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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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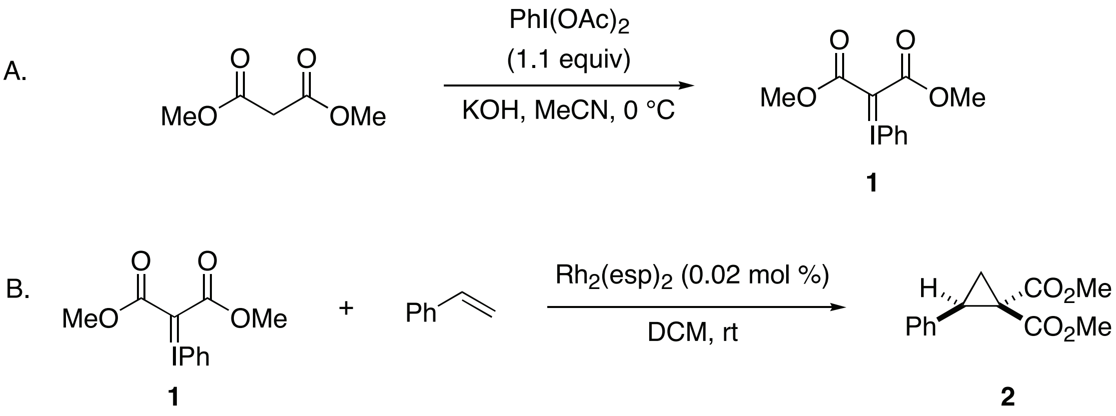
SYNTHESIS OF DIMETHYL 2-PHENYLCYCLOPROPANE-1,1-DICARBOXYLATE USING AN IODONIUM YLIDE DERIVED FROM DIMETHYL MALONATE



Submitted by Sébastien R. Goudreau, David Marcoux and
André B. Charette.[1]
Checked by David Hughes.

1. Procedure

*A. Bis(methoxycarbonyl)(phenyliodinio)methanide (**1**).* A 1-L, 3-necked round-bottomed flask (Note 1) equipped with a 3-cm oval Teflon-coated magnetic stir bar (Note 2) is fitted with a gas inlet adapter connected to a nitrogen line and a gas bubbler, and a septum through which is inserted a thermocouple probe (Note 3). The third neck is fitted with a ground glass stopper, which is removed for solvent and solids additions. To the flask is added potassium hydroxide (30.2 g, 85%, 0.45 mol, 5.0 equiv) (Note 4) and acetonitrile (300 mL) (Note 5). The solution is cooled to 5 °C with an ice/water bath and then dimethyl malonate (11.9 g, 90.0 mmol, 1.00 equiv) is added via a weighed 20-mL syringe over 5 min, forming a viscous slurry (Note 2). $PhI(OAc)_2$ (32.0 g, 99.3 mmol, 1.10 equiv) is added in one portion. The viscous heterogeneous mixture is stirred vigorously for 2 h at 0 to 5 °C and gradually becomes a viscous creamy suspension (Note 6). Water (150 mL) is added in one portion, resulting in a temperature rise to 10 °C. The mixture is stirred for 2 min at this temperature (Note 7), then filtered through a 350-mL medium porosity sintered glass funnel (Note 8). The flask is rinsed with room temperature water (100 mL), and this rinse is used to slurry wash the filter cake (Note 9). The cake is washed a second time with water (100 mL) (Note 10). The white solid is next slurry-washed with Et_2O (150 mL). The solids are dried to constant weight under vacuum (20 mmHg) at 30 °C for 25 h to afford bis(methoxycarbonyl)(phenyliodinio)methanide **1** (23.9 g, 79 %) (Note 11) as an off-white crystalline solid (Notes 12, 13, and 14).

*B. Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (**2**).* A 250-mL 3-necked round-bottomed flask equipped with a 2-cm oval Teflon-coated magnetic stir bar is fitted with a gas inlet adapter connected to a nitrogen line and a gas bubbler, and a septum through which is inserted a thermocouple probe (Note 3). The third neck is fitted with a ground glass stopper, which is removed for solvent and solids additions. To the flask is added bis[rhodium(α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid)] (5 mg, 0.007 mmol, 0.02 mol %) (Note 15), dichloromethane (80 mL) and styrene (3.90 g, 37.4 mmol, 1.00 equiv), and the stirred solution is cooled to 2 °C using an ice/water bath. Iodonium ylide **1** (14.7 g, 43.9 mmol, 1.2 equiv) is added in four portions (3.5 – 4.0 g each) at 5 min intervals (Notes 16 and 17). After the last addition, the ice/water bath is removed. The mixture is allowed to warm to room temperature and is stirred for 1 h at 18–20 °C (Note 18). Aqueous 10% thiourea (50 mL) is added in one portion and the biphasic solution is stirred for 15 min at 20 °C. The mixture is transferred to a 250-mL separatory funnel along with a dichloromethane rinse (15 mL) of the flask. The layers are separated and the aqueous layer is extracted with dichloromethane (2 × 20 mL) (Note 19). The organic layers are combined and vacuum filtered through a bed of Na_2SO_4 (20 g) on top of a Celite© cake (20 g) in a 150-mL sintered-glass funnel. The cake is washed with dichloromethane (2 x 50 mL). The filtrate is concentrated by rotary evaporation (40 °C bath, 100 mmHg initial, lowered to 20 mmHg) to afford 18 g of a yellow, oily mixture of cyclopropane **2** and iodobenzene. This oil is purified by chromatography on SiO_2 (Note 20) to afford dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (**2**) (8.07–8.34 g, 92–95% yield) as a yellowish oil (Notes 21 and 22).

