

Supporting Information

Spatially Resolved Fluoroalkylation and Alkylation of Graphene by Direct Laser Writing

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Materials

CVD graphene on a 1×1 cm² polymethyl methacrylate (PMMA) substrate was purchased from ACS Material Co. (USA). All other chemicals were purchased from Sigma Aldrich Co. (Germany) and used without further treatment. Si/SiO₂ wafers (300 nm oxide layer) were purchased from Fraunhofer-Institute in Erlangen. Before use, the Si/SiO₂ wafers were cleaned by immersing them in isopropanol for ultrasonic treatment (300 W) for 5 min.

Raman Spectroscopy

The Raman spectroscopic characterization was performed on a Horiba Jobin Yvon LabRAM Aramis. A laser (Olympus LMPlanFI50x, NA 0.50) with an excitation wavelength of 532 nm, intensity of 8 mW, and a spot size of ~ 1 μm was used. The spectrometer was calibrated by using crystalline graphite. Spectral data was obtained through a motorized x-y table in a continuous line scan mode (SWIFT-module). The temperature-dependent Raman measurements were performed in a LinkAM stage THMS 600, equipped with a liquid nitrogen pump MS94 for temperature stabilization under a constant flow of nitrogen. The measurements were carried out on Si/SiO₂ wafers with a heating rate of 10 °C/min.

The Statistical Raman mappings were carried out on a confocal Raman microscope (WITec, alpha 300RA) using the green laser with an excitation wavelength of 532 nm, integration time of 1s, and the intensity of 2 mW.

Experimental Section

All chemicals used were of analytical grade and purchased from Aldrich Co. The solvents were purified before use by distillation. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel (neutral, fluorescence indicator F254) precoated plates. ^1H NMR spectra were recorded at frequencies of 600 MHz (Bruker Ascend 600, probe head CPDCH600S3 C/H-D-05Z), carbon-13 spectra at 151 MHz. The NMR spectra of the fluorinated compounds were recorded at Bruker Ascend 500, probe head PATBO500S1BB-H/F-D-05ZFB, with frequencies of 471 MHz (^{19}F) and 126 MHz (^{13}C). All chemical shifts of ^1H and ^{13}C are given in ppm and have been converted to the δ scale and are referenced against the DMSO signal as an internal standard. The ^{19}F shifts are referenced against an externally measured C_6F_6 probe, $\delta = -164.9$ ppm.

Synthesis of silver(I) perfluorocarboxylates

According to known procedures [1-3], silver(I) carbonate (7.4 mMol - 21.3 mMol) reacted with the equimolar amount of perfluorinated carboxylic acids (7.4 mMol - 21.3 mMol) under room temperature and in the absence of light in an aqueous ethanolic solution within 24 hours. After filtration, the precipitate was washed with ethanol and dried. (G_{F1} - G_{F8}).

Silver(I) perfluoropropanoate, $\text{C}_3\text{F}_5\text{-COOAg}$ [509-09-1] (G_{F1})

Yield 4.78 g (80 %), δ_{C} (126 MHz, $\text{DMSO-}d_6$) 107.26, 119.13, 158.81 ppm; δ_{F} (471 MHz, $\text{DMSO-}d_6$) -84.06 (3F), -120.40 (2F) ppm.

Silver(I) perfluorobutanoate, $\text{C}_3\text{F}_7\text{-COOAg}$ [3794-64-7] (G_{F2})

Yield 5.61 g (98 %), δ_{C} (126 MHz, $\text{DMSO-}d_6$) 108.78, 108.91, 117.81, 158.43 ppm; δ_{F} (471 MHz, $\text{DMSO-}d_6$) -82.46 (3F), -117.87 (2F), -128.52 (2F) ppm.

Silver(I) perfluoropentanoate, $\text{C}_4\text{F}_9\text{-COOAg}$ [2795-30-4] (G_{F3})

Yield 4.65 g (94 %), δ_{C} (126 MHz, $\text{DMSO-}d_6$) 108.47, 109.22, 110.57, 117.21, 158.52 ppm; δ_{F} (471 MHz, $\text{DMSO-}d_6$) -82.92 (3F), -117.27 (2F), -125.01 (2F), -127.79 (2F) ppm.

Silver(I) perfluorohexanoate, $\text{C}_5\text{F}_{11}\text{-COOAg}$ [336-02-7] (G_{F4})

Yield 4.62 g (98 %), δ_C (126 MHz, DMSO- d_6) 108.13, 109.28, 110.21, 111.04, 116.90, 158.33 ppm; δ_F (471 MHz, DMSO- d_6) -82.70 (3F), -117.09 (2F), -124.39 (2F), -124.60 (2F), -127.29 (2F) ppm.

Silver(I) perfluoroheptanoate, C₆F₁₃-COOAg [424-05-5] (G_{F5})

Yield 4.26 g (94 %), δ_C (126 MHz, DMSO- d_6) 108.00, 109.31, 109.03, 110.68, 111.13, 116.73, 158.35 ppm; δ_F (471 MHz, DMSO- d_6) -82.68 (3F), -117.07 (2F), -123.86 (2F), -124.20 (2F), -125.03 (2F), -128.17 (2F) ppm.

Silver(I) perfluorooctanoate, C₇F₁₅-COOAg [335-93-3] (G_{F6})

Yield 4.07 g (92 %), δ_C (126 MHz, DMSO- d_6) 107.89, 109.32, 109.81, 110.38, 110.74, 111.14, 116.62, 158.34 ppm; δ_F (471 MHz, DMSO- d_6) -82.67 (3F), -117.08 (2F), -123.70 (2F), -124.23 (b, 2 x 2F), -124.93 (2F), -128.18 (2F) ppm.

Silver(I) perfluorononanoate, C₈F₁₇-COOAg [7358-16-9] (G_{F7})

Yield 3.38 g (78 %), δ_C (126 MHz, DMSO- d_6) 107.86, 109.32, 109.72, 110.29, 110.46, 110.78, 111.17, 116.58, 158.32 ppm; δ_F (471 MHz, DMSO- d_6) -82.67 (3F), -117.09 (2F), -123.68 (2F), -124.16 (b, 3x2F), -124.91 (2F), -128.17 (2F) ppm.

Silver(I) perfluorodecanoate, C₉F₁₉-COOAg [5784-82-7] (G_{F8})

Yield 2.58 g (47 %), δ_C (126 MHz, DMSO- d_6) 107.82, 109.34, 109.67, 110.18, 110.33, 110.47, 110.78, 111.14, 116.54, 158.43 ppm; δ_F (471 MHz, DMSO- d_6) -82.96 (3F), -117.20 (2F), -123.81 (2F), -124.27 (b, 4x2F), -125.06 (2F), -128.38 (2F) ppm.

Synthesis of silver(I) carboxylates

According to known procedure ^[4,5], carboxylic acid (26.0 mMol – 48.3 mMol) was dissolved in the absence of light in the equimolar amount of 1M aqueous KOH (26.0 – 48.3 mMol), followed by the addition of an equimolar amount of 1M aqueous AgNO₃ solution. After 24 h stirring and subsequent filtration under vacuum, the precipitate was washed with ice cold water (55 mL – 90 mL) and dried. (G_{H1} – G_{H6}).

Silver(I) propanoate, C₂H₅-COOAg [5489-14-5] (G_{H1})

Yield 5.67 g (65 %), δ_H (600 MHz, DMSO- d_6) 0.99 (t, *J* 7.6 Hz, 3H, CH₃), 2.09 (q, *J* 7.6, 2H, CH₂) ppm; δ_C (151 MHz, DMSO- d_6) 11.29, 29.63, 177.72 ppm.

Silver(I) butanoate, C₃H₇-COOAg [5076-24-4] (G_{H2})

Yield 7.00 g (79 %), δ_{H} (600 MHz, DMSO-*d*₆) 0.86 (t, *J* 7.4 Hz, 3H, CH₃), 1.51 (tq (*pseudo*-hext), *J* 7.4 Hz, 2H, CH₂-CH₃), 2.08 (t, *J* 7.3, 2H, OOC-CH₂) ppm; δ_{C} (151 MHz, DMSO-*d*₆) 14.19, 19.71, 38.75, 176.96 ppm.

Silver(I) pentanoate, C₄H₉-COOAg [35363-46-3] (G_{H3})

Yield 6.50 g (81 %), δ_{H} (600 MHz, DMSO-*d*₆) 0.85 (t, *J* 7.4 Hz, 3H, CH₃), 1.27 (m, 2H, CH₂), 1.47 (m, 2H, CH₂), 2.09 (t, *J* 7.4, 2H, OOC-CH₂) ppm; δ_{C} (151 MHz, DMSO-*d*₆) 13.88, 22.21, 28.67, 36.36, 177.10 ppm.

Silver(I) hexanoate, C₅H₁₁-COOAg [32461-90-8] (G_{H4})

Yield 5.50 g (77 %), δ_{H} (600 MHz, DMSO-*d*₆) 0.85 (t, *J* 7.1 Hz, 3H, CH₃), 1.25 (m, 4H, 2xCH₂), 1.49 (m, 2H, CH₂), 2.07 (t, *J* 7.4, 2H, OOC-CH₂) ppm; δ_{C} (151 MHz, DMSO-*d*₆) 13.95, 22.04, 26.18, 31.42, 36.61, 177.10 ppm.

Silver(I) heptanoate, C₆H₁₃-COOAg [32461-91-9] (G_{H5})

Yield 5.46 g (73 %), δ_{H} (600 MHz, DMSO-*d*₆) 0.84 (t, *J* 7.0 Hz, 3H, CH₃), 1.24 (m, 6H, 3xCH₂), 1.47 (m, 2H, CH₂), 2.07 (t, *J* 7.4, 2H, OOC-CH₂) ppm; δ_{C} (151 MHz, DMSO-*d*₆) 13.96, 22.08, 26.24, 28.78, 31.21, 36.29, 177.78 ppm.

Silver(I) octanoate, C₇H₁₅-COOAg [24927-67-1] (G_{H6})

Yield 6.49 g (91 %), δ_{H} (600 MHz, DMSO-*d*₆) 0.86 (t, *J* 7.0 Hz, 3H, CH₃), 1.26 (m, 8H, 4xCH₂), 1.49 (m, 2H, CH₂), 2.05 (t, *J* 7.4, 2H, OOC-CH₂) ppm; δ_{C} (151 MHz, DMSO-*d*₆) 13.67, 21.83, 26.24, 28.39, 28.94, 31.06, 36.28, 176.83 ppm.

2D-patterning of graphene via laser-writing. The Si/SiO₂ wafer was first cleaned by immersing it in isopropanol, followed by ultrasonic treatment (300 W) for 5 min. Then, a graphene monolayer was deposited to this wafer by a wet transfer technique. Here, the PMMA-supported graphene, floating on top of a water surface, was fished onto the prepared Si/SiO₂ wafer. The PMMA layer was easily removed by dissolution with acetone overnight. Afterward, the wafers were immersed in a solution of respective reagents (9 mmol/mL, see below for details) dissolved in isopropanol for 30 min. Subsequently, a drop of the solution was applied onto the wafer, respectively, resulting

in the generation of a thin and homogeneous crystalline film atop the graphene by evaporating the solvent with argon. The laser writing procedure was carried out using a green laser ($\lambda_{exc} = 532 \text{ nm}$, 50x objective magnification, irradiation time 1s, 8mW) for the photolysis of the reactants. This process generates highly reactive fluoroalkylated and alkylated radicals that selectively bound to the underlying graphene exclusively in the laser-irradiated areas (Figure S1 and S2). Finally, washing away the excess reagents with isopropanol gives rise to the target-pattered graphene architectures. The employed photoactive compounds are: (I) fluoroalkyl silver carboxylates, including $C_3AgF_5O_2$, $C_4AgF_7O_2$, $C_5AgF_9O_2$, $C_6AgF_{11}O_2$, $C_7AgF_{13}O_2$, $C_8AgF_{15}O_2$, $C_8AgF_{15}O_2$, and $C_8AgF_{15}O_2$, and (II) alkyl silver carboxylates containing $C_3H_5AgO_2$, $C_4H_7AgO_2$, $C_5H_9AgO_2$, $C_6H_{11}AgO_2$, $C_7H_{13}AgO_2$, and $C_8H_{15}AgO_2$.

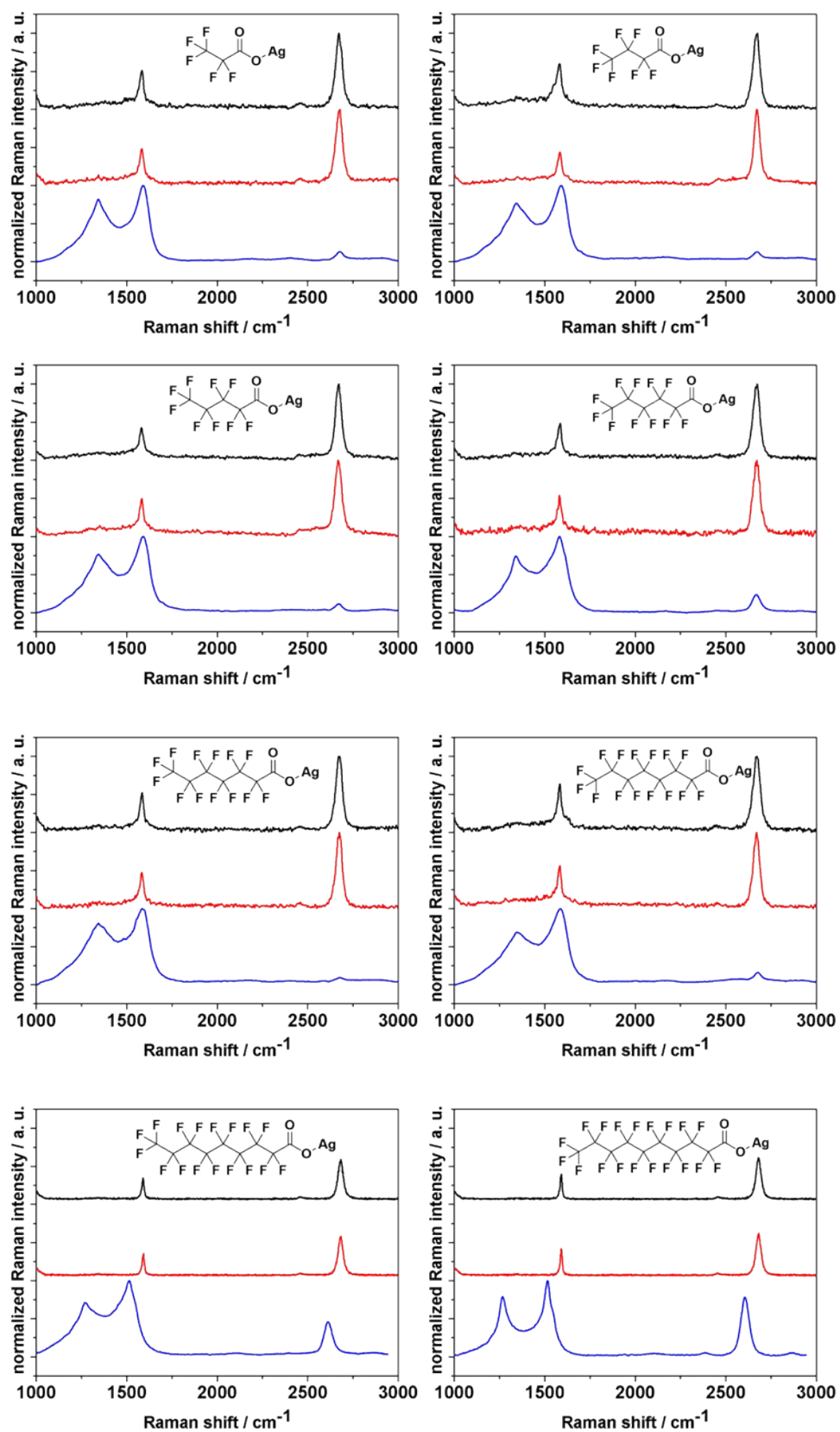


Figure S1. Normalized mean Raman spectra of pristine graphene (black line), non-irradiated areas (red line), and irradiated areas of samples G_{F1} - G_{F8} (blue line).

