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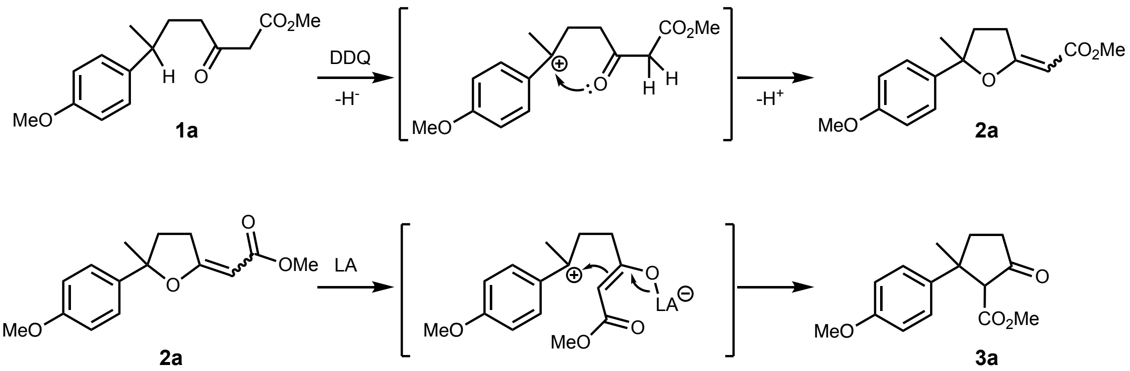
1. Table and Scheme

Table S1 [1,3]-Rearrangement from (*E*)-**2a** to **3a**

entry	acid	mol%	time (h)	yield (%) of **3a**
1	TfOH	100	6	65
2	$BF_3 \cdot OEt_2$	100	18	71
3	$BiCl_3$	100	14	66
4	Me_3SiOTf	100	13	63
5	$Sc(OTf)_3$	100	13	94
6	$Sc(OTf)_3$	30	6	86
7[a]	$Sc(OTf)_3$	30	6	87

[a] (*Z*)-**2a** was used



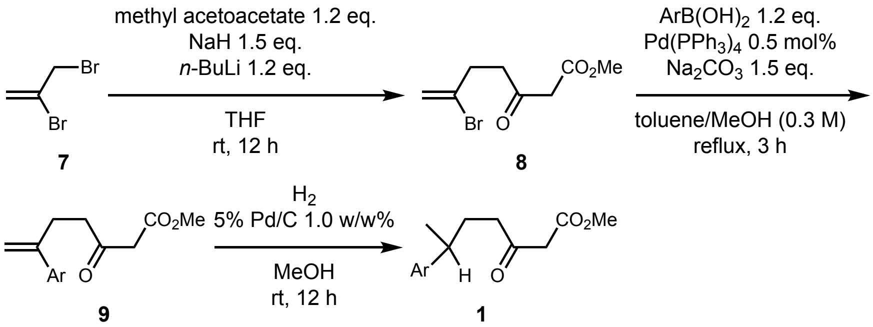
Scheme S1. Proposed reaction mechanism

2. General Information

Reagents and solvents for syntheses were commercially purchased and air and/or moisture sensitive reactions were carried out by using dry solvents under an argon atmosphere. TLC analysis was performed using Merck TLC Silica gel 60 F_{254}. Preparative thin-layer chromatography (PTLC) was conducted using Merck PLC Silica gel 60 F_{254} 0.5 mm. Flash silica gel column chromatography was performed on Wako Wakosil® C-300. IR spectra were recorded on a Jasco FT/IR-4700 spectrometer with ATR PRO ONE in ATR mode using diamond prism. ^{1}H and ^{13}C NMR spectra were measured on a Bruker spectrometer at 500 and 125 MHz. $CDCl_3$ was used as a solvent and the residual solvent peaks were used as an internal standard (^{1}H NMR: 7.26 ppm; ^{13}C NMR: 77.0 ppm). High resolution (HR) mass spectra (MS) were measured on JEOL JMS-T100LP using electrospray ionization (ESI). Optical rotation values were recorded on a Jasco P-1010 polarimeter. The reactions at high temperature was performed with EYELA ChemiStation.

3. Synthesis and Characterization Data of Compounds

3-1. Preparation of substrates 1



Scheme S2. Preparation of methyl 6-aryl-3-oxoheptanoate (1)

Methyl 6-bromo-3-oxohept-6-enoate (8)

Sodium hydride (3.00 g, 60% in mineral oil, 75.0 mmol) was suspended in THF (40 mL) under an argon atmosphere and the suspension was cooled to 0 °C. Methyl acetoacetate (6.97 g, 60.0 mmol) in THF (40 mL) was added dropwise to the suspension over 15 min and the mixture was stirred for 1 hour. At this stage, the suspension became homogeneous solution. 1.25 M *n*-BuLi in hexane (48.0 mL, 60.0 mmol) was added dropwise to the solution over 30 min and the mixture was stirred for 1 hour. 2,3-Dibromopropene (**7**) (10.0 g, 50.0 mmol) in THF (70 mL) was added dropwise to the solution over 10 min at 0 °C and the mixture was stirred for 12 hours at room temperature. The reaction was quenched by addition of 2 M HCl aq. (60 mL) and the organic layer was separated. The aqueous layer was extracted with EtOAc (60 mL×2). The combined organic layer was washed with brine, dried over Na_2SO_4 and filtered through a cotton plug. The filtrate was concentrated in vacuo and the residue was purified by silica gel chromatography with hexane/EtOAc (5/1) to give methyl 6-bromo-3-oxohept-6-enoate (**8**) (9.87 g, 84% yield) as a yellow oil; IR (ATR): ν 2953, 1743, 1716, 1631, 1436, 1407, 1322, 1254, 1200, 1156, 1110, 1083, 996, 894 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.64 (1H, m), 5.43 (1H, m), 3.75 (3H, s), 3.48 (3H, s), 2.85 (2H, t, J = 7.5 Hz), 2.73 (2H, t, J = 7.5 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 200.6, 172.9, 132.2, 117.9, 51.2, 49.1, 41.3, 35.1 ppm; HRMS (*m*/*z*) for $C_8H_{11}O_3{}^{79}Br(Na^+)$: calculated 256.9789, found 256.9807.

General procedure of preparation of methyl 6-aryl-3-oxohept-6-enoate (9)

Aryl bronic acid (1.2 eq.) and sodium carbonate (1.5 eq.) were suspended in MeOH (1.5-15.0 mL) under an argon atmosphere. Methyl 6-bromo-3-oxohept-6-enoate (**8**) (1.00-10.0 mmol) in toluene (1.5-15.0 mL) was added to the suspension. Tetrakis(triphenylphosphine)palladium (0.5 mol%) was added and the mixture was stirred for 3 hours at 80 °C. The reaction was quenched by addition of 0.1 M phosphate buffer (pH 7) and the organic layer was separated. The aqueous layer was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered through a cotton plug. The filtrate was concentrated in vacuo and the residue was purified by silica gel chromatography with EtOAc/hexane to give methyl 6-aryl-3-oxohept-6-enoate (**9**).

Methyl 6-(4-methoxyphenyl)-3-oxohept-6-enoate (9a): yellow oil; 83% yield (10.0 mmol scale); IR (ATR): ν 2952, 1746, 1715, 1607, 1512, 1438, 1322, 1286, 1249, 1181, 1033, 896, 838 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.33 (2H, d, *J* = 8.9 Hz), 6.87 (2H, d, *J* = 8.9 Hz), 5.23 (1H, m), 4.99 (1H, m), 3.81 (3H, s), 3.72 (3H, s), 3.42 (2H, s), 2.79 (2H, t, *J* = 7.8 Hz), 2.68 (2H, t, *J* = 7.8 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.0, 167.5, 159.3, 146.0, 132.8, 127.2, 113.8, 111.5, 55.3, 52.3, 49.1, 41.9, 29.0 ppm; HRMS (*m*/*z*) for $C_{15}H_{18}O_4(Na^+)$: calculated 285.1103, found 285.1083.

Methyl 6-(2-methoxyphenyl)-3-oxohept-6-enoate (9b): colorless oil; 97% yield (1.00 mmol scale); IR (ATR): ν 2952, 1746, 1715, 1630, 1598, 1490, 1455, 1436, 1319, 1241, 1181, 1094, 1047, 1026, 905, 756 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.26 (1H, ddd, *J* = 8.2, 7.8, 1.8 Hz), 7.11 (1H, dd, *J* = 7.4, 1.8 Hz), 6.92 (1H, ddd, *J* = 7.8, 7.4, 1.0 Hz), 6.87 (1H, dd, *J* = 8.2, 1.0 Hz), 5.15 (1H, m), 5.04 (1H, m), 3.81 (3H, s), 3.71 (3H, s), 3.39 (2H, s), 2.79 (2H, t, *J* = 7.6 Hz), 2.59 (2H, t, *J* = 7.6 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.2, 167.8, 156.5, 147.1, 131.1, 130.2, 128.8, 120.6, 115.0, 110.7, 55.4, 52.3, 49.0, 41.8, 30.2 ppm; HRMS (*m*/*z*) for $C_{15}H_{18}O_4(Na^+)$: calculated 285.1103, found 285.1090.

Methyl 6-(3-methoxyphenyl)-3-oxohept-6-enoate (9c): colorless oil; 71% yield (1.00 mmol scale); IR (ATR): ν 2952, 1746, 1715, 1598, 1576, 1488, 1435, 1320, 1287, 1235, 1081, 1047, 903, 791 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.26 (1H, dd, *J* = 8.2, 7.9 Hz), 6.97-6.91 (2H, m), 6.83 (1H, dd, *J* = 8.2, 2.5 Hz), 5.30 (1H, br), 5.09 (1H, br), 3.82 (3H, s), 3.72 (3H, s), 3.42 (2H, s), 2.80 (2H, t, *J* = 7.5 Hz), 2.69 (2H, t, *J* = 7.5 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 201.8, 167.5, 159.7, 146.7, 142.0, 129.4, 118.6, 113.3, 113.0, 112.1, 55.3, 52.3, 49.1, 41.8, 29.1 ppm; HRMS (*m*/*z*) for $C_{15}H_{18}O_4(Na^+)$: calculated 285.1103, found 285.1090.

Methyl 6-(4-acetamidophenyl)-3-oxohept-6-enoate (9d): colorless oil; 83% yield (2.00 mmol scale); IR (ATR): ν 3306, 2952, 1743, 1713, 1668, 1596 , 1525, 1437, 1403, 1371, 1318, 1257, 1187, 1081, 1017, 899, 844 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.46 (2H, d, *J* = 8.5 Hz), 7.37 (1H, br s), 7.34 (2H, d, *J* = 8.5 Hz), 5.27 (1H, br), 5.04 (1H, br), 3.71 (3H, s), 3.42 (2H, s), 2.78 (2H, t, *J* = 7.6 Hz), 2.68 (2H, t, *J* = 7.6 Hz), 2.17 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 201.9, 168.2, 167.5, 145.9, 137.4, 136.3, 126.7, 119.8, 112.6, 52.4, 49.1, 41.8, 28.9, 24.6 ppm; HRMS (*m*/*z*) for $C_{16}H_{19}NO_4(Na^+)$: calculated 312.1212, found 312.1197.

Methyl 6-(benzofuran-5-yl)-3-oxohept-6-enoate (9e): colorless oil; 82% yield (3.02 mmol scale); IR (ATR): ν 2952, 1745, 1715, 1628, 1469, 1437, 1406, 1323, 1265, 1195, 1133, 1113, 1030, 886, 819, 745 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.62 (1H, d, *J* = 2.2 Hz), 7.59 (1H, d, *J* = 1.8 Hz), 7.46 (1H, dd, *J* = 8.6, 0.9 Hz), 7.33 (1H, dd, *J* = 8.6, 1.9 Hz), 6.76 (1H, dd, *J* = 2.2, 0.9 Hz), 5.28 (1H, br), 5.09 (1H, m), 3.70 (3H, s), 3.42 (2H, s), 2.87 (2H, t, *J* = 7.5 Hz), 2.70 (2H, t, *J* = 7.5 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.0, 167.5, 154.6, 147.0, 145.5, 135.5, 127.6, 122.9, 118.7, 112.8, 111.2, 106.7, 52.3, 49.1, 41.9, 29.6 ppm; HRMS (*m/z*) for $C_{16}H_{16}O_4(Na^+)$: calculated 295.0946, found 295.0960.

Methyl 6-(2,4-dimethoxyphenyl)-3-oxohept-6-enoate (9f): colorless oil; 93% yield (1.00 mmol scale); IR (ATR): ν 2952, 1746, 1715, 1606, 1576, 1504, 1455, 1438, 1411, 1302, 1279, 1208, 1160, 1096, 1034, 902, 835 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.03 (1H, d, *J* = 8.8 Hz), 6.44 (1H, d, *J* = 2.3 Hz), 6.44 (1H, dd, *J* = 8.9, 2.3 Hz), 5.10 (1H, br), 5.00 (1H, br), 3.81 (3H, s), 3.79 (3H, s), 3.71 (3H, s), 3.39 (2H, s), 2.77 (2H, t, *J* = 7.6 Hz), 2.57 (2H, t, *J* = 7.6 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.3, 167.6, 160.5, 157.9, 146.7, 130.5, 123.7, 114.7, 104.2, 98.7, 55.4, 55.4, 52.3, 49.0, 42.0, 30.3 ppm; HRMS (*m/z*) for $C_{16}H_{20}O_5(Na^+)$: calculated 315.1208, found 315.1237.

Methyl 6-(3,4-dimethoxyphenyl)-3-oxohept-6-enoate (9g): colorless oil; 95% yield (1.00 mmol scale); IR (ATR): ν 2952, 1745, 1714, 1602, 1577, 1515, 1439, 1412, 1321, 1253, 1229, 1174, 1145, 1025, 895, 858, 813 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.94 (1H, dd, *J* = 8.1, 2.0 Hz), 6.92 (1H, d, *J* = 2.0 Hz), 6.83 (1H, d, *J* = 8.1 Hz), 5.23 (1H, br), 5.01 (1H, br), 3.90 (3H, s), 3.89 (3H, s), 3.72 (3H, s), 3.42 (2H, s), 2.80 (2H, t, *J* = 7.5 Hz), 2.70 (2H, t, *J* = 7.5 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.0, 167.5, 148.9 (2C), 146.3, 133.3, 1118.5, 111.9, 111.0, 109.5, 55.9, 55.9, 52.3, 49.1, 41.9, 29.1 ppm; HRMS (*m/z*) for $C_{16}H_{20}O_5(Na^+)$: calculated 315.1208, found 315.1231.

Methyl 6-(2,5-dimethoxyphenyl)-3-oxohept-6-enoate (9h): colorless oil; 92% yield (1.00 mmol scale); IR (ATR): ν 2951, 1746, 1715, 1630, 1580, 1493, 1464, 1427, 1419, 1312, 1264, 1218, 1180, 1151, 1084, 1045, 1025, 906, 807 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.79 (2H, m), 6.70 (1H, dd, *J* = 2.3, 1.2 Hz), 5.15 (1H, br), 5.05 (1H, br), 3.77 (3H, s), 3.76 (3H, s), 3.71 (3H, s), 3.40 (2H, s), 2.79 (2H, t, *J* = 7.6 Hz), 2.60 (2H, t, *J* = 7.6 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.1, 167.6, 153.5, 150.8, 146.9, 132.1, 116.3, 115.2, 112.9, 111.9, 56.1, 55.7, 52.3, 48.9, 41.8, 30.1 ppm; HRMS (*m/z*) for $C_{16}H_{20}O_5(Na^+)$: calculated 315.1208, found 315.1237.

Methyl 3-oxo-6-phenylhept-6-enoate (9i): yellow oil; 80% yield (10.0 mmol scale); IR (ATR): ν 2952, 1745, 1715, 1652, 1627, 1601, 1574, 1495, 1437, 1407, 1362, 1320, 1244, 1196, 1154, 1135, 1102, 1081, 1028, 997, 903, 780, 708 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.39-7.28 (5H, m), 5.30 (1H, br), 5.08 (1H, br), 3.71 (3H, s), 3.42 (3H, s), 2.82 (2H, t, *J* = 7.6 Hz), 2.69 (2H, t, *J* = 7.6 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 201.9, 167.5, 146.7, 140.4, 128.5, 127.7, 126.1, 113.1, 52.4, 49.1, 41.8, 29.0 ppm; HRMS (*m/z*) for $C_{14}H_{16}O_3(Na^+)$: calculated 255.0997, found 255.1026.

Methyl 3-oxo-6-(*p*-tolyl)hept-6-enoate (9j): colorless oil; 90% yield (1.00 mmol scale); IR (ATR): ν 2952, 1746, 1715, 1653, 1626, 1514, 1437, 1406, 1362, 1322, 1243, 1220, 1196, 1152, 1133, 1080, 1019, 997, 898, 826, 772, 737 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.28 (2H, d, *J* = 8.0 Hz), 7.14 (2H, d, *J* = 8.0 Hz), 5.27 (1H, br), 5.03 (1H, br), 3.72 (3H, s), 3.41 (2H, s), 2.80 (2H, t, *J* = 7.6 Hz), 2.69 (2H, t, *J* = 7.6 Hz), 2.35 (3H, s) ppm; ^{13}C NMR ($CDCl_3$):

δ 202.0, 167.5, 146.5, 137.5, 137.4, 129.2, 125.9, 112.3, 52.3, 49.1, 41.9, 29.0, 21.1 ppm; HRMS (*m*/*z*) for $C_{15}H_{18}O_5(Na^+)$: calculated 269.1154, found 269.1156.

Methyl 6-(naphthalen-2-yl)-3-oxohept-6-enoate (9k) : colorless oil; 80% yield (2.04 mmol scale); IR (ATR): ν 3054, 2952, 1746, 1715, 1625, 1436, 1406, 1320, 1270, 1199, 896, 861, 822, 754 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.84-7.80 (4H, m), 7.55 (1H, dd, *J* = 8.7, 1.7 Hz), 7.50-7.45 (2H, m), 5.46 (1H, br s), 5.19 (1H, br s), 3.70 (3H, s), 3.43 (2H, s), 2.94 (2H, t, *J* = 7.5 Hz), 2.75 (2H, t, *J* = 7.5 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.0, 167.5, 146.5, 137.6, 133.4, 132.9, 128.2, 128.1, 127.6, 126.3, 126.0, 124.7, 124.5, 113.7, 52.4, 49.1, 41.9, 29.0 ppm; HRMS (*m*/*z*) for $C_{18}H_{18}O_3(Na^+)$: calculated 305.1154, found 305.1139.

Methyl 6-(4-methoxy-3-methylphenyl)-3-oxohept-6-enoate (9l): yellow oil; 83% yield (4.80 mmol scale); IR (ATR): ν 2952, 1745, 1715, 1626, 1606, 1505, 1438, 147, 1323, 1296, 1250, 1200, 1174, 1141, 1108, 1082, 1032, 998, 889, 817 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.25-7.17 (2H, m), 6.78 (1H, d, *J* = 9.1 Hz), 5.21 (1H, br), 4.97 (1H, br), 3.83 (3H, s), 3.72 (3H, s), 3.42 (2H, s), 2.78 (2H, t, *J* = 7.5 Hz), 2.69 (2H, t, *J* = 7.5 Hz), 2.22 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 202.1, 167.5, 157.5, 146.2, 132.3, 128.5, 126.5, 124.4, 111.3, 109.7, 55.4, 52.3, 49.1, 42.0, 29.1, 16.3 ppm; HRMS (*m*/*z*) for $C_{16}H_{20}O_4(Na^+)$: calculated 299.1259, found 299.1230.

Methyl 6-(2,5-dimethoxy-4-methylphenyl)-3-oxohept-6-enoate (9m): colorless oil; 90% yield (1.00 mmol scale); IR (ATR): ν 2951, 1746, 1715, 1628, 1503, 1465, 1437, 1397, 1374, 1319, 1210, 1043, 903, 868 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.69 (1H, s), 6.61 (1H, m), 5.14 (1H, br), 5.05 (1H, br), 3.79 (3H, s), 3.76 (3H, s), 3.70 (3H, s), 3.40 (2H, s), 2.79 (2H, t, *J* = 7.6 Hz), 2.60 (2H, t, *J* = 7.6 Hz), 2.22 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 202.2, 167.6, 151.6, 150.1, 147.1, 128.8, 126.7, 114.8, 114.4, 112.7, 56.3, 56.1, 52.3, 49.0, 41.8, 30.3, 16.2 ppm; HRMS (*m*/*z*) for $C_{17}H_{22}O_5(Na^+)$: calculated 329.1365, found 329.1371.

Methyl 6-(3-methoxy-4-methylphenyl)-3-oxohept-6-enoate (9n): colorless oil; 80% yield (1.00 mmol scale); IR (ATR): ν 2952, 1746, 1715, 1653, 1626, 1609, 1573, 1507, 1437, 1407, 1319, 1239, 1203, 1175, 1136, 1100, 1081, 1038, 995, 896, 858, 820 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.08 (1H, d, *J* = 7.6 Hz), 6.88 (1H, dd, *J* = 7.6, 1.6 Hz), 6.84 (1H, d, *J* = 1.6 Hz), 5.27 (1H, br), 5.05 (1H, br), 3.84 (3H, s), 3.71 (3H, s), 3.42 (2H, s), 2.81 (2H, t, *J* = 7.5 Hz), 2.70 (2H, t, *J* = 7.5 Hz), 2.21 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 202.0, 167.5, 157.7, 146.9, 139.3, 130.5, 126.3, 118.0, 112.4, 107.9, 55.3, 52.3, 49.1, 41.9, 29.2, 15.9 ppm; HRMS (*m*/*z*) for $C_{16}H_{20}O_4(Na^+)$: calculated 299.1259, found 299.1234.

General procedure of preparation of methyl 6-aryl-3-oxoheptanoate (1)

Methyl 6-aryl-3-oxohept-6-enoate (**9**) (0.71-8.30 mmol) was dissolved in MeOH (0.1 M) and 5% Pd/C (1.0 w/w% based on the weight of Pd/C) was added to the solution. The reaction was stirred under H_2 atmosphere with a balloon at room temperature for 12 hours and filtered through Celite®. The filtrate was concentrated in vacuo and the residue was purified by silica gel chromatography with hexane/EtOAc to give methyl 6-aryl-3-oxoheptanoate (**1**).

Methyl 6-(4-methoxyphenyl)-3-oxoheptanoate (1a): colorless oil; 99% yield (8.30 mmol scale); IR (ATR): ν 2954, 1746, 1714, 1611, 1583, 1513, 1438, 1408, 1303, 1247, 1179, 1035, 913, 833 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.07 (2H, d, *J* = 8.6 Hz), 6.84 (2H, d, *J* = 8.6 Hz), 3.79 (3H, s), 3.70 (3H, s), 3.35 (2H, s), 2.65 (1H, m), 2.42 (1H, ddd, *J* = 17.6, 8.8, 6.5 Hz), 2.35 (1H, ddd, *J* = 17.6, 8.8, 5.6 Hz), 1.90 (1H, m), 1.80 (1H, m), 1.23 (3H, d, *J* = 6.9 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.7, 167.6, 158.0, 138.2, 127.9, 113.9, 55.3, 52.3, 49.0, 41.3, 38.4, 31.7, 22.6 ppm; HRMS (*m*/*z*) for $C_{15}H_{20}O_4(Na^+)$: calculated 287.1259, found 287.1251.

Methyl 6-(2-methoxyphenyl)-3-oxoheptanoate (1b): colorless oil; 93% yield (0.97 mmol scale); IR (ATR): ν 2956, 1747, 1715, 1653, 1626, 1599, 1585, 1492, 1456, 1438, 1407, 1364, 1317, 1289, 1240, 1194, 1151, 1093, 1028, 756 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.17 (1H, ddd, *J* = 8.2, 7.5, 1.7 Hz), 7.14 (1H, dd, *J* = 7.5, 1.7 Hz), 6.92 (1H, ddd, *J* = 7.5, 7.5, 1.0 Hz), 6.85 (1H, dd, *J* = 8.2, 1.0 Hz), 3.80 (3H, s), 3.69 (3H, s), 3.36 (2H, s), 3.20 (1H, m), 2.45 (1H, ddd, *J* = 17.4, 9.1, 6.5 Hz), 2.36 (1H, ddd, *J* = 17.4, 8.9, 5.7 Hz), 1.95-1.82 (2H, m), 1.22 (3H, d, *J* = 7.0 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.8, 167.7, 157.1, 134.3, 127.0, 126.8, 120.8, 110.6, 55.3, 52.2, 48.9, 41.3, 31.3, 30.6, 20.9 ppm; HRMS (*m*/*z*) for $C_{15}H_{20}O_4(Na^+)$: calculated 287.1259, found 287.1239.

Methyl 6-(3-methoxyphenyl)-3-oxoheptanoate (1c): colorless oil; 95% yield (0.71 mmol scale); IR (ATR): ν 2957, 1746, 1715, 1654, 1600, 1584, 1487, 1455, 1437, 1407, 1317, 1258, 1196, 1162, 1042, 787 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.20 (1H, dd, *J* = 7.9, 7.8 Hz), 6.75-6.70 (3H, m), 3.79 (3H, s), 3.69 (3H, s), 3.35 (2H, s), 2.67 (1H, m), 2.42 (1H, ddd, *J* = 17.7, 8.9, 6.6 Hz), 2.36 (1H, ddd, *J* = 17.7, 8.9, 5.7 Hz), 1.94-1.78 (2H, m), 1.24 (3H, d, *J* = 6.9 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.7, 167.6, 159.8, 148.0, 129.5, 119.4, 113.0, 111.3, 55.1, 52.3, 49.0, 41.2, 39.2, 31.5, 22.4 ppm; HRMS (*m*/*z*) for $C_{15}H_{20}O_4(Na^+)$: calculated 287.1259, found 287.1242.

Methyl 6-(4-acetamidophenyl)-3-oxoheptanoate (1d): colorless oil; 90% yield (1.58 mmol scale); IR (ATR): ν 3303, 2956, 1745, 1712, 1666, 1602, 1532, 1516, 1437, 1412, 1371, 1316, 1260, 1221, 1183, 1015, 913, 837 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.41 (2H, d, *J* = 8.4 Hz), 7.16 (1H, br s), 7.11 (2H, d, *J* = 8.4 Hz), 3.70 (3H, s), 3.35 (2H, s), 2.67 (1H, m), 2.43 (1H, ddd, *J* = 17.7, 8.8, 6.5 Hz), 2.35 (1H, ddd, *J* = 17.7, 8.8, 5.7 Hz), 2.16 (3H,s), 1.92 (1H, m), 1.80 (1H, m), 1.23 (3H, d, *J* = 6.9 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.6, 168.2, 167.6, 142.3, 136.0, 127.5, 120.2, 52.3, 49.0, 41.2, 38.6, 31.5, 24.5, 22.4 ppm; HRMS (*m*/*z*) for $C_{16}H_{21}NO_4(Na^+)$: calculated 314.1368, found 314.1349.

Methyl 6-(benzofuran-5-yl)-3-oxoheptanoate (1e): colorless oil; 62% yield (1.95 mmol scale); IR (ATR): ν 2955, 1746, 1714, 1469, 1438, 1407, 1320, 1196, 1154, 1131, 1111, 1031, 880, 816, 771, 742 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.60 (1H, d, *J* = 2.2 Hz), 7.42 (1H, d, *J* = 8.5 Hz), 7.37 (1H, d, *J* = 1.8 Hz), 7.09 (1H, dd, *J* = 8.5, 1.8 Hz), 6.72 (1H, dd, *J* = 2.2, 0.9 Hz), 3.68 (3H, s), 3.34 (2H, s), 2.80 (1H, m), 2.44 (1H, ddd, *J* = 17.7, 9.1, 6.5 Hz), 2.36 (1H, ddd, *J* = 17.7, 8.9, 5.5 Hz), 1.98 (1H, m), 1.88 (1H, m), 1.30 (3H, d, *J* = 6.9 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.7, 16.7.6, 153.8, 145.2, 140.7, 127.6, 123.4, 119.1, 111.3, 106.5, 52.3, 49.0, 41.3, 39.1, 31.9, 23.1 ppm; HRMS (*m*/*z*) for $C_{16}H_{18}O_4(Na^+)$: calculated 297.1103, found 297.1098.

Methyl 6-(2,4-dimethoxyphenyl)-3-oxoheptanoate (1f): colorless oil; 91% yield (0.93 mmol scale); IR (ATR): ν 2954, 1746, 1714, 1610, 1586, 1505, 1455, 1438, 1415, 1290, 1260, 1207, 1156, 1036 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.03 (1H, d, *J* = 8.2 Hz), 6.46 (1H, dd, *J* = 8.2, 2.4 Hz), 6.44 (1H, d, *J* = 2.4 Hz), 3.79 (3H, s), 3.78 (3H, s), 3.70 (3H, s), 3.37 (2H, s), 3.09 (1H, m), 2.44 (1H, ddd, *J* = 17.3, 9.2, 6.5 Hz), 2.35 (1H, ddd, *J* = 17.3, 9.0, 5.7 Hz), 1.91-1.78 (2H, m), 1.19 (3H, d, *J* = 7.0 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 203.0, 167.7, 159.0, 158.0, 127.2, 126.7, 104.3, 98.6, 55.3 (2C), 52.3, 49.0, 41.3, 30.9, 30.8, 21.1 ppm; HRMS (*m*/*z*) for $C_{16}H_{22}O_5(Na^+)$: calculated 317.1365, found 317.1340.

Methyl 6-(3,4-dimethoxyphenyl)-3-oxoheptanoate (1g): colorless oil; 80% yield (0.95 mmol scale); IR (ATR): ν 2953, 1745, 1714, 1517, 1454, 1418, 1319, 1258, 1144, 1028, cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.80 (1H, d, *J* = 8.0 Hz), 6.70-6.67(2H, m), 3.88 (3H, s), 3.86 (3H, s), 3.70 (3H, s), 3.36 (2H, s), 2.64 (1H, m), 2.43 (1H, ddd, *J* = 17.7, 8.8, 6.6 Hz), 2.37 (1H, ddd, *J* = 17.7, 8.7, 5.6 Hz), 1.91 (1H, m), 1.80 (1H, m), 1.24 (3H, d, *J* = 6.9 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.7, 167.6, 149.0, 147.4, 138.9, 118.8, 111.2, 110.2, 55.9, 55.9, 52.3, 49.1, 41.2, 38.8, 31.7, 22.6 ppm; HRMS (*m*/*z*) for $C_{16}H_{22}O_5(Na^+)$: calculated 317.1365, found 317.1339.

Methyl 6-(2,5-dimethoxyphenyl)-3-oxoheptanoate (1h): colorless oil; 92% yield (0.93 mmol scale); IR (ATR): ν 2962, 1746, 1705, 1497, 1439, 1409, 1375, 1315, 1273, 1214, 1177, 1116, 1086, 1034, 1009, 867, 837, 803 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.78 (1H, d, *J* = 8.8 Hz), 6.72 (1H, d, *J* = 3.0 Hz), 6.69 (1H, dd, *J* = 8.8, 3.0 Hz), 3.78 (6H, s), 3.70 (3H, s), 3.37 (2H, s), 3.16 (1H, m), 2.45 (1H, ddd, *J* = 17.5, 9.1, 6.5 Hz), 2.36 (1H, ddd, *J* = 17.5, 9.0, 5.6 Hz), 1.89 (1H, m), 1.82 (1H, m), 1.20 (3H, d, *J* = 7.0 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.8, 167.7, 153.9, 151.4, 135.8, 113.6, 111.6, 110.7, 56.1, 55.6, 52.2, 49.0, 41.2, 31.4, 30.7, 20.9 ppm; HRMS (*m*/*z*) for $C_{16}H_{22}O_5(Na^+)$: calculated 317.1365, found 317.1336.

Methyl 3-oxo-6-phenylheptanoate (1i): colorless oil; 96% yield (8.00 mmol scale); IR (ATR): ν 2955, 1746, 1714, 1651, 1494, 1452, 1437, 1407, 1318, 1246, 1193, 1015, 912, 763, 703 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.31-7.15 (5H, m), 3.70 (3H, s), 3.35 (2H, s), 2.69 (1H, m), 2.43 (1H, ddd, *J* = 17.7, 9.1, 6.5 Hz), 2.36 (1H, ddd, *J* = 17.7, 8.9, 5.7 Hz), 1.93 (1H, m), 1.85 (1H, m), 1.26 (3H, d, *J* = 6.9 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.5, 167.6, 146.2, 128.5, 127.0, 126.3, 52.3, 49.0, 41.2, 39.2, 31.5, 22.4 ppm; HRMS (*m*/*z*) for $C_{14}H_{18}O_3(Na^+)$: calculated 257.1154, found 257.1164.

Methyl 3-oxo-6-(*p*-tolyl)heptanoate (1j): colorless oil; 91% yield (0.90 mmol scale); IR (ATR): ν 2954, 1747, 1715, 1515, 1436, 1318, 1241, 1194, 818 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.10 (2H, d, *J* = 8.0 Hz), 7.04 (2H, d, *J* = 8.0 Hz), 3.70 (3H, s), 3.35 (2H, s), 2.66 (1H, m), 2.43 (1H, ddd, *J* = 17.7, 9.5, 6.1 Hz), 2.36 (1H, ddd, *J* = 17.7, 9.0, 5.7 Hz), 2.32 (3H, s), 1.92 (1H, m), 1.82 (1H, m), 1.24 (3H, d, *J* = 7.0 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.7, 167.6, 143.1, 135.7, 129.2, 126.9, 52.3, 49.0, 41.3, 38.8, 31.6, 22.6, 21.0 ppm; HRMS (*m*/*z*) for $C_{15}H_{20}O_3(Na^+)$: calculated 271.1310, found 271.1316.

Methyl 6-(naphthalen-2-yl)-3-oxoheptanoate (1k): colorless oil; 84% yield (1.64 mmol scale); IR (ATR): ν 3049, 2954, 1746, 1714, 1631, 1600, 1436, 1406, 1365, 1320, 1269, 1202, 1175, 858, 822, 750 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.82-7.78 (3H, m), 7.59 (1H, br s), 7.45 (2H, m), 7.32 (1H, dd, *J* = 8.5, 1.4 Hz), 3.66 (3H, s), 3.34 (2H, s), 2.88 (1H, m), 2.46 (1H, ddd, *J* = 17.8, 9.1, 6.5 Hz), 2.38 (1H, ddd, *J* = 17.8, 8.9, 5.6 Hz), 2.06-1.91 (2H, m), 1.35 (3H, d, *J* = 6.9 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.6, 167.6, 143.6, 133.6, 132.3, 128.3, 127.6, 127.6, 126.0, 125.4, 125.4, 125.3, 52.3, 49.0, 41.3, 39.3, 31.3, 22.5 ppm; HRMS (*m*/*z*) for $C_{18}H_{20}O_3(Na^+)$: calculated 307.1310, found 307.1282.

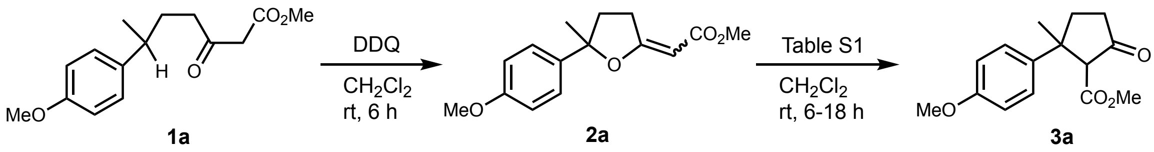
Methyl 6-(4-methoxy-3-methylphenyl)-3-oxoheptanoate (1l): colorless oil; 95% yield (3.86 mmol scale); IR (ATR): ν 2952, 1747, 1714, 1505, 1438, 1306, 1252, 1136, 1033 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.94 (2H, m), 6.75 (1H, d, *J* = 7.9 Hz), 3.81 (3H, s), 3.70 (3H, s), 3.36 (2H, s), 2.60 (1H, m), 2.42 (1H, ddd, *J* = 17.6, 9.2, 6.5 Hz), 2.36 (1H, ddd, *J* = 17.6, 8.9, 5.7 Hz), 2.20 (3H, s), 1.90 (1H, m), 1.79 (1H, m), 1.22 (3H, d, *J* = 6.9 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.8, 167.6, 156.2, 137.8, 129.3, 126.6, 125.0, 110.0, 55.4, 52.3, 49.0, 41.4, 38.4, 31.7, 22.7, 16.3 ppm; HRMS (*m*/*z*) for $C_{16}H_{22}O_4(Na^+)$: calculated 301.1416, found 301.1390. Its NMR spectra were identical with those reported previously.[1]

Methyl 6-(2,5-dimethoxy-4-methylphenyl)-3-oxoheptanoate (1m): colorless oil; 94% yield (0.90 mmol scale); IR (ATR): ν 2952, 1746, 1714, 1504, 1464, 1399, 1316, 1241, 1208, 1046 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.68 (1H, m), 6.62 (1H, s), 3.78 (3H, s), 3.75 (3H, s), 3.70 (3H, s), 3.37 (2H, s), 3.14 (1H, m), 2.47 (1H, ddd, *J* = 17.5, 9.2, 6.5 Hz), 2.36 (1H, ddd, *J* = 17.5, 9.0, 5.5 Hz), 2.20 (3H, s), 1.90 (1H, m), 1.82 (1H, m), 1.21 (3H, d, *J* = 7.0 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 202.9, 167.7, 152.0, 150.8, 132.3, 124.8, 114.3, 109.7, 56.3, 56.2, 52.2, 49.0, 41.3, 31.4, 30.8, 21.2, 16.1 ppm; HRMS (*m*/*z*) for $C_{17}H_{24}O_5(Na^+)$: calculated 331.1521, found 331.1513

Methyl 6-(3-methoxy-4-methylphenyl)-3-oxoheptanoate (1n): colorless oil; 83% yield (0.80 mmol scale); IR (ATR): ν 2953, 1747, 1715, 1612, 1581, 1506, 1455, 1414, 1312, 1255, 1163, 1135, 1039 cm^{-1}; ^1H NMR

(CDCl3): δ 7.05 (1H, d, *J* = 7.5 Hz), 6.65 (1H, dd, *J* = 7.5, 1.6 Hz), 6.62 (1H, d, *J* = 1.6 Hz), 3.82 (3H, s), 3.70 (3H, s), 3.36 (2H, s), 2.66 (1H, m), 2.44 (1H, ddd, *J* = 17.7, 8.9, 6.6 Hz), 2.38 (1H, ddd, *J* = 17.7, 8.8, 5.7 Hz), 2.18 (3H, s), 1.93 (1H, m), 1.83 (1H, m), 1.25 (3H, d, *J* = 6.9 Hz) ppm; ^{13}C NMR (CDCl3): δ 202.7, 167.6, 157.8, 145.2, 130.6, 124.4, 118.6, 108.8, 55.3, 52.3, 49.1, 41.3, 39.2, 31.6, 22.6, 15.8 ppm; HRMS (*m*/*z*) for $C_{16}H_{22}O_4(Na^+)$: calculated 301.1416, found 301.1395

3-2. Dehydrogenative O-alkylation to 2a and Lewis acid-catalyzed [1,3]-rearrangement to 3a



Scheme S3. Dehydrogenative O-alkylation to 2a and Lewis acid-catalyzed [1,3]-rearrangement to 3a

Methyl 2-(5-(4-methoxyphenyl)-5-methyldihydrofuran-2(3H)-ylidene)acetate (2a)

Methyl 6-(4-methoxyphenyl)-3-oxoheptanoate (**1a**) (26.4 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (1.0 mL) and DDQ (34.0 mg, 0.15 mmol) was added to the solution. The reaction was stirred under an argon atmosphere at room temperature for 6 hours. The reaction was quenched by addition of ascorbic acid (35.2 mg, 0.20 mmol), water (1 mL) and saturated $NaHCO_3$ aq. (4 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 mL×3). The combined organic layer was washed with brine, dried over Na_2SO_4 and filtered through a cotton plug. The filtrate was concentrated in vacuo and the residue was purified by preparative thin layer chromatography with hexane/EtOAc (5/1) to give methyl 2-(5-(4-methoxyphenyl)-5-methyldihydrofuran-2(3H)-ylidene)acetate (**2a**).

(*E*)-**2a**: colorless oil; 18.0 mg, 69% yield; IR (ATR): ν 2947, 1705, 1642, 1514, 1435, 1359, 1303, 1248, 1181, 1118, 1075, 1038, 948, 832 cm^{-1}; ^1H NMR (CDCl3): δ 7.24 (2H, d, *J* = 8.9 Hz), 6.87 (2H, d, *J* = 8.9 Hz), 5.42 (1H, dd, *J* =1.9, 1.7 Hz), 3.79 (3H, s), 3.66 (3H, s), 3.28 (1H, dddd, *J* = 18.5, 8.8, 5.2, 1.7 Hz), 2.98 (1H, dddd, *J* = 18.5, 8.8, 8.2, 1.9 Hz), 2.32 (1H, ddd, *J* = 12.4, 8.8, 5.2 Hz), 2.19 (1H, ddd, *J* = 12.4, 8.8, 8.2 Hz), 1.65 (3H, s) ppm; ^{13}C NMR (CDCl3): δ 176.1, 169.1, 158.8, 136.8, 125.6, 113.8, 89.9, 89.4, 55.3, 50.6, 37.4, 30.6, 28.5 ppm; HRMS (*m*/*z*) for $C_{15}H_{18}O_4(Na^+)$: calculated 285.1102, found 285.1130.

(*Z*)-**2a**: colorless oil; 1.4 mg, 5% yield; IR (ATR): ν 2947, 1712, 1646, 1613, 1514, 1436, 1375, 1298, 1249, 1229, 1168, 1146, 1076, 1036, 964, 902, 834 cm^{-1}; ^1H NMR (CDCl3): δ 7.31 (2H, d, *J* = 8.8 Hz), 6.87 (2H, d, *J* = 8.8 Hz), 4.88 (1H, dd, *J* =1.4, 1.1 Hz), 3.80 (3H, s), 3.71 (3H, s), 2.77 (1H, dddd, *J* = 16.9, 8.5, 5.0, 1.1 Hz), 2.61 (1H, dddd, *J* = 16.9, 8.6, 8.3, 1.4 Hz), 2.29 (1H, ddd, *J* = 12.2, 8.3, 5.0 Hz), 2.16 (1H, ddd, *J* = 12.2, 8.6, 8.5 Hz), 1.72 (3H, s) ppm; ^{13}C NMR (CDCl3): δ 171.4, 166.4, 158.8, 136.9, 125.6, 113.8, 92.6, 88.0, 55.3, 50.7, 36.6, 32.0, 29.1 ppm; HRMS (*m*/*z*) for $C_{15}H_{18}O_4(Na^+)$: calculated 285.1102, found 285.1086.

General procedure of Lewis acid-catalyzed [1,3]-rearrangement from 2a to 3a

Methyl 2-(5-(4-methoxyphenyl)-5-methyldihydrofuran-2(3H)-ylidene)acetate (**2a**) (10.0 mg, 0.038 mmol) was disolved in CH_2Cl_2 (1.0 mL) and acid catalyst (30-100 mol%) was added to the solution. The reaction was stirred under an argon atmosphere for 6-18 hours at room temperature. The reaction was quenched by addition of saturated $NaHCO_3$ aq. (2 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 mL×3). The combined organic layer was washed with brine, dried over Na_2SO_4 and filtered through a cotton plug. The filtrate was concentrated in vacuo and the residue was purified by preparative thin layer chromatography with hexane/EtOAc (5/1) to give methyl 2-(4-methoxyphenyl)-2-methyl-5-oxocyclopentane-1-carboxylate (**3a**). Since **3a** was a mixture of keto and enol forms (keto/enol = 2.3/1) as well as the diastereomers in keto forms judged by ^{1}H NMR, the structure was fully identified after conversion to a ketone **10** by dealkoxycarboxylation (see section 3-5 in S17).

3-3. General procedure of dehydrogenative O-alkylation of 1 to 2

Methyl 6-aryl-3-oxoheptanoate (**1**) (0.10 mmol) was dissolved in CH_2Cl_2 (1.0 mL) and DDQ (34.0 mg, 0.15 mmol) was added to the solution. The reaction was stirred under an argon atmosphere at room temperature for 6-24 hours. The reaction was quenched by addition of ascorbic acid (35.2 mg, 0.20 mmol), water (1 mL) and saturated $NaHCO_3$ aq. (4 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 mL×3). The combined organic layer was washed with brine, dried over Na_2SO_4 and filtered through a cotton plug. The filtrate was concentrated in vacuo and the residue was purified by preparative thin layer chromatography with hexane/EtOAc to give methyl 2-(5-aryl-5-methyldihydrofuran-2(3H)-ylidene)acetate (**2**)

Methyl 2-(5-(4-acetamidophenyl)-5-methyldihydrofuran-2(3H)-ylidene)acetate (2d)

(*E*)-**2d**: colorless oil; 15.6 mg, 54% yield; IR (ATR): ν 3309, 2978, 2947, 1667, 1637, 1603, 1533, 1436, 1406, 1360, 1317, 1258, 1187, 1117, 1073, 1041, 948 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.46 (2H, d, J = 8.6 Hz), 7.27 (2H, d, J = 8.6 Hz), 5.43 (1H, br s), 3.67 (3H, s), 3.28 (1H, dddd, J = 18.5, 8.7, 5.2, 1.6 Hz), 2.95 (1H, dddd, J = 18.5, 8.8, 8.4, 1.8 Hz), 2.32 (1H, ddd, J = 12.5, 8.8, 5.2 Hz), 2.19 (1H, ddd, J = 12.5, 8.7, 8.4 Hz), 2.18 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 176.0, 169.1, 168.5, 140.6, 137.2, 125.0, 119.9, 89.9, 89.6, 50.7, 37.4, 30.5, 28.4, 24.5 ppm; HRMS (m/z) for $C_{16}H_{19}NO_4(Na^+)$: calculated 312.1212, found 312.1190.

(*Z*)-**2d**: colorless oil; 1.7 mg, 6% yield; ^{1}H NMR ($CDCl_3$): δ 7.45 (2H, d, J = 8.5 Hz), 7.32 (2H, d, J = 8.5 Hz), 4.89 (1H, br s), 3.71 (3H, s), 2.77 (1H, ddd, J = 16.9, 8.5, 5.0 Hz), 2.60 (1H, dddd, J = 16.9, 8.4, 8.3, 1.3 Hz), 2.28 (1H, ddd, J = 12.2, 8.3, 5.0 Hz), 2.17 (1H, m), 2.17 (3H, s), 1.70 (3H, s) ppm; HRMS (m/z) for $C_{16}H_{19}NO_4(Na^+)$: calculated 312.1212, found 312.1192.

Methyl 2-(5-(benzofuran-5-yl)-5-methyldihydrofuran-2(3H)-ylidene)acetate (2e)

(*E*)-**2e**: colorless oil; 8.4 mg, 31% yield; IR (ATR): ν 2977, 2947, 1704, 1642, 1469, 1436, 1360, 1266, 1189, 1120, 1087, 1040, 950, 885, 822, 773 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.56 (1H, d, J = 2.2 Hz), 7.50 (1H, d, J = 1.8

Hz), 7.40 (1H, d, *J* = 8.7 Hz), 7.18 (1H, dd, *J* = 8.7, 1.8 Hz), 6.69 (1H, dd, *J* = 2.2, 1.0 Hz), 5.40 (1H, dd, *J* = 1.9, 1.6 Hz), 3.60 (3H, s), 3.24 (1H, dddd, *J* = 18.5, 8.7, 5.2, 1.6 Hz), 2.91 (1H, dddd, *J* = 18.5, 8.7, 8.4, 1.9 Hz), 2.34 (1H, ddd, *J* = 12.4, 8.7, 5.2 Hz), 2.20 (1H, ddd, *J* = 12.4, 8.7, 8.4 Hz), 1.65 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 176.0, 169.1, 154.1, 145.7, 139.5, 127.4 120.9, 116.9, 111.3, 106.7, 90.3, 89.6, 50.7, 37.8, 30.5, 29.0 ppm; HRMS (*m*/*z*) for $C_{16}H_{16}O_4(Na^+)$: calculated 295.0946, found 295.0945.

(*Z*)-**2e**: colorless oil; 0.8 mg, 3% yield; ^{1}H NMR ($CDCl_3$): δ 7.67 (1H, d, *J* = 1.8 Hz), 7.62 (1H, d, *J* = 2.2 Hz), 7.47(1H, d, *J* = 8.6 Hz), 7.31 (1H, dd, *J* = 8.6, 1.8 Hz), 6.77 (1H, br s), 4.91 (1H, br s), 3.73 (3H, s), 2.79 (1H, ddd, *J* = 16.9, 8.5, 5.0 Hz), 2.62 (1H, ddd, *J* = 16.9, 8.4, 8.3 Hz), 2.37 (1H, ddd, *J* = 12.2, 8.3, 5.0 Hz), 2.24 (1H, ddd, *J* = 12.2, 8.5, 8.4 Hz), 1.78 (3H, s) ppm; HRMS (*m*/*z*) for $C_{16}H_{16}O_4(Na^+)$: calculated 295.0946, found 295.0938.

Methyl 2-(5-(2,4-dimethoxyphenyl)-5-methyldihydrofuran-2(3H)-ylidene)acetate (2f)

(*E*)-**2f**: colorless oil; 10.5 mg, 35% yield; IR (ATR): ν 2943, 1705, 1641, 1614, 1584, 1504, 1456, 1436, 1416, 1360, 1315, 1285, 1259, 1208, 1161, 1119, 1069, 1040, 949, 876, 827 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.25 (1H, d, *J* = 8.6 Hz), 6.47 (1H, d, *J* = 2.4 Hz), 6.43 (1H, dd, *J* = 8.6, 2.4 Hz), 5.43 (1H, br), 3.82 (3H, s), 3.79 (3H, s), 3.66 (3H, s), 3.24 (1H, dddd, *J* = 18.5, 8.7, 5.0, 1.5 Hz), 2.78 (1H, dddd, *J* = 18.5, 9.0, 8.7, 1.9 Hz), 2.47 (1H, ddd, *J* = 12.7, 9.0, 5.0 Hz), 2.20 (1H, ddd, *J* = 12.7, 8.7, 8.7 Hz), 1.66 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 176.6, 169.2, 160.3, 156.3, 126.1, 125.1, 103.6, 99.4, 89.7, 89.0, 55.4, 55.2, 50.6, 35.6, 30.7, 26.4 ppm; HRMS (*m*/*z*) for $C_{16}H_{20}O_5(Na^+)$: calculated 315.1208, found 315.1237

(*Z*)-**2f**: colorless oil; 1.0 mg, 3% yield; ^{1}H NMR ($CDCl_3$): δ 7.48 (1H, d, *J* = 9.1 Hz), 6.47-6.45 (2H, m, *J* = 2.4 Hz), 4.86 (1H, dd, *J* = 1.3, 1.1 Hz), 3.81 (3H, s), 3.79 (3H, s), 3.72 (3H, s), 2.74 (1H, dddd, *J* = 16.8, 8.8, 5.4, 1.1 Hz), 2.55 (1H, dddd, *J* = 16.8, 8.5, 8.4, 1.3 Hz), 2.43 (1H, ddd, *J* = 12.6, 8.4, 5.4 Hz), 2.18 (1H, ddd, *J* = 12.6, 8.8, 8.5 Hz), 1.72 (3H, s) ppm; HRMS (*m*/*z*) for $C_{16}H_{20}O_5(Na^+)$: calculated 315.1208, found 315.1237.

Methyl 2-(5-(3,4-dimethoxyphenyl)-5-methyldihydrofuran-2(3H)-ylidene)acetate (2g)

(*E*)-**2g**: colorless oil; 23.1 mg, 79% yield; IR (ATR): ν 2945, 1704, 1640, 1516, 1437, 1410, 1359, 1261, 1225, 1177, 1118, 1091, 1029, 949, 874, 821 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.86-6.82 (3H, m), 6.47 (1H, d, *J* = 2.4 Hz), 5.43 (1H, br), 3.88 (3H, s), 3.86 (3H, s), 3.67 (3H, s), 3.29 (1H, dddd, *J* = 18.5, 8.6, 5.3, 1.5 Hz), 2.99 (1H, dddd, *J* = 18.5, 8.8, 8.1, 1.8 Hz), 2.34 (1H, ddd, *J* = 12.5, 8.8, 5.3 Hz), 2.19 (1H, ddd, *J* = 12.5, 8.5, 8.1 Hz), 1.65 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 176.0, 169.0, 148.9, 148.3, 137.4, 116.5, 111.0, 108.1, 89.9, 89.5, 56.0 (2C), 50.7, 37.4, 30.6, 28.5 ppm; HRMS (*m*/*z*) for $C_{16}H_{20}O_5(Na^+)$: calculated 315.1208, found 315.1216.

(*Z*)-**2g**: colorless oil; 1.7 mg, 6% yield; ^{1}H NMR ($CDCl_3$): δ 7.00 (1H, d, *J* = 2.1 Hz), 6.90 (1H, dd, *J* = 8.4, 2.1 Hz), 6.83 (1H, d, *J* = 8.4 Hz), 4.88 (1H, dd, *J* = 1.4, 1.1 Hz), 3.89 (3H, s), 3.87 (3H, s), 3.71 (3H, s), 2.78 (1H, dddd, *J* = 16.9, 8.6, 4.9, 1.1 Hz), 2.61 (1H, dddd, *J* = 16.9, 8.4, 8.4, 1.4 Hz), 2.31 (1H, ddd, *J* = 12.3, 8.4, 4.9 Hz), 2.16 (1H, ddd, *J* = 12.3, 8.6, 8.4 Hz), 1.73 (3H, s) ppm; HRMS (*m*/*z*) for $C_{16}H_{20}O_5(Na^+)$: calculated 315.1208, found 315.1190.

Methyl 2-(5-methyl-5-phenyldihydrofuran-2(3H)-ylidene)acetate (2i)

(*E*)-**2i**: colorless oil; 5.0 mg, 22% yield; IR (ATR): ν 2948, 1706, 1644, 1469, 1435, 1377, 1359, 1288, 1189, 1119, 1066, 1041, 949, 876, 824, 766, 726, 701 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.36-7.27 (5H, m), 5.44 (1H, br), 3.67 (3H, s), 3.29 (1H, dddd, *J* = 18.5, 8.7, 5.2, 1.6 Hz), 2.96 (1H, dddd, *J* = 18.5, 8.7, 8.4, 1.8 Hz), 2.35 (1H, ddd, *J* = 12.4, 8.7, 5.2 Hz), 2.22 (1H, ddd, *J* = 12.4, 8.7, 8.4 Hz), 1.67 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 176.0, 169.1, 144.8, 128.5, 127.3, 124.3, 90.0, 89.6, 50.7, 37.4, 30.5, 28.5 ppm; HRMS (*m*/*z*) for $C_{14}H_{16}O_3(Na^+)$: calculated 255.0997, found 255.1007

(*Z*)-**2i**: colorless oil; 0.7 mg, 3% yield; ^1H NMR ($CDCl_3$): δ 7.41-7.33 (5H, m), 4.88 (1H, dd, *J* = 1.4, 1.2 Hz), 3.72 (3H, s), 2.78 (1H, dddd, *J* = 16.8, 8.5, 5.1, 1.2 Hz), 2.61 (1H, dddd, *J* = 16.8, 8.5, 8.3, 1.4 Hz), 2.32 (1H, ddd, *J* = 12.3, 8.3, 5.1 Hz), 2.19 (1H, ddd, *J* = 12.3, 8.5, 8.5 Hz), 1.74 (3H, s) ppm; HRMS (*m*/*z*) for $C_{14}H_{16}O_3(Na^+)$: calculated 255.0997, found 255.0975.

Methyl 2-(5-methyl-5-(*p*-tolyl)dihydrofuran-2(3H)-ylidene)acetate (2j)

(*E*)-**2j**: colorless oil; 7.9 mg, 32% yield; IR (ATR): ν 2977, 2946, 1706, 1643, 1515, 1435, 1376, 1358, 1314, 1288, 1188, 1117, 1074, 1041, 1020, 949, 876 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.20 (2H, d, *J* = 8.3 Hz), 7.14 (2H, d, *J* = 8.3 Hz), 5.43 (1H, dd, *J* = 1.9, 1.6 Hz), 3.67 (3H, s), 3.28 (1H, dddd, *J* = 18.5, 8.7, 5.2, 1.6 Hz), 2.96 (1H, dddd, *J* = 18.5, 8.8, 8.5, 1.9 Hz), 2.33 (1H, ddd, *J* = 12.4, 8.8, 5.2 Hz), 2.33 (3H, s), 2.20 (1H, ddd, *J* = 12.4, 8.7, 8.5 Hz), 1.65 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 176.1, 169.1, 141.8, 137.0, 129.1, 124.2, 90.1, 89.4, 50.6, 37.4, 30.5, 28.5, 21.0 ppm; HRMS (*m*/*z*) for $C_{15}H_{18}O_3(Na^+)$: calculated 269.1154, found 269.1166.

(*Z*)-**2j**: colorless oil; 0.7 mg, 3% yield; ^1H NMR ($CDCl_3$): δ 7.29 (2H, d, *J* = 8.1 Hz), 7.15 (2H, d, *J* = 8.1 Hz), 4.87 (1H, dd, *J* = 1.3, 1.1 Hz), 3.71 (3H, s), 2.76 (1H, dddd, *J* = 16.9, 8.5, 5.0, 1.1 Hz), 2.60 (1H, dddd, *J* = 16.9, 8.6, 8.3, 1.3 Hz), 2.33 (3H, s), 2.30 (1H, ddd, *J* = 12.2, 8.3, 5.0 Hz), 2.16 (1H, ddd, *J* = 12.2, 8.6, 8.5 Hz), 1.72 (3H, s) ppm; HRMS (*m*/*z*) for $C_{15}H_{18}O_3(Na^+)$: calculated 269.1154, found 269.1135.