2. Notes

1. No special exclusion of water is needed.
2. The procedure was checked using both magnetic stirring and mechanical stirring. The reaction mixture is viscous and poorly mixed using magnetic stirring at 700 rpm, but no difference in yield was obtained with

the two methods of agitation. Adding more solvent for better stirring proved to be detrimental for the yield.

3. The internal temperature is monitored using a J-Kem Gemini digital thermometer with a Teflon-coated T-Type thermocouple probe (12-inch length, 1/8 inch outer diameter, temperature range –200 to +250 °C).

4. The submitters used potassium hydroxide pellets (88% purity) purchased from American Chemicals Ltd. and used as received. The checkers used powdered KOH (85%) obtained from Sigma Aldrich. An excess of potassium hydroxide was optimal for both yield and reproducibility. The checker obtained a 69% yield at this scale using 2.5 equiv KOH instead of 5 equiv.

5. The following reagents and solvents in Step A were obtained from Sigma-Aldrich and used without further purification: acetonitrile (Chromatosolv, 99.9%), dimethyl malonate (98%), and diethyl ether (ACS reagent, anhydrous, BHT-inhibited). Iodosobenzene diacetate (98%) was purchased from Acros and used as received. Deionized tap water was used throughout.

6. Reaction time of 2 h provided the optimal yield. The reaction was not monitored.

7. Vigorous stirring for 2 min is sufficient to dissolve all remaining potassium hydroxide.

8. The filtration took about 10 min.

9. The cake is slurry-washed as follows: 1) the vacuum line is disconnected from the filter flask, 2) water (100 mL) is added to the cake, 3) the cake is mixed for approx. 20 s with a spatula to ensure full contact of all solids with water, 4) the vacuum line is reconnected to the filter flask to remove the cake wash. It is important that the solvent wash be completely removed between each wash.

10. The second cake wash is carried out as a displacement wash, with the vacuum remaining on and no mixing of the cake.

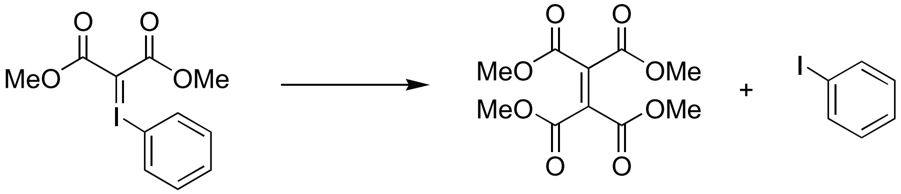
11. After drying to constant weight, the solids contained approx 2 wt% water based on ^{1}H NMR analysis in dry DMSO-d_6. Corrected yield is 77%.

12. Bis(methoxycarbonyl)(phenyliodinio)methanide **1** has the following physical and spectroscopic data: mp 100–104 °C (softens to gum; full melt at 120 °C); IR (neat) 3081, 2982, 2948, 2899, 1668, 1585, 1575, 1562, 1435, 1425, 1320, 1060, 990 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 3.75 (s, 6 H), 7.40–7.44 (m, 2 H), 7.52–7.56 (m, 1 H), 7.74–7.76 (m, 2 H);

^{13}C NMR (100 MHz, DMSO-d_6) δ: 50.7, 58.0 (broad), 116.0, 130.5, 131.1, 131.2, 166.0.

13. The ylide **1** is poorly soluble and unstable in organic solvents. DMSO-d_6 was the optimum solvent for NMR analysis. Samples analyzed within 10 min of dissolution in this solvent indicated product purity >98%. The resonance of the C(2) carbon is broad (δ: 58 ppm) and requires acquisition for several hours to obtain an observable signal. The resonance of this carbon is similar to that reported for the phenyliodonium ylide derived from methyl acetoacetate (68 ppm).[2] In solution, the product decomposes to iodobenzene and dimer **3** (Note 14).

