Electronic supplementary information for the manuscript

"Synthesis of different types of alkoxy fullerene derivatives from chlorofullerene $C_{60}Cl_6$"

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Experimental procedures and selected spectroscopic data

Chlorofullerene $C_{60}Cl_6$ was prepared as described in P. A. Troshin et al., *Fullerenes, Nanotubes, Carbon Nanostruct.*, **2003**, *11*, 165 and stored in dark.

General procedure for the synthesis of alkoxyfullerenes $C_{60}(OR)_5H$ and $C_{60}(OR)_5Br$ using Bu_4NBr as a reagent

Compounds **1a,d**, **2e-f,h-j** and **3a-b,d,g,i-j** were synthesized according to the following procedure. A triple-neck round-bottom 100 mL flask was evacuated and filled with argon three times. Afterwards, 100 mg of $C_{60}Cl_6$ (0.11 mmol) and 50 mL of dry chlorobenzene were introduced into the flask in a stream of argon. The mixture was stirred magnetically until complete dissolving of $C_{60}Cl_6$ with the formation of a transparent orange solution and then an appropriate amount of the corresponding alcohol (1.1-110 mmol, 10-1000 eq.) was added in one portion. Afterwards, a solution of the Bu_4NBr (1.1 mmol, 10 eq.) in 30 ml of dry chlorobenzene was added dropwise to the stirred reaction mixture. In order to obtain compounds **1a,d** the reaction mixture was stirred 30 minutes at room temperature and then diluted by toluene and poured on top of a silica gel column. The target products **1a,d** were eluted using toluene-acetonitrile mixtures (97-99%:1-3% v/v). The obtained solutions of **1a,d** were concentrated at the rotary evaporator, washed with hexanes and dried in air. Compounds **1a,d** were obtained as dark-orange powders.

For preparation of compounds **3a-b, d ,g, i-j**, the reaction mixture was stirred 1 h at 55°C after addition of Bu_4NBr solution. Then the reaction mixture was concentrated at the rotary evaporator, the residue was dissolved in toluene and poured on the top of a silica gel column. The target products **3a-b, d, g, i-j** were eluted using toluene-acetonitrile mixtures (97-99% : 1-3% v/v). Compounds **3g, i-j** were eluted using toluene-THF mixtures (70-90% : 10-30% v/v). The obtained solutions of **3a-b, d, g, i-j** were concentrated at the rotary evaporator, washed with hexanes and dried in air. Compounds **3a-b, d, g, i-j** were obtained as dark-orange powders.

Compounds **2e-f, h-j** were isolated as byproducts or even the main products in the reactions between $C_{60}Cl_6$ and the corresponding alcohols under the reaction conditions specified above.

General procedure for the DMSO-promoted synthesis of alkoxyfullerenes $C_{60}(OR)_5Br$

Compounds **3a-b, d, g, i-j** were also prepared using the DMSO-promoted synthesis according to the following procedure. A corresponding alcohol (1.61 mmol) and 3 ml of dry DMSO were added to the stirred solution of $C_{60}Cl_6$ (100 mg, 0.11 mmol) in 150 ml of dry chlorobenzene. Afterwards, a solution of the Bu_4NBr (207 mg, 0.6 mmol) in 50 ml of dry chlorobenzene was added dropwise. The reaction mixture was stirred 30 minutes at room temperature and then diluted by hexanes and poured on top of a silica gel column. The target products **3a-b, d, g, i-j** were eluted using toluene-acetonitrile mixtures (98-99% : 1-2% v/v). The obtained solutions were concentrated at the rotary evaporator, the residues were washed with hexanes and dried in air. The target compounds were obtained as dark-orange powders with 53-70% isolated yields.

1a (Yield 45%). ^{1}H NMR (500 MHz, $CDCl_3$:CS_2 1:1, δ, ppm): 3.87 (s, 3H), 3.95 (s, 6H), 3.96 (s, 6H), 4.81 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$:CS_2 1:1, δ, ppm): 55.44 (O<u>C</u>H$_3$), 55.61 (O<u>C</u>H$_3$), 55.88 (O<u>C</u>H$_3$), 59.53 (<u>C</u>$_{sp3\ fullerene\ cage}$-H), 78.13 (<u>C</u>$_{sp3\ fullerene\ cage}$ -O), 80.38 (<u>C</u>$_{sp3\ fullerene\ cage}$ -O), 82.34 (<u>C</u>$_{sp3\ fullerene\ cage}$ -O), 140.47, 140.87, 142.97, 143.00, 143.11, 143.49, 143.53, 143.98, 144.43, 144.63, 145.21, 145.65, 146.08, 146.48, 146.81, 147.19, 147.26, 147.72, 147.92, 148.11, 148.18, 148.25, 148.46, 149.18, 149.34, 149.75, 152.07, 154.01.

APCI MS: m/z=875 ([M-H]$^-$).

$C_{65}H_{16}O_5$ (876.82): calcd. C 89.04, H 1.84; found C 89.29, H 1.84.

1d (Yield 43%). ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 0.97-1.06 (m, 15H), 1.47-1.61 (m, 10H), 1.75-1.85 (m, 10H), 4.12 (t, 2H, *J* = 6.4 Hz), 4.16-4.44 (m, 8H), 4.80 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 14.00 (<u>C</u>H$_3$), 14.03 (<u>C</u>H$_3$), 14.07 (<u>C</u>H$_3$), 19.47 (<u>C</u>H$_2$CH$_3$), 19.51 (<u>C</u>H$_2$CH$_3$), 19.54 (<u>C</u>H$_2$CH$_3$), 32.23 (OCH$_2$<u>C</u>H$_2$), 32.28 (OCH$_2$<u>C</u>H$_2$), 32.34 (OCH$_2$<u>C</u>H$_2$), 59.49 (<u>C</u>$_{sp3\ fullerene\ cage}$-H), 67.18 (O<u>C</u>H$_2$), 67.89 (O<u>C</u>H$_2$), 68.18 (O<u>C</u>H$_2$), 77.60 (<u>C</u>$_{sp3\ fullerene\ cage}$-O), 79.81 (<u>C</u>$_{sp3\ fullerene\ cage}$-O), 81.78 (<u>C</u>$_{sp3\ fullerene\ cage}$-O), 140.66, 140.81, 142.86, 143.12, 143.35, 143.36, 143.39, 144.05, 144.26, 144.60, 145.25, 145.66, 146.19, 146.55, 146.78, 147.04, 147.15, 147.25, 147.67, 148.07, 148.14, 148.18, 148.57, 148.86, 149.06, 149.22, 152.47, 154.10.

APCI MS: m/z=1086 ([M-H]$^-$).

$C_{80}H_{46}O_5$ (1087.22): calcd. C 88.38, H 4.26; found C 88.15, H 4.27.

2e (Yield 90%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 1.37-1.39 (m, 12H), 4.96-5.04 (m, 2H).

ESI MS: m/z=838 ([M]$^-$).

Spectroscopic data for compound **2e** were reported previously [A. Avent, P. R. Birkett, A. Darwish, S. Houlton, R. Taylor, K .S .T. Thomson, X. W. Wei. *J. Chem. Soc. Perkin Trans.* 2, 2001, 782].

2f (Yield 73%). ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 1.18-1.22 (m, 12H), 1.98-2.07 (m, 8H), 4.85 (p, 2H, *J* = 5.8 Hz).

^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 10.03 ($\underline{C}H_3$), 10.06 ($\underline{C}H_3$), 28.00 ($\underline{C}H_2$), 28.15 ($\underline{C}H_2$), 79.35 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 79.62 ($\underline{C}$H), 138.54, 139.40, 140.50, 141.27, 142.28, 142.31, 143.02, 143.11, 143.17, 143.29, 143.30, 143.32, 143.77, 143.88, 144.22, 144.31, 144.34, 144.48, 145.60, 145.81, 146.53, 146.82, 146.99, 147.38, 147.49, 148.91, 149.32, 150.78.

ESI MS: m/z=894 ($[M]^-$).

2h (Yield 34%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 3.46 (s, 6H), 3.68 (dd, 4H, *J* = 5.5; 3.9 Hz), 3.88 (dd, 4H, *J* = 5.5; 3.9 Hz), 4.11 (t, 4H, *J* = 4.9 Hz), 4.78-4.86 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 59.18 ($\underline{C}H_3$), 67.32 ($\underline{C}H_2$), 70.86 ($\underline{C}H_2$), 70.92 ($\underline{C}H_2$), 72.14 ($\underline{C}H_2$), 79.75 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 138.57, 139.88, 140.73, 141.23, 142.25, 142.32, 142.90, 143.15, 143.27, 143.31, 143.35, 143.39, 143.64, 143.77, 143.80, 144.22, 144.30, 144.45, 144.48, 145.76, 145.87, 146.58, 146.69, 146.88, 146.99, 147.05, 147.40, 148.21, 149.00, 149.62.

ESI MS: m/z=958 ($[M]^-$).

$C_{70}H_{22}O_6$ (958.92): calcd. C 87.68, H 2.31; found C 87.42, H 2.32.

2i (Yield 36%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 3.40 (s, 6H), 3.59 (dd, 4H, *J* = 5.6; 3.8 Hz), 3.72 (dd, 4H, *J* = 5.6; 3.8 Hz), 3.77-3.79 (m, 4H), 3.88-3.90 (m, 4H), 4.08-4.10 (t, 4H, *J* = 4.8 Hz), 4.75-4.83 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 59.13 ($\underline{C}H_3$), 67.30 ($\underline{C}H_2$), 70.68 ($\underline{C}H_2$), 70.81 ($\underline{C}H_2$), 70.82 ($\underline{C}H_2$), 71.00 ($\underline{C}H_2$), 72.03 ($\underline{C}H_2$), 79.74 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 138.57, 139.87, 140.73, 141.23, 142.25, 142.31, 142.89, 143.12, 143.15, 143.27, 143.30, 143.35, 143.39, 143.63, 143.76, 143.80, 144.22, 144.29, 144.44, 144.48, 145.75, 145.87, 146.58, 146.68, 146.87, 146.97, 147.05, 147.39, 148.22, 148.99, 149.62.

ESI MS: m/z=1053 ($[M+Li]^+$).

$C_{74}H_{30}O_8$ (1047.03): calcd. C 84.89, H 2.89; found C 84.67, H 2.91.

2j (Yield 21%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 1.54 (s, 18H), 2.95-2.98 (t, 4H, *J* = 6.4 Hz), 4.81-4.90 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 28.27 (COOC($\underline{C}H_3$)$_3$), 36.75 ($\underline{C}H_2$), 63.70 ($\underline{C}H_2$), 79.73 (COO$\underline{C}$(CH$_3$)$_3$), 80.92 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 138.57, 139.84, 140.72, 141.26, 142.25, 142.31, 142.90, 143.14, 143.29, 143.31, 143.34, 143.38, 143.63, 143.82, 144.23, 144.30, 144.43, 144.49, 145.75, 145.86, 146.58, 146.66, 146.89, 146.96, 147.05, 147.39, 148.26, 148.99, 149.62, 170.54 ($\underline{C}$OO).

ESI MS: m/z=1033 ($[M+Na]^+$).

3a (Yield 25%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 3.94 (s, 3H), 3.98 (s, 6H), 4.06 (s, 6H).

^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 55.50 ($\underline{C}H_3$), 56.00 ($\underline{C}H_3$), 58.34 ($\underline{C}H_3$), 65.69 ($\underline{C}_{sp3\ fullerene\ cage}$-Br), 77.57 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 80.05 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 81.51 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 138.02, 142.22, 142.42, 142.60, 142.94, 142.98, 143.35, 143.56, 143.86, 144.37, 144.49, 144.92, 145.02, 145.36, 146.77, 146.95, 147.18, 147.34, 147.35, 147.71, 148.23, 148.33, 148.34, 148.45, 149.02, 149.18, 151.24, 154.65.

ESI MS: m/z=875 ($[M-Br]^-$).

$C_{65}H_{15}BrO_5$ (955.72): calcd. C 81.69, H 1.58, Br 8.36; found C 81.47, H 1.59, Br 8.33.

3b (Yield 38%). ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 1.45-1.48 (m, 9H), 1.53 (t, 6H, J = 7.0 Hz), 4.22-4.32 (m, 8H), 4.46-4.51 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 15.35 ($\underline{C}H_3$), 15.84 ($\underline{C}H_3$), 16.08 ($\underline{C}H_3$), 63.76 ($O\underline{C}H_2$), 64.24 ($O\underline{C}H_2$), 66.16 ($\underline{C}_{sp3\ fullerene\ cage}$-Br), 66.95 ($O\underline{C}H_2$), 79.54 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 81.46 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 138.28, 142.50, 142.67, 142.81, 143.24, 143.47, 143.59, 144.13, 144.36, 144.73, 145.08, 145.26, 145.49, 146.94, 147.32, 147.46, 147.79, 147.81, 148.31, 148.44, 148.56, 148.76, 149.07, 149.21, 151.88, 154.66.

ESI MS: m/z=945 ($[M-Br]^-$).

3d (Yield 30%). ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 0.96-1.05 (m, 15H), 1.46-1.63 (m, 10H), 1.78-1.89 (m, 10H), 4.15-4.24 (m, 8H), 4.39-4.43 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 13.96 ($\underline{C}H_3$), 14.06 ($\underline{C}H_3$), 14.14 ($\underline{C}H_3$), 19.31 ($\underline{C}H_2CH_3$), 19.56 ($\underline{C}H_2CH_3$), 19.58 ($\underline{C}H_2CH_3$), 31.86 ($OCH_2\underline{C}H_2$), 32.28 ($OCH_2\underline{C}H_2$), 32.39 ($OCH_2\underline{C}H_2$), 66.29 ($\underline{C}_{sp3\ fullerene\ cage}$-Br), 67.88 ($O\underline{C}H_2$), 68.50 ($O\underline{C}H_2$), 70.98 ($O\underline{C}H_2$), 79.57 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 81.35 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 138.34, 142.58, 142.65, 142.87, 143.11, 143.15, 143.47, 143.59, 144.14, 144.36, 144.79, 145.02, 145.26, 145.53, 146.93, 147.32, 147.46, 147.48, 147.79, 148.31, 148.43, 148.53, 148.56, 148.84, 149.05, 149.19, 151.95, 154.80.

APCI MS: m/z=1086 ($[M-Br]^-$), 1166 ($[M]^-$), 866 ([M-3(O*n*Bu)-Br]$^-$).

$C_{80}H_{45}BrO_5$ (1166.11): calcd. C 82.40, H 3.89, Br 6.86; found C 82.23, H 3.91, Br 6.84.

3g (Yield 33%). ^{1}H NMR (500 MHz, $CDCl_3$:CD_3OD 10:1, δ, ppm): 3.40 (s, 3H), 3.44 (s, 6H), 3.47 (s, 6H), 3.75-3.90 (m, 10H), 4.30-4.44 (m, 8H), 4.48-4.56 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$:CD_3OD 10:1, δ, ppm): 58.89 ($O\underline{C}H_3$), 58.99 ($O\underline{C}H_3$), 59.17 ($O\underline{C}H_3$), 65.94 ($\underline{C}_{sp3\ fullerene\ cage}$-Br), 67.38 ($\underline{C}H_2$), 67.88 ($\underline{C}H_2$), 69.94 ($\underline{C}H_2$), 71.49 ($\underline{C}H_2$), 71.84 ($\underline{C}H_2$), 71.91 ($\underline{C}H_2$), 77.28 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 79.51 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 81.48 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 137.90, 142.34, 142.38, 142.66, 143.03, 143.48, 143.63, 143.99, 144.45, 144.71, 145.07, 145.09,

145.40, 146.93, 147.29, 147.32, 147.46, 147.47, 147.81, 148.30, 148.45, 148.57, 148.58, 149.12, 149.27, 151.49, 154.63.

ESI MS: m/z=1095 ([M-Br]$^-$).

$C_{75}H_{35}BrO_{10}$ (1175.98): calcd. C 76.60, H 3.00, Br 6.79; found C 76.51, H 3.03, Br 6.77.

3i (Yield 11%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 3.36-3.39 (m, 15H), 3.52-3.81 (m, 40H), 3.87-3.98 (m, 10H), 4.33-4.44 (m, 8H), 4.51-4.62 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 59.14 (O$\underline{C}H_3$), 66.05 ($\underline{C}_{sp3\ fullerene\ cage}$-Br), 67.59 ($\underline{C}H_2$), 67.92 ($\underline{C}H_2$), 68.14 ($\underline{C}H_2$), 70.11 ($\underline{C}H_2$), 70.25 ($\underline{C}H_2$), 70.36 ($\underline{C}H_2$), 70.53 ($\underline{C}H_2$), 70.66 ($\underline{C}H_2$), 70.76 ($\underline{C}H_2$), 70.87 ($\underline{C}H_2$), 71.93 ($\underline{C}H_2$), 72.02 ($\underline{C}H_2$), 72.49 ($\underline{C}H_2$), 79.50 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 81.54 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 137.99, 142.36, 142.42, 142.43, 142.68, 143.03, 143.49, 143.63, 144.01, 144.44, 144.71, 145.05, 145.17, 145.42, 146.94, 146.99, 147.32, 147.46, 147.49, 147.83, 148.34, 148.42, 148.46, 148.59, 149.14, 149.28, 151.56, 154.66.

APCI MS: m/z=1536 ([M-Br]$^-$), 1389 ([M-Br-OR+H_2O]$^-$).

3j. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 1.42 (s, 9H), 1.45-1.46 (m, 36H), 2.73-2.82 (m, 10H), 4.36-4.58 (m, 10H).

^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 28.26 ($\underline{C}H_3$), 28.30 ($\underline{C}H_3$), 28.34 ($\underline{C}H_3$), 36.39 ($\underline{C}H_2$), 36.43 ($\underline{C}H_2$), 36.72 ($\underline{C}H_2$), 63.90 ($\underline{C}H_2$), 64.56 ($\underline{C}H_2$), 65.73 ($\underline{C}_{sp3\ fullerene\ cage}$-Br), 66.49 ($\underline{C}H_2$), 77.01 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 79.52 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 80.67 ($\underline{C}(CH_3)_3$), 80.75 ($\underline{C}(CH_3)_3$), 80.78 ($\underline{C}(CH_3)_3$), 81.29 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 138.12, 142.55, 142.59, 142.79, 143.00, 143.59, 143.73, 144.07, 144.55, 144.79, 145.11, 145.22, 145.54, 147.01, 147.32, 147.40, 147.56, 147.57, 147.91, 148.42, 148.47, 148.54, 148.65, 149.19, 149.34, 151.68, 154.91, 170.46 ($\underline{C}OO$), 170.50 ($\underline{C}OO$), 170.62 ($\underline{C}OO$).

APCI MS: m/z=1446 ([M-Br]$^-$).

$C_{95}H_{65}BrO_{15}$ (1526.43): calcd. C 74.75, H 4.29, Br 5.23; found C 74.73, H 4.30, Br 5.21.

General procedure for the synthesis of epoxide-type alkoxyfullerenes $C_{60}(OR)_4O$

Compounds **4b-c,i** were synthesized according to the following procedure. A triple-neck round-bottom 100 mL flask was evacuated and filled with argon three times. Afterwards, 100 mg of $C_{60}Cl_6$ (0.11 mmol) and 50 mL of toluene were introduced into the flask in a stream of argon. The mixture was stirred magnetically until complete dissolving of $C_{60}Cl_6$ with the formation of transparent orange solution. Afterwards, an excess of the corresponding alcohol (11 mmol, 100 eq.) and 0.1 ml of distilled water were added in one portion. Then a solution of the Bu_4NBr (345 mg, 1.1 mmol) in 30 ml of toluene was added dropwise. The reaction mixture was stirred 12 hours at room temperature and then diluted by toluene and poured on top of a silica gel column.

The target products **4b-c,i** were eluted using toluene-acetonitrile mixtures (97-99% : 1-3% v/v) after elution of corresponding bromides. The obtained solutions of **4b-c,i** were concentrated at the rotary evaporator, washed with hexanes and dried in air. Compounds **4b-c,i** were obtained as dark-orange powders.

4b (Yield 31%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 1.46 (t, 6H, *J* = 7.0 Hz), 1.52 (t, 6H, *J* = 7.0 Hz), 4.23-4.33 (m, 6H), 4.45-4.51 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 15.83 ($\underline{C}H_3$), 16.07 ($\underline{C}H_3$), 63.81 ($\underline{C}H_2$), 64.46 ($\underline{C}H_2$), 76.19 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 76.98 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 77.24 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 79.46 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 137.25, 142.43, 142.69, 142.75, 143.45, 143.59, 143.62, 144.11, 144.39, 144.85, 145.03, 145.26, 145.42, 146.93, 147.28, 147.43, 147.49, 147.77, 148.29, 148.33, 148.43, 148.58, 148.61, 148.68, 149.10, 149.19, 151.55, 154.40.

APCI MS: m/z=916 ($[M]^-$).

$C_{68}H_{20}O_5$ (916.88): calcd. C 89.08, H 2.20; found C 88.94, H 2.21.

4c (Yield 17%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 1.09-1.14 (m, 12H), 1.82-1.96 (m, 8H), 4.13-4.22 (m, 6H), 4.35-4.40 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 10.90 ($\underline{C}H_3$), 11.04 ($\underline{C}H_3$), 23.46 ($\underline{C}H_2$), 23.63 ($\underline{C}H_2$), 69.85 ($\underline{C}H_2$), 70.47 ($\underline{C}H_2$), 76.17 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 79.49 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 137.34, 142.51, 142.73, 142.77, 143.46, 143.60, 143.62, 144.11, 144.39, 144.90, 145.02, 145.25, 145.45, 146.93, 147.28, 147.43, 147.50, 147.77, 148.16, 148.33, 148.43, 148.56, 148.61, 148.71, 149.10, 149.18, 151.64, 154.40.

APCI MS: m/z=972 ($[M]^-$).

4i (Yield 25%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 3.37 (s, 12H), 3.55 (dd, 8H, *J* = 5.5; 3.8 Hz), 3.65-3.70 (m, 16H), 3.76-3.78 (m, 8H), 3.89 (dt, 8H, *J* = 9.9; 4.9 Hz), 4.27-4.46 (m, 8H).

^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 59.07 ($\underline{C}H_3$), 67.79 ($\underline{C}H_2$), 68.66 ($\underline{C}H_2$), 70.51 ($\underline{C}H_2$), 70.59 ($\underline{C}H_2$), 70.68 ($\underline{C}H_2$), 70.70 ($\underline{C}H_2$), 70.80 ($\underline{C}H_2$), 71.97 ($\underline{C}H_2$), 76.65 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 77.24 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 77.51 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 81.86 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 140.44, 142.15, 143.09, 143.20, 143.61, 143.70, 144.37, 144.43, 144.77, 145.17, 145.20, 146.37, 146.47, 146.71, 146.85, 147.05, 147.10, 147.18, 147.22, 147.26, 147.42, 147.73, 148.02, 149.50, 149.66, 150.00, 150.71.

APCI MS: m/z=1411 ($[M+Na]^+$).

$C_{88}H_{60}O_{17}$ (1389.41): calcd. C 76.07, H 4.35; found C 76.04, H 4.36.

General procedure for the synthesis of alkoxyfullerenes $C_{60}(OR)_5Cl$ using triethylamine as a base

Compounds **5a-e,g-i** were synthesized according to the following procedure. An excess of the corresponding alcohol (1.1-110 mmol, 10-1000 eq.) and triethylamine (542 mg, 5.36 mmol) were added to the stirred solution of $C_{60}Cl_6$ (100 mg, 0.11 mmol) in 70 ml of toluene. The reaction mixture was kept under stirring at room temperature for 30 minutes and then concentrated at the rotary evaporator. The residue was dissolved in toluene and poured on top of a silica gel column. The target products **5a-e** were eluted using toluene-acetonitrile mixtures (97-99% : 1-3% v/v). Compounds **5g-i** were eluted using toluene-tetrahydrofuran mixtures (70-90% : 10-30% v/v). The obtained solutions of **5a-e,g-i** were concentrated at the rotary evaporator, washed with hexanes and dried in air. Compounds **5a-e,g-i** were obtained as dark-orange powders with 38-52% yields.

5a. ^{1}H NMR (600 MHz, bromobenzene-D5, δ, ppm): 3.83 (s, 6H), 3.86 (s, 3H), 3.94 (s, 6H).

^{13}C NMR (150 MHz, bromobenzene-D5, δ, ppm): 55.44 ($\underline{C}H_3$), 55.91 ($\underline{C}H_3$), 58.45 ($\underline{C}H_3$), 73.90 ($\underline{C}_{sp3\ fullerene\ cage}$-Cl), 77.64 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 80.10 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 82.07 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 138.08, 142.10, 142.39, 142.64, 143.40, 143.62, 143.77, 144.39, 144.44, 144.49, 145.05, 145.09, 145.36, 146.76, 147.15, 147.31, 147.33, 147.63, 147.73, 148.19, 148.30, 148.38, 148.43, 148.94, 149.07, 151.38, 154.43.

ESI MS: m/z=875 ($[M-Cl]^-$).

Spectroscopic data for compound **5a** were reported previously [A. Avent, P. R. Birkett, A. Darwish, S. Houlton, R. Taylor, K .S .T. Thomson, X. W. Wei. *J. Chem. Soc. Perkin Trans.* 2, 2001, 782].

5b. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 1.43-1.51 (m, 15H), 4.20-4.43 (m, 10H).

ESI MS: m/z=945 ($[M-Cl]^-$).

Spectroscopic data for compound **5b** were reported previously [A. Avent, P. R. Birkett, A. Darwish, S. Houlton, R. Taylor, K .S .T. Thomson, X. W. Wei. *J. Chem. Soc. Perkin Trans.* 2, 2001, 782].

5c. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 1.02 (t, 3H, J = 7.4 Hz), 1.09-1.13 (m, 12H), 1.81-1.94 (m, 10H), 4.13-4.20 (m, 8H), 4.27-4.31 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 10.59 ($\underline{C}H_3$), 10.89 ($\underline{C}H_3$), 10.99 ($\underline{C}H_3$), 23.30 ($\underline{C}H_2$), 23.45 ($\underline{C}H_2$), 23.62 ($\underline{C}H_2$), 69.94 ($\underline{C}H_2O$), 70.27 ($\underline{C}H_2O$), 72.97 ($\underline{C}H_2O$), 73.86 ($\underline{C}_{sp3\ fullerene\ cage}$-Cl), 79.41 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 81.67 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 138.21, 142.52, 142.57, 142.69, 143.11, 143.51, 143.62, 144.04, 144.36, 144.51, 144.74, 145.15, 145.31, 145.50, 146.98, 147.36, 147.51, 147.79, 148.18, 148.34, 148.45, 148.52, 148.61, 148.82, 149.05, 149.19, 151.85, 154.27.

APCI MS: m/z=1015 ($[M-Cl]^-$).

$C_{75}H_{35}ClO_5$ (1051.53): calcd. C 85.67, H 3.35, Cl 3.37; found C 85.74, H 3.37, Cl 3.35.

5d. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 0.96-1.04 (m, 15H), 1.45-1.63 (m, 10H), 1.78-1.87 (m, 10H), 4.16-4.22 (m, 8H), 4.30-4.35 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 13.97 ($\underline{C}H_3$), 14.08 ($\underline{C}H_3$), 19.29 ($\underline{C}H_2$), 19.54 ($\underline{C}H_2$), 32.06 ($\underline{C}H_2$), 32.27 ($\underline{C}H_2$), 32.40 ($\underline{C}H_2$), 67.92 ($\underline{C}H_2O$), 68.43 ($\underline{C}H_2O$), 71.22 ($\underline{C}H_2O$), 73.86 ($\underline{C}_{sp3\ fullerene\ cage}$-Cl), 79.43 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 81.68 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 138.23, 142.54, 142.59, 142.69, 143.52, 143.63, 144.04, 144.38, 144.48, 144.75, 145.15, 145.32, 145.51, 146.98, 147.37, 147.51, 147.53, 147.80, 148.21, 148.34, 148.46, 148.52, 148.62, 148.83, 149.05, 149.19, 151.89, 154.34.

APCI MS: m/z=1085 ([M-Cl]$^-$).

$C_{80}H_{45}ClO_5$ (1121.66): calcd. C 85.66, H 4.04, Cl 3.16; found C 85.50, H 4.05, Cl 3.18.

5e. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 1.44 (dd, 18H, J = 11.1; 5.7 Hz), 1.47 (d, 6H, J = 6.0 Hz), 1.51 (d, 6H, J = 6.1 Hz), 4.69-4.77 (m, 1H), 4.84-4.97 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 24.02 ($\underline{C}H_3$), 24.32 ($\underline{C}H_3$), 24.43 ($\underline{C}H_3$), 24.46 ($\underline{C}H_3$), 70.32 ($\underline{C}H$), 70.59 ($\underline{C}H$), 72.76 ($\underline{C}H$), 74.20 ($\underline{C}_{sp3\ fullerene\ cage}$-Cl), 76.52 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 78.57 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 81.86 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 138.28, 142.60, 142.94, 143.43, 143.53, 143.77, 143.95, 144.29, 144.46, 144.60, 144.86, 145.06, 145.19, 145.41, 146.98, 147.40, 147.55, 147.57, 147.80, 148.31, 148.44, 148.48, 148.50, 148.60, 149.03, 149.15, 152.72, 154.90.

APCI MS: m/z=1015 ([M-Cl]$^-$).

$C_{75}H_{35}ClO_5$ (1051.53): calcd. C 85.67, H 3.35, Cl 3.37; found C 85.58, H 3.39, Cl 3.38.

