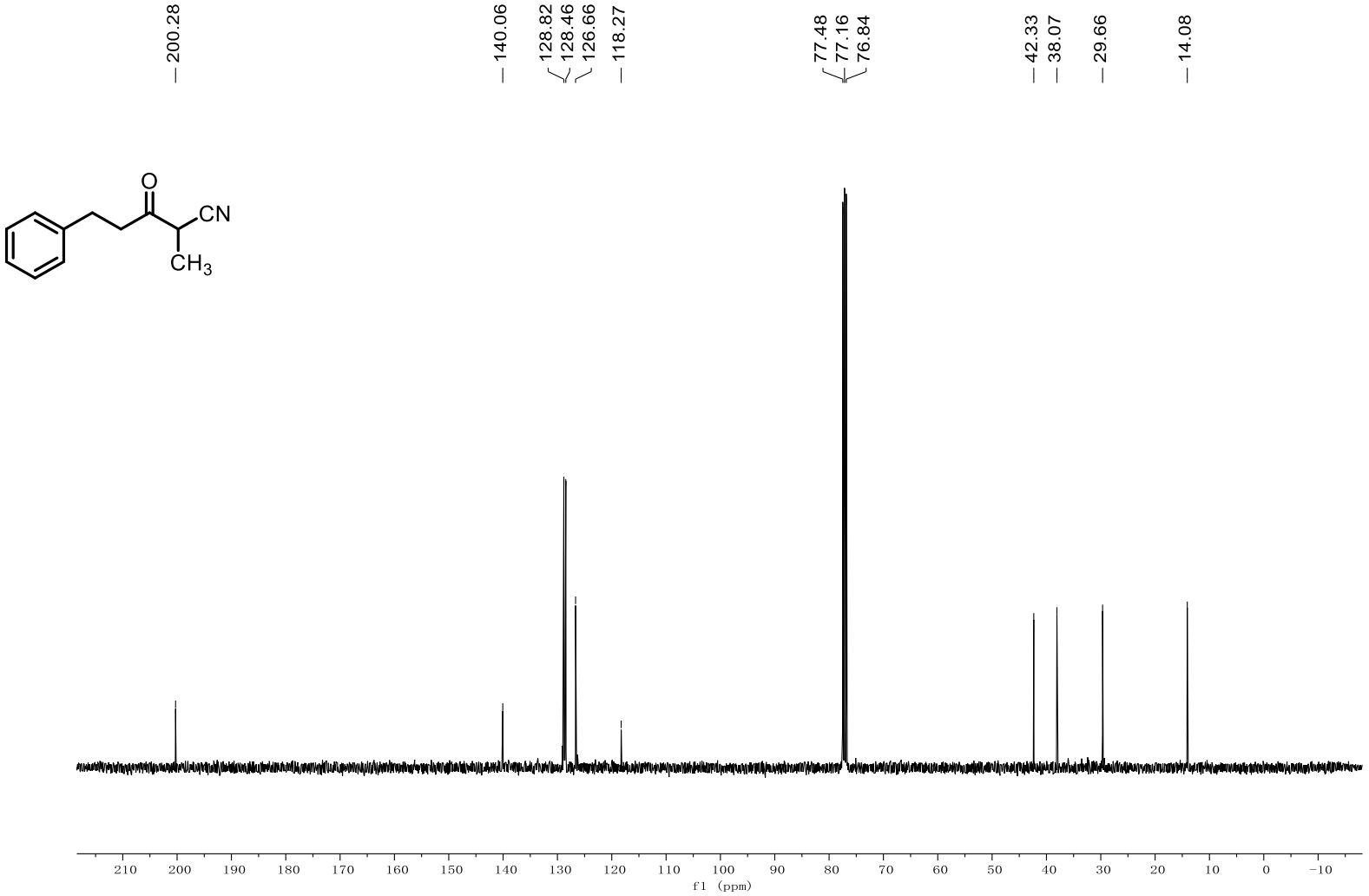
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (2*S*,3*S*,4*S*,5*S*,6*R*)-2-(Acetoxymethyl)-6-(4-(2-cyanopropanoyl)phenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (28)



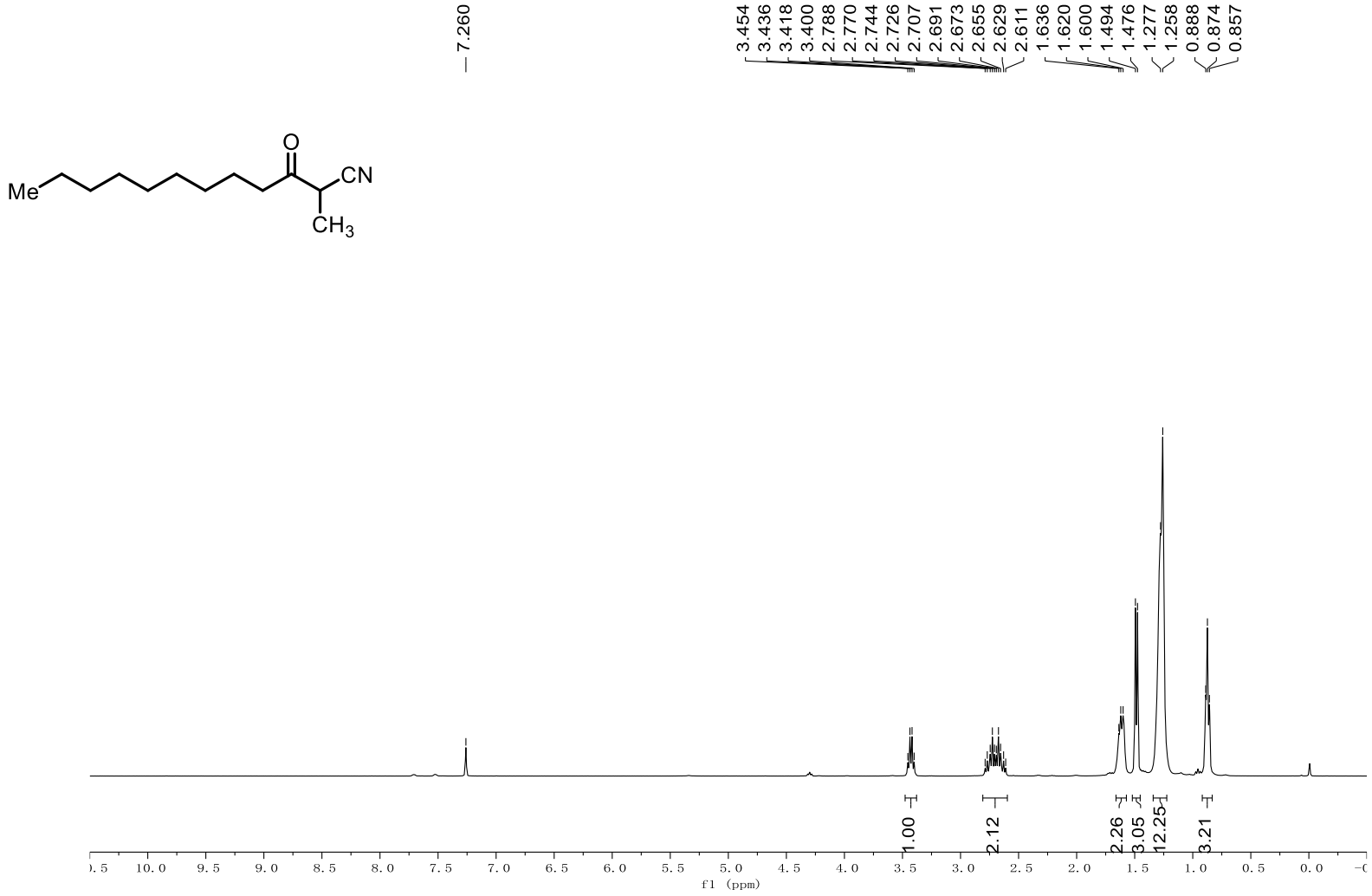
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxo-5-phenylpentanenitrile (29)



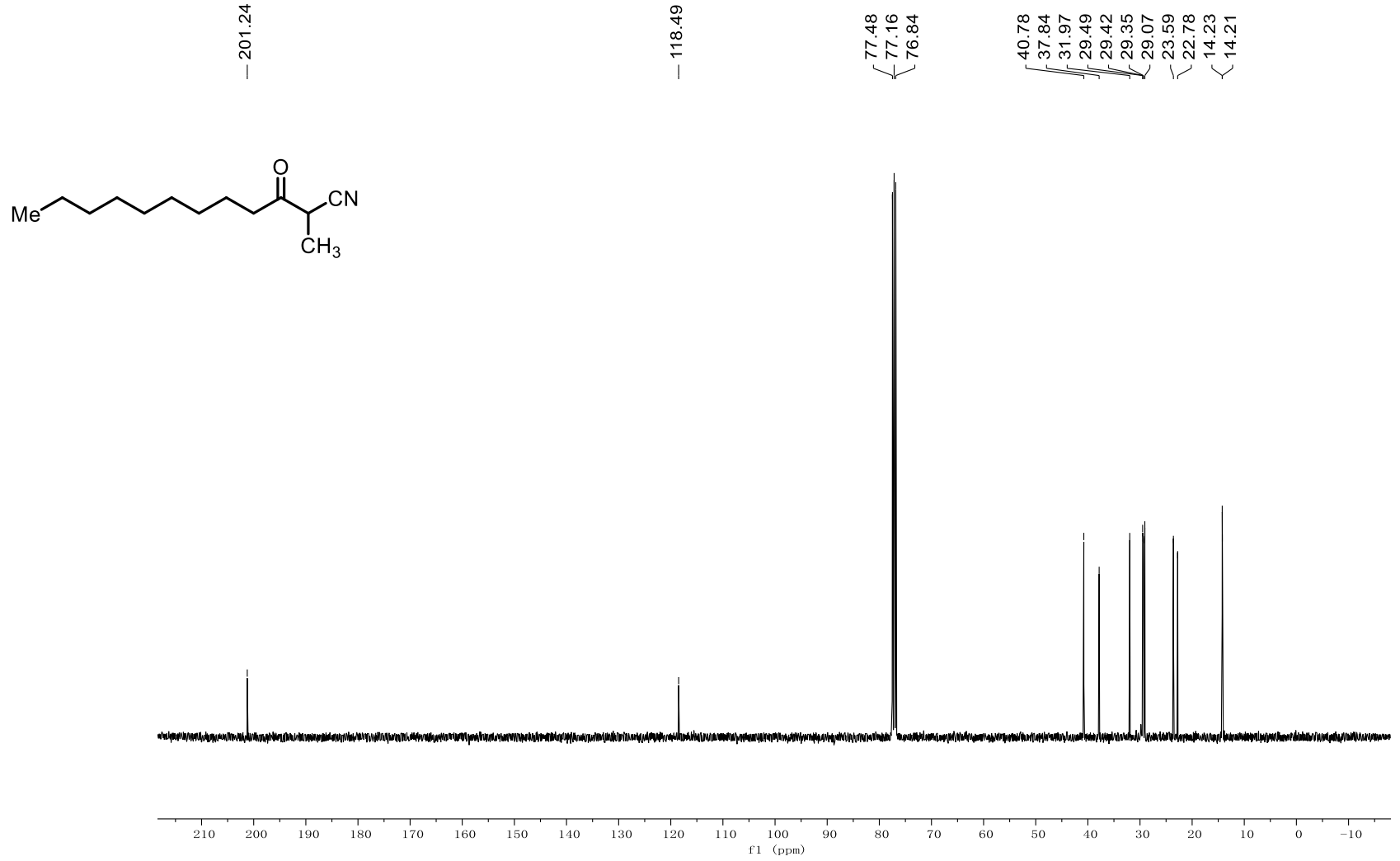
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxo-5-phenylpentanenitrile (29)



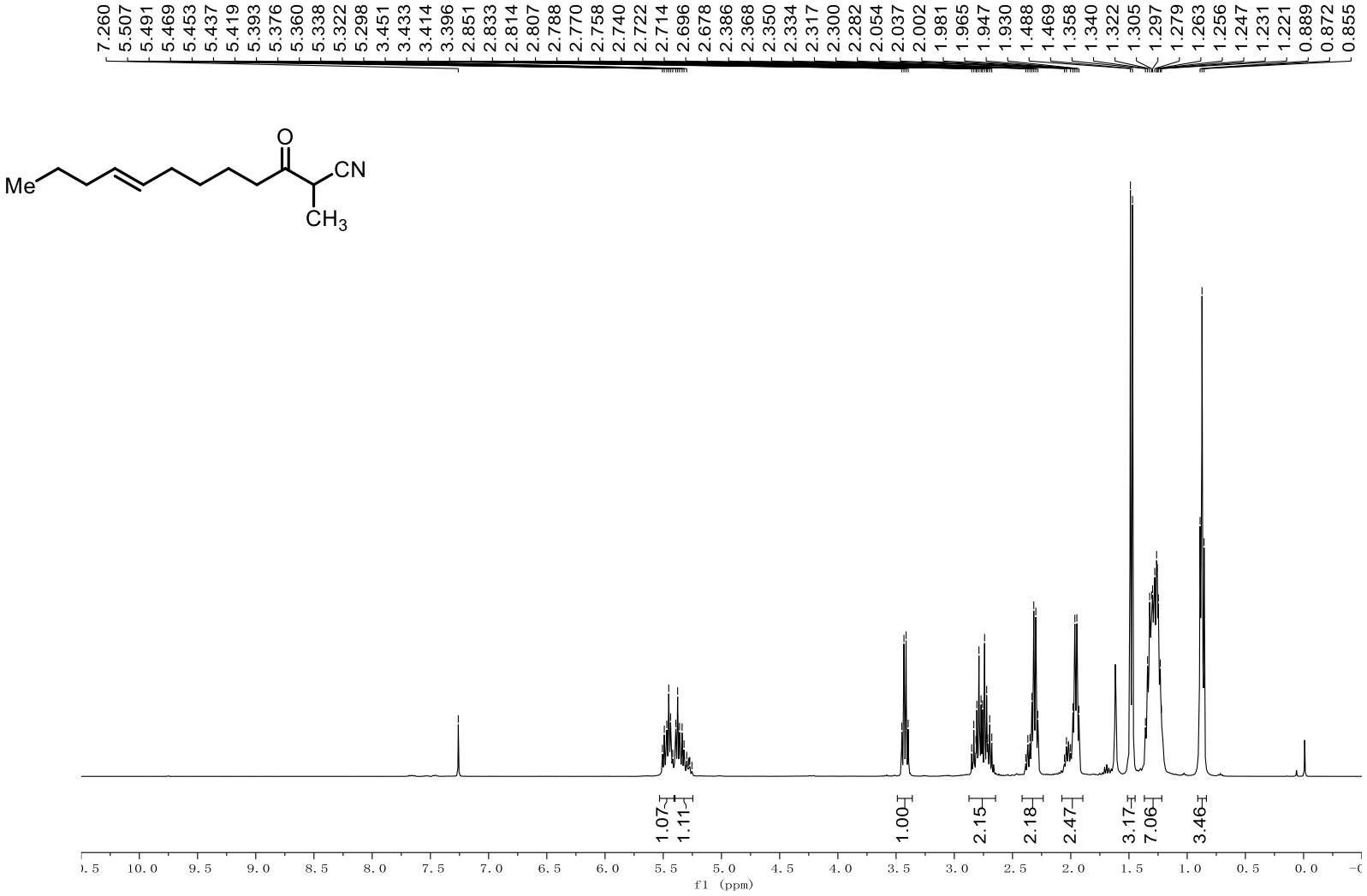
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxododecanenitrile (30)



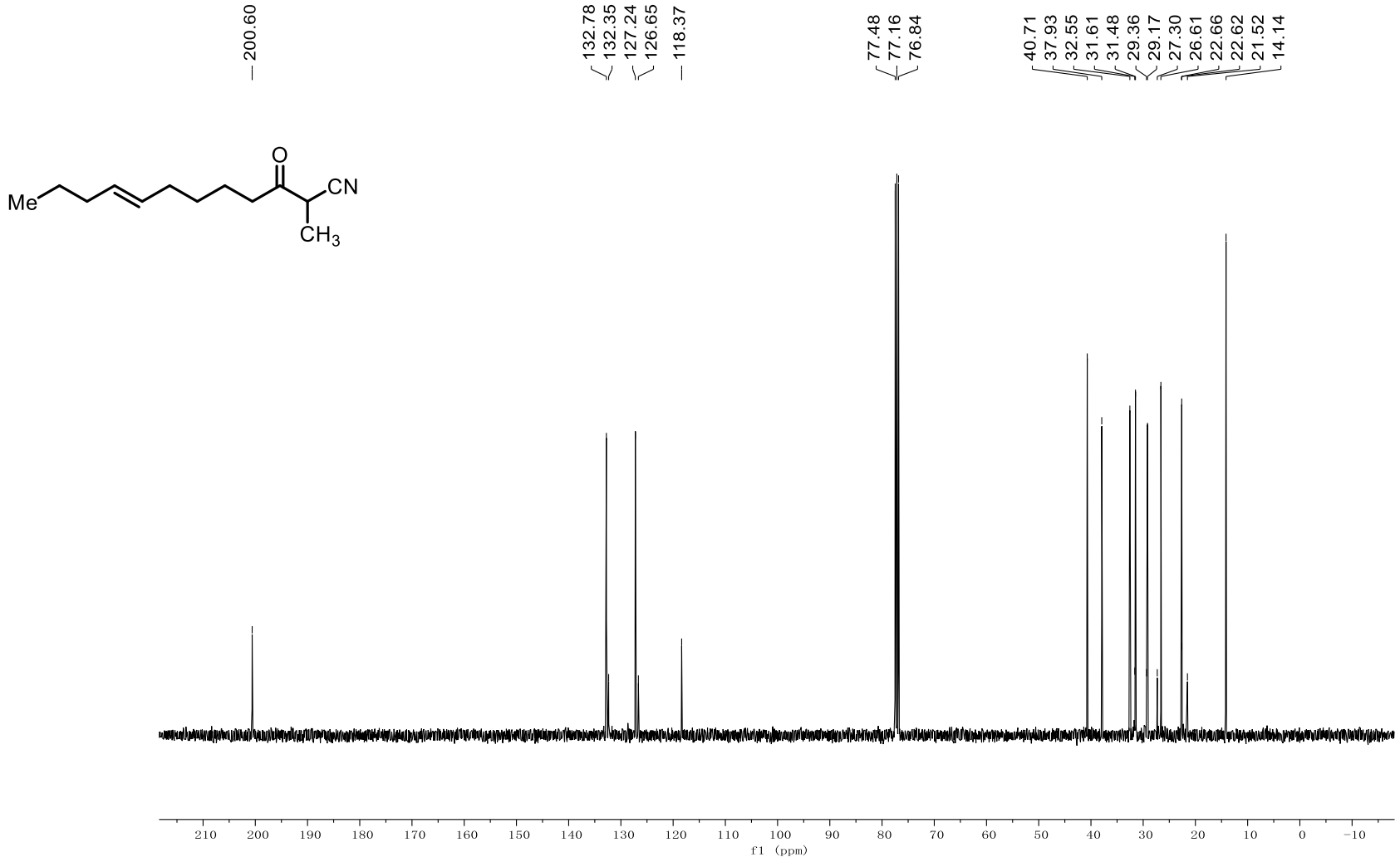
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-3-oxododecanenitrile (30)



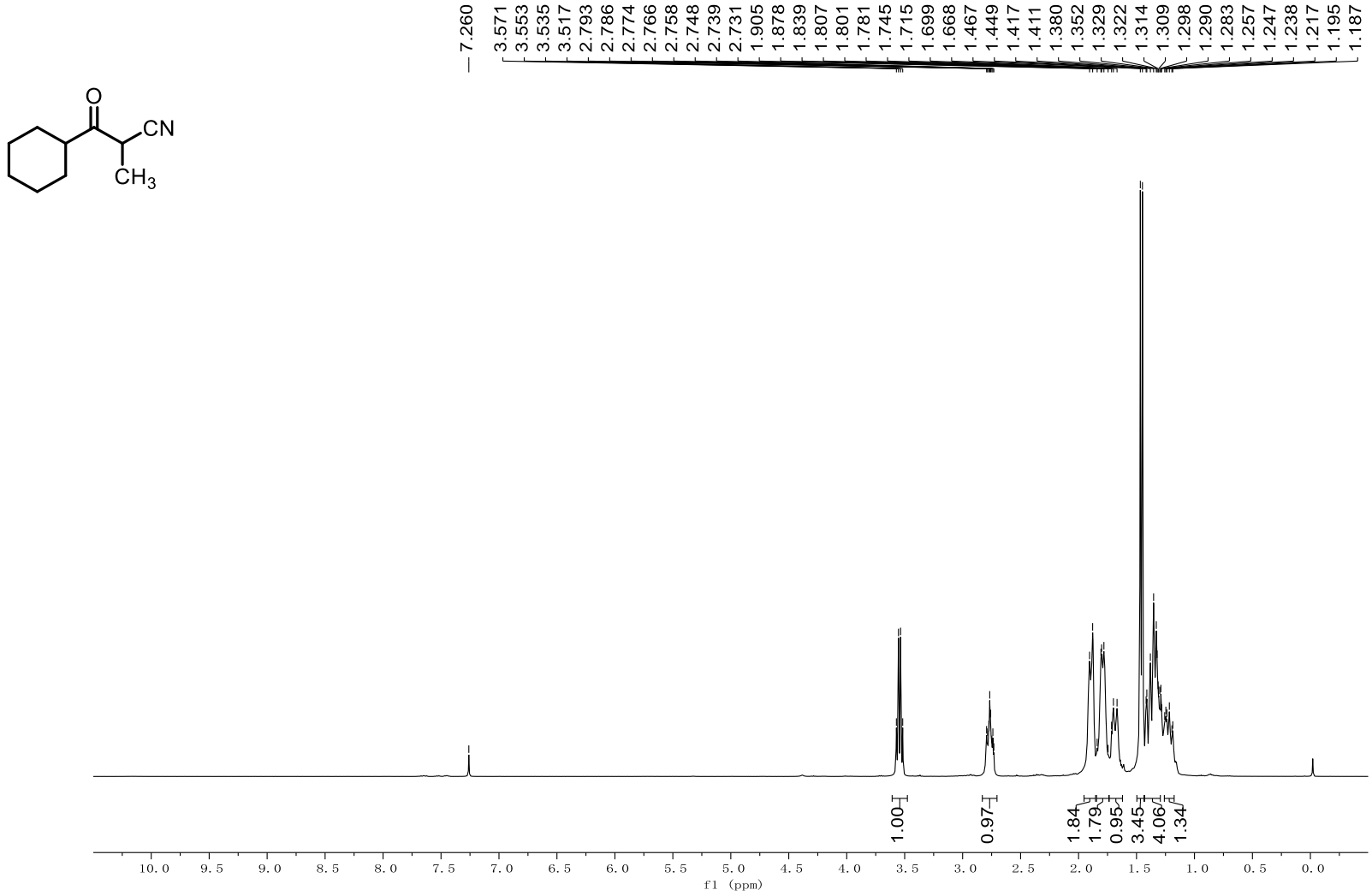
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*E*)-2-Methyl-3-oxododec-8-enenitrile (31) with minor (*Z*)-31



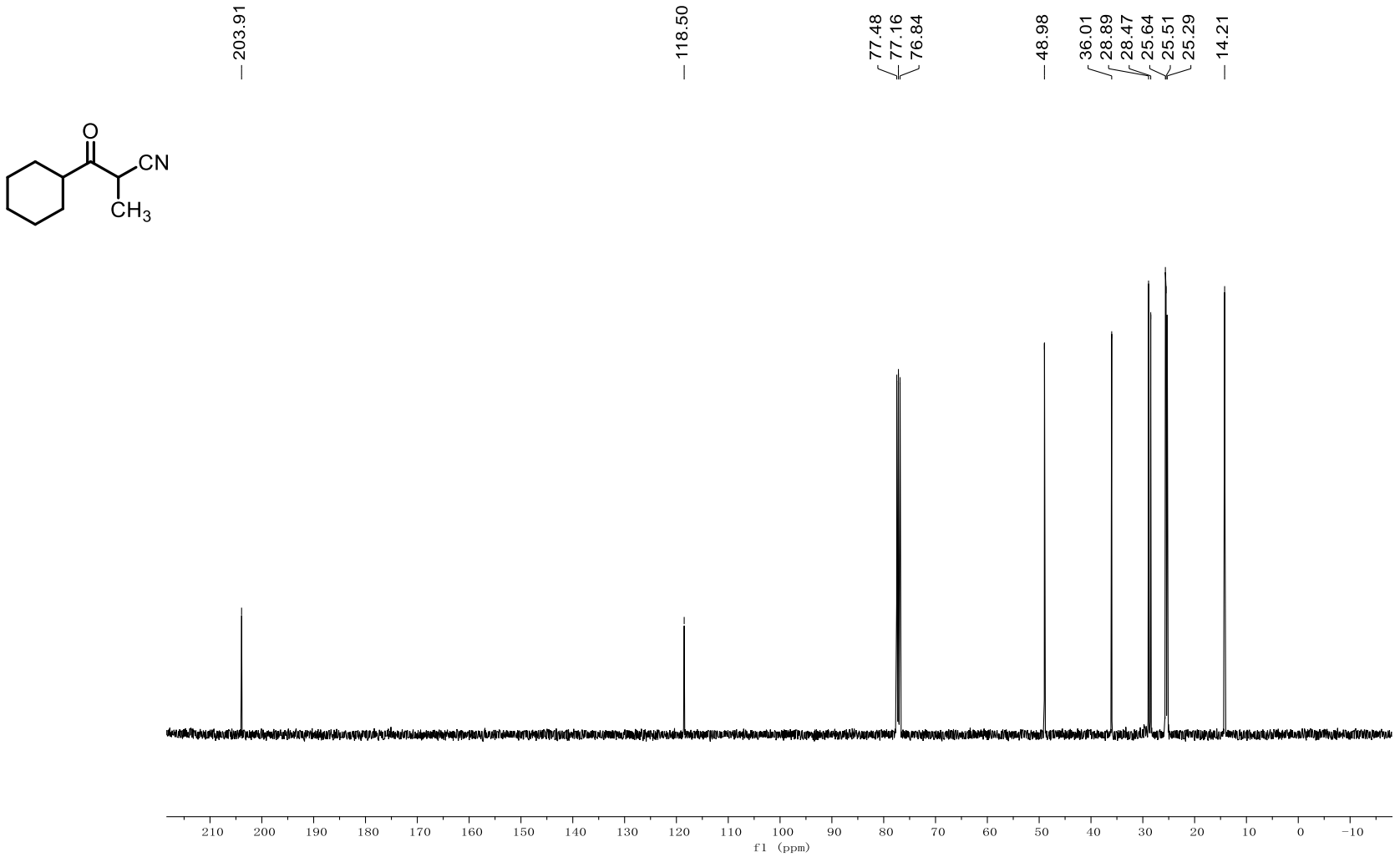
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-2-Methyl-3-oxododec-8-enenitrile (31) with minor (*Z*)-31



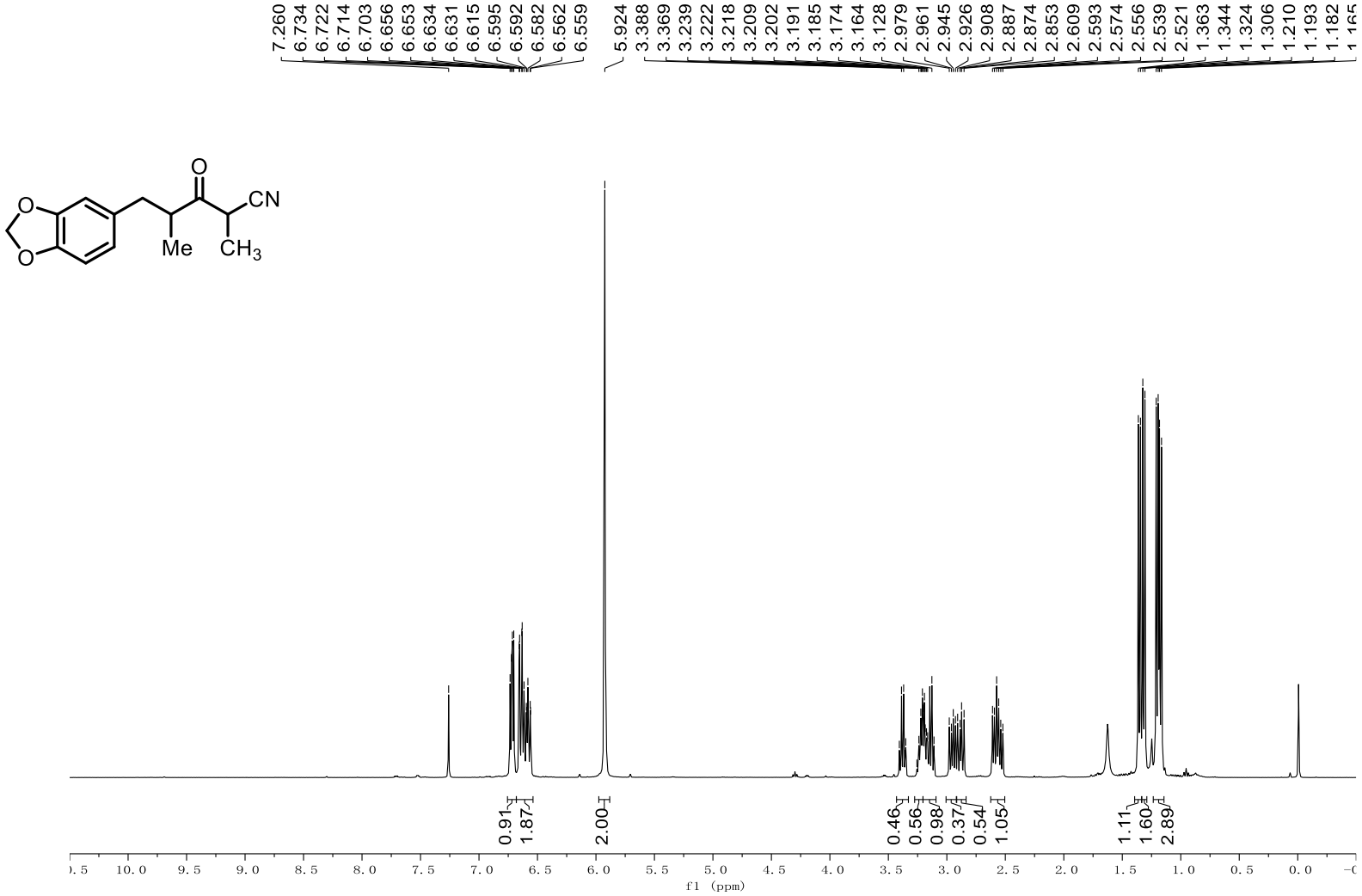
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-Cyclohexyl-2-methyl-3-oxopropanenitrile (32)



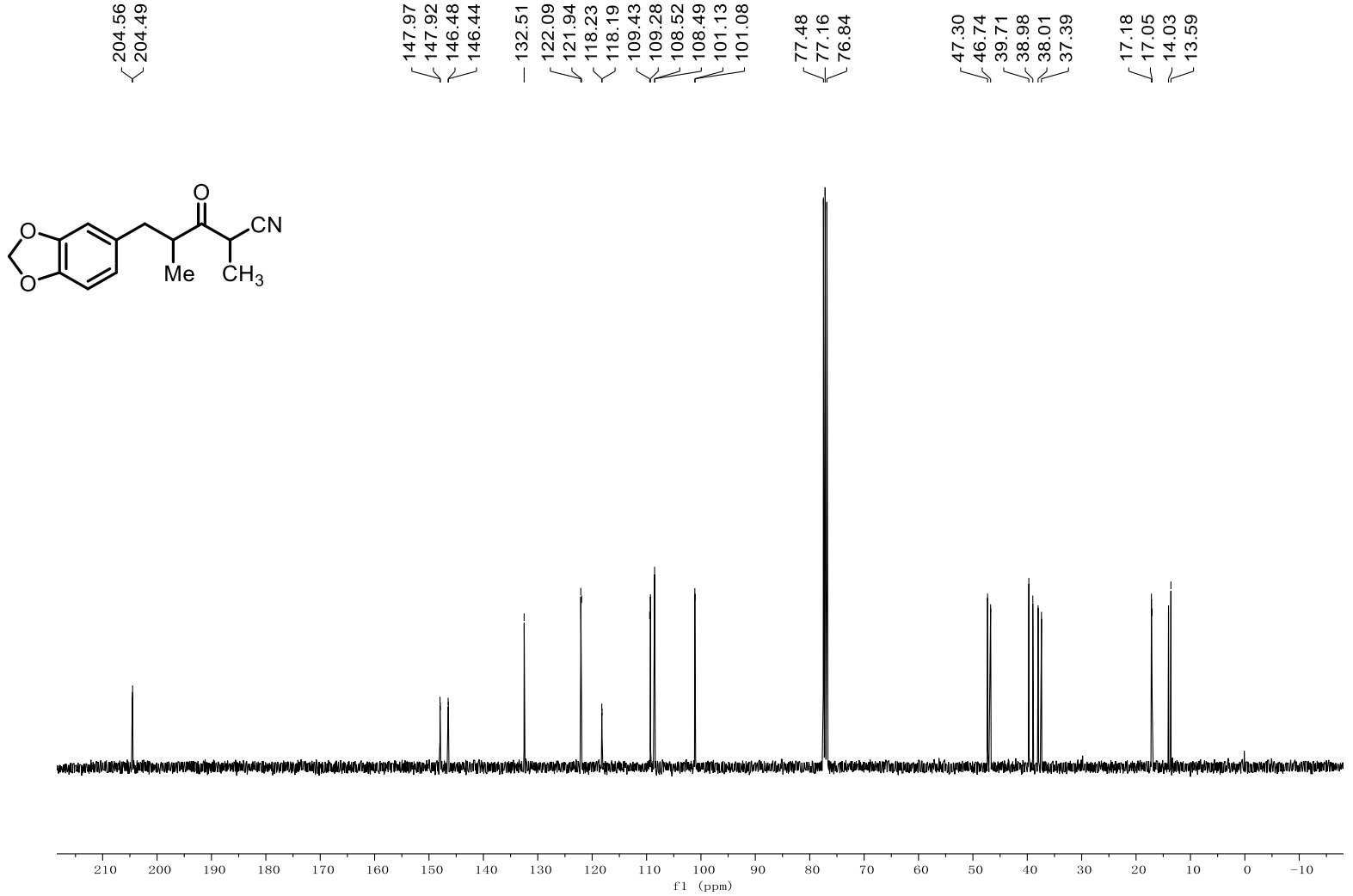
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-Cyclohexyl-2-methyl-3-oxopropanenitrile (32)



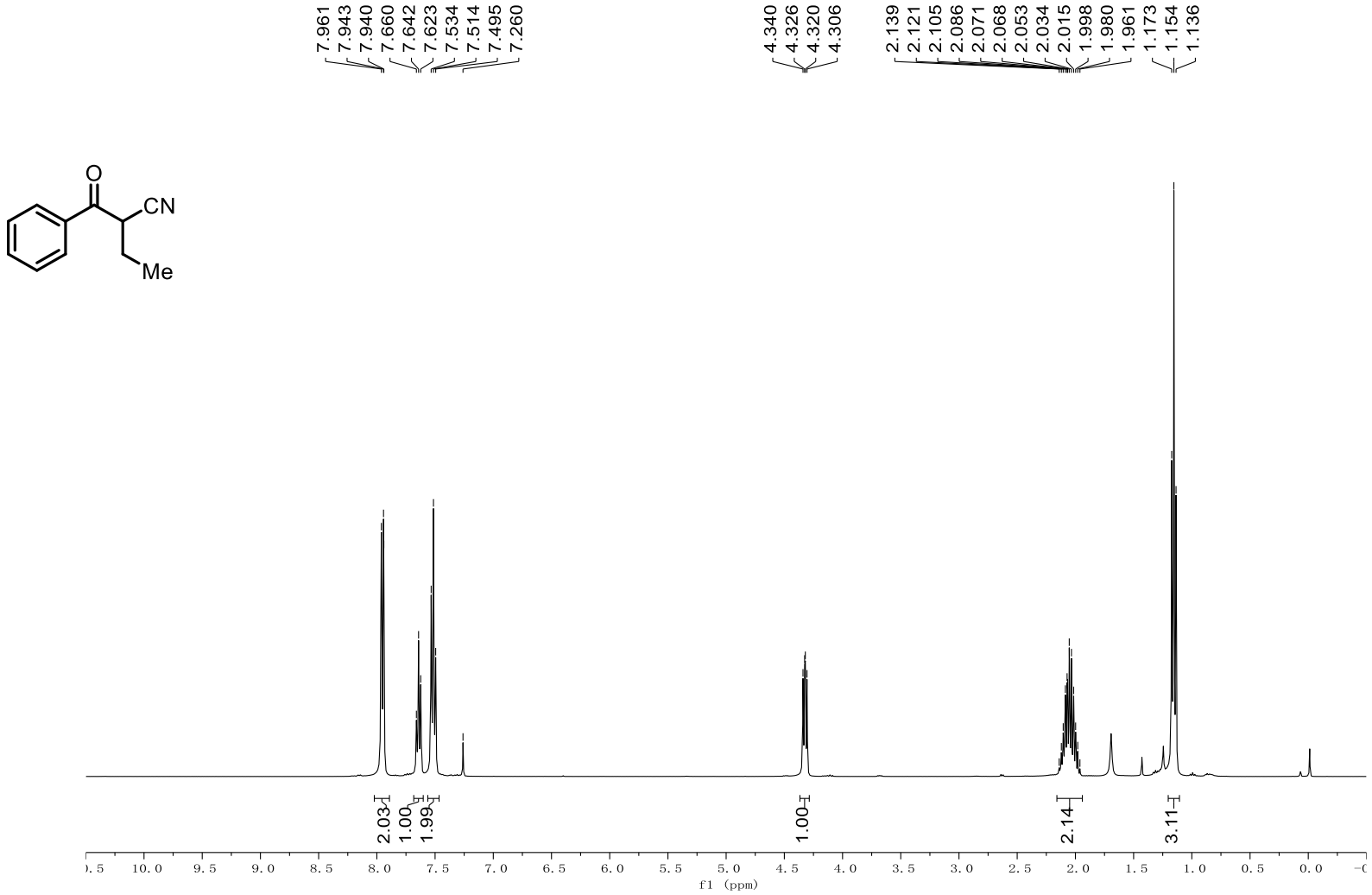
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5-(Benzo[*d*][1,3]dioxol-5-yl)-2,4-dimethyl-3-oxopentanenitrile (33)



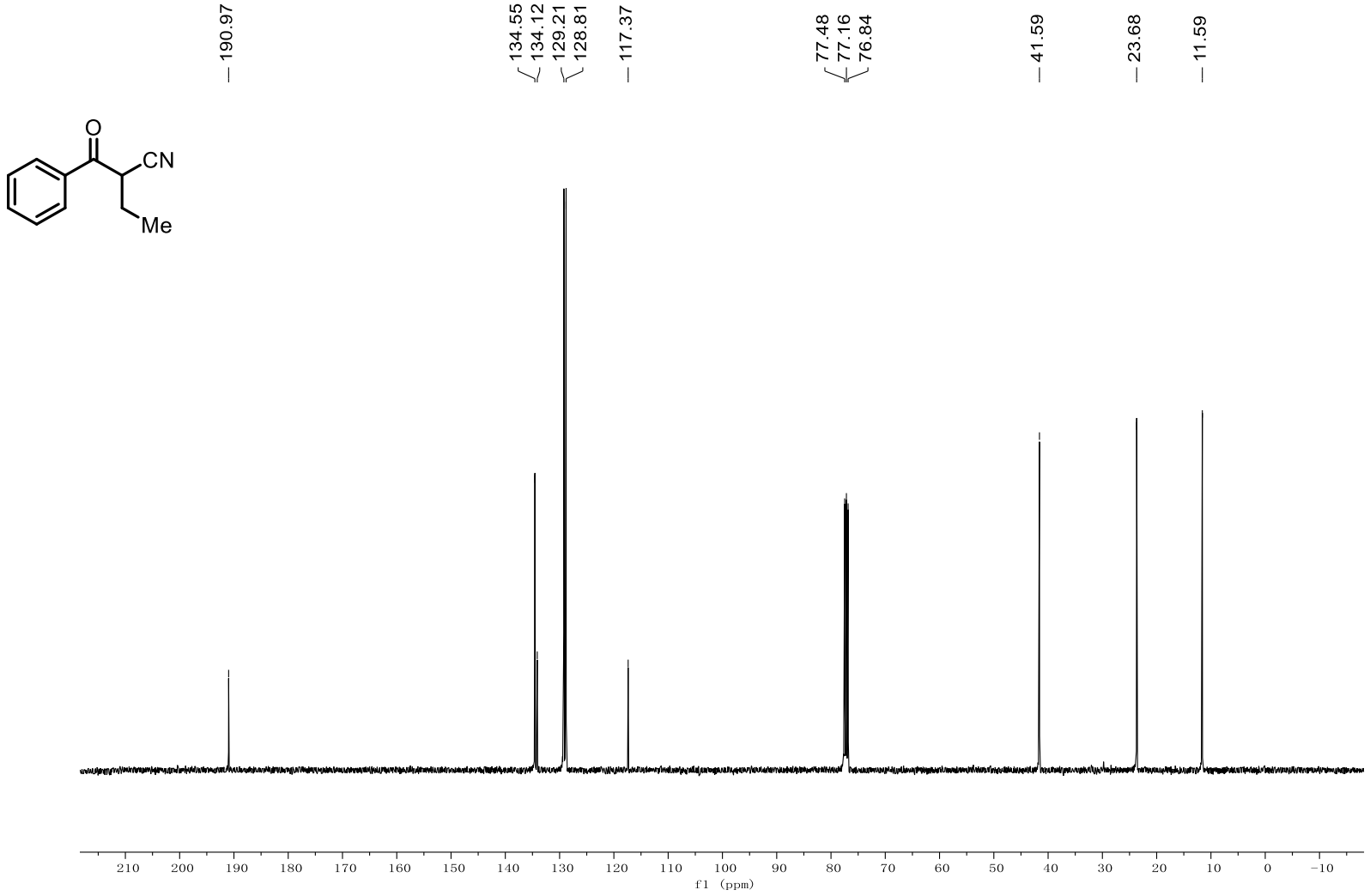
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5-(Benzo[*d*][1,3]dioxol-5-yl)-2,4-dimethyl-3-oxopentanenitrile (33)



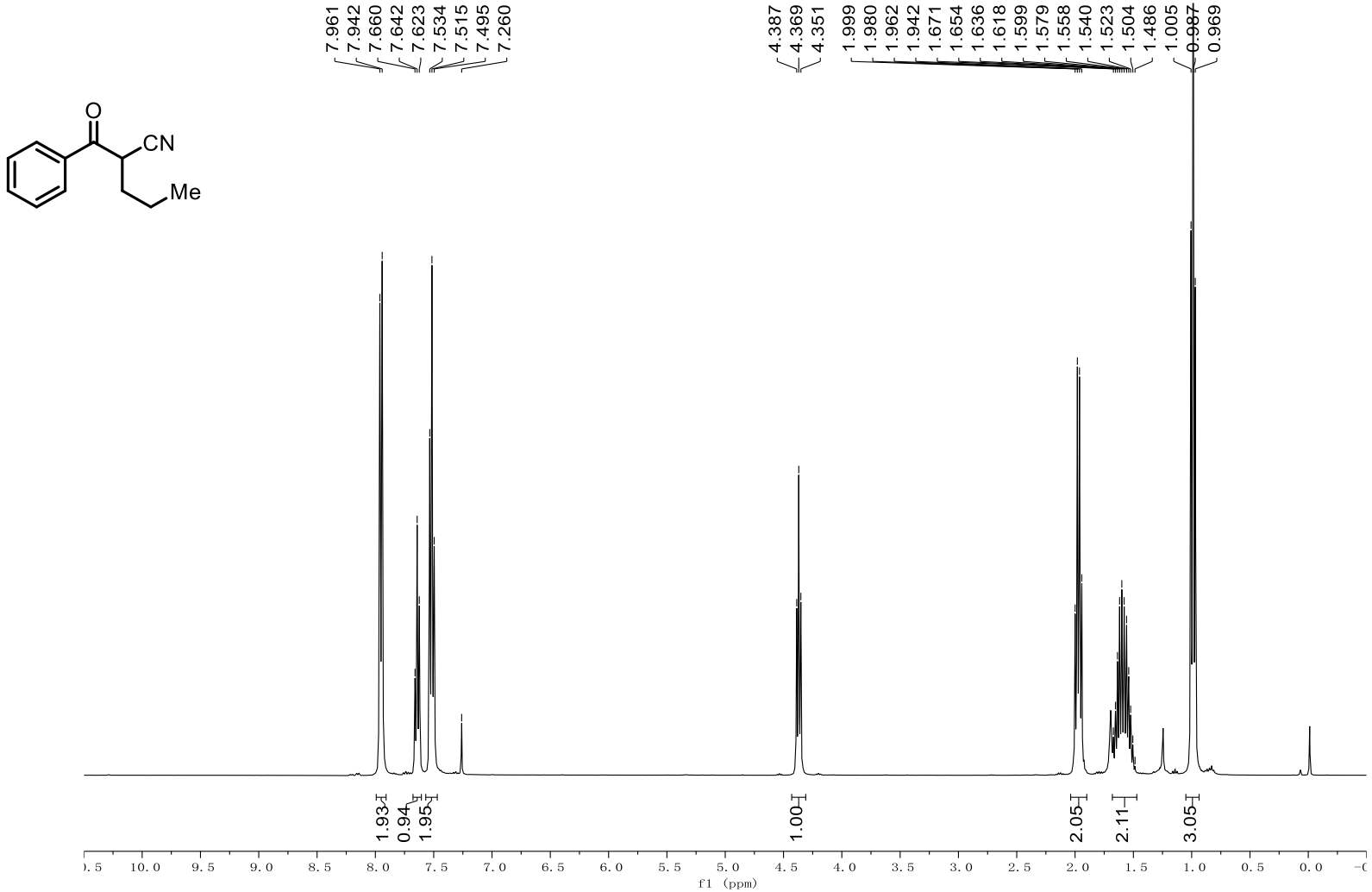
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Benzoylbutanenitrile (34)



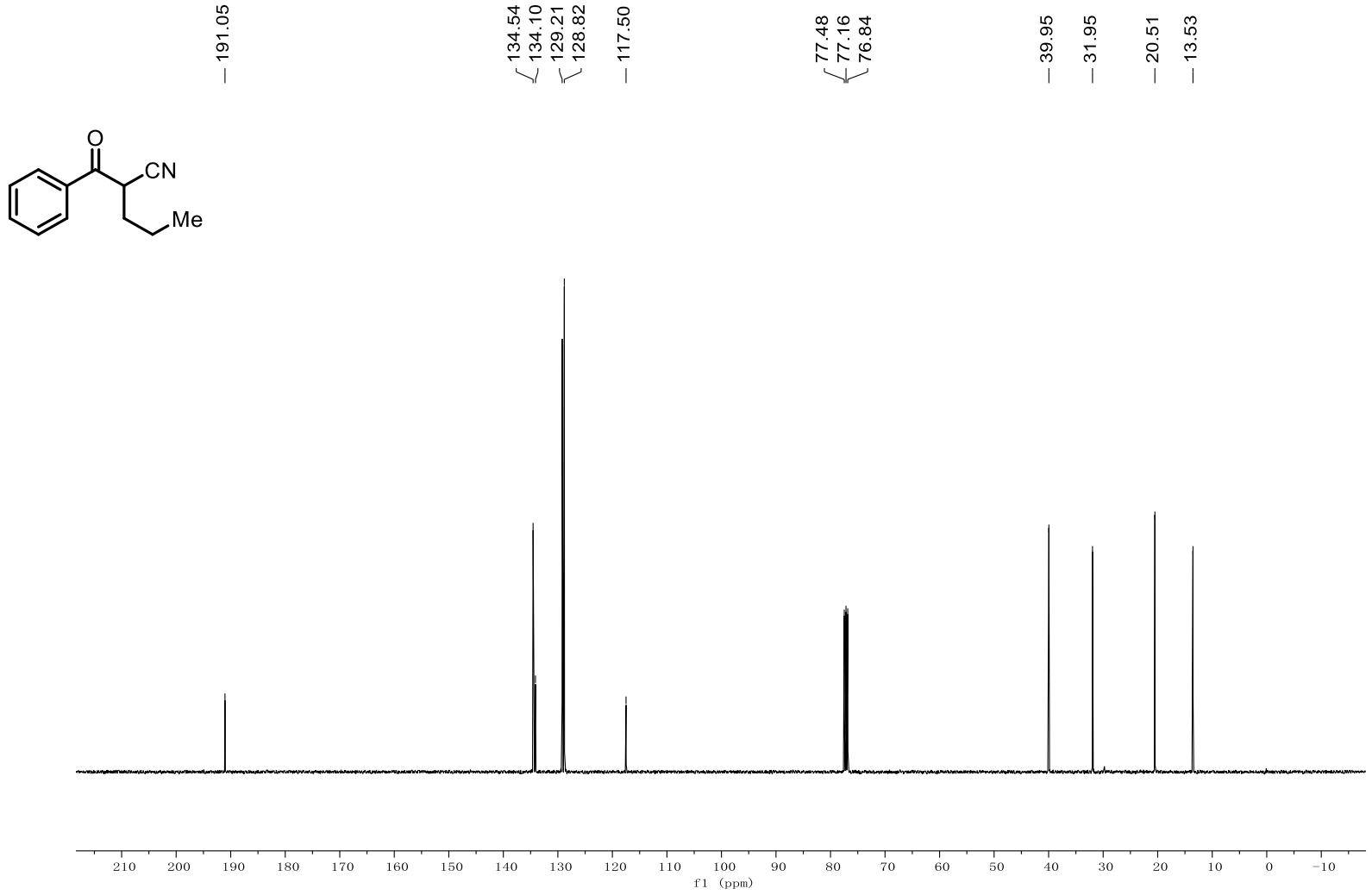
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Benzoylbutanenitrile (34)



