Electronic Supplementary Information for the manuscript:

Diversion of the Arbuzov reaction: alkylation of C-Cl instead of phosphonic ester formation on the fullerene cage

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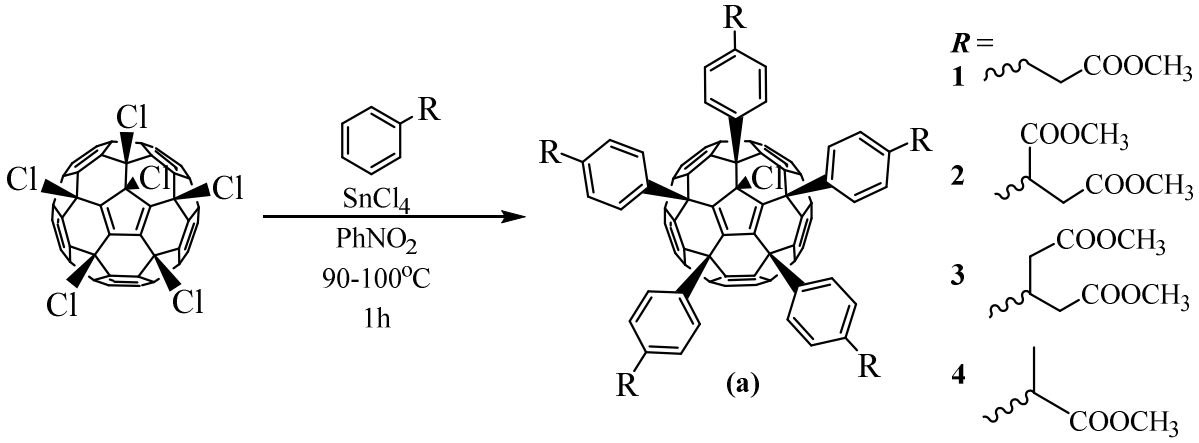
Table of contents

Experimental procedures

Chlorofullerene $C_{60}Cl_6$ was prepared as described in P. A. Troshin et al., *Fullerenes, Nanotubes, Carbon Nanostruct.*, **2003**, *11*, 165. Methyl esters of hydrocinnamic (**1**), phenylsuccinic (**2**), 3-phenylglutaric (**3**) and 2-phenylpropanoic (**4**) acids were synthesized from commercially available acids using standard procedure (esterification in methanol in presence of catalytic amount of sulfuric acid). Methyl esters were distilled in vacuo and dried over 4Å molecular sieves. Toluene for alkylation reactions was distilled and dried over sodium flakes (water content – 22 ppm).

Synthesis of $C_{60}Ar_5Cl$ derivatives 1a-4a

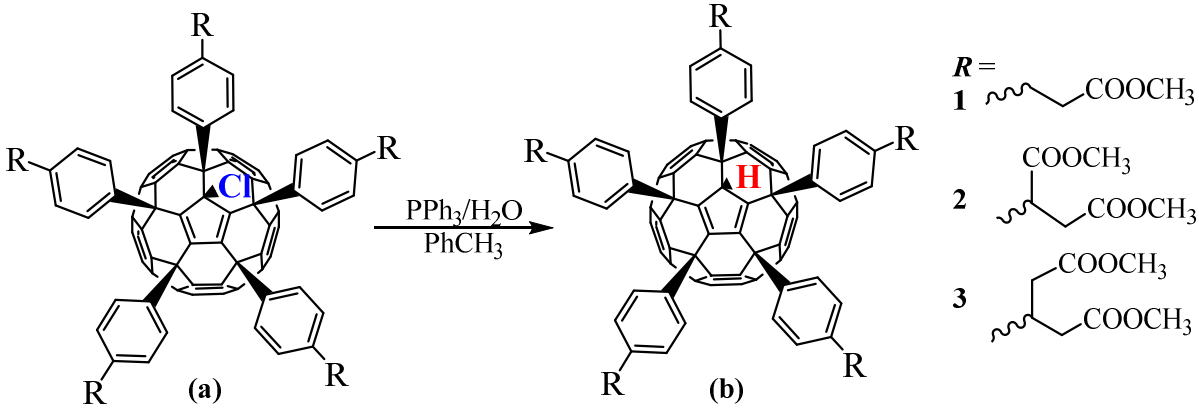


The arylation of $C_{60}Cl_6$ in nitrobenzene was performed following the previously established procedure (O. A. Troshina, P. A. Troshin, A. S. Peregudov, V. I. Kozlovskiy, J. Balzarini and R. N. Lyubovskaya, *Org. Biomol. Chem.*, **2007**, *5*, 2783).

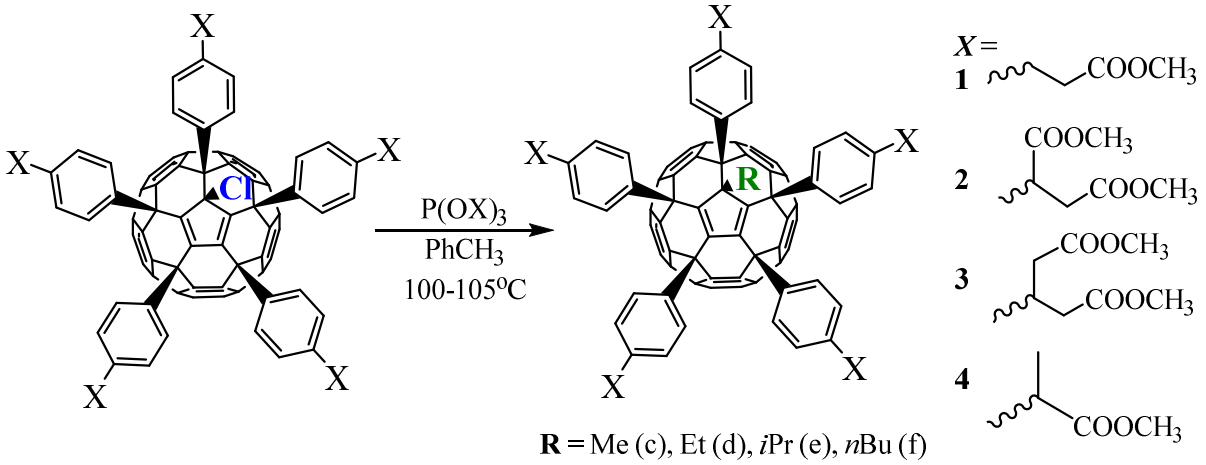
Nitrobenzene was carefully distilled and dried over 4Å molecular sieves for two days. Content of water (<7 ppm) was defined using Mettler Toledo C10SX Karl Fischer titrator.

Synthesis of $C_{60}Ar_5H$ derivatives 1b-4b

Replacement of Cl in $C_{60}Ar_5Cl$ with H was achieved using Ph_3P/H_2O treatment reported by group of R. Taylor (A.G. Avent *et al*., *J. Chem. Soc., Chem. Commun.,* 1994, 1463).

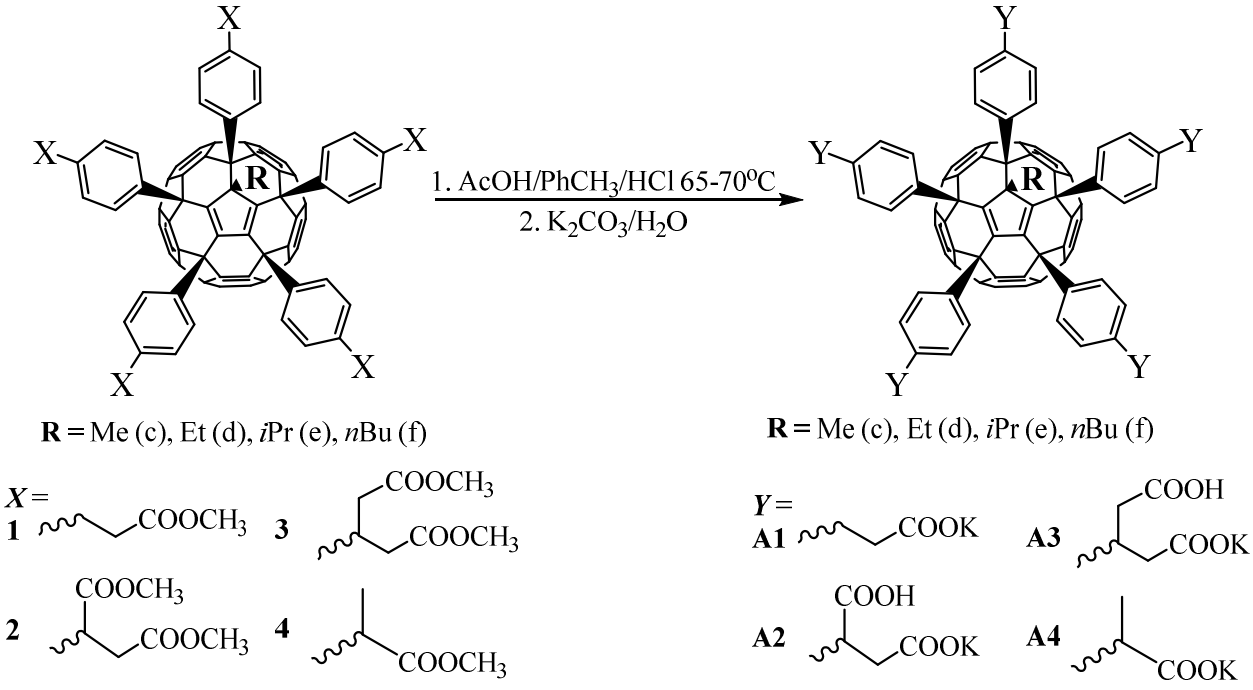


General procedure for the synthesis of $C_{60}Ar_5R$ derivatives 1c-f to 4c-d



A triple-neck round-bottom 50 mL flask equipped with a magnetic stirring bar, thermometer (0-150°C), stopper and condenser was evacuated and filled with argon three times. Compound $C_{60}Ar_5Cl$ (0.07 mmol) and dry toluene (50 mL) were introduced to the flask in a steam of argon and the mixture was stirred for 10 min until complete dissolution of $C_{60}Ar_5Cl$. Phosphite $P(OR)_3$ (1.75 mmol, 25 eq.) was added in a steam of argon and reaction mixture was heated at reflux and stirred for 1h. Dynamics of the reaction was controlled by HPLC. When the signal of $C_{60}Ar_5Cl$ was not observed by HPLC, reaction mixture was cooled to room temperature and poured on the top of the silica gel column. The target product was eluted using toluene/methanol mixtures (97-90% : 3-10% v/v). The obtained solutions were concentrated at the rotary evaporator, washed with acetonitrile and dried in air. Compounds $C_{60}Ar_5R$ (**1c-f, 2c,d,f, 3d** and **4c-d**) were obtained as bright-orange powders.

General procedure for the synthesis of polycarboxylic acids A1a-f to A4a-d



Compounds **A1(a-f), A2(a-d,f), A3(a,b,d)** and **A4(a,c,d)** were synthesized according to the following procedure. Fullerene derivative $C_{60}Ar_5X$ (X=H, Cl, Me, Et, *i*Pr, *n*Bu) (0.07 mmol), toluene (25 mL), acetic acid (25 mL) and HCl (5 ml) were introduced into a two-necked round bottom 100mL flask equipped with a teflon-coated magnetic stirring bar, condenser and thermometer (0-100^{o}C). The mixture was stirred at 65-70^{o}C for 3-4 days and concentrated using a rotary evaporator to afford an orange powder, which was washed with acetonitrile and dried in air.

Water-soluble salts of the fullerene derivatives were obtained as follows. Fullerene-based polycarboxylic acid (0.07 mmol), distilled water (20 mL) and stoichiometric amount of anhydrous potassium carbonate (24.2 mg 0.175 mmol) were placed into a single-necked flask and the reaction mixture was intensively stirred until complete dissolution. Than the solution was filtered through a PES syringe filter (average pore size 0.45 μm) and freeze-dried for 8 h to afford an orange powder of water-soluble salt with quantitative yield.

X-ray crystallography for 1c

Data collection for single crystal of **1c** (0.050 × 0.040 × 0.015 mm3) was carried out with a MAR225 CCD detector at 100 K using synchrotron radiation at the BESSY storage ring, BL 14.3 (λ = 0.8950 Å, PSF of the Free University of Berlin, Germany). The structure was solved using SHELXD and refined against $|F^2|$ with SHELXL-2014/7. Absorption correction was not applied. Crystal data for **1c**: $C_{111}H_{58}O_{10}$, M = 1551.58, monoclinic, $P2_1/c$, a = 21.893(2), b = 16.150(1), c = 20.433(1) Å, β = 95.293(5), V = 7193.7(9) Å^3, Z = 4, Anisotropic refinement with 13833 reflections and 1020 parameters yielded a conventional R1 = 0.1818 for 7916 reflections with I > 2σ (I) and wR2 = 0.3908 for all reflections. Terminal carboxylated alkyl groups were refined with very large thermal parameters due to long distances from the fullerene cage. All methylene and methyl hydrogen atoms were placed into geometrically calculated positions and refined in the riding mode. For more details see CCDC 1893318.

Selected spectroscopic data

Compounds **1a** and **1b** have been synthesized and fully characterized earlier (*Mendeleev Commun.,* 2012, **22**, 254–256).

1c (Yield 95%). ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 1.46 (s, 3H), 2.54 (t, 2H, J = 7.8 Hz), 2.65 – 2.73 (m, 8H), 2.83 (t, 2H, J = 7.8 Hz), 2.98 - 3.06 (m, 8H), 3.62 (s, 3H), 3.68 (s, 6H), 3.73 (s, 6H), 6.94 (d, 2H, J = 8.3 Hz), 7.13 (d, 2H, J = 8.3 Hz), 7.17 (m, 8H), 7.64 (d, 4H, J = 7.2 Hz), 7.75 (d, 4H, J = 8.2 Hz).

^{13}C NMR (151 MHz, $CDCl_3$, δ, ppm): 30.27 ($\underline{C}H_2$), 30.58 ($\underline{C}H_2$), 30.60 ($\underline{C}H_2$), 34.38 ($\underline{C}H_3$, cage-bonded), 35.29 ($\underline{C}H_2$), 35.59 ($\underline{C}H_2$), 35.70 ($\underline{C}H_2$), 51.63 ($\underline{C}H_3$), 51.68 ($\underline{C}H_3$), 51.72 ($\underline{C}H_3$), 57.91 ($\underline{C}_{sp3\ fullerene\ cage}$),

60.78 ($\underline{C}_{sp3\ fullerene\ cage}$), 62.17 ($\underline{C}_{sp3\ fullerene\ cage}$), 62.22 ($\underline{C}_{sp3\ fullerene\ cage}$), 127.99, 128.39, 128.52, 128.60, 128.80, 129.02, 129.16, 130.13, 136.04, 137.72, 139.15, 140.00, 140.17, 140.78, 142.65, 142.72, 143.80, 143.86, 144.01, 144.24, 144.29, 144.32, 144.37, 144.85, 145.45, 145.74, 147.08, 147.27, 147.31, 147.81, 148.08, 148.21, 148.31, 148.45, 148.57, 148.72, 151.71, 153.10, 157.24, 160.14, 173.19 ($\underline{C}OOCH_3$), 173.23 ($\underline{C}OOCH_3$).

ESI MS: m/z= 1552 ($[M]^-$).

Elemental analysis: $C_{111}H_{58}O_{10}$ (M_w=1551.68): calcd., %: C 85.92, H 3.77; found, %: C 85.67, H 3.82.

1d (Yield 92%). ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 0.91 (t, 3H, *J* = 7.1 Hz), 1.49 (q, 2H, *J* = 7.0 Hz), 2.55 – 2.59 (m, 2H), 2.67-2.73 (m, 8H), 2.87 (t, 2H, *J* = 7.8 Hz), 2.97-3.07 (m, *J* = 22.8, 8H), 3.64 (s, 3H), 3.69 (s, 6H), 3.72 (s, 6H), 7.00 (d, 2H, *J* = 8.3 Hz), 7.15-7.19 (m, 8H), 7.26 (d, 2H, *J* = 8.3 Hz), 7.60 (d, 4H, *J* = 8.2 Hz), 7.71 (d, 4H, *J* = 8.2 Hz).
^{13}C NMR (151 MHz, $CDCl_3$, δ, ppm): 9.64 ($CH_2\underline{C}H_3$), 30.27 ($\underline{C}H_2$), 30.54 ($\underline{C}H_2$), 30.61 ($\underline{C}H_2$), 33.59 ($\underline{C}H_2CH_3$), 35.27 ($\underline{C}H_2$), 35.55 ($\underline{C}H_2$), 35.71 ($\underline{C}H_2$), 51.66 ($\underline{C}H_3$), 51.69 ($\underline{C}H_3$), 58.41 ($\underline{C}_{sp3\ fullerene\ cage}$), 60.91 ($\underline{C}_{sp3\ fullerene\ cage}$), 63.24 ($\underline{C}_{sp3\ fullerene\ cage}$), 65.48 ($\underline{C}_{sp3\ fullerene\ cage}$), 127.89, 128.07, 128.47, 128.54, 128.79, 129.01, 130.88, 136.96, 138.60, 139.24, 140.04, 140.14, 141.02, 142.66, 143.59, 143.90, 144.01, 144.12, 144.17, 144.32, 144.36, 144.70, 144.74, 145.33, 145.54, 147.09, 147.30, 147.37, 147.66, 147.86, 148.07, 148.20, 148.28, 148.47, 148.57, 148.71, 148.80, 151.47, 153.33, 155.82, 156.94, 173.22 ($\underline{C}OOCH_3$).
ESI MS: m/z= 1565 ($[M]^-$).

Elemental analysis: $C_{112}H_{60}O_{10}$ (M_w=1565.70): calcd., %: C 85.92, H 3.86; found, %: C 85.63, H 3.97

1e (Yield 80%). ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 0.59 (d, 6H, *J* = 6.2 Hz), 2.41 (m, 1H), 2.60 (t, 2H, *J* = 7.7 Hz), 2.65 (t, 4H, *J* = 7.7 Hz), 2.74 (t, 4H, *J* = 7.6 Hz), 2.89 (t, 2H, *J* = 7.5 Hz), 2.95 (t, 4H, *J* = 7.5 Hz), 3.08 (t, 4H, *J* = 7.5 Hz), 3.65 (s, 3H), 3.68 (s, 6H), 3.73 (s, 6H), 7.08 (d, 2H, *J* = 7.9 Hz), 7.12 (d, 4H, *J* = 7.7 Hz), 7.26 (d, 4H, *J* = 7.7 Hz), 7.54– 7.63 (m, 6H), 7.93 (d, 4H, *J* = 7.8 Hz).
^{13}C NMR (151 MHz, $CDCl_3$, δ, ppm): 22.53 ($CH(\underline{C}H_3)_2$), 30.30 ($\underline{C}H_2$), 30.48 ($\underline{C}H_2$), 30.62 ($\underline{C}H_2$), 35.22 ($\underline{C}H(CH_3)_2$), 35.36 ($\underline{C}H_2$), 35.53 ($\underline{C}H_2$), 35.71 ($\underline{C}H_2$), 51.66 ($\underline{C}H_3$), 51.71 ($\underline{C}H_3$), 58.24 ($\underline{C}_{sp3\ fullerene\ cage}$), 61.25 ($\underline{C}_{sp3\ fullerene\ cage}$), 63.10 ($\underline{C}_{sp3\ fullerene\ cage}$), 71.65($\underline{C}_{sp3\ fullerene\ cage}$), 127.58, 128.56, 128.63, 128.74, 129.09, 131.54, 138.20, 138.80, 139.16, 140.00, 140.18, 142.54, 142.66, 142.74, 143.27, 143.66, 143.94, 144.10, 144.25, 144.33, 144.75, 145.28, 145.56, 147.20, 147.34, 147.53, 147.86, 147.95, 148.23, 148.28, 148.55, 148.58, 148.73, 148.89, 150.12, 154.74, 157.44, 158.40, 173.21 ($\underline{C}OOCH_3$), 173.23 ($\underline{C}OOCH_3$).
ESI MS: m/z= 1579 ($[M]^-$).

Elemental analysis: $C_{113}H_{62}O_{10}$ (M_w=1579.73): calcd., %: C 85.92, H 3.96; found, %: C 85.66, H 3.99

1f (Yield 95%). ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 0.62 (t, 3H, *J* = 7.3 Hz), 0.79-0.87 (m, 2H), 1.37–1.49 (m, 4H), 2.57 (t, 2H, *J* = 7.8 Hz), 2.65– 2.74 (m, 8H), 2.87 (t, 2H, *J* = 7.7 Hz), 2.96– 3.06 (m, 8H),

3.64 (s, 3H), 3.69 (s, 6H), 3.72 (s, 6H), 7.00 (d, 2H, *J* = 8.2 Hz), 7.14 – 7.18 (m, 8H), 7.27 (d, 2H, *J* = 8.2 Hz), 7.59 (d, 4H, *J* = 8.1 Hz), 7.72 (d, 4H, *J* = 8.1 Hz).

^{13}C NMR (151 MHz, $CDCl_3$, δ, ppm): 14.21 ($\underline{C}H_3(CH_2)_3$), 22.24 ($CH_3(\underline{C}H_2)_3$), 27.48 ($CH_3(\underline{C}H_2)_3$), 30.30 ($\underline{C}H_2$), 30.55 ($\underline{C}H_2$), 30.60 ($\underline{C}H_2$), 35.36 ($\underline{C}H_2$), 35.65 ($\underline{C}H_2$), 35.80 ($\underline{C}H_2$), 40.38 ($CH_3(\underline{C}H_2)_3$), 51.65 ($\underline{C}H_3$), 51.68 ($\underline{C}H_3$), 51.70 ($\underline{C}H_3$), 58.34 ($\underline{C}_{sp3\ fullerene\ cage}$), 60.95 ($\underline{C}_{sp3\ fullerene\ cage}$), 63.20 ($\underline{C}_{sp3\ fullerene\ cage}$), 65.37 ($\underline{C}_{sp3\ fullerene\ cage}$), 127.82, 128.18, 128.36, 128.46, 128.69, 128.86, 129.01, 130.83, 137.01, 138.54, 139.25, 140.10, 140.17, 140.95, 142.66, 143.65, 143.96, 144.03, 144.09, 144.11, 144.29, 144.33, 144.38, 144.77, 145.42, 145.55, 147.09, 147.31, 147.38, 147.70, 147.87, 148.10, 148.20, 148.29, 148.49, 148.59, 148.74, 148.82, 151.48, 153.51, 156.60, 156.96, 173.18 ($\underline{C}OOCH_3$), 173.21 ($\underline{C}OOCH_3$).

ESI MS: m/z= 1594 ($[M]^-$).

Elemental analysis: $C_{114}H_{64}O_{10}$ (M_w=1593.76): calcd., %: C 85.91, H 4.05; found, %: C 85.30, H 4.25.

2a (Yield 80%)**.** ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 2.53 – 2.86 (m, 5H), 3.07 – 3.37 (m, 5H), 3.60 – 3.88 (m, 30H), 3.95-4.23 (m, 5H), 6.95–7.39 (m, 12H), 7.51 – 7.72 (m, 4H), 7.76 – 7.97 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 37.45 ($\underline{C}H_2$), 37.48 ($\underline{C}H_2$), 37.52 ($\underline{C}H_2$), 37.55 ($\underline{C}H_2$), 37.58 ($\underline{C}H_2$), 46.57 ($\underline{C}H$), 46.74 ($\underline{C}H$), 46.75 ($\underline{C}H$), 51.91 ($\underline{C}H_3$), 51.97 ($\underline{C}H_3$), 52.01 ($\underline{C}H_3$), 52.42 ($\underline{C}H_3$), 52.47 ($\underline{C}H_3$), 52.52 ($\underline{C}H_3$), 57.80 ($\underline{C}_{sp3\ fullerene\ cage}$), 128.24, 60.44 ($\underline{C}_{sp3\ fullerene\ cage}$), 63.12 ($\underline{C}_{sp3\ fullerene\ cage}$), 75.98 ($\underline{C}_{sp3\ fullerene\ cage}$-Cl), 125.31, 126.87, 127.55, 127.74, 128.26, 128.43, 128.72, 128.94, 129.53, 130.55, 136.77, 137.52, 137.61, 138.24, 138.74, 143.00, 143.19, 143.57, 143.72, 143.87, 144.28, 144.38, 144.46, 144.64, 145.14, 145.22, 146.44, 147.30, 147.45, 147.93, 148.26, 148.36, 148.54, 148.74, 148.78, 148.84, 148.86, 150.18, 150.89, 153.73, 156.47, 171.78 ($\underline{C}OOCH_3$), 171.82 ($\underline{C}OOCH_3$), 171.86 ($\underline{C}OOCH_3$), 173.12 ($\underline{C}OOCH_3$), 173.17 ($\underline{C}OOCH_3$).

ESI MS: m/z= 1828 ($[M\text{-}Cl]^-$).

Elemental analysis: $C_{120}H_{65}ClO_{20}$ (M_w=1862.27): calcd., %: C 77.40, H 3.52; found, %: C 77.31, H 3.77.

2b (Yield 95%)**.** ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 2.59 – 2.78 (m, 5H), 3.08 - 3.37 (m, 5H), 3.63 – 3.80 (m, 30H), 4.02 – 4.20 (m, 5H), 5.20 (s, 1H), 7.06 (d, 2H, *J* = 8.1 Hz), 7.08 - 7.12 (m, 4H), 7.23 – 7.27 (m, 4H), 7.33 (d, 2H, *J* = 7.5 Hz), 7.51 (d, 4H, *J* = 8.0 Hz), 7.67 – 7.73 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 37.39 ($\underline{C}H_2$), 37.42 ($\underline{C}H_2$), 37.45 ($\underline{C}H_2$), 37.49 ($\underline{C}H_2$), 37.53 ($\underline{C}H_2$), 46.56 ($\underline{C}H$), 46.68 ($\underline{C}H$), 46.72 ($\underline{C}H$), 51.99 ($\underline{C}H_3$), 52.02 ($\underline{C}H_3$), 52.43 ($\underline{C}H_3$), 52.47 ($\underline{C}H_3$), 52.53 ($\underline{C}H_3$), 58.46 ($\underline{C}_{sp3\ fullerene\ cage}$), 58.60 ($\underline{C}_{sp3\ fullerene\ cage}$), 60.62 ($\underline{C}_{sp3\ fullerene\ cage}$), 62.81 ($\underline{C}_{sp3\ fullerene\ cage}$-H), 127.74, 128.02, 128.15, 128.22, 128.33, 128.52, 128.60, 128.63, 128.91, 129.02, 136.88, 137.29, 137.50, 139.15, 143.25, 143.60, 144.17, 144.25, 144.33, 144.44, 144.97, 145.24, 145.49, 145.73, 146.91, 147.11, 147.21, 147.79, 148.13, 148.19, 148.31, 148.44, 148.73, 148.80, 148.86, 151.32, 151.88, 152.49, 155.83, 155.87, 171.75 ($\underline{C}OOCH_3$), 173.05 ($\underline{C}OOCH_3$), 173.11 ($\underline{C}OOCH_3$), 173.14 ($\underline{C}OOCH_3$).

ESI MS: m/z= 1827 ($[M\text{-}H]^-$).

Elemental analysis: $C_{120}H_{66}O_{20}$ (M_w=1827.83): calcd., %: C 78.85, H 3.64; found, %: C 78.55, H 3.89.

2c (Yield 95%). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 1.47 (s, 3H), 2.47 – 2.81 (m, 5H), 3.06 – 3.33 (m, 5H), 3.55 – 3.83 (m, 30H), 3.92–4.27 (m, 5H), 6.97 - 7.07 (m, 2H), 7.13 - 7.21 (m, 2H), 7.21 – 7.36 (m, 8H), 7.52 – 7.61 (m, 2H), 7.62 – 7.82 (m, 8H).

^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 34.35 ($\underline{C}H_3$, cage-boned), 37.48 ($\underline{C}H_2$), 37.54 ($\underline{C}H_2$), 46.49 ($\underline{C}H$), 46.73 ($\underline{C}H$), 51.91 ($\underline{C}H_3$), 51.97 ($\underline{C}H_3$), 52.02 ($\underline{C}H_3$), 52.41 ($\underline{C}H_3$), 52.52 ($\underline{C}H_3$), 57.82 ($\underline{C}_{sp3\ fullerene\ cage}$), 60.70 ($\underline{C}_{sp3\ fullerene\ cage}$), 62.18 ($\underline{C}_{sp3\ fullerene\ cage}$), 62.30 ($\underline{C}_{sp3\ fullerene\ cage}$), 127.57, 128.09, 128.36, 128.63, 128.85, 129.21, 130.45, 130.93, 136.41, 137.49, 139.11, 142.05, 142.83, 143.67, 144.11, 144.32, 144.45, 144.68, 145.28, 145.55, 147.10, 147.29, 147.33, 147.84, 148.17, 148.25, 148.36, 148.51, 148.68, 148.79, 148.82, 151.33, 152.80, 156.98, 171.76 ($\underline{C}OOCH_3$), 171.80 ($\underline{C}OOCH_3$), 173.07 ($\underline{C}OOCH_3$), 173.11 ($\underline{C}OOCH_3$), 173.14 ($\underline{C}OOCH_3$), 173.18 ($\underline{C}OOCH_3$).

ESI MS: m/z= 1841 ($[M]^-$).

Elemental analysis: $C_{121}H_{68}O_{20}$ (M_w=1841.86): calcd., %: C 78.91, H 3.72; found, %: C 79.02, H 3.80.

2d (Yield 94%)**.** ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 0.91 (t, 3H, *J* = 6.9 Hz), 1.51 (m, 2H), 2.56 – 2.84 (m, 5H), 3.10 – 3.33 (m, 5H), 3.60 – 3.80 (m, 30H), 3.98 – 4.21 (m, 5H), 7.00 – 7.14 (m, 2H), 7.14 – 7.37 (m, 10H), 7.59– 7.67 (m, 4H), 7.69 – 7.82 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 9.67 ($CH_2\underline{C}H_3$), 33.79 ($\underline{C}H_2CH_3$), 37.47 ($\underline{C}H_2$), 37.49 ($\underline{C}H_2$), 37.53 ($\underline{C}H_2$), 46.51 ($\underline{C}H$), 46.71 ($\underline{C}H$), 46.75 ($\underline{C}H$), 51.94 ($\underline{C}H_3$), 51.97 ($\underline{C}H_3$), 52.01 ($\underline{C}H_3$), 52.47 ($\underline{C}H_3$), 52.53 ($\underline{C}H_3$), 52.55 ($\underline{C}H_3$), 58.29 ($\underline{C}_{sp3\ fullerene\ cage}$), 60.83 ($\underline{C}_{sp3\ fullerene\ cage}$), 63.20 ($\underline{C}_{sp3\ fullerene\ cage}$), 65.53 ($\underline{C}_{sp3\ fullerene\ cage}$), 125.31, 127.20, 127.48, 128.04, 128.24, 128.29, 128.36, 129.05, 129.16, 131.17, 136.45, 137.43, 138.36, 139.93, 142.31, 142.76, 143.44, 143.72, 144.11, 144.21, 144.35, 144.45, 144.55, 145.15, 145.37, 147.12, 147.33, 147.41, 147.93, 148.17, 148.26, 148.34, 148.54, 148.68, 148.83, 148.87, 151.05, 153.03, 155.89, 156.74, 171.78 ($\underline{C}OOCH_3$), 173.11 ($\underline{C}OOCH_3$), 173.16 ($\underline{C}OOCH_3$), 173.18 ($\underline{C}OOCH_3$).

ESI MS: m/z= 1856 ($[M]^-$).

Elemental analysis: $C_{122}H_{70}O_{20}$ (M_w=1855.88): calcd., %: C 78.96, H 3.80; found, %: C 78.77, H 3.78.

2f (Yield 85%)**.** ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 0.48 - 0.57 (m, 3H), 0.69 – 0.82 (m, 2H), 1.33 – 1.48 (m, 4H), 2.82 – 2.55 (m, 5H), 7.18 – 7.26 (m, 10H), 3.34 – 3.09 (m, 5H), 3.82 – 3.60 (m, 30H), 3.98 - 4.23 (m, 5H), 7.03 – 7.11 (m, 2H), 7.57 - 7.63 (m, 4H), 7.68 - 7.75 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$, δ, ppm): 13.88 ($\underline{C}H_3(CH_2)_3$), 22.14 ($CH_3(\underline{C}H_2)_3$), 27.67 46.53 ($\underline{C}H$), ($CH_3(\underline{C}H_2)_3$), 37.42 ($\underline{C}H_2$), 37.45 ($\underline{C}H_2$), 37.48 ($\underline{C}H_2$), 37.51 ($\underline{C}H_2$), 37.53 ($\underline{C}H_2$), 40.86 ($CH_3(\underline{C}H_2)_3$), 46.69 ($\underline{C}H$), 46.71 ($\underline{C}H$), 46.73 ($\underline{C}H$), 46.75 ($\underline{C}H$), 51.89 ($\underline{C}H_3$), 51.95 ($\underline{C}H_3$), 51.99 ($\underline{C}H_3$), 52.37 ($\underline{C}H_3$), 52.44 ($\underline{C}H_3$), 52.46 ($\underline{C}H_3$), 52.50 ($\underline{C}H_3$), 58.22 ($\underline{C}_{sp3\ fullerene\ cage}$), 60.89 ($\underline{C}_{sp3\ fullerene\ cage}$), 63.10 ($\underline{C}_{sp3\ fullerene\ cage}$), 65.49 ($\underline{C}_{sp3\ fullerene\ cage}$), 127.02, 127.47, 127.95, 128.23, 128.47, 128.83, 129.23, 130.91, 136.60, 137.52, 138.45, 139.84, 142.22, 142.76, 143.49, 143.78, 144.12, 144.20, 144.36, 144.47, 144.57, 145.22, 145.34, 147.10, 147.31, 147.39, 147.91, 148.17, 148.24, 148.33, 148.54, 148.68, 148.84, 148.87, 151.05, 153.20, 156.74, 171.72 ($\underline{C}OOCH_3$), 173.06 ($\underline{C}OOCH_3$), 173.09 ($\underline{C}OOCH_3$), 173.13 ($\underline{C}OOCH_3$), 173.15 ($\underline{C}OOCH_3$).

ESI MS: m/z= 1919 ([M+Cl]$^-$).

Elemental analysis: $C_{124}H_{74}O_{20}$ (M_w=1883.94): calcd., %: C 79.06, H 3.96; found, %: C 78.80, H 4.13.

