Supporting Information

Design, Preparation, X-ray Crystal Structure, and Reactivity of *o*-Alkoxyphenyliodonium Bis(methoxycarbonyl)methanide, a Highly Soluble Carbene Precursor

Chenjie Zhu[a,b], *Akira Yoshimura*[a], *Lei Ji*[a], *Yunyang Wei*[b], *Victor N. Nemykin*[a,]*, *and Viktor V. Zhdankin*[a,]*

[a] Department of Chemistry and Biochemistry, University of Minnesota Duluth, Duluth, Minnesota 55812, USA

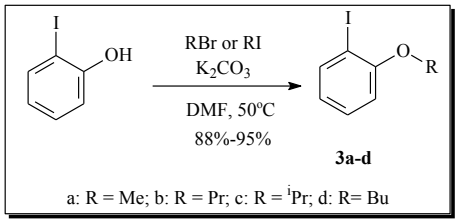
[b] School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

Table of Contents

1. General experimental remarks

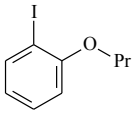
All reactions were performed under dry nitrogen atmosphere with flame-dried glassware. All commercial reagents were ACS reagent grade and used without further purification. Dichloromethane was distilled from CaH_2 immediately prior to use. Diethyl ether was distilled from Na/benzophenone. All commercial 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. Preparation and characterization of ethers of 2-iodophenol 3a-d.



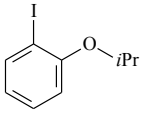
To a solution of 2-iodophenol (10.0 mmol) in dry DMF (20 mL) potassium carbonate (50.0 mmol) was added under stirring. After 10 min the appropriate alkyl bromide or alkyl iodide (15.0 mmol) was added to the reaction mixture. The reaction was stirred at 50 °C for 3 h. The solvent was evaporated in vacuum 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.[1]



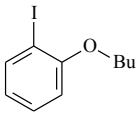
Reaction of propyl iodide with 2-iodophenol (2.2 g, 10.0 mmol) according to the general procedure afforded 2.2 g (85%) of product **3b**, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 7.5, 1H), 7.32-7.22 (m, 1H), 6.81 (d, J = 8, 1H), 6.69 (t, J = 7.5, 1H), 3.97 (t, J = 6.3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

1-Iodo-2-isopropoxybenzene 3c.[1]



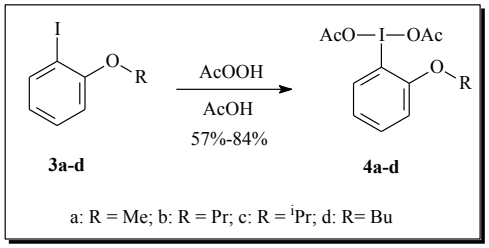
Reaction of isopropyl bromide with 2-iodophenol (2.2 g, 10.0 mmol) according to the general procedure afforded 2.4 g (90%) of product **3c**, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (dd, J = 7.5, 1.5 Hz, 1H), 7.29-7.24 (m, 1H), 6.82 (dd, J = 8.3, 1.0 Hz, 1H), 6.68 (td, J = 7.5,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



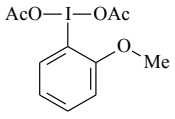
Reaction of butyl bromide with 2-iodophenol (2.2 g, 10.0 mmol) according to the general procedure afforded 2.6 g (95%) of product **3d**, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.3-7.22 (m, 1H), 6.79 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.68 (td, *J* = 7.8,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

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



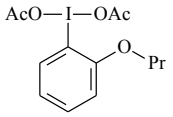
The mixture of acetic anhydride (30 mL) and 30% H_2O_2 (10 mL) was stirred at 40°C overnight, then the appropriate 2-iodophenol derivative **1** (5.0 mmol) was added and the mixture was stirred at 40°C for 8 h. Then the reaction mixture was concentrated in vacuum and washed with water followed by hexanes 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 **3** without additional recrystallization.

1-Diacetoxy-2-methoxyphenyl-λ^3-iodane 4a.



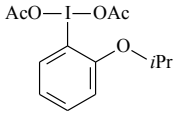
Reaction of 1-iodo-2-methoxybenzene **3a** (1.17 g, 5 mmol) with peracetic acid according to the general procedure afforded 1.51 g (87%) of product **4a**, isolated as light yellow solid, mp 140-142 °C (lit.[2], mp 139-140 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.62-7.56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



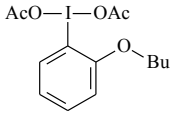
Reaction of 1-iodo-2-propoxybenzene **3b** (0.90 g, 3.43 mmol) with peracetic acid according to the general procedure afforded 1.19 g (85%) of product **4b**, isolated as light yellow solid, mp 98-100 °C (lit.[2], mp 97.2-98 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8 Hz, 1H), 7.62-7.48 (m,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



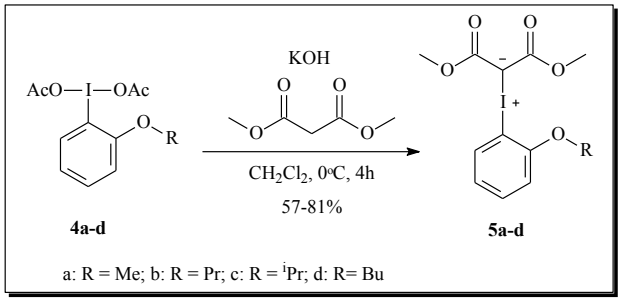
Reaction of 1-iodo-2-isopropoxybenzene **3c** (0.90 g, 3.43 mmol) with peracetic acid according to the general procedure afforded 0.63 g (53%) of product **4c**, isolated as light yellow solid, mp 84-86 °C (lit.[2], mp 84.2-84.8 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (dd, *J* = 7.8, 1.3 Hz, 1H),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



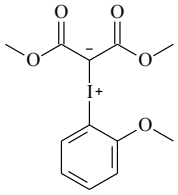
Reaction of 1-iodo-2-butoxybenzene **3d** (1.00 g, 3.62 mmol) with peracetic acid according to the general procedure afforded 1.08 g (72%) of product **4d**, isolated as light yellow solid, mp 73-75 °C (lit.[2], mp 75-76 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8 Hz, 1H), 7.58 (t, *J* = 8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

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



To a stirred solution of KOH (15 mmol) in CH_2Cl_2 (15 mL) was added dimethyl malonate (4.0 mmol). The heterogeneous mixture was cooled at 0 °C (ice/water bath) and stirred vigorously for 10 min to produce a milky white suspension. Then the appropriate 1-diacetoxy-2-alkoxyphenyl-λ^3-iodanes **4** (3.0 mmol) was added and the reaction mixture was stirred vigorously for 4.0 h at 0°C. The reaction mixture was then filtered and washed three times with CH_2Cl_2 (10 mL). 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, which was further recrystallized from CH_2Cl_2/Hexane.

Bis(methoxycarbonyl)-2-methoxyphenyliodinio-methanide 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-white solid, mp 126 °C (with decomposition); IR (KBr) cm^{-1}: 3080, 2977, 2939, 2886, 1685, 1565, 1433, 1308, 1006, 813; ^1H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 3.85-3.88 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.6, 158.1, 139.5, 135.4, 129.5, 122.5, 111.0, 85.9, 56.3, 53.4. Anal. Calcd for $C_{12}H_{13}IO_5$: C, 39.58; H, 3.60; Found: C, 39.62; H, 3.59.

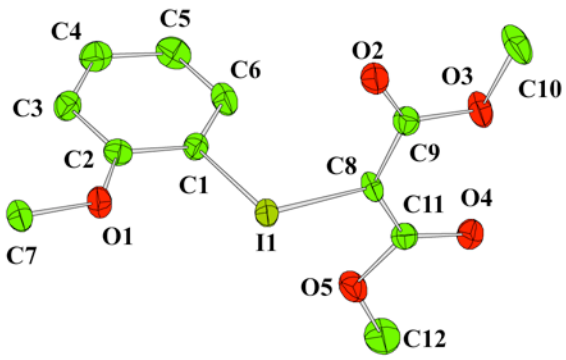
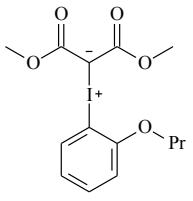


Figure 1. X-ray crystal structure of bis(methoxycarbonyl) -2-methoxyphenyliodinio-methanide **5a**.

Single crystals of product **5a** suitable for X-ray crystallographic analysis were obtained by slow evaporation of the CH_2Cl_2-hexane solution of **5a**. X-ray diffraction data were collected on Rigacu RAPID II diffractometer 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** $C_{12}H_{13}I_1O_5$: M = 364.14; monoclinic, space group P21/n; a = 8.5395(5), b = 7.7736(5); c = 19.6400(13) Å; b = 90.848(6); V = 1303.61(14) $Å^3$; Z= 4; μ = 2.467mm^{-1}, 11928 reflections measured, 2971 unique; final R_1 = 0.0448, R_w = 0.1206. A cif file containing crystallographic data for compound **5a** is provided as Supporting Information with this article.

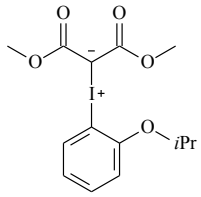
Bis(methoxycarbonyl) - 2- propoxyphenyliodinio-methanide 5b.



Reaction of 1-diacetoxy-2-propoxyphenyl-$λ^3$-iodane **4b** (1.14 g, 3.0 mmol) according to

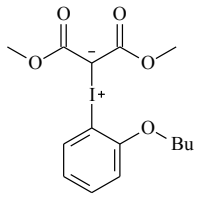
the general procedure afforded 0.95 g (81%) of product **5b**, isolated as off-white solid, mp 132 °C (with decomposition); IR (KBr) cm^{-1}: 3068, 2970, 2931, 1605, 1587, 1486, 1364, 1306, 1077, 986; ^1H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 3.96-3.99 (m, 2H), 3.86-3.90 (m, 6H), 1.84-1.87 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.6, 157.6, 139.4, 135.4, 129.4, 122.3, 112.1, 86.7, 70.7, 53.4, 22.5, 10.8. Anal. Calcd for $C_{14}H_{17}IO_5$: C, 42.87; H, 4.37; Found: C, 42.95; H, 4.31.

Bis(methoxycarbonyl)-2- isopropoxyphenyliodinio-methanide 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 117 °C (with decomposition); IR (KBr) cm^{-1}: 3040, 2954, 2927, 1590, 1534, 1352, 1321, 1031; ^1H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.25-7.28 (m, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 4.53-4.57 (m, 1H), 3.87 (s, 6H), 1.39 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.7, 156.8, 139.6, 135.4, 129.2, 122.4, 114.4, 88.6, 72.1, 53.4, 21.9. Anal. Calcd for $C_{14}H_{17}IO_5$: C, 42.87; H, 4.37; Found: C, 43.03; H, 4.29.

Bis(methoxycarbonyl)-2-butoxyphenyliodinio-methanide 5d.



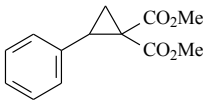
Reaction of 1-diacetoxy-2-propoxyphenyl-λ^3-iodane **4d** (1.18 g, 3.0 mmol) according to

the general procedure afforded 0.69 g (57%) of product **5d**, isolated as off-white solid, mp 106 °C (with decomposition); IR (KBr) cm^{-1}: 3027, 2974, 2921, 1683, 1546, 1348, 1279, 1137, 948; ^1H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.27-7.29 (m, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 4.02 (t, *J* = 6.5 Hz, 2H), 3.85-3.88 (m, 6H), 1.81-1.83 (m, 2H), 1.54-1.58 (m, 2H), 0.97-1.01 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.7, 157.7, 139.4, 135.4, 129.4, 122.3, 112.1, 86.7, 68.9, 53.4, 31.2, 19.4, 13.8. Anal. Calcd for $C_{15}H_{19}IO_5$: C, 44.35; H, 4.71; Found: C, 44.87; H, 4.24.

5. General procedure for the cyclopropanation of olefins with iodonium ylide 5a.

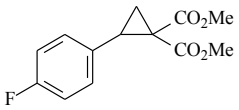
To a solution of the $Rh_2(OAc)_4$ (5 mol %) in 3 mL of CH_2Cl_2 were added alkene (5.0 mmol) and **5a** (1 mmol). The reaction was stirred at room temperature. The solution was then concentrated and purified by chromatography on silica gel to give the corresponding cyclopropanedicarboxylates **6**.

Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate 6a.[3]



Reaction of styrene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.21 g (90%) of product, isolated as colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ 7.28-7.17 (m, 5H), 3.77 (s, 3H), 3.34 (s, 3H), 3.23 (t, *J* = 8.0 Hz, 1H), 2.19 (dd, *J* = 8.0, 5.0 Hz, 1H), 1.73 (dd, *J* = 9.0, 5.0 Hz, 1H)

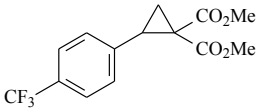
Dimethyl 2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate 6b.[3]



Reaction of 4-fluorostyrene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.24 g (95%) of product, isolated as colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ 7.16-7.19 (m, 2H), 6.95-6.99 (m, 2H), 3.80 (s, 3H), 3.40 (s, 3H), 3.20 (t, *J* = 8.5 Hz, 1H), 2.16 (dd, *J* = 8.0,

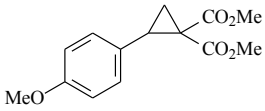
5.0 Hz, 1H), 1.74 (dd, *J* = 9.0, 5.0 Hz, 1H).

Dimethyl 2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate 6c.[5]



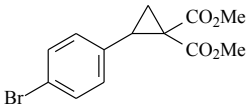
Reaction of 4-(trifluoromethyl)styrene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.29 g (96%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.80 (s, 3H), 3.39 (s, 3H), 3.26 (t, *J* = 8.0 Hz, 1H), 2.21 (dd, *J* = 8.0, 5.0 Hz, 1H), 1.79 (dd, *J* = 9.0, 5.0 Hz, 1H).

Dimethyl 2-(4-methoxylphenyl)cyclopropane-1,1-dicarboxylate 6d.[3]



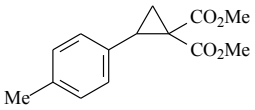
Reaction of 4-vinylanisole (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.21 g (81%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 3.77 (s, 3H), 3.76 (s, 3H), 3.38 (s, 3H), 3.18 (t, *J* = 8.5 Hz, 1H), 2.14 (dd, *J* = 8.0, 5.0 Hz, 1H), 1.71 (dd, *J* = 9.0, 5.0 Hz, 1H).

Dimethyl 2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate 6e.[4]



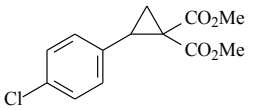
Reaction of 4-bromostyrene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.28 g (91%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 3.41 (s, 3H), 3.17 (t, *J* = 9.0 Hz, 1H), 2.15 (dd, *J* = 8.0, 5.0 Hz, 1H), 1.75 (dd, *J* = 9.0, 5.0 Hz, 1H).

Dimethyl 2-(4-methylphenyl)cyclopropane-1,1-dicarboxylate 6f.[3]



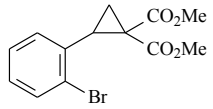
Reaction of 4-methylstyrene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.21 g (83%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (s, 4H), 3.78 (s, 3H), 3.38 (s, 3H), 3.19 (t, *J* = 8.0 Hz, 1H), 2.30 (s, 3H), 2.17 (dd, *J* = 8.0, 5.0 Hz, 1 H), 1.72 (dd, *J* = 9.0, 5.0 Hz, 1H).

Dimethyl 2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate 6g.[5]



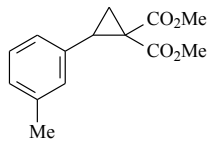
Reaction of 4-chlorostyrene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.25 g (93%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 3.40 (s, 3H), 3.18 (t, *J* = 8.0 Hz, 1H), 2.14 (dd, *J* = 8.0, 5.0 Hz, 1H), 1.74 (dd, *J* = 9.0, 5.0 Hz, 1H).

Dimethyl 2-(2-bromophenyl)cyclopropane-1,1-dicarboxylate 6h.[5]



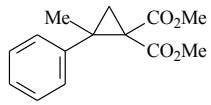
Reaction of 2-bromostyrene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.22 g (71%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.21-7.28 (m, 1H), 7.02-7.13 (m, 2H), 3.81 (s, 3H), 3.36 (s, 3H), 3.32-3.34 (m, 1H), 2.25 (dd, *J* = 8.0, 5.0 Hz, 1H), 1.79 (dd, *J* = 9.0, 5.0 Hz, 1H).

Dimethyl 2-(3-methylphenyl)cyclopropane -1,1-dicarboxylate 6i.[6]



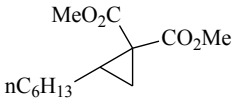
Reaction of 3-methylstyrene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.19 g (76%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (t, *J* = 7.5 Hz, 1H), 7.04 (s, 1H), 7.02 (s, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 3.78 (s, 3H), 3.38 (s, 3H), 3.18 (t, *J* = 8.0 Hz, 1H), 2.30 (s, 3H), 2.17 (dd, *J* = 8.0, 5.0 Hz, 1H), 1.72 (dd, *J* = 9.0, 5.0 Hz, 1H).

Dimethyl 2-methyl-2-phenylcyclopropane-1,1-dicarboxylate 6j.[7]



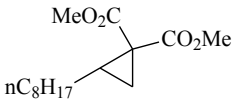
Reaction of α-methylstyrene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.18 g (73%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, *J* = 4.5 Hz, 4H), 7.22-7.23 (m, 1H), 3.83 (s, 3H), 3.33 (s, 3H), 2.22 (d, *J* = 5.5 Hz, 1H), 1.70 (d, *J* = 5.5Hz, 1H), 1.52 (s, 3H).

Dimethyl 2-hexylcyclopropane-1,1-dicarboxylate 6k.[5]



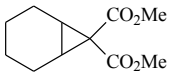
Reaction of 1-octene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.19 g (81%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.76 (s, 3H), 3.72 (s, 3H), 1.82-1.93 (m, 1H), 1.10-1.49 (m, 12H), 0.84 (m, 3H).

Dimethyl 2-octylcyclopropane-1,1-dicarboxylate 6l.[9]



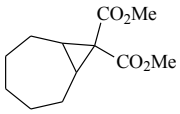
Reaction of 1-decene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.21 g (78%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.76 (s, 3H), 3.72 (s, 3H), 1.88-1.96 (m, 1H), 1.12-1.51 (m, 16H), 0.88 (t, *J* = 7.0 Hz, 3H).

7,7-Dimethoxycarbonylbicyclo[4.1.0]heptane 6m.[8]



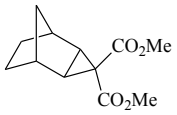
Reaction of cyclohexene (1.0 mmol) with $Cu(acac)_2$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.13 g (61%) of product, isolated as white solid: colorless needles (recrystallized from dichloromethane-hexane); mp 90-92 °C (lit.[7], mp 91-93 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.78 (s, 3H), 3.68 (s, 3H), 1.81-1.99 (m, 6H), 1.24-1.29 (m, 2H), 0.99-1.01 (m, 2H).

8,8-Dimethoxycarbonylbicyclo[5.1.0]octane 6n.[5]



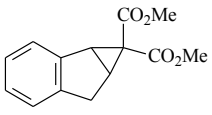
Reaction of cycloheptene (1.0 mmol) with $Cu(acac)_2$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.12 g (55%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.76 (s, 3H), 3.69 (s, 3H), 2.09-2.17 (m, 2H), 1.75-1.91 (m, 5H), 1.26-1.42 (m, 2H), 1.07-1.22 (m, 3H)

Dimethoxycarbonyltricyclo[3.2.1.0]octane 6o.



