Supporting Information

Hydroxyapatite Supported Palladium (PdHAP) Catalyzed Efficient Synthesis of *(E)*-2-Alkene-4-yn Carboxylic Esters. Intense Fluorescence Emission of Selected Compounds

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Experimental procedure for peptide synthesis

Synthesis of (*E*)-5-naphthalen-1-yl-pent-2-en-4-ynoic acid (2)

(a) A solution of 5-naphthalen-1-yl-pent-2-en-4-ynoic acid butyl ester **I** (278 mg, 1 mmol) in THF (4.0 mL) and aqueous LiOH solution (1.0 M, 3 mL, 3 mmol) was stirred at room temperature for 18 h. After evaporation of THF the residue was diluted with water (3 mL) and extracted with EtOAc. The aqueous phase was cooled to 0 ^{o}C, acidified with cold 10% H_2SO_4 and extracted with EtOAc. The combined organic extract was dried over Na_2SO_4 and concentrated under reduced pressure to give compound **2** (182 mg, 82%).

(b) **Synthesis of methyl ester protected tryptophan hydrochloride**

A slurry of tryptophan (2.04 g, 10 mmol) in methanol (10 mL) was added in portions to a cooled (0-5^{o}C) solution of $SOCl_2$ (1 mL) in MeOH (10 mL) and the mixture was sonicated in an ultrasound bath to make a clear solution. It was then stirred at room temperature 10 h. The reaction mixture was concentrated and extracted with ether (3x15 mL). Then ether extract was evaporated to leave a solid product which was dried in vacuum to give the corresponding methyl ester.

(c) **Synthesis of peptide (3)**

The HCL-free tryptophan methyl ester in ethyl acetate (5 mL) was added to a cooled solution of compound **2** (5 mmol, 1.11 g) in DMF (2.5 mL) and *N*-hydroxybenzotriazole (HOBT) (675 ml, 5 mmol) and the reaction mixture was stirred for five min followed by addition of DCC (1.03 g, 5 mmol). The whole solution was stirred for 48 h and extracted with ethyl acetate (20 mL). The extract was filtered through sintered funnel and the residue was washed with EtOAc. The combined organic extract was then washed with 2N HCl, brine, satd. Na_2CO_3 solution, brine, and dried over Na_2SO_4. Solvent was evaporated

to leave the crude product which was purified by column chromatography using ethyl acetate and pet-ether as eluent (40:60) to afford the pure peptide (3).

(d) **Fluorescence measurement parameters**

The steady state absorption and emission spectra were recorded in a Shimadzu UV-2401 spectrophotometer and a spex fluoromax-3 spectrofluorimeter, respectively. All absorbance and fluorescence experiments were carried out in 1 cm quartz cells, using freshly prepared solutions, thermostatted at 25 ^{o}C. Quantum yields were determined using a fluorescent dye (coumarin 480, C480) in cyclohexane as the reference compound with a reported quantum yield of 1.05. For all the compounds (fig. 1 and 2) the excitation wave length used was 300 nm.

TEM images of nonstoichiometric Pd-HAP before (Fig. a) and after (Fig. b) reaction, taken on a JEM-2011 (JEOL) microscope

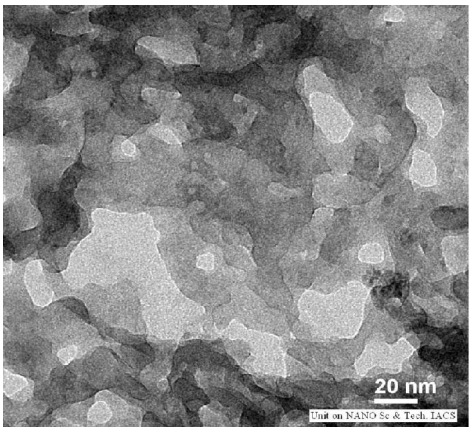


Figure a

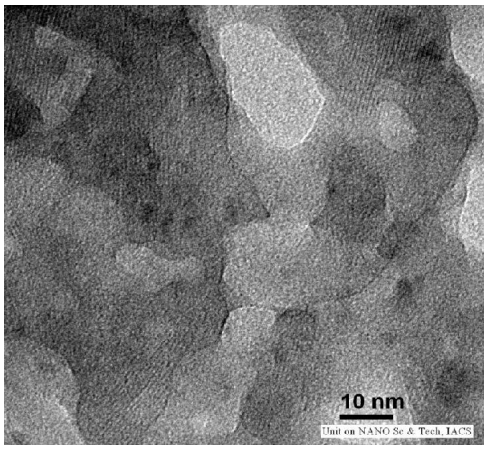


Figure b

Characterization Data of the Unknown Compounds in entries 2,4,6,7,8,9,11,14 and 15 in Table 3

5-Phenyl-pent-2-en-4-ynoic acid tert-butyl ester [entry 2, Table 3]. Light yellow liquid: IR (neat): 2906, 2868, 2195, 1716, 1620, 1309, 1253, 1176, 1028 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.50 (s, 9H), 6.25 (d, *J* = 15.8 Hz, 1H), 6.89 (d, *J* = 15.8 Hz, 1H), 7.30-7.36 (m, 3H), 7.46-7.52 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.2 (3C), 81.1, 86.6, 97.7, 122.5, 124.1, 128.5 (2C), 129.3, 132.0 (2C), 132.2, 165.3; HRMS Calcd for $C_{15}H_{16}O_2$ $[M+Na]^+$: 251.1048; Found: 251.1056.

5-*p*-Tolyl-pent-2-en-4-ynoic acid butyl ester [entry 4, Table 3]. Yellowish liquid; IR (neat): 2960, 2933, 2200, 1714, 1620, 1489, 1311, 1251, 1173, 1092, 1024, 827 cm^{-1}; ^1H NMR δ 0.97 (t, *J* = 7.3 Hz, 3H), 1.38-1.46 (m, 2H), 1.63-1.72 (m, 2H), 2.38 (s, 3H), 4.19 (t, *J* = 6.6 Hz, 2H), 6.30 (d, *J* = 15.8 Hz, 1H), 6.99 (d, *J* = 15.8 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR δ 13.8, 19.2, 21.7, 30.8, 64.7, 86.0, 98.8, 119.3, 125.4, 129.4 (2C), 129.7, 132.0 (2C), 139.8, 166.2; HRMS Calcd for $C_{16}H_{18}O_2$ $[M+Na]^+$: 265.1307; Found : 265.1311.

5-(4-Chloro-phenyl)-pent-2-en-4-ynoic acid butyl ester [entry 6, Table 3]. Yellow liquid: IR (neat): 2963, 2880, 2197, 1716, 1621, 1395, 1270, 1180, 1020 cm^{-1}; ^1H NMR δ 0.95 (t, *J* = 7.3 Hz, 3H), 1.34-1.47 (m, 2H), 1.61-1.71 (m, 2H), 4.18 (t, *J* = 6.6 Hz, 2H), 6.31 (d, *J* = 15.8 Hz, 1H), 6.95 (d, *J* = 15.8 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR δ 13.8, 19.3, 30.8, 64.8, 87.4, 97.0, 120.8, 124.8, 129.0 (2C), 130.6, 133.3 (2C), 135.6, 166.0; HRMS Calcd for $C_{15}H_{15}ClO_2$ $[M+Na]^+$: 285.0625; Found: 285.0648.

5-(2-Bromo-phenyl)-pent-2-en-4-ynoic acid butyl ester [entry 7, Table 3]. Yellow liquid: IR (neat): 2958, 2931, 2202, 1715, 1618, 1467, 1315, 1259, 1174, 1026 cm^{-1}; ^1H NMR δ 0.87 (t, *J* = 7.4 Hz, 3H), 1.29-1.37 (m, 2H), 1.54-1.63 (m, 2H), 4.11 (t, *J* = 6.6 Hz, 2H), 6.30 (d, *J* = 15.8 Hz, 1H), 6.92 (d, *J* = 15.8 Hz, 1H), 7.12-7.21 (m, 2H), 7.41

(dd, *J* = 8.2 Hz, 1.5 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR δ 13.8, 19.2, 30.8, 64.8, 90.6, 96.3, 124.5, 124.6, 125.9, 127.2, 130.5, 131.0, 132.7, 133.8, 165.9; HRMS Calcd for $C_{15}H_{15}BrO_2$ $[M+Na]^+$: 329.0153, 331.0134; Found: 329.0151, 331.0147.

5-(2-Bromo-phenyl)-pent-2-en-ynoic acid butyl ester [entry 8, Table 3]. Yellow liquid: IR (neat): 2978, 2931, 2203, 1708, 1616, 1469, 1323, 1151, 958, 754 cm^{-1}; ^{1}H NMR δ 1.51 (s, 9H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.91 (d, *J* = 15.8 Hz, 1H), 7.19-7.28 (m, 2H), 7.48 (dd, *J* = 7.7 Hz, 1.4 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR δ 28.2 (3C), 81.3, 90.7, 95.7, 123.6, 124.7, 125.9, 127.2, 130.3, 132.6, 132.7, 133.7, 165.1; HRMS Calcd for $C_{15}H_{15}BrO_2$ $[M+Na]^+$: 329.0153, 331.0134; Found: 329.0155, 331.0150.

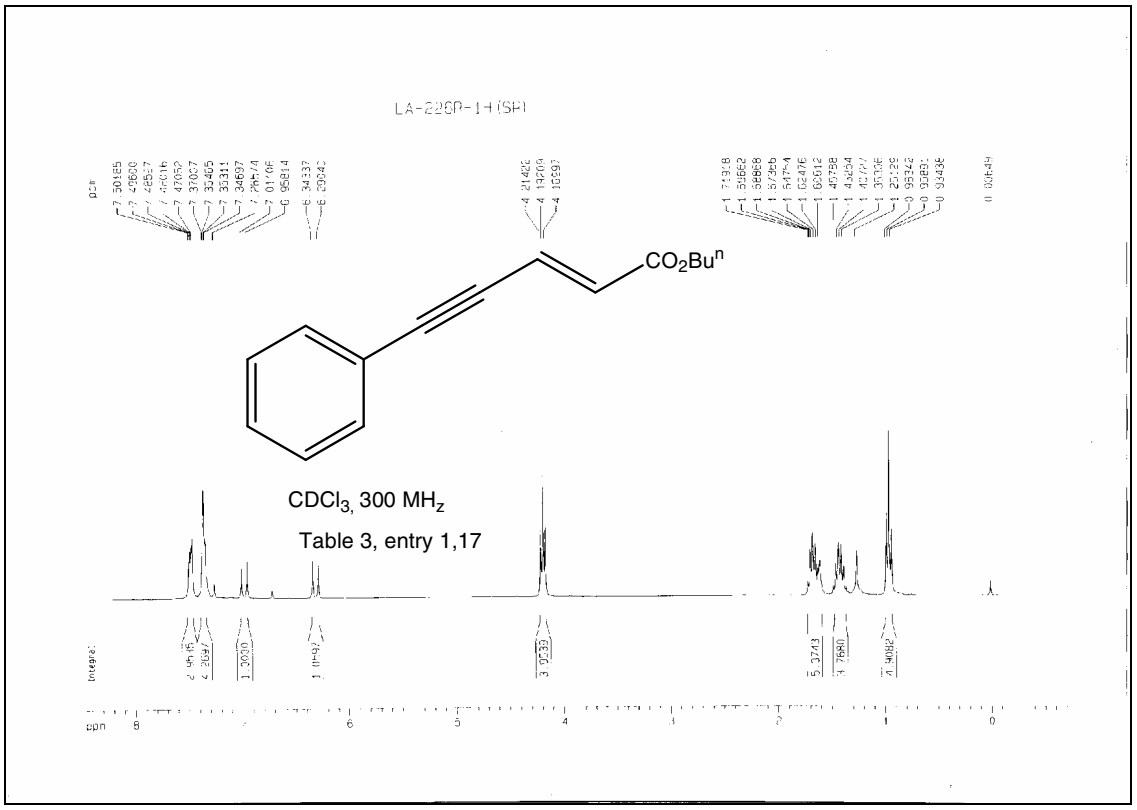
5-(4-Fluoro-phenyl)-pent-2-en-4-ynoic acid butyl ester [entry 9, Table 3]. Yellowish liquid: IR (neat): 2960, 2935, 2874, 2202, 1715, 1620, 1597, 1506, 1313, 1232, 1155, 1024, 837 cm^{-1}; ^{1}H NMR δ 0.95 (t, *J* = 7.3 Hz, 3H), 1.34-1.47 (m, 2H), 1.61-1.71 (m, 2H), 4.15 (t, *J* = 6.6 Hz, 2H), 6.29 (d, *J* = 15.8 Hz, 1H), 6.95 (d, *J* = 15.8 Hz, 1H), 7.04 (t, *J* = 8.6 Hz, 2H), 7.44-7.48 (m, 2H); ^{13}C NMR δ 13.8, 19.3, 30.8, 64.8, 86.2, 97.2, 115.8, 116.1, 118.5, 124.9, 130.3, 134.0, 134.2, 161.5, 164.9, 166.1; HRMS Calcd for $C_{15}H_{15}FO_2$ $[M+Na]^+$: 269.0954, Found: 269.0947.

5-(3-Methoxy-phenyl)-pent-2-en-4-ynoic acid butyl ester [entry 11, Table 3]. Yellow liquid: IR (neat): 2965, 2929, 2200, 1716, 1460, 1325, 1251, 1020, 920 cm^{-1}; ^{1}H NMR δ 0.87 (t, *J* = 7.3 Hz, 3H), 1.29-1.37 (m, 2H), 1.53-1.63 (m, 2H), 3.72 (s, 3H), 4.10 (t, *J* = 6.6 Hz, 2H), 6.23 (d, *J* = 15.9 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 15.9 Hz, 1H), 6.92 (s, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR δ 13.8, 19.2, 30.7, 55.4, 64.8, 86.2, 98.2, 116.0, 116.7, 123.2, 124.6, 125.0, 129.6, 130.2, 159.5, 166.1; HRMS Calcd for $C_{16}H_{18}O_3$ $[M+Na]^+$: 281.1154; Found : 281.1151.

Non-2-en-4-ynoic acid butyl ester [entry 14, Table 3]. Colorless liquid: IR (neat): 2959, 2933, 2873, 2214, 1716, 1620, 1466, 1299, 1157, 962 cm^{-1}; ^{1}H NMR δ 0.89-0.95 (m, 6H), 1.35-1.65 (m, 8H), 2.34-2.39 (m, 2H) 4.16 (t, *J* = 6.5 Hz, 2H), 6.14 (d, *J* = 15.8 Hz, 1H), 6.74 (dt, *J* = 15.8 Hz, 2.2 Hz, 1H); ^{13}C NMR δ 13.7, 13.8, 19.3, 19.6, 22.1, 30.5, 30.8, 64.6, 78.1, 100.9, 126.2, 129.4, 166.4; HRMS Calcd for $C_{13}H_{20}O_2$ $[M+Na]^+$: 231.1361; Found: 231.1362.

