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Regioselective synthesis of novel derivatives of *neo* oxo carboxylic acids with two different functional groups from linear carboxylic acid chlorides

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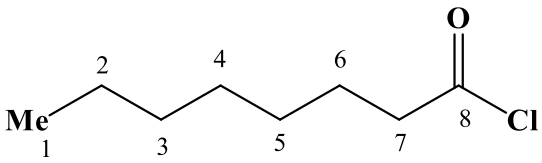
1. EXPERIMENTAL SECTION

All reagents used were purchased from ordinary suppliers and were dried over anhydrous $CaCl_2$. All samples were weighted and introduced into the reactions in air. The reactions were monitored by GC on a Focus GC Thermo Scientific instrument. All products were characterized by elemental analysis, ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, and MS spectrometry. NMR spectra were recorded on a Bruker AMX-400 (operating frequencies 400.13, 100.61 и 376.49 MHz respectively). Chemical shifts (^{1}H, ^{13}C) are given relative to $SiMe_4$ and are referenced to signals of benzene-d_6 (δ_H 7.23 ppm, δ_C 128.0 ppm) or $CDCl_3$ (δ_H 7.32 ppm, δ_C 76.91 ppm) as solvents. ^{19}F chemical shifts are given relative to CCl_3F. The $^{13}C\{^{1}H\}$ NMR spectra of all compounds were registered using the *JMODECHO* mode. ^{19}F NMR spectra were recorded with full ^{1}H–^{19}F decoupling. Liquid chromatography-mass spectrometry measurements were performed on a Shimadzu LCMS-2020 (Japan) instrument using electrospray ionization (ESI) and a single quadrupole mass detector. Acetonitrile as a mobile phase was of HPLC grade.

The typical method for the synthesis of bifunctional products with two different groups from acyl halide of octanoic or nonanoic acid. Octanoyl or nonanoyl chloride, R^1H (fluorobenzene or 2-bromothiophene), and $AlBr_3$ were stirred at –20°C in anhydrous CH_2Br_2 for 0.5 - 1 h (a molar ratio [RCOCl]:[R^1H]:[$AlBr_3$] = 1:1:(2-4). Then CBr_4 was added in amounts for the overall molar ratio [RCOCl]:[$CBr_4 \cdot 2AlBr_3$] to be 1:2, and the mixture was brought into contact with carbon monoxide (**caution, a poison!**) under atmospheric pressure under stirring. After stirring for 2 h at –20°C, the appropriate alcohol (R^2OH) was introduced to the reaction mixture, and the reaction left to warm to 0°C over 20-30 min. A total molar ratio [RCOCl]:[$CBr_4 \cdot 2AlBr_3$]:[R^1H]:[R^2H] = 1:2:1:(1-5). Then water (10 ml) and $CHCl_3$ (30 ml) were carefully added to the reaction products. The organic layer was separated and the aqueous one was extracted with $CHCl_3$ (10 ml). The combined organic extracts were washed with H_2O until neutral pH, and dried over Na_2SO_4. The organic extract was concentrated using a rotary evaporator and purified by column chromatography (silica gel) using hexane-acetone (5:1) as an eluent.

2. Starting compounds

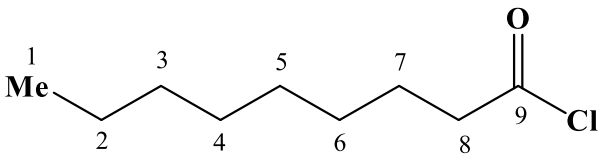
Octanoyl chloride (Aldrich >99%)



^{1}H NMR (400.13 MHz, C_6D_6): 0.96 (t, 3H, $^{3}J_{HH}$ = 7.0 Hz, $^{1}CH_3$), 1.04–1.36 (m, 10H, $^{2–6}CH_2$); 2.37 (t, $^{3}J_{HH}$ = 7.0 Hz, $^{7}CH_2$).

^{13}C NMR (100.61 MHz, C_6H_6): 13.95 ($^{1}CH_3$); 22.61 ($^{2}CH_2$); 24.87 ($^{6}CH_2$); 28.18 ($^{4}CH_2$); 28.72 ($^{5}CH_2$); 31.54 ($^{3}CH_2$); 46.73 ($^{7}CH_2$); 172.97 (^{8}C).

Nonanoyl chloride (Aldrich >95- 98%)



^{1}H NMR (400.13 MHz, C_6D_6): 0.96 (t, $^{3}J_{HH}$ = 7.0 Hz, $^{1}CH_3$); 1.00–1.38 (m, 12H, $^{2–7}CH_2$); 2.37 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H, $^{8}CH_2$).

^{13}C NMR (100.61 MHz, C_6H_6): 14.1 ($^{1}CH_3$); 22.7 ($^{2}CH_2$); 24.9 ($^{7}CH_2$); 28.2 ($^{6}CH_2$); 29.0 ($^{5}CH_2$); 29.1 ($^{4}CH_2$); 31.8 ($^{3}CH_2$); 46.7 ($^{8}CH_2$); 173.0 (^{9}CO).

3. Bifunctional products from acylhalide of octanoic acid

3.1. Synthesis of isopropyl 7-(4-fluorophenyl)-2,2-dimethyl-7-oxoheptanoate (3a)

$C_7H_{15}COCl$ – 0.370 g (2.27 mmol).

CBr_4 – 1.524 g (4.60 mmol).

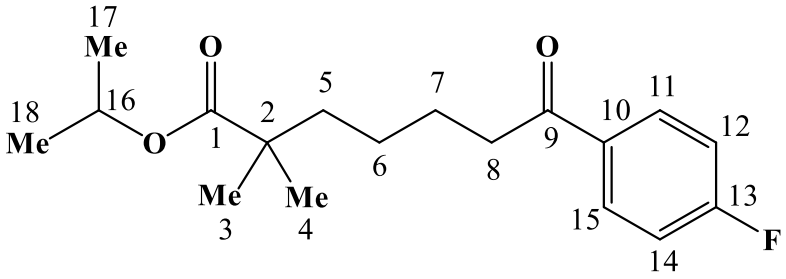
$AlBr_3$ – 2.450 g (9.19 mmol).

CH_2Br_2 – 4.5 ml.

$R^1H = C_6H_5F$ – 0.221 g (2.29 mmol).

$R^2OH = Pr^iOH$ – 0.50 g (8,32 mmol).

Yield 0.39 g (56 %).



Anal. Calcd for $C_{18}H_{25}FO_3$ (308.39 g/mol): C, 70.10; H, 8.17; F, 6.16. Found: C, 70.06; H, 8.06; F, 6.02.

^{1}H NMR (400.13 MHz, $CDCl_3$): 1.15 (s, 6H, $^{3,4}CH_3$); 1.21 (d, $^3J_{HH}$ = 6.2 Hz, 6H, $^{17,18}CH_3$); 1.30-1.35 (m, 2H, $^6CH_2$); 1.54-1.58 (m, 2H, $^5CH_2$); 1.71 (dt, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.4 Hz, 2H, $^7CH_2$); 2.94 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $^8CH_2$); 4.96-4.99 (m, 1H, ^{16}CH); 7.12 (dd, $^3J_{HF}$ = $^3J_{HH}$ = 8.6 Hz, 2H, $^{12,14}CH$); 7.96-7.99 (m, 2H, $^{11,15}CH$).

^{13}C NMR (100.61 MHz, $CDCl_3$): 21.47 ($^{17,18}CH_3$); 24.39 ($^7CH_2$); 24.44 ($^6CH_2$); 24.85 ($^{3,4}CH_3$); 38.04 ($^8CH_2$); 40.14 ($^5CH_2$); 41.78 (^2C); 66.96 (^{16}CH); 115.34 (d, $^2J_{CF}$ = 21.7 Hz, $^{12,14}CH$); 130.38 (d, $^3J_{CF}$ = 9.4 Hz, $^{11,15}CH$); 133.21 (d, $^4J_{CF}$ = 3.0 Hz, ^{10}C); 165.35 (d, $^1J_{CF}$ = 254.0 Hz, ^{13}C); 177.06 (^1CO); 198.22 (^9CO).

^{19}F NMR (376.49 MHz, $CDCl_3$): –105.66.

MS (ESI, m/z): 309 $[M+H]^+$; 221 $[M–COOCH(CH_3)_2]^+$.

3.2. Synthesis of 2,2,2-trifluoroethyl 7-(4-fluorophenyl)-2,2-dimethyl-7-oxoheptanoate (3b)

$C_7H_{15}COCl$ – 0.358 g (2.20 mmol).

CBr_4 – 1.462 g (4.40 mmol).

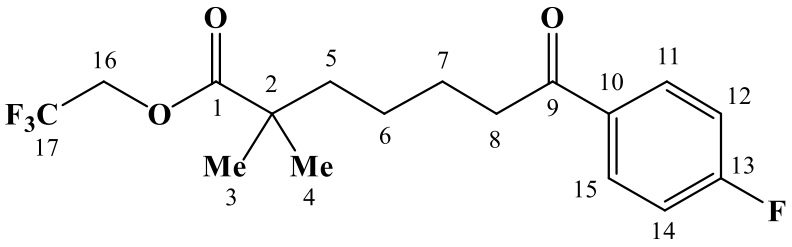
$AlBr_3$ – 2.35 g (8.81 mmol).

CH_2Br_2 – 4 ml.

$R^1H = C_6H_5F$ – 0.212 g (2.21 mmol).

$R^2OH = CF_3CH_2OH$ – 0.91 g (9.10 mmol).

Yield 0.47 g (61 %).



Anal. Calcd for $C_{17}H_{20}O_3F_4$ (348.34 g/mol): C, 58.62; H, 5.79; F, 21.82%. Found: C, 59.69; H, 5.61; F, 21.46%.

^{1}H NMR (400.13 MHz, $CDCl_3$): 1.26 (s, 6H, $^{3,4}CH_3$); 1.32-1.41 (m, 2H, $^6CH_2$); 1.64-1.68 (m, 2H, $^5CH_2$); 1.76 (dt, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.5 Hz, 2H, $^7CH_2$); 2.97 (t, $^3J_{HH}$ = 7.4 Hz, 2H, $^8CH_2$); 4.51 (q, $^3J_{HF}$ = 8.5 Hz, 2H, $^{16}CH_2$); 7.15 (dd, $^3J_{HF}$ = $^3J_{HH}$ = 8.6 Hz, 2H, $^{12,14}CH$); 7.99-8.03 (m, 2H, $^{11,15}CH$).

^{13}C NMR (100.61 MHz, $CDCl_3$): 24.17 ($^7CH_2$); 24.34 ($^6CH_2$); 24.66 ($^{3,4}CH_3$); 37.92 ($^8CH_2$); 39.93 ($^5CH_2$); 42.24 (^2C); 59.87 (q, $^2J_{CF}$ = 36.3 Hz, $^{16}CH_2$); 115.37 (d, $^2J_{CF}$ = 21.8 Hz, $^{12,14}CH$); 127.87 (q, $^1J_{CF}$ = 277.3 Hz, $^{17}CF_3$); 130.37 (d, $^3J_{CF}$ = 9.3 Hz, $^{11,15}CH$); 133.19 (d, $^4J_{CF}$ = 3.0 Hz, ^{10}C); 165.42 (d, $^1J_{CF}$ = 254.0 Hz, ^{13}C); 175.96 (^1CO); 198.13 (^9CO).

^{19}F NMR (376.49 MHz, $CDCl_3$): –74.97 ($^{17}CF_3$); –106.74 (^{13}CF).

MS (ESI, m/z): 349 $[M+H]^+$; 221 $[M–COOCH_2CF_3]^+$; 83 $[CH_2CF_3]^+$.

3.3. Synthesis of 2,2,3,3,3-pentafluoropropyl 7-(4-fluorophenyl)-2,2-dimethyl-7-oxoheptanoate (3c)

$C_7H_{15}COCl$ – 0.370 g (2.27 mmol).

CBr_4 – 1.51 g (4.55 mmol).

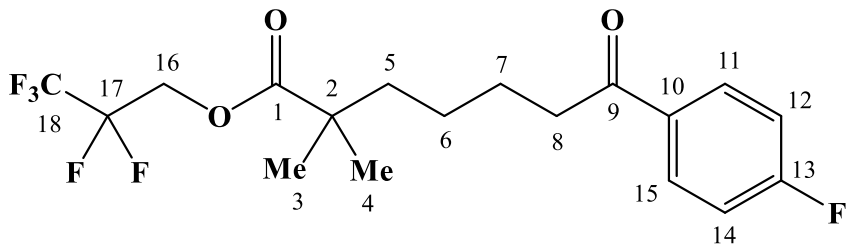
$AlBr_3$ – 2.43 g (9.11 mmol).

CH_2Br_2 – 4 ml.

$R^1H = C_6H_5F$ – 0.278 g (2.27 mmol).

$R^2OH = CF_3CF_2CH_2OH$ – 1.204 g (8.02 mmol).

Yield 0.58 g (64 %).



Anal. Calcd for $C_{18}H_{20}F_6O_3$ (398.35 g/mol): C, 54.27; H, 5.06; F, 28.62%. Found: C, 54.33; H, 5.20%; F, 28.23%.

^{1}H NMR (400.13 MHz, $CDCl_3$): 1.26 (s, 6H, $^{3,4}CH_3$); 1.32-1.40 (m, 2H, $^6CH_2$); 1.64-1.68 (m, 2H, $^5CH_2$); 1.76 (dt, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.5 Hz, 2H, $^7CH_2$); 2.98 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $^8CH_2$); 4.58 (t, $^3J_{HF}$ = 12.8 Hz, 2H, $^{16}CH_2$); 7.16 (dd, $^3J_{HF}$ = $^3J_{HH}$ = 8.6 Hz, 2H, $^{12,14}CH$); 8.00-8.04 (m, 2H, $^{11,15}CH$).

^{13}C NMR (100.61 MHz, $CDCl_3$): 24.26 ($^7CH_2$); 24.43 ($^6CH_2$); 24.71 ($^{3,4}CH_3$); 38.01 ($^8CH_2$); 40.01 ($^5CH_2$); 42.39 (^2C); 58.97 (t, $^2J_{CF}$ = 28.0 Hz, $^{16}CH_2$); 112.07 (tq, $^1J_{CF}$ = 250.4 Hz, $^2J_{CF}$ = 38.1 Hz, $^{17}CF_2$); 115.47 (d, $^2J_{CF}$ = 21.9 Hz, $^{12,14}CH$); 118.36 (qt, $^1J_{CF}$ = 285.6 Hz, $^2J_{CF}$ = 34.7 Hz, $^{18}CF_3$); 130.47 (d, $^3J_{CF}$ = 9.4 Hz, $^{11,15}CH$); 133.27 (d, $^4J_{CF}$ = 3.2 Hz, ^{10}C); 165.54 (d, $^1J_{CF}$ = 254.3 Hz, ^{13}C); 176.03 (^1CO); 198.23 (^9CO).