Reaction of norbornene (1.0 mmol) with $Cu(acac)_2$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 76 mg (34%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.83 (s, 3H), 3.59 (s, 3H), 2.91 (d, J = 7.5 Hz, 2H), 1.52-1.42 (m, 4H), 1.28-1.20 (m, 2H), 0.75 (d, J = 8.0 Hz, 2H).

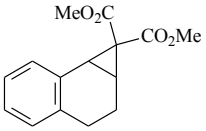
Dimethyl cyclopropane-indene-1,1-dicarboxylate 6p.[5]



Reaction of indene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general

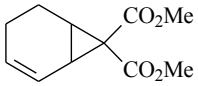
procedure, purified by chromatography on silica gel to afforded 0.19 g (83%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34-7.42 (m, 1H), 7.08-7.22 (m, 3H), 3.74 (s, 3H), 3.25-3.24 (m, 3H), 3.23 (s, 3H), 2.66-2.69 (m, 1H).

Dimethyl 2,3-dihydro-1*H*-cyclopropane-naphthalene-1,1-dicarboxylate 6q.[5]



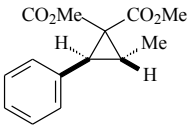
Reaction of 1, 2-dihydronaphthalene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.21 g (80%) of product, isolated as white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.35 (m, 1H), 7.08-7.19 (m, 2H), 6.96-7.02 (m, 1H), 3.75 (s, 3H), 3.53 (s, 3H), 2.82 (m, 2H), 2.58-2.76 (m, 1H), 2.18-2.46 (m, 3H).

Dimethyl bicyclo[4.1.0]hept-2-ene-7,7-dicarboxylate 6r.[10]



Reaction of 1,3-cyclohexadiene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.14 g (66%) of product, isolated as white solid, mp 37-39 °C (lit.[10], mp 38-39 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.88-5.92 (m, 1H), 5.68-5.72 (m, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 2.24-1.89 (m, 5H), 1.67-1.71 (m, 1H).

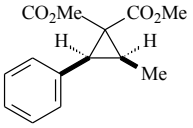
***Trans*-dimethyl 2-methyl-3-phenylcyclopropane-1,1-dicarboxylate 6s.[5]**



Reaction of *trans*-β-methylstyrene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 52 mg (21%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ7.29-7.16 (m, 5H), 3.78 (s, 3H), 3.36 (s, 3H), 3.06 (d, J = 8.0 Hz, 1H), 2.57 (dq, J = 8.0, 6.5 Hz, 1H), 1.27 (d, J =

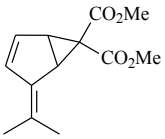
6.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 168.5, 167.8, 135.2, 128.9, 128.0, 127.6, 52.6, 52.0, 43.2, 37.9, 25. 2, 12.7. The relative stereochemistry was established by NOESY.

Cis-dimethyl 2-methyl-3-phenylcyclopropane-1,1-dicarboxylate 6t.[5]



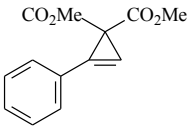
Reaction of *cis*-β-methylstyrene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.18 g (72%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.04 (m, 5H), 3.70 (s, 3H), 3.54 (s, 3H), 3.02 (d, J = 10.5 Hz, 1H), 1.94-2.06 (m, 1H), 1.24 (d, J = 8.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 177.6, 167.9, 133.5, 130.2, 128.1, 126.5, 52.5, 52.0, 27.4, 34.9, 26.8, 10.4. The relative stereochemistry was established by NOESY.

Dimethyl bicycle[3.1.0]hex-2-ene-6,6-dicarboxylate 6u.[11]



Reaction of 6,6-dimethylfulvene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.13 g (53%) of product, isolated as yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.23 (d, J = 5.5 Hz, 1H), 5.92-5.97 (m, 1H), 3.72 (s, 3H), 3.59 (s, 3H), 2.98-3.14 (m, 2H), 2.19 (s, 6H).

Dimethyl 2-phenylcycloprop-2-ene-1,1-dicarboxylate 7.[12]

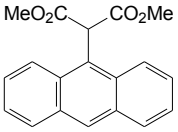


Reaction of phenylacetylene (1.0 mmol) with $Rh_2(OAc)_4$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.16 g (68%) of product **7**, isolated as pale yellow solid, mp 69-71 °C (lit.[12], mp 67-70 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62-7.64 (m, 2H), 7.43-7.44 (m, 3H), 6.89 (s, 1H), 3.73 (s, 6H).

6. General procedure for C-H insertion reactions using 5a.

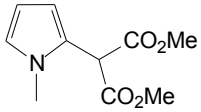
To a solution of the substrate (1 mmol) in 5 mL of CH_2Cl_2 were added **5a** (1.5 mmol) and $BF_3 \cdot Et_2O$ (3.0 mmol) at 0-5°C. Alternatively, the reaction can be conducted in the absence of $BF_3 \cdot Et_2O$ by refluxing a mixture of ylide **5a** (1.5 equiv), substrate (1.0 equiv), and CH_2Cl_2 (3 mL). The solution was then concentrated and purified by chromatography on silica gel to give the corresponding C-H insertion product.

Dimethyl 2-(anthracen-9-yl)malonate (Table 2, entries 1-4).[13]



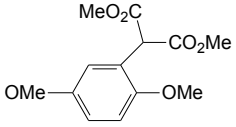
Reaction of anthracene (1.0 mmol) with $BF_3 \cdot Et_2O$ (3.0 mmol) according to the general procedure, purified by chromatography on silica gel to afforded 0.16 g (51%) of product, isolated as white solid, mp 129-131 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48 (s, 1H), 8.24 (d, J = 9.0 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H), 7.53-7.56 (m, 2H), 7.44-7.48 (m, 2H), 6.10 (s, 1H), 3.71 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.3, 131.7, 130.7, 129.4, 129.2, 126.7, 124.9, 124.8, 124.2, 52.8, 51.6.

2-bis(methoxycarbonyl)methyl pyrrole (Table 2, entries 5-8).[14]



Reaction of *N*-methyl pyrrole (1.0 mmol) with $BF_3 \cdot Et_2O$ (3.0 mmol) according to the general procedure, purified by chromatography on silica gel to afforded 0.1 g (48%) of product, isolated as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.65 (t, J = 2.5 Hz, 1H), 6.23-6.24 (m, 1H), 6.13 (t, J = 4.0 Hz, 1H), 4.79 (s, 1H), 3.81 (s, 6H), 3.62 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.9, 123.8, 123.0, 109.9, 107.3, 52.9, 50.3, 34.3.

Dimethyl 2-(2,5-dimethoxyphenyl)malonate (Table 2, entries 9-12).[15]

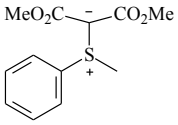


Reaction of *p*-dimethoxybenzene (1.0 mmol) with $BF_3 \cdot Et_2O$ (3.0 mmol) according to the general procedure, purified by chromatography on silica gel to afforded 0.17 g (62%) of product, isolated as off-orange solid, mp 89-91 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.95 (t, J = 2.0 Hz, 1H), 6.85-6.86 (m, 2H), 5.16 (s, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.78 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.9, 153.6, 151.2, 122.5, 115.7, 114.1, 111.9, 56.4, 55.7, 52.8, 50.8.

7. General procedure for the transylidation with various nucleophiles using 5a

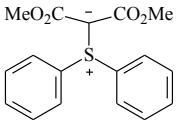
To a solution of the $Rh_2(OAc)_4$ (1 mol %) in 5 mL of CH_2Cl_2 were added the substrate (1.0 mmol) and **5a** (1.2 mmol). The reaction was stirred at room temperature. The solution was then concentrated and purified by chromatography on silica gel to give the corresponding C-S, C-N, or C-P ylides **8**.

Thiophenium bismethoxycarbonylmethylide 8a.[17,18]



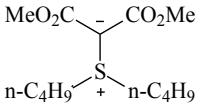
Reaction of thioanisole (1.0 mmol) with $Rh_2(OAc)_4$ (1 mol %) according to the general procedure, purified by chromatography on silica gel to afforded 0.23 g (91%) of product, isolated as reddish solid, mp 123-125 °C (lit.[17], mp 126-127 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61-7.63 (m, 1H), 7.48-7.49 (m, 2H), 7.28-7.30 (m, 2H), 3.71 (s, 6H), 2.49 (s, 3H).

Dimethyl-2-(diphenylsulfuranylidene)malonate 8b.[22]



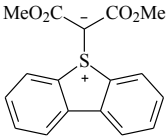
Reaction of diphenyl sulfoxide (1.0 mmol) with $Rh_2(OAc)_4$ (1 mol %) according to the general procedure, purified by chromatography on silica gel to afforded 0.29 g (93%) of product, isolated as colorless solid, mp 128-130 °C (lit.[22], mp 126-127 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63-7.65 (m, 4H), 7.49-7.53 (m, 6H), 3.69 (s, 6H).

Dimethyl-2-(dibutylsulfuranylidene)malonate 8c.[19]



Reaction of dibutyl sulfide (1.0 mmol) with $Rh_2(OAc)_4$ (1 mol %) according to the general procedure, purified by chromatography on silica gel to afforded 0.22 g (80%) of product, isolated as colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.67 (s, 6H), 2.76-2.82 (m, 4H), 1.56-1.62 (m, 4H), 1.35-1.45 (m, 3H), 0.90 (t, J = 7.5 Hz, 6H).

Dibenzothiophenium bismethoxycarbonylmethylide 8d.[21]



Reaction of dibenzothiophene (1.0 mmol) with $Rh_2(OAc)_4$ (1 mol %) according to the general procedure, purified by chromatography on silica gel to afforded 0.26 g (82%) of product, isolated as white solid, mp 159-160 °C (lit.[21], mp 160-161 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (d, J = 7.5 Hz, 2H), 7.77 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 8.0 Hz, 2H), 7.51 (t, J = 8.0 Hz, 2H), 3.85 (s, 3H), 3.29 (s, 3H).

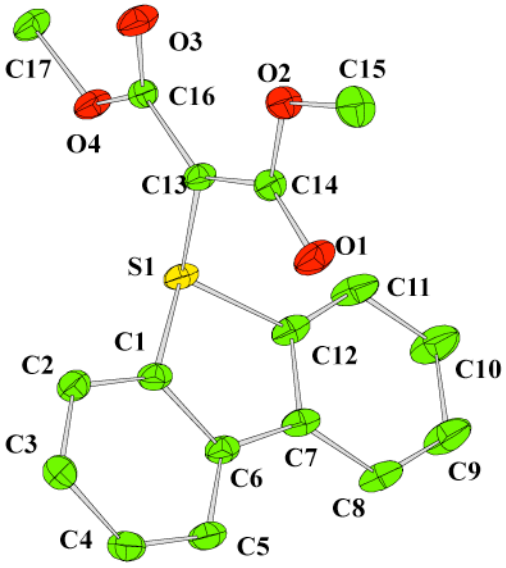
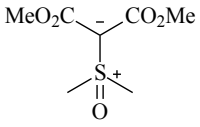


Figure 2. X-ray crystal structure of product **8d**.

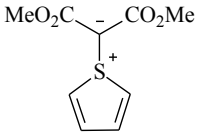
Single crystals of dibenzothiophenium bismethoxycarbonylmethylide **8d** suitable for X-ray crystallographic analysis were obtained by slow evaporation of CH_2Cl_2-hexane solution of the compound. X-ray diffraction data were collected on Rigacu RAPID II diffractometrer using graphite-monochromated MoKα 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 direct method (SIR-2004) using CrystalStructure 4.0 program and refined by full-matrix least-squares refinement on F^2 using Crystals for Windows program. Disordered solvent molecule was eliminated from the unit cell using SQUIZE procedure implemented into Crystals for Windows program. Crystal data for $C_{17}H_{14}S_1O_4$: M = 314.36; monoclinic, space group P21/c; a = 5.5663(3), b = 17.8925(9); c = 16.0834(11) Å; b = 90.338(6); V = 1601.80(16) $Å^3$; Z= 4; μ = 0.216 mm^{-1}, 13884 reflections measured, 3663 unique; final R_1 = 0.0447, R_w = 0.1247. A cif file containing crystallographic data for dibenzothiophenium bismethoxycarbonylmethylide is provided as Supporting Information with this article.

Dimethyl sulfoxonium biscarbomethoxymethylide 8e.[23]



Reaction of dimethyl sulfoxide (1.0 mmol) with $Rh_2(OAc)_4$ (1 mol %) according to the general procedure, purified by chromatography on silica gel to afforded 0.15 g (74%) of product, isolated as yellowish solid, mp 159-160 °C (lit.[23], mp 157-158 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.73 (s, 6H), 3.67 (s, 6H).

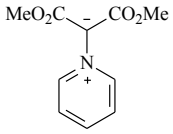
Thiophenium bis(methoxycarbonyl)methylide 8f.[20]



Reaction of thiophene (1.0 mmol) with $Rh_2(OAc)_4$ (1 mol %) according to the general procedure, purified by chromatography on silica gel to afforded 0.17 g (83%) of product, isolated as off-yellow solid, mp 148-150 °C (lit.[20], mp 145-146 °C); ^{1}H NMR (500 MHz,

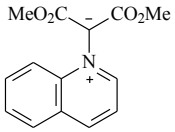
$CDCl_3$): δ 7.19-7.20 (m, 2H), 6.96-6.98 (m, 2H), 3.69 (s, 6H).

2-Pyridinium bis(methoxycarbonyl)methylide 8g.[24]



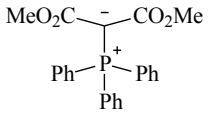
Reaction of pyridine (1.0 mmol) with $Rh_2(OAc)_4$ (1 mol %) according to the general procedure, purified by chromatography on silica gel to afforded 0.18 g (85%) of product, isolated as yellowish solid, mp 184-185 °C (lit.[24], mp 185-186 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.59 (d, *J* = 7.0 Hz, 2H), 8.19 (t, *J* = 7.5 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 2H), 3.71 (s, 6H).

Quinolinium bis(methoxycarbonyl)methylide 8h.[25]



Reaction of quinoline (1.0 mmol) with $Cu(acac)_2$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.24 g (91%) of product, isolated as red solid, mp 199-201 °C (lit.[25], mp 197 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.92 (d, *J* = 2.0 Hz, 1H), 8.14 (t, *J* = 9.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.0 Hz, 1H), 7.52 (t, *J* = 7.0 Hz, 1H), 7.36-7.38 (m, 1H), 3.79 (s, 6H).

Triphenylphosphonium bis(methoxycarbonyl)methylide 8i.[25]



Reaction of triphenylphosphine (1.0 mmol) with $Cu(acac)_2$ (5 mol%) according to the general procedure, purified by chromatography on silica gel to afforded 0.26 g (67%) of product, isolated as red solid, mp 179-181 °C (lit.[25], mp 183 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69-7.74 (m, 6H), 7.53-7.56 (m, 3H), 7.45-7.49 (m, 6H), 3.34 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.4 (d, *J* (PC) = 13.75 Hz), 133.3 (d, *J* (PC) = 10.00 Hz),

131.9 (d, *J* (PC) = 2.75 Hz), 128.5 (d, *J* (PC) = 12.75 Hz), 126.8, 126.1, 53.7, 52.8, 50.1; ^{31}P NMR (81.0 MHz, $CDCl_3$): δ 26.8.

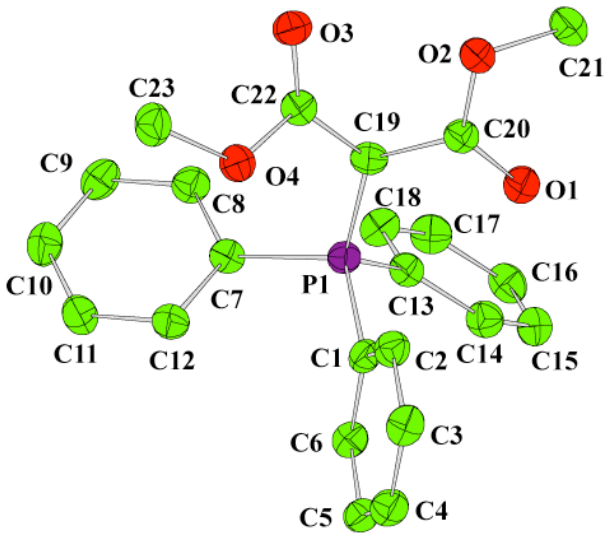


Figure 3. X-ray crystal structure of triphenylphosphonium bis(methoxycarbonyl)methylide **8i**.

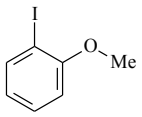
Single crystals of product **8i** suitable for X-ray crystallographic analysis were obtained by slow evaporation of the CH_2Cl_2-hexane solution. X-ray diffraction data were collected on Rigacu RAPID II diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 123 K. Multi-scan absorption correction was applied to the data using CrystalClear 2.0 program (Rigaku Inc. 2010). The structure was solved by direct method (SIR-2004) using CrystalStructure 4.0 program and refined by full-matrix least-squares refinement on F^2 using Crystals for Windows program. Crystal data for $C_{23}H_{21}P_1O_4$: M = 392.39; triclinic, space group P-1; a = 9.3953(5), b = 10.2384(5); c = 10.6318(7) Å; a = 95.355(7), b = 92.172(7), g = 109.933(8); V = 954.58(11) Å^3; Z= 2; μ = 0.171 mm^{-1}, 31331 reflections measured, 4371 unique; final R_1 = 0.0519, R_w = 0.1062. A cif file containing crystallographic data for triphenylphosphonium bis(methoxycarbonyl)methylide is provided as Supporting Information with this article.

