Electronic Supplementary Information

Efficient conversion of the nitronate into nitrile oxide using Cyanuric Chloride. One-Pot synthesis of bicyclic isoxazolines and isoxazoles from nitroalkenes.

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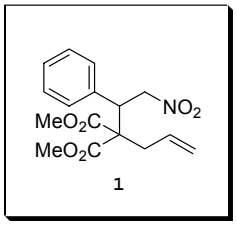
Table of Contents

General. All reactions were performed in oven-dried glassware under a positive pressure of nitrogen when the reactions were sensitive to moisture or oxygen. Solvent was dried over molecular sieves 4 Å. All other commercially available reagents were used as received without purification. Analytical thin layer chromatography was performed with E. Merck silica gel 60F glass plates and flash chromatography by use of E. Merck silica gel 60 (230-400 mesh). MS or HRMS were measured by JEOL JMS-D300 or JEOL JMS-HX110 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Gemini-200 or Bruker Aavance EX 400 or 500 FT NMR. Elemental analyses were analyzed by HERAEUS VarioEL-III (for CHN). ^{1}H NMR data are reported with the solvent resonance as the internal standard relative to $CDCl_3$-TMS (δ = 0.00) as follows; chemical shift (δ), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broadened, m = multiplet), coupling constants (J, given in Hz). ^{13}C NMR chemical shifts (δ) are recorded in parts per million (ppm) relative to $CDCl_3$ (δ = 77.23) as internal standards**.** High-resolution mass spectra (HRMS) are reported in *m/z*.

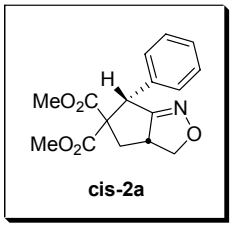
Characterization Data of Compounds

3,3-Dimethoxycarbonyl-1-nitro-2-phenylhex-5-ene (1)



Purified by column chromatography (ethyl acetate–hexanes 1:20) after concentration in vacuo to give a colorless oil; IR ($CHCl_3$) ν 3034, 2955, 2246, 1739, 1640, 1602, 1495, 1456, 1436, 1300, 1255, 1218, 1141, 1083 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (m, 3H), 7.13-7.10 (m, 2H), 5.79-5.70 (m, 1H), 5.15-4.96 (m, 4H), 4.20 (dd, J = 10.8, 7.4 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 2.58 (dd, J = 14.4, 6.7 Hz, 1H), 2.28 (dd, J = 14.4, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.05, 169.88, 134.81, 131.78, 128.78, 128.50, 119.79, 78.27, 60.80, 52.71, 52.67, 46.76, 38.45; HRMS (CI) *m/z* calcd. for $C_{16}H_{19}NO_6$ (M^+) 321.1212, found 321.1205.

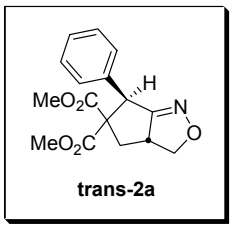
***cis*-5,5-Dimethoxycarbonyl-6-phenyl-3a,4-dihydro-3H,6H-cyclopenta[c]isoxazole (*cis*-2a)**



cis-2a

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a colorless oil; IR ($CHCl_3$) ν 3033, 2954, 2873, 1732, 1648, 1603, 1497, 1456, 1435, 1274, 1212, 1167, 1100, 1080, 1010 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 5H), 5.02 (d, J = 1.2 Hz, 1H), 4.64 (dd, J = 9.7, 8.5 Hz, 1H), 4.10 (dd, J = 12.3, 8.5 Hz, 1H), 3.90-3.80 (m, 1H), 3.81 (s, 3H), 3.11 (s, 3H), 2.70 (dd, J = 13.6, 11.2 Hz, 1H), 2.56 (dd, J = 13.6, 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.33, 170.46, 168.43, 135.38, 129.82, 128.11, 127.90, 75.09, 72.20, 53.42, 52.23, 51.88, 46.71, 35.14; HRMS (CI) *m/z* calcd for $C_{16}H_{17}O_5$ (M^+) 303.1107, found 303.1109.

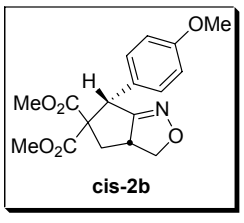
***trans*-5,5-Dimethoxycarbonyl-6-phenyl-3a,4-dihydro-3H,6H-cyclopenta[c]isoxazole (*trans*-2a)**



trans-2a

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a colorless oil; IR ($CHCl_3$) ν 3004, 2954, 2870, 1732, 1649, 1604, 1497, 1455, 1435, 1280, 1259, 1208, 1176, 1102, 1078, 1009 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30-7.20 (m, 5H), 5.01 (d, J = 1.4 Hz, 1H), 4.68 (dd, J = 9.6, 7.7 Hz, 1H), 4.62-4.56 (m, 1H), 3.91 (dd, J = 12.0, 7.7 Hz, 1H), 3.81 (s, 3H), 3.04 (s, 3H), 2.87 (dd, J = 12.8, 7.6 Hz, 1H), 1.80 (dd, J = 12.8, 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.80, 170.65, 169.60, 135.63, 128.59, 128.24, 127.64, 75.08, 71.42, 55.34, 53.12, 52.10, 45.88, 36.47; HRMS (CI) *m/z* calcd for $C_{16}H_{17}O_5$ (M^+) 303.1107, found 303.1111.

***cis*-5,5-Dimethoxycarbonyl-6-(4-methoxylphenyl)-3a,4-dihydro-3H,6H-cyclopenta[c]isoxazole (*cis*-2b)**

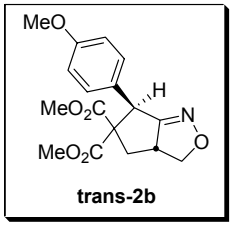


cis-2b

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a colorless oil; IR ($CHCl_3$) ν 3462, 3001, 2954, 2840, 2252, 2053, 1731, 1612, 1583, 1515, 1460, 1435, 1362, 1251, 1213, 1180, 1100, 1032, 945, 908, 891, 868, 838 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23-7.20

(m, 2H), 6.84-6.80 (m, 2H), 4.97 (s, 1H), 4.63 (dd, J = 9.5, 8.2 Hz, 1H), 4.08 (dd, J = 12.3, 8.2 Hz, 1H), 3.90-3.81 (s, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.18 (s, 3H), 2.67 (dd, J = 13.6, 11.1 Hz, 1H), 2.54 (dd, J = 13.6, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.57, 170.86, 168.79, 159.33, 131.13, 127.40, 113.69, 75.33, 70.17, 55.38, 53.56, 52.53, 51.95, 46.27, 35.16; HRMS (CI) *m/z* calcd for $C_{17}H_{19}NO_6$ (M^+) 333.1212, found 333.1215.

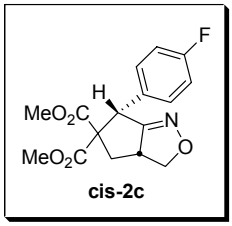
***trans*-5,5-Dimethoxycarbonyl-6-(4-methoxylphenyl)-3a,4-dihydro-3H,6H-cyclopenta[c]isoxazole (*trans*-2b)**



trans-2b

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a colorless oil; IR ($CHCl_3$) ν 2950, 1731, 1610 ,1514, 1434, 1369, 1278, 1250, 1207, 1179, 1102, 1077, 1031, 836, 788 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.12 (m, 2H), 6.83-6.79 (m, 2H), 4.96 (d, J = 1.32 Hz, 1H), 4.67 (dd, J = 9.6, 7.7 Hz, 1H), 4.63-4.52 (m, 1H), 3.88 (s, 3H), 3.77 (s, 3H), 3.12 (s, 3H), 2.85 (dd, J = 12.9, 7.6 Hz, 1H), 1.79 (dd, J = 12.8, 11.1 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 171.29, 171.01, 170.02, 159.26, 129.99, 128.80, 113.89, 75.34, 71.60, 55.50, 55.48, 53.35, 52.49, 45.53, 36.61; HRMS (CI) *m/z* calcd for $C_{17}H_{19}NO_6$ (M^+) 333.1212, found 333.1215.

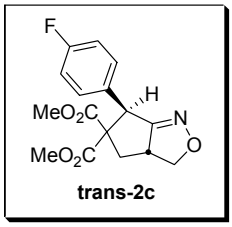
***cis*-5,5-Dimethoxycarbonyl-6-(4-fluorophenyl)-3a,4-dihydro-3H,6H-cyclopenta[c]isoxazole (*cis*-2c)**



cis-2c

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a colorless oil; IR ($CHCl_3$) ν 3445, 2955, 1730, 1606, 1510, 1435, 1365, 1275, 1216, 1161, 1100, 1075, 842 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 2H), 7.02-6.96 (m, 2H), 5.01 (s, 1H), 4.65 (dd, J = 9.7, 8.2 Hz, 1H), 4.10 (dd, J = 12.2, 8.2 Hz, 1H), 4.13-4.08 (m, 1H), 3.82 (s, 3H), 3.18 (s, 3H), 2.67 (dd, J = 13.7, 11.0 Hz, 1H), 2.54 (dd, J = 13.7, 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.47, 170.30, 168.72, 162.58 (d, J = 246 Hz), 131.84 (d, J = 8 Hz), 131.15 (d, J = 3 Hz), 115.28 (d, J = 21 Hz), 75.50, 70.10, 53.70, 52.61, 51.91, 46.26, 35.25; HRMS (CI) *m/z* calcd for $C_{16}H_{16}FNO_5$ (M^+) 321.1013, found 321.1014.

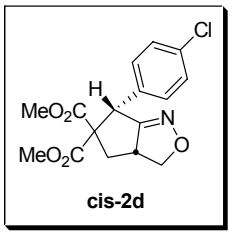
***trans*-5,5-Dimethoxycarbonyl-6-(4-fluorophenyl)-3a,4-dihydro-3H,6H-cyclopenta[c]isoxazole (*trans*-2c)**



trans-2c

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a white solid with the melting point of 140-141 ^{o}C; IR ($CHCl_3$) ν 2994, 2950, 2868, 1731, 1605, 1509, 1435, 1279, 1259, 1207, 1174, 1099, 1077, 1012, 849 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.19 (m, 2H), 7.01-6.95 (m, 2H), 4.99 (d, *J* = 1.2 Hz, 1H), 4.68 (dd, *J* = 9.6, 7.8 Hz, 1H), 4.63 -4.49 (m, 1H), 3.92 (dd, *J* = 12.7, 7.8 Hz, 1H) 3.81 (s, 3H), 3.12 (s, 3H), 2.85 (dd, *J* = 12.8 , 7.6 Hz, 1H), 1.81 (dd, *J* = 12.8, 11.3 Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.91, 170.84, 169.82, 162.43 (d, *J* = 246 Hz), 132.59 (d, *J* = 3 Hz), 130.62 (d, *J* = 8 Hz), 115.42 (d, *J* = 21 Hz), 75.39, 71.63, 55.42, 53.43, 52.48, 45.44, 36.67; HRMS (CI) *m/z* calcd for $C_{16}H_{16}FNO_5$ (M^+) 321.1013, found 321.1014.

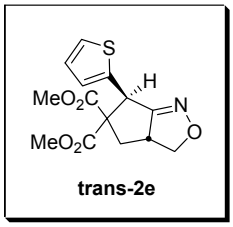
***cis*-5,5-Dimethoxycarbonyl-6-(4-chlorophenyl)-3a,4-dihydro-3H,6H-cyclopenta[c]isoxazole (*cis*-2d)**



cis-2d

Purified by column chromatography (ethyl acetate–hexanes 1:10) after concentration in vacuo to give a colorless oil; IR ($CHCl_3$) ν 3460, 3001, 2954, 1731, 1646, 1596, 1494, 1435, 1415, 1362, 1273, 1213, 1167, 1092, 1016, 942, 908, 838 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 4H), 4.99 (d, *J* = 1.04 Hz, 1H), 4.65 (dd, *J* = 9.7, 8.2 Hz, 1H), 4.10 (dd, *J* = 12.2, 8.2 Hz, 1H), 3.92-3.82 (m, 1H), 3.82 (s, 3H), 3.19 (s, 3H), 2.67 (dd, *J* = 13.7, 10.9 Hz, 1H), 2.55 (dd, *J* = 13.7, 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.40, 170.03, 168.66, 134.19, 133.90, 131.49, 128.54, 75.52, 70.09, 53.74, 52.68, 51.91, 46.37, 35.28; HRMS(CI) *m/z* calcd for $C_{16}H_{16}ClNO_5$ (M^+) 337.0717, found 337.0716.