14. The product showed no degradation based on NMR analysis after drying for 25 h at 30 °C. As a dry solid, the product degrades slowly at room temperature (over 2 weeks) to form mainly dimer **3** and iodobenzene, but it can be stored at –20 °C for months without significant degradation. The submitters observed rapid degradation of the ylide when not properly dried. However, its degradation never led to an explosion. Indeed, the exothermic degradation can be described as a rapid "melting" of the ylide to produce a hot iodobenzene solution, fumes, and black solids. Care should be taken when an oily solid is obtained, meaning the workup/drying process was not correctly done. The checkers ran the procedure 3 times as written or with slight variations with no issues with decomposition.


3

Dimer **3** was not isolated and characterized, but ^1H and ^{13}C NMR spectral data are consistent with reported literature NMR data.[3]

15. The following reagents and solvents used in Step B were obtained from Sigma-Aldrich and used without further purification: bis[rhodium(α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid)] (abbr. as $Rh_2(esp)_2$), dichloromethane (ACS reagent, 99.5%), thiourea, Celite 545, silica gel (230-400 mesh, 60 Å), ethyl acetate (ACS reagent, >99.5%), and hexanes (ACS reagent, >98.5%). Styrene (99.5%) was purchased from Acros and used as received. Sodium sulfate was obtained from Fisher Scientific.

16. After each addition the mixture warms to 9–11 °C within one minute, then is cooled to <5 °C prior to the next addition of the ylide.

17. The mixture is heterogeneous after addition of the ylide and is stirred at 500 rpm.

18. The submitters followed the progress of the reaction by GC analysis (Agilent 6890 Series GC, Column: HP-5HS30m x 0.25 mm, Agilent 5973EI mass detector, temperature of the injector: 250 °C, temperature of the detector: 250 °C) using a 5 °C/min gradient from 40 to 270 °C and 63 psi H_2. Styrene has a t_r = 5.48 min, iodobenzene has a t_r = 7.73 min, cyclopropane **2** has t_r = 15.9 min. The checker followed the reaction by ^{1}H NMR as follows. A drop of the reaction mixture was added to 1 mL of $CDCl_3$ and analyzed by ^{1}H NMR. The styrene resonances at 5.8 and 6.8 ppm were integrated relative to the cyclopropane resonances at 1.8 and 2.2 ppm of the product to assess conversion. If more than 2% styrene remained, an additional amount of the ylide was added at room temperature to drive the reaction to completion.

19. The solids present in these extractions are kept with the aq. phase.

20. A 5 cm glass column is wet-packed (hexanes) with SiO_2 (170 g) topped with 0.5 cm sand. The crude reaction product **2** is loaded neat on the column and eluted as follows: hexanes (200 mL), 10 % EtOAc in hexanes (500 mL), 20% EtOAc in hexanes (800 mL). The first 5 fractions are collected as 100 mL fractions, then the remaining as 50 mL fractions. TLC (UV visualization) is used to follow the chromatography. The R*f* value of the title compound is 0.5 (20% EtOAc/hexanes). Fractions 13-19 are concentrated by rotary evaporation (40 °C bath, 20 mmHg), then vacuum dried (20 mmHg) at 22 °C for 20 h to constant weight (8.07–8.34 g). The product contains <0.2 wt % EtOAc by ^{1}H NMR analysis.

21. An analytically pure sample is prepared by crystallization of **2** as follows. Compound **2** (600 mg, isolated by chromatography as described in Note 20) is dissolved in MeOH (5 mL) at 22 °C, transferred to a 10-mL syringe, then filtered through a 0.45 micron PTFE syringe filter into a 25-mL Erlenmeyer flask. Water (1.5 mL) is added and the solution is swirled to mix. The flask is capped and held in a –15 °C freezer for 2 days, affording crystals. The crystalline solid is vacuum filtered using a 15-mL medium porosity sintered glass funnel, then dried for 15 h at 22 °C in a vacuum oven (20 mmHg) to constant weight (420 mg, 70% yield).

22. Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (**2**) has the following physical and spectroscopic properties: mp 40–41°C; IR (neat)

2953, 1726, 1436, 1332, 1277, 1217, 1130 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 1.76 (dd, *J* = 9.2, 5.3 Hz, 1 H), 2.22 (dd, *J* = 8.1, 5.3 Hz, 1 H), 3.25 (t, *J* = 8.7 Hz, 1 H), 3.37 (s, 3 H), 3.81 (s, 3 H), 7.20–7.30 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.3, 32.7, 37.4, 52.4, 53.0, 127.6, 128.3, 128.6, 134.8, 167.2, 170.4; HRMS (EI) *m/z* calcd. for $C_{13}H_{14}O_4$ ($[M]^+$) 234.09; found 234.20; Anal. calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02; found: C, 66.67; H, 5.88.

