Supplementary Material (ESI) for OBC

Benzoyl Radicals from (Hetero)aromatic Aldehydes. Decatungstate Photocatalyzed Synthesis of Substituted Aromatic Ketones.

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1) Selected absorption spectra of starting aldehydes, TBADT and reaction mixture.

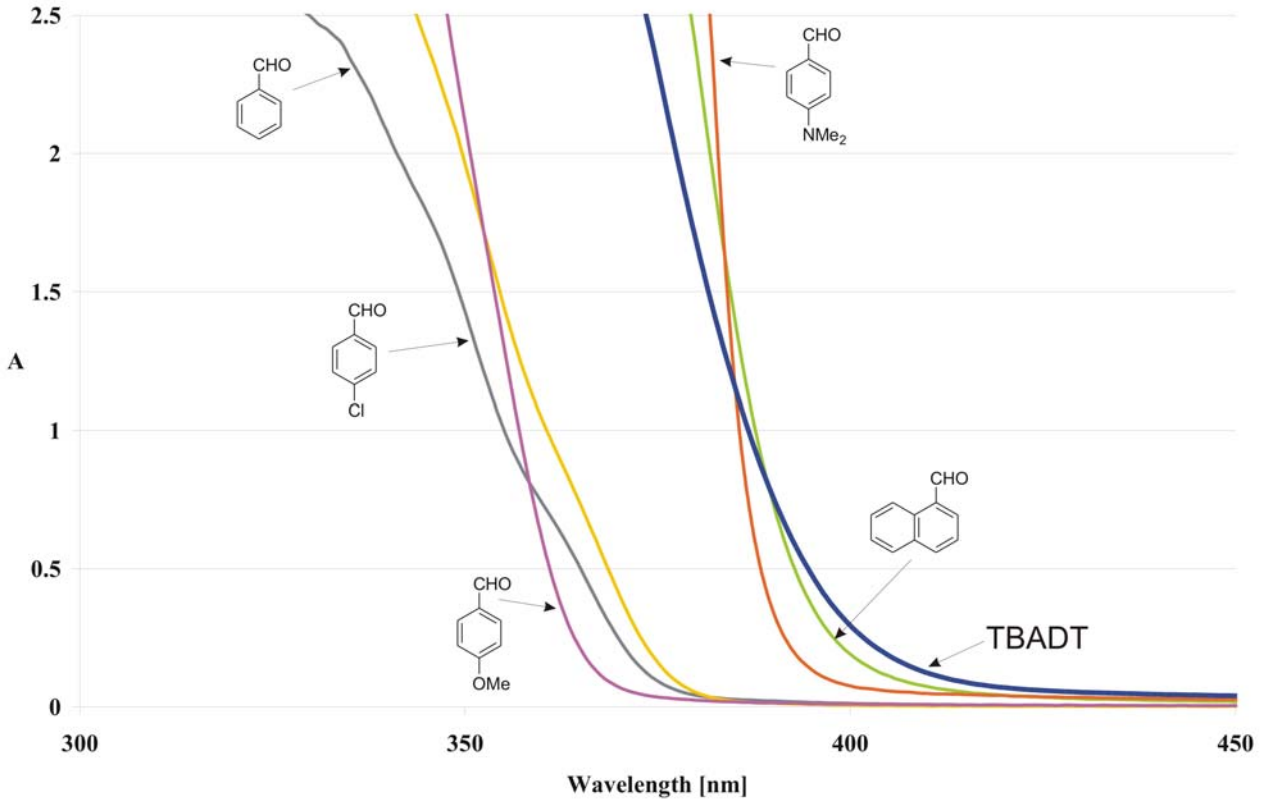


Figure S1 Absorption spectra of selected aldehydes (0.1 M) and of TBADT (0.002 M, these are the concentration used in preparative experiments).

As it is apparent from Figure S1, when the competitive absorption of the aldehyde is not overwhelming (as for aldehydes **1a-c**) the reaction occurred whereas where the absorption is comparable with TBADT (e.g. for napthaldehyde and 4-aminobenzaldehyde) no acylation took place.

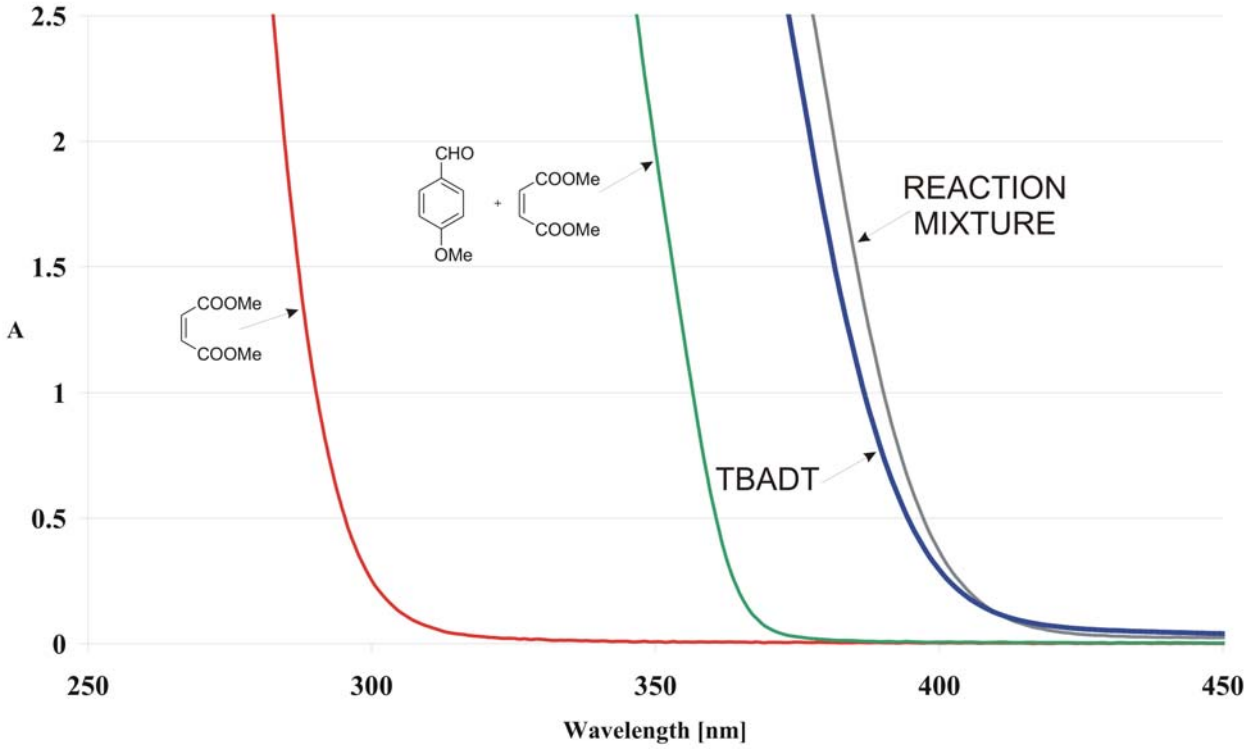
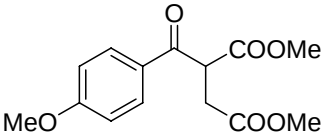


Figure S2 Selected absorption spectra concerning the TBADT photocatalyzed reaction between dimethyl maleate (**2a**) and anisaldehyde (**1a**) in MeCN.

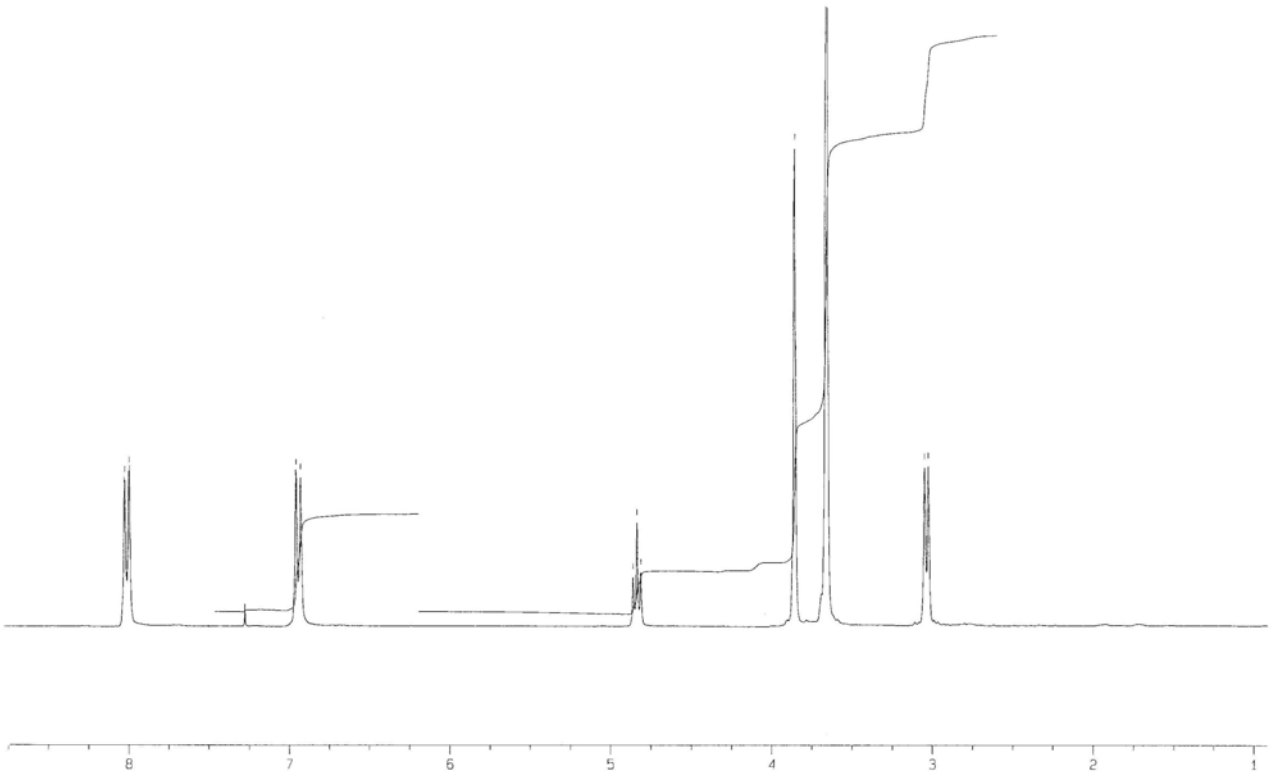
Figure S2 ruled out both a possible competitive absorption of the olefin (e.g. dimethyl maleate) used as radical traps and the formation of ground state complexes. In fact the absorption spectra of TBADT is virtually superimposable to that of the overall reaction mixture containing aldehyde **1a** and olefin **2a** confirming again that the photocatalyst is by far the main absorbing species in solution.

2) ^{1}H-NMR and ^{13}C-NMR spectra of compounds 3-9, 11-15

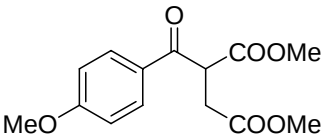
Compound 3.



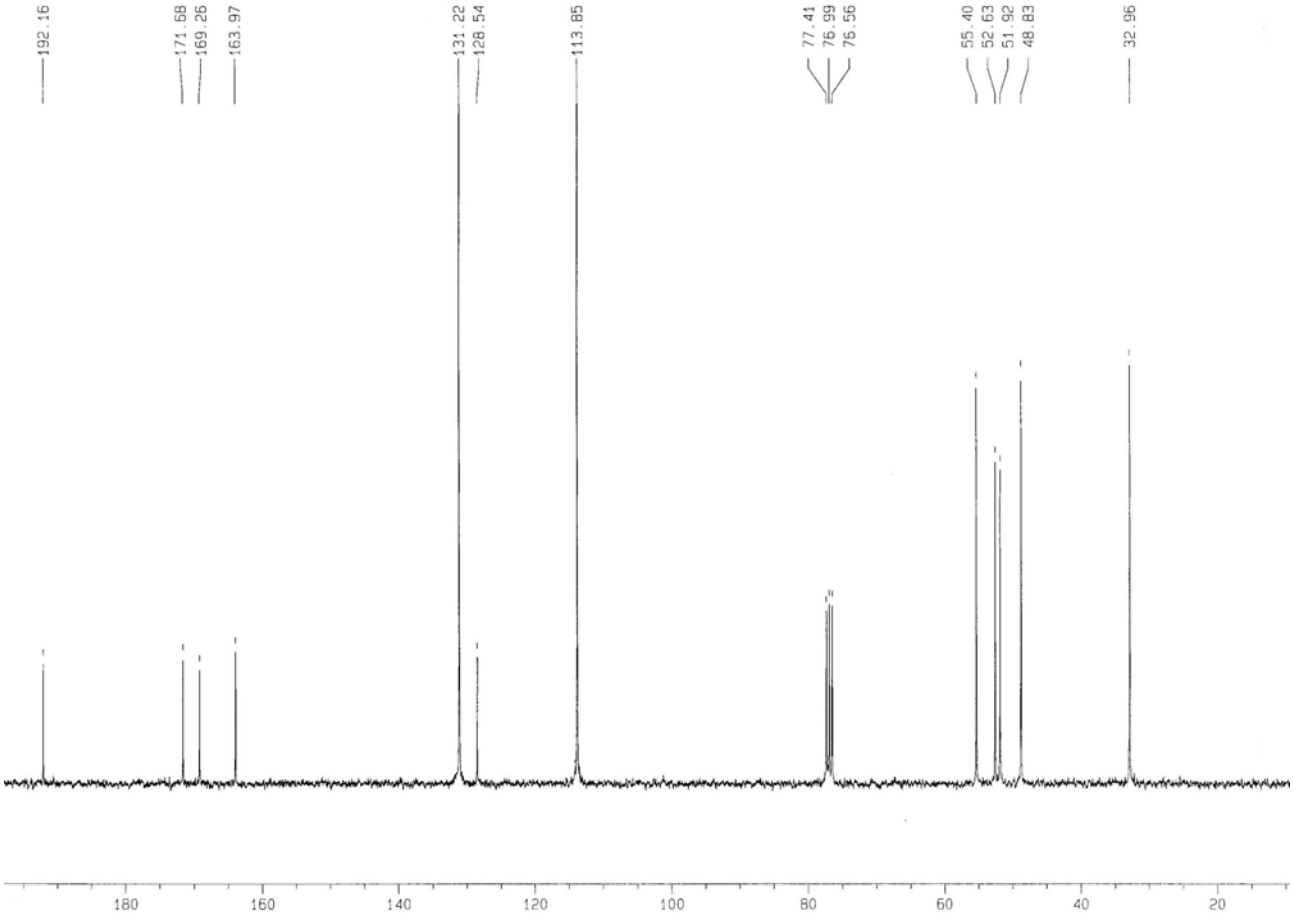
^{1}H-NMR



Compound 3.