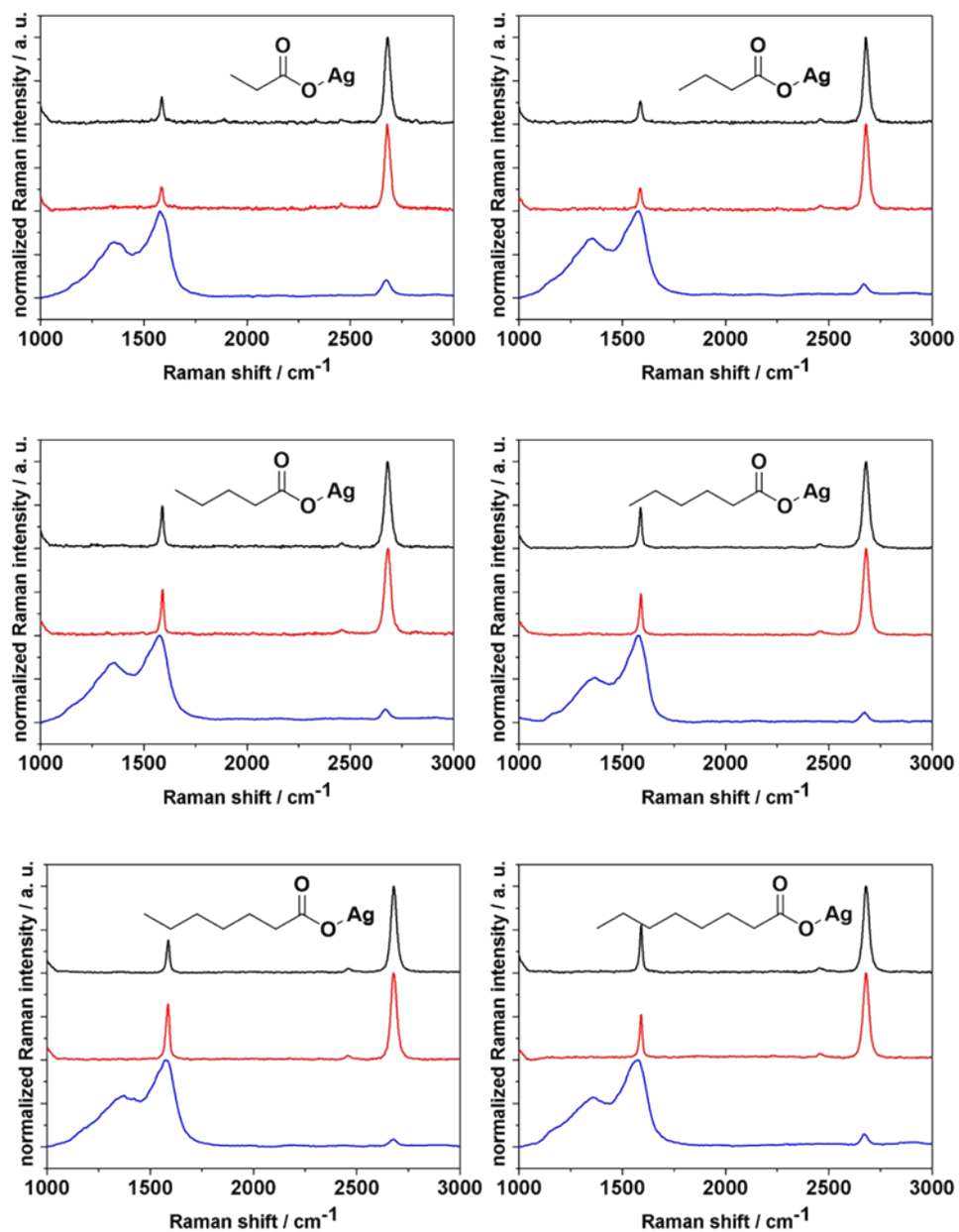


Figure S2. Normalized mean Raman spectra of pristine graphene (black line), non-irradiated areas (red line), and irradiated areas of samples **G_{H1}**-**G_{H6}** (blue line).

Temperature-Dependent Raman analysis. Temperature-dependent Raman spectroscopy measurements were conducted to investigate the thermal stability of the addend binding in the fluoroalkylated graphene (Figure S3) and alkylated graphene (Figure S4). The temperature-dependent Raman measurements were performed in a Linkam state, equipped with a liquid nitrogen pump for temperature stabilization under a constant flow of nitrogen to determine the thermal stability and the reversibility of the covalent addend binding. The measurements were carried out on Si/SiO₂ wafers with a heating rate of 10 °C/min and the developments of the Raman-specific bands were recorded. For samples **G_{F1}-G_{F8}**, as the temperature rises to 350°C, the I_D/I_G ratio shows a continuous increase, reaching a value of approximate 1.0 (Figure S3). Overall, the behavior of all samples is very similar, with a maximum I_D/I_G ratio of 0.95 - 1.0. However, a further increase in the temperature to 400°C leads to a sharp decline of the D band, resulting in an I_D/I_G ratio < 0.1, indicative of complete defunctionalization. As such, the intact sp²-carbon lattice of graphene is restored. Samples **G_{H1}-G_{H6}** exhibit a similar trend in D-peak behavior during heat treatments below 350 °C, where the intensity of the D-peak continuously increases with rising temperature until the I_D/I_G ratio reaches 0.9 (Figure S4). A further increase of the temperature to 400 °C results in the complete disappearance of the D-, G-, and 2D-band. This suggests that, unlike **G_{H1}-G_{H6}**, the high-temperature processing leads to the disintegration of the graphene network rather than the cleavage of the bond between graphene and addends.

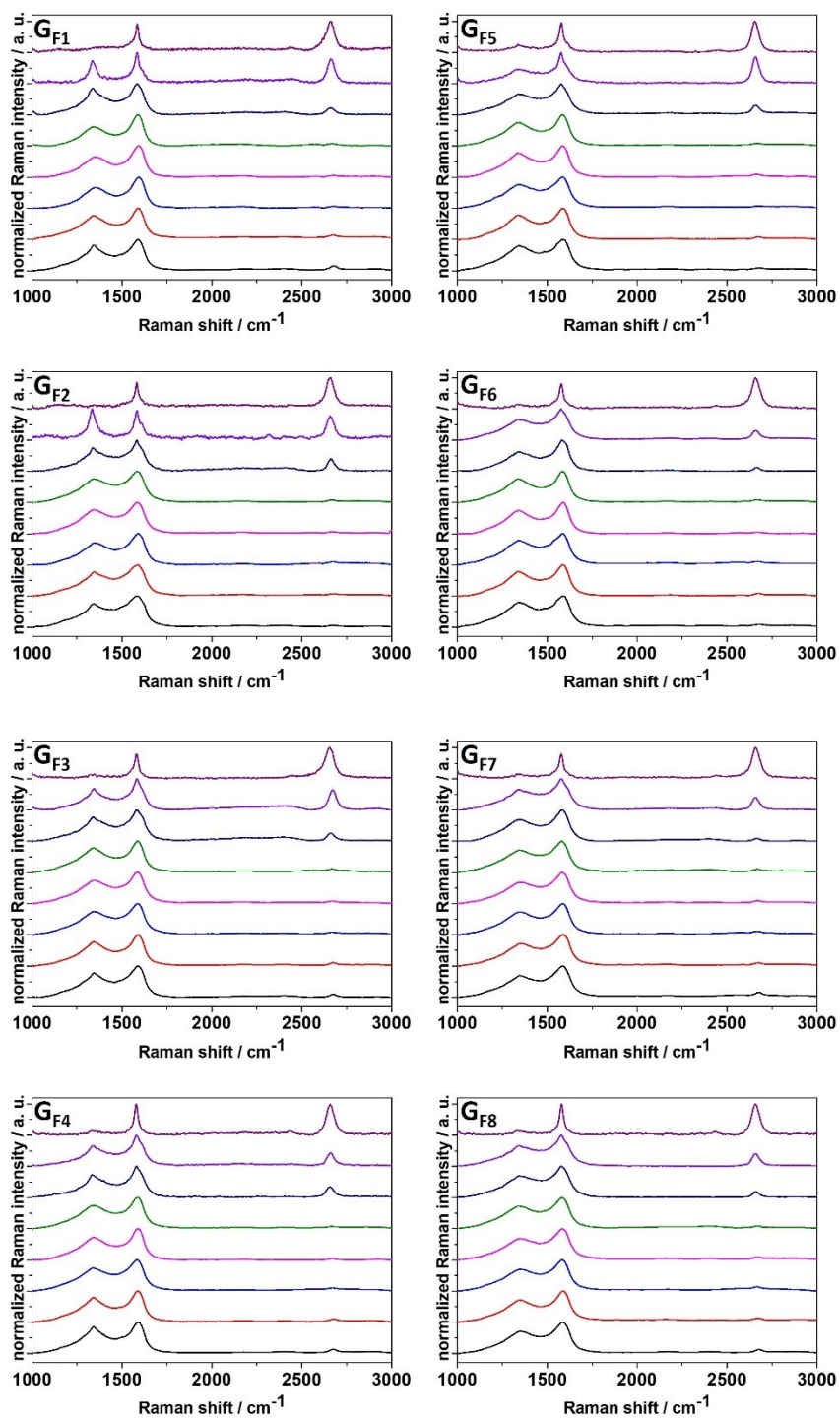


Figure S3. Temperature-dependent Raman spectra of samples G_{F1} - G_{F8} .

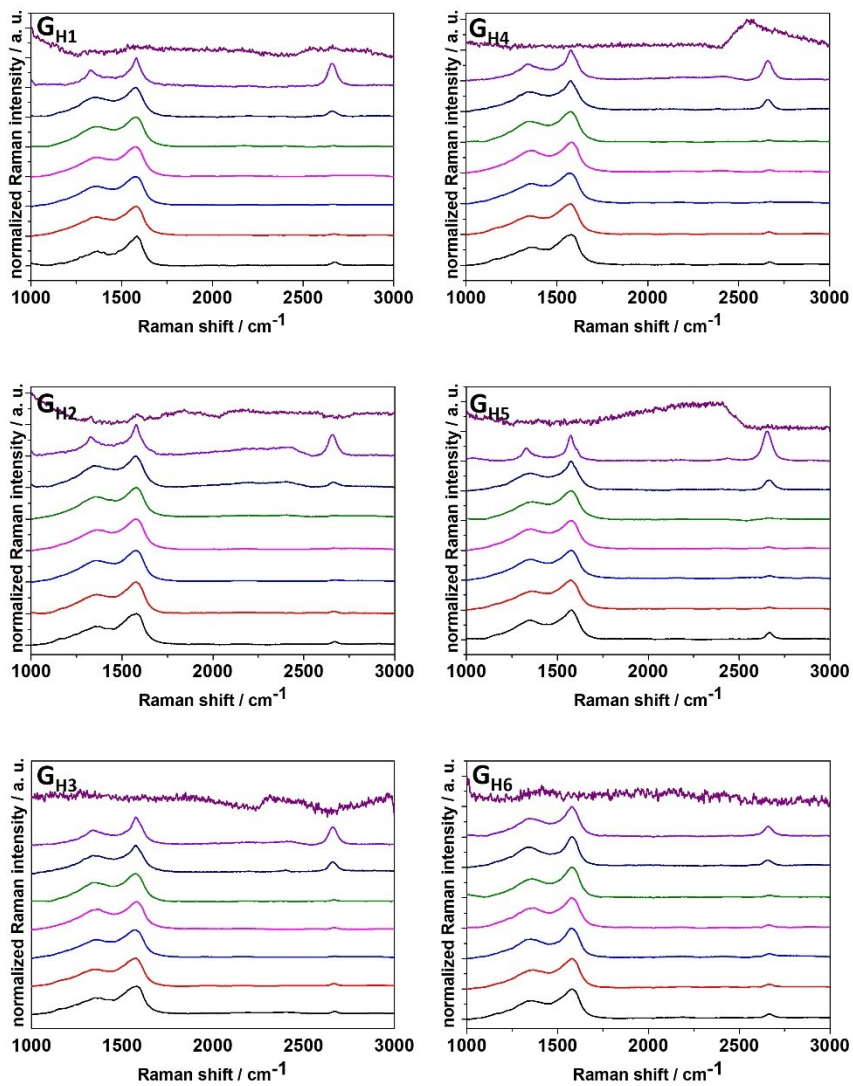


Figure S4. Temperature-dependent Raman spectra of samples G_{H1} - G_{H6} .

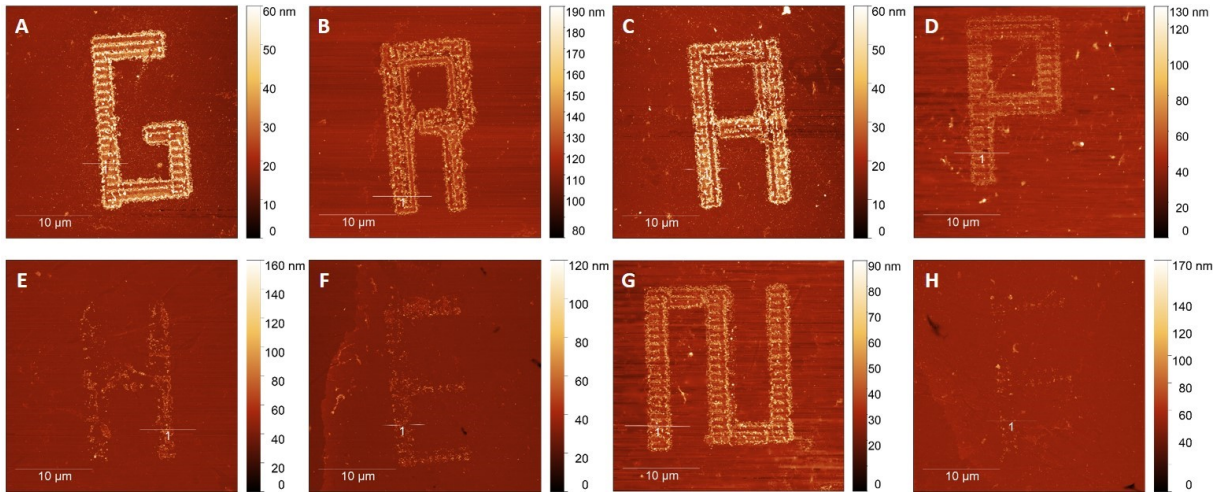


Figure S5. AFM images of the samples G_{F1} (A), G_{F2} (B), G_{F3} (C), G_{F4} (D), G_{F5} (E), G_{F6} (F), G_{F7} (G), and G_{F8} (H).