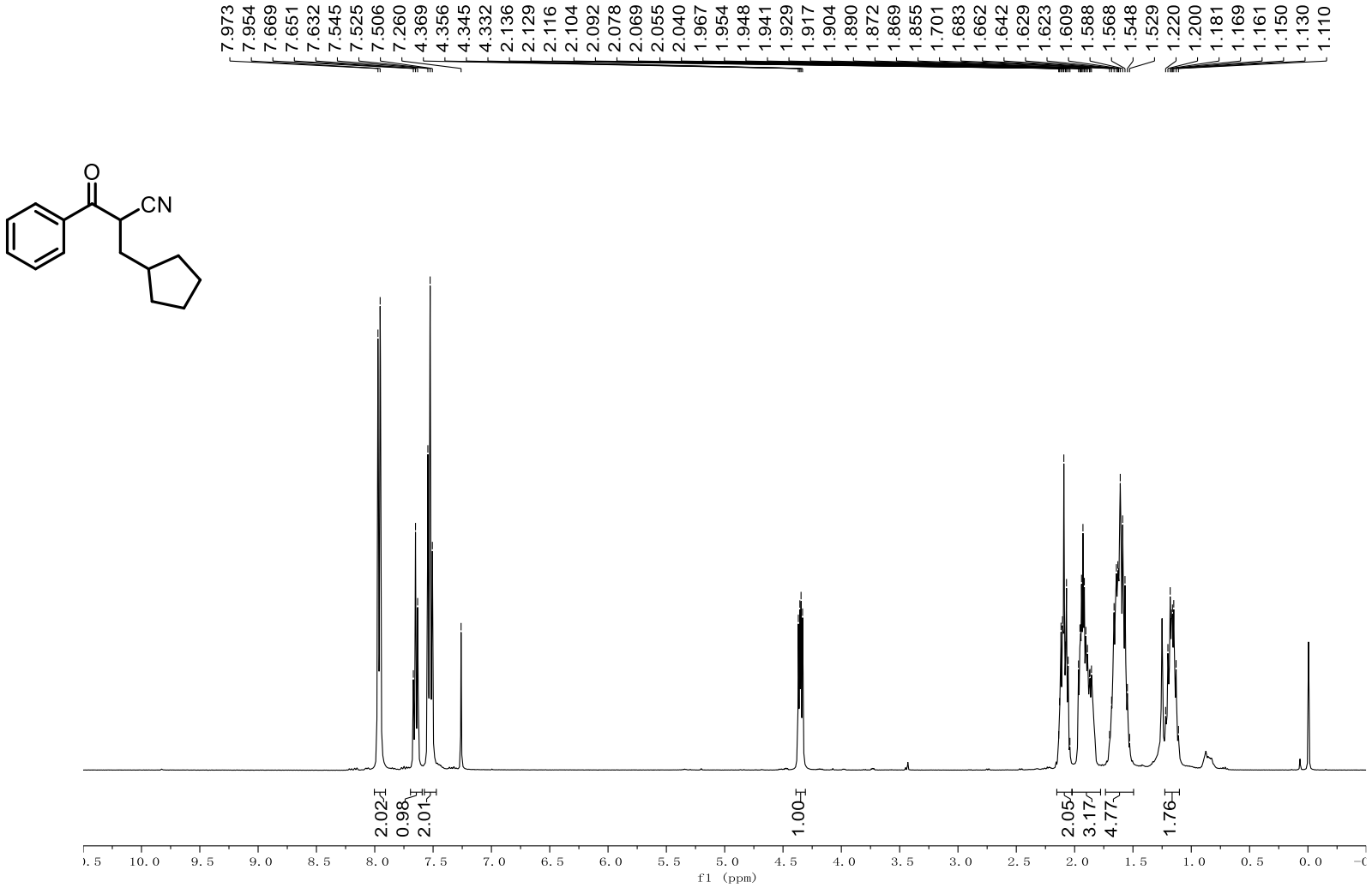
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Benzoylpentanenitrile (35)



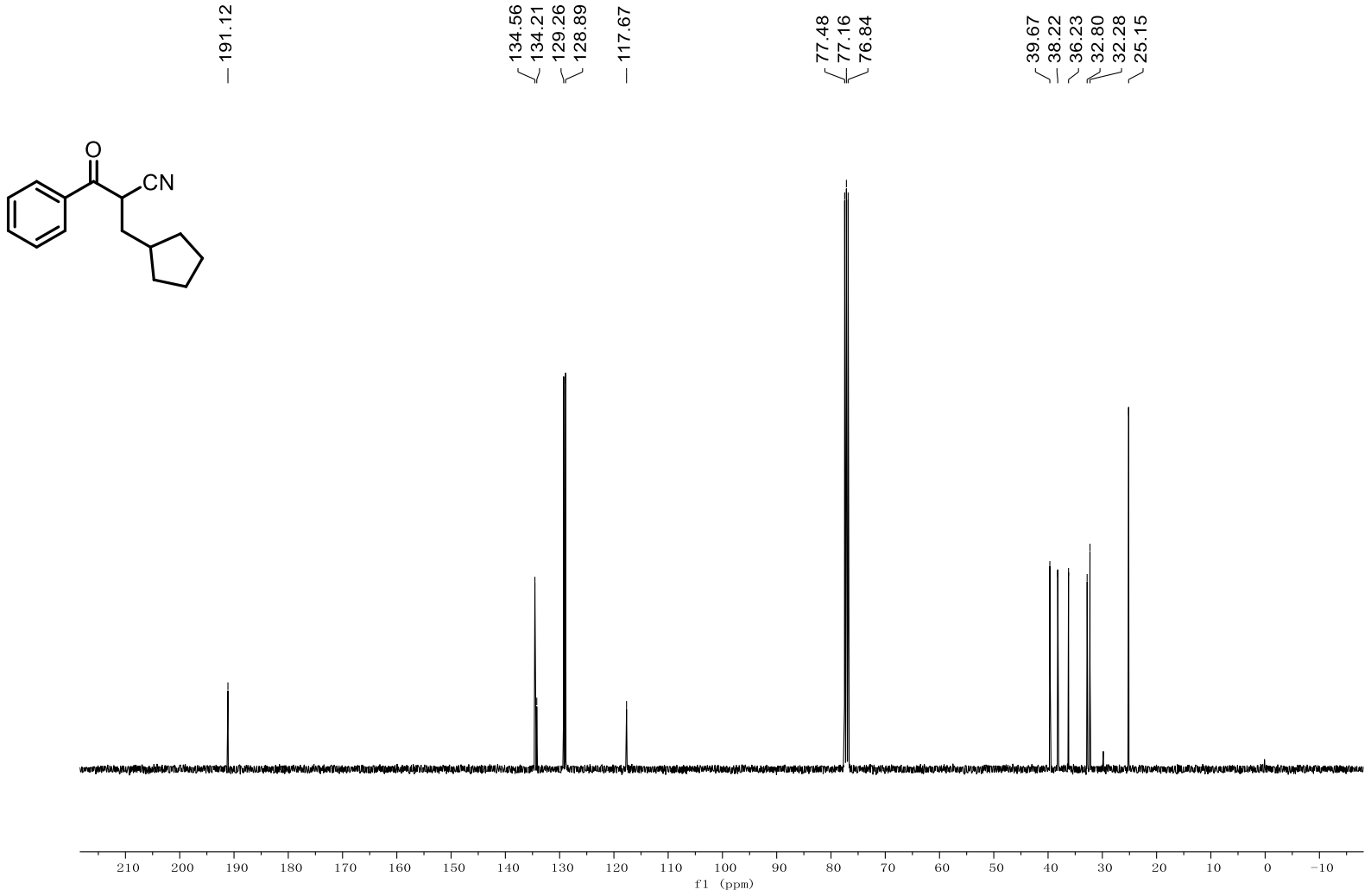
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Benzoylpentanenitrile (35)



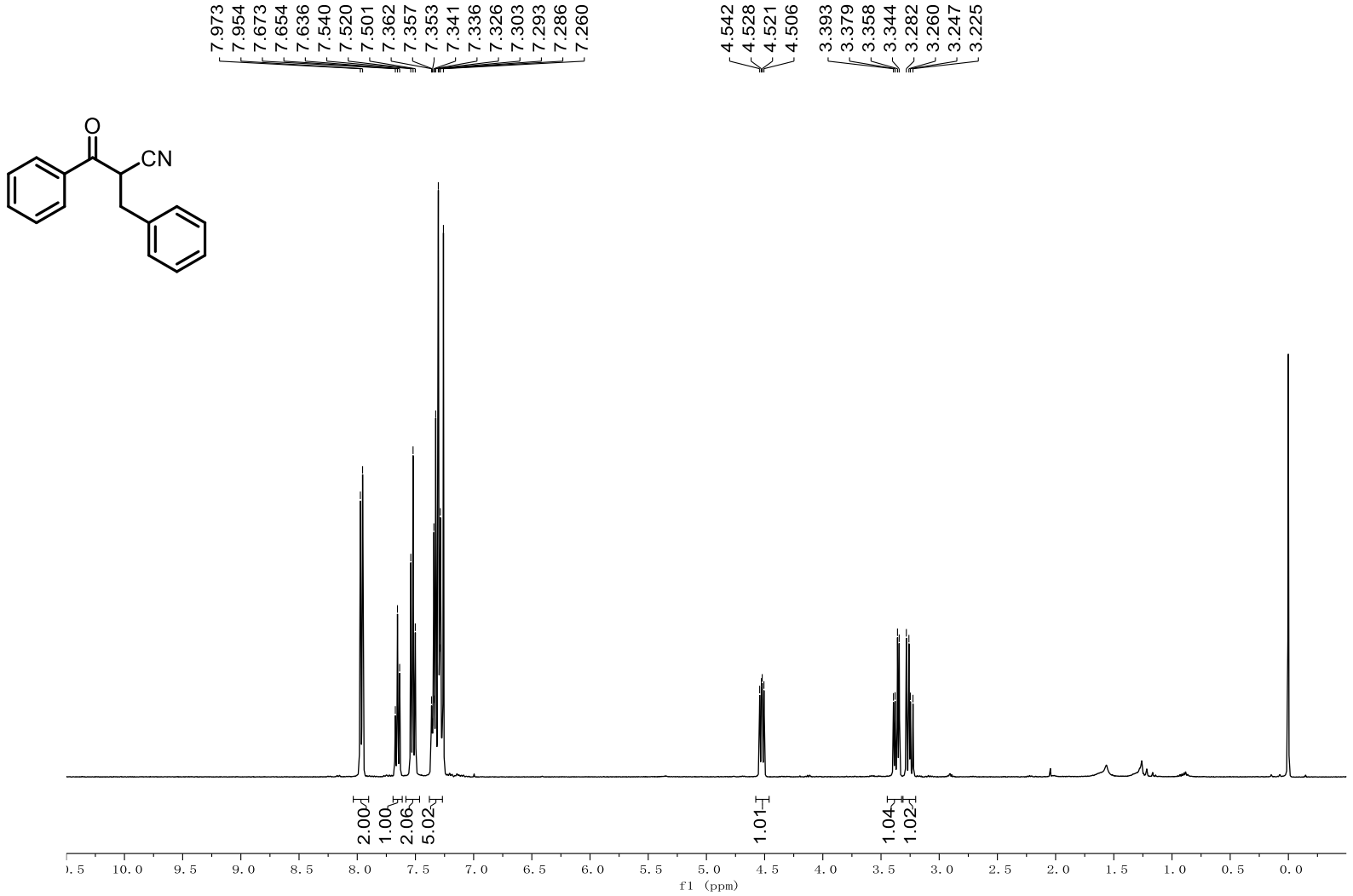
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(Cyclopentylmethyl)-3-oxo-3-phenylpropanenitrile (36)



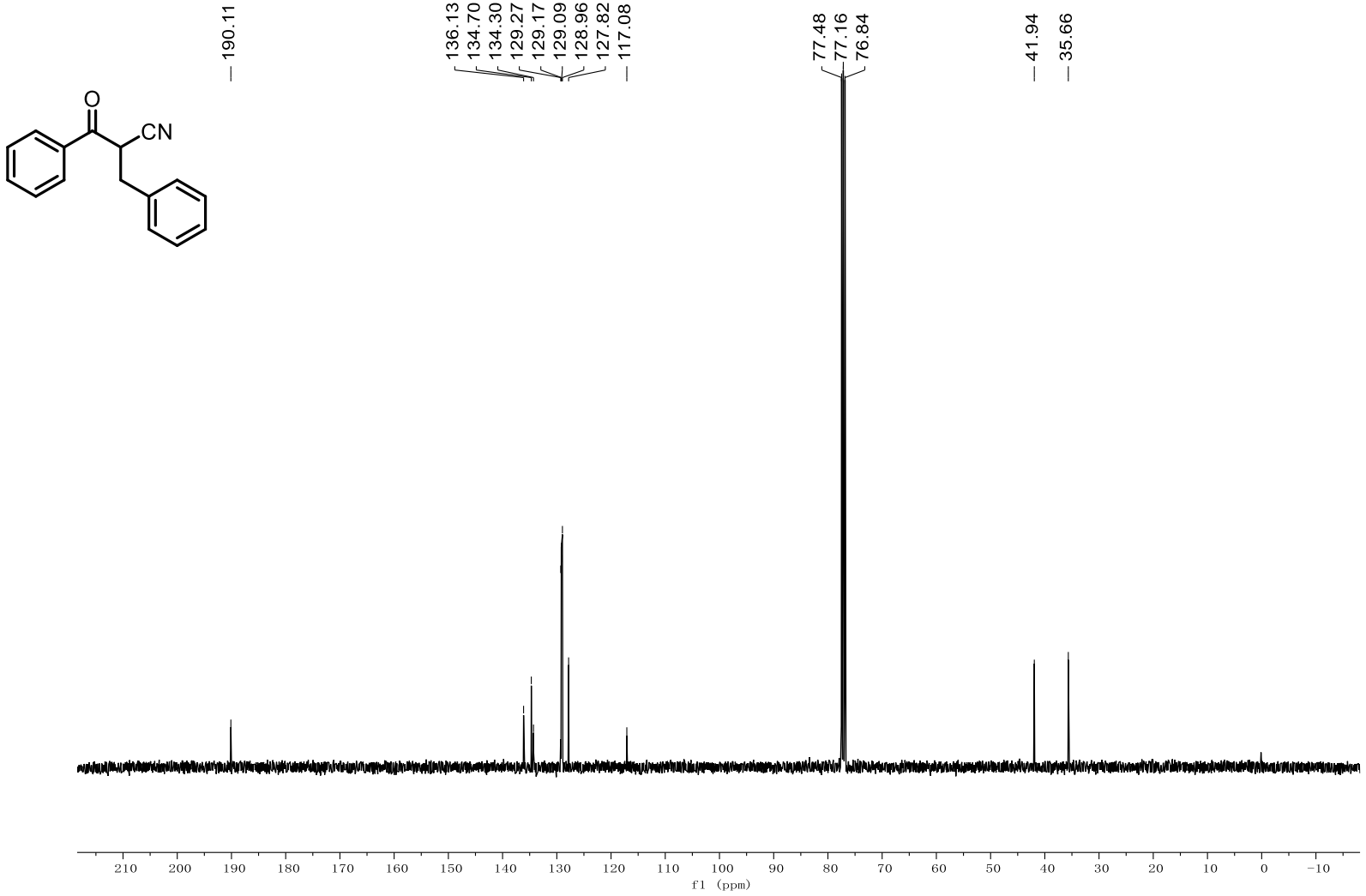
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(Cyclopentylmethyl)-3-oxo-3-phenylpropanenitrile (36)



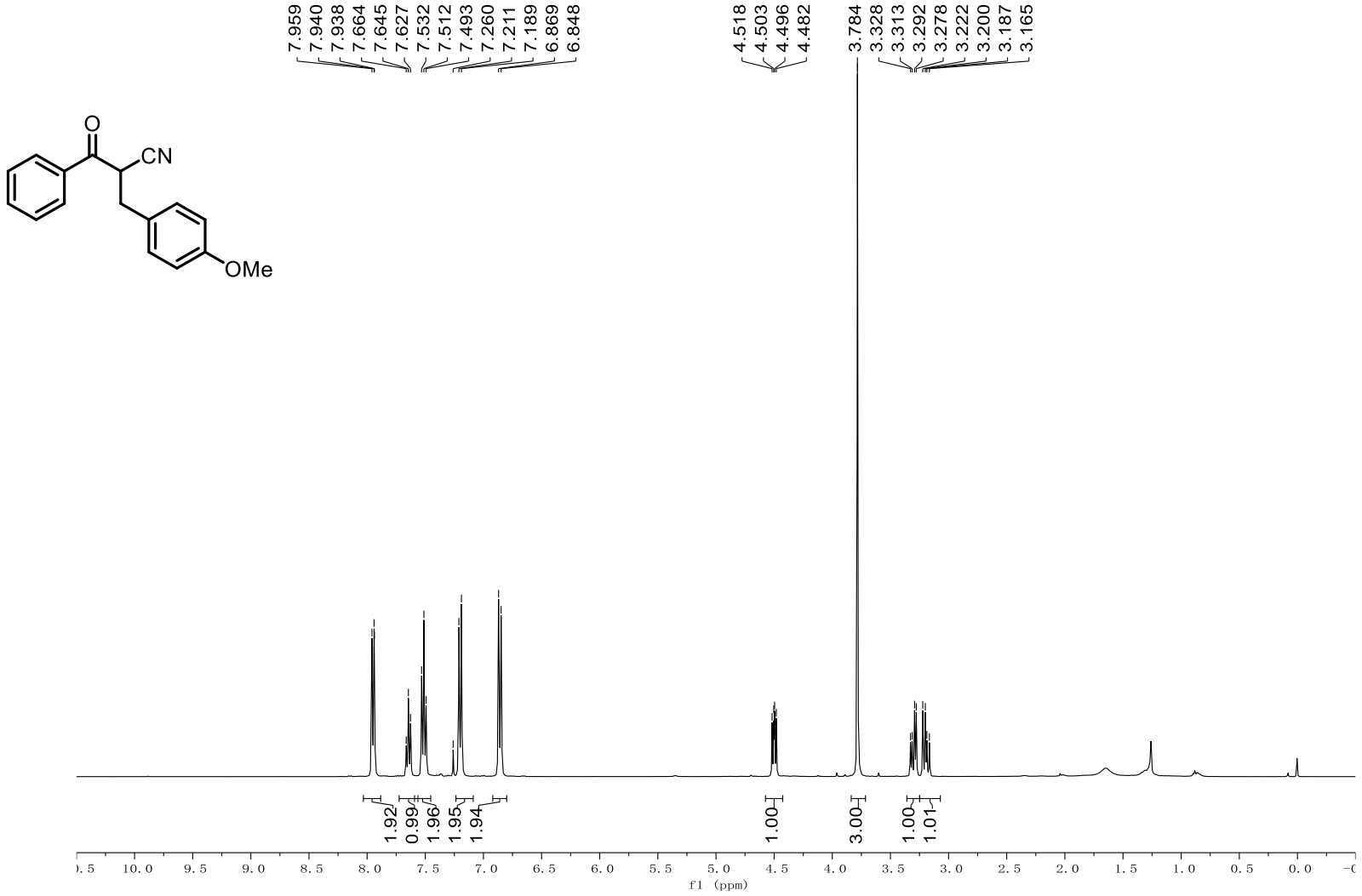
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Benzyl-3-oxo-3-phenylpropanenitrile (37)



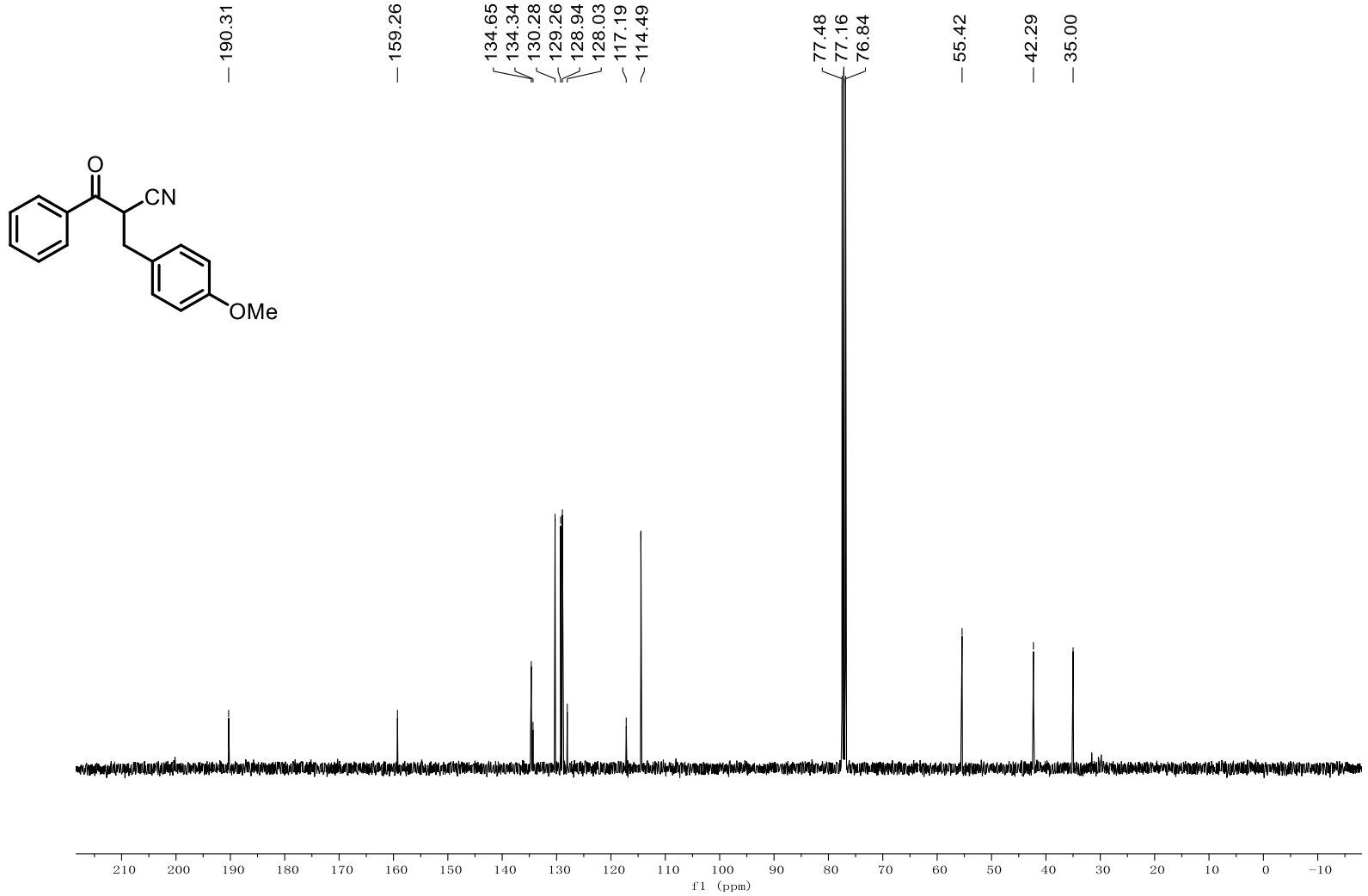
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Benzyl-3-oxo-3-phenylpropanenitrile (37)



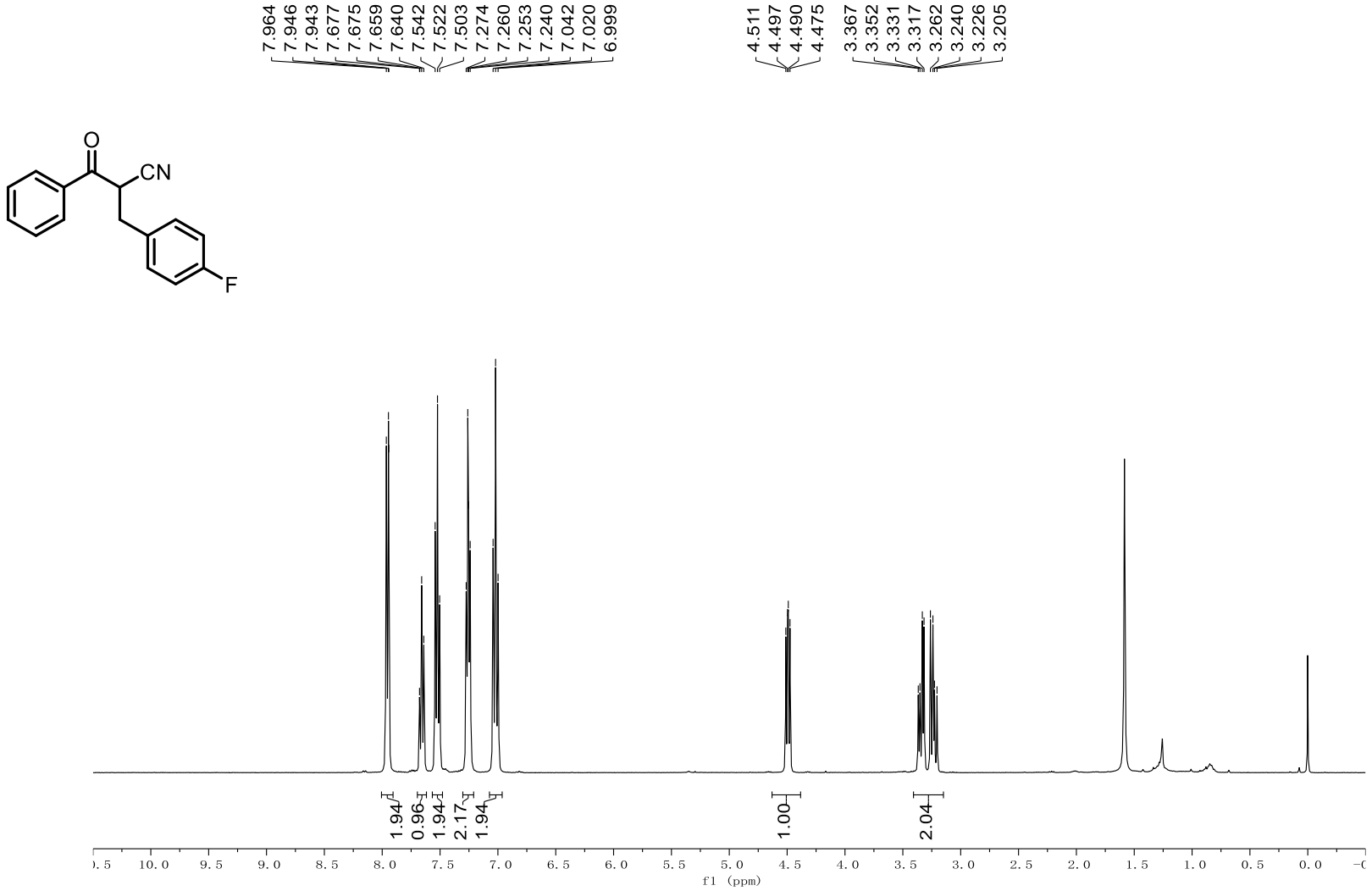
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(4-Methoxybenzyl)-3-oxo-3-phenylpropanenitrile (38)



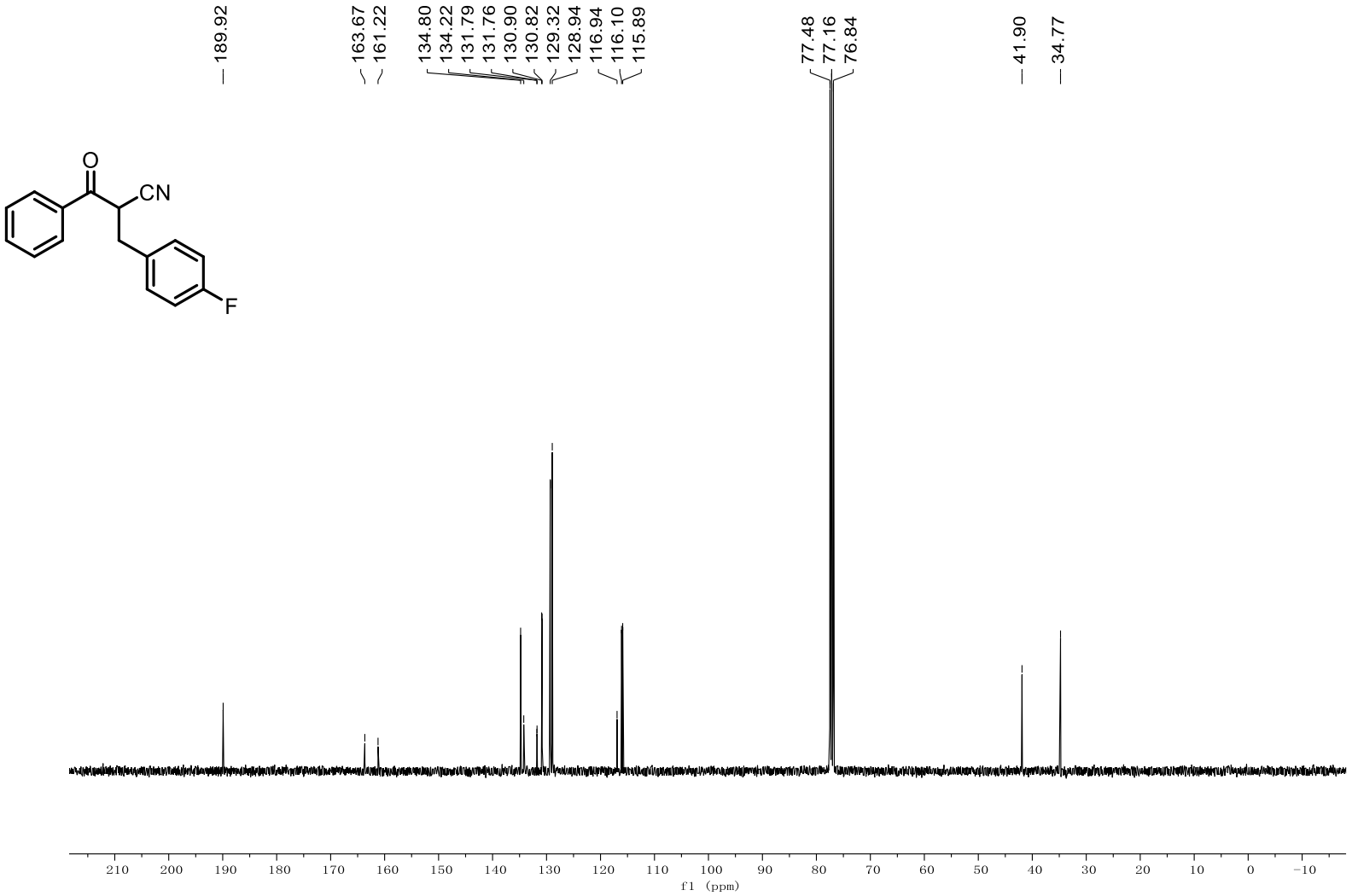
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(4-Methoxybenzyl)-3-oxo-3-phenylpropanenitrile (38)



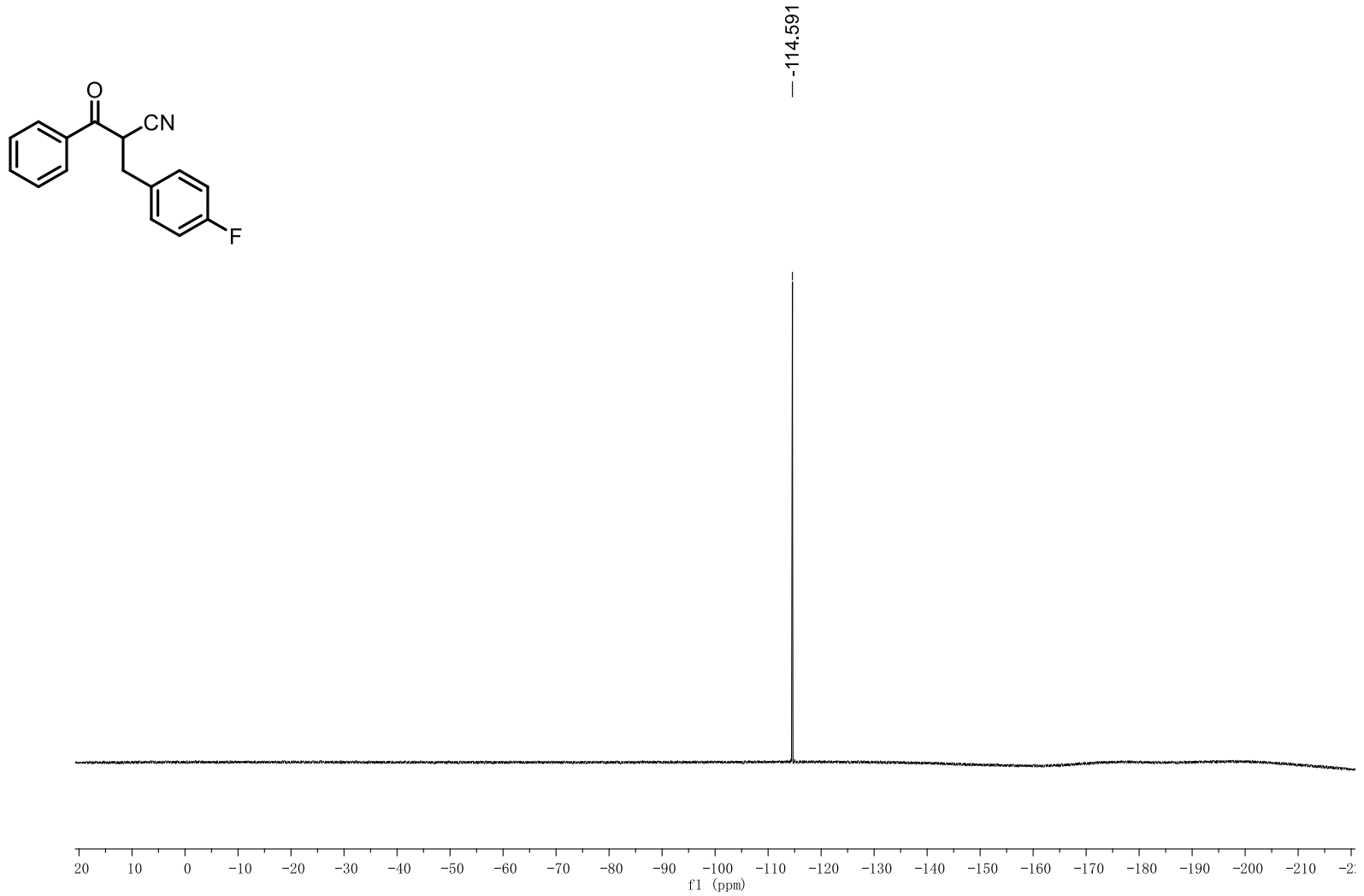
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(4-Fluorobenzyl)-3-oxo-3-phenylpropanenitrile (39)



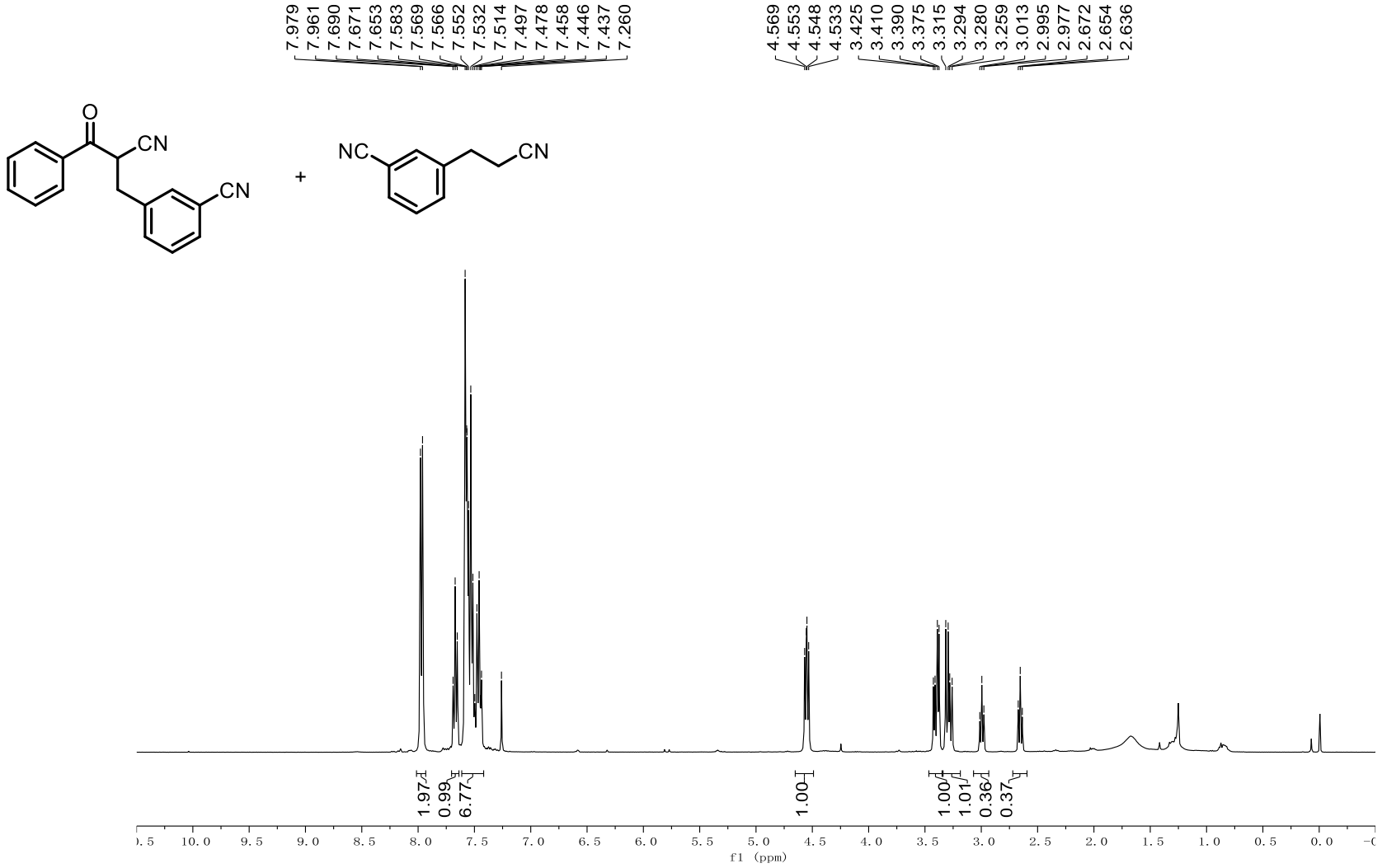
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(4-Fluorobenzyl)-3-oxo-3-phenylpropanenitrile (39)



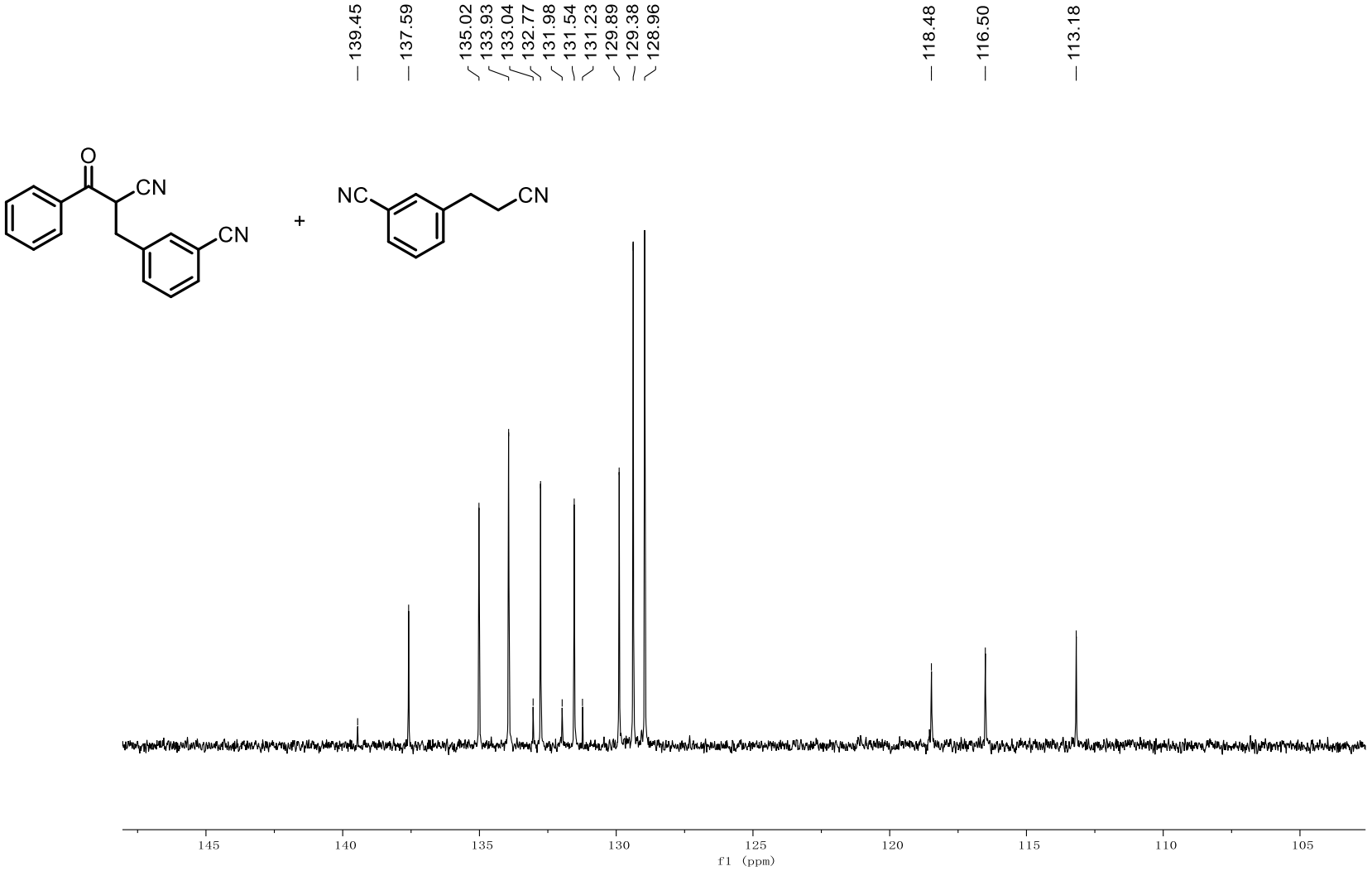
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-(4-Fluorobenzyl)-3-oxo-3-phenylpropanenitrile (39)



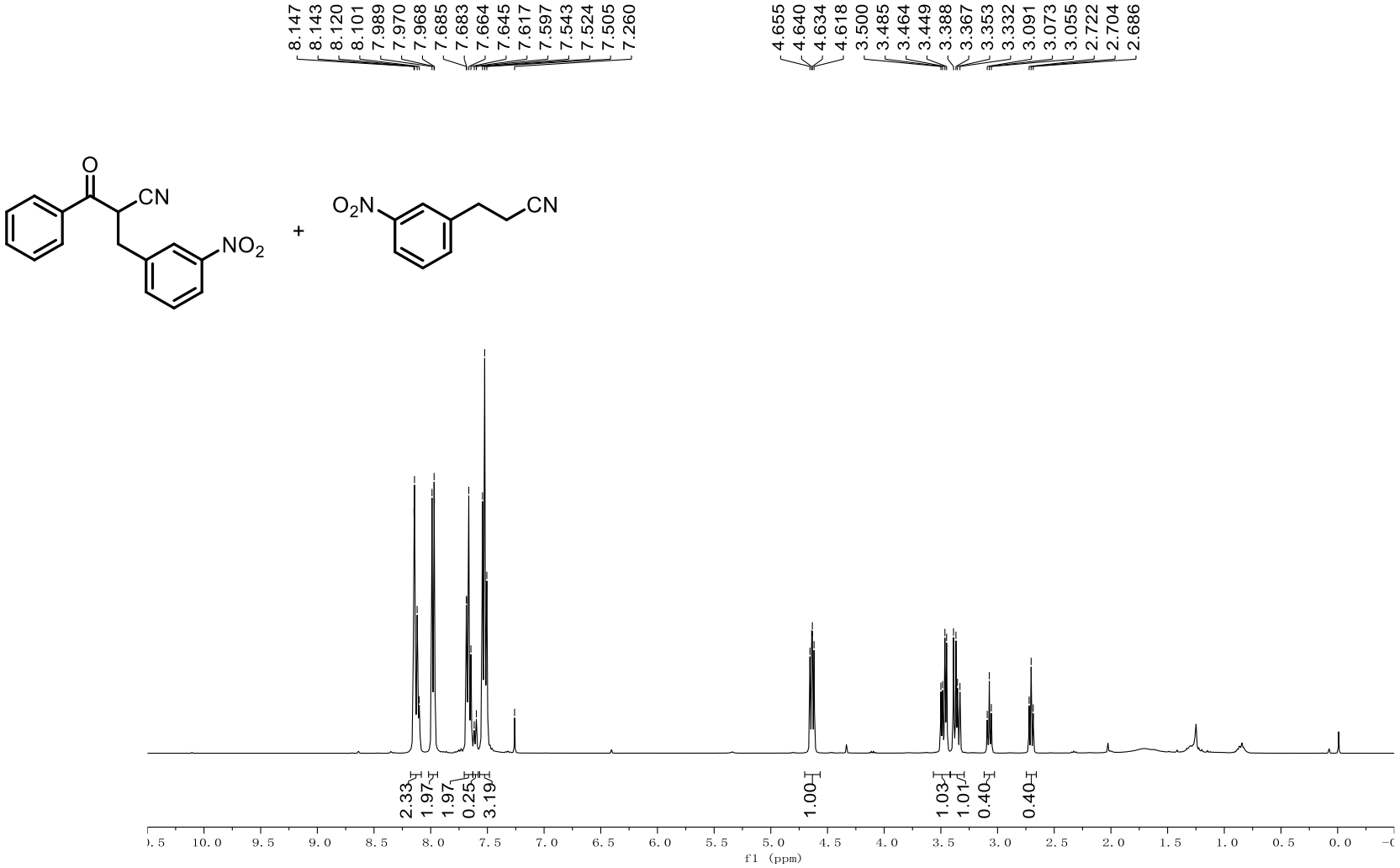
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-(2-Cyano-3-oxo-3-phenylpropyl)benzonitrile (40) and 3-(3-Cyanophenyl)propanenitrile



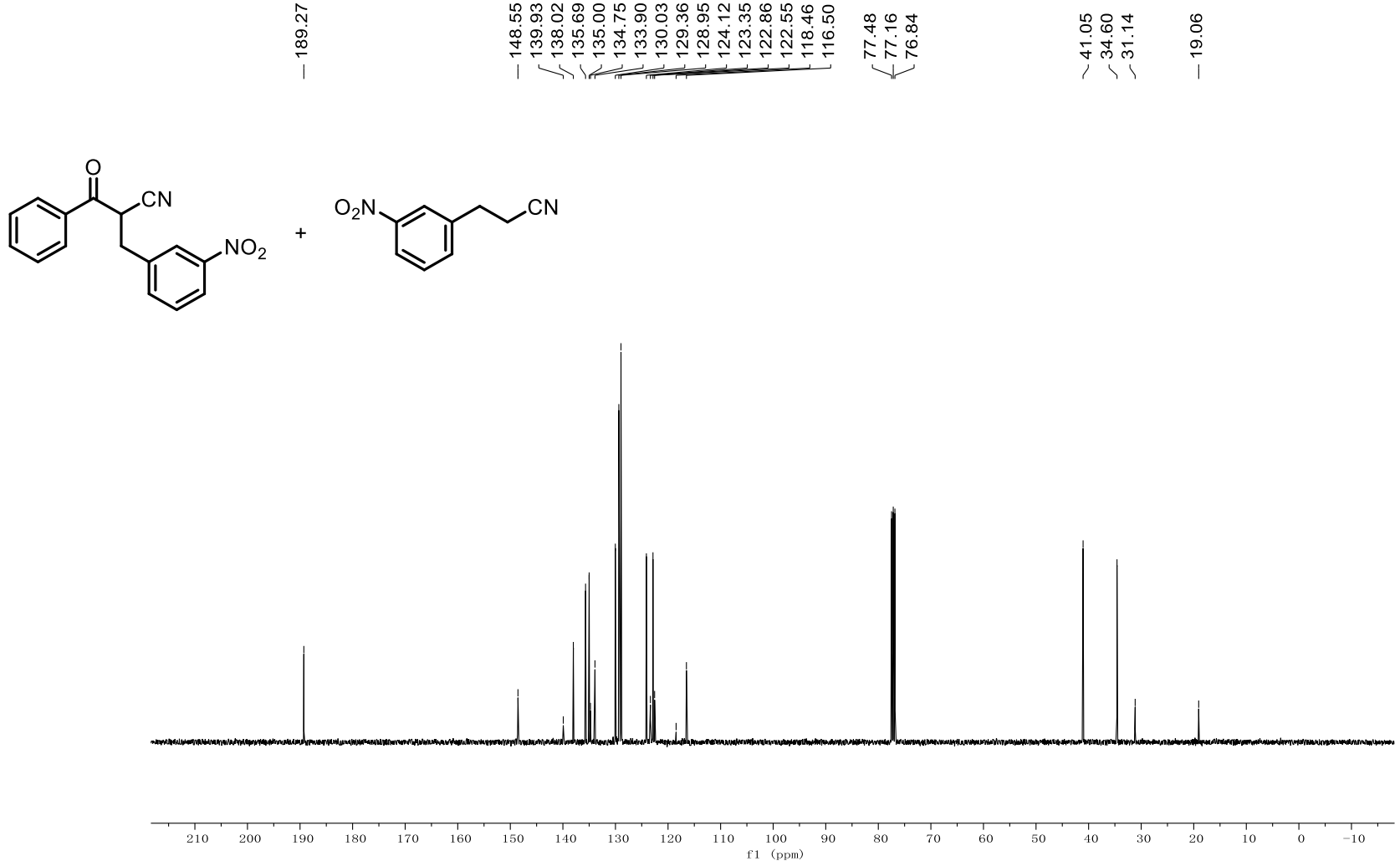
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-(2-Cyano-3-oxo-3-phenylpropyl)benzonitrile (40) and 3-(3-Cyanophenyl)propanenitrile