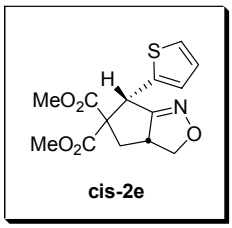
***trans*-5,5-Dimethoxycarbonyl-6-(4-chlorophenyl)-3a,4-dihydro-3H,6H-cyclopenta[c]isoxazole (*trans*-2d)**



trans-2e

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a colorless oil; IR ($CHCl_3$) ν 3463, 3000, 2953, 2869, 1732, 1647, 1595, 1492, 1435, 1412, 1362, 1275, 1258, 1208, 1175, 1090, 1015, 930, 908, 889, 868, 842 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 2H), 7.20-7.16 (m, 2H), 4.98 (d, J = 1.7 Hz , 1H), 4.68 (dd, J = 9.6, 7.8 Hz, 1H), 4.63-4.52 (m, 1H), 3.92 (dd, J = 12.3, 7.9 Hz , 1H), 3.81 (s, 3H), 3.13 (s, 3H), 2.85 (ddd, J = 8.2, 7.6, 0.4 Hz, 1H), 1.81 (dd, J = 12.8, 11.2 Hz , 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.78, 170.64, 169.72, 135.30, 133.89, 130.26, 128.65, 75.40, 71.60, 55.41, 53.47, 52.51, 45.53, 36.69; HRMS (CI) *m/z* calcd for $C_{16}H_{16}ClNO_5$ (M^+) 337.0717, found 337.0716.

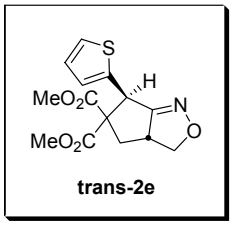
cis-5,5-Dimethoxycarbonyl-6-(2-thienyl)-3a,4-dihydro-3H,6H-cyclopenta[c]isoxazole (_cis_-2e)



cis-2e

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a colorless oil; IR ($CHCl_3$) ν 3108, 3000, 2953, 2879, 1731, 1434, 1361, 1279, 1246, 1208, 1175, 1077, 1042, 943, 905, 886, 864, 711 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, J = 5.1, 0.8 Hz, 1H), 7.09 (d, J = 3.5 Hz, 1H), 6.95 (dd, J = 5.1, 3.5 Hz, 1H), 5.28 (s, 1H), 4.65 (dd, J = 9.7, 8.2 Hz, 1H), 4.12 (dd, J = 12.4, 8.1 Hz, 1H), 3.91-3.82 (m, 1H), 3.82 (s, 3H), 3.32 (s, 3H), 2.64 (dd, J = 13.7, 10.1 Hz, 1H), 2.52 (dd, J = 13.7, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.14, 169.88, 168.66, 136.30, 128.52, 126.64, 125.90, 75.83, 70.05, 52.62, 52.81, 51.29, 42.42, 34.56; HRMS (CI) *m/z* calcd for $C_{14}H_{15}NO_5S$ (M^+) 309.0671, found 309.0670.

trans-5,5-Dimethoxycarbonyl-6-(2-thienyl)-3a,4-dihydro-3H,6H-cyclopenta[c]isoxazole (_trans_-2e)

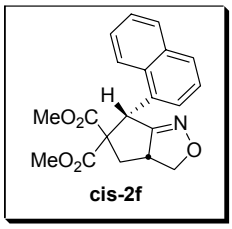


trans-2e

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a colorless oil; IR ($CHCl_3$) ν 3583, 3000, 2953, 2857, 1731, 1434, 1281, 1266, 1208, 1175, 1100, 1077, 1009, 886, 852, 821, 788, 706 cm^{-1}; ^1H NMR

(400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 4.9, 1.4 Hz, 1H), 6.94-6.91 (m, 2H), 5.19 (d, *J* = 1.6 Hz, 1H), 4.68 (dd, *J* = 9.7, 7.8 Hz, 1H), 4.63-4.53 (m, 1H), 3.92 (dd, *J* = 12.2, 7.8 Hz, 1H), 3.82 (s, 3H), 3.29 (s, 3H), 2.91 (dd, *J* = 13.1, 7.9 Hz, 1H), 1.86 (dd, *J* = 13.1, 10.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.66, 170.01, 169.51, 138.86, 127.21, 126.93, 125.59, 75.71, 71.20, 54.11, 53.49, 52.83, 41.82, 36.05; HRMS (CI) *m/z* calcd for $C_{14}H_{15}NO_5S$ (M^+) 309.0671, found 309.0670.

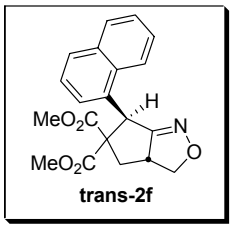
cis-5,5-Dimethoxycarbonyl-6-(naphthalen-1-yl)-3a,4-dihydro-3H,6H-cyclopenta[c]isoxazole (_cis_-2f)



cis-2f

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a white solid which decompose at 190 °C; IR ($CHCl_3$) *ν* 3043, 2994, 2939, 2846, 1750, 1723, 1508, 1448, 1432, 1283, 1247, 1204, 1174, 1166, 1152, 887 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.4 Hz, 1H), 7.82 (d , *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.57-7.53 (m, 1H), 7.49-7.45 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.38-7.37 (m, 1H), 6.06 (s, 1H), 4.69 (dd, *J* = 9.5, 8.4 Hz, 1H), 4.14 (dd, *J* = 12.3, 8.2 Hz, 1H), 4.03-3.81 (m, 1H), 3.85 (s, 3H), 2.82 (t, *J* = 13.0 Hz, 1H), 2.66 (dd, *J* = 13.3, 7.4 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.16, 171.88, 168.15, 133.73, 132.78, 128.78, 128.74, 128.09, 126.50, 125.81, 125.27, 123.81, 75.04, 71.28, 53.88, 52.72, 51.83, 41.12, 36.06; HRMS (CI) *m/z* calcd for $C_{20}H_{19}NO_5$ (M^+) 353.1263, found 353.1263.

trans-5,5-Dimethoxycarbonyl-6-(naphthalen-1-yl)-3a,4-dihydro-3H,6H-cyclopenta[c]isoxazole (_trans_-2f)

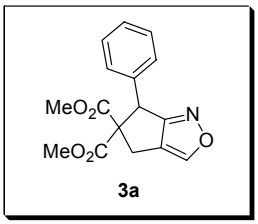


trans-2f

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a white solid with the melting point of 146-148 °C; IR ($CHCl_3$) *ν* 3463, 3049, 3002, 2953, 2872, 1732, 1639, 1597, 1511, 1435, 1398, 1361, 1300,

1276, 1255, 1221, 1205, 1103, 1073, 1016, 924, 904, 887, 791 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.60-7.55 (m, 1H), 7.51-7.47 (m, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 5.83 (s, 1H), 4.74 (dd, *J* = 9.7, 8.0 Hz, 1H), 4.69-4.58 (m, 1H), 4.00 (dd, *J* = 11.7, 8.0 Hz, 1H), 3.81 (s, 3H), 3.03 (dd, *J* = 12.7, 7.8 Hz, 1H), 2.61 (s, 3H), 1.85 (dd, *J* = 12.7, 11.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.78, 171.08, 169.79, 134.71, 133.75, 132.54, 128.78, 128.65, 126.74, 126.24, 126.08, 125.13, 124.67, 75.40, 71.60, 56.01, 53.53, 51.89, 41.94, 37.64; HRMS (CI) *m/z* calcd for $C_{20}H_{19}NO_5$ (M^+) 353.1263, found 353.1263.

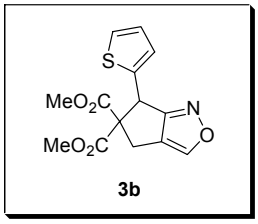
5,5-Dimethoxycarbonyl-6-phenyl-4-dihydro-6H-cyclopenta[c]isoxazole (3a)



3a

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a white solid with the melting point of 135-136 °C; IR ($CHCl_3$) *ν* 3583, 3461, 3127, 2954, 1753, 1731, 1621, 1497, 1434, 1400, 1281, 1261, 1214, 1162, 1144, 1074, 1048, 941, 898, 863, 819 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.30-7.20 (m, 3H), 7.19-7.16 (m, 2H), 5.32 (s, 1H), 3.80 (s, 3H), 3.72 (dd, *J* = 16.6, 1.4 Hz, 1H), 3.21 (s, 3H), 3.14 (dd, *J* = 16.6, 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.02, 171.13, 168.81, 150.43, 136.16, 129.06, 128.56, 128.21, 121.39, 73.01, 53.51, 52.53, 48.72, 29.70; HRMS (CI) *m/z* calcd for $C_{16}H_{15}NO_5$ (M^+) 301.0950, found 301.0955.

5,5-Dimethoxycarbonyl-6-(2-thienyl)-4-dihydro-6H-cyclopenta[c]isoxazole (3b)

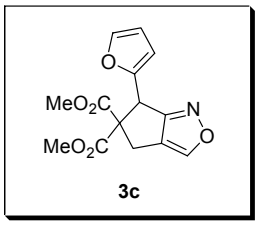


3b

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a white solid with the melting point of 129-130 °C; IR ($CHCl_3$) *ν* 3439, 3109, 2954, 2785, 1732, 1626, 1433, 1409, 1271, 1214, 1174, 1116, 1065, 941, 888, 853, 823, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.23-7.21 (m, 1H), 6.94-6.91 (m, 2H), 5.53 (s, 1H), 3.81 (s, 3H), 3.68 (dd, *J* = 16.5, 1.2 Hz, 1H),

3.41 (s, 3H), 3.14 (dd, J = 16.5, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.51, 170.71, 168.55, 150.62, 137.44, 127.55, 126.82, 125.89, 120.66, 72.88, 53.54, 52.84, 44.07, 29.26; HRMS (CI) *m/z* calcd for $C_{14}H_{13}NO_5S$ (M^+) 307.0514, found 307.0513.

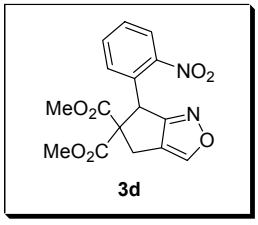
5,5-Dimethoxycarbonyl-6-(2-furyl)-4-dihydro-6H-cyclopenta[c]isoxazole (3c)



3c

Purified by column chromatography (ethyl acetate–hexanes 1:10) after concentration in vacuo to give a white solid which decompose at 134 ^{o}C; IR ($CHCl_3$) ν 3126, 2956, 2774, 1732, 1624, 1499, 1448, 1434, 1400, 1274, 1257, 1216, 1163, 1144, 1069, 1045, 1013, 931, 885, 816 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.33-7.32 (m, 1H), 6.30-6.29 (m, 1H), 6.21 (d, J = 3.2 Hz, 1H), 5.38 (s, 1H), 3.80 (s, 3H), 3.73 (dd, J = 16.4, 1.1 Hz, 1H), 3.49 (s, 3H), 3.15 (dd, J = 16.4, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.54, 169.89, 168.51, 150.55, 149.25, 143.02, 120.92, 110.69, 109.22, 71.57, 53.63, 53.12, 42.74, 29.54; HRMS (CI) *m/z* calcd for $C_{14}H_{13}NO_6$ (M^+) 291.0743, found 291.0746.

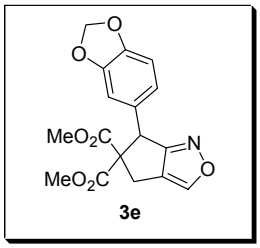
5,5-Dimethoxycarbonyl-6-(2-nitrophenyl)-4-dihydro-6H-cyclopenta[c]isoxazole (3d)



3d

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a white solid with the melting point of 134-135 ^{o}C; IR ($CHCl_3$) ν 3126, 2957, 1736, 1627, 1531, 1435, 1408, 1356, 1274, 1214, 1168, 1067, 944, 900, 864, 848, 824, 786 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.89 (dd, J = 7.9, 1.4 Hz, 1H), 7.50-7.41 (m, 2H), 7.02 (d, J = 7.5 Hz, 1H), 6.26 (s, 1H), 3.78 (s, 3H), 3.76 (d, J = 16.8 Hz, 1H), 3.28 (s, 3H), 3.21 (dd, J = 16.8, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.56, 170.32, 168.47, 150.95, 150.38, 132.83, 131.02, 130.65, 129.15, 125.12, 121.55, 72.92, 53.80, 52.94, 42.49, 29.97; HRMS (CI) m/z calcd for $C_{16}H_{14}N_2O_7$ (M+) 346.0800, found 346.0813.