Methyl (E)-2-(5-methyl-5-(naphthalen-2-yl)dihydrofuran-2(3H)-ylidene)acetate (2k)

(*E*)-**2k**: colorless oil; 15.9 mg, 56% yield; IR (ATR): ν 2978, 2947, 1706, 1643, 1435, 1359, 1287, 1191, 1117, 1091, 1042, 947, 822, 771, 749 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.85-7.77 (4H, m), 7.51-7.46 (2H, m), 7.42 (1H, dd, *J* = 8.6, 1.9 Hz), 5.52 (1H, d, *J* = 1.9, 1.6 Hz), 3.68 (3H, s), 3.34 (1H, dddd, *J* = 18.4, 8.7, 5.1, 1.6 Hz), 2.99 (1H, dddd, *J* = 18.4, 8.8, 8.5, 1.9 Hz), 2.46 (1H, ddd, *J* = 12.5, 8.8, 5.1 Hz), 2.30 (1H, ddd, *J* = 12.5, 8.7, 8.5 Hz), 1.76 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 176.0, 169.1, 142.0, 133.0, 132.5, 128.4, 128.2, 127.6, 126.4, 126.1, 122.8, 122.8, 90.2, 89.7, 50.7, 37.3, 30.5, 28.4 ppm; HRMS (*m*/*z*) for $C_{18}H_{28}O_3(Na^+)$: calculated 305.1154, found 305.1142.

(*Z*)-**2k**: colorless oil; 1.3 mg, 5% yield; ^{1}H NMR ($CDCl_3$): δ 7.86-7.81 (4H, m), 7.50-7.44 (3H, m), 4.92 (1H, br s), 3.75 (3H, s), 2.81 (1H, ddd, *J* = 16.6, 8.7, 4.7 Hz), 2.64 (1H, ddd, *J* = 16.6, 8.4, 8.3 Hz), 2.43 (1H, ddd, *J* = 12.3, 8.3, 4.7 Hz), 2.26 (1H, ddd, *J* = 12.3, 8.7, 8.4 Hz), 1.83 (3H, s) ppm; HRMS (*m*/*z*) for $C_{18}H_{28}O_3(Na^+)$: calculated 305.1154, found 305.1148.

Methyl 2-(5-(4-methoxy-3-methylphenyl)-5-methyldihydrofuran-2(3H)-ylidene)acetate (2l).

(*E*)-**2l**: colorless oil; 22.7 mg, 82% yield; IR (ATR): ν 2975, 2947, 1705, 1642, 155, 1435, 1359, 1249, 1117, 1091, 1037, 949, 873, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.11 (1H, dd, *J* = 8.4, 2.3 Hz), 7.07 (1H, d, *J* = 2.3 Hz), 6.77 (1H, d, *J* = 8.4 Hz), 5.42 (1H, d, *J* = 1.9, 1.6 Hz), 3.81 (3H, s), 3.67 (3H, s), 3.28 (1H, dddd, *J* = 18.4, 8.7, 5.2, 1.6 Hz), 2.98 (1H, dddd, *J* = 18.4, 8.8, 8.3, 1.9 Hz), 2.33 (1H, ddd, *J* = 12.5, 8.8, 5.3 Hz), 2.21 (3H, s), 2.17 (1H, ddd, *J* = 12.5, 8.8, 8.3 Hz), 1.64 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 176.2, 169.2, 157.0, 136.3, 126.8, 126.7, 122.7, 109.6, 90.0, 89.3, 55.4, 50.6, 37.4, 30.6, 28.5, 16.4 ppm; HRMS (*m*/*z*) for $C_{16}H_{20}O_4(Na^+)$: calculated 299.1259, found 299.1237.

(*Z*)-**2l**: colorless oil; 1.5 mg, 5% yield; ^{1}H NMR ($CDCl_3$): δ 7.21 (1H, dd, *J* = 8.5, 2.3 Hz), 7.11 (1H, d, *J* = 2.3 Hz), 6.87 (1H, d, *J* = 8.5 Hz), 4.87 (1H, d, *J* = 1.4, 1.1 Hz), 3.81 (3H, s), 3.71 (3H, s), 2.75 (1H, dddd, *J* = 16.9, 8.5, 4.9, 1.1 Hz), 2.61 (1H, dddd, *J* = 16.9, 8.5, 8.3, 1.4 Hz), 2.29 (1H, ddd, *J* = 12.2, 8.3, 4.9 Hz), 2.22 (3H, s), 2.14 (1H, ddd, *J* = 12.2, 8.5, 8.5 Hz), 1.71 (3H, s) ppm; HRMS (*m*/*z*) for $C_{16}H_{20}O_4(Na^+)$: calculated 299.1259, found 299.1234.

Methyl 2-(5-(2,5-dimethoxy-4-methylphenyl)-5-methyldihydrofuran-2(3H)-ylidene)acetate (2m)

(*E*)-**2m**: colorless oil; 11.1 mg, 36% yield; IR (ATR): ν 2946, 1708, 1643, 154, 1465, 1435, 1396, 1372, 1359, 1277, 1212, 1119, 1088, 1062, 1042, 948, 873, 824, 773 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.88 (1H, s), 6.71 (1H, s), 5.46 (1H, br), 3.79 (3H, s), 3.77 (3H, s), 3.67 (3H, s), 3.24 (1H, dddd, *J* = 18.5, 8.8, 5.2, 1.3 Hz), 2.90 (1H, dddd, *J* = 18.5, 9.0, 8.5, 1.7 Hz), 2.48 (1H, ddd, *J* = 12.8, 9.0, 5.2 Hz), 2.25 (1H, ddd, *J* = 12.8, 8.8, 8.5 Hz), 2.20 (3H, s), 1.67 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 176.5, 169.2, 151.4, 148.7, 130.6, 126.3, 114.5, 108.4, 89.8, 89.1, 56.0, 55.7, 50.6, 35.7, 30.7, 26.2, 16.1 ppm; HRMS (*m*/*z*) for $C_{17}H_{22}O_5(Na^+)$: calculated 329.1365, found 329.1380.

(*Z*)-**2m**: colorless oil; 0.8 mg, 3% yield; ^{1}H NMR ($CDCl_3$): ^{1}H NMR ($CDCl_3$): δ 7.21 (1H, s), 6.70 (1H, s), 4.87 (1H, br), 3.79 (3H, s), 3.79 (3H, s), 3.71 (3H, s), 2.75 (1H, dddd, *J* = 16.4, 9.0, 5.2, 1.3 Hz), 2.57-2.44 (2H, m), 2.20 (1H, m), 2.20 (3H, s), 1.74 (3H, s) ppm; HRMS (*m*/*z*) for $C_{17}H_{22}O_5(Na^+)$: calculated 329.1365, found 329.1381.

Methyl 2-(5-(3-methoxy-4-methylphenyl)-5-methyldihydrofuran-2(3H)-ylidene)acetate (2n)

(*E*)-**2n**: colorless oil; 11.3 mg, 41% yield; IR (ATR): ν 2976, 2947, 1706, 1643, 1582, 1506, 1456, 1435, 1406, 1376, 1360, 1313, 1262, 1233, 1188, 1118, 1092, 1040, 950, 875, 822 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.08 (1H, d, *J* = 7.5 Hz), 6.79-6.77 (2H, m), 5.44 (1H, dd, *J* = 1.9, 1.6 Hz), 3.83 (3H, s), 3.67 (3H, s), 3.28 (1H, dddd, *J* = 18.5, 8.7, 5.2, 1.6 Hz), 2.97 (1H, dddd, *J* = 18.5, 8.8, 8.4, 1.9 Hz), 2.35 (1H, ddd, *J* = 12.5, 8.8, 5.2 Hz), 2.20 (1H, ddd, *J* = 12.5, 8.7, 8.4 Hz), 2.19 (3H, s), 1.66 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 176.1, 169.1, 157.7, 143.7, 130.5, 125.7, 116.1, 106.2. 90.2, 89.5, 55.3, 50.7, 37.4, 30.6, 28.6, 15.8 ppm; HRMS (*m/z*) for $C_{16}H_{20}O_4(Na^+)$: calculated 299.1259, found 299.1231.

(*Z*)-**2n**: colorless oil; 1.1 mg, 4% yield; IR (ATR): ^{1}H NMR ($CDCl_3$): δ 7.09 (1H, d, *J* = 7.7 Hz), 6.96 (1H, d, *J* = 1.7 Hz), 6.82 (1H, dd, *J* =7.7, 1.7 Hz), 4.88 (1H, dd, *J* = 1.4, 1.1 Hz), 3.83 (3H, s), 3.71 (3H, s), 2.77 (1H, dddd, *J* = 16.9, 8.6, 4.8, 1.1 Hz), 2.60 (1H, dddd, *J* = 16.9, 8.6, 8.6, 1.4 Hz), 2.33 (1H, ddd, *J* = 12.2, 8.3, 4.8 Hz), 2.17-2.13 (1H, m), 2.19 (3H, s), 1.73 (3H, s) ppm; HRMS (*m/z*) for $C_{16}H_{20}O_4(Na^+)$: calculated 299.1259, found 299.1259.

3-4. General procedure of [1,3]-rearrangement from 2 to 3

Methyl 2-(5-aryl-5-methyldihydrofuran-2(3H)-ylidene)acetate (**2**) (0.02-0.10 mmol) was disolved in CH_2Cl_2 (1.0 mL) and $Sc(OTf)_3$ (30 mol%) was added to the solution. The reaction was stirred under an argon atmosphere for 2-24 hours at room temperature, 40 °C or 80 °C. The reaction was quenched by addition of saturated $NaHCO_3$ aq. (2 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 mL×3). The combined organic layer was washed with brine, dried over Na_2SO_4 and filtered through a cotton plug. The filtrate was concentrated in vacuo and the residue was purified by preparative thin layer chromatography with hexane/EtOAc to give methyl 2-aryl-2-methyl-5-oxocyclopentane-1-carboxylate (**3**). Since **3** was a mixture of keto and enol forms as well as the diastereomers in keto forms judged by ^{1}H NMR, the structure was fully identified after conversion to a ketone **10** by dealkoxycarboxylation.

Methyl 2-(4-methoxyphenyl)-2-methyl-5-oxocyclopentane-1-carboxylate (3a) (keto/enol = 2.3/1, *dr* of keto forms = 1.3/1 judged by ^{1}H NMR): colorless oil; 86% yield (0.10 mmol scale); HRMS (*m/z*) for $C_{15}H_{18}O_4(Na^+)$: calculated 285.1103, found 285.1086.

Methyl 2-(4-acetamidophenyl)-2-methyl-5-oxocyclopentane-1-carboxylate (3d) (keto/enol = 2.1/1, *dr* of keto forms = 1.5/1 judged by ^{1}H NMR): colorless oil; 78% yield (0.07 mmol scale); HRMS (*m/z*) for $C_{16}H_{19}NO_4(Na^+)$: calculated 312.1212, found 312.1187.

Methyl 2-(benzofuran-5-yl)-2-methyl-5-oxocyclopentane-1-carboxylate (3e) (keto/enol = 1.8/1, *dr* of keto forms = 1.2/1 judged by ^{1}H NMR): colorless oil; 85% yield (0.04 mmol scale); HRMS (*m/z*) for $C_{16}H_{16}O_4(Na^+)$: calculated 295.0946, found 295.0929.

Methyl 2-(2,4-dimethoxyphenyl)-2-methyl-5-oxocyclopentane-1-carboxylate (3f) (keto/enol = 7.1/1, *dr* of keto forms = 1.9/1 judged by ^{1}H NMR): colorless oil; 84% yield (0.03 mmol scale); HRMS (*m*/*z*) for $C_{16}H_{20}O_5(Na^+)$: calculated 315.1208, found 315.1220.

Methyl 2-(3,4-dimethoxyphenyl)-2-methyl-5-oxocyclopentane-1-carboxylate (3g) (keto/enol = 1.3/1, *dr* of keto forms = 1.3/1 judged by ^{1}H NMR): colorless oil; 78% yield (0.07 mmol scale); HRMS (*m*/*z*) for $C_{16}H_{20}O_5(Na^+)$: calculated 315.1208, found 315.1216.

Methyl 2-methyl-5-oxo-2-phenylcyclopentane-1-carboxylate (3i) (keto/enol = 2.3/1, *dr* of keto forms = 1.3/1 judged by ^{1}H NMR): colorless oil; 94% yield (0.04 mmol scale); HRMS (*m*/*z*) for $C_{14}H_{16}O_3(Na^+)$: calculated 255.0997, found 255.0980.

Methyl 2-methyl-5-oxo-2-(*p*-tolyl)cyclopentane-1-carboxylate (3j) (keto/enol = 2.6/1, *dr* of keto forms = 1.1/1 judged by ^{1}H NMR): colorless oil; 88% yield (0.02 mmol scale); HRMS (*m*/*z*) for $C_{15}H_{18}O_3(Na^+)$: calculated 269.1154, found 269.1179.

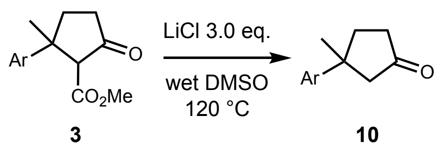
Methyl 2-methyl-2-(naphthalen-2-yl)-5-oxocyclopentane-1-carboxylate (3k) (keto/enol = 3.6/1, *dr* of keto forms = 1.0/1 judged by ^{1}H NMR): colorless oil; 83% yield (0.06 mmol scale); HRMS (*m*/*z*) for $C_{18}H_{18}O_3(Na^+)$: calculated 305.1154, found 305.1129.

Methyl 2-(4-methoxy-3-methylphenyl)-2-methyl-5-oxocyclopentane-1-carboxylate (3l) (keto/enol = 2.5/1, *dr* of keto forms = 1.4/1 judged by ^{1}H NMR): colorless oil; 82% yield (0.08 mmol scale); HRMS (*m*/*z*) for $C_{16}H_{20}O_4(Na^+)$: calculated 299.1259, found 299.1255.

Methyl 2-(2,5-dimethoxy-4-methylphenyl)-2-methyl-5-oxocyclopentane-1-carboxylate (3m) (keto/enol = 8.8/1, *dr* of keto forms = 1.5/1 judged by ^{1}H NMR): colorless oil; 86% yield (0.03 mmol scale); HRMS (*m*/*z*) for $C_{17}H_{22}O_5(Na^+)$: calculated 329.1365, found 329.1365.

Methyl 2-(3-methoxy-4-methylphenyl)-2-methyl-5-oxocyclopentane-1-carboxylate (3n) (keto/enol = 2.5/1, *dr* of keto forms = 1.4/1 judged by ^{1}H NMR): colorless oil; 75% yield (0.05 mmol scale); HRMS (*m*/*z*) for $C_{16}H_{20}O_4(Na^+)$: calculated 299.1259, found 299.1248.

3-5. General procedure of dealkoxycarbonylation of 3 to 10



Scheme S4. Dealkoxycarbonylation of methyl 2-aryl-2-methyl-5-oxocyclopentane-1-carboxylate (3)

Methyl 2-aryl-2-methyl-5-oxocyclopentane-1-carboxylate (**3**) (0.02-0.06 mmol) was dissolved in DMSO/H_2O (25/1, 1.0 mL) and LiCl (3.0 eq.) was added to the solution. The reaction was stirred for 16 hours at 120 °C. The reaction was quenched by addition of water (2 mL). The aqueous layer was extracted with EtOAc (2 mL×3). The combined organic layer was washed with water and brine, dried over Na_2SO_4 and filtered through a cotton plug. The filtrate was concentrated in vacuo and the residue was purified by preparative thin layer chromatography with hexane/EtOAc to 3-aryl-3-methylcyclopentan-1-one (**10**).

3-(4-Methoxyphenyl)-3-methylcyclopentan-1-one (10a): color less oil; 83% yield (0.03 mmol scale); ^{1}H NMR ($CDCl_3$): δ 7.21 (2H, d, *J* = 8.9 Hz), 6.88 (2H, d, *J* = 8.9 Hz), 3.80 (3H, s), 2.62 (1H, d, *J* = 17.6 Hz), 2.43 (1H, d, *J* = 17.6 Hz), 2.44-2.19 (4H, m), 1.37 (3H, s) ppm. Its NMR spectra were identical with those reported previously.[2]

***N*-(4-(1-methyl-3-oxocyclopentyl)phenyl)acetamide (10d)**: colorless oil; 90% yield (0.04 mmol scale); IR (ATR): ν 3305, 2956, 1736, 1666, 1601, 1531, 1519, 1405, 1371, 1321, 1264, 1158, 1020, 838 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.46 (2H, d, *J* = 8.6 Hz), 7.28 (1H, br s), 7.23 (2H, d, *J* = 8.6 Hz), 2.62 (1H, d, *J* = 17.7 Hz), 2.44 (1H, d, *J* = 17.7 Hz), 2.39-2.20 (4H, m), 2.17 (3H, s), 1.36 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 218.5, 168.3, 144.4, 136.1, 126.1, 120.2, 52.3, 43.5, 36.7, 35.9, 29.4, 24.5 ppm; HRMS (*m*/*z*) for $C_{14}H_{17}NO_2(Na^+)$: calculated 254.1157, found 254.1187.

3-(Benzofuran-5-yl)-3-methylcyclopentan-1-one (10e): colorless oil; 90% yield (0.04 mmol scale); IR (ATR): ν 2918, 1740, 1684, 1540, 1471, 1404, 1318, 1270, 1167, 1131, 1112, 1029, 811, 771, 741 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.62 (1H, d, *J* = 2.2 Hz), 7.49 (1H, d, *J* = 1.9 Hz), 7.47 (1H, d, *J* = 8.6 Hz), 7.24 (1H, dd, *J* = 8.6, 1.9 Hz), 6.75 (1H, dd, *J* = 2.2, 0.9 Hz), 2.72 (1H, d, *J* = 17.4 Hz), 2.55 (1H, d, *J* = 17.4 Hz), 2.52-2.32 (4H, m), 1.43 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 218.6, 153.5, 145.5, 143.2, 127.5, 122.2, 117.7, 111.4, 106.6, 52.8, 43.9, 36.8, 36.3, 30.0 ppm.

3-(2,4-Dimethoxyphenyl)-3-methylcyclopentan-1-one (10f): colorless oil; 89% yield (0.03 mmol scale); IR (ATR): ν 2952, 1739, 1610, 1581, 1505, 1464, 1408, 1308, 1267, 1208, 1160, 1034, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.09 (1H, d, *J* = 8.5 Hz), 6.48 (1H, d, *J* = 2.5 Hz), 6.45 (1H, dd, *J* = 8.5, 2.5 Hz), 3.80 (6H, s), 2.63 (1H, d, *J* = 18.1 Hz), 2.58 (1H, d, *J* = 18.1 Hz), 2.41-2.26 (4H, m), 1.36 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 220.2, 160.0, 158.7, 125.7, 126.7, 103.6. 99.5, 55.3, 55.0, 52.5, 42.2, 36.4, 35.1, 26.4 ppm; HRMS (*m*/*z*) for $C_{14}H_{18}O_3(Na^+)$: calculated 257.1154, found 257.1182.

3-(3,4-Dimethoxyphenyl)-3-methylcyclopentan-1-one (10g): colorless oil; 93% yield (0.06 mmol scale); IR (ATR): ν 2953, 2834, 1738, 1605, 1588, 1519, 1464, 1408, 1328, 1255, 1172, 1146, 1027, 810 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.84-6.80 (3H, m), 3.89 (3H, s), 3.87 (3H, s), 2.64 (1H, d, *J* = 17.6 Hz), 2.44 (1H, d, *J* = 17.6 Hz), 2.43-2.20 (4H, m), 1.39 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 218.5, 149.0, 147.6, 141.1, 117.4, 111.2. 109.3, 56.0, 55.9, 52.5, 43.5, 36.8, 36.2, 29.5 ppm; $C_{14}H_{18}O_3(Na^+)$: calculated 257.1154, found 257.1183.

3-Methyl-3-phenylcyclopentan-1-one (10i): colorless oil; 85% yield (0.02 mmol scale); ^1H NMR ($CDCl_3$): δ 7.36-7.21 (5H, m), 2.66 (1H, d, *J* = 17.6 Hz), 2.48 (1H, d, *J* = 17.6 Hz), 2.46-2.26 (4H, m), 1.39 (3H, s) ppm. Its NMR spectra were identical with those reported previously.[3]

3-Methyl-3-(*p*-tolyl)cyclopentan-1-one (10j): colorless oil; 90% yield (0.02 mmol scale); ^1H NMR ($CDCl_3$): δ 7.18 (2H, d, *J* = 8.3 Hz), 7.15 (2H, d, *J* = 8.3 Hz), 2.64 (1H, d, *J* = 17.5 Hz), 2.45 (1H, d, *J* = 17.5 Hz), 2.39-2.25 (4H, m), 2.35 (3H, s), 1.37 (3H, s) ppm. Its NMR spectra were identical with those reported previously.[4]

3-Methyl-3-(naphthalen-2-yl)cyclopentan-1-one (10k): colorless oil; 78% yield (0.05 mmol scale); IR (ATR): ν 3054, 2955, 1739, 1599, 1505, 1451, 1404, 1376, 1316, 1279, 1245, 1152, 857, 820, 748 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.85-7.81 (3H, m), 7.67 (1H, d, *J* = 1.8 Hz), 7.50-7.44 (3H, m), 2.79 (1H, d, *J* = 17.6 Hz), 2.57 (1H, d, *J* = 17.6 Hz), 2.50-2.34 (4H, m), 1.48 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 218.5, 145.7, 133.3, 132.0, 128.4, 127.9, 127.5, 126.3, 125.8, 124.5, 123.4, 52.3, 44.0, 36.8, 35.9, 29.3 ppm; HRMS (*m*/*z*) for $C_{16}H_{16}O(Na^+)$: calculated 247.1099, found 247.1127.

3-(4-Methoxy-3-methylphenyl)-3-methylcyclopentan-1-one (10l): colorless oil; 90% yield (0.04 mmol scale); IR (ATR): ν 2948, 1735, 1507, 1461, 1401, 1267, 1249, 1173, 1138, 1029, 884 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.07-7.05 (2H, m), 6.79 (1H, d, *J* = 9.1 Hz), 3.82 (3H, s), 2.63 (1H, d, *J* = 17.6 Hz), 2.42 (1H, d, *J* = 17.6 Hz), 2.44-2.18 (4H, m), 2.23 (3H, s), 1.36 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 218.6, 157.8, 147.5, 130.6, 124.8, 117.2, 107.5, 55.3, 52.5, 43.8, 36.8, 36.0, 29.4, 15.7 ppm; HRMS (*m*/*z*) for $C_{14}H_{18}O_3(Na^+)$: calculated 241.1205, found 241.1226.

3-(2,5-Dimethoxy-4-methylphenyl)-3-methylcyclopentan-1-one (6): colorless oil; 97% yield (0.03 mmol scale); ^1H NMR ($CDCl_3$): δ 6.71 (2H, br), 2.66 (1H, d, *J* = 18.1 Hz), 2.60 (1H, d, *J* = 18.1 Hz), 2.43-2.29 (4H, m), 2.21 (3H, s), 1.39 (3H, s) ppm. Its NMR spectra were identical with those reported previously.[5]

3-(3-Methoxy-4-methylphenyl)-3-methylcyclopentan-1-one (10n): colorless oil; 72% yield (0.04 mmol scale); IR (ATR): ν 2953, 1740, 1613, 1577, 1516, 1464, 1404, 1319, 1269, 1248, 1172, 1140, 1039 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.09 (1H, d, *J* = 7.7 Hz), 6.78 (1H, dd, *J* = 7.7, 1.8 Hz), 6.74 (1H, d, *J* = 1.8 Hz), 3.84 (3H, s), 2.66 (1H, d, *J* = 17.5 Hz), 2.45 (1H, d, *J* = 17.5 Hz), 2.44-2.24 (4H, m), 2.20 (3H, s), 1.36 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 218.9, 156.2, 140.1, 128.00, 126.6, 123.5, 109.8, 55.4, 52.6, 43.1, 36.8, 36.1, 29.5, 16.4 ppm; HRMS (*m/z*) for $C_{14}H_{18}O_3(Na^+)$: calculated 241.1205, found 241.1233.

3-6. One-pot conversion of 1l to 3l

Method A: Methyl 6-(4-methoxy-3-methylphenyl)-3-oxoheptanoate (**1l**) (27.6 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (1.0 mL). DDQ (34.0 mg, 0.15 mmol) and $Sc(OTf)_3$ (14.8 mg, 0.030 mmol) were added to the solution. The reaction was stirred under an argon atmosphere at room temperature for 8 hours. The reaction was quenched by addition of ascorbic acid (35.2 mg, 0.20 mmol), water (1 mL) and saturated $NaHCO_3$ aq. (4 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 mL×3). The combined organic layer was washed with brine, dried over Na_2SO_4 and filtered through a cotton plug. The filtrate was concentrated in vacuo and the residue was purified by preparative thin layer chromatography with hexane/EtOAc (5/1) to give methyl 2-(4-methoxy-3-methylphenyl)-2-methyl-5-oxocyclopentane-1-carboxylate (**3l**) (14.4 mg, 52% yield) as a colorless oil. Substrate **1l** (5.3 mg, 19% yield) was recovered.

Method B: Methyl 6-(4-methoxy-3-methylphenyl)-3-oxoheptanoate (**1l**) (27.6 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (1.0 mL) and DDQ (34.0 mg, 0.15 mmol) was added to the solution. The reaction was stirred under an argon atmosphere at room temperatura. After 6 hours, $Sc(OTf)_3$ (14.8 mg, 0.030 mmol) was added to the reaction mixture and the reaction was stirred at room temperature for 2 hours. The reaction was quenched by addition of ascorbic acid (35.2 mg, 0.20 mmol), water (1 mL) and saturated $NaHCO_3$ aq. (4 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 mL×3). The combined organic layer was washed with brine, dried over Na_2SO_4 and filtered through a cotton plug. The filtrate was concentrated in vacuo and the residue was purified by preparative thin layer chromatography with hexane/EtOAc (5/1) to give methyl 2-(4-methoxy-3-methylphenyl)-2-methyl-5-oxocyclopentane-1-carboxylate (**3l**) (17.7 mg, 64% yield) as a colorless oil.

3-7. Methylation of 3l to 5

(±)-Methyl (1*SR*,2*RS*)-2-(4-methoxy-3-methylphenyl)-1,2-dimethyl-5-oxocyclopentane-1-carboxylate ((±)-5)[1]

Methyl 2-(4-methoxy-3-methylphenyl)-2-methyl-5-oxocyclopentane-1-carboxylate (**3l**) (18.3 mg, 0.066 mmol) was dissolved in acetone (1.0 mL). K_2CO_3 (13.8 mg, 0.10 mmol) and MeI (8 μL, 0.128 mmol) were added to the solution. The reaction was stirred at room temperature for 14 hours. The reaction mixture was filtered through Celite® pad and washed with EtOAc (5 mL). The filtrate was concentrated in vacuo and the residue was purified by preparative thin layer chromatography with hexane/EtOAc (5/1) to give (±)-methyl (1*SR*,2*RS*)-2-(4-methoxy-3-methylphenyl)-1,2-dimethyl-5-oxocyclopentane-1-carboxylate ((±)-**5**) (14.0 mg, 73% yield) as a colorless oil; ^{1}H NMR ($CDCl_3$): δ 7.15 (1H, dd, *J* = 8.5, 2.3 Hz), 7.13 (1H, d, *J* = 2.3 Hz), 6.76 (1H, d, *J* = 8.5 Hz), 3.81 (3H, s), 3.31 (3H, s), 3.03 (1H, m), 2.72 (1H, ddd, *J* = 19.4, 9.4, 1.3 Hz) , 2.48 (1H, ddd, *J* = 19.4, 11.0, 9.0 Hz), 2.21 (3H, s), 1.97 (1H, ddd, *J* = 12.5, 9.0, 1.3 Hz), 1.40 (3H, s), 1.28 (3H, s) ppm; ^{13}C NMR ($CDCl_3$): δ 216.2, 171.2, 156.5, 135.8, 128.2, 126.1, 124.1, 109.5, 64.7, 55.2, 51.2, 49.4, 35.8, 31.4, 25.6. 16.5, 14.9 ppm. Its NMR spectra were identical with those reported previously.[1]

3-8. [1,3]-Rearrangement of 2l to3l using an asymmetric Cu catalyst (*S*,*S*)-4[6]

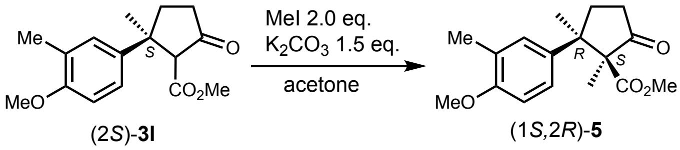
Preparation of asymmetric Cu catalyst (*S*,*S*)-4[6]

$CuCl_2$ (13.4 mg, 0.10 mmol), $AgSbF_6$ (68.7 mg, 0.20 mmol) and (*S*,*S*)-(-)-2,2'-Isopropylidenebis(4-*tert*-butyl-2-oxazoline) (29.4 mg, 0.10 mmol) were suspended in CH_2Cl_2 (2 mL) under an argon atmosphere. The suspension was stirred in the dark at room temperature. After 14 hours, the suspension was filtered through Celite® pad under air and washed with CH_2Cl_2 (5 mL). The filtrate was concentrated in vacuo to give (*S*,*S*)-**4**[6] (78.8 mg, 91%) as a light blue solid.

(2*S*)-Methyl 2-(4-methoxy-3-methylphenyl)-2-methyl-5-oxocyclopentane-1-carboxylate ((2*S*)-3l)

Methyl 2-(5-(4-methoxy-3-methylphenyl)-5-methyldihydrofuran-2(3H)-ylidene)acetate (**2l**) (27.6 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (1.0 mL). Prepared (*S*,*S*)-**4** (25.9 mg, 0.030 mmol) in CH_2Cl_2 (0.3 mL) was added to the solution. The reaction was stirred under an argon atmosphere at room temperature for 24 hours. The reaction was quenched by addition of saturated $NaHCO_3$ aq. (2 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 mL×3). The combined organic layer was washed with brine, dried over Na_2SO_4 and filtered through a cotton plug. The filtrate was concentrated in vacuo and the residue was purified by preparative thin layer chromatography with hexane/EtOAc (5/1) to gieve (2*S*)-methyl 2-(4-methoxy-3-methylphenyl)-2-methyl-5-oxocyclopentane-1-carboxylate ((2*S*)-**3l**) (18.0 mg, 65% yield) as a colorless oil.

Determination of of enantiomeric excess of enantiomerically enriched 5

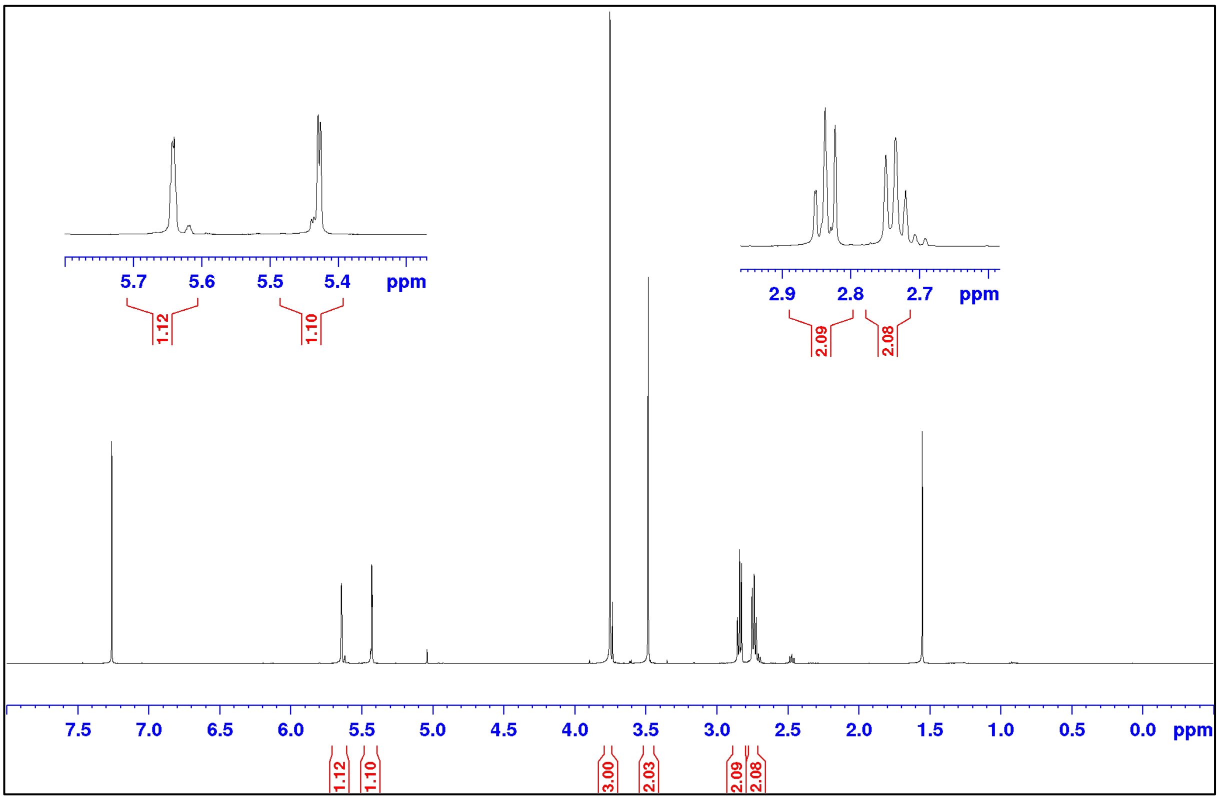


Scheme S5. Determination of enantiomeric excess of enantiomerically enriched 5

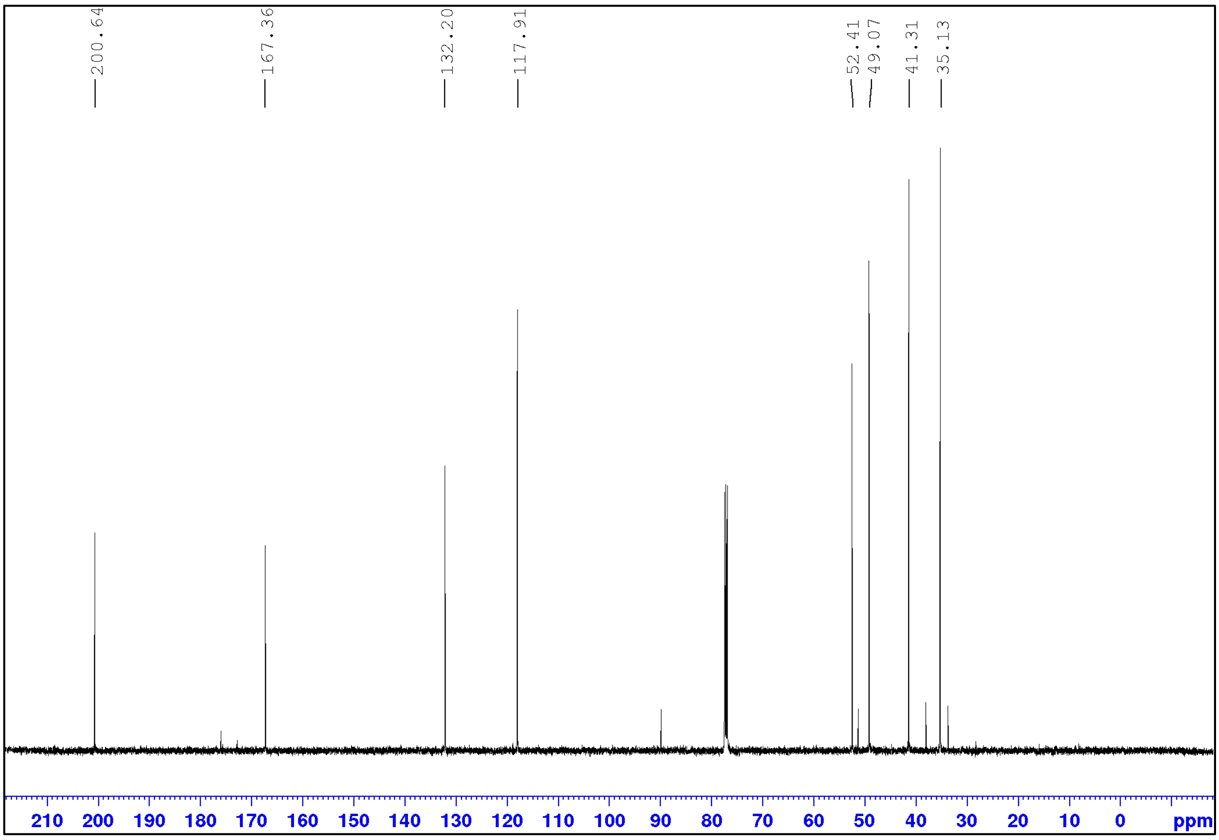
Enantiomeric excess and absolute configuration of (2*S*)-**3l** were determined after the conversion into methylated product **5**. (2*S*)-**3l** was converted to (1*S*,2*R*)-**5** by following the procedure described for (±)-**3l** to (±)-**5**. $[\alpha]^{22}_{D}$ = –31.4 (*c* = 0.6, $CHCl_3$) {lit.[1] $[\alpha]^{25}_{D}$ = +126.3 (*c* = 0.6, $CHCl_3$ for (1*R*,2*S*)-**5**)}. Enantiomeric excess was determined by HPLC analysis: [column, Daicel Chiralcel® OD-H, 0.46 x 25 cm; hexane/2-propanol = 98:2, flow rate 0.5 mL/min, detected at 270 nm], t_R (min) = 17.8 for (1*R*, 2*S*)-**5**, t_R (min) = 20.0 for (1*S*, 2*R*)-**5**.

4. ^{1}H and ^{13}C NMR Spectra

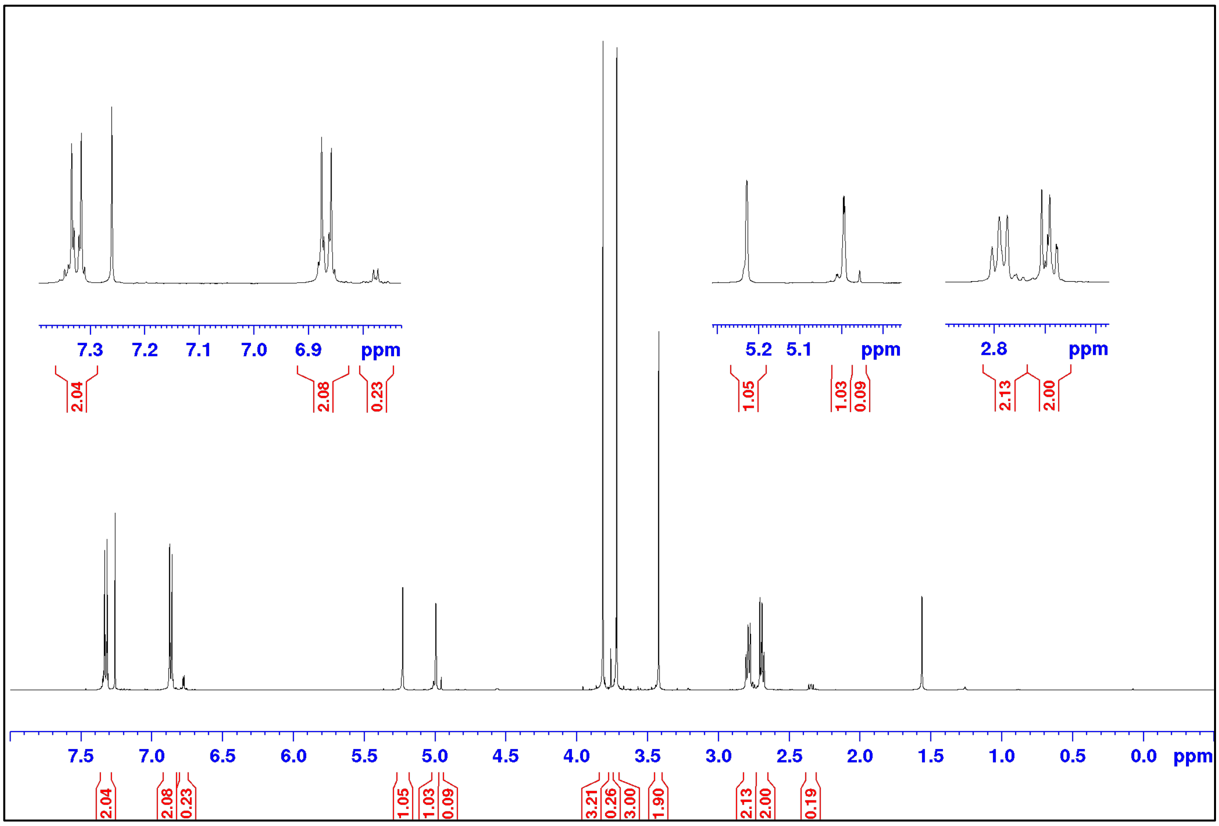
^{1}H NMR (500 MHz, $CDCl_3$) of **8**



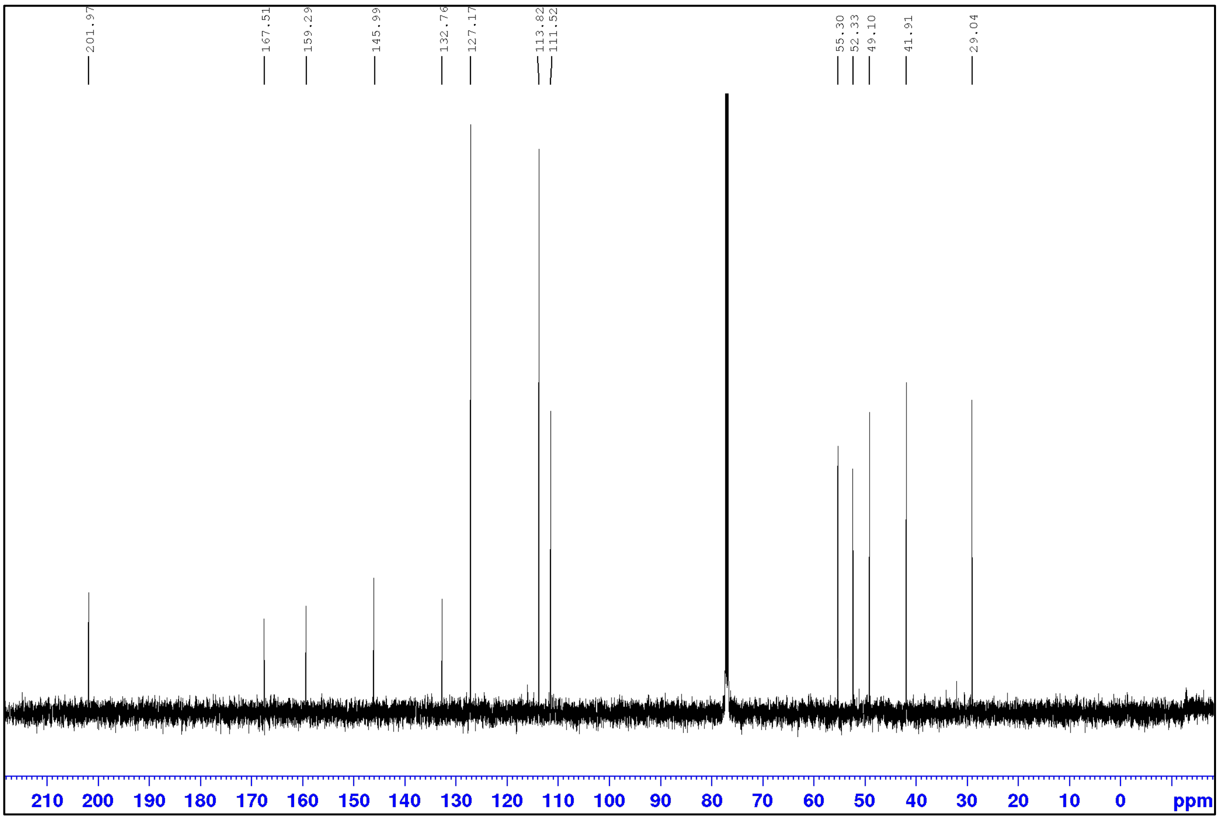
^{13}C NMR (125 MHz, $CDCl_3$) of **8**



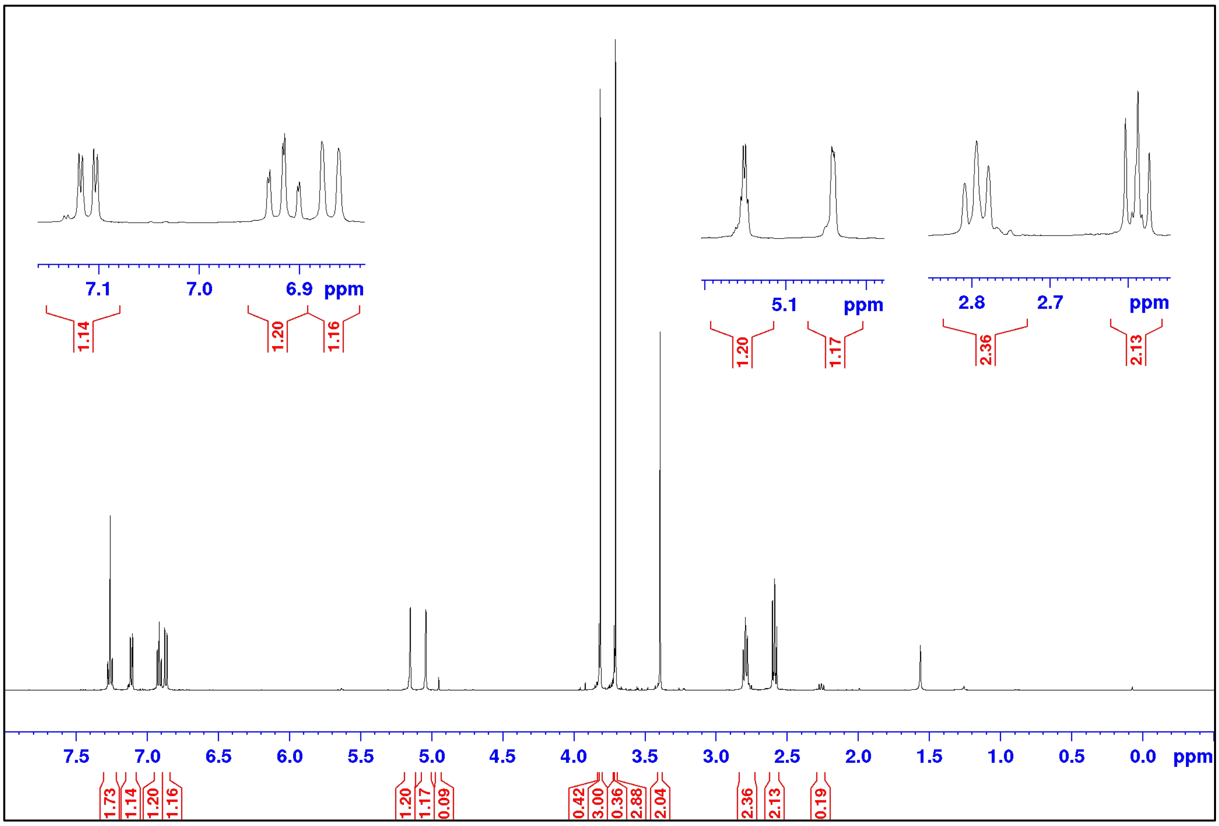
^{1}H NMR (500 MHz, $CDCl_3$) of **9a**



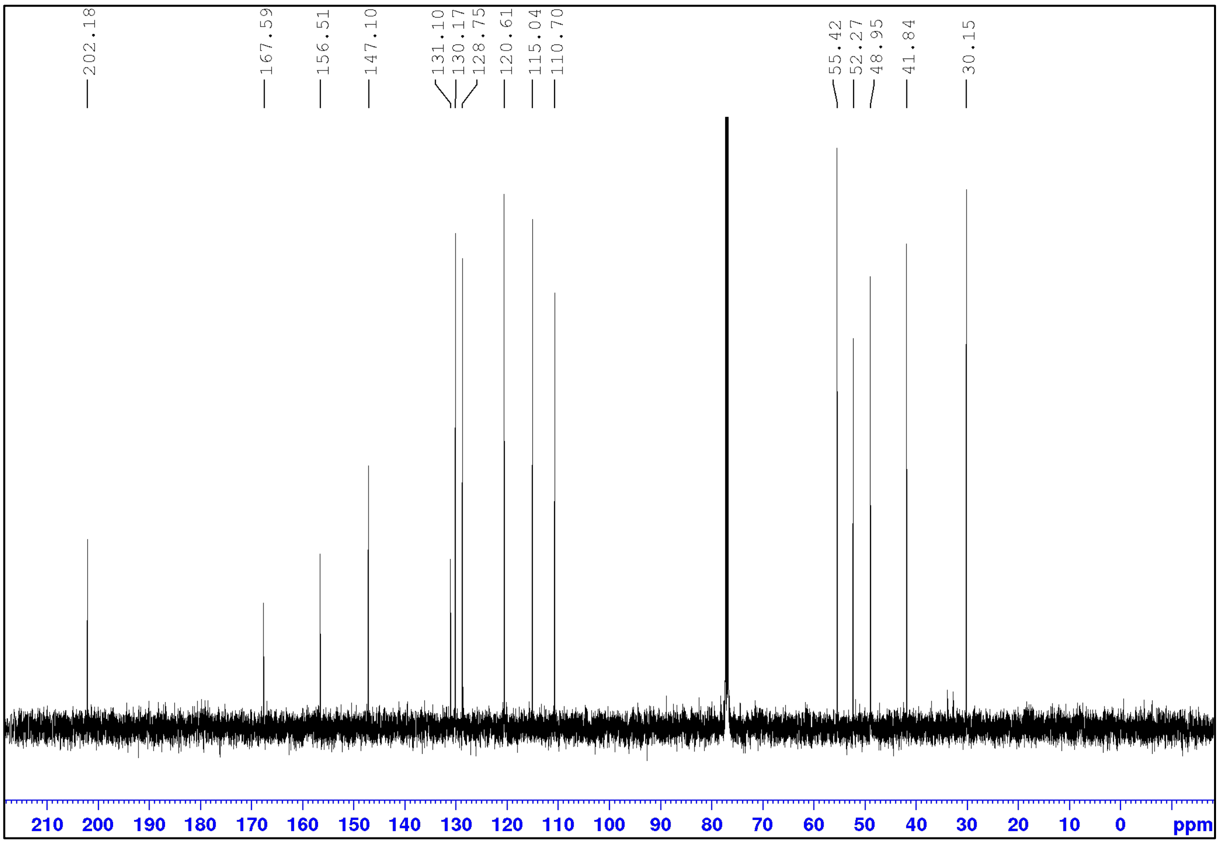
^{13}C NMR (125 MHz, $CDCl_3$) of **9a**



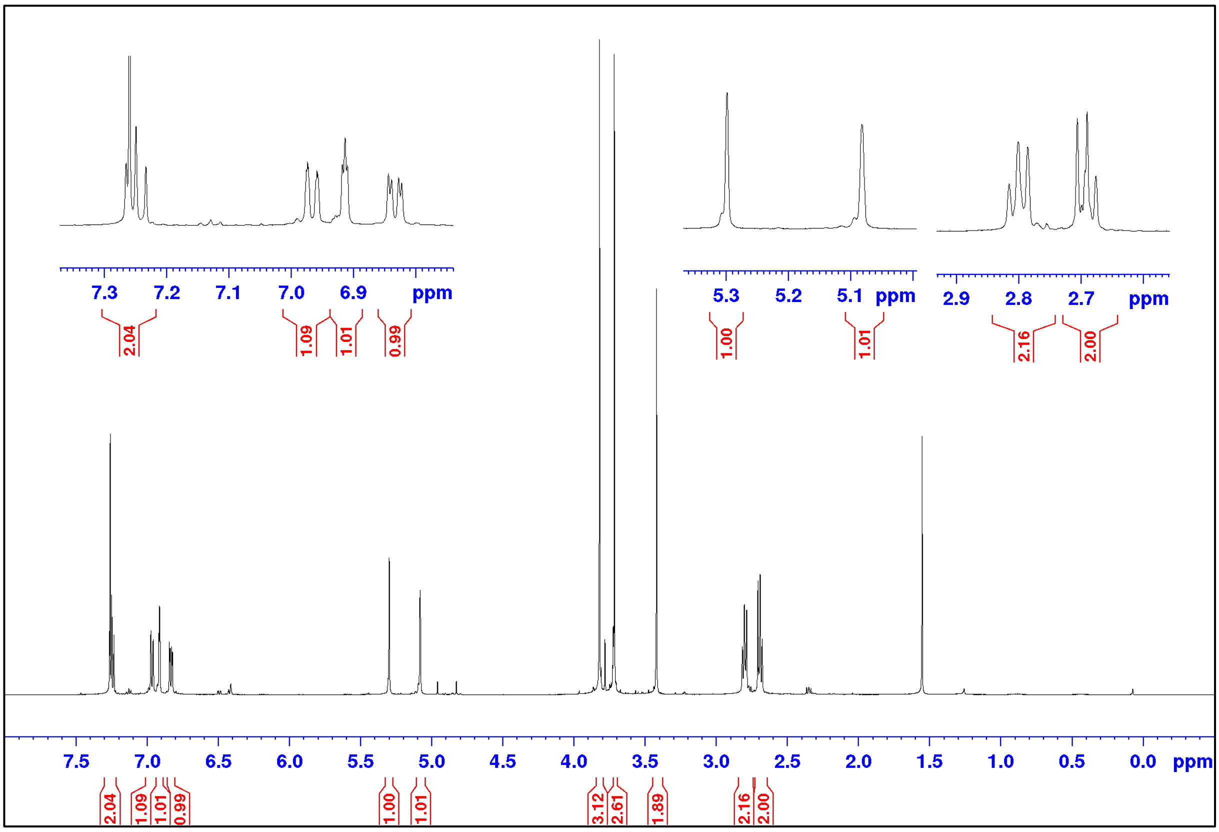
[1]H NMR (500 MHz, $CDCl_3$) of **9b**



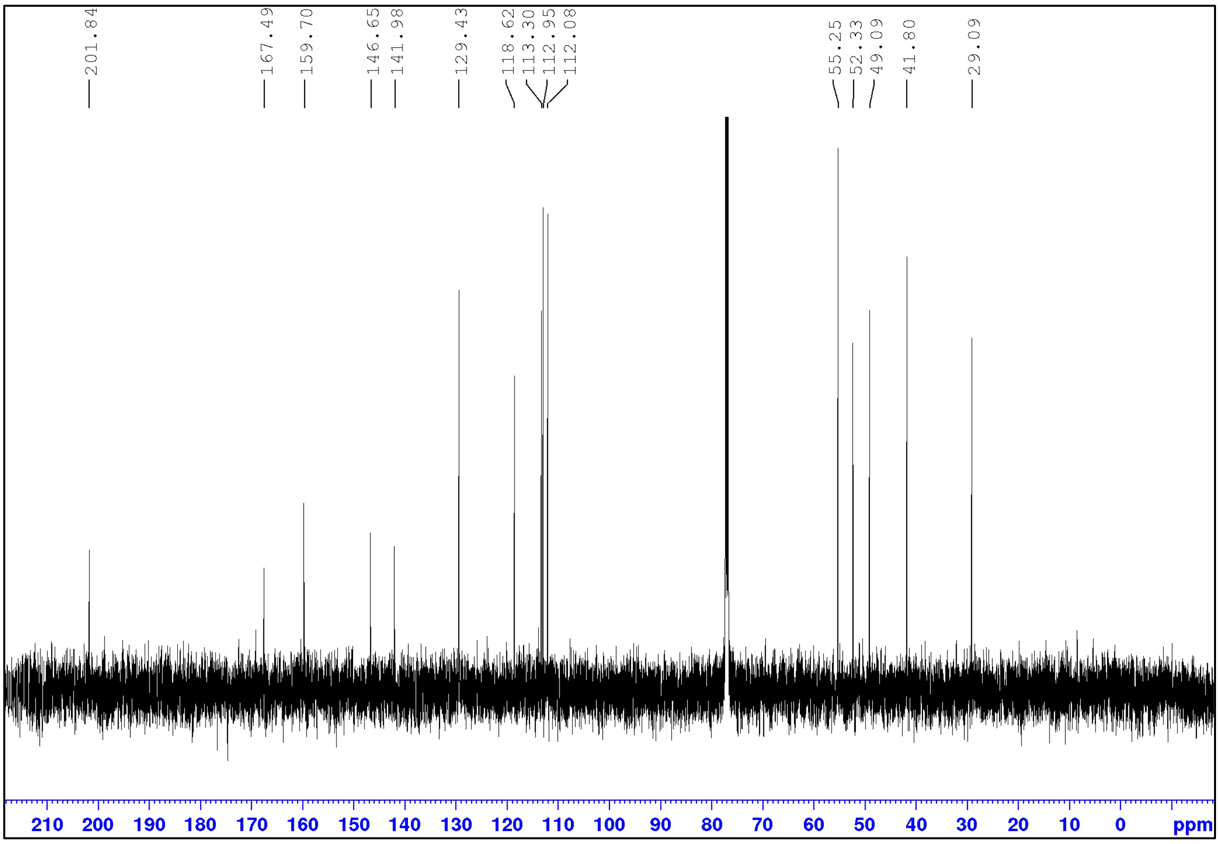
[13]C NMR (125 MHz, $CDCl_3$) of **9b**



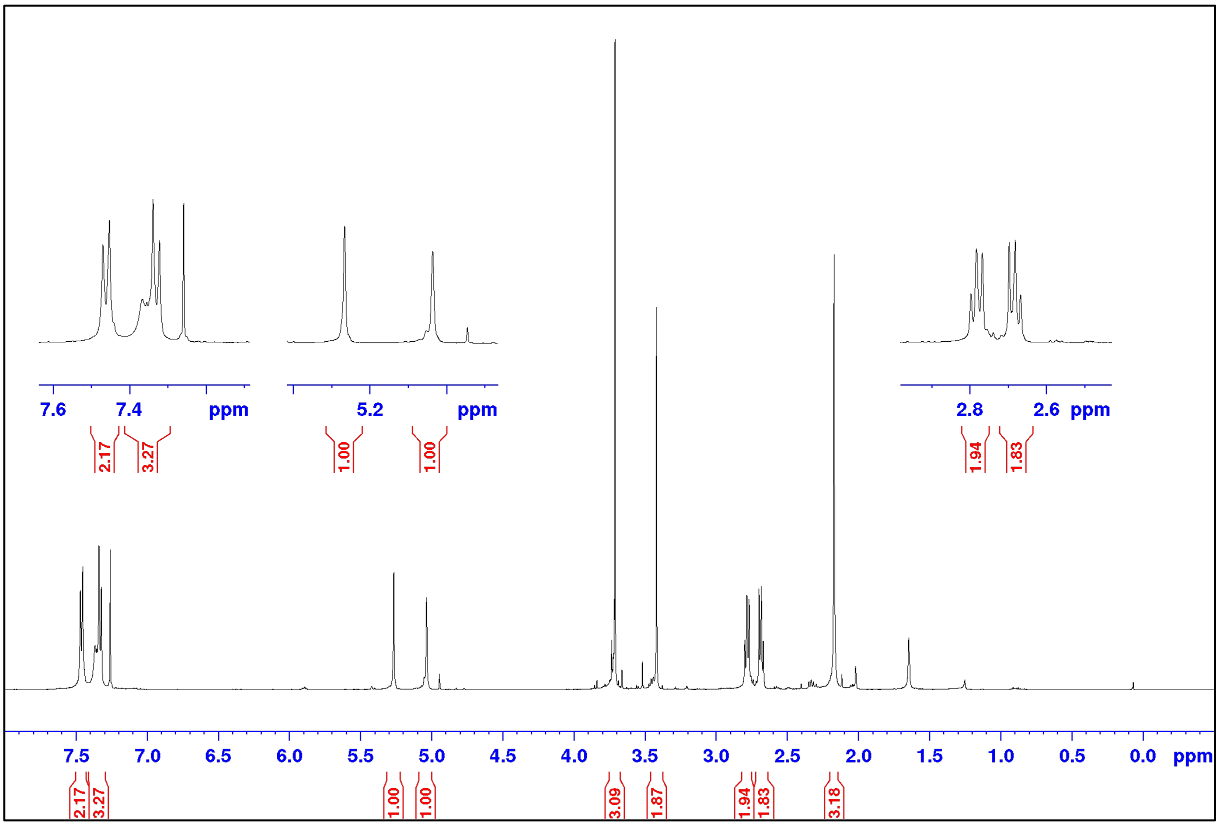
^{1}H NMR (500 MHz, $CDCl_3$) of **9c**



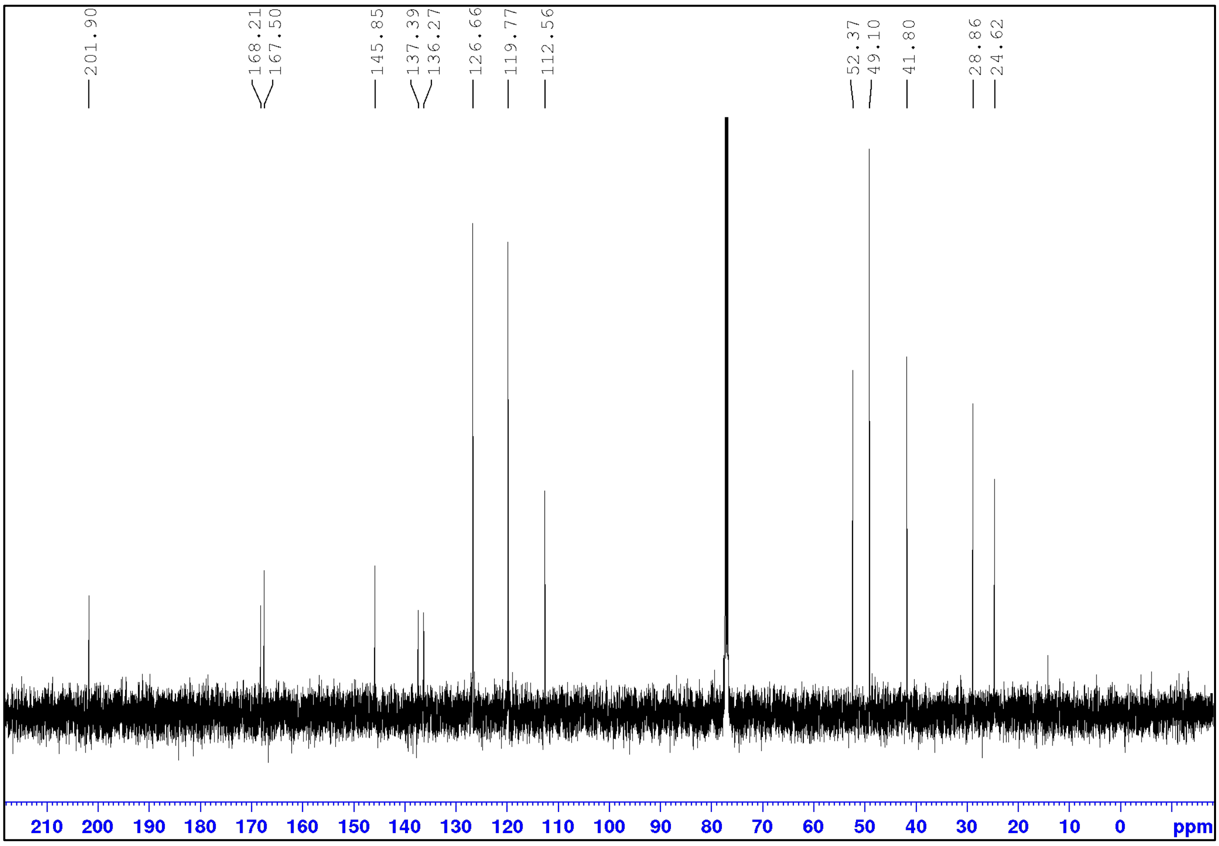
^{13}C NMR (125 MHz, $CDCl_3$) of **9c**