3a (Yield 87%)**.** ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 2.54 – 2.86 (m, 20H), 3.51 – 3.75 (m, 35H), 7.02 (d, 2H, *J* = 8.3 Hz), 7.16 (d, 2H, *J* = 8.3 Hz), 7.19 (d, 4H, *J* = 8.1 Hz), 7.24 (d, 4H, *J* = 8.1 Hz), 7.52 (d, 4H, *J* = 8.1 Hz), 7.82 (d, 4H, *J* = 8.1 Hz).
^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 37.79 (C$\underline{H}$), 37.99 (C$\underline{H}$), 38.10 (C$\underline{H}$), 40.17 (C$\underline{H}_2$), 40.38 (C$\underline{H}_2$), 40.42 (C$\underline{H}_2$), 40.44 (C$\underline{H}_2$), 40.49 (C$\underline{H}_2$), 51.59 (C$\underline{H}_3$), 51.70 (C$\underline{H}_3$), 51.71 (C$\underline{H}_3$), 51.74 (C$\underline{H}_3$), 57.92 ($\underline{C}_{sp3\ fullerene\ cage}$), 60.49 ($\underline{C}_{sp3\ fullerene\ cage}$), 63.12 ($\underline{C}_{sp3\ fullerene\ cage}$), 76.36 ($\underline{C}_{sp3\ fullerene\ cage}$-Cl), 125.31, 126.66, 127.54, 127.67, 127.77, 127.98, 128.24, 128.34, 128.41, 128.54, 128.75, 128.89, 129.05, 130.32, 136.03, 137.40, 141.94, 142.27, 142.35, 142.52, 142.94, 143.36, 143.43, 143.72, 143.75, 144.04, 144.23, 144.32, 144.43, 144.59, 145.24, 145.37, 146.67, 147.27, 147.30, 147.44, 147.91, 148.21, 148.33, 148.52, 148.72, 148.78, 148.84, 150.41, 151.06, 153.57, 156.65, 171.89 ($\underline{C}OOCH_3$), 171.92 ($\underline{C}OOCH_3$), 171.94 ($\underline{C}OOCH_3$).
ESI MS: m/z= 1896 ([M-Cl]$^-$).

Elemental analysis: $C_{125}H_{75}ClO_{20}$ (M_w=1932.41): calcd., %: C 77.69, H 3.91; found, %: C 77.48, H 4.05.

3b (Yield 95%)**.** ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 2.58– 2.84 (m, 20H), 3.52 – 3.74 (m, 35H), 5.20 (s, 1H), 7.07 – 7.11 (m, 6H), 7.21 (d, 4H, *J* = 8.2 Hz), 7.31 (d, 2H, *J* = 8.2 Hz), 7.45 (d, 4H, *J* = 8.2 Hz), 7.64 (d, 4H, *J* = 8.2 Hz).
^{13}C NMR (151 MHz, $CDCl_3$, δ, ppm): 37.74 (C$\underline{H}$), 37.90 (C$\underline{H}$), 37.96 (C$\underline{H}$), 40.27 (C$\underline{H}_2$), 40.37 (C$\underline{H}_2$), 40.42 (C$\underline{H}_2$), 40.45 (C$\underline{H}_2$), 51.71 (C$\underline{H}_3$), 51.74 (C$\underline{H}_3$), 51.78 (C$\underline{H}_3$), 58.61 ($\underline{C}_{sp3\ fullerene\ cage}$), 58.66 ($\underline{C}_{sp3\ fullerene\ cage}$), 60.70 ($\underline{C}_{sp3\ fullerene\ cage}$), 62.89 ($\underline{C}_{sp3\ fullerene\ cage}$-H), 127.53, 127.67, 127.76, 128.01, 128.34, 128.40, 128.49, 128.58, 131.98, 132.09, 132.15, 138.48, 141.88, 142.16, 142.30, 143.16, 143.75, 144.09, 144.17, 144.19, 144.28, 144.29, 144.37, 144.43, 145.39, 145.65, 145.93, 145.95, 146.90, 147.10, 147.19, 147.74, 147.76, 148.09, 148.13, 148.28, 148.40, 148.69, 148.73, 148.80, 151.69, 152.14, 152.44, 156.01, 171.89 ($\underline{C}OOCH_3$).
ESI MS: m/z= 1896 ([M-H]$^-$).

Elemental analysis: $C_{125}H_{76}O_{20}$ (M_w=1897.96): calcd., %: C 79.10, H 4.04; found, %: C 78.82, H 4.10.

3d (Yield 91%)**.** ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 0.79 (t, 3H, *J* = 7.1 Hz), 1.42 (q, 2H, *J* = 6.7 Hz), 2.54 – 2.89 (m, 20H), 3.51 – 3.77 (m, 35H), 7.04 (d, 2H, *J* = 8.4 Hz), 7.19 – 7.25 (m, 10H), 7.58 (d, 4H, *J* = 8.3 Hz), 7.65 (d, 4H, *J* = 8.3 Hz).
^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 9.45 ($CH_2\underline{C}H_3$), 33.58 ($\underline{C}H_2CH_3$), 37.63 (C$\underline{H}$), 38.02 (C$\underline{H}$), 38.05 (C$\underline{H}$), 40.12 (C$\underline{H}_2$), 40.40 (C$\underline{H}_2$), 40.42 (C$\underline{H}_2$), 40.47 (C$\underline{H}_2$), 40.54 (C$\underline{H}_2$), 51.60 (C$\underline{H}_3$), 51.66 (C$\underline{H}_3$), 51.71 (C$\underline{H}_3$), 58.40 ($\underline{C}_{sp3\ fullerene\ cage}$), 60.91 ($\underline{C}_{sp3\ fullerene\ cage}$), 63.18 ($\underline{C}_{sp3\ fullerene\ cage}$), 65.42 ($\underline{C}_{sp3\ fullerene\ cage}$), 126.78, 127.51, 127.78, 128.16, 129.01, 130.87, 137.52, 139.07, 141.46, 141.67, 142.23, 142.32, 142.70, 143.59, 143.93, 144.05, 144.08, 144.14, 144.30, 144.40, 144.70, 144.74, 145.30, 145.47, 147.10, 147.32, 147.39,

147.49, 147.90, 148.12, 148.22, 148.31, 148.51, 148.62, 148.77, 148.84, 171.89 ($\underline{C}OOCH_3$), 171.92 ($\underline{C}OOCH_3$).

Elemental analysis: $C_{127}H_{80}O_{20}$ (M_w=1926.02): calcd., %: C 79.20, H 4.19; found, %: C 78.93, H 4.23.

4a (Yield 75%)**.** ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 1.40 – 1.69 (m, 15H), 3.56 – 3.83 (m, 20H), 7.06 (d, 2H, *J* = 8.5 Hz), 7.22 (d, 4H, *J* = 5.3 Hz), 7.24 – 7.36 (m, 6H), 7.55 - 7.67 (m, 4H), 7.81– 7.95 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 18.39 ($\underline{C}H_3$), 18.54 ($\underline{C}H_3$), 18.57 ($\underline{C}H_3$), 44.87 ($\underline{C}H$), 45.06 ($\underline{C}H$), 52.07 ($\underline{C}H_3$), 52.12 ($\underline{C}H_3$), 57.87 ($\underline{C}_{sp3\ fullerene\ cage}$), 60.51 ($\underline{C}_{sp3\ fullerene\ cage}$), 63.22($\underline{C}_{sp3\ fullerene\ cage}$), 76.01 ($\underline{C}_{sp3\ fullerene\ cage}$-Cl), 126.55, 127.29, 127.91, 127.95, 128.06, 128.80, 129.20, 129.67, 130.35, 130.49, 136.26, 137.71, 139.37, 140.22, 140.34, 142.56, 142.94, 143.34, 143.37, 143.67, 143.76, 143.99, 144.23, 144.34, 144.43, 144.60, 145.27, 145.33, 147.31, 147.45, 147.92, 148.22, 148.33, 148.52, 148.73, 148.79, 148.85, 150.41, 151.04, 153.82, 156.70, 174.69 ($\underline{C}OOCH_3$), 174.78 ($\underline{C}OOCH_3$).

ESI MS: m/z= 1537 ($[M\text{-}Cl]^-$).

Elemental analysis: $C_{110}H_{55}ClO_{10}$ (M_w=1572.09): calcd., %: C 84.04, H 3.53; found, %: C 84.31, H 3.30.

4c (Yield 94%)**.** ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 1.42 (d, 3H, *J* = 7.2 Hz), 1.51 (s, 3H), 1.53 – 1.59 (m, 12H), 3.52 – 3.87 (m, 20H), 7.00 – 7.07 (m, 2H), 7.16 – 7.22 (m, 2H), 7.23 – 7.33 (m, 8H), 7.63 – 7.71 (m, 4H), 7.73 – 7.81 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 18.46 ($\underline{C}H_3$), 18.60 ($\underline{C}H_3$), 18.65 ($\underline{C}H_3$), 34.48 ($\underline{C}H_3$, cage-boned), 44.81 ($\underline{C}H$), 45.04 ($\underline{C}H$), 45.08 ($\underline{C}H$), 45.09 ($\underline{C}H$), 52.07 ($\underline{C}H_3$), 52.12 ($\underline{C}H_3$), 57.87 ($\underline{C}_{sp3\ fullerene\ cage}$), 60.78 ($\underline{C}_{sp3\ fullerene\ cage}$), 62.22 ($\underline{C}_{sp3\ fullerene\ cage}$), 62.25 ($\underline{C}_{sp3\ fullerene\ cage}$), 126.95, 127.31, 127.73, 127.76, 127.95, 128.04, 128.47, 128.64, 129.03, 130.29, 136.96, 138.55, 138.58, 138.62, 139.03, 140.13, 140.17, 141.61, 142.77, 143.79, 144.06, 144.16, 144.29, 144.41, 144.79, 145.40, 145.68, 147.11, 147.30, 147.34, 147.83, 148.13, 148.24, 148.35, 148.50, 148.63, 148.78, 151.53, 153.07, 153.10, 157.20, 160.12, 160.20, 160.26, 174.76 ($\underline{C}OOCH_3$), 174.80 ($\underline{C}OOCH_3$).

ESI MS: m/z= 1551 ($[M]^-$).

Elemental analysis: $C_{111}H_{58}O_{10}$ (M_w=1551.68): calcd., %: C 85.92, H 3.77; found, %: C 85.66, H 4.04.

4d (Yield 92%)**.** ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 0.91– 1.00 (m, 3H), 1.45 (d, 3H, *J* = 7.2 Hz), 1.52 – 1.61 (m, 14H), 3.54-3.86 (m, 20H) 7.04 – 7.14 (m, 2H), 7.21 – 7.34 (m, 10H), 7.60 – 7.69 (m, 4H), 7.73 – 7.81 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$, δ, ppm): 9.71 ($CH_2\underline{C}H_3$), 18.50 ($\underline{C}H_3$), 18.54 ($\underline{C}H_3$), 18.60 ($\underline{C}H_3$), 33.80 ($\underline{C}H_2CH_3$), 44.84 ($\underline{C}H$), 45.02 ($\underline{C}H$), 45.05 ($\underline{C}H$), 45.08 ($\underline{C}H$), 52.13 ($\underline{C}H_3$), 58.36 ($\underline{C}_{sp3\ fullerene\ cage}$), 60.91 ($\underline{C}_{sp3\ fullerene\ cage}$), 63.29 ($\underline{C}_{sp3\ fullerene\ cage}$), 65.56 ($\underline{C}_{sp3\ fullerene\ cage}$), 126.92, 127.24, 127.69, 127.83, 127.90, 128.05, 128.12, 129.03, 130.98, 131.02, 137.83, 139.04, 139.42, 140.11, 141.87, 142.69, 143.57, 143.82, 144.05, 144.16, 144.32, 144.40, 144.69, 145.27, 145.50, 147.11, 147.33, 147.40, 147.51, 147.90, 148.11,

148.22, 148.31, 148.51, 148.61, 148.77, 148.85, 151.26, 153.24, 153.28, 153.33, 155.94, 156.95, 174.78 ($\underline{C}OOCH_3$), 174.81 ($\underline{C}OOCH_3$).
ESI MS: m/z= 1565 ($[M]^-$).

Elemental analysis: $C_{112}H_{60}O_{10}$ (M_w=1565.70): calcd., %: C 85.92, H 3.86; found, %: C 85.78, H 4.15.

A1c. ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 1.42 (s, 3H), 2.41 (t, 2H, *J* = 7.6 Hz), 2.52 – 2.60 (m, 8H), 2.67 (t, 2H, *J* = 6.8 Hz), 2.81 – 2.89 (m, 8H), 6.97 (d, 2H, *J* = 8.3 Hz), 7.03 (d, 2H, *J* = 8.0 Hz), 7.23 (d, 8H, *J* = 8.1 Hz), 7.61 (d, 4H, *J* = 8.1 Hz), 7.67 (d, 4H, *J* = 8.1 Hz), 12.16 (br.s, 5H).
^{13}C NMR (151 MHz, DMSO-d_6, δ, ppm): 30.02 ($\underline{C}H_2$), 30.35 ($\underline{C}H_2$), 30.44 ($\underline{C}H_2$), 34.51 ($\underline{C}H_3$, cage-bonded), 35.08 ($\underline{C}H_2$), 35.44 ($\underline{C}H_2$), 35.67 ($\underline{C}H_2$), 57.81 ($\underline{C}_{sp3\ fullerene\ cage}$), 60.88 ($\underline{C}_{sp3\ fullerene\ cage}$), 62.14 ($\underline{C}_{sp3\ fullerene\ cage}$), 62.25 ($\underline{C}_{sp3\ fullerene\ cage}$), 128.17, 128.56, 128.67, 129.29, 129.54, 129.81, 135.16, 136.76, 140.22, 140.40, 141.16, 141.30, 142.36, 142.58, 143.86, 143.95, 144.02, 144.10, 144.20, 144.22, 144.68, 144.80, 145.62, 145.92, 146.95, 147.19, 147.66, 147.95, 148.02, 148.19, 148.31, 148.38, 148.57, 148.61, 152.10, 153.42, 157.41, 160.42, 174.17 ($\underline{C}OOH$), 174.21 ($\underline{C}OOH$), 174.23 ($\underline{C}OOH$).
Elemental analysis: $C_{106}H_{48}O_{10}$ (M_w=1481.54): calcd., %: C 85.94, H 3.27; found, %: C 85.86, H 3.44.

A1d. ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 0.86 (t, 3H, *J* = 6.9 Hz), 1.34 – 1.43 (m, 2H), 2.44 (t, 2H, *J* = 7.6 Hz), 2.53 – 2.59 (m, 8H), 2.69 (t, 2H, *J* = 7.3 Hz), 2.79 – 2.90 (m, 8H), 7.03 (d, 2H, *J* = 8.2 Hz), 7.15 (d, 2H, *J* = 8.1 Hz), 7.19 – 7.26 (m, 8H), 7.52 (d, 4H, *J* = 8.1 Hz), 7.62 (d, 4H, *J* = 8.1 Hz).
^{13}C NMR (151 MHz, DMSO-d_6, δ, ppm): 9.79 ($CH_2\underline{C}H_3$), 30.02 ($\underline{C}H_2$), 30.31 ($\underline{C}H_2$), 30.41 ($\underline{C}H_2$), 33.87 ($\underline{C}H_2CH_3$), 35.10 ($\underline{C}H_2$), 35.44 ($\underline{C}H_2$), 35.70 ($\underline{C}H_2$), 58.41 ($\underline{C}_{sp3\ fullerene\ cage}$), 61.01 ($\underline{C}_{sp3\ fullerene\ cage}$), 63.24 ($\underline{C}_{sp3\ fullerene\ cage}$), 65.41 ($\underline{C}_{sp3\ fullerene\ cage}$), 127.85, 128.59, 129.19, 129.52, 130.55, 135.96, 137.65, 140.37, 140.52, 141.38, 142.51, 143.77, 143.88, 143.99, 144.01, 144.23, 144.47, 144.50, 144.72, 145.40, 145.74, 146.98, 147.23, 147.26, 147.76, 147.95, 148.03, 148.18, 148.33, 148.39, 148.57, 148.69, 151.76, 153.71, 156.04, 157.20, 174.16 ($\underline{C}OOH$), 174.19 ($\underline{C}OOH$).
Elemental analysis: $C_{107}H_{50}O_{10}$ (M_w=1495.57): calcd., %: C 85.93, H 3.37; found, %: C 85.74, H 3.50.

A1e. ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 0.55 (d, 6H, *J* = 6.4 Hz), 2.35 – 2.38 (m, 1H), 2.46 – 2.54 (m, 6H), 2.62 (t, 4H, *J* = 7.6 Hz), 2.75 (t, 2H, *J* = 7.4 Hz), 2.81 (t, 4H, *J* = 7.4 Hz), 2.93 (t, 4H, *J* = 7.3 Hz), 7.14 (d, 2H, *J* = 8.3 Hz), 7.18 (d, 4H, *J* = 8.3 Hz), 7.35 (d, 4H, *J* = 8.3 Hz), 7.50 – 7.57 (m, 6H), 7.86 (d, 4H, *J* = 8.2 Hz), 12.16 (br. s, 5H).
^{13}C NMR (126 MHz, DMSO-d_6, δ, ppm): 22.67 ($CH(\underline{C}H_3)_2$), 30.12 ($\underline{C}H_2$), 30.25 ($\underline{C}H_2$), 30.47 ($\underline{C}H_2$), 35.20 ($\underline{C}H(CH_3)_2$), 35.29 ($\underline{C}H_2$), 35.42 ($\underline{C}H_2$), 35.75 ($\underline{C}H_2$), 58.29 ($\underline{C}_{sp3\ fullerene\ cage}$), 61.39 ($\underline{C}_{sp3\ fullerene\ cage}$), 63.14 ($\underline{C}_{sp3\ fullerene\ cage}$), 71.55 ($\underline{C}_{sp3\ fullerene\ cage}$), 128.30, 128.54, 128.69, 129.32, 131.47, 137.39, 137.83, 140.37, 141.21, 141.52, 142.09, 142.43, 143.19, 143.33, 143.83, 143.93, 144.04, 144.12, 144.27, 144.45, 144.52, 145.41, 145.80, 147.14, 147.30, 147.47, 147.86, 147.92, 148.08, 148.20, 148.21, 148.41, 148.49, 148.62, 148.81, 150.46, 155.26, 157.75, 158.59, 174.15 ($\underline{C}OOH$), 174.19 ($\underline{C}OOH$).
Elemental analysis: $C_{108}H_{52}O_{10}$ (M_w=1509.59): calcd., %: C 85.93, H 3.47; found, %: C 85.69, H 3.52.

A1f. ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 0.57 (t, 3H, *J* = 7.2 Hz), 0.66-0.81 (m, 2H), 1.31– 1.47 (m, 4H), 2.43 (t, 2H, *J* = 7.7 Hz), 2.52– 2.60 (m, 8H), 2.72 (t, 2H, *J* = 7.6 Hz), 2.80– 2.91 (m, 8H), 7.04 (d, 2H, *J* = 6.5 Hz), 7.13 – 7.25 (m, 10H), 7.52 (d, 4H, *J* = 7.9 Hz), 7.65 (d, 4H, *J* = 8.1 Hz).
^{13}C NMR (126 MHz, DMSO-d_6, δ, ppm): 14.44 ($\underline{C}H_3(CH_2)_3$), 22.36 ($CH_3(\underline{C}H_2)_3$), 27.57 ($CH_3(\underline{C}H_2)_3$), 30.07 ($\underline{C}H_2$), 30.32 ($\underline{C}H_2$), 30.43 ($\underline{C}H_2$), 35.23 ($\underline{C}H_2$), 35.52 ($\underline{C}H_2$), 35.83 ($\underline{C}H_2$), 40.67 ($CH_3(\underline{C}H_2)_3$), 58.34 ($\underline{C}_{sp3\ fullerene\ cage}$), 61.08 ($\underline{C}_{sp3\ fullerene\ cage}$), 63.23 ($\underline{C}_{sp3\ fullerene\ cage}$), 65.38 ($\underline{C}_{sp3\ fullerene\ cage}$), 128.00, 128.49, 128.62, 129.06, 129.35, 130.60, 136.05, 137.60, 140.42, 140.46, 141.39, 141.41, 142.14, 142.52, 143.83, 143.89, 144.00, 144.04, 144.23, 144.24, 144.41, 144.56, 144.72, 145.00, 145.52, 145.71, 146.96, 147.21, 147.25, 147.73, 147.94, 148.01, 148.15, 148.33, 148.38, 148.56, 148.68, 151.81, 153.90, 156.91, 157.19, 174.12 ($\underline{C}$OOH), 174.16 ($\underline{C}$OOH).
Elemental analysis: $C_{109}H_{54}O_{10}$ (M_w=1523.62): calcd., %: C 85.93, H 3.57; found, %: C 86.04, H 3.66.

A2a. ^{1}H NMR (500 MHz, DMSO-d_6, acetone-d_6, CS_2, δ, ppm): 2.89– 3.10 (m, 5H), 3.36 – 3.56 (m, 5H), 4.21– 4.52 (m, 5H), 7.04– 7.35 (m, 4H), 7.53– 7.64 (m, 4H), 7.65– 7.91 (m, 8H), 7.92– 8.22 (m, 4H).
^{13}C NMR (126 MHz, DMSO-d_6, acetone-d_6, CS_2, δ, ppm): 37.97 ($\underline{C}H_2$), 37.99 ($\underline{C}H_2$), 38.09 ($\underline{C}H_2$), 38.19 ($\underline{C}H_2$), 38.23 ($\underline{C}H_2$), 38.29 ($\underline{C}H_2$), 47.14 ($\underline{C}$H), 47.43 ($\underline{C}$H), 58.20 ($\underline{C}_{sp3\ fullerene\ cage}$), 61.57 ($\underline{C}_{sp3\ fullerene\ cage}$), 71.91 ($\underline{C}_{sp3\ fullerene\ cage}$), 79.11 ($\underline{C}_{sp3\ fullerene\ cage}$-Cl), 125.26, 125.92, 125.95, 128.84, 128.93, 129.12, 129.24, 129.74, 131.56, 137.62, 138.42, 138.86, 139.40, 139.59, 143.28, 143.64, 144.23, 144.41, 144.45, 144.83, 144.96, 145.95, 146.23, 147.69, 147.99, 148.23, 148.35, 148.53, 148.60, 148.90, 148.99, 149.05, 149.17, 149.27, 152.46, 156.46, 159.84, 173.25 ($\underline{C}$OOH), 173.39 ($\underline{C}$OOH), 173.60 ($\underline{C}$OOH), 174.54 ($\underline{C}$OOH), 174.96 ($\underline{C}$OOH).
Elemental analysis: $C_{110}H_{45}ClO_{20}$ (M_w=1722.00): calcd., %: C 76.73, H 2.63; found, %: C 76.52, H 2.85.

A2b. ^{1}H NMR (500 MHz, DMSO-d_6, acetone-d_6, CS_2, δ, ppm): 2.31 – 2.66 (m, 5H), 2.85– 3.07 (m, 5H), 3.71 – 4.25 (m, 5H), 5.68 (s, 1H), 6.69 (d, 1H, *J* = 8.4 Hz), 6.92– 7.44 (m, 12 H), 7.49 –7.89 (m, 6H).
^{13}C NMR (126 MHz, DMSO-d_6, acetone-d_6, CS_2, δ, ppm): 37.46 ($\underline{C}H_2$), 37.53 ($\underline{C}H_2$), 37.56 ($\underline{C}H_2$), 37.63 ($\underline{C}H_2$), 46.82 ($\underline{C}$H), 46.92 ($\underline{C}$H), 46.99 ($\underline{C}$H), 58.62 ($\underline{C}_{sp3\ fullerene\ cage}$), 58.83 ($\underline{C}_{sp3\ fullerene\ cage}$), 60.87 ($\underline{C}_{sp3\ fullerene\ cage}$), 62.85 ($\underline{C}_{sp3\ fullerene\ cage}$-H), 128.35, 128.49, 128.55, 128.59, 128.75, 138.15, 138.85, 139.52, 143.10, 143.95, 144.07, 144.12, 144.24, 144.35, 144.43, 144.78, 145.70, 145.90, 147.12, 147.23, 147.72, 147.90, 148.04, 148.11, 148.24, 148.31, 148.37, 148.63, 148.67, 148.75, 148.84, 156.68, 157.07, 172.74 ($\underline{C}$OOH), 172.81 ($\underline{C}$OOH), 174.09 ($\underline{C}$OOH).
Elemental analysis: $C_{110}H_{46}O_{20}$ (M_w=1687.56): calcd., %: C 78.29, H 2.75; found, %: C 78.15, H 3.02.

A2c. ^{1}H NMR (600 MHz, acetone-d_6, CS_2, δ, ppm): 1.46 – 1.54 (m, 3H), 2.39 – 2.52 (m, 1H), 2.53 – 2.75 (m, 4H), 2.90 – 3.00 (m, 1H), 3.01 – 3.17 (m, 4H), 6.97 – 7.19 (m, 4H), 7.21 – 7.46 (m, 8H), 7.49 – 7.96 (m, 8H).
^{13}C NMR (151 MHz, acetone-d_6, CS_2, δ, ppm): 34.29 ($\underline{C}H_3$, cage-boned), 37.60 ($\underline{C}H_2$), 37.65 ($\underline{C}H_2$), 37.78 ($\underline{C}H_2$), 37.82 ($\underline{C}H_2$), 37.86 ($\underline{C}H_2$), 47.02 ($\underline{C}$H), 47.22 ($\underline{C}$H), 47.27 ($\underline{C}$H), 58.51 ($\underline{C}_{sp3\ fullerene\ cage}$), 61.55 ($\underline{C}_{sp3\ fullerene\ cage}$), 62.89 ($\underline{C}_{sp3\ fullerene\ cage}$), 62.94 ($\underline{C}_{sp3\ fullerene\ cage}$), 128.98, 129.12, 129.15, 129.39,

129.42, 129.55, 137.29, 139.06, 142.04, 143.50, 144.02, 144.62, 144.65, 144.67, 144.72, 144.77, 144.98, 145.13, 145.14, 145.60, 145.63, 145.66, 146.28, 146.31, 146.46, 146.49, 147.77, 147.98, 148.02, 148.50, 148.79, 148.87, 149.01, 149.15, 149.27, 149.43, 172.77 (COOH), 172.85 (COOH), 172.86 (COOH), 172.95 (COOH), 174.08 (COOH), 174.13 (COOH), 174.22 (COOH).

Elemental analysis: $C_{111}H_{48}O_{20}$ (M_w=1701.59): calcd., %: C 78.35, H 2.84; found, %: C 78.13, H 3.08.

A2d. ^{1}H NMR (500 MHz, DMSO-d_6, acetone-d_6, CS_2, δ, ppm): 0.81 – 1.00 (m, 3H), 1.39-1.57 (m, 2H), 2.40 – 2.68 (m, 5H), 2.82 – 3.08 (m, 5H), 3.75 – 4.04 (m, 5H), 6.96 – 7.41 (m, 12H), 7.50 – 7.94 (m, 8H).

^{13}C NMR (126 MHz, DMSO-d_6, acetone-d_6, CS_2, δ, ppm): 9.35 (CH_2CH_3), 33.69 (CH_2CH_3), 37.06 (CH_2), 37.23 (CH_2), 37.27 (CH_2), 46.20 (CH), 46.41 (CH), 46.48 (CH), 57.93 ($C_{sp3\ fullerene\ cage}$), 60.57 ($C_{sp3\ fullerene\ cage}$), 62.79 ($C_{sp3\ fullerene\ cage}$), 65.11 ($C_{sp3\ fullerene\ cage}$), 127.66, 128.29, 128.58, 130.42, 136.80, 137.75, 138.49, 138.73, 138.83, 138.85, 141.13, 142.15, 143.28, 143.51, 143.64, 143.85, 144.20, 144.94, 145.23, 146.60, 146.85, 146.88, 147.40, 147.59, 147.65, 147.81, 147.97, 148.03, 148.21, 148.33, 151.10, 153.14, 156.60, 172.55 (COOH), 173.61 (COOH), 173.75 (COOH), 173.77 (COOH), 173.82 (COOH).

Elemental analysis: $C_{112}H_{50}O_{20}$ (M_w=1715.61): calcd., %: C 78.41, H 2.94; found, %: C 78.31, H 3.22.

A2f. ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 0.45 – 0.54 (m, 3H), 0.61 – 0.71 (m, 2H), 1.26 – 1.35 (m, 2H), 1.46 – 1.59 (m, 2H), 2.56 – 2.67 (m, 5H), 2.83 – 3.07 (m, 5H), 3.79 – 4.11 (m, 5H), 7.09 – 7.018 (m, 4H), 7.59 – 7.64 (m, 8H), 7.74 (d, 4H, J = 7.6 Hz), 12.47 (s, 5H).

^{13}C NMR (126 MHz, DMSO-d_6, δ, ppm): 14.22 ($CH_3(CH_2)_3$), 22.39 ($CH_3(CH_2)_3$), 28.16 ($CH_3(CH_2)_3$), 37.78, 37.80, 37.83, 37.98, 38.04, 38.10, 39.39, 39.55, 39.72, 39.89, 39.98, 40.05, 40.14, 40.22, 40.31, 40.39, 40.48, 40.73, 46.75, 46.92, 47.10, 58.21 ($C_{sp3\ fullerene\ cage}$), 61.08 ($C_{sp3\ fullerene\ cage}$), 63.11 ($C_{sp3\ fullerene\ cage}$), 65.70 ($C_{sp3\ fullerene\ cage}$), 128.23, 128.66, 128.71, 128.88, 130.86, 137.24, 138.37, 138.60, 139.33, 139.51, 141.51, 142.55, 143.86, 143.92, 143.96, 144.04, 144.18, 144.27, 144.61, 145.49, 145.69, 147.00, 147.24, 147.28, 147.79, 148.00, 148.03, 148.20, 148.39, 148.63, 148.75, 151.54, 153.93, 157.14, 173.02 (COOH), 173.05 (COOH), 173.07 (COOH), 173.11 (COOH), 174.19 (COOH), 174.32 (COOH), 174.34 (COOH), 174.41 (COOH), 174.45 (COOH).

Elemental analysis: $C_{114}H_{54}O_{20}$ (M_w=1743.67): calcd., %: C 78.53, H 3.12; found, %: C 78.29, H 3.16.

A3a. ^{1}H NMR (500 MHz, DMSO-d_6, acetone-d_6, CS_2, δ, ppm): 2.40 – 2.77 (m, 20H), 3.44 – 3.61 (m, 5H), 7.06 – 7.18 (m, 4H), 7.23 – 7.35 (m, 8H), 7.41 – 7.49 (m, 4H), 7.68 – 7.80 (m, 4H).

^{13}C NMR (126 MHz, DMSO-d_6, acetone-d_6, CS_2, δ, ppm): 37.60 (CH), 37.97 (CH), 38.02 (CH), 38.08 (CH), 38.14 (CH), 58.09 ($C_{sp3\ fullerene\ cage}$), 60.64 ($C_{sp3\ fullerene\ cage}$), 63.29 ($C_{sp3\ fullerene\ cage}$), 76.26 ($C_{sp3\ fullerene\ cage}$-Cl), 127.54, 127.73, 128.19, 128.25, 128.30, 128.38, 128.58, 128.65, 129.29, 130.10, 135.00, 136.37, 137.19, 141.70, 142.90, 143.12, 143.54, 143.75, 143.84, 144.05, 144.10, 144.17, 144.22, 144.31, 144.43, 144.56, 144.83, 145.54, 145.73, 145.90, 146.09, 146.75, 146.90, 147.01, 147.09, 147.22, 147.31, 147.44, 147.72, 147.91, 148.02, 148.14, 148.25, 148.35, 148.49, 148.63, 148.69, 148.81, 150.94, 151.21, 153.60, 156.97, 173.17 (COOH). * signals of the CH_2 groups are overlapped with DMSO-d_6 signals.

Elemental analysis: $C_{115}H_{55}ClO_{20}$ (M_w=1792.14): calcd., %: C 77.07, H 3.09; found, %: C 76.83, H 3.25.

A3b. ^{1}H NMR (500 MHz, DMSO-d_6, acetone-d_6, CS_2, δ, ppm): 2.39 – 2.76 (m, 20H), 3.46 – 3.64 (m, 5H), 5.49 (s, 1H), 7.07 – 7.25 (m, 8H), 7.30 (d, 4H, *J* = 8.3 Hz), 7.46 (d, 4H, *J* = 8.3 Hz), 7.71 (d, 4H, *J* = 8.3 Hz).

^{13}C NMR (126 MHz, DMSO-d_6, acetone-d_6, CS_2,δ, ppm): 37.69 (CH), 37.97 (CH), 38.08 (CH), 58.72 ($C_{sp3\ fullerene\ cage}$), 58.79 ($C_{sp3\ fullerene\ cage}$), 60.88 ($C_{sp3\ fullerene\ cage}$), 62.72 ($C_{sp3\ fullerene\ cage}$-H), 127.71, 128.17, 128.23, 128.30, 128.43, 128.54, 128.64, 129.25, 137.19, 137.71, 143.09, 143.27, 143.30, 143.60, 143.81, 143.98, 144.01, 144.07, 144.20, 144.30, 144.83, 145.73, 145.90, 146.09, 146.75, 146.89, 147.08, 147.21, 147.71, 148.00, 148.21, 148.34, 148.36, 148.58, 148.64, 152.35, 152.73, 152.86, 156.72, 173.16 (COOH), 173.18 (COOH). * signals of the CH_2 groups are overlapped with DMSO-d_6 signals.

Elemental analysis: $C_{115}H_{56}O_{20}$ (M_w=1757.69): calcd., %: C 78.58, H 3.21; found, %: C 78.30, H 3.44.

A3d. ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 0.77 (t, 3H, *J* = 6.9 Hz), 1.44 – 1.53 (m, 2H), 2.35 – 2.79 (m, 20H), 3.43 – 3.59 (m, 5H), 7.00 – 7.20 (m, 6H), 7.25 (d, 4H, *J* = 8.0 Hz), 7.29 (d, 4H, *J* = 8.0 Hz), 7.54 (d, 6H, *J* = 7.6 Hz).

^{13}C NMR (126 MHz, DMSO-d_6, δ, ppm): 9.66 (CH_2CH_3), 33.95 (CH_2CH_3), 37.60 (CH), 38.05 (CH), 38.29 (CH), 58.53 ($C_{sp3\ fullerene\ cage}$), 61.12 ($C_{sp3\ fullerene\ cage}$), 63.34 ($C_{sp3\ fullerene\ cage}$), 65.33 ($C_{sp3\ fullerene\ cage}$), 127.75, 127.86, 128.46, 128.72, 130.56, 136.26, 137.79, 140.85, 142.55, 143.13, 143.84, 143.89, 143.92, 143.97, 144.09, 144.29, 144.56, 144.74, 145.44, 145.82, 147.04, 147.32, 147.85, 147.91, 148.07, 148.24, 148.45, 148.65, 148.78, 151.63, 154.00, 155.75, 157.39, 173.31 (COOH). * signals of the CH_2 groups are overlapped with DMSO-d_6 signals.

Elemental analysis: $C_{117}H_{60}O_{20}$ (M_w=1785.75): calcd., %: C 78.69, H 3.39; found, %: C 78.46, H 3.51.

A4a. ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 1.18 – 1.51 (m, 15H), 3.51 – 3.91 (m, 5H), 6.97 – 7.21 (m, 4H), 7.22 – 7.43 (m, 8H), 7.55 – 7.71 (m, 4H), 7.75 – 7.94 (m, 4H).

