Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Catalytic carbonyl-ene reaction with ketones: evidence for a retro-ene process

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Supporting Information

Contents:

1. Analysis

^{1}H NMR and ^{13}C NMR spectra were recorded by using BRUKER AC200 (200 MHz) and BRUKER AVANCE 500 (500 MHz) spectrometers. ^{1}H NMR spectra are reported relative to the chemical shift of $CHCl_3$ at 7.26 ppm. ^{13}C NMR spectra are reported relative to $CDCl_3$ at 77.16 ppm. Column chromatography was performed with silica gel (spherical, neutral, 63–200 µm, Geduran Si 60, Merck KGaA). Analytical TLC was performed on 0.2 mm precoated Kieselgel60 F254 plates (Merck). GC/MS analysis were performed by using a Shimadzu QP2010 gas chromatograph (conditions: carrier gas, He; injector and detector temperatures, 250 °C; injected volume 0.5 µL; split ratio, 1/100; (pressure, 180 kPa); SLB-5 ms capillary column (thickness: 0.25 µm, length: 30 m, inside diameter: 0.25 mm); temperature program, 60-250 °C at 28 °C min $^{-1}$, and 250 °C for 10 min, coupled to a mass selective detector. Mass spectra were obtained by electron ionisation at 70 eV, *m/z* 35-400, source temperature 250 °C; only the most abundant ions are given.

1a: Diethyl 2-(3-Methylbut-2-enyl)-2-(3-oxobutyl) malonate. (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): 4.89 (1H; t; J=7.5 Hz); 4.10 (4H; q; J=7.1 Hz); 2.33-2.41 (2H; m); 2.52 (2H; d; J=7.4 Hz); 2.06 (3H; s); 2.01-2.09 (2H; m); 1.61 (3H; s); 1.54 (3H; s); 1.17 (6H; t; J=7.1 Hz).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): 207.6; 171.4 (2C); 135.8; 117.6; 61.4 (2C); 57.0; 38.9; 32.2; 30.0; 26.5; 26.1; 18.1; 14.2 (2C).
EI-MS (70 eV): 298 (0) [$M^{\cdot+}$], 136 (65), 135 (34), 109 (16), 108 (17), 93 (16), 79 (14), 69 (45), 55 (15), 43 (100), 41 (62).
HRMS (ES+) calculated for $C_{16}H_{26}O_5$ (MH^+) 298,1780, obtained 298,1783.

2a: Diethyl 4-hydroxy-4-methyl-3-(prop-1-en-2-yl)cyclohexane-1,1-dicarboxylate. (colorless oil)

Cis diastereoisomer*:*

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 4.74-4.89 (2H; m); 4.15 (2H; q; J=7.1 Hz); 4.09 (2H; q; J=7.1 Hz); 1.95-2.05 (1H; m); 2.02-2.04 (2H. m); 1.76 (3H; s); 1.58-1.63 (1H; m); 1.42-1.52 (1H; m); 1.15 (3H; t; J=7.1 Hz); 1.15 (3H; t; J=7.1 Hz); 1.06 (3H; s).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 171.0; 170.1; 146.0; 111.6; 68.3; 60.3; 60.0; 54.0; 47.9; 35.5; 31.0; 28.7; 25.3; 24.0; 13.1; 13.0.
EI-MS (70 eV): 298 (0) [$M^{\cdot+}$], 230 (31); 173 (37), 160 (19), 138 (30); 127 (23); 111 (21); 82 (21); 55 (26); 43 (100), 41 (30).

Trans diastereoisomer*:*

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 4.75 (1H; s); 4.96 (1H; s); 4.21 (2H; q; J=7.1 Hz); 4.17 (2H; q; J=7.1 Hz); 2.21-2.37 (3H; m); 1.77 (3H; m); 1.75-1.82 (2H; m); 1.55-1.75 (2H; m); 1.22 (3H; t; J=7.1 Hz); 1.19 (3H; t; J=7.1 Hz); 1.13 (3H; s).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 172,2; 170,6; 145,0; 114,6; 71,6; 61,6; 61,4; 55,1; 50,6; 38,2; 33,3; 28,9; 23,1; 21,8; 14,1; 14,0.
EI-MS (70 eV): 298 (0) [$M^{\cdot+}$], 230 (26); 173 (33), 160 (19), 138 (30); 127 (21); 111 (19); 82 (20); 55 (24); 43 (100), 41 (31).

3a: Diethyl 4-methyl-3-(prop-1-en-2-yl)cyclohex-3-ene-1,1-dicarboxylate. (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 4.86 (1H; s); 4.58 (1H; s); 4.11 (4H; q; J=7.1 Hz); 2.45-2.58 (2H; m); 1.98-2.06 (2H; m); 2.05 (2H; d; J=4.9 Hz); 1.73 (3H; s); 1.52 (3H; s); 1.17 (6H; t; J=7.1 Hz).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 171.4 (2C); 146.4; 131.3; 125.5; 113.1; 61.3 (2C); 53.7; 34.3; 28.5; 28.0; 21.9; 19.8; 14.2 (2C).
EI-MS (70 eV): 280 (0) [$M^{\cdot+}$], 207 (41), 133 (100), 119 (23), 105 (59), 93 (43), 91 (68), 79 (18), 77 (32), 43 (16), 41 (55).

4a: Diethyl 4-methylcyclohex-3-ene-1,1-dicarboxylate. CAS Registry Number : 2698-65-9. (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 5.25-5.35 (1H; m); 4.12 (4H; q; J=7.1 Hz); 2.41-2.51 (2H; m); 2.02-2.12 (2H; m); 1.87-1.97 (2H; m); 1.56 (3H; s); 1.16 (6H; t; J=7.1 Hz).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 170.8 (2C); 132.2; 117.0; 60.2 (2C); 51.8; 29.7; 26.8; 26.1; 22.3; 13.1 (2C).

1b: Diethyl 2-(3-methylbut-2-enyl)-2-(3-oxo-3-phenylpropyl)malonate. CAS Registry Number 1523334-60-2. (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 7.34-7.90 (5H; m); 4.95 (1H; t; J=7.5 Hz); 4.12 (4H; q; J=7.1 Hz); 2.88-2.96 (2H; m); 2.59-2.62 (2H; m); 2.19-2.27 (2H; m); 1.62 (3H; s); 1.56 (3H; s); 1.17 (6H; t; J=7.1 Hz).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 199.0; 171.3 (2C); 136.7; 135.7; 133.0; 128.6 (2C); 128.02 (2C); 117.6; 61.2 (2C); 57.0; 33.9; 32.2; 27.1; 26.0; 18.0; 14.0 (2C).
EI-MS (70 eV): 360 (0) [$M^{\cdot+}$], 173 (10), 135 (11), 106 (8), 105 (100), 79 (7), 77 (38), 69 (17), 55 (8), 43 (8), 41 (30).

4b: Diethyl 4-phenylcyclohex-3-ene-1,1-dicarboxylate. CAS Registry Number 109397-15-1. (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 7.29 (2H; t; J=7.2Hz); 7.22 (1H; t; J=7.2 Hz); 7.34-7.36 (2H; m); 6.06-6.09 (1H; m); 4.20 (4H; q; J=7.1 Hz); 2.77 (2H; m); 2.50 (2H; t; J=8.5 Hz, J=2 Hz); 2.29 (2H; t; J=6.3 Hz); 1.25 (6H; t; J=7.1Hz).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 171.5 (2C); 141.2; 135.6; 128.2 (2C); 126.9; 125.0 (2C); 121.1; 61.3 (2C); 52.7; 31.1; 27.9; 24.5; 14.0 (2C).
EI-MS (70 eV): 302 (8) [$M^{\cdot+}$], 228 (67), 227 (19), 156 (18), 155 (100), 154 (18), 153 (18), 128 (18), 115 (27), 91 (37), 77 (35).

5b: Diethyl 9,9-dimethyl-3,4-dihydro-1H-fluorene-2,2(9H)-dicarboxylate. (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 7.12-7.35 (4H; m); 4.14-4.23 (4H; m); 2.32-2.39 (2H; m); 2.79-2.82 (2H; m); 2.49-2.56 (2H; m); 1.25 (6H; s); 1.25 (6H; t; J=7.1 Hz).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 171.5 (2C); 153.6; 146.9; 142.5; 131.2; 126.1; 124.5; 120.9; 118.0; 61.4 (2C); 54.1; 48.8; 28.1; 27.7; 23.5 (2C); 19.5; 14.0 (2C).
EI-MS (70 eV): 342 (27) [$M^{\cdot+}$], 269 (29), 268 (100), 195 (77), 181 (27), 179 (35), 173 (27), 166 (23), 165 (48), 141 (24).

1c: Diethyl 2-(4-methylpent-3-enyl)-2-(3-oxobutyl)malonate. (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 4.95 (1H; t; J=7.5 Hz); 4.10 (4H; q; J=7.1 Hz); 2.33-2.41 (2H; m); 2.05-2.13 (2H; m); 2.07 (3H; s); 1.79-1.83 (4H; m); 1.60 (3H; s); 1.51 (3H; s); 1.19 (6H; t; J=7.1 Hz).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 207.4; 171.4 (2C); 132.6; 123.0; 61.2 (2C); 56.6; 38.7; 33.3; 29.9; 26.4; 25.6; 22.8; 17.6; 14.1 (2C).
EI-MS (70 eV): 312 (0) [$M^{\cdot+}$], 230 (67), 173 (90), 138 (68), 82 (72), 43 (100).

5c: Ethyl 5-methyl-2-oxo-3-oxa-bicyclo[3.3.2]decane-1-carboxylate. CAS Registry Number 85696-88-4. (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 4.05-4.19 (2H; m); 2.51-2.57 (1H; m); 2.02-2.07 (2H; m); 1.92-2.00 (1H; m); 1.87-1.95 (2H; m); 1.69-1.83 (2H; m); 1.69-1.79 (2H; m); 1.34 (3H; s); 1.13-1.27 (3H; m).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 173.5; 171.9; 83.3; 62.1; 52.3; 38.5; 31.3; 30.5; 30.0; 25.1; 21.1; 14.4.
EI-MS (70 eV): 312 (0) [$M^{\cdot+}$], 109 (58), 108 (58), 69 (88), 43 (100), 41 (49).

1d: Diethyl 2-(but-2-enyl)-2-(3-oxobutyl)malonate mixture of *Z/E,* (85/15). (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C) *Z* isomer: δ ppm 5,14-5,51 (2H; m); 4,11 (4H; q; J=7,16 Hz); 2,43-3,51 (4H; m); 2,07 (3H; s); 2,00-2,08 (2H; m); 1,56 (3H; s); 1,18 (6H , t).

^{13}C NMR (50 MHz, $CDCl_3$, 20 °C) *Z* isomer: δ ppm 207,4; 171,1 (2C); 129,9; 124,4; 61,2 (2C); 56,8; 38,6; 36,7; 29,8; 26,3; 18,0; 14,1 (2C).
EI-MS (70 eV) *Z* isomer: 284 (0) [$M^{\cdot+}$], 167 (11), 123 (21), 122 (81), 121 (17), 95 (17), 93 (10), 79 (13), 55 (33), 43 (100), 41 (15).
HRMS (ES^+) calculated for $C_{15}H_{24}O_5$ (MH^+) 284,1623, obtained 284,1626.

3d: Diethyl 3-ethyl-4-methylcyclohex-3-ene-1,1-dicarboxylate. (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 4.2 (4H; q; J=7.1 Hz); 2.49 (2H; ~s); 2.04-2.07 (2H; m); 2.10 (2H; t; J=6.2 Hz); 1.97-2.04 (2H; m); 1.60 (3H; s); 1.25 (6H; t; J=7.1 Hz); 0.98 (3H; t; J=7.5 Hz).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C) : δ ppm 170.8 (2C); 127.7; 123.2; 60.1 (2C); 52.7; 33.0; 27.8; 27.0; 25.0; 17.2; 13.0 (2C); 11.2.
EI-MS (70 eV) : 268 (14) [$M^{\cdot+}$], 194 (58), 165 (25), 121 (97), 93 (100), 91 (27).

5d: Ethyl 5-ethyl-2-oxo-3-(3-oxobutyl)-tetrahydrofuran-3-carboxylate. (colorless oil)

Mixture of 2 isomers (45/55)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 4.33-4.45 (1H; m); 4.16 (2H; q; J=7.1 Hz); 2.59-2.70 (1H; m); 2.32-2.45 (1H; m); 2.15-2.22 (1H; m); 2.07 (3H; s); 2.04-2.21 (2H; m); 1.68-1.76 (1H; m); 1.67-1.74 (1H; m); 1.56-1.64 (1H; m); 1.23 (3H; t; J=7.1 Hz); 0.95 (3H; t; J=7.5 Hz).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 206.9; 174.0; 169.6; 79.7; 62.3; 54.9; 38.7; 38.6; 29.9; 28.3; 28.2; 14.1; 9.4.
IE-SM (70 eV): 256 (0) [$M^{\cdot+}$], 186 (53), 122 (29), 81 (16); 43 (100).

1e: Diethyl 2-cinnamyl-2-(3-oxobutyl)malonate. (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 7.4-7.2 (m. 5H); 6.50 (1H; d; J=15.8 Hz); 6.10 (1H; dt; J=15.8 Hz; J=7.1Hz); 4.1 (4H; q; J=7.1 Hz); 2.70 (2H; d; J=7.3 Hz); 2.44 (2H; t; J=8.5 Hz); 2.11 (2H; t; J=8.5 Hz); 2.07 (3H; s); 1.18 (6H; t; J=7.1 Hz).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 207.3; 170.9 (2C); 136.9; 134.0; 128.5 (2C); 127.4; 126.2 (2C); 123.7; 61.4 (2C); 57.0; 38.7; 37.4; 29.9; 26.8; 14.1 (2C).
EI-MS (70 eV): 346 (0) [$M^{\cdot+}$], 184 (54), 183 (14), 155 (14), 141 (23), 128 (17), 117 (100) , 116 (11), 115 (62), 91 (37), 43 (94).

3e: (*E*)-Diethyl 4-methyl-5-phenylcyclohept-4-ene-1,1-dicarboxylate. (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 7.13-7.34 (5H; m); 4.12 (2H; q; J=7.1 Hz); 4.07 (2H; q; J=7.1 Hz); 3.39 (2H; ~s); 2.40 (2H; ~s); 2.07-2.16 (4H; m); 1.73 (3H; s); 1.16 (6H; t; J=7.1 Hz).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 172.0 (2C); 140.4;128.9 (2C); 128.6 (2C); 127.5; 126.2; 126.2; 61.5 (2C); 54.0; 39.3; 34.8; 29.3; 28.3; 19.5; 14.4 (2C).
EI-MS (70 eV): 330 (2) [M.+], 93 (26), 92 (18), 91 (100), 77 (11), 65 (9).

1f: Diethyl 2-(2-methylallyl)-2-(3-oxobutyl)malonate. (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 4.75 (1H; s); 4.70 (1H; s); 4.12 (4H; q; J=7.1 Hz); 2.64 (2H; s); 2.33-2.40 (2H; m); 2.04-2.12 (2H; m); 2.07 (3H; s); 1.58 (3H; s); 1.19 (6H; t; J=7.1 Hz).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 207.3; 171.3 (2C); 140.4; 115.8; 61.3 (2C); 56.0; 41.1; 38.7; 29.9; 26.4; 23.0; 14.0 (2C).
EI-MS (70 eV): 284 (0) [M.+], 211 (31), 165 (25), 122 (56), 43 (100).

2f: (*Z*)-diethyl 5-hydroxy-3,5-dimethylcyclohept-2-ene-1,1-dicarboxylate. (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 5.30 (1H; ~s); 4.16 (2H; q; J=7.1 Hz); 4.05 (2H; q; J=7.1 Hz); 2.79-2.85 (1H; m); 2.68-2.74 (1H; m); 2.56-2.63 (1H; m); 2.40-2.48 (1H; m); 2.24-2.30 (1H; m); 2.20-2.29 (1H; m); 1.65 (3H; ~s); 1.51 (3H; s); 1.16 (3H; t; J=7.1 Hz); 1.16 (3H; t; J=7.1Hz).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 174.1; 169.1; 129.4; 117.8; 81.7; 61.1 (2C); 53.9; 46.3; 43.1; 34.1; 27.3; 26.5; 13.0 (2C).
EI-MS (70 eV): 284 (0) [$M^{\cdot+}$], 238 (3), 127 (60), 123 (30), 93 (31), 43 (100).

3f: (2*Z*,4*Z*)-Diethyl 3,4-dimethylcyclohepta-2,4-diene-1,1-dicarboxylate. (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 4,25 (2H; q; J=7,1 Hz); 2,79 (1H; ddd; J=17,9 Hz, J=9,6 Hz, J=5,7 Hz); 2,66 (1H; d; J=13,6 Hz); 2,50 (1H; ddd; J=17,9 Hz, J=9,6 Hz, J=5,7 Hz); 2,21 (2H; td; J=9,5

Hz, J=5,6 Hz); 2,09 (1H; ddd; J=13,6 Hz); 2,16 (3H; s); 1,48 (3H; s); 1,42 (3H; s); 1,30 (3H; t; J=7,1 Hz).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 205,9; 172,7; 169,5; 81,2; 61,2; 54,3; 44,0; 37,6; 28,9; 28,7; 28,7; 27,3; 12,9.
EI-MS (70 eV): 256 (0) [$M^{\cdot+}$], 186 (40), 122 (46), 95 (14), 81 (15), 43 (100).

1g: Diethyl 2-(3-methylbut-2-enyl)-2-(3-oxopropyl)malonate. CAS Registry Number: 1396789-01-7. (colorless oil)

^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 9.67 (1H; t; J=1.3 Hz); 4.88 (1H; t; J=6.1 Hz); 4.12 (4H; q; J=7.1 Hz); 2.53 (2H; d; J=7.4 Hz); 2.35-2.43 (2H; m); 2.06-2.14 (2H; m); 1.55 (3H; s); 1.52 (3H; s); 1.18 (6H; t).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 201.0; 171.1 (2C); 135.9; 117.2; 65.8 (2C); 61.3; 39.2; 31.9; 30.9; 26.0; 17.9; 15.2 (2C).
EI-MS (70 eV): 286 (0) [$M^{\cdot+}$], 160 (23), 119 (27), 109 (23), 93 (27), 79 (24), 69 (80), 67 (26), 55 (31), 43 (31), 41 (100).
HRMS (ES^+) calculated for $C_{15}H_{24}O_5$ (MH^+) 284,1623, obtained 284,1626.

2g: Diethyl 4-hydroxy-3-(prop-1-en-2-yl)cyclohexane-1,1-dicarboxylate. (Colorless oil)

1st diastereoisomer:
^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 4.80-4.98 (2H; m); 4.13-4.20 (4H; m); 3.91 (1H; q; J=2.2 Hz); 2.14-2.21 (1H; m); 2.04-2.11 (2H; m); 1.98-2.14 (2H; m); 1.92-1.98 (1H; m); 1.77 (3H; s); 1.60-1.69 (1H; m); 1.20-1.25 (6H; m).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C): δ ppm 172.1; 171.1; 146.0; 111.7; 64.3; 61.3; 61.1; 54.9; 44.4; 28.7; 28.2; 24.3; 22.7; 14.0; 14.0.
EI-MS (70 eV): 284 (100) [M.+], 266 (0,1), 193 (55), 160 (42), 119 (100), 41 (52).

2^{d} diastereoisomer:
^{1}H NMR (200 MHz, $CDCl_3$, 20 °C): δ ppm 4.82-4.89 (2H; m); 3.44 (1H; dt; J=10.6 Hz, J=4.1 Hz); 4.03-4.25 (4H; m); 1.67 (3H; s); 1.32-2.41 (7H; m); 1.13-1.25 (6H; m).
^{13}C NMR (50 MHz, $CDCl_3$, 20 °C) : δ ppm 170.9; 169.5; 144.0; 112.6; 68.8; 60.6; 60.3; 53.7; 49.1; 33.7; 29.4; 28.7; 18.2; 13.1; 13.0.
EI-MS (70 eV): 284 (0) [M.+], 266 (0,2), 193 (58), 160 (77),119 (100), 41 (57).

2. ESI-MS measurements

Mass spectrometry measurements were performed on a quadrupole ion trap instrument (LCQ Deca; Thermo Fisher) operated with Xcalibur (version 1.3, Thermoquest Finnigan) software package. The spectra were scanned in the *m/z* range from 50 to 2000. For minimizing small changes in intensity ratio associated with the *m/z* range, an optimization procedure carried out was conducted on the ion $[In^{3+}(OTf^{-})_2(\mathbf{1a})]^{+}$ (*m/z* 711). Under these conditions, the intensity ratios are highly repeatable. The spray conditions were as follows: flow rate 3 µL min^{-1}; electrospray ionization voltage: 3.1 kV; capillary temperature: 200 °C; drying and nebulizer gas: nitrogen. The capillary voltage was adjusted according to the Xcalibur tune procedure.
The helium buffer gas pressure in the ion trap was set automatically by the regulated inlet at about 2×10^{-3} Pa (ion gauge reading). Each spectrum was acquired with 5 micro-scans and with a maximum ion injection time of 200 ms. Confirmation of the composition of ions was obtained from isotopic simulations and tandem mass spectrometry in some cases.[40] Stock solutions of **1a** and indium triflate at 2 10^{-3} mol/L in nitromethane were mixed to provide a final solution in the same concentration ratio of bulk synthesis.