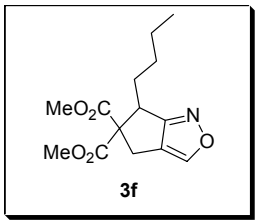
5,5-Dimethoxycarbonyl-6-(1,3-benzodioxol-5-yl)-4-dihydro-6H-cyclopenta[c]isoxazole (3e)



3e

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a white solid with the melting point of 93-94 ^{o}C; IR ($CHCl_3$) ν 3115, 2955, 2780, 1732, 1627, 1504, 1489, 1444, 1408, 1364, 1267, 1216, 1066, 1038, 931, 881, 825, 785 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 6.72-6.66 (m, 3H), 5.91-5.90 (m, 2H), 5.23 (s, 1H), 3.79 (s, 3H), 3.66 (dd, *J* = 18.1, 1.0 Hz, 1H), 3.33 (s, 3H), 3.11 (dd, *J* = 16.5, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.91, 170.96, 168.70, 150.45, 147.69, 147.37, 129.49, 122.49, 121.16, 109.38, 108.15, 101.22, 72.74, 53.38, 52.58, 48.31, 29.46; HRMS (CI) *m/z* calcd for $C_{17}H_{15}NO_7$ (M^+) 345.0849, found 345.0847.

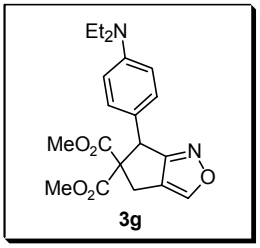
5,5-Dimethoxycarbonyl-6-(n-butyl)-4-dihydro-6H-cyclopenta[c]isoxazole (3f)



3f

Purified by column chromatography (ethyl acetate–hexanes 1:10) after concentration in vacuo to give a white solid with the melting point of 63-64 ^{o}C; IR ($CHCl_3$) ν 3583, 3461, 2956, 2863, 1735, 1629, 1454, 1435, 1401, 1268, 1215, 1163, 1119, 1066, 954, 938, 872, 835, 820, 792, 665 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 3.86 (dd, *J* = 11.3, 3.9 Hz, 1H), 3.762 (s, 3H), 3.760 (s, 3H) 3.48 (dd, *J* = 16.4, 1.3 Hz, 1H), 3.09 (dd, *J* = 16.4, 1.3 Hz, 1H), 1.69-1.25 (m, 6H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.51, 171.20, 169.65, 149.54, 120.06, 70.40, 53.37, 52.92, 43.43, 29.56, 29.45, 28.98, 22.63, 12.06; HRMS (CI) *m/z* calcd for $C_{14}H_{19}NO_5$ (M^+) 281.1263, found 281.1258.

5,5-Dimethoxycarbonyl-6-(4-diethylamino-phenyl)-4-dihydro-6H-cyclopenta[c]isoxazole (3g)

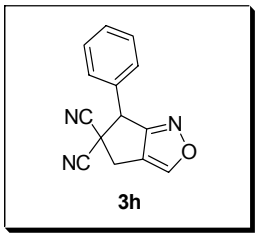


3g

Purified by column chromatography (methanol– chloroform1:50) after concentration in vacuo to white solid with the melting point of 104-106 ^{o}C; IR

($CHCl_3$) ν 3668, 3451, 2953, 2291, 1793, 1733, 1613, 1521, 1457, 1435, 1372, 1269, 1163, 1147, 1096; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.05-6.95 (m, 2H), 6.62-6.57 (m, 2H), 5.21 (s, 1H), 3.79 (s, 3H), 3.69 (dd, J = 16.5, 1.3 Hz, 1H), 3.35-3.27 (m, 4H), 3.29 (s, 3H), 3.10 (dd, J = 16.5, 1.3 Hz, 1H), 1.11 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.42, 171.19, 168.86, 149.95, 147.39, 129.63, 122.03, 121.67, 111.69, 72.71, 53.16, 52.37, 47.96, 44.30, 29.29, 12.44; HRMS (CI) *m/z* calcd for $C_{20}H_{24}N_2O_5$ (M^+) 372.1685, found 372.1691.

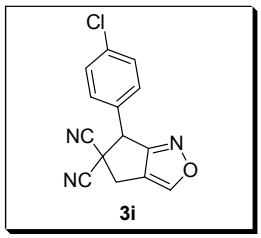
5,5-Dinitrile-6-phenyl-4-dihydro-6H-cyclopenta[c]isoxazole (3h)



3h

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a white solid with the melting point of 143-144 ^{o}C; IR ($CHCl_3$) ν 3583, 3137, 2923, 1708, 1630 ,1499, 1455, 1406, 1261, 1070 ,950, 847, 805 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.48 (s, 5H), 5.04 (s, 1H), 3.70 (d, *J* = 15.7 Hz, 1H), 3.58 (dd, *J* = 15.7, 1.4 Hz ,1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.48, 152.65, 131.05, 130.36, 129.65, 128.86, 118.56, 114.51, 113.33, 53.59, 48.30, 34.53; HRMS (CI) *m/z* calcd for $C_{14}H_9N_3O$ (M^+) 235.0746, found 235.0746.

5,5-Dinitrile-6-(4-chlorophenyl)-4-dihydro-6H-cyclopenta[c]isoxazole (3i)

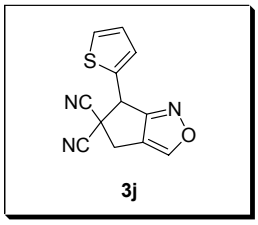


3i

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a white solid with the melting point of 108-109 ^{o}C; IR ($CHCl_3$) ν 3479, 3139, 3003, 2920, 2252, 2126, 1911, 1710, 1630, 1597, 1577, 1494, 1446, 1405, 1362, 1296, 1260, 1224, 1112, 1092, 1071, 1016, 950, 903, 867, 833, 806, 745 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.43-7.49 (m, 4H), 5.02 (s, 1H), 3.71 (d, *J* = 15.7 Hz, 1H), 3.58 (dd, *J* = 15.7, 1.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.09,

152.85, 136.63, 130.25, 129.94, 129.42, 118.47, 114.21, 113.22, 52.99, 48.24, 34.50; HRMS (CI) *m/z* calcd for $C_{14}H_8ClN_3O$ (M^+) 269.0356, found 269.0357.

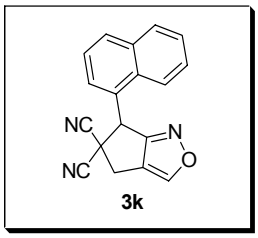
5,5-Dinitrile-6-(2-thienyl)-4-dihydro-6H-cyclopenta[c]isoxazole (3j)



3j

Purified by column chromatography (ethyl acetate–hexanes 1:10) after concentration in vacuo to give a white solid with the melting point of 129-130 ^oC; IR ($CHCl_3$) ν 3583, 3115, 2923, 2774, 2252, 1728, 1709, 1630, 1509, 1444, 1408, 1365, 1296, 1237, 1120, 1070, 1043, 947, 856, 795 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.44 (dd, *J* = 5.1, 0.7 Hz, 1H), 7.33 (d, *J* = 3.7 Hz, 1H), 7.12 (dd, *J* = 5.1, 3.7 Hz, 1H), 5.31 (s, 1H), 3.71 (d, *J* = 15.7, 1H), 3.57 (dd, *J* = 15.7, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.49, 152.86, 132.36, 129.25, 128.03, 127.94, 118.01, 114.28, 113.03, 49.18, 48.78, 34.23; HRMS (CI) *m/z* calcd for $C_{12}H_7N_3OS$ (M^+) 241.0310, found 241.0313.

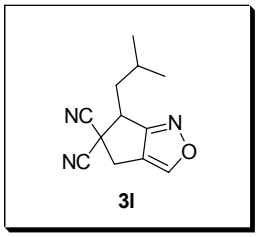
5,5-Dinitrile-6-(naphthalen-1-yl)-4-dihydro-6H-cyclopenta[c]isoxazole (3k)



3k

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a white solid with the melting point of 180-181 ^oC; IR ($CHCl_3$) ν 3583, 3137, 3054, 2939, 1709, 1630, 1598, 1514, 1443, 1409, 1360, 1293, 1223, 1071, 949, 803, 781 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.24 (d, *J* = 8.6 Hz, 1H), 7.96 (dd, *J* = 8.1, 2.5 Hz, 2H) 7.72-7.68 (m, 1H), 7.63-7.59 (m, 1H), 7.50 (t, *J* = 7.8 Hz , 1H), 7.36 (d, *J* = 7.1 Hz, 1H), 5.98 (s, 1H), 3.78-3.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.04, 152.72, 134.24, 131.73, 131.04, 129.67, 128.03, 127.72, 127.52, 126.83, 125.51, 122.45, 118.96, 115.22, 113.21, 48.81, 47.26, 35.18; HRMS (CI) *m/z* calcd for $C_{18}H_{11}N_3O$ (M^+) 285.0902, found 285.0902.

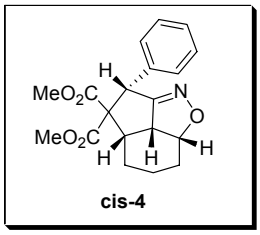
5,5-Dinitrile-6-(iso-butyl)-4-dihydro-6H-cyclopenta[c]isoxazole (3l)



3l

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a colorless oil; IR ($CHCl_3$) ν 2960, 2923, 2873, 2247, 1706, 1630, 1506, 1469, 1445, 1403, 1370, 1305, 1278, 1220, 1168, 1069, 943, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 3.82 (dd, *J* = 9.4, 6.4 Hz, 1H), 3.59 (dd, *J* = 15.7, 0.6 Hz, 1H), 3.48 (dd, *J* = 15.7, 1.4 Hz, 1H), 2.08-2.18 (m, 1H), 1.97 (ddd, *J* = 13.7, 9.3, 6.2 Hz, 1H), 1.84 (ddd, *J* = 13.7, 8.3, 6.2 Hz, 1H), 1.09 (d, *J* = 6.4 Hz, 3H), 1.07 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.02, 151.68, 117.52, 114.79, 113.49, 46.07, 44.91, 38.45, 34.73, 25.79, 22.91, 22.02; HRMS (CI) *m/z* calcd for $C_{12}H_{13}N_3O$ (M^+) 215.1059, found 215.1060.

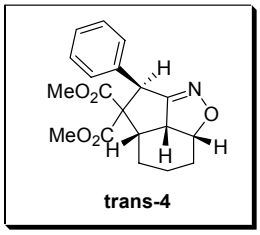
***cis*-4,4-Dimethoxycarbonyl-3-phenyl-4a,5,6,7,7a,7b-hexahydro-3H-indeno[1,7-cd]isoxazole (*cis*-4)**