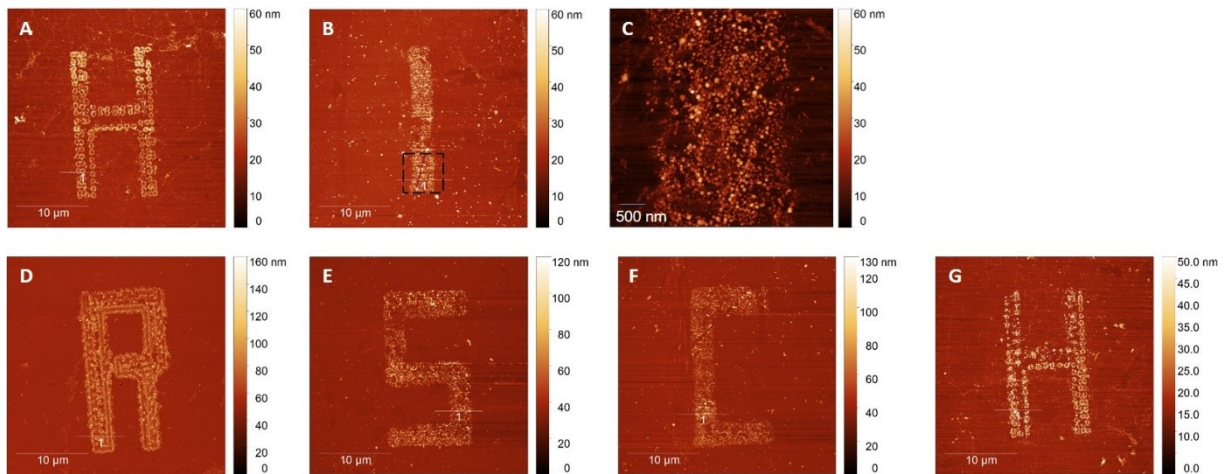
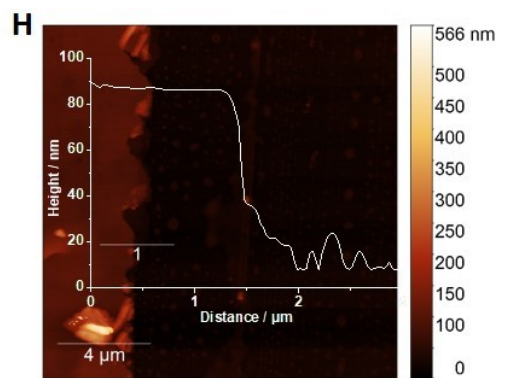
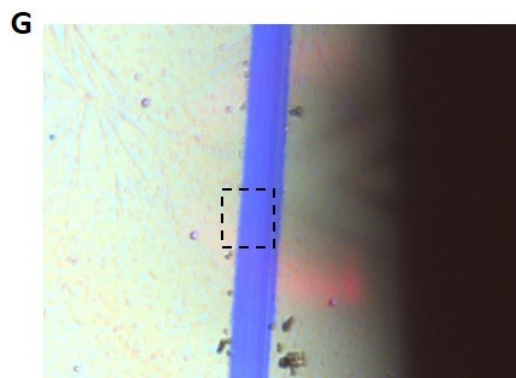
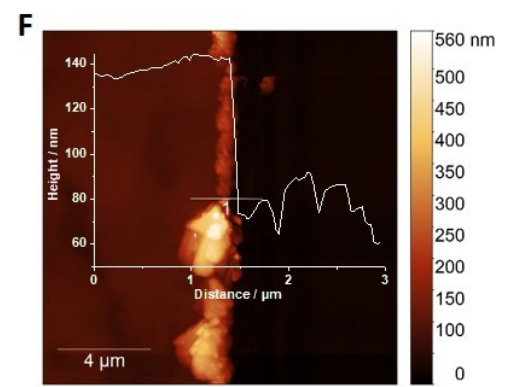
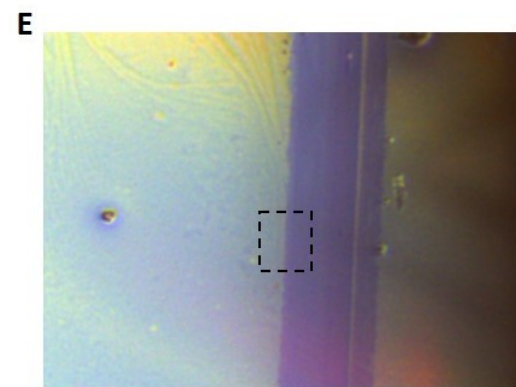
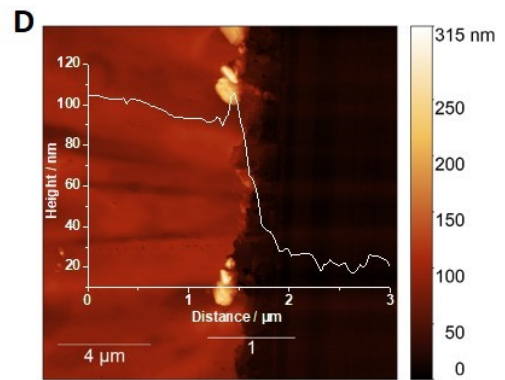
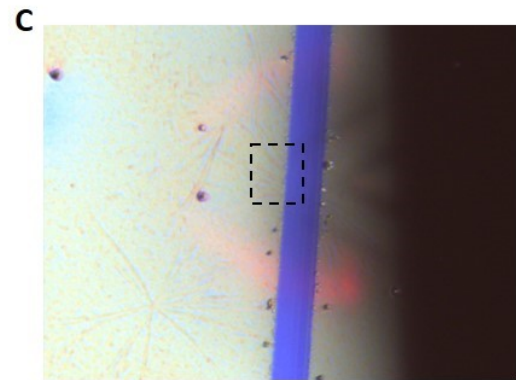
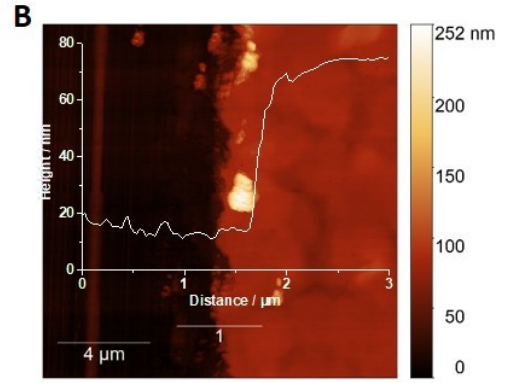
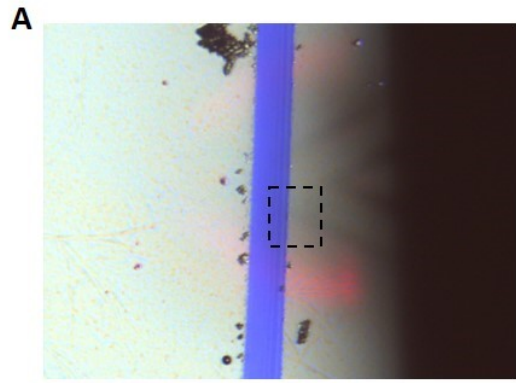


Figure S6. AFM images of the samples G_{H1} (A), G_{H2} (B), G_{H3} (D), G_{H4} (E), G_{H5} (F), and G_{H6} (G), and AFM image of the zoomed-in region marked by a black square (C).



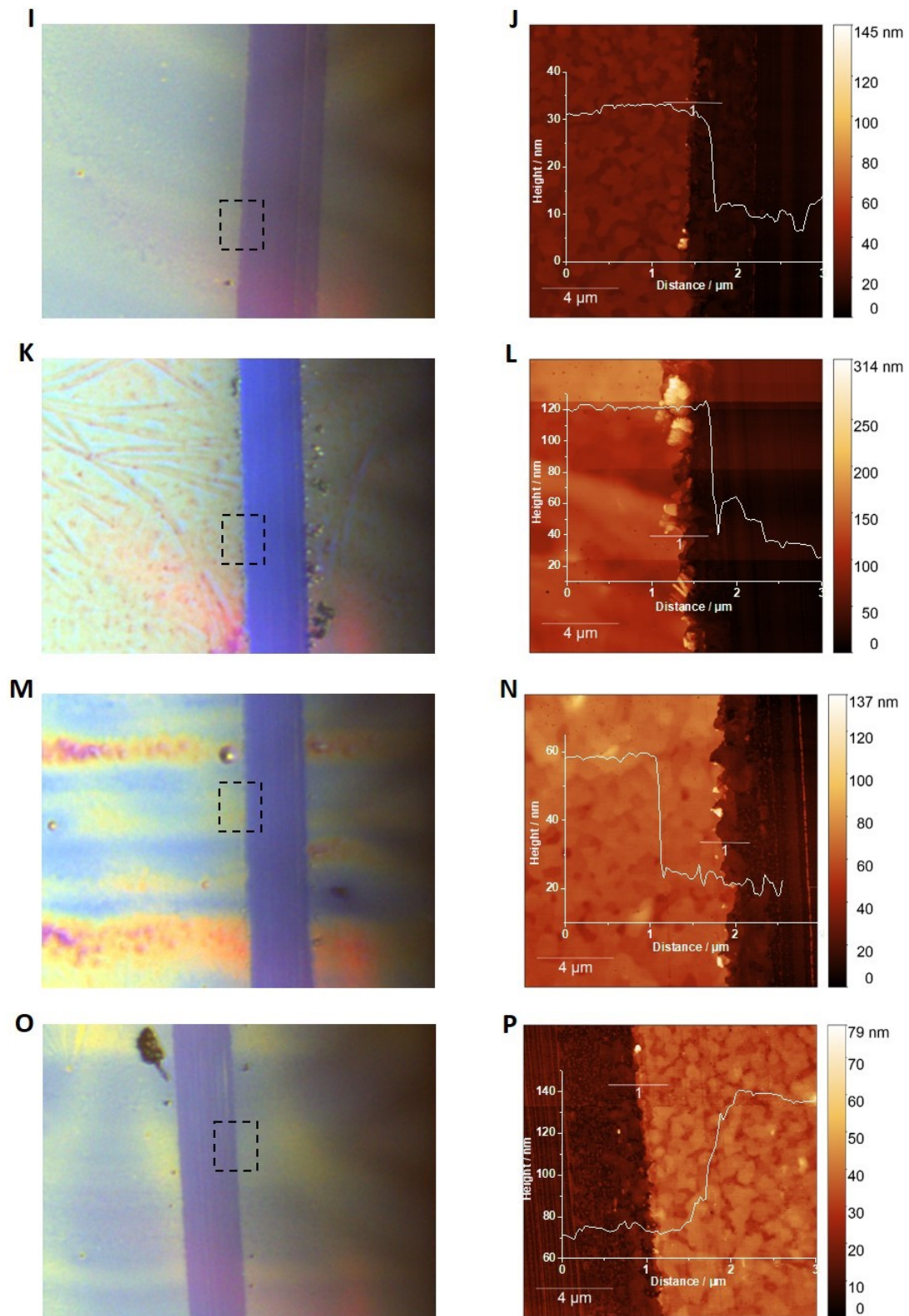
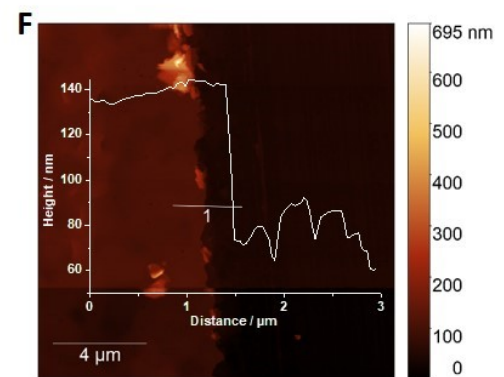
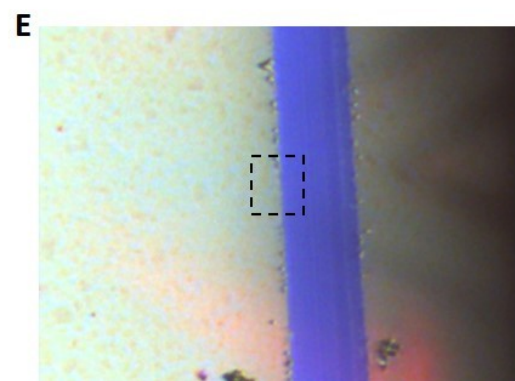
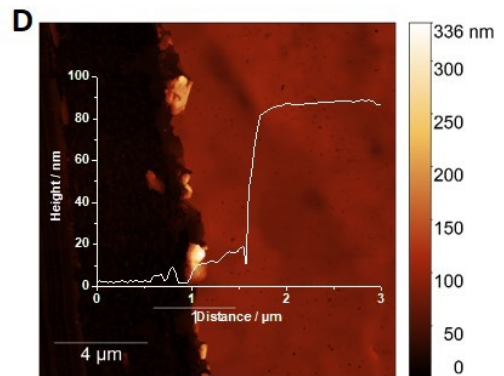
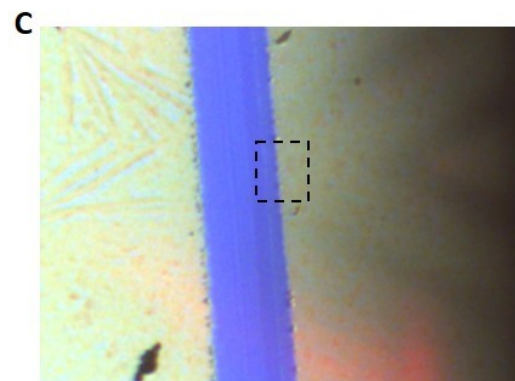
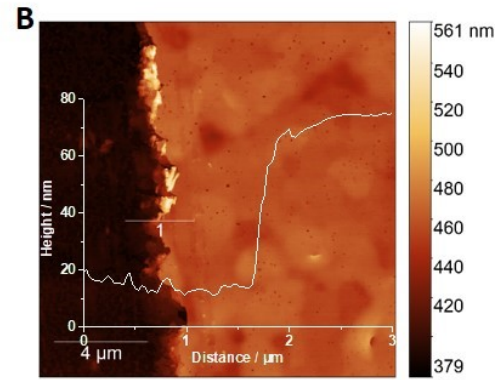
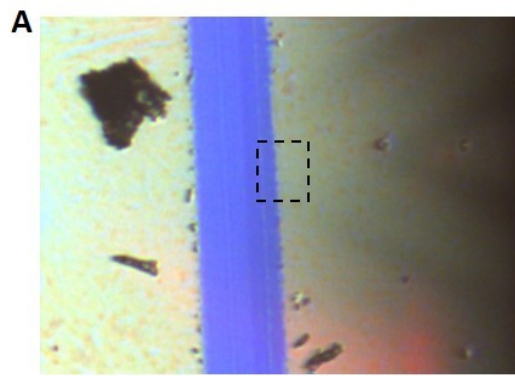


Figure S7. Optical images and corresponding AFM images of precursor film in samples G_{F1} (A, B), G_{F2} (C, D), G_{F3} (E, F), G_{F4} (G, H), G_{F5} (I, J), G_{F6} (K, L), G_{F7} (M, N), and G_{F8} (O, P). To facilitate the AFM measurements the scratches shown in optical images are implemented on purpose. The black square denotes the location where the AFM characterization has been carried out.



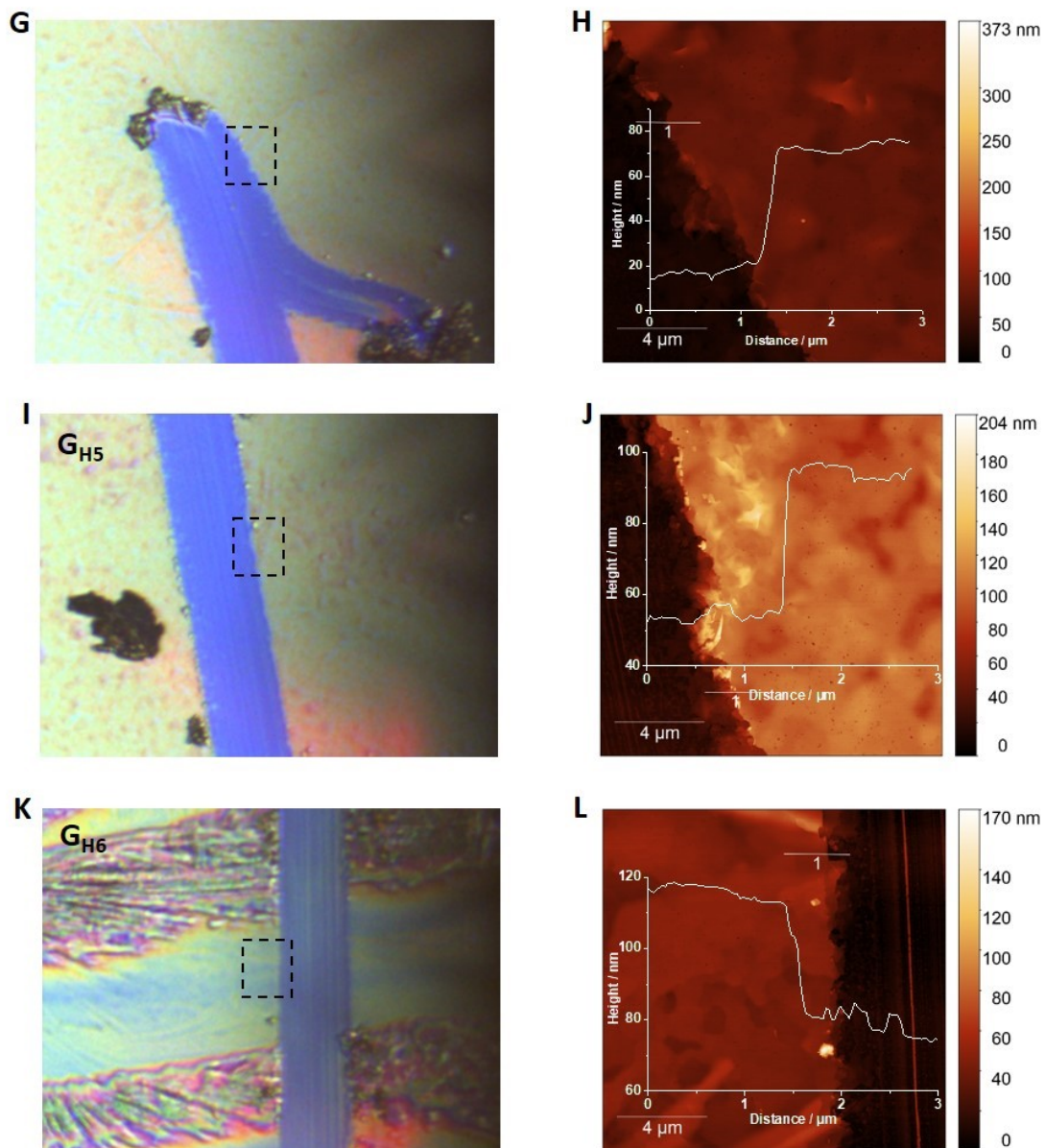


Figure S7. Optical images and corresponding AFM images of precursor film in samples G_{H1} (A, B), G_{H2} (C, D), G_{H3} (E, F), G_{H4} (G, H), G_{H5} (I, J), and G_{H6} (K, L). In order to facilitate the AFM measurements the scratches shown in optical images are implemented on purpose. The black square denotes the location where the AFM characterization has been carried out.

