Supporting Information

New highly soluble dimedone-derived iodonium ylides: preparation, X-ray structure, and reaction with carbodiimide leading to oxazole derivatives

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1. *General experimental remarks*

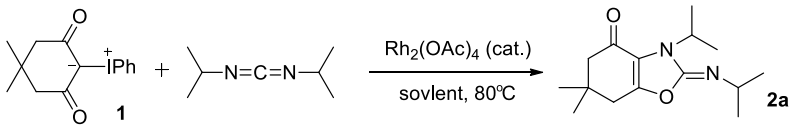
All reactions were performed under dry argon atmosphere with flame-dried glassware. All commercial reagents were ACS reagent grade and used without further purification. Dichloromethane was distilled from CaH_2 immediately prior to use. Diethyl ether was distilled from Na/benzophenone. All commercial reagents were ACS reagent grade and used without further purification. Melting points were determined in an open capillary tube with a Mel-temp II melting point apparatus. Infrared spectra were recorded as a KBr pellet on a Perkin-Elmer 1600 series FT-IR spectrophotometer. NMR spectra were recorded on a Varian Inova 500 MHz NMR spectrometer at 500 MHz (^{1}H NMR) and 125 MHz (^{13}C NMR). Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C chemical shifts are referenced relative to the tetramethylsilane. GC-MS analysis was carried out with a HP 5890A Gas Chromatograph using a 5970 Series mass selective detector. Microanalyses were carried out by Atlantic Microlab, Inc., Norcross, Georgia.

2. *Optimization study of the reaction with diisopropylcarbodiimide using ylide 1*

The initial experiments were carried out using the original ylide **1** and diisopropylcarbodiimide (DIC) as the model substrate. A strong solvent dependence was observed in this reaction (Table S1). CH_2Cl_2 and $CHCl_3$ were initially chosen as the solvents, because ylide **1** can only dissolve in these two solvents. However, we have found that ylide **1** in the presence of $Rh_2(OAc)_4$ reacts with CH_2Cl_2 to give 2-chloro-3-(chloromethoxy)cyclohex-2-en-1-one **11b** in 74% yield (Scheme S1). Compound **11b** probably originates from the ylide **11a**, which, in turn, results from reaction of the intermediate metallocarbene with the solvent CH_2Cl_2. Ylide formation between 1,3-dioxocarbenes and benzyl or acyl halides to afford the corresponding

haloenones is well documented, and has been preparatively exploited.[1] Meanwhile, the reaction of ylide **1** in $CHCl_3$ affords phenyl 2-iododimedonyl ether **12** in 80% yield, which is a well known rearrangement product of ylide **1**.[2] To prevent formation of these by-products, the reactions were carried out either without solvent, or in inert solvents such as fluorobenzene, which shows low reactivity with carbenes. However, the rearrangement product **12** was also the dominant product in neat DIC as solvent (Table S1, entry 3). Using aromatic solvents such as benzene, fluorobenzene, chlorobenzene afforded the corresponding "C-H insertion" product **13** (Scheme S1) (Table S1, entries 4-6).[1a,3] The use of 4-fluorotoluene as a solvent in an attempt to block the *para*- position to the fluorine also did not show any improvement (Table S1, entry 7). Hexafluorobenzene seems to be an ideal solvent for this reaction, because carbenes (or carbenoids) are reported to be unreactive toward this solvent,[3] however, the catalyst $Rh_2(OAc)_4$ is completely insoluble in hexafluorobenzene (Table S1, entry 9). Other solvents including nitromethane, dimethoxyethane, tetrachloroethane, pentane, hexane, TFE (trifluoroethanol), and HFIP (hexafluoroisopropanol) were also tested. All these solvents are poor choices for this reaction because of low reactant/catalyst solubility, formation of byproducts, and overall low yields of product **2a** (Table S1, entries 11-17). Among all the solvent we tested, $PhCF_3$ was the most efficient solvent, giving the highest yield of product **2a** and the lowest yield of byproducts (Table S1, entry 10).

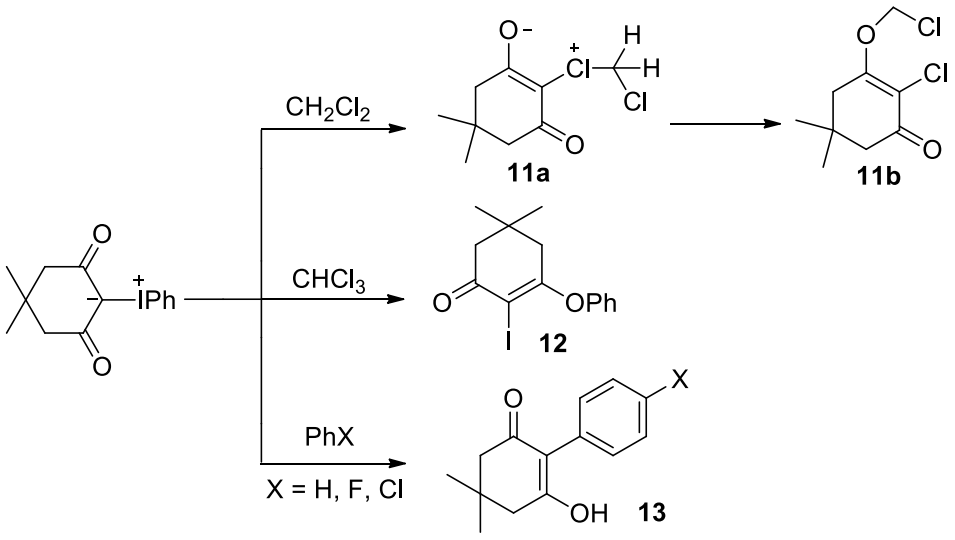
Table S1 The solvent effects in the reaction of ylide **1** with DIC[a]



Entry	Solvent	Time(h)	Yield of **2**(%)[b]
1	CH_2Cl_2	2	0 (74[c])
2	$CHCl_3$	0.5	9 (80[d])

3	--[e]	4	23 (61[d])
4	Ph	4	49 (26[f])
5	PhF	4	53 (29[f])
6	PhCl	4	33 (35[f])
7	4-MePhF	4	29(23[d])
8	PhMe	4	42(19[d])
9	Hexafluorobenzene	8	22
10	**$PhCF_3$**	**3**	**62 (5[f])**
11	Nitromethane	4	(17[g])
12	Dimethoxyethane	4	(12[g])
13	Tetrachloroethane	4	(14[g])
14	Pentane	4	0
15	Hexane	4	0
16	Trifluoroethanol	4	0
17	Hexafluoroisopropanol	4	(8[g])

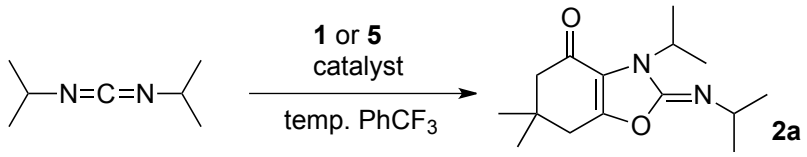
[a] Reaction conditions: ylide **1** (1 equiv), DIC (2 equiv), $Rh_2(OAc)_4$ (0.05 equiv), solvent (3 mL), argon protect, and 80 °C unless otherwise noted. [b] Isolated yields. [c] Yield of product **11b**; [d] Yield of rearrangement product **12**. [e] DIC (2 mL) was used as solvent. [f] Yield of product **13**. [g] In parentheses are NMR yields using 1,1,2,2-tetrachloroethane as an internal standard.



Scheme S1. The reactions of ylide **1** with different solvents.

3. Optimization study of the reaction with diisopropylcarbodiimide using ylide 5

Table S2. Comparison and optimization ylide **5** and **1** in the reaction with DIC[a]

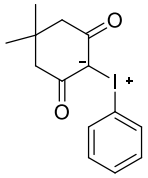


Entry	Ylide	Catalyst	Temp(°C)	Time(h)	Yield(%)[b]
1	**5b**	$Rh_2(OAc)_4$	80	0.5	79
2	**5b**	$Rh_2(OAc)_4$	r.t.	12	81
3	**1**	$Rh_2(OAc)_4$	r.t.	24	37(22[c])
4	**5b**	$Cu(OTf)_2$	r.t.	12	46
5	**5b**	CuOTf[d]	r.t.	12	17 (42[e])
6	**5b**	$BF_3{\cdot}Et_2O$	r.t.	12	--
7	**5b**	$Cu(acac)_2$	r.t.	12	78
8	**1**	$Cu(acac)_2$	r.t.	48	23(15[c])
9	**5b**	CuCl	r.t.	12	13 (44[e])
10	**5b**	$CuCl_2{\cdot}2H_2O$	r.t.	12	(21)
11	**5b**	CuBr	r.t.	12	9 (47[e])
12	**5b**	$CuBr_2$	r.t.	12	(19)
13	**5b**	CuI	r.t.	12	(--)
14	**5b**	--[f]	r.t.	48	--
15[g]	**5b**	$Cu(acac)_2$	r.t.	12	69
16[h]	**5b**	$Cu(acac)_2$	r.t.	12	79
17	**5a**	$Cu(acac)_2$	r.t.	12	71 (74)
18	**5b**	$Cu(acac)_2$	r.t.	12	75 (77)
19	**5c**	$Cu(acac)_2$	r.t.	12	70 (75)
20	**5d**	$Cu(acac)_2$	r.t.	12	67 (70)

[a] Reaction conditions: **1** or **5b** (1 equiv), DIC (1.5 equiv), catalyst (0.05 equiv), $PhCF_3$ (3 mL) and argon protect, unless otherwise noted. [b] Isolated yields. In parentheses are NMR yields using 1,1,2,2-tetrachloroethane as an internal standard. [c] Yield of reaction time is 12h. [d] $(CuOTf)_2{\cdot}C_6H_6$ was used as the source of CuOTf. [e] Yield of rearrangement product. [f] no catalyst was used. [g] 1 equiv of DIC was used. [h] 2 equiv of DIC was used.

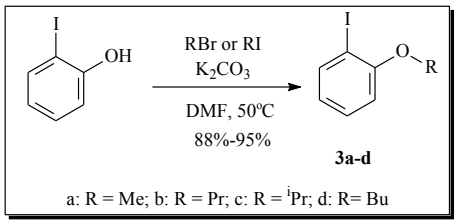
4. Preparation and characterization of ylide 1

2-Phenyliodonio-5,5-dimethyl-1,3-dioxacyclohexanemethylide[1a].



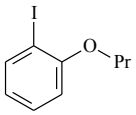
The ylide **1** was prepared by a slightly modified literature procedure,[1a] to a stirred solution of KOH (15 mmol) in MeOH (30 mL) was added 5,5-dimethyl-1,3-cyclohexanedione (10.0 mmol). The mixture was cooled at 0°C (ice/water bath), then diacetoxyiodo benzene (11.0 mmol) was added and the reaction mixture was stirred vigorously for 4.0 h at 0°C. The reaction mixture was quenched with ice cold water (20 mL), then extracted with dichloromethane for four times. The yellow solution was then concentrated under reduced pressure below 20 °C, and dried in vacuum to afforded ylide **1**, isolated as white solid, mp 132-133 °C (lit.[1a] mp 132-134°C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82-7.84 (m, 2H), 7.51-7.54 (m, 1H), 7.34-7.38 (m, 2H), 2.51 (s, 4H), 1.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.4, 133.9, 131.6, 131.5, 111.9, 94.5, 50.8, 32.1, 28.1.

5. Preparation and characterization of ethers of 2-iodophenol 3a-d.



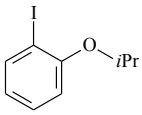
To a solution of 2-iodophenol (10.0 mmol) in dry DMF (20 mL) potassium carbonate (50.0 mmol) was added under stirring. After 10 min the appropriate alkyl bromide or alkyl iodide (15.0 mmol) was added to the reaction mixture. The reaction was stirred at 50 °C for 3 h. The solvent was evaporated in vacuum and the residue was extracted with ethyl acetate. Then the mixture was separated by column chromatography using the mixture EtOAc/hexanes (1:3) to afford the pure product **3**.

1-Iodo-2-propoxybenzene (3b).[4]



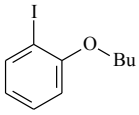
Reaction of propyl iodide with 2-iodophenol (2.2 g, 10.0 mmol) according to the general procedure afforded 2.2 g (85%) of product **3b**, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.5 Hz, 1H), 7.32-7.22 (m, 1H), 6.81 (d, *J* = 8 Hz, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 3.97 (t, *J* = 6.3 Hz, 2H), 1.91-1.80 (m, 2H), 1.1 (t, *J* = 7.5 Hz, 3H).

1-Iodo-2-isopropoxybenzene (3c).[4]



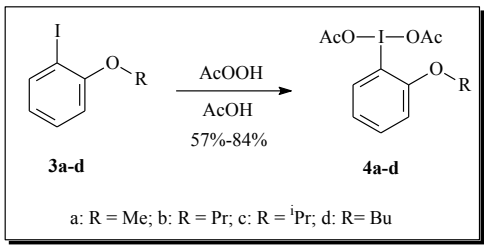
Reaction of isopropyl bromide with 2-iodophenol (2.2 g, 10.0 mmol) according to the general procedure afforded 2.4 g (90%) of product **3c**, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.29-7.24 (m, 1H), 6.82 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.68 (td, *J* = 7.5, 1.0 Hz, 1H), 4.55 (sept, *J* = 6.3 Hz, 1H), 1.38 (d, *J* = 6.3 Hz, 6H).

1-Iodo-2-butoxybenzene (3d).[4]



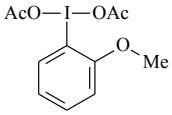
Reaction of butyl bromide with 2-iodophenol (2.2 g, 10.0 mmol) according to the general procedure afforded 2.6 g (95%) of product **3d**, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.3-7.22 (m, 1H), 6.79 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.68 (td, *J* = 7.8, 1.1 Hz, 1H), 4.0 (t, *J* = 6.5 Hz, 2H), 1.85-1.77 (m, 2H), 1.61-1.51 (m, 2H), 0.99 (t, *J* = 7.5 Hz, 3H).

6. Preparation and characterization of 1-diacetoxy-2-alkoxyphenyl-λ^3-iodanes 4.



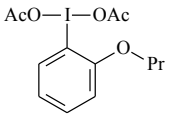
The mixture of acetic anhydride (30 mL) and 30% H_2O_2 (10 mL) was stirred at 40°C overnight, then the appropriate 2-iodophenol derivative **3** (5.0 mmol) was added and the mixture was stirred at 40 °C for 8 h. Then the reaction mixture was concentrated in vacuum and washed with water followed by hexanes several times, then dried in vacuum to give products **4** in the form of light yellow solids, which can be used for the preparation of iodonium ylides **5** without additional recrystallization.

1-Diacetoxy-2-methoxyphenyl-λ^3-iodane (4a).[4]



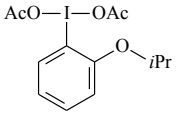
Reaction of 1-iodo-2-methoxybenzene **3a** (1.17 g, 5 mmol) with peracetic acid according to the general procedure afforded 1.51 g (87%) of product **4a**, isolated as light yellow solid, mp 140-142 °C (lit.[2], mp 139-140 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.62-7.56 (m, 1H), 7.2-7.14 (m, 1H), 7.04 (td, *J* = 7.6, 1.4 Hz, 1H), 3.99 (s, 3H), 1.97 (s, 6H).

1-Diacetoxy-2-propoxyphenyl-λ^3-iodane (4b).[4]



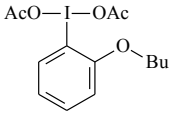
Reaction of 1-iodo-2-propoxybenzene **3b** (0.90 g, 3.43 mmol) with peracetic acid according to the general procedure afforded 1.19 g (85%) of product **4b**, isolated as light yellow solid, mp 98-100 °C (lit.[2], mp 97.2-98 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8 Hz, 1H), 7.62-7.48 (m, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.06-6.98 (m, 1H), 4.11 (t, *J* = 5.5 Hz, 1H), 2.0 (s, 6H), 1.92 - 1.82 (m, 2H), 1.07 (t, J = 7.5 Hz, 3H).

1-Diacetoxy-2-isopropoxyphenyl-λ^3-iodane (4c).[4]



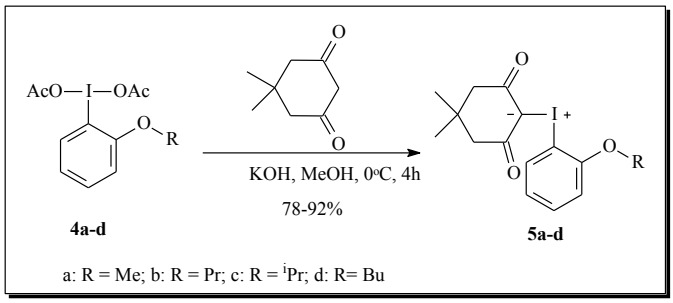
Reaction of 1-iodo-2-isopropoxybenzene **3c** (0.90 g, 3.43 mmol) with peracetic acid according to the general procedure afforded 0.63 g (53%) of product **4c**, isolated as light yellow solid, mp 84-86 °C (lit.[2], mp 84.2-84.8 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.58-7.48 (m, 1H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.0 (t, *J* = 7.8 Hz, 1H), 4.73 (sept, *J* = 6 Hz, 1H), 1.97 (s, 6H), 1.41 (d, *J* = 6 Hz, 6H).

