Supplementary Material (ESI) for Chemical Communications

Supporting Information

Boronic Acid Catalyzed Ene Carbocyclization of Acetylenic Dicarbonyl Compounds

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General Information

All reactions were performed under an atmosphere of dry nitrogen unless otherwise stated. All glass apparatus was oven dried and cooled under vacuum before use.

Solvents used are dry solvents. Petroleum ether refers to the distilled light petroleum fraction (40-65 ℃). Anhydrous toluene was distilled over CaH_2. Commercial reagents were used as purchased without any further purification.

Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. In all cases of chromatography, distilled solvents were used as eluents. Flash chromatographic purification of products was carried out using Merck Kieselgel 60 silica gel (230-400 mesh). Thin-layer chromatography was carried out using Merck Kieselgel 60 F_{254} (230-400 mesh) fluorescence treated silica plates which were visualized under UV light (250 nm) or by staining with aqueous potassium permanganate solutions or anisaldehyde solutions as appropriate.

All ^{1}H and ^{13}C NMR spectra were recorded using a Bruker 500 MHz and Bruker 400 MHz spectrometers, use ppm for measurement and were internally referenced to residual proteochloroform. Chemical shifts (δ) are given in parts per million (ppm), and coupling constants (J) are given in Hertz (Hz). The ^{1}H NMR spectra are reported as δ/ppm downfield from tetramethylsilane (multiplicity, number of protons, assignment, coupling constant J/Hz). The ^{13}C NMR spectra are reported as δ/ppm. DEPT135 and two-dimensional NMR spectroscopy (COSY, HMQC) were used where appropriate to assist the assignment of signals in the ^{1}H and ^{13}C NMR spectra. Low resolution mass spectrometry (ES) was recorded on a Fissions VG Trio 2000 quadropole mass spectrometer. High resolution mass spectra

(accurate mass) were recorded on a Thermo Finnigan Mat 95XP mass spectrometer. Infrared spectra (IR) were recorded on an ATI Mattson Genesis Series FTIR spectrometer from a thin film deposited onto a sodium chloride plate and only diagnostic absorbances (λ_{max}) are reported.

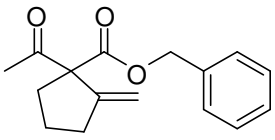
Substrates **1a-n, 1p-q** were prepared by treating the appropriate unsubstituted 1, 3-dicarbonyl compounds with NaH and performing the nucleophilic substitution of the obtained anions on 1-pentynyl-5-chloride in the presence of KI.[S1] Pentynyl β-ketoamide **1o** was obtained applying the same procedure from the corresponding unsubstituted β-ketoamide, which was obtained by aminolysis of ethyl 3-oxo-3-phenylpropanoate with aniline in presence of 3-nitro-benzeneboronic acid.[S2]

General procedure for the ene carbocyclization of acetylenic dicarbonyl compounds catalyzed by boronic acids

To a mixture of 1, 3-dicarbonyl compounds **1a-q** (0.2 mmol) and 3-NO_2-benzeneboronic acid **4g** (1.7 mg, 0.01 mmol), dry toluene (5 mL) was added. The resulting solutions were refluxed at 125 °C until complete consumption of the starting materials was indicated by TLC. The solvent was then removed under reduced pressure and the obtained crude product was purified by flash column chromatography to give the carbocyclic products (**2a-q**) described below.

Synthesis and characterization of compounds 2a-q

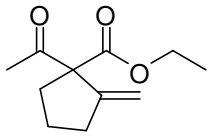
1-Acetyl-2-methylene-cyclopentanecarboxylic acid benzyl ester (2a)



Compound **2a** (46 mg) was obtained according to the general procedure in 90% yield as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.31 (m, 5H), 5.28 (t, *J* = 1.5 Hz, 1H), 5.21 (t, *J* = 2.0 Hz, 1H), 5.18 (s, 2H), 2.47-2.39 (m, 3H), 2.22-2.18 (m, 1H), 2.17 (s, 3H), 1.79-1.69 (m, 2H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 203.4, 170.9, 148.5, 135.4, 128.5 (2C), 128.3, 128.1 (2C), 112.3, 70.4, 67.2, 35.0, 34.0, 24.1, 22.9; **IR**: ν_{max} (film)/cm^{-1} 3028, 2959, 2882, 1711, 1650, 1498, 1453, 1434, 1375, 1354, 1259, 1227, 1179, 1139, 1084, 1060, 970, 902; **MS (ES)** m/z (rel. intensity %) 281 (M+Na$^+$, 100); **HRMS (ES)** calcd. $C_{16}H_{18}O_3Na$ (M+Na$^+$) 281.1148, found 281.1158.

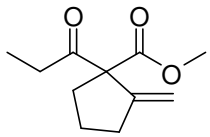
1-Acetyl-2-methylene-cyclopentanecarboxylic acid ethyl ester (2b)



Compound **2b** (36 mg) was obtained according to the general procedure in 92% yield as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.29 (t, *J* = 2.0 Hz, 1H), 5.23 (t, *J* = 2.0 Hz, 1H), 4.23-4.19 (m, 2H), 2.46-2.37 (m, 3H), 2.22 (s, 3H), 2.20-2.13 (m, 1H), 1.79-1.63 (m, 2H), 1.27 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 203.6, 171.1, 148.7, 112.0, 70.4, 61.5, 35.0, 34.0, 26.7, 24.1, 14.0; **IR**: ν_{max} (film)/cm^{-1} 2956, 2336, 1734, 1721, 1653, 1559, 1354, 1235, 1140, 1093, 897; **MS (ES)** m/z (rel. intensity %) 219 (M+Na$^+$, 100); **HRMS (ES)** calcd. $C_{11}H_{16}O_3Na$ (M+Na$^+$) 219.0992, found 219.0984.

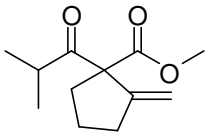
1-Propionyl-2-methylene-cyclopentanecarboxylic acid methyl ester (2c)



Compound **2c** (22 mg) was obtained according to the general procedure in 56% yield as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.28 (t, *J* = 2.0 Hz, 1H), 5.21 (t, *J* = 2.0 Hz, 1H), 3.74 (s, 3H), 2.61 (dq, *J* = 21.5, 7.5 Hz, 1H), 2.57-2.37 (m, 4H), 2.18 (ddd, *J* = 13.5, 7.0, 7.0 Hz, 1H), 1.78-1.64 (m, 2H), 1.06 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 206.6, 171.8, 148.7, 112.1, 70.2, 52.6, 35.1, 33.9, 32.2, 24.1, 8.5; **IR**: ν_{max} (film)/cm^{-1} 3276, 2953, 2341, 1739, 1713, 1458, 1437, 1339, 1259, 1231, 1171, 1122, 1008, 897; **MS (ES)** m/z (rel. intensity %) 219 ($M+Na^+$, 100); **HRMS (ES)** calcd. $C_{11}H_{16}O_3Na$ ($M+Na^+$) 219.0992, found 219.0996.

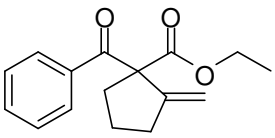
1-Isobutyryl-2-methylenecyclopentanecarboxylic methyl ester (2d)



Compound **2d** (37 mg) was obtained according to the general procedure in 88% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (t, *J* = 2.0 Hz, 1H), 5.17 (t, *J* = 2.3 Hz, 1H), 3.67 (s, 3H), 2.91 (sept., *J* = 6.7 Hz, 1H), 2.41-2.36 (m, 2H), 2.35-2.29 (m, 1H), 2.23-2.16 (m, 1H), 1.69-1.57 (m, 2H), 1.04 (d, *J* = 6.7 Hz, 3H), 1.00 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.1, 171.7, 148.3, 112.3, 70.8, 52.5, 37.3, 34.6, 33.8, 24.0, 20.7, 20.6; **IR**: ν_{max} (film)/cm^{-1} 3433, 2971, 2875, 2097, 1744, 1714, 1646, 1469, 1434, 1263, 1236, 1095, 1008, 899; **MS (ES)** m/z (rel. intensity %) 233 ($M+Na^+$, 100); **HRMS (ES)** calcd. $C_{12}H_{18}O_3Na_1$ ($M+Na^+$) 233.1144, found 233.1148.

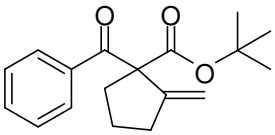
1-Benzoyl-2-methylene-cyclopentanecarboxylic acid ethyl ester (2e)



Compound **2e** (40 mg) was obtained according to the general procedure in 97% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 5.29 (t, *J* = 2.0 Hz, 1H), 5.14 (t, *J* = 2.0 Hz, 1H), 4.12-3.99 (m, 2H), 2.78 (td, *J* = 13.5, 8.0 Hz, 1H), 2.47-2.42 (m, 2H), 2.15-2.08 (m, 1H), 1.79 (d, *J* = 12.5, 7.5 Hz, 1H), 1.68-1.58 (m, 1H), 0.98 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.4, 171.8, 149.5, 135.4, 132.7, 128.8 (2C), 128.4 (2C), 111.8, 67.4, 61.6, 36.8, 34.3, 24.4, 13.7; **IR**: ν_{max} (film)/cm^{-1} 2976, 2957, 1734, 1685, 1447, 1264, 1242, 1217, 1155, 1077, 899, 885; **MS (ES)** m/z (rel. intensity %) 281 ($M+Na^+$, 100); **HRMS (ES)** calcd. $C_{16}H_{18}O_3Na$ ($M+Na^+$) 281.1148, found 281.1154.

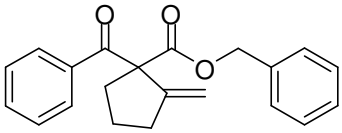
1-Benzoyl-2-methylene-cyclopentanecarboxylic acid *tert*-butyl ester (2f)



Compound **2f** (53 mg) was obtained according to the general procedure in 93% yield as a colorless oil.

^{1}H NMR (400 MHz) δ 7.80 (td, *J* = 1.7, 8.6 Hz, 2H), 7.47-7.43 (m, 1H), 7.37-7.33 (m, 2H), 5.29 (t, *J* = 2.0 Hz, 1H), 5.16 (t, *J* = 2.2 Hz, 1H), 2.80-2.72 (m, 1H), 2.43 (tdd, *J* = 2.1, 7.4, 9.5 Hz, 2H), 2.11-2.04 (m, 1H), 1.77 (tdd, *J* = 7.2, 12.4, 14.6 Hz, 1H), 1.66-1.59 (m, 1H), 1.20 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.7, 169.6, 148.9, 134.7, 131.5, 127.8, 127.5, 127.3, 127.0, 110.2, 81.0, 67.8, 35.7, 33.5, 26.6, 21.2; **IR**: ν_{max} (film)/cm^{-1} 2976, 2876, 1728, 1686, 1448, 1368, 1271, 1251, 1150, 1078, 1122, 842, 703; **MS (ES)** m/z (rel. intensity %) 309 ($M+Na^+$, 100); **HRMS (ES)** calcd. $C_{18}H_{22}O_3Na_1$ ($M+Na^+$) 309.1453, found 309.1461.

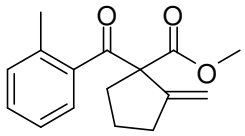
1-Benzoyl-2-methylene-cyclopentanecarboxylic acid benzyl ester (2g)



Compound **2g** (63 mg) was obtained according to the general procedure in 98% yield as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.33 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.27-7.20 (m, 3H), 7.05 (d, *J* = 6.5 Hz, 2H), 5.33 (t, *J* = 2.0 Hz, 1H), 5.17 (t, *J* = 2.0 Hz, 1H), 5.08 (s, 2H), 2.86 (ddd, *J* = 13.5, 7.0, 7.0 Hz, 1H), 2.53-2.50 (m, 2H), 2.20 (ddd, *J* = 13.5, 7.0, 7.0 Hz, 1H), 1.93-1.82 (m, 1H), 1.75-1.68 (m, 1H); **^{13}C NMR** (125.8 MHz, $CDCl_3$) δ 195.2, 171.6, 149.3, 135.2, 134.9, 132.6, 128.8 (2C), 128.4 (2C), 128.4 (2C), 128.3 (2C), 128.2, 112.0, 67.4 (2C), 36.9, 34.3, 24.3; **IR**: ν_{max} (film)/cm^{-1} 3065, 2956, 2341, 1734, 1682, 1653, 1559, 1448, 1264, 1239, 1212, 1156, 1070, 1000, 902, 791, 697; **MS (ES)** m/z (rel. intensity %) 321 ($M+H^+$, 81); **HRMS (ES)** calcd. $C_{21}H_{21}O_3$ ($M+H^+$) 321.1485, found 321.1492.

1-(2-Methylbenzoyl)-2-methylene-cyclopentanecarboxylic acid methyl ester (2h)

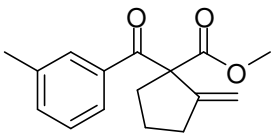


Compound **2h** (38 mg) was obtained according to the general procedure in 76% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.22 (m, 2H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 5.28 (t, *J* = 2.0 Hz, 1H), 5.17 (t, *J* = 2.0 Hz, 1H), 3.59 (s, 3H), 2.60 (dt, *J* = 13.0, 6.5 Hz, 1H), 2.49-2.38 (m, 2H), 2.33 (s, 3H), 2.11 (dt, *J* = 13.0, 7.5Hz, 1H), 1.75-1.59 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.2, 172.0, 149.2, 137.9, 137.5, 131.7, 130.4, 126.4, 125.1, 112.6, 69.8, 52.7, 36.9, 34.3, 24.4, 20.8; **IR**: ν_{max} (film)/cm^{-1} 2953, 1735, 1688, 1453, 1432, 1237, 1219, 1155, 897, 885; **MS (ES)** m/z (rel. intensity %) 259 ($M+H^+$, 40),

281 (M+Na$^+$, 100); **HRMS (ES)** calcd. $C_{16}H_{19}O_3$ (M+H$^+$) 259.1329, found 259.1339.

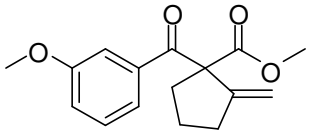
1-(3-Methylbenzoyl)-2-methylene-cyclopentanecarboxylic acid methyl ester (2i)



Compound **2i** (50 mg) was obtained according to the general procedure in 96% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.28-7.19 (m, 2H), 5.28 (t, *J* = 2.0 Hz, 1H), 5.11 (t, *J* = 2.0 Hz, 1H), 3.59 (s, 3H), 2.76 (dt, *J* = 13.5, 7.0 Hz, 1H), 2.46-2.42 (m, 2H), 2.32 (s, 3H), 2.18 (dt, *J* = 13.0, 7.5 Hz, 1H), 1.90-1.79 (m, 1H), 1.68-1.58 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.4, 171.4, 148.4, 137.4, 134.2, 132.5, 128.4, 127.2, 124.9, 110.9, 66.5, 51.7, 35.9, 33.3, 23.3, 20.4; **IR**: ν_{max} (film)/cm^{-1} 2952, 1734, 685, 1600, 1583, 1433, 1269, 1228, 1148, 1079, 1046, 897; **MS (ES)** m/z (rel. intensity %) 259 (M+H$^+$, 100); **HRMS (ES)** calcd. $C_{16}H_{19}O_3$ (M+H$^+$) 259.1329, found 259.1335.

