Cleavage of Oxygen-Sulfur Double Bond and Carbon-Sulfur Bond: Unnatural Highly Selective Electrophilic Addition of Allenylic Sulfoxides

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Supporting Information

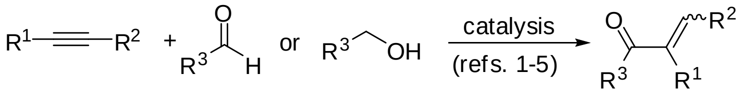
Table of Conents

General Information:

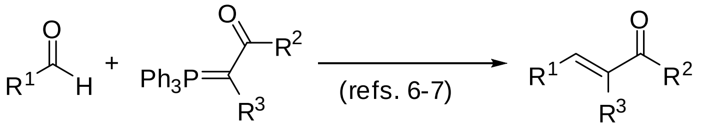
Anhydrous $CHCl_3$ was dried over P_2O_5 under reflux for 5 hours and distilled before use. Commercial anhydrous EtOH was used. Et_3N was dried over KOH and distilled freshly before use. CH_2Cl_2 was dried over CaH_2 under reflux for 3 hours and distilled before use. THF was dried over sodium wire with benzophenone as indicator and distilled freshly before use. The petroleum ether (30-60 ^{o}C) for chromatography was distilled before use. Other reagents were used without further treatment.

The known methods for the synthesis of enones or enals:

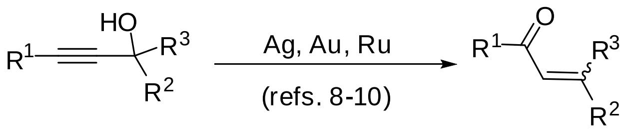
Transition metal-catalyzed hydroacylation of alkynes with aldehydes or alcohols usually affords *E/Z* mixtures of *α,β*-enones together with an issue of regioselectivity referring to the alkynes.[1-4] When Lewis acids were used in such transformations, *E/Z* >99/1 can be achieved only when the group of R^1 is larger than the R^2.[5] In addition, these methodologies are limited to incorporate substituents into the β position of the enones or enals. The Witting reaction between ylides and aldehydes afforded *Z/E* mixtures.[6-7] When R^2 = quinolyl and R^3 = H, the reaction could afford the enals with the ratio of *E/Z* up to 99/1.[6] Isomerization of propargylic alcohols catalyzed by Ag, Au, and Ru complexes could also afford enones.[8-10] However, poor *E/Z* ratio were observed and these methodologies cannot incorporate substituents into the α positions. The aldol addition between ketones and aldehydes is an efficient approach to *α,β*-unsaturated ketones, however, this methodology cannot be used widely because of the regioselectivity arise from the unsymmetric ketones.[11]



Catalyst	R^1	R^2	R^3	*E*/*Z*	Regioselectivity	ref.
Ni (0)-PR_3	aryl, alkyl	aryl, alkyl	aryl, alkyl	44/56 ~ 95/5	>40/60	1
Rh	alkyl	alkyl	2-hydroxyphenyl	only *E* isomer	--	2a
	aryl, alkyl	H	aryl, alkyl	--	only branched enones	2a-b
Ru	CH_3	CH_3	aryl, alkyl	>95/5	--	3
	CH_2CH_2OBn	CH_3	*p*-BrPh	>95/5	5/1	3
Ir	aryl, alkyl	CH_3	aryl, alkyl	16/84 ~ 86/14	--	4
	Ph	CH_3	CH_3	98/2	--	4
	CH_3	CH_3	Ph	9/91	--	4
Lewis acid	aryl	H, alkyl	aryl, alkyl	>15/1 ~ 99/1	--	5



R^1 = aryl, R^3 = H, *E*/*Z* = 84/16 ~ 92/8 ref. 6
only when R^1 = quinolyl, R^3 = Ph, *E*/*Z* = 99/1;
R^1 = Ph, R^3 =CH_3, *E*/*Z* = 98/2;
R^1 = *m*-$BnOC_6H_4$, R^3 = CH_3, *E*/*Z* = 95/5.
R^1 = alkyl, R^3 = H, *E*/*Z* = 1/1 ~93/7 ref. 7a
R^1 = alkyl, R^3 = alkyl, *E*/*Z* = 1/1 ~ 95/5 refs. 7



Ag: *E*/*Z* = 46/54 ~ 79/21 ref. 8
Au: *E*/*Z* = 63/37 ~ 93/7; refs. 9
only when R^1 = C_6H_{13}-*n*, R^2 = H, R^3 = Ph, *E*/*Z* = 97/3;
R^1 = Bu-*n*, R^2 = CH_3, R^3 = Bu-*t*, *E*/*Z* = 97/3.
Ru: *E*/*Z* = 1/2 ~ 2/1 refs. 10

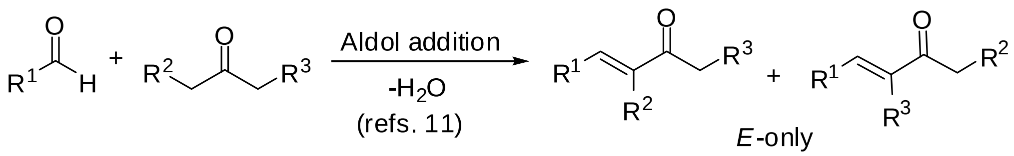
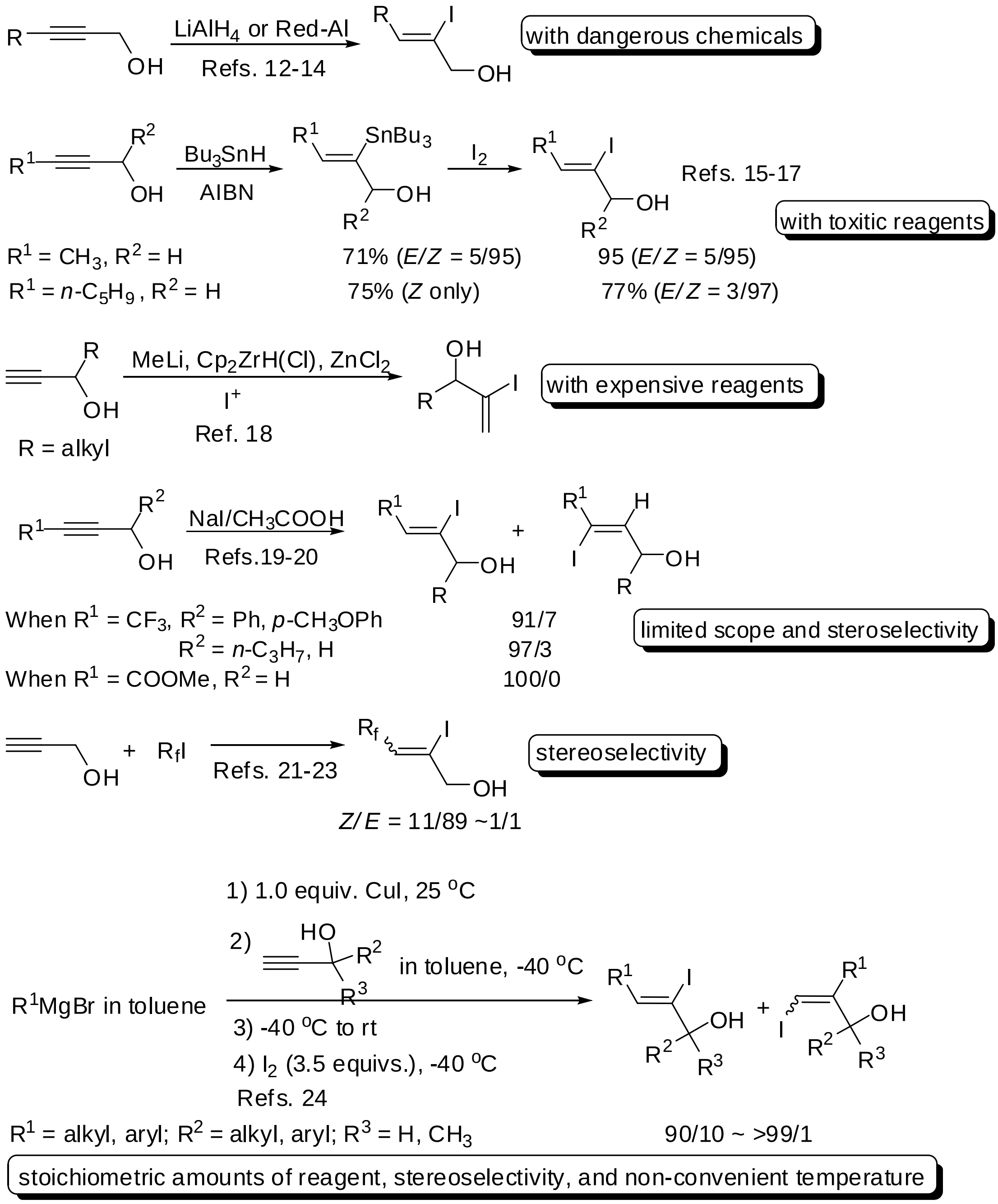
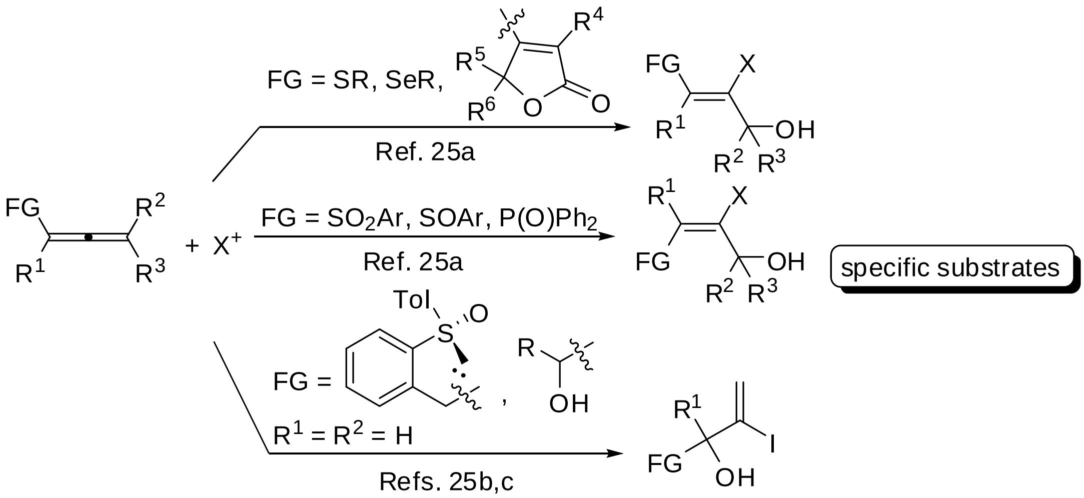


Figure 1. The known methods for the synthesis of enones or enals

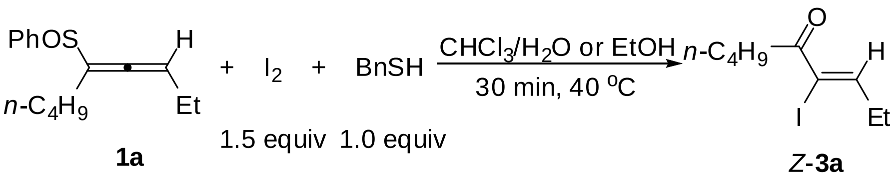
The known methods for the synthesis of *α*-iodoallylic alcohols:


LiAlH4 or Red-Al
Refs. 12-14
with dangerous chemicals
Bu3SnH
AIBN
I2
Refs. 15-17
with toxitic reagents
R1 = CH3, R2 = H
71% (E/Z = 5/95)
95 (E/Z = 5/95)
R1 = n-C5H9 , R2 = H
75% (Z only)
77% (E/Z = 3/97)
MeLi, Cp2ZrH(Cl), ZnCl2
I+
Ref. 18
R = alkyl
with expensive reagents
NaI/CH3COOH
Refs.19-20
When R1 = CF3, R2 = Ph, p-CH3OPh
91/7
R2 = n-C3H7, H
97/3
When R1 = COOMe, R2 = H
100/0
limited scope and steroselectivity
Refs. 21-23
Z/E = 11/89 ~1/1
stereoselectivity
R1MgBr in toluene
1) 1.0 equiv. CuI, 25 oC
2)
in toluene, -40 oC
3) -40 oC to rt
4) I2 (3.5 equivs.), -40 oC
Refs. 24
R1 = alkyl, aryl; R2 = alkyl, aryl; R3 = H, CH3
90/10 ~ >99/1
stoichiometric amounts of reagent, stereoselectivity, and non-convenient temperature



Supplementary Table S1-S4:

Table S1. Effect of H_2O or EtOH [a]

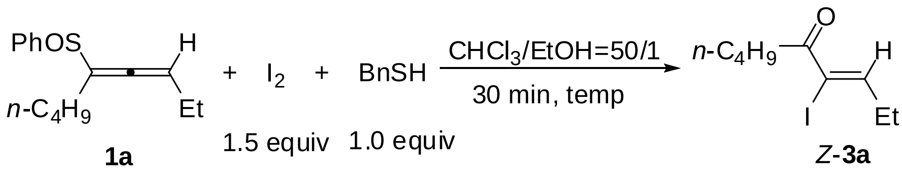


entry	H_2O or EtOH	yield of *Z*-**3a** (%) [b]
1	0	0
2	27 μL H_2O (5.0 equiv)	0
3	54 μL H_2O (10.0 equiv)	2
4	270 μL H_2O (50.0 equiv)	1
5	86 μL EtOH (5.0 equiv)	46
6	75 μL EtOH (4.4 equiv)	50
7	100 μL EtOH (5.9 equiv)	51
8	**120 μL EtOH (7.1 equiv)**	**53**
9	150 μL EtOH (8.9 equiv)	48
10	300 μL EtOH (17.7 equiv)	44
11 [c]	600 μL EtOH (35.5 equiv)	8

[a] A solution of **1a** (0.3 mmol), $CHCl_3$ (4 mL, dried under reflux over P_2O_5 for 5 hours and

distilled), and anhydrous EtOH or H_2O was treated with I_2 (0.45 mmol) for 5 min at 40 °C followed by the addition of a solution of BnSH in $CHCl_3$ (0.15 M, 2 mL, dried under reflux over P_2O_5 for 5 hours and distilled) with stirring. After being stirred for 30 min, the mixture was quenched with 6 mL of water followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$ at 40 °C. [b] The yields were determined by ^1H NMR analysis with CH_2Br_2 as the internal standard. [c] 64% of *E*-**2a** was formed.

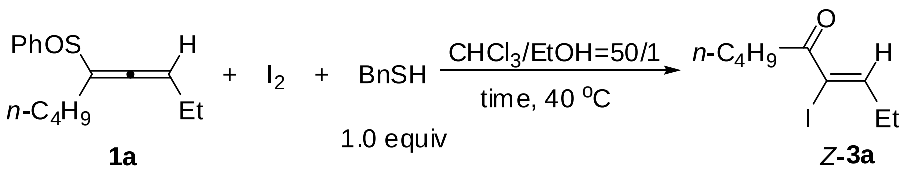
Table S2. Effect of temperature on the yield of *Z*-3a[a]



entry	temp (℃)	yield of *Z*-**3a** (%) [b]
1 [c]	10	7
2 [d]	20	47
3	30	48
5	**40**	**53**
6	50	47
7	60	45

[a] A solution of **1a** (0.3 mmol), $CHCl_3$ (4 mL, dried under reflux over P_2O_5 for 5 hours and distilled), and EtOH (30 μL) was treated with I_2 (0.45 mmol) for 5 min followed by the addition of a solution of BnSH in $CHCl_3$ (0.15 M, 2 mL, dried under reflux over P_2O_5 for 5 hours and distilled) with stirring. After being stirred for 30 min, the mixture was quenched with 6 mL of water followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$. [b] The yields were determined by ^1H NMR analysis with CH_2Br_2 as the internal standard. [c] 58% of *E*-**2a** was formed under this condition. [d] The reaction was complete in 45 min.

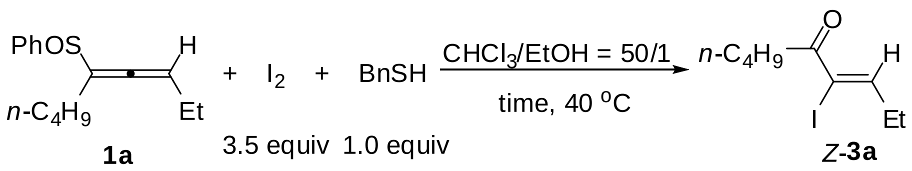
Table S3. Effect of the loading of I_2 on the reaction of nona-3,4-dien-5-ylphenyl sulfoxide 1a with I_2 in the BnSH [a]



entry	I_2 (equiv)	time (min)	yield of *Z*-**3a** (%) [b]
1	1.0	30	28
2	2.0	30	62
3	2.5	15	70
4	3.0	15	76
5	**3.5**	**15**	**81**
6	4.0	15	80
7	5.0	15	80

[a] A solution of **1a** (0.3 mmol), $CHCl_3$ (4 mL, dried under reflux over P_2O_5 for 5 hours and distilled), and anhydrous EtOH (30 μL) was treated with I_2 for 5 min at 40 °C followed by the addition of a solution of BnSH in $CHCl_3$ (0.15 M, 2 mL, dried under reflux over P_2O_5 for 5 hours and distilled) with stirring. After the reaction completed, the mixture was quenched with 6 mL of water followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$ at 40 °C. [b] The yields were determined by ^1H NMR analysis with CH_2Br_2 as the internal standard.

Table S4. Concentration effect on the reaction of nona-3,4-dien-5-ylphenyl sulfoxide 1a with I_2 in the presence of BnSH [a]



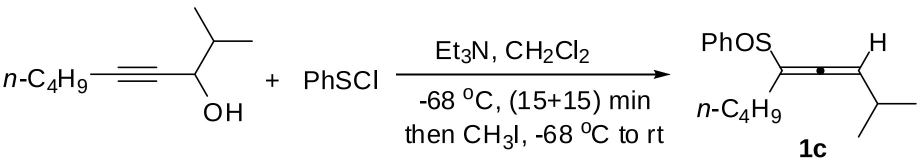
entry	c (mmol/mL)	time (min)	yield of *Z*-**3a** (%) [b]
1	0.05	15	83
2 [c]	0.05	180	0
3	0.1	15	85
4	**0.2**	**15**	**89 (82 [d])**
5 [e]	0.3	15	76

[a] A solution of **1a** (0.3 mmol), $CHCl_3$ (dried under reflux over P_2O_5 for 5 hours and distilled), and anhydrous EtOH was treated with I_2 (1.05 mmol) for 5 min at 40 °C followed by the addition of a solution of BnSH (0.3 mmol) in $CHCl_3$ (dried under reflux over P_2O_5 for 5 hours and distilled) with stirring. After the reaction completed, the mixture was quenched with 6 mL of water followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$ at 40 °C. [b] The yields were determined by ^{1}H NMR analysis with CH_2Br_2 as the internal standard. [c] The reaction was conducted in the absence of BnSH. [d] Isolated yield. [e] 0.6 mmol **1a** and 2 mL of $CHCl_3$ were used.

Preparation of Starting 1,2-Allenylic Sulfoxides 1c, 1d, and 1l

Synthesis of the starting materials: Compounds **1a-b**, **1h-o**, and **1q-r** were prepared according to the known procedures [28-30]. Compounds **1c**, **1d**, **1e**, **1f**, **1g**, and **1p** were prepared as follows:

1. 2-Methylnona-3,4-dien-5-yl phenyl sulfoxide (1c)   wmy-3-132

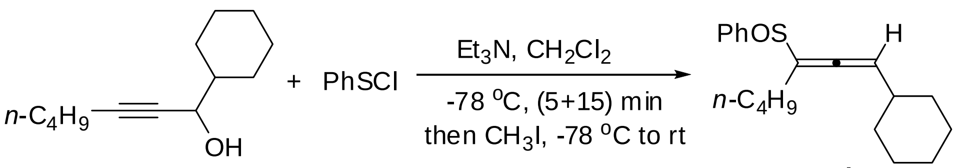


1c
51%

Typical Procedure[28]**:** To a dried three-neck round bottom flask were added 2-methylnon-4-yn-3-ol (1.5417 g, 10 mmol), CH_2Cl_2 (20 mL), and triethylamine (1.55 mL, d = 0.72 g/mL, 1.116 g, 10 mmol) sequentially. After the mixture was cooled to -68 ^oC, a solution of sulfenyl chloride (1.4531 g, 10 mmol) was added dropwise within 15 min. After being stirred at -68 ^oC for another 15 min, methyl iodide (0.3 mL, d = 2.28 g/mL, 0.684 g, 4.8 mmol) was added, then the resulting mixture was allowed to warm up naturally to room temperature followed by quenching with water (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (10 mL). The combined organic layer was dried over anhydrous Na_2SO_4. Filtration, evaporation and chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 15/1 ~ 8/1) of the crude product afforded **1c** (1.3464 g, 51%) as an oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.68-7.56 (m, 2 H, ArH), 7.55-7.40 (m, 3 H, ArH), 5.78-5.64 (m, 1 H, =CH), 2.53-2.34 (m, 1 H), 2.33-2.14 (m, 1 H), 1.94-1.76 (m, 1 H), 1.46-1.16 (m, 4 H, 2 × CH_2), 1.14-0.96 (m, 6 H, 2 × CH_3), 0.87-0.73 (m, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.2, 200.1, 143.8, 143.4, 130.5, 130.4, 128.73, 128.70, 124.5, 124.3, 114.7, 114.4, 106.4, 106.2, 29.5, 28.4, 28.3, 22.7, 22.6, 22.3, 22.22, 22.19, 21.9, 13.6; IR (neat) ν (cm^{-1}) 3058, 2960, 2930, 2871, 1951, 1578, 1465, 1443, 1379, 1364, 1293, 1083, 1049, 1022; MS (70 eV, EI) *m/z* (%) 262 (M^+, 1.30), 81 (100); Anal. Cacld. for $C_{16}H_{22}OS$: C, 73.23, H, 8.45; Found: C, 72.93, H, 8.46.

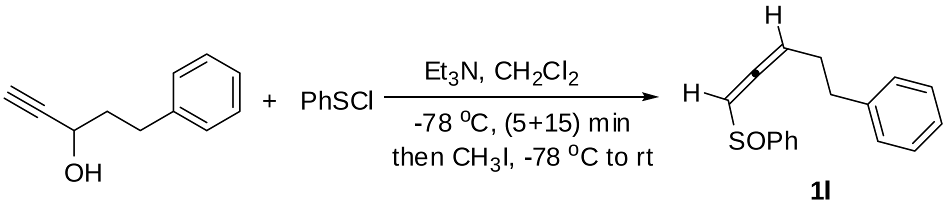
The following compounds were prepared according to this Typical Procedure.

2. 1-Cyclohexylhepta-1,2-dien-3-yl phenyl sulfoxide (1d) wmy-3-182



The reaction of 1-cyclohexylhept-2-yn-1-ol (1.9414 g, 10 mmol), triethylamine (1.50 mL, d = 0.72 g/mL, 1.08 g, 10.7 mmol), sulfenyl chloride (1.4476 g, 10 mmol), and methyl iodide (0.3 mL, d = 2.28 g/mL, 0.684 g, 4.8 mmol) in CH_2Cl_2 (20 mL) at -78 °C afforded **1d** (1.2546 g, 41%) (eluent: petroleum ether / ethyl acetate = 20/1 ~ 10/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.56 (m, 2 H, ArH), 7.56-7.40 (m, 3 H, ArH), 5.73-5.62 (m, 1 H, =CH), 2.32-1.98 (m, 2 H), 1.92-1.58 (m, 6 H), 1.45-0.98 (m, 9 H), 0.80 (t, J = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.7, 200.6, 143.9, 143.5, 130.5, 130.4, 128.8, 128.7, 124.6, 124.4, 114.3, 114.1, 104.9, 104.8, 37.5, 37.4, 32.83, 32.80, 32.7, 29.58, 29.56, 25.8, 25.7, 22.8, 22.6, 22.0, 13.6; IR (neat) ν (cm^{-1}) 3057, 2956, 2926, 2852, 1950, 1584, 1475, 1444, 1082, 1049, 1022; MS (70 eV, EI) *m/z* (%) 303 (M^++1, 8.98), 302 (M^+, 3.07), 81 (100); Anal. Cacld. for $C_{19}H_{26}OS$: C, 75.45, H, 8.66; Found: C, 75.45, H, 8.73.

3. 5-Phenylpenta-1,2-dienyl phenyl sulfoxide (1l)

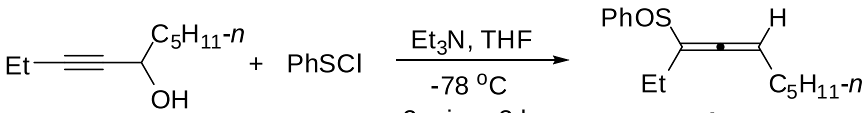


1l
58%

The reaction of 5-phenylpent-1-yn-3-ol (1.6165 g, 10.1 mmol), triethylamine (1.50 mL, d = 0.72 g/mL, 1.08 g, 10.7 mmol), sulfenyl chloride (1.4631 g, 10.1 mmol), and methyl iodide (0.3 mL, d = 2.28 g/mL, 0.684 g, 4.8 mmol) in CH_2Cl_2 (20 mL) at -78 °C afforded **1l** (1.5727 g, 58%) (eluent: petroleum ether / ethyl acetate = 20/1 ~ 10/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.58 (m, 1 H, ArH), 7.58-7.51 (m, 1 H, ArH), 7.51-7.36 (m, 3 H, ArH), 7.34-7.21 (m, 2 H, ArH), 7.21-7.04 (m, 3 H, ArH), 6.08-5.90 (m, 1 H, =CH), 5.77-5.62 (m, 1 H, =CH), 2.79-2.56 (m, 2 H, CH_2), 2.50-2.24 (m, 2 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.6, 203.4, 144.6, 144.5, 140.42, 140.38, 130.8, 129.0, 128.3, 128.2, 126.1, 126.0, 124.0, 123.9, 102.9, 98.4, 98.3, 34.6, 29.7, 29.5; IR (neat) ν (cm^{-1}) 3060, 3026, 2923, 2856, 1748, 1603, 1581, 1496, 1475, 1454, 1443, 1304, 1083, 1046; MS (70 eV, EI) *m/z* (%) 268 (M^+, 1.01), 91 (100); Anal. Calcd. for $C_{17}H_{16}OS$: C, 76.08, H, 6.01; Found: C, 75.76, H, 6.05.

Preparation of Starting 1,2-Allenylic Sulfoxides 1e, 1f, and 1g

1. Deca-3,4-dien-3-yl phenyl sulfoxide (1e)   wmy-4-153

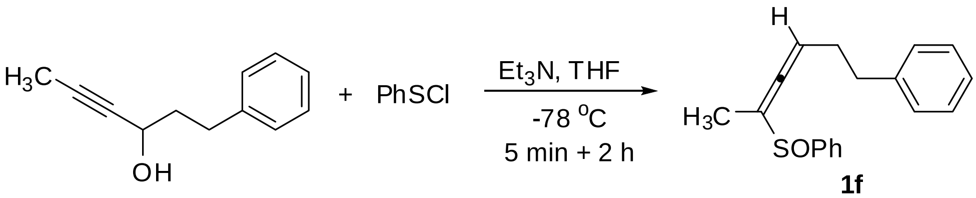


1e
73%

Typical Procedure[31]: To a dried three-neck round bottom flask were added dec-3-yn-5-ol (0.8412 g, 5.0 mmol), THF (10 mL), and triethylamine (1.0 mL, d = 0.72 g/mL, 0.72 g, 7.1 mmol) sequentially. After the mixture was cooled to -78 ^{o}C, a solution of sulfenyl chloride (1.0117 g, 7.0 mmol) was added dropwise in 2 min. After being stirred at -78 ^{o}C for 3 hours, water (10 mL) was added to quench the reaction. Then the mixture was extracted with Et_2O (20 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation and chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 20/1) of the crude product afforded **1e** (0.9534 g, 73%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66-7.26 (m, 5 H, ArH), 5.81-5.66 (m, 1 H, =CH), 2.36-2.05 (m, 3 H), 1.91-1.73 (m, 1 H), 1.55-1.23 (m, 6 H), 1.03-0.82 (m, 6 H, 2 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.51, 201.48, 143.9, 143.6, 130.6, 130.5, 128.89, 128.85, 124.5, 124.4, 115.0, 114.9, 99.8, 99.6, 31.25, 31.20, 28.70, 28.67, 22.42, 22.39, 16.42, 16.37, 14.01, 13.98, 12.0; IR (neat) ν (cm^{-1}) 3056, 2959, 2930, 2857, 1953, 1578, 1474, 1458, 1443, 1378, 1299, 1085, 1048; MS (70 eV, EI) *m/z* (%) 263 (M^++1, 3.66), 262 (M^+, 17.37), 191 (100); Anal. Cacld. for $C_{16}H_{22}OS$: C, 73.23, H, 8.45; Found: C, 72.90, H, 8.52.

The following compounds were prepared according to this Typical Procedure.

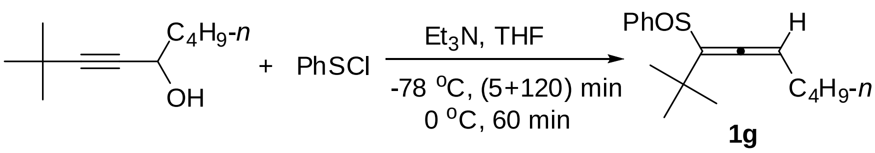
2. 6-Phenylhexa-2,3-dien-2-yl phenyl sulfoxide (1f) wmy-4-154



1f
49%

The reaction of 1-phenylhex-4-yn-3-ol (0.8707 g, 5.0 mmol), triethylamine (1.0 mL, d = 0.72 g/mL, 0.72 g, 7.1 mmol), and sulfenyl chloride (1.0214 g, 7.1 mmol) in THF (10 mL) at -78 °C afforded **1f** (0.6898 g, 49%) (eluent: petroleum ether / ethyl acetate = 20/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-7.55 (m, 1 H, ArH), 7.55-7.24 (m, 6 H, ArH), 7.24-7.12 (m, 3 H, ArH), 5.76-5.56 (m, 1 H, =CH), 2.86-2.65 (m, 2 H, CH_2), 2.57-2.35 (m, 2 H, CH_2), 1.70-1.57 (m, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.12, 202.09, 143.6, 143.4, 140.8, 140.7, 130.72, 130.70, 129.0, 128.54, 128.47, 126.25, 126.16, 124.44, 124.38, 108.8, 108.6, 97.0, 96.7, 35.1, 35.0, 30.4, 30.0, 9.4; IR (neat) ν (cm^{-1}) 3060, 3026, 2920, 2856, 1956, 1603, 1580, 1496, 1474, 1453, 1443, 1389, 1090, 1048, 1011; MS (70 eV, EI) *m/z* (%) 283 (M^++1, 3.58), 282 (M^+, 16.45), 177 (100); Anal. Calcd. for $C_{18}H_{18}OS$: C, 76.56, H, 6.42; Found: C, 76.77, H, 6.34.

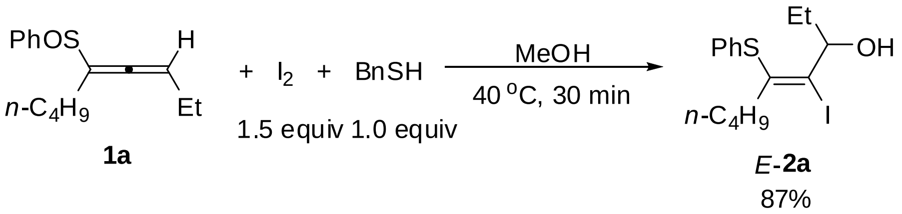
3. 2,2-Dimethylnona-3,4-dien-3-yl phenyl sulfoxide (1g) wmy-4-97



1g
63%

The reaction of 2,2-dimethylnon-3-yn-5-ol (1.6809 g, 10 mmol), triethylamine (1.70 mL, d = 0.72 g/mL, 1.224 g, 12.1 mmol), and sulfenyl chloride (1.7347 g, 12 mmol) in THF (20 mL) at -78 °C afforded **1g** (1.7428 g, 63%) (eluent: petroleum ether / ethyl acetate = 20/1 ~ 10/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.53 (m, 2 H, ArH), 7.53-7.38 (m, 3 H, ArH), [5.51 (t, *J* = 6.9 Hz, 0.58 H, =CH), 5.22 (t, *J* = 7.2 Hz, 0.45 H, =CH)], 1.96 (q, *J* = 6.8 Hz, one proton in CH_2), 1.60 (q, *J* = 6.8 Hz, one proton in CH_2), 1.36-1.22 (m, 11 H, 3 × CH_3 + CH_2), 1.22-1.10 (m, 1 H, one proton in CH_2), 1.04-0.91 (m, 1 H, one proton in CH_2), [0.87 (t, *J* = 7.1 Hz, 1.69 H, CH_3), 0.79 (t, *J* = 7.2 Hz, 1.75 H, CH_3)]; ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.3, 199.6, 144.6, 144.5, 130.34, 130.27, 128.5, 126.5, 125.5, 125.0, 124.7, 100.1, 99.9, 35.3, 35.1, 31.0, 30.5, 30.1, 29.9, 28.1, 27.6, 22.1, 22.0, 13.7, 13.6; IR (neat) ν (cm^{-1}) 3059, 2962, 2930, 2870, 1948, 1578, 1475, 1462, 1444, 1391, 1363, 1236, 1085, 1048; MS (70 eV, EI) *m/z* (%) 277 (M^++1, 1.79), 276 (M^+, 9.70), 163 (100); Anal. Cacld. for $C_{17}H_{24}OS$: C, 73.86, H, 8.75; Found: C, 73.86, H, 8.89.

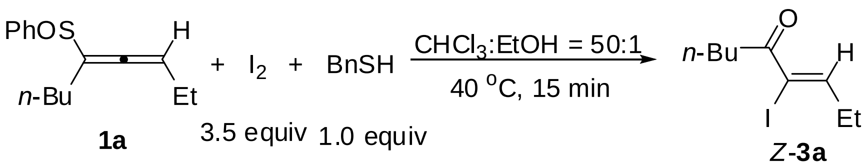
The Reaction of 1,2-Allenylic Sulfoxide 1a Affording *E*-4-Iodo-5-phenylthio-4-nonen-3-ol (*E*-2a) wmy-4-40



A solution of **1a** (74.9 mg, 0.3 mmol) in MeOH (4 mL) was treated with I_2 (115.2 mg, 0.45 mmol) for 5 min at 40 °C followed by the addition of a solution of BnSH (37.6 mg, 0.3 mmol) in MeOH (2 mL) with stirring. After being stirred at for 30 min, the mixture was quenched with 6 mL of water followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$ at 40 °C. The mixture was extracted with ether (20 mL × 3) and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1) afforded *E*-**2a** (99.1 mg, 87%): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.20 (m, 5 H, ArH), 4.55 (q, *J* = 6.9 Hz, 1 H, CH), 2.58-2.44 (m, 1 H, one protone in CH_2), 2.36-2.23 (m, 1 H, one protone in CH_2), 2.01 (d, *J* = 6.9 Hz, 1 H, OH), 1.76-1.42 (m, 4 H, 2 × CH_2), 1.34-1.19 (m, 2 H, CH_2), 0.93-0.81 (m, 6 H, 2 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.7, 134.3, 130.4, 129.0, 127.1, 120.1, 74.2, 41.4, 31.0, 29.9, 22.2, 13.8, 9.5; IR (neat) ν (cm^{-1}) 3399, 3072, 3058, 2959, 2929, 2872, 2858, 1582, 1477, 1460, 1439, 1379, 1327, 1099, 1058, 1023; MS (70 eV, EI) *m/z* (%) 376 (M^+, 11.09), 139 (100); HRMS (EI) Cacld for $C_{15}H_{21}OSI$ (M^+): 376.0358; Found: 376.0361.

Preparation of *Z*-1-Iodo-1-alkenyl Ketones *Z*-3a-*Z*-3f

1. (*Z*)-4-Iodonon-3-en-5-one (*Z*-3a) wmy-3-83

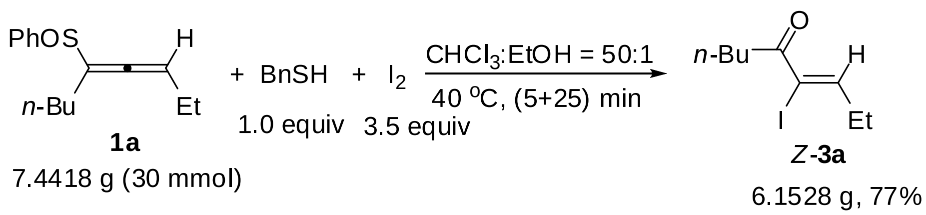


1a

Z-**3a**
82%

A solution of **1a** (74.8 mg, 0.3 mmol), $CHCl_3$ (1 mL), and EtOH (30 μL) was treated with I_2 (267.2 mg, 1.05 mmol) for 5 min at 40 °C followed by the addition of a solution of BnSH in $CHCl_3$ (0.6 M, 0.5 mL) with stirring. After being stirred for 15 min at 40 °C, the mixture was quenched with 6 mL of water followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$. The mixture was extracted with Et_2O (20 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether ~ petroleum ether/ether = 300/1) afforded *Z*-**3a** (66.1 mg, 82%): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (t, J = 6.9 Hz, 1 H, =CH), 2.83 (t, J = 7.4 Hz, 2 H, $COCH_2$), 2.49-2.37 (m, 2 H, CH_2), 1.69-1.56 (m, 2 H, CH_2), 1.44-1.23 (m, 2 H, CH_2), 1.14 (t, J = 7.5 Hz, 3 H, CH_3), 0.92 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.9, 152.9, 111.9, 37.4, 31.4, 27.0, 22.2, 13.8, 11.9; IR (neat) ν (cm^{-1}) 2960, 2929, 2872, 1682, 1604, 1461, 1379, 1290, 1248, 1170, 1121, 1085; MS (70 eV, EI) *m/z* (%) 266 (M^+, 1.19), 237 (100); HRMS (EI) Cacld for $C_9H_{15}OI$ (M^+): 266.0168; Found: 266.0167.

A large scale reaction:

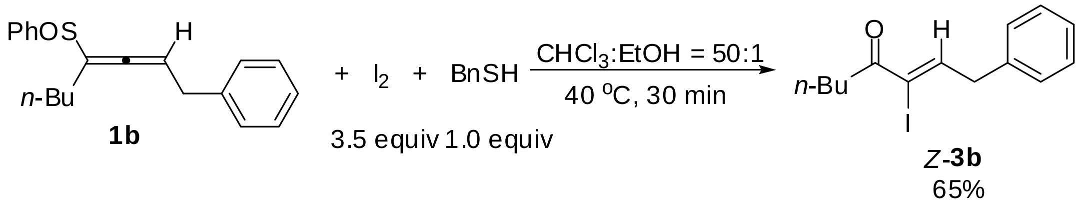


A solution of **1a** (7.4418 g, 30 mmol), $CHCl_3$ (100 mL), and EtOH (3 mL) was treated with I_2 (26.6772 g, 105 mmol) for 5 min at 40 °C, then a solution of BnSH (3.5 mL, d = 1.06 g/mL, 3.71 g, 30 mmol) in $CHCl_3$ (50 mL) was added within 5 min.

After being stirred for 25 min at 40 °C, the mixture was quenched with 10 mL of water followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$. The mixture was extracted with Et_2O (20 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether ~ petroleum ether/ether = 300/1) afforded *Z*-**3a** (6.1528 g, 77%).

The following compounds were prepared according to this procedure.

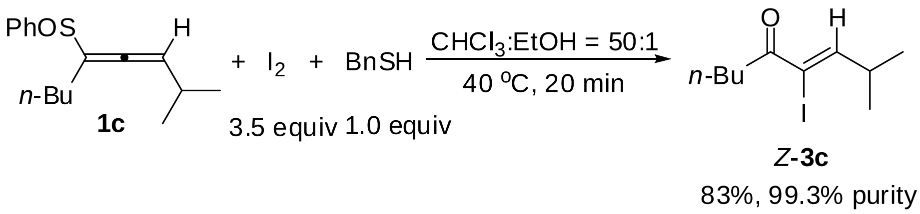
2. (*Z*)-3-Iodo-1-phenyloct-2-en-4-one (*Z*-3b) wmy-3-170



The reaction of **1b** (93.1 mg, 0.3 mmol), 30 μL of EtOH, 1 mL of $CHCl_3$, I_2 (266.6 mg, 1.05 mmol), and BnSH in $CHCl_3$ (0.6 M, 0.5 mL) at 40 °C with stirring for 30 min afforded *Z*-**3b** (63.8 mg, 65%) (eluent: petroleum ether ~ petroleum ether/ether = 300/1 ~ petroleum ether/ether = 100/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.21 (m, 5 H, ArH), 7.11 (t, J = 6.9 Hz, 1 H, =CH), 3.77 (d, J = 6.6 Hz, 2 H, CH_2Ar), 2.80 (t, J = 7.5 Hz, 2 H, $COCH_2$), 1.68-1.55 (m, 2 H, CH_2), 1.42-1.23 (m, 2 H, CH_2), 0.90 (t, J = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.9, 149.7, 137.1, 128.8, 128.6, 126.9, 113.1, 44.2, 37.5, 26.9, 22.2, 13.8; IR (neat) ν

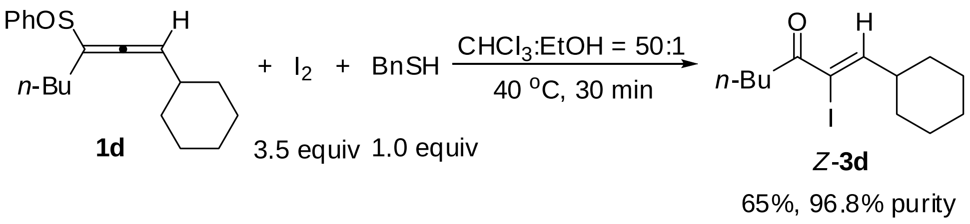
(cm^{-1}) 3063, 3027, 2957, 2926, 2867, 1682, 1598, 1495, 1453, 1251, 1145, 1100; MS (70 eV, EI) *m/z* (%) 328 (M^+, 20.68), 57 (100); HRMS (EI) Cacld for $C_{14}H_{17}OI$ (M^+): 328.0324; Found: 328.0329.

3. (*Z*)-4-Iodo-2-methylnon-3-en-5-one (*Z*-3c) wmy-4-7



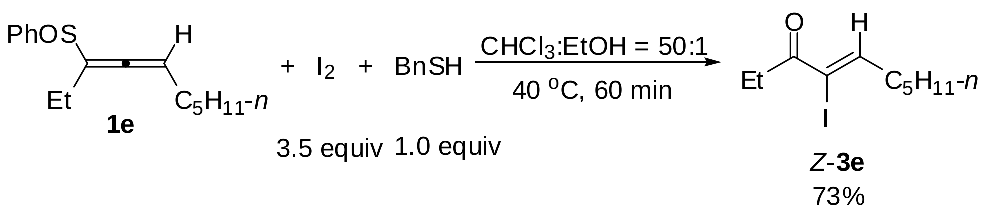
The reaction of **1c** (79.1 mg, 0.3 mmol), 30 μL of EtOH, 1 mL of $CHCl_3$, I_2 (267.4 mg, 1.05 mmol), and BnSH in $CHCl_3$ (0.6 M, 0.5 mL) at 40 °C with stirring for 20 min afforded *Z*-**3c** (70.6 mg, 83%, 99.3% purity) (eluent: petroleum ether ~ petroleum ether/ether = 300/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.74 (d, *J* = 8.4 Hz, 1 H, =CH), 2.92-2.77 (m, 3 H, $COCH_2$ + CH), 1.77-1.56 (m, 2 H, CH_2), 1.44-1.23 (m, 2 H, CH_2), 1.12 (d, *J* = 6.6 Hz, 6 H, 2 × CH_3), 0.92 (t, *J* = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.1, 157.1, 109.6, 37.5, 37.3, 27.0, 22.2, 20.7, 13.8; IR (neat) ν (cm^{-1}) 2960, 2931, 2870, 1682, 1602, 1465, 1412, 1382, 1363, 1329, 1267, 1166, 1128, 1086; MS (70 eV, EI) *m/z* (%) 280 (M^+, 0.76), 237 (100); HRMS (EI) Cacld for $C_{10}H_{17}OI$ (M^+): 280.0324; Found: 280.0317.

4. (*Z*)-1-Cyclohexyl-2-iodohept-1-en-3-one (*Z*-3d) wmy-4-9



The reaction of **1d** (90.4 mg, 0.3 mmol), 30 μL of EtOH, 1 mL of $CHCl_3$, I_2 (267.3 mg, 1.05 mmol), and BnSH in $CHCl_3$ (0.6 M, 0.5 mL) at 40 °C with stirring for 30 min afforded *Z*-**3d** (62.0 mg, 65%, 96.8% purity) (eluent: petroleum ether ~ petroleum ether/ether = 300/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.75 (d, J = 8.7 Hz, 1 H, =CH), 2.80 (t, J = 7.5 Hz, 2 H, $COCH_2$), 2.60-2.50 (m, 1 H, CH), 1.87-1.52 (m, 7 H), 1.50-1.13 (m, 7 H), 0.92 (t, J = 7.2 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.2, 155.7, 109.9, 46.7, 37.5, 30.7, 27.1, 25.7, 25.2, 22.3, 13.8; IR (neat) ν (cm^{-1}) 2959, 2927, 2852, 1682, 1601, 1448, 1315, 1278, 1259, 1224, 1169, 1129, 1088; MS (70 eV, EI) *m/z* (%) 321 (M^++1, 44.69), 320 (M^+, 6.73), 95 (100); HRMS (EI) Cacld for $C_{13}H_{21}OI$ (M^+): 320.0637; Found: 320.0631.

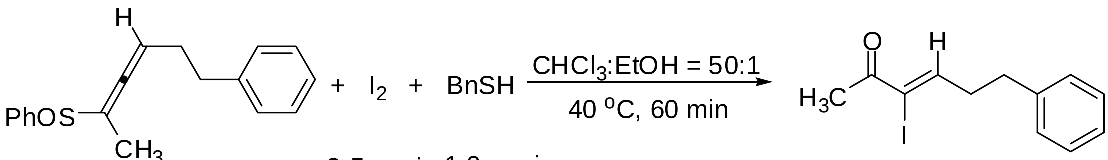
5. (*Z*)-4-Iododec-4-en-3-one (*Z*-3e) wmy-4-156



The reaction of **1e** (79.2 mg, 0.3 mmol), 30 μL of EtOH, 1 mL of $CHCl_3$, I_2 (267.7 mg, 1.05 mmol), and BnSH in $CHCl_3$ (0.6 M, 0.5 mL) at 40 °C with stirring for 60 min afforded *Z*-**3e** (61.7 mg, 73%) (eluent: petroleum ether ~ petroleum ether/ether = 300/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 (t, J = 6.8 Hz, 1 H,

=CH), 2.86 (q, J = 7.2 Hz, 2 H, $COCH_2$), 2.42 (q, J = 7.4 Hz, 2 H, CH_2), 1.64-1.44 (m, 2 H, CH_2), 1.44-1.24 (m, 4 H, 2 × CH_2), 1.16 (t, J = 7.4 Hz, 3 H, CH_3), 0.92 (t, J = 6.9 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.3, 151.9, 112.0, 37.9, 31.4, 31.1, 27.3, 22.4, 13.9, 9.0; IR (neat) ν (cm^{-1}) 2953, 2929, 2858, 1688, 1603, 1458, 1373, 1166, 1119, 1061; MS (70 eV, EI) *m/z* (%) 281 (M^++1, 3.34), 280 (M^+, 27.12), 57 (100); HRMS (EI) Cacld for $C_{10}H_{17}OI$ (M^+): 280.0324; Found: 280.0325.

6. (*Z*)-3-Iodo-6-phenylhex-3-en-2-one (*Z*-3f) wmy-4-159

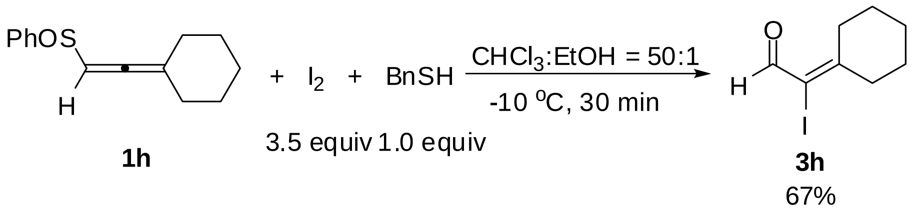


1f *Z*-**3f** 68%

The reaction of **1f** (85.2 mg, 0.3 mmol), 30 μL of EtOH, 1 mL of $CHCl_3$, I_2 (267.4 mg, 1.05 mmol), and BnSH in $CHCl_3$ (0.6 M, 0.5 mL) at 40 °C with stirring for 60 min afforded *Z*-**3f** (61.9 mg, 68%) (eluent: petroleum ether ~ petroleum ether/ether = 100/1 ~ petroleum ether/ether = 50/1): Oil; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.28 (m, 2 H, ArH), 7.27-7.19 (m, 3 H, ArH), 7.03 (t, J = 6.8 Hz, 1 H, =CH), 2.90-2.82 (m, 2 H, $COCH_2$), 2.80-2.69 (m, 2 H, CH_2), 2.46 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.4, 152.0, 140.1, 128.5, 128.2, 126.4, 113.1, 39.4, 33.5, 25.2; IR (neat) ν (cm^{-1}) 3061, 3026, 2924, 2858, 1682, 1603, 1496, 1454, 1428, 1356, 1299, 1228, 1168, 1087, 1030; MS (70 eV, EI) *m/z* (%) 301 (M^++1, 1.03), 300 (M^+, 8.51), 91 (100); HRMS (EI) Cacld for $C_{12}H_{13}OI$ (M^+): 300.0011; Found: 300.0013.

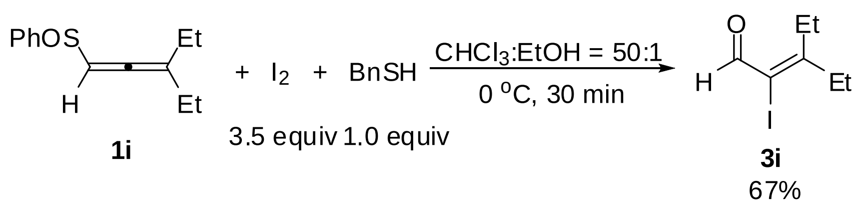
Preparation of 2-Iodo-2-enals with the Same Substituents at the 3-Position 3h-3k

1. 2-Cyclohexylidene-2-iodoacetaldehyde (3h)[32]



The reaction of **1h** (69.4 mg, 0.3 mmol), 30 μL of EtOH, 1 mL of $CHCl_3$, I_2 (267.3 mg, 1.05 mmol), and BnSH in $CHCl_3$ (0.6 M, 0.5 mL) at -10 °C with stirring for 30 min afforded **3h** (49.9 mg, 67%) (eluent: petroleum ether ~ petroleum ether/ether = 300/1 ~petroleum ether/ether = 80/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.17 (d, J = 0.9 Hz, 1 H, CHO), 2.98 (t, J = 5.1 Hz, 2 H, =CCH_2), 2.74 (t, J = 5.7 Hz, 2 H, =CCH_2), 1.68-1.59 (m, 6 H, 3 × CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.8, 171.8, 105.5, 44.5, 33.6, 28.7, 27.8, 26.1; IR (neat) ν (cm^{-1}) 2931, 2855, 1678, 1577, 1445, 1388, 1348, 1314, 1268, 1235, 1222, 1133, 1109, 1091, 1058; MS (70 eV, EI) *m/z* (%) 250 (M^+, 100).

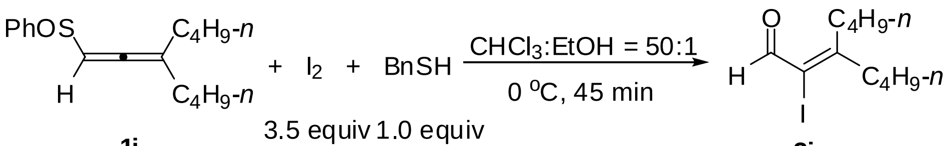
2. 3-Ethyl-2-iodopent-2-enal (3i) wmy-3-186



The reaction of **1i** (66.6 mg, 0.3 mmol), 30 μL of EtOH, 1 mL of $CHCl_3$, I_2 (267.1 mg, 1.05 mmol), and BnSH in $CHCl_3$ (0.6 M, 0.5 mL) at 0 °C with stirring for 30 min afforded **3i** (48.2 mg, 67%) (eluent: petroleum ether ~ petroleum ether/ether = 300/1

~petroleum ether/ether = 100/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.07 (s, 1 H, CHO), 2.84 (q, *J* = 7.6 Hz, 2 H, $=CCH_2$), 2.59 (q, *J* = 7.6 Hz, 2 H, $=CCH_2$), 1.21 (t, *J* = 7.7 Hz, 3 H, CH_3), 1.14 (t, *J* = 7.7 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.6, 174.8, 106.4, 37.8, 27.0, 14.6, 11.3; IR (neat) ν (cm^{-1}) 2972, 2932, 2872, 1684, 1578, 1460, 1379, 1205, 1122, 1084, 1063; MS (70 eV, EI) *m/z* (%) 238 (M^+, 100); HRMS (EI) Cacld for $C_7H_{11}OI$ (M^+): 237.9855; Found: 237.9850.