1-Diacetoxy-2-butoxyphenyl-λ^3-iodane (4d).[4]



Reaction of 1-iodo-2-butoxybenzene **3d** (1.00 g, 3.62 mmol) with peracetic acid according to the general procedure afforded 1.08 g (72%) of product **4d**, isolated as light yellow solid, mp 73-75 °C (lit.[2], mp 75-76 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8 Hz, 1H), 7.58 (t, *J* = 8 Hz, 1H), 7.13 (d, *J* = 8 Hz, 1H), 7.01 (t, *J* = 8 Hz, 1H), 4.15 (t, *J* = 5.8 Hz, 1H), 1.96 (s, 6H), 1.88-1.78 (m, 2H), 1.6-1.48 (m, 2H), 0.98 (t, *J* = 7 Hz, 3H).

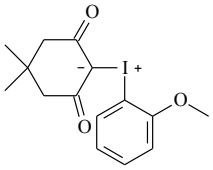
7. Preparation and characterization of 2-alkoxyphenyliodonium ylides 5.



To a stirred solution of KOH (10 mmol) in MeOH (15 mL) was added 5,5-dimethyl-1,3-cyclohexanedione (5.0 mmol). The mixture was cooled at 0 °C (ice/water bath), then the appropriate 1-diacetoxy-2-alkoxyphenyl-λ^3-iodanes **4** (5.2 mmol) was added and the reaction mixture was stirred vigorously for 4.0 h at 0 °C. After reaction, the mixture was quenched with ice cold water, the resulting white precipitate

was filtered and mother liquor was extracted with dichloromethane. The yellow solution was then concentrated under reduced pressure below 20 °C, and dried in vacuum to give products **5** in the form of off-white solid. The resultant white solid was mixed with the first crop and further recrystallized from CH_2Cl_2/Hexane.

1,3-Dicarbonyl Phenyl Iodonium Ylide (5a).



Reaction of 1-diacetoxy-2-methoxyphenyl-λ^3-iodane **4a** (1.06 g, 3.0 mmol) according to the general procedure afforded 0.82 g (75%) of product **5a**, isolated as off-yellow solid, mp 157-159 °C; IR (KBr) cm^{-1}: 3012, 2977, 2379, 2201, 1529, 1437, 1342, 1318; ^1H NMR (500 MHz, $CDCl_3$): δ 7.39-7.43 (m, 1H), 7.21-7.22 (m, 1H), 6.93-6.98 (m, 2H), 3.96 (s, 3H), 2.57 (s, 4H), 1.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.3, 155.6, 132.1, 129.8, 124.0, 112.1, 100.3, 87.4, 56.8, 50.8, 32.1, 28.4. Anal. Calcd for $C_{15}H_{17}IO_3$: C, 48.40; H, 4.60; Found: C, 48.38; H, 4.62.

Single crystals of product **5a** suitable for X-ray crystallographic analysis were obtained by slow evaporation of the solution of **5a** in dichloromethane-hexane solution. X-ray diffraction data were collected on Rigaku RAPID II diffractometrer using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 123 K. Multi-scan absorption correction was applied to the data using CrystalClear 2.0 program (Rigaku Inc. 2010). The structure was solved by Patterson method (PATTY) using CrystalStructure 4.0 program and refined by full-matrix least-squares refinement on F^2 using Crystals for Windows program. Crystal data for **5a** $C_{15}H_{17}IO_3$: M 372.20, triclinic, space group P-1, a = 7.9997(3), b = 9.0944(3), c = 10.6971(7) Å, α = 73.485(5)°, β = 86.480(6)°, γ = 69.563(5)°, V = 698.55(7) $Å^3$, Z = 2, μ = 2.293mm^{-1}, 22505 reflections measured, 3200 unique; final R_1 = 0.0151, R_w = 0.0401. CCDC-894818 contains the supplementary crystallographic data for compound **5a**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ UK; fax: (+44) 1223-336-033, or deposit@ccdc.cam.ac.uk).

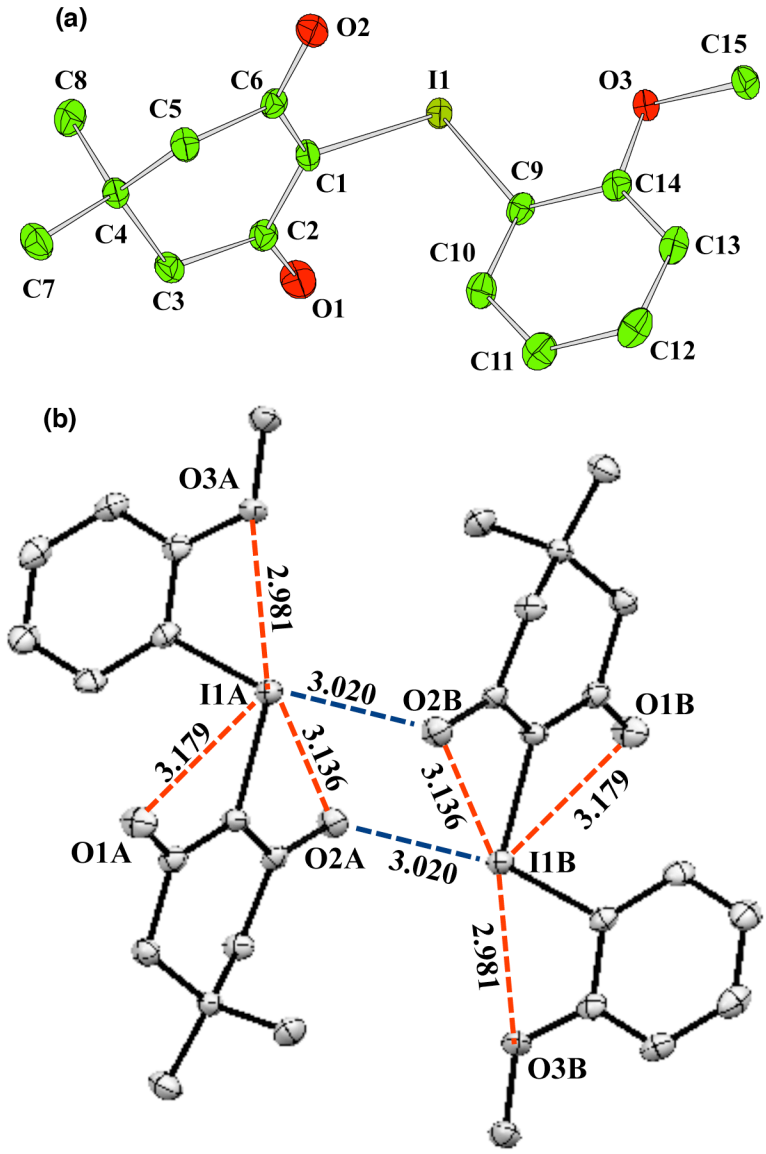
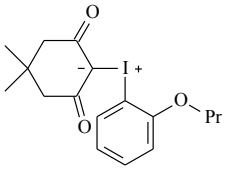


Figure S1. (a) Molecular structure of compound **5a**. (b) Intra- and inter-molecular interactions in **5a** dimer.

1,3-Dicarbonyl Phenyl Iodonium Ylide (5b).



Reaction of 1-diacetoxy-2-propoxyphenyl-λ^3-iodane **4b** (1.14 g, 3.0 mmol) according to the general procedure afforded 0.95 g (81%) of product **5b**, isolated as off-white solid,

mp 151-152 °C; IR (KBr) cm^{-1}: 2960, 2357, 1564, 1447, 1349, 1317; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.40 (m, 1H), 7.16-7.18 (m, 1H), 6.94-6.98 (m, 1H), 6.91-6.92 (m, 1H), 4.08 (t, *J* = 6 Hz, 2H), 2.58 (s, 4H), 1.86-1.90 (m, 2H), 1.16 (s, 6H), 1.09 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.4, 155.1, 131.9, 129.4, 123.8, 112.8, 100.6, 86.9, 71.3, 50.8, 32.0, 28.4, 22.3, 10.5. Anal. Calcd for $C_{17}H_{21}IO_3$: C, 51.01; H, 5.29; Found: C, 51.11; H, 5.32.

Single crystals of product **5b** suitable for X-ray crystallographic analysis were obtained by slow evaporation of the solution of **5b** in dichloromethane-hexane. X-ray diffraction data were collected on Rigaku RAPID II diffractometrer using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 123 K. Multi-scan absorption correction was applied to the data using CrystalClear 2.0 program (Rigaku Inc. 2010). The structure was solved by Patterson method (PATTY) using CrystalStructure 4.0 program and refined by full-matrix least-squares refinement on F^2 using Crystals for Windows program. Crystal data for **5b** $C_{17}H_{21}IO_3$: M 400.26, orthorhombic, space group P bca, a = 28.076(2), b = 16.5298(13), c = 7.1600(5) Å, α = β = γ = 90°, V = 3322.9(4) $Å^3$, Z = 8, μ = 1.935 mm^{-1}, 9590 reflections measured, 3441 unique; final R_1 = 0.0462, R_w = 0.0764. CCDC-894819 contains the supplementary crystallographic data for compound **5b**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ UK; fax: (+44) 1223-336-033, or deposit@ccdc.cam.ac.uk).

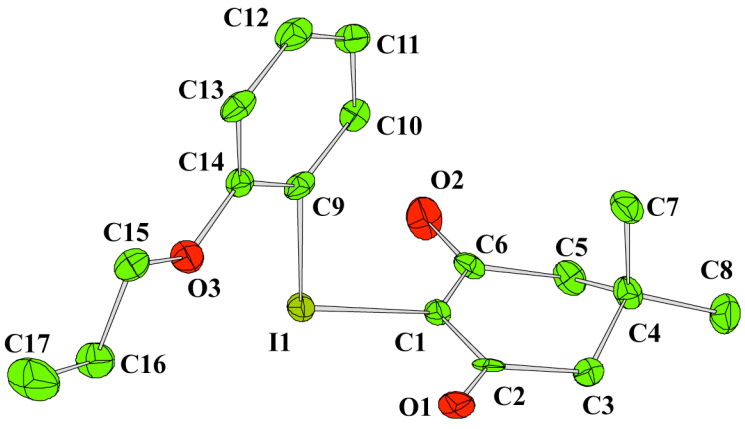
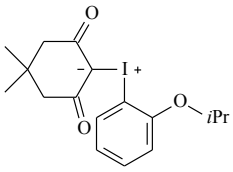


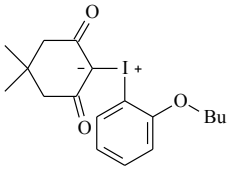
Figure S2. Molecular structure of compound **5b**.

1,3-Dicarbonyl Phenyl Iodonium Ylide (5c).



Reaction of 1-diacetoxy-2-isopropoxyphenyl-λ^3-iodane **4c** (1.14 g, 3.0 mmol) according to the general procedure afforded 0.78 g (67%) of product **5c**, isolated as off-white solid, mp 147-149 °C; IR (KBr) cm^{-1}: 3007, 2409, 1529, 1459, 1346, 1329; ^1H NMR (500 MHz, $CDCl_3$): δ 7.37 (t, J = 8.0 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 6.90-6.96 (m, 2H), 4.68-4.71 (m, 1H), 2.58 (s, 4H), 1.43 (d, J = 6.0 Hz, 6H), 1.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.4, 154.0, 131.8, 129.4, 123.7, 113.7, 101.7, 86.7, 73.0, 50.8, 32.0, 28.4, 22.1. Anal. Calcd for $C_{17}H_{21}IO_3$: C, 51.01; H, 5.29; Found: C, 51.09; H, 5.22.

1,3-Dicarbonyl Phenyl Iodonium Ylide (5d).

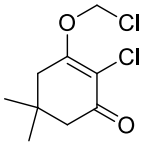


Reaction of 1-diacetoxy-2-propoxyphenyl-λ^3-iodane **4d** (1.18 g, 3.0 mmol) according to the general procedure afforded 0.69 g (57%) of product **5d**, isolated as off-white solid, mp 153-154 °C; IR (KBr) cm^{-1}: 2967, 2369, 1518, 1462, 1284, 1330; ^1H NMR (500 MHz, $CDCl_3$): δ 7.38 (t, J = 8.0 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 6.90-6.97 (m, 2H), 4.12 (t, J = 6.5 Hz, 2H), 2.58 (s, 4H), 1.80-1.85 (m, 2H), 1.51-1.55 (m, 2H), 1.16 (s, 6H), 1.00 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 189.3, 155.1, 131.9, 129.3, 123.8, 112.7, 100.6, 86.7, 69.5, 50.8, 32.0, 30.9, 28.4, 19.2, 13.7. Anal. Calcd for $C_{18}H_{23}IO_3$: C, 52.19; H, 5.60; Found: C, 52.11; H, 5.68.

8. General procedure for the reaction with carbodiimides

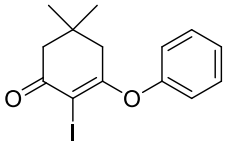
To a solution of the $Rh_2(OAc)_4$ or $Cu(acac)_2$ (5 mol %) in 3 mL of $PhCF_3$ were added carbodiimide (1.5 mmol) and **5b** (1 mmol). The reaction was stirred at room temperature under argon gas. The solution was then concentrated and purified by chromatography or Prep-TLC on silica gel to give the corresponding product.

2-Chloro-3-(chloromethoxy)-5,5-dimethylcyclohex-2-en-1-one (11b)[5].



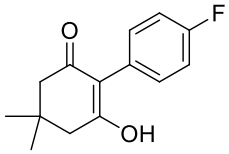
Reaction of ylide **1** (0.5 mmol) in CH_2Cl_2 according to the general procedure afforded 82 mg (74%) of product, isolated as yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.84 (s, 2H), 2.70 (s, 2H), 2.45 (s, 2H), 1.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.1, 165.2, 115.2, 74.5, 50.6, 39.5, 32.4, 28.2.

2-Iodo-3-phenoxy-5,5-dimethyl-2-cyclohexanone (12)[2].



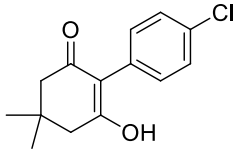
Reaction of ylide **1** (0.5 mmol) in $CHCl_3$ according to the general procedure afforded 137 mg (80%) of product, isolated as off-white solid, mp 164-165 °C (lit.[2] mp 165-166 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.43 (m, 2H), 7.26-7.28 (m, 1H), 7.03-7.05 (m, 2H), 2.49 (s, 2H), 2.31 (s, 2H), 1.05 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.9, 173.4, 153.2, 130.1, 125.8, 120.6, 85.5, 50.1, 42.5, 33.1, 27.8.

2-(4-Fluoro-phenyl)-5,5-dimethyl-cyclohexane-1,3-dione[1a].



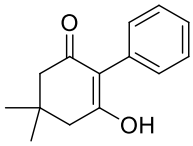
Reaction of ylide **1** (0.5 mmol) in fluorobenzene according to the general procedure afforded 30 mg (29%) of product, isolated as white solid, mp 181-182 °C (lit.[1a] mp 180-182 °C); ^{1}H NMR (500 MHz, CD_3OD): δ 7.14-7.15 (m, 2H), 7.02-7.04 (m, 2H), 2.42 (s, 4H), 1.16 (s, 6H).

2-(4-Chloro-phenyl)-5,5-dimethyl-cyclohexane-1,3-dione[1a].



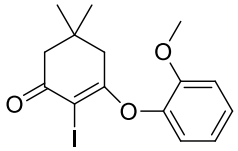
Reaction of ylide **1** (0.5 mmol) in chlorobenzene according to the general procedure afforded 31 mg (35%) of product, isolated as white solid, mp 192-193 °C (lit.[1a] mp 190-192 °C); ^{1}H NMR (500 MHz, CD_3OD): δ 7.32 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 2.42 (s, 4H), 1.15 (s, 6H).

2-Phenyl-5,5-dimethyl-cyclohexane-1,3-dione[6].



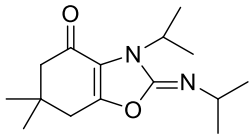
Reaction of ylide **1** (0.5 mmol) in benzene according to the general procedure afforded 25 mg (26%) of product, isolated as white solid, mp 154-156 °C; ^{1}H NMR (500 MHz, CD_3OD): δ 7.22-7.27 (m, 5H), 2.43 (s, 4H), 1.14 (s, 6H).

2-Iodo-3-(2-methoxyphenoxy)-5,5-dimethylcyclohex-2-enone.



Reaction of phenyl iodonium ylide **5a** (0.17 g, 0.5 mmol) in $CHCl_3$ according to the general procedure afforded 0.82 g (75%) of product, isolated as yellow soid, mp 124-126 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22-7.25 (m, 1H), 7.09-7.11 (m, 1H), 6.96-7.00 (m, 2H), 3.83 (s, 3H), 2.47 (s, 2H), 2.22 (s, 2H), 1.02 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.0, 175.0, 151.1, 142.1, 127.1, 122.4, 121.3, 112.9, 82.5, 56.1, 50.1, 41.5, 32.8, 27.9.

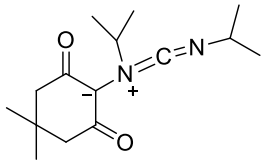
3-Isopropyl-2-(isopropylimino)-6,6-dimethyl-2,3,6,7-tetrahydrobenzo[*d*]oxazol--4(5*H*)-one (2a).