5g. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 3.41 (s, 3H), 3.46 (s, 6H), 3.47 (s, 6H), 3.76-3.87 (m, 10H), 4.35-4.42 (m, 8H), 4.46-4.49 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 59.04 ($\underline{C}H_3$), 59.16 ($\underline{C}H_3$), 59.21 ($\underline{C}H_3$), 67.48 ($\underline{C}H_2O$), 67.85 ($\underline{C}H_2O$), 70.24 ($\underline{C}H_2O$), 71.64 ($\underline{C}H_2O$), 71.85 ($\underline{C}H_2O$), 71.89 ($\underline{C}H_2O$), 73.64 ($\underline{C}_{sp3\ fullerene\ cage}$-Cl), 76.90 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 79.36 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 81.82 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 137.78, 142.08, 142.35, 142.68, 143.51, 143.66, 143.90, 144.40, 144.45, 144.69, 145.19, 145.39, 146.98, 147.34, 147.50, 147.52, 147.76, 147.81, 148.29, 148.33, 148.47, 148.54, 148.64, 149.11, 149.25, 151.44, 154.14.

APCI MS: m/z=1095 ([M-Cl]$^-$).

$C_{75}H_{35}ClO_{10}$ (1131.53): calcd. C 79.61, H 3.12, Cl 3.13; found C 79.37, H 3.15, Cl 3.12.

5h. ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 3.35 (s, 3H), 3.39 (s, 6H), 3.40 (s, 6H), 3.51-3.52 (m, 2H), 3.57-3.59 (m, 8H), 3.69-3.70 (m, 2H), 3.72-3.74 (m, 4H), 3.76-3.78 (m, 4H), 3.85-3.89 (m, 6H), 3.92-3.94 (m, 4H), 4.35-4.41 (m, 8H), 4.45-4.48 (m, 2H).

^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 59.05 ($\underline{C}H_3$), 59.08 ($\underline{C}H_3$), 67.61 ($\underline{C}H_2O$), 68.05 ($\underline{C}H_2O$), 70.33 ($\underline{C}H_2O$), 70.57 ($\underline{C}H_2O$), 70.59 ($\underline{C}H_2O$), 70.66 ($\underline{C}H_2O$), 70.72 ($\underline{C}H_2O$), 72.00

($\underline{C}H_2O$), 72.03 ($\underline{C}H_2O$), 72.06 ($\underline{C}H_2O$), 73.66 ($\underline{C}_{sp3\ fullerene\ cage}$-Cl), 76.93 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 79.32 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 81.83 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 137.82, 142.08, 142.36, 142.69, 143.49, 143.64, 143.88, 144.35, 144.42, 144.63, 145.13, 145.19, 145.36, 146.97, 147.34, 147.51, 147.68, 147.81, 148.34, 148.35, 148.46, 148.54, 148.62, 149.11, 149.24, 151.41, 154.13.

APCI MS: m/z=1373 ($[M+Na]^+$).

5i. ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 3.36 (s, 3H), 3.37-3.38 (m, 12H), 3.50-3.57 (m, 10H), 3.60-3.71 (m, 20H), 3.73-3.79 (m, 10H), 3.83-3.93 (m, 10H), 4.33-4.47 (m, 10H).

^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 59.06 ($\underline{C}H_3$), 67.58 ($\underline{C}H_2O$), 68.02 ($\underline{C}H_2O$), 68.66 ($\underline{C}H_2O$), 70.32 ($\underline{C}H_2O$), 70.55 ($\underline{C}H_2O$), 70.58 ($\underline{C}H_2O$), 70.59 ($\underline{C}H_2O$), 70.63 ($\underline{C}H_2O$), 70.69 ($\underline{C}H_2O$), 70.71 ($\underline{C}H_2O$), 70.77 ($\underline{C}H_2O$), 70.80 ($\underline{C}H_2O$), 71.93 ($\underline{C}H_2O$), 71.96 ($\underline{C}H_2O$), 73.69 ($\underline{C}_{sp3\ fullerene\ cage}$-Cl), 76.93 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 79.32 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 81.87 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 137.81, 142.08, 142.35, 142.69, 143.49, 143.63, 143.88, 144.37, 144.42, 144.63, 145.14, 145.20, 145.36, 146.97, 147.05, 147.34, 147.52, 147.69, 147.81, 148.34, 148.47, 148.55, 148.62, 149.11, 149.25, 151.42, 154.10.

APCI MS: m/z=1536 ($[M-Cl]^-$).

$C_{95}H_{75}ClO_{20}$ (1572.05): calcd. C 72.58, H 4.81, Cl 2.26; found C 72.49, H 4.85, Cl 2.24.

Synthesis of 3j-H and 3j-K

Compound **3j** (80 mg, 0.05 mmol) was dissolved in 15 mL of CH_2Cl_2 and quenched with trifluoroacetic acid (1 mL) at room temperature. The solvent and excess of CF_3COOH were removed *in vacuo*; the residue was washed with ethyl acetate and then dried in air. Acid **3j-H** was obtained as an orange powder with 98% yield.

Afterwards, **3j-H** (62 mg, 0.05 mmol) was suspended in distilled water (10 mL) and then aqueous solution of K_2CO_3 (17 mg, 0.125 mmol, in 3 mL of water) was added. The obtained solution was filtered *via* syringe PES filter and freeze-dried. Compound **3j-K** was obtained as an orange light powder with virtually quantitative yield.

3j-H. ^{1}H NMR (500 MHz, acetone-D6, δ, ppm): 2.73-2.83 (m, 10H), 4.35-4.60 (m, 10H).

^{13}C NMR (125 MHz, acetone-D6, δ, ppm): 34.42 ($\underline{C}H_2$), 34.71 ($\underline{C}H_2$), 34.80 ($\underline{C}H_2$), 64.18 ($\underline{C}H_2$), 64.25 ($\underline{C}H_2$), 64.32 ($\underline{C}H_2$), 64.46 ($\underline{C}H_2$), 66.55 ($\underline{C}_{sp3\ fullerene\ cage}$-Br), 76.88 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 79.40 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 79.45 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 81.43 ($\underline{C}_{sp3\ fullerene\ cage}$-O), 137.01, 138.34, 142.50, 142.60, 142.73, 142.74, 142.79, 142.84, 142.92, 143.21, 143.49, 143.51, 143.66, 143.71, 144.12, 144.16, 144.46, 144.51, 144.69, 145.04, 145.18, 145.22, 145.31, 145.36, 145.60, 146.92, 146.96, 147.35, 147.47, 147.49, 147.72, 147.84, 148.32, 148.35, 148.43, 148.46, 148.55, 148.76,

149.02, 149.10, 149.17, 149.23, 149.82, 151.70, 152.00, 154.65, 155.16, 171.68 (COO), 171.99 (COO), 172.12 (COO), 172.19 (COO), 172.63 (COO).

X-ray crystallography for 3b·

Synchrotron X-ray data for single crystal of **3b** (0.03 × 0.03 × 0.01 mm^3) were collected at 100 K on BL14.2 at the BESSY storage ring (Berlin, Germany) using a MAR225 detector, λ = 0.8551 Å. The structures was solved and anisotropically refined using SHELX package. Absorption correction was not applied. Crystal data for **3b**: $C_{70}H_{25}BrO_5$, M = 1025.81, orthorhombic, *Pnma*, a = 19.765(1), b = 17.350(1), c = 24.003(2) Å, V = 8231.2(9) $Å^3$, Z = 8, D_{calc} = 1.656 g cm^{-3}. Anisotropic refinement with 9880 reflections and 866 parameters yielded a conventional R_1 = 0.104 for 4087 reflections with $I > 2\sigma(I)$ and wR_2 = 0.269 for all reflections. All methylene and methyl hydrogen atoms were placed into geometrically calculated positions and refined in the riding mode. Both $C_{60}(OC_2H_5)Br$ molecules are located on a mirror plane so that two halves are independent. Due to approximate fivefold symmetry, both molecules are disordered around pseudo C_5 axes with OC_2H_5 groups disordered over two positions each. Br atoms are disordered over 2-4 positions. For more details see CCDC 1496548.

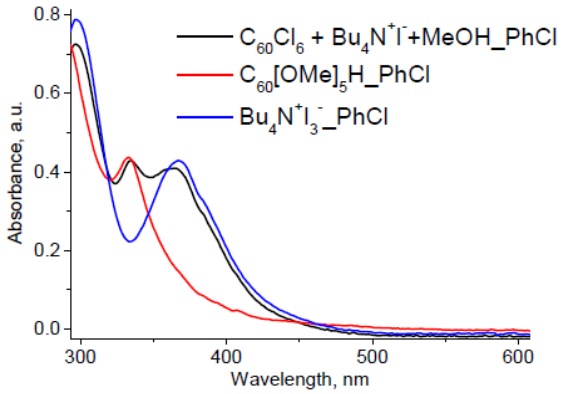

Fig. S1. UV-VIS spectra of the $C_{60}Cl_6$+ Bu_4NI+MeOH reaction mixture and solutions of $C_{60}[OMe]_5H$ and Bu_4NI_3 in chlorobenzene

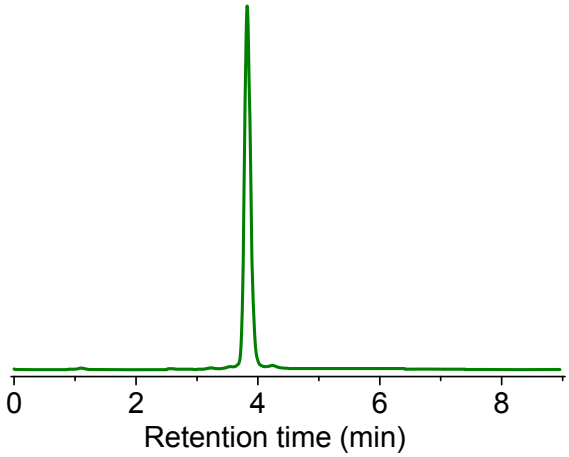

Fig. S2. HPLC profile of compound **5g** (Orbit C18 column, 150 x 4.6 mm, acetonitrile/toluene 70/30 v/v, flow rate 1 mL min^{-1})

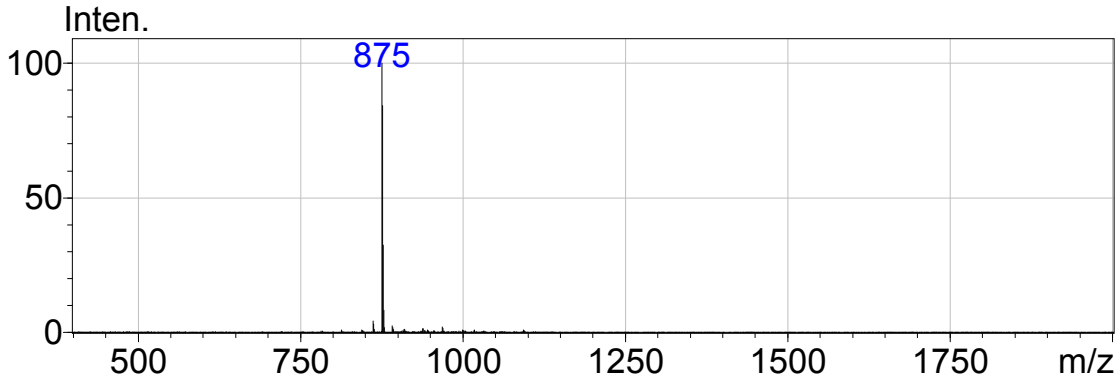

Fig. S3. APCI MS spectrum of compound **1a**

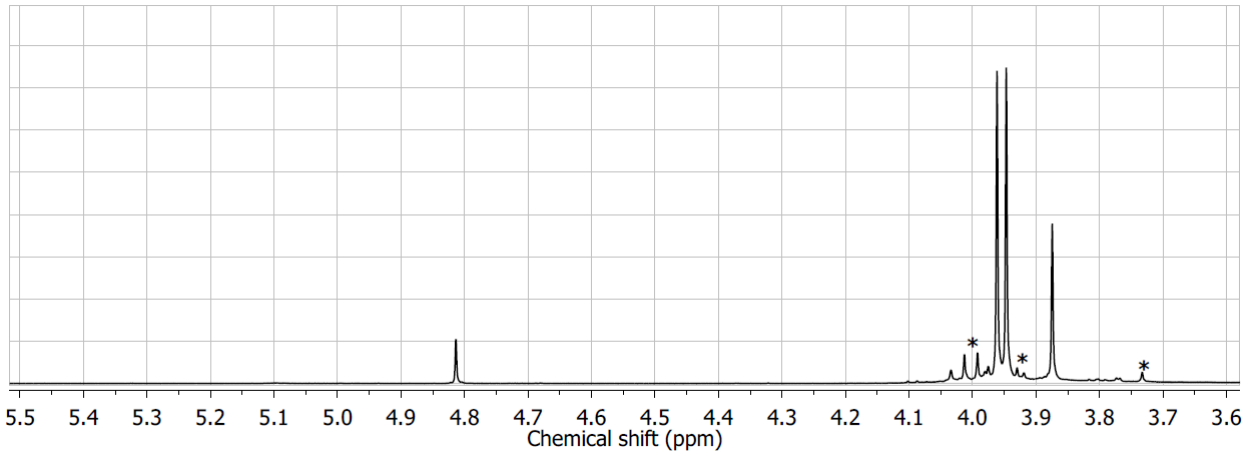

Fig. S4. ^{1}H NMR spectrum of compound **1a** (* denotes signals of the hydrolysis products)

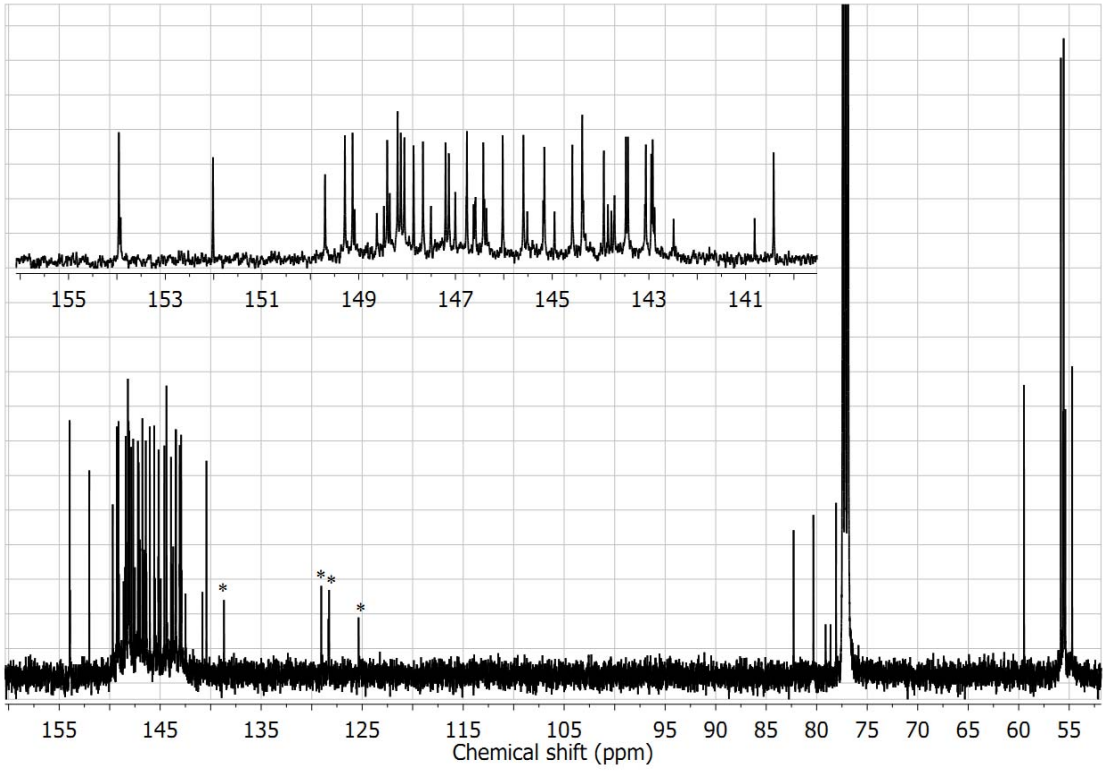

Fig. S5. ^{13}C NMR spectrum of compound **1a** (* denotes signals of toluene impurity)