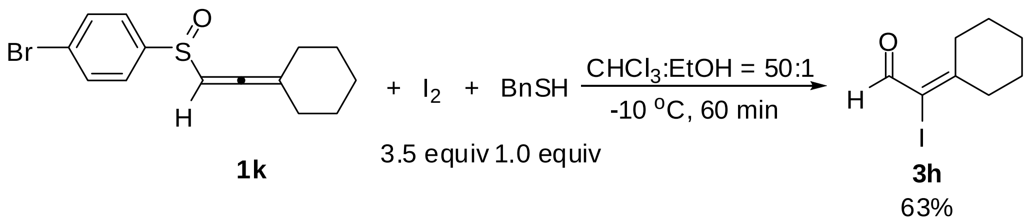
3. 3-Butyl-2-iodohept-2-enal (3j)   wmy-3-191



1j **3j** 75%

The reaction of **1j** (82.3 mg, 0.3 mmol), 30 μL of EtOH, 1 mL of $CHCl_3$, I_2 (267.4 mg, 1.05 mmol), and BnSH in $CHCl_3$ (0.6 M, 0.5 mL) at 0 °C with stirring for 45 min afforded **3j** (66.1 mg, 75%) (eluent: petroleum ether ~ petroleum ether/ether = 300/1 ~petroleum ether/ether = 200/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.05 (s, 1 H, CHO), 2.80 (t, *J* = 7.8 Hz, 2 H, $=CCH_2$), 2.55 (t, *J* = 7.7 Hz, 2 H, $=CCH_2$), 1.62-1.33 (m, 8 H, 4 × CH_2), 1.02-0.88 (m, 6 H, 2 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.6, 172.9, 107.2, 44.7, 34.1, 32.3, 29.3, 22.9, 22.5, 13.8, 13.7; IR (neat) ν (cm^{-1}) 2958, 2930, 2861, 2721, 1683, 1578, 1465, 1381, 1078; MS (70 eV, EI) *m/z* (%) 294 (M^+, 45.99), 55 (100); HRMS (EI) Cacld for $C_{11}H_{19}OI$ (M^+): 294.0481; Found: 294.0488.

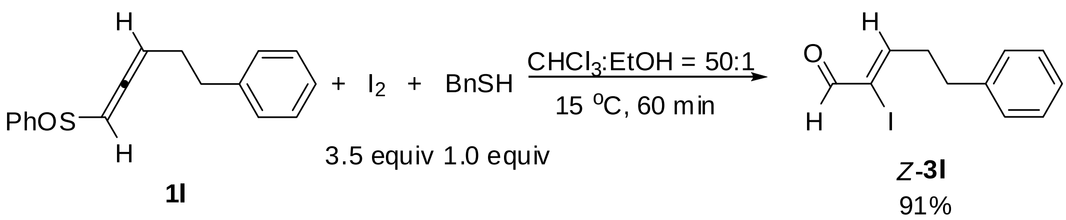
4. 2-Cyclohexylidene-2-iodoacetaldehyde (3h)   wmy-4-71



The reaction of **1k** (93.4 mg, 0.3 mmol), 30 μL of EtOH, 1 mL of $CHCl_3$, I_2 (266.8 mg, 1.05 mmol), and BnSH in $CHCl_3$ (0.6 M, 0.5 mL) at -10 °C with stirring for 60 min afforded **3h** (47.6 mg, 63%) (eluent: petroleum ether ~ petroleum ether/ether = 300/1 ~petroleum ether/ether = 80/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.10 (s, 1 H, CHO), 2.91 (t, J = 5.4 Hz, 2 H, $=CCH_2$), 2.67 (t, J = 6.0 Hz, 2 H, $=CCH_2$), 1.74-1.55 (m, 6 H, 3 × CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.8, 171.8, 105.5, 44.5, 33.6, 28.7, 27.8, 26.1.

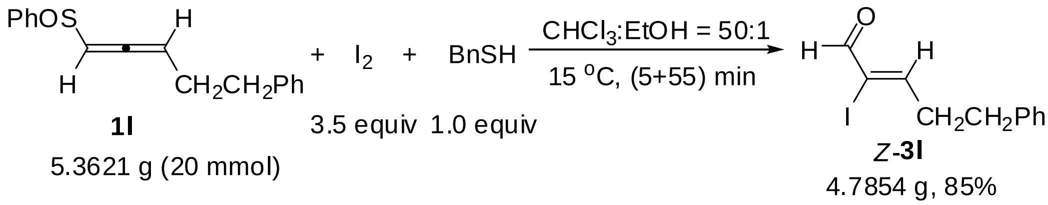
Preparation of *Z*-2-Iodo-2-enals *Z*-3l-*Z*-3o

1. (*Z*)-2-Iodo-5-phenylpent-2-enal (*Z*-3l) wmy-3-173



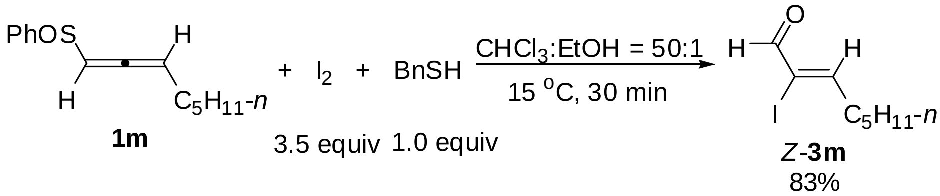
The reaction of **1l** (80.9 mg, 0.3 mmol), 30 μL of EtOH, 1 mL of $CHCl_3$, I_2 (266.3 mg, 1.05 mmol), and BnSH in $CHCl_3$ (0.6 M, 0.5 mL) at 15 °C with stirring for 60 min afforded *Z*-**3l** (78.3 mg, 91%) (eluent: petroleum ether ~ petroleum ether/ether = 300/1 ~ petroleum ether/ether = 100/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (s, 1 H, CHO), 7.38-7.10 (m, 6 H, ArH + =CH), 2.92-2.76 (m, 4 H, 2 × CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.5, 160.9, 139.6, 128.4, 128.1, 126.2, 112.2, 37.7, 33.0; IR (neat) ν (cm^{-1}) 3081, 3063, 3026, 2924, 2846, 2816, 2724, 1694, 1604, 1496, 1454, 1188, 1113, 1075; MS (70 eV, EI) *m/z* (%) 286 (M$^+$, 2.95), 91 (100); HRMS (EI) Cacld for $C_{11}H_{11}OI$ (M$^+$): 285.9855; Found: 285.9852.

A large scale reaction:



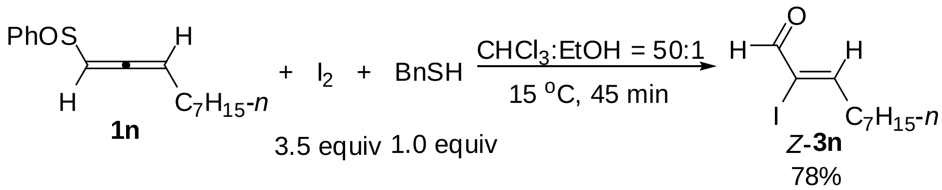
A solution of **1l** (5.3621 g, 20 mmol), $CHCl_3$ (70 mL), and EtOH (2 mL) was treated with I_2 (17.7872 g, 70 mmol) for 5 min at 15 °C. Then a solution of BnSH (2.35 mL, d = 1.06 g/mL, 2.491 g, 20 mmol) in $CHCl_3$ (30 mL) was added within 5 min. After being stirred for 55 min at 15 °C, the mixture was quenched with 20 mL of water followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$. The mixture was extracted with Et_2O (50 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether ~ petroleum ether/ether = 300/1 ~ petroleum ether/ether = 100/1) afforded *Z*-**3l** (4.7854 g, 84%).

2. (*Z*)-2-Iodooct-2-enal (*Z*-3m) wmy-3-172



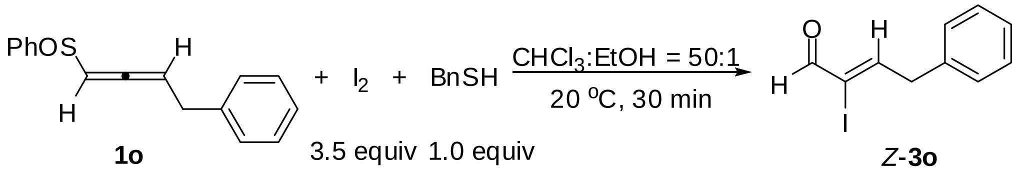
The reaction of **1m** (70.6 mg, 0.3 mmol), 30 μL of EtOH, 1 mL of $CHCl_3$, I_2 (267.7 mg, 1.05 mmol), and BnSH in $CHCl_3$ (0.6 M, 0.5 mL) at 15 °C with stirring for 30 min afforded *Z*-**3m** (63.4 mg, 83%) (eluent: petroleum ether ~ petroleum ether/ether = 300/1 ~ petroleum ether/ether = 100/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (s, 1 H, CHO), 7.21 (t, *J* = 7.1 Hz, 1 H, =CH), 2.55 (q, *J* = 7.3 Hz, 2 H, CH_2), 1.63-1.50 (m, 2 H, CH_2), 1.49-1.31 (m, 4 H, 2 × CH_2), 0.92 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.9, 162.7, 111.7, 36.5, 31.3, 27.1, 22.3, 13.8; IR (neat) ν (cm^{-1}) 2956, 2927, 2858, 2810, 2726, 1695, 1606, 1465, 1380, 1199, 1141, 1082; MS (70 eV, EI) *m/z* (%) 252 (M^+, 12.81), 41 (100); HRMS (EI) Cacld for $C_8H_{13}OI$ (M^+): 252.0011; Found: 252.0014.

3. (*Z*)-2-Iododec-2-enal (*Z*-3n)   wmy-3-176



The reaction of **1n** (78.9 mg, 0.3 mmol), 30 μL of EtOH, 1 mL of $CHCl_3$, I_2 (266.5 mg, 1.05 mmol), and BnSH in $CHCl_3$ (0.6 M, 0.5 mL) at 15 °C with stirring for 45 min afforded *Z*-**3n** (65.7 mg, 78%) (eluent: petroleum ether ~ petroleum ether/ether = 300/1 ~ petroleum ether/ether = 100/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (s, 1 H, CHO), 7.20 (t, *J* = 6.9 Hz, 1 H, =CH), 2.55 (q, *J* = 7.3 Hz, 2 H, CH_2), 1.65-1.50 (m, 2 H, CH_2), 1.46-1.17 (m, 8 H, 4 × CH_2), 0.89 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.9, 162.7, 111.7, 36.5, 31.6, 29.2, 28.9, 27.4, 22.5, 14.0; IR (neat) ν (cm^{-1}) 2926, 2856, 2806, 2726, 1698, 1605, 1465, 1379, 1185, 1140, 1086; MS (70 eV, EI) *m/z* (%) 280 (M^+, 1.76), 55 (100); HRMS (EI) Cacld for $C_{10}H_{17}OI$ (M^+): 280.0324; Found: 280.0324.

4. (*Z*)-2-Iodo-4-phenylbut-2-enal (*Z*-3o) wmy-4-50

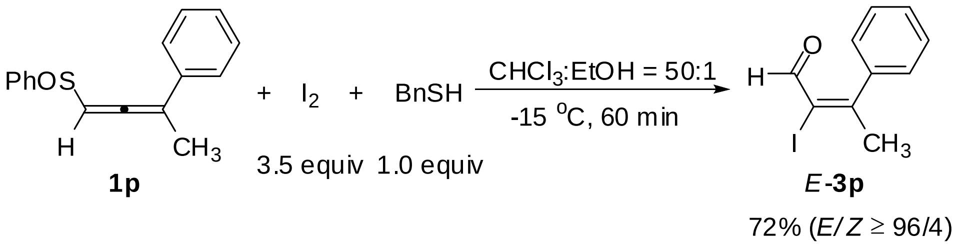


1o **Z-3o** 37%

The reaction of **1o** (76.6 mg, 0.3 mmol), 30 μL of EtOH, 1 mL of $CHCl_3$, I_2 (267.4 mg, 1.05 mmol), and BnSH in $CHCl_3$ (0.6 M, 0.5 mL) at 20 °C with stirring for 30 min afforded *Z*-**3o** (30.5 mg, 37%) (eluent: petroleum ether ~ petroleum ether/ether = 300/1 ~petroleum ether/ether = 80/1): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (s, 1 H, CHO), 7.42-7.20 (m, 6 H, ArH + =CH), 3.82 (d, *J* = 7.2 Hz, 2 H, CH_2Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.9, 160.2, 136.4, 129.0, 128.7, 127.2, 112.1, 42.7; IR (neat) ν (cm^{-1}) 3027, 2922, 2820, 1695, 1599, 1494, 1453, 1113, 1072; MS (70 eV, EI) *m/z* (%) 272 (M^+, 33.00), 115 (100); HRMS (EI) Cacld for $C_{10}H_9OI$ (M^+): 271.9698; Found: 271.9692.

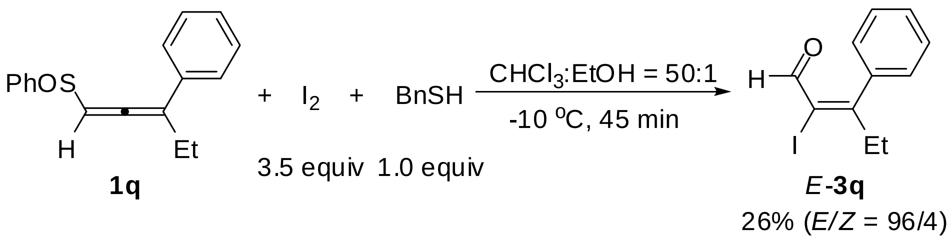
Preparation of *E*-2-iodo-3-phenyl-2-enals *E*-3p- *E*-3q

1. (*E*)-2-Iodo-3-phenylbut-2-enal (*E*-3p) wmy-4-68



The reaction of **1p** (76.7 mg, 0.3 mmol), 30 μL of EtOH, 1 mL of $CHCl_3$, I_2 (267.6 mg, 1.05 mmol), and BnSH in $CHCl_3$ (0.6 M, 0.5 mL) at -15 °C stirred for 60 min afforded the crude product (The *E/Z* ratio of the product is 96/4 as determined by ^{1}H NMR analysis with CH_2Br_2 as the internal standard.). Purification (eluent: petroleum ether ~ petroleum ether/ether = 300/1 ~petroleum ether/ether = 100/1) afforded *E*-**3p** (58.9 mg, 72%, *E/Z* ≥ 98/2, if any): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (s, 1 H, CHO), 7.48-7.39 (m, 3 H, ArH), 7.30-7.21 (m, 2 H, ArH), 2.63 (s, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.9, 167.3, 139.2, 129.3, 128.6, 128.2, 110.3, 33.6; IR (neat) ν (cm^{-1}) 3054, 3021, 2923, 2847, 2718, 1674, 1578, 1560, 1489, 1442, 1375, 1123, 1025; MS (70 eV, EI) *m/z* (%) 272 (M^+, 50.38), 115 (100); Anal. Calcd. for $C_{10}H_9OI$: C, 44.14, H, 3.33; Found: C, 44.17, H, 3.44.

2. (*E*)-2-Iodo-3-phenylpent-2-enal (*E*-3q) Wmy-4-113



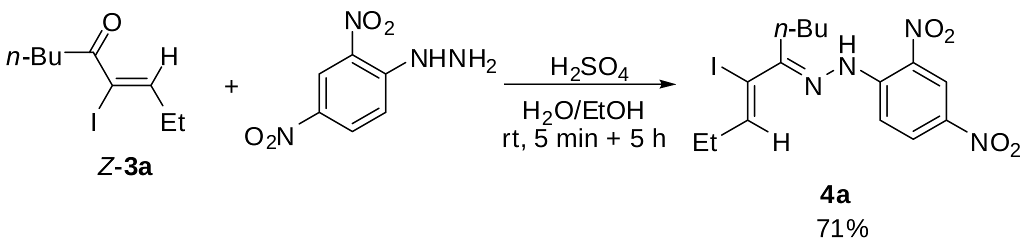
The reaction of **1q** (80.7 mg, 0.3 mmol), 30 μL of EtOH, 1 mL of $CHCl_3$, I_2 (267.5 mg, 1.05 mmol), and BnSH in $CHCl_3$ (0.6 M, 0.5 mL) at -10 °C stirred for 45 min afforded the crude product (The *E/Z* ratio of the product is 96/4 as determined by

^{1}H NMR analysis with CH_2Br_2 as the internal standard.). Purification (eluent: petroleum ether ~ petroleum ether/ether = 300/1 ~ petroleum ether/ether = 100/1) afforded only *E*-**3q** (22.8 mg, 26%): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (s, 1 H, CHO), 7.48-7.33 (m, 3 H, ArH), 7.25-7.14 (m, 2 H, ArH), 2.94 (q, *J* = 7.5 Hz, 2 H, CH_2), 1.05 (t, *J* = 7.5 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.3, 172.3, 138.1, 129.2, 128.55, 128.49, 109.4, 39.5, 11.3; IR (neat) ν (cm^{-1}) 3051, 2973, 2932, 2849, 2724, 1679, 1575, 1561, 1442, 1377, 1284, 1128, 1068; MS (70 eV, EI) *m/z* (%) 286 (M^+, 100); HRMS (EI) Cacld for $C_{11}H_{11}OI$ (M^+): 285.9855; Found: 285.9856.

The reaction of 3 with 2,4- dinitrophenylhydrazine affording 4

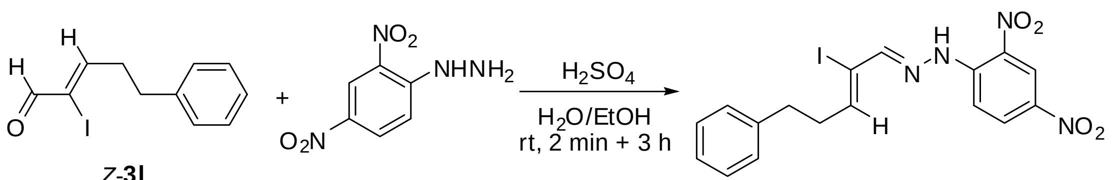
1. (*E*)-1-(2,4-Dinitrophenyl)-2-((*Z*)-4-iodonon-3-en-5-ylidene)hydrazine (4a)

wmy-4-61



To a solution of 2,4-dinitrophenylhydrazine (198.4 mg, 1.0 mmol), H_2SO_4 (1.5 mL, 98%), EtOH (15 mL), and H_2O (45 mL) was added a solution of *Z*-**3a** (291.8 mg, 1.1 mmol) in EtOH (5 mL) dropwise within 5 min. After being stirred for 5 hours at room temperature, the mixture was extracted with EtOAc (50 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1) afforded **4a** (318.4 mg, 71%) as solid: mp 113.1-114.0 °C (EtOAc/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.38 (s, 1 H, NH), 9.14 (d, *J* = 2.7 Hz, 1 H, ArH), 8.42-8.34 (dd, J_1 = 9.5 Hz , J_2 = 2.5 Hz, 1 H, ArH), 8.16 (d, *J* = 9.6 Hz, 1 H, ArH), 6.37 (t, *J* = 6.8 Hz, 1 H, =CH), 2.72 (t, *J* = 7.8 Hz, 2 H, CH_2), 2.57-2.43 (m, 2 H, CH_2), 1.67-1.44 (m, 4 H, 2 × CH_2), 1.15 (t, *J* = 7.5 Hz, 3 H, CH_3), 1.01 (t, *J* = 7.1 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 145.5, 145.0, 138.5, 130.2, 129.8, 123.3, 117.6, 106.8, 31.7, 28.0, 27.2, 22.9, 13.7, 12.6; IR (KBr) ν (cm^{-1}) 3312, 3106, 2963, 2932, 2872, 1617, 1593, 1503, 1422, 1335, 1311, 1257, 1221, 1135, 1110; MS (70 eV, EI) *m/z* (%) 446 (M^+, 12.42), 41 (100); Anal. Calcd. for $C_{15}H_{19}IN_4O_4$: C, 40.37, H, 4.29, N, 12.56; Found: C, 40.58, H, 4.29, N, 12.53.

2. (*E*)-1-(2,4-Dinitrophenyl)-2-((*Z*)-2-iodo-5-phenylpent-2-enylidene)hydrazine (4l) wmy-3-195



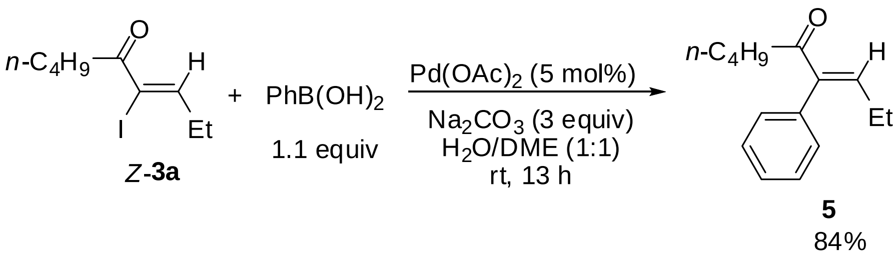
Z-**3l**

4l
81%

To a solution of 2,4-dinitrophenylhydrazine (199.1 mg, 1.0 mmol), H_2SO_4 (1.5 mL, 98%), EtOH (15 mL), and H_2O (45 mL) was added a solution of *Z*-**3l** (314.8 mg, 1.1 mmol) in EtOH (5 mL) dropwise within 3 min. After being stirred for 3 hours at room temperature, the mixture was extracted with EtOAc (50 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **4l** (379.1 mg, 81%) as solid: mp 193.9-194.2 °C (EtOAc/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.27 (s, 1 H, NH), 9.13 (d, J = 2.4 Hz, 1 H, ArH), 8.42-8.33 (dd, J_1 = 9.0 Hz, J_2 = 2.6 Hz, 1 H, ArH), 8.06 (d, J = 9.3 Hz, 1 H, ArH), 7.39 (s, 1 H, =CH), 7.37-7.28 (m, 2 H, ArH), 7.26-7.18 (m, 3 H, ArH), 6.52-6.45 (m, 1 H, =CH), 2.93-2.75 (m, 4 H, 2 × CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.0, 147.5, 144.9, 140.3, 138.6, 130.2, 129.6, 128.6, 128.4, 126.4, 123.3, 117.4, 101.8, 38.1, 34.0; IR (KBr) ν (cm^{-1}) 3414, 3303, 3090, 3022, 2930, 2858, 1616, 1585, 1515, 1504, 1421, 1332, 1314, 1139, 1091, 1077; MS (70 eV, EI) *m/z* (%) 466 (M^+, 4.17), 91 (100); Anal. Calcd. for $C_{17}H_{15}IN_4O_4$: C, 43.79, H, 3.24, N, 12.02; Found: C, 43.90, H, 3.13, N, 11.88.

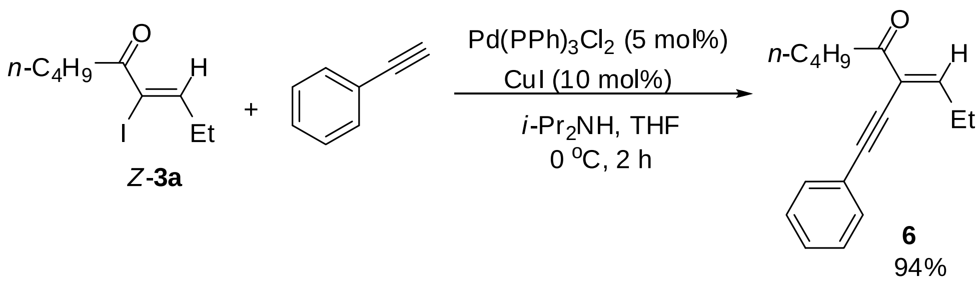
The Synthetic Application of the *Z*-3a Affording 5-6

1. (*E*)-4-Phenylnon-3-en-5-one (5)   Wmy-4-30



To a solution of *Z*-**3a** (79.9 mg, 0.3 mmol) in 1,2-dimethoxyethane (1.5 mL) were added Na_2CO_3 (95.8 mg, 0.9 mmol), H_2O (1.5 mL), phenyl boronic acid (40.4 mg, 0.33 mmol), and $Pd(OAc)_2$ (3.5 mg, 0.016 mmol) sequentially. The mixture was stirring at room temperature under nitrogen for 13 h. After the reaction complete, 10 mL of ethyl ether was added. Filtration and evaporation, then column chromatography on silia gel (eluent: petroleum ether/ethyl ether = 100:1) gave **5** (54.8 mg, 84%): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.26 (m, 3 H, ArH), 7.14-7.06 (m, 2 H, ArH), 6.84 (t, J = 7.5 Hz, 1 H, =CH), 2.54 (t, J = 7.5 Hz, 2 H, CH_2), 2.13-1.98 (m, 2 H, CH_2), 1.63-1.50 (m, 2 H, CH_2), 1.37-1.20 (m, 2 H, CH_2), 1.01 (t, J = 7.5 Hz, 3 H, CH_3), 0.87 (t, J = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.3, 144.1, 142.2, 136.3, 129.5, 128.2, 127.3, 39.2, 26.6, 22.9, 22.3, 13.9, 13.3; IR (neat) ν (cm^{-1}) 3051, 3024, 2960, 2933, 2873, 1690, 1619, 1597, 1494, 1459, 1442, 1378, 1266, 1143, 1072, 1029; MS (70 eV, EI) *m/z* (%) 216 (M^+, 6.03), 131 (100); HRMS (EI) Cacld for $C_{15}H_{20}O$ (M^+): 216.1514; Found: 216.1518.

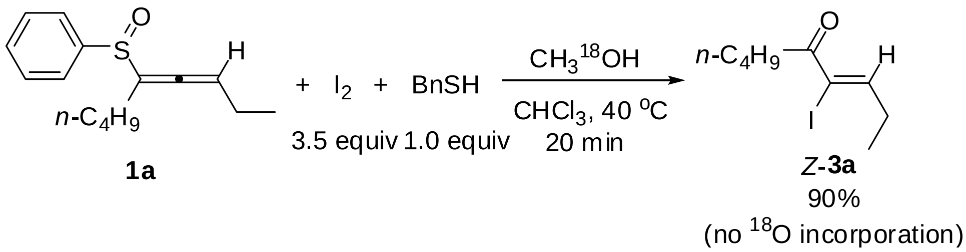
2. (*E*)-4-(Phenylethynyl)non-3-en-5-one (6)   Wmy-4-60



To a solution of *Z*-**3a** (80.3 mg, 0.3 mmol) in THF (1 mL) were added $Pd(PPh_3)_2Cl_2$ (10.6 mg, 0.015 mmol), a solution of phenylacetylene (46.1 mg, 0.45 mmol) in THF (1 mL), CuI (5.8 mg, 0.03 mmol), and a solution of *i*-Pr_2NH (48.6 mg, 0.48 mmol) in THF (1 mL) sequentially. The mixture was stirring at 0 °C over a period of 2 h under nitrogen. After the reaction complete, 5 mL of ethyl ether was added. Filtration, evaporation and column chromatography on silica gel (eluent: petroleum ether/ethyl ether = 80:1) gave **6** (68.4 mg, 94%): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57-7.43 (m, 2 H, ArH), 7.42-7.27 (m, 3 H, ArH), 7.13 (t, *J* = 7.7 Hz, 1 H, =CH), 2.85 (t, *J* = 7.4 Hz, 2 H, CH_2), 2.58-2.45 (m, 2 H, CH_2), 1.73-1.60 (m, 2 H, CH_2), 1.46-1.30 (m, 2 H, CH_2), 1.13 (t, *J* = 7.7 Hz, 3 H, CH_3), 0.94 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.8, 151.9, 131.3, 128.5, 128.3, 123.9, 122.9, 97.0, 84.2, 40.0, 26.1, 24.2, 22.3, 13.9, 12.6; IR (neat) ν (cm^{-1}) 2960, 2933, 2873, 1700, 1601, 1587, 1490, 1459, 1442, 1378, 1254, 1165, 1141, 1099, 1067, 1019; MS (70 eV, EI) *m/z* (%) 240 (M^+, 31.03), 57 (100); HRMS (EI) Cacld for $C_{17}H_{20}O$ (M^+): 240.1514; Found: 240.1512.

Experiments for Mechanistic Study:

1. $CH_3^{18}OH$ as additive for the reaction   wmy-4-119

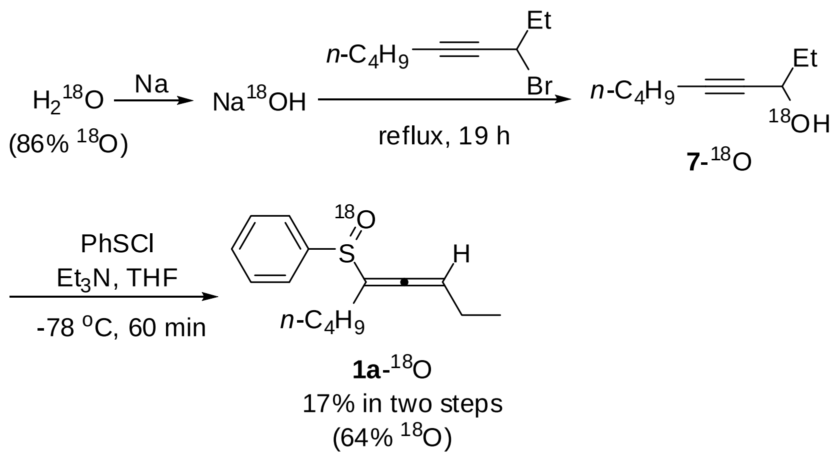


A solution of **1a** (74.2 mg, 0.3 mmol), $CHCl_3$ (1 mL), and $CH_3^{18}OH$ (30 μL) was treated with I_2 (267.4 mg, 1.05 mmol) for 5 min at 40 °C followed by the addition of a solution of BnSH in $CHCl_3$ (0.6 M, 0.5 mL) with stirring. After being stirred for 20 min at 40 °C, the mixture was quenched with 6 mL of water followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$. The mixture was extracted with Et_2O (20 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether ~ petroleum ether/ether = 300/1) afforded *Z*-**3a** (71.6 mg, 90%): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (t, *J* = 6.8 Hz, 1 H, =CH), 2.83 (t, *J* = 7.5 Hz, 2 H, $COCH_2$), 2.51-2.36 (m, 2 H, CH_2), 1.71-1.54 (m, 2 H, CH_2), 1.44-1.22 (m, 2 H, CH_2), 1.15 (t, *J* = 7.5 Hz, 3 H, CH_3), 0.92 (t, *J* = 7.2 Hz, 3 H, CH_3).

2. Isotopic distribution experiments

1). Synthesis of Nona-3,4-dien-5-yl phenyl sulfoxide-^{18}O 1a-^{18}O

wmy-5-62, wmy-5-65



Na (0.4611 g, 2.0 mmol) was added to 1.0 mL of ^{18}O-labelled water (86% $H_2{}^{18}O$) in a reaction tube. Then 3-bromonon-4-yne (1.0153 g, 5.0 mmol) was added into the tube in a glove box. The resulting mixture was refluxed for 19 h with continuous stirring under N_2 atmosphere. The resulting mixture was allowed to cool down naturally to room temperature followed by quenching with water (5 mL), extracted with Et_2O (10 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation and chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1) of the impurity crude product **7**-^{18}O (0.3134 g) as an oil.

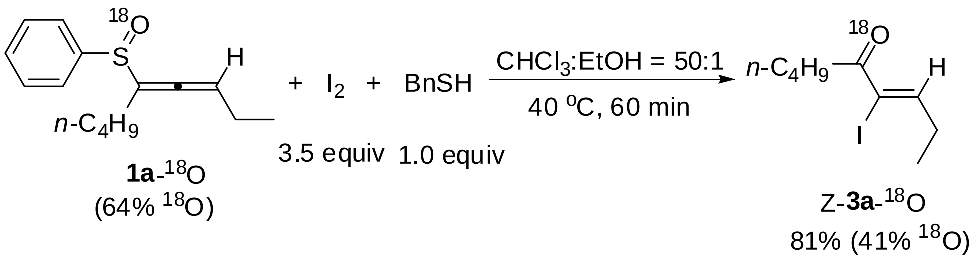
To a dried reaction tube were added crude product non-4-yn-3-ol (^{18}O) **7**-^{18}O (0.3134 g) prepared above, THF (10 mL), and triethylamine (0.4 mL, d = 0.72 g/mL, 0.288 g, 2.85 mmol) sequentially under N_2 atmosphere. After the mixture was cooled to -78 ^{o}C, a solution of sulfenyl chloride (0.3821 g, 2.64 mmol) was added dropwise within 2 min. After being stirred at -78 ^{o}C for 60 min, water (5 mL) was added to quench the reaction. The resulting mixture was extracted with Et_2O (10 mL × 3), washed by brine, dried over anhydrous Na_2SO_4. Filtration, evaporation and chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 20/1) of the product afforded **1a**-^{18}O (0.2174 g, 17% in two steps, 64% ^{18}O) as an oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.56 (m, 2 H, ArH), 7.56-7.36 (m, 3 H, ArH), 5.83-5.66 (m, 1 H, =CH), 2.29-2.07 (m, 3 H, CH_2 + one proton in CH_2), 1.93-1.70 (m, 1 H, one proton in CH_2), 1.40-1.14 (m, 4 H, 2 × CH_2), 1.14-0.96 (m, 3 H, CH_3), 0.90-0.73 (m, 3 H, CH_3); IR (neat) ν (cm^{-1}) 3057, 2961, 2931, 2872, 1951, 1581, 1475, 1457, 1443, 1378, 1322, 1303, 1083, 1049, 1022; MS (70 eV, EI) *m/z* (%) 250 (M (^{18}O)$^+$, 30.46), 248 (M (^{16}O)$^+$, 15.12), 221 ((M (^{18}O)-Et)$^+$, 100), 219 ((M (^{16}O)-Et)$^+$, 46.94); HRMS (EI) Cacld for $C_{15}H_{20}{}^{16}OS$ (M$^+$): 248.1235; Found: 248.1232; HRMS (EI) Cacld for $C_{15}H_{20}{}^{18}OS$ (M$^+$): 250.1277; Found: 250.1279.

The ^{18}O% of **1a**-^{18}O was detemined by MS spectrum. The natural abundance of the stable isotopes of some common elements has been reported by literatures. The presence and number of sulphur atoms is usually indicated by the contribution of ^{34}S to the M+2 peak. Various combinations of C, H, O will thus give rise to the intensity of the M+2 peak. According to the theoretical calculations, the ratio $C_{15}H_{20}{}^{16}OS$: $C_{15}H_{20}{}^{18}OS$ = 100:4.5. Thus the intensity of M+2 ($C_{15}H_{20}{}^{18}OS$) peak will be 4.5 percent of the intensity of the molecular peak M ($C_{15}H_{20}{}^{16}OS$). The relative abundances of 221 [M (^{18}O)-Et]$^+$, 219 [(M (^{16}O)-Et)$^+$ of **1a**-^{18}O are 100, 46.94. (The intensity of (M-Et)$^+$ could be calculated due to the contribution from Et to M+2 is extremely small.) The ^{18}O% of **1a**-^{18}O can be calculated as follow: (100-46.94*4.5%)/(100-46.94*4.5%+46.94)=67.6% (See pages 102-104).

In additional, the spurious contributions to the isotope peak intensities from weak background peaks or from impurities in the sample must be considered. The spurious contribution of **1a** to M+2: (3.65-45.44*4.5%)/(3.65-45.44*4.5%+45.44)=3.4% (See pages 106-107).

So the ^{18}O% of **1a**-^{18}O is 67.%-3.41% ≈ 64%.

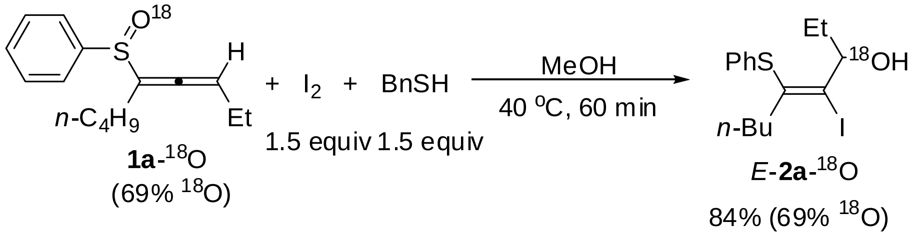
(*Z*)-4-Iodonon-3-en-5-one-^{18}O *Z*-3a-^{18}O wmy-5-66



A solution of **1a**-^{18}O (89.4 mg, 0.36 mmol, 64% ^{18}O), $CHCl_3$ (1.2 mL), and EtOH (36 μL) was treated with I_2 (320.7 mg, 1.26 mmol) for 5 min at 40 °C followed by the addition of a solution of BnSH in $CHCl_3$ (44.7mg, 0.36 mmol, 0.5 mL) with stirring. After being stirred for 60 min at 40 °C, the mixture was quenched with 6 mL of water followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$. The mixture was extracted with Et_2O (20 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether ~ petroleum ether/ether = 300/1) afforded *Z*-**3a**-^{18}O (77.4 mg, 81%, 41% ^{18}O): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (t, *J* = 6.9 Hz, 1 H, =CH), 2.82 (t, *J* = 7.5 Hz, 2 H, $COCH_2$), 2.49-2.36 (m, 2 H, CH_2), 1.70-1.53 (m, 2 H, CH_2), 1.41-1.28 (m, 2 H, CH_2), 1.14 (t, *J* = 7.5 Hz, 3 H, CH_3), 0.93 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 152.9, 111.9, 37.5, 31.5, 27.1, 22.3, 13.8, 12.0; IR (neat) ν (cm^{-1}) 2959, 2932, 2872, 1682, 1605, 1457, 1413, 1378, 1323, 1280, 1171, 1121, 1085, 1019; MS (70 eV, EI) *m/z* (%) 268 (M (^{18}O)$^+$, 0.91), 266 (M (^{16}O)$^+$, 1.36), 239 ((M (^{18}O)-Et)$^+$, 65.81), 237 ((M (^{16}O)-Et)$^+$, 91.50), 53 (100); HRMS (EI) Cacld for $C_9H_{15}{}^{16}OI$ (M^+): 266.0168; Found: 266.0171; HRMS (EI) Cacld for $C_9H_{15}{}^{18}OI$ (M^+):

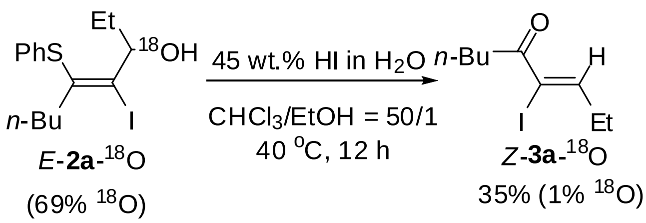
268.0210; Found: 268.0204. The ^{18}O% of *Z*-**3a**-^{18}O was detemined by MS spectrum: 41.8%-0.6% ≈ 41% (see pages 110-114).

_E_-4-Iodo-5-phenylthio-4-nonen-3-ol-^{18}O (_E_-2a-^{18}O) wmy-6-44



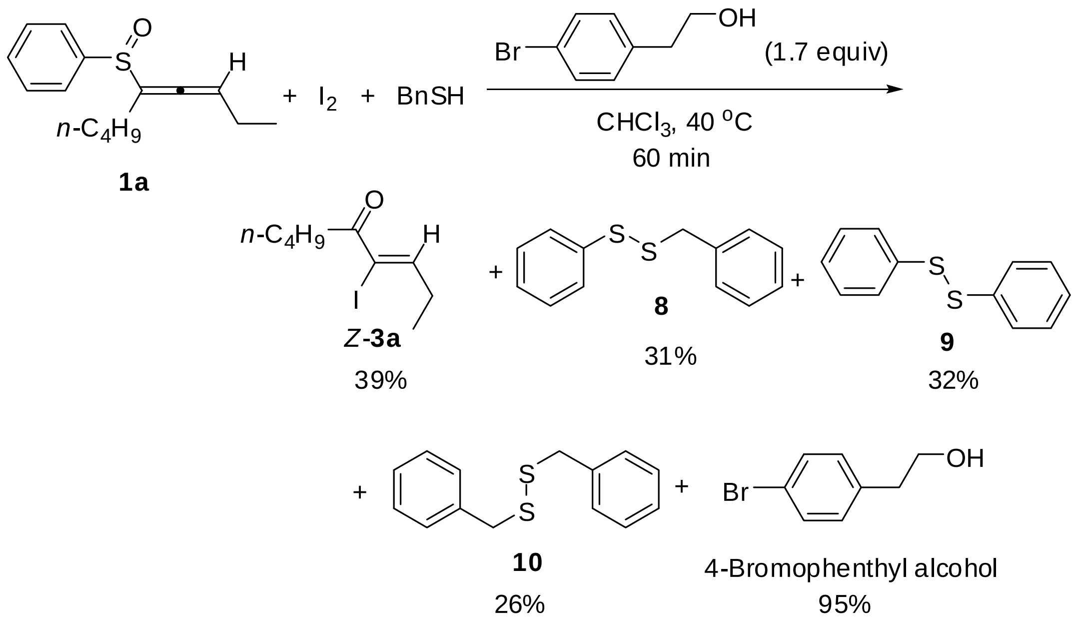
A solution of **1a**-^{18}O (163.2 mg, 0.65 mmol, 69% ^{18}O) in MeOH (8 mL) was treated with I_2 (248.3 mg, 0.98 mmol) for 5 min at 40 °C followed by the addition of a solution of BnSH (121.0 mg, 0.98 mmol) in MeOH (2 mL) with stirring. After being stirred at for 60 min, the mixture was quenched with 5 mL of water at 40 °C followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$. The mixture was extracted with ether (10 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) afforded *E*-**2a**-^{18}O (208.0 mg, 84%, 69% ^{18}O): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.16 (m, 5 H, ArH), 4.56 (t, *J* = 6.8 Hz, 1 H, CH), 2.58-2.44 (m, 1 H, one protone in CH_2), 2.36-2.22 (m, 1 H, one protone in CH_2), 2.01 (bs, 1 H, OH), 1.74-1.40 (m, 4 H, 2 × CH_2), 1.34-1.16 (m, 2 H, CH_2), 0.94-0.77 (m, 6 H, 2 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.6, 134.3, 130.3, 129.0, 127.0, 120.1, 74.2, 41.3, 30.9, 29.9, 22.2, 13.8, 9.5; IR (neat) ν (cm^{-1}) 3386, 3058, 2959, 2929, 2872, 1582, 1476, 1461, 1439, 1379, 1327, 1237, 1098, 1055, 1024, 1002; MS (70 eV, EI) *m/z* (%) 378 (M (^{18}O)$^+$, 3.07), 376 (M (^{16}O)$^+$, 1.20), 141 (100); HRMS (EI) Cacld for $C_{15}H_{21}{}^{18}OSI$ (M^+): 378.0400; Found: 378.408; HRMS (EI) Cacld for $C_{15}H_{21}{}^{16}OSI$ (M^+): 376.0358; Found: 376.0352. The ^{18}O% of *E*-**2a**-^{18}O was detemined by MS spectrum: 71.5%-1.7% ≈ 69% (see pages 117-121).

***E*-2a-^{18}O reacted with 45% HI aqueous affording *Z*-3a: wmy-6-45:**



A solution of *E*-**2a**-^{18}O (123.8 mg, 0.33 mmol, 69% ^{18}O), $CHCl_3$ (6 mL), and EtOH (0.12 mL) was treated with 45 wt.% HI in H_2O (0.66 mmol, 188 μL) for 12 hours at 40 ^{o}C. The reaction was quenched with 5 mL of water, extracted with Et_2O (10 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether/ether = 300/1) afforded *Z*-**3a**-^{18}O (30.5 mg, 35%, 1% ^{18}O): Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (t, *J* = 6.8 Hz, 1 H, =CH), 2.83 (t, *J* = 7.5 Hz, 2 H, $COCH_2$), 2.52-2.36 (m, 2 H, CH_2), 1.74-1.56 (m, 2 H, CH_2), 1.46-1.28 (m, 2 H, CH_2), 1.15 (t, *J* = 7.5 Hz, 3 H, CH_3), 0.92 (t, *J* = 7.4 Hz, 3 H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 153.0, 111.9, 37.5, 31.5, 27.1, 22.3, 13.8, 12.0; MS (70 eV, EI) *m/z* (%) 268 (M (^{18}O)$^+$, 0.04), 266 (M (^{16}O)$^+$, 1.16), 239 ((M (^{18}O)-Et)$^+$, 1.84), 237 ((M (^{16}O)-Et)$^+$, 100). The ^{18}O% of *Z*-**3a**-^{18}O was detemined by MS spectrum: 1.8%-0.6% ≈ 1% (See pages 122 and 123).

3. 4-Bromophenthyl alcohol as additive for the reaction wmy-4-109



A solution of **1a** (75.1 mg, 0.3 mmol), $CHCl_3$ (1 mL), and 4-bromophenthyl alcohol (101.9 mg, 0.51 mmol) was treated with I_2 (266.8 mg, 1.05 mmol) for 5 min at 40 °C followed by the addition of a solution of BnSH in $CHCl_3$ (0.6 M, 0.5 mL) with stirring. After being stirred for 60 min at 40 °C, the mixture was quenched with 6 mL of water followed by the addition of a saturated aqueous solution of $Na_2S_2O_3$. The mixture was extracted with Et_2O (20 mL × 3), washed with brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether ~ petroleum ether/ether = 300/1 ~ petroleum ether/ethyl acetate = 10/1) afforded *Z*-**3a** (31.3 mg, 39%), **8**[33] (21.9 mg, 31%), **9** (10.5 mg, 32%), **10** (9.6 mg, 26%), and 4-bromophenthyl alcohol (96.8 mg, 95%).

Z-**3a**: Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (t, *J* = 6.8 Hz, 1 H, =CH), 2.83 (t, *J* = 7.4 Hz, 2 H, $COCH_2$), 2.50-2.36 (m, 2 H, CH_2), 1.72-1.54 (m, 2 H, CH_2), 1.45-1.24 (m, 2 H, CH_2), 1.15 (t, *J* = 7.7 Hz, 3 H, CH_3), 0.92 (t, *J* = 7.2 Hz, 3 H, CH_3).

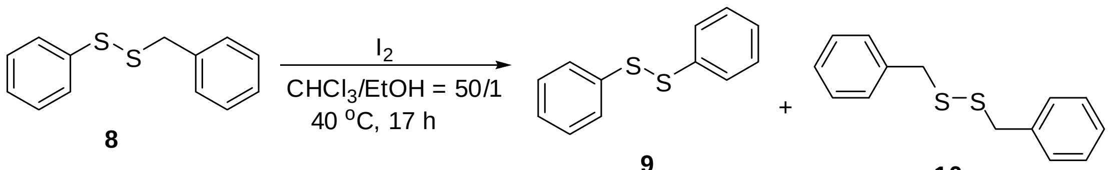
8[33]: Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.39 (m, 2 H, ArH), 7.34-7.12 (m, 8 H, ArH), 3.93 (s, 2 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0, 136.6, 129.4, 128.9, 128.5, 127.7, 127.5, 126.8, 43.4; IR (neat) ν (cm^{-1}) 3060, 3028, 2925, 2852, 1945, 1876, 1578, 1494, 1476, 1453, 1438, 1299, 1230, 1199, 1068, 1024; MS (70 eV, EI) *m/z* (%) 233 (M^++1, 2.82), 232 (M^+, 17.13), 91 (100).

9: Oil; CAS: 882-33-7. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.45 (m, 4 H, ArH), 7.36-7.14 (m, 6 H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0, 129.0, 127.5, 127.1; IR (neat) ν (cm^{-1}) 3072, 3058, 2926, 2852, 1578, 1476, 1438, 1296, 1068, 1023; MS (70 eV, EI) *m/z* (%) 219 (M^++1, 6.45), 218 (M^+, 50.76), 109 (100).

10: Oil; CAS: 3076-69-5. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.17 (m, 10 H, ArH), 3.59 (s, 4 H, 2 × CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.3, 129.4, 128.4, 127.4, 43.3; IR (neat) ν (cm^{-1}) 3084, 3061, 3028, 2956, 2923, 2849, 1601, 1494, 1453, 1414, 1229, 1198, 1070, 1028; MS (70 eV, EI) *m/z* (%) 247 (M^++1, 2.67), 246 (M^+, 14.02), 91 (100).

4-Bromophenthyl alcohol: Oil; CAS: 4654-39-1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.1 Hz, 2 H, ArH), 7.06 (d, *J* = 8.1 Hz, 2 H, ArH), 3.77 (t, *J* = 6.0 Hz, 2 H, CH_2), 2.76 (t, *J* = 6.0 Hz, 2 H, CH_2), 2.29 (bs, 1 H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 131.4, 130.6, 120.1, 63.0, 38.4.

4. The reaction of 1-benzyl-2-phenyldisulfane 8 with I_2 wmy-5-137



8 46% recovery; **9** 52%; **10** 54%

A solution of **8** (232.6 mg, 1.0 mmol), $CHCl_3$ (10 mL), and EtOH (0.2 mL) was treated with I_2 (255.1 mg, 1.0 mmol) at 40 °C with stirring. After being stirred for 17 h at 40 °C, the mixture was quenched with a saturated aqueous solution of $Na_2S_2O_3$. The mixture was extracted with Et_2O (20 mL × 3) and dried over anhydrous Na_2SO_4. Filtration, evaporation, and column chromatography on silica gel (petroleum ether) afforded, **8** (107.8 mg, 46%), **9** (57.1 mg, 52%), **10** (64.9 mg, 54%).

8: Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.36 (m, 2 H, ArH), 7.32-7.10 (m, 8 H, ArH), 3.91 (s, 2 H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.0, 136.5, 129.3, 128.8, 128.5, 127.6, 127.5, 126.7, 43.3.

9: Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.38 (m, 4 H, ArH), 7.30-7.08 (m, 6 H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.9, 129.0, 127.4, 127.0.

10: Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.15 (m, 10 H, ArH), 3.59 (s, 4 H, 2 × CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.3, 129.4, 128.4, 127.4, 43.2.

