

Highly Enantioselective Michael Addition of Malononitrile to α,β -Unsaturated Ketones

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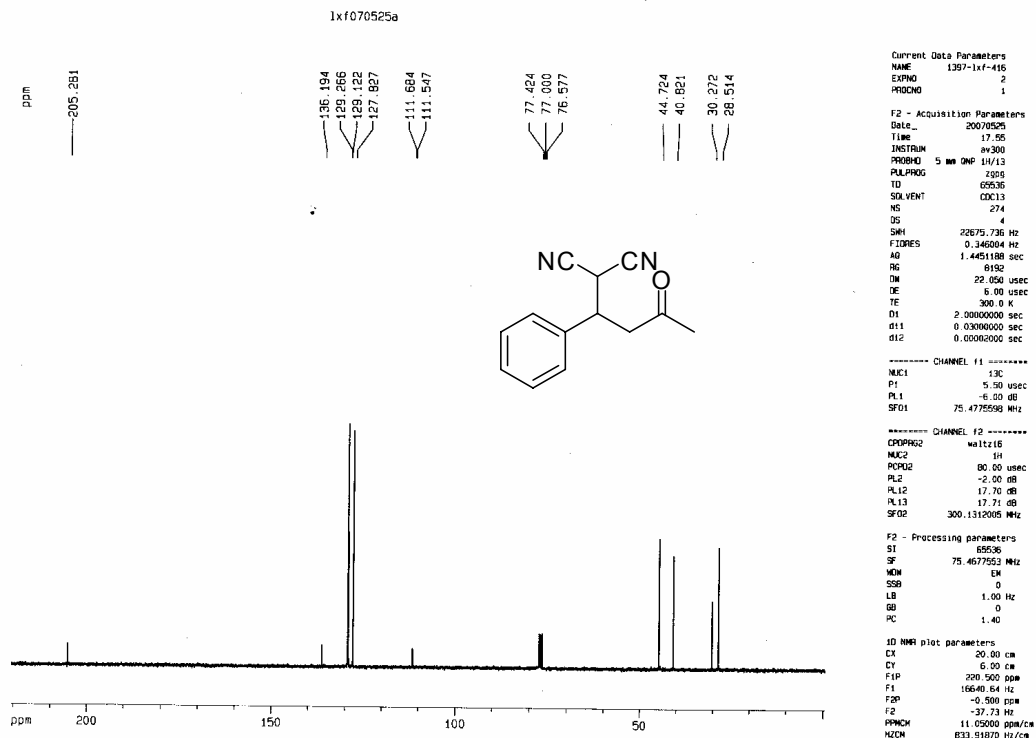
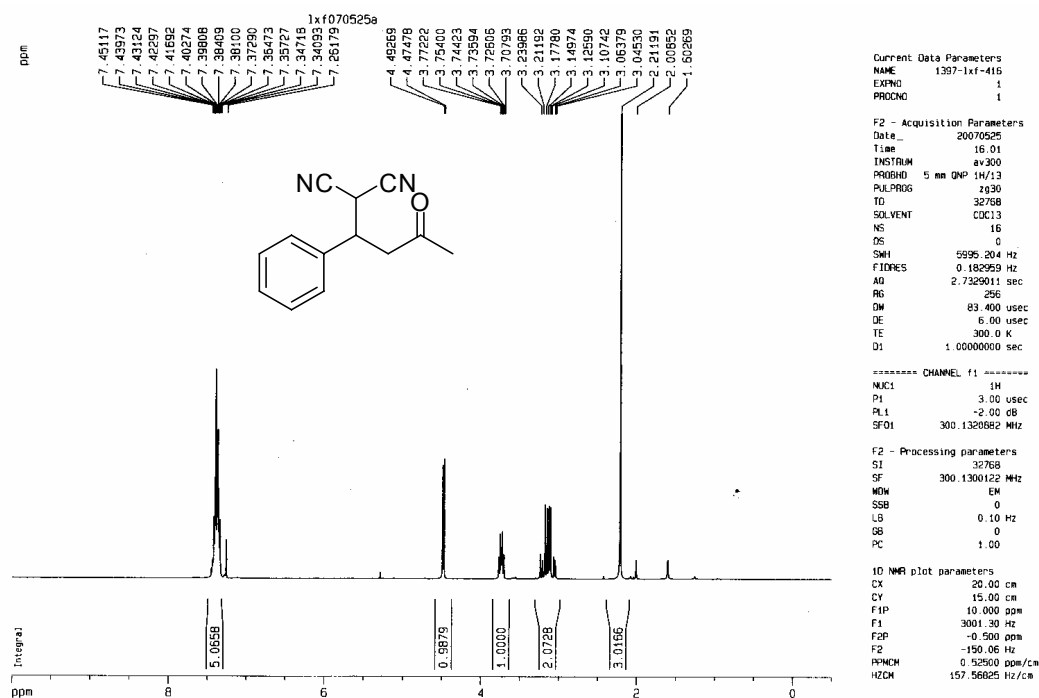
^c West China School of Pharmacy, Sichuan University, Chengdu 610041, China

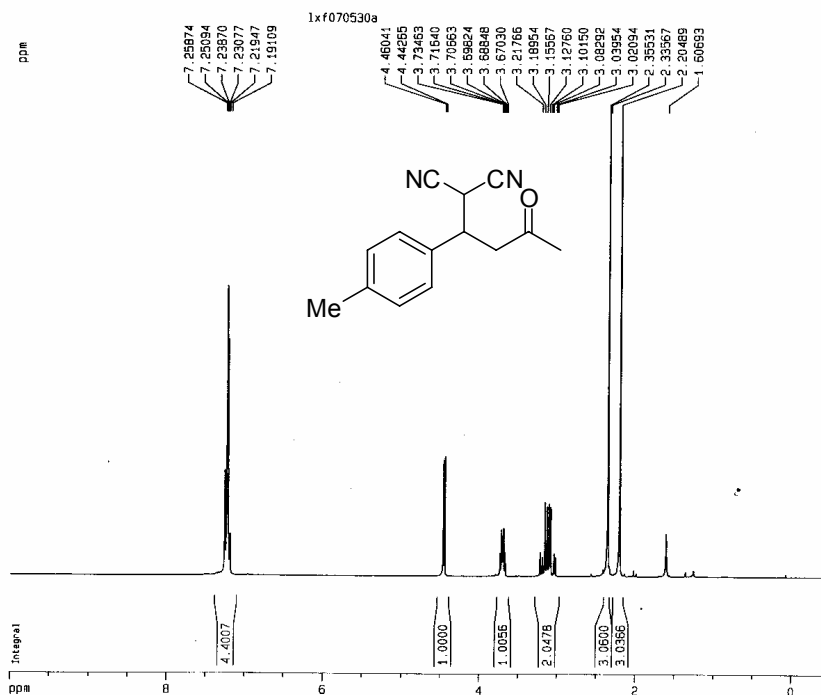
Supplementary Information

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1. ^1H NMR and ^{13}C NMR spectra





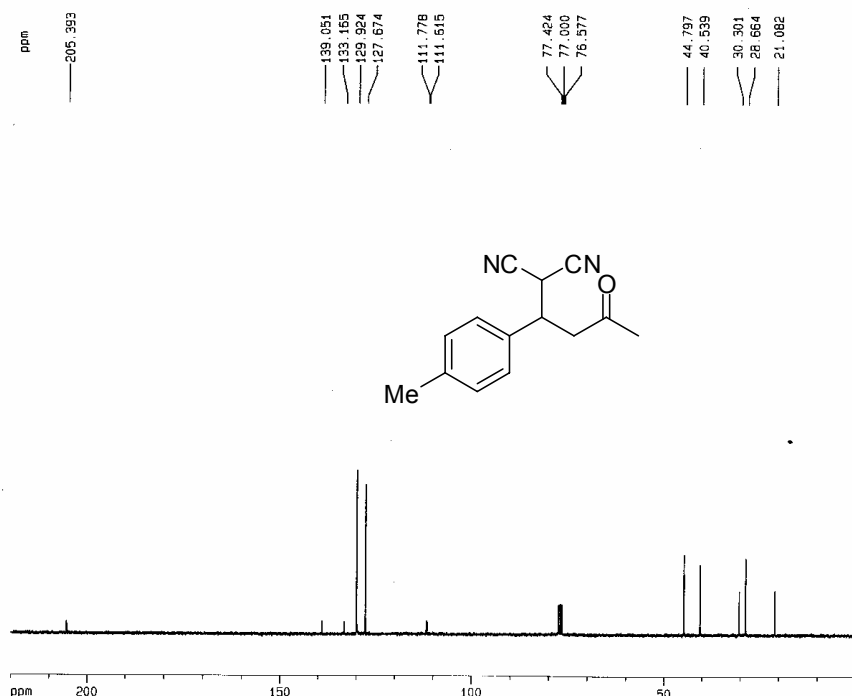
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TE 300.0 K
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CY 15.00 cm
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F2P -0.500 ppm
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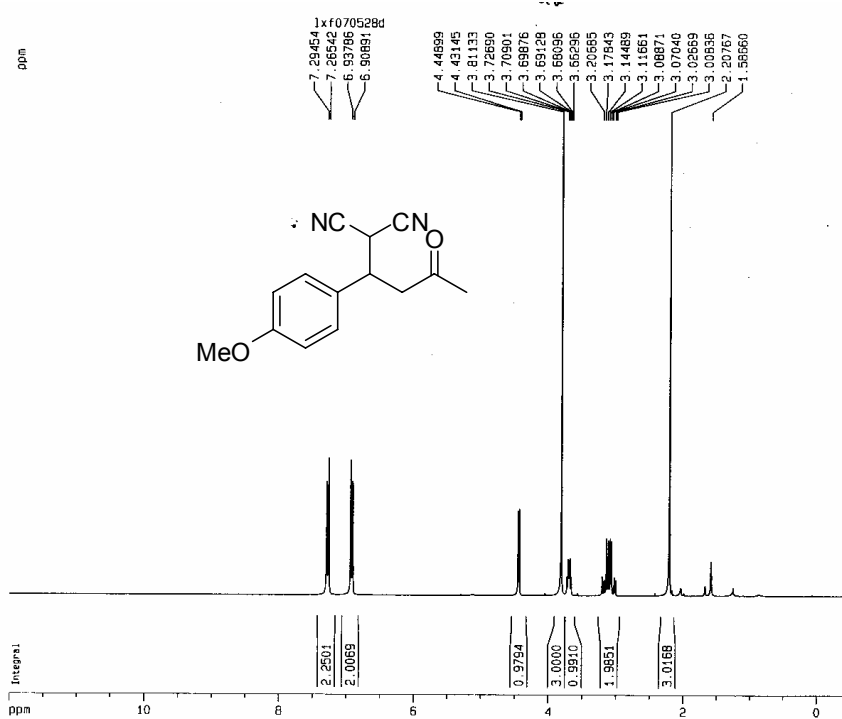
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FIDRES 0.346064 Hz
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RG 8192
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DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

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PL1 -6.00 dB
SF01 75.4775936 MHz

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PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SF02 300.1312005 MHz

F2 - Processing parameters
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LB 1.00 Hz
GB 0
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1D NMR plot parameters
CX 20.00 cm
CY 4.00 cm
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F2 -37.73 Hz
PFWHM 11.02500 ppm/cm
HZOM 632.03192 Hz/cm



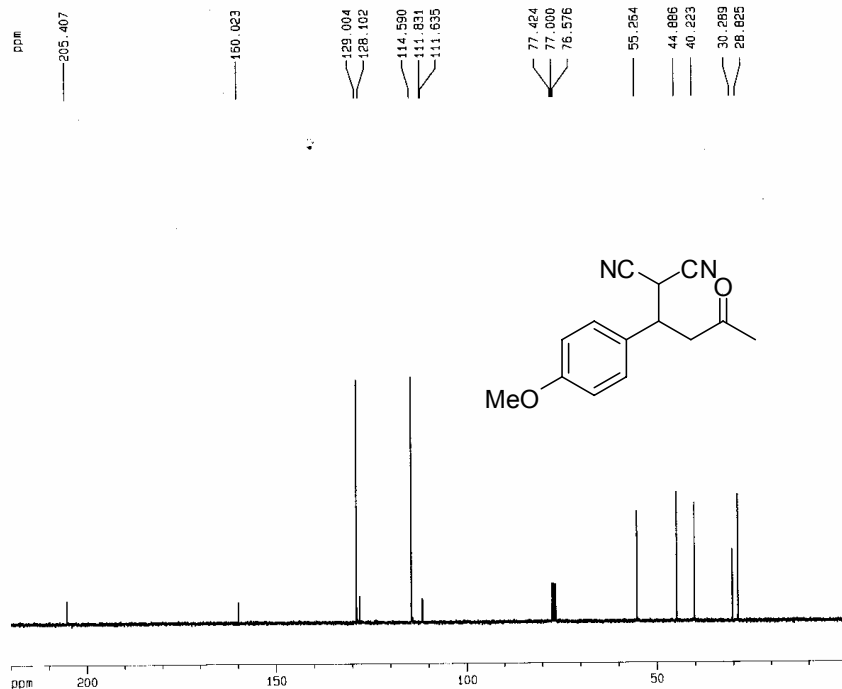
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SOLVENT CDCl3
NS 16
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SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 256
DM 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

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PL1 -2.00 dB
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F2 - Processing parameters
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SF 300.1300122 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 12.00 cm
F1P 12.000 ppm
F1 3601.56 Hz
F2P -0.500 ppm
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HZCM 187.58125 Hz/cm



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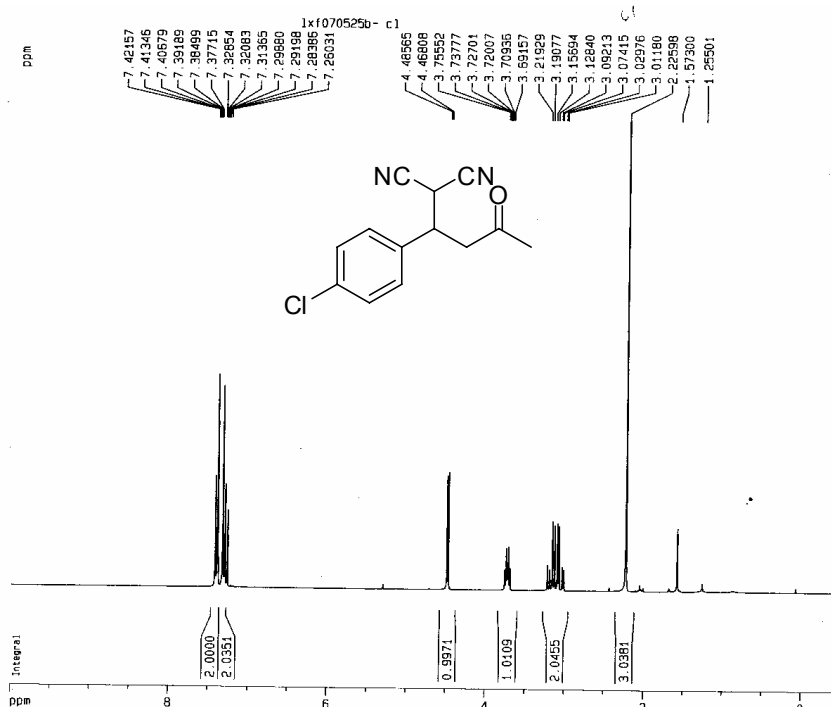
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FIDRES 0.348054 Hz
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DE 6.00 usec
TE 300.0 K
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NUC1 13C
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PL1 -6.00 dB
SF01 75.4775598 MHz

===== CHANNEL f2 =====
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NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SF02 300.1312005 MHz

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GB 0
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1D NMR plot parameters
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CY 6.00 cm
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F2P -0.005 ppm
F2 -0.38 Hz
PCHM 11.00025 ppm/cm
HZCM 830.16425 Hz/cm



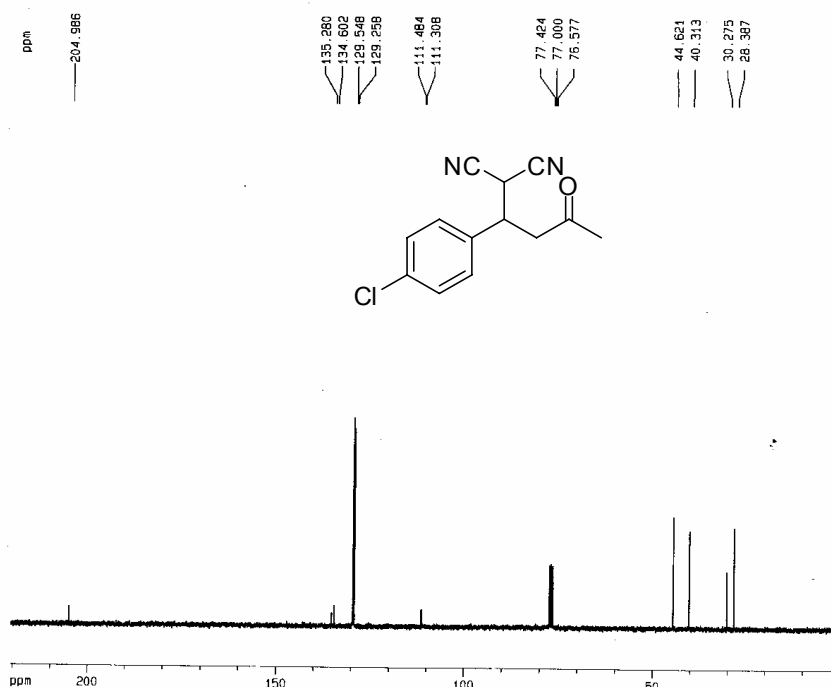
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SOLVENT CDCl3
NS 32
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 256
DM 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.0000000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320082 MHz

F2 - Processing parameters
SI 32768
SF 300.1300122 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 15.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PPMCH 0.52500 ppm/cm
HZCM 157.56825 Hz/cm