^{13}C-NMR



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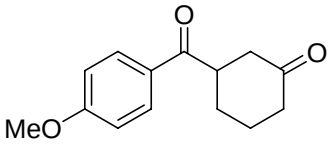
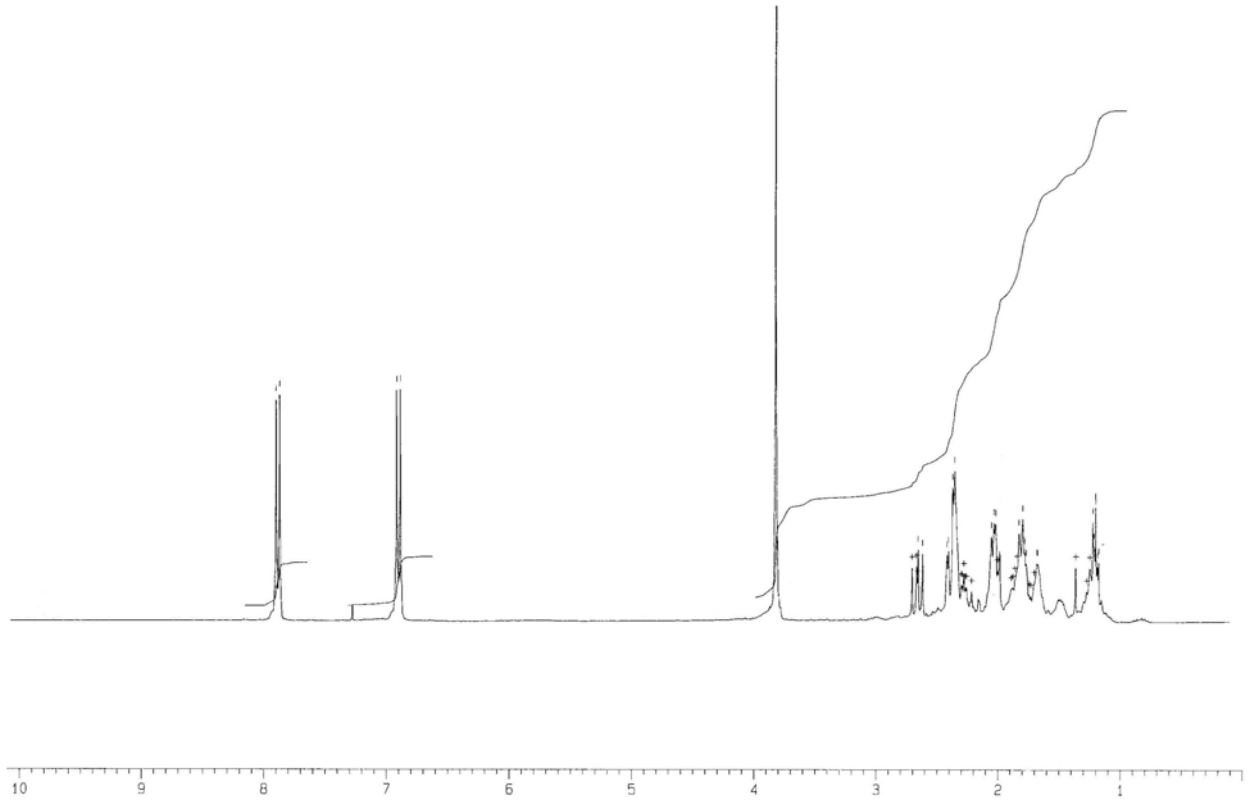
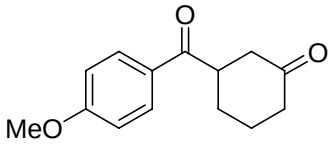


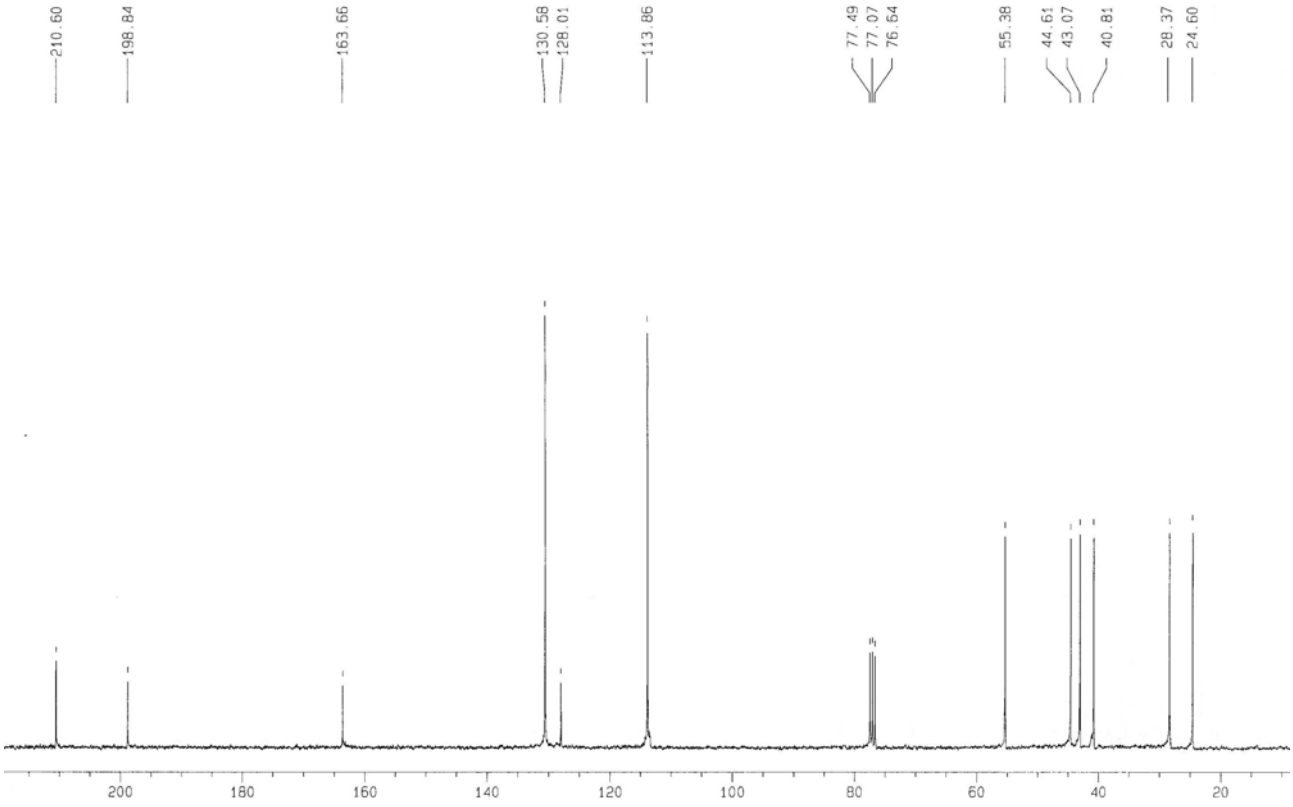
^{1}H-NMR



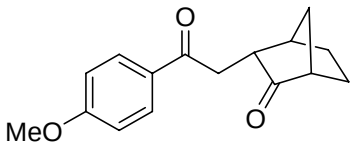
Compound 4.



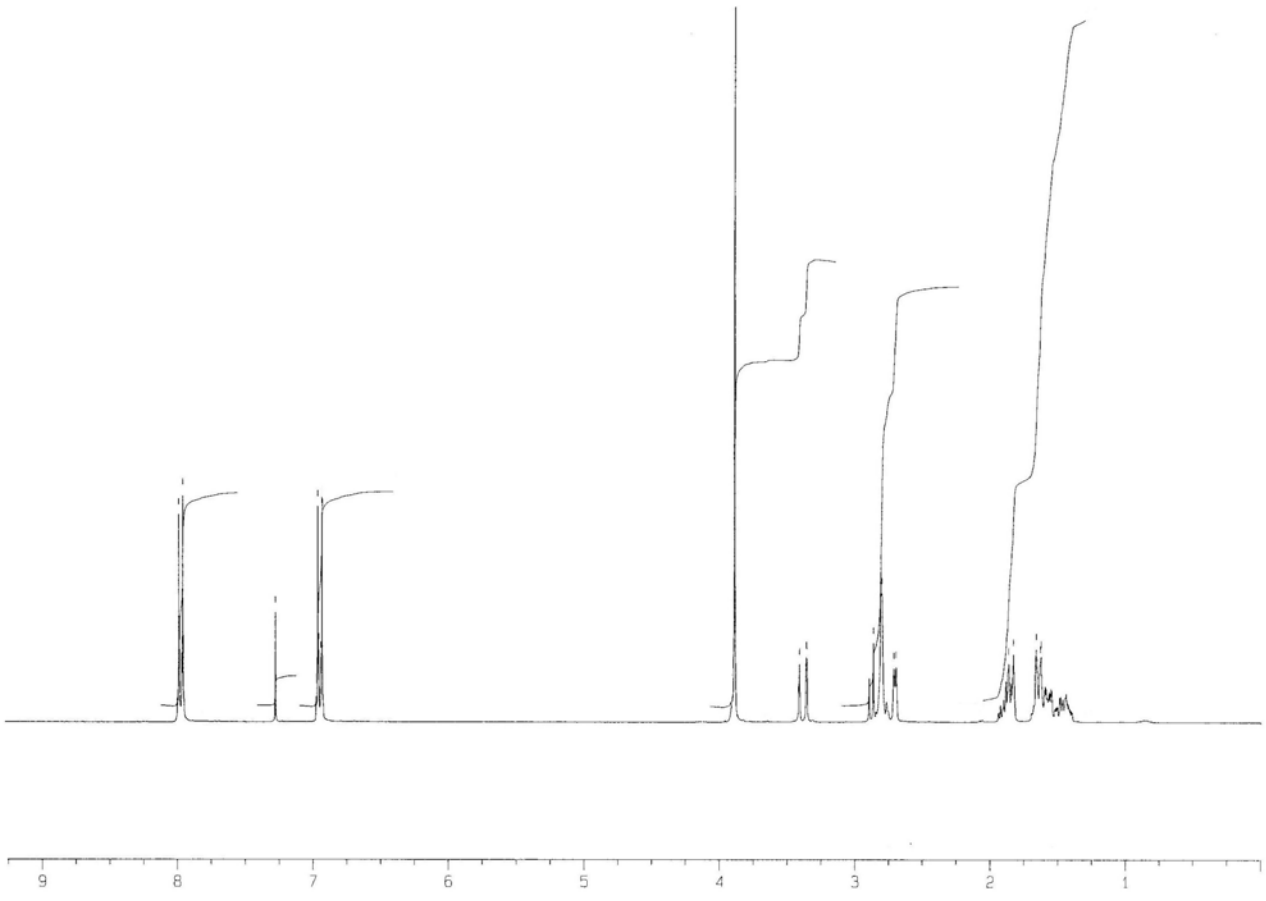
^{13}C-NMR



Compound 5.



^{1}H-NMR ($CDCl_3$)



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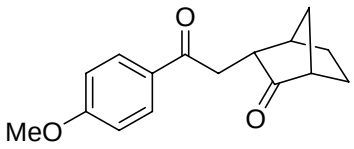
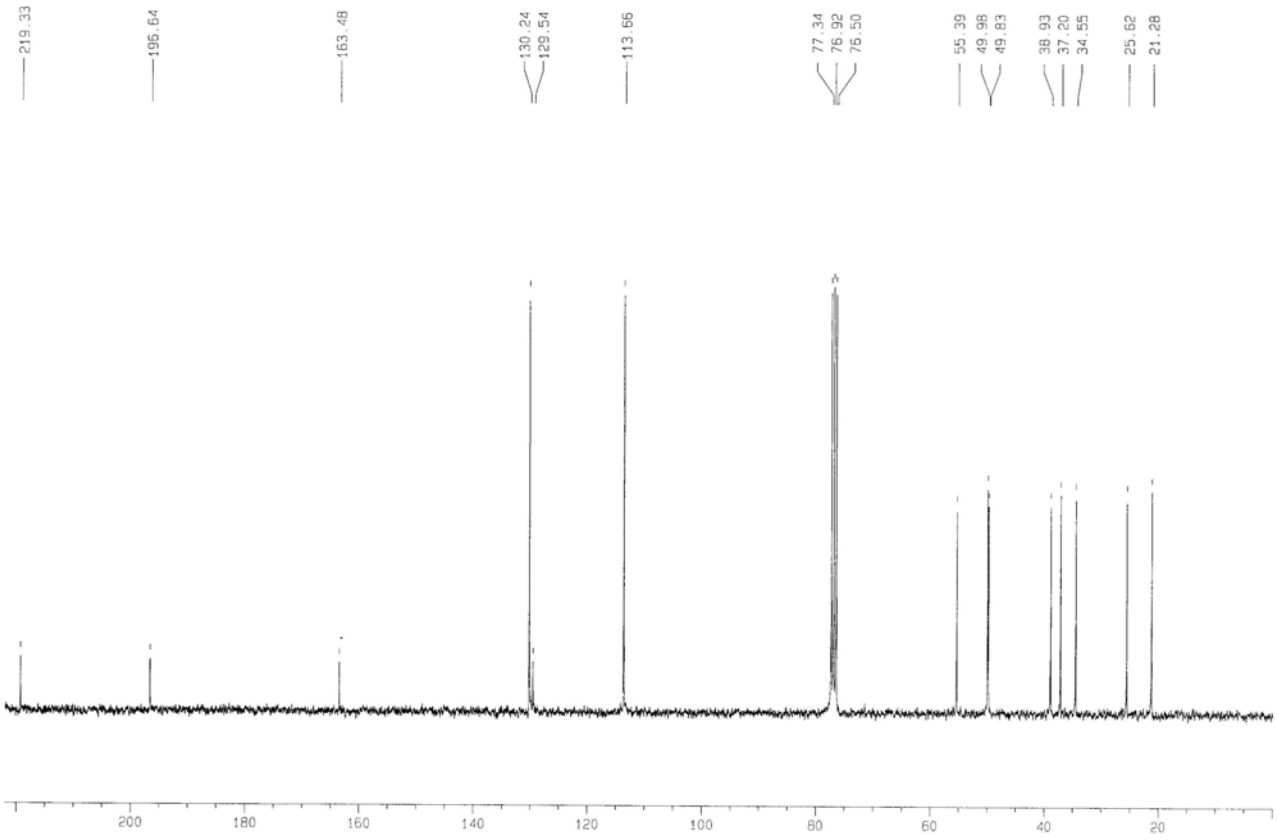
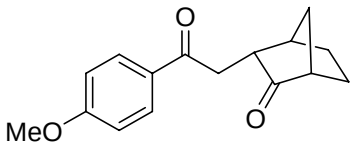