^{19}F NMR (376.49 MHz, $CDCl_3$): –83.83 ($^{18}CF_3$); –105.65 (^{13}CF); –123.49 ($^{17}CF_2$).

MS (ESI, m/z): 399 $[M+H]^+$; 221 $[M–COOCH_2CF_2CF_3]^+$.

3.4. Synthesis of butyl 7-(5-bromothiophen-2-yl)-2,2-dimethyl-7-oxoheptanoate (3d)

$C_7H_{15}COCl$ – 0.443 g (2.72 mmol).

CBr_4 – 1.805 g (5.44 mmol).

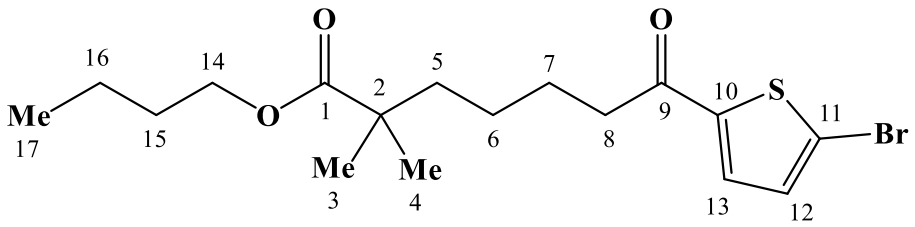
$AlBr_3$ – 2.90 g (10.8 mmol).

CH_2Br_2 – 5 ml.

R^1H = 2-bromothiophene – 0.44 g (2.70 mmol).

R^2OH = BuOH – 0.81 g (10.9 mmol).

Yield 0.68 g (64 %).



Anal. Calcd for $C_{17}H_{25}BrSO_3$ (388.07 g/mol): C, 52.44; H, 6.47; Br, 20.52; S, 8.23%. Found: C, 51.97; H, 6.51; Br, 21.10; S, 8.21%

^{1}H NMR (400.13 MHz, $CDCl_3$): 0.97 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $^{17}CH_3$); 1.19 (s, 6H, $^{3,4}CH_3$); 1.29-1.44 (m, 4H, $^6CH_2$, $^{16}CH_2$); 1.57-1.65 (m, 4H, $^5CH_2$, $^{15}CH_2$); 1.73 (dt, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.4 Hz, 2H, $^7CH_2$); 2.85 (t, $^3J_{HH}$ = 7.4 Hz, 2H, $^8CH_2$); 4.08 (t, $^3J_{HH}$ = 7.4 Hz, 2H, $^{14}CH_2$); 7.13 (d, $^3J_{HH}$ = 4.0 Hz, 1H, ^{12}CH); 7.47 (d, $^3J_{HH}$ = 4.1 Hz, 1H, ^{13}CH).

^{13}C NMR (100.61 MHz, $CDCl_3$): 13.72 ($^{17}CH_3$); 19.18 ($^{16}CH_2$); 24.69 ($^{7}CH_2$); 24.88 ($^{6}CH_2$); 25.16 ($^{3,4}CH_3$); 30.68 ($^{15}CH_2$); 38.49 ($^{8}CH_2$); 40.39 ($^{5}CH_2$); 42.20 (^{2}C); 64.14 ($^{14}CH_2$); 122.31 (^{11}C); 131.19 (^{12}CH); 131.77 (^{13}CH); 145.84 (^{10}C); 177.90 (^{1}CO); 192.03 (^{9}CO).

MS (ESI, m/z): 389 $[M+H]^+$; 287 $[M–COOC_4H_9]^+$.

3.5. Synthesis of isopropyl 7-(5-bromothiophen-2-yl)-2,2-dimethyl-7-oxoheptanoate (3e)

$C_7H_{15}COCl$ – 0.378 g (2.32 mmol).

CBr_4 – 1.54 g (4.64 mmol).

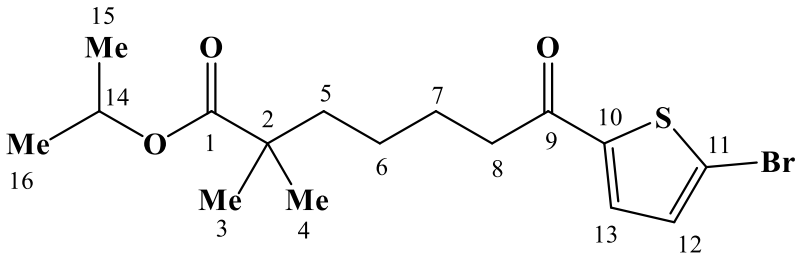
$AlBr_3$ – 2.48 g (9.79 mmol).

CH_2Br_2 – 4.3 ml.

R^1H = 2-bromothiophene – 0.379 g (2.32 mmol).

R^2OH = Pr^iOH – 0.725 g (12.06 mmol).

Yield 0.46 g (53 %).



Anal. Calcd for $C_{16}H_{23}BrSO_3$ (375.32 g/mol): C, 51.20; H, 6.18; Br, 21.29; S, 8.54%. Found: C, 50.73; H, 5.91; Br, 21.45; S, 8.27%.

^{1}H NMR (400.13 MHz, $CDCl_3$): 1.16 (s, 6H, $^{3,4}CH_3$); 1.23 (d, $^3J_{HH}$ = 6.2 Hz, 6H, $^{15,16}CH_3$); 1.28-1.36 (m, 2H, $^{6}CH_2$); 1.54-1.58 (m, 2H, $^{5}CH_2$); 1.72 (dt, 2H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.4 Hz, $^{7}CH_2$); 2.85 (t, 2H, $^3J_{HH}$ = 7.4 Hz, $^{8}CH_2$); 4.99 (hept, $^3J_{HH}$ = 6.2 Hz, 1H, ^{14}CH); 7.12 (d, $^3J_{HH}$ = 3.9 Hz, 1H, ^{12}CH); 7.46 (d, $^3J_{HH}$ = 3.8 Hz, 1H, ^{13}CH).

^{13}C NMR (100.61 MHz, $CDCl_3$): 21.52 ($^{15,16}CH_3$); 24.42 ($^{7}CH_2$); 24.70 ($^{6}CH_2$); 24.89 ($^{3,4}CH_3$); 38.26 ($^{8}CH_2$); 40.06 ($^{5}CH_2$); 41.78 (^{2}C); 67.02 (^{14}CH); 122.10 (^{11}C); 130.98 (^{12}CH); 131.58 (^{13}CH); 146.62 (^{10}C); 177.08 (^{1}CO); 191.86 (^{9}CO).

MS (ESI, m/z): 375 $[M+H]^+$; 287 $[M–COOCH(CH_3)_2]^+$.

3.6. Synthesis of 2,2,2-trifluoroethyl 7-(5-bromothiophen-2-yl)-2,2-dimethyl-7-oxoheptanoate (3f)

$C_7H_{15}COCl$ – 0.415 g (2.55 mmol).

CBr_4 – 1.655 g (4.99 mmol).

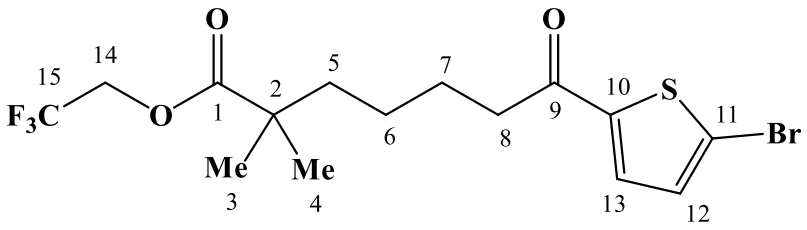
$AlBr_3$ – 1.66 g (9.97 mmol).

CH_2Br_2 – 3.5 ml.

R^1H = 2-bromothiophene – 0.407 g (2.49 mmol).

R^2OH = CF_3CH_2OH – 0.78 g (7.79 mmol).

Yield 0.53 g (50 %).



Anal. Calcd for $C_{15}H_{18}BrF_3SO_3$ (415.27 g/mol): C, 43.39; H, 4.37; F, 13.73; Br, 19.24; S, 7.72%. Found: C, 43.47; H, 4.48; F, 13.68; Br, 19.00; S, 7.68%.

^{1}H NMR (400.13 MHz, $CDCl_3$): 1.23 (s, 6H, $^{3,4}CH_3$); 1.30-1.36 (m, 2H, $^6CH_2$); 1.60-1.64 (m, 2H, $^5CH_2$); 1.72 (p, $^3J_{HH}$ = 7.4 Hz, 2H, $^7CH_2$); 2.84 (t, $^3J_{HH}$ = 7.4 Hz, 2H, $^8CH_2$); 4.48 (q, $^3J_{HF}$ = 8.5 Hz, 2H, $^{14}CH_2$); 7.11 (d, $^3J_{HH}$ = 3.7 Hz, 1H, ^{12}CH); 7.44 (d, $^3J_{HH}$ = 3.7 Hz, 1H, ^{13}CH).

^{13}C NMR (100.61 MHz, $CDCl_3$): 24.44 ($^7CH_2$); 24.57 ($^6CH_2$); 24.84 ($^{3,4}CH_3$); 38.27 ($^8CH_2$); 39.97 ($^5CH_2$); 42.36 (^2C); 60.04 (q, $^2J_{CF}$ = 36.6 Hz, $^{14}CH_2$); 122.10 (^{11}C); 122.95 (q, $^1J_{CF}$ = 273.0 Hz, $^{15}CF_3$); 131.08 (^{12}CH); 131.66 (^{13}CH); 145.66 (^{10}C); 176.12 (^1CO); 191.87 (^9CO).

^{19}F NMR (376.49 MHz, $CDCl_3$): –73.80.

MS (ESI, m/z): 415 $[M+H]^+$; 315 $[M–OCH_2CF_3]^+$; 287 $[M–COOCH_2CF_3]^+$; 83 $[CH_2CF_3]^+$.

3.7. Synthesis of 2,2,3,3,3-pentafluoropropyl 7-(5-bromothiophen-2-yl)-2,2-dimethyl-7-oxoheptanoate (3g)

$C_7H_{15}COCl$ – 0.374 g (2.30 mmol).

CBr_4 – 1.528 g (4.61 mmol).

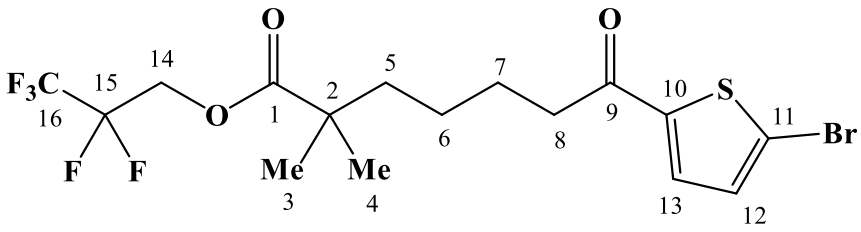
$AlBr_3$ – 2.448 g (9.42 mmol).

CH_2Br_2 – 4 ml.

R^1H = 2-bromothiophene – 0.374 g (2.29 mmol).

R^2OH = $CF_3CF_2CH_2OH$ – 1.505 g (10.03 mmol).

Yield 0.43 g (40 %).



Anal. Calcd for $C_{16}H_{18}BrF_5SO_3$ (465.27 g/mol): C, 41.30; H, 3.90; F, 20.42; Br, 17.17; S, 6.89%. Found: C, 41.16; H, 4.18; F, 19.99; Br, 17.75; S, 7.38%.

^{1}H NMR (400.13 MHz, $CDCl_3$): 1.22 (s, 6H, $^{3,4}CH_3$); 1.27-1.35 (m, 2H, $^{6}CH_2$); 1.59-1.63 (m, 2H, $^{5}CH_2$); 1.72 (dt, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 7.4 Hz, 2H, $^{7}CH_2$); 2.83 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H, $^{8}CH_2$); 4.54 (t, $^{3}J_{HF}$ = 12.8 Hz, 2H, $^{14}CH_2$); 7.11 (d, $^{3}J_{HH}$ = 4.0 Hz, 1H, ^{12}CH); 7.44 (d, $^{3}J_{HH}$ = 4.0 Hz, 1H, ^{13}CH).

^{13}C NMR (100.61 MHz, $CDCl_3$): 24.43 ($^{7}CH_2$); 24.58 ($^{6}CH_2$); 24.79 ($^{3,4}CH_3$); 38.28 ($^{8}CH_2$); 39.96 ($^{5}CH_2$); 42.42 (^{2}C); 59.03 (t, $^{2}J_{CF}$ = 28.2 Hz, $^{14}CH_2$); 113.33 (tq, $^{1}J_{CF}$ = 254.8 Hz, $^{2}J_{CF}$ = 38.0 Hz, $^{15}CF_2$); 115.49 (qt, $^{1}J_{CF}$ = 292.2 Hz, $^{2}J_{CF}$ = 34.7 Hz, $^{16}CF_3$); 122.33 (^{11}C); 131.09 (^{12}CH); 131.65 (^{13}CH); 145.66 (^{10}C); 176.07 (^{1}CO); 191.83 (^{9}CO).

^{19}F NMR (376.49 MHz, $CDCl_3$): –83.71 ($^{16}CF_3$); –123.39 ($^{15}CF_2$).

MS (ESI, m/z): 465 $[M+H]^+$; 287 $[M–COOCH_2CF_2CF_3]^+$.

4. Bifunctional products from acylhalide of nonanoic acid

4.1. Synthesis of 2,2,2-trifluoroethyl 8-(4-fluorophenyl)-2,2-dimethyl-8-oxooctanoate (4a)

$C_8H_{17}COCl$ – 0.362 g (2.05 mmol).

CBr_4 – 1.367 g (4.12 mmol).

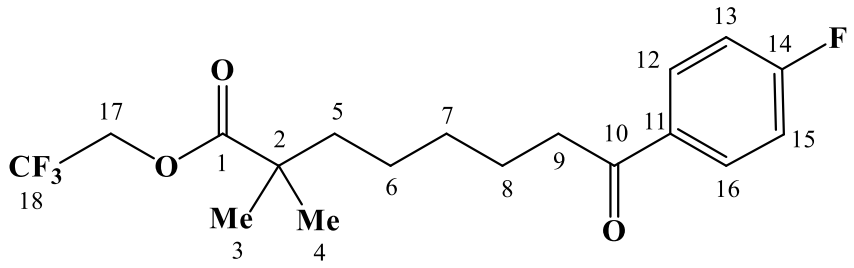
$AlBr_3$ – 2.19 g (8.21 mmol).