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EXPNO 2
PROCNO 1

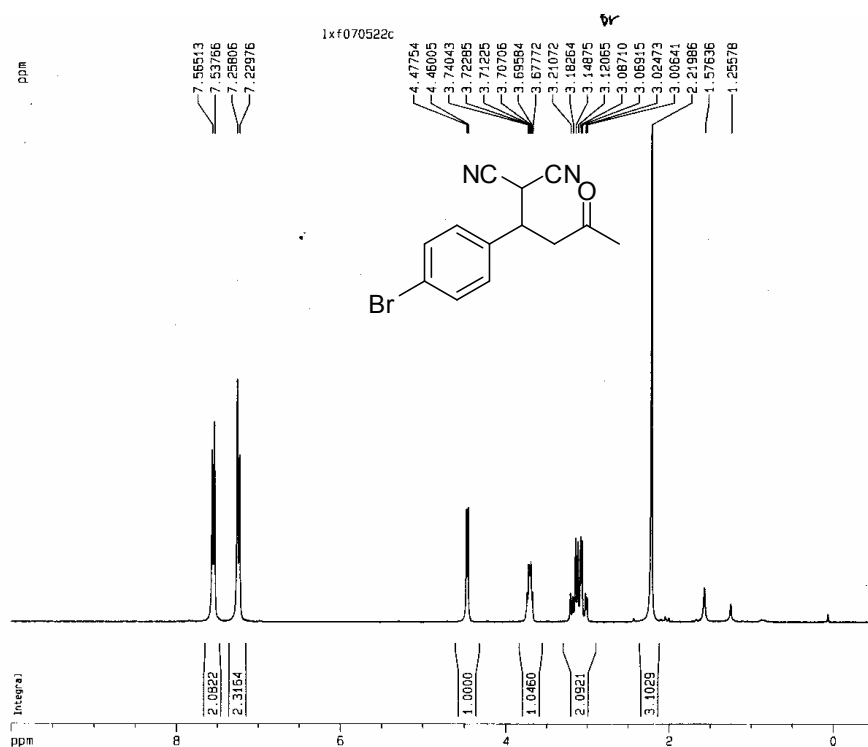
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SOLVENT CDCl3
NS 282
DS 4
SWH 22675.735 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DM 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.0000000 sec
d11 0.0300000 sec
d12 0.0000200 sec

***** CHANNEL f1 *****
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.475598 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 65536
SF 75.4677525 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 5.00 cm
F1P 230.500 ppm
F1 16640.64 Hz
F2P -0.500 ppm
F2 -37.73 Hz
PPMCH 11.05000 ppm/cm
HZCM 833.91864 Hz/cm



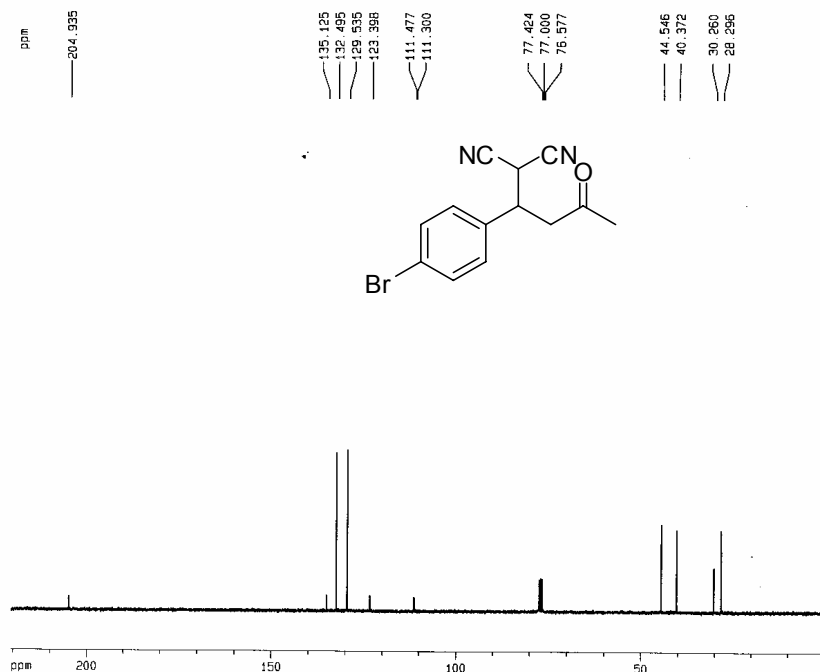
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PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7325011 sec
RG 512
DM 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.0000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz

F2 - Processing parameters
SI 32768
SF 300.130122 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 15.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.05 Hz
PPMCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm



Current Data Parameters
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EXPNO 2
PROCNO 1

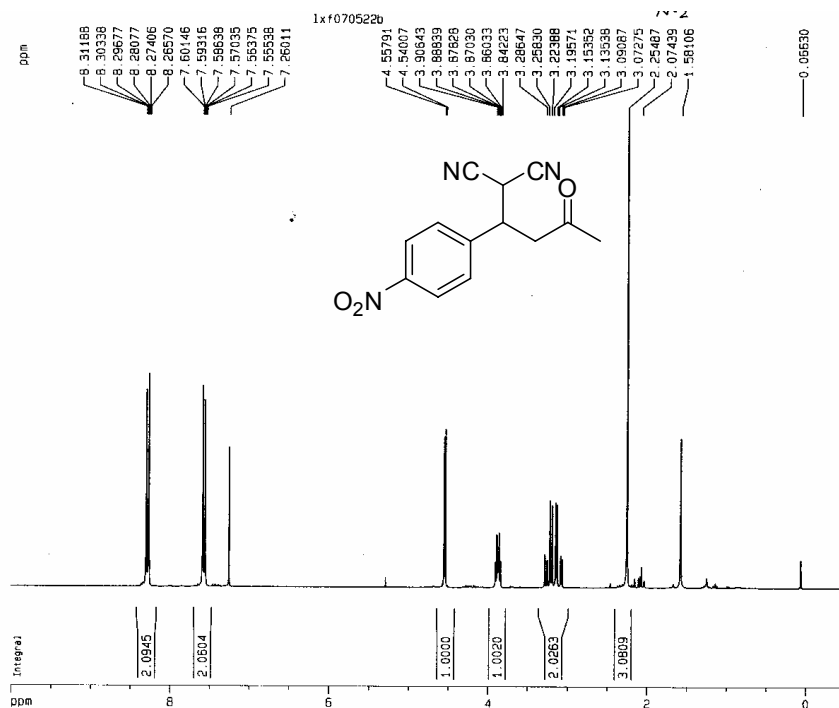
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PULPROG zgpg30
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SOLVENT CDCl3
NS 256
DS 4
SWH 32675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8152
DM 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.0000000 sec
d11 0.0300000 sec
d12 0.0000200 sec

===== CHANNEL f1 =====
NUC1 13C
P1 5.50 usec
PL1 -5.00 dB
SFO1 75.4775988 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 65536
SF 75.4677936 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 4.00 cm
F1P 220.500 ppm
F1 16640.64 Hz
F2P -0.500 ppm
F2 -37.73 Hz
PPMCM 11.05000 ppm/cm
HZCM 833.91864 Hz/cm



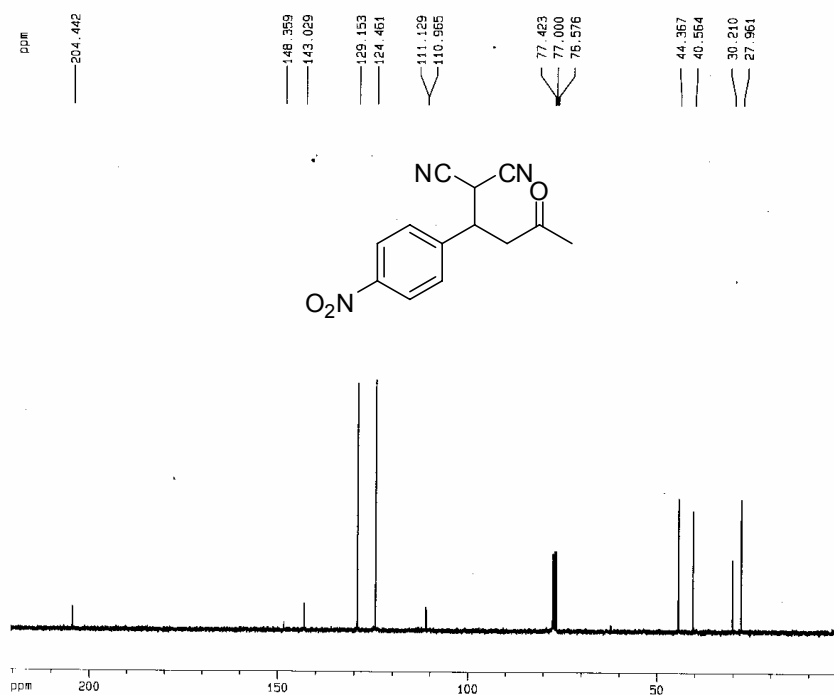
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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz

F2 - Processing parameters
SI 32768
SF 300.1300122 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 20.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PQCM 0.52500 ppm/cm
HZCM 157.56825 Hz/cm



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EXPNO 2
PROCNO 1

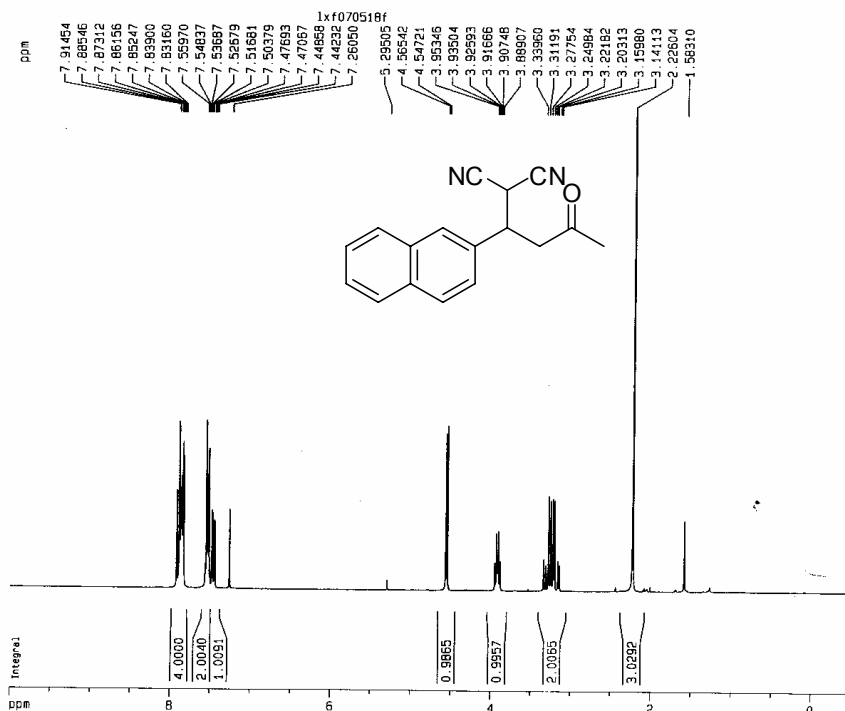
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PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 680
DS 4
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.63000000 sec
d12 0.00002000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775586 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.70 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 65536
SF 75.4677528 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 6.00 cm
F1P 220.500 ppm
F1 16640.64 Hz
F2P -37.73 Hz
F2 -11.05000 ppm/cm
PQCM 11.05000 ppm/cm
HZCM 835.91864 Hz/cm



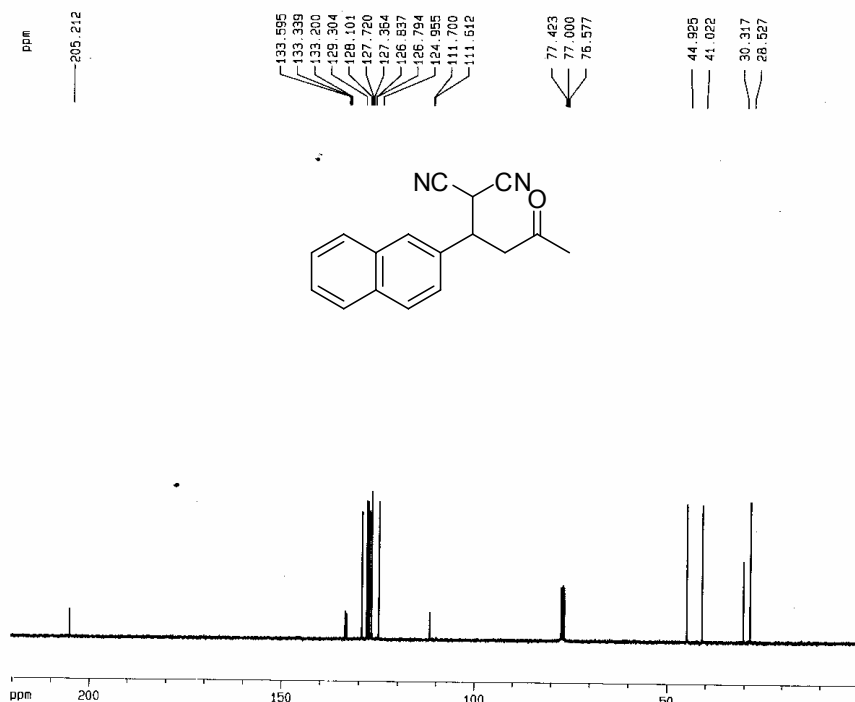
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NS 24
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FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 1024
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DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz

F2 - Processing parameters
SI 32768
SF 300.1300124 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 20.00 cm
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F1 300.130 Hz
F2P -0.500 ppm
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Current Data Parameters
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EXPNO 2
PROCNO 1

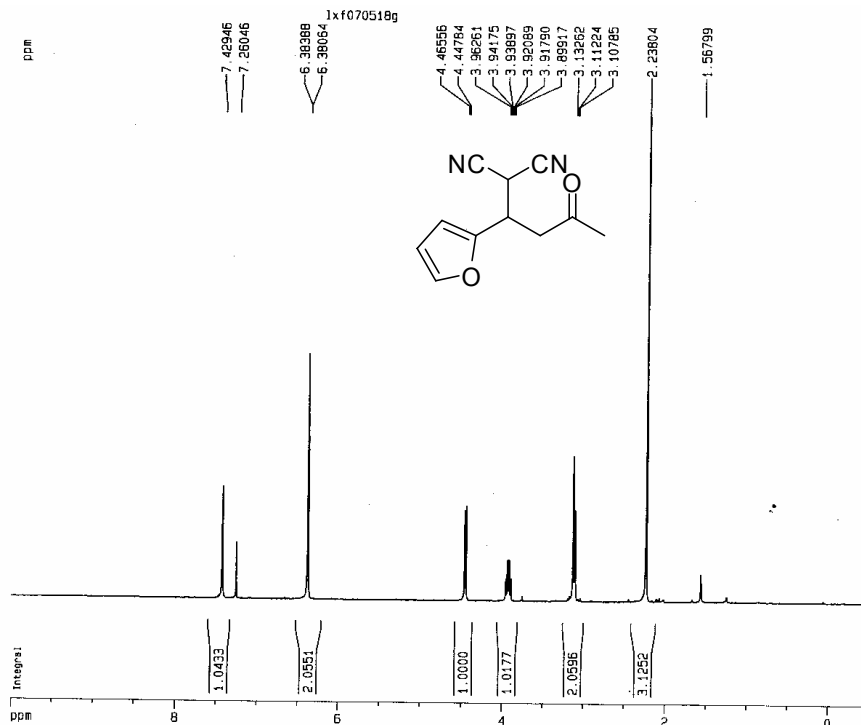
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FIDRES 0.345004 Hz
AQ 1.4451108 sec
RG 0192
DM 22.050 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 5.50 usec
PL1 -6.00 dB
SFO1 75.4775598 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 65536
SF 75.4677543 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
CY 3.50 cm
F1P 220.500 ppm
F1 16640.64 Hz
F2P -0.500 ppm
F2 -37.73 Hz
PPMCH 11.05000 ppm/cm
HZCM 833.91864 Hz/cm



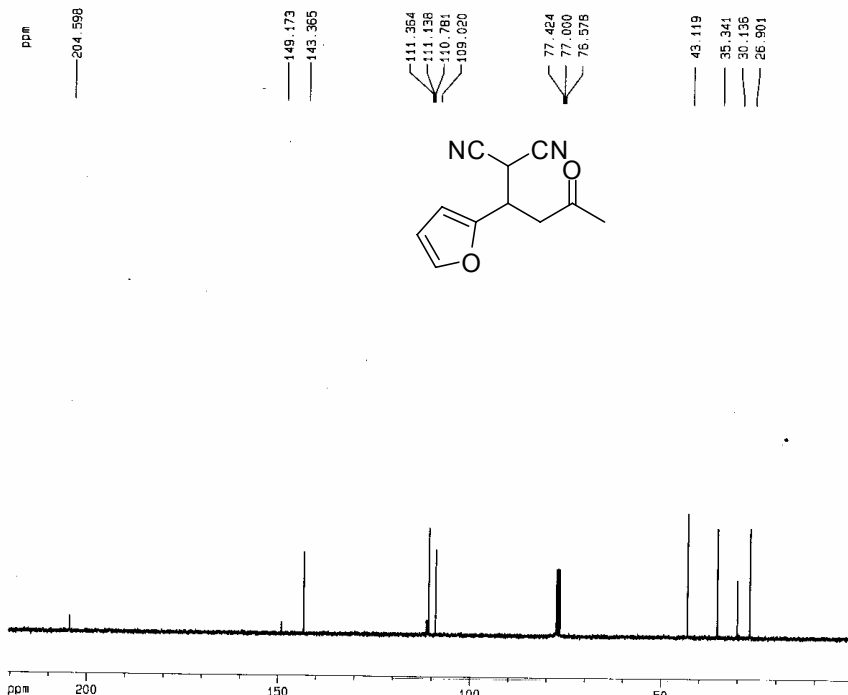
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 NS 8
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 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 1024
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 3.00 usec
 PL1 -2.00 dB
 SFO1 300.1320862 MHz