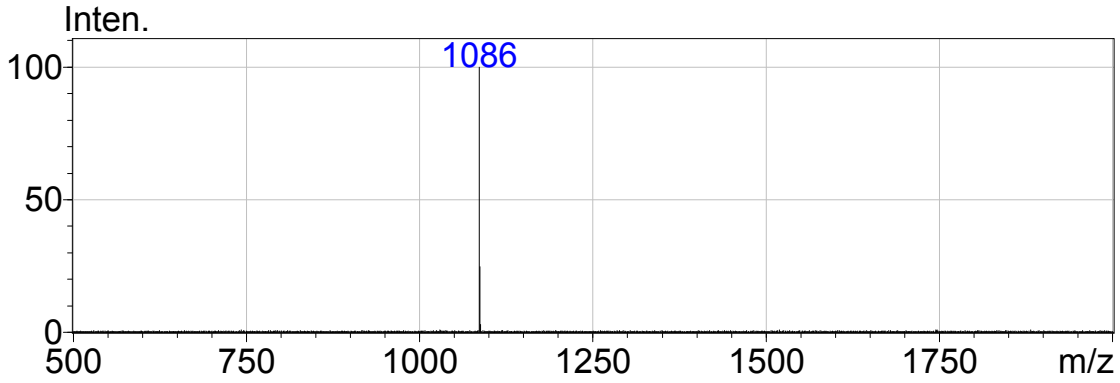

Fig. S6 APCI MS spectrum of compound **1d**

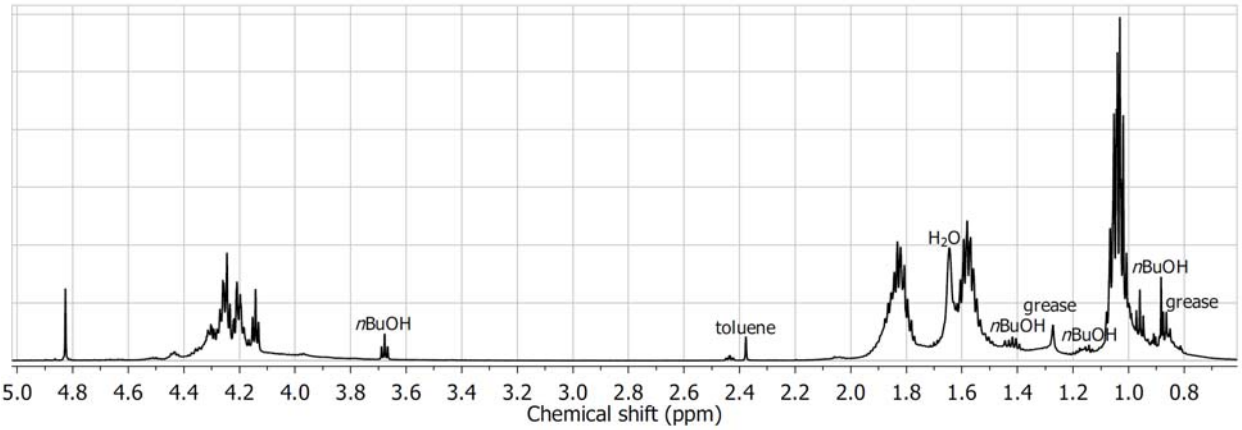

Fig. S7 ^{1}H NMR spectrum of compound **1d**

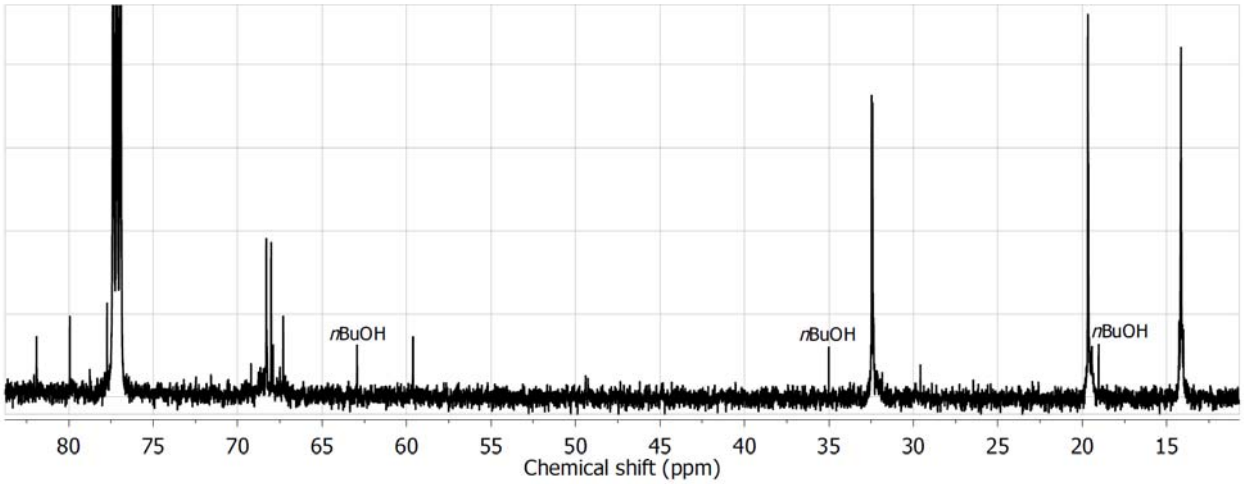

Fig. S8. High-field part of the ^{13}C NMR spectrum of compound **1d**

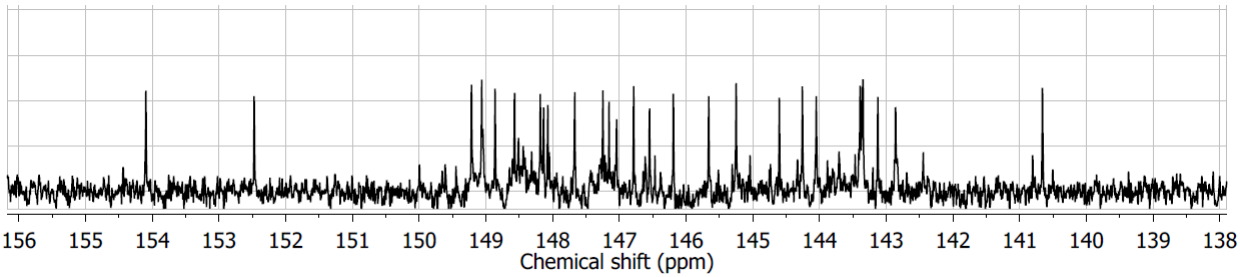

Fig. S9. Low-field part of the ^{13}C NMR spectrum of compound **1d**

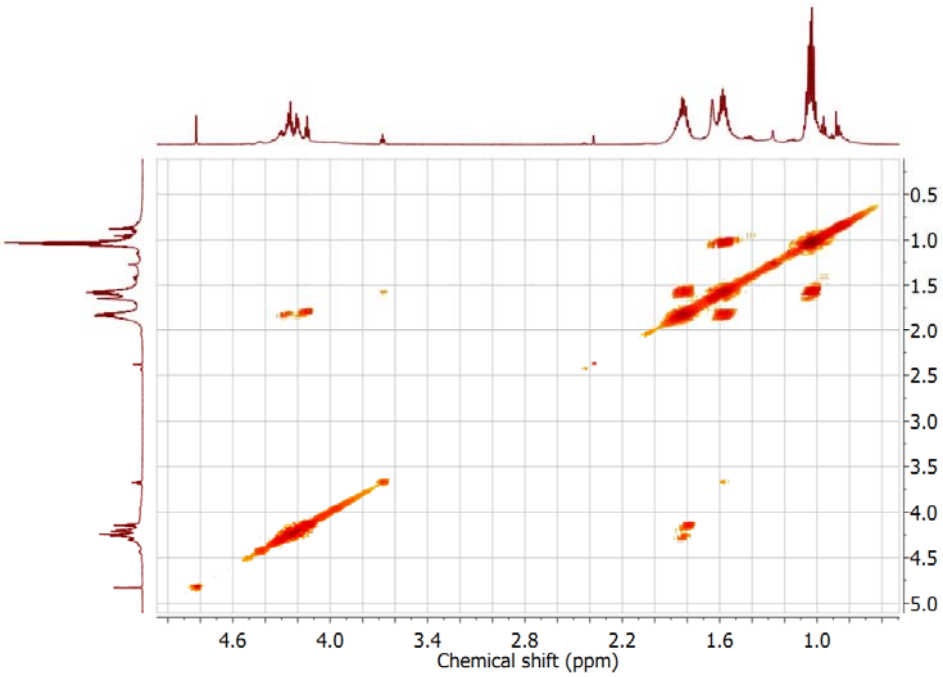

Fig. S10. H-H COSY NMR spectrum of compound **1d**

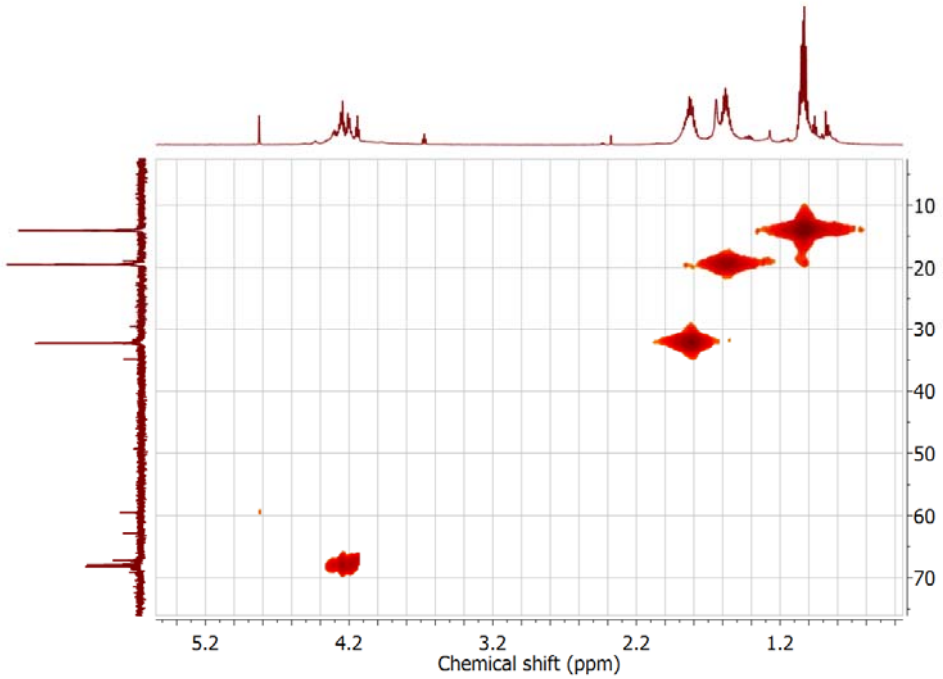

Fig. S11. H-C HSQC NMR spectrum of compound **1d**

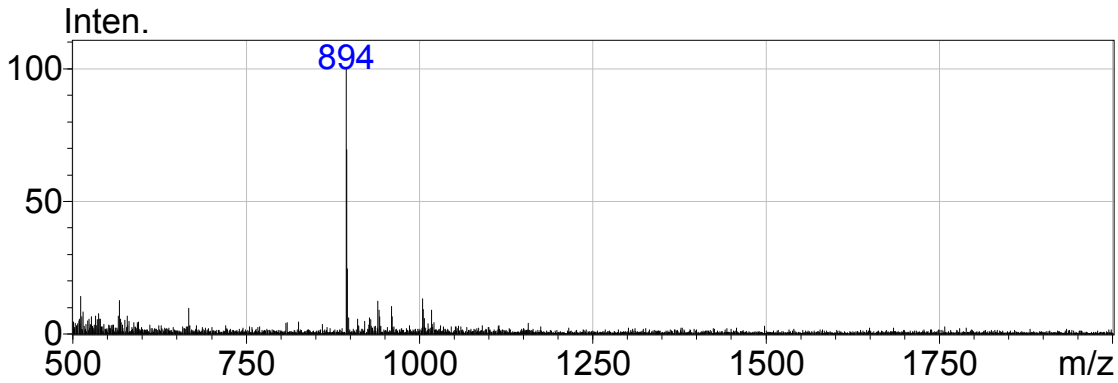

Fig. S12. APCI mass spectrum of compound **2f**

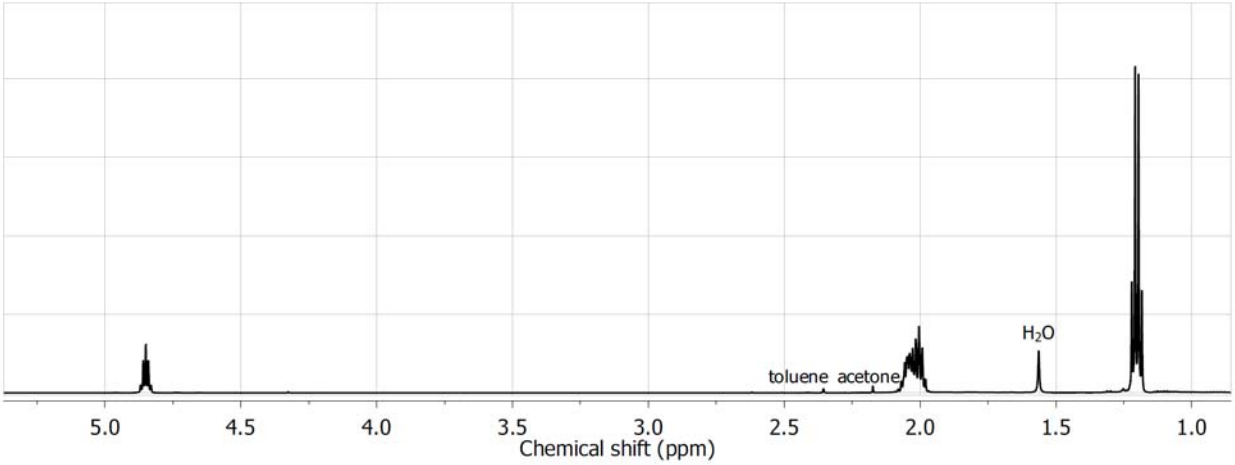

Fig. S13. ^{1}H NMR spectrum of compound **2f**

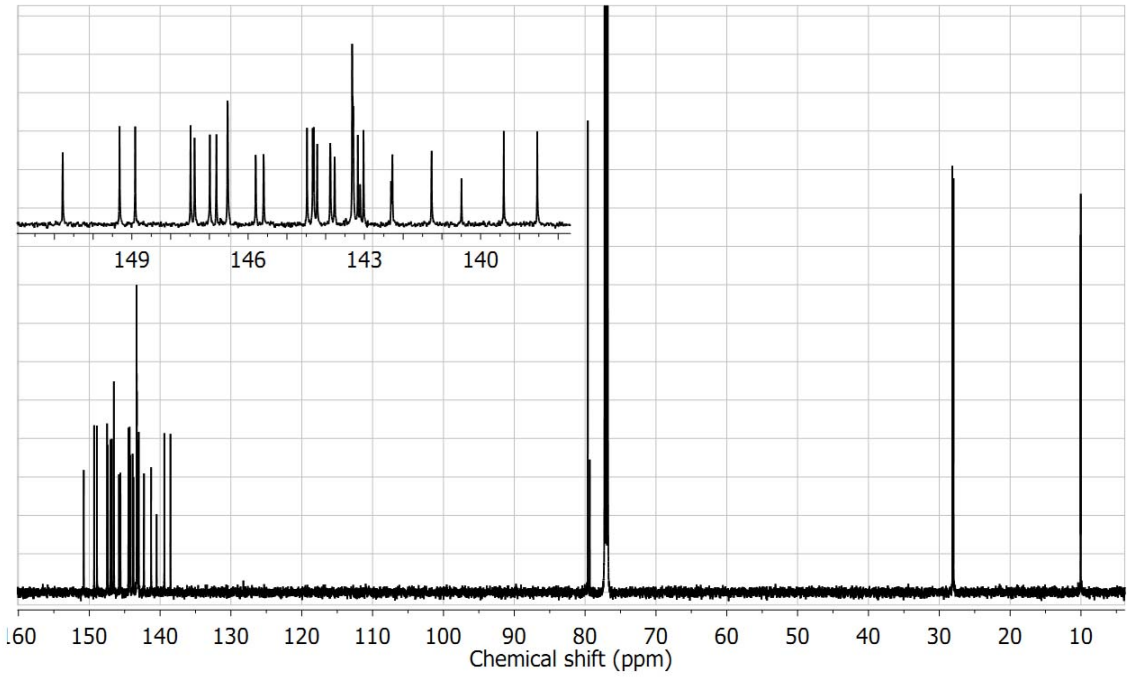

Fig. S14. ^{13}C NMR spectrum of compound **2f**

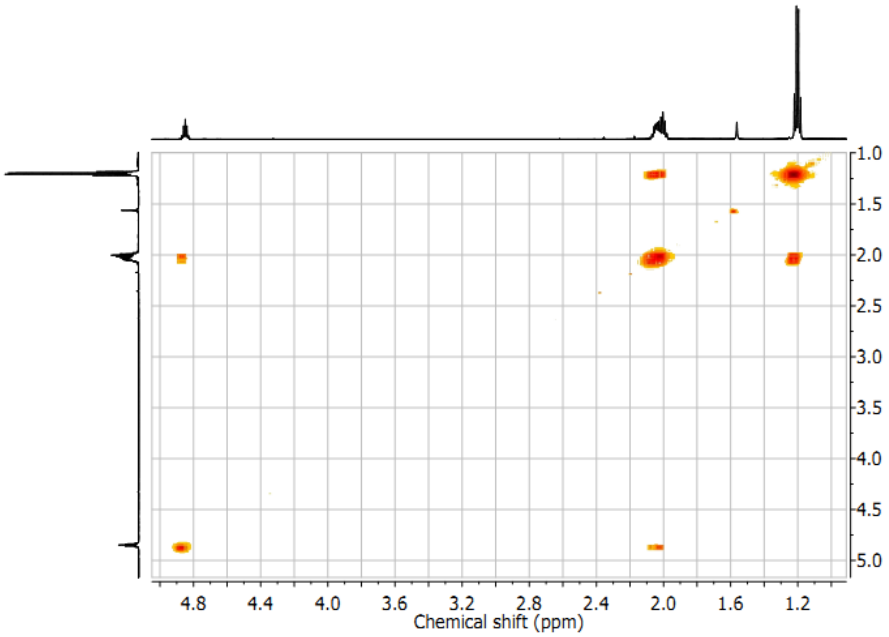

Fig. S15. H-H COSY NMR spectrum of compound **2f**

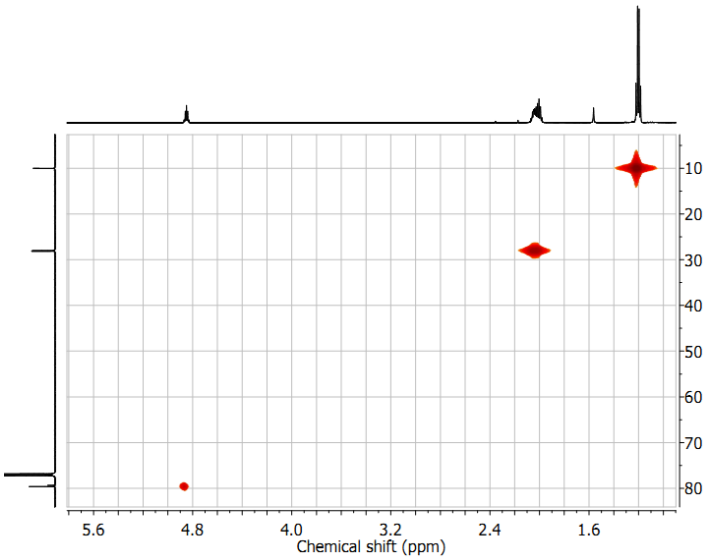

Fig. S16. H-C HSQC NMR spectrum of compound **2f**

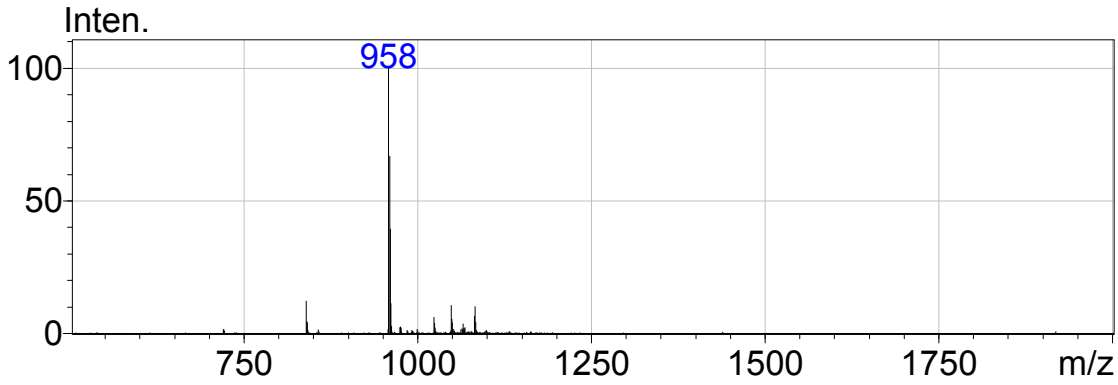

Fig. S17. APCI mass spectrum of compound **2h**

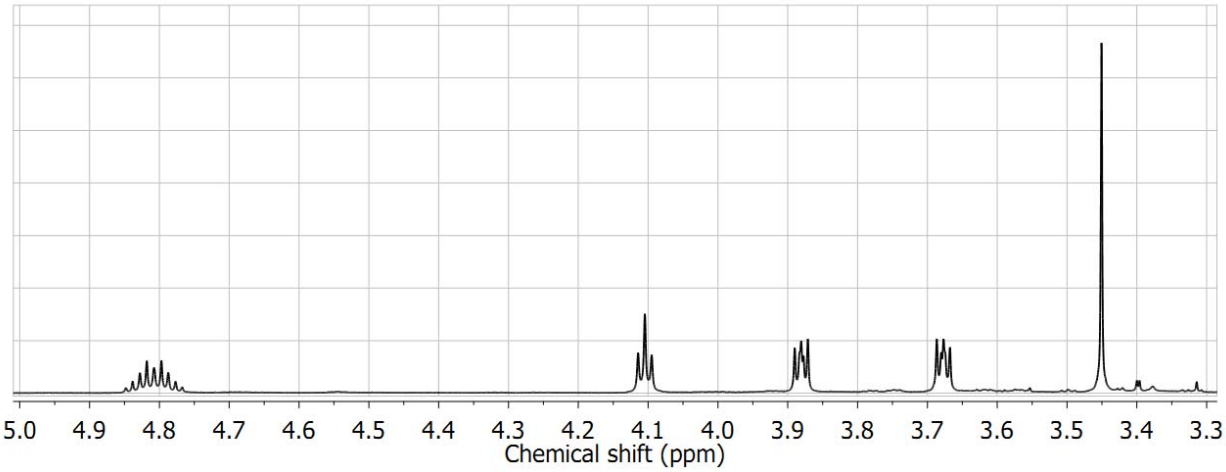

Fig. S18 ^{1}H NMR spectrum of compound **2h**

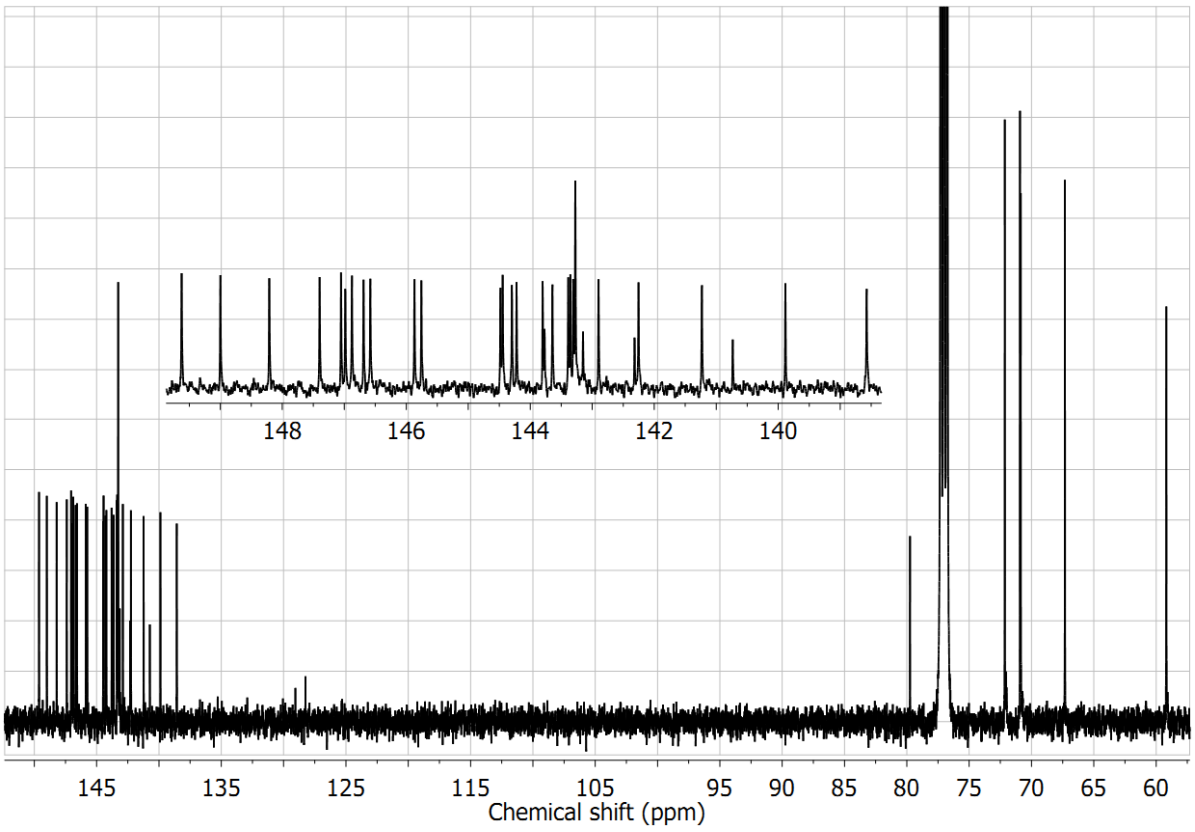

Fig. S19 ^{13}C NMR spectrum of compound **2h**

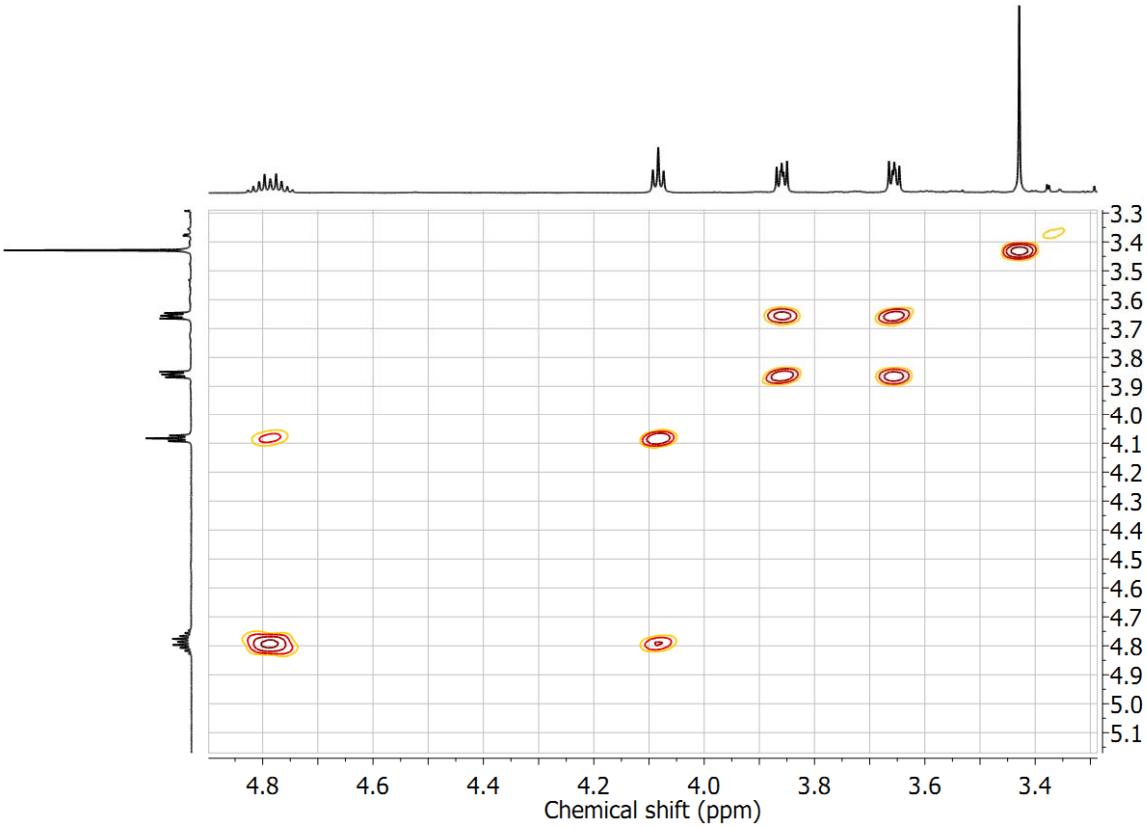

Fig. S20 H-H COSY NMR spectrum of compound **2h**

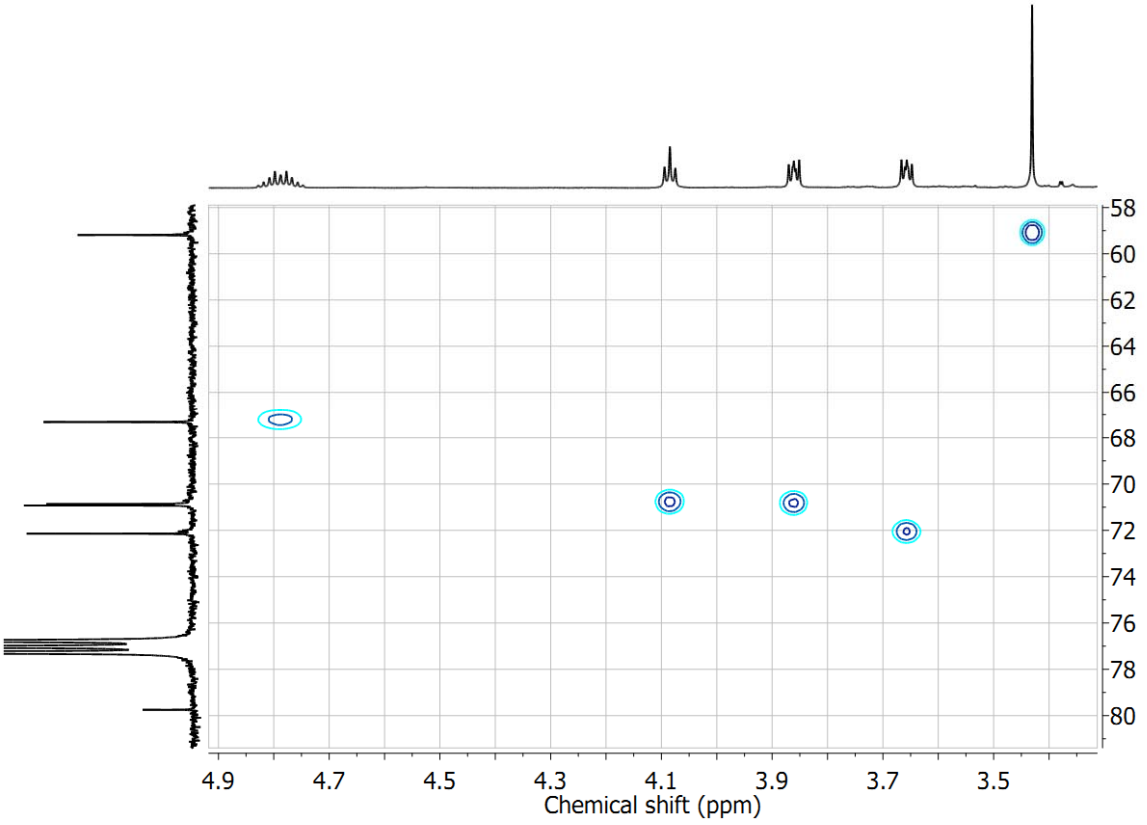

Fig. S21. H-C HSQC NMR spectrum of compound **2h**

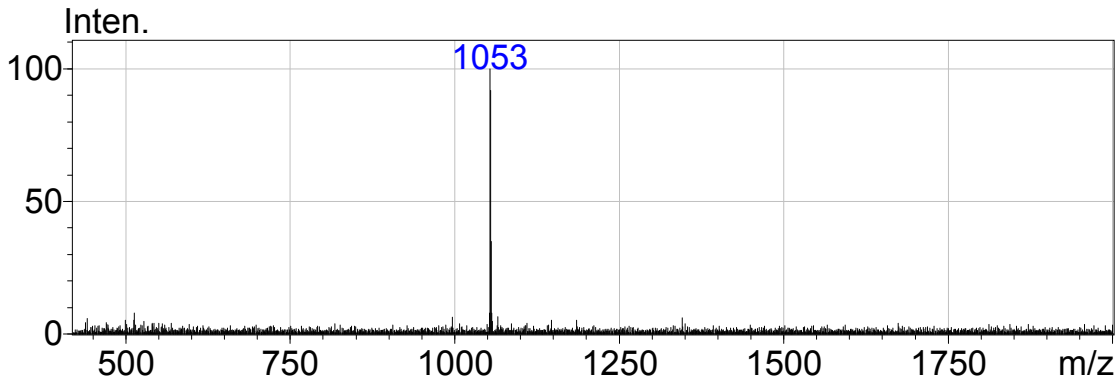

Fig. S22. APCI mass spectrum of compound **2i** ([M+Li]$^+$)

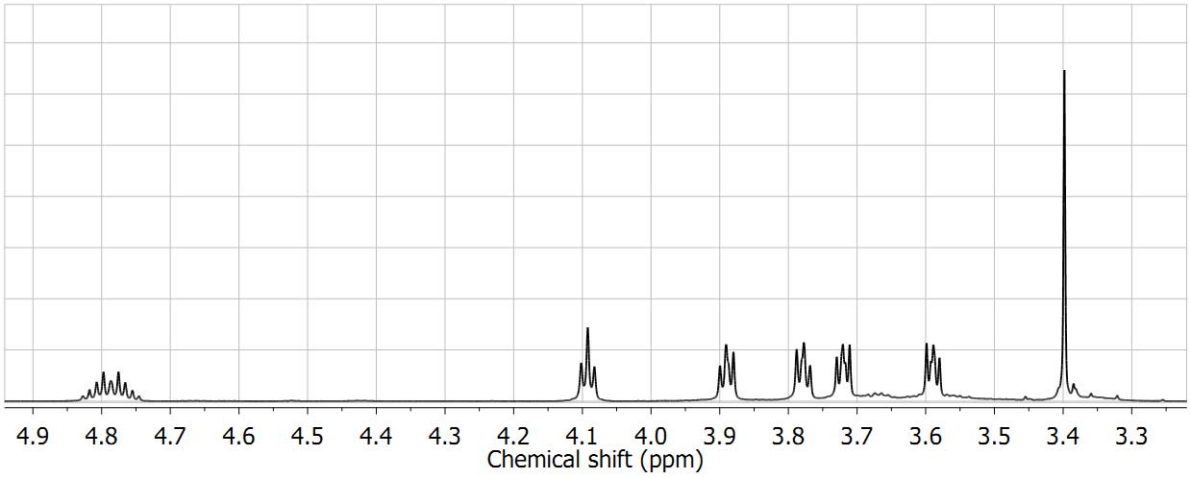

Fig. S23. ^{1}H NMR spectrum of compound **2i**

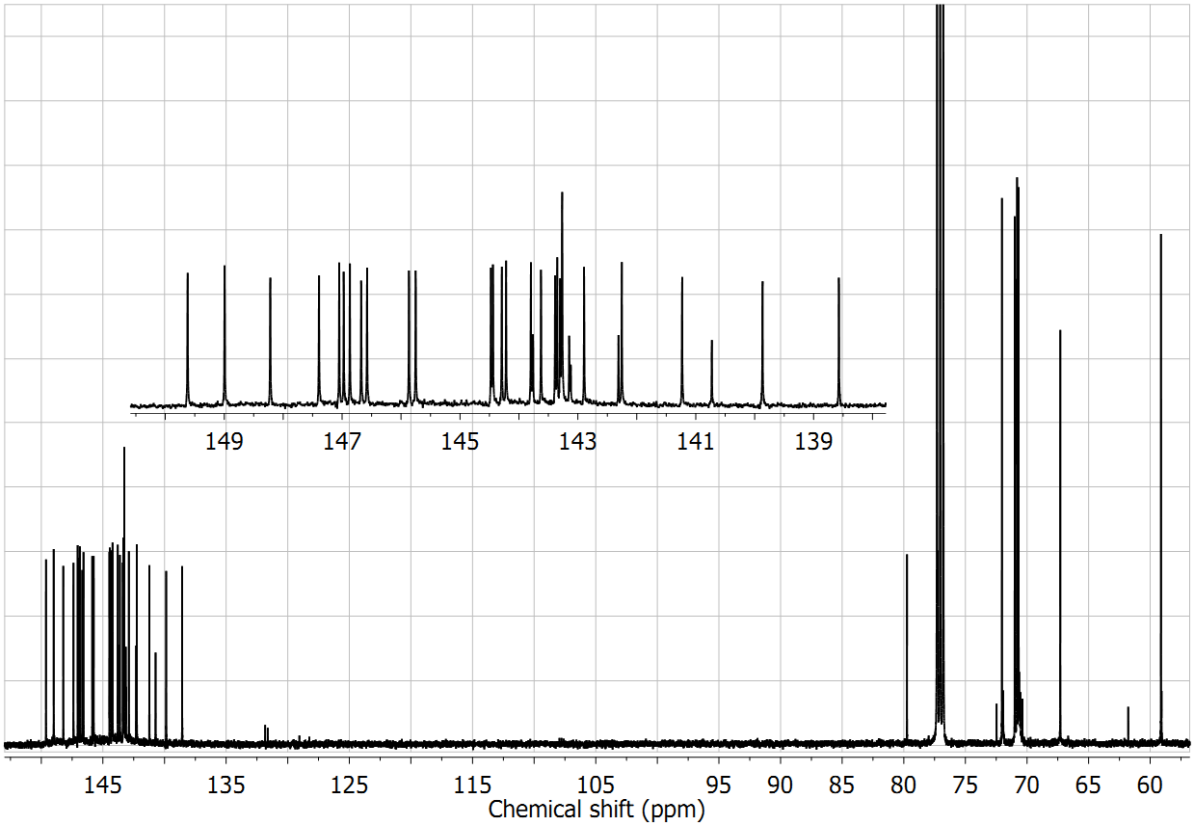

Fig. S24. ^{13}C NMR spectrum of compound **2i**

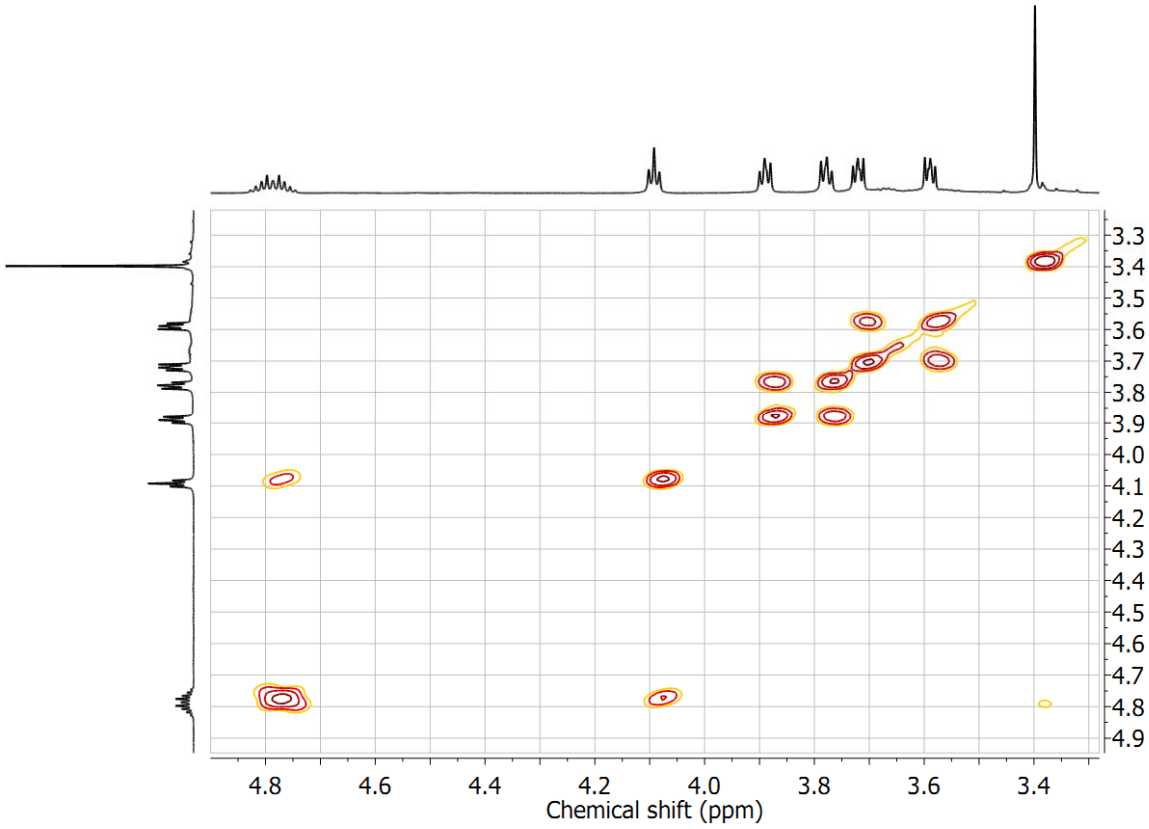

Fig. S25. H-H COSY NMR spectrum of compound **2i**

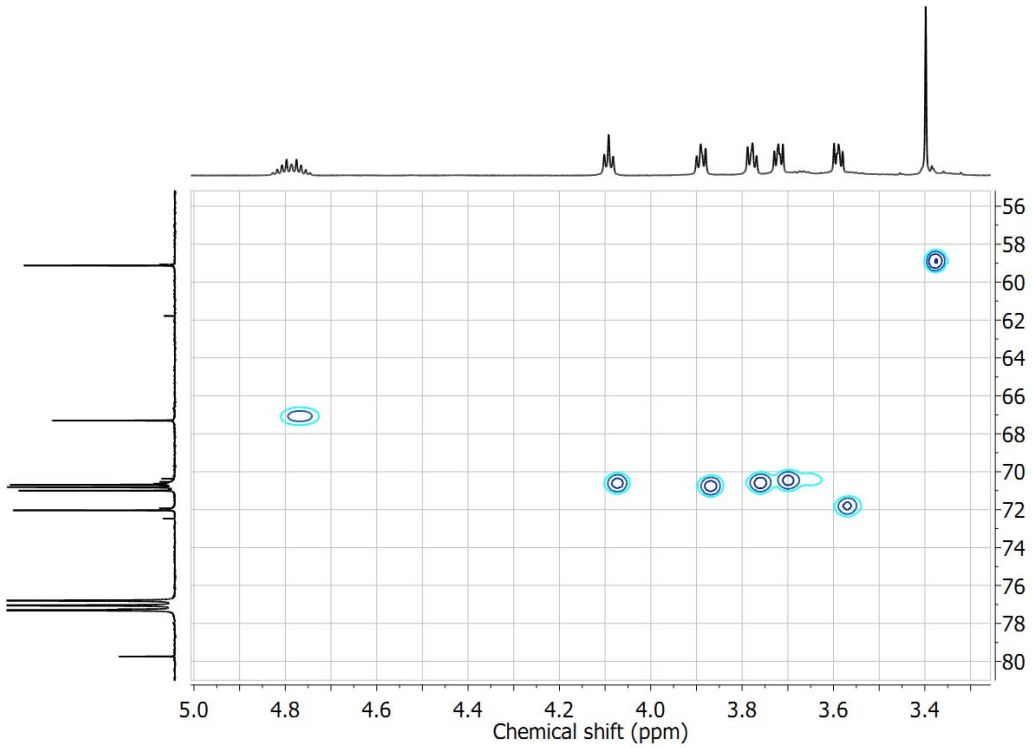

Fig. S26. H-C HSQC NMR spectrum of compound **2i**

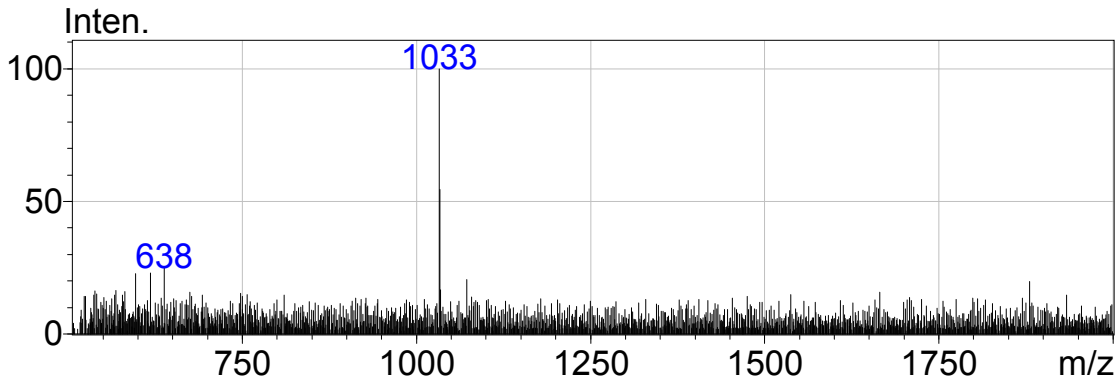

Fig. S27. APCI mass spectrum of compound **2j** ([M+Na]$^+$)