Undec-2-en-4-ynoic acid methyl ester [entry 15, Table 3]. Colorless liquid: IR (neat): 2958, 2931, 2872, 2214, 1716, 1620, 1465, 1299, 1286, 1176, 1157, 962 cm^{-1}; ^1H NMR δ 0.89 (t, *J* = 6.4 Hz, 3H), 1.25-1.43 (m, 6H), 1.50-1.62 (m, 2H), 2.36 (td, *J* = 6.9 Hz, 2.0 Hz, 2H), 3.76 (s, 3H), 6.14 (d, *J* = 15.8 Hz, 1H), 6.76 (dt, *J* = 15.8 Hz, 2.1 Hz, 1H); ^{13}C NMR δ 14.17, 19.9, 22.6, 28.4, 28.7, 31.4, 51.9, 78.1, 101.3, 126.6, 128.9, 166.8; HRMS Calcd for $C_{12}H_{18}O_2$ $[M+Na]^+$: 217.1305; Found: 217.1309.

3-(1H-Indol-3-yl)-2-(5-naphthalen-1-yl-pent-2-en-4-ynoylamino)-propionic acid methyl ester [Scheme 2, Compound 3]. Brownish viscous liquid; IR (neat): 3400, 3300, 3058, 2949, 2932, 2854, 2246, 2191, 1738, 1651, 1614, 1537, 1519, 1437, 1340, 1272, 1207, 1180, 908, 734 cm^{-1}; ^1H NMR δ 3.40 (t, *J* = 8.4 Hz, 2H), 3.69 (s, 3H), 5.06-5.12 (m, 1H), 6.42 (d, *J* = 15.5 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 1.8 Hz, 1H), 7.13 (d, *J* = 15.5 Hz, 1H), 7.12-7.20 (m, 2H), 7.34-7.44 (m, 2H), 7.52-7.58 (m, 3H), 7.68 (d, *J* = 6.9 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 8.28 (d, *J* = 8.1 Hz, 1H), 8.65 (s, 1H); ^{13}C NMR δ 27.6, 52.5, 53.4, 91.6, 95.3, 109.6, 111.5, 118.5, 119.7, 119.9, 122.2, 122.3, 123.1, 125.2, 125.9, 126.6, 127.1, 127.6, 128.4, 129.8, 131.2, 131.9, 133.1, 133.2, 136.2, 164.5, 172.3; HRMS Calcd for $C_{27}H_{22}N_2O_3$ $[M+Na]^+$: 445.1528; Found: 445.1529.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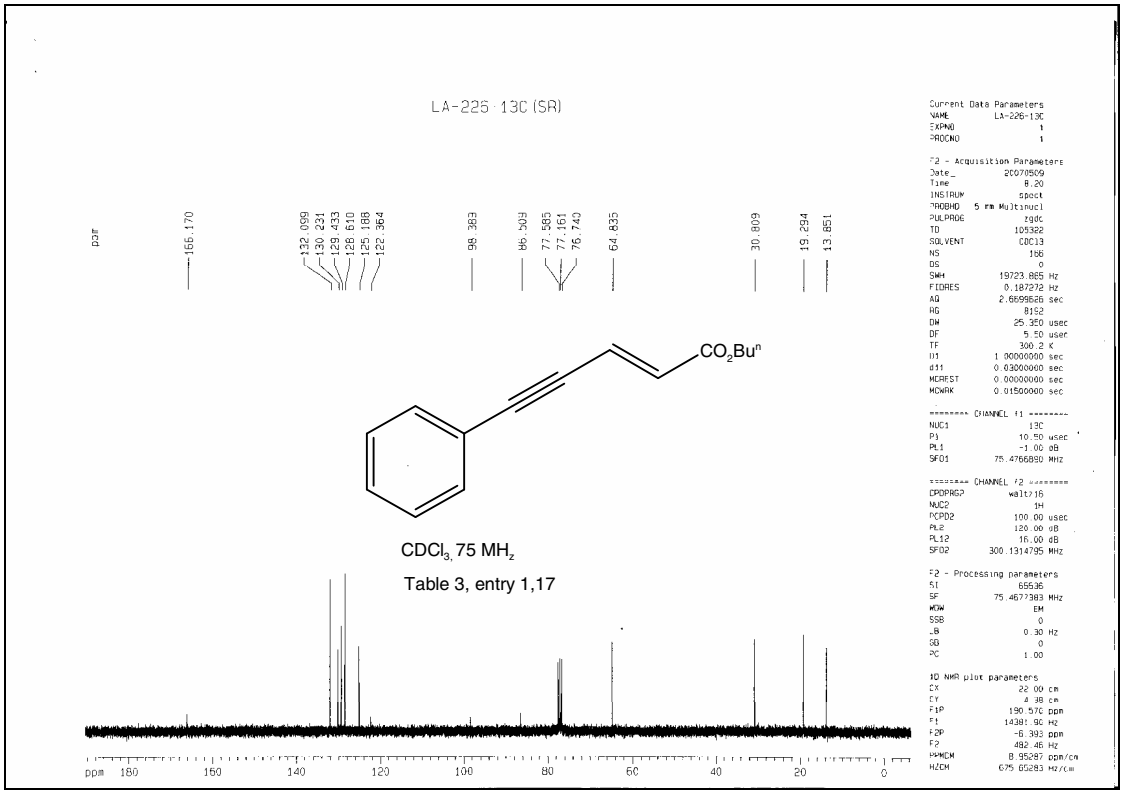
CO_2Bu^n
$CDCl_3$, 300 MH_z
Table 3, entry 1,17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CO_2Bu^n
$CDCl_3$, 75 MH_z
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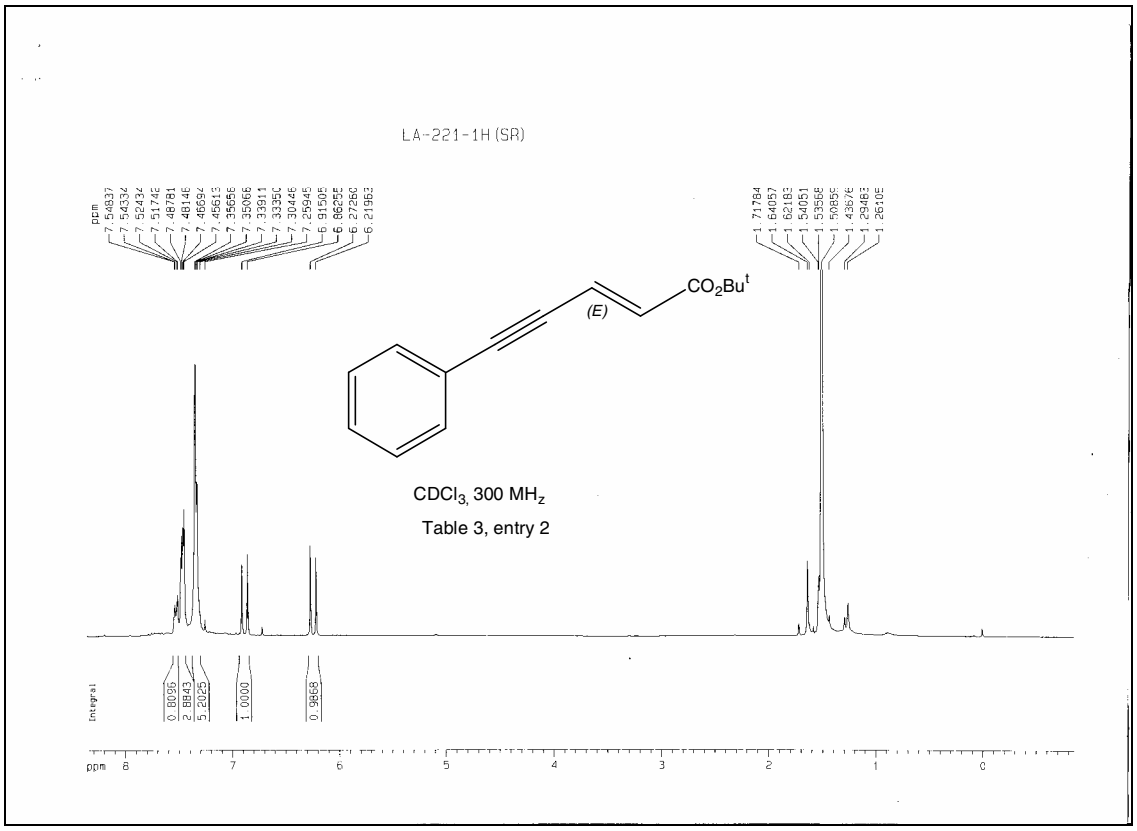
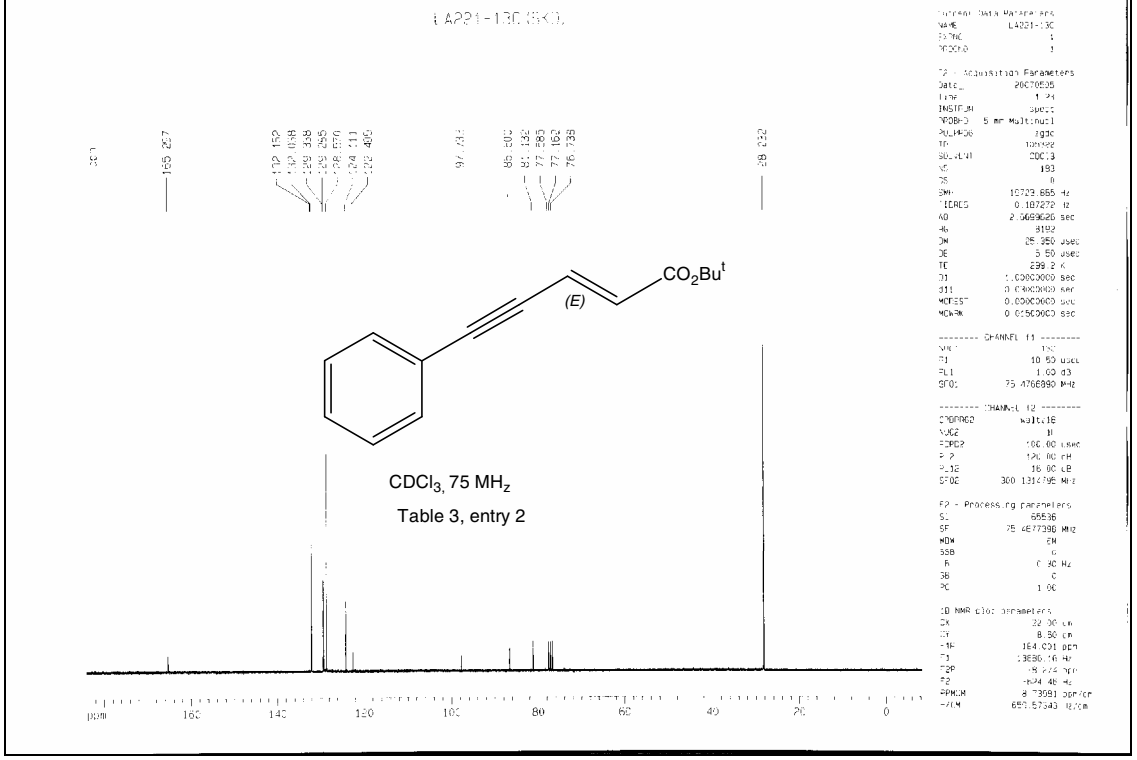