References

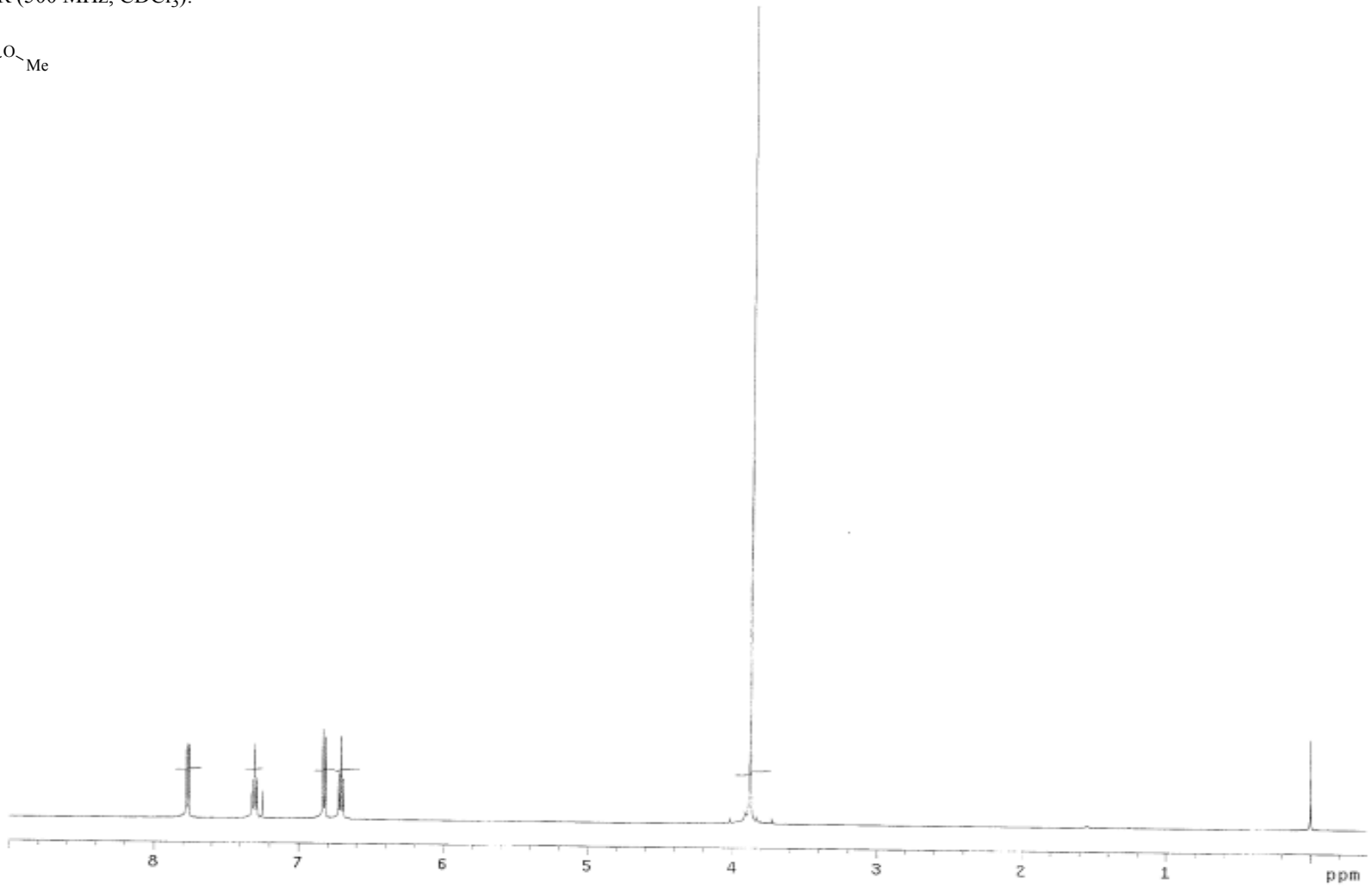
1. Koposov, A. Y.; Karimov, R. R.; Geraskin, I. M.; Nemykin, V. N.; Zhdankin, V. V. *J. Org. Chem.* **2006**, *71*, 8452-8458.
2. Yoshimura, A.; Nemykin, V. N.; Zhdankin, V. V. *Chem. Eur. J.* **2011**, *17*, 10538-10541.
3. Goudreau, S. R.; Marcoux, D.; Charette, A. B. *J. Org. Chem.* **2009**, *74*, 470-473.
4. Ghanem, A.; Lacrampe, F.; Schurig, V. *Helv. Chim. Acta* **2005**, *88*, 216-239.
5. Bobes, F. G.; Fenster, M. D. B.; Kiau, S.; Kolla, L.; Kolotuchin, S.; Soumeillant, M. *Adv. Synth. Catal.* **2008**, *350*, 813-816.
6. Nishimura, T.; Maeda, Y.; Hayashi, T. *Angew. Chem. Int. Ed.* **2010**, *49*, 7324-7327.
7. Smith, A. G.; Slade, M. C.; Johnson, J. S. *Org. Lett.* **2011**, *13*, 1996-1999.
8. Hood, J. N. C.; Lloyd, D.; Macdonald, W. A.; Shepherd, T. M. *Tetrahedron* **1982**, *38*, 3355-3358.
9. Sharpless, K. B.; Gao, Y. *United States Patent* **1994**, 5321143.
10. Backvall, J. E.; Vagberg, J. O.; Zercher, C.; Genet, J. P.; Denis, A. *J. Org. Chem.* **1987**, *52*, 5430-5435.
11. Georgakopoulou, G.; Kalogiros, C.; Hadjiarapoglou, L. P. *Synlett* **2001**, 1843-1846.
12. Müller, P.; Fernandez, D. *Helv. Chim. Acta* **1995**, *78*, 947-958.
13. Telu, S.; Durmus, S.; Koser, G. F. *Tetrahedron Lett.* **2007**, *48*, 1863-1866.
14. Maryanoff, B. E. *J. Org. Chem.* **1982**, *47*, 3000-3002.
15. Ghosh, S.; Pardo, S. N.; Salomon, R. G. *J. Org. Chem.* **1982**, *47*, 4692-4702.
16. Angelini, T.; Fringuelli, F.; Lanari, D.; Pizzo, F.; Vaccaro, L. *Tetrahedron Lett.* **2010**, *51*, 1566-1569.
17. Ando, W.; Yagihara, T.; Tozune, S.; Imai, I.; Suzuki, J.; Toyama, T.; Nakaido, S.; Migita, T. *J. Org. Chem.* **1972**, *37*, 1721-1727.
18. Haruo, M. *Sulfur Lett.* **1986**, *4*, 223-228.
19. Huang, X.; Goddard, R.; Maulide, N. *Angew. Chem. Int. Ed.* **2010**, *49*, 8979-8983.
20. Gillespie, R. J.; Porter, A. E. A. *J. Chem. Soc., Perkin Trans. 1* **1979**. 2624-2628.
21. Stoffregen, S. A.; Heying, M.; Jenks, W. S. *J. Am. Chem. Soc.* **2007**, *129*, 15746-15747.
22. Huang, X.; Goddard, R.; Maulide, N. *Angew. Chem. Int. Ed.* **2010**, *49*, 8979-8983.

23. Ando, W.; Yagihara, T.; Tozune, S.; Imai, I.; Suzuki, J.; Toyama, T.; Nakaido, S.; Migita, T. *J. Org. Chem.* **1972**, *37*, 1721-1727.
24. Shevchenko, V. V.; Zhegalova, N. G.; Borzenko, A. O.; Nikolaev, V. A. *Helv. Chim. Acta* **2008**, *91*, 501-509.
25. Neilands, O.; Kalnina, S. *Zhurnal Organicheskoi Khimii*, **1968**, *4*, 140-147.

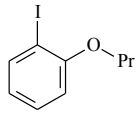
^{1}H NMR (500 MHz, $CDCl_3$):



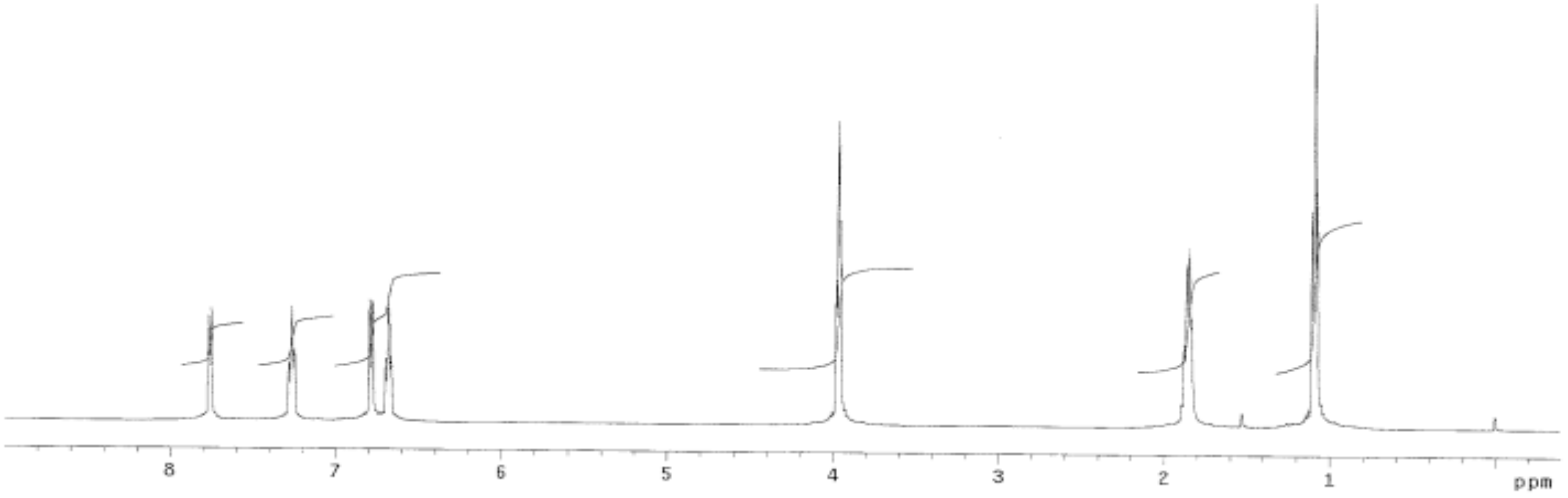
3a



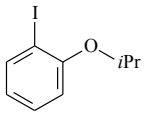
^{1}H NMR (500 MHz, $CDCl_3$):



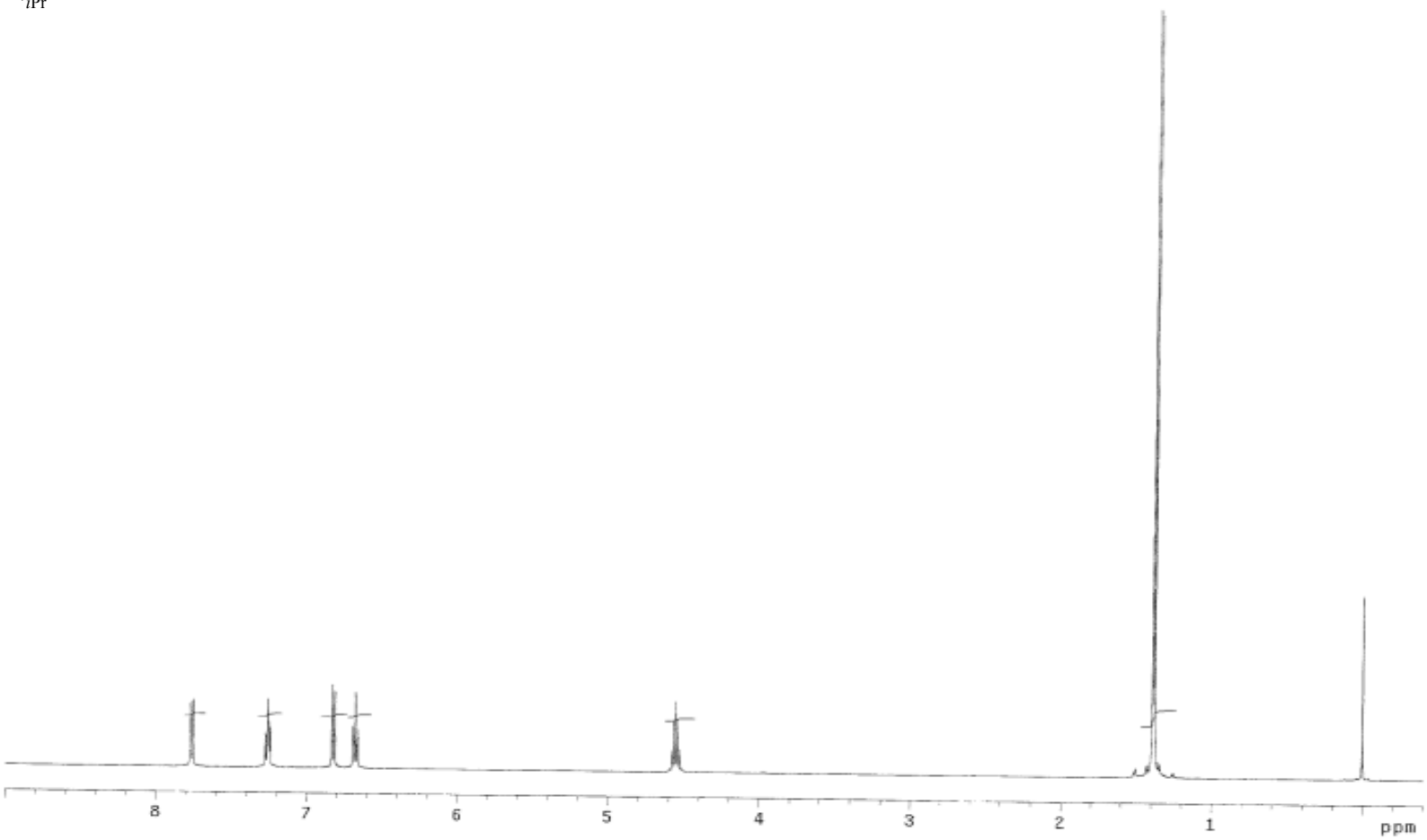
3b



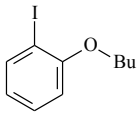
^{1}H NMR (500 MHz, $CDCl_3$):



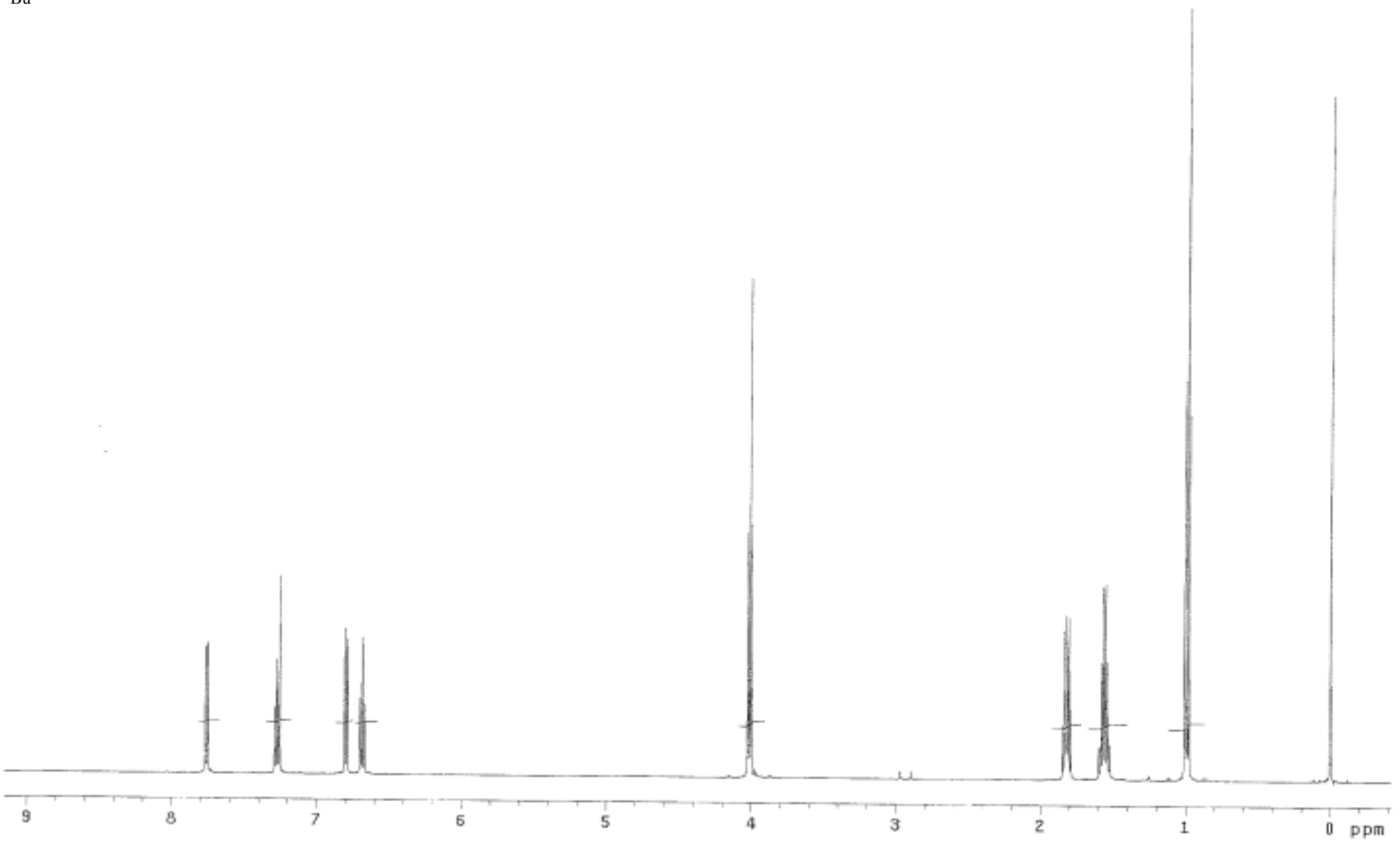
3c



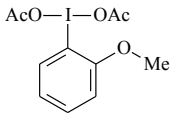
^{1}H NMR (500 MHz, $CDCl_3$):



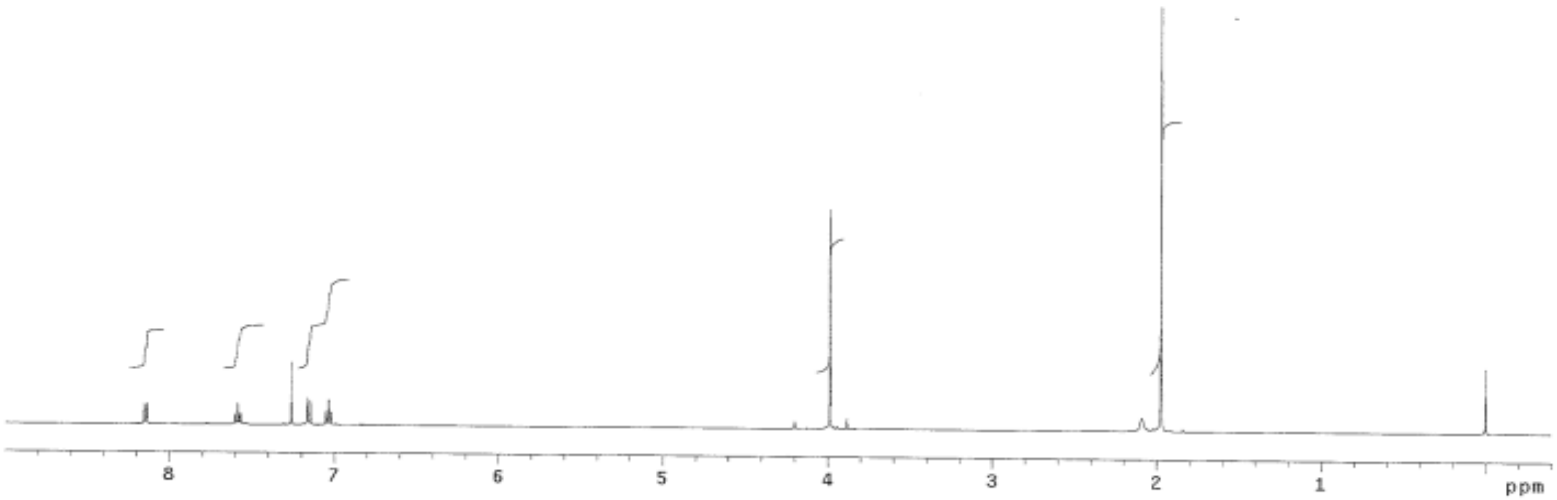
3d



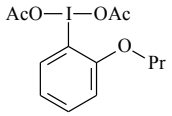
^{1}H NMR (500 MHz, $CDCl_3$):