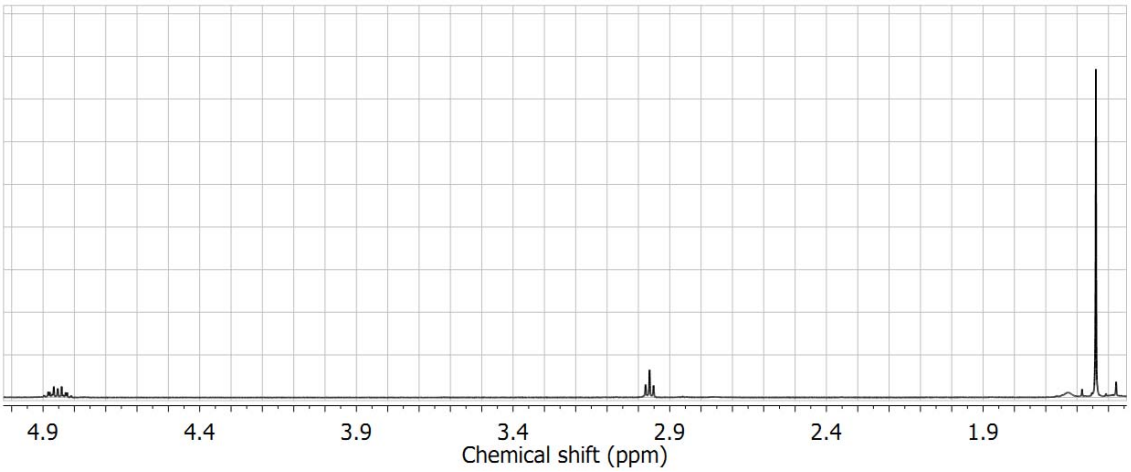

Fig. S28. ^{1}H NMR spectrum of compound **2j**

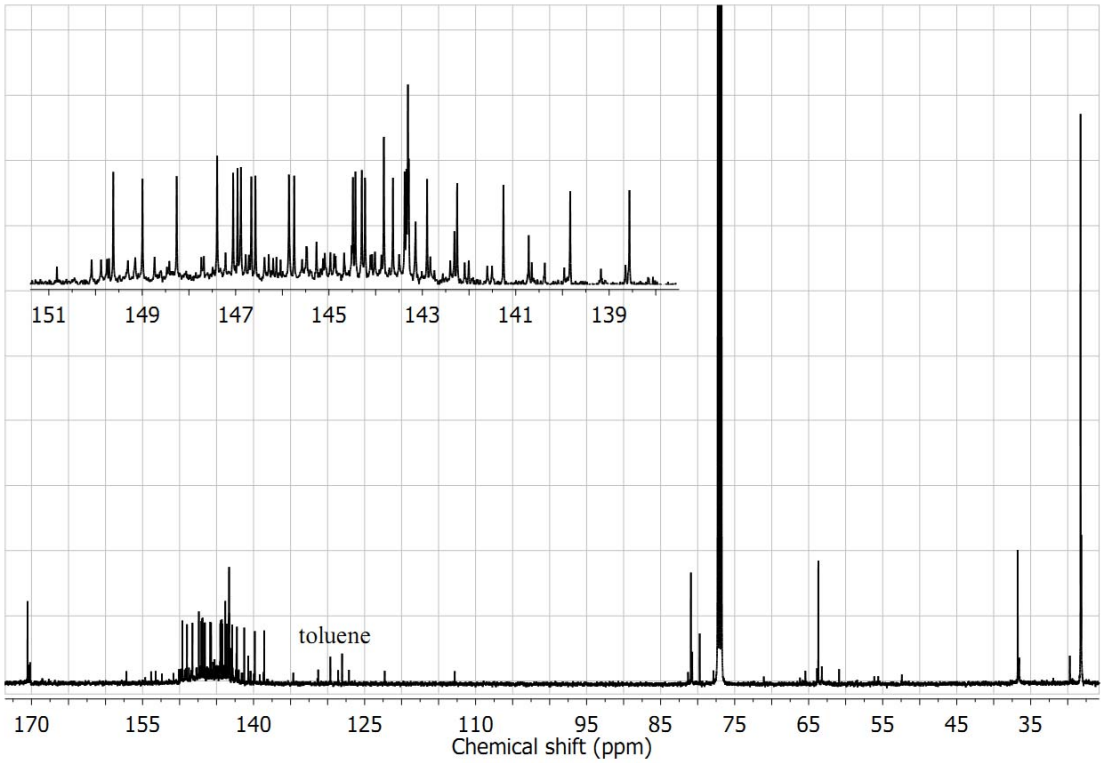

Fig. S29. ^{13}C NMR spectrum of compound **2j**

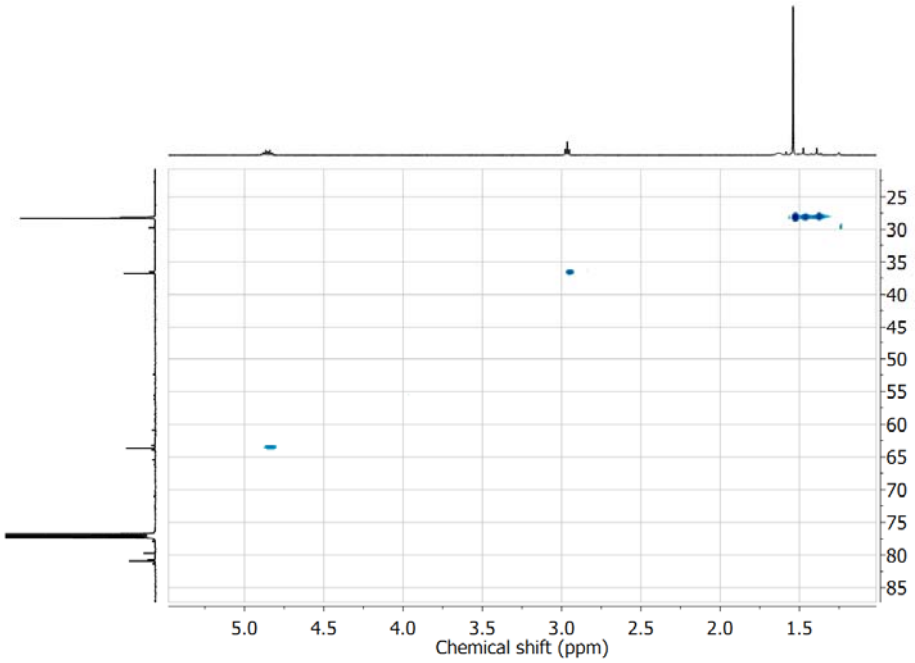

Fig. S30. H-C HSQC NMR spectrum of compound **2j**

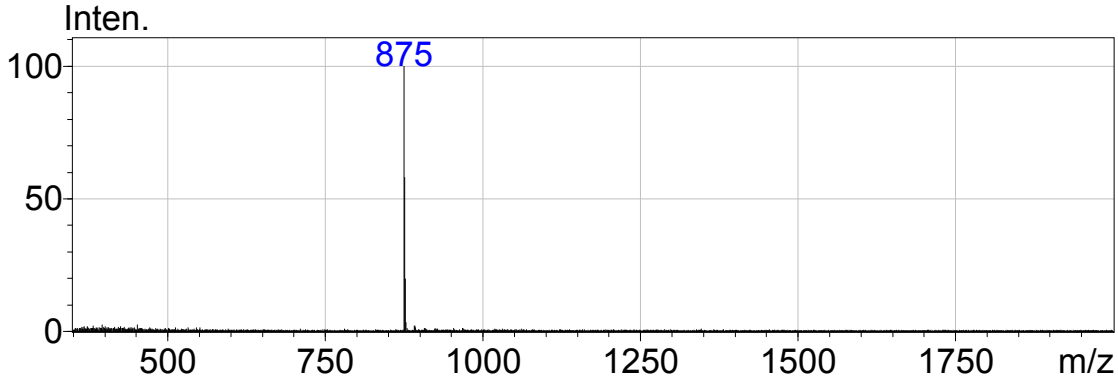

Fig. S31. ESI MS spectrum of compound **3a**

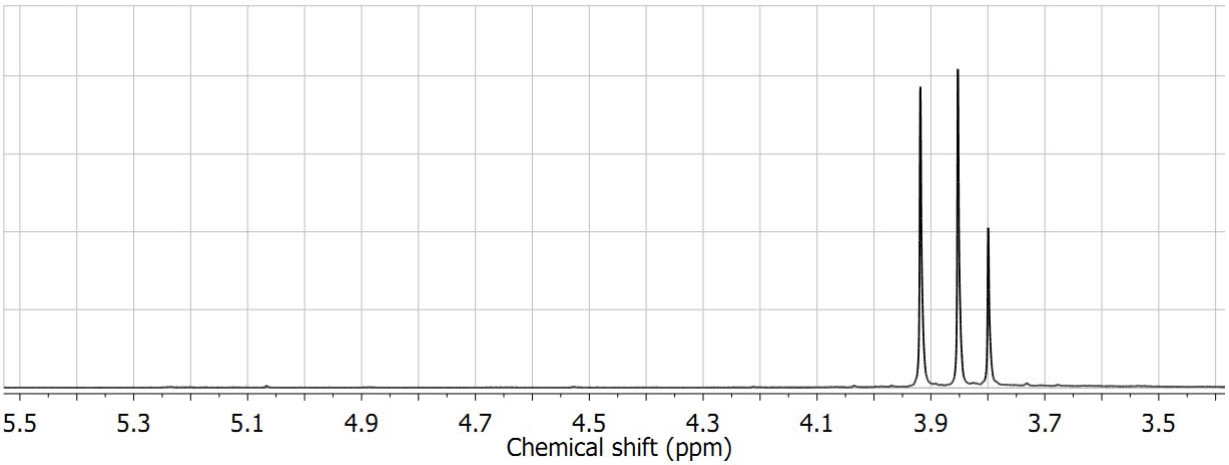

Fig. S32. ^{1}H NMR spectrum of compound **3a**

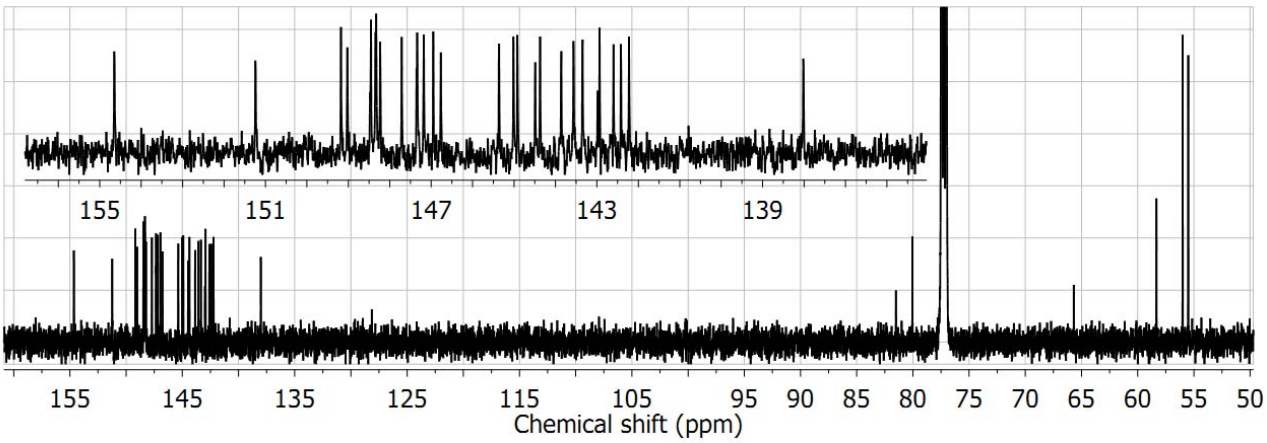

Fig. S33. ^{13}C NMR spectrum of compound **3a**

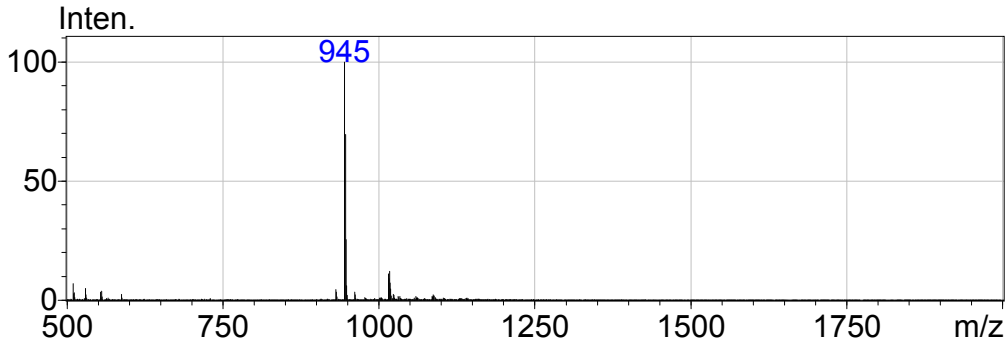

Fig. S34 ESI MS spectrum of compound **3b**

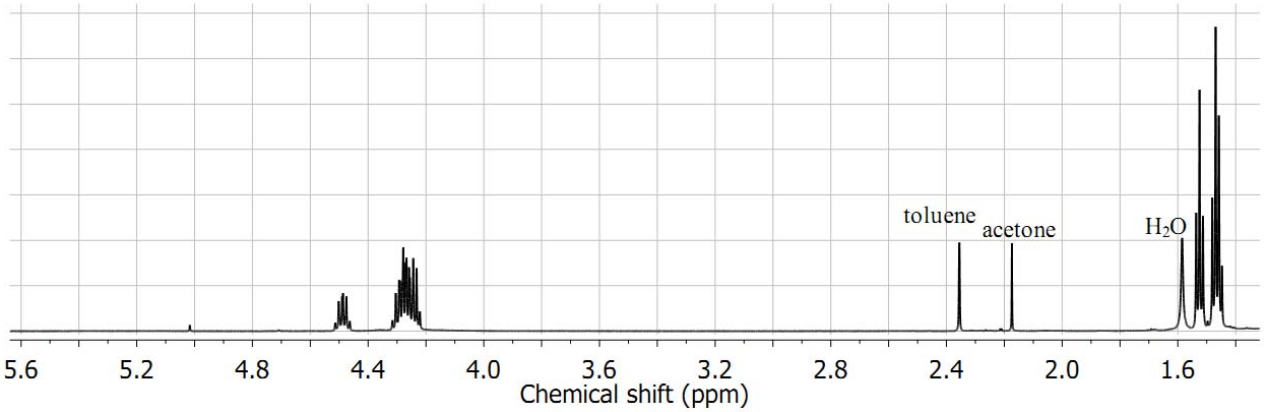

Fig. S35 ^{1}H NMR spectrum of compound **3b**

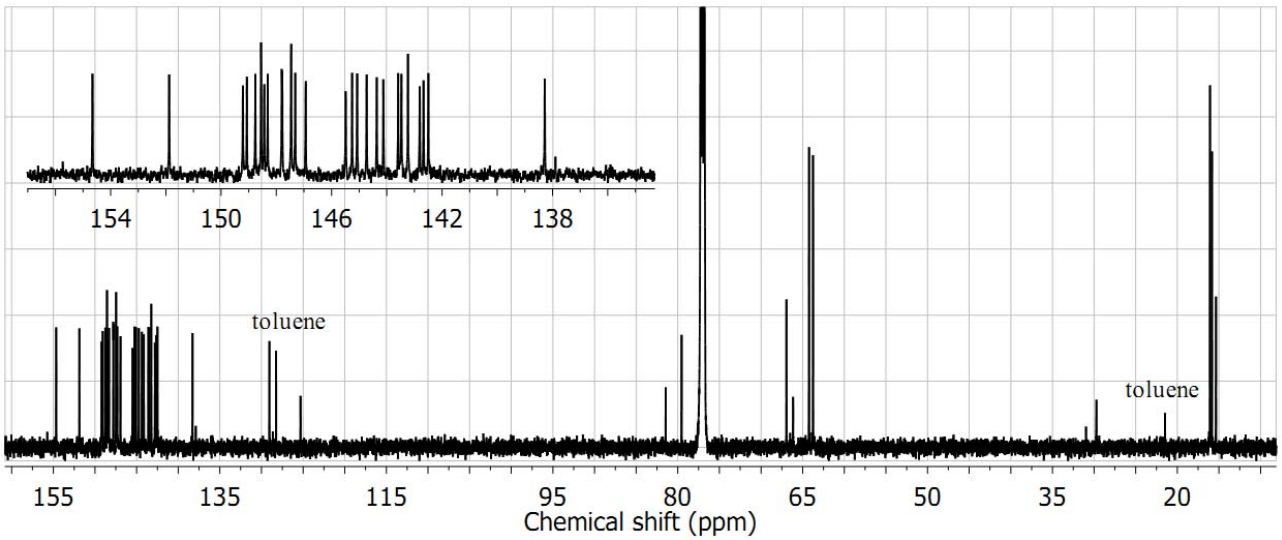

Fig. S36. ^{13}C NMR spectrum of compound **3b**

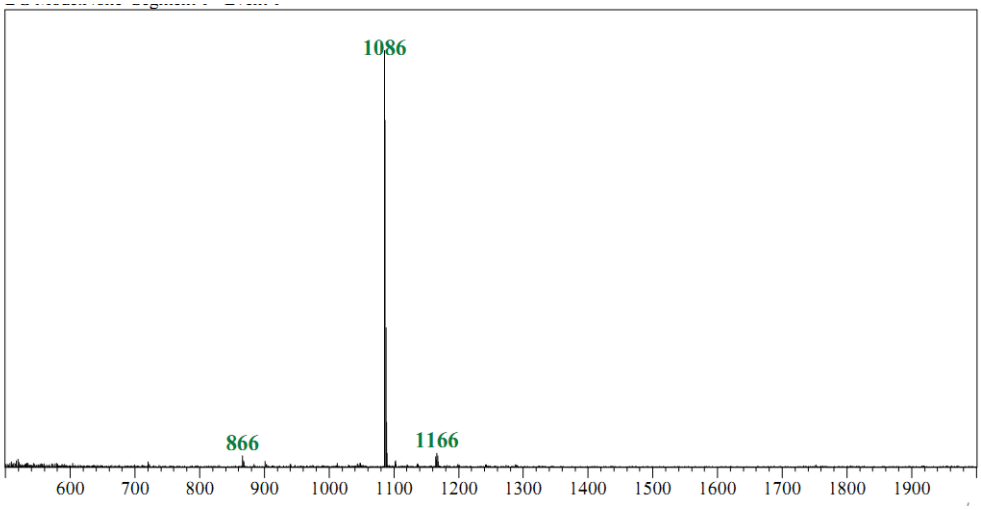

Fig. S37. APCI mass spectrum of compound **3d**

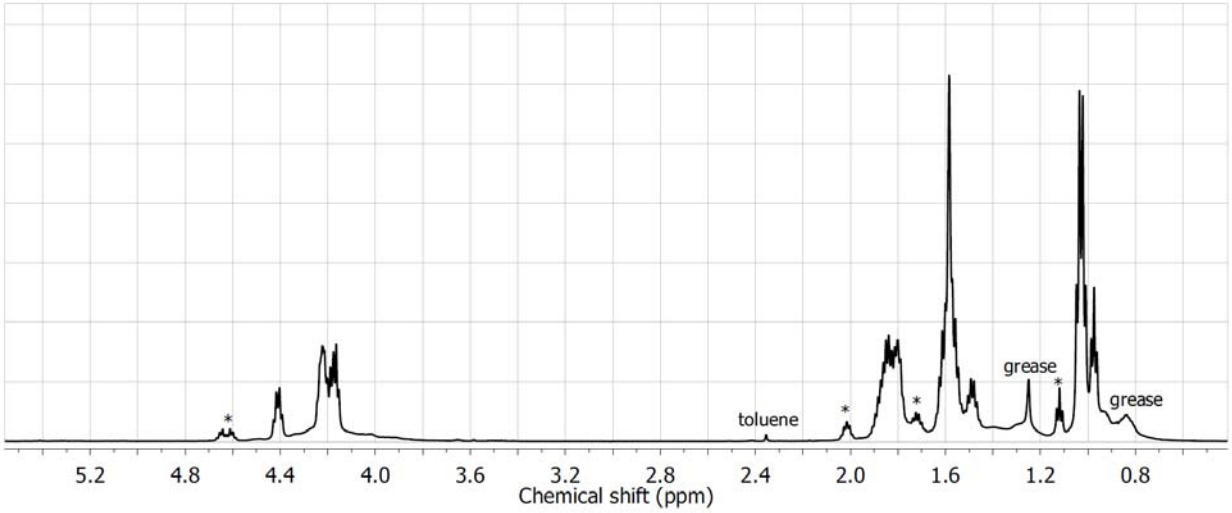

Fig. S38. ^{1}H NMR spectrum of compound **3d** ("*" denotes signals of $C_{60}(OC_4H_9)_2$ impurity)