1-(3-Methoxybenzoyl)-2-methylene-cyclopentanecarboxylic acid methyl ester (2j)

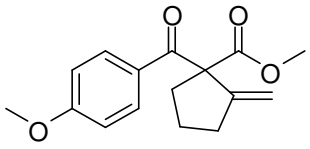


Compound **2j** (54 mg) was obtained according to the general procedure in 98% yield as a white solid.

Mp 65-66 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 2.5, 1.5 Hz, 1H), 7.29 (td, *J* = 7.5, 1.5 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.00 (ddd, *J* = 7.5, 2.5, 1.5 Hz, 1H), 5.29 (t, *J* = 2.0 Hz, 1H), 5.12 (t, *J* = 2.0 Hz, 1H), 3.76 (s, 3H),

3.59 (s, 3H), 2.77 (dt, *J* = 13.5, 7.0 Hz, 1H), 2.44 (tt, *J* = 7.5, 2.0 Hz, 2H), 2.19 (dt, *J* = 13.0, 6.5 Hz, 1H), 1.90-1.79 (m, 1H), 1.75-1.66 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.0, 172.3, 159.7, 149.3, 136.6, 129.4, 121.1, 119.3, 113.3, 112.0, 67.6, 55.4, 52.7, 36.9, 34.3, 24.3; **IR**: ν_{max} (film)/cm^{-1} 2951, 1737, 1688, 1596, 1581, 1432, 1266, 1233, 1150, 1038; **MS (ES)** m/z (rel. intensity %) 297 ($M+Na^+$, 100); **HRMS (ES)** calcd. $C_{16}H_{18}O_4Na$ ($M+Na^+$) 267.0992, found 267.0996.

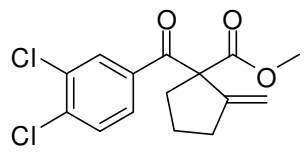
1-(3-Methoxybenzoyl)-2-methylene-cyclopentanecarboxylic acid methyl ester (2k)



Compound **2k** (50 mg) was obtained according to the general procedure in 91% yield as a white solid.

Mp 53-54 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 9.0 Hz, 2H), 5.28 (t, *J* = 2.0 Hz, 1H), 5.11 (t, *J* = 2.0 Hz, 1H), 3.79 (s, 3H), 3.60 (s, 3H), 2.75 (td, *J* = 13.5, 7.0 Hz, 1H), 2.46-2.41 (m, 2H), 2.11 (dt, *J* = 13.0, 7.0 Hz, 1H), 1.88-1.78 (m, 1H), 1.74-1.64 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.1, 172.6, 163.1, 149.5, 131.2 (2C), 127.9, 113.7 (2C), 111.8, 67.3, 55.5, 52.7, 37.0, 34.3, 24.3; **IR**: ν_{max} (film)/cm^{-1} 2952, 1733, 1679, 1601, 1575, 1511, 1308, 1252, 1173, 1157, 1027, 843; **MS (ES)** m/z (rel. intensity %) 297 ($M+Na^+$, 100); **HRMS (ES)** calcd. $C_{16}H_{18}O_4Na$ ($M+Na^+$) 297.1097, found 297.1092.

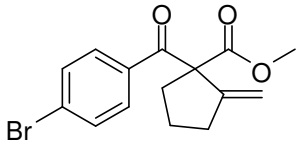
1-(3,4-Dichlorobenzoyl)-2-methylene-cyclopentanecarboxylic acid methyl ester (2l)



Compound **2l** (53 mg) was obtained according to the general procedure in 95% yield as a white solid.

Mp 56-57 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 2.0 Hz, 1H), 7.53 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 5.30 (t, *J* = 2.0 Hz, 1H), 5.10 (t, *J* = 2.0 Hz, 1H), 3.62 (s, 3H), 2.74 (dt, *J* = 13.5, 7.0 Hz, 1H), 2.44 (tt, *J* = 7.0, 2.0 Hz, 2H), 2.07 (dt, *J* = 13.5, 7.0 Hz, 1H), 1.85-1.75 (m, 1H), 1.69-1.59 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.1, 171.9, 148.9, 137.4, 134.9, 133.3, 130.9, 130.5, 127.6, 112.4, 67.4, 53.0, 36.7, 34.2, 24.3; **IR**: ν_{max} (film)/cm^{-1} 2948, 1740, 1692, 1581, 1463, 1432, 1382, 1269, 1238, 1214, 1158, 1030, 899; **MS (ES)** m/z (rel. intensity %) 334 (M+Na$^+$, 100); **HRMS (ES)** calcd. $C_{15}H_{14}O_3Cl_2Na$ (M+Na$^+$) 335.0212, found 335.0225.

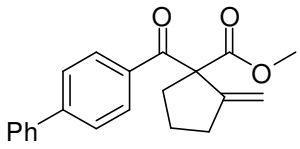
1-(4-Bromobenzoyl)-2-methylene-cyclopentanecarboxylic acid methyl ester (2m)



Compound **2m** (58 mg) was obtained according to the general procedure in 90% yield as a white solid.

Mp 75-77 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 5.29 (t, *J* = 2.0 Hz, 1H), 5.10 (t, *J* = 2.0 Hz, 1H), 3.60 (s, 3H), 2.75 (dt, *J* = 13.5, 7.0 Hz, 1H), 2.44 (tt, *J* = 7.5, 2.0 Hz, 2H), 2.14 (dt, *J* = 13.5, 7.0 Hz, 1H), 1.91-180 (m, 1H), 1.75-1.65 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.2, 172.2, 149.1, 134.0, 131.8 (2C), 130.3 (2C), 127.9, 112.2, 67.4, 52.8, 36.7, 34.2, 24.3; **IR**: ν_{max} (film)/cm^{-1} 2948, 1730, 1685, 1451, 1427, 1392, 1266, 1249, 1083, 915, 883; **MS (ES)** m/z (rel. intensity %) 344, 346 (M+Na$^+$, 100); **HRMS (ES)** calcd. $C_{15}H_{15}O_3BrNa$ (M+Na$^+$) 345.0097, found 345.0111.

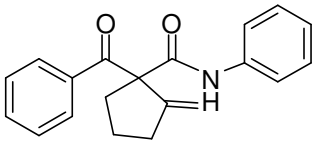
1-(Biphenylcarbonyl)-2-methylene-cyclopentanecarboxylic acid methyl ester (2n)



Compound **2n** (62 mg) was obtained according to the general procedure in 96% yield as a white solid.

Mp 163-165 ℃; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.66-7.61 (m, 4H), 7.47 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.40 (t, *J* = 7.0 Hz, 1H), 5.38 (t, *J* = 2.0 Hz, 1H), 5.22 (t, *J* = 2.0 Hz, 1H), 3.69 (s, 3H), 2.87 (ddd, *J* = 13.5, 7.0, 7.0 Hz, 1H), 2.55-2.52 (m, 2H), 2.23 (ddd, *J* = 13.5, 7.0, 7.0 Hz, 1H), 1.92-1.83 (m, 1H), 1.77-1.69 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.7, 172.5, 149.3, 145.4, 139.7, 133.8, 129.5 (2C), 129.0 (2C), 128.3, 127.2 (2C), 127.1 (2C), 112.0, 67.5, 52.8, 36.9, 34.3, 24.3; **IR**: ν_{max} (film)/cm^{-1} 2952, 2341, 1729, 1680, 1600, 1452, 1424, 1264, 1250, 1080, 912, 884, 848, 746; **MS (ES)** m/z (rel. intensity %) 321 (M+H$^+$, 100); **HRMS (ES)** calcd. $C_{21}H_{21}O_3$ (M+H$^+$) 321.1485, found 321.1487.

1-Benzoyl-2-methylene-N-phenylcyclopentanecarboxamide (2o)

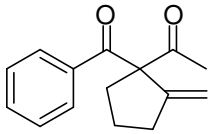


Compound **2p** (46 mg) was obtained according to the general procedure in 75% yield as a yellowish solid.

Mp 90-91 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.76-7.73 (m, 2H), 7.45-7.41 (m, 3H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.28-7.23 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 5.40 (t, *J* = 2.0 Hz, 1H), 5.27 (t, *J* = 2.5 Hz, 1H), 2.72 (ddd, *J* = 12.5, 7.0, 5.5 Hz, 1H), 2.60-2.54 (m, 2H), 2.43 (ddd, *J* = 13.0, 8.5, 7.5 Hz, 1H), 1.84-1.68 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.3, 168.4, 152.2, 137.5, 136.2, 132.5, 129.1 (2C), 129.0 (2C), 128.4 (2C), 124.8, 120.0 (2C), 113.1, 71.6, 37.2, 34.1, 23.9; **IR**: ν_{max} (film)/cm^{-1} 3346, 2953, 1662, 1597, 1524, 1498, 1439, 1315, 1238, 1153, 883; **MS (ES)** m/z (rel. intensity %) 306 (M+H$^+$,

25%), 328 ($M+Na^+$, 100%); **HRMS (ES)**: calcd $C_{20}H_{20}O_2N$ ($M+H^+$) 306.1489, found 306.1494.

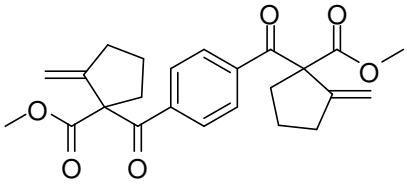
1-Acetyl-1-benzoyl-2-methylene-cyclopentane (2p)



Compound **2q** (35 mg) was obtained according to the general procedure in 95% yield as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.41 (dd, *J* = 7.5, 7.4 Hz, 2H), 5.41 (t, *J* = 2.0 Hz, 1H), 5.12 (t, *J* = 2.2 Hz, 1H), 2.74 (ddd, *J* = 13.3, 6.5, 6.5 Hz, 1H), 2.57-2.46 (m, 2H), 2.25-2.19 (m, 1H), 2.23 (s, 3H), 1.85-1.73 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.5, 197.9, 148.9, 135.3, 132.8, 129.3, 128.4, 113.2, 75.4, 35.8, 34.2, 27.2, 24.2; **IR**: ν_{max} (film)/cm^{-1} 2957, 2359, 1684, 1596, 1579, 1447, 1355, 1234, 1151, 1007, 894, 782, 704; **MS (ES)** m/z (rel. intensity %) 229.1 ($M+H^+$, 94); **HRMS (ES)** calcd. $C_{15}H_{17}O_2$ ($M+H^+$) 229.1218, found 229.1223.

1,4-Phenylene bis((1-carboxyethyl-2-methylenecyclopentyl)methanone) (2q)



Compound **2o** (39 mg) was obtained according to the general procedure in 95% yield as a white solid.

MP 100-101 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (s, 4H), 5.30 (t, *J* = 1.8 Hz, 2H), 5.11 (t, *J* = 2.1 Hz, 2H), 3.61 (s, 6H), 2.75 (td, *J* = 6.9, 13.5 Hz, 2H), 2.45 (tt, *J* = 1.9, 7.6 Hz, 4H), 2.12-2.06 (m, 2H), 1.80 (pd, *J* = 7.4, 12.7 Hz, 2H), 1.68-1.60 (m, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.7, 172.0, 148.9, 138.3, 128.8, 112.3, 67.6, 52.9, 36.6, 34.2, 24.3; **IR**: ν_{max} (film)/cm^{-1} 2953, 1738, 1688, 1433, 1266, 1245, 1219, 1157, 1083, 999, 899, 862; **MS (ES)** m/z (rel.

intensity %) 433 ($M+Na^+$, 100); **HRMS (ES)** calcd. $C_{24}H_{26}O_6Na_1$ ($M+Na^+$) 433.1619, found 433.1622.

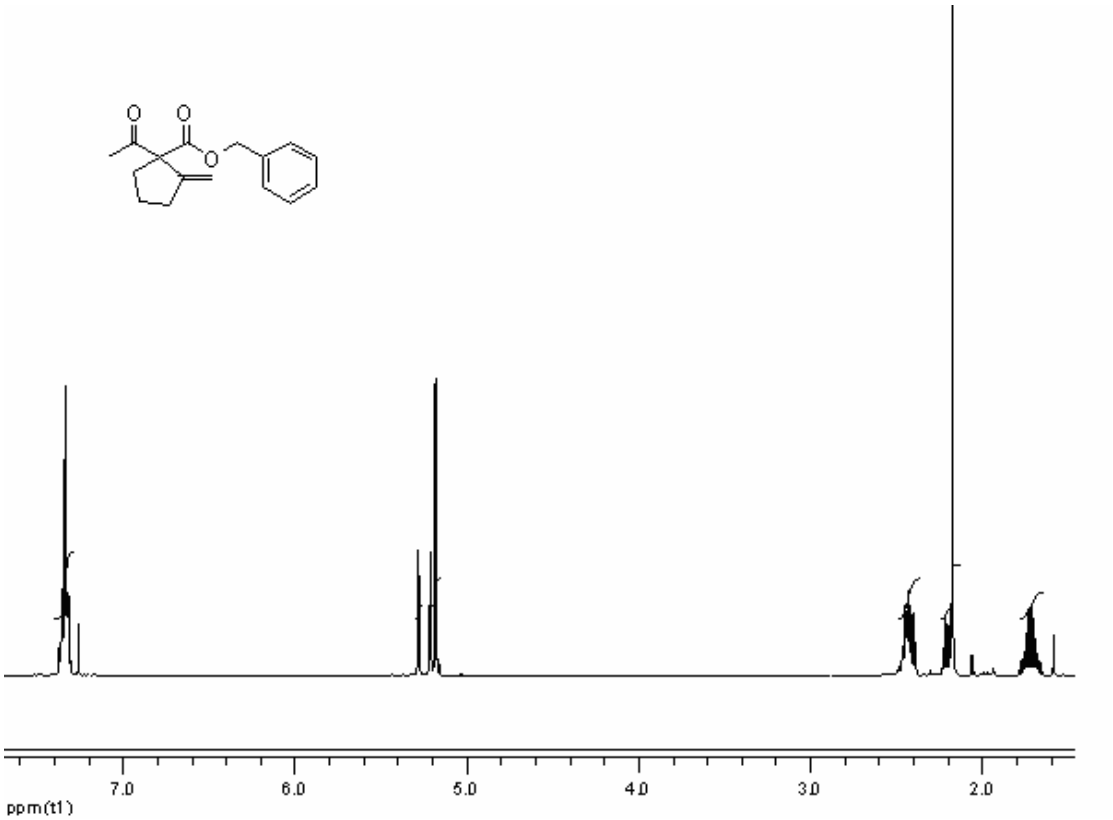
References

[S1] D. Brillon, P. Deslongchamps, *Can. J. Chem.*, 1987, **65**, 43.