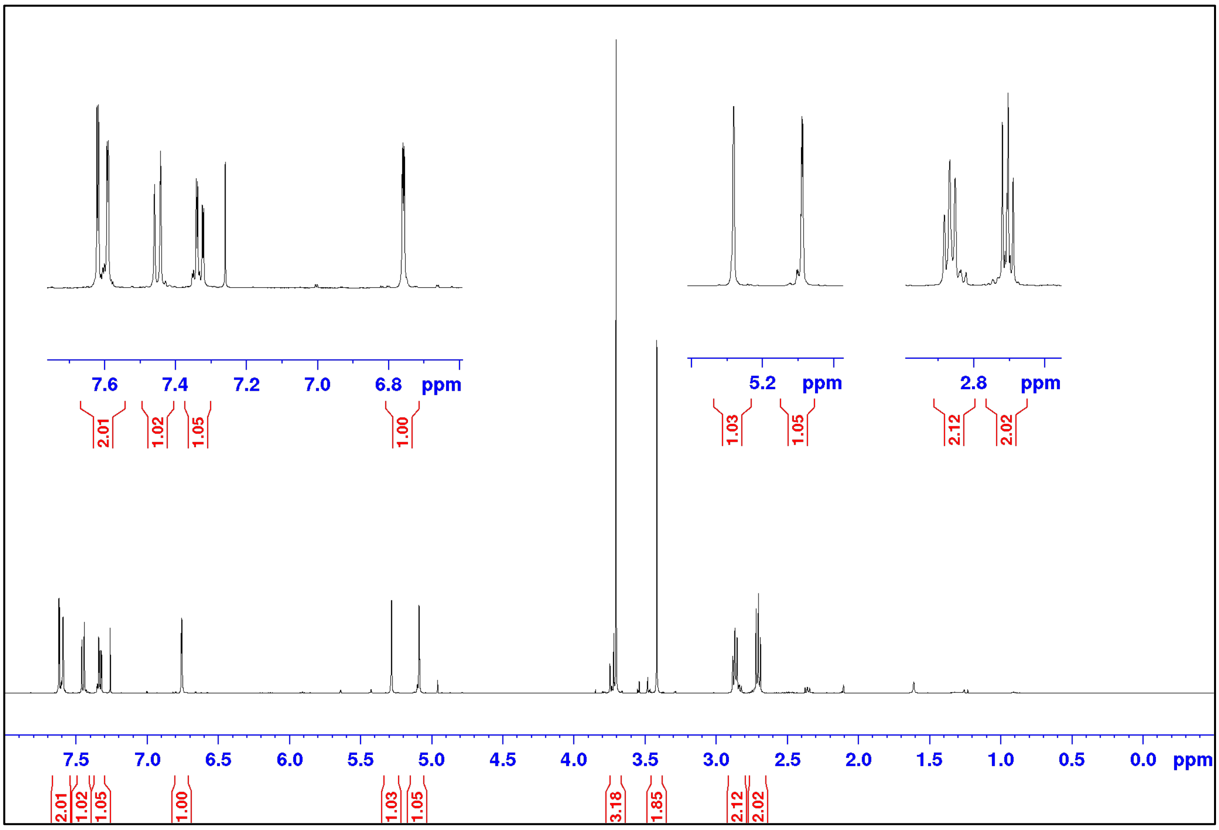
^{1}H NMR (500 MHz, $CDCl_3$) of **9d**



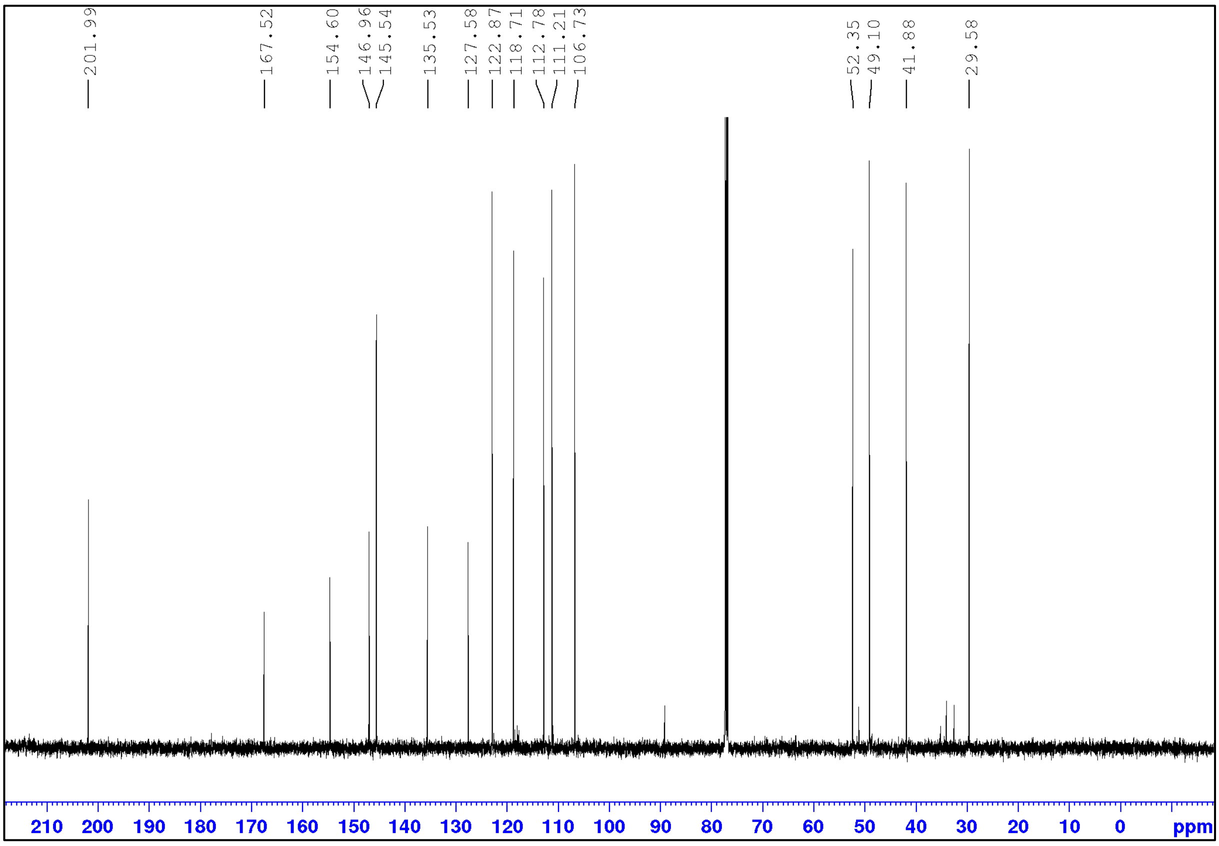
^{13}C NMR (125 MHz, $CDCl_3$) of **9d**



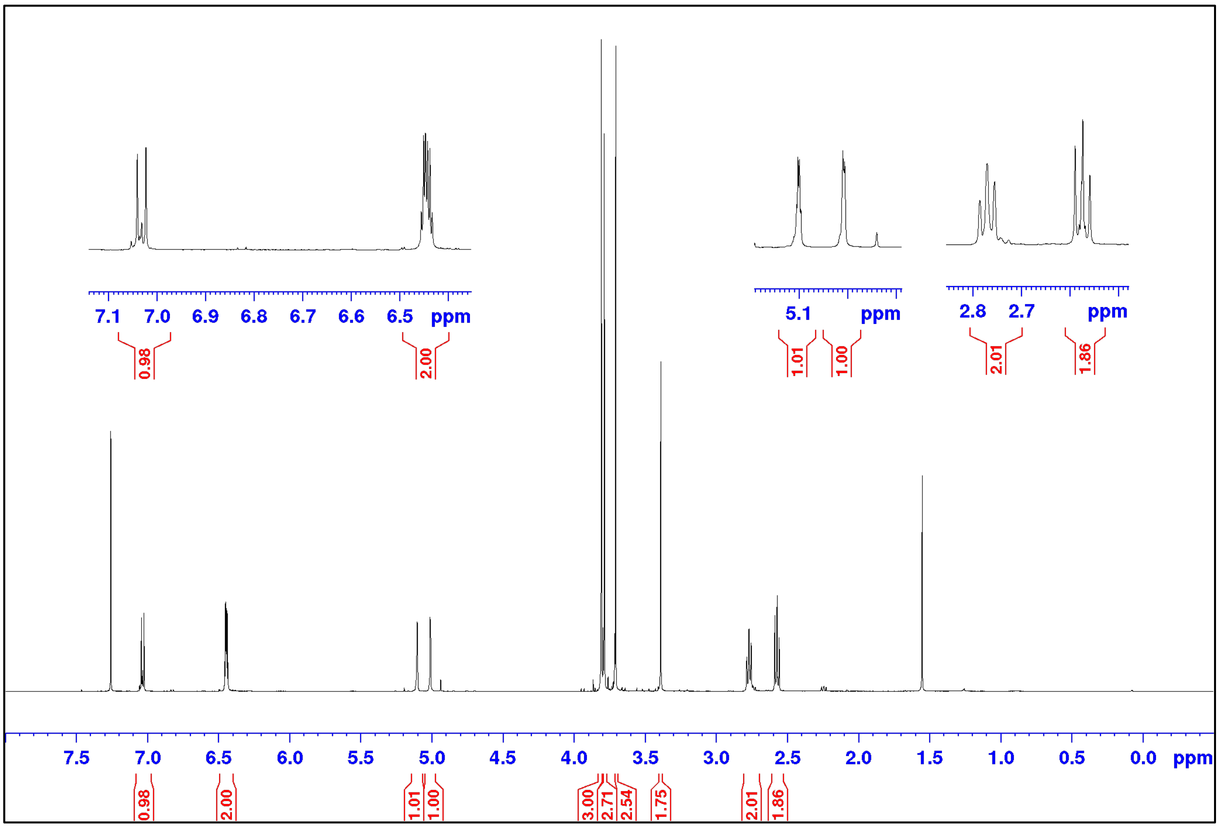
[1]H NMR (500 MHz, $CDCl_3$) of **9e**



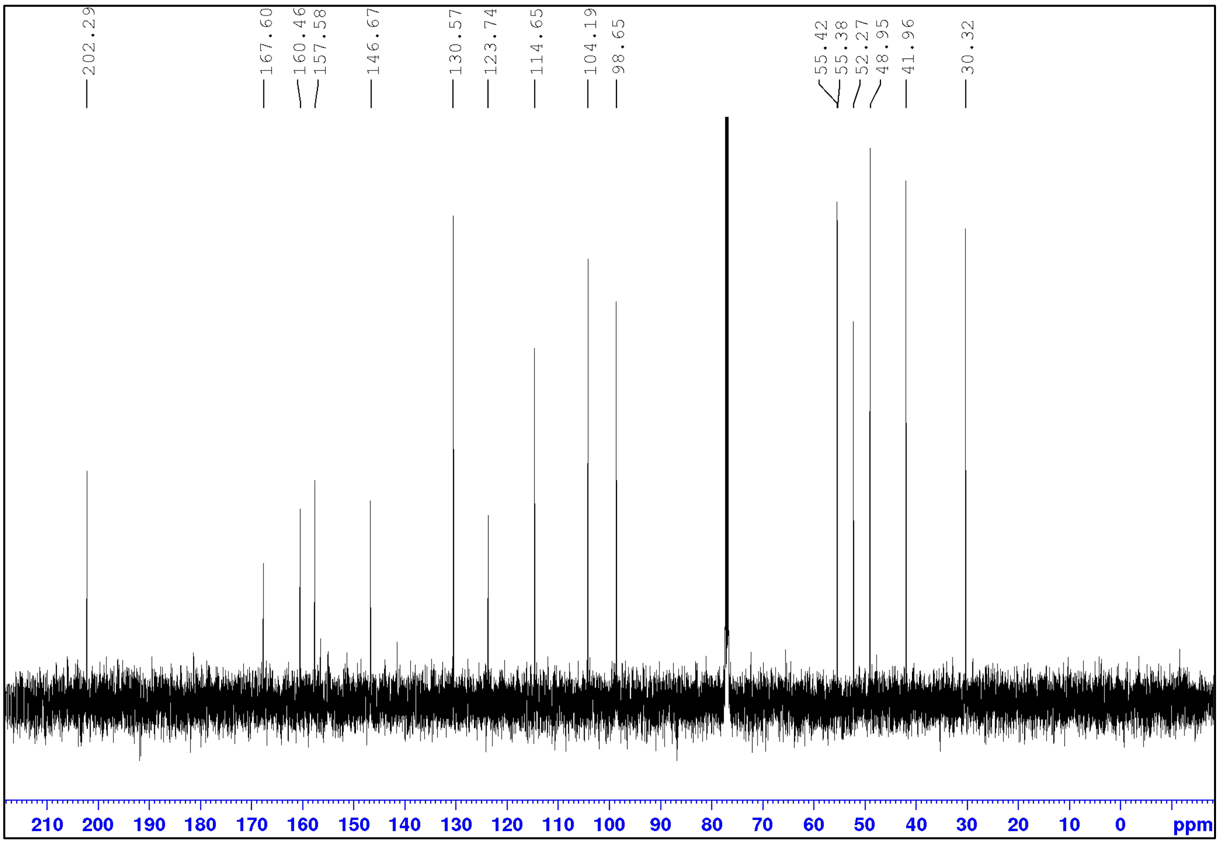
[13]C NMR (125 MHz, $CDCl_3$) of **9e**



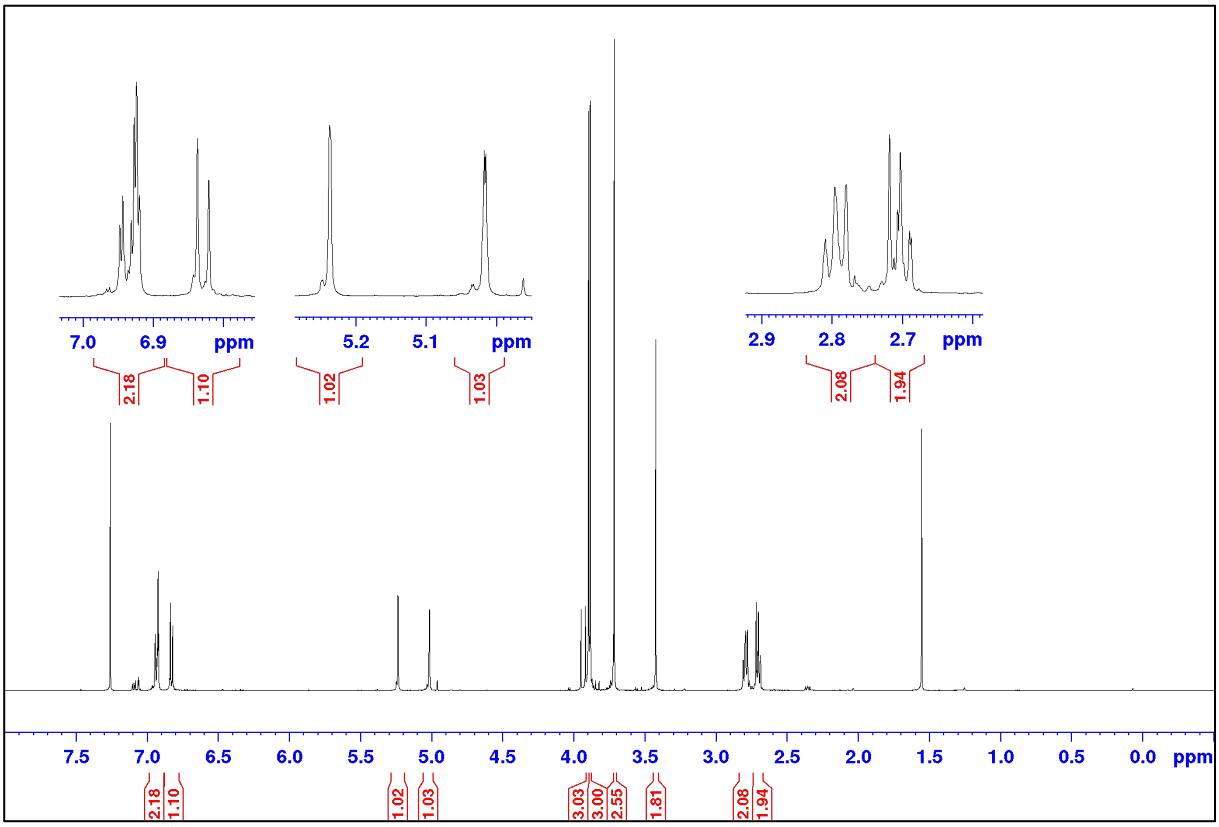
[1]H NMR (500 MHz, $CDCl_3$) of **9f**



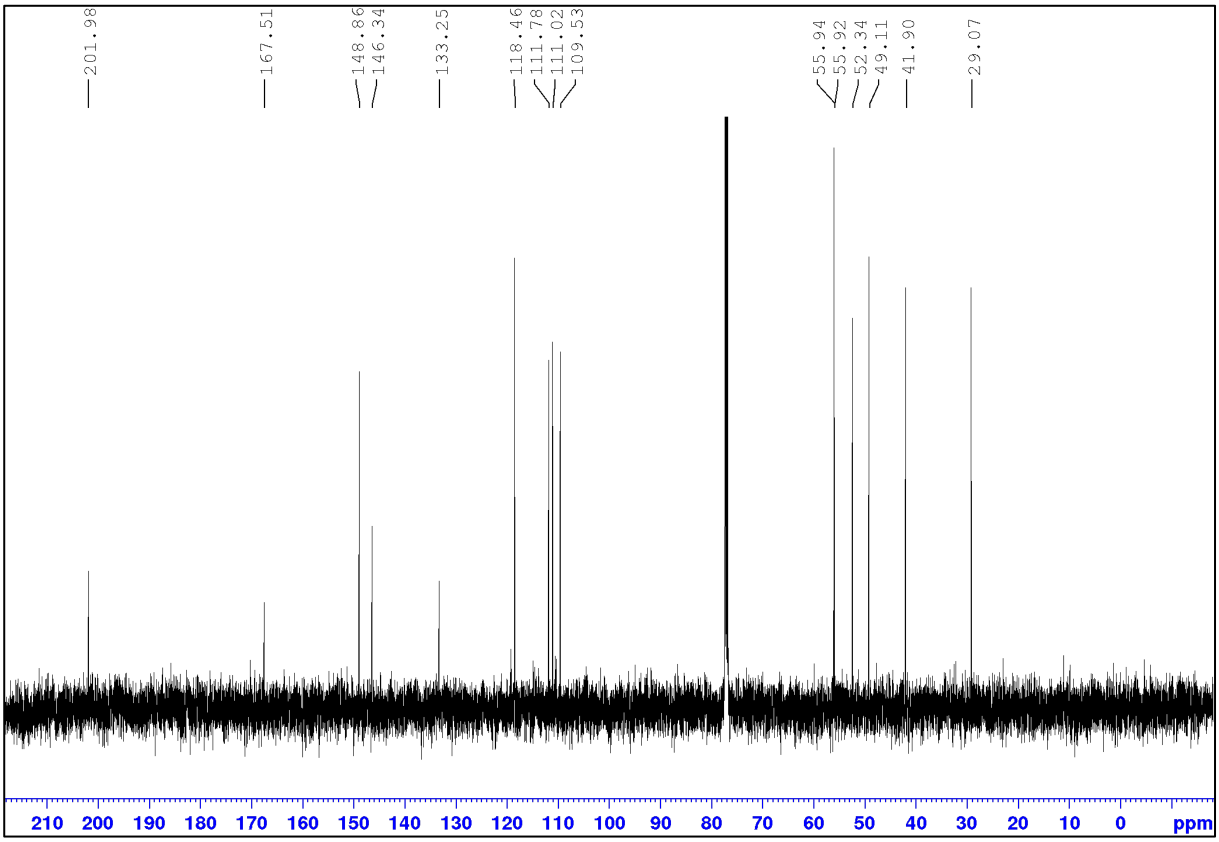
[13]C NMR (125 MHz, $CDCl_3$) of **9f**



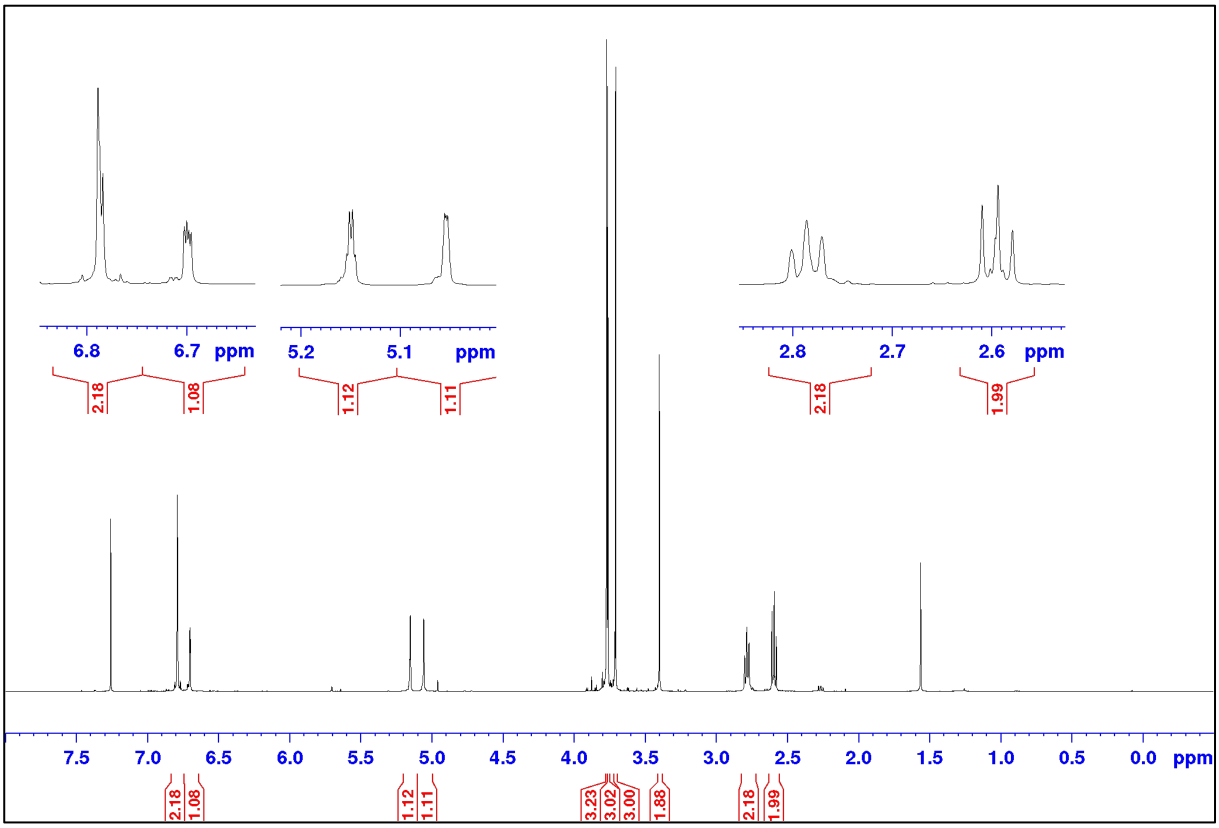
[1]H NMR (500 MHz, $CDCl_3$) of **9g**



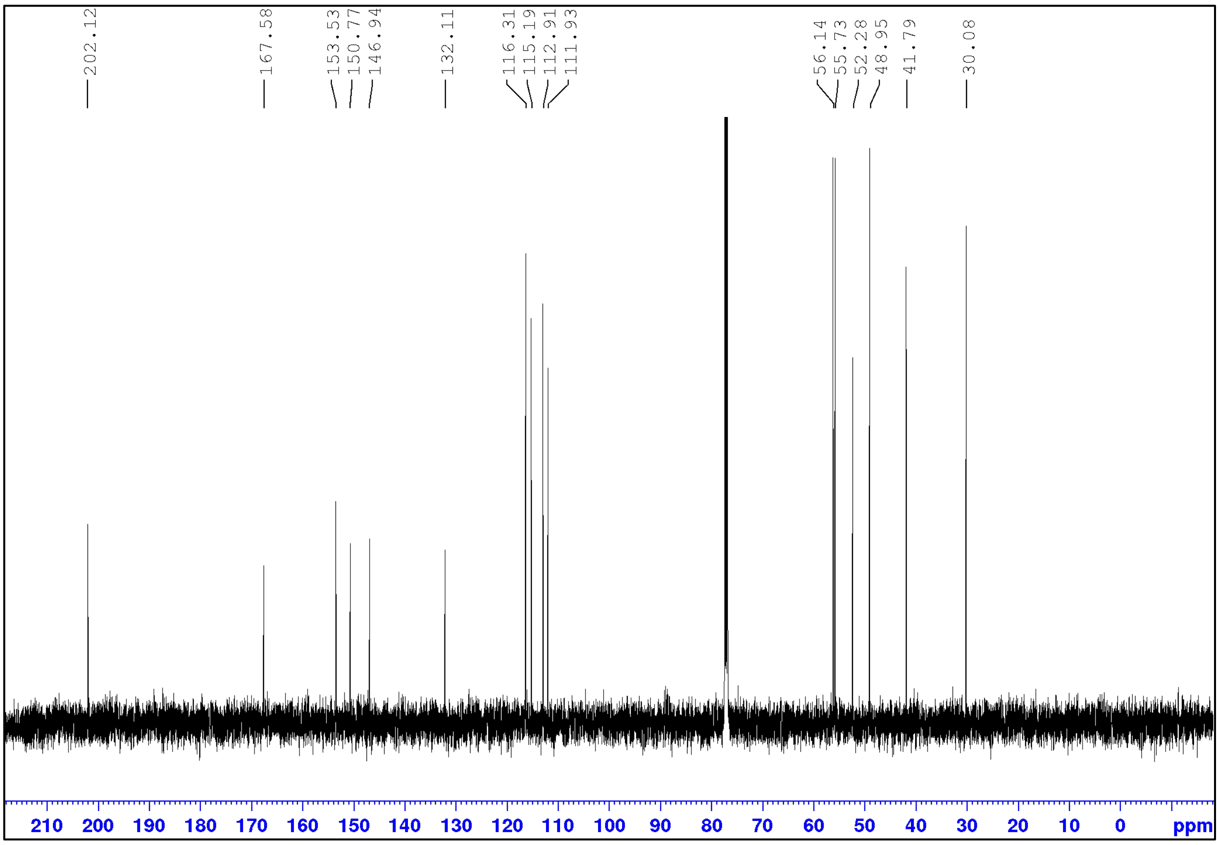
[13]C NMR (125 MHz, $CDCl_3$) of **9g**



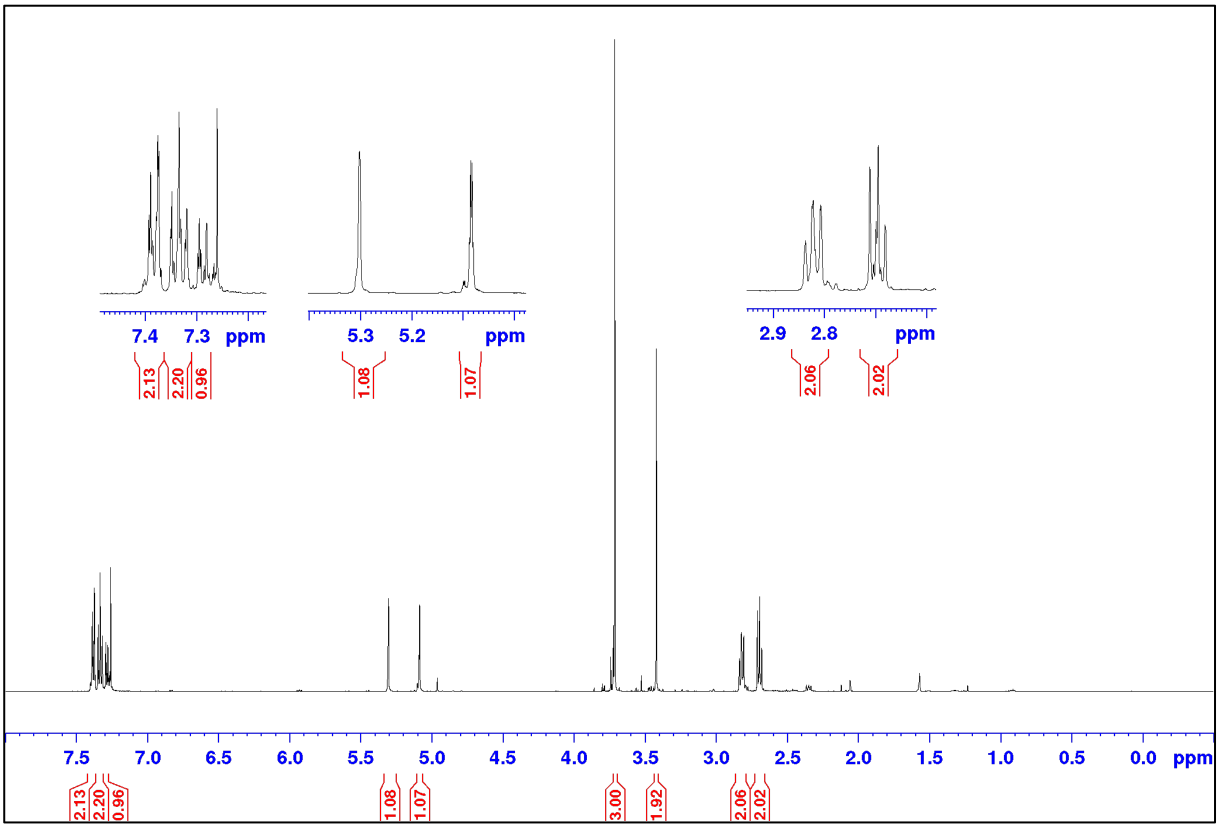
^{1}H NMR (500 MHz, $CDCl_3$) of **9h**



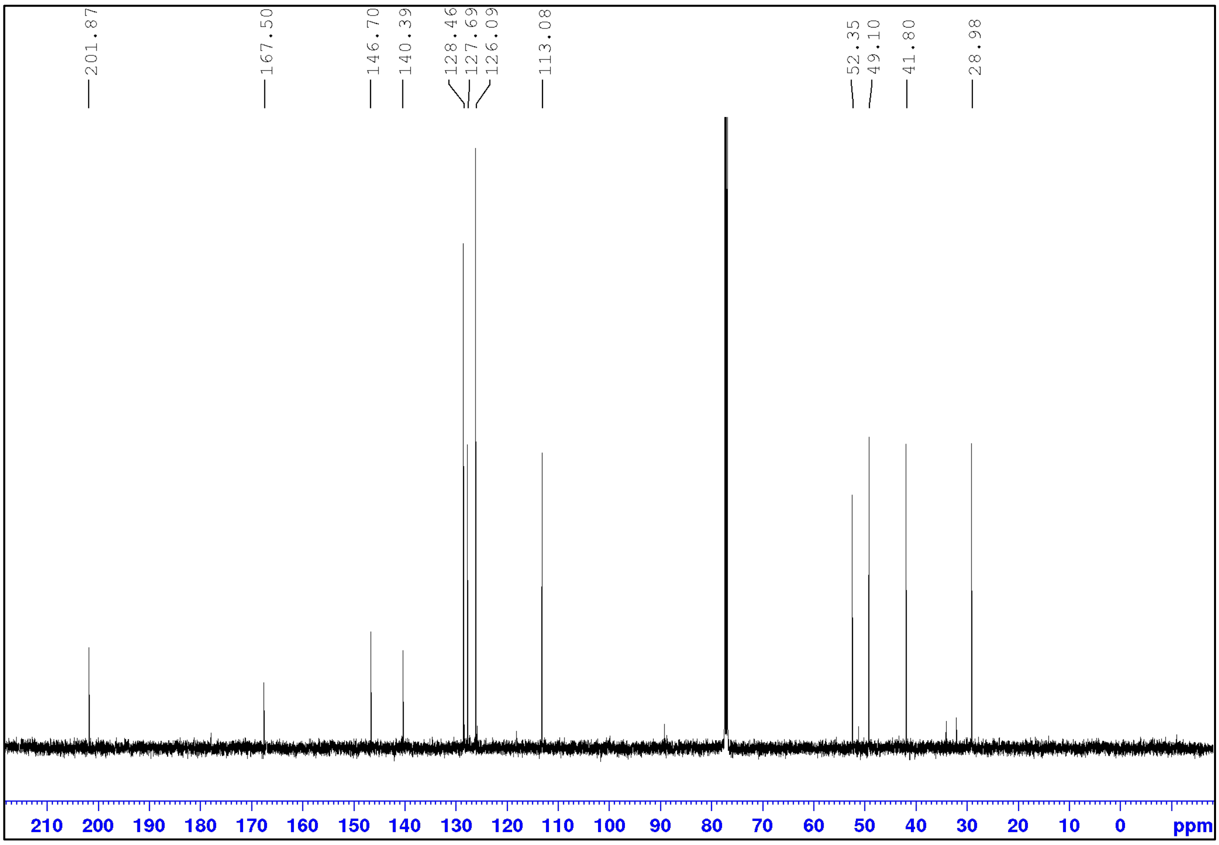
^{13}C NMR (125 MHz, $CDCl_3$) of **9h**



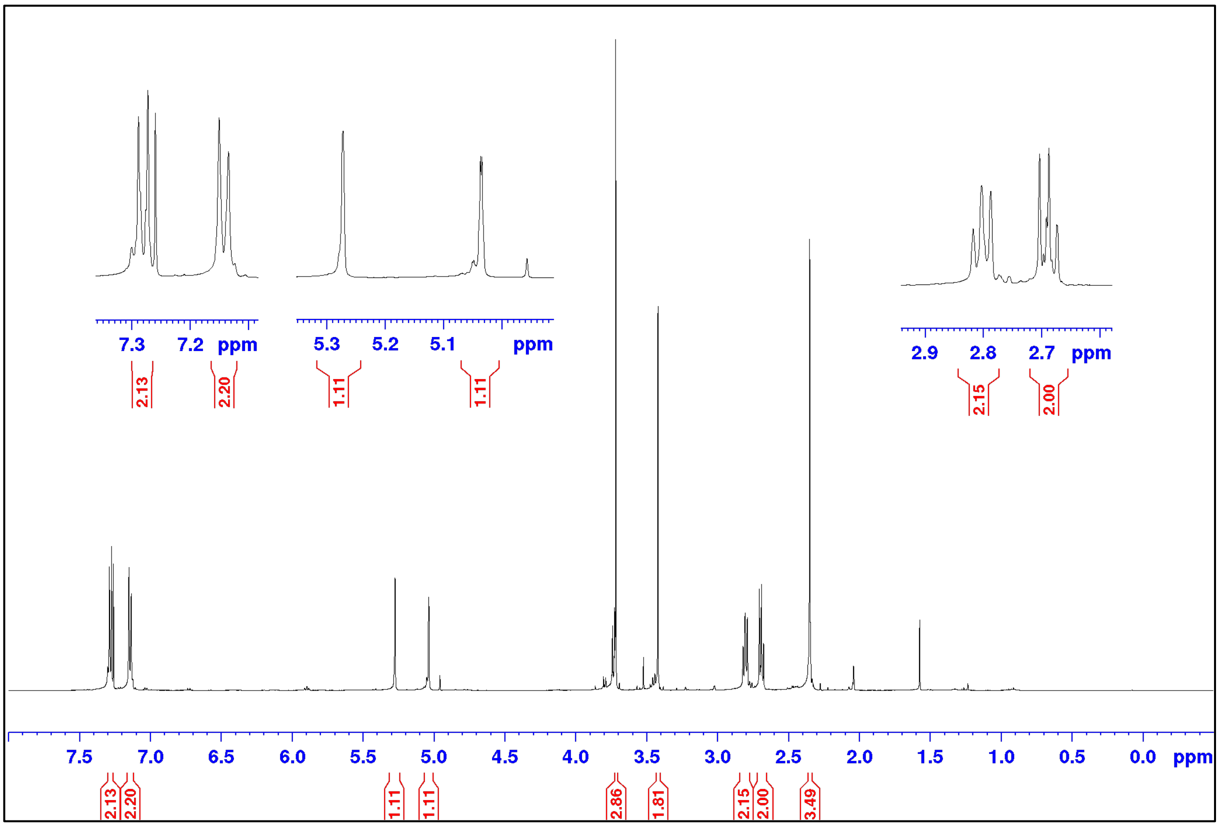
[1]H NMR (500 MHz, $CDCl_3$) of **9i**



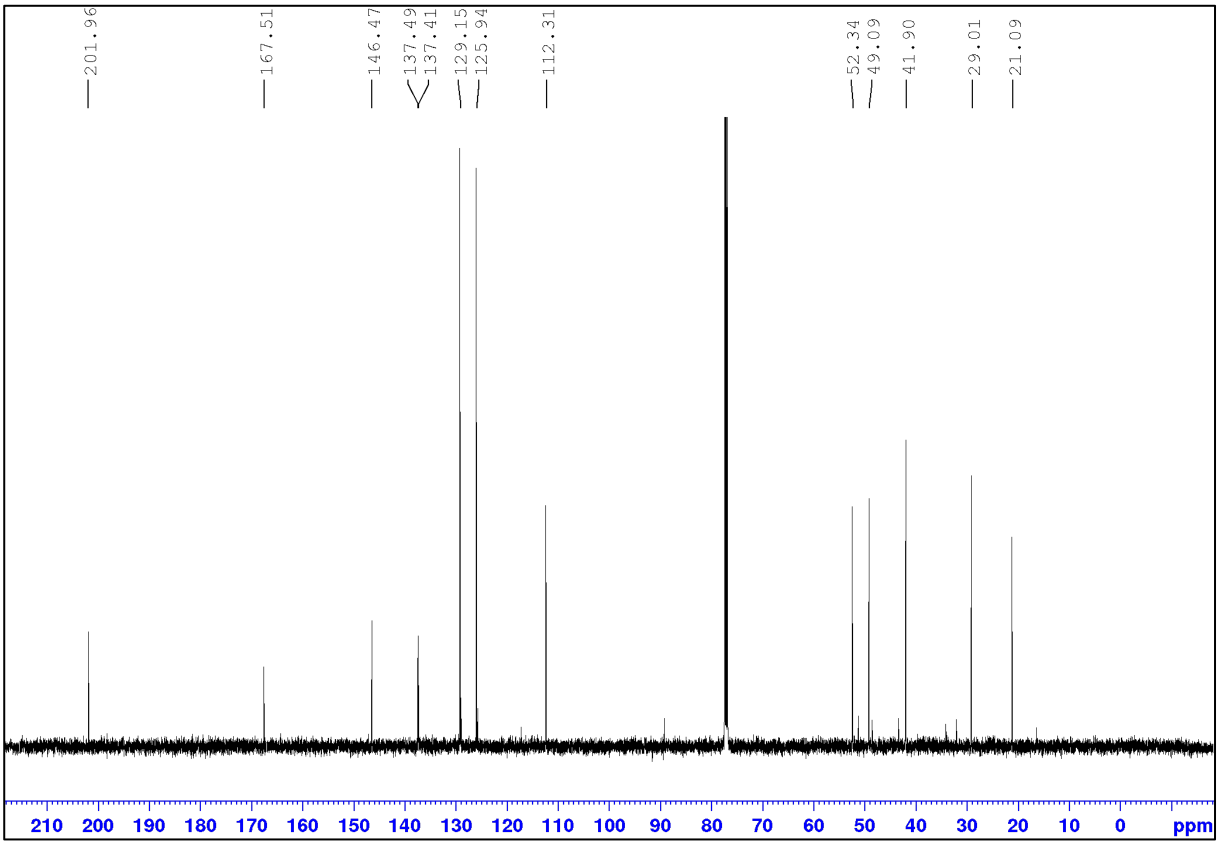
[13]C NMR (125 MHz, $CDCl_3$) of **9i**



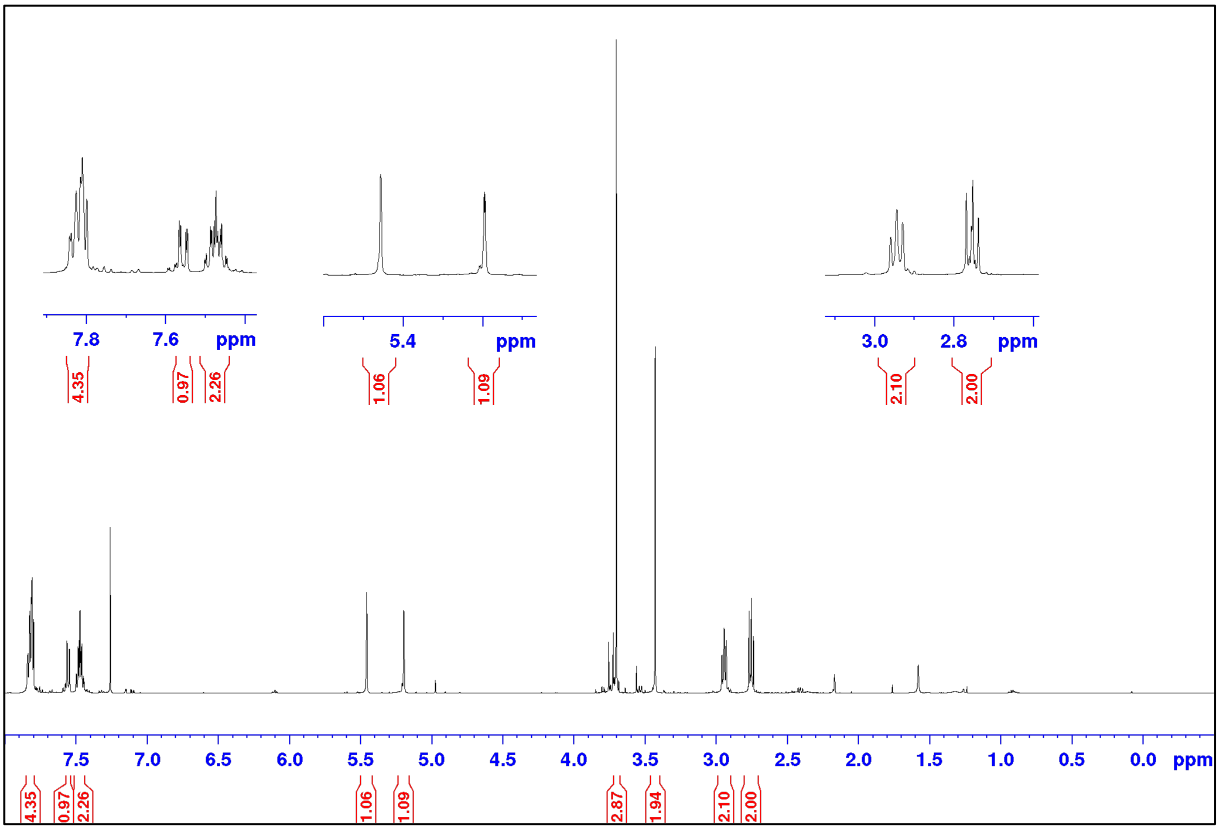
^{1}H NMR (500 MHz, $CDCl_3$) of **9j**



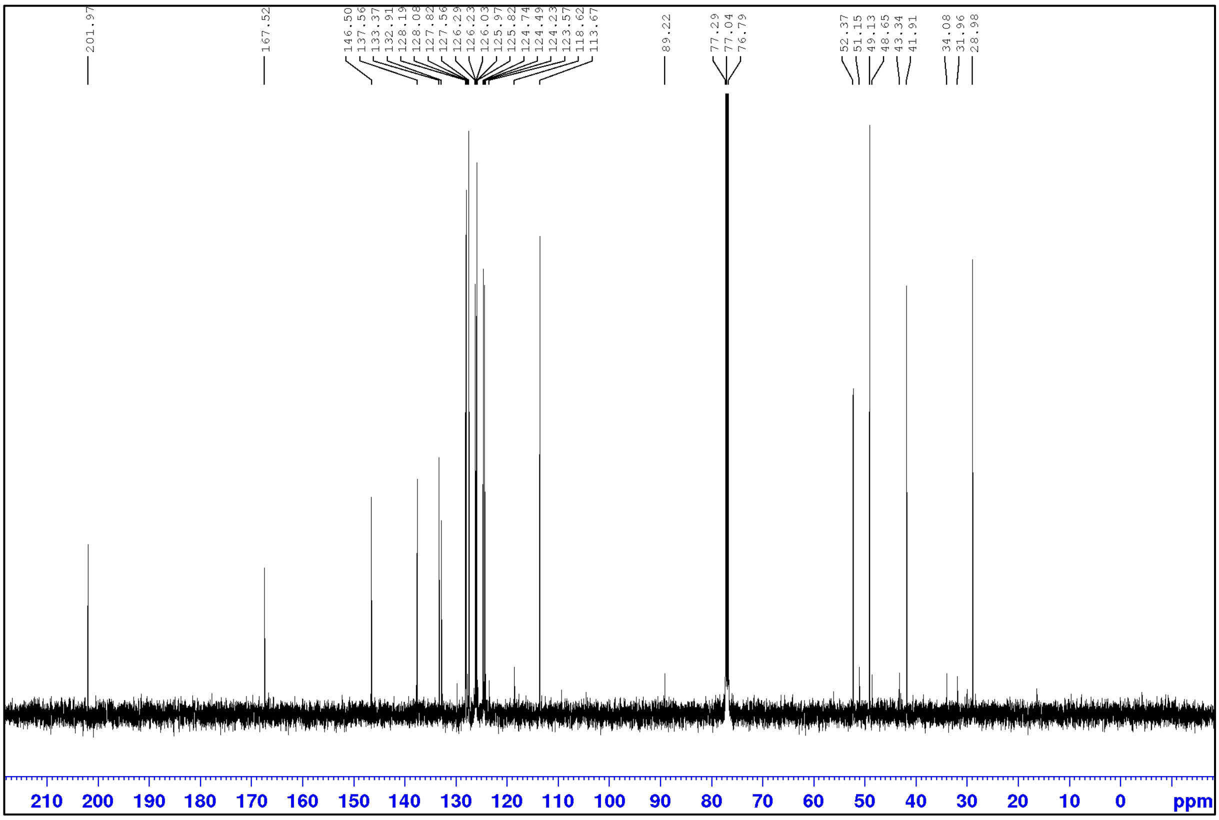
^{13}C NMR (125 MHz, $CDCl_3$) of **9j**



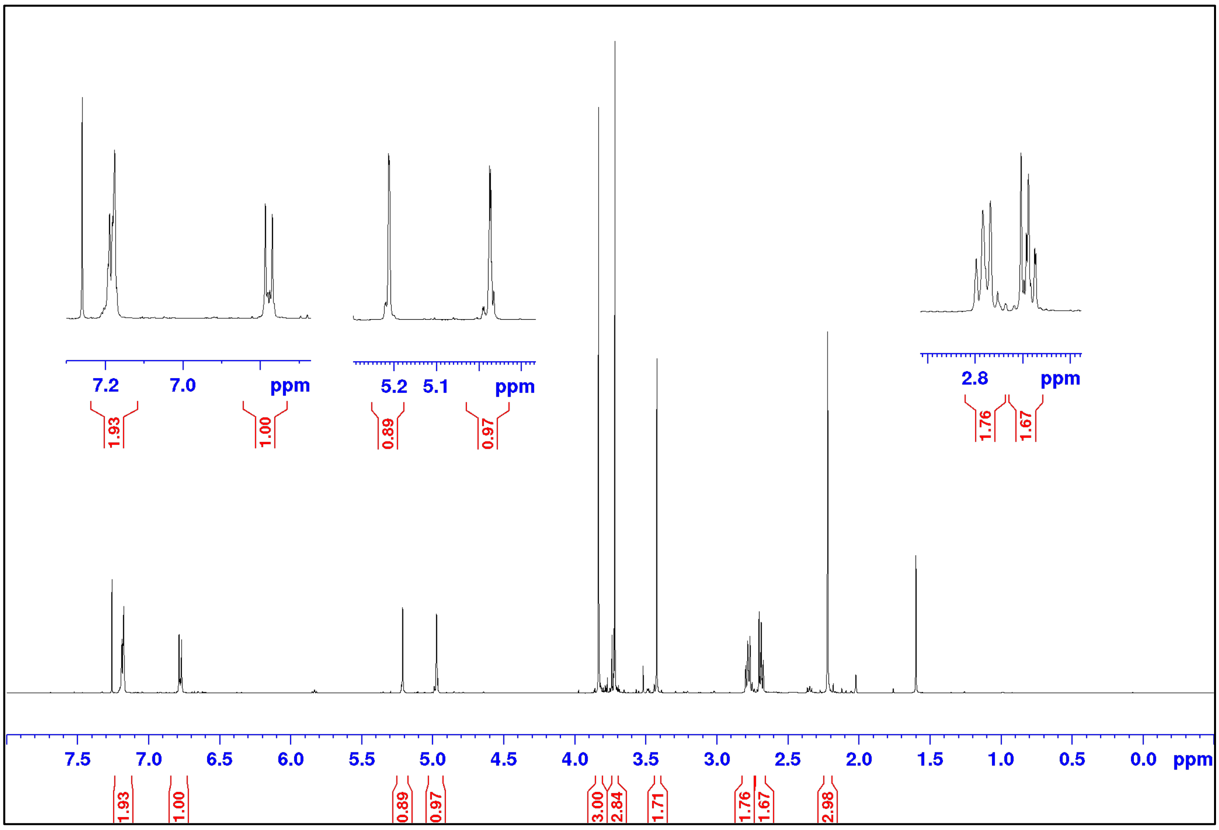
^{1}H NMR (500 MHz, $CDCl_3$) of **9k**



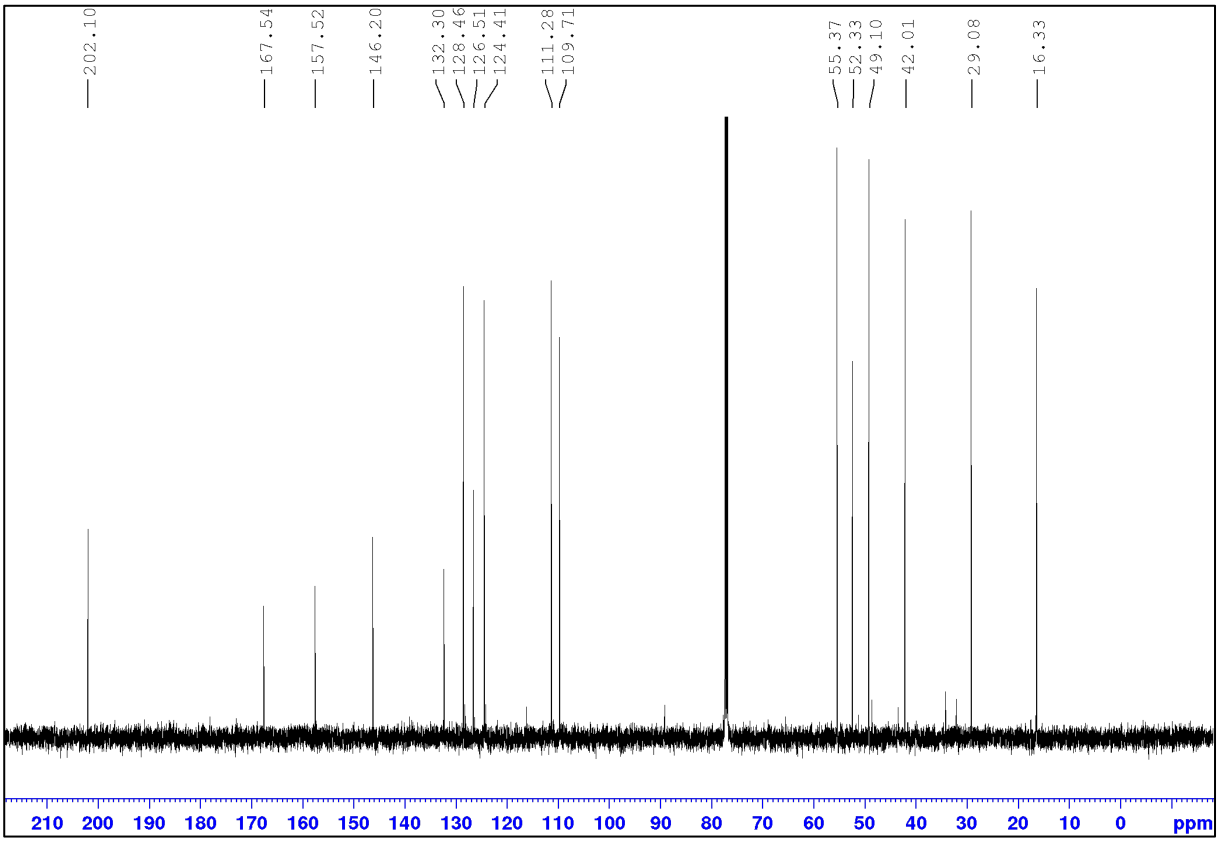
^{13}C NMR (125 MHz, $CDCl_3$) of **9k**