CH_2Br_2 – 4 ml.

$R^1H = C_6H_5F$ – 0.197 g (2.05 mmol).

$R^2OH = CF_3CH_2OH$ – 1.04 g (10.40 mmol).

Yield 0.49 g (66 %).



Anal. Calcd for $C_{18}H_{22}F_4O_3$ (362.36 g/mol): C, 59.66; H, 6.12; F, 20.97% Found: C, 59.71; H, 6.11; F, 20.45%

^{1}H NMR (400.13 MHz, $CDCl_3$): 1.25 (s, 6H, $^{3,4}CH_3$); 1.31-1.44 (m, 4H, $^{6,7}CH_2$); 1.60-1.64 (m, 2H, $^5CH_2$); 1.73-1.81 (m, 2H, $^8CH_2$); 2.97 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $^9CH_2$); 4.51 (q, $^3J_{HF}$ = 8.5 Hz, 2H, $^{17}CH_2$); 7.16 (dd, $^3J_{HF} = {}^3J_{HH}$ = 8.5 Hz, 2H, $^{13,15}CH$); 8.00-8.04 (m, 2H, $^{12,16}CH$).

^{13}C NMR (100.61 MHz, $CDCl_3$): 23.87 ($^7CH_2$); 24.55 ($^6CH_2$); 24.78 ($^{3,4}CH_3$); 29.47 ($^8CH_2$); 38.15 ($^9CH_2$); 40.11 ($^5CH_2$); 42.34 (^2C); 59.94 (q, $^2J_{CF}$ = 36.6 Hz, $^{17}CH_2$); 115.47 (d, $^2J_{CF}$ = 21.9 Hz, $^{13,15}CH$); 122.97 (q, $^1J_{CF}$ = 277.5 Hz, $^{18}CF_3$); 130.50 (d, $^3J_{CF}$ = 9.4 Hz, $^{12,16}CH$); 133.32 (d, $^4J_{CF}$ = 3.1 Hz, ^{11}C); 165.51 (d, $^1J_{CF}$ = 254.5 Hz, ^{14}C); 176.18 (^1CO); 198.52 (^{10}CO).

^{19}F NMR (376.49 MHz, $CDCl_3$): –73.88 ($^{18}CF_3$); –105.70 (^{14}CF).

MS (ESI, m/z): 363 $[M+H]^+$; 235 $[M–COOCH_2CF_3]^+$; 83 $[CH_2CF_3]^+$.

4.2. Synthesis of 2,2,3,3,3-pentafluoropropyl 8-(4-fluorophenyl)-2,2-dimethyl-8-oxooctanoate (4b)

$C_8H_{17}COCl$ – 0.373 g (2.11 mmol).

CBr_4 – 1.405 g (4.24 mmol).

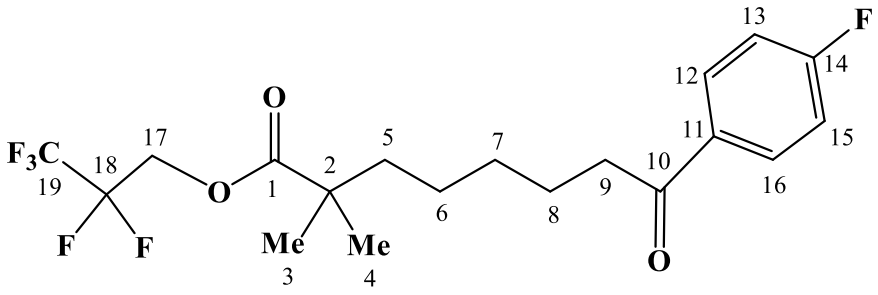
$AlBr_3$ – 2.05 g (7.69 mmol).

CH_2Br_2 – 4 ml.

$R^1H = C_6H_5F$ – 0.203 g (2.11 mmol).

$R^2OH = CF_3CF_2CH_2OH$ – 1.053 g (7.02 mmol).

Yield 0.44 g (50 %).



Anal. Calcd for $C_{19}H_{22}F_6O_3$ (412.37 g/mol): C, 55.34; H, 5.38; F, 27.64%. Found: C, 55.78; H, 5.03; F, 27.35%.

^{1}H NMR (400.13 MHz, $CDCl_3$): 1.25 (s, 6H, $^{3,4}CH_3$); 1.29-1.44 (m, 4H, $^{6,7}CH_2$); 1.59-1.63 (m, 2H, $^5CH_2$); 1.73-1.81 (m, 2H, $^8CH_2$); 2.97 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $^9CH_2$); 4.57 (t, $^3J_{HF}$ = 12.8 Hz, 2H, $^{17}CH_2$); 7.16 (dd, $^3J_{HF}$ = $^3J_{HH}$ = 8.6 Hz, 2H, $^{13,15}CH$); 8.00-8.04 (m, 2H, $^{12,16}CH$).

^{13}C NMR (100.61 MHz, $CDCl_3$): 23.87 ($^7CH_2$); 24.55 ($^6CH_2$); 24.72 ($^{3,4}CH_3$); 29.46 ($^8CH_2$); 38.14 ($^9CH_2$); 40.10 ($^5CH_2$); 42.40 (^2C); 54.95 (t, $^2J_{CF}$ = 28.2 Hz, $^{17}CH_2$); 112.07 (tq, $^1J_{CF}$ = 254.7 Hz, $^2J_{CF}$ = 37.9 Hz, $^{18}CF_2$); 115.46 (d, $^2J_{CF}$ = 21.9 Hz, $^{13,15}CH$); 115.51 (qt, $^1J_{CF}$ = 286.0 Hz, $^2J_{CF}$ = 34.7 Hz, $^{19}CF_3$); 130.49 (d, $^3J_{CF}$ = 9.4 Hz, $^{12,16}CH$); 133.33 (d, $^4J_{CF}$ = 3.1 Hz, ^{11}C); 165.52 (d, $^1J_{CF}$ = 254.0 Hz, ^{14}C); 176.13 (^1CO); 198.49 (^{10}CO).

^{19}F NMR (376.49 MHz, $CDCl_3$): –83.84 ($^{19}CF_3$); –105.73 (^{14}CF); –123.47 ($^{18}CF_2$);.

MS (ESI, m/z): 413 $[M+H]^+$; 235 $[M–COOCH_2CF_2CF_3]^+$.

4.3. Synthesis of isopropyl 8-(5-bromothiophen-2-yl)-2,2-dimethyl-8-oxooctanoate (4c)

$C_8H_{17}COCl$ – 0.366 g (2.07 mmol).

CBr_4 – 1.37 g (4.130 mmol).

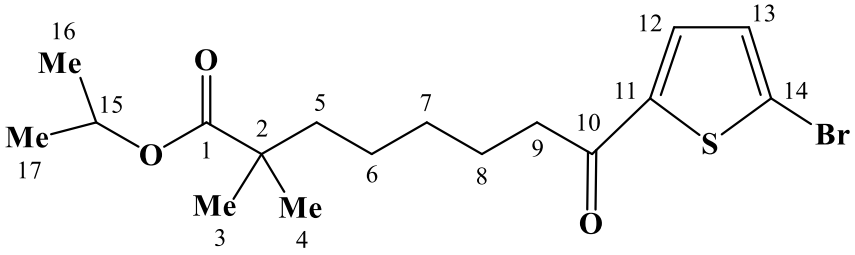
$AlBr_3$ – 2.27 g (8.51 mmol).

CH_2Br_2 – 4 ml.

R^1H = 2-bromothiophene – 0.388 g (2.38 mmol).

R^2OH = Pr^iOH – 0.363 g (6.04 mmol).

Yield 0.52 g (64 %).



Anal. Calcd for $C_{17}H_{25}BrSO_3$ (388.35 g/mol): C, 52.44; H, 6.47; Br, 20.52; S, 8.23%. Found: C, 52.18; H, 6.27; Br, 20.19; S, 8.01%.

^{1}H NMR (400.13 MHz, $CDCl_3$): 1.16 (s, 6H, $^{3,4}CH_3$); 1.23 (d, $^{3}J_{HH}$ = 6.3 Hz, 6H, $^{16,17}CH_3$); 1.28-1.40 (m, 4H, $^{6,7}CH_2$); 1.51-1.55 (m, 2H, $^{5}CH_2$); 1.74 (dt, 2H, $^{3}J_{HH}$ = 7.5 Hz, $^{3}J_{HH}$ = 7.4 Hz, $^{8}CH_2$); 2.83 (t, 2H, $^{3}J_{HH}$ = 7.4 Hz, $^{9}CH_2$); 5.0 (hept, $^{3}J_{HH}$ = 6.2 Hz, 1H, ^{15}CH); 7.12 (d, $^{3}J_{HH}$ = 4.0 Hz, 1H, ^{13}CH); 7.47 (d, $^{3}J_{HH}$ = 4.0 Hz, 1H, ^{14}CH).

^{13}C NMR (100.61 MHz, $CDCl_3$): 21.54 ($^{16,17}CH_3$); 24.22 ($^{7}CH_2$); 24.46 ($^{6}CH_2$); 24.30 ($^{3,4}CH_3$); 29.45 ($^{8}CH_2$); 38.26 ($^{9}CH_2$); 40.15 ($^{5}CH_2$); 41.81 (^{2}C); 66.95 (^{15}CH); 122.10 (^{12}C); 130.98 (^{13}CH); 131.60 (^{14}CH); 145.62 (^{11}C); 177.19 (^{1}CO); 192.06 (^{10}CO).

MS (ESI, m/z): 389 $[M+H]^+$; 301 $[M–COOCH(CH_3)_2]^+$.

4.4. Synthesis of 2,2,2-trifluoroethyl 8-(5-bromothiophen-2-yl)-2,2-dimethyl-8-oxooctanoate (4d)

$C_8H_{17}COCl$ – 0.373 g (2.11 mmol).

CBr_4 – 1.399 g (4.22 mmol).

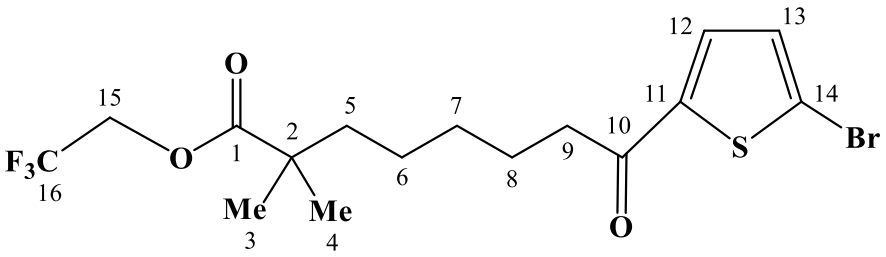
$AlBr_3$ – 2.248 g (8.43 mmol).

CH_2Br_2 – 3.7 ml.

R^1H = 2-bromothiophene – 0.344 g (2.11 mmol).

R^2OH = CF_3CH_2OH – 1.04 g (10.40 mmol).

Yield 0.35 g (39 %).



Anal. Calcd for $C_{16}H_{20}BrF_3SO_3$ (429.29 g/mol): C, 44.77; H, 4.70; Br, 18.61; S, 7.47%. Found: C, 44.98; H, 4.61; Br, 18.31; S, 7.07%.

^{1}H NMR (400.13 MHz, $CDCl_3$): 1.25 (s, 6H, $^{3,4}CH_3$); 1.29-1.43 (m, 4H, $^{6,7}CH_2$); 1.59-1.63 (m, 2H, $^{5}CH_2$); 1.72-1.80 (m, 2H, $^{8}CH_2$); 2.86 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H, $^{9}CH_2$); 4.52 (q, $^{3}J_{HF}$ = 8.5 Hz, 2H, $^{15}CH_2$); 7.14 (d, $^{3}J_{HH}$ = 4.0 Hz, 1H, ^{13}CH); 7.48 (d, $^{3}J_{HH}$ = 4.0 Hz, 1H, ^{14}CH).

^{13}C NMR (100.61 MHz, $CDCl_3$): 24.16 ($^{7}CH_2$); 24.45 ($^{6}CH_2$); 24.77 ($^{3,4}CH_3$); 29.37 ($^{8}CH_2$); 38.32 ($^{9}CH_2$); 40.03 ($^{5}CH_2$); 42.31 (^{2}C); 59.93 (q, $^{2}J_{CF}$ = 36.5 Hz, $^{15}CH_2$); 122.19 (^{12}C); 122.91 (q, $^{1}J_{CF}$ = 277.3 Hz, $^{16}CF_3$); 131.04 (^{13}CH); 131.64 (^{14}CH); 145.72 (^{11}C); 176.13 (^{1}CO); 192.07 (^{10}CO).

^{19}F NMR (376.49 MHz, $CDCl_3$): –73.82.

MS (ESI, m/z): 429 $[M+H]^+$; 301 $[M–COOCH_2CF_3]^+$; 83 $[CH_2CF_3]^+$.

4.5. Synthesis of 2,2,3,3,3-pentafluoropropyl 8-(5-bromothiophen-2-yl)-2,2-dimethyl-8-oxooctanoate (4e)

$C_8H_{17}COCl$ – 0.334 g (1.89 mmol).

CBr_4 – 1.253 g (3.78 mmol).

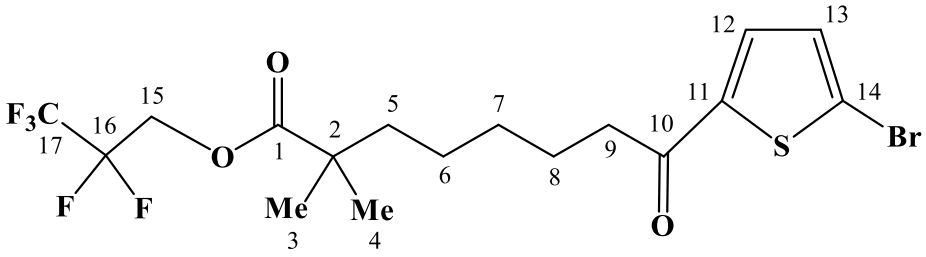
$AlBr_3$ – 2.013 g (7.55 mmol).

CH_2Br_2 – 3.4 ml.

R^1H = 2-bromothiophene – 0.308 g (1.89 mmol).

R^2OH = $CF_3CF_2CH_2OH$ – 0.753 g (5.01 mmol).

Yield 0.41 g (45 %).



Anal. Calcd for $C_{17}H_{20}BrF_5SO_3$ (479.30 g/mol): C, 42.60; H, 4.21; Br, 16.67; F, 19.82; S, 6.69%. Found: C, 42.50; H, 4.37; Br, 16.49; F, 19.67; S, 6.65%.