cis-4

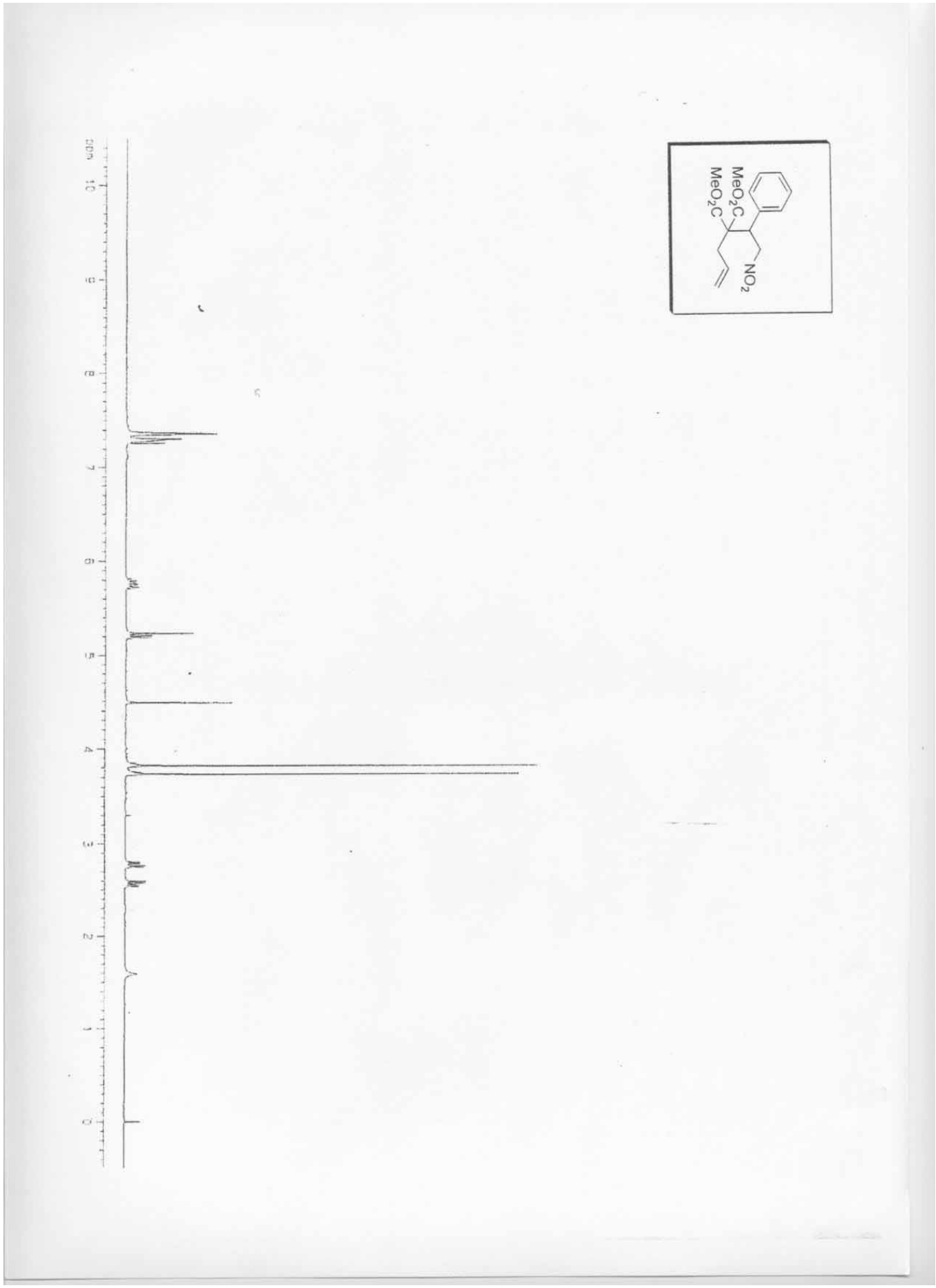
Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a white solid with the melting point of 189-190 ^oC; IR ($CHCl_3$) ν 3032, 2952, 2864, 1729, 1645, 1497, 1455, 1435, 1355, 1313, 1280, 1254, 1205, 1180, 1079, 1044 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.23 (m, 5H), 5.02 (s, 1H), 4.81 (dd, *J* = 17.2, 8.8 Hz, 1H), 3.84 (s, 3H), 3.77 (dd, *J* = 9.2, 8.2 Hz, 1H), 3.26 (s, 3H), 2.99-2.92 (m, 1H), 2.27-2.24 (m, 1H), 2.18-2.13 (m, 1H), 1.74-1.70 (m, 1H), 1.61-1.41 (m, 2H), 1.02-0.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.91, 169.77, 166.70, 135.65, 129.94, 127.99, 127.57, 75.66, 74.20, 54.22, 53.48, 51.54, 46.57, 41.90, 29.02, 25.43, 19.78; HRMS (CI) *m/z* calcd for $C_{19}H_{21}NO_5$ (M^+) 343.1420, found 303.1109; Elemental analysis calculated for $C_{19}H_{21}NO_5$: C, 66.46; H, 6.16: N, 4.08. Found: C, 66.40; H, 6.15; N, 3.93.

***trans*-4,4-Dimethoxycarbonyl-3-phenyl-4a,5,6,7,7a,7b-hexahydro-3H-indeno[1,7-cd]isoxazole (*trans*-4)**



trans-4

Purified by column chromatography (ethyl acetate–hexanes 1:5) after concentration in vacuo to give a white solid with the melting point of 154-155 ^{o}C; IR ($CHCl_3$) ν 3032, 2954, 1730, 1644, 1601, 1497, 1456, 1435, 1280, 1254, 1207, 1078 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.21 (m, 5H), 5.05 (d, J = 2.0 Hz, 1H), 4.85 (dd , J = 17.2, 8.8 Hz, 1H), 4.60 (dd, J = 8.6, 8.2 Hz, 1H), 3.79 (s, 3H), 3.00 (s, 3H), 2.95-2.90 (m, 1H), 2.11-2.06 (m, 1H), 1.69-1.63 (m, 2H), 1.39-1.29 (m, 1H), 1.08-0.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.24, 169.81, 169.41, 135.63, 128.75, 128.28, 127.64, 77.02, 56.99, 52.64, 52.01, 44.71, 40.51, 28.49, 24.28, 20.28; HRMS (CI) *m/z* calcd for $C_{19}H_{21}NO_5$ (M^+) 343.1420, found 303.1109; Elemental analysis calculated for $C_{19}H_{21}NO_5$: C, 66.46; H, 6.16: N,4.08. Found: C,66.41; H, 6.15; N, 3.93.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MeO2C
NO2