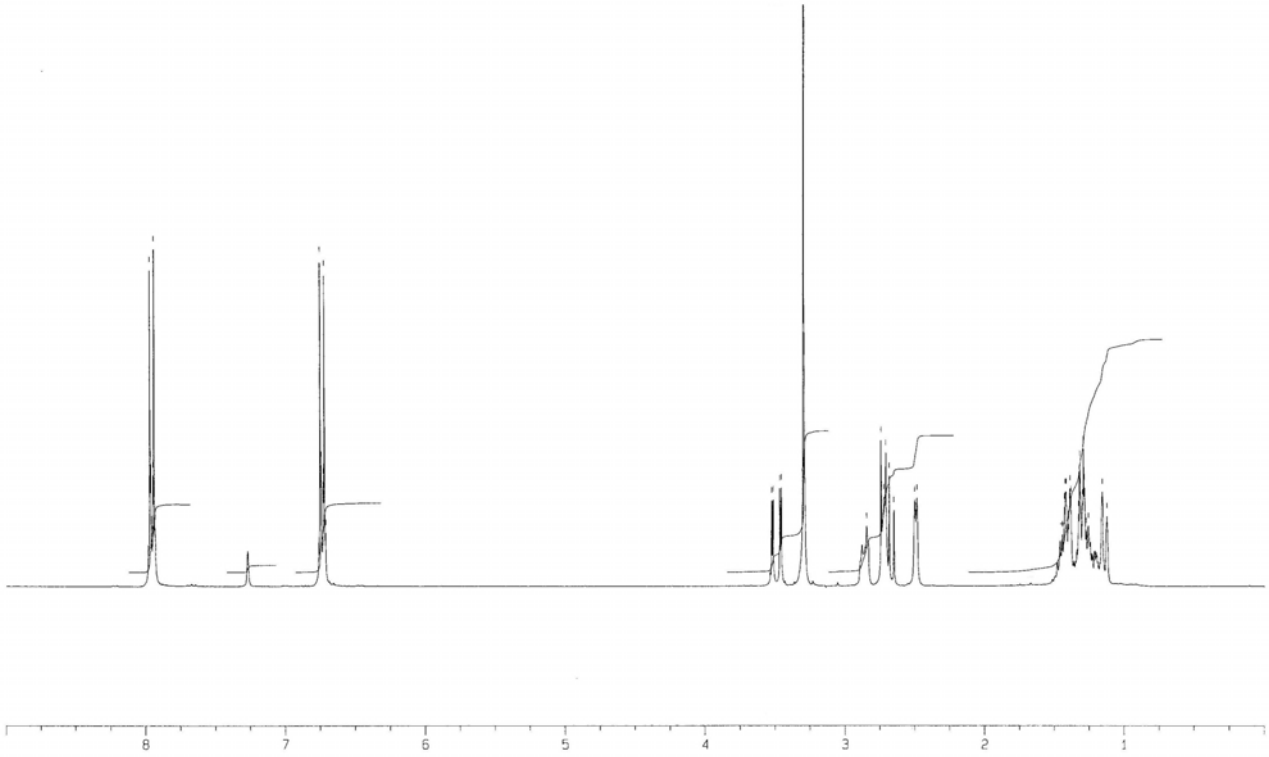
^{13}C-NMR



Compound 5.



^{1}H-NMR (C_6D_6)



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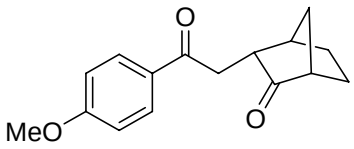
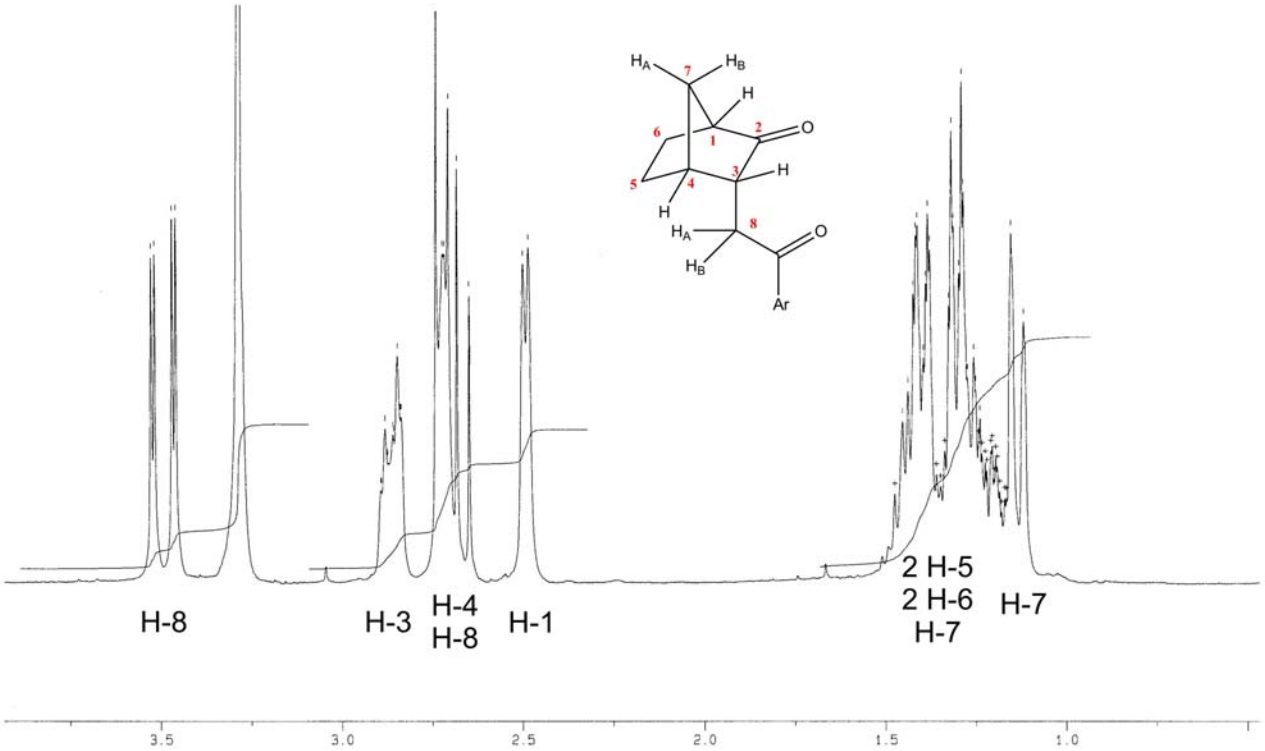


^{1}H-NMR (C_6D_6, enlarged portion)



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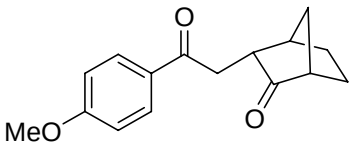
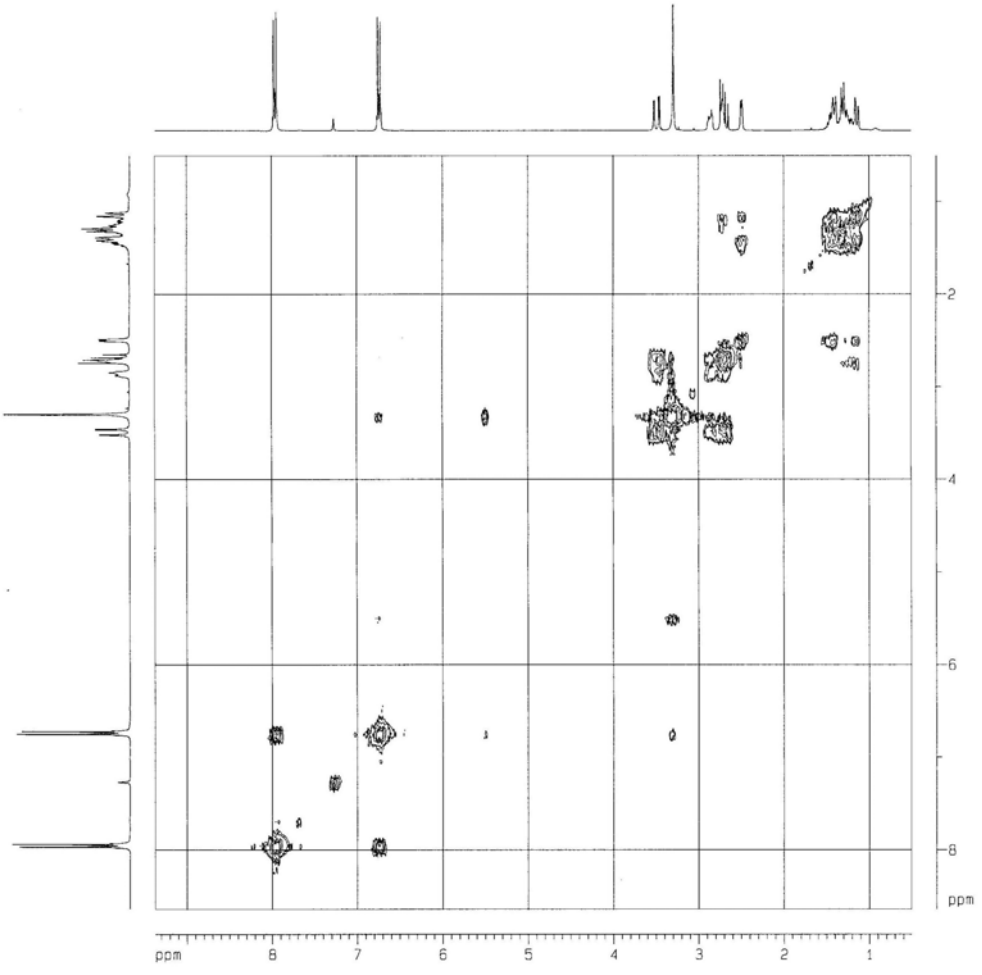


Long-range COSY



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PROCNO	1

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FIDRES	3.229373 Hz
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RG	362
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DE	6.00 usec
TE	303.2 K
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D1	2.00000000 sec
D6	0.10000000 sec
IN0	0.0003040 sec
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PL1	-2.00 dB
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FnMODE	QF

F2 - Processing parameters

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SSB	0
LB	0.00 Hz
GB	0
PC	1.00

F1 - Processing parameters

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SSB	0
LB	0.00 Hz
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2D NMR plot parameters

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F2PH1	0.507 ppm
F2H1	152.29 Hz
F1PL0	8.642 ppm
F1L0	2593.69 Hz
F1PH1	0.507 ppm
F1H1	152.29 Hz
F2PPMCM	0.59108 ppm/cm
F2HZCM	177.40524 Hz/cm
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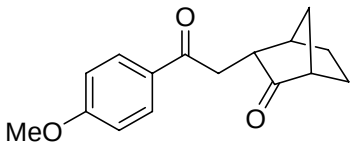
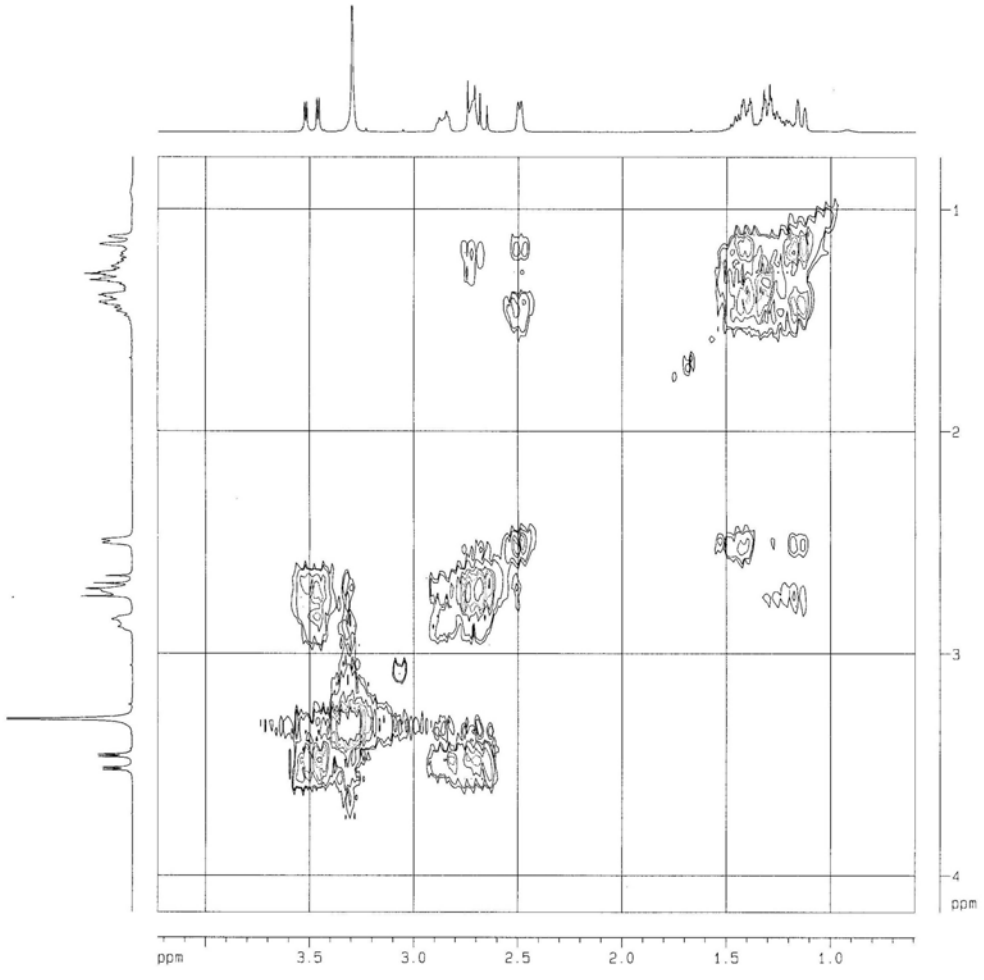
F1HZCM	162.76042 Hz/cm

Compound 5.