^{1}H NMR (400.13 MHz, $CDCl_3$): 1.24 (s, 6H, $^{3,4}CH_3$); 1.29-1.41 (m, 4H, $^{6,7}CH_2$); 1.58-1.62 (m, 2H, $^5CH_2$); 1.76 (dt, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.3 Hz, 2H, $^8CH_2$); 2.85 (t, $^3J_{HH}$ = 7.3 Hz, 2H, $^9CH_2$); 4.57 (t, $^3J_{HF}$ = 12.8 Hz, 2H, $^{15}CH_2$); 7.13 (d, $^3J_{HH}$ = 4.0 Hz, 1H, ^{13}CH); 7.47 (d, $^3J_{HH}$ = 4.0 Hz, 1H, ^{14}CH).

^{13}C NMR (100.61 MHz, $CDCl_3$): 24.15 ($^7CH_2$); 24.45 ($^6CH_2$); 24.70 ($^{3,4}CH_3$); 29.46 ($^8CH_2$); 38.30 ($^9CH_2$); 40.00 ($^5CH_2$); 42.34 (^{2}C); 58.90 (t, $^2J_{CF}$ = 28.2 Hz, $^{15}CH_2$); 112.01 (tq, $^1J_{CF}$ = 254.9 Hz, $^2J_{CF}$ = 38.0 Hz, $^{16}CF_2$); 118.30 (qt, $^1J_{CF}$ = 285.9 Hz, $^2J_{CF}$ = 35.0 Hz, $^{17}CF_3$); 122.18 (^{12}C); 131.03 (^{13}CH); 131.63 (^{14}CH); 145.72 (^{11}C); 176.06 (^{1}CO); 192.01 (^{10}CO).

^{19}F NMR (376.49 MHz, $CDCl_3$): –83.80 ($^{17}CF_3$); –123.43 ($^{16}CF_2$).

MS (ESI, m/z): 479 $[M+H]^+$; 301 $[M–COOCH_2CF_2CF_3]^+$.

5. ^{1}H, ^{13}C and ^{19}F NMR spectra of starting $C_nH_{2n+1}COCl$ (n = 7–9) and bifunctional products obtained from them

5.1. Starting octanoyl and nonanoyl chlorides

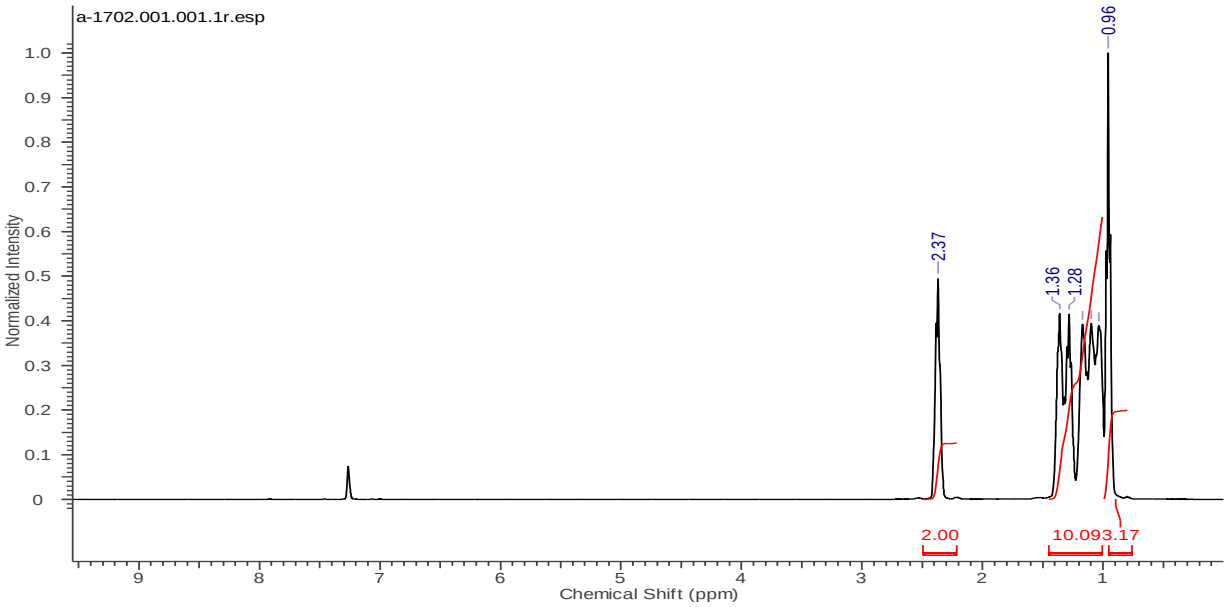


Figure S1. ^{1}H NMR spectrum of starting $C_7H_{15}COCl$ recorded in C_6D_6.

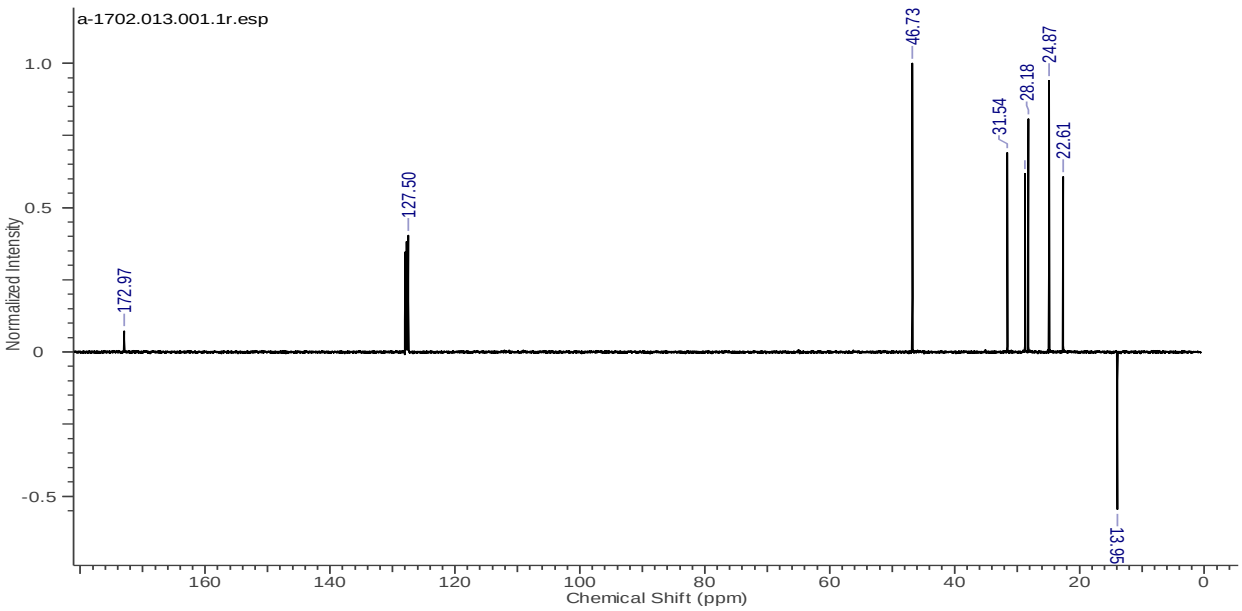


Figure S2: ^{13}C NMR spectrum of starting $C_7H_{15}COCl$ recorded in C_6D_6.

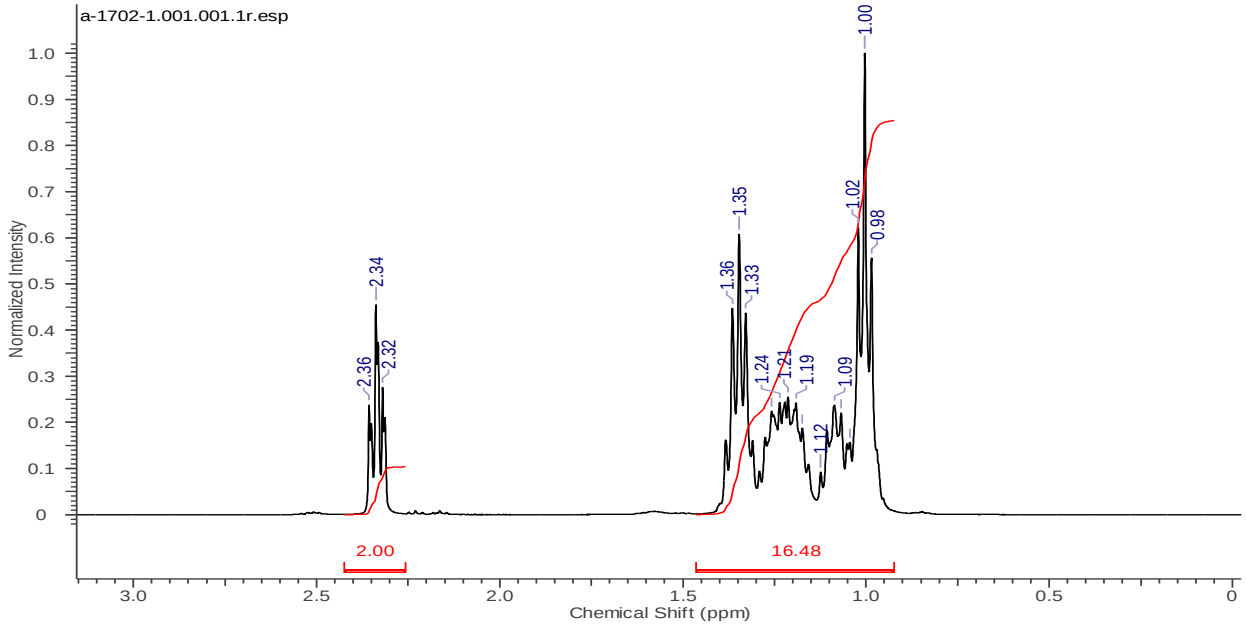


Figure. S3. ^{1}H NMR spectrum of starting $C_8H_{17}COCl$ (Aldrich< 95- 98 %) recorded in C_6D_6.

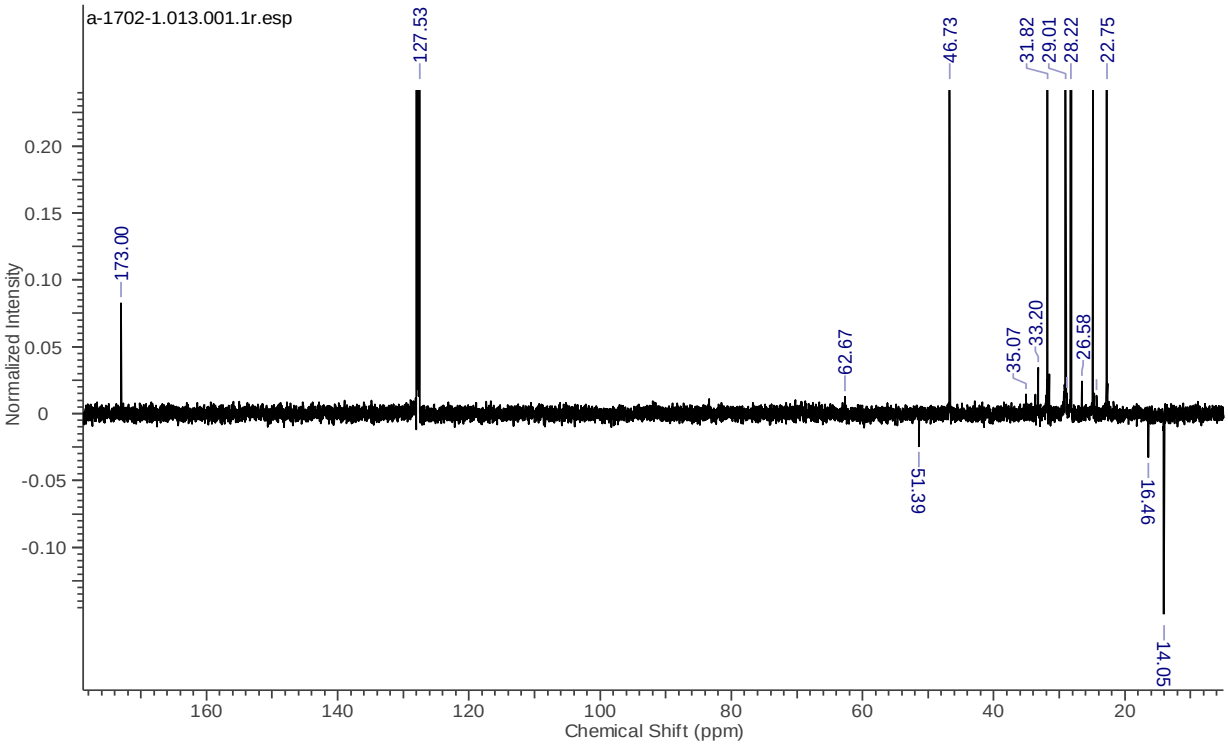


Figure. S4a. ^{13}C NMR spectrum of starting $C_8H_{17}COCl$ recorded in C_6D_6.

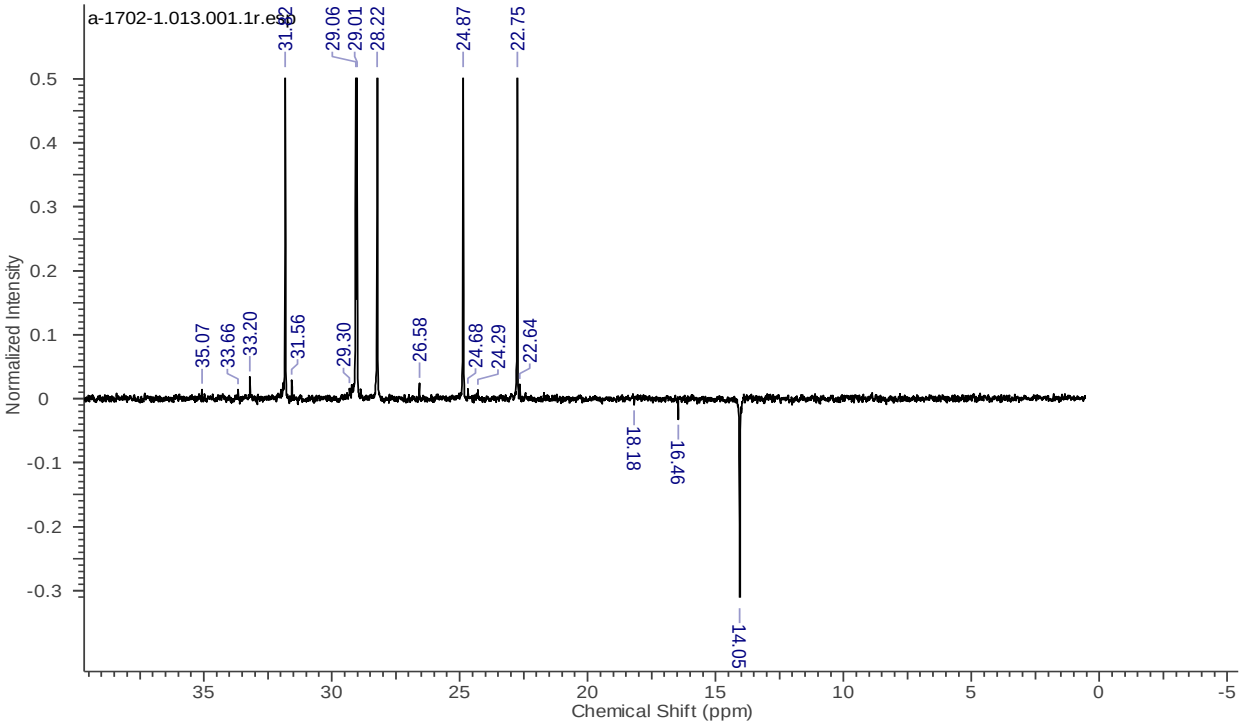


Figure S4b. ^{13}C NMR spectrum of $C_8H_{17}COCl$ recorded in C_6D_6.