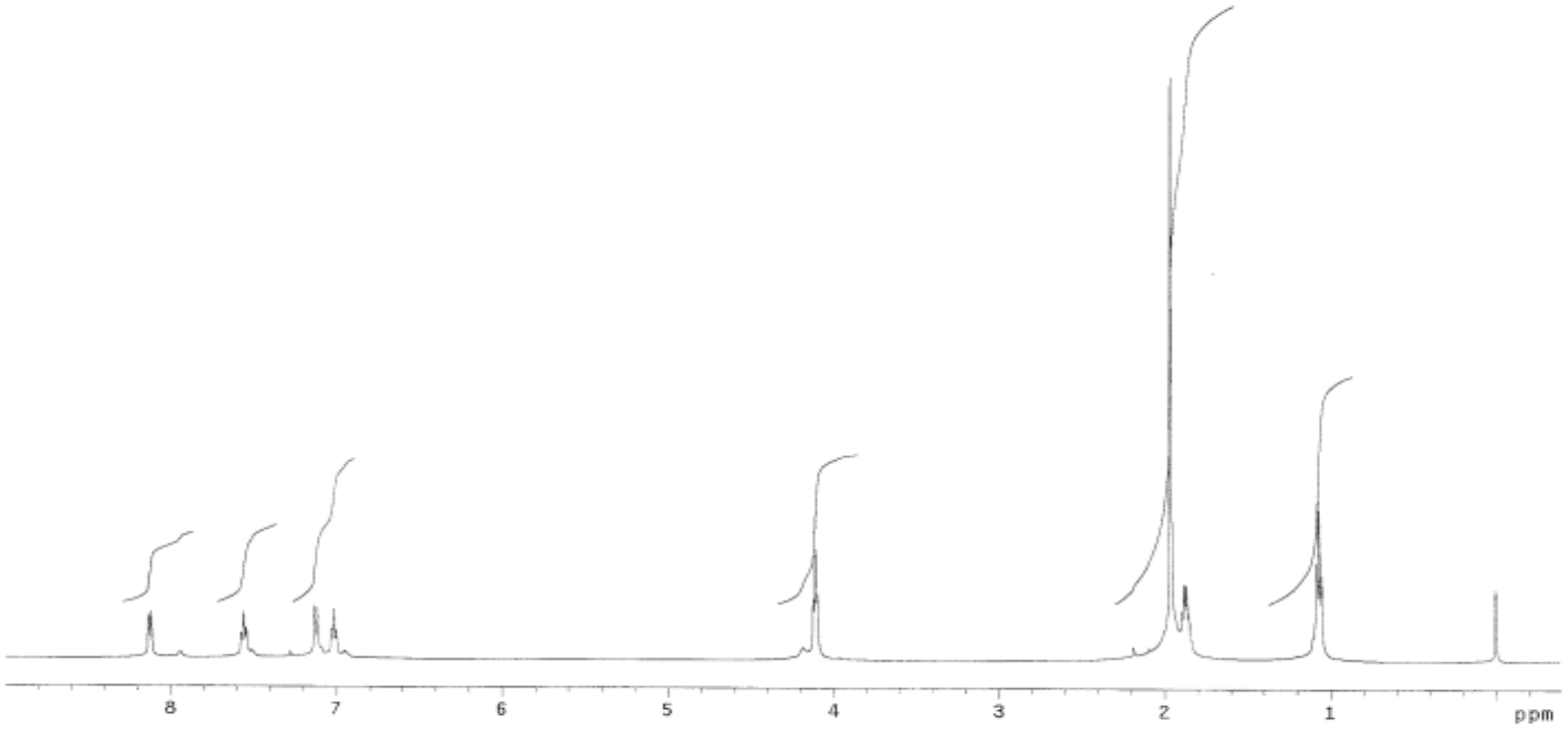
4a



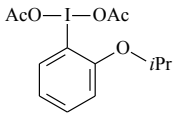
^{1}H NMR (500 MHz, $CDCl_3$):



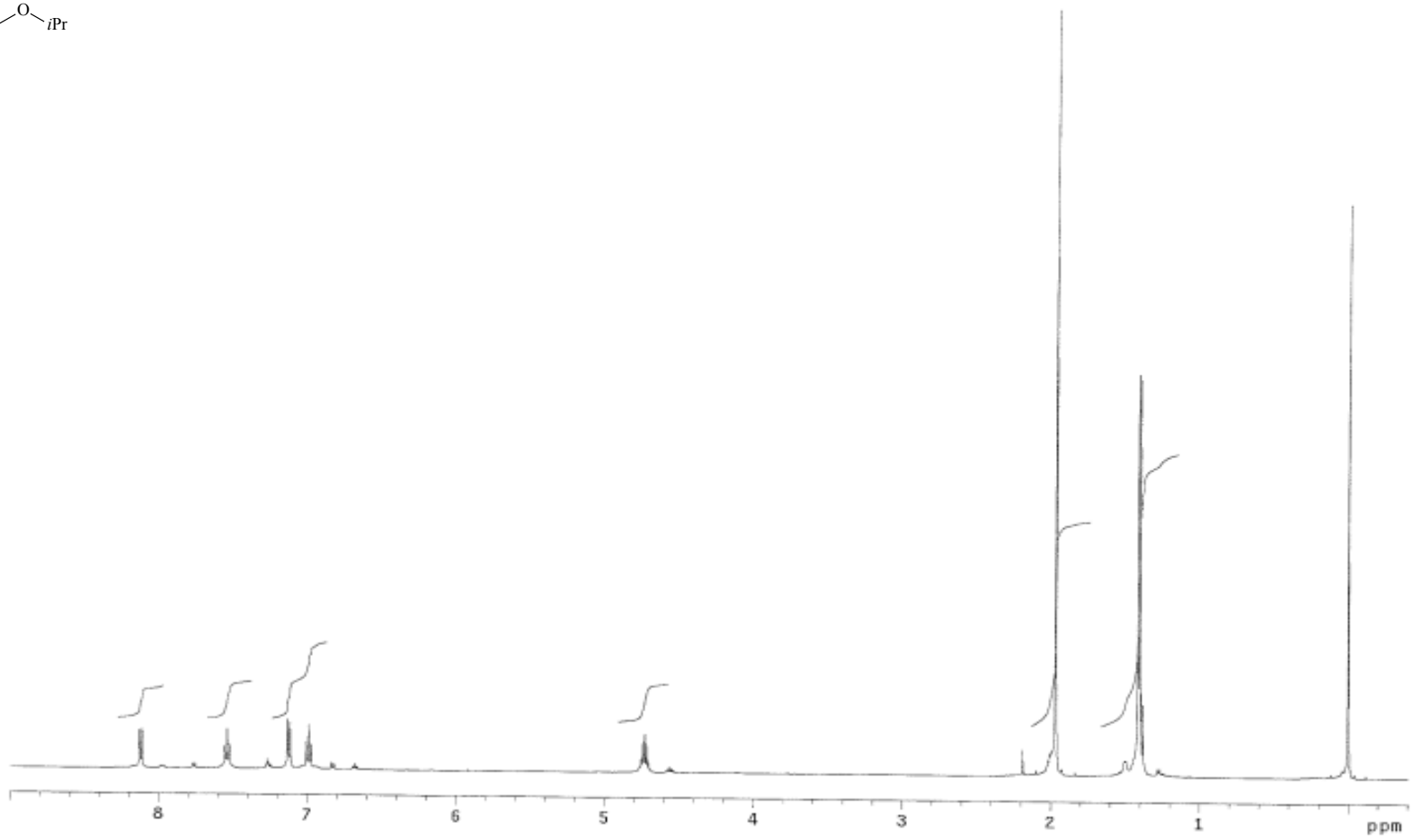
4b



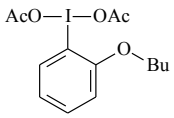
^{1}H NMR (500 MHz, $CDCl_3$):



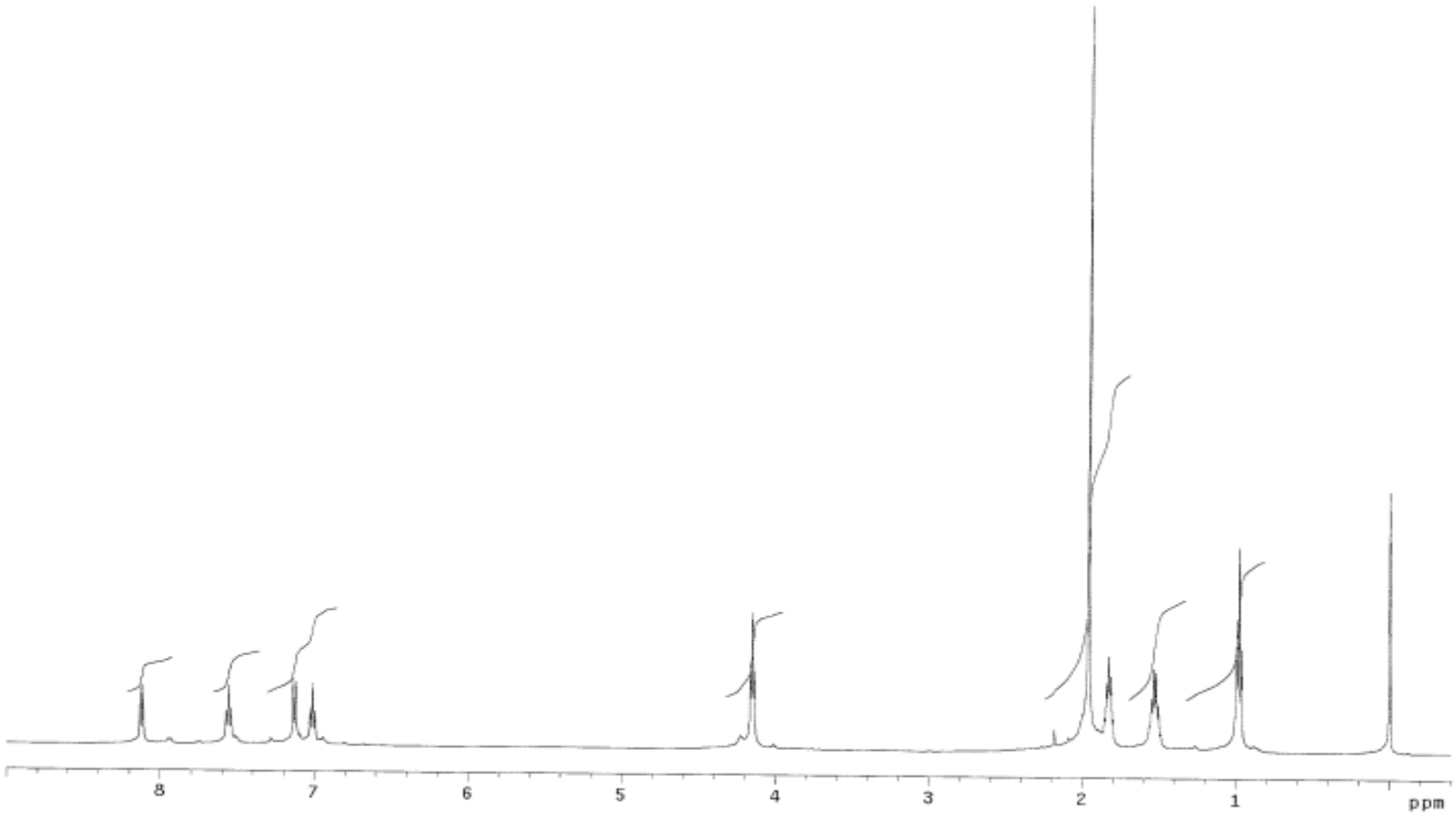
4c



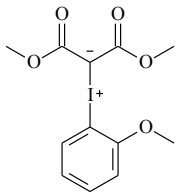
^{1}H NMR (500 MHz, $CDCl_3$):



4d

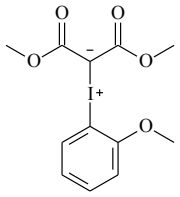


^{1}H NMR (500 MHz, $CDCl_3$):



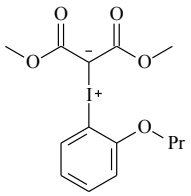
5a

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



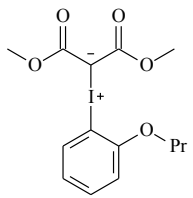
5a

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



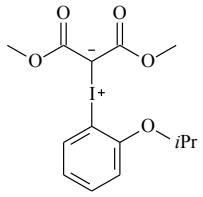
5b

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

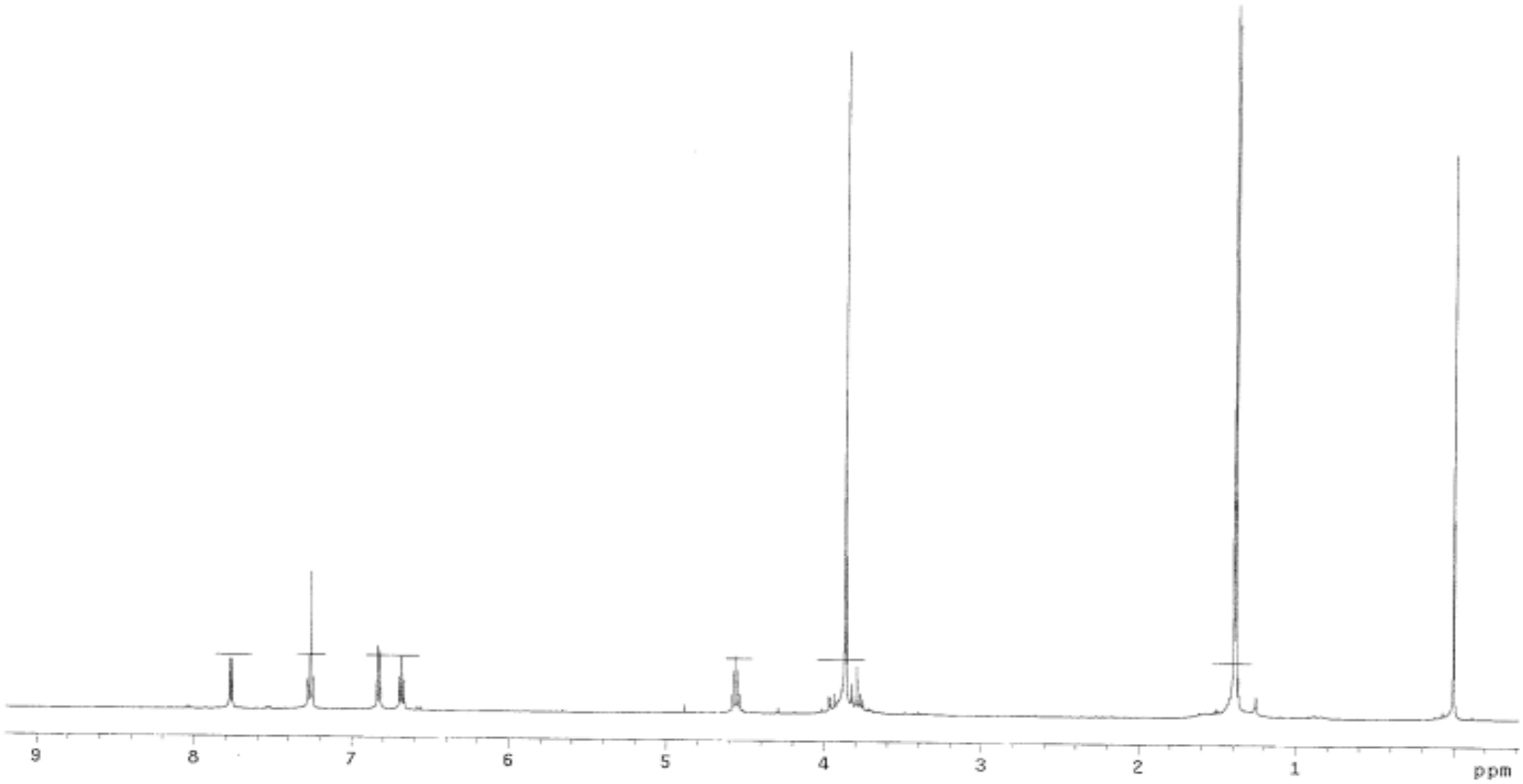


5b

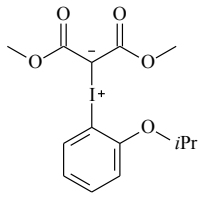
^{1}H NMR (500 MHz, $CDCl_3$):



5c

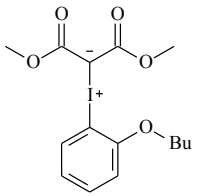


^{13}C NMR (125 MHz, $CDCl_3$):



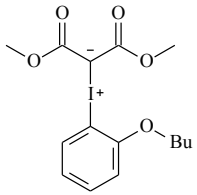
5c

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



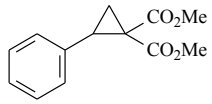
5d

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



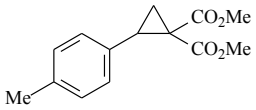
5d

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

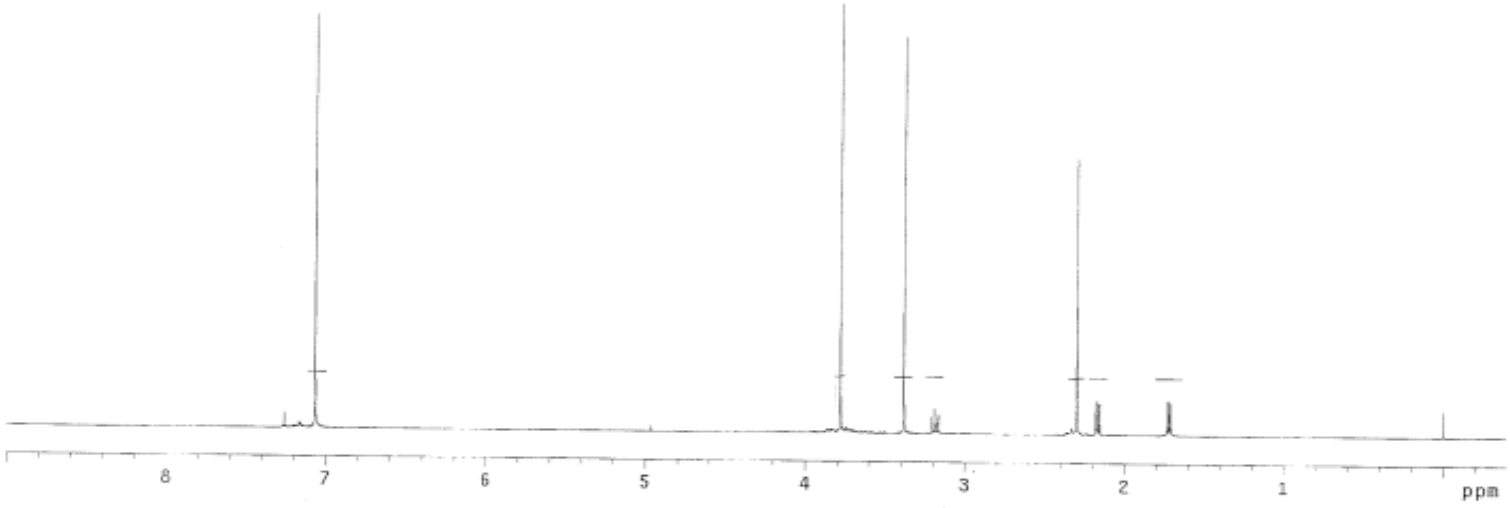


6a

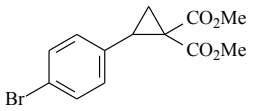
^{1}H NMR (500 MHz, $CDCl_3$):



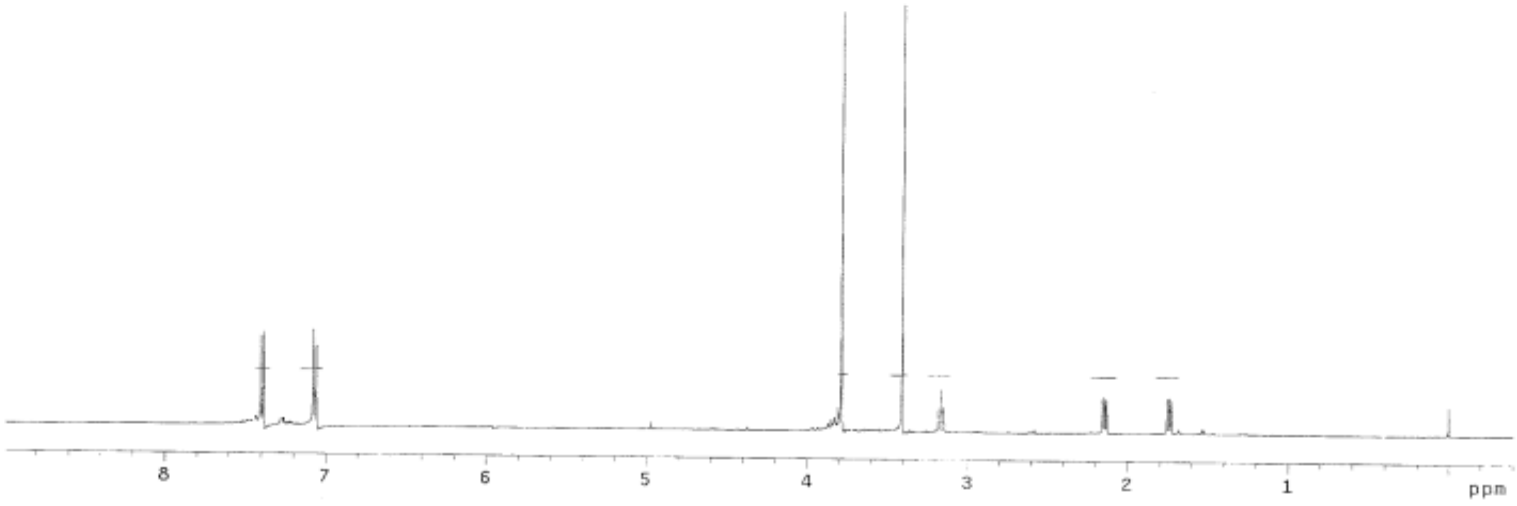
6f



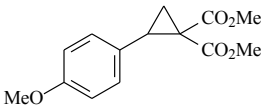
^{1}H NMR (500 MHz, $CDCl_3$):