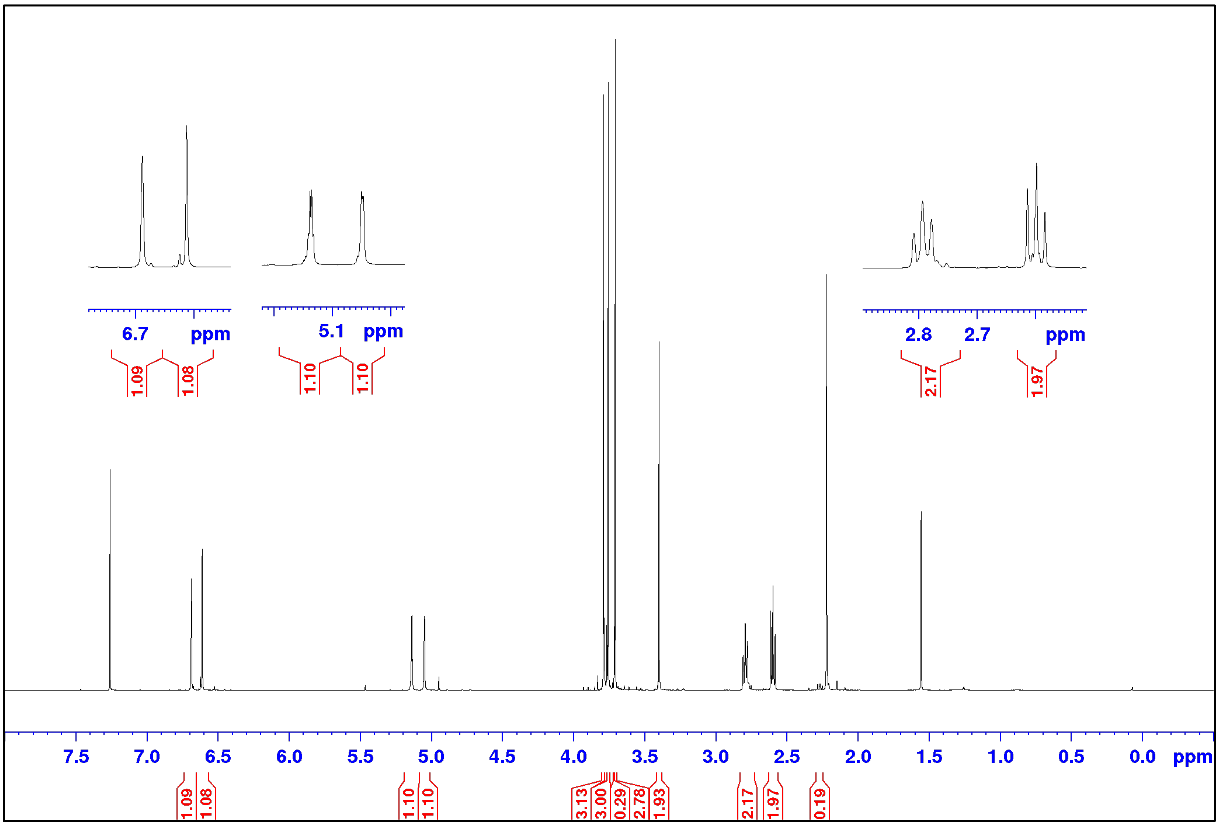
^{1}H NMR (500 MHz, $CDCl_3$) of **9l**



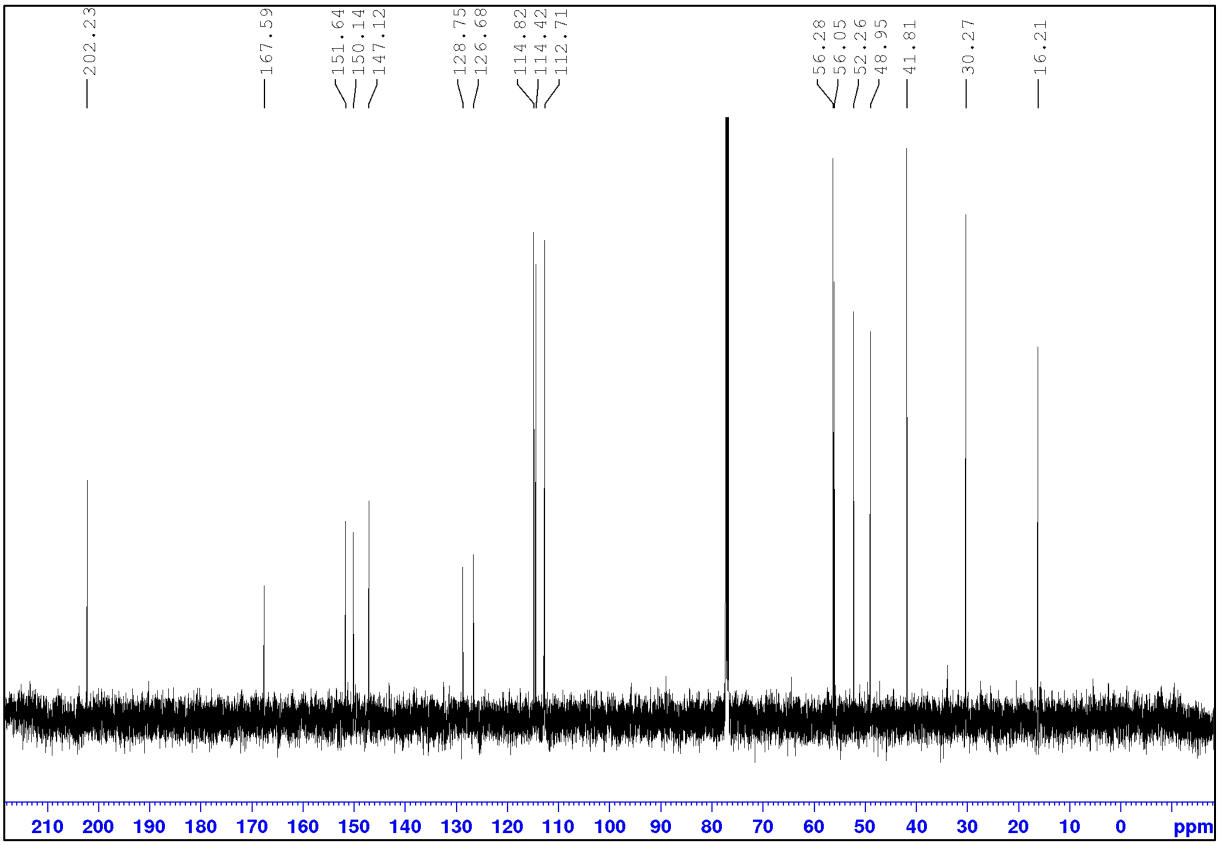
^{13}C NMR (125 MHz, $CDCl_3$) of **9l**



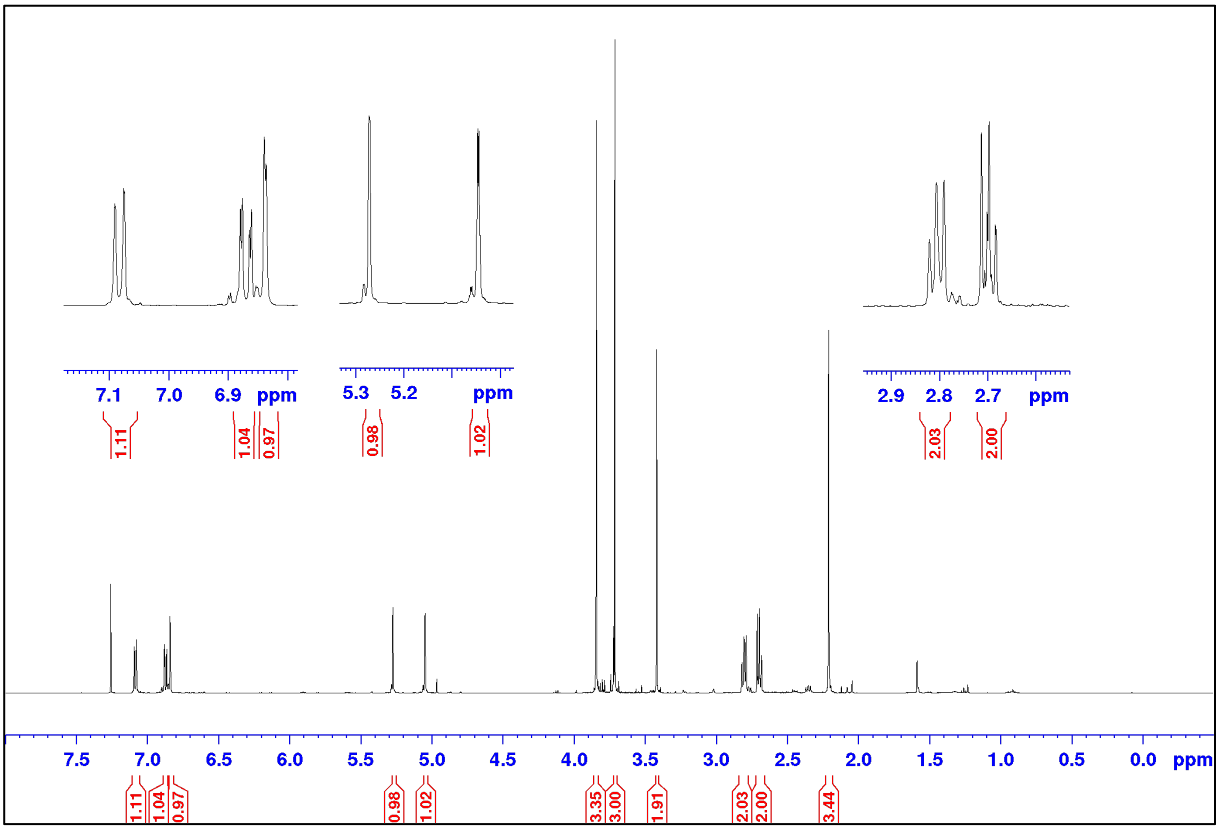
^{1}H NMR (500 MHz, $CDCl_3$) of **9m**



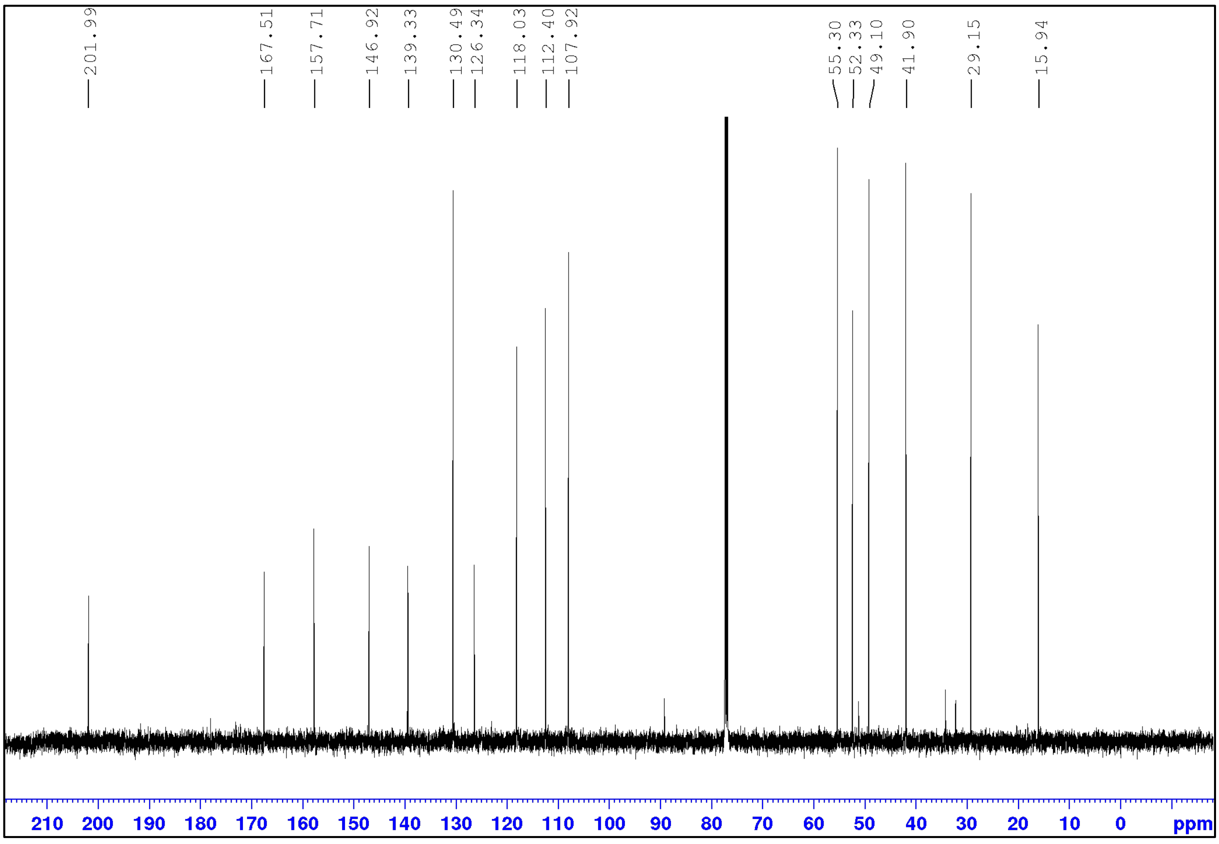
^{13}C NMR (125 MHz, $CDCl_3$) of **9m**



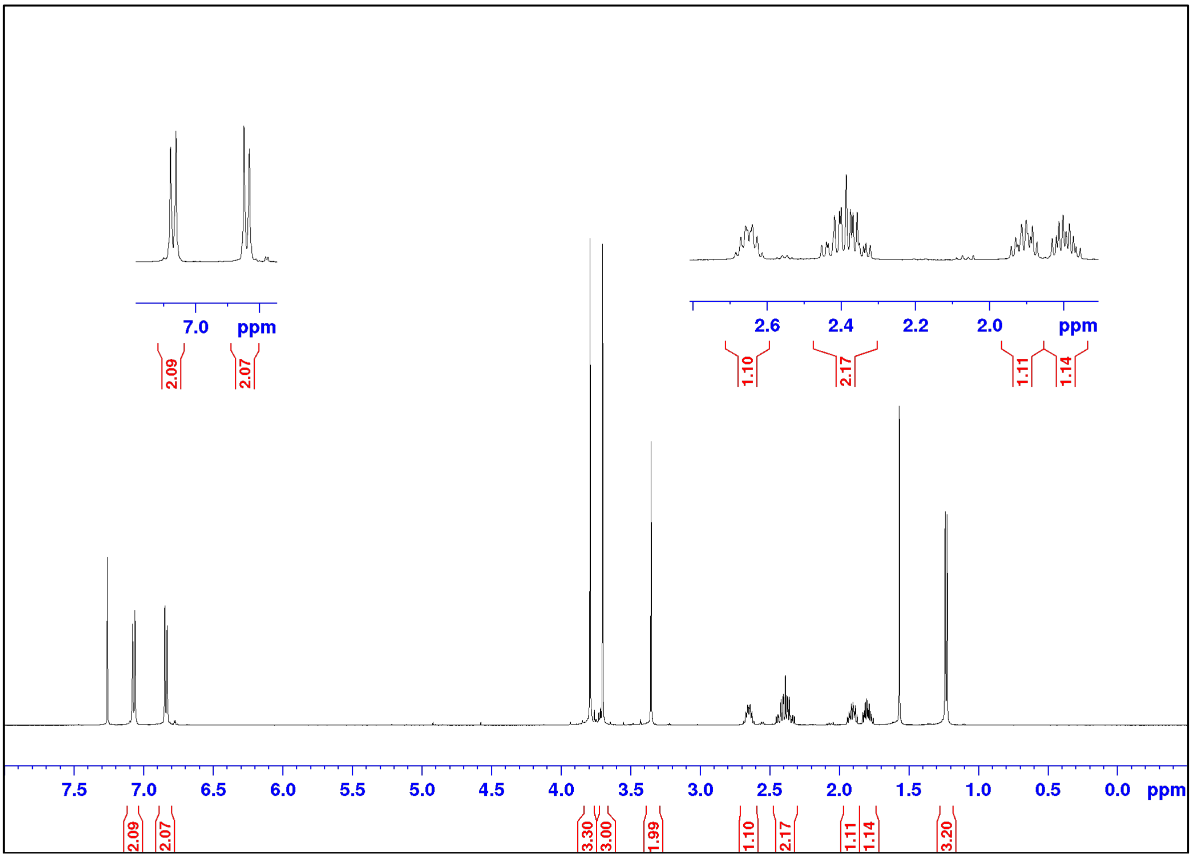
^{1}H NMR (500 MHz, $CDCl_3$) of **9n**



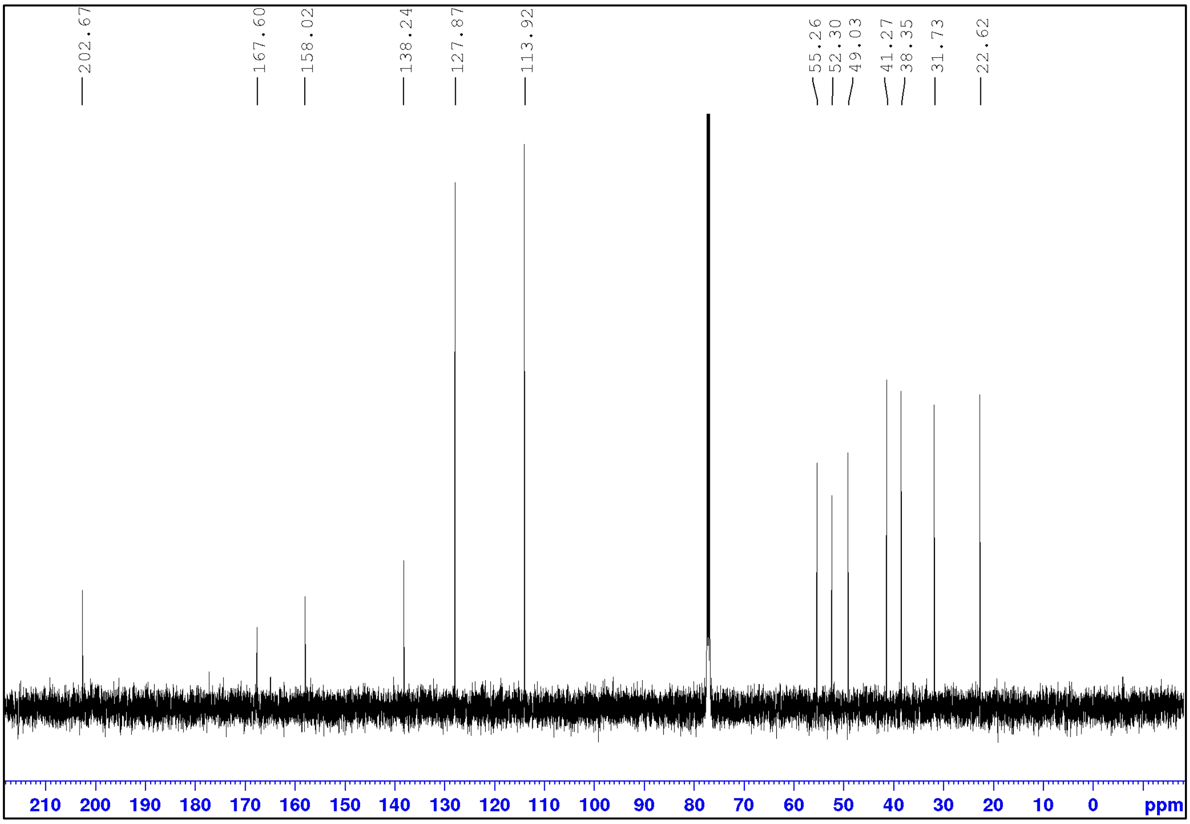
^{13}C NMR (125 MHz, $CDCl_3$) of **9n**



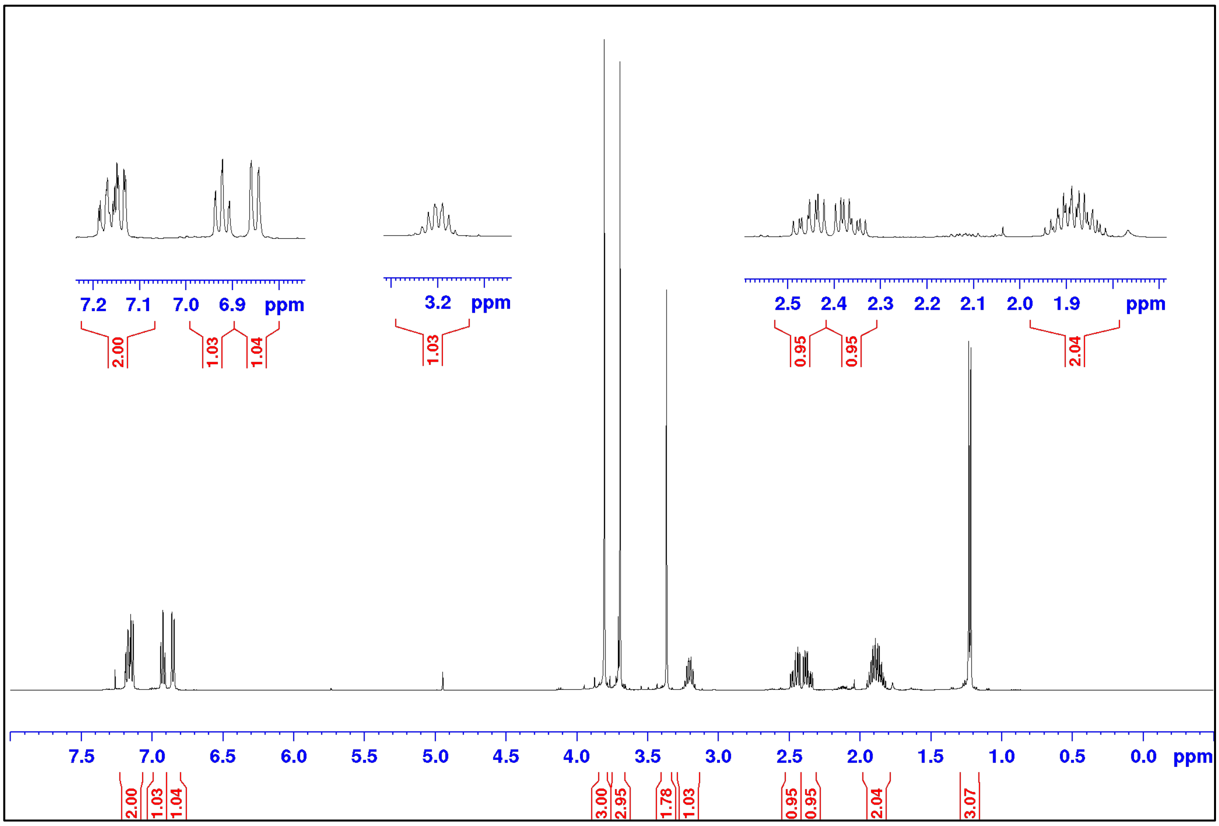
^{1}H NMR (500 MHz, $CDCl_3$) of **1a**



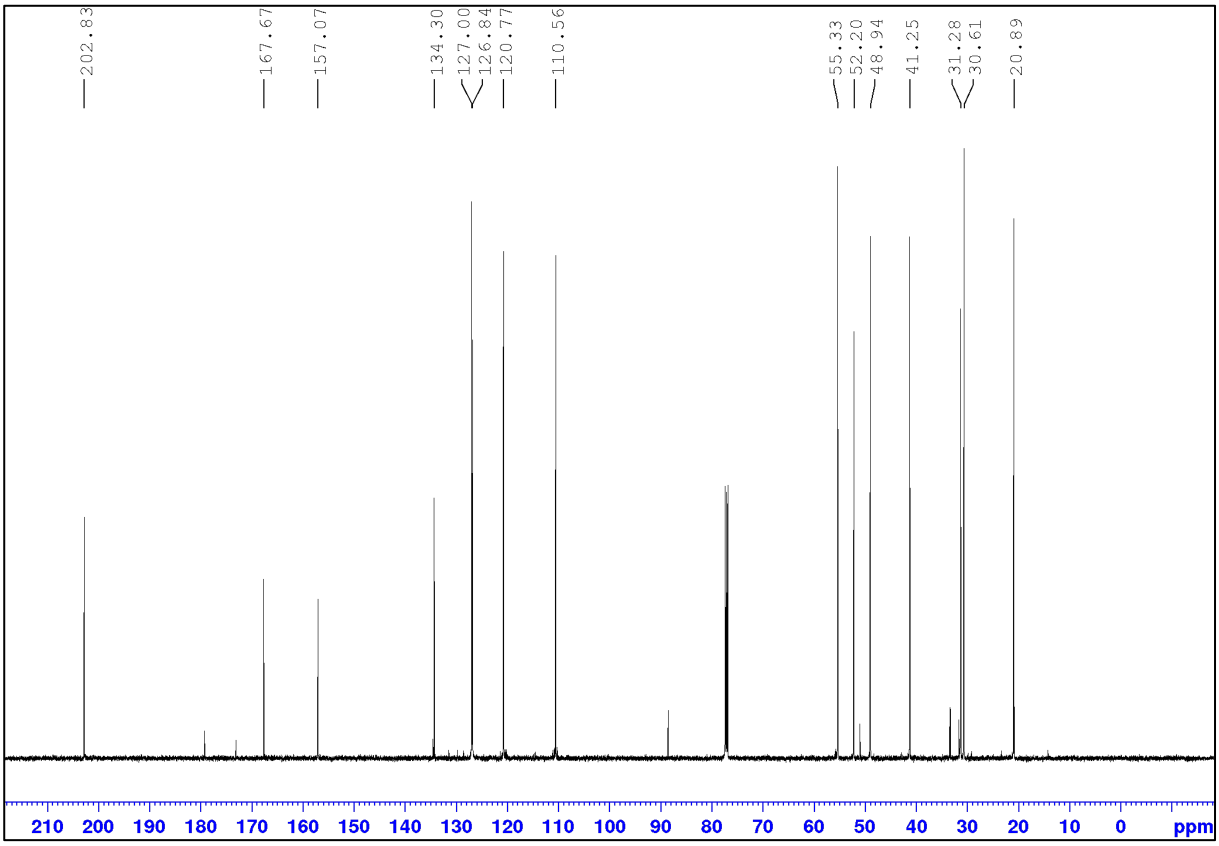
^{13}C NMR (125 MHz, $CDCl_3$) of **1a**



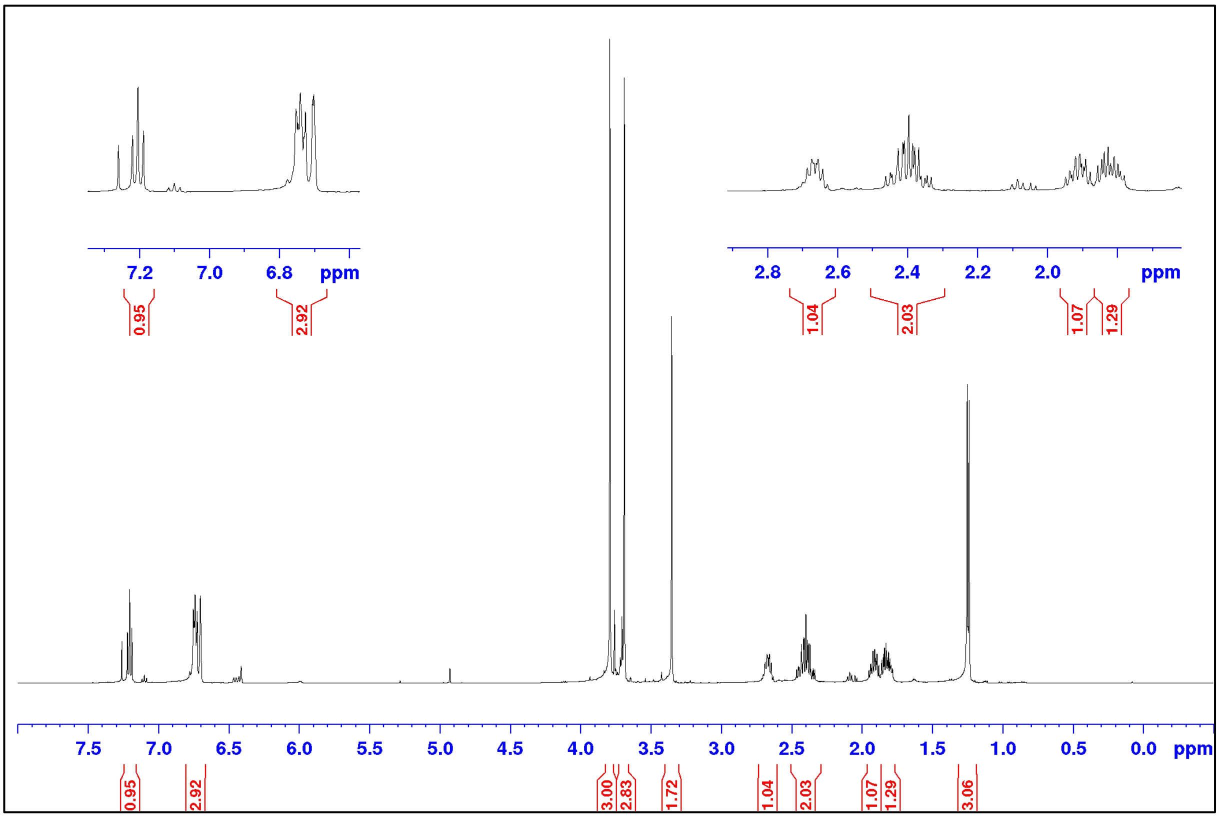
^{1}H NMR (500 MHz, $CDCl_3$) of **1b**



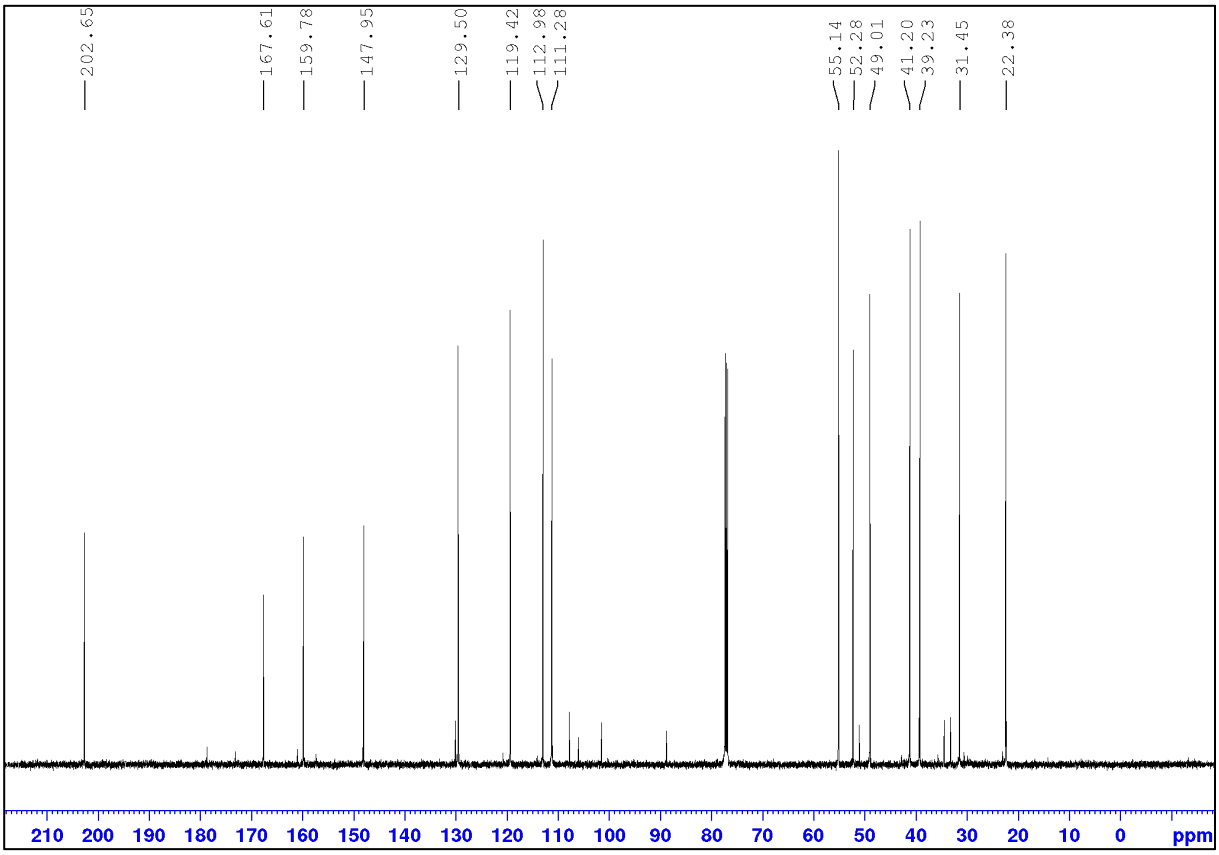
^{13}C NMR (125 MHz, $CDCl_3$) of **1b**



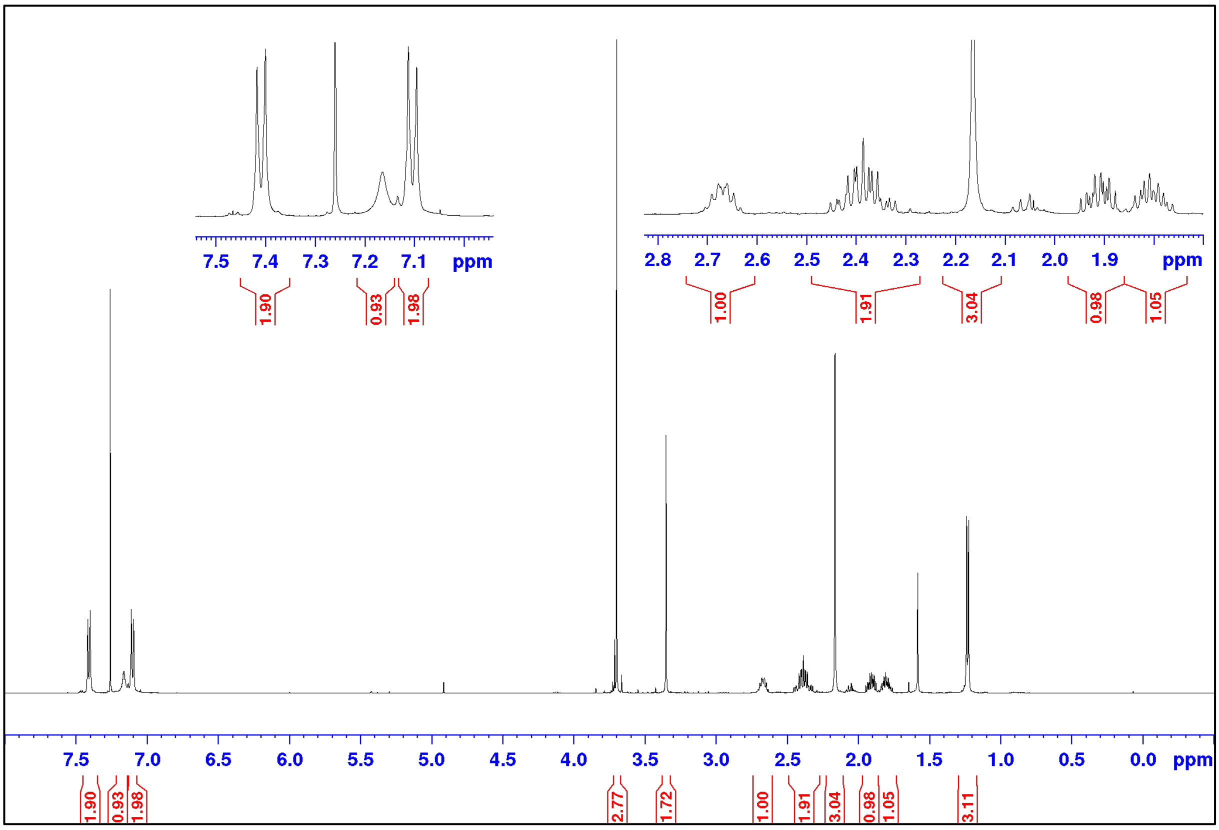
^{1}H NMR (500 MHz, $CDCl_3$) of **1c**



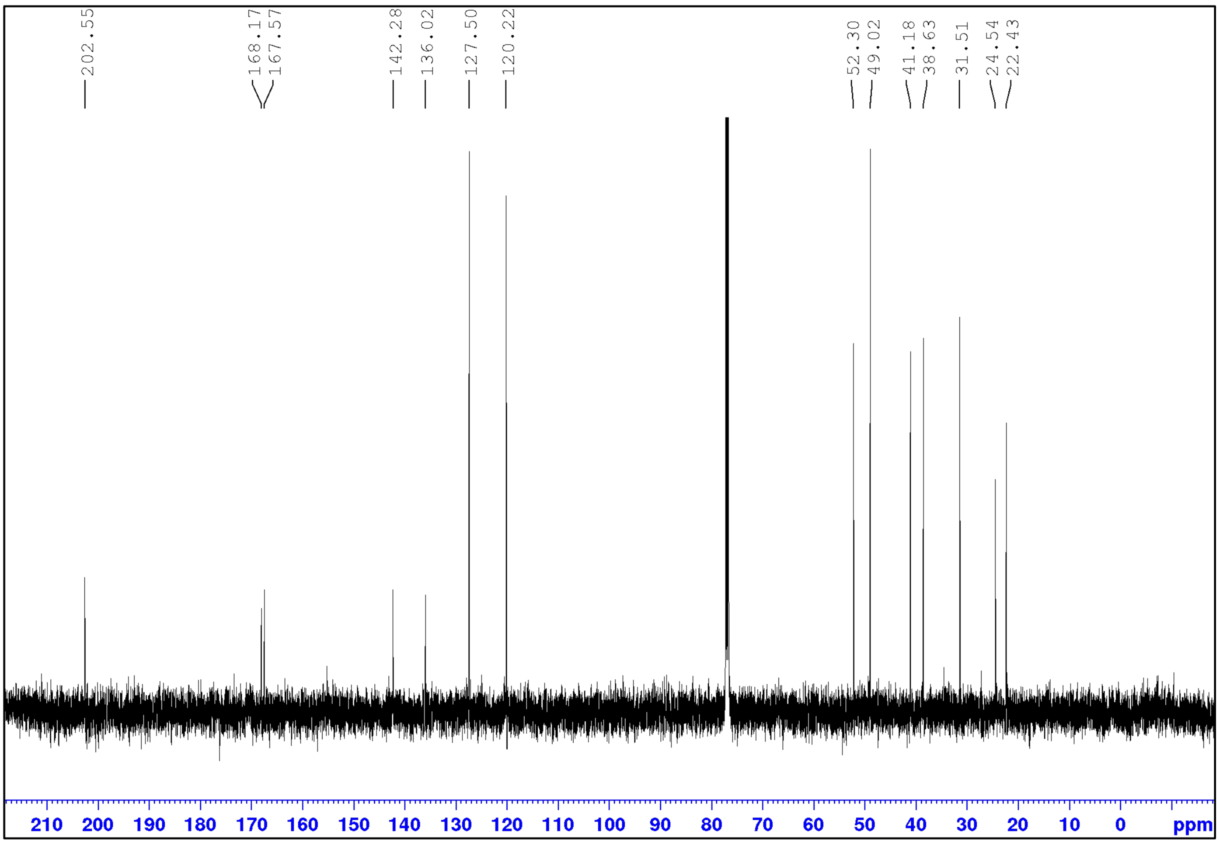
^{13}C NMR (125 MHz, $CDCl_3$) of **1c**



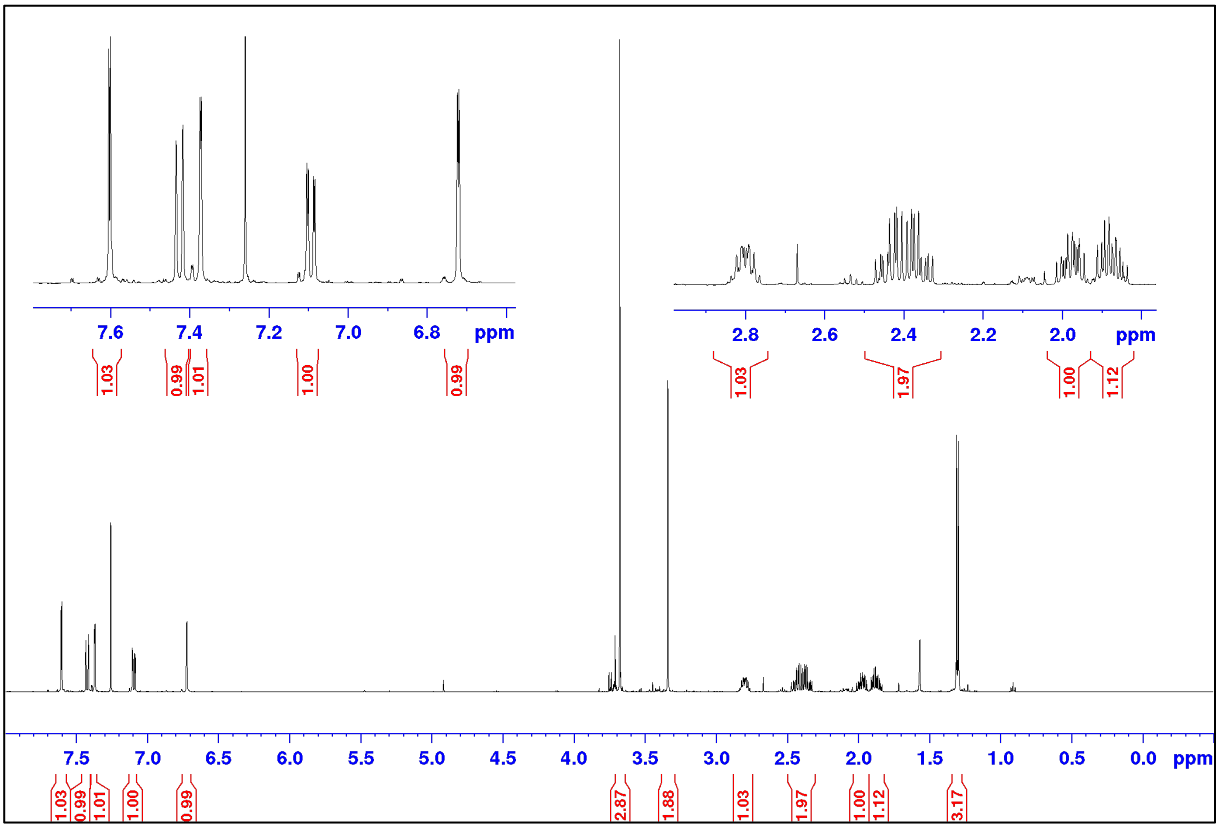
[1]H NMR (500 MHz, $CDCl_3$) of **1d**



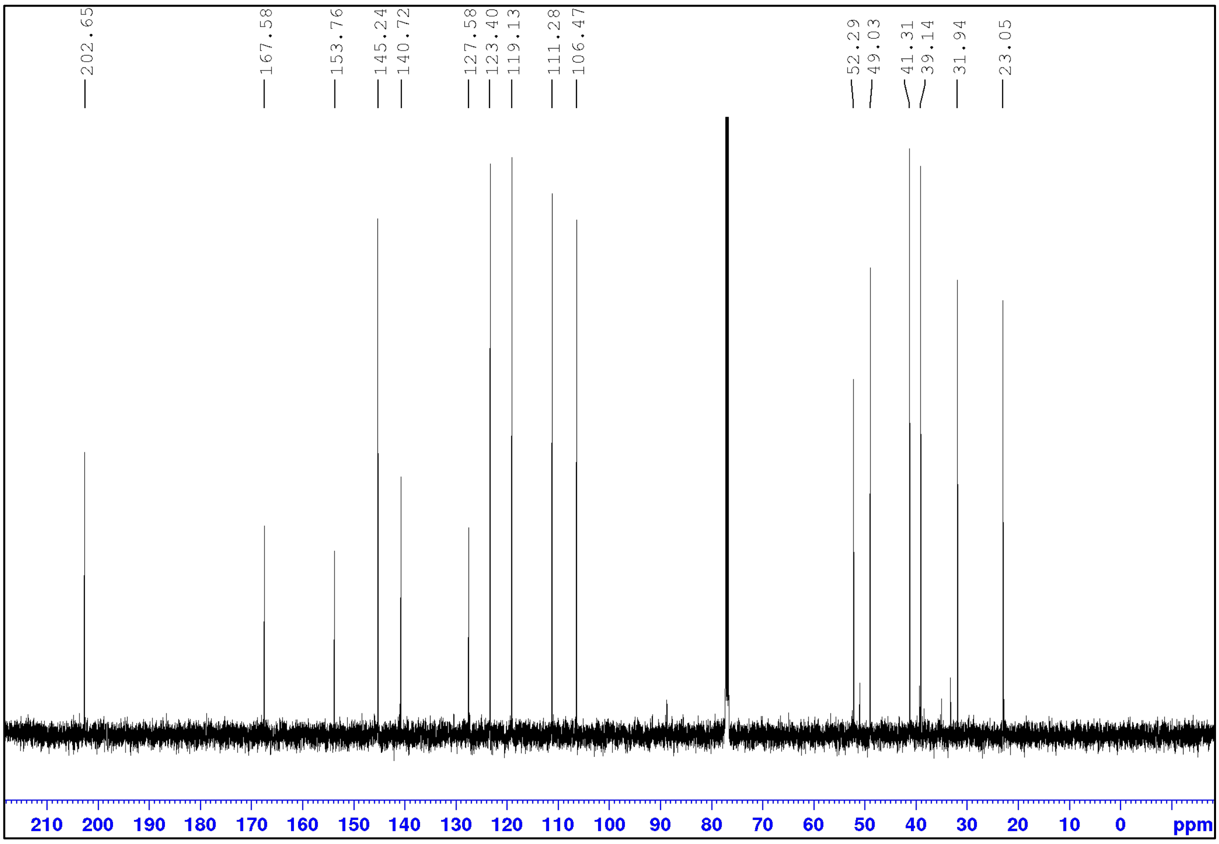
[13]C NMR (125 MHz, $CDCl_3$) of **1d**



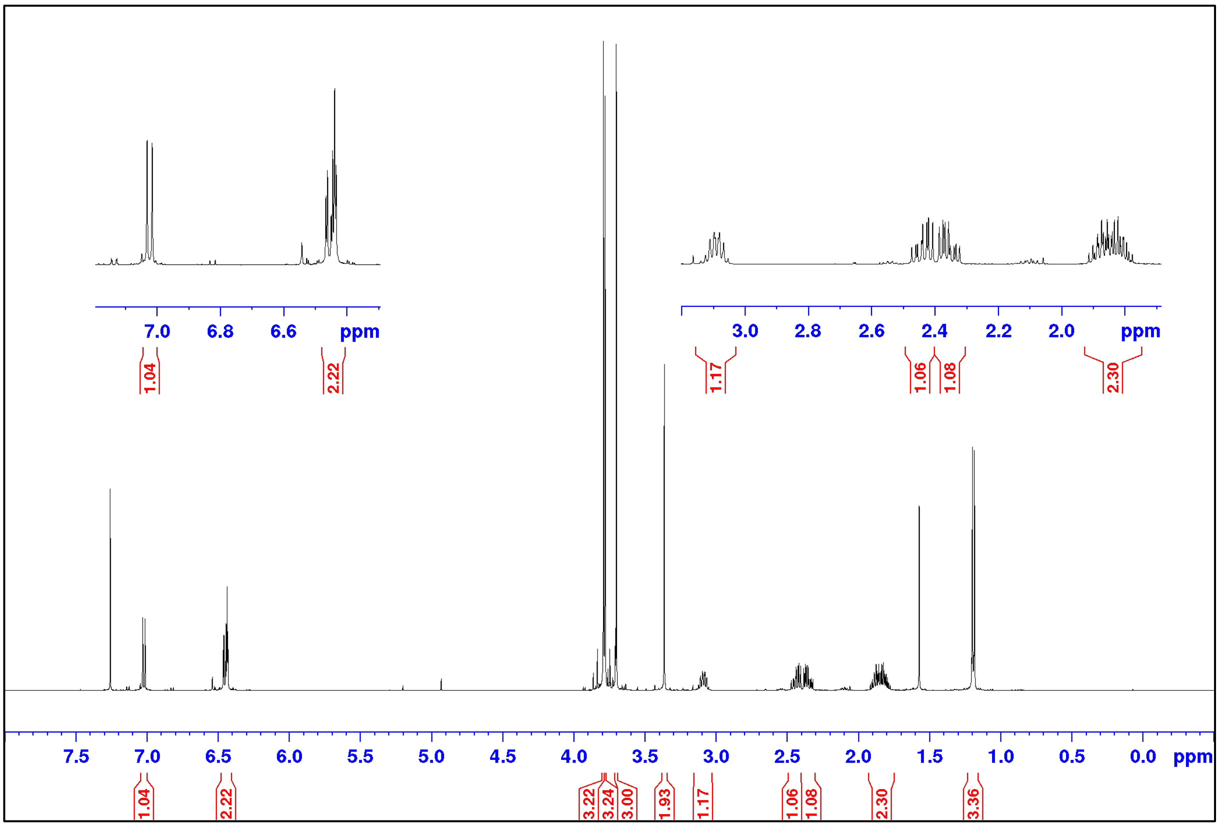
^{1}H NMR (500 MHz, $CDCl_3$) of **1e**



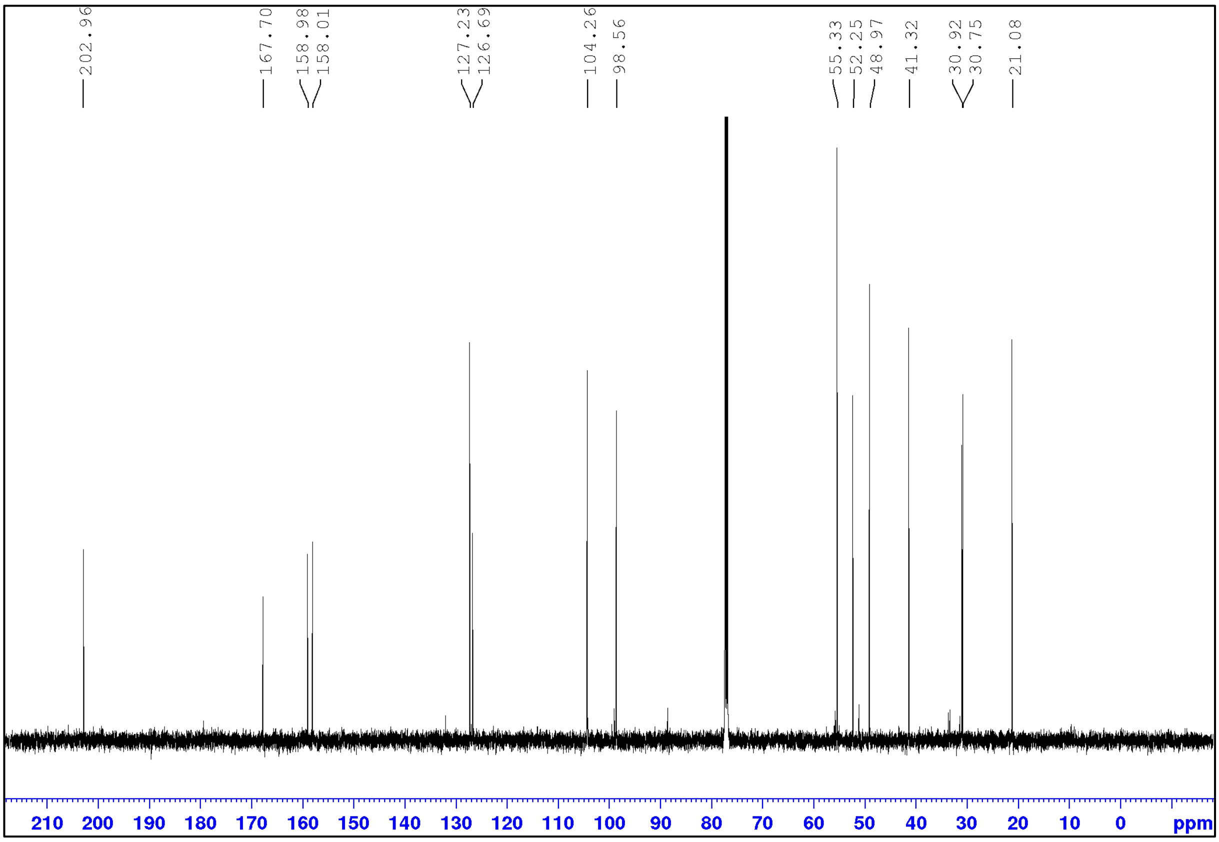
^{13}C NMR (125 MHz, $CDCl_3$) of **1e**