5.2. Bifunctional products from octanoyl chloride

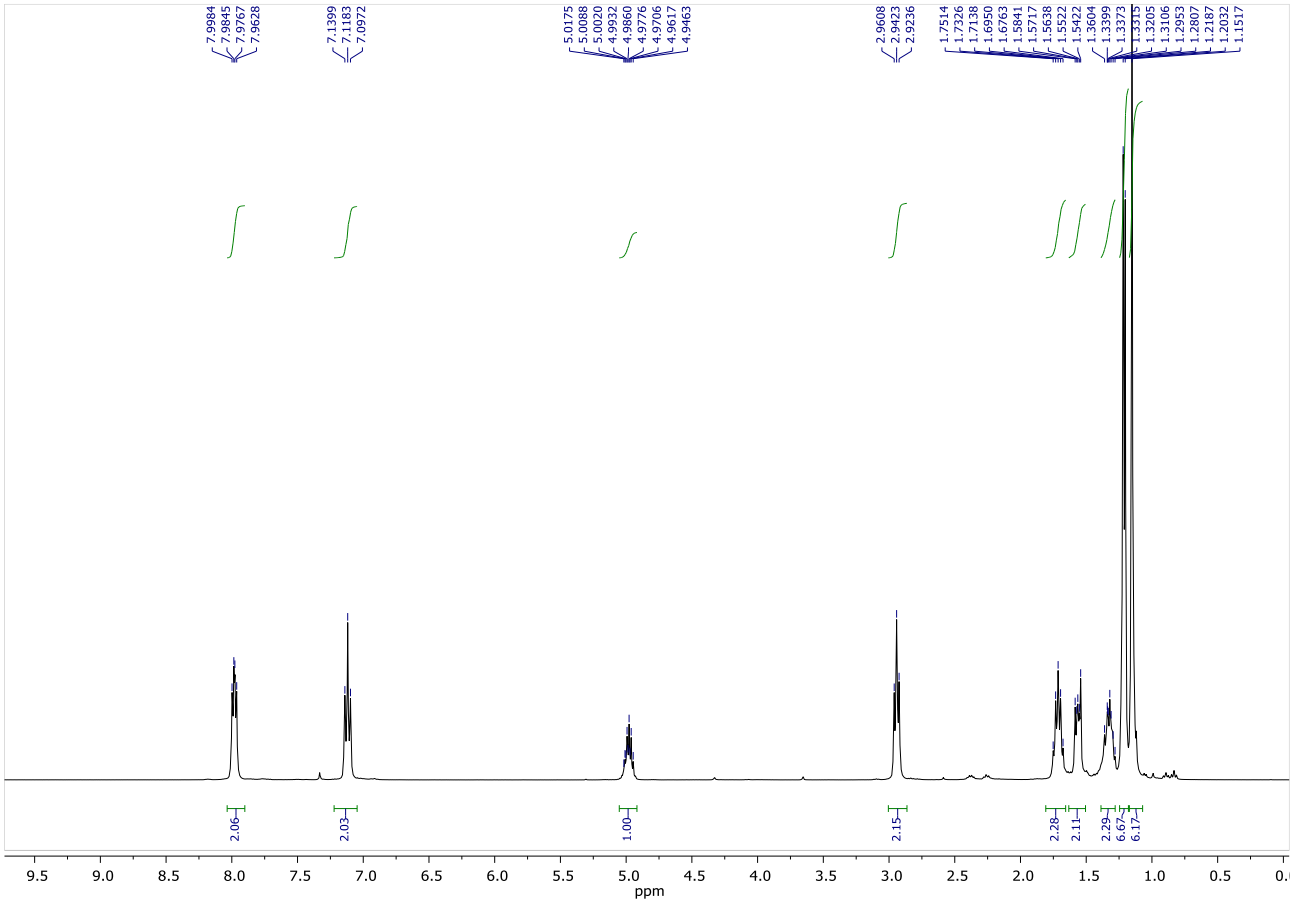


Figure S5. ^{1}H NMR spectrum of (**3a**) recorded in $CDCl_3$.

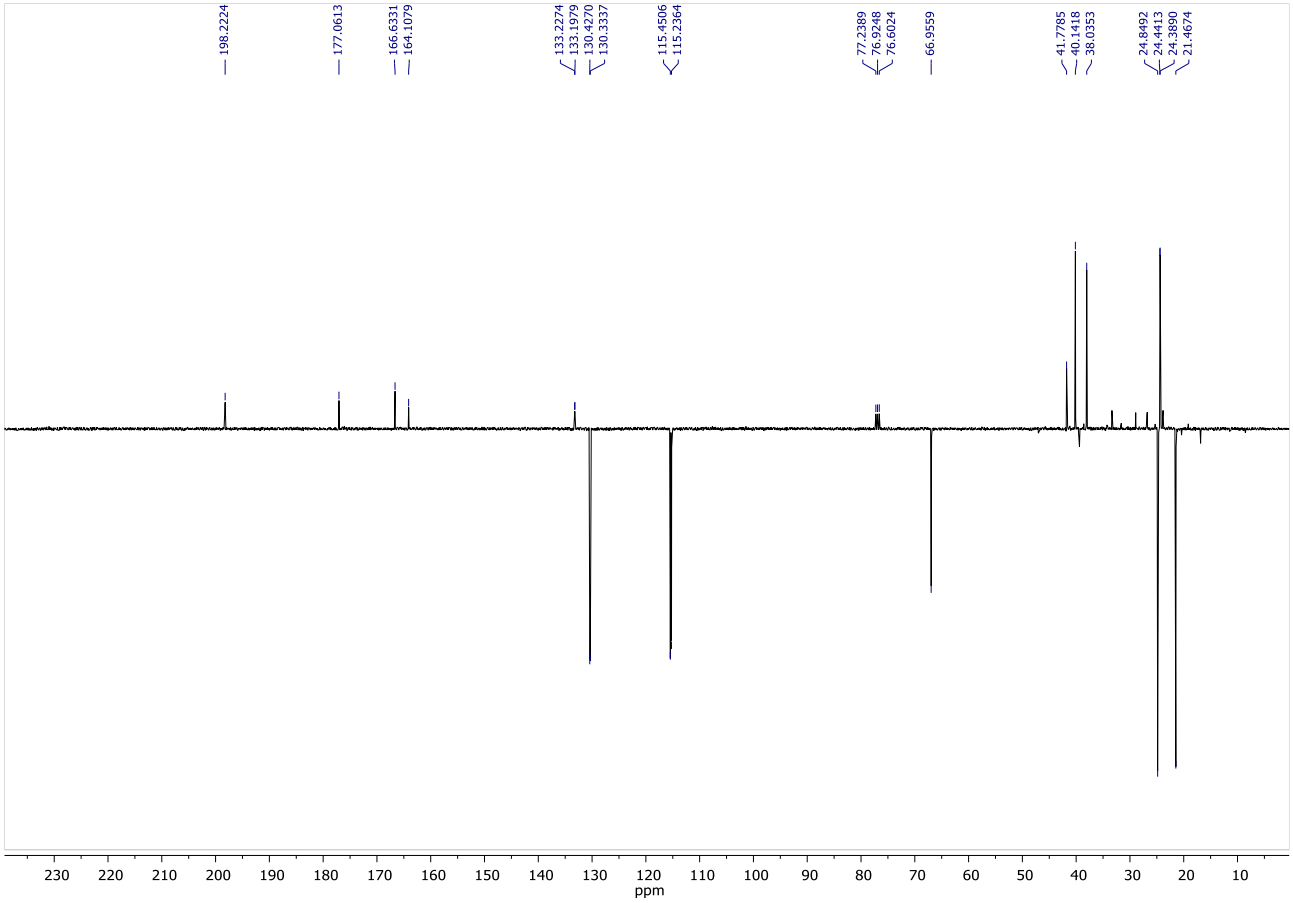


Figure S6. ^{13}C NMR spectrum of (**3a**) recorded in $CDCl_3$

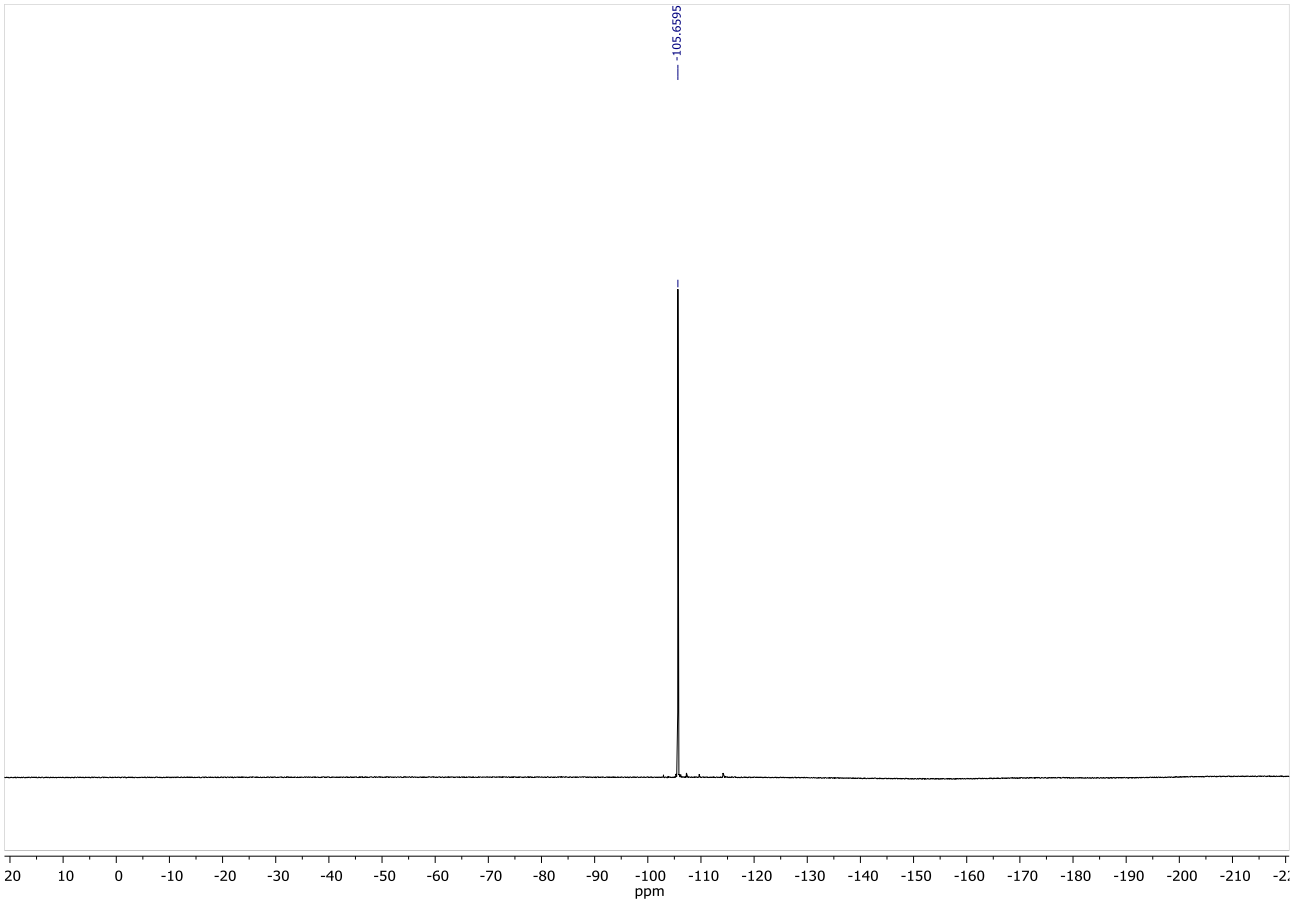


Figure S7. ^{19}F NMR spectrum of (**3a**) recorded in $CDCl_3$

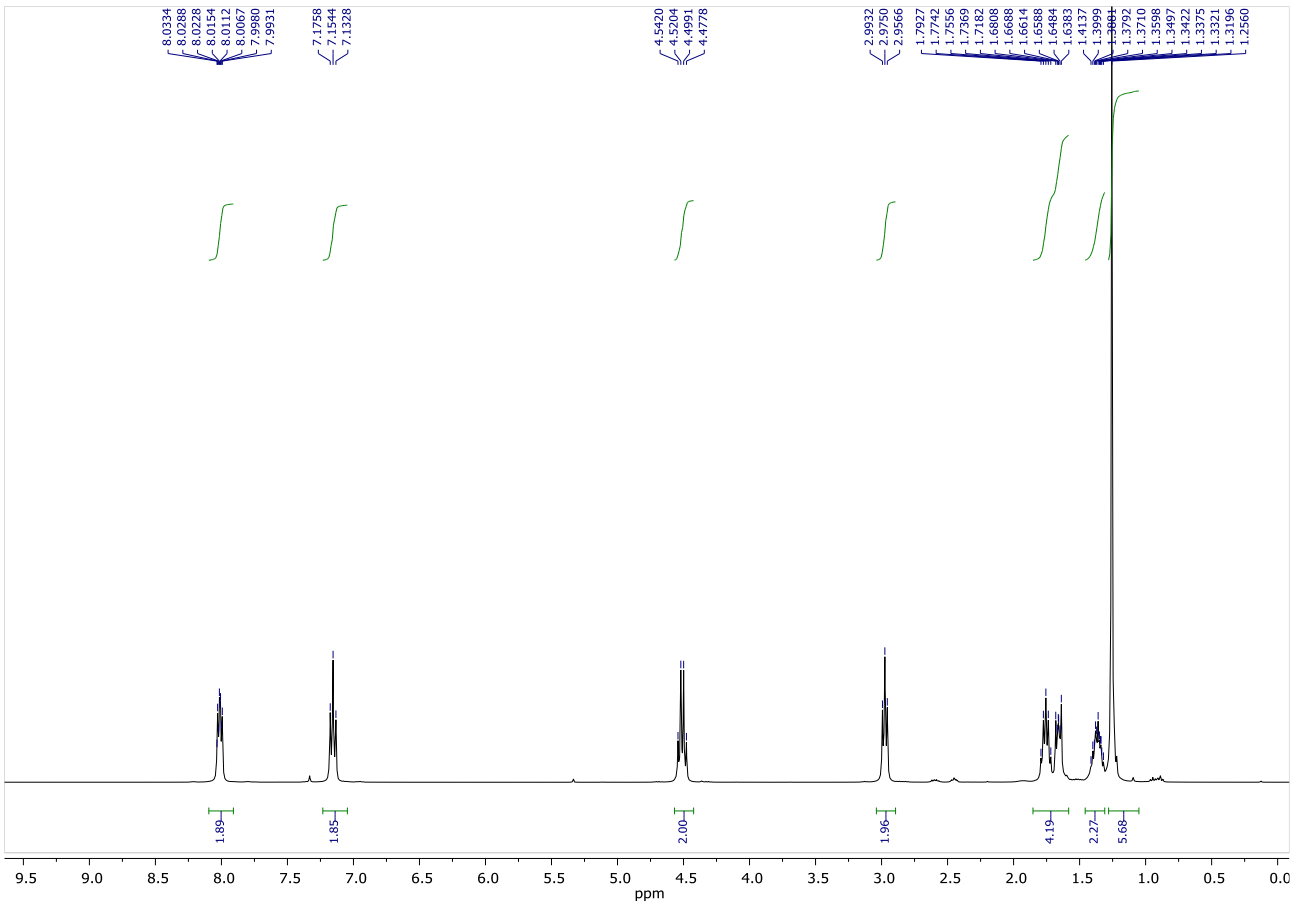


Figure S8. ^{1}H NMR spectrum of (**3b**) recorded in $CDCl_3$.