Long-range COSY (enlarged portion)

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FIDRES               3.229373 Hz
AQ                   0.1548788 sec
RG                          362
DW                      151.200 usec
DE                        6.00 usec
TE                      303.2 K
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======== CHANNEL f1 ========
NUC1                       1H
P1                       9.70 usec
PL1                     -2.00 dB
SFO1                300.1316507 MHz

F1 - Acquisition parameters
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TD                          128
SFO1                 300.1317 MHz
FIDRES                25.834988 Hz
SW                       11.018 ppm
FnMODE                        QF

F2 - Processing parameters
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SF                   300.1300000 MHz
WDW                         SINE
SSB                            0
LB                          0.00 Hz
GB                             0
PC                          1.00

F1 - Processing parameters
SI                           256
MC2                           QF
SF                   300.1300000 MHz
WDW                         SINE
SSB                            0
LB                          0.00 Hz
GB                             0

2D NMR plot parameters
CX2                         15.00 cm
CY1                         15.00 cm
F2PLO                        4.230 ppm
F2LO                      1269.65 Hz
F2PHI                        0.593 ppm
F2HI                       178.12 Hz
F1PLO                        4.166 ppm
F1LO                      1250.27 Hz
F1PHI                        0.766 ppm
F1HI                       229.79 Hz
F2PPMCM                  0.24248 ppm/cm
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F1HZCM                  68.03213 Hz/cm
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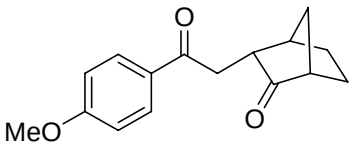
Compound 5.



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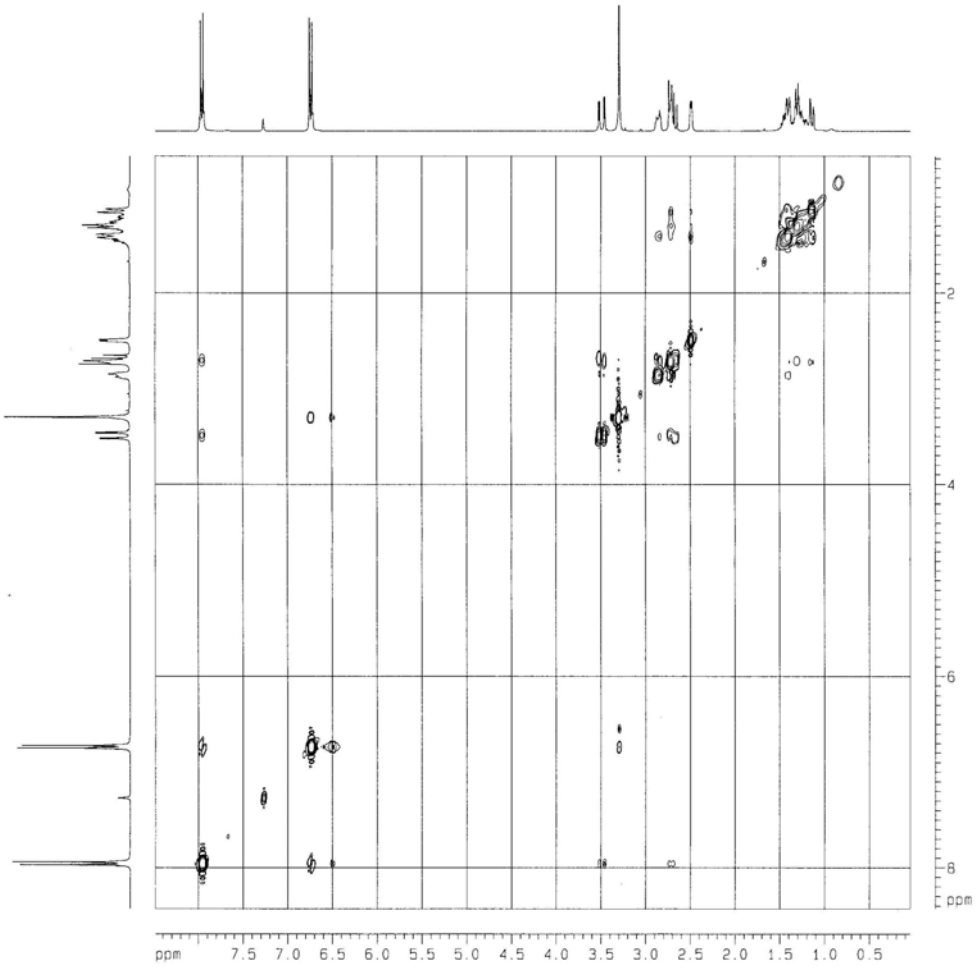


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PROCNO                    1

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TD                     1024
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DS                       16
SWH                3906.250 Hz
FIDRES             3.814697 Hz
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RG                       256
DW                 128.000 usec
DE                   6.00 usec
TE                  296.2 K
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D8                 1.00000000 sec
IN0                0.00025630 sec
MCREST             0.00000000 sec
MCWRK              3.00000000 sec

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PL1                   -2.00 dB
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F1 - Acquisition parameters
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FnMODE                 TPPI

F2 - Processing parameters
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SSB                        2
LB                      0.00 Hz
GB                         0
PC                      1.00

F1 - Processing parameters
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MC2                    TPPI
SF                300.1300000 MHz
WDW                     SINE
SSB                        2
LB                      0.00 Hz
GB                         0

2D NMR plot parameters
CX2                    15.00 cm
CY1                    15.00 cm
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F2LO                2545.94 Hz
F2PHI                  0.043 ppm
F2HI                  12.98 Hz
F1PLO                  8.430 ppm
F1LO                2530.00 Hz
F1PHI                  0.571 ppm
F1HI                 171.47 Hz
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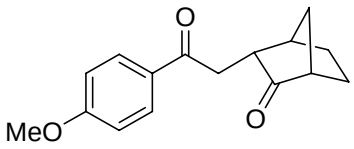
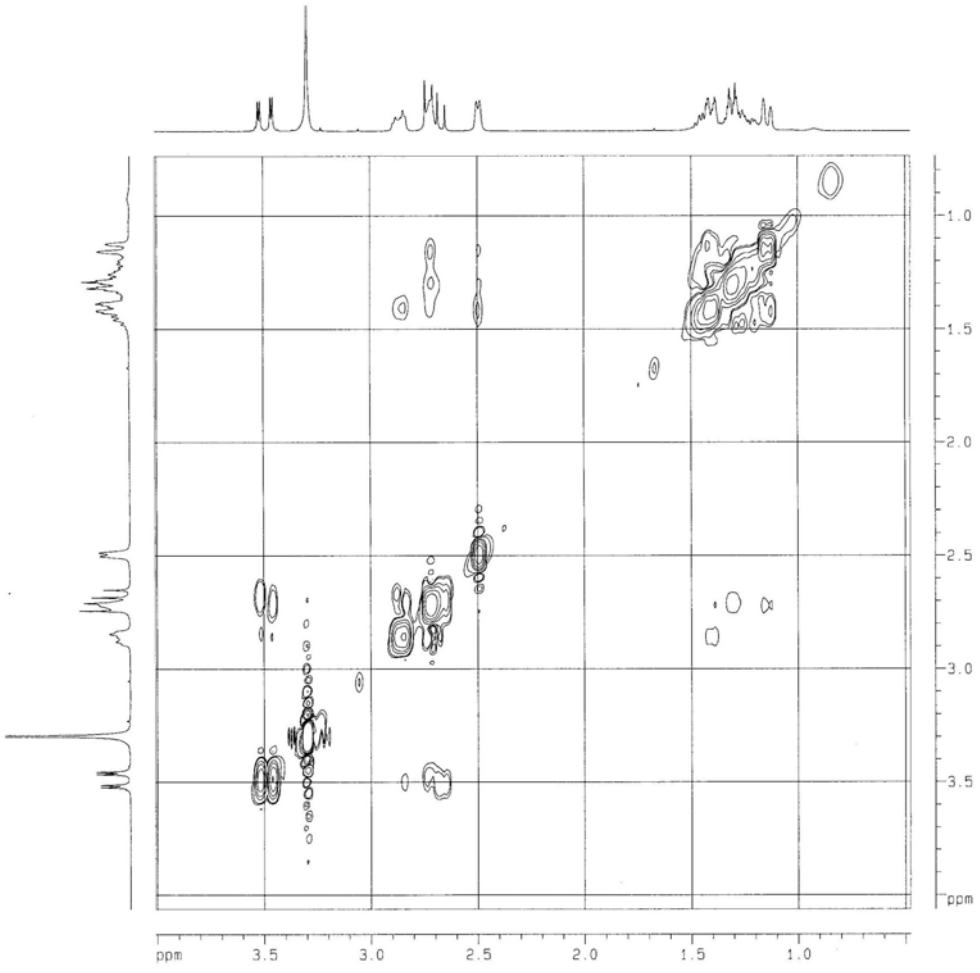
Compound 5.



NOESY (enlarged portion)

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SOLVENT               CDCl3
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DS                      16
SWH                3906.250 Hz
FIDRES             3.814697 Hz
AQ                 0.1311220 sec
RG                      256
DW                 128.000 usec
DE                   6.00 usec
TE                  298.2 K
d0                 0.00011542 sec
D1                 3.00000000 sec
D8                 1.00000000 sec
IN0                0.00025630 sec
MCREST             0.00000000 sec
MCWRK              3.00000000 sec

======== CHANNEL f1 ========
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PL1                    -2.00 dB
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F1 - Acquisition parameters
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FIDRES            15.240929 Hz
SW                    13.000 ppm
FnMODE                  TPPI

F2 - Processing parameters
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WDW                     SINE
SSB                        2
LB                      0.00 Hz
GB                         0
PC                      1.00

F1 - Processing parameters
SI                      1024
MC2                     TPPI
SF              300.1300000 MHz
WDW                     SINE
SSB                        2
LB                      0.00 Hz
GB                         0

2D NMR plot parameters
CX2                    15.00 cm
CY1                    15.00 cm
F2PLO                  4.009 ppm
F2LO                 1203.17 Hz
F2PHI                  0.475 ppm
F2HI                  142.68 Hz
F1PLO                  4.063 ppm
F1LO                 1219.28 Hz
F1PHI                  0.736 ppm
F1HI                  221.00 Hz
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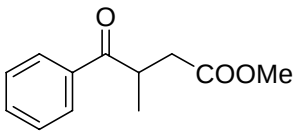
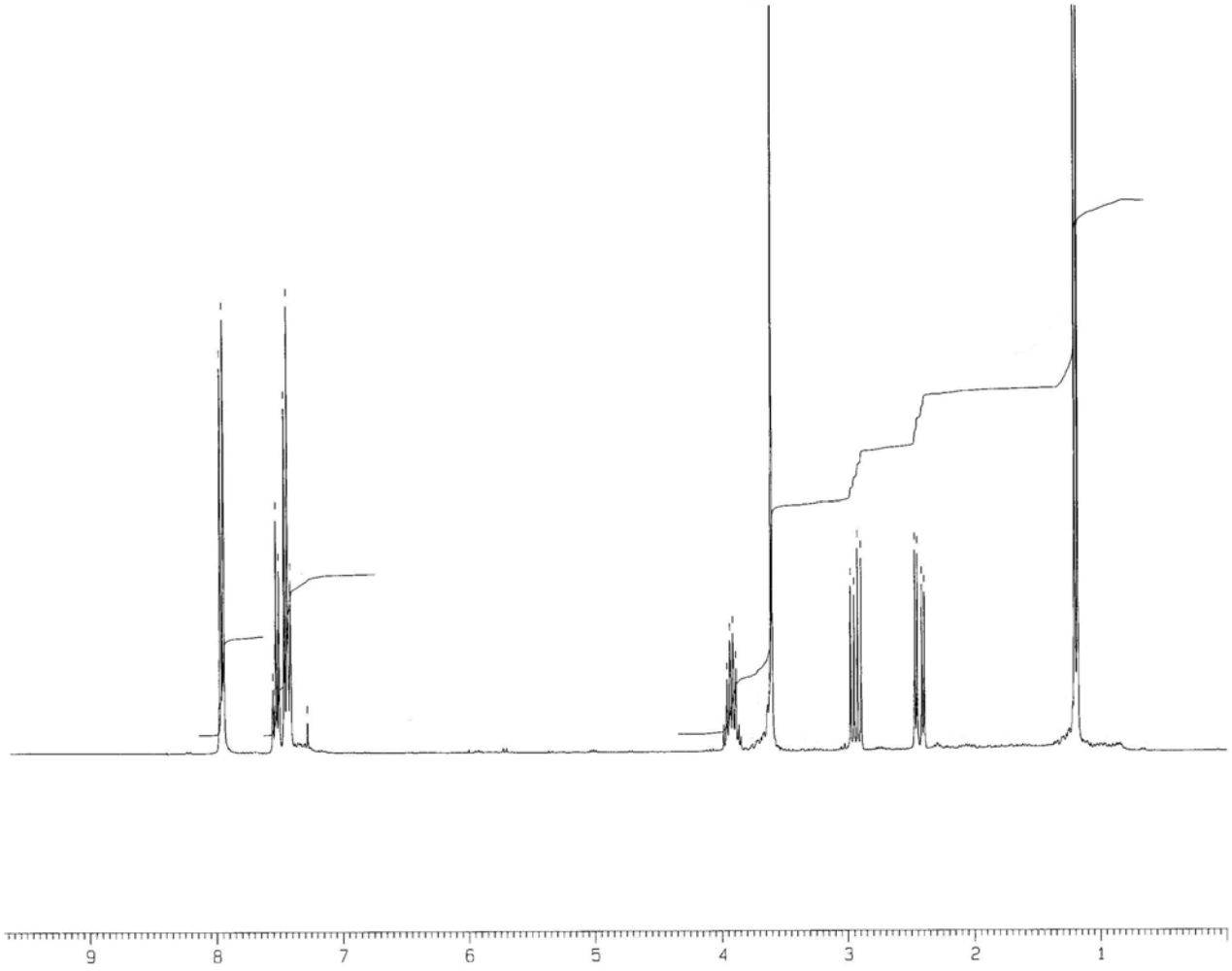
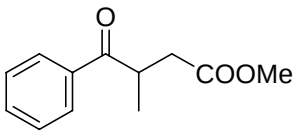
Compound 6.