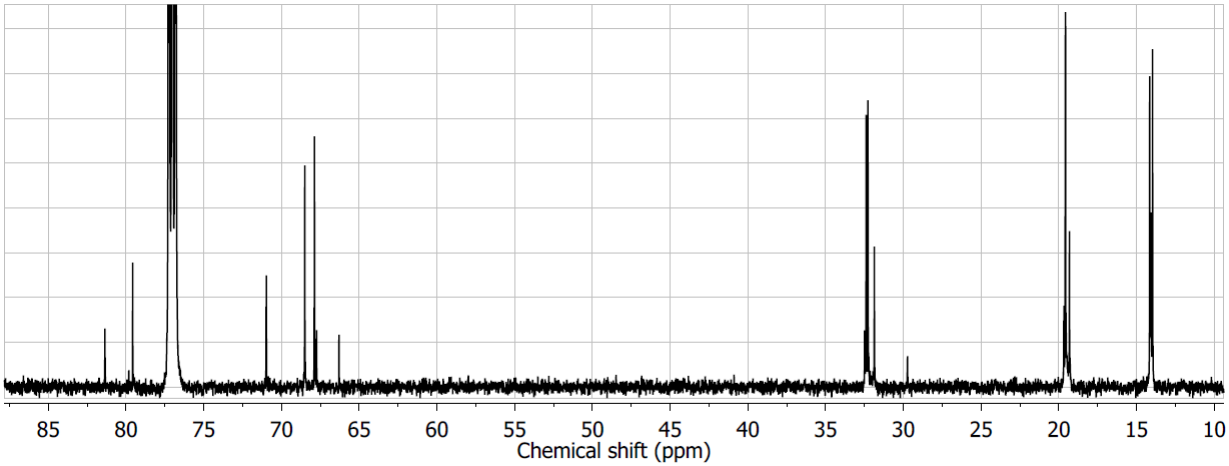

Fig. S39. High-field part of the ^{13}C NMR spectrum of compound **3d**

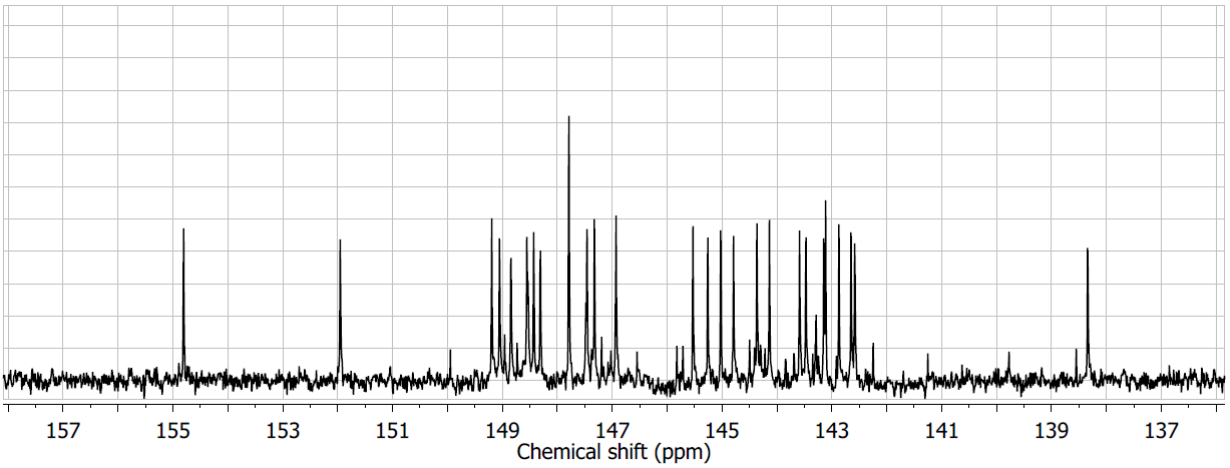

Fig. S40. Low-field part of the ^{13}C NMR spectrum of compound **3d**

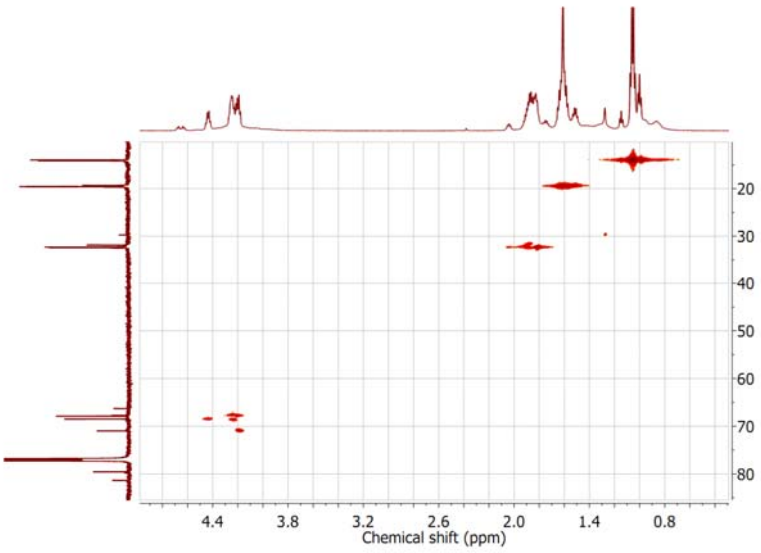

Fig. S41. H-C HSQC NMR spectrum of compound **3d**

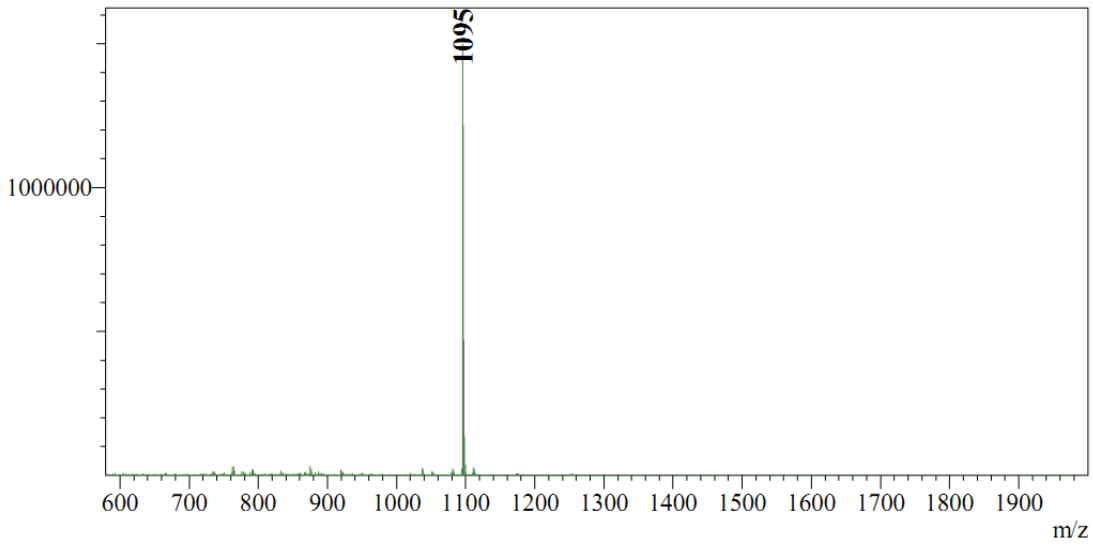

Fig. S42. ESI mass spectrum of compound **3g**

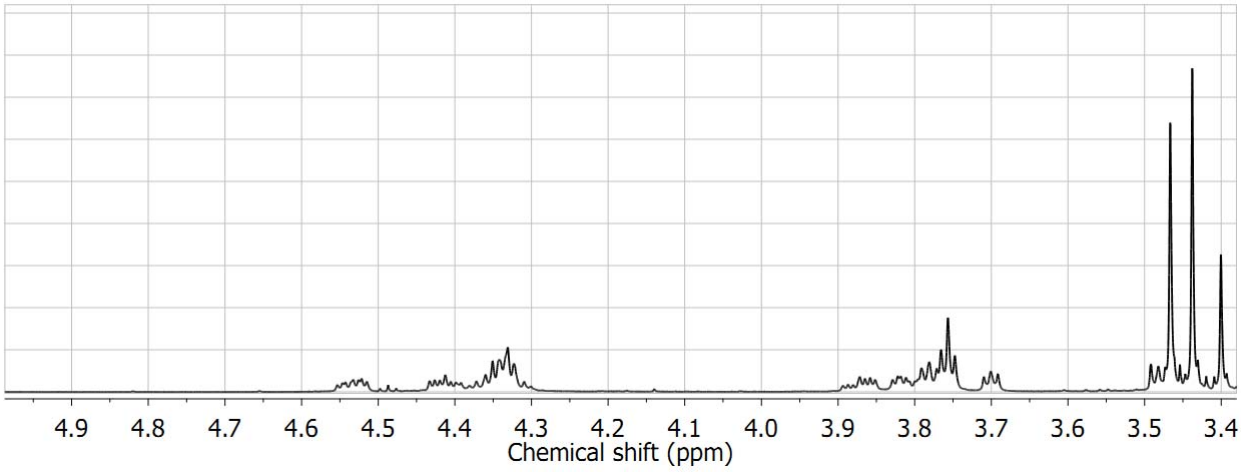

Fig. S43. ^{1}H NMR spectrum of compound **3g**

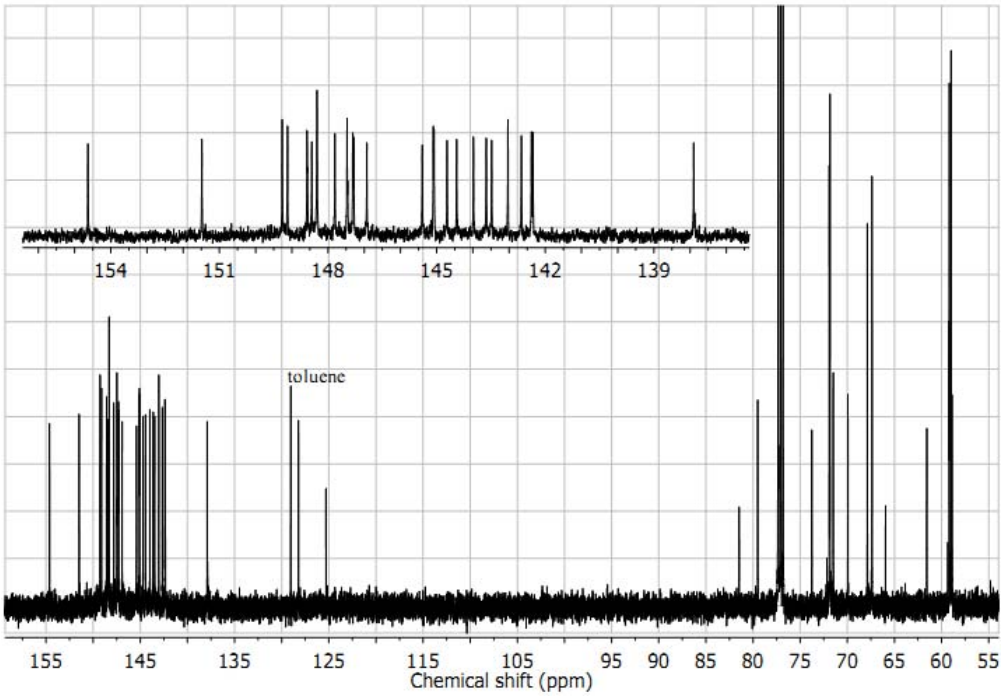

Fig. S44. ^{13}C NMR spectrum of compound **3g**

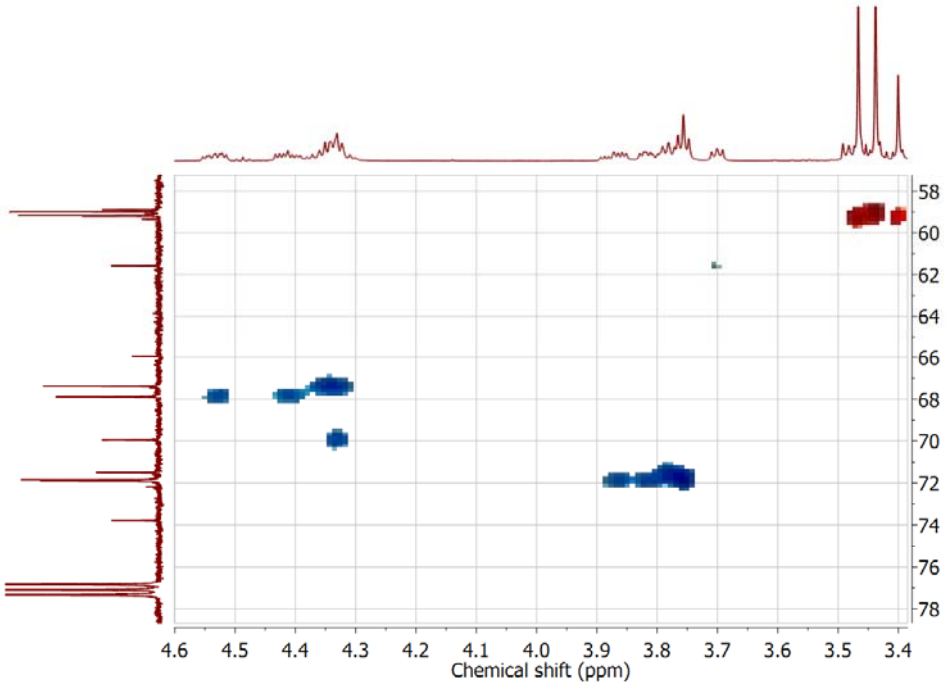

Fig. S45. H-C HSQC NMR spectrum of compound **3g**

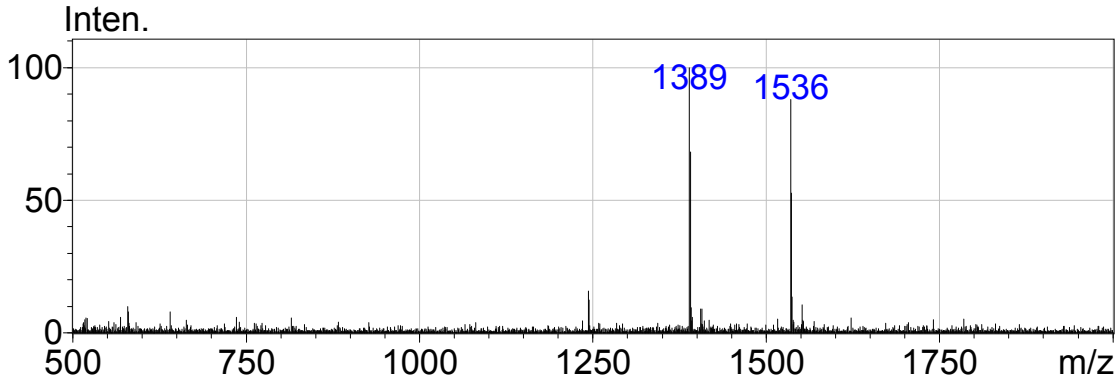

Fig. S46. APCI mass spectrum of compound **3i**: 1536 ([M-Br]$^-$), 1389 ([M-Br-OR+H_2O]$^-$)

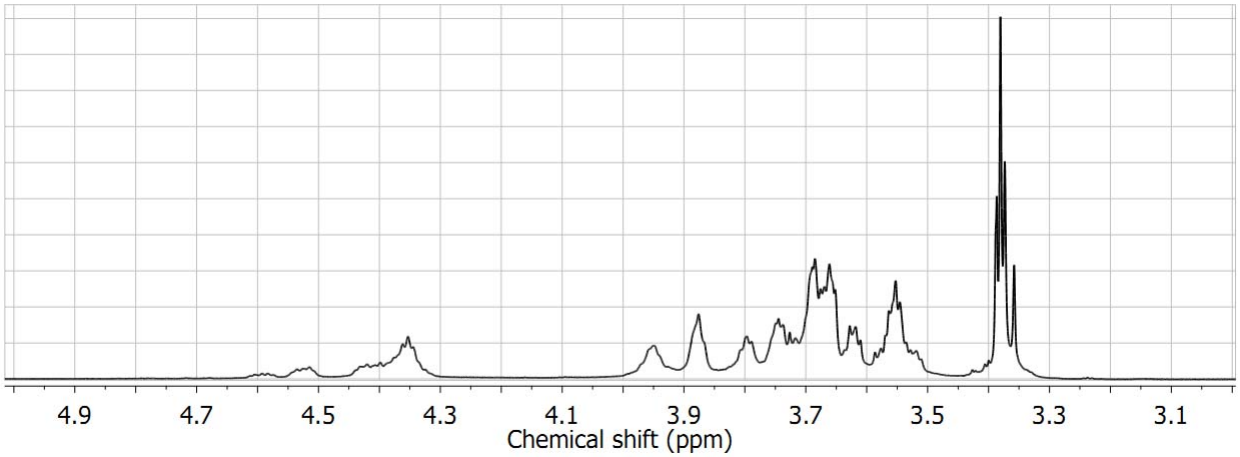

Fig. S47 ^{1}H NMR spectrum of compound **3i**

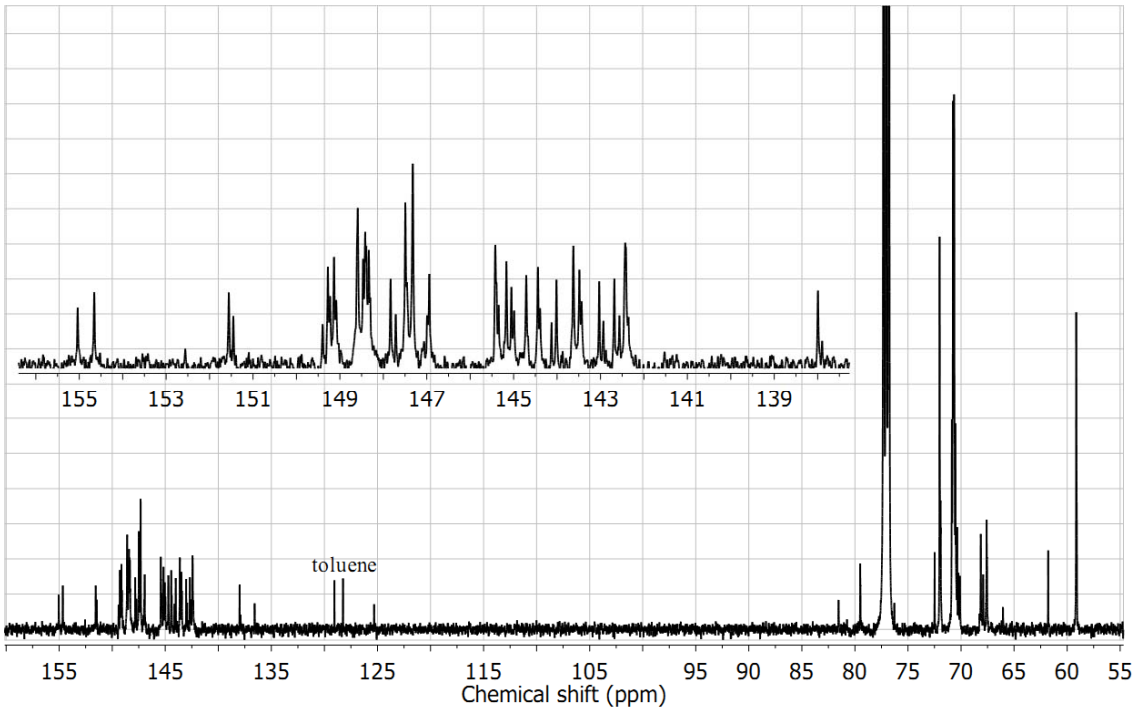

Fig. S48 ^{13}C NMR spectrum of compound **3i**

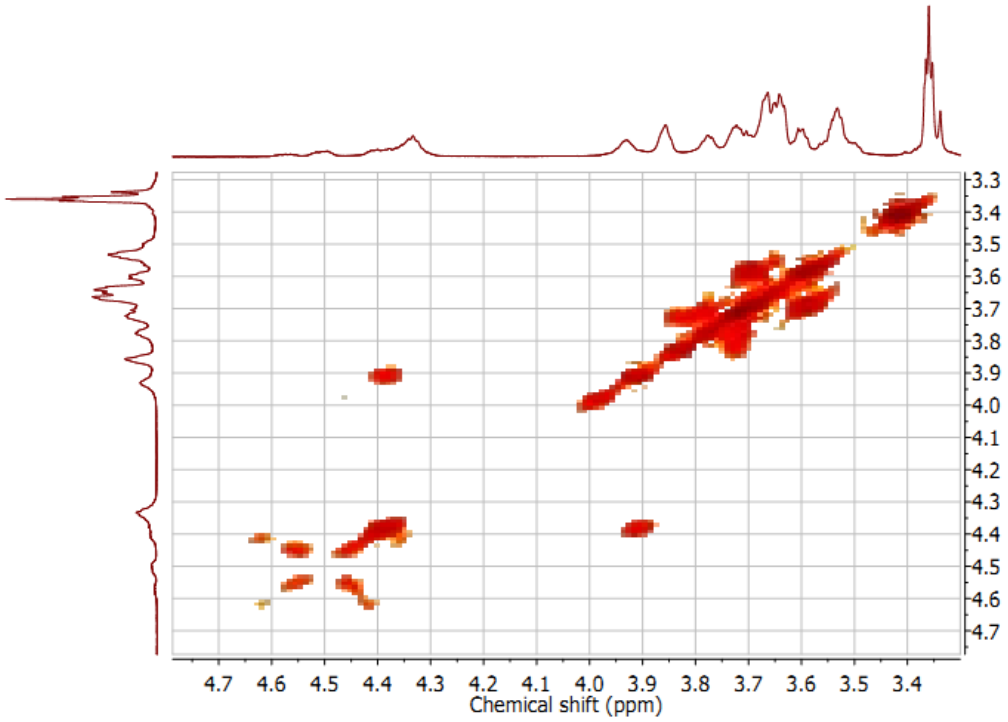

Fig. S49. H-H COSY NMR spectrum of compound **3i**

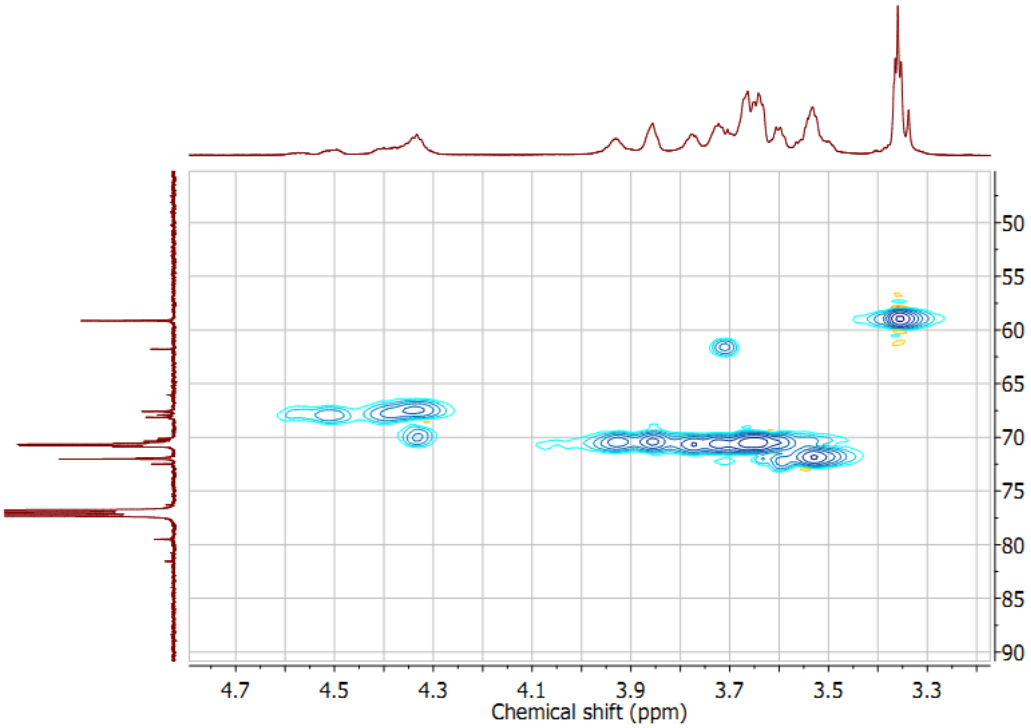

Fig. S50. H-C HSQC NMR spectrum of compound **3i**

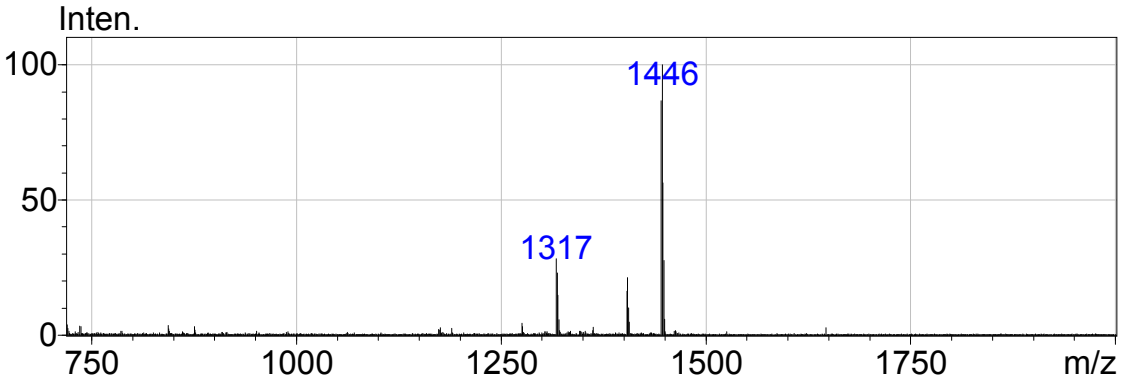

Fig. S51. APCI mass spectrum of compound **3j** (1446 $[M\text{-}Cl]^-$, 1404 $[M\text{-}Cl\text{-}C(CH_3)_2]^-$, 1317 $[M\text{-}Cl\text{-}OC_2H_4COOC(CH_3)_3+O]^-$).

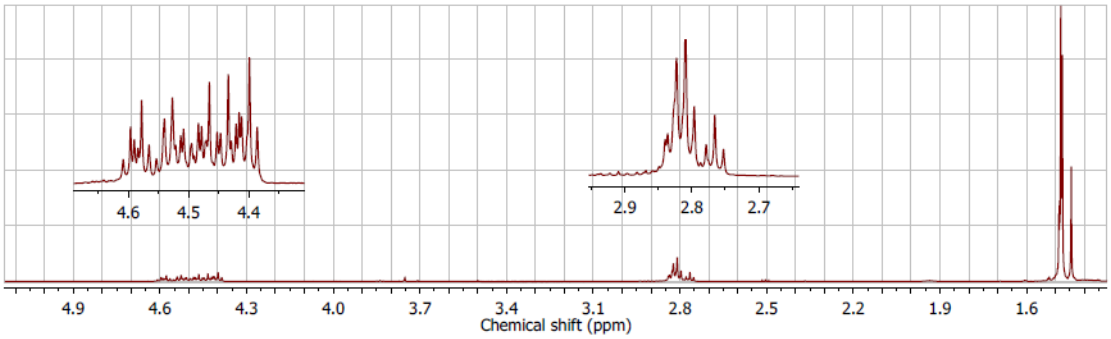

Fig. S52. ^1H NMR spectrum of compound **3j**

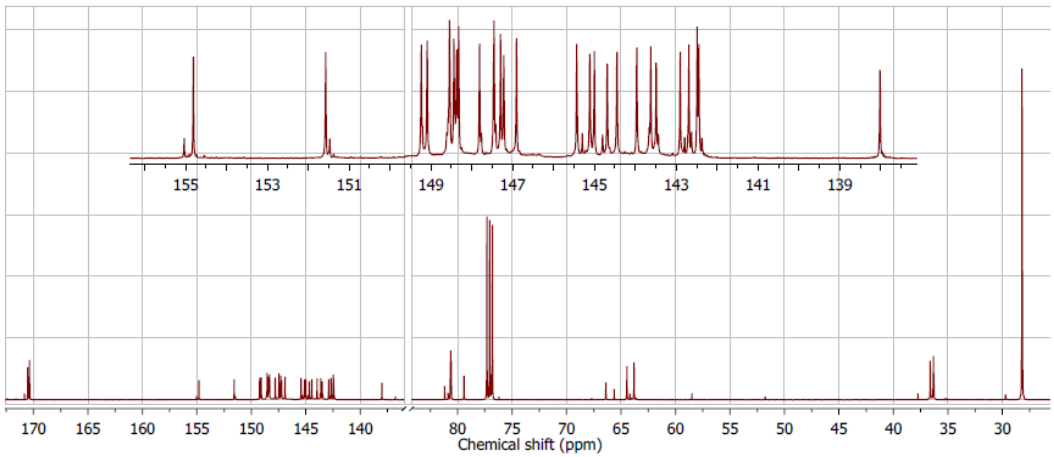

Fig. S53. ^{13}C NMR spectrum of compound **3j**

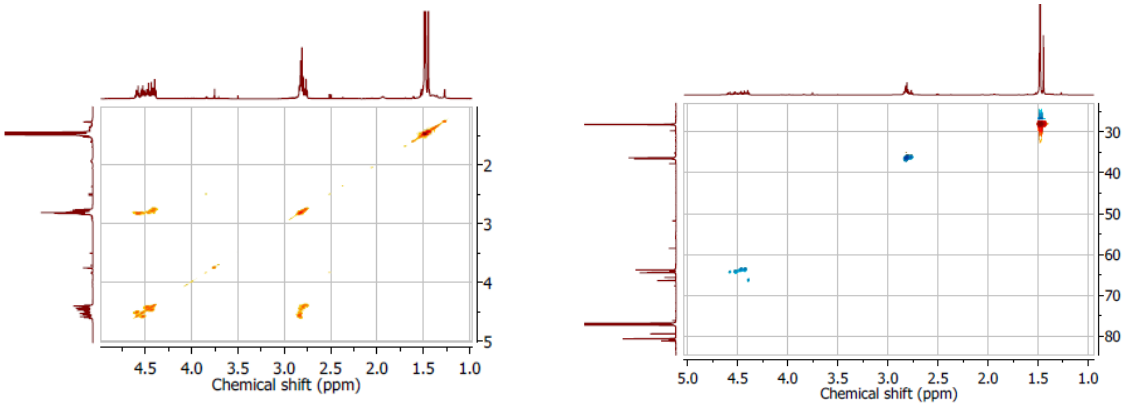

Fig. S54. H-H COSY NMR spectrum of compound **3j** (left) and H-C HSQC NMR spectrum of compound **3j** (right)

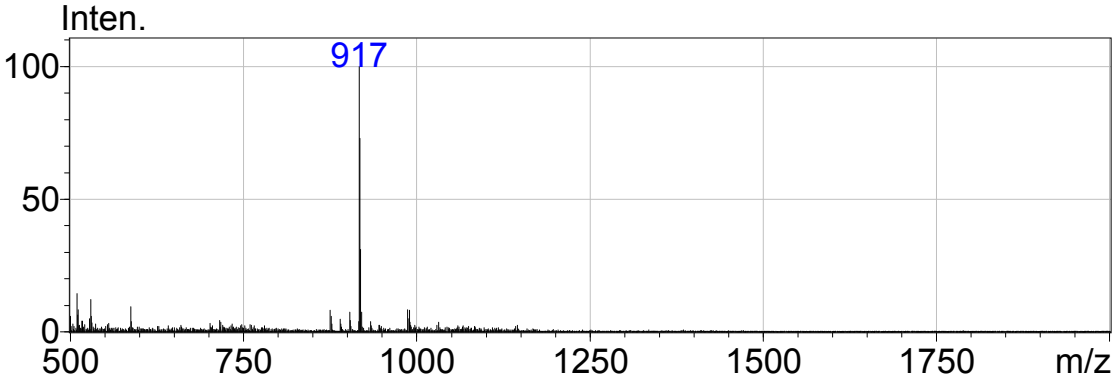

Fig. S55 APCI MS spectrum of compound **4b**

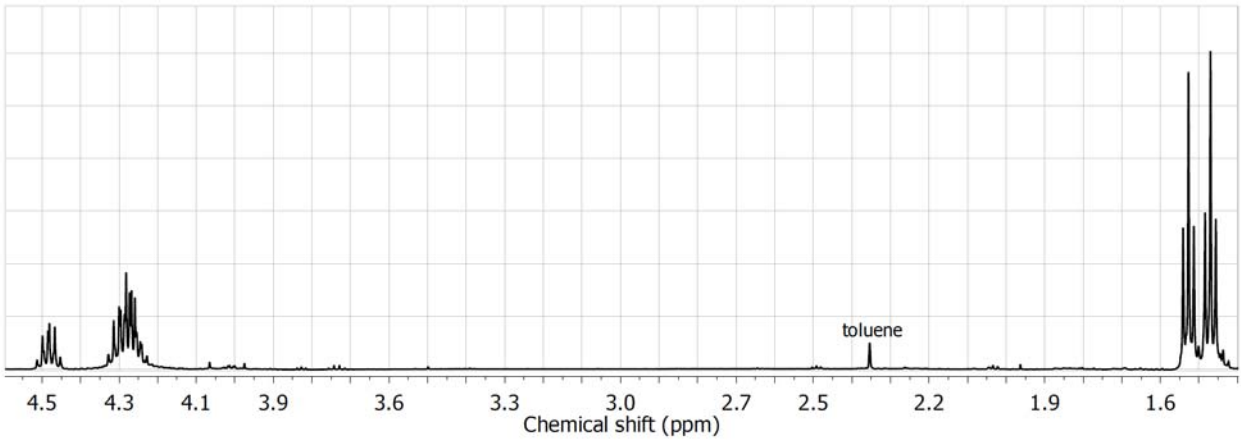

Fig. S56. ^{1}H NMR spectrum of compound **4b**

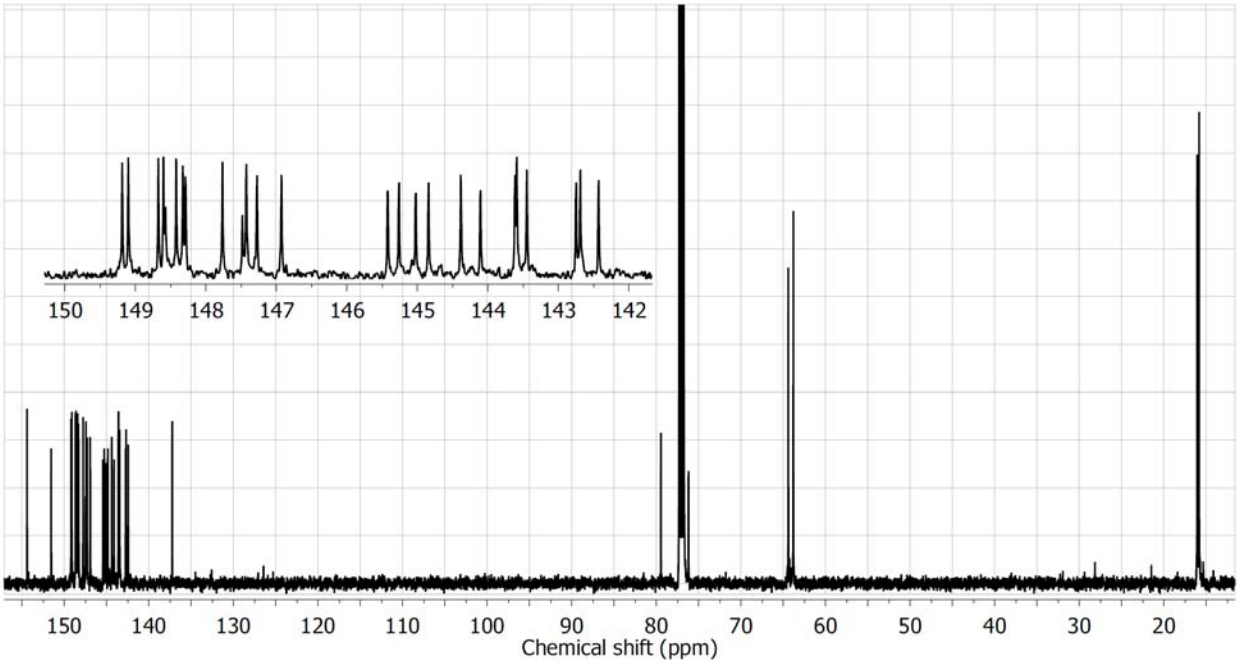

Fig. S57. ^{13}C NMR spectrum of compound **4b** (* denotes signals of unknown impurity)