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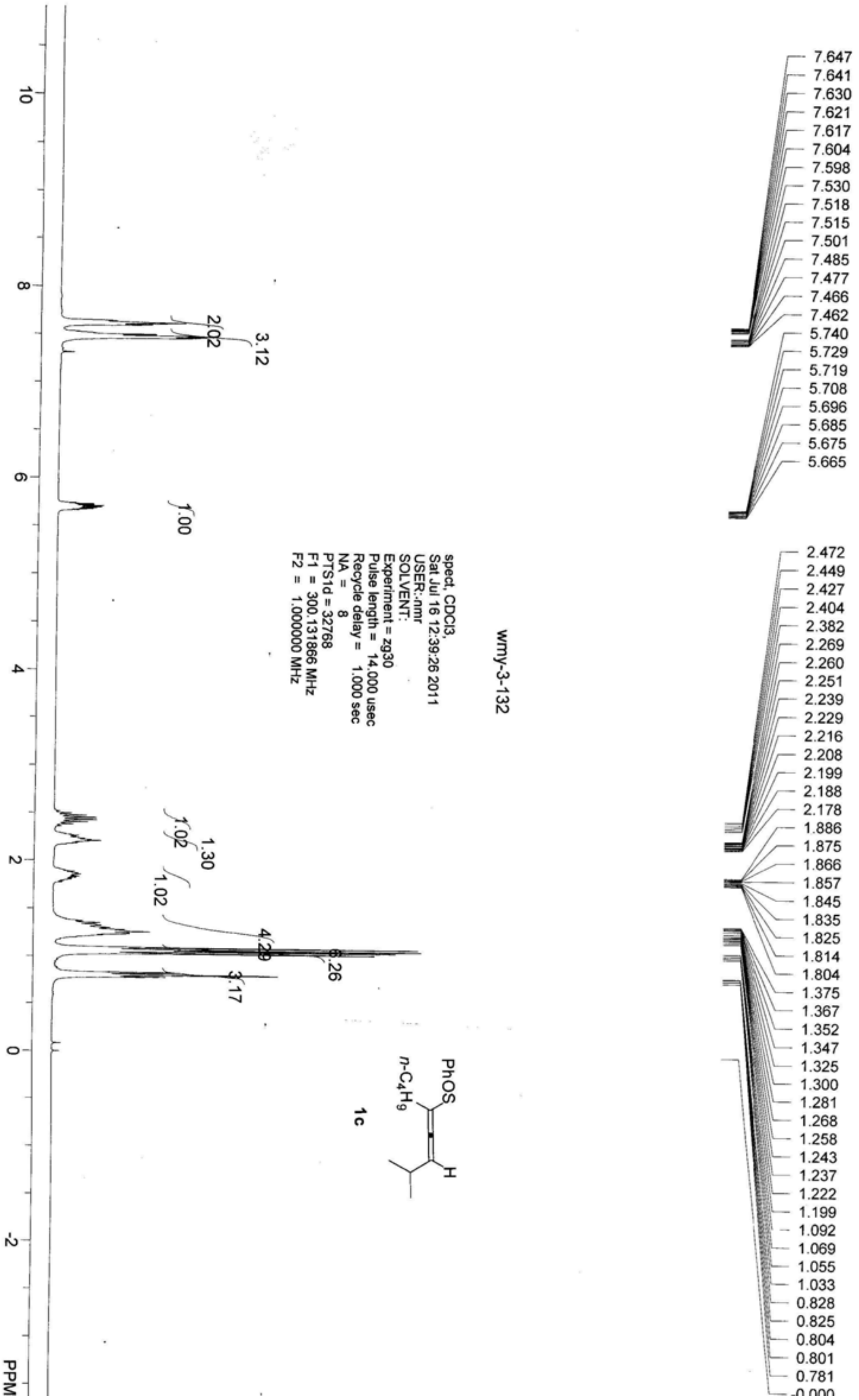
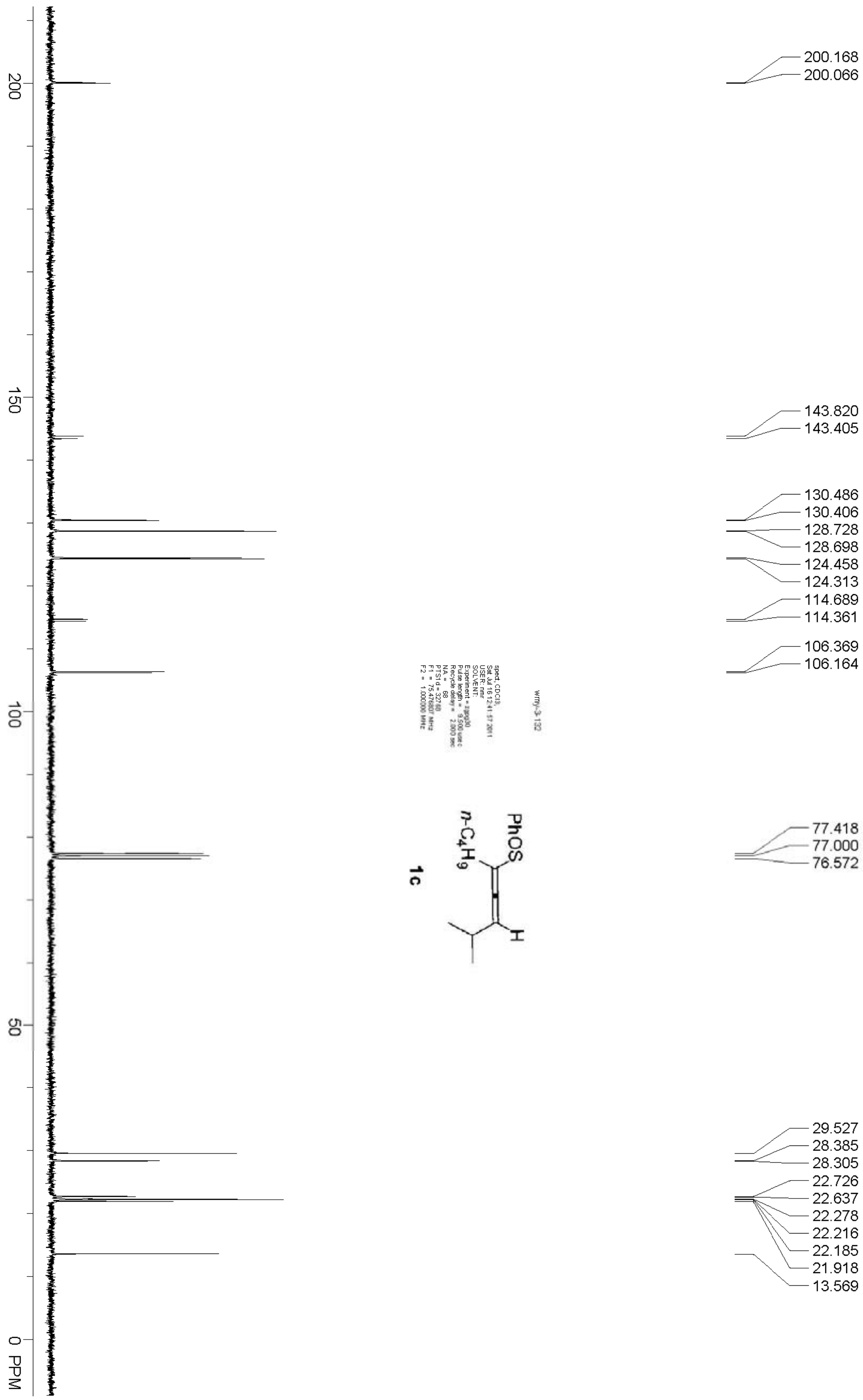
$^1H/^{13}C$ NMR Spectra of These Compounds

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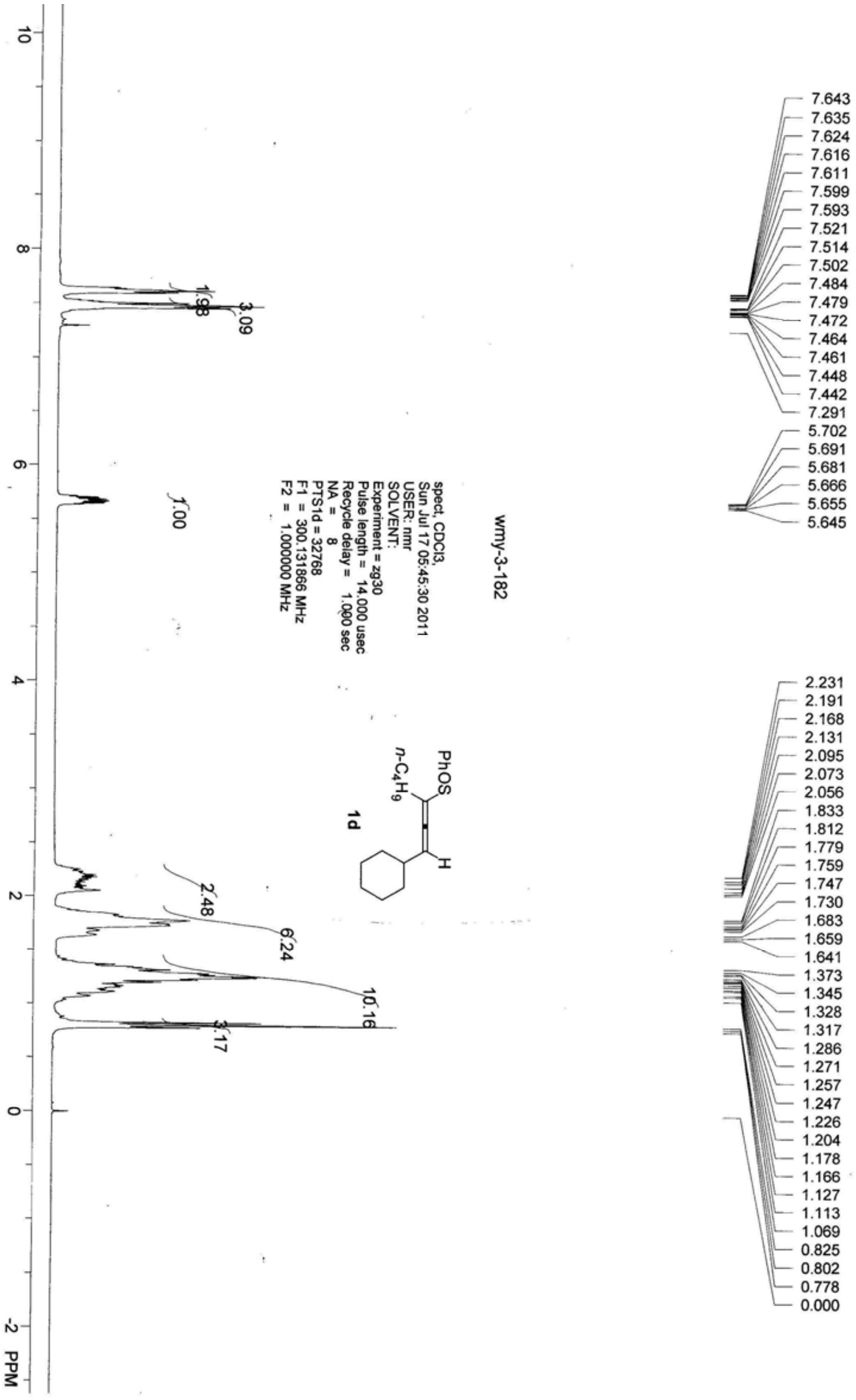
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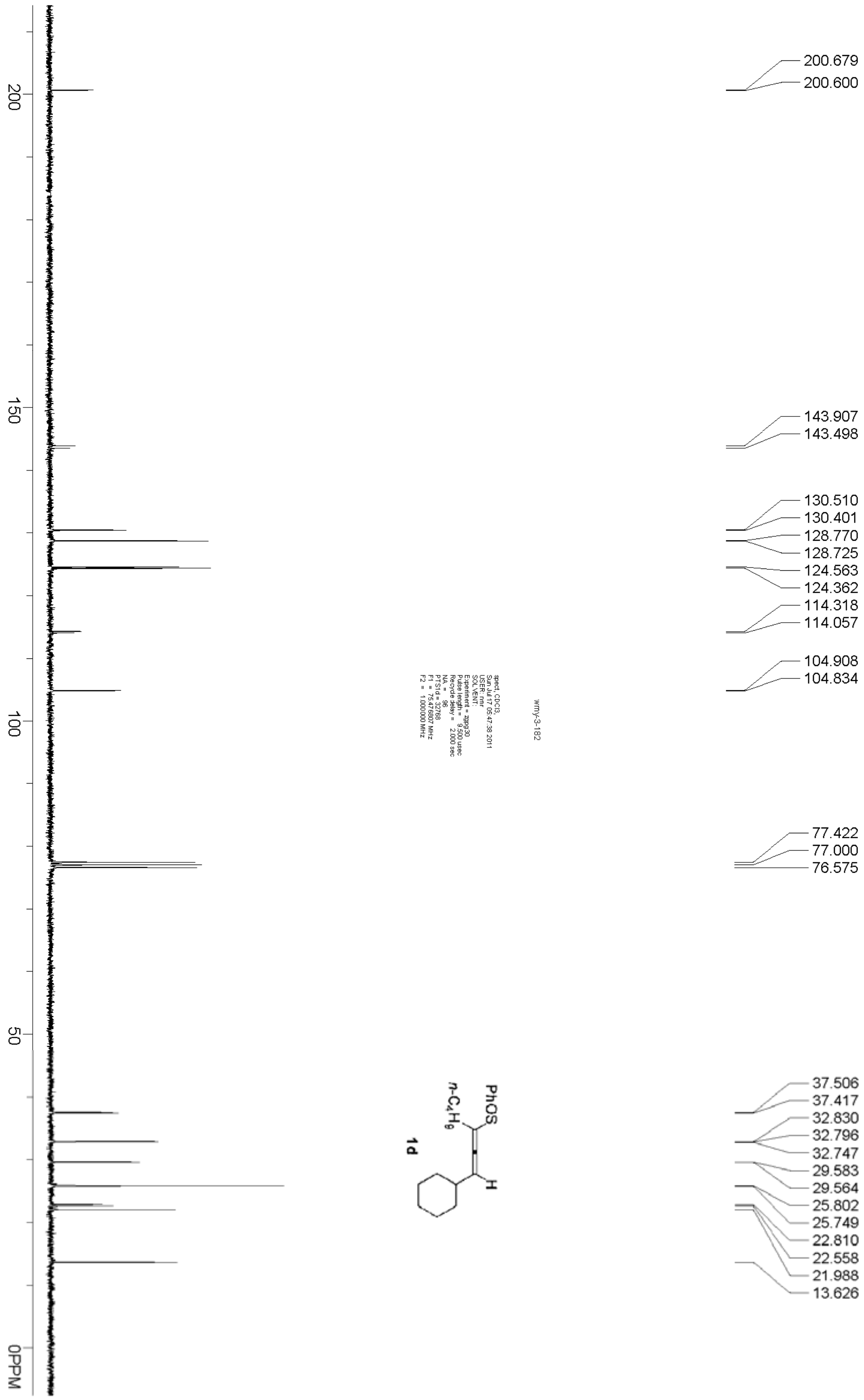
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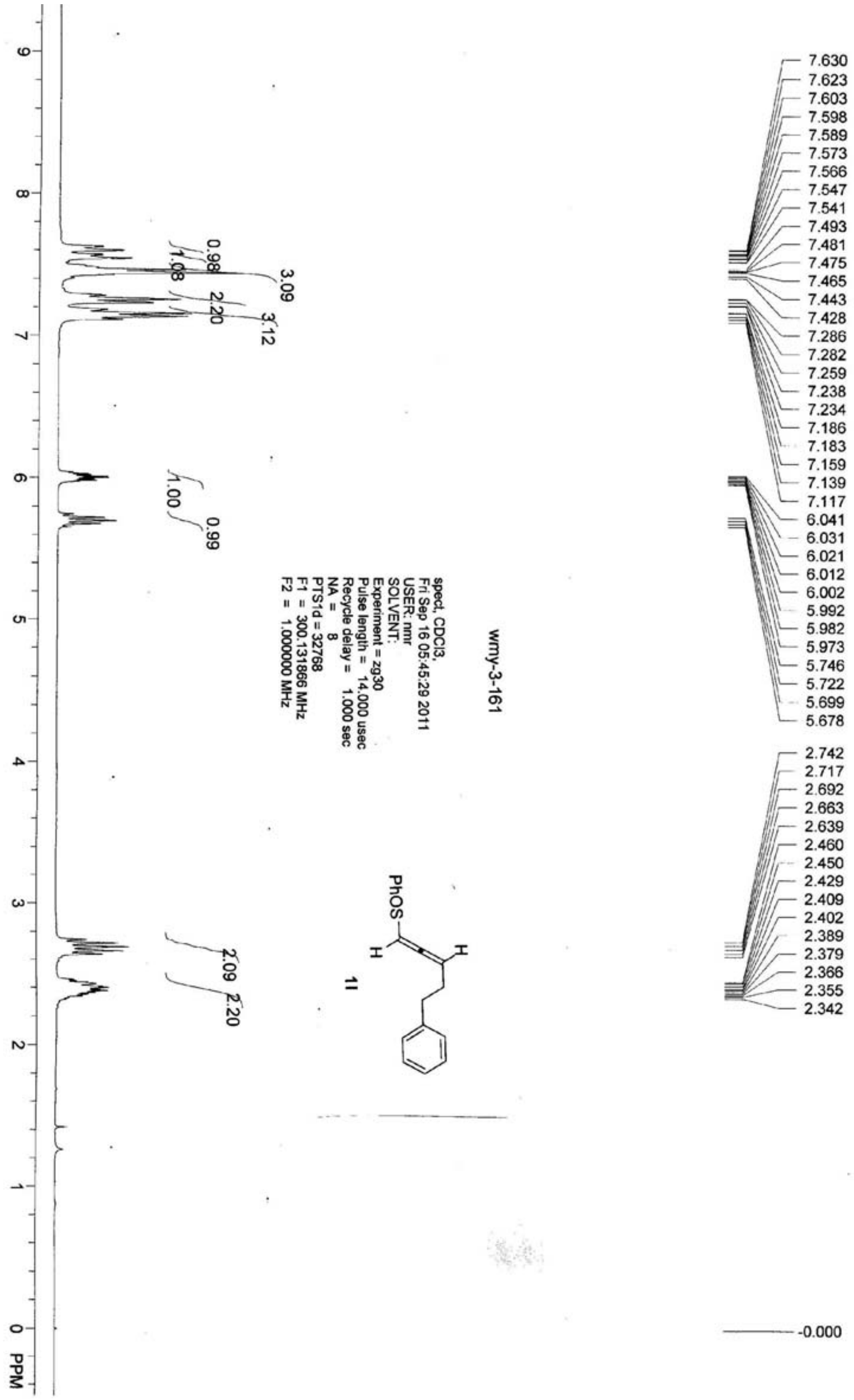
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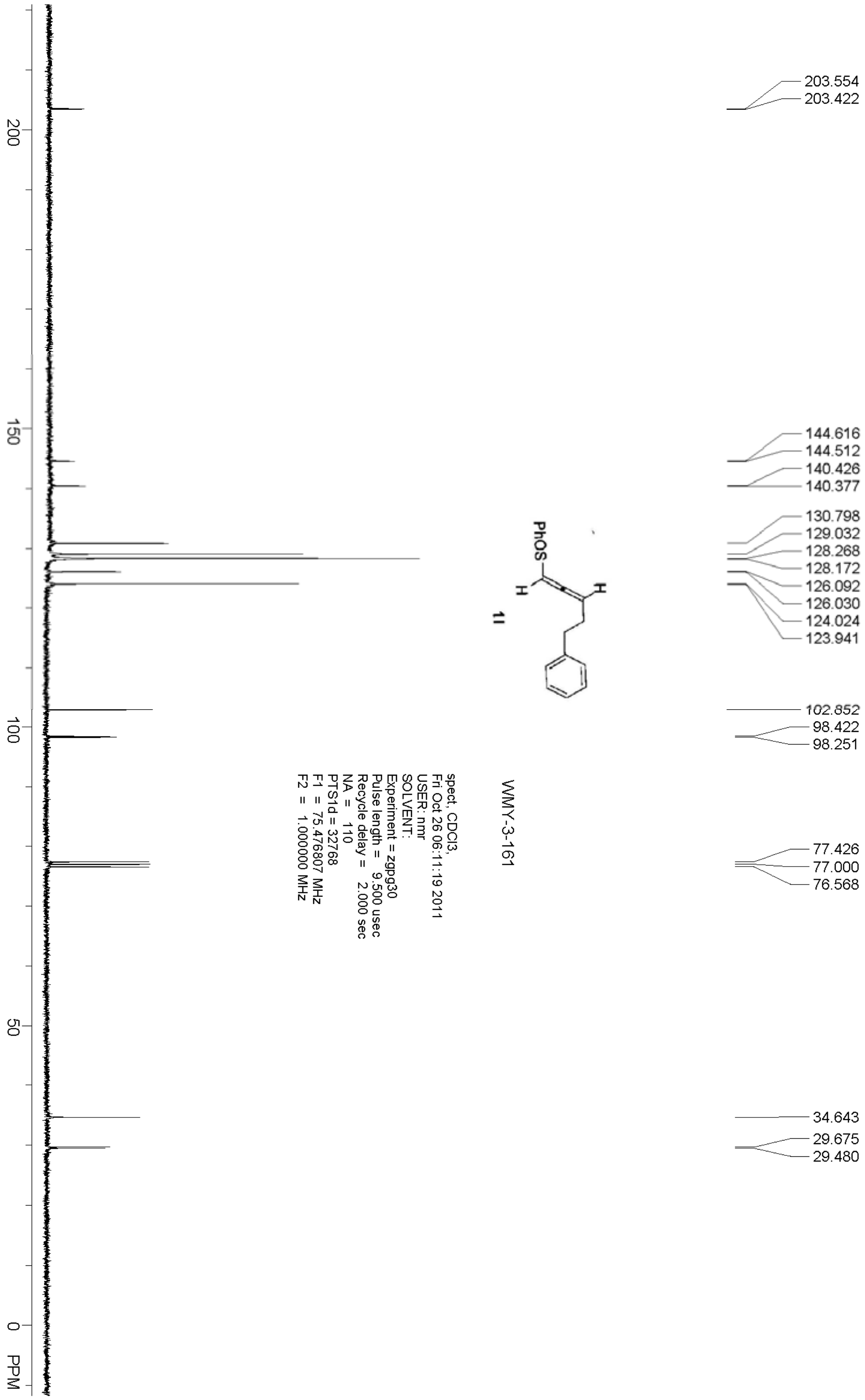
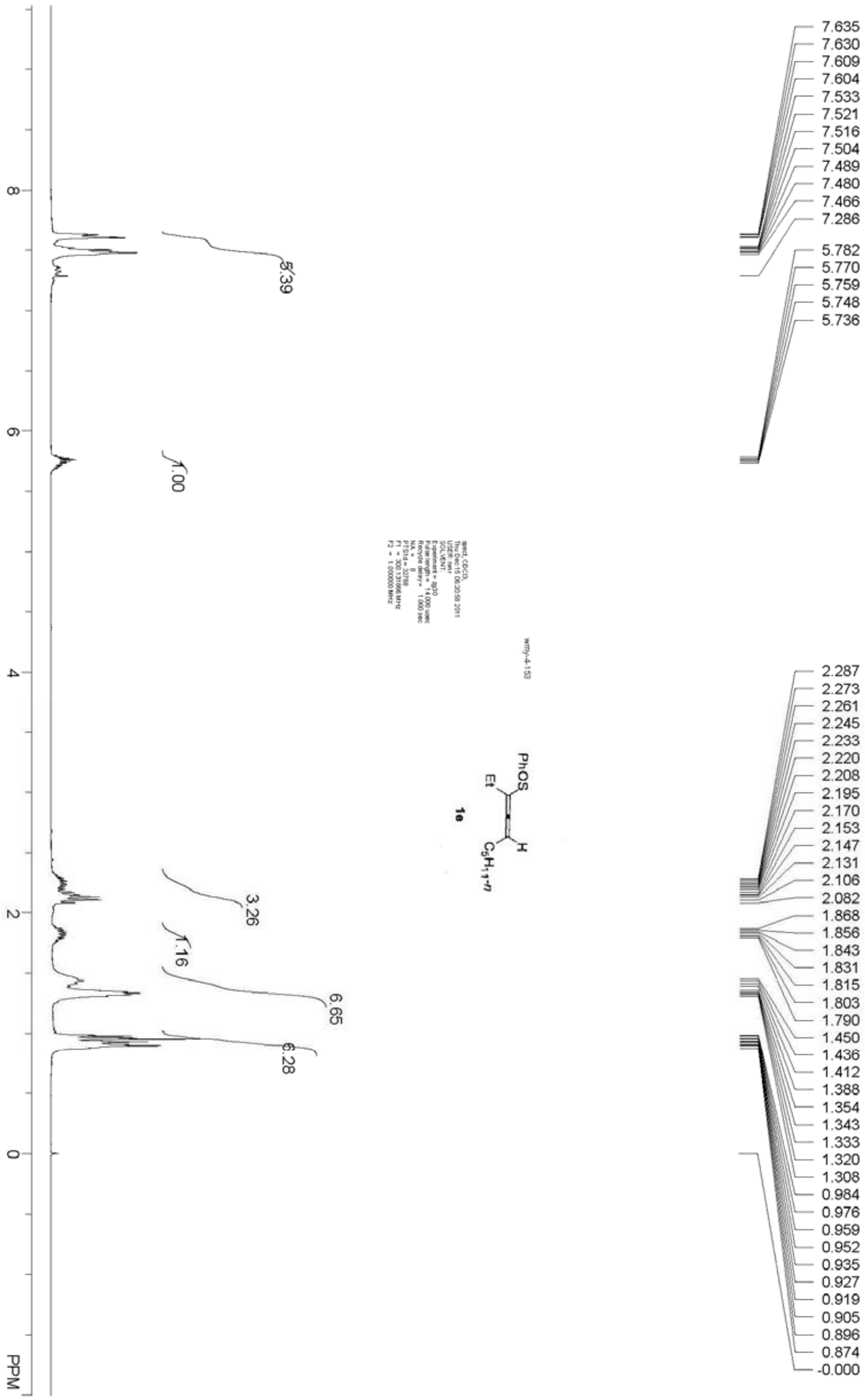
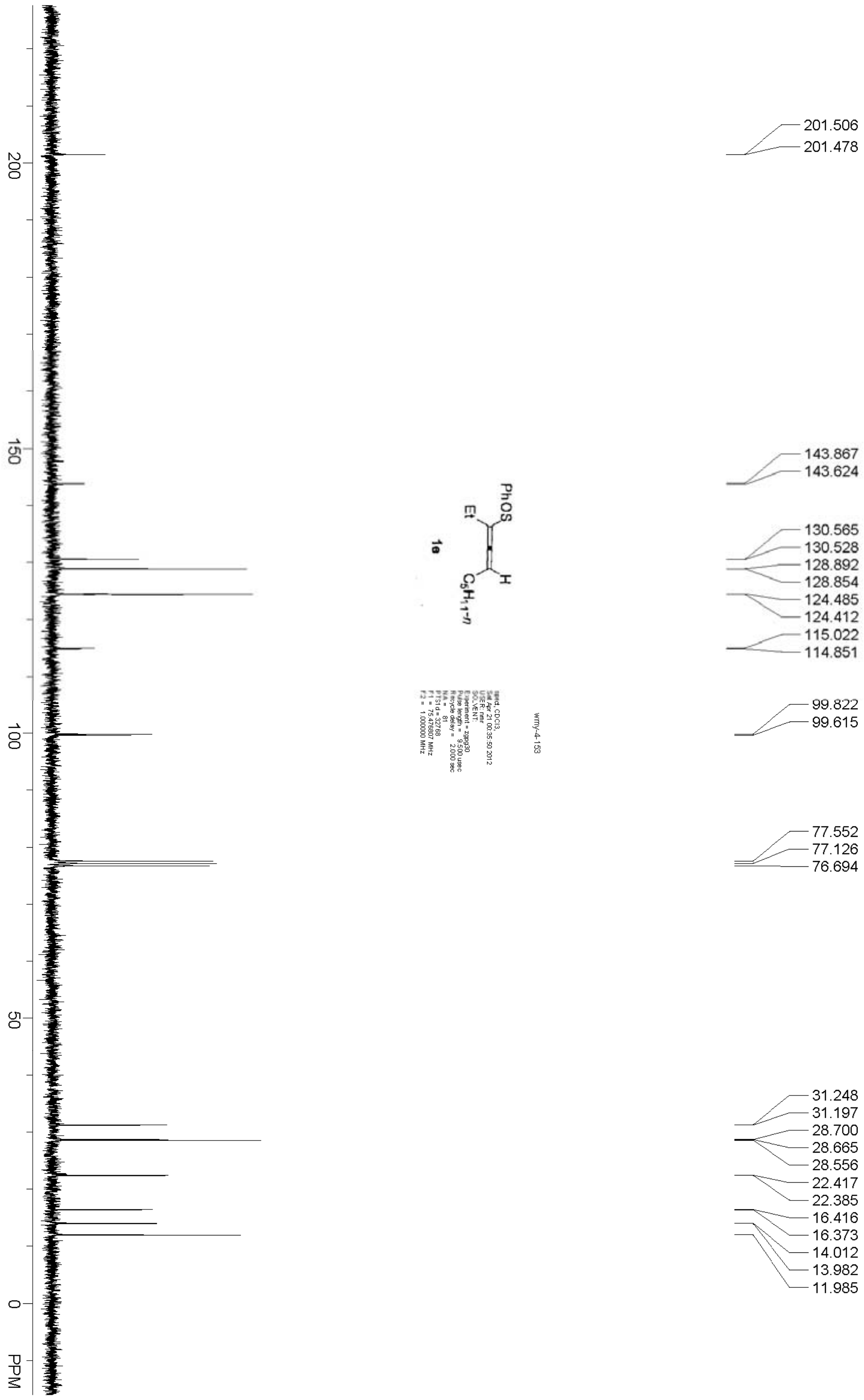
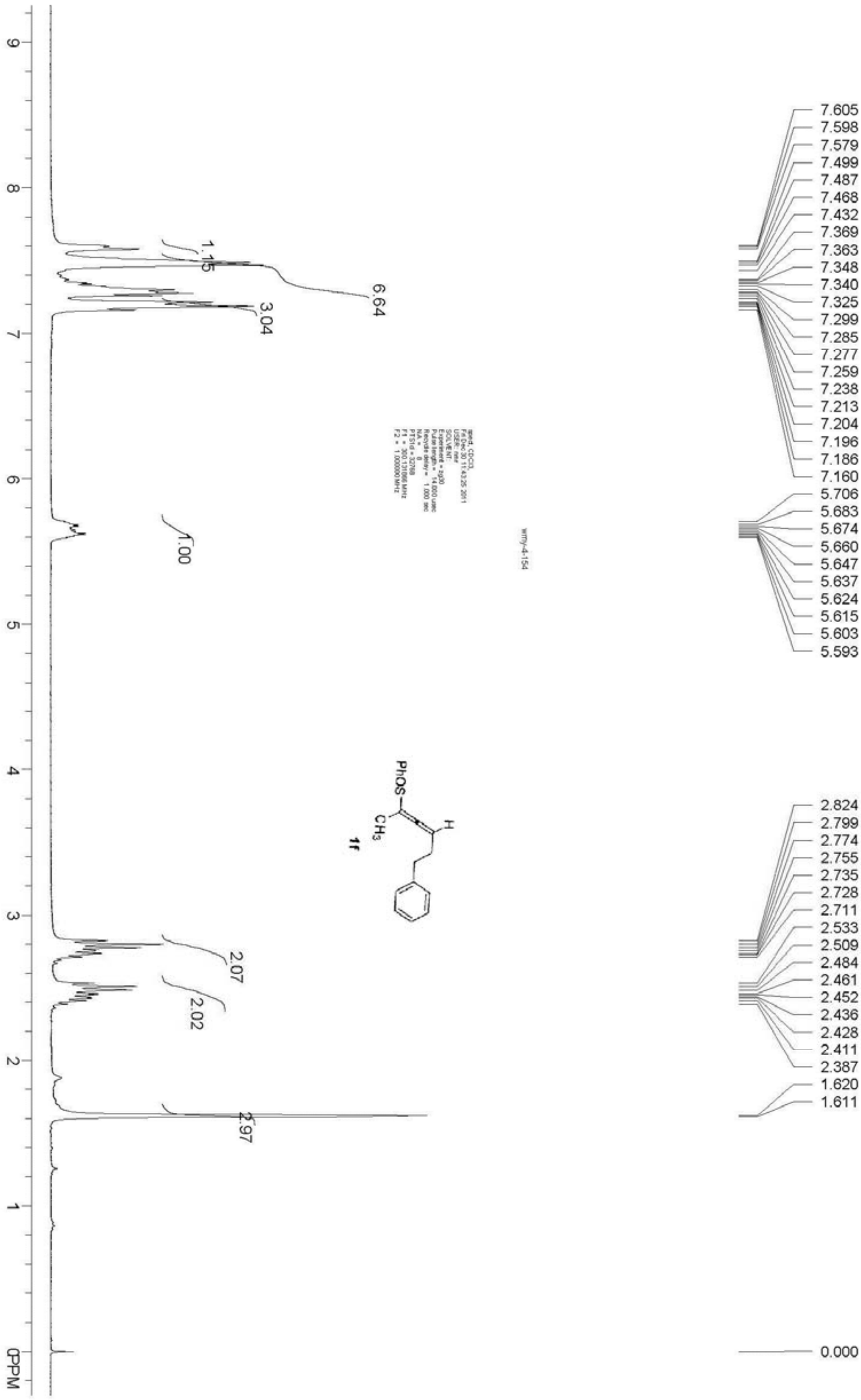
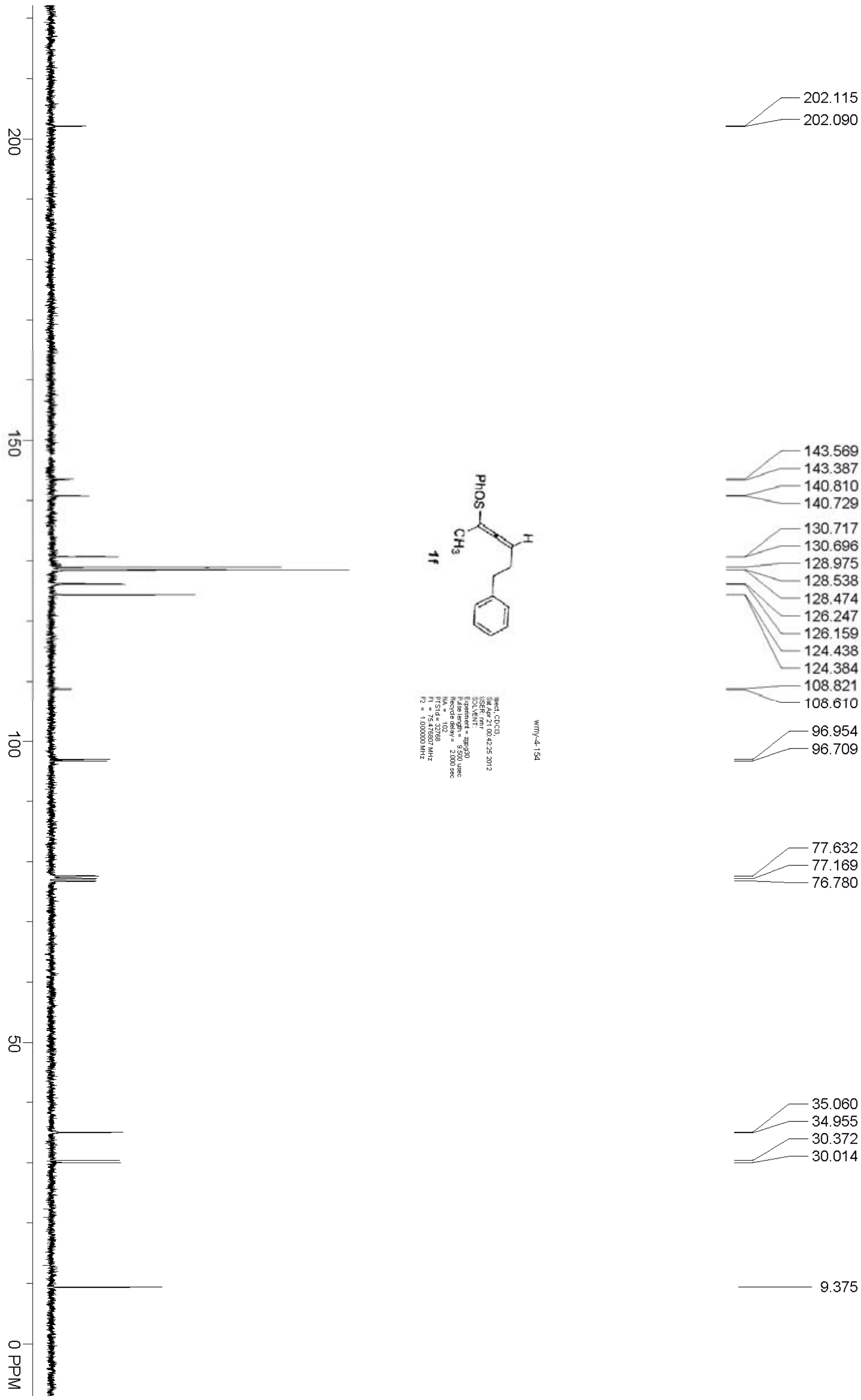
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
PhOS
H
H
1l
0.98
1.08
3.09
2.20
3.12
1.00
0.99
2.09
2.20
9
8
7
6
5
4
3
2
1
0
PPM
7.630
7.623
7.603
7.598
7.589
7.573
7.566
7.547
7.541
7.493
7.481
7.475
7.465
7.443
7.428
7.286
7.282
7.259
7.238
7.234
7.186
7.183
7.159
7.139
7.117
6.041
6.031
6.021
6.012
6.002
5.992
5.982
5.973
5.746
5.722
5.699
5.678
2.742
2.717
2.692
2.663
2.639
2.460
2.450
2.429
2.409
2.402
2.389
2.379
2.366
2.355
2.342
-0.000

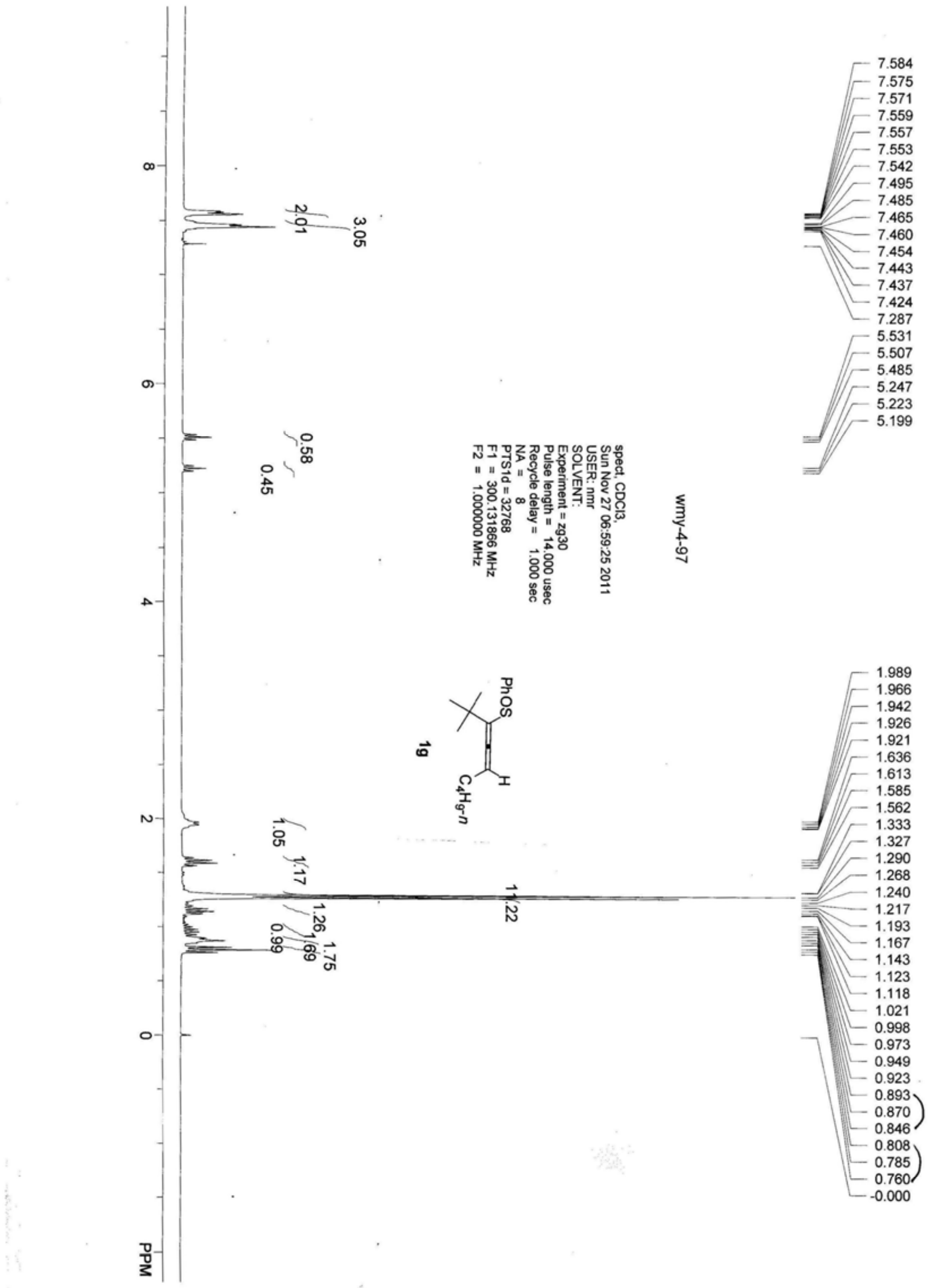

203.554
203.422
144.616
144.512
140.426
140.377
130.798
129.032
128.268
128.172
126.092
126.030
124.024
123.941
102.852
98.422
98.251
77.426
77.000
76.568
34.643
29.675
29.480
PhOS
H
H
1l
WMY-3-161
spect. CDCl3,
Fri Oct 26 06:11:19 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 110
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
200
150
100
50
0
PPM

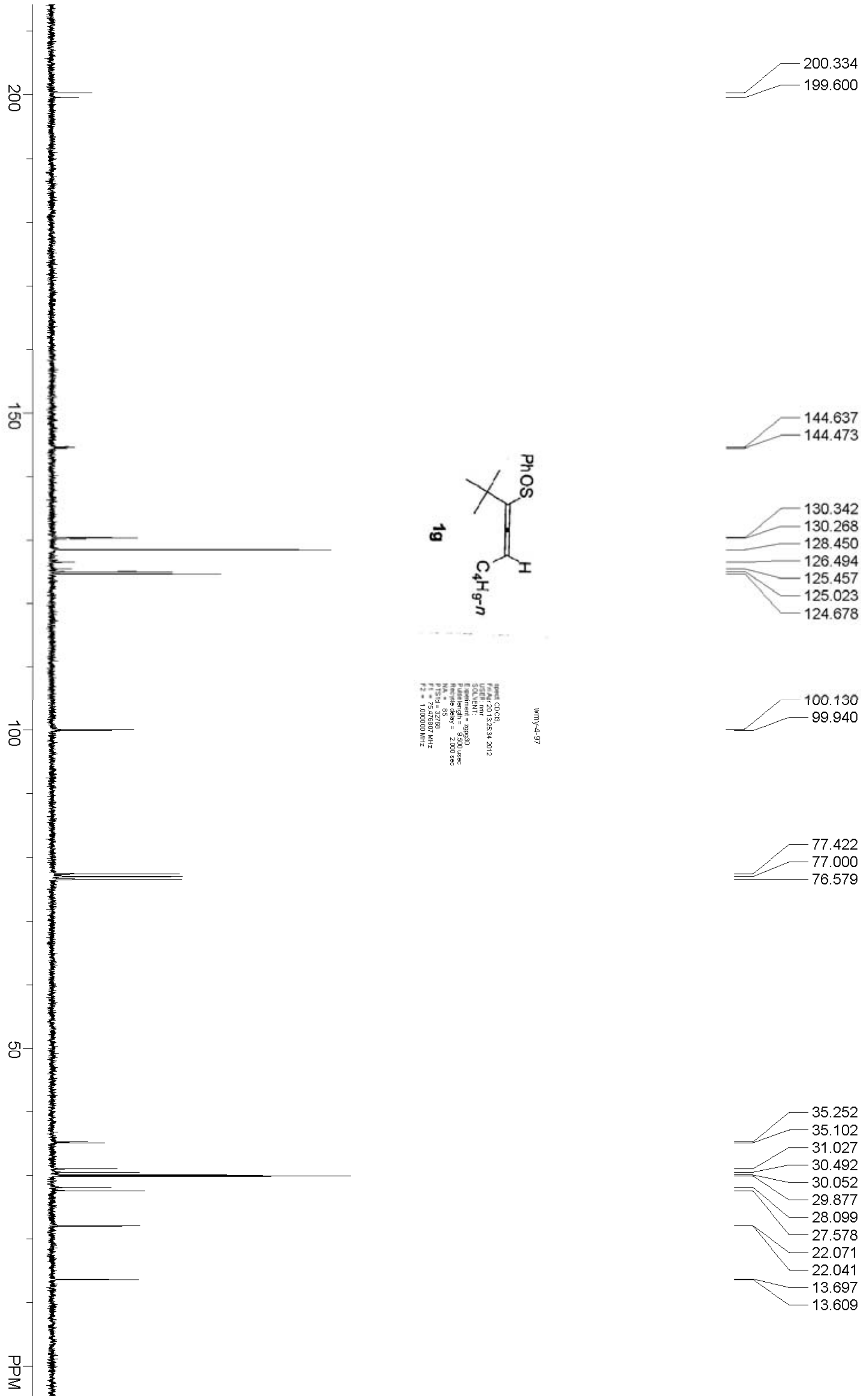

7.635
7.630
7.609
7.604
7.533
7.521
7.516
7.504
7.489
7.480
7.466
7.286
5.782
5.770
5.759
5.748
5.736
2.287
2.273
2.261
2.245
2.233
2.220
2.208
2.195
2.170
2.153
2.147
2.131
2.106
2.082
1.868
1.856
1.843
1.831
1.815
1.803
1.790
1.450
1.436
1.412
1.388
1.354
1.343
1.333
1.320
1.308
0.984
0.976
0.959
0.952
0.935
0.927
0.919
0.905
0.896
0.874
-0.000
5.39
1.00
3.26
1.16
6.65
6.28
wmy-4-153
PhOS
Et
H
C_5H_{11}-n
1e
8
6
4
2
0
PPM

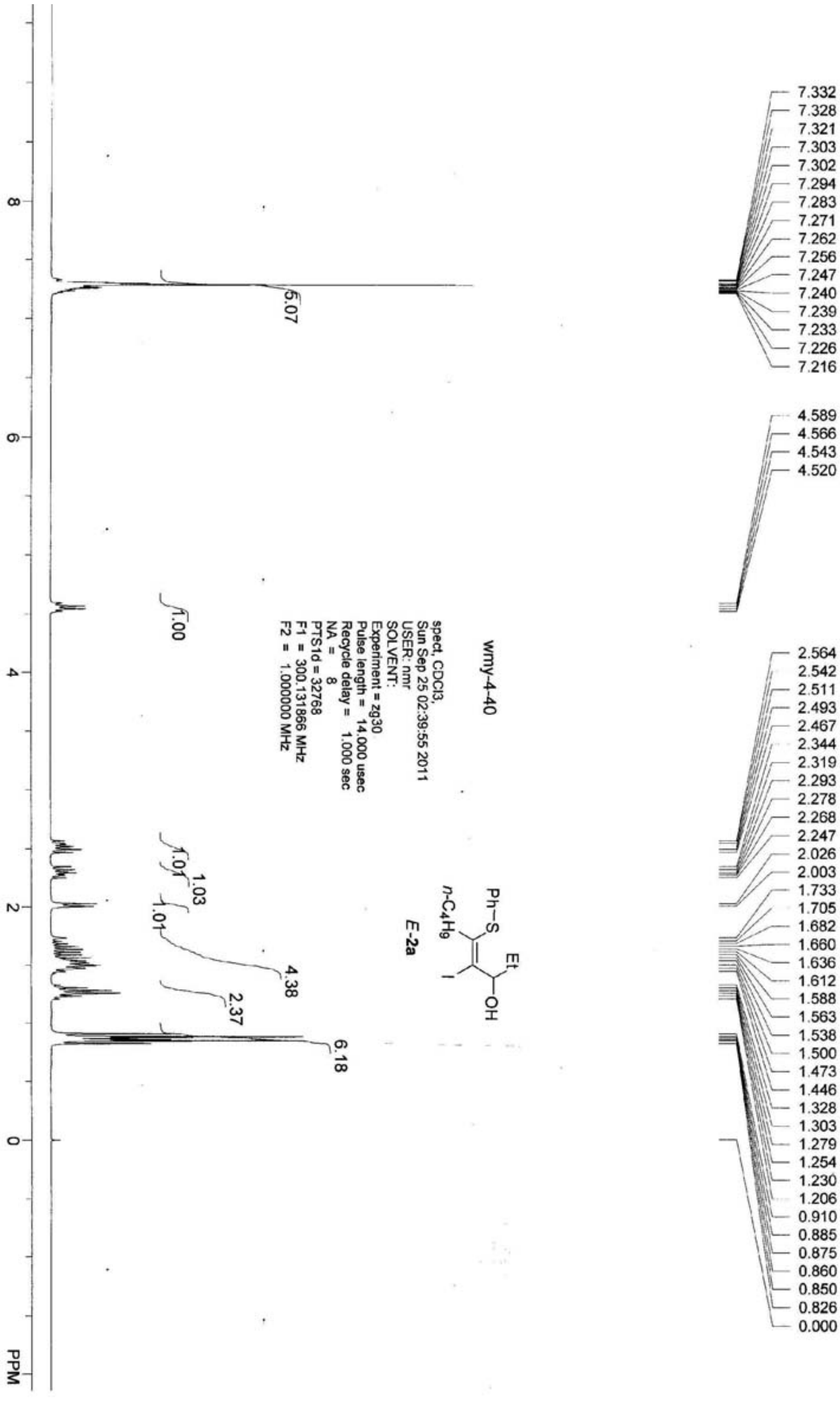

201.506
201.478
143.867
143.624
130.565
130.528
128.892
128.854
124.485
124.412
115.022
114.851
99.822
99.615
77.552
77.126
76.694
31.248
31.197
28.700
28.665
28.556
22.417
22.385
16.416
16.373
14.012
13.982
11.985
200
150
100
50
0
PPM
PhOS
Et
H
C5H11-n
1e
wmy-4-153

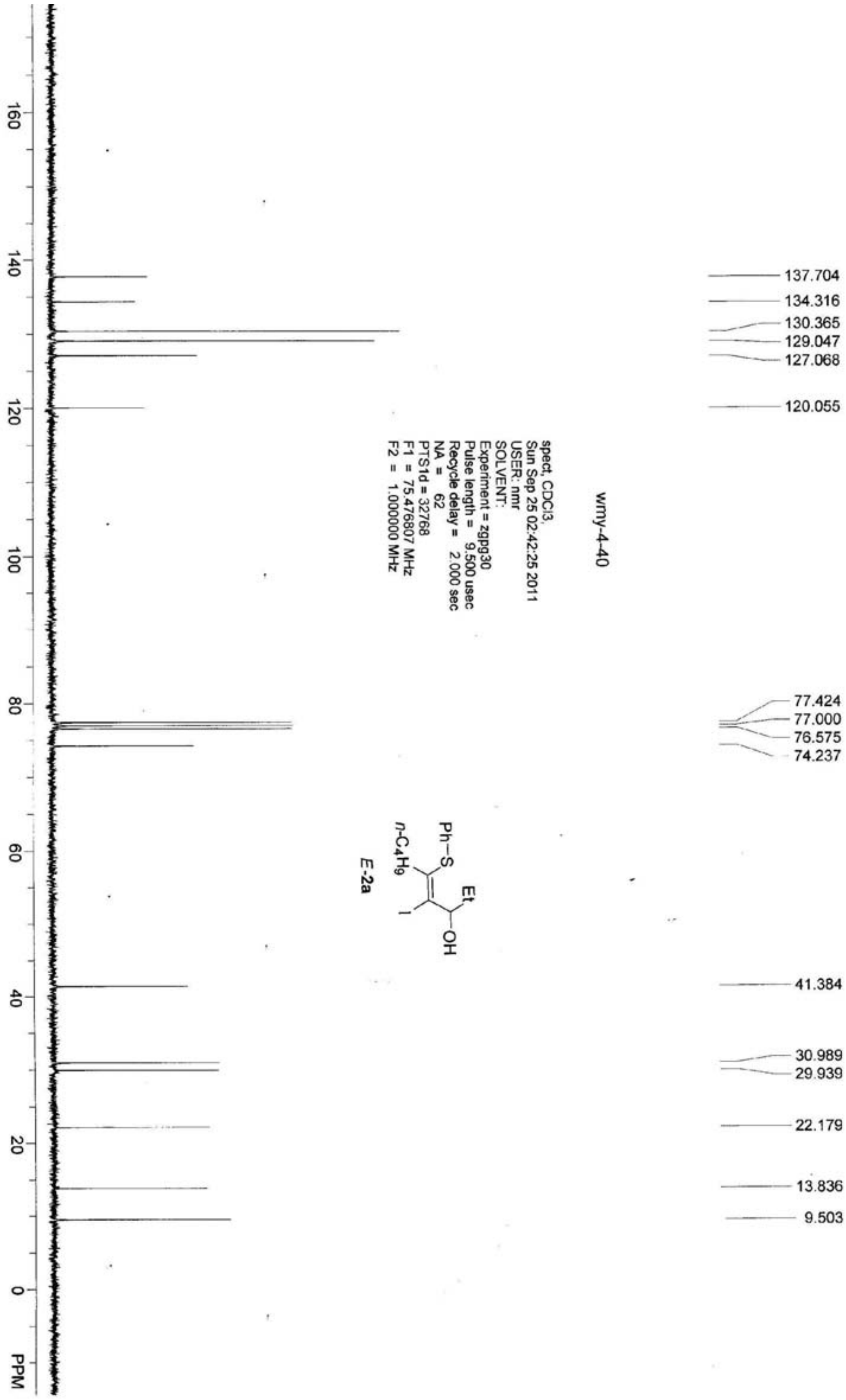

7.605
7.598
7.579
7.499
7.487
7.468
7.432
7.369
7.363
7.348
7.340
7.325
7.299
7.285
7.277
7.259
7.238
7.213
7.204
7.196
7.186
7.160
5.706
5.683
5.674
5.660
5.647
5.637
5.624
5.615
5.603
5.593
2.824
2.799
2.774
2.755
2.735
2.728
2.711
2.533
2.509
2.484
2.461
2.452
2.436
2.428
2.411
2.387
1.620
1.611
0.000
1.15
6.64
3.04
1.00
2.07
2.02
2.97
PhOS
CH3
H
1f
wmy-4-154
PPM

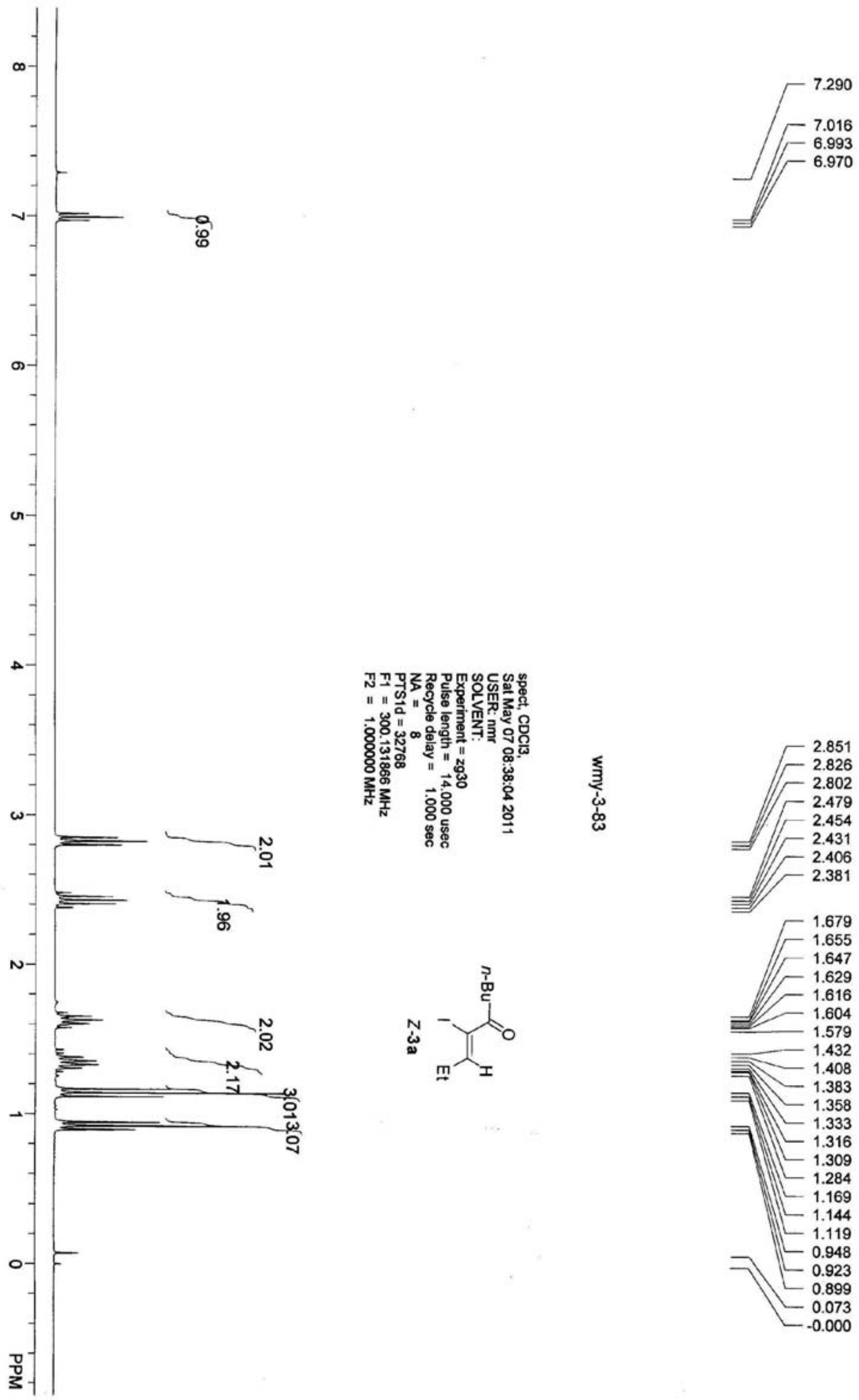

202.115
202.090
143.569
143.387
140.810
140.729
130.717
130.696
128.975
128.538
128.474
126.247
126.159
124.438
124.384
108.821
108.610
96.954
96.709
77.632
77.169
76.780
35.060
34.955
30.372
30.014
9.375
PhOS
CH3
H
1f
wmy-4-154
200
150
100
50
0 PPM