- On-line reaction monitoring using the Sheath Liquid Inlet.

A new ESI source configuration was employed to reduce the reactants mixing dead time. In this set-up, a $In(OTf)_3$ solution was injected through the Sheath Liquid Inlet of the ESI source while the **1a** solution was injected using the normal Sample Inlet. This results in two separated coaxial flows that will be mixed only in the Taylor cone, less than one second before the ionization (Figure 1).
The optimized spray conditions were as follows: flow rate 3 µL min^{-1} for both the **1a** solution and $In(OTf)_3$ solution; electrospray ionization voltage: 3.1 kV; capillary temperature: 200 °C; drying and nebulizer gas: nitrogen. The optimized concentrations of the employed solutions were as follows: indium triflate at 10^{-4} mol L^{-1} in nitromethane; **1a** at 10^{-3} mol L^{-1} in nitromethane.

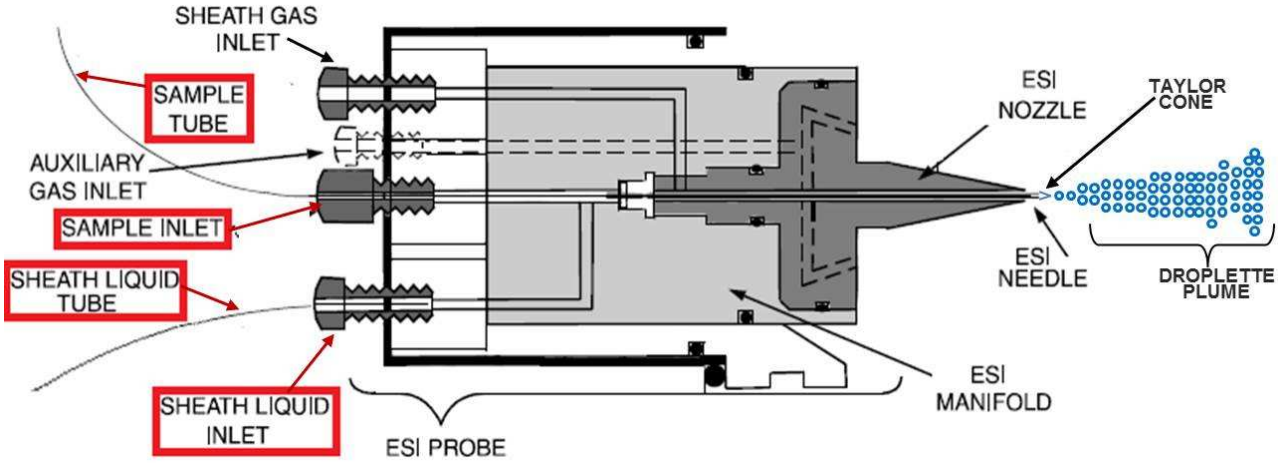
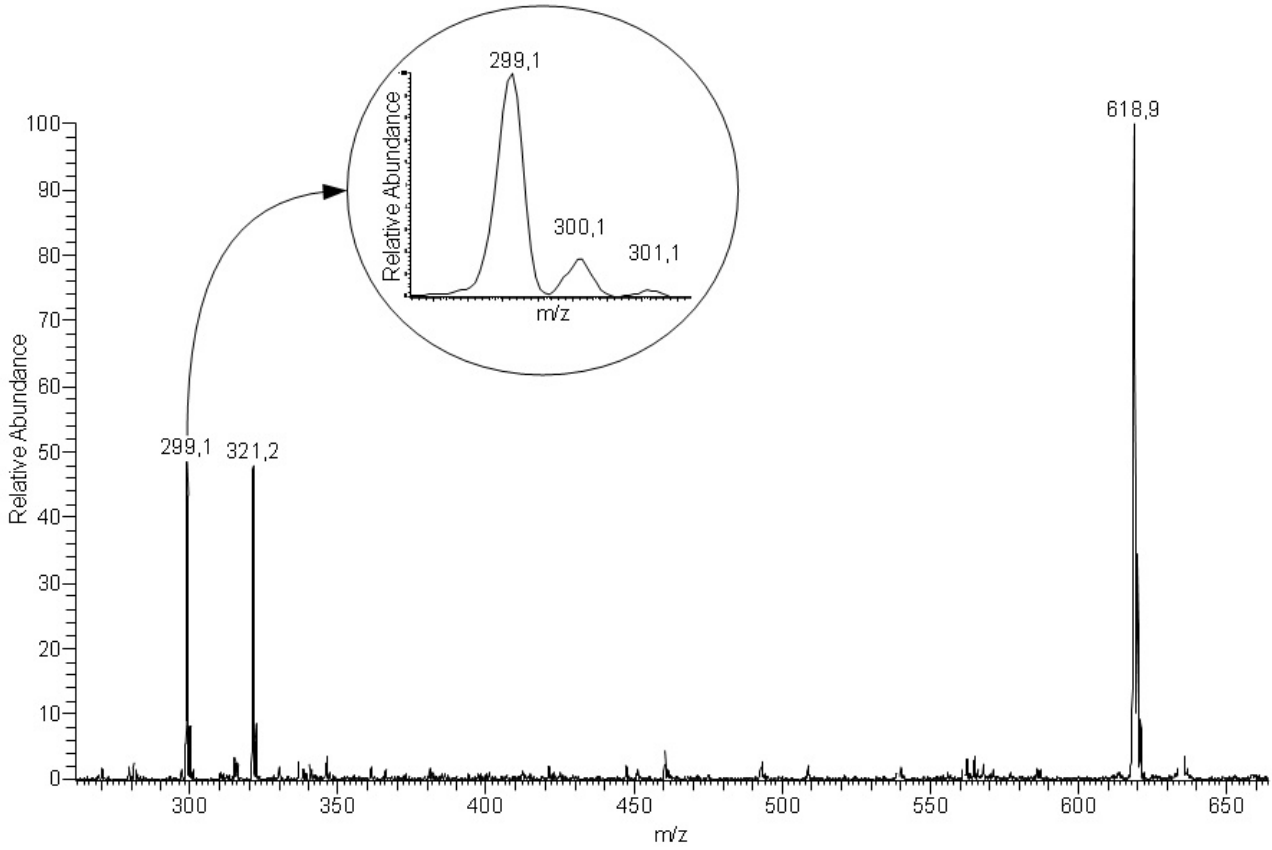


Figure 1. Mixing of the reactant and catalyst using the Sheath Liquid Inlet.

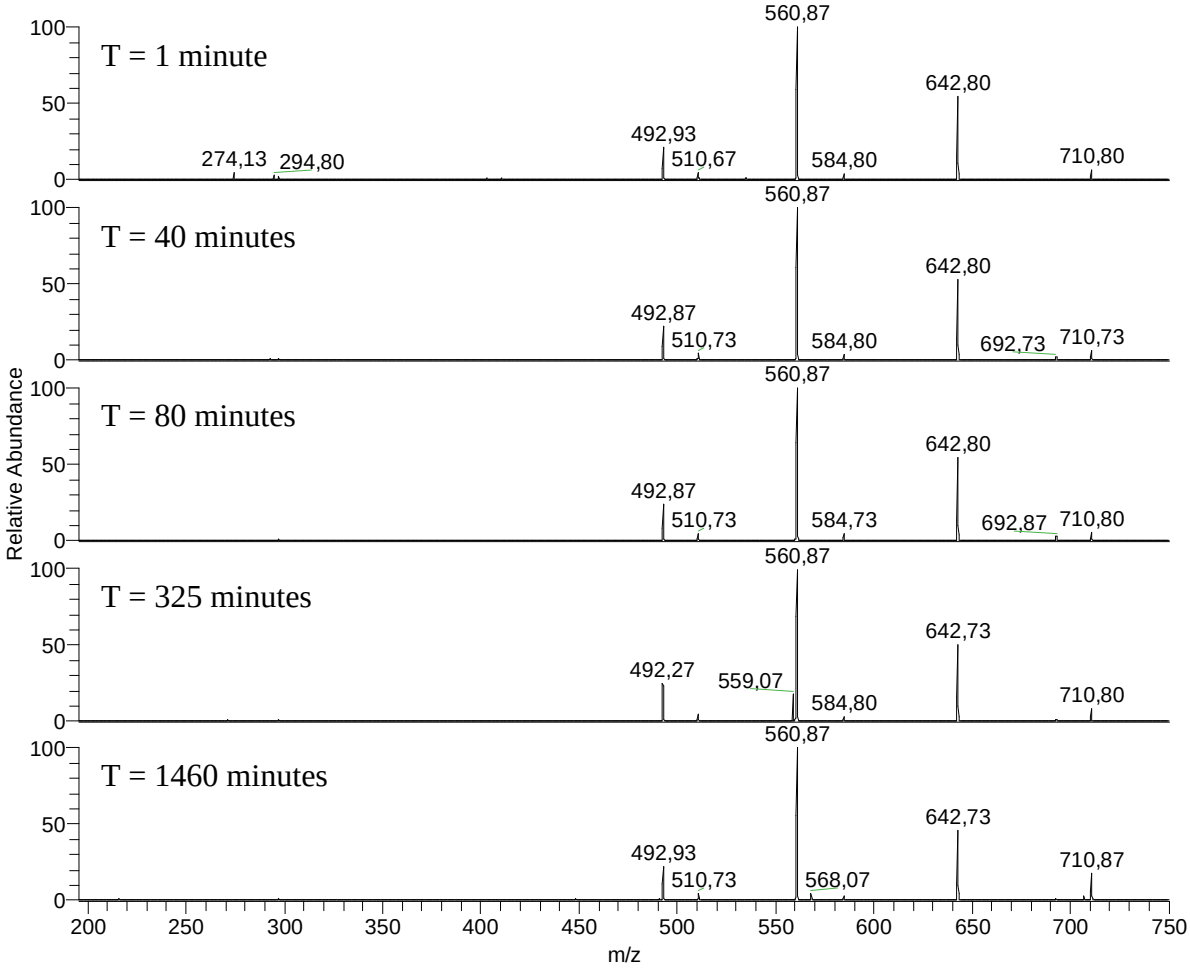
- Positive ion mode ESI-MS spectrum of nitromethane solution of the compound **1a**:

Ion at *m/z* 299.1 corresponds to [**1a**+H^+]; Ion at *m/z* 321.2 corresponds to [**1a**+Na^+]; Ion at *m/z* 618.9 corresponds to [$(\mathbf{1a})_2$+Na^+] adduct.



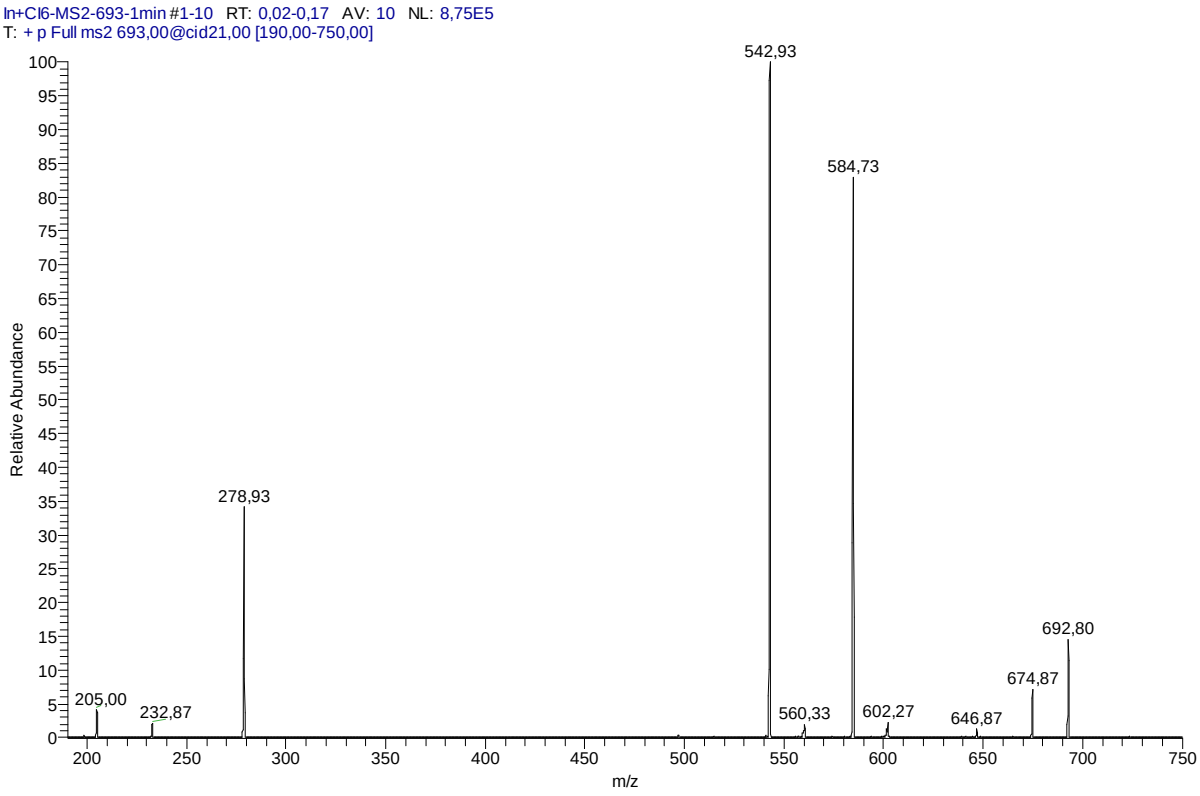
- Positive ion mode **ESI-MS/MS** spectrum of nitromethane solution of the compound **1a** mixed with $In(OTf)_3$ over time:

Ion at *m/z* 710.87 corresponds to [**1a** + $In(OTf)_2^+$]; No modifications of the fragmentation pattern is observed over time making [**1a** + $In(OTf)_2^+$] and [**2a** + $In(OTf)_2^+$] undistinguishable.



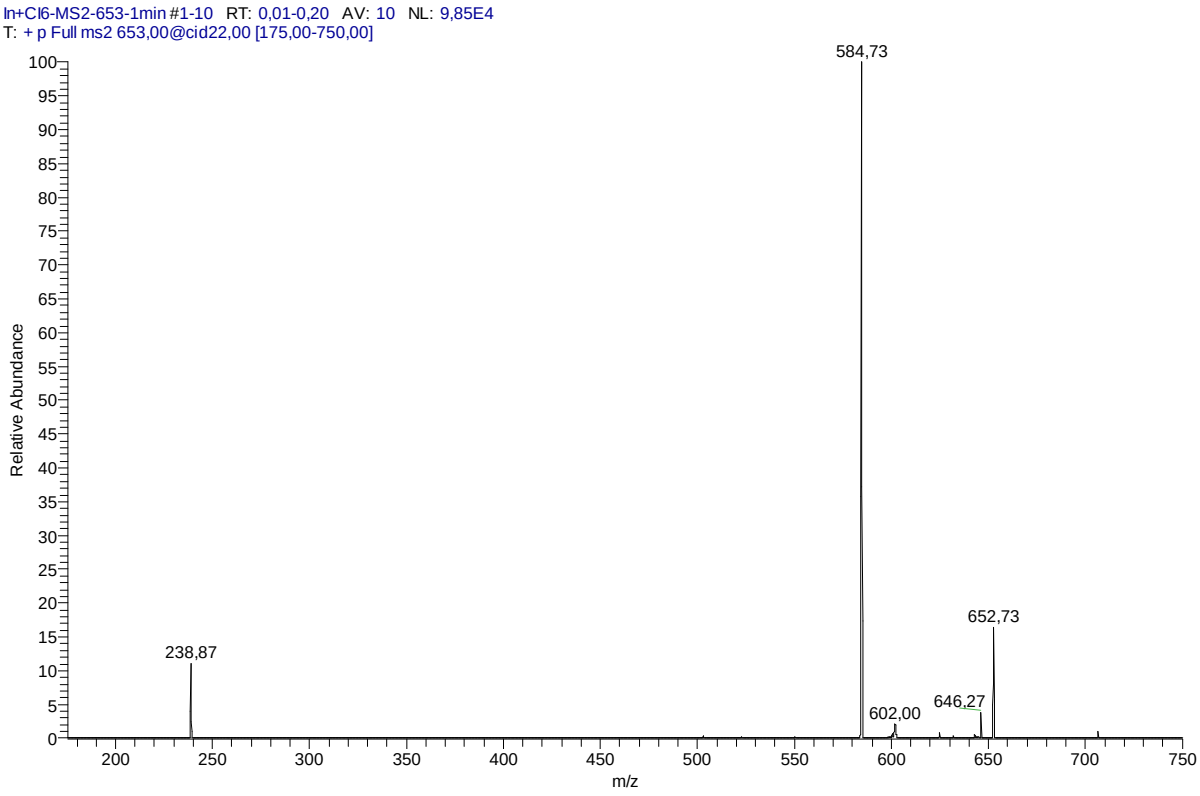
- Positive ion mode **ESI-MS/MS** spectrum of nitromethane solution of the compound **1a** mixed with $In(OTf)_3$ over time:

Ion at *m/z* 692.80 corresponds to [**3a** + $In(OTf)_2^+$]



- Positive ion mode ESI-MS/MS spectrum of nitromethane solution of the compound **1a** mixed with $In(OTf)_3$ over time:

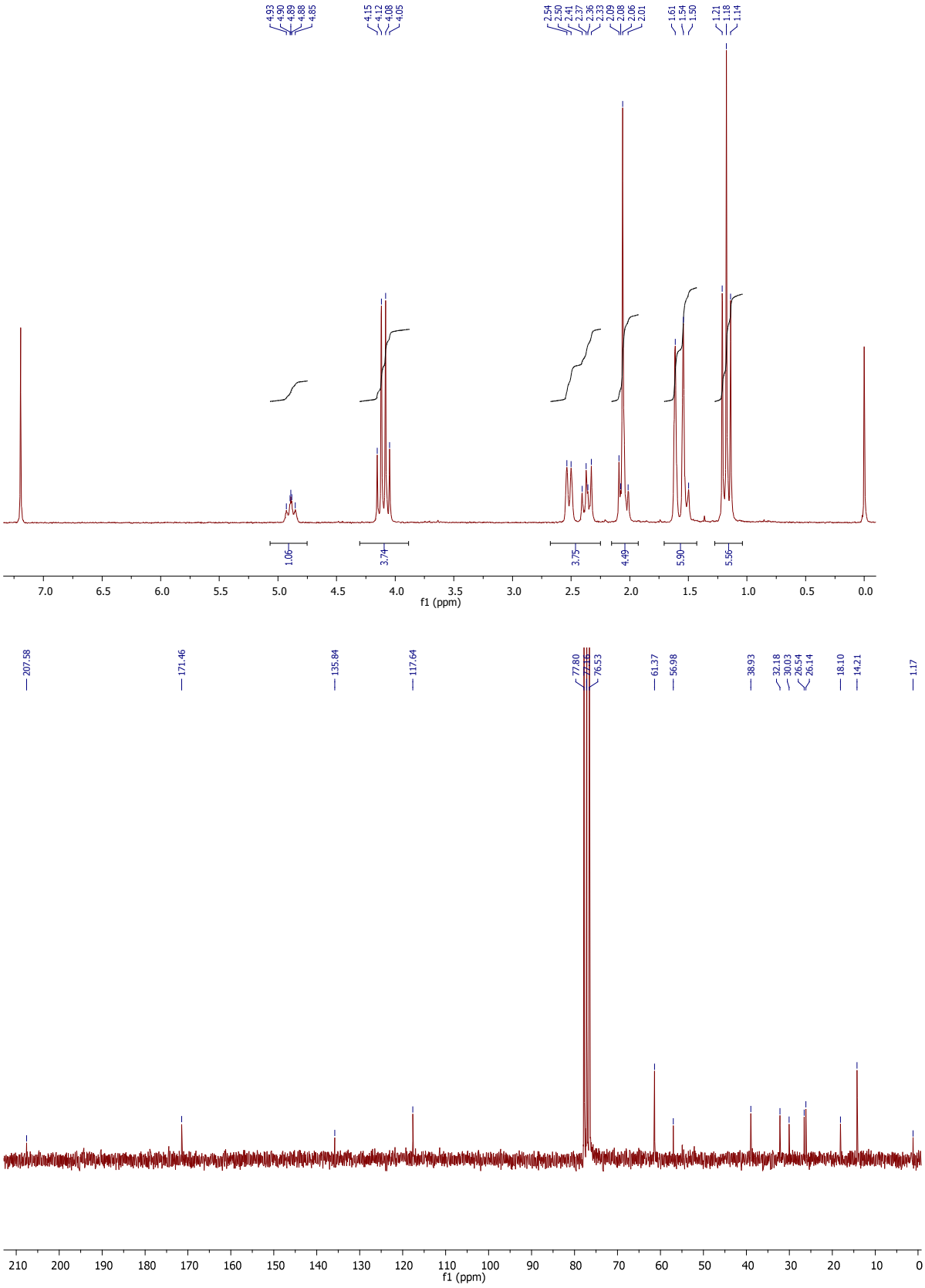
Ion at *m/z* 652.73 corresponds to [**4a** + $In(OTf)_2^+$]