^{13}C NMR (126 MHz, DMSO-d_6, δ, ppm): 18.80 (CH_3), 18.84 (CH_3), 19.01 (CH_3), 44.42 (CH), 44.69 (CH), 44.72 (CH), 57.81 ($C_{sp3\ fullerene\ cage}$), 60.56 ($C_{sp3\ fullerene\ cage}$), 63.16 ($C_{sp3\ fullerene\ cage}$), 76.29 ($C_{sp3\ fullerene\ cage}$-Cl), 128.43, 128.55, 128.65, 140.95, 141.12, 141.69, 142.03, 142.82, 143.51, 143.78, 144.10, 144.45, 145.47, 147.24, 147.35, 147.82, 148.12, 148.19, 148.42, 148.60, 148.67, 148.76, 150.60, 156.85, 174.48 (COOH), 174.57 (COOH), 175.47 (COOH), 175.63 (COOH).

Elemental analysis: $C_{105}H_{45}ClO_{10}$ (M_w=1501.96): calcd., %: C 83.97, H 3.02; found, %: C 83.86, H 3.23.

A4c. ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 1.26 (d, 3H, *J* = 7.2 Hz), 1.41 – 1.33 (m, 12H), 1.54 (s, 3H), 3.54 – 3.62 (m, 1H), 3.67 – 3.78 (m, 4H), 6.99– 7.16 (m, 4H), 7.23– 7.39 (m, 8H), 7.69 – 7.84 (m, 8H).

^{13}C NMR (126 MHz, DMSO-d_6, δ, ppm): 18.63 (CH_3), 18.79 (CH_3), 18.83 (CH_3), 18.95 (CH_3), 19.12 (CH_3), 34.54 (CH_3, cage-bonded), 44.43 (CH), 44.65 (CH), 44.73 (CH), 57.79 ($C_{sp3\ fullerene\ cage}$), 60.92 ($C_{sp3\ fullerene\ cage}$), 62.24 ($C_{sp3\ fullerene\ cage}$), 62.33 ($C_{sp3\ fullerene\ cage}$), 128.28, 128.32, 128.53, 128.67, 128.73, 136.02, 137.59, 140.68, 141.10, 141.67, 142.64, 143.91, 143.97, 144.09, 144.15, 144.28, 144.67, 144.80, 145.70,

145.98, 147.06, 147.28, 147.69, 147.77, 148.06, 148.10, 148.28, 148.41, 148.49, 148.68, 148.73, 152.11, 153.44, 157.39, 160.62, 175.48 (COOH), 175.67 (COOH).

Elemental analysis: $C_{106}H_{48}O_{10}$ (M_w=1481.54): calcd., %: C 85.94, H 3.27; found, %: C 85.90, H 3.45.

A4d. ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm): 0.93 (t, 3H, *J* = 7.0 Hz), 1.28 (d, 3H, *J* = 7.1 Hz), 1.35 – 1.44 (m, 12H), 1.45 – 1.57 (m, 2H), 3.57 – 3.66 (m, 1H), 3.68 – 3.82 (m, 4H), 7.01 – 7.20 (m, 4H), 7.20 – 7.36 (m, 8H), 7.55 – 7.69 (m, 4H), 7.70 – 7.80 (m, 4H).

^{13}C NMR (126 MHz, DMSO-d_6, δ, ppm): 9.79 (CH_2CH_3), 18.67 (CH_3), 18.89 (CH_3), 18.92 (CH_3), 18.99 (CH_3), 19.09 (CH_3), 34.20 (CH_2CH_3), 44.47 (CH), 44.62 (CH), 44.69 (CH), 58.39 ($C_{sp3\ fullerene\ cage}$), 61.06 ($C_{sp3\ fullerene\ cage}$), 63.28 ($C_{sp3\ fullerene\ cage}$), 65.57 ($C_{sp3\ fullerene\ cage}$), 128.02, 128.04, 128.40, 128.63, 128.68, 128.73, 129.37, 136.91, 137.82, 138.61, 138.71, 140.71, 141.75, 141.85, 141.89, 142.58, 143.95, 144.08, 144.31, 144.70, 145.74, 147.06, 147.31, 147.34, 147.85, 148.05, 148.10, 148.25, 148.43, 148.48, 148.67, 148.79, 151.70, 157.16, 175.51 (COOH), 175.67 (COOH).

Elemental analysis: $C_{107}H_{50}O_{10}$ (M_w=1495.57): calcd., %: C 85.93, H 3.37; found, %: C 85.68, H 3.52.

DFT study of the mechanism of the inversed Arbuzov reaction

To understand the mechanism of the reversed Arbuzov reaction the fullerene derivative $C_{60}Ph_5Cl$, which does not contain any substituents on the phenyl groups (**Fig. T1**), and the trialkyl phosphite $P(OMe)_3$ were used. Quantum-chemical calculations using density functional theory PBE (J.P. Perdew *et al, Phys. Rev. Lett.,* **1996**, *77*, 3865) were carried out using the extended basis H: (5s1p) / [3s1p], C, O, P, Cl: (5s5p2d) / [3s3p2d] for SBK pseudopotential (W.J. Stevens, *et al., J. Chem. Phys.,* **1984**, *81*, 6026). Calculations were performed using the "PRIRODA" program package (D.N. Laikov, *Chem. Phys. Lett.,* **1997**, *281*, 151) at the Joint Supercomputer Center of the Russian Academy of Sciences. The relative energies were calculated taking into account zero point energy (ZPE) at zero temperature. The states transition had only one vibration with imaginary frequency. Electronic density distribution was analyzed in terms of Hirshfeld's atomic charges (F. L. Hirshfeld, *Theor. Chim. Acta*, **1977**, *44*, 129).

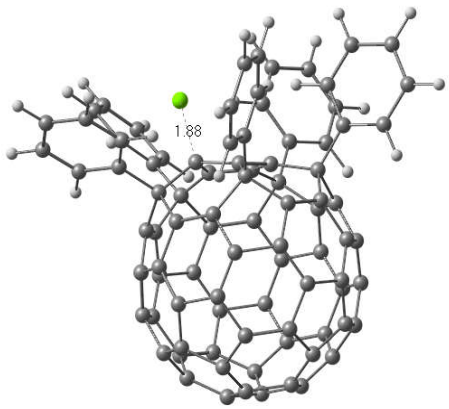


Fig. T1. The calculated structure of $C_{60}Ph_5Cl$

Prereactional Van der Waals complex (**Fig. T2**) is formed between the reagents with a small energy gain of 1.4 kcal/mol. In this adduct with Cl-P distance equal to 3.40Å, a partial transfer of the electron density occurs and the fragment $P(OMe)_3$ acquires a charge +0.044. Dipole moment of the adduct (5.0 Debye) is much less than the sum of the coaxial dipole moments of the $C_{60}Ph_5Cl$ and $P(OMe)_3$, equal to 6.1 and 1.6 Debye, respectively.

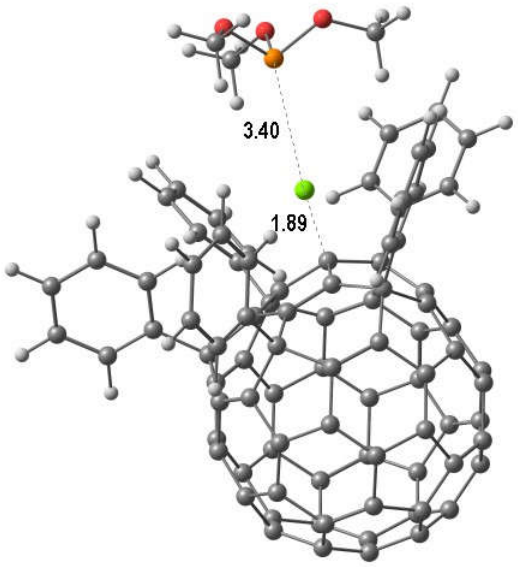


Fig. T2. The calculated structure of the adduct of $C_{60}Ph_5Cl$ and $P(OMe)_3$

The electron affinity of the $C_{60}Ph_5Cl$ at fixed geometry is 2.5 eV. However, the radical anion $C_{60}Ph_5Cl^{\bullet-}$ is unstable due to the elimination of the Cl- ion. In this case, a weakly bound complex is formed, in which Cl- ion located approximately above the center of the five-membered cycle of the radical $C_{60}Ph_5^{\bullet}$ with C-Cl distances of 3.75 ± -0.08 Å (**Fig. T3**).

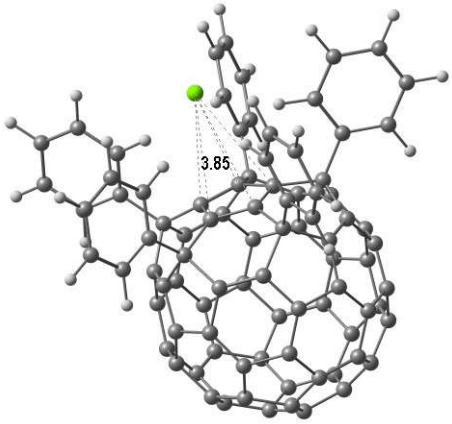


Fig. T3. The calculated structure of the complex of $C_{60}Ph_5^{\bullet}$ and Cl^-

The charge on the Cl atom and the spin density are equal to -0.44 and 0.14, respectively. Therefore, the total electron transfer in the adduct $C_{60}Ph_5Cl...P(OMe)_3$ is associated with the elimination of the Cl^- ion and attaching of this particle to the radical cation $P(OMe)_3^{\bullet+}$. Finally, the radical pair $C_{60}Ph_5^{\bullet}$ $ClP(OMe)_3^{\bullet}$ is formed. Its structure in the triplet state is shown in **Fig. T4**. The distances C-P and C-Cl are equal to ~

6.5 and 5.6 Å, respectively. These distances significantly exceed the sum of Van der Waals radii of the atoms. Due to the weak overlap of the electron shells, each of the ions has a spin density of ~1. Formation of a radical pair leads to increase in the energy of the system by 7.5 kcal/mol with respect to the initial adduct.

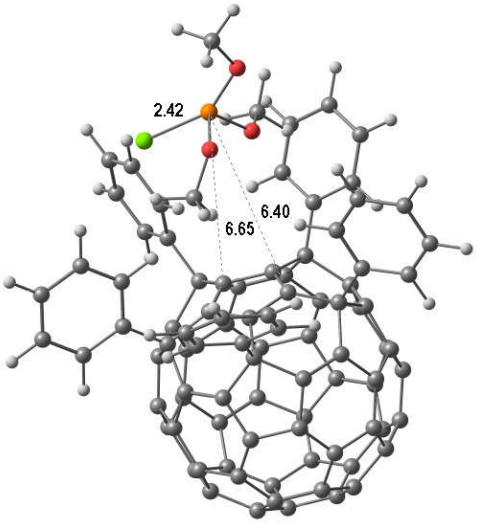


Fig. T4. The calculated structure of the radical pair $C_{60}Ph_5^{\bullet}$…$ClP(OMe)_3^{\bullet}$.

The affinity to the electron of $C_{60}Ph_5^{\bullet}$ (3.2 eV) and the ionization potential of $ClP(OMe)_3^{\bullet}$ (5.7 eV) is more favorable for electron transfer than the affinity to the electron of $C_{60}Ph_5Cl$ (2.4 eV) and the ionization potential of $P(OMe)_3$ (7.9 eV). At the second electron transfer, ion pair $C_{60}Ph_5^{-}$ $ClP(OMe)_3^{+}$ is formed with an energy increase of 4.8 kcal/mol. Structure of this ion pair is shown in **Fig. T5**. The distance P-C (5.21 Å) is practically the same as in the initial adduct. The $ClP(OMe)_3$ fragment has a charge of +0.72. Taking into account the dipole moment of the ion pair (24.8 Debye), it is possible to estimate the dipole length of 8.2 Å, which is comparable to the distance between the center of the fullerene framework and the P atom (7.5 Å).

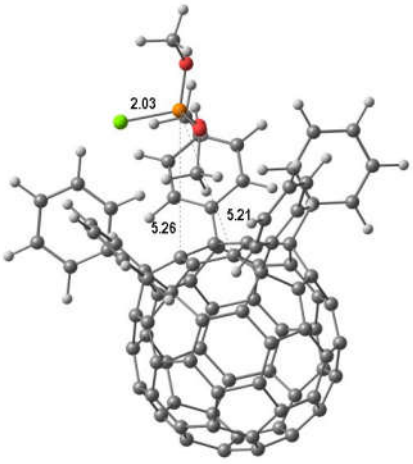


Fig. T5 The calculated structure of the ion pair $C_{60}Ph_5^{-}$…$ClP(OMe)_3^{+}$

In the ion pair, the methyl group is close to the fullerene framework (the distance C-C is 3.26Å), and has a charge of +0.16. This facilitates the transfer of Me^+ carbocation to the $C_{60}Ph_5^-$ anion to form the product of the reversed Arbuzov reaction with quite insignificant energy barrier (1.3 kcal / mol). The structure of the transition state is shown in **Fig. T6**. The transition state has a dipole moment of 20.4 Debye, and the charge on the methyl group decreases slightly to +0.12.

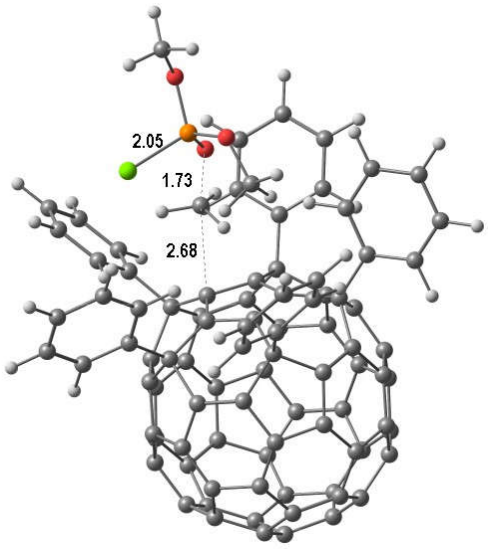


Fig. T6. The calculated structure of the transition state of methyl transfer

The transition state is very early, the distance C(Me)-C (2.68 Å) is much longer than the length of a single C-C bond. The energy gain (55.5 kcal/mol) of the ion pair transformation into the post-reaction complex $C_{60}Ph_5Me…OPCl(OMe)_2$ is large (**Fig. T7**). The binding energy of $C_{60}Ph_5Me$ and $OPCl(OMe)_2$ is equal to 5.1 kcal / mol.

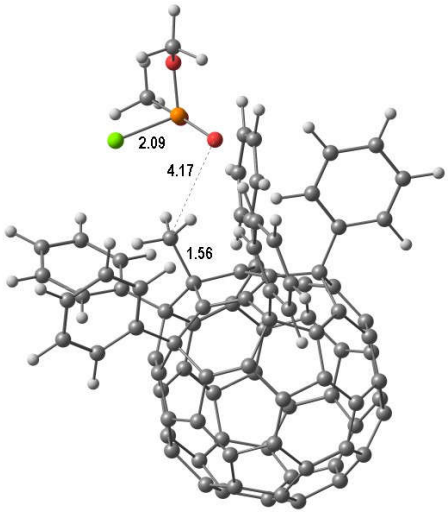


Fig. T7. The calculated structure of the post-reaction complex $C_{60}Ph_5Me…OPCl(OMe)_2$

The radical pair in the singlet state is unstable due to the possibility of recombination with the formation of an intermediate product with a P-C bond (**Fig. T8**). Product with a P-C bond has higher energy (by 4.7 kcal/mol) than the energy of triplet radical pair. This energy ratio is caused by a decrease of the energy of the triplet state in the presence of open shells due to the exchange interactions. Cleavage of MeCl and formation of the reaction product of Arbuzov reaction $C_{60}Ph_5$-$PO(OMe)_2$ is energetically favorable.

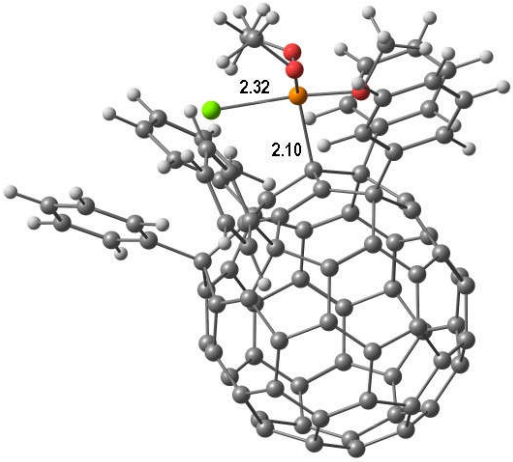


Fig. T8. The calculated structure of intermediate product $C_{60}Ph_5$-$PCl(OMe)_3$

However, the direct cleavage of MeCl from $C_{60}Ph_5$-$PO(OMe)_2$ occurs with formation of a four-term transition state and therefore has a high activation energy. The model calculation for the simplified $RPCl(OMe)_3$ system, where the fullerene derivative residue replaced with the R=Me group, yields a value of 32.2 kcal/mol for the activation energy. The structure of the transition state is shown in **Fig. T9**.

On the other hand, heterolytic cleavage of the P-Cl bond resulting in the formation of contact ion pair $RP(OMe)_3^+$ Cl^- (See **Fig. T10**) with P-Cl distance equal to 3.76 Å requires a small energy expenses of 3.9 kcal/mol. Closeness of the Cl^- ion and a positively charged methyl group creates conditions for nucleophilic attack and formation of the final product of the Arbuzov reaction.

The activation barrier along this reaction path is considerably less and equal to 19.4 kcal/mol. The structure of the transition state is shown in **Fig. T11**. For the favorable orientation of the ion Cl- the P-Cl distance increases to 4.9 Å. In the transition state the charges of the Cl atom and CH_3 fragment are equal to -0.56 and +0.10, what leads to the appearance of notable dipole moment of 12.3 Debye. If there are no steric hindrances for solvate interactions in the solution, a decrease in the energy barrier is expected.

In the intermediate product $C_{60}Ph_5$-$PCl(OMe)_3$ short Van der Waals contacts of the Cl atom with H and C atoms (2.7 and 3.9 Å) create prohibition for a significant increase in the P-Cl distance required for heterolytic cleavage of the P-Cl bond. Thus, steric hindrances from the phenyl substituents surrounding the chlorine atom induce a nonclassical course of the Arbuzov reaction.

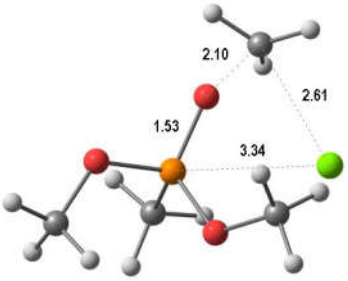


Fig. T9. The calculated structure of a four-term transition state state of CH_3^+ transfer to Cl^-

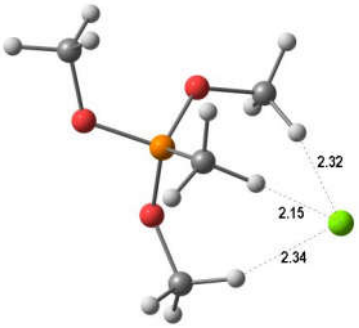


Fig. T10. The calculated structure of the contact ion pair $RP(OMe)_3^+$ Cl^-

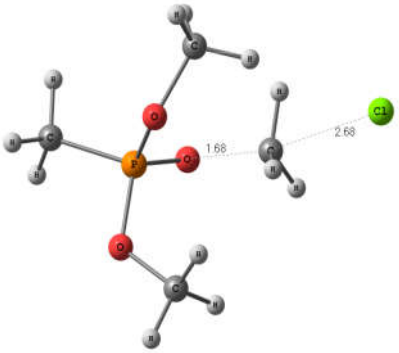


Fig. T11. The calculated structure of the transition state of CH_3^+ transfer

The total energy scheme of the transformations considered is shown in **Fig. T12**

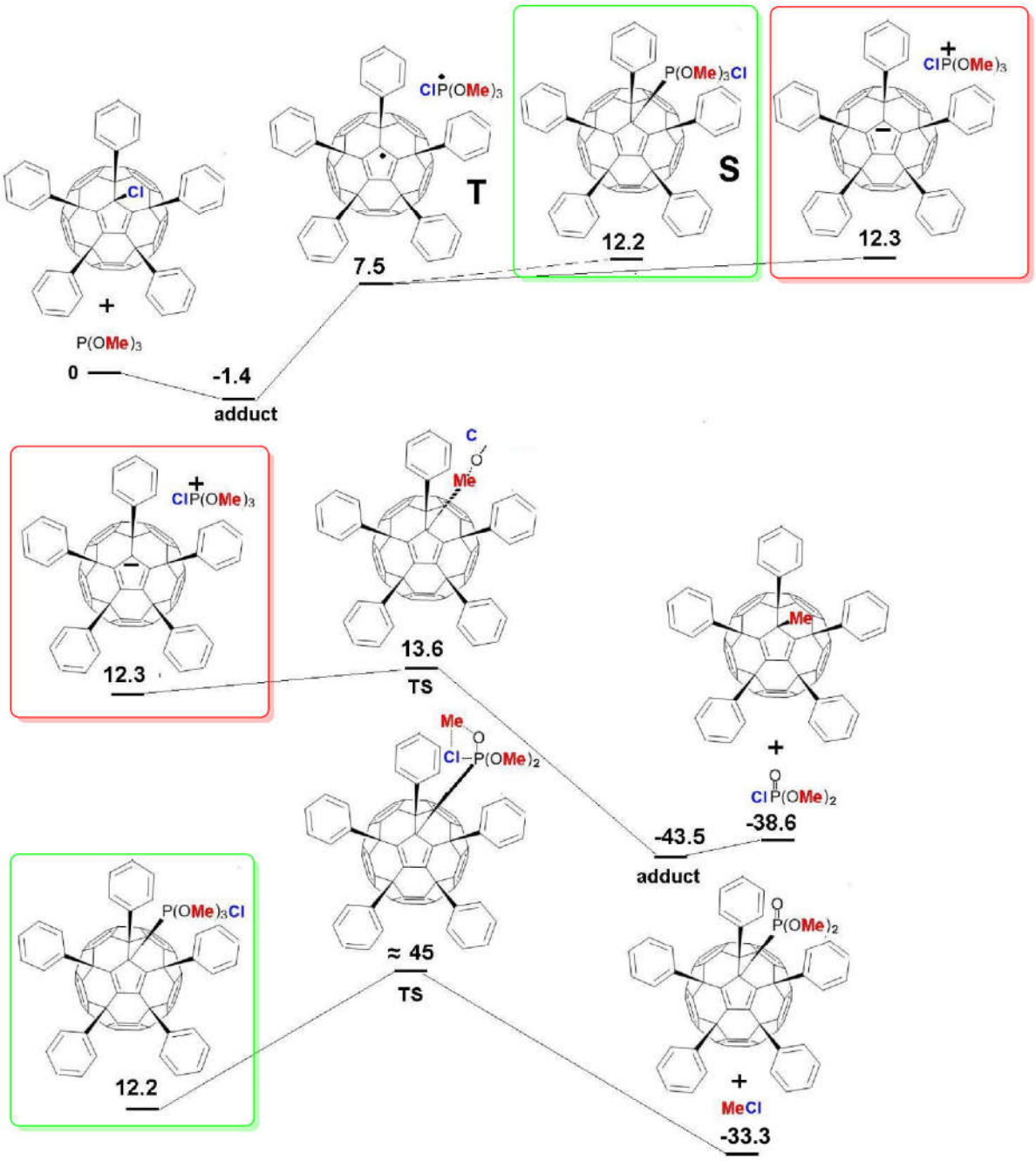


Fig. T12. The total energy scheme of the reaction between $C_{60}Ph_5Cl$ and $P(OMe)_3$

Biological assays

Antiviral activity assays

Activity of the fullerene derivatives against two herpes viruses (Herpes Simplex virus type 1 (HSV1) and human cytomegalovirus (HCMV)) was investigated using standard *in vitro* assays. HSV-sensitive Vero cells and CMV-sensitive human embryo lung fibroblasts (HELF) were used to evaluate the cytotoxicity of the compounds. Antiviral activity was evaluated by monitoring the ability of the compound to inhibit a plaque formation (plaque reduction test) in the cells infected with corresponding viruses. Selectivity indices (SI) were calculated as CC_{50}/EC_{50} (CC_{50} - concentration of the compound reducing the viability of the cells by 50% within 1 (HSV1) or 3 (HCMV) days after its addition to the culture medium, EC_{50} - concentration of compound providing the 50% inhibition of the plaque-forming activity). A detailed description of the general experimental procedures (cytotoxicity and antiviral assays) is provided in the previous publication (N. E. Fedorova, R.R. Klimova, Yu. A. Tulenev, E.V. Chichev, A. B. Kornev, P. A. Troshin and A.A. Kushch, *Mendeleev Commun.*, **2012**, 22, 254–256).

Activity of the fullerene derivatives against influenza viruses (Influenza A/H1N1 A/Ned/378/05, Influenza A/H3N2 A/HK/7/87, and Influenza B B/Ned/537/05) was investigated using standard *in vitro* assays. MDCK (Madin Darby canine kidney cells) were used to evaluate the cytotoxicity and antiviral activity of the compounds. Details were reported previously (A. B. Kornev, A. S. Peregudov, V. M. Martynenko, J. Balzarini, B. Hoorelbeke, P. A. Troshin, *Chem. Commun*., **2011**, *47*, 8298–8300).

Activity of the fullerene derivatives against HIV-1 (NL4.3WT and BaL) viruses was investigated using standard *in vitro* assays. TZM-bl cell line was used to evaluate the cytotoxicity and antiviral activity of the compounds (O. A. Troshina, P. A. Troshin, A. S. Peregudov, V. I. Kozlovskiy, J. Balzarini and R. N. Lyubovskaya, *Org. Biomol. Chem.*, **2007**, *5*, 2783).

A detailed description of the general experimental procedures on ascertainment of the early effect (1 h) of two water-soluble fullerene derivatives **A2a** and **A2c** on human embryonic lung fibroblasts (HELFs) is provided in the previous publication (E. S. Ershova, V. A. Sergeeva, V. J. Tabakov, L. A. Kameneva, L. N. Porokhovnik, I. I. Voronov, S. V. Kostyuk, *Oxid. Med. Cell. Longev.*, **2016**, 9895245).

Table S1. Cytotoxicity of the fullerene derivatives in HELF cell line

Compound	**Cytotoxicity**		
	Acute cytotoxicity (AC_{50}), μg/mL	**Chronic cytotoxicity (CC_{50}), μg/mL**	**Maximal tolerated dose (MTD), μg/mL**
A1a	269	248	5
A1b	259	206	5
A1c	256	242	5
A1d	256	192	5
A1e	258	141	5
A1f	260	225	5
A2a	Precipitated in culture media		
A2b	46	34	1
A2c	Precipitated in culture media		
A2d	Precipitated in culture media		
A2f	Precipitated in culture media		
A3a	1329	1331	25
A3b	1575	1306	25
A3d	1288	1288	25
A4a	Precipitated in culture media		
A4c	861	846	25
A4d	863	846	25

Table S2. Cytotoxicity of the fullerene derivatives to the Vero cell culture

Compound	**Cytotoxicity**		
	Acute cytotoxicity (AC_{50}), μg/mL	**Chronic cytotoxicity (CC_{50}), μg/mL**	**Maximal tolerated dose (MTD), μg/mL**
A1a	393	300	50
A1b	536	500	100
A1c	388	200	10
A1d	300	200	10
A1e	200	100	10
A1f	125	100	10
A2a	Precipitated in culture media		
A2b	>100	100	10
A2c	Precipitated in culture media		
A2d	Precipitated in culture media		
A2f	Precipitated in culture media		
A3a	1270	400	100
A3b	>2000	2100	1000
A3d	690	658	125
A4a	Precipitated in culture media		
A4c	<250	<125	<125
A4d	<250	<125	<125

Table S3. Antiviral activity of the water-soluble fullerene derivatives against human cytomegalovirus (HCMV)

Compound	CC_{50}, µg/mL	Exposure scheme							
		Microbicidal[a]		Prophylactic[b]		Virulicide[c]		Therapeutic[d]	
		EC_{50}, µg/mL	SI	EC_{50}, µg/mL	SI	EC_{50}, µg/mL	SI	EC_{50}, µg/mL	SI
A1a	248	3	83	2.1	**118**	6.3	39	-	-
A1b	206	-	-	2.1	98	2.5	82	20	10
A1c	242	2	**121**	1.4	**173**	7	35	-	-
A1d	192	3.5	55	2.1	91	2.5	77	4.3	45
A1e	141	1.9	74	1.8	78	9.1	15	-	-
A1f	225	2.6	87	1.8	**125**	4.2	50	-	-
A2b	34	-	**-**	-	**-**	-	**-**	-	-
A3a	1331	8	**166**	42	32	10	**133**	-	-
A3b	1306	11	**118**	-	**-**	-	**-**	-	-
A3d	1288	-	**-**	-	**-**	-	**-**	23	56
A4c	846	-	-	-	**-**	25.6	33	10.2	83
A4d	846	60	14	-	**-**	16	53	9.7	87

[a] cells were incubated for 1 h with the compounds and then were infected with virus

[b] cells were incubated for 48 h with the compounds and then were infected with virus

[c] the mixture of virus and compounds was introduced into the cell culture for 1 hour, then washed and fresh culture medium was added

[d] cells were infected with the virus and after 1 hour the compounds were introduced

Table S4. Antiviral activity of the water-soluble fullerene derivatives against herpes simplex virus type 1 (HSV1)

Compound	CC_{50}, µg/mL	Exposure scheme							
		Microbicidal[a]		Prophylactic[b]		Virulicide[c]		Therapeutic[d]	
		EC_{50}, µg/mL	SI	EC_{50}, µg/mL	SI	EC_{50}, µg/mL	SI	EC_{50}, µg/mL	SI
A1a	300	3.4	88	-	-	5.5	54.5	17	18
A1b	500	4	**125**	-	-	-	-	17.2	29
A1c	200	-	-	19.7	10	-	-	-	-
A1d	200	-	-	-	-	6	33	12.4	16
A1e	100	5	20	72.4	1.3	5.5	18	-	-
A1f	100	-	-	-	-	-	-	-	-
A2b	100	9	11	-	-	28	3.5	22	4.5
A3a	400	4.4	91	-	-	-	-	15	27
A3b	2100	5.5	**382**	-	-	-	-	-	-
A3d	658	13.1	50	2.54	**259**	5.0	**133**	10	66
A4c	<125	3.2	<39	0.36	**<347**	n/i	n/i	-	-
A4d	<125	5.3	<24	-	**-**	1.9	<66	-	-

a, b, c, d - as in *the Table S3*

Table S5. Antiviral activity of the water-soluble fullerene derivatives against influenza viruses

Compound	Cytotoxicity, µM		Antiviral activity EC_{50}[c], µM					
			Influenza A/H1N1 A/Ned/378/05		Influenza A/H3N2 A/HK/7/87		Influenza B B/Ned/537/05	
	CC_{50}[a]	MCC[b]	visual CPE score	MTS	visual CPE score	MTS	visual CPE score	MTS
A1a	17.4	20	>100	>100	>100	>100	>100	>100
A1b	1.5	20	>100	>100	>100	>100	>100	>100
A1c	44	≥20	>100	>100	**0.4**	**0.5**	>100	>100
A1d	41.3	≥20	>100	>100	**0.2**	**0.1**	>100	>100
A2a	90.1	100	**2.1**	**0.5**	**0.5**	**0.9**	**1.8**	**0.8**
A2b	6.6	100	>100	>100	>100	>100	>100	>100
A2c	1	20	>100	>100	>100	>100	>100	>100
A2d	1.5	20	>100	>100	>100	>100	>100	>100
Zanamivir	>100	>100	0.08	0.01	9	3	0.2	0.01
Amandatin	>100	>100	>100	0.5	20	1.3	>100	>100

[a]CC_{50} - 50% cytotoxic concentration, as determined by measuring the cell viability with the colorimetric formazan-based MTS assay. [b]MCC - minimum compound concentration that causes a microscopically detectable alteration of normal cell morphology. [c]EC_{50} - 50% effective concentration, or concentration producing 50% inhibition of virus-induced cytopathic effect, as determined by visual scoring of the CPE, or by measuring the cell viability with the colorimetric formazan-based MTS assay.

Table S6. Antiviral activity of the water-soluble fullerene derivatives against human immunodeficiency virus (HIV-1)

Compound	**Cytotoxicity** CC_{50}[a] **, µM**	**Antiviral activity** EC_{50}[b] **, µM**	
	TZM-bl	**HIV-1 NL4.3**	**HIV-1 BaL**
A1a	35.9	2.81	3.61
A1b	43.0	3.02	12.30
A1c	40.6	3.18	3.41
A1d	40.9	4.20	4.29
A2a	51.0	0.99	13.66
A2b	**> 100**	**0.35**	8.37
A2c	**> 100**	**0.15**	12.70
A2d	**> 100**	**0.16**	7.78

[a]CC_{50} -50% cytotoxic concentration in TZM-bl cell cultures. [b]EC_{50} - 50% effective concentration or compound concentration required to inhibit HIV- induced cytopathogenic effect in TZM-bl cell cultures.