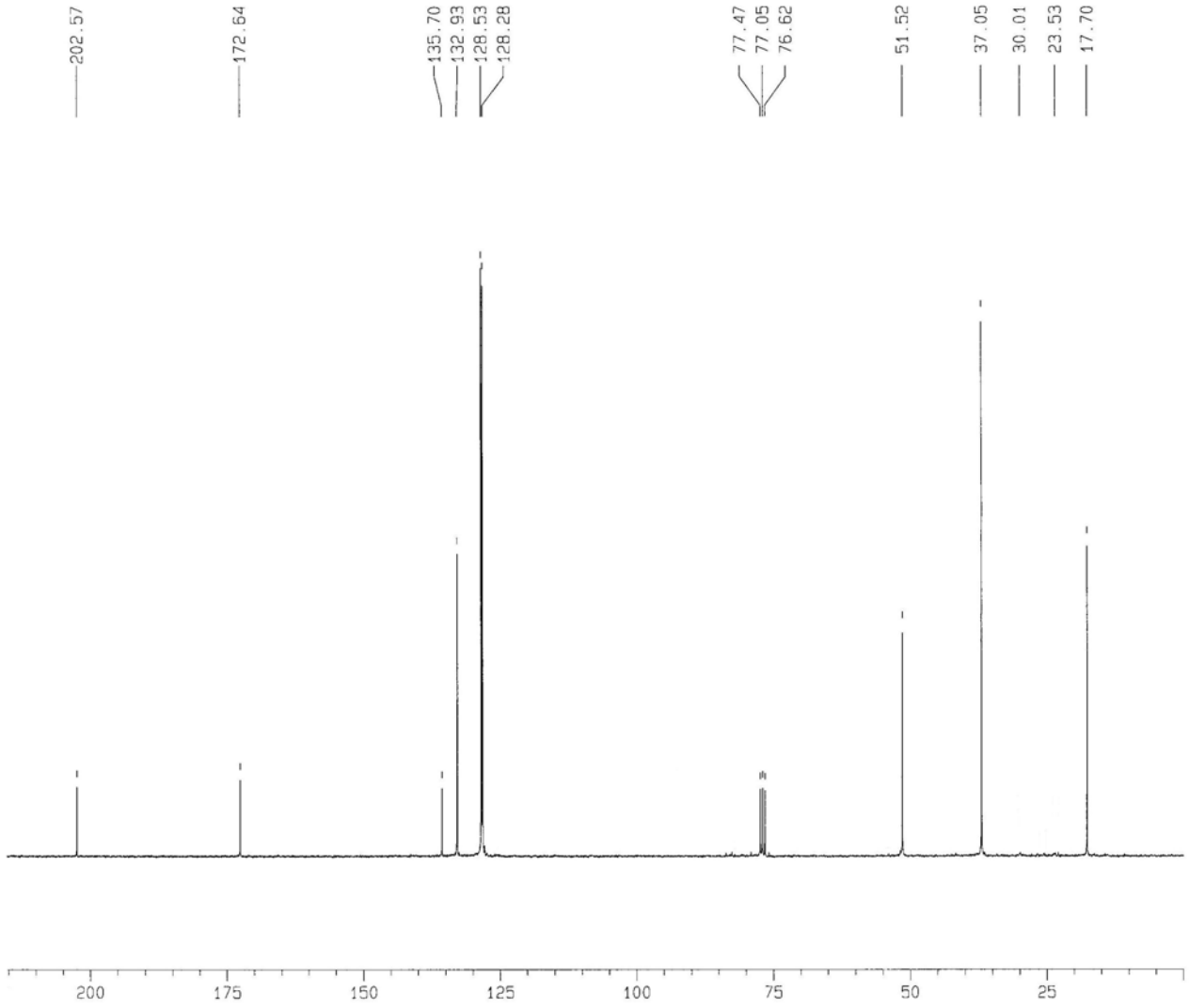
^{1}H-NMR



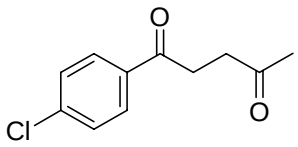
Compound 6.



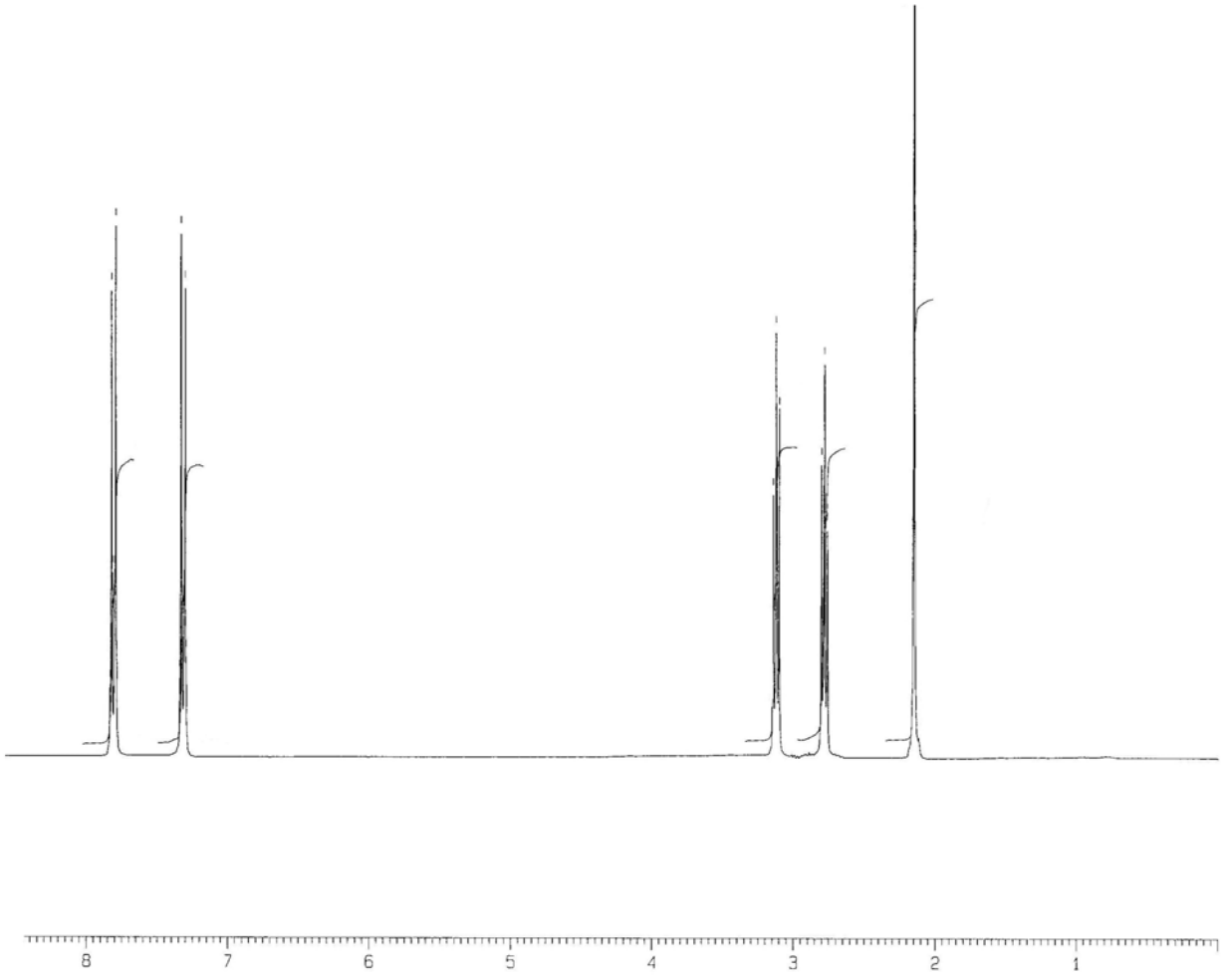
^{13}C-NMR



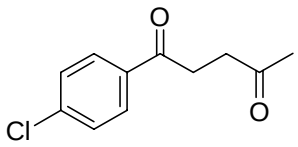
Compound 7.



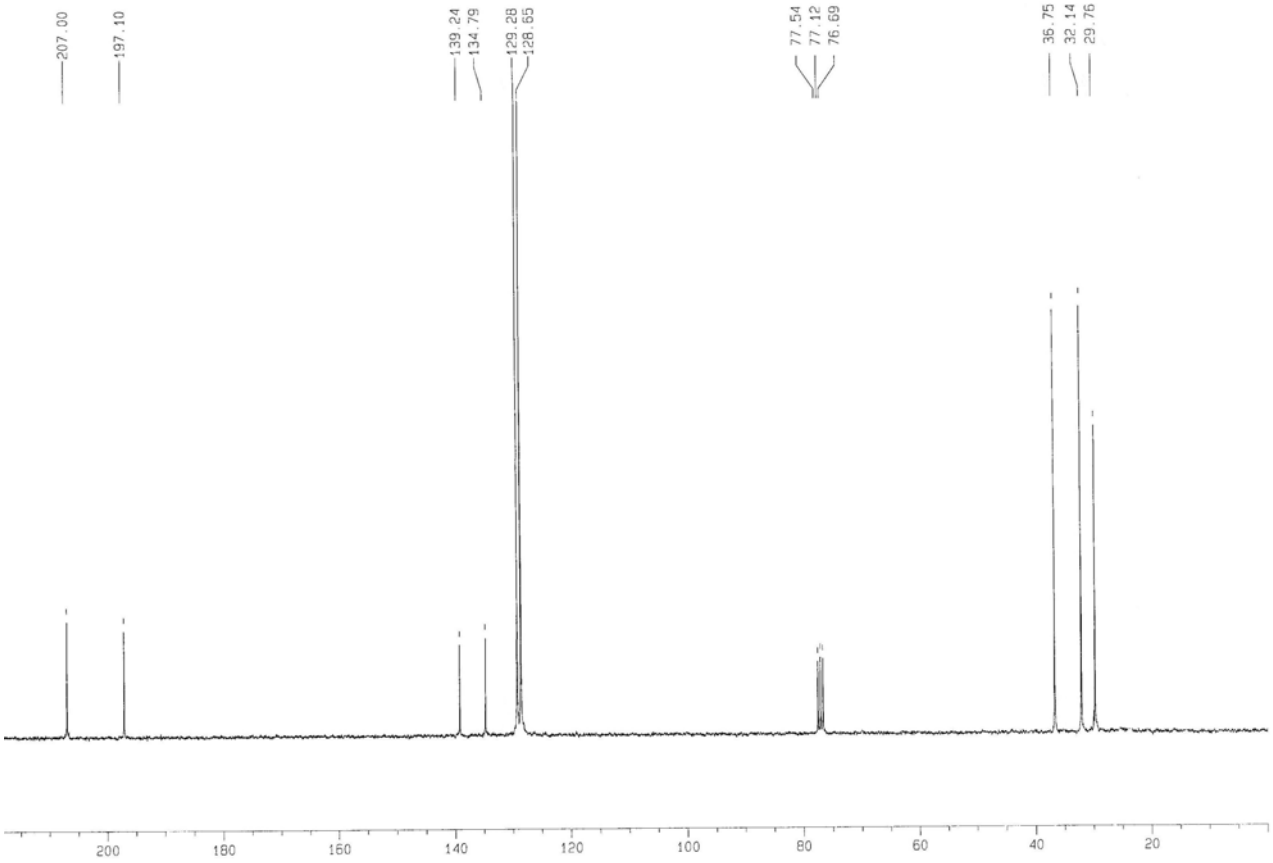
^{1}H-NMR



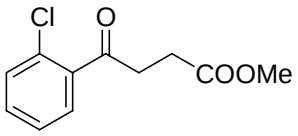
Compound 7.



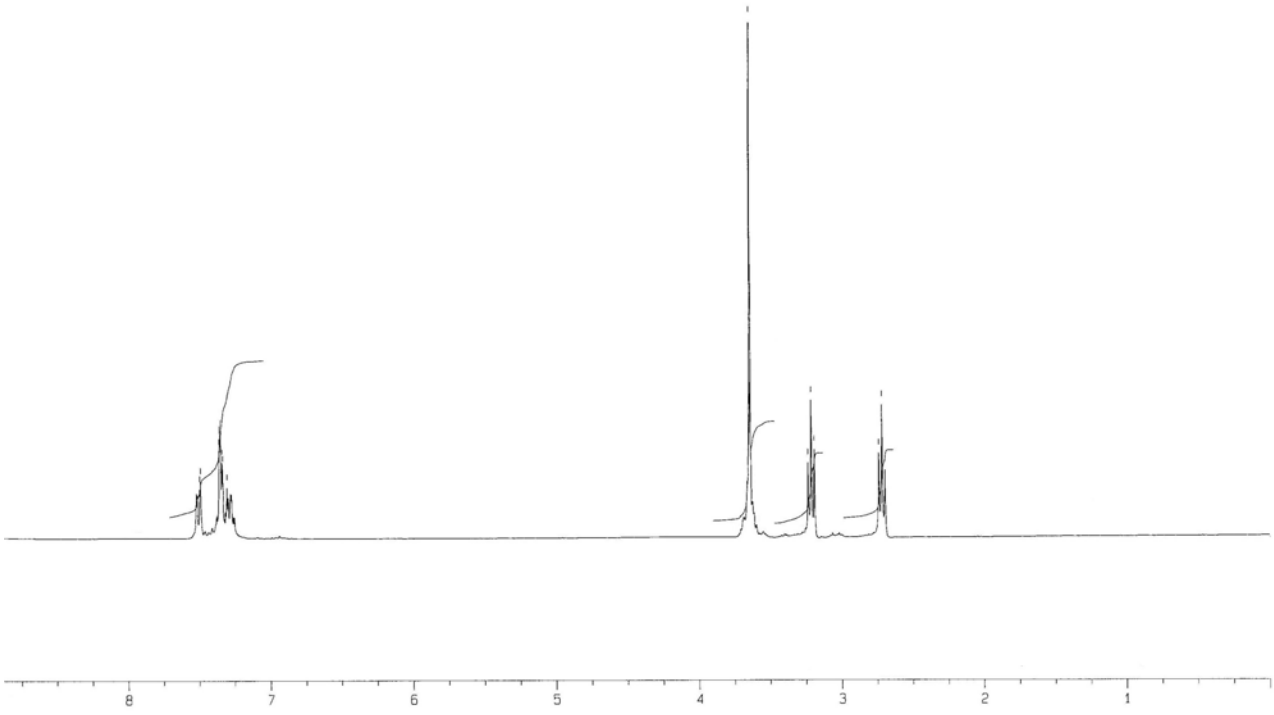
^{13}C-NMR



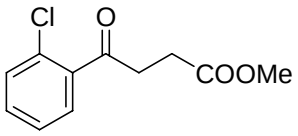
Compound 8.