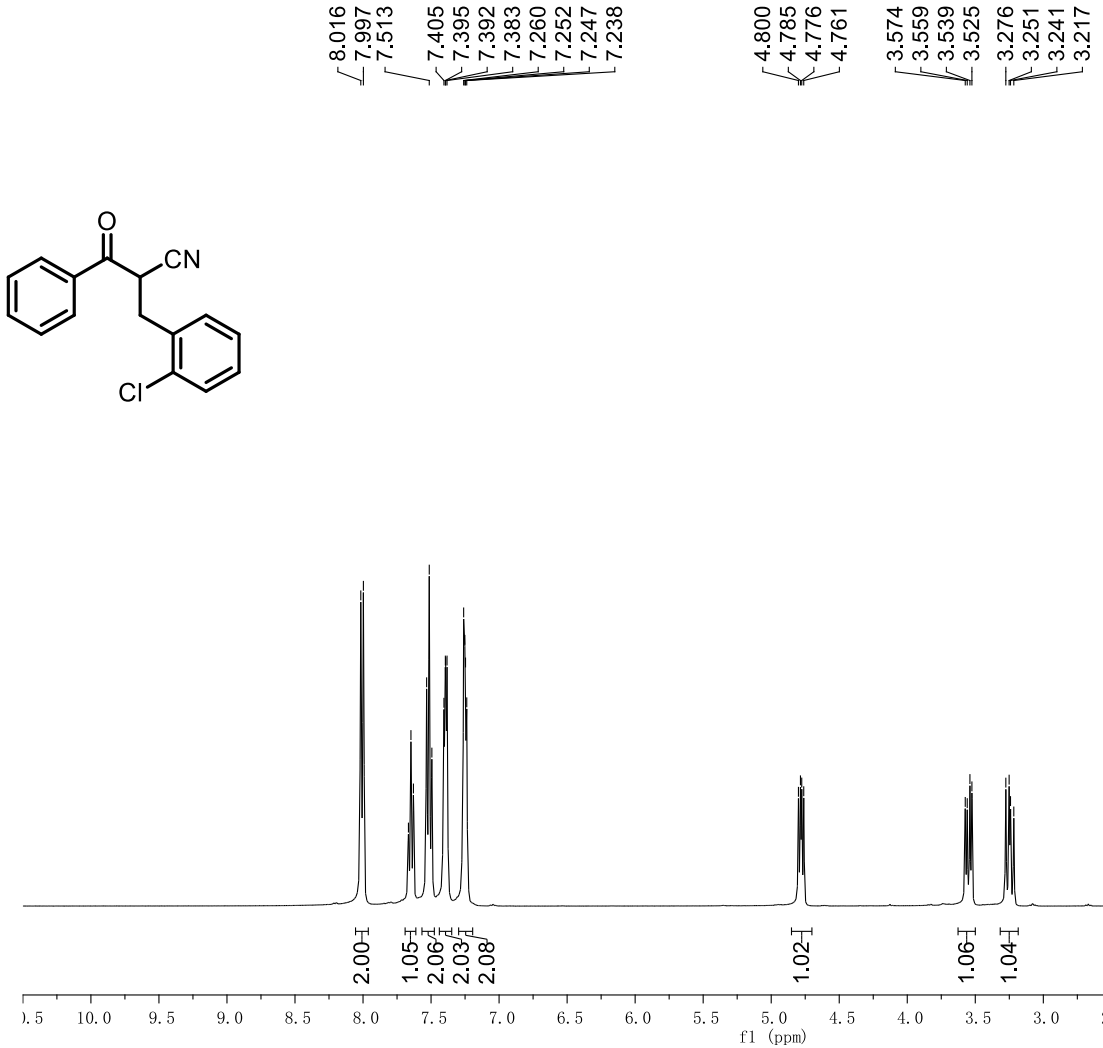
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(3-Nitrobenzyl)-3-oxo-3-phenylpropanenitrile (41) and 3-(3-Nitrophenyl)propanenitrile



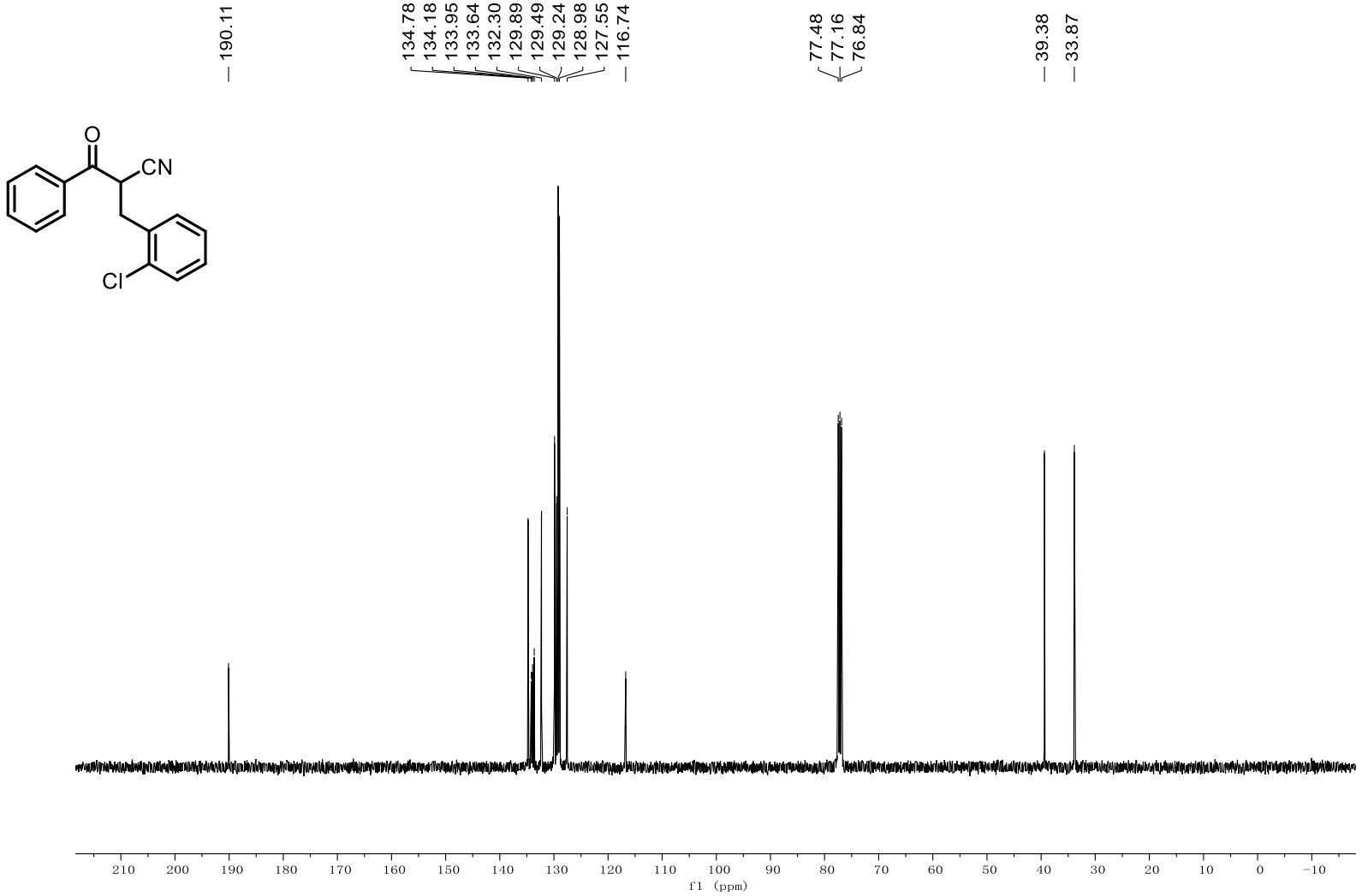
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(3-Nitrobenzyl)-3-oxo-3-phenylpropanenitrile (41) and 3-(3-Nitrophenyl)propanenitrile



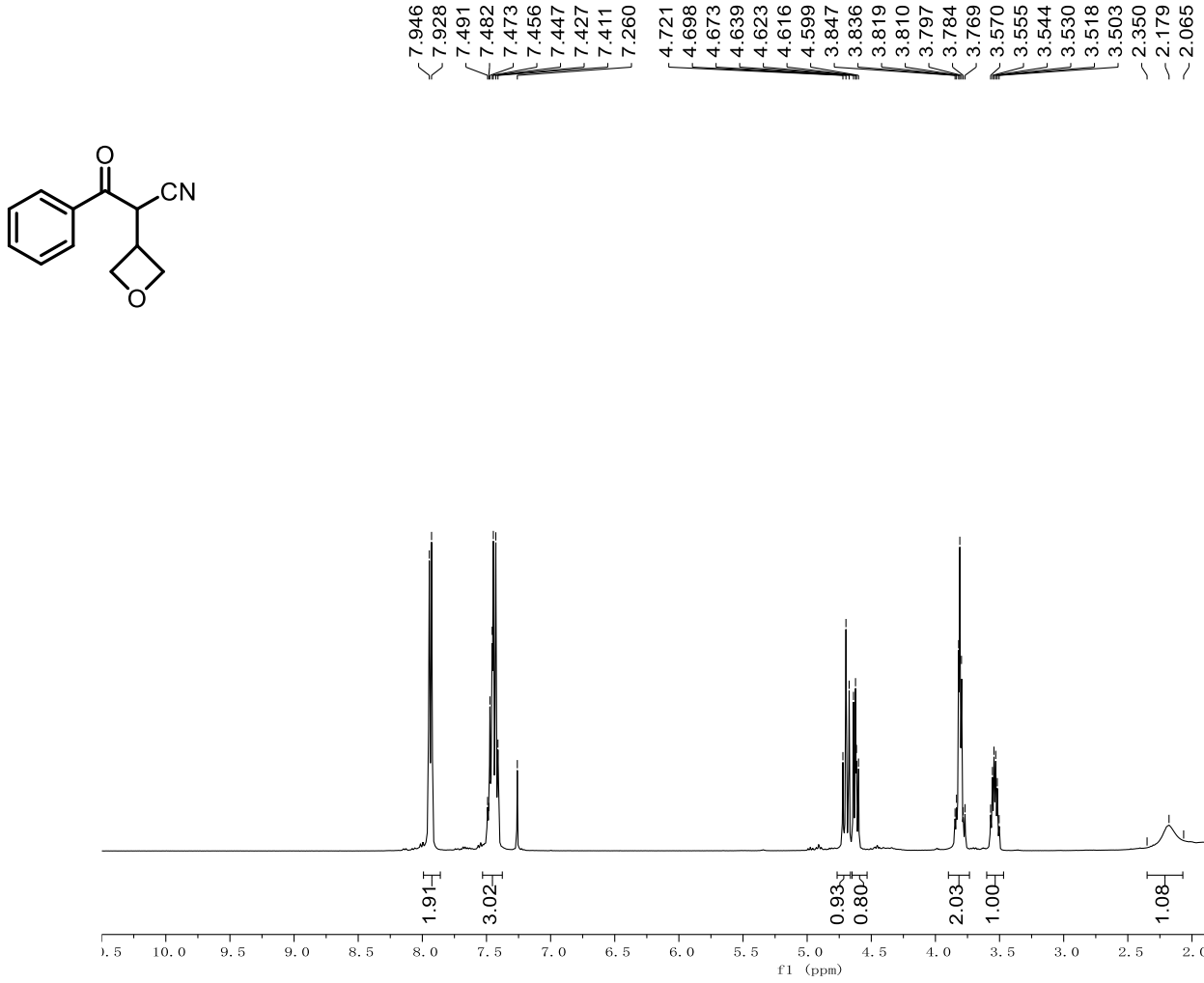
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(2-Chlorobenzyl)-3-oxo-3-phenylpropanenitrile (42)



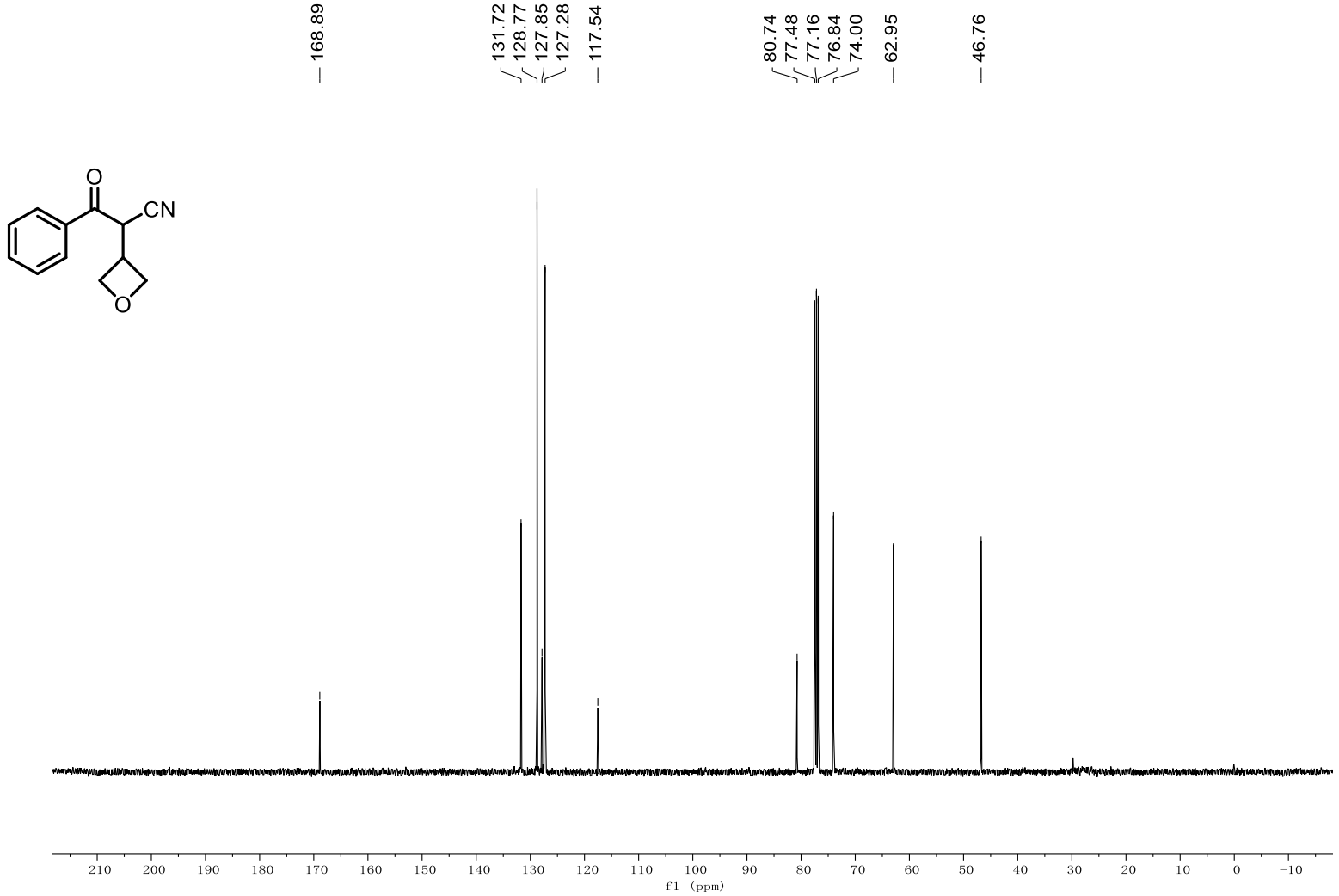
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(2-Chlorobenzyl)-3-oxo-3-phenylpropanenitrile (42)



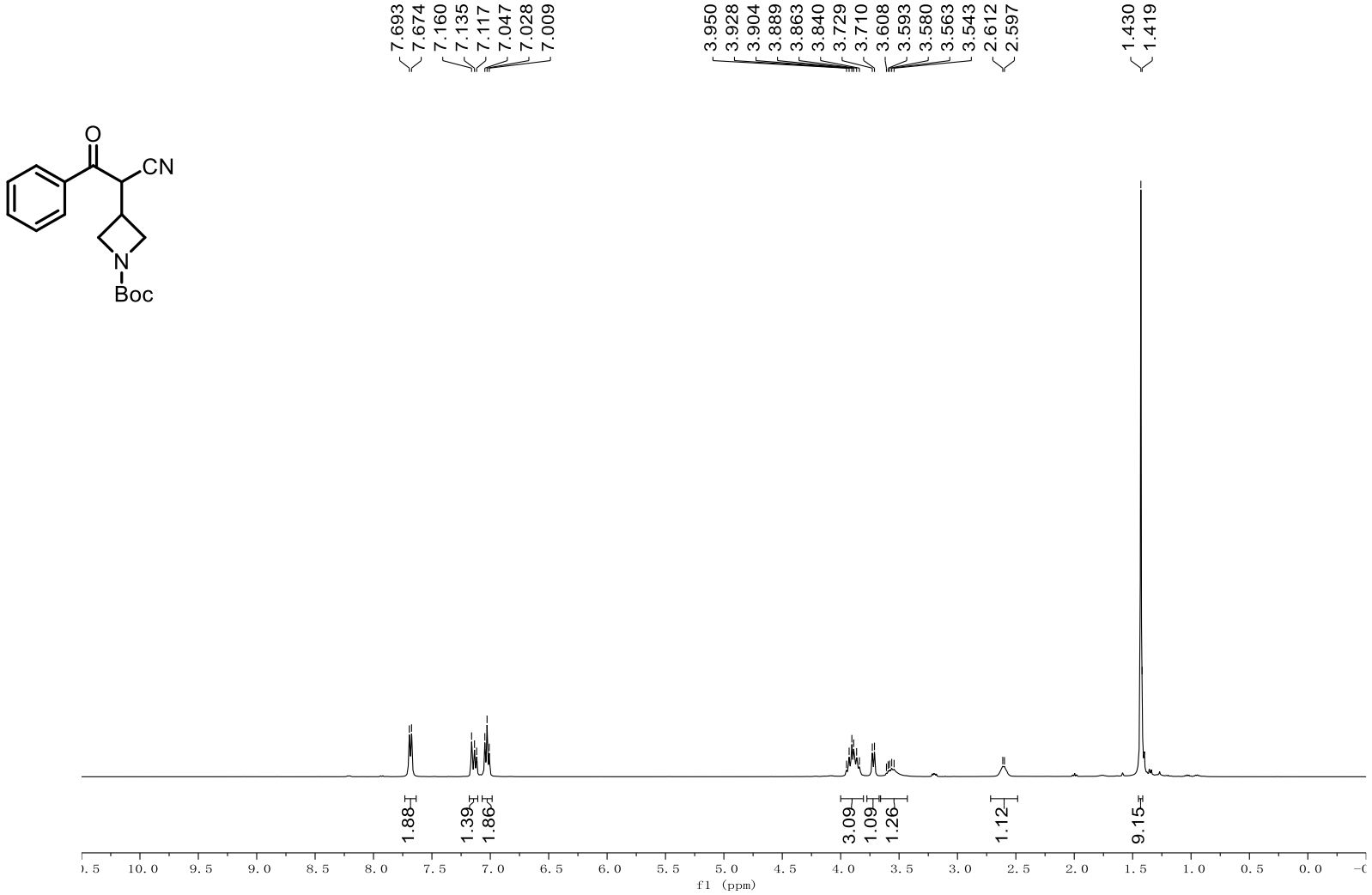
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(Oxetan-3-yl)-3-oxo-3-phenylpropanenitrile (43)



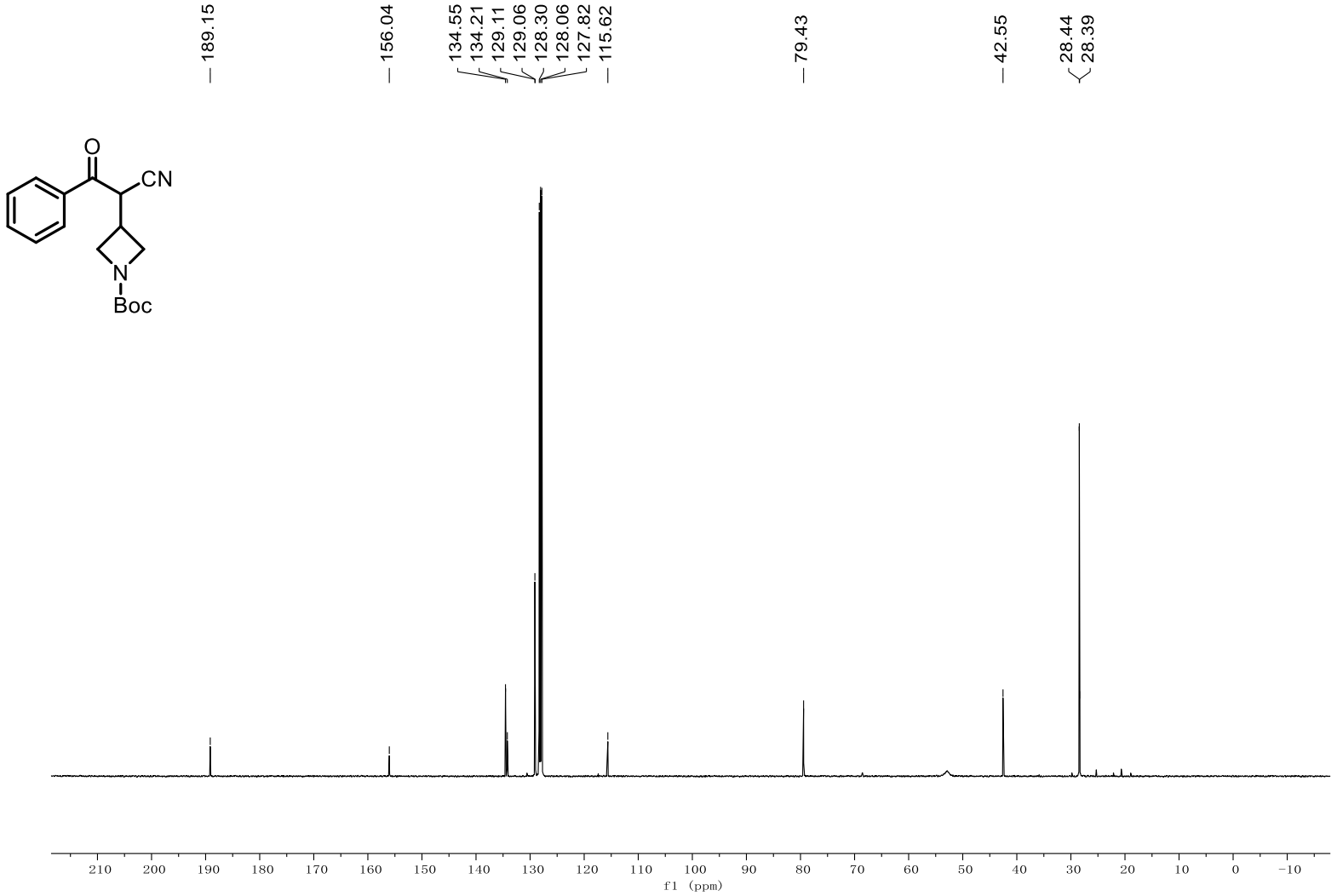
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(Oxetan-3-yl)-3-oxo-3-phenylpropanenitrile (43)



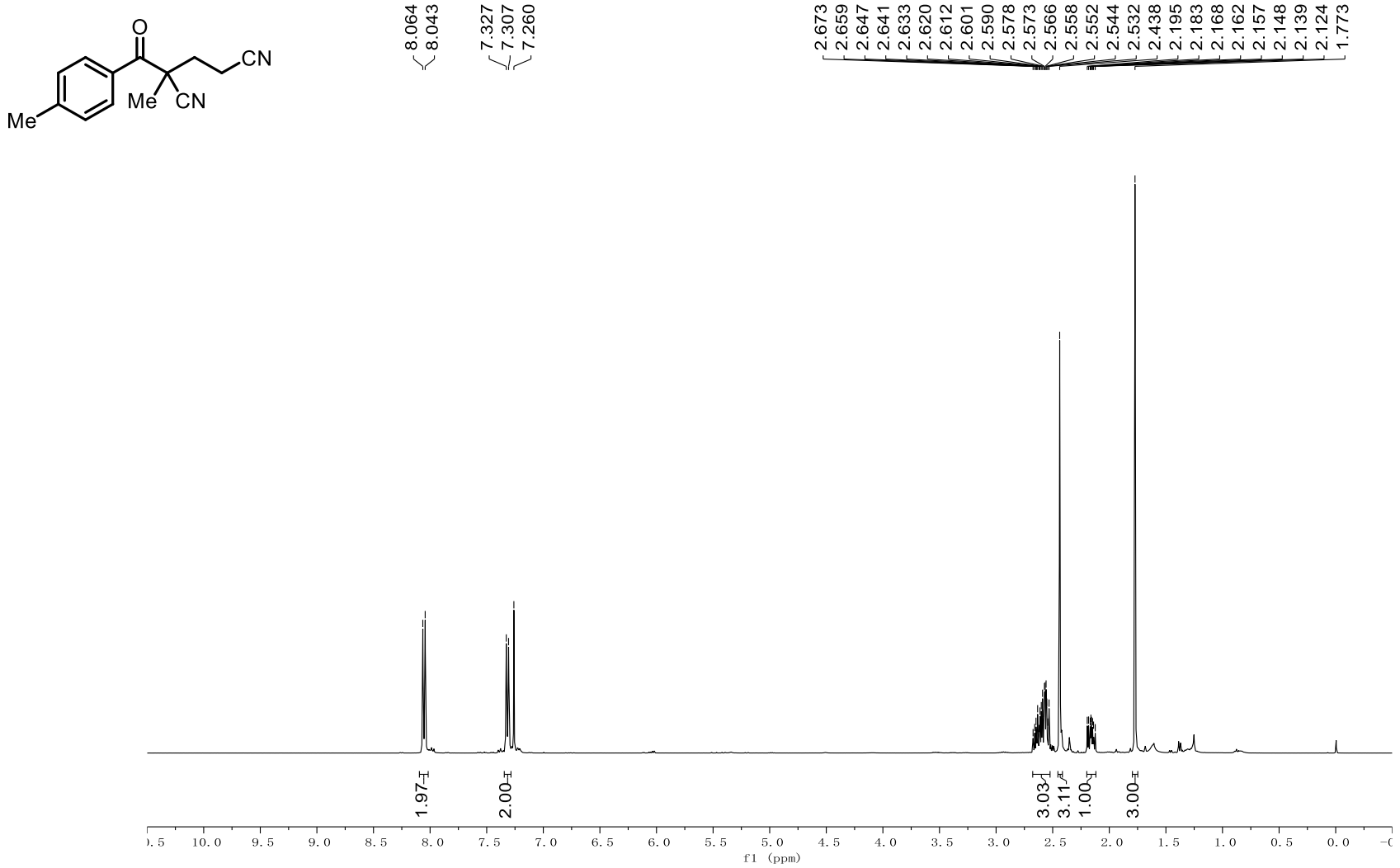
^{1}H NMR (400 MHz, Benzene-d_6) spectrum of *tert*-Butyl 3-(1-cyano-2-oxo-2-phenylethyl)azetidine-1-carboxylate (44)



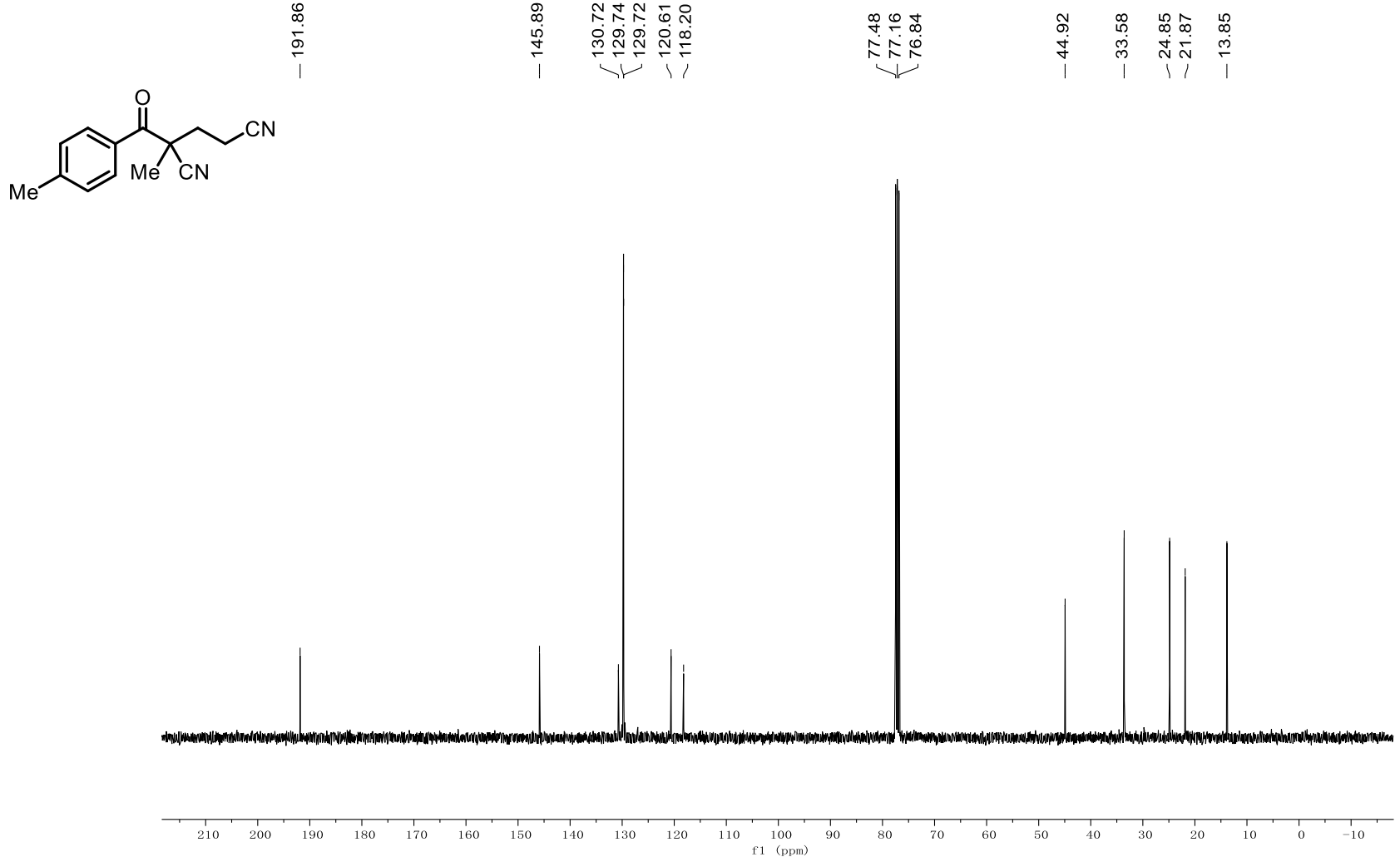
^{13}C NMR (100 MHz, Benzene-d_6) spectrum of *tert*-Butyl 3-(1-cyano-2-oxo-2-phenylethyl)azetidine-1-carboxylate (44)



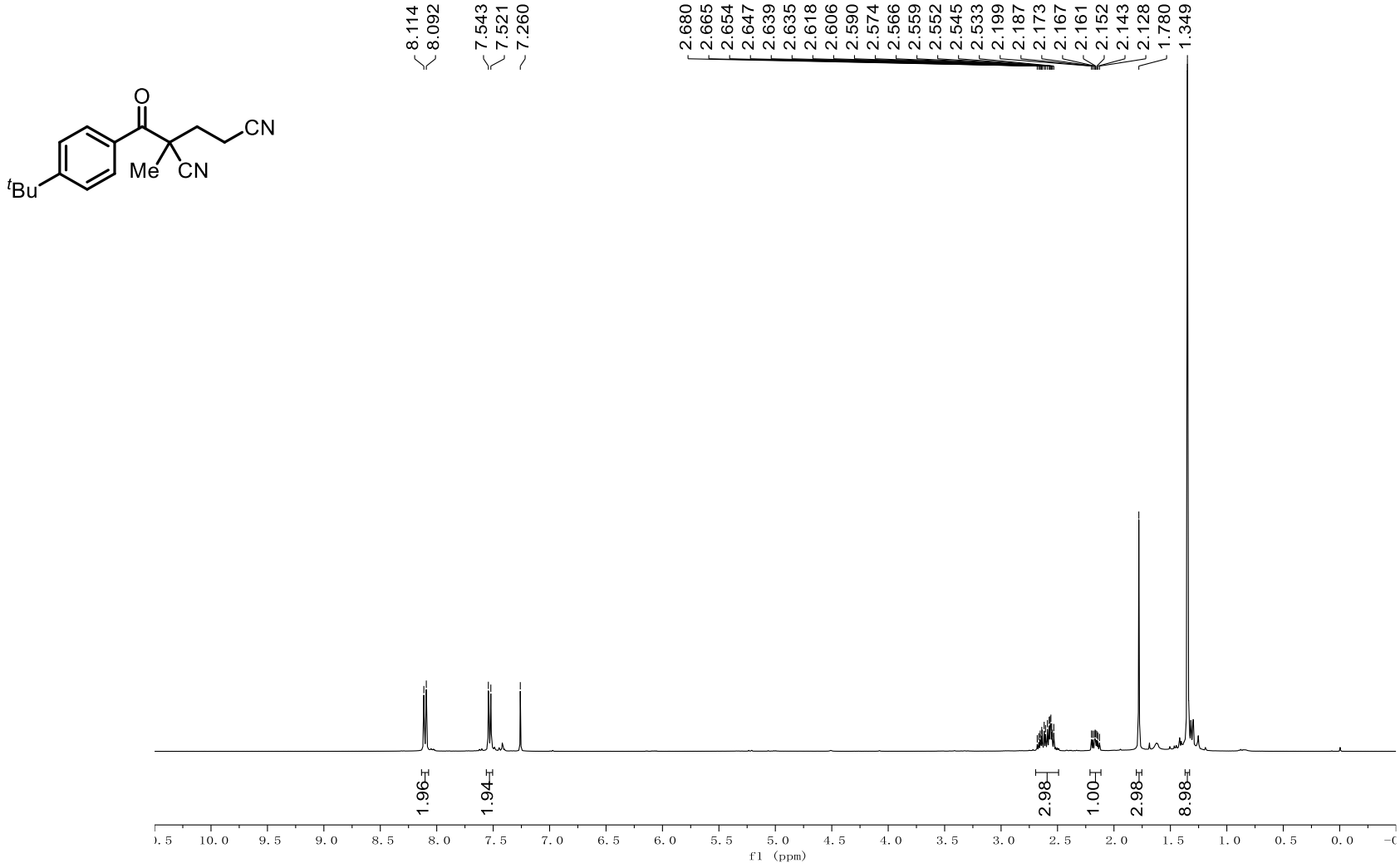
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(4-methylbenzoyl)pentanedinitrile (45)



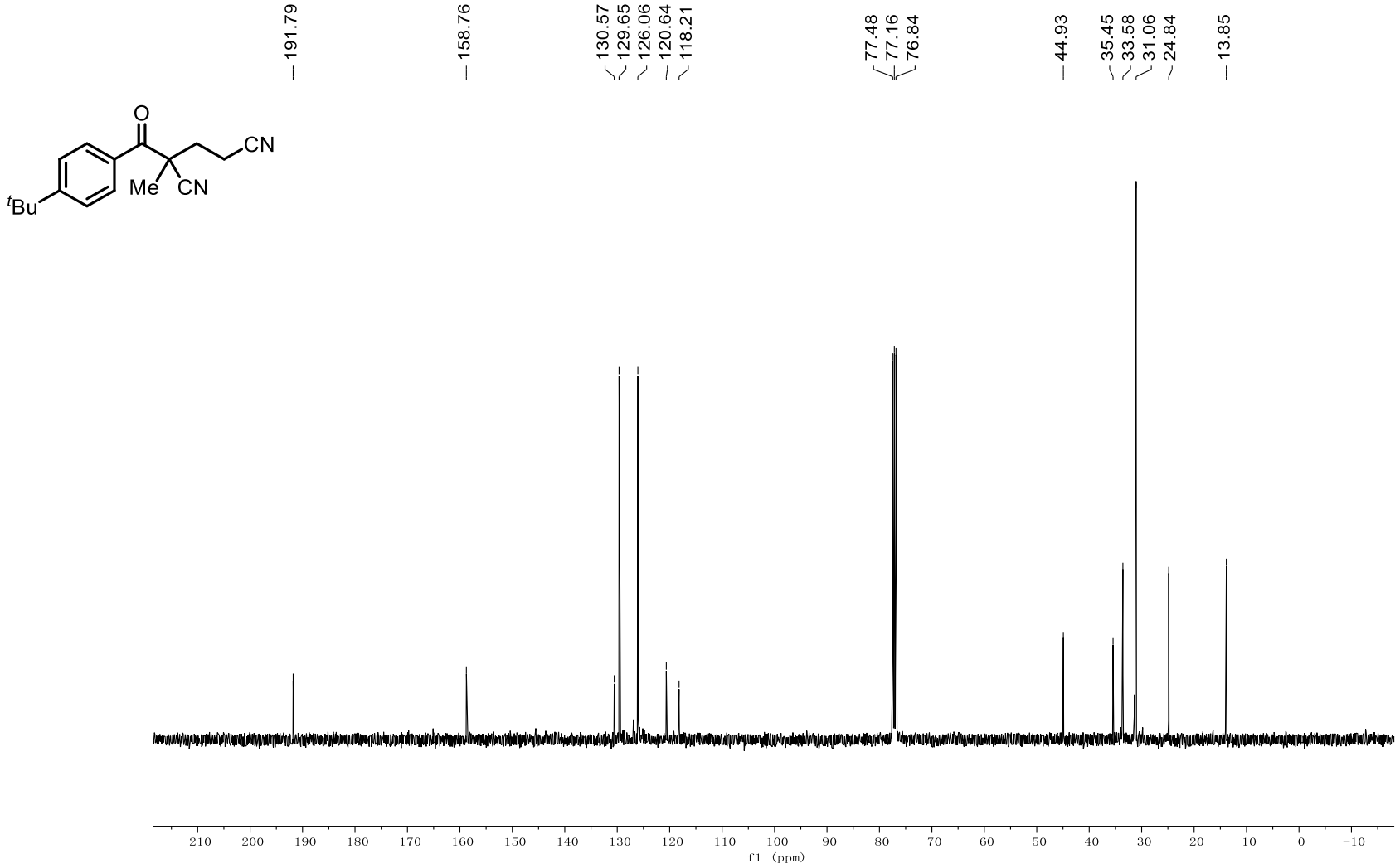
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(4-methylbenzoyl)pentanedinitrile (45)



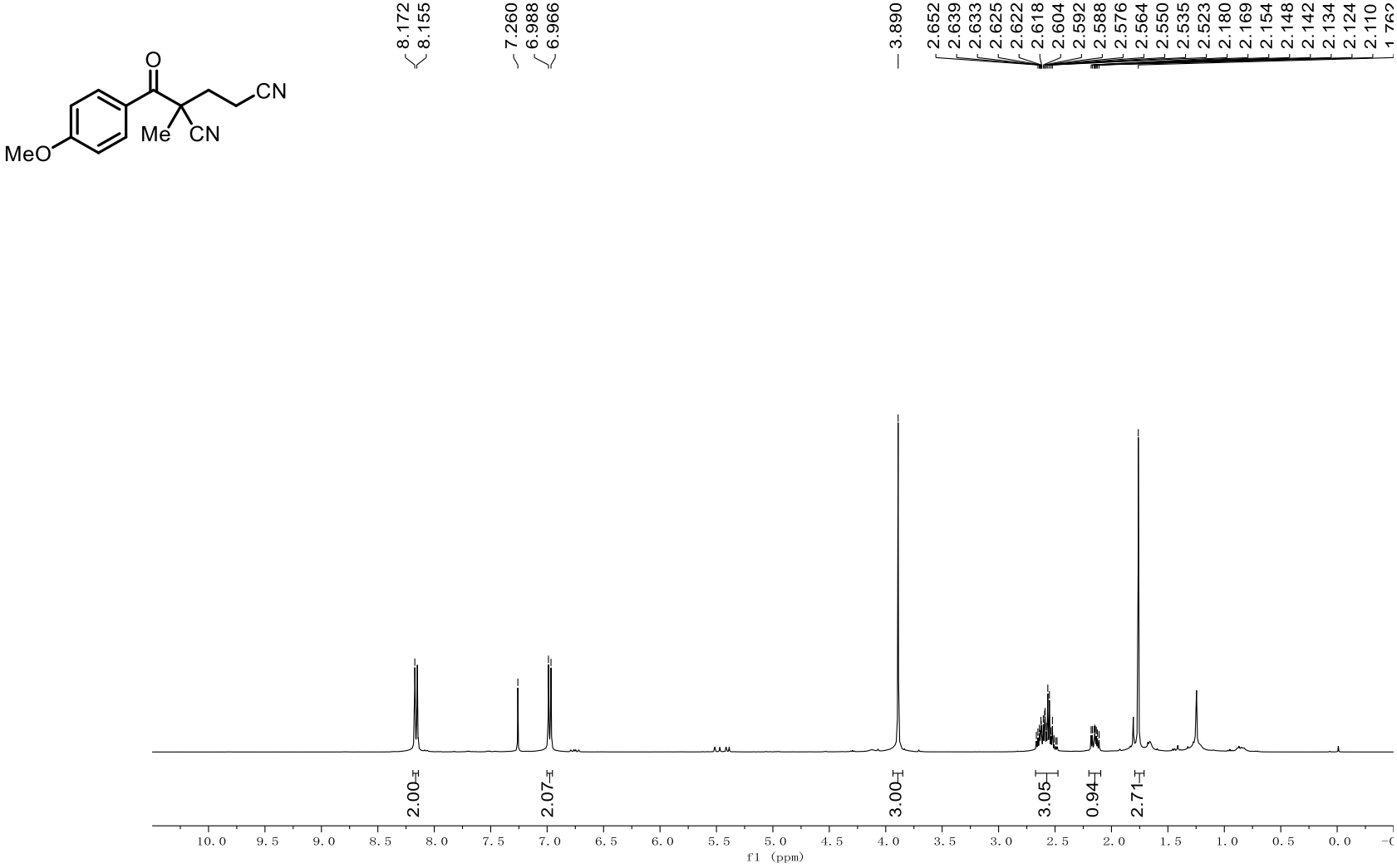
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(4-(*tert*-Butyl)benzoyl)-2-methylpentanedinitrile (46)



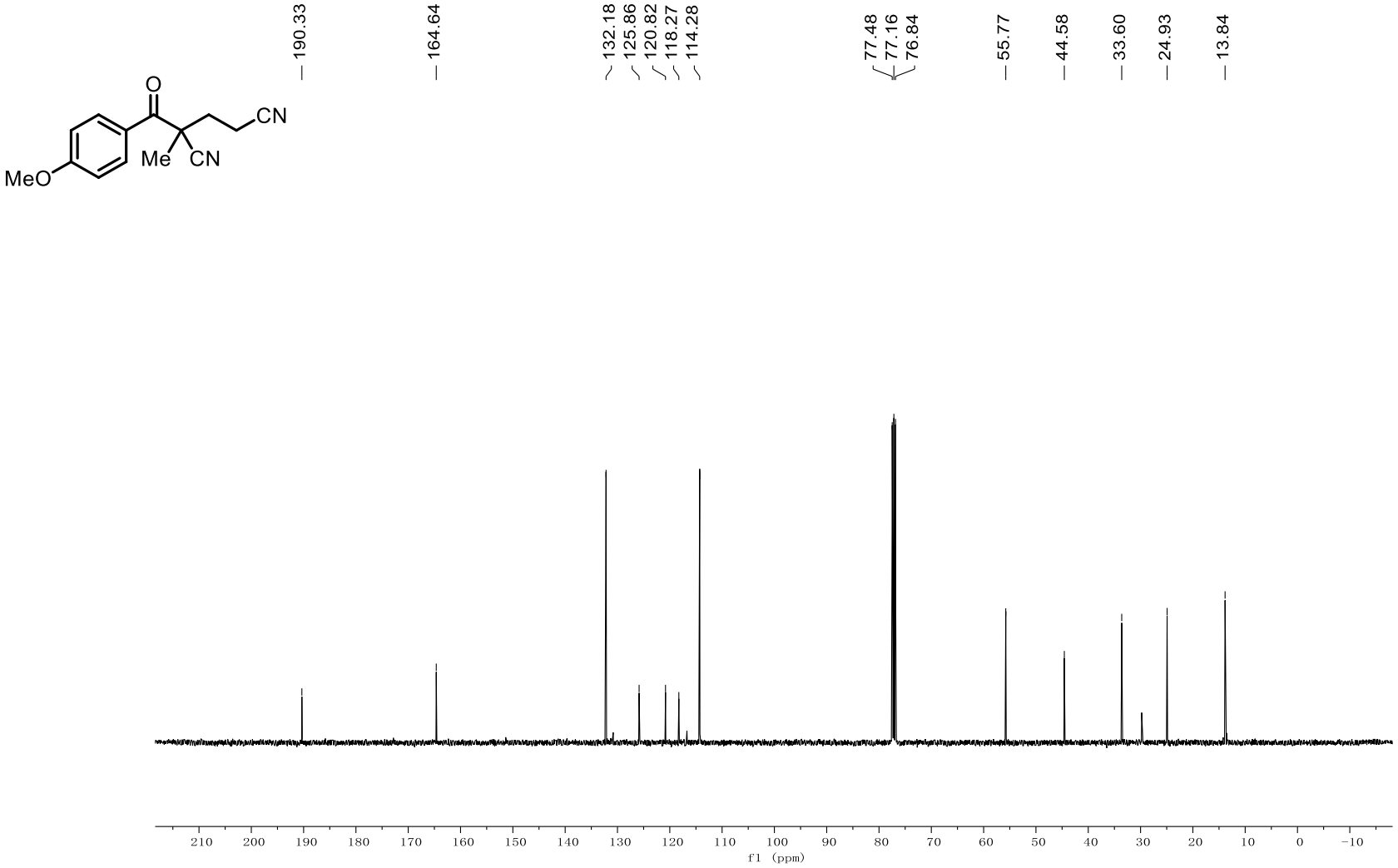
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(4-(*tert*-Butyl)benzoyl)-2-methylpentanedinitrile (46)



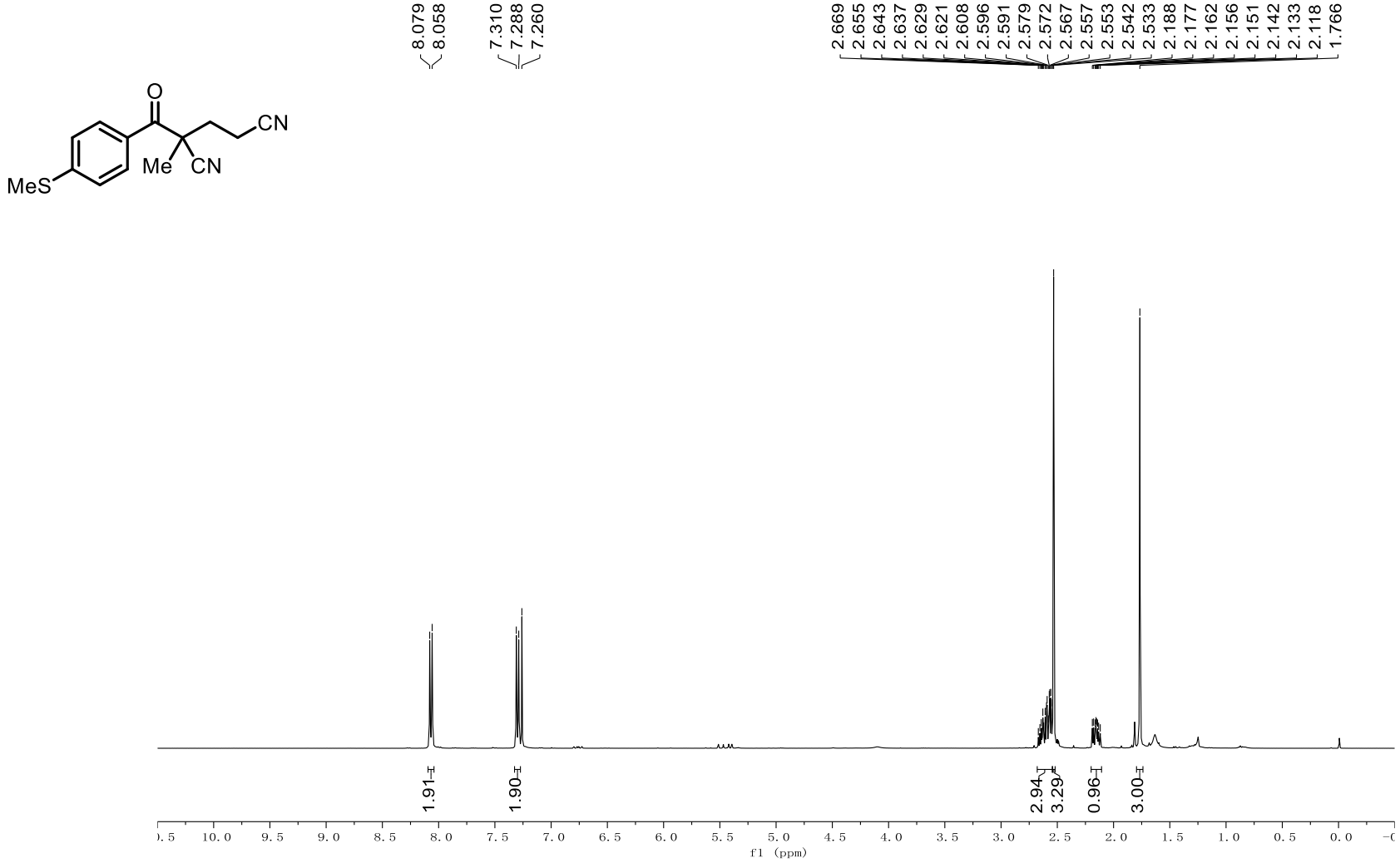
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(4-Methoxybenzoyl)-2-methylpentanedinitrile (47)