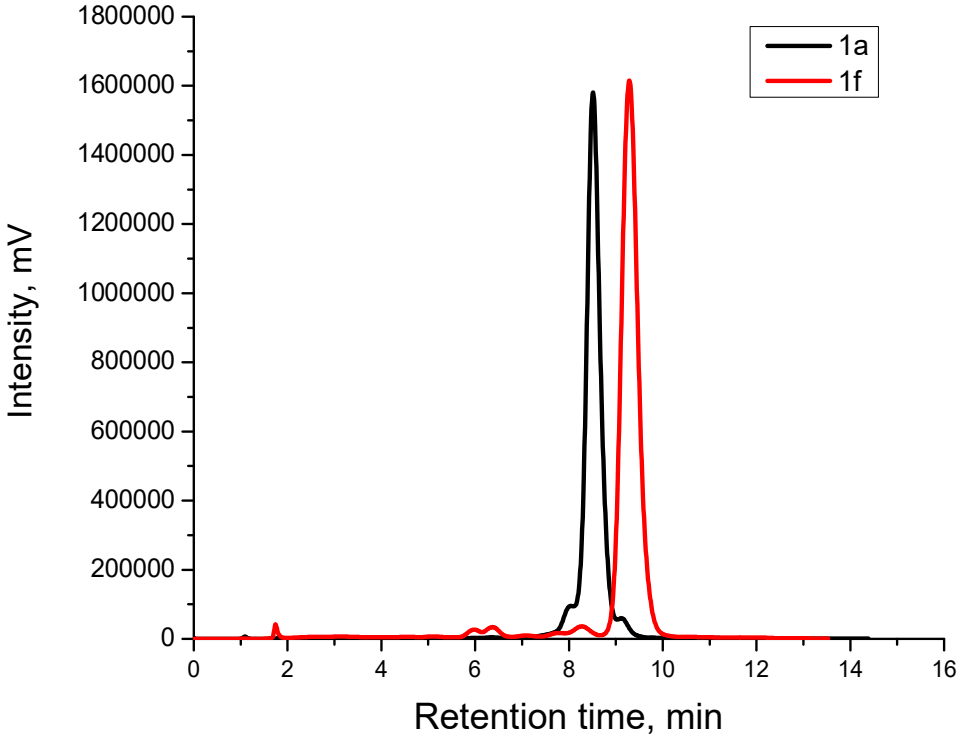


Fig. S1 HPLC profile of the reaction mixture of the alkylation reaction of **1a** with $P(OBu)_3$, resulting in formation of **1f** (C18 Cosmosil column, elution with toluene/acetonitrile mixtures 20%/80% v/v, 30°C, flow rate 1 mL/min)

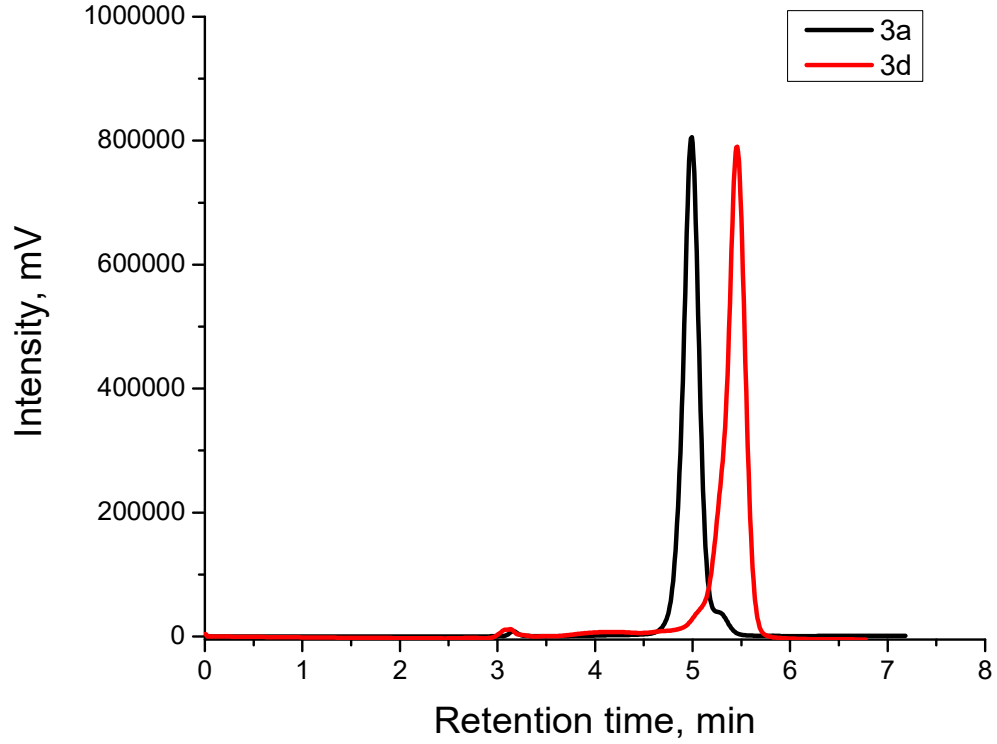


Fig. S2. HPLC profile of the reaction mixture of the alkylation reaction of **3a** with $P(OEt)_3$, resulting in formation of **3d** (C18 Cosmosil column, elution with toluene/acetonitrile mixtures 20%/80% v/v, 30°C, flow rate 1 mL/min)

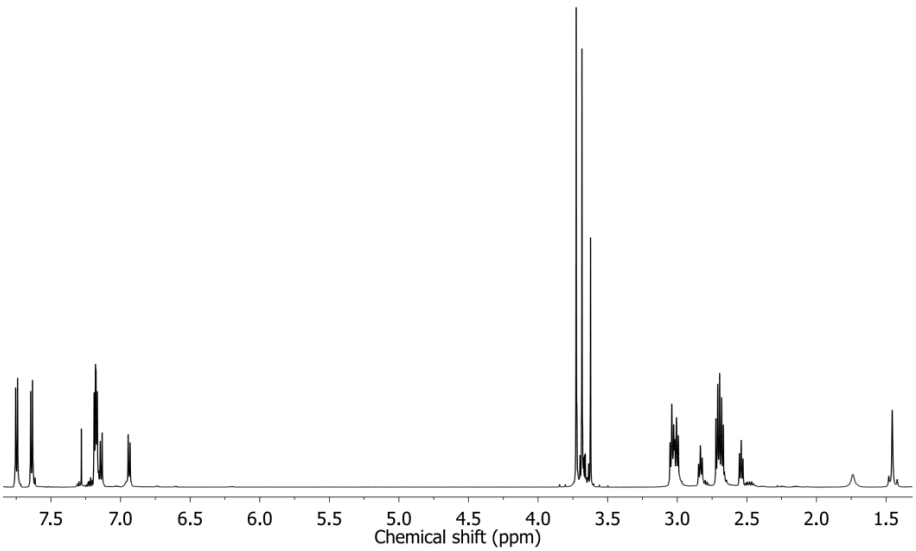


Fig. S3 ^{1}H NMR spectrum of compound **1c**

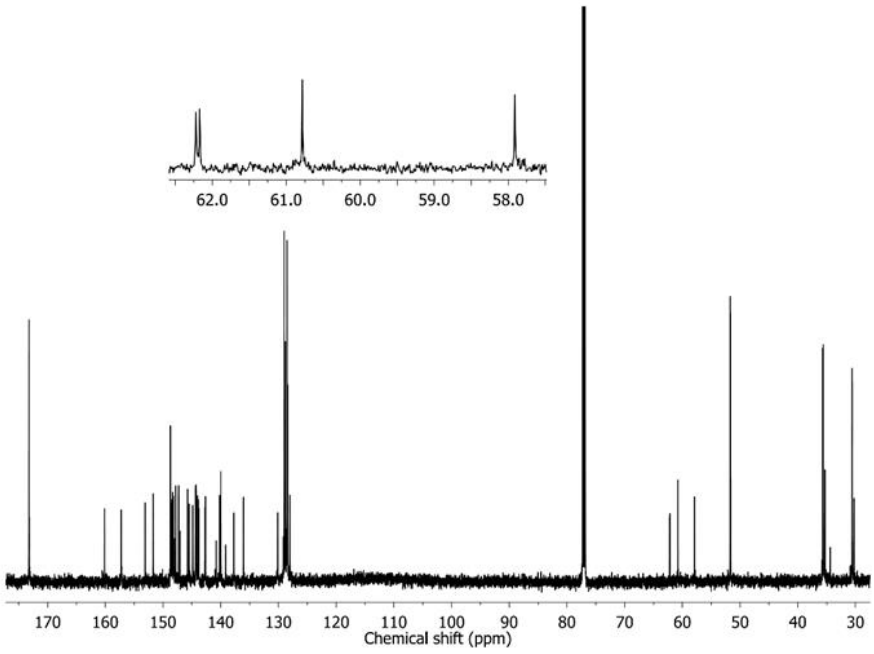


Fig. S4 ^{13}C NMR spectrum of compound **1c**

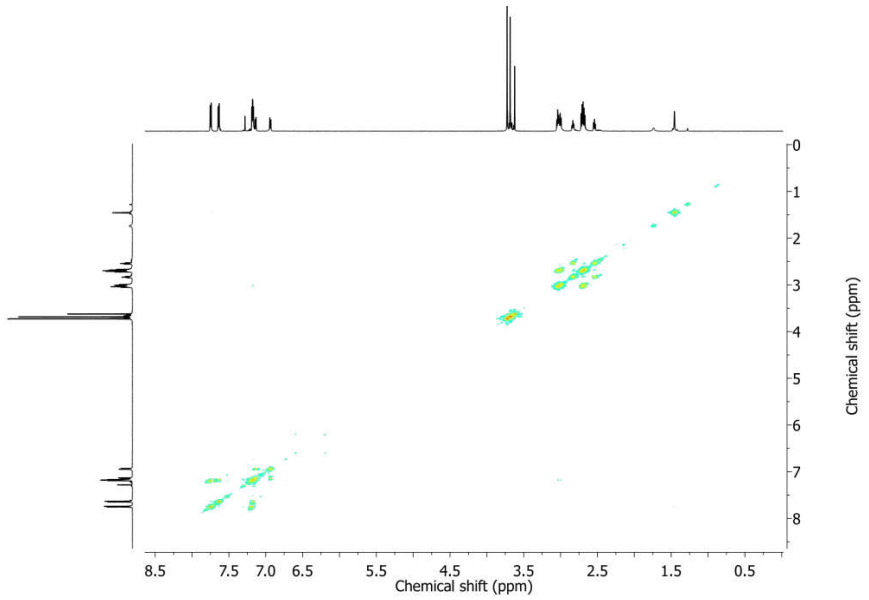


Fig. S5 ^{1}H-^{1}H COSY NMR spectrum of compound **1c**

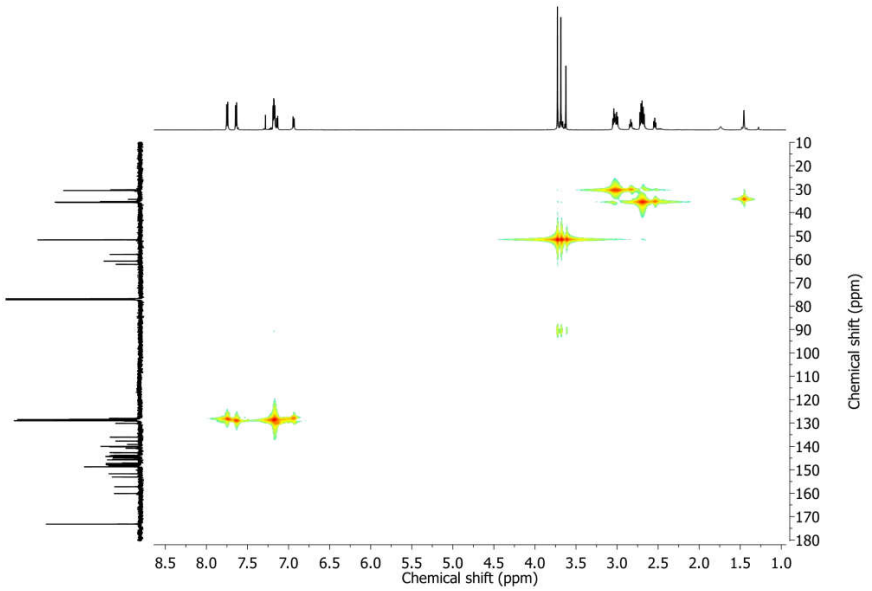


Fig. S6 ^{1}H-^{13}C HSQC NMR spectrum of compound **1c**

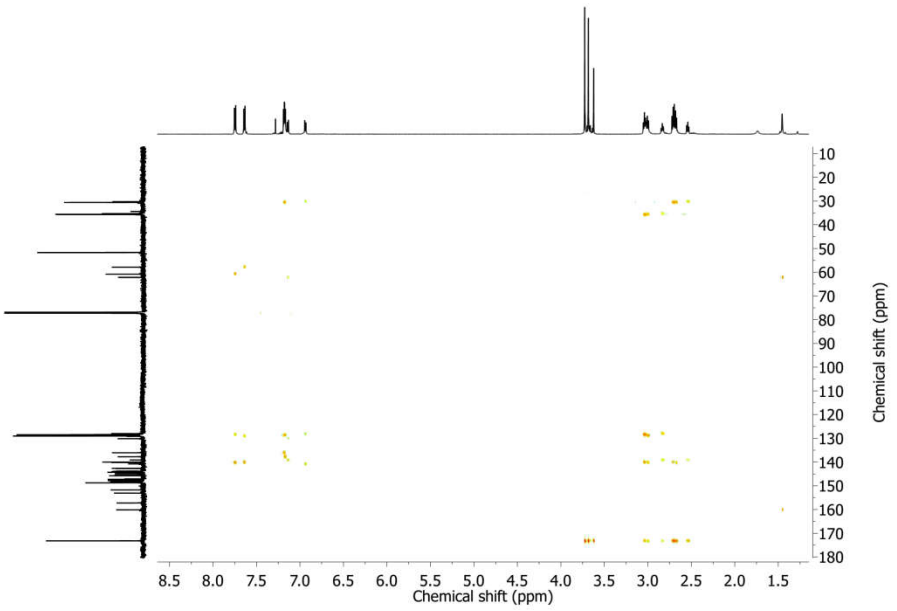


Fig. S7 ^{1}H-^{13}C HMBC NMR spectrum of compound **1c**

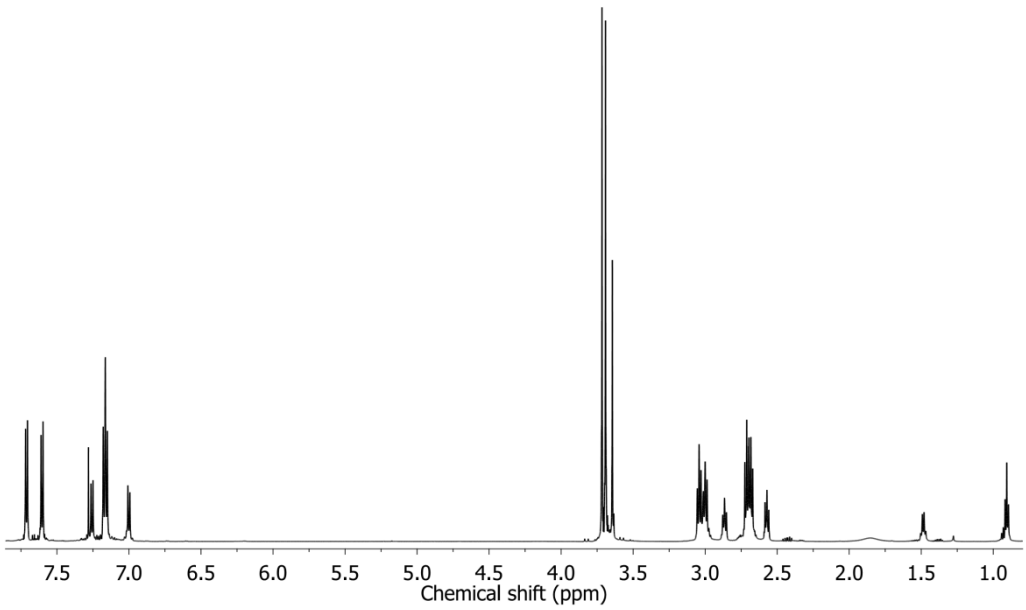


Fig. S8 ^{1}H NMR spectrum of compound **1d**

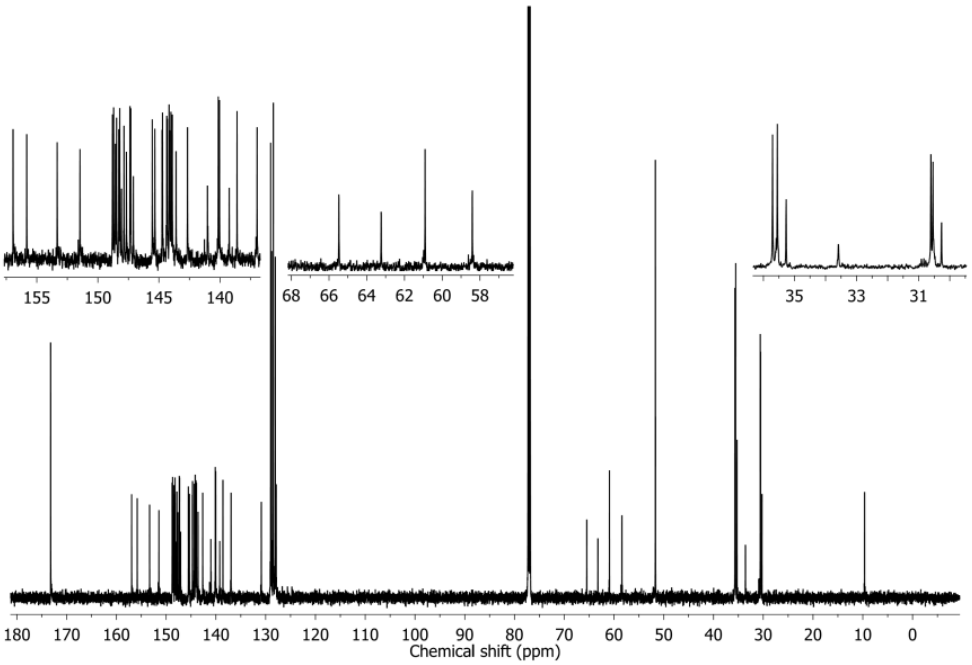


Fig. S9 ^{13}C NMR spectrum of compound **1d**

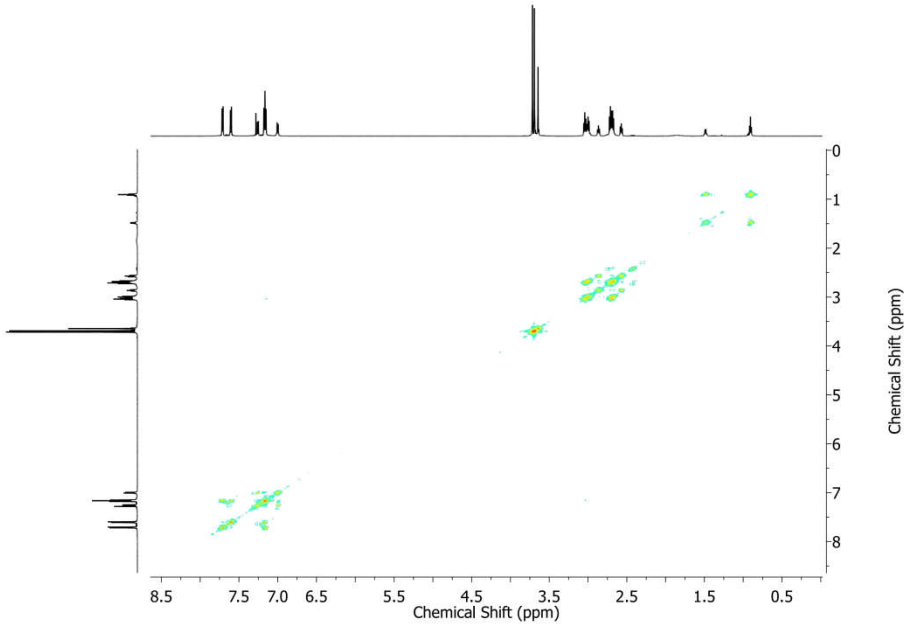


Fig. S10 ^{1}H-^{1}H COSY NMR spectrum of compound **1d**

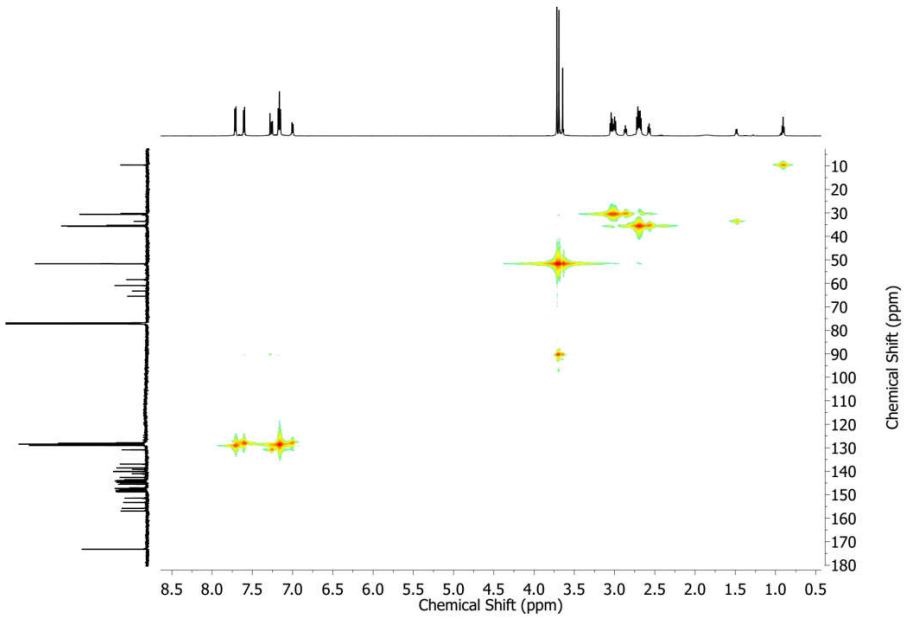


Fig. S11 ^{1}H-^{13}C HSQC NMR spectrum of compound **1d**

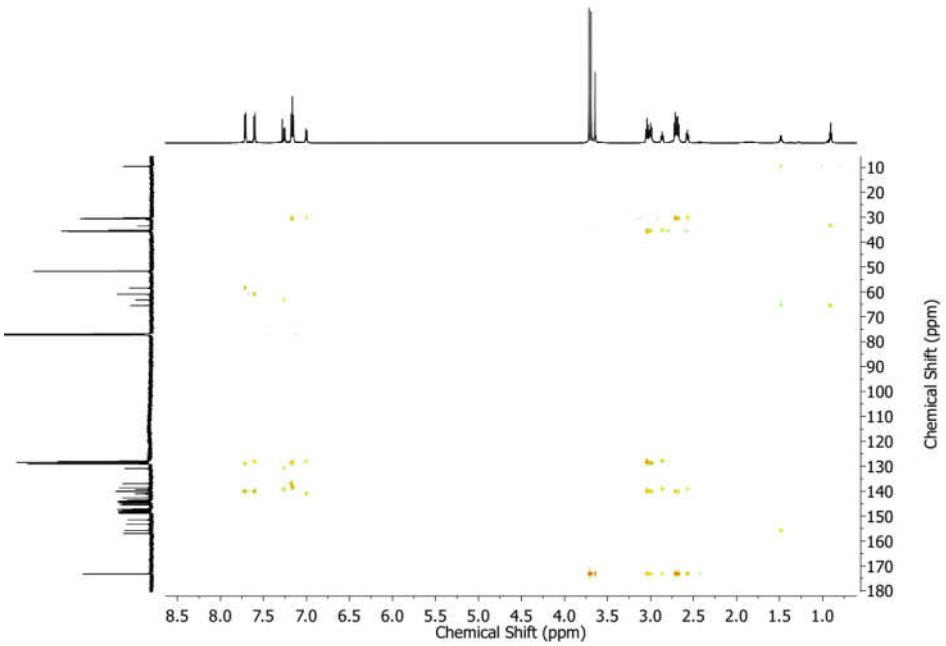


Fig. S12 ^{1}H-^{13}C HMBC NMR spectrum of compound **1d**

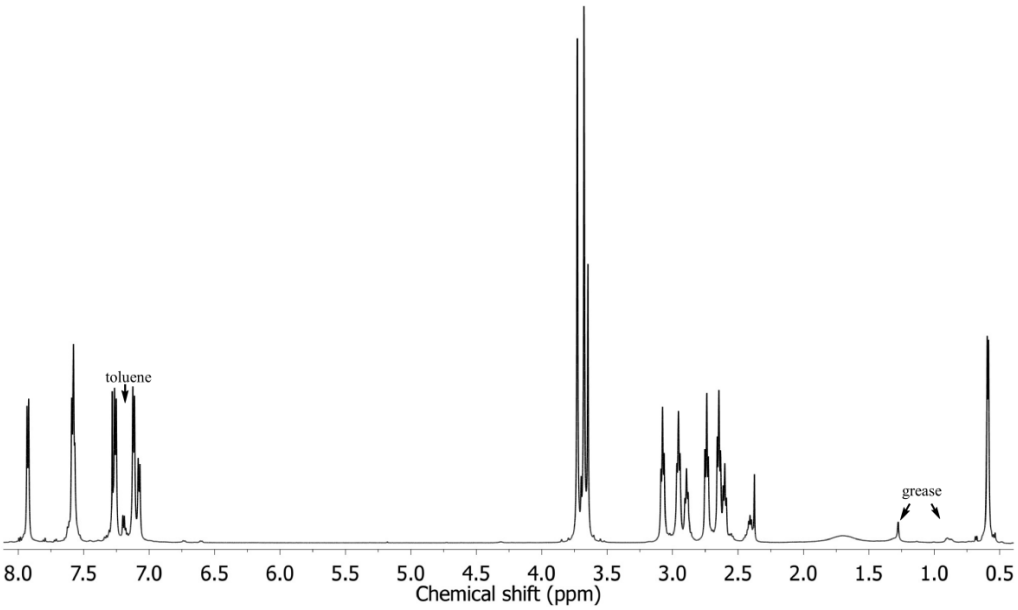


Fig. S13 ^{1}H NMR spectrum of compound **1e**

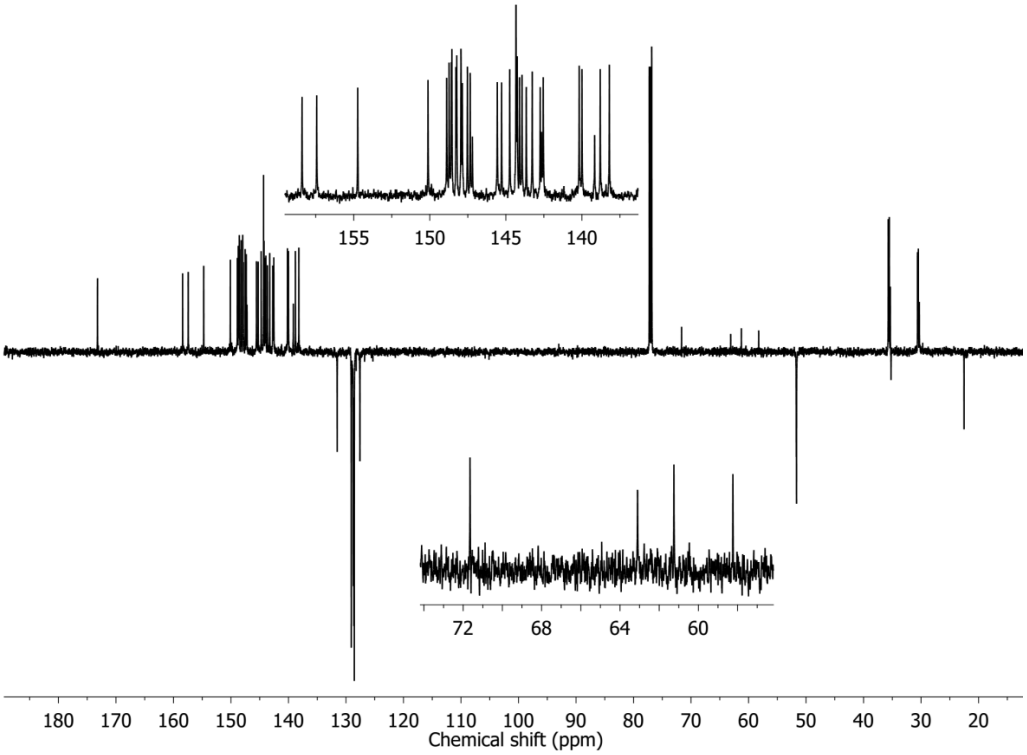


Fig. S14 ^{13}C NMR spectrum of compound **1e**

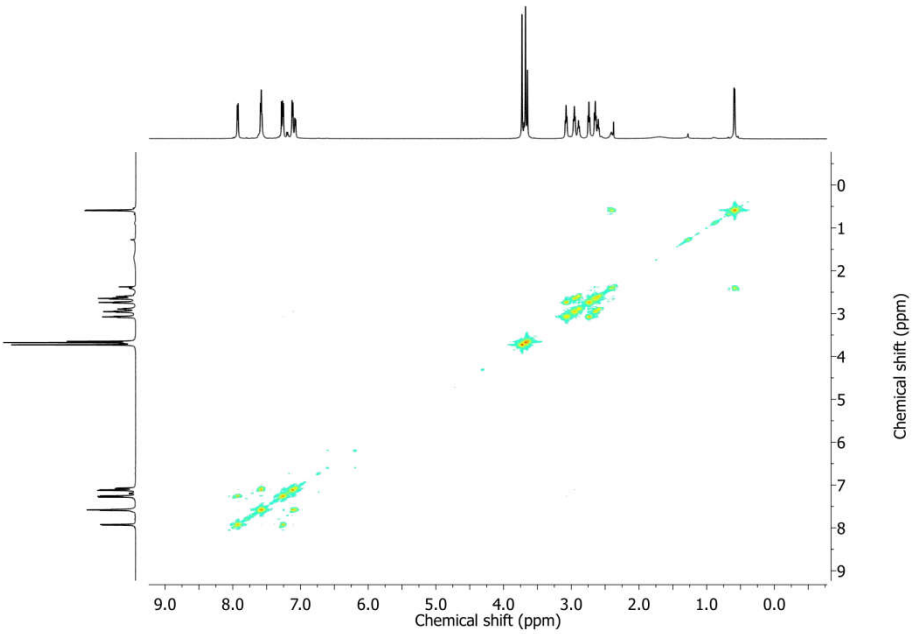


Fig. S15 ^{1}H-^{1}H COSY NMR spectrum of compound **1e**

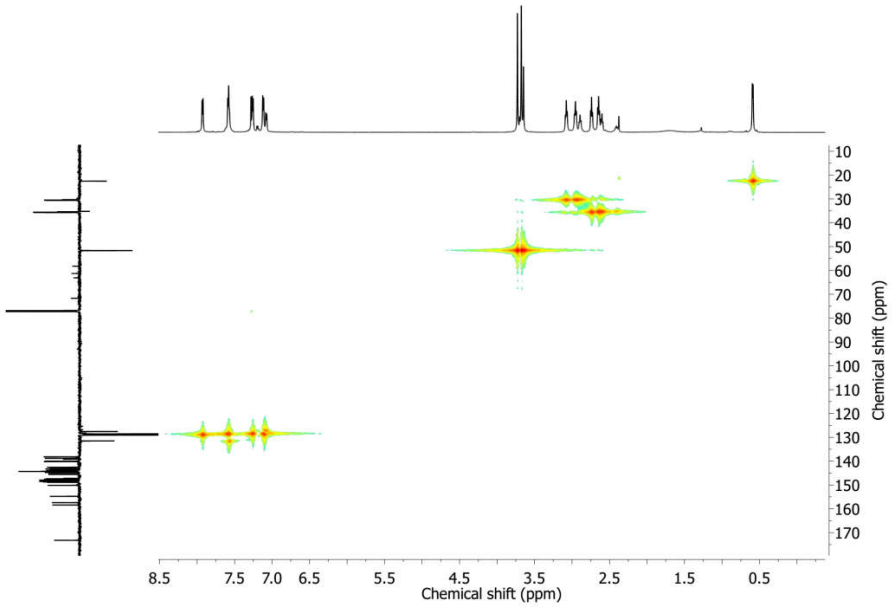


Fig. S16 ^{1}H-^{13}C HSQC NMR spectrum of compound **1e**

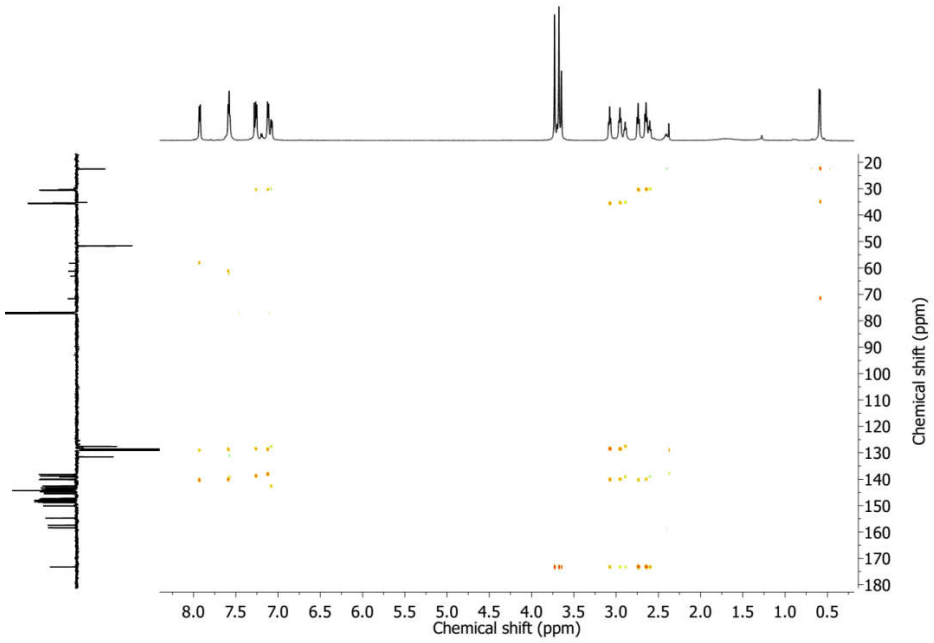


Fig. S17 ^{1}H-^{13}C HMBC NMR spectrum of compound **1e**

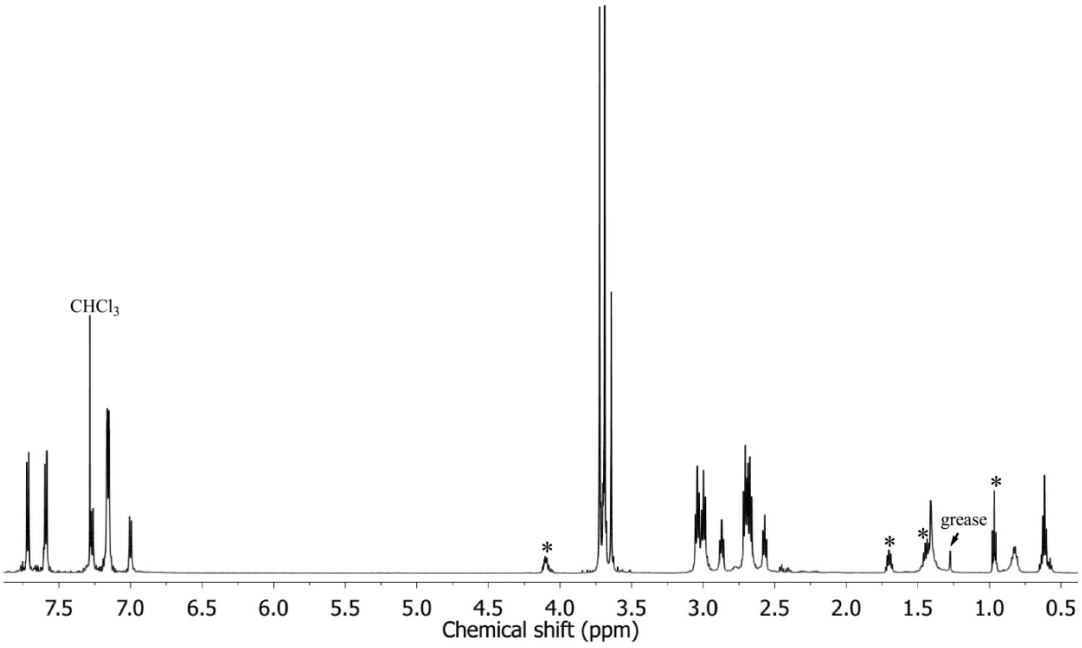


Fig. S18 ^{1}H NMR spectrum of compound **1f** (* denotes impurity of $P(OBu)_3$)