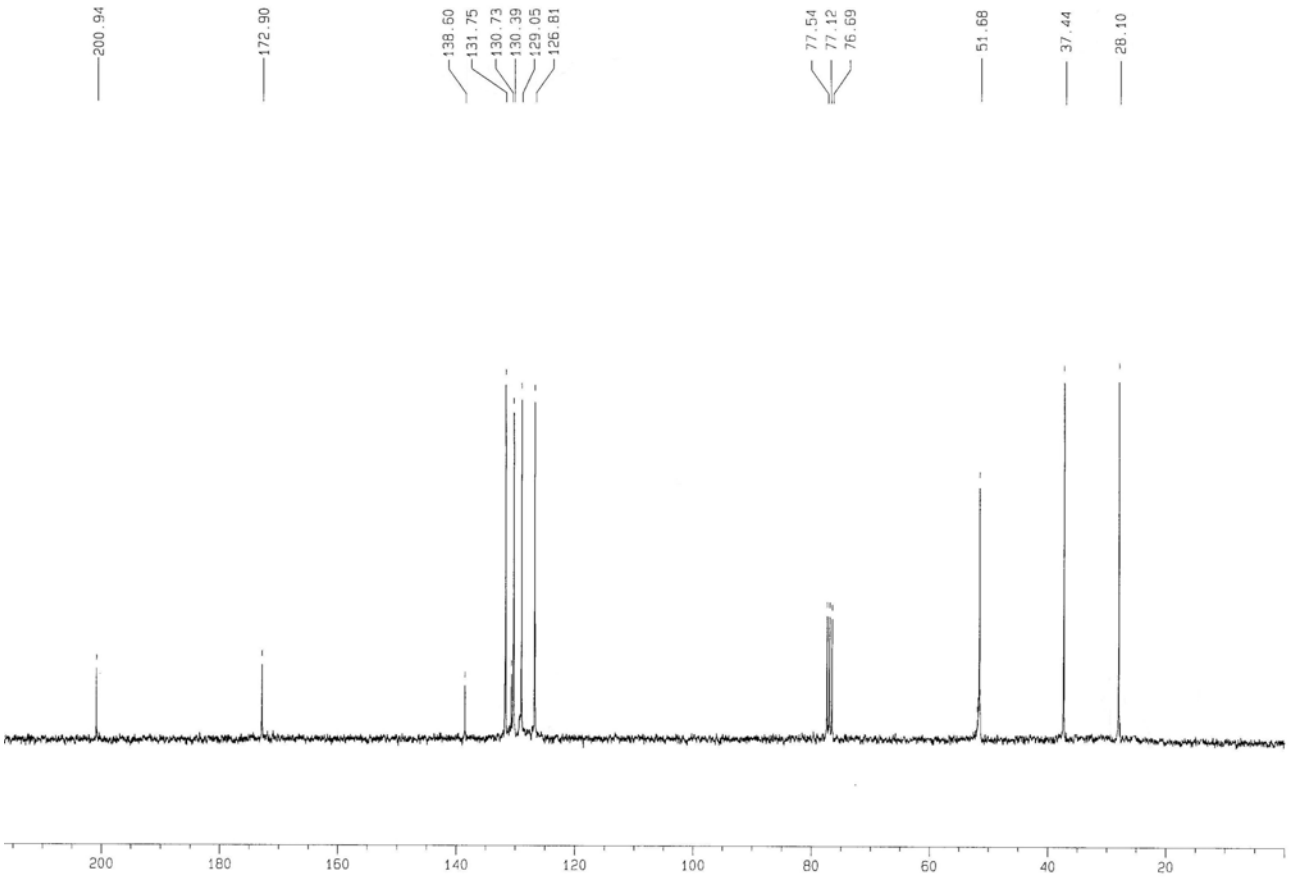
^{1}H-NMR



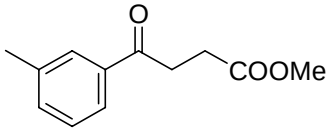
Compound 8.



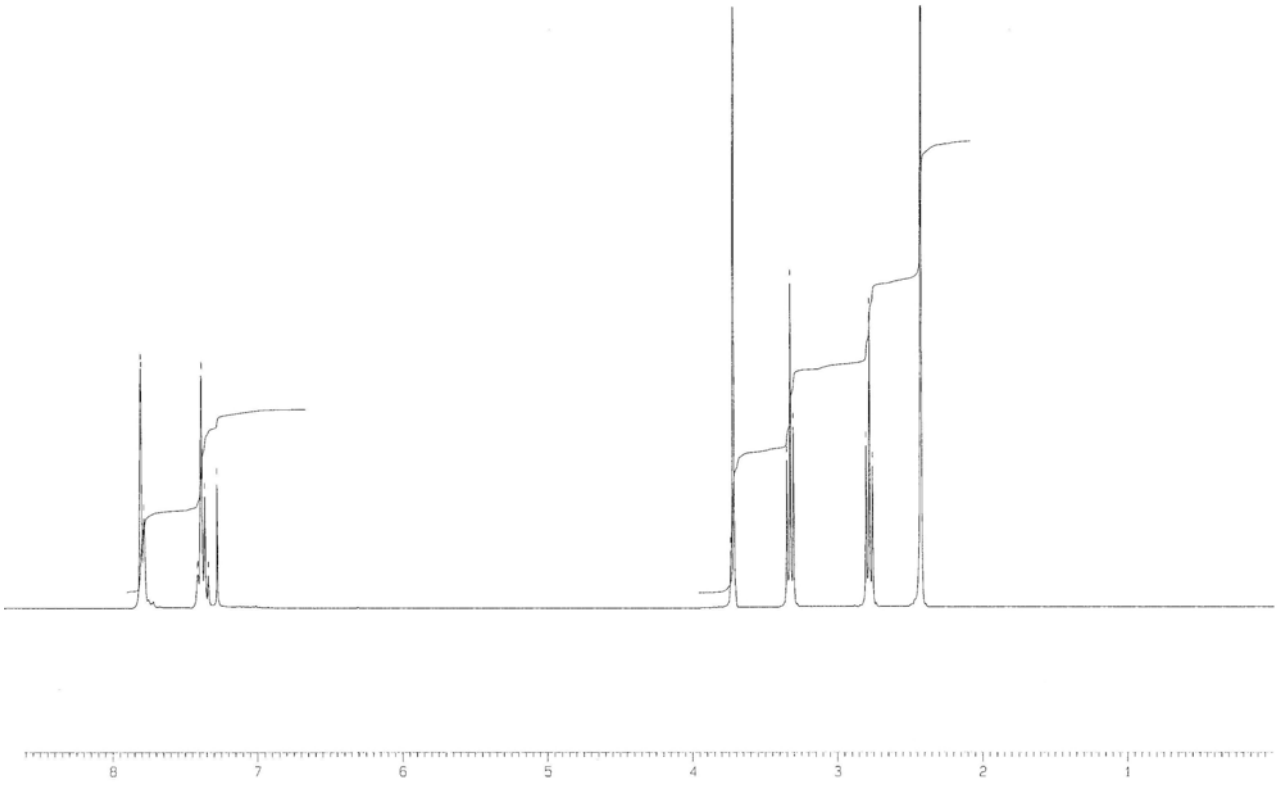
^{13}C-NMR



Compound 9.



^{1}H-NMR



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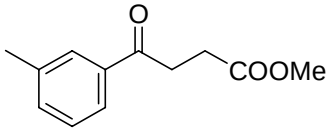
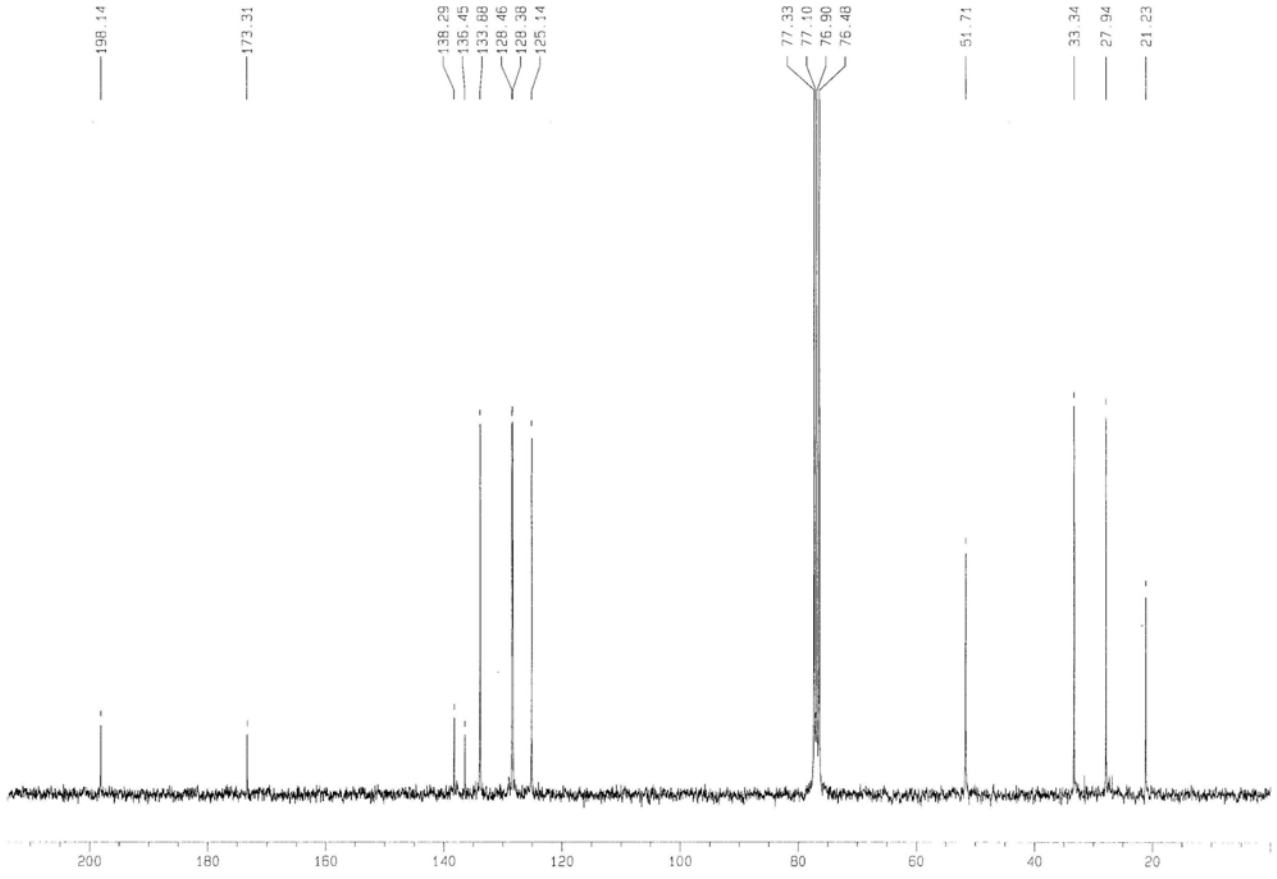


^{13}C-NMR



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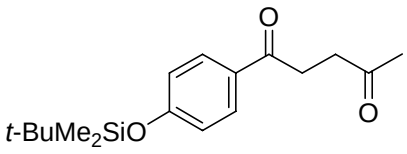

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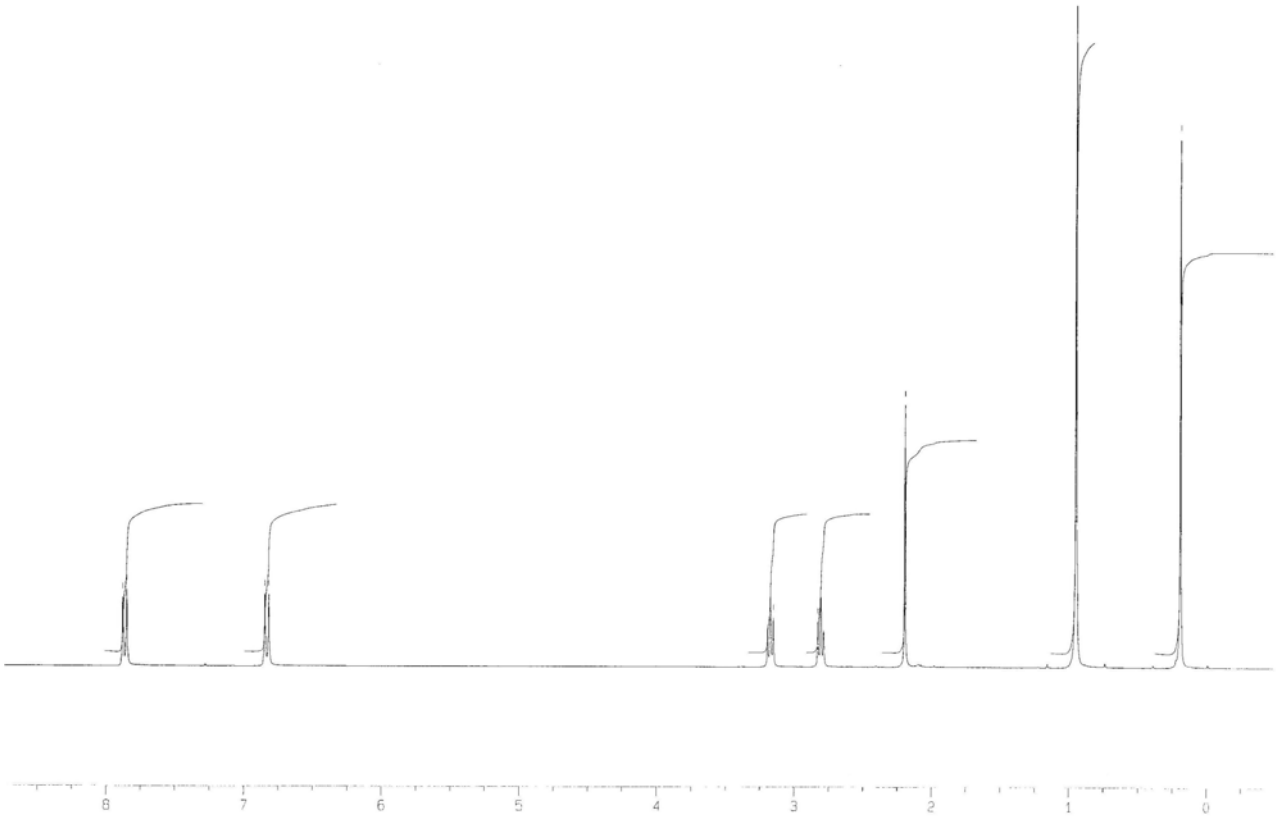

