Supporting information for:

Alkynylcopper(I) Polymers and their Use in a Mechanistic Study of Alkyne-Azide Click Reactions

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General experimental

All infrared spectra were obtained using a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer; thin film spectra were acquired using sodium chloride plates.

All ^1H and ^{13}C NMR spectra were measured at 400.13 and 100.62 MHz using a Bruker DPX 400 MHz spectrometer or a Bruker Avance 400 MHz spectrometer. The solvent used for NMR spectroscopy was $CDCl_3$ (unless stated otherwise) using TMS (tetramethylsilane) as the internal reference. Chemical shifts are given in parts per million (ppm) and *J* values are given in Hertz (Hz).

Analysis by GCMS utilised a Fisons GC 8000 series (AS 800), using a 15 m x 0.25 mm DB-5 column and an electron impact low resolution mass spectrometer.

Melting points were recorded using an Stuart Scientific melting point apparatus SMP3 and are uncorrected.

Microanalyses were performed on a Exeter Analytical Inc. CE-440 Elemental Analyser.

All chromatographic manipulations used silica gel as the adsorbent. Reactions were monitored using thin layer chromatography (TLC) on aluminium backed plates with Merck Kiesel 60 F254 silica gel. TLC visualised by UV radiation at a wavelength of 254 nm, or stained by exposure to an ethanolic solution of phosphomolybdic acid (acidified with concentrated sulphuric acid), followed by charring where appropriate. Purification by column chromatography used Merck Kiesel 60 H silica adsorbent.

The reactions requiring anhydrous conditions were carried out using flame dried glassware, under a nitrogen atmosphere unless otherwise stated. Reaction solvents were obtained commercially dry, except light petroleum (b.p. 40-60 ºC) which was distilled from calcium chloride prior to use. Ethyl acetate was distilled over calcium sulfate or chloride. Dichloromethane was distilled over calcium hydride. Tetrahydrofuran (THF) was distilled under a nitrogen atmosphere from the sodium/benzophenone ketyl radical.

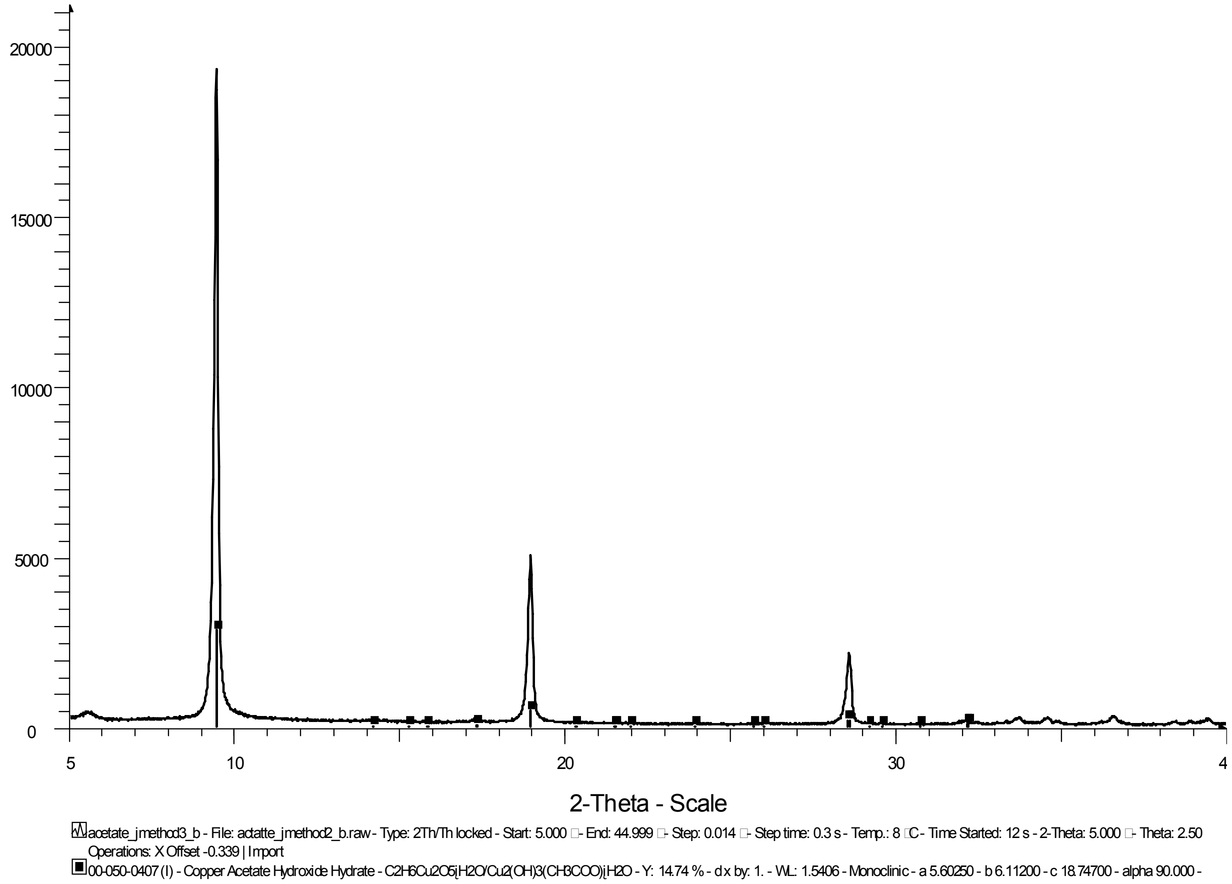
Microwave reactions were performed in a Biotage Initiator EXP 8 reactor in 2-5 mL crimped vials.

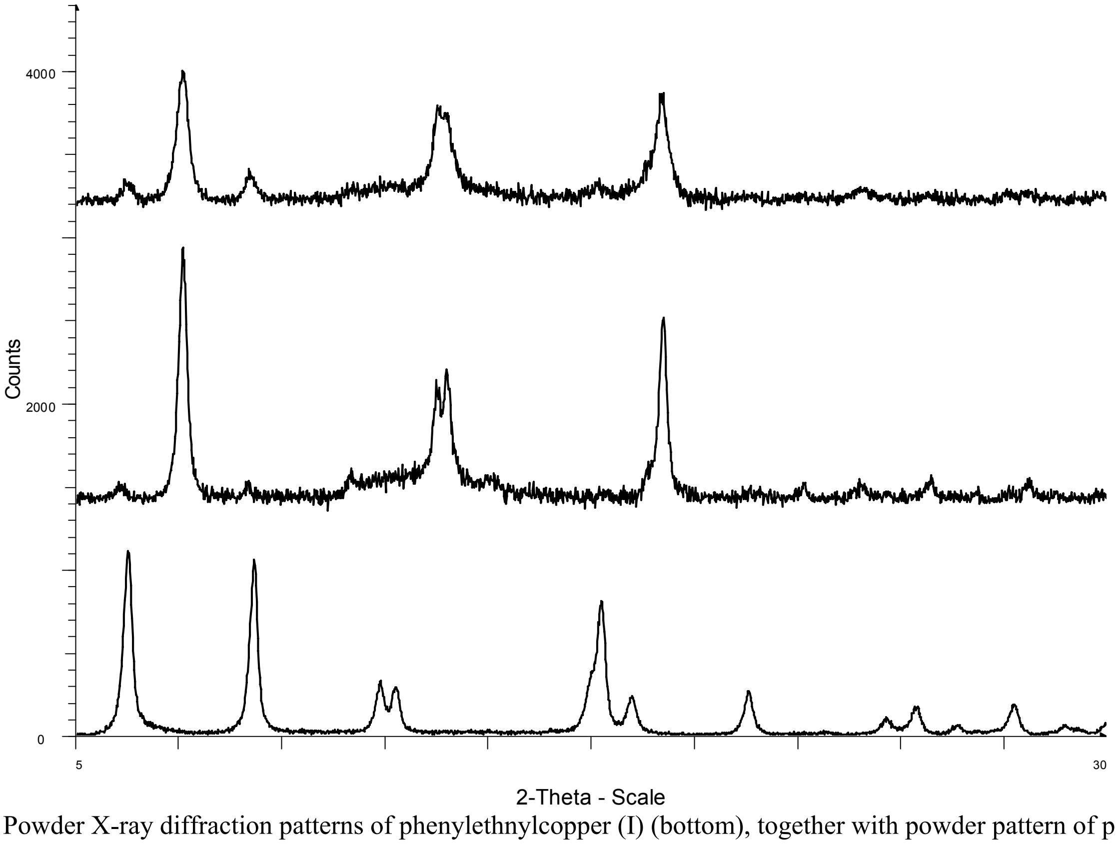
Powder refraction data were recorded on a Bruker Avance powder defractometer operating with monocremated $Cu_{K\alpha 1}$ radiation over the 2θ range 5-60º using a 0.0147 2θ step.

Mass spectra were recorded on a Thermo Fisher Exactive with a ion max source and ESI probe fitted with a Advion triversa nanomate. Mass range 20-2000 with a resolution of better than 100000.

Synthesis of $Cu_2(OH)_3OAc{\bullet}H_2O$

$Cu(OAc)_2{\cdot}H_2O$ (4.00 g, 20.1 mmol) was dissolved in H_2O (200 mL) and stirred at room temperature. NaOH (200 mL, 0.1 M) was added slowly with vigorous stirring. The reaction mixture was left to stir for 7 days. The reaction mixture was centrifuged at 2000 rpm for 15 min. The aqueous phase was decanted and replaced with deionised water and the centrifuged for a further 15 min. The process was then repeated using ethanol and finally dichloromethane to afford the product as a pale green solid. The structure was then confirmed by powder x-ray diffraction (below) and found to be mono hydrated by combustion analysis. (Found: C 9.31, H 2.86% $Cu_2(OH)_3OAc{\cdot}H_2O$ requires C 9.41, H 3.16%).



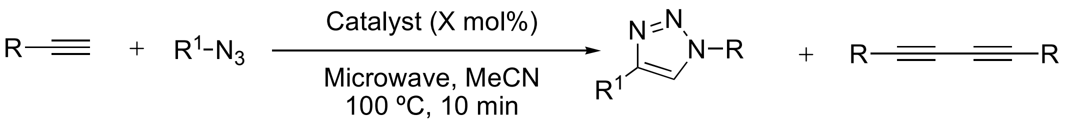


Powder X-ray diffraction patterns of phenylethnylcopper (I) (bottom), together with powder pattern of polymeric tolylethnylcopper (I) (middle) and recovered polymeric tolylethynylcopper (I) as described in Scheme 4.

Representative synthesis of the ladder polymers:

$Cu_2(OH)_3OAc$ (0.20 g, 0.78 mmol) was suspended in acetonitrile (4 mL) in a Biotage microwave tube. Phenylacetylene (0.24 g, 2.4 mmol) was added. The reaction mixture was heated under microwave irradiation at 100°C for 10 mins (with 20 s pre-stirring, set at normal absorbance). The mixture was diluted with dichloromethane (4 mL) filtered and washed with dichloromethane. The yellow filter cake was dried and analysed by x-ray powder diffraction and found to be the ladder polymer **2** (0.12 g, 92%). The filtrate was evaporated under reduced pressure to afford the Glaser product as a colourless solid (0.15 g, 95%).

Representative click reaction using copper hydroxy acetate:



$Cu_2(OH)_3OAc.H_2O$ (0.11 g, 0.48 mmol) was suspended in acetonitrile (4 mL) in a Biotage microwave tube. Phenylacetylene (0.77 g, 7.5 mmol) and benzyl azide (0.64 g, 4.8 mmol) were added. The reaction mixture was heated under microwave irradiation at 100°C for 10 mins (with 20 s pre-stirring, set at normal absorbance). The mixture was diluted with dichloromethane (4 mL) filtered and washed with dichloromethane. The filtrate was evaporated under reduced pressure to afford the crude title compound as a pale yellow solid. Purification by silica gel column chromatography with light petroleum:ethyl acetate (gradient elution 20:1–5:1) as eluent afforded the Glazer product as colourless crystals (0.075 g,77% yield w.r.t Cu) and the triazole product as colourless crystals (1.08 g, 97%, w.r.t the benzyl azide).

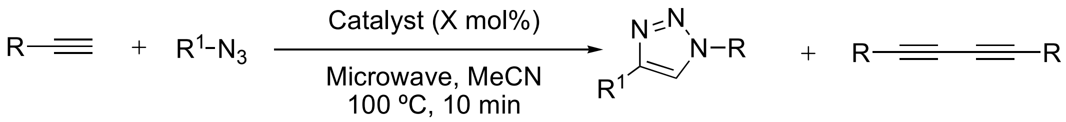
Representative click reaction using the copper(I) ladder complexes:

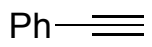
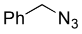
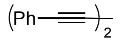
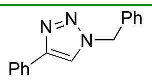
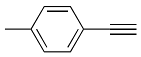
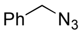
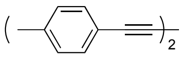
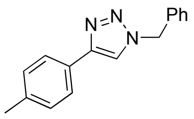
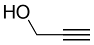
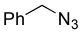
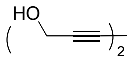
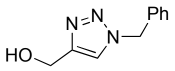
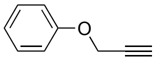
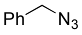
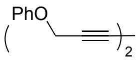
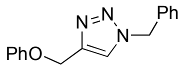
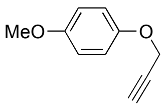
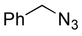
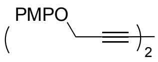
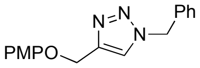
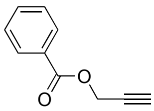
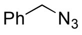
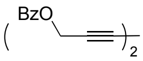
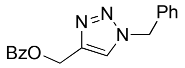
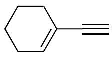
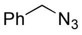
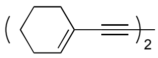
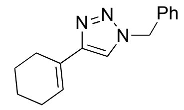
$[CuCCPh]_n$ (0.078 g, 0.48 mmol) was suspended in acetonitrile (4 mL) in a Biotage microwave tube. Phenylacetylene (0.77 g, 7.5 mmol) and benzyl azide (0.64 g, 4.8 mmol) were added. The reaction mixture was heated under microwave irradiation at 100°C for 10 mins (with 20 s pre-stirring, set at normal absorbance). The mixture was diluted with dichloromethane (4 mL) filtered and washed with dichloromethane. The filtrate was evaporated under reduced pressure to afford the crude title compound as a pale yellow solid. Purification by silica gel column chromatography with light petroleum:ethyl acetate (gradient elution 20:1–5:1) as eluent afforded the the triazole product as colourless crystals (0.97 g, 86%). Repetition of the experiment using $[CuCCPh]_n$ prepared by the Owsley and Castro method[i] gave an identical result.

Formation of $[CuCCPh]_n$ using the Sharpless and Fokin click reaction protocol:

Phenyl acetylene (0.310 g, 3.0 mmol) was suspended in a 1:1 mixture of water and tert-butyl alcohol (12 mL). Sodium ascorbate (0.3 mmol, 300 mL of freshly prepared 1M solution in water) was added, followed by copper(II) sulfate pentahydrate (7.5 mg, 0.03 mmol, in 100 mL of water). The heterogeneous mixture was stirred vigorously and turned brown and viscous. After approx. 15 min a yellow precipitate was formed. The reaction mixture was centrifuged at 2000 rpm for 15 min. The aqueous/tert-butanol phase was decanted and replaced with deionised water and centrifuged for a further 15 min. The process was then repeated using ethanol and finally dichloromethane to afford the product as a yellow solid. Which was characterised by x-ray powder diffraction to be the $[CuCCPh]_n$ ladder complex.

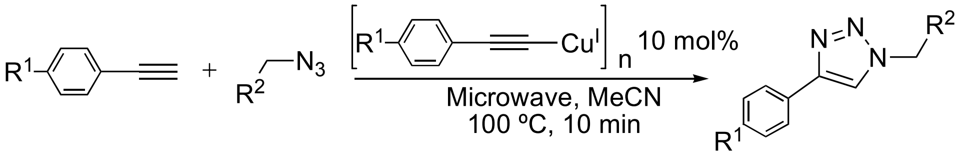
Table including additional experiments: Reaction of Azides with Terminal Alkynes Using Copper(II) hydroxy acetate as Pre-catalyst

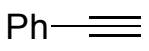
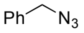
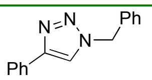
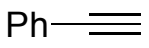
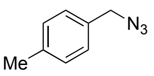
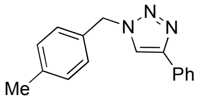
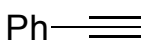
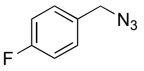
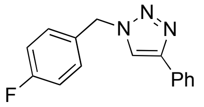
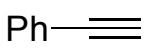
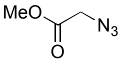
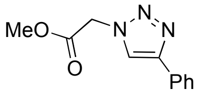
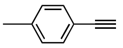
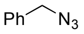
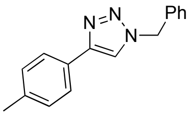
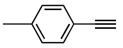
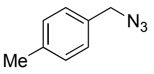
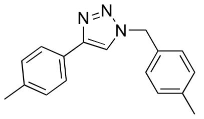
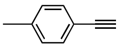
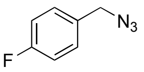
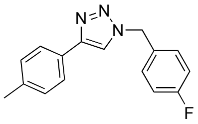
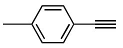
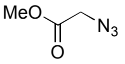
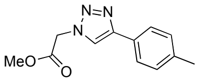


Entry	Catalyst/pre-catalyst (mol%)	Alkyne	Azide	Glaser Product	Yield (%)[a,b]	Click Product	Yield (%)[a]
1	Cu$_2$(OH)$_3$OAc (10 mol%)				77		92
2	[(CuCCPh)$_2$]$_n$ (10 mol%)				0		86
3	Cu$_2$(OH)$_3$OAc (10 mol%)				70		89
2	Cu$_2$(OH)$_3$OAc (10 mol%)				74		79
3	Cu$_2$(OH)$_3$OAc (10 mol%)				81		73
4	Cu$_2$(OH)$_3$OAc (10 mol%)				84		73
5	Cu$_2$(OH)$_3$OAc (10 mol%)				79		85
6	Cu$_2$(OH)$_3$OAc (10 mol%)				87		86

[a] Isolated yield; [b] Yield calculated w.r.t. the mmol of Cu$_2$(OH)$_3$OAc used.

Table including additional experiments: Reactions of Azides Catalyzed by Polymeric Arylethynylcopper(I) Compounds

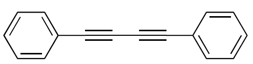


Entry	Catalyst (mol%)	Alkyne	Azide	Click Product	Yield (%)^a
1	$[(CuCCPh)_2]_n$ (10 mol%)				86
2	$[(CuCCPh)_2]_n$ (10 mol%)				60
3	$[(CuCCPh)_2]_n$ (10 mol%)				82
4	$[(CuCCPh)_2]_n$ (10 mol%)				88
5	$[(CuCC\text{-}4\text{-}Tol)_2]_n$				75
6	$[(CuCC\text{-}4\text{-}Tol)_2]_n$				74
7	$[(CuCC\text{-}4\text{-}Tol)_2]_n$				88
8	$[(CuCC\text{-}4\text{-}Tol)_2]_n$				76

Compound Data:

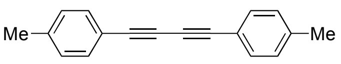
The Glazer Products:

1,4-Diphenylbuta-1,3-diyne:[ii]



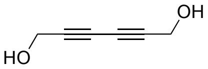
Colourless crystals. ^1H NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 7.54-7.52 (2 H, m), 7.38-7.26 (3 H, m); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 132.5, 129.2, 128.4, 121.8, 81.6, 73.9.

1,4-Di[4-methylphenyl]buta-1,3-diyne:[iii]



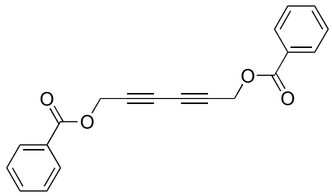
Colourless crystals. ^1H NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 7.41 (2 H, d, *J* 8.1 Hz), 7.14 (2 H, d, *J* 8.1 Hz), 2.36 (3 H, s); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 139.5, 132.4, 129.4, 118.8, 81.6, 73.5, 21.7.

1,4-Di[hydroxymethyl]buta-1,3-diyne:[iv]



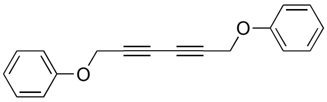
Colourless crystals. ^{1}H NMR (400 MHz, CDCl$_3$/DMSO-d$_6$, 25°C, TMS) δ = 5.48 (2 H, t, *J* 6.0 Hz), 4.23 (4 H, d, *J* 6 Hz); ^{13}C NMR (400 MHz, CDCl$_3$/DMSO-d$_6$, 25°C, TMS) δ = 79.5, 67.9, 49.3.

1,4-Di[benzoyloxymethyl]buta-1,3-diyne:[v]



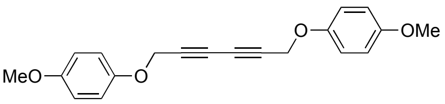
Colourless crystals. ^{1}H NMR (400 MHz, CDCl$_3$, 25°C, TMS) δ = 7.99-7.98 (4 H, m), 7.53-7.50 (2 H, m), 7.41-7.36 (4 H, m), 4.92 (4 H, s); ^{13}C NMR (400 MHz, CDCl$_3$, 25°C, TMS) δ = 165.6, 133.5, 129.9, 129.2, 128.5, 73.7, 70.6, 52.8.

1,4-Di[phenoxymethyl]buta-1,3-diyne:[vi]



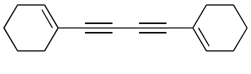
Colourless crystals. ^{1}H NMR (400 MHz, CDCl$_3$, 25°C, TMS) δ = 7.25-7.12 (4 H, m), 6.99-6.86 (6 H, m), 7.41-7.36 (4 H, m), 4.67 (4 H, s); ^{13}C NMR (400 MHz, CDCl$_3$, 25°C, TMS) δ = 157.4, 129.7, 121.8, 114.9, 74.6, 71.0, 56.2.

1,4-Di[4-methoxyphenoxymethyl]buta-1,3-diyne:[vii]



Colourless crystals. ^{1}H NMR (400 MHz, CDCl$_3$, 25°C, TMS) δ = 6.93-6.84 (8 H, m), 4.72 (4 H, s), 3.80 (6 H, s); ^{13}C NMR (400 MHz, CDCl$_3$, 25°C, TMS) δ = 154.6, 151.5, 116.2, 114.7, 74.9, 70.9, 57.1, 55.7.

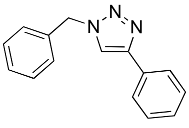
1,4-Di[1-cyclohexenyl]buta-1,3-diyne[viii]



Yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25°C, TMS) δ = 6.26 (2 H, s), 2.13-2.12 (8 H, m), 1.64-1.58 (8 H, m); ^{13}C NMR (400 MHz, CDCl$_3$, 25°C, TMS) δ = 138.1, 120.0, 82.7, 71.6, 28.7, 25.9, 22.1, 21.3.