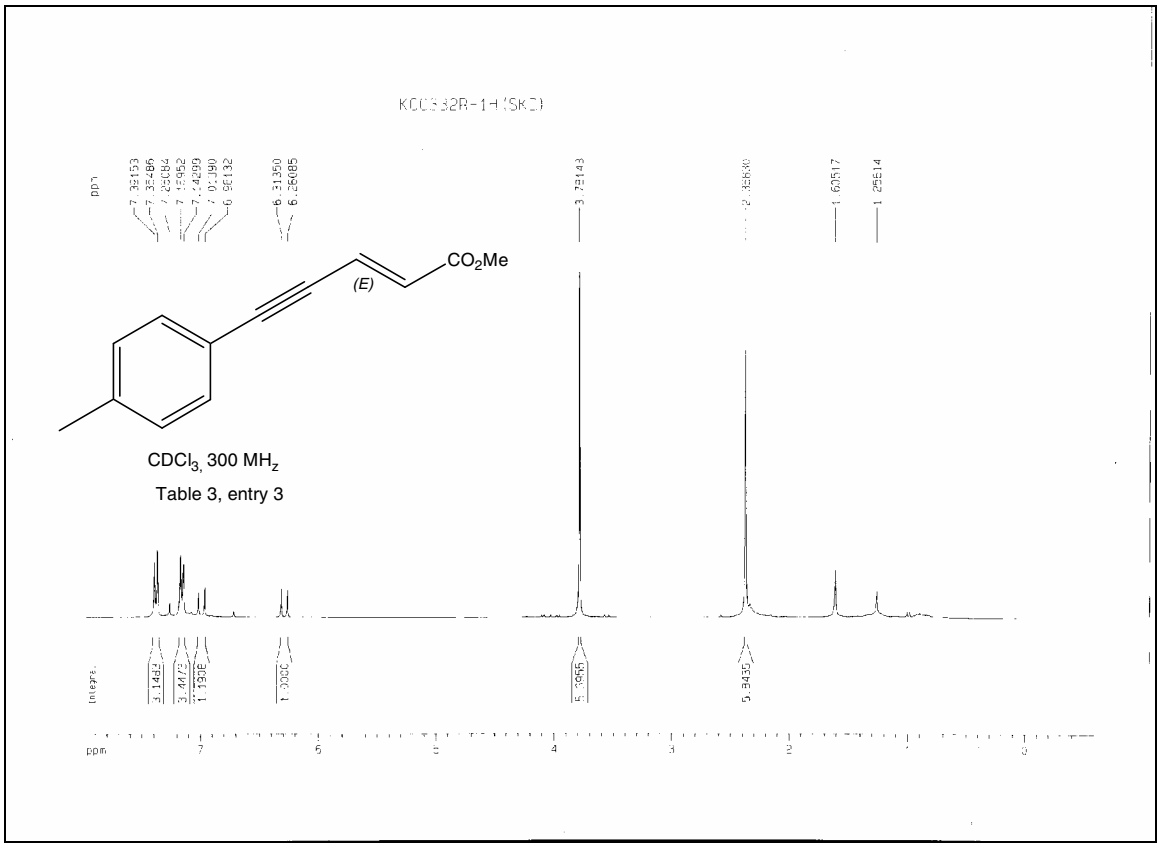
CDCl$_3$, 300 MH$_z$

Table 3, entry 2



CDCl$_3$, 75 MH$_z$

Table 3, entry 2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(E)
CDCl3, 300 MHz
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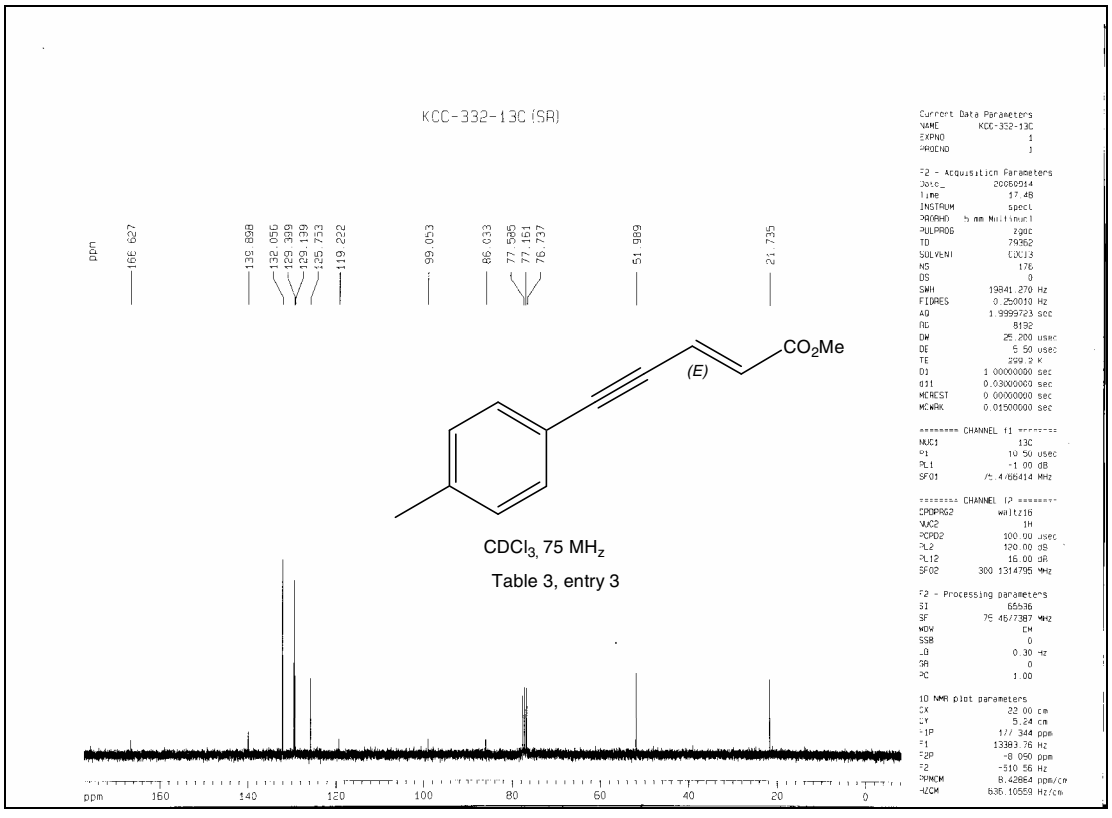
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(E)
CDCl3, 75 MHz
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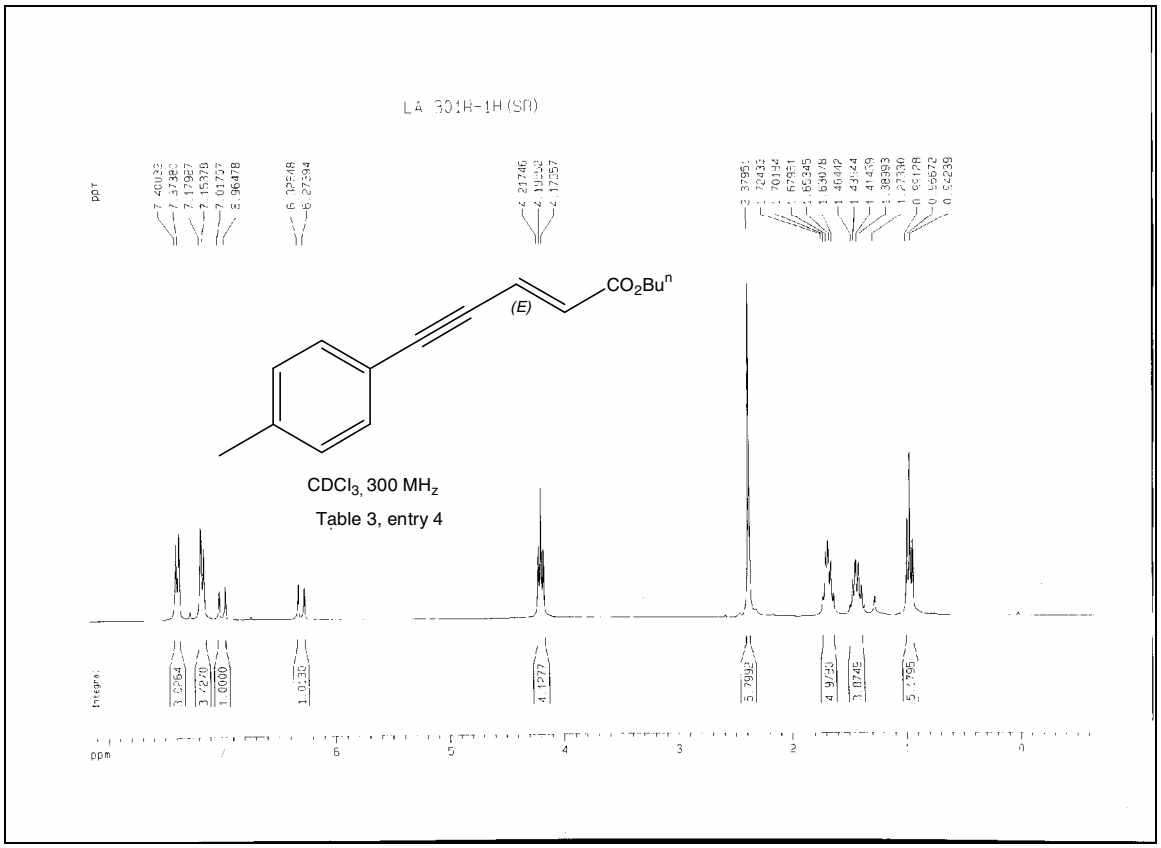
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CO2Bun
(E)
CDCl3, 300 MHz
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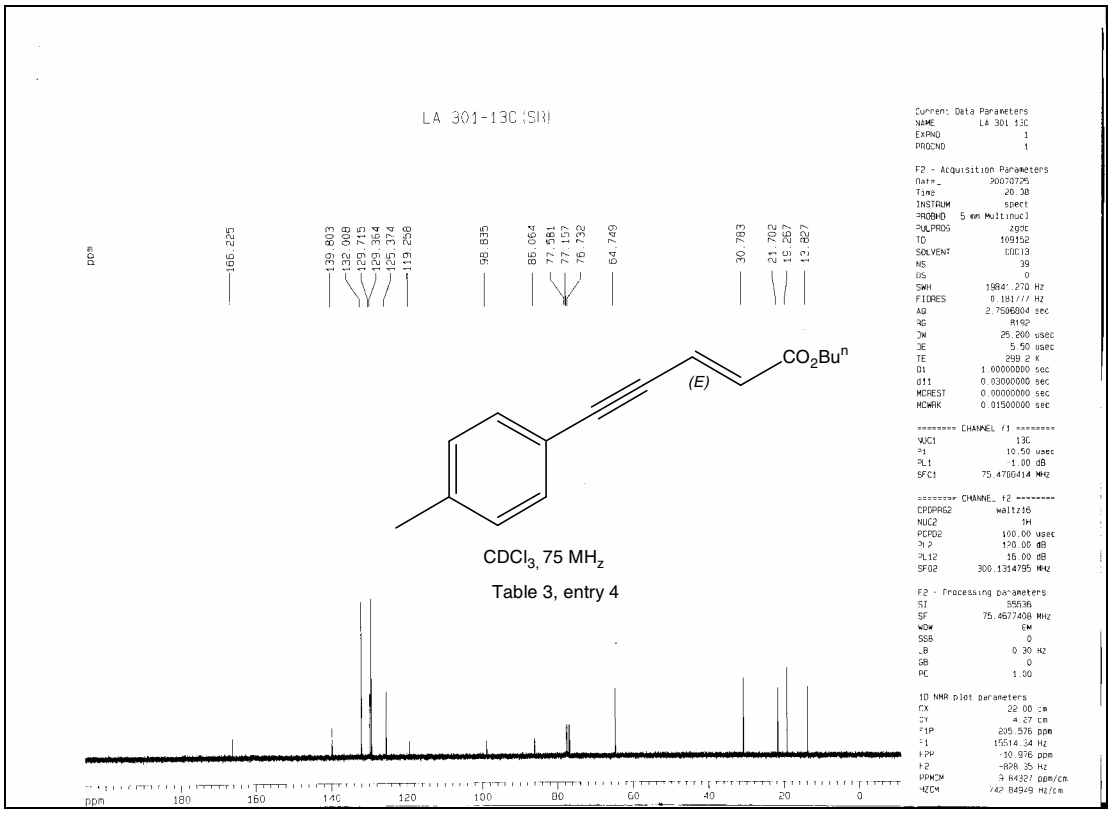
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CO2Bun
(E)
CDCl3, 75 MHz
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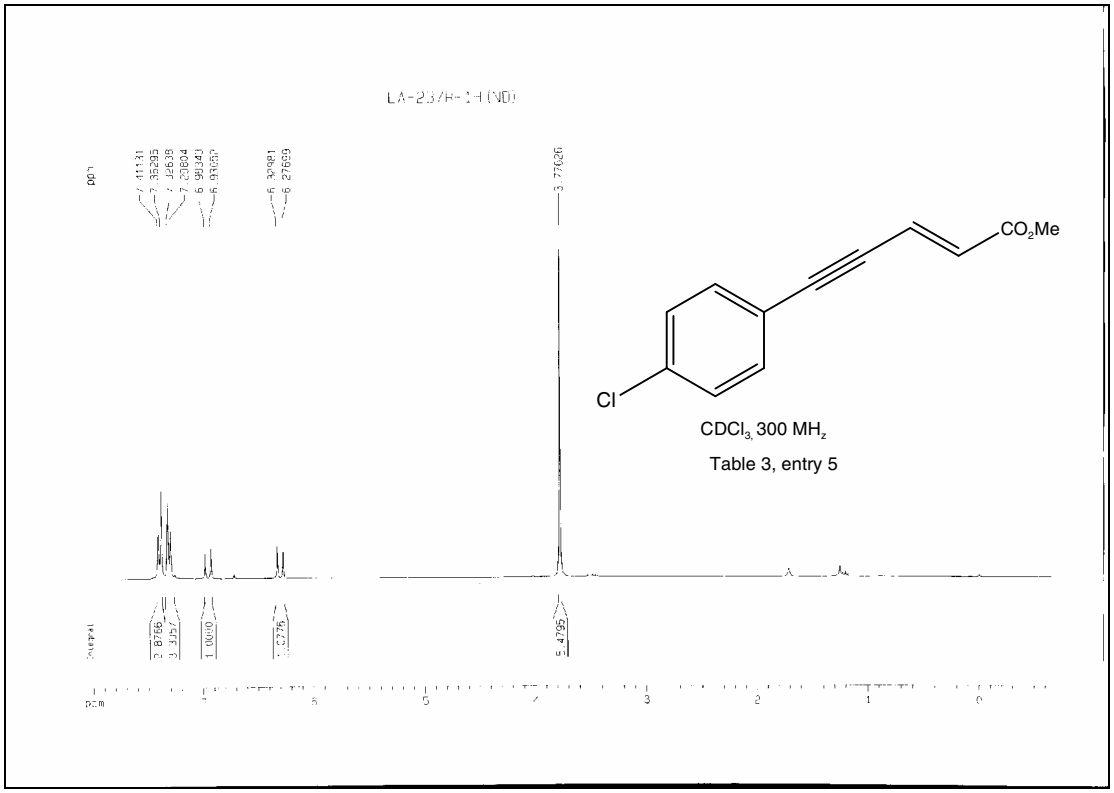
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Cl
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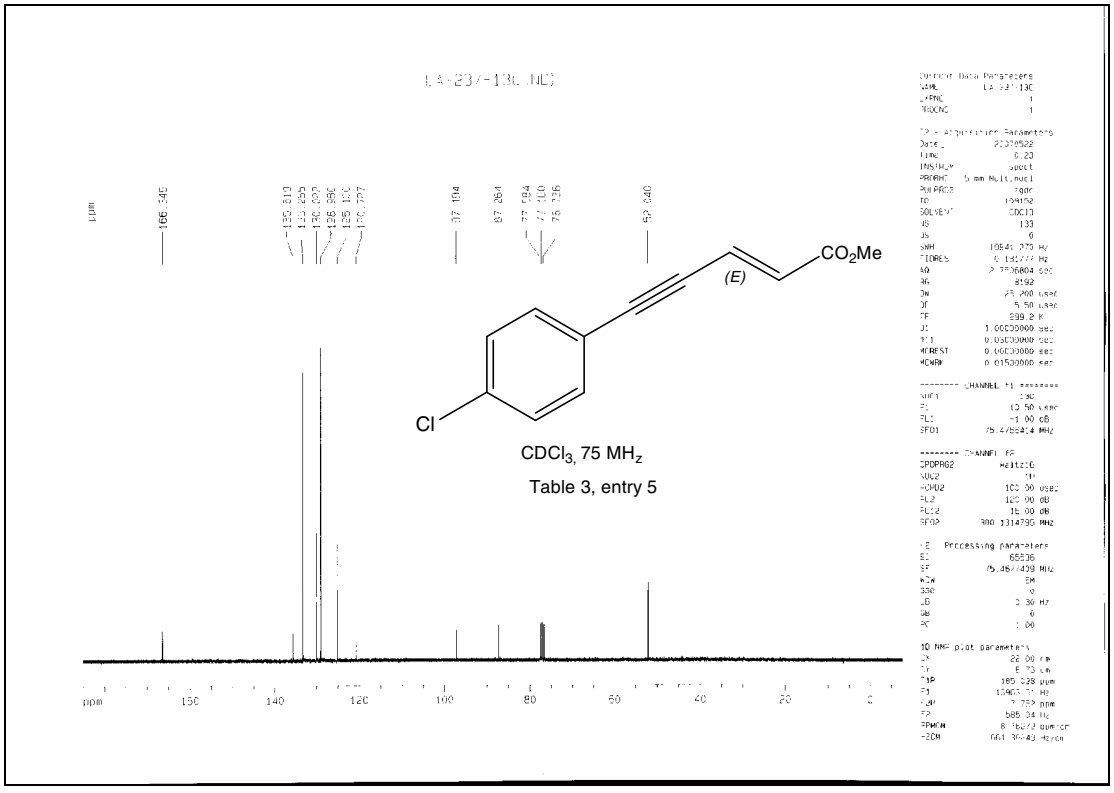
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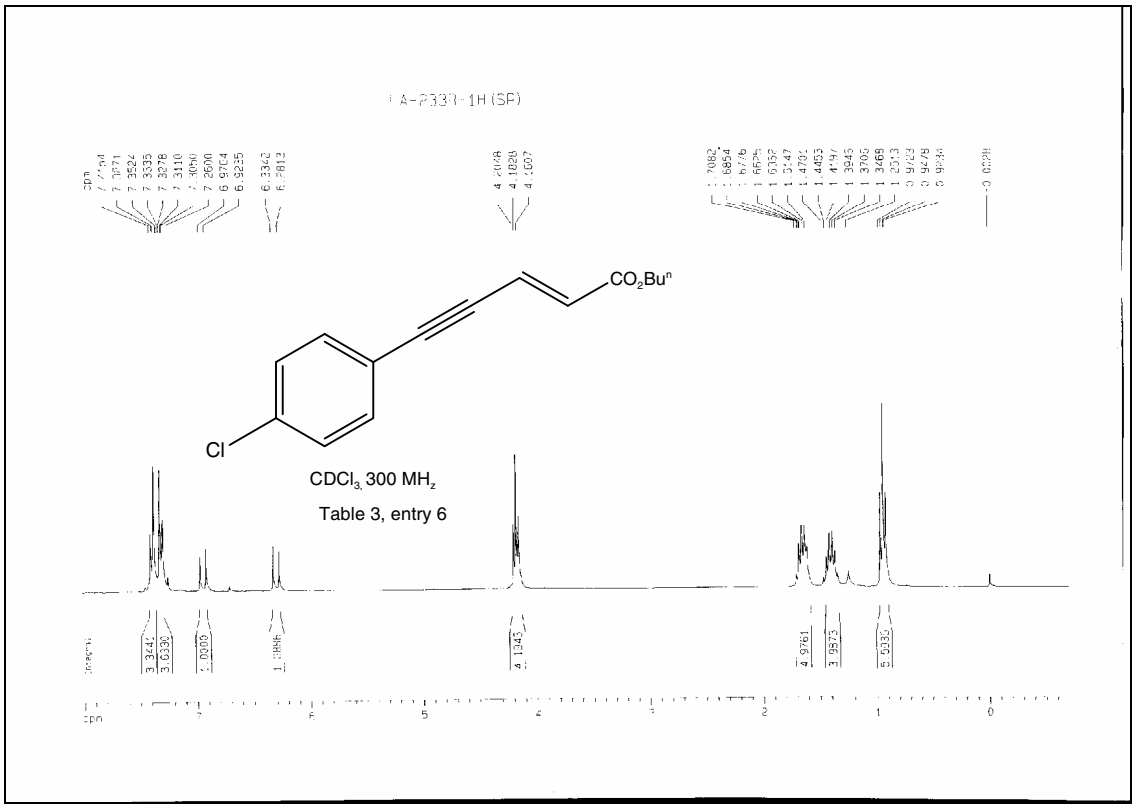
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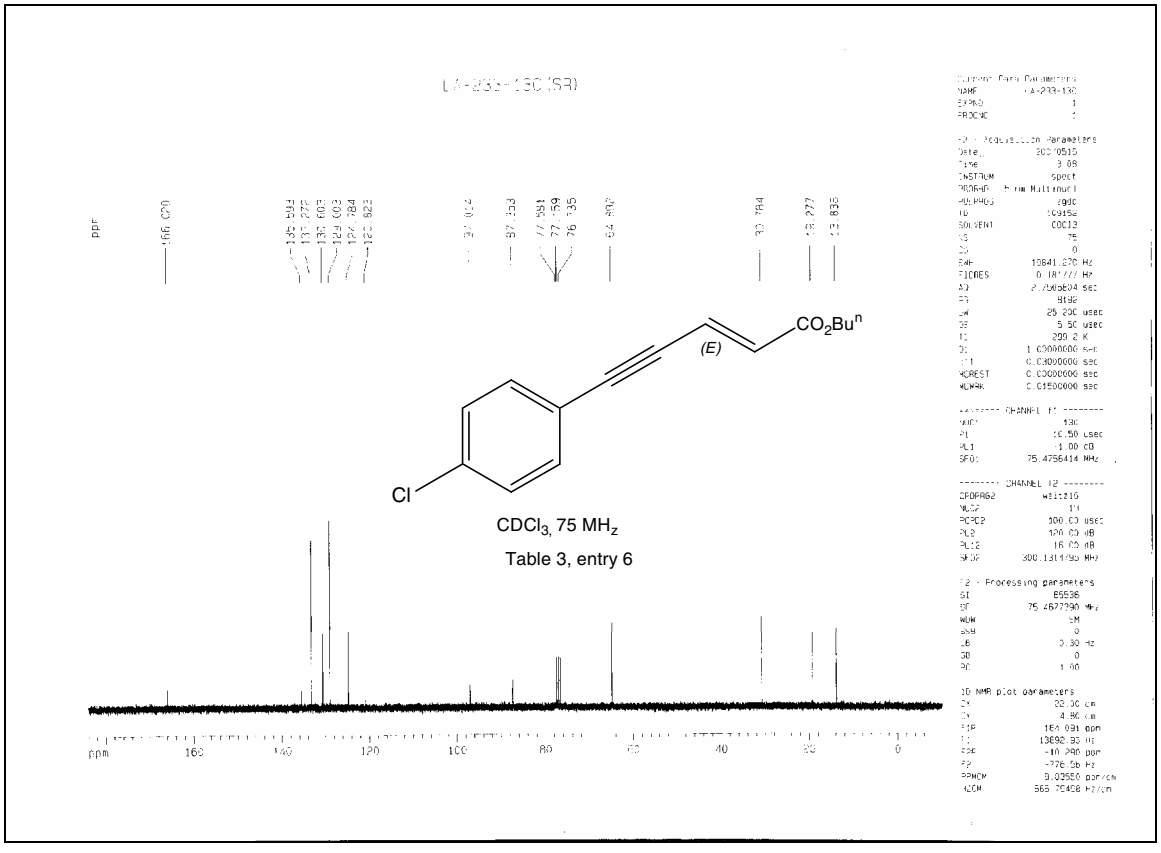
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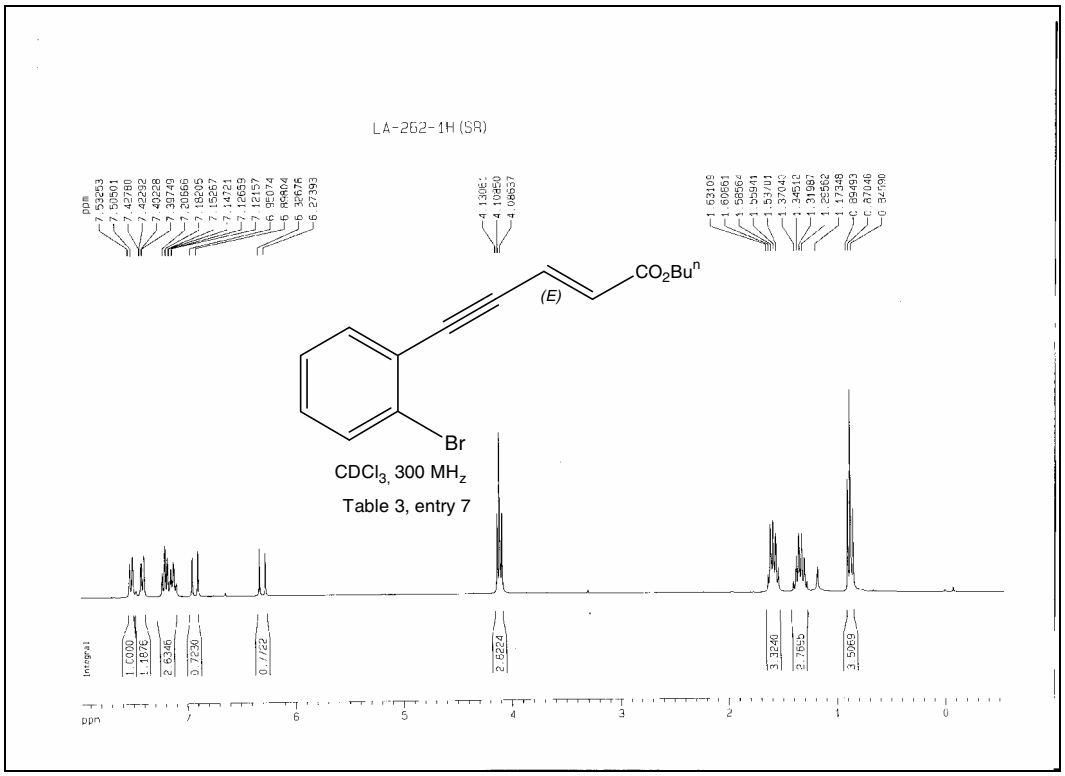
(E)
Cl
CDCl3, 75 MHz
Table 3, entry 6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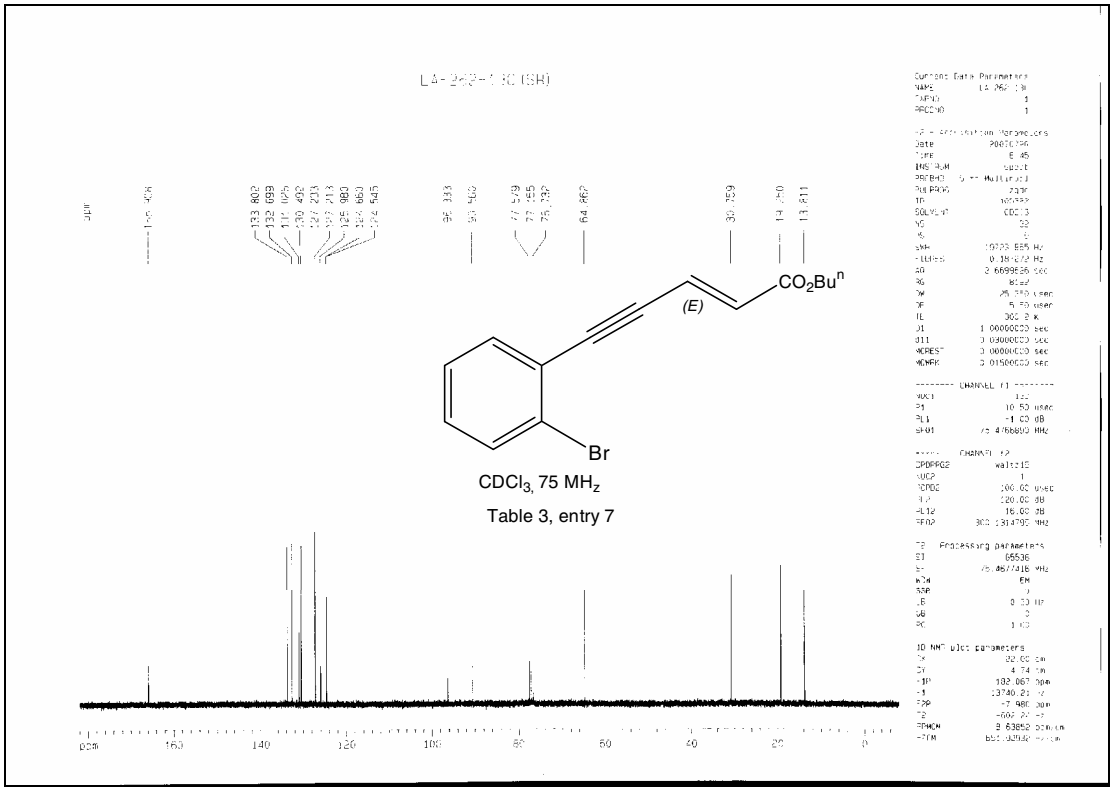
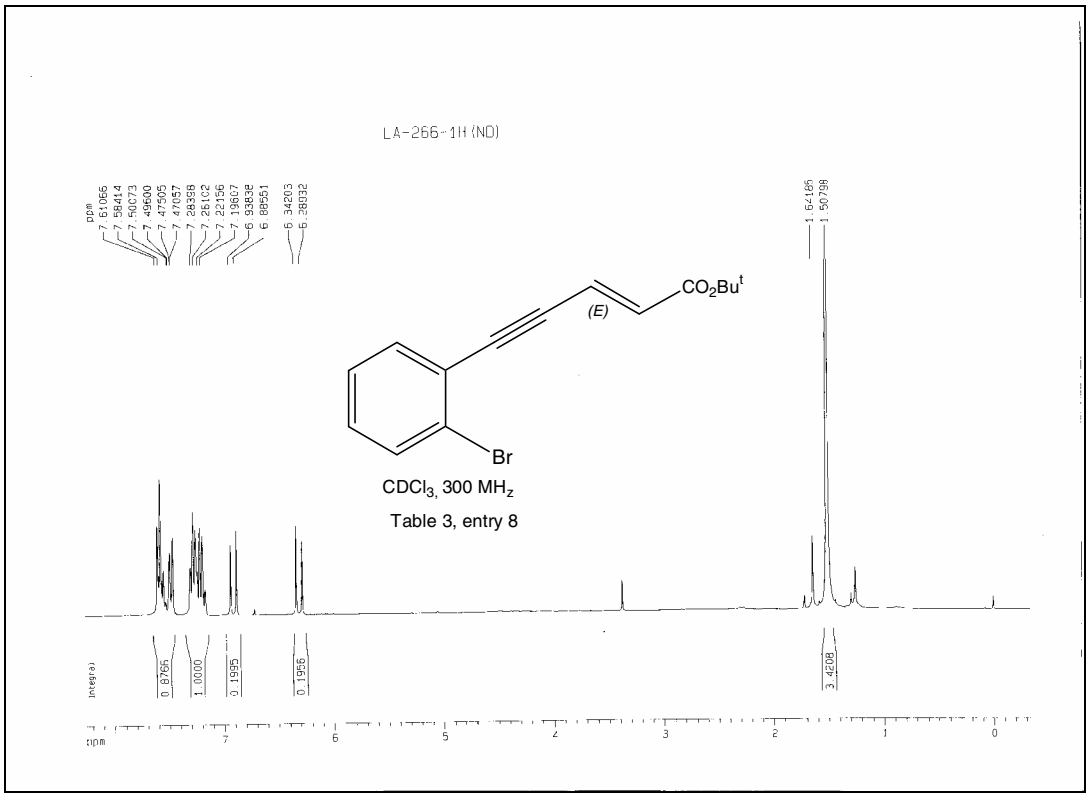