Safety and Waste Disposal Information

All hazardous materials should be handled and disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

Activated cyclopropanes represent an important class of synthons, often acting as electrophiles or involved in cycloaddition reactions. The most straightforward and convergent approach to these cyclopropanes remains the reaction of olefins with metal carbenes, which are derived from the decomposition of diazo compounds or iodonium ylides (Scheme 1).[4,5] In the case of the synthesis of 1,1-cyclopropane diesters, the decomposition of diazomalonate derivatives is well known and has been proven to be efficient. González-Bobes and co-workers have developed a very efficient method to synthesize these cyclopropanes[6] using 0.1 mol% of $Rh_2(esp)_2$, 1.3 equivalent of the diazomalonate and 1.0 equivalent of the alkene to achieve good to excellent yields. The reaction proceeds smoothly with mono-substituted aliphatic or aromatic alkenes and good reactivity was observed with disubstituted alkenes. Lower yields were obtained with styrene derivatives bearing strong electron-withdrawing groups.

Although dimethyl diazomalonate is a relatively stable compound, it is both explosive and shock sensitive. Moreover, its synthesis requires at least one equivalent of azide, which is also explosive.[4a] This presents a challenge when reactions are performed on large scale. Nevertheless, these problems can be overcome through the use of iodonium ylides.[7] Indeed, differential scanning calorimetry (DSC) analyses indicate that the iodonium ylide derived from dimethyl malonate is safer than the corresponding diazo compound. Moreover, it is readily accessible in one step from iodosobenzene diacetate, which itself is a stable white solid.[8]

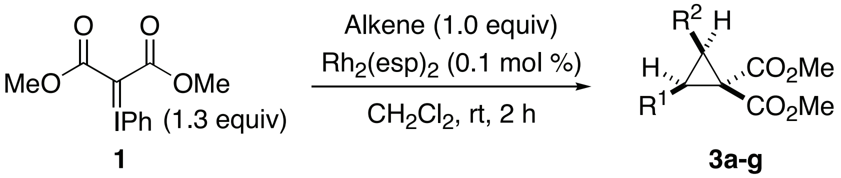
Previous methods to synthesize this compound reported by Müller[9] and Hadjiarapoglou[2] described the treatment dimethyl malonate with iodosobenzene diacetate in presence of an excess of potassium hydroxide in methanol. The product was extracted with a large amount of dichloromethane and concentrated under reduced pressure to yield an off-white solid that was purified by dissolving it in a minimum amount of chloroform followed by precipitation with hexane. However, when the reaction is performed on larger scale, reduced yields are observed. We determined that the lower yield was due to the workup and the removal of the solvent. Once the product crystallizes, it becomes very insoluble and dissolving the solid leads to degradation. Furthermore, a large amount of dichloromethane is needed during the workup and this leads to a longer concentration time. Since the product is not very stable in solution, the excess time and the temperature needed on larger scale to remove the methanol and the dichloromethane results in a larger percentage of degradation, hence lower yields.

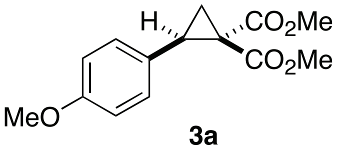
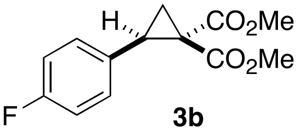
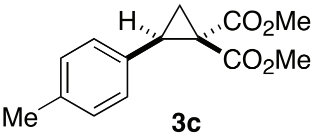
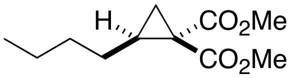
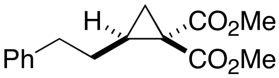
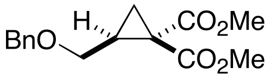
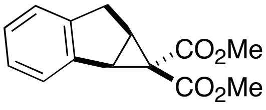
The synthesis of the iodonium ylide of dimethyl malonate herein described has many advantages. First, the isolated yield is higher (77–79%) compared to the previous methods (56% and 61% for Müller and Hadjiarapoglou respectively), and no extraction/concentration steps are needed. Second, the product is obtained from a simple filtration and without need for further purification. Finally, it is suitable for large scale synthesis.

As discussed above, the cyclopropanation reaction using 1.1 to 1.2 equivalent of iodonium ylide derived from dimethyl malonate and 1.0 equivalent of styrene gives an excellent yield (92–95%). The low catalyst loading required (0.02 mol% of $Rh_2(esp)_2$) makes this process a very efficient and inexpensive way to prepare dimethyl 2-phenylcyclopropane-1,1-dicarboxylate. With other alkenes, similar efficiency (0.1 mol% of $Rh_2(esp)_2$) was obtained using the González-Bobes conditions while substituting the diazomalonate for the iodonium ylide (Table 1).[6]

A drawback of using iodonium ylides compare to diazo compounds is the stoichiometric formation of iodobenzene byproduct instead of molecular nitrogen. However, the volatility and low polarity of iodobenzene compared to 1,1-cyclopropane diesters permits facile separation by evaporation or by chromatography on silica gel. Consequently, we have not encountered problems in its removal from the desired cyclopropanes.