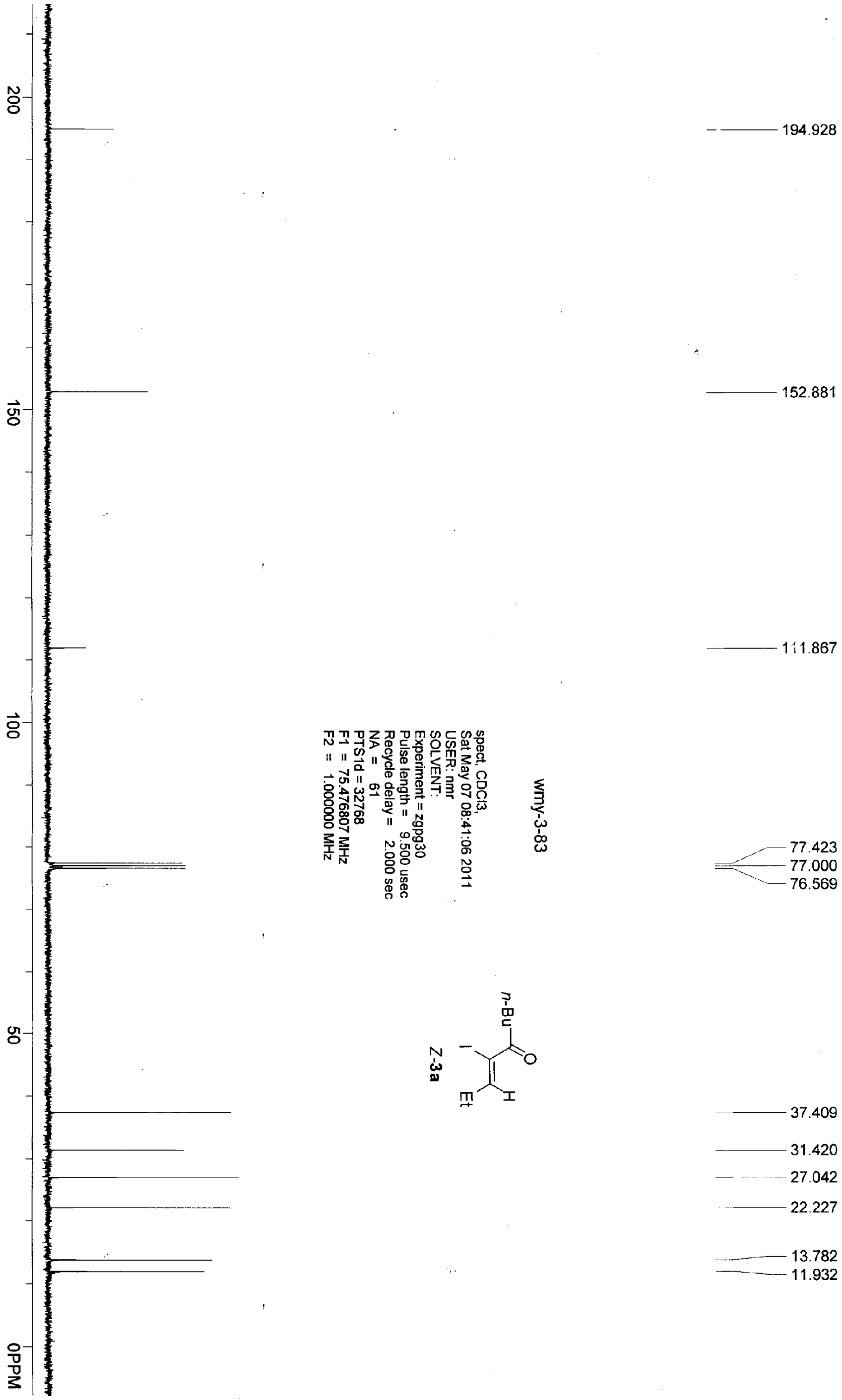

wmy-4-97
spect, CDCl3,
Sun Nov 27 06:59:25 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
PhOS
H
C4H9-n
1g
7.584
7.575
7.571
7.559
7.557
7.553
7.542
7.495
7.485
7.465
7.460
7.454
7.443
7.437
7.424
7.287
5.531
5.507
5.485
5.247
5.223
5.199
1.989
1.966
1.942
1.926
1.921
1.636
1.613
1.585
1.562
1.333
1.327
1.290
1.268
1.240
1.217
1.193
1.167
1.143
1.123
1.118
1.021
0.998
0.973
0.949
0.923
0.893
0.870
0.846
0.808
0.785
0.760
-0.000
2.01
3.05
0.58
0.45
1.05
1.17
11.22
1.26
0.99
1.69
1.75
PPM

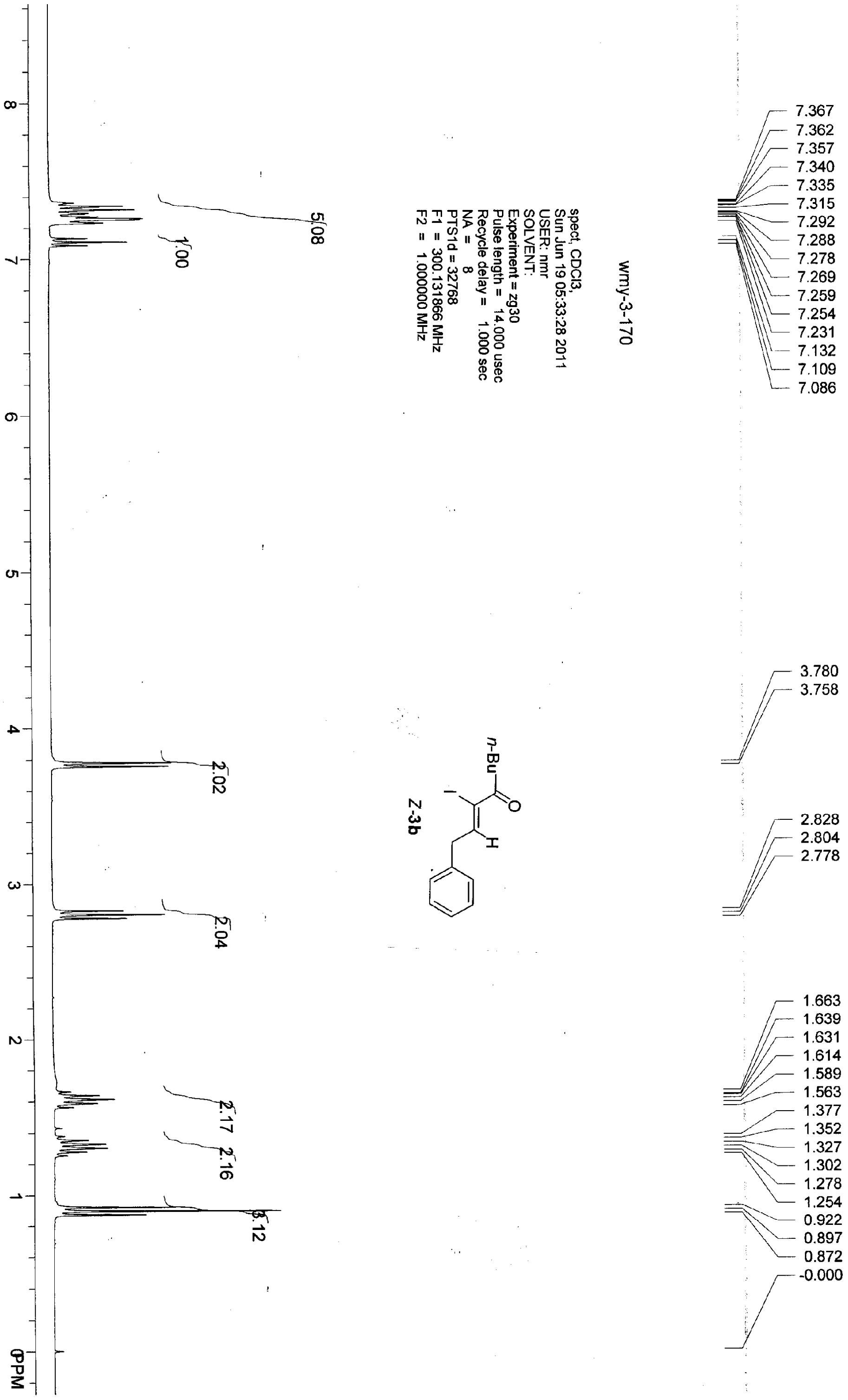

200
150
100
50
PPM
PhOS
H
C4H9-n
1g
wmy-4-97
200.334
199.600
144.637
144.473
130.342
130.268
128.450
126.494
125.457
125.023
124.678
100.130
99.940
77.422
77.000
76.579
35.252
35.102
31.027
30.492
30.052
29.877
28.099
27.578
22.071
22.041
13.697
13.609

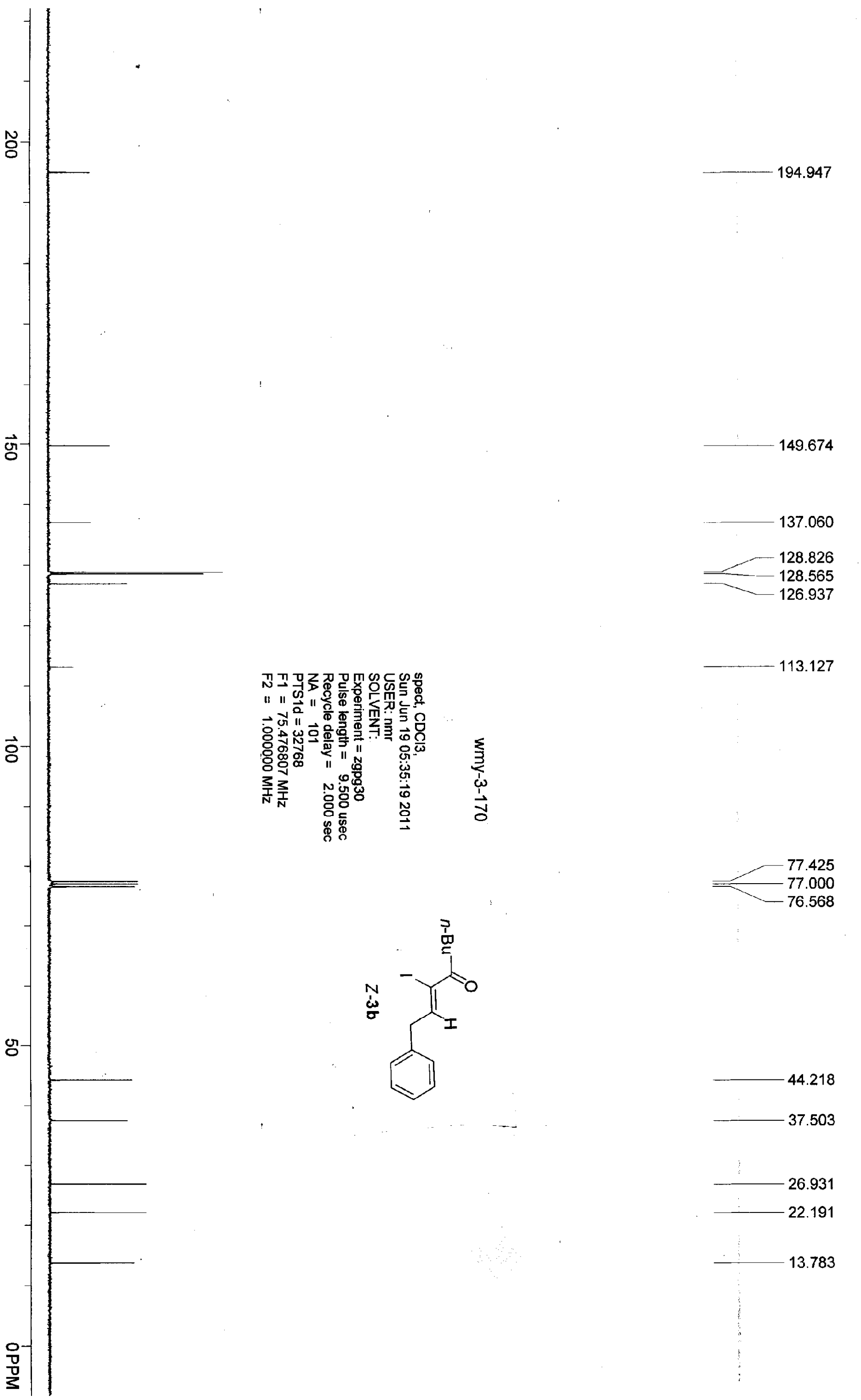

wmy-4-40
spect, CDCl3,
Sun Sep 25 02:39:55 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
Ph–S
Et
OH
n-C4H9
I
E-2a
5.07
1.00
1.01
1.03
1.01
4.38
2.37
6.18
PPM
7.332
7.328
7.321
7.303
7.302
7.294
7.283
7.271
7.262
7.256
7.247
7.240
7.239
7.233
7.226
7.216
4.589
4.566
4.543
4.520
2.564
2.542
2.511
2.493
2.467
2.344
2.319
2.293
2.278
2.268
2.247
2.026
2.003
1.733
1.705
1.682
1.660
1.636
1.612
1.588
1.563
1.538
1.500
1.473
1.446
1.328
1.303
1.279
1.254
1.230
1.206
0.910
0.885
0.875
0.860
0.850
0.826
0.000

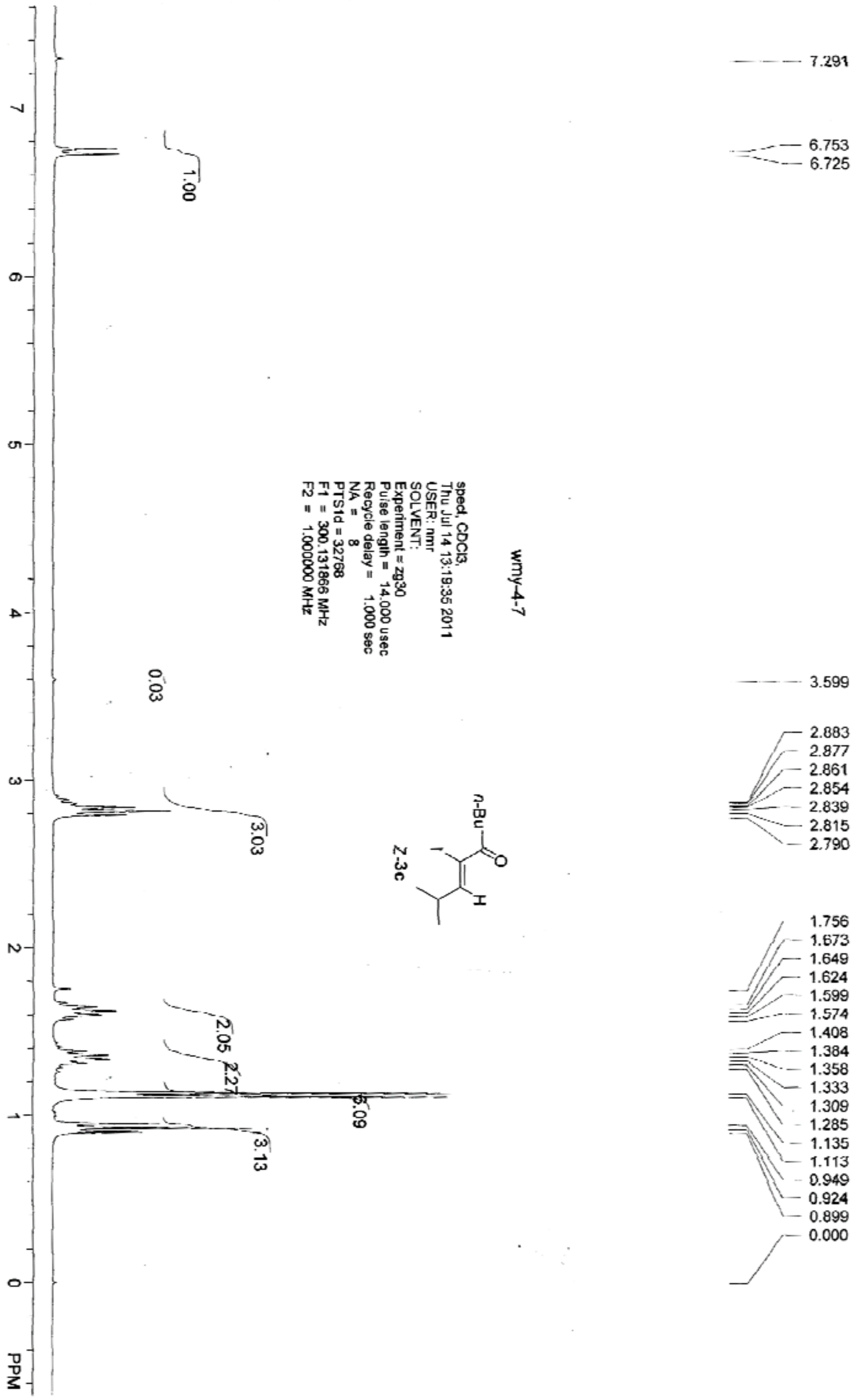

wmy-4-40
spect, CDCl3,
Sun Sep 25 02:42:25 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 62
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
137.704
134.316
130.365
129.047
127.068
120.055
77.424
77.000
76.575
74.237
41.384
30.989
29.939
22.179
13.836
9.503
Ph–S
Et
OH
I
n-C4H9
E-2a
160
140
120
100
80
60
40
20
0
PPM

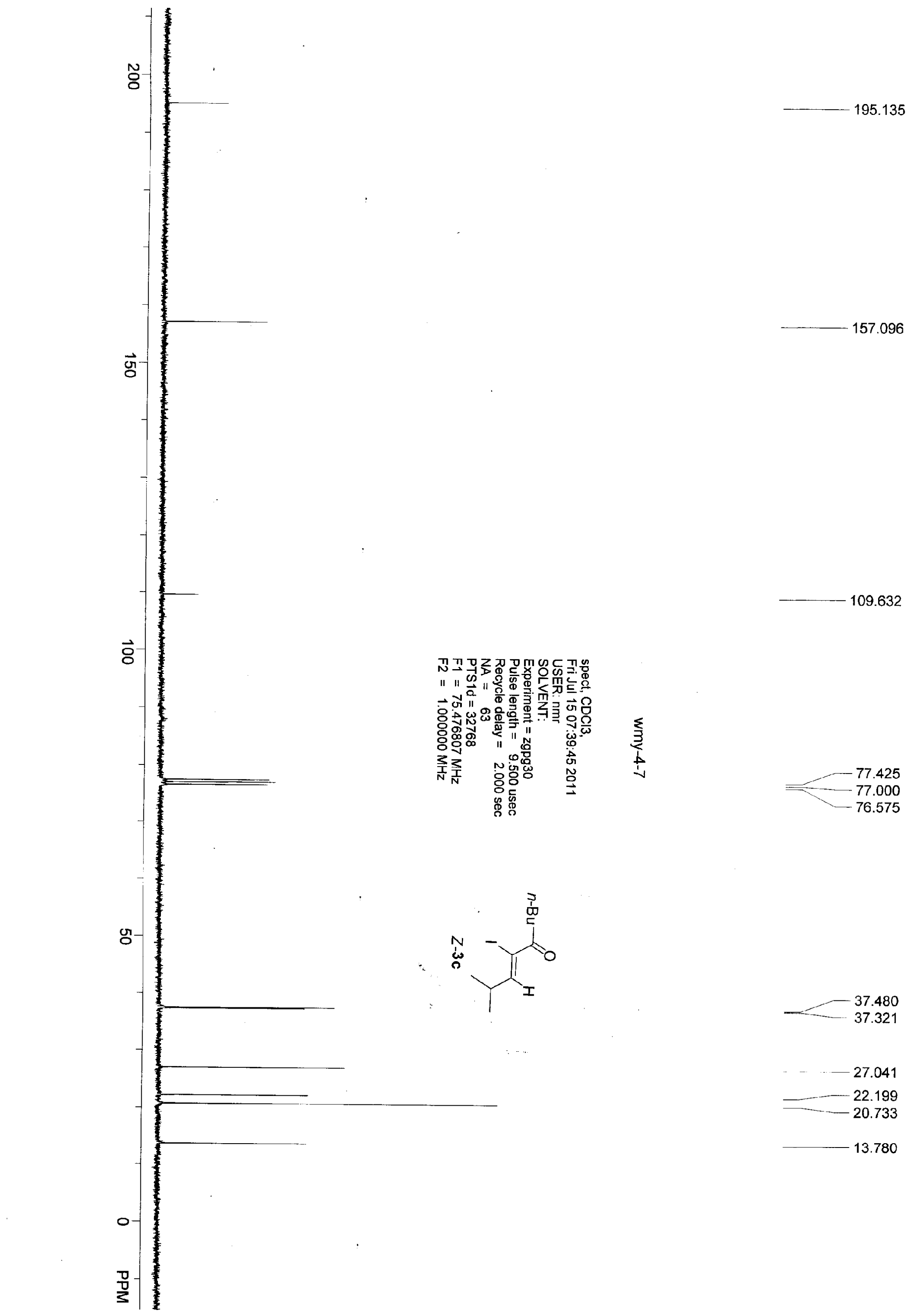

wmy-3-83
spect, CDCl3
Sat May 07 08:38:04 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
n-Bu
O
H
I
Et
Z-3a
7.290
7.016
6.993
6.970
2.851
2.826
2.802
2.479
2.454
2.431
2.406
2.381
1.679
1.655
1.647
1.629
1.616
1.604
1.579
1.432
1.408
1.383
1.358
1.333
1.316
1.309
1.284
1.169
1.144
1.119
0.948
0.923
0.899
0.073
-0.000
0.99
2.01
1.96
2.02
2.17
3.01
3.07
PPM

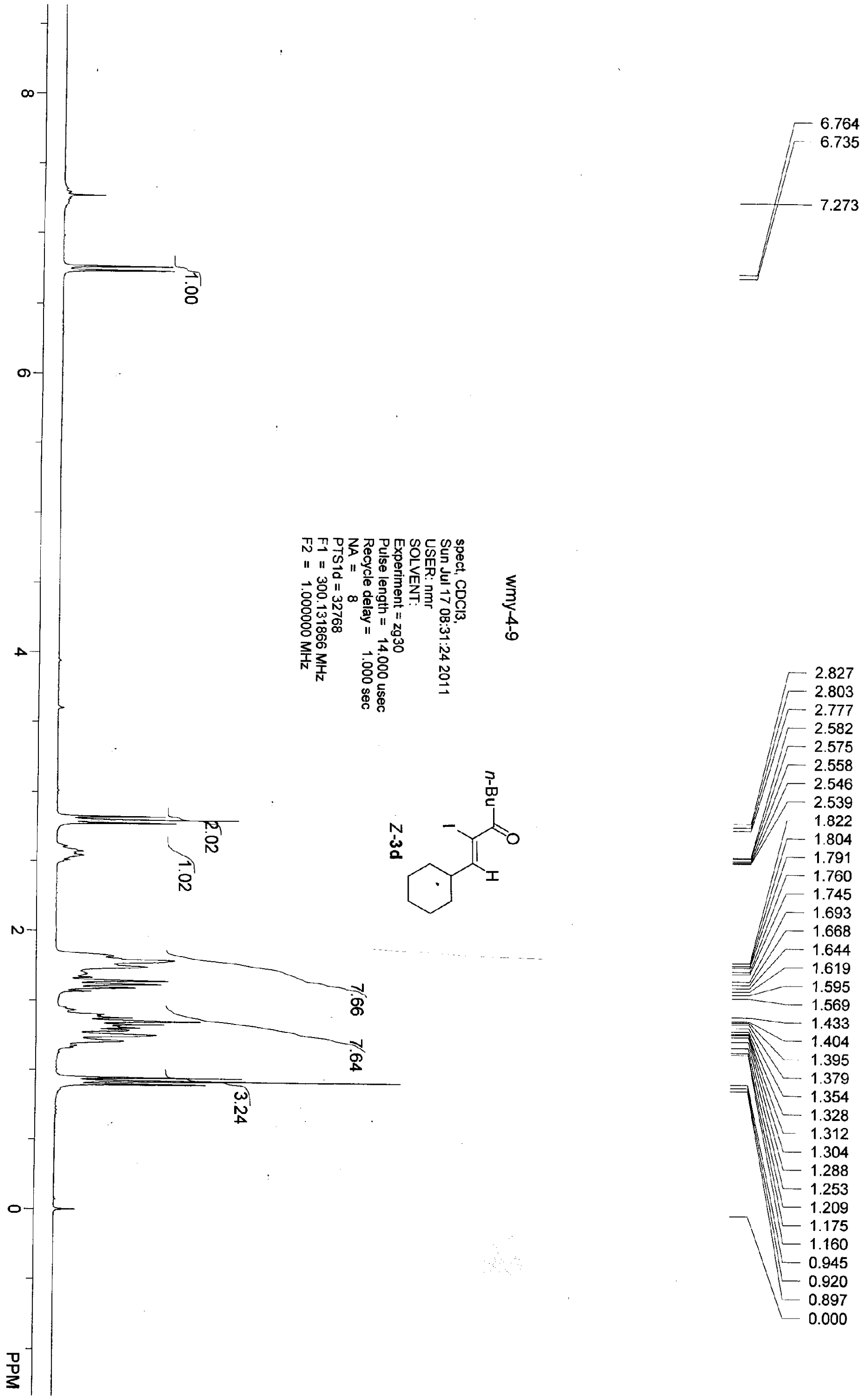

194.928
152.881
111.867
77.423
77.000
76.569
37.409
31.420
27.042
22.227
13.782
11.932
wmy-3-83
spect, CDCl3,
Sat May 07 08:41:06 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 61
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
n-Bu
O
H
I
Et
Z-3a
200
150
100
50
0PPM

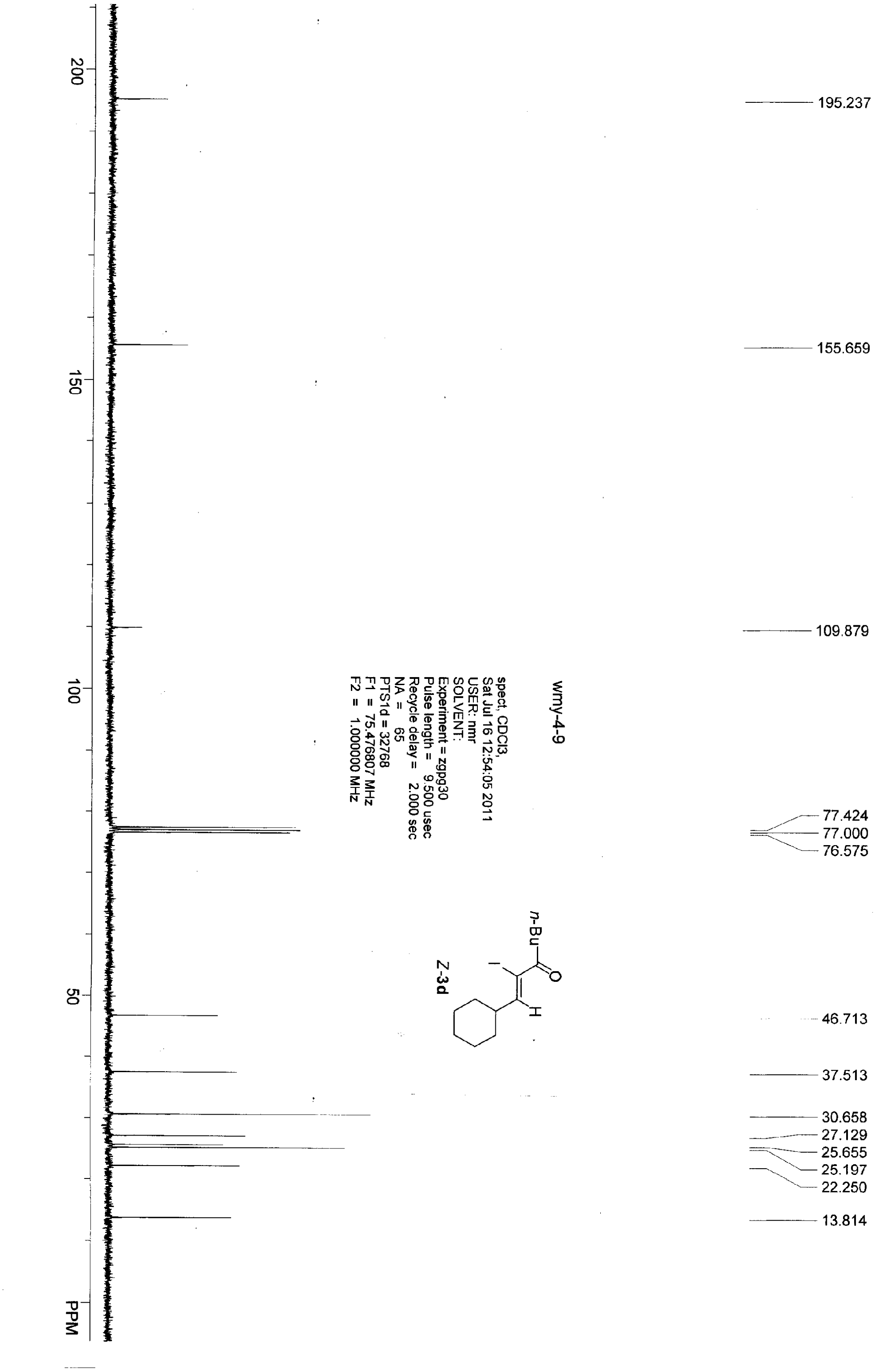

wmy-3-170
spect, CDCl3,
Sun Jun 19 05:33:28 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
n-Bu
O
H
I
Z-3b
7.367
7.362
7.357
7.340
7.335
7.315
7.292
7.288
7.278
7.269
7.259
7.254
7.231
7.132
7.109
7.086
3.780
3.758
2.828
2.804
2.778
1.663
1.639
1.631
1.614
1.589
1.563
1.377
1.352
1.327
1.302
1.278
1.254
0.922
0.897
0.872
-0.000
5.08
1.00
2.02
2.04
2.17
2.16
3.12
8
7
6
5
4
3
2
1
0
PPM

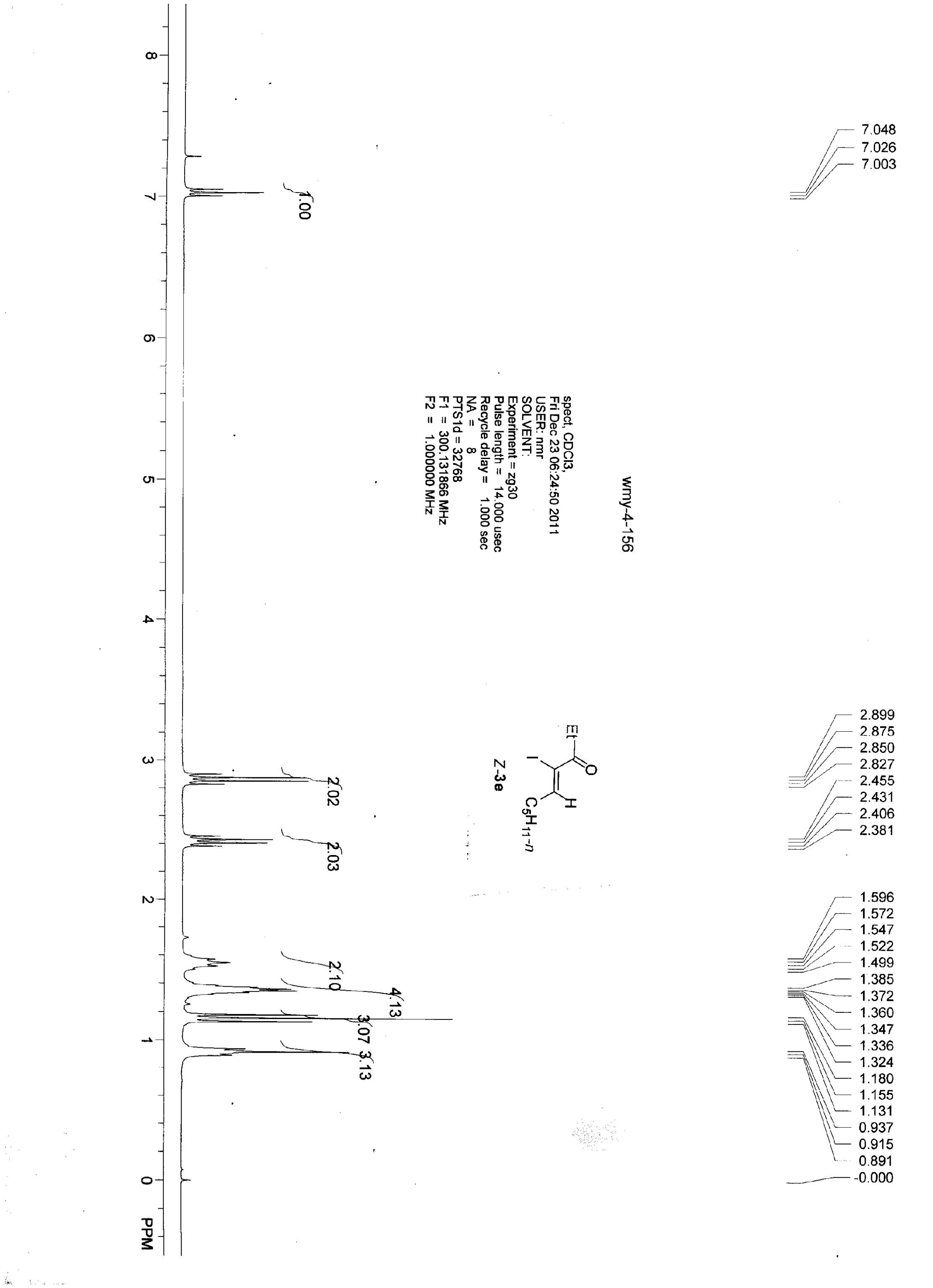

wmy-3-170
spect, CDCl3.
Sun Jun 19 05:35:19 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 101
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
n-Bu
O
H
I
Z-3b
194.947
149.674
137.060
128.826
128.565
126.937
113.127
77.425
77.000
76.568
44.218
37.503
26.931
22.191
13.783
200
150
100
50
0PPM

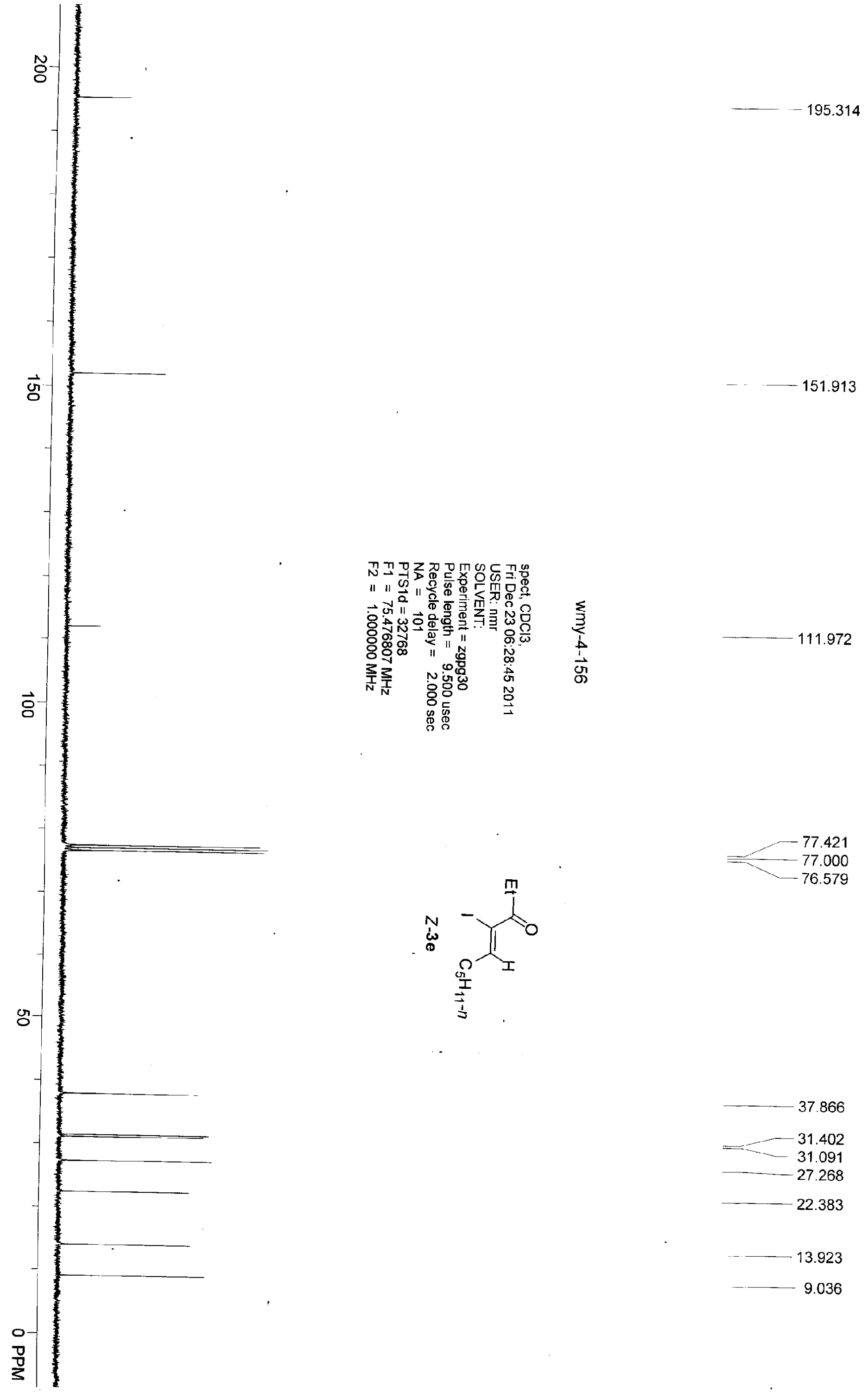

wmy-4-7
sped, CDCl3,
Thu Jul 14 13:19:35 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
n-Bu
O
I
H
Z-3c
1.00
0.03
3.03
2.05
2.27
6.09
3.13
PPM
7.291
6.753
6.725
3.599
2.883
2.877
2.861
2.854
2.839
2.815
2.790
1.756
1.673
1.649
1.624
1.599
1.574
1.408
1.384
1.358
1.333
1.309
1.285
1.135
1.113
0.949
0.924
0.899
0.000

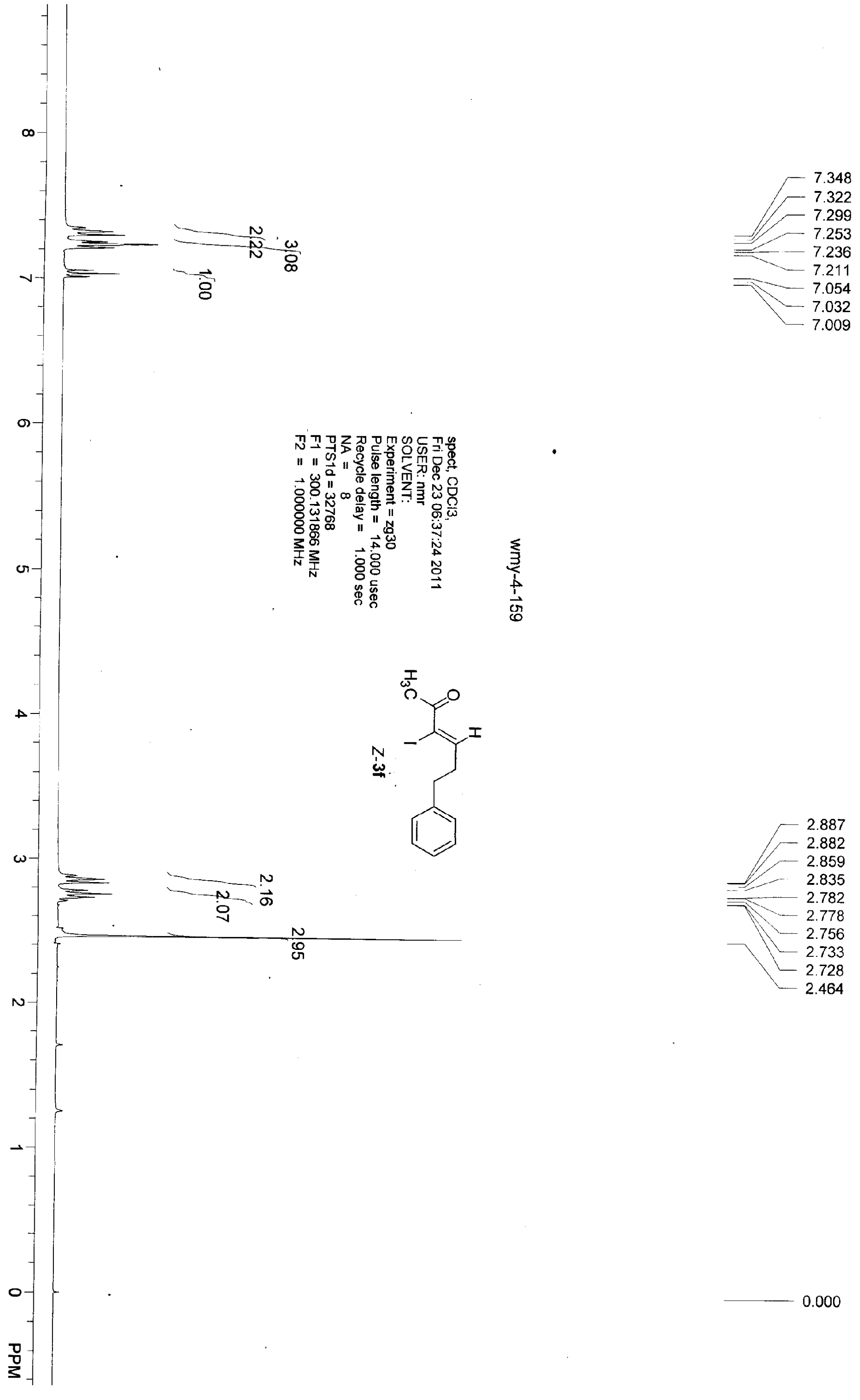

wmy-4-7
spect, CDCl3,
Fri Jul 15 07:39:45 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 63
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
n-Bu
O
H
I
Z-3c
195.135
157.096
109.632
77.425
77.000
76.575
37.480
37.321
27.041
22.199
20.733
13.780
200
150
100
50
0
PPM

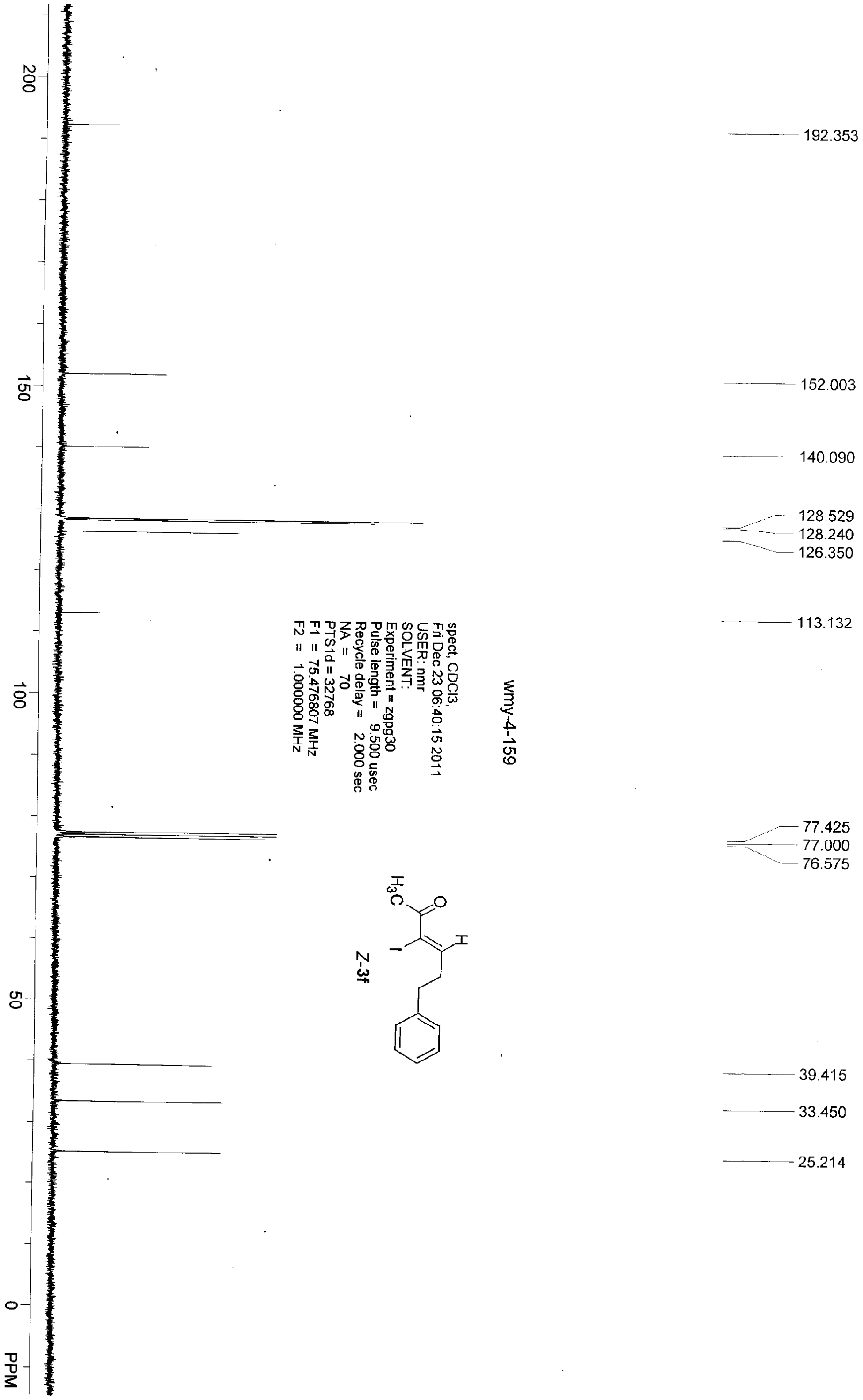

wmy-4-9
spect, CDCl3,
Sun Jul 17 08:31:24 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
n-Bu
O
I
H
Z-3d
1.00
2.02
1.02
7.66
7.64
3.24
8
6
4
2
0
PPM
6.764
6.735
7.273
2.827
2.803
2.777
2.582
2.575
2.558
2.546
2.539
1.822
1.804
1.791
1.760
1.745
1.693
1.668
1.644
1.619
1.595
1.569
1.433
1.404
1.395
1.379
1.354
1.328
1.312
1.304
1.288
1.253
1.209
1.175
1.160
0.945
0.920
0.897
0.000

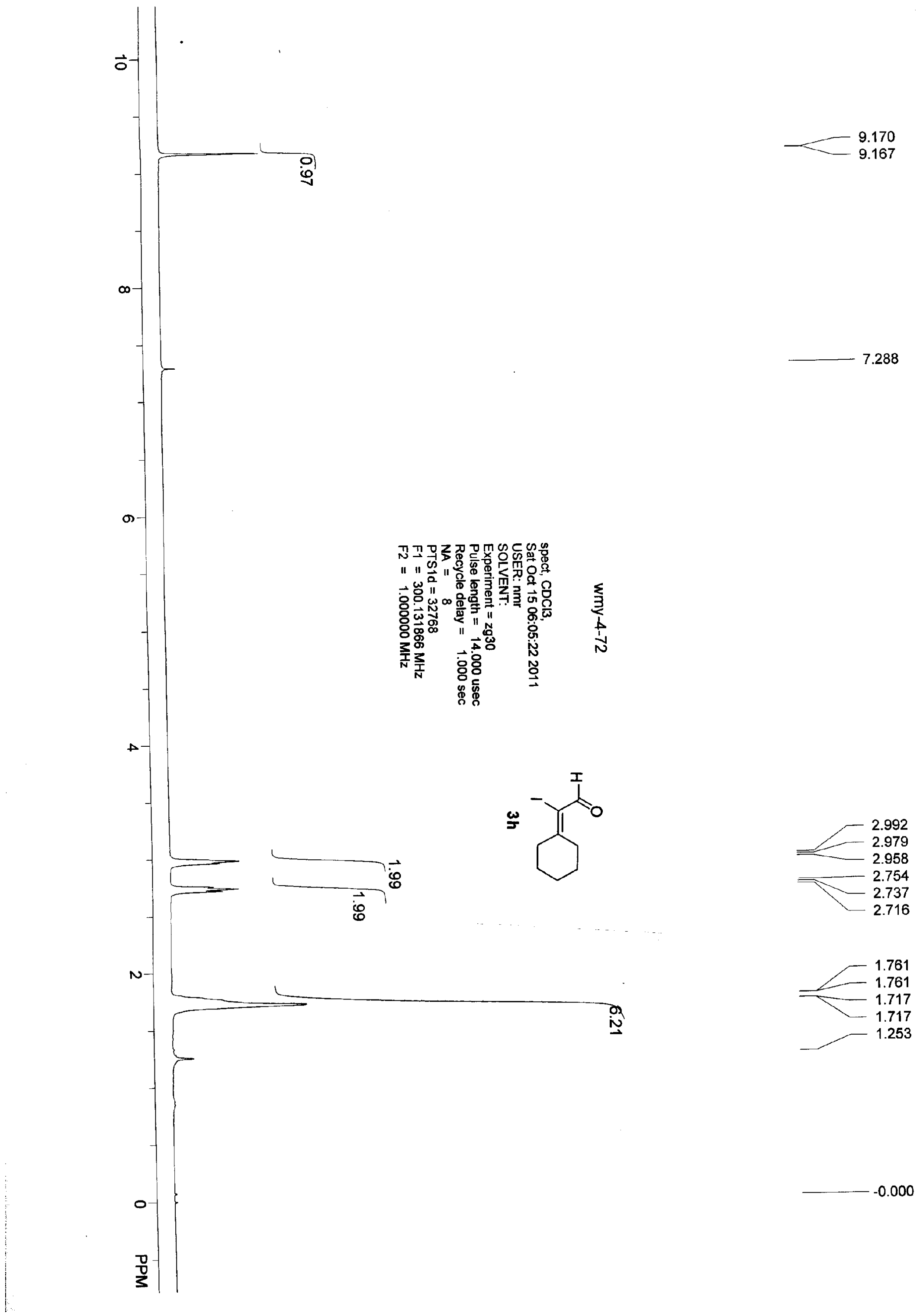

wmy-4-9
spect, CDCl3,
Sat Jul 16 12:54:05 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 65
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
n-Bu
O
H
I
Z-3d
195.237
155.659
109.879
77.424
77.000
76.575
46.713
37.513
30.658
27.129
25.655
25.197
22.250
13.814
200
150
100
50
PPM

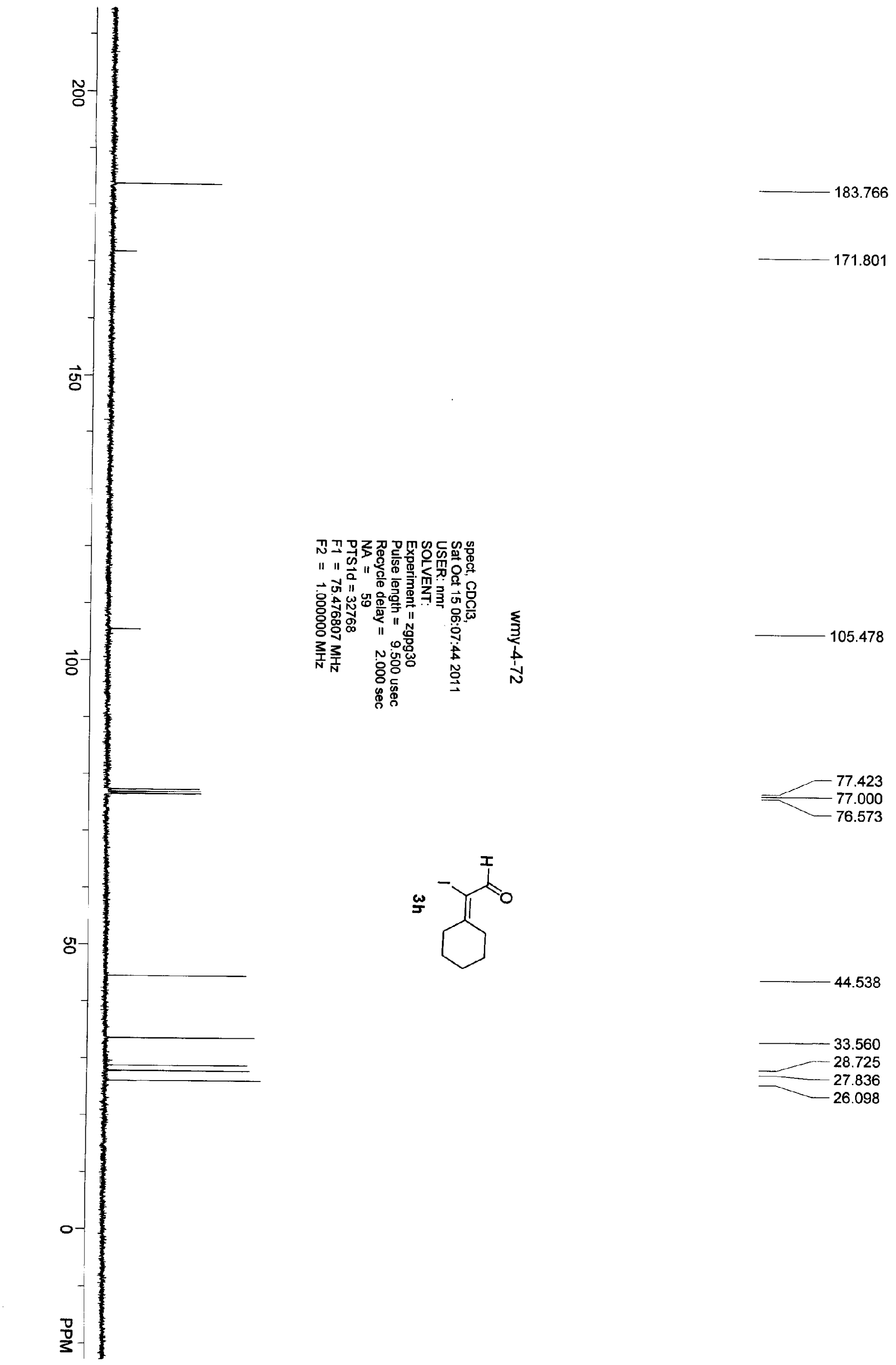

wmy-4-156
spect, CDCl3,
Fri Dec 23 06:24:50 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
Et
O
H
I
C5H11-n
Z-3e
7.048
7.026
7.003
2.899
2.875
2.850
2.827
2.455
2.431
2.406
2.381
1.596
1.572
1.547
1.522
1.499
1.385
1.372
1.360
1.347
1.336
1.324
1.180
1.155
1.131
0.937
0.915
0.891
-0.000
1.00
2.02
2.03
2.10
4.13
3.07
3.13
8
7
6
5
4
3
2
1
0
PPM