Reaction of phenyl iodonium ylide **5b** (1.0 mmol) with N, N'- diisopropylcarbodiimide (1.5 mmol) according to the general procedure afforded 0.85 g (81%) of product **2a**, isolated as yellow oil; IR (NaCl) cm^{-1}: 2954, 2866, 1712, 1654, 1387, 1098, 813; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.57-4.61 (m, 1H), 3.77-3.80 (m, 1H), 2.55 (s, 2H), 2.34 (s,

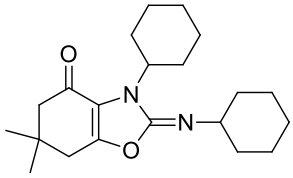
2H), 1.36 (d, J = 6.5 Hz, 6H), 1.15 (s, 6H), 1.13 (d, J = 6.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 186.1, 155.4, 148.2, 122.1, 52.2, 46.8, 46.7, 36.1, 34.5, 28.5, 24.7, 20.1. Anal. Calcd for $C_{15}H_{24}N_2O_2$: C, 68.15; H, 9.15; Found: C, 68.10; H, 9.18.

1-(Isopropyl((isopropylimino)methylene)ammonio)-4,4-dimethyl-2,6-dioxocyclohexan-1-ide (intermediate 10).



Reaction of phenyl iodonium ylide **5b** (1.0 mmol) with N, N'- diisopropylcarbodiimide (1.5 mmol) according to the general procedure afforded 17 mg (15%) of the intermediate **10**, isolated as a yellow oil; IR (KBr) cm^{-1}: 2955, 2868, 1911, 1612, 1582, 1521, 1348, 1146, 829; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.08-5.11 (m, 1H), 3.87-3.89 (m, 1H), 2.44-2.45 (m, 2H), 2.40-2.41 (m, 2H), 1.41-1.43 (m, 6H), 1.18 (s, 6H), 1.09-1.11 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.8, 160.9, 140.6, 108.9, 46.1, 45.8, 45.6, 40.8, 36.1, 30.0, 24.1, 18.8.

3-Cyclohexyl-2-(cyclohexylimino)-6,6-dimethyl-2,3,6,7-tetrahydrobenzo[*d*]oxazol-4(5*H*)-one (2b).



Reaction of phenyl iodonium ylide **5b** (1.0 mmol) with N, N'- dicyclohexylcarbodiimide (1.5 mmol) according to the general procedure afforded 0.82 g (84%) of product **2b**, isolated as yellow solid, mp 127-129 °C; IR (KBr) cm^{-1}: 2946, 2870, 1719, 1645, 1377, 1102, 834; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.13-4.20 (m, 1H), 3.39-3.43 (m, 1H), 2.54 (s, 2H), 2.33 (s, 2H), 2.10-2.19 (m, 2H), 1.73-1.77 (m, 6H), 1.58-1.64 (m, 4H), 1.21-1.33 (m, 8H), 1.14 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 186.1, 155.4, 148.1, 129.4, 122.1, 115.6, 54.8, 54.4, 52.3, 36.2, 34.8, 34.4, 29.6, 28.5, 25.9, 25.1. Anal. Calcd for $C_{21}H_{32}N_2O_2$: C, 73.22; H, 9.36; Found: C, 73.18; H, 9.31.

Single crystals of product **2b** suitable for X-ray crystallographic analysis were obtained by slow evaporation of the solution of **2b** in acetone-hexane. X-ray diffraction data were collected on Rigacu RAPID II diffractometrer using graphite-monochromated CuKα radiation (λ = 1.54187 Å) at 123 K. Multi-scan absorption correction was applied to the data using CrystalClear 2.0 program (Rigaku Inc. 2010). The structure was solved by Patterson method (PATTY) using CrystalStructure 4.0 program and refined by full-matrix least-squares refinement on F^2 using Crystals for Windows program. Crystal data for **2b** $C_{21}H_{32}N_2O_2$: M 344.50, monoclinic, space group $P_{21/c}$, a = 9.32650(10), b = 5.97390(10), c = 34.571(3) Å, β = 91.198(6)°, V = 1925.72(17) $Å^3$, Z = 4, μ = 0.595 mm^{-1}, 22422 reflections measured, 3567 unique; final R_1 = 0.0426, R_w = 0.0727. CCDC-894817 contains the supplementary crystallographic data for compound **2b**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ UK; fax: (+44) 1223-336-033, or deposit@ccdc.cam.ac.uk).

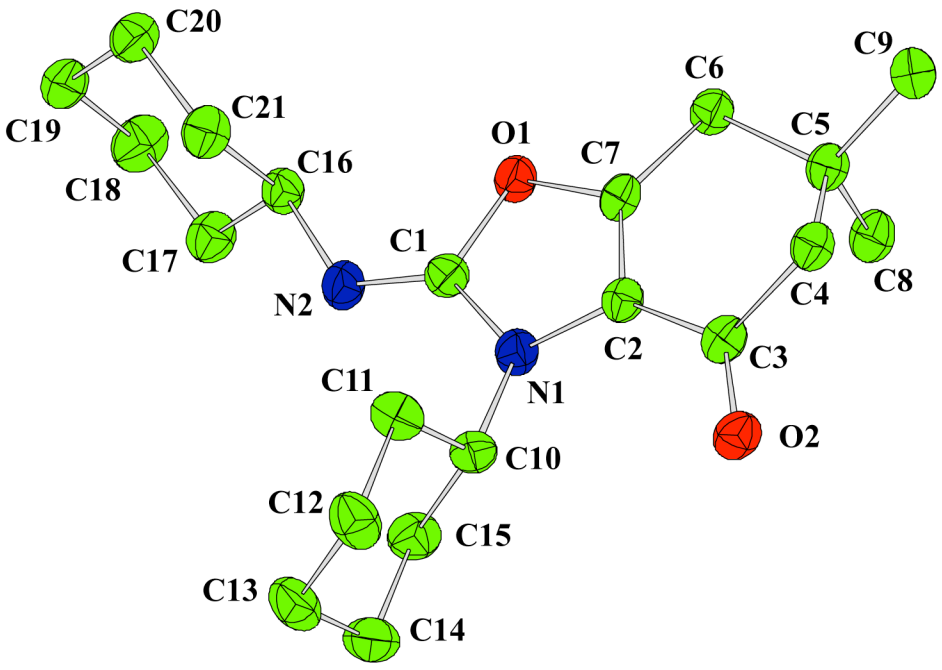
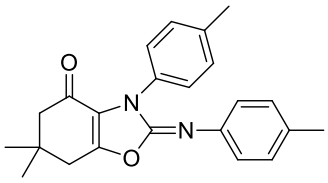


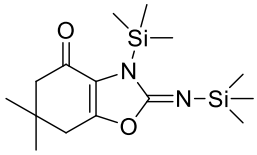
Figure S3. Molecular structure of compound **2b**.

6,6-dimethyl-3-*p*-tolyl-2-(*p*-tolylimino)-2,3,6,7-tetrahydrobenzo[*d*]oxazol-4(*5H*)-one (2c).



Reaction of phenyl iodonium ylide **5b** (1.0 mmol) with 1,3-di-*p*-tolylcarbodiimide (1.5 mmol) according to the general procedure afforded 0.57 g (77%) of product **2c**, isolated as yellow oil; IR (KBr) cm^{-1}: 2953, 2947, 2882, 1720, 1639, 1365, 1087, 826; ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.22 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 2.72 (s, 2H), 2.46 (s, 2H), 2.35 (s, 3H), 2.23 (s, 3H), 1.12 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 185.8, 156.4, 148.1, 143.5, 136.8, 133.1, 131.5, 129.6, 129.1, 127.1, 123.1, 121.2, 118.6, 51.7, 35.2, 34.9, 27.6, 21.1. Anal. Calcd for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; Found: C, 76.72; H, 6.85.

6,6-dimethyl-3-(trimethylsilyl)-2-(trimethylsilylimino)-2,3,6,7-tetrahydrobenzo[*d*]oxazol-4(*5*H)-one (2e).

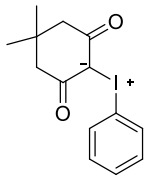


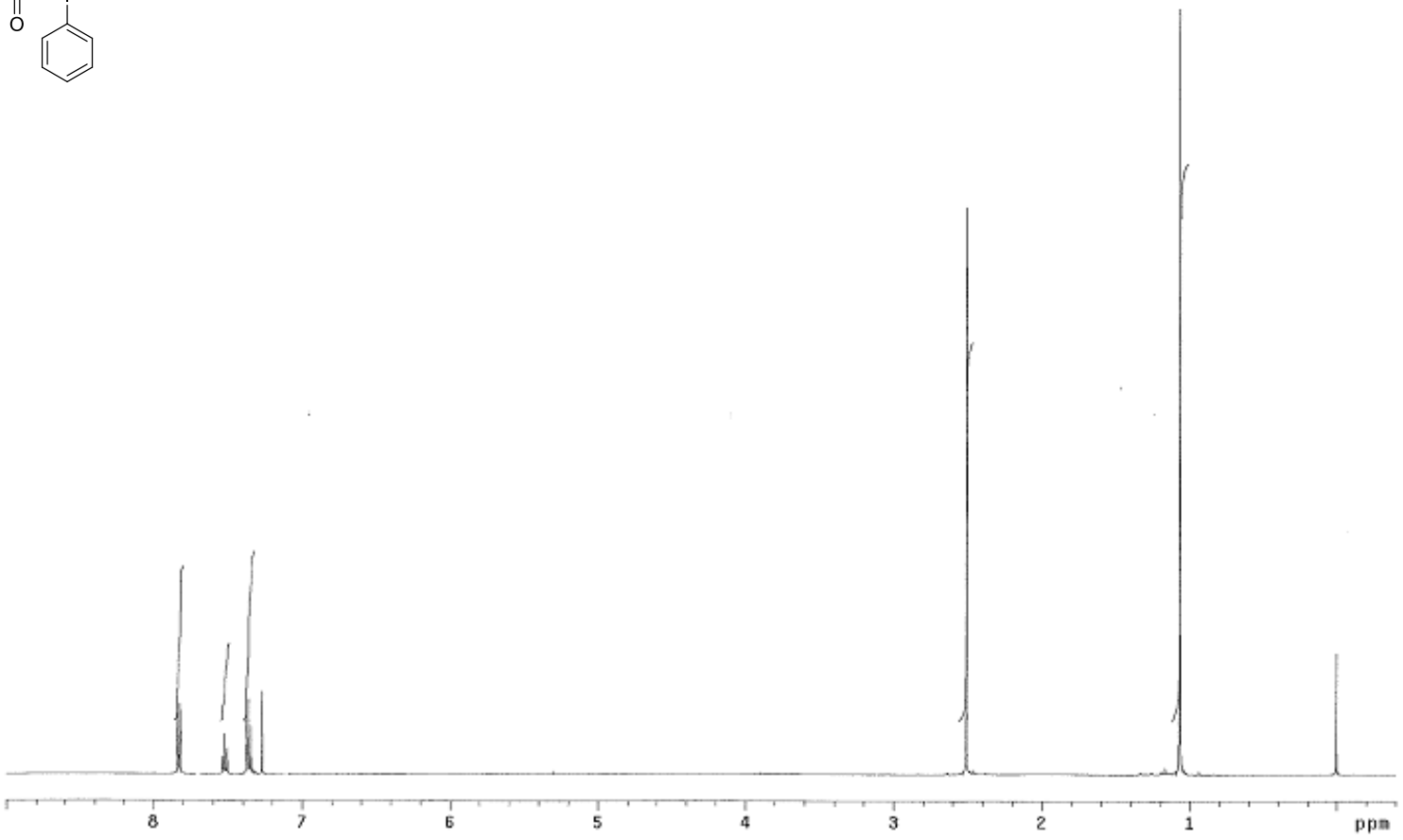
Reaction of phenyl iodonium ylide **5b** (1.0 mmol) with bis(trimethylsilyl)carbodiimide (1.5 mmol) according to the general procedure afforded 0.82 g (86%) of product **2e**, isolated as yellow oil; IR (KBr) cm^{-1}: 2948, 2941, 2879, 1716, 1649, 1355, 1069, 893; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.57 (s, 2H), 2.36 (s, 2H), 1.18 (s, 6H), 0.2-0.7 (m, 18H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 186.2, 155.4, 148.2, 122.7, 51.6, 36.2, 34.5, 28.6, 0.2. Anal. Calcd for $C_{15}H_{28}N_2O_2Si_2$: C, 55.51; H, 8.70; Found: C, 55.37; H, 8.76.

References:

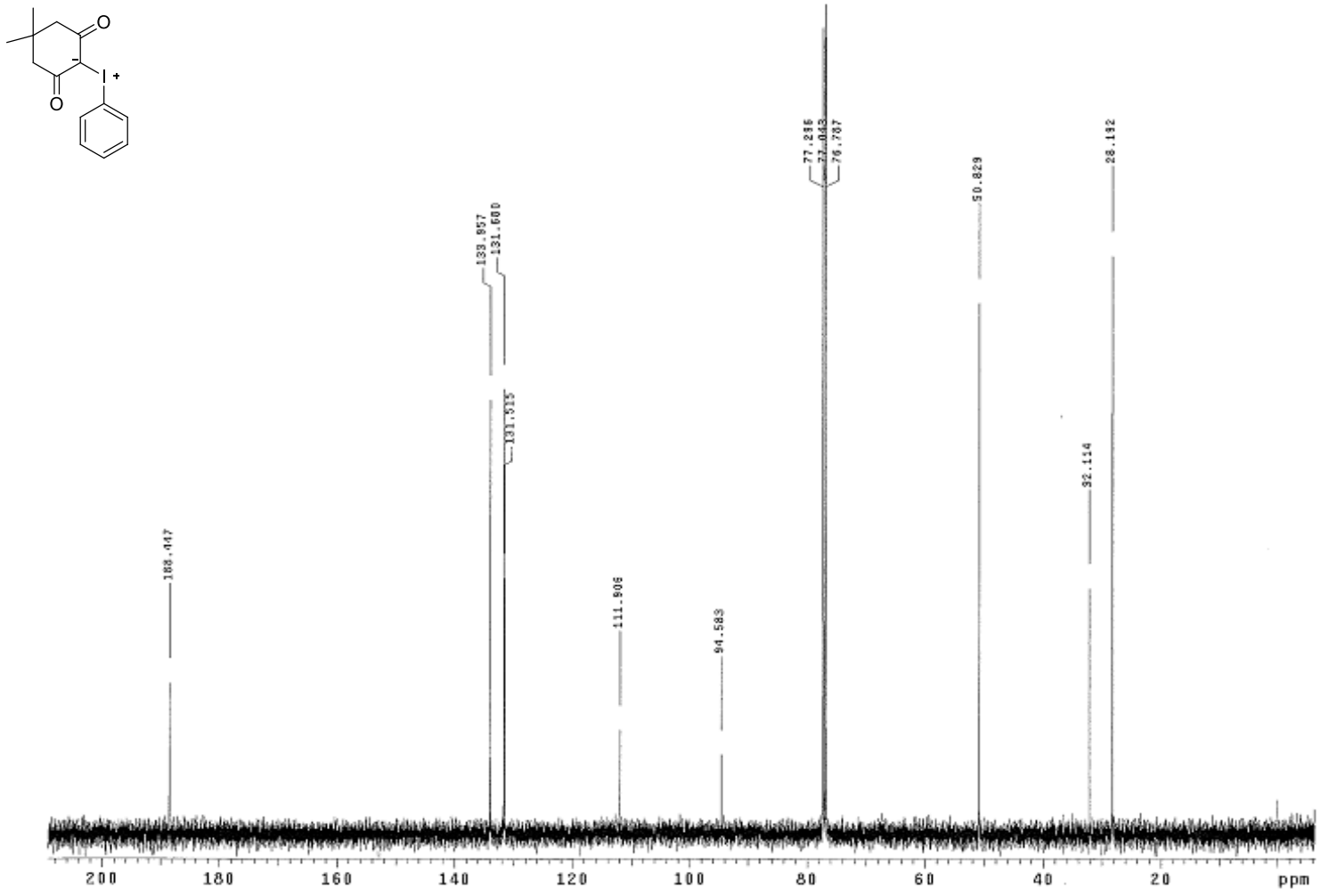
1. (*a*) R. M. Moriarty, S. Tyagi, D. Ivanov and M. Constantinescu, *J. Am. Chem. Soc.*, 2008, **130**, 7564-7565; (*b*) Y. R. Lee, Y. U. Jung, *J. Chem. Soc., Perkin Trans. 1* **2002**, 1309-1313; (*c*) S.-Y. Gu, M.-D. Su, *J. Phys. Chem. A* **2007**, *111*, 6587-6591.
2. R. M. Moriarty, B. R. Bailey, O. Prakash and I. Prakash, *J. Am. Chem. Soc.*, 1985, **107**, 1375-1378.
3. (*a*) M. C. Pirrung, J. Zhang, K. Lackey, D. D. Sternbach and F. Brown, *J. Org. Chem.*, 1995, **60**, 2112-2124; (*b*) T. N. Wheeler, *J. Org. Chem.*, 1979, **44**, 4906-4912; (*c*) M. J. Rosenfeld, B. K. R. Shankar and H. Shechter, *J. Org. Chem.*, 1988, **53**, 2699-2705.
4. (*a*) C. Zhu, A. Yoshimura, L. Ji, Y. Wei, V. N. Nemykin and V. V. Zhdankin, *Org. Lett.*, 2012, **14**, 3170-3173; (*b*) A. Yoshimura, V. N. Nemykin and V. V. Zhdankin, *Chem. Eur. J.*, 2011, **17**, 10538-10541.
5. P. Müller, Y. F. Allenbach and G. Bernardinelli, *Helv. Chim. Acta*, 2003, **86**, 3164-3178.
6. T. N. Wheeler, *J. Org. Chem.*, 1979, **44**, 4906-4912.