F2 - Processing parameters
 SI 32768
 SF 300.1300124 MHz
 WDW EM
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 CY 12.00 cm
 F1P 10.600 ppm
 F1 3001.30 Hz
 F2P -0.500 ppm
 F2 -150.06 Hz
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 HZCM 157.56825 Hz/cm



Current Data Parameters
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 PROCNO 1

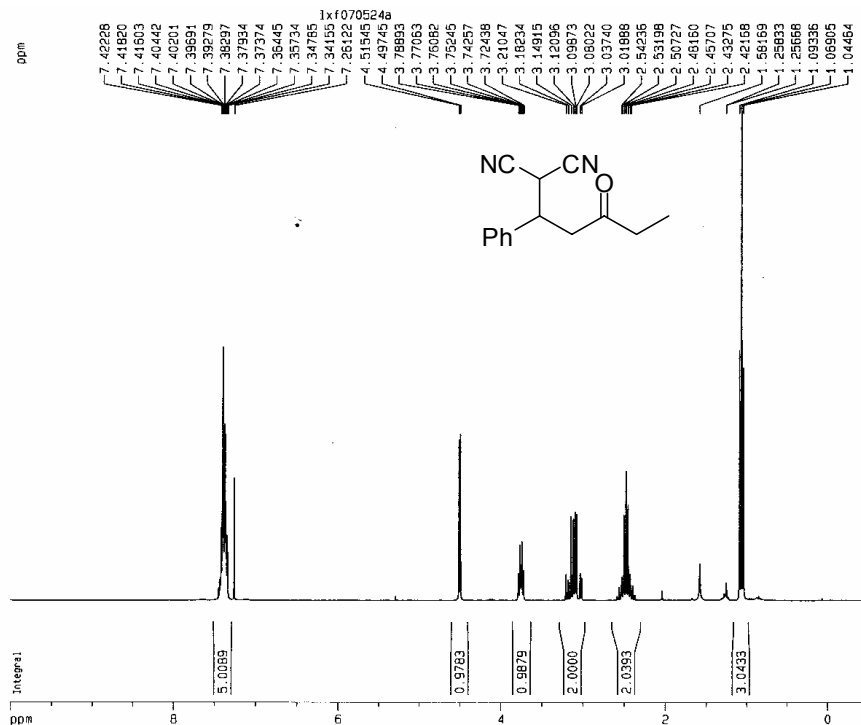
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 NS 866
 DS 4
 SWH 22675.736 Hz
 FIDRES 0.346004 Hz
 AQ 1.4451188 sec
 RG 8192
 DW 22.050 usec
 DE 6.00 usec
 TE 300.0 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 d12 0.00020000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 5.50 usec
 PL1 -8.00 dB
 SFO1 75.4775598 MHz

===== CHANNEL f2 =====
 CPOPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -2.00 dB
 PL12 17.70 dB
 PL13 17.71 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 65536
 SF 75.4677526 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 20.00 cm
 CY 3.00 cm
 F1P 220.500 ppm
 F1 16640.64 Hz
 F2P -37.73 Hz
 F2 11.95000 ppm/cm
 HZCM 833.91864 Hz/cm



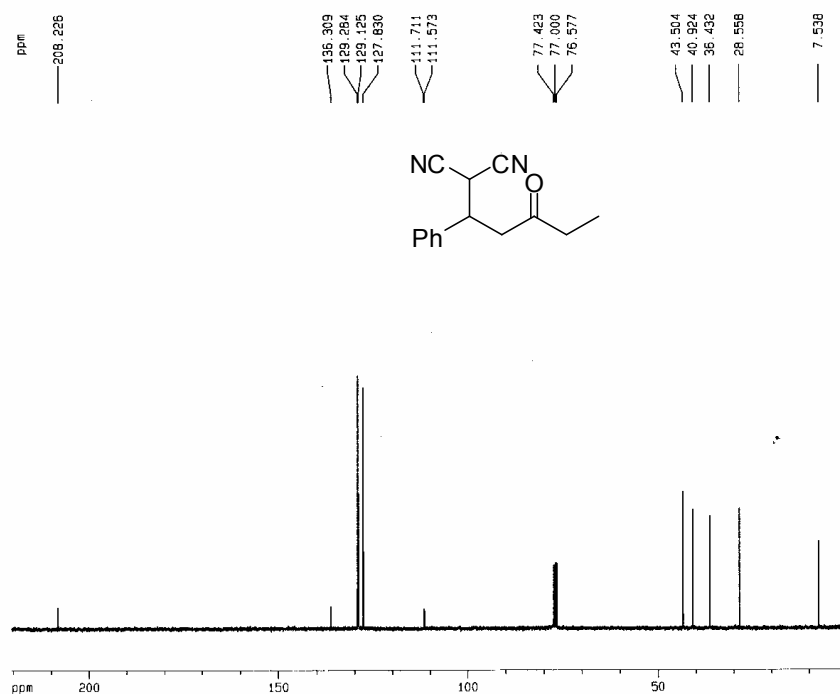
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PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 512
DM 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 3.00 usec
PL1 -2.00 dB
SFO1 300.1320882 MHz

F2 - Processing parameters
SI 32768
SF 300.1300122 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 12.00 cm
F1P 10.000 ppm
F1 3001.30 Hz
F2P -0.500 ppm
F2 -150.06 Hz
PRACH 0.32500 ppm/cm
HZCM 157.56825 Hz/cm



Current Data Parameters
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PROCNO 1

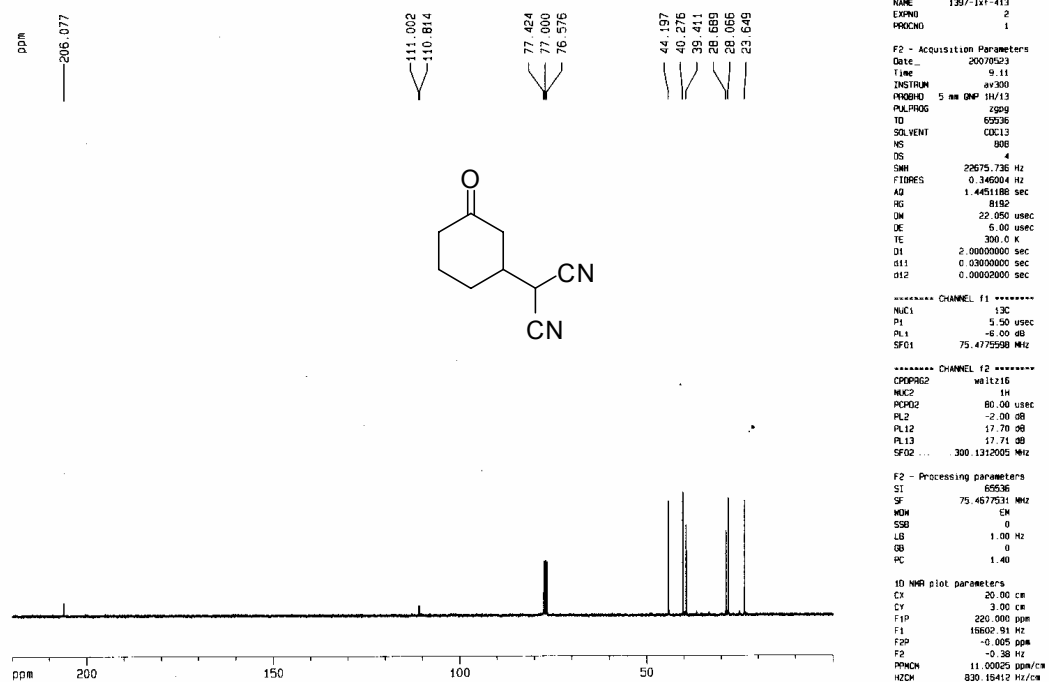
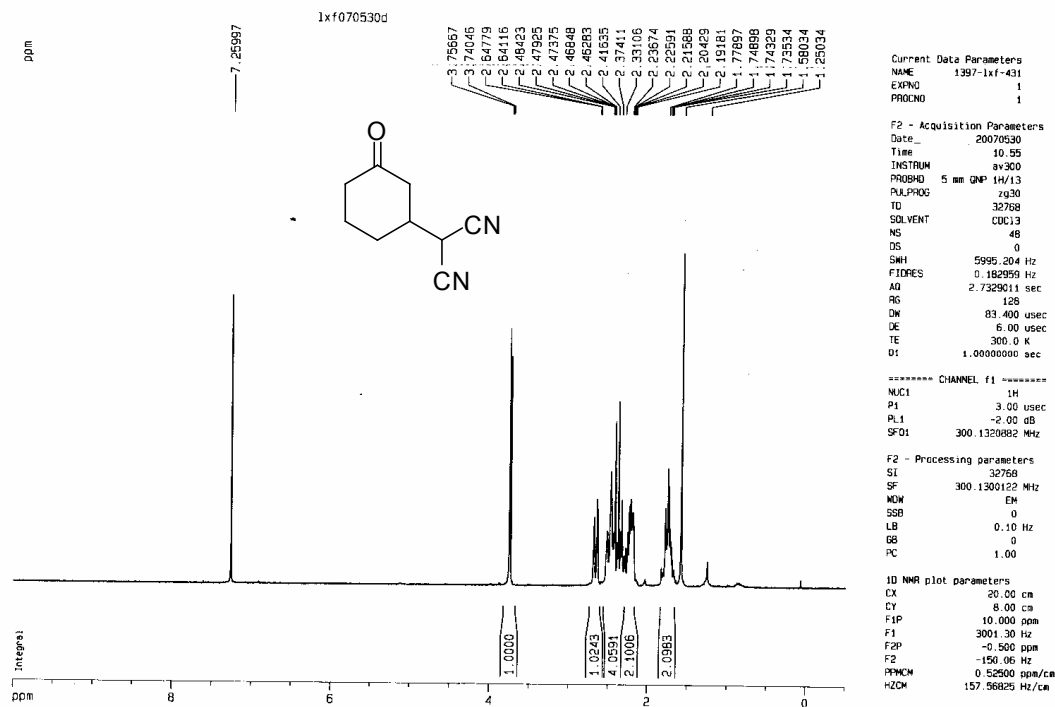
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NS 744
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FIDRES 0.346004 Hz
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d12 0.00002000 sec

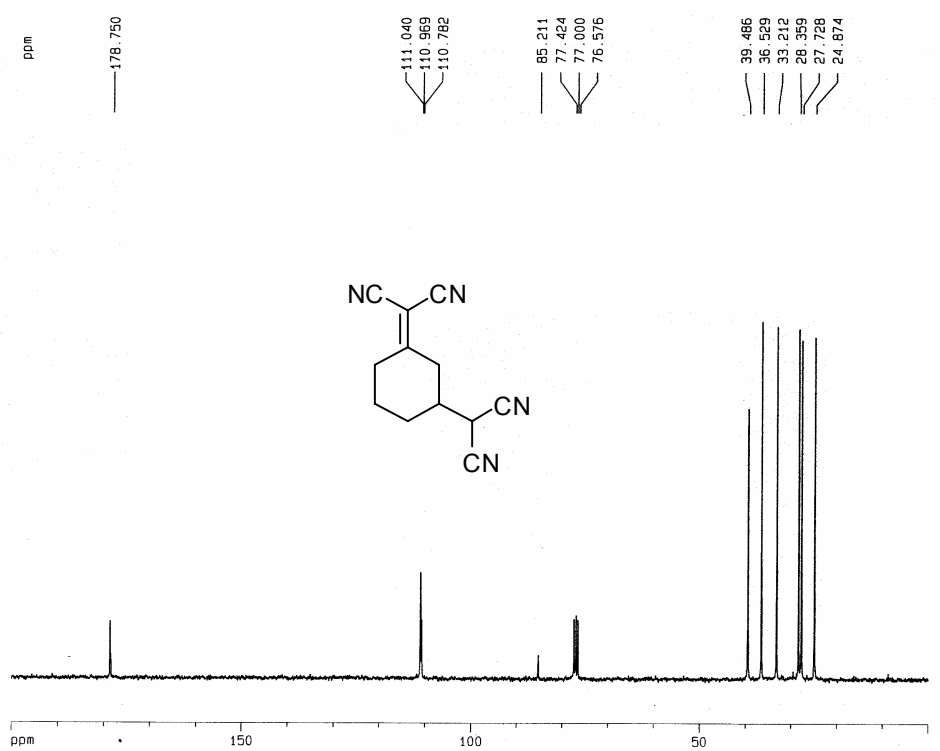
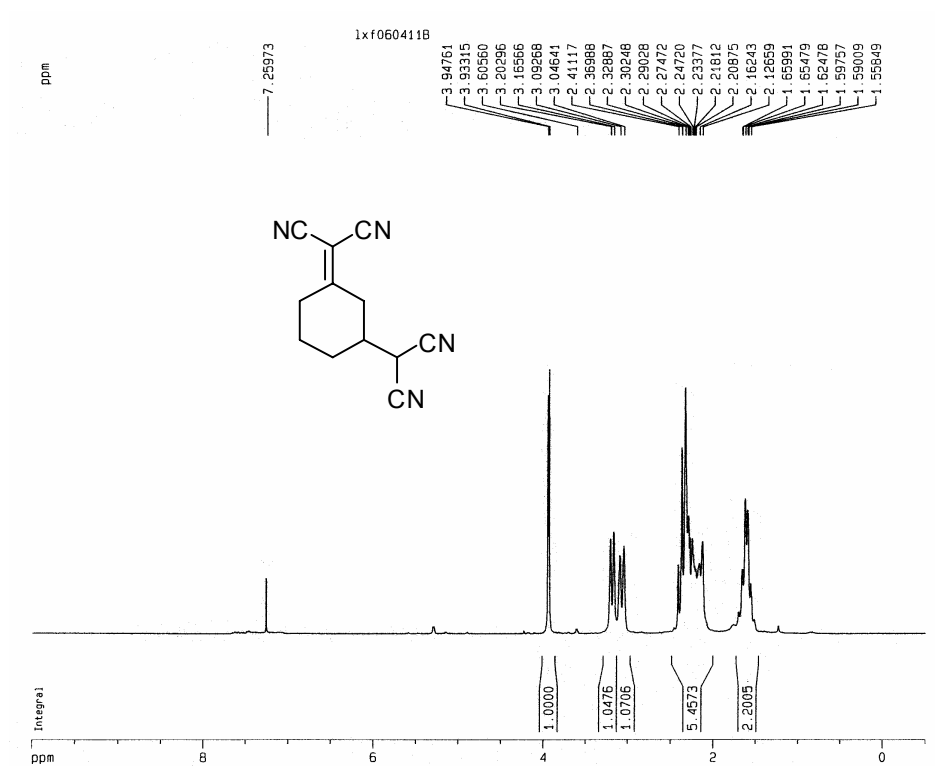
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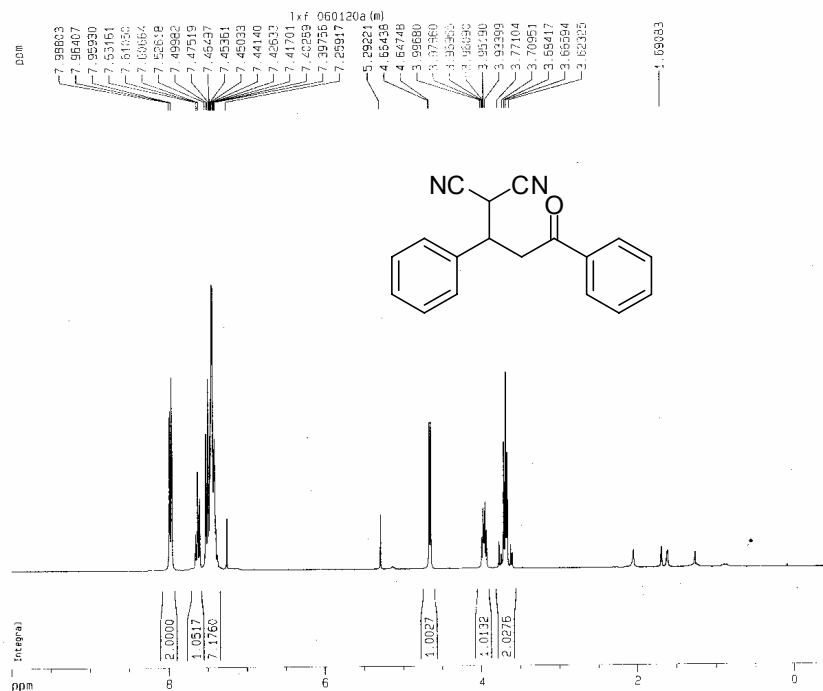
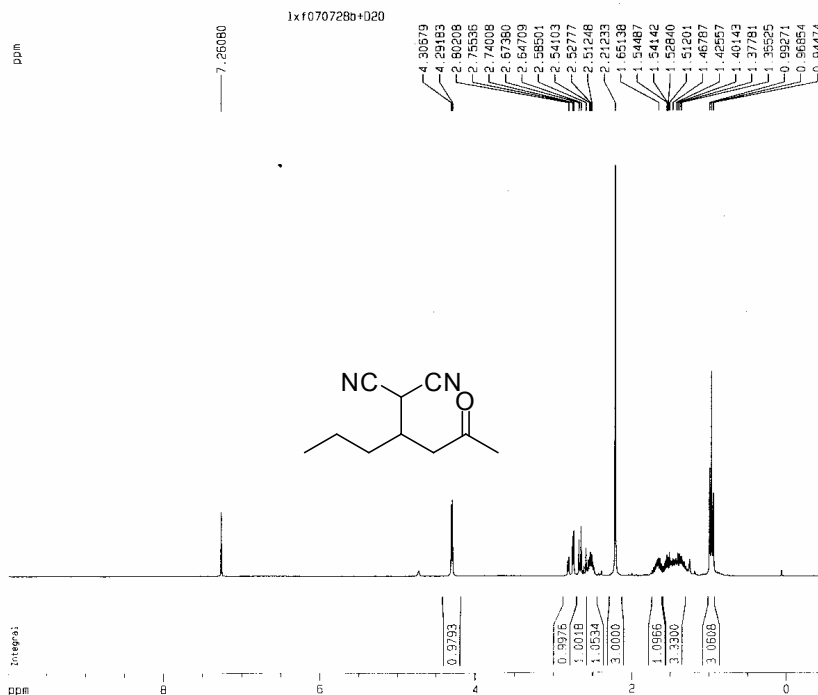
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NUC2 1H
PCPD2 80.00 usec
PL2 -2.00 dB
PL12 17.70 dB
PL13 17.71 dB
SFO2 300.1312005 MHz