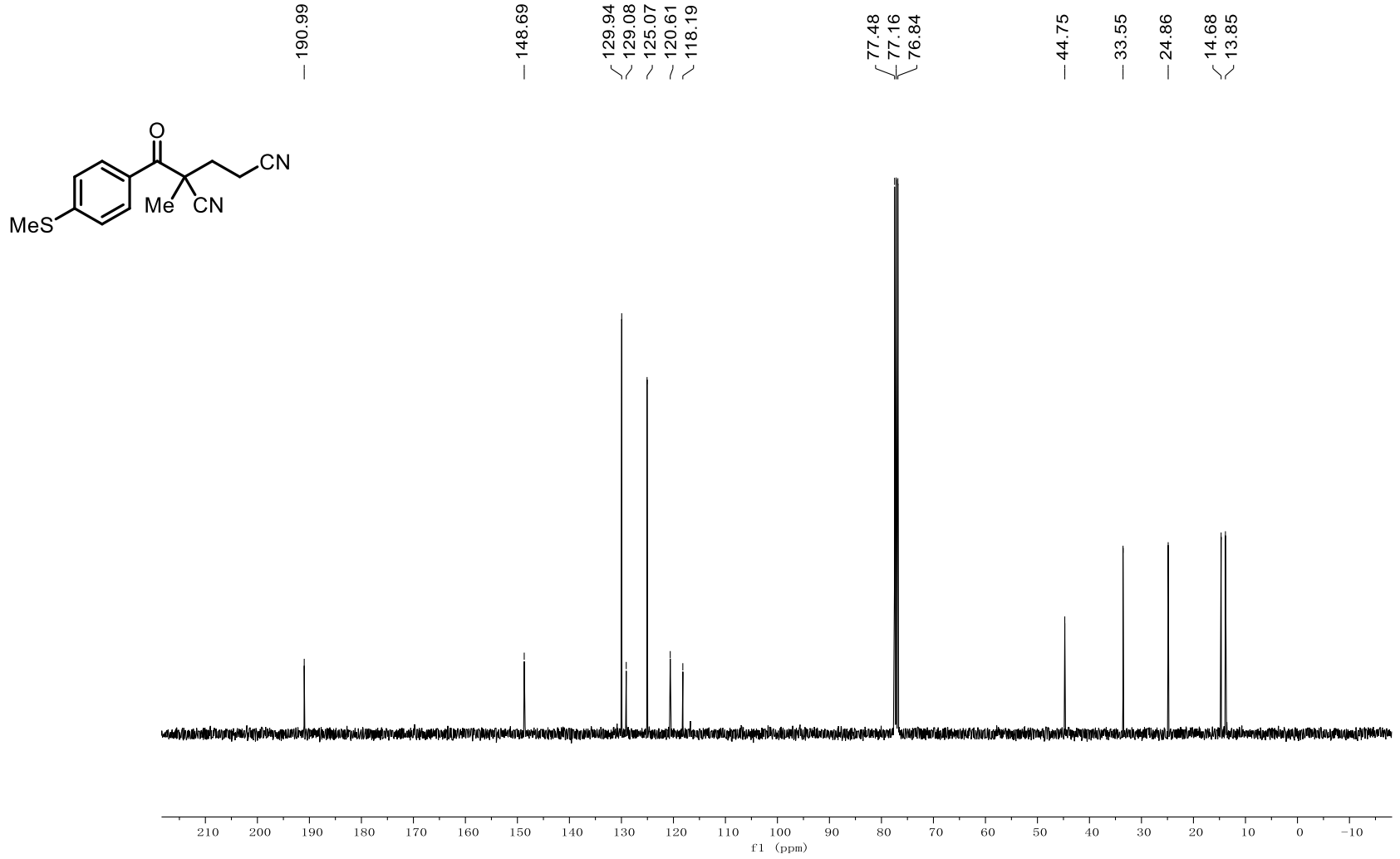
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(4-Methoxybenzoyl)-2-methylpentanedinitrile (47)



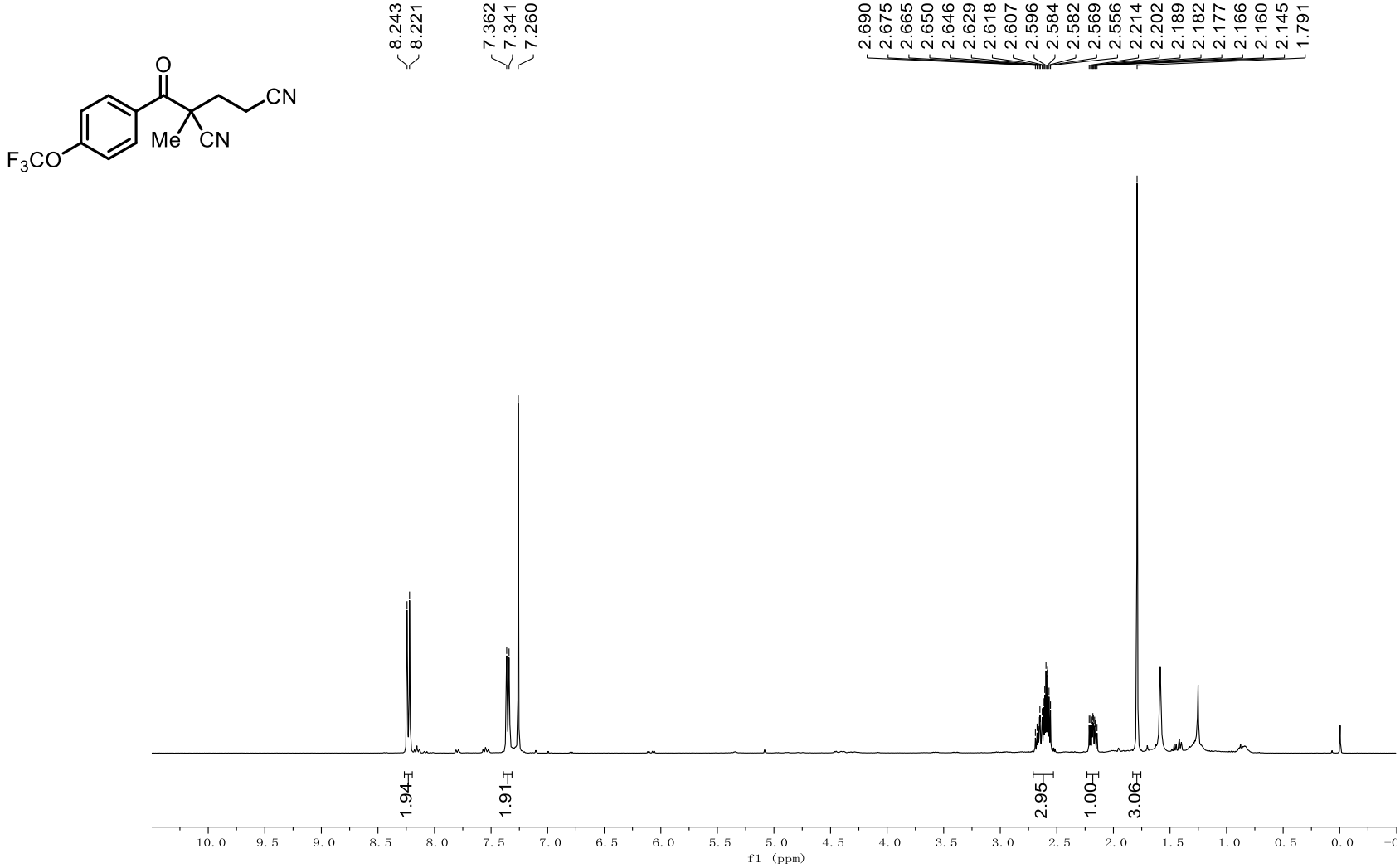
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(4-(methylthio)benzoyl)pentanedinitrile (48)



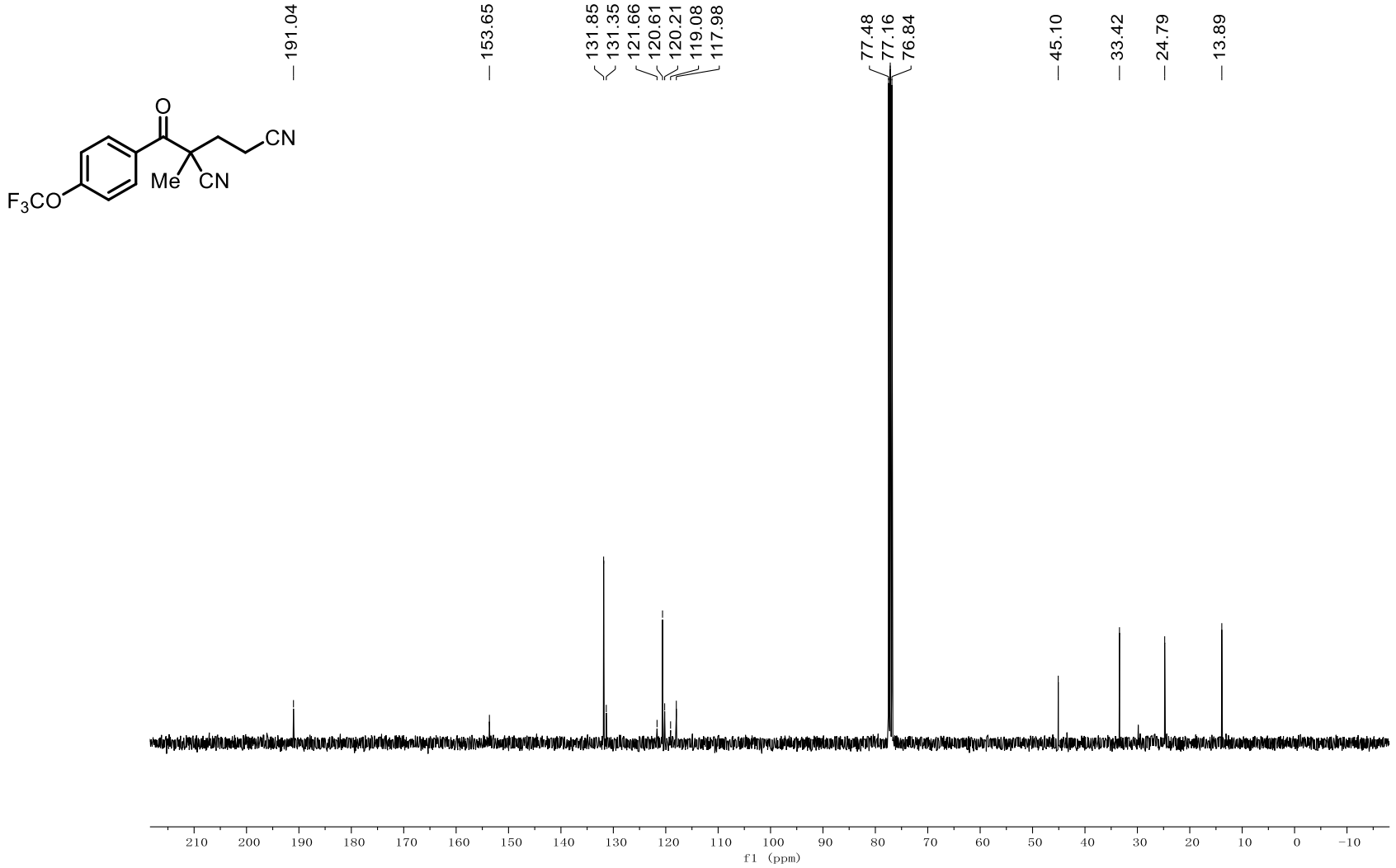
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(4-(methylthio)benzoyl)pentanedinitrile (48)



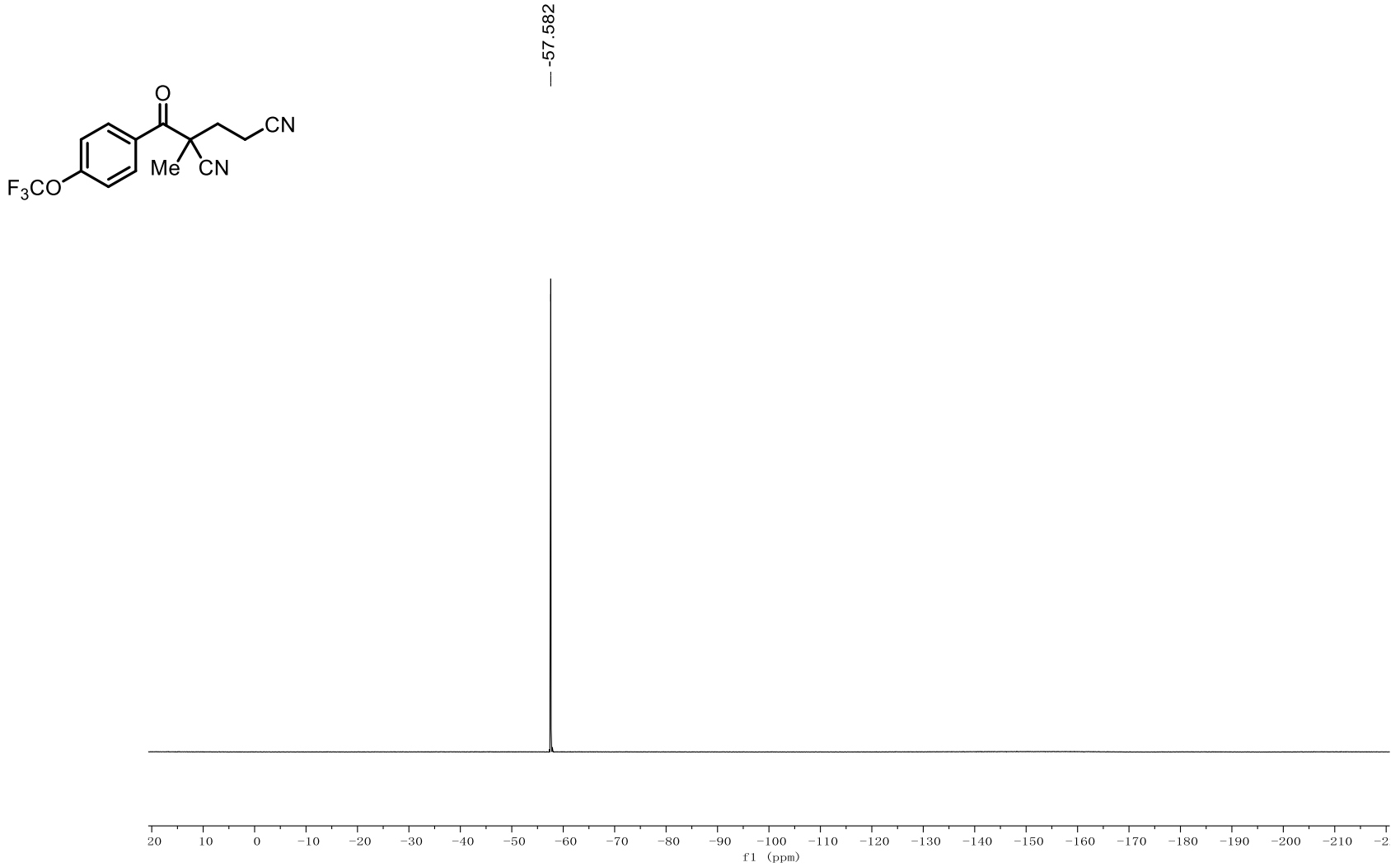
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(4-(trifluoromethoxy)benzoyl)pentanedinitrile (49)



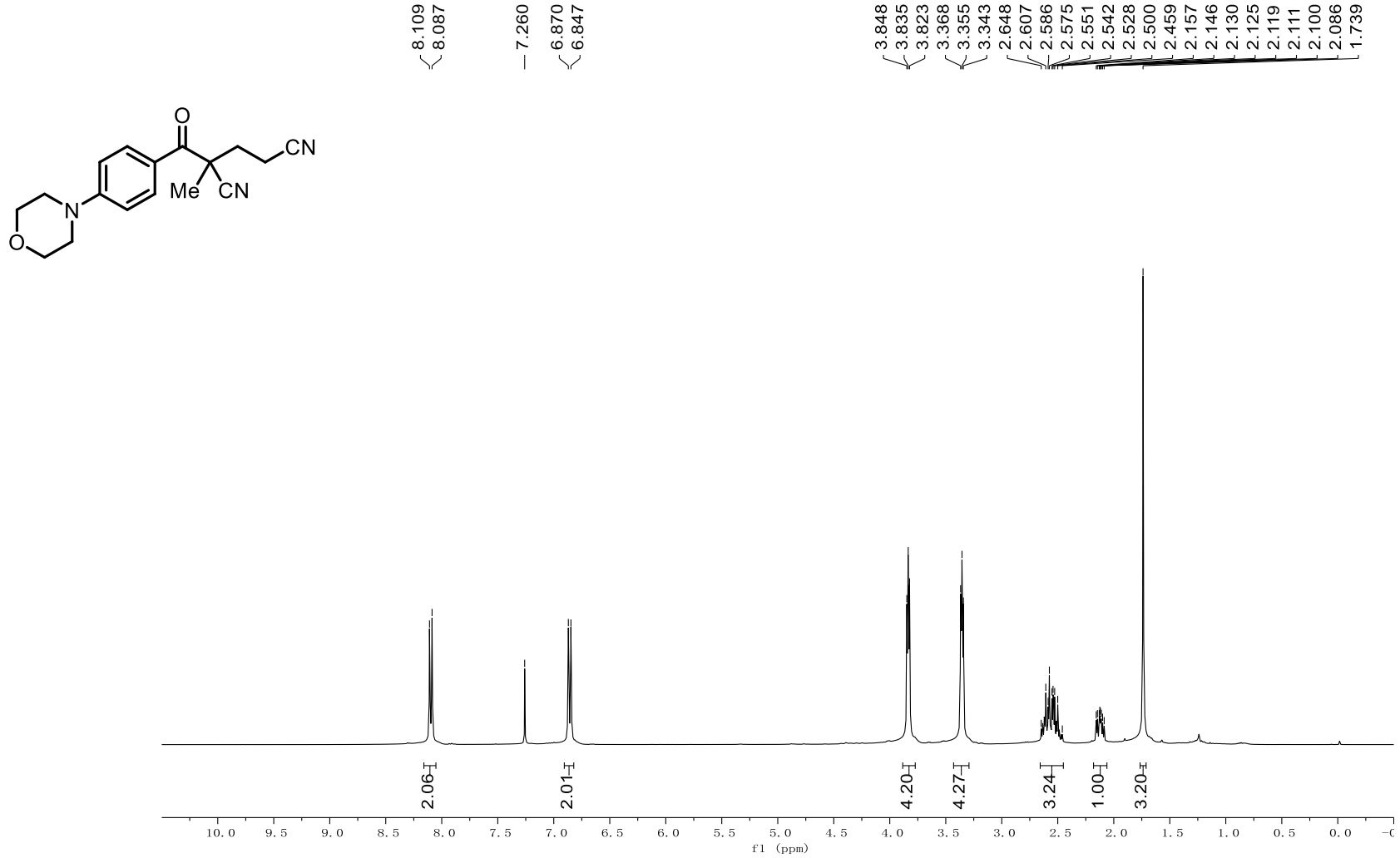
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(4-(trifluoromethoxy)benzoyl)pentanedinitrile (49)



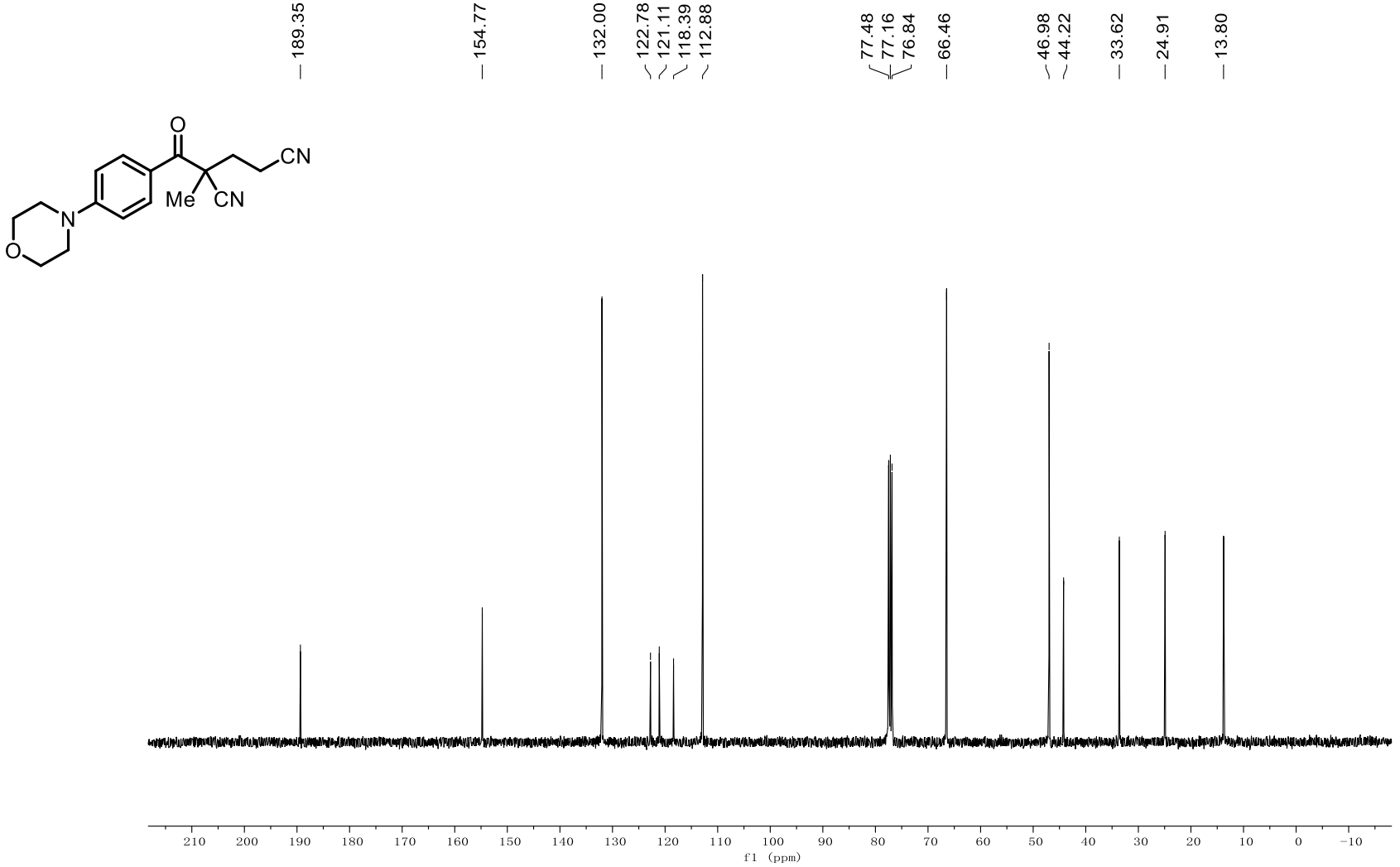
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(4-(trifluoromethoxy)benzoyl)pentanedinitrile (49)



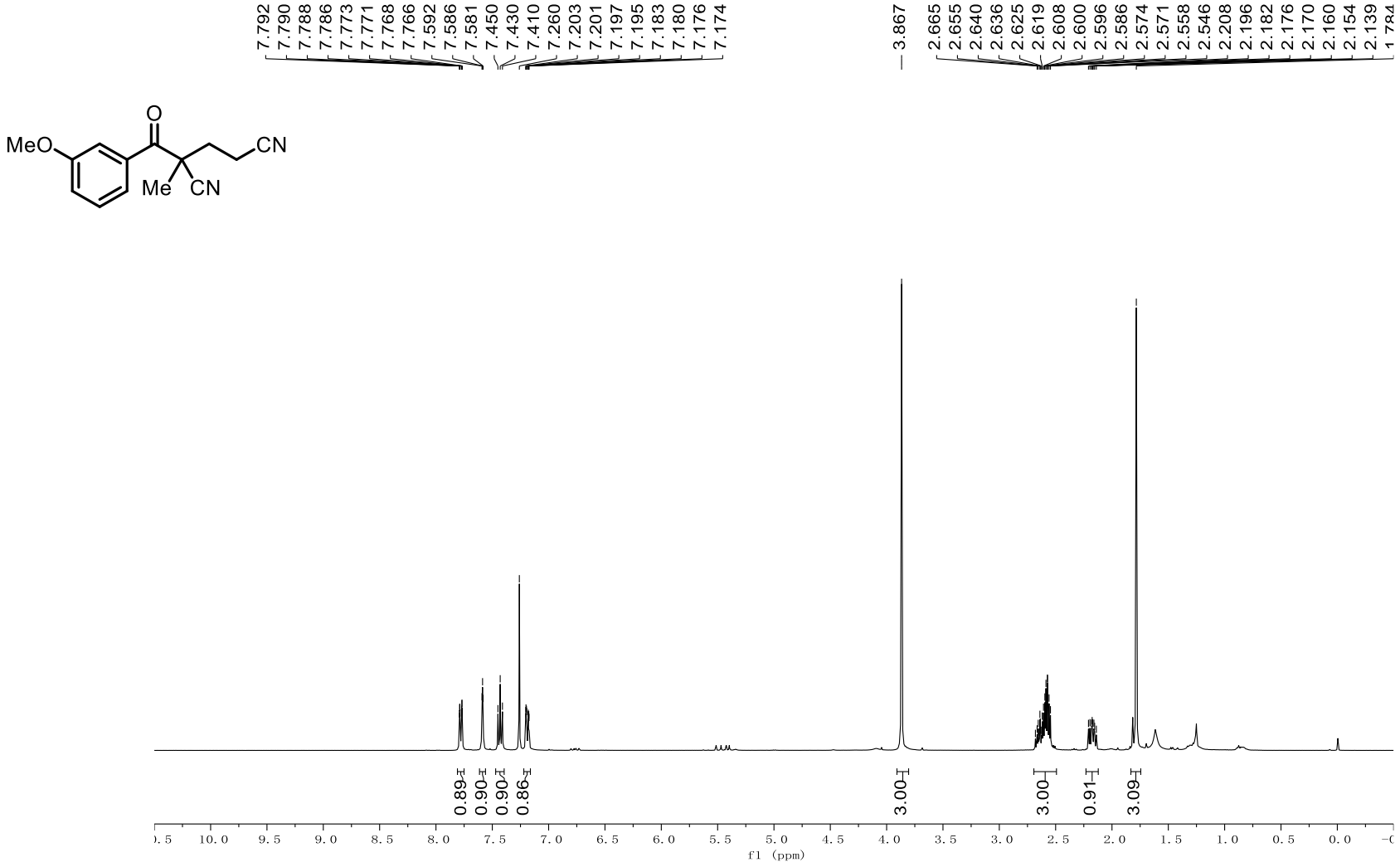
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(4-morpholinobenzoyl)pentanedinitrile (50)



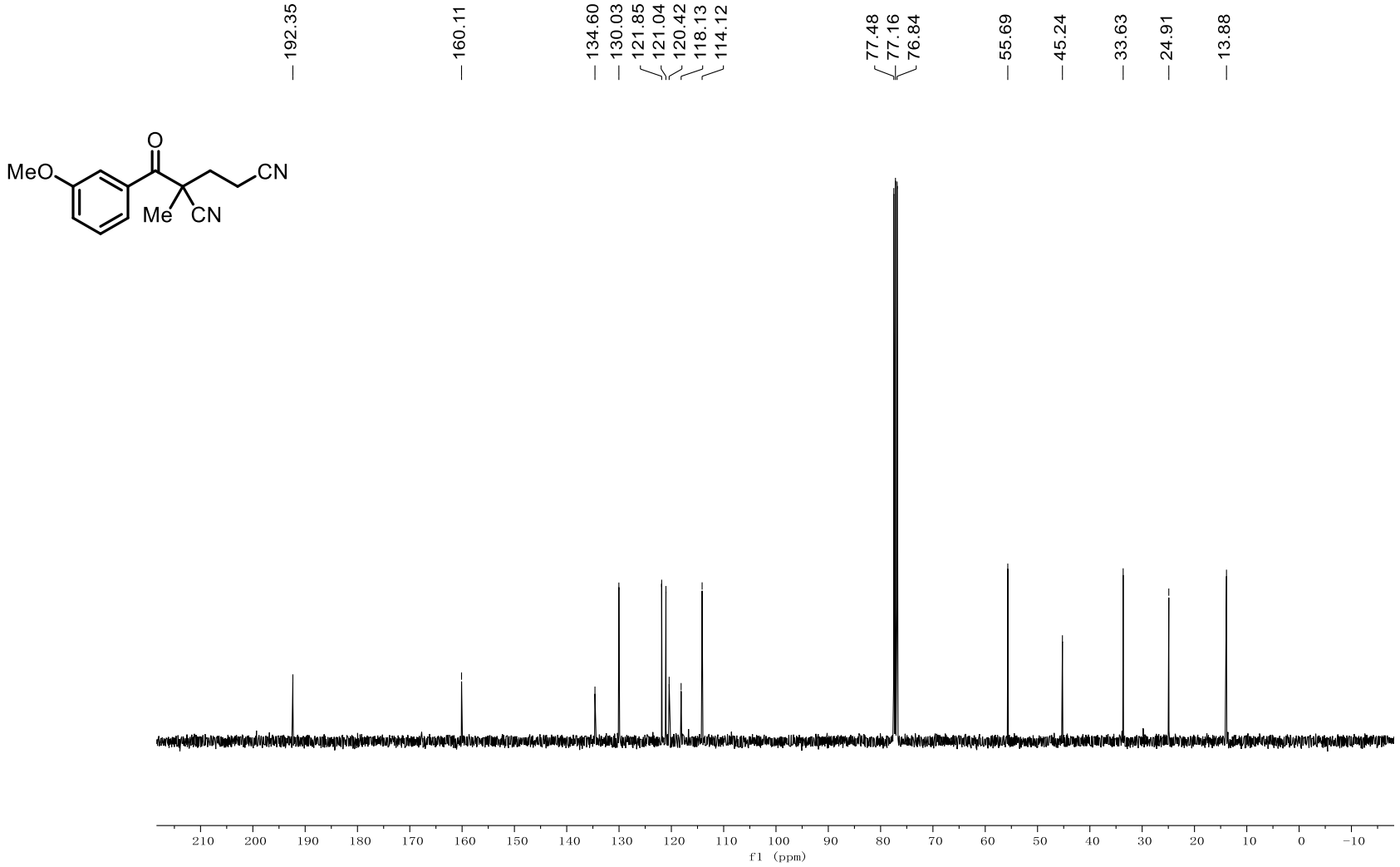
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(4-morpholinobenzoyl)pentanedinitrile (50)



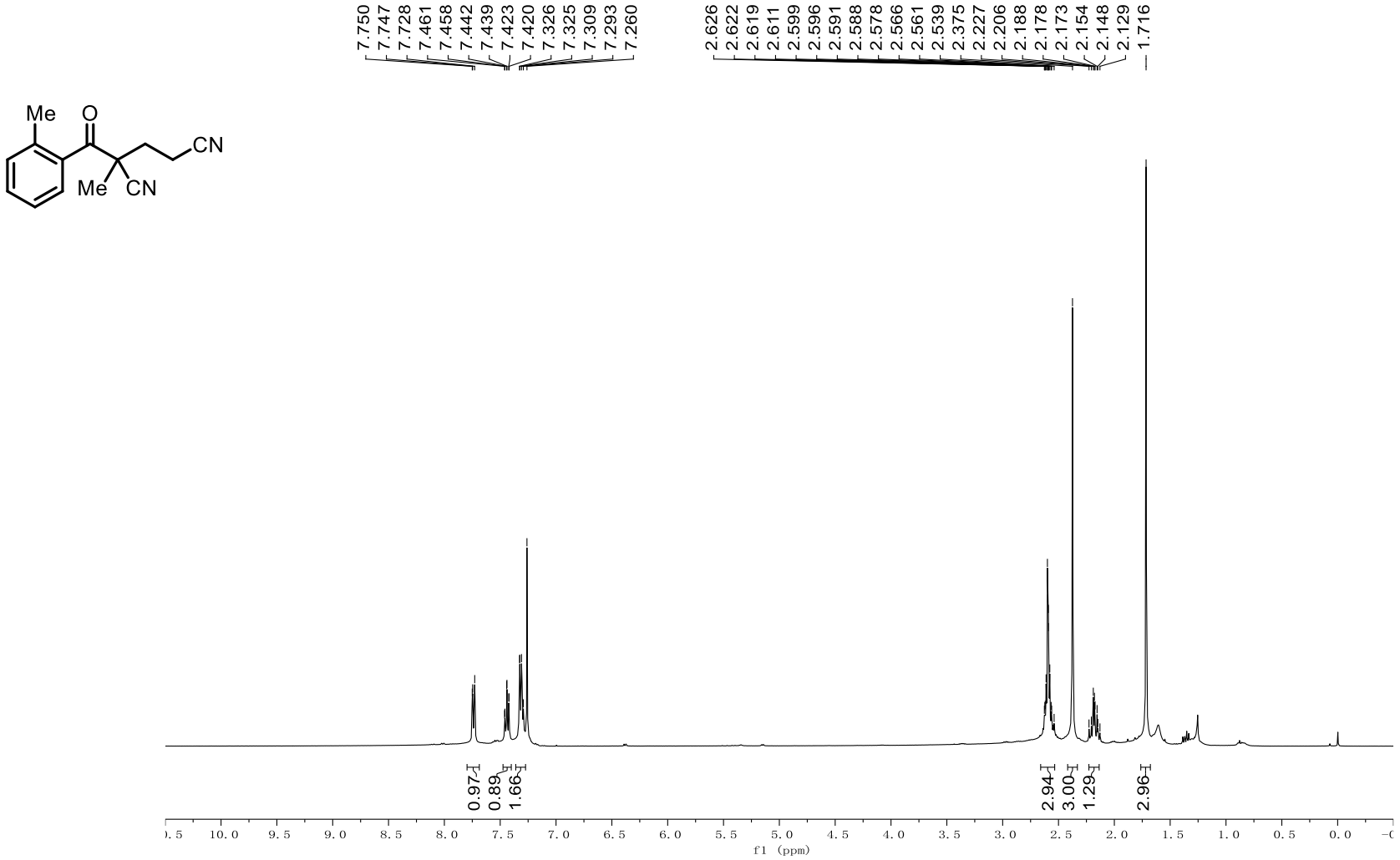
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(3-Methoxybenzoyl)-2-methylpentanedinitrile (51)



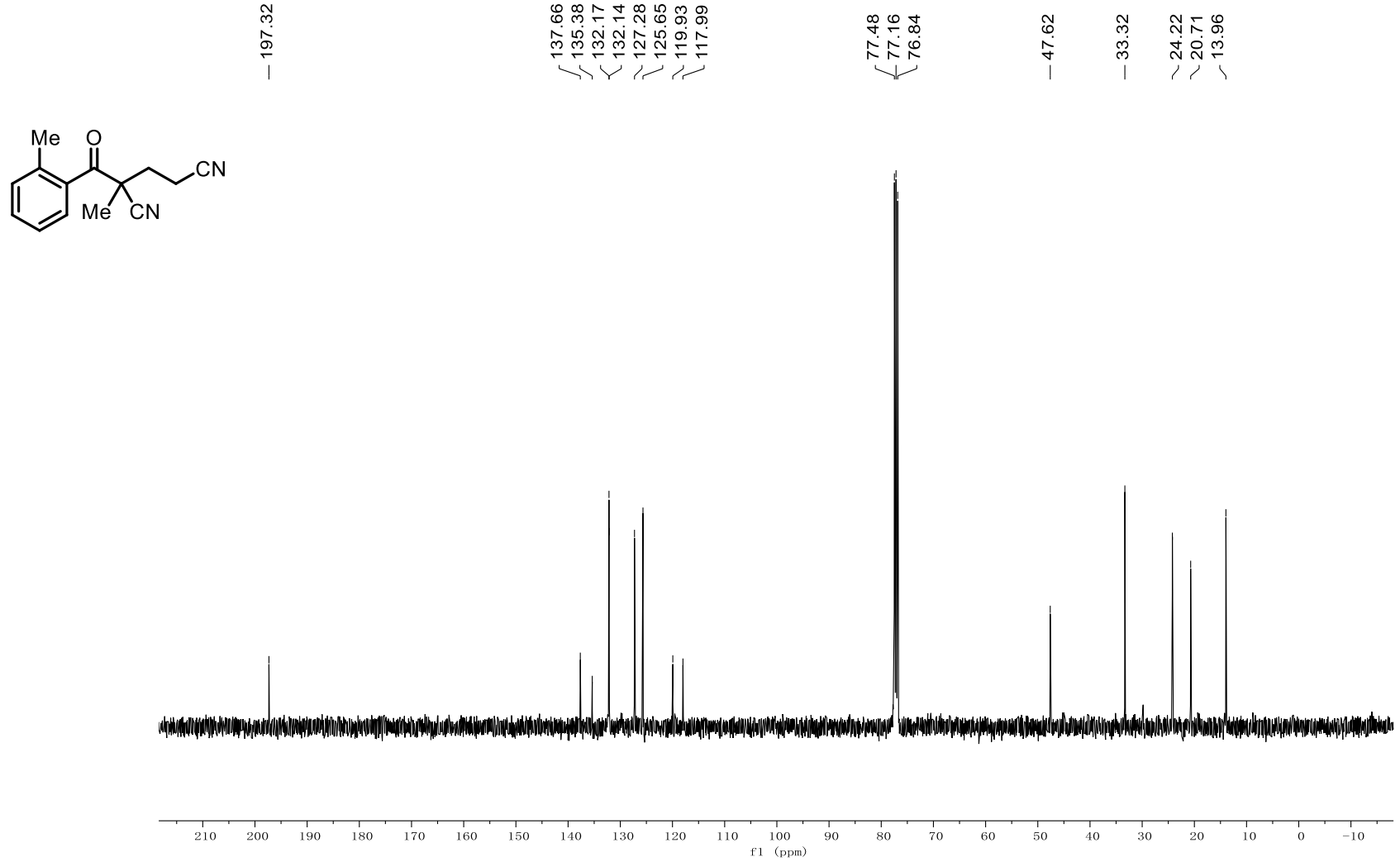
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(3-Methoxybenzoyl)-2-methylpentanedinitrile (51)



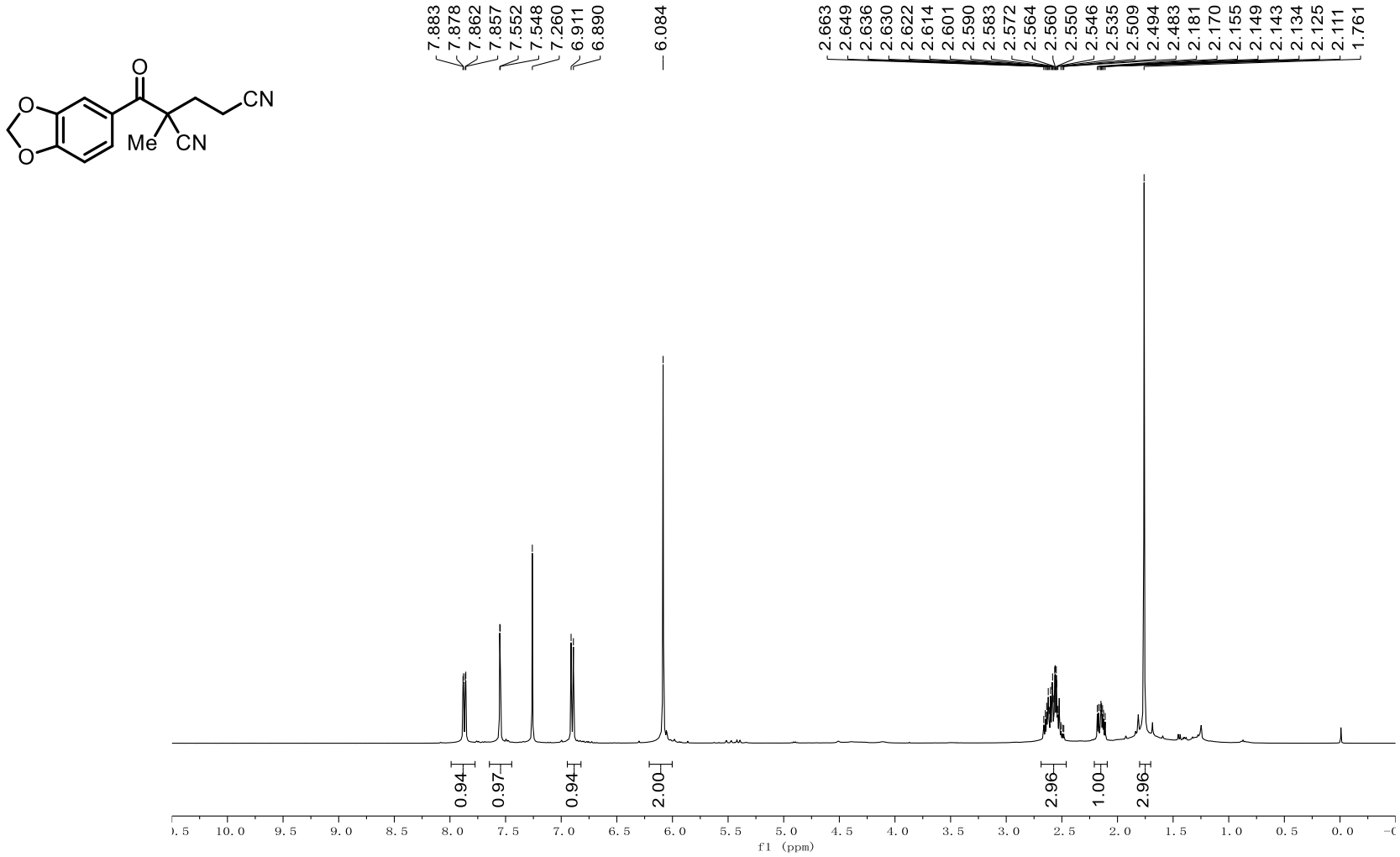
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(2-methylbenzoyl)pentanedinitrile (52)



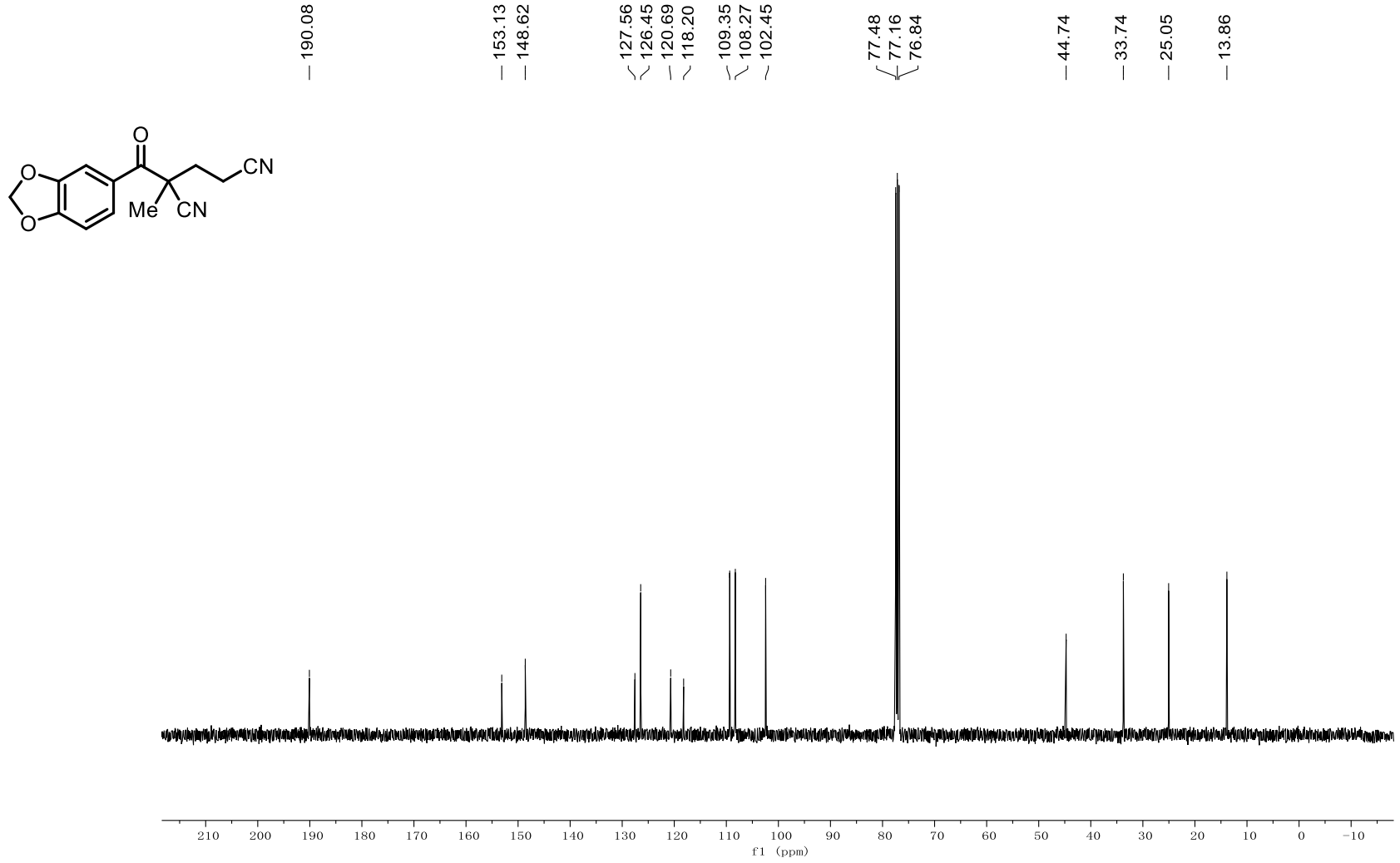
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(2-methylbenzoyl)pentanedinitrile (52)



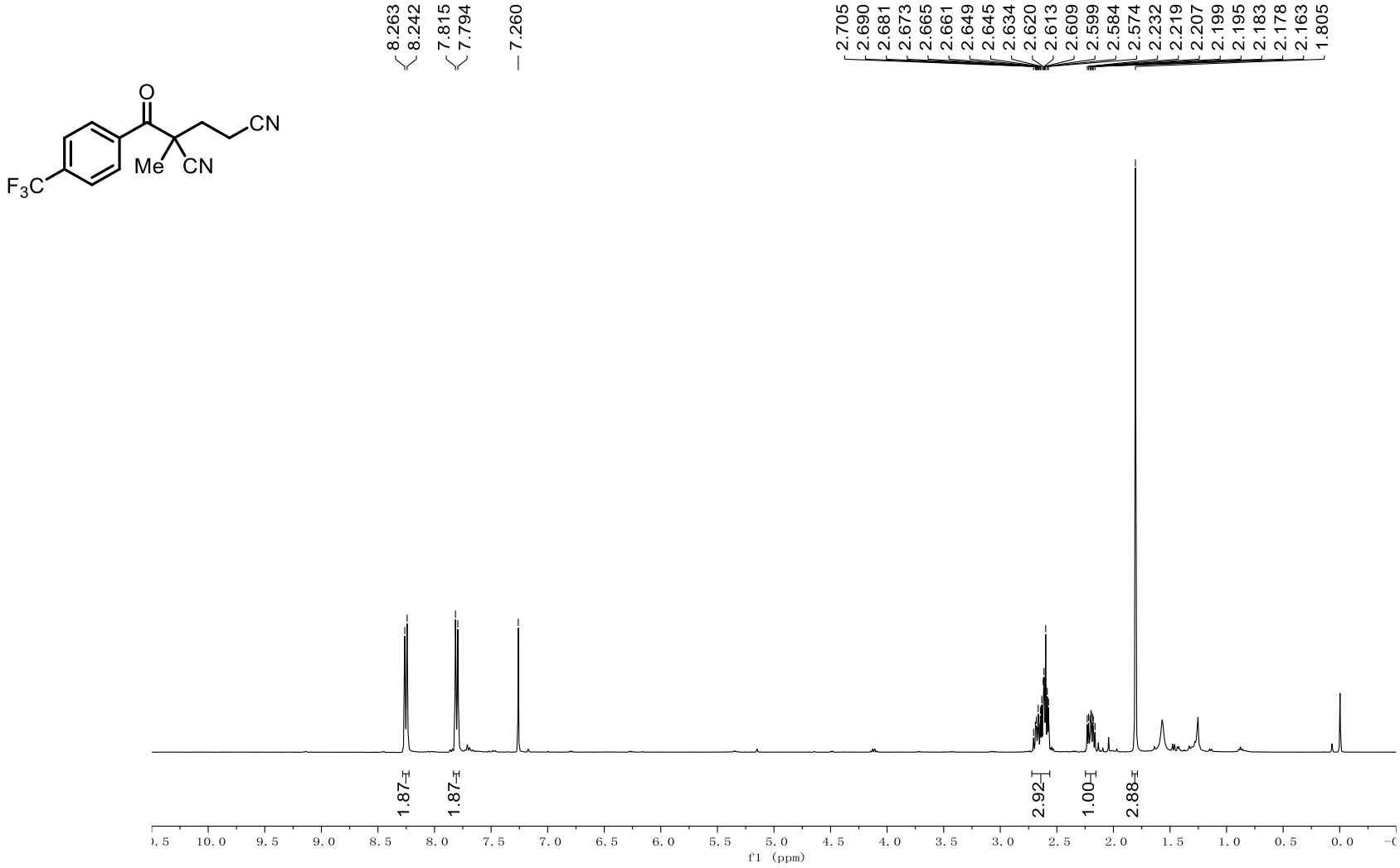
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(Benzo[*d*][1,3]dioxole-5-carbonyl)-2-methylpentanedinitrile (53)