^{1}H NMR (500 MHz, $CDCl_3$):

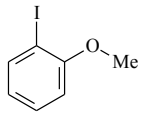


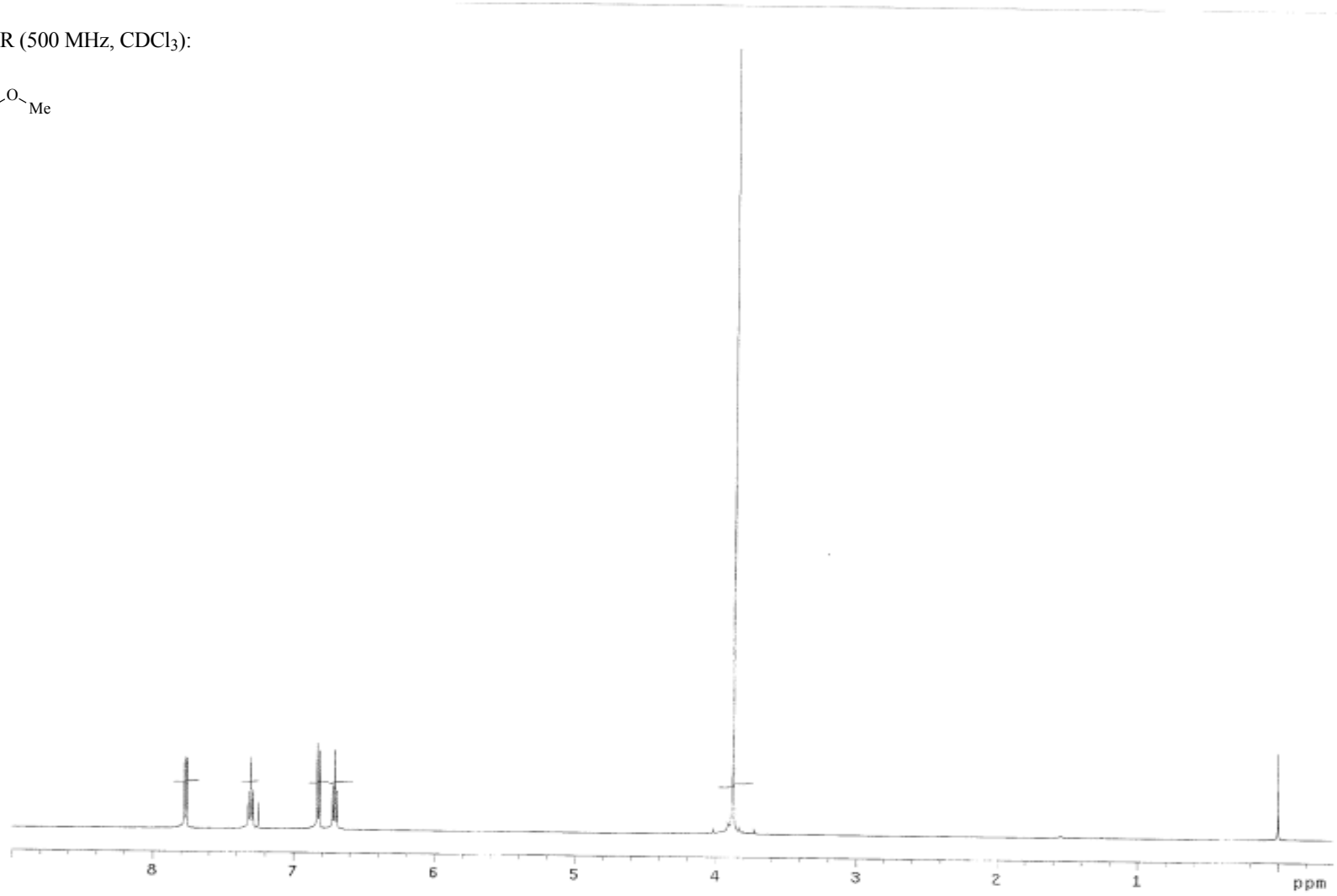


^{13}C NMR (125 MHz, $CDCl_3$):



^{1}H NMR (500 MHz, $CDCl_3$):





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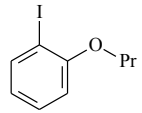

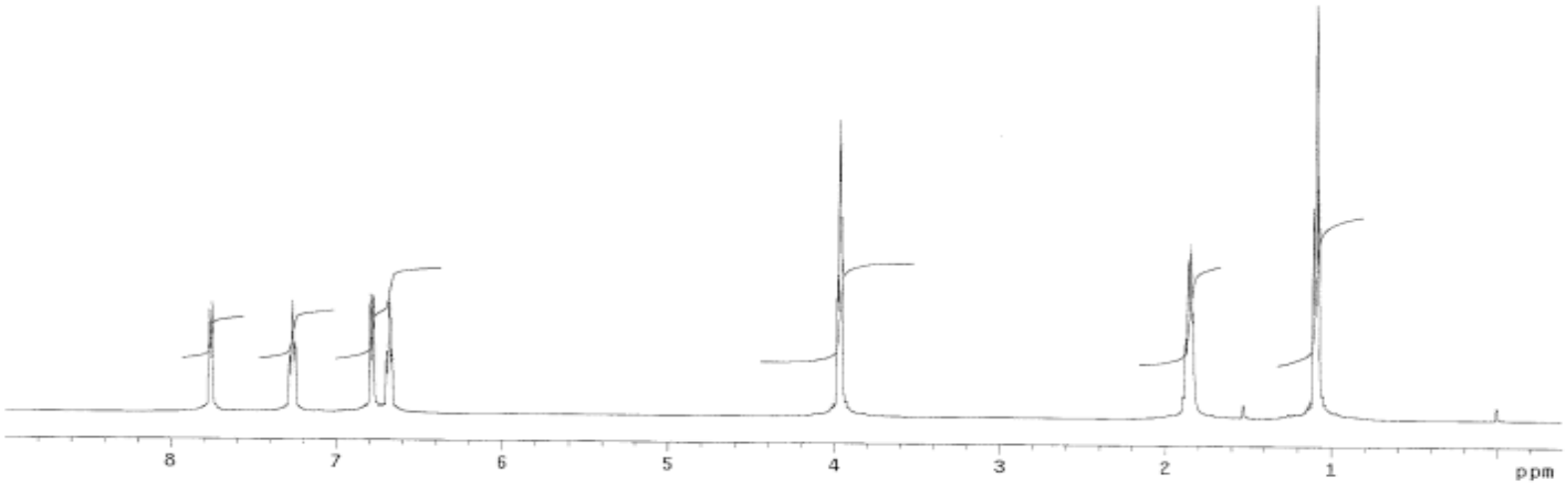

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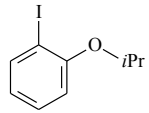

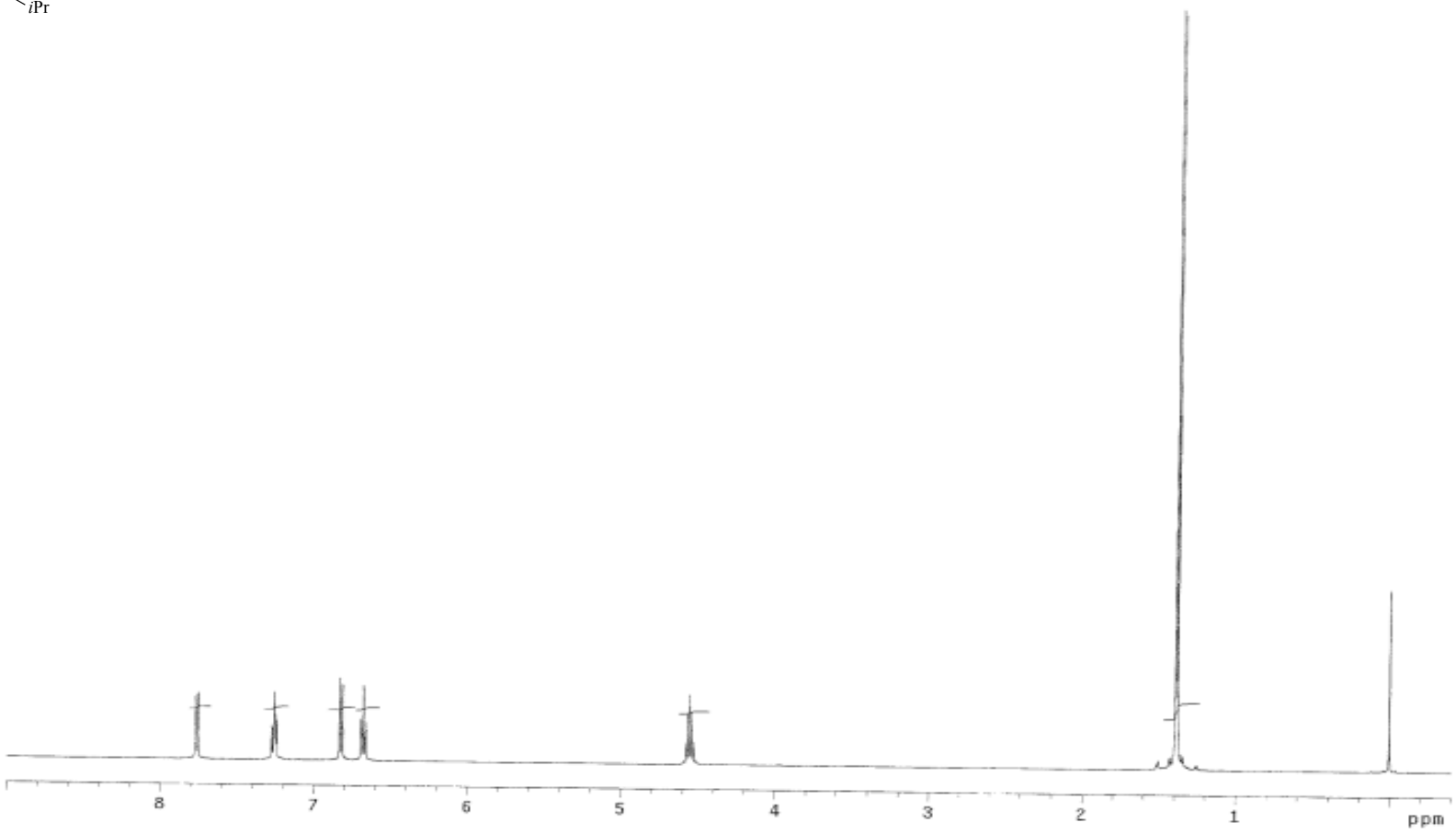

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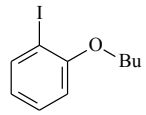
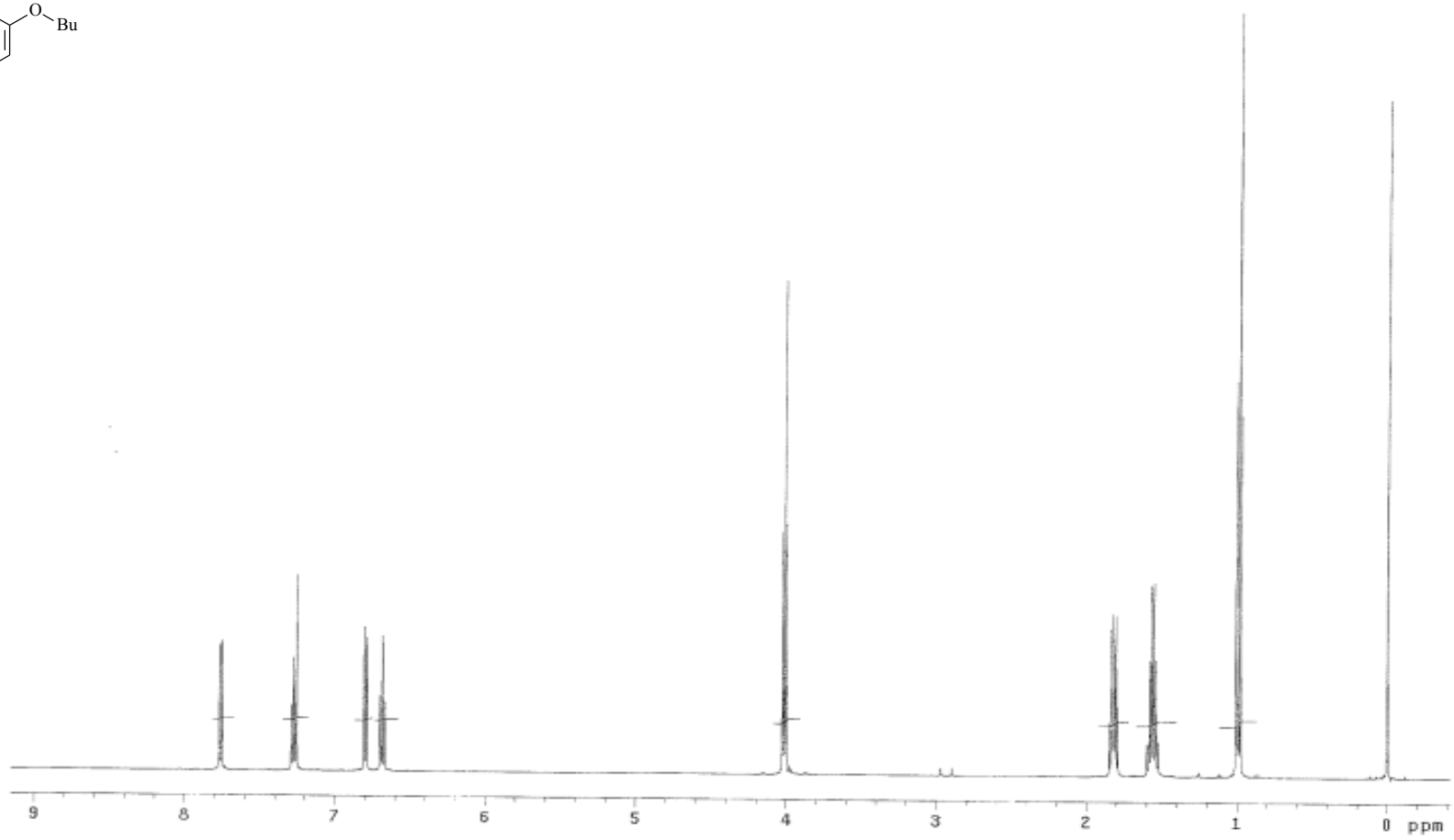
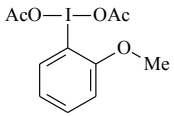
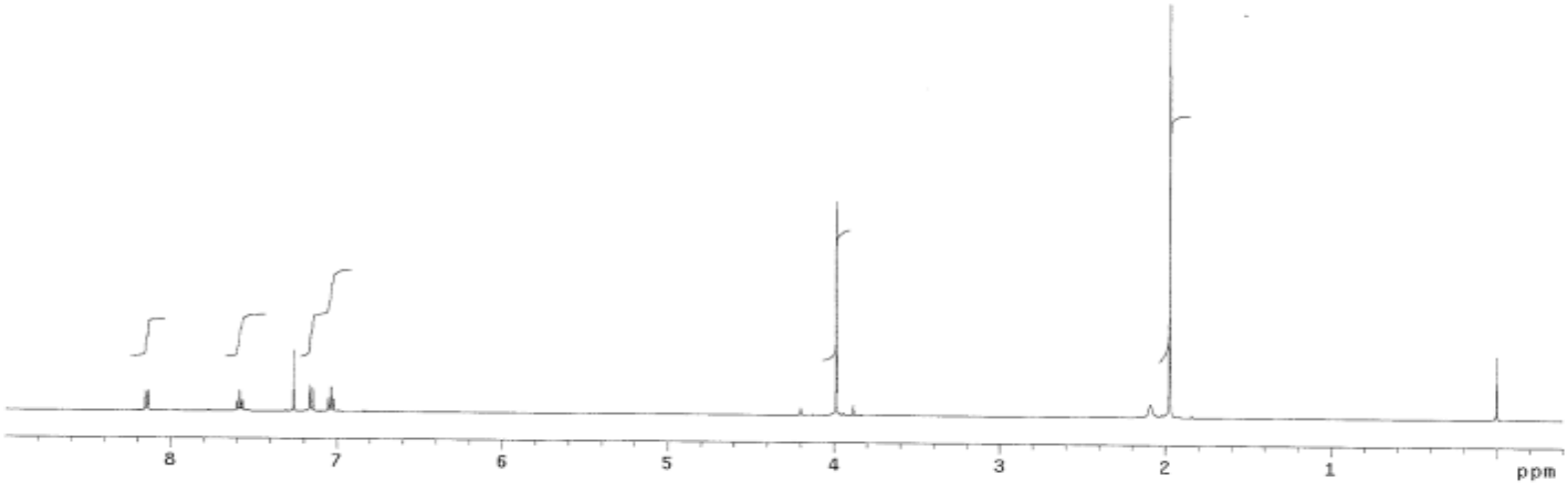