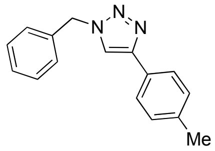
The Triazole Products:

Triazole prepared from phenyl acetylene and benzyl azide:[ix]



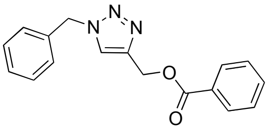
Colourless crystals. ^{1}H (400 MHz, CDCl$_3$) δ = 7.74 (2 H, d, *J* 1.4 Hz), 7.60 (1 H, s), 7.35-7.19 (8 H, m), 5.58 (2 H, s); ^{13}C NMR (400 MHz, CDCl$_3$, 25°C, TMS) δ = 148.3, 134.7, 130.6, 129.2, 128.8, 128.2, 128.1, 125.7, 119.6, 54.2.

Triazole prepared from tolyl acetylene and benzyl azide: [x]



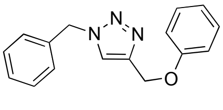
Colourless crystals. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 7.20 (2 H, d, *J* 7.9 Hz), 7.25-7.38 (5 H, m), 7.67 (1 H, s), 7.68 (2 H, d, *J* 8.2 Hz), 5.57 (2 H, s); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 148.3, 138.0, 134.7, 129.5, 129.1, 128.9, 128.1, 127.7, 125.6, 119.2, 54.2, 21.3.

Triazole prepared from propargyl benzoate and benzyl azide:[xi]



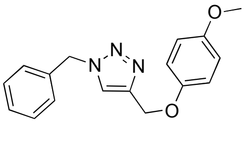
Colourless crystals. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 8.02 (2 H, dd, *J* 0.4, 7.2 Hz), 7.61 (1 H, s), 7.44 – 7.57 (1 H, m), 7.34 – 7.42 (5 H, m), 7.26 – 7.31 (2 H, m), 5.53 (2 H, s), 5.45 (2 H, s).
^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 166.4, 143.4, 134.4, 133.2, 129.8, 129.2, 128.9, 128.4, 128.2, 123.8, 58.1, 54.3.

Triazole prepared from propargyl phenyl ether and benzyl azide:[xii]



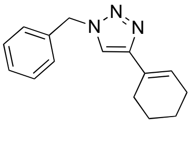
Colourless crystals. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 7.53 (1 H, s), 7.29–7.31 (8 H, m), 6.95-6.98 (2 H, m) 5.52 (2 H, s), 5.18 (2H, s); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 158.2, 144.8, 134.5, 129.6, 129.2, 128.8, 128.2, 122.7, 121.3, 114.8, 62.1, 54.3.

Triazole prepared from propargyl 4-methoxyphenyl ether and benzyl azide:



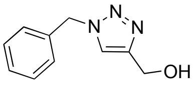
Colourless crystals. M.p. 112.0-113.2 ºC; (Found: C 69.09, H 5.77, N 14.12% $C_{17}H_{17}N_3O_2$ requires 69.14, H 5.80, N 14.23%); ν max (film) /cm^{-1} 3054.3, 2986.1, 2305.8, 1506.4, 1265.1, 1230.7, 1040.0;^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 7.52 (1H, s), 7.35 – 7.37 (3 H, m), 7.26 – 7.27 (2 H, m), 6.89 – 6.91 (2 H, m), 6.80 – 6.84 (2 H, m), 5.53 (2 H, s), 5.13 (2 H, s), 3.76 (3 H, s); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 154.2, 152.3, 144.9, 134.5, 129.2, 128.8, 128.1, 122.5, 115.9, 114.7, 62.9, 55.7, 54.2; m/z Found: 296.1391, $C_{17}H_{18}N_3O_2$ (M+H) requires 296.1394.

Triazole prepared from 1-ethynylcyclohexene and benzyl azide: [xiii]



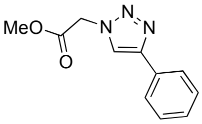
Colourless crystals. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 7.24 – 7.37 (6 H, m), 6.49 – 6.51 (1 H, t, *J* 2.0 Hz), 5.51 (2 H, s), 2.16-2.34 (4 H, m), 1.64-1.75 (4 H, m); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 150.0, 135.0, 129.1, 128.6, 128.0, 127.3, 125.1, 118.2, 54.0, 26.4, 25.3, 22.4, 22.2.

Triazole prepared from propargyl alcohol and benzyl azide:[xiv]



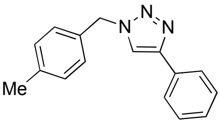
Colourless crystals. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS) $\delta = 7.46$ (1 H, s), 7.36-7.31 (3 H, m), 7.28-7.25 (2 H, m), 5.50 (2 H, s), 4.75 (2 H, s), 3.02; ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS) $\delta = 133.5$, 128.1, 127.8, 127.3, 127.1, 120.9, 55.1, 53.2.

Triazole prepared from phenyl acetylene and methyl azido acetate:



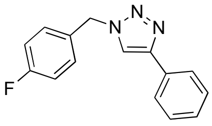
Colourless crystals. M.p. 81.4-82.3 (Found: C 60.58, H 5.13, N 19.08% $C_{11}H_{11}N_3O_2$ requires C 60.82, H 5.10, N 19.34%); ν max (film) /cm^{-1} 3053.1, 2934.7, 1756.0, 1439.1; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS) $\delta = 7.92$ (1 H, s), 7.84 (2 H, d, *J* 0.4 Hz), 7.43 (2 H, t, *J* 7.2 Hz), 7.35 (1 H, t, *J* 7.2 Hz), 5.22 (2 H, s), 3.82 (3 H, s); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS) $\delta = 166.8$, 148.3, 130.3, 128.9, 128.3, 128.0, 121.0, 53.1, 50.8; m/z Found: 218.0929, $C_{11}H_{12}O_2N_3$ M+H requires 218.0924.

Triazole prepared from phenyl acetylene and 4-methylbenzyl azide:[xv]



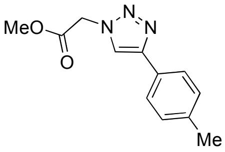
Colourless crystals. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS) $\delta = 7.78$ (2 H, d, *J* 7.2 Hz), 7.63 (1 H, s), 7.41-7.18 (9 H, m), 5.22 (2 H, s), 2.35 (3 H, s); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS) $\delta = 148.1$, 138.7, 131.7, 130.7, 129.8, 128.8, 128.14, 128.12, 125.7, 119.5, 54.0, 21.2.

Triazole prepared from phenyl acetylene and 4-fluorobenzyl azide:[xvi]



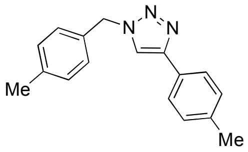
Pale yellow solid. (Found: C 70.78, H 4.84, N 16.33% $C_{15}H_{12}N_3F$ requires C 71.13, H 4.78, N 16.59%); ν max (film) /cm^{-1} 3054.2, 2986.0, 2305.8, 1512.3, 1422.4; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS) $\delta = 7.81$ (1 H, d, *J* 1.6 Hz), 7.79 (1 H, s), 7.41-7.26 (4 H, m), 7.10-7.06 (2 H), 5.55 (2 H, s);^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS) $\delta = 164.1$, 161.6, 148.3, 130.60, 130.57, 130.4, 130.0, 129.9, 128.9, 128.3, 119.4, 116.27, 116.05, 53.5.

Triazole prepared from 4-tolyl acetylene and methyl azido acetate:



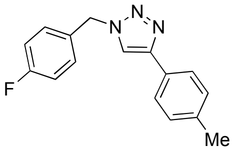
Colourless crystals. M.p. 116.1-117.0 ºC (Found: C 62.33, H 5.69, N 17.80% $C_{12}H_{13}N_3O_2$ requires 62.54, H 5.67, N 18.17%); ν max (film) /cm^{-1} 3053.1, 2934.7, 1756.0, 1439.1; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS) $\delta = 7.87$ (1 H, s), 7.72 (2 H, d, *J* 8.1 Hz), 7.22 (2 H, d, *J* 8.1 Hz), 5.20 (2 H, s), 3.80 (3 H, s), 2.37 (3 H, s); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS) $\delta = 166.8$, 148.3, 138.2, 129.5, 127.5, 125.7, 120.7, 53.1, 50.8, 21.3; m/z Found: 232.1084, $C_{12}H_{14}O_2N_3$ (M+H) requires 232.181.

Triazole prepared from 4-tolyl acetylene and 4-methylbenzyl azide:[xvii]



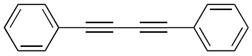
Colourless crystals. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 7.68 (2 H, d, *J* 7.6 Hz), 7.59 (1 H, bs), 7.26 – 7.11 (6 H, m), 5.50 (2 H, s), 2.35 (6 H, s);^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 148.0, 138.7, 137.9, 131.8, 129.8, 129.5, 128.1, 127.9, 125.6, 119.1, 54.0, 21.3, 21.2.

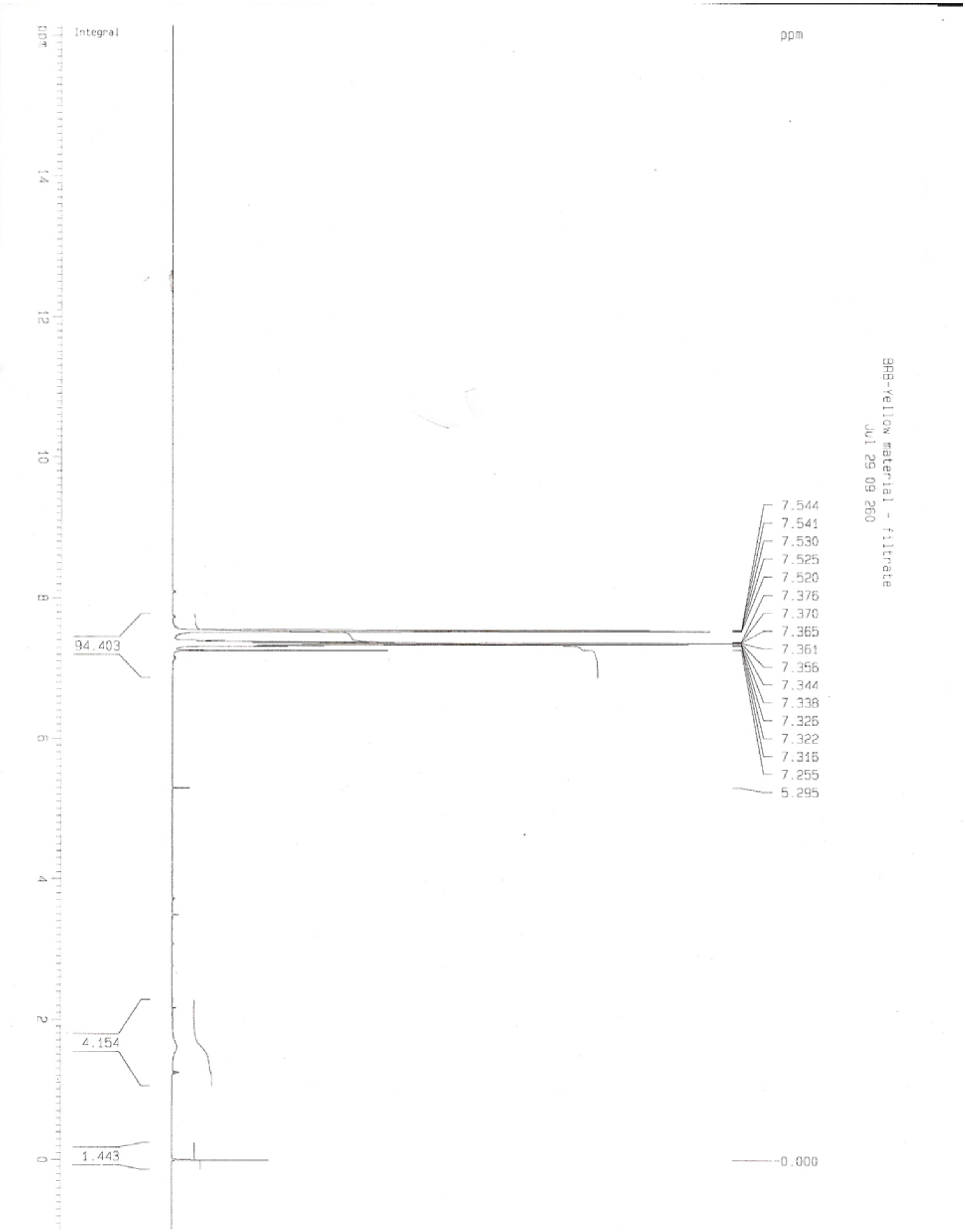
Triazole prepared from 4-tolyl acetylene and 4-fluorobenzyl azide:

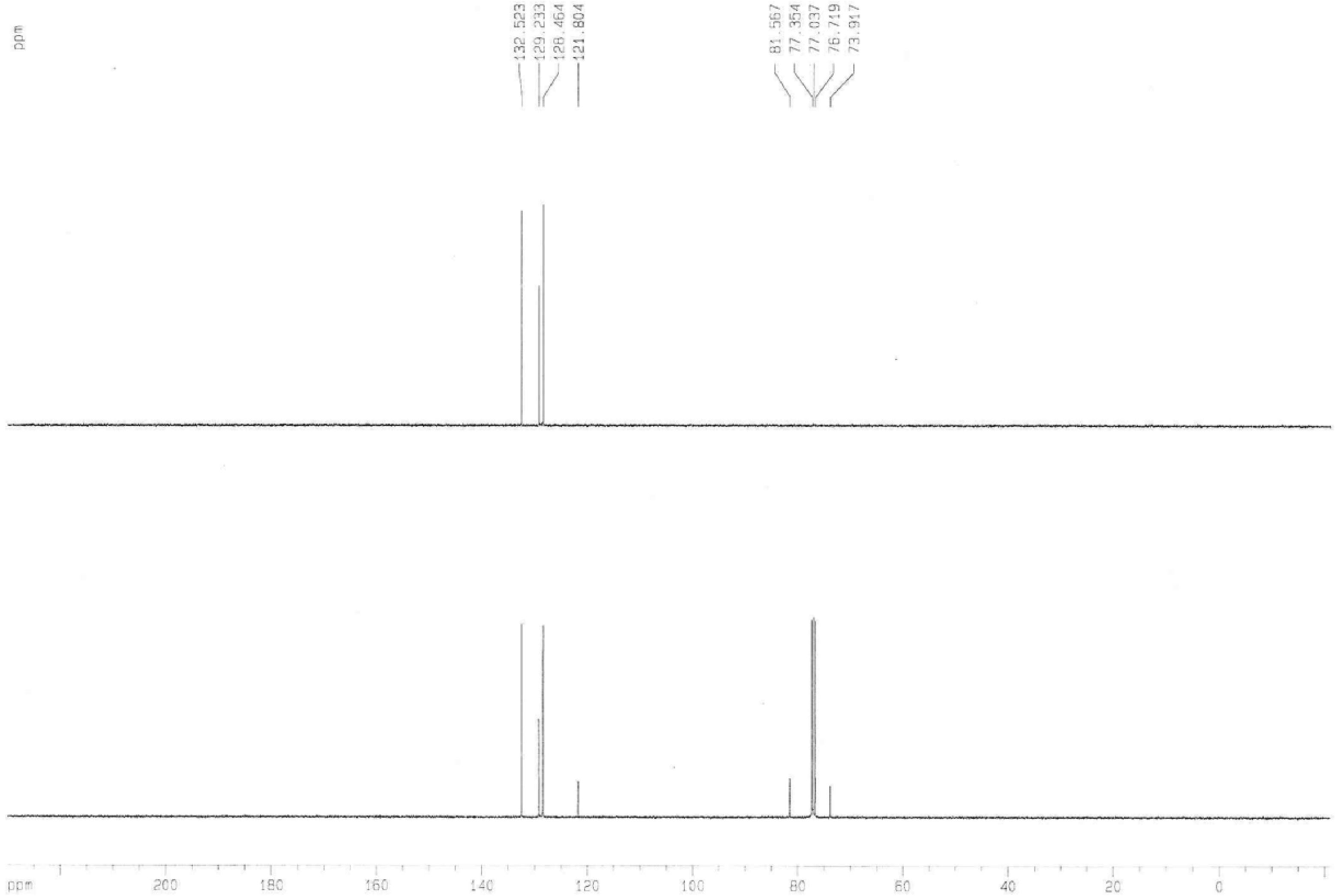


Pale yellow crystals. M.p. 150.1-151.3 ºC; (Found: C 72.71, H 5.27, N 15.44% $C_{16}H_{14}N_3F$ requires 71.89, H 5.28, N 15.72%)ν max (film) /cm^{-1} 3053.3, 1422.0, 1264.9; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 7.69 (2 H, d, *J* 8.1 Hz), 7.61 (1 H, s), 7.32 – 7.29 (8 H, m), 7.06 (1 H, t, *J* 2.04 Hz), 5.54 (2 H, s), 2.37 (3 H, s); ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS) δ = 148.4, 138.1, 130.6, 130.0, 129.9, 129.5, 125.6, 119.0, 116.3, 116.1, 53.5, 21.3; m/z Found: 268.1248, $C_{16}H_{15}N_3F$ (M+H) requires 268.1250.

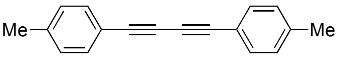
NMR spectra for the Glaser products:

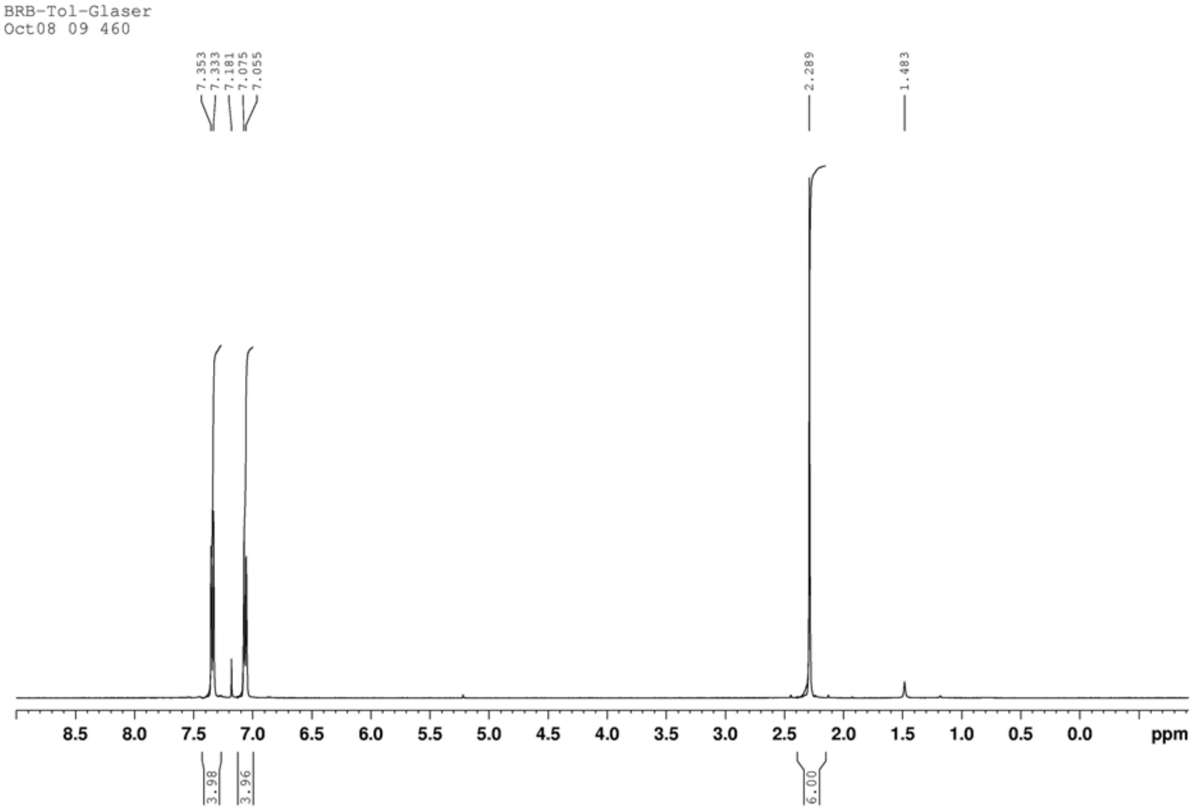






BRB-Yellow material - filtrate
Jul 29 09 261


Me
Me


BRB-Tol-Glaser
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7.0
6.5
6.0
5.5
5.0
4.5
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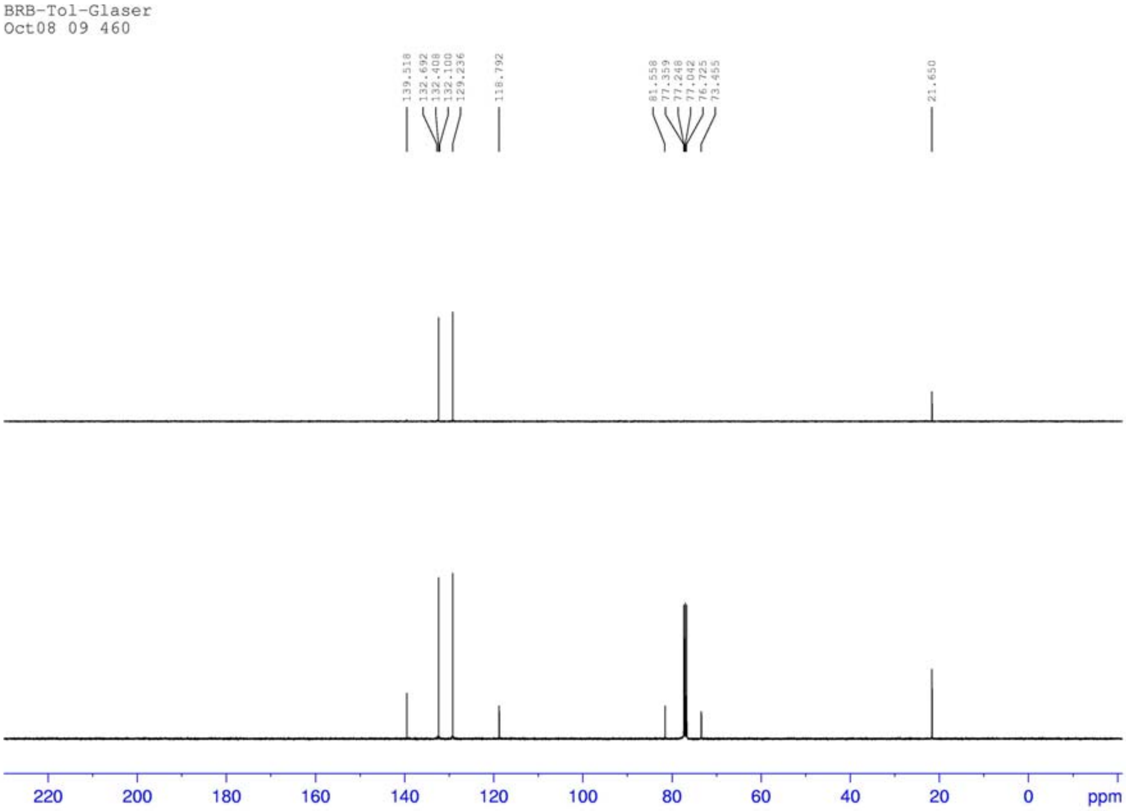
6.00