Removal of the silver nanoparticles. Silver nanoparticles are produced during the laser-writing process and confined to the laser-irradiated regions, presenting the identical patterns as organic addends. To visualize the regular distributions of silver nanoparticles, AFM measurements were performed on graphene samples after laser writing and subsequent removal of excess reagents, revealing a pattern-dependent arrangement of these silver nanoparticles (Figure S5 and S6). On the other hand, the resulting silver particles can be easily removed by a two-step treatment consisting of washing with diluted nitric acid (0.3 mol/L for 10 min) and sequential ultrasonication (30W) in diluted nitric acid (1 min) and isopropanol (1min). For example, after laser writing and subsequent rinse of the residues of reagents, the letter pattern "I" remains visible as shown in the optical image (Figure S 9A) due to the generation of silver particles. This was further confirmed by AFM analysis, which showed that the pattern was composed of silver nanoparticles (Figure S6B and S6C). However, upon washing treatment by submerging the sample in diluted nitric acid (0.3 mol/L) for 10 minutes and a sequential ultrasonic treatment (30 W) in diluted nitric acid (0.3 mol/L) (1 min) and isopropanol (1 min), the patterned silver nanoparticles were eliminated (Figure S9B). The successful removal of silver nanoparticles was corroborated by AFM measurements, where the distinct letter pattern "I" was disappeared (Figure S9C).

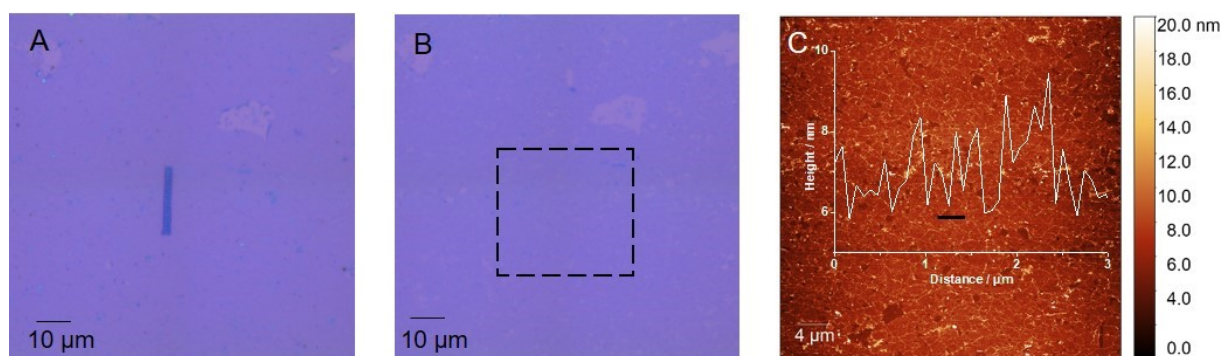
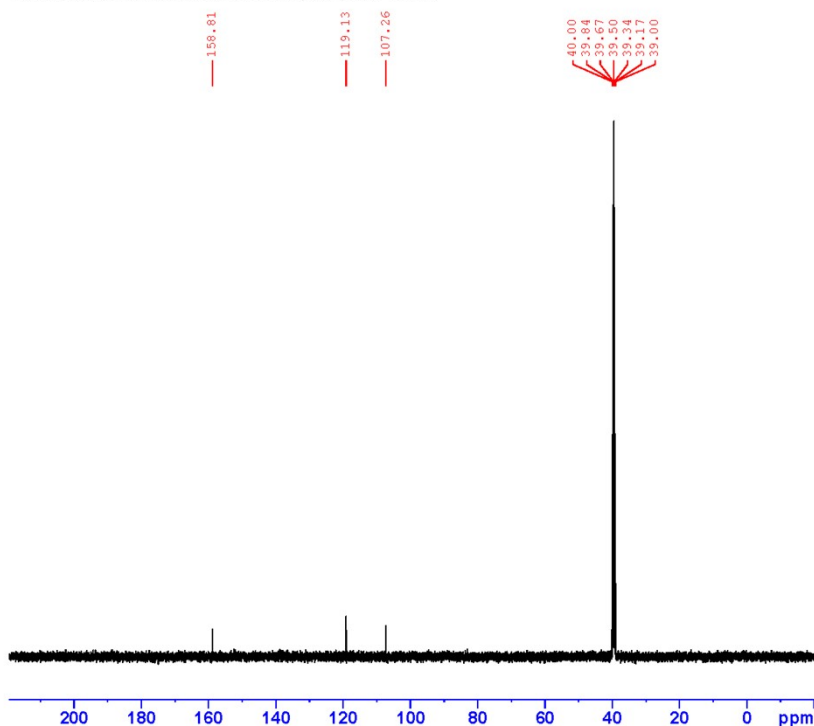


Figure S9. Optical images of G_{H2} before (A) and after (B) removal of silver nanoparticles and the corresponding AFM image after depletion of silver nanoparticles. The black square denotes the location where the AFM characterization has been carried out.

#000669/ROHDE/SRP21/DMSO/13C{19F}/25°C/CHP



Current Data Parameters
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EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
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PULPROG zgig30
TD 32768
SOLVENT DMSO
NS 16
DS 4
SWH 30120.482 Hz
FIDRES 1.838408 Hz
AQ 0.5439488 sec
RG 101
DW 16.600 usec
DE 6.50 usec
TE 298.2 K
D1 6.0000000 sec
D11 0.0300000 sec
TD0 8
SFO1 125.8231741 MHz
NUC1 13C
FO 5.83 usec
F1 17.50 usec
PLW1 17.13599968 W
SFO2 470.7428960 MHz
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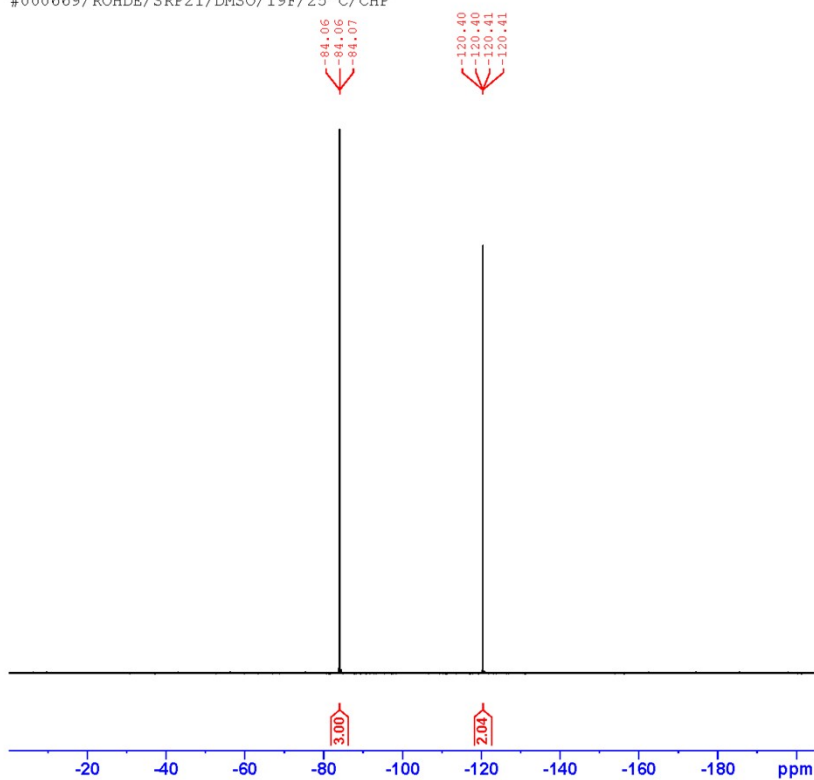
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SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Silver carboxylate G₁ F₅C₃-COOAg

¹⁹F₅C₃-COOAg

Figure S10. G_{F1}, δ_C (126 MHz, DMSO-d₆).

#000669/ROHDE/SRP21/DMSO/19F/25°C/CHP



Current Data Parameters
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PROCNO 1

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AQ 1.3631488 sec
RG 101
DW 5.200 usec
DE 6.50 usec
TE 298.1 K
D1 4.0000000 sec
TE0 1
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P0 7.33 usec
P1 22.00 usec
PLW1 39.5000000 W

F2 - Processing parameters
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PC 1.00

Silver carboxylate G₁ F₅C₃-COOAg

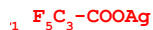
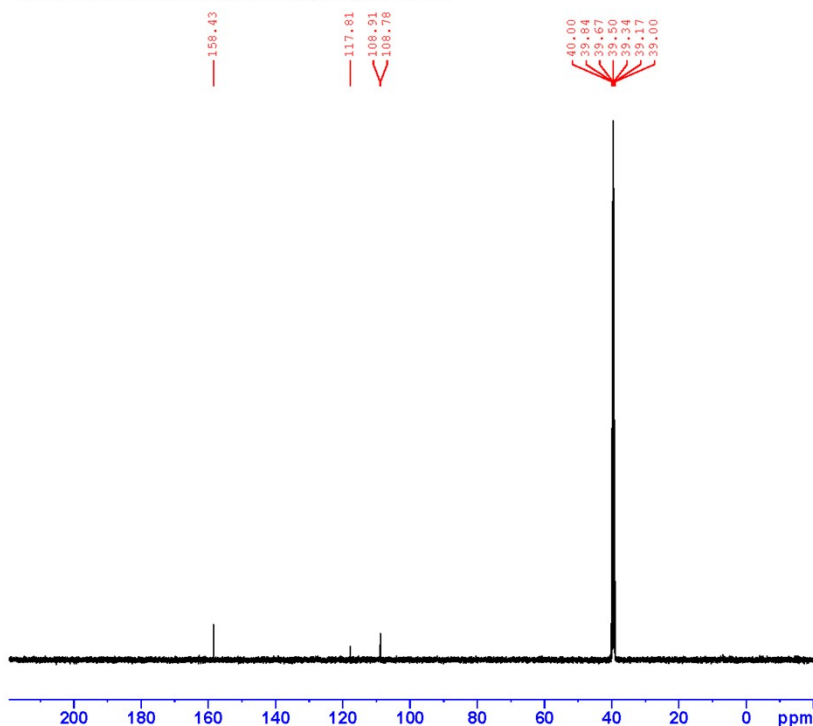


Figure S11. G_{F1}, δ_F (471 MHz, DMSO-d₆).

#000668/ROHDE/SRP20/CDC13/13C{19F}/25°C/CHP



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PROCNO 1

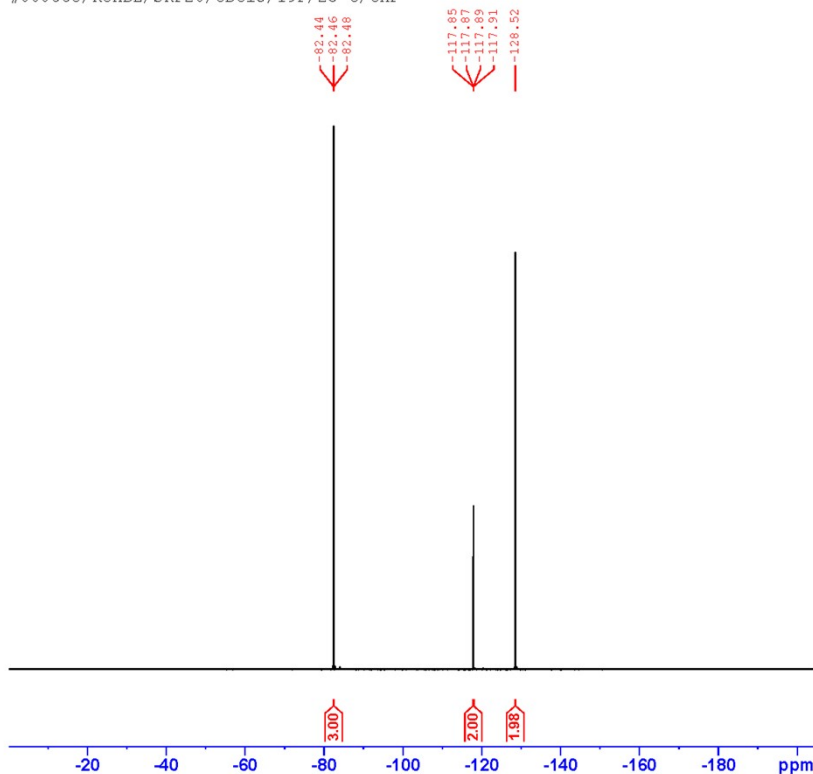
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Date_ 20210311
Time 15.23 h
INSTRUM CAB AV4 500 MHz BASIC
PROBHD E128651_0010 (
PULPROG zgig
TD 32768
SOLVENT DMSO
NS 184
DS 0
SWH 30120.482 Hz
FIDRES 1.838408 Hz
AQ 0.5439488 sec
RG 101
DW 16.600 usec
DE 6.50 usec
TE 298.1 K
D1 8.0000000 sec
D11 0.0300000 sec
TD0 1
SF01 125.8231741 MHz
NUC1 13C
P1 17.50 usec
PLW1 17.1359968 W
SFO2 470.7414836 MHz
NUC2 19F
CFDPRG2 garp4
PCPD2 59.32 usec
PLW2 39.5000000 W
PLW12 5.46224022 W

F2 - Processing parameters
SI 32768
SF 125.8106538 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Silver carboxylate G₂ F₇C₃-COOAg

Figure S12. G_{F_2} , δ_C (126 MHz, DMSO- d_6).

#000668/ROHDE/SRP20/CDC13/19F/25°C/CHP



Current Data Parameters
NAME S5ro000668.8R-P20
EXPNO 1
PROCNO 1

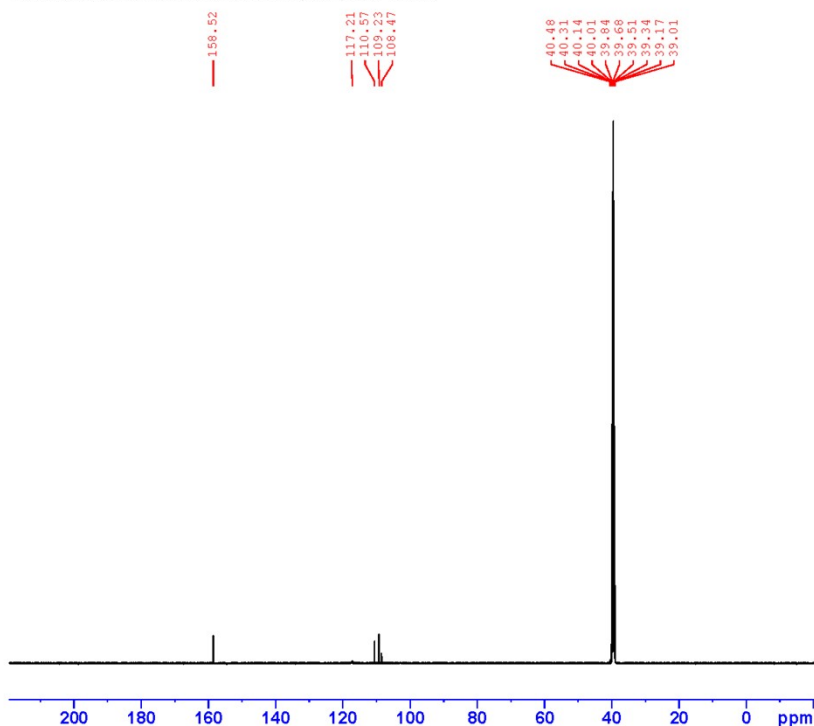
F2 - Acquisition Parameters
Date_ 20210311
Time 14.43 h
INSTRUM CAB AV4 500 MHz BASIC
PROBHD Z128651_0010 (
PULPROG zg30
TD 262144
SOLVENT DMSO
NS 8
DS 0
SWH 96153.844 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 101
DW 5.200 usec
DE 6.50 usec
TE 298.1 K
D1 4.0000000 sec
TD0 1
SF01 470.7428956 MHz
NUC1 19F
P1 7.33 usec
PLW1 22.00 usec
PLW1 39.5000000 W

F2 - Processing parameters
SI 131072
SF 470.7910701 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Silver carboxylate G₂ F₇C₃-COOAg

Figure S13. G_{F_2} , δ_F (471 MHz, DMSO- d_6).