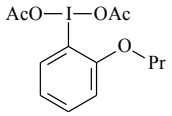


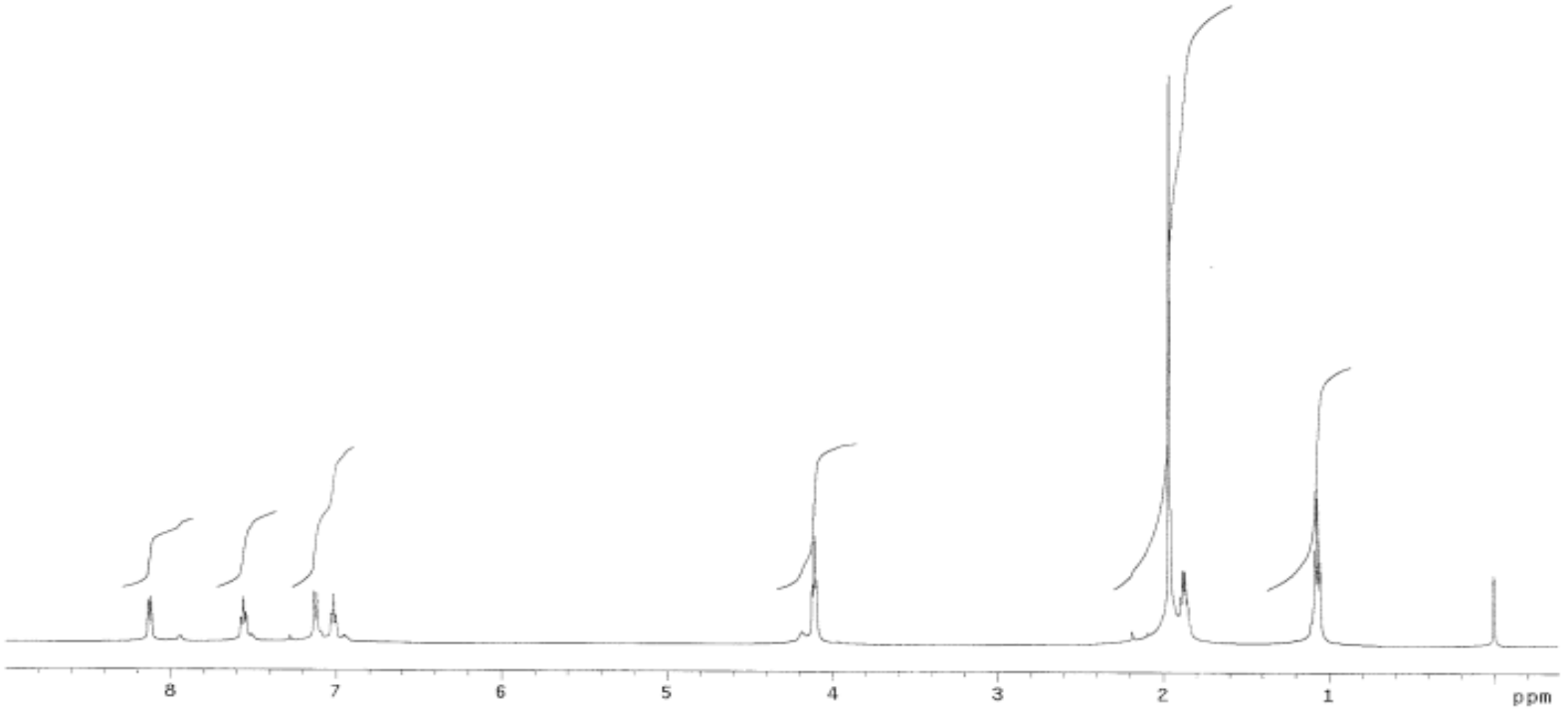
^{1}H NMR (500 MHz, $CDCl_3$):



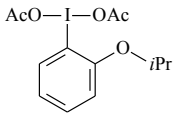


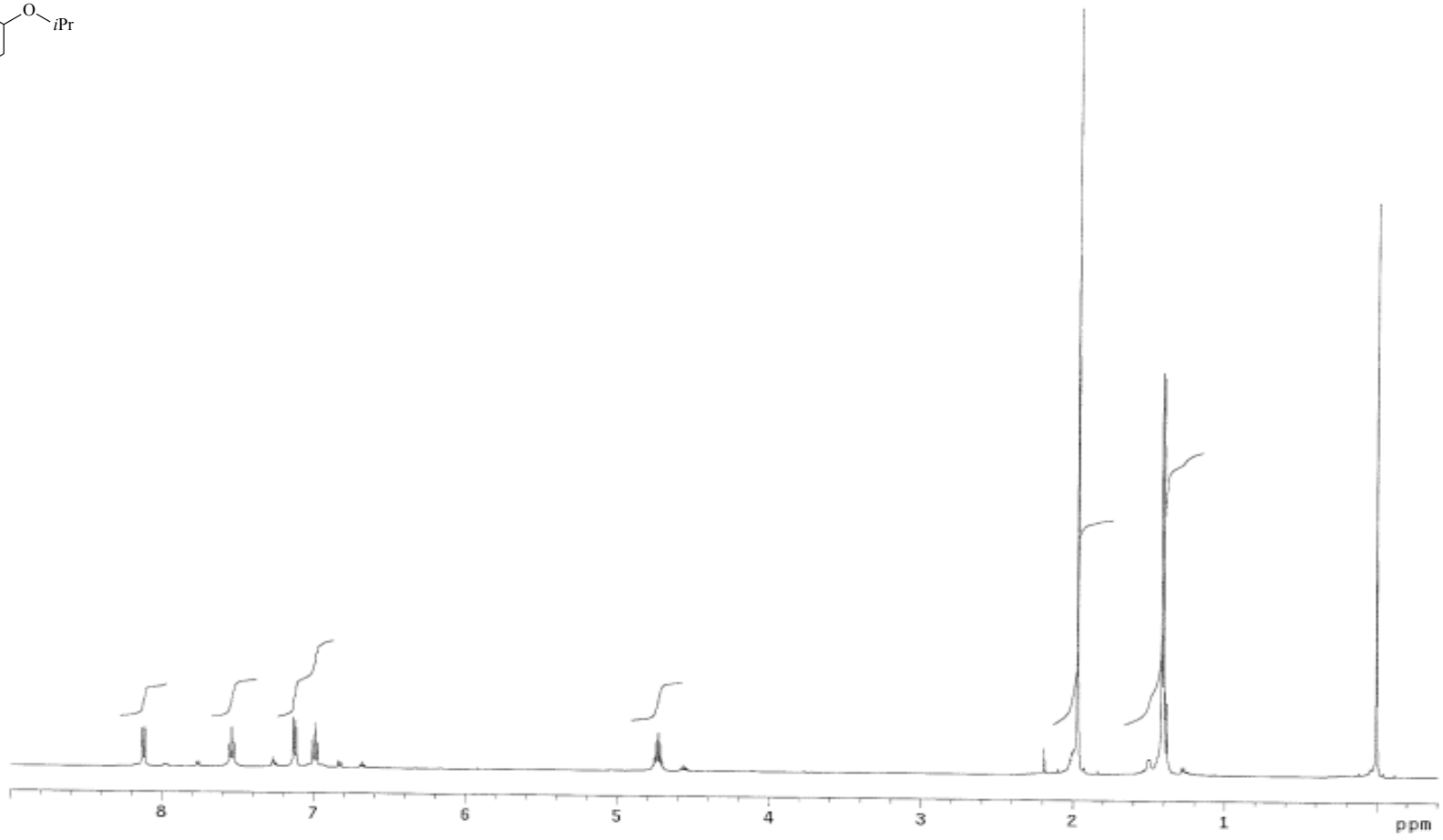
^{1}H NMR (500 MHz, $CDCl_3$):





^{1}H NMR (500 MHz, $CDCl_3$):





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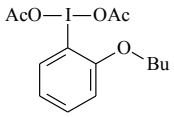
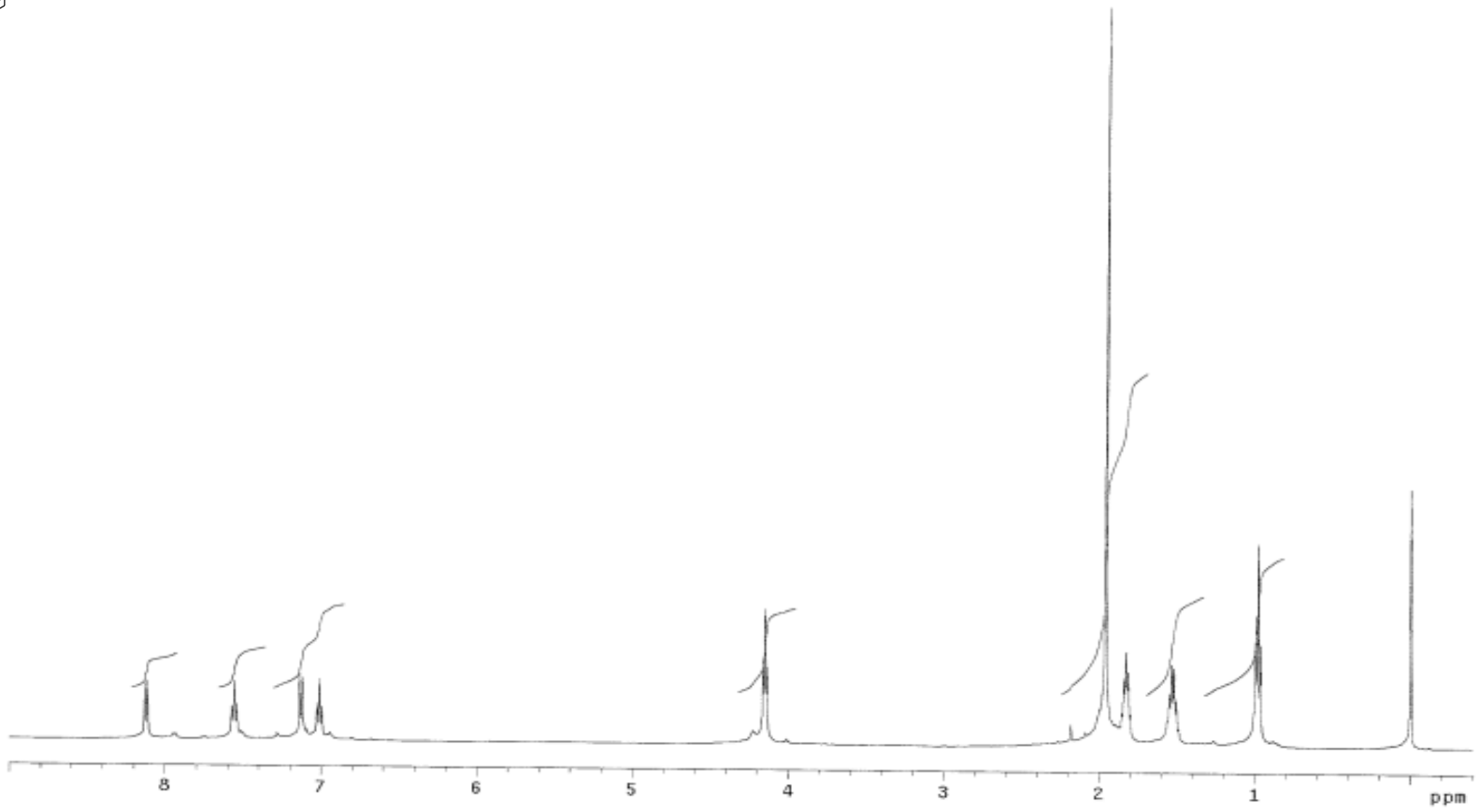
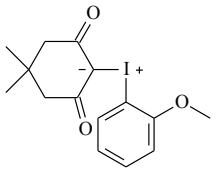
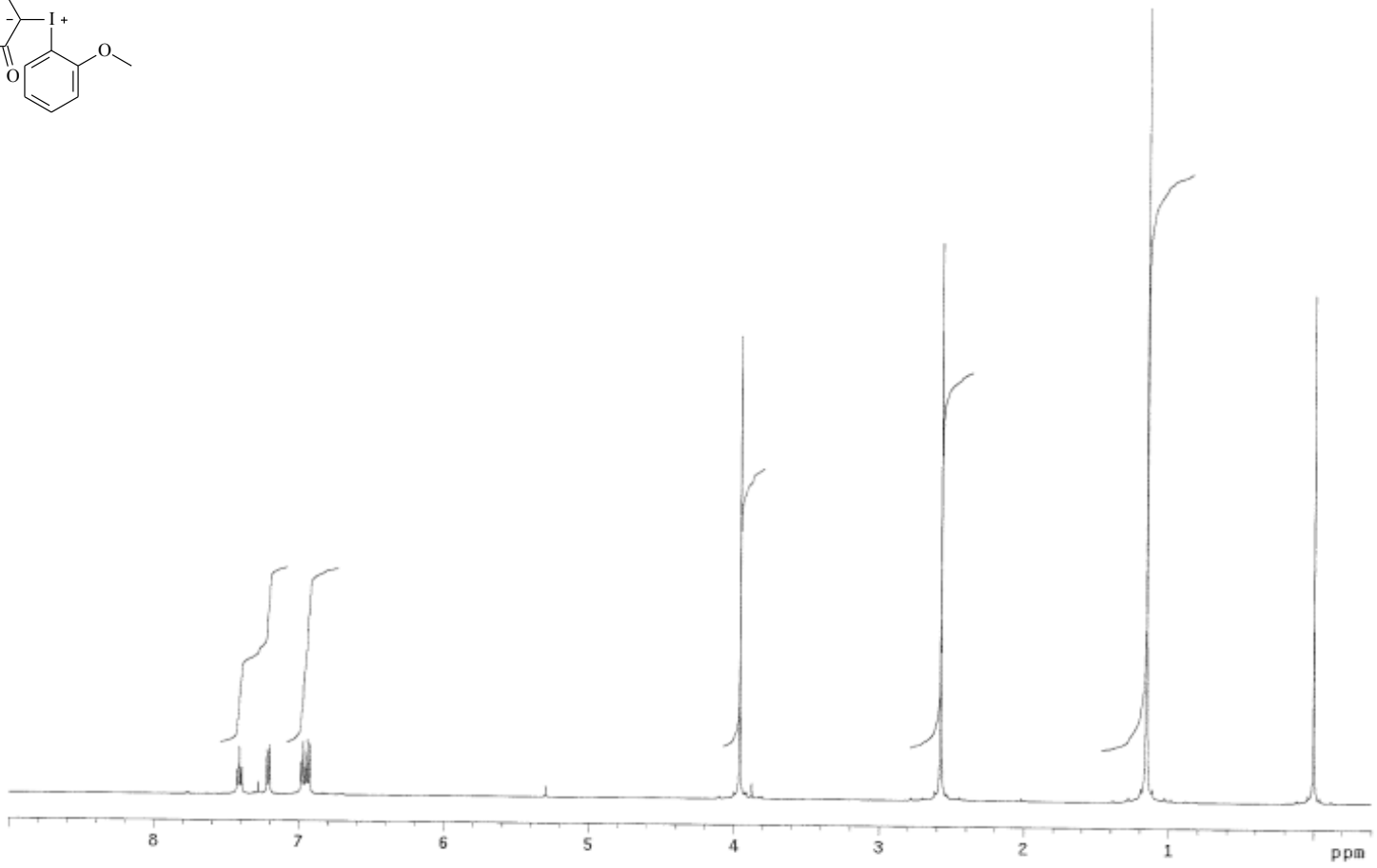


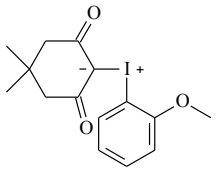


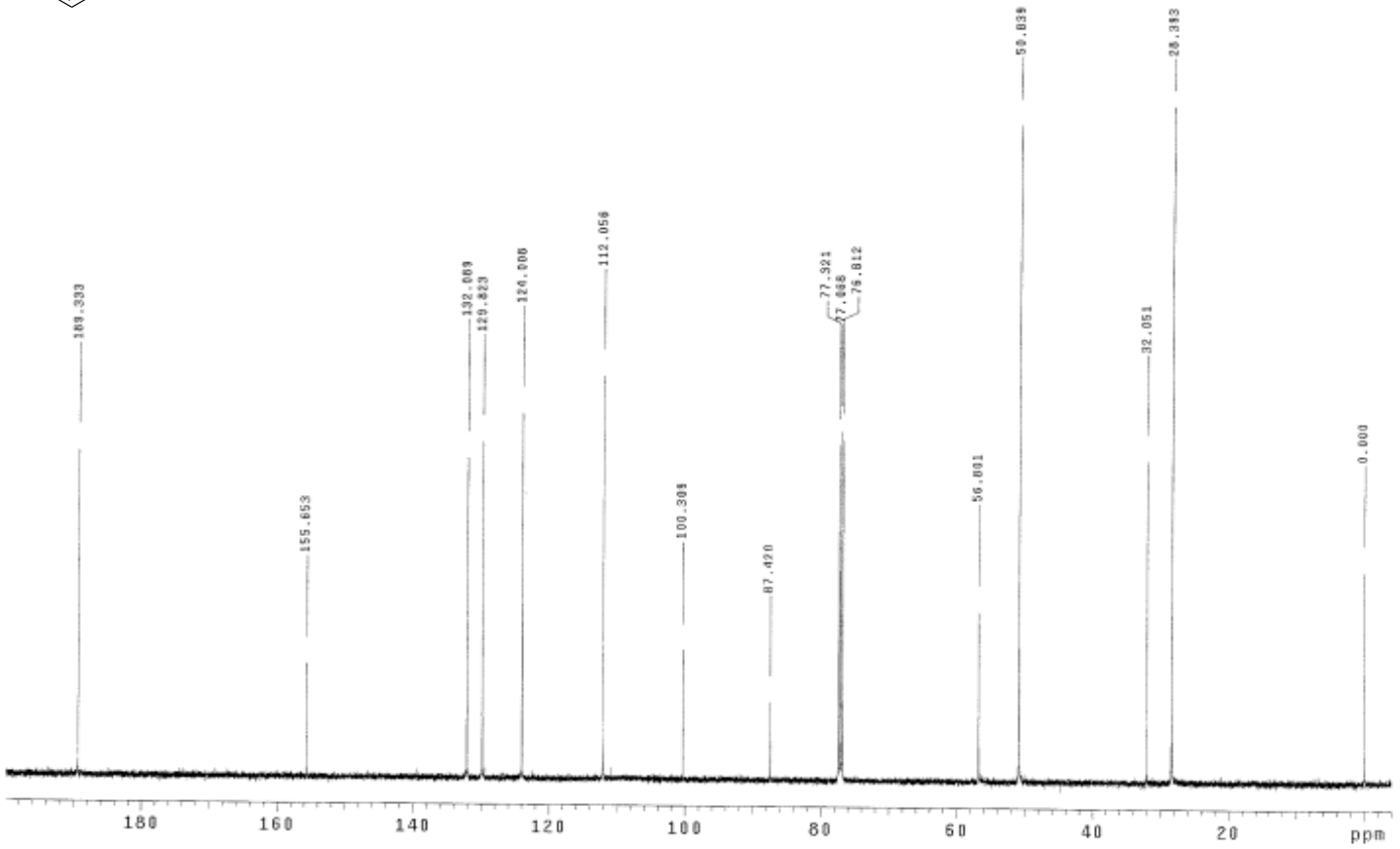
^{1}H NMR (500 MHz, $CDCl_3$):