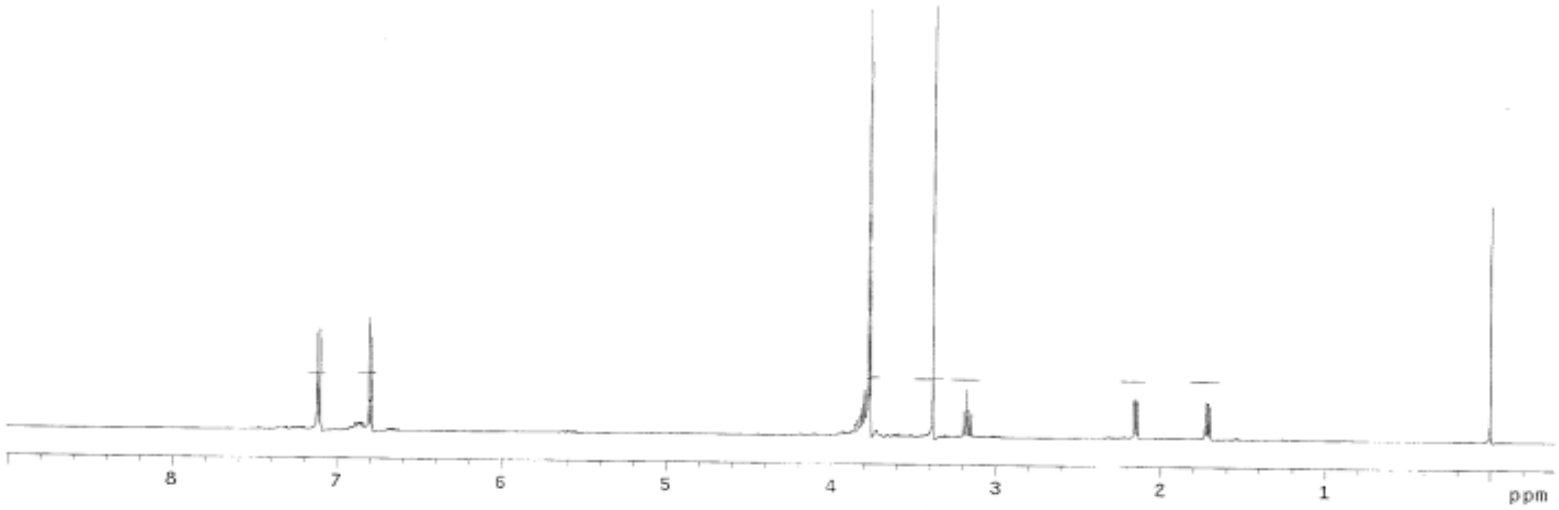
6e



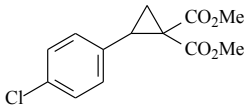
^{1}H NMR (500 MHz, $CDCl_3$):



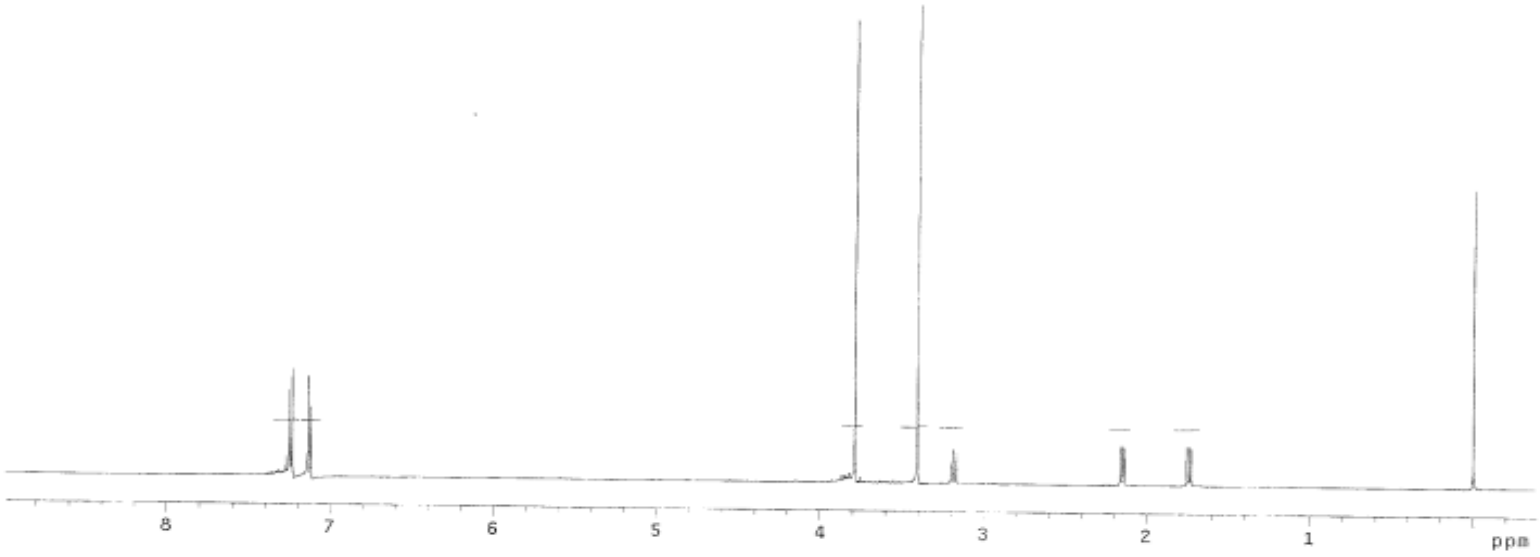
6d



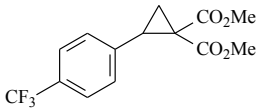
^{1}H NMR (500 MHz, $CDCl_3$):



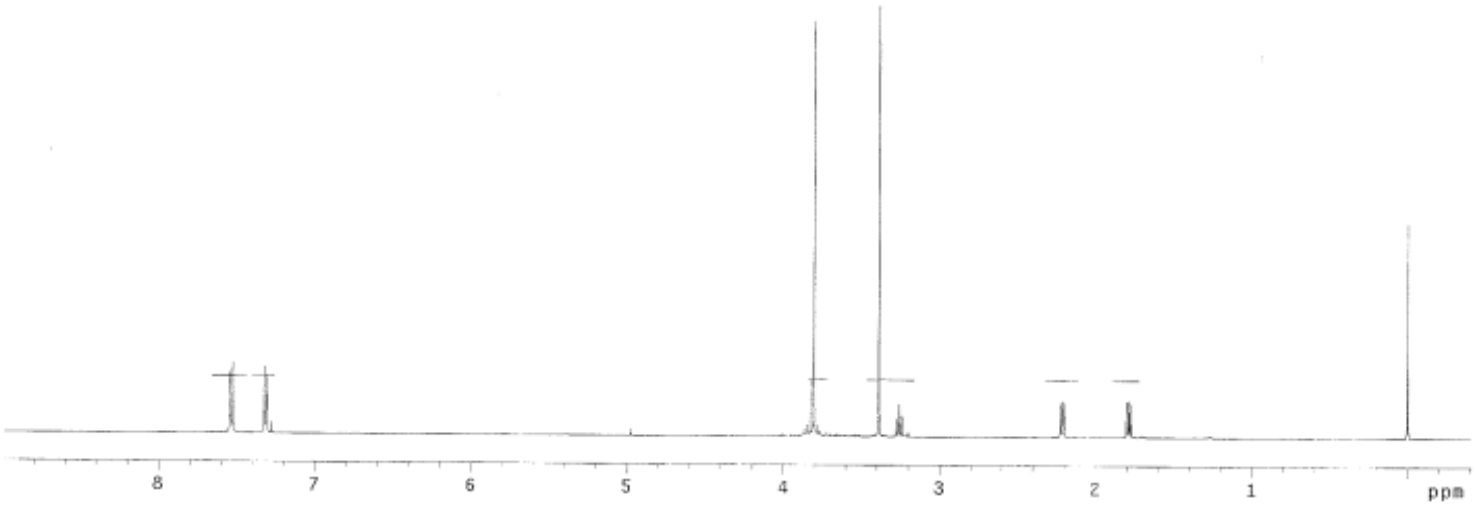
6g



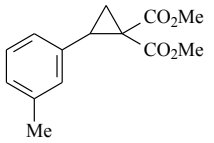
^{1}H NMR (500 MHz, $CDCl_3$):



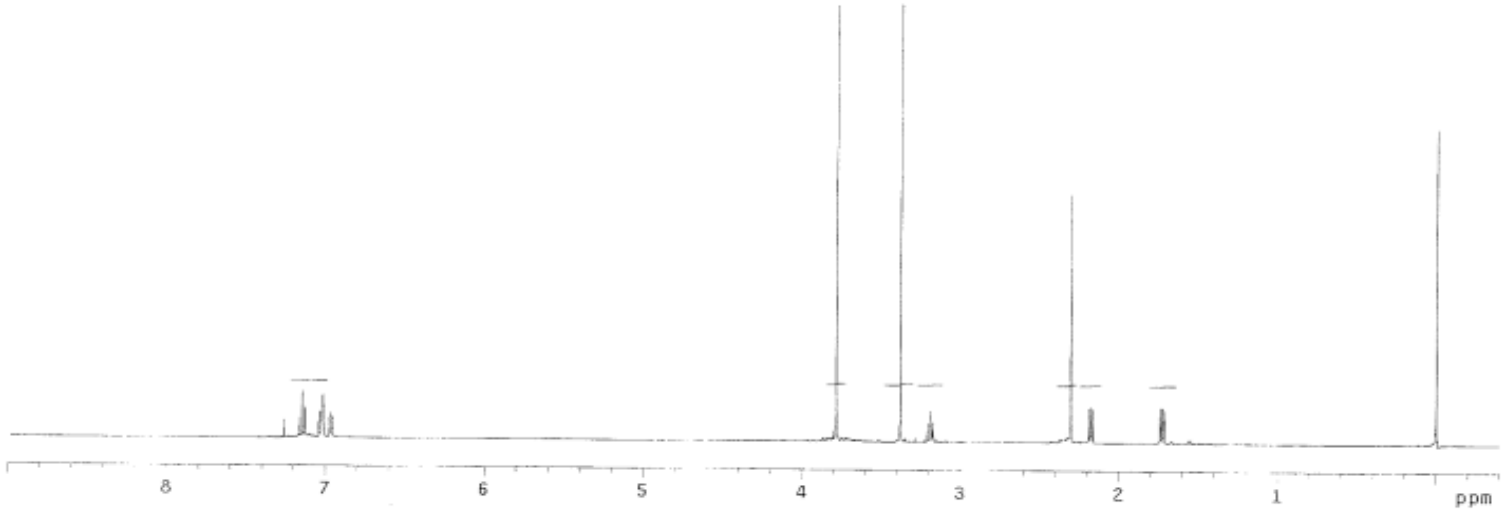
6c



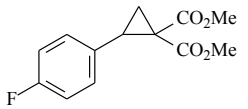
^{1}H NMR (500 MHz, $CDCl_3$):



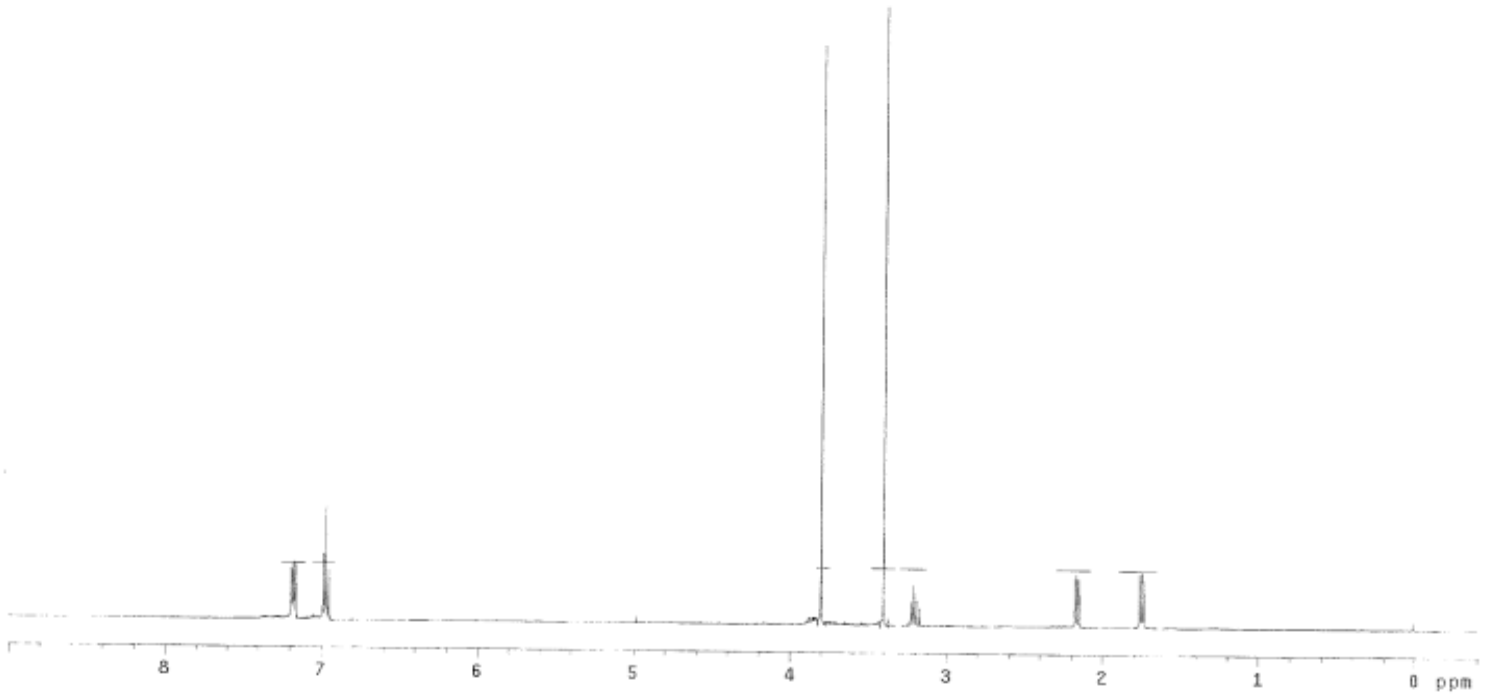
6i



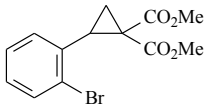
^{1}H NMR (500 MHz, $CDCl_3$):



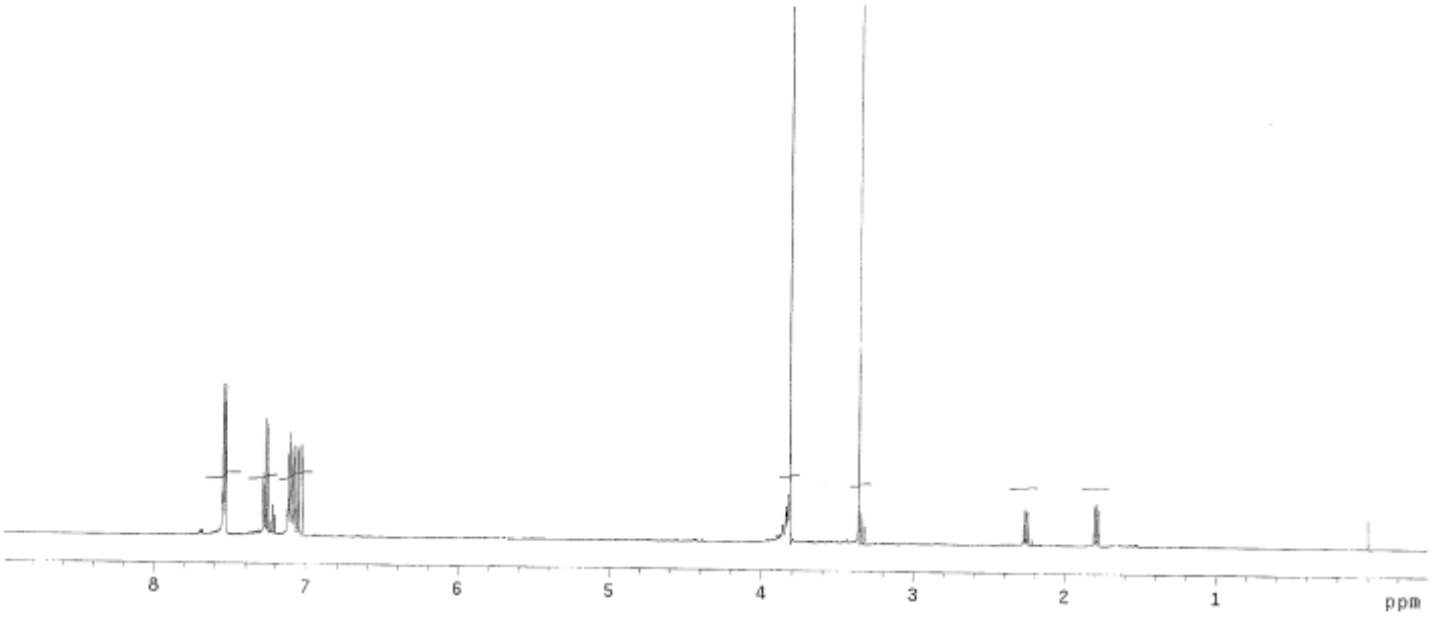
6b



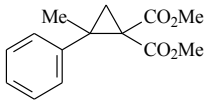
^{1}H NMR (500 MHz, $CDCl_3$):