MeO2C
MeO2C
NO2
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140
120
100
80
60
40
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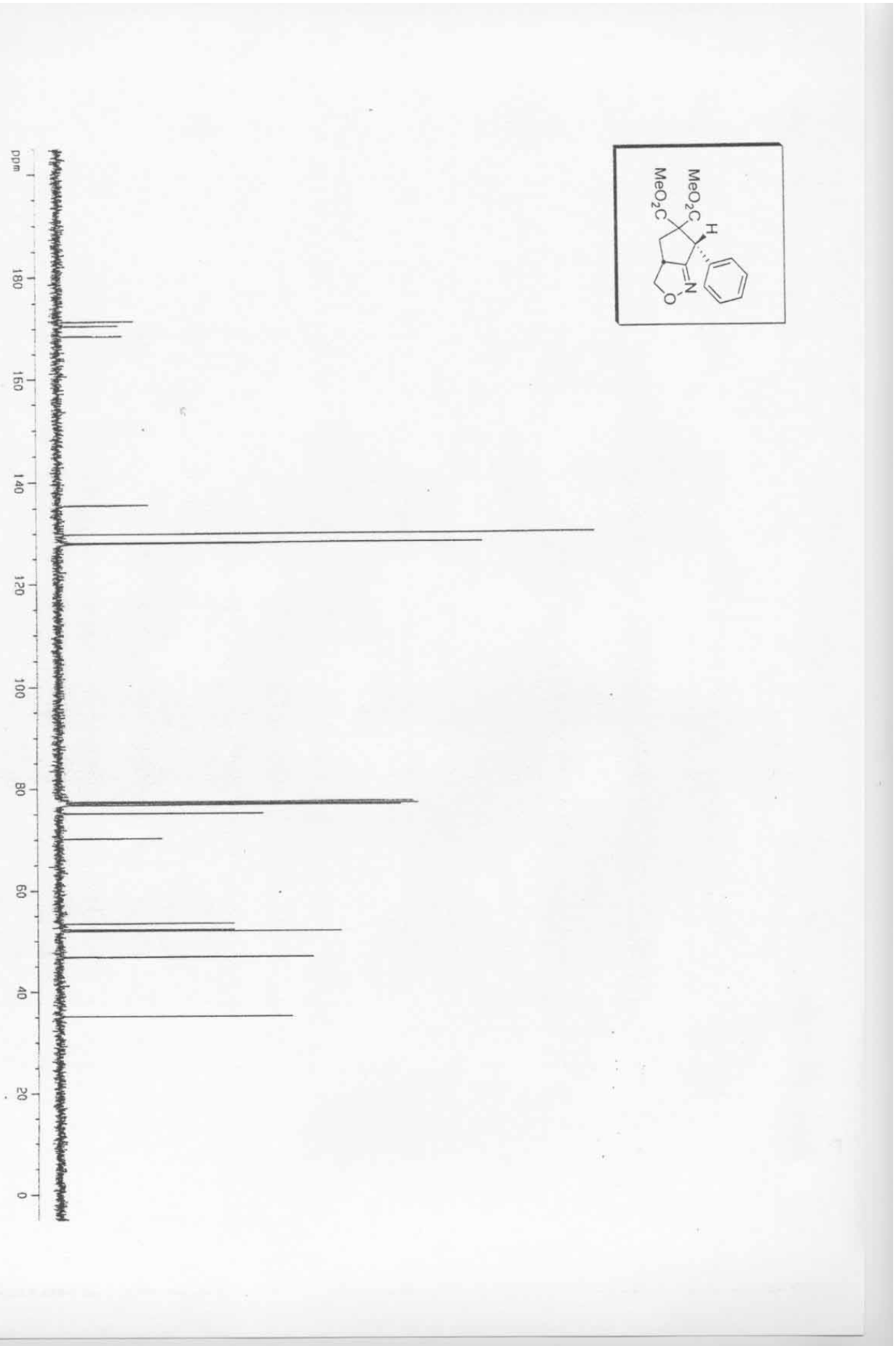
9
8
7
6
5
4
3
2
1
0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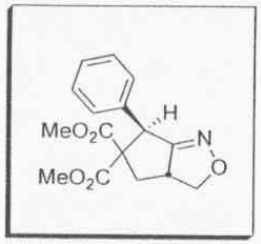
H
N
O
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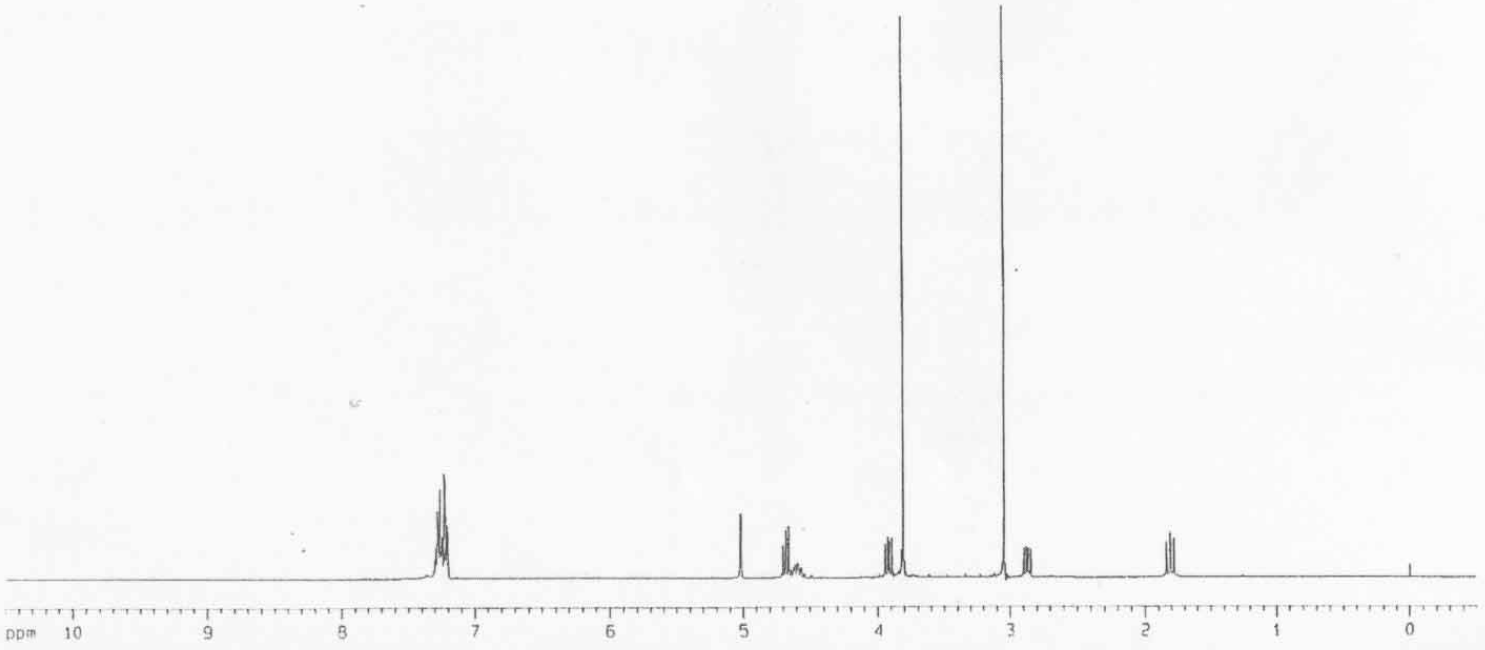
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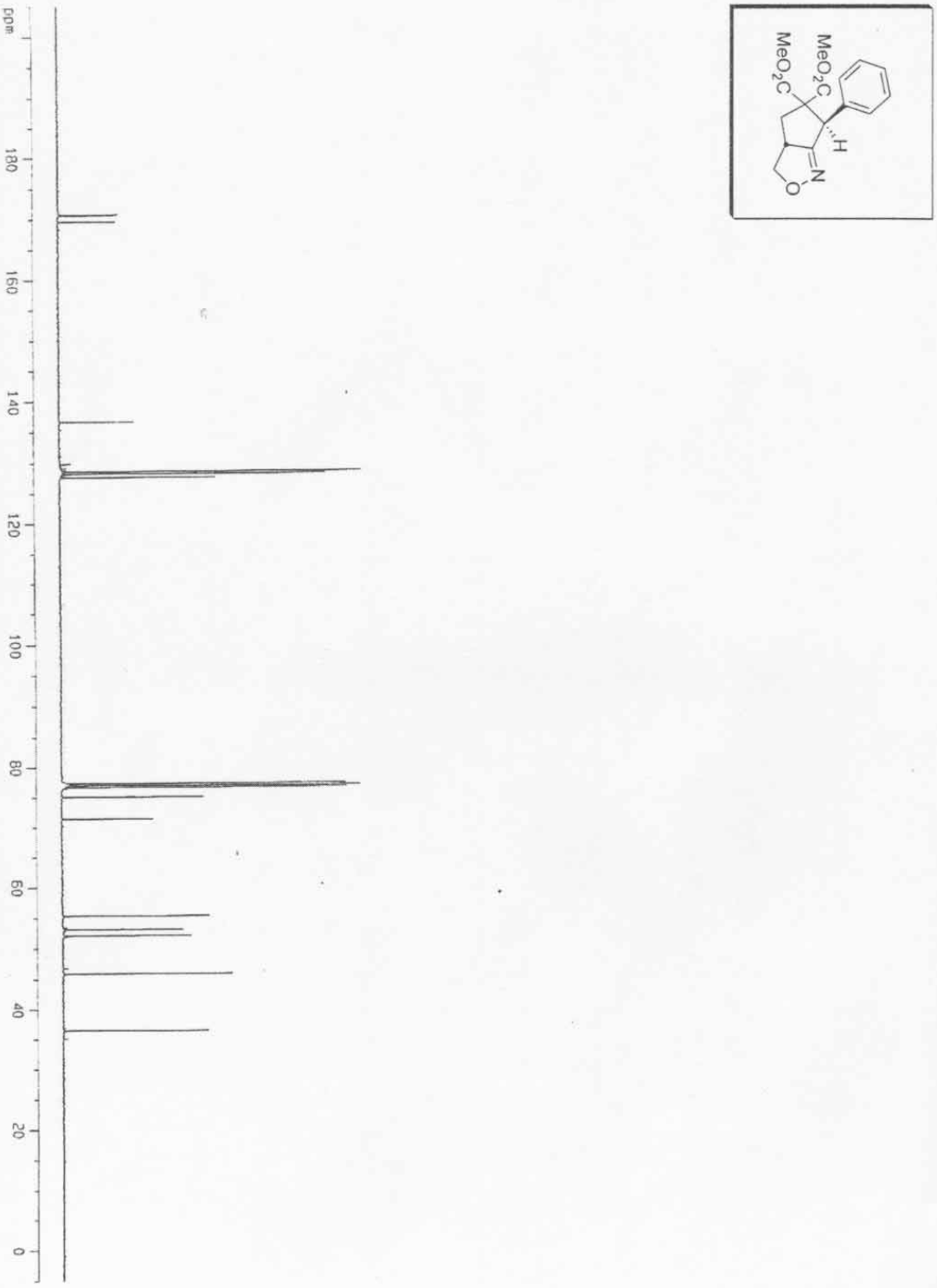