BRB-Tol-Glaser
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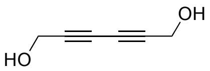
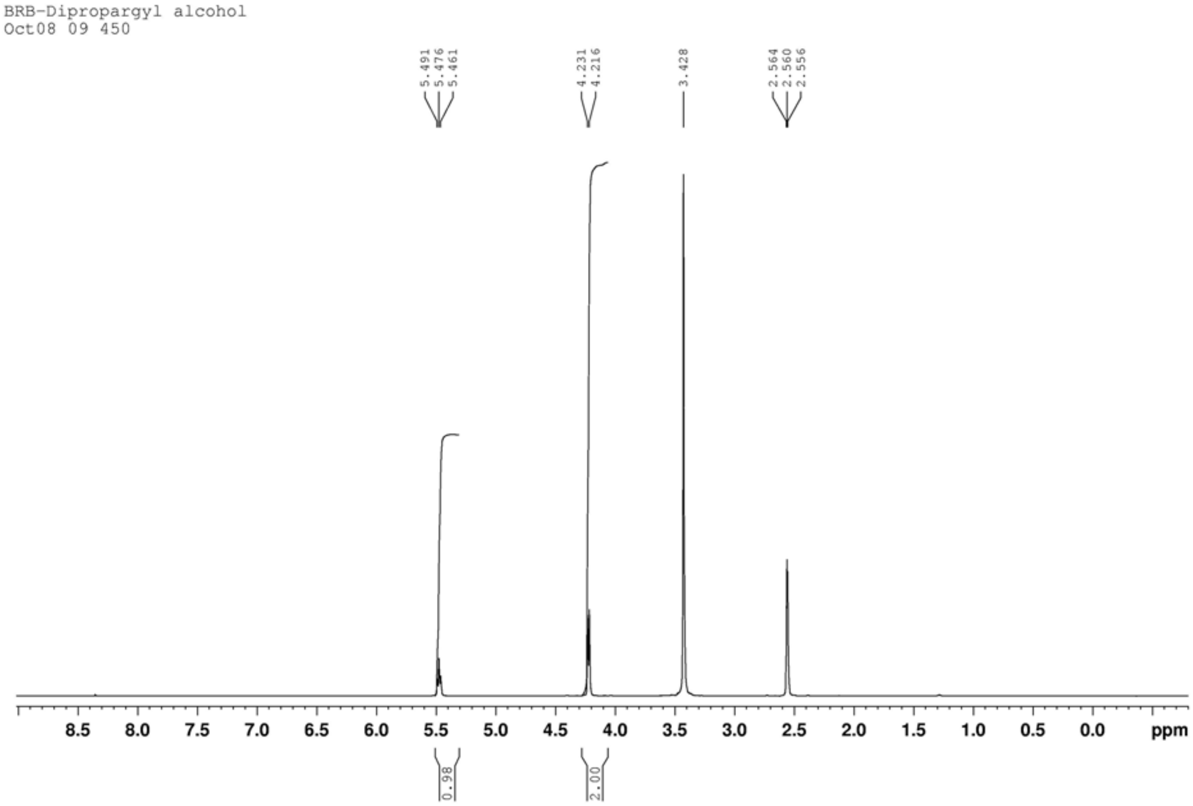
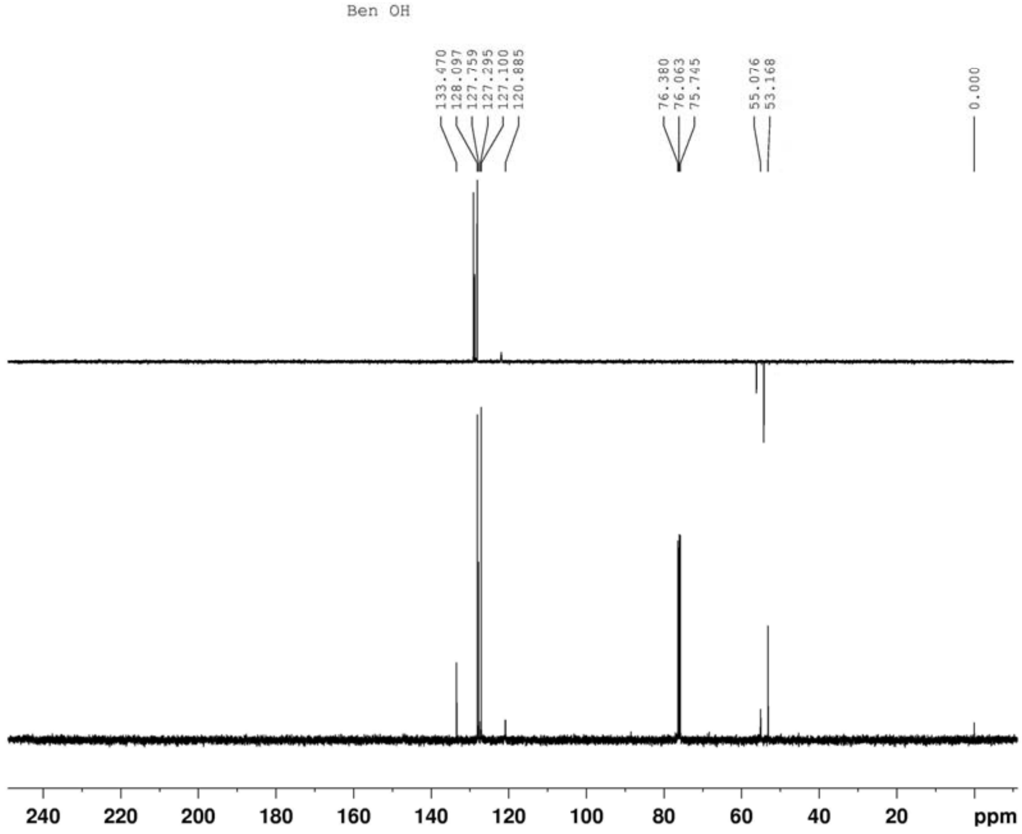
0
ppm