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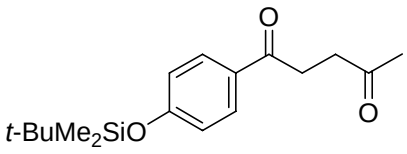

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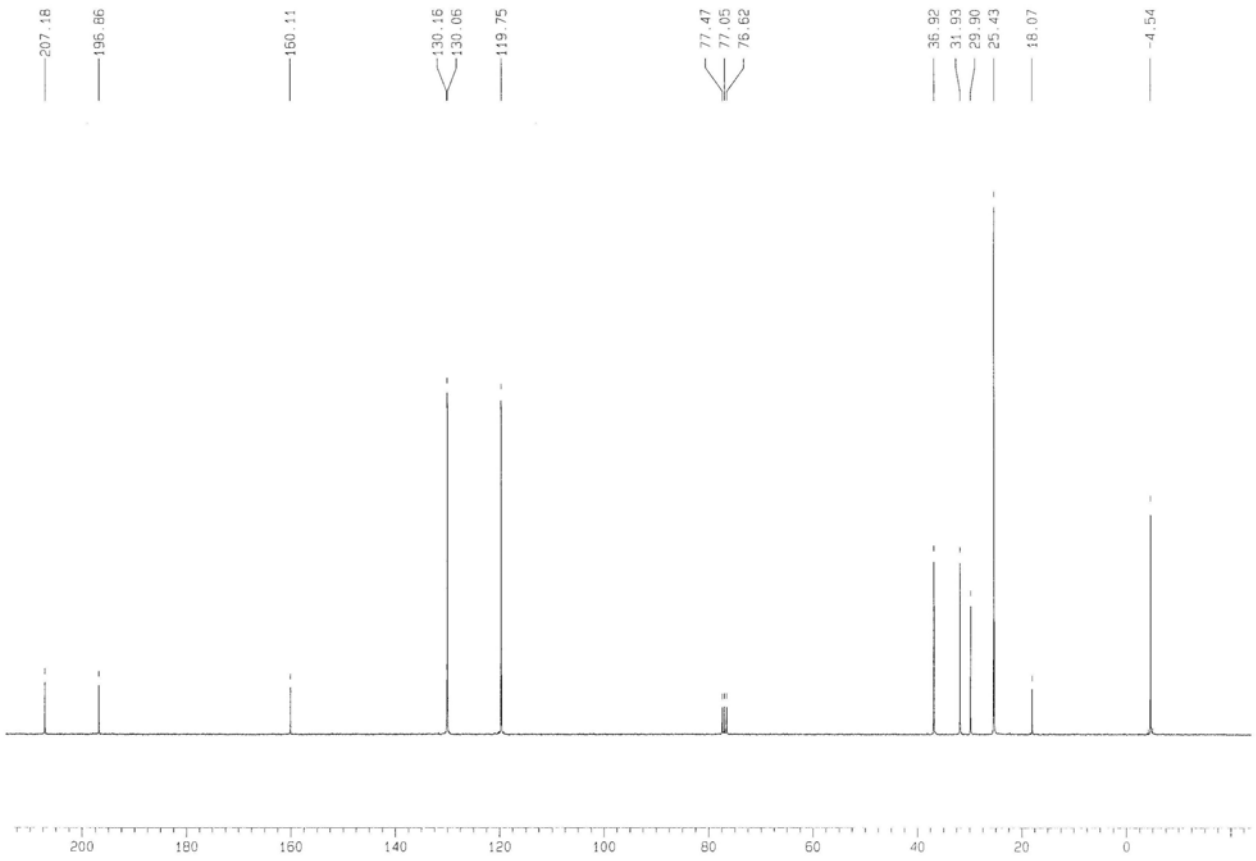

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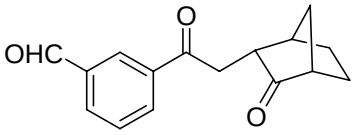
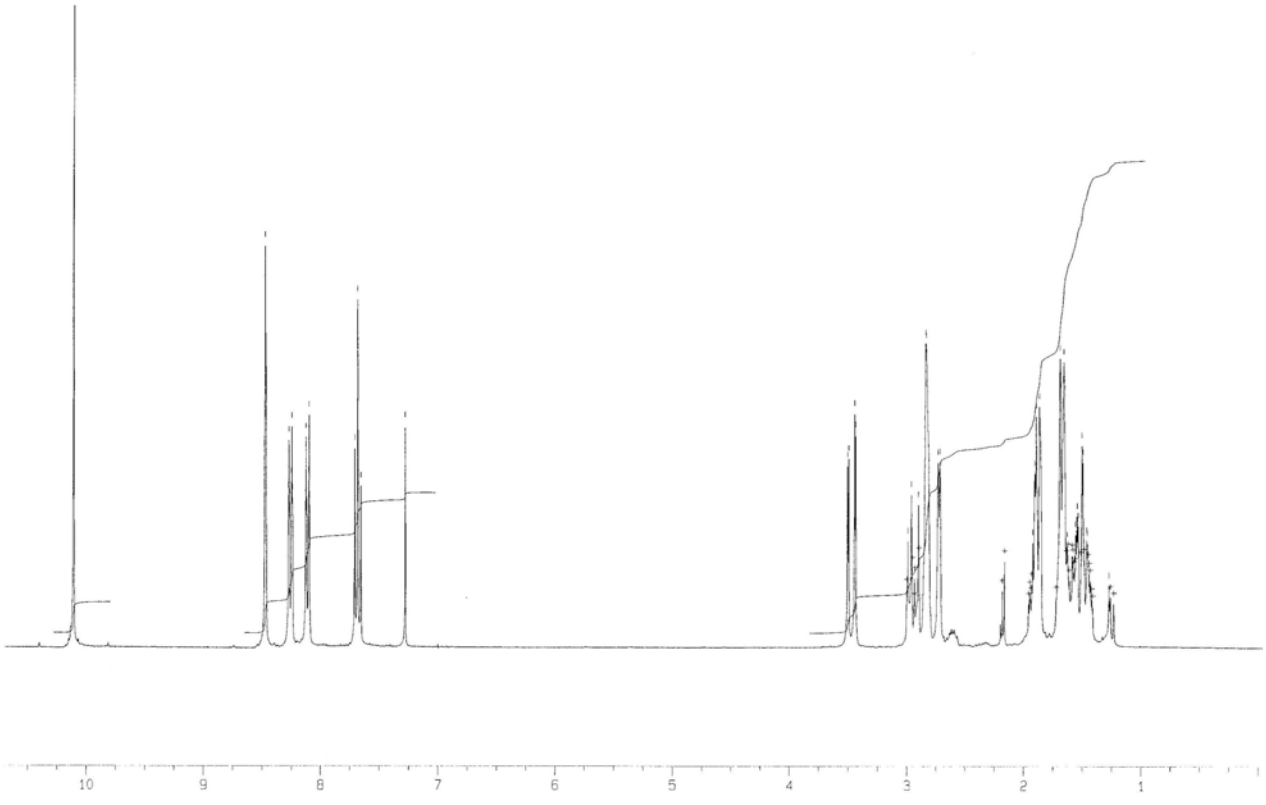


^{1}H-NMR



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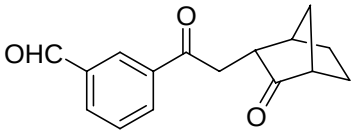

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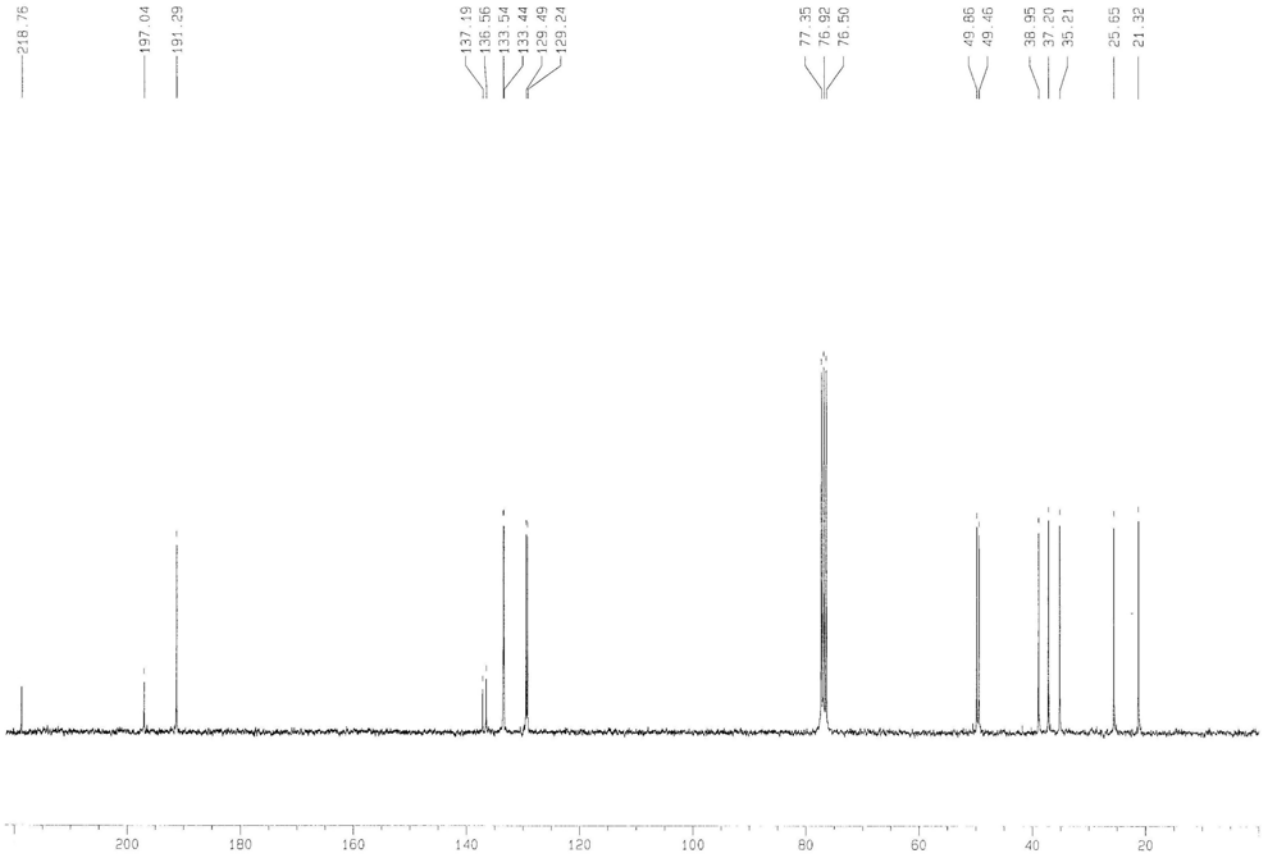

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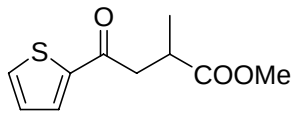

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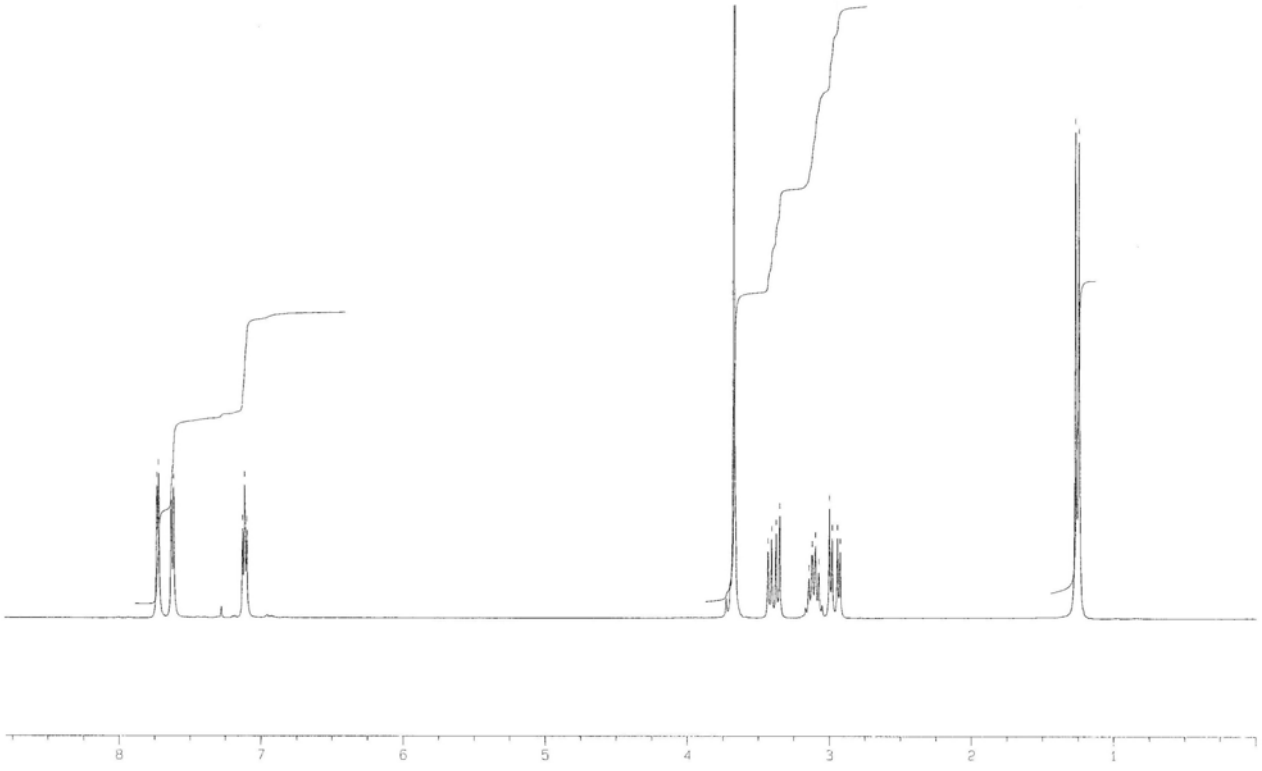