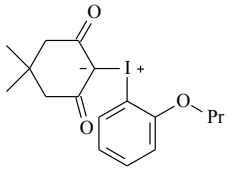


^{13}C NMR (125 MHz, $CDCl_3$):

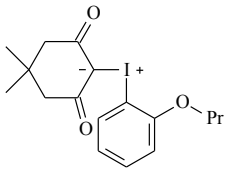


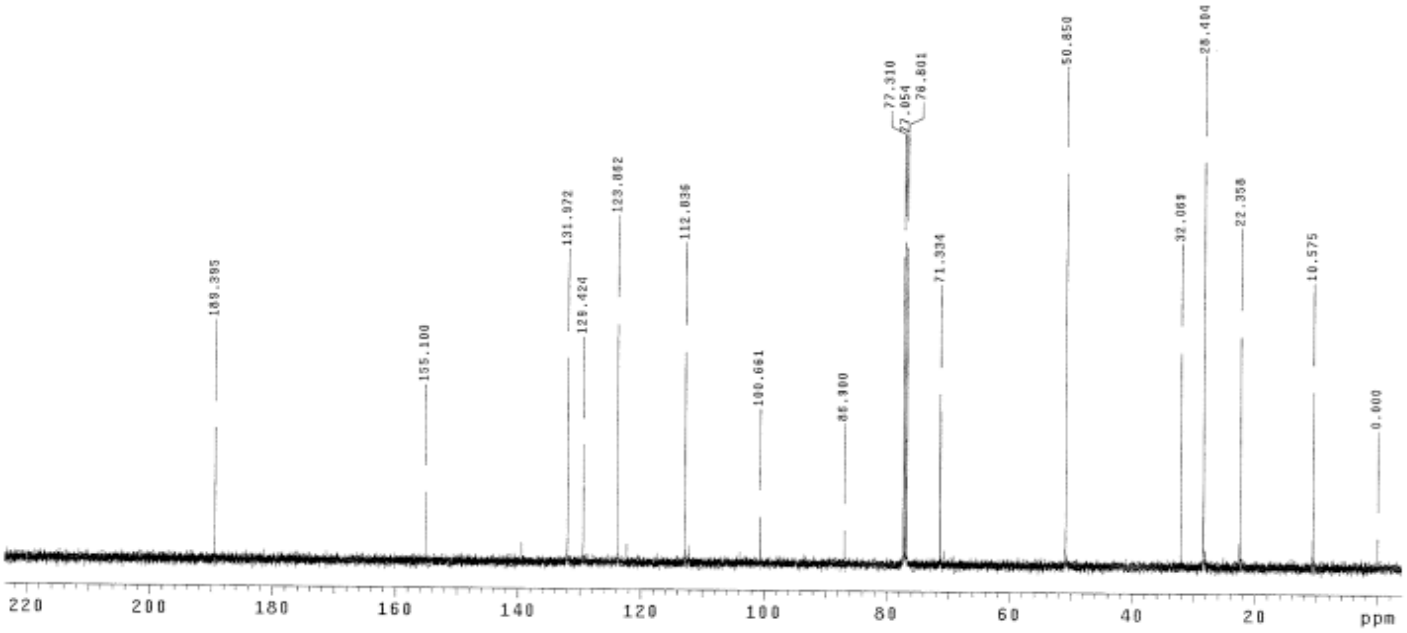


^{1}H NMR (500 MHz, $CDCl_3$):



^{13}C NMR (125 MHz, $CDCl_3$):





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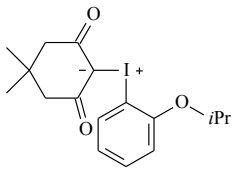

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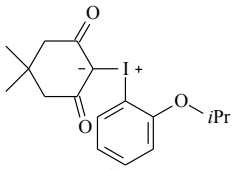

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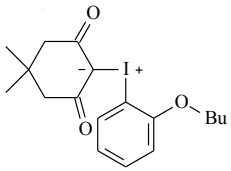

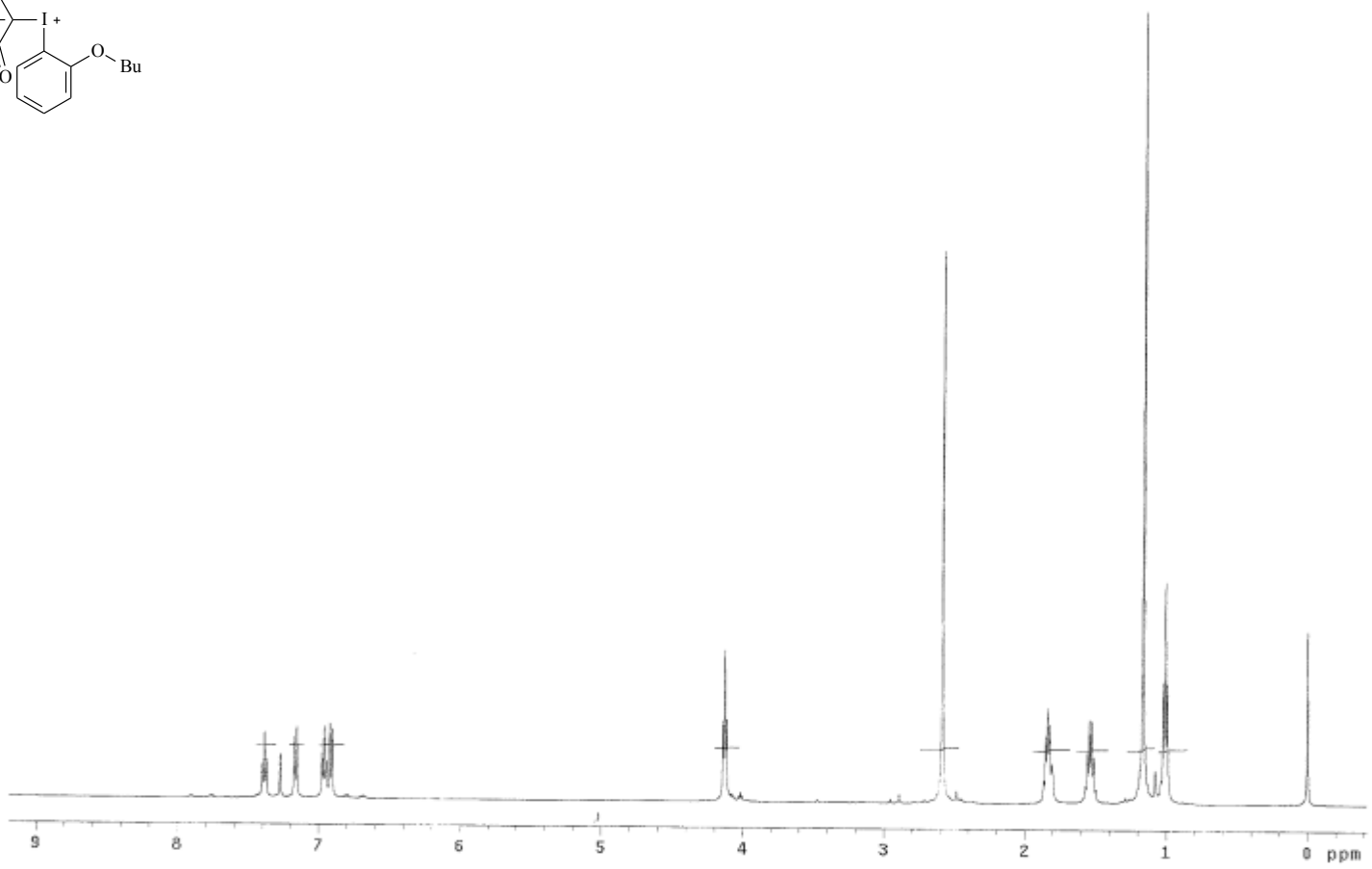

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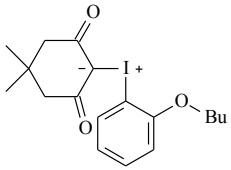
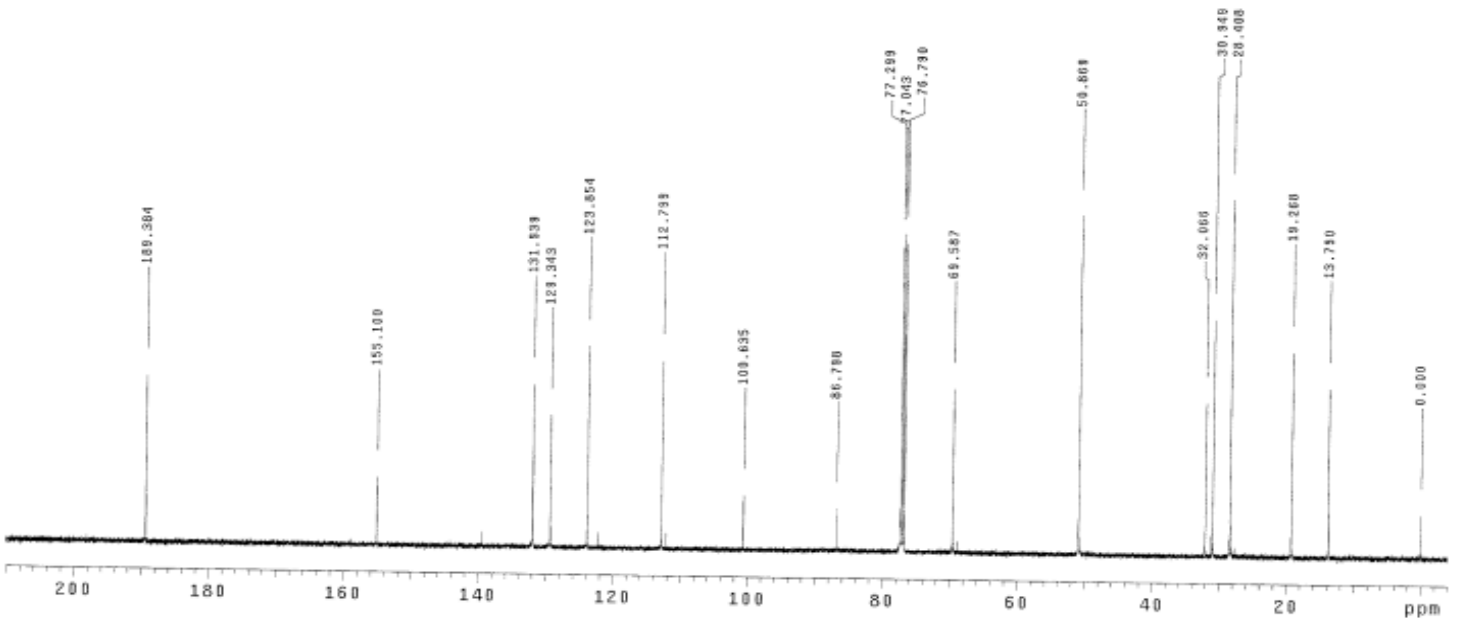
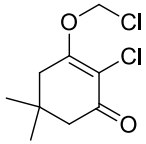
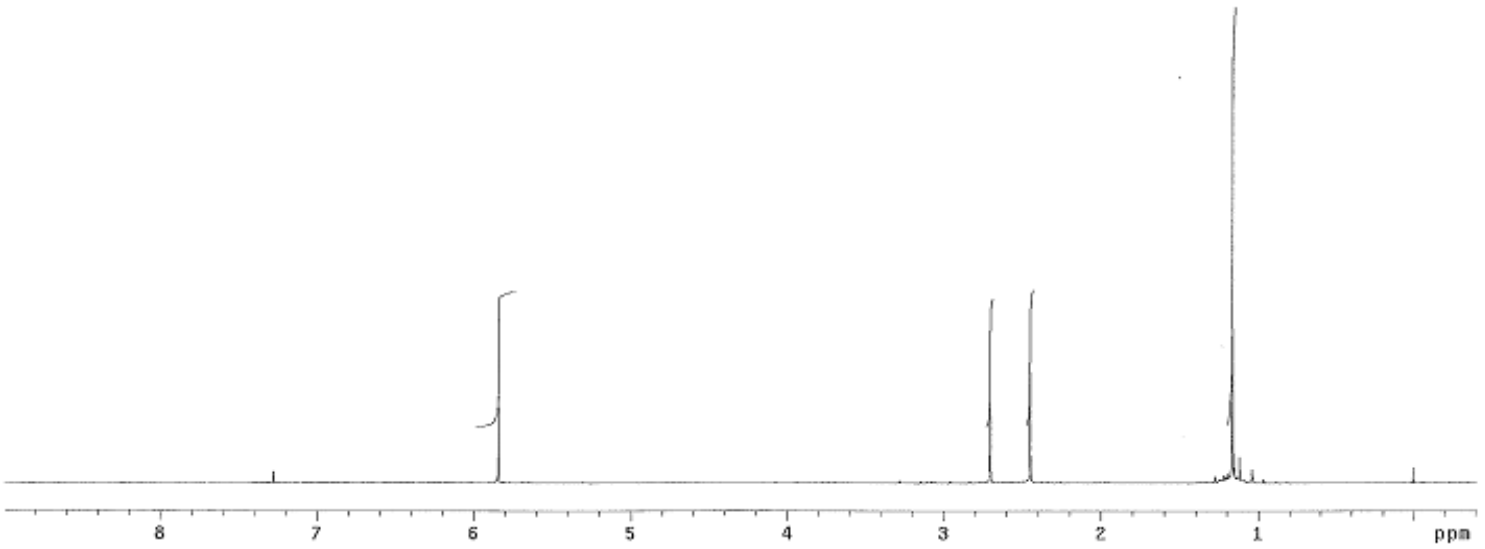


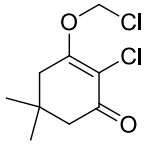


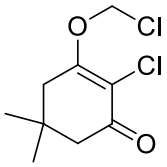
^{1}H NMR (500 MHz, $CDCl_3$):





^{13}C NMR (125 MHz, $CDCl_3$):