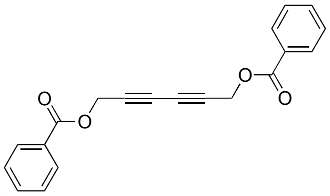
```
Current Data Parameters
NAME             Oct09-2009
EXPNO                    11
PROCNO                    1

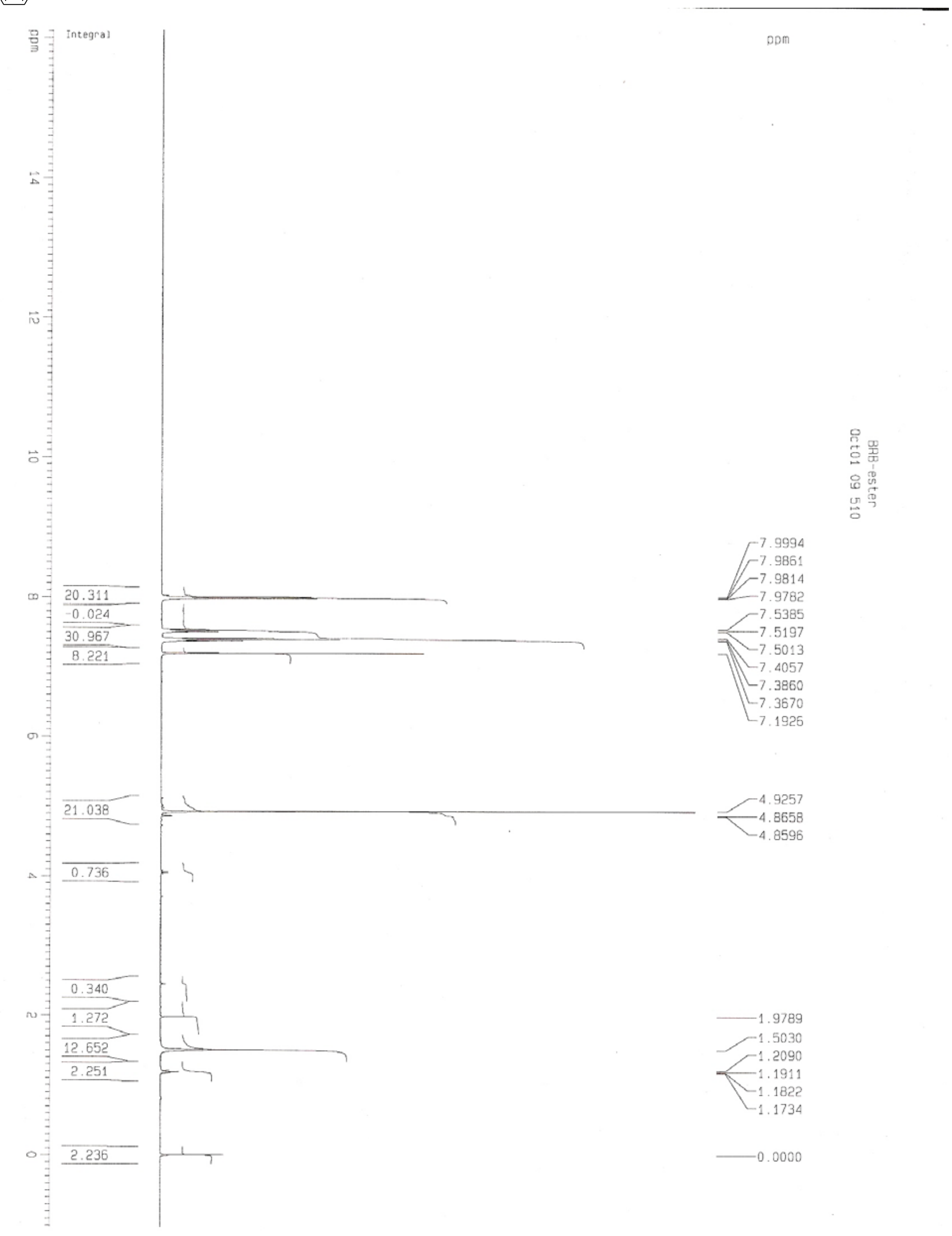
F2 - Acquisition Parameters
Date_              20091009
Time                  12.05
INSTRUM               av400
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      139
DS                        2
SWH              26178.010 Hz
FIDRES            0.399445 Hz
AQ               1.2517875 sec
RG                    16384
DW                   19.100 usec
DE                     6.00 usec
TE                    298.0 K
D1               1.00000000 sec
d11              0.03000000 sec
DELTA            0.89999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     9.75 usec
PL1                    8.00 dB
SFO1            100.6248425 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                    4.00 dB
PL12                  18.99 dB
PL13                  20.00 dB
SFO2            400.1316005 MHz

F2 - Processing parameters
SI                   131072
SF              100.6128721 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```


O
O
O
O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Integral
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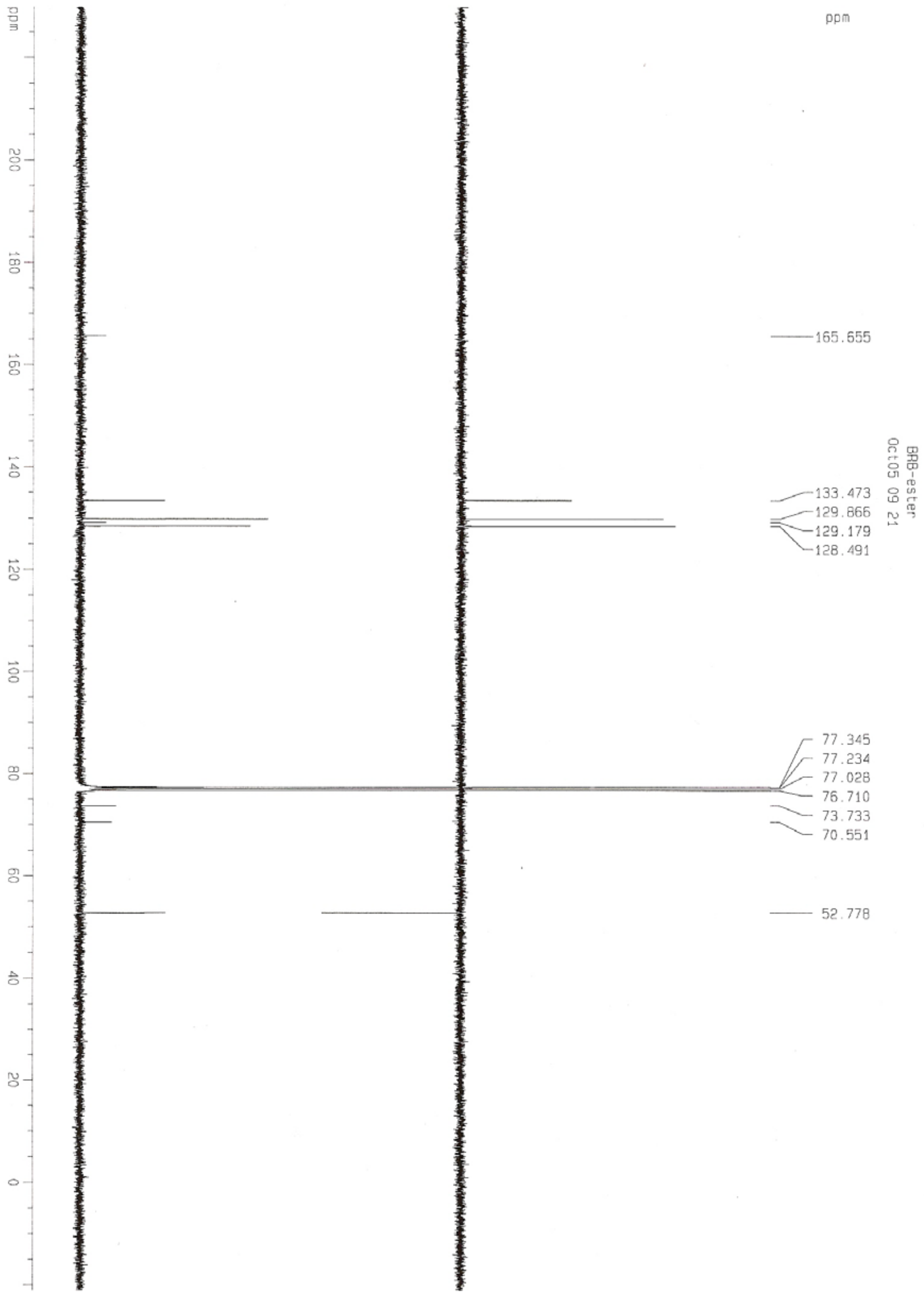
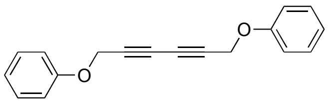
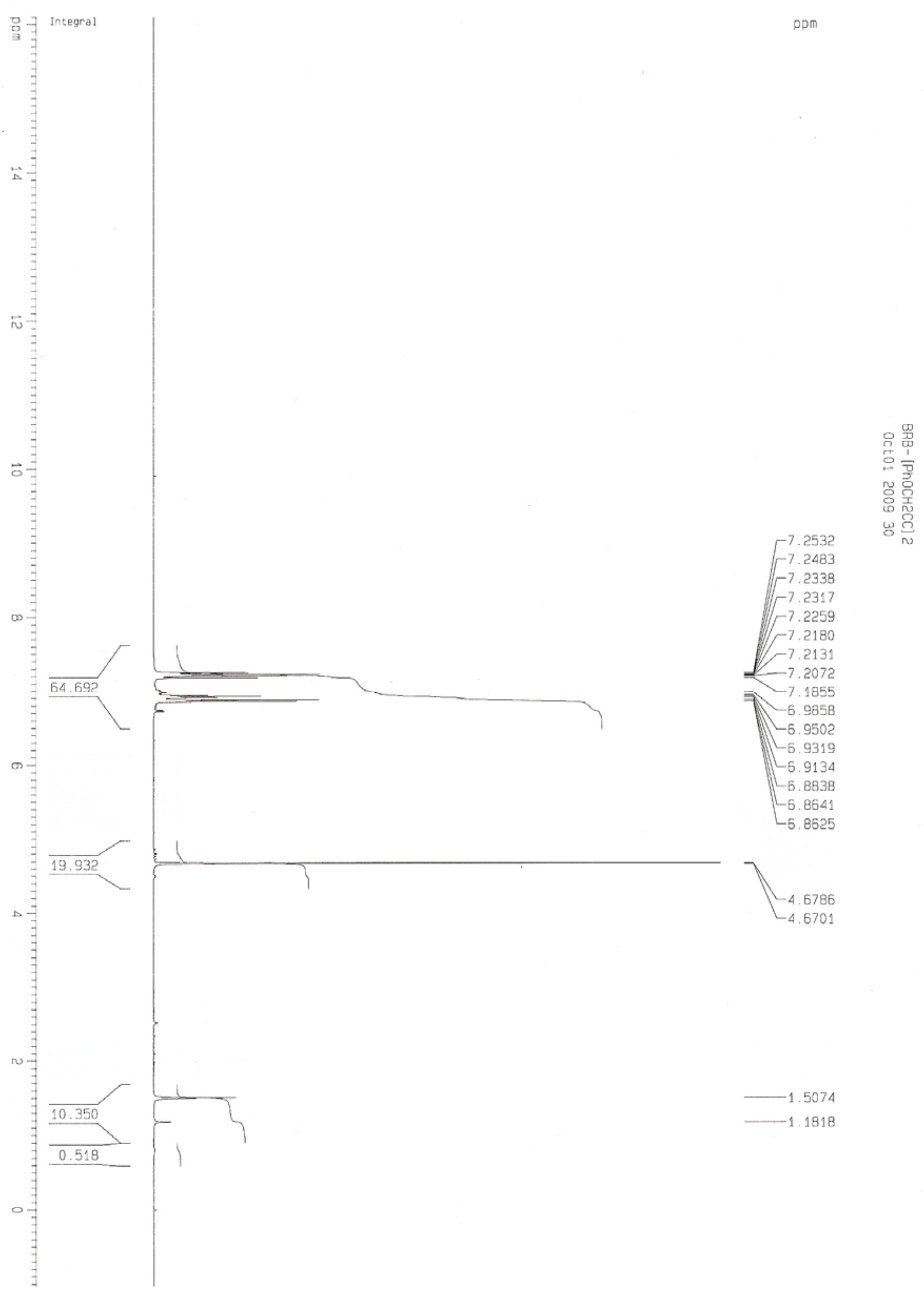
12
10
8
6
4
2
0
20.311
-0.024
30.967
8.221
21.038
0.736
0.340
1.272
12.652
2.251
2.236
ppm
BRB-ester
Oct01 09 510
7.9994
7.9861
7.9814
7.9782
7.5385
7.5197
7.5013
7.4057
7.3860
7.3670
7.1926
4.9257
4.8658
4.8596
1.9789
1.5030
1.2090
1.1911
1.1822
1.1734
0.0000


ppm
200
180
160
140
120
100
80
60
40
20
0
ppm
165.655
133.473
129.866
129.179
128.491
77.345
77.234
77.028
76.710
73.733
70.551
52.778
BRB-ester
Oct05 09 21

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Integral
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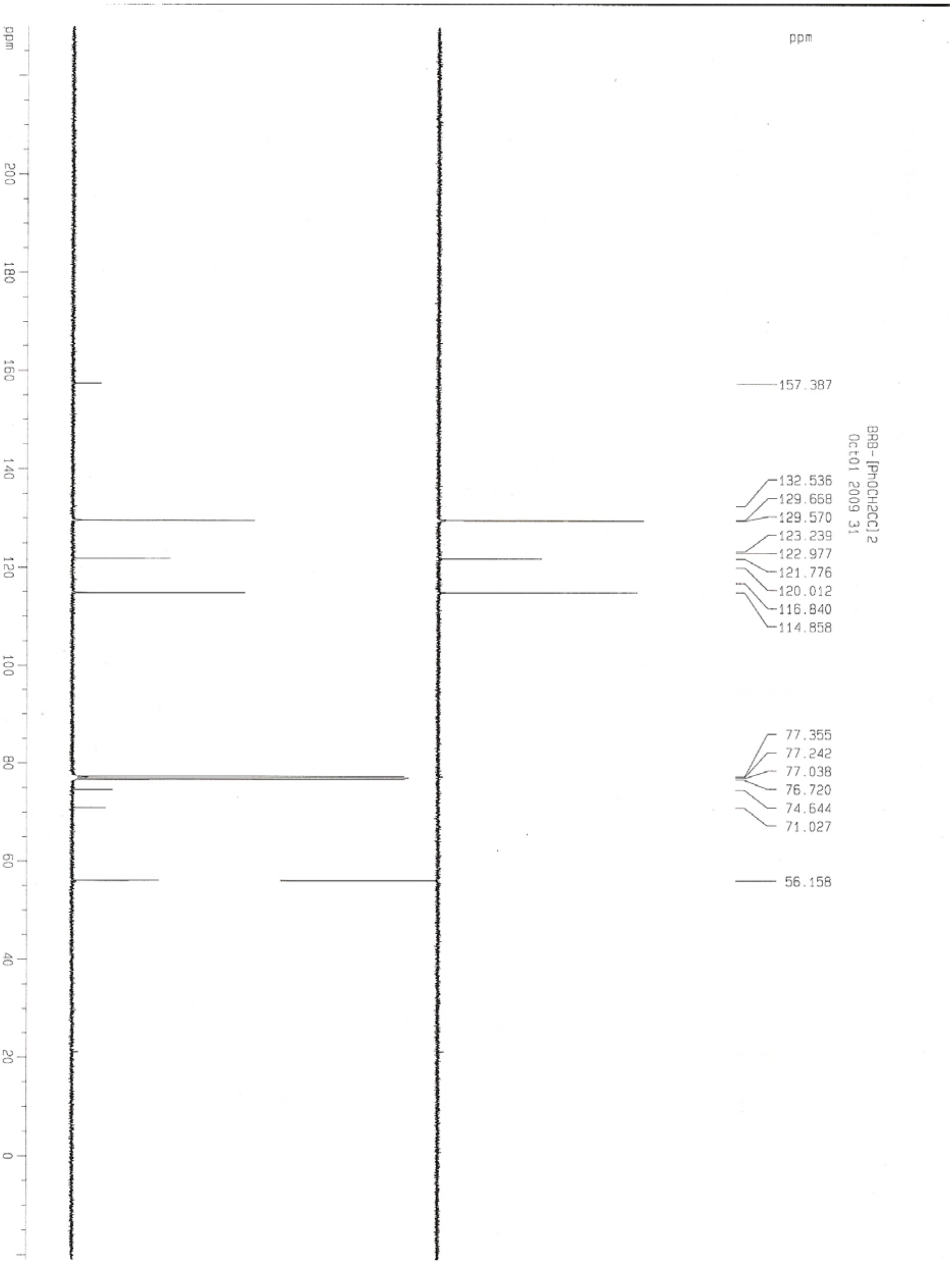
12
10
8
6
4
2
0
64.692
19.932
10.350
0.518
ppm
7.2532
7.2483
7.2338
7.2317
7.2259
7.2180
7.2131
7.2072
7.1855
6.9858
6.9502
6.9319
6.9134
6.8838
6.8641
6.8625
4.6786
4.6701
1.5074
1.1818
BRB-[PhOCH2CC]2
Oct01 2009 30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200
180
160
140
120
100
80
60
40
20
0
ppm
157.387
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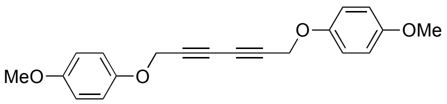
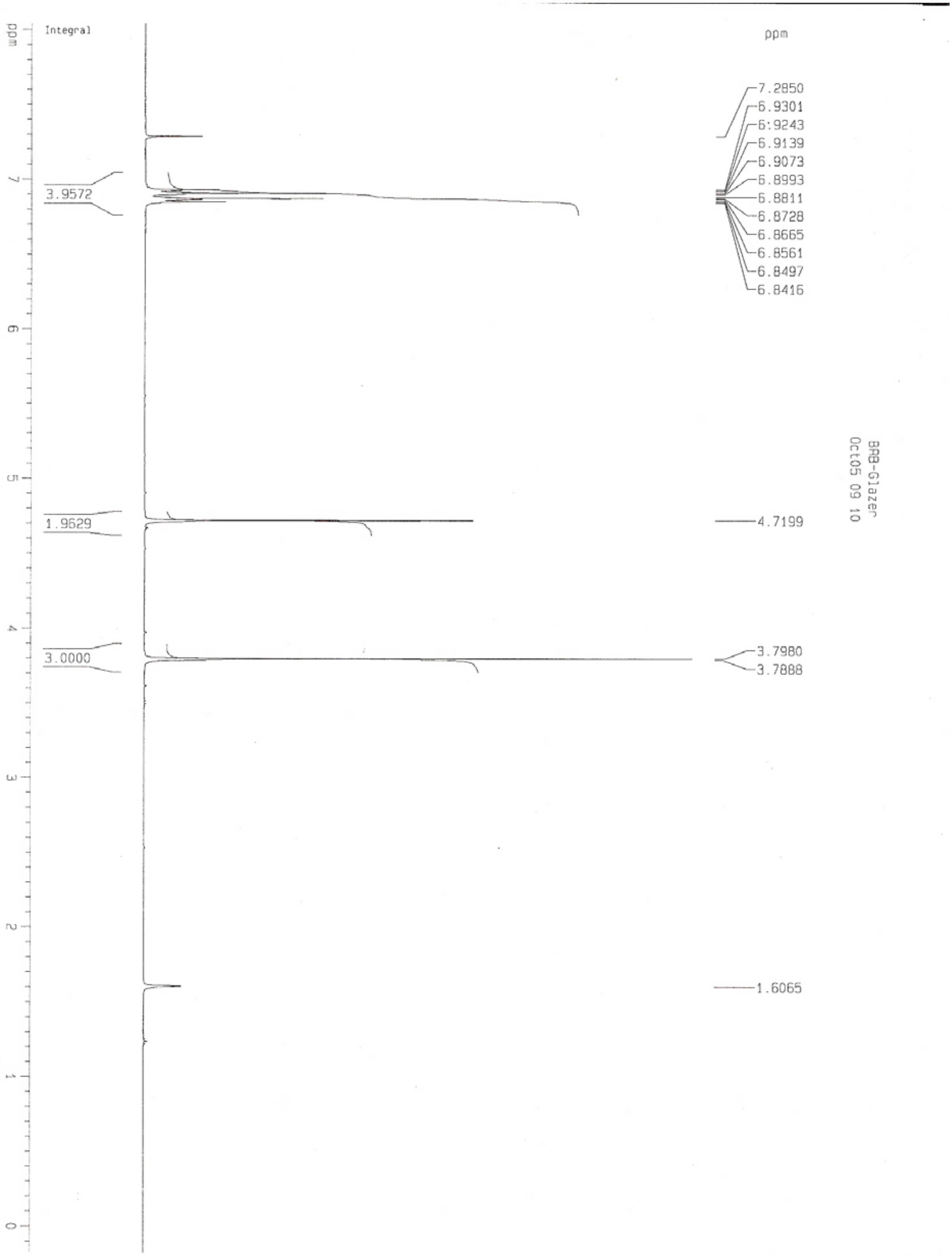
Oct01 2009 31
132.536
129.668
129.570
123.239
122.977