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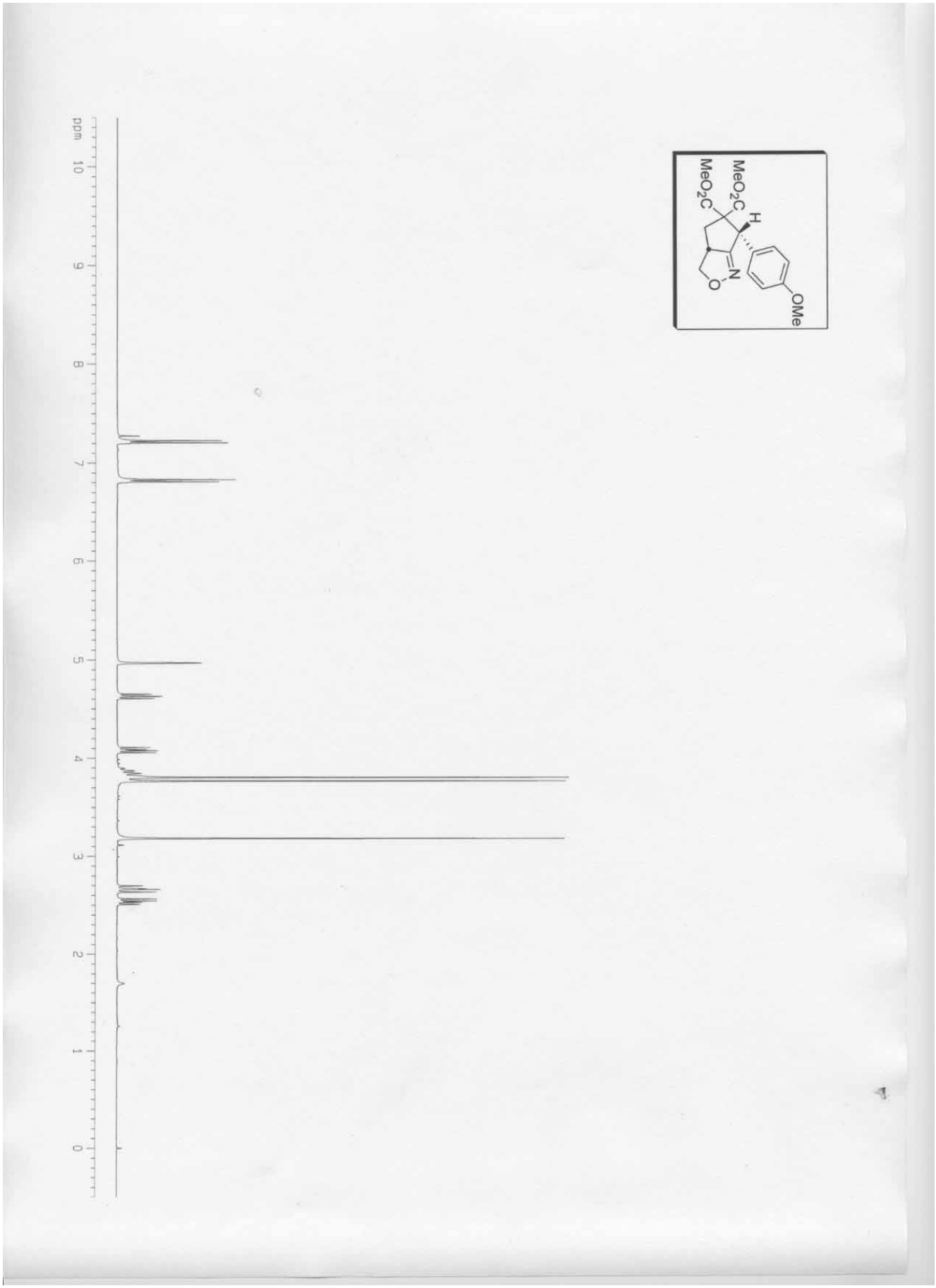
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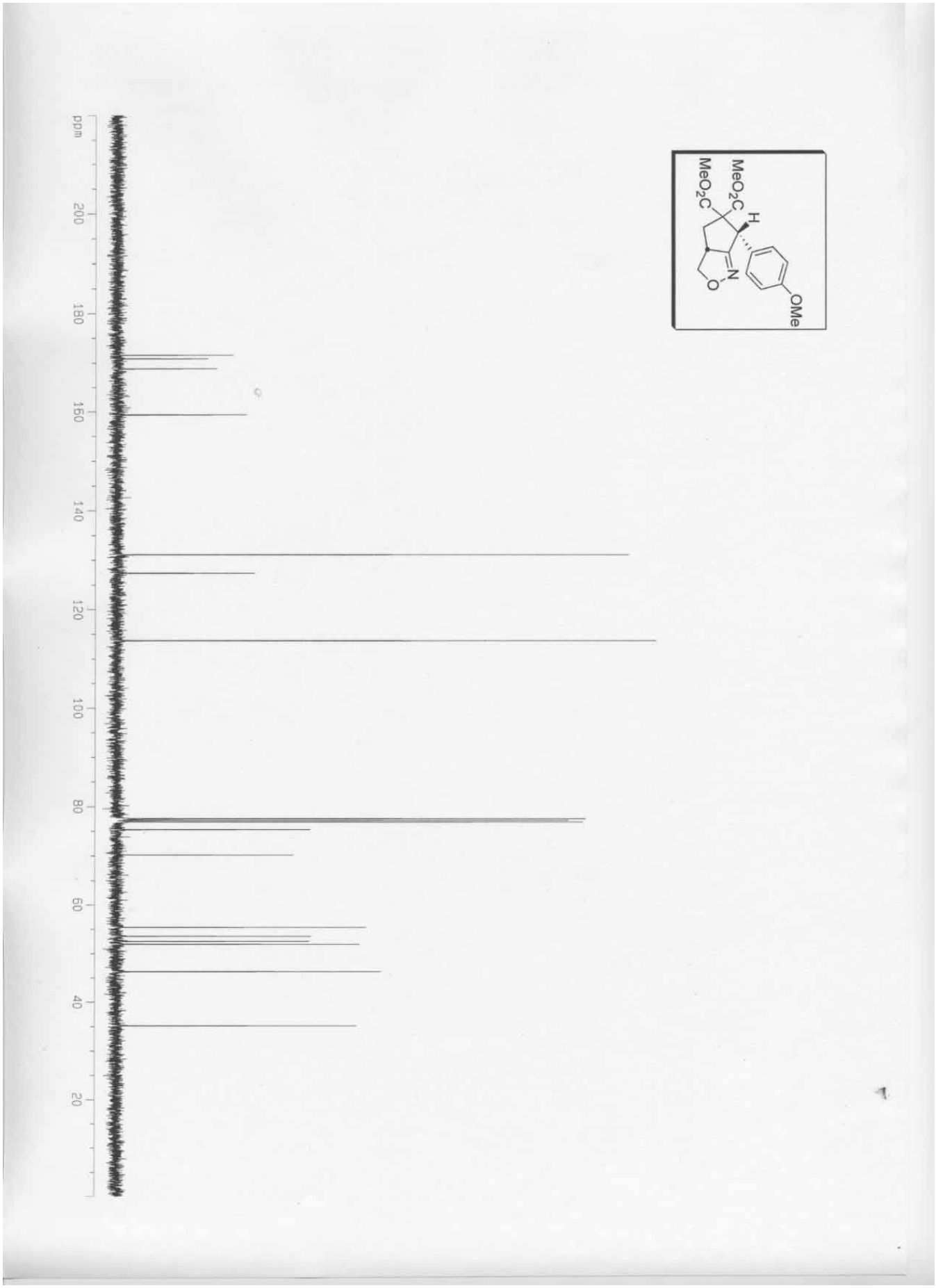
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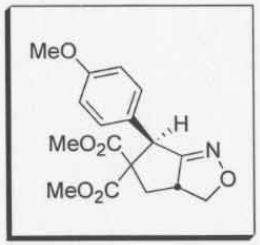
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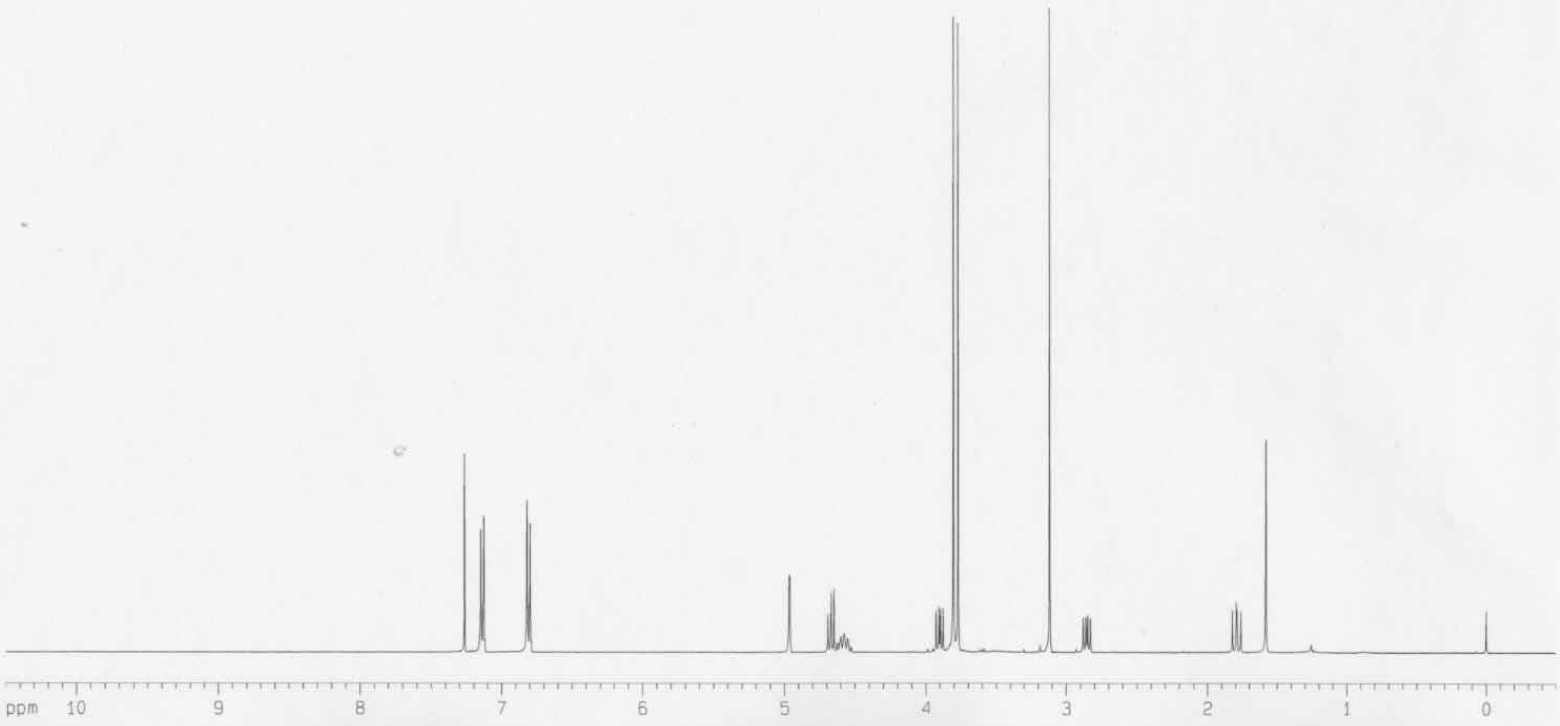
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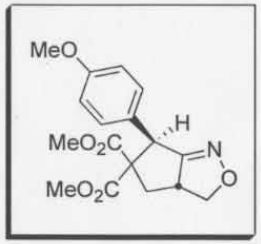
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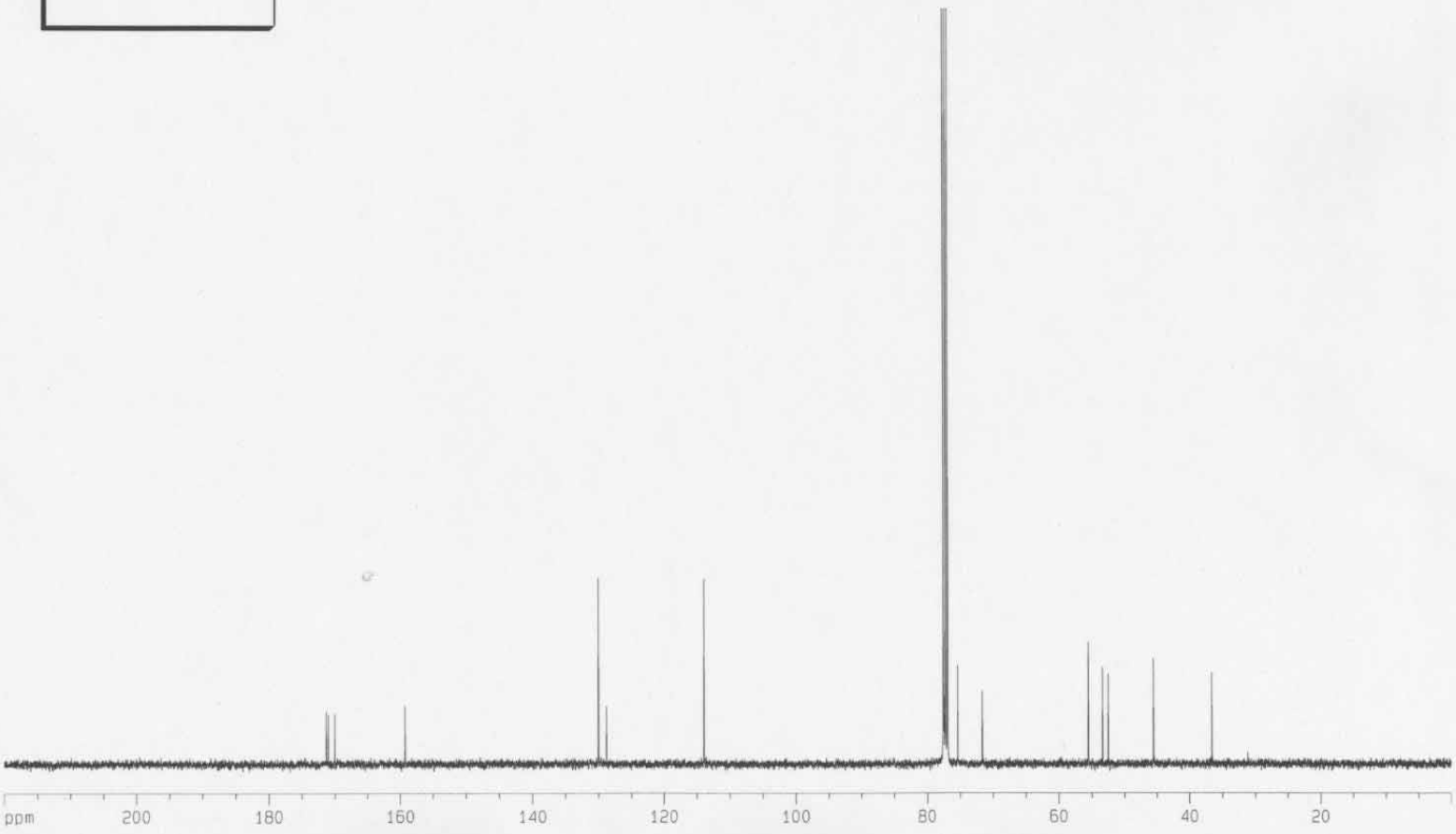