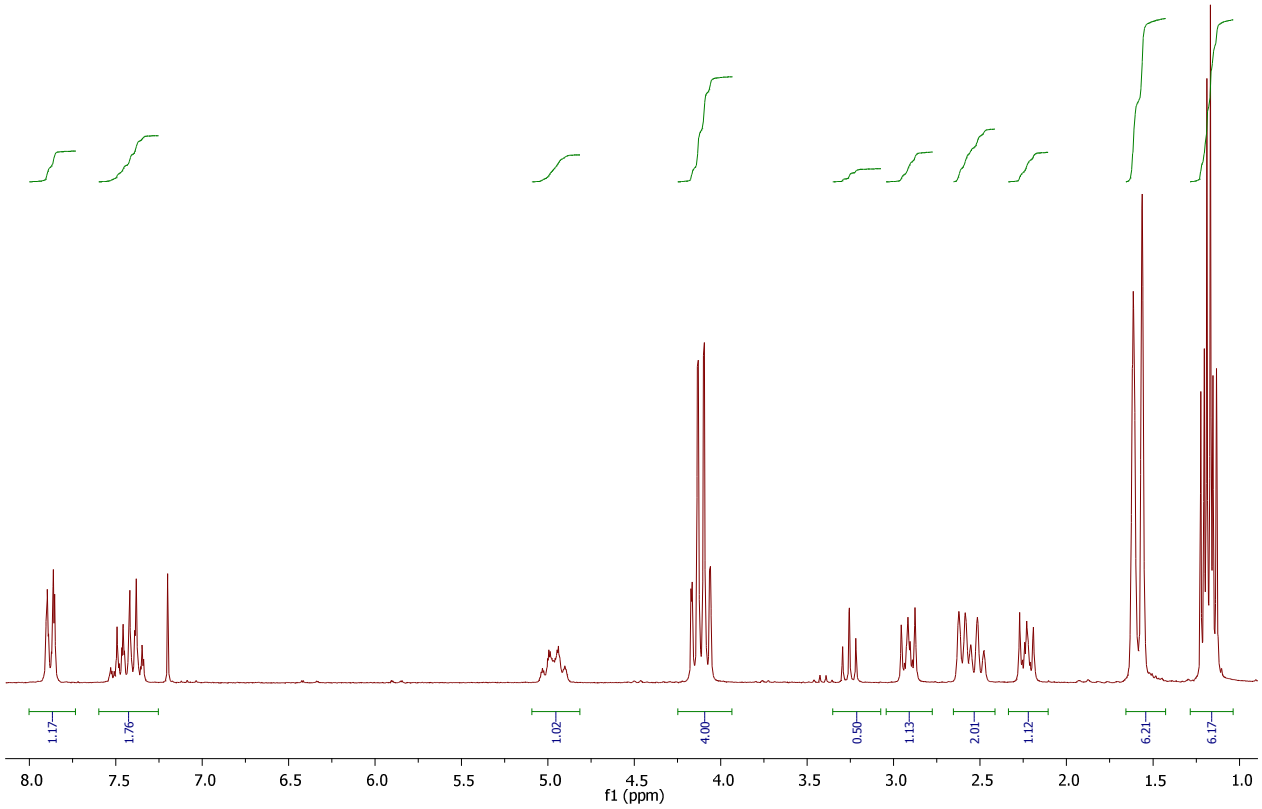
3. NMR spectra

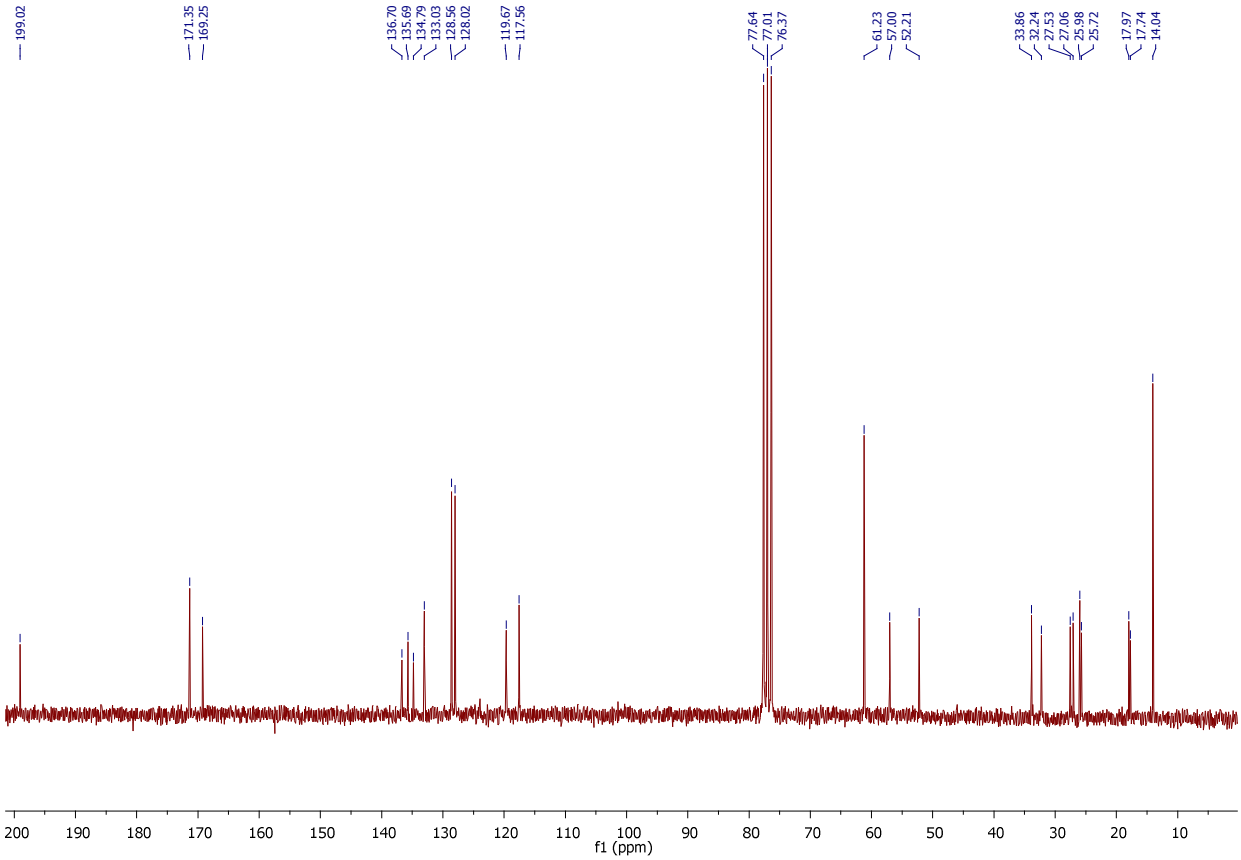
^{1}H and ^{13}C NMR spectra

Compound **1a**:

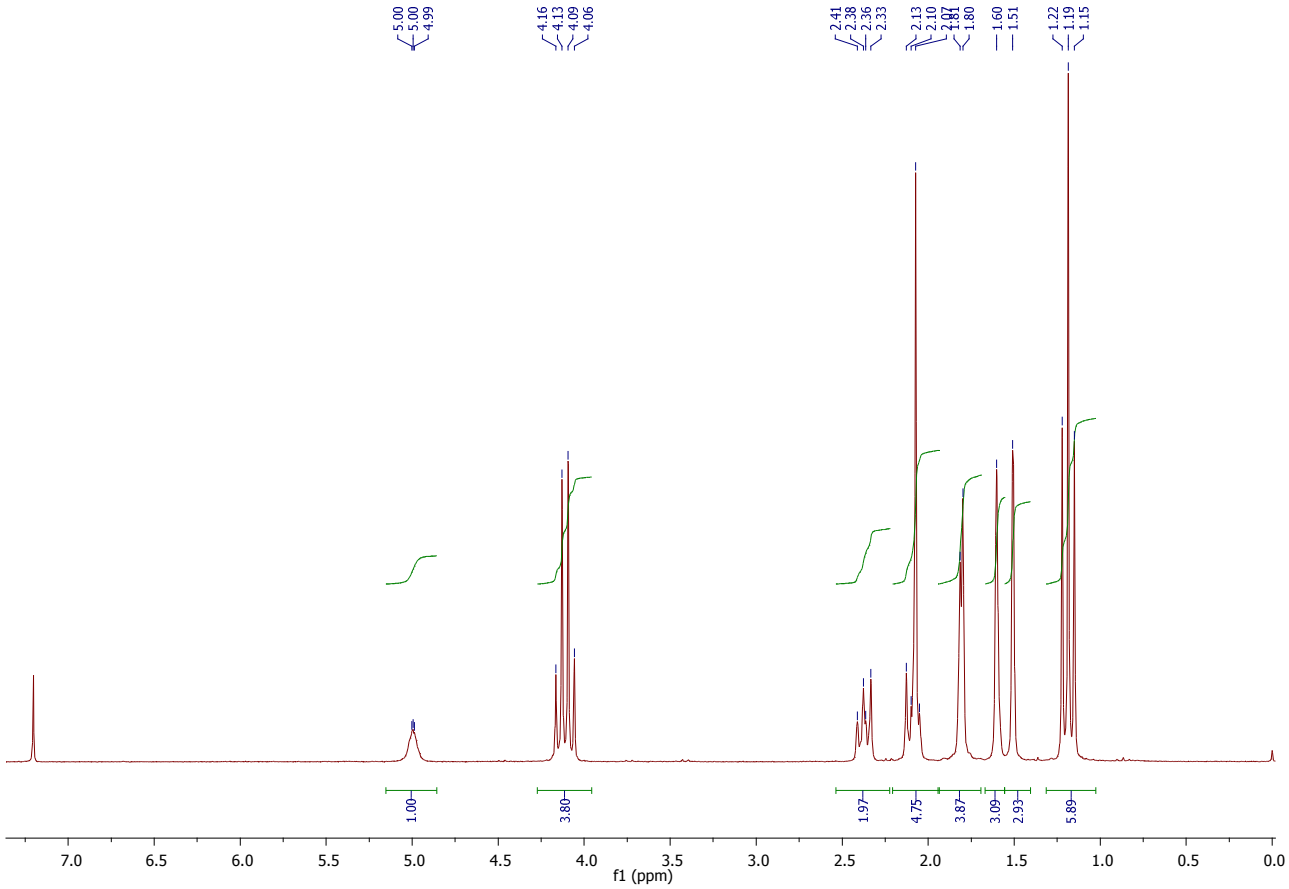


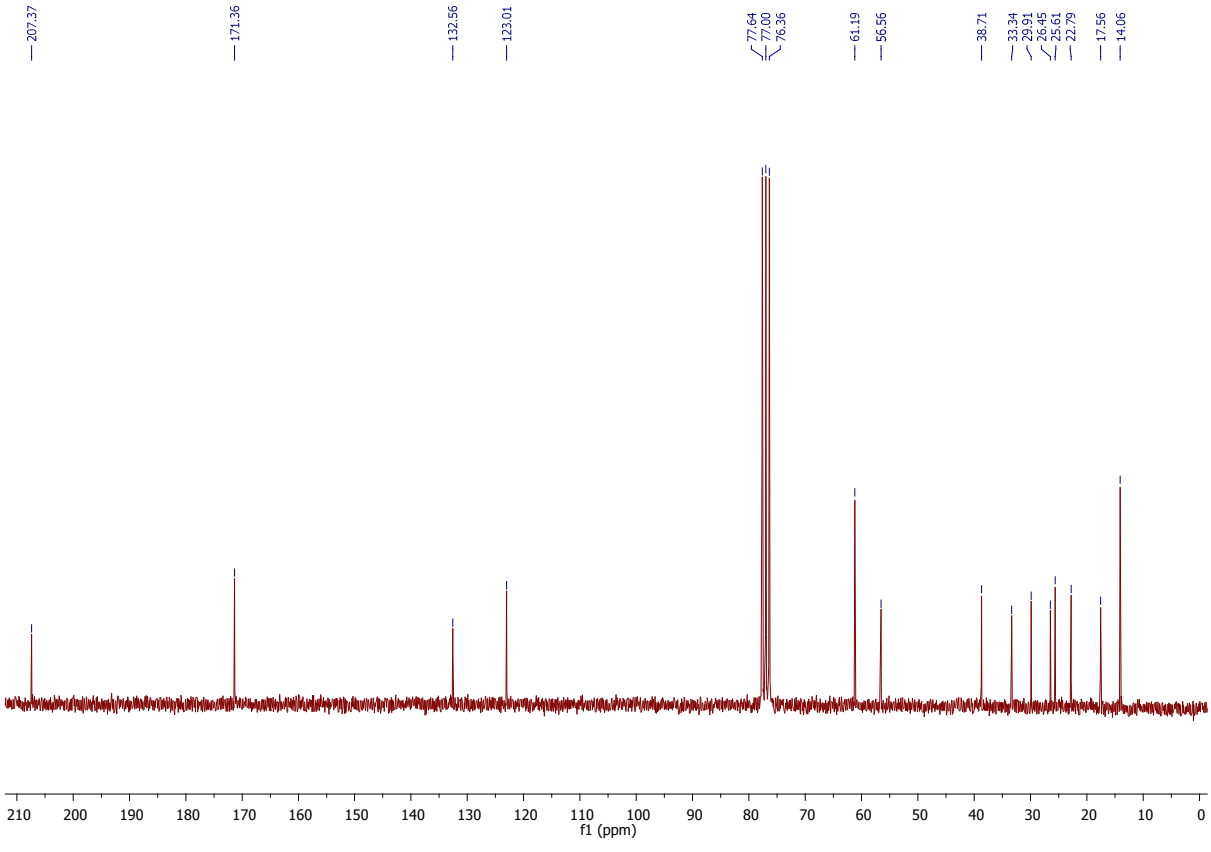
Compound **1b**:


1.17
1.76
1.02
4.00
0.50
1.13
2.01
1.12
6.21
6.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

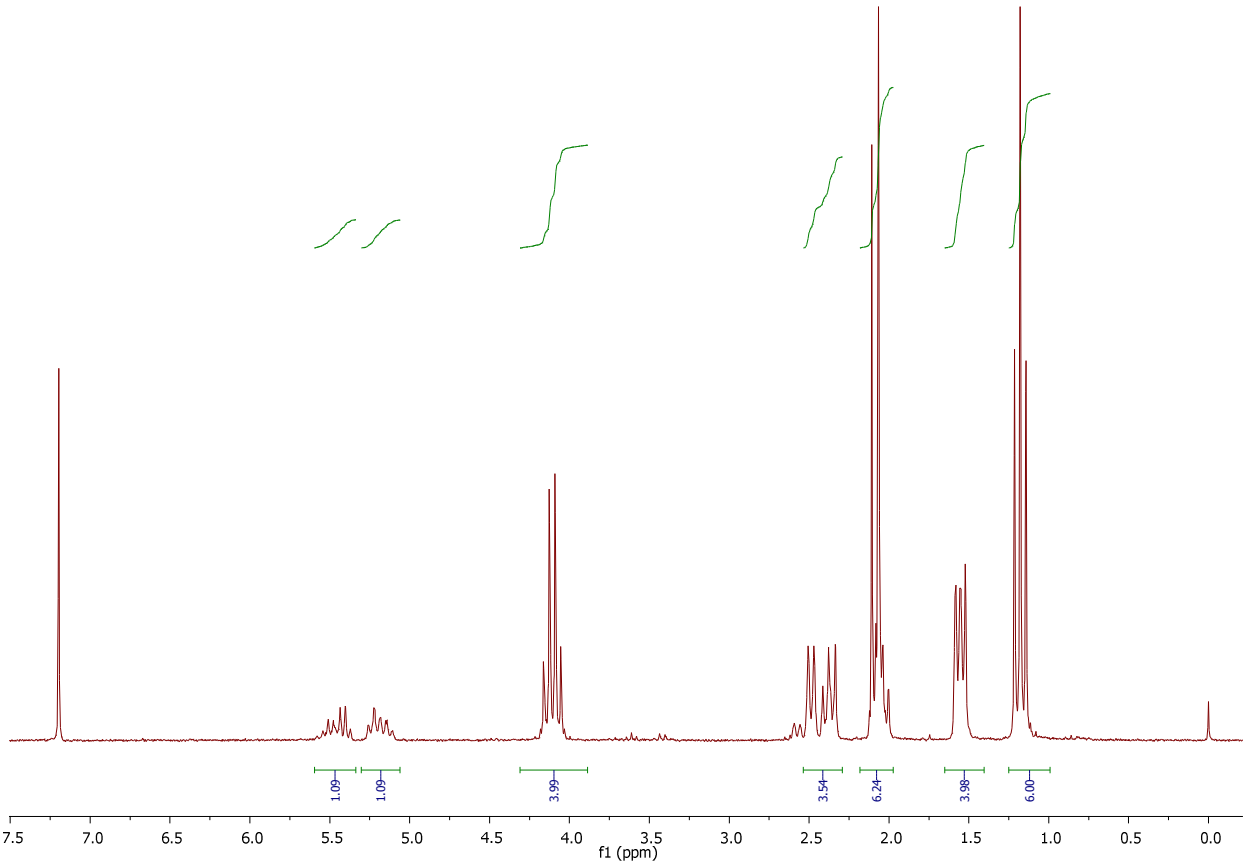

199.02
171.35
169.25
136.70
135.69
134.79
133.03
128.56
128.02
119.67
117.56
77.64
77.01
76.37
61.23
57.00
52.21
33.86
32.24
27.53
27.06
25.98
25.72
17.97
17.74
14.04
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

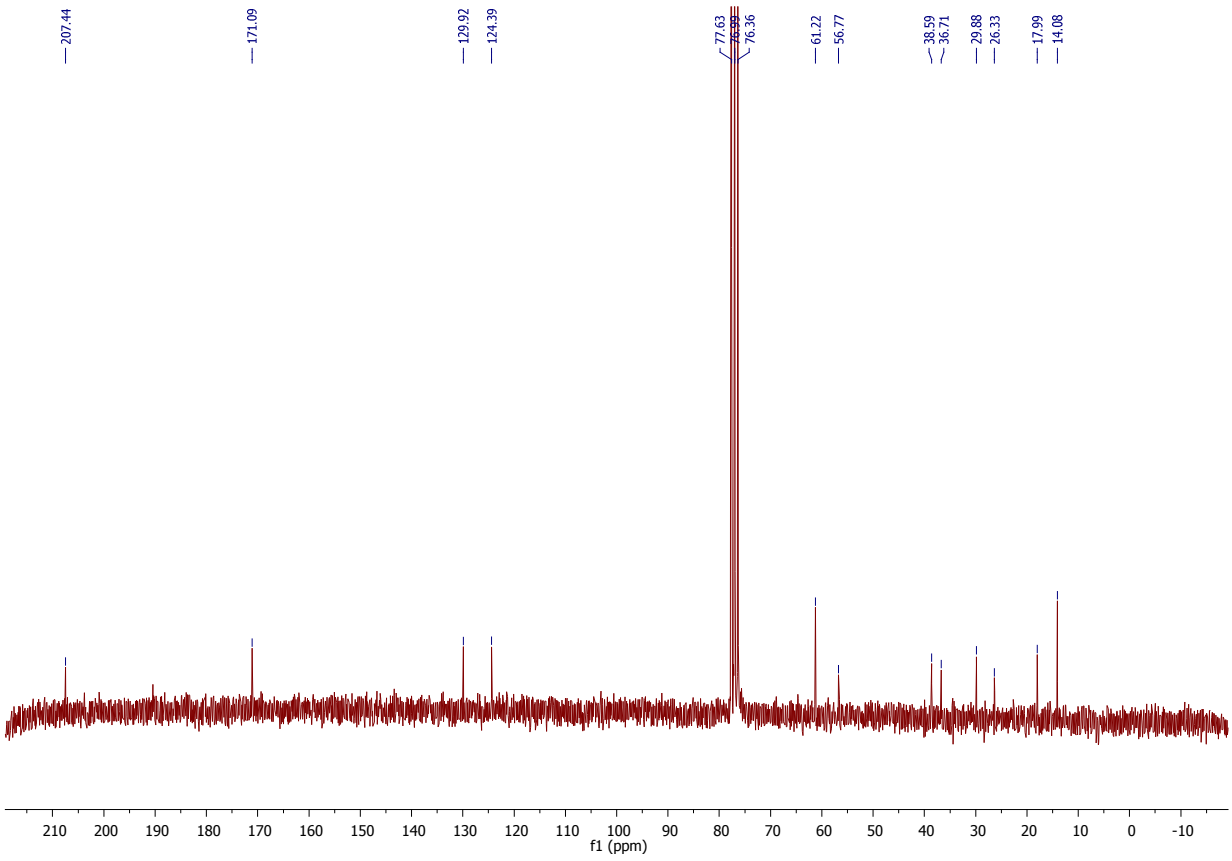
Compound **1c**:


5.00
5.00
4.99
4.16
4.13
4.09
4.06
2.41
2.38
2.36
2.33
2.13
2.10
2.07
1.81
1.80
1.60
1.51
1.22
1.19
1.15
1.00
3.80
1.97
4.75
3.87
3.09
2.93
5.89
f1 (ppm)

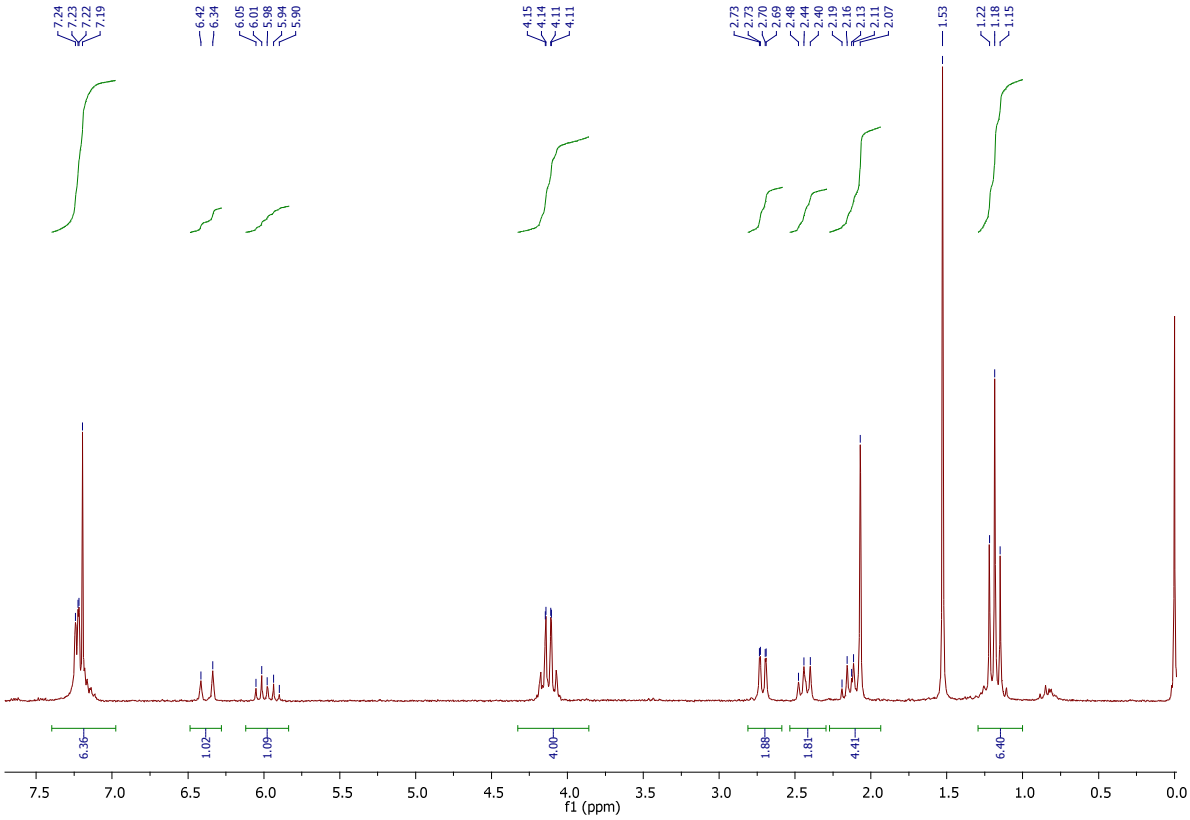

207.37
171.36
132.56
123.01
77.64
77.00
76.36
61.19
56.56
38.71
33.34
29.91
26.45
25.61
22.79
17.56
14.06
f1 (ppm)

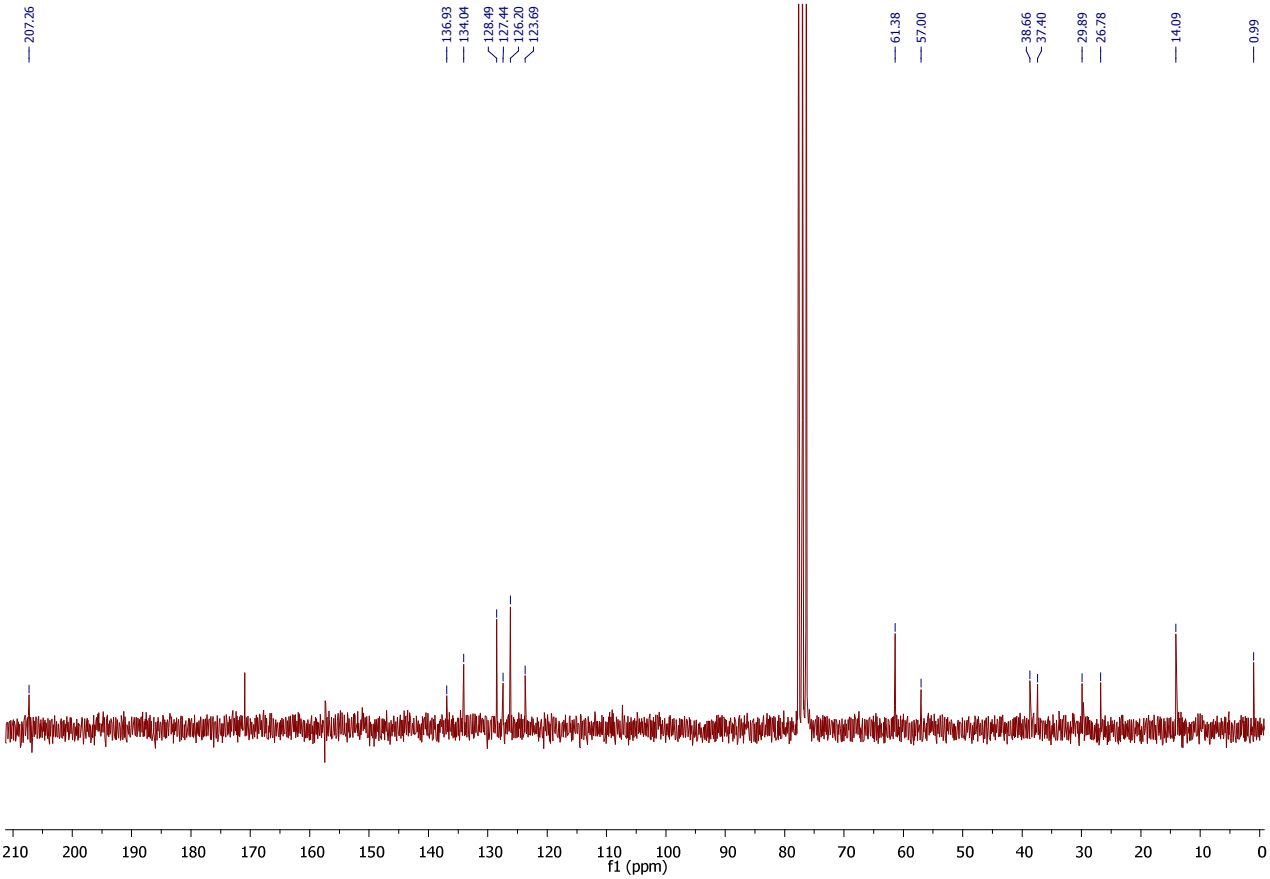
Compound **1d**:


1.09
1.09
3.99
3.54
6.24
3.98
6.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

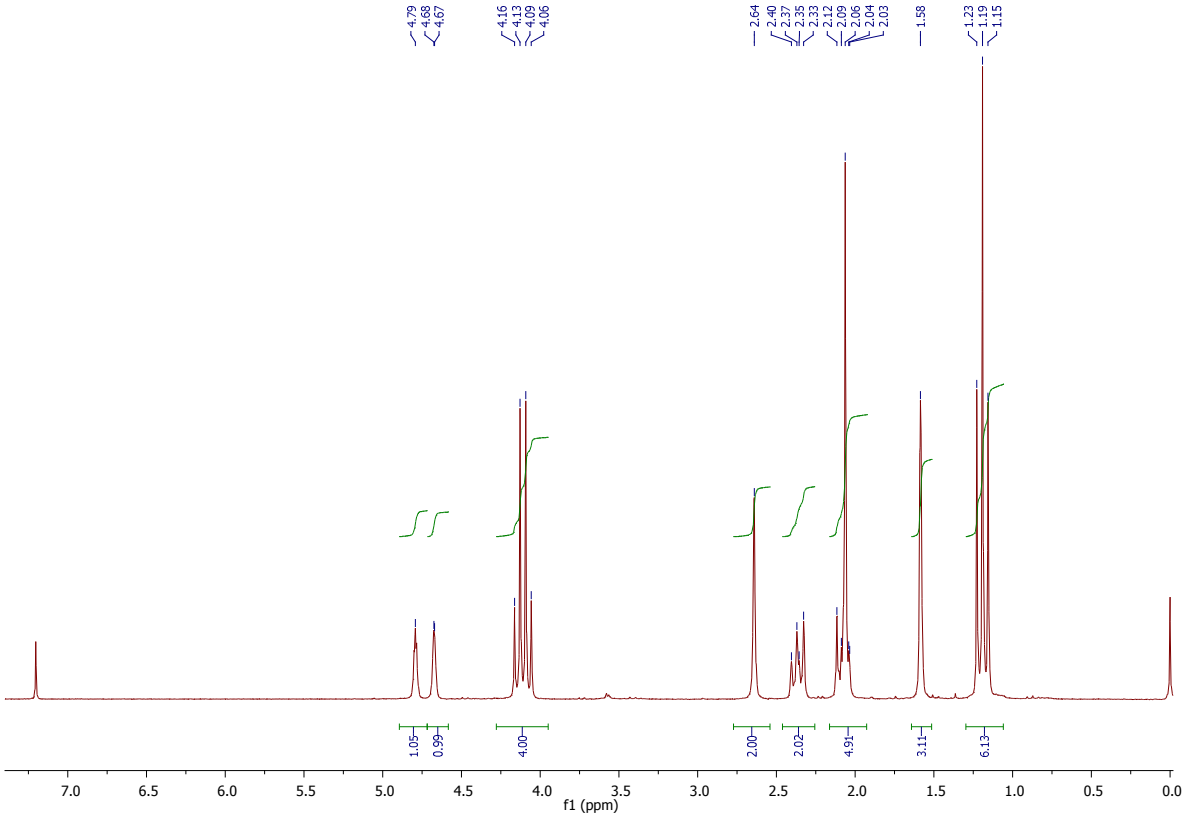

207.44
171.09
129.92
124.39
77.63
76.99
76.36
61.22
56.77
38.59
36.71
29.88
26.33
17.99
14.08
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

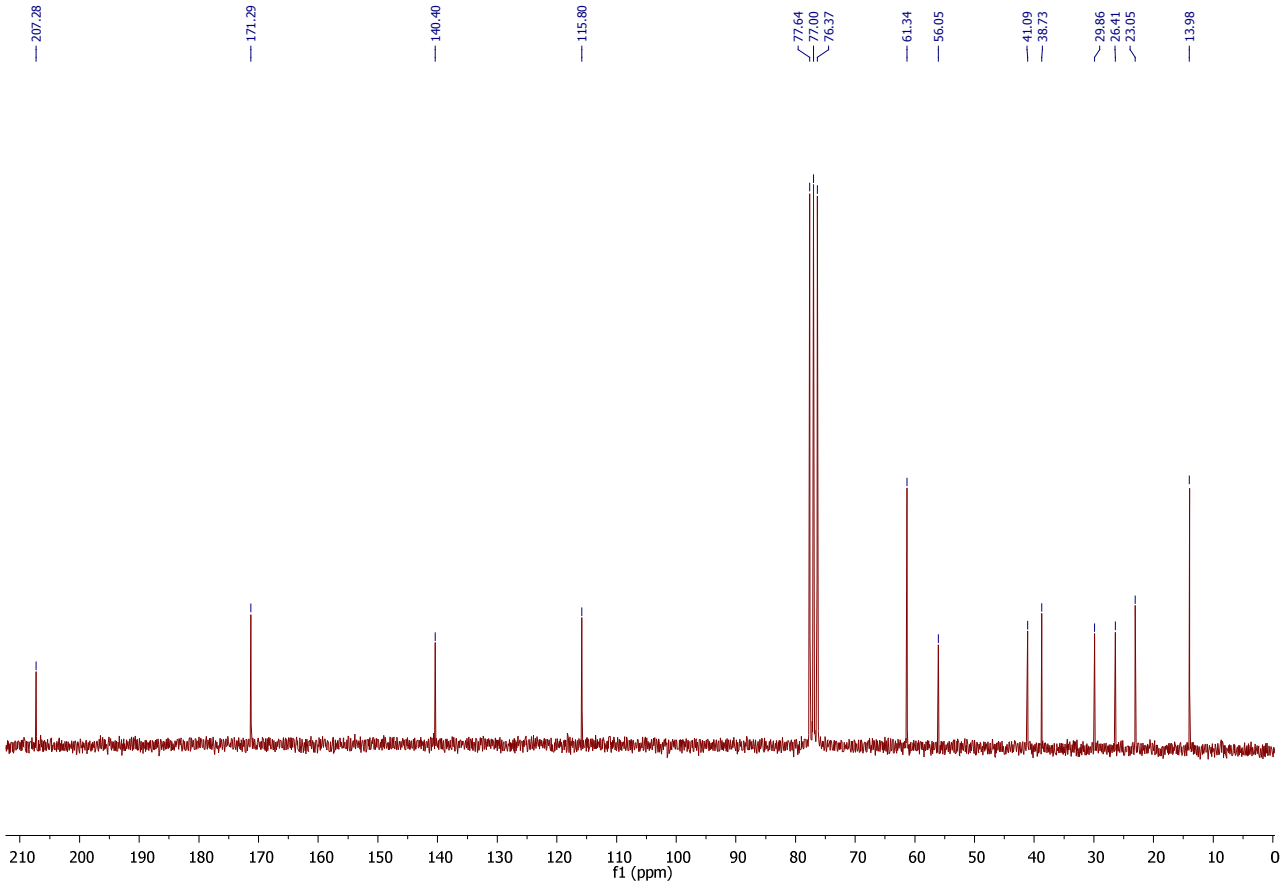
Compound **1e**:


7.24
7.23
7.22
7.19
6.42
6.34
6.05
6.01
5.98
5.94
5.90
4.15
4.14
4.11
4.11
2.73
2.73
2.70
2.69
2.48
2.44
2.40
2.19
2.16
2.13
2.11
2.07
1.53
1.22
1.18
1.15
6.36
1.02
1.09
4.00
1.88
1.81
4.41
6.40
f1 (ppm)

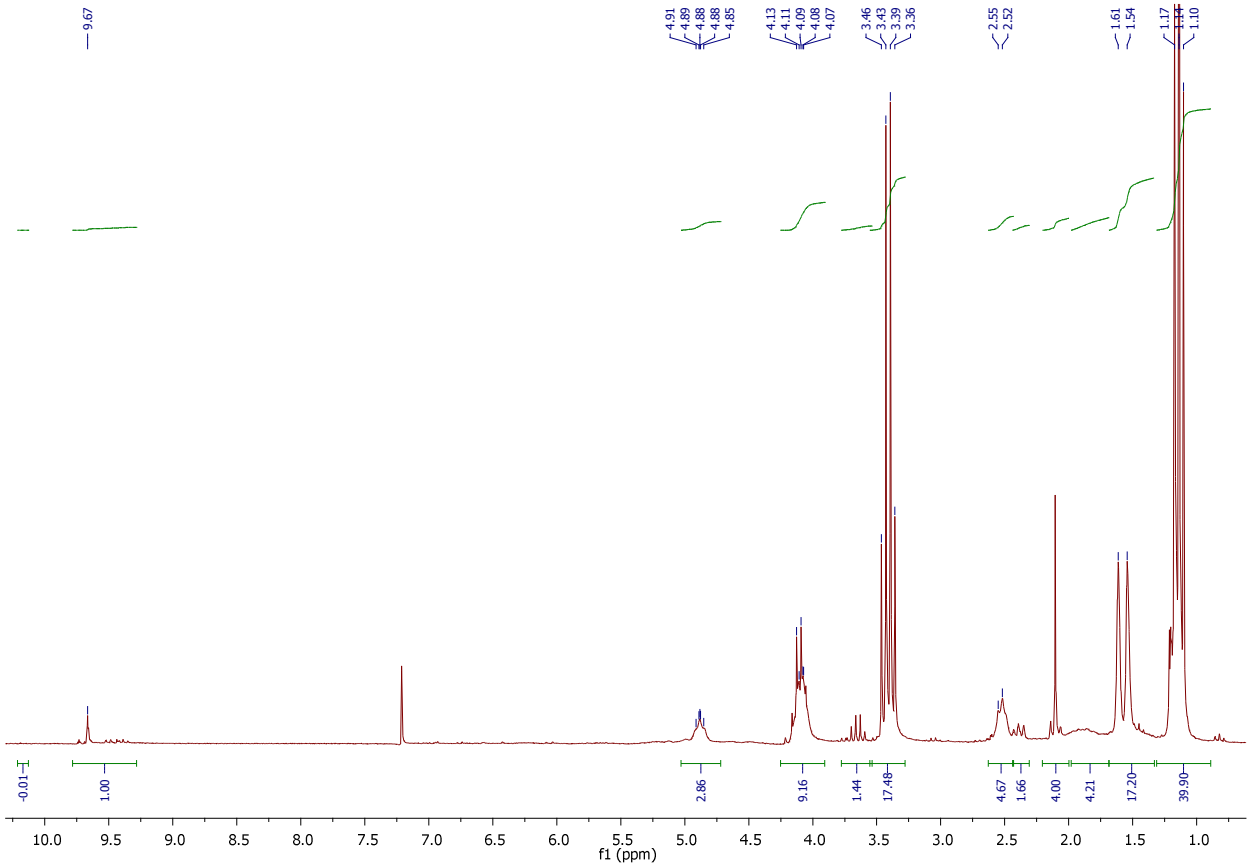

207.26
136.93
134.04
128.49
127.44
126.20
123.69
61.38
57.00
38.66
37.40
29.89
26.78
14.09
0.99
f1 (ppm)

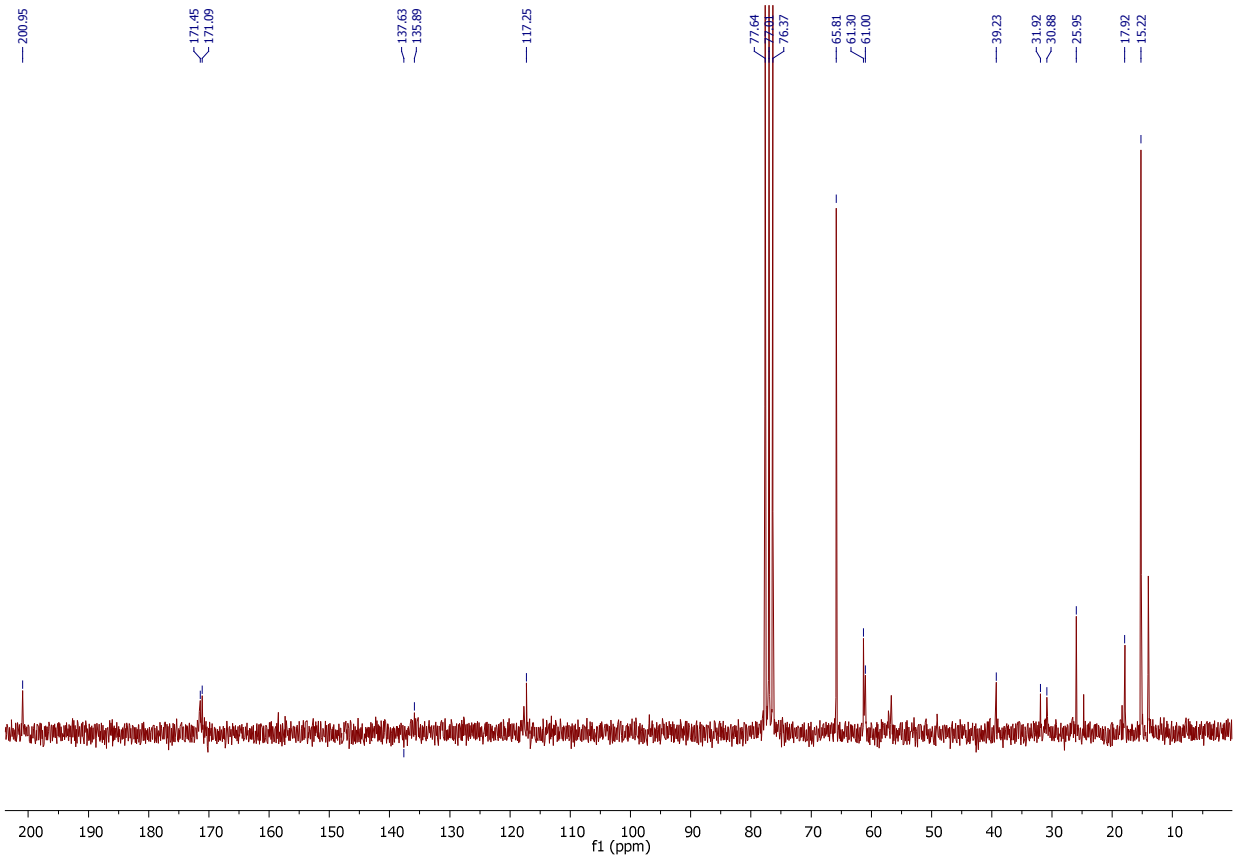
Compound **1f**:


4.79
4.68
4.67
4.16
4.13
4.09
4.06
2.64
2.40
2.37
2.35
2.33
2.12
2.09
2.06
2.04
2.03
1.58
1.23
1.19
1.15
1.05
0.99
4.00
2.00
2.02
4.91
3.11
6.13
f1 (ppm)

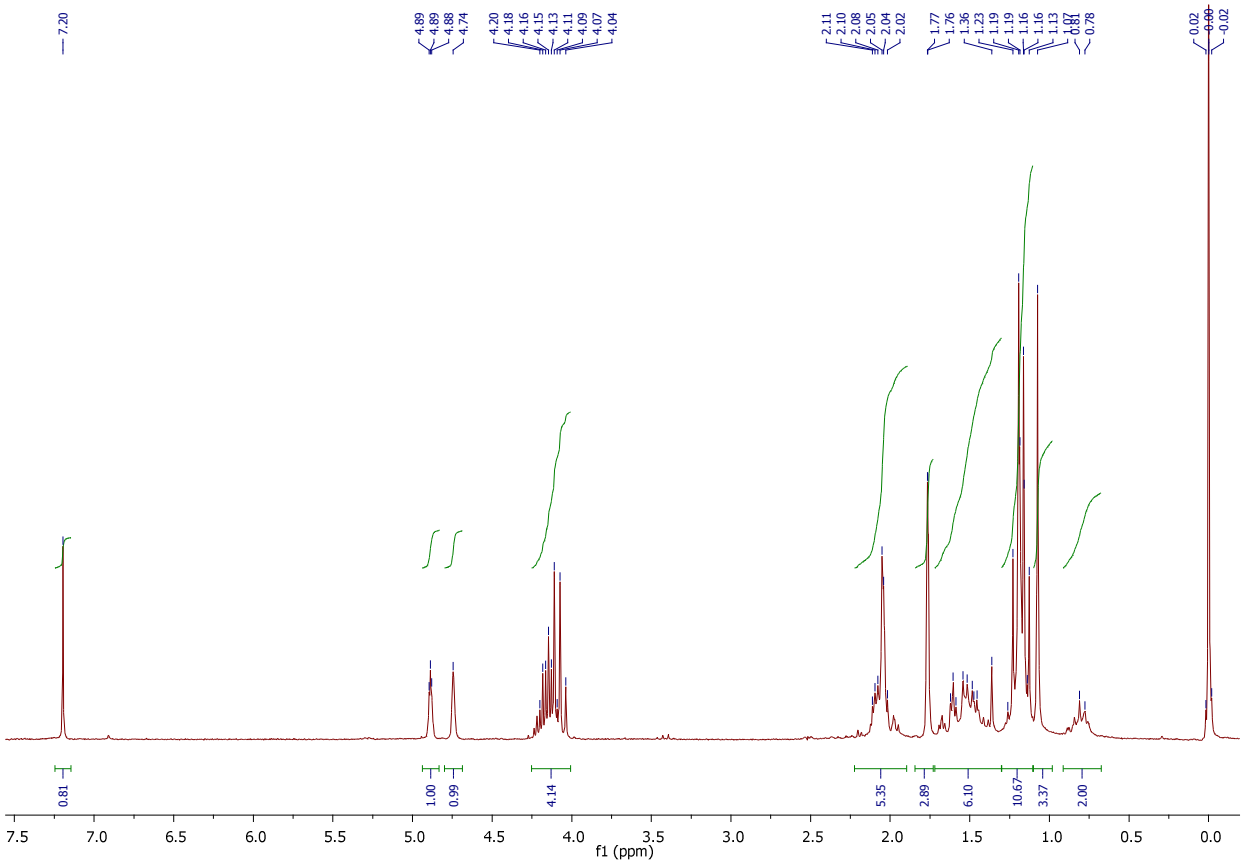

207.28
171.29
140.40
115.80
77.64
77.00
76.37
61.34
56.05
41.09
38.73
29.86
26.41
23.05
13.98
f1 (ppm)

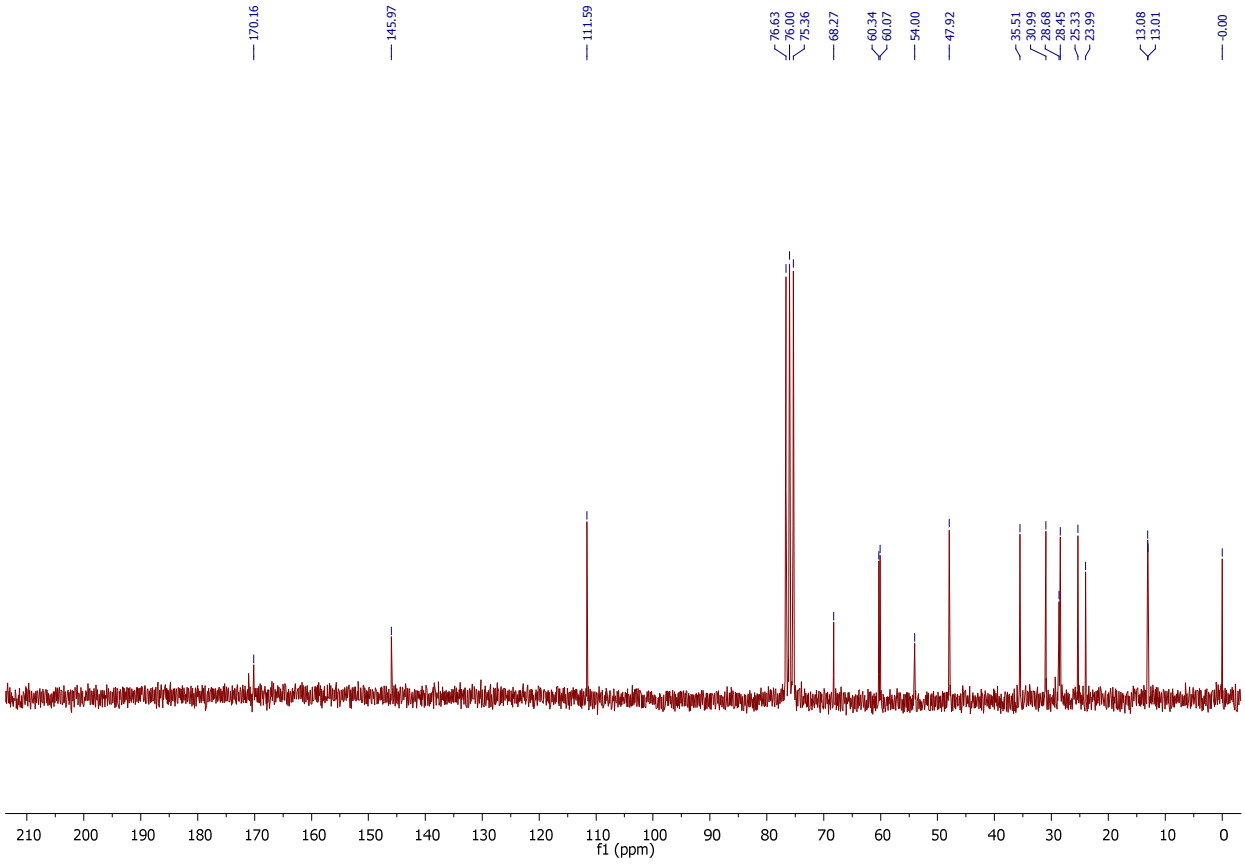
Compound **1g**:


9.67
4.91
4.89
4.88
4.88
4.85
4.13
4.11
4.09
4.08
4.07
3.46
3.43
3.39
3.36
2.55
2.52
1.61
1.54
1.17
1.14
1.10
-0.01
1.00
2.86
9.16
1.44
17.48
4.67
1.66
4.00
4.21
17.20
39.90
f1 (ppm)

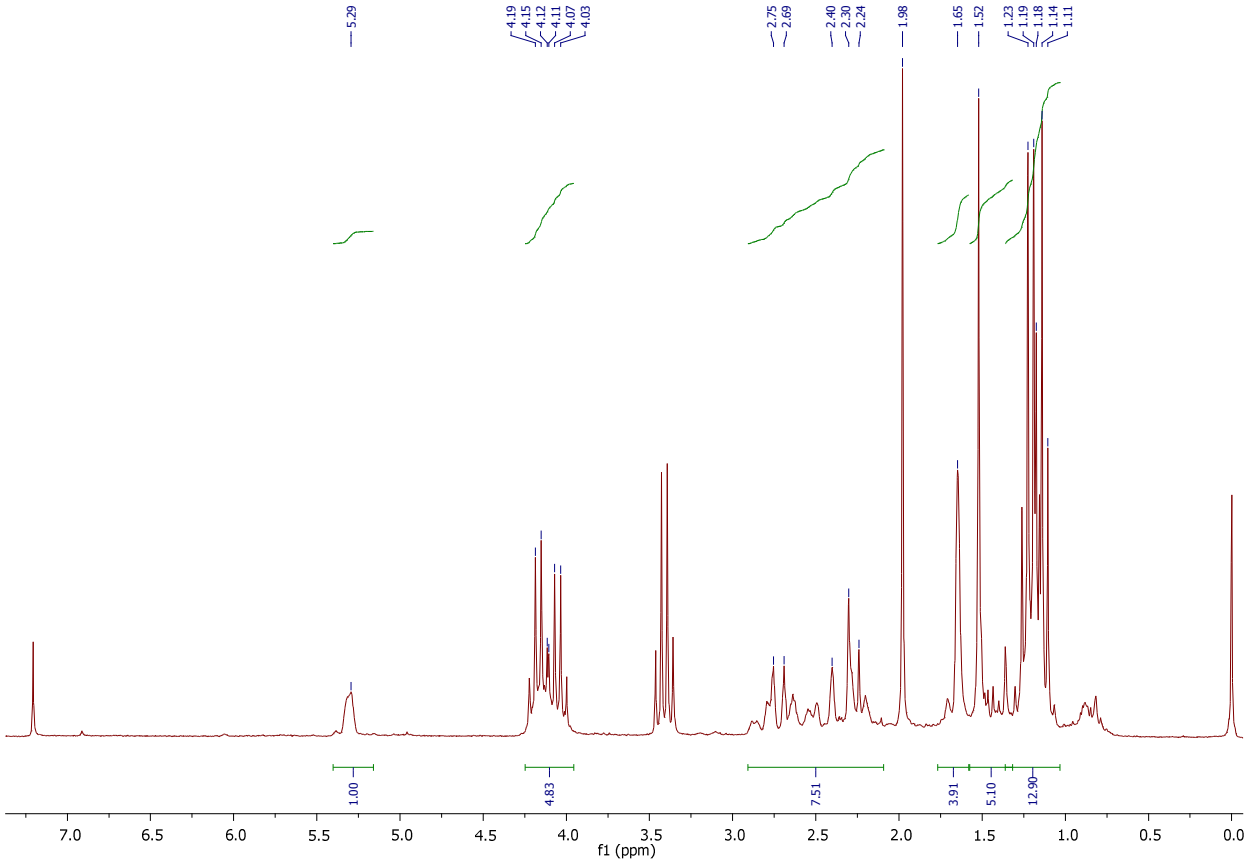

200.95
171.45
171.09
137.63
135.89
117.25
77.64
77.00
76.37
65.81
61.30
61.00
39.23
31.92
30.88
25.95
17.92
15.22
f1 (ppm)

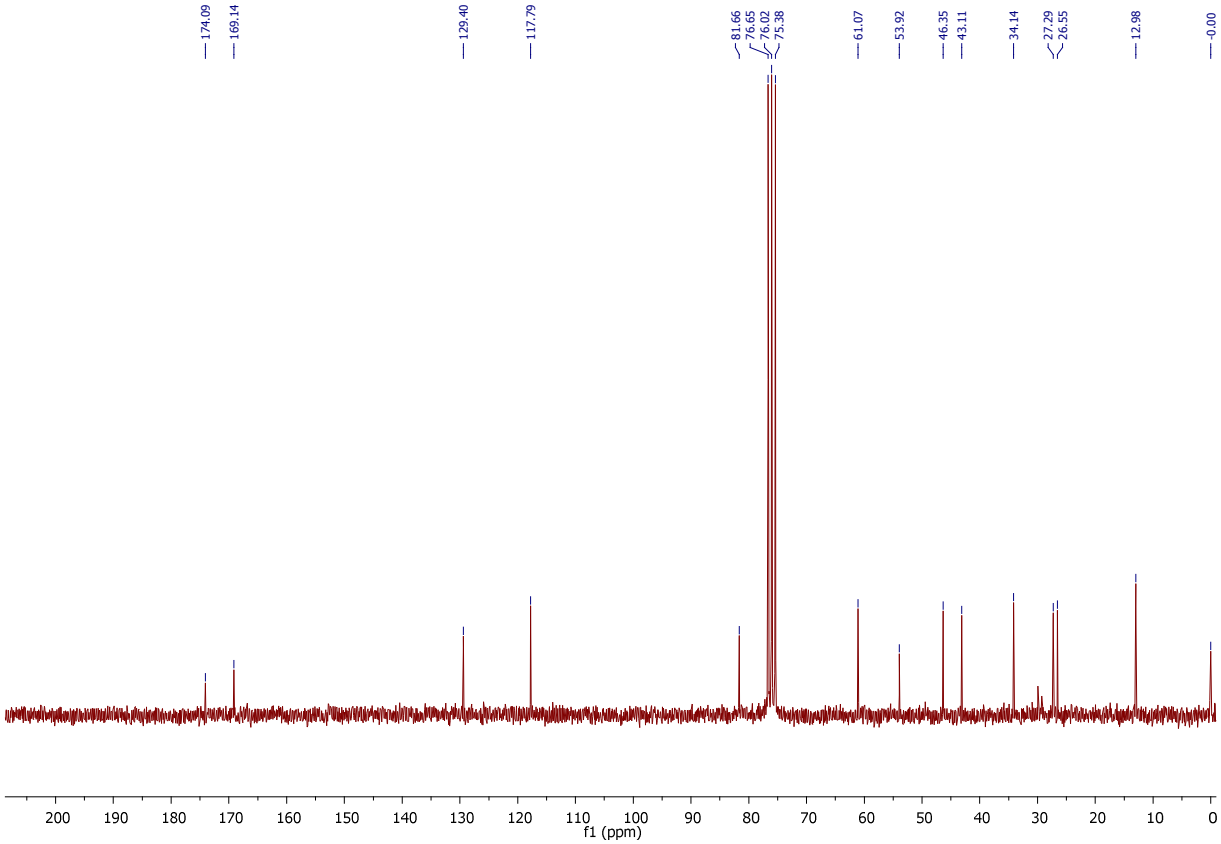
Compound **2a**:


7.20
4.89
4.89
4.88
4.74
4.20
4.18
4.16
4.15
4.13
4.11
4.09
4.07
4.04
2.11
2.10
2.08
2.05
2.04
2.02
1.77
1.76
1.36
1.23
1.19
1.19
1.16
1.16
1.13
0.87
0.87
0.78
0.02
0.00
-0.02
0.81
1.00
0.99
4.14
5.35
2.89
6.10
10.67
3.37
2.00
f1 (ppm)

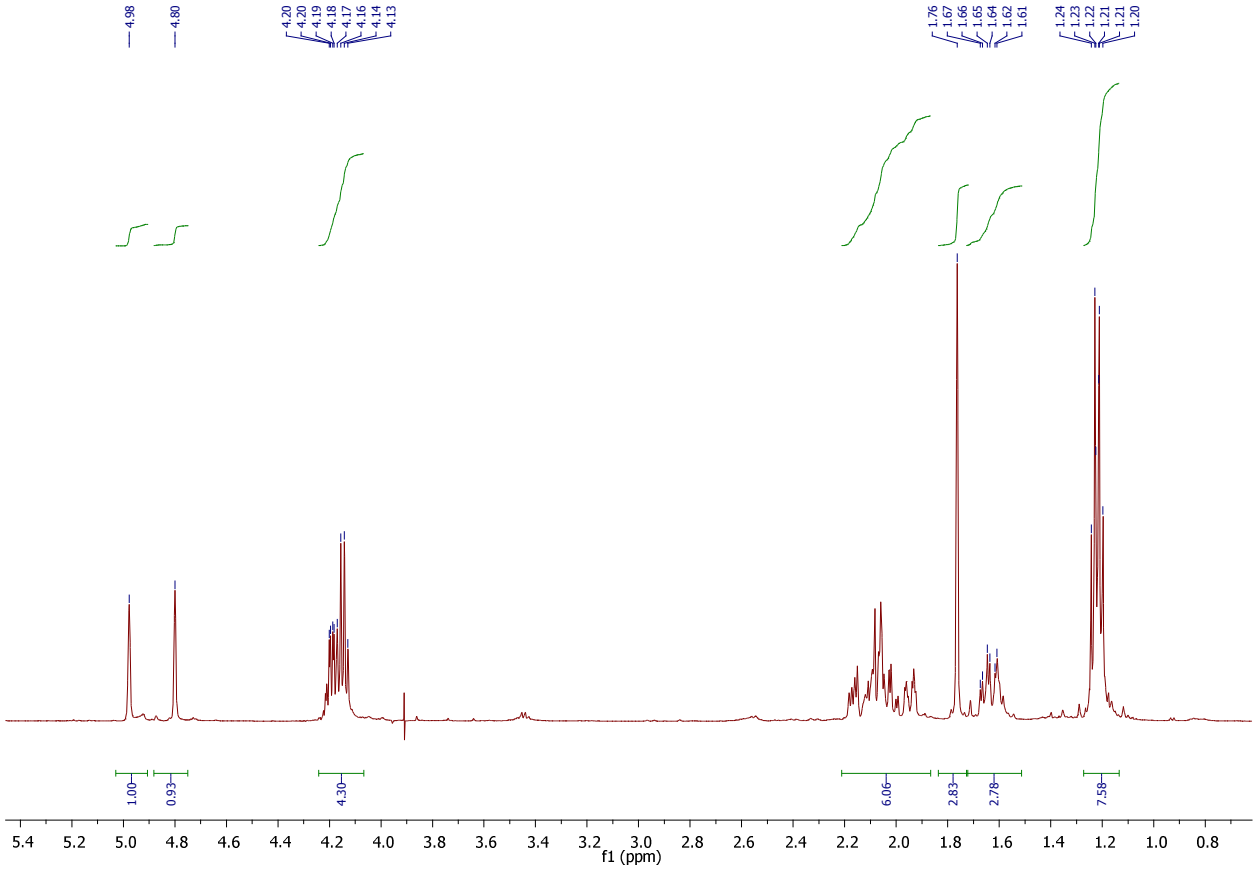

170.16
145.97
111.59
76.63
76.00
75.36
68.27
60.34
60.07
54.00
47.92
35.51
30.99
28.68
28.45
25.33
23.99
13.08
13.01
-0.00
f1 (ppm)