121.776
120.012
116.840
114.858
77.355
77.242
77.038
76.720
74.644
71.027
56.158


MeO
O
O
OMe


ppm
Integral
3.9572
1.9629
3.0000
ppm
7.2850
6.9301
6.9243
6.9139
6.9073
6.8993
6.8811
6.8728
6.8665
6.8561
6.8497
6.8416
4.7199
3.7980
3.7888
1.6065
BRB-Glazer
Oct05 09 10
7
6
5
4
3
2
1
0

Supplementary Material (ESI) for Chemical Communications
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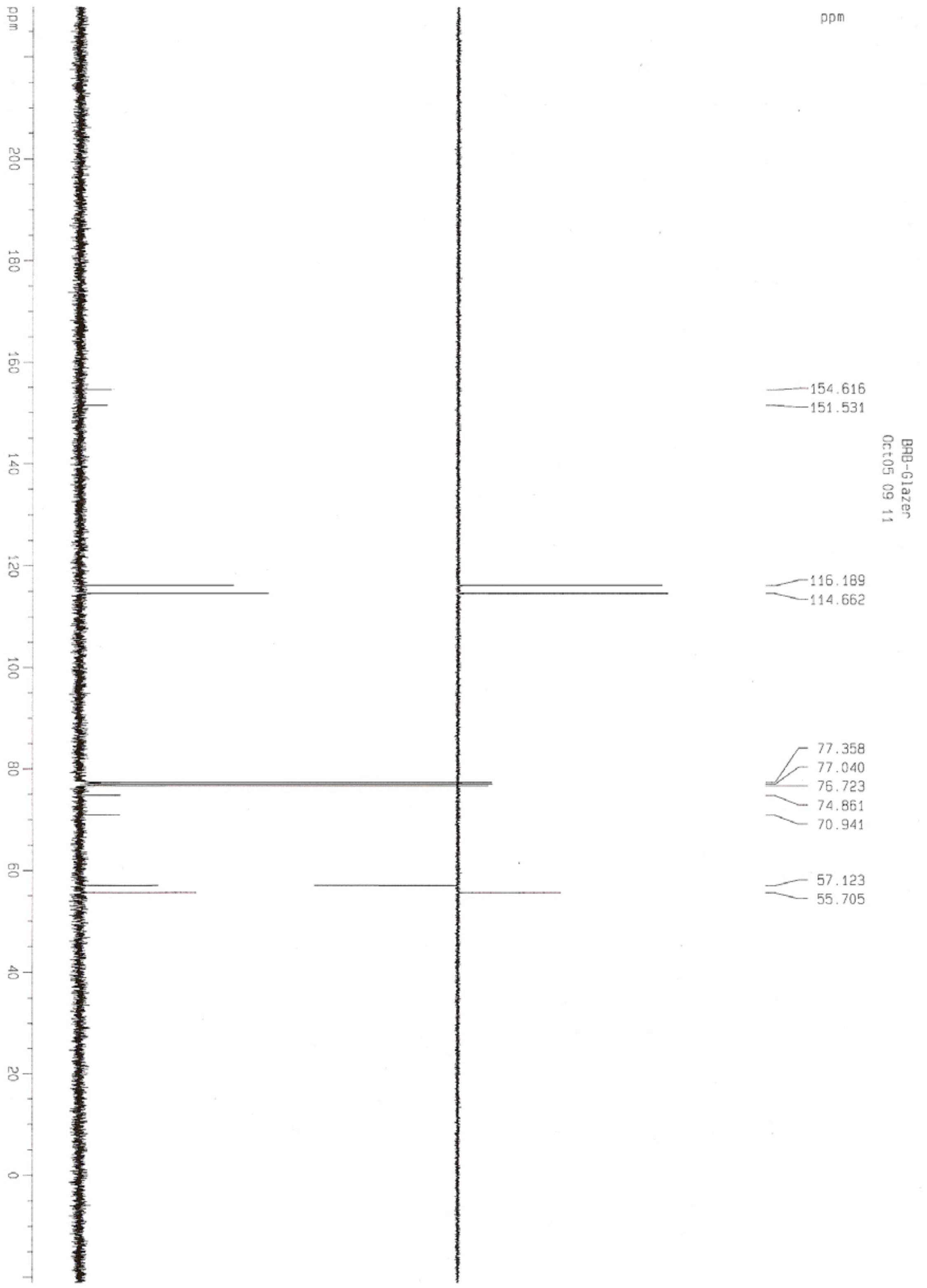

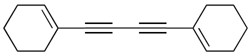

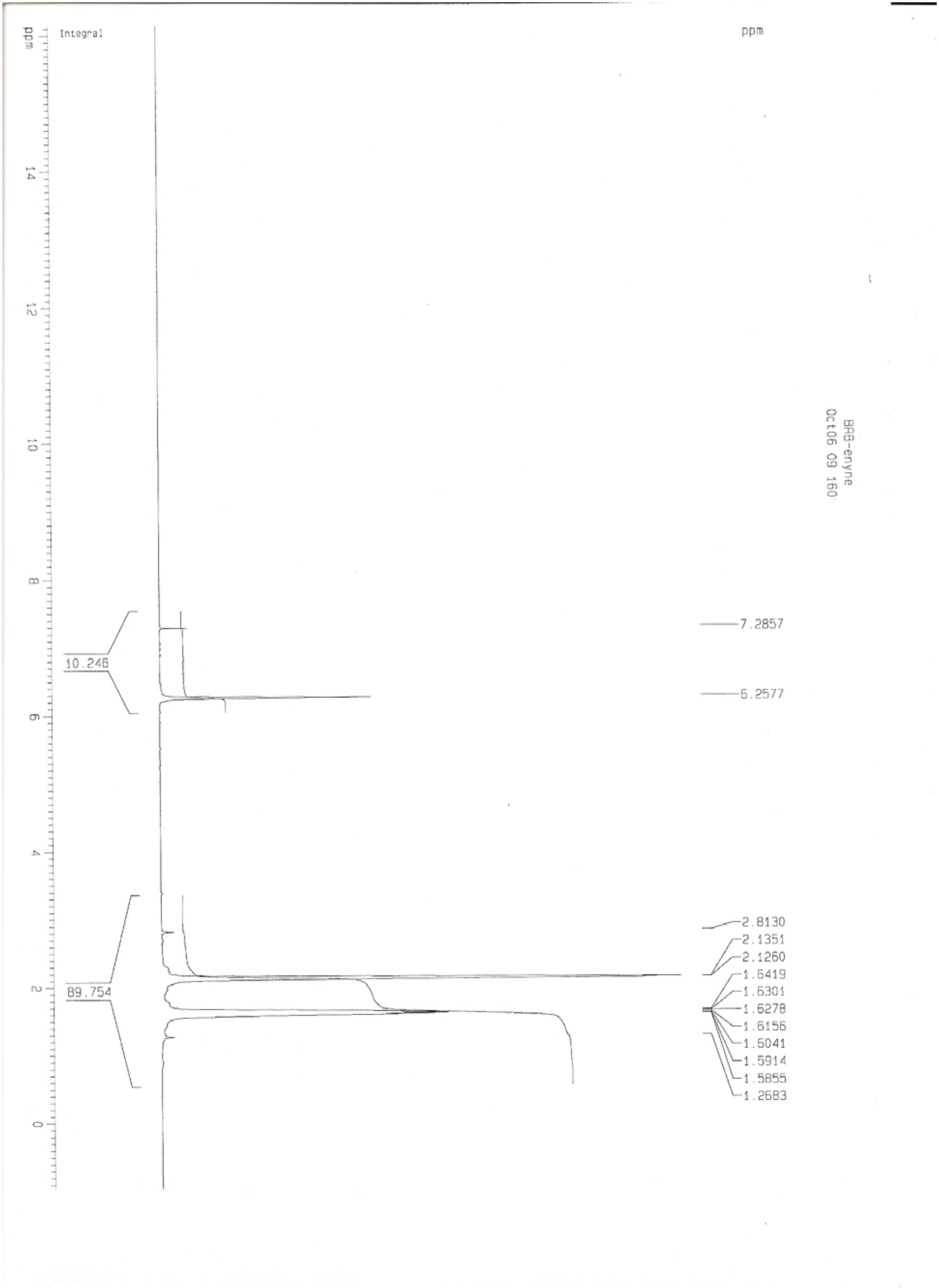
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Integral
ppm
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12
10
8
6
4
2
0
10.246
89.754
7.2857
6.2577
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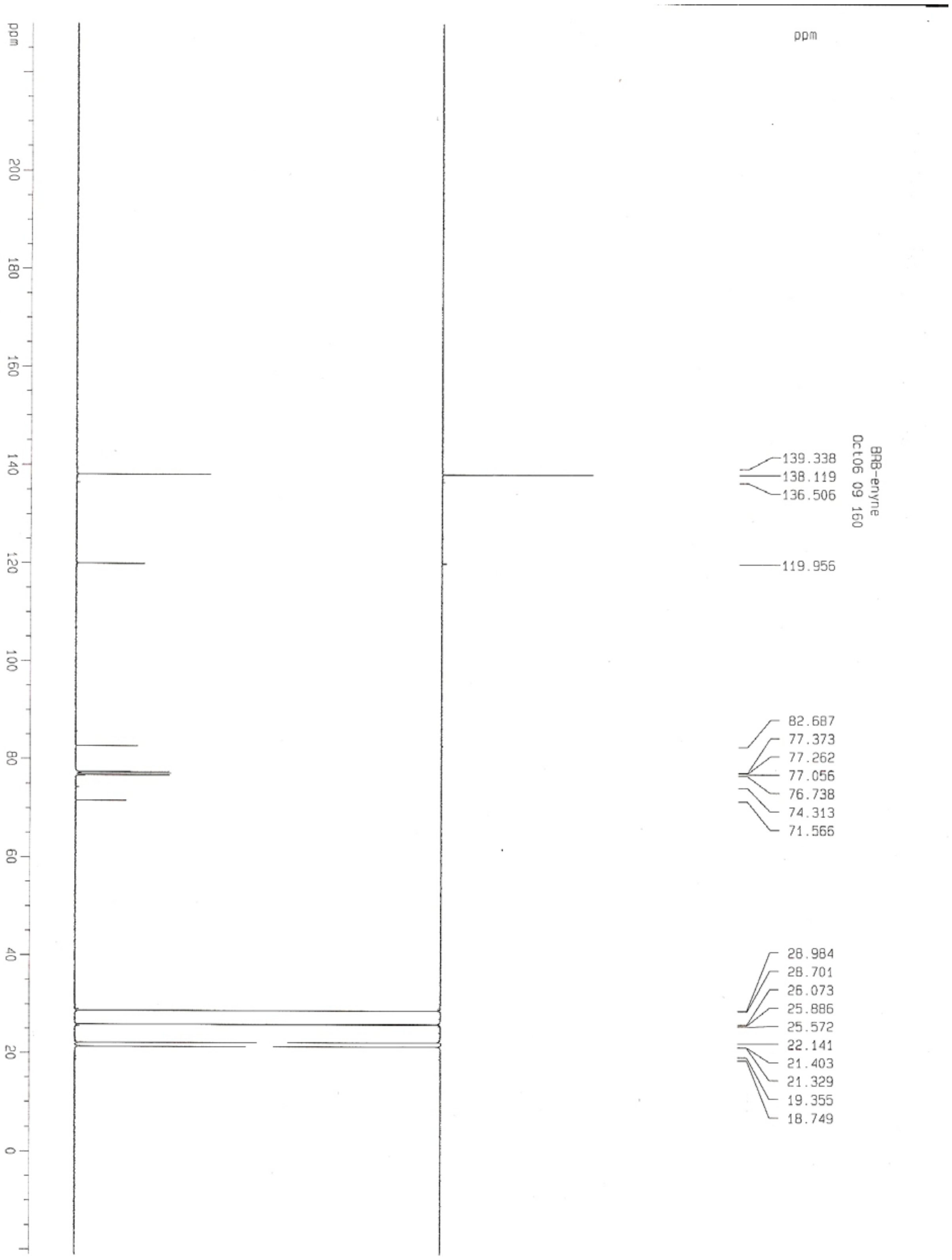
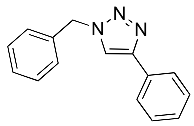
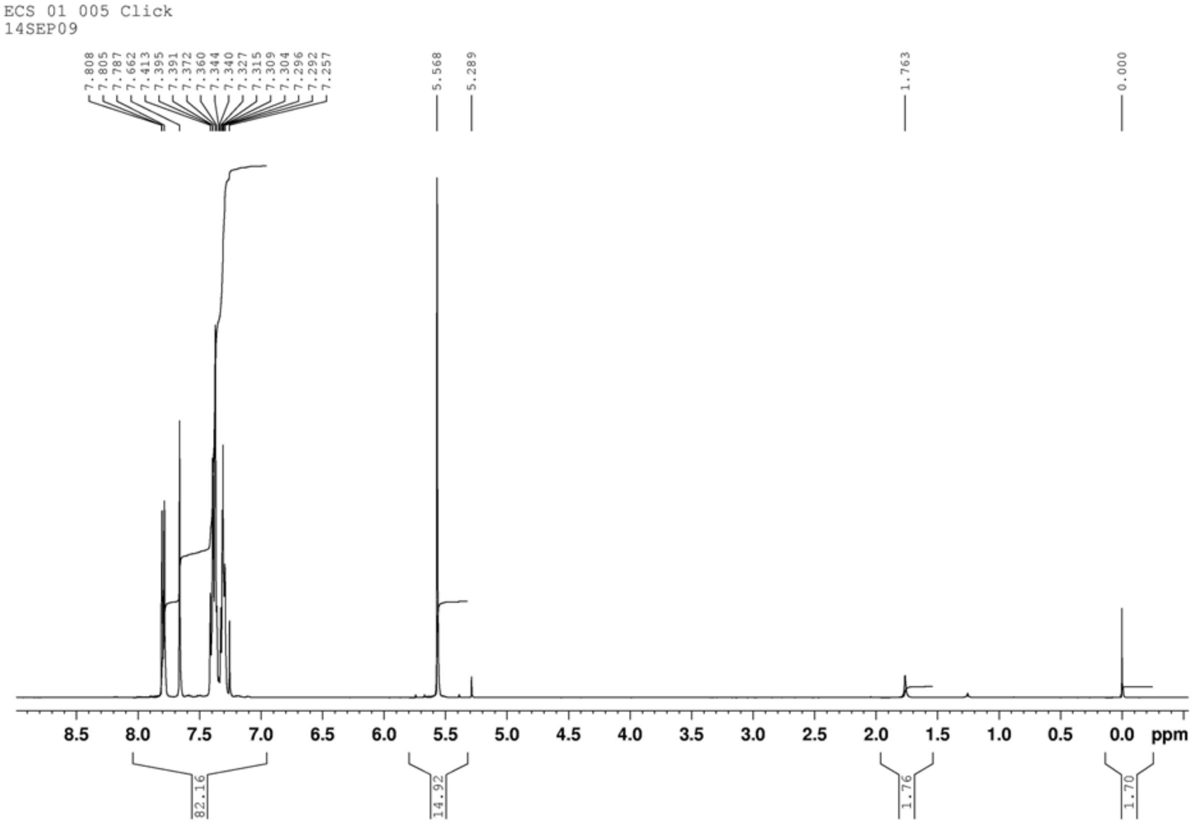
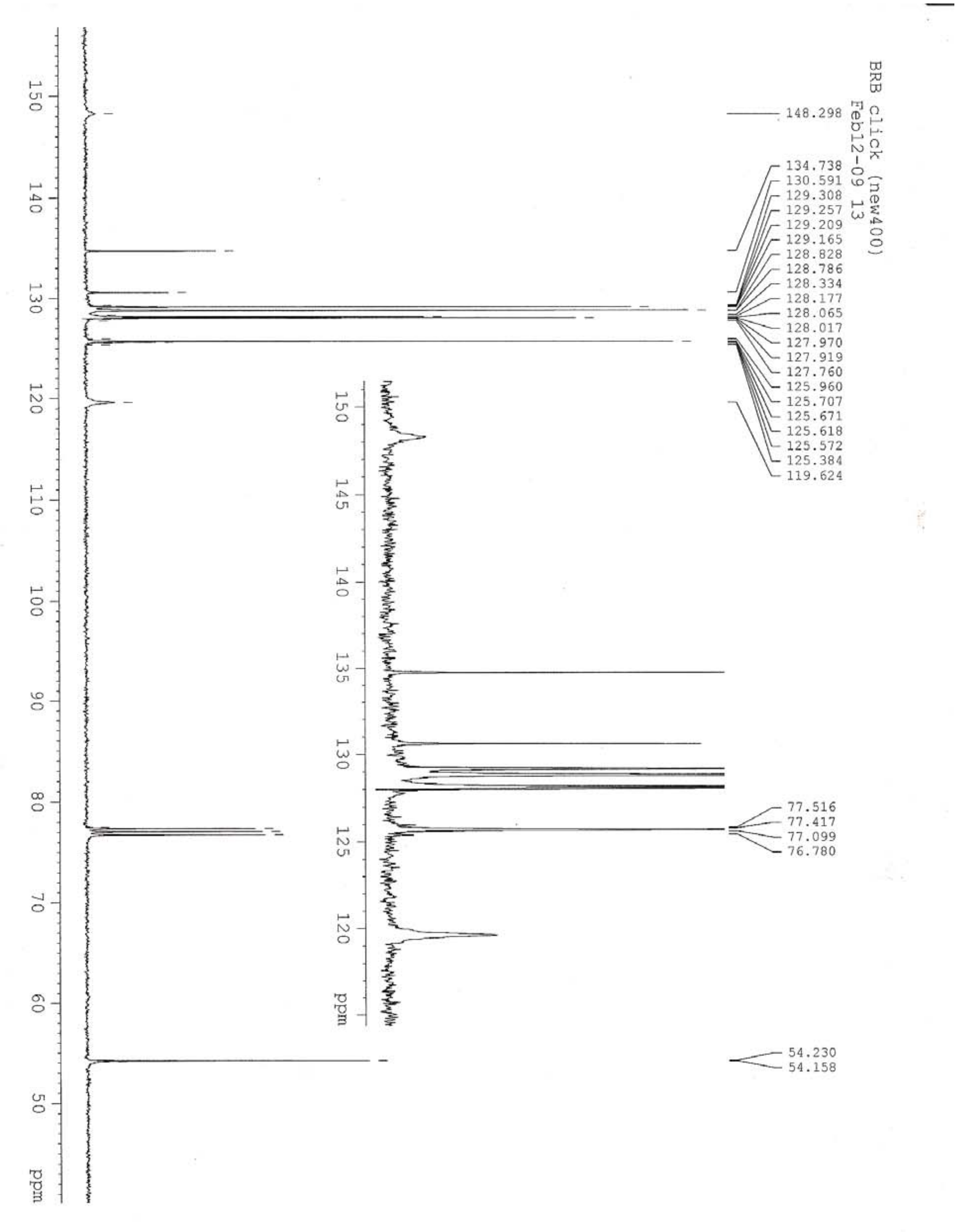
2.1351
2.1260
1.6419
1.6301
1.6278
1.6156
1.6041
1.5914
1.5855
1.2683
BRB-enyne
Oct06 09 160

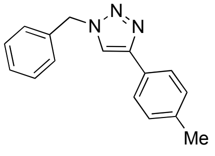

BRB-enyne
Oct06 09 160
ppm
200
180
160
140
120
100
80
60
40
20
0
139.338
138.119
136.506
119.956
82.687
77.373
77.262
77.056
76.738
74.313
71.566
28.984
28.701
26.073
25.886
25.572
22.141
21.403
21.329
19.355
18.749

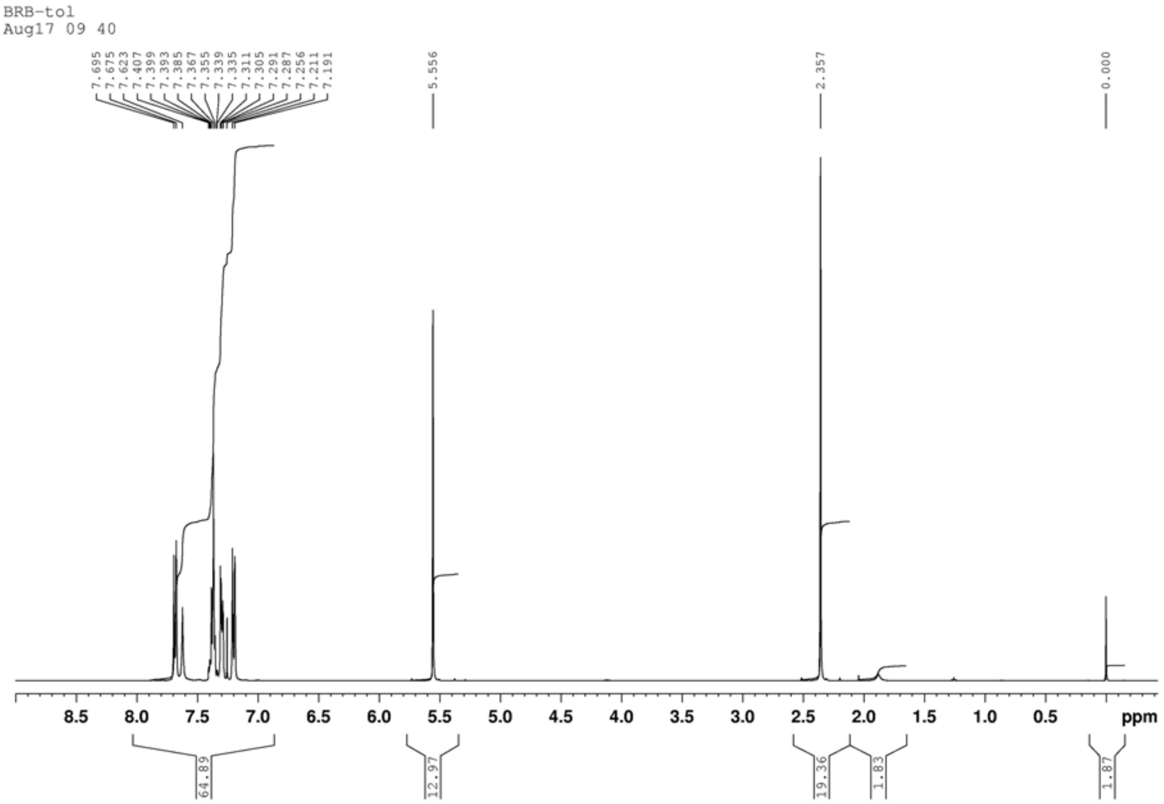
NMR spectra for the triazoles:






BRB click (new400)
Feb12-09 13
148.298
134.738
130.591
129.308
129.257
129.209
129.165
128.828
128.786
128.334
128.177
128.065
128.017
127.970
127.919
127.760
125.960
125.707
125.671
125.618
125.572
125.384
119.624
77.516
77.417
77.099
76.780
54.230
54.158
150
140
130
120
110
100
90
80
70
60
50
ppm
150
145
140
135
130
125
120
ppm


N
N
N
Me


BRB-tol
Aug17 09 40
7.695
7.675
7.623
7.407
7.399
7.393
7.385
7.367
7.355
7.339
7.335
7.311
7.305
7.291
7.287
7.256
7.211
7.191
5.556
2.357
0.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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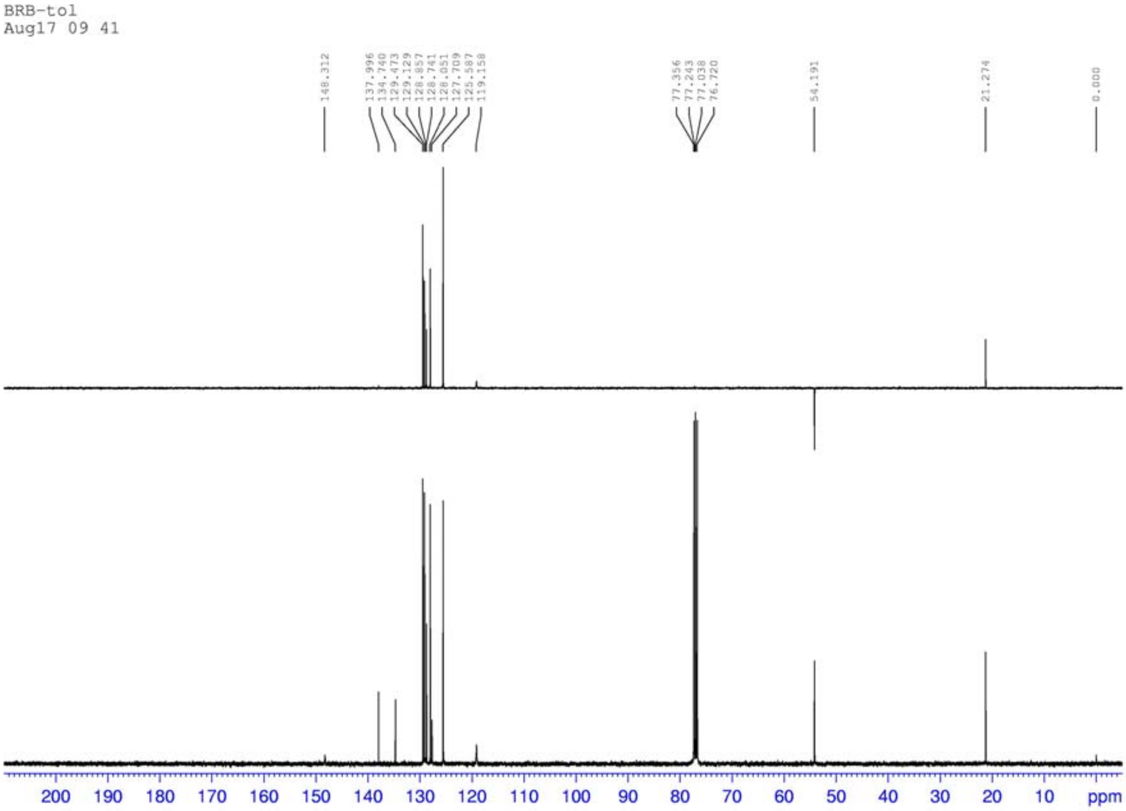
12.97
19.36
1.83
1.87


BRB-tol
Aug17 09 41
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137.996
134.740
129.473
129.129
128.857
128.741
128.051
127.709
125.587
119.158
77.356
77.243
77.038
76.720
54.191
21.274
0.000
200
190
180
170
160
150
140
130
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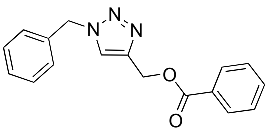
50
40
30
20
10
ppm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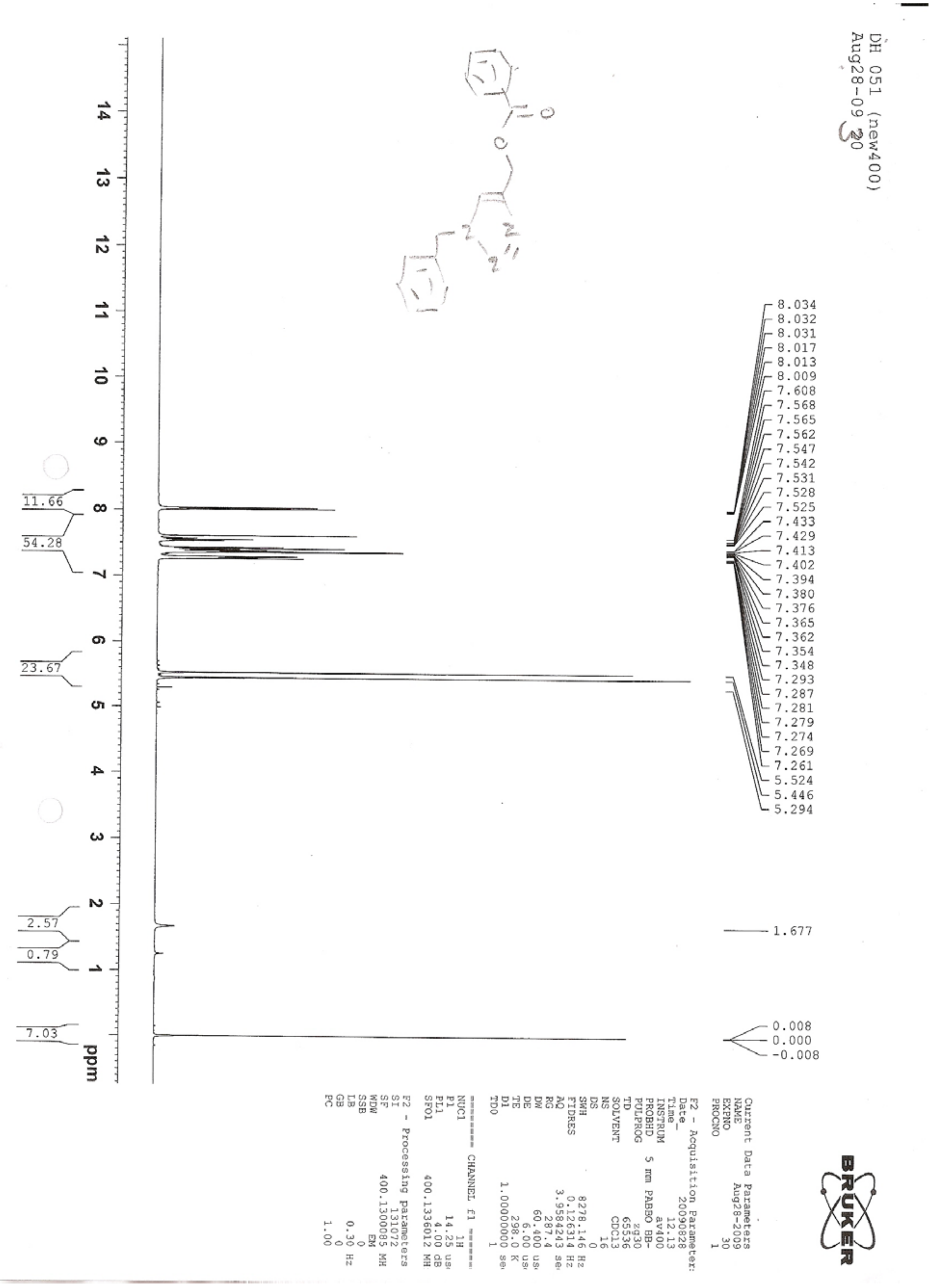
N
N
O
O

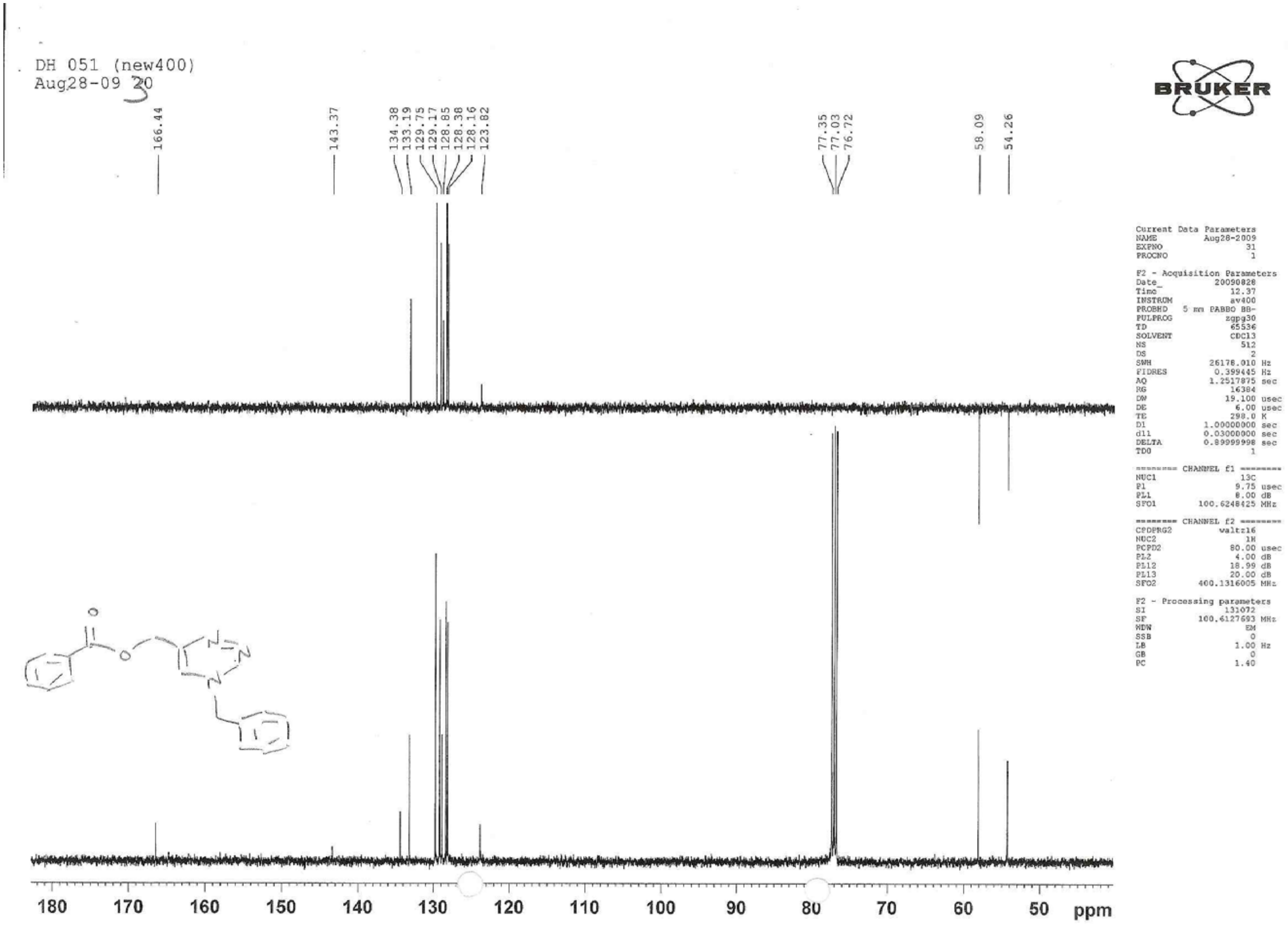