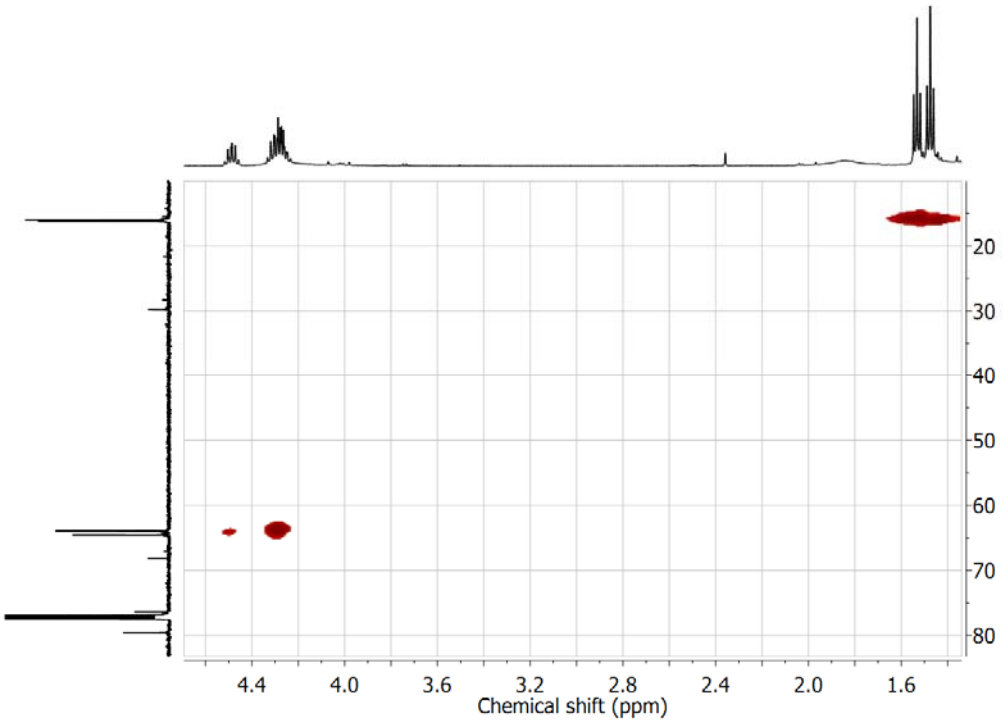

Fig. S58. H-C HSQC NMR spectrum of compound **4b**

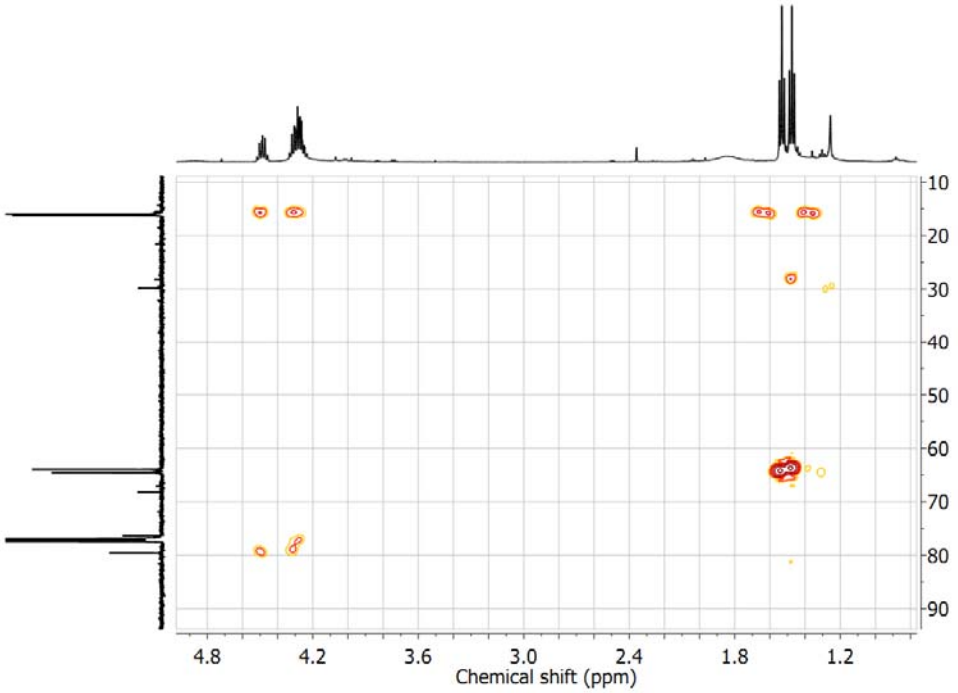

Fig. S59. H-C HMBC NMR spectrum of compound **4b**

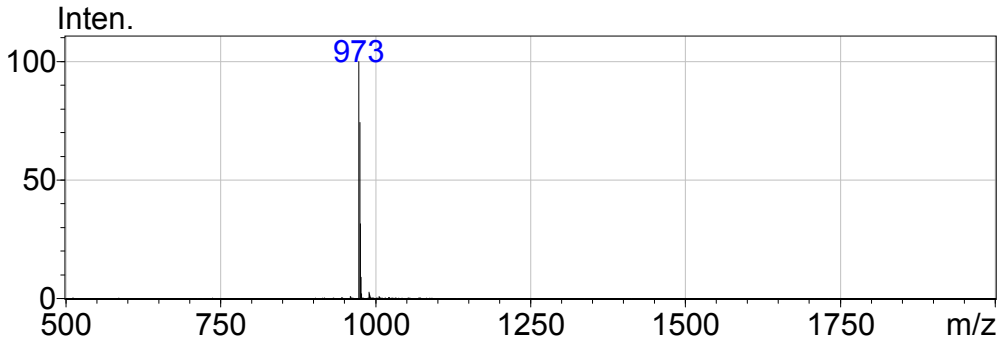

Fig. S60. APCI MS spectrum of compound **4c**

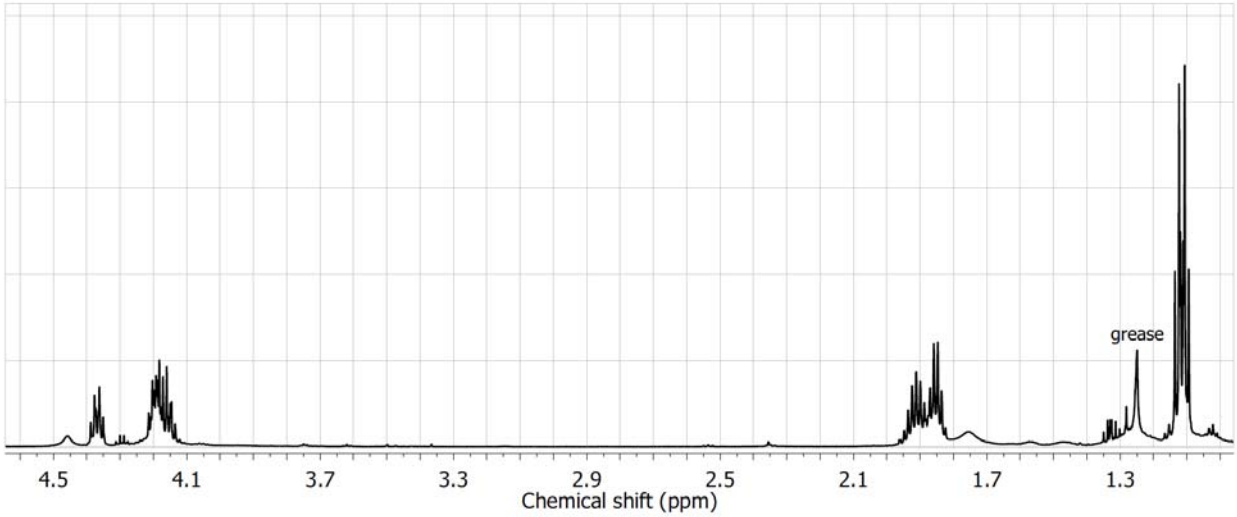

Fig. S61. ^{1}H NMR spectrum of compound **4c**

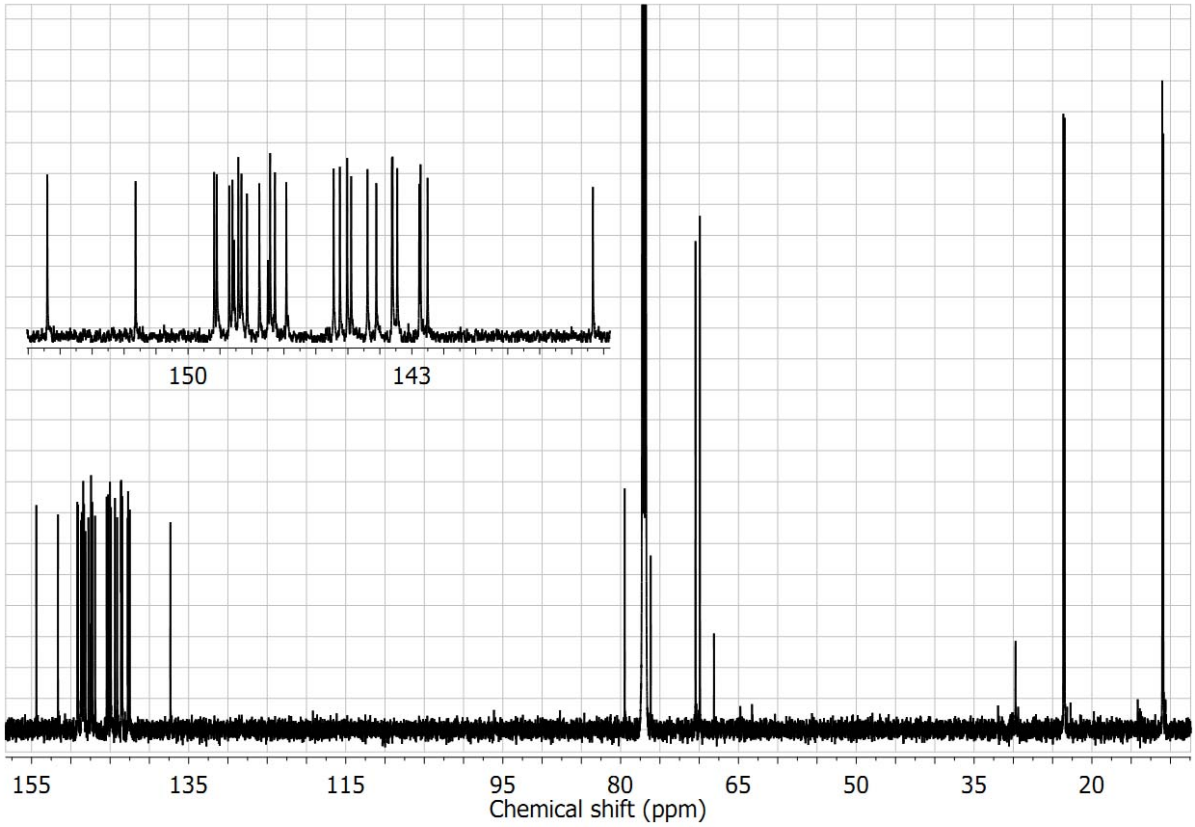

Fig. S62. ^{13}C NMR spectrum of compound **4c**

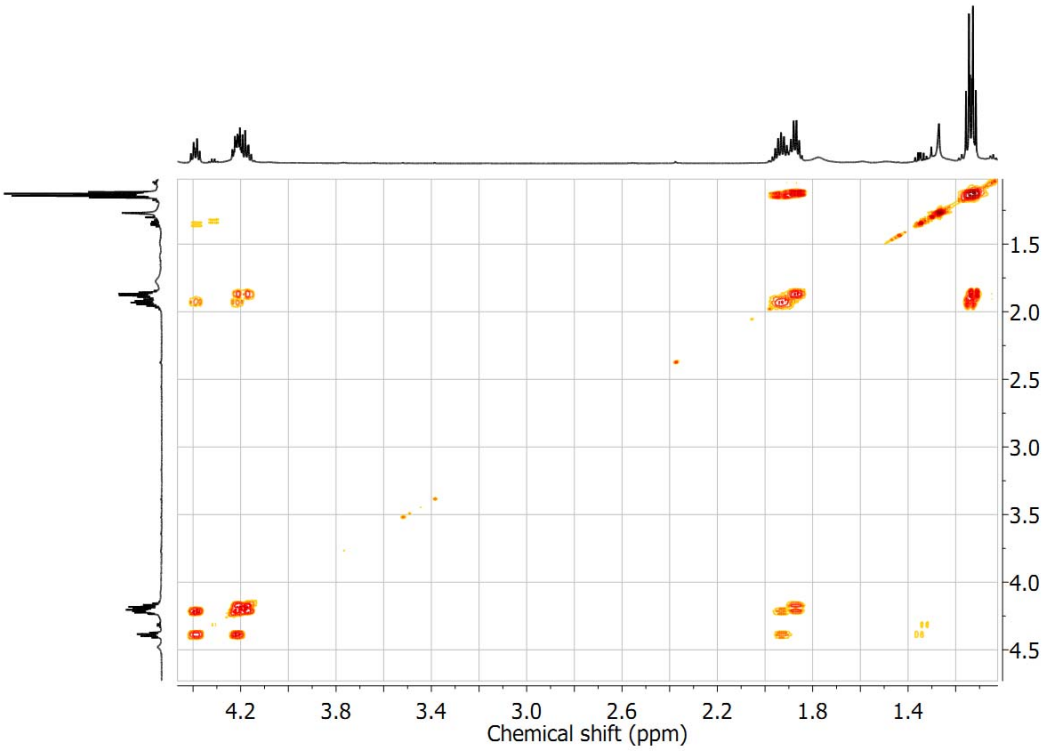

Fig. S63. H-H COSY NMR spectrum of compound **4c**

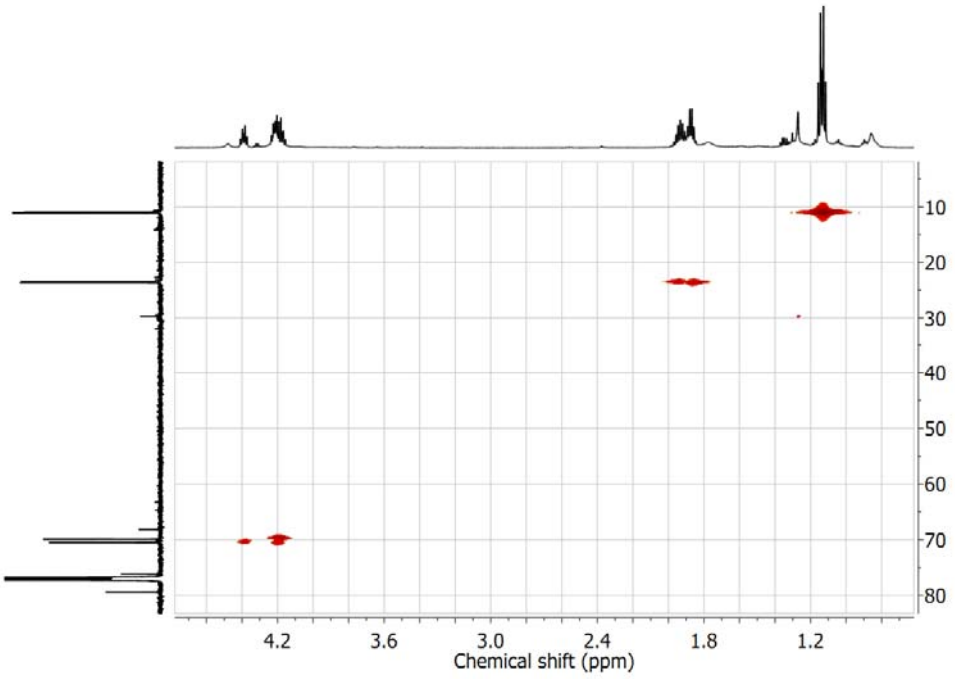

Fig. S64. H-C HSQC NMR spectrum of compound **4c**

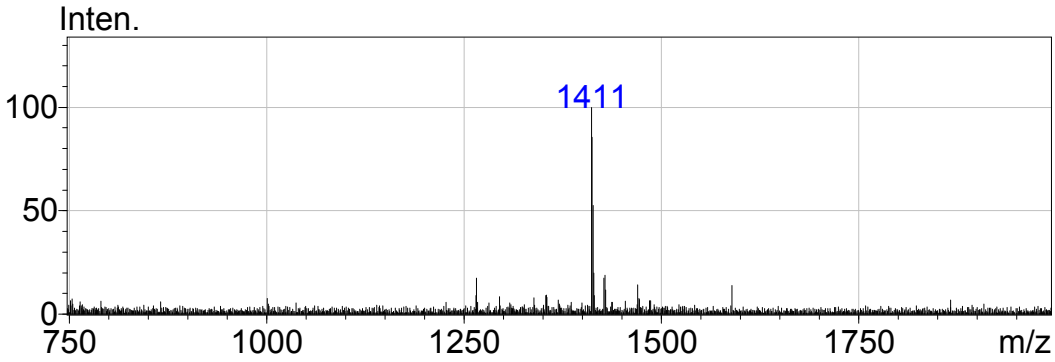

Fig. S65. APCI MS spectrum of compound **4i** ($[M+Na]^+$)