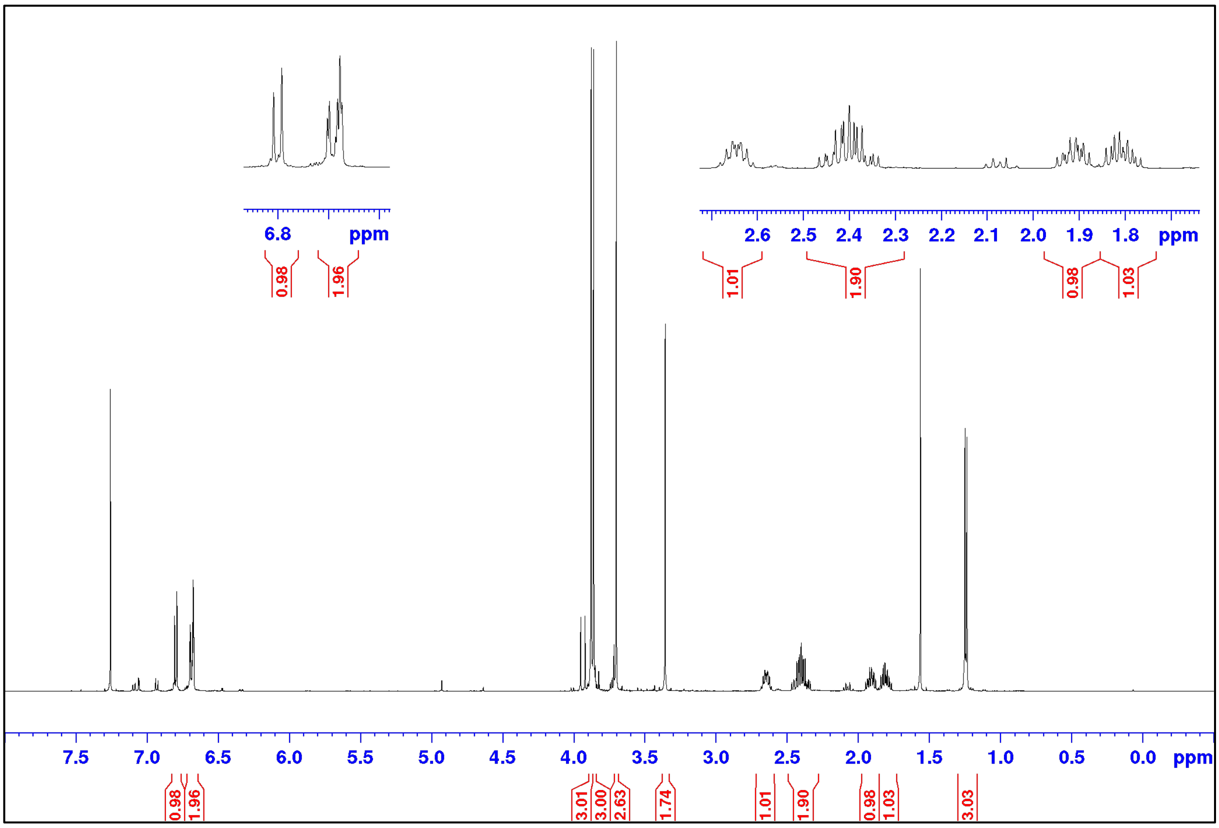
^{1}H NMR (500 MHz, $CDCl_3$) of **1f**



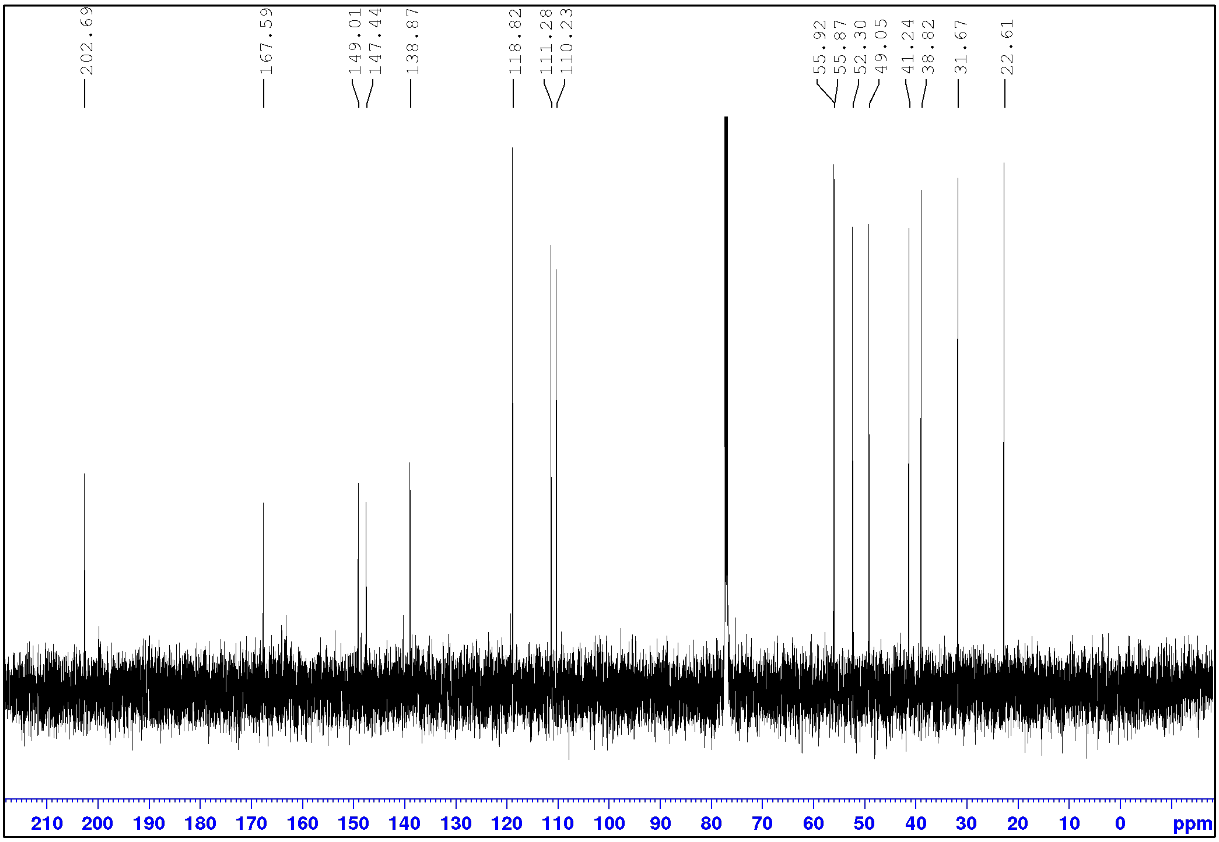
^{13}C NMR (125 MHz, $CDCl_3$) of **1f**



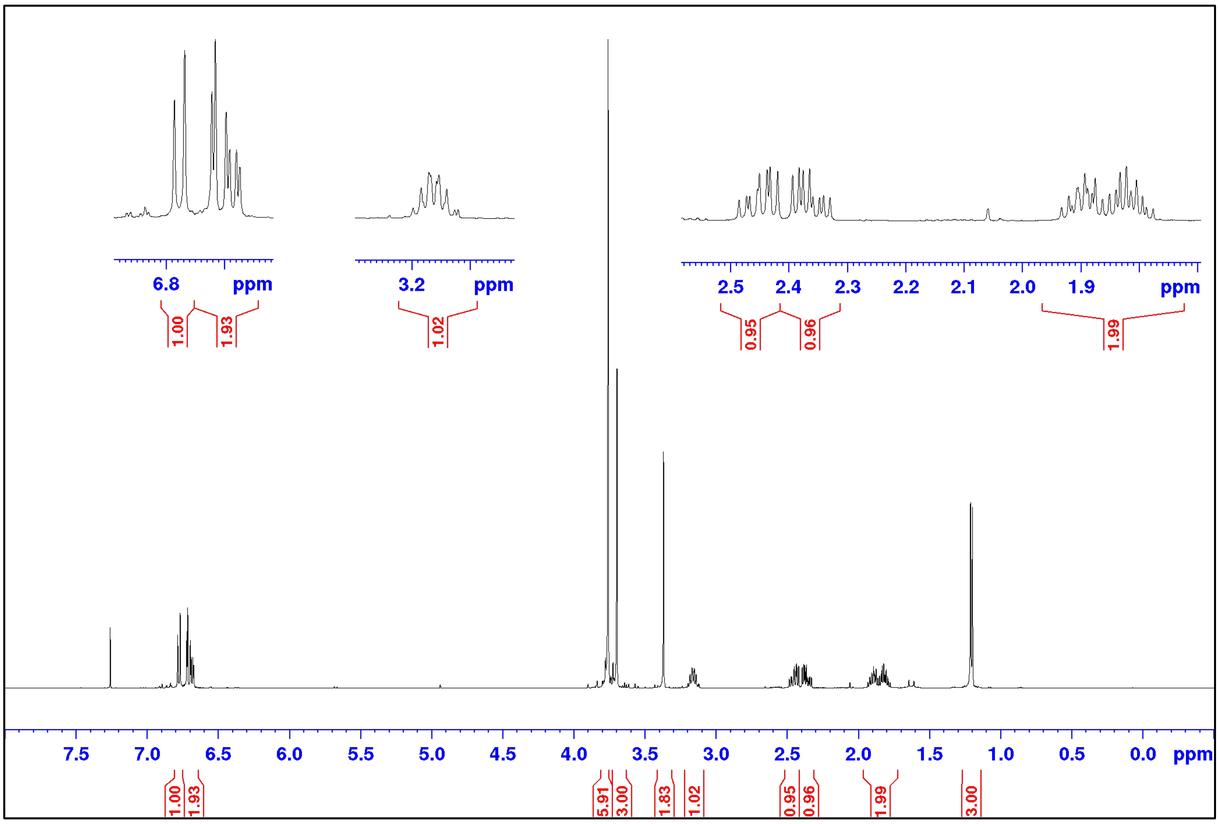
^{1}H NMR (500 MHz, $CDCl_3$) of **1g**



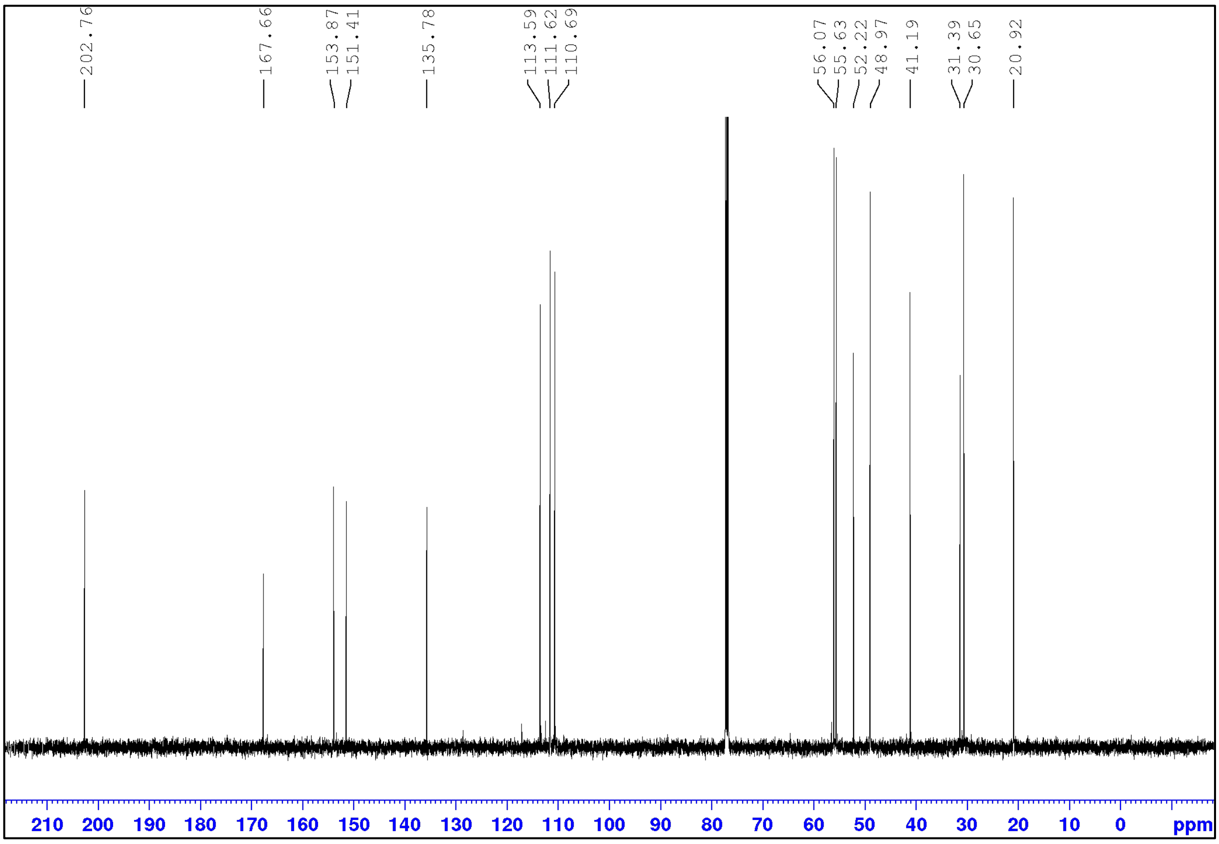
^{13}C NMR (125 MHz, $CDCl_3$) of **1g**



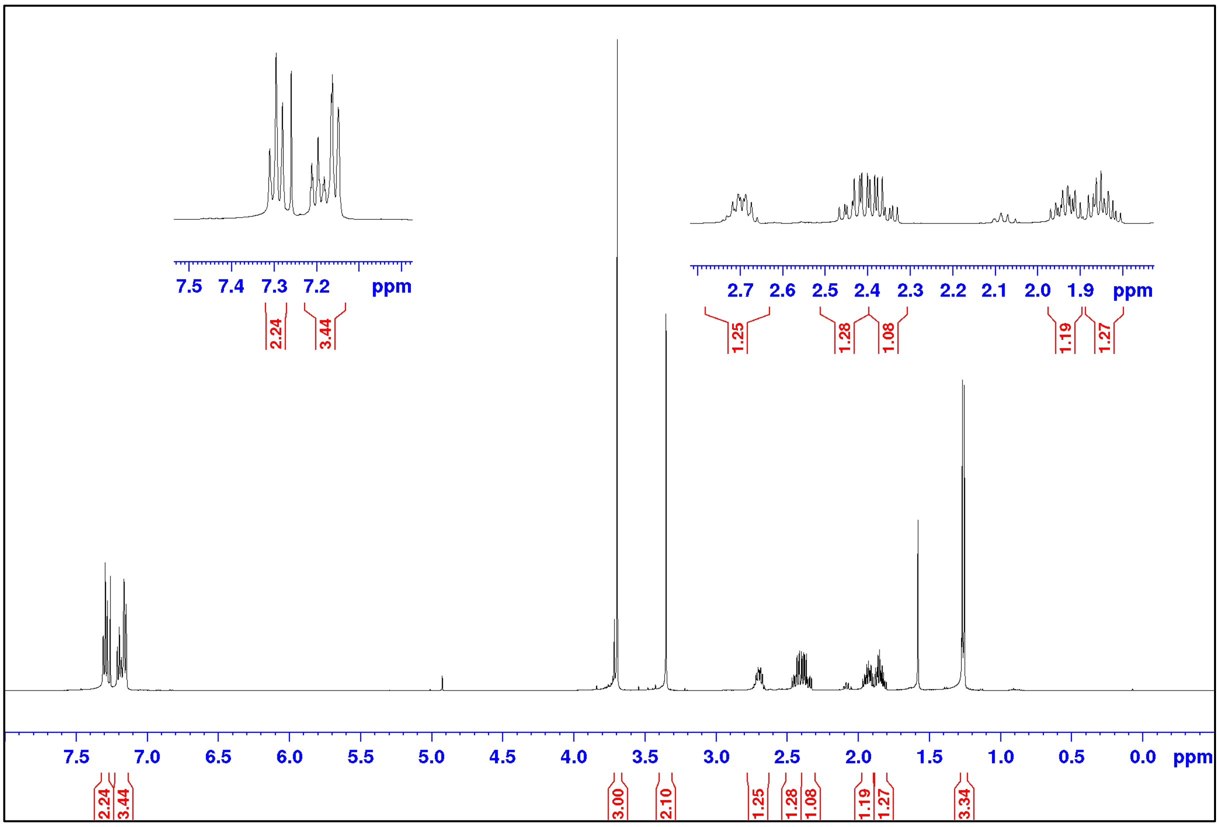
^{1}H NMR (500 MHz, $CDCl_3$) of **1h**



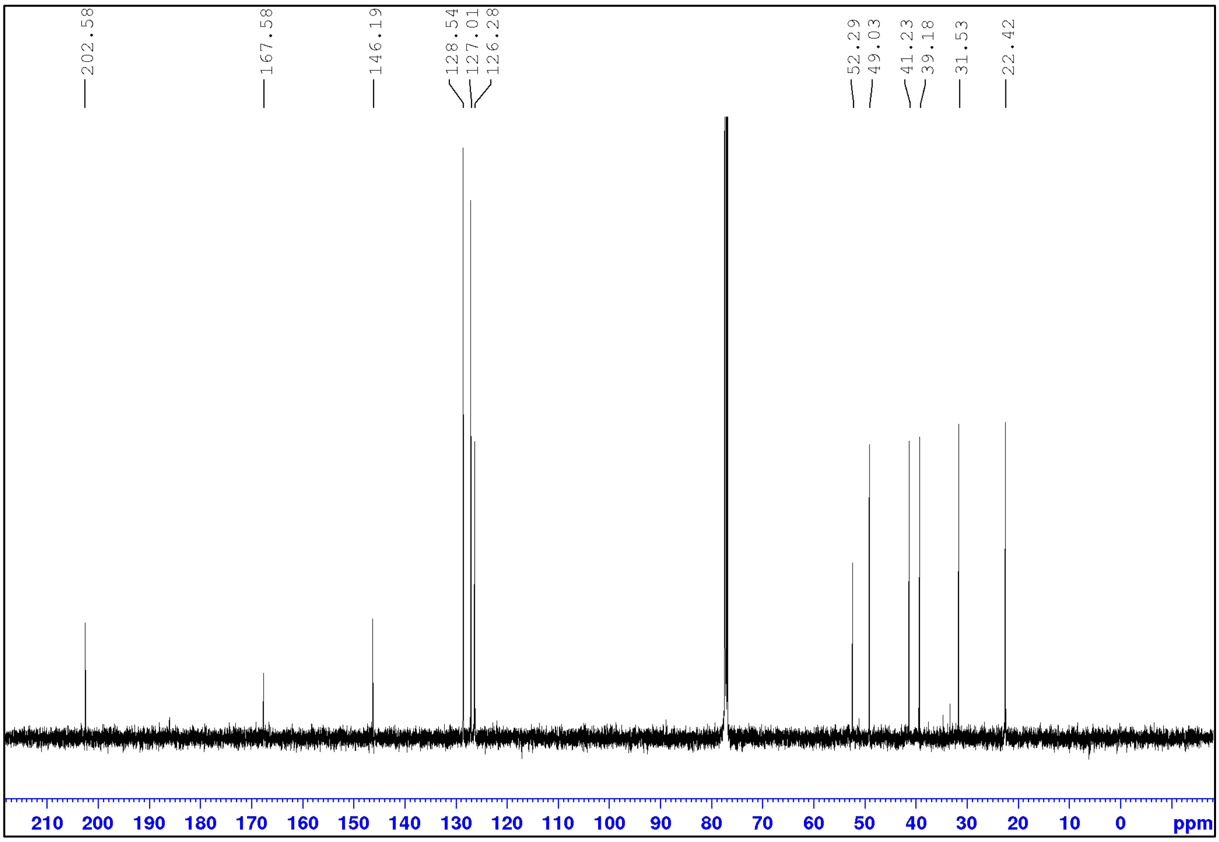
^{13}C NMR (125 MHz, $CDCl_3$) of **1h**



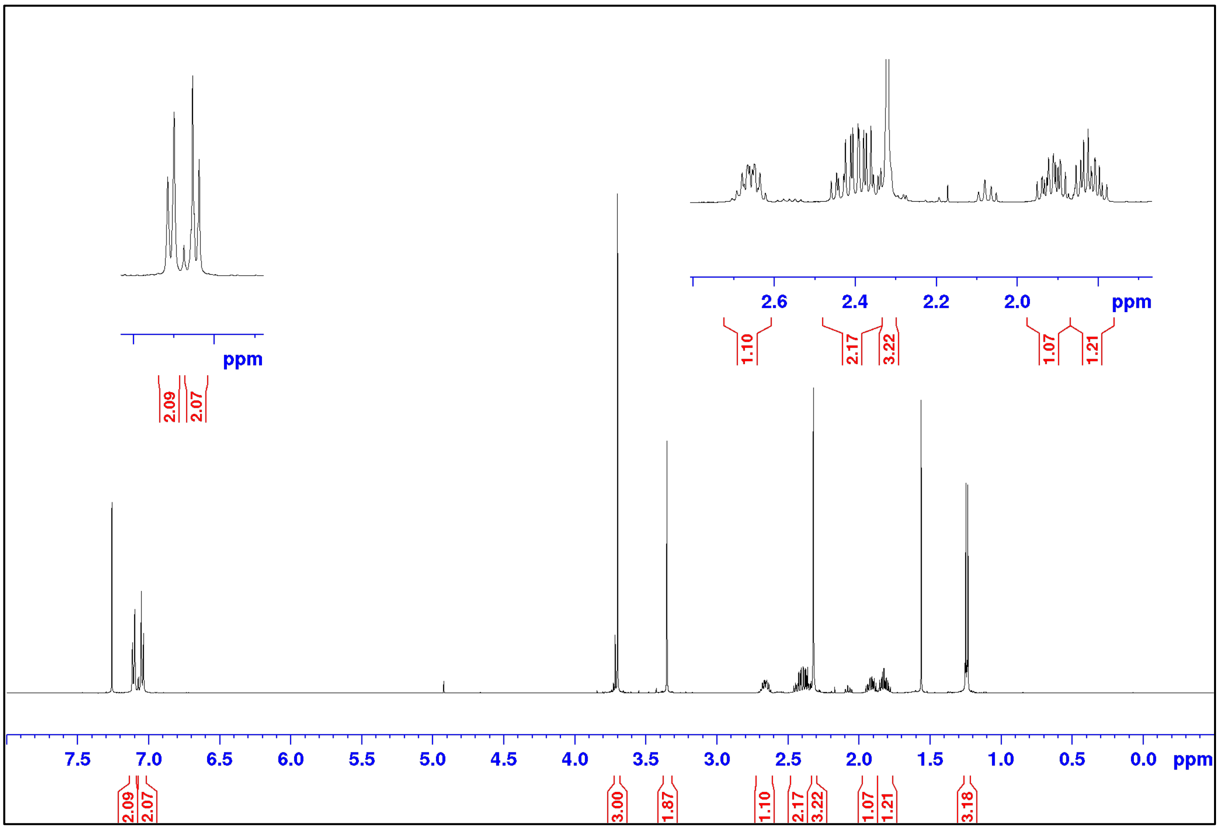
^{1}H NMR (500 MHz, $CDCl_3$) of **1i**



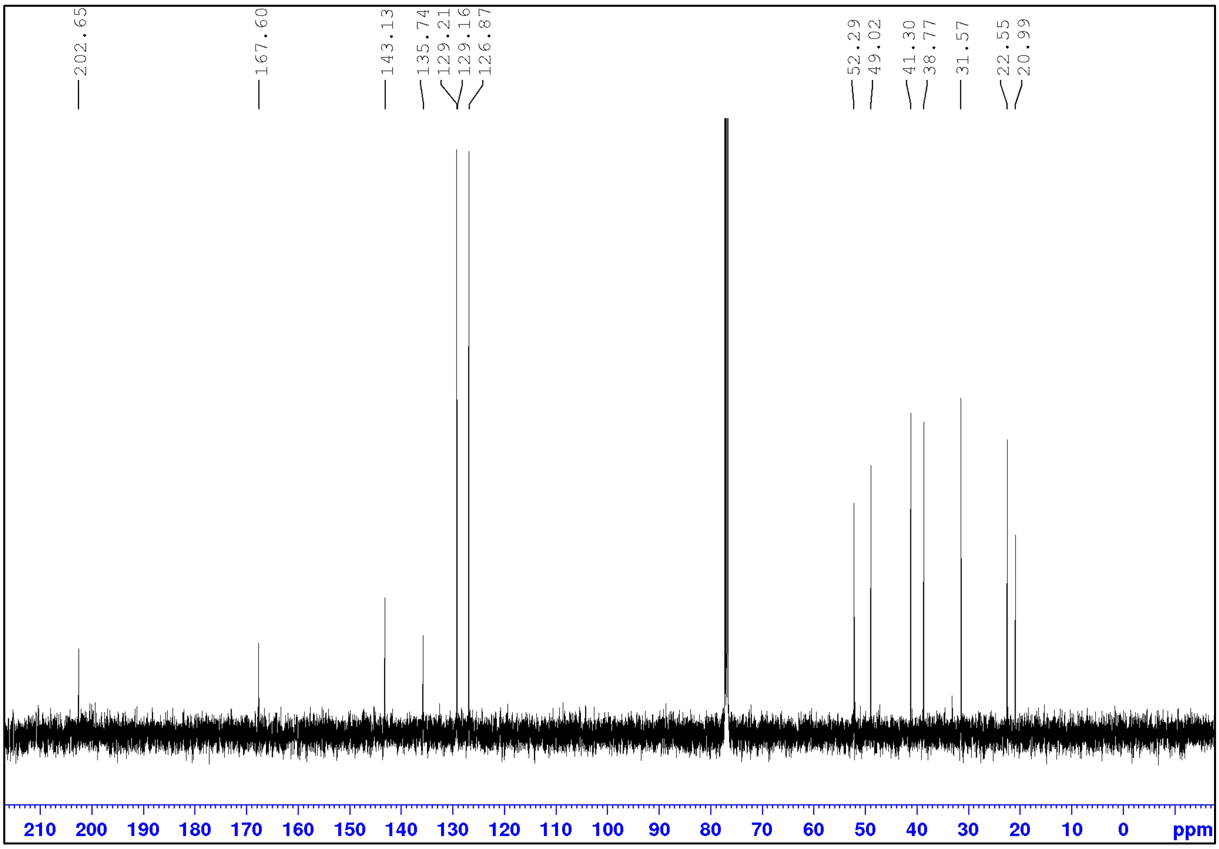
^{13}C NMR (125 MHz, $CDCl_3$) of **1i**



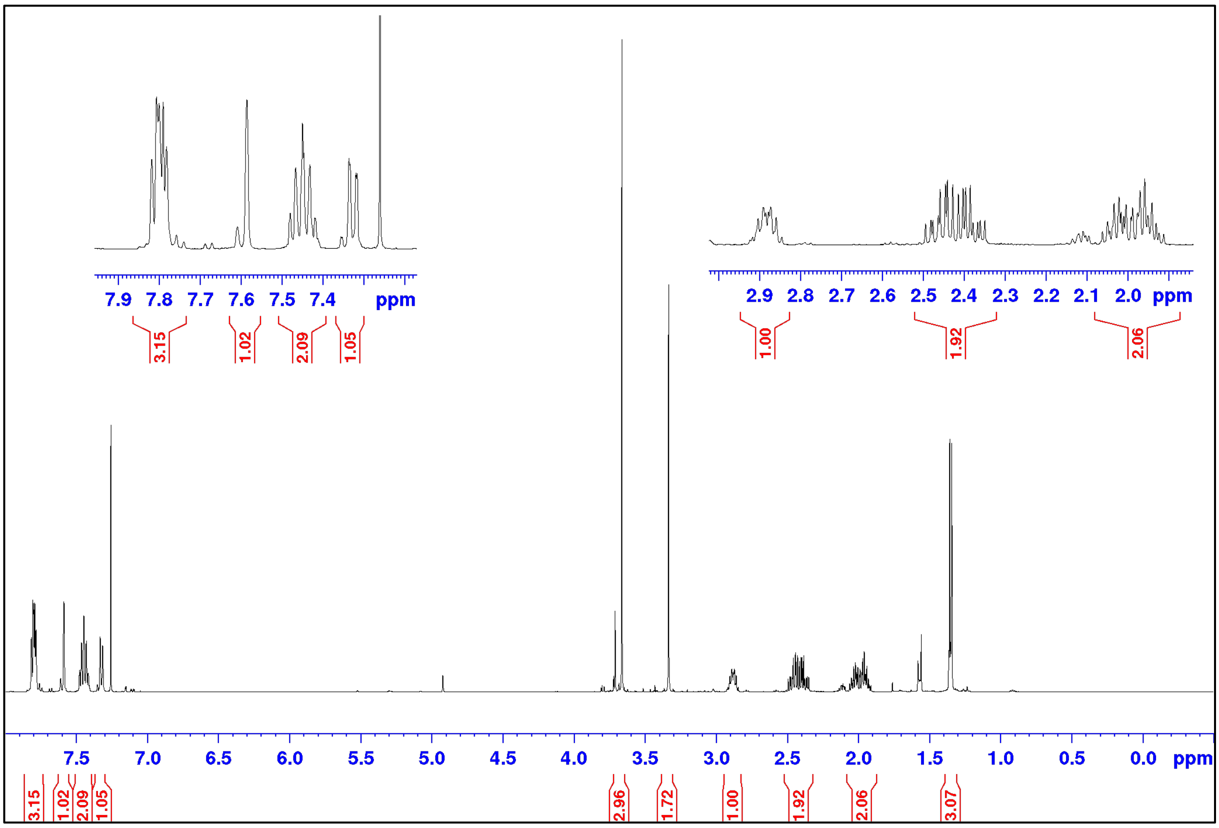
^{1}H NMR (500 MHz, $CDCl_3$) of **1j**



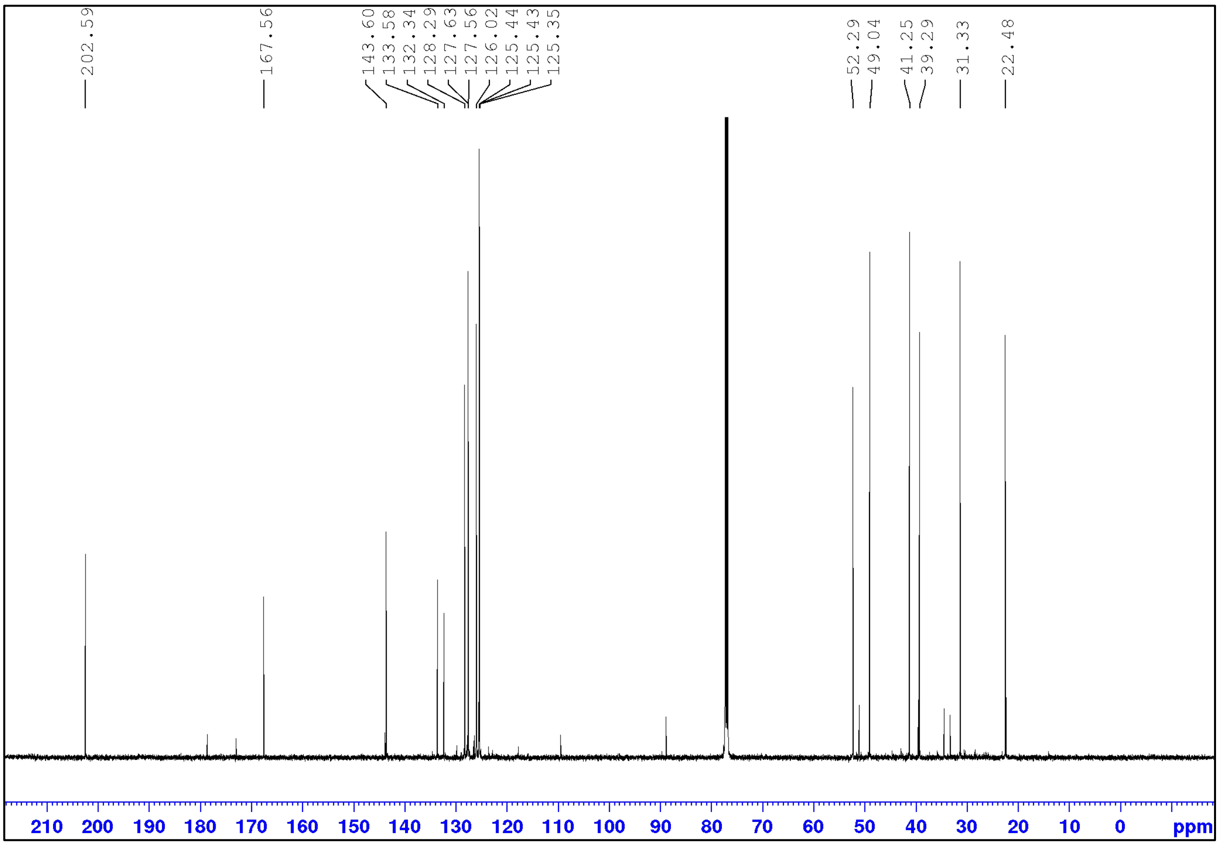
^{13}C NMR (125 MHz, $CDCl_3$) of **1j**



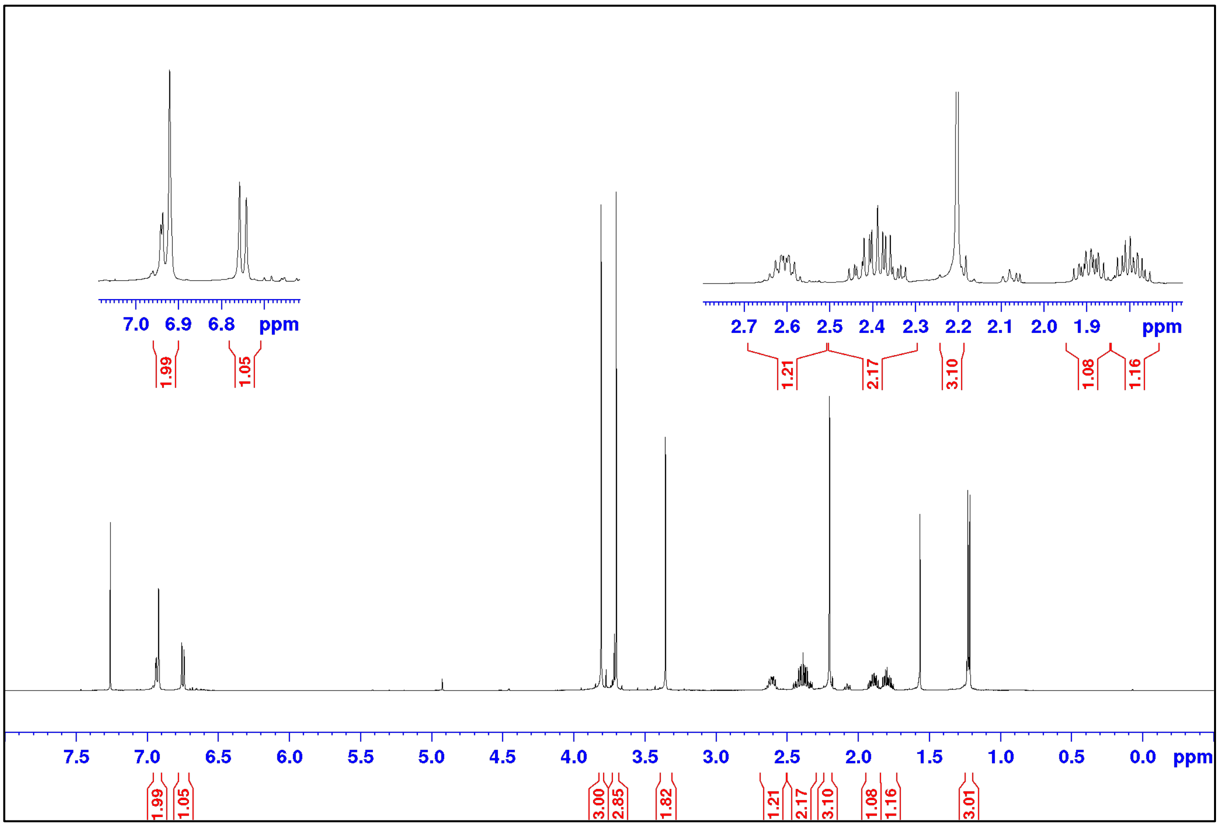
^{1}H NMR (500 MHz, $CDCl_3$) of **1k**



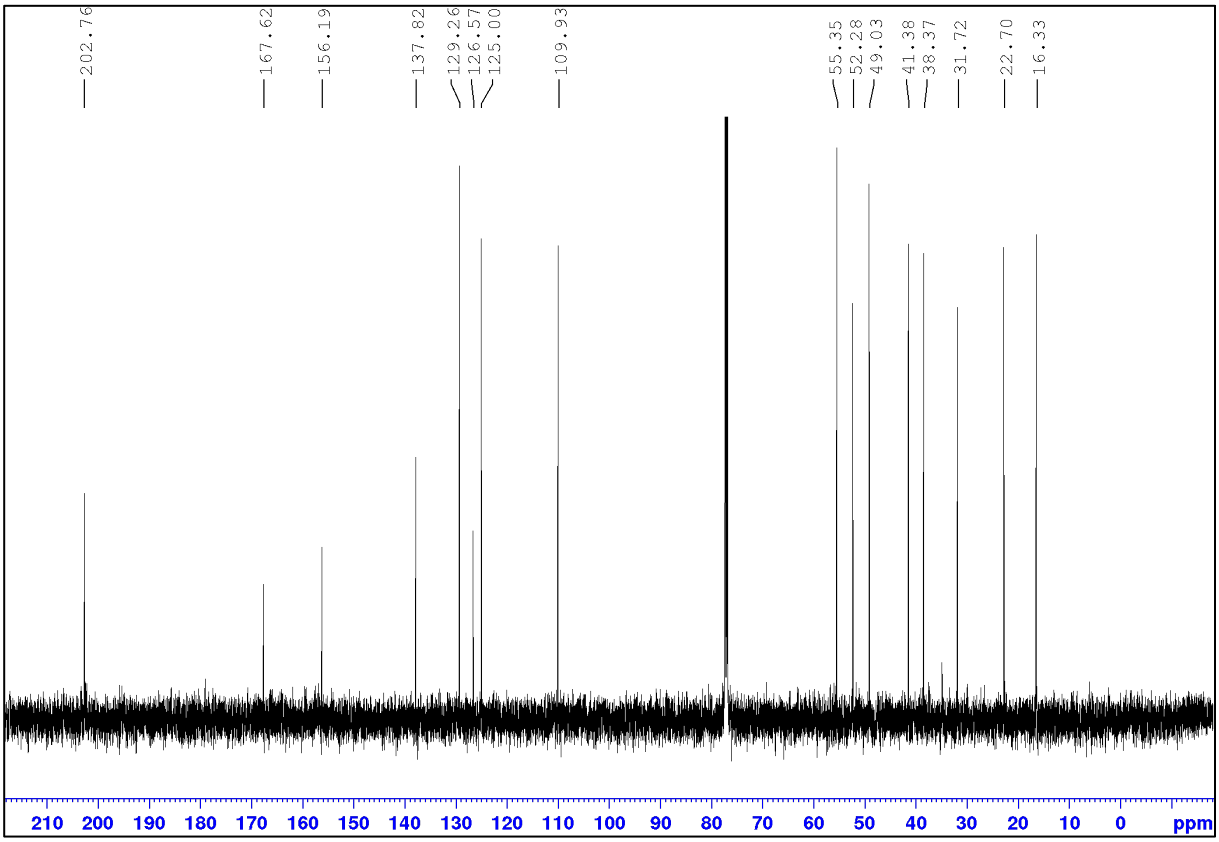
^{13}C NMR (125 MHz, $CDCl_3$) of **1k**



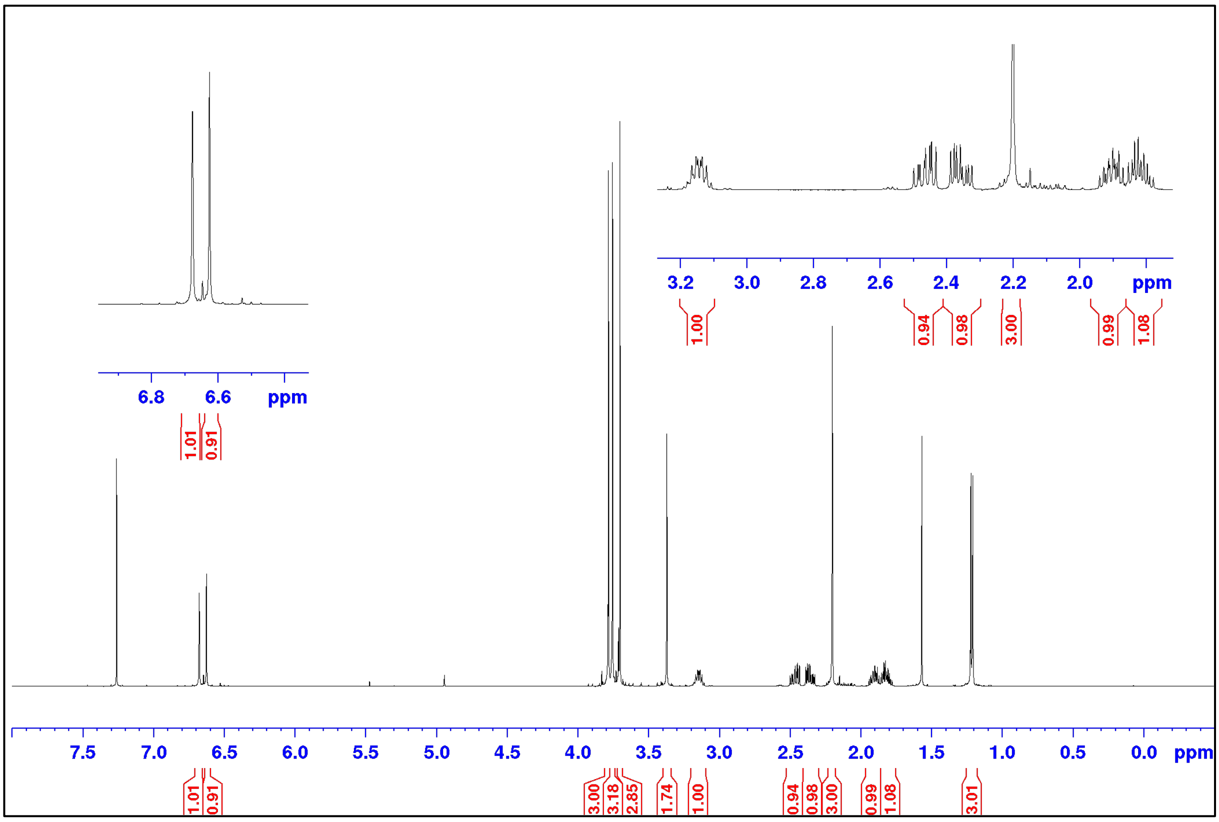
^{1}H NMR (500 MHz, $CDCl_3$) of **1l**



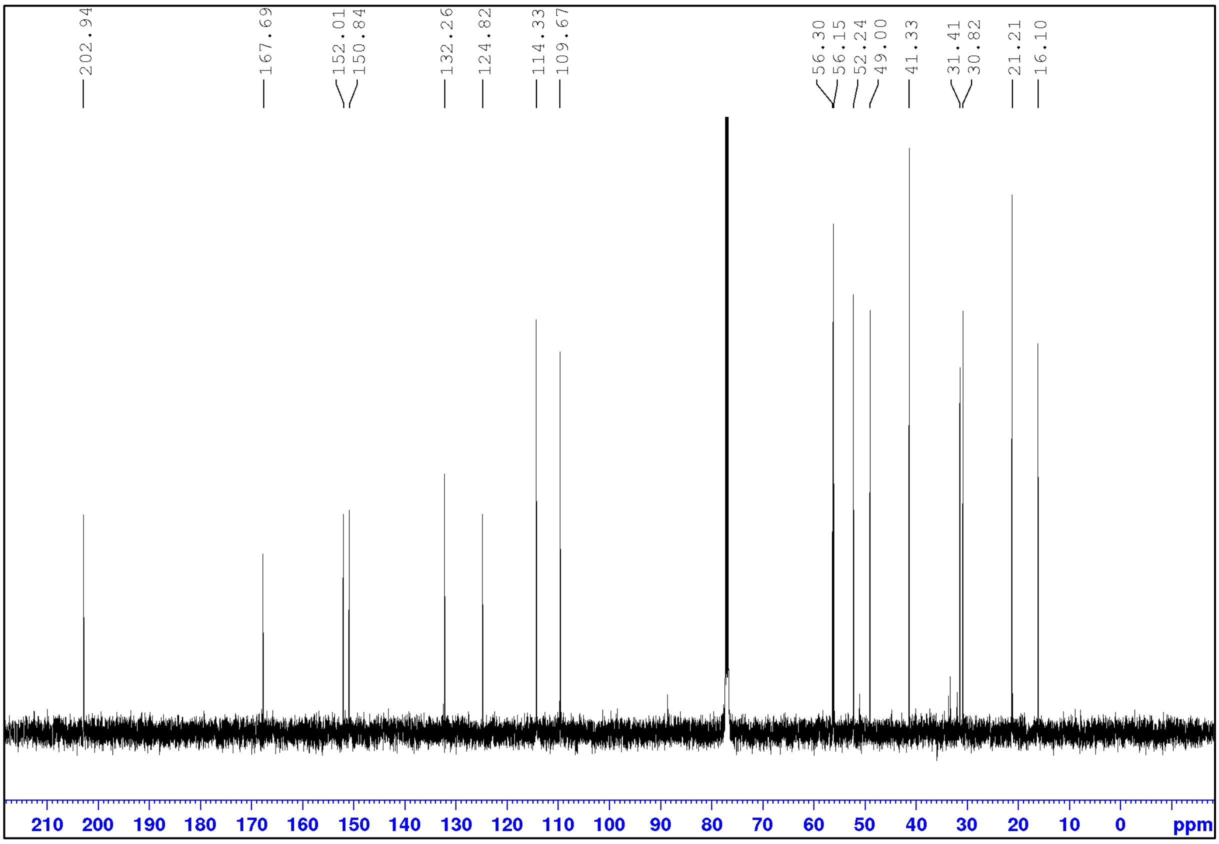
^{13}C NMR (125 MHz, $CDCl_3$) of **1l**



[1]H NMR (500 MHz, $CDCl_3$) of **1m**



[13]C NMR (125 MHz, $CDCl_3$) of **1m**



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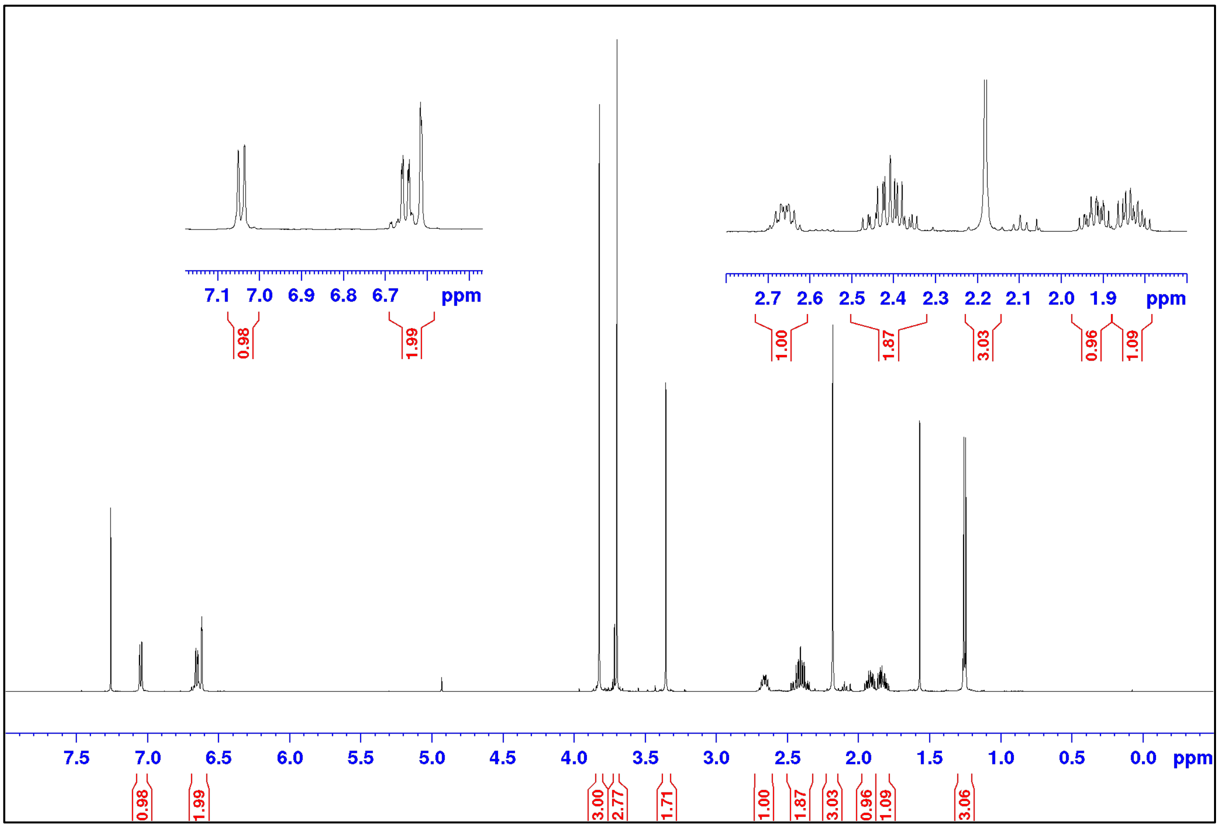
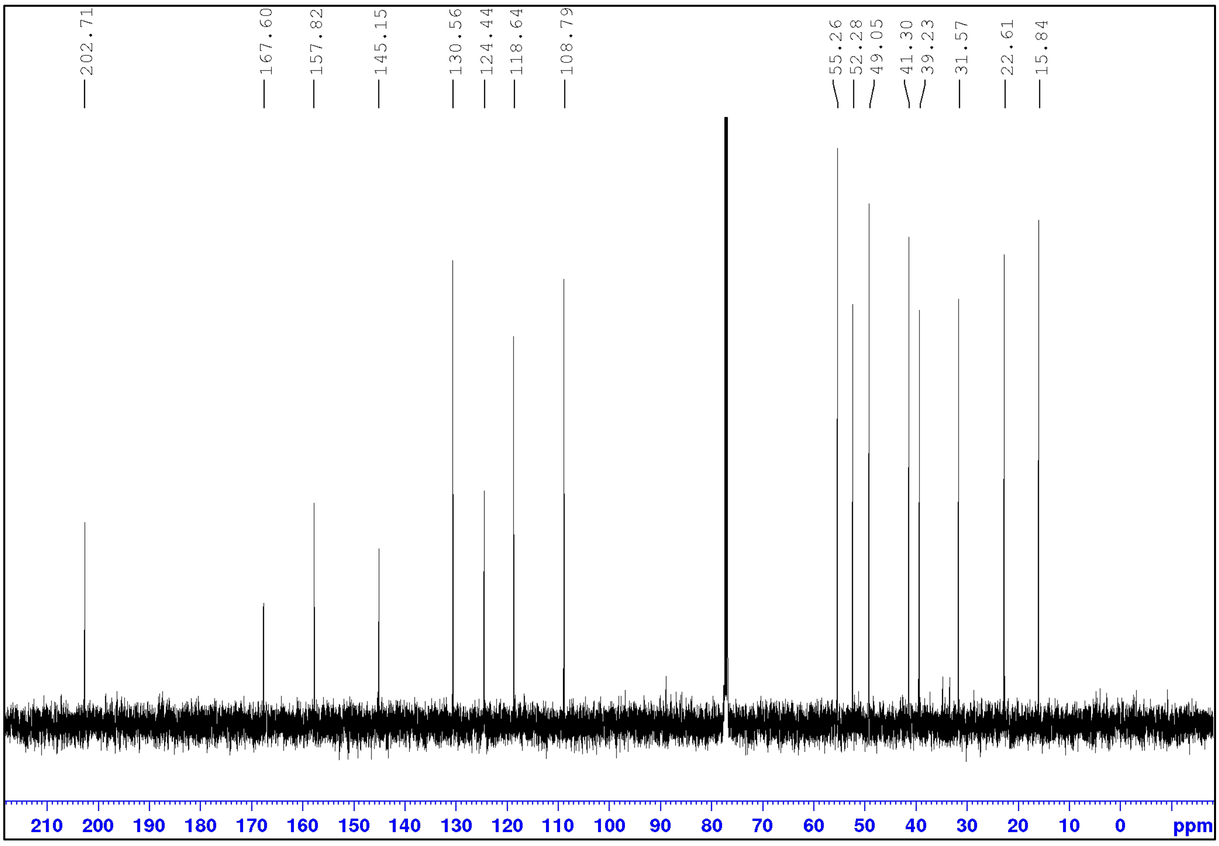
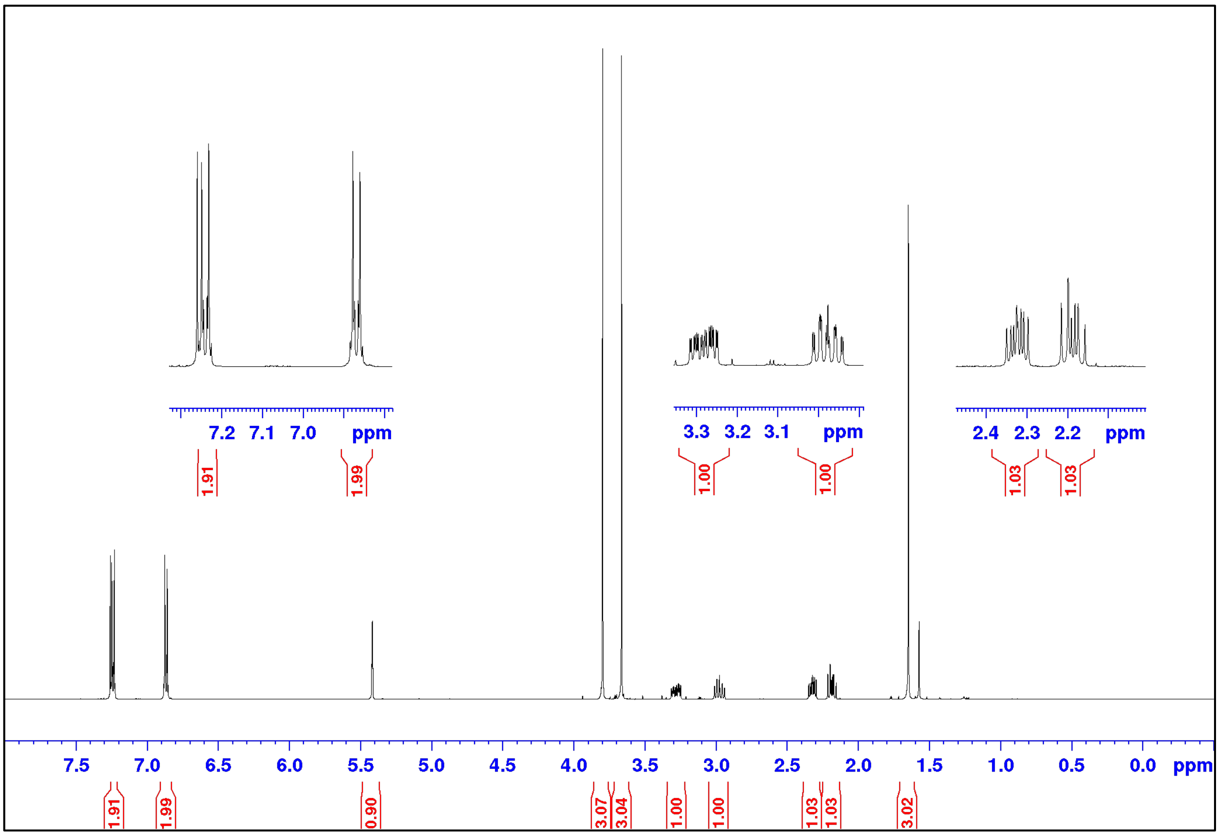


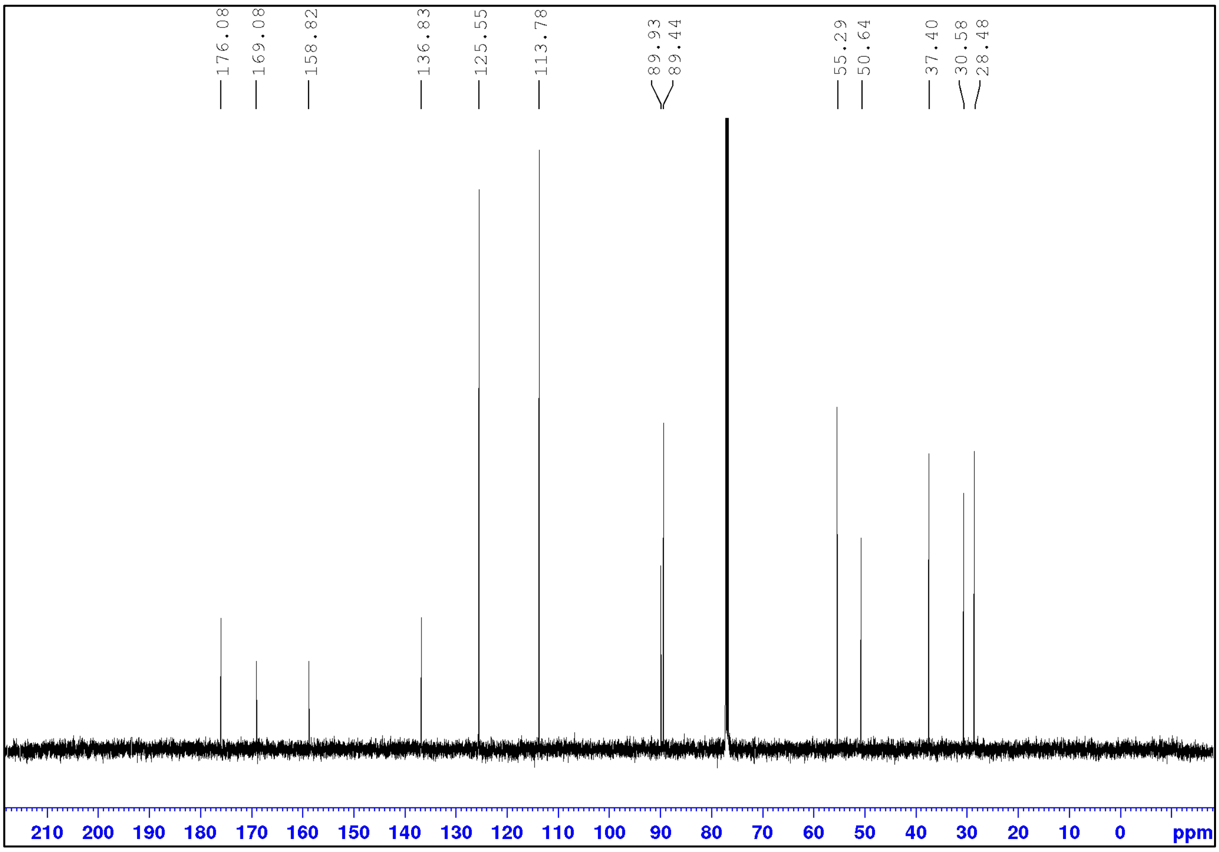
^{13}C NMR (125 MHz, $CDCl_3$) of **1n**