```
Current Data Parameters
NAME          Aug28-2009
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameter:
Date_           20090828
Time               12.13
INSTRUM            av400
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 se
RG                 287.4
DW                60.400 us
DE                  6.00 us
TE                 298.0 K
D1           1.00000000 se
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.25 us
PL1                 4.00 dB
SFO1        400.1336012 MH

F2 - Processing parameters
SI                131072
SF          400.1300085 MH
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



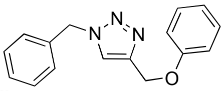
```
Current Data Parameters
NAME          Aug28-2009
EXPNO                 31
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090828
Time               12.37
INSTRUM            av400
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     2
SWH            26178.010 Hz
FIDRES          0.399445 Hz
AQ             1.2517875 sec
RG                 16384
DW                19.100 usec
DE                  6.00 usec
TE                 298.0 K
D1            1.00000000 sec
d11           0.03000000 sec
DELTA         0.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.75 usec
PL1                 8.00 dB
SFO1         100.6248425 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 4.00 dB
PL12               18.99 dB
PL13               20.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                131072
SF           100.6127693 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```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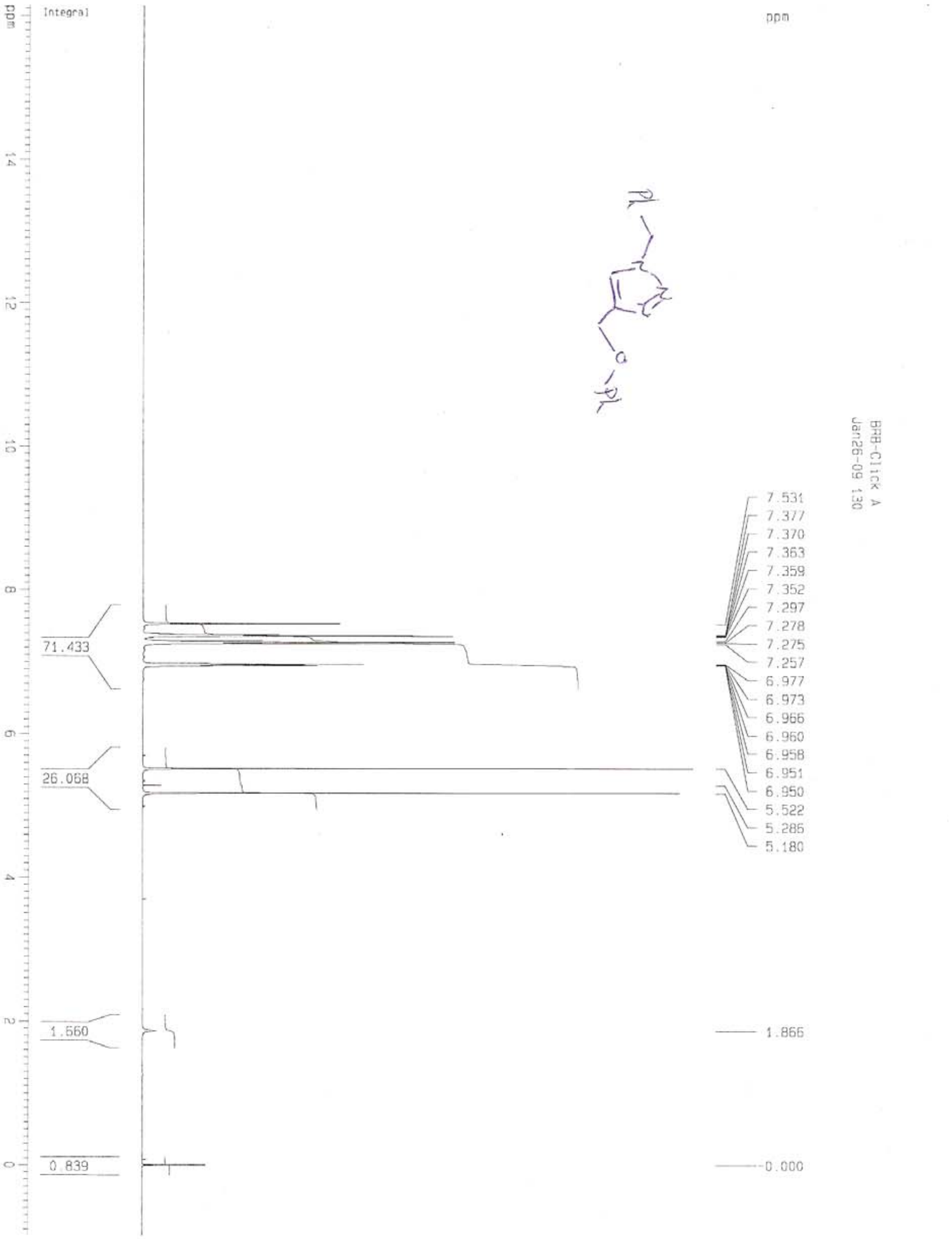
N
N
O


ppm
Integral
14
12
10
8
6
4
2
0
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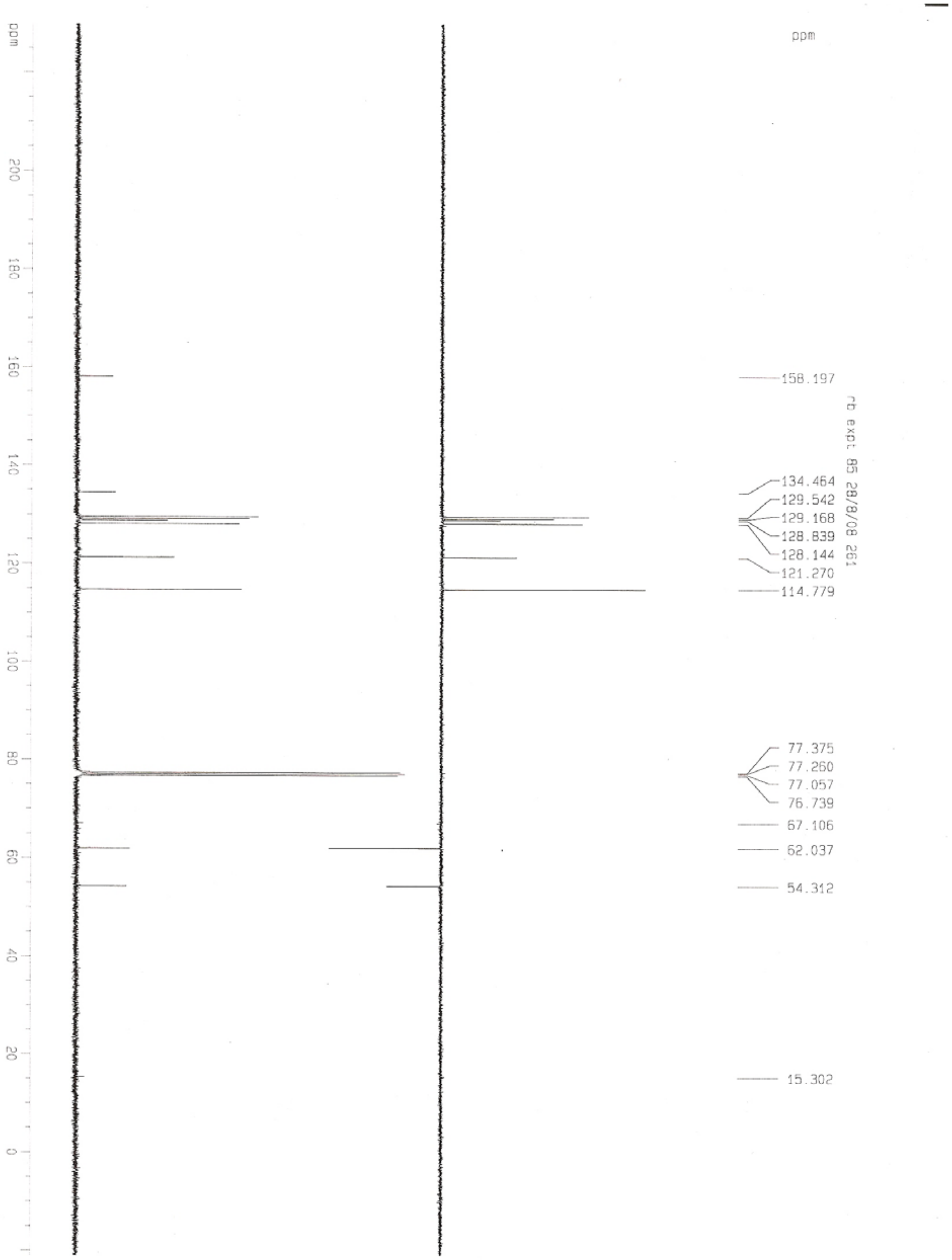
26.068
1.660
0.839
ppm
Ph
N
N
N
O
Ph
BRB-Click A
Jan26-09 130
7.531
7.377
7.370
7.363
7.359
7.352
7.297
7.278
7.275
7.257
6.977
6.973
6.966
6.960
6.958
6.951
6.950
5.522
5.285
5.180
1.866
0.000


ppm
200
180
160
140
120
100
80
60
40
20
0
ppm
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rb expt 85 28/8/08 261
134.464
129.542
129.168
128.839
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121.270
114.779
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77.260
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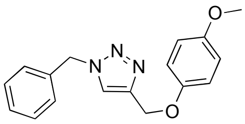
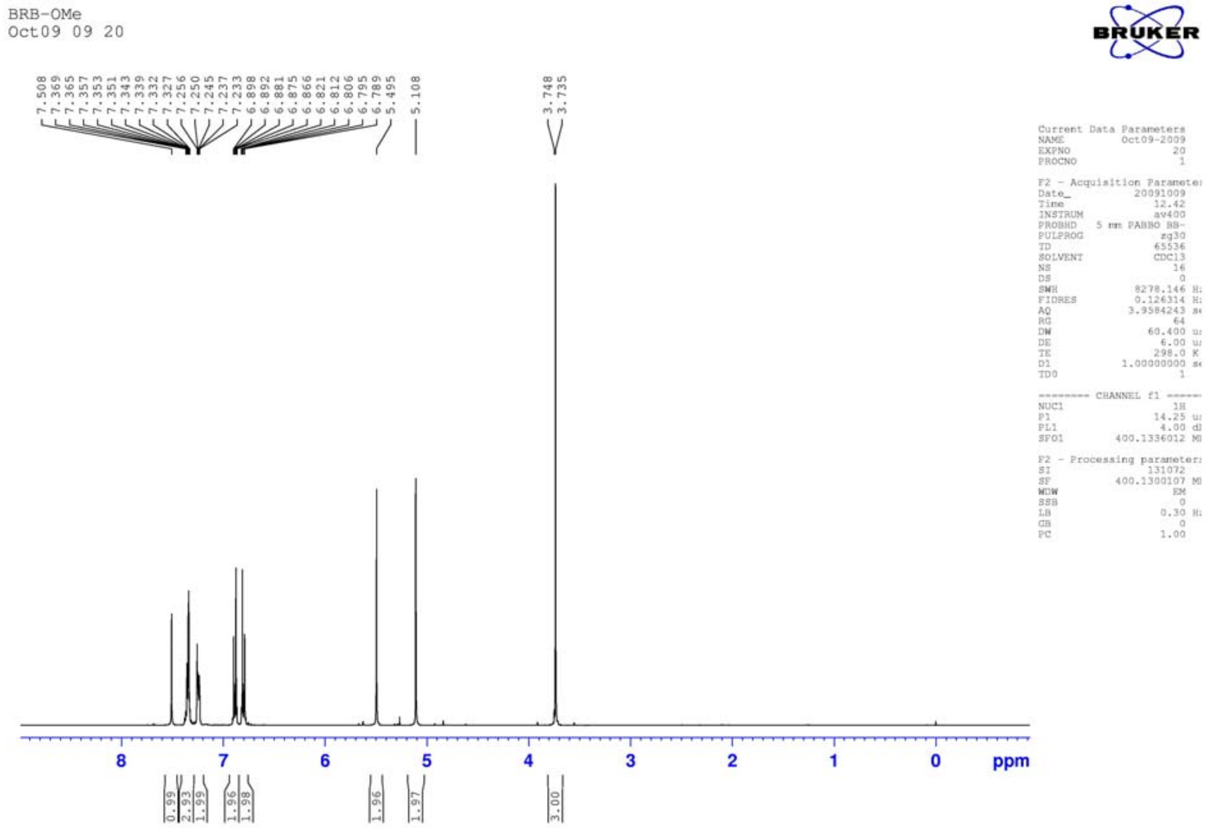
67.106
62.037
54.312
15.302


O
N
N
N
O


BRB-OMe
Oct09 09 20
7.508
7.369
7.365
7.357
7.353
7.351
7.343
7.339
7.332
7.327
7.256
7.250
7.245
7.237
7.233
6.898
6.892
6.881
6.875
6.866
6.821
6.812
6.806
6.795
6.789
5.495
5.108
3.748
3.735
8
7
6
5
4
3
2
1
0
ppm
0.99
2.93
1.99
1.96
1.98
1.96
1.97
3.00
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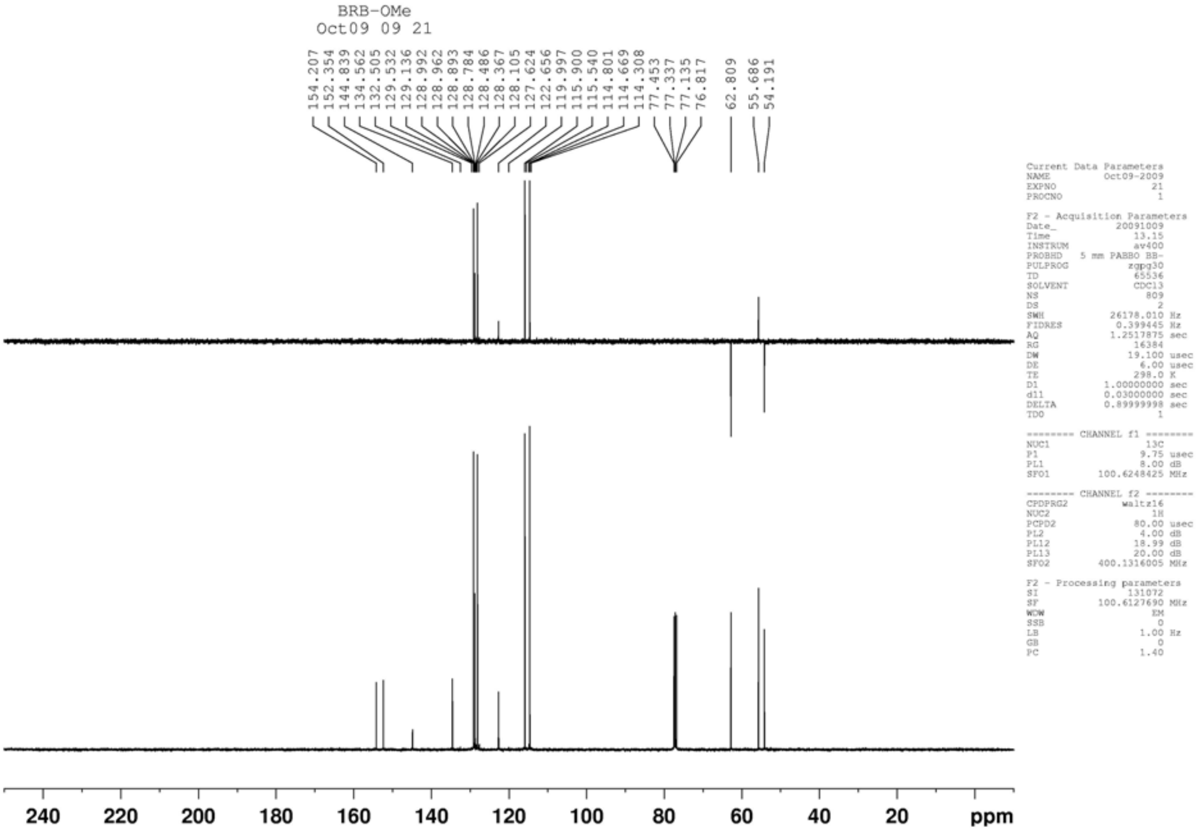
NAME Oct09-2009
EXPNO 20
PROCNO 1
F2 - Acquisition Paramete
Date_ 20091009
Time 12.42
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8278.146 H
FIDRES 0.126314 H
AQ 3.9584243 s
RG 64
DW 60.400 u
DE 6.00 u
TE 298.0 K
D1 1.00000000 s
TD0 1
======== CHANNEL f1 =====
NUC1 1H
P1 14.25 u
PL1 4.00 d
SFO1 400.1336012 M
F2 - Processing parameter
SI 131072
SF 400.1300107 M
WDW EM
SSB 0
LB 0.30 H
GB 0
PC 1.00


BRB-OMe
Oct09 09 21
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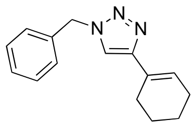
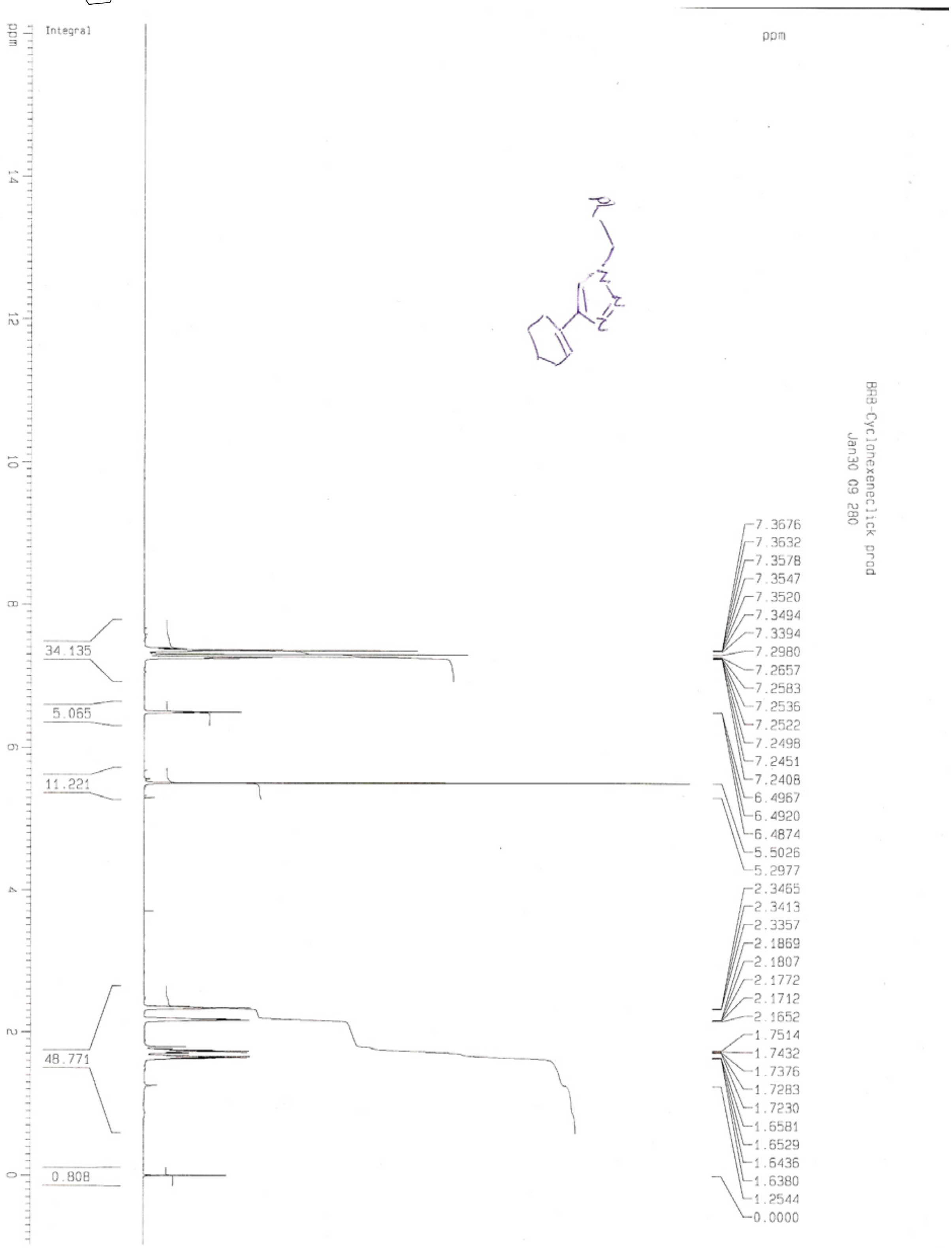
152.354
144.839
134.562
132.505
129.532
129.136
128.992
128.962
128.893
128.784
128.486
128.367
128.105
127.624
122.656
119.997
115.900
115.540
114.801
114.669
114.308
77.453
77.337
77.135
76.817
62.809
55.686
54.191
240
220
200
180
160
140
120
100
80
60
40
20
ppm
Current Data Parameters
NAME Oct09-2009
EXPNO 21
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091009
Time 13.15
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 809
DS 2
SWH 26178.010 Hz
FIDRES 0.399445 Hz
AQ 1.2517875 sec
RG 16384
DW 19.100 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.75 usec
PL1 8.00 dB