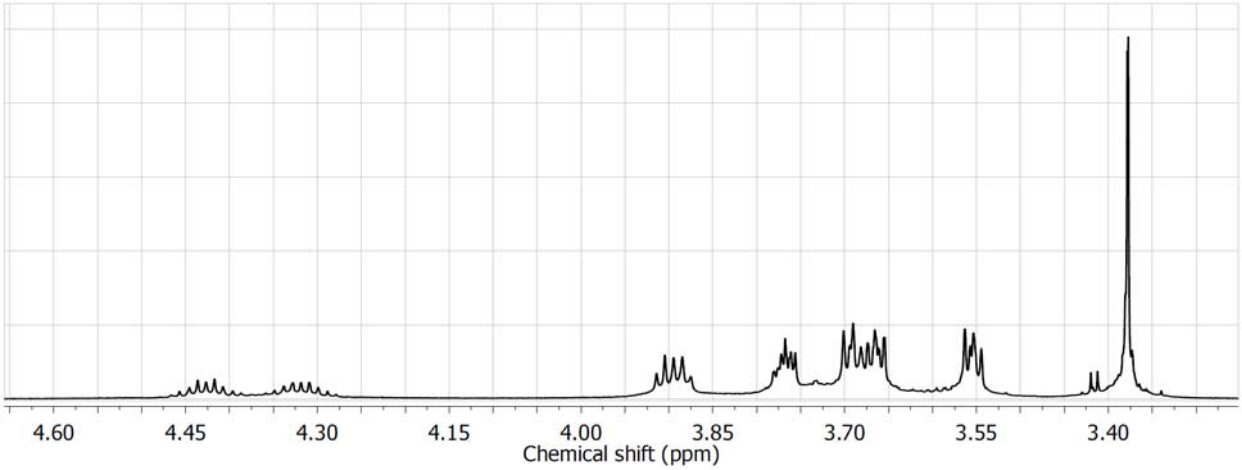

Fig. S66. ^1H NMR spectrum of compound **4i**

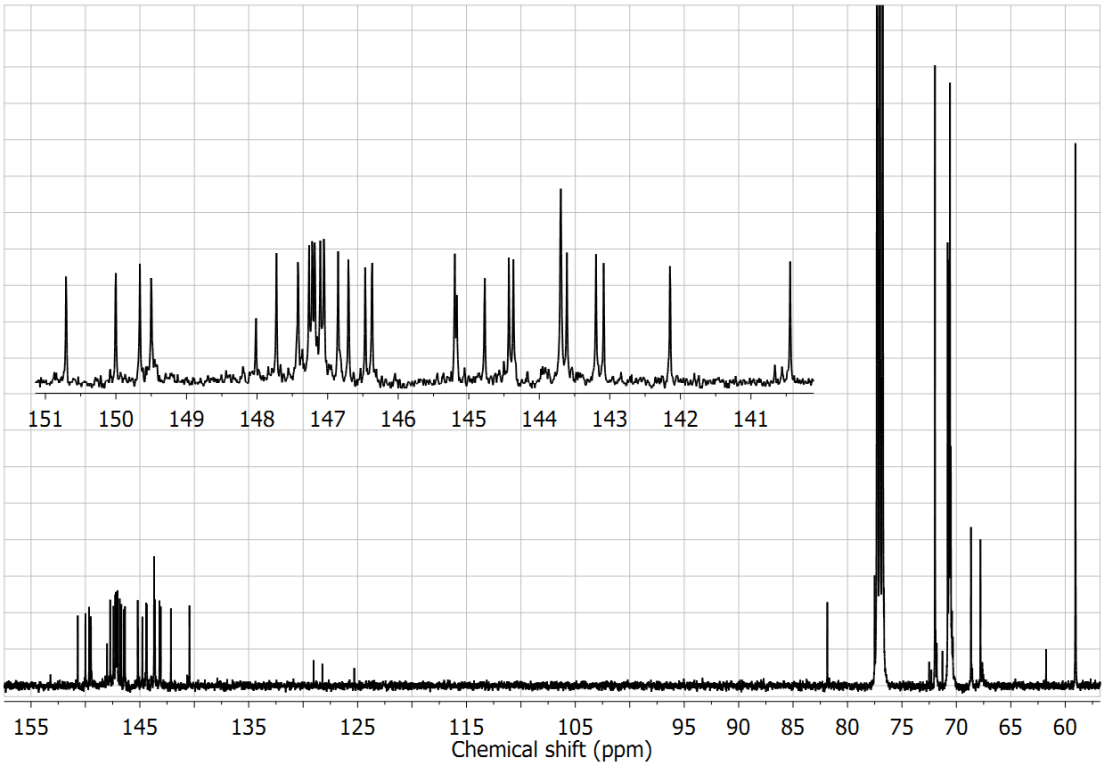

Fig. S67. ^{13}C NMR spectrum of compound **4i**

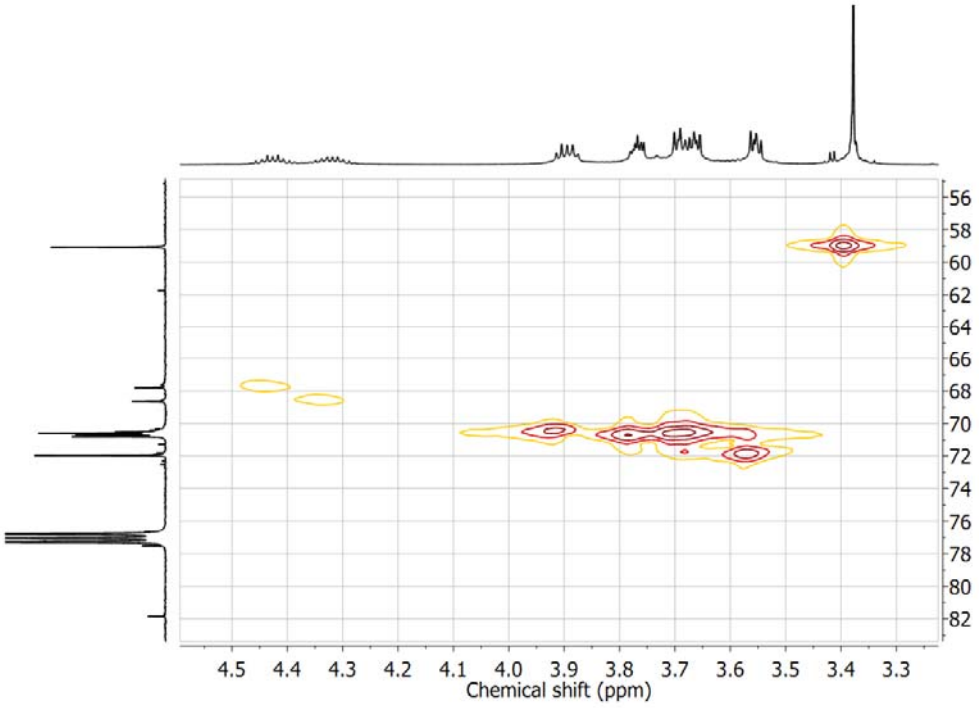

Fig. S68. H-C HSQC NMR spectrum of compound **4i**

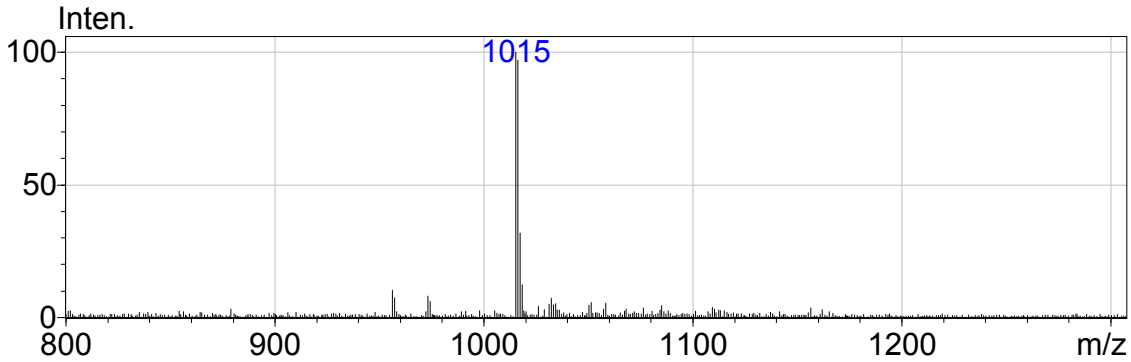

Fig. S69. APCI MS spectrum of compound **5c**

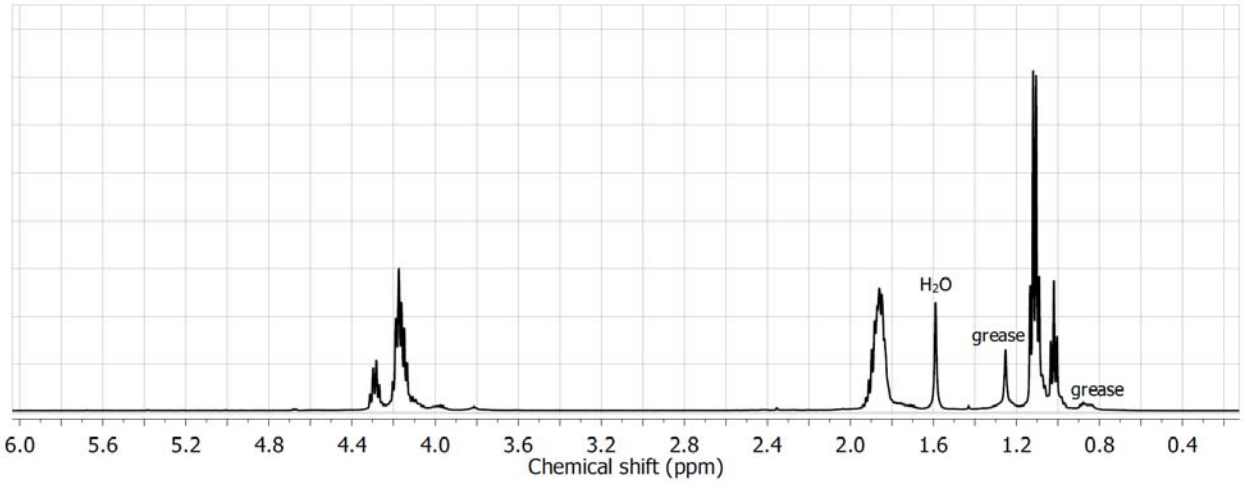

Fig. S70. ^{1}H NMR spectrum of compound **5c**

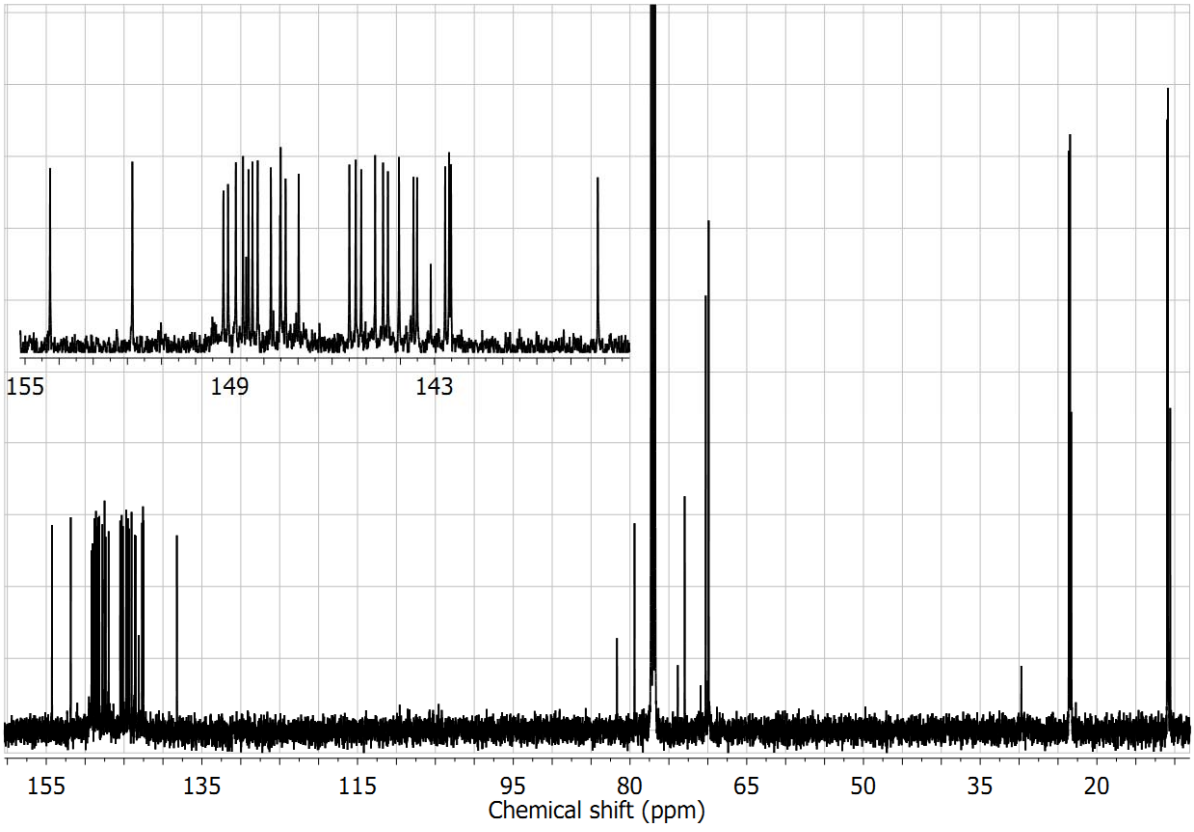

Fig. S71. ^{13}C NMR spectrum of compound **5c**

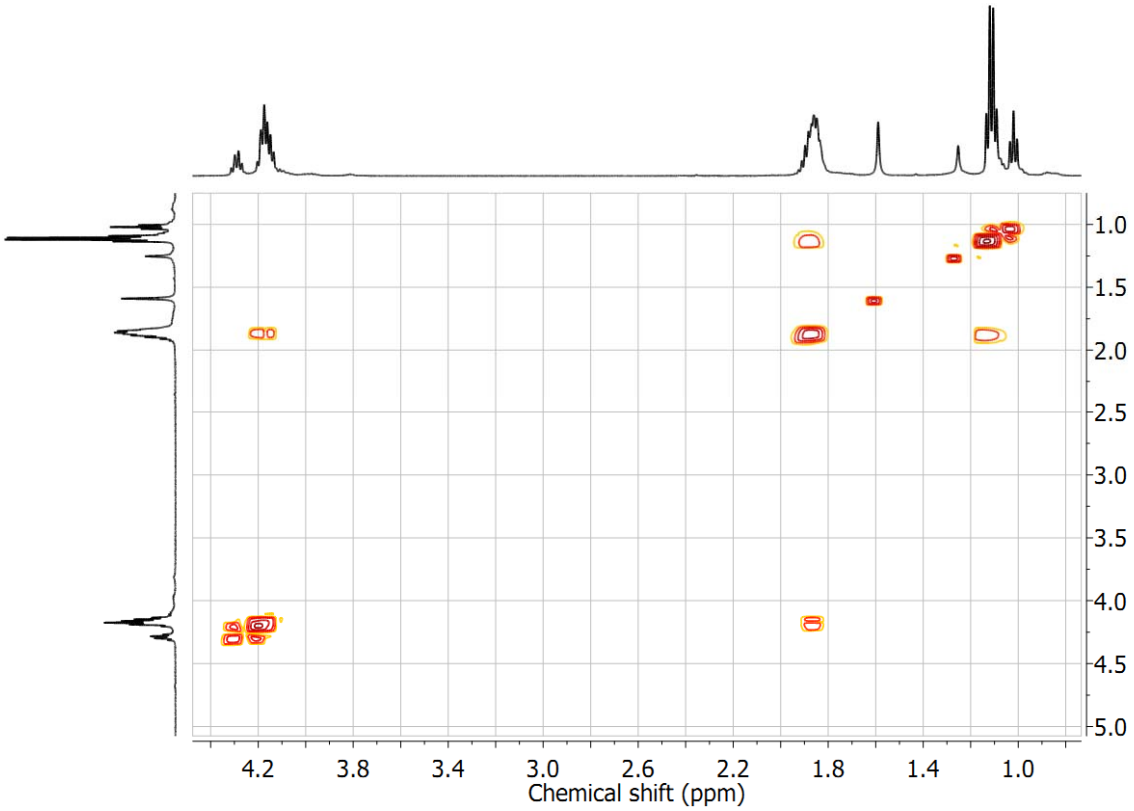

Fig. S72. H-H COSY NMR spectrum of compound **5c**

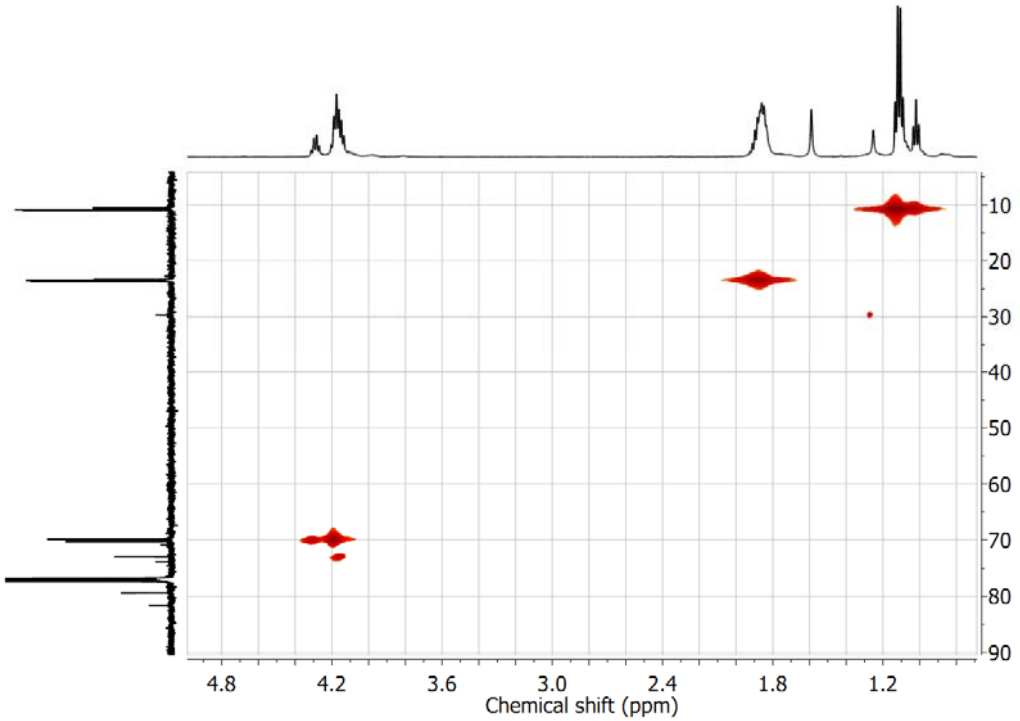

Fig. S73. H-C HSQC NMR spectrum of compound **5c**

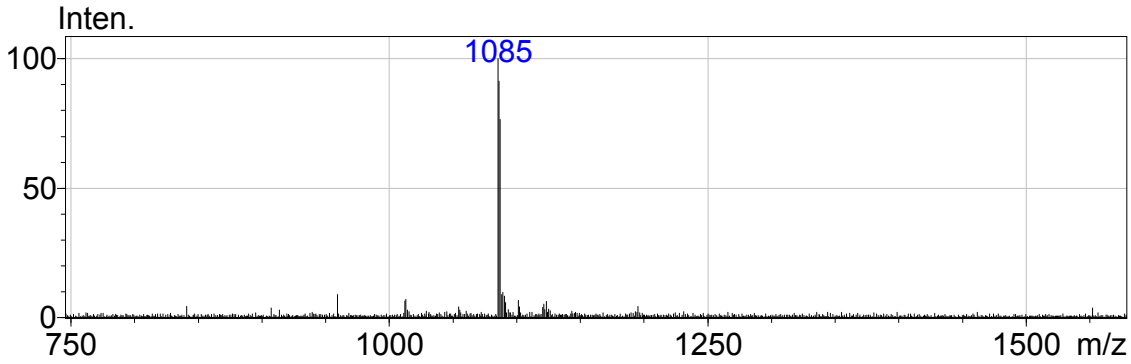

Fig. S74. APCI MS spectrum of compound **5d**

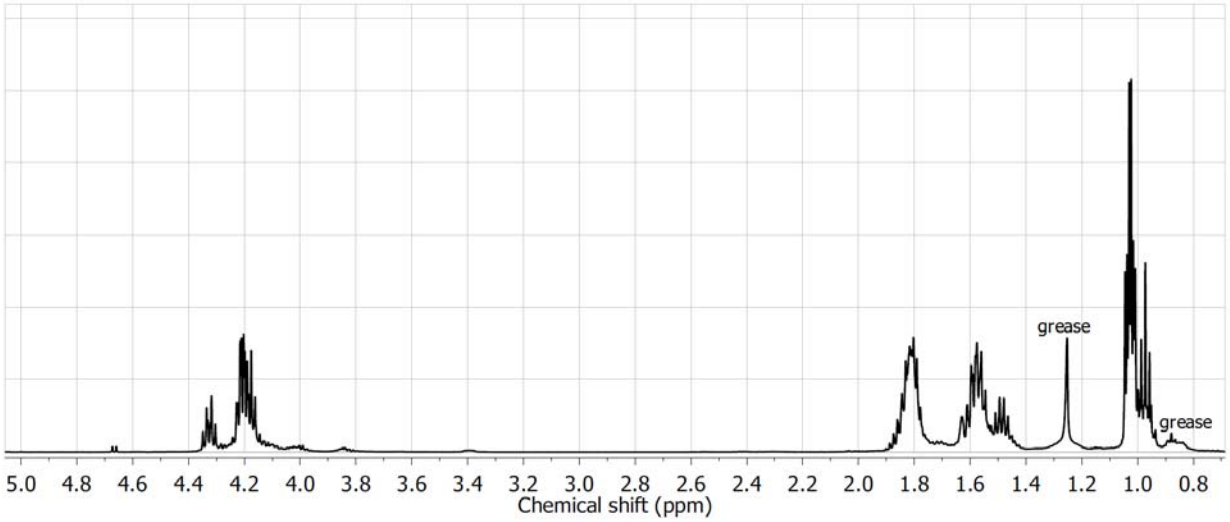

Fig. S75. ^{1}H NMR spectrum of compound **5d**

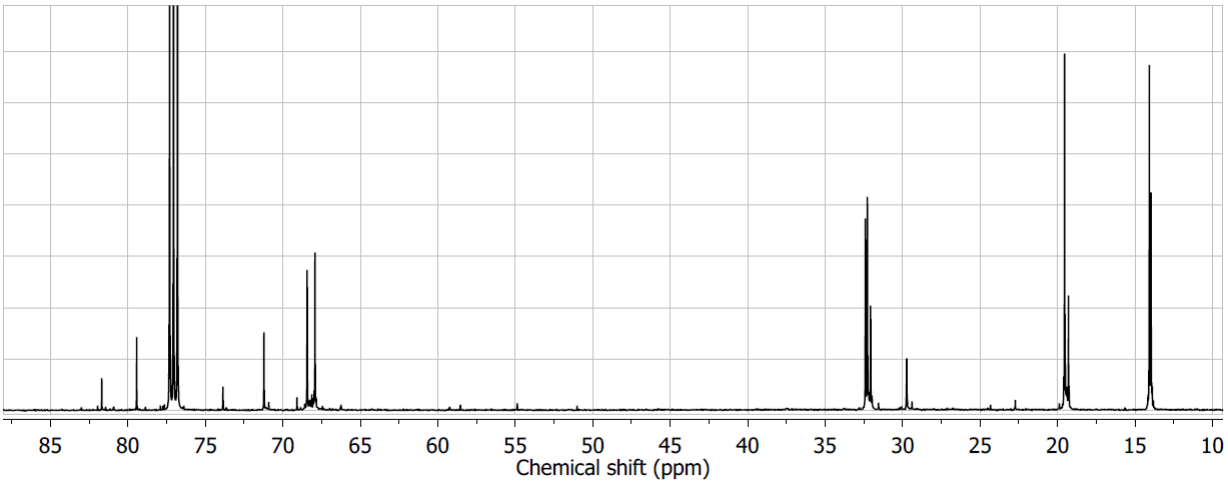

Fig. S76. High-field part of the ^{13}C NMR spectrum of compound **5d**

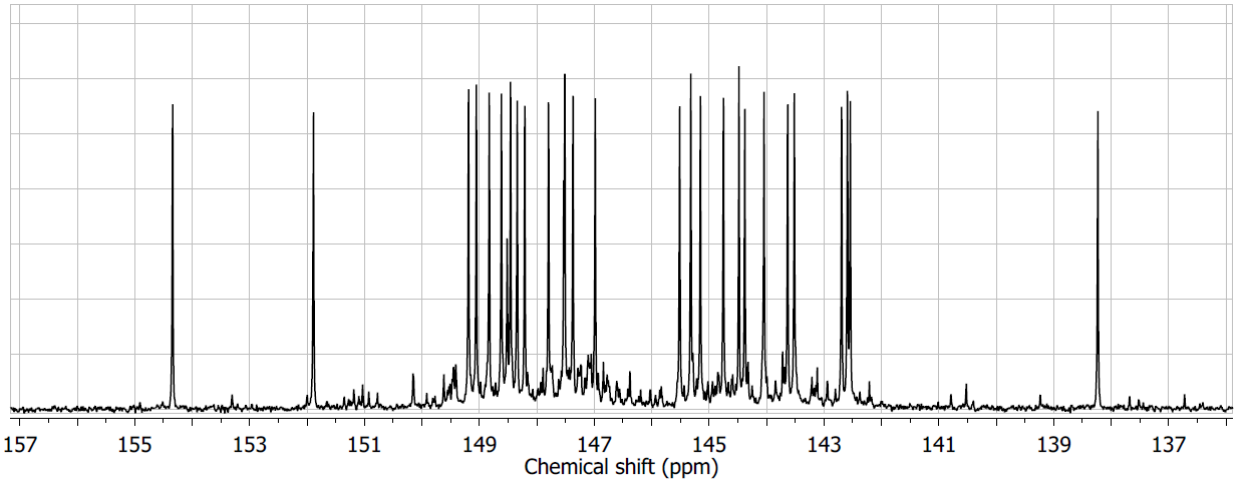

Fig. S77. Low-field part of the ^{13}C NMR spectrum of compound **5d**

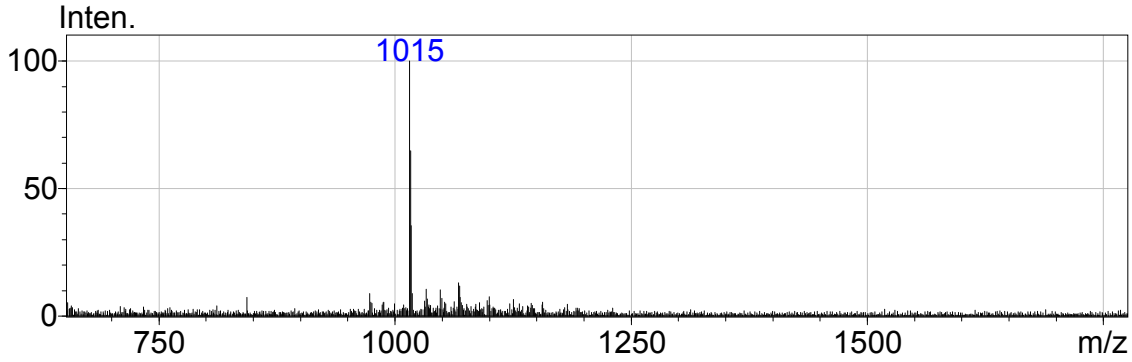

Fig. S78. APCI MS spectrum of compound **5e**

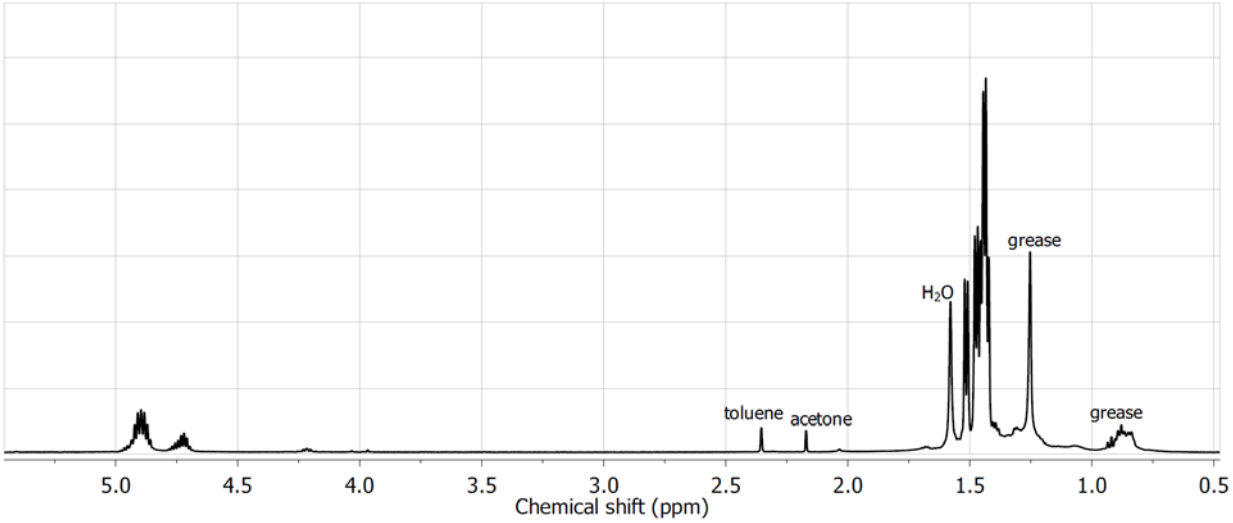

Fig. S79. ^{1}H NMR spectrum of compound **5e**

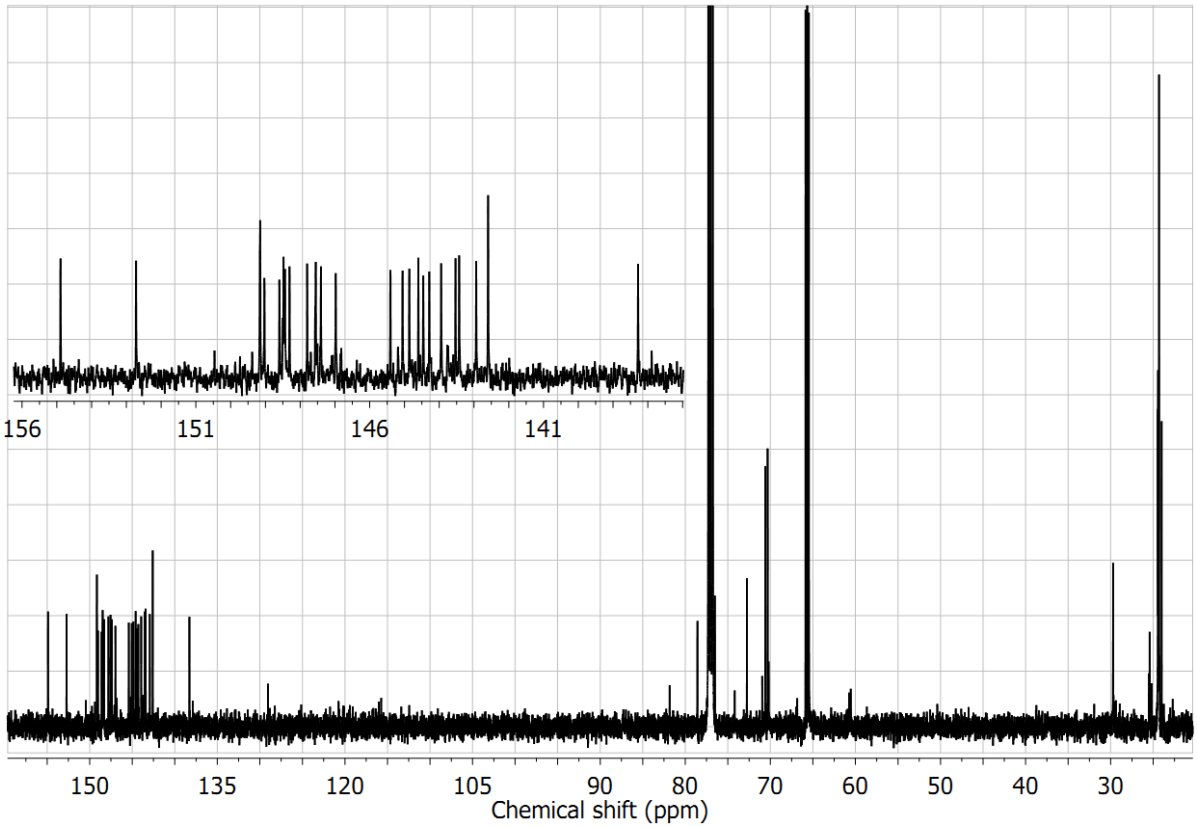

Fig. S80. ^{13}C NMR spectrum of compound **5e**

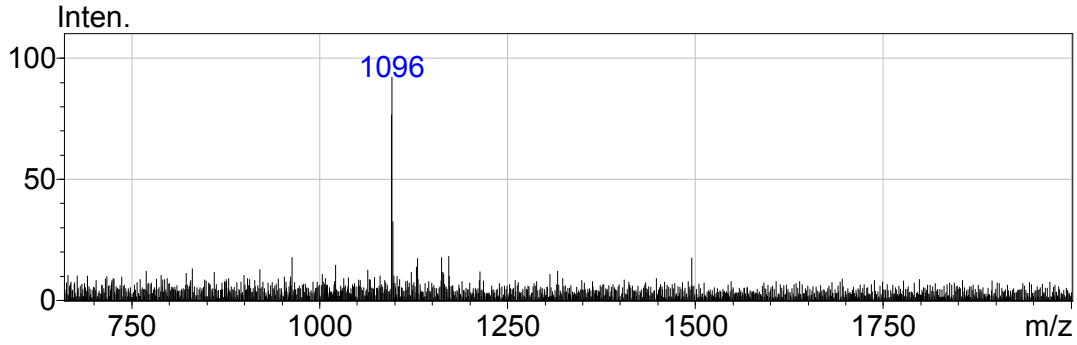

Fig. S81. APCI MS spectrum of compound **5g**

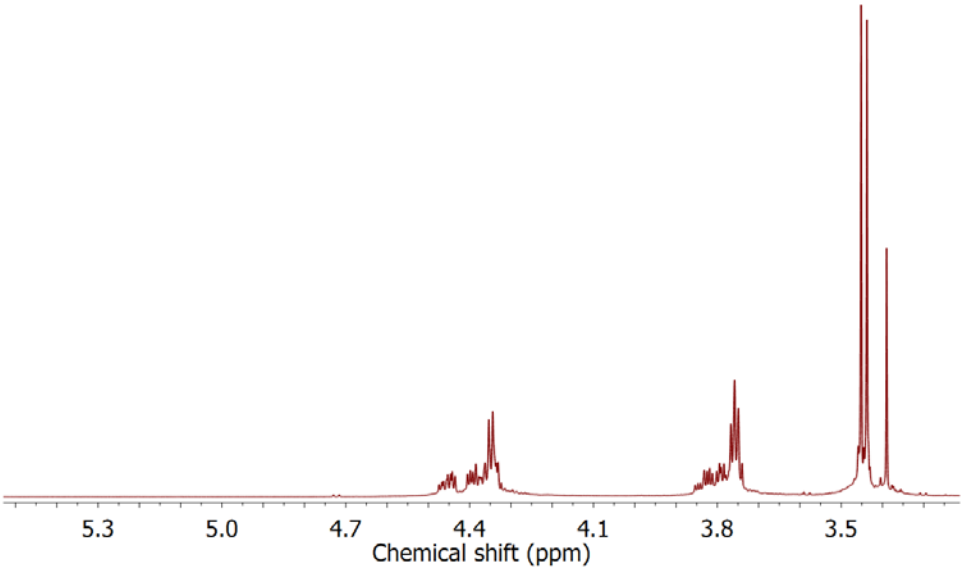

Fig. S82. ^{1}H NMR spectrum of compound **5g**

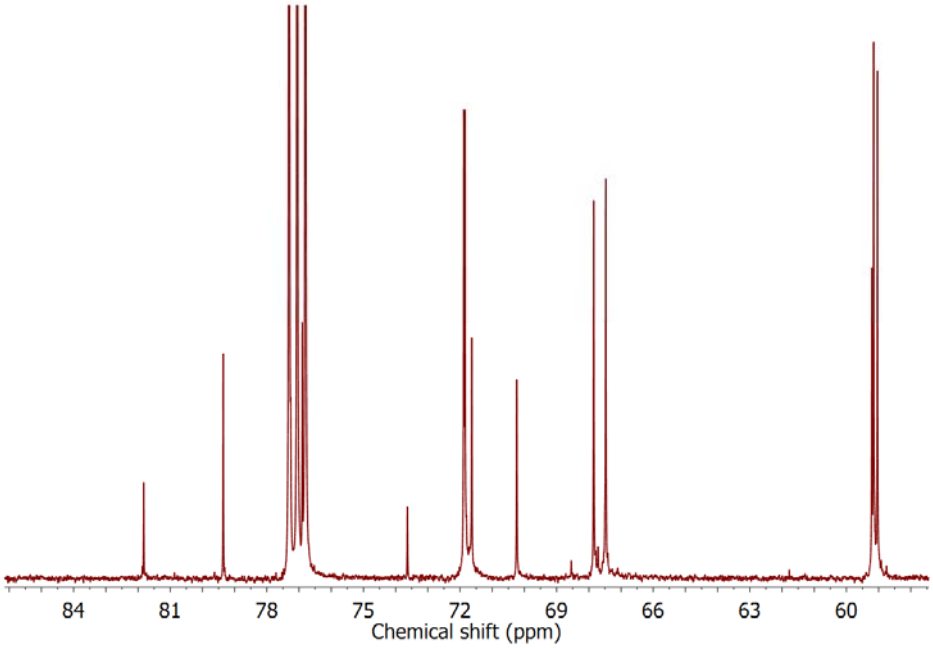

Fig. S83. High-field part of the ^{13}C NMR spectrum of compound **5g**

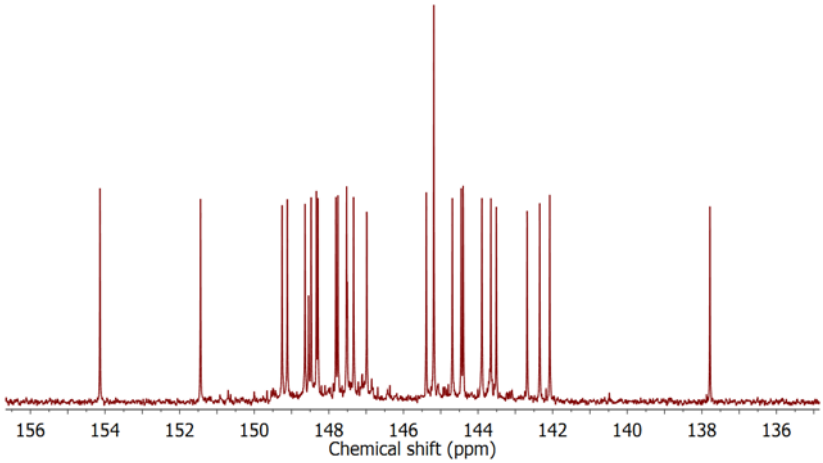

Fig. S84. Low-field part of the ^{13}C NMR spectrum of compound **5g**

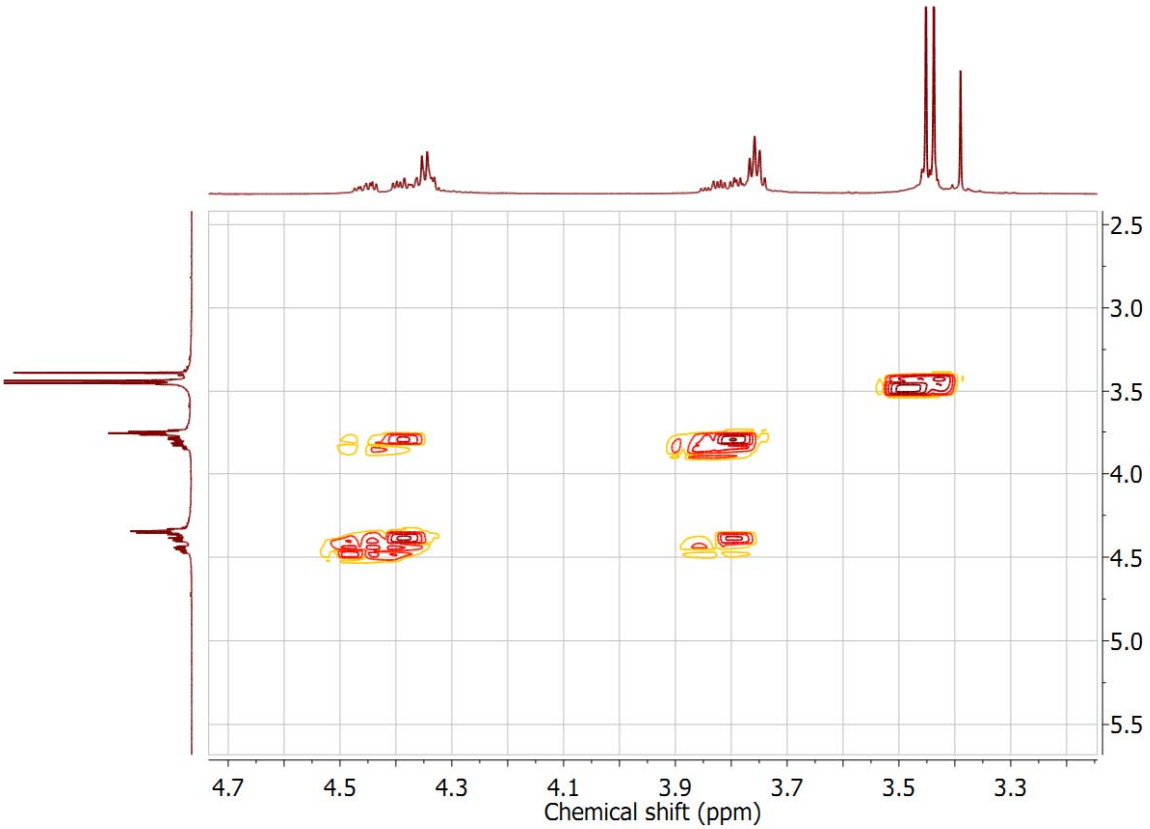

Fig. S85. H-H COSY NMR spectrum of compound **5g**

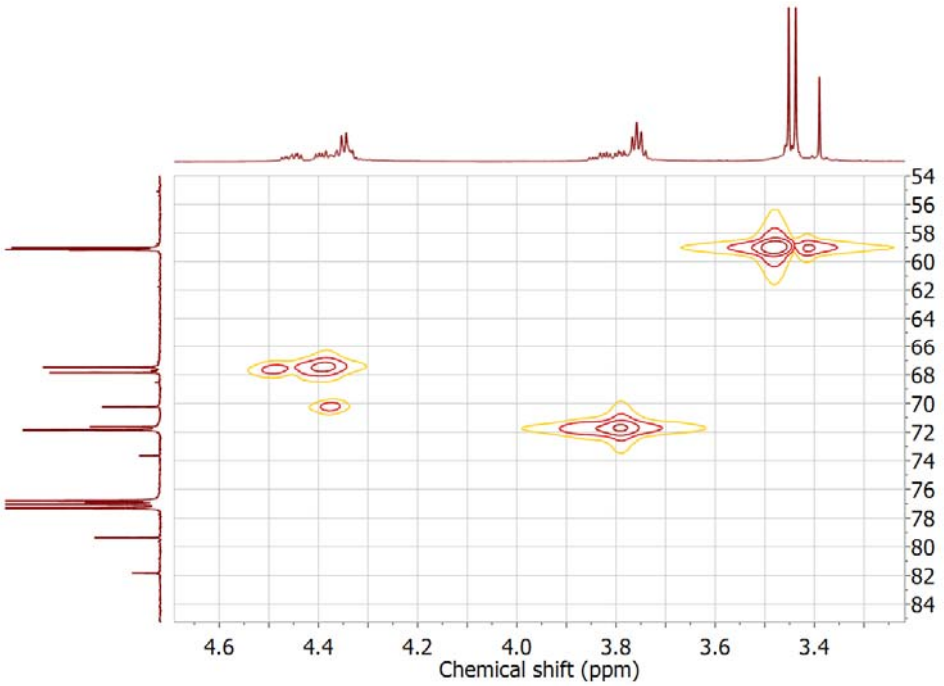

Fig. S86. H-C HSQC NMR spectrum of compound **5g**

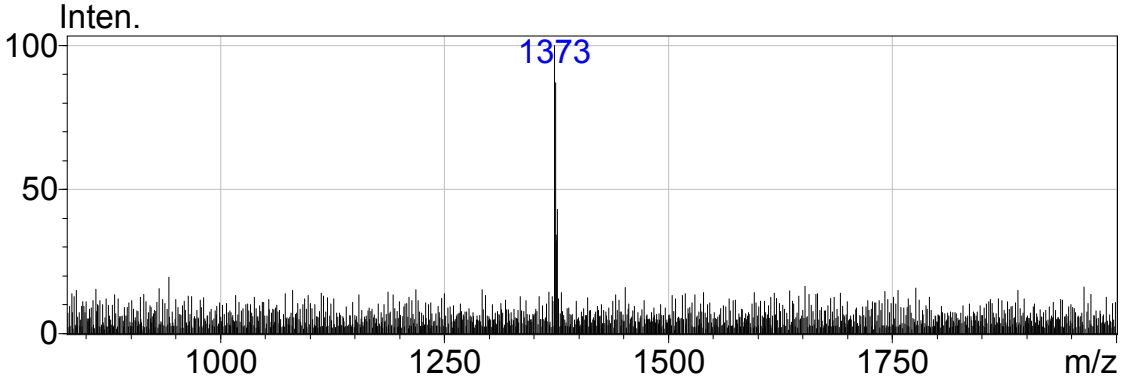

Fig. S87. APCI MS spectrum of compound **5h** ([M+Na]$^+$)