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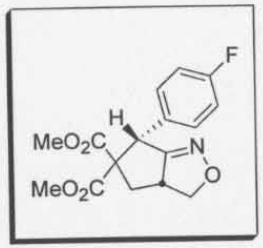
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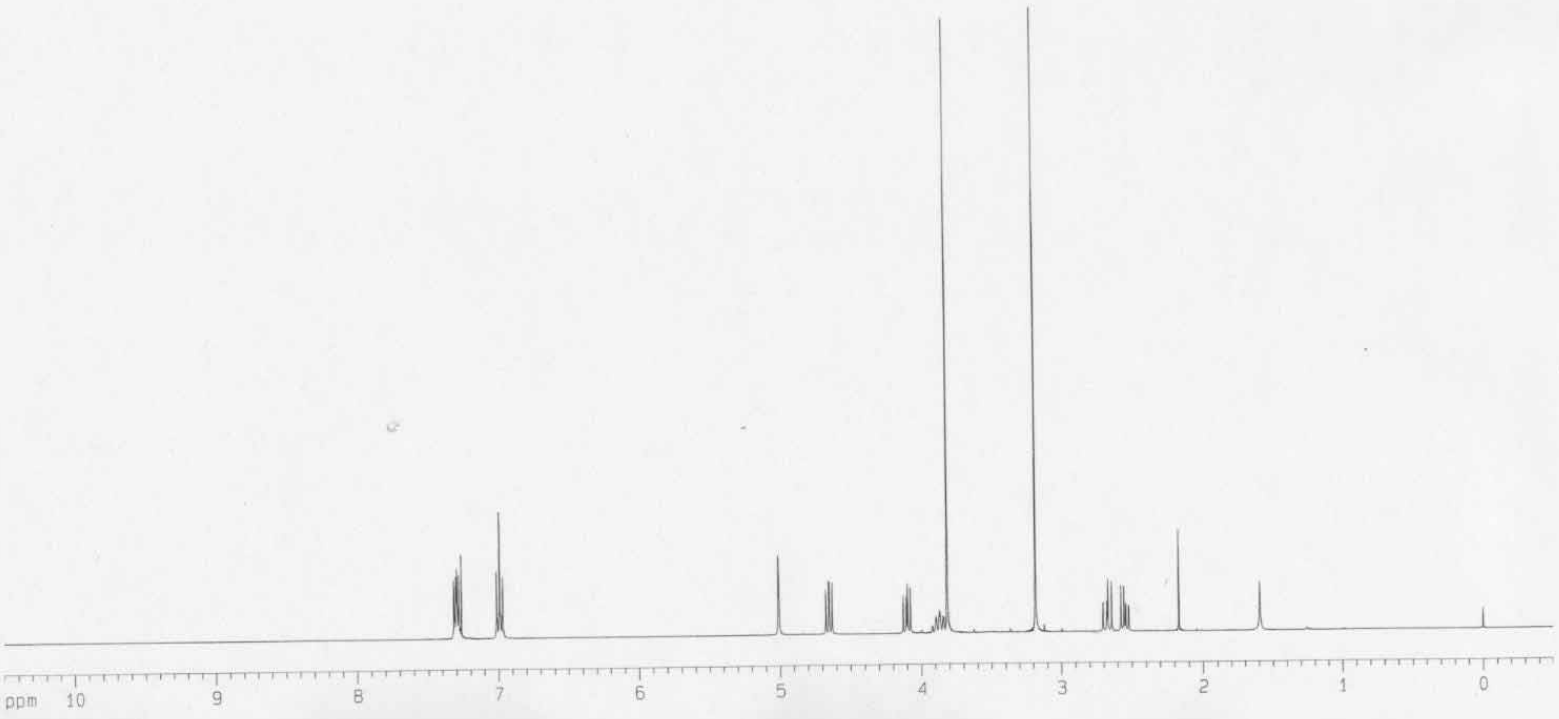
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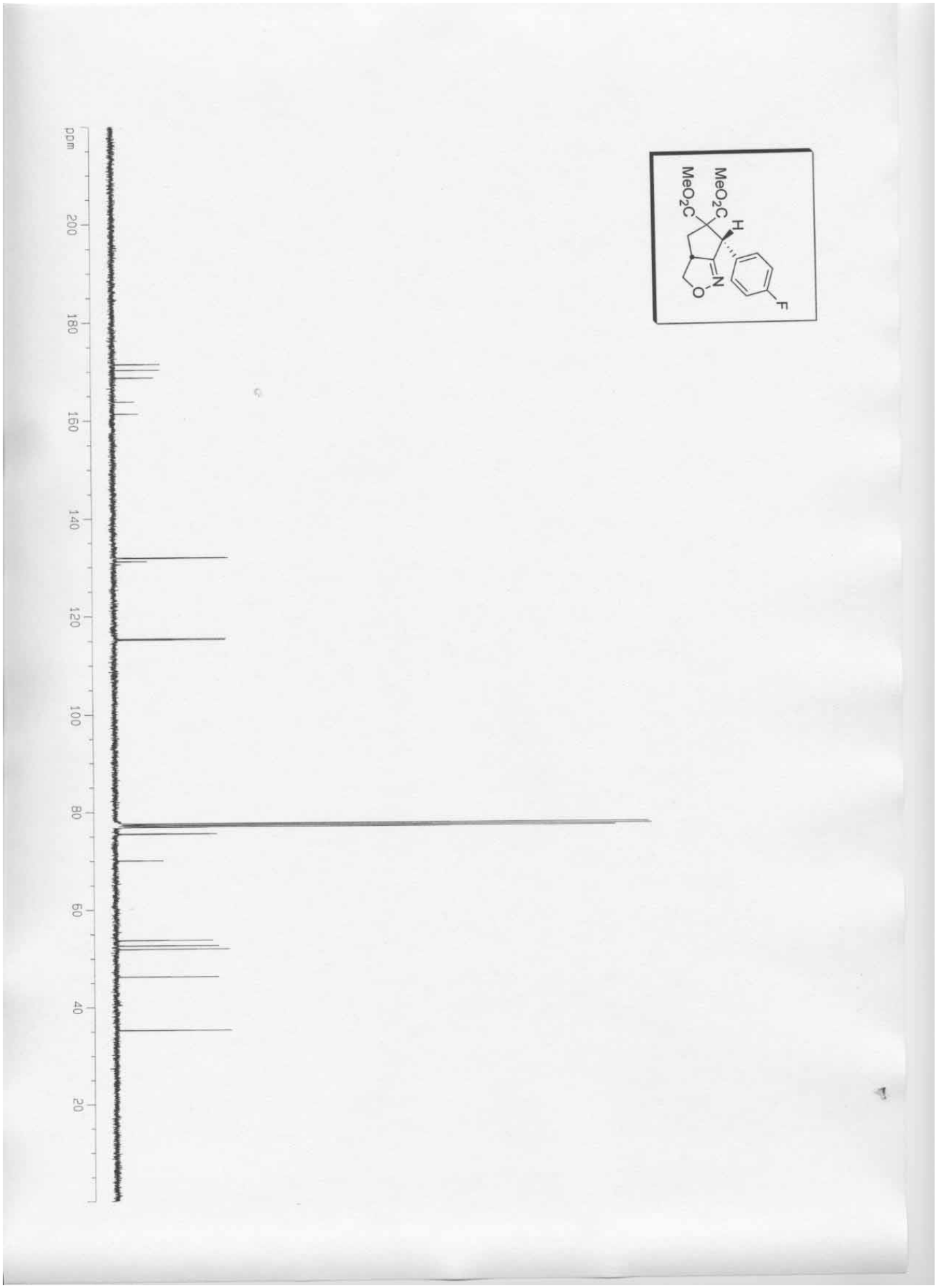
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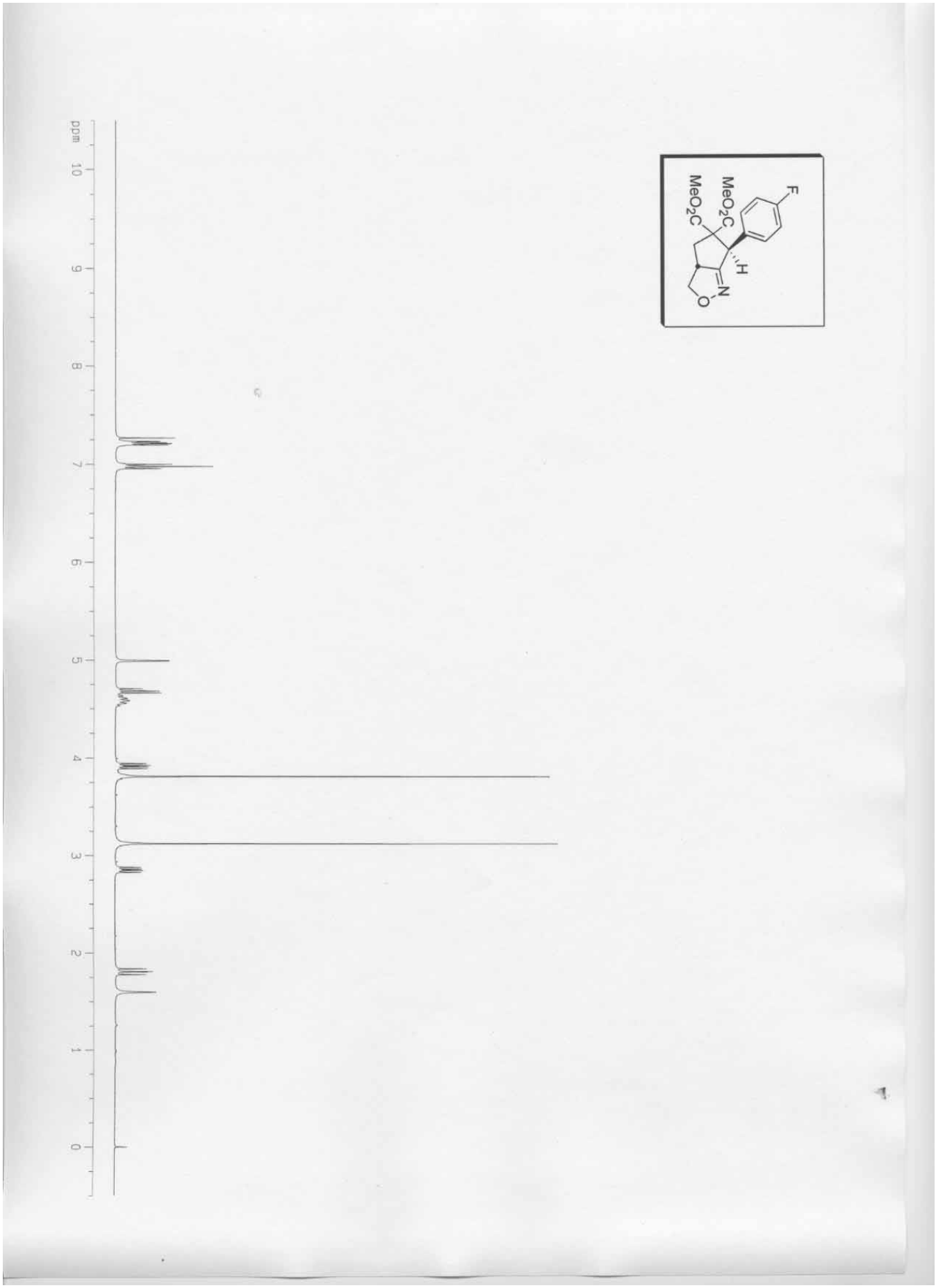
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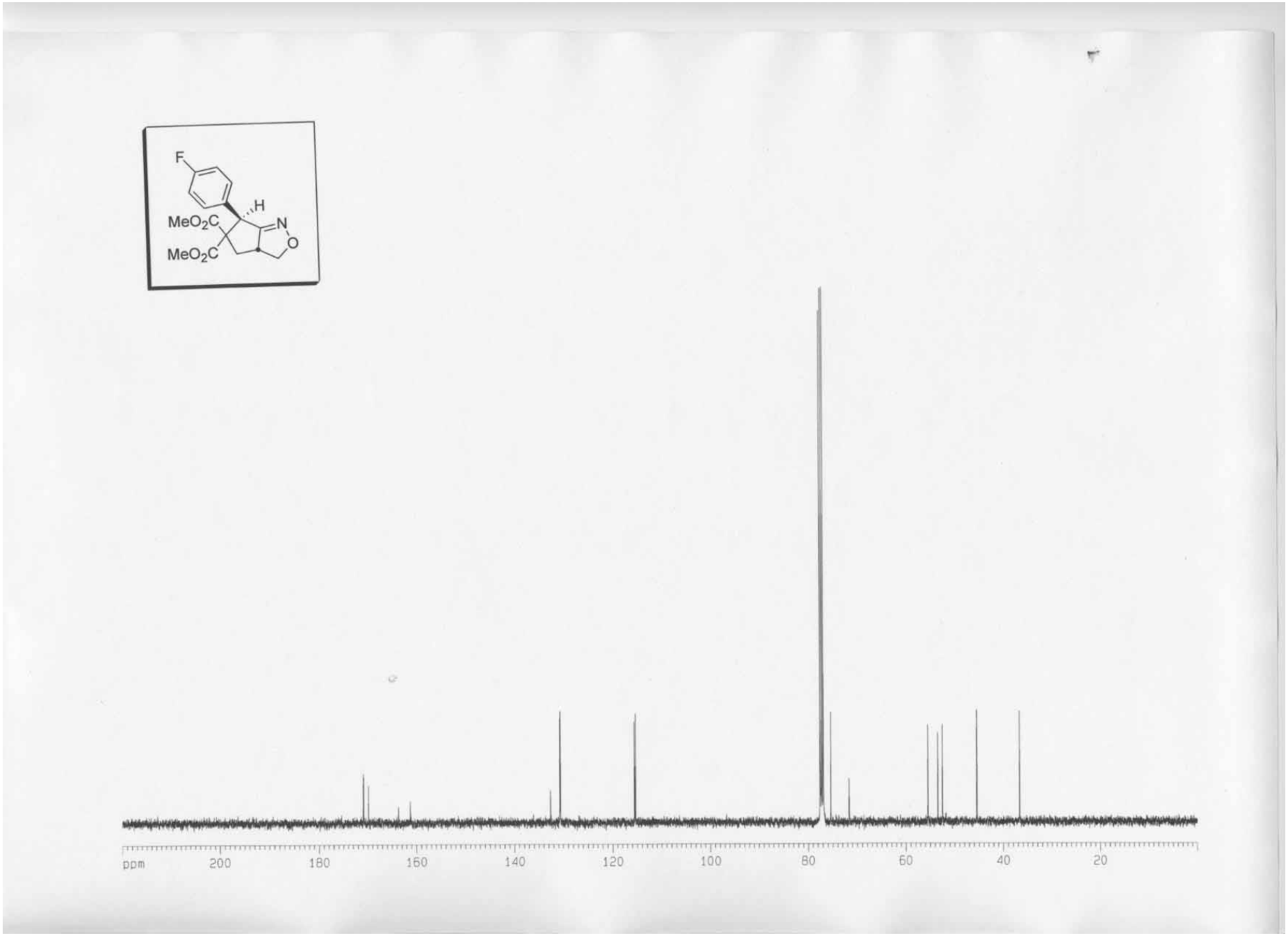