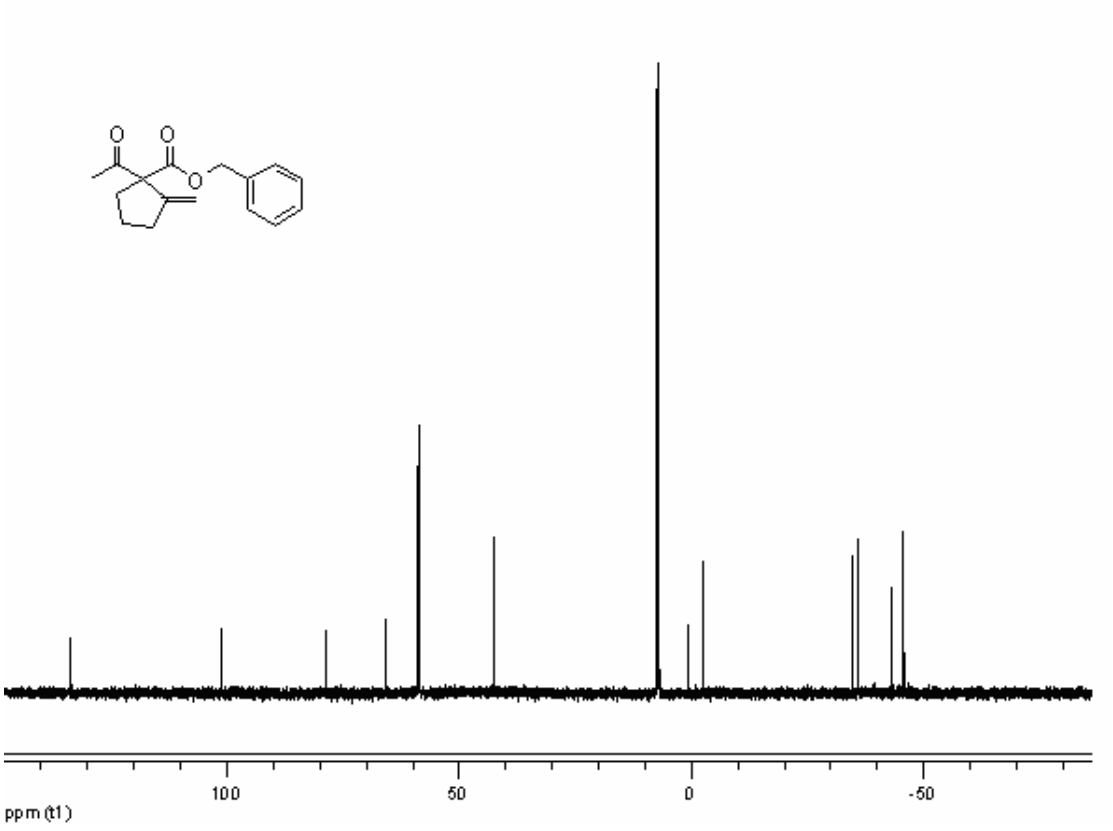
[S2] H. R. Tale, A. D. Sagar, H. D. Santan, R. N. Adude, *Synlett*, 2006, **3**, 415.