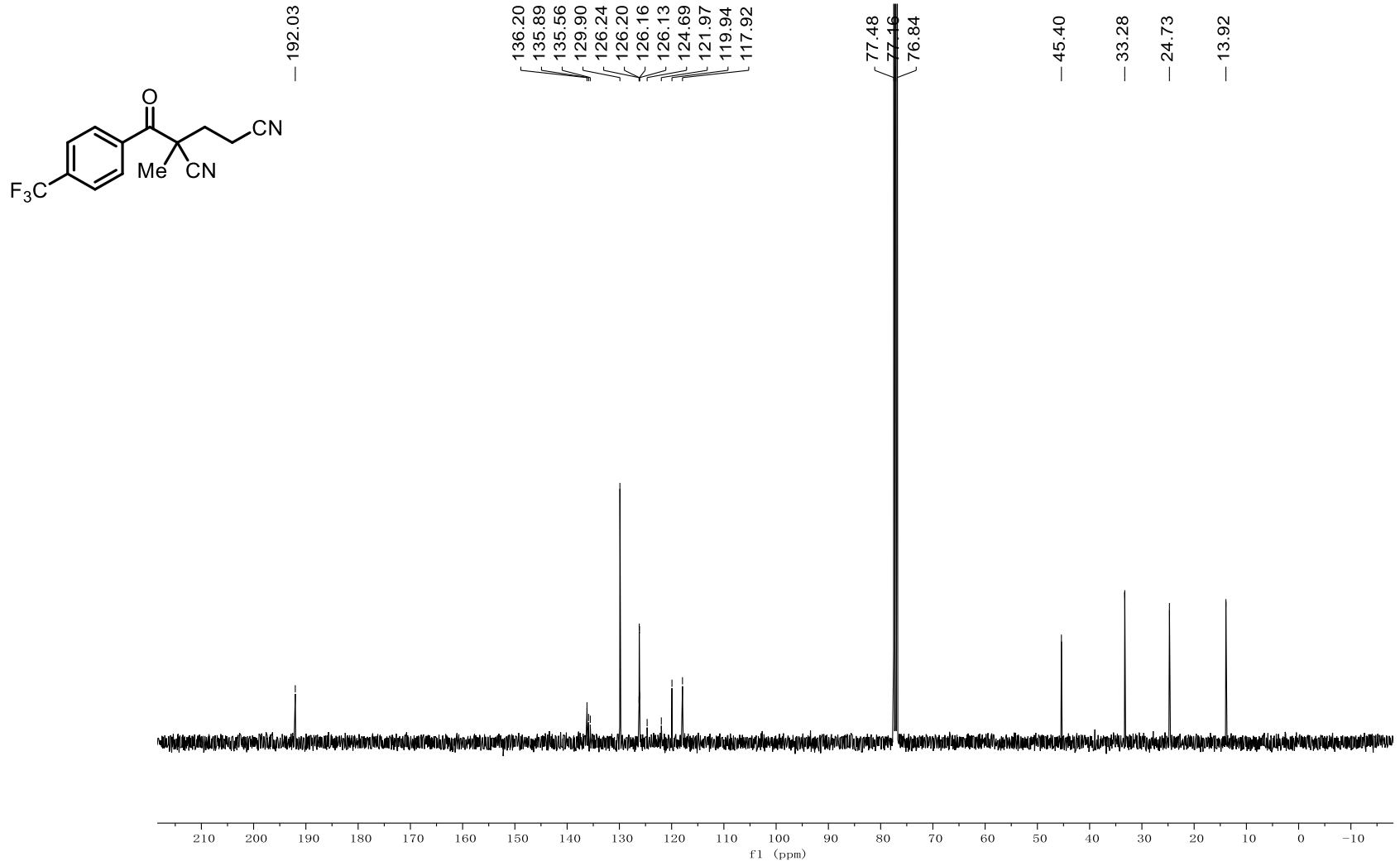
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(Benzo[*d*][1,3]dioxole-5-carbonyl)-2-methylpentanedinitrile (53)



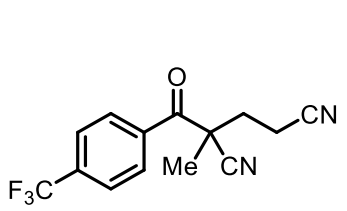
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(4-(trifluoromethoxy)benzoyl)pentanedinitrile (54)

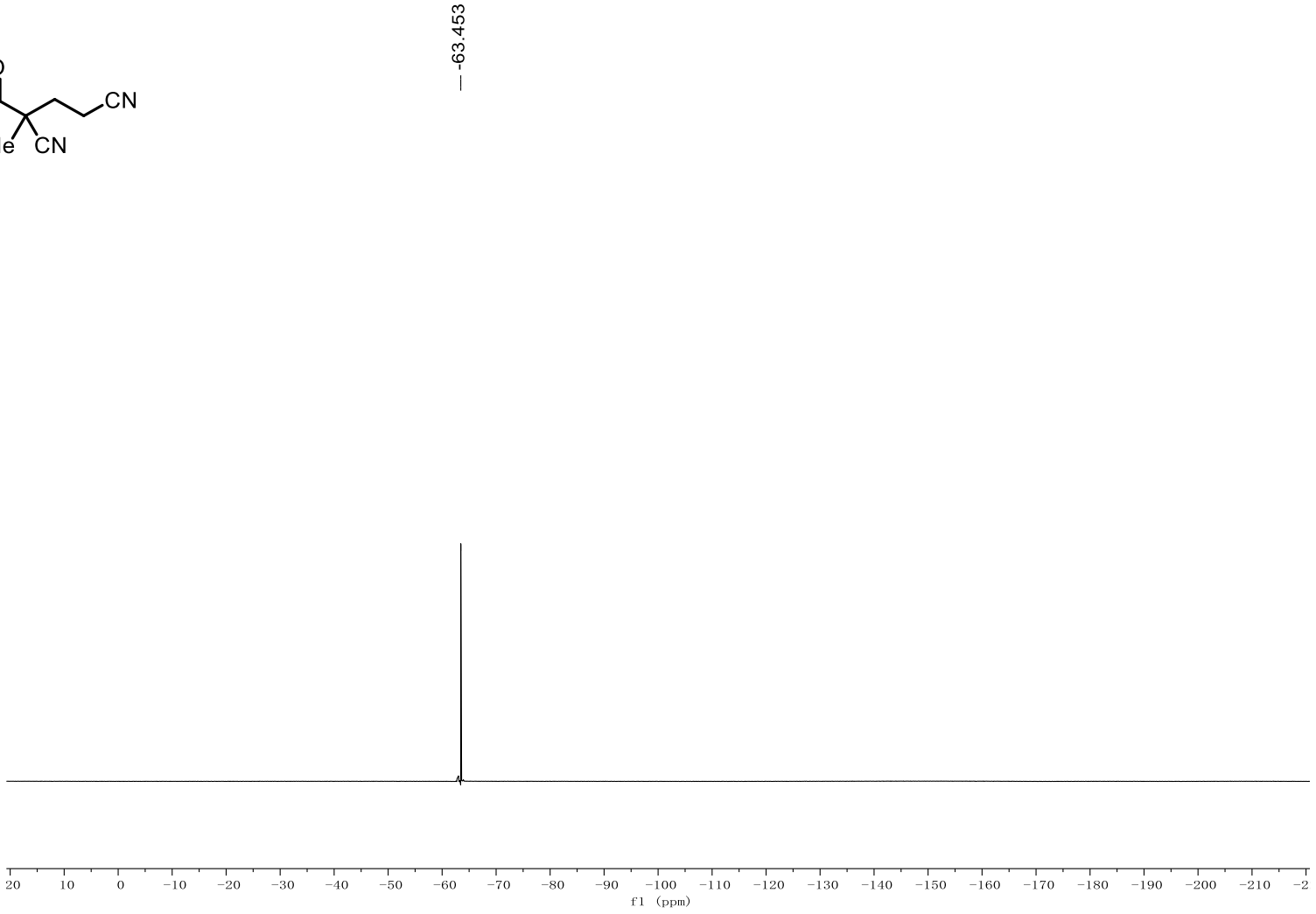


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(4-(trifluoromethoxy)benzoyl)pentanedinitrile (54)

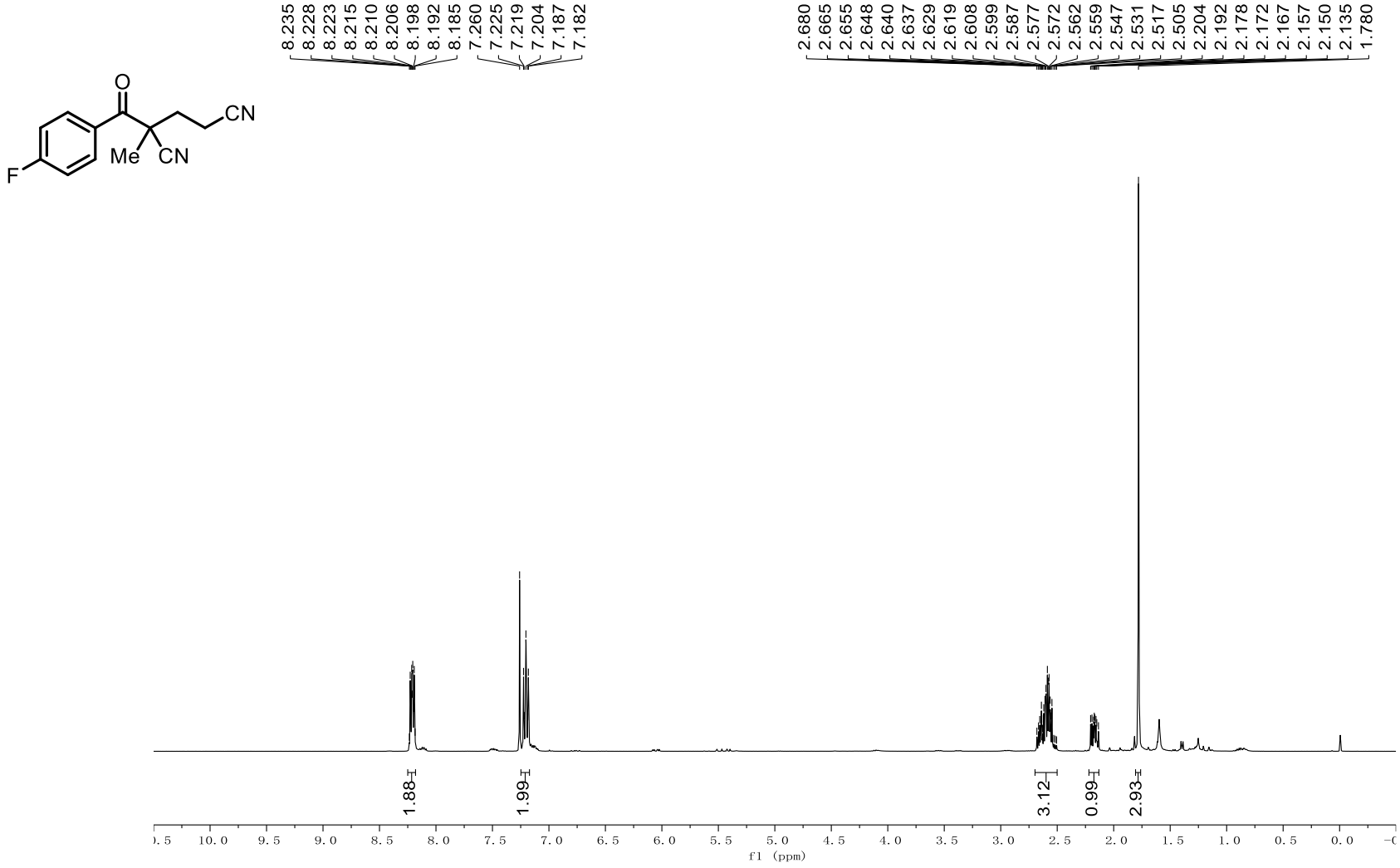


^{19}F NMR (376 MHz, CDCl3) spectrum of 2-Methyl-2-(4-(trifluoromethoxy)benzoyl)pentanedinitrile (54)

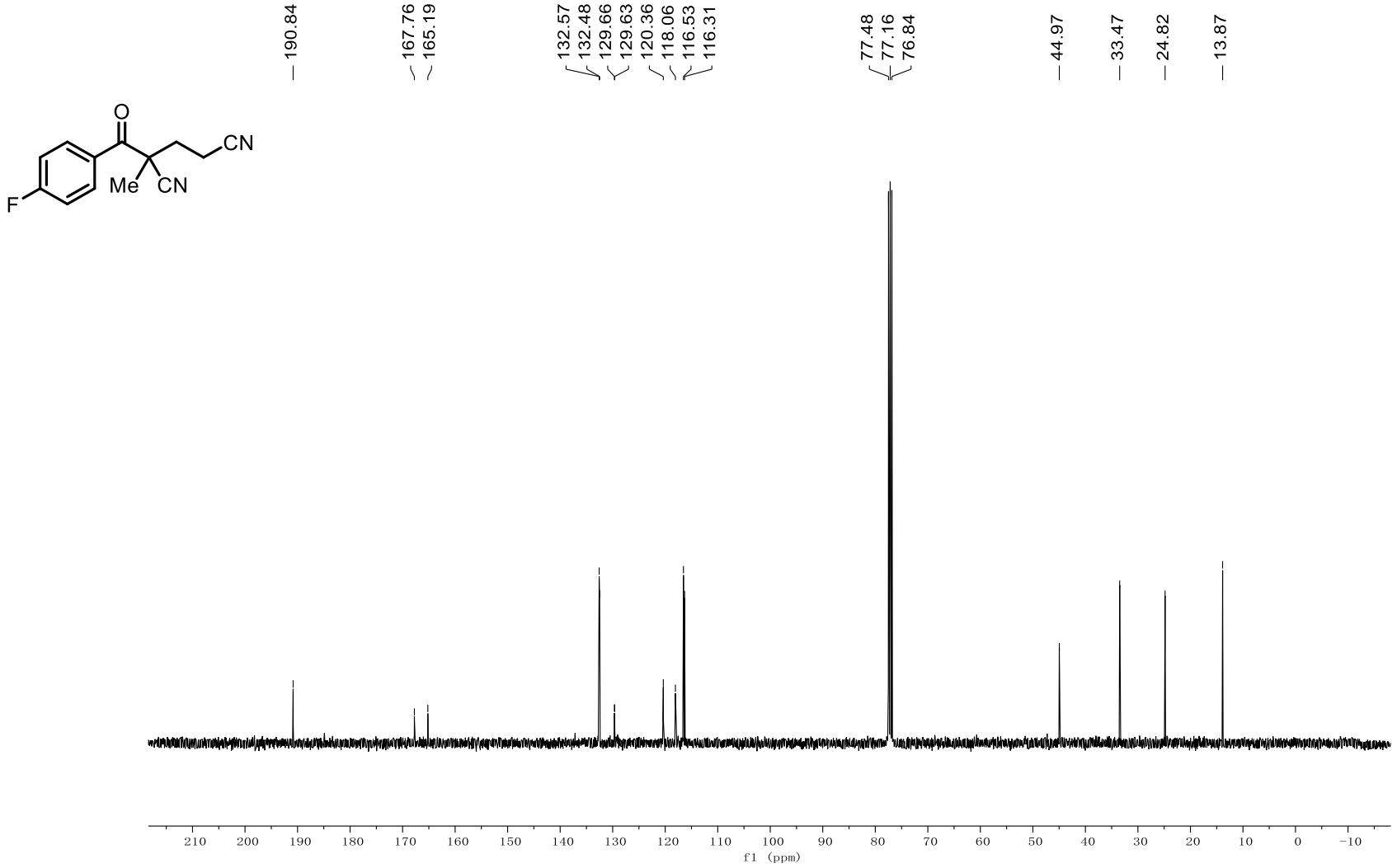




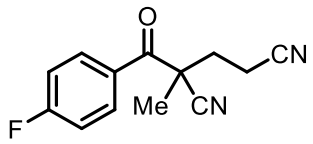
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(4-Fluorobenzoyl)-2-methylpentanedinitrile (55)

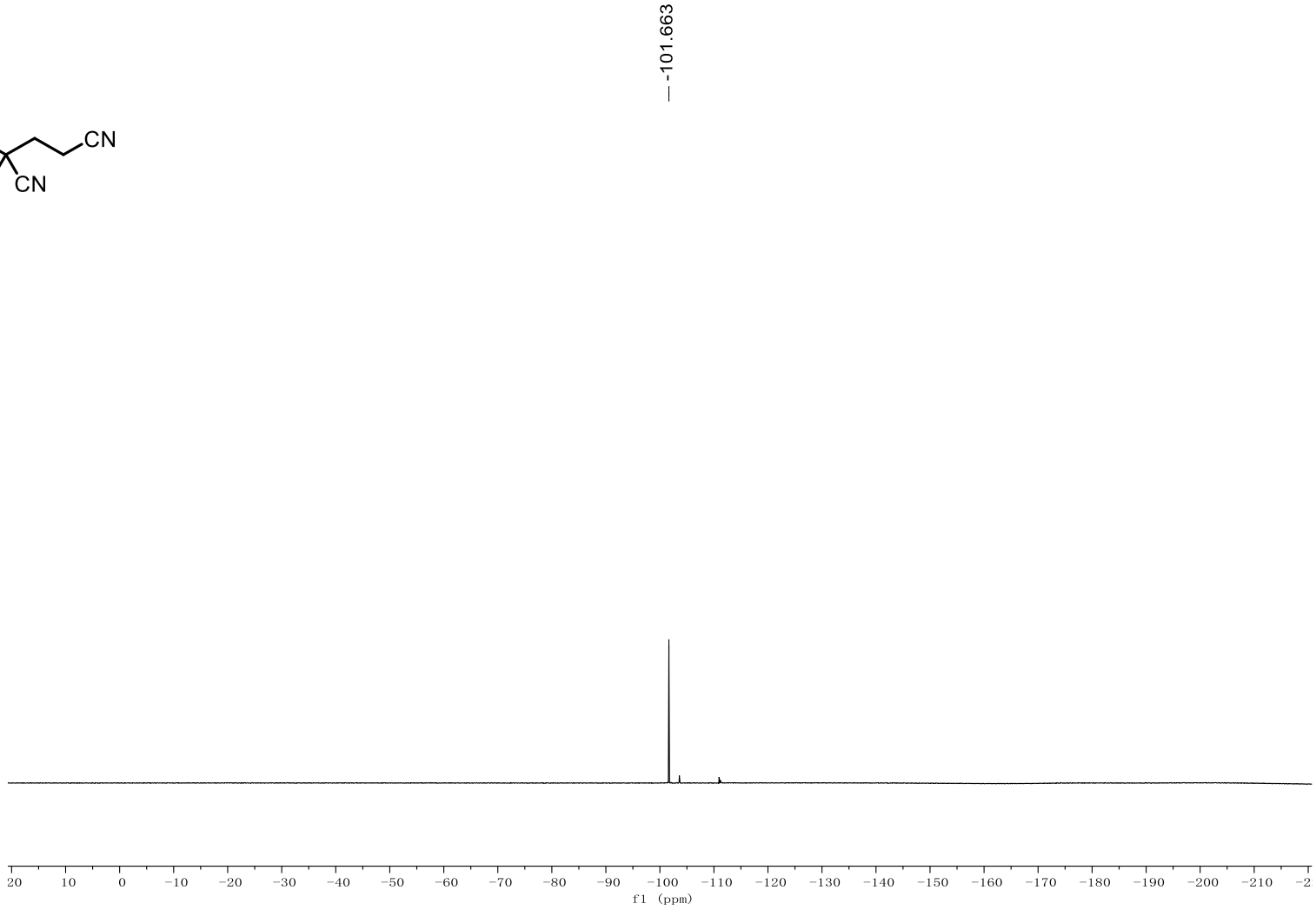


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(4-Fluorobenzoyl)-2-methylpentanedinitrile (55)

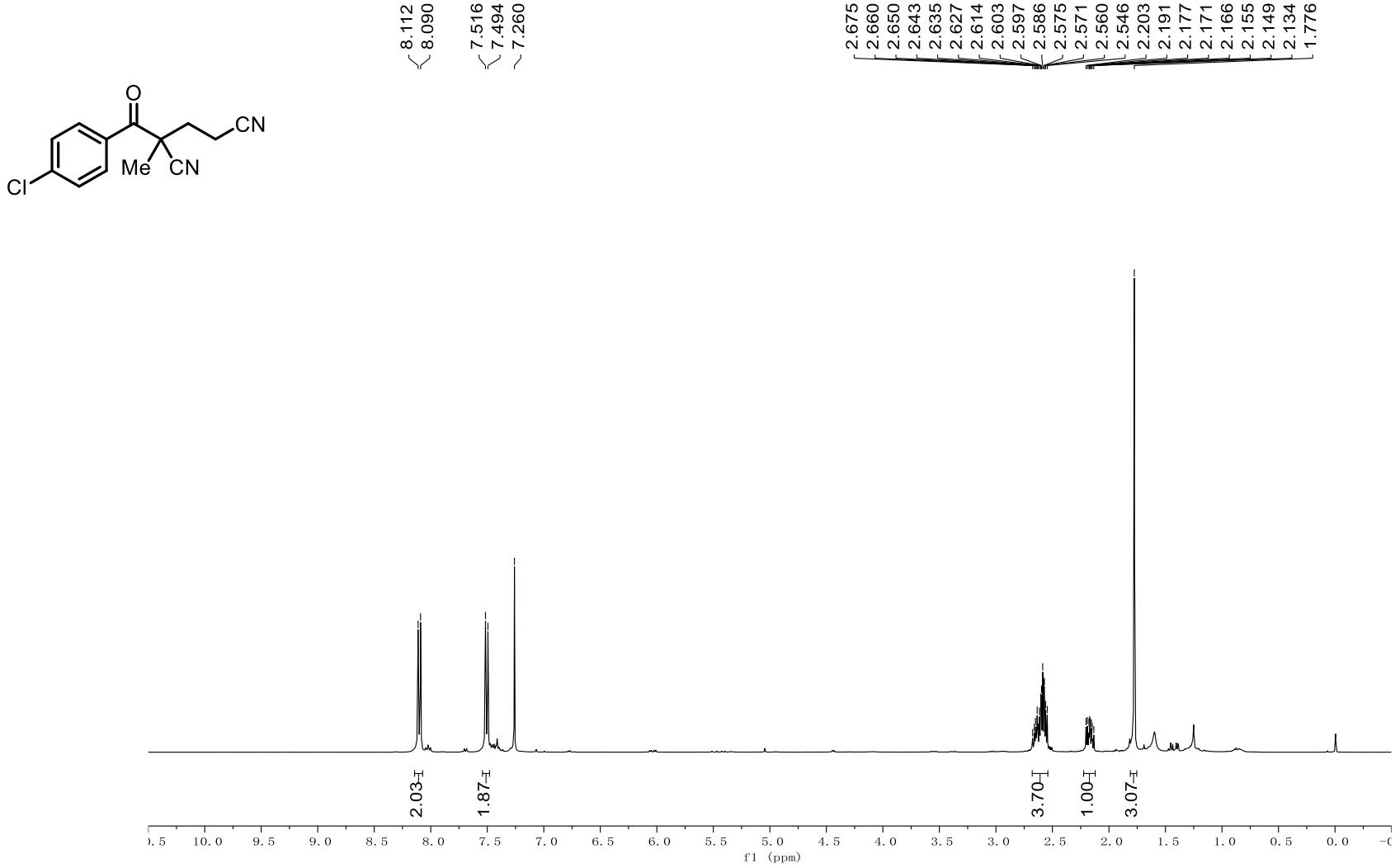


^{19}F NMR (376 MHz, CDCl3) spectrum of 2-(4-Fluorobenzoyl)-2-methylpentanedinitrile (55)

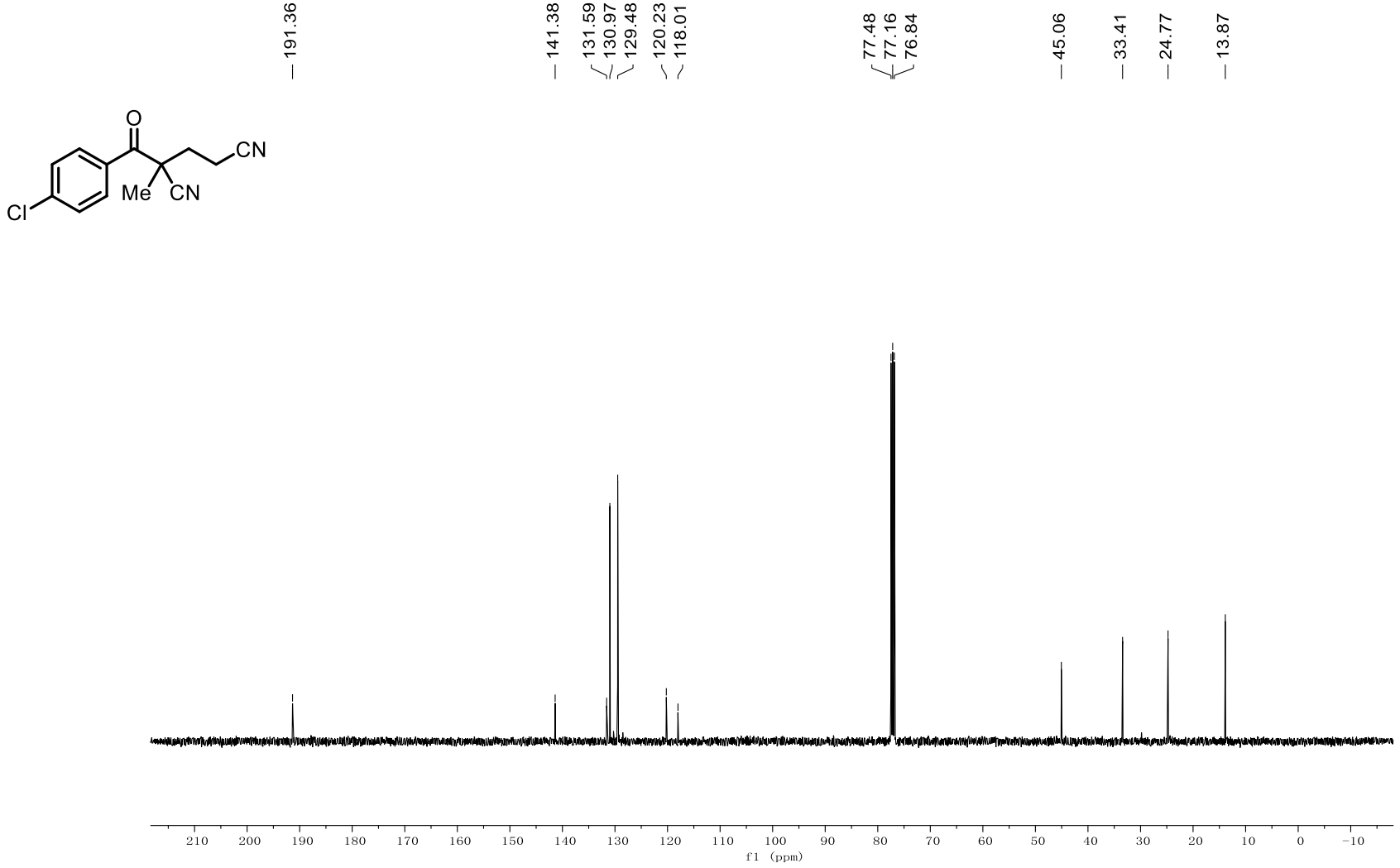




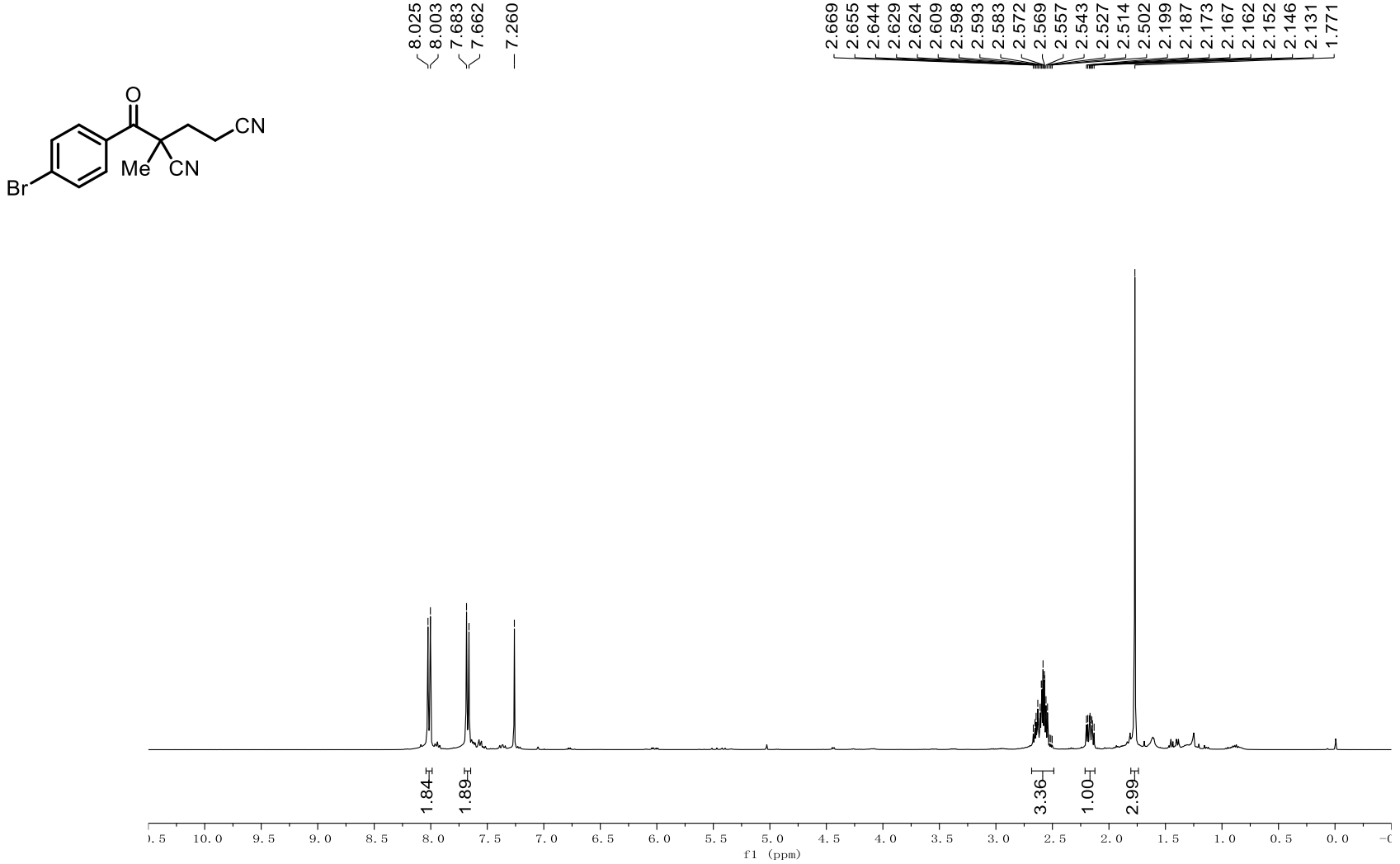
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(4-Chlorobenzoyl)-2-methylpentanedinitrile (56)



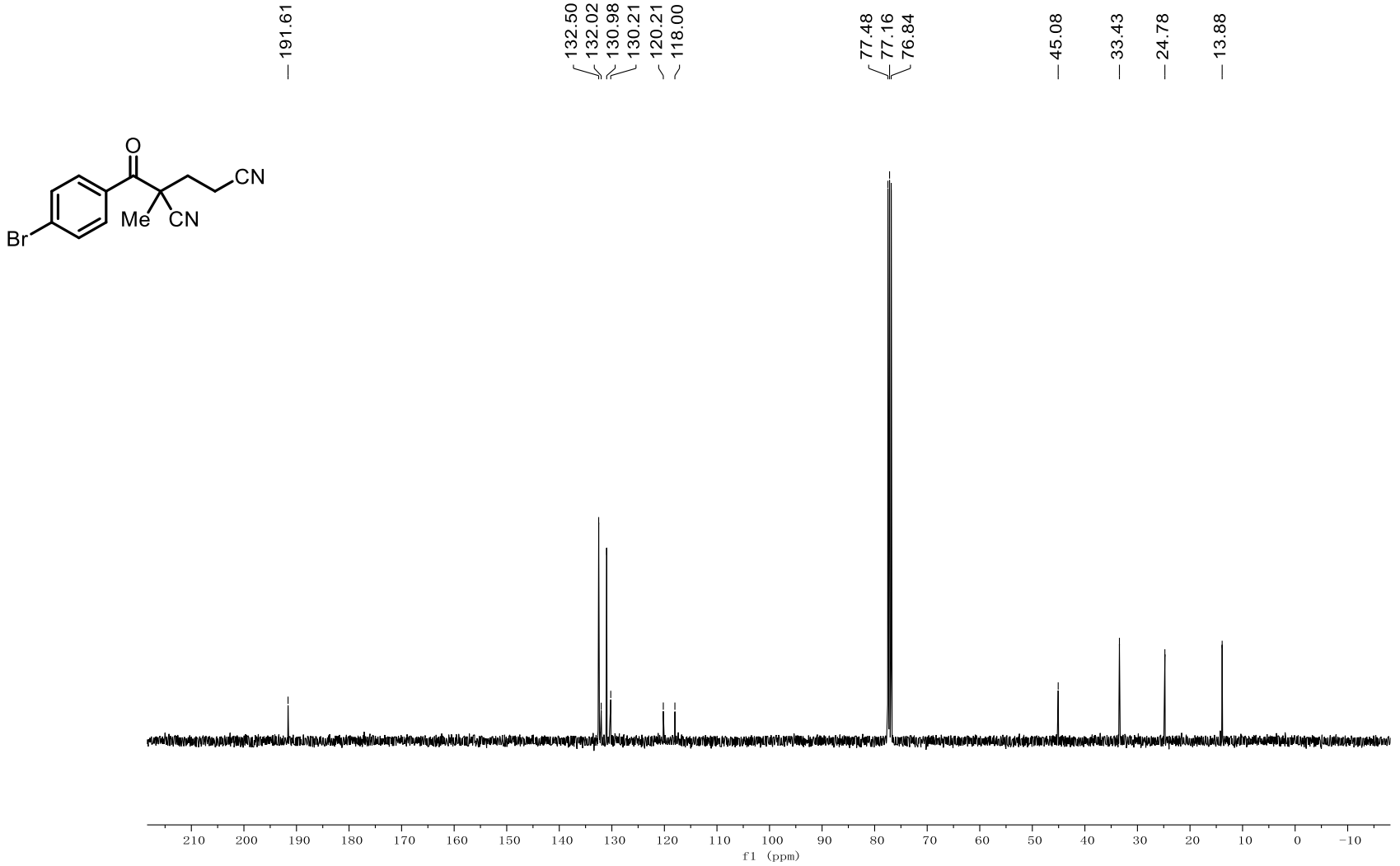
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(4-Chlorobenzoyl)-2-methylpentanedinitrile (56)



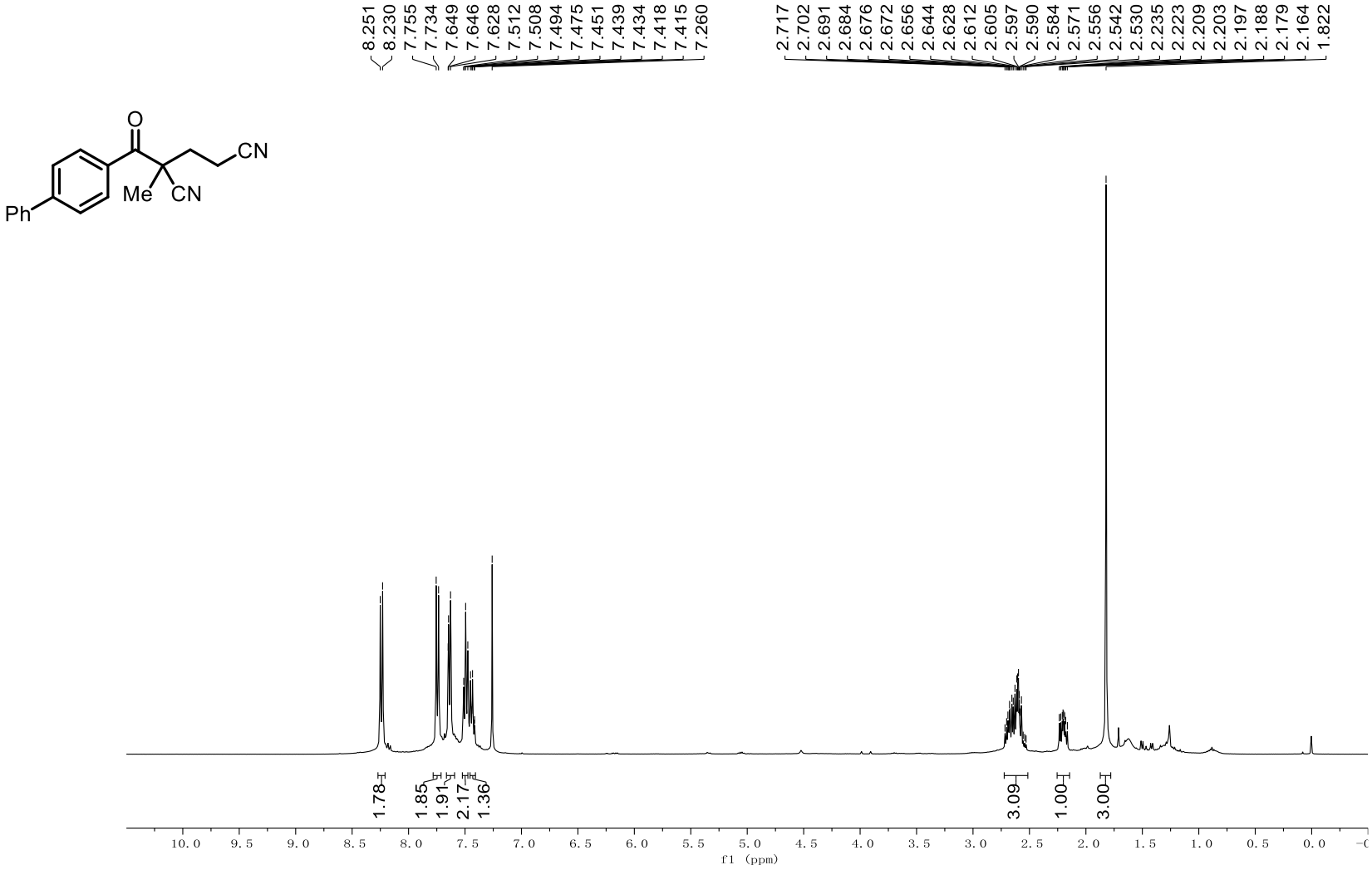
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(4-Bromobenzoyl)-2-methylpentanedinitrile (57)



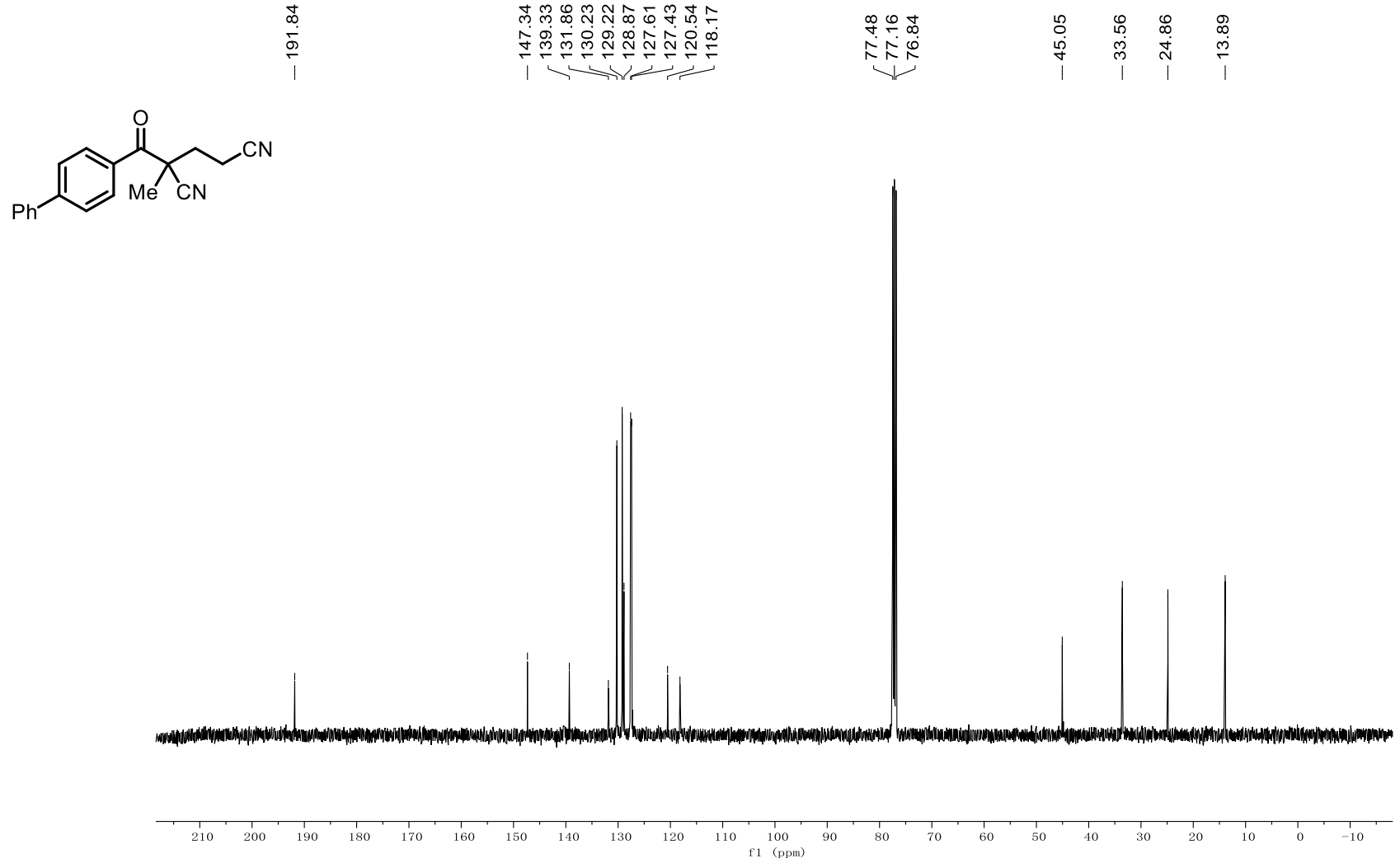
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(4-Bromobenzoyl)-2-methylpentanedinitrile (57)



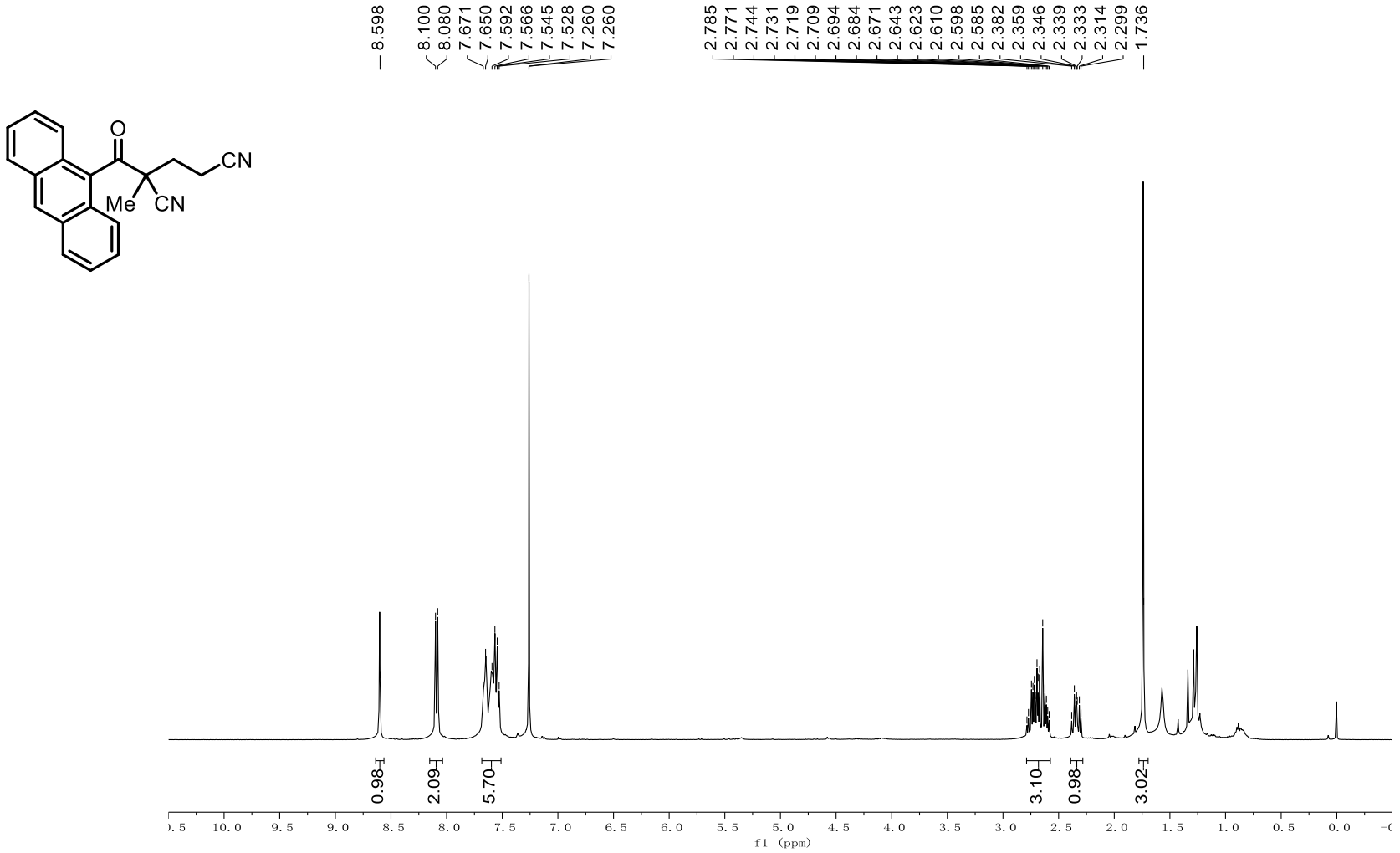
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-([1,1'-Biphenyl]-4-carbonyl)-2-methylpentanedinitrile (58)