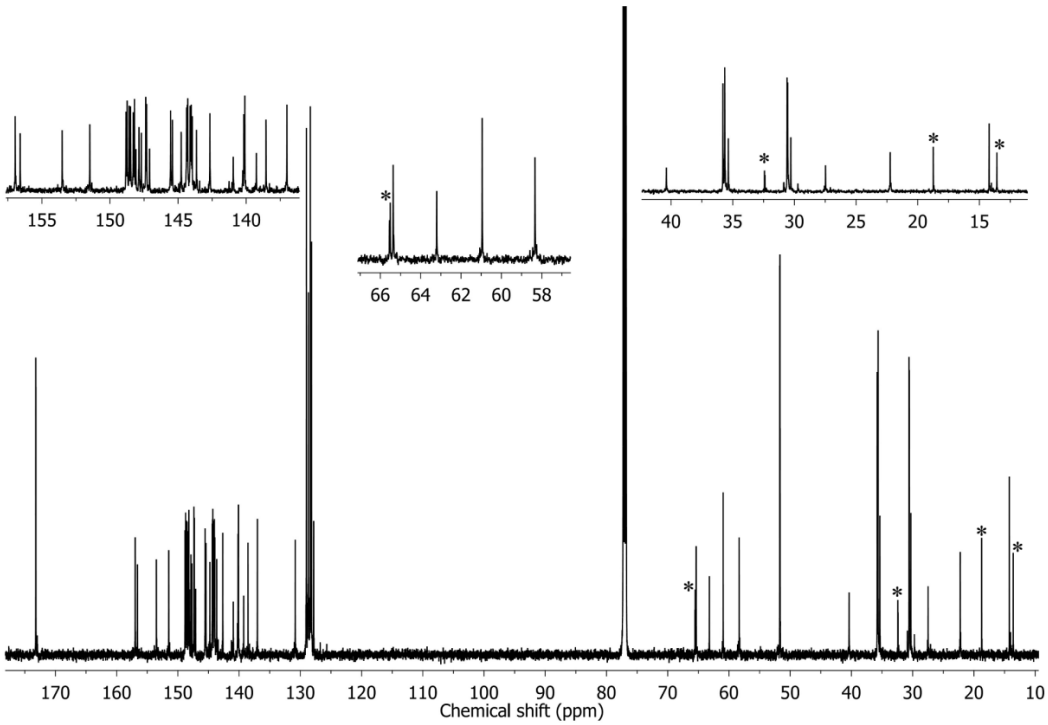


Fig. S19 ^{13}C NMR spectrum of compound **1f** (* denotes impurity of $P(OBu)_3$)