#000670/ROHDE/SRP22/DMSO/13C{19F}/25°C/CHP



Current Data Parameters
NAME S5ro000670.SR-P22
EXPNO 2
PROCNO 1

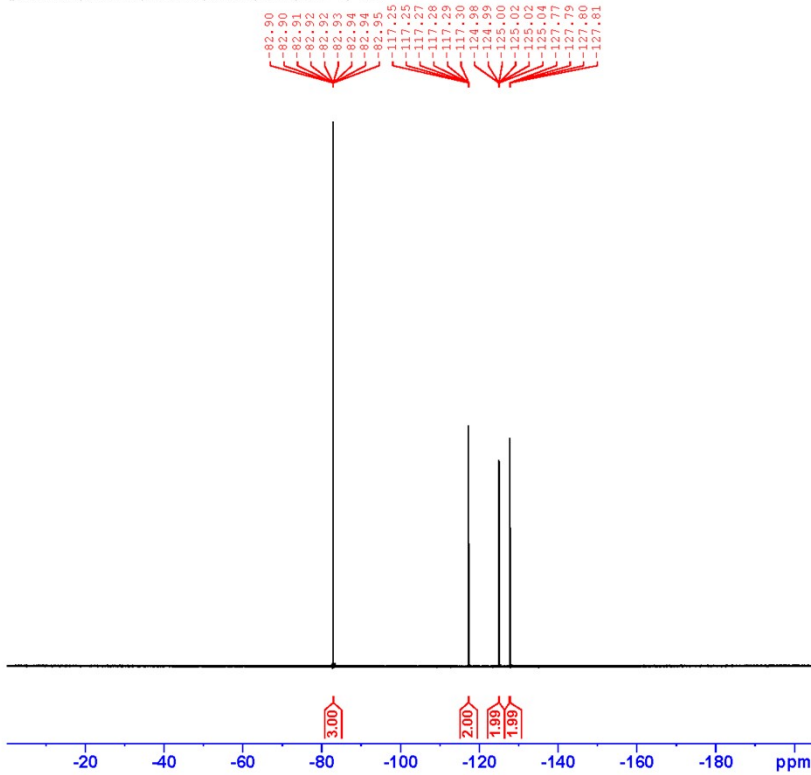
F2 - Acquisition Parameters
Date_ 20210311
Time 20.05 h
INSTRUM CAB AV4 500 Mhz BASIC
PROBHD z128651_0010 (z)
PULPROG zgpg30
TD 32768
SOLVENT DMSO
NS 1024
DS 4
SWH 30120.482 Hz
FIDRES 1.838408 Hz
AQ 0.5439488 sec
RG 101
DM 16.600 usec
DE 6.50 usec
TE 298.1 K
D1 7.00000000 sec
D11 0.03000000 sec
TDO 1
SF01 125.8231741 MHz
NUC1 13C
P0 5.83 usec
P1 17.50 usec
PLW1 17.13599968 W
SFO2 470.7407774 MHz
NUC2 19F
CPDPRG2 garp4
PCPD2 58.33 usec
PLW2 39.50000000 W
PLW12 5.61830378 W

F2 - Processing parameters
SI 32768
SF 125.8106521 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Silver carboxylate G₃ F₃C₄-COOAg

Figure S14. G_{F3}, δ_C (126 MHz, DMSO-*d*₆).

#000670/ROHDE/SRP22/DMSO/19F/25°C/CHP



Current Data Parameters
NAME s5ro000670.SR-P22
EXPNO 1
PROCNO 1

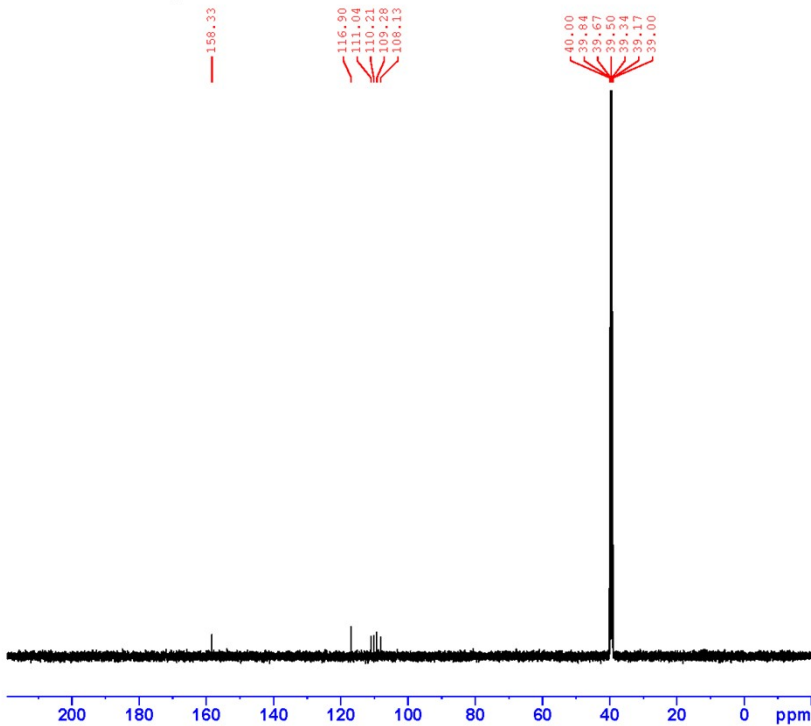
F2 - Acquisition Parameters
Date_ 20210311
Time_ 17.43 h
INSTRUM CAB AV4 500 MHz BASIC
PROBHD Z128651 0010 (
PULPROG zg30
TD 262144
SOLVENT DMSO
NS 8
DS 0
SWH 96153.844 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 101
DW 5.200 usec
DE 6.50 usec
TE 298.1 K
D1 4.00000000 sec
TD0 1
SFO1 470.7428956 MHz
NUC1 19F
P0 7.33 usec
F1 22.00 usec
PLW1 39.50000000 W

F2 - Processing parameters
SI 121072
SF 470.7910701 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Silver carboxylate G₃ F₃C-COOAg

Figure S15. G_{F3}, δ_F (471 MHz, DMSO-d₆).

#000677/ROHDE/SR_P23/DMSO/13C{19F}/25°C/CHP



Current Data Parameters
NAME s5ro000677.SR-P23
EXPNO 2
PROCNO 1

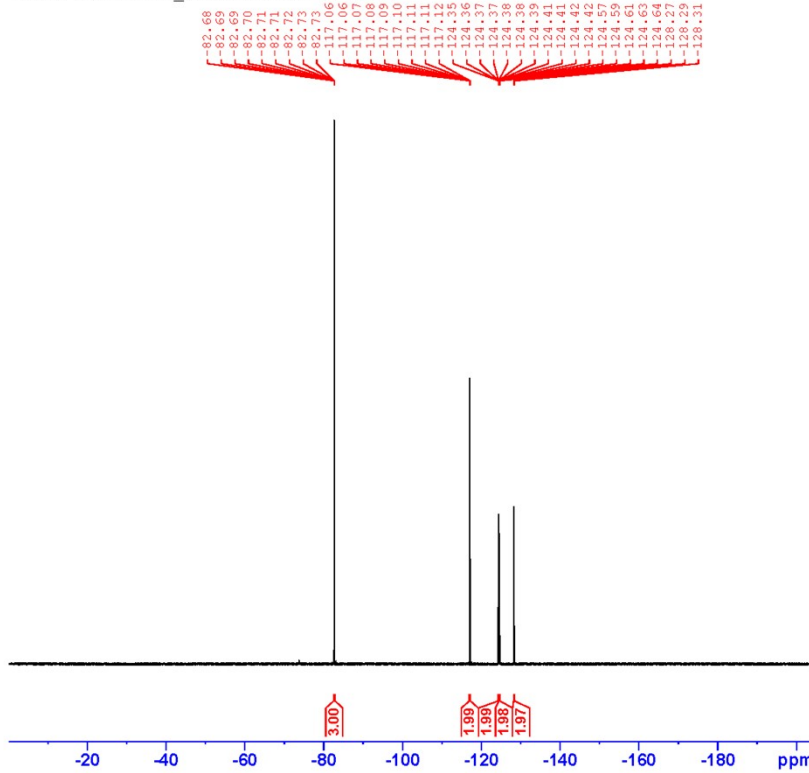
F2 - Acquisition Parameters
Date_ 20210318
Time_ 19.37 h
INSTRUM CAB AV4 500 MHz BASIC
PROBHD Z128651 0010 (
PULPROG zgig30
TD 32768
SOLVENT DMSO
NS 41
DS 4
SWH 30120.482 Hz
FIDRES 1.938408 Hz
AQ 0.5439488 sec
RG 101
DW 16.600 usec
DE 6.50 usec
TE 298.2 K
D1 6.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.8231741 MHz
NUC1 13C
P0 5.83 usec
F1 17.50 usec
PLW1 17.13599968 W
SFO2 470.7417190 MHz
NUC2 19F
CPDPRG2 garp4
PCPD2 49.65 usec
PLW2 39.50000000 W
PLW12 7.80319977 W

F2 - Processing parameters
SI 22768
SF 125.8106541 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Silver carboxylate G₄ F₁₁C₃-COOAg

Figure S16. G_{F4}, δ_C (126 MHz, DMSO-d₆).

#000677/ROHDE/SR_P23/DMSO/19F/25°C/CHP



Current Data Parameters
NAME S5ro000677.SR-F23
EXPNO 1
PROCNO 1

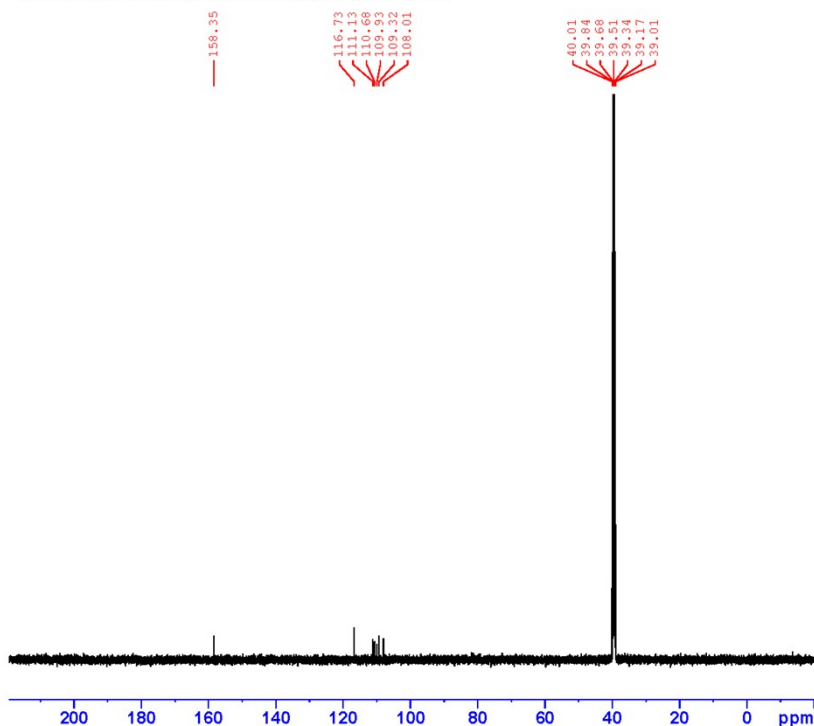
F2 - Acquisition Parameters
Date_ 20210318
Time_ 19.26 h
INSTRUM CAB AV4 500 MHz BASIC
PROBHD Z128651_0010 (
PULPROG zg30
TD 262144
SOLVENT DMSO
NS 16
DS 0
SWH 96153.844 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 101
DM 5.200 usec
DE 6.50 usec
TE 298.2 K
D1 4.0000000 sec
TD0 1
SFO1 470.7428956 MHz
NUC1 19F
P0 7.33 usec
F1 22.00 usec
PLW1 39.5000000 W

F2 - Processing parameters
SI 131072
SF 470.7910701 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Silver carboxylate G4 F13C5-COOAg

Figure S17. G_{F4} , δ_F (471 MHz, DMSO- d_6).

#000678/ROHDE/SR-P24/DMSO/13C{19F}/25°C/CHP



Current Data Parameters
NAME s5ro000678.SR-P24
EXPNO 2
PROCNO 1

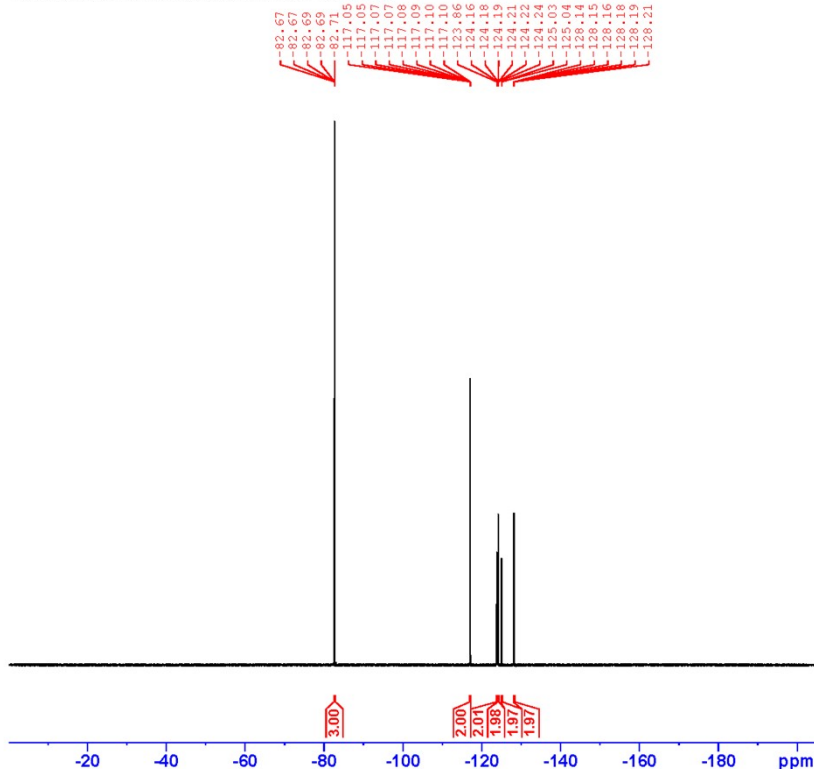
F2 - Acquisition Parameters
Date_ 20210318
Time 20.50 h
INSTRUM CAB AV4 500 MHz BASIC
PROBHD Z128651_0010 ()
PULPROG zgig30
TD 32768
SOLVENT DMSO
NS 64
DS 4
SWH 30120.482 Hz
FIDRES 1.838408 Hz
AQ 0.5439488 sec
RG 101
DW 16.600 usec
DE 6.50 usec
TE 298.1 K
D1 7.00000000 sec
D11 0.03000000 sec
TD0 1
SF01 125.8231741 MHz
NUC1 13C
P0 5.83 usec
P1 17.50 usec
PLW1 17.1359968 W
SFO2 470.7414836 MHz
NUC2 19F
CFDPRG2 garp4
PCPD2 49.65 usec
PLW2 39.5000000 W
PLW12 7.80319977 W

F2 - Processing parameters
SI 32768
SF 125.8106531 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Silver carboxylate G₅ F₁₃C₆-COOAg

Figure S18. G₅, δ_C (126 MHz, DMSO-*d*₆).