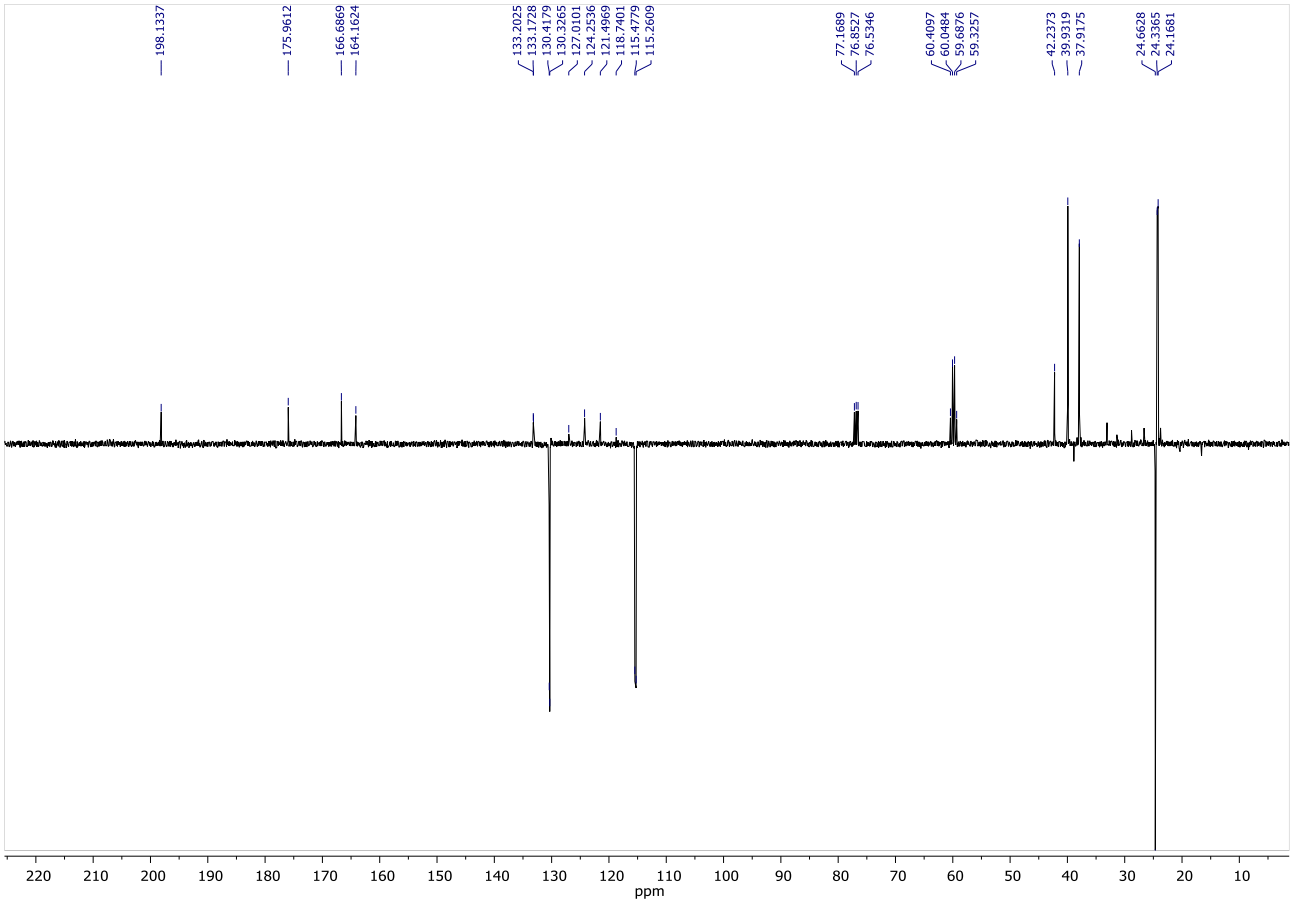


Figure S9. ^{13}C NMR spectrum of (**3b**) recorded in $CDCl_3$

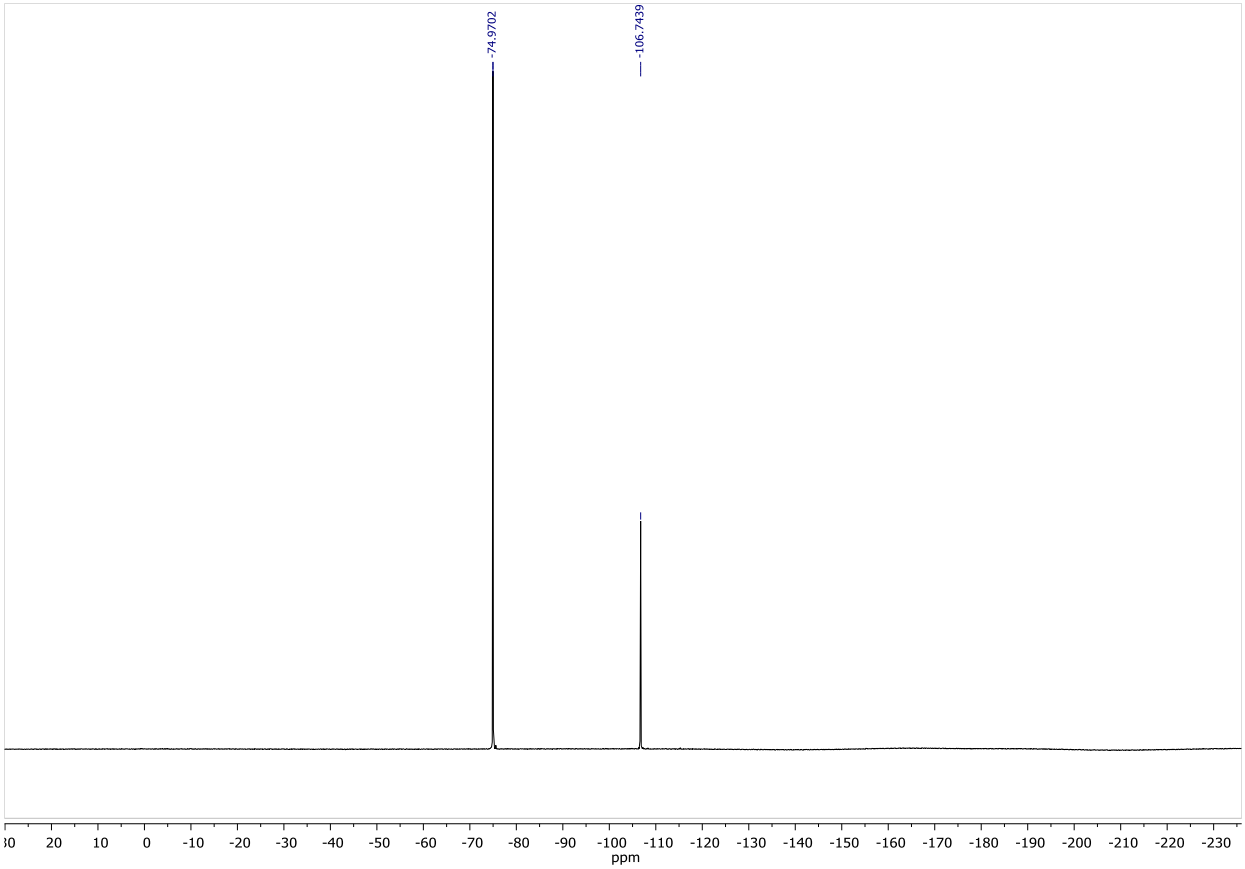


Figure S10. ^{19}F NMR spectrum of (**3b**) recorded in $CDCl_3$

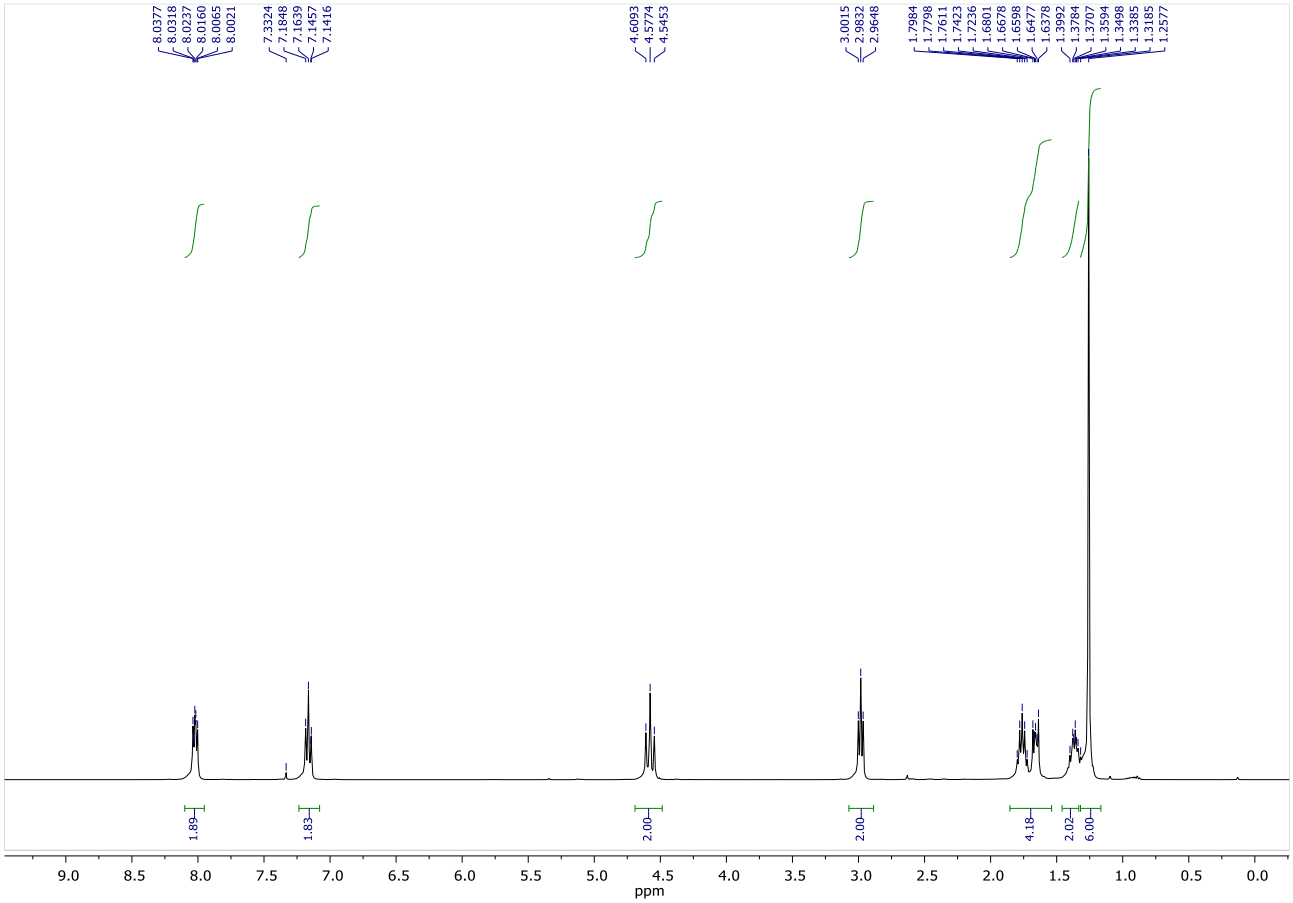


Figure S11. ^{1}H NMR spectrum of (**3c**) recorded in $CDCl_3$.