(E)
CO2Bun
Br
CDCl3, 75 MHz
Table 3, entry 7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6.88551
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6.28032
1.64166
1.50798
CO2But
(E)
Br
CDCl3, 300 MHz
Table 3, entry 8
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0.1966
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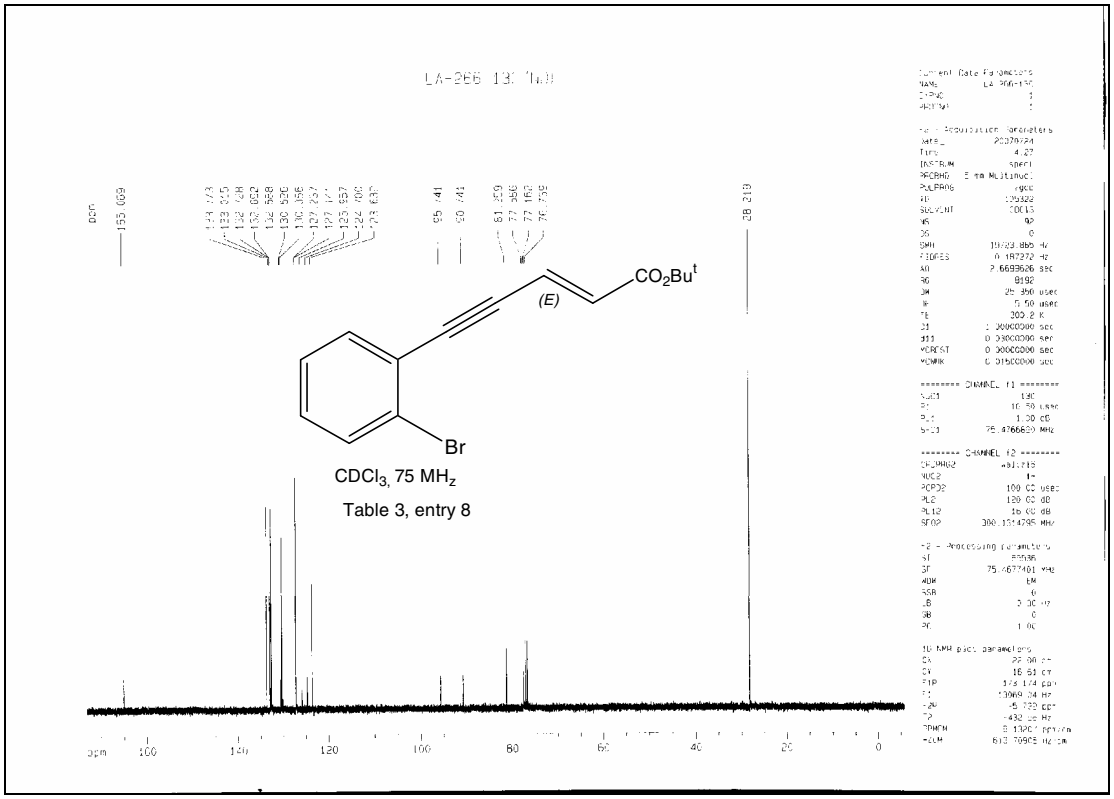
ppm