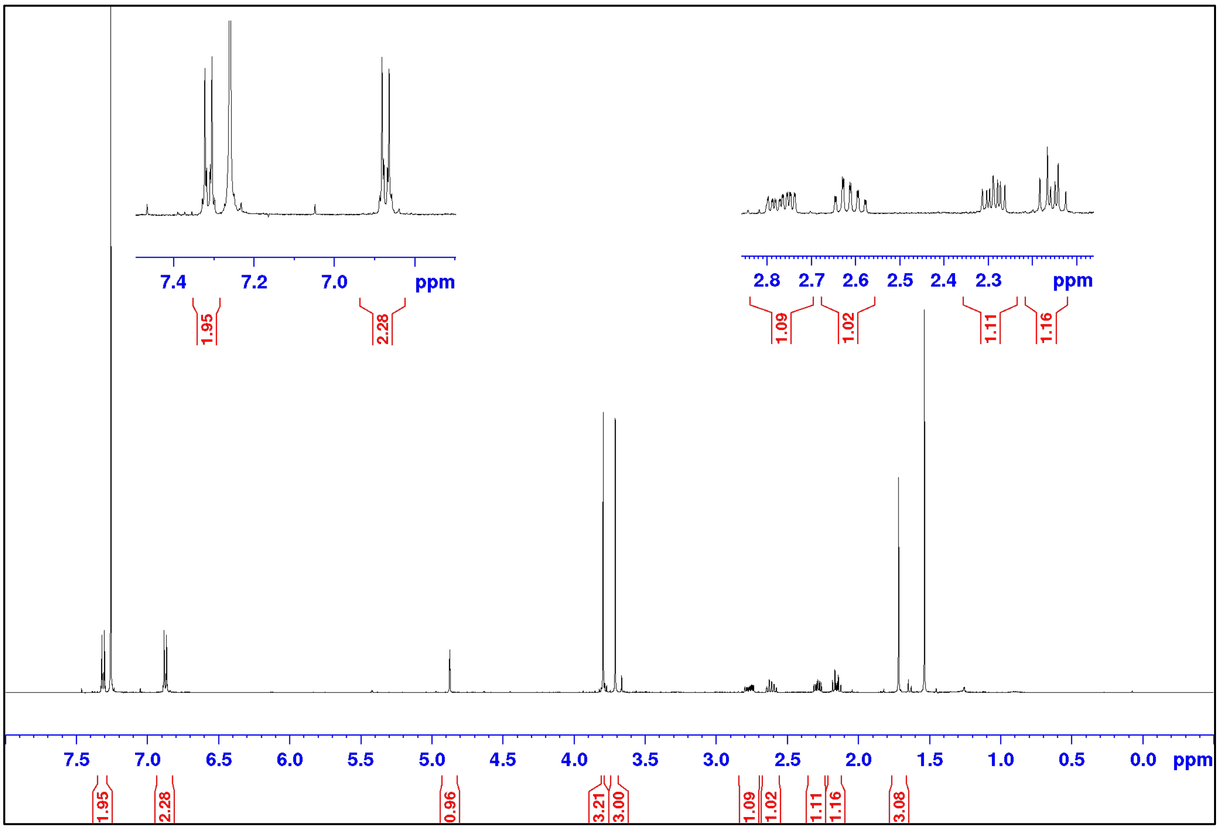
^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-**2a**



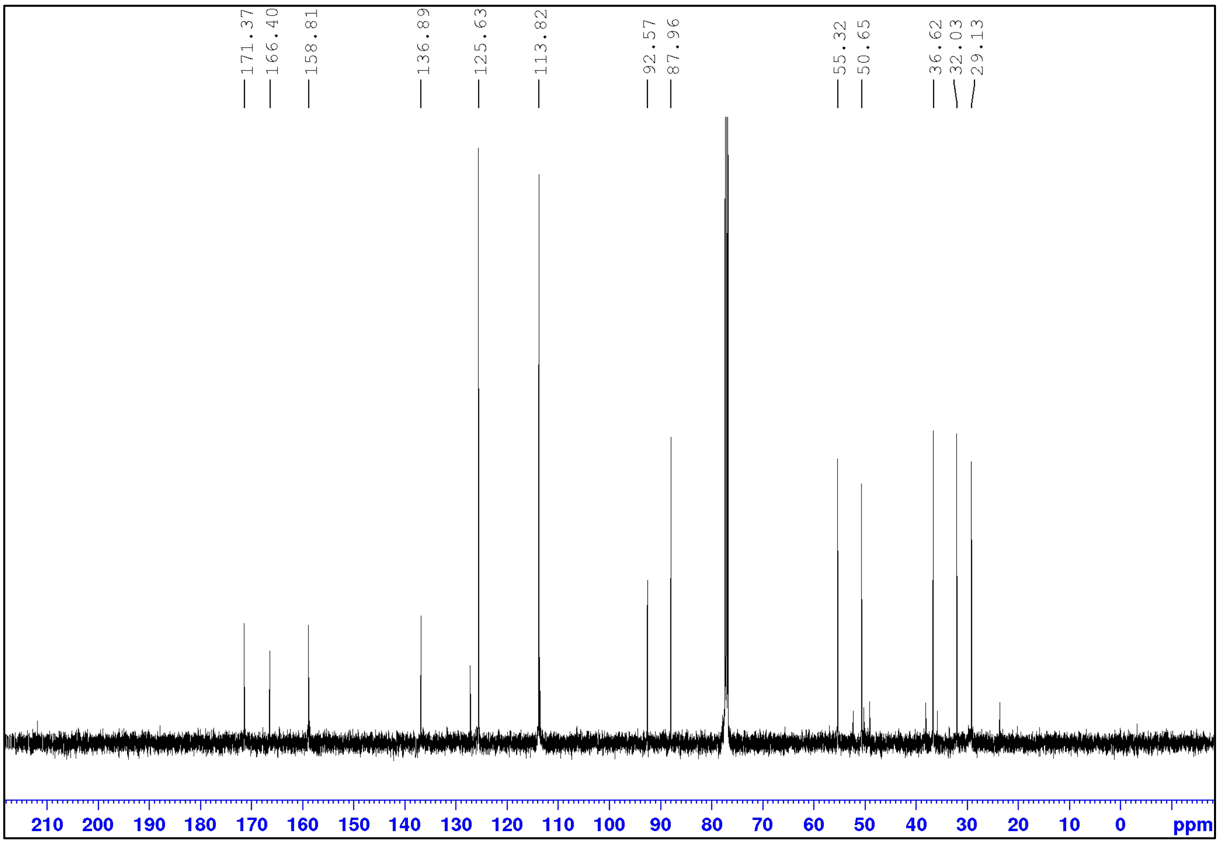
^{13}C NMR (125 MHz, $CDCl_3$) of (*E*)-**2a**



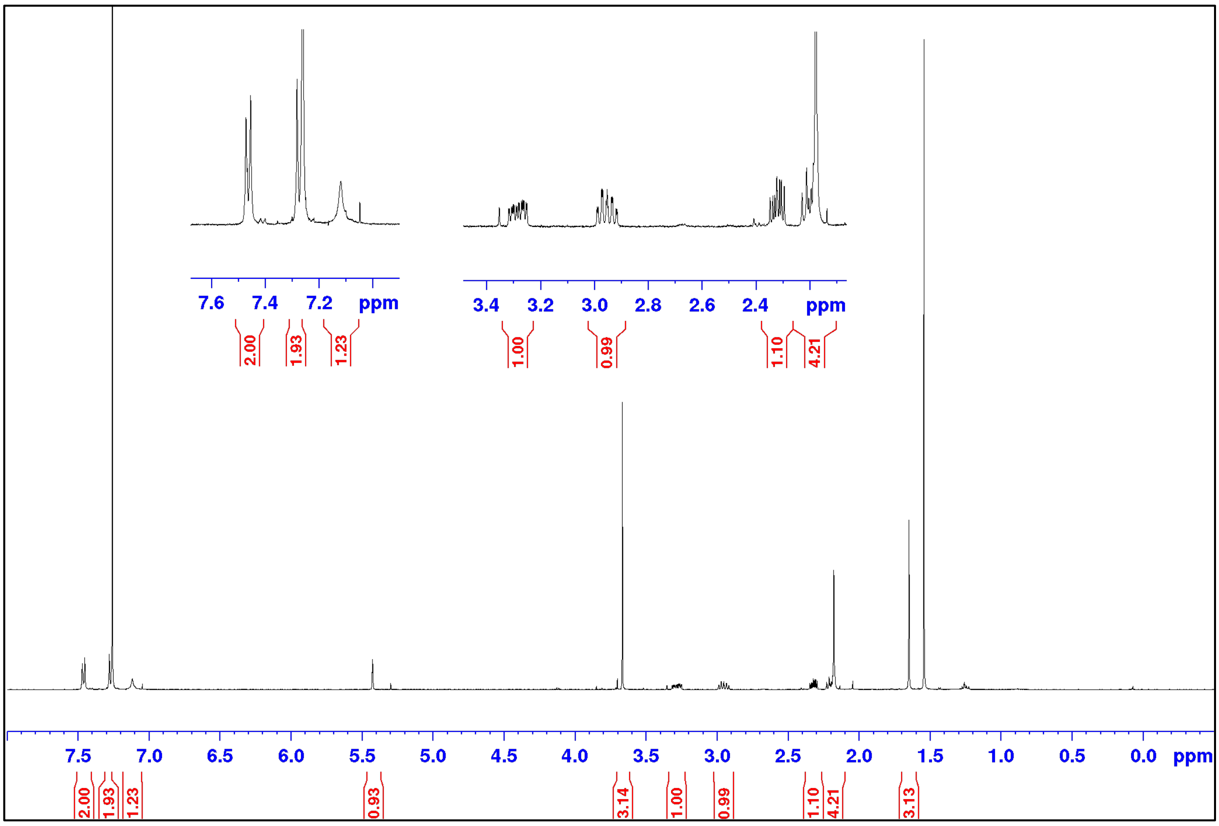
[1]H NMR (500 MHz, CDCl$_3$) of (*Z*)-**2a**



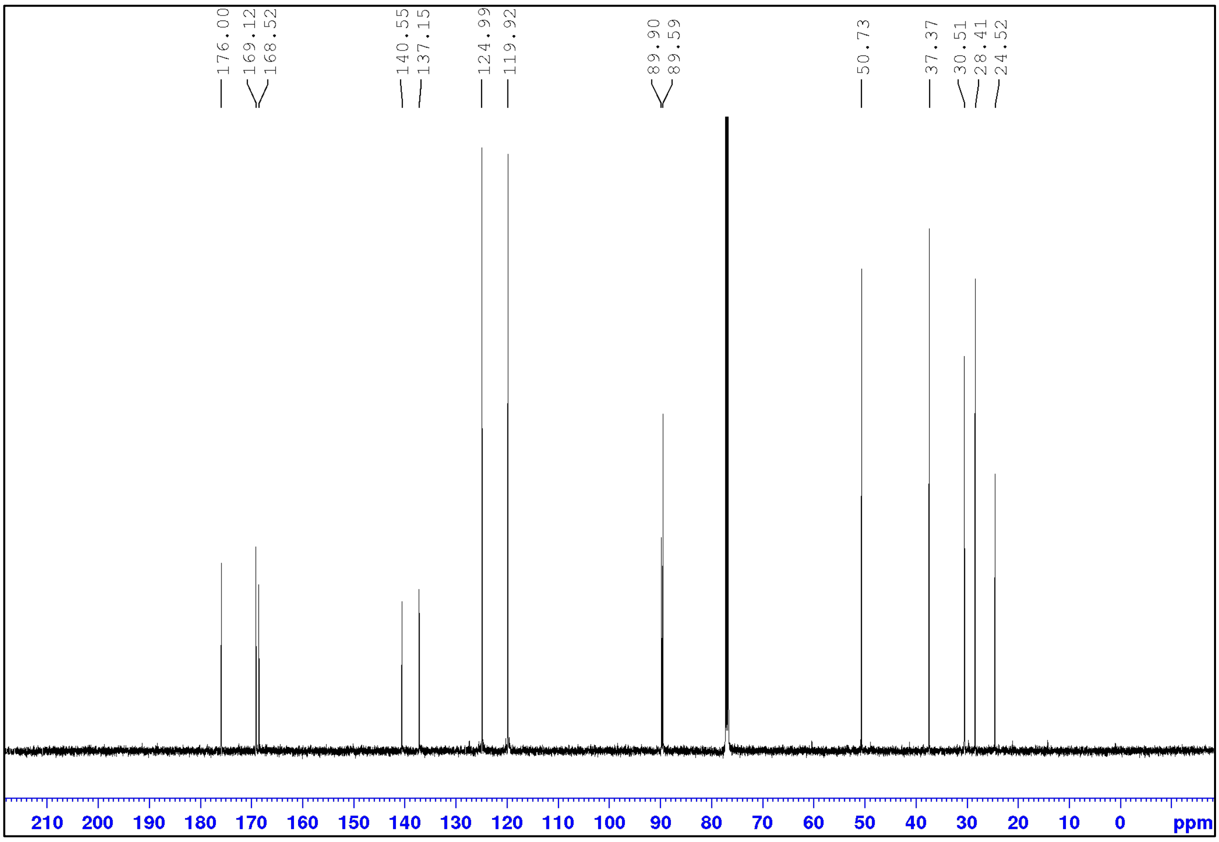
[13]C NMR (125 MHz, CDCl$_3$) of (*Z*)-**2a**



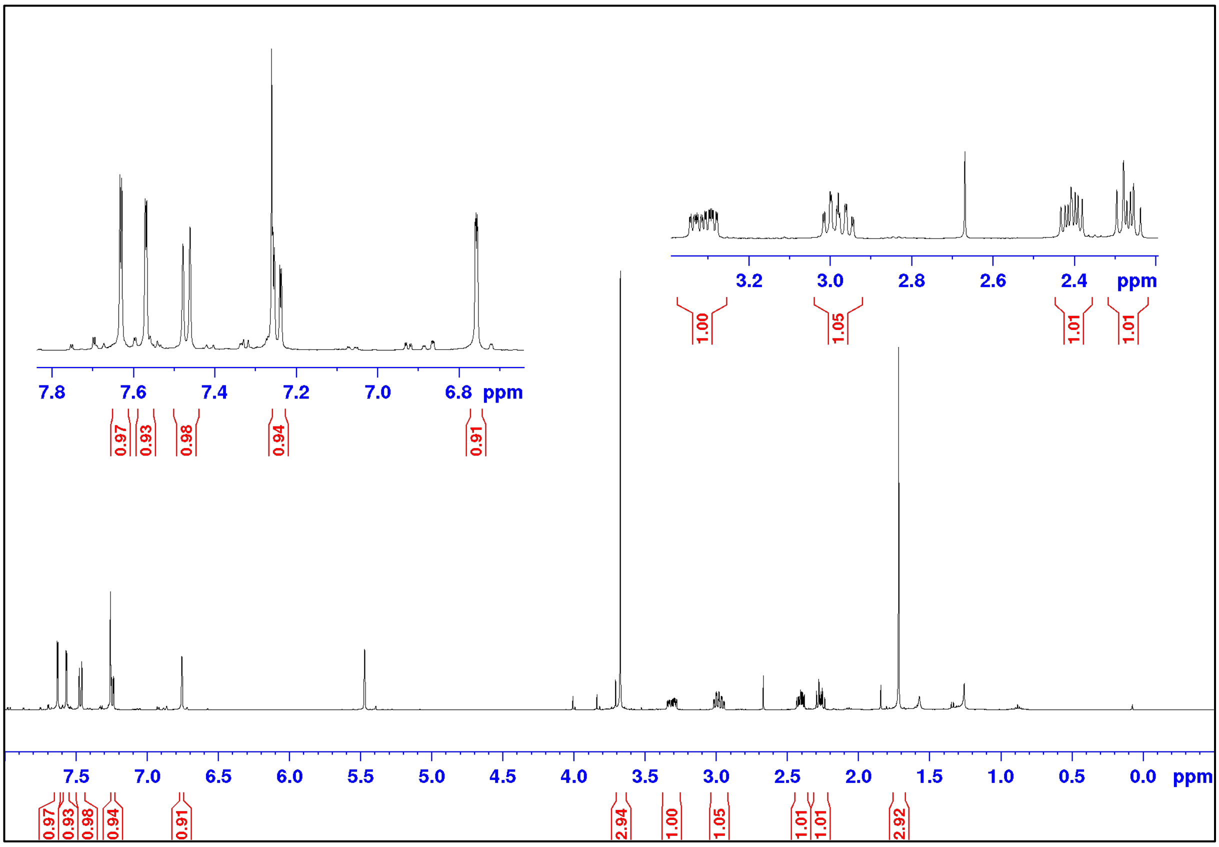
^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-**2d**



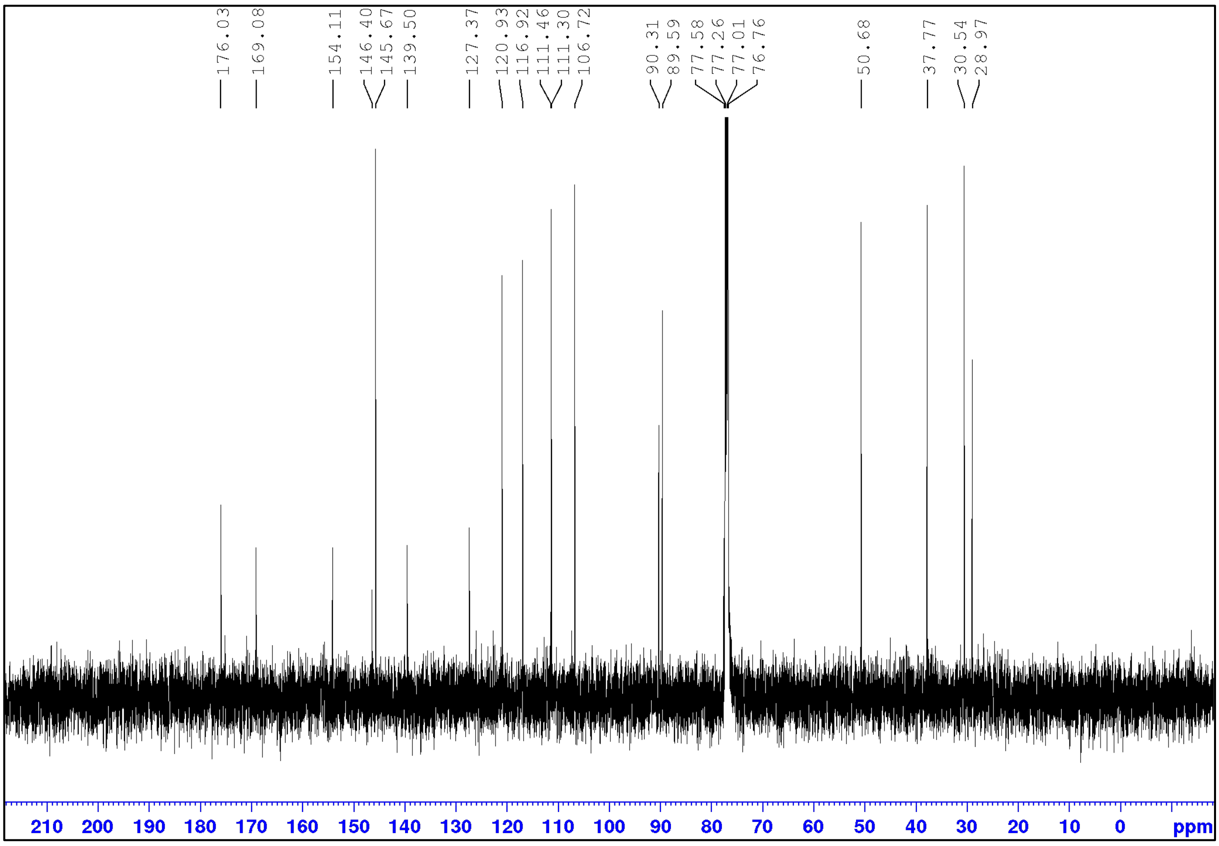
^{13}C NMR (125 MHz, $CDCl_3$) of (*E*)-**2d**



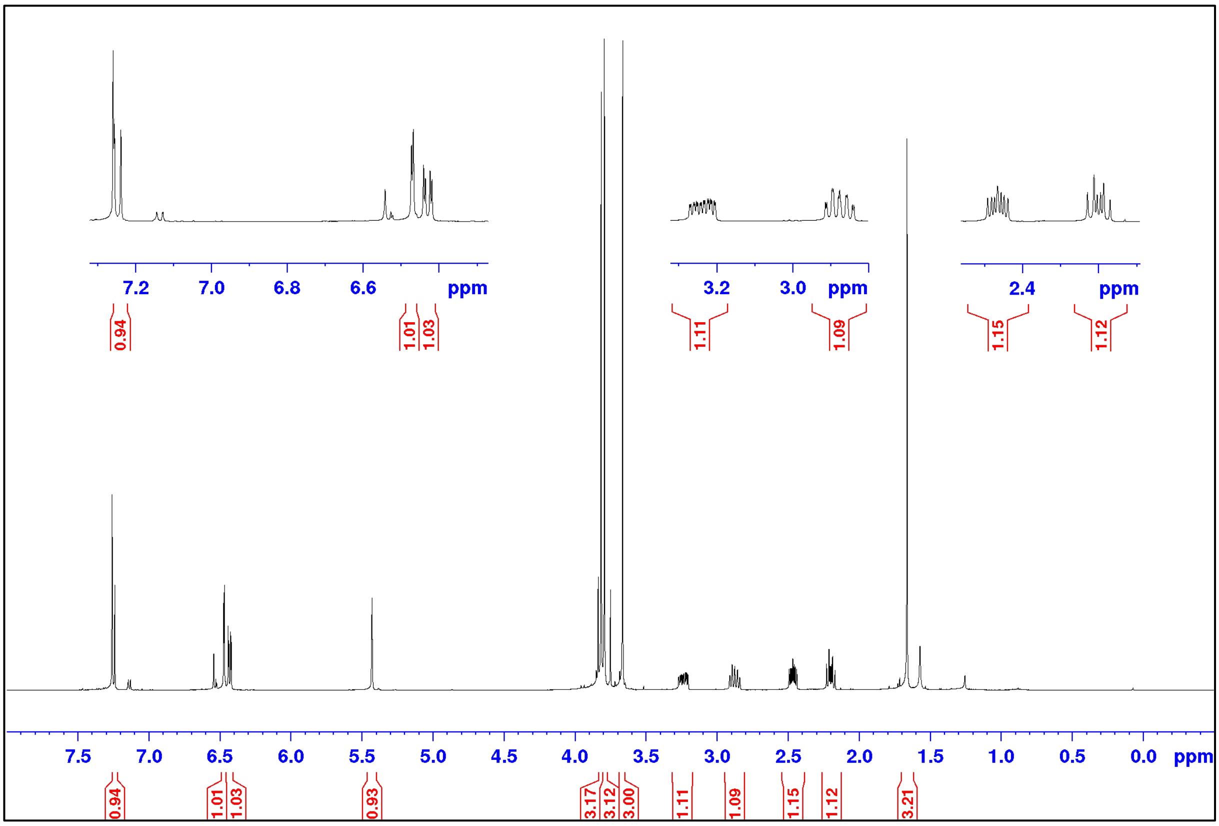
^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-**2e**



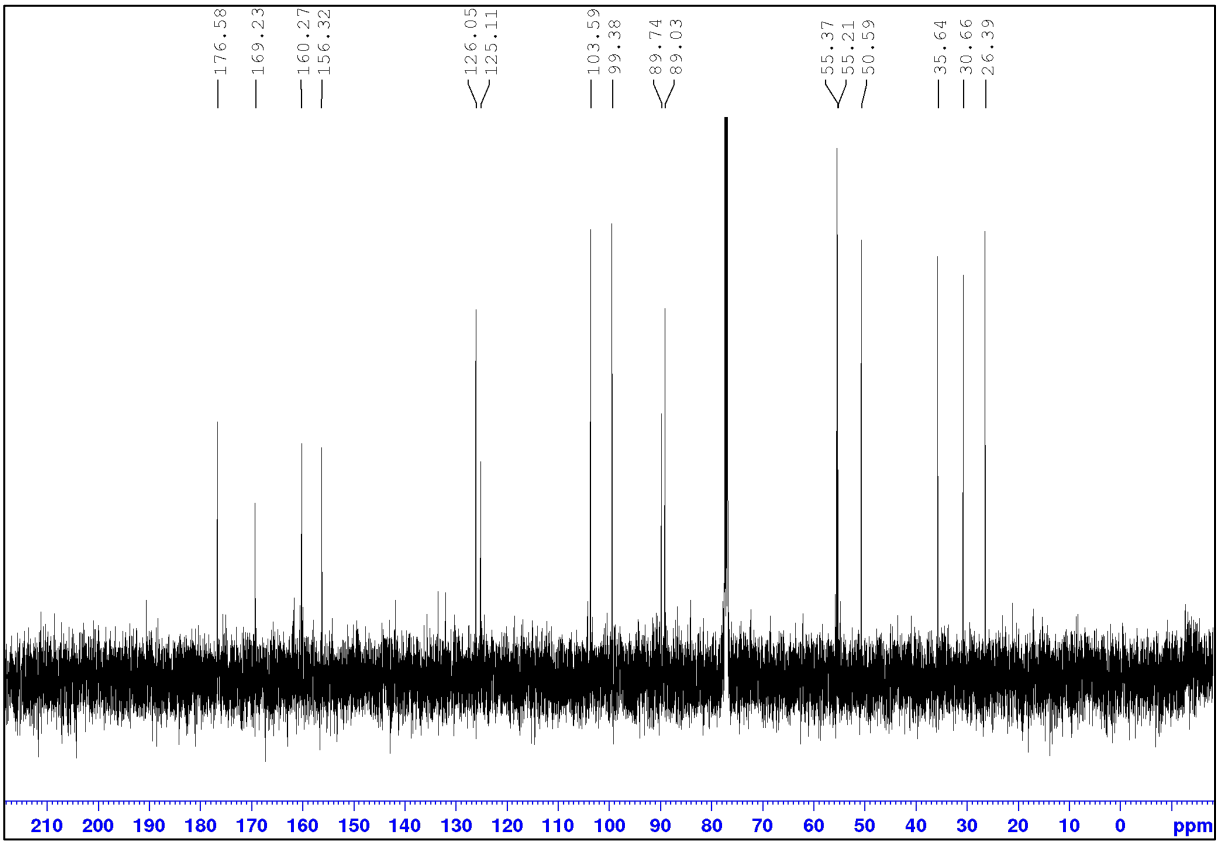
^{13}C NMR (125 MHz, $CDCl_3$) of (*E*)-**2e**



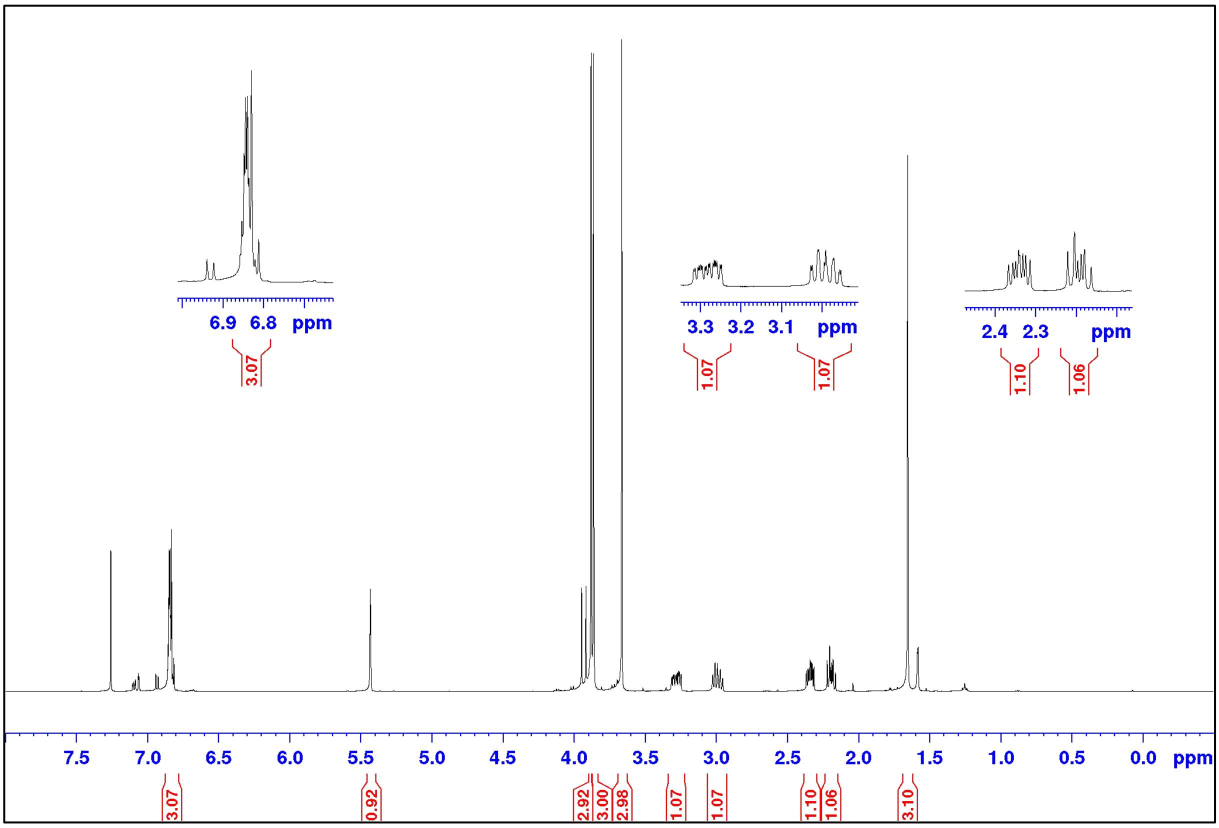
[1]H NMR (500 MHz, $CDCl_3$) of (*E*)-**2f**



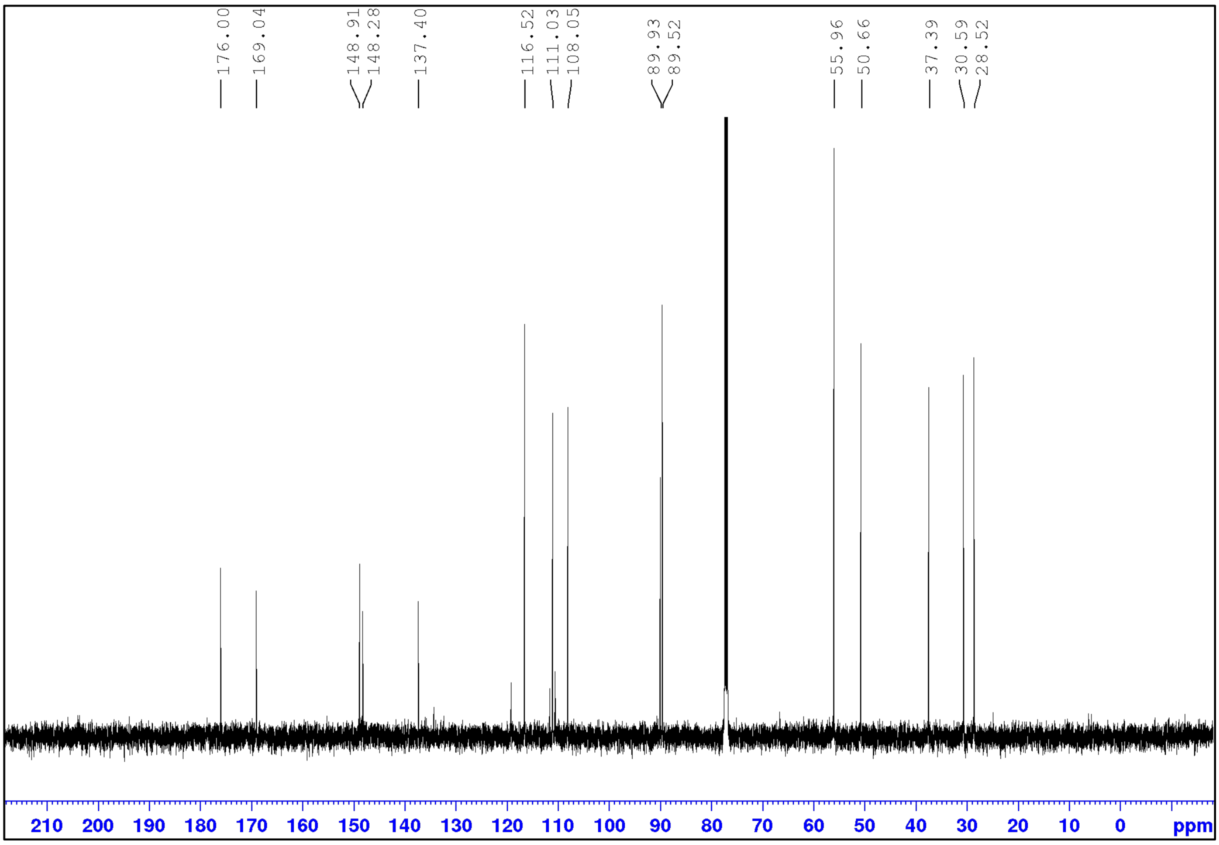
[13]C NMR (125 MHz, $CDCl_3$) of (*E*)-**2f**



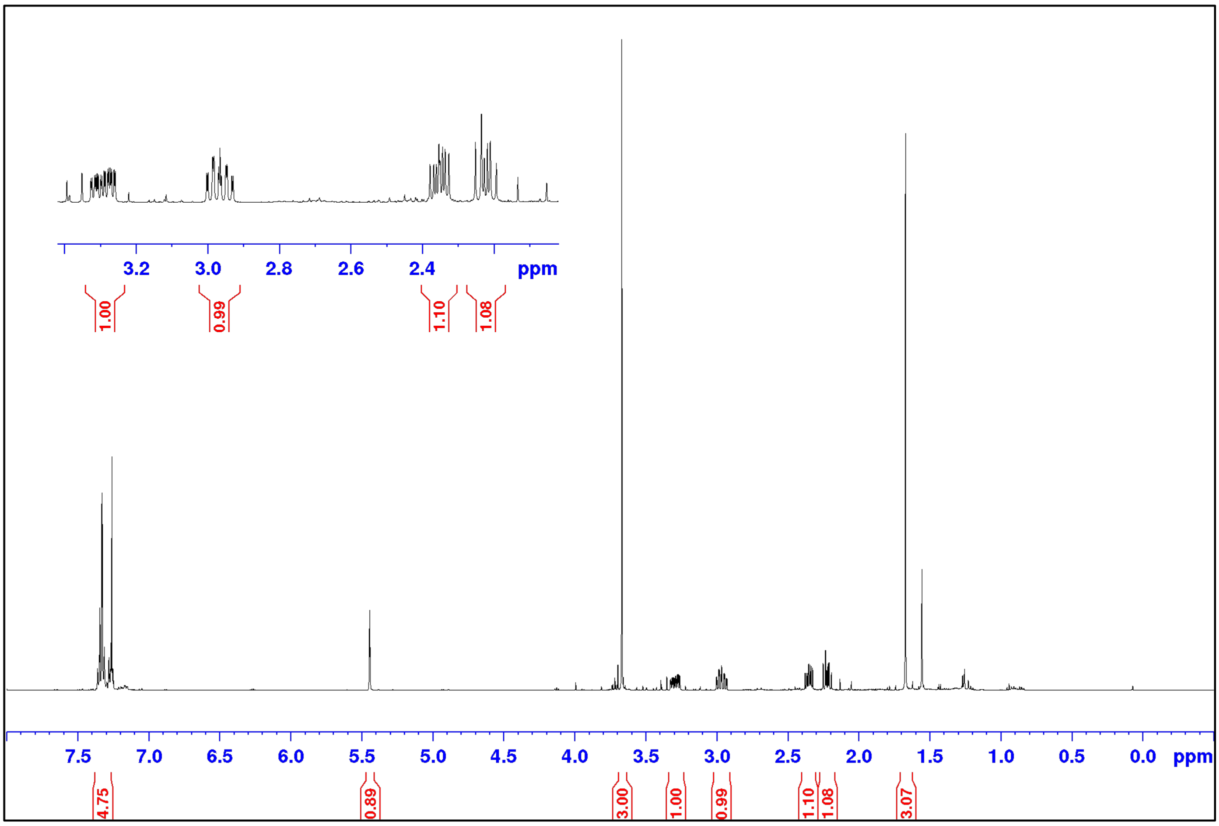
^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-**2g**



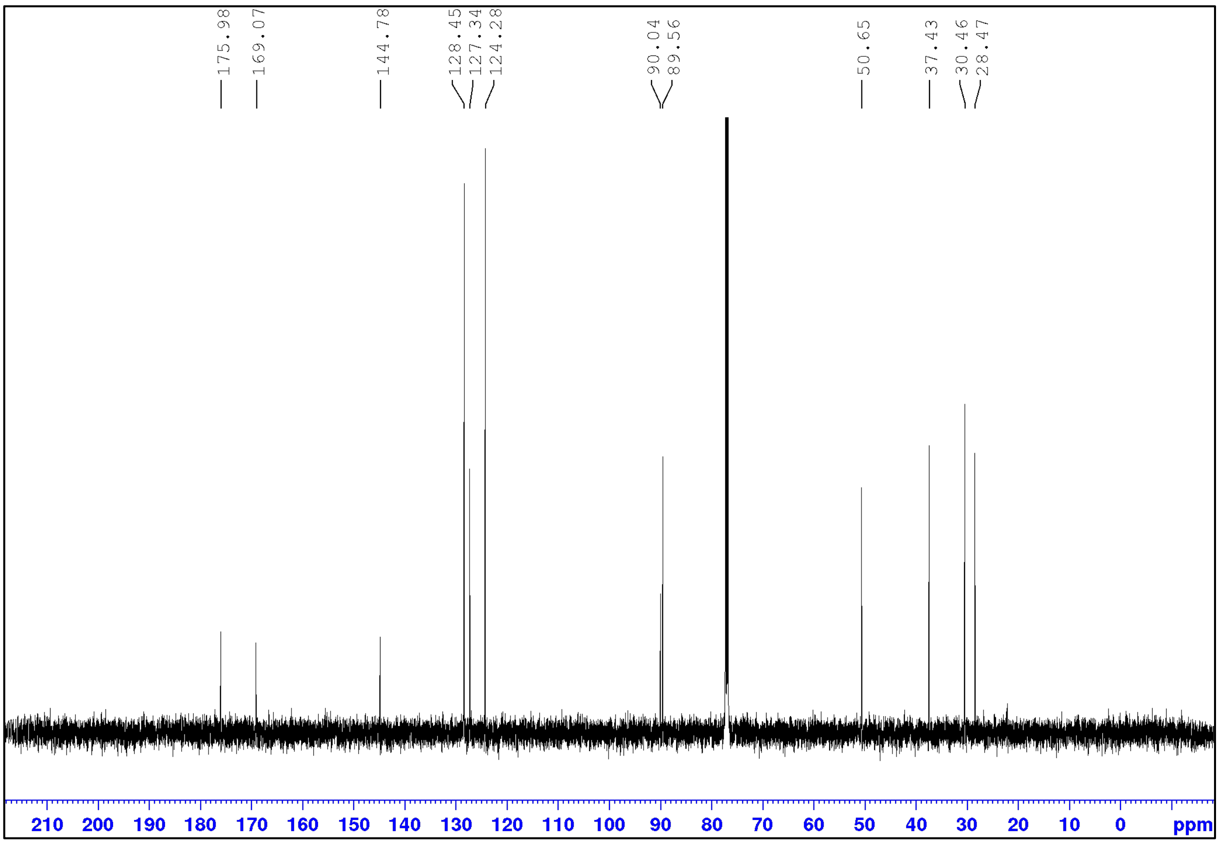
^{13}C NMR (125 MHz, $CDCl_3$) of (*E*)-**2g**



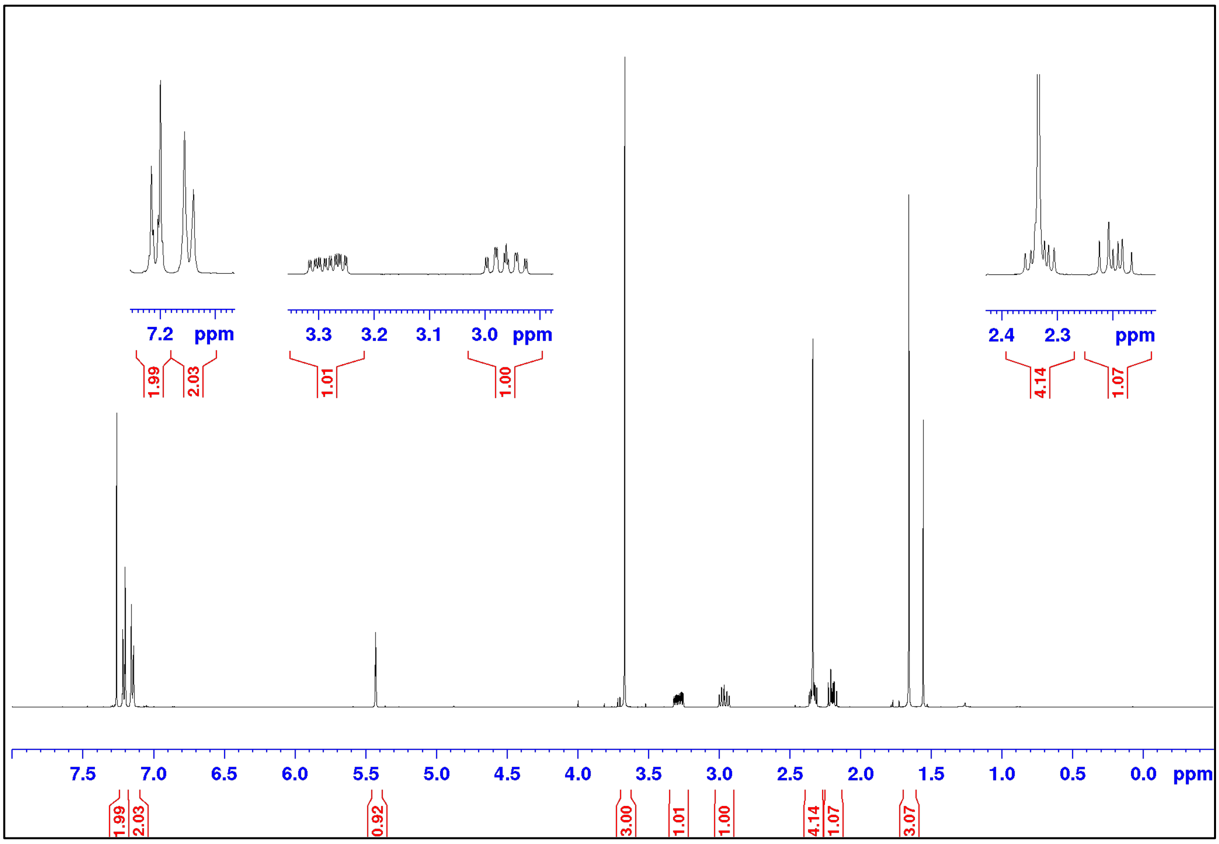
¹H NMR (500 MHz, $CDCl_3$) of (*E*)-**2i**



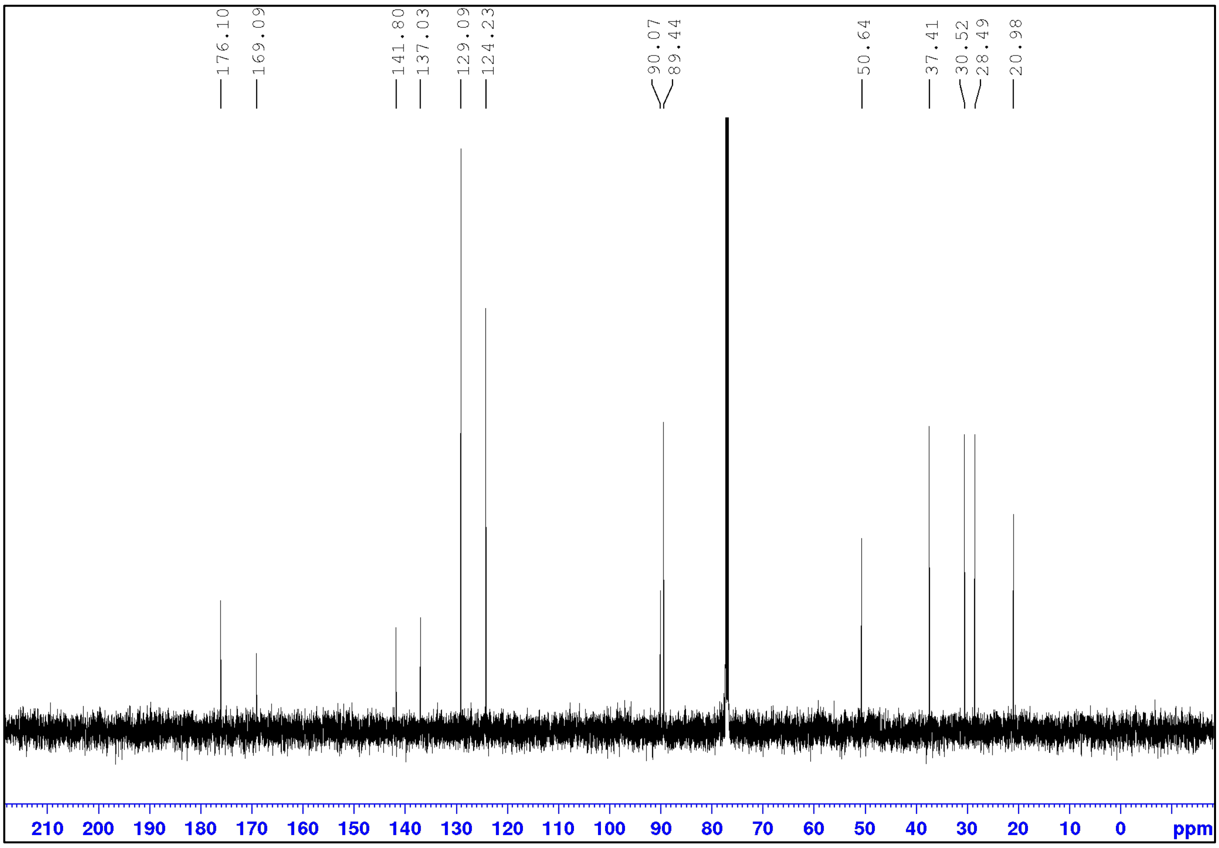
¹³C NMR (125 MHz, $CDCl_3$) of (*E*)-**2i**



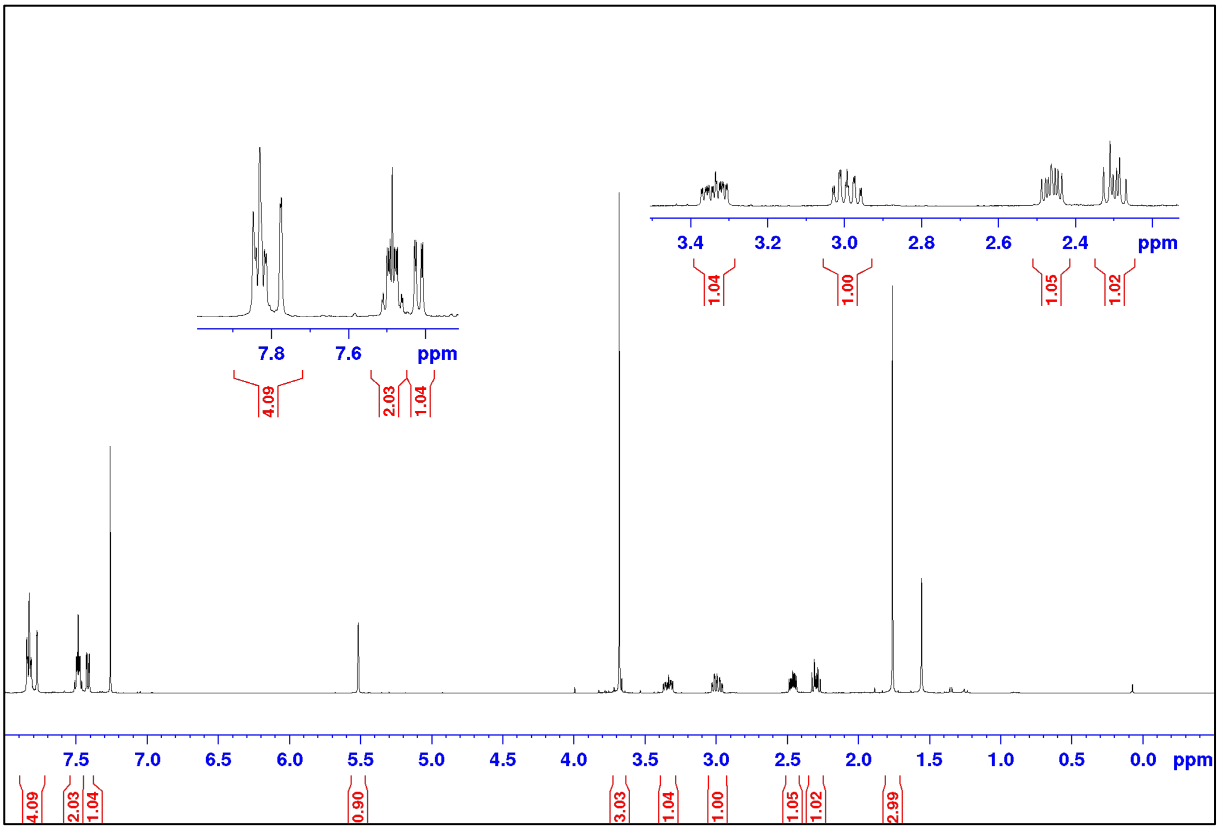
^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-**2j**



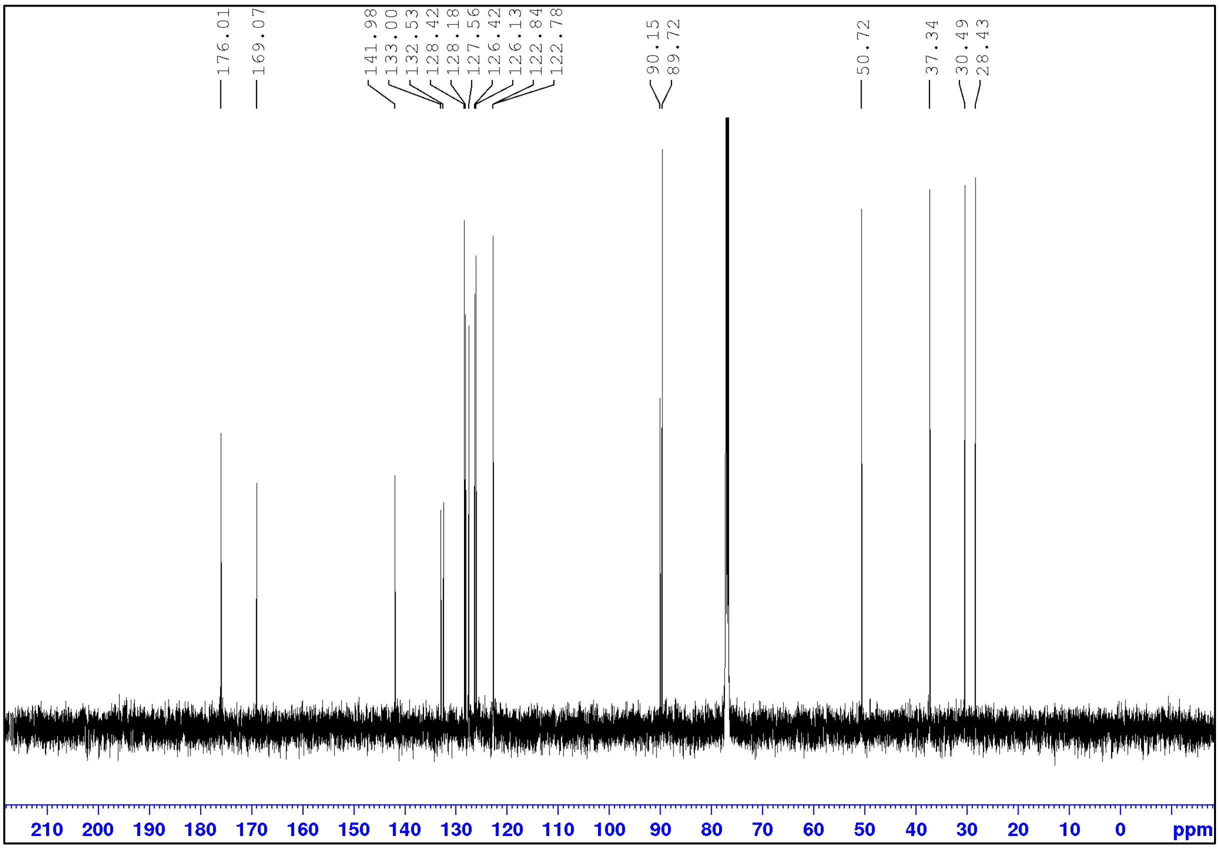
^{13}C NMR (125 MHz, $CDCl_3$) of (*E*)-**2j**



^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-**2k**



^{13}C NMR (125 MHz, $CDCl_3$) of (*E*)-**2k**



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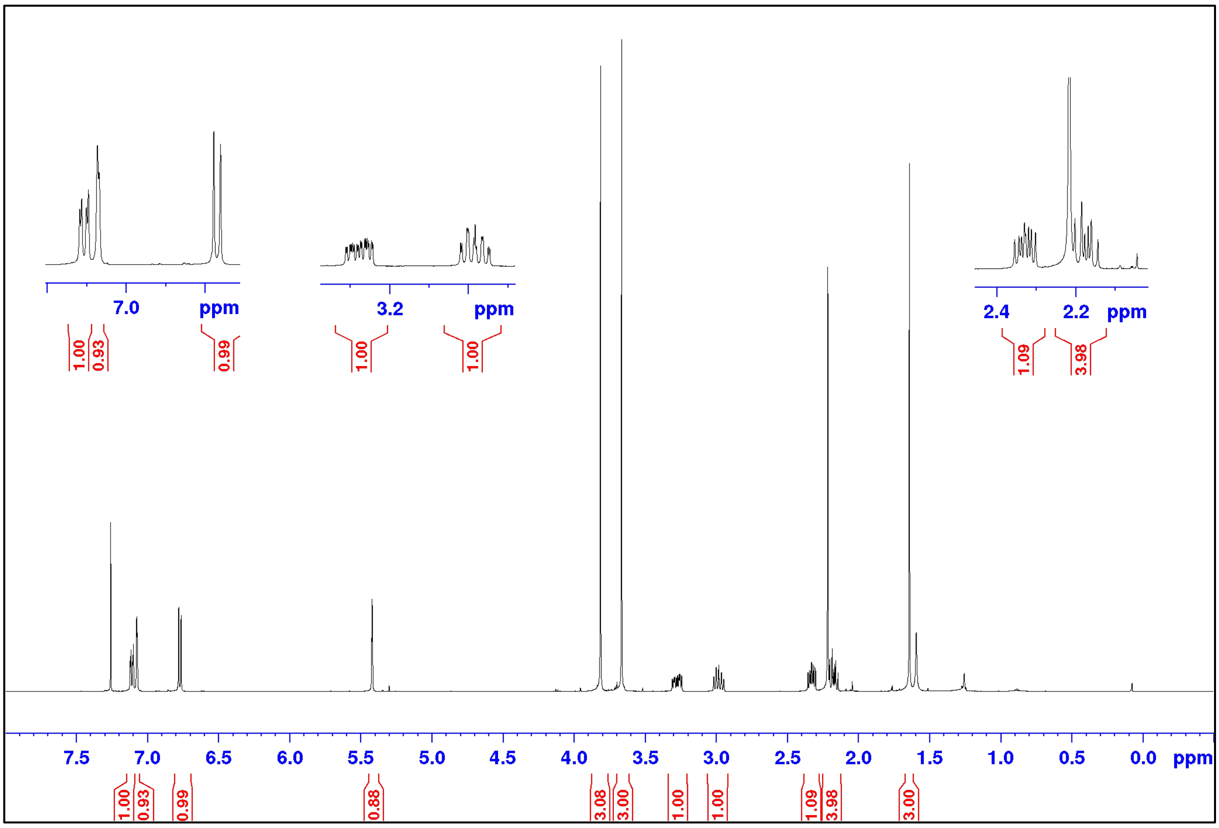
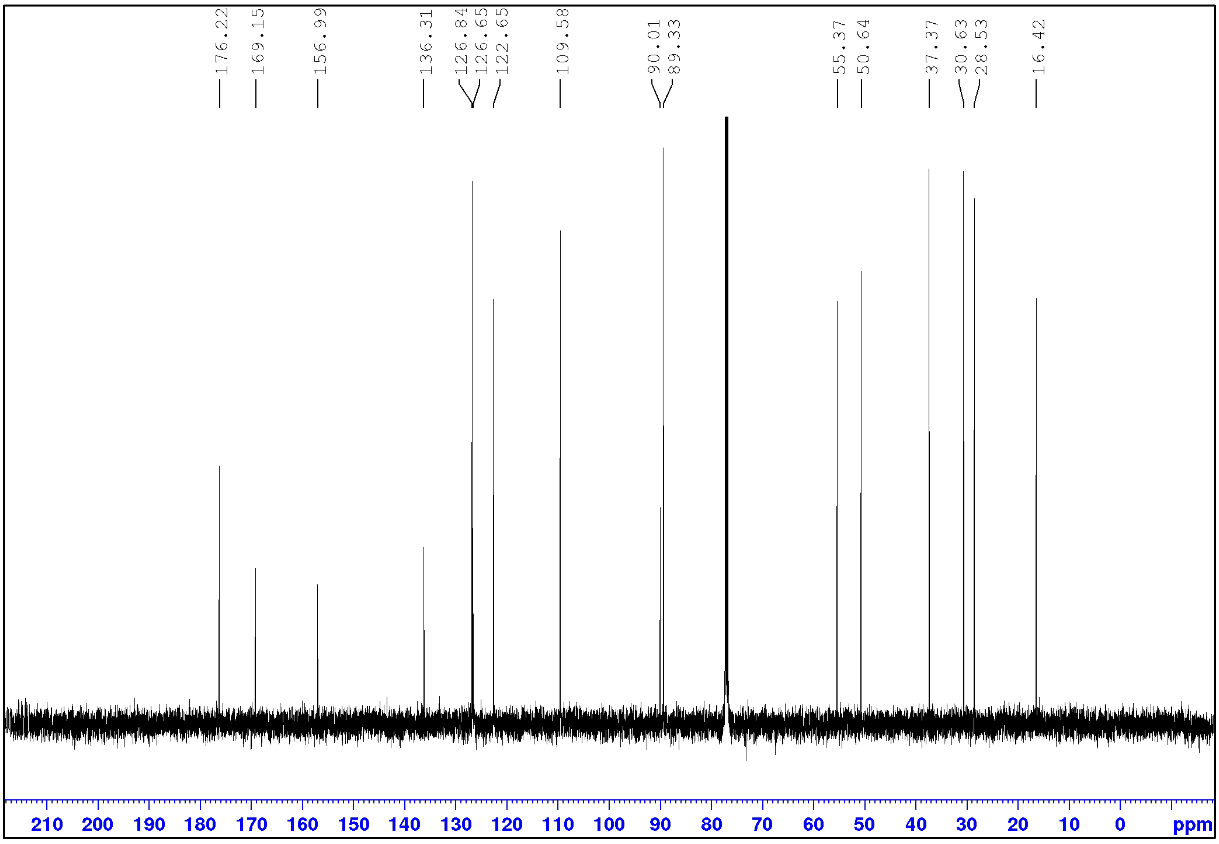