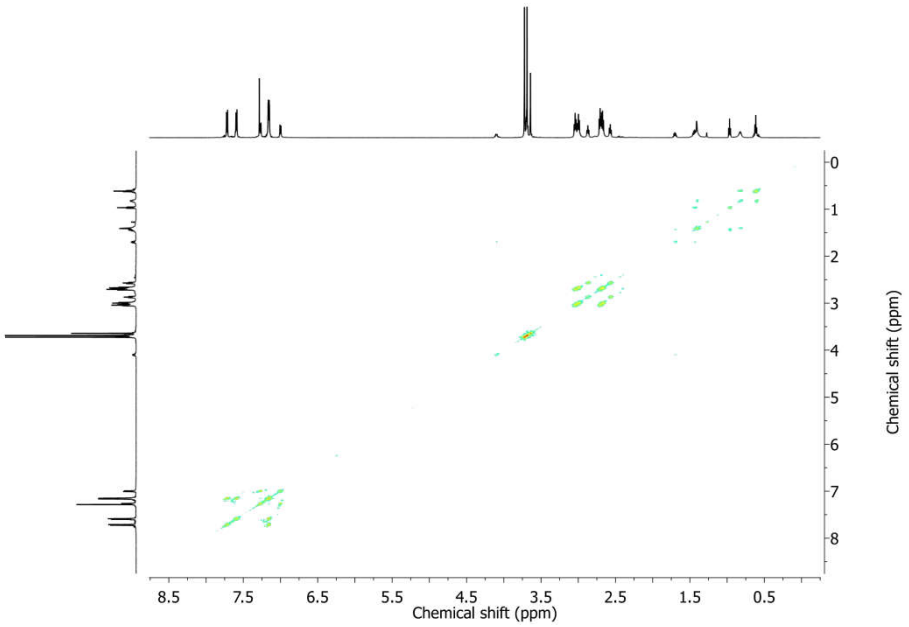


Fig. S20 ^{1}H-^{1}H COSY NMR spectrum of compound **1f**

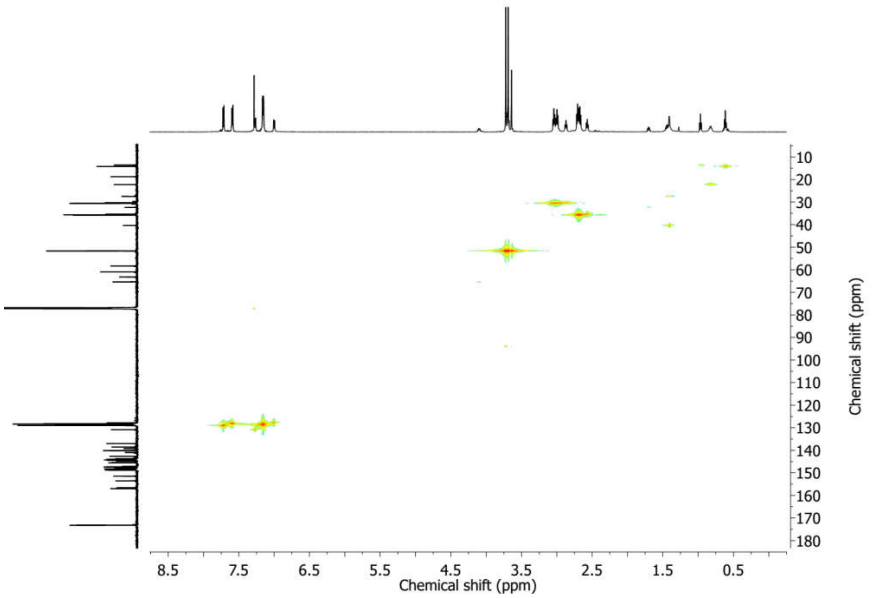


Fig. S21 ^{1}H-^{13}C HSQC NMR spectrum of compound **1f**

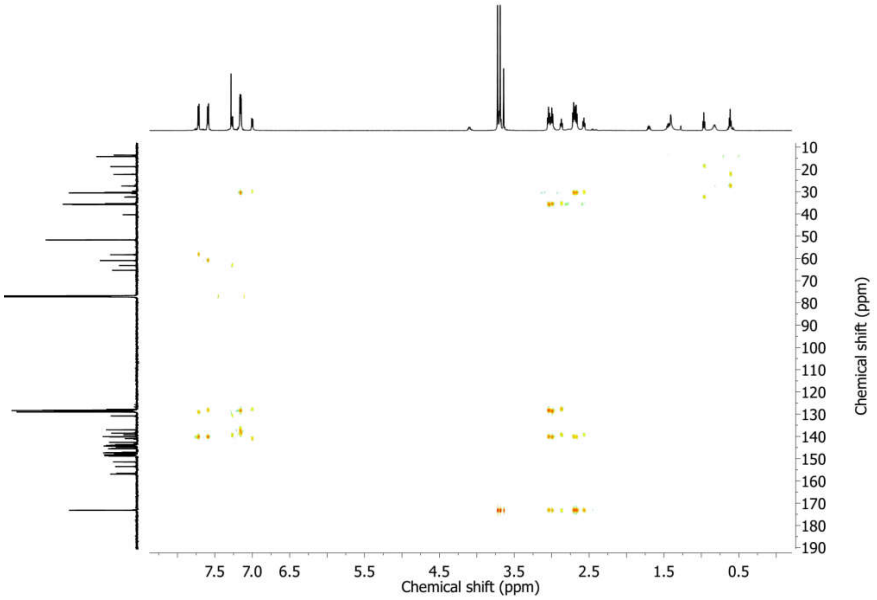


Fig. S22 ^{1}H-^{13}C HMBC NMR spectrum of compound **1f**

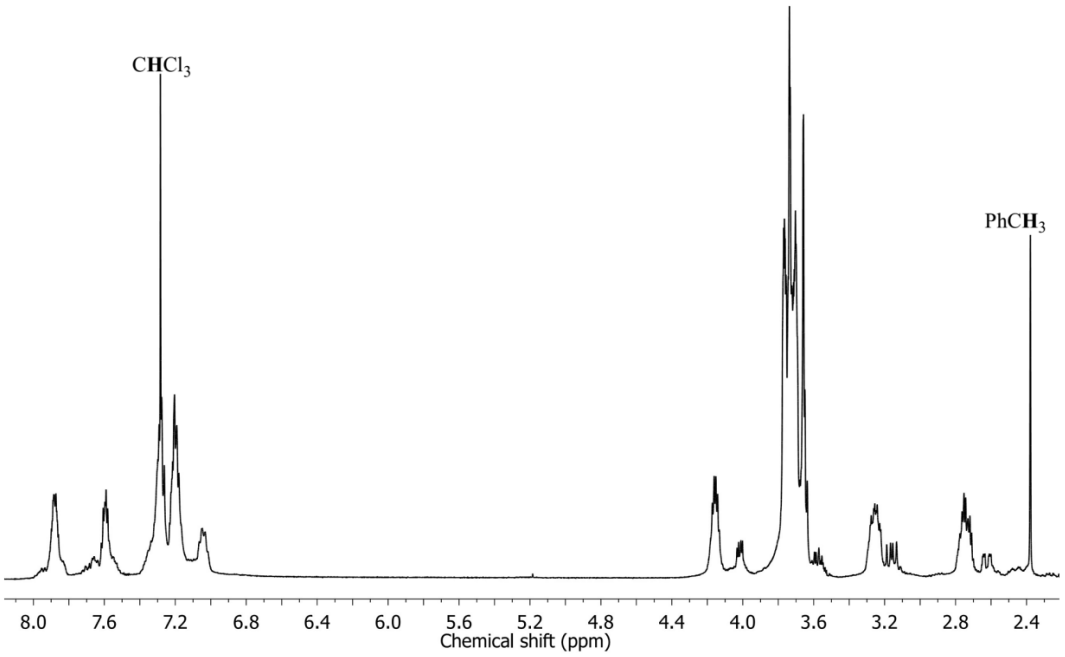


Fig. S23 ^{1}H NMR spectrum of compound **2a**

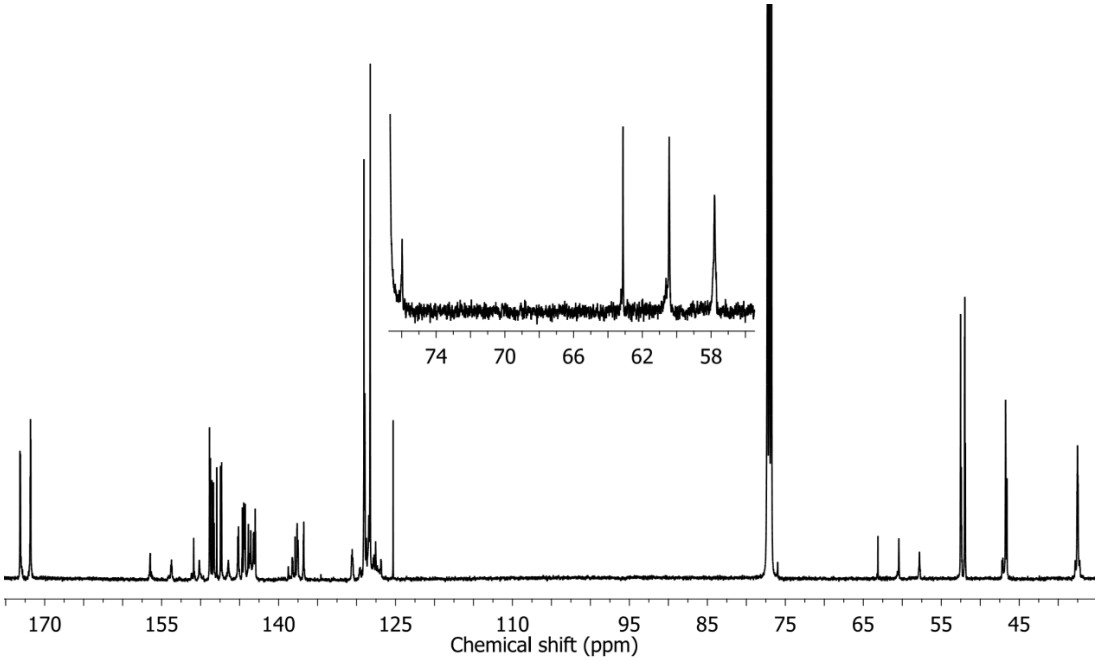


Fig. S24 ^{13}C NMR spectrum of compound **2a**

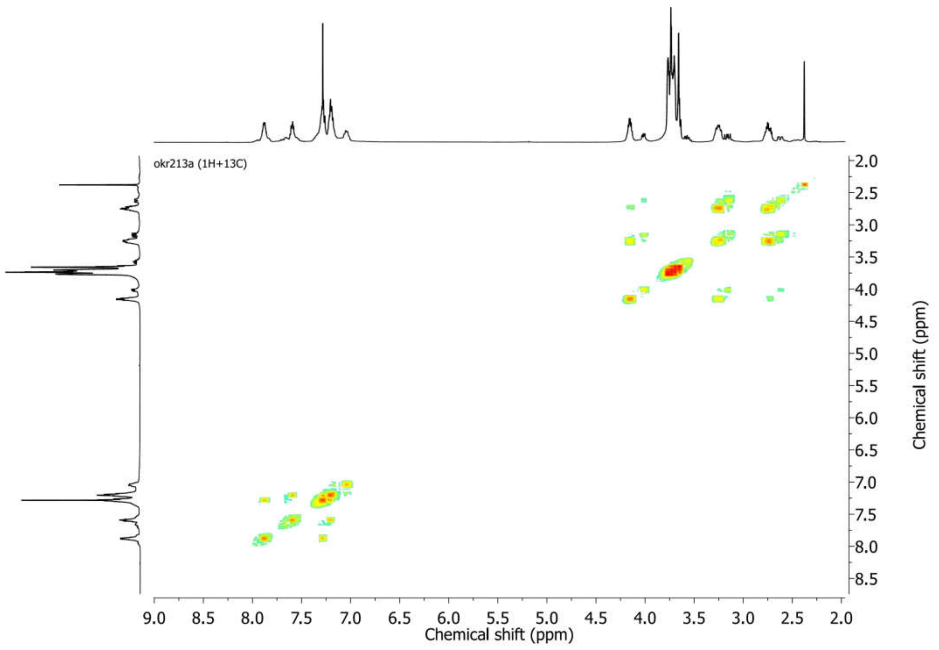


Fig. S25 ^{1}H-^{1}H COSY NMR spectrum of compound **2a**

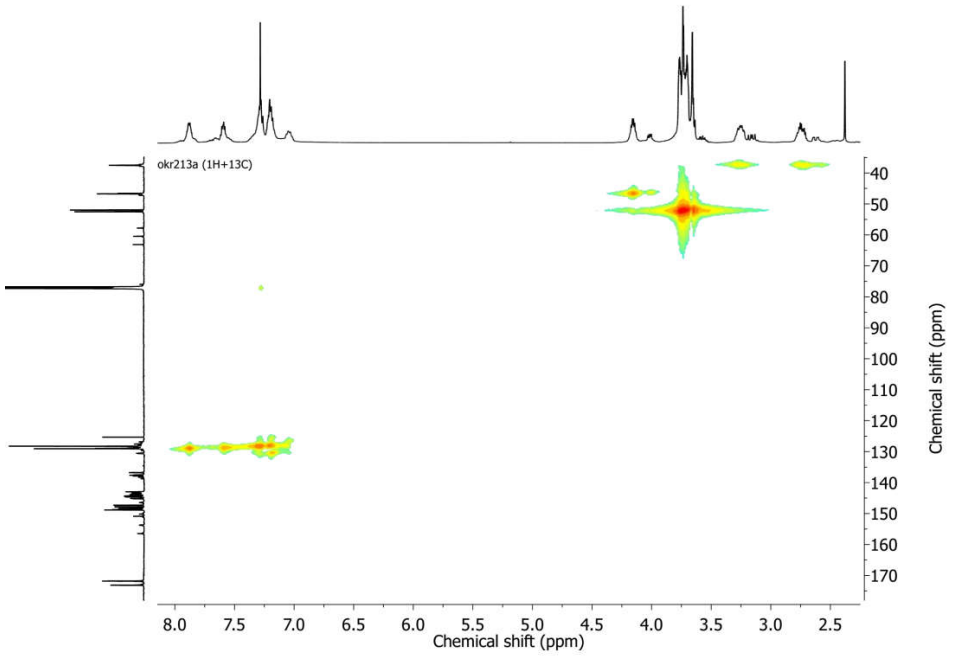


Fig. S26 ^{1}H-^{13}C HSQC NMR spectrum of compound **2a**

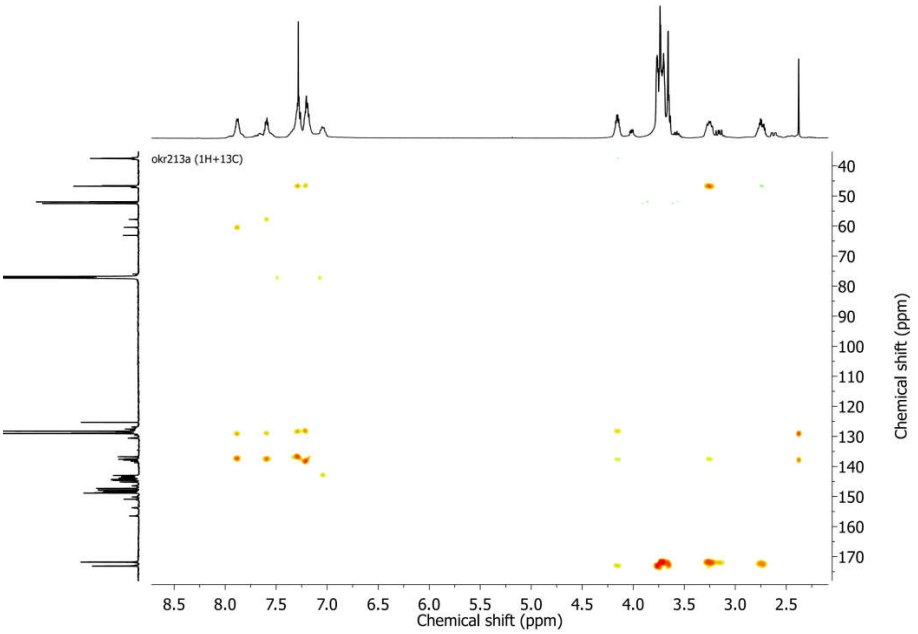


Fig. S27 ^{1}H-^{13}C HMBC NMR spectrum of compound **2a**

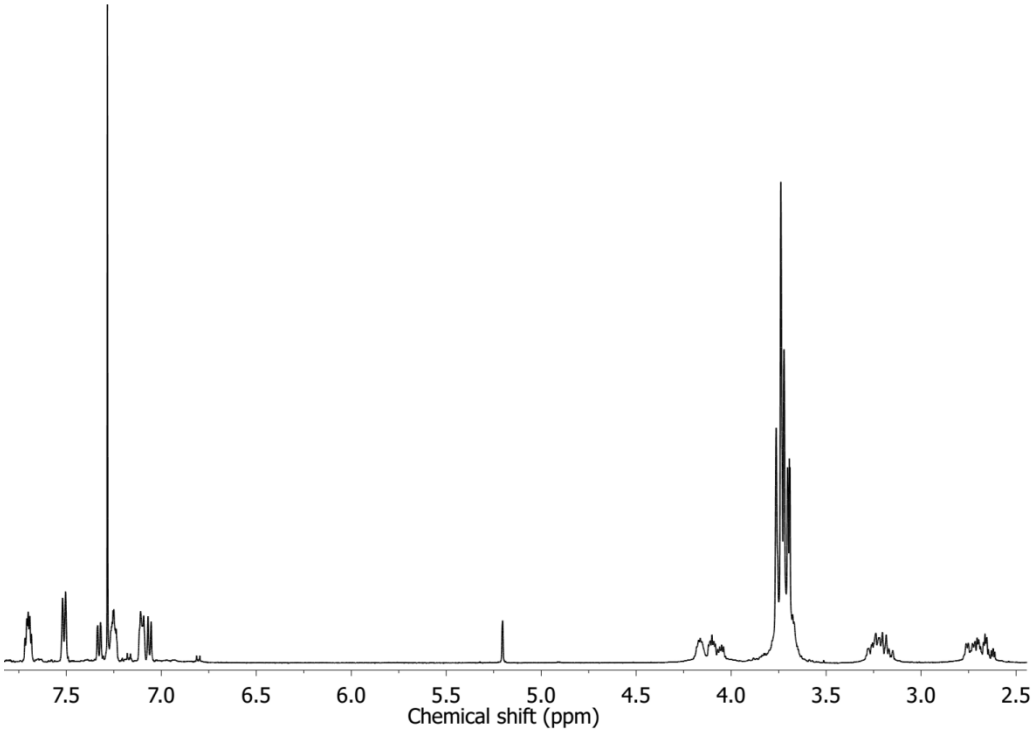


Fig. S28 ^{1}H NMR spectrum of compound **2b**

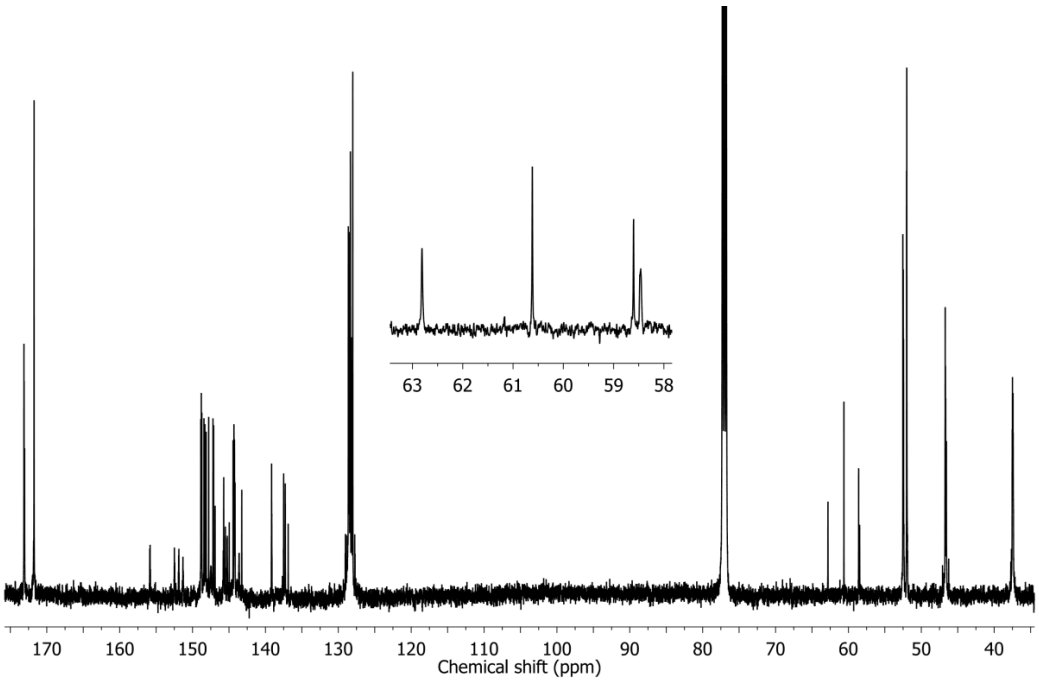


Fig. S29 ^{13}C NMR spectrum of compound **2b**

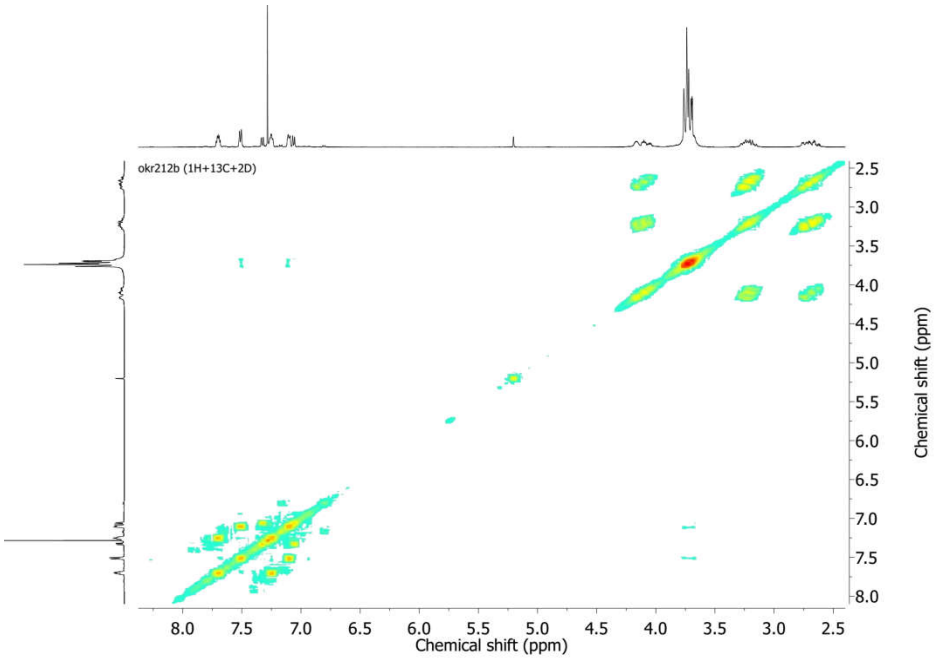


Fig. S30 ^{1}H-^{1}H COSY NMR spectrum of compound **2b**

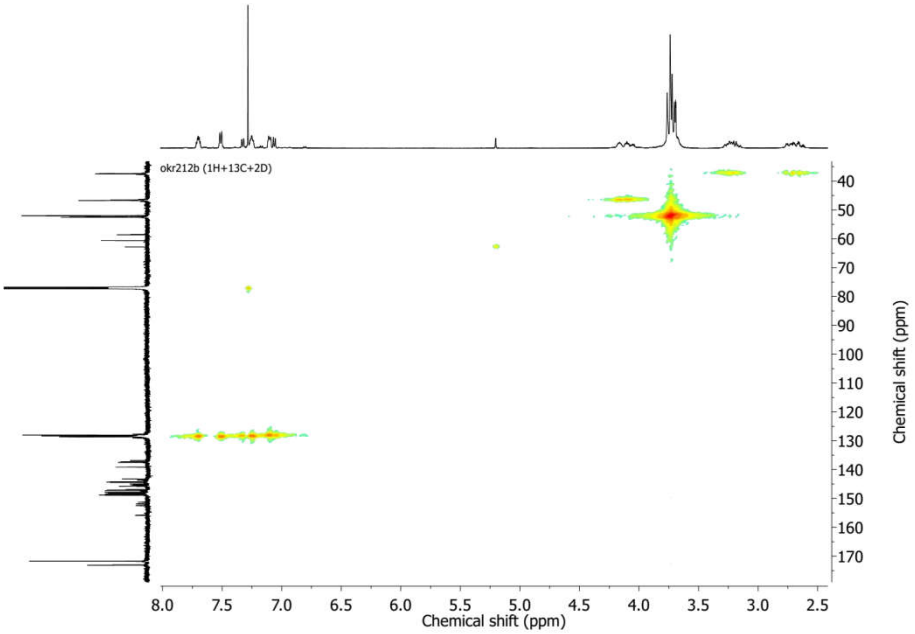


Fig. S31 ^{1}H-^{13}C HSQC NMR spectrum of compound **2b**

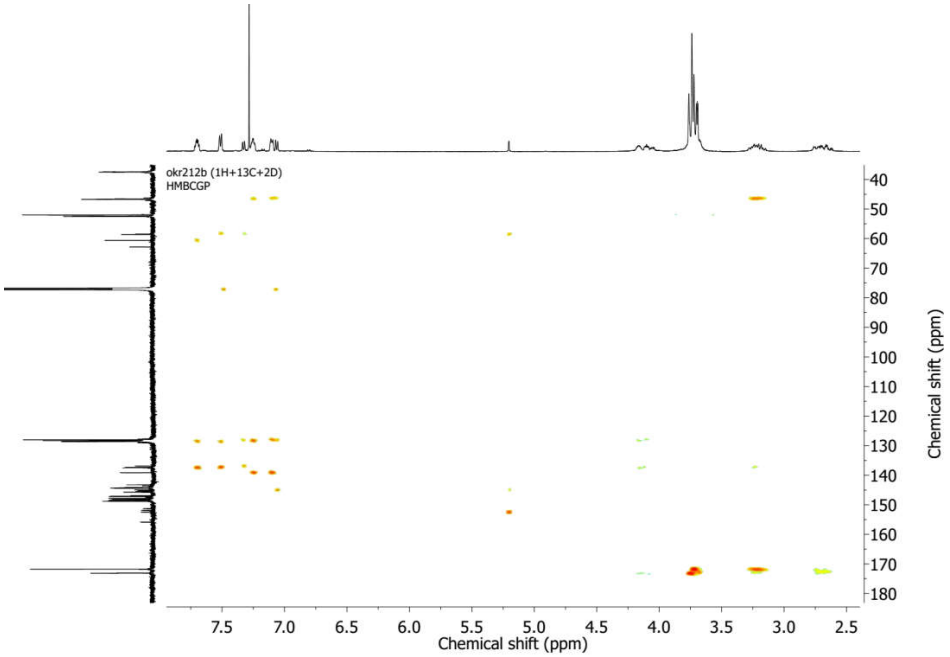


Fig. S32 ^{1}H-^{13}C HMBC NMR spectrum of compound **2b**

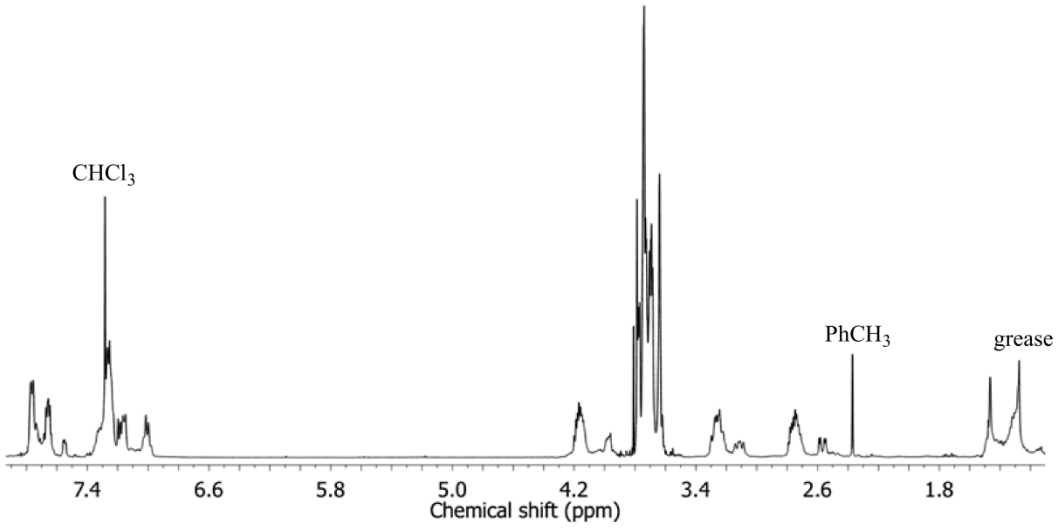


Fig. S33 ^{1}H NMR spectrum of compound **2c**

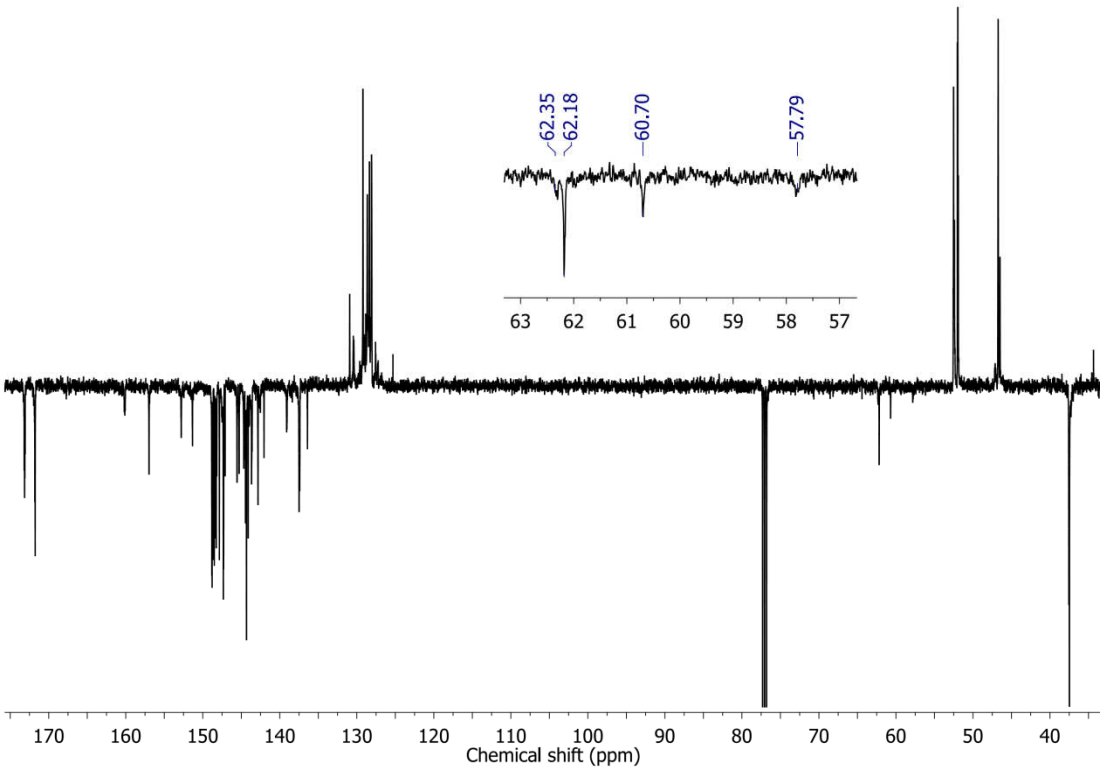


Fig. S34 ^{13}C NMR spectrum of compound **2c**

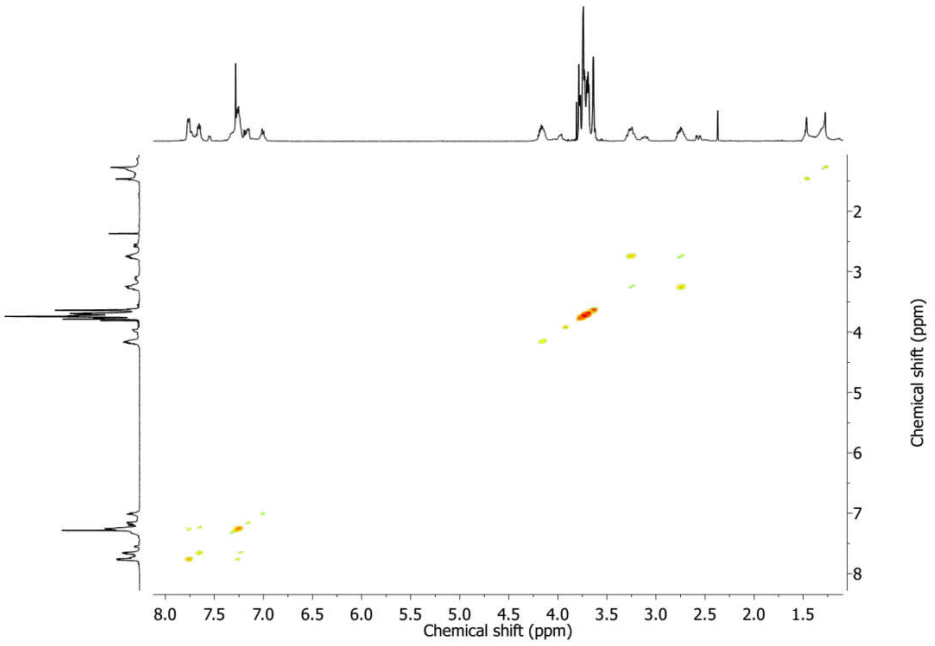


Fig. S35 ^{1}H-^{1}H COSY NMR spectrum of compound **2c**

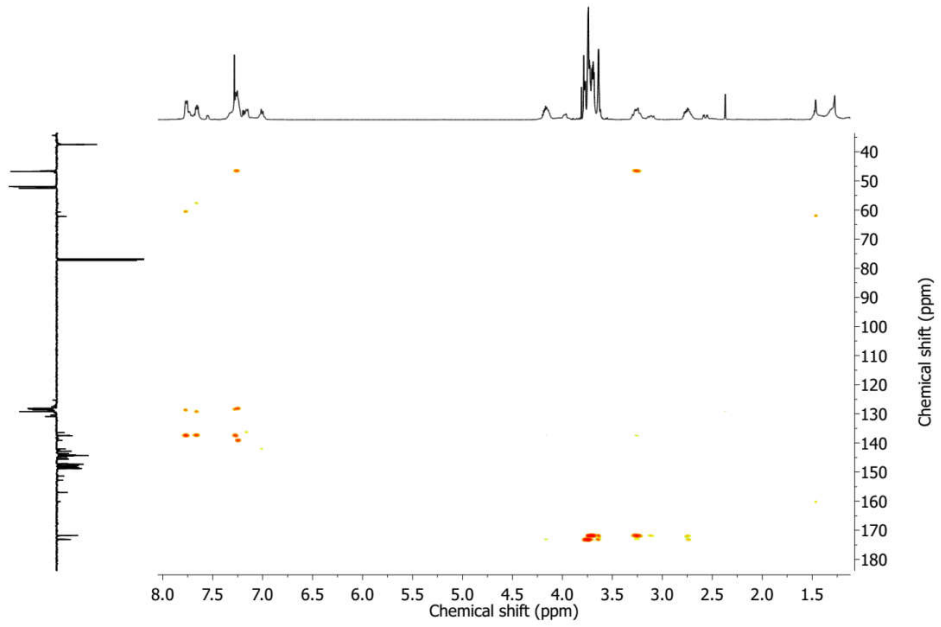


Fig. S36 ^{1}H-^{13}C HSQC NMR spectrum of compound **2c**

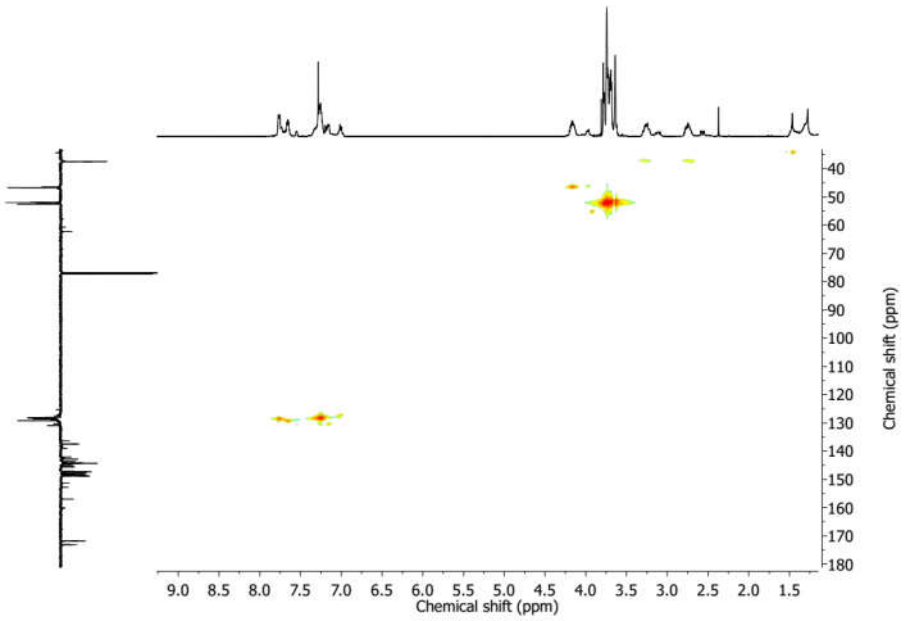


Fig. S37 ^{1}H-^{13}C HMBC NMR spectrum of compound **2c**

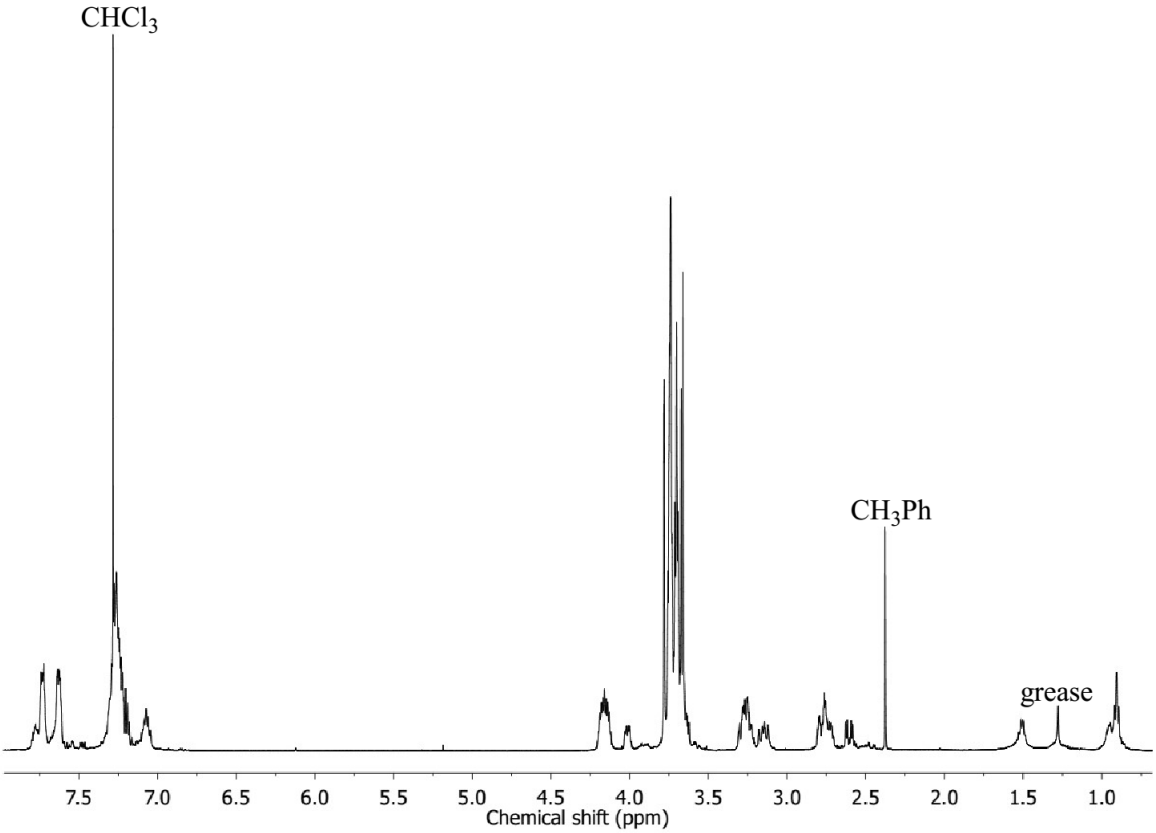


Fig. S38 ^{1}H NMR spectrum of compound **2d**

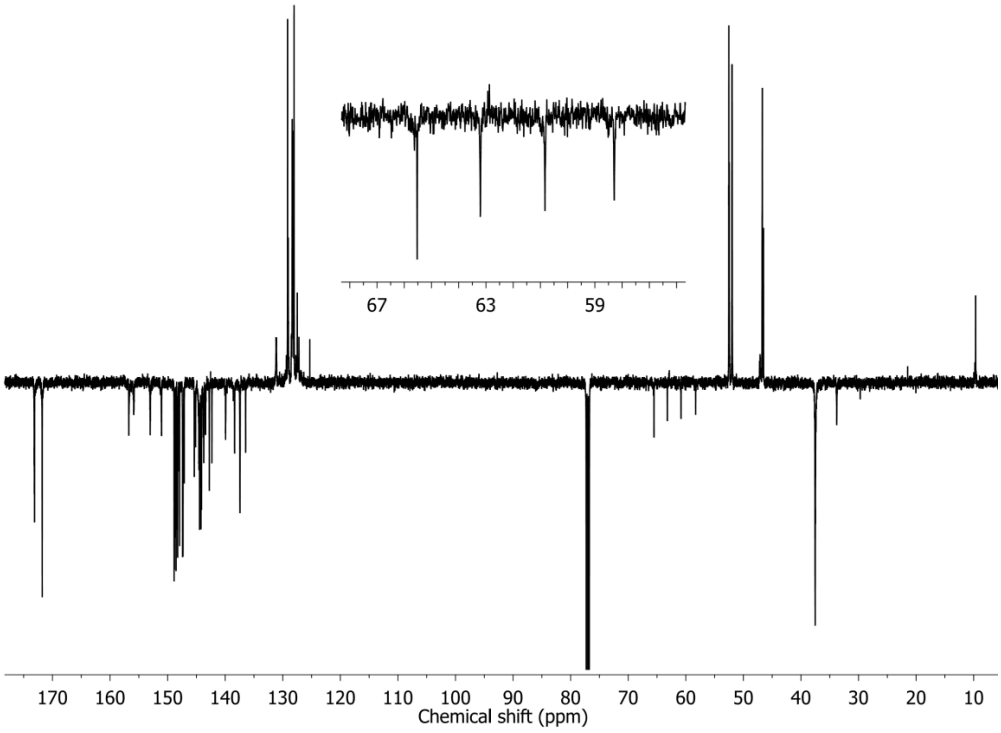


Fig. S39 ^{13}C NMR spectrum of compound **2d**

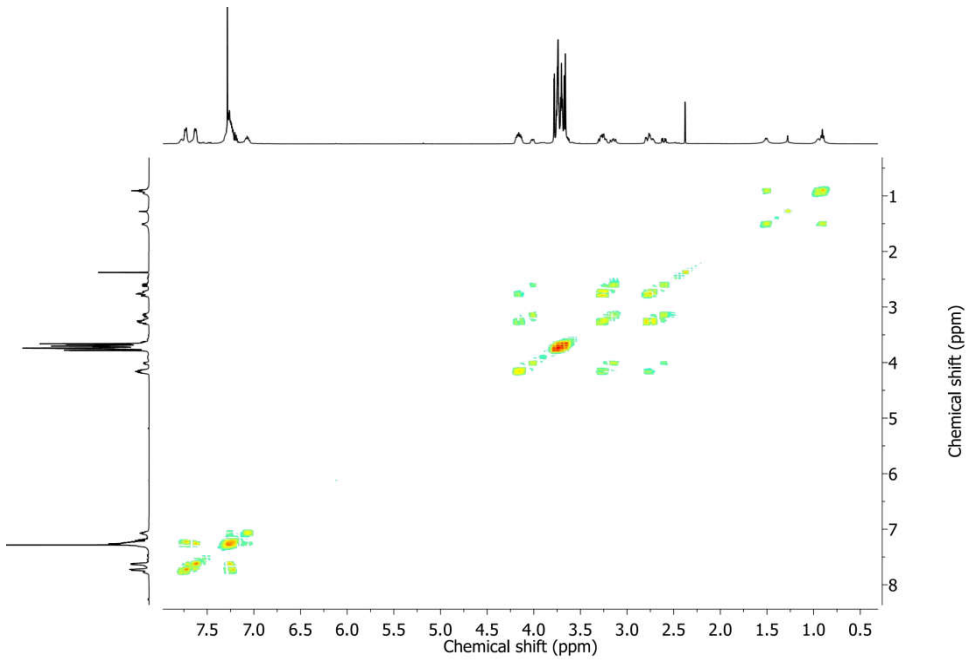


Fig. S40 ^{1}H-^{1}H COSY NMR spectrum of compound **2d**

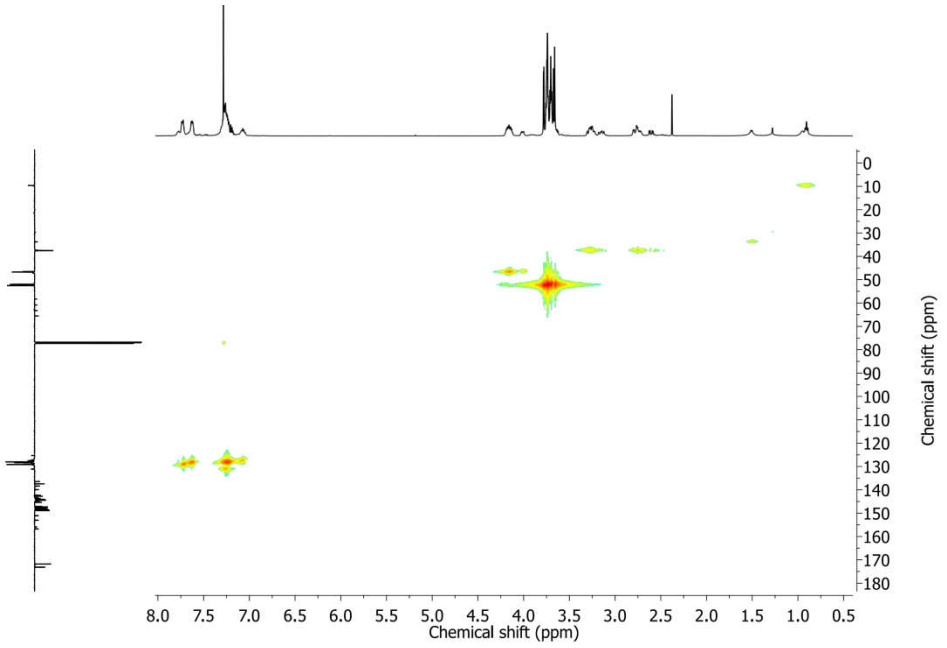


Fig. S41 ^{1}H-^{13}C HSQC NMR spectrum of compound **2d**

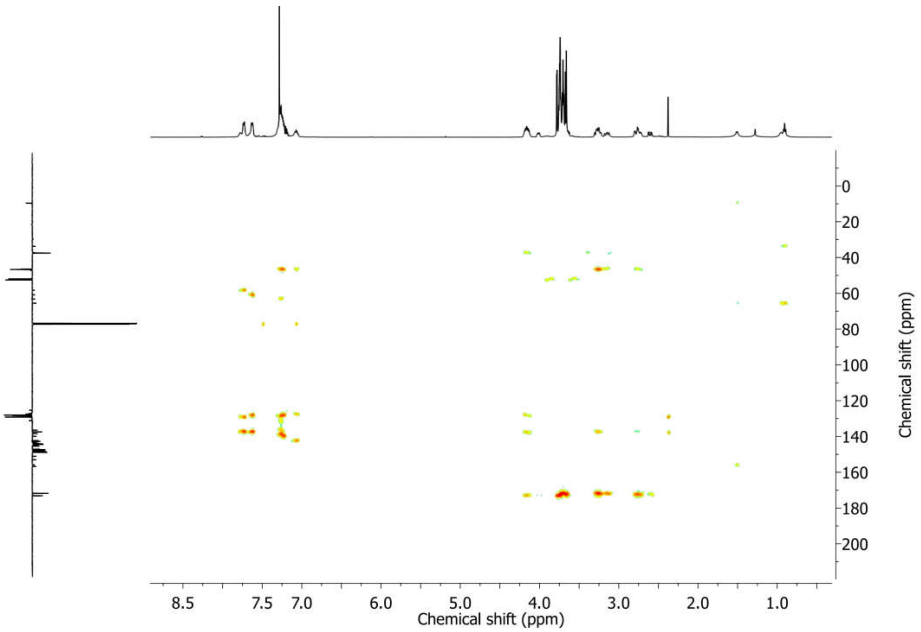


Fig. S42 ^{1}H-^{13}C HMBC NMR spectrum of compound **2d**

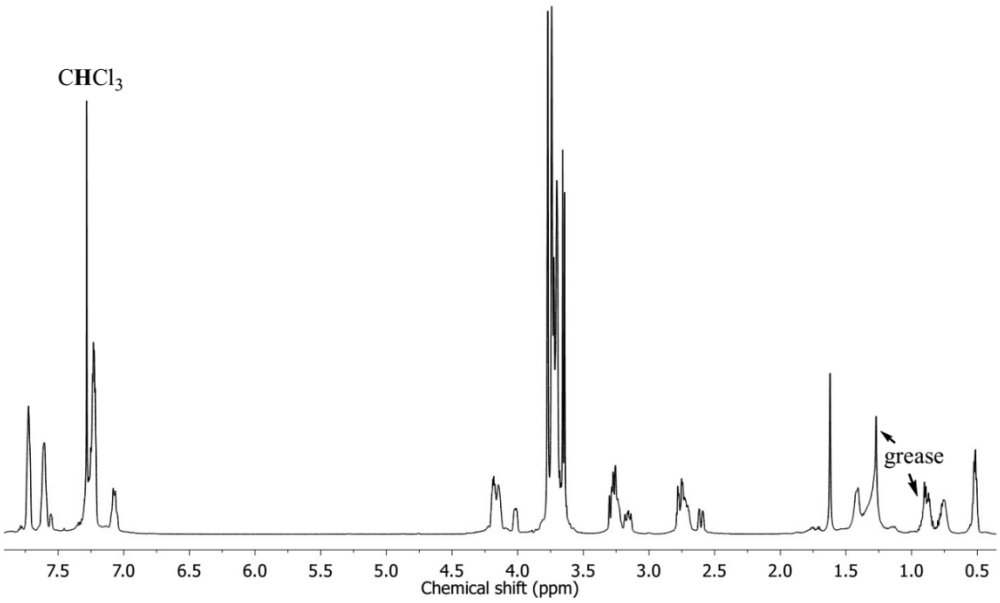