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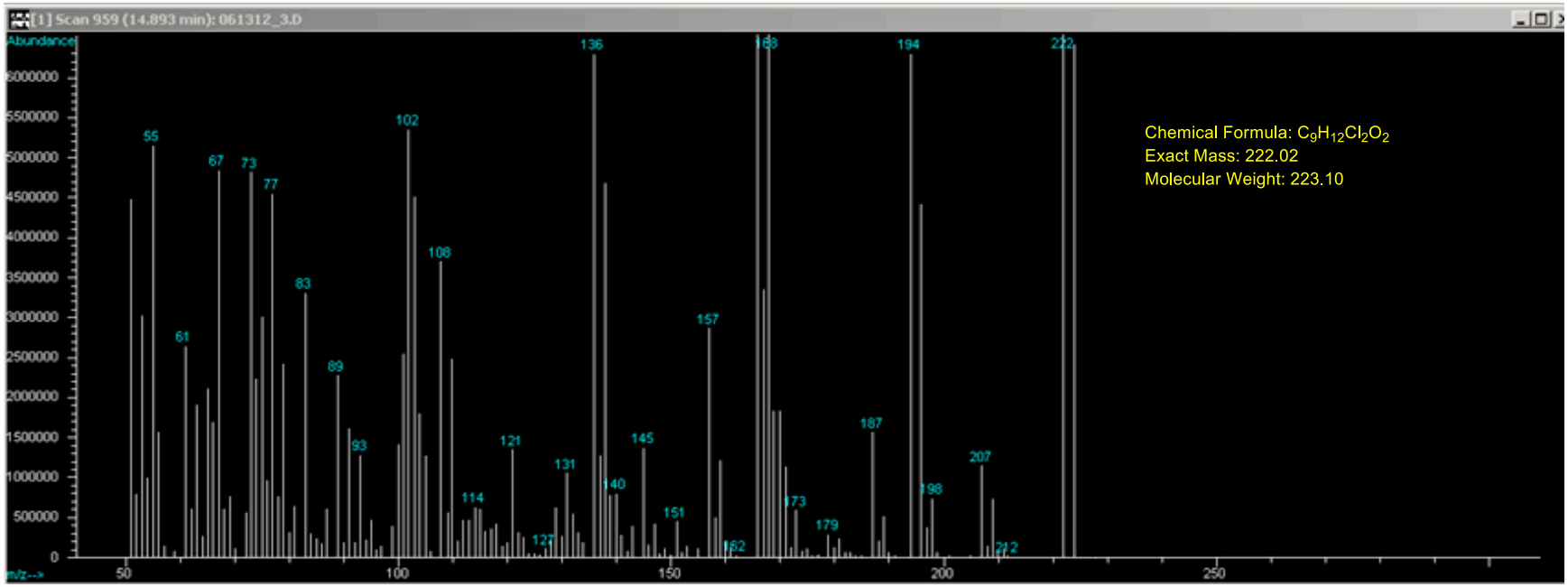
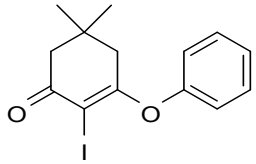
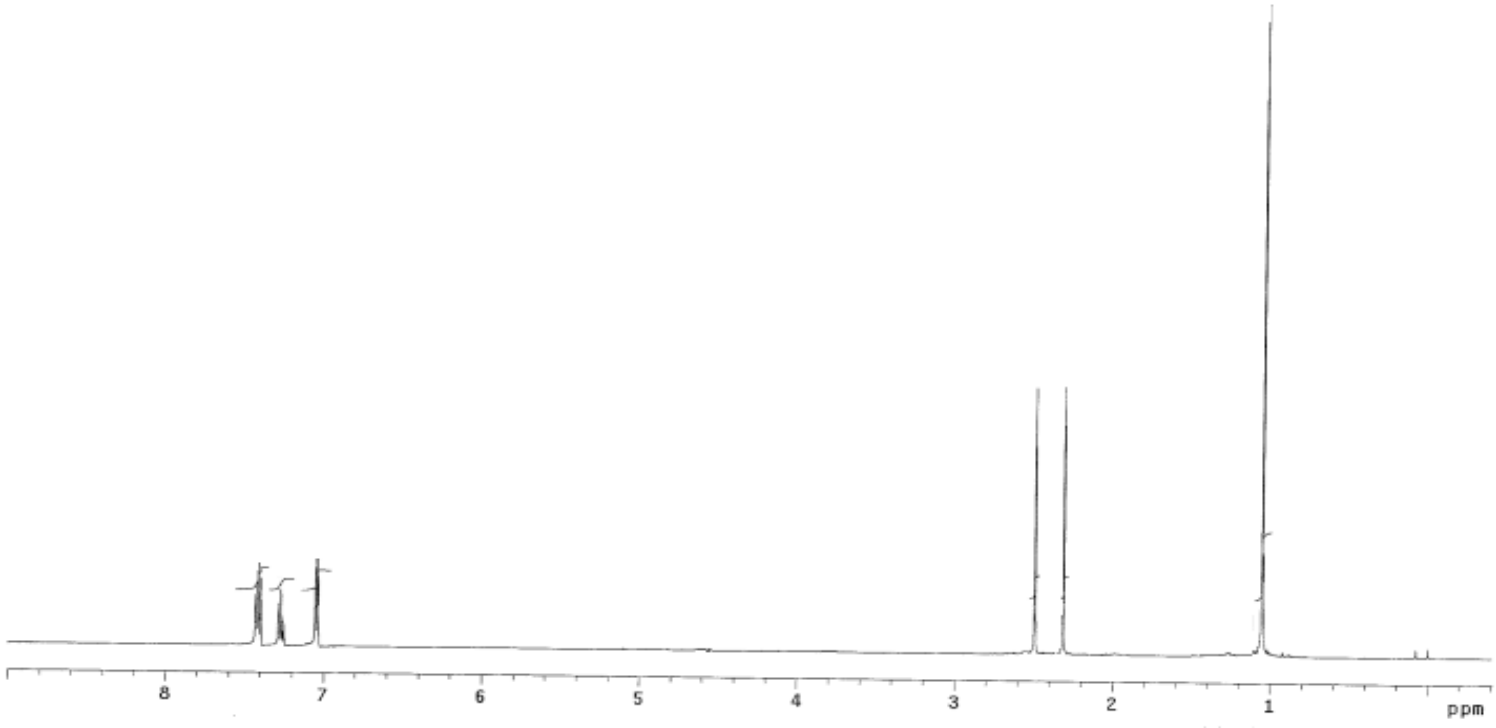


^{1}H NMR (500 MHz, $CDCl_3$):





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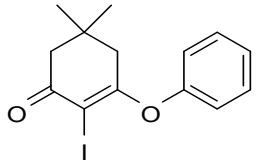

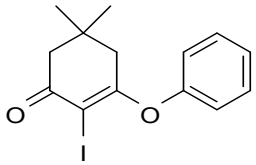

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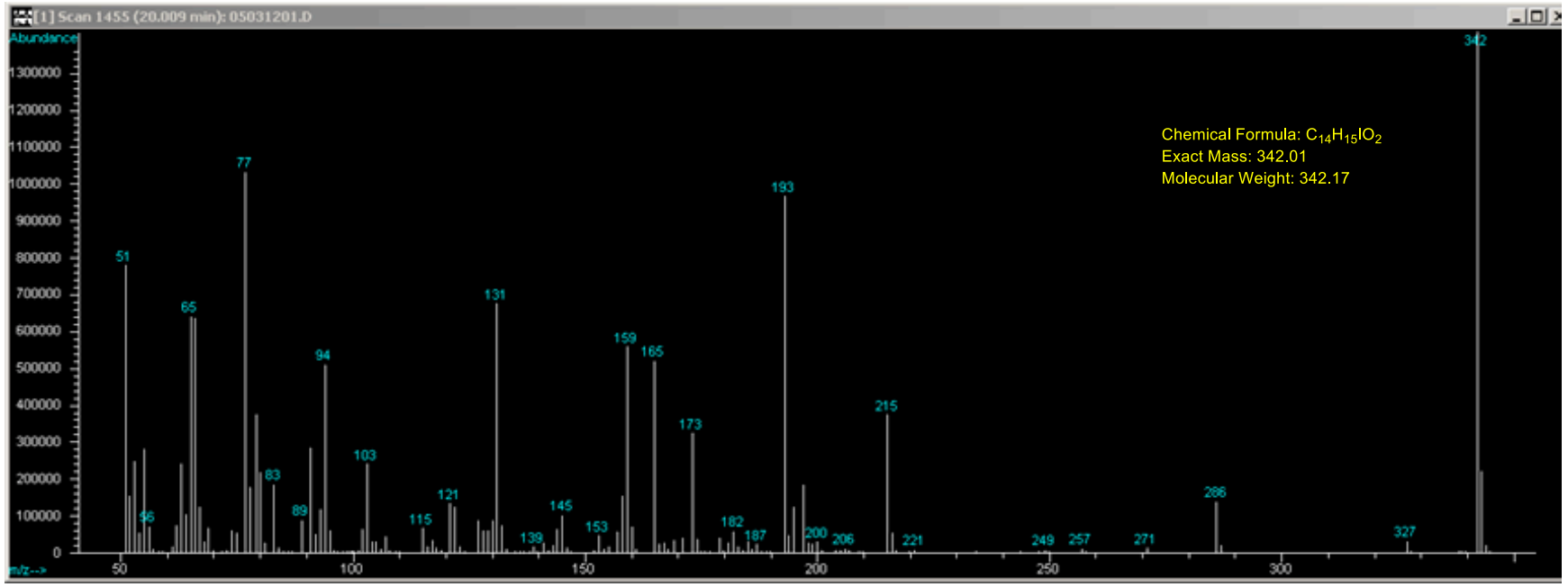
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Abundance
m/z-->
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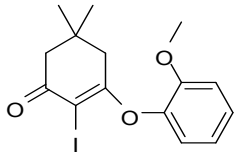

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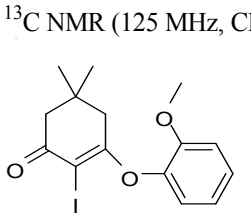

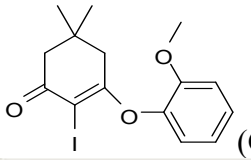

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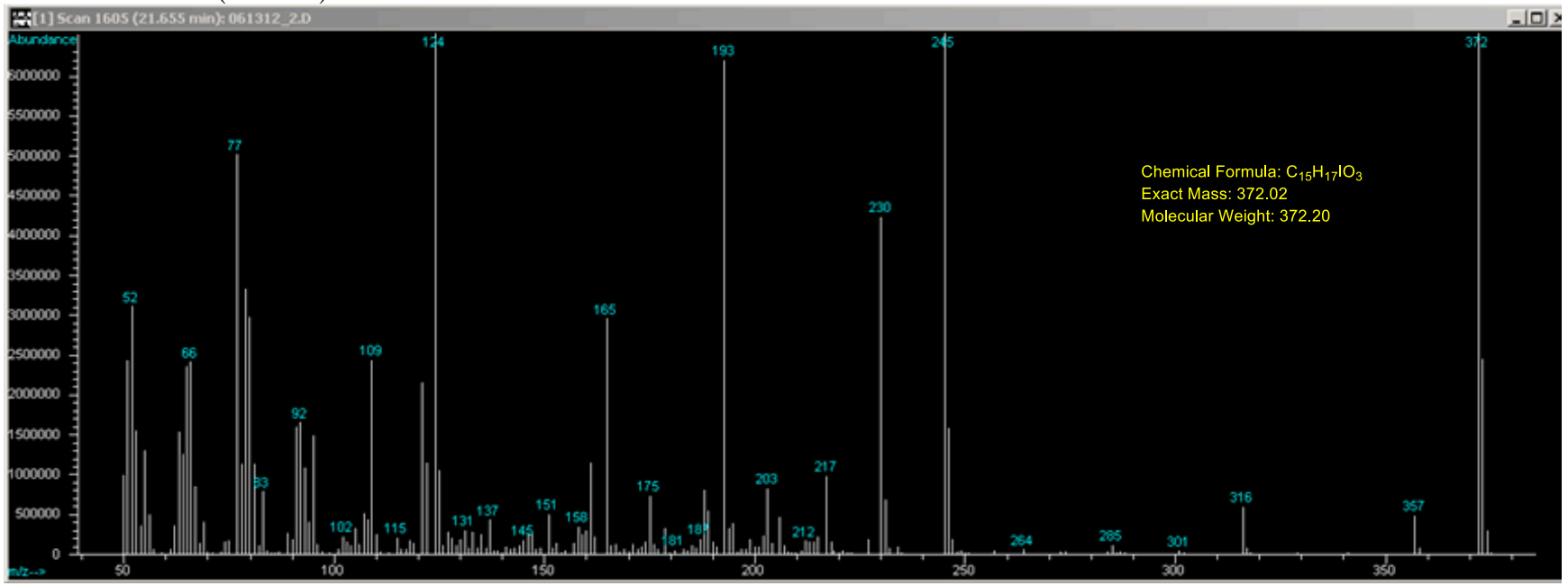
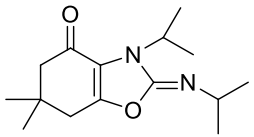
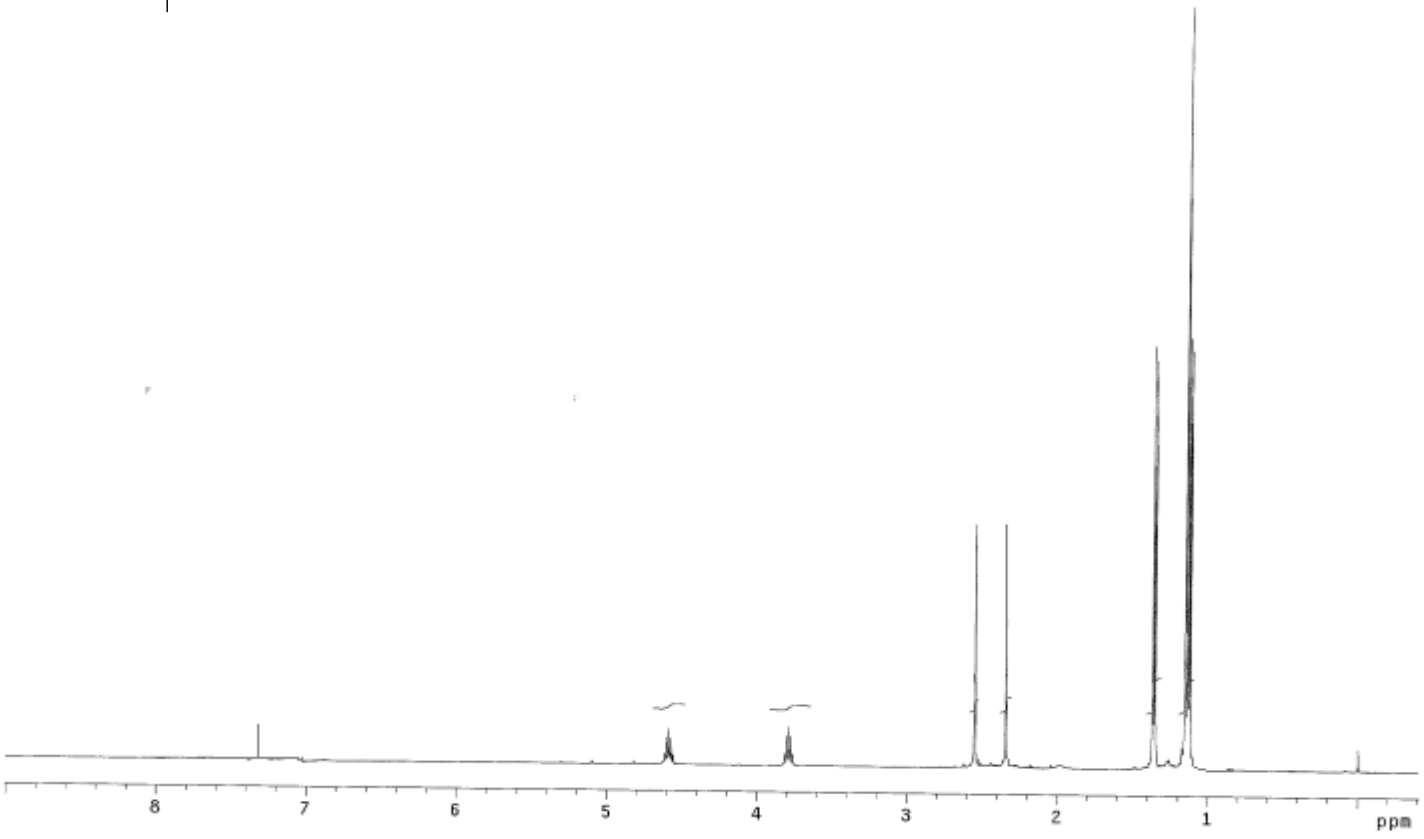
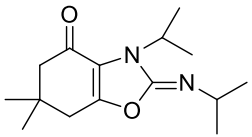


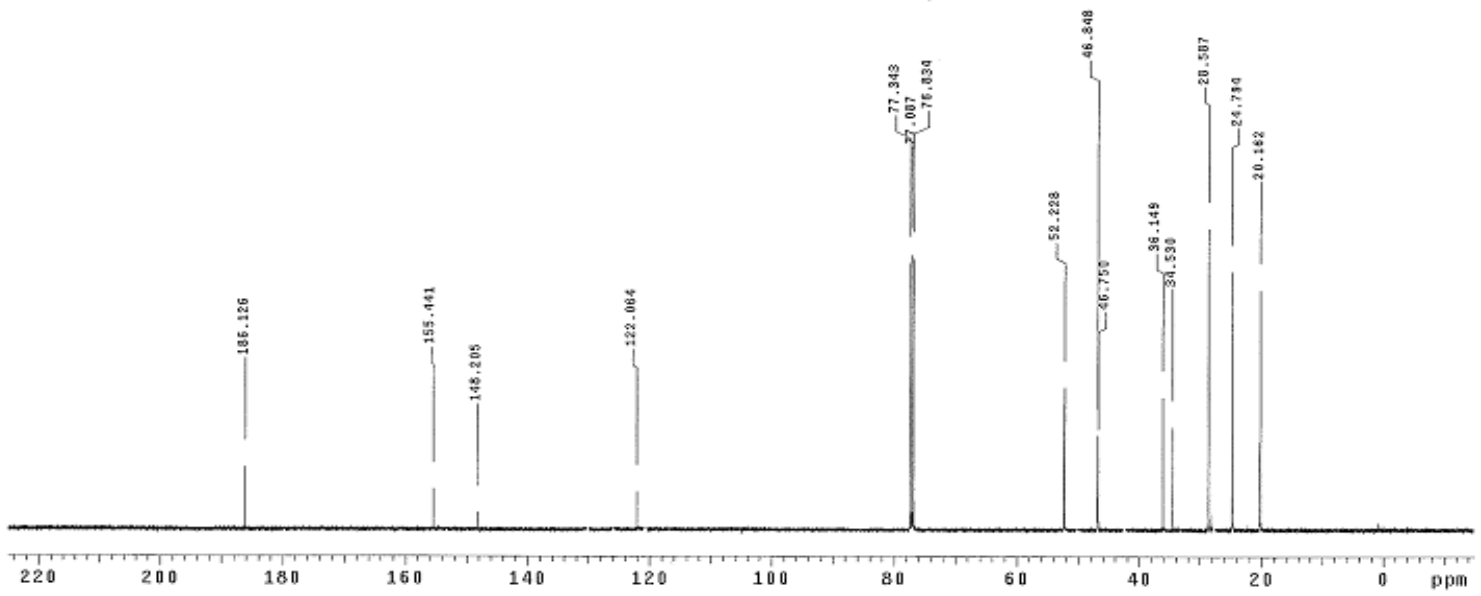
^{1}H NMR (500 MHz, $CDCl_3$):