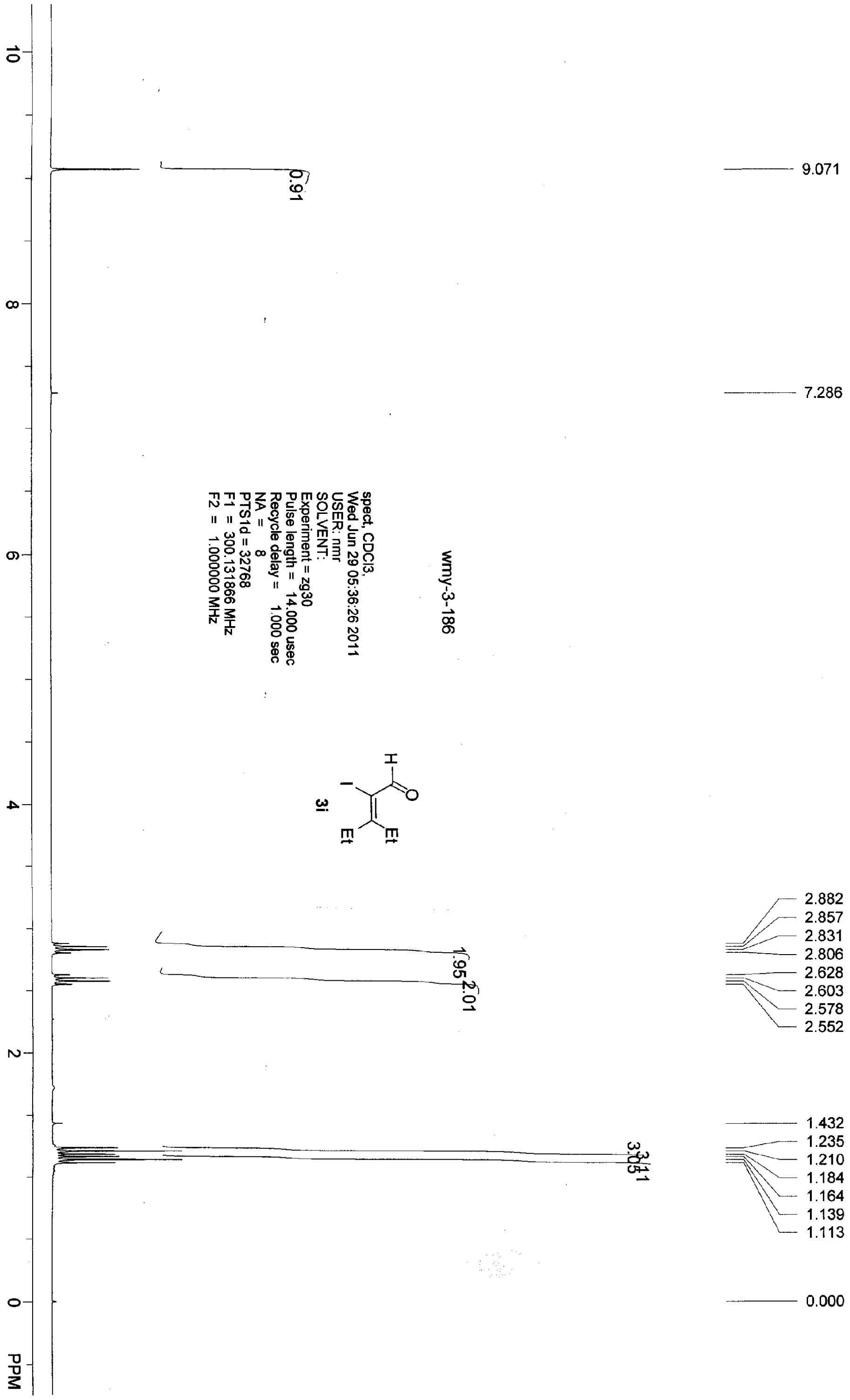

wmy-4-156
spect, CDCl3,
Fri Dec 23 06:28:45 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 101
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
Et
O
H
I
C5H11-n
Z-3e
195.314
151.913
111.972
77.421
77.000
76.579
37.866
31.402
31.091
27.268
22.383
13.923
9.036
200
150
100
50
0 PPM

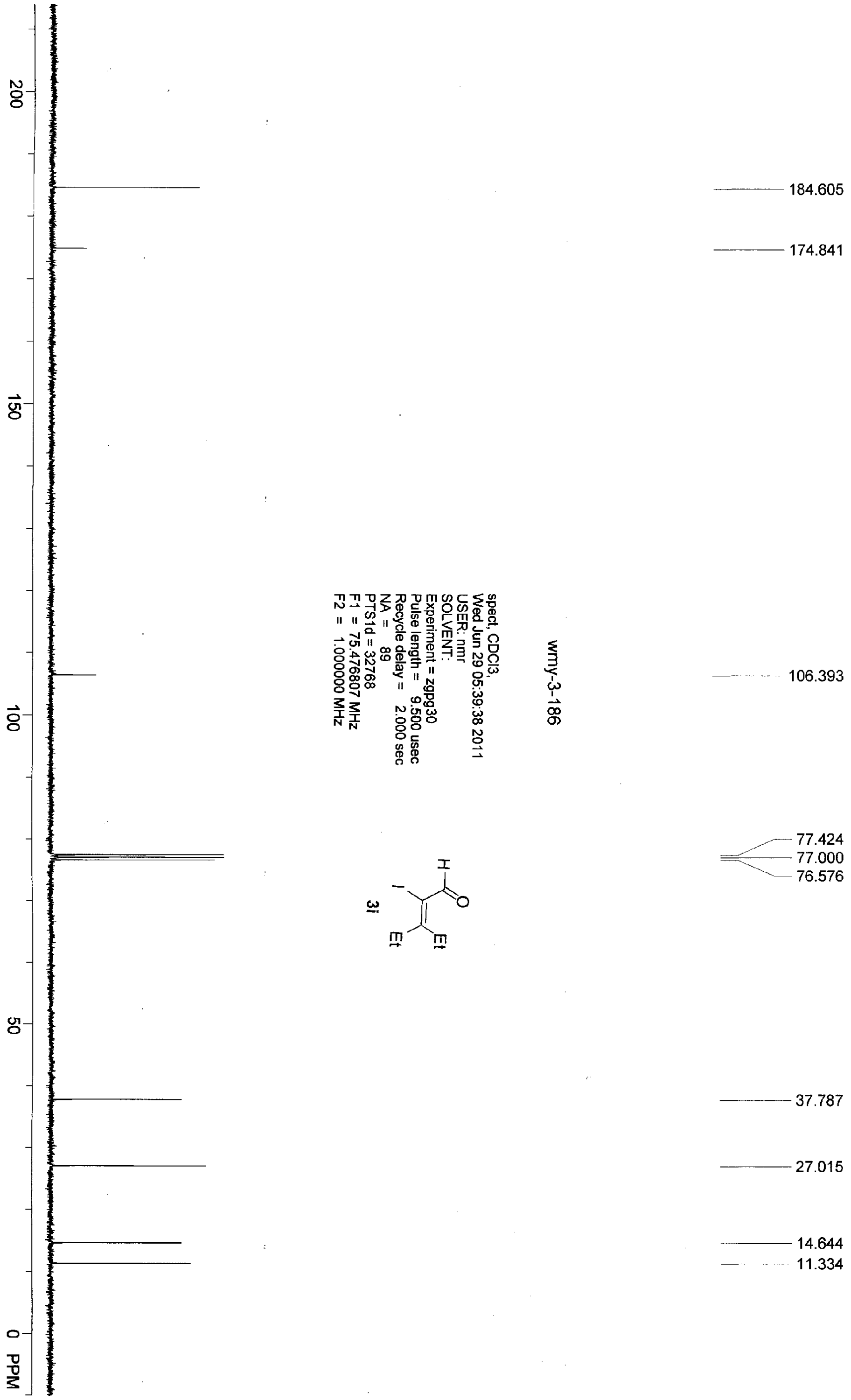

wmy-4-159
spect, CDCl3,
Fri Dec 23 06:37:24 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
Z-3f
7.348
7.322
7.299
7.253
7.236
7.211
7.054
7.032
7.009
2.887
2.882
2.859
2.835
2.782
2.778
2.756
2.733
2.728
2.464
0.000
3.08
2.22
1.00
2.16
2.07
2.95
PPM

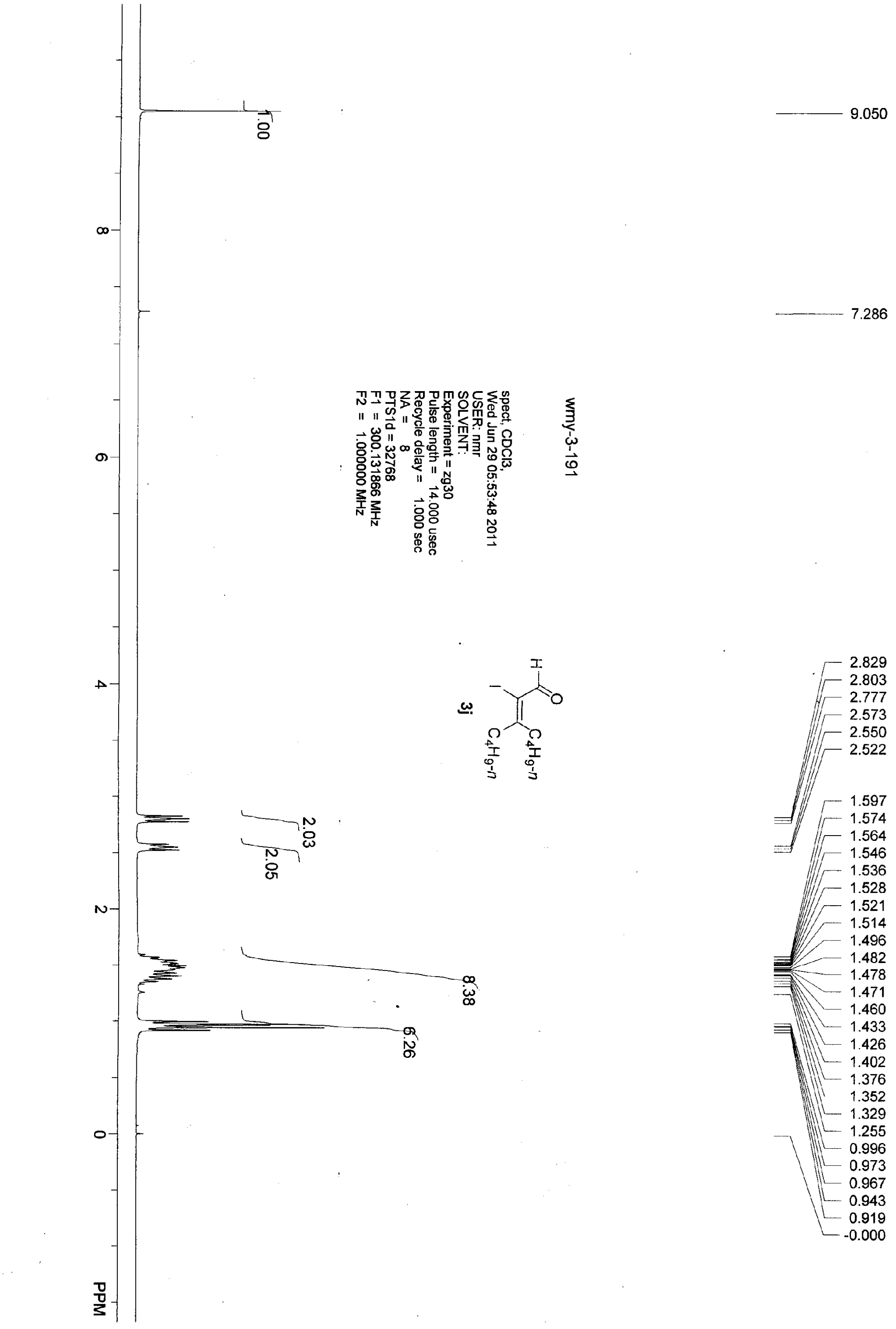

wmy-4-159
spect, CDCl3,
Fri Dec 23 06:40:15 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 70
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
192.353
152.003
140.090
128.529
128.240
126.350
113.132
77.425
77.000
76.575
39.415
33.450
25.214
Z-3f
200
150
100
50
0
PPM

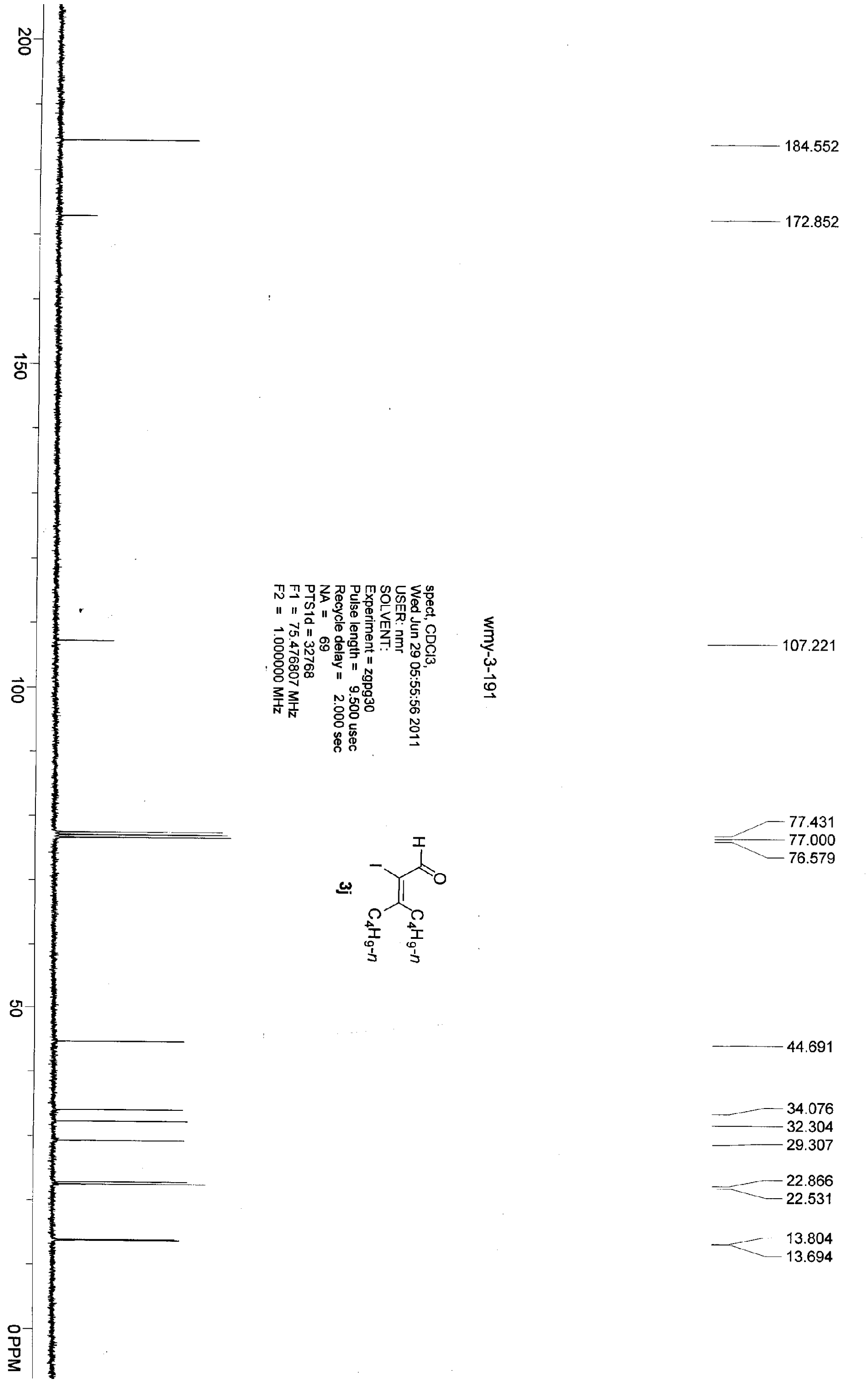

wmy-4-72
spect, CDCl3,
Sat Oct 15 06:05:22 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
3h
9.170
9.167
7.288
2.992
2.979
2.958
2.754
2.737
2.716
1.761
1.761
1.717
1.717
1.253
-0.000
0.97
1.99
1.99
6.21
PPM

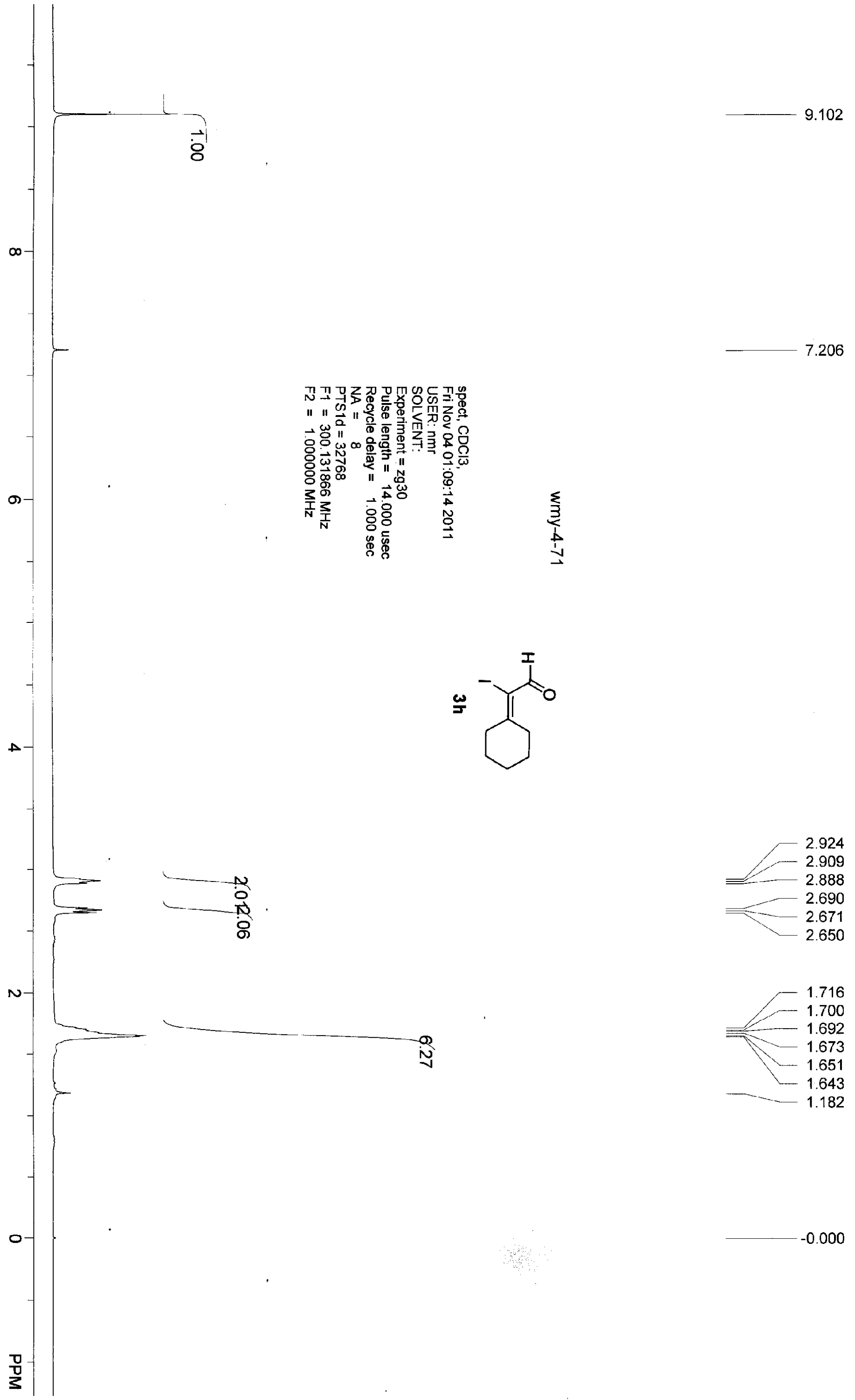

wmy-4-72
spect, CDCl3,
Sat Oct 15 06:07:44 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 59
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
3h
183.766
171.801
105.478
77.423
77.000
76.573
44.538
33.560
28.725
27.836
26.098
200
150
100
50
0
PPM

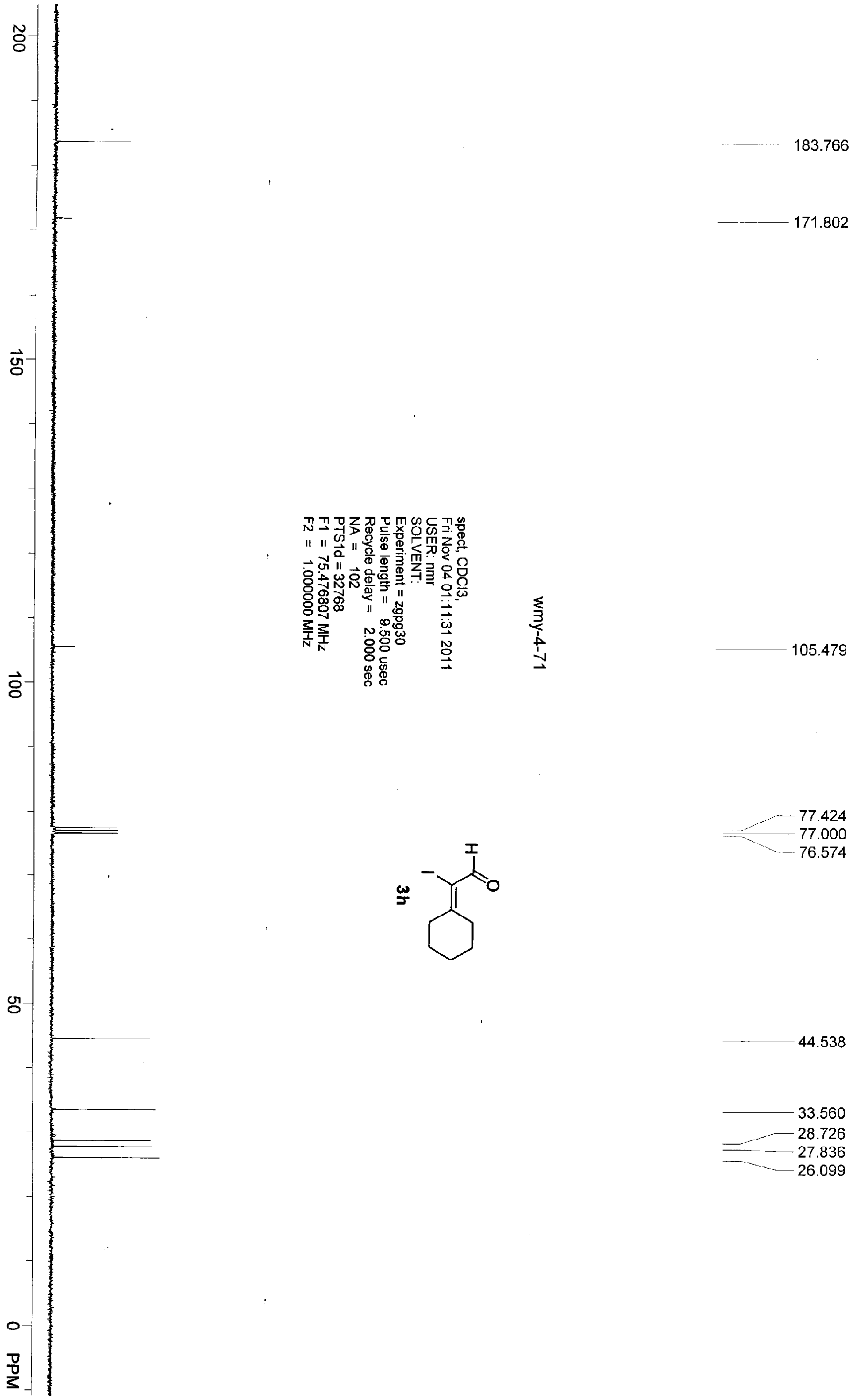

wmy-3-186
spect, CDCl3,
Wed Jun 29 05:36:26 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
3i
9.071
7.286
2.882
2.857
2.831
2.806
2.628
2.603
2.578
2.552
1.432
1.235
1.210
1.184
1.164
1.139
1.113
0.000
0.91
1.95
2.01
3.05
3.11
10
8
6
4
2
0
PPM

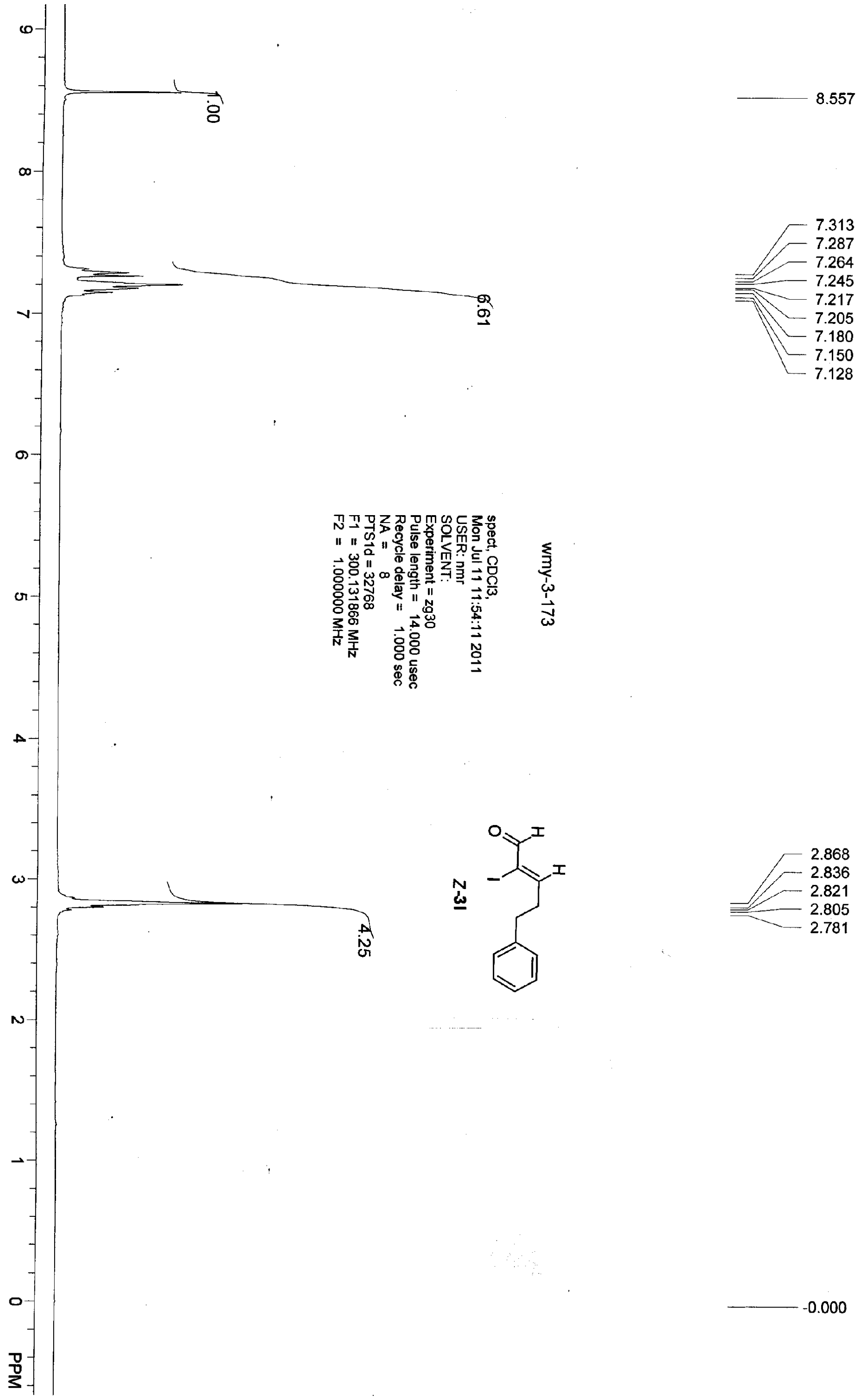

wmy-3-186
spect, CDCl3,
Wed Jun 29 05:39:38 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 89
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
3i
184.605
174.841
106.393
77.424
77.000
76.576
37.787
27.015
14.644
11.334
200
150
100
50
0 PPM

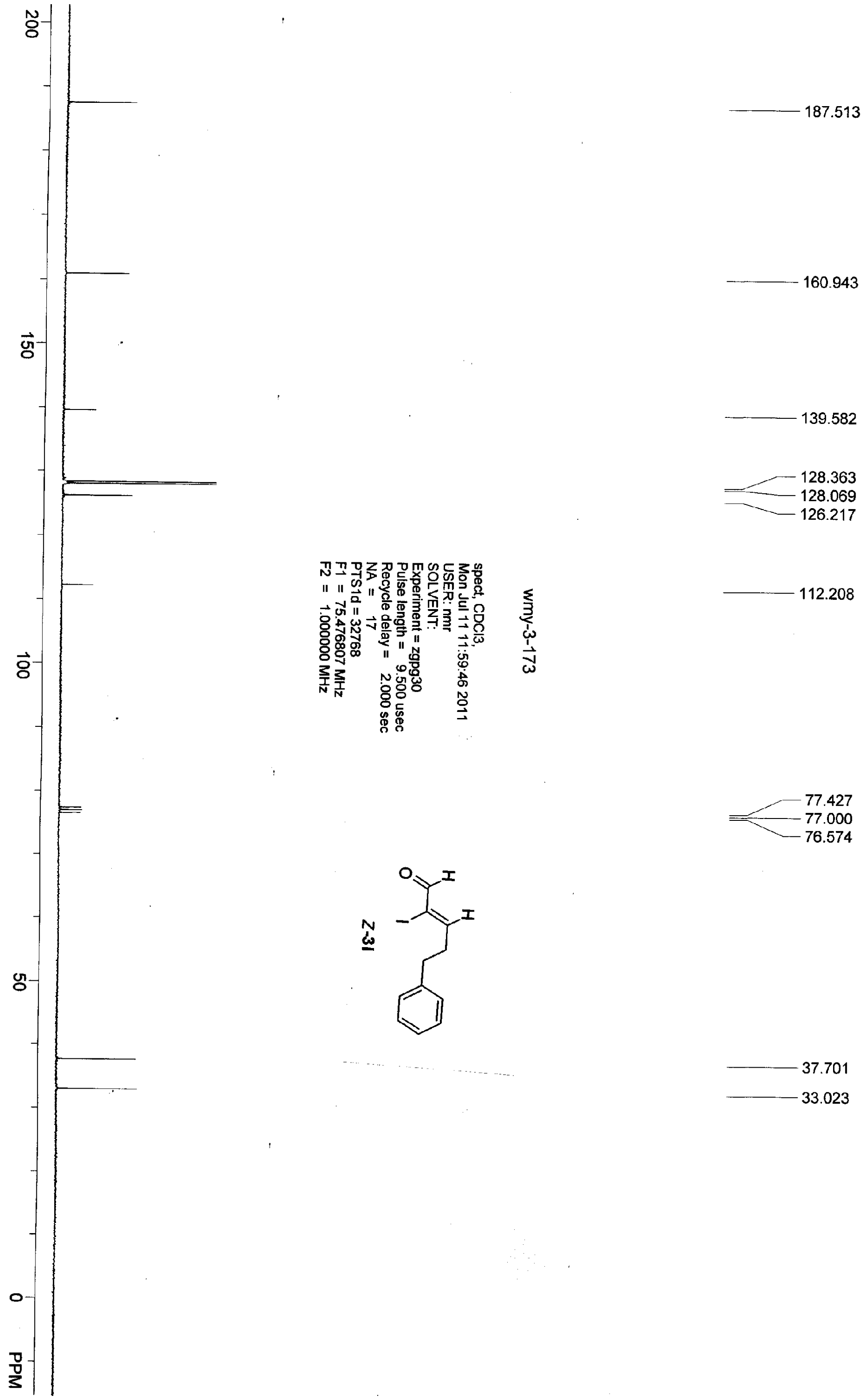

wmy-3-191
spect, CDCl3,
Wed Jun 29 05:53:48 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
3j
C4H9-n
C4H9-n
H
O
I
1.00
2.03
2.05
8.38
6.26
9.050
7.286
2.829
2.803
2.777
2.573
2.550
2.522
1.597
1.574
1.564
1.546
1.536
1.528
1.521
1.514
1.496
1.482
1.478
1.471
1.460
1.433
1.426
1.402
1.376
1.352
1.329
1.255
0.996
0.973
0.967
0.943
0.919
-0.000
8
6
4
2
0
PPM

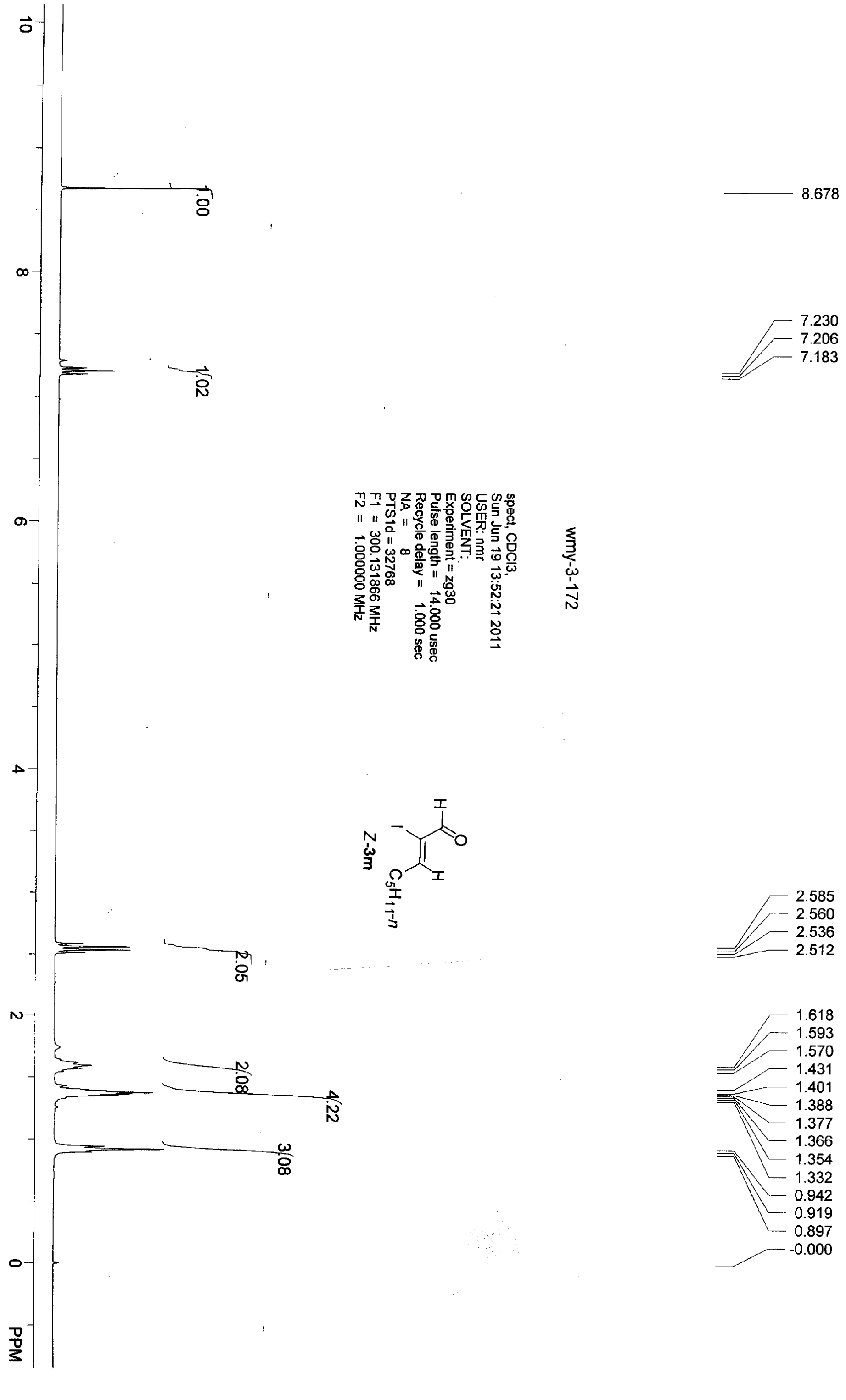

wmy-3-191
spect, CDCl3,
Wed Jun 29 05:55:56 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 69
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
3j
184.552
172.852
107.221
77.431
77.000
76.579
44.691
34.076
32.304
29.307
22.866
22.531
13.804
13.694
200
150
100
50
0PPM

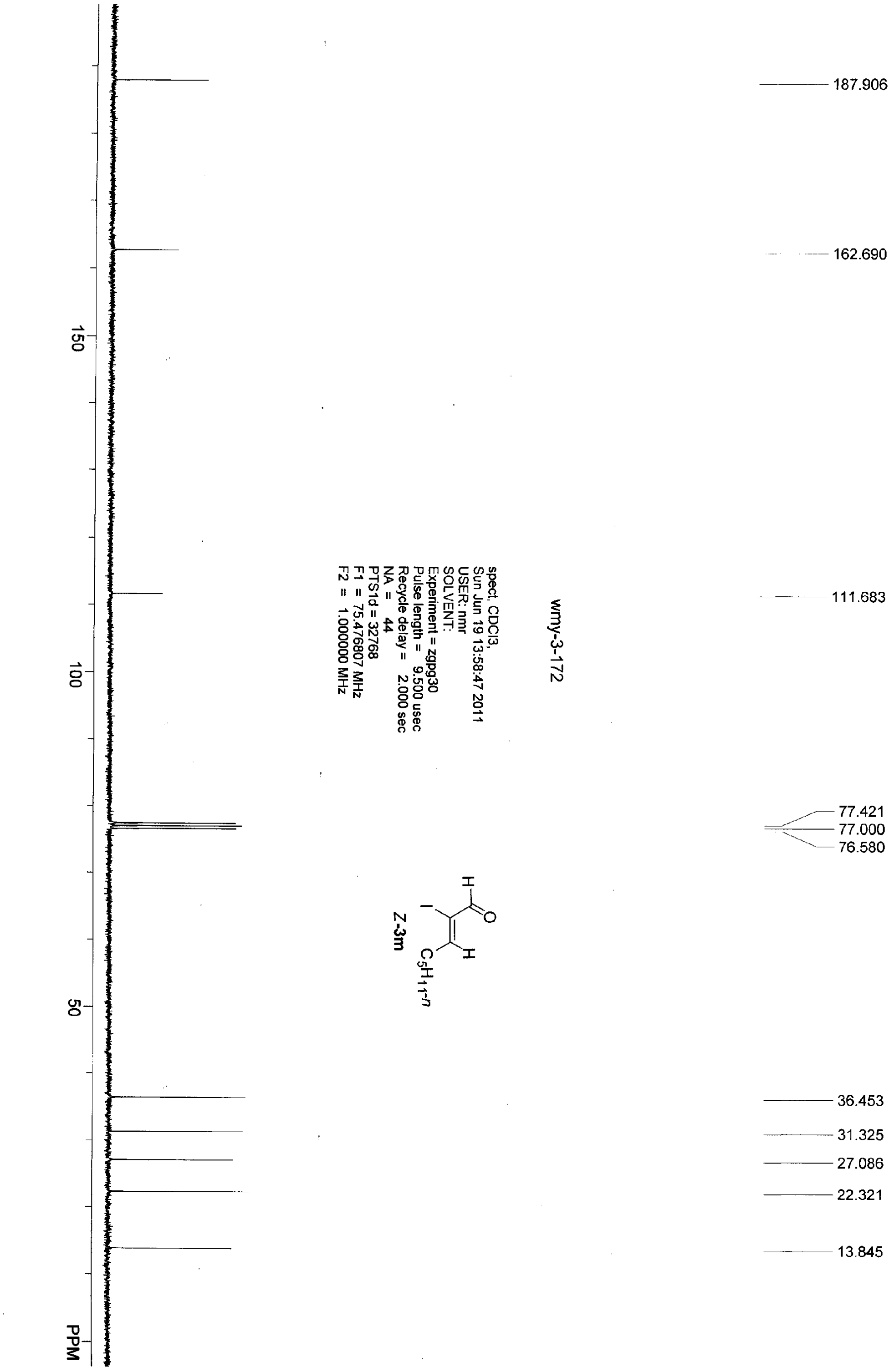

wmy-4-71
spect, CDCl3,
Fri Nov 04 01:09:14 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
3h
9.102
7.206
2.924
2.909
2.888
2.690
2.671
2.650
1.716
1.700
1.692
1.673
1.651
1.643
1.182
-0.000
1.00
2.01
2.06
6.27
PPM

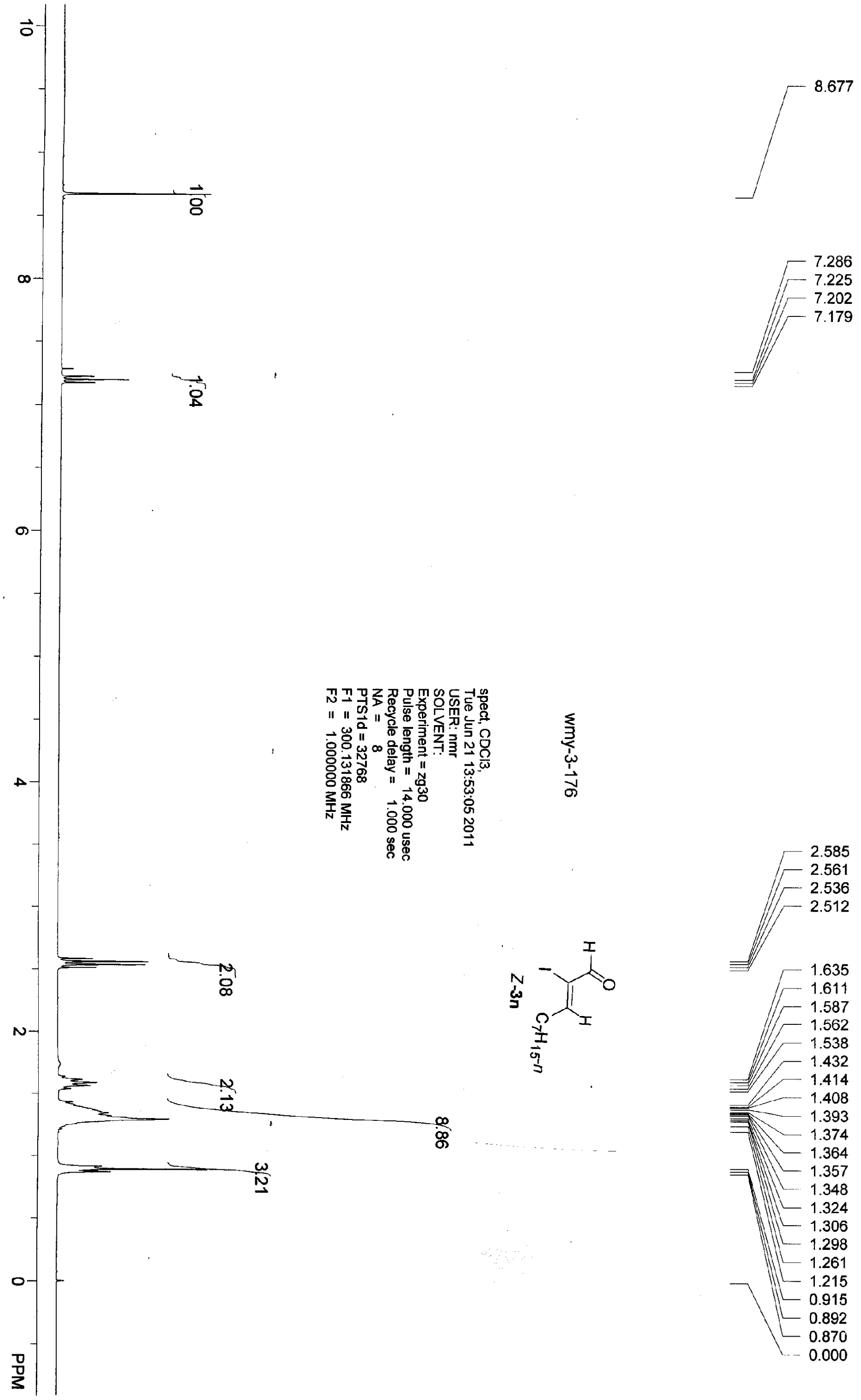

wmy-4-71
spect. CDCl3,
Fri Nov 04 01:11:31 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 102
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
3h
183.766
171.802
105.479
77.424
77.000
76.574
44.538
33.560
28.726
27.836
26.099
200
150
100
50
0
PPM

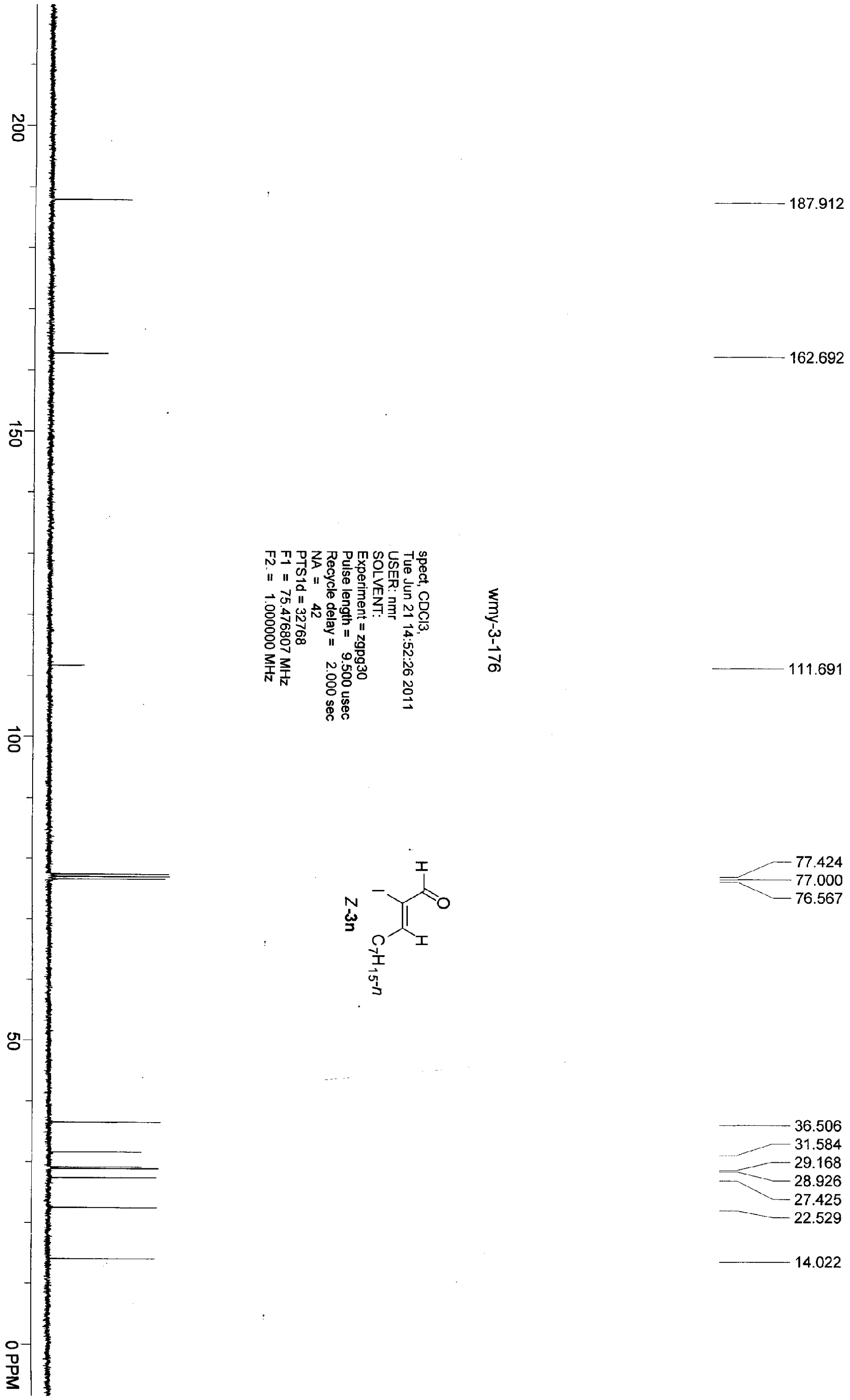

wmy-3-173
spect, CDCl3,
Mon Jul 11 11:54:11 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
Z-31
8.557
7.313
7.287
7.264
7.245
7.217
7.205
7.180
7.150
7.128
2.868
2.836
2.821
2.805
2.781
-0.000
1.00
6.61
4.25
PPM

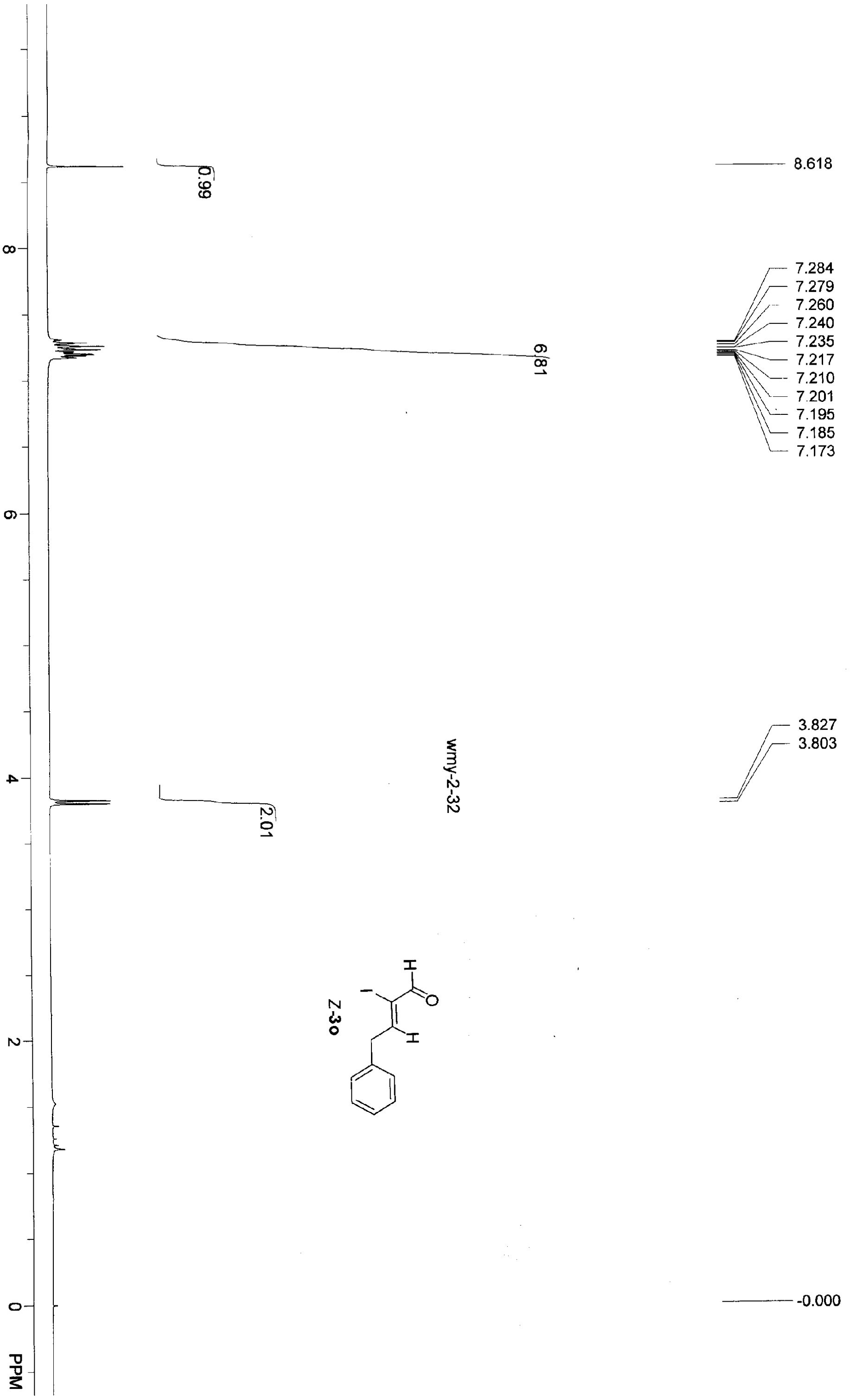

187.513
160.943
139.582
128.363
128.069
126.217
112.208
77.427
77.000
76.574
37.701
33.023
wmy-3-173
spect, CDCl3,
Mon Jul 11 11:59:46 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 17
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
Z-3l
200
150
100
50
0
PPM


wmy-3-172
spect, CDCl3,
Sun Jun 19 13:52:21 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
Z-3m
8.678
7.230
7.206
7.183
2.585
2.560
2.536
2.512
1.618
1.593
1.570
1.431
1.401
1.388
1.377
1.366
1.354
1.332
0.942
0.919
0.897
-0.000
1.00
1.02
2.05
2.08
4.22
3.08
PPM