Table 1. Scope of the Cyclopropanation Using $Rh_2(esp)_2$ and Iodonium Ylide 1



entry	product	yield (%)^a
1	 **3a**	78
2	 **3b**	95
3	 **3c**	95
4	 **3d**	94
5	 **3e**	93
6	 **3f**	69
7^b	 **3g**	84

[a] Isolated yields. [b] Reaction time = 16 h.

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dimethyl 2-diazomalonate has 2 large DSC exotherms: (1) 103.3–211.7 °C, –719.7 J/g; (2) 215–300 °C, –220.1 J/g.

9. Müller, P.; Fernández, D. *Helv. Chim. Acta* **1995**, *78*, 947–958.

Appendix
Chemical Abstracts Nomenclature; (Registry Number)

Potassium hydroxide; (1310-58-3)
Dimethyl malonate; (108-59-8)
Iodosobenzene diacetate; (3240-34-4)
Bis[rhodium(α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid)]; (819050-89-0)
Styrene; (100-42-5)
Thiourea; (62-56-6)

André B. Charette was born in 1961 in Montréal, Quebec. Upon completion of his B.Sc. from Université de Montréal in 1983, he pursued his graduate studies at the University of Rochester, earning his M.Sc. (1985) and Ph.D. (1987) with Robert Boeckman Jr. Following NSERC postdoctoral fellowship at Harvard University with D. A. Evans, he began his academic career at Université Laval in 1989. In 1992, he returned to his alma mater, where he is today Full Professor and holder of an NSERC/Merck Frosst/Boehringer Ingelheim Industrial Chair and a Canada Research Chair. His research focuses on the development of new methods for the stereoselective synthesis of organic compounds. Recent honors include a Cope Scholar Award (2007), the Prix Marie-Victorin (2008) and the Alfred Bader Award (2009).

Sébastien R. Goudreau was born in 1981 in Sherbrooke (Canada). He completed his undergraduate degree in chemistry at the Université de Sherbrooke in 2005. Following these studies he then joined the Charette group at the Université de Montréal where he is currently completing his Ph.D. studies as a NSERC postgraduate fellow. His Ph.D. research focuses on the development of new enantioselective methods to access activated cyclopropanes, and the application of these cyclopropanes in synthesis.

David Marcoux received his B.Sc. degree in chemistry at the Université du Québec à Trois-Rivières (Canada) in 2005. He then moved to the Université de Montréal as a NSERC predoctoral fellow where he received his Ph.D. degree in chemistry in 2009 under the mentorship of Professor André B. Charette. His graduate work is oriented towards the synthesis and used of tetraarylphophonium salts as a solubility control group in organic chemistry as well as towards the stereoselective Rh(II)-catalyzed cyclopropanation of olefins using diazo reagents bearing two acceptor groups. Since 2010, he has joined Professor David A. Evans at Harvard University as a NSERC postdoctoral fellow.

2009-099
iodonium ylide
Dried 60 h at 30 degrees
nmr400b c-13

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Current Data Parameters
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PROCNO               1

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DS                   4
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DW              19.000 usec
DE                7.00 usec
TE               300.0 K
D1          0.10000000 sec
d11         0.03000000 sec
TD0                 40

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P1                4.00 usec
PL1               0.00 dB
SFO1       100.5584512 MHz

======== CHANNEL f2 ========
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PCPD2           100.00 usec
PL2             120.00 dB
PL12             24.50 dB
SFO2       399.8719994 MHz