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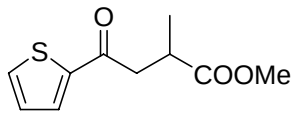
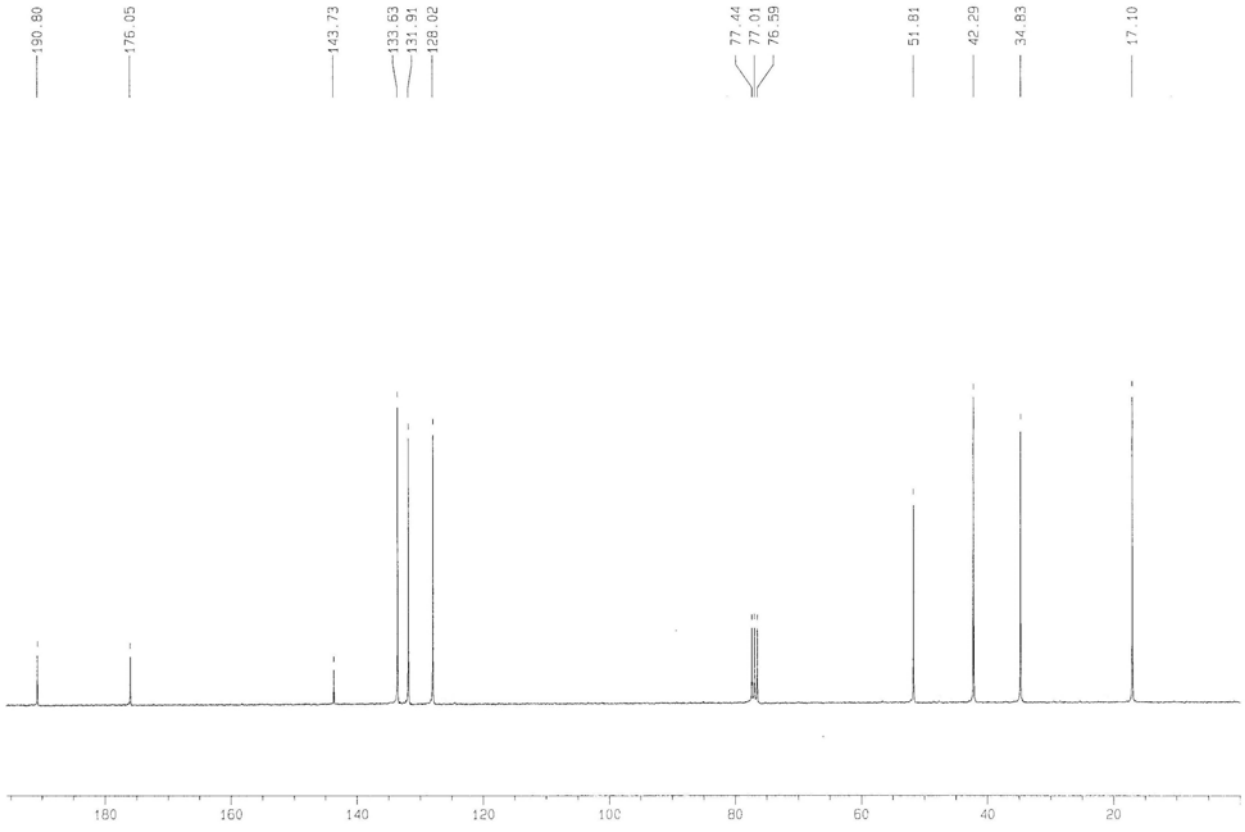


^{13}C-NMR



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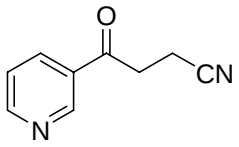
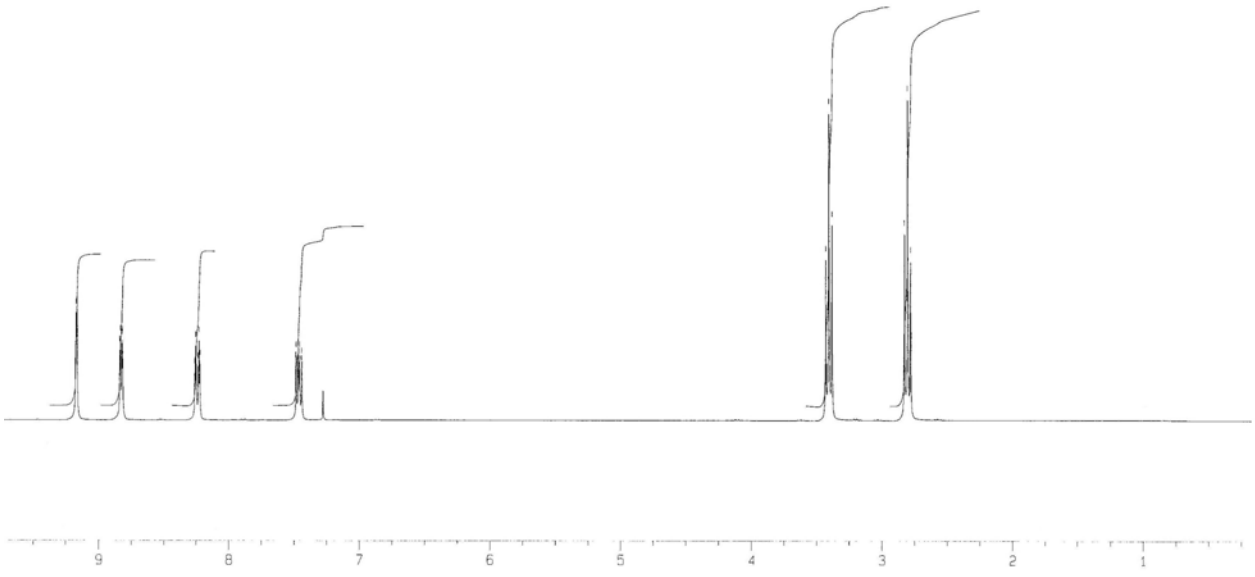


^{1}H-NMR



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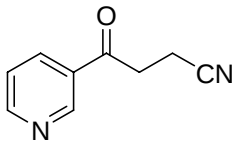
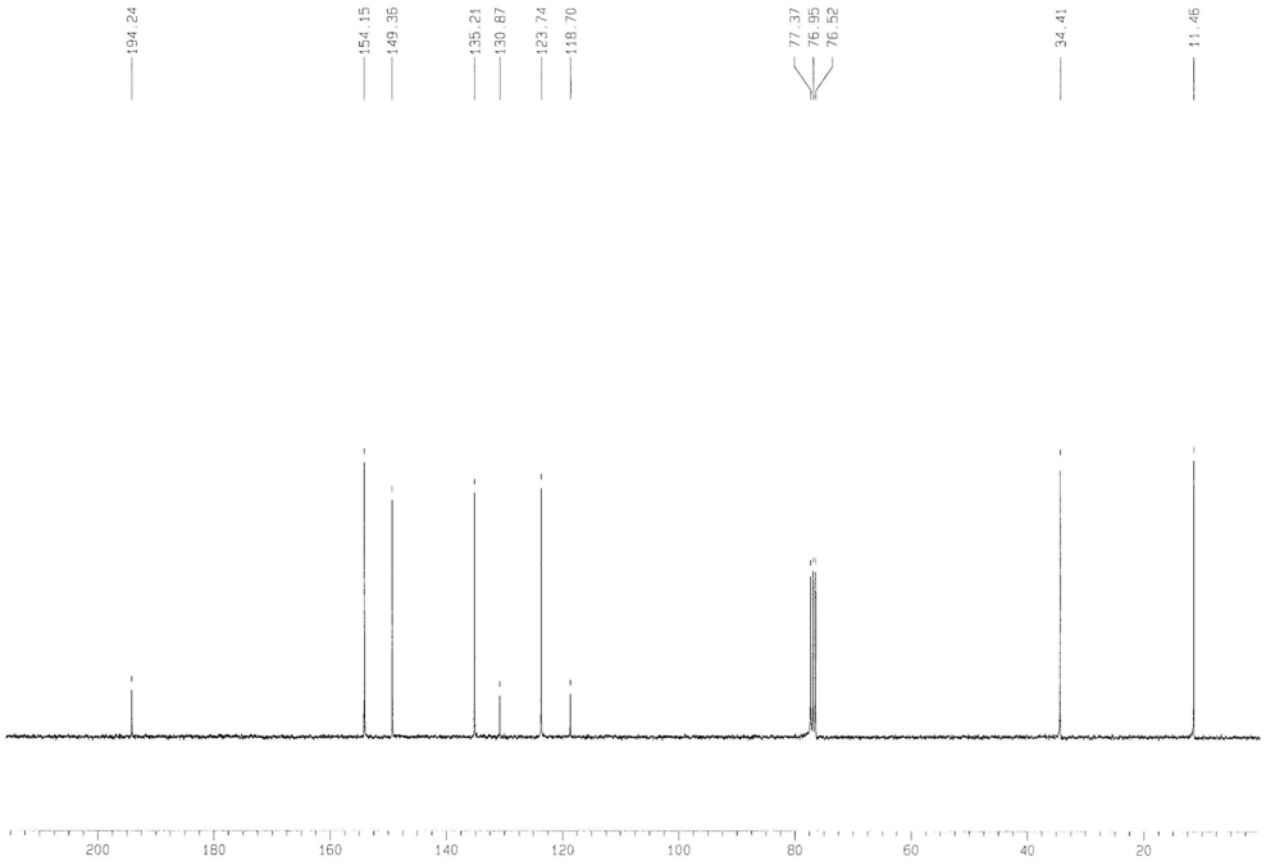


^{13}C-NMR



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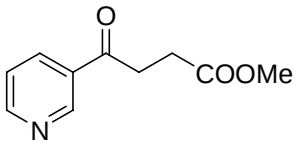

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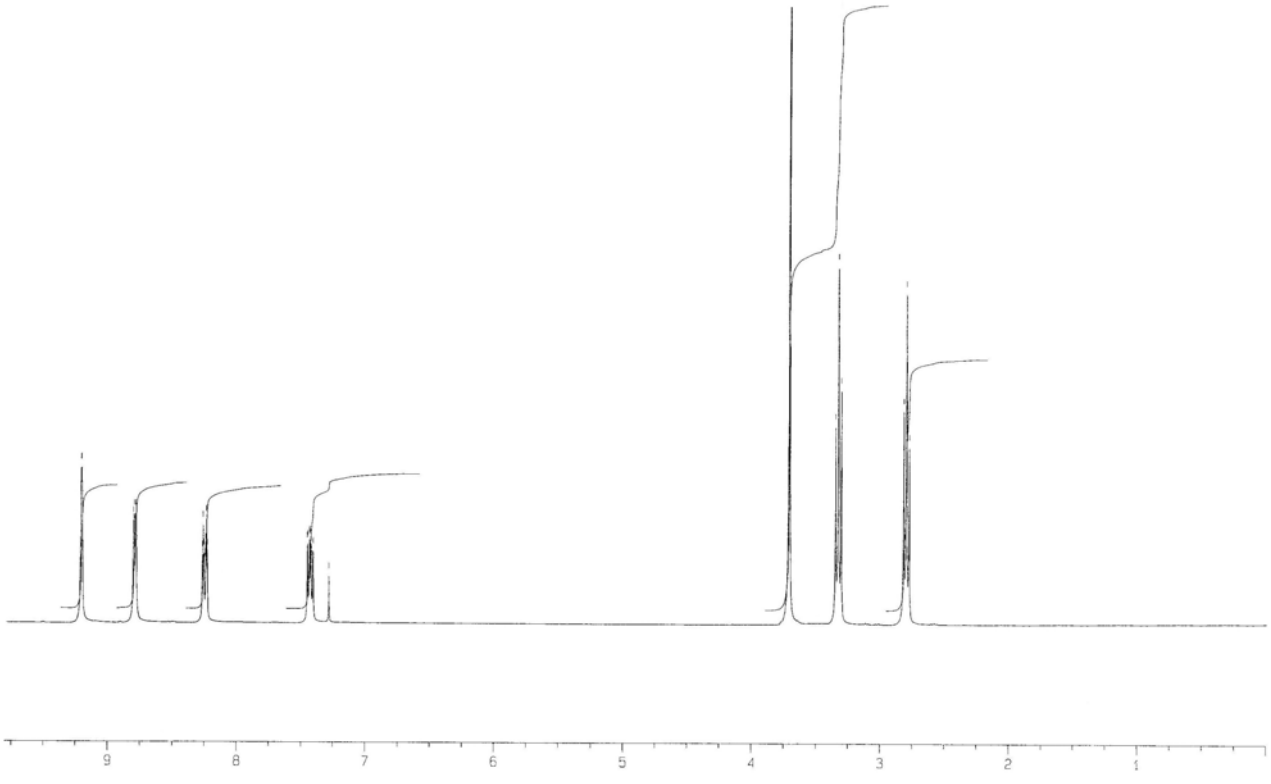

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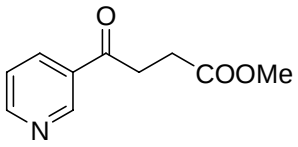

^{13}C-NMR