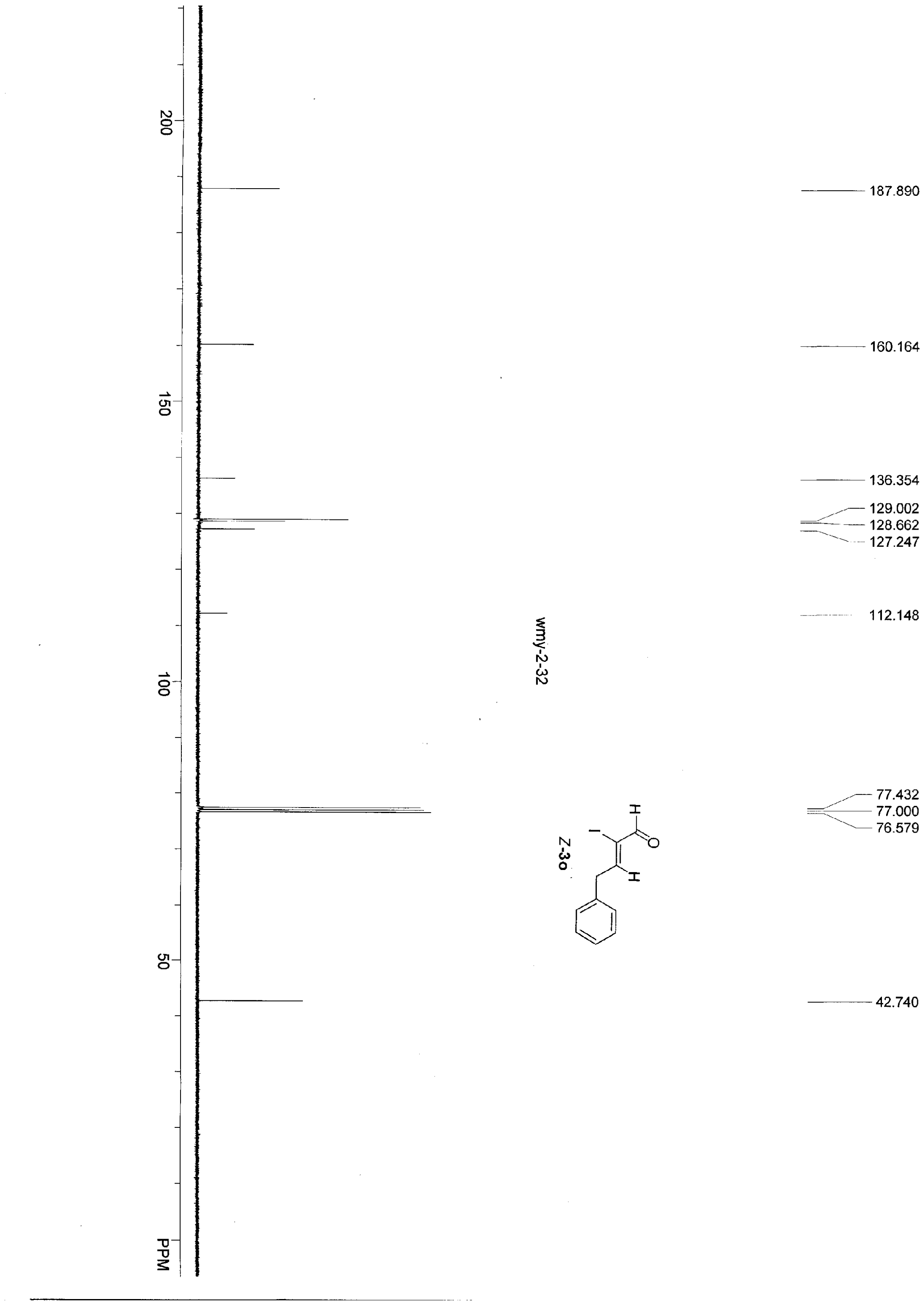

187.906
162.690
111.683
77.421
77.000
76.580
36.453
31.325
27.086
22.321
13.845
wmy-3-172
spect, CDCl3,
Sun Jun 19 13:58:47 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 44
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
Z-3m
150
100
50
PPM

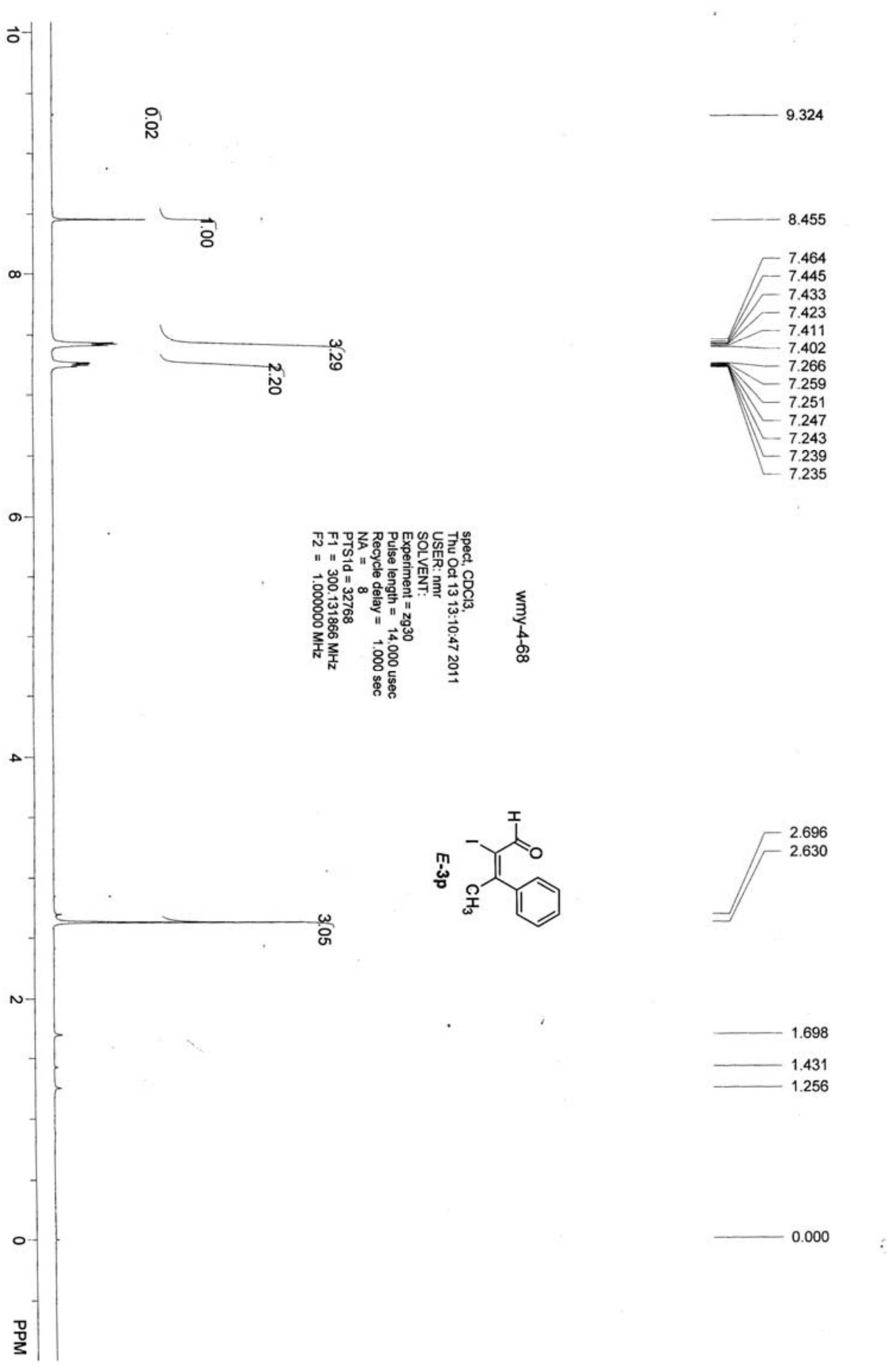

wmy-3-176
spect, CDCl3,
Tue Jun 21 13:53:05 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
Z-3n
8.677
7.286
7.225
7.202
7.179
2.585
2.561
2.536
2.512
1.635
1.611
1.587
1.562
1.538
1.432
1.414
1.408
1.393
1.374
1.364
1.357
1.348
1.324
1.306
1.298
1.261
1.215
0.915
0.892
0.870
0.000
1.00
1.04
2.08
2.13
8.86
3.21
PPM

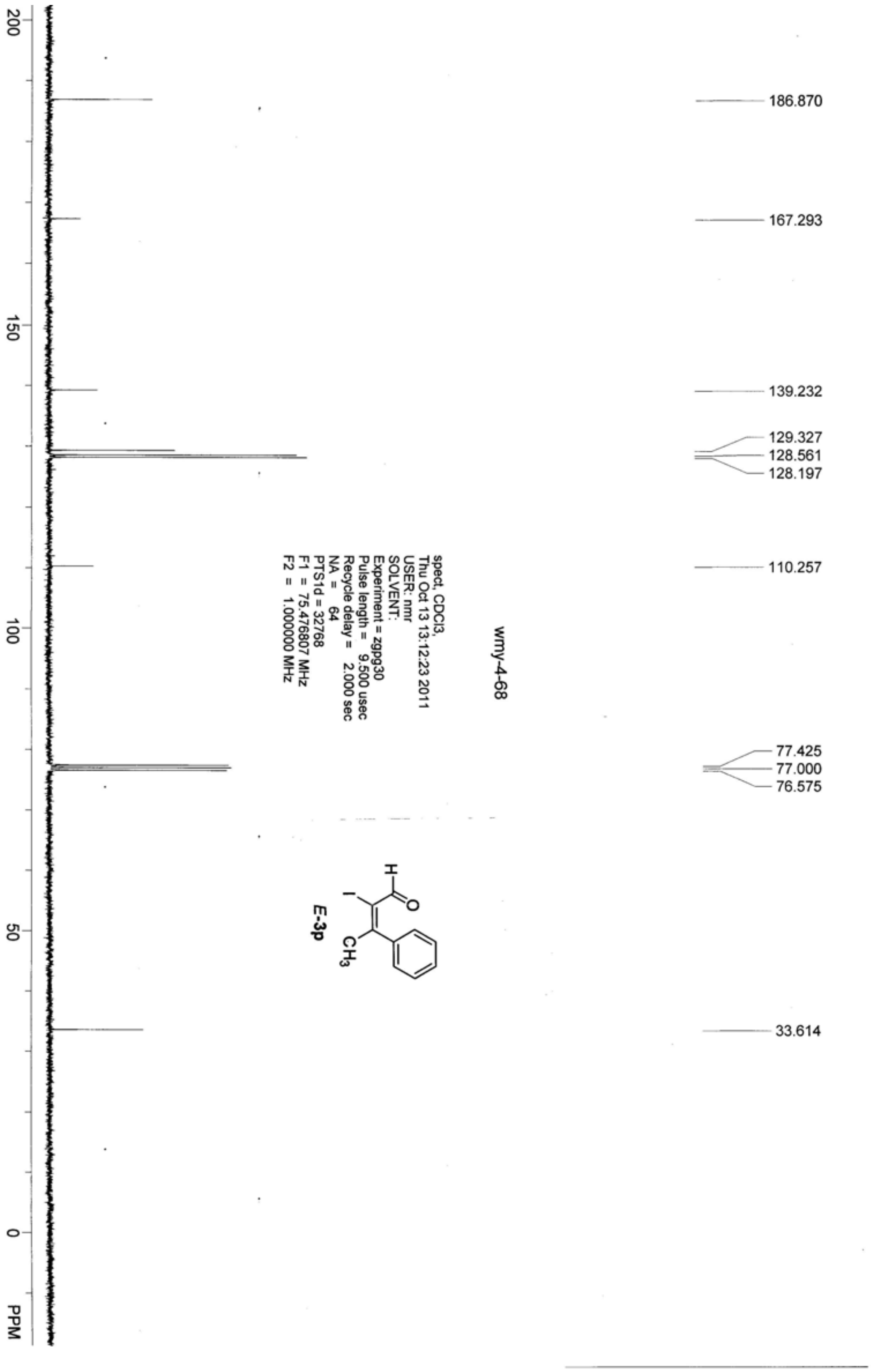

wmy-3-176
spect, CDCl3,
Tue Jun 21 14:52:26 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 42
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
Z-3n
187.912
162.692
111.691
77.424
77.000
76.567
36.506
31.584
29.168
28.926
27.425
22.529
14.022
200
150
100
50
0 PPM

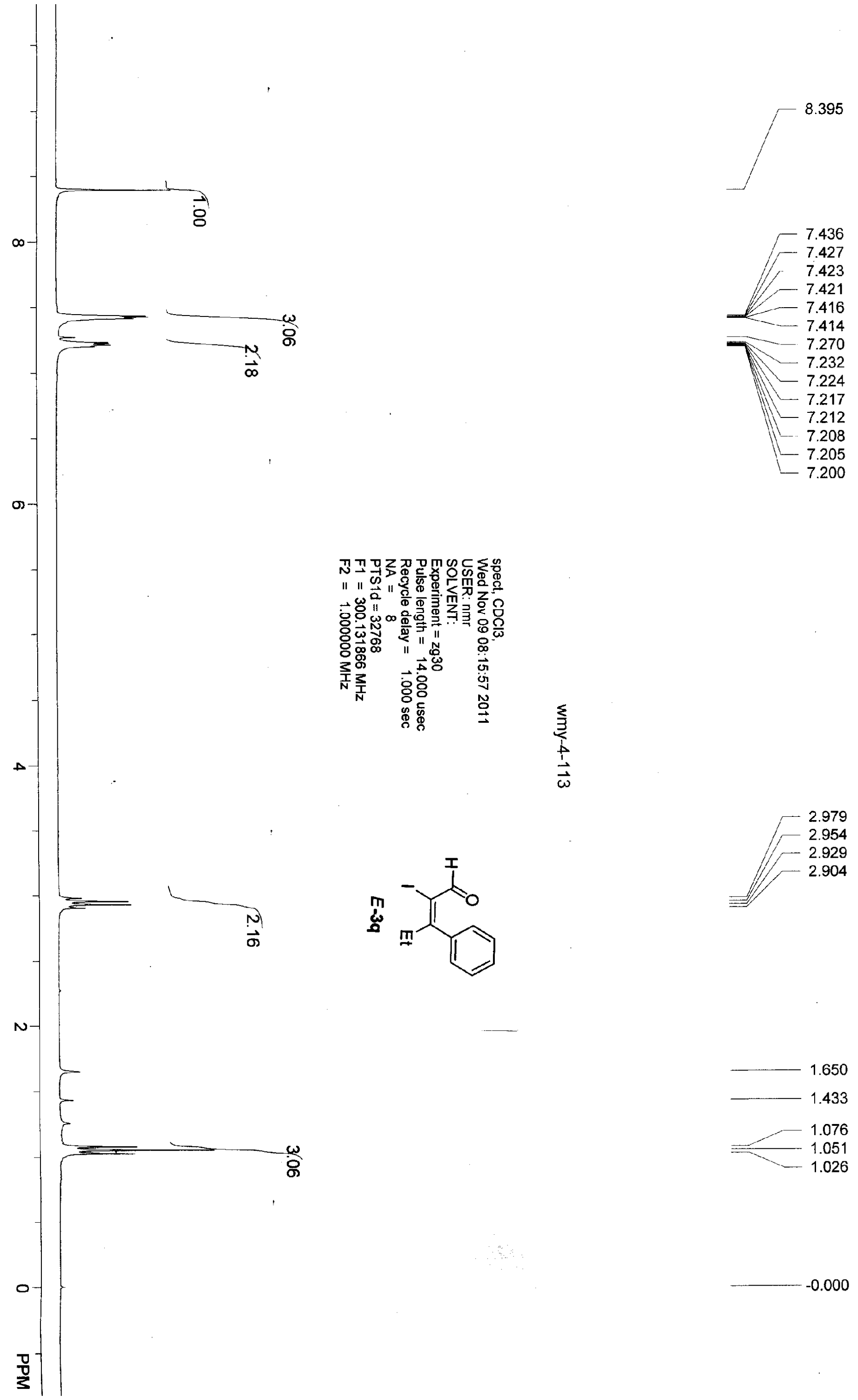

8.618
7.284
7.279
7.260
7.240
7.235
7.217
7.210
7.201
7.195
7.185
7.173
3.827
3.803
-0.000
0.99
6.81
2.01
wmy-2-32
Z-3o
8
6
4
2
0
PPM

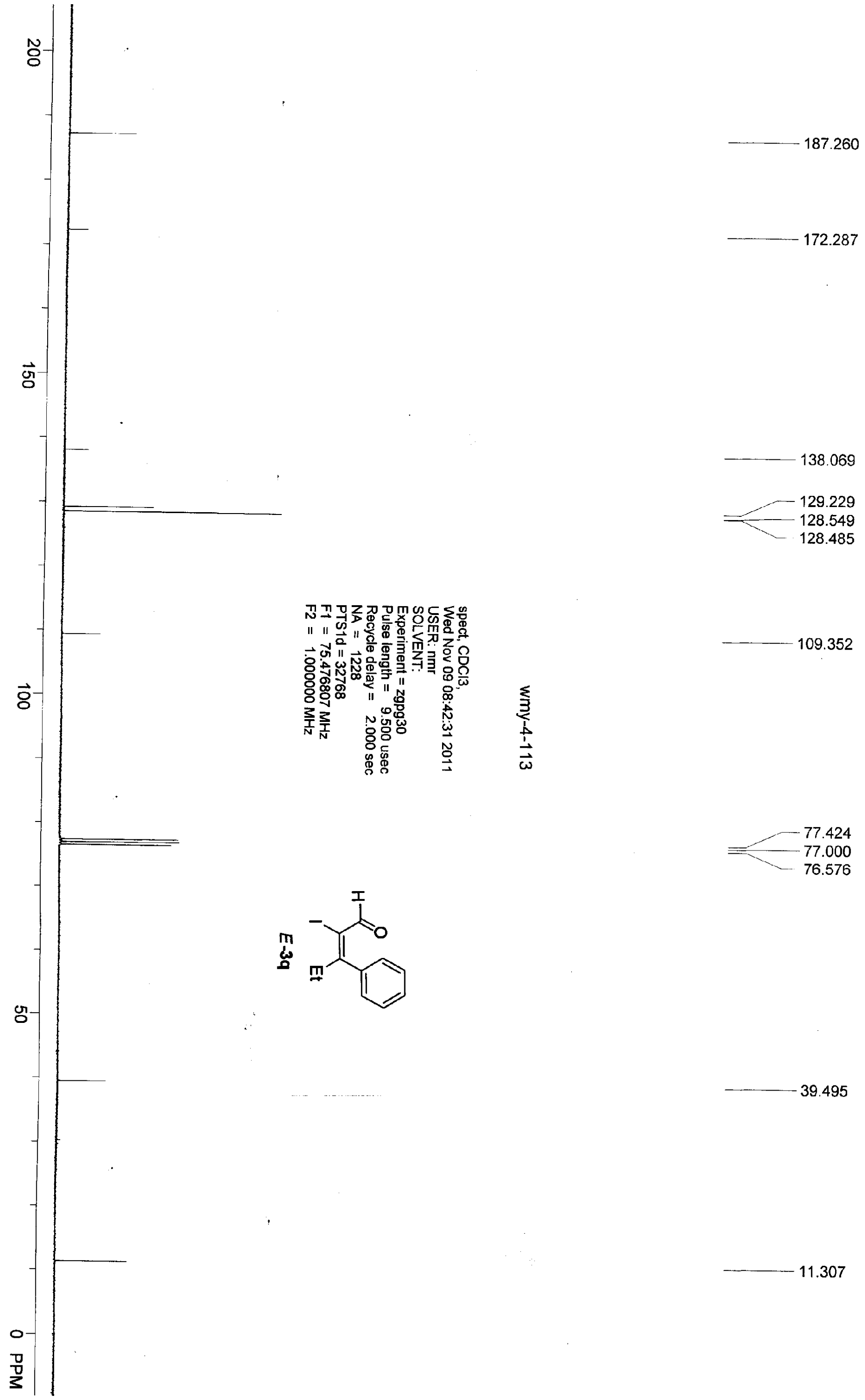
Electronic Supplementary Material (ESI) for Chemical Science

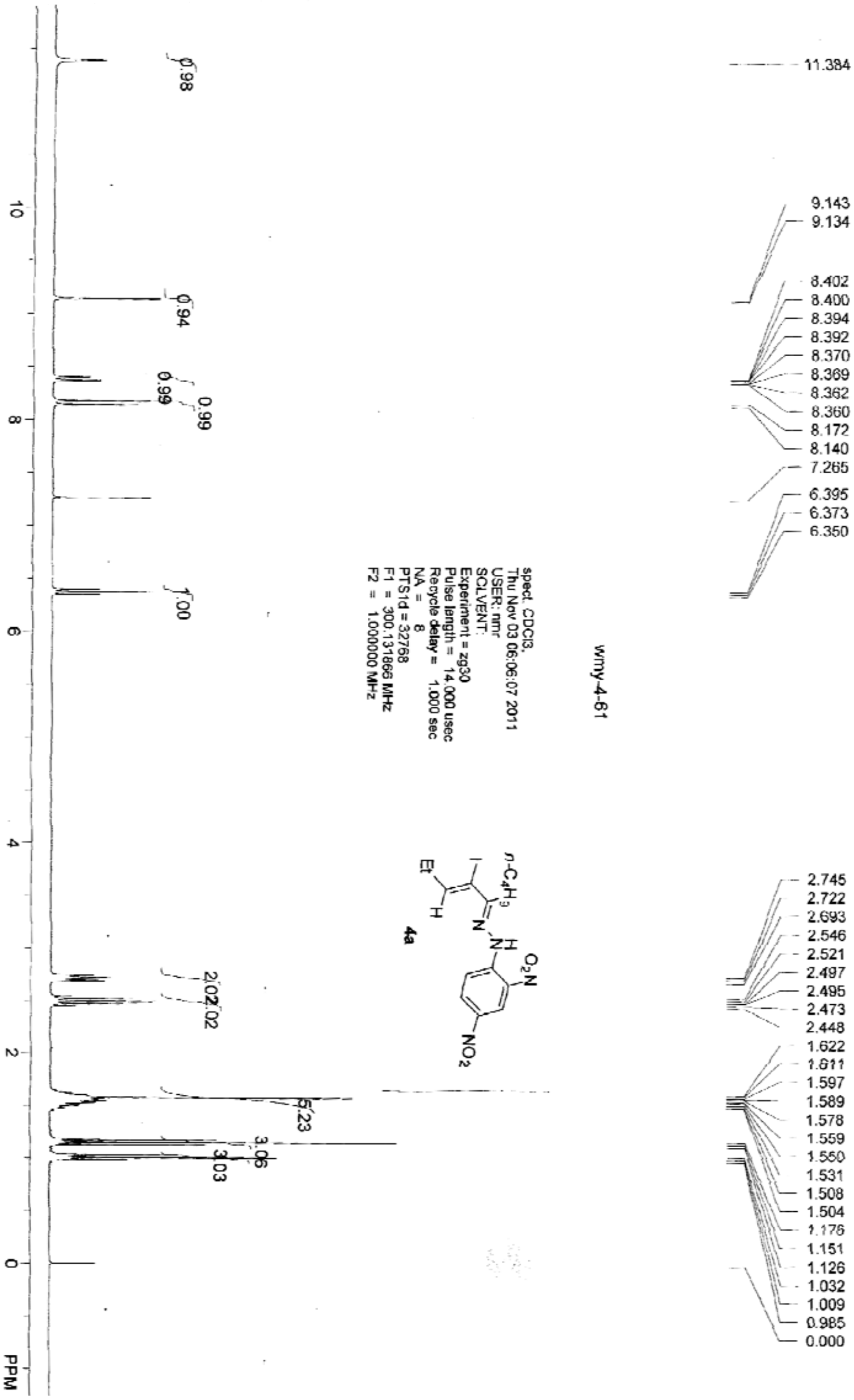


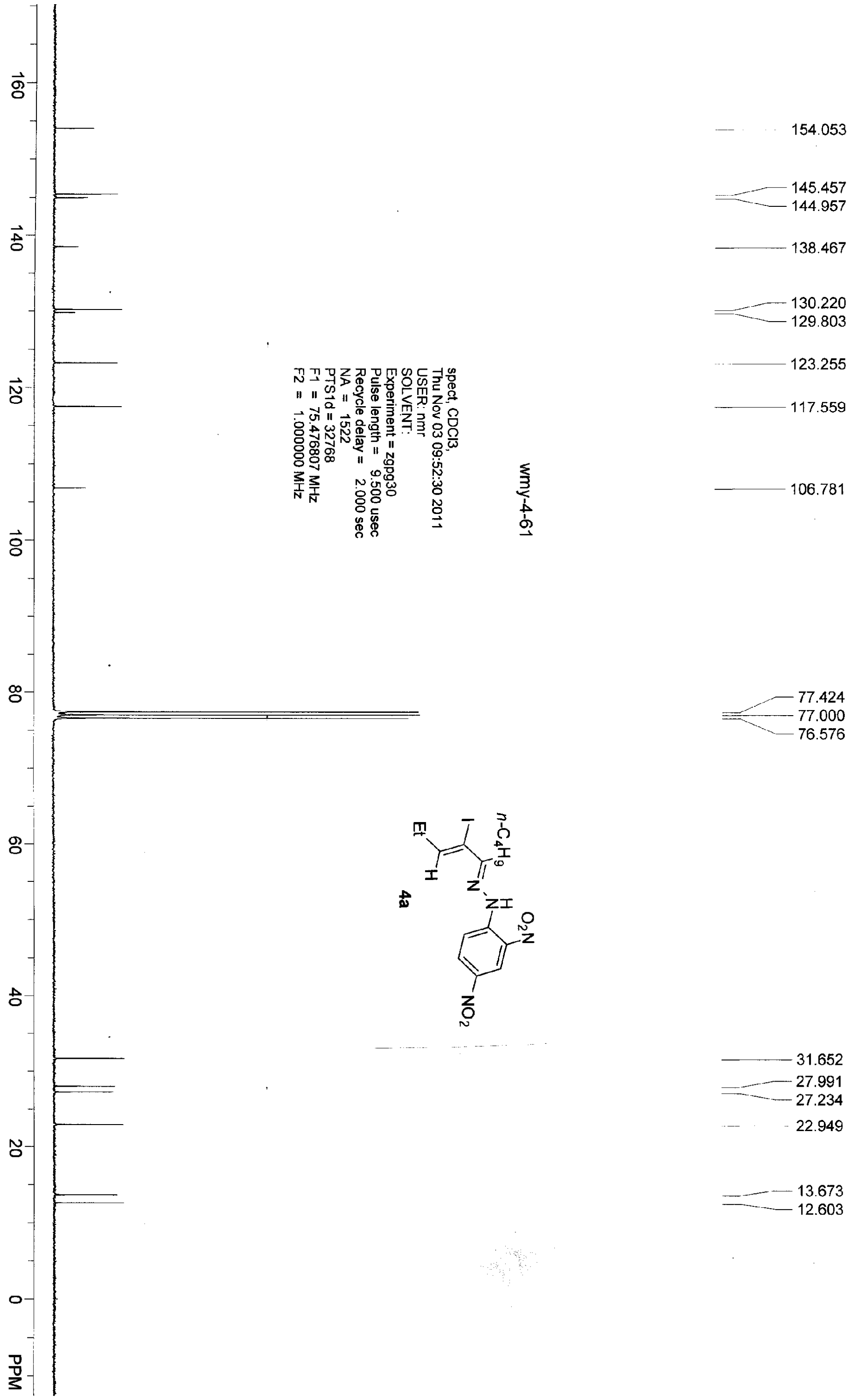

wmy-4-68
spect, CDCl3,
Thu Oct 13 13:10:47 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
E-3p
9.324
8.455
7.464
7.445
7.433
7.423
7.411
7.402
7.266
7.259
7.251
7.247
7.243
7.239
7.235
2.696
2.630
1.698
1.431
1.256
0.000
0.02
1.00
3.29
2.20
3.05
PPM

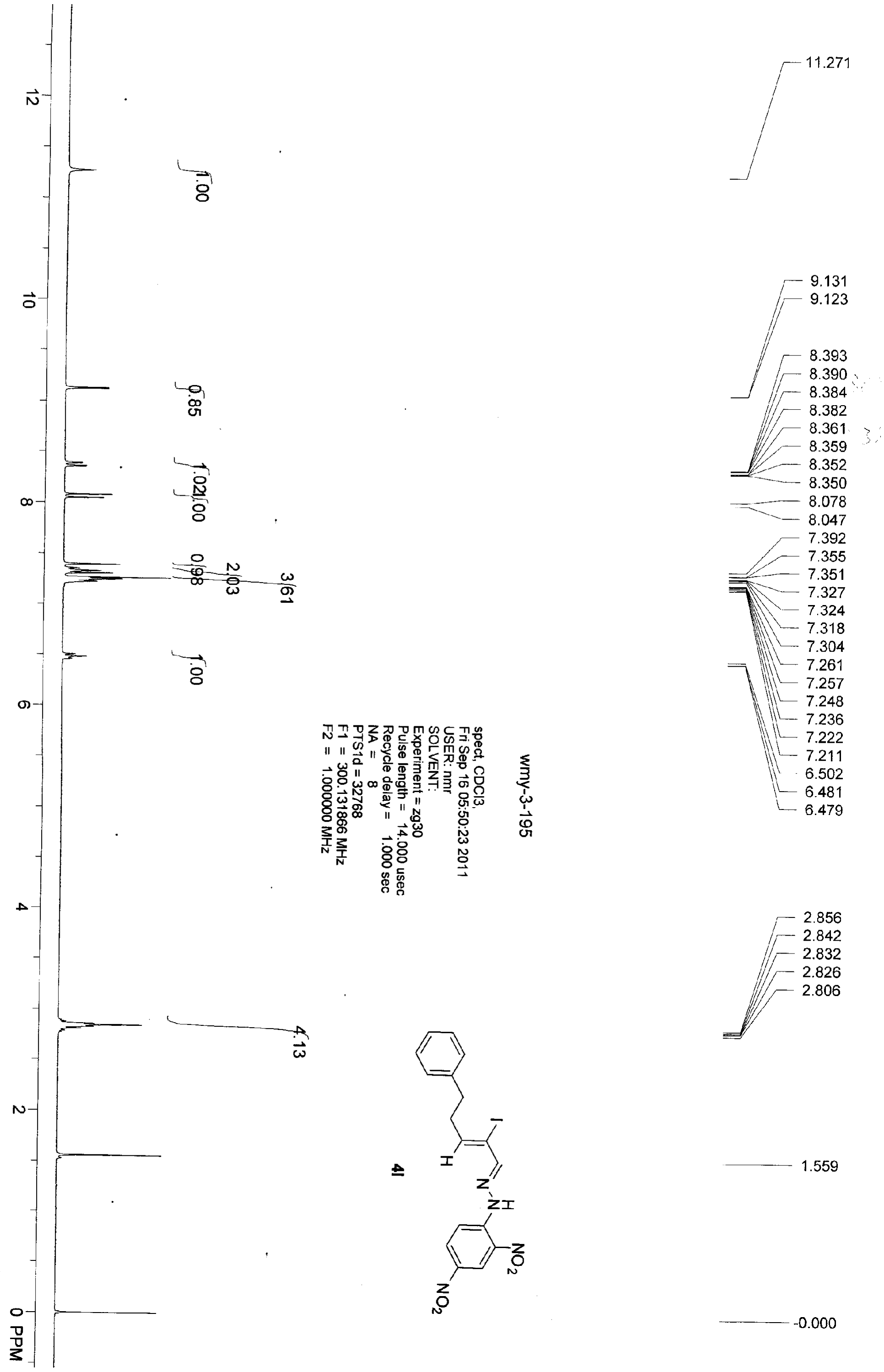

wmy-4-68
spect, CDCl3,
Thu Oct 13 13:12:23 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 64
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
186.870
167.293
139.232
129.327
128.561
128.197
110.257
77.425
77.000
76.575
33.614
E-3p
200
150
100
50
0
PPM

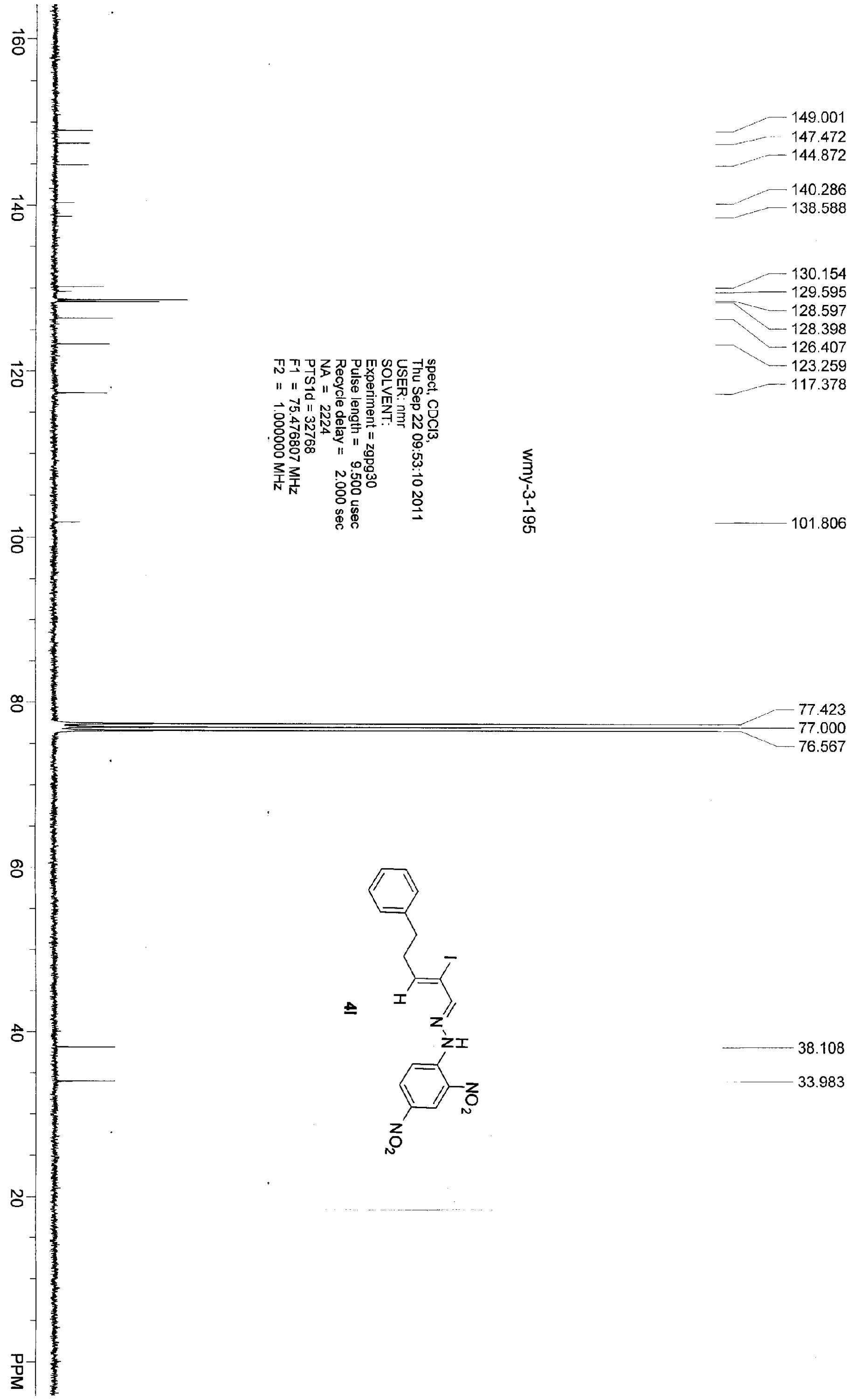

wmy-4-113
spect, CDCl3,
Wed Nov 09 08:15:57 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
H
O
I
Et
E-3q
8.395
7.436
7.427
7.423
7.421
7.416
7.414
7.270
7.232
7.224
7.217
7.212
7.208
7.205
7.200
2.979
2.954
2.929
2.904
1.650
1.433
1.076
1.051
1.026
-0.000
1.00
3.06
2.18
2.16
3.06
8
6
4
2
0
PPM

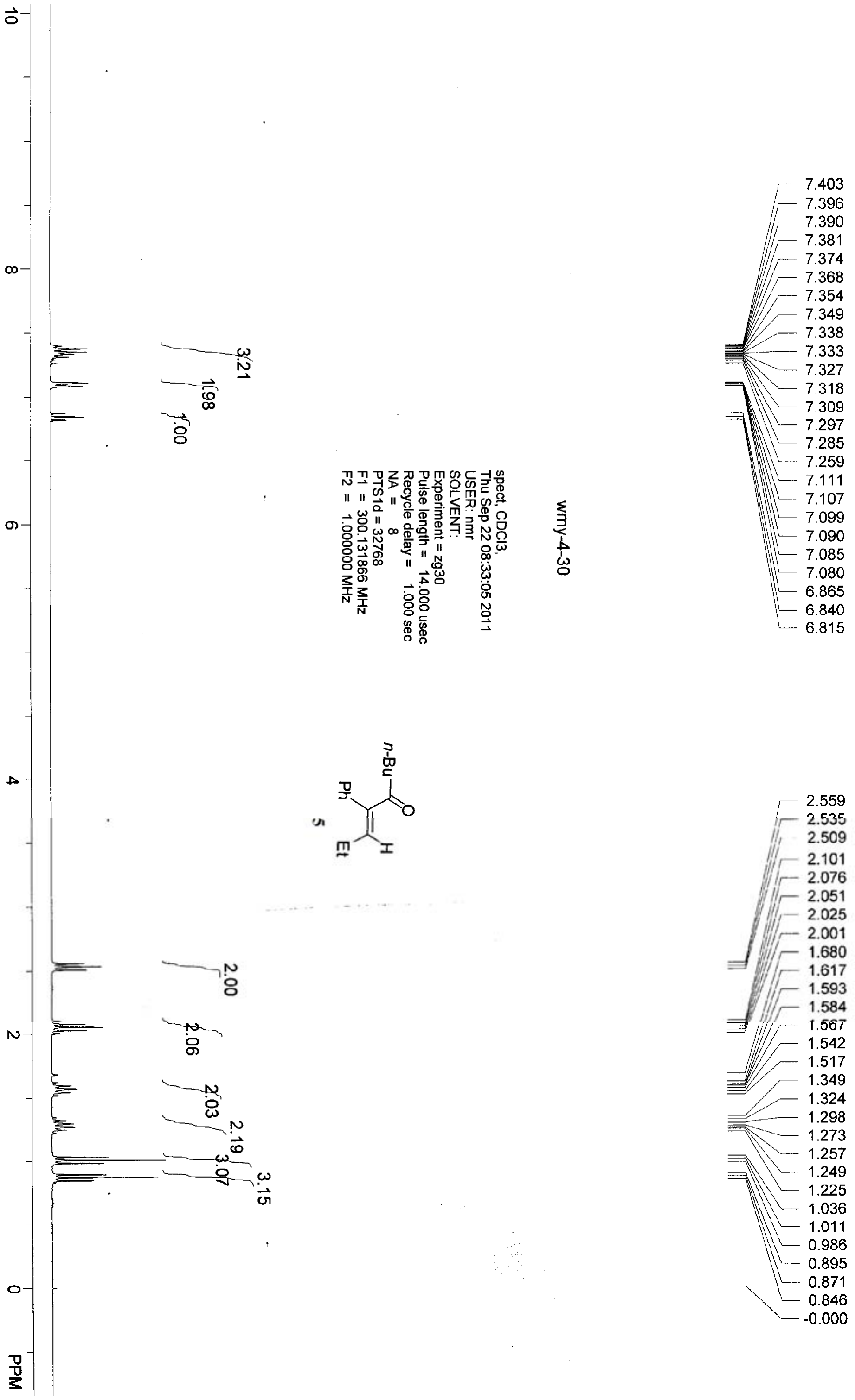

wmy-4-113
spect, CDCl3,
Wed Nov 09 08:42:31 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 1228
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
187.260
172.287
138.069
129.229
128.549
128.485
109.352
77.424
77.000
76.576
39.495
11.307
200
150
100
50
0 PPM
H
O
I
Et
E-3q


wmy-4-61
spect. CDCl3,
Thu Nov 03 06:06:07 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
4a
11.384
9.143
9.134
8.402
8.400
8.394
8.392
8.370
8.369
8.362
8.360
8.172
8.140
7.265
6.395
6.373
6.350
2.745
2.722
2.693
2.546
2.521
2.497
2.495
2.473
2.448
1.622
1.611
1.597
1.589
1.578
1.559
1.550
1.531
1.508
1.504
1.176
1.151
1.126
1.032
1.009
0.985
0.000
0.98
0.94
0.99
0.99
1.00
2.02
2.02
5.23
3.06
3.03
PPM


wmy-4-61
spect, CDCl3,
Thu Nov 03 09:52:30 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 1522
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
154.053
145.457
144.957
138.467
130.220
129.803
123.255
117.559
106.781
77.424
77.000
76.576
31.652
27.991
27.234
22.949
13.673
12.603
n-C4H9
I
Et
H
N
H
N
O2N
NO2
4a
160
140
120
100
80
60
40
20
0
PPM


wmy-3-195
spect, CDCl3,
Fri Sep 16 05:50:23 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
11.271
9.131
9.123
8.393
8.390
8.384
8.382
8.361
8.359
8.352
8.350
8.078
8.047
7.392
7.355
7.351
7.327
7.324
7.318
7.304
7.261
7.257
7.248
7.236
7.222
7.211
6.502
6.481
6.479
2.856
2.842
2.832
2.826
2.806
1.559
-0.000
1.00
0.85
1.02
1.00
0.98
2.03
3.61
1.00
4.13
12
10
8
6
4
2
0 PPM
4l


wmy-3-195
spect, CDCl3,
Thu Sep 22 09:53:10 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 2224
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
149.001
147.472
144.872
140.286
138.588
130.154
129.595
128.597
128.398
126.407
123.259
117.378
101.806
77.423
77.000
76.567
38.108
33.983
4l
I
H
N
H
NO2
NO2
160
140
120
100
80
60
40
20
PPM


wmy-4-30
spect, CDCl3,
Thu Sep 22 08:33:05 2011
USER: nmr
SOLVENT:
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Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
n-Bu
O
H
Ph
Et
5
7.403
7.396
7.390
7.381
7.374
7.368
7.354
7.349
7.338
7.333
7.327
7.318
7.309
7.297
7.285
7.259
7.111
7.107
7.099
7.090
7.085
7.080
6.865
6.840
6.815
2.559
2.535
2.509
2.101
2.076
2.051
2.025
2.001
1.680
1.617
1.593
1.584
1.567
1.542
1.517
1.349
1.324
1.298
1.273
1.257
1.249
1.225
1.036
1.011
0.986
0.895
0.871
0.846
-0.000
3.21
1.98
1.00
2.00
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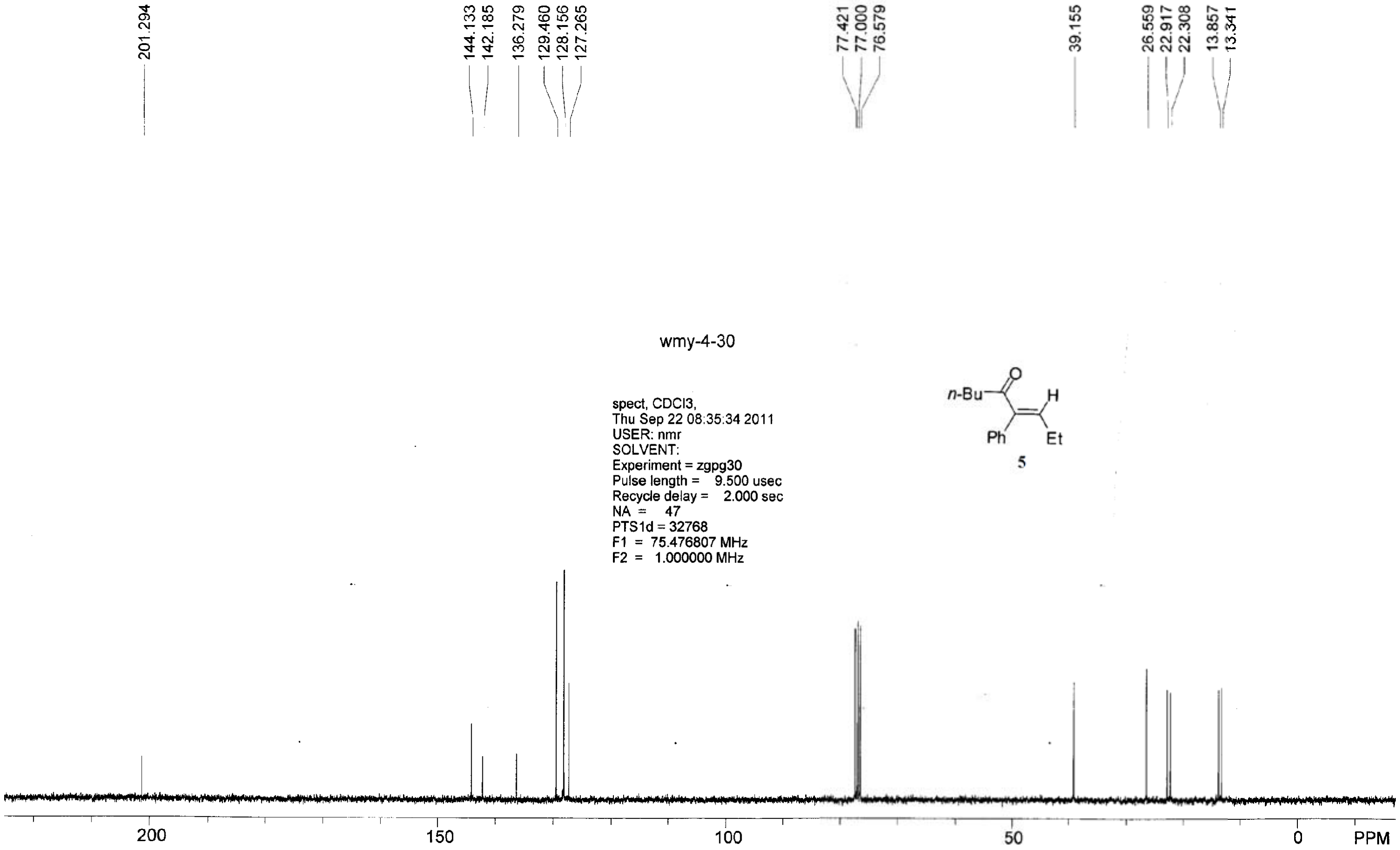
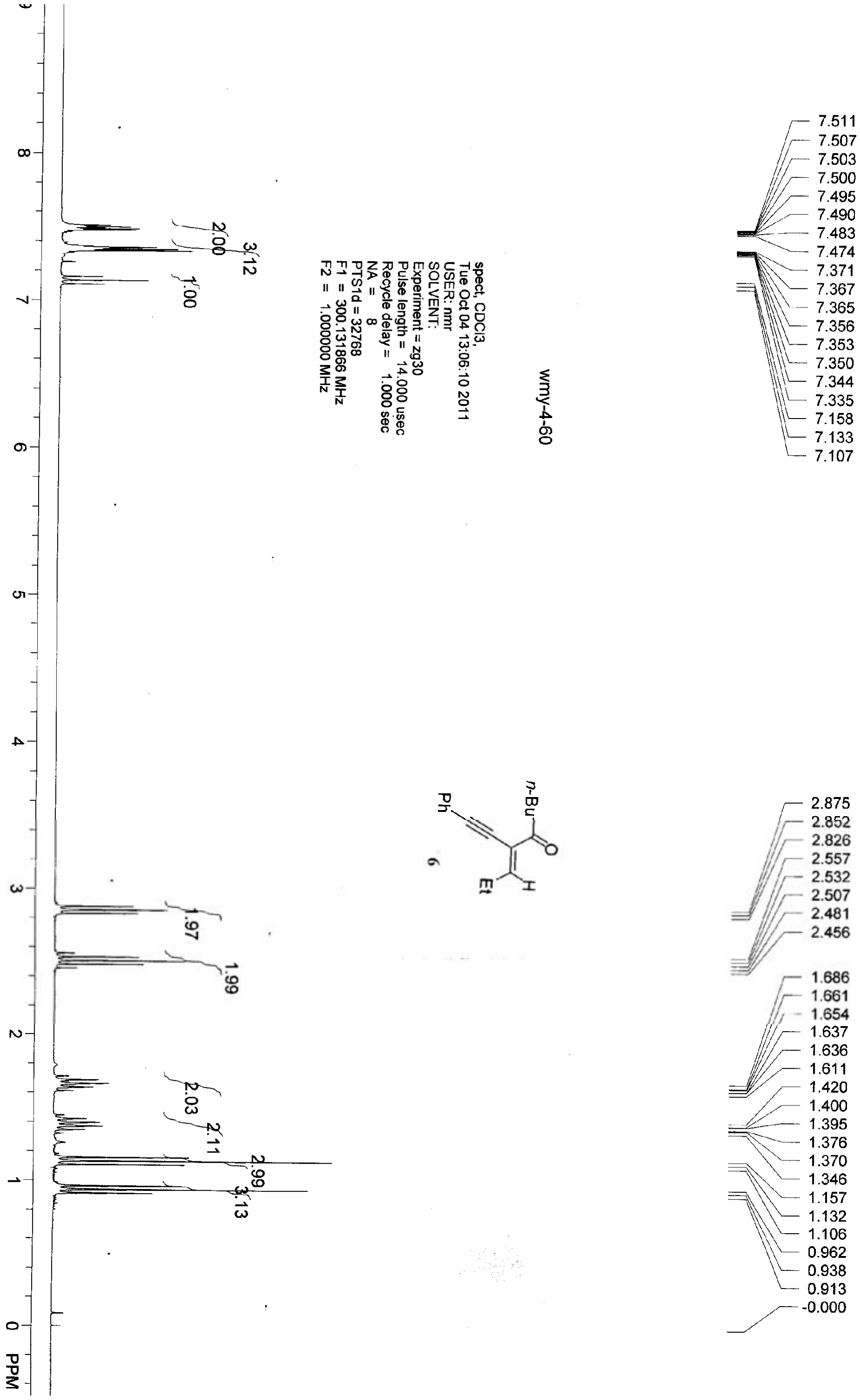
2.03
2.19
3.07
3.15
10
8
6
4
2
0
PPM