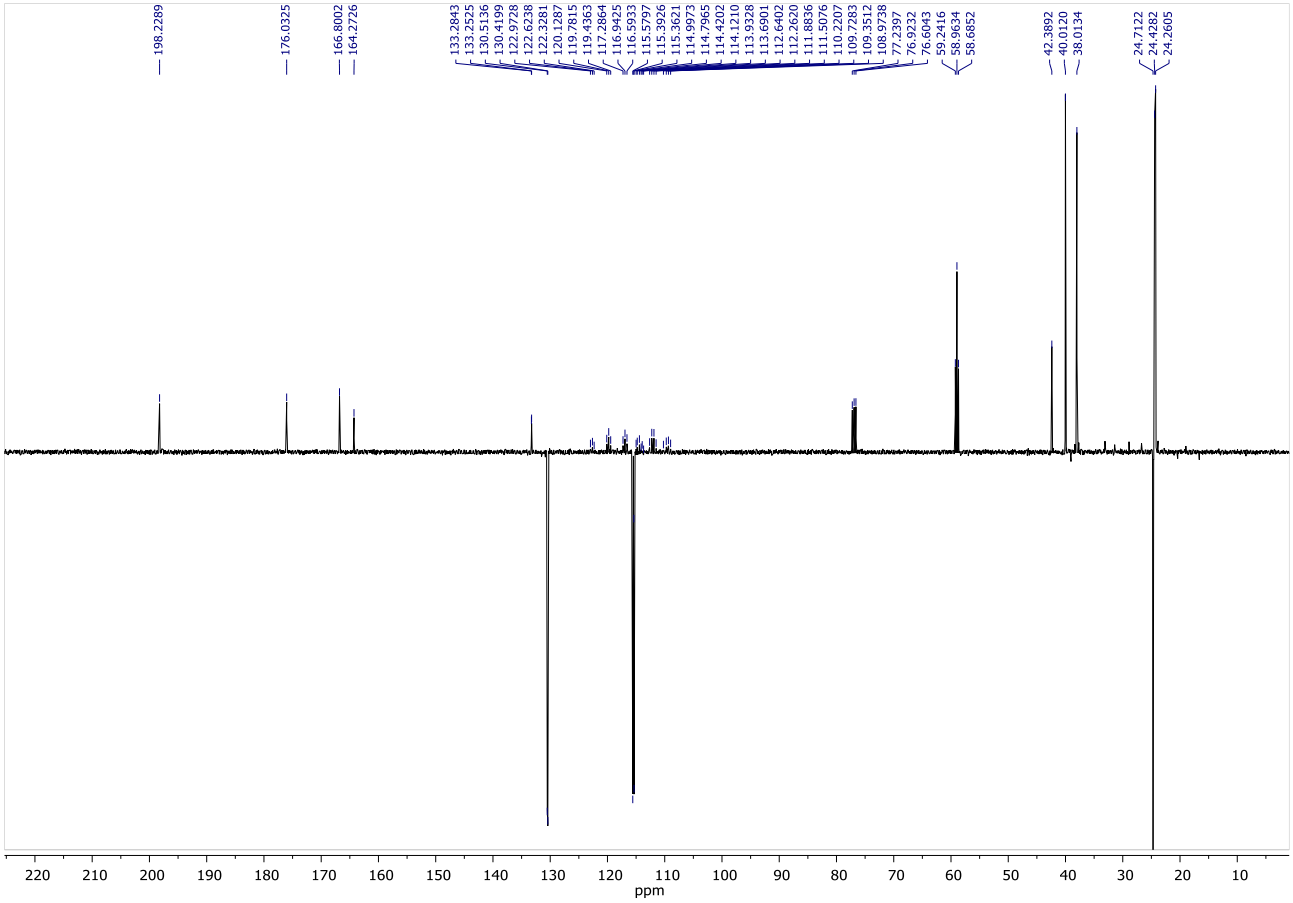


Figure S12. ^{13}C NMR spectrum of (**3c**) recorded in $CDCl_3$

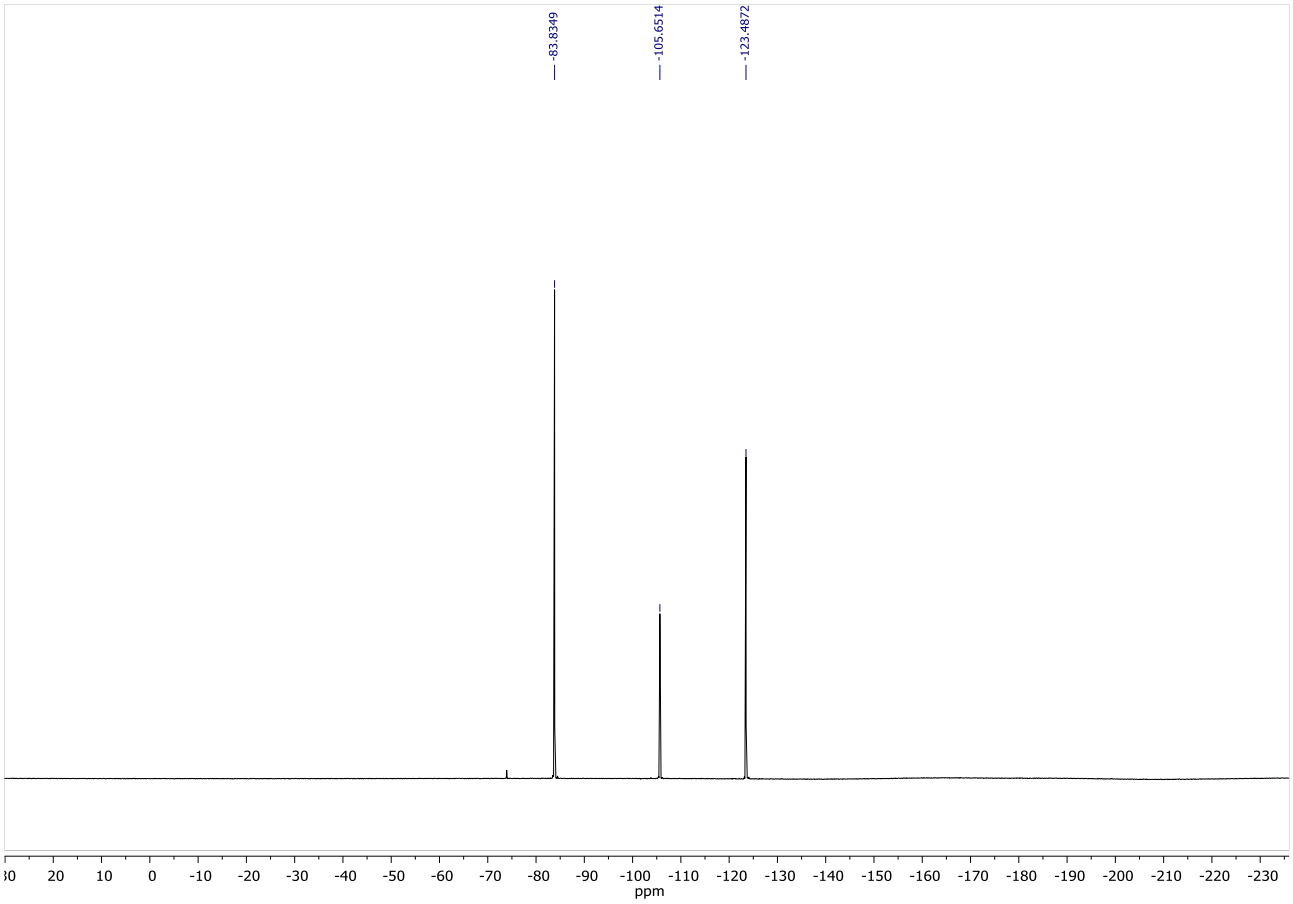


Figure S13. ^{19}F NMR spectrum of (**3c**) recorded in $CDCl_3$

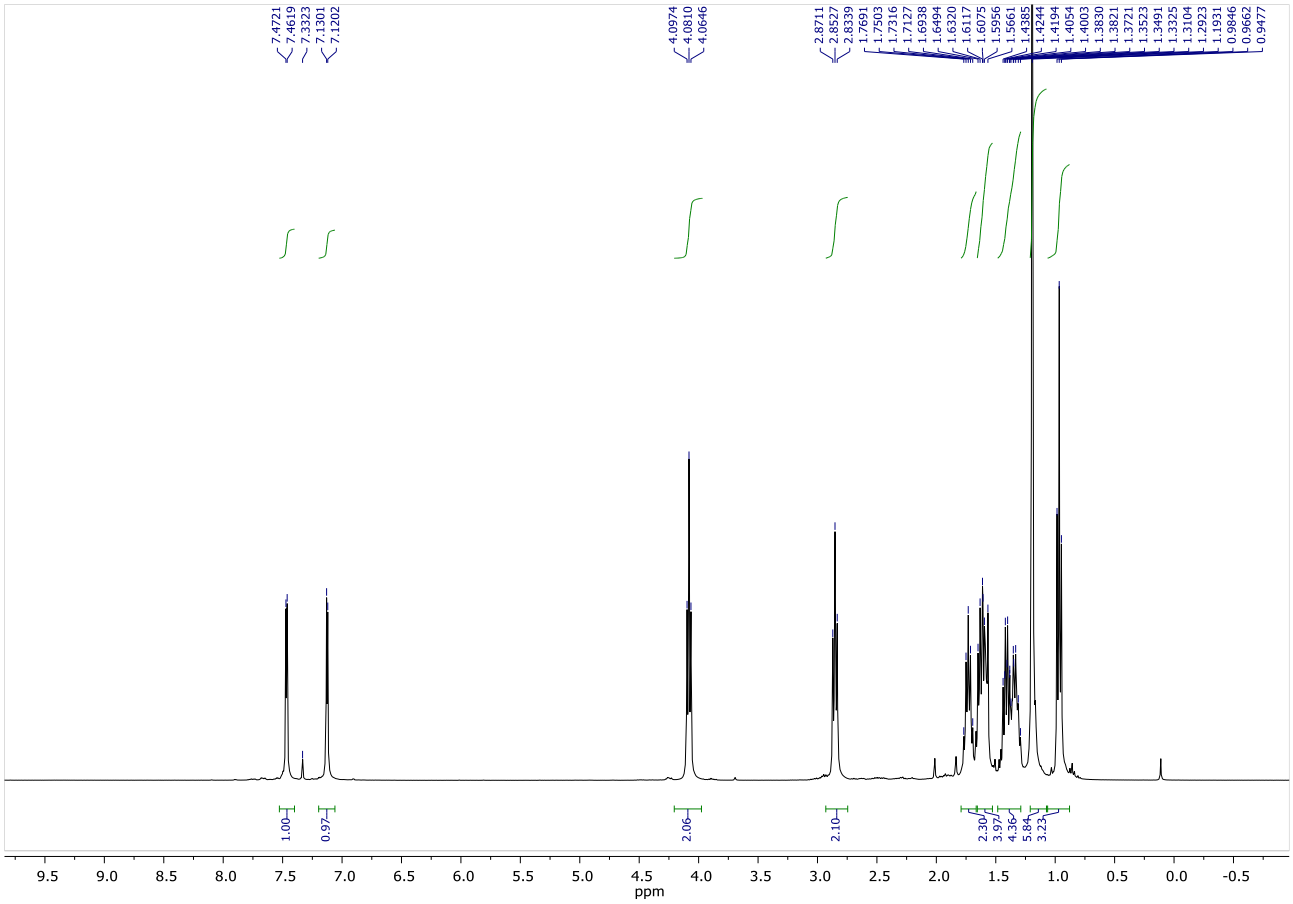


Figure S14. ^{1}H NMR spectrum of (**3d**) recorded in $CDCl_3$

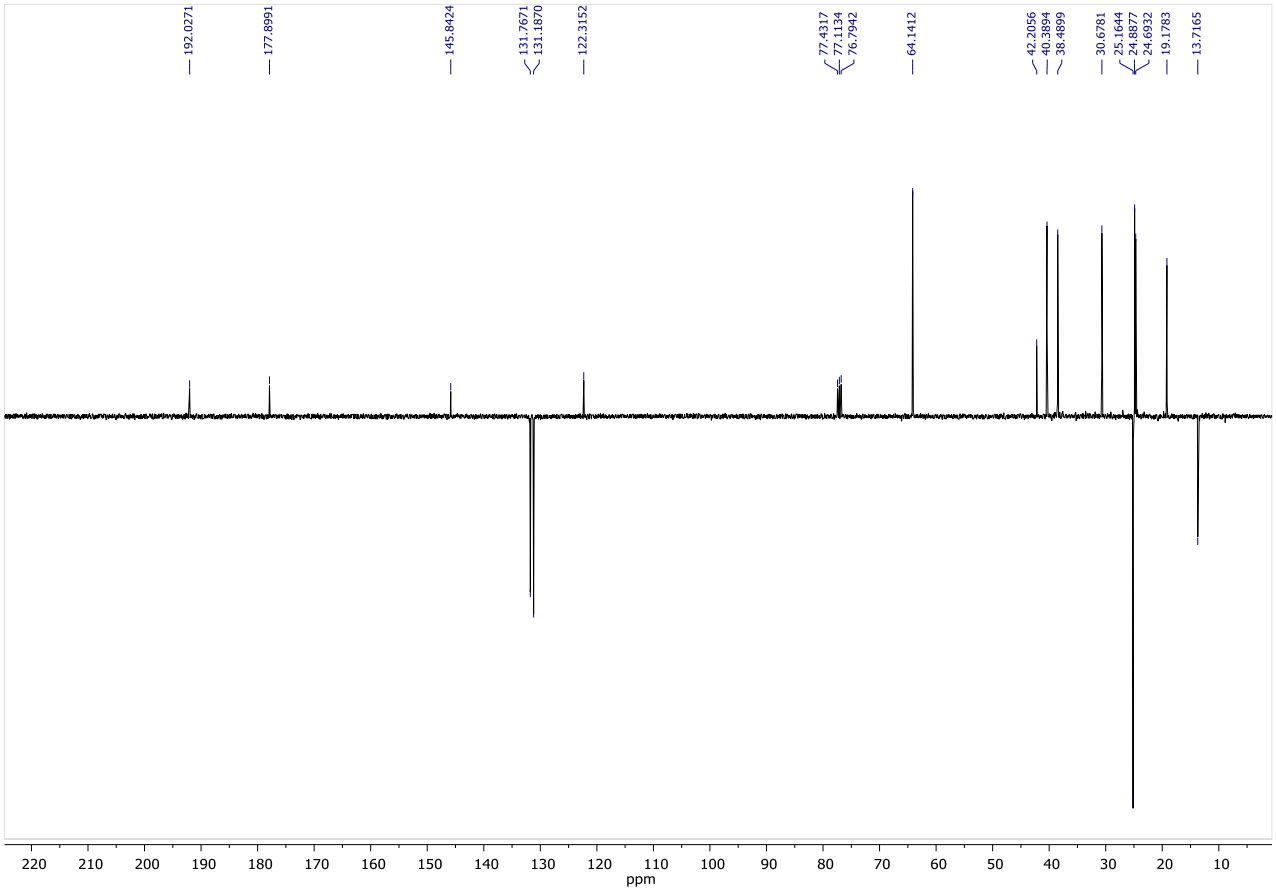


Figure S15. ^{13}C NMR spectrum of (**3d**) recorded in $CDCl_3$