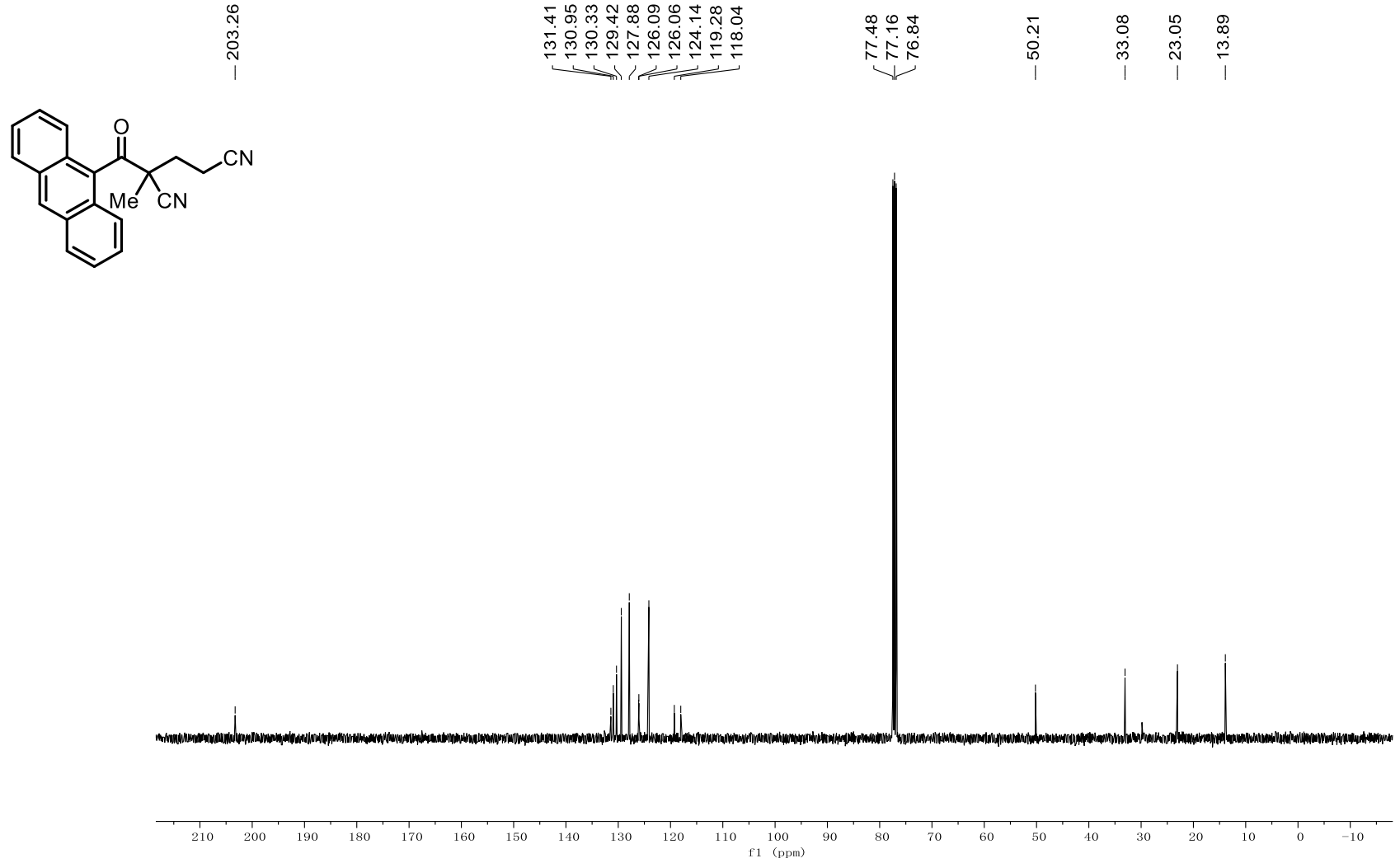
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-([1,1'-Biphenyl]-4-carbonyl)-2-methylpentanedinitrile (58)



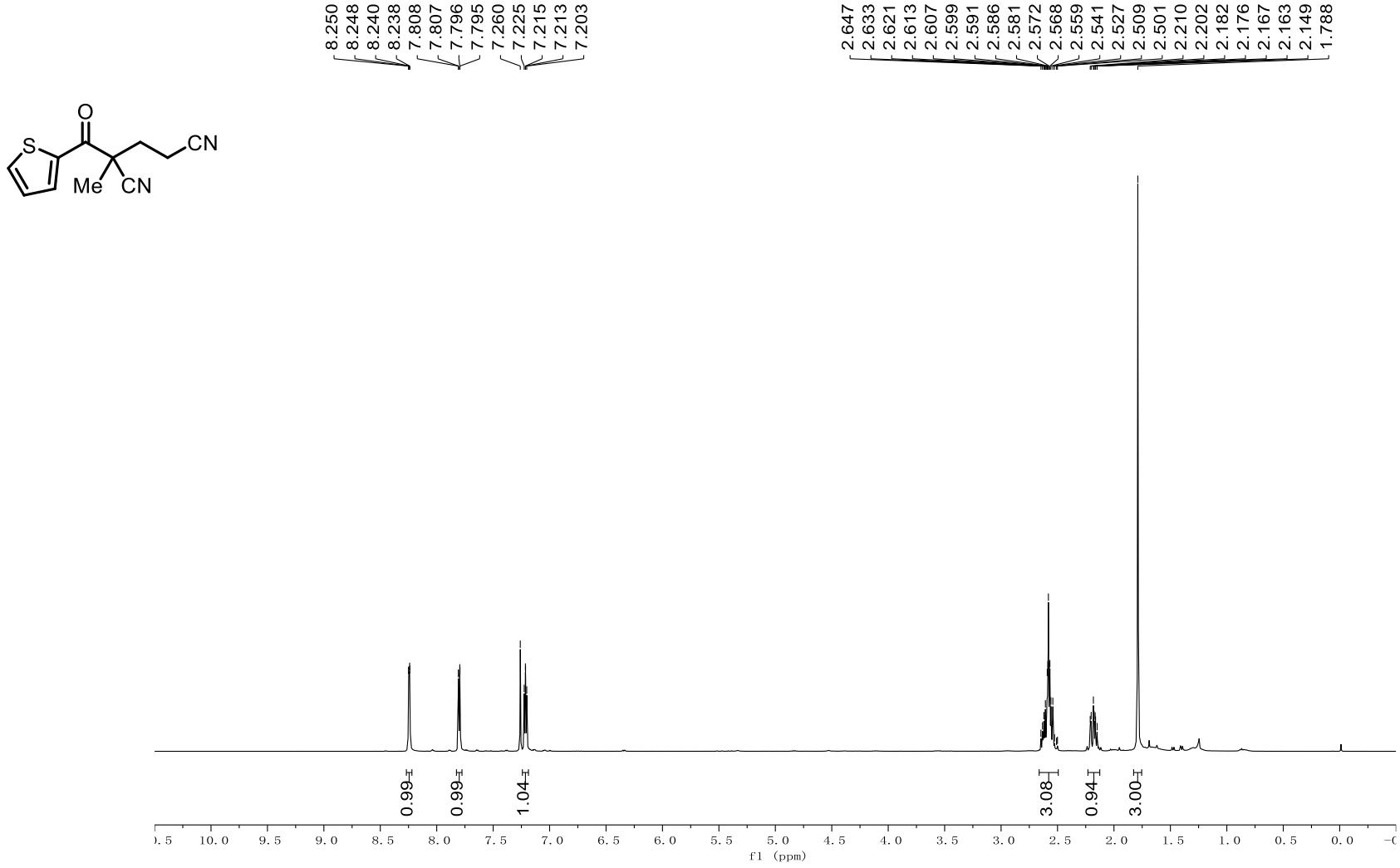
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(Anthracene-9-carbonyl)-2-methylpentanedinitrile (59)



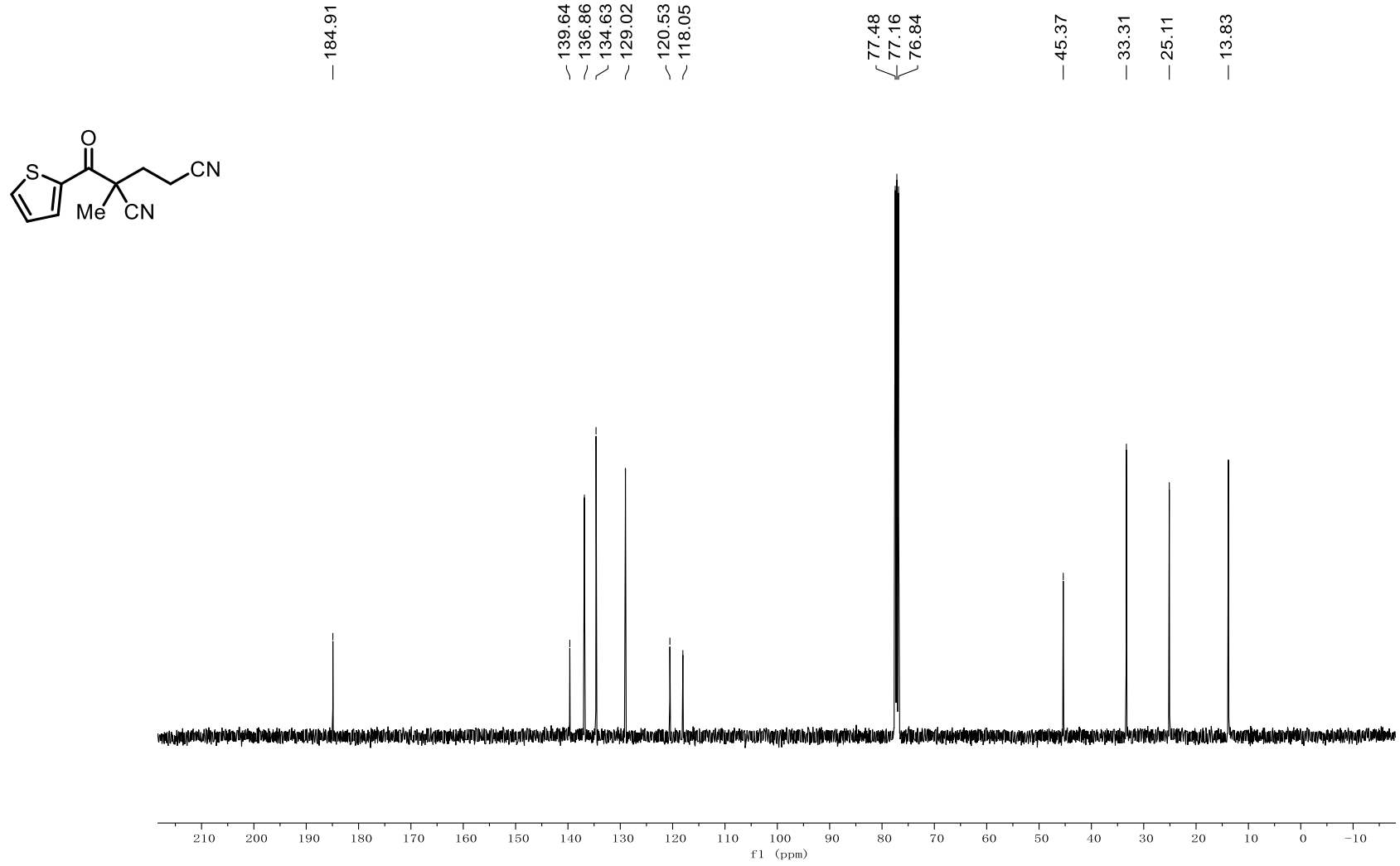
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(Anthracene-9-carbonyl)-2-methylpentanedinitrile (59)



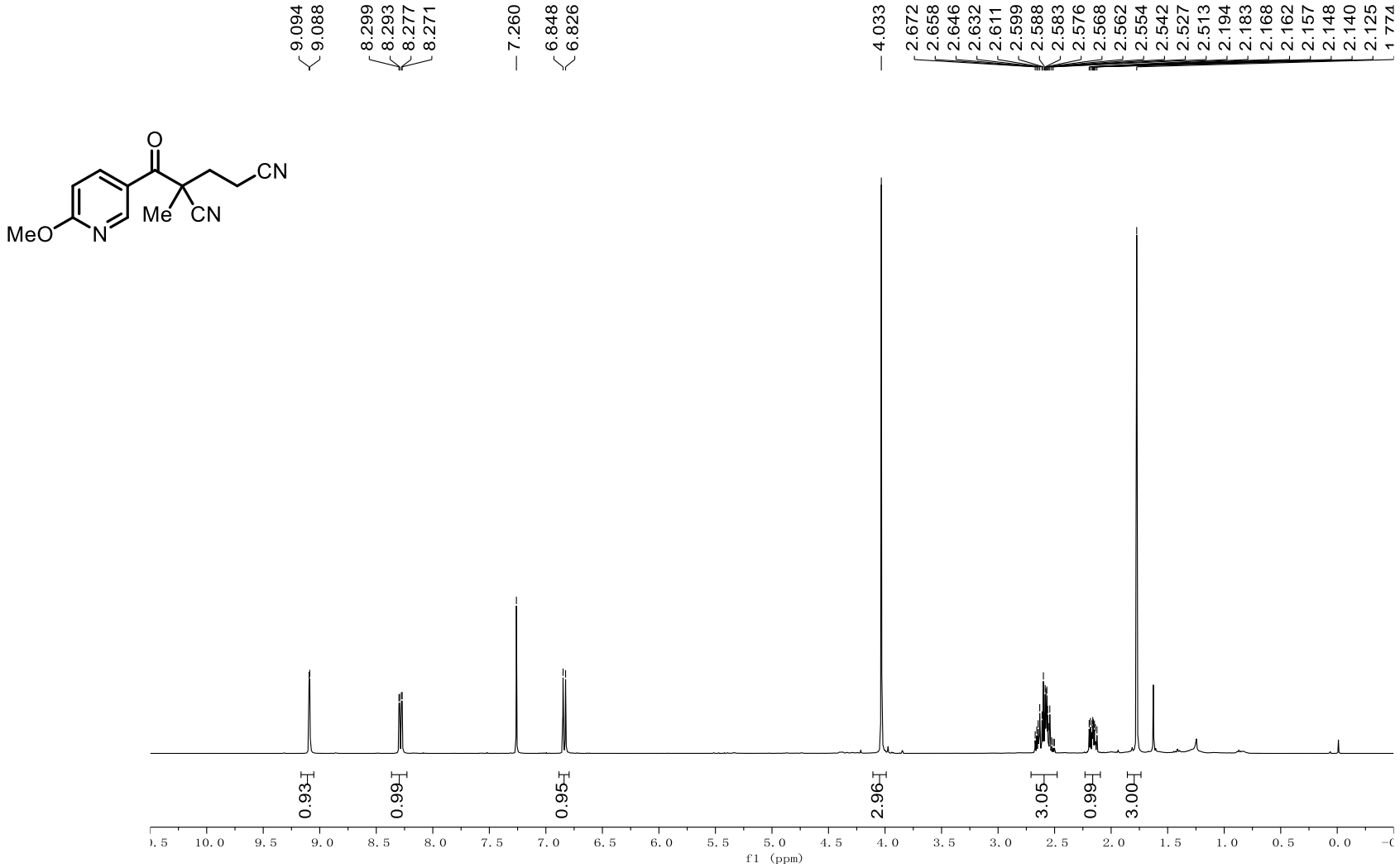
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(thiophene-2-carbonyl)pentanedinitrile (60)



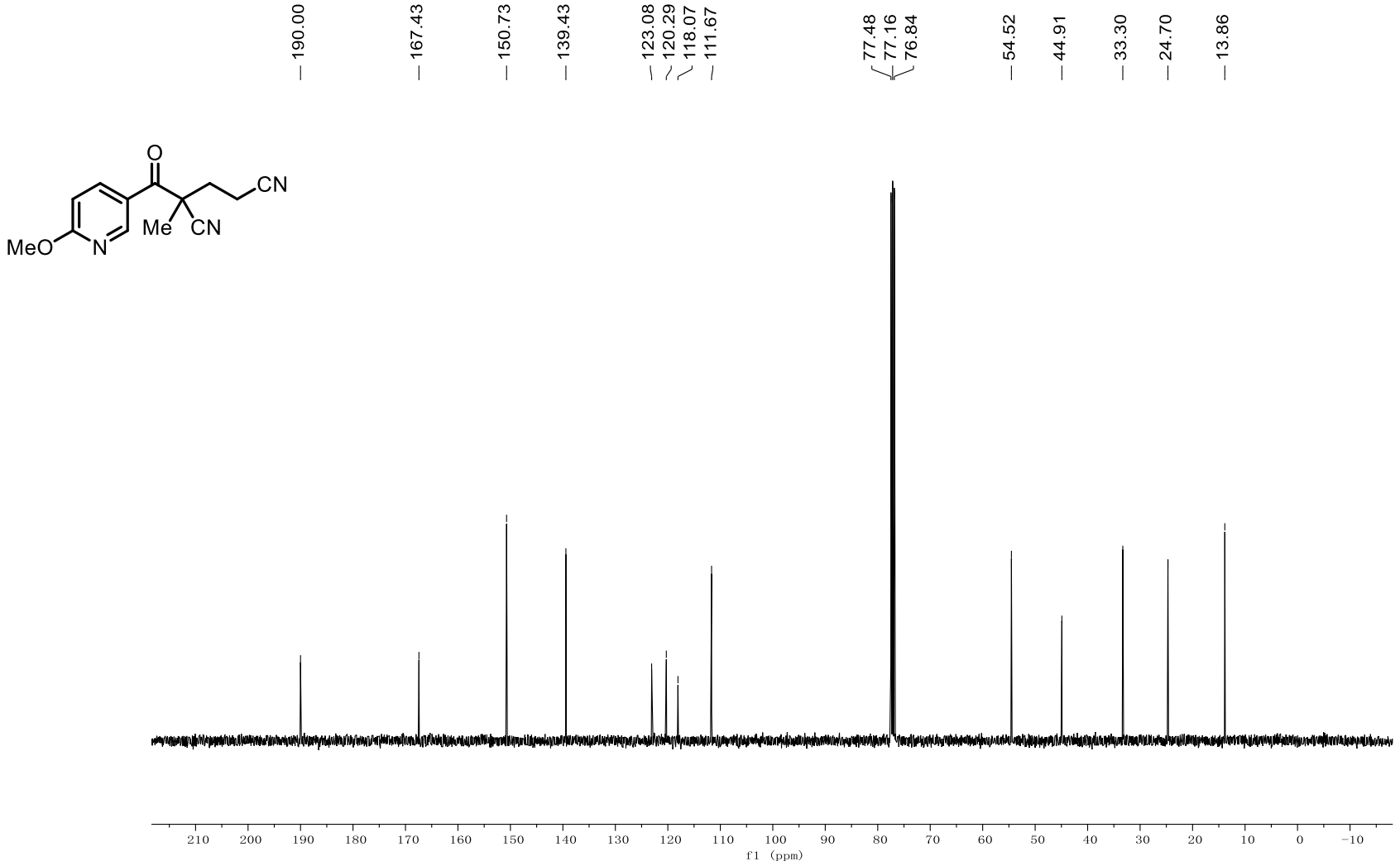
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(thiophene-2-carbonyl)pentanedinitrile (60)



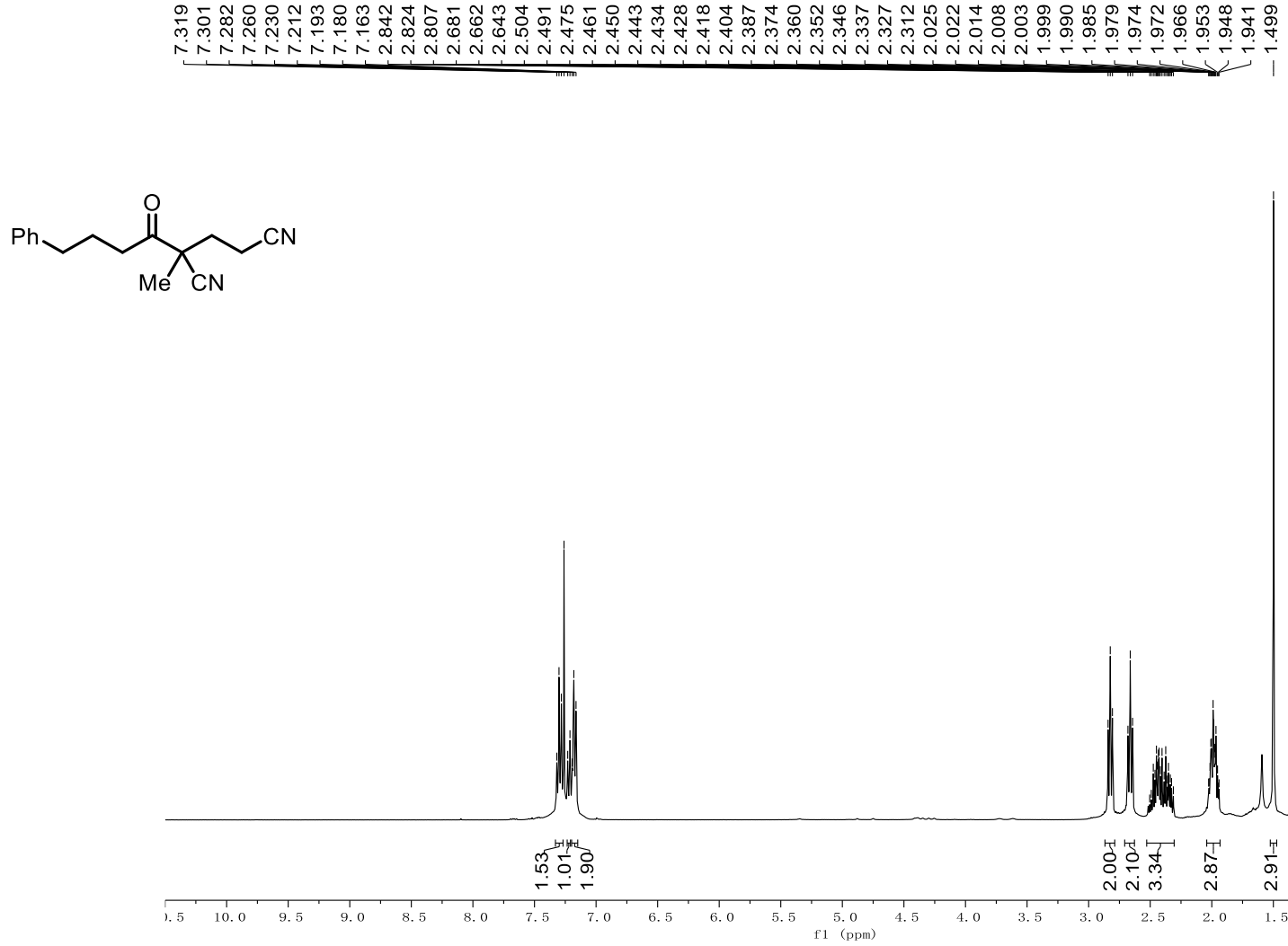
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(6-Methoxynicotinoyl)-2-methylpentanedinitrile (61)



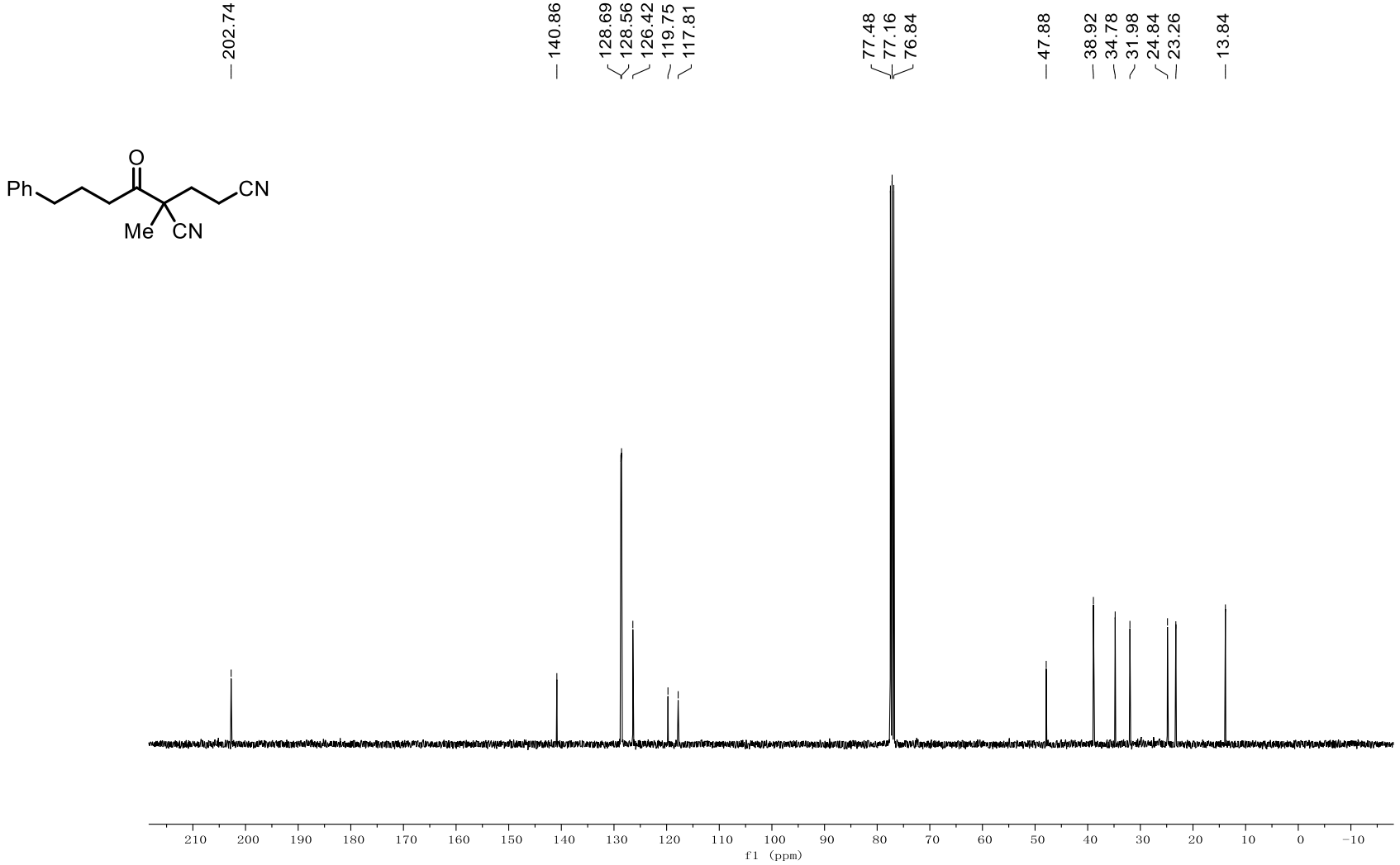
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(6-Methoxynicotinoyl)-2-methylpentanedinitrile (61)



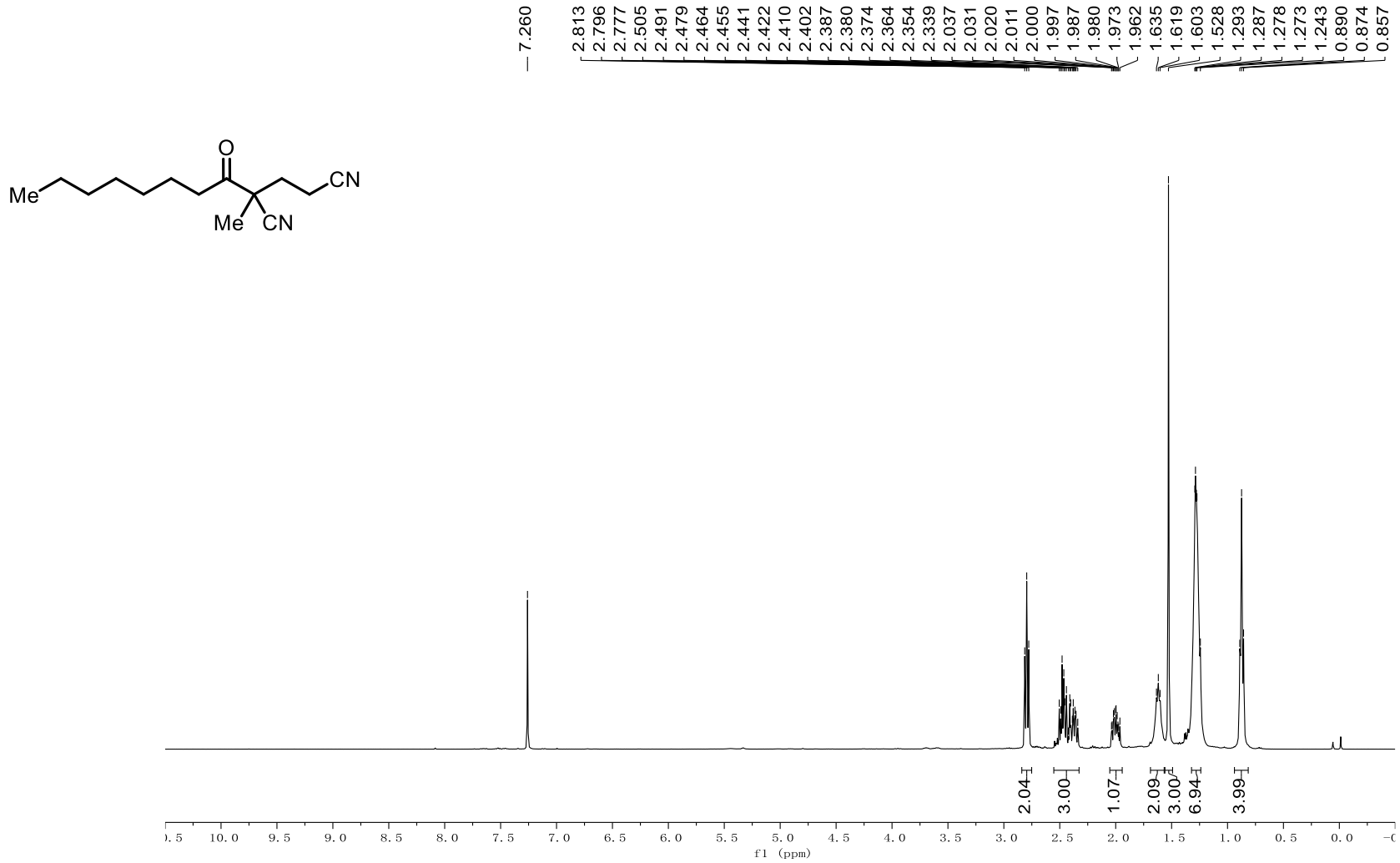
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(4-phenylbutanoyl)pentanedinitrile (62)



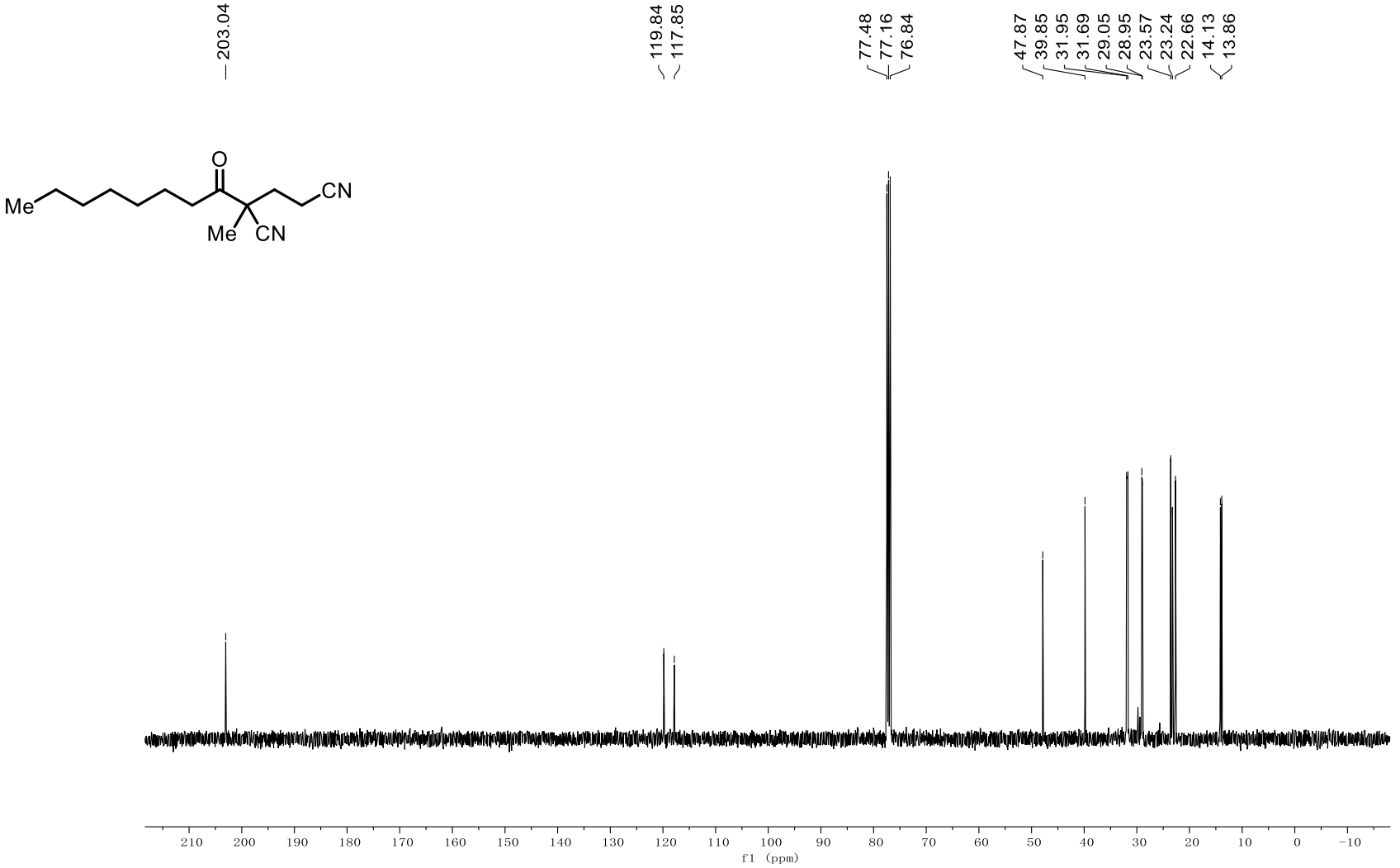
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(4-phenylbutanoyl)pentanedinitrile (6)



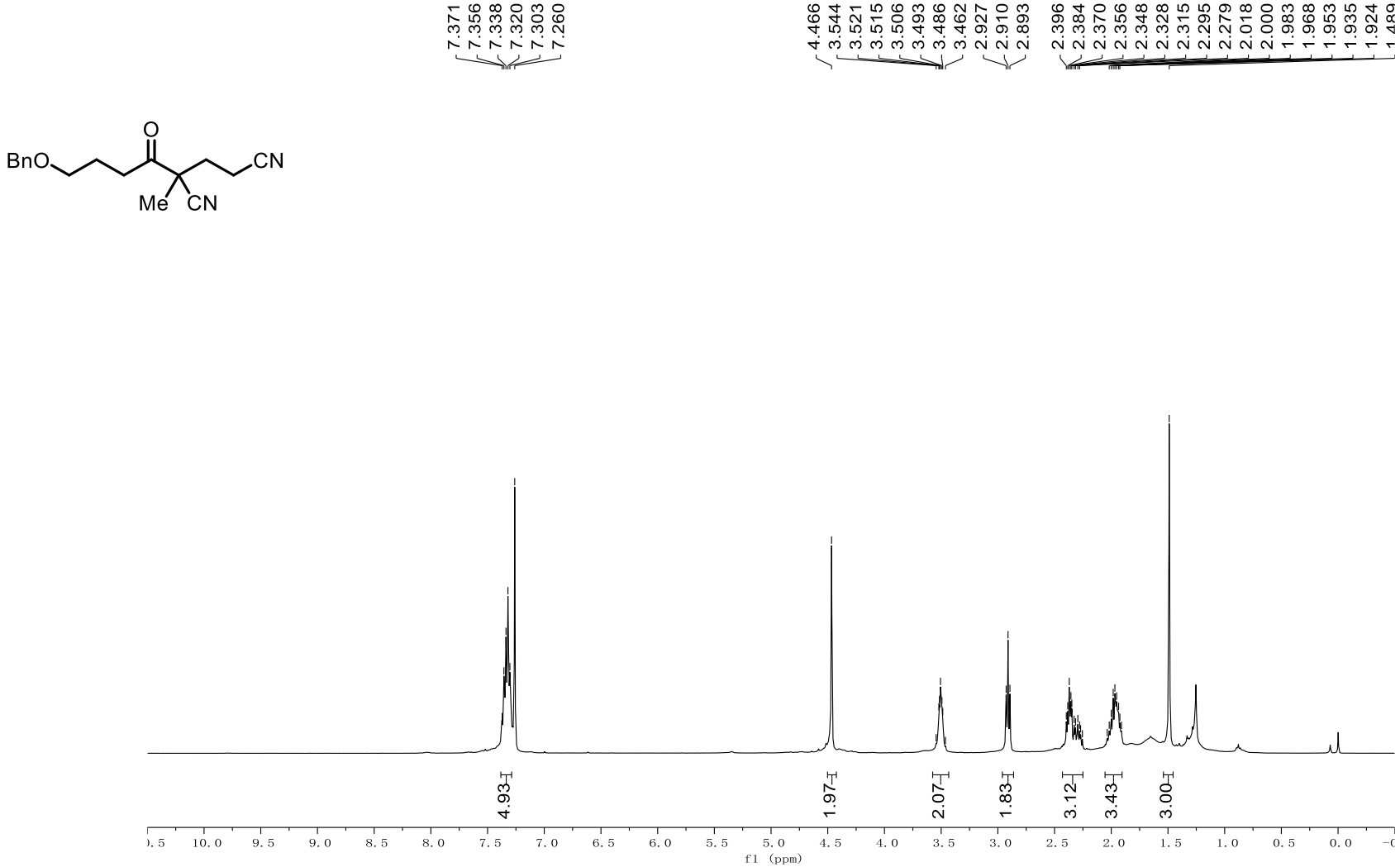
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-2-octanoylpentanedinitrile (63)



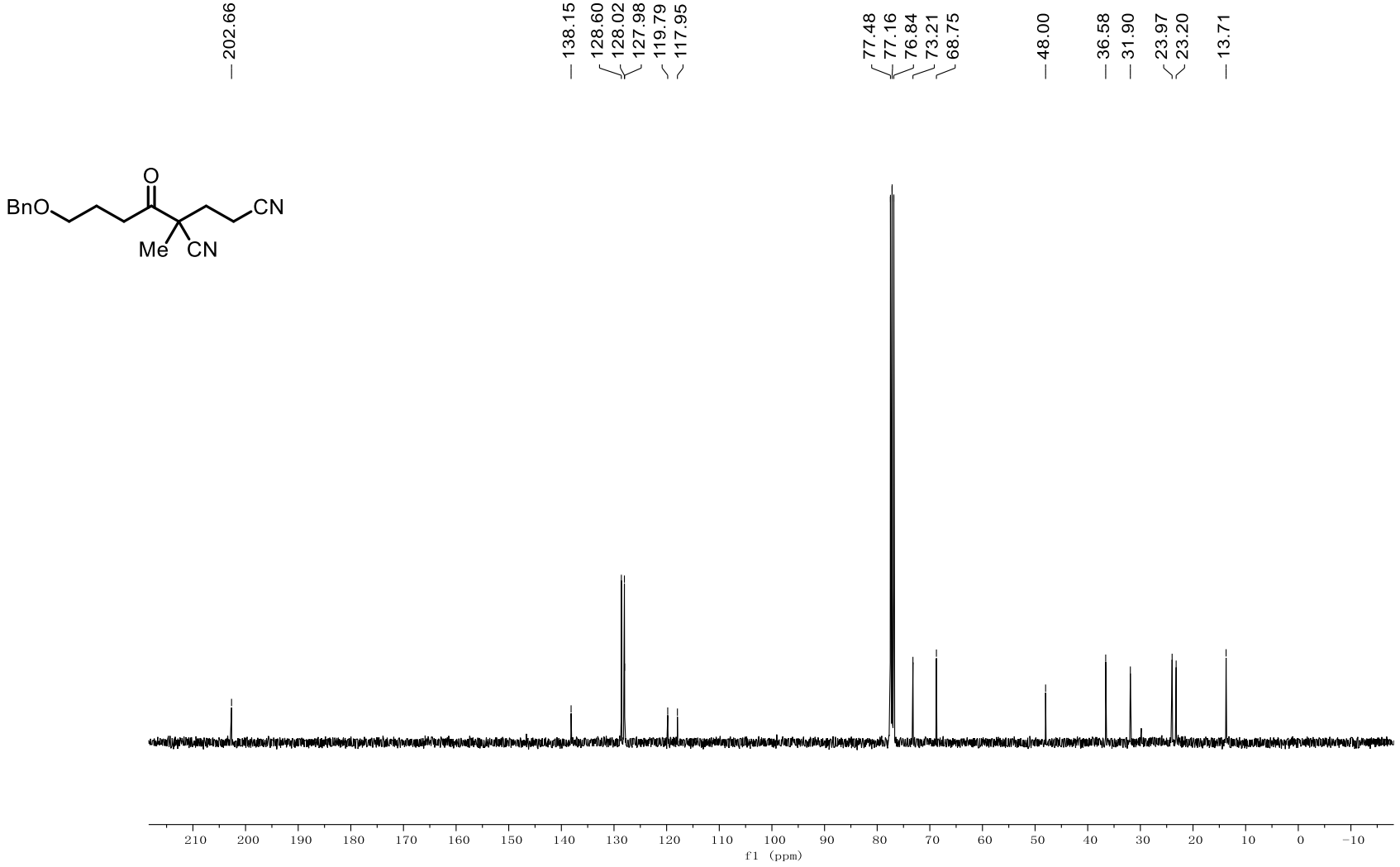
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-2-octanoylpentanedinitrile (63)



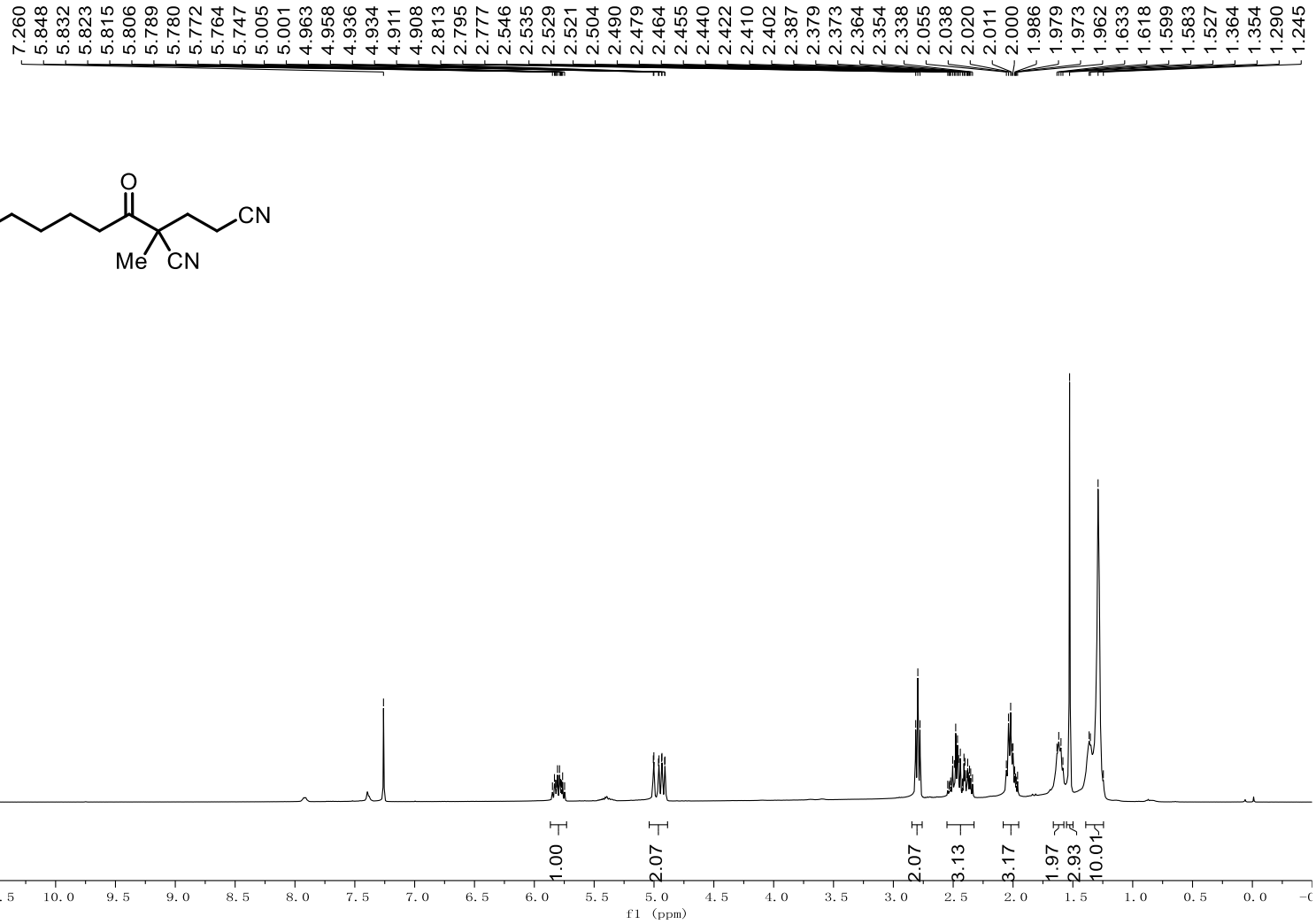
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(4-(Benzyloxy)butanoyl)-2-methylpentanedinitrile (64)



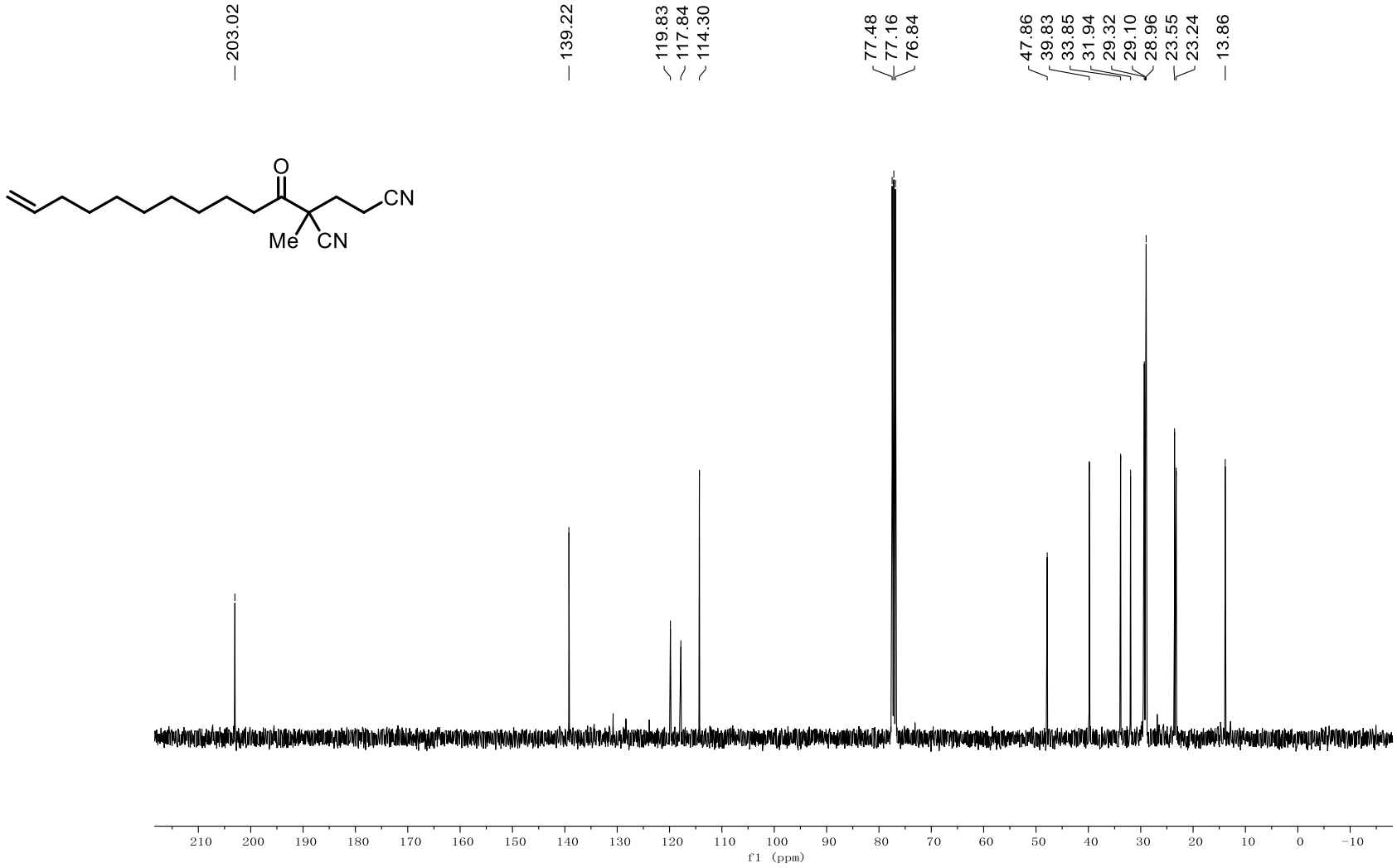
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(4-(Benzyloxy)butanoyl)-2-methylpentanedinitrile (64)