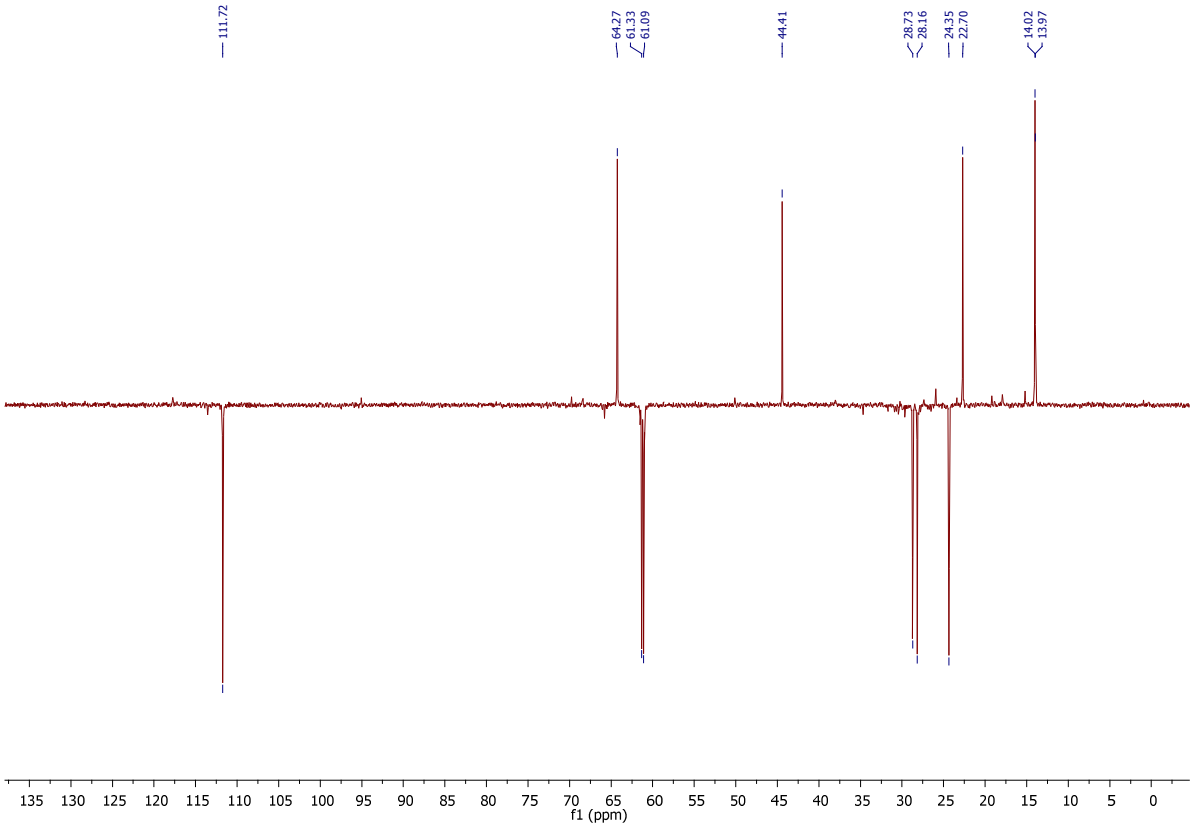
Compound **2f**:


5.29
4.19
4.15
4.12
4.11
4.07
4.03
2.75
2.69
2.40
2.30
2.24
1.98
1.65
1.52
1.23
1.19
1.18
1.14
1.11
1.00
4.83
7.51
3.91
5.10
12.90
f1 (ppm)

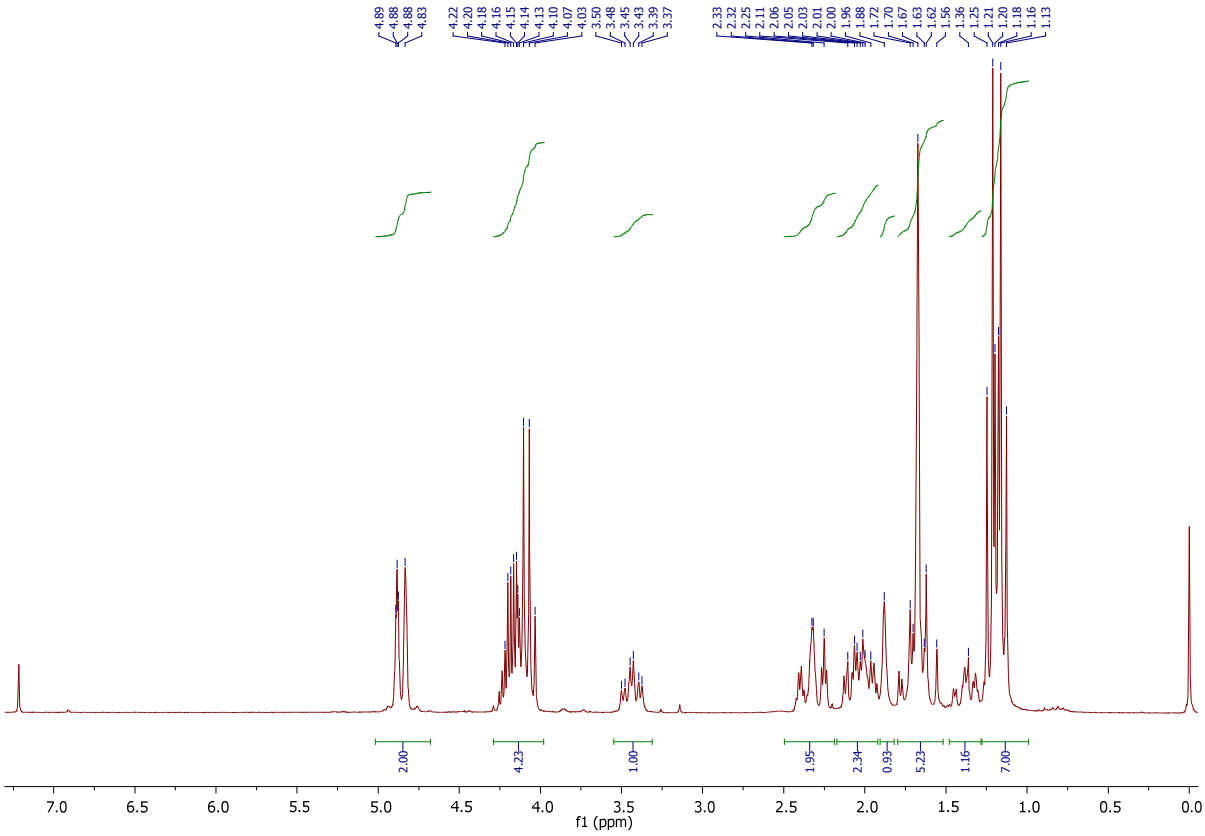

174.09
169.14
129.40
117.79
81.66
76.65
76.02
75.38
61.07
53.92
46.35
43.11
34.14
27.29
26.55
12.98
-0.00
f1 (ppm)

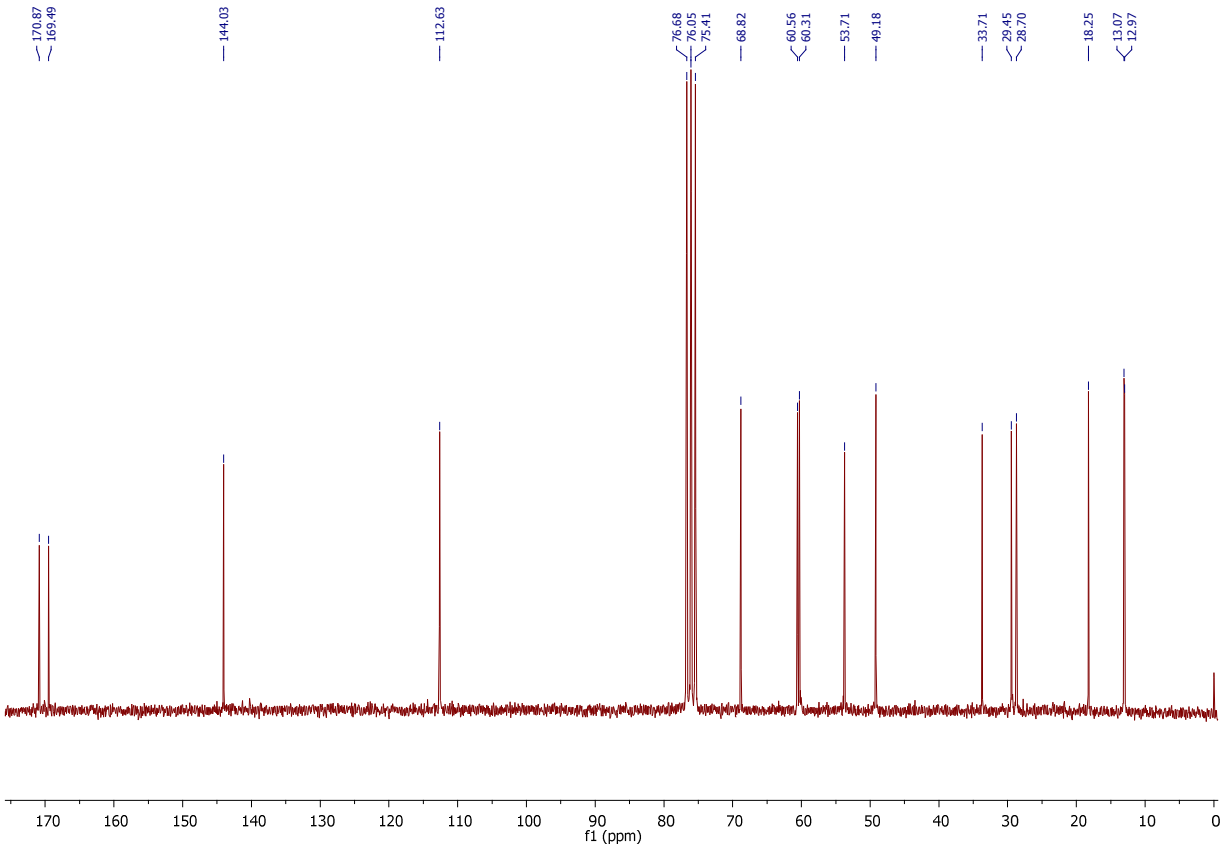
Compound **2g**-*cis*,



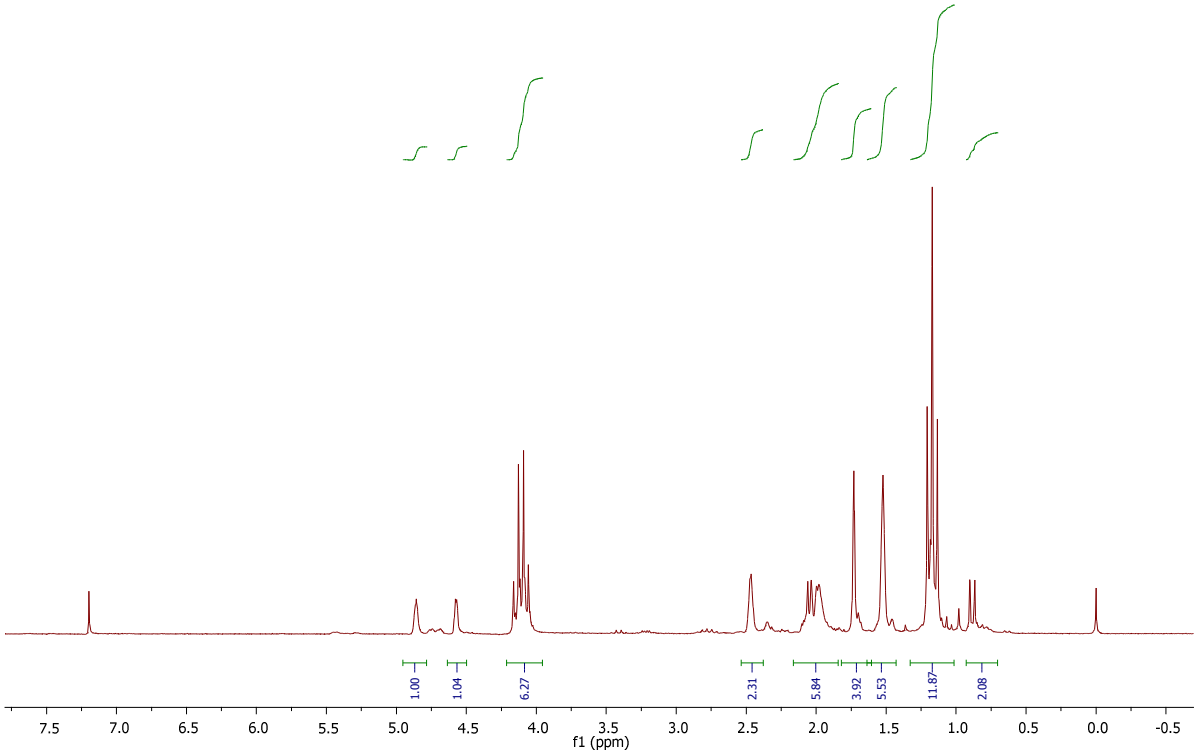


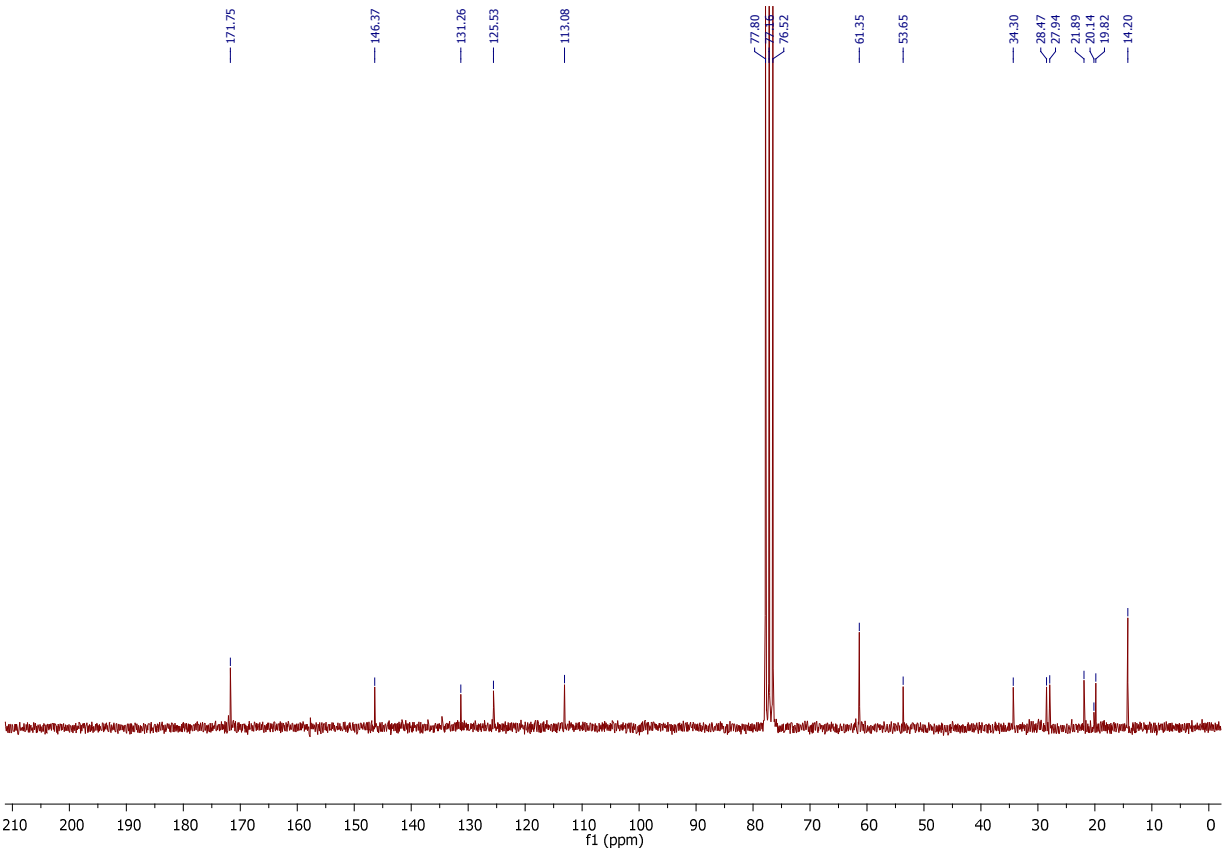
Compound **2g**-*trans*:



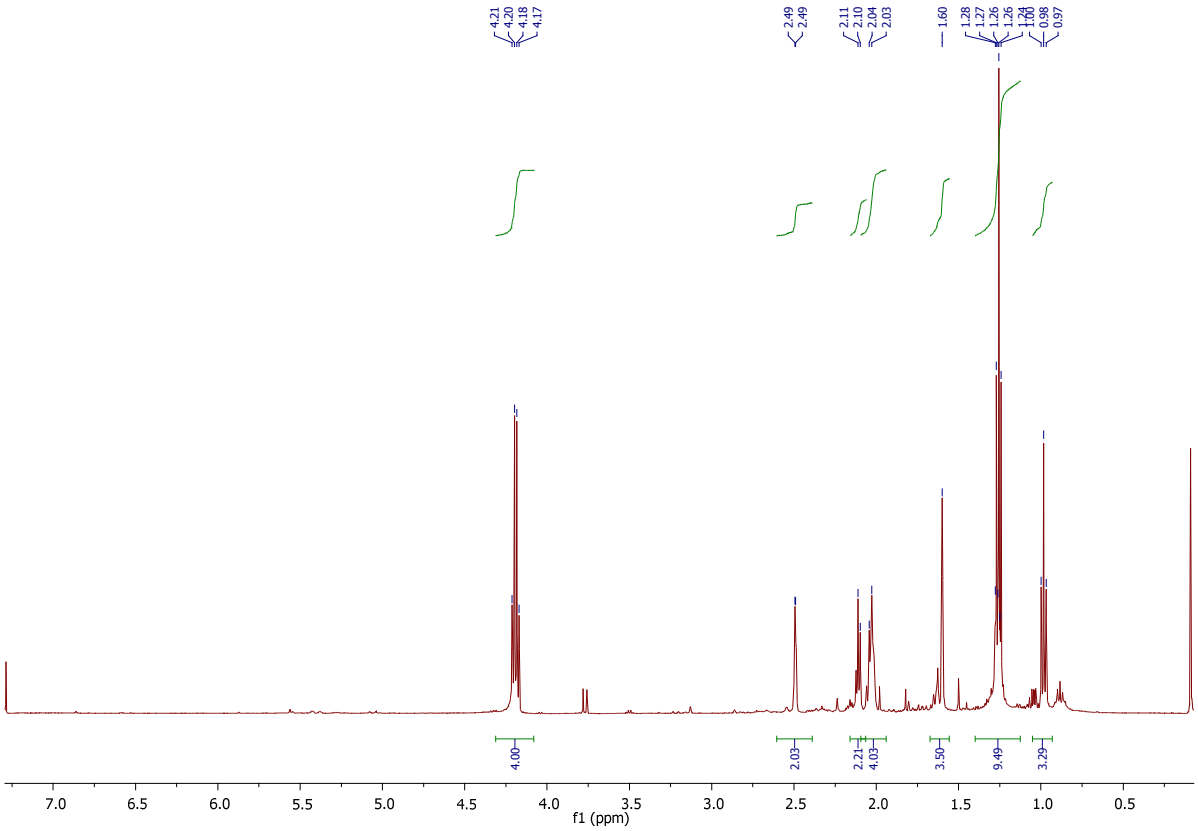


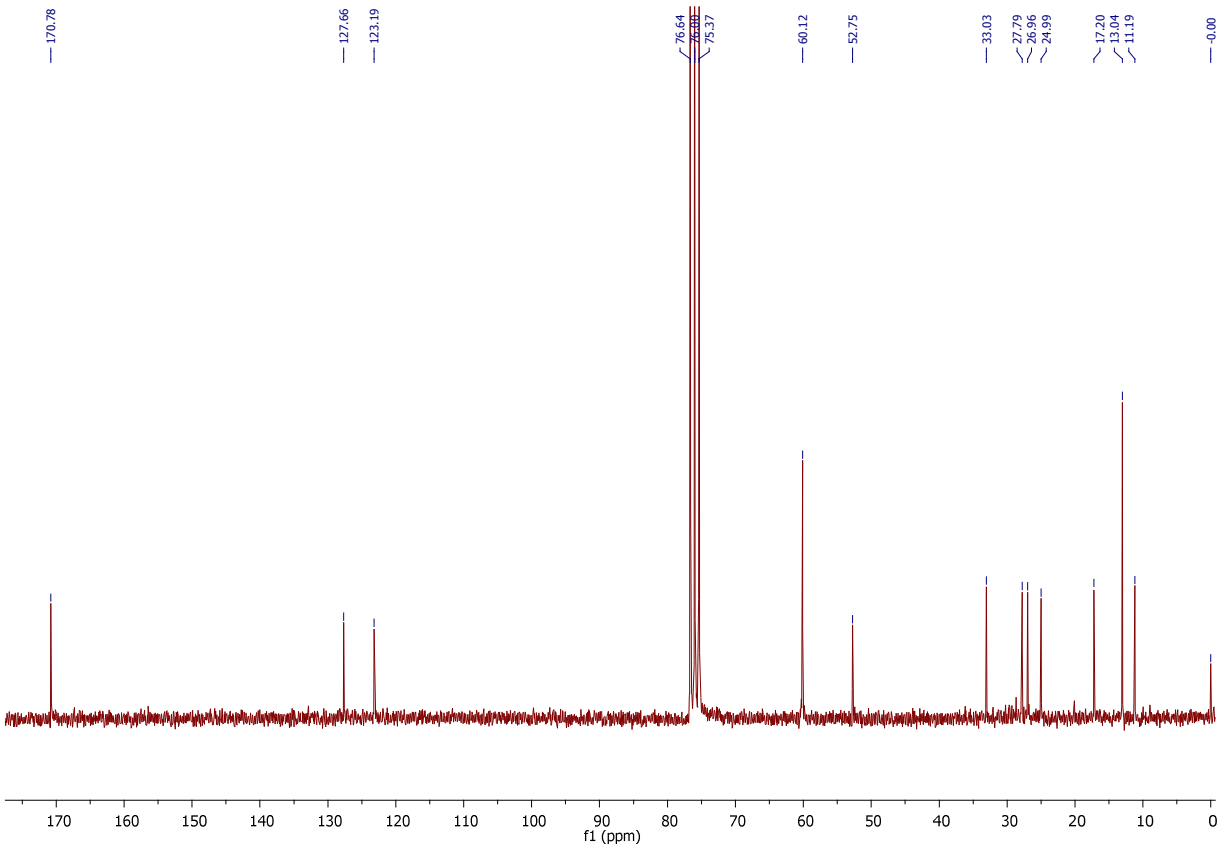
Compound **3a**:


1.00
1.04
6.27
2.31
5.84
3.92
5.53
11.87
2.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

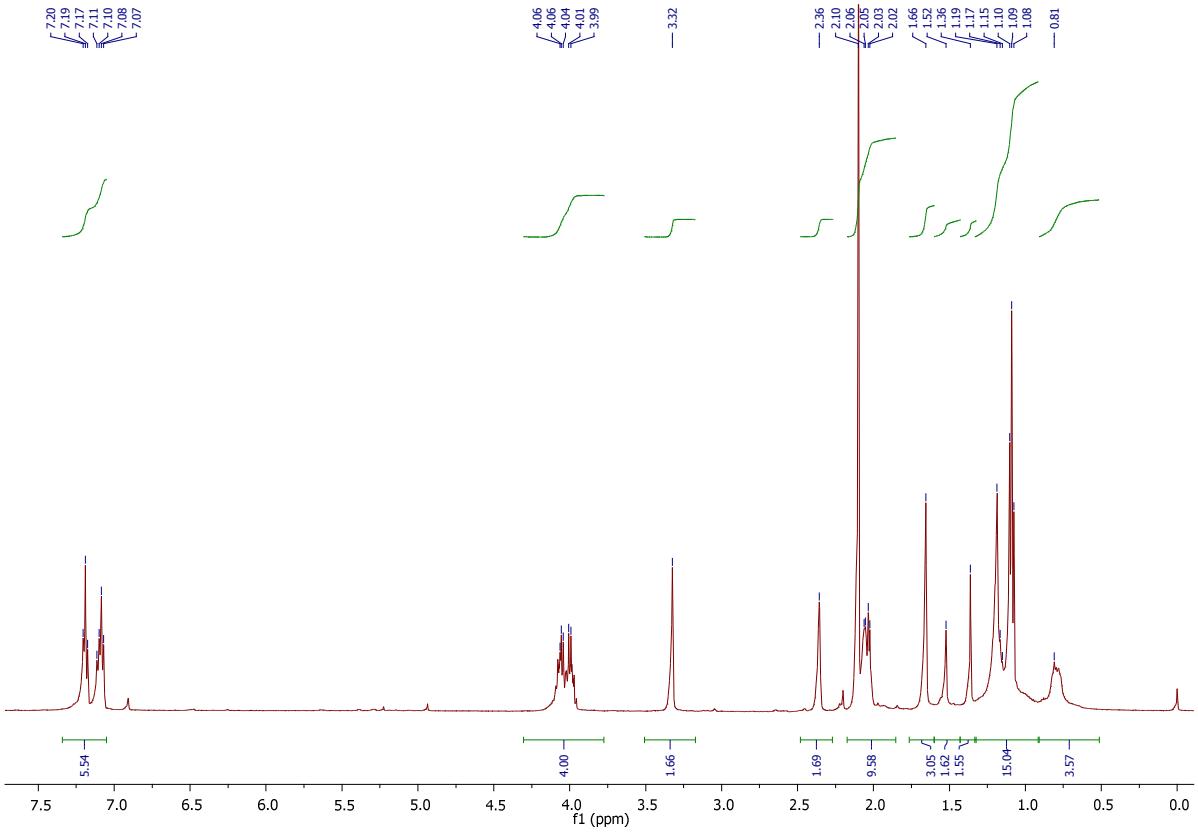

171.75
146.37
131.26
125.53
113.08
77.80
77.16
76.52
61.35
53.65
34.30
28.47
27.94
21.89
20.14
19.82
14.20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

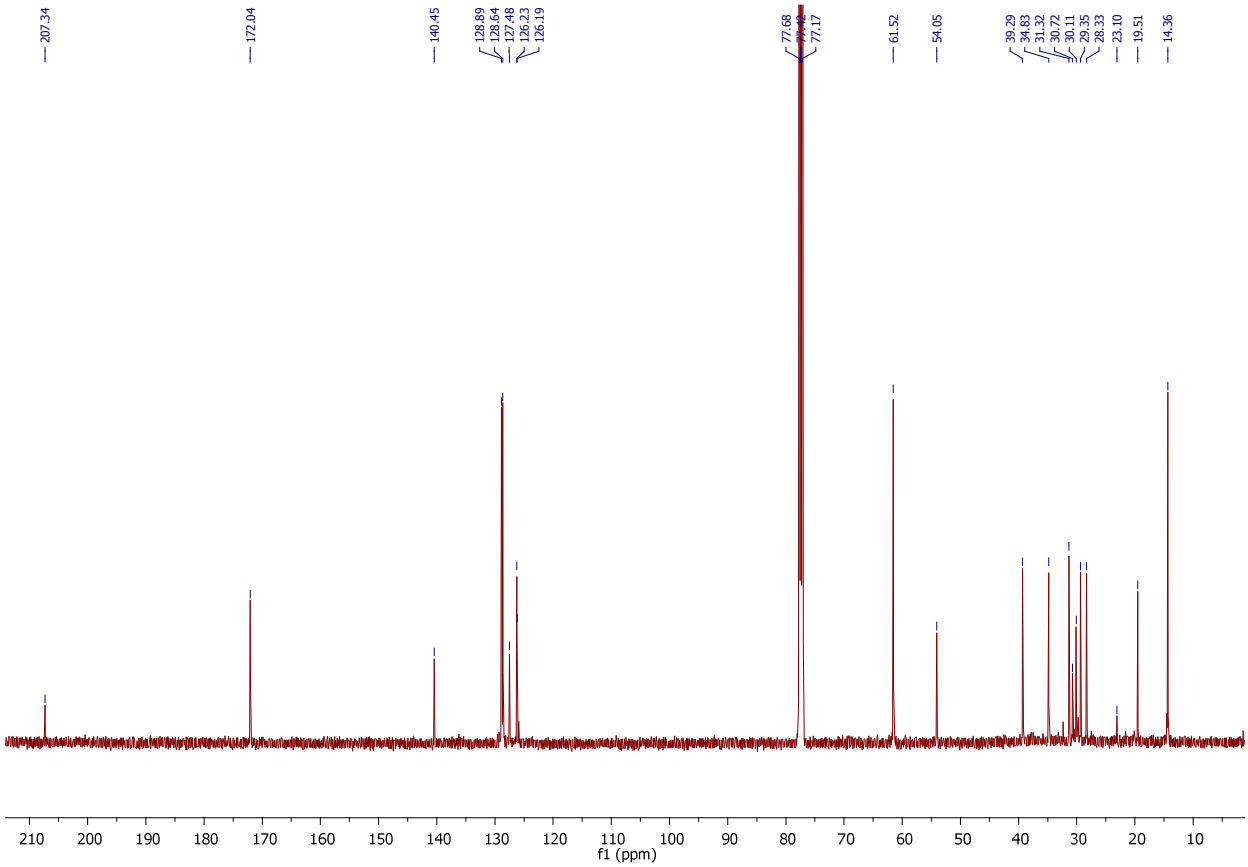
Compound **3d**:


4.21
4.20
4.18
4.17
2.49
2.49
2.11
2.10
2.04
2.03
1.60
1.28
1.27
1.26
1.26
1.00
0.98
0.97
4.00
2.03
2.21
4.03
3.50
9.49
3.29
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

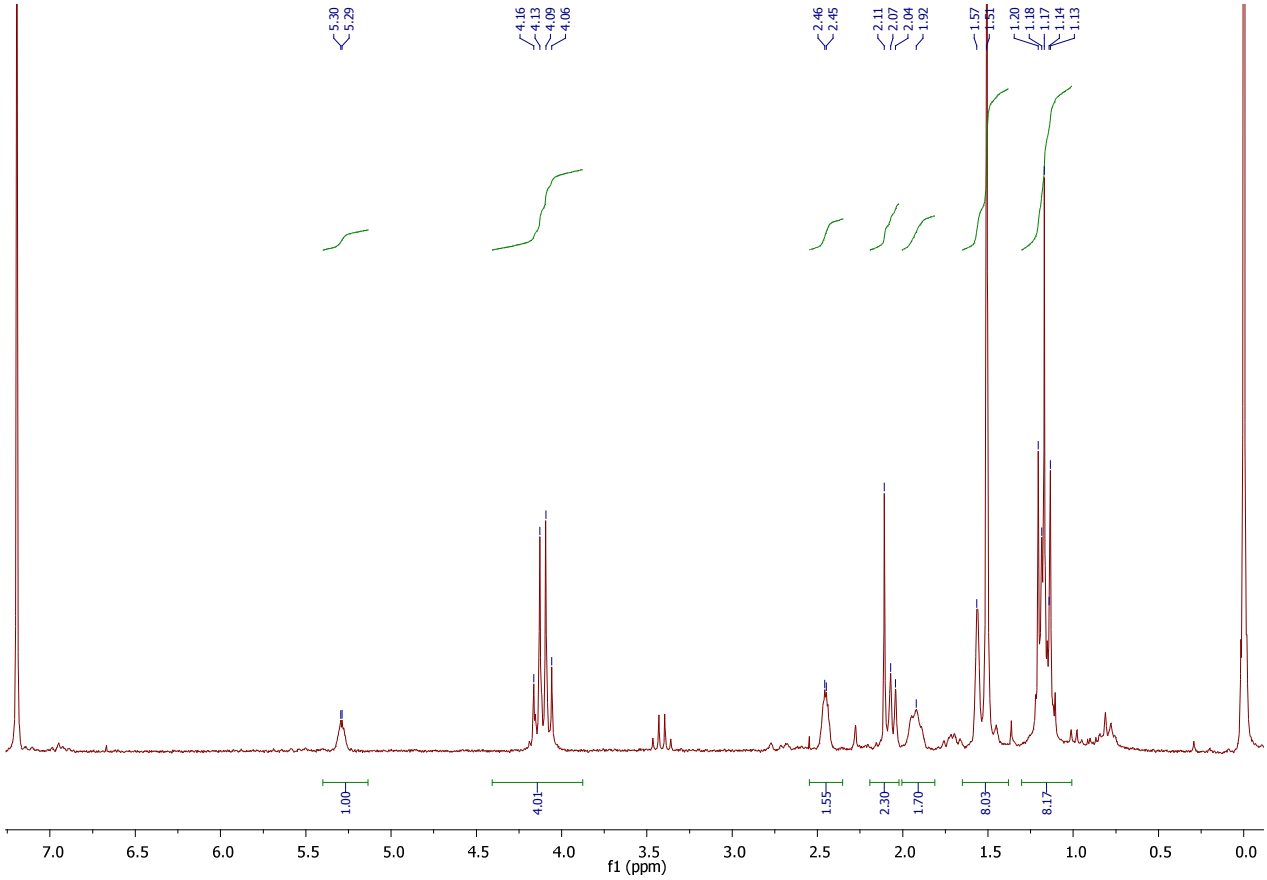

170.78
127.66
123.19
76.64
76.88
75.37
60.12
52.75
33.03
27.79
26.96
24.99
17.20
13.04
11.19
-0.00
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

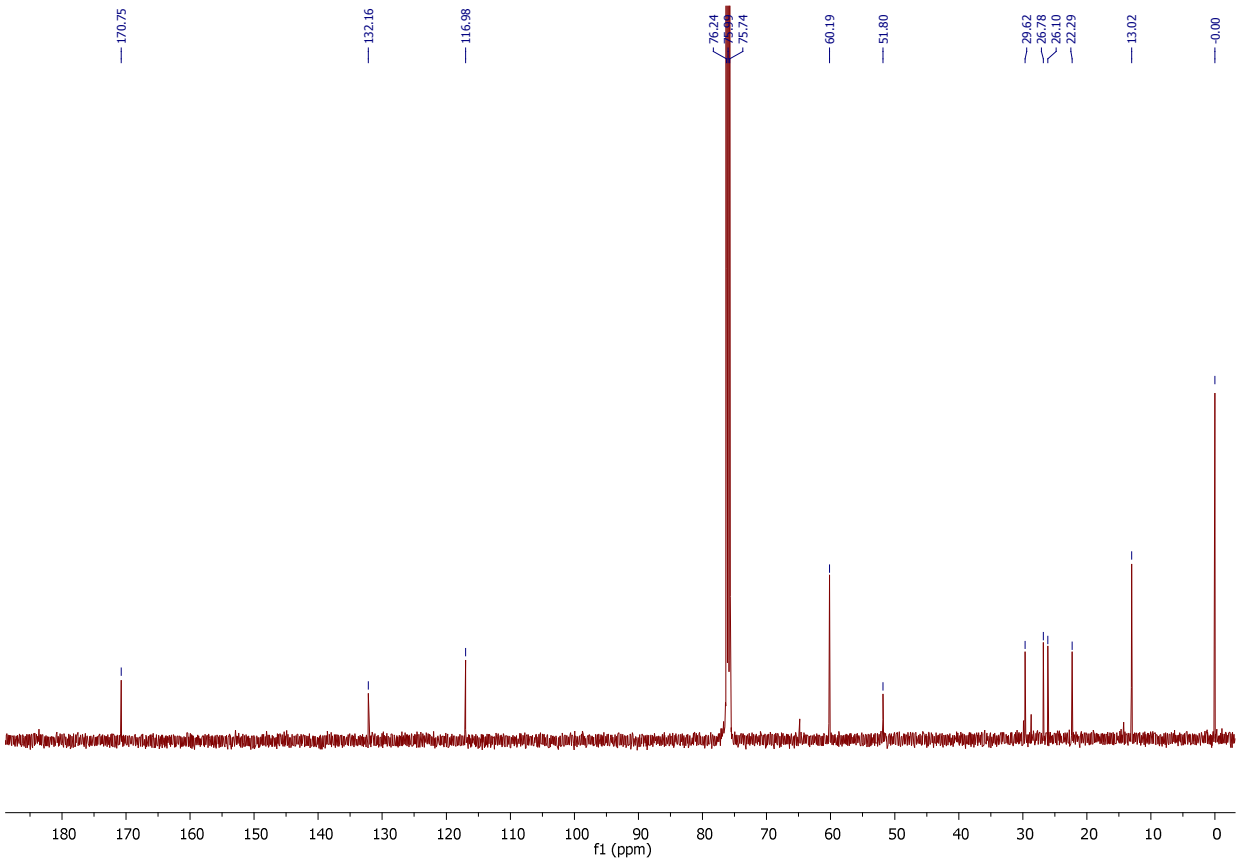
Compound **3e**:


7.20
7.19
7.17
7.11
7.10
7.08
7.07
4.06
4.06
4.04
4.01
3.99
3.32
2.36
2.10
2.06
2.05
2.03
2.02
1.66
1.52
1.36
1.19
1.17
1.15
1.10
1.09
1.08
0.81
5.54
4.00
1.66
1.69
9.58
3.05
1.62
1.55
15.04
3.57
f1 (ppm)

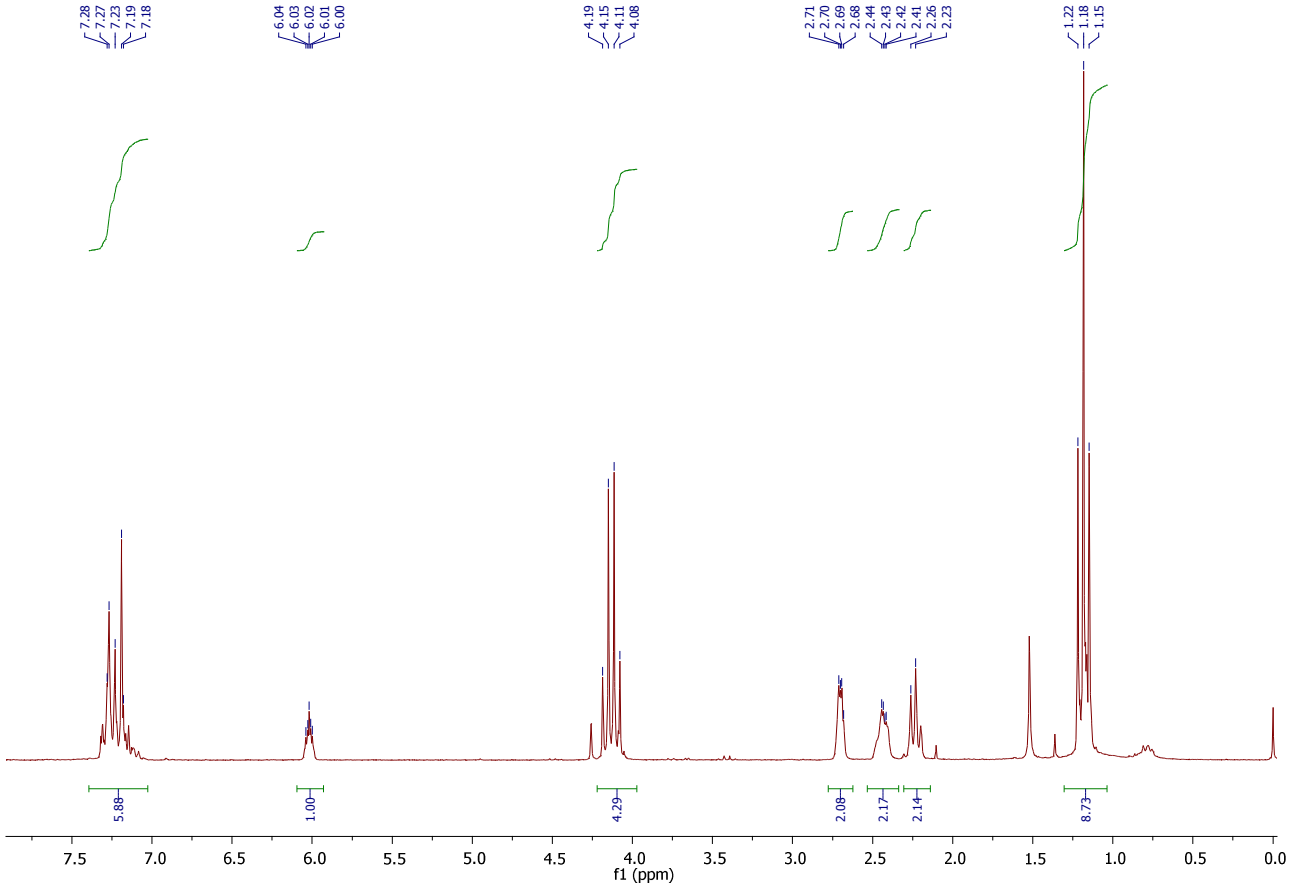

207.34
172.04
140.45
128.89
128.64
127.48
126.23
126.19
77.68
77.42
77.17
61.52
54.05
39.29
34.83
31.32
30.72
30.11
29.35
28.33
23.10
19.51
14.36
f1 (ppm)

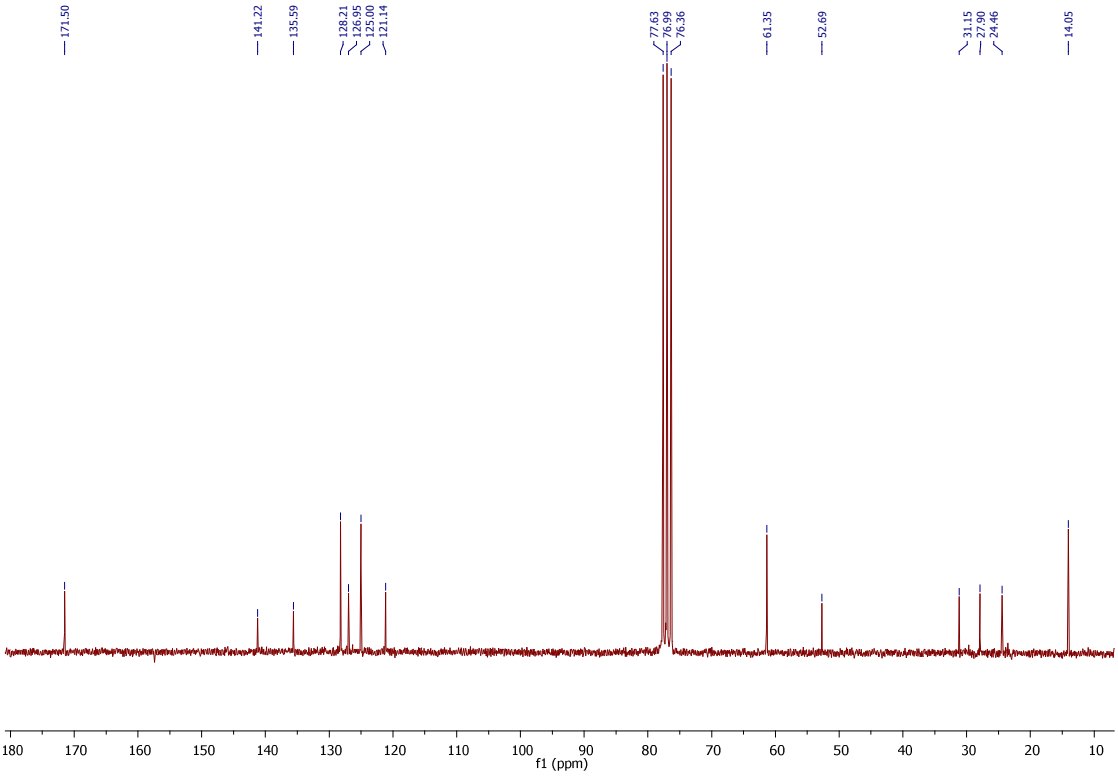
Compound **4a**:


5.30
5.29
4.16
4.13
4.09
4.06
2.46
2.45
2.11
2.07
2.04
1.92
1.57
1.51
1.20
1.18
1.17
1.14
1.13
1.00
4.01
1.55
2.30
1.70
8.03
8.17
f1 (ppm)

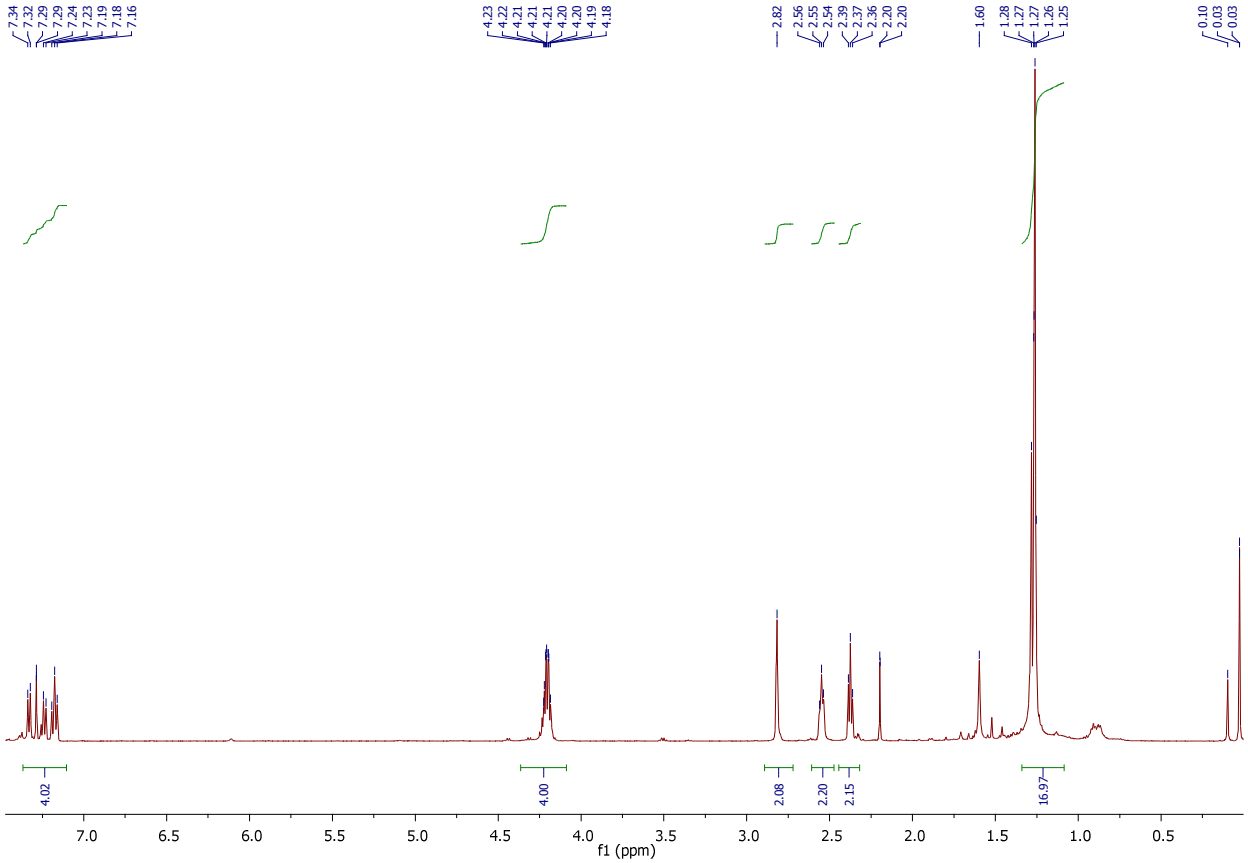

170.75
132.16
116.98
76.24
75.74
60.19
51.80
29.62
26.78
26.10
22.29
13.02
-0.00
f1 (ppm)

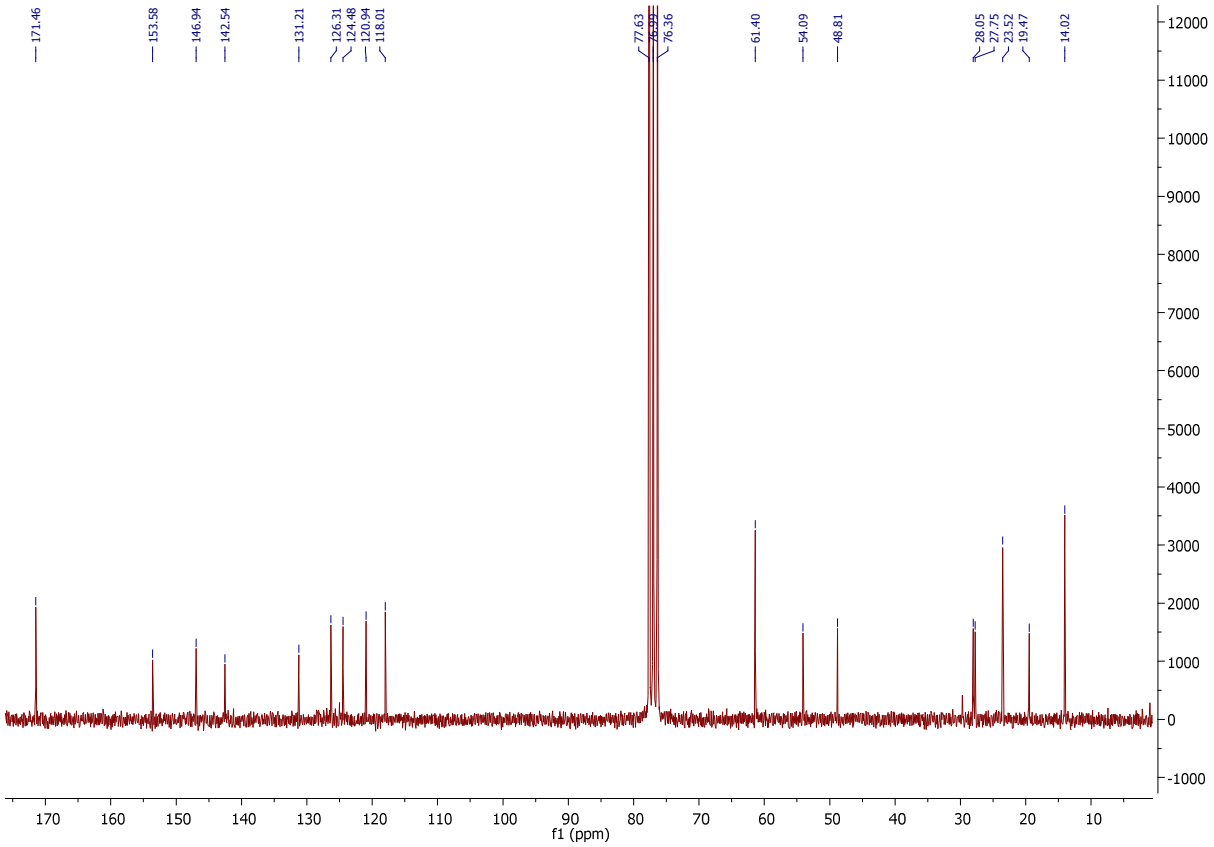
Compound **4b**:


7.28
7.27
7.23
7.19
7.18
6.04
6.03
6.02
6.01
6.00
4.19
4.15
4.11
4.08
2.71
2.70
2.69
2.68
2.44
2.43
2.42
2.41
2.26
2.23
1.22
1.18
1.15
5.88
1.00
4.29
2.08
2.17
2.14
8.73
f1 (ppm)

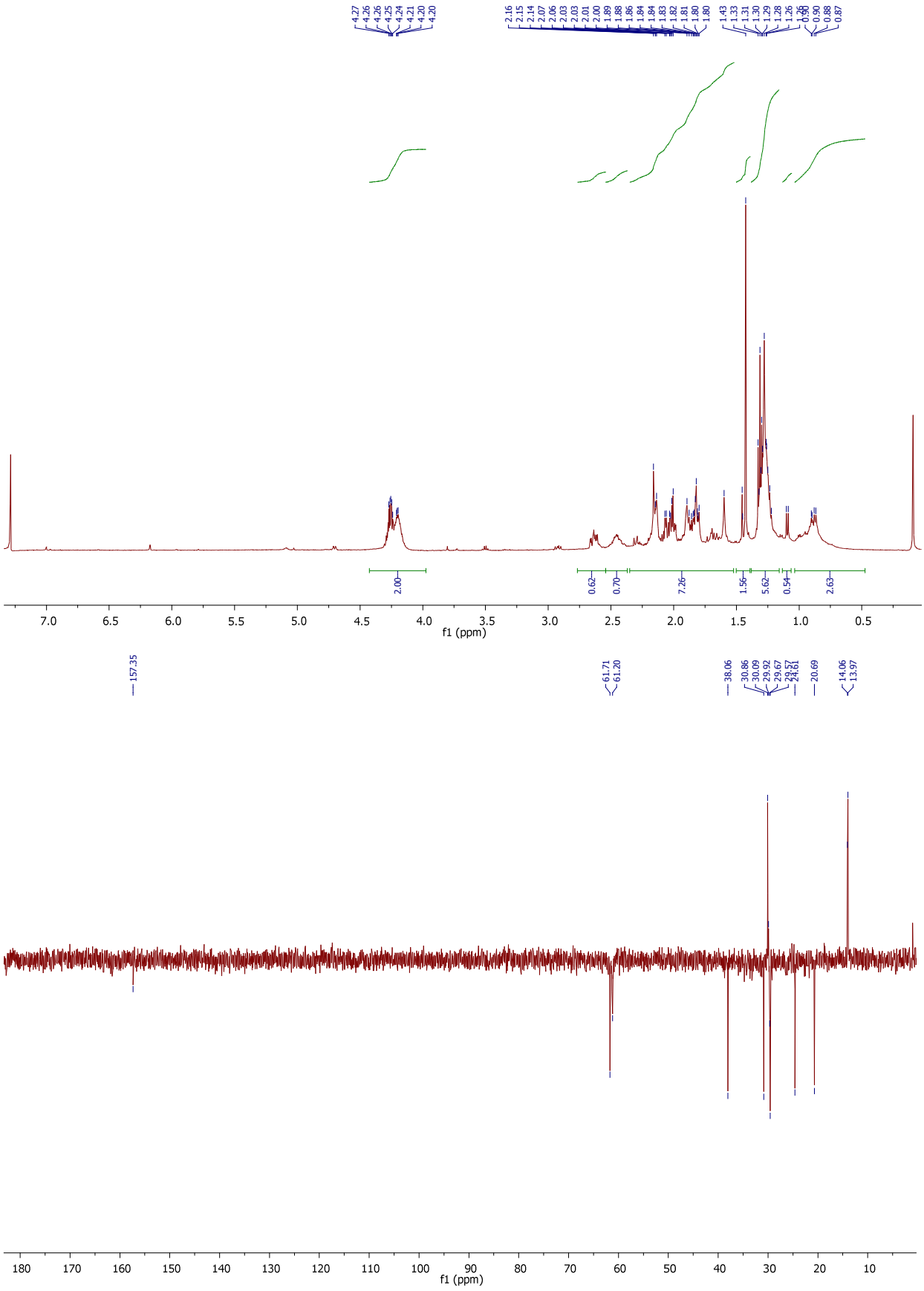

171.50
141.22
135.59
128.21
126.95
125.00
121.14
77.63
76.99
76.36
61.35
52.69
31.15
27.90
24.46
14.05
f1 (ppm)

Compound **5b**:

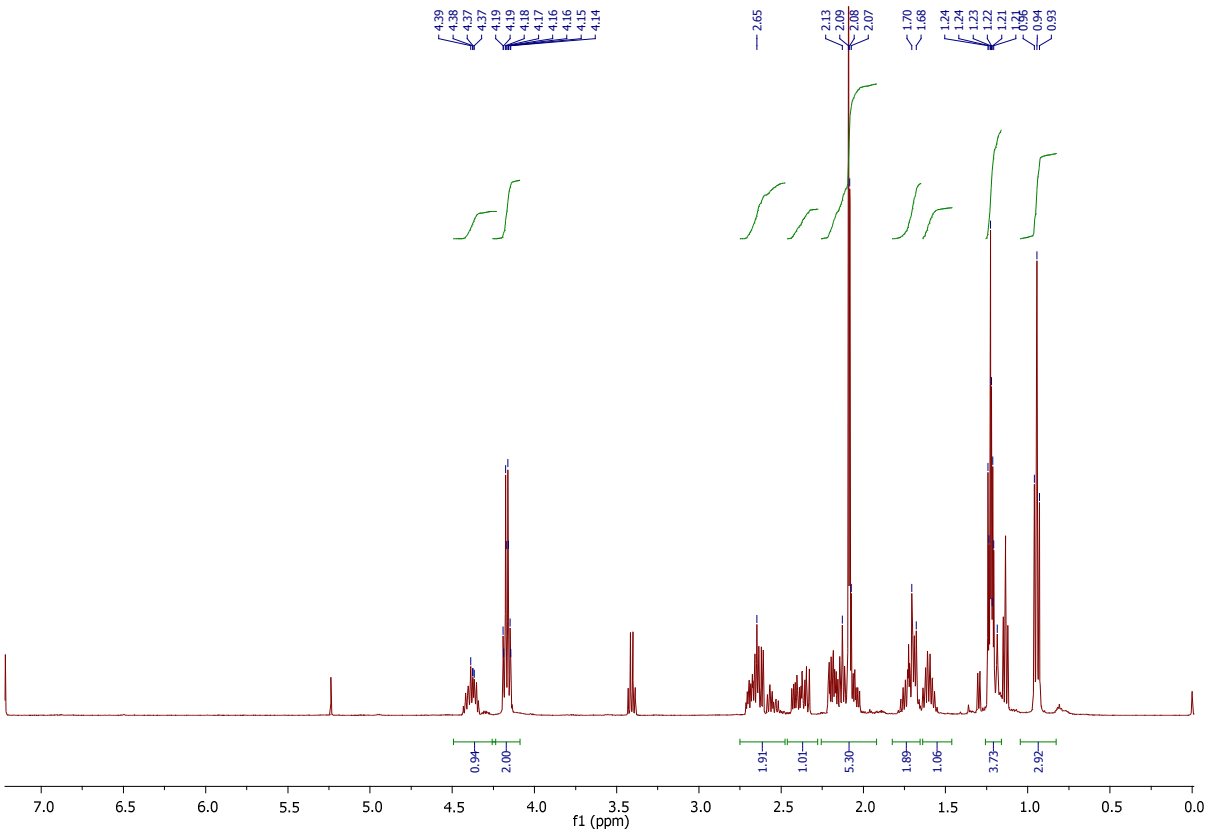

7.34
7.32
7.29
7.29
7.24
7.23
7.19
7.18
7.16
4.23
4.22
4.21
4.21
4.21
4.20
4.20
4.19
4.18
2.82
2.56
2.55
2.54
2.39
2.37
2.36
2.20
2.20
1.60
1.28
1.27
1.27
1.26
1.25
0.10
0.03
0.03
4.02
4.00
2.08
2.20
2.15
16.97
f1 (ppm)

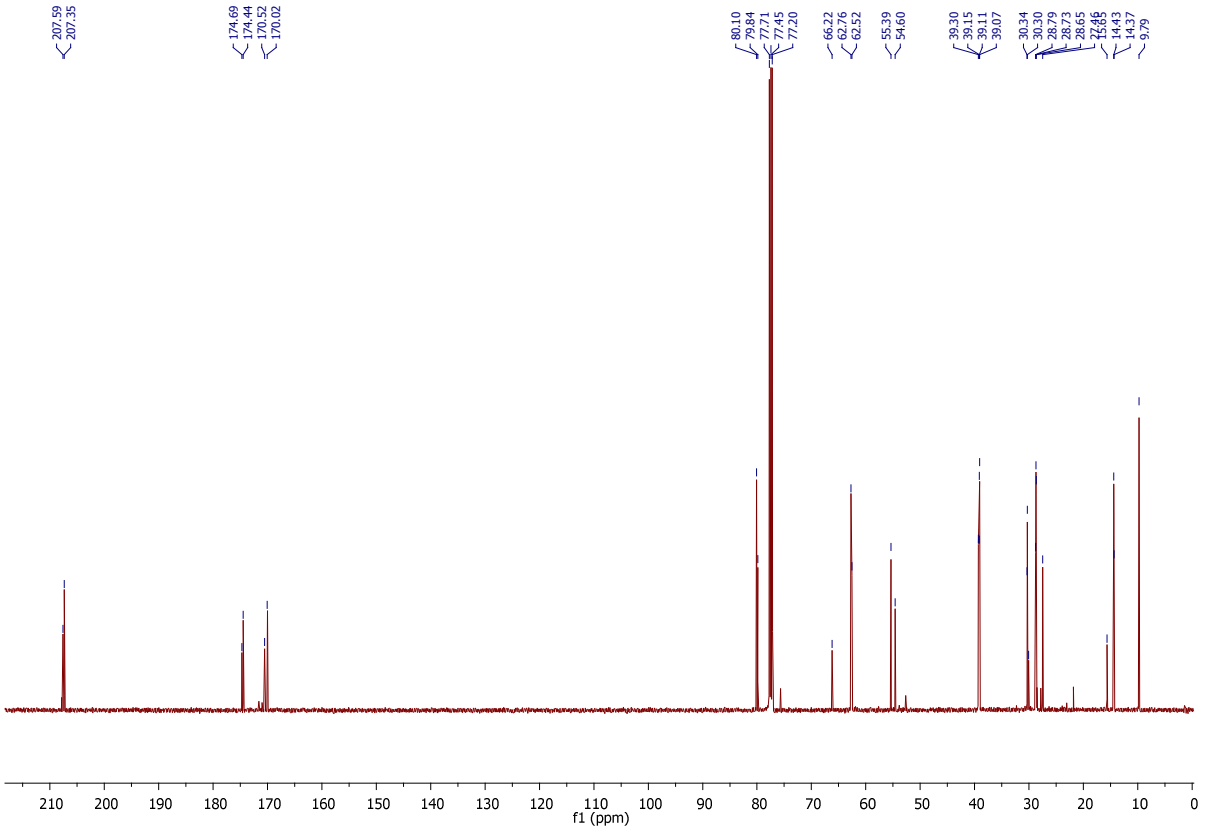

171.46
153.58
146.94
142.54
131.21
126.31
124.48
120.94
118.01
77.63
76.99
76.36
61.40
54.09
48.81
28.05
27.75
23.52
19.47
14.02
f1 (ppm)

Compound **5c**:


4.27
4.26
4.26
4.25
4.24
4.21
4.20
4.20
2.16
2.15
2.14
2.07
2.06
2.03
2.03
2.01
2.00
1.89
1.88
1.86
1.84
1.84
1.83
1.82
1.81
1.80
1.80
1.43
1.33
1.31
1.30
1.29
1.28
1.26
0.90
0.88
0.87
2.00
0.62
0.70
7.26
1.56
5.62
0.54
2.63
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
157.35
61.71
61.20
38.06
30.86
30.09
29.92
29.67
29.57
24.61
20.69
14.06
13.97
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Compound **5d**:


4.39
4.38
4.37
4.37
4.19
4.19
4.18
4.17
4.16
4.16
4.15
4.14
2.65
2.13
2.09
2.08
2.07
1.70
1.68
1.24
1.24
1.23
1.22
1.21
0.96
0.94
0.93
0.94
2.00
1.91
1.01
5.30
1.89
1.06
3.73
2.92
f1 (ppm)


207.59
207.35
174.69
174.44
170.52
170.02
80.10
79.84
77.71
77.45
77.20
66.22
62.76
62.52
55.39
54.60
39.30
39.15
39.11
39.07
30.34
30.30
28.79
28.73
28.65
14.43
14.37
9.79
f1 (ppm)