LA-266 13C (1H)
ppm
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90.741
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77.160
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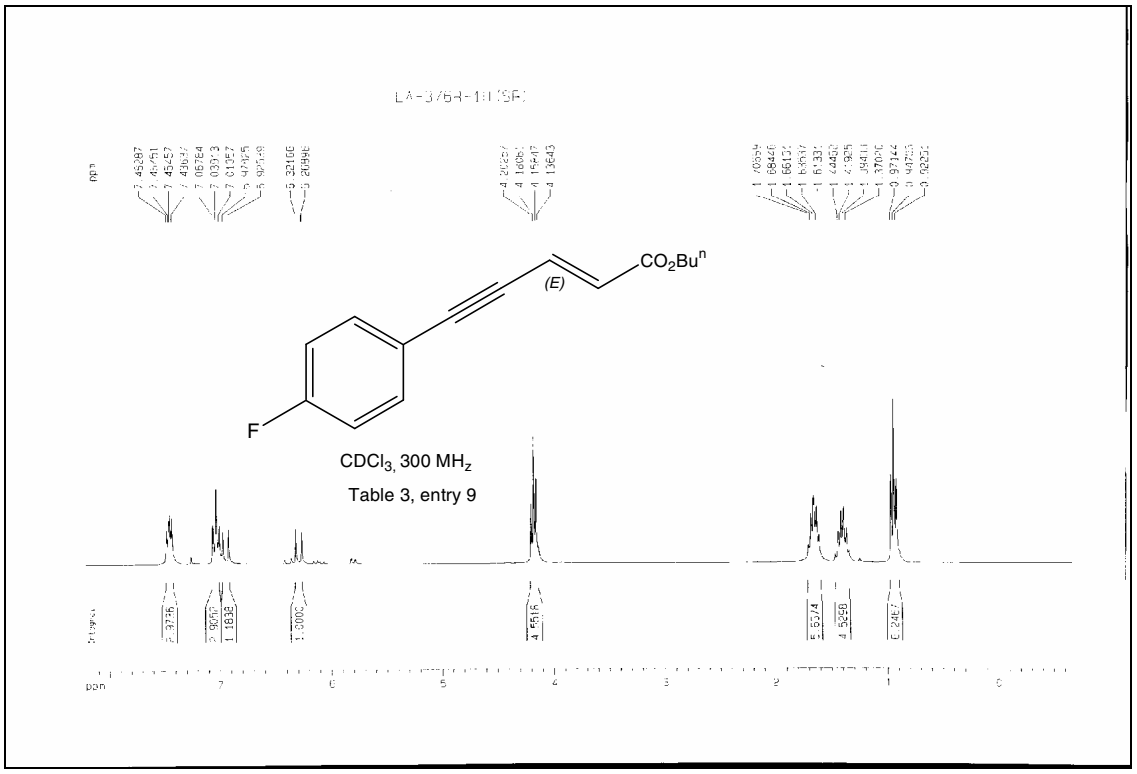
CO2But
(E)
Br
CDCl3, 75 MHz
Table 3, entry 8
ppm


(E)
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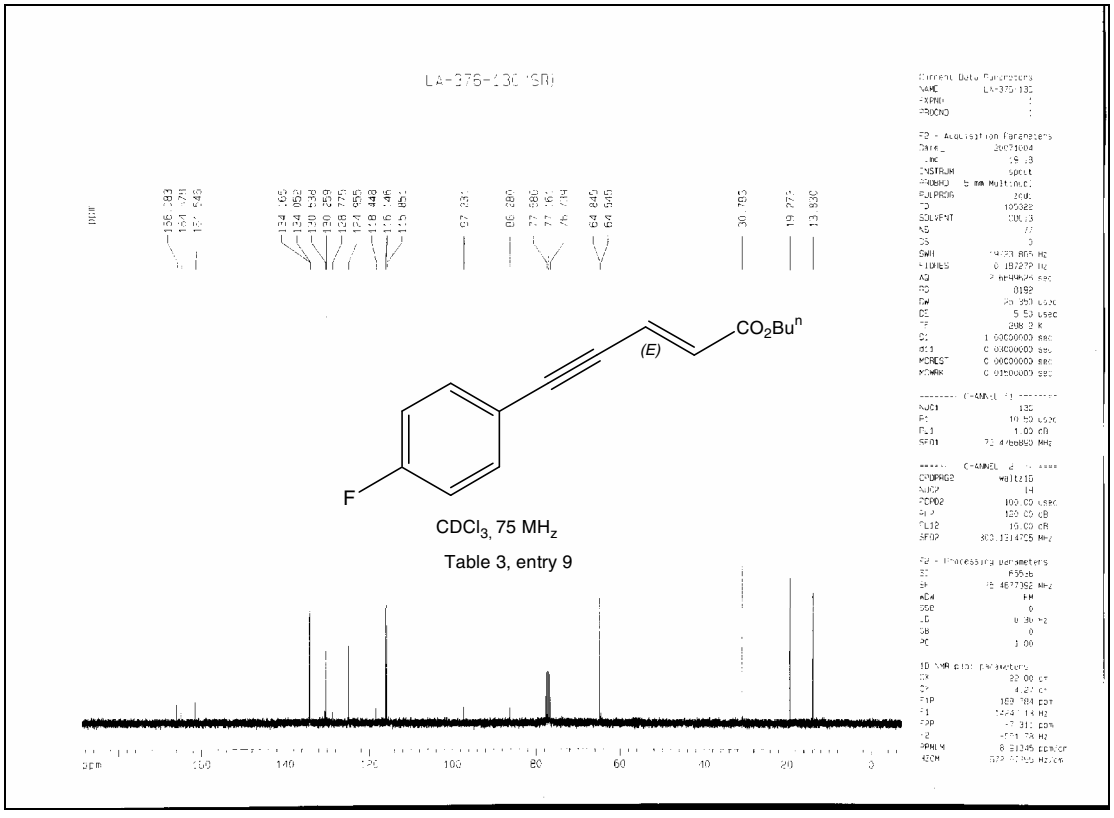
F
$CDCl_3$, 300 MH_z
Table 3, entry 9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F
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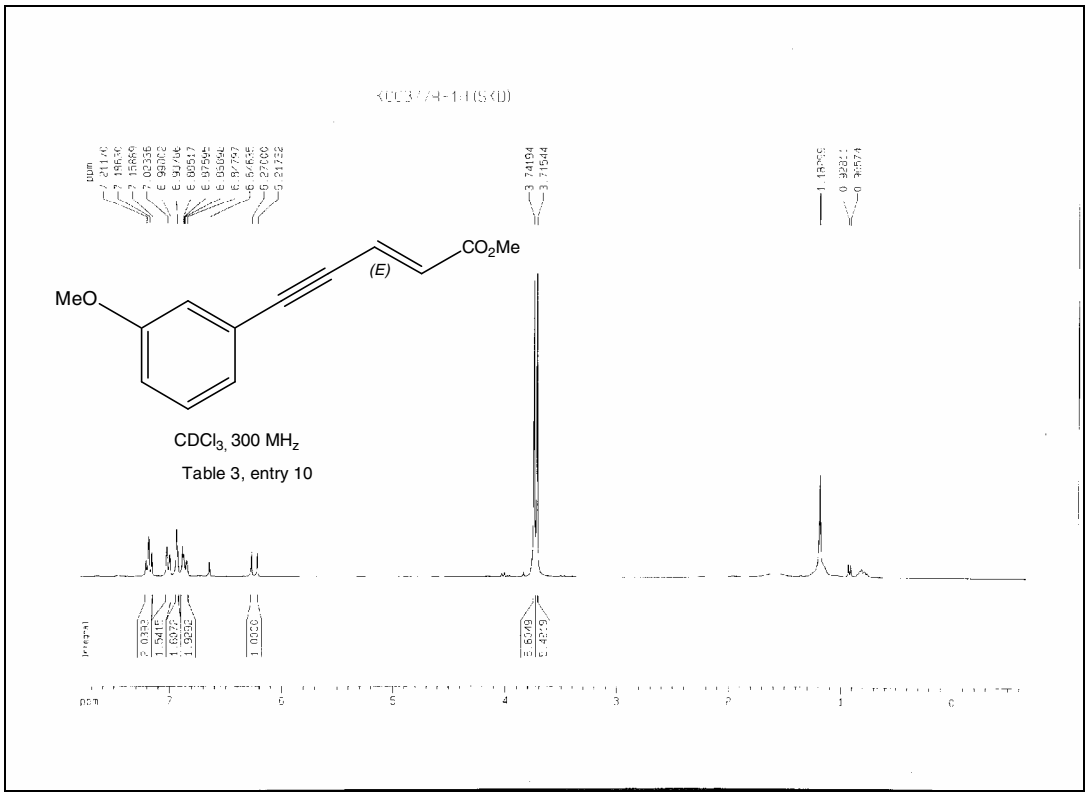