Electronic Supplementary Material (ESI) for Chemical Science

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spect, CDCl3,
Tue Oct 04 13:06:10 2011
USER: nmr
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Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
n-Bu
O
H
Et
Ph
6
7.511
7.507
7.503
7.500
7.495
7.490
7.483
7.474
7.371
7.367
7.365
7.356
7.353
7.350
7.344
7.335
7.158
7.133
7.107
2.875
2.852
2.826
2.557
2.532
2.507
2.481
2.456
1.686
1.661
1.654
1.637
1.636
1.611
1.420
1.400
1.395
1.376
1.370
1.346
1.157
1.132
1.106
0.962
0.938
0.913
-0.000
2.00
3.12
1.00
1.97
1.99
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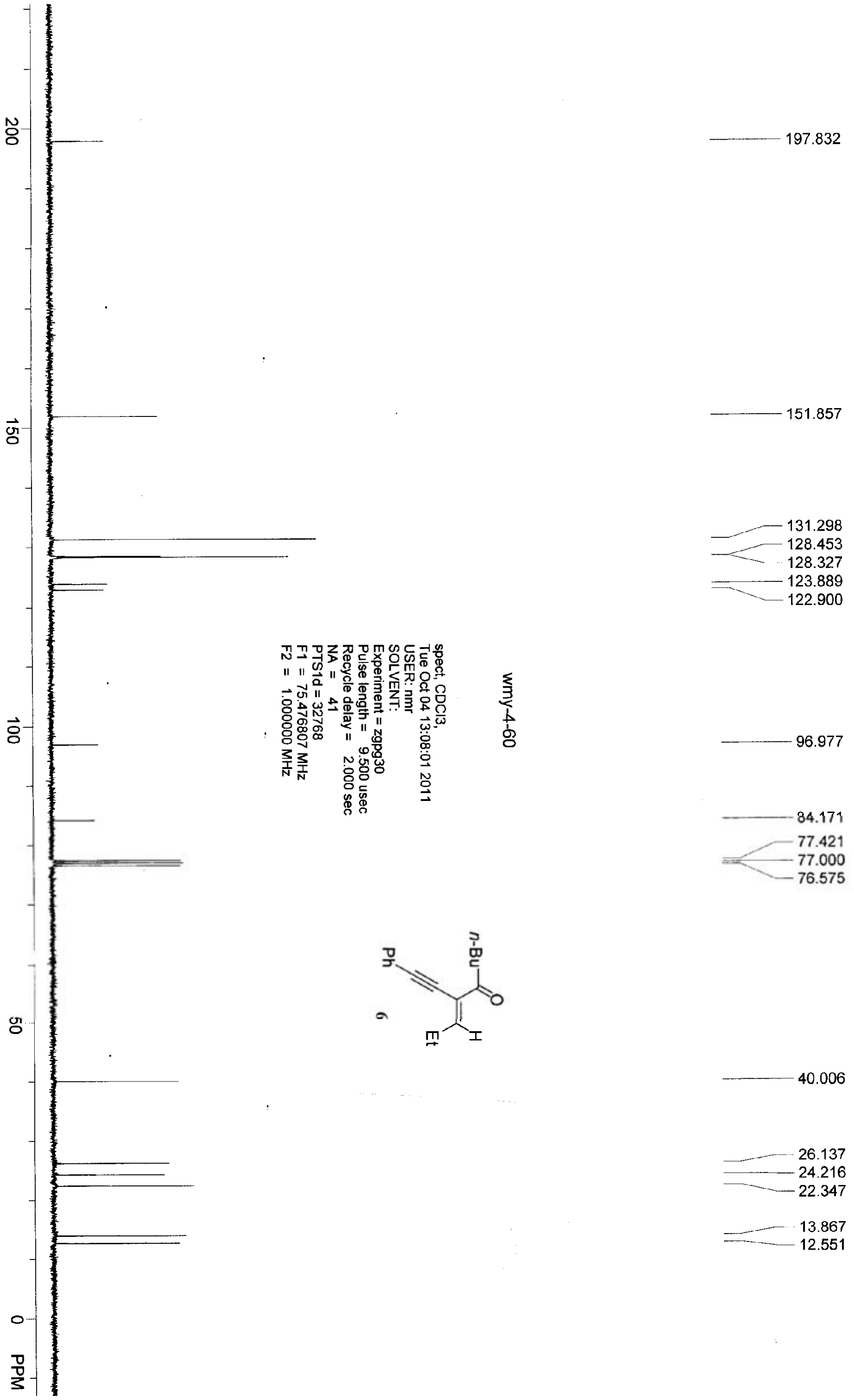
2.11
2.99
3.13
8
7
6
5
4
3
2
1
0
PPM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Recycle delay = 2.000 sec
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O
H
Et
Ph
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131.298
128.453
128.327
123.889
122.900
96.977
84.171
77.421
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26.137
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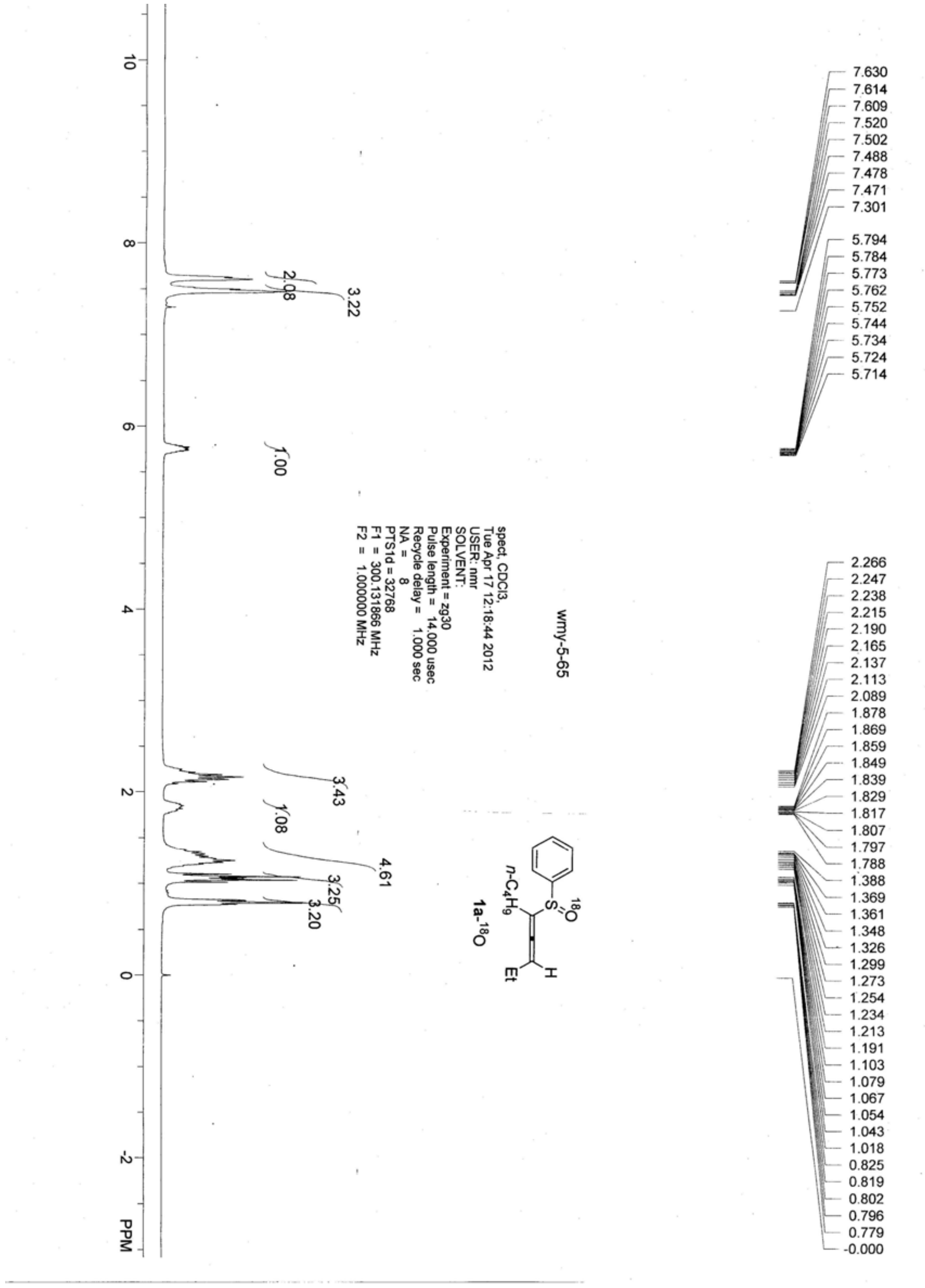
12.551
200
150
100
50
0
PPM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spect, CDCl3,
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USER: nmr
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Recycle delay = 1.000 sec
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PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
18O
S
n-C4H9
H
Et
1a-18O
2.08
3.22
1.00
3.43
1.08
4.61
3.25
3.20
10
8
6
4
2
0
-2
PPM
7.630
7.614
7.609
7.520
7.502
7.488
7.478
7.471
7.301
5.794
5.784
5.773
5.762
5.752
5.744
5.734
5.724
5.714
2.266
2.247
2.238
2.215
2.190
2.165
2.137
2.113
2.089
1.878
1.869
1.859
1.849
1.839
1.829
1.817
1.807
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1.273
1.254
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1.191
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1.043
1.018
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0.796
0.779
-0.000

Sample Information

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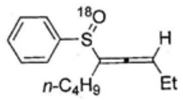
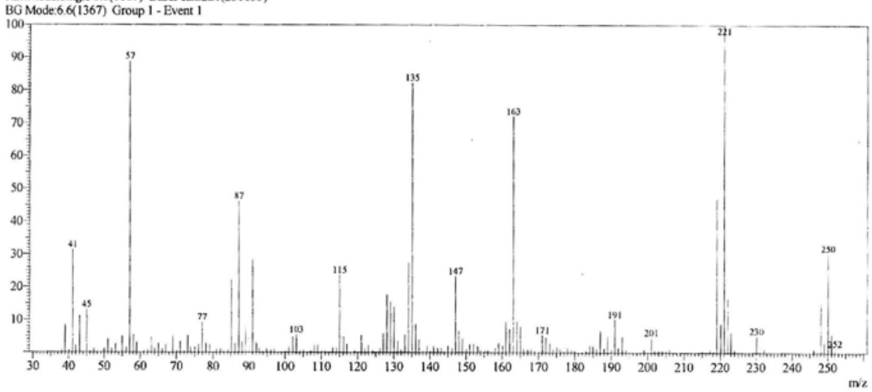


1a-^{18}O

Spectrum

Line#:1 R.Time:6.0(Scan#:1187)
MassPeaks:168
RawMode:Single 6.0(1187) BasePeak:221(230655)
BG Mode:6.6(1367) Group 1 - Event 1



Mass Table
Line#:1 R.Time:6.0(Scan#:1187)
MassPeaks:168
RawMode:Single 6.0(1187) BasePeak:221(230655)
BG Mode:6.6(1367) Group 1 - Event 1

#	m/z	Abs. Int.	Rel. Int.	#	m/z	Abs. Int.	Rel. Int.
1	38.10	2151	0.93	25	66.05	2385	1.03
2	39.05	19938	8.64	26	67.00	5548	2.41
3	40.10	1678	0.73	27	69.00	11315	4.91
4	41.10	72418	31.40	28	70.10	1289	0.56
5	42.05	5125	2.22	29	71.05	8006	3.47
6	43.05	25913	11.23	30	72.10	1135	0.49
7	44.00	458	0.20	31	73.10	11880	5.15
8	45.00	30271	13.12	32	73.85	3791	1.64
9	46.05	1053	0.46	33	75.00	3711	1.61
10	47.10	2791	1.21	34	76.05	5822	2.52
11	50.00	2929	1.27	35	77.05	21291	9.23
12	51.05	9501	4.12	36	78.05	6472	2.81
13	52.05	2962	1.28	37	79.10	5572	2.42
14	53.15	6353	2.75	38	81.00	2218	0.96
15	55.00	11717	5.08	39	82.05	2959	1.28
16	56.15	3842	1.67	40	82.90	1622	0.70
17	57.10	204816	88.80	41	84.10	1849	0.80
18	58.10	12657	5.49	42	85.10	51466	22.31
19	59.00	7102	3.08	43	86.05	6090	2.64
20	61.05	1047	0.45	44	87.10	106495	46.17
21	62.05	2089	0.91	45	88.05	7830	3.39
22	63.05	10591	4.59	46	89.00	20140	8.73
23	64.00	2748	1.19	47	90.05	10535	4.57
24	65.05	6274	2.72	48	91.05	65254	28.29

#	m/z	Abs. Int.	Rel. Int.	#	m/z	Abs. Int.	Rel. Int.
49	92.05	7037	3.05	106	155.20	1682	0.73
50	92.80	3062	1.33	107	156.10	1460	0.63
51	93.85	1158	0.50	108	158.05	3426	1.49
52	94.90	2663	1.15	109	159.00	7126	3.09
53	96.05	1743	0.76	110	160.10	5026	2.18
54	97.05	2673	1.16	111	161.05	21761	9.43
55	99.15	438	0.19	112	162.10	16521	7.16
56	100.10	1135	0.49	113	163.05	166187	72.05
57	101.05	3509	1.52	114	164.10	21974	9.53
58	102.05	11092	4.81	115	165.05	18209	7.89
59	103.10	12632	5.48	116	165.95	2428	1.05
60	104.15	1368	0.59	117	167.10	2098	0.91
61	105.10	1740	0.75	118	168.00	2297	1.00
62	107.05	1043	0.45	119	169.00	1162	0.50
63	108.00	5351	2.32	120	171.05	12255	5.31
64	109.05	5416	2.35	121	172.05	10970	4.76
65	110.05	1351	0.59	122	173.10	7151	3.10
66	110.95	1202	0.52	123	174.05	2384	1.03
67	113.15	3486	1.51	124	175.10	4140	1.79
68	114.10	3663	1.59	125	175.90	2390	1.04
69	115.05	54617	23.68	126	176.95	3146	1.36
70	116.10	11231	4.87	127	178.05	3260	1.41
71	117.05	6151	2.67	128	179.10	1817	0.79
72	119.10	1254	0.54	129	180.00	1078	0.47
73	121.00	12289	5.33	130	183.10	1188	0.52
74	122.00	2799	1.21	131	184.10	5097	2.21
75	123.00	5359	2.32	132	184.95	4875	2.11
76	124.20	1153	0.50	133	186.05	2616	1.13
77	126.15	2894	1.25	134	187.05	15263	6.62
78	127.10	13484	5.85	135	188.05	3022	1.31
79	128.10	40850	17.71	136	189.00	11999	5.20
80	129.10	35886	15.56	137	190.05	2718	1.18
81	130.10	32222	13.97	138	191.00	23254	10.08
82	131.10	8414	3.65	139	192.00	3372	1.46
83	132.05	1809	0.78	140	193.05	11455	4.97
84	133.05	12614	5.47	141	194.05	2080	0.90
85	134.05	63581	27.57	142	199.00	2108	0.91
86	135.10	189876	82.32	143	201.05	10621	4.60
87	136.05	20092	8.71	144	201.90	1596	0.69
88	137.00	9234	4.00	145	203.00	1423	0.62
89	138.10	1263	0.55	146	204.00	1470	0.64
90	139.10	5103	2.21	147	205.00	1546	0.67
91	140.05	1323	0.57	148	205.95	2640	1.14
92	141.00	4599	1.99	149	207.05	238	0.10
93	142.10	3185	1.38	150	208.00	80	0.03
94	143.10	3226	1.40	151	215.00	1102	0.48
95	144.05	1543	0.67	152	217.15	1953	0.85
96	145.00	4942	2.14	153	218.05	1358	0.59
97	146.15	3274	1.42	154	219.05	108261	46.94
98	147.05	53878	23.36	155	220.05	20638	8.95
99	148.00	15172	6.58	156	221.05	230655	100.00
100	149.05	9950	4.31	157	222.00	38194	16.56
101	150.15	2605	1.13	158	223.00	14209	6.16
102	151.05	5952	2.58	159	224.00	1844	0.80
103	152.05	6198	2.69	160	230.10	11598	5.03
104	153.20	4924	2.13	161	231.10	3252	1.41
105	154.00	2022	0.88	162	232.20	2740	1.19

#	m/z	Abs. Int.	Rel. Int.	#	m/z	Abs. Int.	Rel. Int.
163	246.10	2492	1.08	166	250.10	70249	30.46
164	248.10	34866	15.12	167	251.10	13151	5.70
165	249.10	7194	3.12	168	252.05	3286	1.42

The relative abundances of 221 [M (^{18}O)-Et]$^+$, 219 [M (^{16}O)-Et]$^+$ are 100, 46.94.

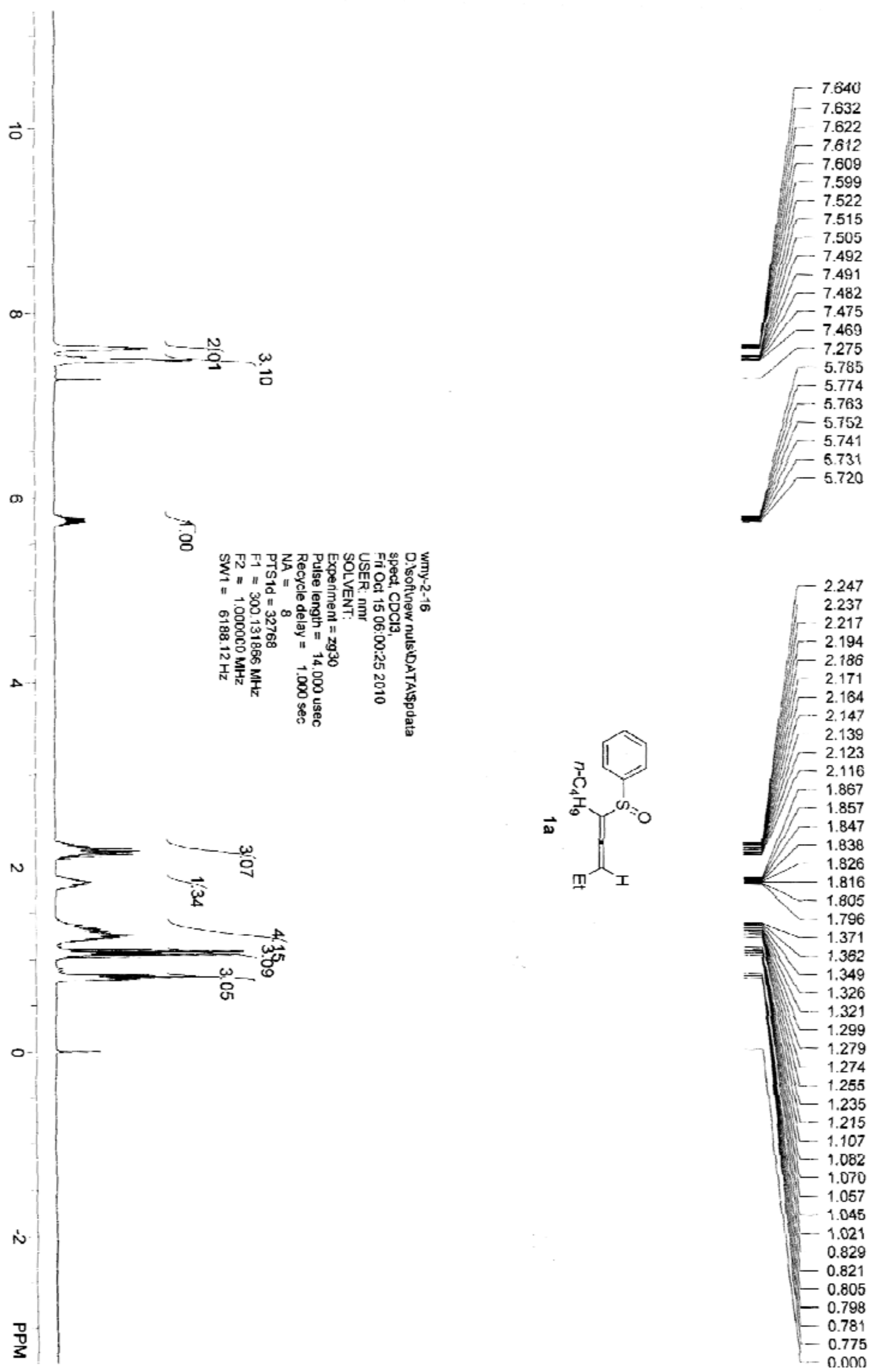
(100-46.94*4.5%)/(100-46.94*4.5%+46.94)=67.59%

$C_{13}H_{15}S\,^{16}O$

Chemical Formula: $C_{13}H_{15}{}^{16}OS$
Exact Mass: 219.0844
Molecular Weight: 219.3181
m/z: 219.0844 (100.0%), 220.0877 (14.1%), 221.0802 (4.5%)
Elemental Analysis: C, 71.19; H, 6.89; O, 7.29; S, 14.62

$C_{13}H_{15}S\,^{18}O$

Chemical Formula: $C_{13}H_{15}{}^{18}OS$
Exact Mass: 221.0886
Molecular Weight: 221.3224
m/z: 221.0886 (100.0%), 222.0920 (14.1%), 223.0844 (4.5%)
Elemental Analysis: C, 70.55; H, 6.83; O, 8.13; S, 14.49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spect, CDCl3,
Fri Oct 15 06:00:25 2010
USER: nmr
SOLVENT:
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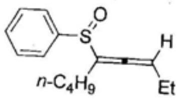
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
SW1 = 6188.12 Hz
1a
PPM



1a

Sample Information

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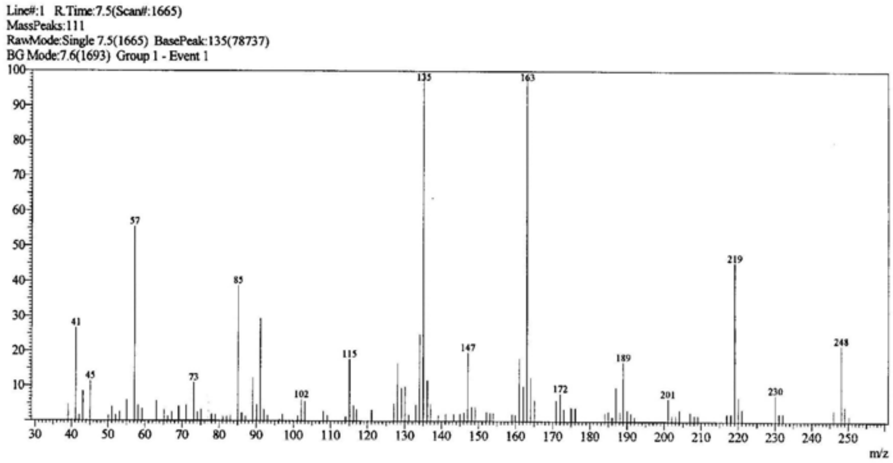
H:\zju\zj.qgr

Spectrum



Mass Table
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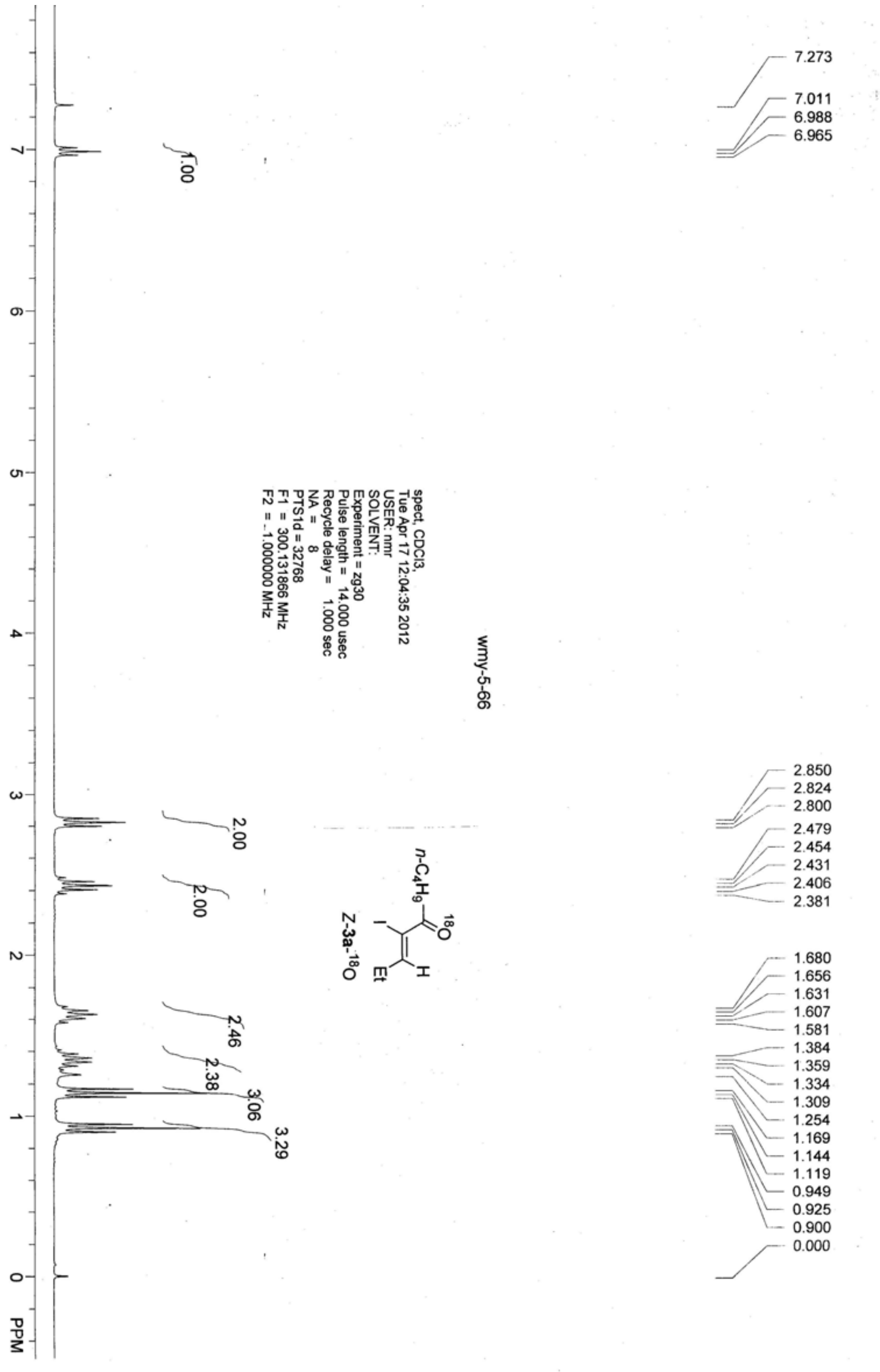
MassPeaks:111
RawMode:Single 7.5(1665) BasePeak:135(78737)
BG Mode:7.6(1693) Group 1 - Event 1

#	m/z	Abs. Int.	Rel. Int.	#	m/z	Abs. Int.	Rel. Int.
1	39.15	3647	4.63	25	77.05	5758	7.31
2	40.10	307	0.39	26	78.00	1506	1.91
3	41.15	20983	26.65	27	79.00	1430	1.82
4	42.15	1255	1.59	28	81.05	1090	1.38
5	43.15	6618	8.41	29	82.10	1046	1.33
6	44.10	205	0.26	30	83.05	1252	1.59
7	45.15	8994	11.42	31	85.10	30605	38.87
8	50.10	1212	1.54	32	86.10	1839	2.34
9	51.10	3222	4.09	33	87.05	1155	1.47
10	52.05	1299	1.65	34	89.05	9720	12.34
11	53.15	2007	2.55	35	90.10	3631	4.61
12	55.10	4736	6.01	36	91.10	23181	29.44
13	57.15	43742	55.55	37	92.05	2618	3.32
14	58.10	3401	4.32	38	93.00	1302	1.65
15	59.20	2735	3.47	39	96.20	384	0.49
16	63.05	4524	5.75	40	97.05	1505	1.91
17	65.15	2524	3.21	41	101.15	1150	1.46
18	66.20	1046	1.33	42	102.10	4847	6.16
19	67.15	2101	2.67	43	103.05	4494	5.71
20	69.05	3313	4.21	44	108.00	2185	2.78
21	71.10	3657	4.64	45	109.10	1340	1.70
22	73.10	8638	10.97	46	114.05	1040	1.32
23	74.10	1993	2.53	47	115.10	13989	17.77
24	75.05	2671	3.39	48	116.15	3585	4.55

#	m/z	Abs. Int.	Rel. Int.	#	m/z	Abs. Int.	Rel. Int.
49	117.00	2646	3.36	81	173.00	2876	3.65
50	121.10	2556	3.25	82	174.95	3229	4.10
51	127.10	3913	4.97	83	176.05	3123	3.97
52	128.10	13116	16.66	84	184.05	2013	2.56
53	129.10	7420	9.42	85	185.00	2326	2.95
54	130.10	7855	9.98	86	186.00	1046	1.33
55	131.10	1459	1.85	87	187.05	7674	9.75
56	133.05	3721	4.73	88	188.05	2192	2.78
57	134.05	19661	24.97	89	189.00	13414	17.04
58	135.05	78737	100.00	90	190.10	2505	3.18
59	136.10	9250	11.75	91	191.05	1856	2.36
60	137.05	3883	4.93	92	192.00	1046	1.33
61	139.05	1361	1.73	93	201.00	5142	6.53
62	141.15	1658	2.11	94	202.00	1442	1.83
63	143.30	1596	2.03	95	203.05	1343	1.71
64	145.00	1660	2.11	96	204.05	2627	3.34
65	146.05	2009	2.55	97	206.95	2075	2.64
66	147.10	15542	19.74	98	208.05	1334	1.69
67	148.15	3293	4.18	99	209.00	1340	1.70
68	149.05	3191	4.05	100	216.95	1882	2.39
69	152.15	2160	2.74	101	218.05	1752	2.23
70	153.15	1847	2.35	102	219.00	35776	45.44
71	153.90	1916	2.43	103	220.05	5428	6.89
72	159.10	1596	2.03	104	221.05	2876	3.65
73	159.90	1506	1.91	105	230.10	5999	7.62
74	161.05	14187	18.02	106	231.10	1801	2.29
75	162.15	7965	10.12	107	232.15	1869	2.37
76	163.05	77181	98.02	108	246.00	2633	3.34
77	164.10	9929	12.61	109	248.10	17280	21.95
78	165.10	4796	6.09	110	249.10	3490	4.43
79	170.95	4774	6.06	111	250.25	1379	1.75
80	172.05	6300	8.00				

The relative abundances of 221 [M (^{18}O)-Et]$^+$, 219 [M (^{16}O)-Et]$^+$ are 3.65, 45.44.

$$(3.65-45.44*4.5\%)/(3.65-45.44*4.5\%+45.44)=3.41\%$$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spect, CDCl3,
Tue Apr 17 12:04:35 2012
USER: nmr
SOLVENT:
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Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = .1.000000 MHz
Z-3a-18O
7.273
7.011
6.988
6.965
2.850
2.824
2.800
2.479
2.454
2.431
2.406
2.381
1.680
1.656
1.631
1.607
1.581
1.384
1.359
1.334
1.309
1.254
1.169
1.144
1.119
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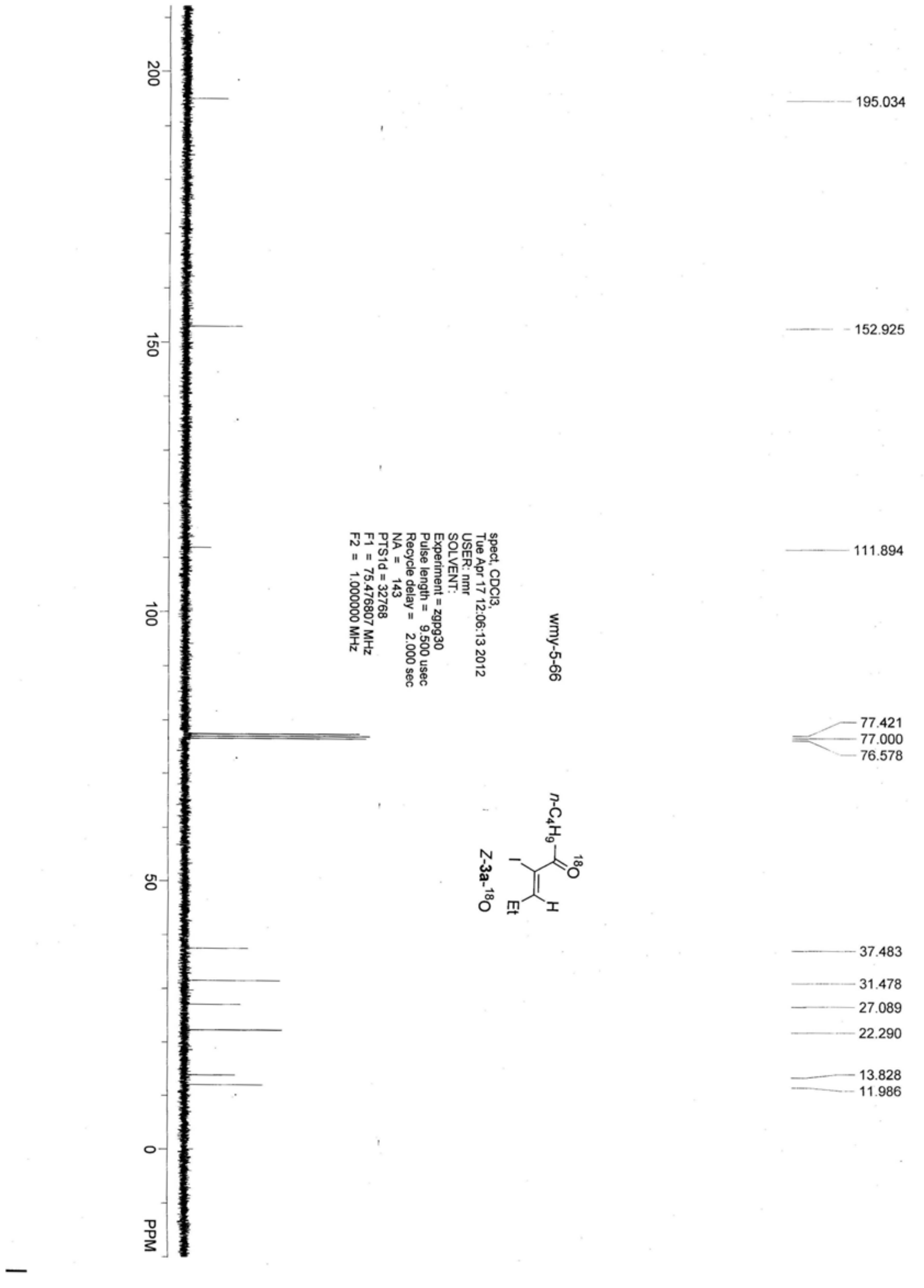
0.900
0.000
1.00
2.00
2.00
2.46
2.38
3.06
3.29
PPM


wmy-5-66
spect, CDCl3,
Tue Apr 17 12:06:13 2012
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 143
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
195.034
152.925
111.894
77.421
77.000
76.578
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31.478
27.089
22.290
13.828
11.986
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100
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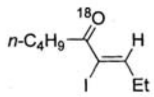
PPM
Z-3a-18O

Electronic Supplementary Material (ESI) for Chemical Science

Sample Information

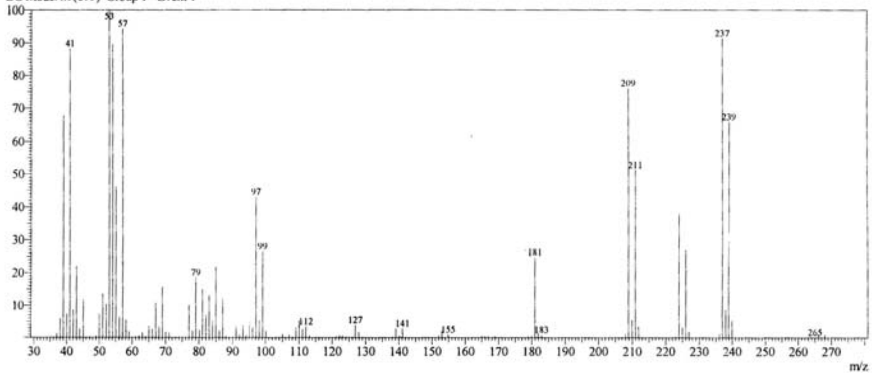
E:\msm\wmy-5-66_2012-4-6_3.qgd



Z-**3a**-^{18}O

Spectrum

Line#:1 R.Time:4.5(Scan#:757)
MassPeaks:156
RawMode:Single 4.5(757) BasePeak:53(2678104)
BG Mode:4.9(879) Group 1 - Event 1



Mass Table
Line#:1 R.Time:4.5(Scan#:757)
MassPeaks:156
RawMode:Single 4.5(757) BasePeak:53(2678104)
BG Mode:4.9(879) Group 1 - Event 1

#	m/z	Abs. Int.	Rel. Int.	#	m/z	Abs. Int.	Rel. Int.
1	36.15	1674	0.06	25	60.05	6521	0.24
2	37.05	32984	1.23	26	61.05	11907	0.44
3	38.10	158063	5.90	27	62.00	21198	0.79
4	39.05	1813495	67.72	28	63.05	44368	1.66
5	40.10	195874	7.31	29	64.05	11770	0.44
6	41.05	2364334	88.28	30	65.05	94443	3.53
7	42.05	230797	8.62	31	66.05	71268	2.66
8	43.05	590276	22.04	32	67.05	288166	10.76
9	44.05	73685	2.75	33	68.05	94629	3.53
10	45.05	316291	11.81	34	69.05	419786	15.67
11	46.00	7903	0.30	35	70.05	45490	1.70
12	47.05	9311	0.35	36	71.05	44774	1.67
13	48.05	1585	0.06	37	72.10	5300	0.20
14	49.00	17118	0.64	38	73.05	7728	0.29
15	50.00	195218	7.29	39	74.05	9095	0.34
16	51.05	363604	13.58	40	75.05	8266	0.31
17	52.10	279255	10.43	41	76.15	6486	0.24
18	53.05	2678104	100.00	42	77.05	269995	10.08
19	54.05	2400709	89.64	43	78.05	58299	2.18
20	55.05	1236411	46.17	44	79.05	497902	18.59
21	56.10	172525	6.44	45	80.10	62796	2.34
22	57.10	2529065	94.43	46	81.05	398603	14.88
23	58.10	148753	5.55	47	82.05	185392	6.92
24	59.05	53670	2.00	48	83.05	344311	12.86

#	m/z	Abs. Int.	Rel. Int.	#	m/z	Abs. Int.	Rel. Int.
49	84.05	141353	5.28	103	140.15	16981	0.63
50	85.05	585462	21.86	104	141.10	74871	2.80
51	86.10	57079	2.13	105	142.10	6230	0.23
52	87.10	320129	11.95	106	151.95	17304	0.65
53	88.05	18527	0.69	107	152.95	56198	2.10
54	89.05	5070	0.19	108	153.95	2668	0.10
55	90.15	3296	0.12	109	154.90	24849	0.93
56	91.05	88501	3.30	110	156.90	3012	0.11
57	92.10	26103	0.97	111	163.95	3314	0.12
58	93.10	101887	3.80	112	164.95	14662	0.55
59	94.15	19063	0.71	113	165.90	13516	0.50
60	95.10	187274	6.99	114	166.90	14455	0.54
61	96.10	84214	3.14	115	167.90	1527	0.06
62	97.10	1153552	43.07	116	168.95	11919	0.45
63	98.10	141585	5.29	117	169.90	1129	0.04
64	99.10	708745	26.46	118	170.85	5502	0.21
65	100.10	54879	2.05	119	178.95	12514	0.47
66	101.10	3617	0.14	120	179.95	14467	0.54
67	102.10	2049	0.08	121	180.95	661573	24.70
68	103.10	7673	0.29	122	181.90	38188	1.43
69	104.10	3097	0.12	123	182.90	24039	0.90
70	105.10	28997	1.08	124	183.90	1188	0.04
71	106.05	7262	0.27	125	184.90	1162	0.04
72	107.05	23044	0.86	126	192.85	1336	0.05
73	108.05	7277	0.27	127	193.80	3415	0.13
74	109.10	83071	3.10	128	194.95	3093	0.12
75	110.10	140406	5.24	129	195.90	3302	0.12
76	111.05	68747	2.57	130	196.90	1871	0.07
77	112.10	91570	3.42	131	205.95	2086	0.08
78	113.10	17340	0.65	132	206.95	2759	0.10
79	114.15	1850	0.07	133	207.95	29674	1.11
80	115.00	3558	0.13	134	208.90	2038230	76.11
81	116.10	1057	0.04	135	209.95	144752	5.41
82	117.15	2348	0.09	136	210.95	1373512	51.29
83	118.05	1526	0.06	137	211.90	90130	3.37
84	119.15	6605	0.25	138	212.90	2679	0.10
85	120.15	2802	0.10	139	222.95	12665	0.47
86	121.15	12652	0.47	140	223.95	1014487	37.88
87	122.15	19920	0.74	141	224.95	82010	3.06
88	123.05	13584	0.51	142	225.95	721593	26.94
89	124.15	9325	0.35	143	226.90	49569	1.85
90	125.10	9180	0.34	144	227.95	2184	0.08
91	125.95	8251	0.31	145	235.00	1177	0.04
92	126.90	103833	3.88	146	236.05	31688	1.18
93	127.95	45511	1.70	147	236.95	2450420	91.50
94	128.85	5403	0.20	148	237.95	229233	8.56
95	131.10	1033	0.04	149	238.95	1762487	65.81
96	133.10	320	0.01	150	239.90	142146	5.31
97	134.05	1098	0.04	151	240.90	5649	0.21
98	135.05	1036	0.04	152	265.05	1249	0.05
99	136.15	1239	0.05	153	266.00	36438	1.36
100	137.15	2801	0.10	154	267.00	8466	0.32
101	138.15	9082	0.34	155	268.00	24346	0.91
102	139.10	73847	2.76	156	268.90	5393	0.20

The relative abundances of 239 [M (^{18}O)-Et]$^+$, 237 [M (^{16}O)-Et]$^+$ are 65.81, 91.50.

$$\frac{[\mathrm{M}\ (^{18}\mathrm{O})\text{-Et}]^+}{[\mathrm{M}\ (^{18}\mathrm{O})\text{-Et}]^+ + [\mathrm{M}\ (^{16}\mathrm{O})\text{-Et}]^+} = \frac{65.81}{65.81+91.50} = 41.835\%$$

$C_8H_{10}I^{16}O$

Chemical Formula: $C_8H_{10}I^{16}O$
Exact Mass: 248.9776
Molecular Weight: 249.0644
m/z: 248.9776 (100.0%), 249.9810 (8.7%)
Elemental Analysis: C, 38.58; H, 4.05; I, 50.95; O, 6.42

$C_8H_{10}I^{18}O$

Chemical Formula: $C_8H_{10}I^{18}O$
Exact Mass: 250.9819
Molecular Weight: 251.0686
m/z: 250.9819 (100.0%), 251.9852 (8.7%)
Elemental Analysis: C, 38.27; H, 4.01; I, 50.55; O, 7.17

Electronic Supplementary Material (ESI) for Chemical Science
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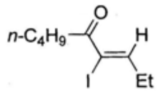
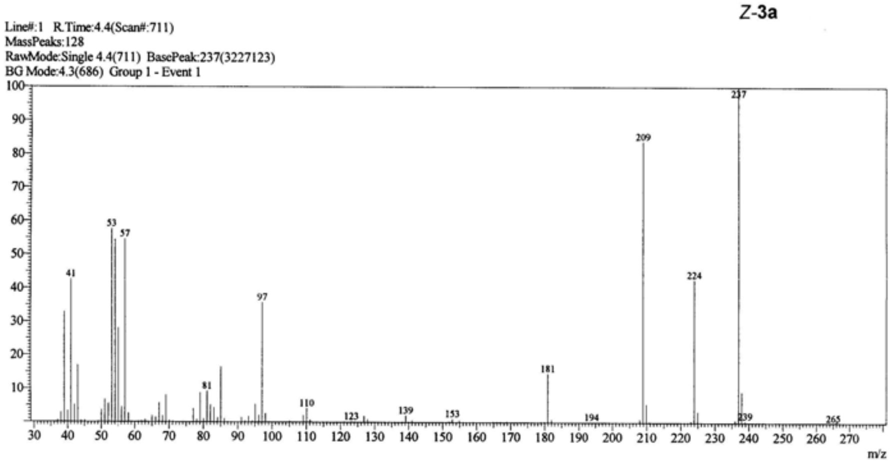
Sample Information

E:\msm\wmy-3-83_2011-7-4_5.qgd



Z-3a

Spectrum



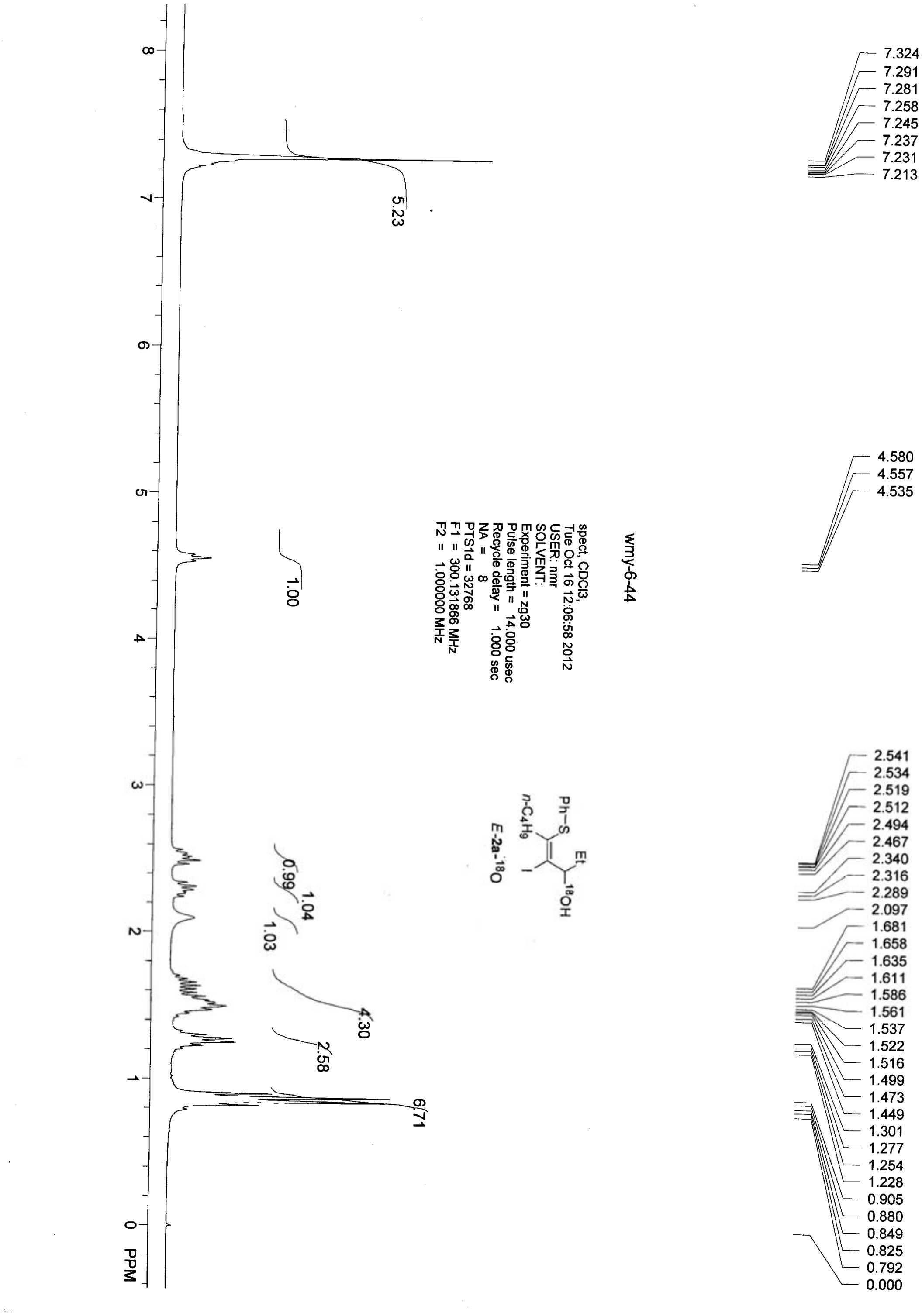
Mass Table
Line#:1 R.Time:4.4(Scan#:711)
MassPeaks:128
RawMode:Single 4.4(711) BasePeak:237(3227123)
BG Mode:4.3(686) Group 1 - Event 1

#	m/z	Abs. Int.	Rel. Int.	#	m/z	Abs. Int.	Rel. Int.
1	36.00	4259	0.13	25	61.05	8801	0.27
2	37.05	18702	0.58	26	61.95	12951	0.40
3	38.05	91704	2.84	27	63.05	26477	0.82
4	39.05	1061994	32.91	28	64.05	7385	0.23
5	40.05	109710	3.40	29	65.05	59458	1.84
6	41.05	1377324	42.68	30	66.05	47386	1.47
7	42.05	164423	5.10	31	67.05	185732	5.76
8	43.05	547514	16.97	32	68.05	60281	1.87
9	44.05	14932	0.46	33	69.05	259047	8.03
10	45.05	17654	0.55	34	70.05	18155	0.56
11	46.05	2245	0.07	35	71.05	10215	0.32
12	47.10	1119	0.03	36	72.05	2440	0.08
13	49.05	9309	0.29	37	73.05	1539	0.05
14	50.00	115577	3.58	38	74.00	6002	0.19
15	51.00	215786	6.69	39	75.00	3406	0.11
16	52.05	178792	5.54	40	76.05	3697	0.11
17	53.05	1860685	57.66	41	77.05	129498	4.01
18	54.05	1757780	54.47	42	78.05	28688	0.89
19	55.05	905906	28.07	43	79.05	283074	8.77
20	56.05	143675	4.45	44	80.05	33699	1.04
21	57.05	1762054	54.60	45	81.05	298916	9.26
22	58.10	87289	2.70	46	82.05	166564	5.16
23	59.00	8230	0.26	47	83.05	140799	4.36
24	60.05	2828	0.09	48	84.10	45250	1.40

#	m/z	Abs. Int.	Rel. Int.	#	m/z	Abs. Int.	Rel. Int.
49	85.05	532319	16.50	89	140.95	20323	0.63
50	86.10	34099	1.06	90	151.90	10855	0.34
51	87.00	3935	0.12	91	152.90	33878	1.05
52	89.05	2703	0.08	92	153.95	2654	0.08
53	90.15	1479	0.05	93	154.90	18852	0.58
54	91.05	45800	1.42	94	163.85	2411	0.07
55	92.10	15506	0.48	95	164.90	8772	0.27
56	93.10	56910	1.76	96	165.95	7192	0.22
57	94.10	16002	0.50	97	166.95	8590	0.27
58	95.05	174018	5.39	98	167.95	1522	0.05
59	96.10	69404	2.15	99	168.90	10226	0.32
60	97.05	1155444	35.80	100	178.95	8632	0.27
61	98.05	86844	2.69	101	179.95	7847	0.24
62	99.00	5462	0.17	102	180.95	472019	14.63
63	103.05	4027	0.12	103	181.95	28741	0.89
64	104.15	1592	0.05	104	182.90	1562	0.05
65	105.10	13620	0.42	105	192.80	1409	0.04
66	106.05	3988	0.12	106	193.85	3769	0.12
67	107.10	6761	0.21	107	194.90	2466	0.08
68	108.10	5105	0.16	108	195.85	1325	0.04
69	109.10	64631	2.00	109	205.75	1621	0.05
70	110.10	133284	4.13	110	206.95	2903	0.09
71	111.10	22759	0.71	111	207.95	31324	0.97
72	111.90	1530	0.05	112	208.90	2702919	83.76
73	114.80	1393	0.04	113	209.90	178177	5.52
74	117.30	1318	0.04	114	210.85	11772	0.36
75	119.00	2937	0.09	115	220.90	1726	0.05
76	120.15	1036	0.03	116	221.95	1031	0.03
77	121.10	7306	0.23	117	222.95	15165	0.47
78	122.10	2690	0.08	118	223.90	1375593	42.63
79	123.15	8950	0.28	119	224.90	104665	3.24
80	124.10	8681	0.27	120	225.85	6547	0.20
81	125.95	1925	0.06	121	234.95	1205	0.04
82	126.90	62526	1.94	122	235.95	23282	0.72
83	127.95	29915	0.93	123	236.95	3227123	100.00
84	128.90	2356	0.07	124	237.90	294095	9.11
85	137.15	1325	0.04	125	238.90	17948	0.56
86	138.15	4412	0.14	126	265.05	1006	0.03
87	139.10	65801	2.04	127	266.00	38471	1.19
88	139.90	7145	0.22	128	267.05	5884	0.18

The relative abundances of 239 [M (^{18}O)-Et]$^+$, 237 [M (^{16}O)-Et]$^+$ are 0.56, 100.

$$\frac{[\mathrm{M}\ (^{18}\mathrm{O})\text{-Et}]^+}{[\mathrm{M}\ (^{18}\mathrm{O})\text{-Et}]^+ + [\mathrm{M}\ (^{16}\mathrm{O})\text{-Et}]^+} = \frac{0.56}{0.56+100} = 0.557\%$$


wmy-6-44
spect, CDCl3,
Tue Oct 16 12:06:58 2012
USER: nmr
SOLVENT:
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Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
Ph–S
Et
18OH
n-C4H9
I
E-2a-18O
5.23
1.00
0.99
1.04
1.03
4.30
2.58
6.71
8
7
6
5
4
3
2
1
0
PPM
7.324
7.291
7.281
7.258
7.245
7.237
7.231
7.213
4.580
4.557
4.535
2.541
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2.519
2.512
2.494
2.467
2.340
2.316
2.289
2.097
1.681
1.658
1.635
1.611
1.586
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1.516
1.499
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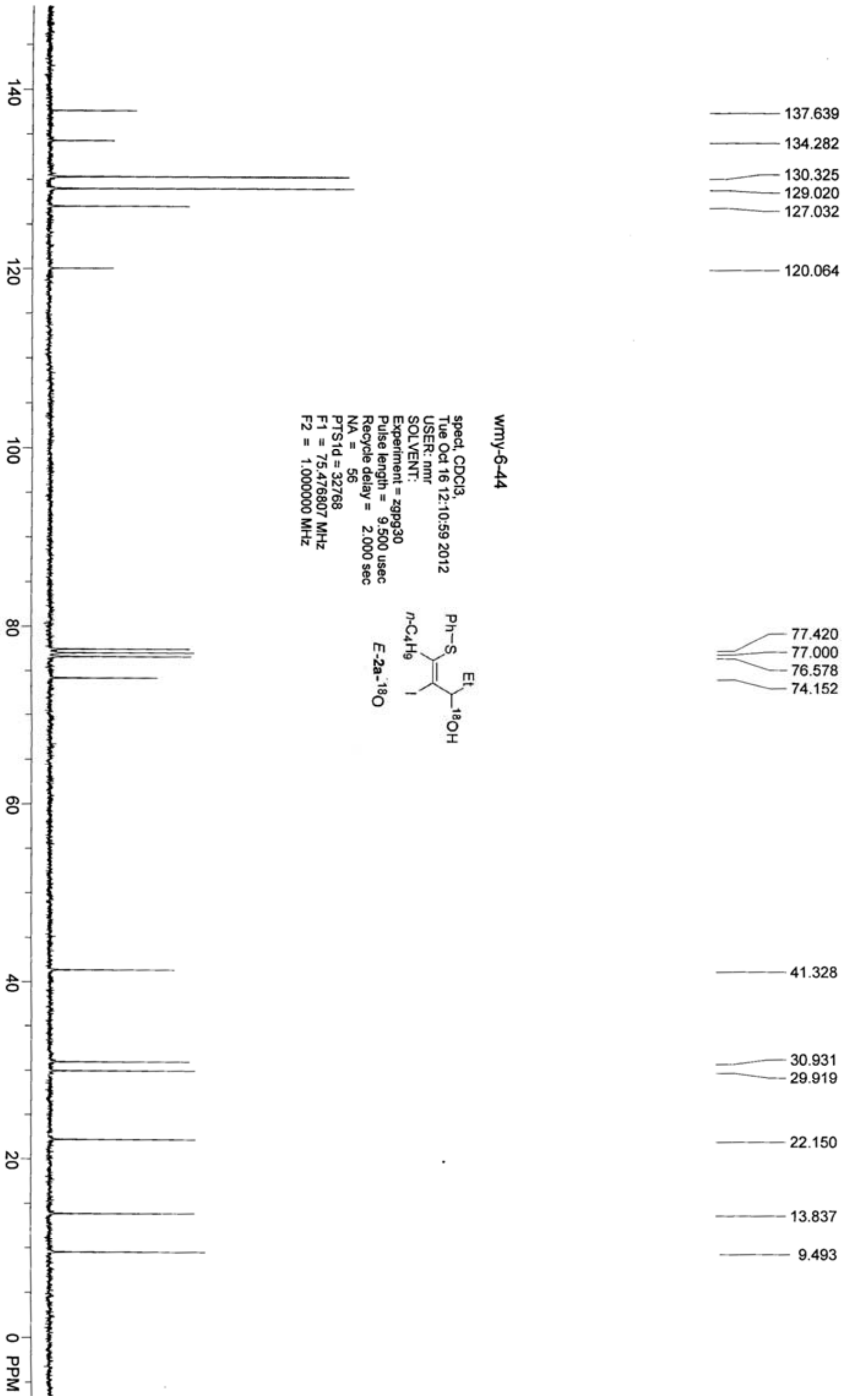
wmy-6-44
spect, CDCl3,
Tue Oct 16 12:10:59 2012
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Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 56
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F1 = 75.476807 MHz
F2 = 1.000000 MHz
E-2a-18O
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134.282
130.325
129.020
127.032
120.064
77.420
77.000
76.578
74.152
41.328
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9.493
PPM