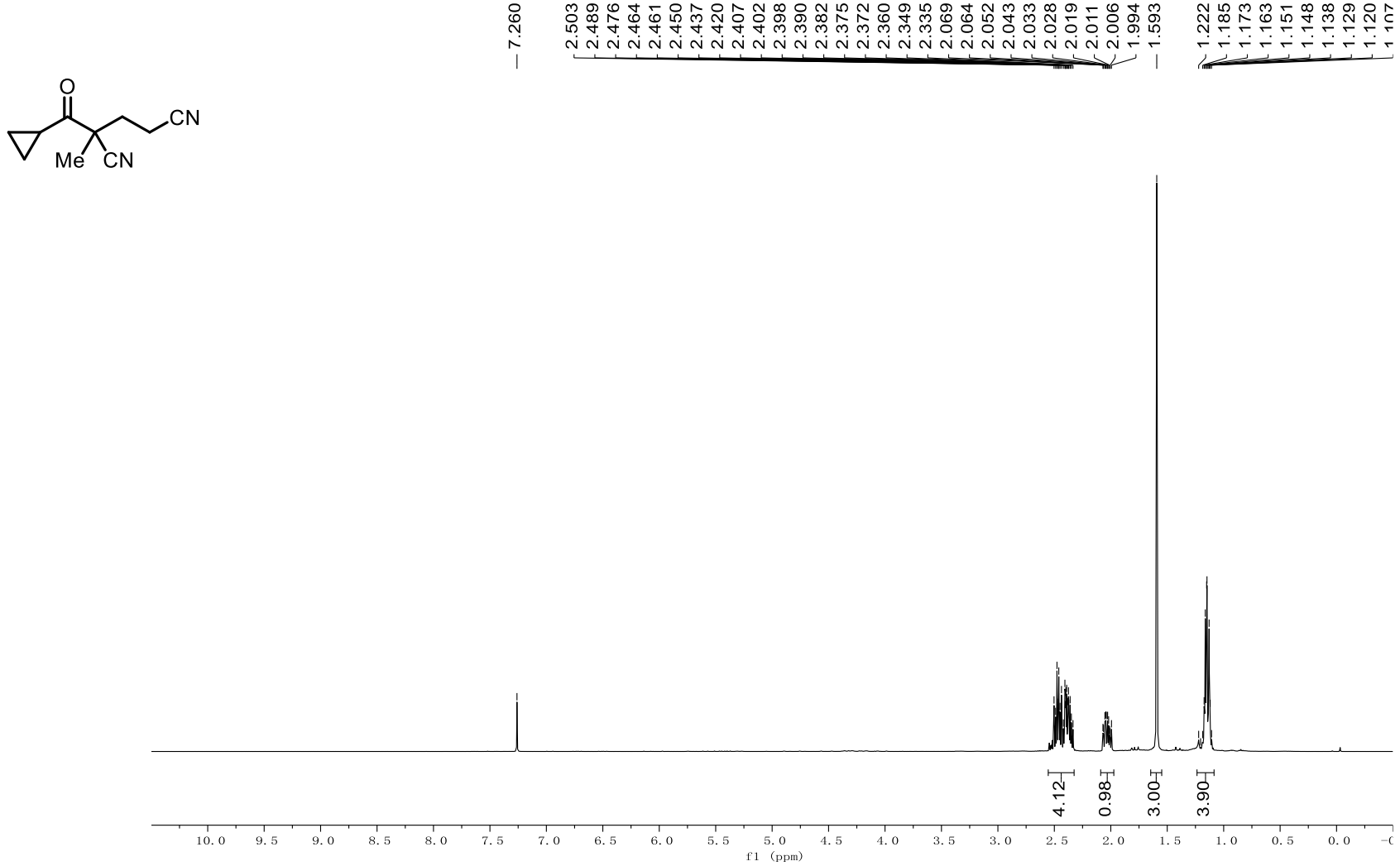
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(undec-10-enoyl)pentanedinitrile (65)



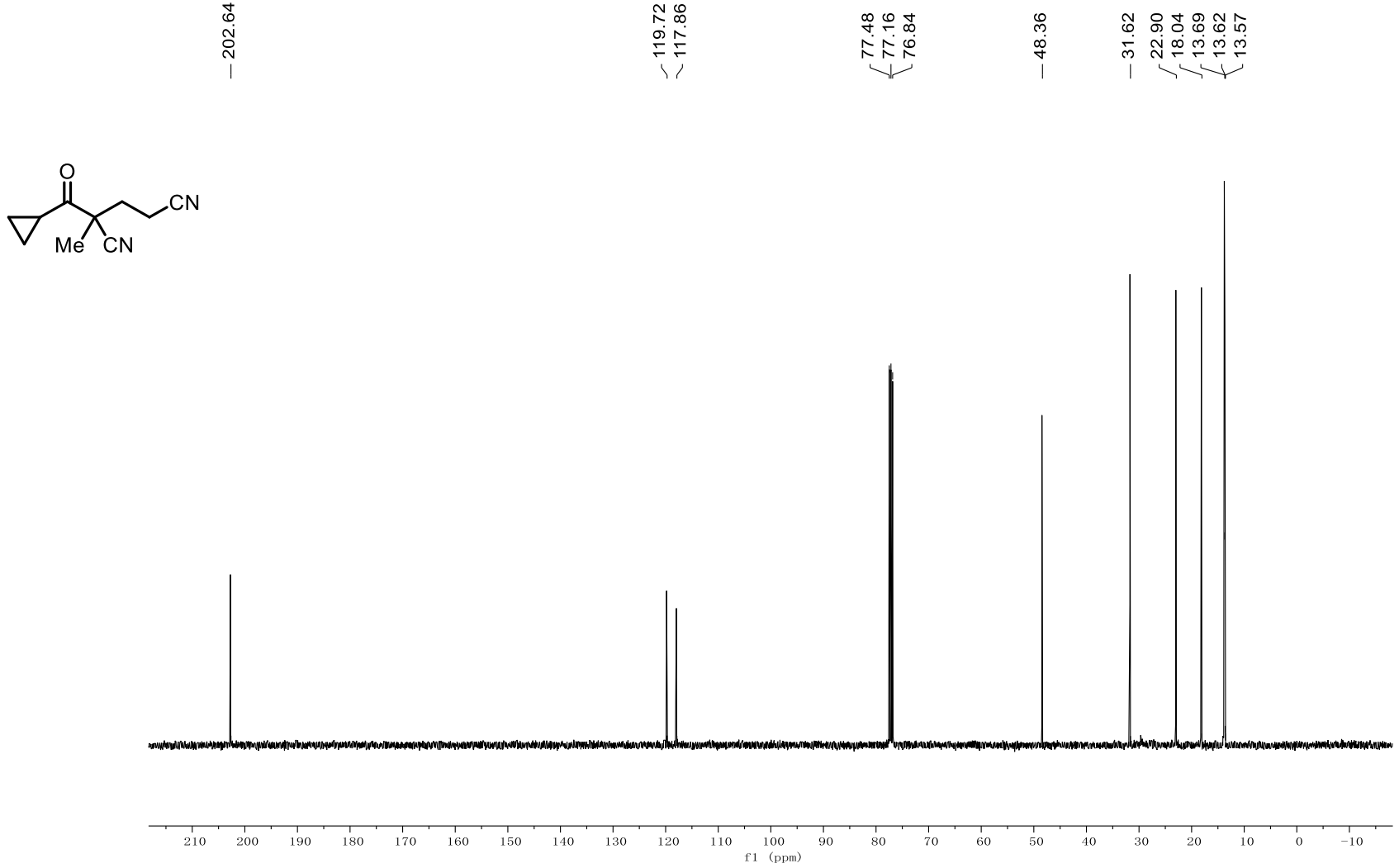
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Methyl-2-(undec-10-enoyl)pentanedinitrile (65)



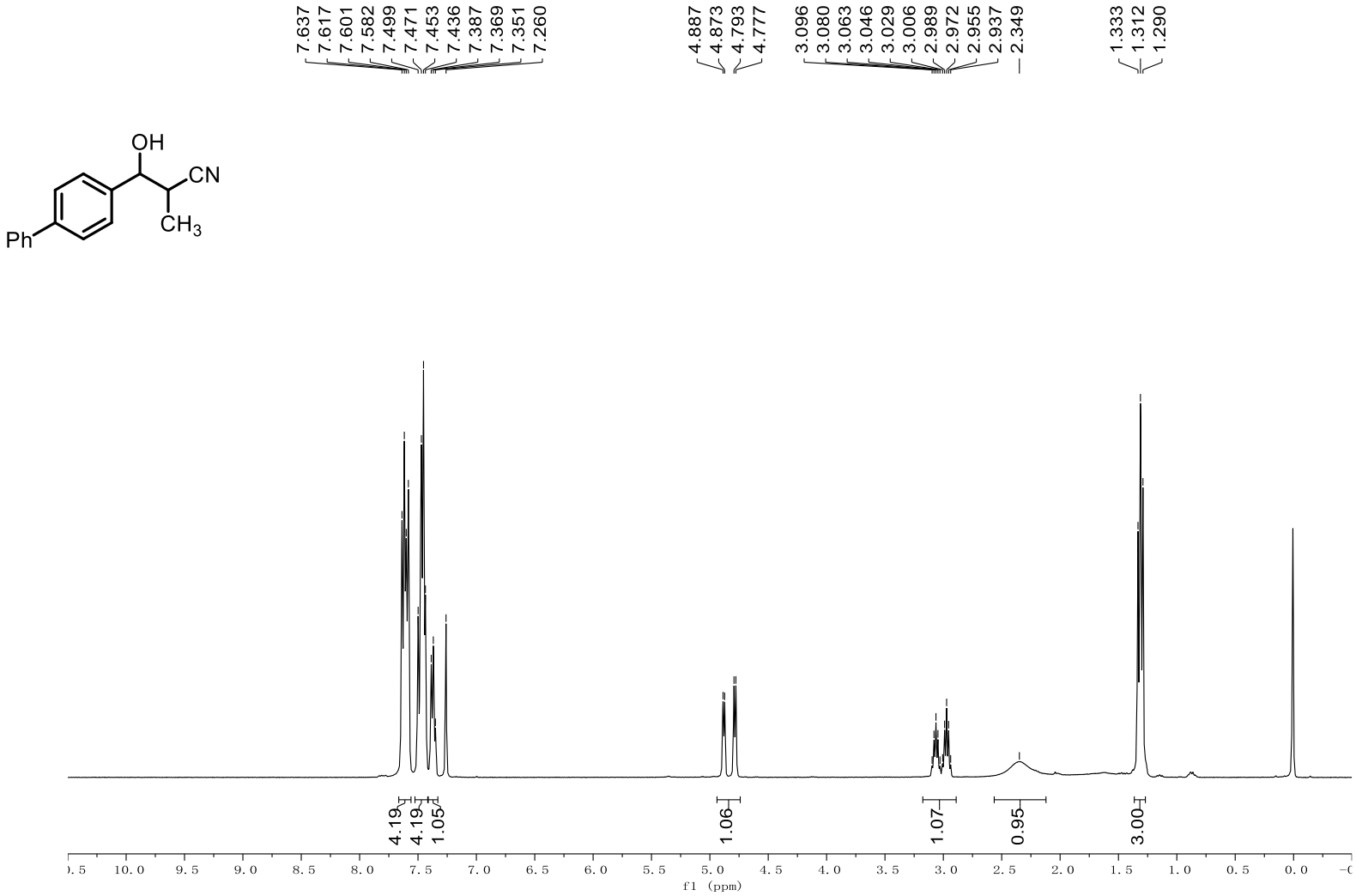
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(Cyclopropanecarbonyl)-2-methylpentanedinitrile (66)



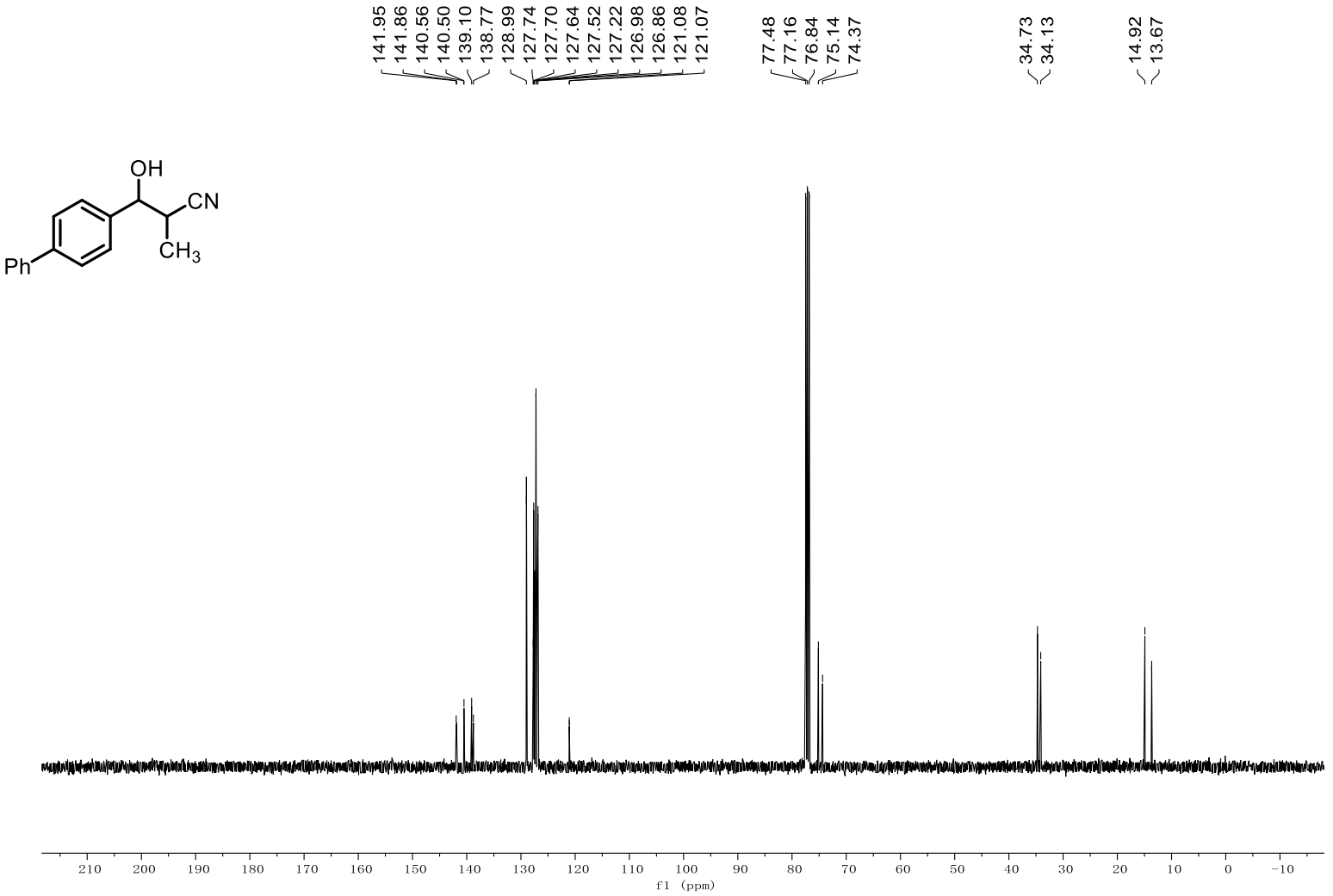
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(Cyclopropanecarbonyl)-2-methylpentanedinitrile (66)



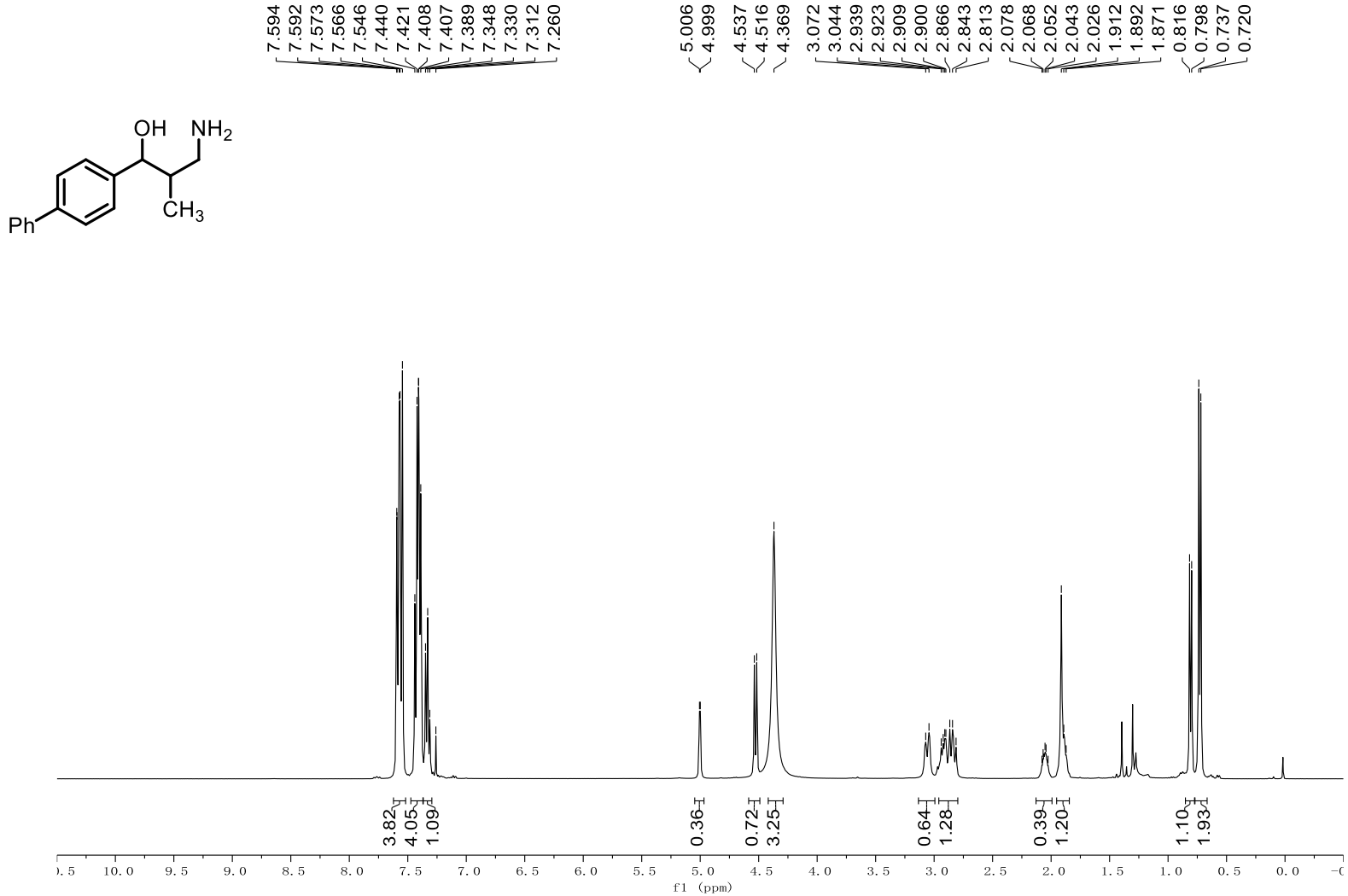
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-([1,1'-Biphenyl]-4-yl)-3-hydroxy-2-methylpropanenitrile (67)



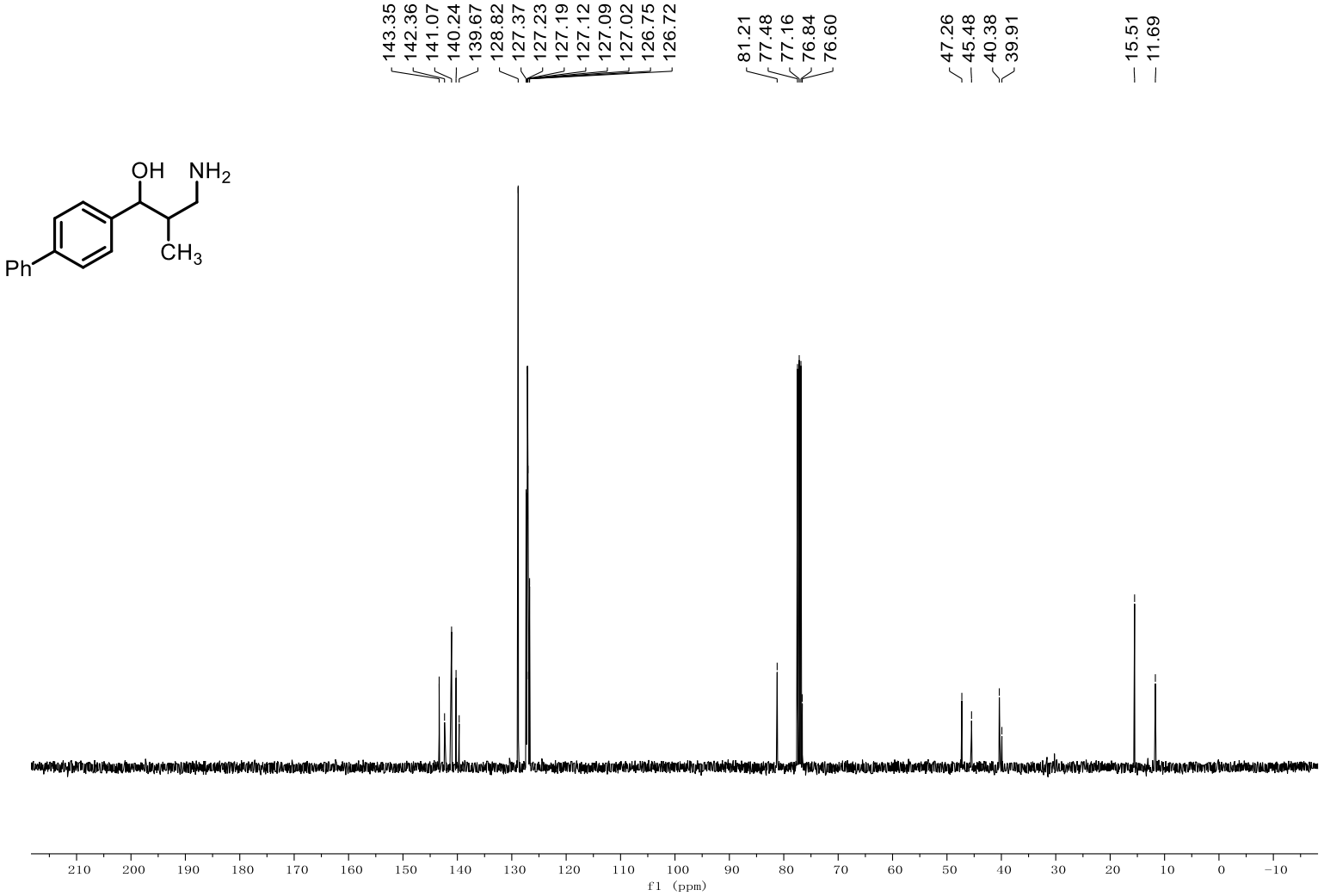
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-([1,1'-Biphenyl]-4-yl)-3-hydroxy-2-methylpropanenitrile (67)



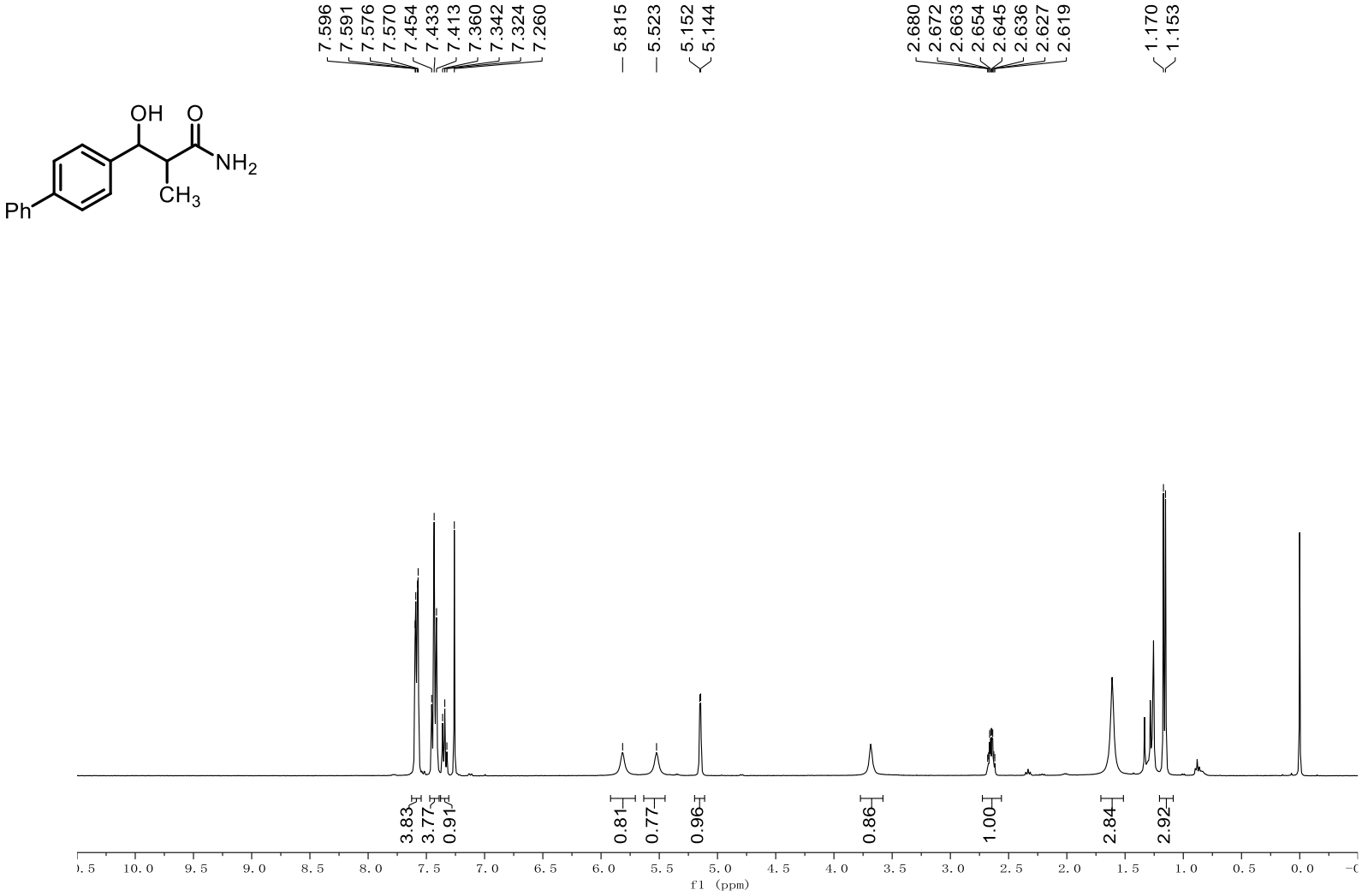
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-([1,1'-Biphenyl]-4-yl)-3-amino-2-methylpropan-1-ol (68)



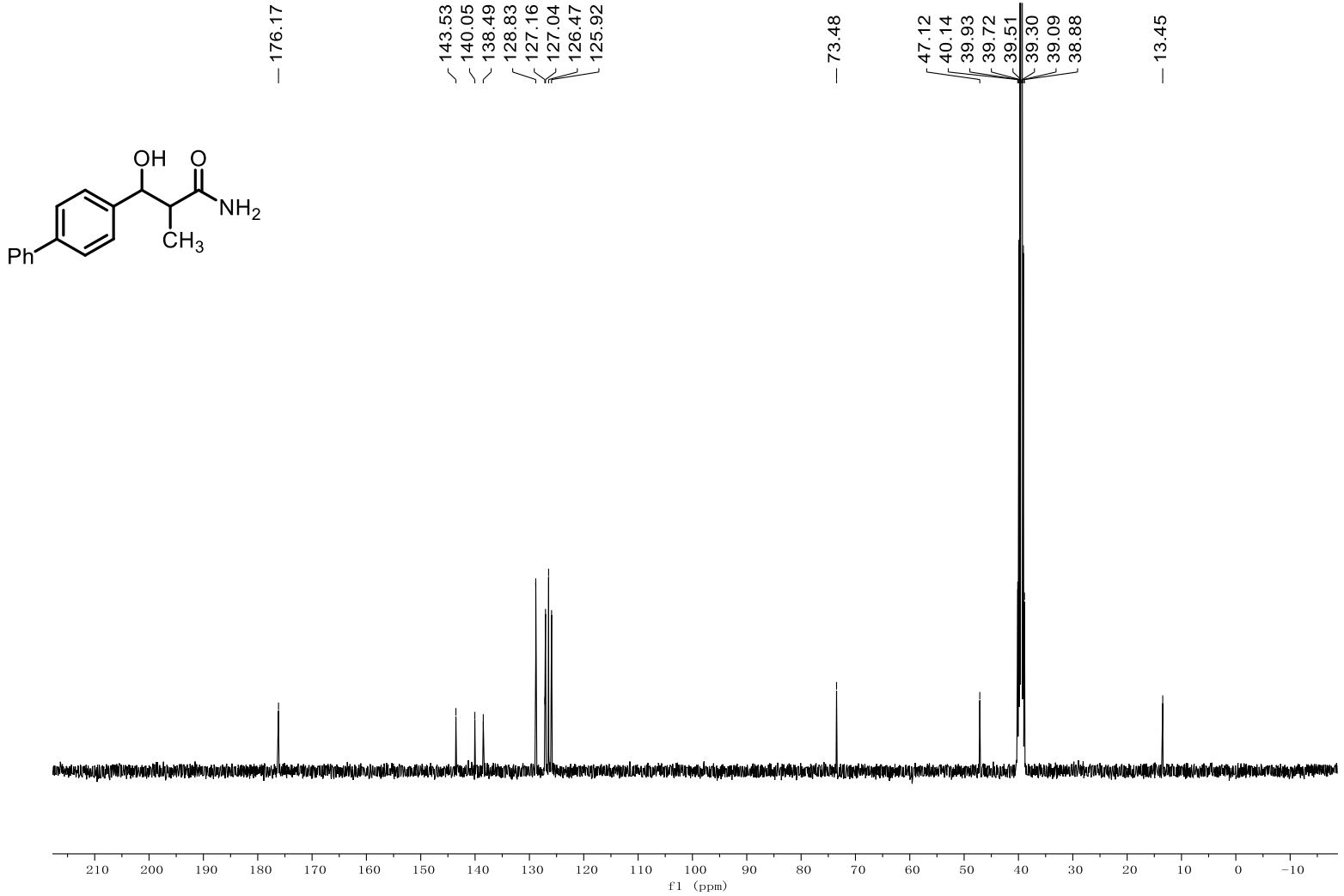
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 1-([1,1'-Biphenyl]-4-yl)-3-amino-2-methylpropan-1-ol (68)



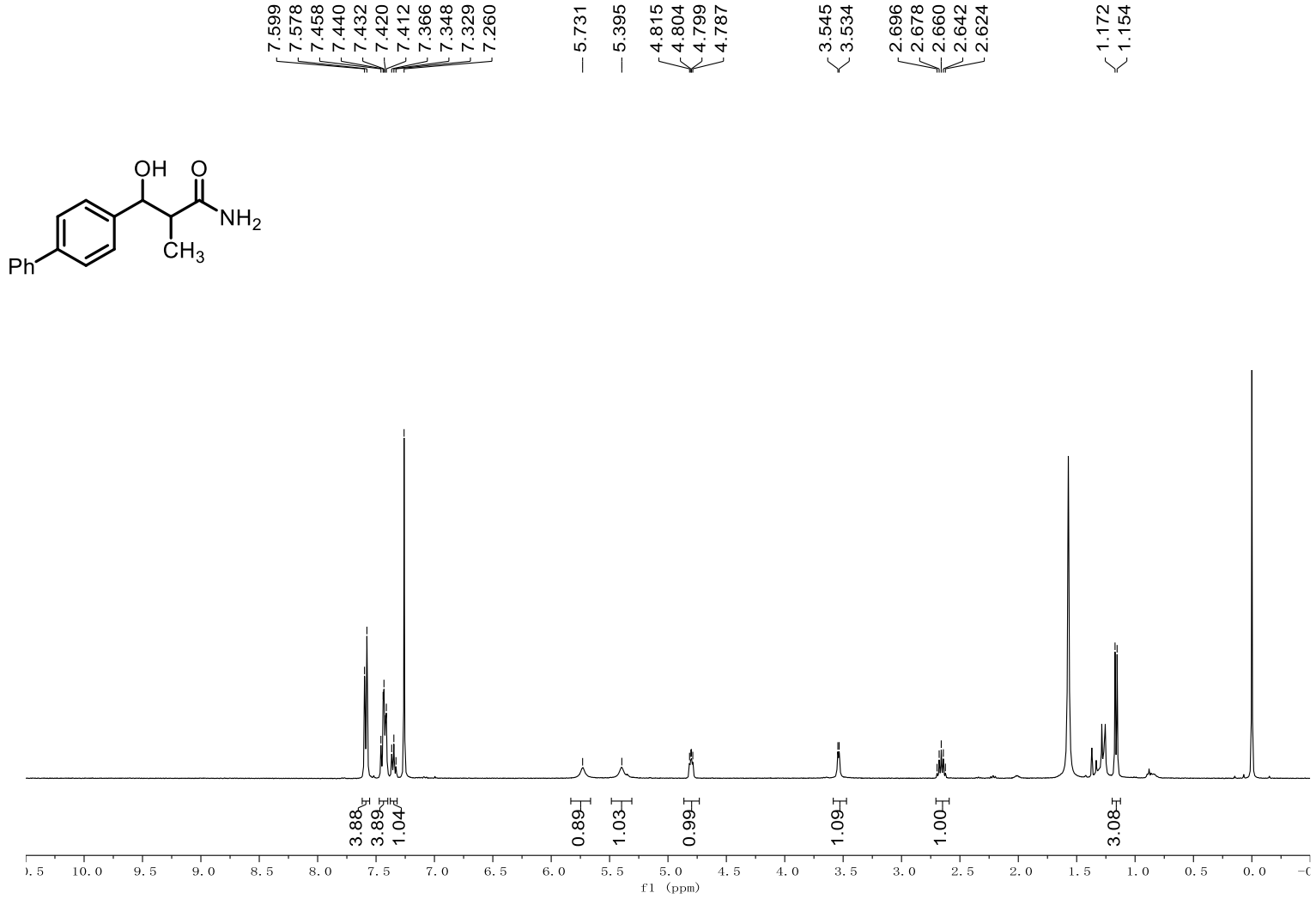
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-([1,1'-Biphenyl]-4-yl)-3-hydroxy-2-methylpropanamide (69) *Major isomer*



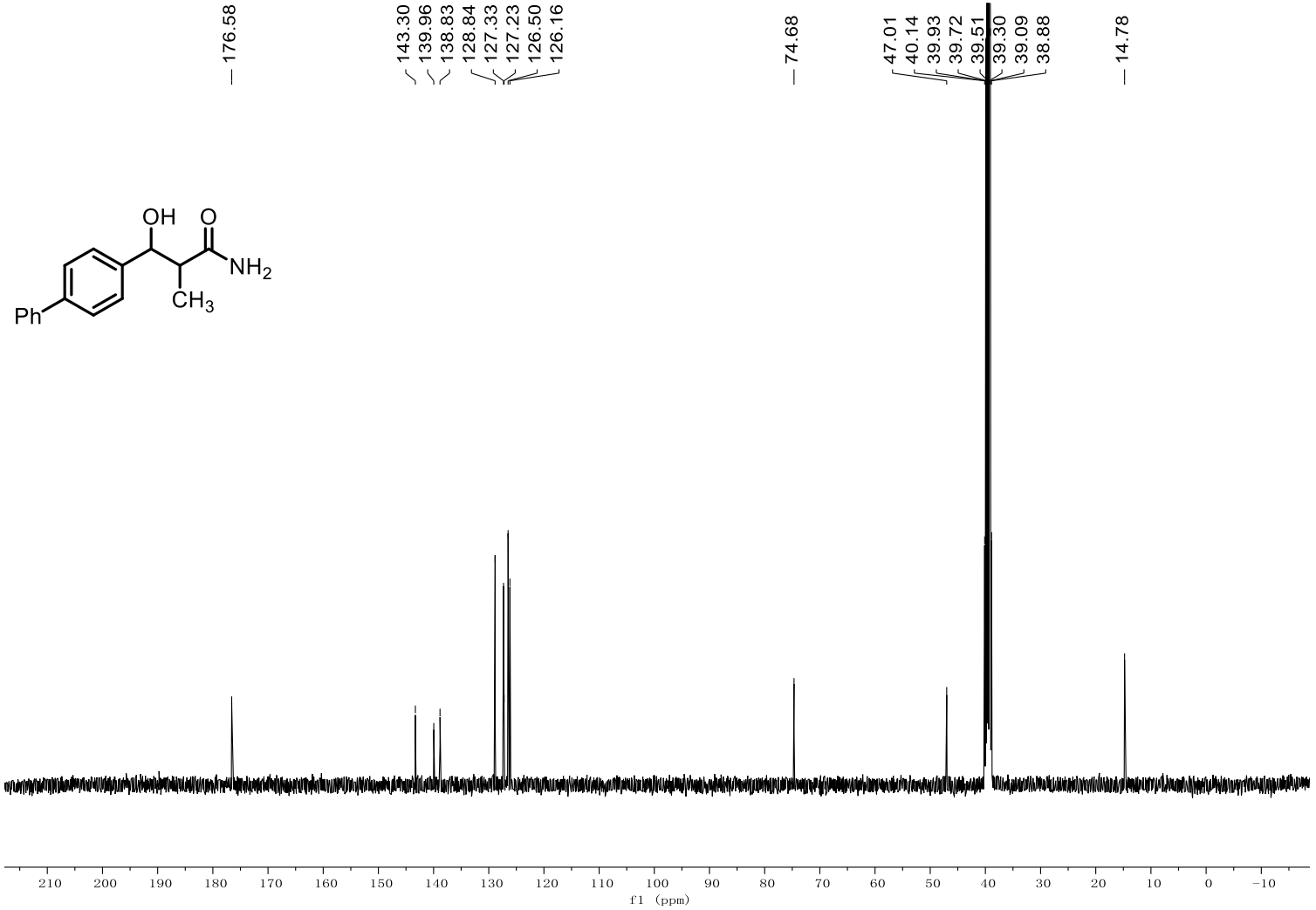
^{13}C NMR (100 MHz, DMSO-*d*$_6$) spectrum of 3-([1,1'-biphenyl]-4-yl)-3-hydroxy-2-methylpropanamide (69) *Major isomer*



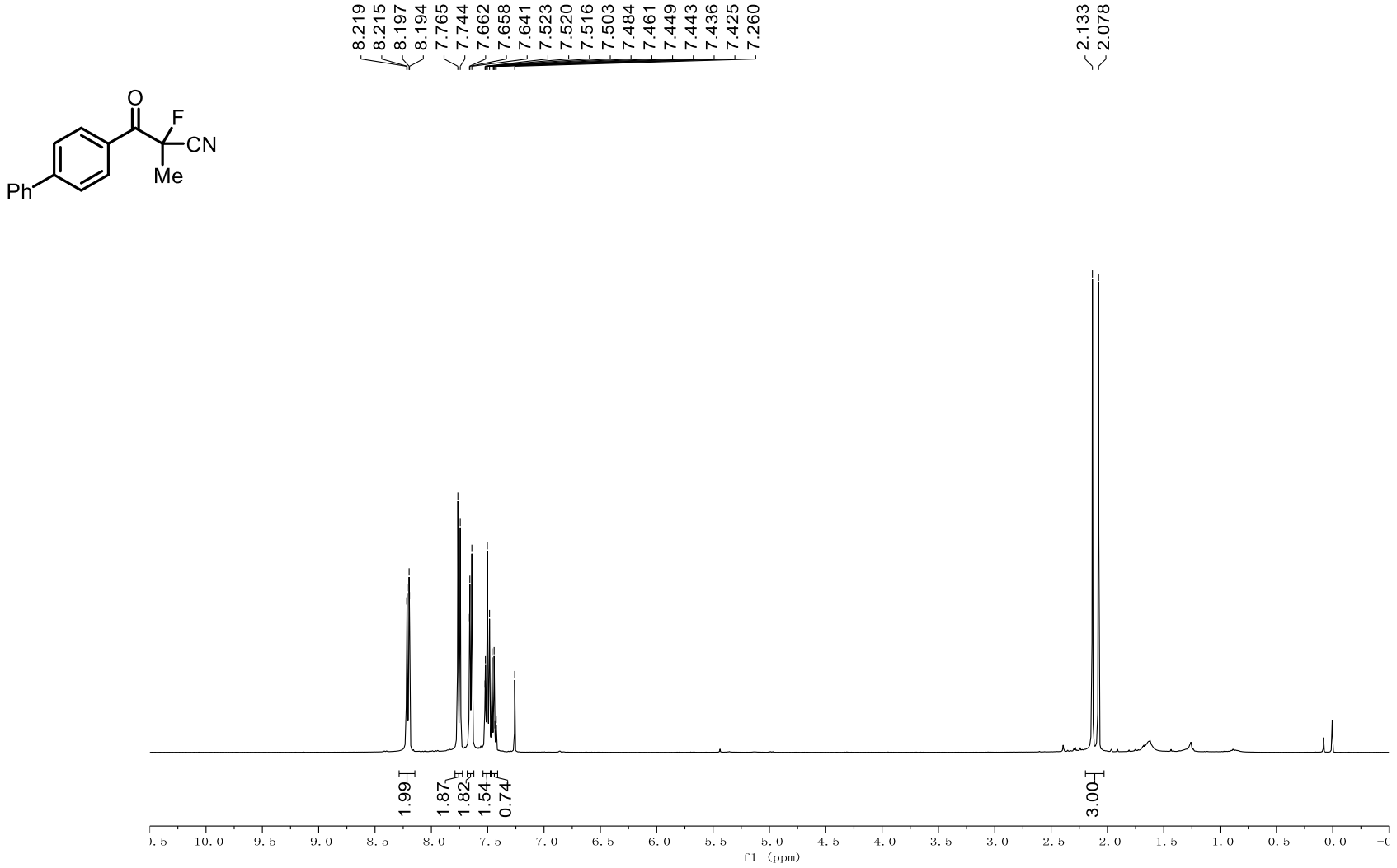
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-([1,1'-biphenyl]-4-yl)-3-hydroxy-2-methylpropanamide (69) *Minor isomer*



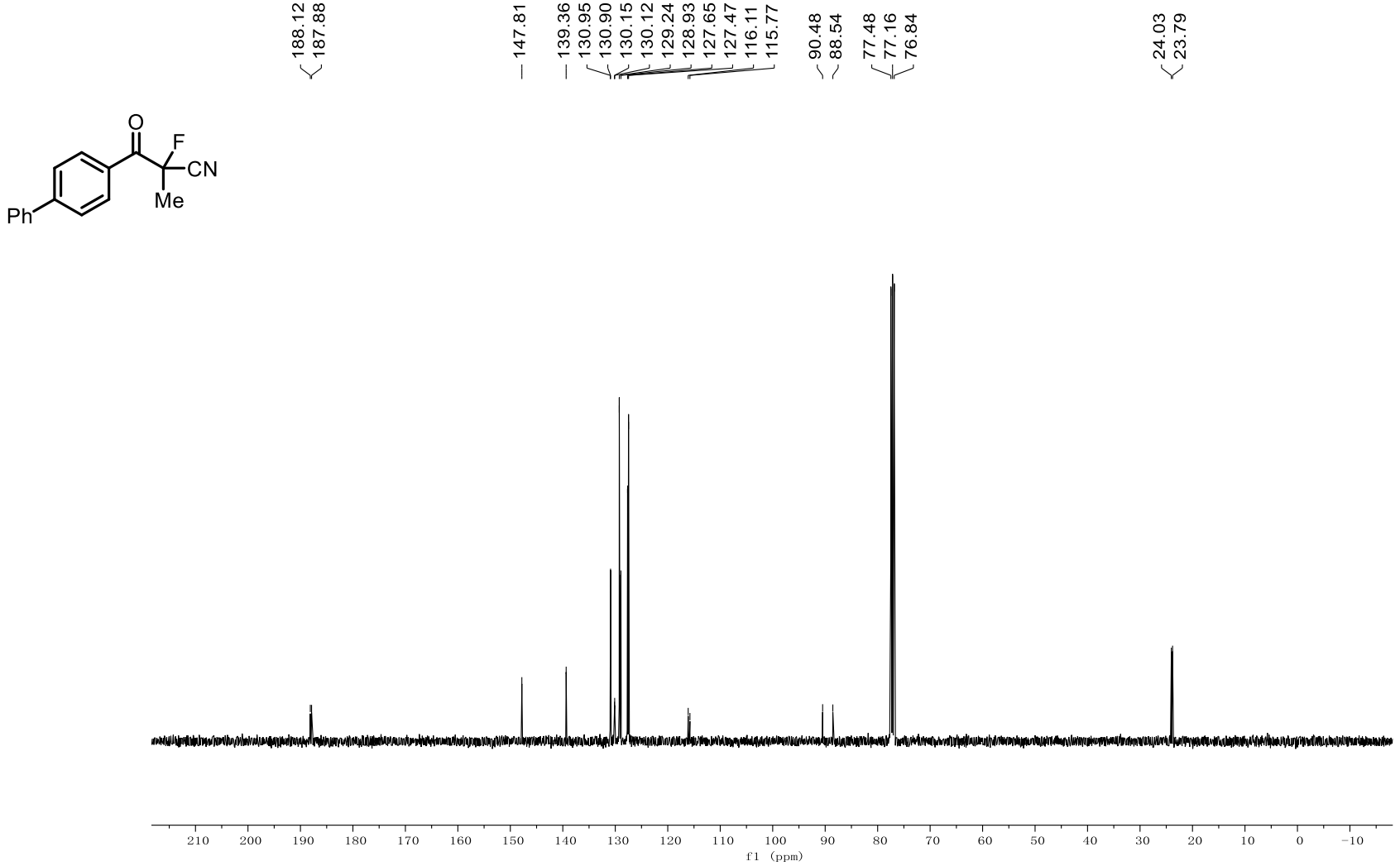
^{13}C NMR (100 MHz, DMSO-*d*$_6$) spectrum of 3-([1,1'-biphenyl]-4-yl)-3-hydroxy-2-methylpropanamide (69) *Minor isomer*



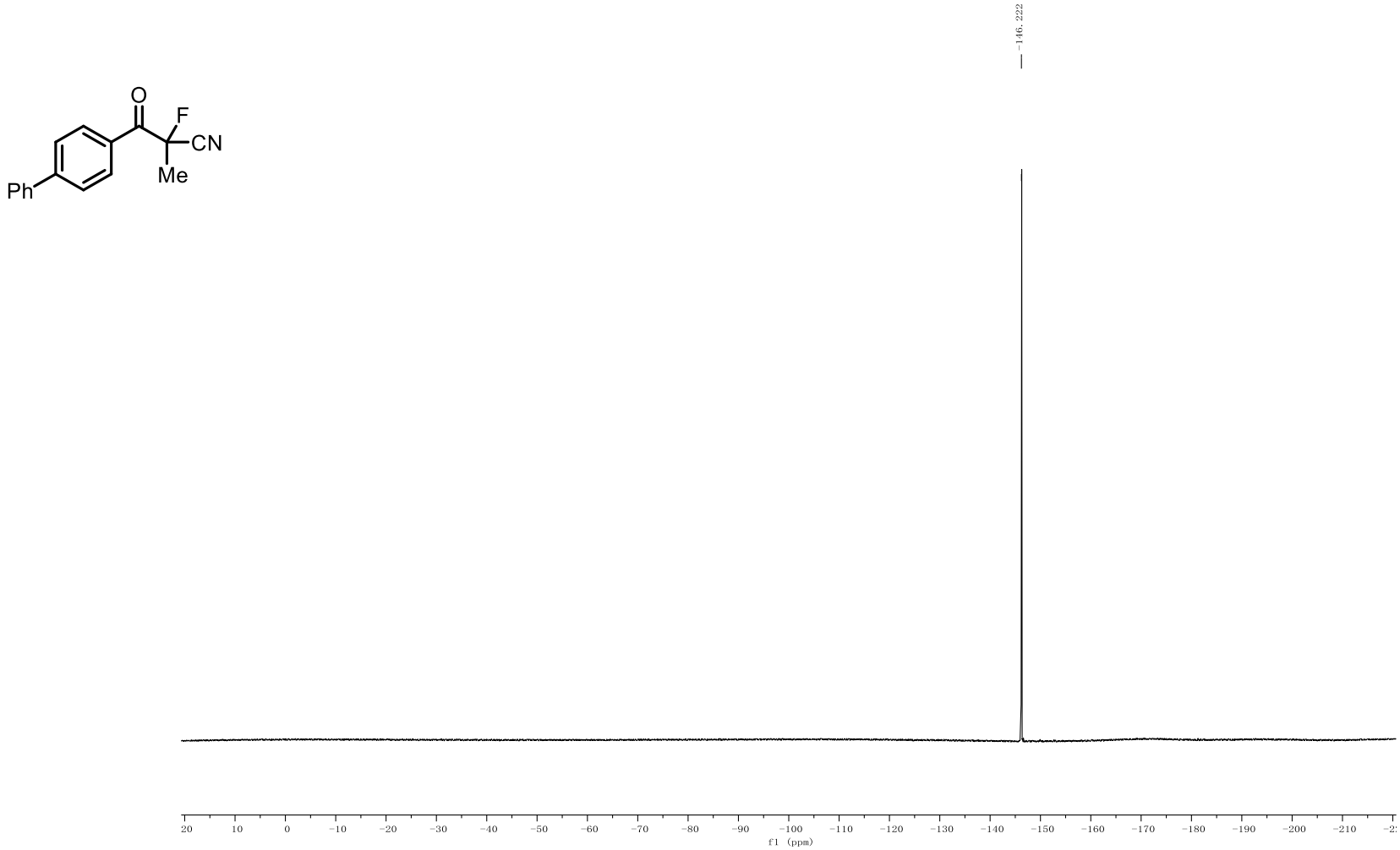
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-([1,1'-Biphenyl]-4-yl)-2-fluoro-2-methyl-3-oxopropanenitrile (70)



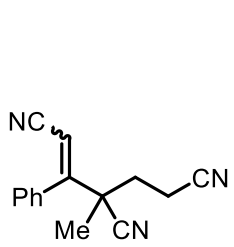
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-([1,1'-Biphenyl]-4-yl)-2-fluoro-2-methyl-3-oxopropanenitrile (70)