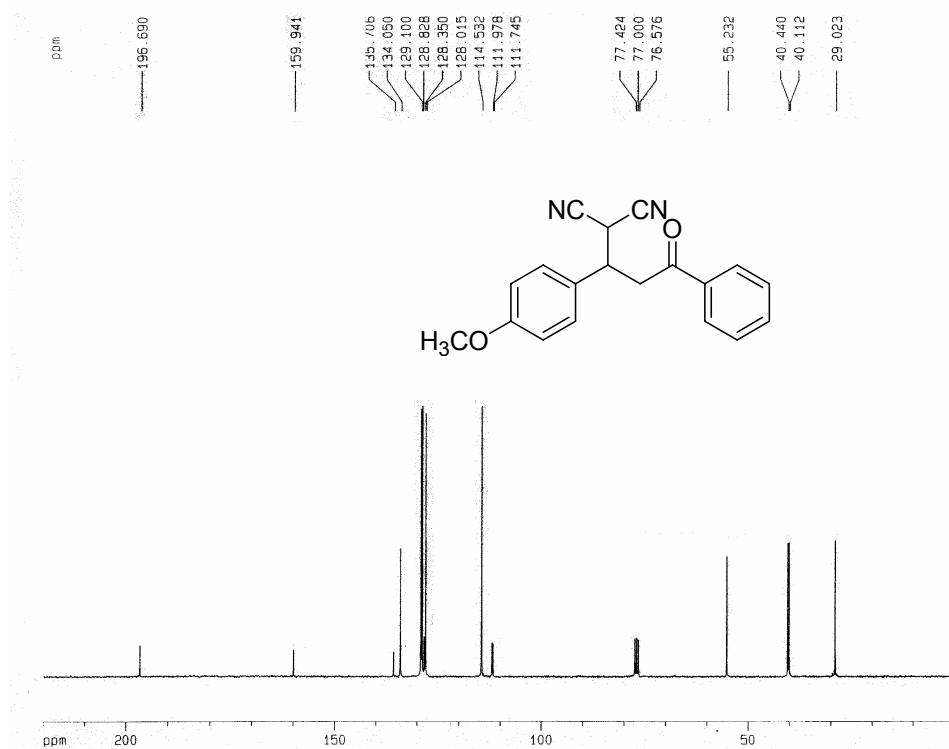
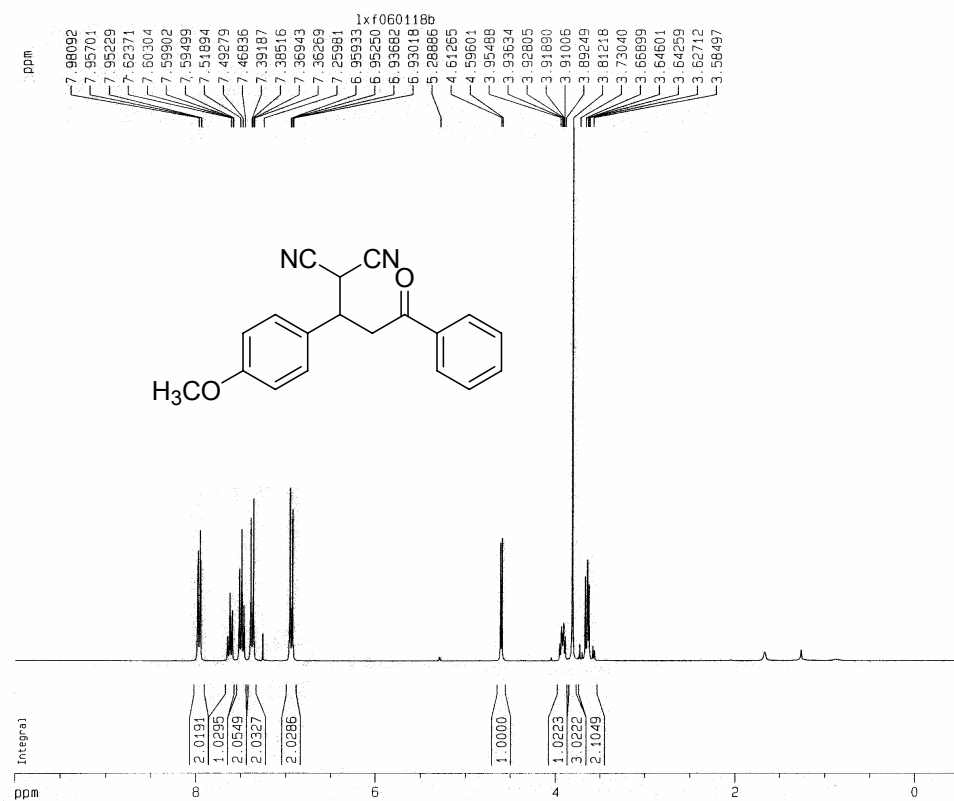
F2 - Processing parameters
SI 65536
SF 75.4677536 MHz
WDW EN
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

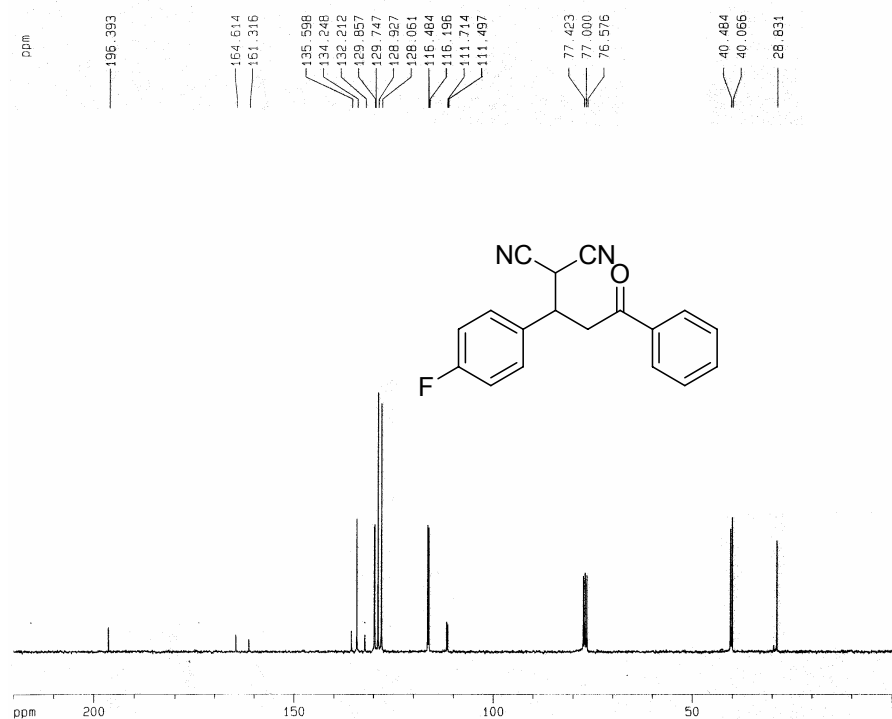
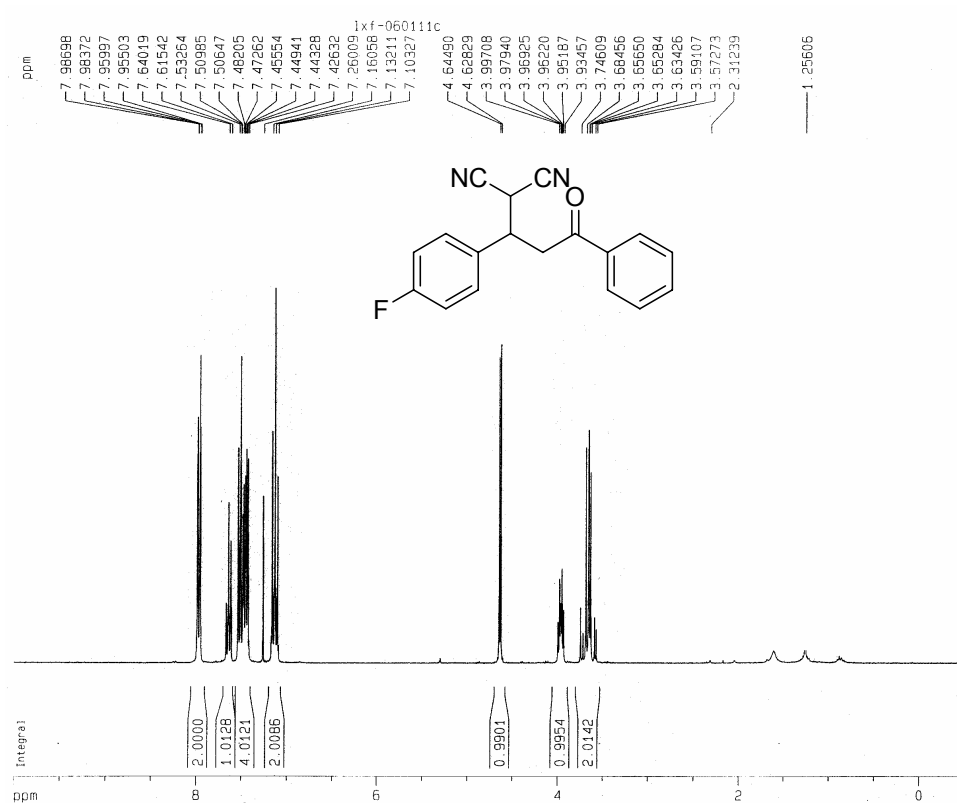
1D NMR plot parameters
CX 20.00 cm
CY 6.00 cm
F1P 220.500 ppm
F1 15640.54 Hz
F2P -0.500 ppm
F2 -37.73 Hz
PRACH 11.05000 ppm/cm
HZCM 833.51864 Hz/cm

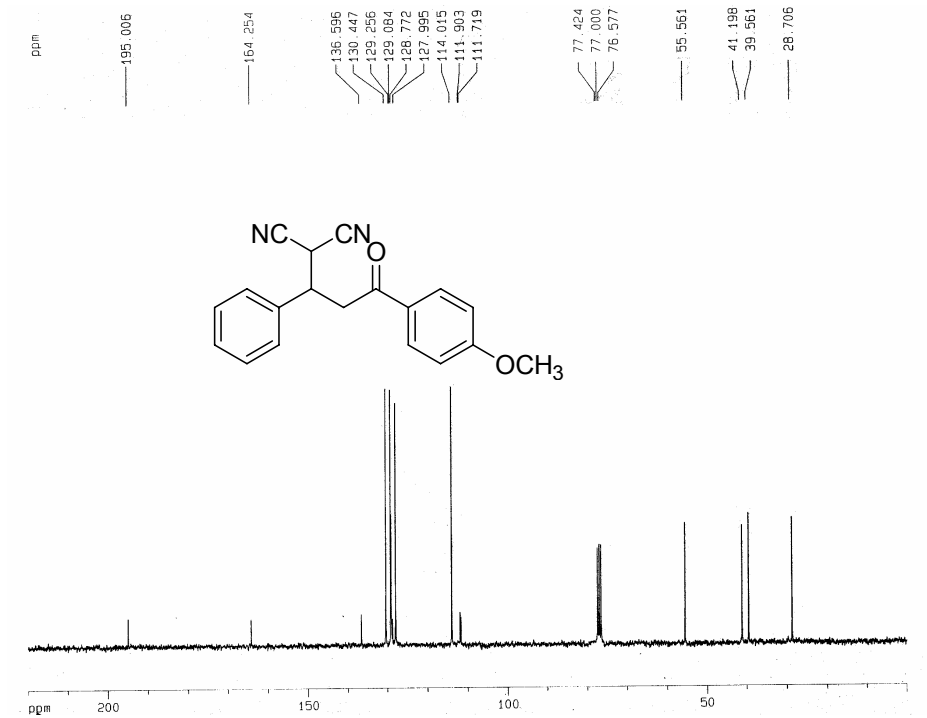
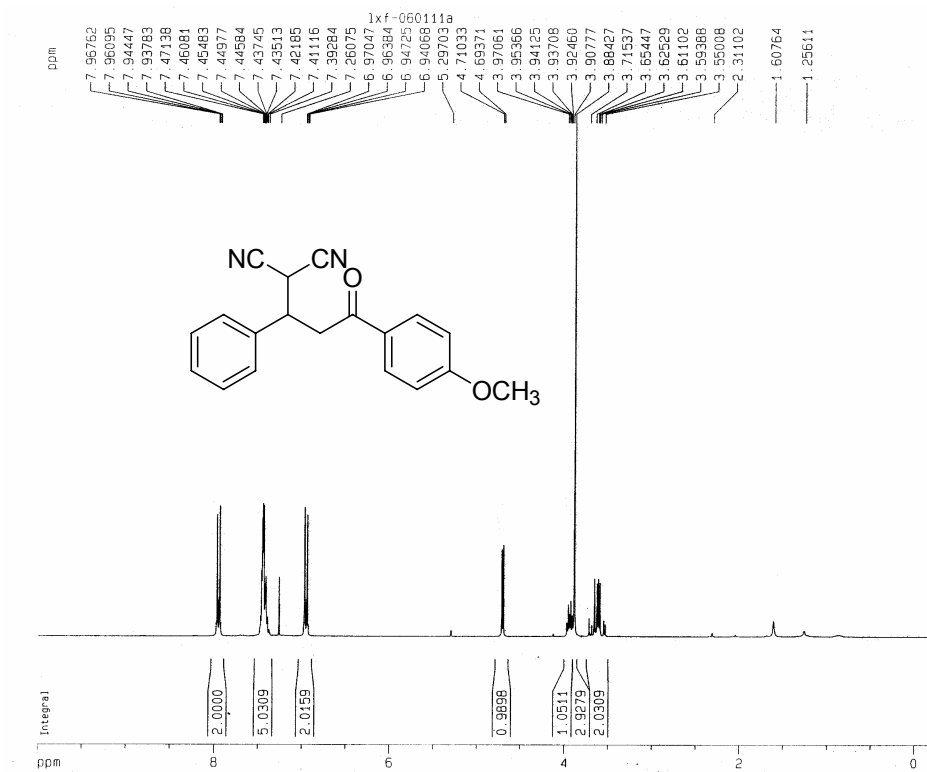




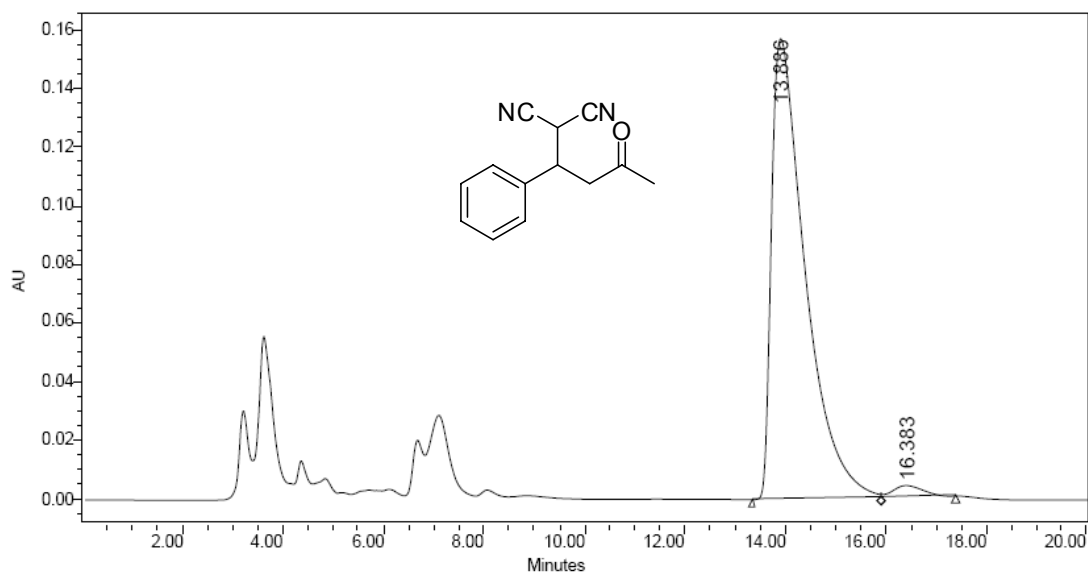
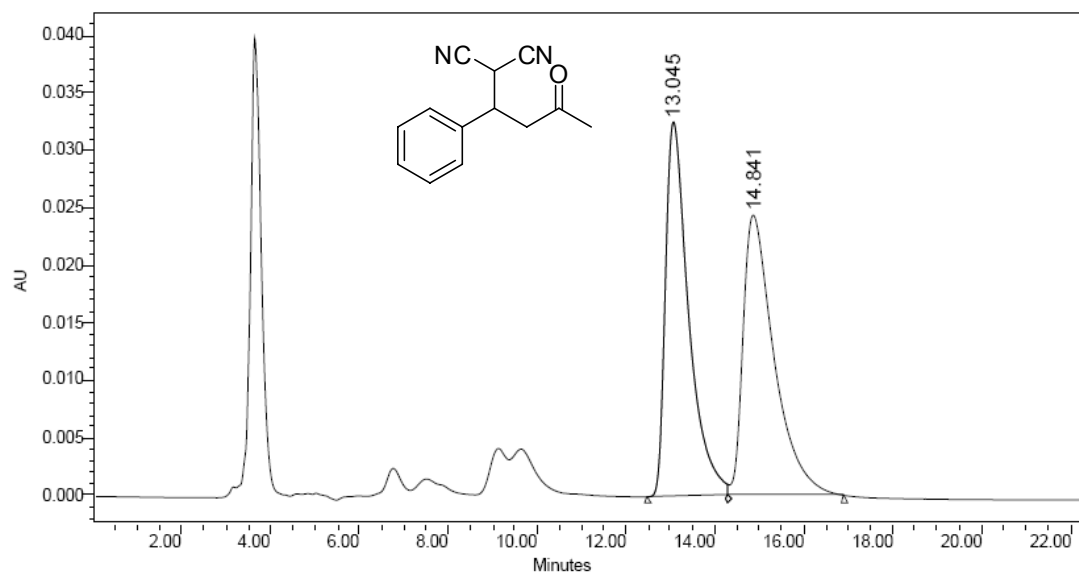