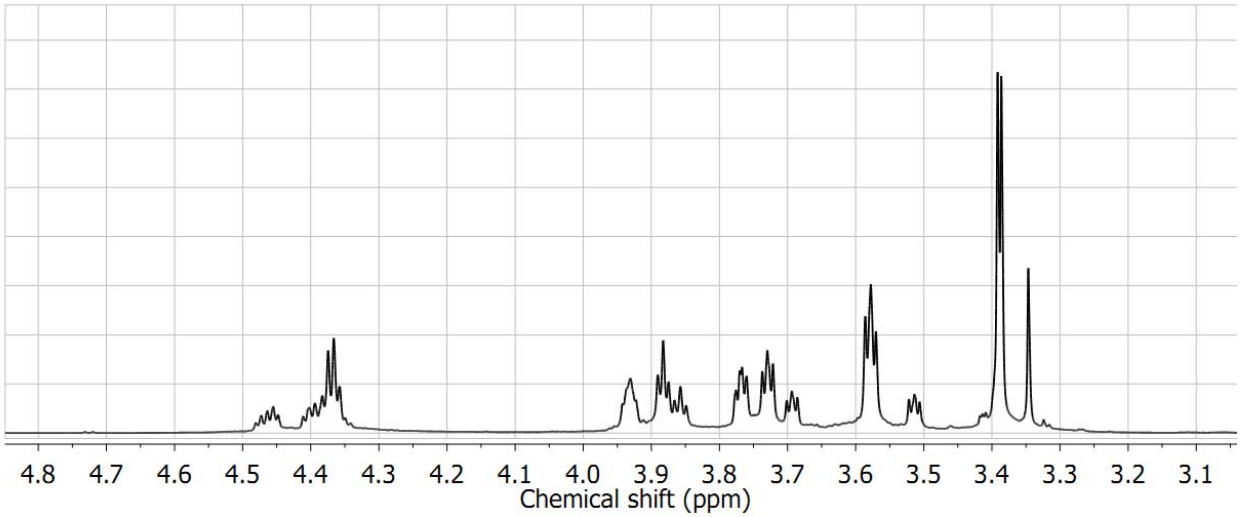

Fig. S88. ^{1}H NMR spectrum of compound **5h**

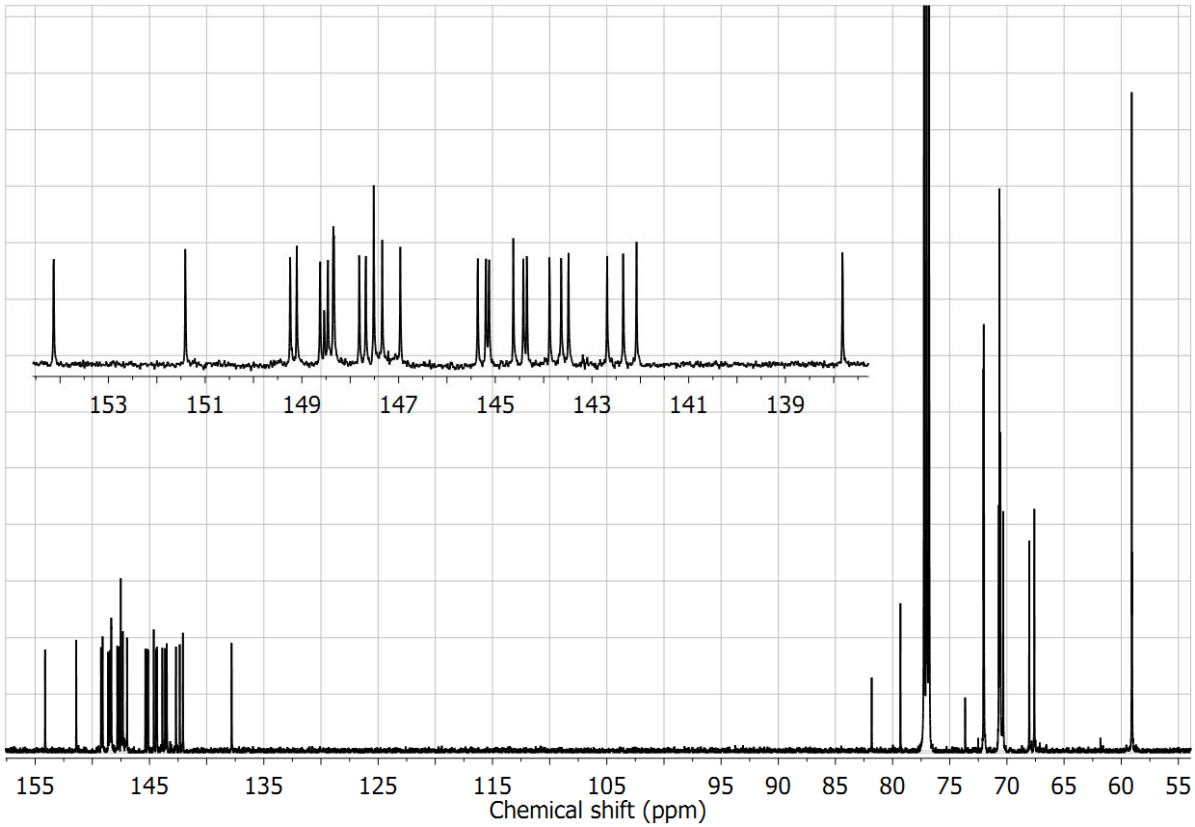

Fig. S89. ^{13}C NMR spectrum of compound **5h**

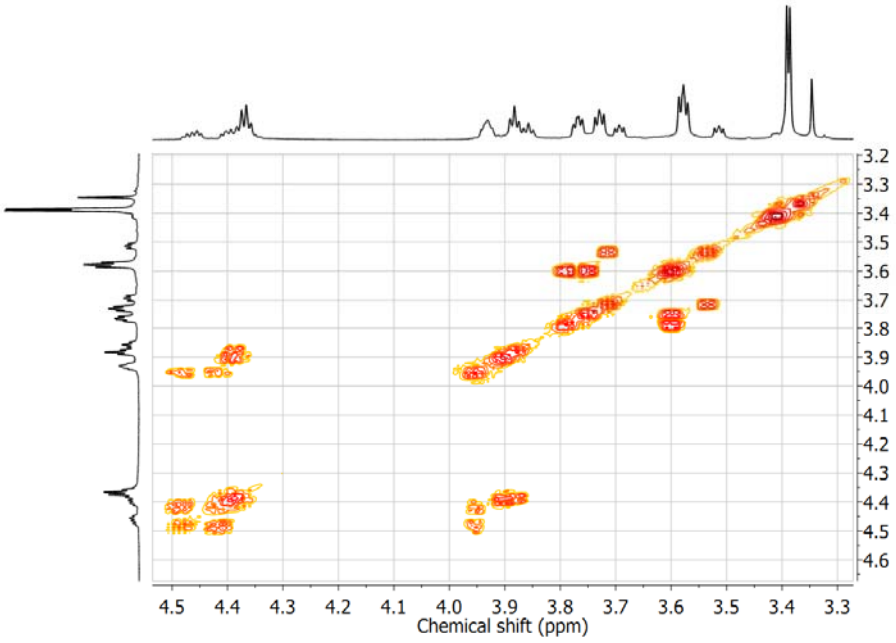

Fig. S90. H-H COSY NMR spectrum of compound **5h**

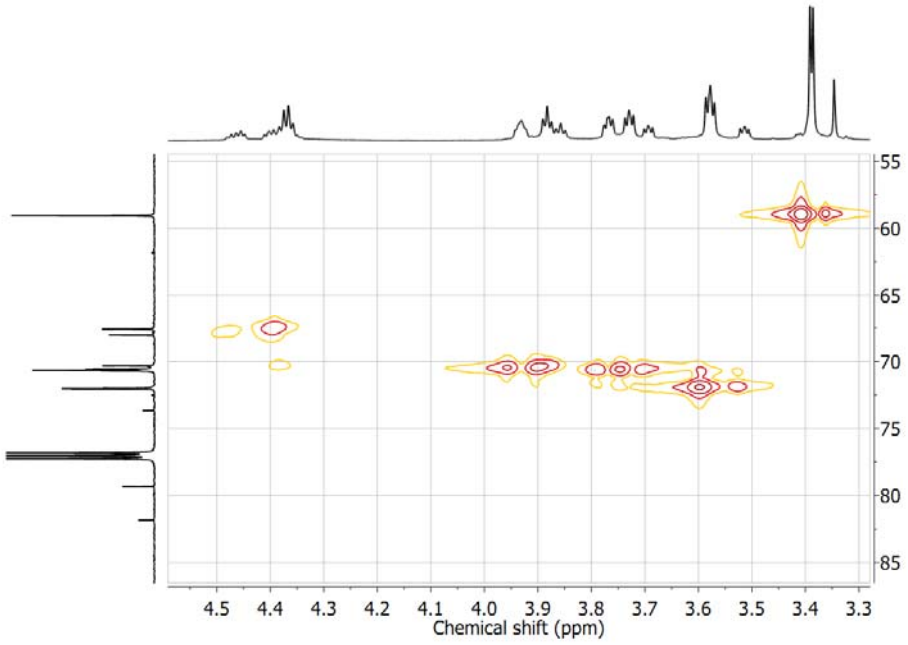

Fig. S91. H-C HSQC NMR spectrum of compound **5h**

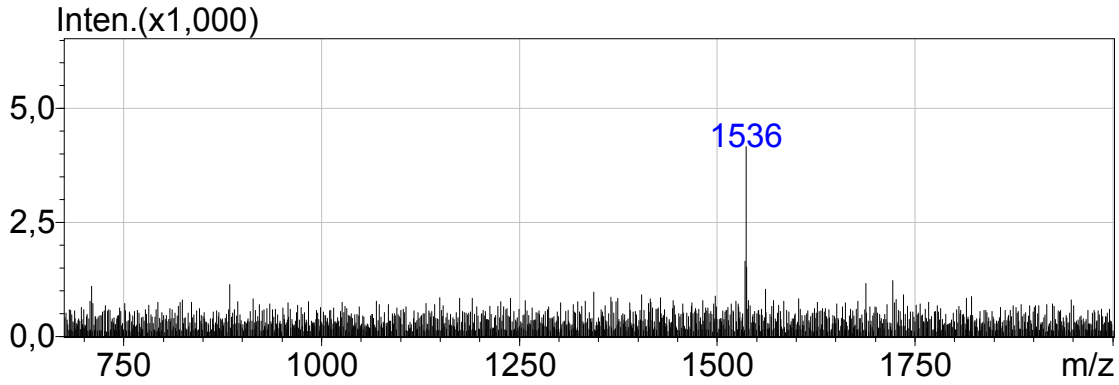

Fig. S92. APCI mass spectrum of compound **5i**

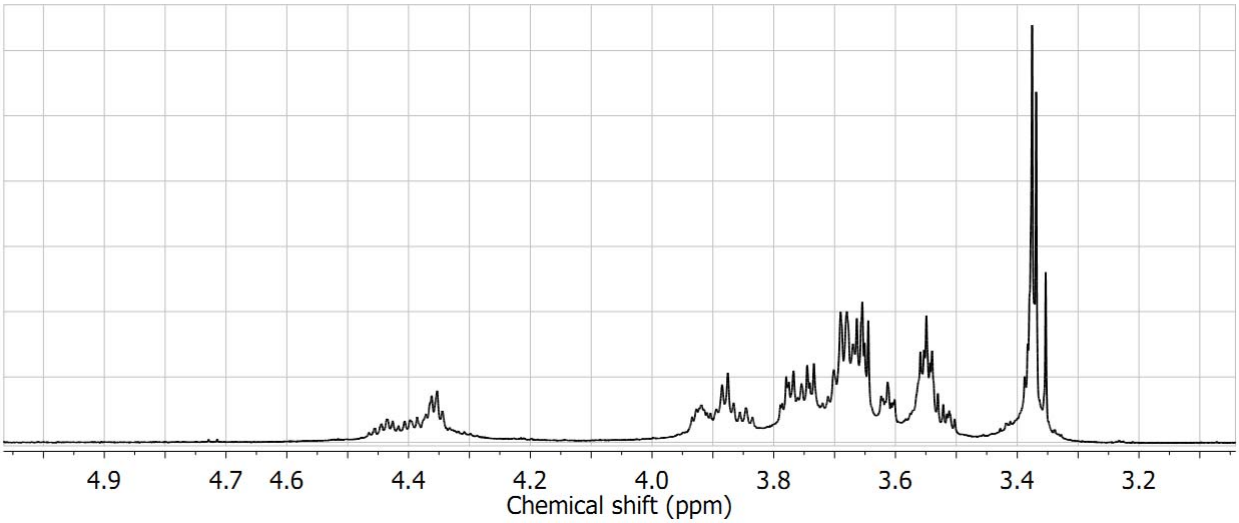

Fig. S93. ^{1}H NMR spectrum of compound **5i**

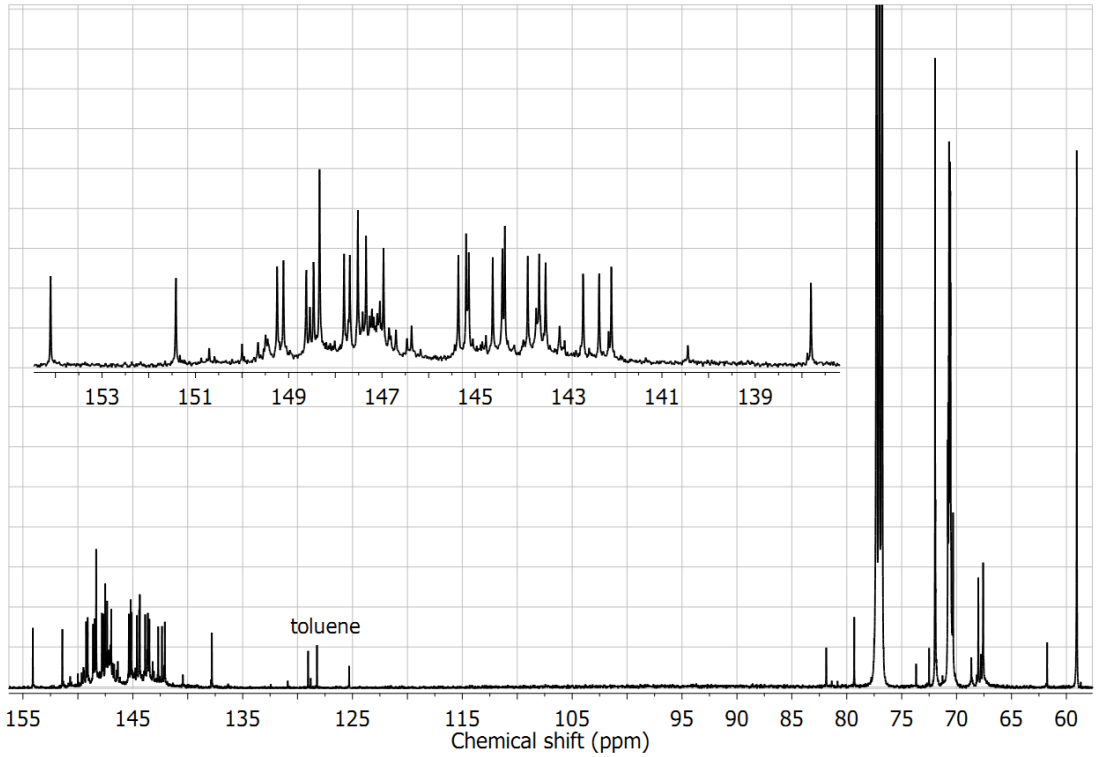

Fig. S94. ^{13}C NMR spectrum of compound **5i**

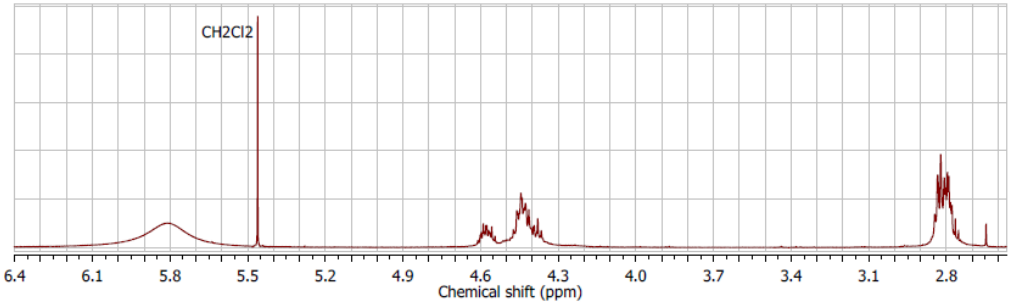

Fig. S95. ^{1}H NMR spectrum of compound **3j-H**

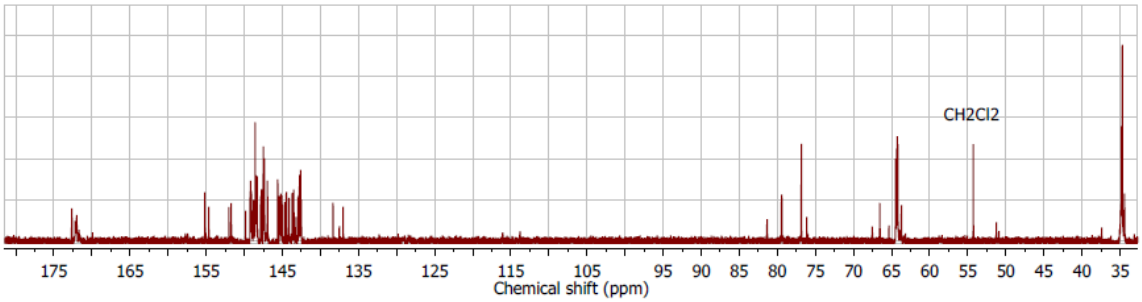

Fig. S96. ^{13}C NMR spectrum of compound **3j-H**

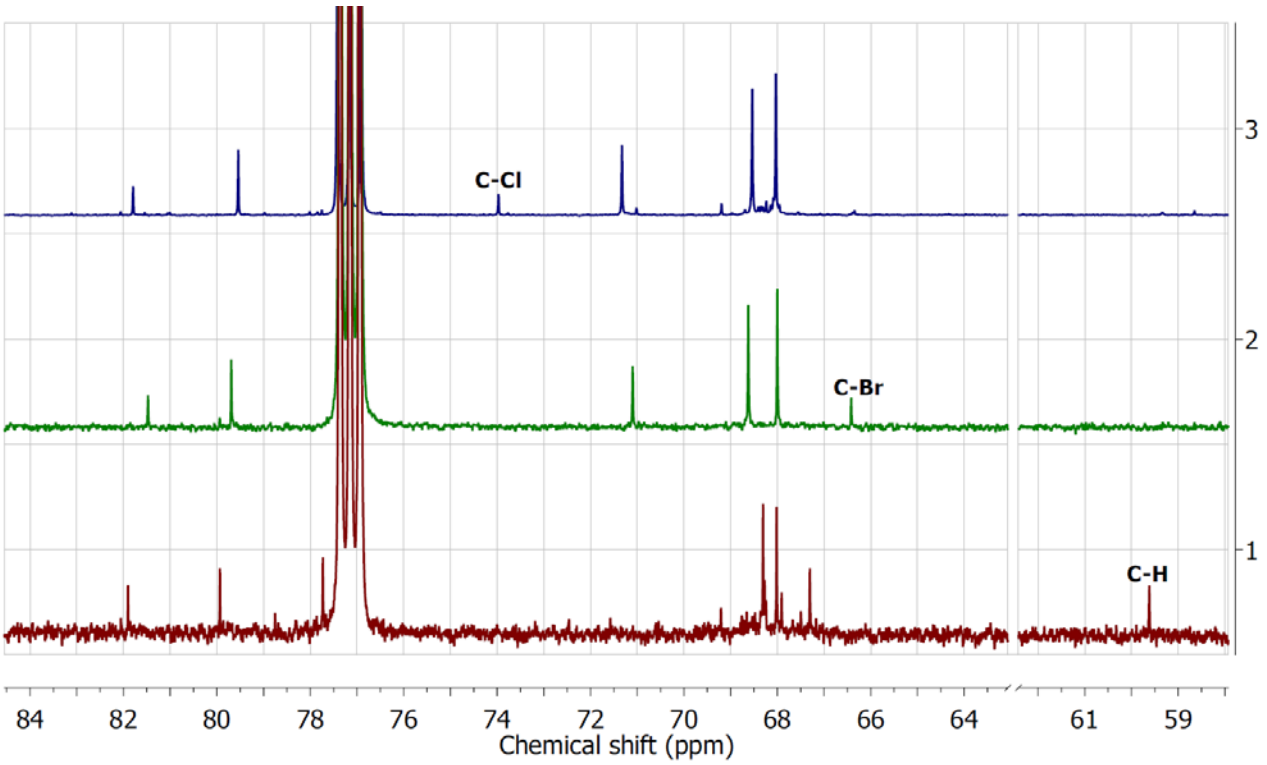

Fig. S97. Comparison of the selected areas in the ^{13}C NMR spectra of compounds $C_{60}(OnBu)_5X$ (X=H (**1**), Br (**2**) and Cl (**3**))

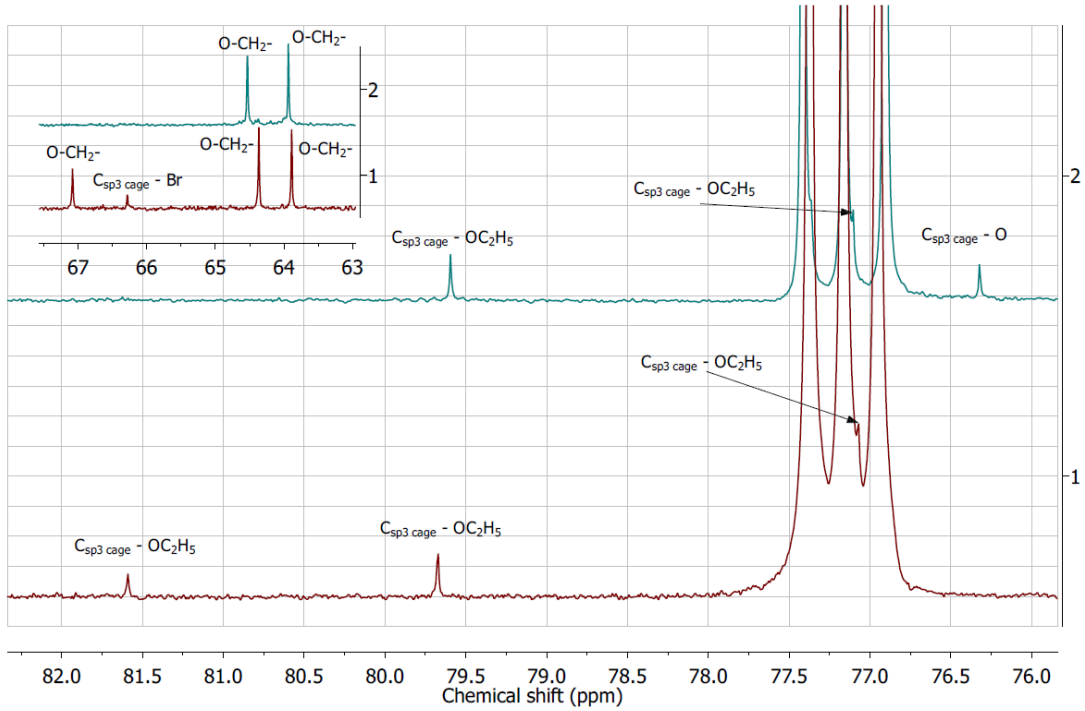

Fig. S98. Comparison of the selected areas in the ^{13}C NMR spectra of compounds $C_{60}(OEt)_5Br$ (1) and $C_{60}(OEt)_4O$ (2)

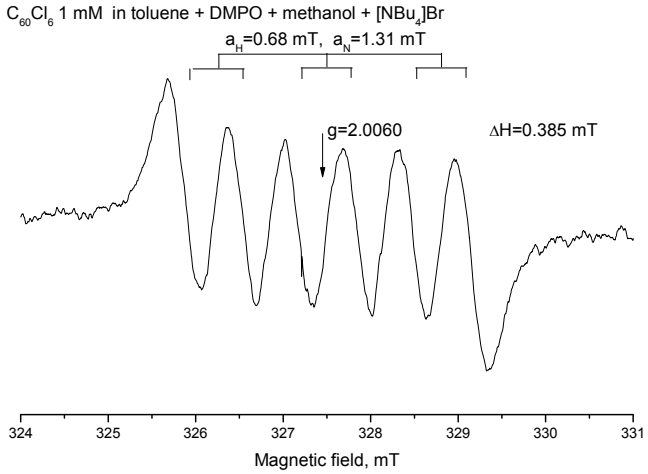

Fig. S99. ESR spectrum of the reaction mixture $C_{60}Cl_6$+DMPO+MeOH+[NBu_4]Br in toluene proving radical nature of the investigated reaction

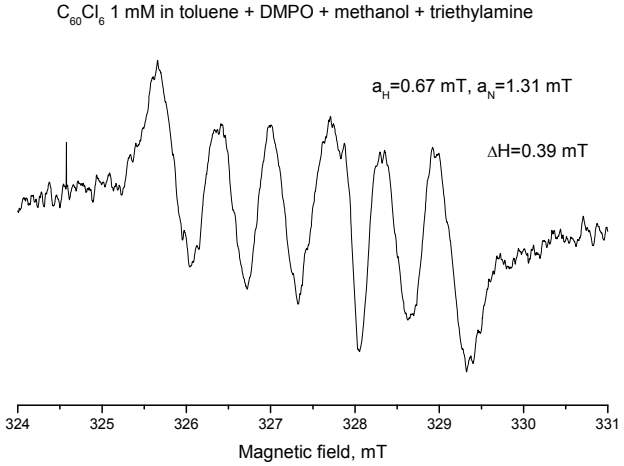

Fig. S100. ESR spectrum of the reaction mixture $C_{60}Cl_6$+DMPO+MeOH+NEt_3 in toluene proving radical nature of the investigated reaction

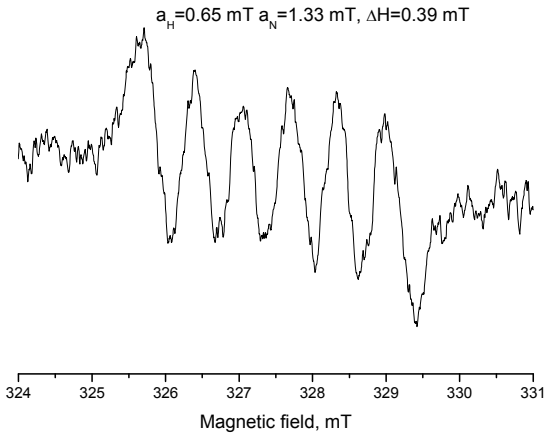

Fig. S101. ESR spectrum of the reaction mixture $C_{60}Cl_6$+DMPO+MeOH+[NBu_4]I in toluene proving radical nature of the investigated reaction