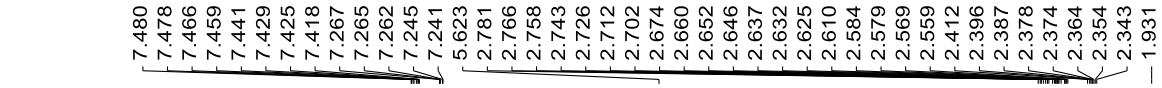


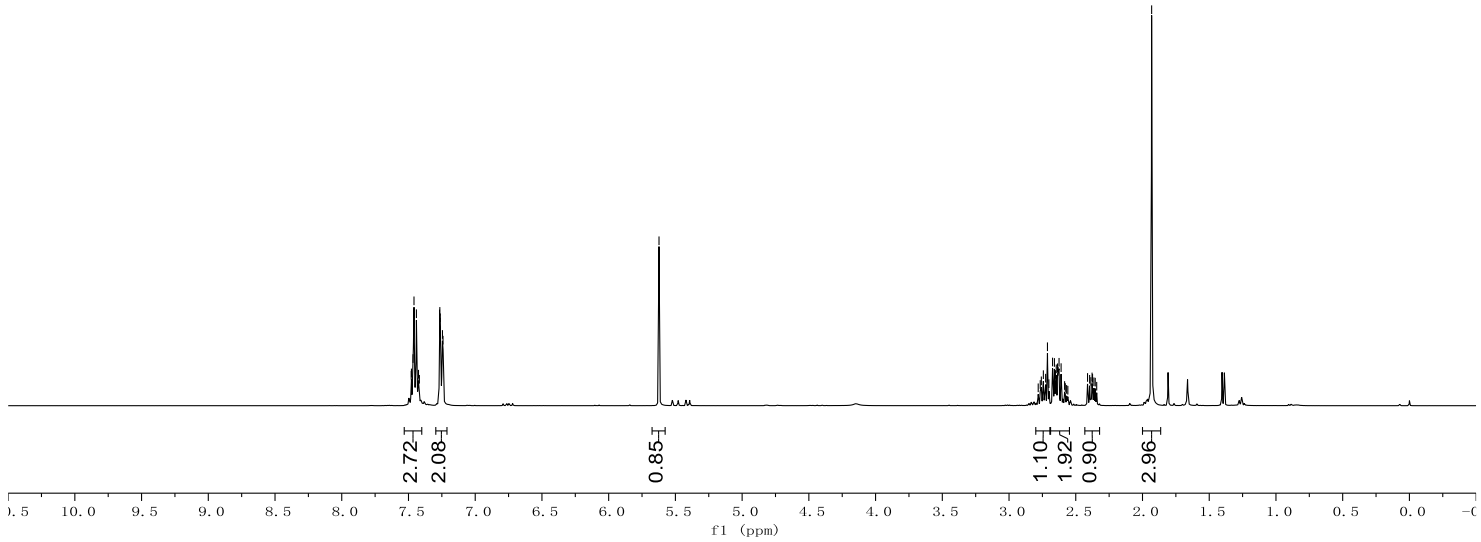
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of 3-([1,1'-Biphenyl]-4-yl)-2-fluoro-2-methyl-3-oxopropanenitrile (70)



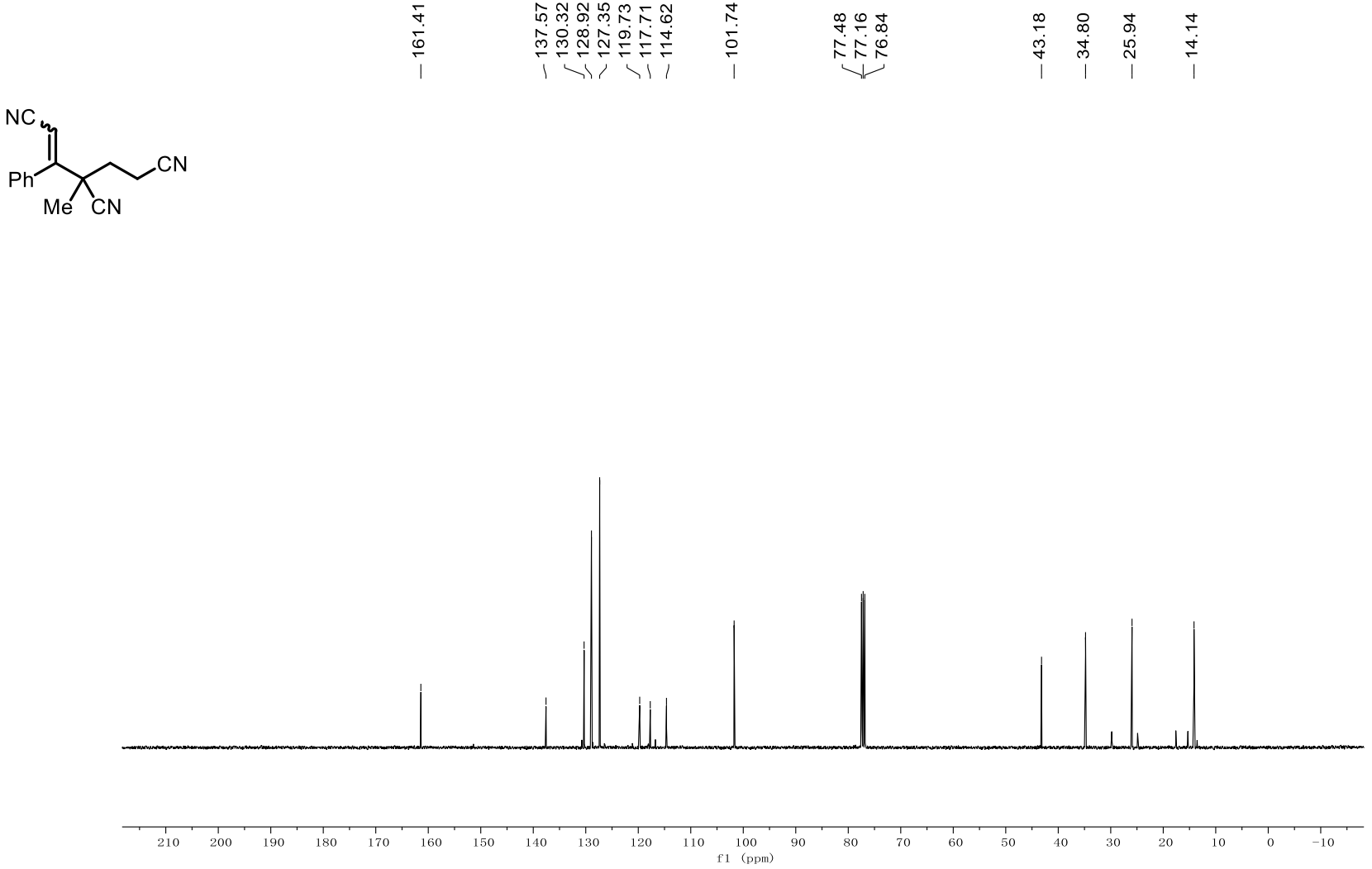
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-Methyl-2-phenylpent-1-ene-1,3,5-tricarbonitrile (71) *Major isomer*



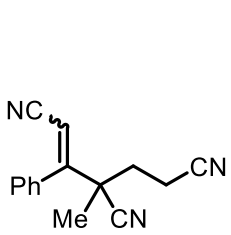


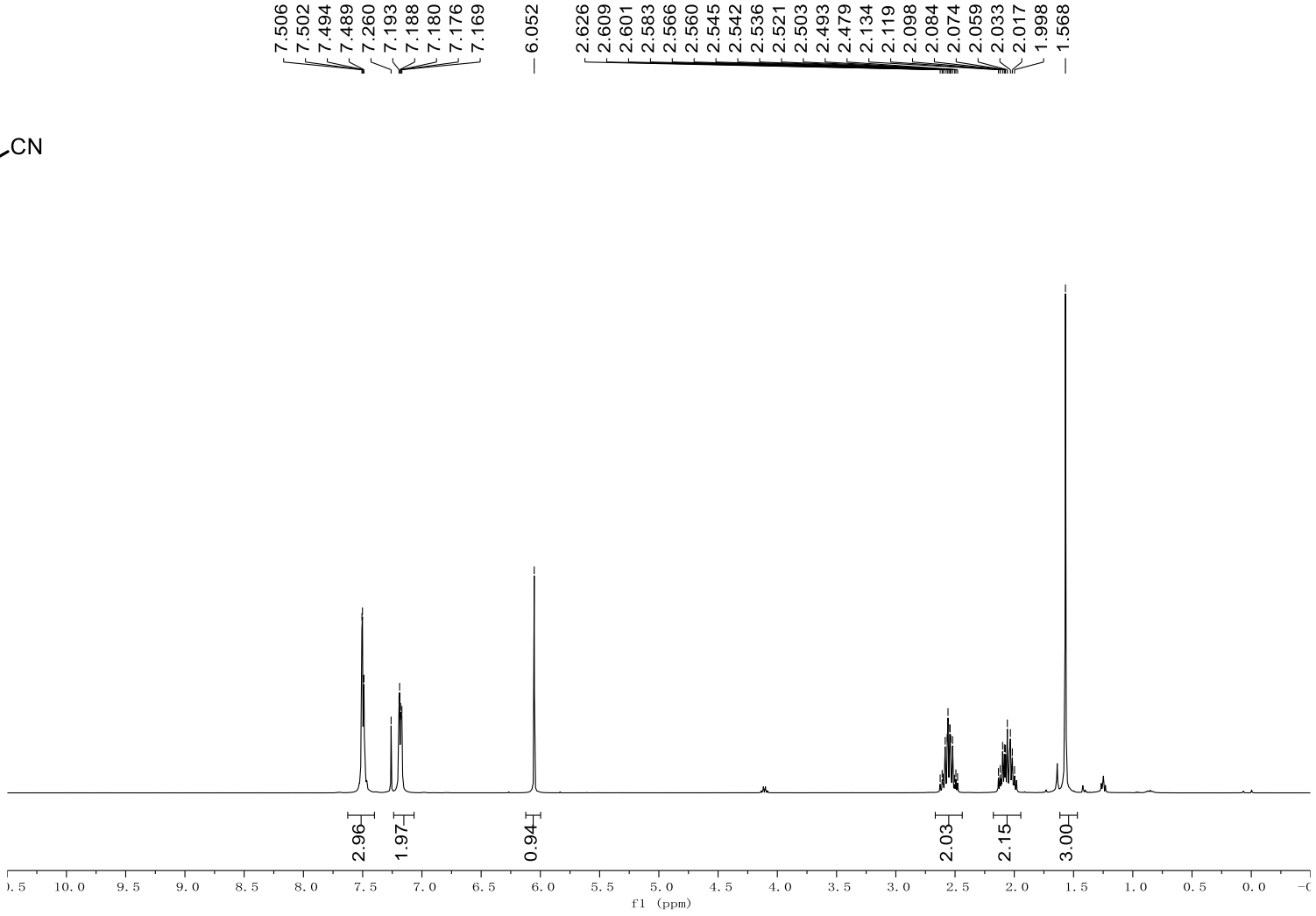


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-Methyl-2-phenylpent-1-ene-1,3,5-tricarbonitrile (71) *Major isomer*

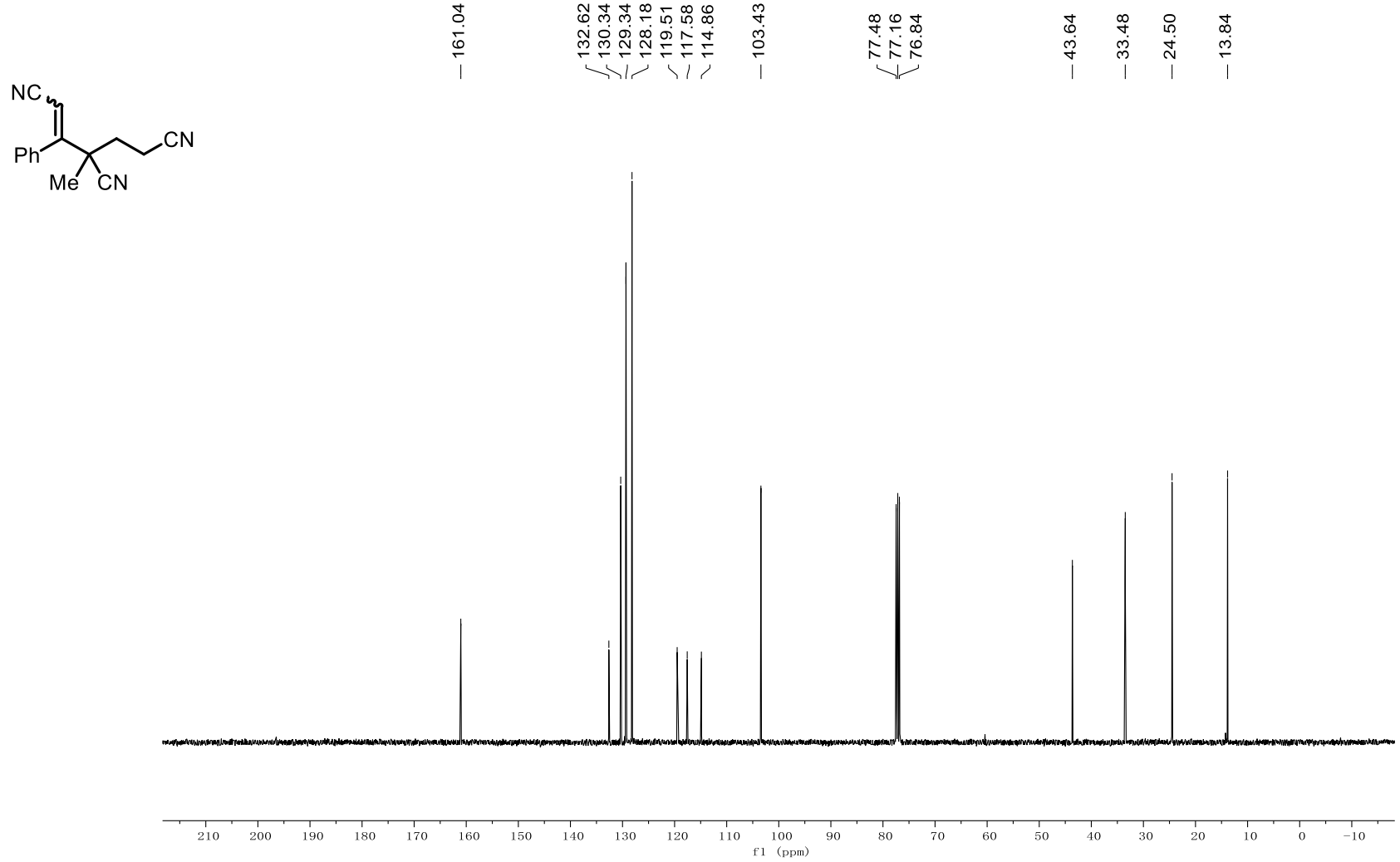


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-Methyl-2-phenylpent-1-ene-1,3,5-tricarbonitrile (71) *Minor isomer*

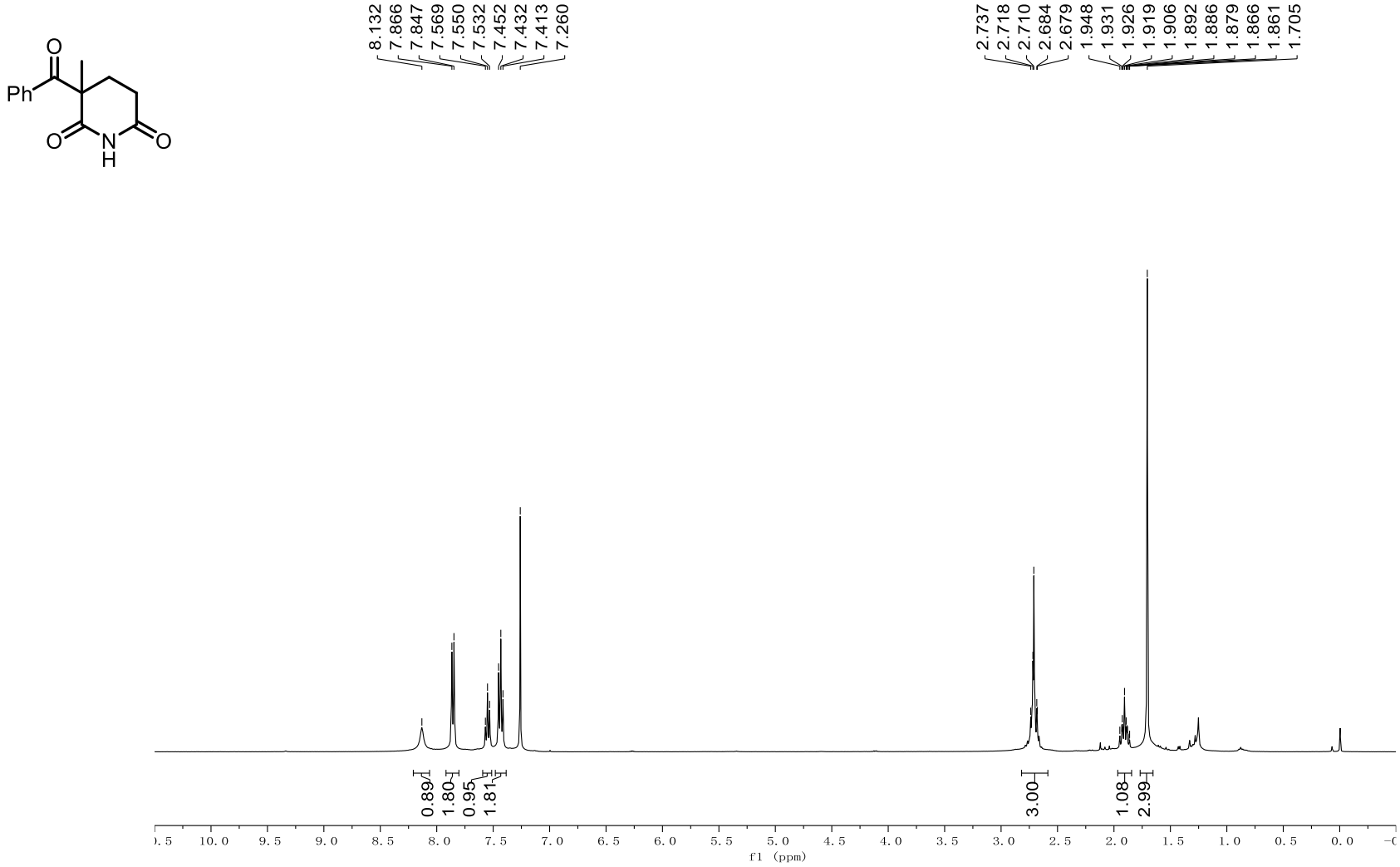




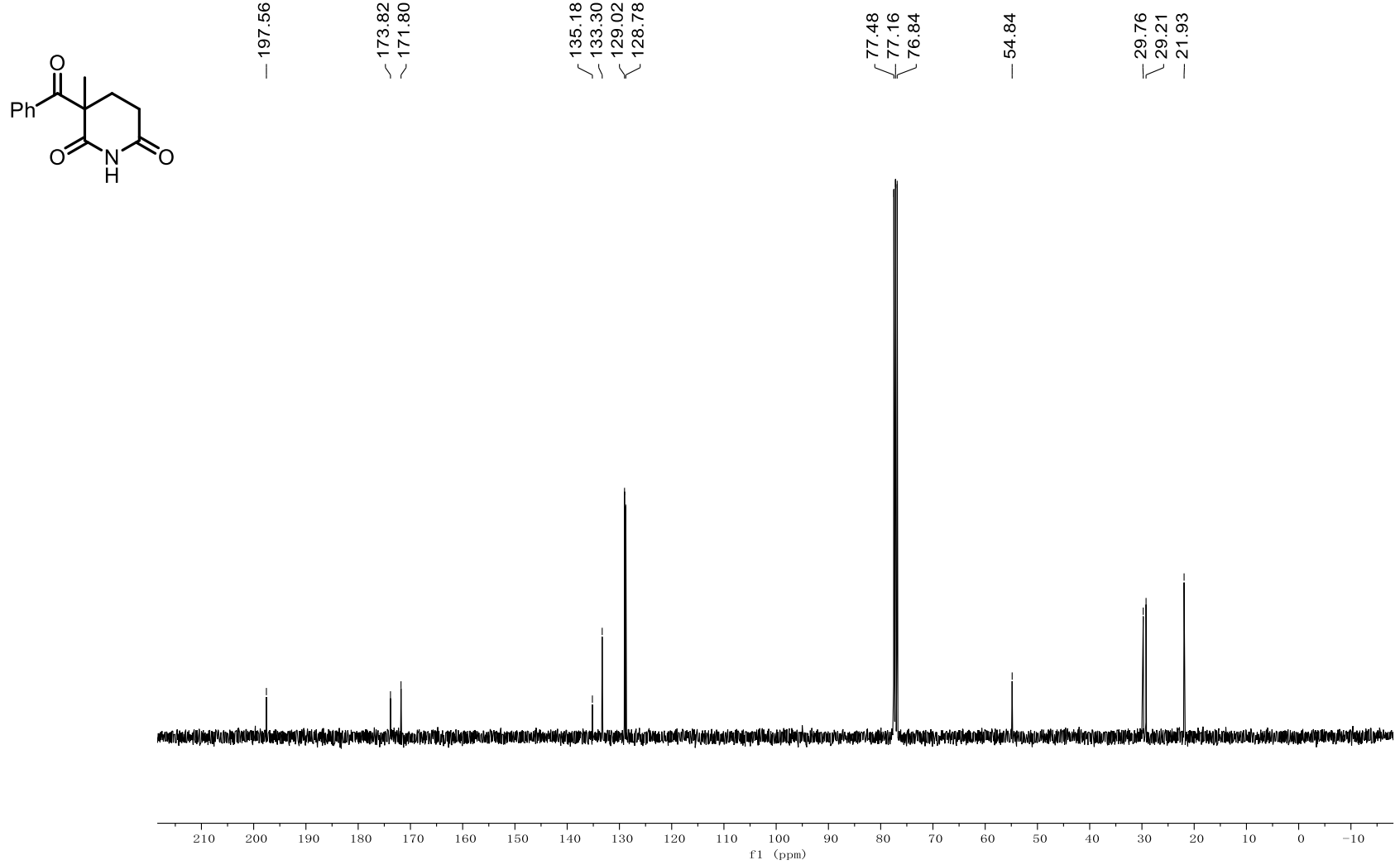
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-Methyl-2-phenylpent-1-ene-1,3,5-tricarbonitrile (71) *Minor isomer*



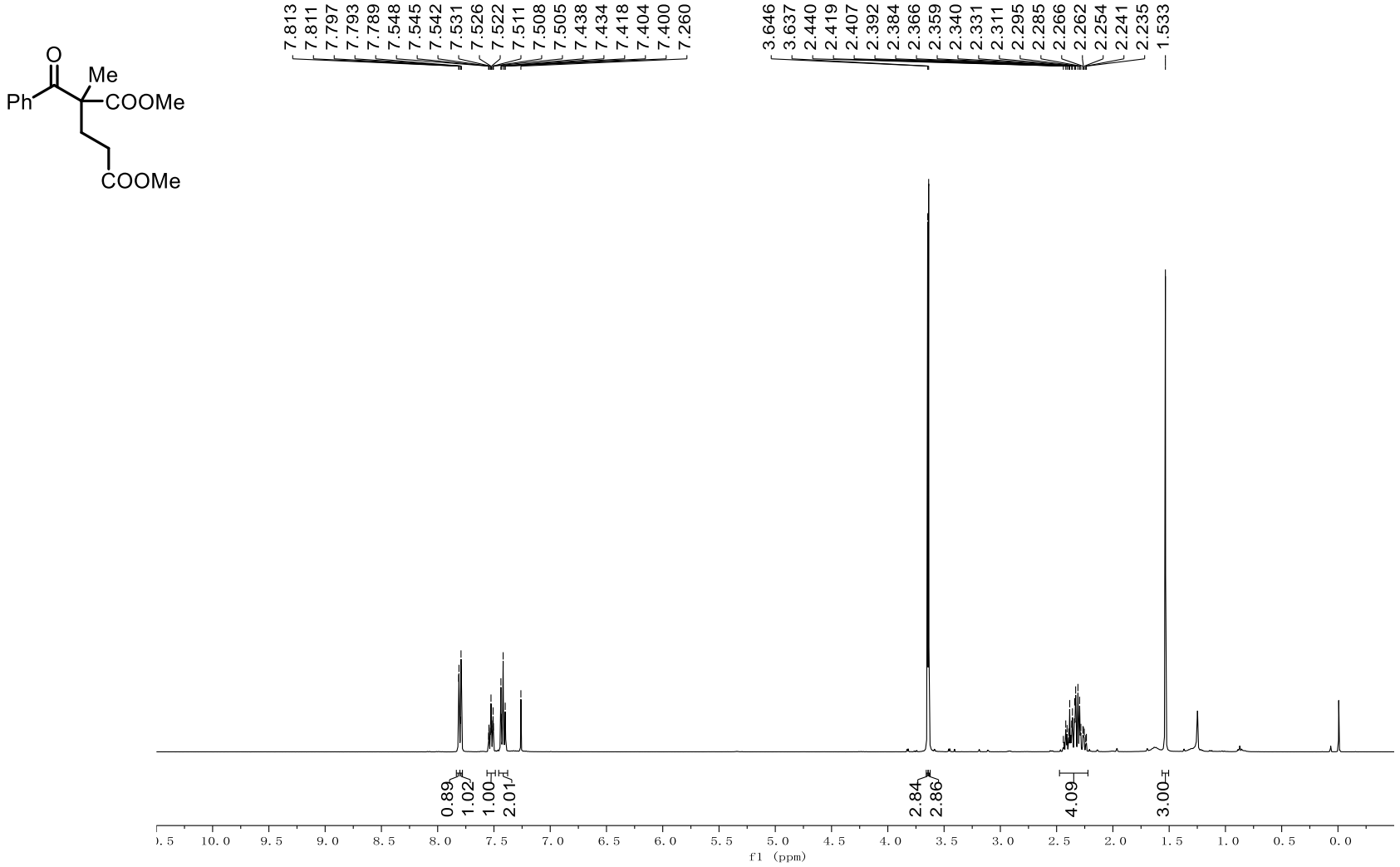
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-Benzoyl-3-methylpiperidine-2,6-dione (72)



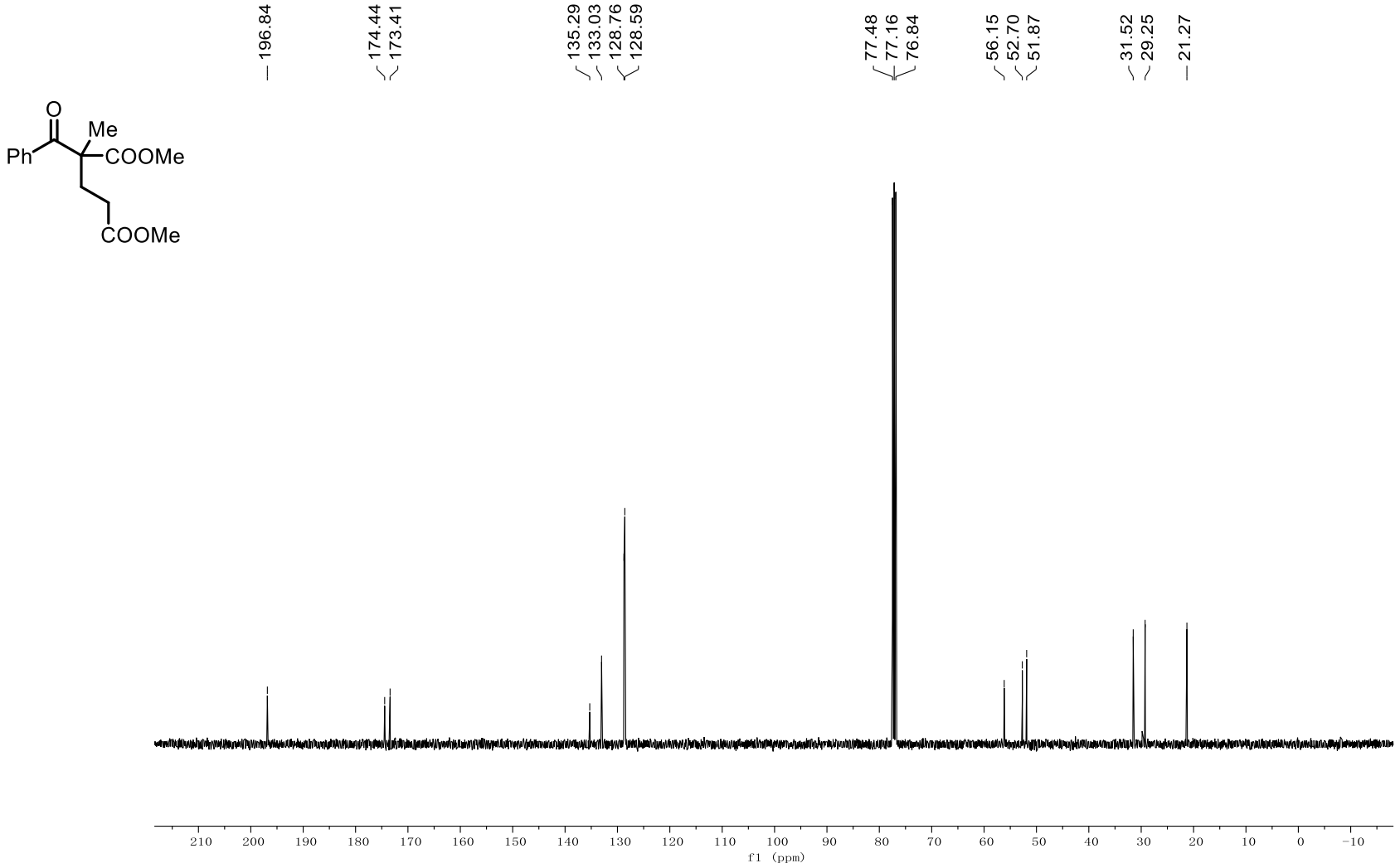
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-Benzoyl-3-methylpiperidine-2,6-dione (72)



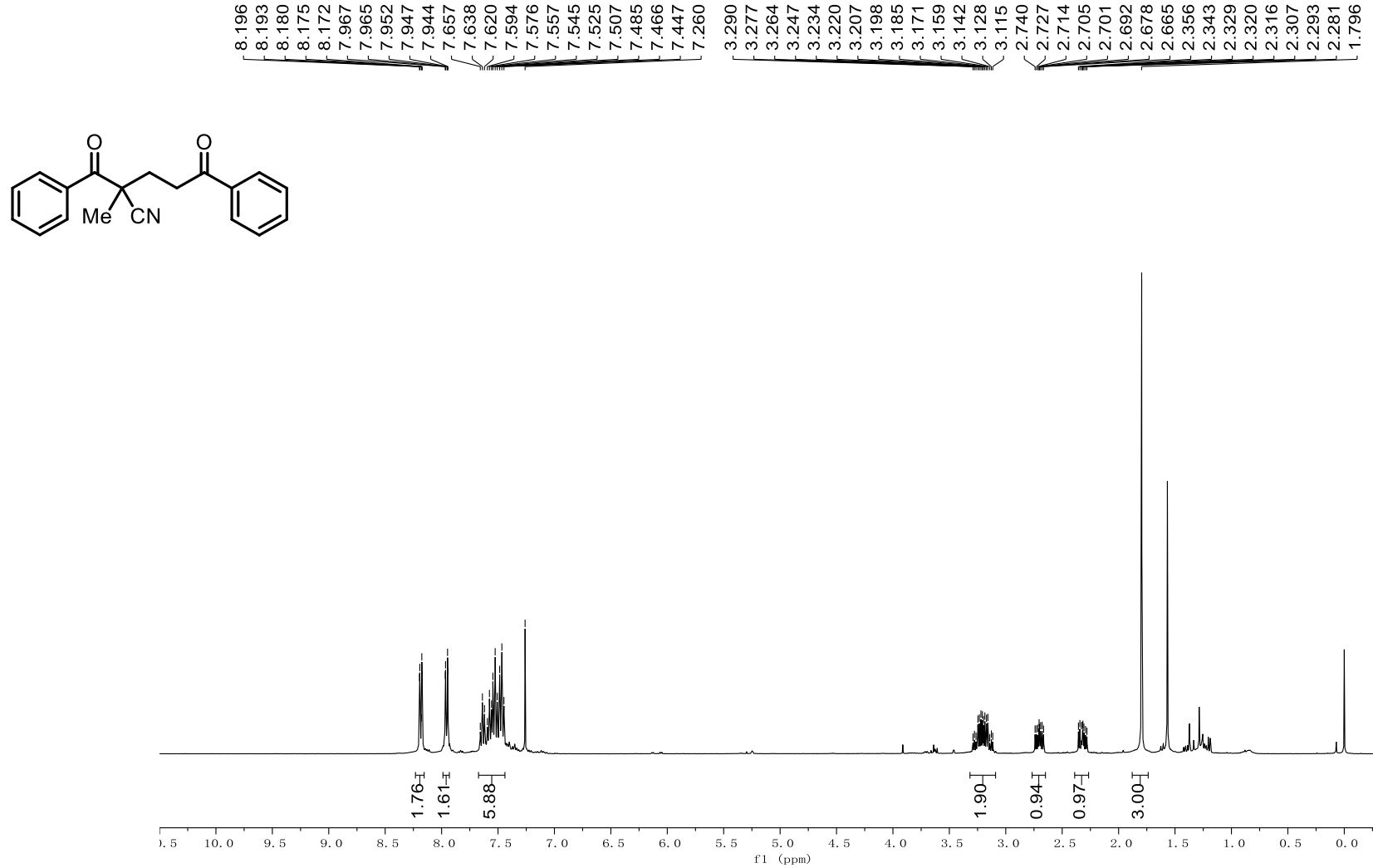
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of Dimethyl 2-benzoyl-2-methylpentanedioate (73)



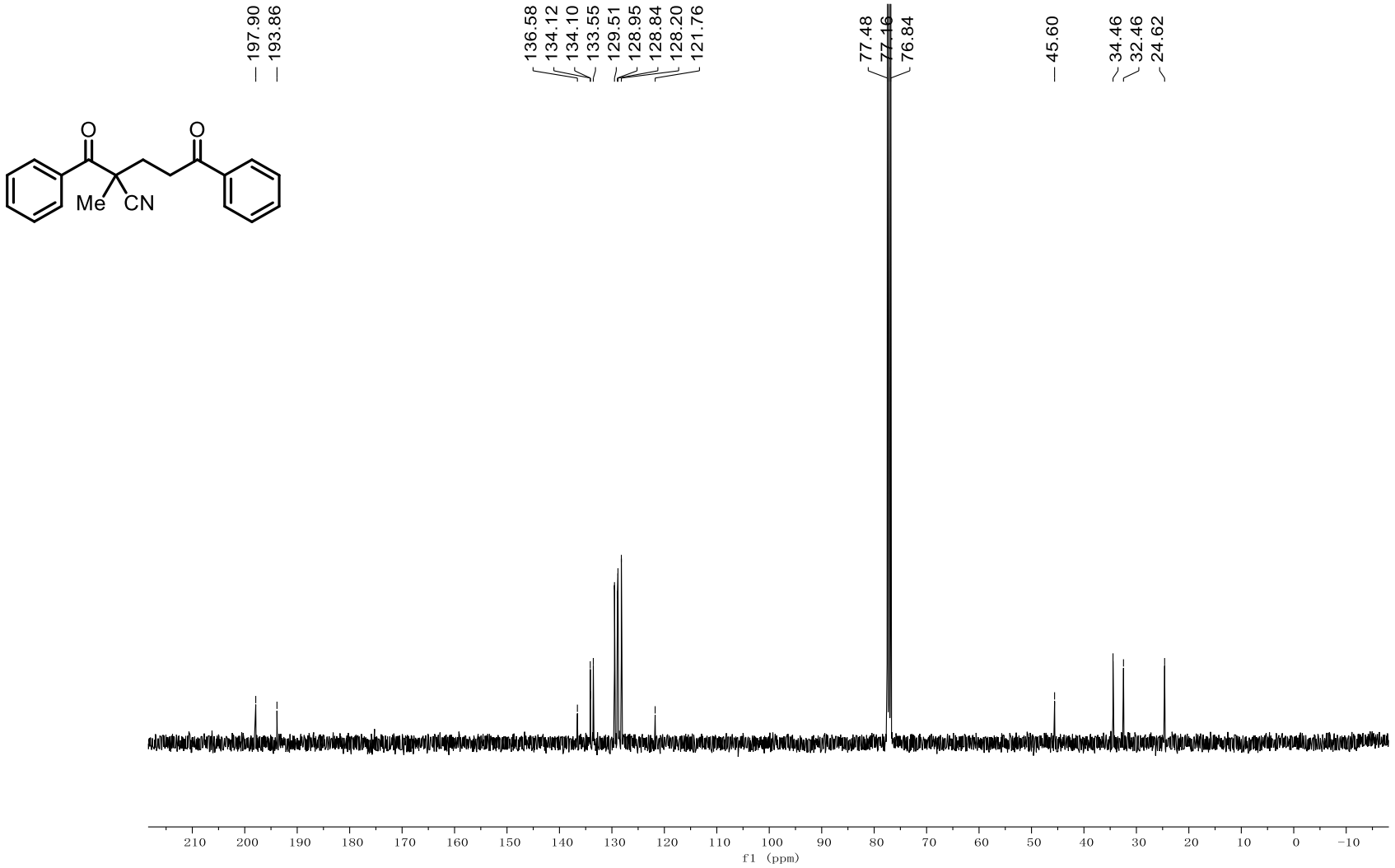
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of Dimethyl 2-benzoyl-2-methylpentanedioate (73)



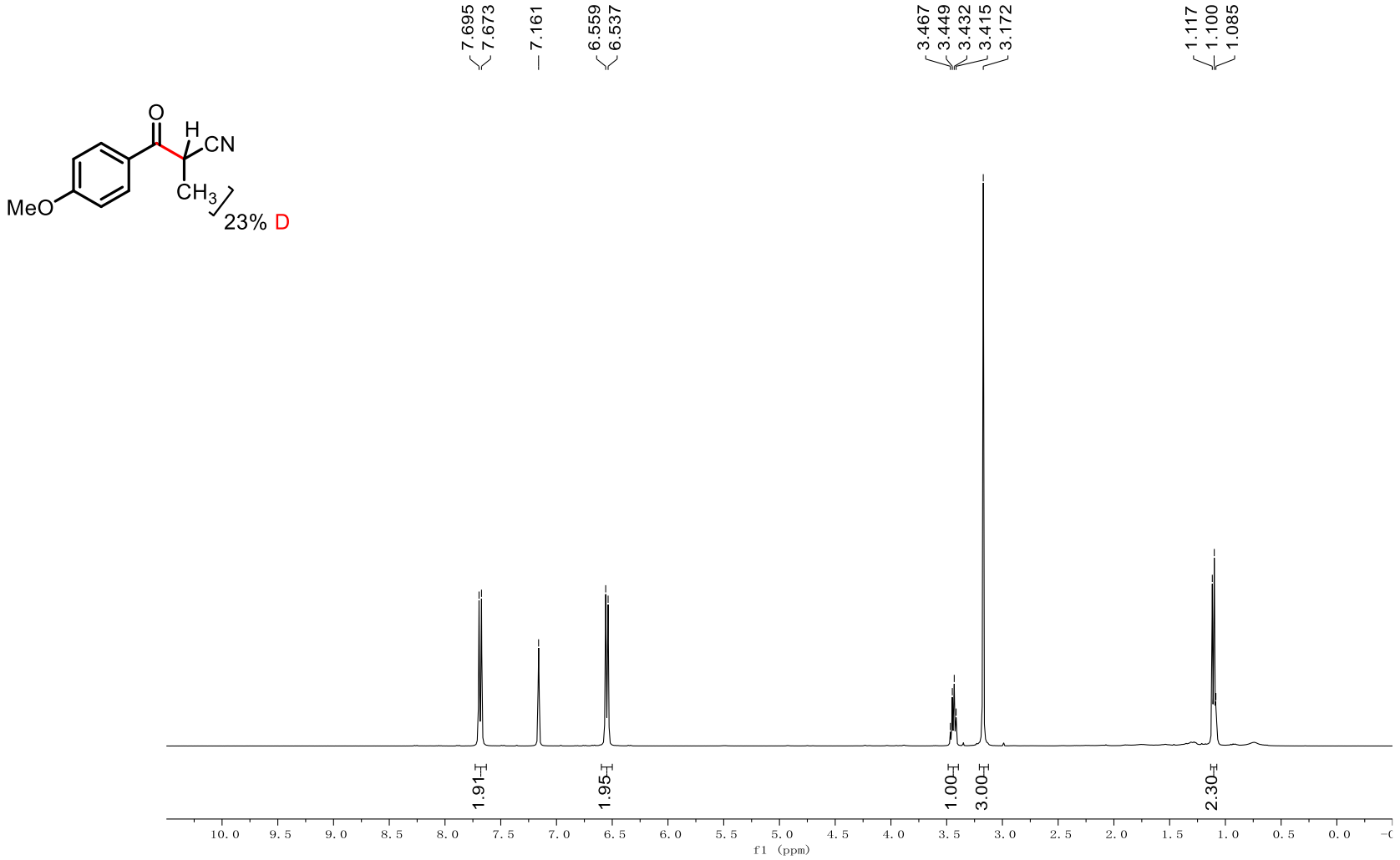
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-Benzoyl-2-methyl-5-oxo-5-phenylpentanenitrile (74)



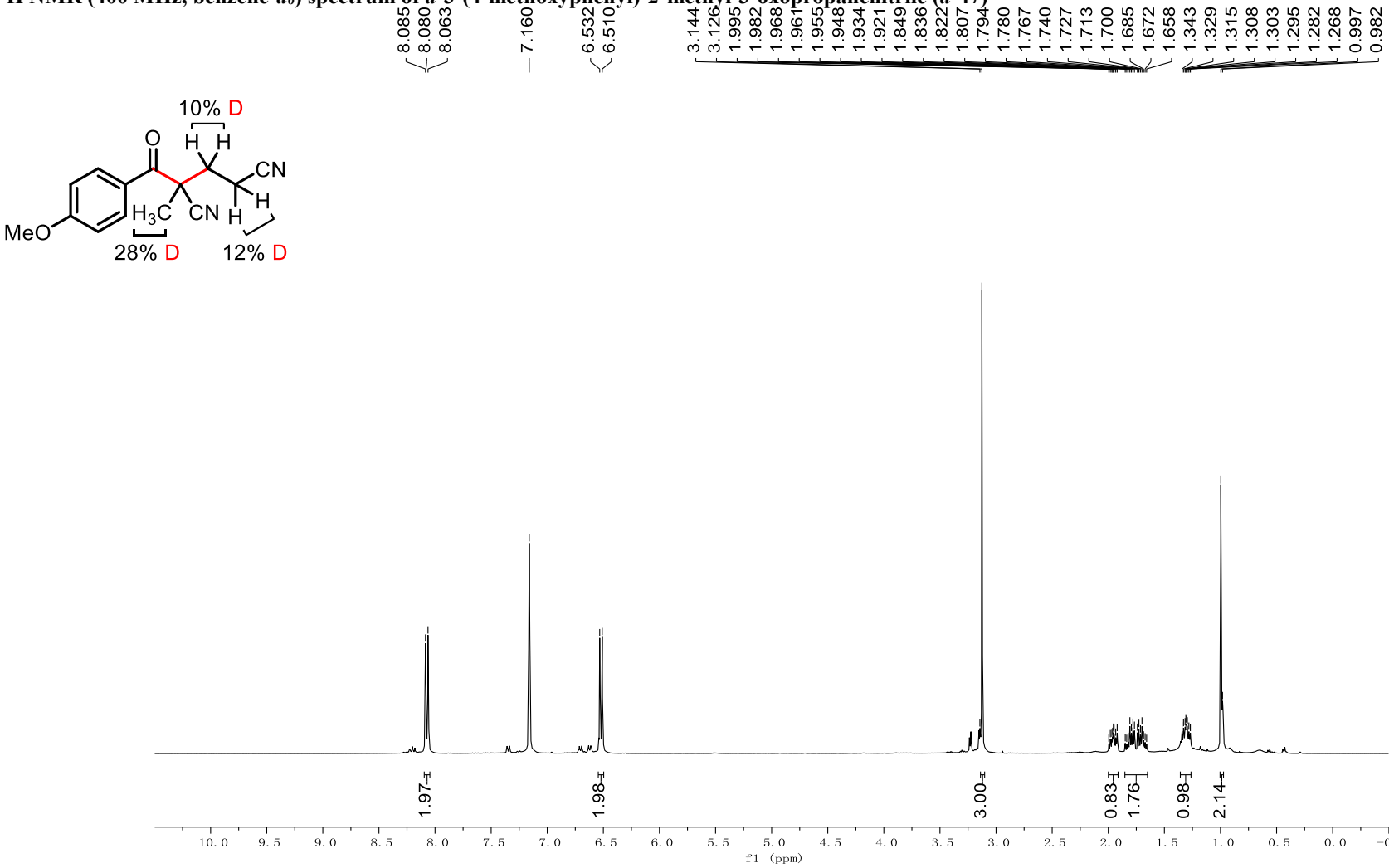
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-Benzoyl-2-methyl-5-oxo-5-phenylpentanenitrile (74)



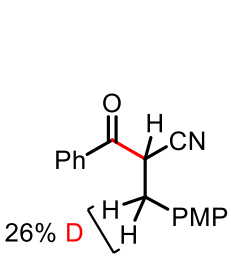
^{1}H NMR (400 MHz, benzene-d_6) spectrum of *d*-3-(4-methoxyphenyl)-2-methyl-3-oxopropanenitrile (*d*-9)

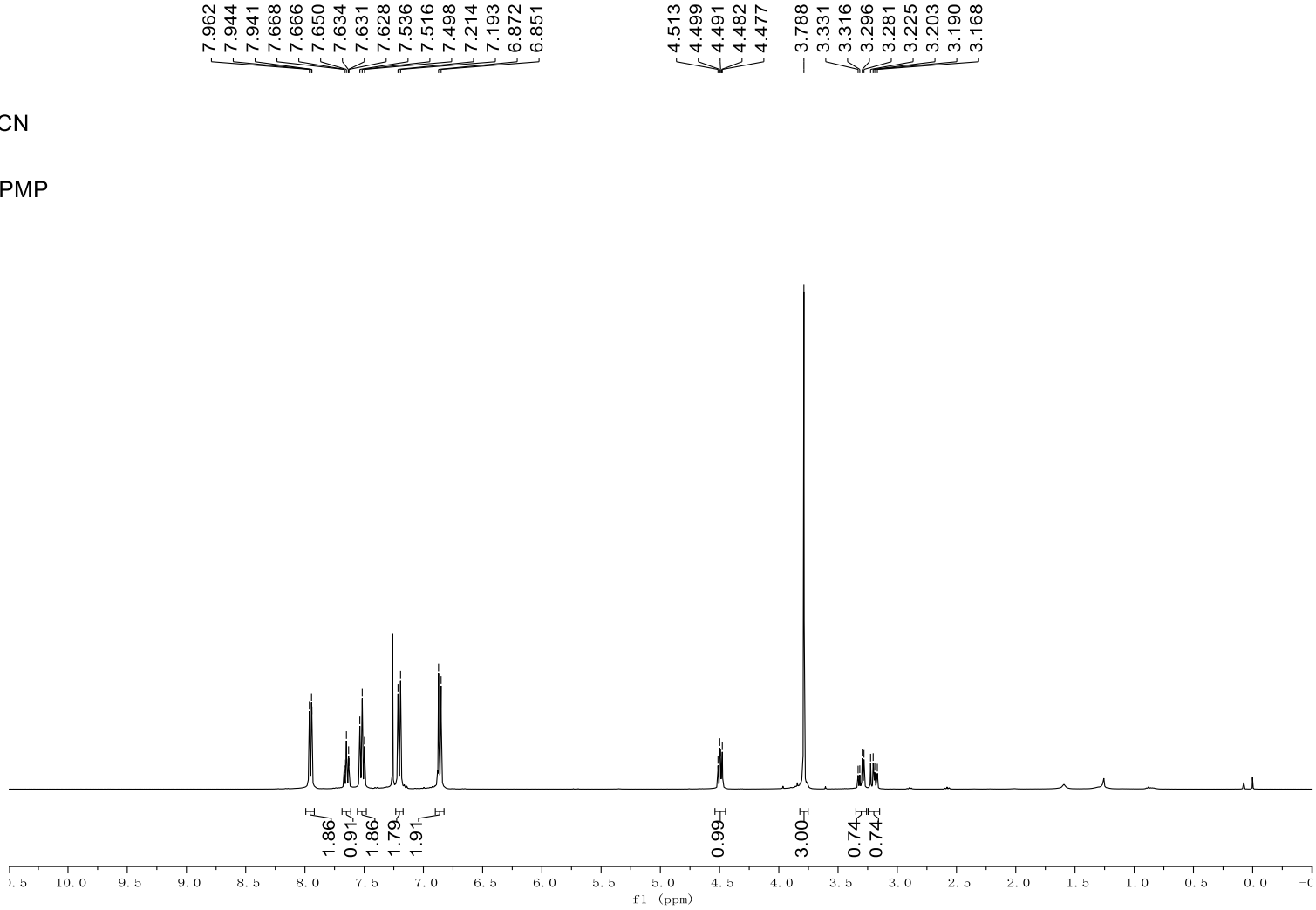


^{1}H NMR (400 MHz, benzene-d_6) spectrum of *d*-3-(4-methoxyphenyl)-2-methyl-3-oxopropanenitrile (*d*-47)



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *d*-3-(4-methoxyphenyl)-2-methyl-3-oxopropanenitrile (*d*-78)





^{1}H NMR (400 MHz, $CDCl_3$) spectrum of *d*-3-(4-methoxyphenyl)-2-methyl-3-oxopropanenitrile (81)