$CDCl_3$, 300 MH_z

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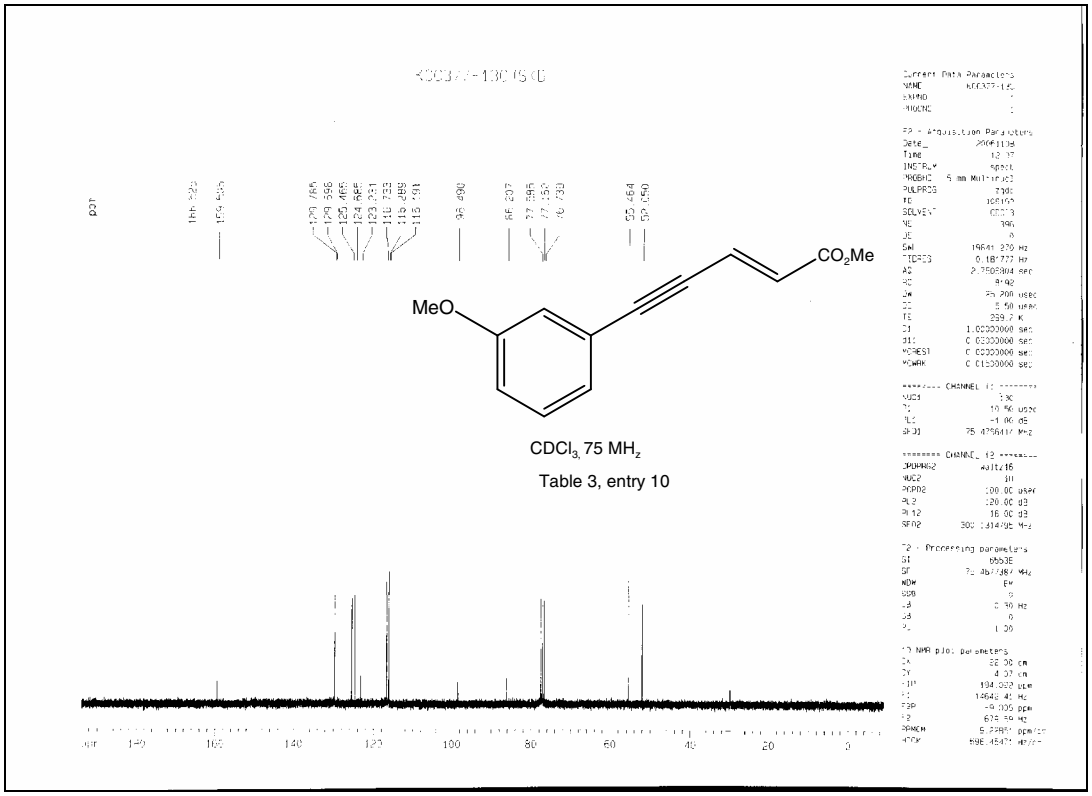
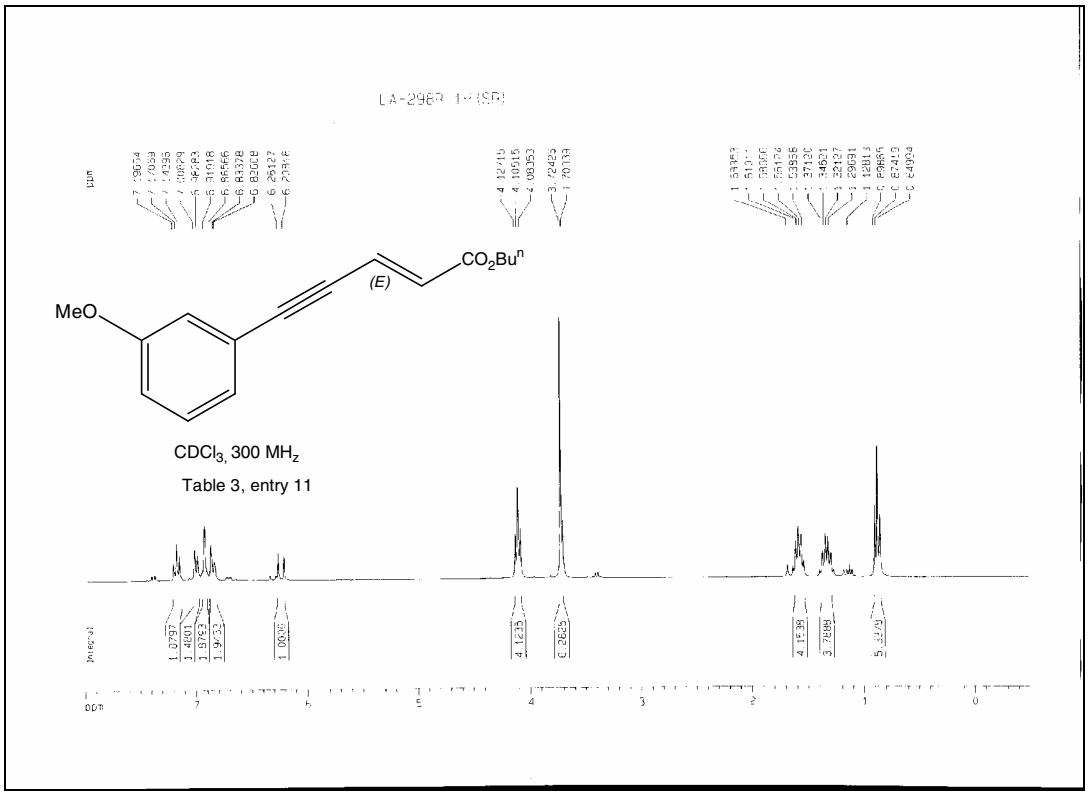
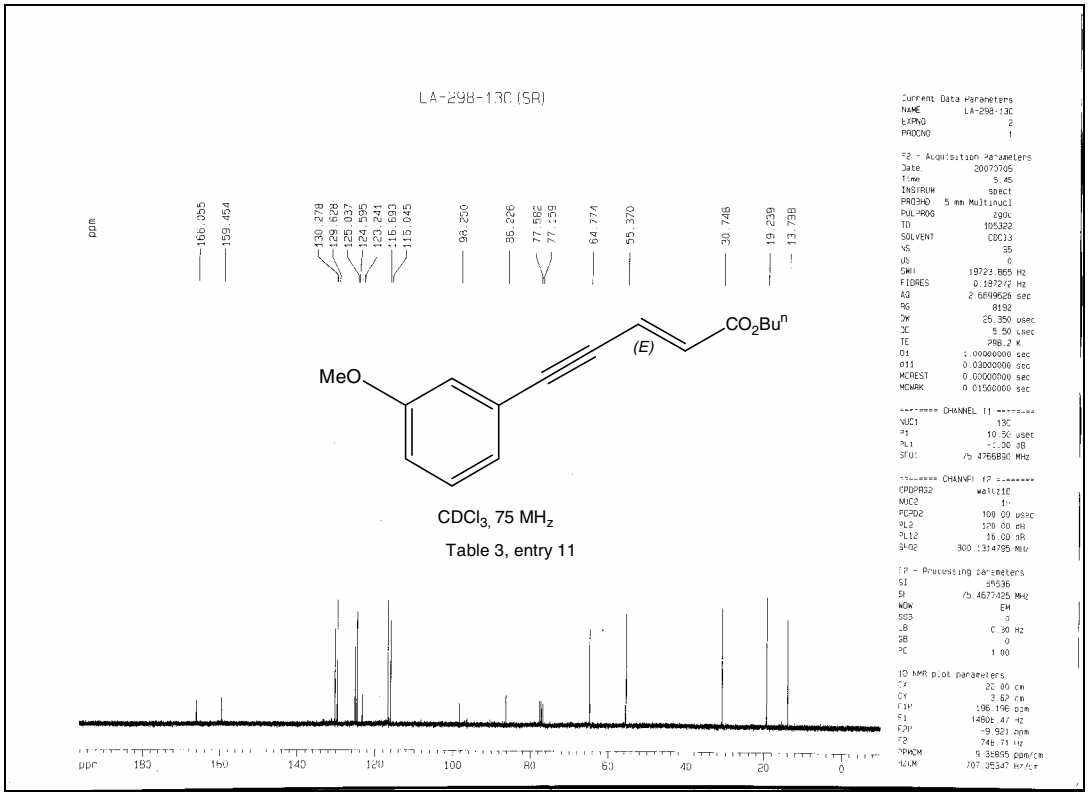
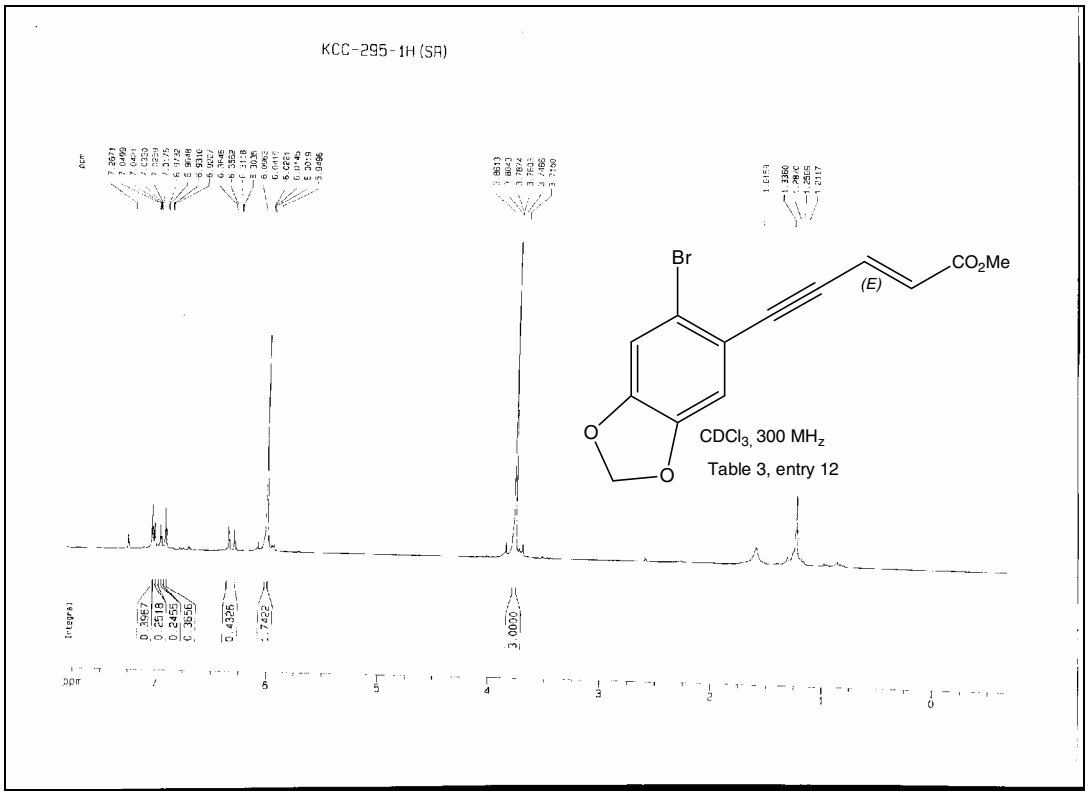