SFO1 100.6248425 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 4.00 dB
PL12 18.99 dB
PL13 20.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 131072
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40


N
N
N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Integral
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12
10
8
6
4
2
0
34.135
5.065
11.221
48.771
0.808
ppm
Ph
N
N
N
BRB-Cyclohexeneclick prod
Jan30 09 280
7.3676
7.3632
7.3578
7.3547
7.3520
7.3494
7.3394
7.2980
7.2657
7.2583
7.2536
7.2522
7.2498
7.2451
7.2408
6.4967
6.4920
6.4874
5.5026
5.2977
2.3465
2.3413
2.3357
2.1869
2.1807
2.1772
2.1712
2.1652
1.7514
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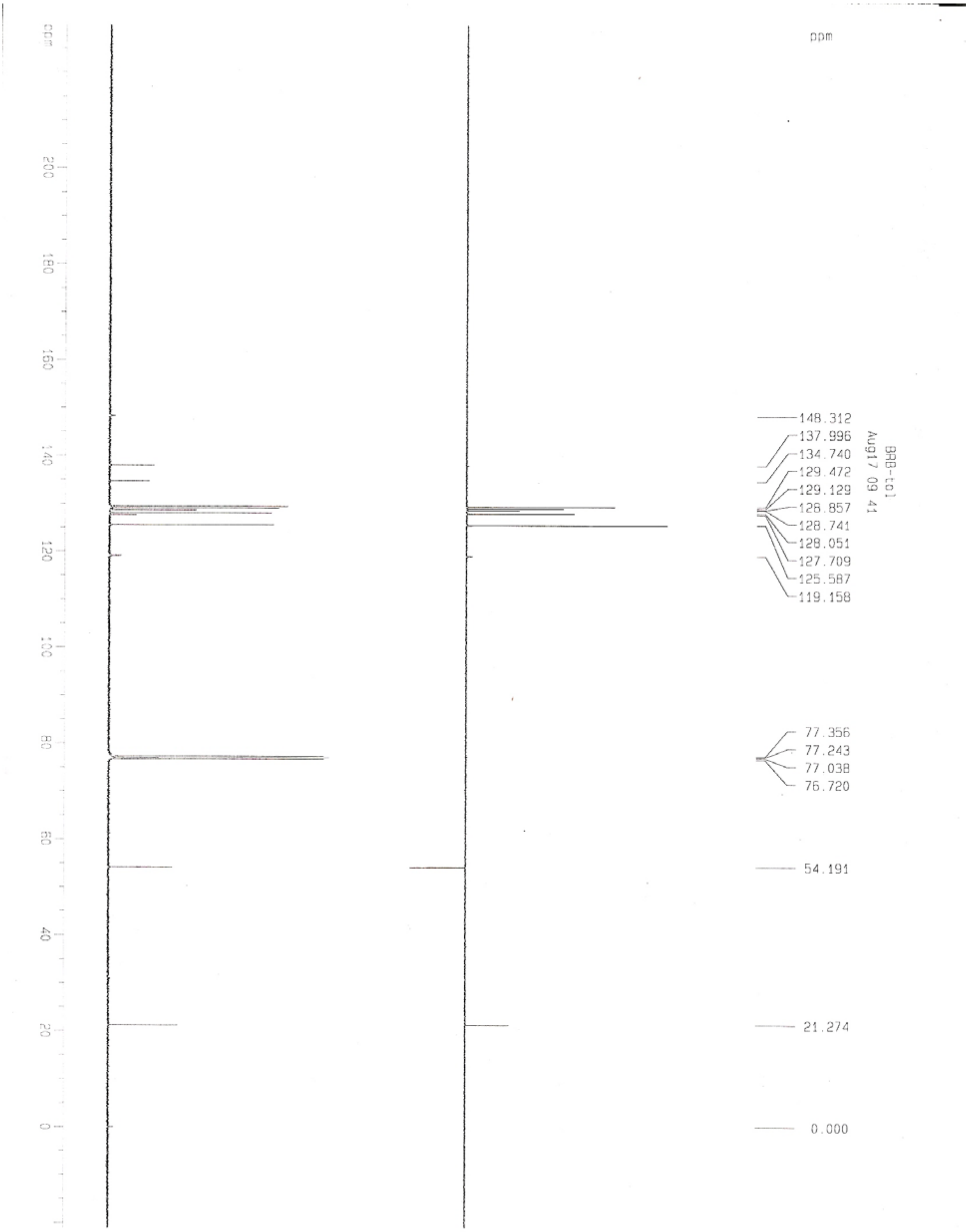
1.2544
0.0000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200
180
160
140
120
100
80
60
40
20
0
ppm
148.312
137.996
134.740
129.472
129.129
128.857
128.741
128.051
127.709
125.587
119.158
77.356
77.243
77.038
76.720
54.191
21.274
0.000
BRB-tol
Aug17 09 41

Supplementary Material (ESI) for Chemical Communications
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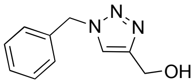

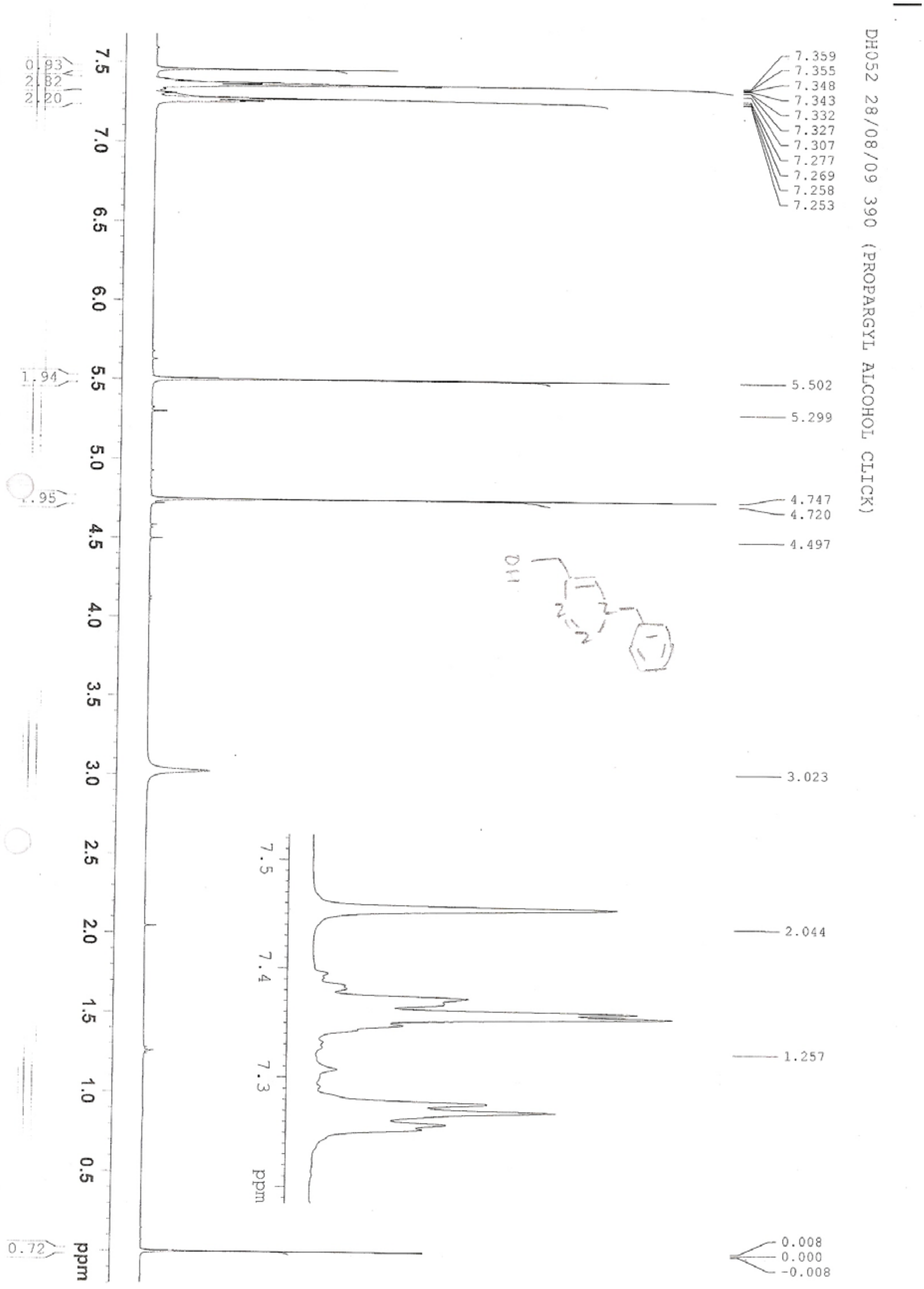

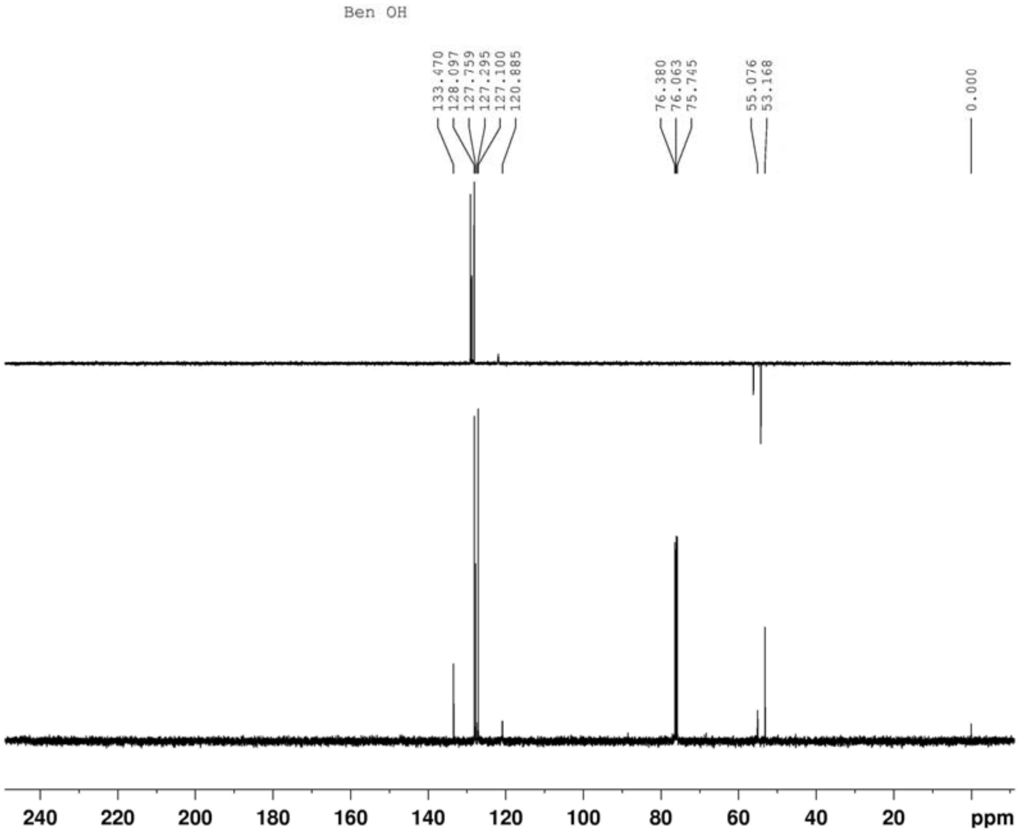

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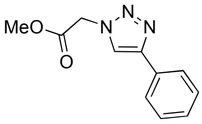
NAME          Oct09-2009
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20091009
Time               12.05
INSTRUM            av400
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   139
DS                     2
SWH           26178.010 Hz
FIDRES         0.399445 Hz
AQ            1.2517875 sec
RG                 16384
DW               19.100 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
d11          0.03000000 sec
DELTA        0.89999998 sec
TD0                    1

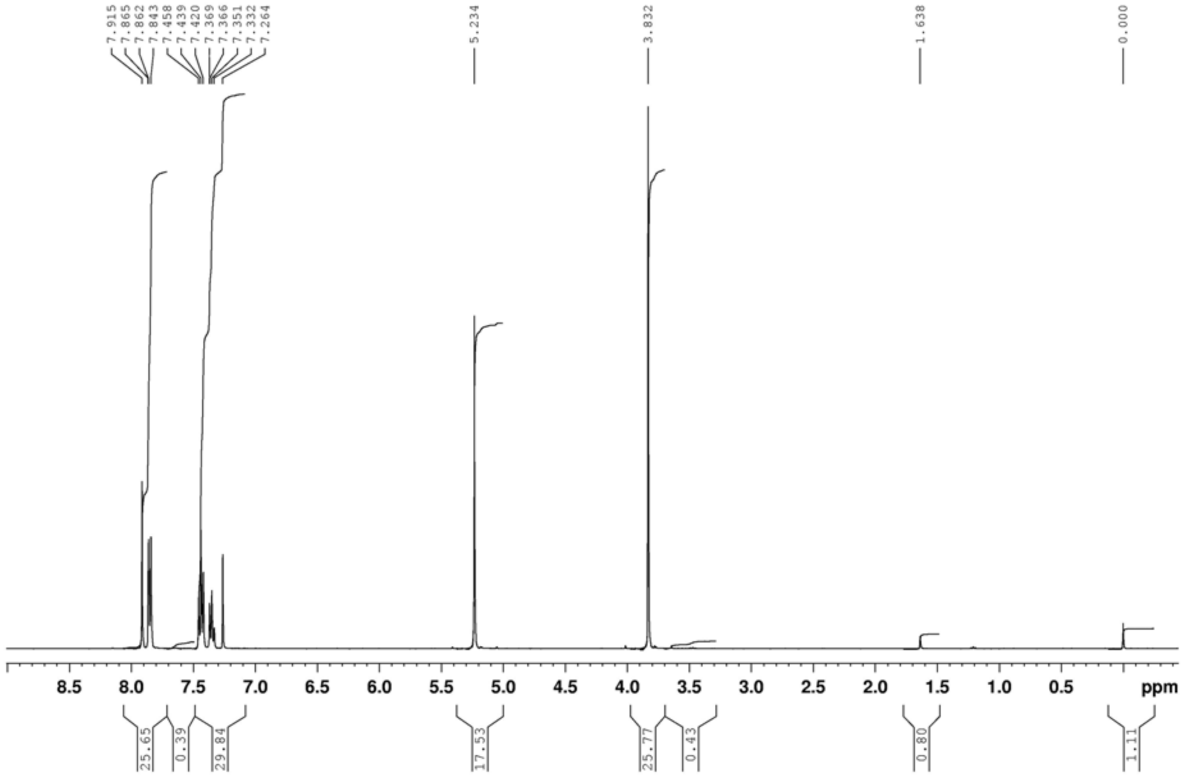
======== CHANNEL f1 ========
NUC1                 13C
P1                  9.75 usec
PL1                 8.00 dB
SFO1         100.6248425 MHz

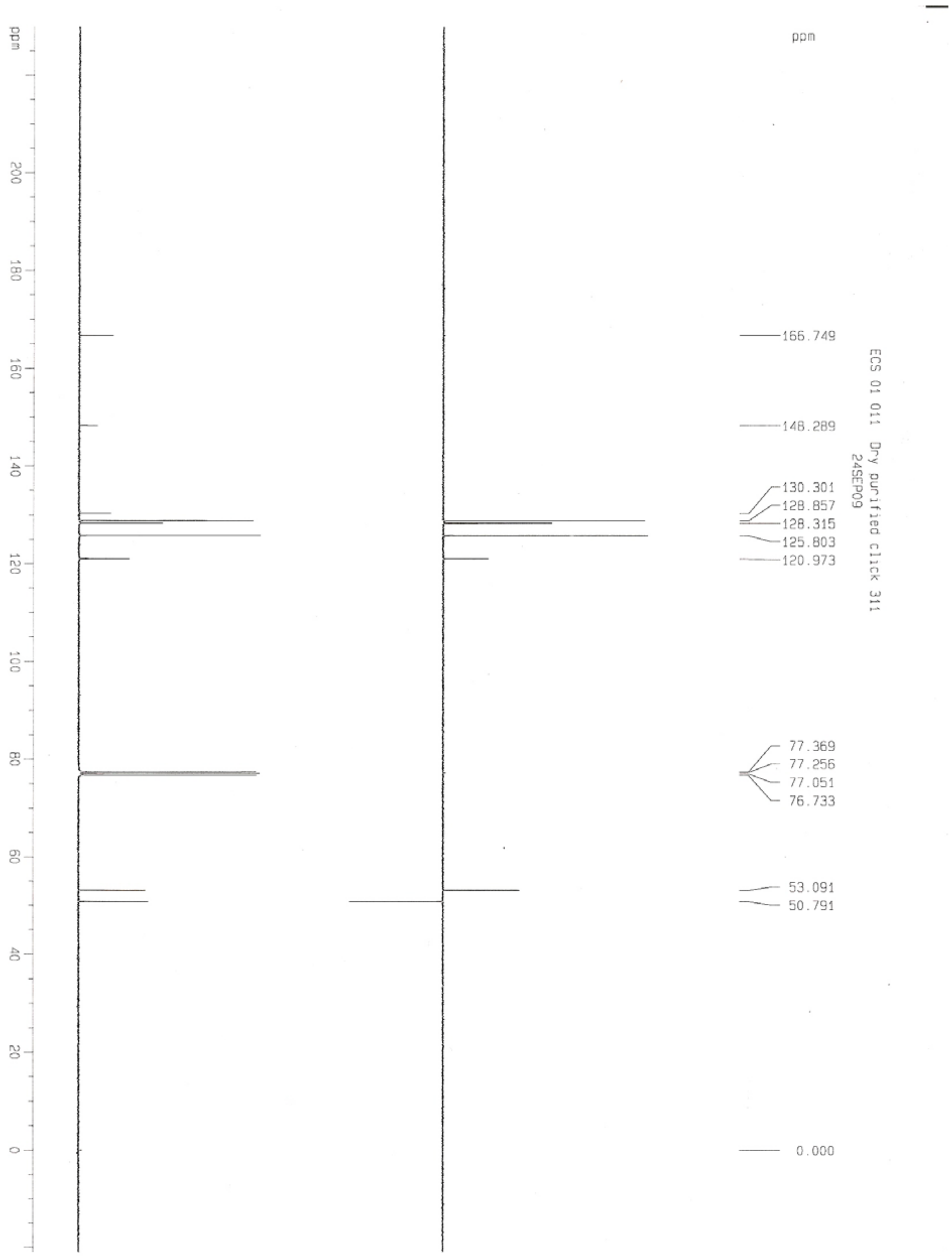
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 4.00 dB
PL12               18.99 dB
PL13               20.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                131072
SF           100.6128721 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



10 ECS/01/011 Rerun purified proton of Click Product 09/OCT/09

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200
180
160
140
120
100
80
60
40
20
0
ppm
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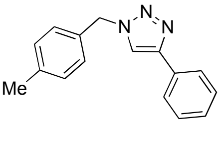
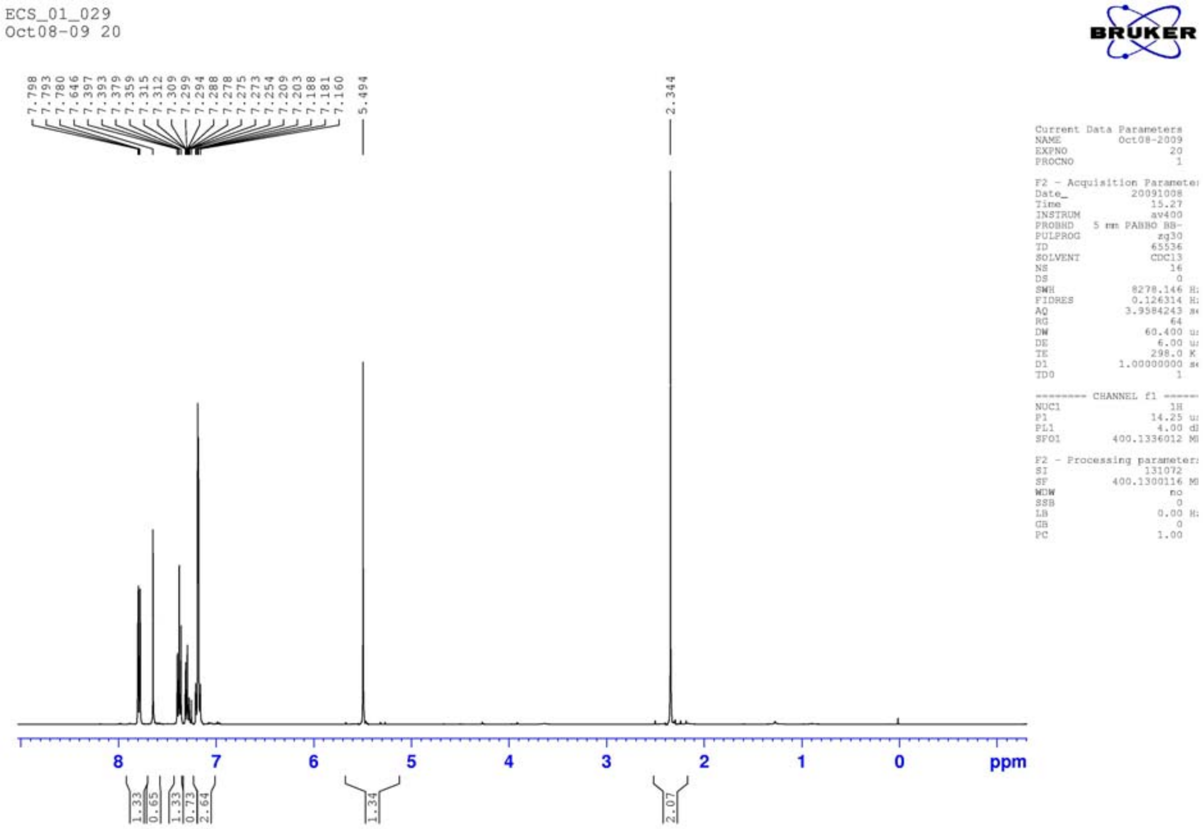
148.289
130.301
128.857
128.315
125.803
120.973
77.369
77.256
77.051
76.733
53.091
50.791
0.000
ECS 01 011 Dry purified click 311
24SEP09


N
N
N
Me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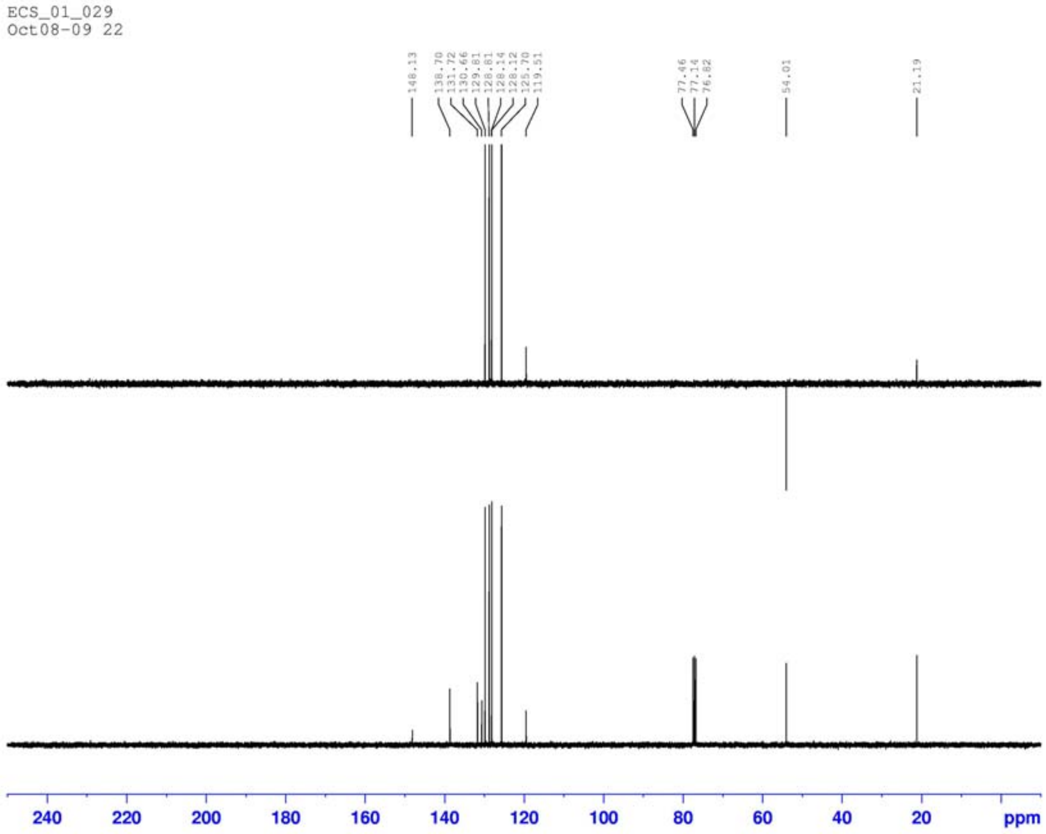
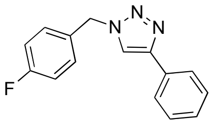
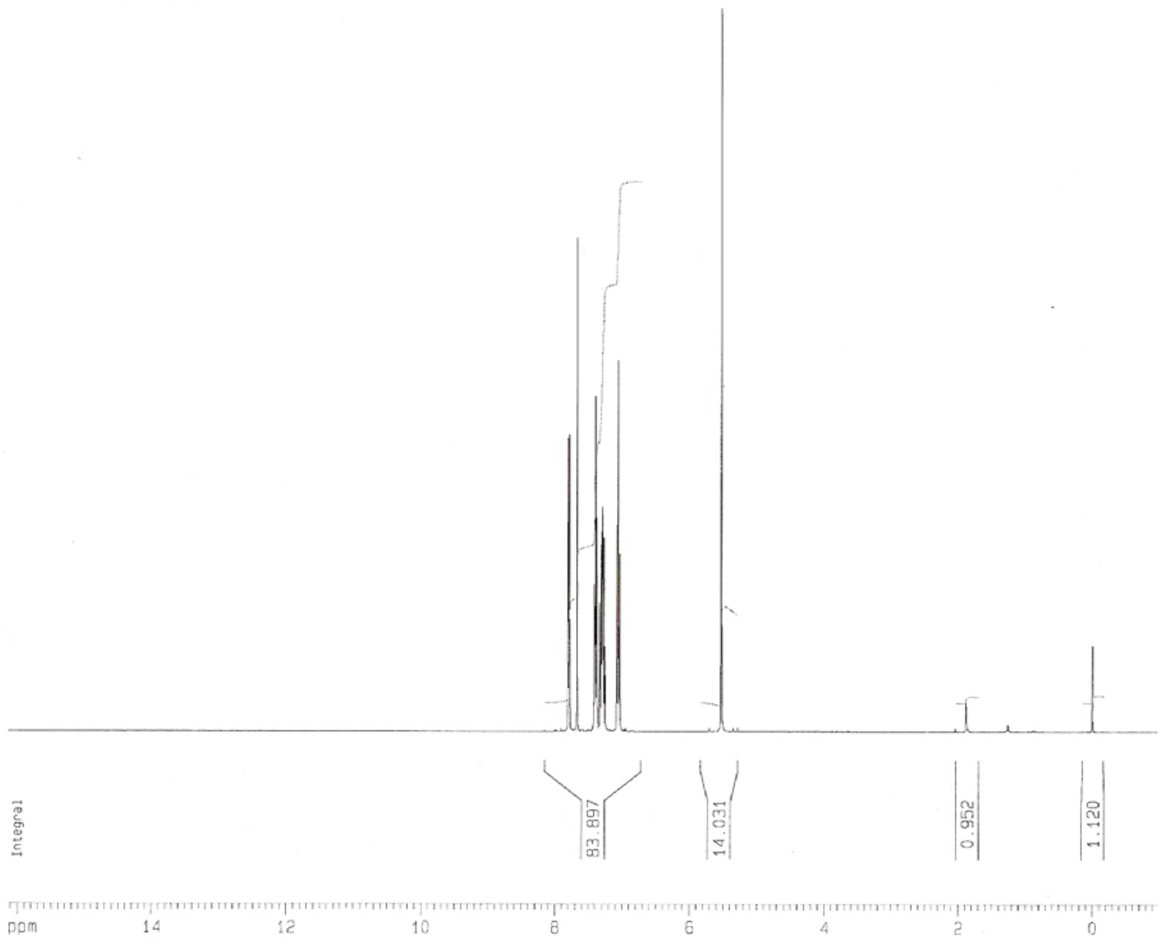
Oct08-09 20
7.798
7.793
7.780
7.646
7.397
7.393
7.379
7.359
7.315
7.312
7.309
7.299
7.294
7.288
7.278
7.275
7.273
7.254
7.209
7.203
7.188
7.181
7.160
5.494
2.344
BRUKER
Current Data Parameters
NAME Oct08-2009
EXPNO 20
PROCNO 1
F2 - Acquisition Paramete
Date_ 20091008
Time 15.27
INSTRUM av400
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8278.146 H
FIDRES 0.126314 H
AQ 3.9584243 s
RG 64
DW 60.400 u
DE 6.00 u
TE 298.0 K
D1 1.00000000 s
TD0 1
======== CHANNEL f1 =====
NUC1 1H
P1 14.25 u
PL1 4.00 d
SFO1 400.1336012 M
F2 - Processing parameter
SI 131072
SF 400.1300116 M
WDW no
SSB 0
LB 0.00 H
GB 0
PC 1.00
8
7
6
5
4
3
2
1
0
ppm
1.33
0.65
1.33
0.73
2.64
1.34
2.07


ECS_01_029
Oct08-09 22
148.13
138.70
131.72
130.66
129.81
128.81
128.14
128.12
125.70
119.51
77.46
77.14
76.82
54.01
21.19
240
220
200
180
160
140
120
100
80
60
40
20
ppm


F
N
N
N

ECS 01 013 dry purified click 320
24SEP09



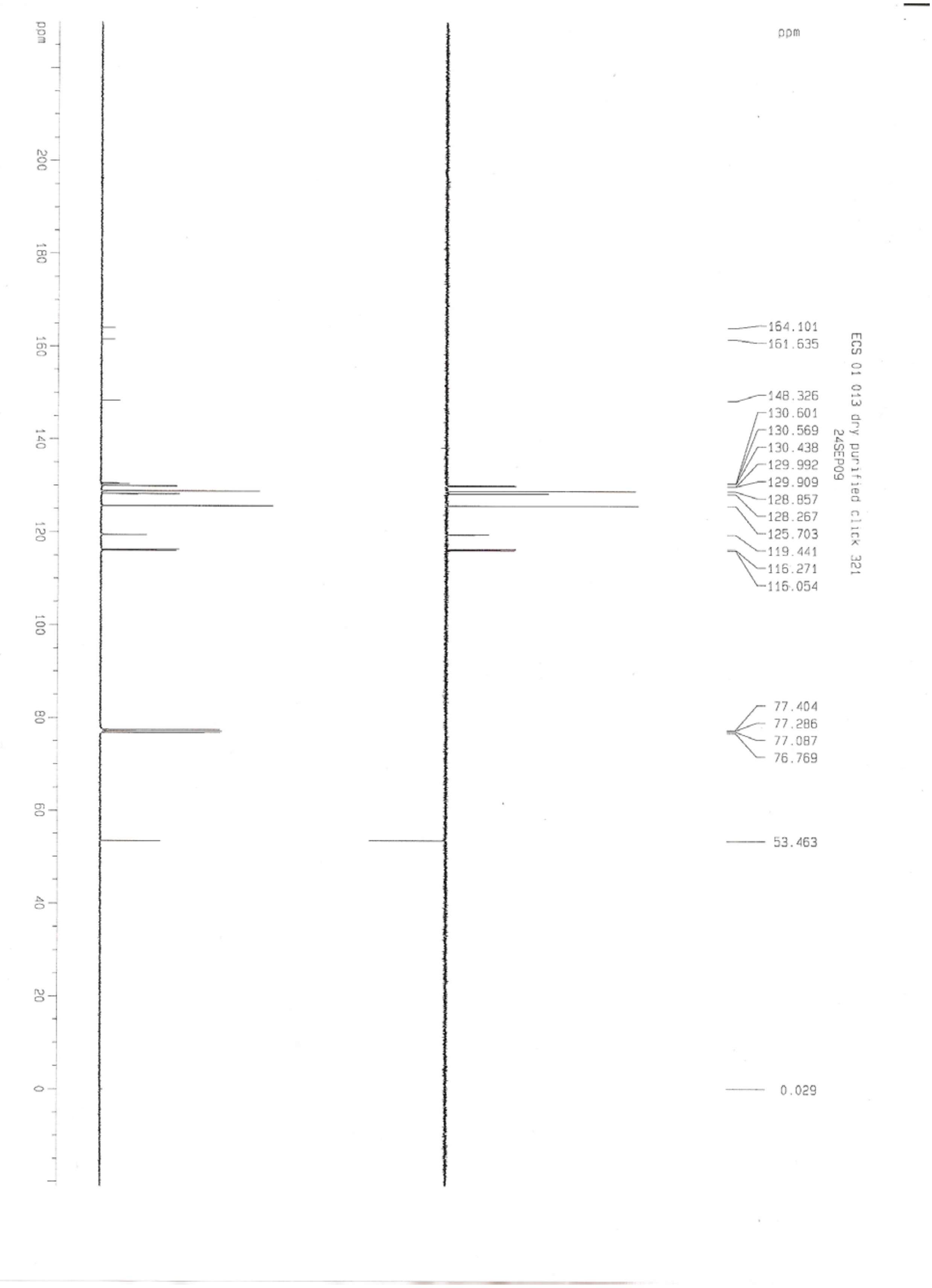
```
Current Data Parameters
NAME          Sep24-2009
EXPNO                320
PROCNO                 1