Fig. S43 ^{1}H NMR spectrum of compound **2f**

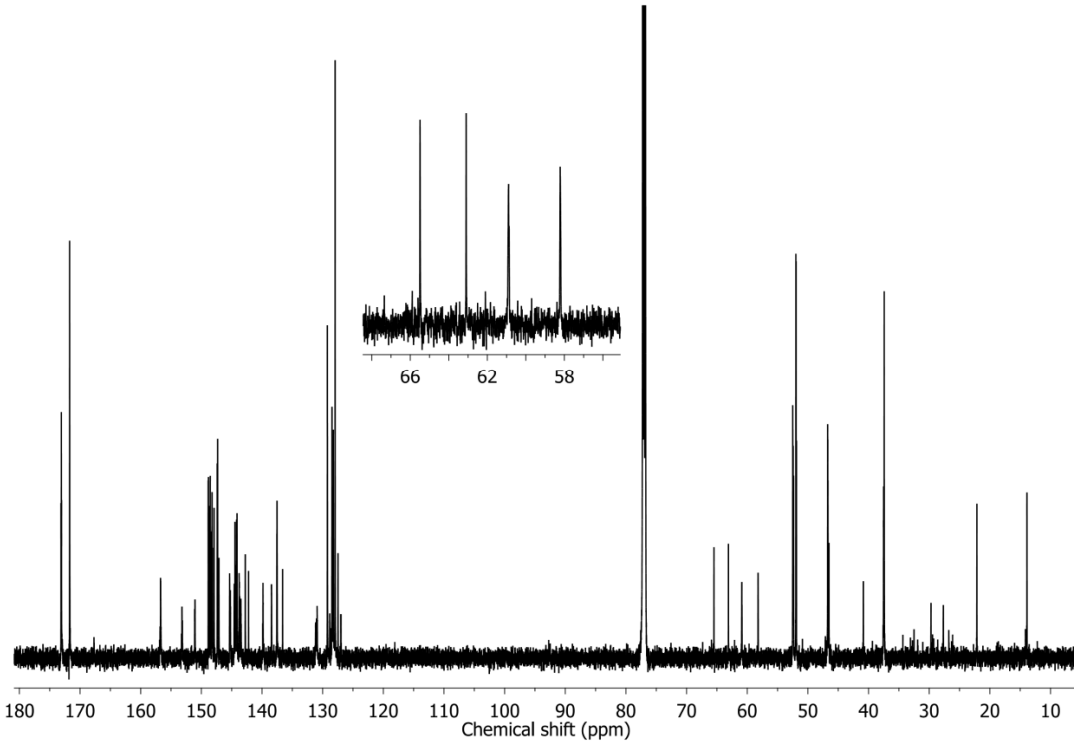


Fig. S44 ^{13}C NMR spectrum of compound **2f**

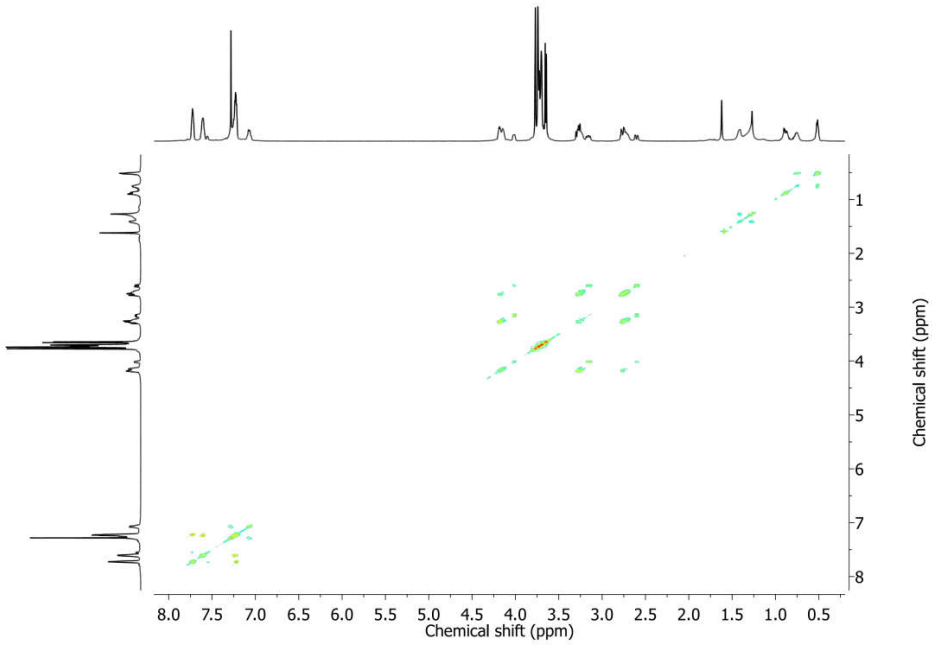


Fig. S45 ^{1}H-^{1}H COSY NMR spectrum of compound **2f**

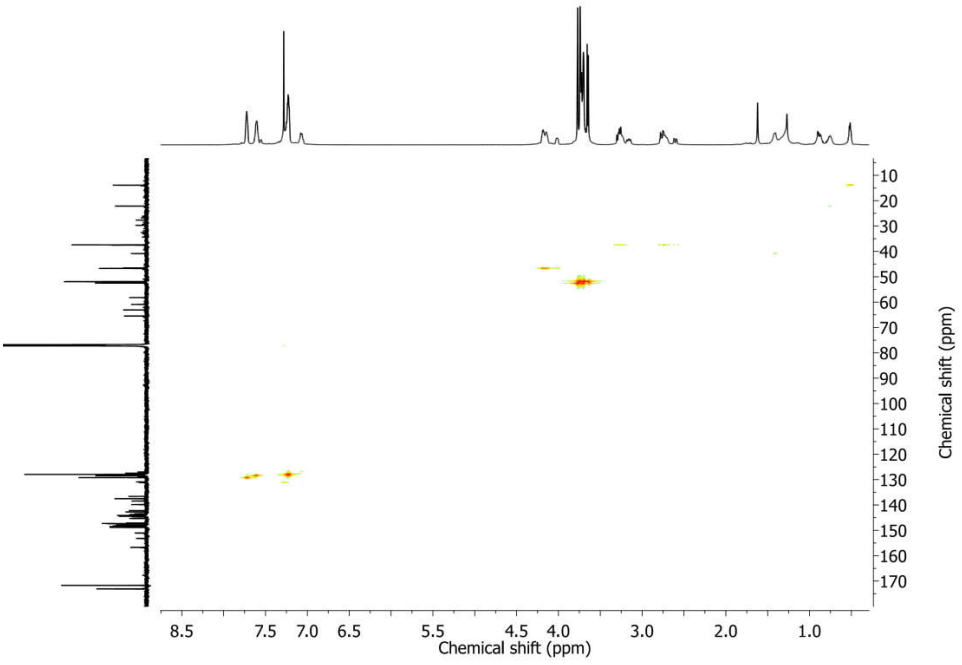


Fig. S46 ^{1}H-^{13}C HSQC NMR spectrum of compound **2f**

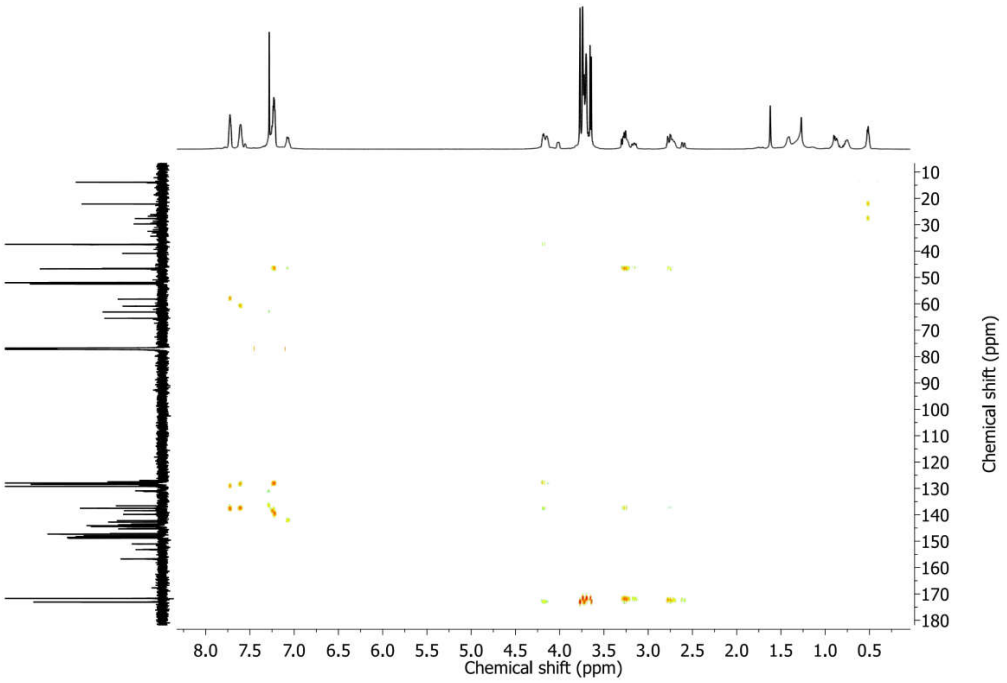


Fig. S47 ^{1}H-^{13}C HMBC NMR spectrum of compound **2f**

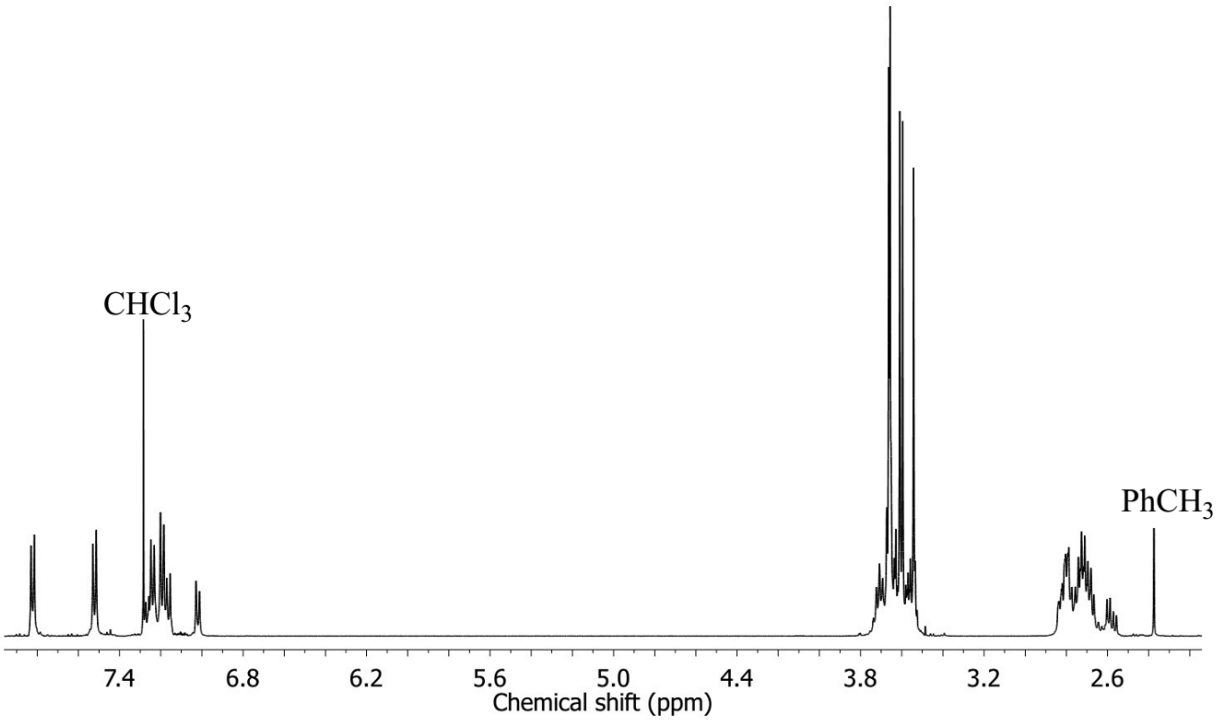


Fig. S48 ^{1}H NMR spectrum of compound **3a**

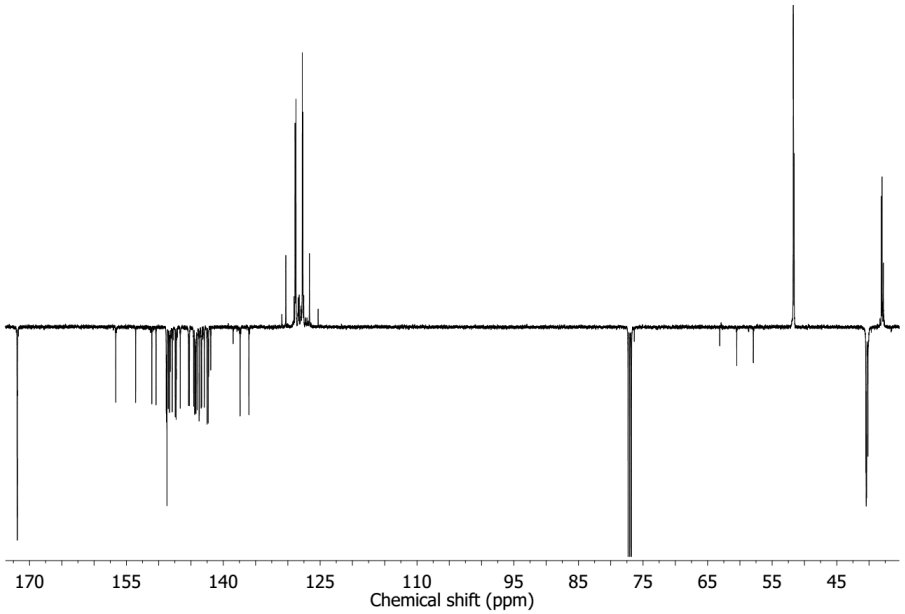


Fig. S49 ^{13}C NMR spectrum of compound **3a**

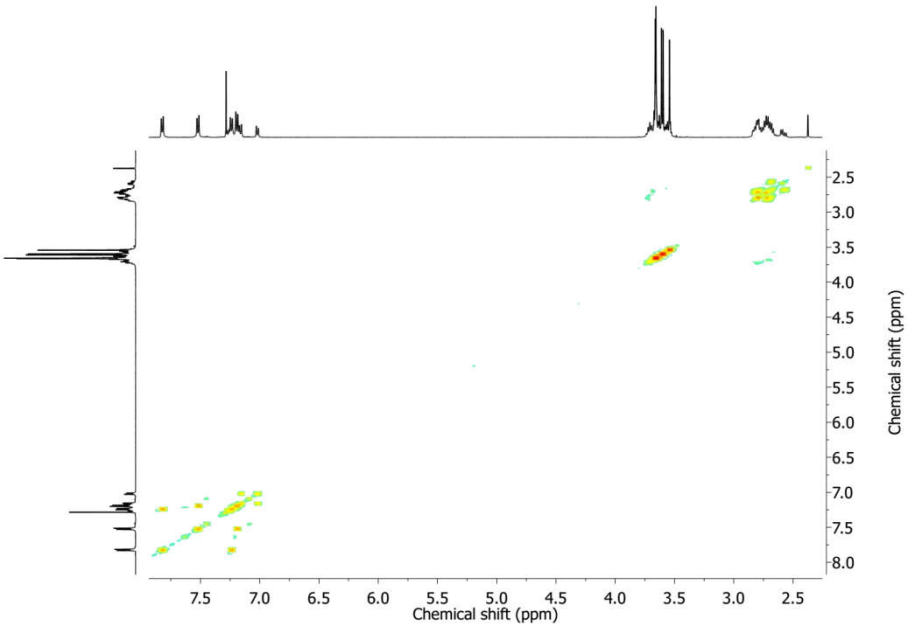


Fig. S50 ^{1}H-^{1}H COSY NMR spectrum of compound **3a**

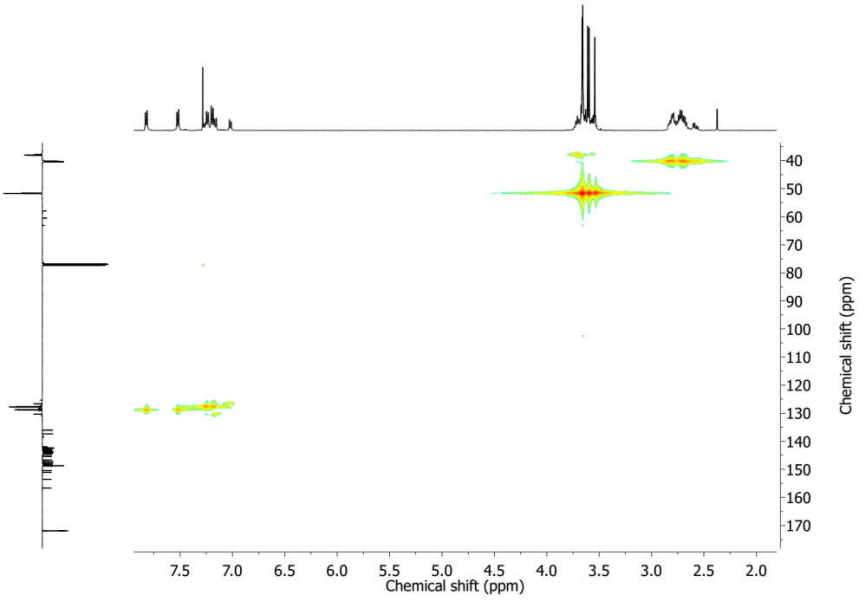


Fig. S51 ^{1}H-^{13}C HSQC NMR spectrum of compound **3a**

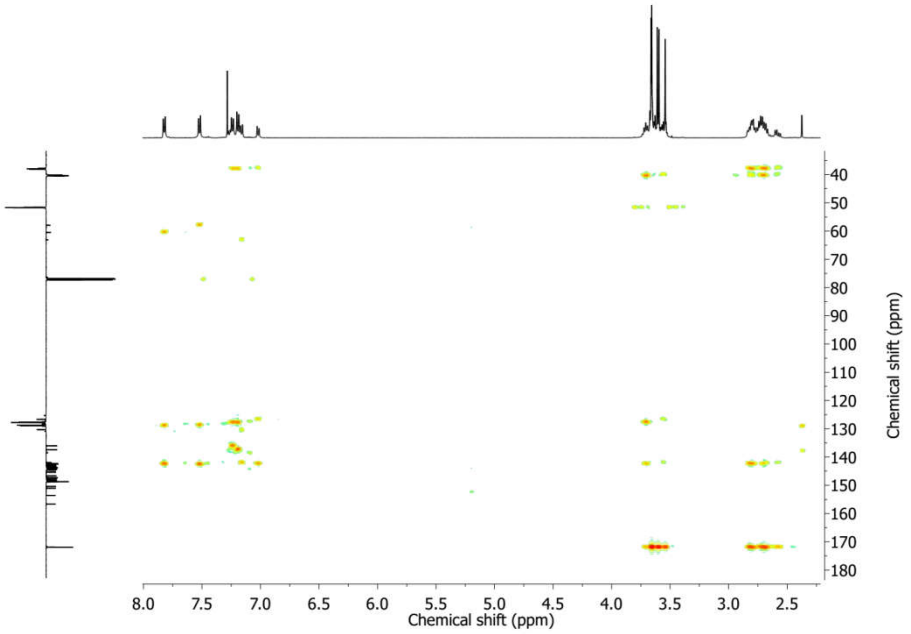


Fig. S52 ^{1}H-^{13}C HMBC NMR spectrum of compound **3a**

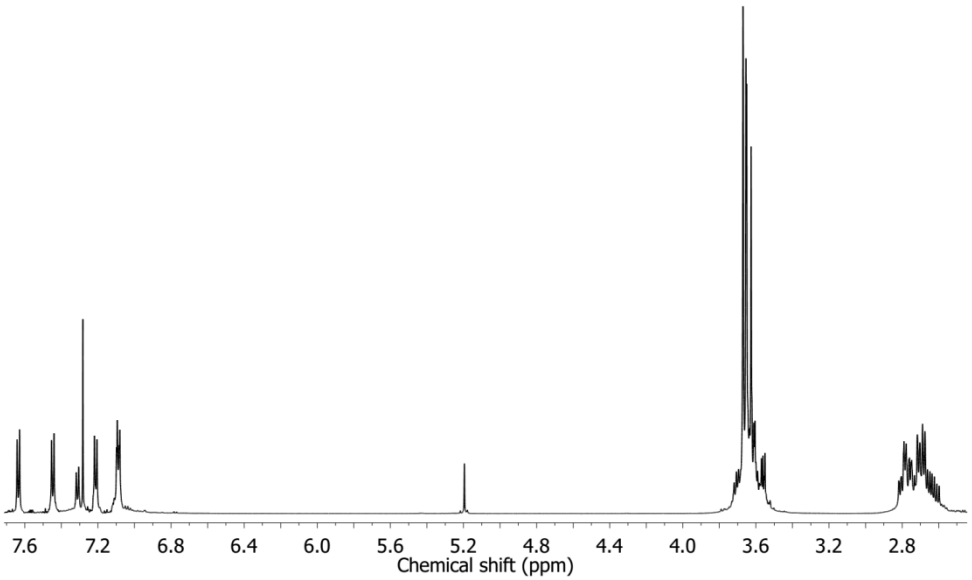


Fig. S53 ^{1}H NMR spectrum of compound **3b**

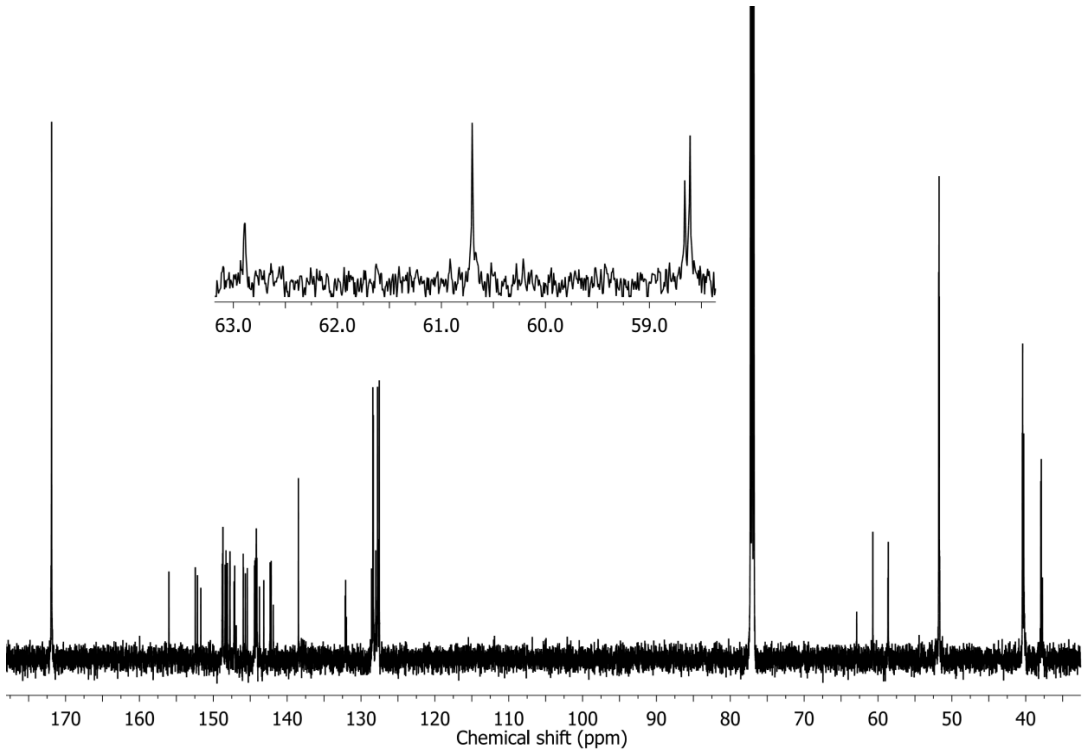


Fig. S54 ^{13}C NMR spectrum of compound **3b**

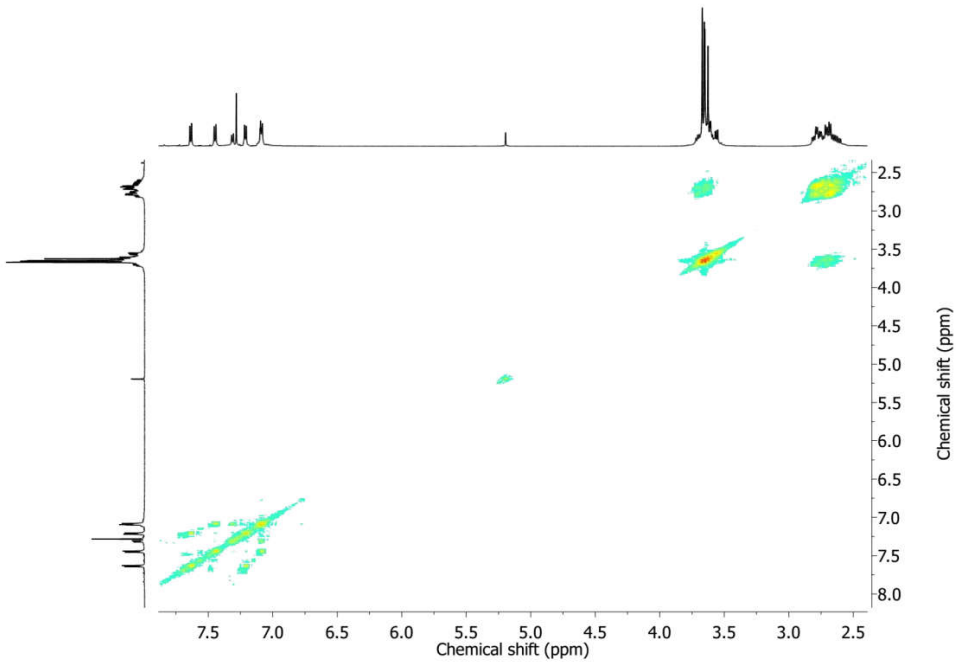


Fig. S55 ^{1}H-^{1}H COSY NMR spectrum of compound **3b**

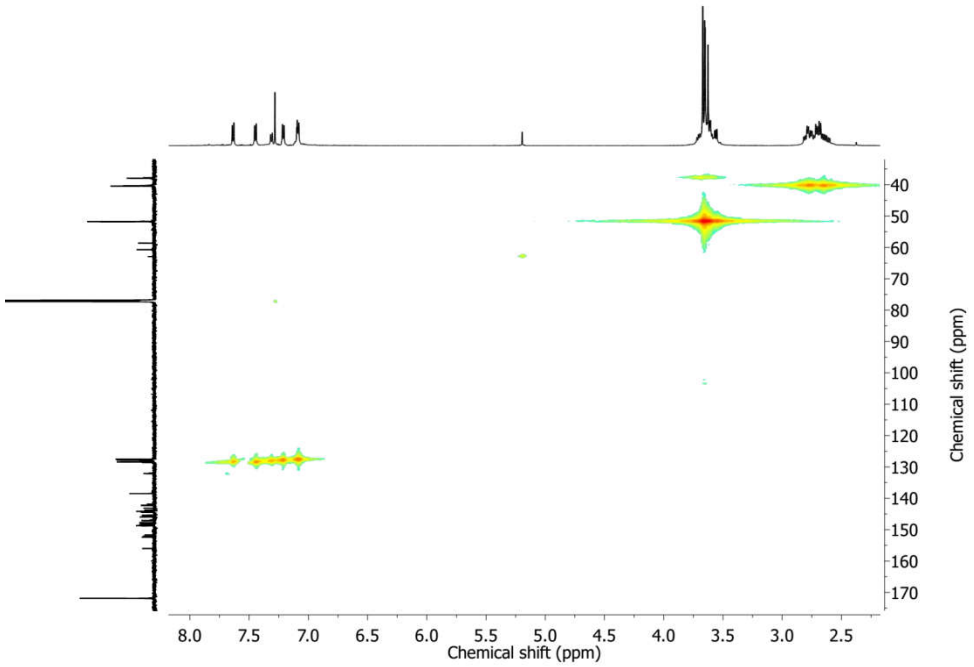


Fig. S56 ^{1}H-^{13}C HSQC NMR spectrum of compound **3b**

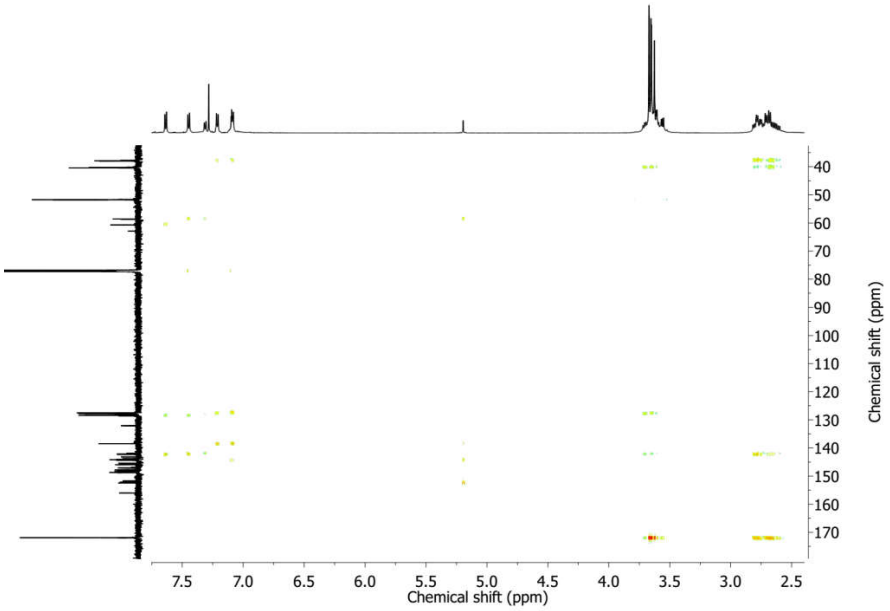


Fig. S57 ^{1}H-^{13}C HMBC NMR spectrum of compound **3b**

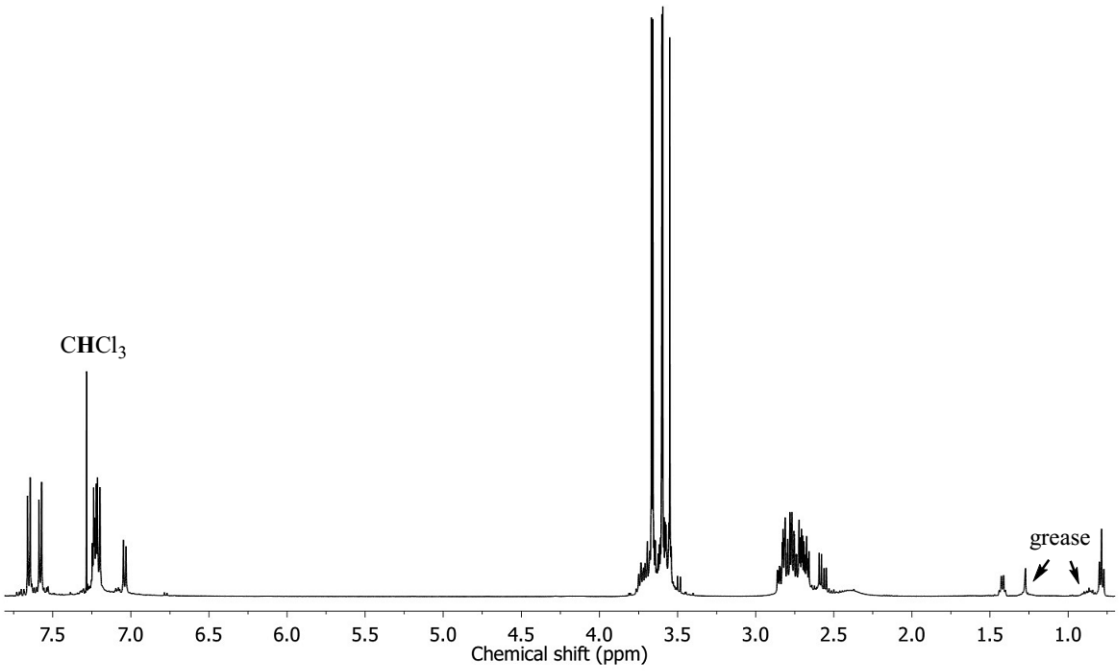


Fig. S58 ^{1}H NMR spectrum of compound **3d**

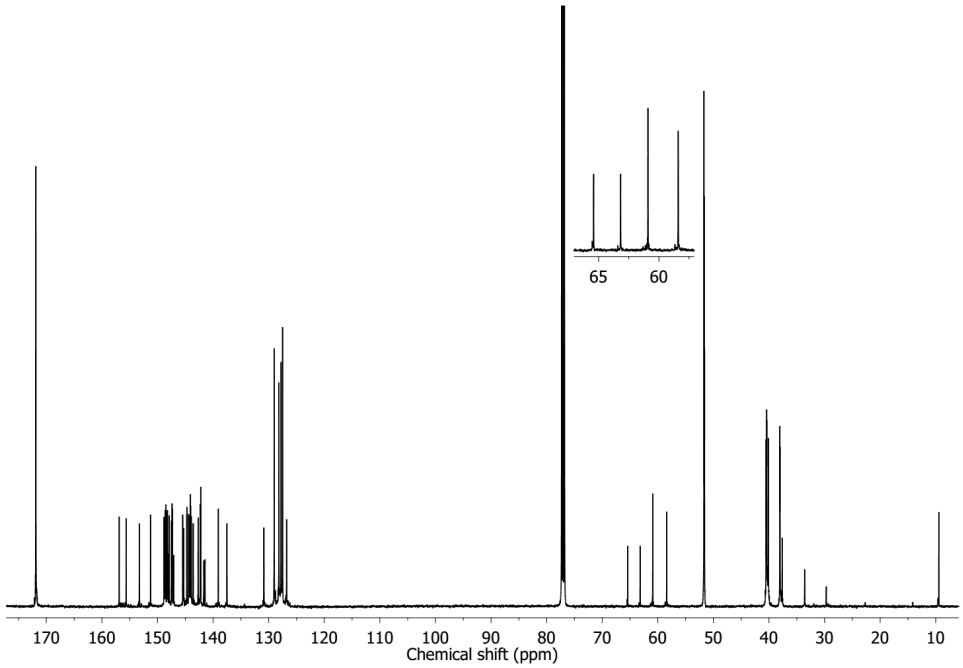


Fig. S59 ^{13}C NMR spectrum of compound **3d**

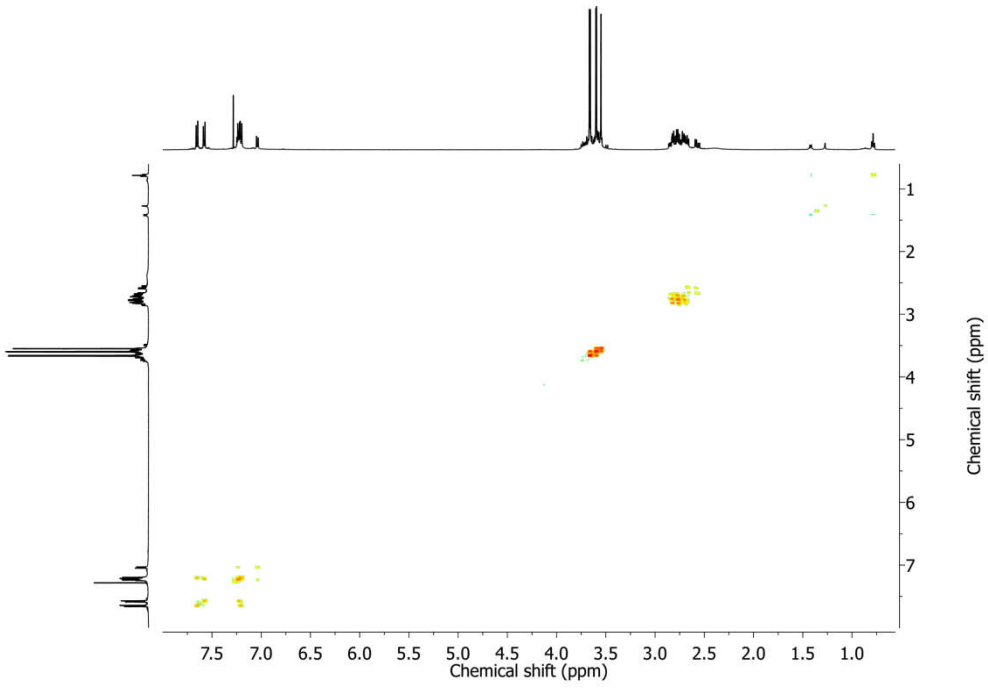


Fig. S60 ^{1}H-^{1}H COSY NMR spectrum of compound **3d**

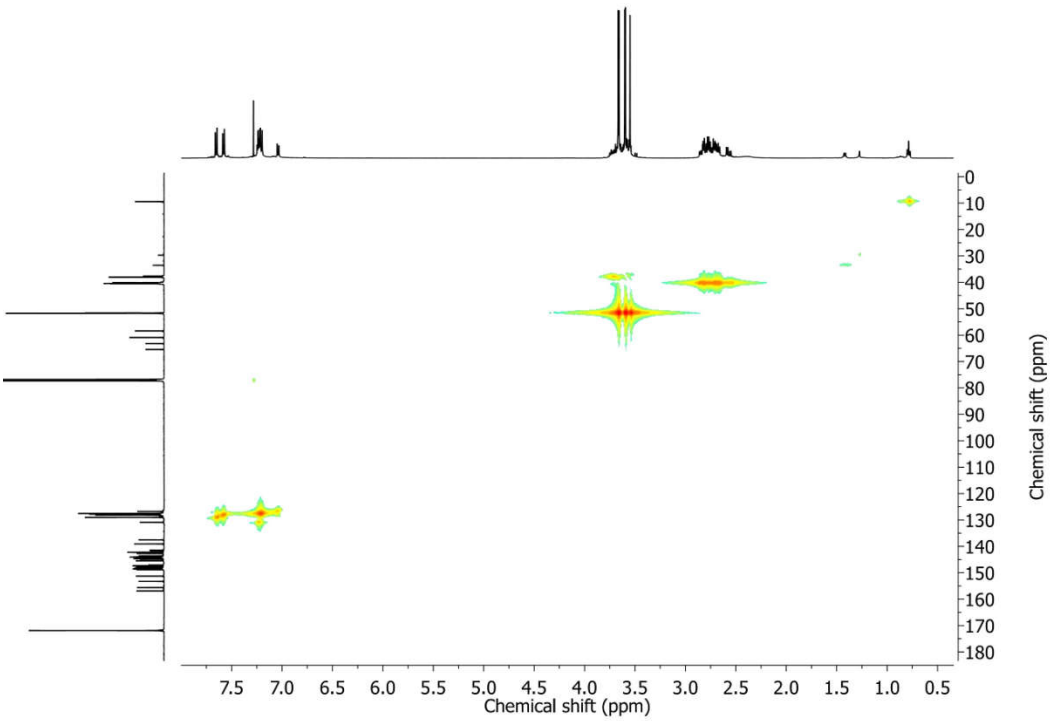


Fig. S61 ^{1}H-^{13}C HSQC NMR spectrum of compound **3d**

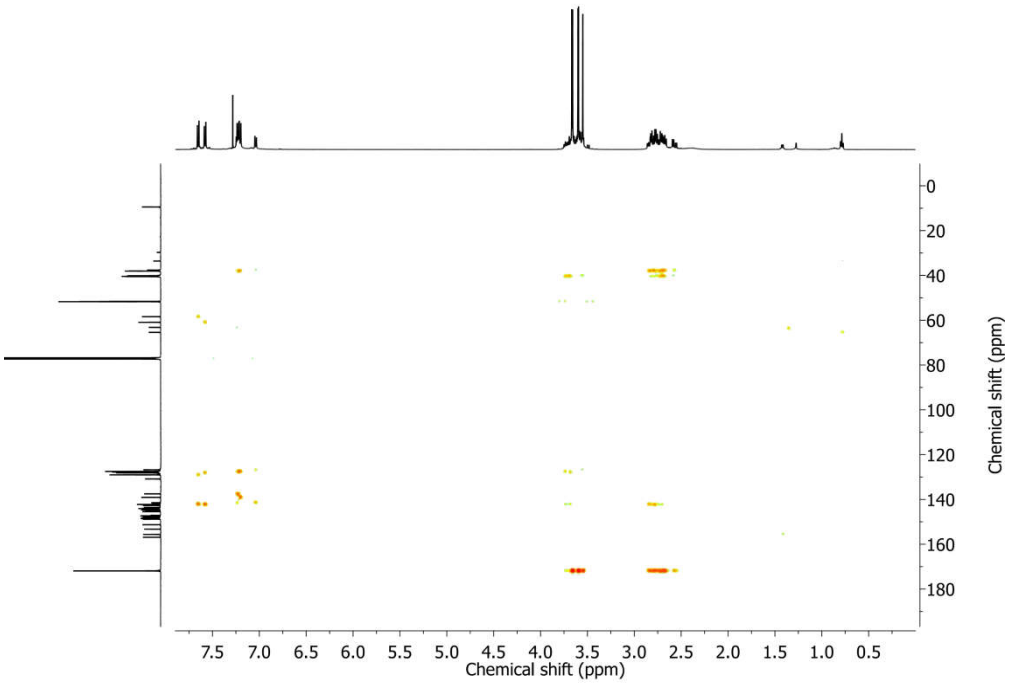


Fig. S62 ^{1}H-^{13}C HMBC NMR spectrum of compound **3d**

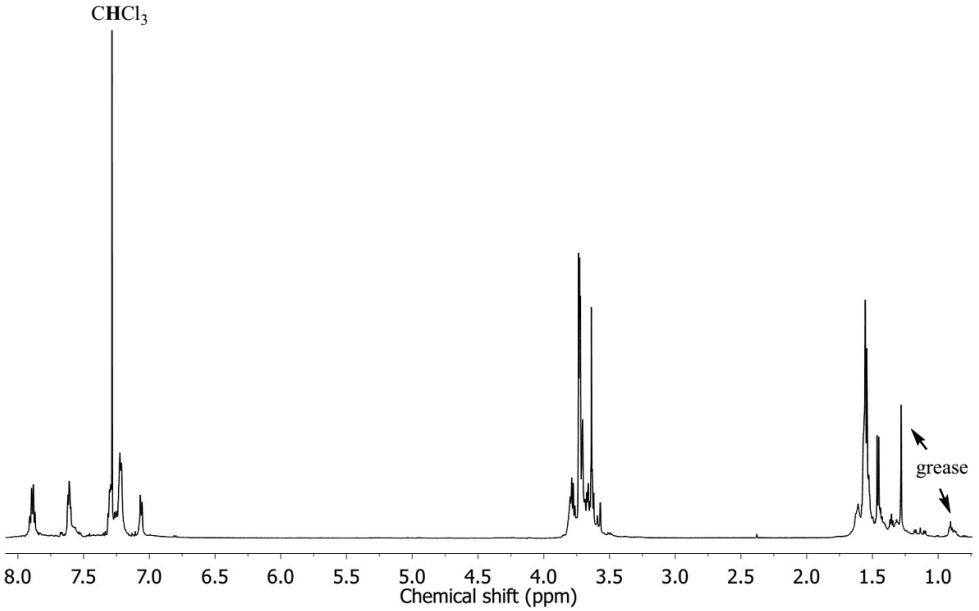


Fig. S63 ^{1}H NMR spectrum of compound **4a**

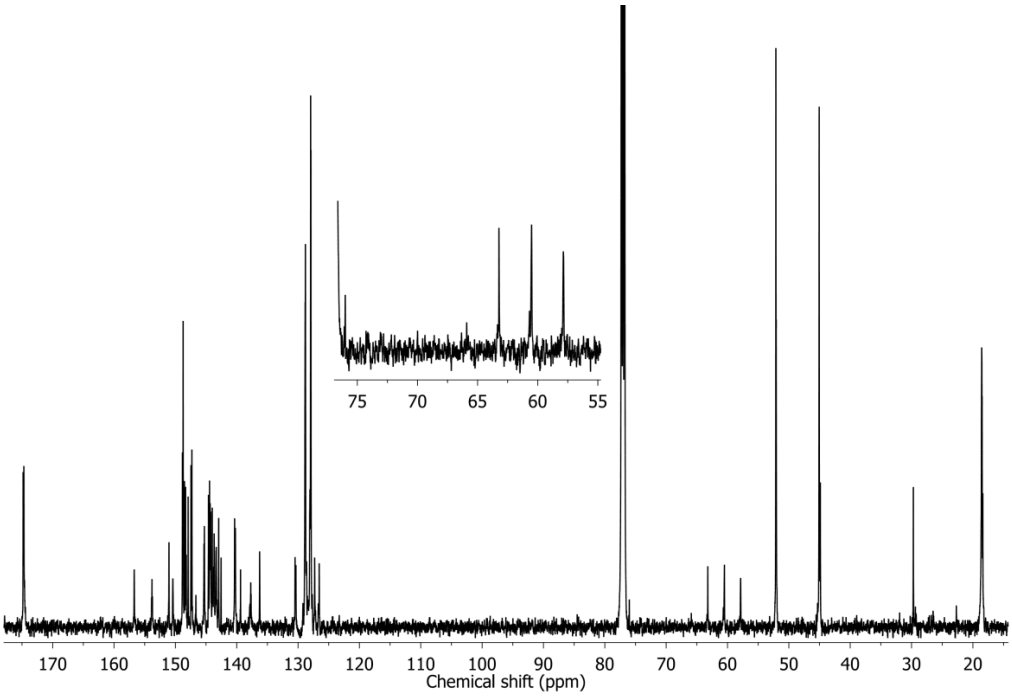


Fig. S64 ^{13}C NMR spectrum of compound **4a**

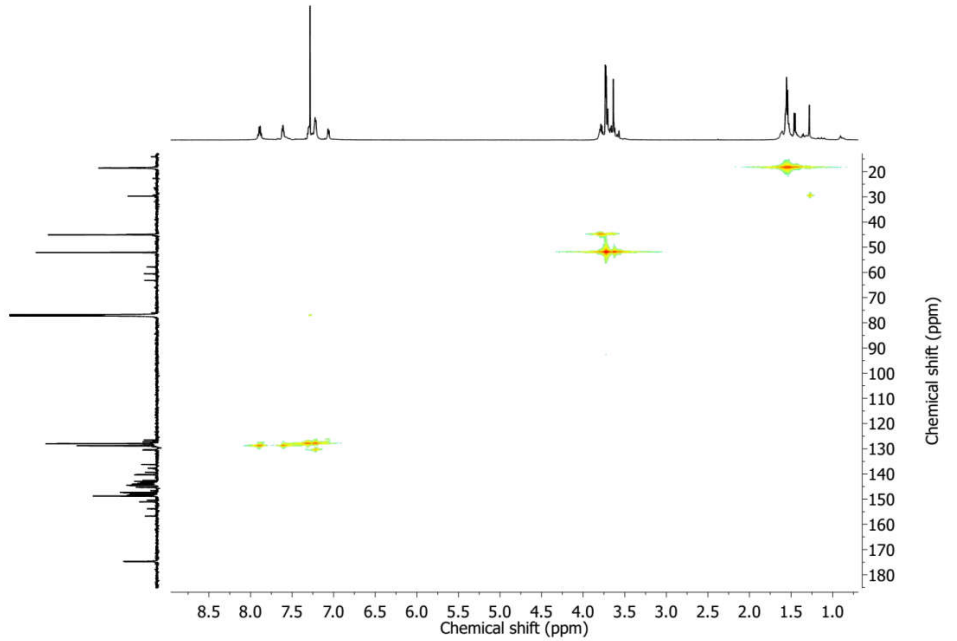


Fig. S65 ^{1}H-^{13}C HSQC NMR spectrum of compound **4a**

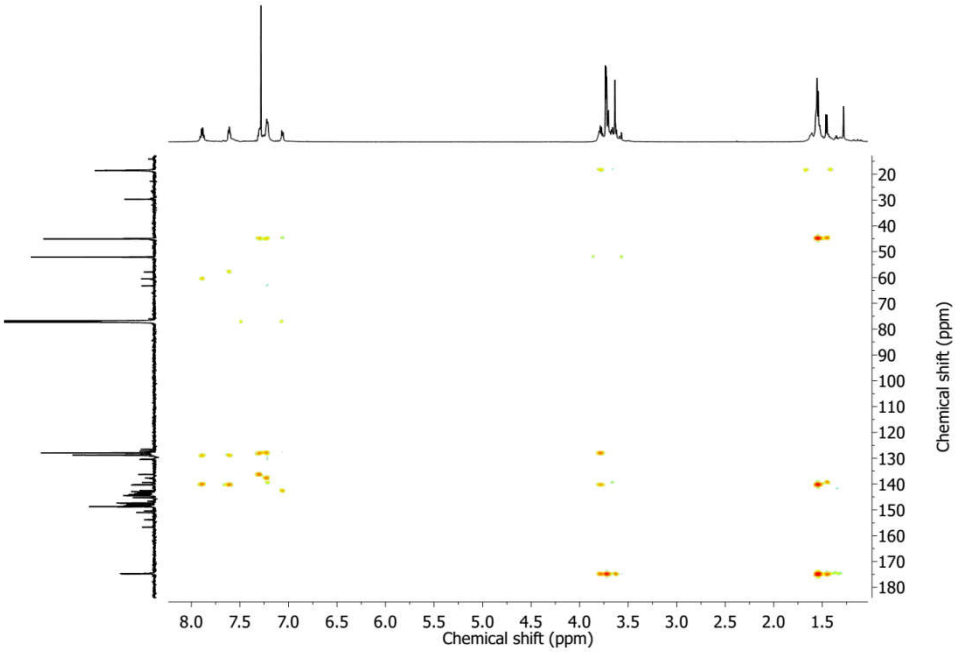