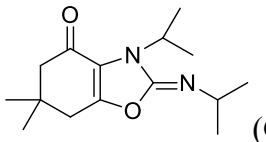




^{13}C NMR (125 MHz, $CDCl_3$):







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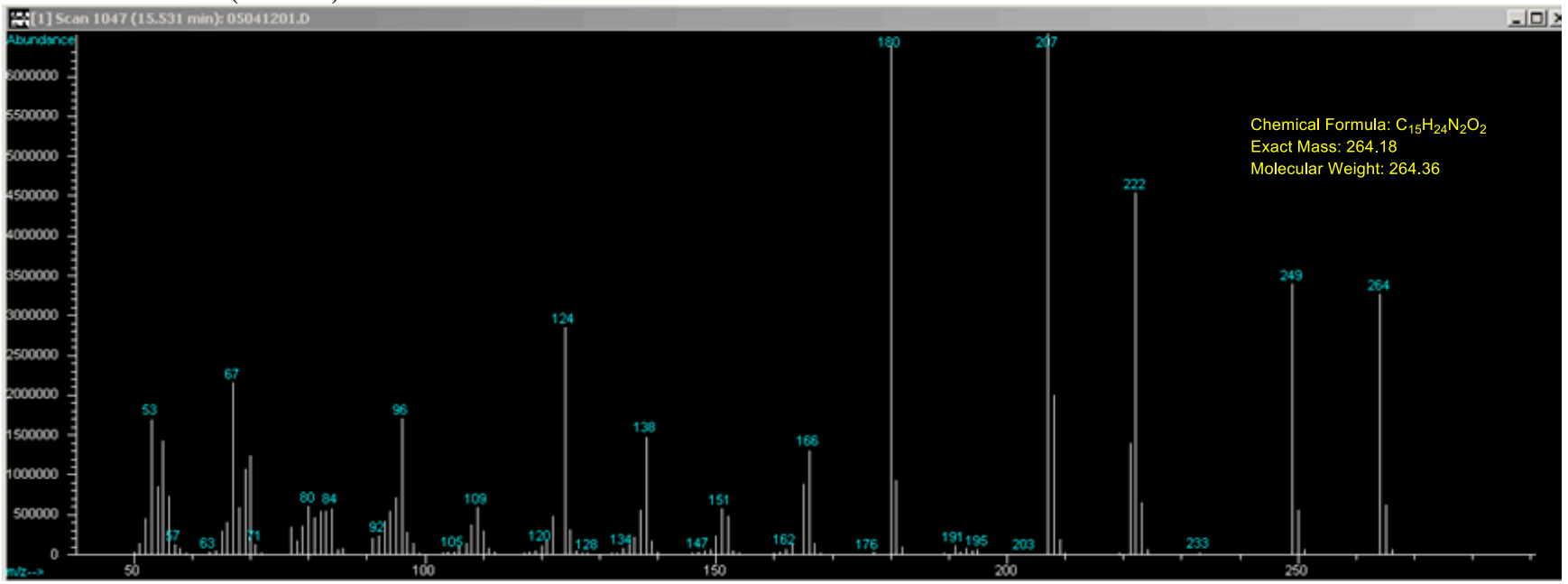
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Molecular Weight: 264.36
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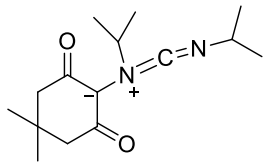
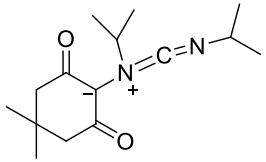
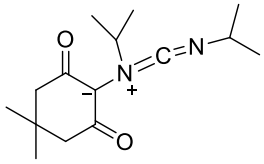
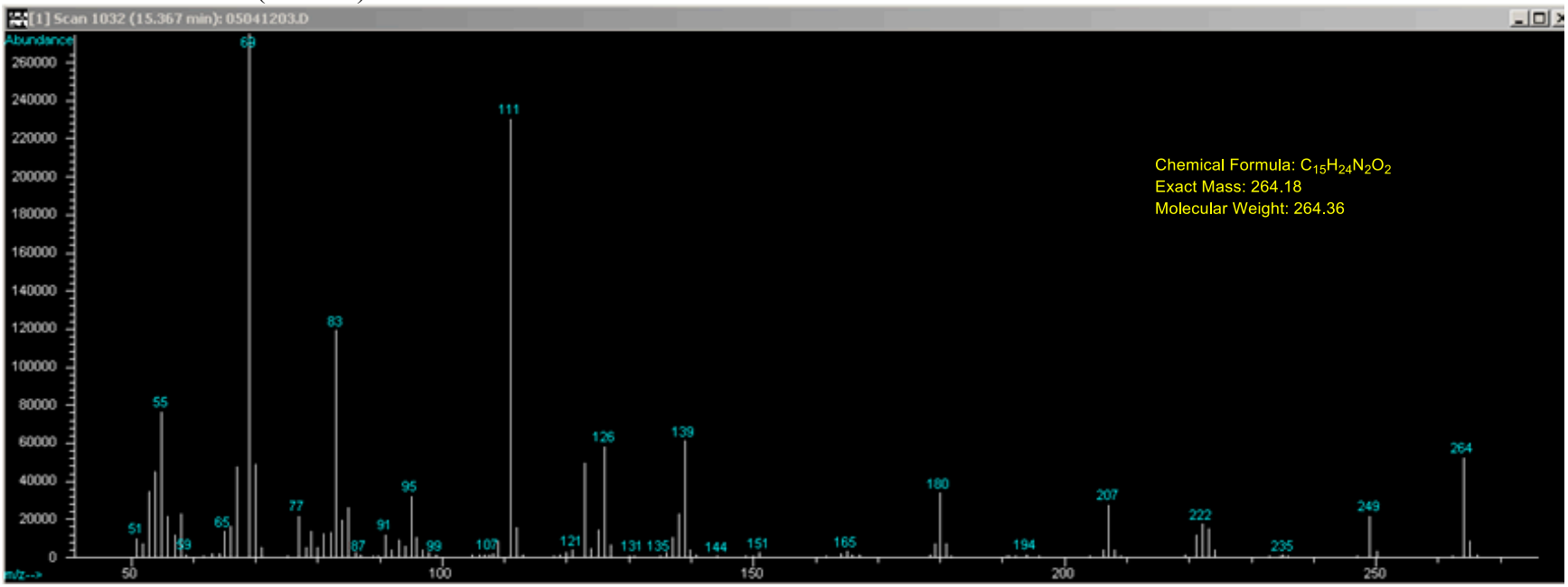


^{13}C NMR (125 MHz, $CDCl_3$):

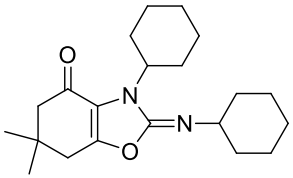




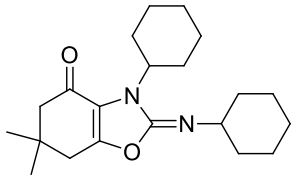
(GC-MS):

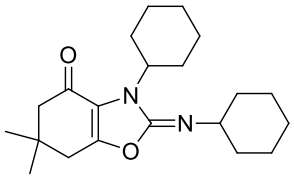


^{1}H NMR (500 MHz, $CDCl_3$):

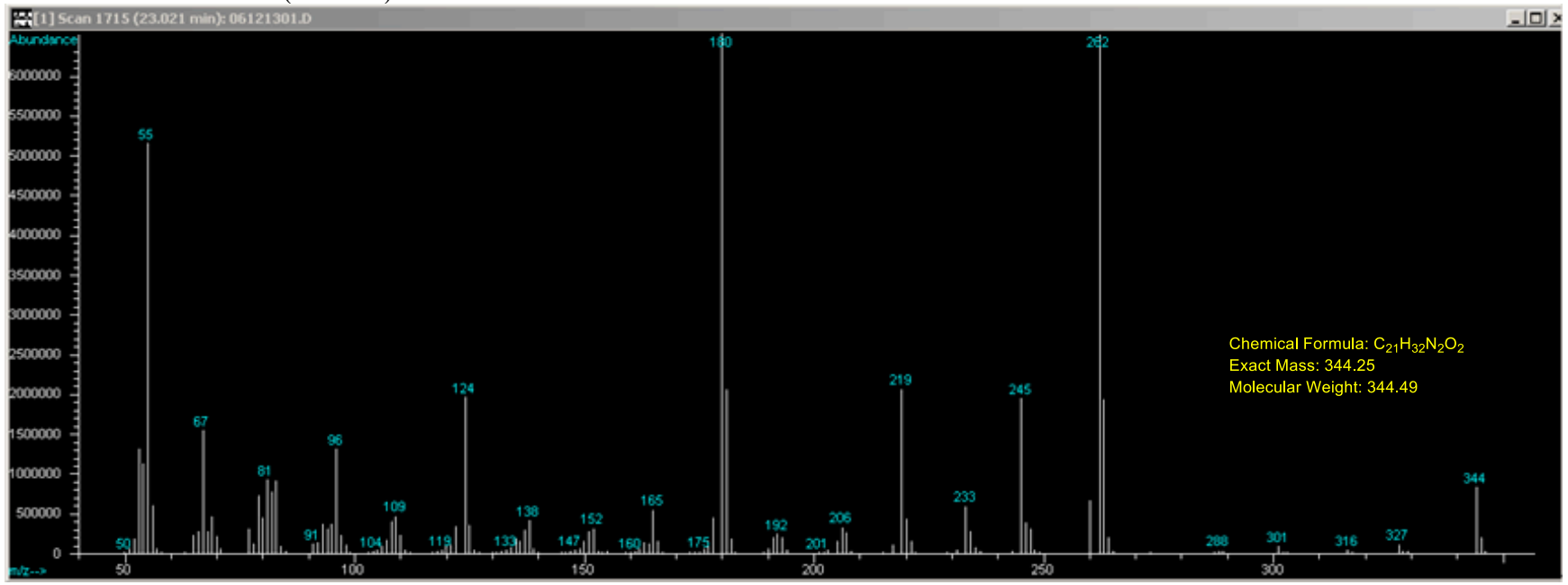


^{13}C NMR (125 MHz, $CDCl_3$):

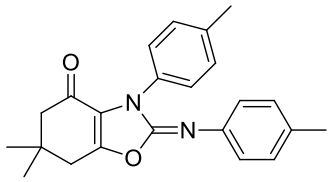


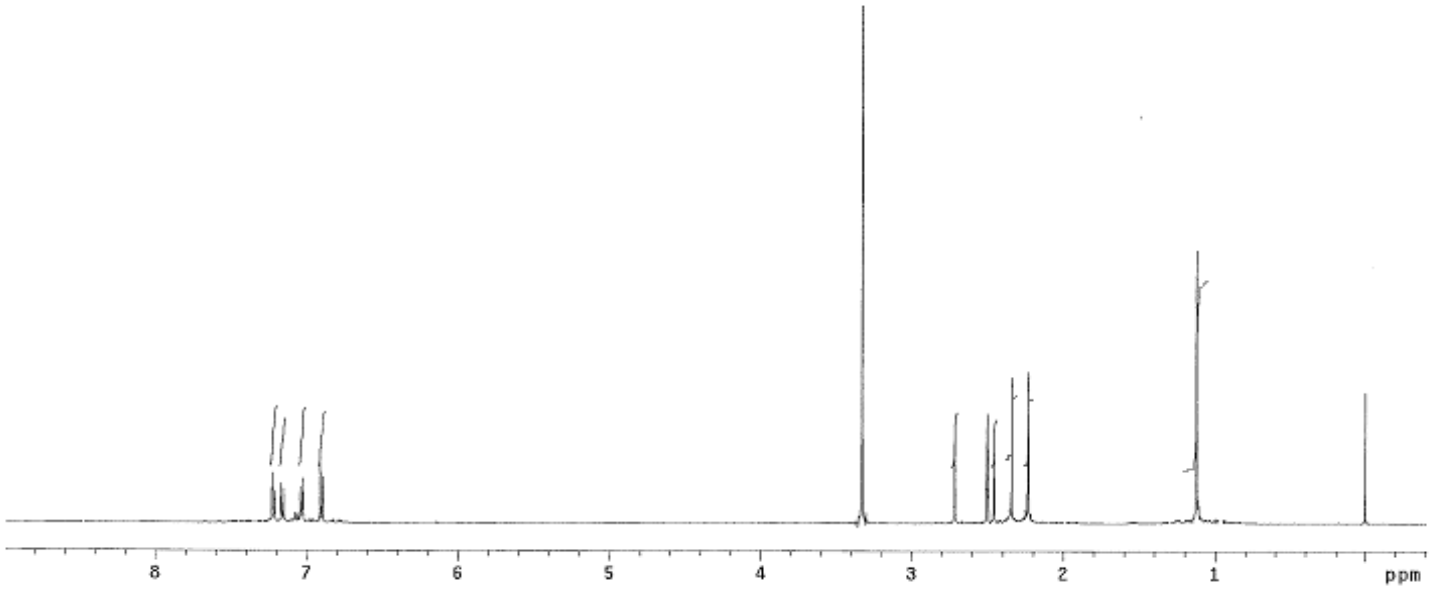


(GC-MS):

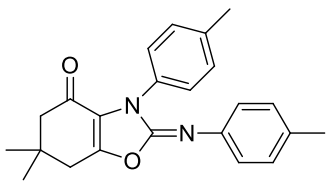


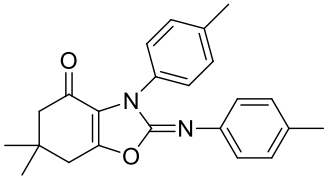
^{1}H NMR (500 MHz, DMSO-d_6):



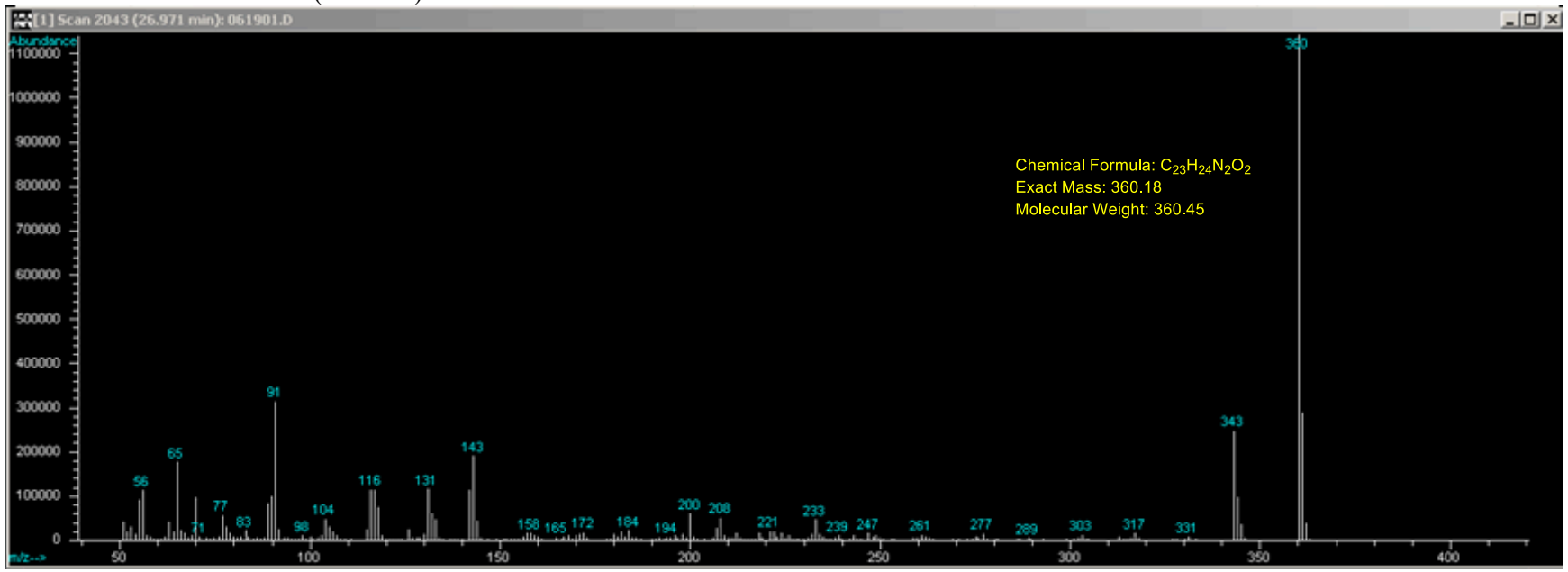


^{13}C NMR (125 MHz, DMSO-d_6):

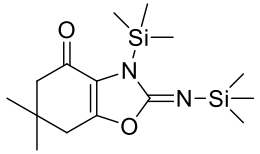




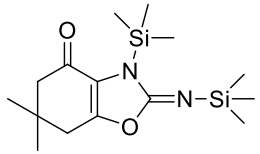
(GC-MS):

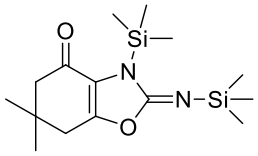


^{1}H NMR (500 MHz, $CDCl_3$):



^{13}C NMR (125 MHz, $CDCl_3$):





(GC-MS):