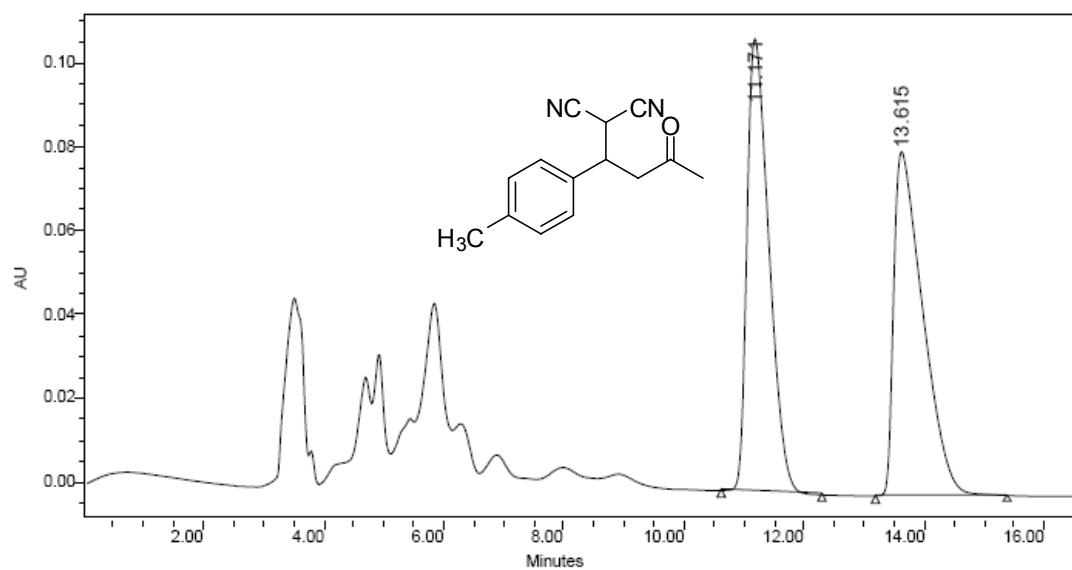




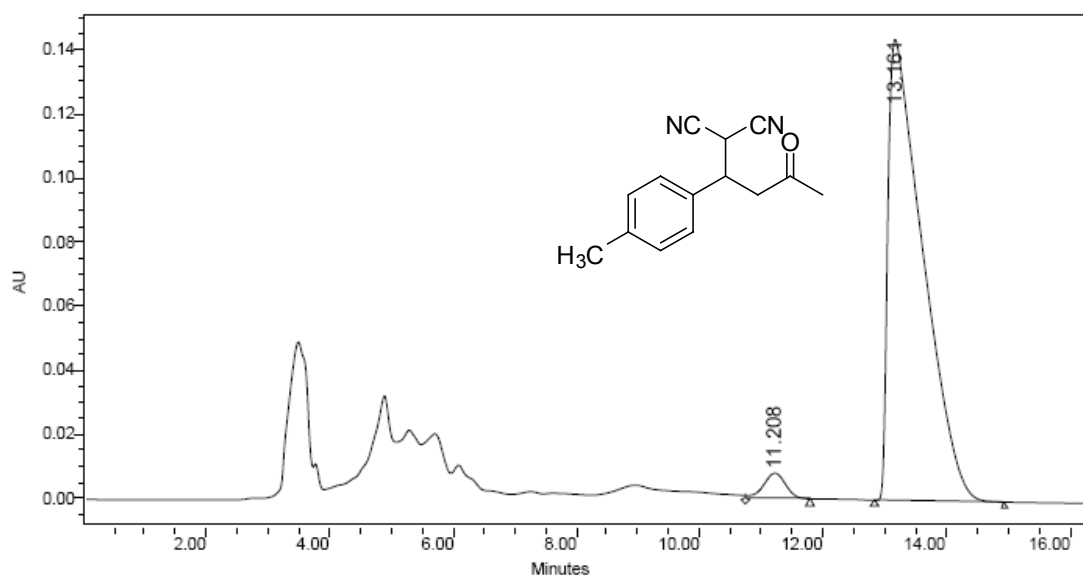


2. HPLC and GC chromatograms

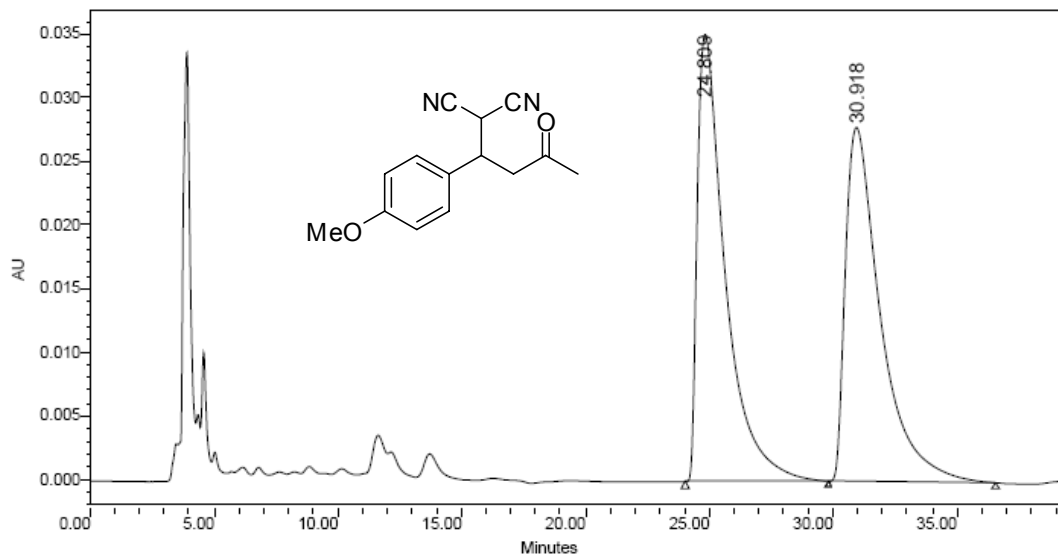




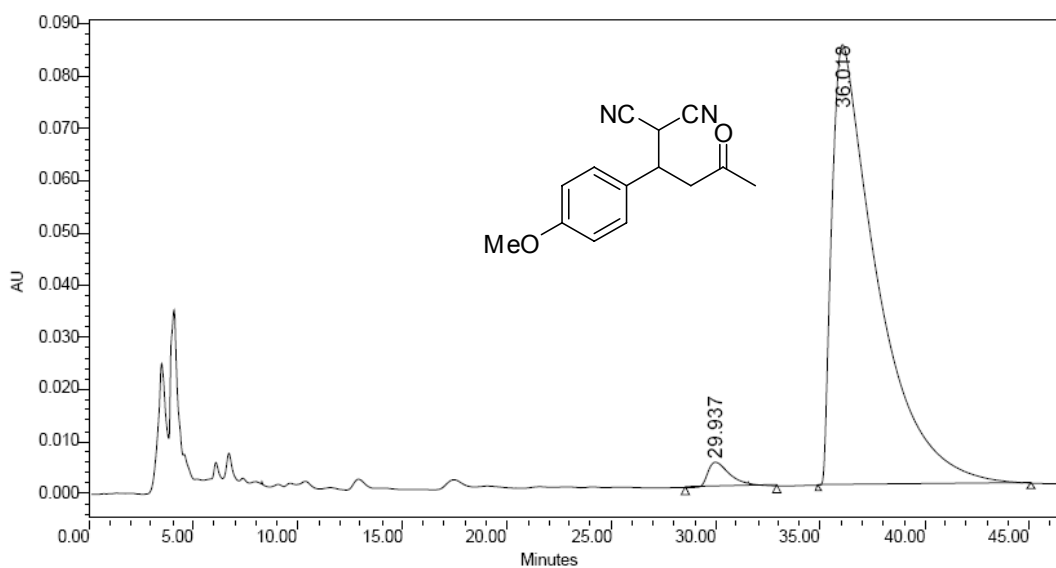
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.171	2740761	49.87	107992	56.85
2	13.615	2754698	50.13	81982	43.15



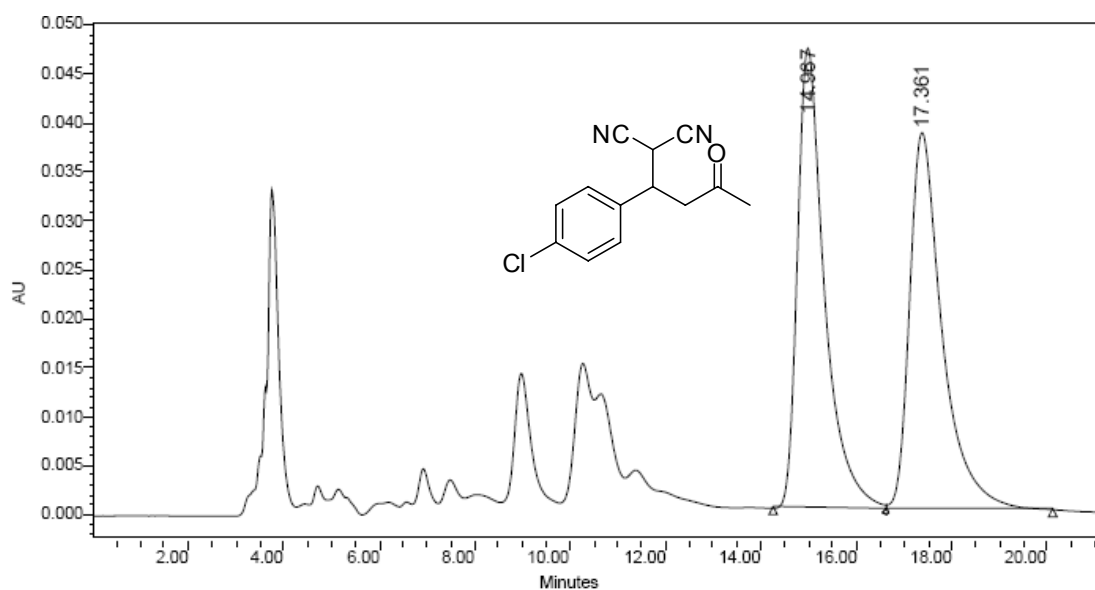
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.208	194707	3.32	7889	5.19
2	13.161	5664096	96.68	143974	94.81



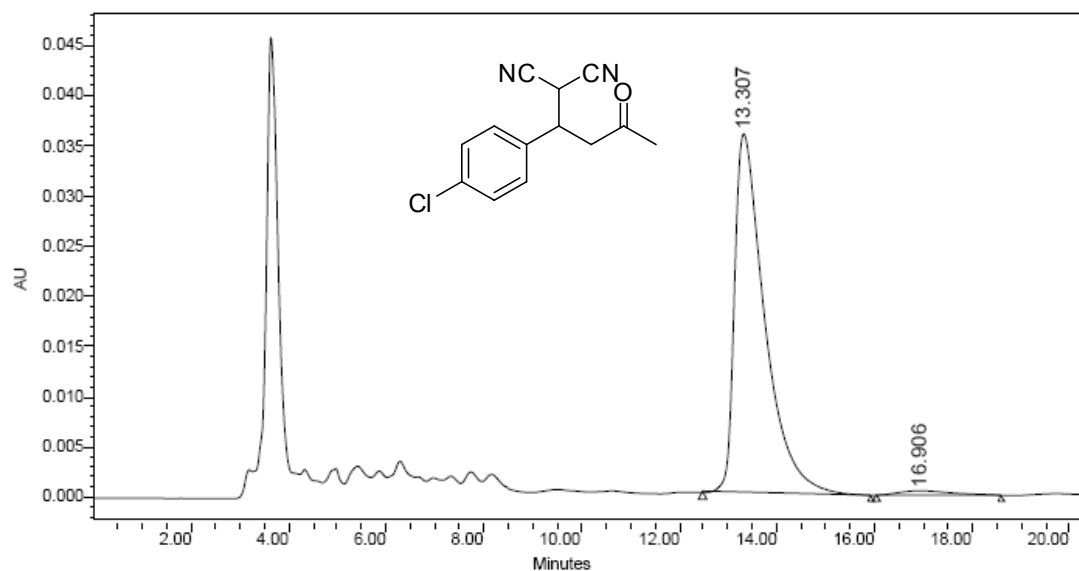
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	24.809	2759581	50.18	35117	55.82
2	30.918	2740317	49.82	27794	44.18



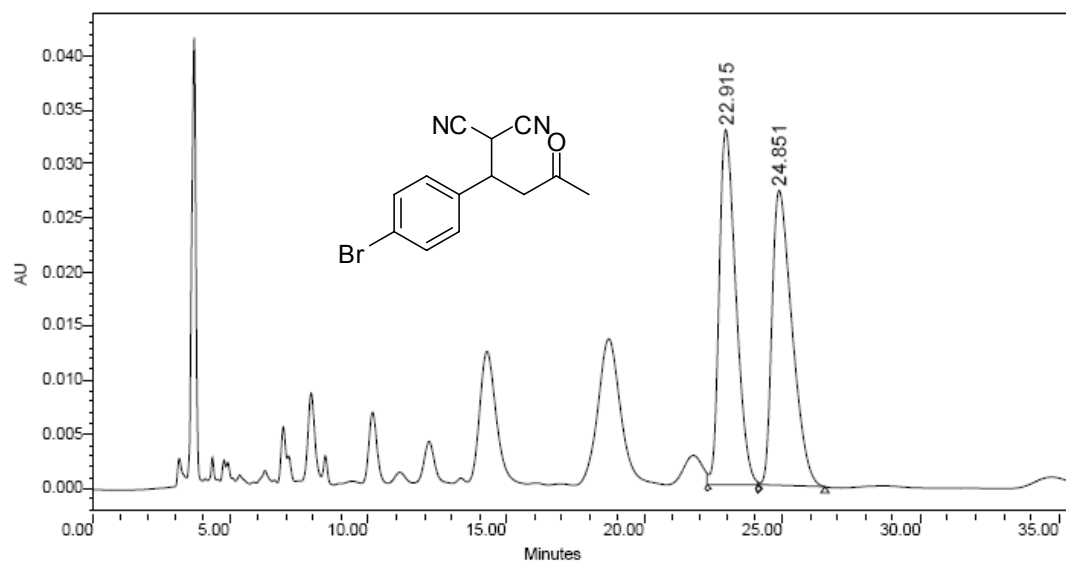
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	29.937	360821	2.76	4748	5.32
2	36.018	12709424	97.24	84430	94.68



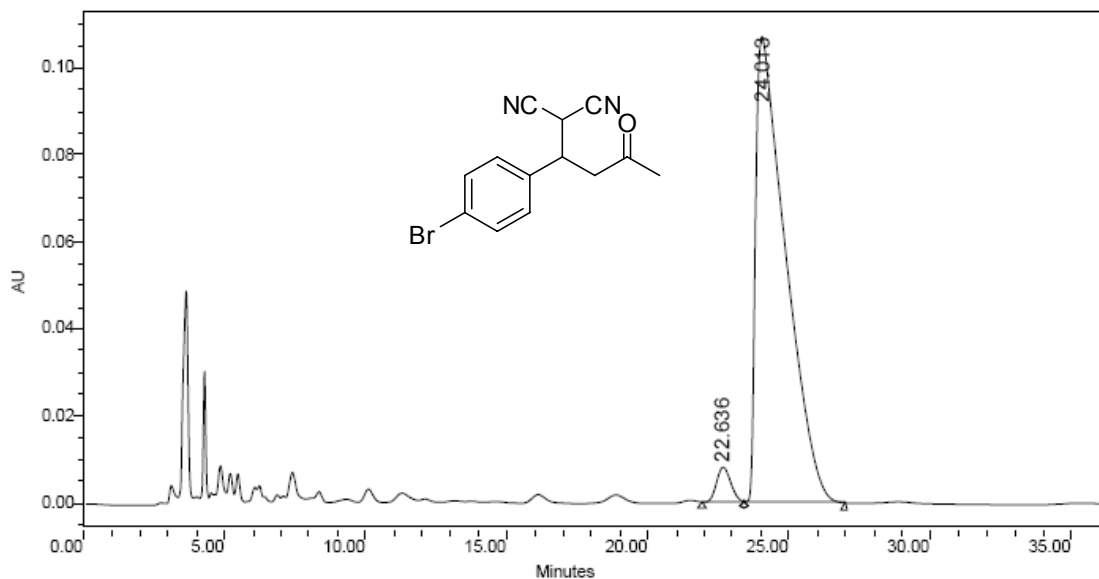
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	14.967	1855268	50.36	46980	55.00
2	17.361	1828621	49.64	38431	45.00