Spectra

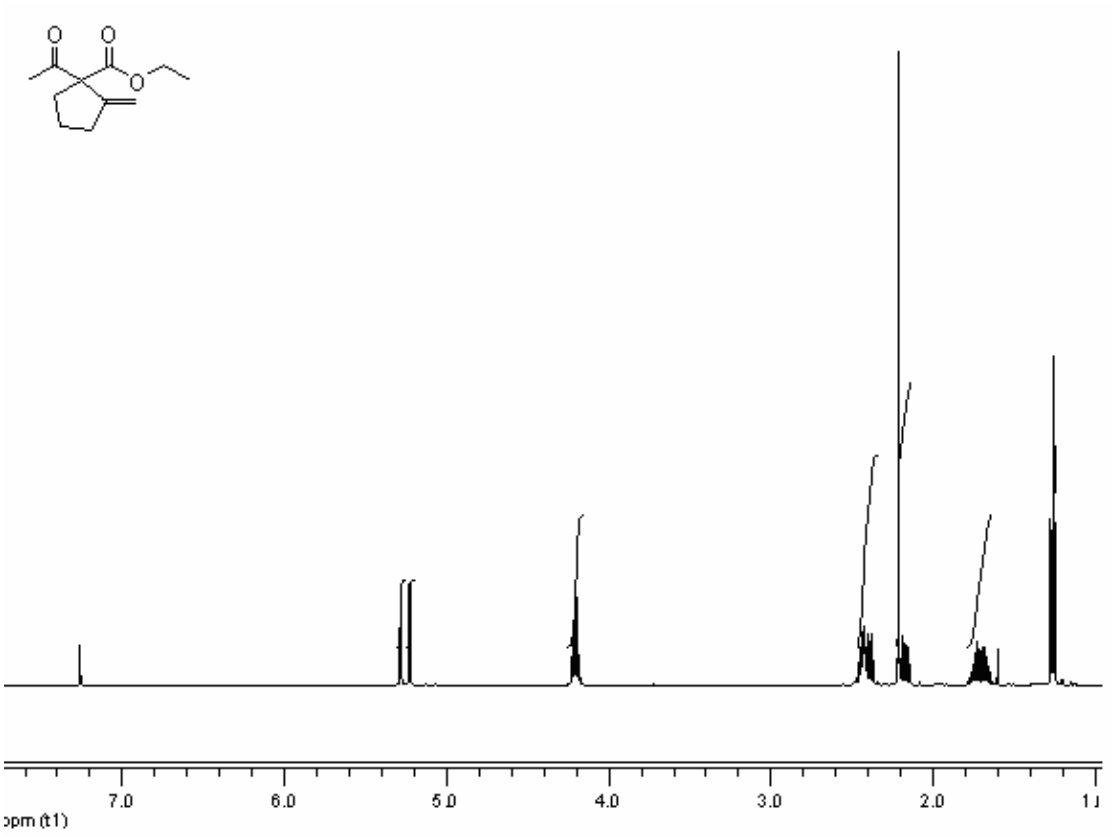
^{1}H NMR of compound 2a



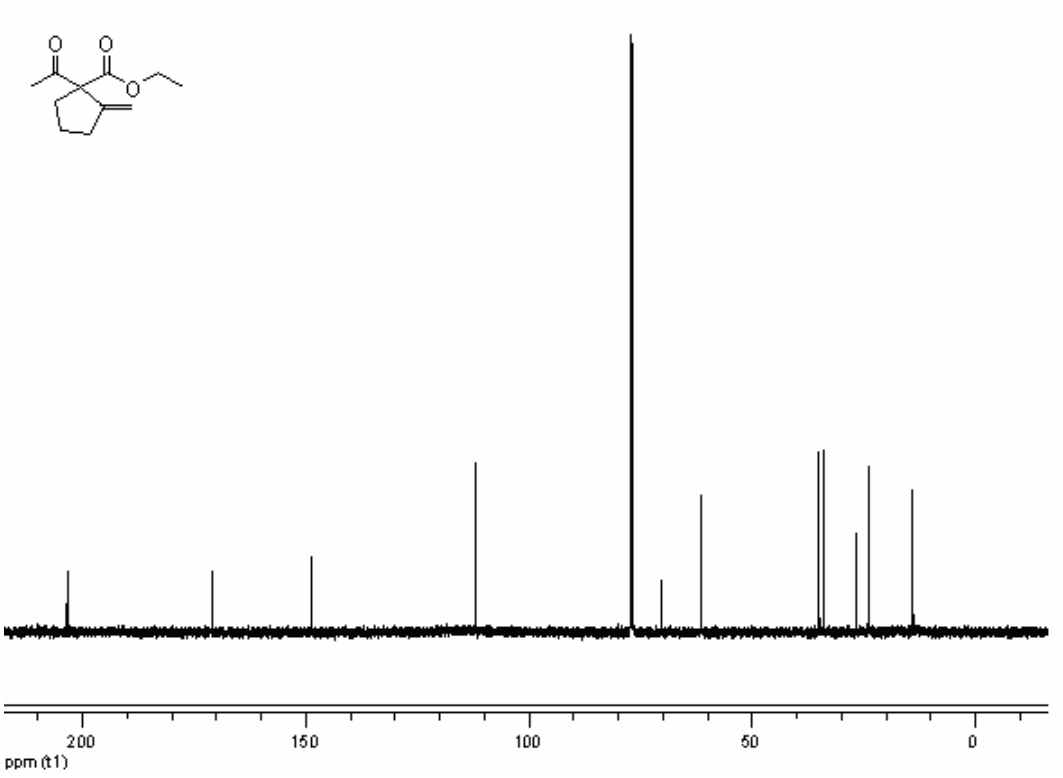
^{13}C NMR of compound 2a



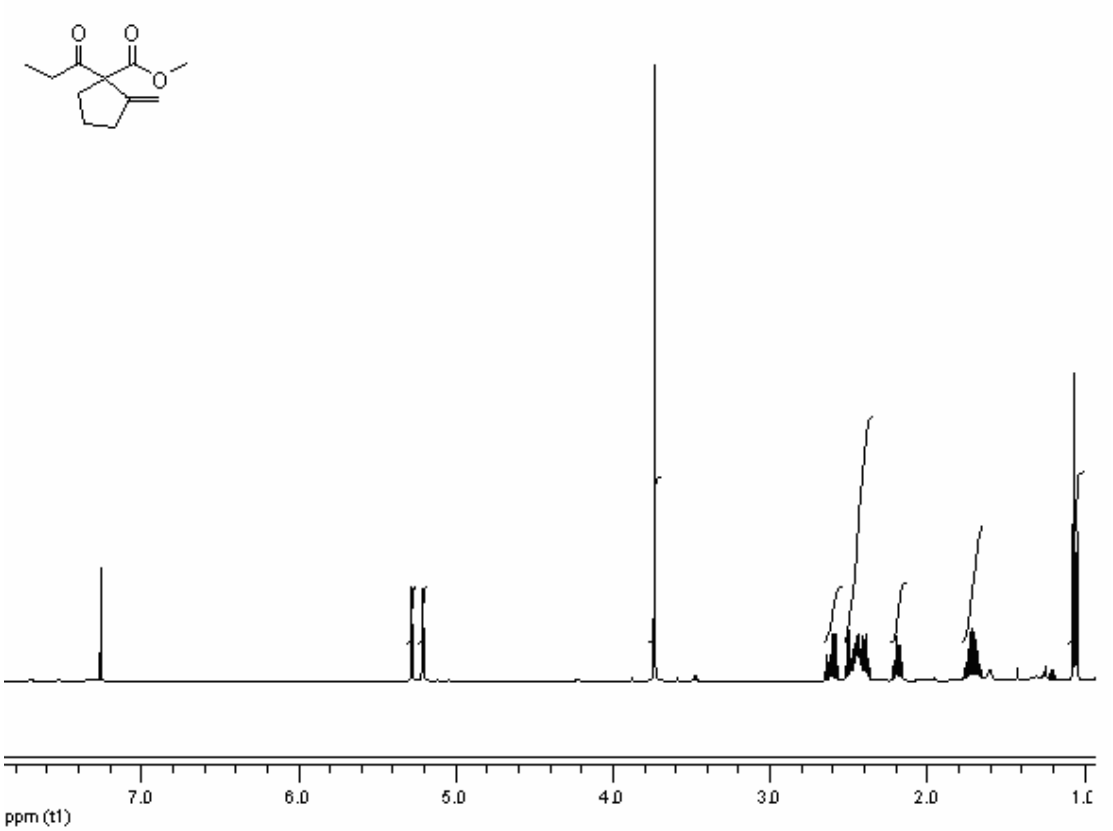
^{1}H NMR of compound 2b



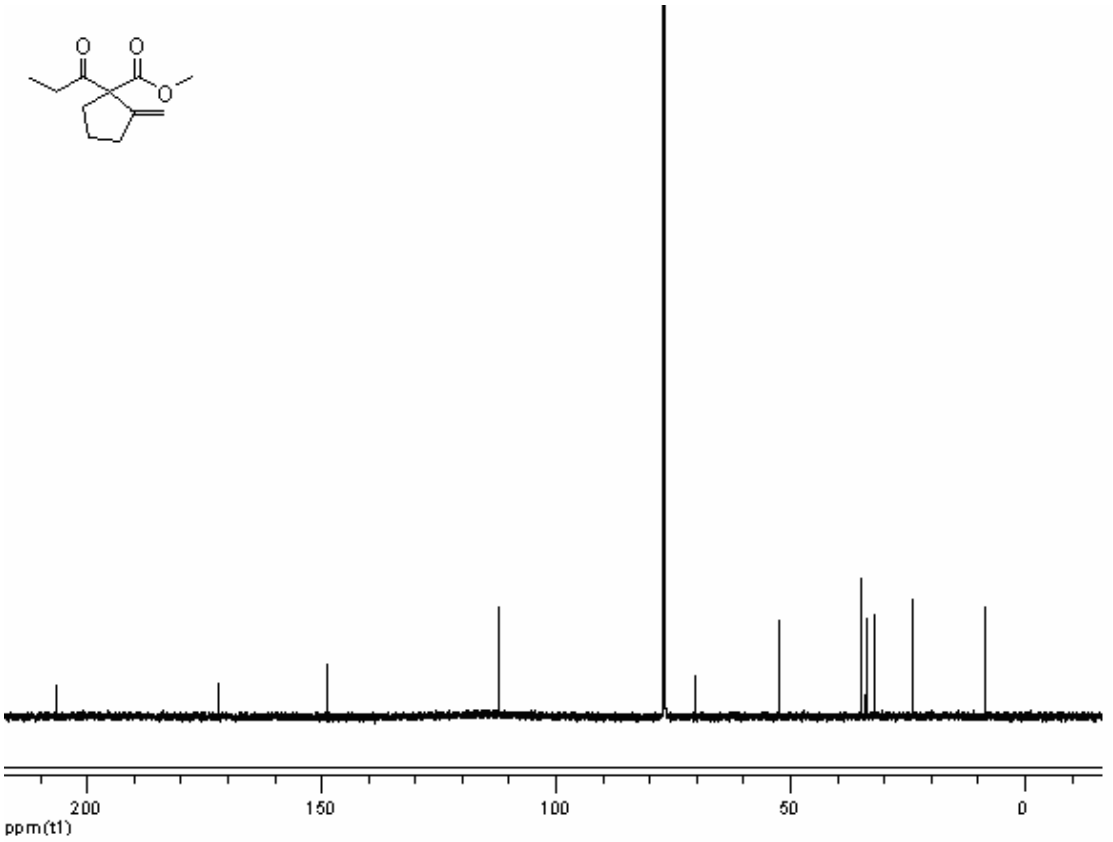
^{13}C NMR of compound 2b



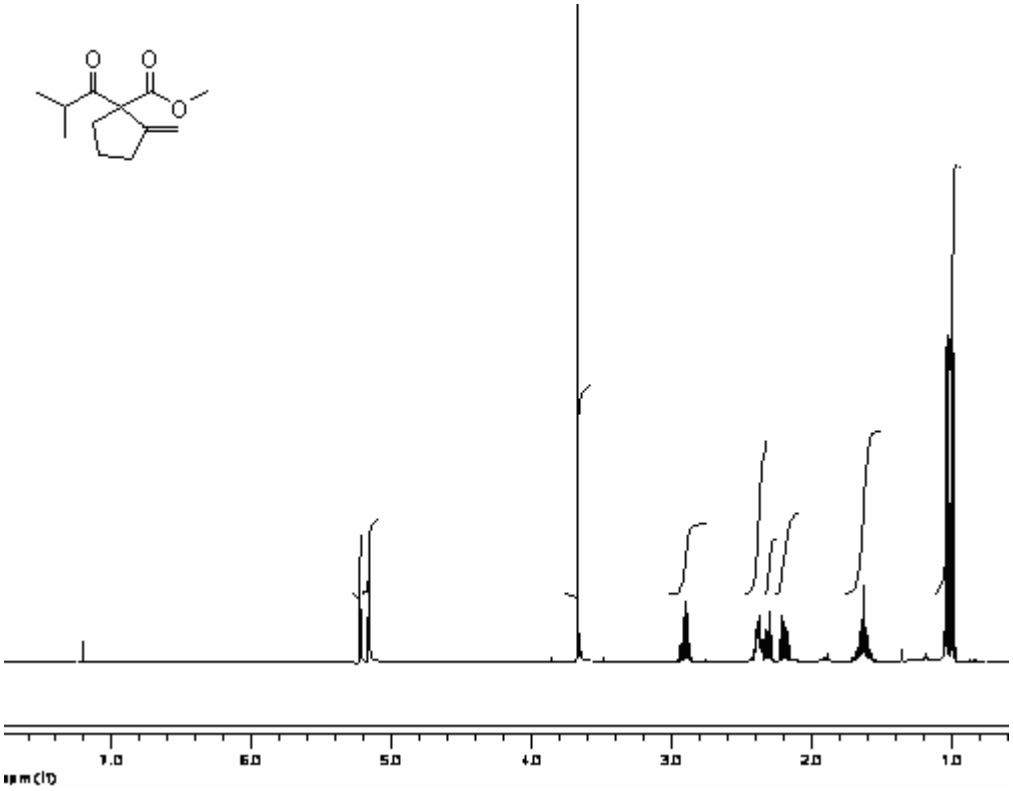
^{1}H NMR of compound 2c



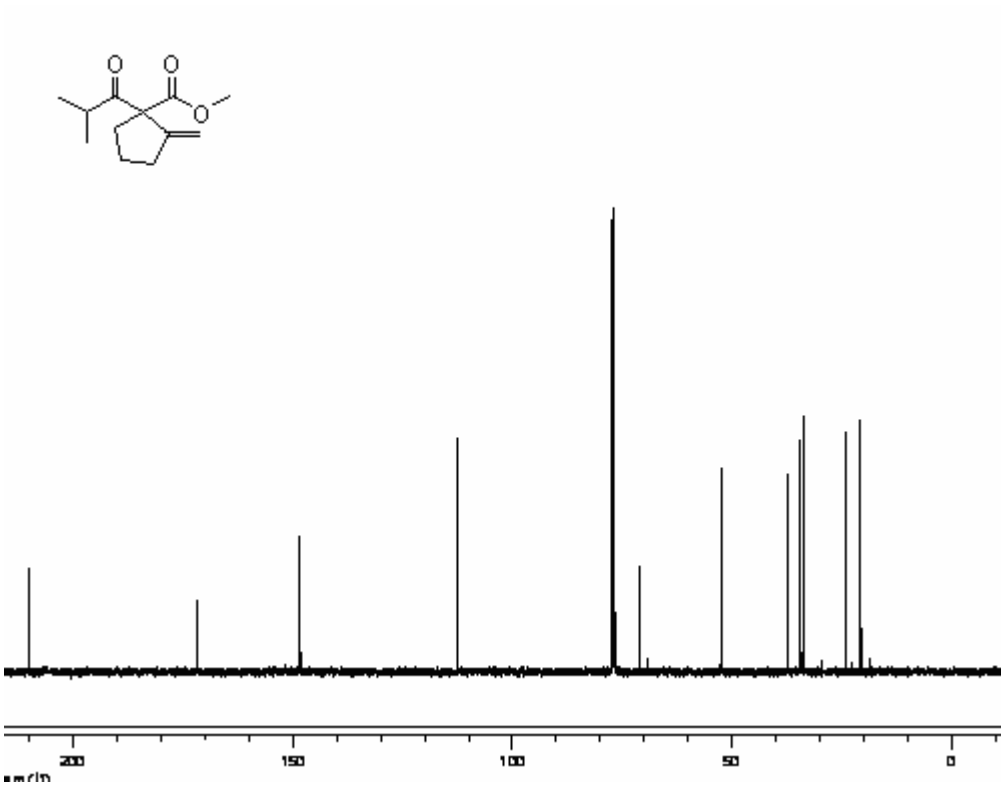
^{13}C NMR of compound 2c



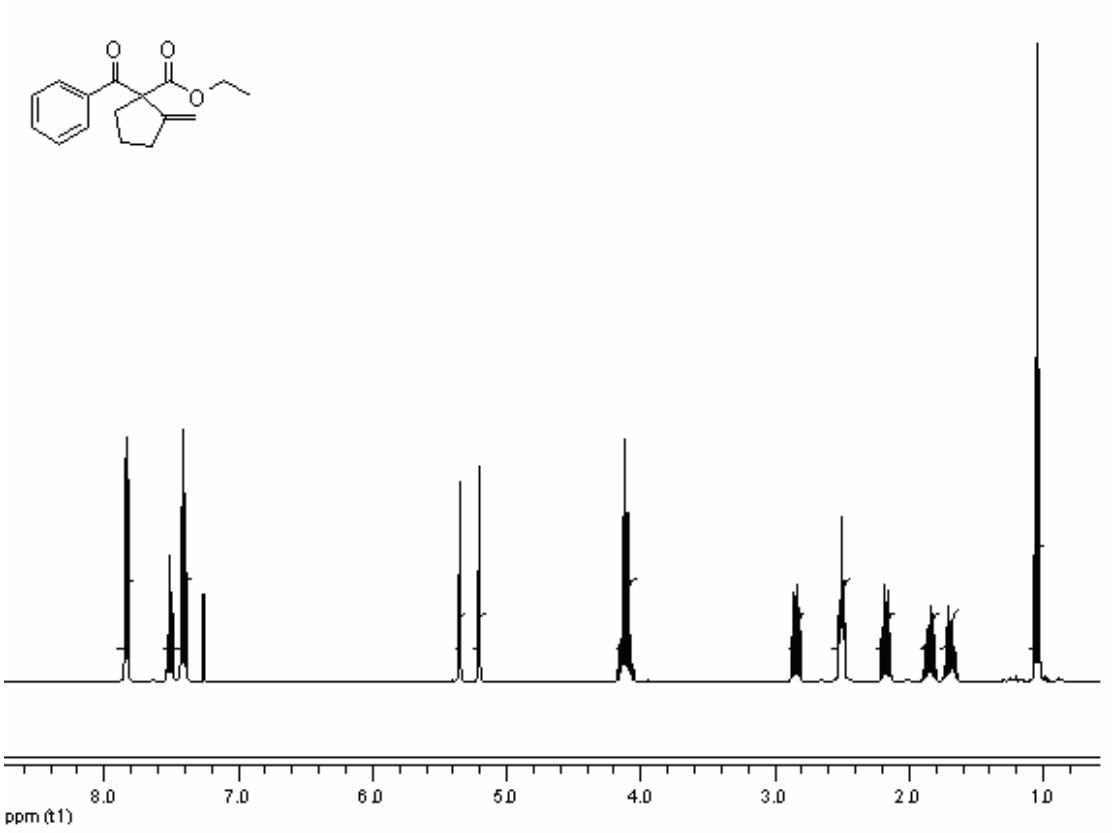