Sample Information

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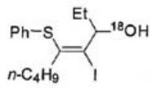
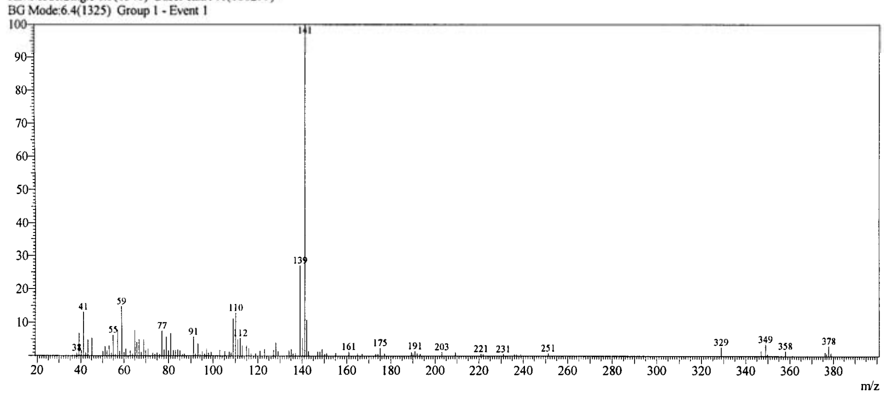


E-**2a**-^{18}O

Spectrum

Line#:1 R.Time:6.5(Scan#:1346)
MassPeaks:116
RawMode:Single 6.5(1346) BasePeak:141(186299)
BG Mode:6.4(1325) Group 1 - Event 1



Mass Table
Line#:1 R.Time:6.5(Scan#:1346)
MassPeaks:116
RawMode:Single 6.5(1346) BasePeak:141(186299)
BG Mode:6.4(1325) Group 1 - Event 1

#	m/z	Abs. Int.	Rel. Int.	#	m/z	Abs. Int.	Rel. Int.
1	38.05	1595	0.86	25	68.00	2226	1.19
2	39.00	12774	6.86	26	69.05	9126	4.90
3	40.05	2932	1.57	27	69.95	3281	1.76
4	41.10	24544	13.17	28	70.95	4042	2.17
5	42.05	2041	1.10	29	73.05	1826	0.98
6	43.10	9028	4.85	30	74.00	1222	0.66
7	45.05	9990	5.36	31	75.05	2030	1.09
8	50.15	2544	1.37	32	76.10	1017	0.55
9	51.10	5382	2.89	33	77.10	14061	7.55
10	52.05	2808	1.51	34	78.10	3552	1.91
11	53.05	5742	3.08	35	79.05	10647	5.72
12	54.05	1750	0.94	36	80.05	3133	1.68
13	55.00	11635	6.25	37	81.00	12640	6.78
14	56.00	858	0.46	38	82.15	3188	1.71
15	57.05	14565	7.82	39	83.10	3174	1.70
16	58.00	2681	1.44	40	84.05	3583	1.92
17	59.05	27640	14.84	41	85.10	3046	1.64
18	60.10	1996	1.07	42	86.15	1097	0.59
19	60.95	4080	2.19	43	86.95	1285	0.69
20	63.00	3135	1.68	44	91.10	10682	5.73
21	64.05	1198	0.64	45	92.05	1363	0.73
22	65.10	14506	7.79	46	93.10	6918	3.71
23	66.00	7816	4.20	47	94.05	1008	0.54
24	67.05	9281	4.98	48	95.05	2511	1.35

#	m/z	Abs. Int.	Rel. Int.	#	m/z	Abs. Int.	Rel. Int.
49	96.15	1298	0.70	83	149.05	3882	2.08
50	97.10	3940	2.11	84	150.15	1040	0.56
51	98.00	1906	1.02	85	151.10	1612	0.87
52	99.10	2291	1.23	86	155.05	1761	0.95
53	103.05	3396	1.82	87	160.95	2351	1.26
54	105.20	2643	1.42	88	164.90	1420	0.76
55	107.20	2406	1.29	89	166.95	1232	0.66
56	108.05	1875	1.01	90	173.05	1227	0.66
57	109.00	20987	11.27	91	174.00	1266	0.68
58	110.05	24060	12.91	92	175.00	4441	2.38
59	111.10	9134	4.90	93	177.10	1350	0.72
60	112.15	9925	5.33	94	189.20	2137	1.15
61	113.05	5874	3.15	95	189.95	1376	0.74
62	115.05	5880	3.16	96	190.85	2675	1.44
63	116.05	4154	2.23	97	191.90	1311	0.70
64	117.00	1535	0.82	98	193.20	1215	0.65
65	119.00	1516	0.81	99	203.05	2219	1.19
66	121.05	2863	1.54	100	209.10	2073	1.11
67	123.10	3711	1.99	101	220.85	1255	0.67
68	127.05	3221	1.73	102	221.85	1033	0.55
69	128.05	7495	4.02	103	231.00	1158	0.62
70	129.10	2719	1.46	104	235.90	1126	0.60
71	133.10	307	0.16	105	236.90	1010	0.54
72	134.05	3138	1.68	106	238.80	1062	0.57
73	135.10	3888	2.09	107	251.20	1580	0.85
74	135.95	1431	0.77	108	328.85	4961	2.66
75	137.00	1497	0.80	109	346.90	3058	1.64
76	139.10	50578	27.15	110	348.95	6631	3.56
77	140.15	9981	5.36	111	349.85	1068	0.57
78	141.15	186299	100.00	112	358.00	2905	1.56
79	142.15	20125	10.80	113	376.00	2239	1.20
80	142.95	2718	1.46	114	376.95	1435	0.77
81	147.05	2473	1.33	115	377.95	5714	3.07
82	148.05	2475	1.33	116	378.90	1810	0.97

Chemical Formula: $C_{15}H_{21}I^{16}OS$

Exact Mass: 376.0358

Molecular Weight: 376.2961

m/z: 376.0358 (100.0%), 377.0391 (17.3%), 378.0316 (4.5%)

Elemental Analysis: C, 47.88; H, 5.63; I, 33.72; O, 4.25; S, 8.52

Chemical Formula: $C_{15}H_{21}I^{18}OS$

Exact Mass: 378.0400

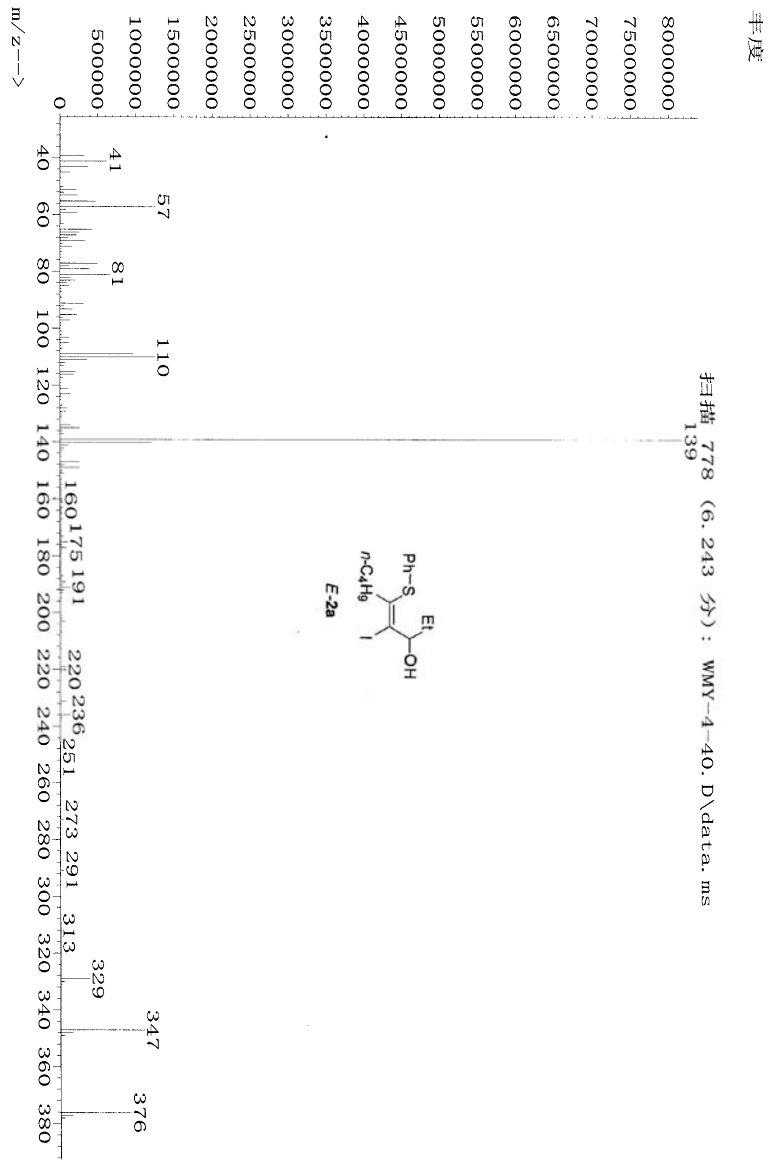
Molecular Weight: 378.2959

m/z: 378.0400 (100.0%), 379.0434 (17.0%), 380.0358 (4.6%)

Elemental Analysis: C, 47.62; H, 5.60; I, 33.55; O, 4.76; S, 8.48

The relative abundances of 378 $[M(^{18}O)]^+$, 376 $[M(^{16}O)]^+$ are 3.07, 1.20

(3.07-1.20*4.5%)/(3.07-1.20*4.5%+1.20)=71.54%


丰度
扫描 778 (6.243 分): WMY-4-40.D\data.ms
m/z-->
E-2a

扫描 778 (6.243 分): WMY-4-40.D\data.ms

37.15	4085	93.15	171200	145.15	17608	196.05	4800	250.15	16105
39.15	322368	95.15	234304	147.05	263680	196.95	4717	251.15	6912
41.15	627840	96.15	42960	148.15	64408	199.05	6817	252.15	1772
43.15	369664	97.15	133632	149.05	261696	201.15	22408	252.95	1463
45.05	133120	98.15	23016	150.15	38344	202.15	37288	254.05	253
46.05	3963	99.05	20192	151.05	56616	203.15	69296	254.95	476
47.05	13652	100.05	13292	152.15	11997	204.15	13782	256.15	433
47.95	406	101.05	34808	153.15	17776	205.15	16146	256.85	861
50.15	51920	102.15	31488	154.15	10932	206.15	13225	258.05	253
51.15	219392	103.15	124952	155.05	27264	207.15	24728	259.85	417
52.15	59472	104.15	22048	156.15	16245	208.15	4246	260.95	394
53.15	237120	105.15	129480	157.15	19816	208.95	9091	262.95	601
55.15	473728	106.15	19064	158.05	11717	210.95	9295	265.05	2413
57.15	1257984	107.15	35536	159.15	12637	212.95	14839	265.95	720
58.15	83744	109.05	974592	160.05	38840	214.05	1364	267.05	2912
59.15	228672	110.05	1252352	161.05	74208	215.15	9105	268.95	14211
60.15	11887	111.05	356416	163.05	83624	216.15	4334	269.95	1461
61.05	10838	112.05	68304	164.05	19696	217.15	2800	270.85	950
62.25	11654	113.05	51264	165.05	30616	219.15	77456	272.95	39640
63.15	51744	115.15	208128	166.95	65456	220.15	80280	273.95	4059
65.15	435584	116.15	186816	168.15	7201	221.15	16440	274.95	3230
66.15	252160	117.15	44952	169.05	15217	222.15	4625	276.05	2800
67.15	231936	118.15	6768	171.05	26856	223.05	4018	276.95	903
68.15	107624	119.15	15331	172.15	16239	224.15	1670	278.05	302
69.05	331008	121.05	111472	173.05	54008	225.05	1914	278.95	3745
70.15	37800	123.05	147136	174.15	19200	226.05	1406	280.05	608
71.05	162432	124.15	19056	175.05	103440	226.95	1739	281.05	1148
72.05	16744	125.05	22264	176.15	27384	228.05	326	281.95	462
73.05	27400	127.05	49728	177.05	88880	229.15	3360	282.55	188
74.05	16776	128.05	100160	178.05	25144	231.15	75688	283.15	255
75.15	22504	129.15	81264	179.05	18512	232.15	16552	285.95	1772
77.15	503680	130.15	20256	181.05	9196	233.15	5022	286.95	2324
78.15	122880	131.15	22864	182.95	13093	234.15	1201	288.15	552
79.15	399104	132.05	4539	184.15	6833	235.95	132864	289.05	3421
81.15	659392	134.05	151936	185.05	10438	236.95	31152	290.95	47184
82.15	131712	135.05	262720	186.15	7191	237.95	9993	291.95	5136
83.15	199488	136.05	38952	187.05	40784	238.95	2238	293.05	2273
84.05	93472	137.15	58088	188.15	24432	239.95	1055	294.05	306
85.05	122456	139.15	8388096	189.15	72976	240.95	1140	295.25	166
86.05	24496	140.15	1204224	190.15	42872	242.05	631	296.85	707
87.05	29336	141.15	112536	191.15	133504	242.95	755	298.05	304
89.05	35808	142.15	53272	192.15	59720	247.15	13853	299.05	2127
91.15	318848	143.15	29144	193.05	31368	248.15	17408	299.95	813
92.15	55200	144.15	11928	194.95	25752	249.15	94552	301.05	1010

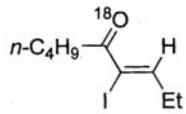
302.05	1062
303.05	1274
304.05	452
305.05	2887
305.95	538
307.05	259
311.15	189
313.05	2491
314.15	322
315.05	748
316.05	239
317.05	944
319.05	8138
320.05	1252
320.95	427
327.05	194
329.05	384384
330.05	57008
331.05	22776
332.05	2685
333.05	368
334.05	8198
335.05	1142
336.05	305
343.05	261
345.05	11488
347.05	1103872
348.05	166336
349.05	63312
350.05	8964
351.05	839
356.05	160
357.15	1594
358.05	11138
359.15	16408
360.05	2668
361.15	1581
361.95	295
371.55	179
374.05	459
376.15	930496
377.15	160448
378.05	57904
379.15	8180
380.05	771
381.15	205

The relative abundances of 378 [M (^{18}O)]$^+$, 376 [M (^{16}O)]$^+$ are 57904, 930496.

(57904-930496*4.5%)/(57904-930496*4.5%+930496)=1.69 %

Sample Information

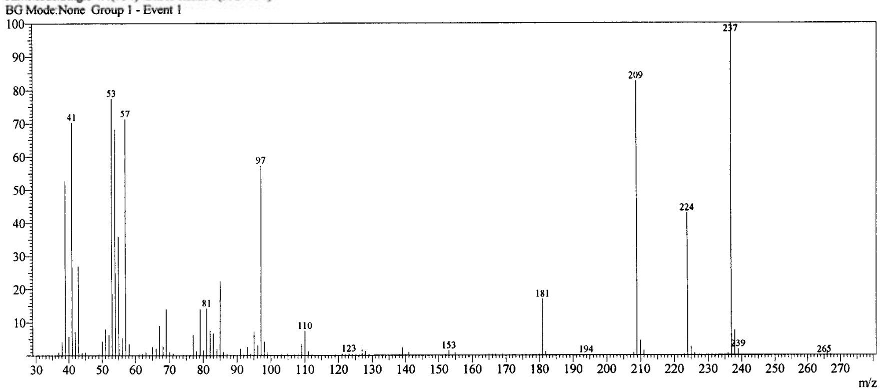
E:\msm\wmy-6-45_2012-10-18_7.qgd



Z-**3a**-^{18}O

Spectrum

Line#:1 R.Time:4.4(Scan#:734)
MassPeaks:141
RawMode:Single 4.4(734) BasePeak:237(3527637)
BG Mode:None Group 1 - Event 1



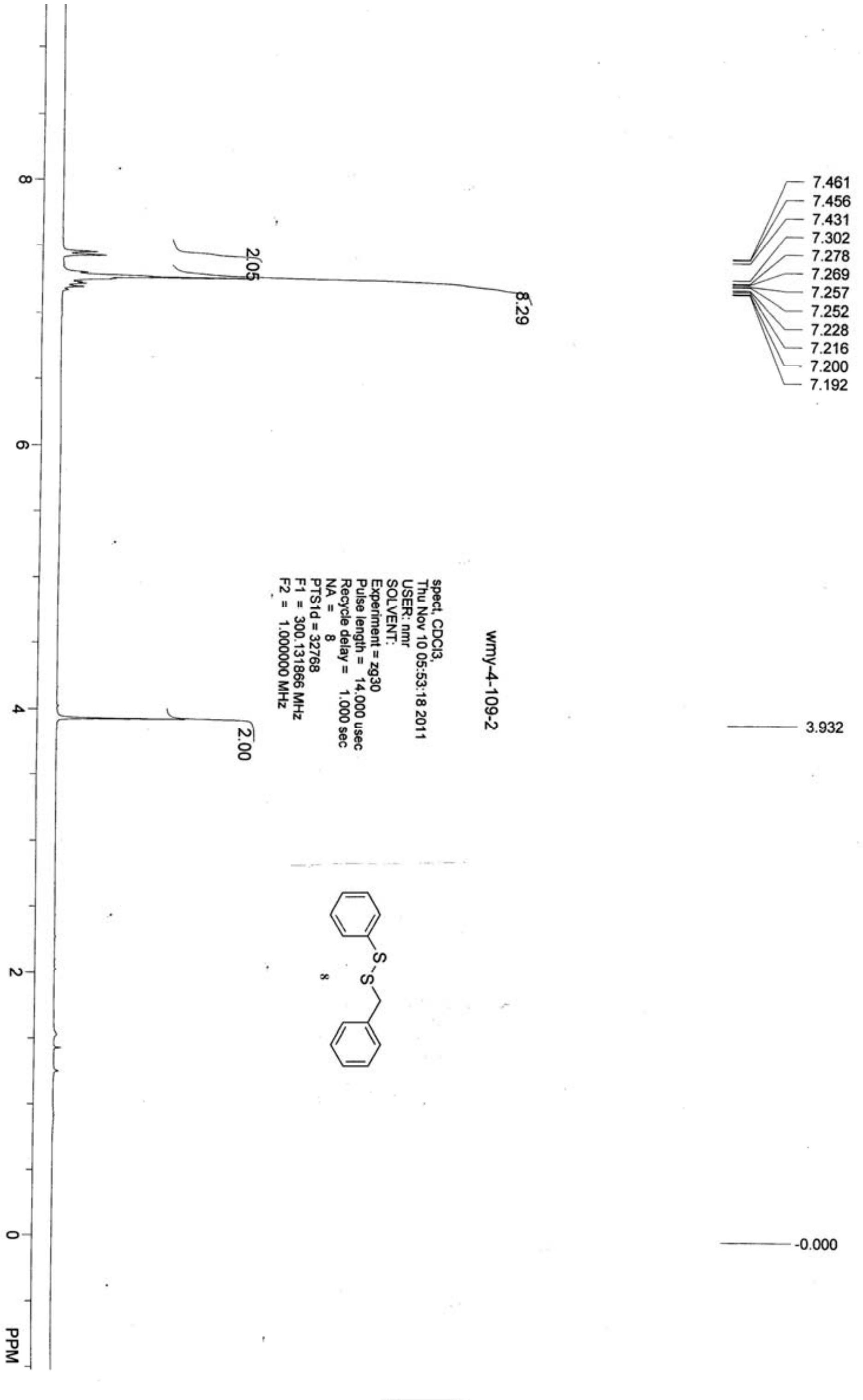
Mass Table
Line#:1 R.Time:4.4(Scan#:734)
MassPeaks:141
RawMode:Single 4.4(734) BasePeak:237(3527637)
BG Mode:None Group 1 - Event 1

#	m/z	Abs. Int.	Rel. Int.	#	m/z	Abs. Int.	Rel. Int.
1	36.05	3150	0.09	25	60.05	2761	0.08
2	37.05	31836	0.90	26	61.00	12972	0.37
3	38.05	144470	4.10	27	62.00	16377	0.46
4	39.05	1855934	52.61	28	63.00	36076	1.02
5	40.10	205938	5.84	29	64.05	12058	0.34
6	41.10	2481183	70.34	30	65.05	90704	2.57
7	42.05	257800	7.31	31	66.05	72224	2.05
8	43.05	952441	27.00	32	67.05	319970	9.07
9	44.05	29123	0.83	33	68.05	100219	2.84
10	45.10	38534	1.09	34	69.05	492858	13.97
11	46.05	3499	0.10	35	70.10	38271	1.08
12	47.00	1196	0.03	36	71.05	24042	0.68
13	47.95	1123	0.03	37	72.05	1978	0.06
14	49.05	13774	0.39	38	73.05	3145	0.09
15	50.05	148163	4.20	39	74.10	7327	0.21
16	51.05	285607	8.10	40	75.00	6290	0.18
17	52.05	225391	6.39	41	76.15	5570	0.16
18	53.05	2735454	77.54	42	77.05	221713	6.29
19	54.05	2408901	68.29	43	78.05	47486	1.35
20	55.05	1269043	35.97	44	79.10	491020	13.92
21	56.10	195071	5.53	45	80.10	52255	1.48
22	57.10	2518937	71.41	46	81.05	503023	14.26
23	58.10	121311	3.44	47	82.05	266321	7.55
24	59.00	11276	0.32	48	83.05	237594	6.74

#	m/z	Abs. Int.	Rel. Int.	#	m/z	Abs. Int.	Rel. Int.
49	84.10	66630	1.89	96	139.10	82162	2.33
50	85.05	792856	22.48	97	139.95	11041	0.31
51	86.05	40178	1.14	98	140.90	32946	0.93
52	87.05	15765	0.45	99	141.90	1068	0.03
53	88.15	1013	0.03	100	151.95	10727	0.30
54	89.05	2787	0.08	101	153.00	49119	1.39
55	90.15	1563	0.04	102	153.95	1821	0.05
56	91.05	72499	2.06	103	154.90	26022	0.74
57	92.05	17854	0.51	104	164.95	12131	0.34
58	93.10	90214	2.56	105	165.95	10754	0.30
59	94.05	17962	0.51	106	166.90	11417	0.32
60	95.05	255886	7.25	107	167.95	1818	0.05
61	96.10	110822	3.14	108	168.90	13305	0.38
62	97.10	2023430	57.36	109	178.90	12306	0.35
63	98.10	142425	4.04	110	179.95	10924	0.31
64	99.05	37005	1.05	111	180.90	598399	16.96
65	100.10	2482	0.07	112	181.90	37036	1.05
66	101.95	1071	0.03	113	182.90	2226	0.06
67	103.00	7794	0.22	114	190.00	1215	0.03
68	104.15	2862	0.08	115	192.95	1414	0.04
69	105.05	27011	0.77	116	193.90	4959	0.14
70	106.15	7482	0.21	117	194.75	2623	0.07
71	107.10	12748	0.36	118	195.80	1612	0.05
72	108.10	7398	0.21	119	205.90	2233	0.06
73	109.10	117465	3.33	120	206.95	4840	0.14
74	110.10	262706	7.45	121	207.95	28953	0.82
75	111.10	41599	1.18	122	208.90	2915078	82.64
76	112.15	7876	0.22	123	209.95	159771	4.53
77	113.10	1055	0.03	124	210.95	51225	1.45
78	115.10	2662	0.08	125	211.95	2069	0.06
79	117.10	1932	0.05	126	219.00	1689	0.05
80	118.05	1068	0.03	127	220.95	1937	0.05
81	119.10	7148	0.20	128	222.95	12195	0.35
82	120.05	2747	0.08	129	223.90	1516479	42.99
83	121.10	13369	0.38	130	224.95	91091	2.58
84	122.05	5611	0.16	131	225.95	24206	0.69
85	123.10	18546	0.53	132	227.00	1234	0.03
86	124.00	11148	0.32	133	235.95	20391	0.58
87	124.95	1546	0.04	134	236.95	3527637	100.00
88	125.95	2301	0.07	135	237.95	264180	7.49
89	126.95	83664	2.37	136	238.95	64847	1.84
90	127.90	57081	1.62	137	239.90	4953	0.14
91	129.10	3705	0.11	138	265.05	1775	0.05
92	133.45	1607	0.05	139	266.00	40806	1.16
93	136.30	2098	0.06	140	267.00	9407	0.27
94	137.15	1351	0.04	141	267.95	1340	0.04
95	138.10	9439	0.27				

The relative abundances of 239 $[M\,(^{18}O)\text{-}Et]^+$, 237 $[M\,(^{16}O)\text{-}Et]^+$ are 1.84, 100

$$\frac{[M\,(^{18}O)\text{-}Et]^+}{[M\,(^{18}O)\text{-}Et]^+ + [M\,(^{16}O)\text{-}Et]^+} = \frac{1.84}{1.84+100} = 1.81\%$$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USER: nmr
SOLVENT:
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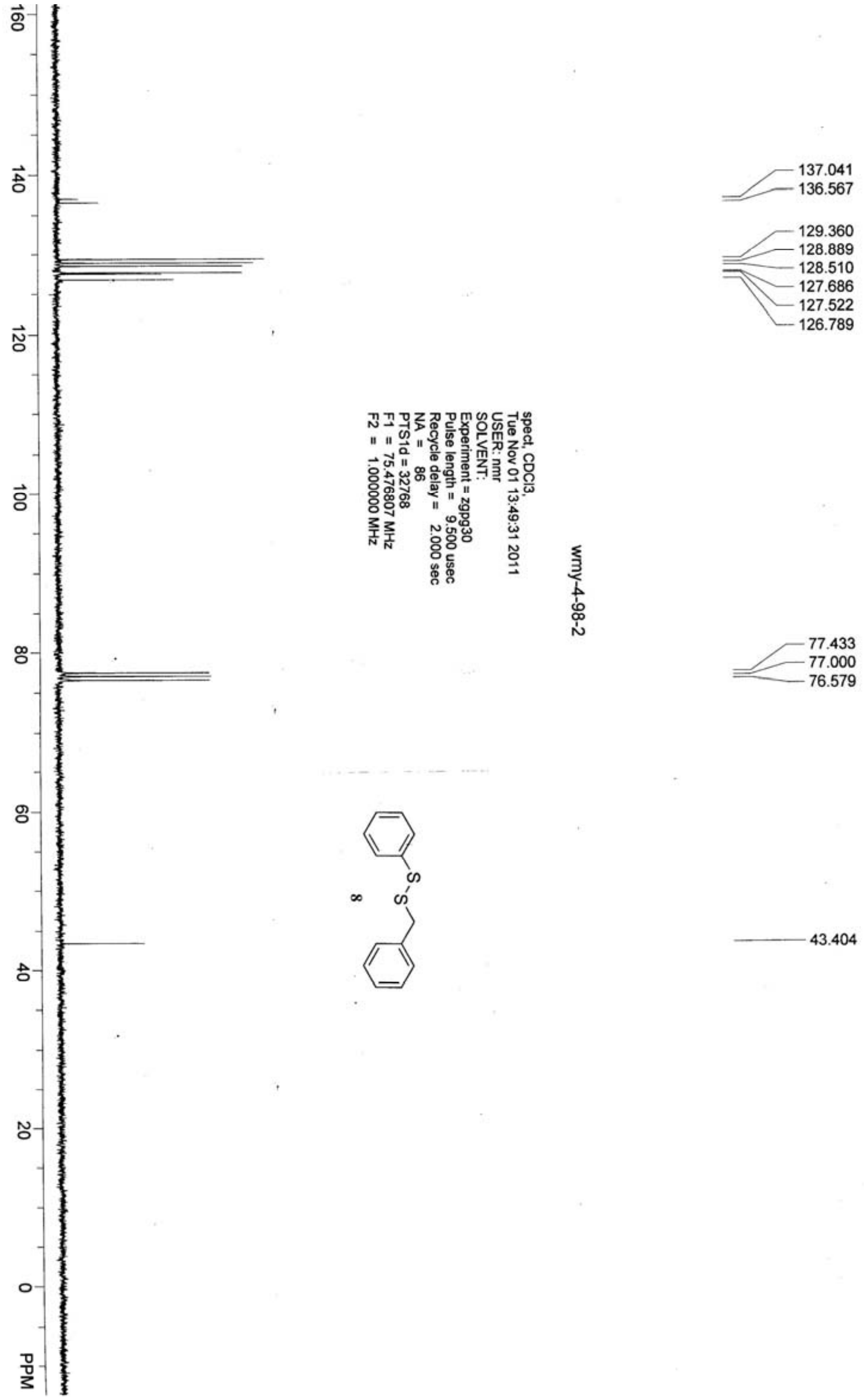
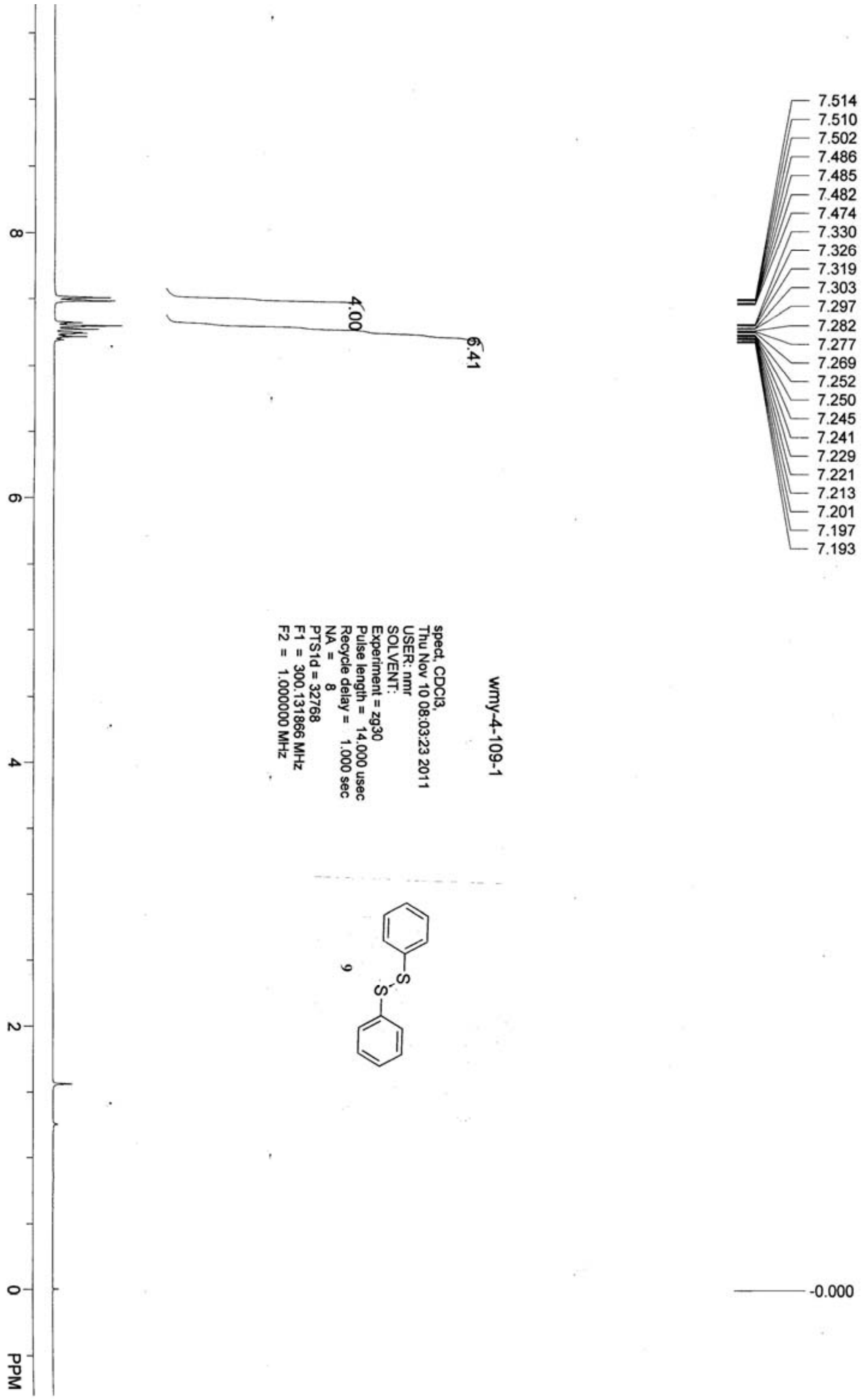
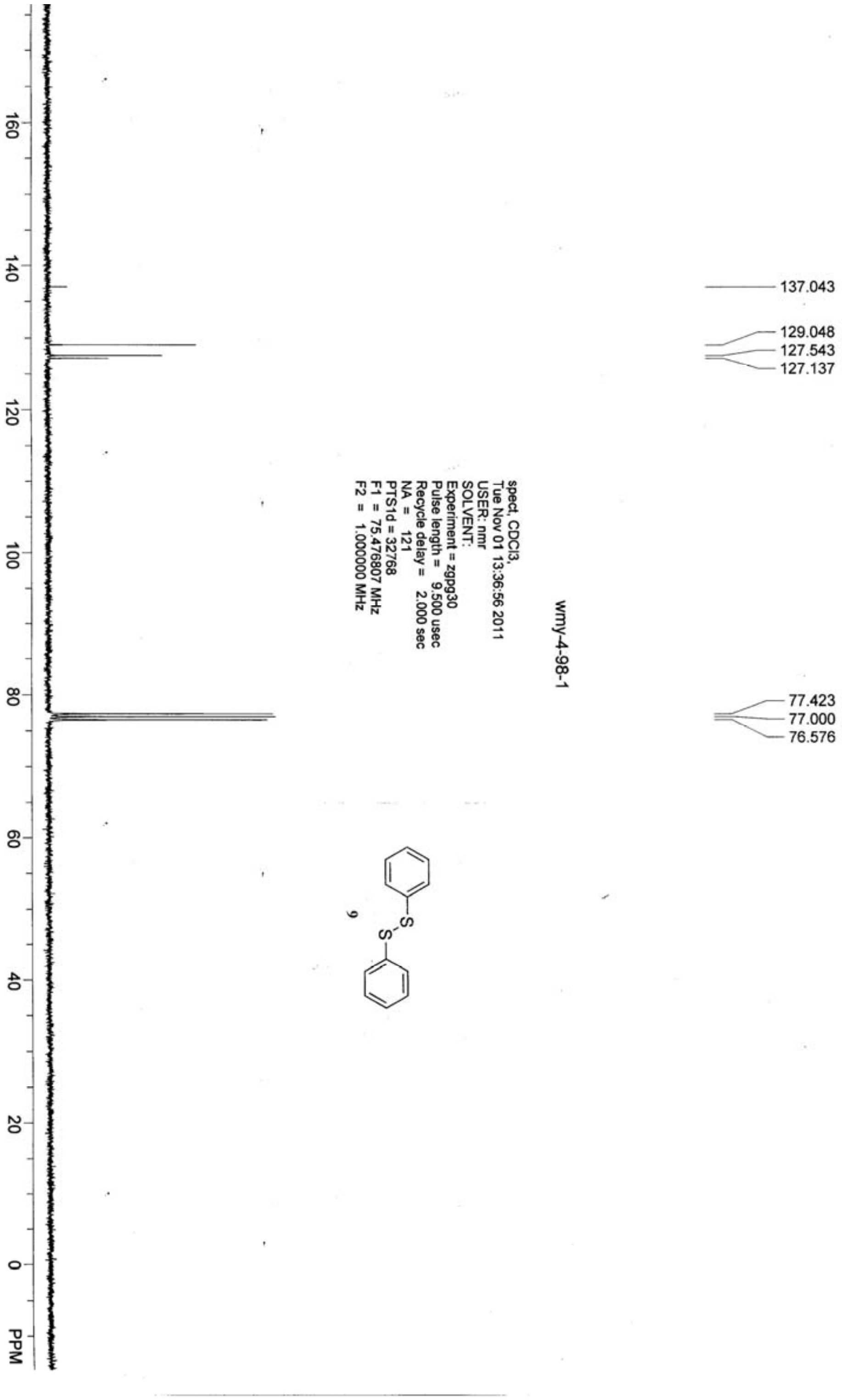
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
7.461
7.456
7.431
7.302
7.278
7.269
7.257
7.252
7.228
7.216
7.200
7.192
3.932
-0.000
2.05
8.29
2.00
S
S
8
PPM


wmy-4-98-2
spect. CDCl3.
Tue Nov 01 13:49:31 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 86
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
137.041
136.567
129.360
128.889
128.510
127.686
127.522
126.789
77.433
77.000
76.579
43.404
S
S
8
160
140
120
100
80
60
40
20
0
PPM


7.514
7.510
7.502
7.486
7.485
7.482
7.474
7.330
7.326
7.319
7.303
7.297
7.282
7.277
7.269
7.252
7.250
7.245
7.241
7.229
7.221
7.213
7.201
7.197
7.193
-0.000
4.00
6.41
wmy-4-109-1
spect, CDCl3,
Thu Nov 10 08:03:23 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
S
S
9
8
6
4
2
0
PPM


137.043
129.048
127.543
127.137
77.423
77.000
76.576
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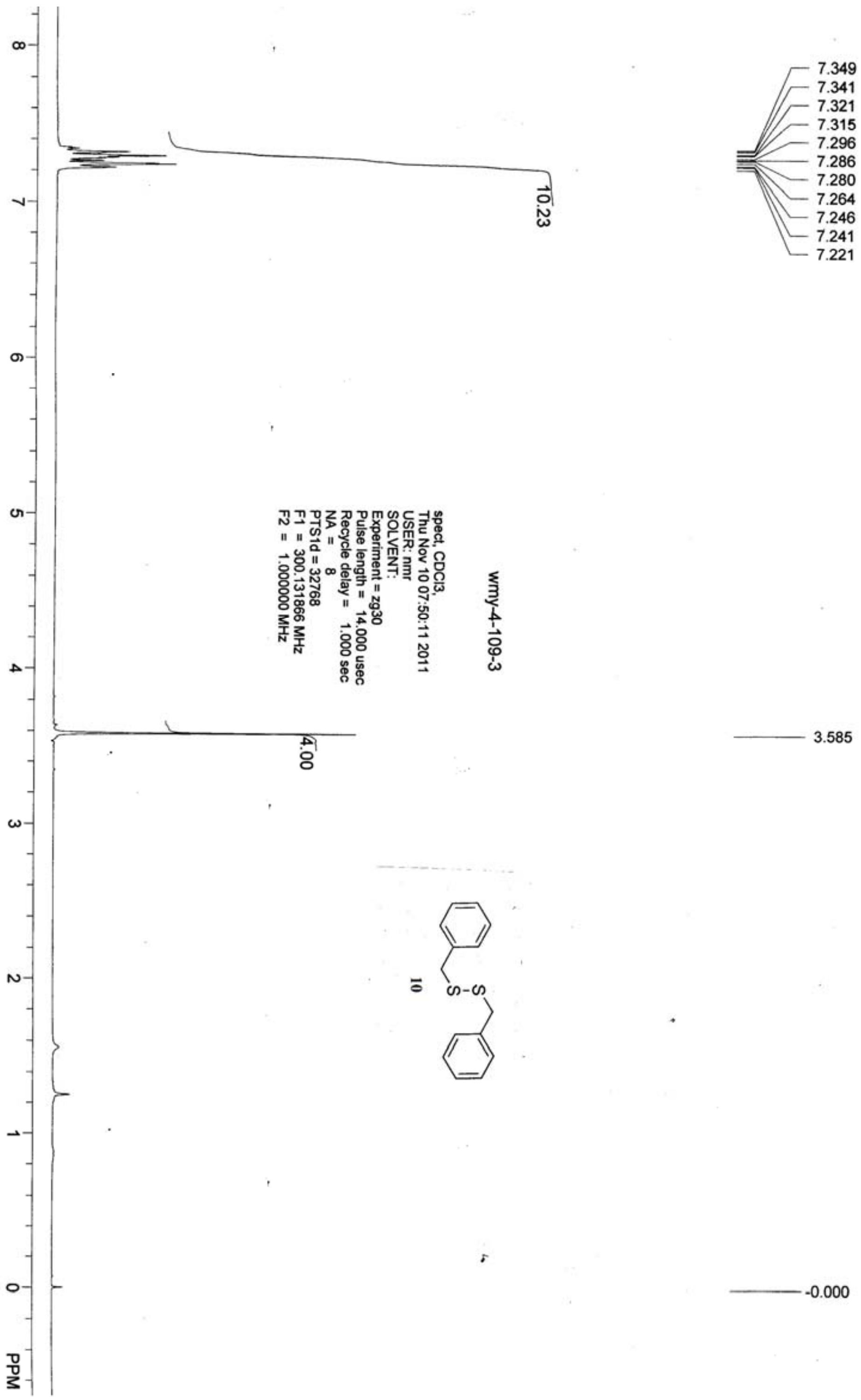
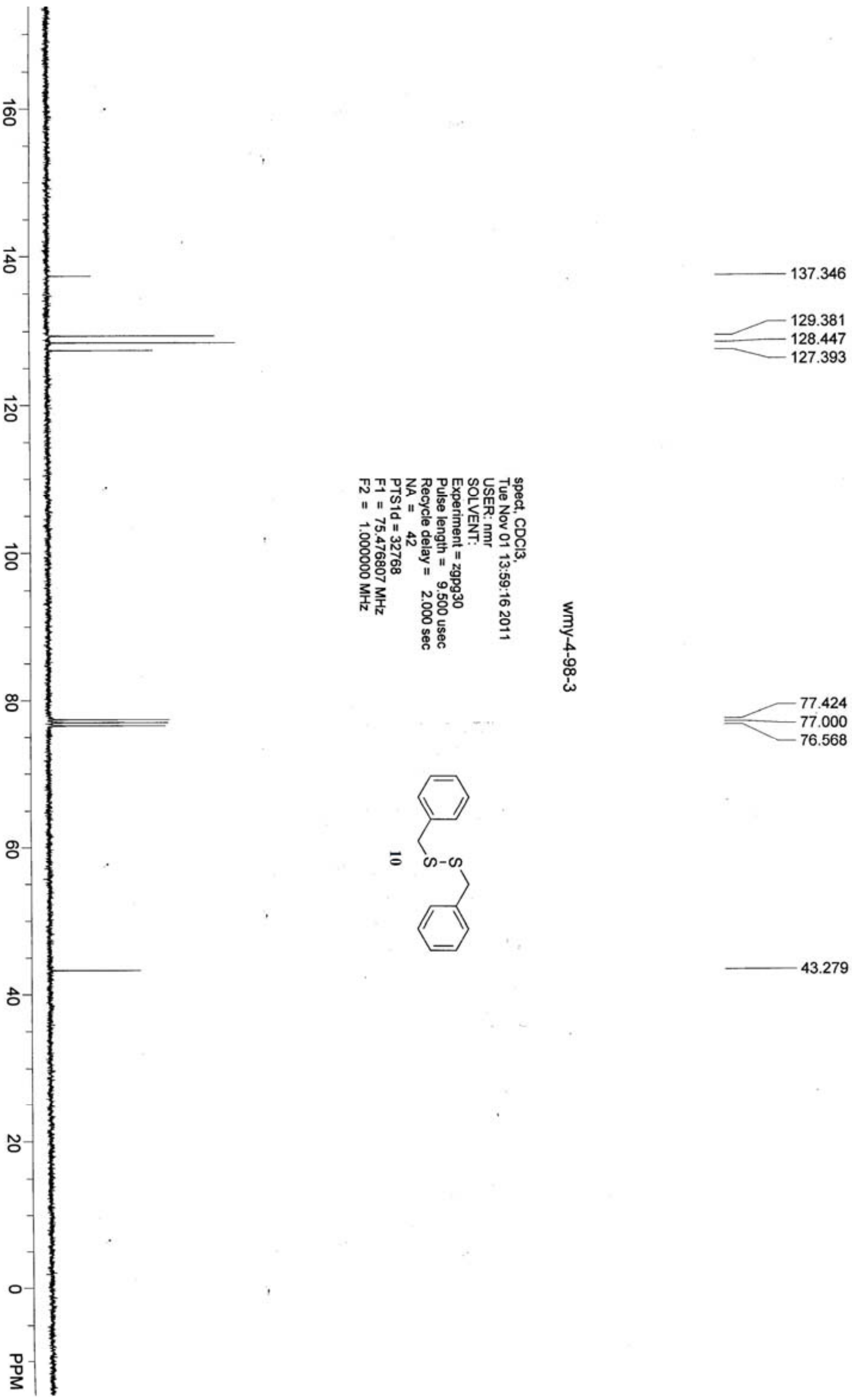
Tue Nov 01 13:36:56 2011
USER: nmr
SOLVENT:
Experiment = zgpg30
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 121
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
S
S
9
PPM


7.349
7.341
7.321
7.315
7.296
7.286
7.280
7.264
7.246
7.241
7.221
10.23
wmy-4-109-3
spect, CDCl3,
Thu Nov 10 07:50:11 2011
USER: nmr
SOLVENT:
Experiment = zg30
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
3.585
4.00
10
-0.000
PPM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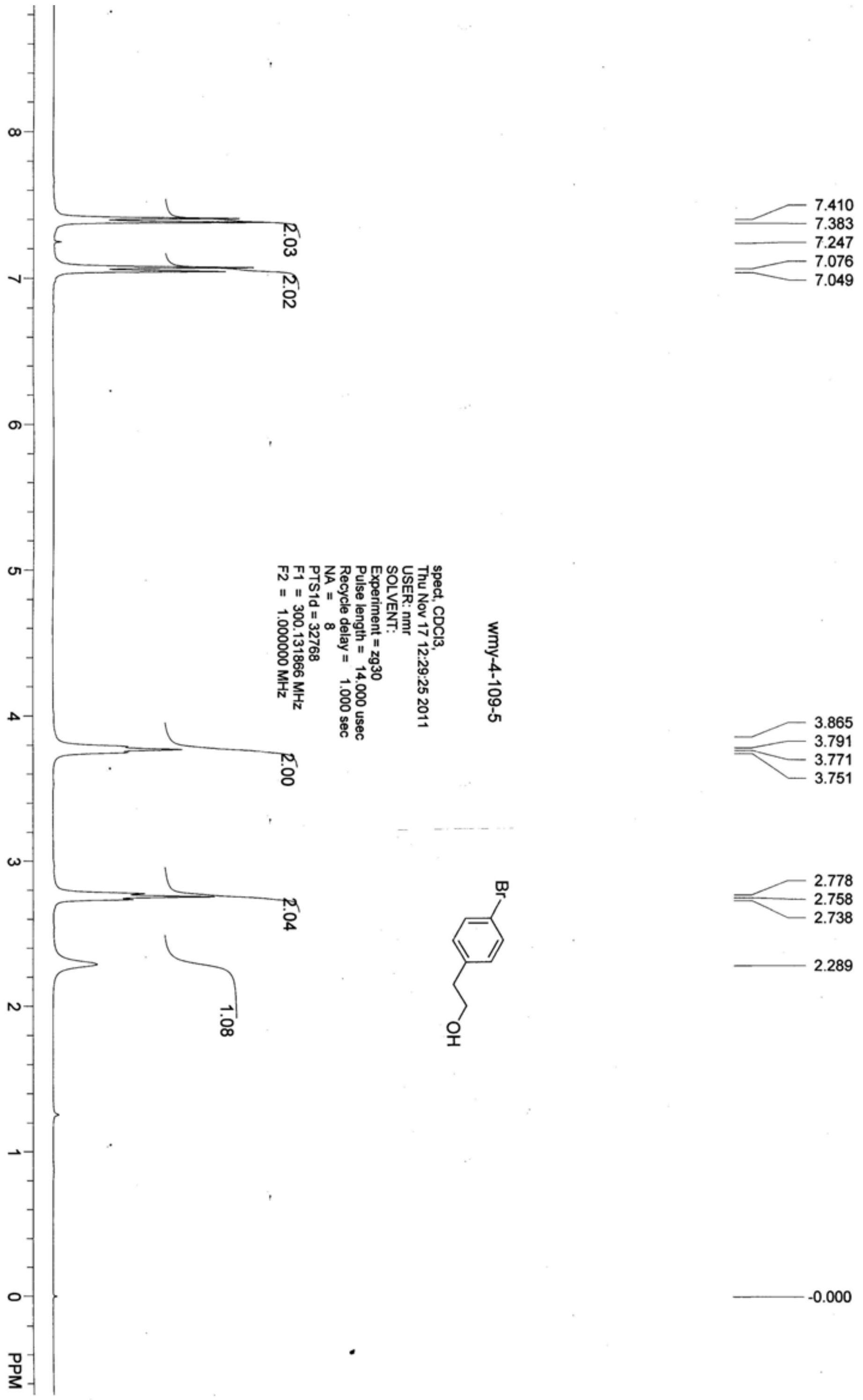
Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 42
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
137.346
129.381
128.447
127.393
77.424
77.000
76.568
43.279
10
160
140
120
100
80
60
40
20
0
PPM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spect CDCl3
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USER: nmr
SOLVENT:
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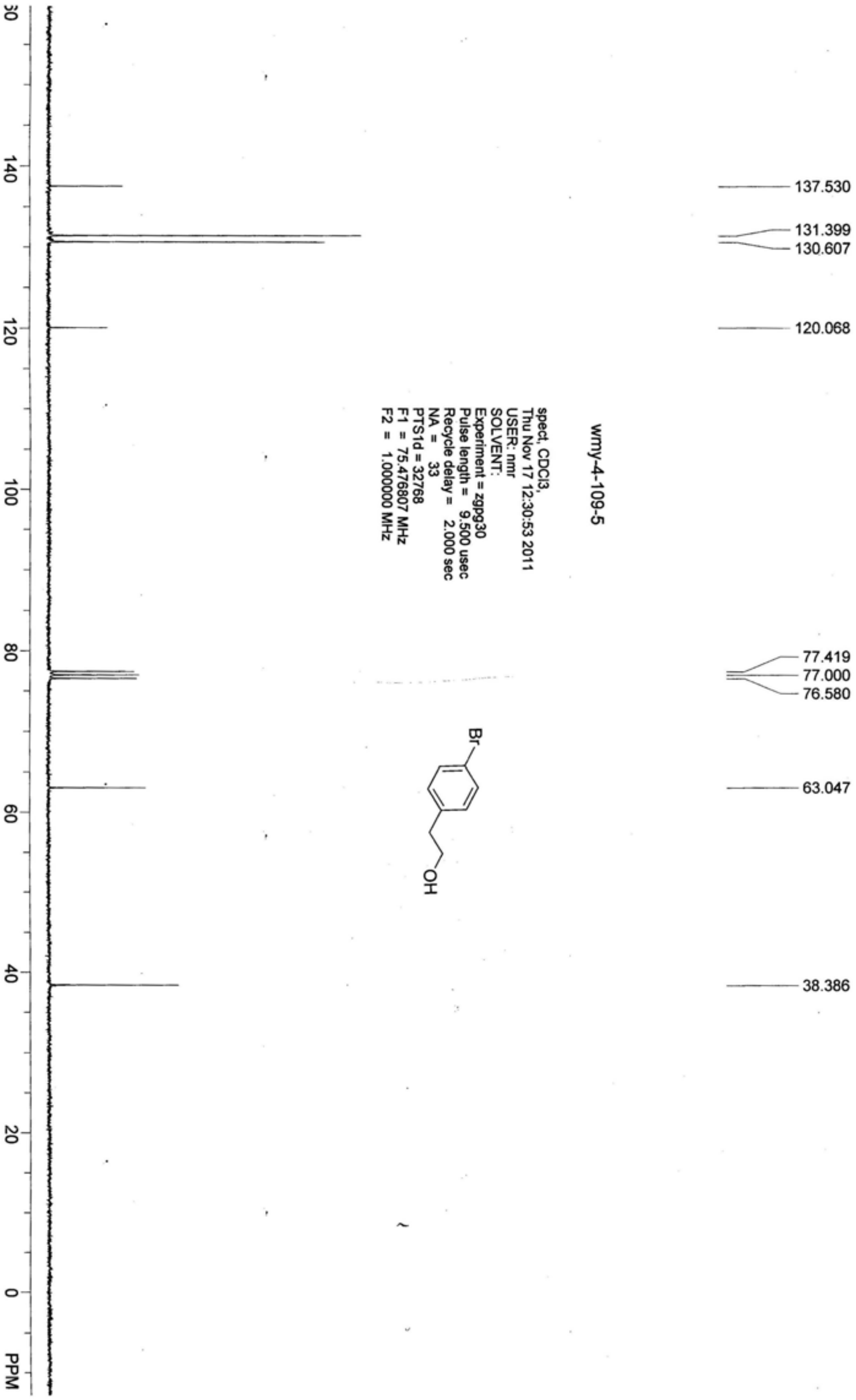
Pulse length = 14.000 usec
Recycle delay = 1.000 sec
NA = 8
PTS1d = 32768
F1 = 300.131866 MHz
F2 = 1.000000 MHz
Br
OH
7.410
7.383
7.247
7.076
7.049
3.865
3.791
3.771
3.751
2.778
2.758
2.738
2.289
-0.000
2.03
2.02
2.00
2.04
1.08
PPM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SOLVENT:
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Pulse length = 9.500 usec
Recycle delay = 2.000 sec
NA = 33
PTS1d = 32768
F1 = 75.476807 MHz
F2 = 1.000000 MHz
137.530
131.399
130.607
120.068
77.419
77.000
76.580
63.047
38.386
Br
OH
PPM