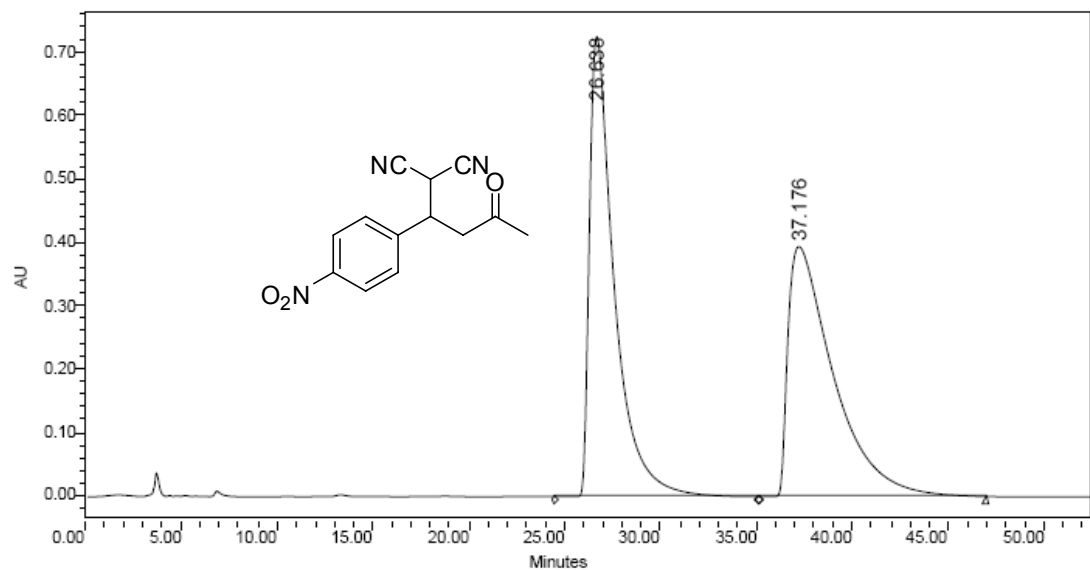
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	13.307	1543654	97.88	35847	98.80
2	16.906	33510	2.12	436	1.20



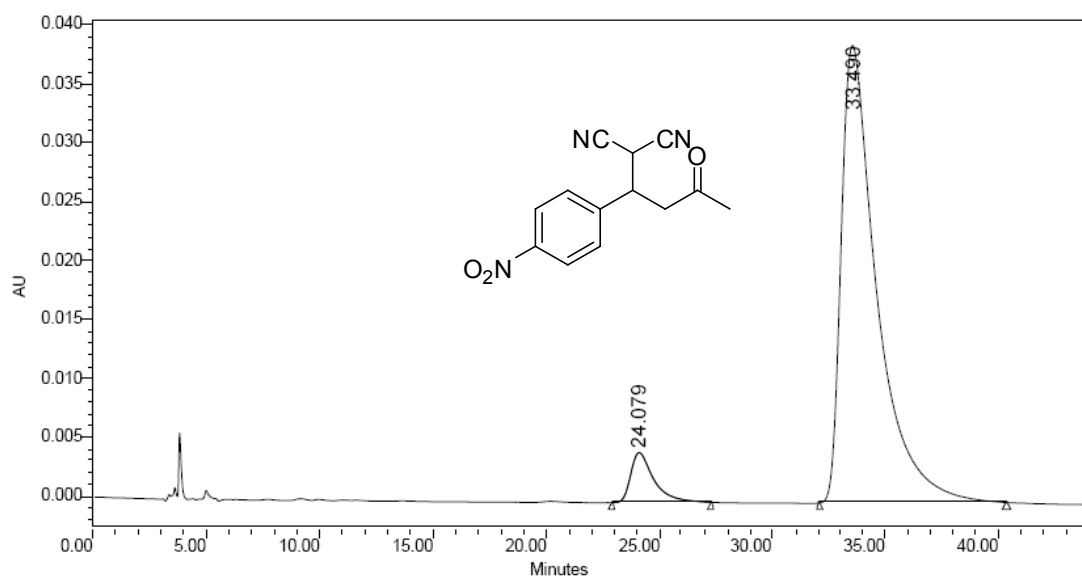
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	22.915	1391156	50.08	32918	54.59
2	24.851	1386609	49.92	27385	45.41



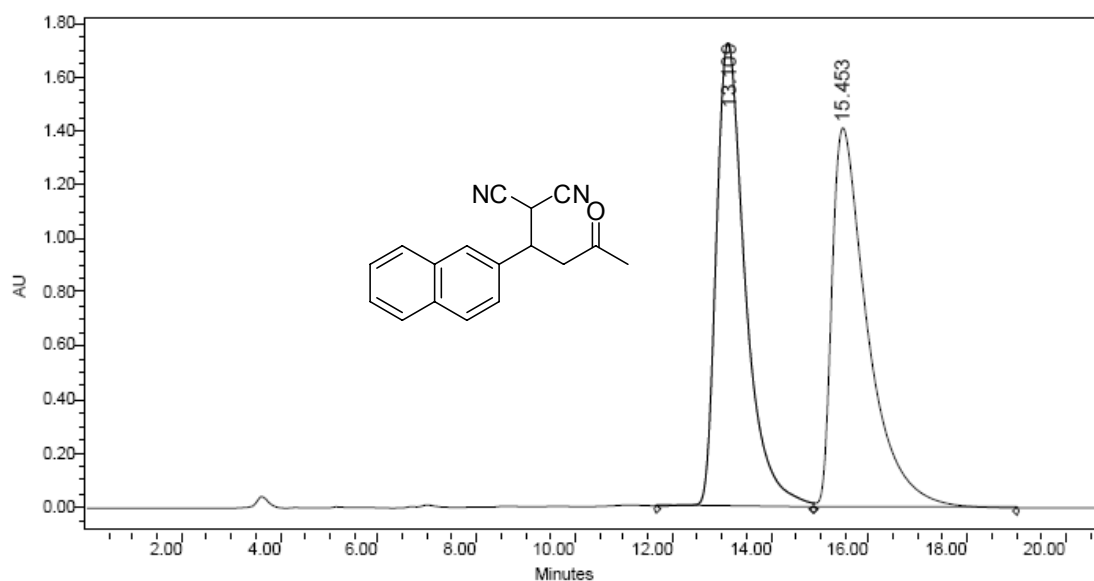
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	22.636	283390	3.46	8025	6.97
2	24.013	7896710	96.54	107072	93.03



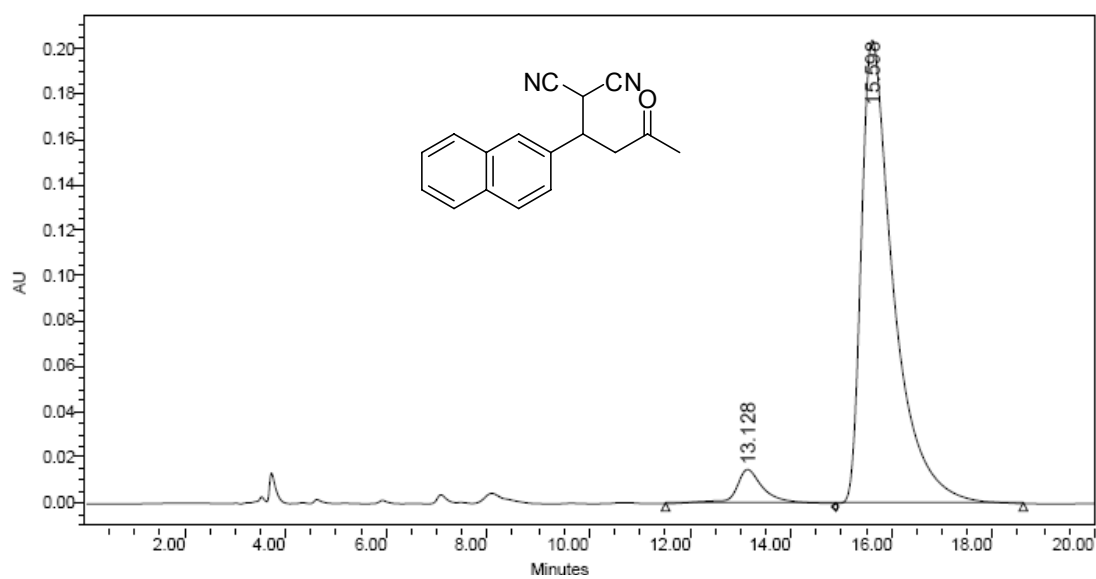
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	26.638	65256292	50.13	726311	64.79
2	37.176	64918943	49.87	394695	35.21



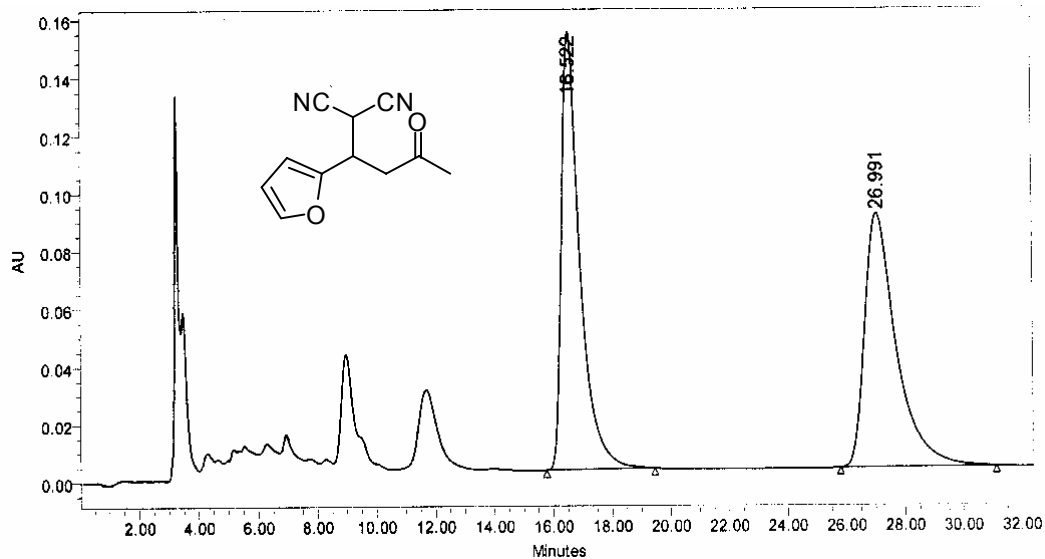
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	24.079	299647	6.61	4231	9.83
2	33.490	4234608	93.39	38815	90.17



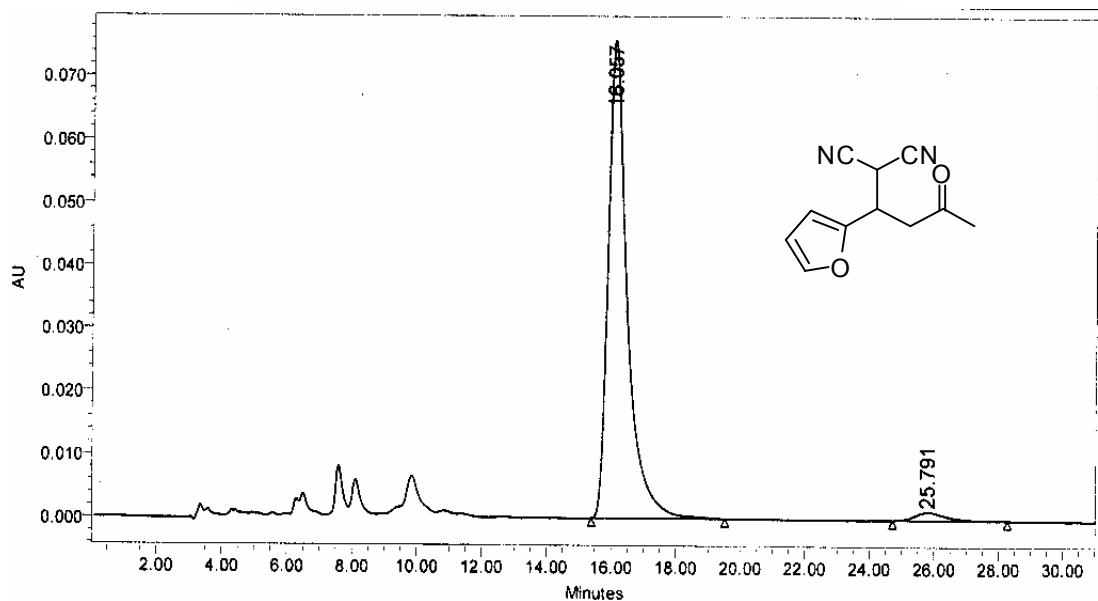
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	13.109	71290217	50.09	1727524	55.03
2	15.453	71031919	49.91	1411912	44.97



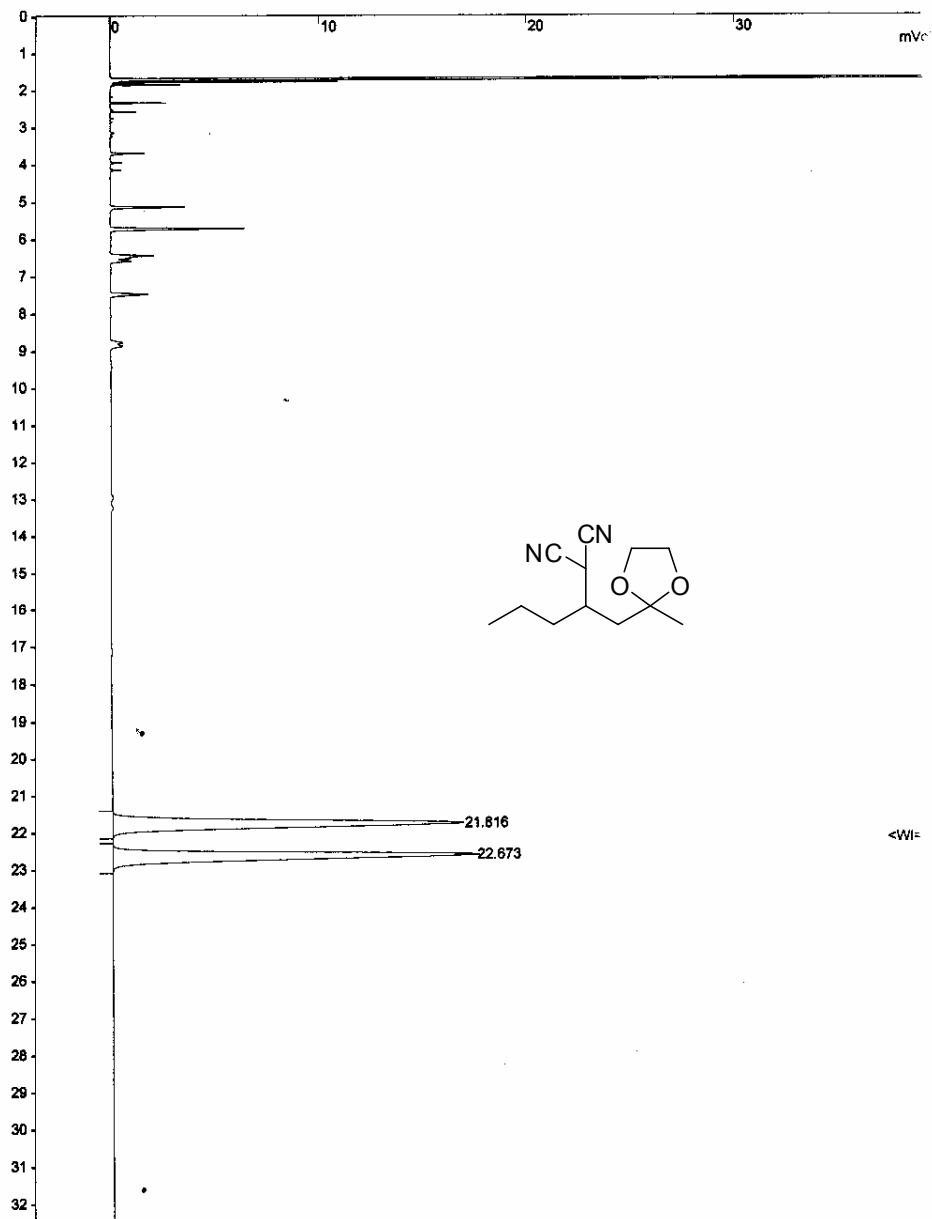
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	13.128	586989	6.09	15024	6.86
2	15.598	9045317	93.91	204059	93.14