#000678/ROHDE/SR-P24/DMSO/19F/25°C/CHP



Current Data Parameters
NAME s5ro000678.SR-P24
EXPNO 1
PROCNO 1

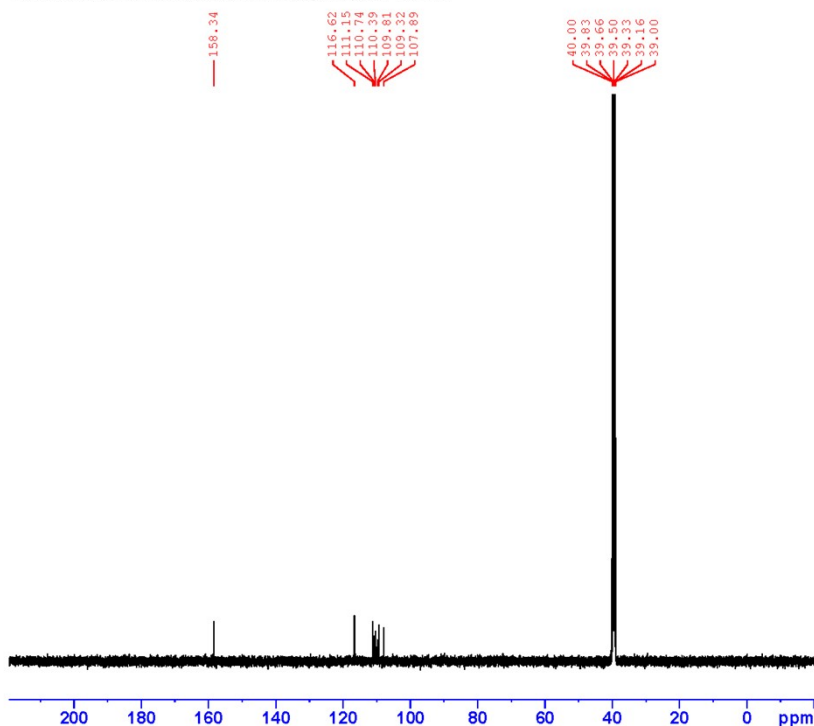
F2 - Acquisition Parameters
Date_ 20210318
Time 20.38 h
INSTRUM CAB AV4 500 MHz BASIC
PROBHD Z128651_0010 ()
PULPROG zg30
TD 262144
SOLVENT DMSO
NS 16
DS 0
SWH 96153.844 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 101
DW 5.200 usec
DE 6.50 usec
TE 298.1 K
D1 4.00000000 sec
D11 1
SF01 470.7428956 MHz
NUC1 19F
P0 7.33 usec
P1 22.00 usec
PLW1 39.5000000 W

F2 - Processing parameters
SI 131072
SF 470.7910701 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Silver carboxylate G₅ F₁₃C₆-COOAg

Figure S19. G₅, δ_F (471 MHz, DMSO-*d*₆).

#000680/ROHDE/SR-P25/DMSO/13C{19F}/25°C/CHP



Current Data Parameters
NAME s5ro000680.SR-P25
EXPNO 2
PROCNO 1

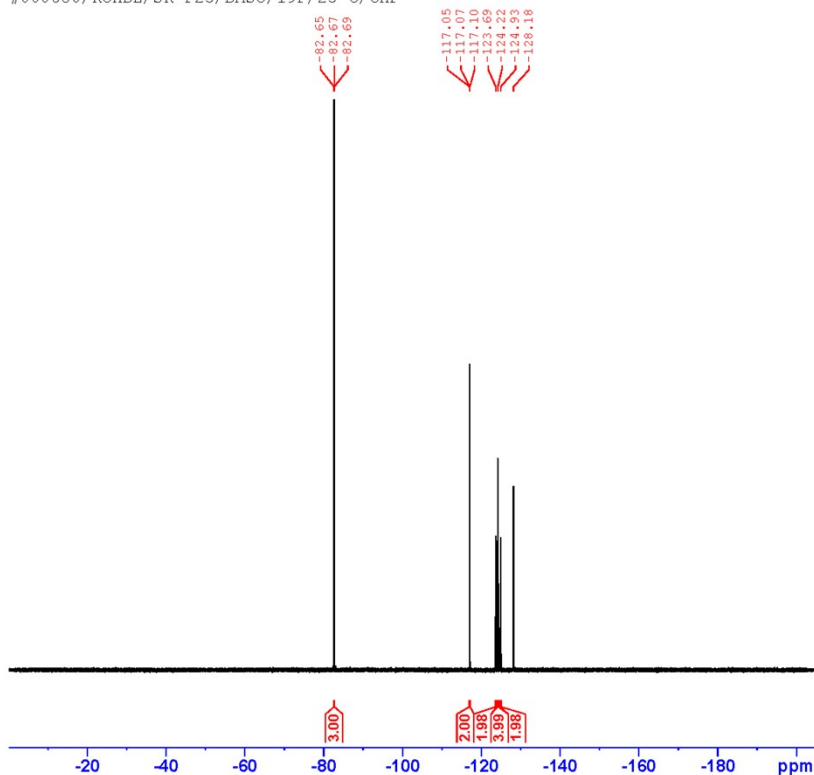
F2 - Acquisition Parameters
Date 20210322
Time 12.25 h
INSTRUM CAB AV4 500 MHz BASIC
PROBHD Z128651_0010 ()
PULPROG zgig30
TD 32768
SOLVENT DMSO
NS 128
DS 4
SWH 30120.482 Hz
FIDRES 1.838488 Hz
AQ 0.5429488 sec
RG 101
DM 16.600 usec
DE 6.50 usec
TE 298.1 K
D1 7.00000000 sec
D11 0.03000000 sec
TD0 1
SF01 125.8231741 MHz
NUC1 13C
P0 5.83 usec
P1 17.50 usec
PLW1 17.1359968 W
SFO2 470.7414836 MHz
NUC2 19F
CPDPRG2 gacp4
PCPD2 49.65 usec
FLW2 39.5000000 W
FLW12 7.80319977 W

F2 - Processing parameters
SI 32768
SF 125.8106546 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Silver carboxylate G₆ F₁₅C₇-COOAg

Figure S20. G_{F6}, δ_C (126 MHz, DMSO-d₆).

#000680/ROHDE/SR-P25/DMSO/19F/25°C/CHP



Current Data Parameters
NAME s5ro000680.SR-P25
EXPNO 1
PROCNO 1

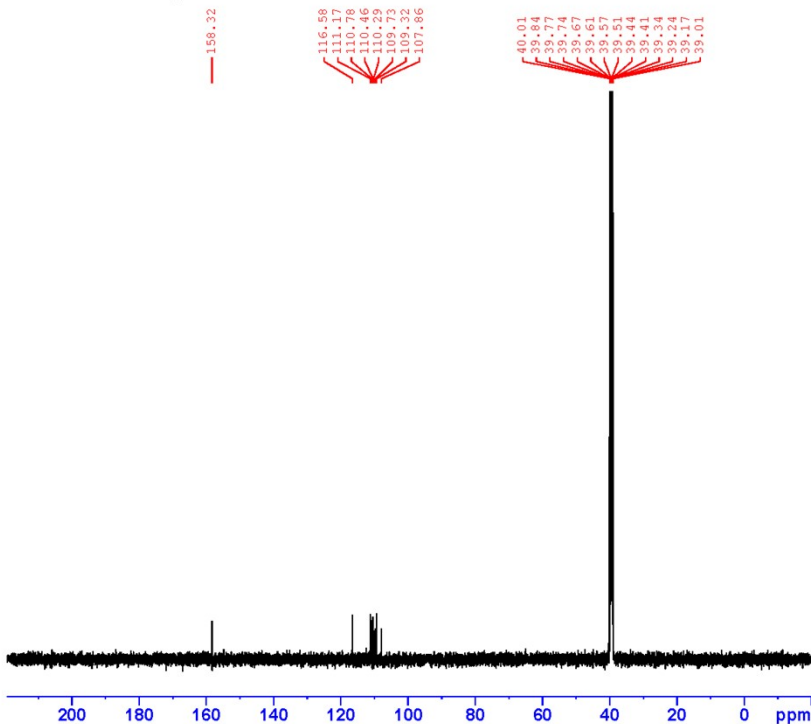
F2 - Acquisition Parameters
Date 20210322
Time 12.03 h
INSTRUM CAB AV4 500 MHz BASIC
PROBHD Z128651_0010 ()
PULPROG zg30
TD 262144
SOLVENT DMSO
NS 16
DS 0
SWH 96153.844 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 101
DM 5.200 usec
DE 6.50 usec
TE 298.2 K
D1 4.00000000 sec
TD0 1
SF01 470.7428956 MHz
NUC1 19F
P0 7.33 usec
P1 22.00 usec
PLW1 39.5000000 W

F2 - Processing parameters
SI 131072
SF 470.7910701 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00

Silver carboxylate G₆ F₁₅C₇-COOAg

Figure S21. G_{F6}, δ_F (471 MHz, DMSO-d₆).

#000681/ROHDE/SR_P26/DMSO/13C{1H,19F}/25°C/CHP



Current Data Parameters
 NAME S5ro000681.SR-P26
 EXFNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20210323
 Time_ 12.27 h
 INSTRUM CAB AV4 500 MHz BASIC
 PROBHD Z173362_0004 (
 PULPROG zgig30
 TD 16384
 SOLVENT DMSO
 NS 160
 DS 4
 SWH 30120.482 Hz
 FIDRES 3.676817 Hz
 AQ 0.2719744 sec
 RG 101
 DW 16.600 usec
 DE 8.50 usec
 TE 298.1 K
 D1 12.0000000 sec
 D11 0.0300000 sec
 TDO 1
 SFO1 125.8231741 MHz
 NUC1 13C
 P0 3.33 usec
 F1 10.00 usec
 PLW1 78.56199646 W
 SFO2 470.7417190 MHz
 NUC2 19F
 CPDPRG2 gatr4
 PCPD2 49.65 usec
 PLW2 46.52899933 W
 PLW12 11.86960030 W

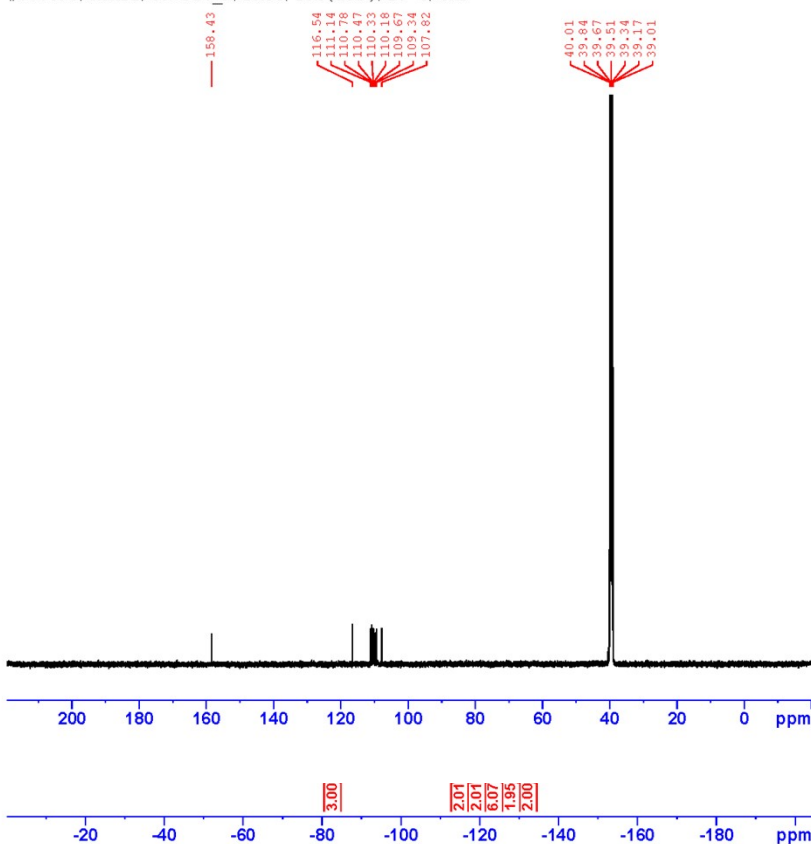
F2 - Processing parameters
 SI 32768
 SF 125.810652 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Silver carboxylate Gr7 F₁₉C₈-COOAg

Figure S22. G_{F7}, δ_C (126 MHz, DMSO-d₆).

Figure S23. G_{F7}, δ_F (471 MHz, DMSO-d₆).

#000693/ROHDE/SR-P26_A/DMSO/13C{19F}/25°C/CHP



Current Data Parameters
 NAME S5ro000693.SR-P26A
 EXFNO 2
 PROCNO 1

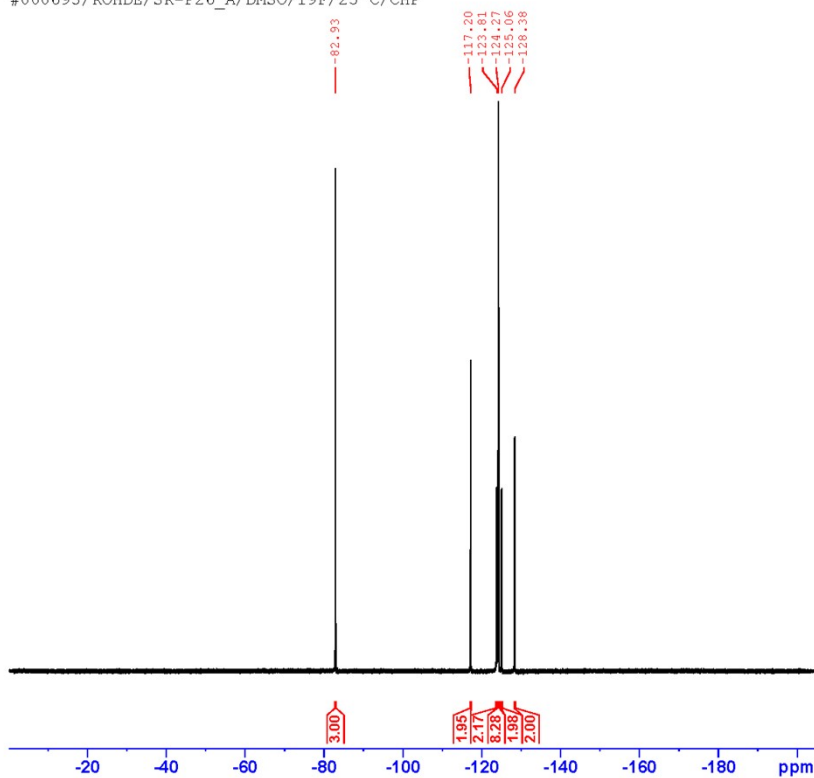
F2 - Acquisition Parameters
 Date_ 20210330
 Time_ 19.35 h
 INSTRUM CAB AV4 500 MHz BASIC
 PROBHD Z128651_0010 (
 PULPROG zgig30
 TD 32768
 SOLVENT DMSO
 NS 1024
 DS 0
 SWH 30120.482 Hz
 FIDRES 1.838408 Hz
 AQ 0.5439488 sec
 RG 101
 DW 16.600 usec
 DE 8.50 usec
 TE 298.1 K
 D1 9.0000000 sec
 D11 0.0300000 sec
 TDO 1
 SFO1 125.8231741 MHz
 NUC1 13C
 P0 5.83 usec
 F1 17.50 usec
 PLW1 17.13599968 W
 SFO2 470.7414836 MHz
 NUC2 19F
 CPDPRG2 gatr4
 PCPD2 49.65 usec
 PLW2 39.5000000 W
 PLW12 7.80319977 W

F2 - Processing parameters
 SI 32768
 SF 125.8106525 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Silver carboxylate Gr8 F₁₉C₉-COOAg

Figure S24. G_{F8}, δ_C (126 MHz, DMSO-d₆).

#000693/ROHDE/SR-P26_A/DMSO/19F/25°C/CHP



Current Data Parameters
NAME s5ro000693.SR-P26A
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210330
Time_ 16.47 h
INSTRUM CAB AV4 500 MHz BASIC
PROBHD Z128651_0010 ()
PULPROG zg30
TD 262144
SOLVENT DMSO
NS 16
DS 0
SWH 96153.844 Hz
FIDRES 0.733596 Hz
AQ 1.3631488 sec
RG 101
DM 5.200 usec
DE 6.50 usec
TE 298.2 K
D1 4.00000000 sec
TD0 1
SF01 470.7428956 MHz
NUC1 19F
P0 7.33 usec
F1 22.00 usec
PLW1 39.50000000 W

F2 - Processing parameters
SI 131072
SF 470.7910701 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Silver carboxylate G₈ F₁₉C₉-CO₂Ag

Figure S25. G₈, δ_F (471 MHz, DMSO-d₆).