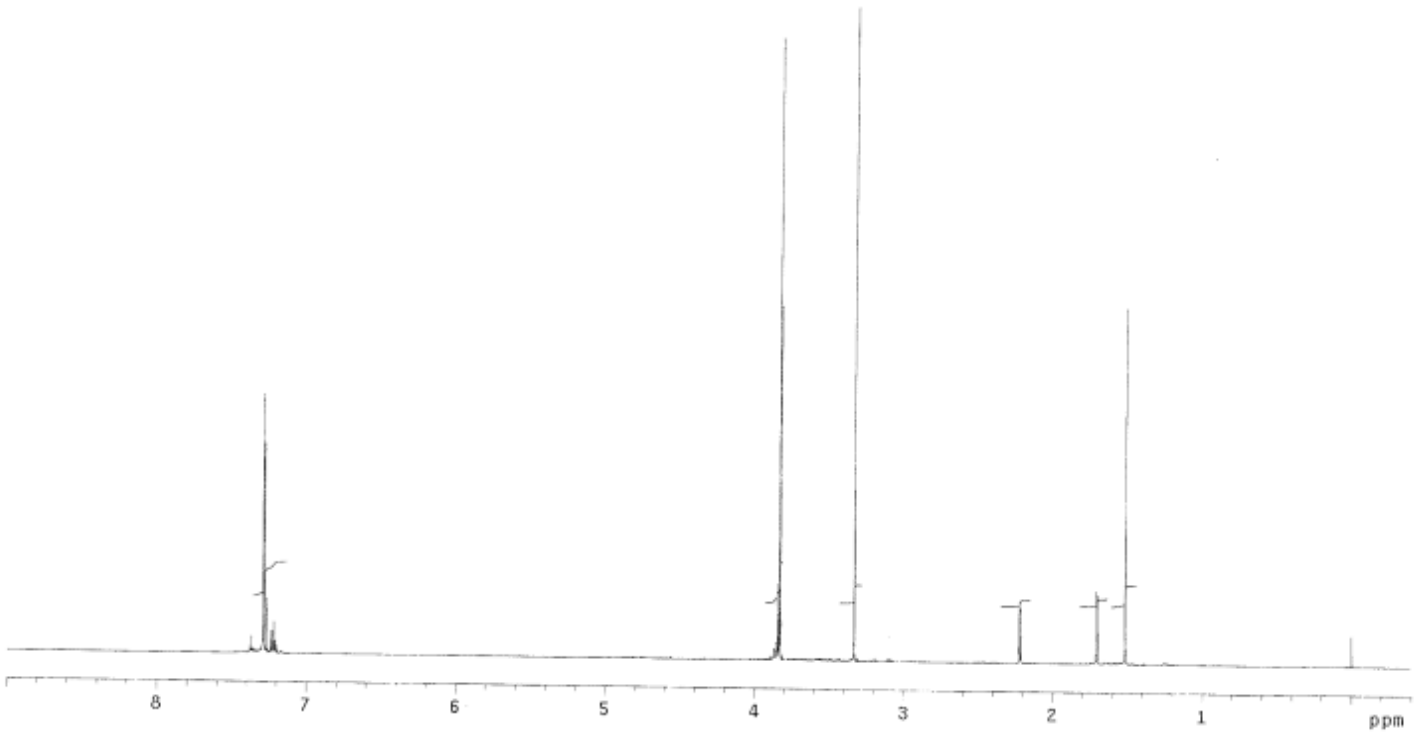
6h



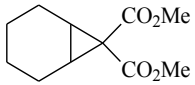
^{1}H NMR (500 MHz, $CDCl_3$):



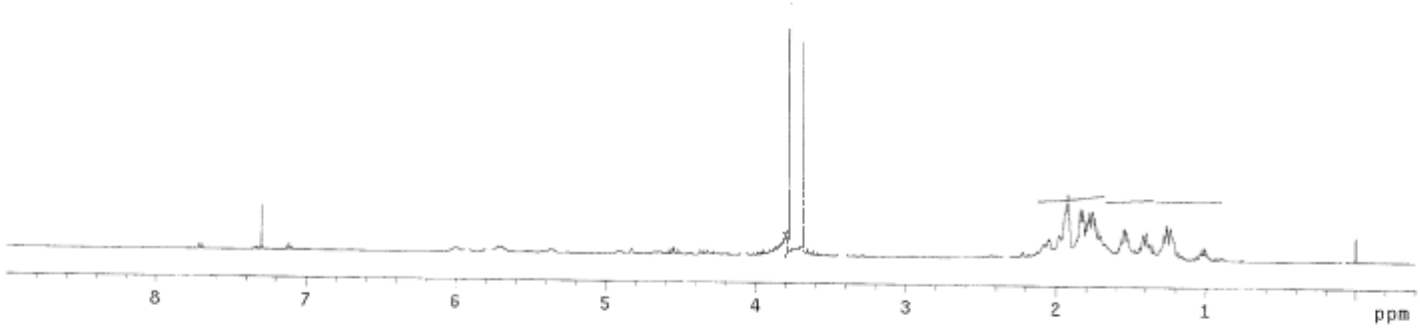
6j



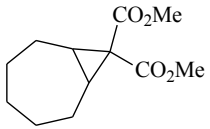
^{1}H NMR (500 MHz, $CDCl_3$):



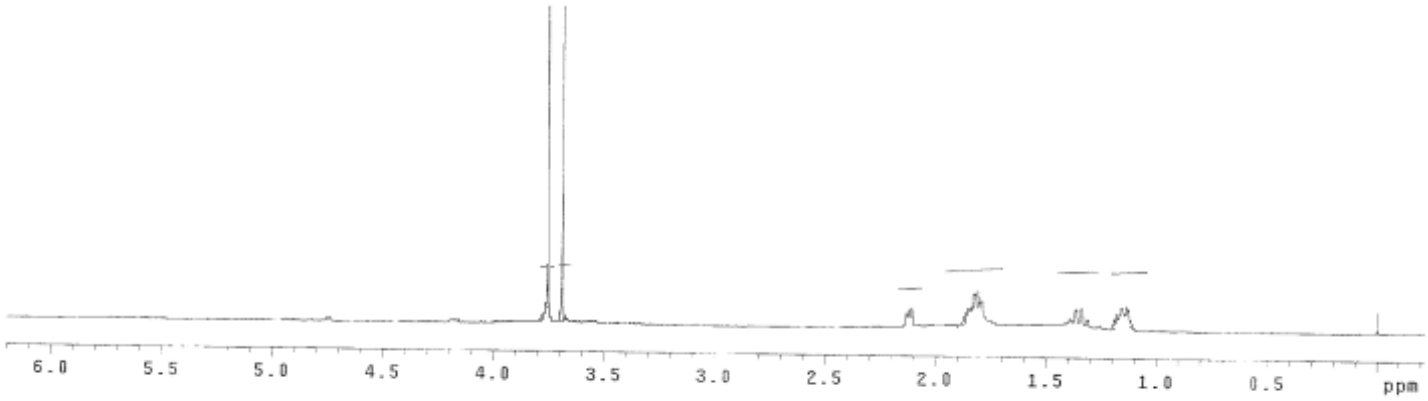
6m



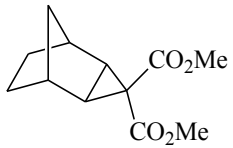
^{1}H NMR (500 MHz, $CDCl_3$):



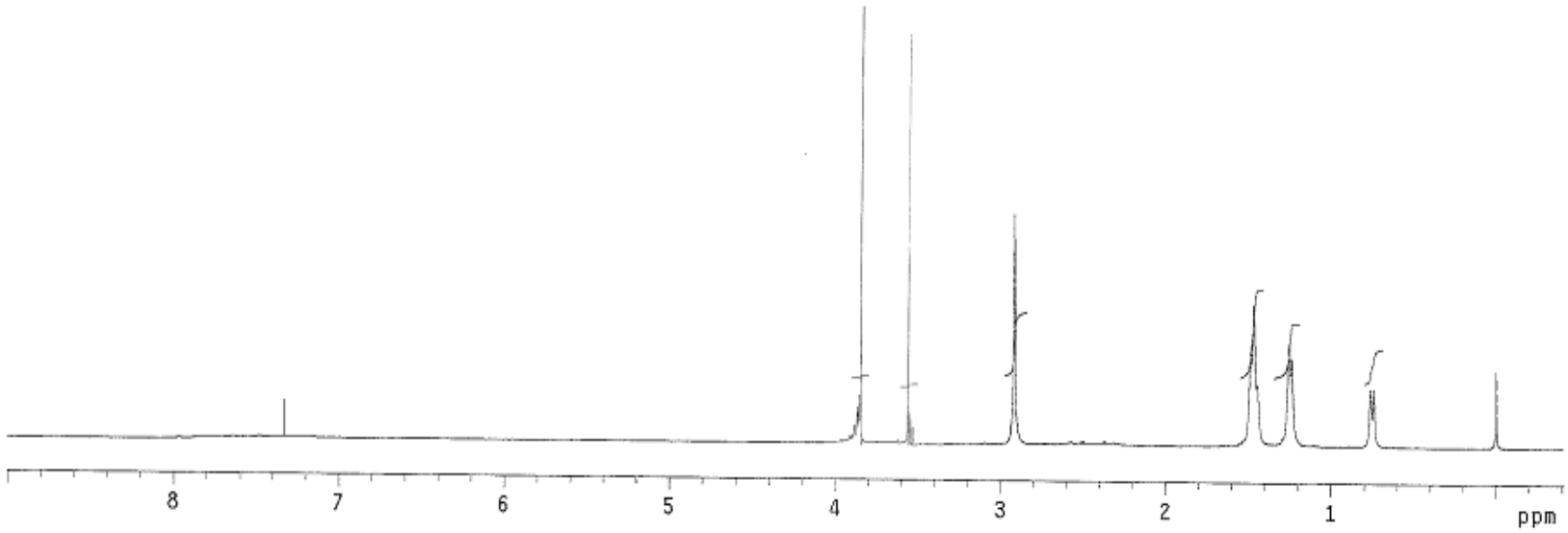
6n



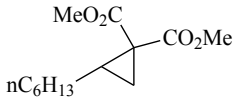
^{1}H NMR (500 MHz, $CDCl_3$):



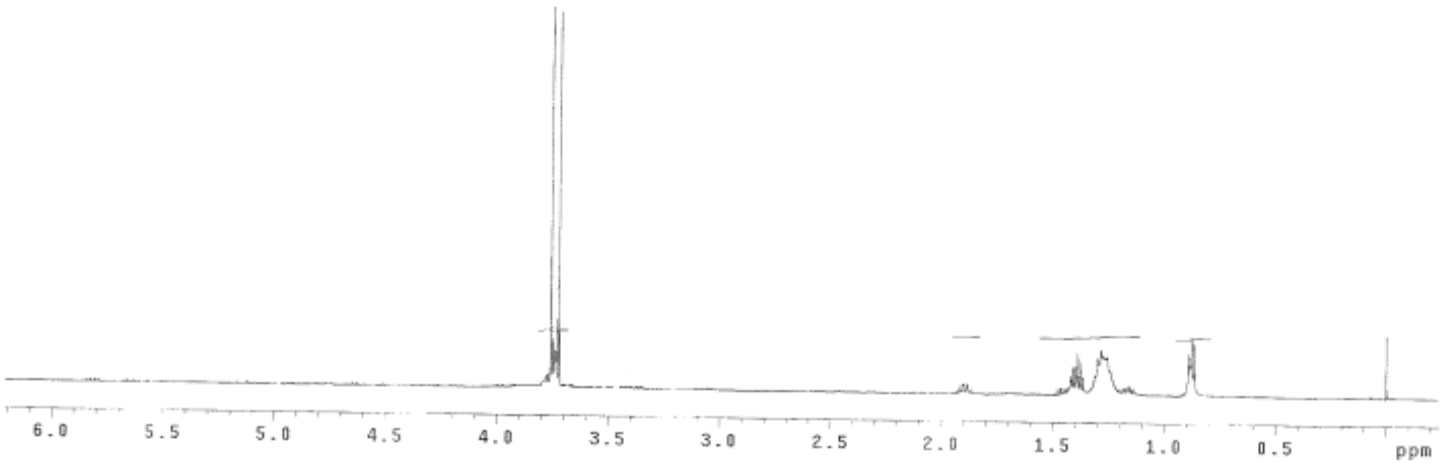
6o



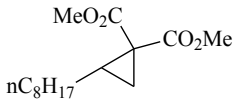
^{1}H NMR (500 MHz, $CDCl_3$):



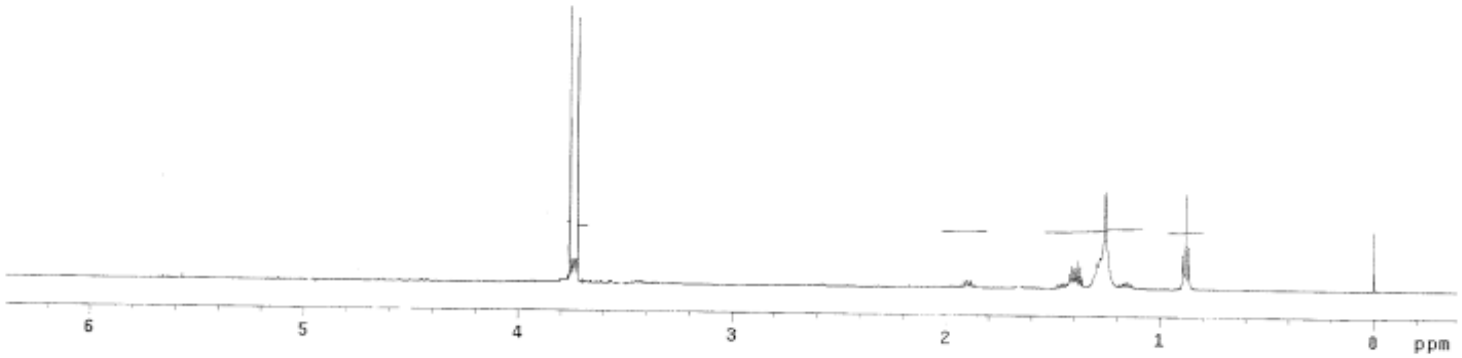
6k



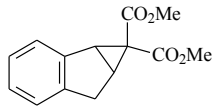
^{1}H NMR (500 MHz, $CDCl_3$):



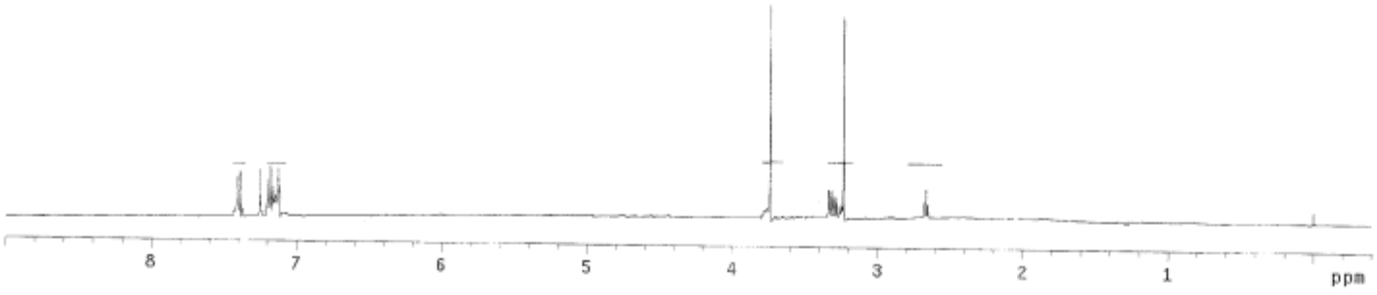
6l



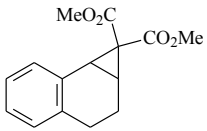
^{1}H NMR (500 MHz, $CDCl_3$):



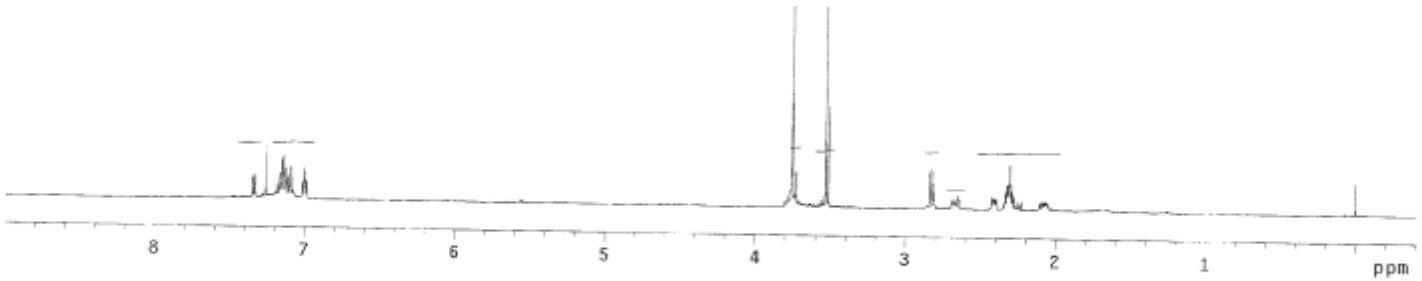
6p



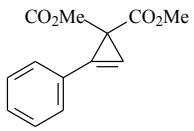
^{1}H NMR (500 MHz, $CDCl_3$):



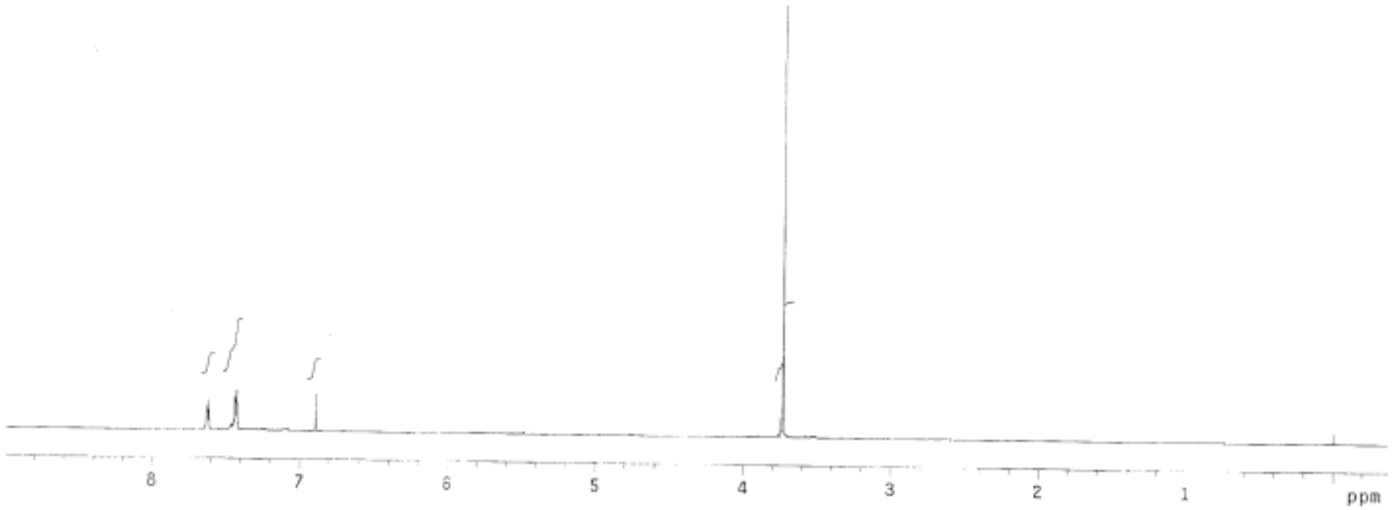
6q



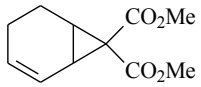
^{1}H NMR (500 MHz, $CDCl_3$):