F2 - Processing parameters
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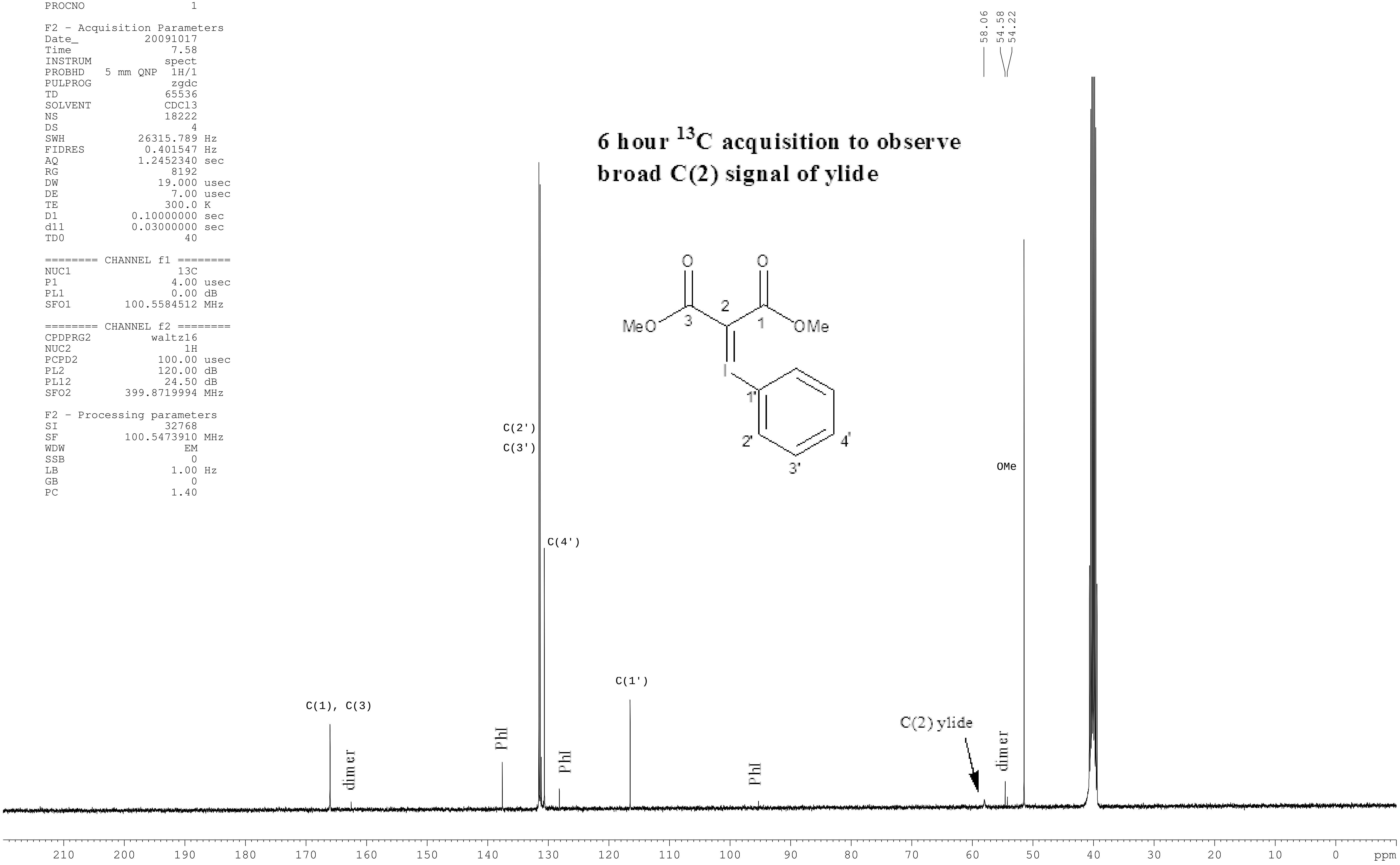
SF         100.5473910 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