^{1}H NMR of compound 2d



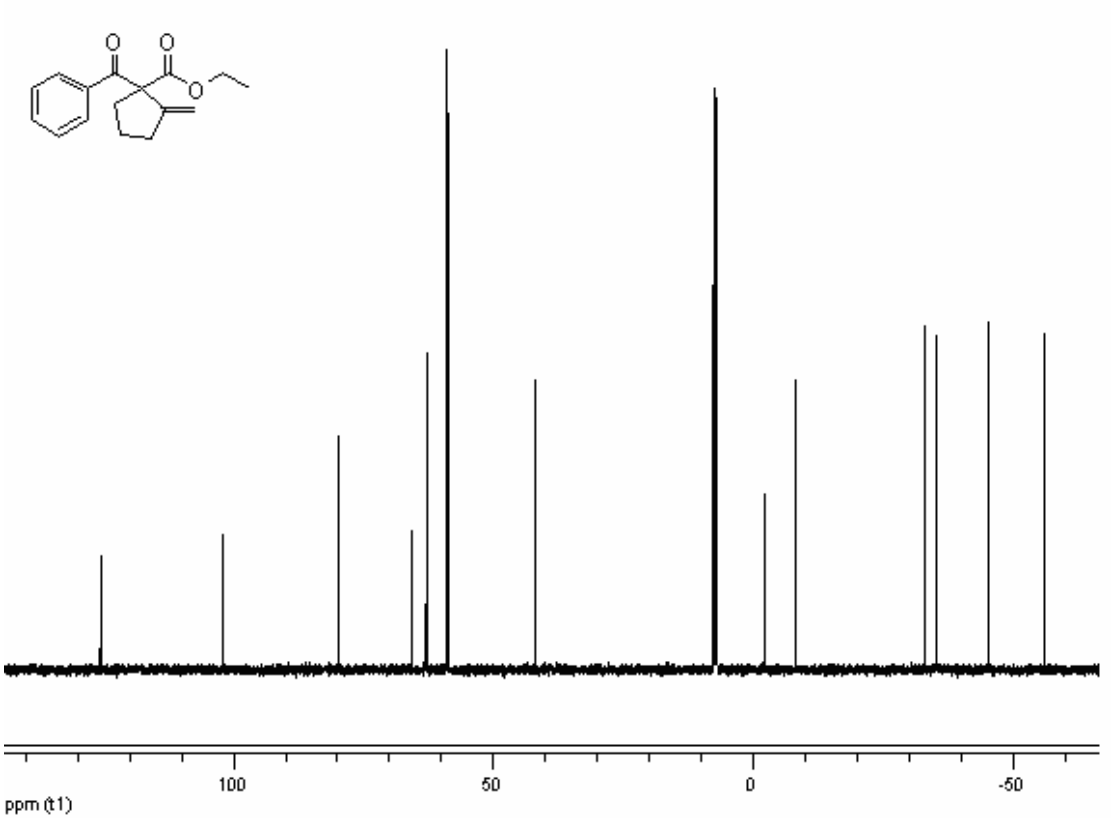
^{13}C NMR of compound 2d



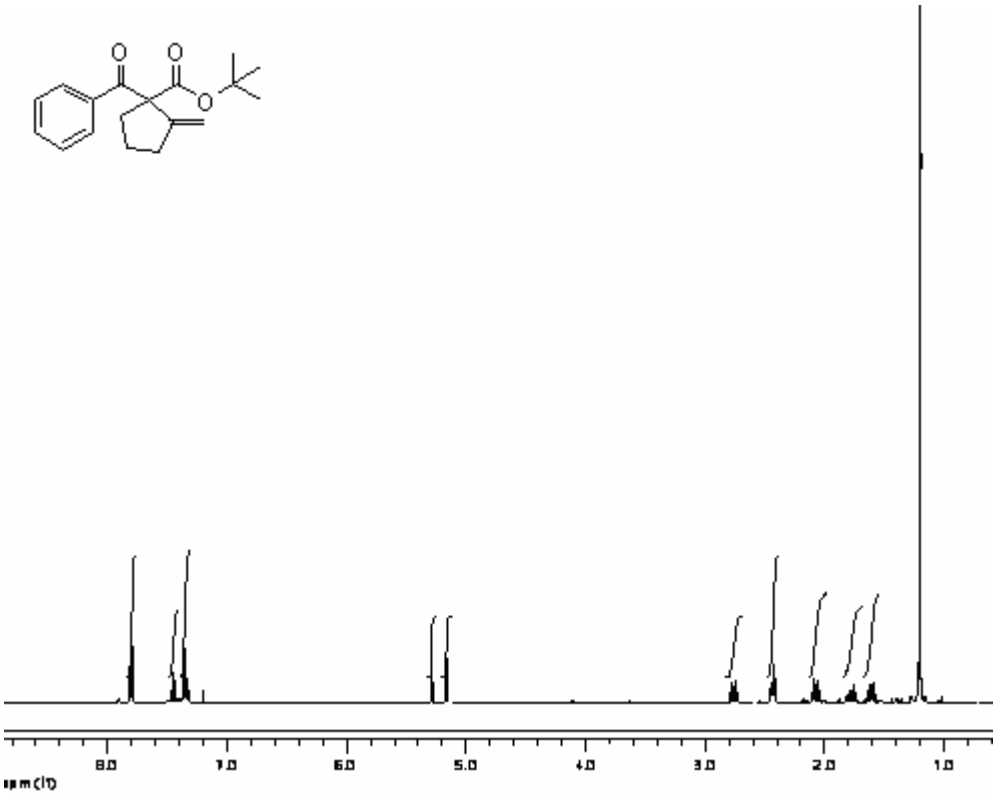
^{1}H NMR of compound 2e



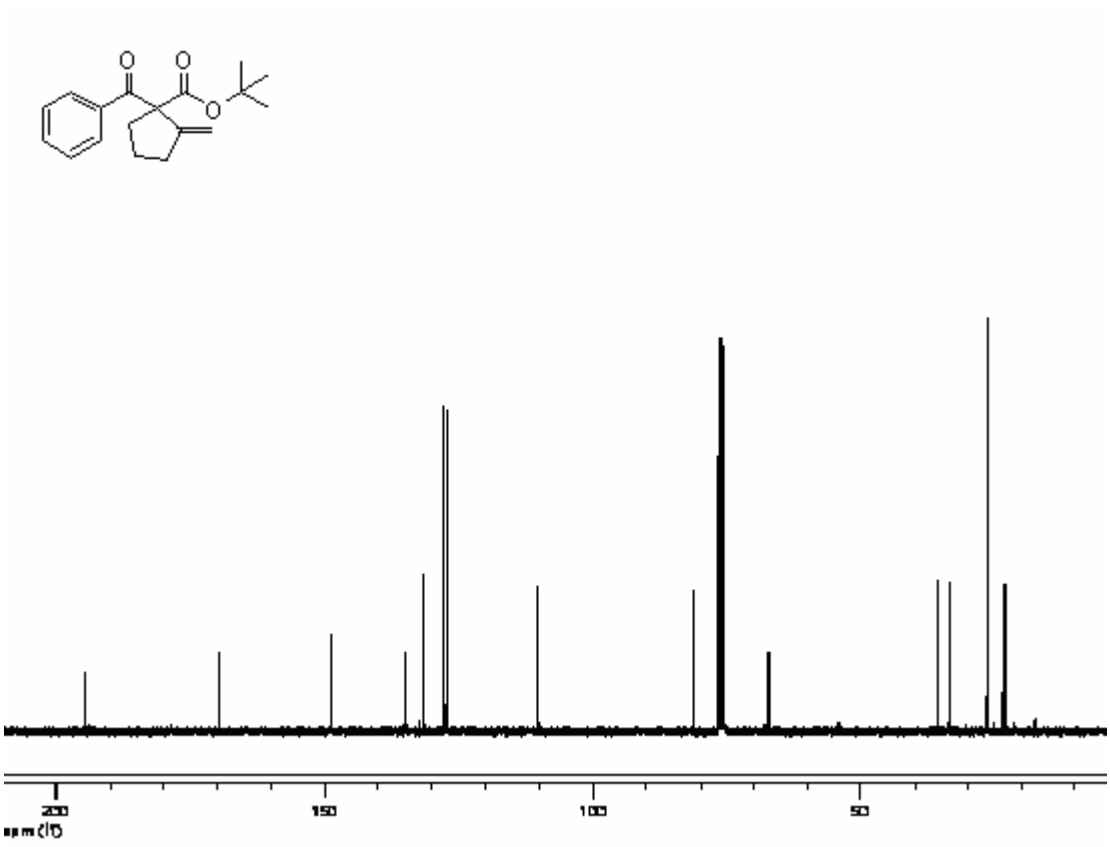
^{13}C NMR of compound 2e



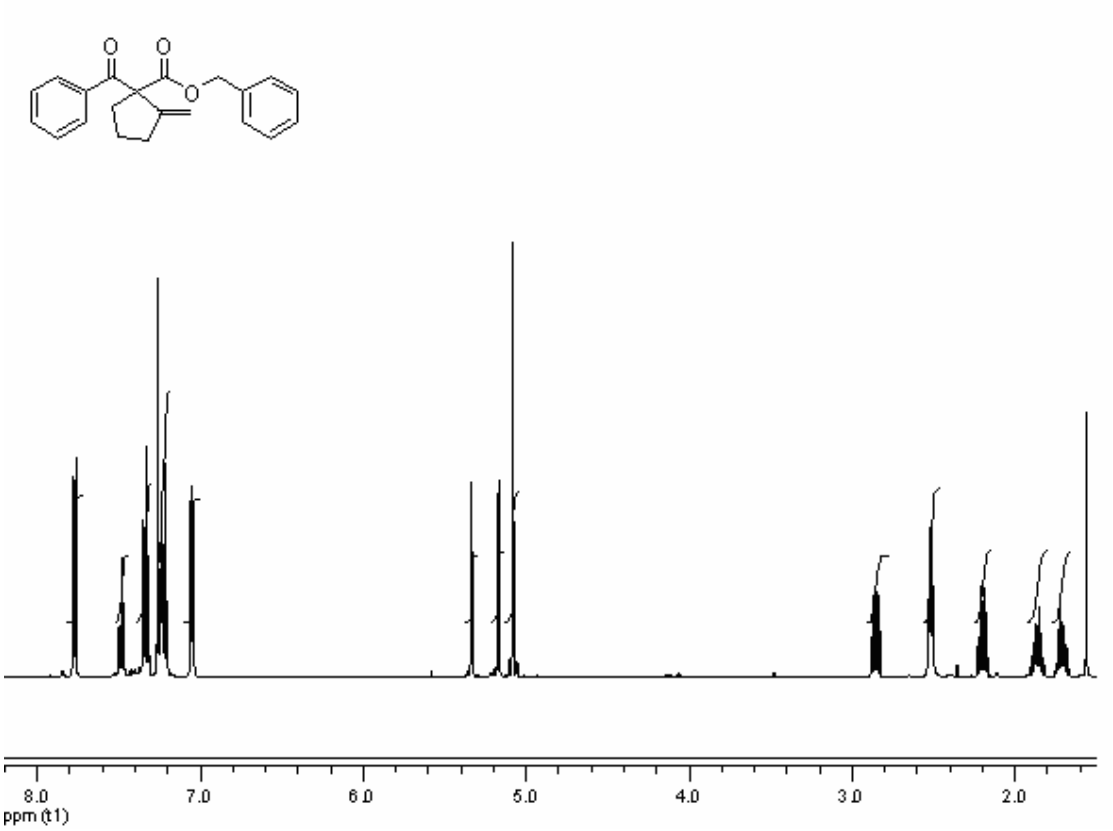
^{1}H NMR of compound 2f



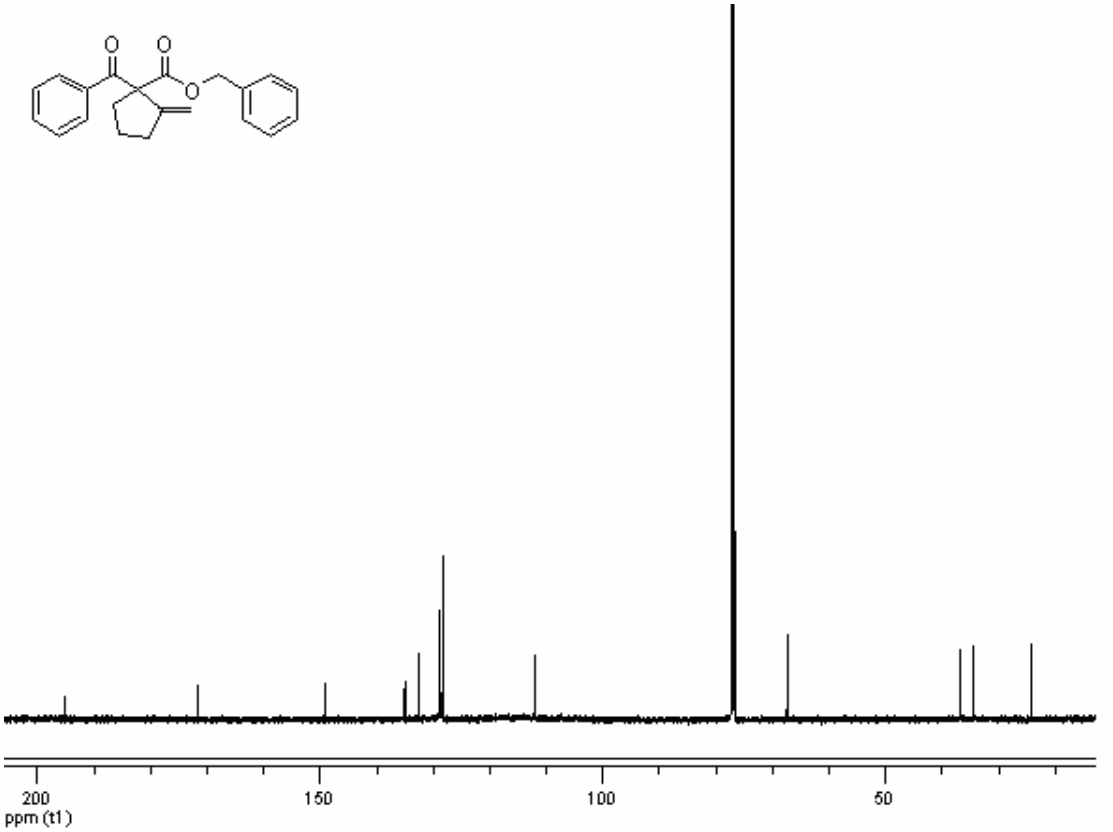
^{13}C NMR of compound 2f



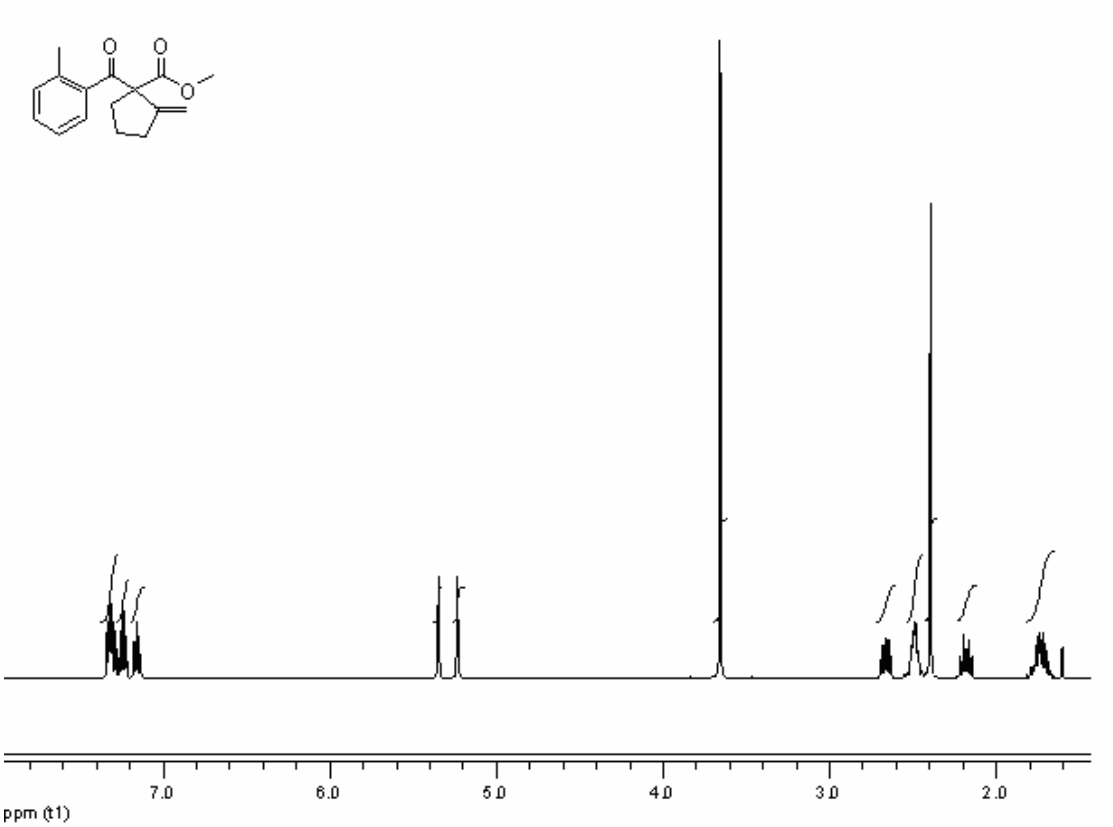
^{1}H NMR of compound 2g



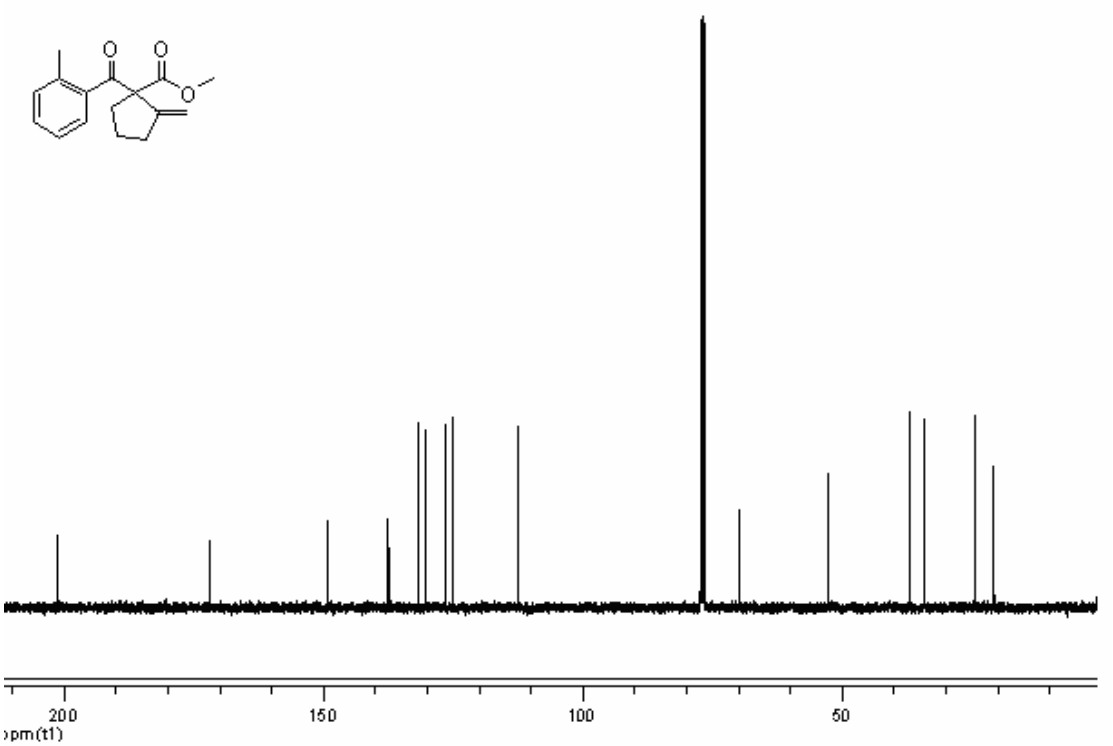