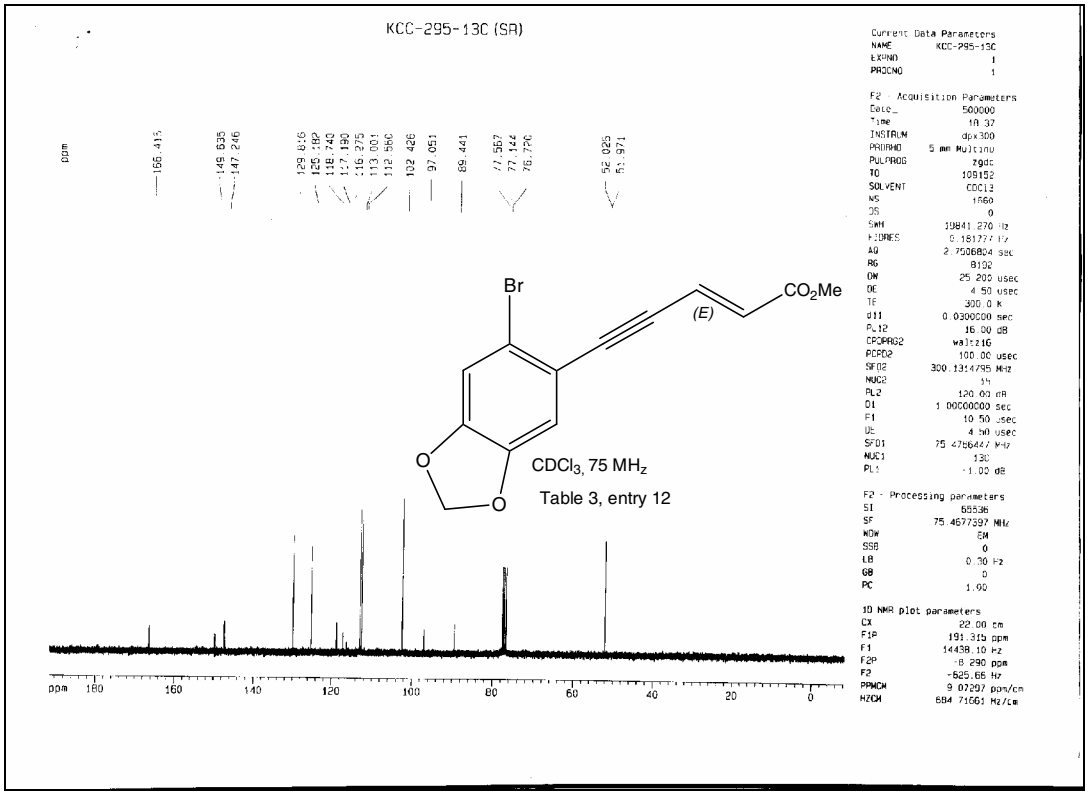
$CDCl_3$, 75 MH_z

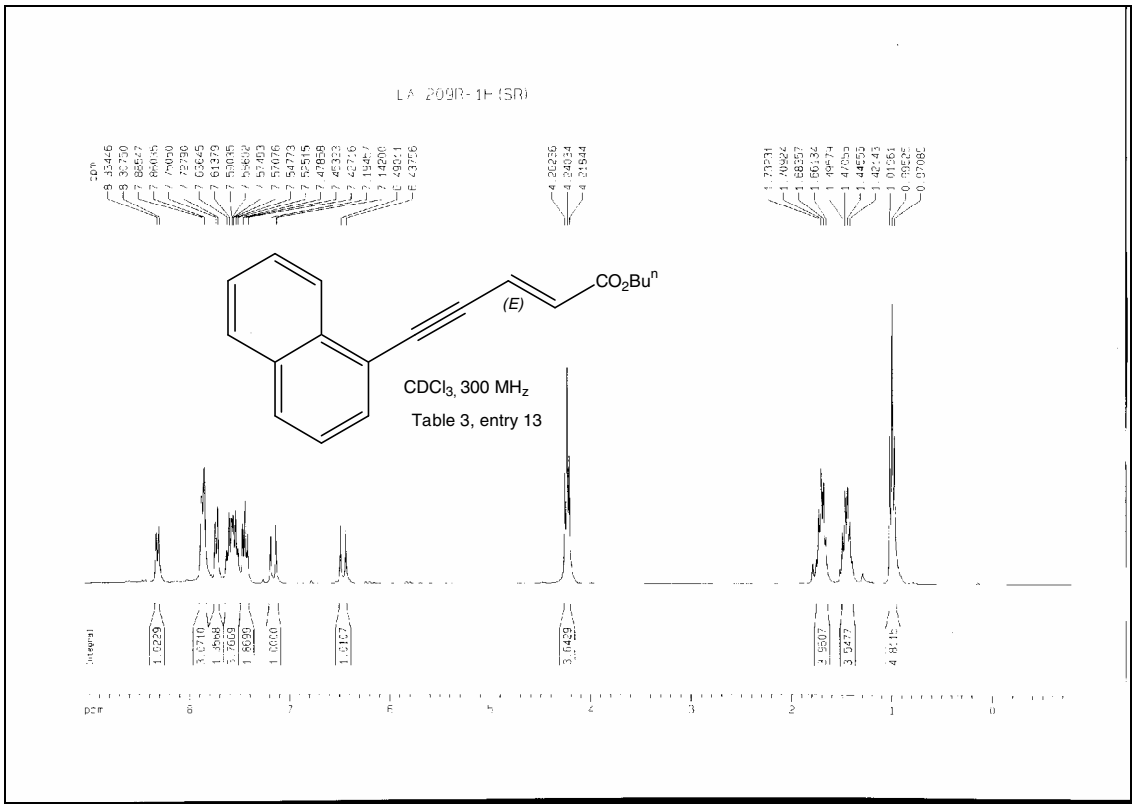
Table 3, entry 10

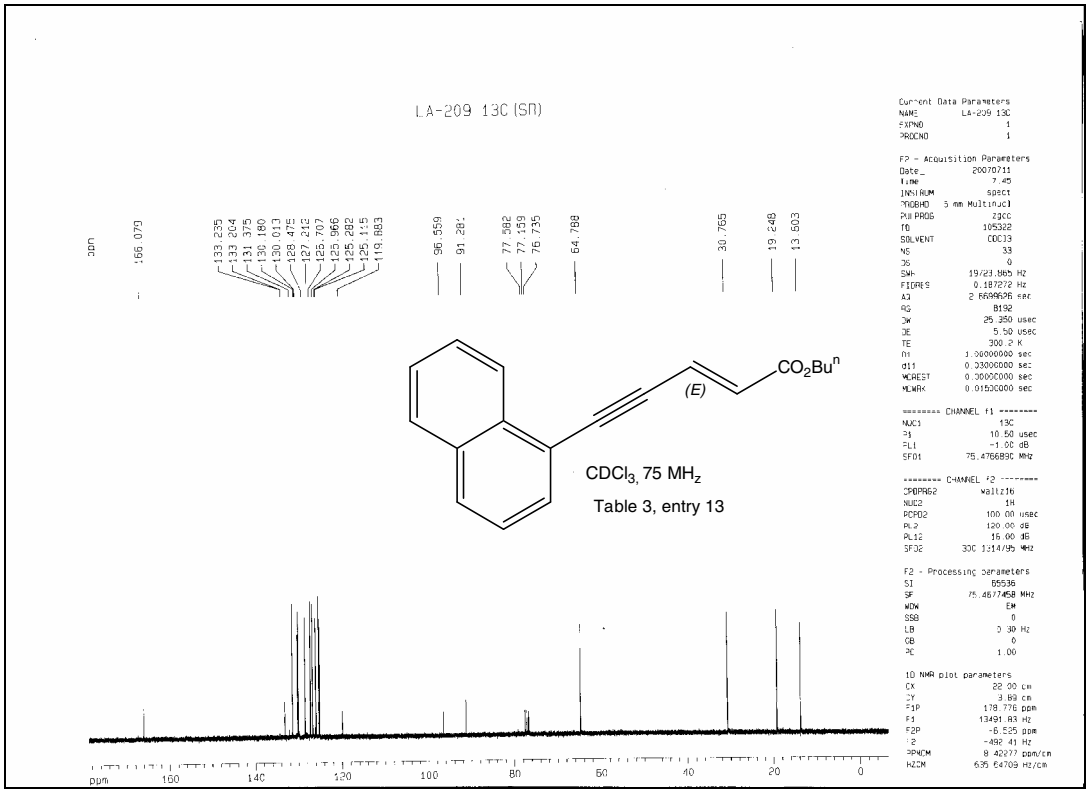

MeO
CO2Bun
(E)
CDCl3, 300 MHz
Table 3, entry 11

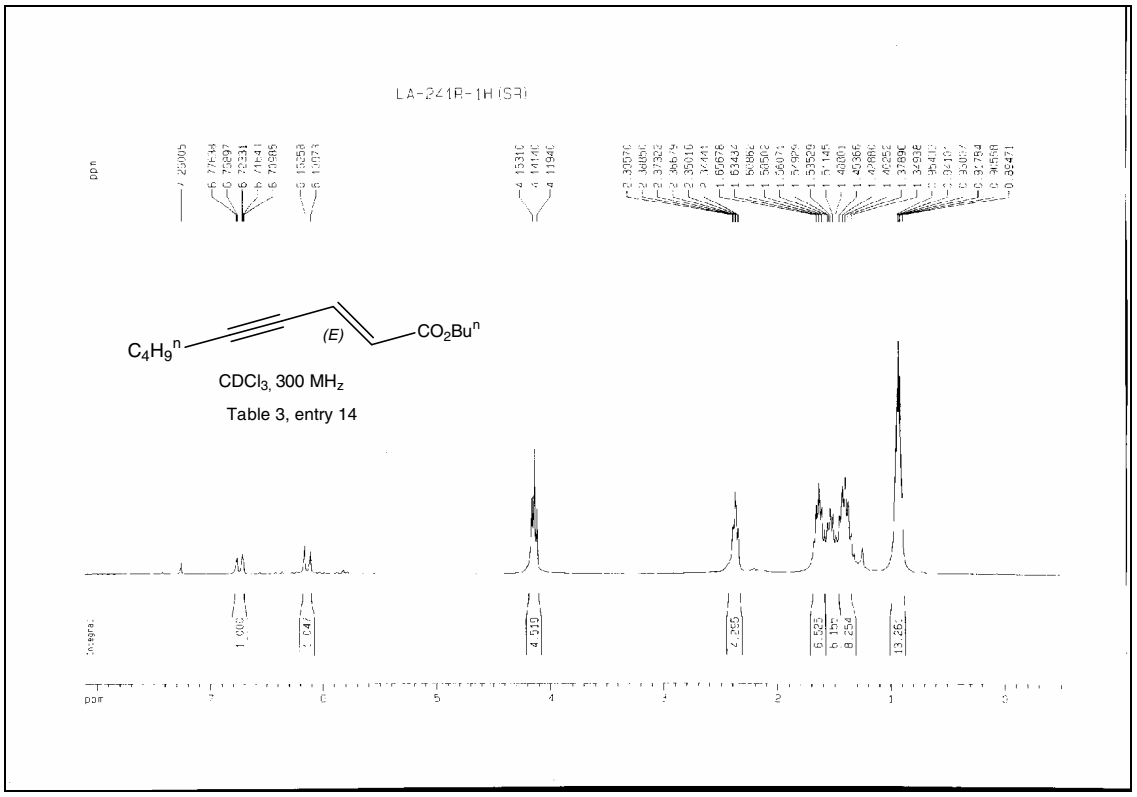

MeO
CO2Bun
(E)
CDCl3, 75 MHz
Table 3, entry 11

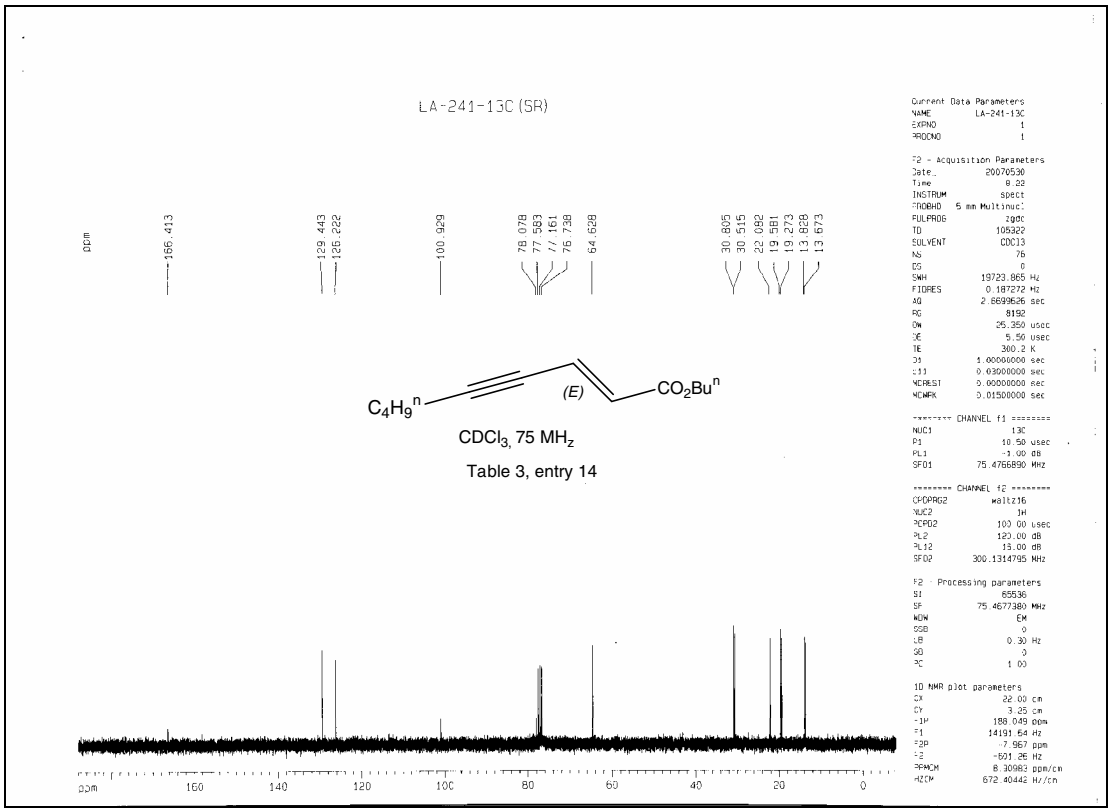

KCC-295-1H (SA)
Br
CO2Me
(E)
O
O
CDCl3, 300 MHz
Table 3, entry 12
Integral
ppm

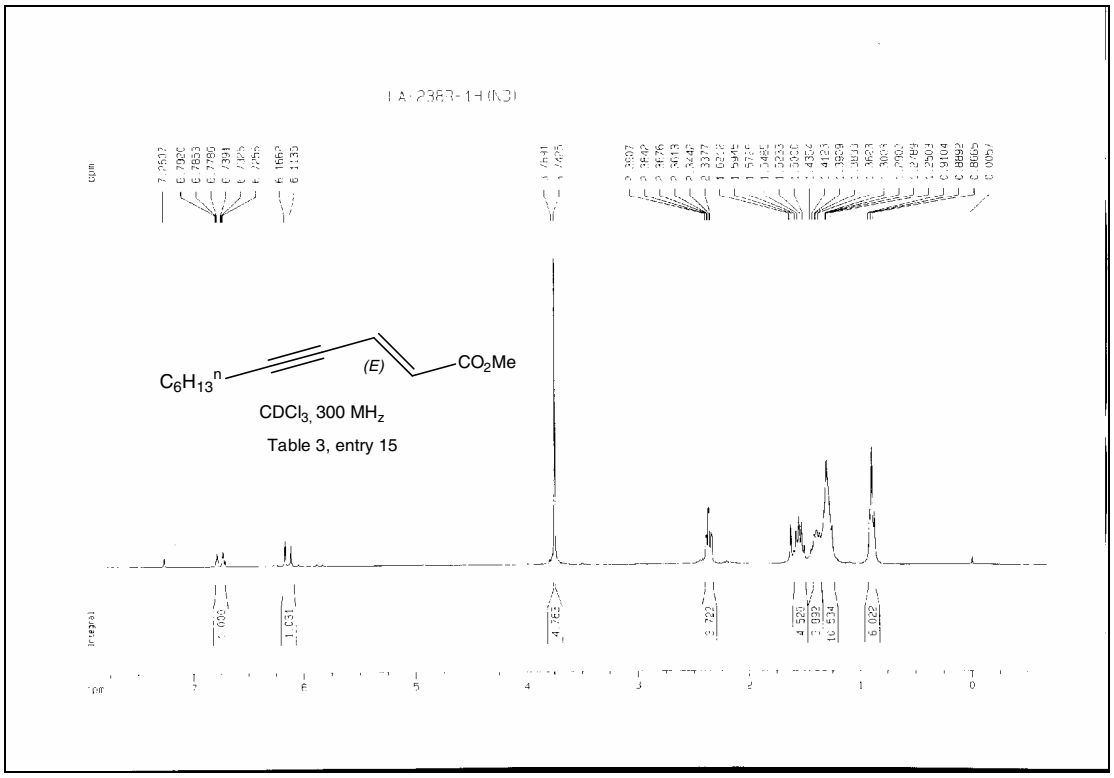

KCC-295-13C (SA)
Br
CO2Me
(E)
O
O
CDCl3, 75 MHz
Table 3, entry 12
ppm
Current Data Parameters
NAME KCC-295-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 500000
Time 10.37
INSTRUM dpx300
PROBHD 5 mm Multinu
PULPROG zgdc
TD 109152
SOLVENT CDCl3
NS 1560
DS 0
SWH 19841.270 Hz
FIDRES 0.181777 Hz
AQ 2.7506804 sec
RG 8192
DW 25.200 usec
DE 4.50 usec
TE 300.0 K
D11 0.03000000 sec
PL12 16.00 dB
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 300.1314795 MHz
NUC2 1H
PL2 120.00 dB
D1 1.00000000 sec
P1 10.50 usec
DE 4.50 usec
SFO1 75.4756447 MHz
NUC1 13C
PL1 -1.00 dB
F2 - Processing parameters
SI 65536
SF 75.4677397 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.00 cm
F1P 191.915 ppm
F1 14438.10 Hz
F2P -8.290 ppm
F2 -625.66 Hz
PPMCM 9.07297 ppm/cm
HZCM 684.71661 Hz/cm