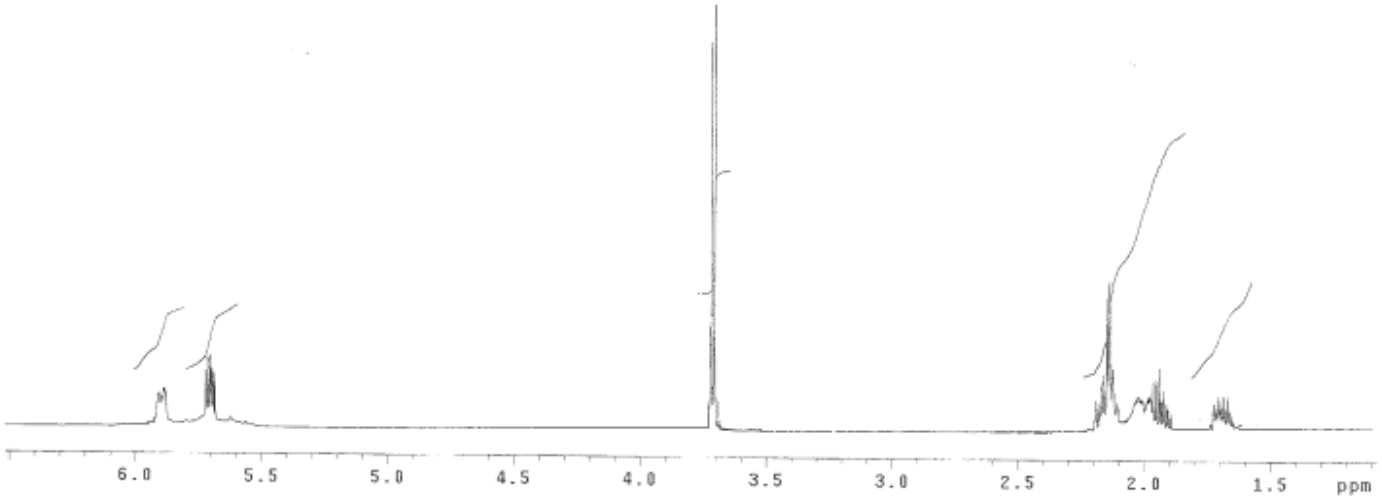
7



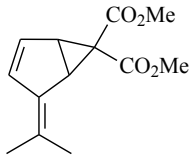
^{1}H NMR (500 MHz, $CDCl_3$):



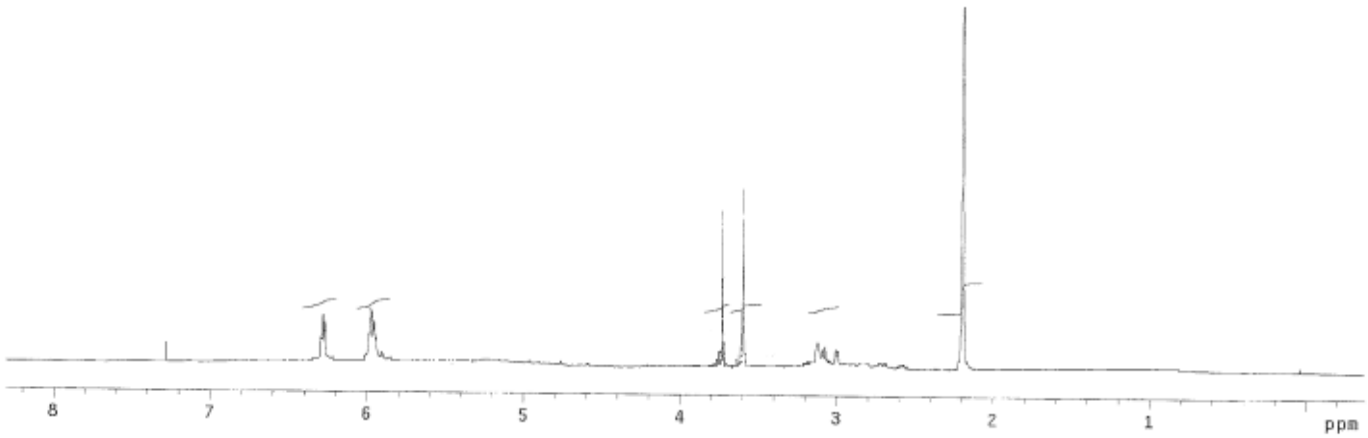
6r



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



6u



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

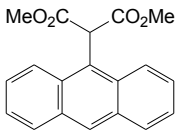


Table 2, entry 1

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

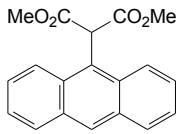
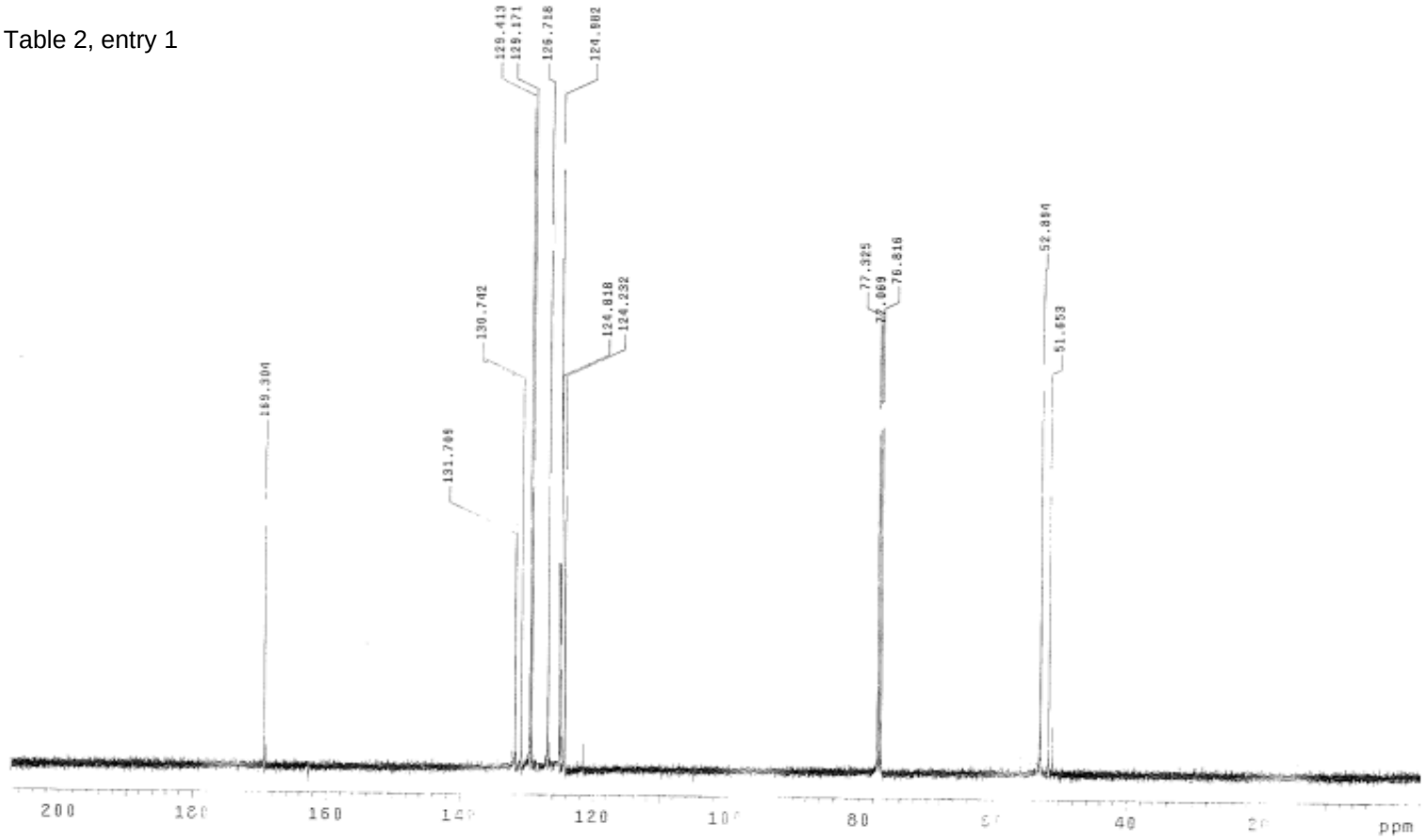


Table 2, entry 1



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

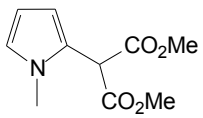


Table 2, entry 5

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

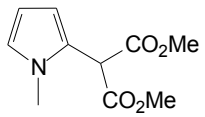
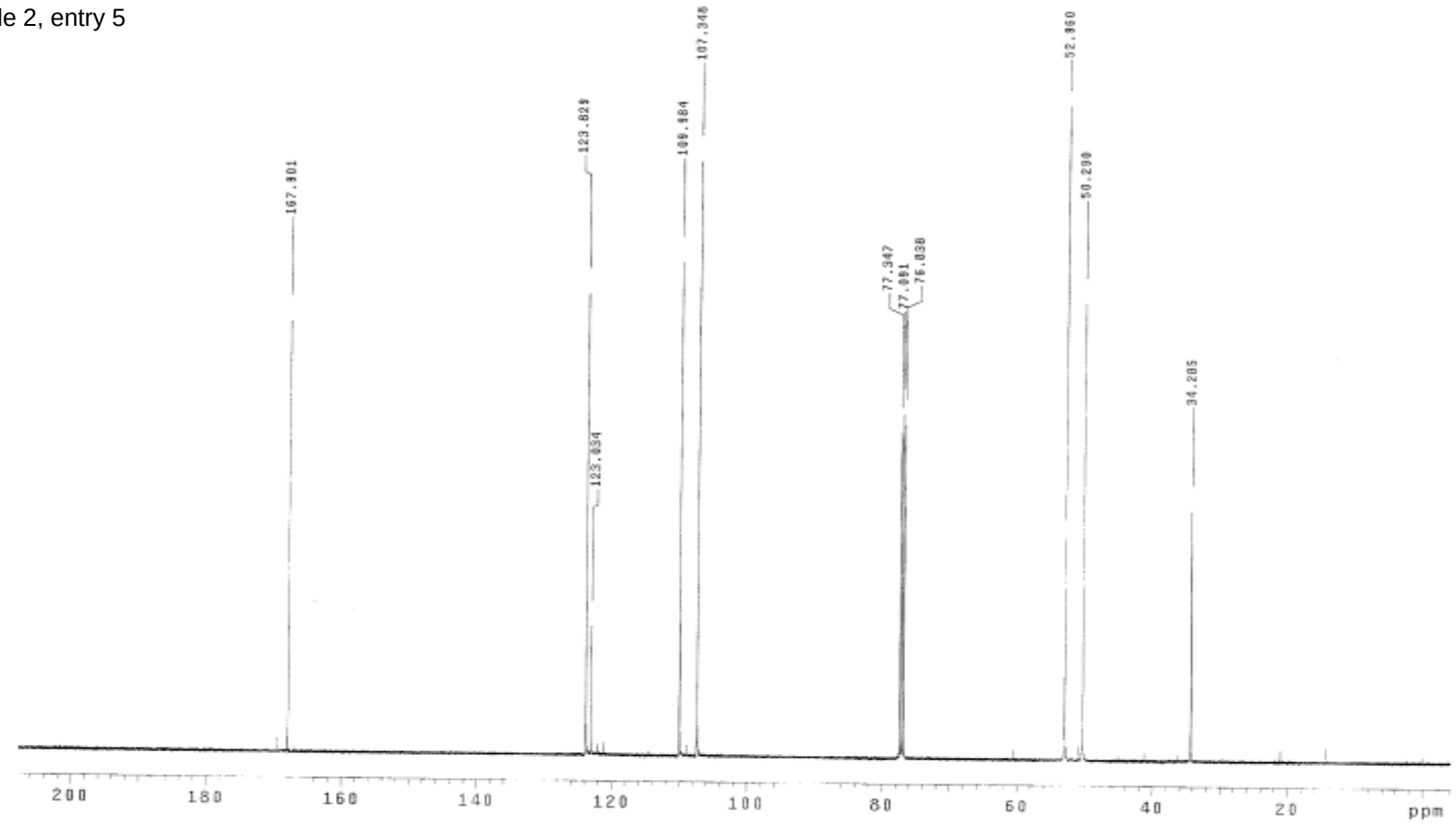


Table 2, entry 5



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

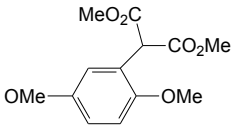


Table 2, entry 9

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

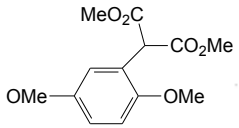
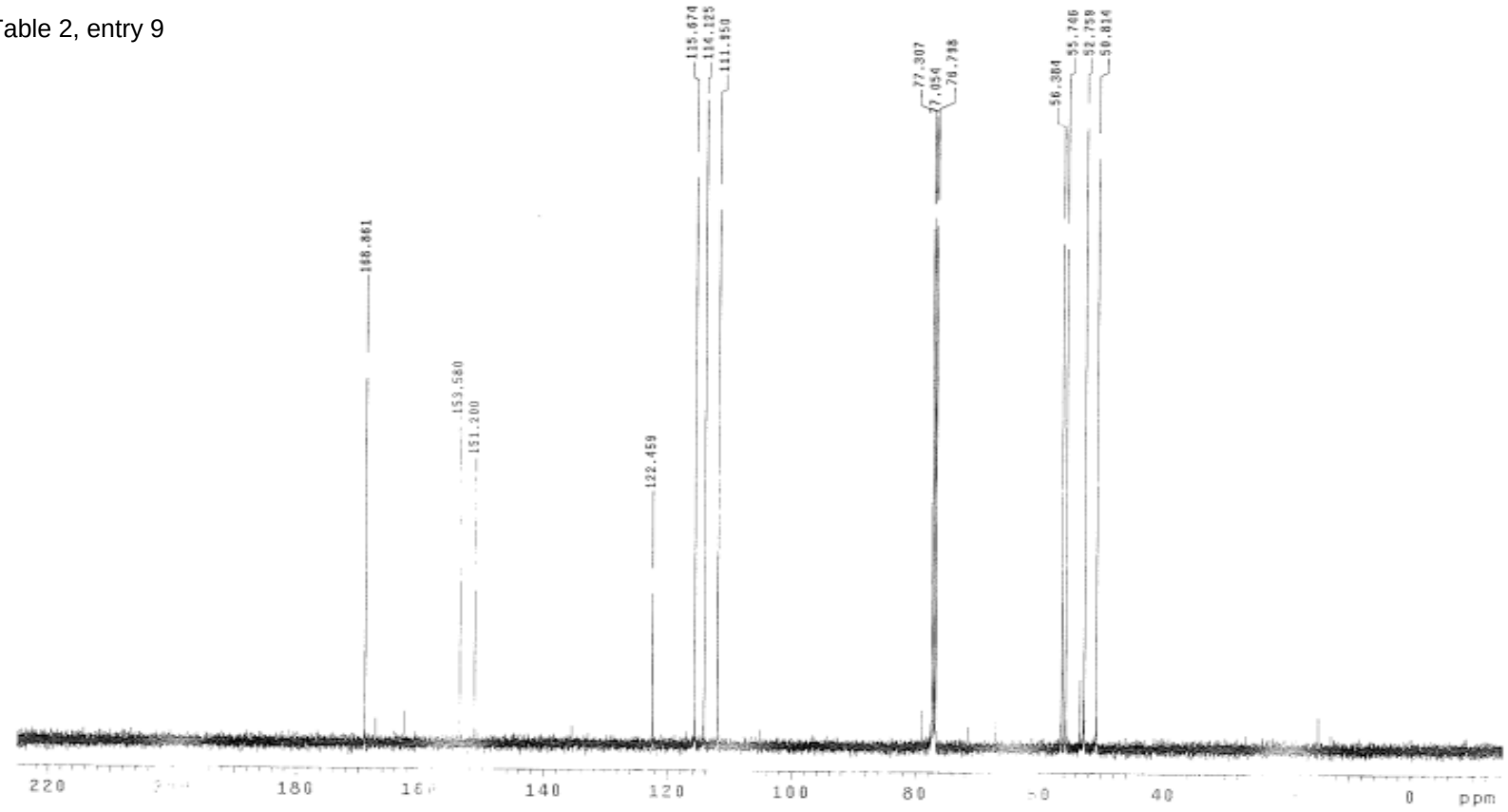
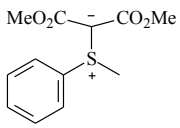


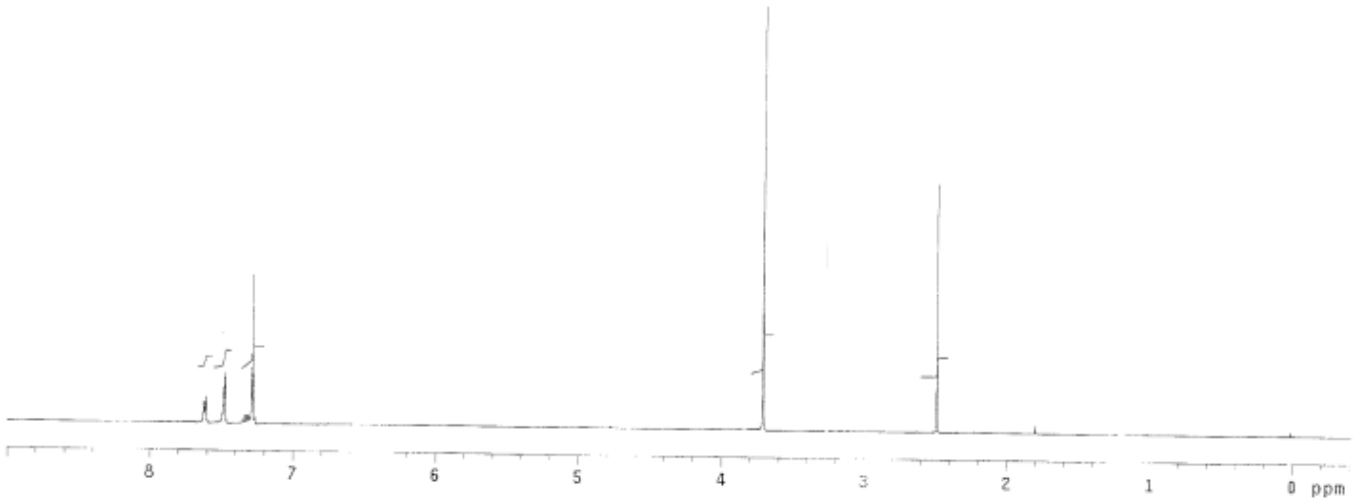
Table 2, entry 9



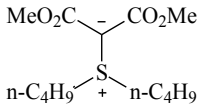
^{1}H NMR (500 MHz, $CDCl_3$):