^{13}C NMR of compound 2g



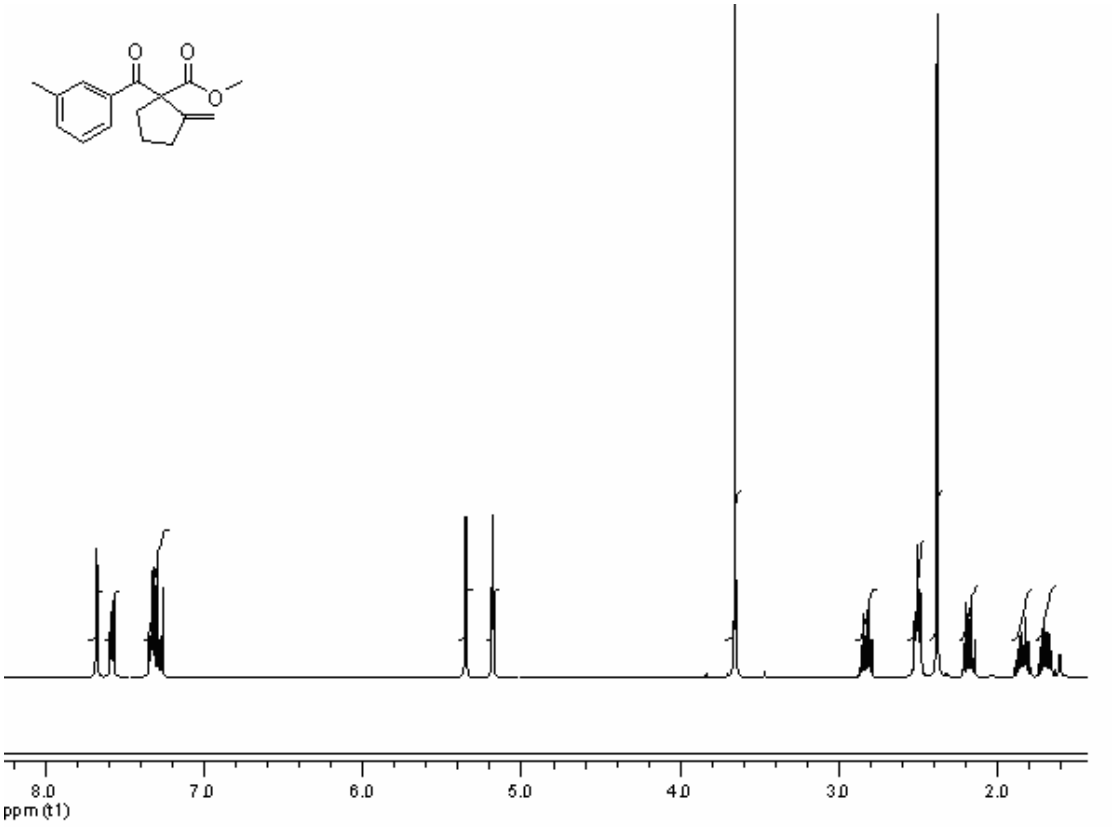
^{1}H NMR of compound 2h



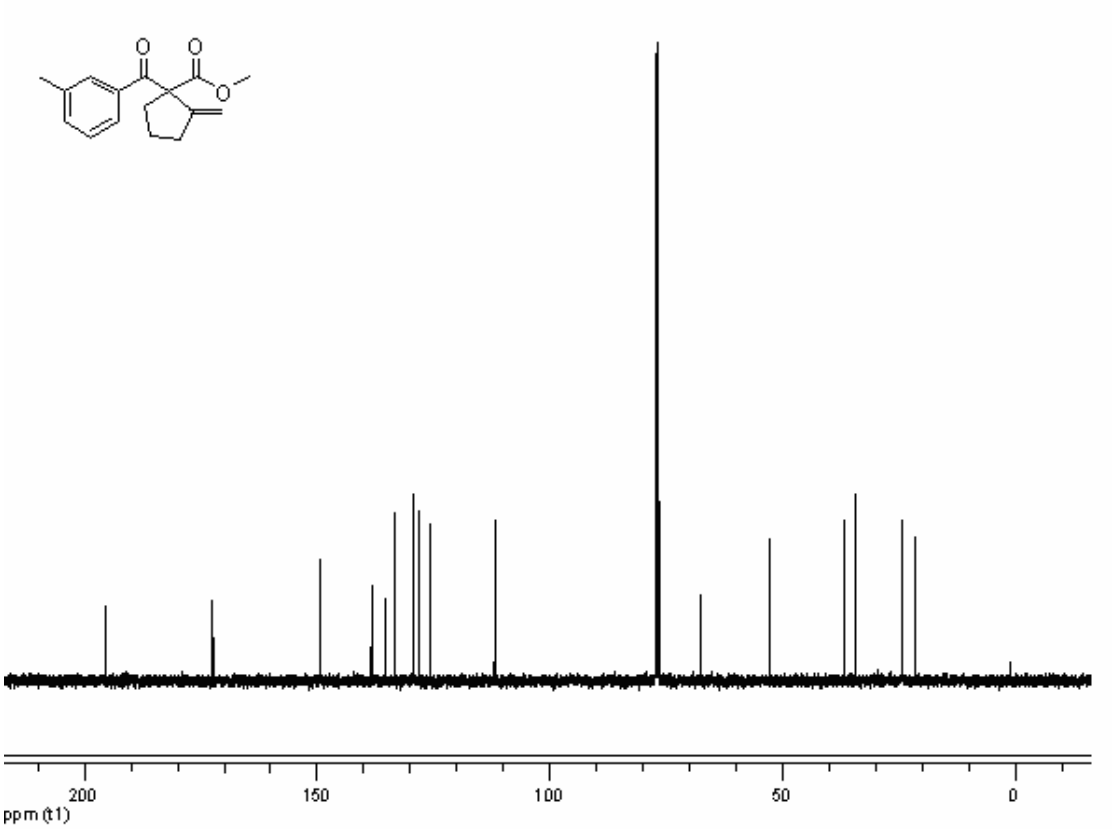
^{13}C NMR of compound 2h



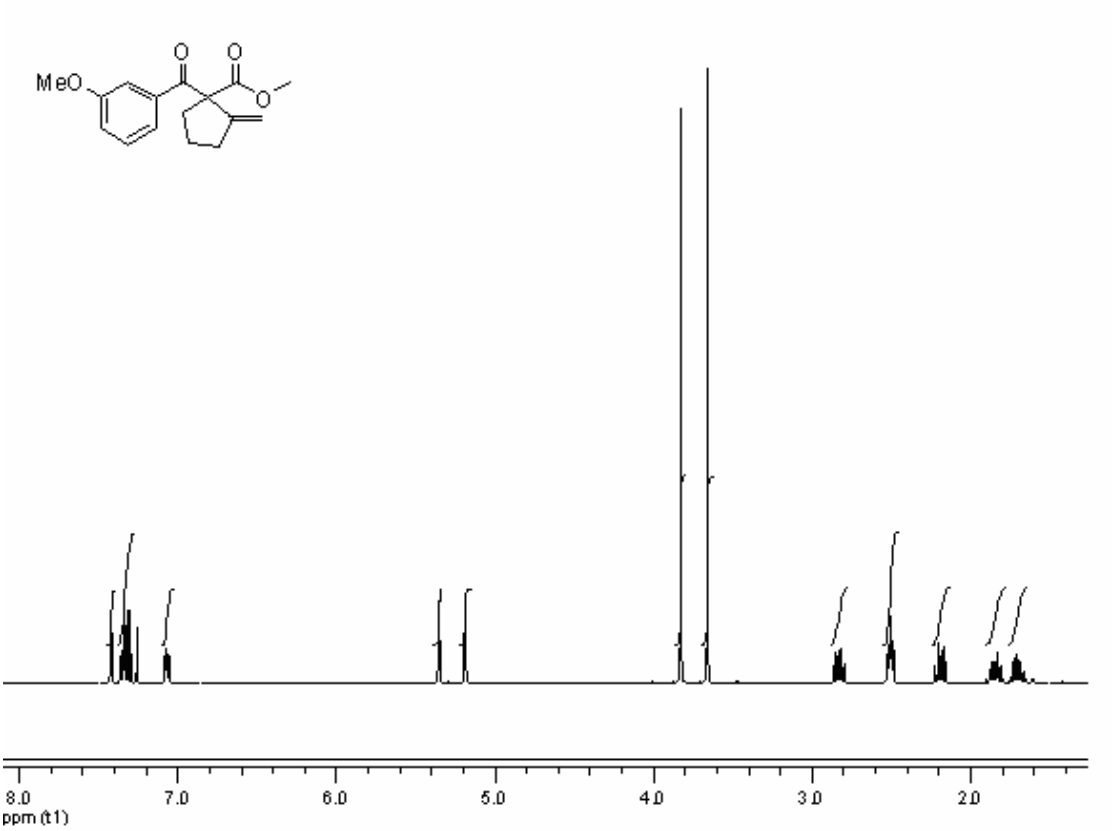
^{1}H NMR of compound 2i



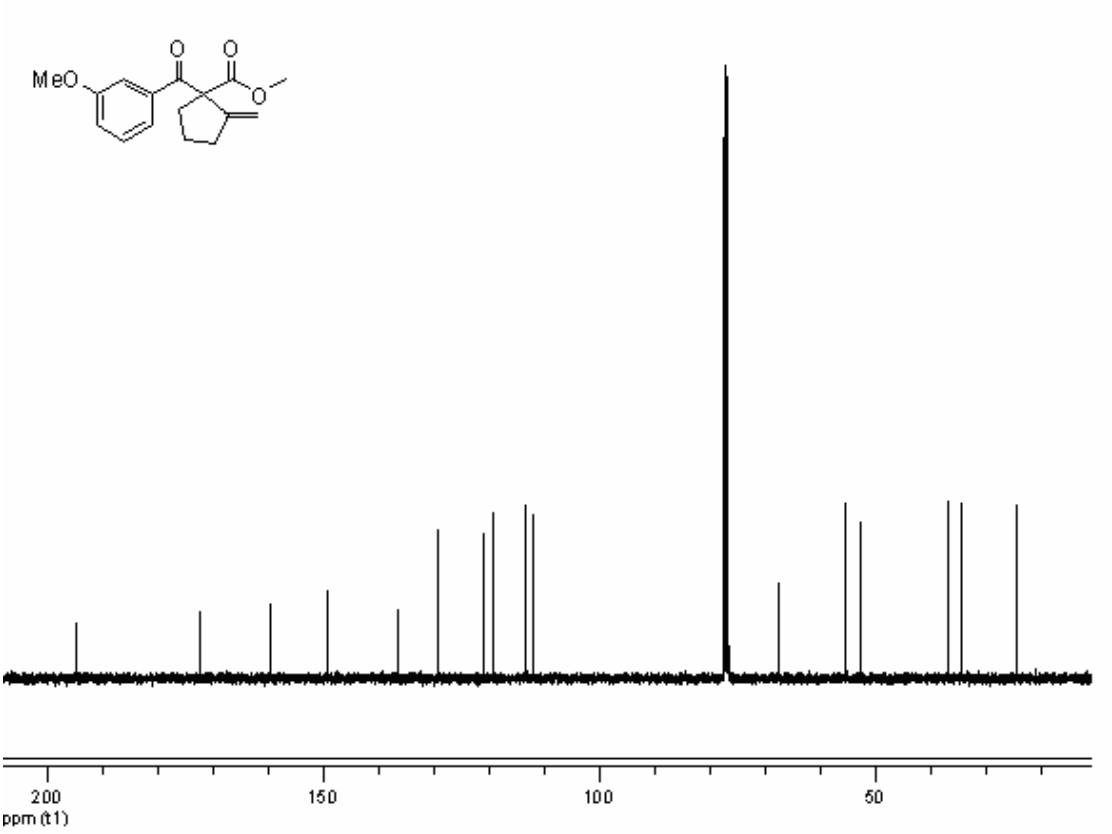
^{13}C NMR of compound 2i



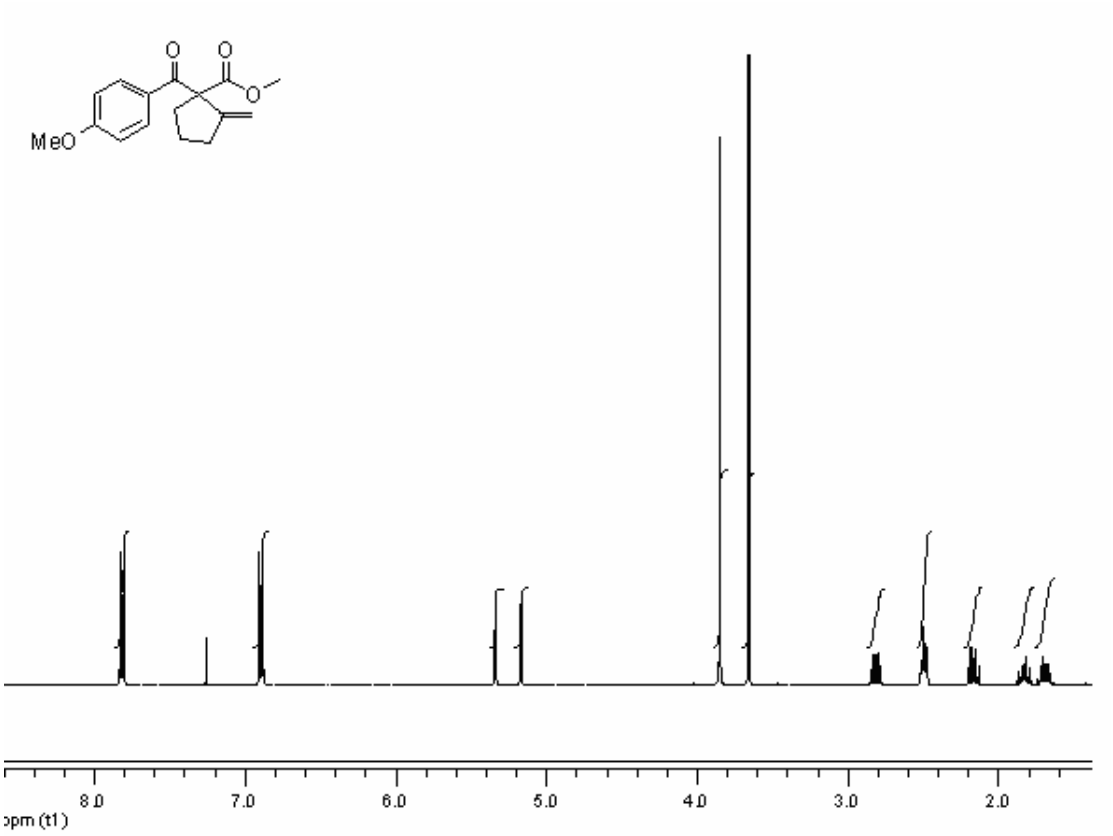
^{1}H NMR of compound 2j



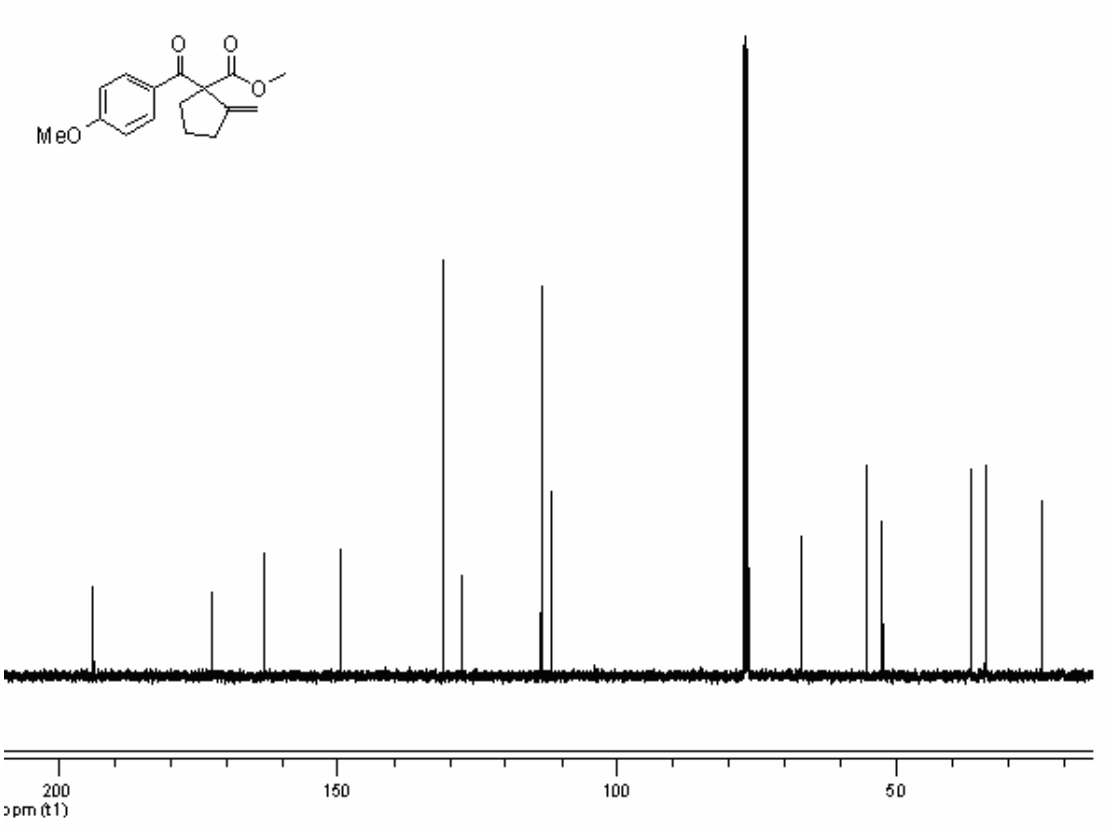
^{13}C NMR of compound 2j



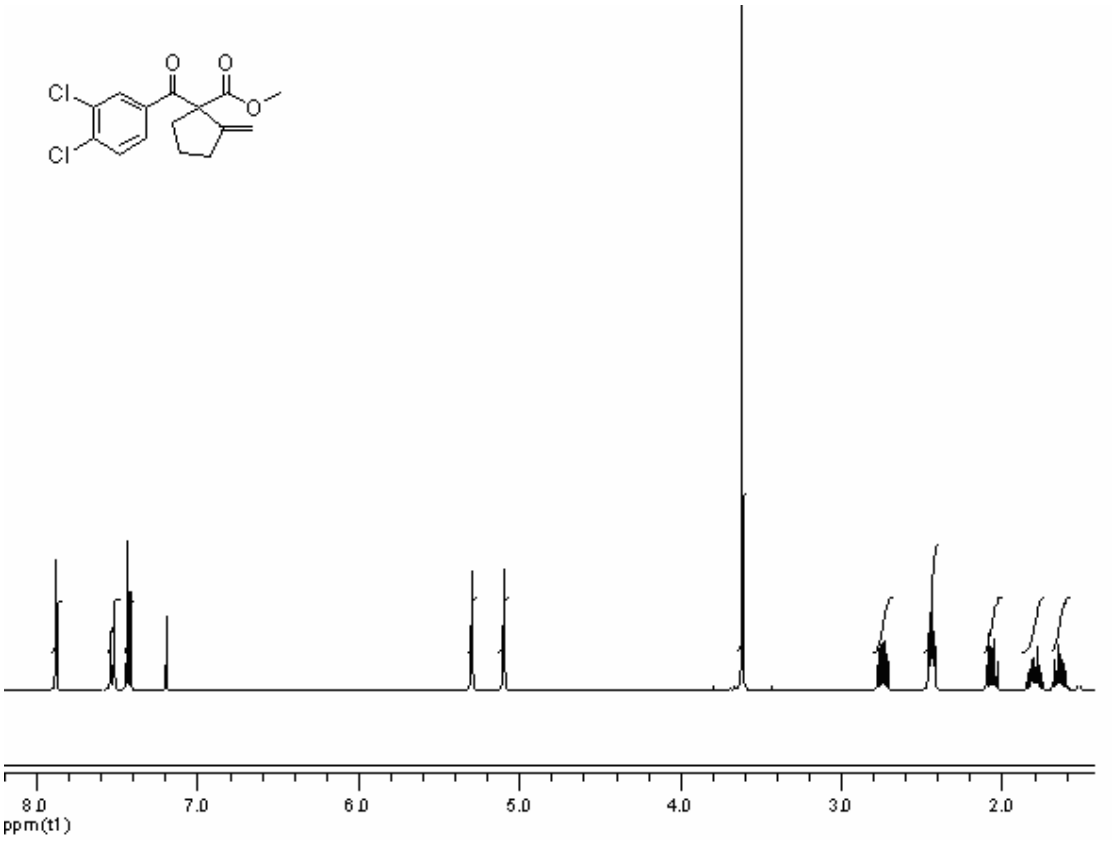