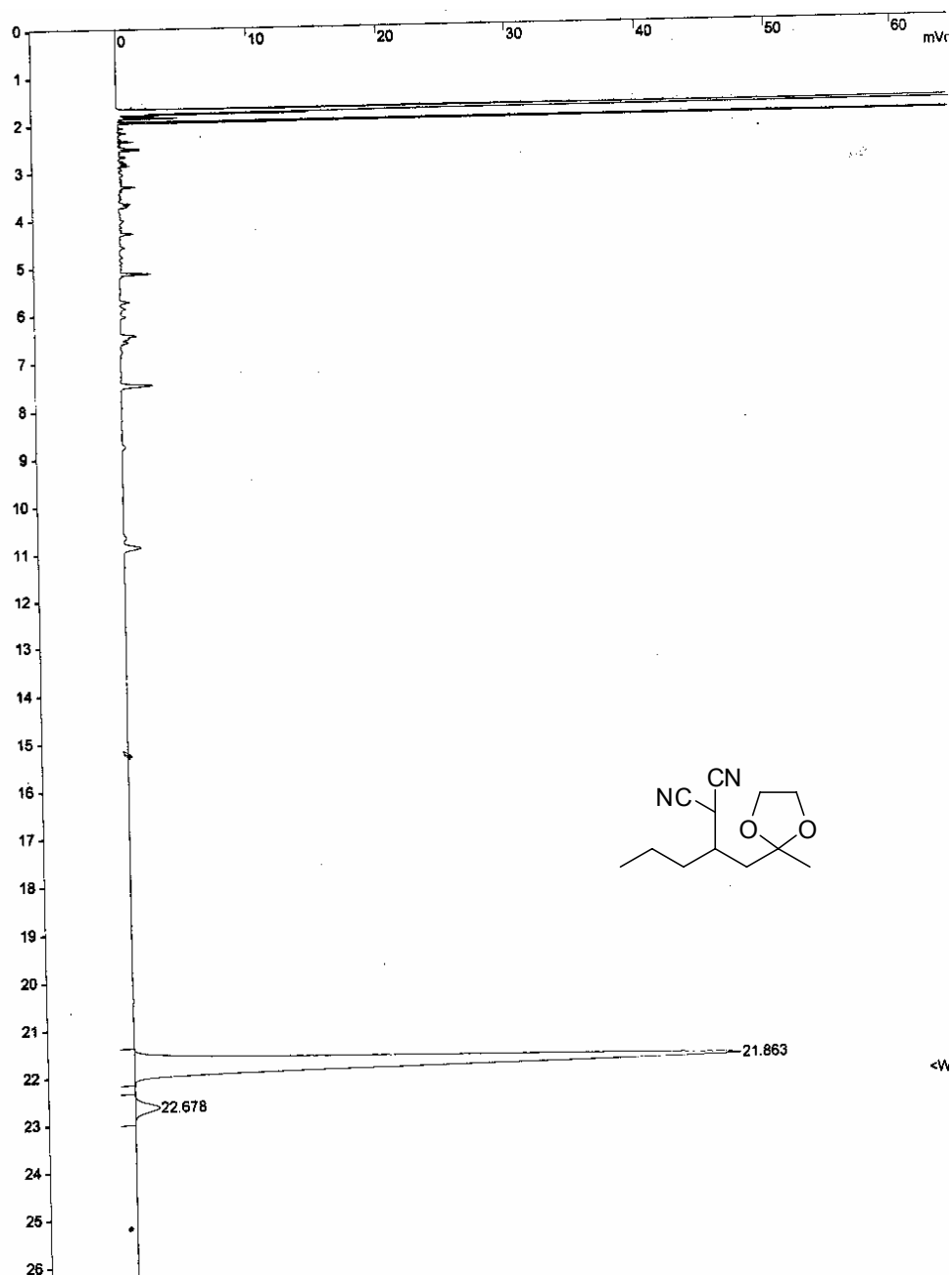
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	16.522	6575994	50.17	151410	63.27
2	26.991	6531305	49.83	87913	36.73



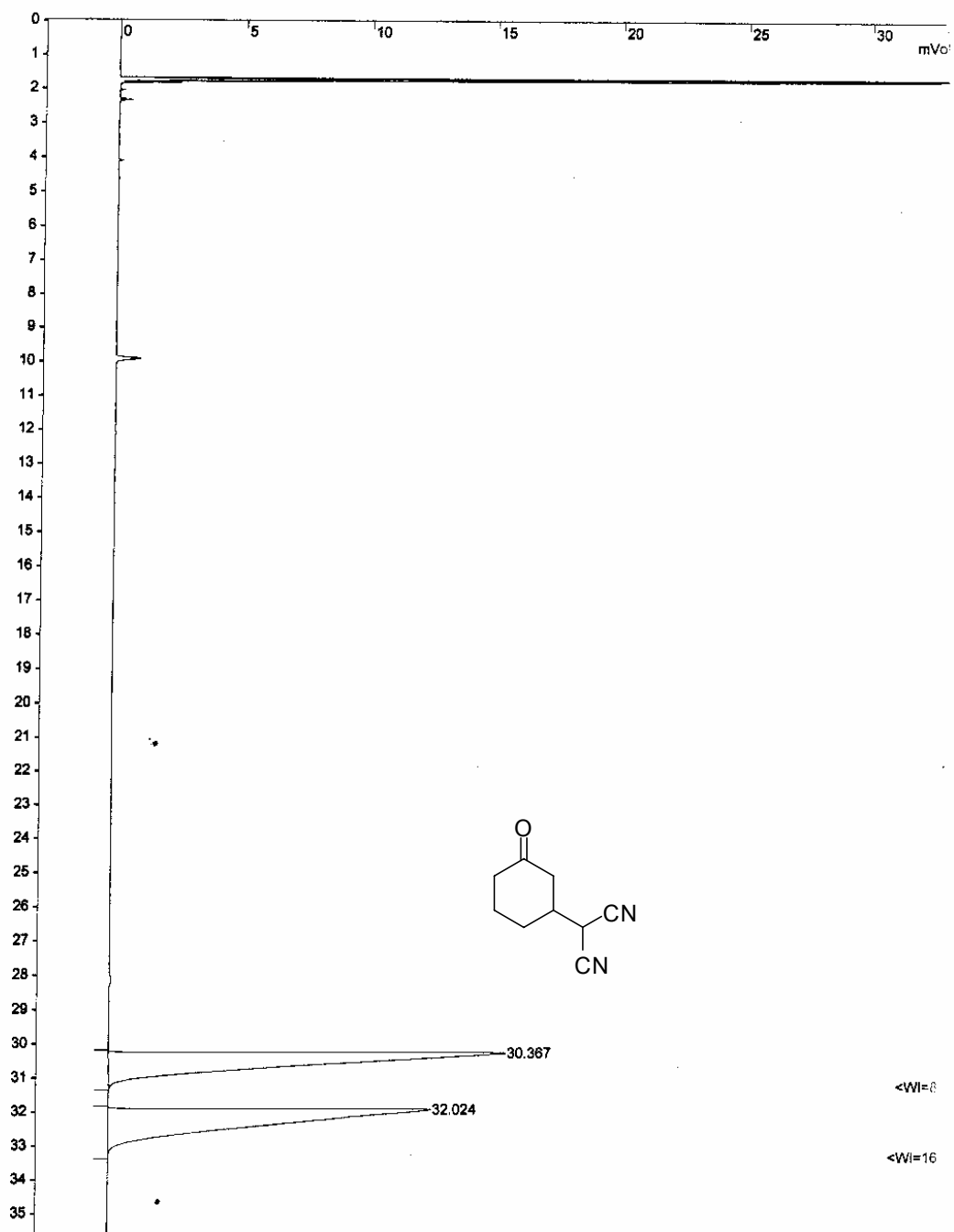
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	16.057	3100566	97.38	75820	98.32
2	25.791	83298	2.62	1294	1.68



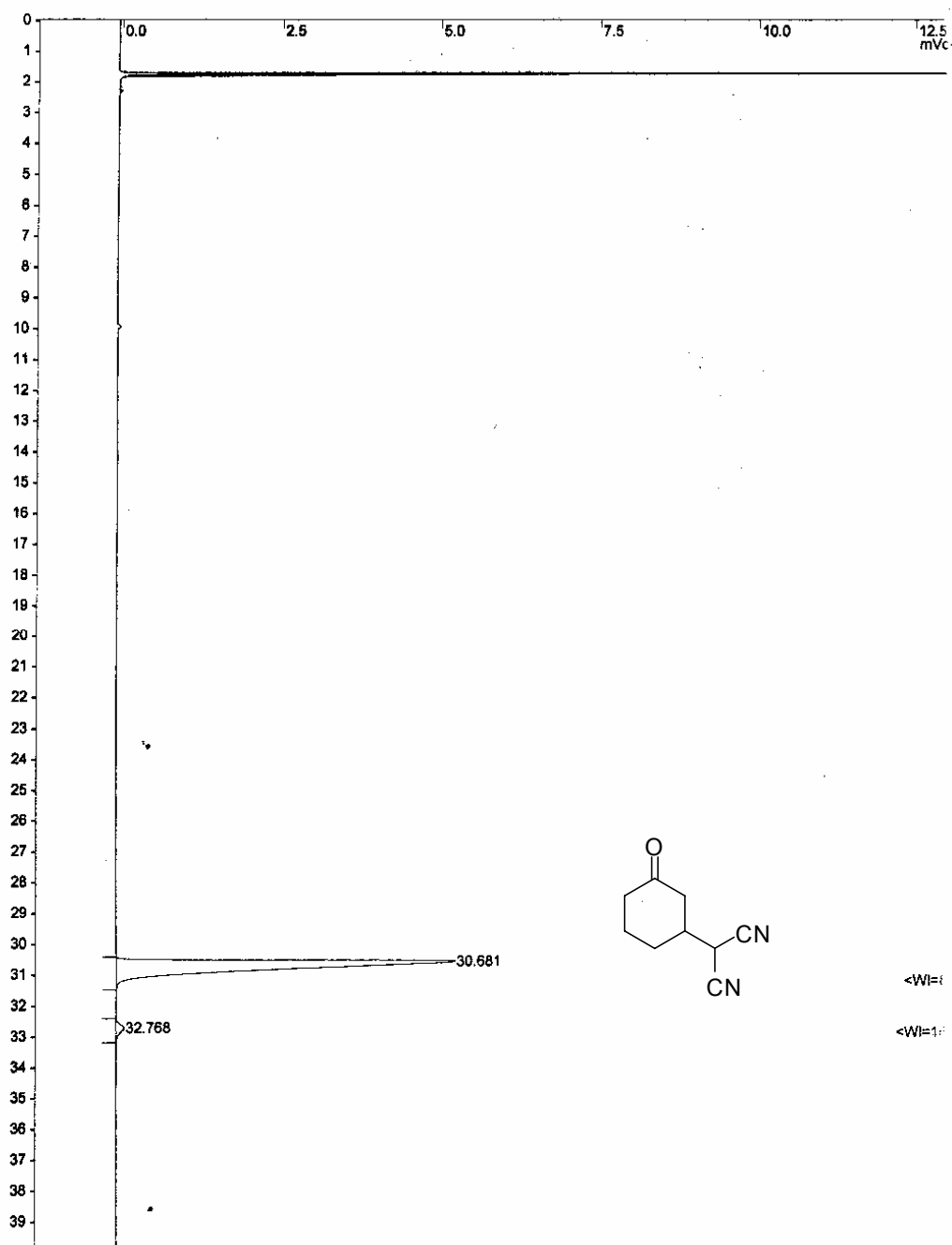
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.9656	21.816	0.000	225432	BB	12.6	U
2		50.0344	22.673	0.000	225742	BB	12.1	
Totals:		100.0000		0.000	451174			



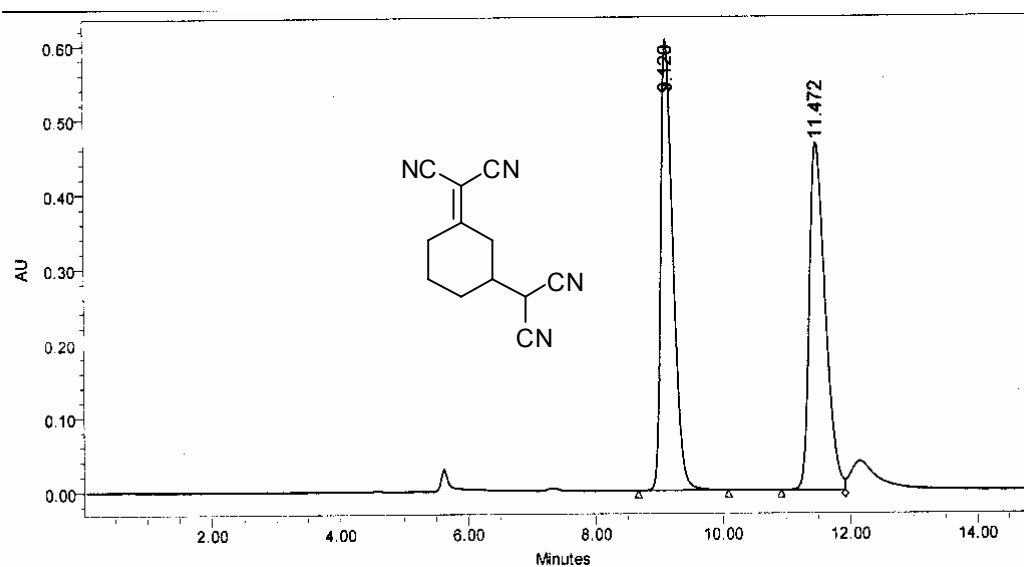
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		96.6250	21.863	0.000	670568	BB	13.5	
2		3.3750	22.678	0.000	23422	BB	11.8	
Totals:		100.0000		0.000	693990			



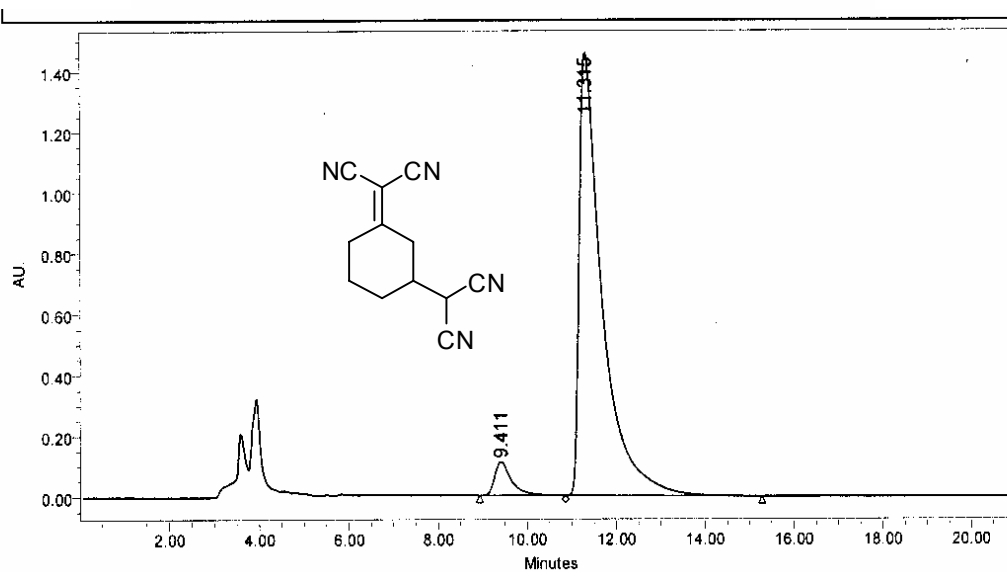
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.9672	30.367	0.000	381238	BB	22.6	
2		50.0328	32.024	0.000	381738	BB	28.6	
Totals:		100.0000		0.000	762976			



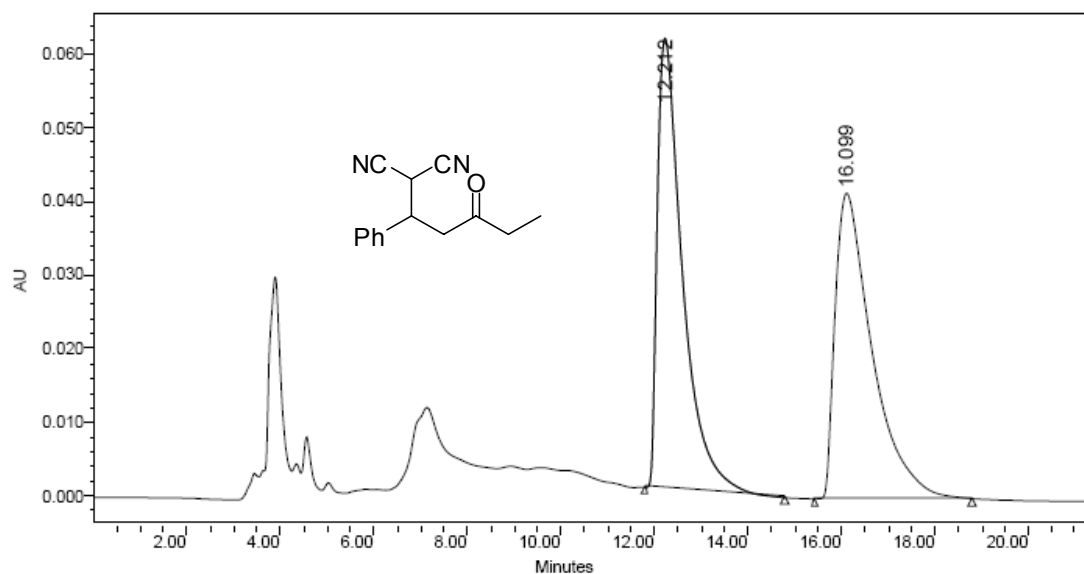
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		97.6672	30.681	0.000	101464	BB	17.6	U
2		2.3328	32.768	0.000	2424	BB	14.7	U
Totals:		100.0000		0.000	103888			



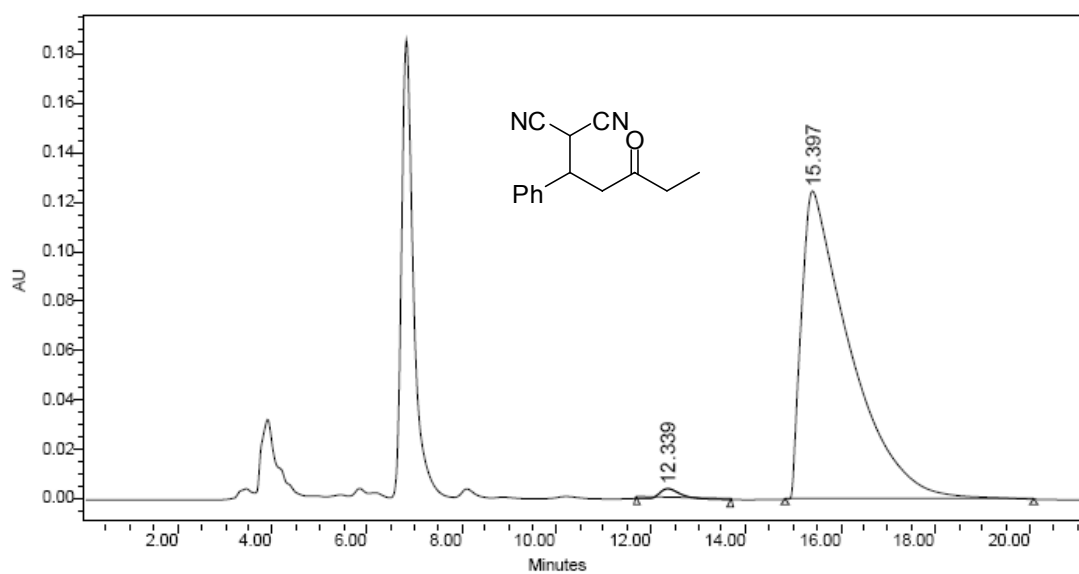
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	9.120	8052059	49.97	605447	56.50
2	11.472	8060940	50.03	466161	43.50