^{13}C NMR (125 MHz, $CDCl_3$) of (*E*)-**2l**



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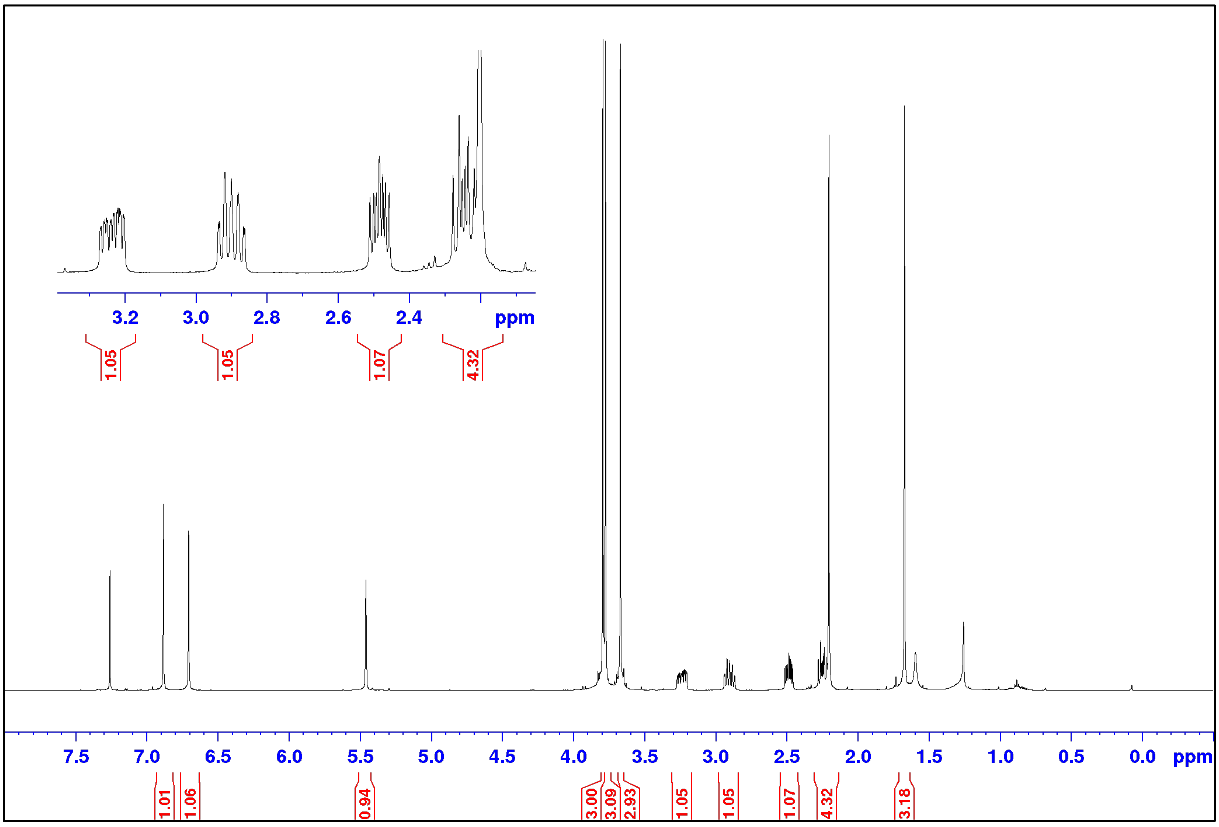

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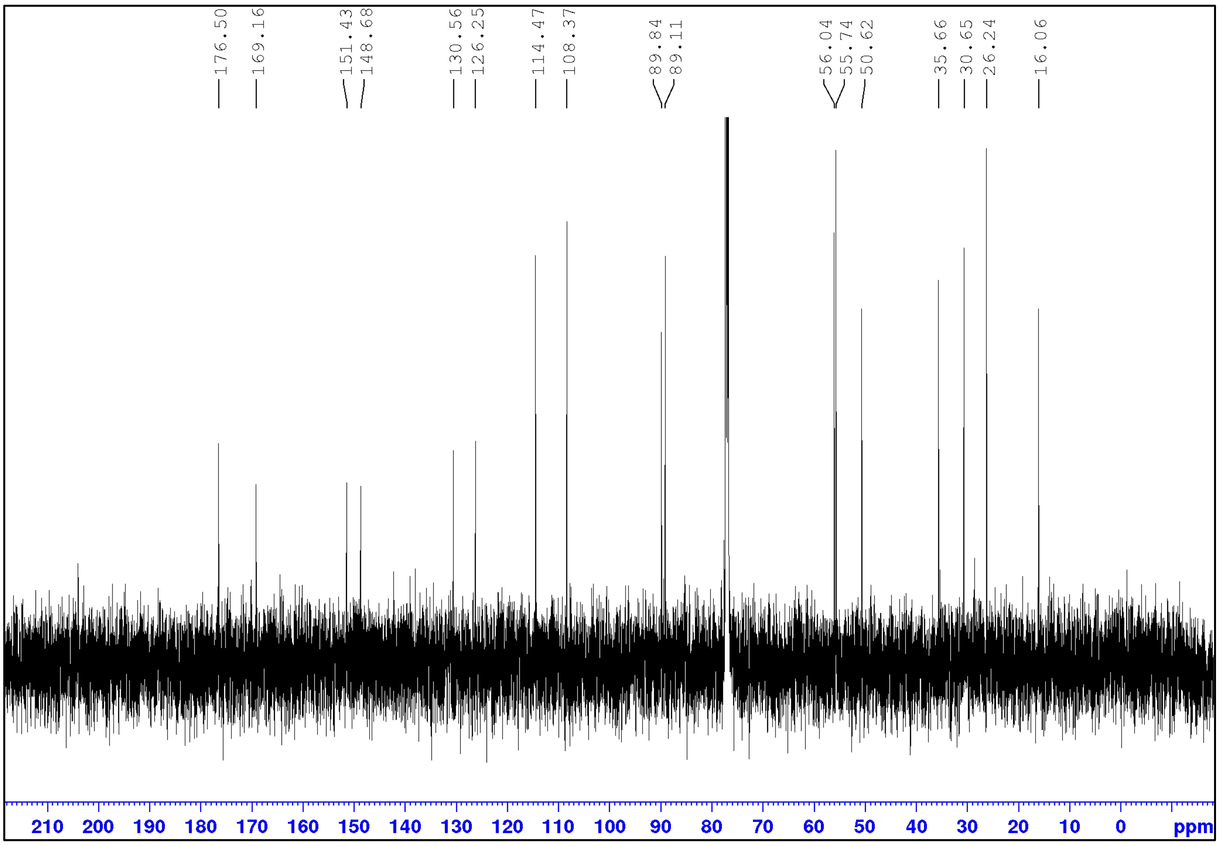
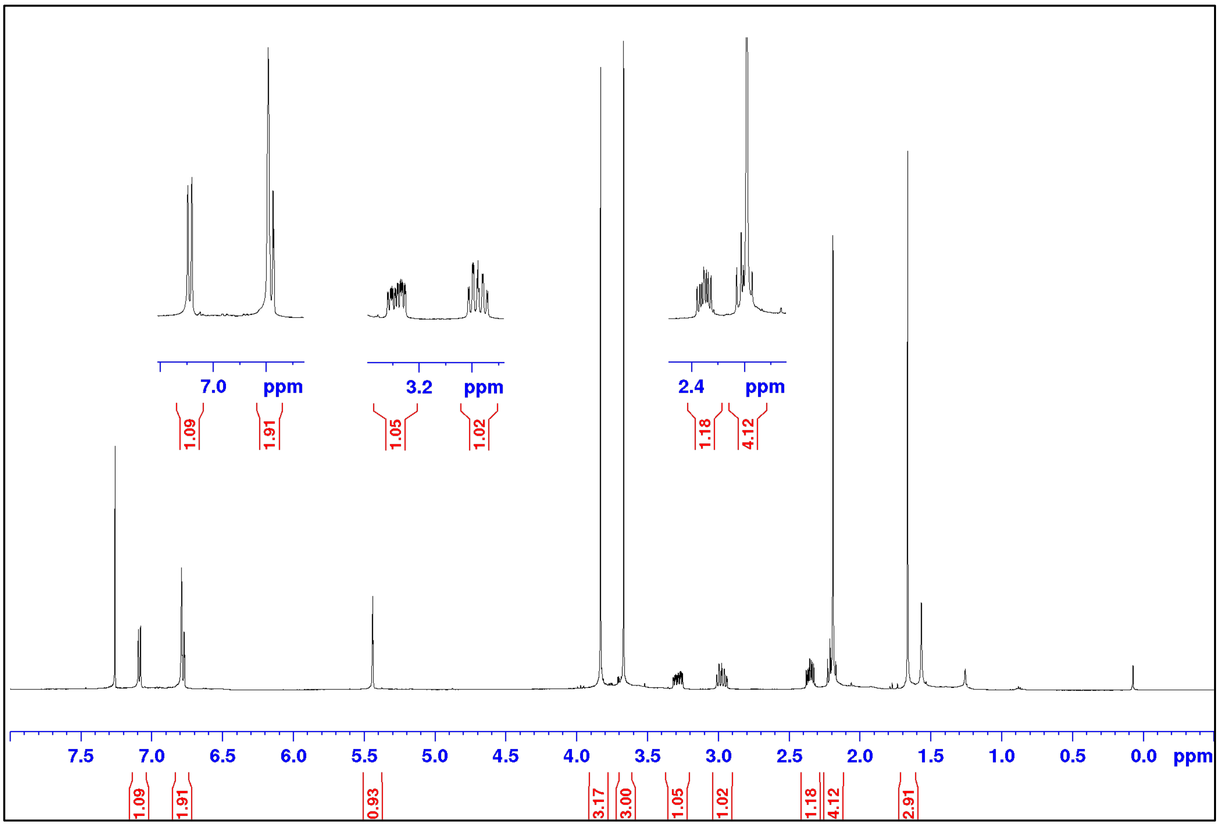
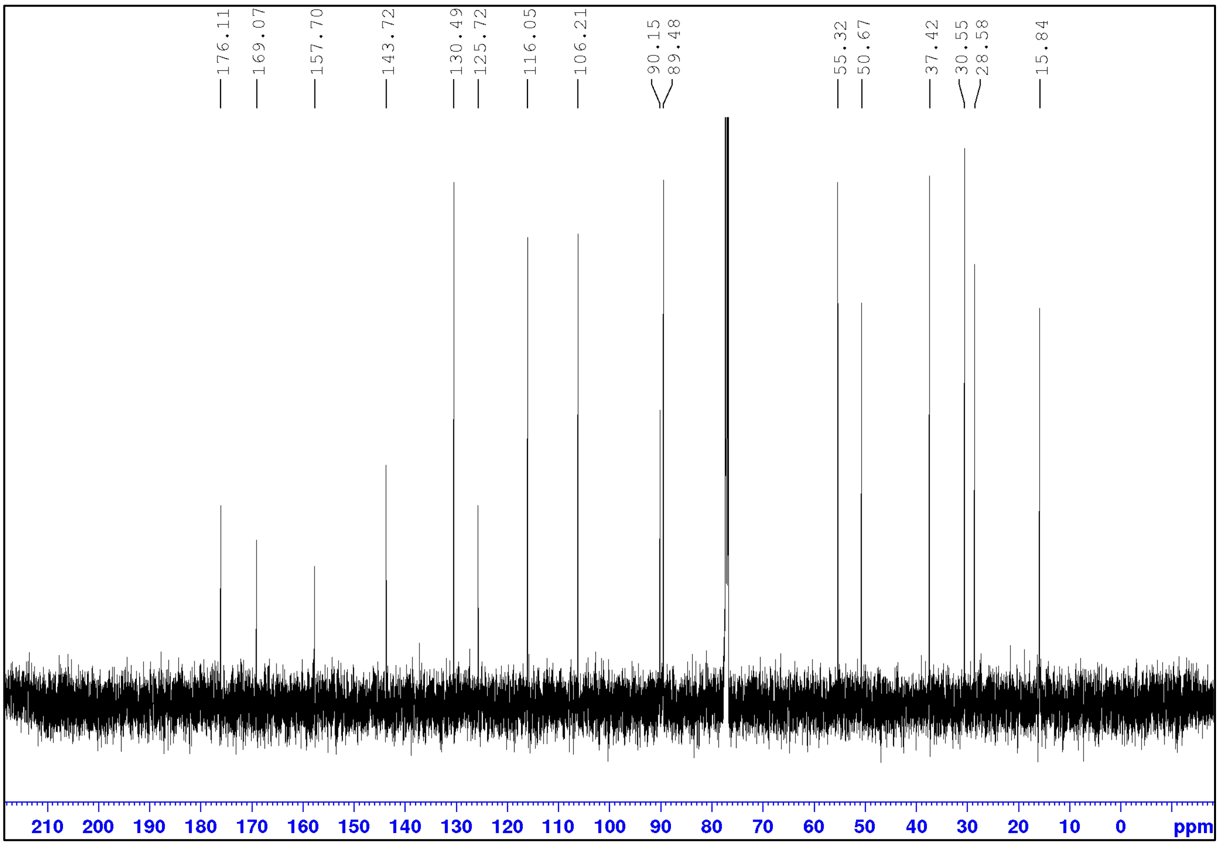


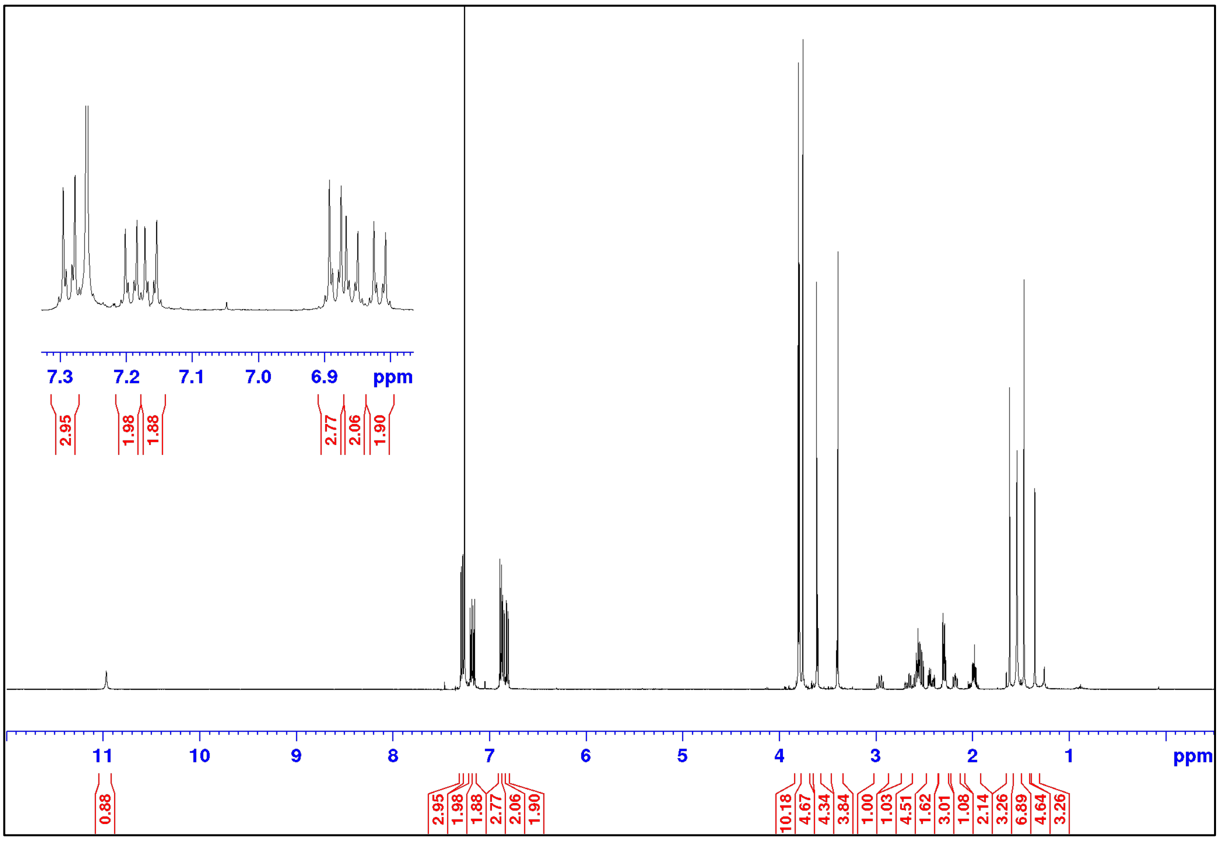
^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-**2n**



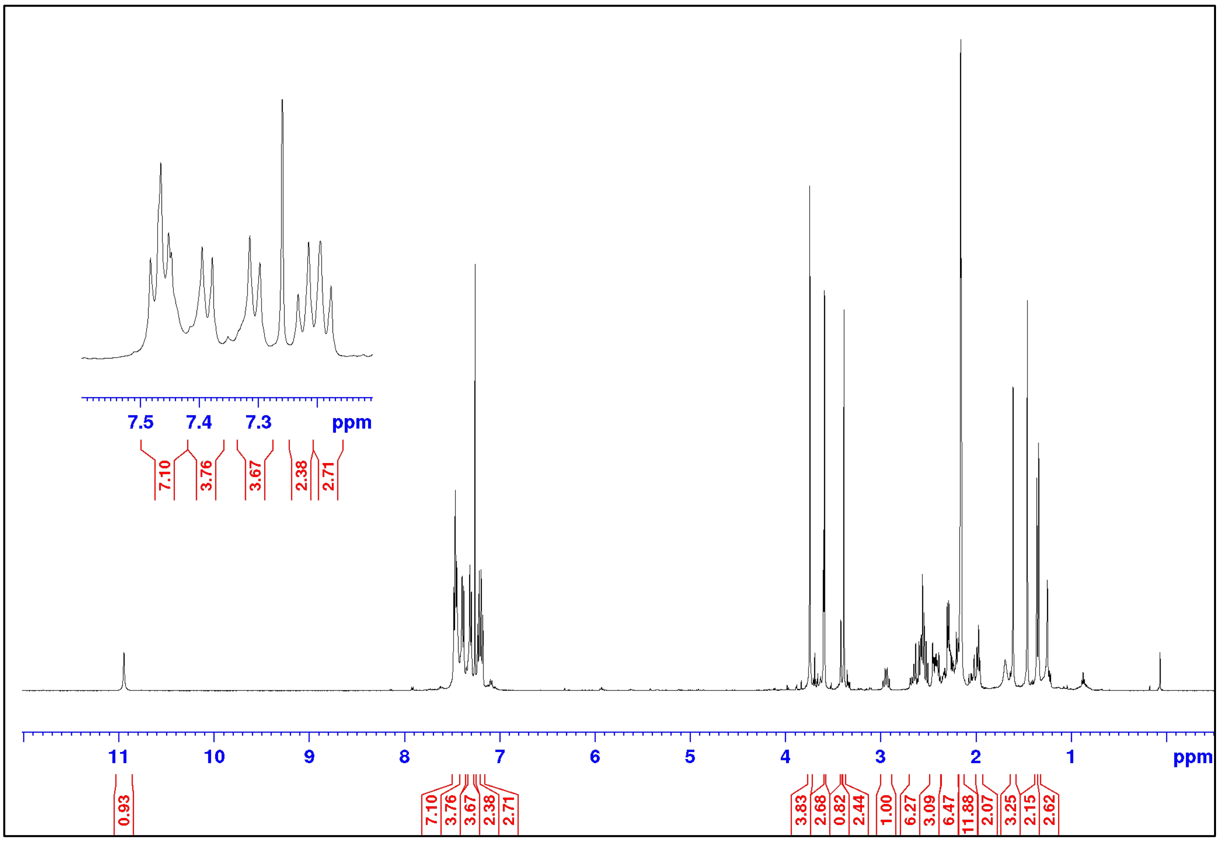
^{13}C NMR (125 MHz, $CDCl_3$) of (*E*)-**2n**



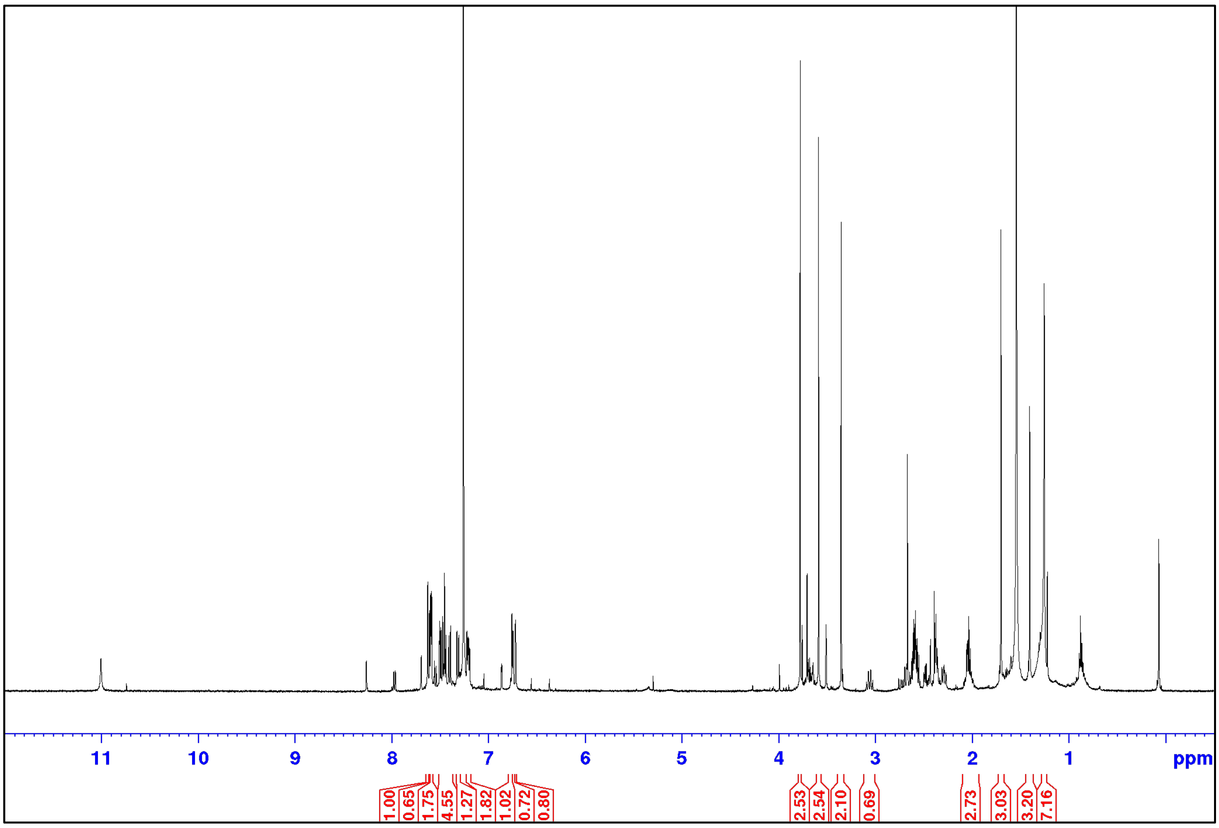
^{1}H NMR (500 MHz, $CDCl_3$) of **3a**



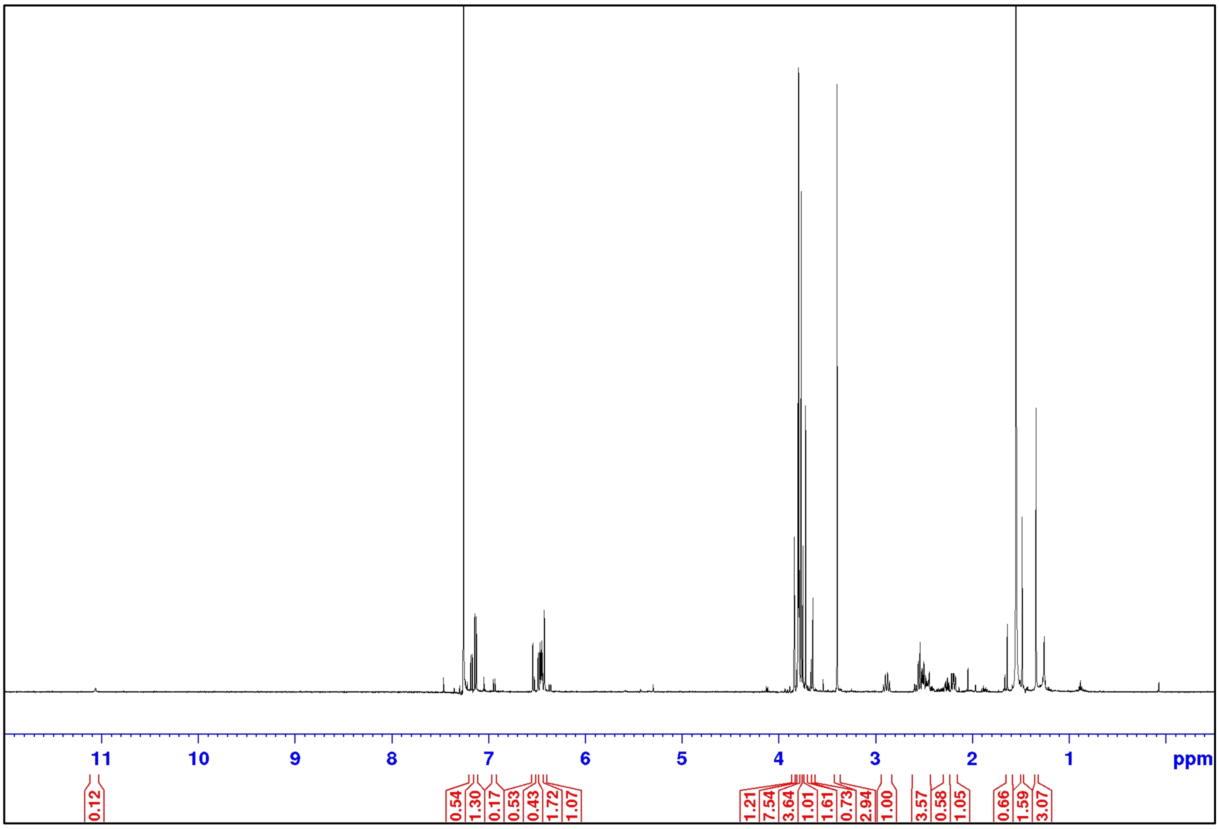
^{1}H NMR (500 MHz, $CDCl_3$) of **3d**



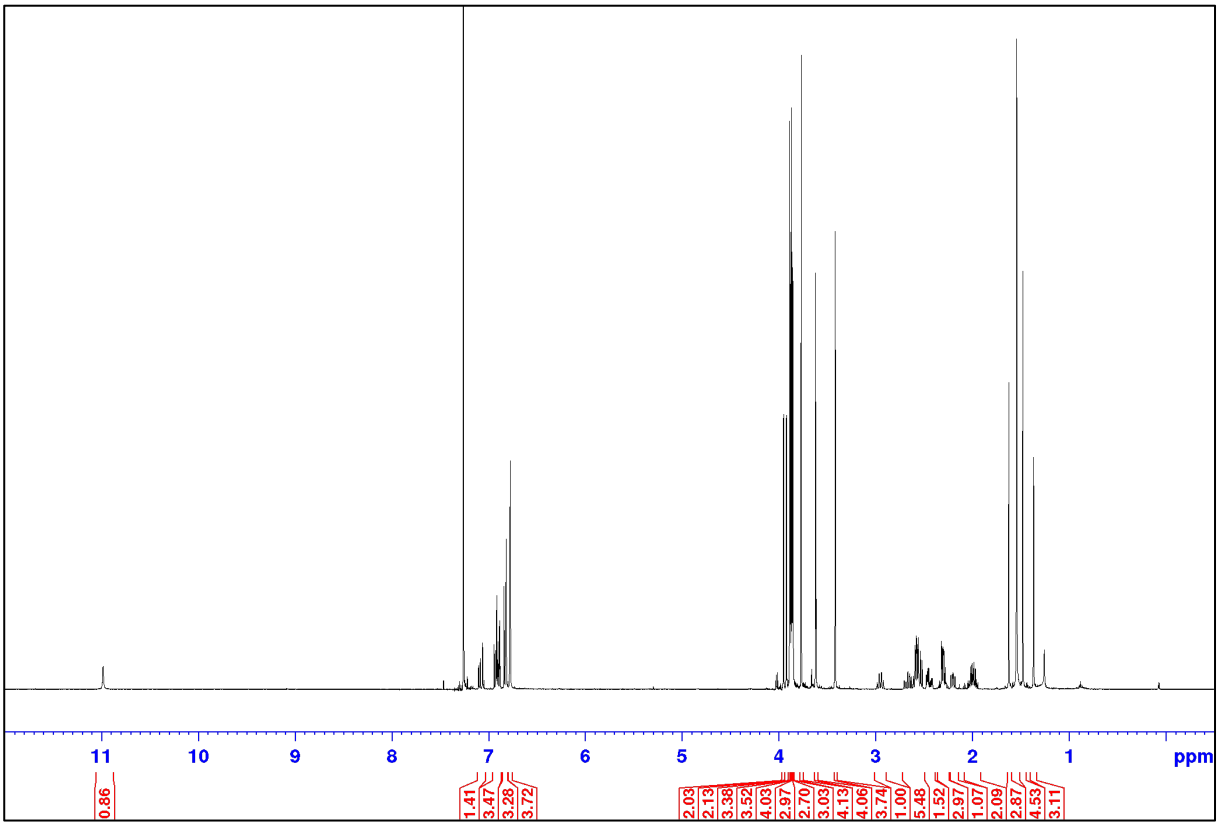
^1H NMR (500 MHz, $CDCl_3$) of **3e**



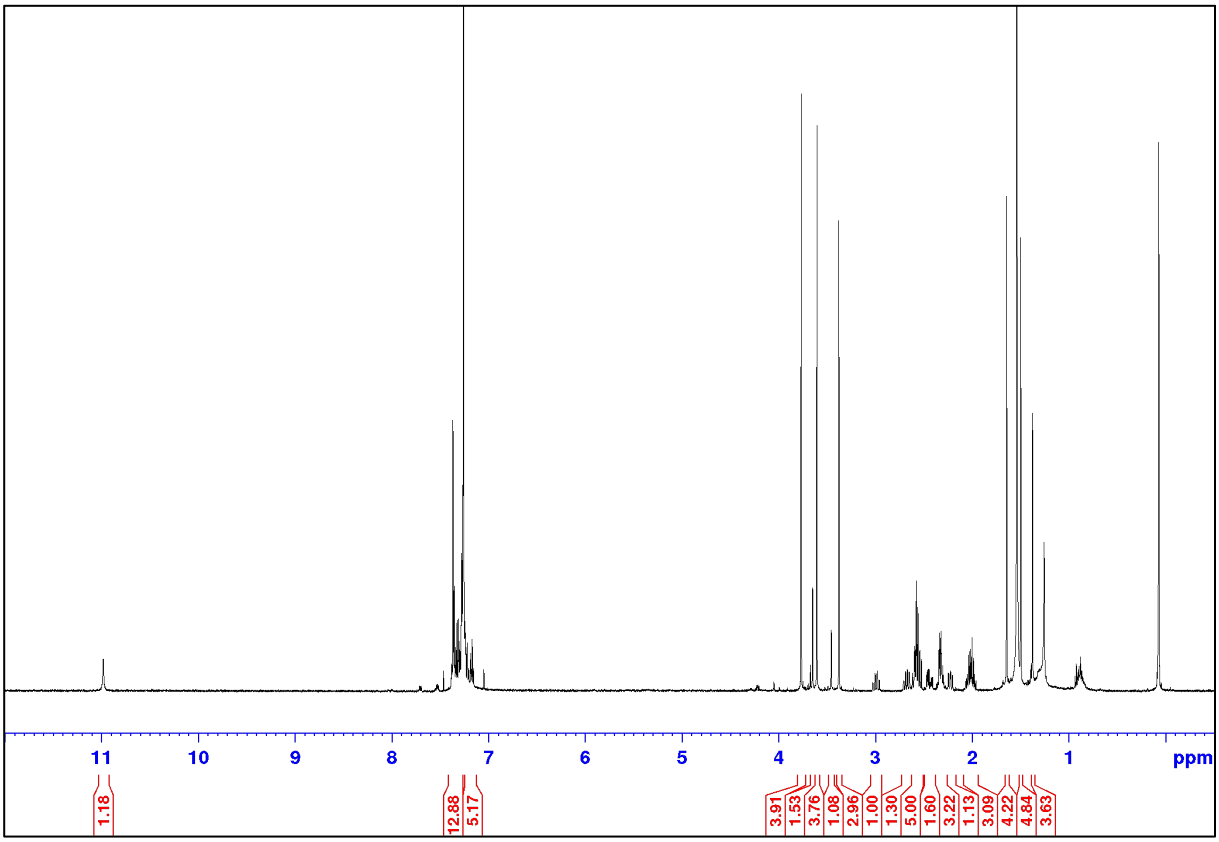
^1H NMR (500 MHz, $CDCl_3$) of **3f**



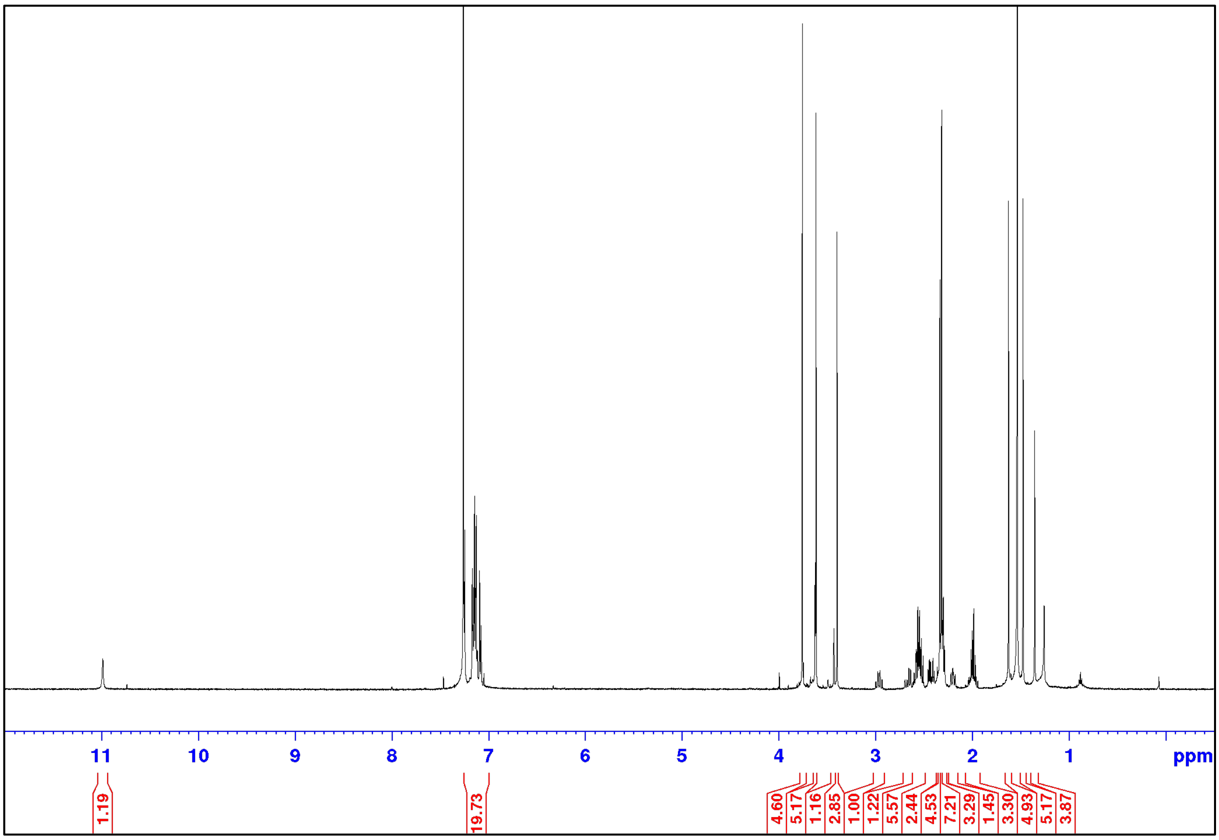
^{1}H NMR (500 MHz, $CDCl_3$) of **3g**



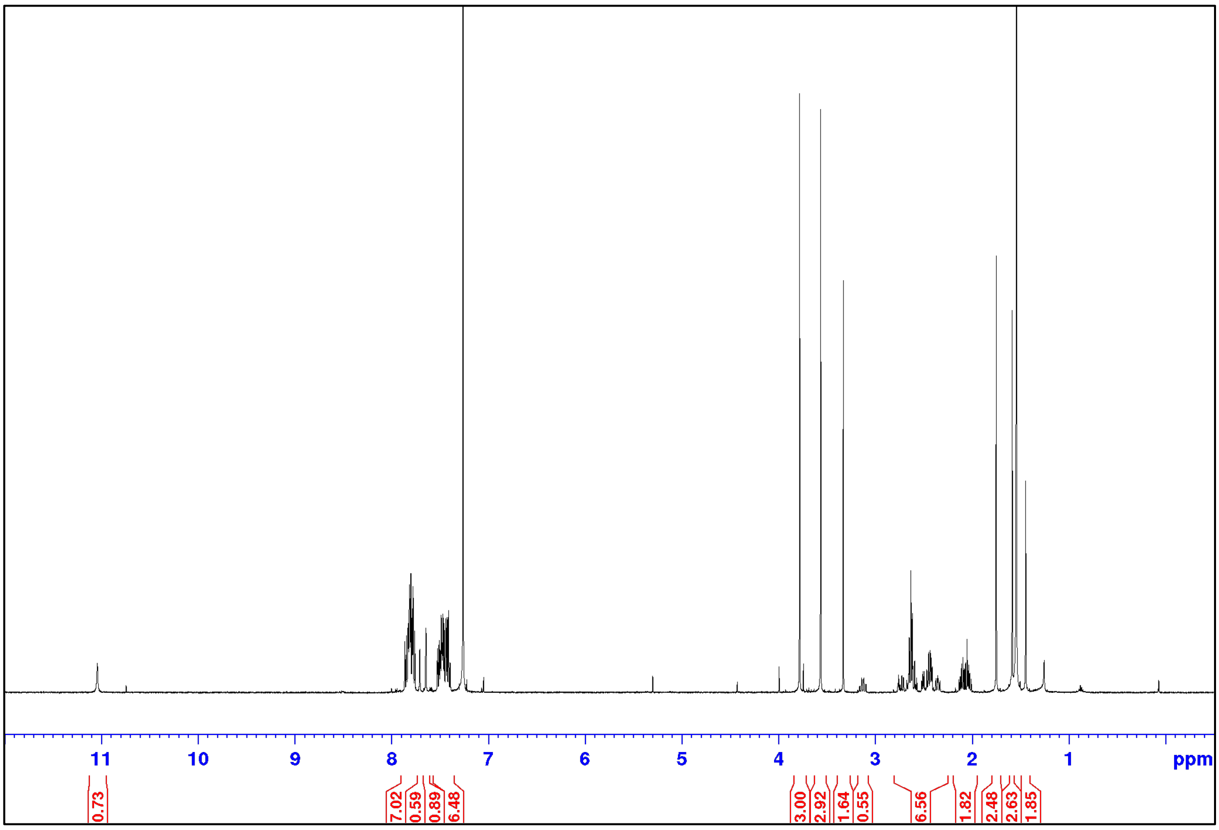
^{1}H NMR (500 MHz, $CDCl_3$) of **3i**



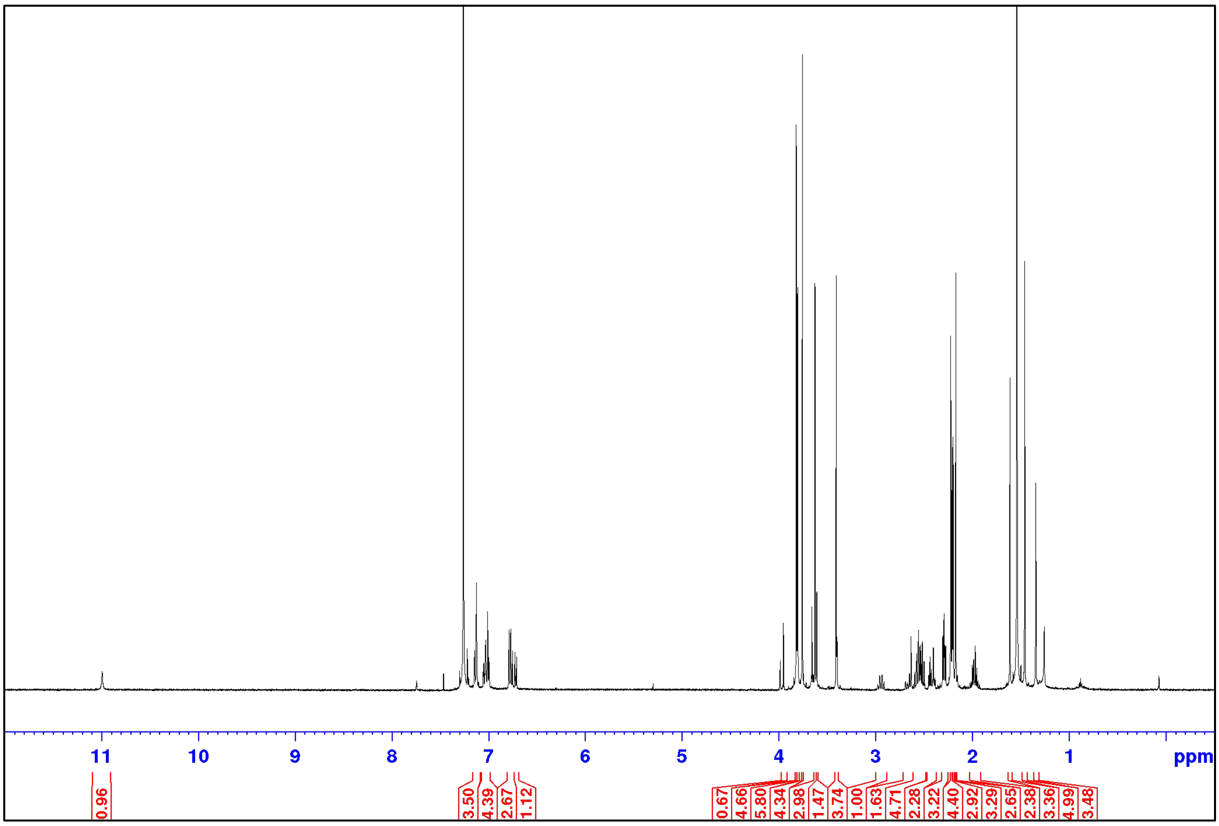
^{1}H NMR (500 MHz, $CDCl_3$) of **3j**



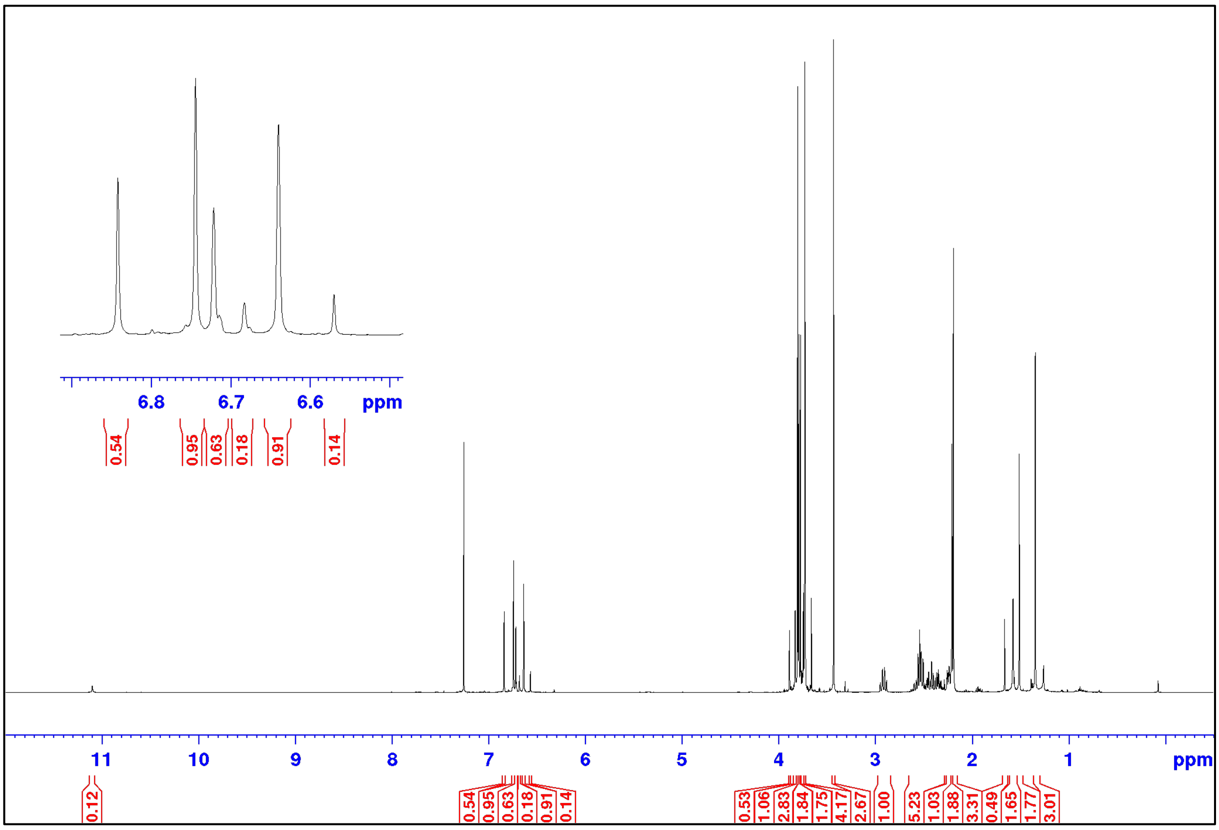
^{1}H NMR (500 MHz, $CDCl_3$) of **3k**



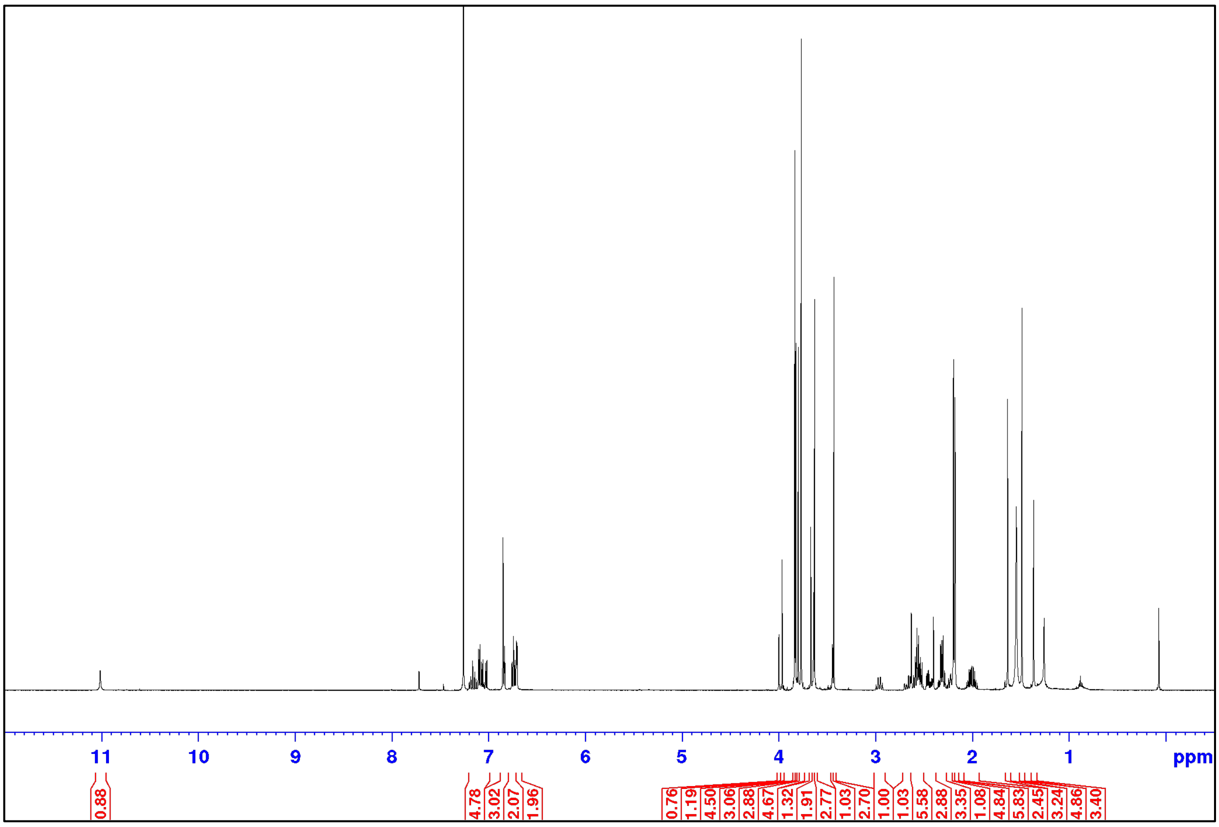
[1]H NMR (500 MHz, $CDCl_3$) of **3l**



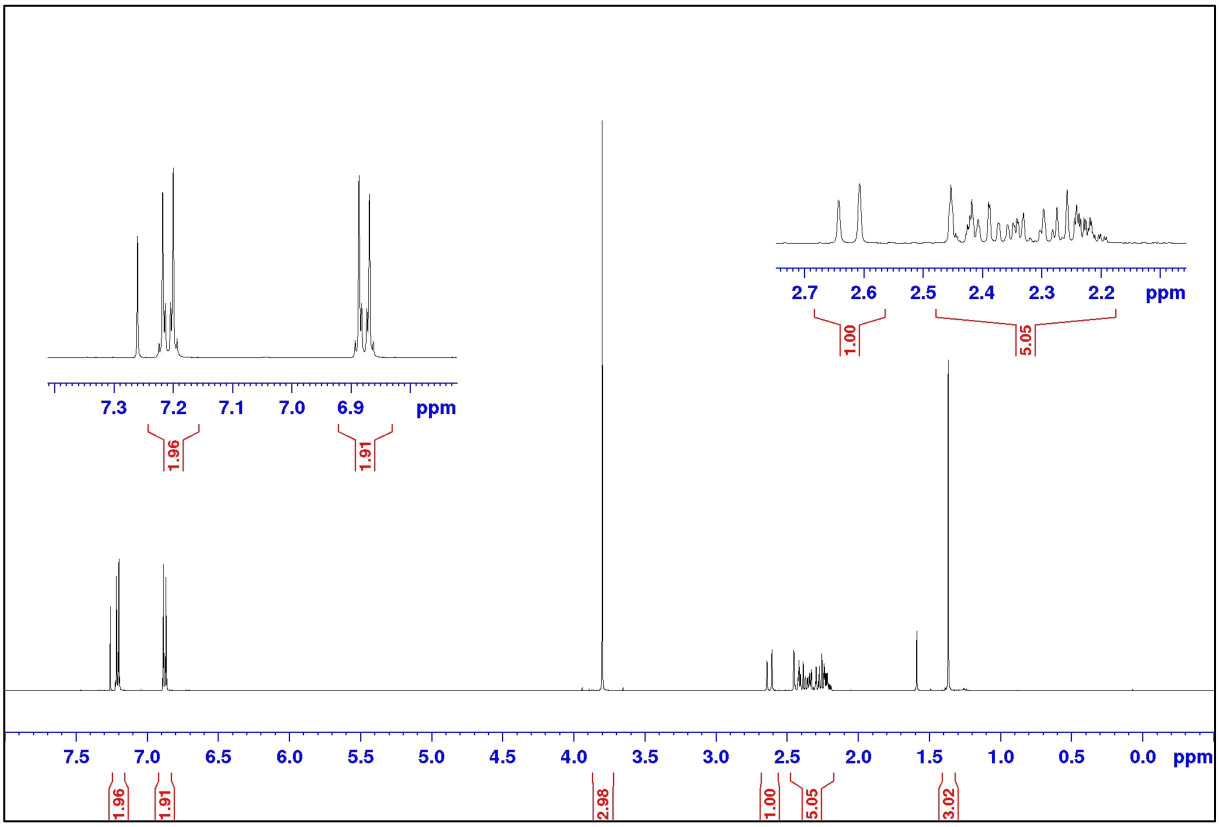
[1]H NMR (500 MHz, $CDCl_3$) of **3m**



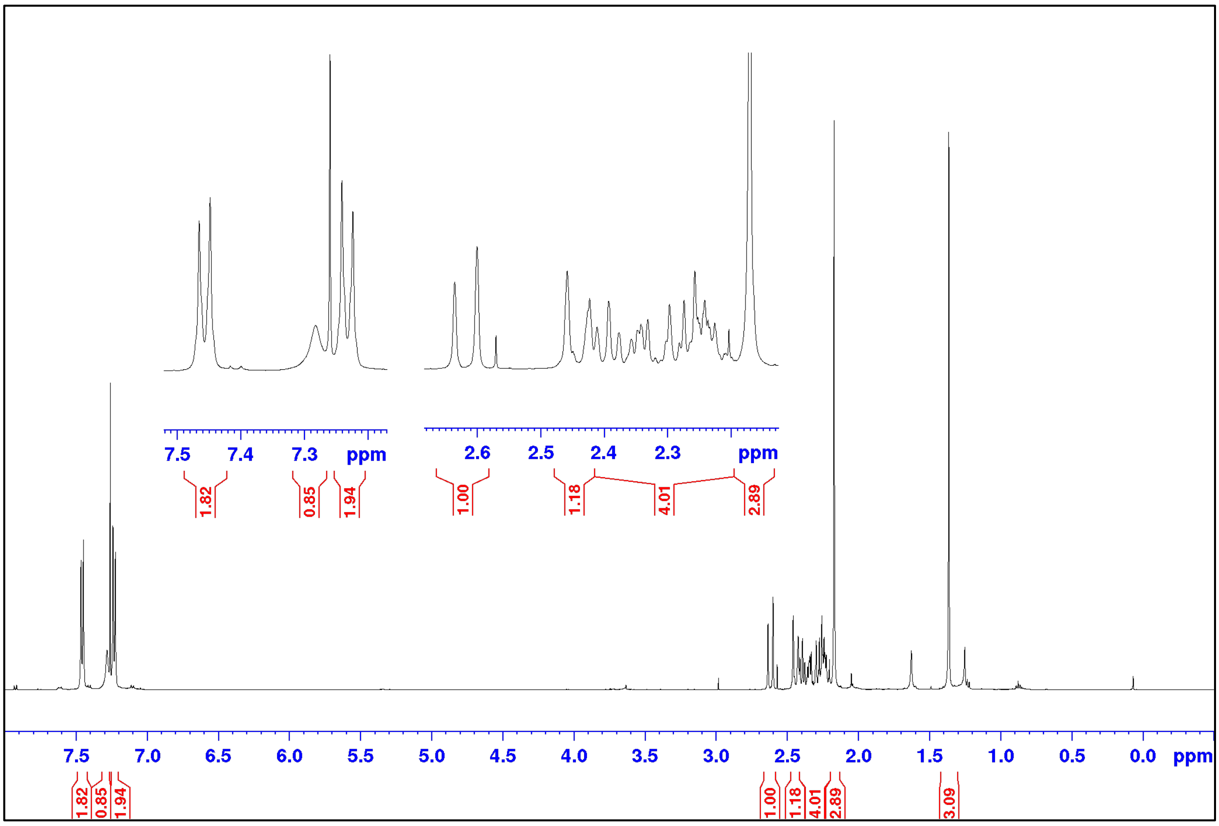
[1]H NMR (500 MHz, $CDCl_3$) of **3n**



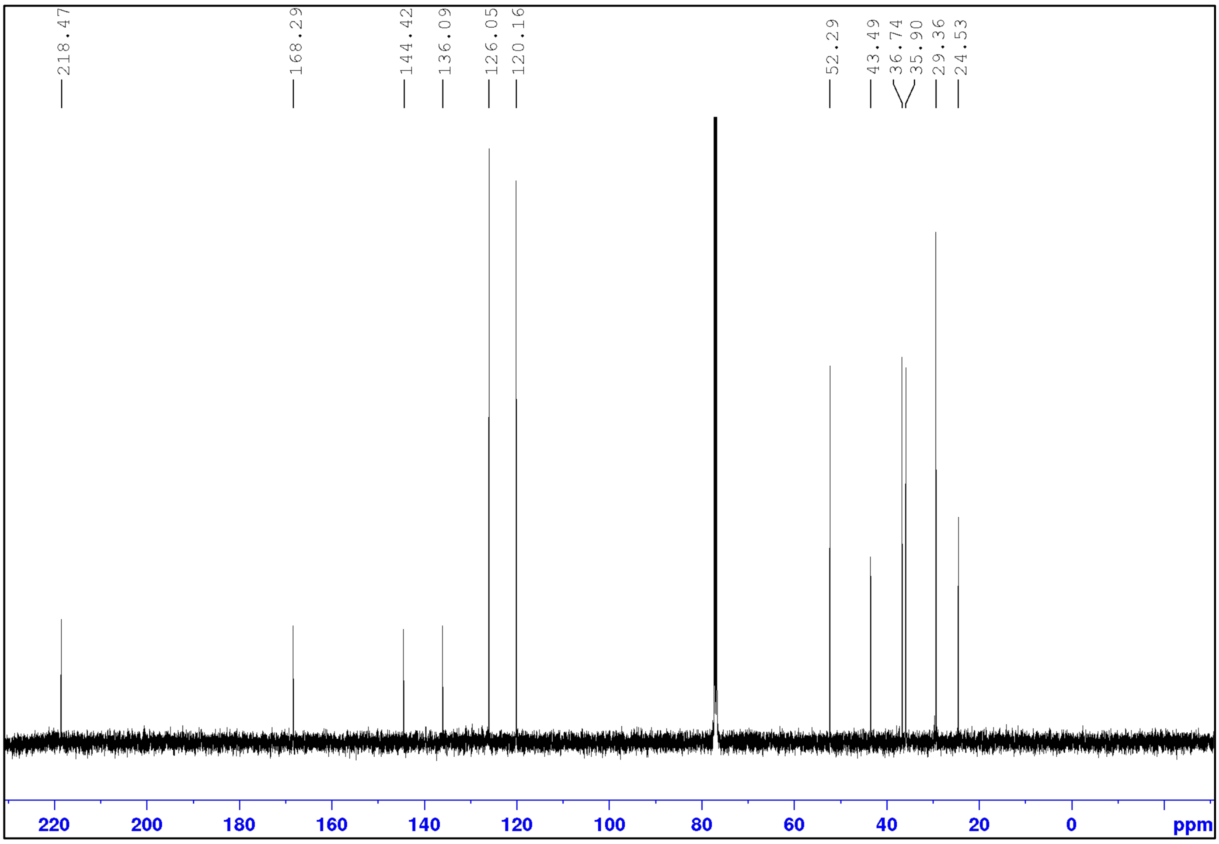
[1]H NMR (500 MHz, $CDCl_3$) of **10a**



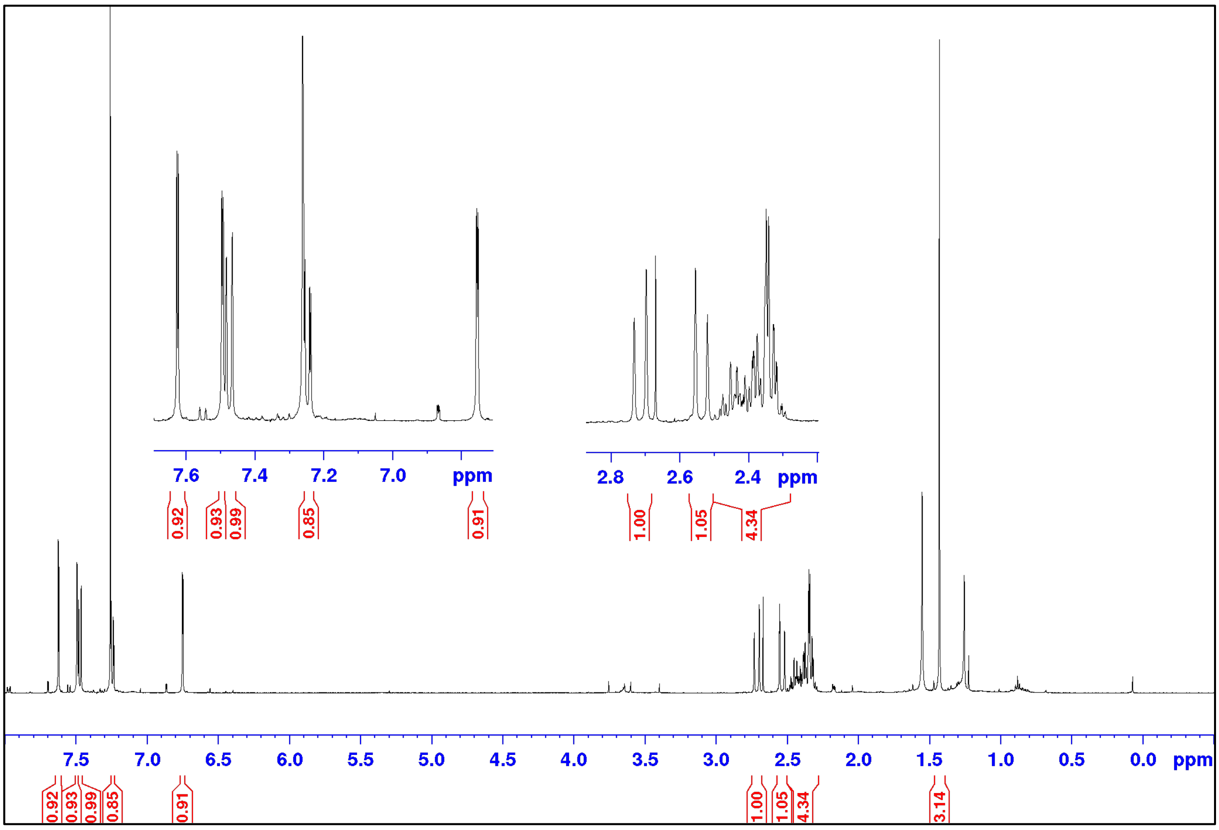
[1]H NMR (500 MHz, $CDCl_3$) of **10d**



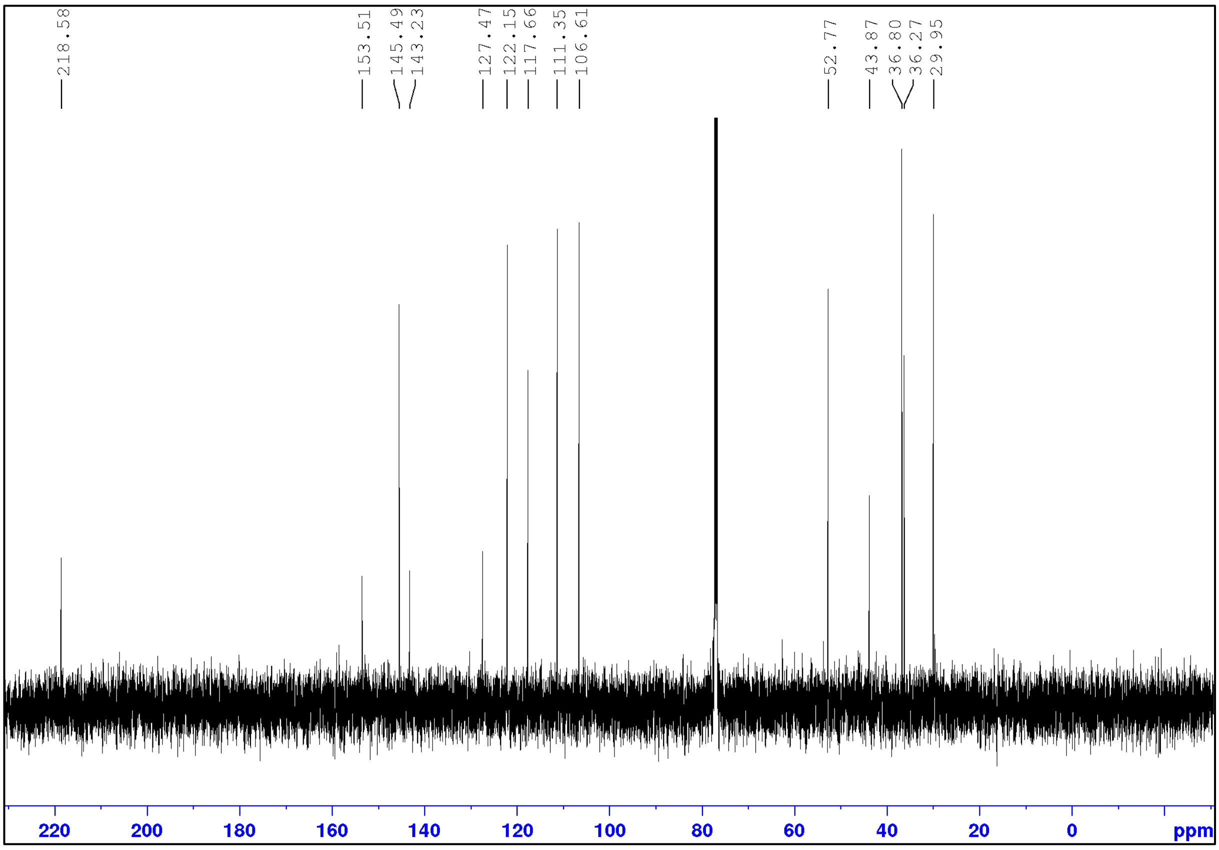
[13]C NMR (125 MHz, $CDCl_3$) of **10d**