^{1}H NMR of compound 2k



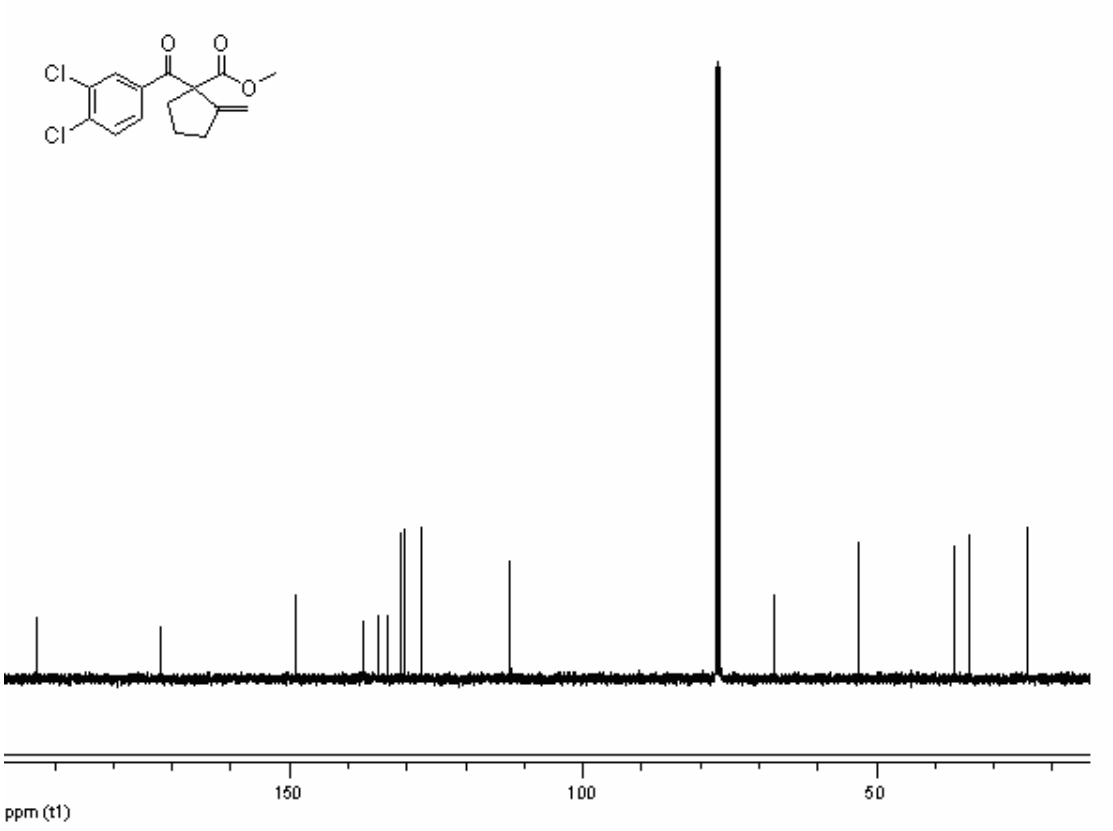
^{13}C NMR of compound 2k



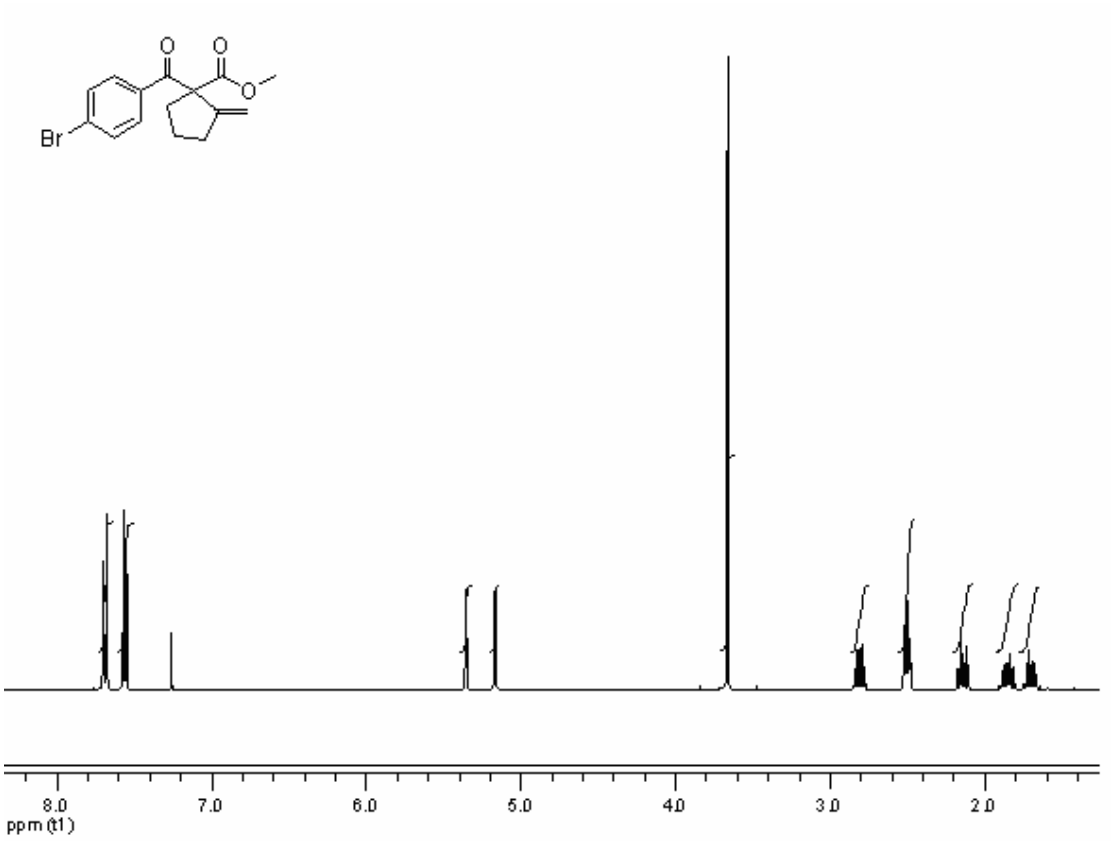
^{1}H NMR of compound 2l



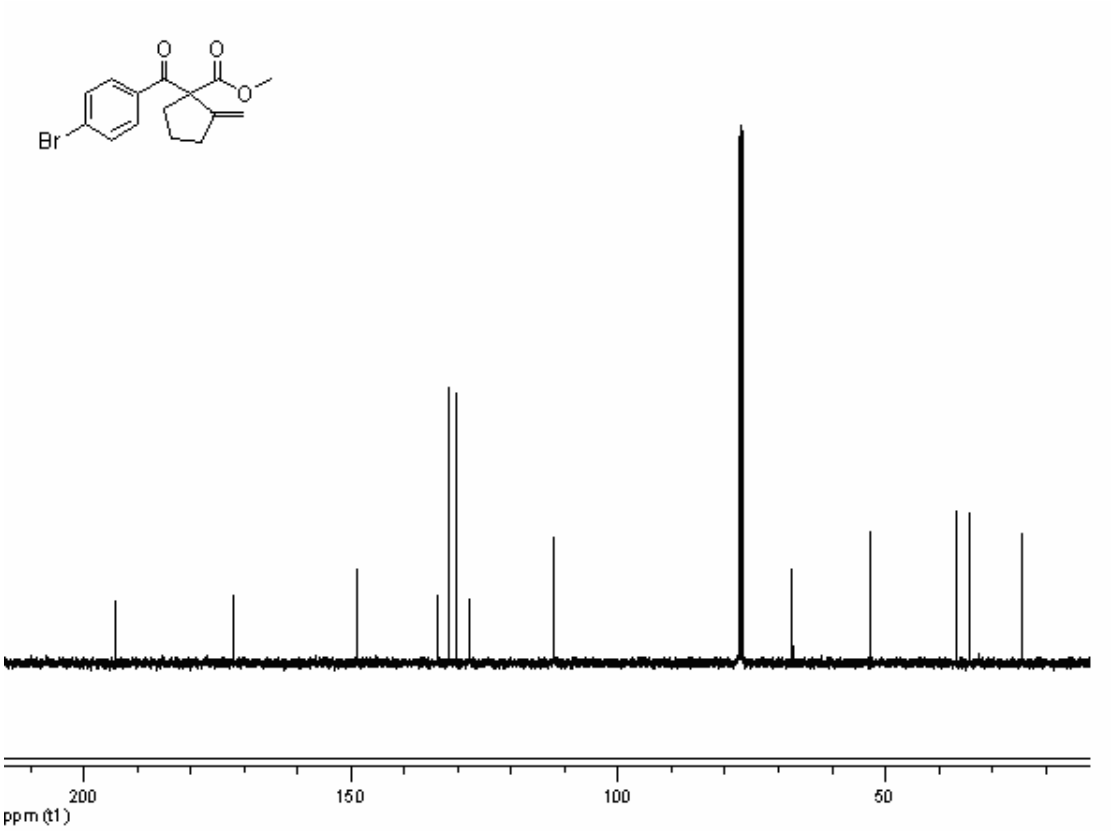
^{13}C NMR of compound 2l



^{1}H NMR of compound 2m



^{13}C NMR of compound 2m



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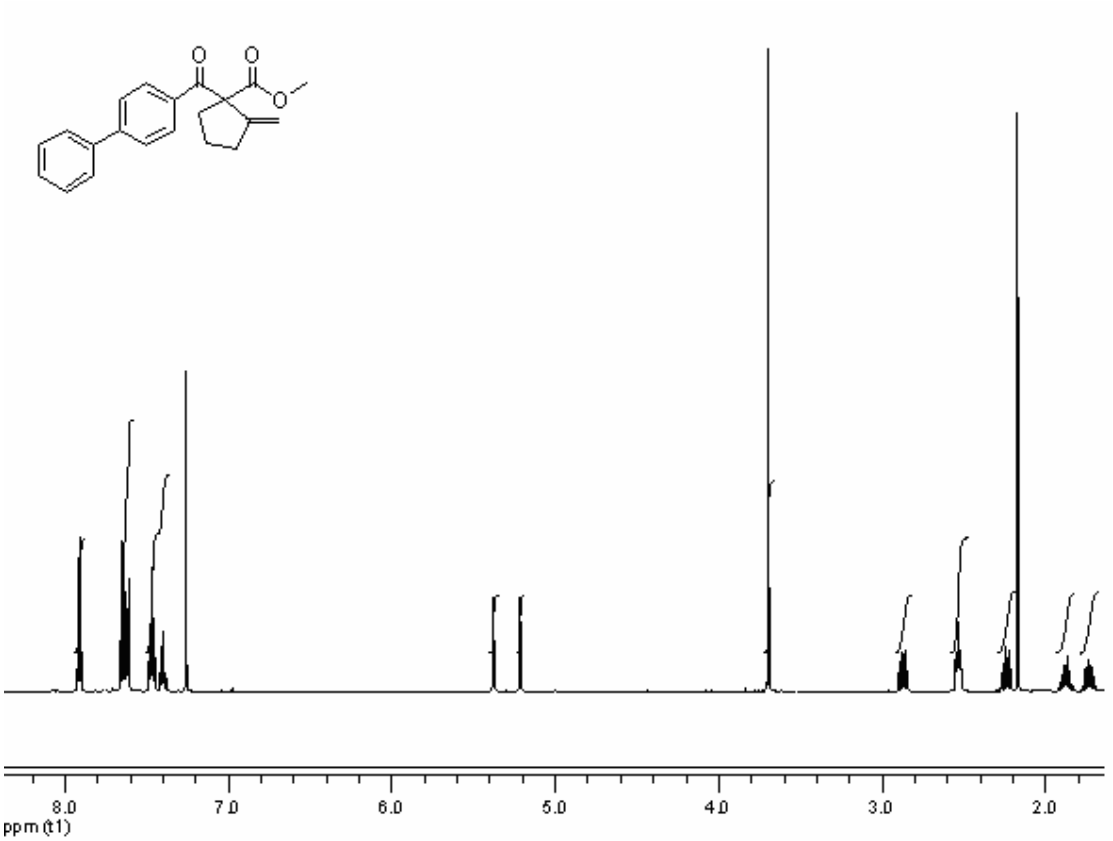

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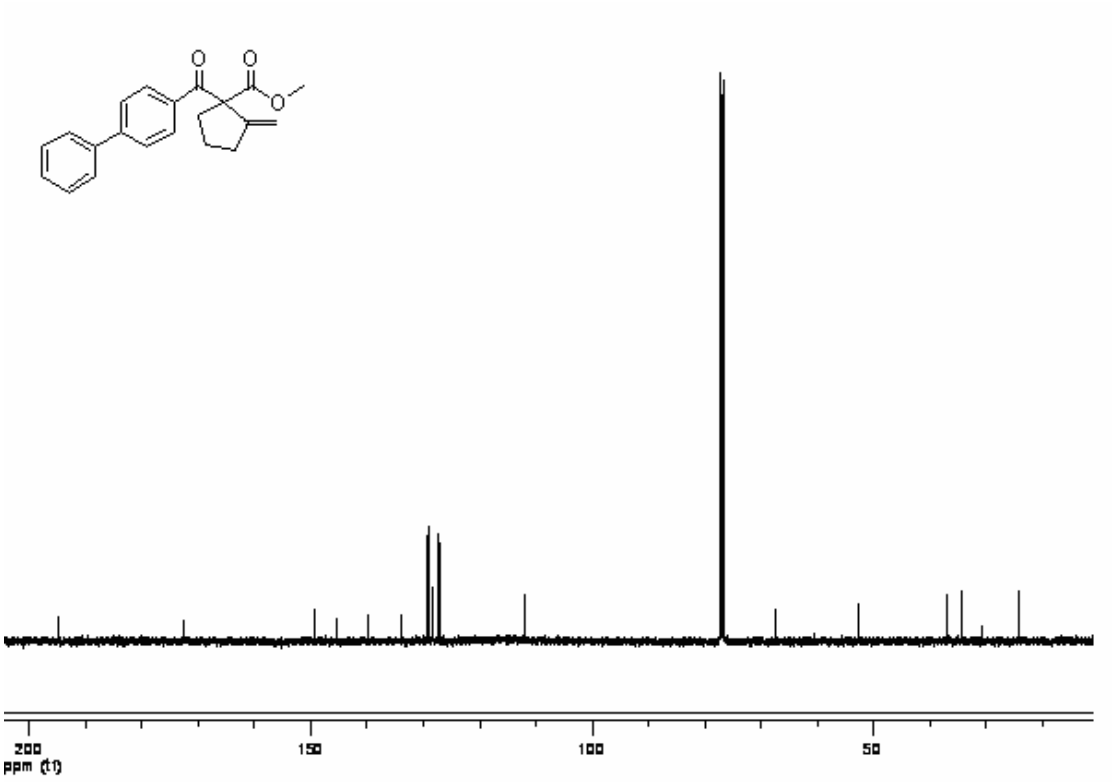