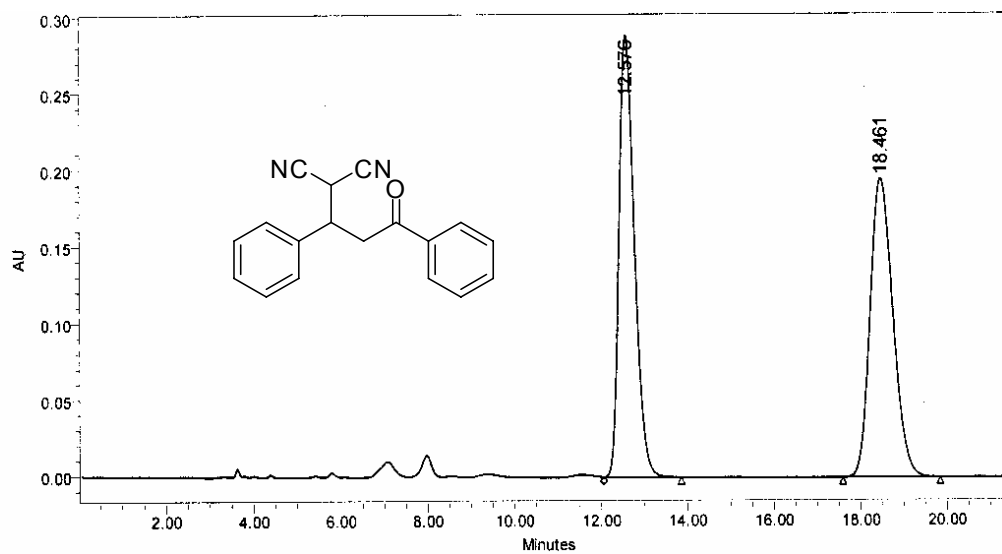
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	9.411	2855996	5.20	109891	7.01
2	11.315	52032832	94.80	1457314	92.99



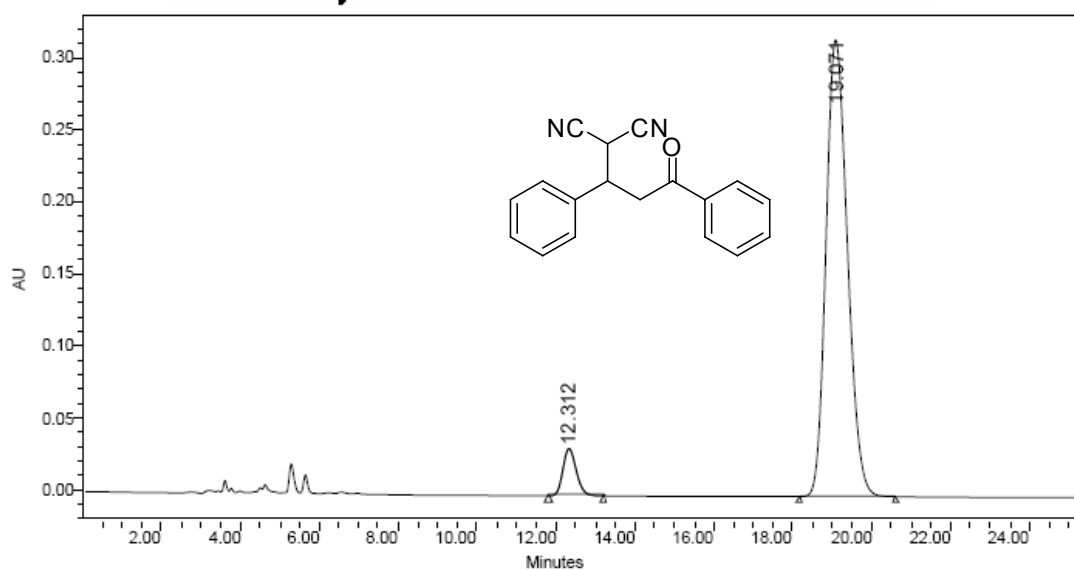
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.212	2299472	50.23	61156	59.57
2	16.099	2278372	49.77	41506	40.43



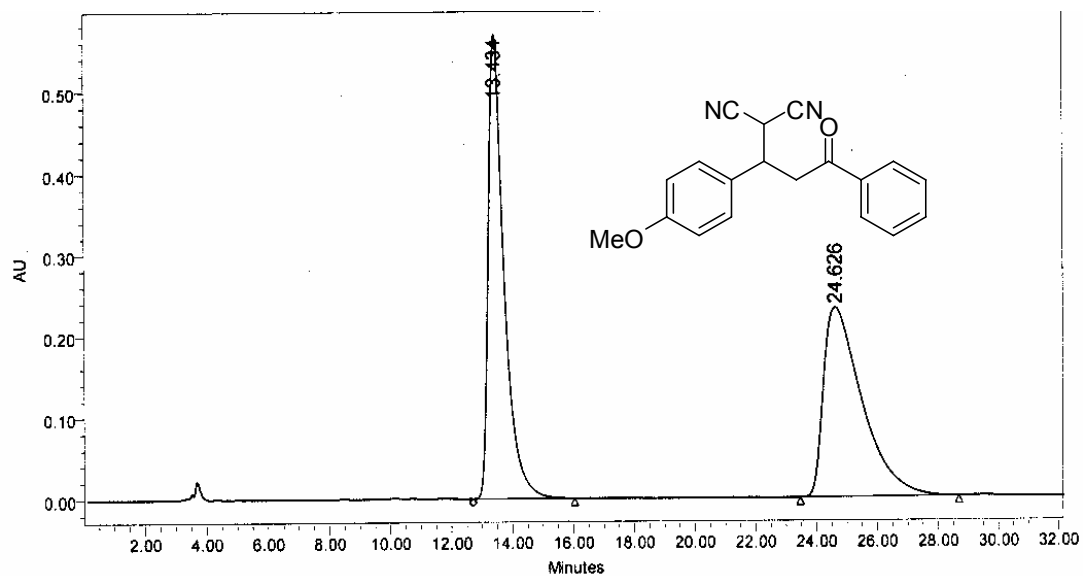
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.339	123473	1.37	4069	3.16
2	15.397	8914597	98.63	124753	96.84



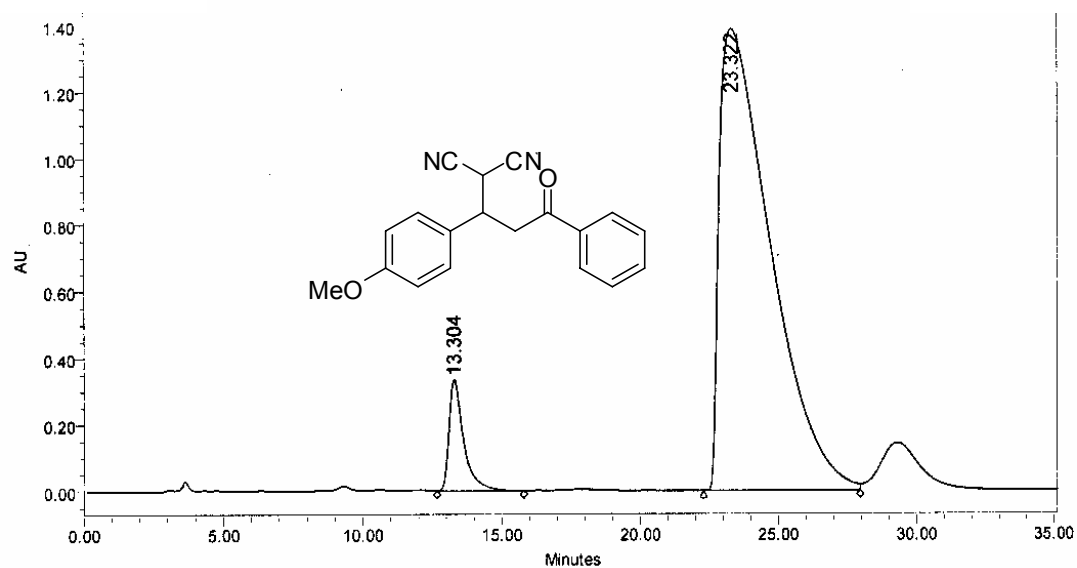
	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	12.576	7121121	49.90	289005	59.66
2	18.461	7148850	50.10	195440	40.34



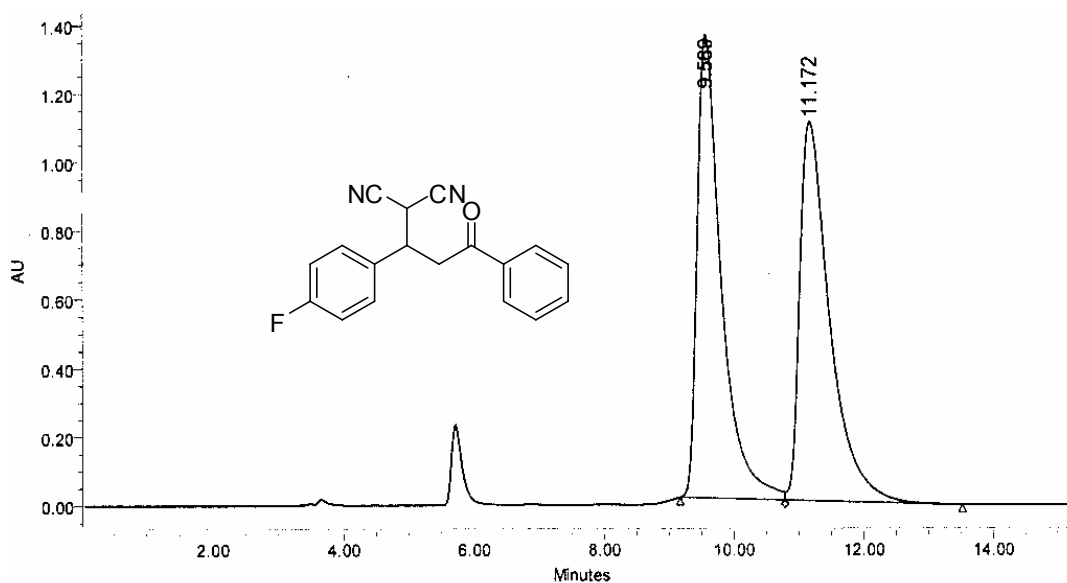
	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	12.312	767410	6.06	32706	9.37
2	19.071	11904956	93.94	316483	90.63



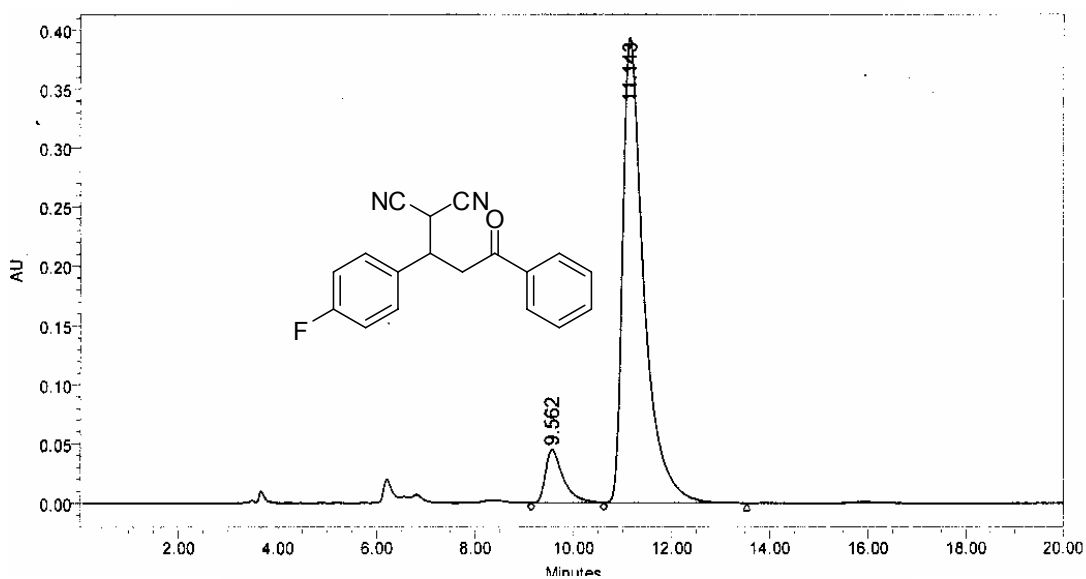
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	13.434	20348142	49.94	569147	71.03
2	24.626	20399379	50.06	232100	28.97



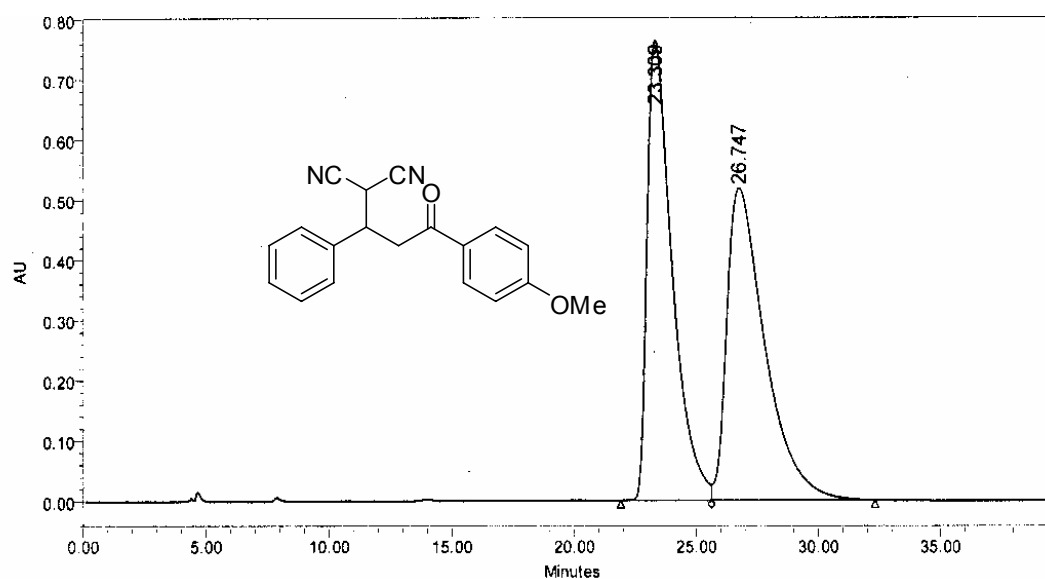
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	13.304	12365124	6.46	336434	19.51
2	23.322	179159110	93.54	1387797	80.49



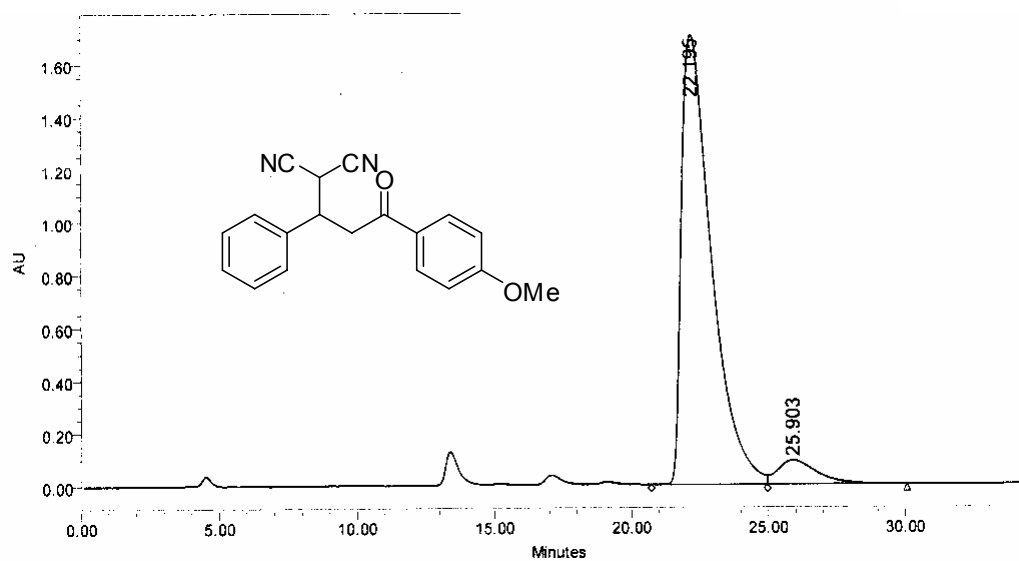
	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	9.569	34947616	49.79	1348936	55.02
2	11.172	35244699	50.21	1102665	44.98



	RT (min)	Area ($\mu\text{V}\cdot\text{sec}$)	% Area	Height (μV)	% Height
1	9.562	1121521	8.70	44817	10.22
2	11.143	11771279	91.30	393775	89.78



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	23.309	54413014	49.24	762426	59.58
2	26.747	56097091	50.76	517258	40.42



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	22.195	130003565	93.47	1706365	94.93
2	25.903	9078451	6.53	91185	5.07