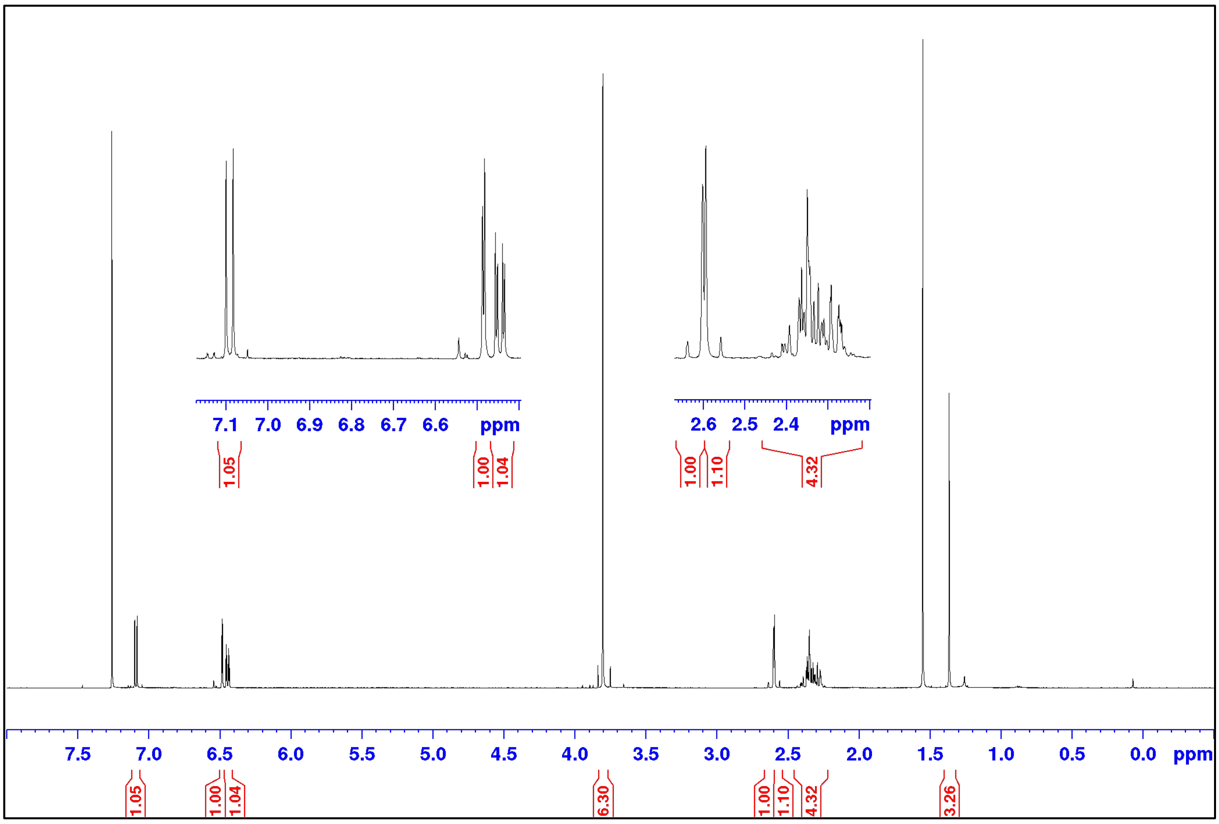
^{1}H NMR (500 MHz, CDCl$_3$) of **10e**



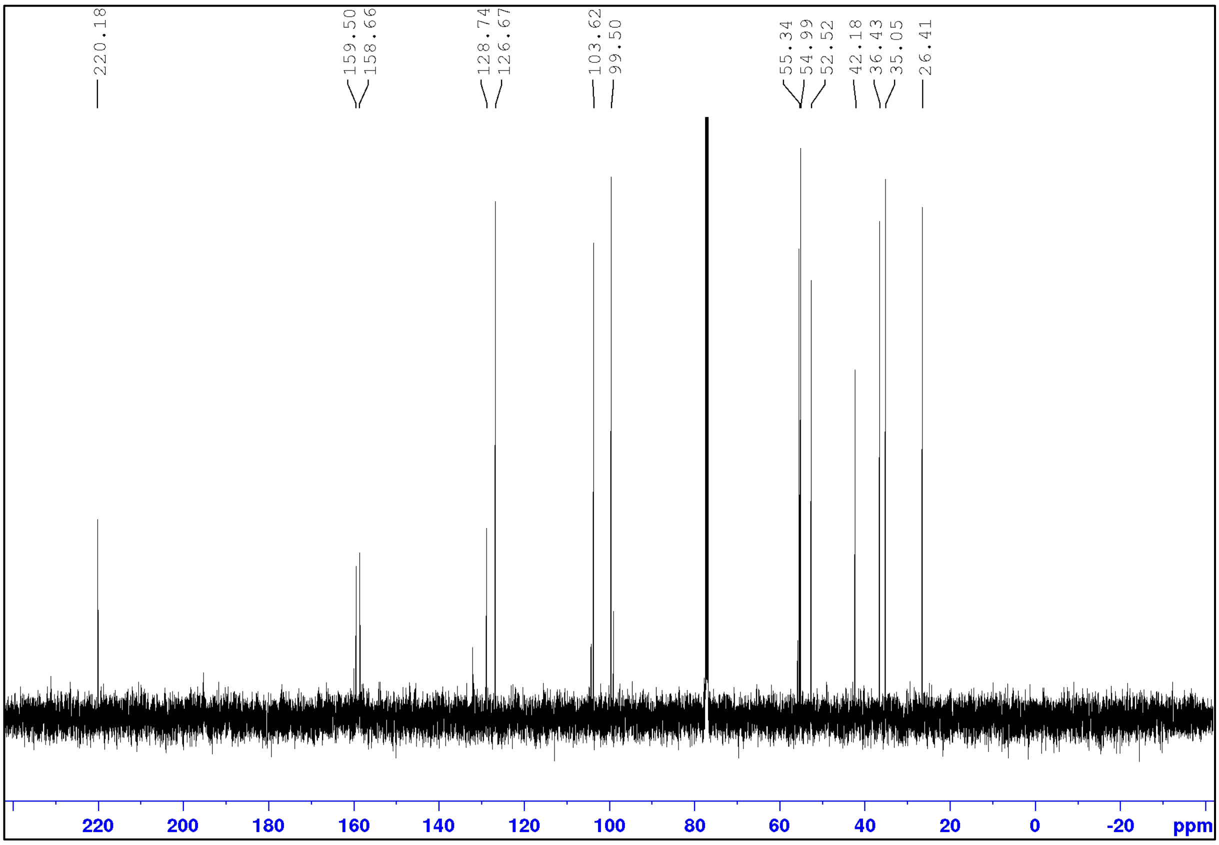
^{13}C NMR (125 MHz, CDCl$_3$) of **10e**



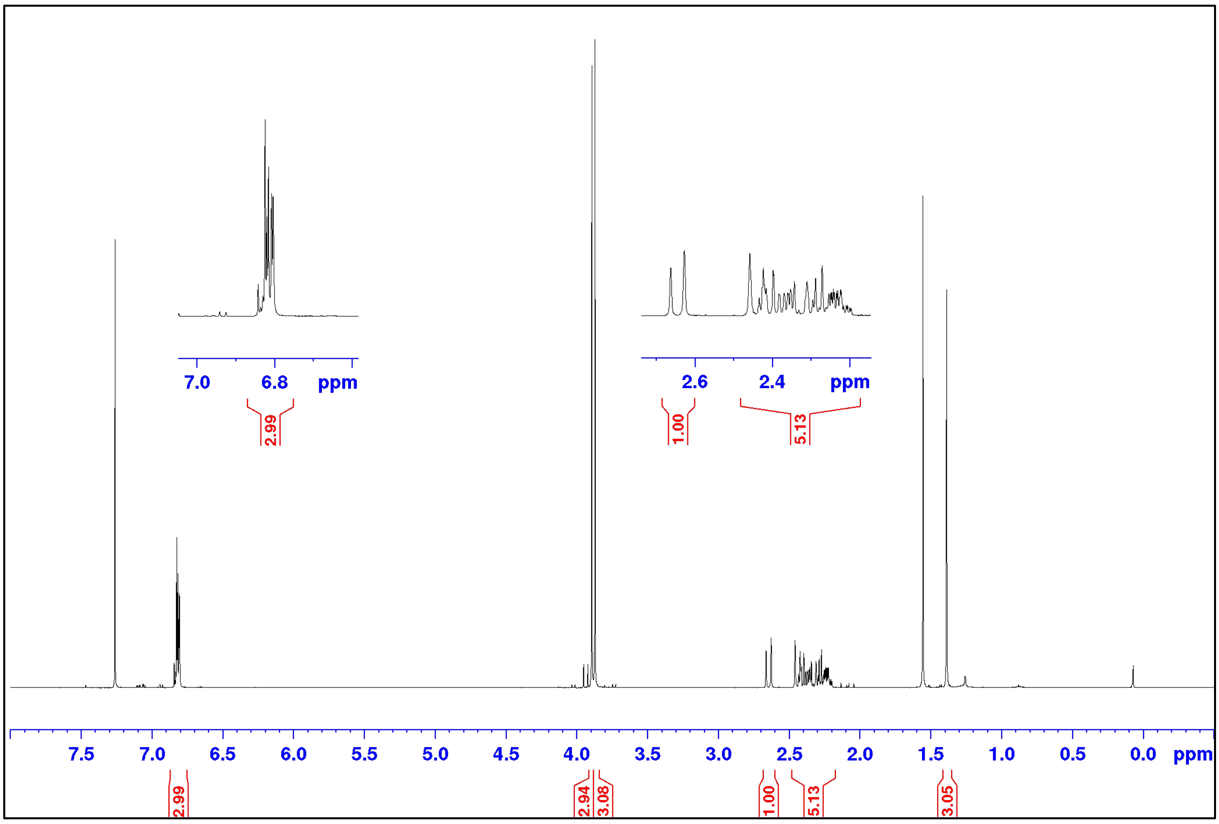
^{1}H NMR (500 MHz, $CDCl_3$) of **10f**



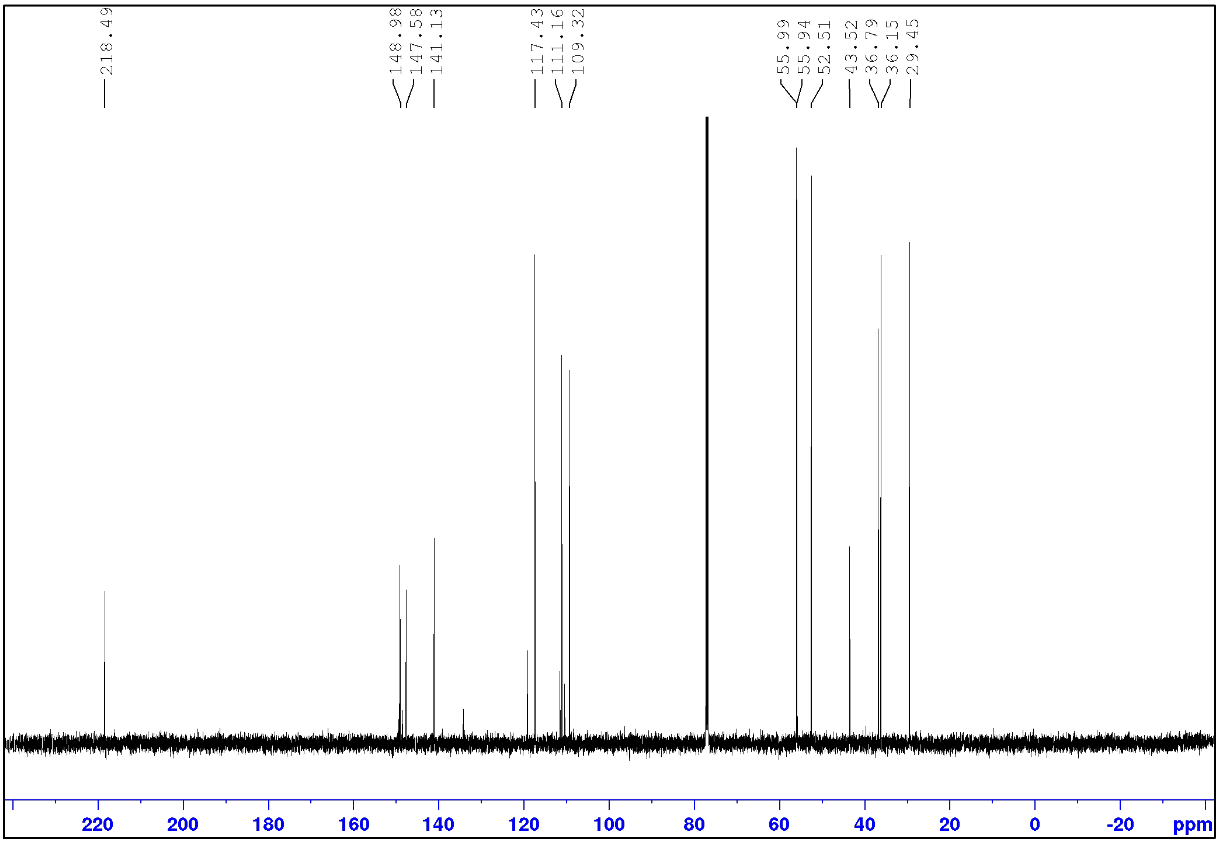
^{13}C NMR (125 MHz, $CDCl_3$) of **10f**



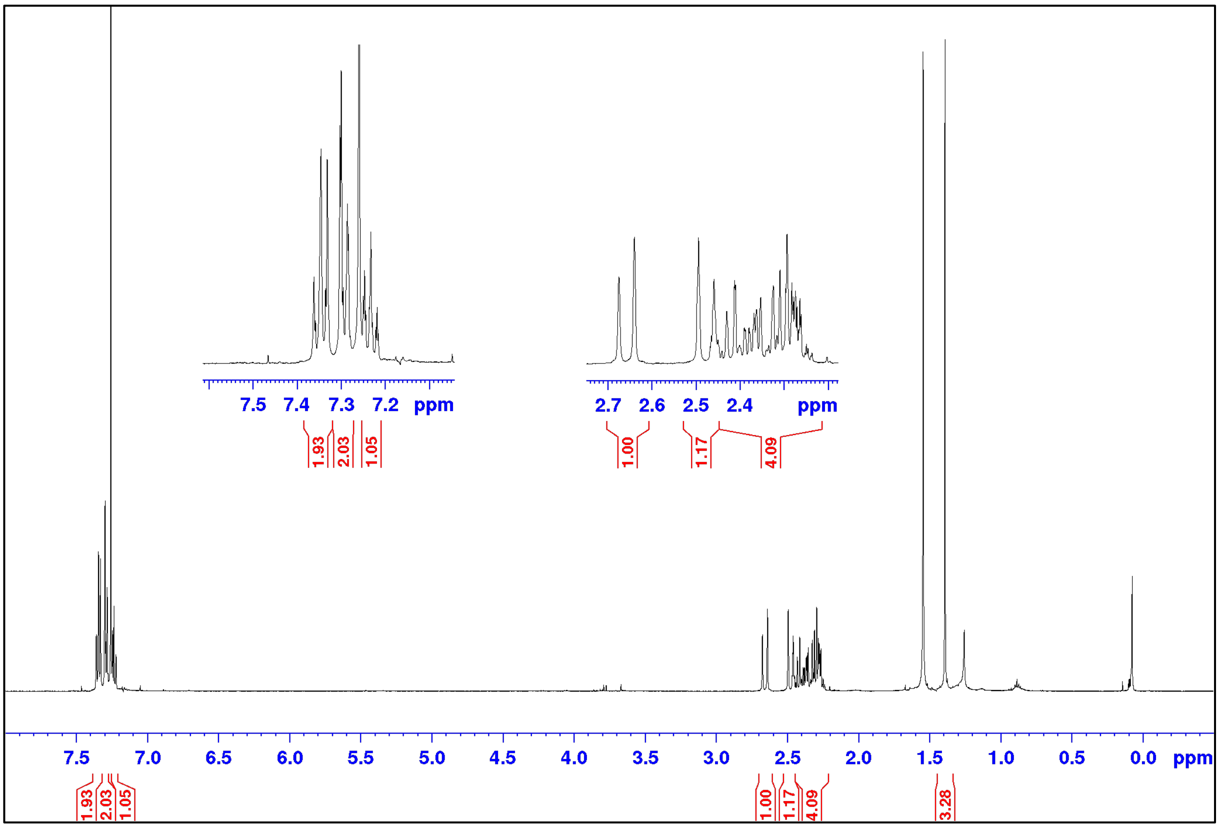
[1]H NMR (500 MHz, $CDCl_3$) of **10g**



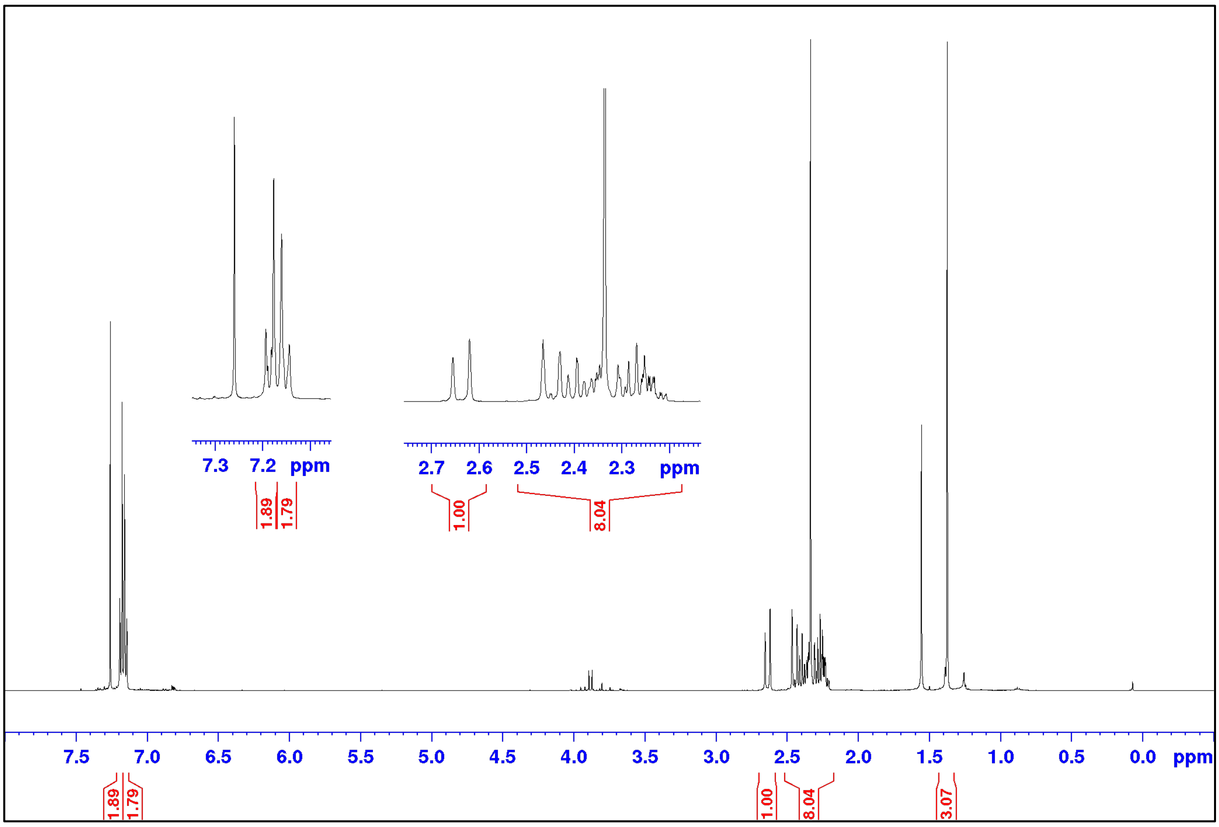
[13]C NMR (125 MHz, $CDCl_3$) of **10g**



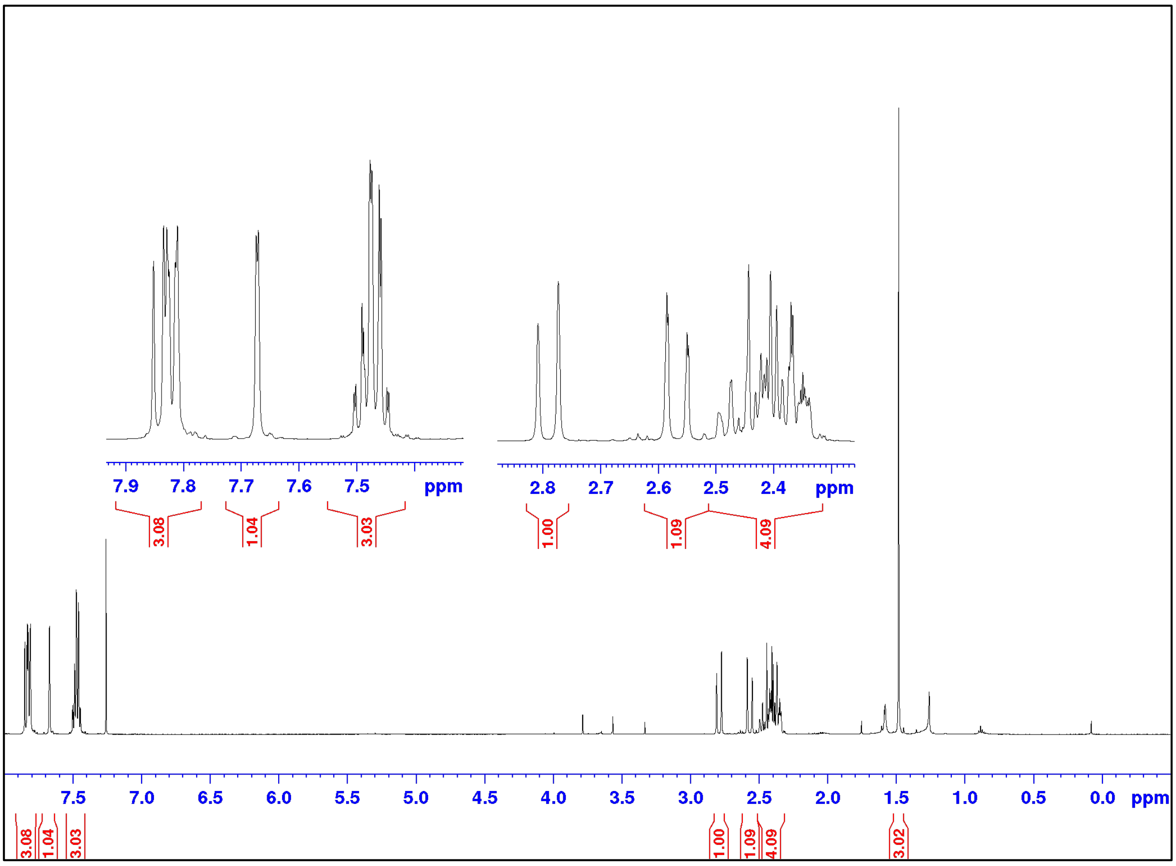
[1]H NMR (500 MHz, $CDCl_3$) of **10i**



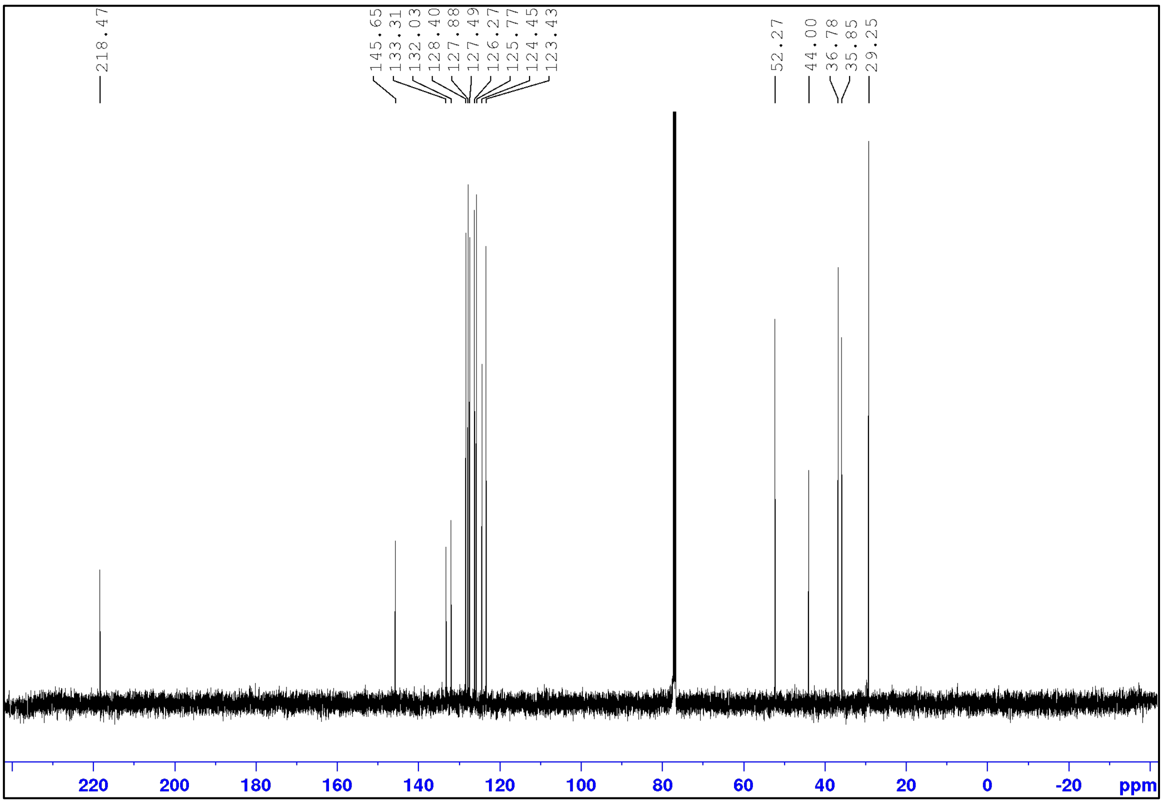
[1]H NMR (500 MHz, $CDCl_3$) of **10j**



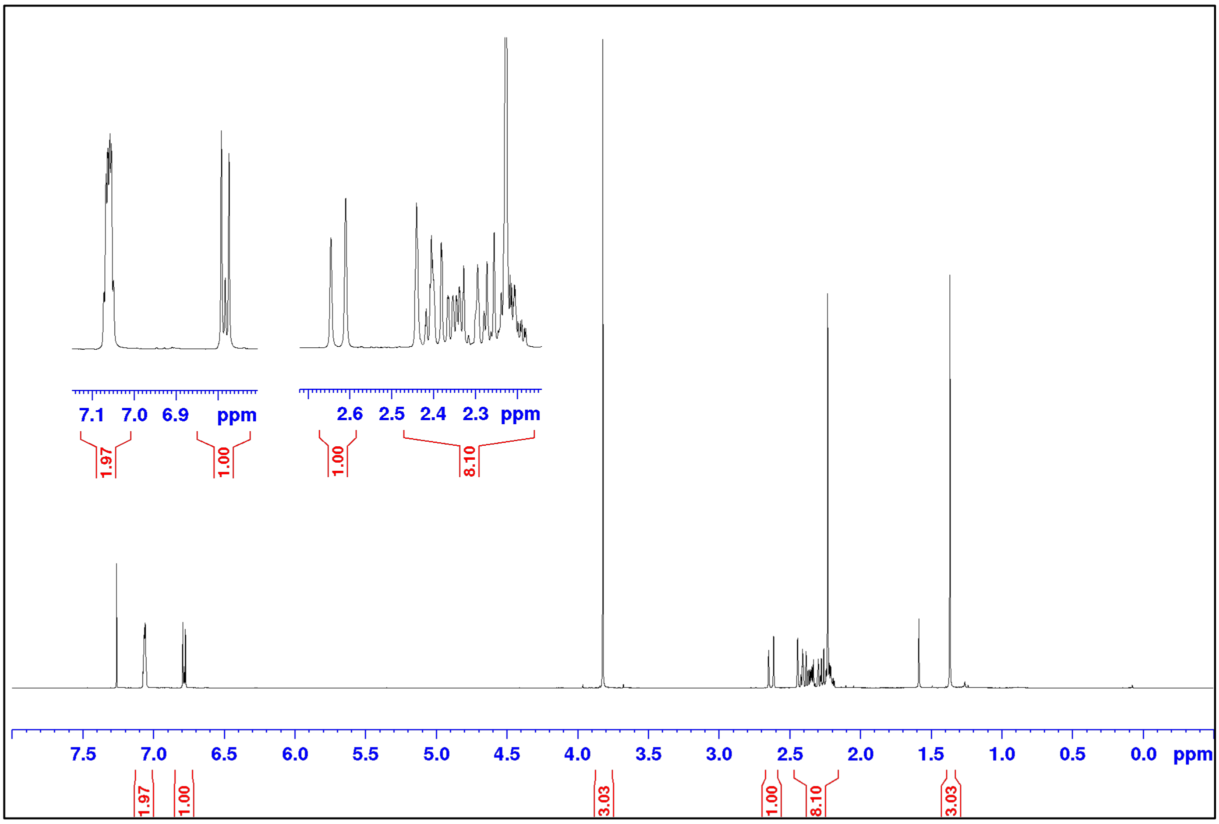
[1]H NMR (500 MHz, $CDCl_3$) of **10k**



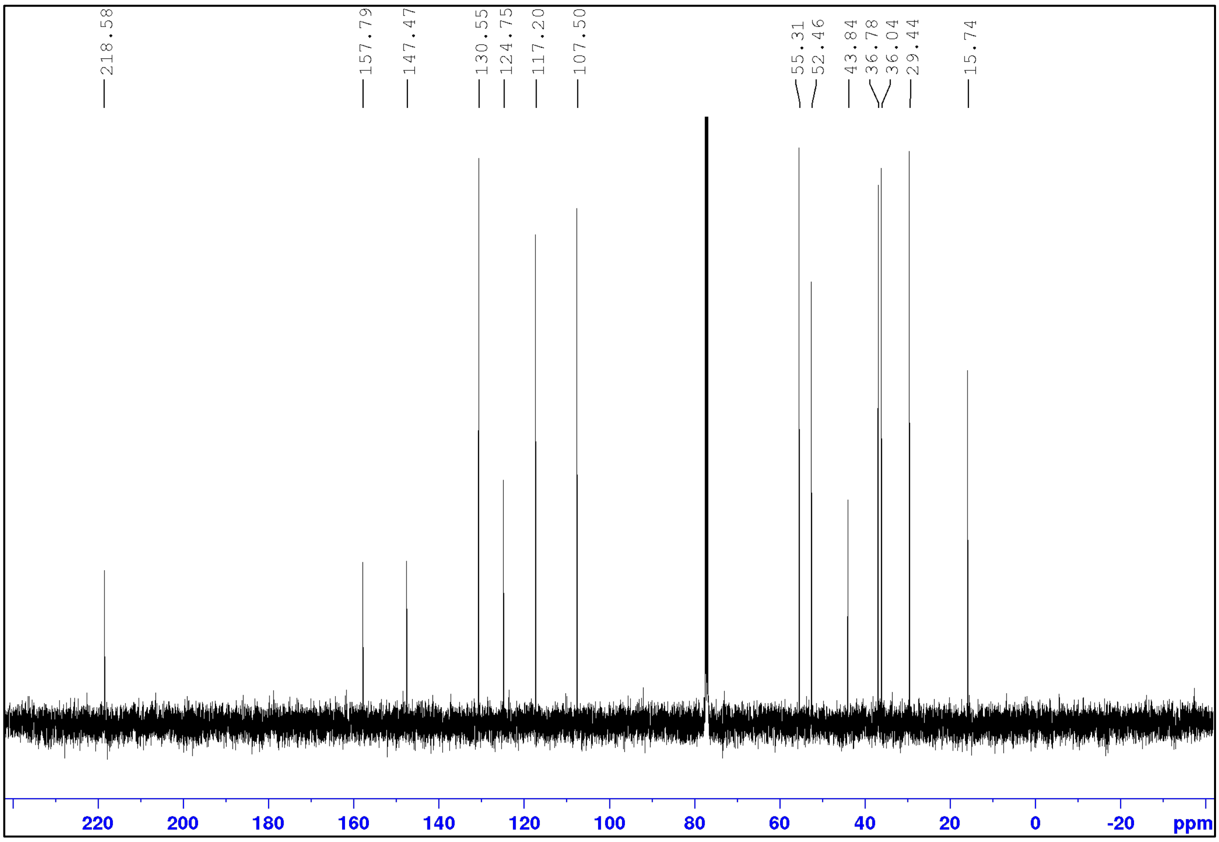
[13]C NMR (125 MHz, $CDCl_3$) of **10k**



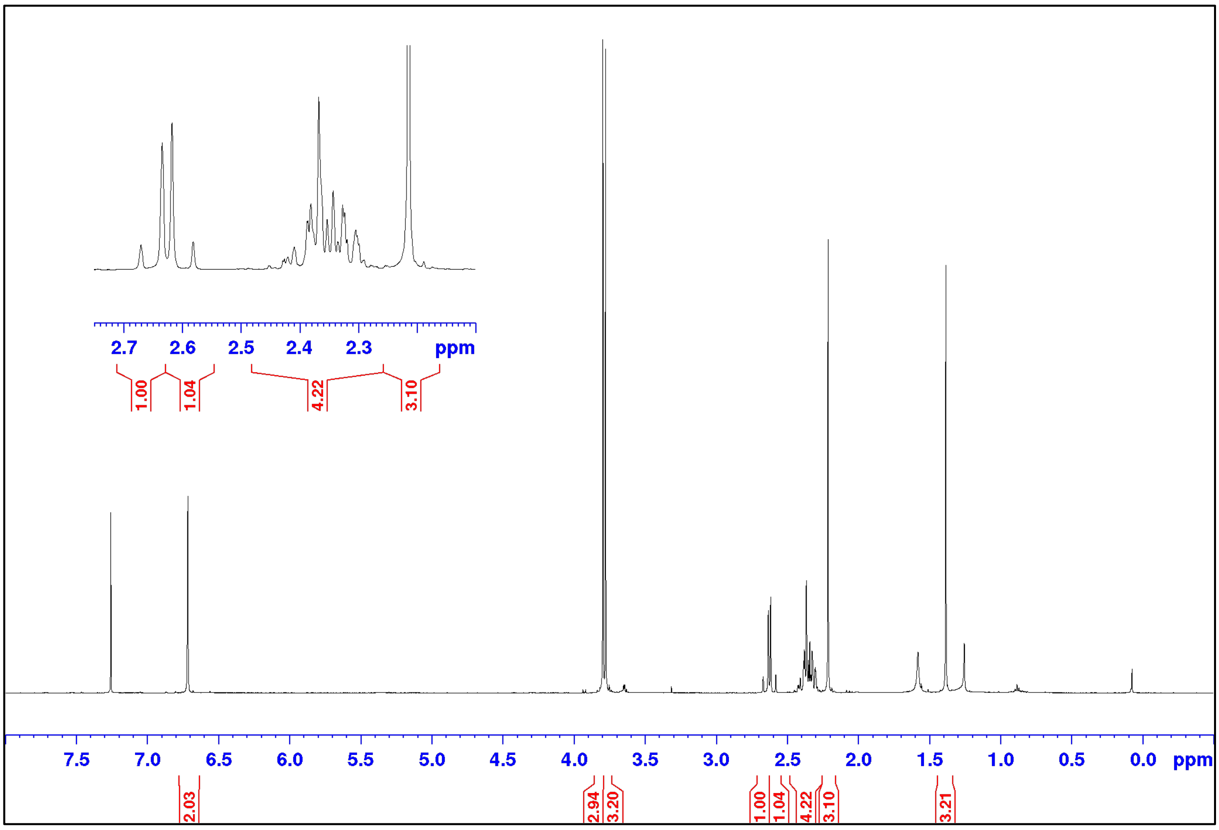
[1]H NMR (500 MHz, $CDCl_3$) of **10l**



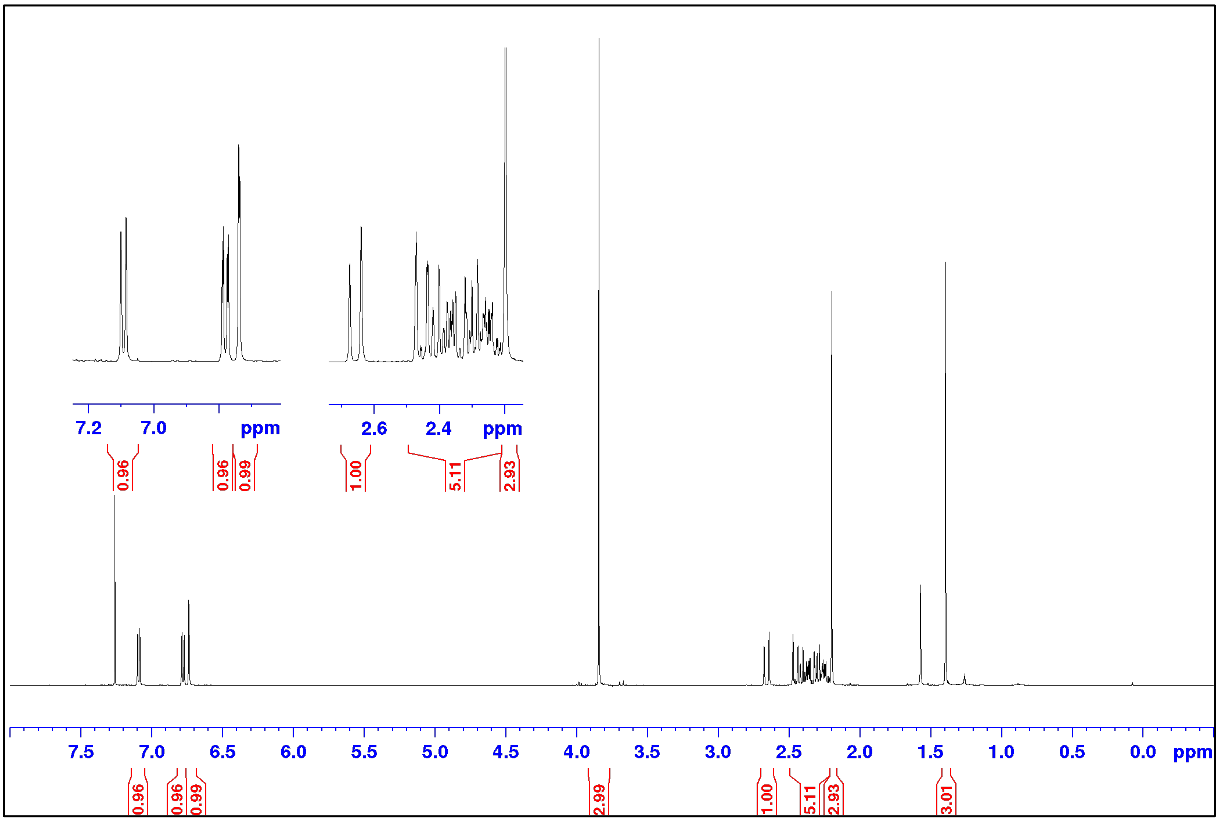
[13]C NMR (125 MHz, $CDCl_3$) of **10l**



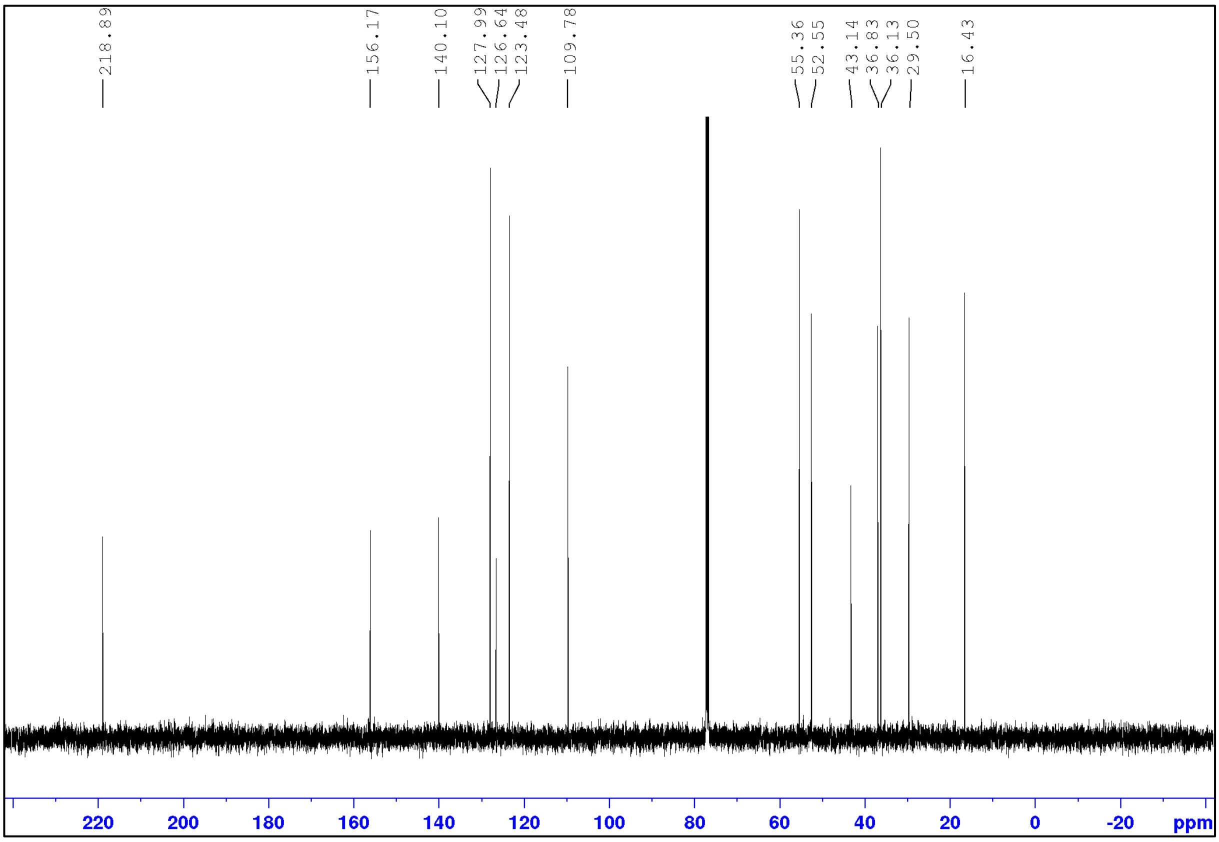
[1]H NMR (500 MHz, $CDCl_3$) of **6**



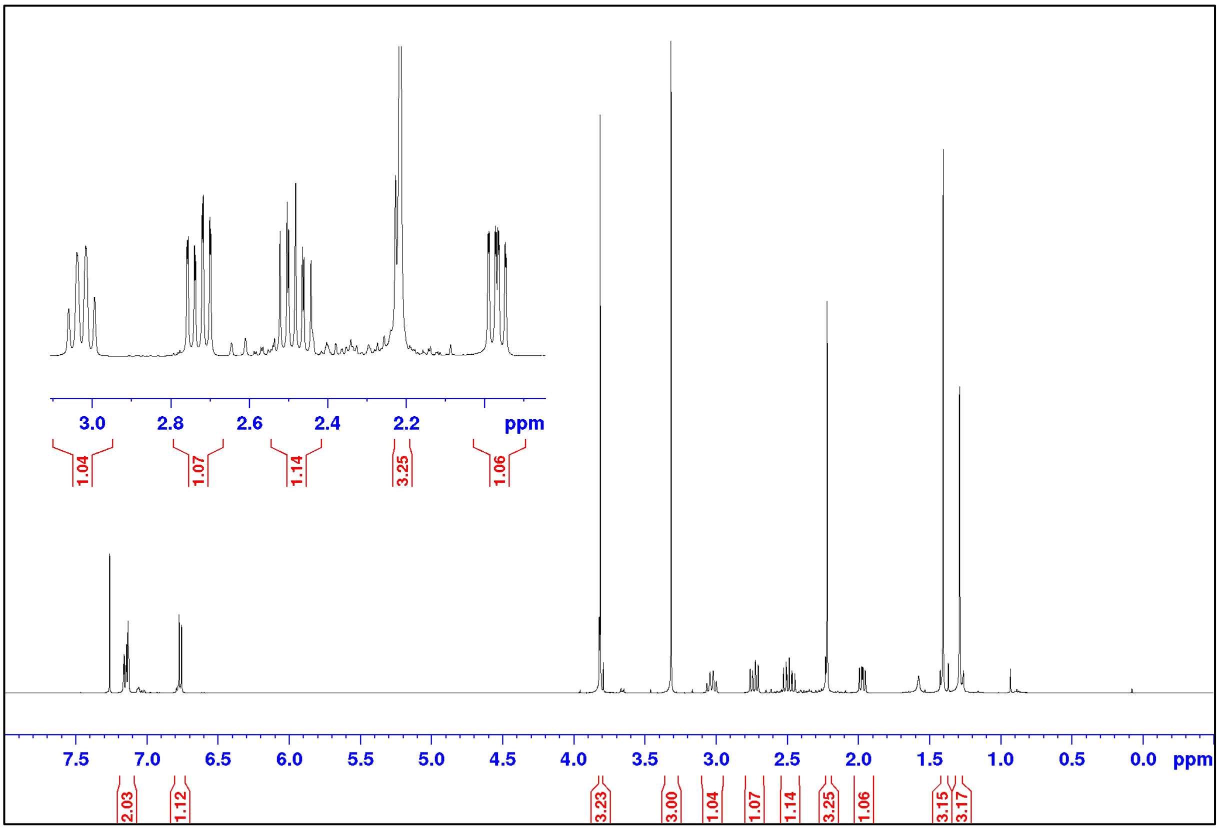
^{1}H NMR (500 MHz, $CDCl_3$) of **10n**



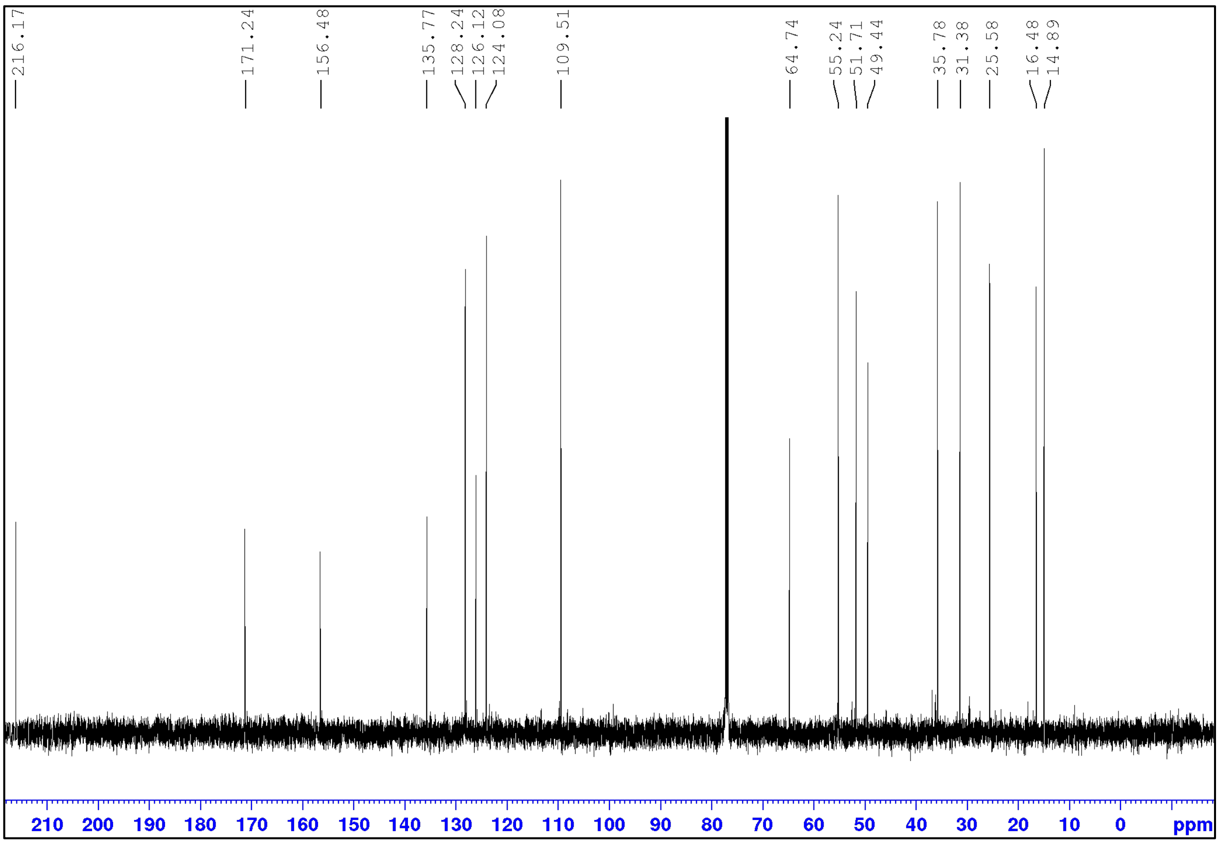
^{13}C NMR (125 MHz, $CDCl_3$) of **10n**



[1]H NMR (500 MHz, $CDCl_3$) of **5**



[13]C NMR (125 MHz, $CDCl_3$) of **5**



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