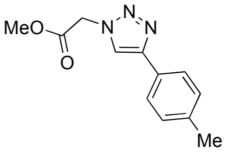
F2 - Acquisition Parameters
Date_           20090925
Time                8.35
INSTRUM           dpx400
PROBHD   5 mm Dual 13C/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6868.132 Hz
FIDRES          0.104799 Hz
AQ             4.7710710 sec
RG                 161.3
DW                72.800 usec
DE                  6.00 usec
TE                 292.2 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

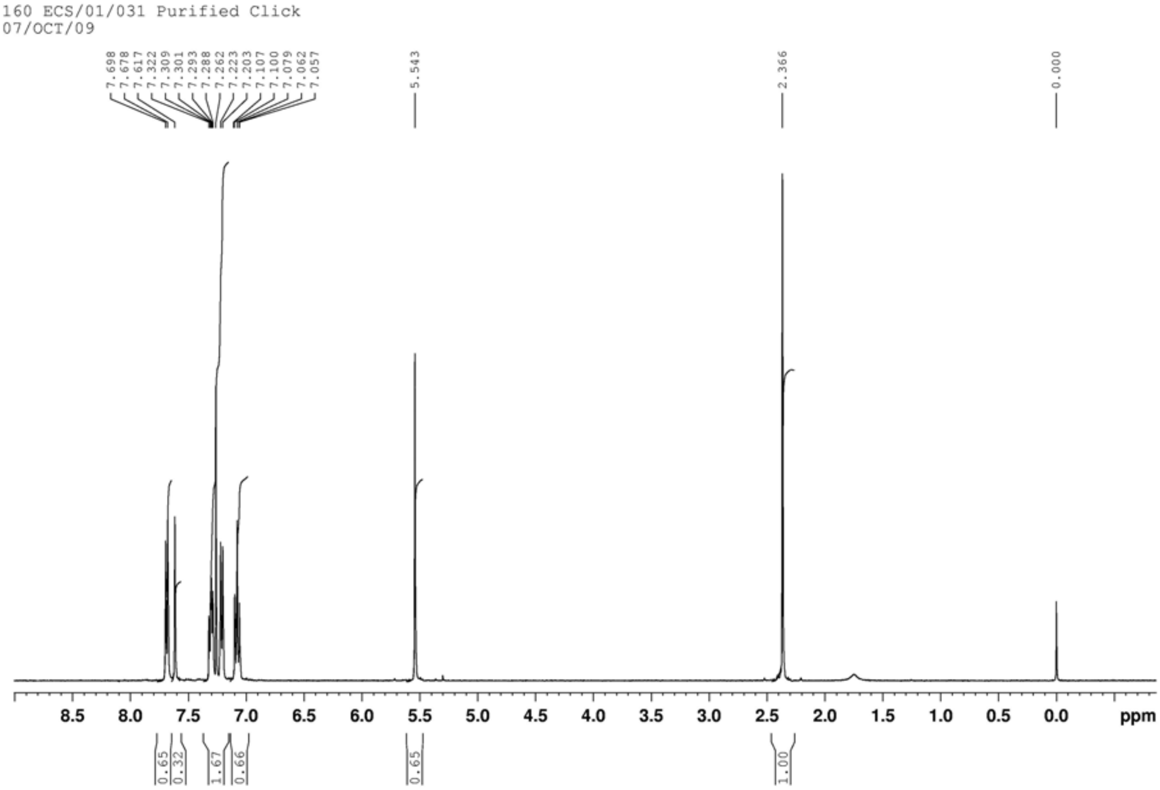
======== CHANNEL f1 ========
NUC1                  1H
P1                 11.75 usec
PL1                -6.00 dB
SF01         400.1330508 MHz

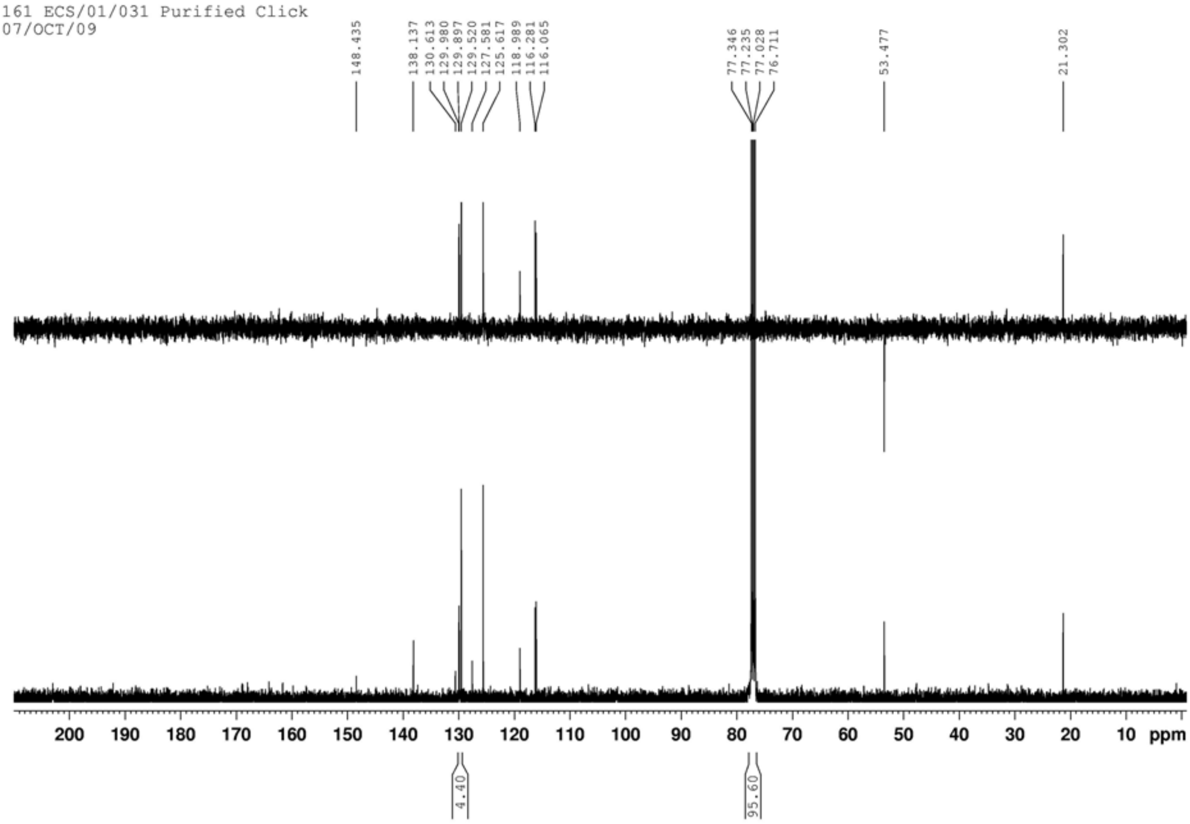
F2 - Processing parameters
SI                131072
SF           400.1300096 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 12.50 cm
F1P               16.140 ppm
F1               6458.25 Hz
F2P               -1.024 ppm
F2               -409.88 Hz
PPMCM            0.85824 ppm/cm
HZCM           343.40656 Hz/cm
```


ECS 01 013 dry purified click 321
24SEP09
ppm
200
180
160
140
120
100
80
60
40
20
0
164.101
161.635
148.326
130.601
130.569
130.438
129.992
129.909
128.857
128.267
125.703
119.441
116.271
116.054
77.404
77.286
77.087
76.769
53.463
0.029


MeO
O
N
N
N
Me


160 ECS/01/031 Purified Click
07/OCT/09
7.698
7.678
7.617
7.322
7.309
7.301
7.293
7.288
7.262
7.223
7.203
7.107
7.100
7.079
7.062
7.057
5.543
2.366
0.000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.65
0.32
1.67
0.66
0.65
1.00


161 ECS/01/031 Purified Click
07/OCT/09
148.435
138.137
130.613
129.980
129.897
129.520
127.581
125.617
118.989
116.281
116.065
77.346
77.235
77.028
76.711
53.477
21.302
200
190
180
170
160
150
140
130
120
110
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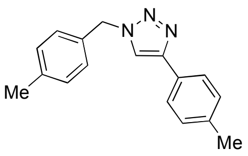
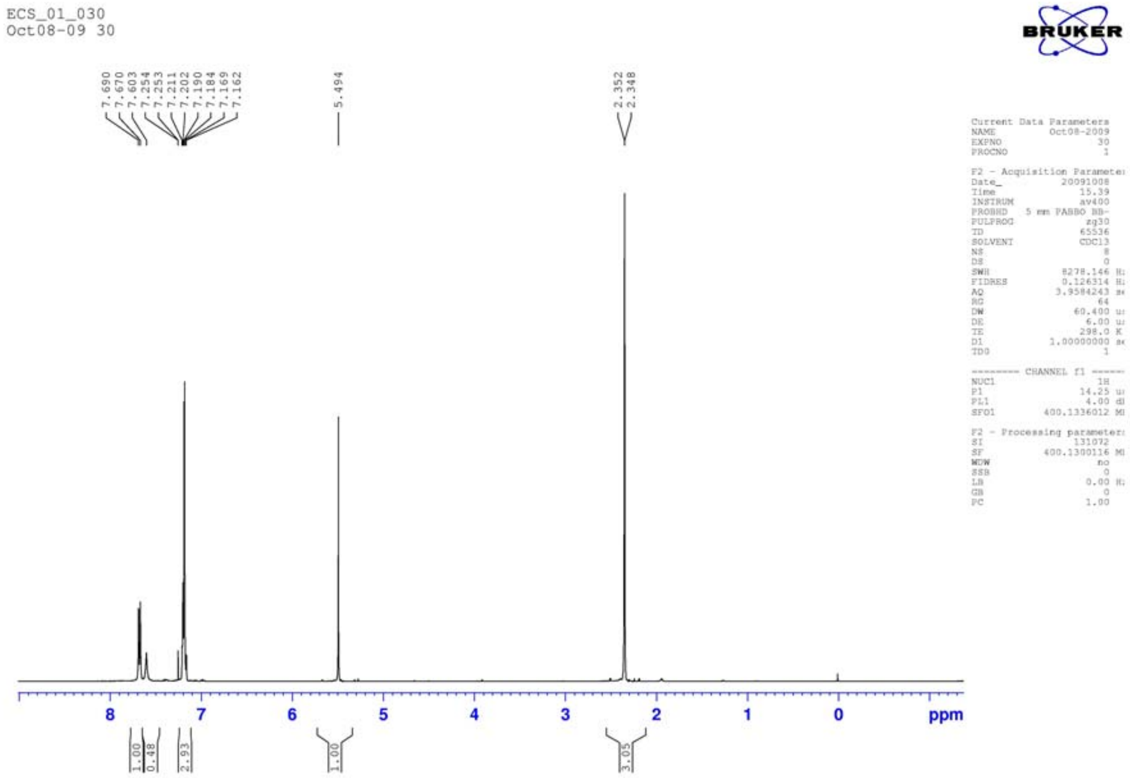
20
10
ppm
4.40
95.60





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Current Data Parameters
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EXPNO                     30
PROCNO                     1

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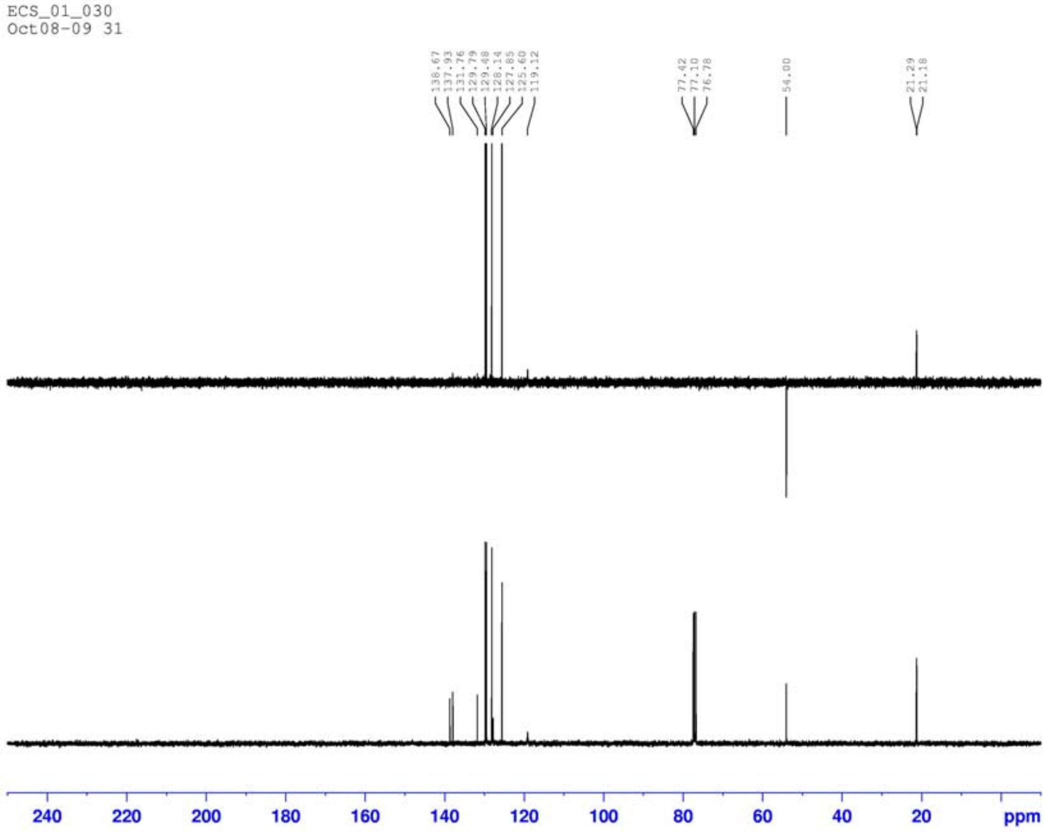
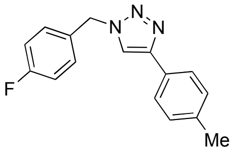
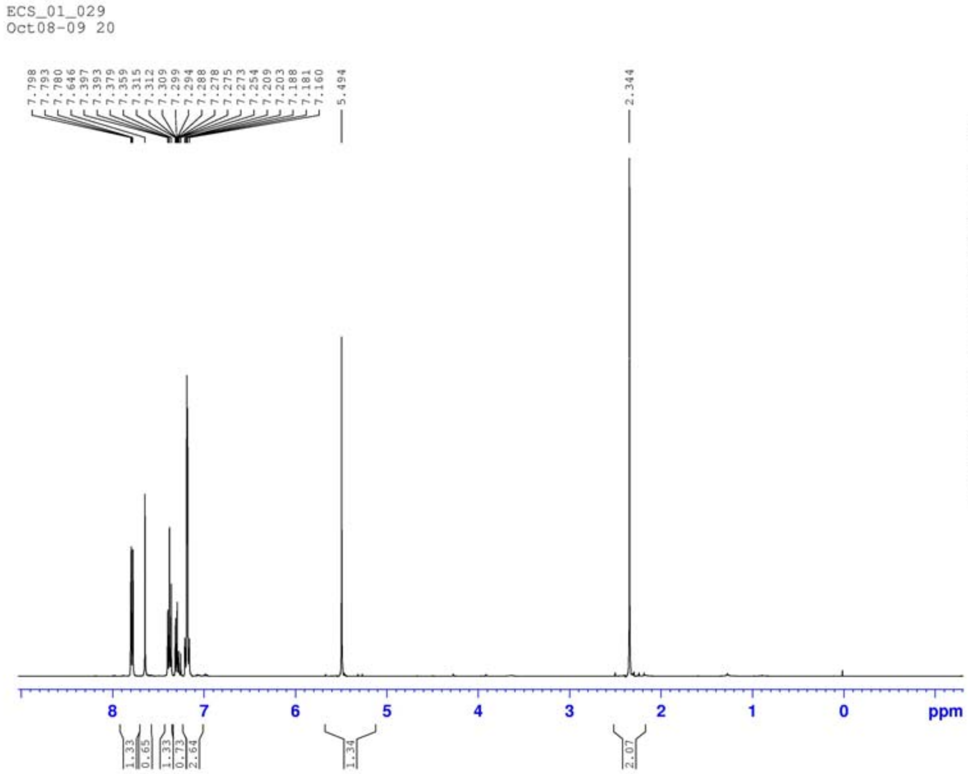
Date_               20091008
Time                   15.39
INSTRUM                av400
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                         8
DS                         0
SWH                 8278.146 H
FIDRES              0.126314 H
AQ                 3.9584243 s
RG                        64
DW                    60.400 u
DE                      6.00 u
TE                     298.0 K
D1                1.00000000 s
TD0                        1

======== CHANNEL f1 =====
NUC1                      1H
P1                     14.25 u
PL1                     4.00 d
SFO1             400.1336012 M

F2 - Processing parameter
SI                    131072
SF               400.1300116 M
WDW                       no
SSB                        0
LB                      0.00 H
GB                         0
PC                      1.00
```







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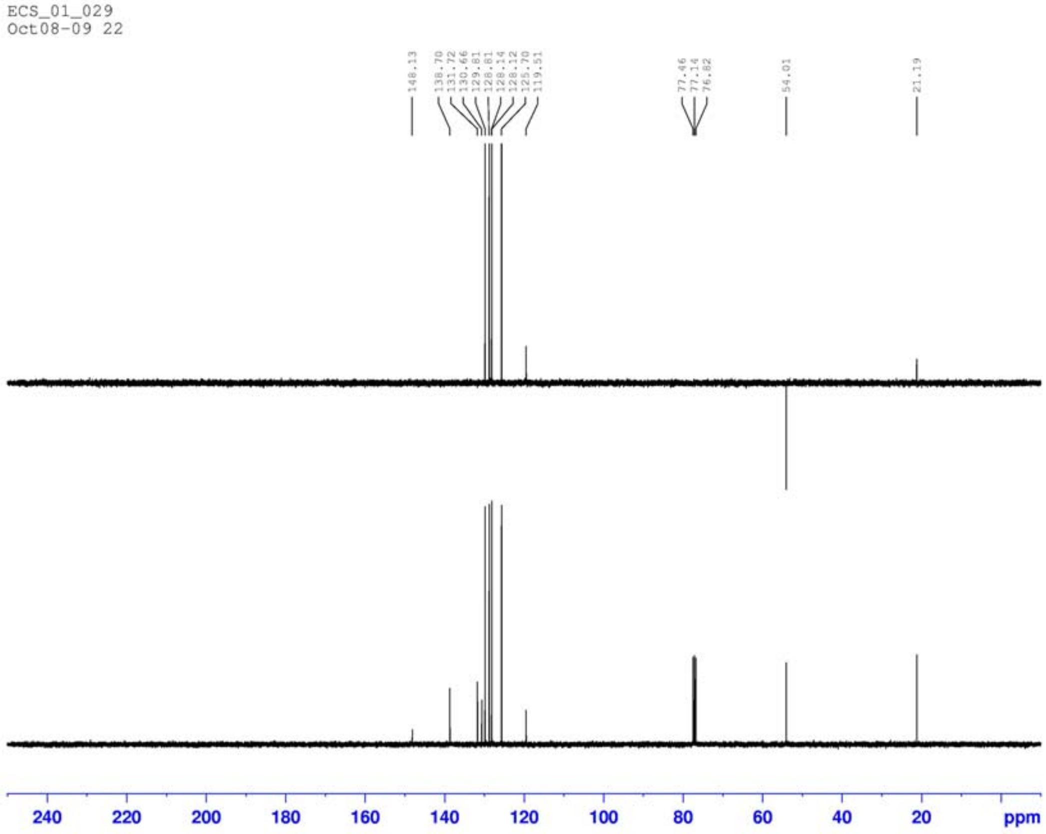
Current Data Parameters
NAME             Oct08-2009
EXPNO                    20
PROCNO                    1

F2 - Acquisition Paramete
Date_              20091008
Time                  15.27
INSTRUM               av400
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8278.146 H
FIDRES             0.126314 H
AQ                3.9584243 s
RG                       64
DW                   60.400 u
DE                     6.00 u
TE                    298.0 K
D1               1.00000000 s
TD0                       1

======== CHANNEL f1 =====
NUC1                     1H
P1                    14.25 u
PL1                    4.00 d
SFO1            400.1336012 M

F2 - Processing parameter
SI                   131072
SF              400.1300116 M
WDW                      no
SSB                       0
LB                     0.00 H
GB                        0
PC                     1.00
```



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