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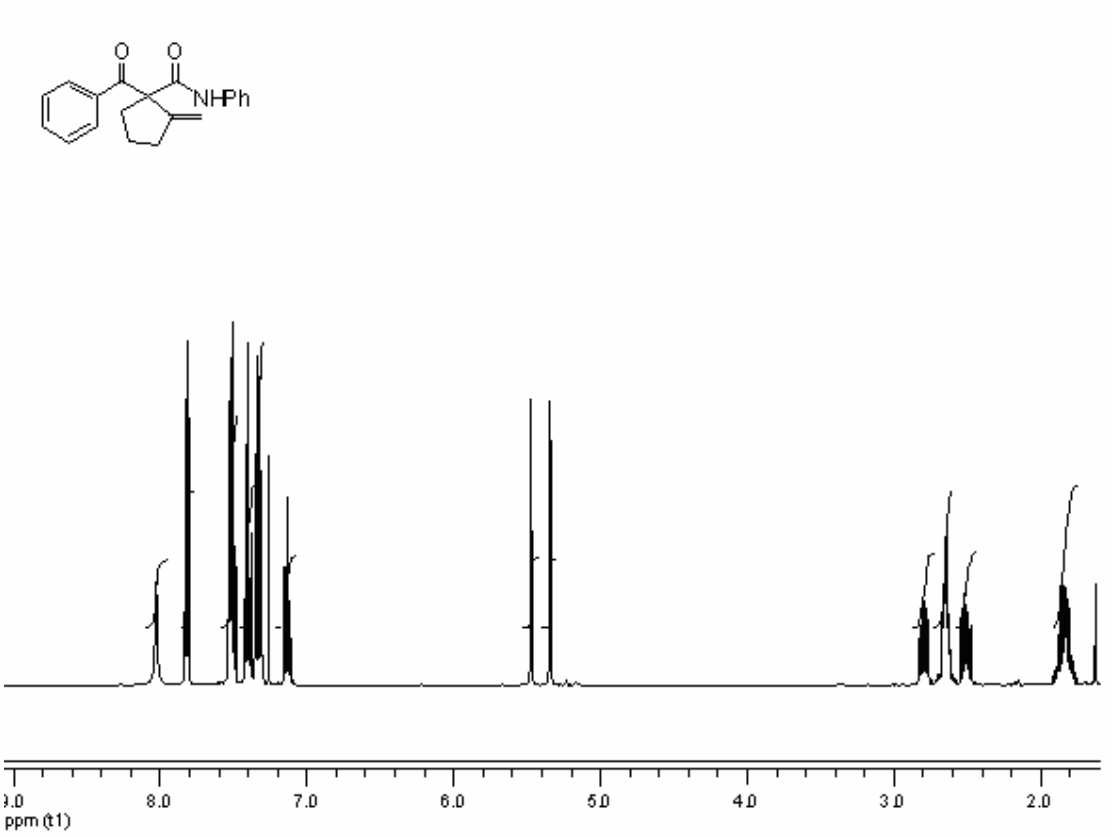
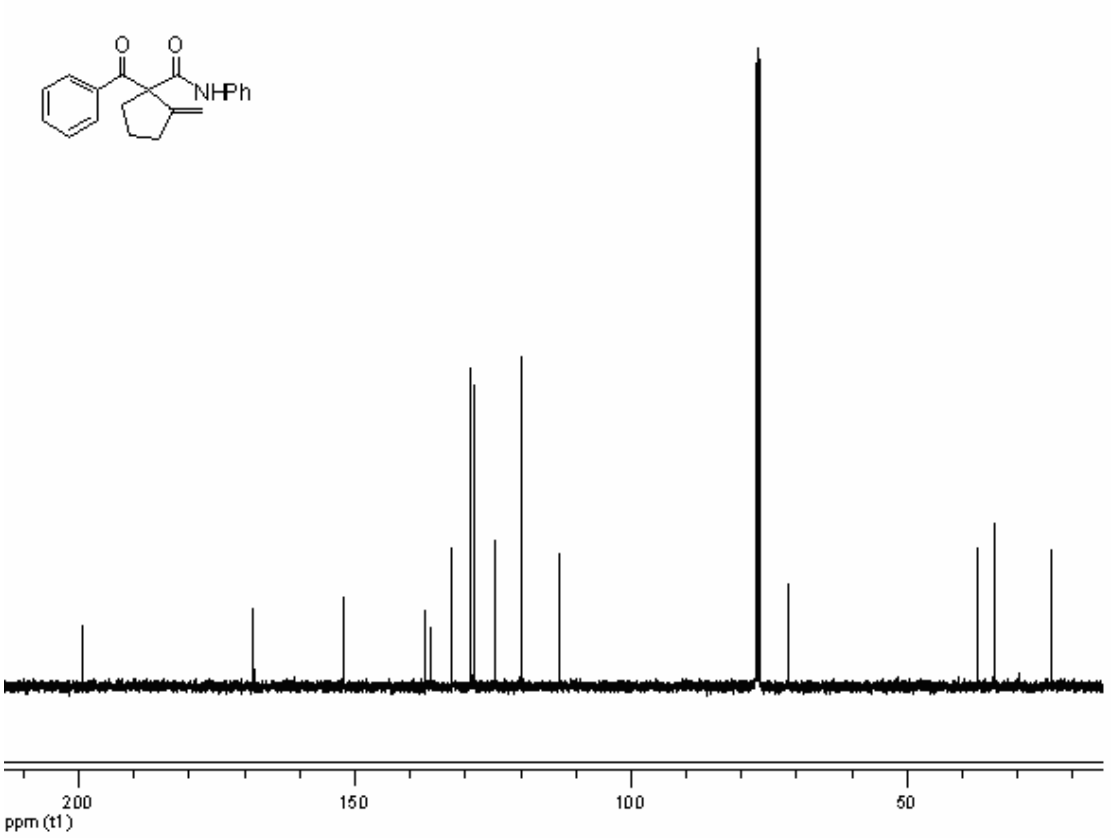
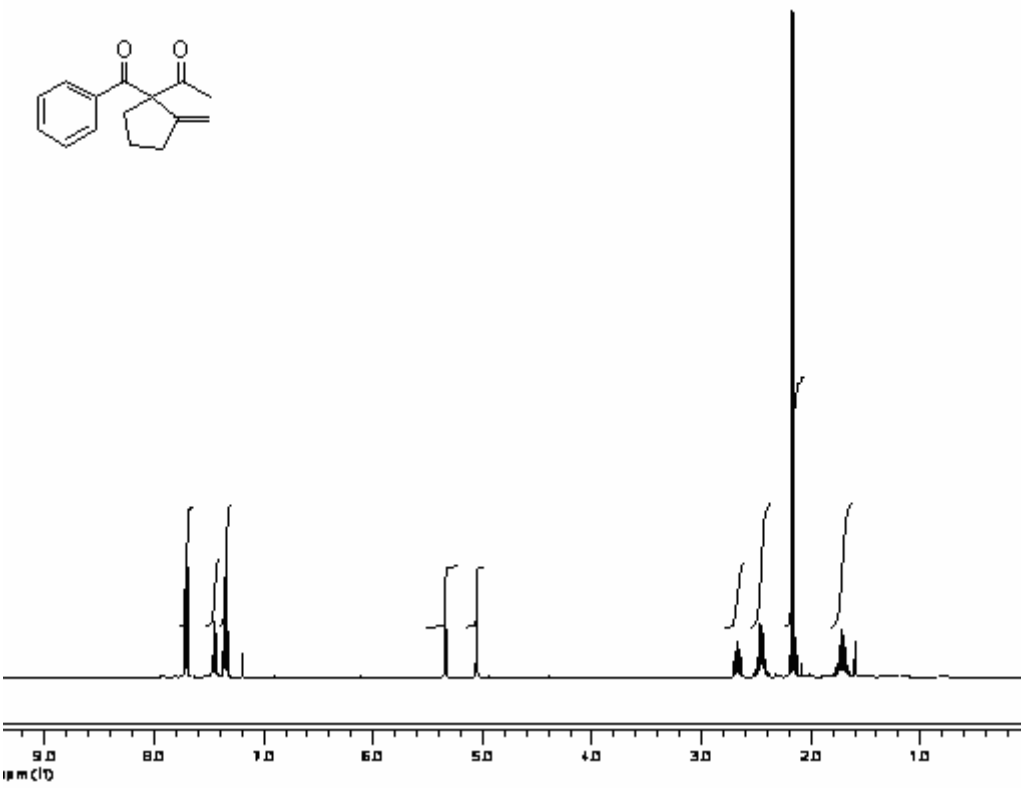


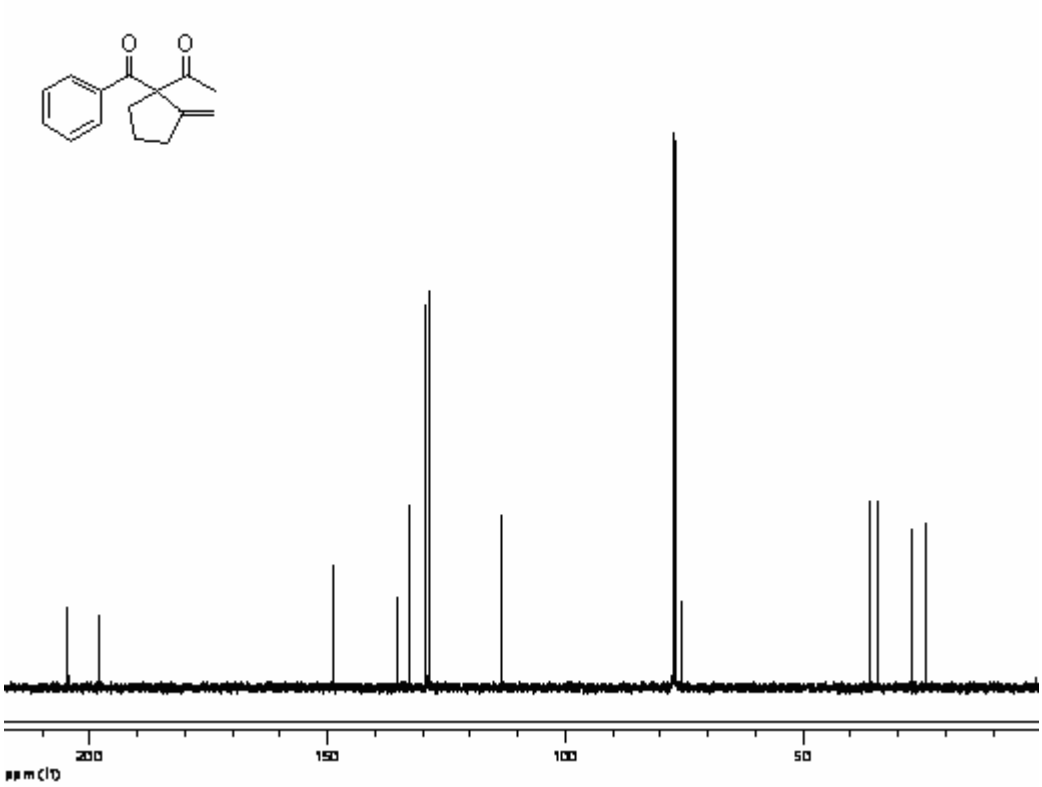
^{13}C NMR of compound 2o



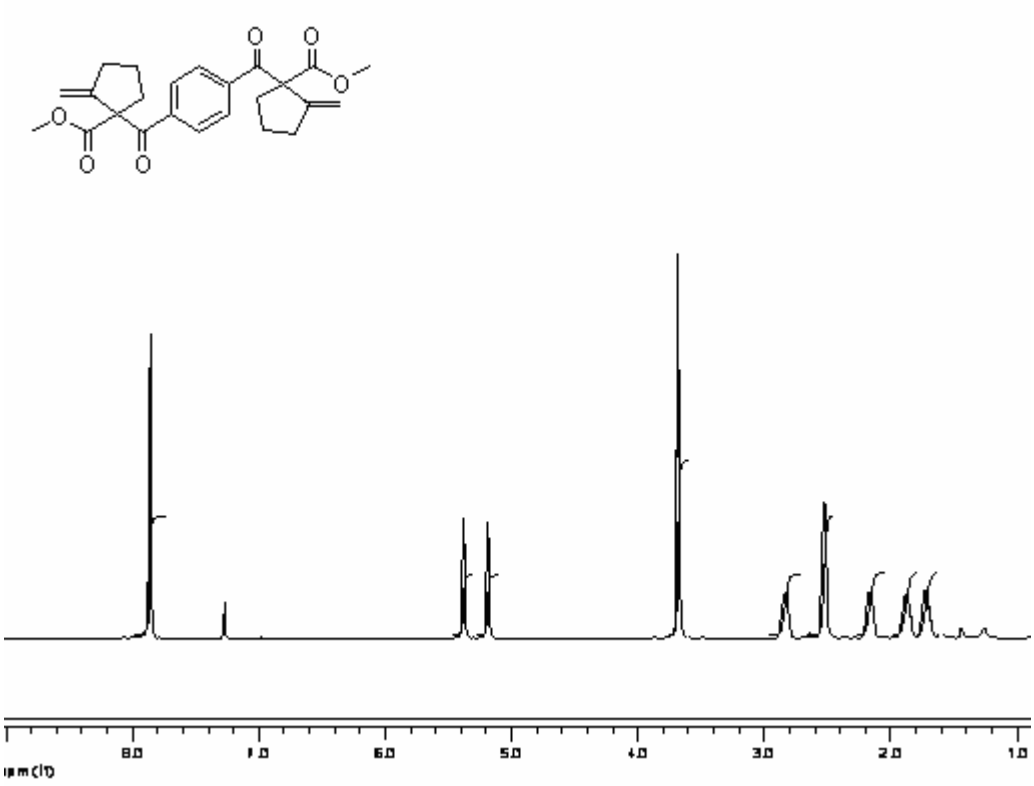
^{1}H NMR of compound 2p



^{13}C NMR of compound 2p



^{1}H NMR of compound 2q



^{13}C NMR of compound 2q