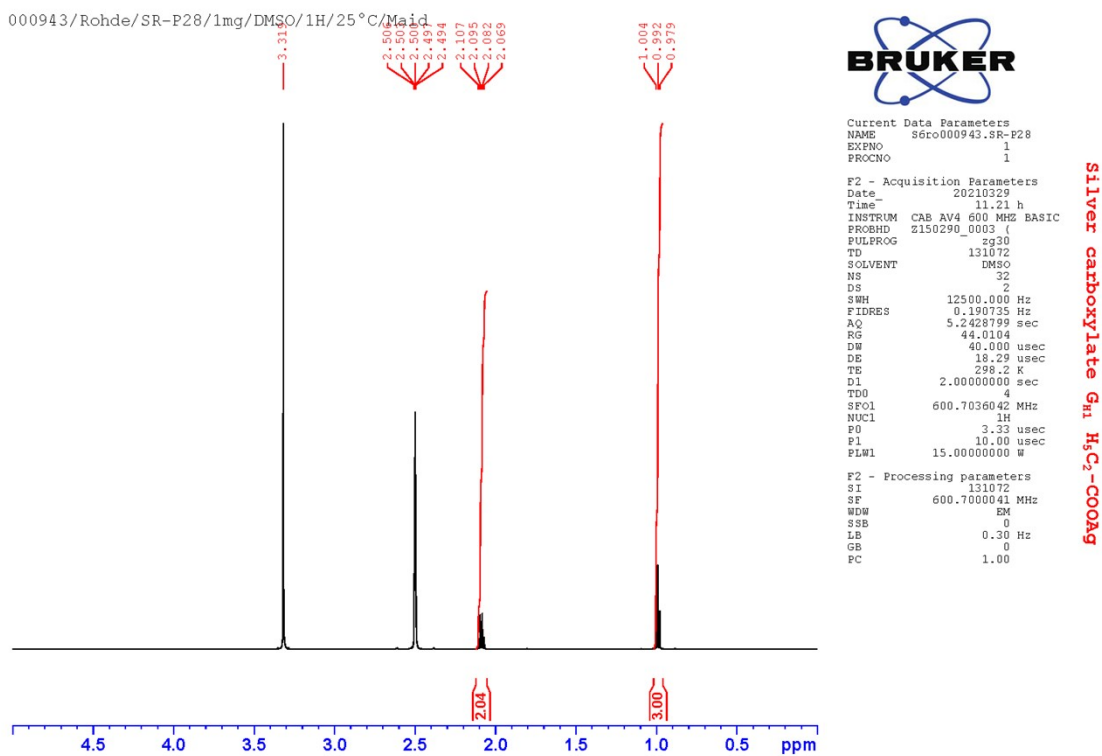
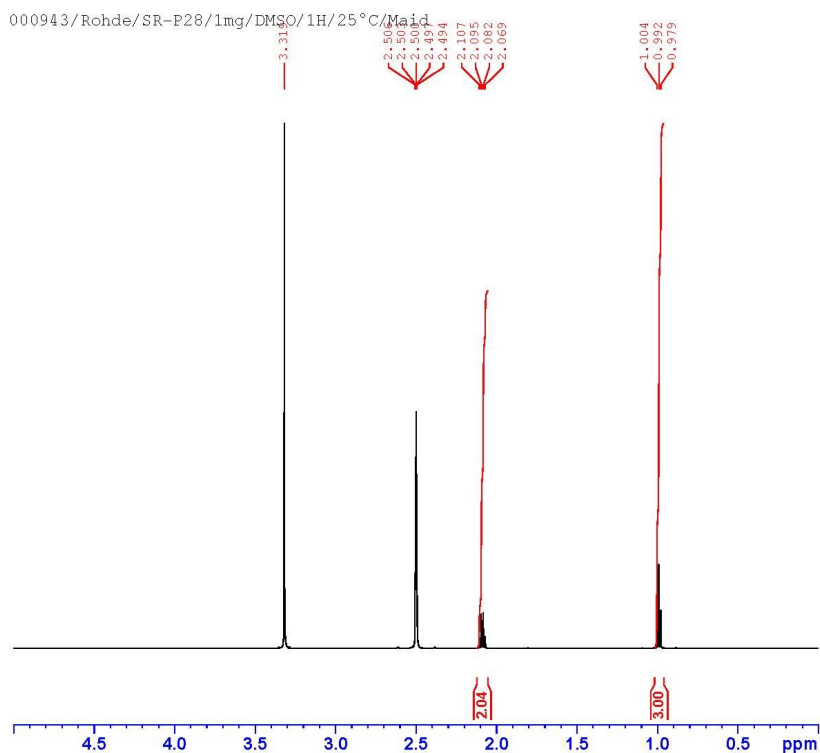
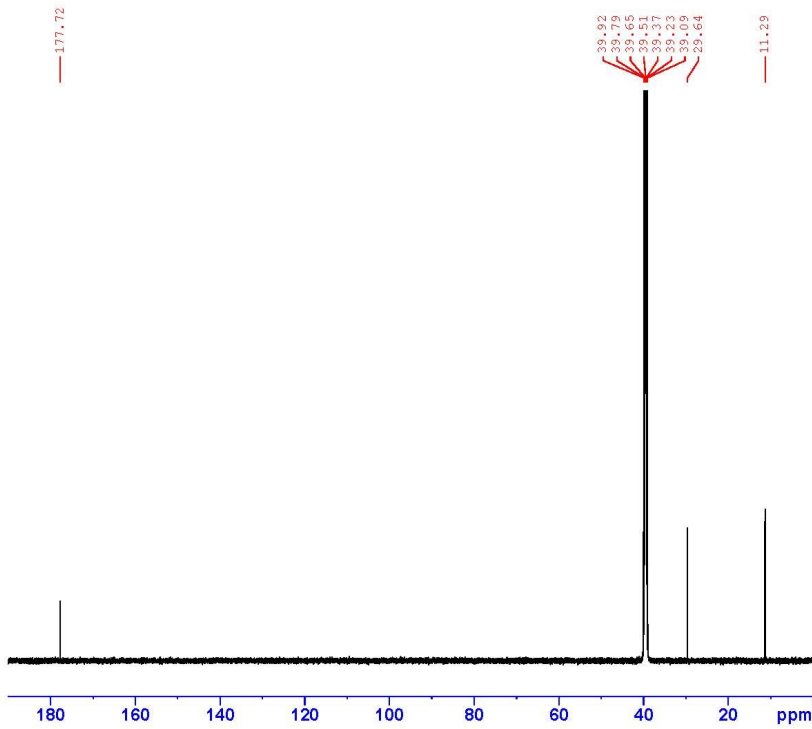


Figure S26. G_{H1}, δ_H (600 MHz, DMSO-d₆)

Figure S27. G_{H1}, δ_C (151 MHz, DMSO-d₆).

000943/Rohde/SR-P28/1mg/DMSO/13C{1H}/25°C/Maid



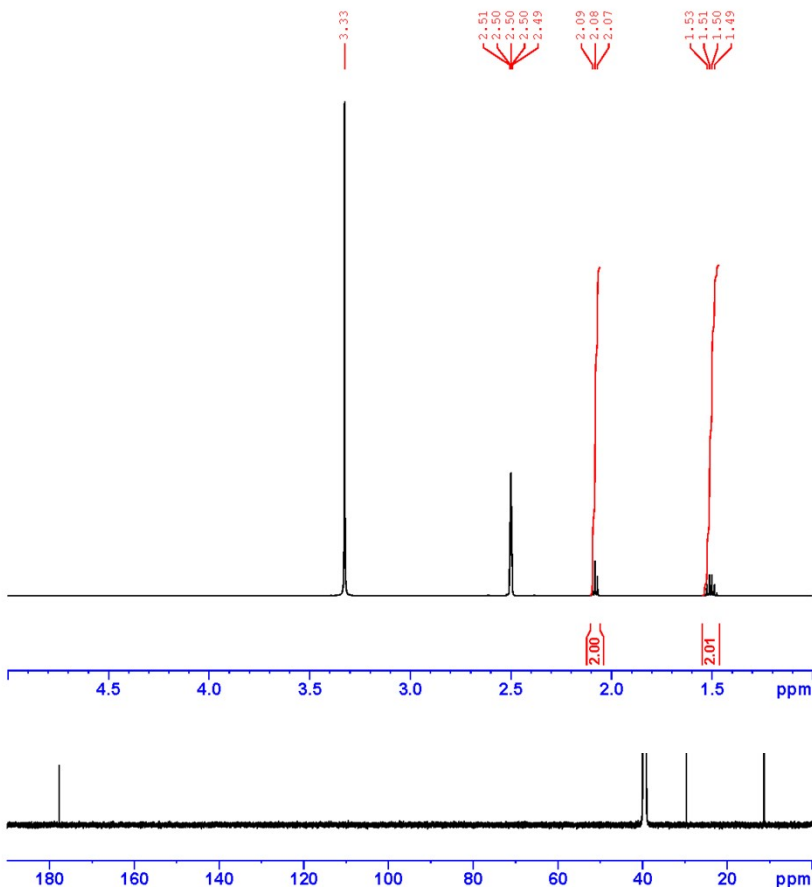
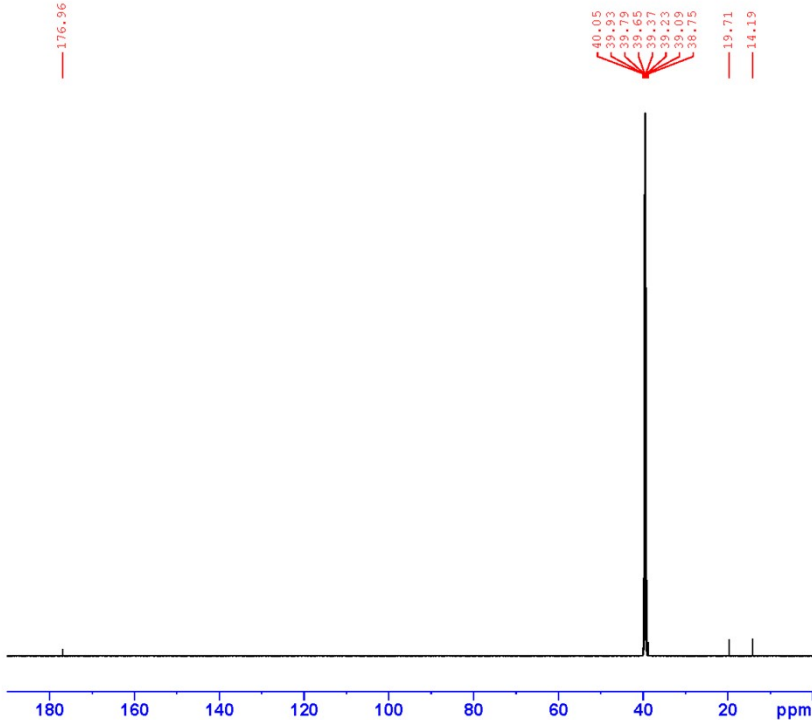
Current Data Parameters
NAME Sgro000943.SR-P28
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110329
Time_ 11.49 h
INSTRUM CAB AV4 600 Mhz BASIC
PROBHD z150290_0003 (4
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 368
DS 4
SWH 35714.285 Hz
FIDRES 1.089913 Hz
AQ 0.9175040 sec
RG 13.0208
DW 14.000 usec
DE 25.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TDO 128
SFO1 151.0612398 MHz
NUC1 13C
P0 3.53 usec
P1 10.60 usec
PLW1 19.89299965 W
SFO2 600.7024028 MHz
NUC2 1H
CPCPRG[2] waltz16
PCPD2 70.00 usec
PLW2 15.00000000 W
PLW12 0.30612001 W
PLW13 0.15398000 W

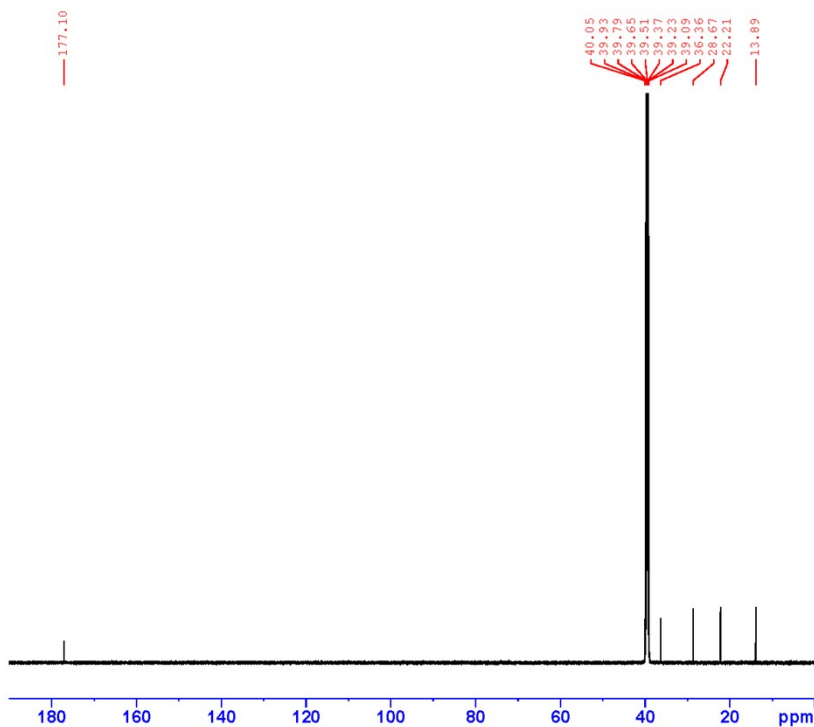
F2 - Processing parameters
SI 131072
SF 151.0462093 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Silver carboxylate G₁ H₅C₂-COOAg

Figure S28. G_{H_2} , δ_H (600 MHz, DMSO- d_6).

Silver carboxylate G₂ H₂C-COOAgFigure S29. G_{H2}, δ_C (151 MHz, DMSO-d₆).Silver carboxylate G₂ H₂C-COOAgFigure S30. G_{H3}, δ_H (600 MHz, DMSO-d₆).

000916/Rohde/SR-P29/1mg/DMSO/13C{1H}/25°C/Maid



Current Data Parameters
NAME S6ro000916.SR-P29
EXPNO 2
PROCNO 1

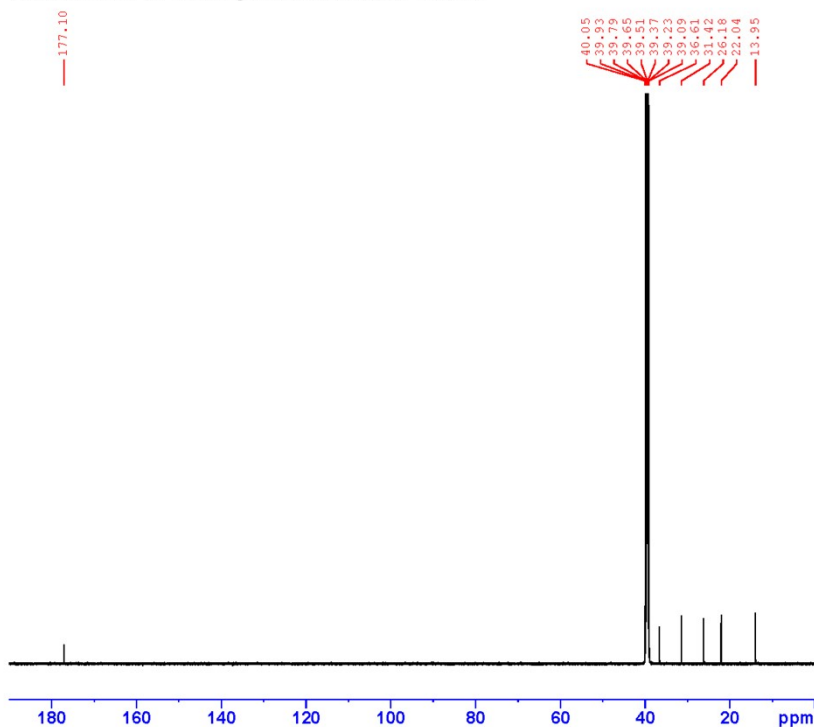
F2 - Acquisition Parameters
Date_ 20210302
Time 14.13 h
INSTRUM CAB AV4 600 MHz BASIC
PROBHD z150290_0003 ()
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 136
DS 4
SWH 35714.285 Hz
FIDRES 1.089913 Hz
AQ 0.9175040 sec
RG 13.0208
DW 14.000 usec
DE 25.00 usec
TE 298.2 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 128
SFO1 151.0612398 MHz
NUC1 13C
P0 3.53 usec
P1 10.60 usec
PLW1 19.89299965 W
SFO2 600.7024028 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 70.00 usec
PLW2 15.0000000 W
PLW12 0.30612001 W
PLW13 0.15398000 W

F2 - Processing parameters
SI 131072
SF 151.0462089 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Silver carboxylate G₁₃ H₃C₄-COOAg

Figure S31. G_{H3}, δ_C (151 MHz, DMSO-d₆).