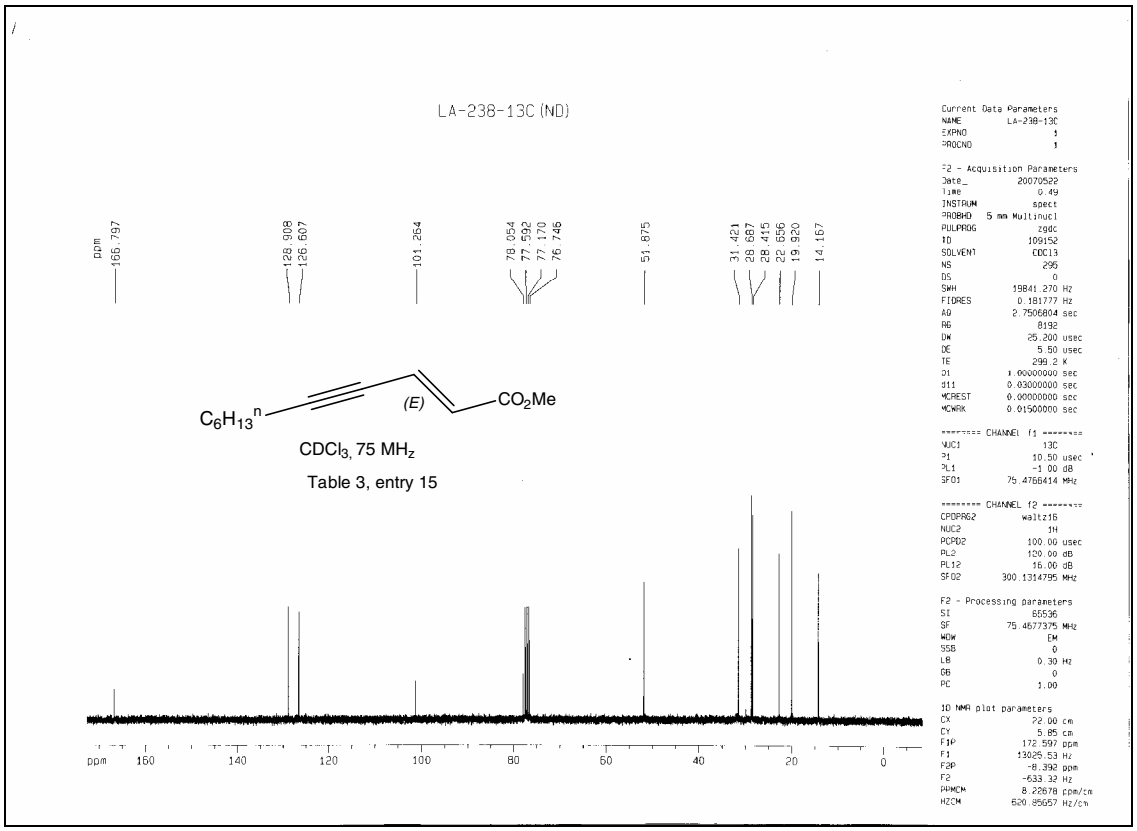

LA-209R-1H (SM)
(E)
CO2Bun
CDCl3, 300 MHz
Table 3, entry 13

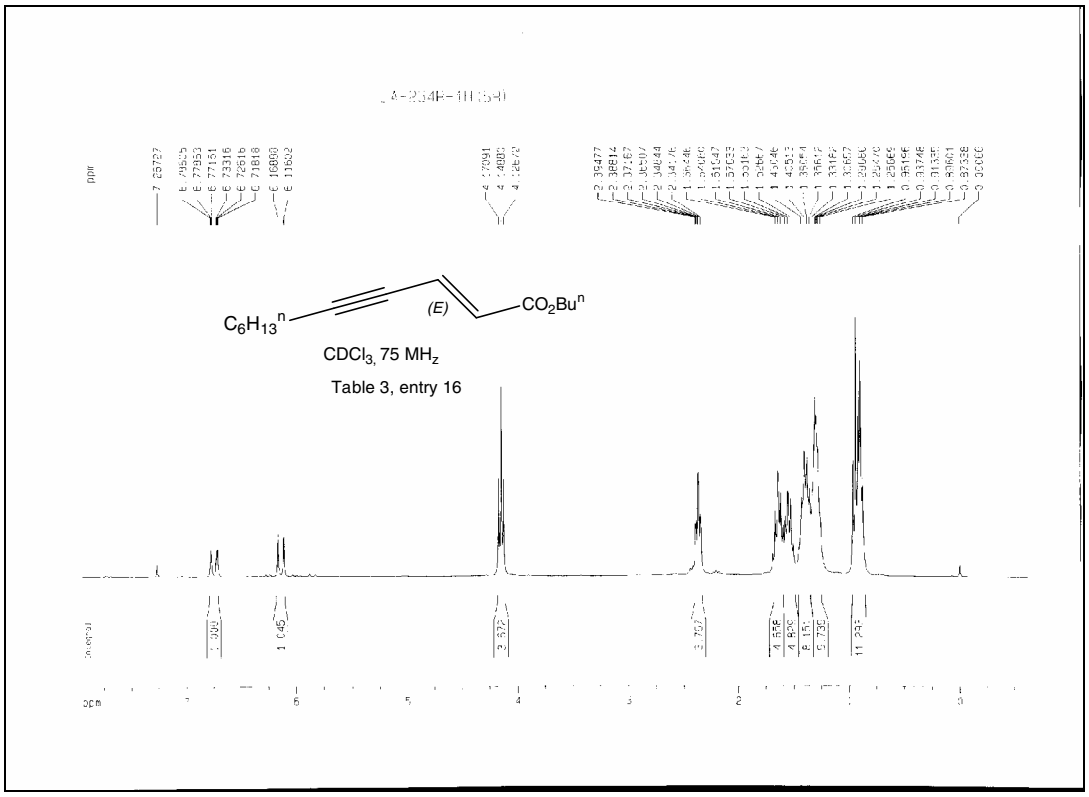

LA-209 13C (SM)
(E)
CO2Bun
CDCl3, 75 MHz
Table 3, entry 13

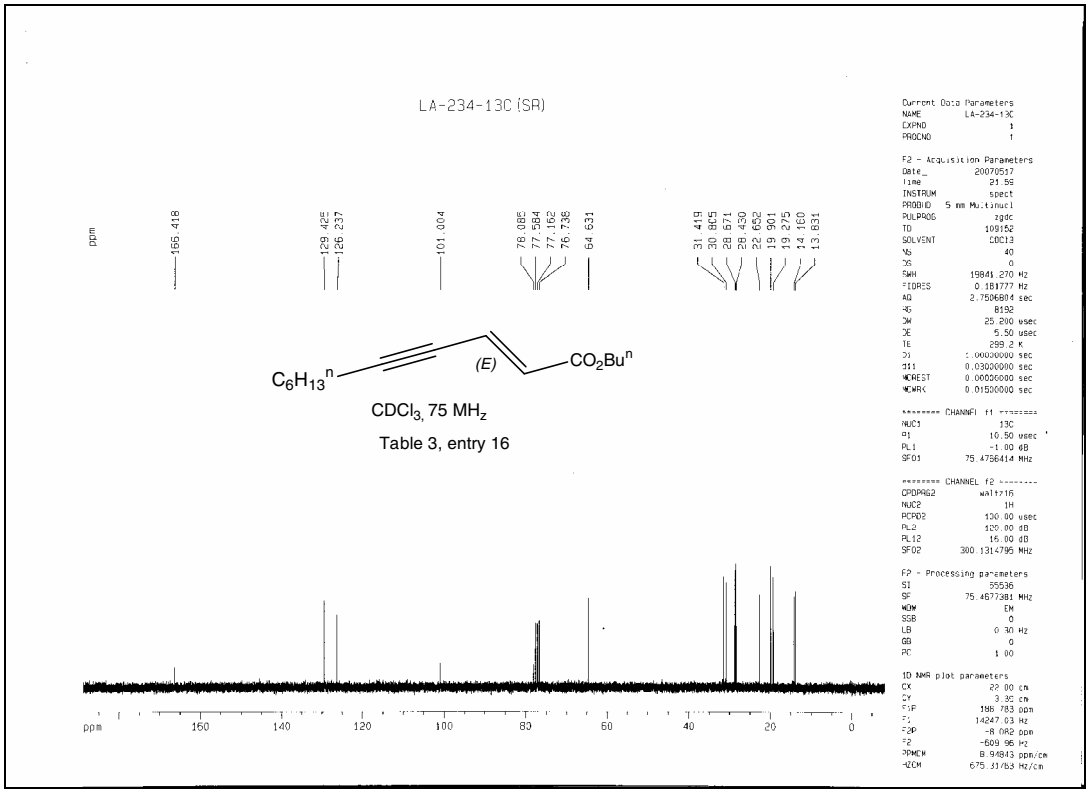

LA-241R-1H(SR)
ppm
(E)
CO2Bu^n
C4H9^n
CDCl3, 300 MHz
Table 3, entry 14
Integral
ppm

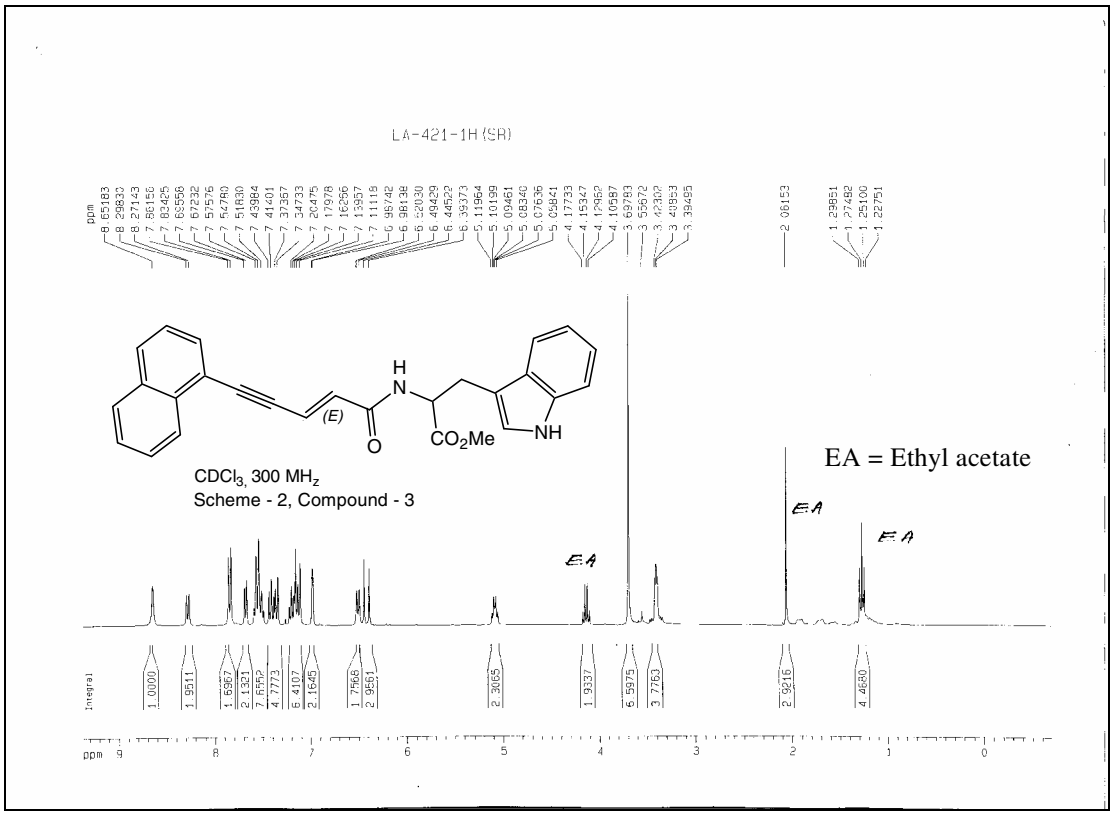

LA-241-13C(SR)
ppm
166.413
129.443
126.222
100.929
78.078
77.583
77.161
76.738
64.628
30.805
30.515
22.082
19.581
19.273
13.828
13.673
(E)
CO2Bu^n
C4H9^n
CDCl3, 75 MHz
Table 3, entry 14
Current Data Parameters
NAME LA-241-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070530
Time 8.28
INSTRUM spect
PROBHD 5 mm Multinuc
PULPROG zgpg
TD 105322
SOLVENT CDCl3
NS 76
DS 0
SWH 19723.865 Hz
FIDRES 0.187272 Hz
AQ 2.6699526 sec
RG 8192
DW 25.350 usec
DE 5.50 usec
TE 300.2 K
D1 1.00000000 sec
D11 0.03000000 sec
DCBEST 0.00000000 sec
DCWFR 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.50 usec
PL1 -1.00 dB
SFO1 75.4766890 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 13.00 dB
SFO2 300.1314795 MHz
F2 - Processing parameters
SI 65536
SF 75.4677380 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.00 cm
CY 9.25 cm
F1P 188.049 ppm
F1 14191.64 Hz
F2P -7.967 ppm
F2 -601.26 Hz
PPMCM 8.30983 ppm/cm
HZCM 672.40442 Hz/cm

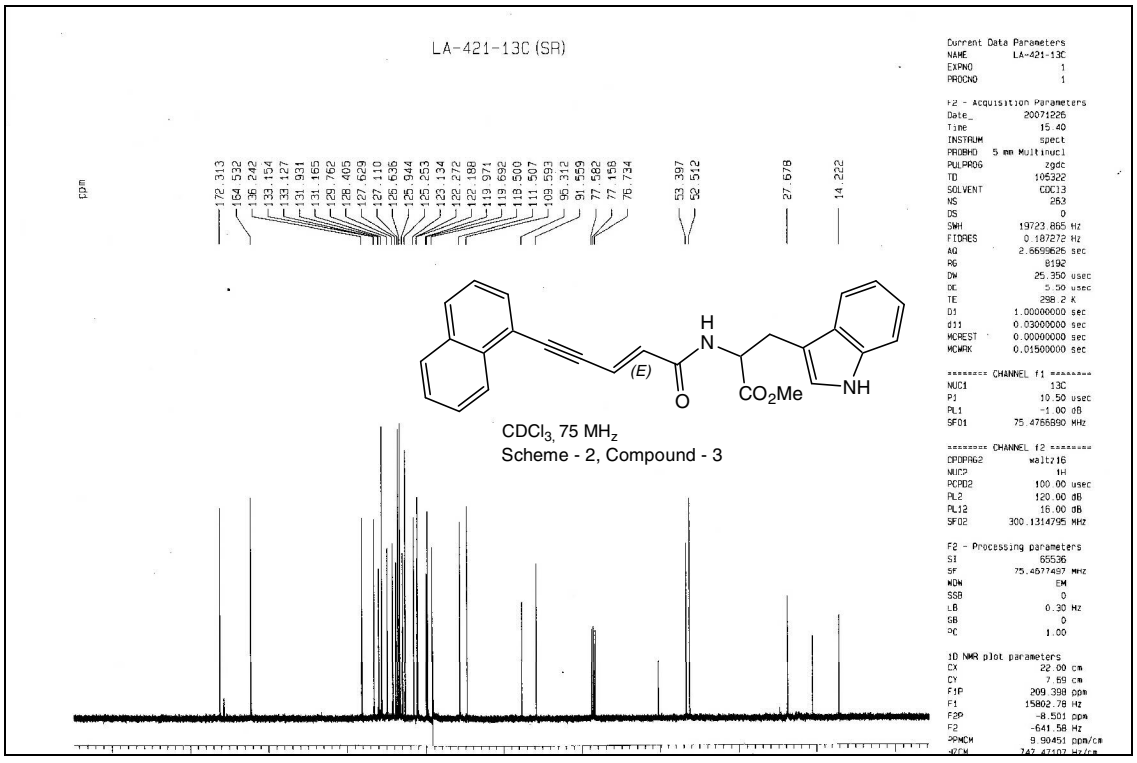

LA-238-1H(ND)
ppm
Integral
1.000
1.031
4.763
3.729
4.526
3.992
16.534
6.022
C_6H_{13}
(E)
CO_2Me
$CDCl_3$, 300 MH_z
Table 3, entry 15


LA-238-13C(ND)
ppm
166.797
128.908
126.607
101.264
78.054
77.592
77.170
76.746
51.875
31.421
28.687
28.415
22.656
19.920
14.167
C_6H_{13}
(E)
CO_2Me
$CDCl_3$, 75 MH_z
Table 3, entry 15
Current Data Parameters
NAME LA-238-13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070522
Time 9.49
INSTRUM spect
PROBHD 5 mm Multinuc
PULPROG zgdc
TD 109152
SOLVENT CDCl3
NS 295
DS 0
SWH 19841.270 Hz
FIDRES 0.181777 Hz
AQ 2.7506804 sec
RG 8192
DW 25.200 usec
DE 5.50 usec
TE 299.2 K
D1 1.00000000 sec
D11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.50 usec
PL1 -1.00 dB
SFO1 75.4766414 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 16.06 dB
SFO2 300.1314795 MHz
F2 - Processing parameters
SI 65536
SF 75.4677375 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.00 cm
CY 5.85 cm
F1P 172.597 ppm
F1 13025.53 Hz
F2P -8.392 ppm
F2 -633.32 Hz
PPMCM 8.22678 ppm/cm
HZCM 620.85657 Hz/cm


(E)
CDCl3, 75 MHz
Table 3, entry 16


LA-234-13C (SR)
(E)
CDCl3, 75 MHz
Table 3, entry 16


LA-421-1H (SR)
CDCl3, 300 MHz
Scheme - 2, Compound - 3
EA = Ethyl acetate
EA
EA
EA


LA-421-13C (SR)
CDCl3, 75 MHz
Scheme - 2, Compound - 3