6 hour ^{13}C acquisition to observe broad C(2) signal of ylide



2009-097
cyclopropane
fr 13-19
vacuum dried overnight
nmr500d c-13

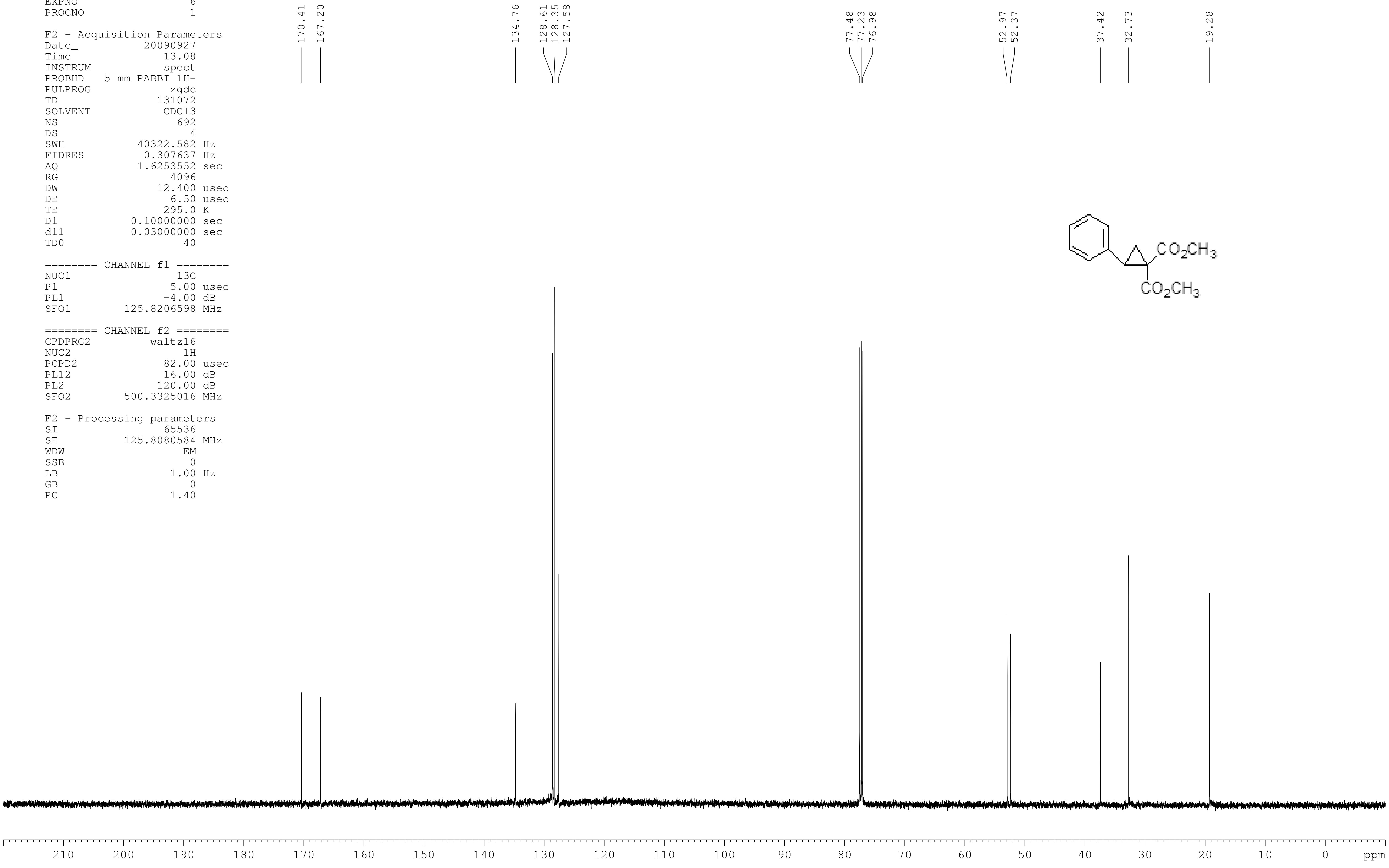
```
Current Data Parameters
NAME          2009-097
EXPNO                6
PROCNO               1

F2 - Acquisition Parameters
Date_         20090927
Time             13.08
INSTRUM          spect
PROBHD   5 mm PABBI 1H-
PULPROG           zgdc
TD              131072
SOLVENT          CDCl3
NS                 692
DS                   4
SWH          40322.582 Hz
FIDRES        0.307637 Hz
AQ           1.6253552 sec
RG                4096
DW              12.400 usec
DE                6.50 usec
TE               295.0 K
D1          0.10000000 sec
d11         0.03000000 sec
TD0                 40

======== CHANNEL f1 ========
NUC1               13C
P1                5.00 usec
PL1              -4.00 dB
SFO1       125.8206598 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            82.00 usec
PL12             16.00 dB
PL2             120.00 dB
SFO2       500.3325016 MHz

F2 - Processing parameters
SI               65536
SF         125.8080584 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```



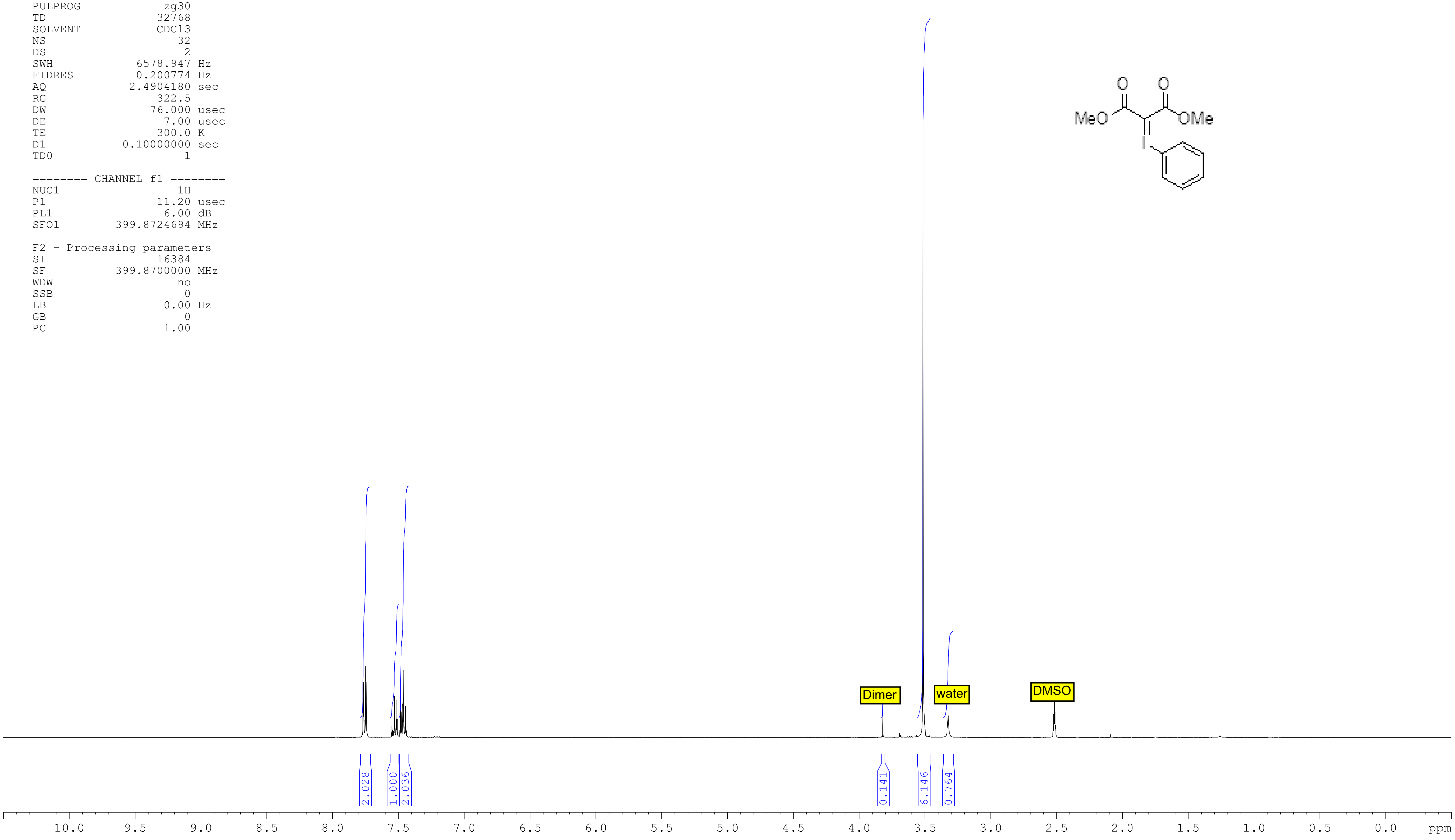
2009-099
iodonium ylide
Vacuum Dried 60 h at 30 degrees
nmr400b h-1