000917/Rohde/SR-P30/1mg/DMSO/13C{1H}/25°C/Maid



Current Data Parameters
NAME S6ro000917.SR-P30
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210302
Time 15.03 h
INSTRUM CAB AV4 600 MHz BASIC
PROBHD z150290_0003 ()
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 496
DS 4
SWH 35714.285 Hz
FIDRES 1.089913 Hz
AQ 0.9175040 sec
RG 13.0208
DW 14.000 usec
DE 25.00 usec
TE 298.1 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 128
SFO1 151.0612398 MHz
NUC1 13C
P0 3.53 usec
P1 10.60 usec
PLW1 19.89299965 W
SFO2 600.7024028 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 70.00 usec
PLW2 15.0000000 W
PLW12 0.30612001 W
PLW13 0.15398000 W

F2 - Processing parameters
SI 131072
SF 151.0462092 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Silver carboxylate G₁₄ H₁C₅-COOAg

Figure S32. G_{H4} , δ_H (600 MHz, DMSO- d_6).

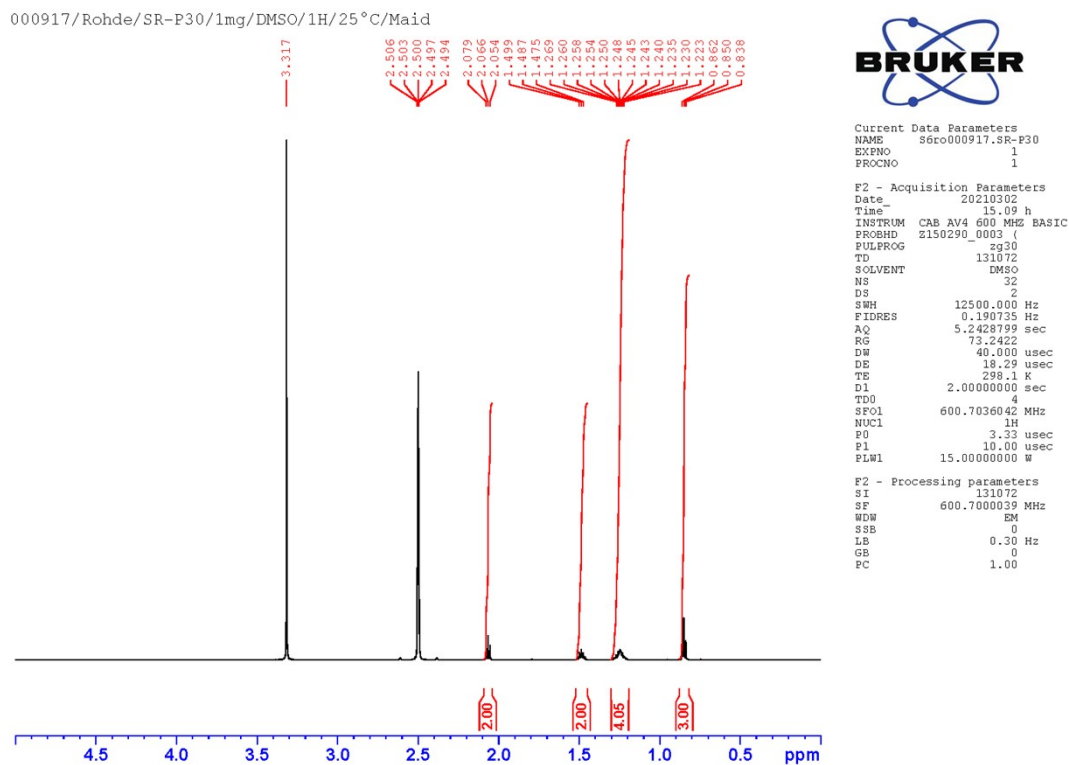
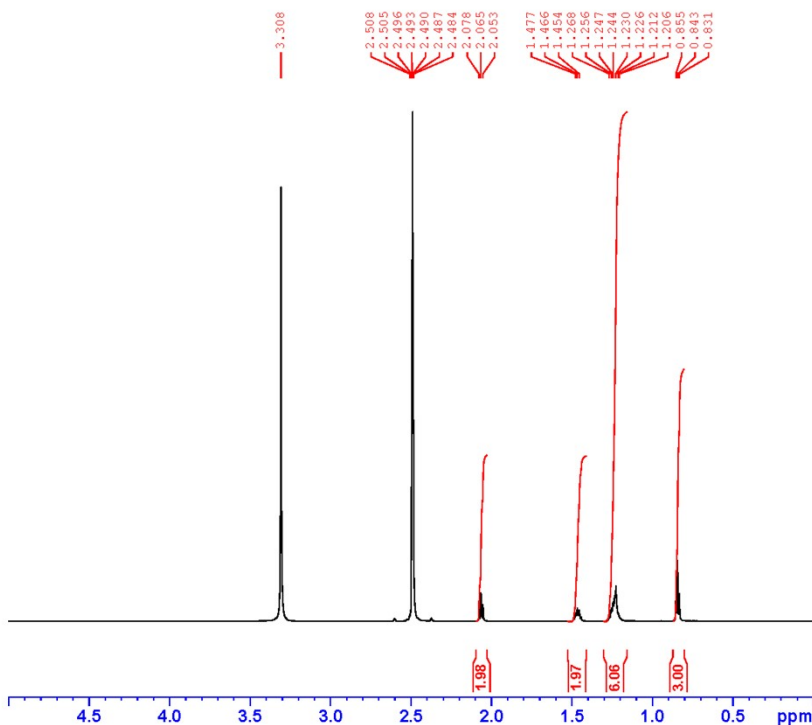


Figure S33. G_{H4} , δ_C (151 MHz, DMSO- d_6)

000944/Rohde/SR-P31/2mg/DMSO/1H/25°C/Maid



Current Data Parameters
NAME S6ro000944.SR-P31
EXFNO 1
PROCNO 1

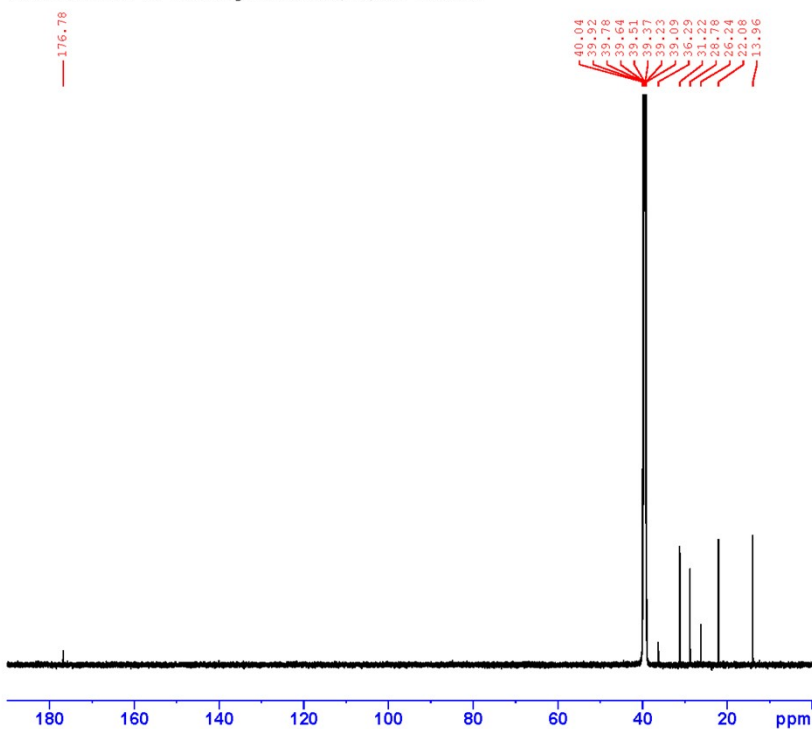
F2 - Acquisition Parameters
Date_ 20210329
Time 11.59 h
INSTRUM CAB AV4 600 MHz BASIC
PROBHD Z150290_0003 (Z150290)
PULPROG zg30
TD 131072
SOLVENT DMSO
NS 32
DS 2
SWH 12500.000 Hz
FIDRES 0.190735 Hz
AQ 5.2428799 sec
RG 52.8125
DW 40.000 usec
DE 18.29 usec
TE 298.1 K
D1 2.0000000 sec
TD0 4
SF01 600.7036042 MHz
NUC1 1H
P0 3.33 usec
P1 10.00 usec
PLW1 15.0000000 W

F2 - Processing parameters
SI 131072
SF 600.7000100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Silver carboxylate G₅ H₁₃C₆-COOAg

Figure S34. G_{H5}, δ_H (600 MHz, DMSO-d₆).

000944/Rohde/SR-P31/2mg/DMSO/13C{1H}/25°C/Maid



Current Data Parameters
NAME S6ro000944.SR-P31
EXFNO 2
PROCNO 1

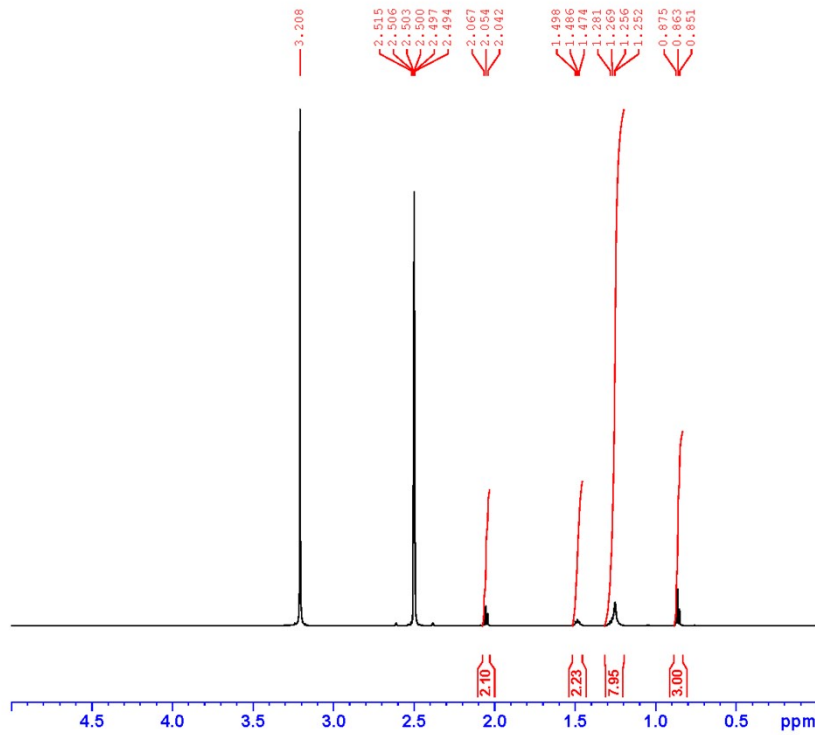
F2 - Acquisition Parameters
Date_ 20210329
Time 12.57 h
INSTRUM CAB AV4 600 MHz BASIC
PROBHD Z150290_0003 (Z150290)
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 904
DS 4
SWH 35714.285 Hz
FIDRES 1.089913 Hz
AQ 0.9175040 sec
RG 13.0208
DW 14.000 usec
DE 25.00 usec
TE 298.1 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 128
SF01 151.0612398 MHz
NUC1 13C
P0 3.53 usec
P1 10.60 usec
PLW1 19.8929995 W
SF02 600.7024028 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD 70.00 usec
PLW2 15.0000000 W
PLW12 0.30612001 W
PLW13 0.15398000 W

F2 - Processing parameters
SI 131072
SF 151.0462097 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Silver carboxylate G₅ H₁₃C₆-COOAg

Figure S35. G_{H5}, δ_C (151 MHz, DMSO-d₆).

000950/Rohde/SR-P32/1mg/DMSO/1H/50°C/Maid



Current Data Parameters
NAME s6ro000950.SR-P32
EXPNO 1
PROCNO 1

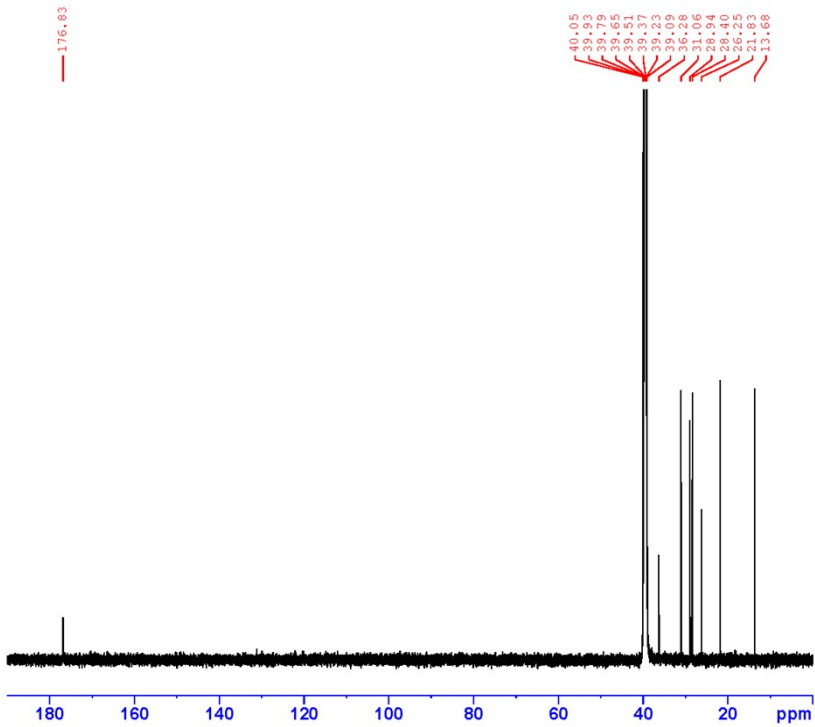
F2 - Acquisition Parameters
Date_ 20210407
Time 12.49 h
INSTRUM CAB AV4 600 MHz BASIC
PROBHD Z150290_0003 ()
PULPROG zg30
TD 131072
SOLVENT DMSO
NS 32
DS 2
SWH 12500.000 Hz
FIDRES 0.190735 Hz
AQ 5.2428799 sec
RG 58.6806
DW 40.000 usec
DE 18.29 usec
TE 323.2 K
D1 2.00000000 sec
TD0 4
SFO1 600.7036042 MHz
NUC1 1H
P0 3.33 usec
P1 10.00 usec
PLW1 15.00000000 W

F2 - Processing parameters
SI 131072
SF 600.7000043 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Silver carboxylate G6 $H_5C_7-COOAg$

Figure S36. G_{H6} , δ_H (600 MHz, DMSO- d_6).

000950/Rohde/SR-P32/1mg/DMSO/1H/50°C/Maid



Current Data Parameters
NAME s6ro000950.SR-P32
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20210407
Time 12.41 h
INSTRUM CAB AV4 600 MHz BASIC
PROBHD Z150290_0003 ()
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 1496
DS 4
SWH 35714.285 Hz
FIDRES 1.089913 Hz
AQ 0.9175040 sec
RG 13.0208
DW 14.000 usec
DE 25.00 usec
TE 323.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1280
SFO1 151.0612398 MHz
NUC1 13C
P0 3.53 usec
P1 10.60 usec
PLW1 19.89259965 W
SFO2 600.7024028 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 70.00 usec
PLW2 15.00000000 W
PLW12 0.30612001 W
PLW13 0.15398000 W

F2 - Processing parameters
SI 131072
SF 151.0462371 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Silver carboxylate G6 $H_5C_7-COOAg$

Figure S37. G_6 , δ_C (151 MHz, DMSO- d_6).

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