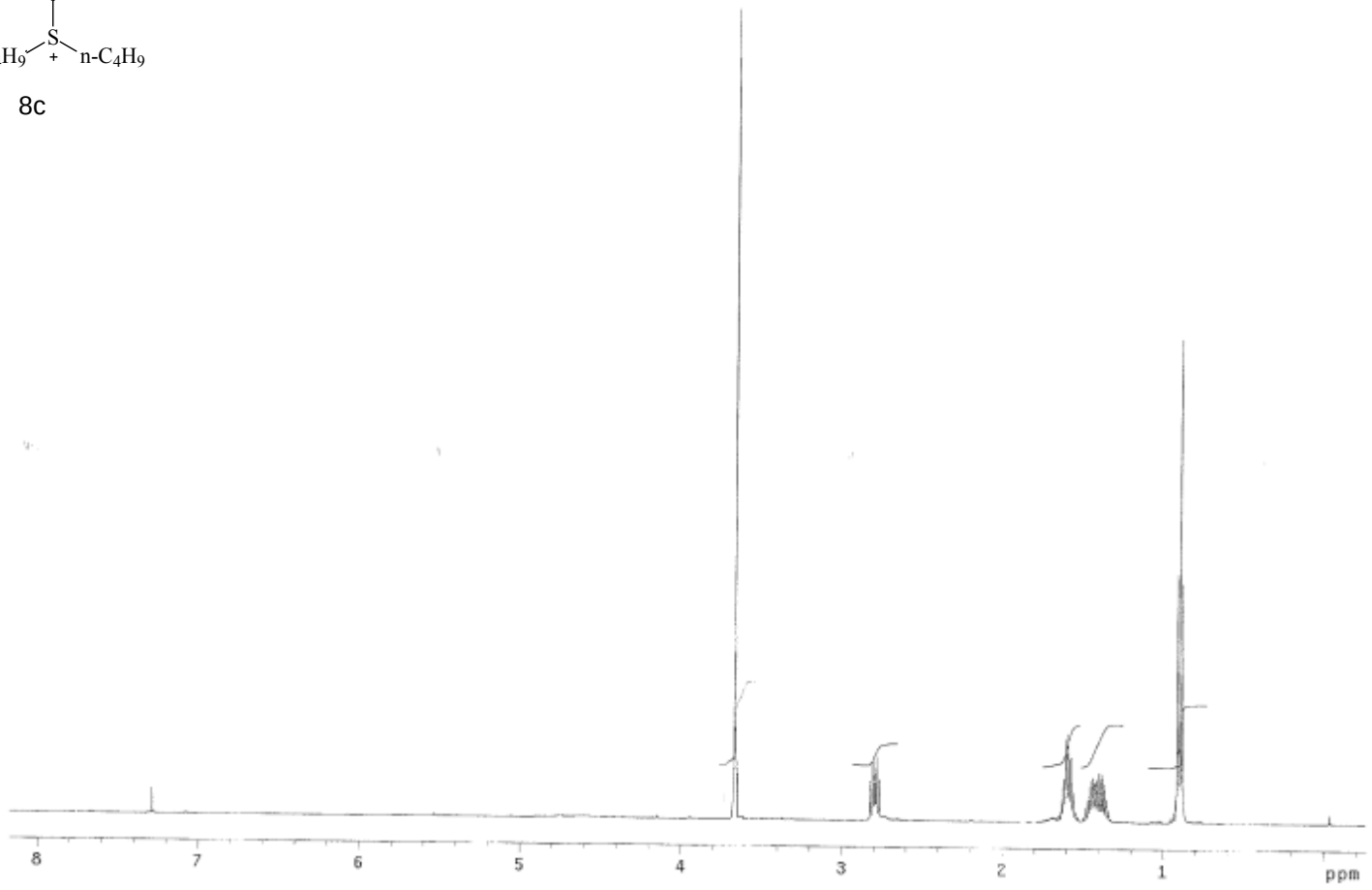
8a



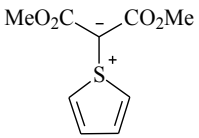
^{1}H NMR (500 MHz, $CDCl_3$):



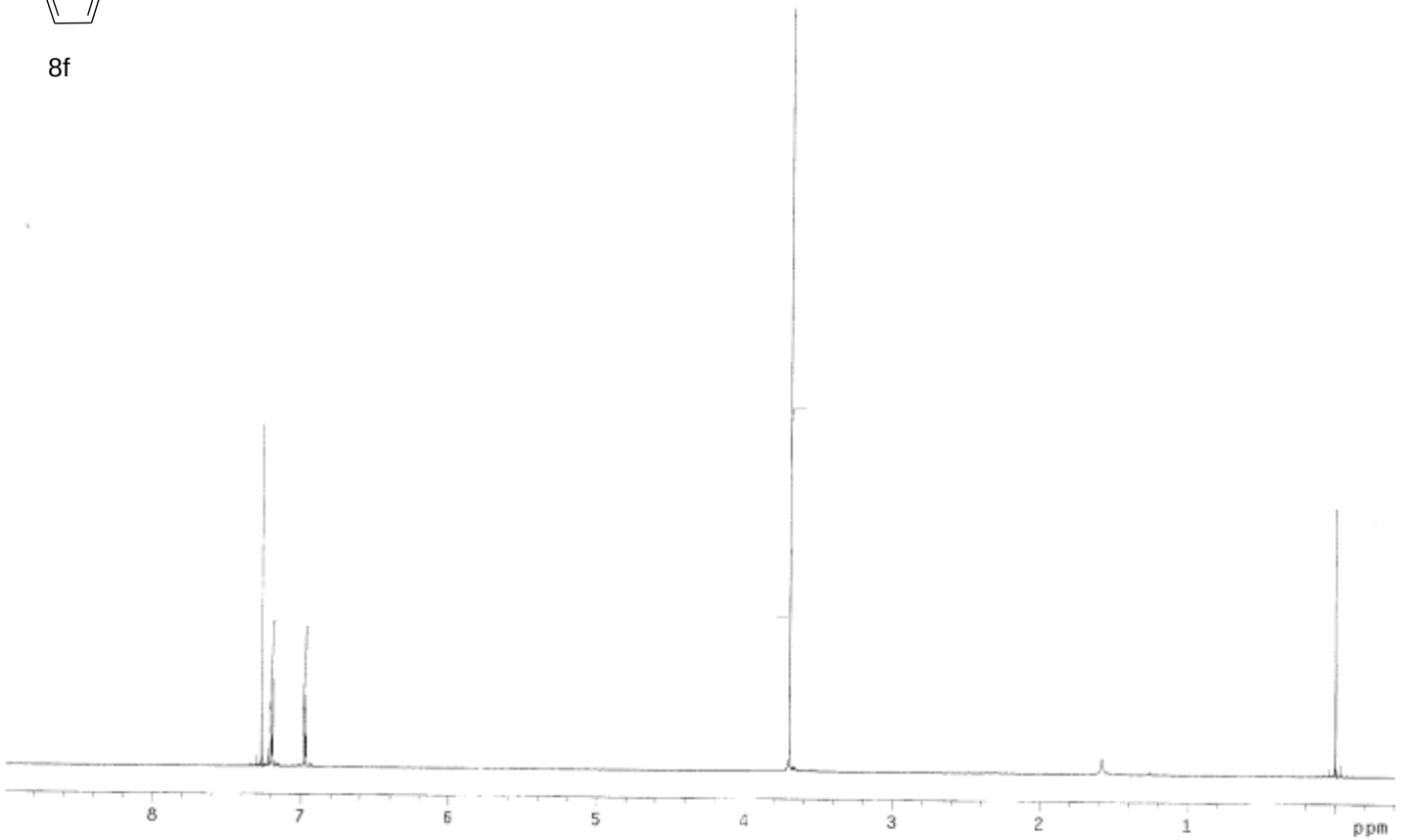
8c



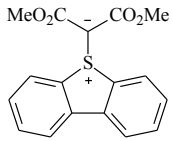
^{1}H NMR (500 MHz, $CDCl_3$):



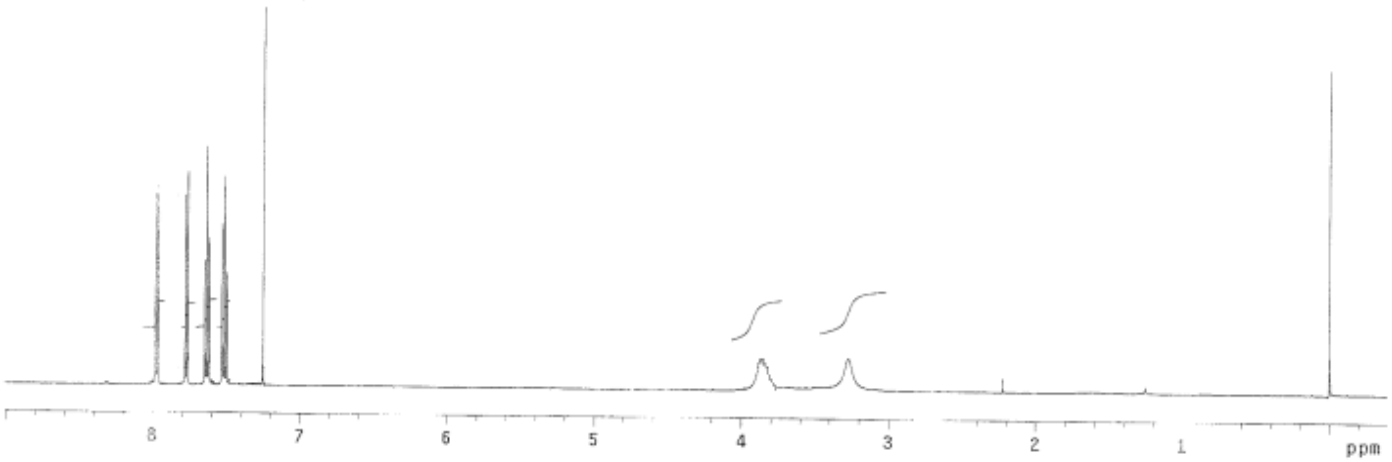
8f



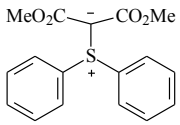
^{1}H NMR (500 MHz, $CDCl_3$):



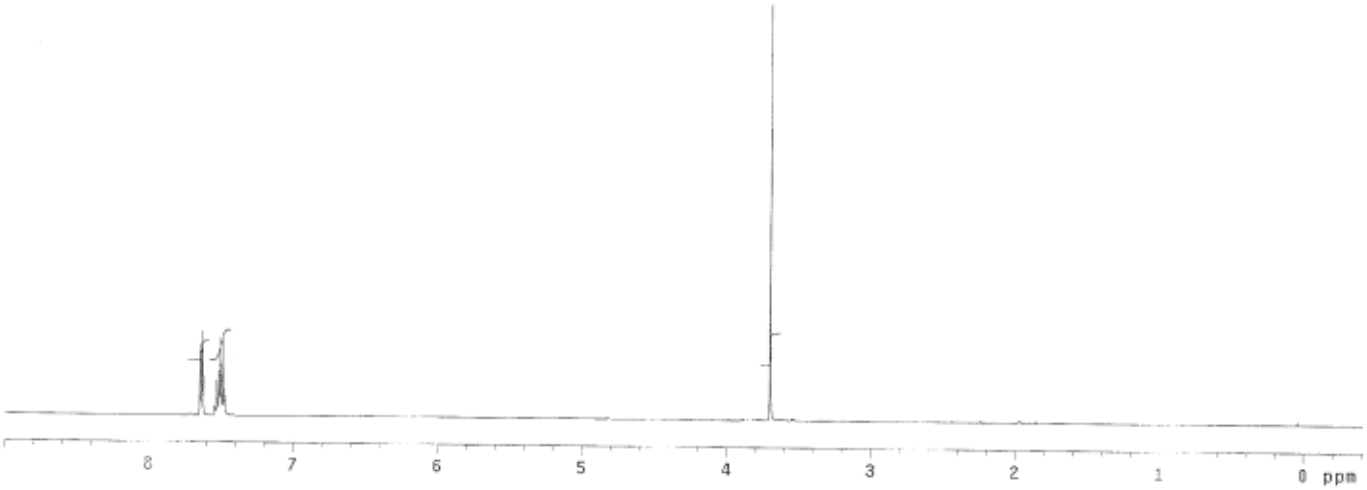
8d



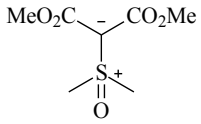
^{1}H NMR (500 MHz, $CDCl_3$):



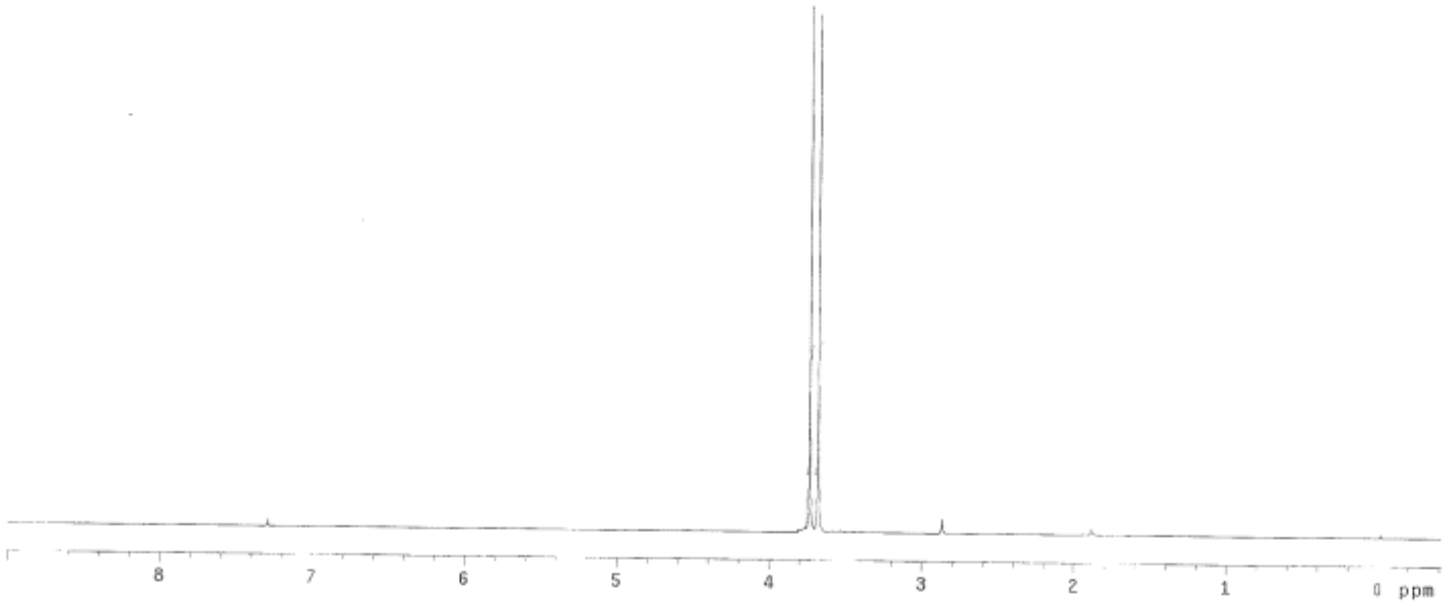
8b



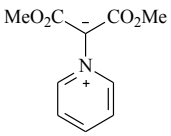
^{1}H NMR (500 MHz, $CDCl_3$):



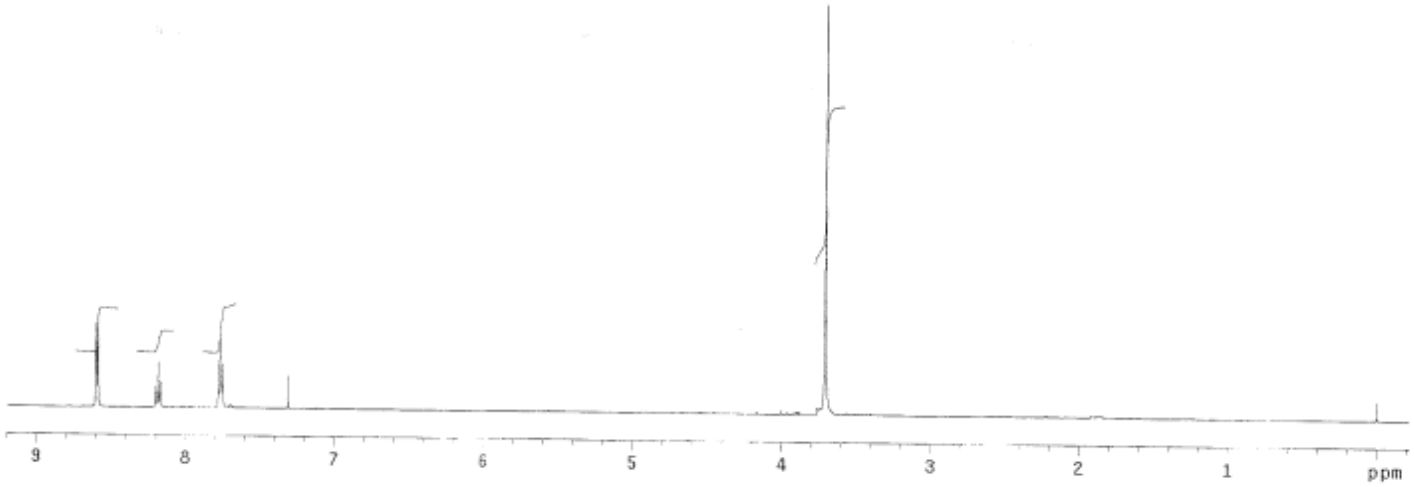
8e



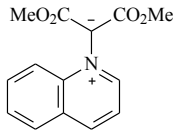
^{1}H NMR (500 MHz, $CDCl_3$):



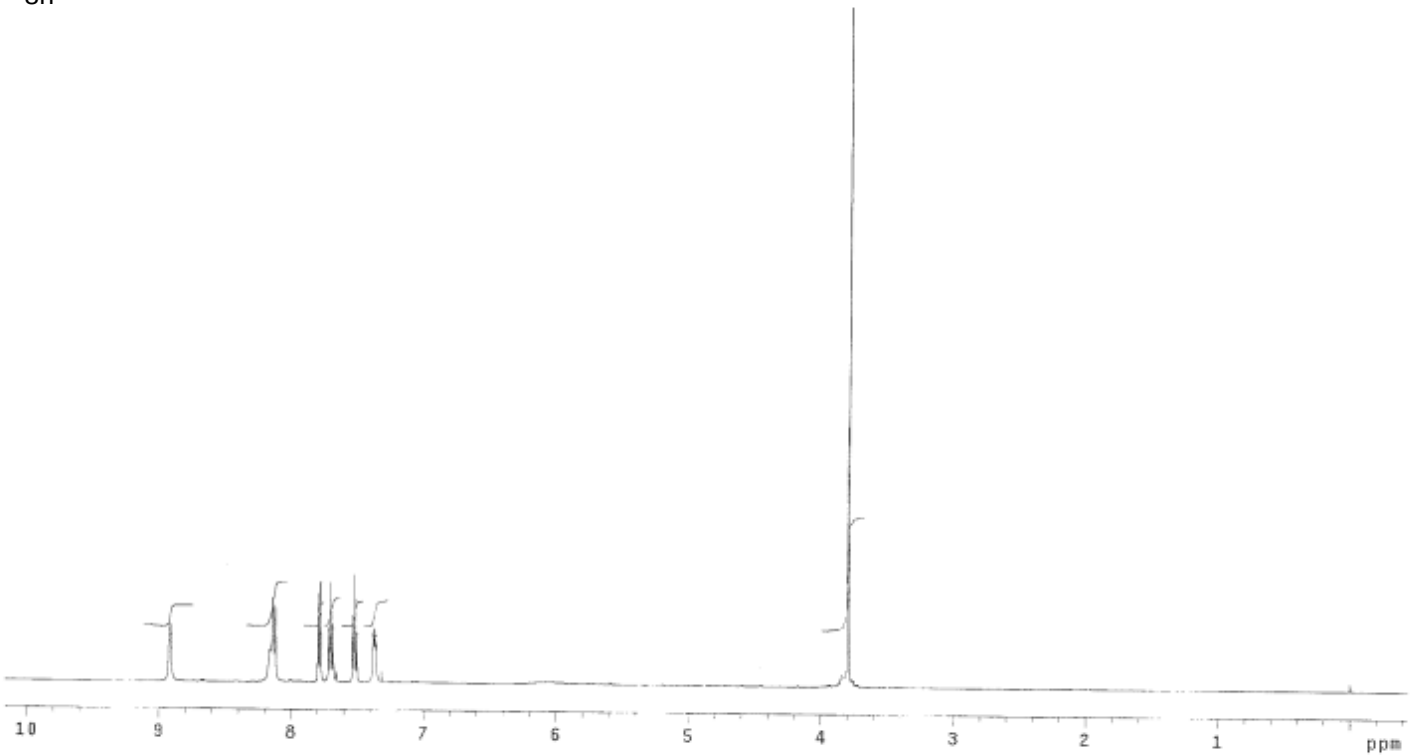
8g



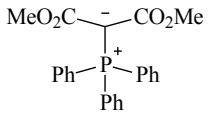
^{1}H NMR (500 MHz, $CDCl_3$):



8h

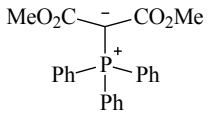


^{1}H NMR (500 MHz, $CDCl_3$):



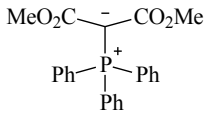
8i

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



8i

^{31}P (81.0 MHz, $CDCl_3$):



8i