Fig. S66 ^{1}H-^{13}C HMBC NMR spectrum of compound **4a**

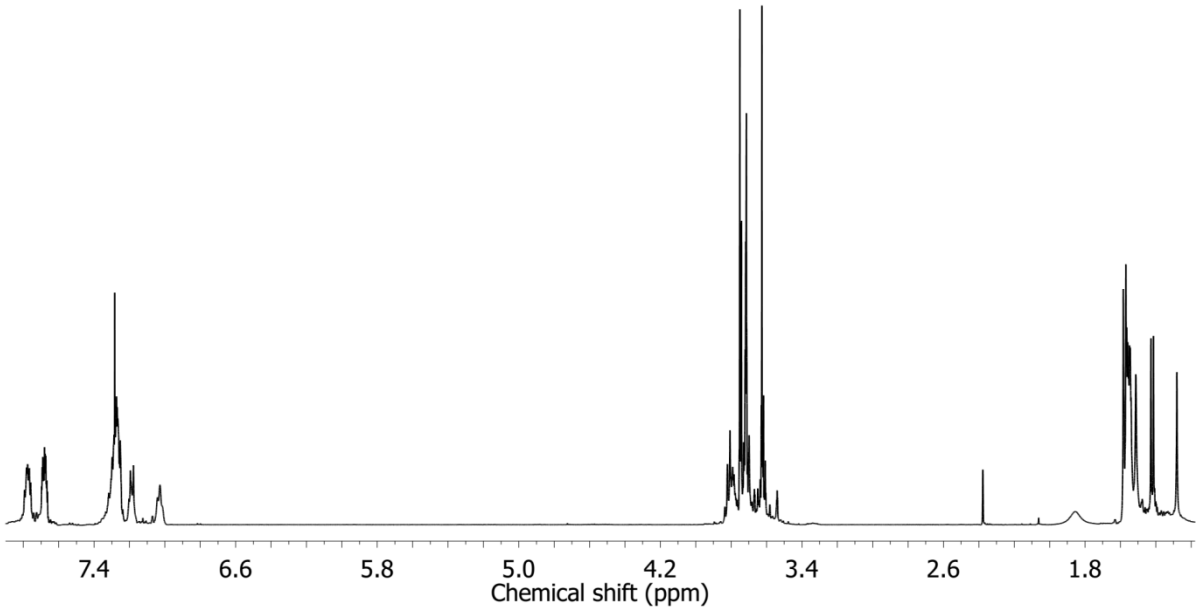


Fig. S67 ^{1}H NMR spectrum of compound **4c**

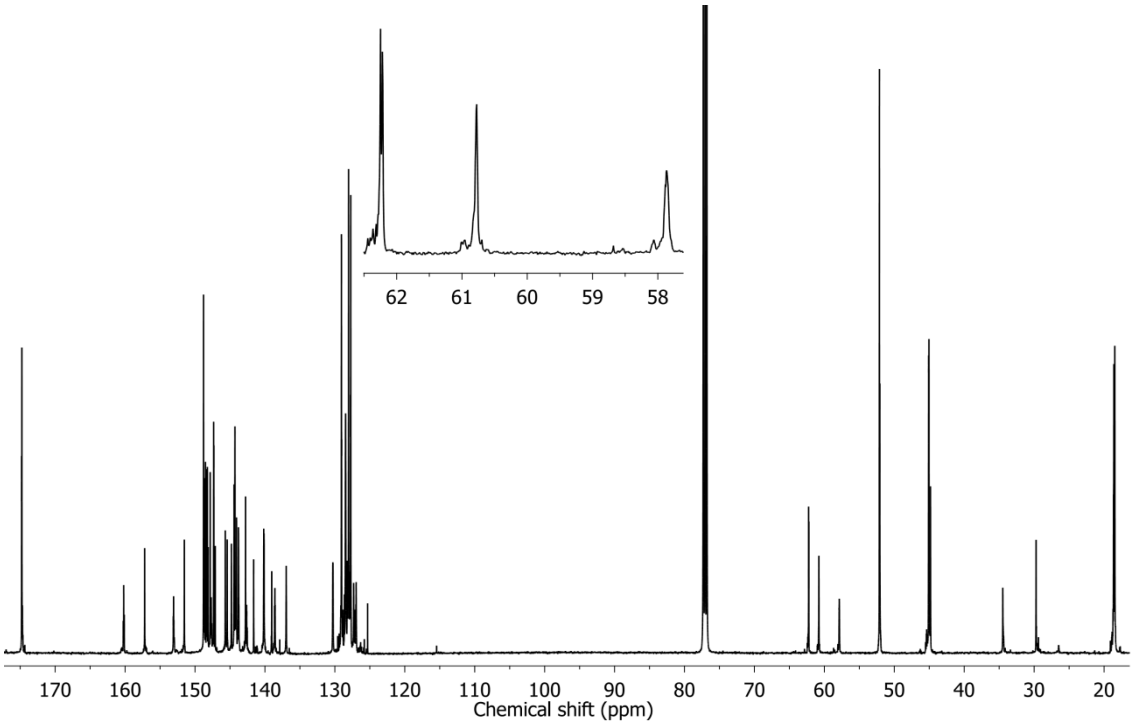


Fig. S68 ^{13}C NMR spectrum of compound **4c**

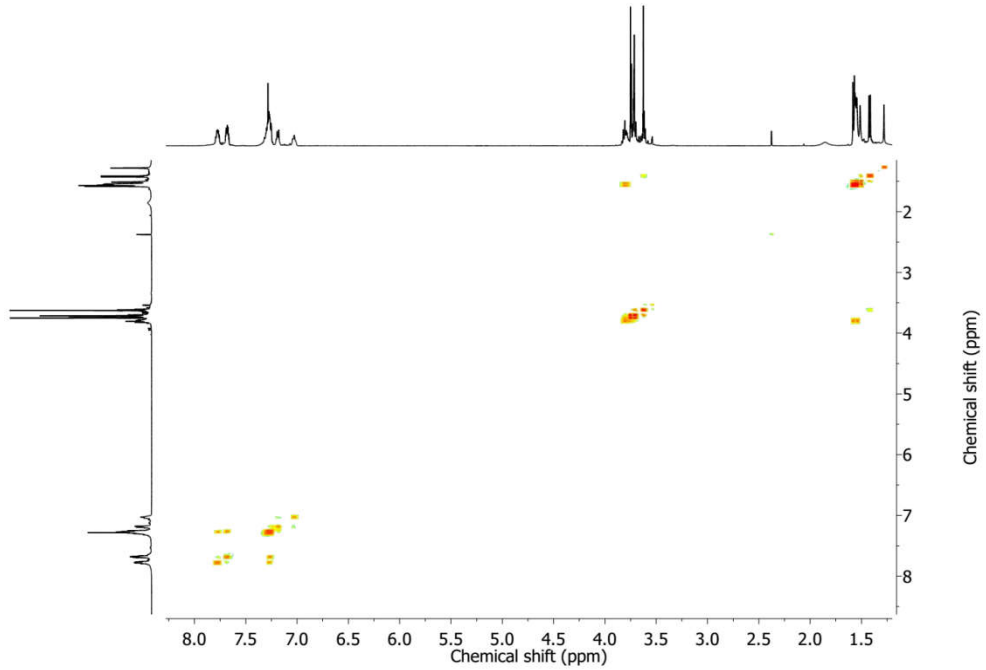


Fig. S69 ^{1}H-^{1}H COSY NMR spectrum of compound **4c**

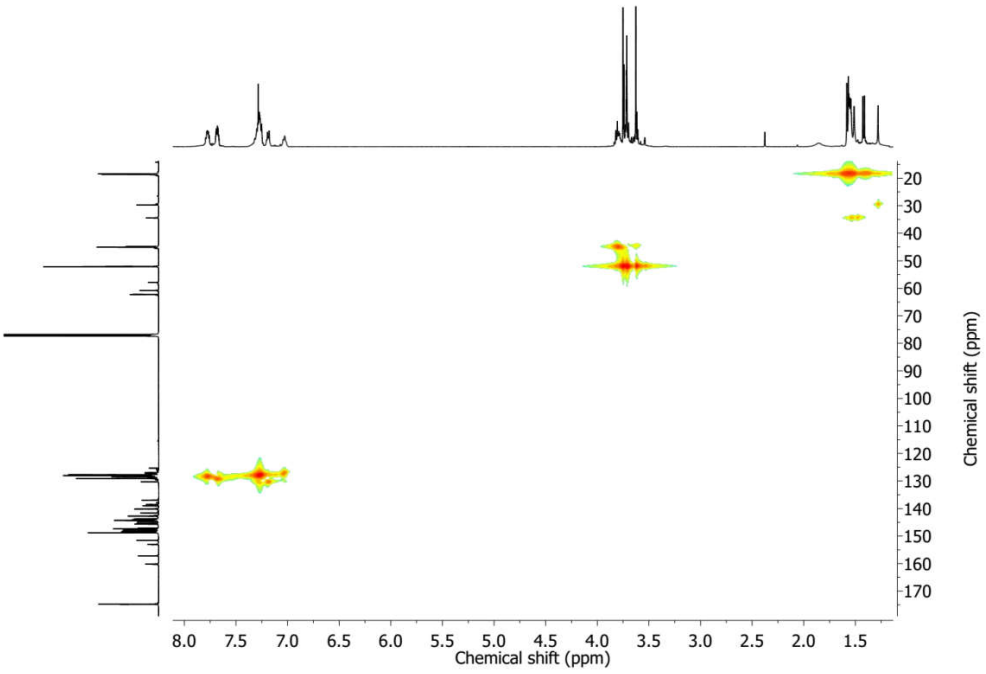


Fig. S70 ^{1}H-^{13}C HSQC NMR spectrum of compound **4c**

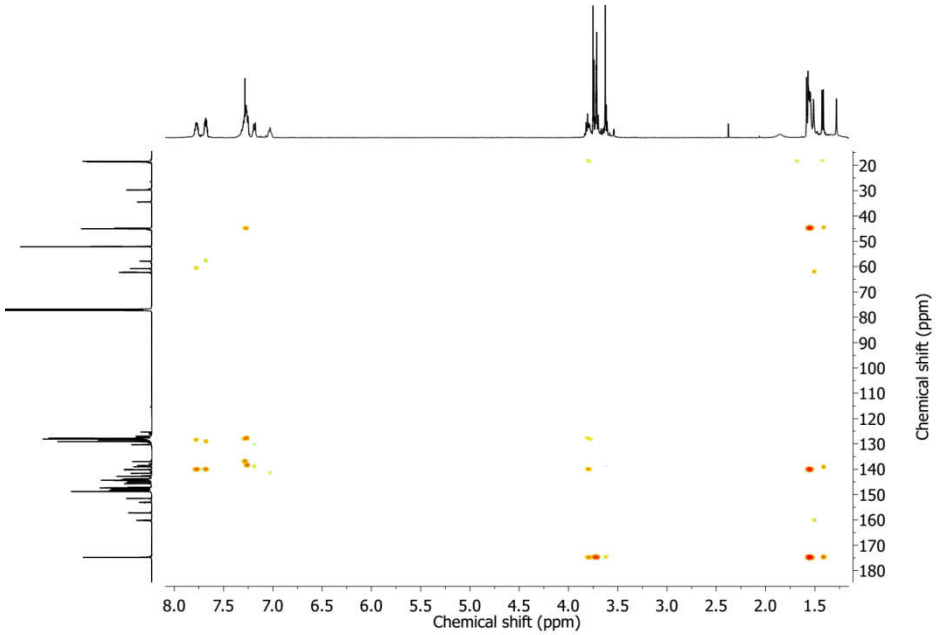


Fig. S71 ^{1}H-^{13}C HMBC NMR spectrum of compound **4c**

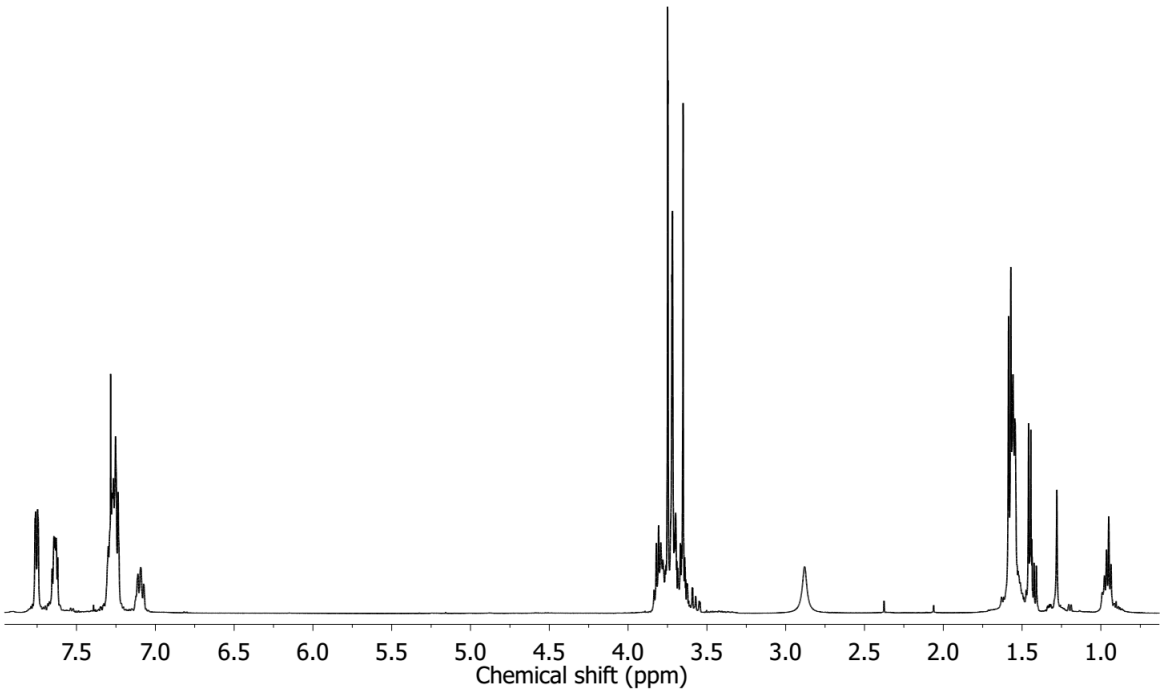


Fig. S72 ^{1}H NMR spectrum of compound **4d**

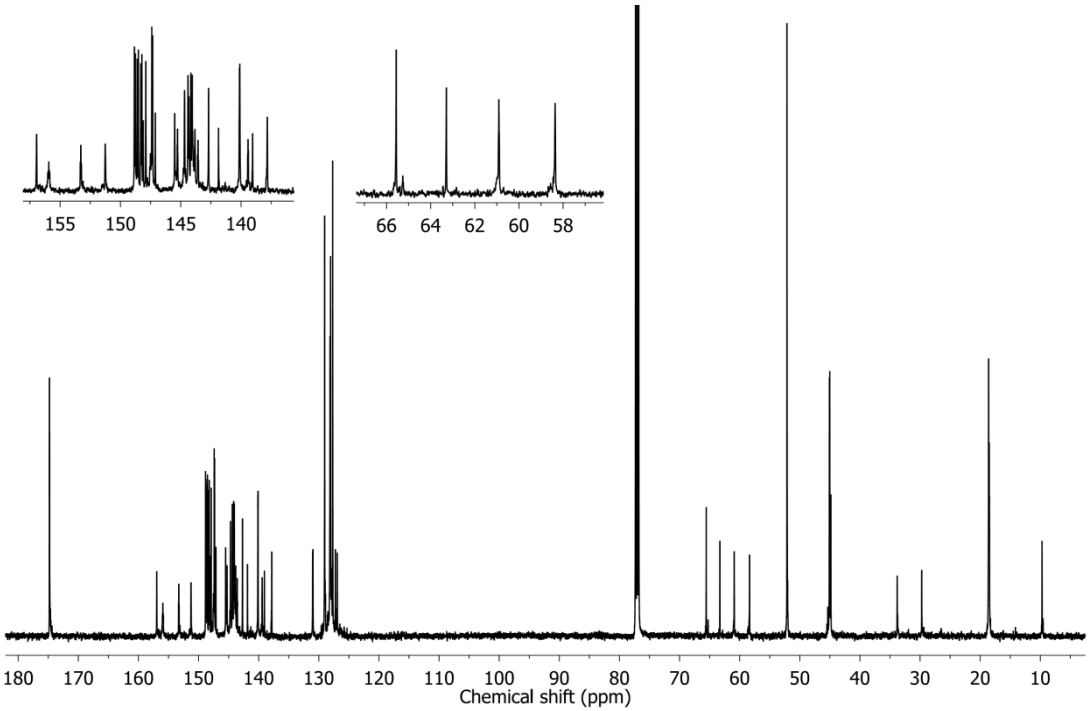


Fig. S73 ^{13}C NMR spectrum of compound **4d**

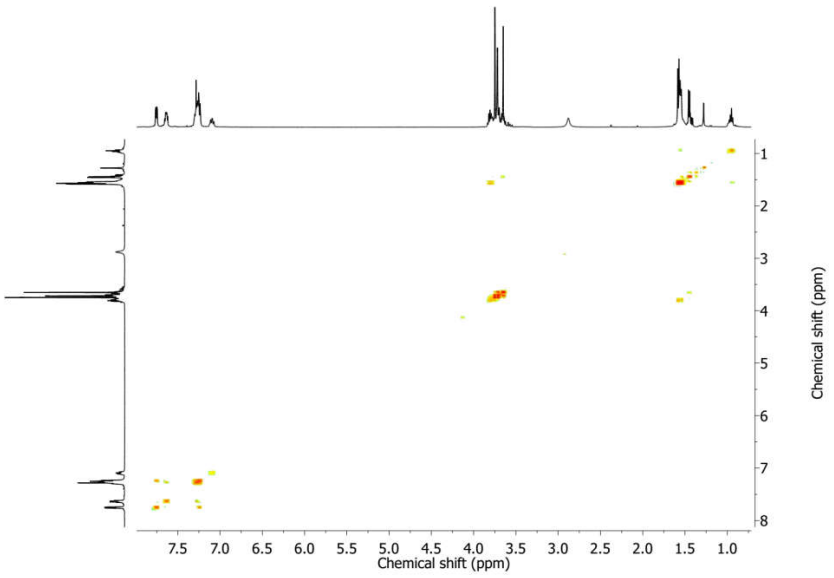


Fig. S74 ^{1}H-^{1}H COSY NMR spectrum of compound **4d**

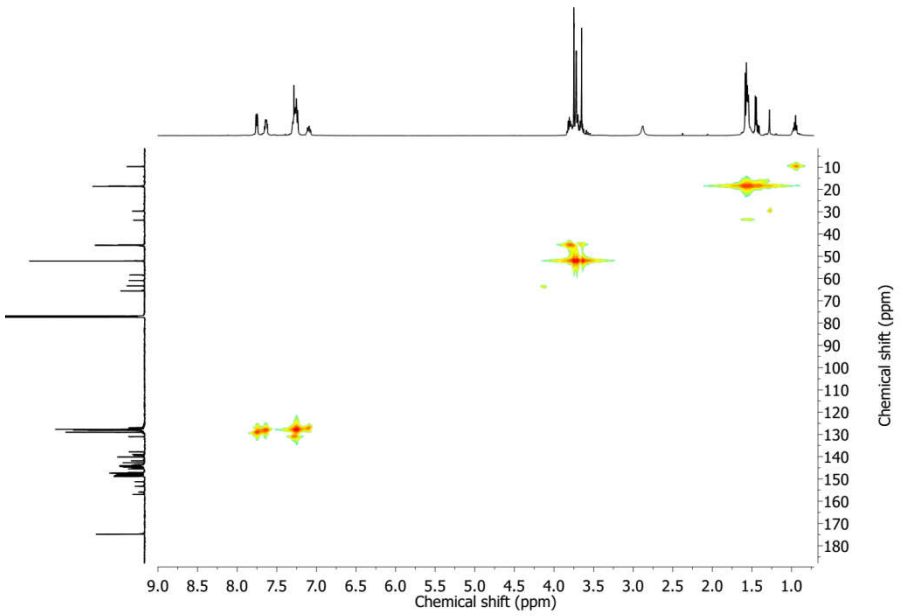


Fig. S75 ^{1}H-^{13}C HSQC NMR spectrum of compound **4d**

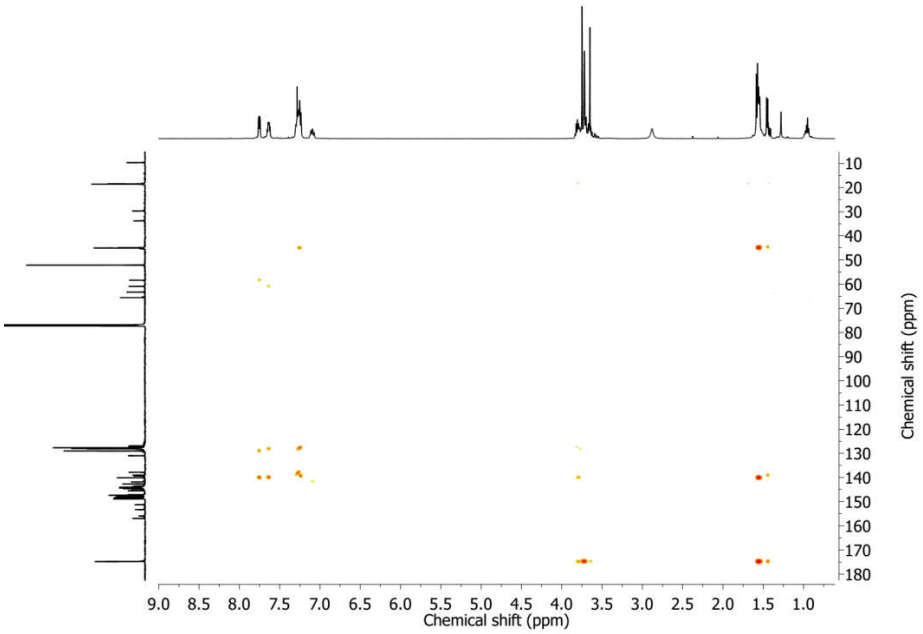


Fig. S76 ^{1}H-^{13}C HMBC NMR spectrum of compound **4d**

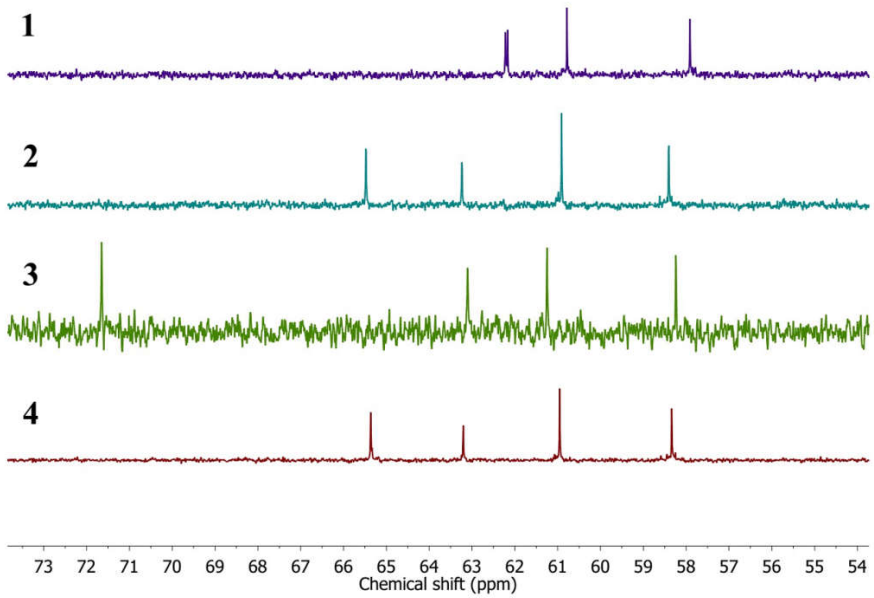


Fig. S77. Comparison of the selected area (Csp^3 atoms of the fullerene cage) in the ^{13}C NMR spectra of compounds $C_{60}R_5Me$ (1), $C_{60}R_5Et$ (2), $C_{60}R_5iPr$ (3), $C_{60}R_5Bu$ (4), ($R=C_6H_4CH_2CH_2COOCH_3$)

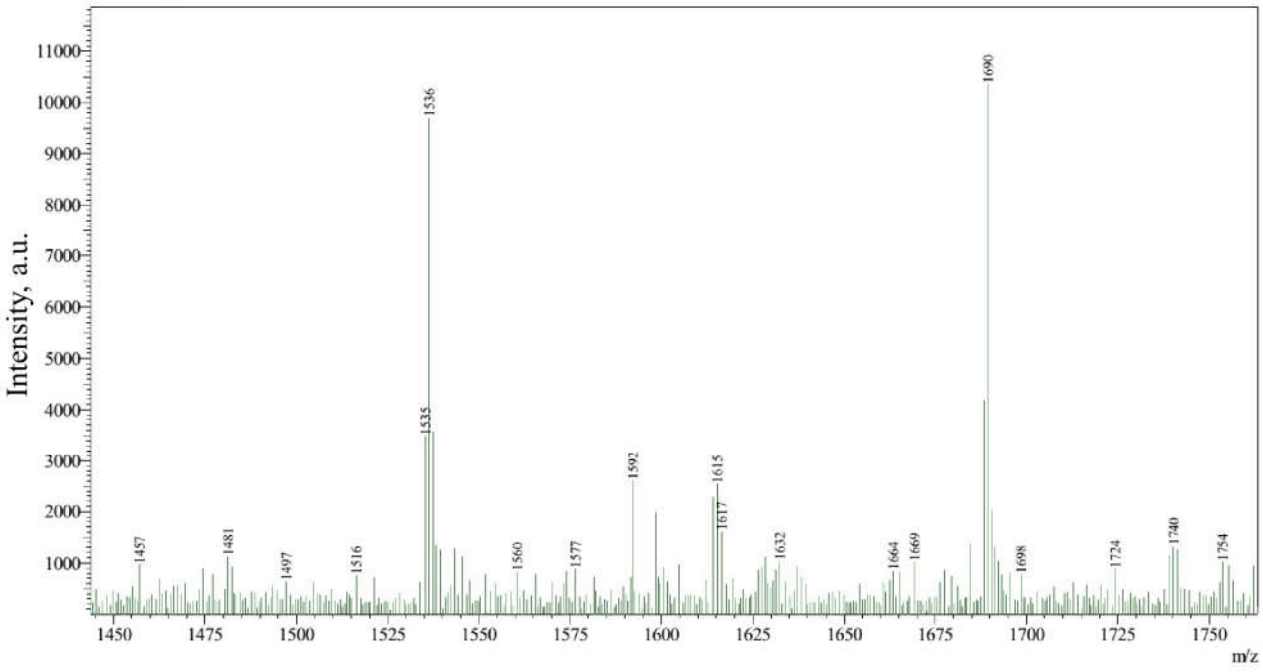


Fig. S78. MS spectra of the reaction mixture of compound **1a** with $P(OPh)_3$

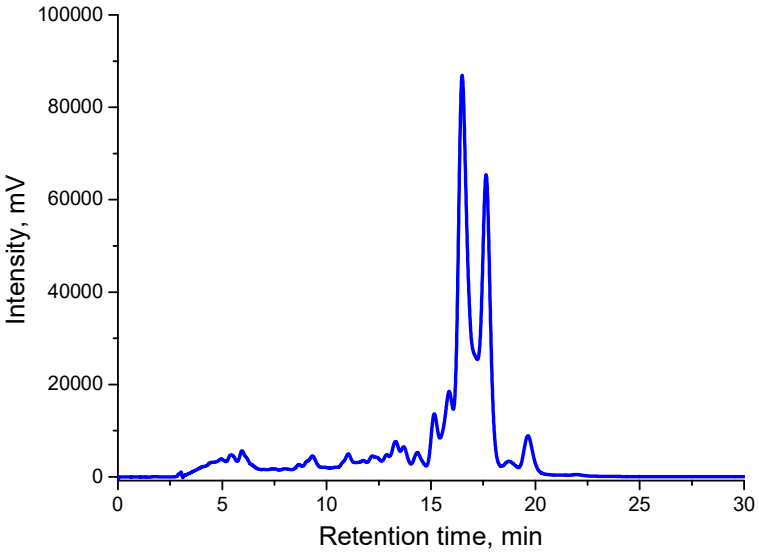


Fig. S79. HPLC profile revealing the formation of a complex mixture of products in the reaction of **1a** with $P(OPh)_3$ (C18 Cosmosil column, elution with toluene/acetonitrile mixtures 20/80 v/v, 30°C, flow rate 1 mL/min)

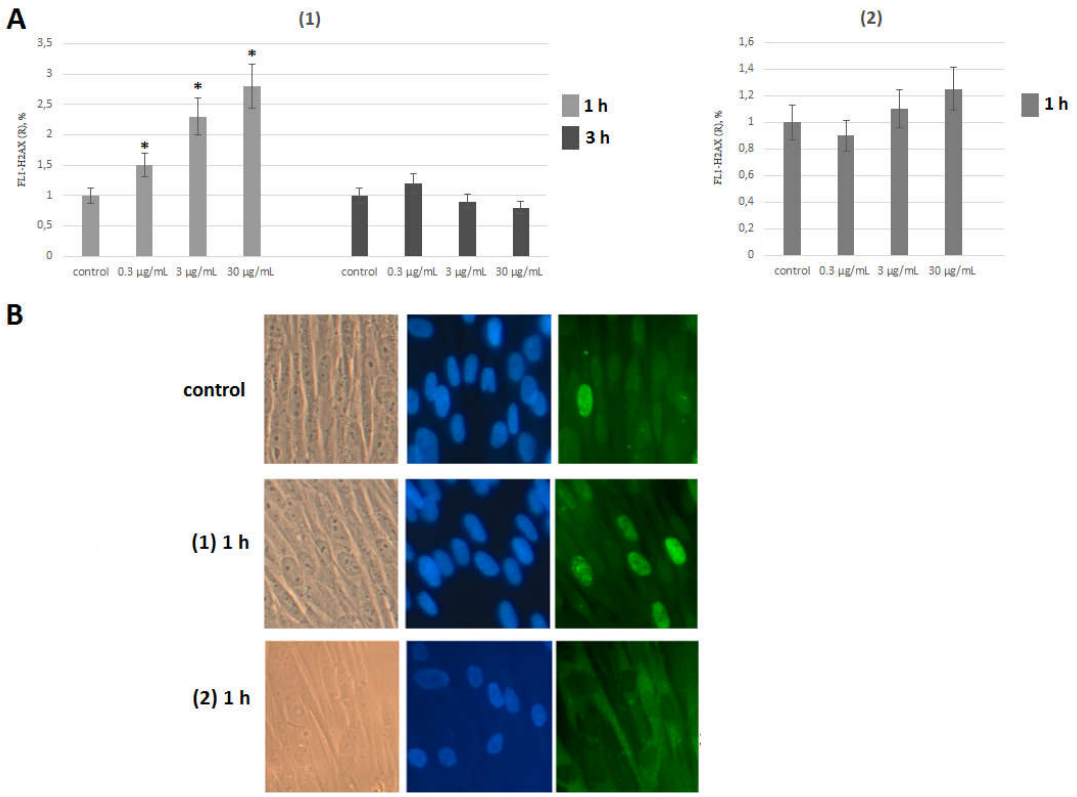


Fig. S80. Compound **A2a** in concentrations of 0.3-30 µg/mL induces DNA damage as reflected by the increased amount of double strand breaks (DSB). A - Flow cytometry detection of DSB in cells exposed to compounds **A2a** (1) or **A2c** (2), (∗) - $p<0.01$. B - Fluorescence microscopy detection of DSB in cells exposed to compounds **A2a** (1) and compound **A2c** (2); cells stained with DAPI and anti-γH2AX antibodies, (∗) - $p<0.01$, nonparametric U test.

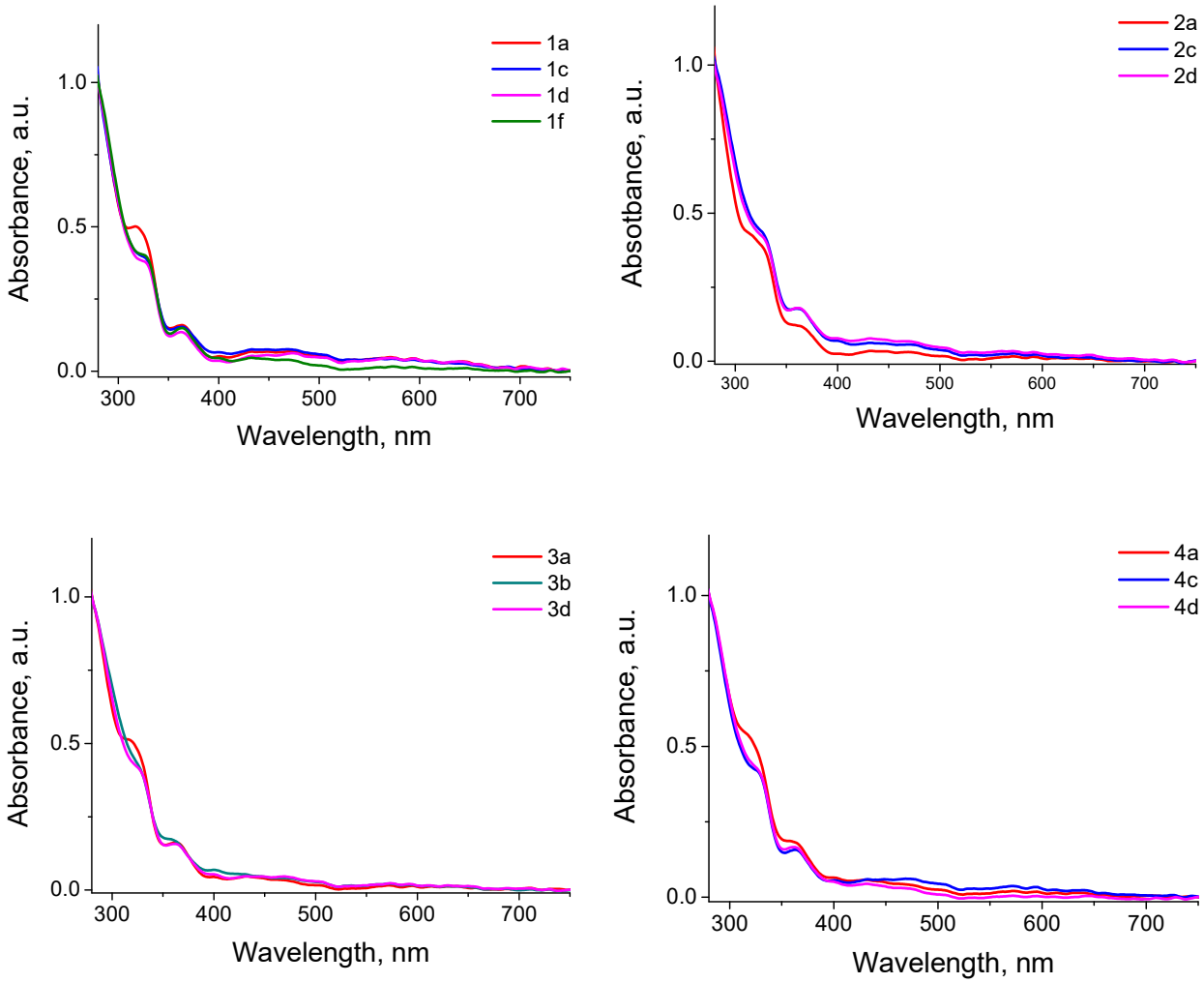


Fig. S81. UV-Vis spectra of some of the synthesized fullerene derivatives