```
Current Data Parameters
NAME             2009-099
EXPNO                  50
PROCNO                  1

F2 - Acquisition Parameters
Date_            20091017
Time                 7.48
INSTRUM             spect
PROBHD   5 mm QNP  1H/1
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     32
DS                      2
SWH              6578.947 Hz
FIDRES           0.200774 Hz
AQ              2.4904180 sec
RG                  322.5
DW                 76.000 usec
DE                   7.00 usec
TE                  300.0 K
D1             0.10000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.20 usec
PL1                  6.00 dB
SFO1          399.8724694 MHz

F2 - Processing parameters
SI                  16384
SF            399.8700000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```



2009-097B
crystallized cyclopropane
nmr400b h-1

```
Current Data Parameters
NAME            2009-097
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20091024
Time               13.36
INSTRUM            spect
PROBHD   5 mm QNP  1H/1
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    64
DS                     2
SWH             6578.947 Hz
FIDRES          0.200774 Hz
AQ             2.4904180 sec
RG                 228.1
DW                76.000 usec
DE                  7.00 usec
TE                 300.0 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.20 usec
PL1                 6.00 dB
SFO1         399.8724694 MHz

F2 - Processing parameters
SI                 16384
SF           399.8700000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```

Peak	?(F1) [ppm]	?(F1) [Hz]	Intensity
1	7.3235	2928.4479	0.33
2	7.3188	2926.5686	0.54
3	7.3144	2924.8091	0.27
4	7.3077	2922.1300	0.34
5	7.3023	2919.9707	1.66
6	7.2976	2918.0913	1.02
7	7.2922	2915.9320	2.12
8	7.2877	2914.1326	0.86
9	7.2840	2912.6531	2.37
10	7.2773	2909.9740	0.71
11	7.2721	2907.8946	1.18
12	7.2680	2906.2552	0.88
13	7.2620	2903.8559	0.30
14	7.2553	2901.1768	0.99
15	7.2453	2897.1781	0.21
16	7.2405	2895.2587	0.24
17	7.2327	2892.1397	1.88
18	7.2286	2890.5003	1.94
19	7.2228	2888.1810	0.55
20	7.2164	2885.6219	0.63
21	7.2126	2884.1024	1.28
22	7.2110	2883.4626	1.17
23	7.2090	2882.6628	1.01
24	3.8227	1528.5830	17.99
25	3.8178	1526.6237	0.57
26	3.3909	1355.9192	20.00
27	3.3862	1354.0398	0.92
28	3.2830	1312.7732	0.59
29	3.2613	1304.0960	0.93
30	3.2398	1295.4988	0.64
31	2.2469	898.4679	1.16
32	2.2340	893.3096	1.29
33	2.2269	890.4705	1.14
34	2.2139	885.2722	1.23
35	1.7932	717.0469	1.46
36	1.7802	711.8486	1.51
37	1.7701	707.8099	1.43
38	1.7571	702.6116	1.37