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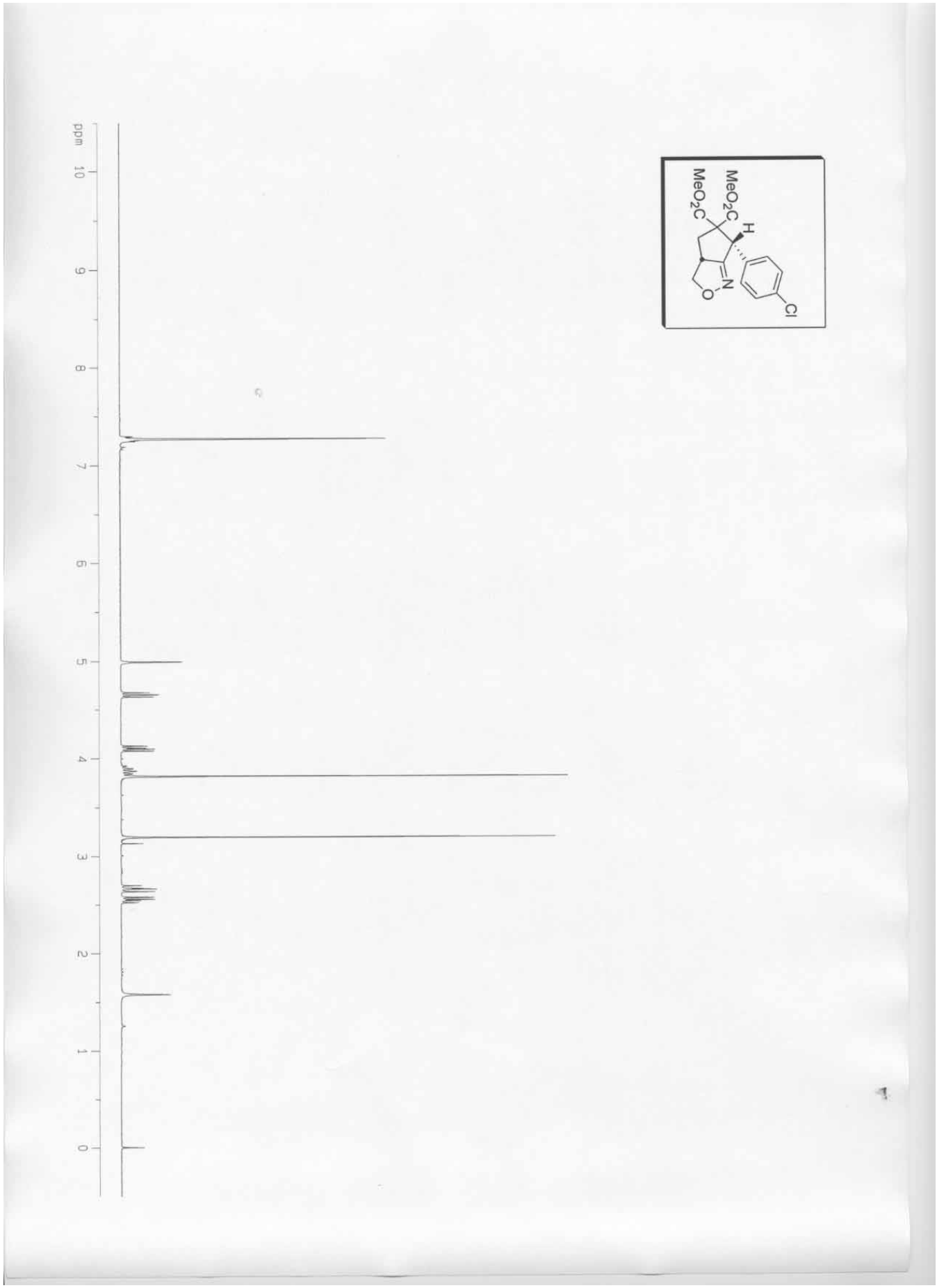
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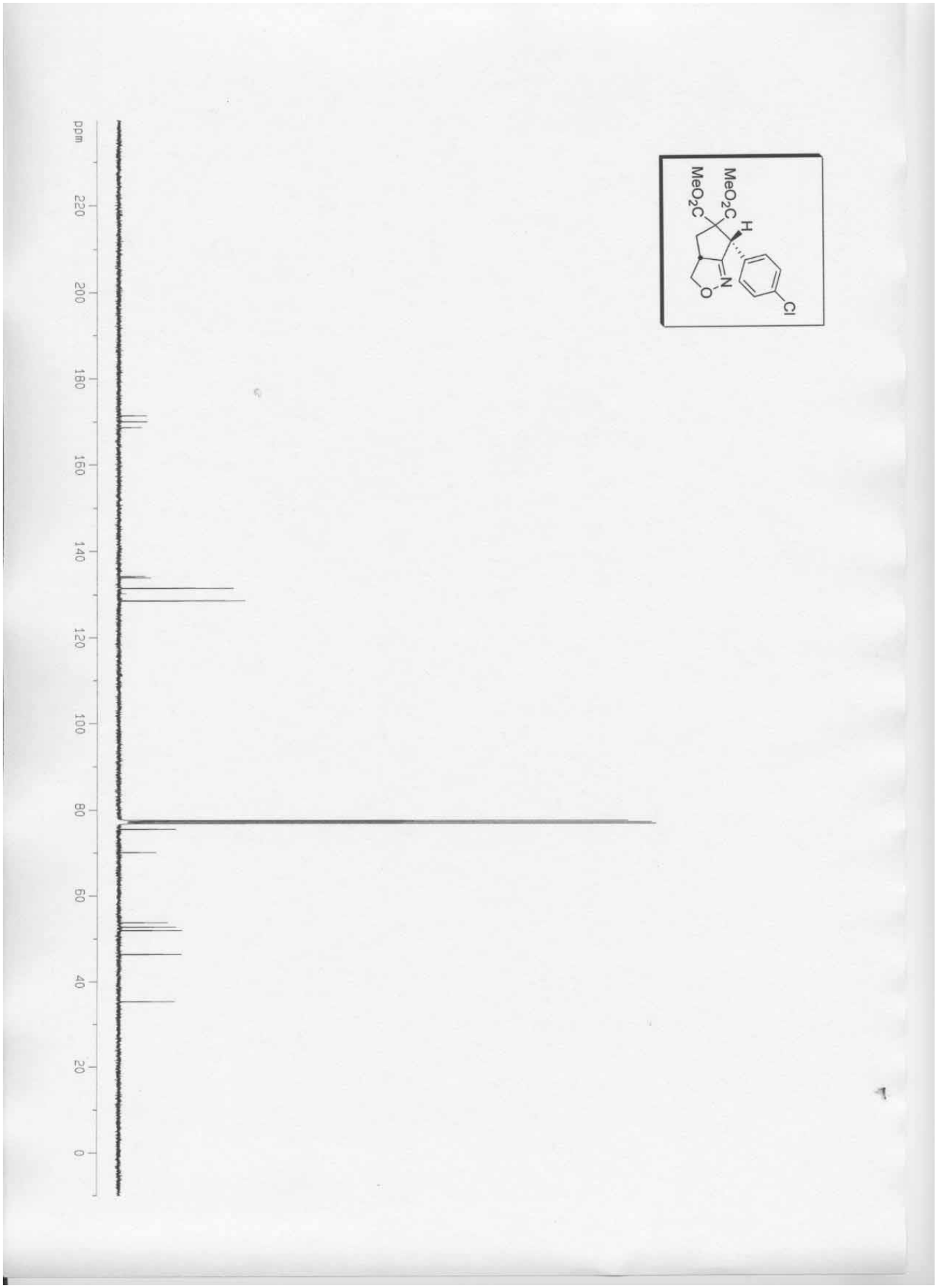
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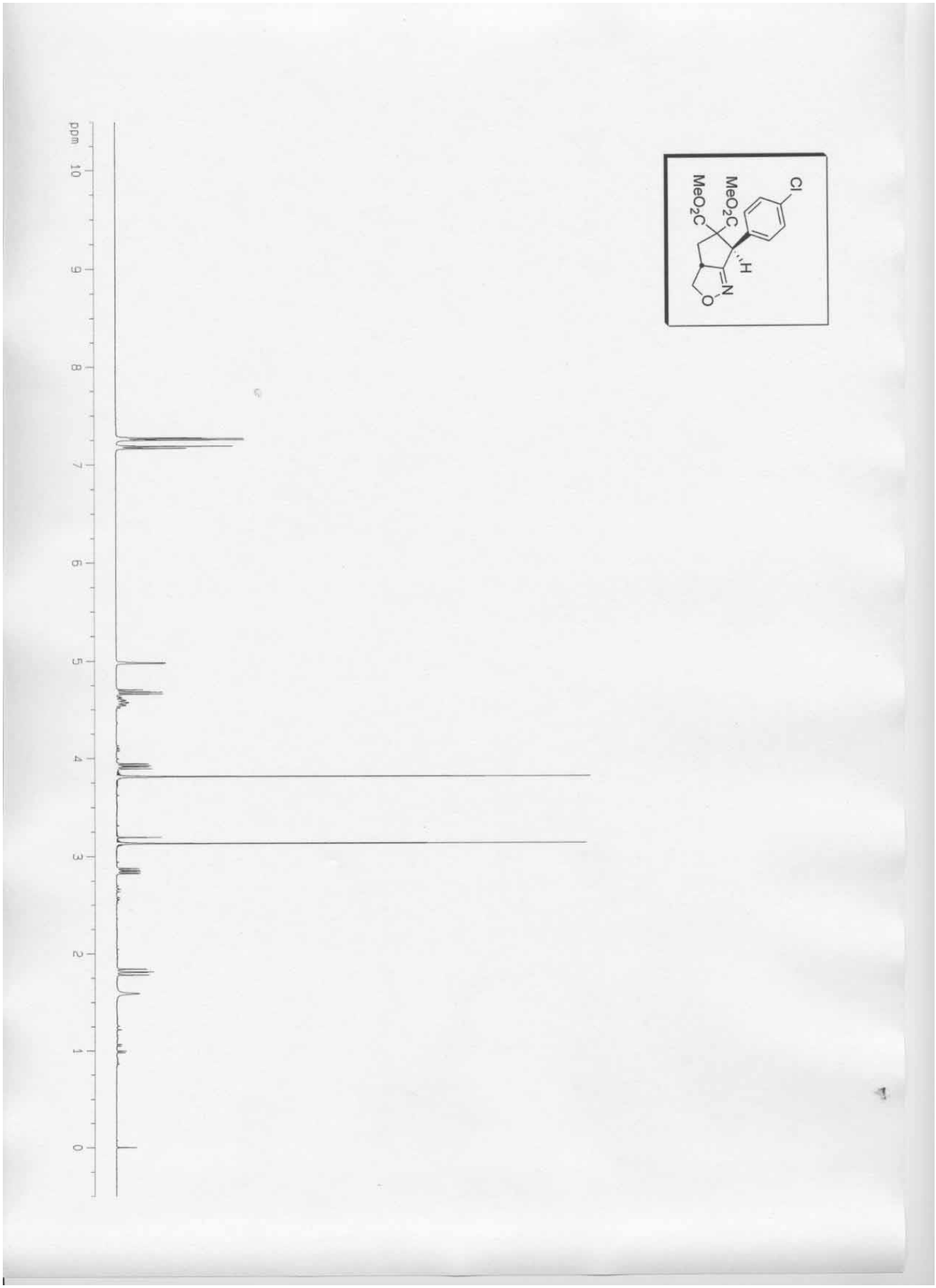
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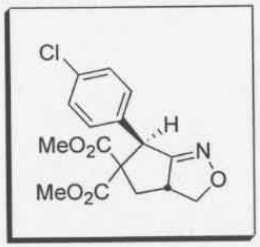
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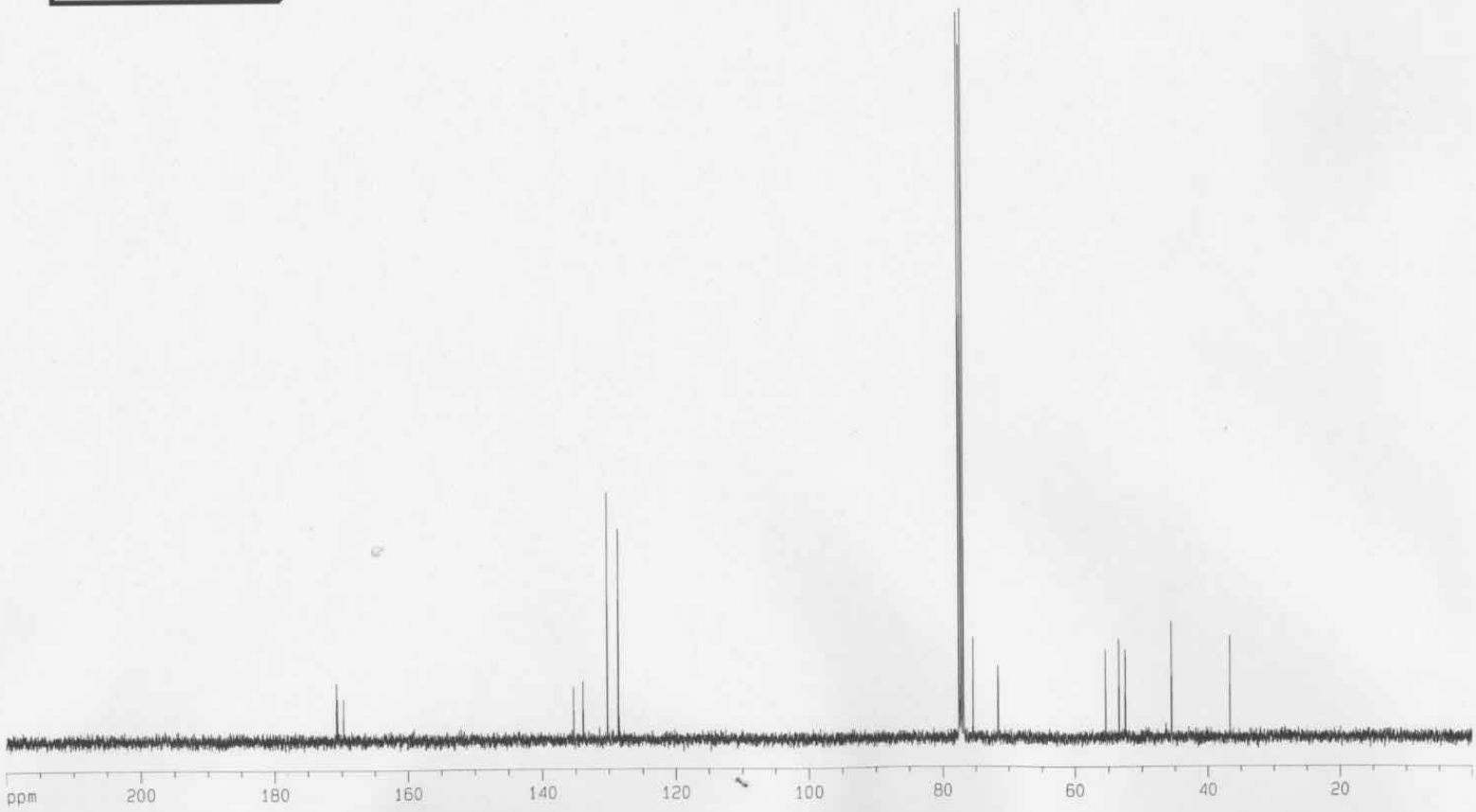
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