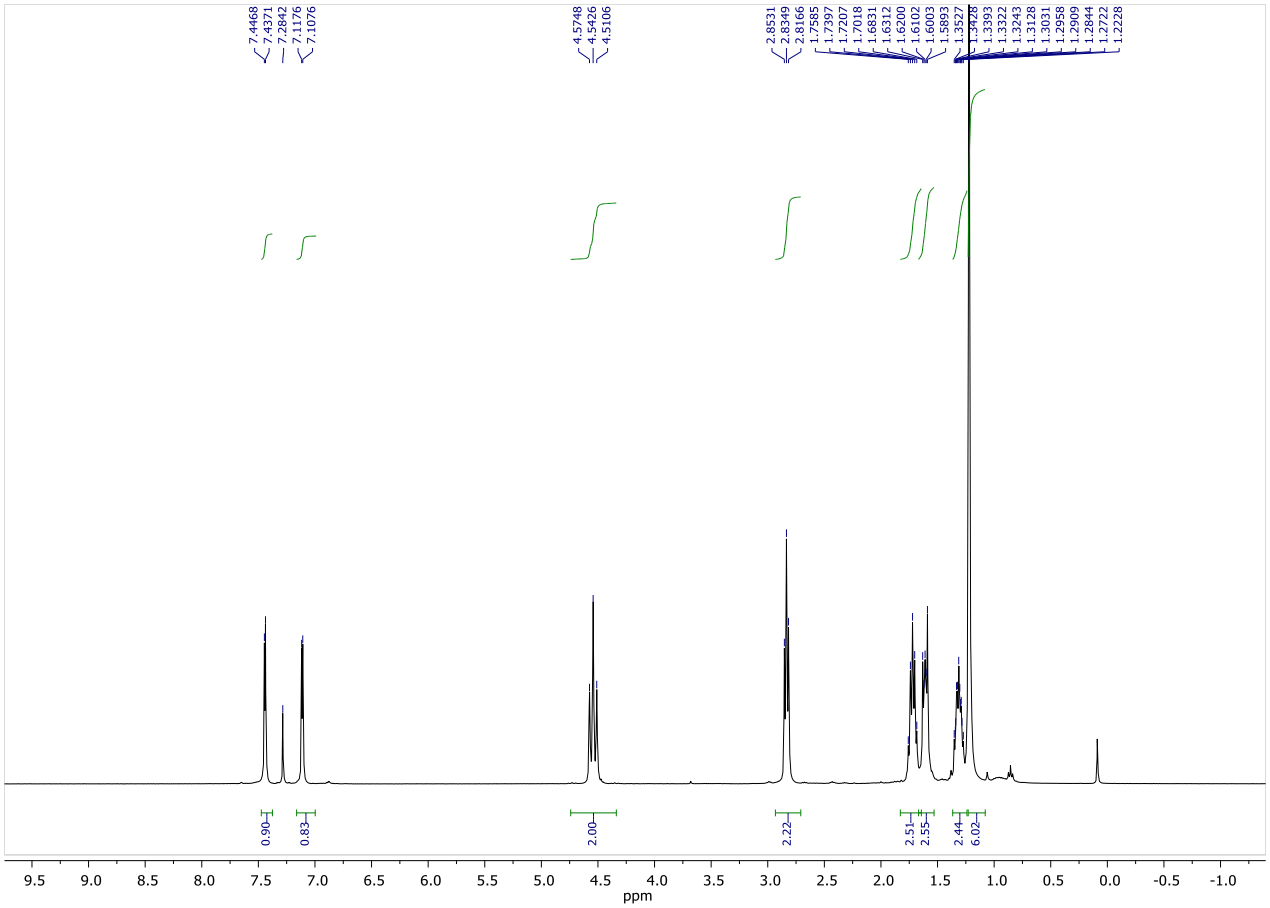


Figure S16. ^{1}H NMR spectrum of (**3e**) recorded in $CDCl_3$

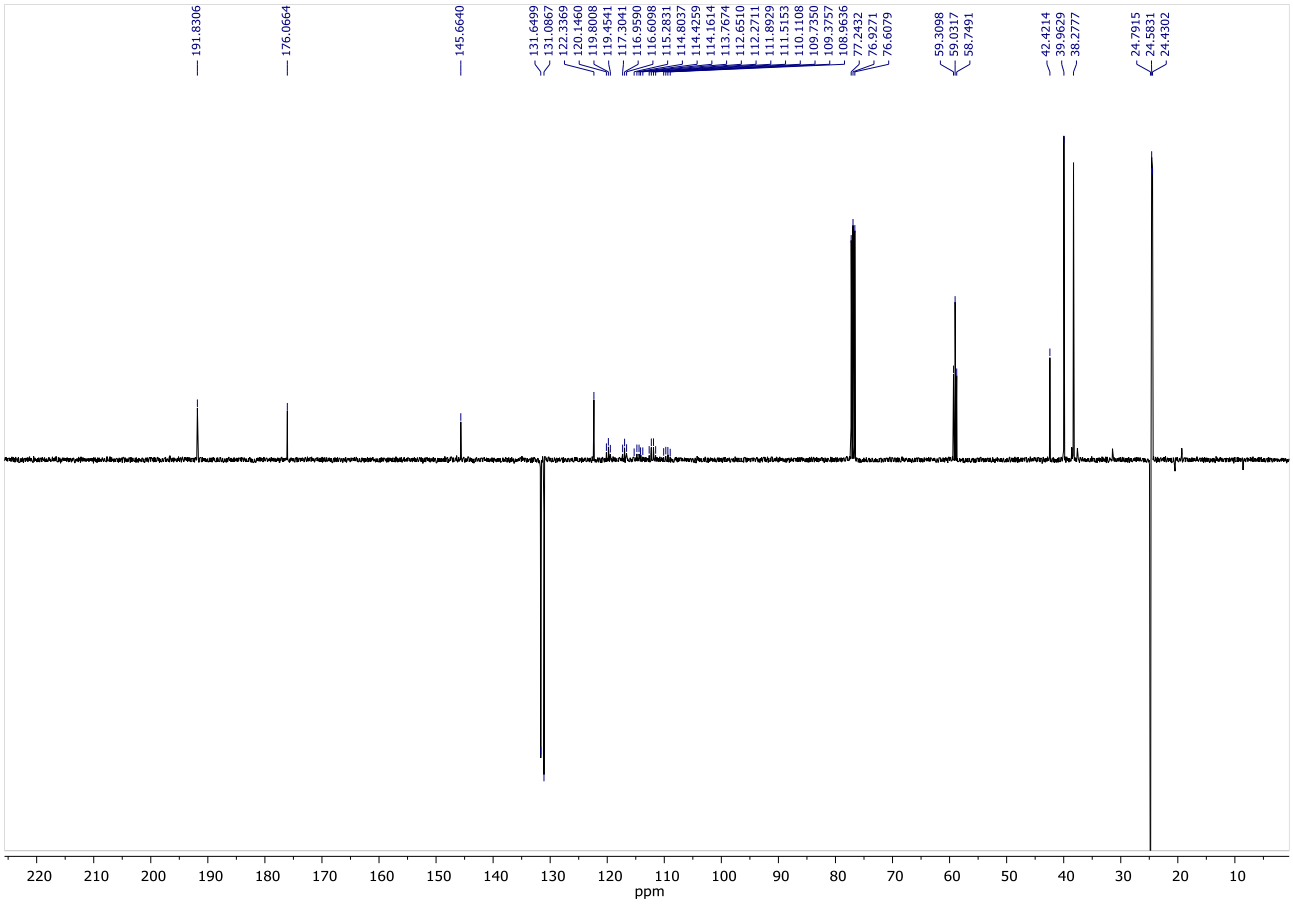


Figure S17. ^{13}C NMR spectrum of (**3e**) recorded in $CDCl_3$

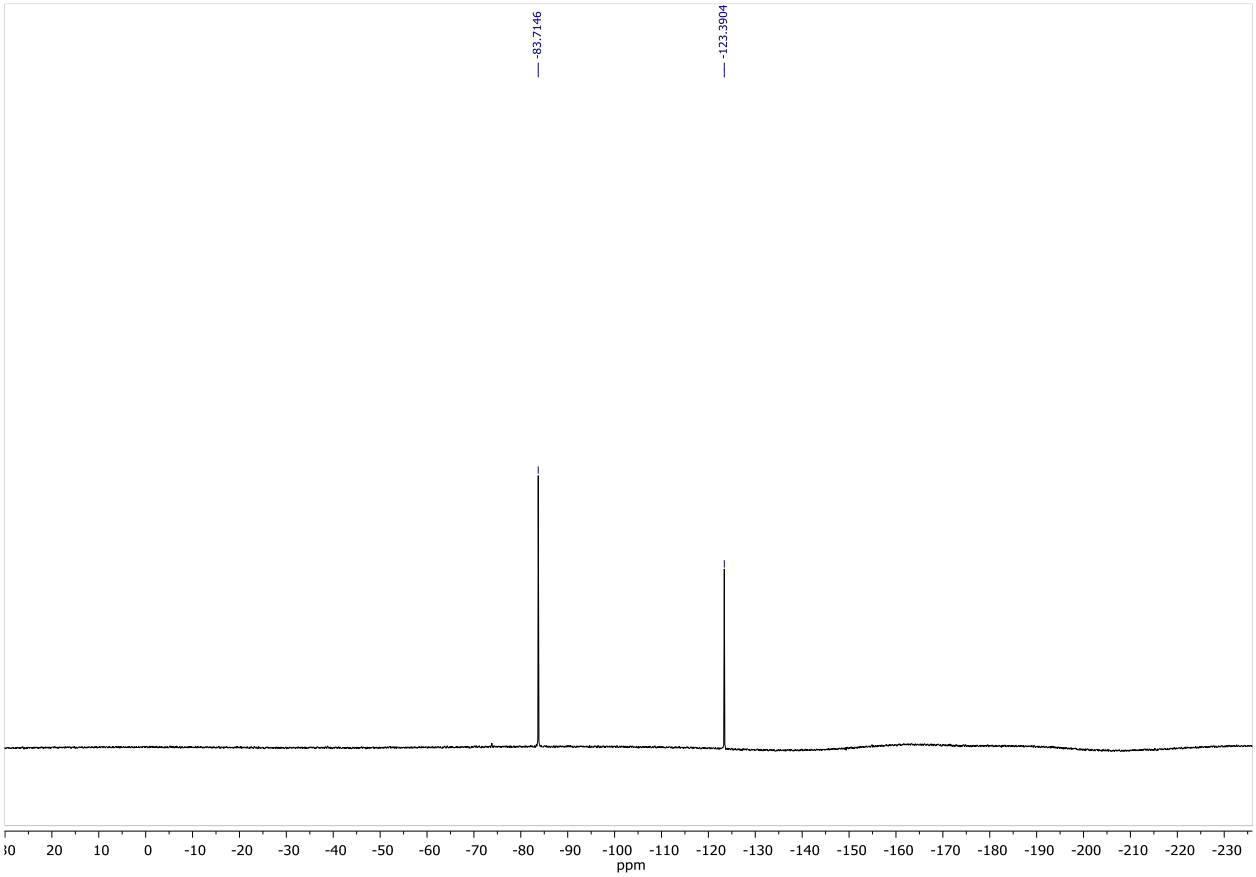


Figure S18. ^{19}F NMR spectrum of (**3e**) recorded in $CDCl_3$

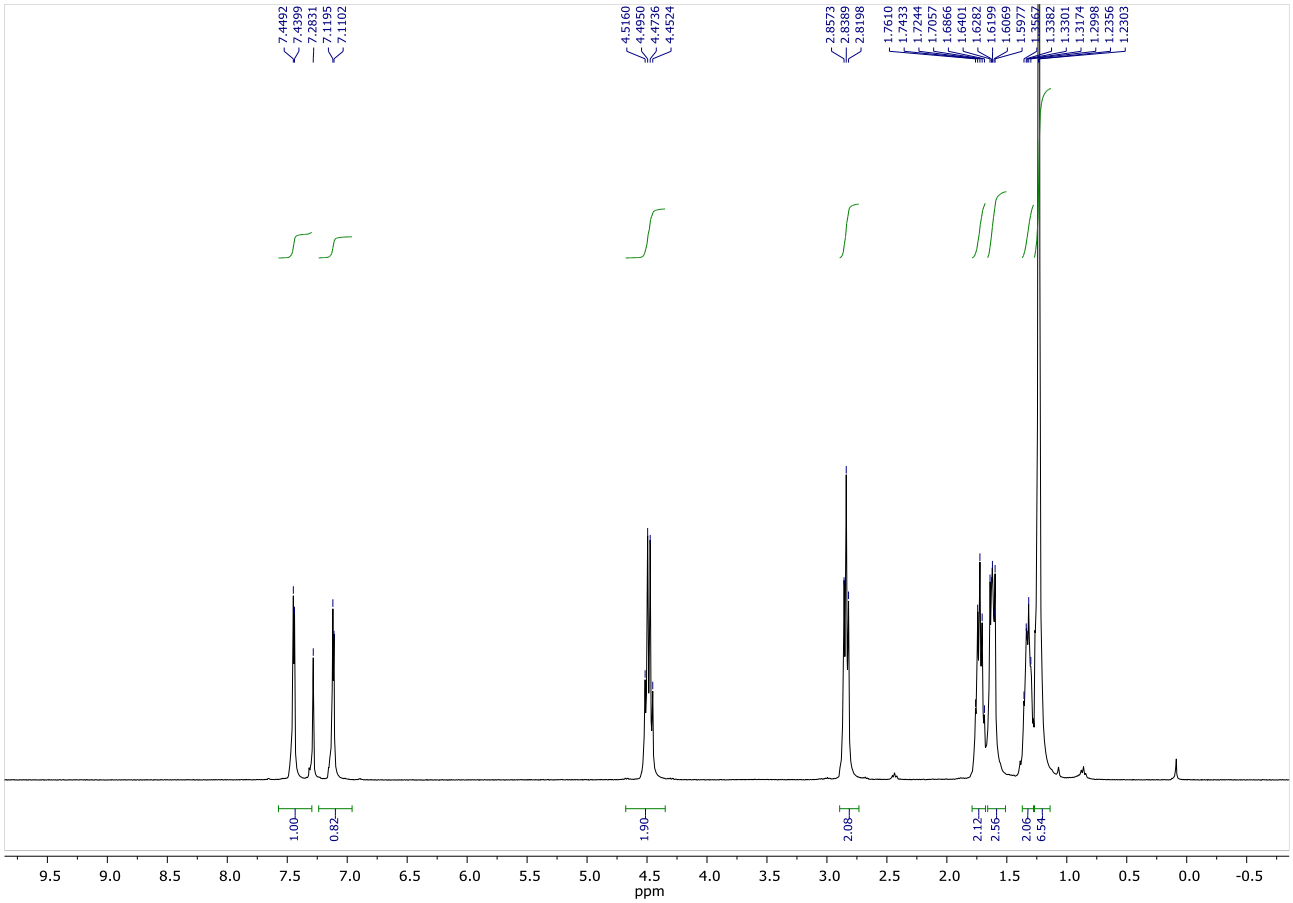


Figure S19. ^{1}H NMR spectrum of (**3f**) recorded in $CDCl_3$

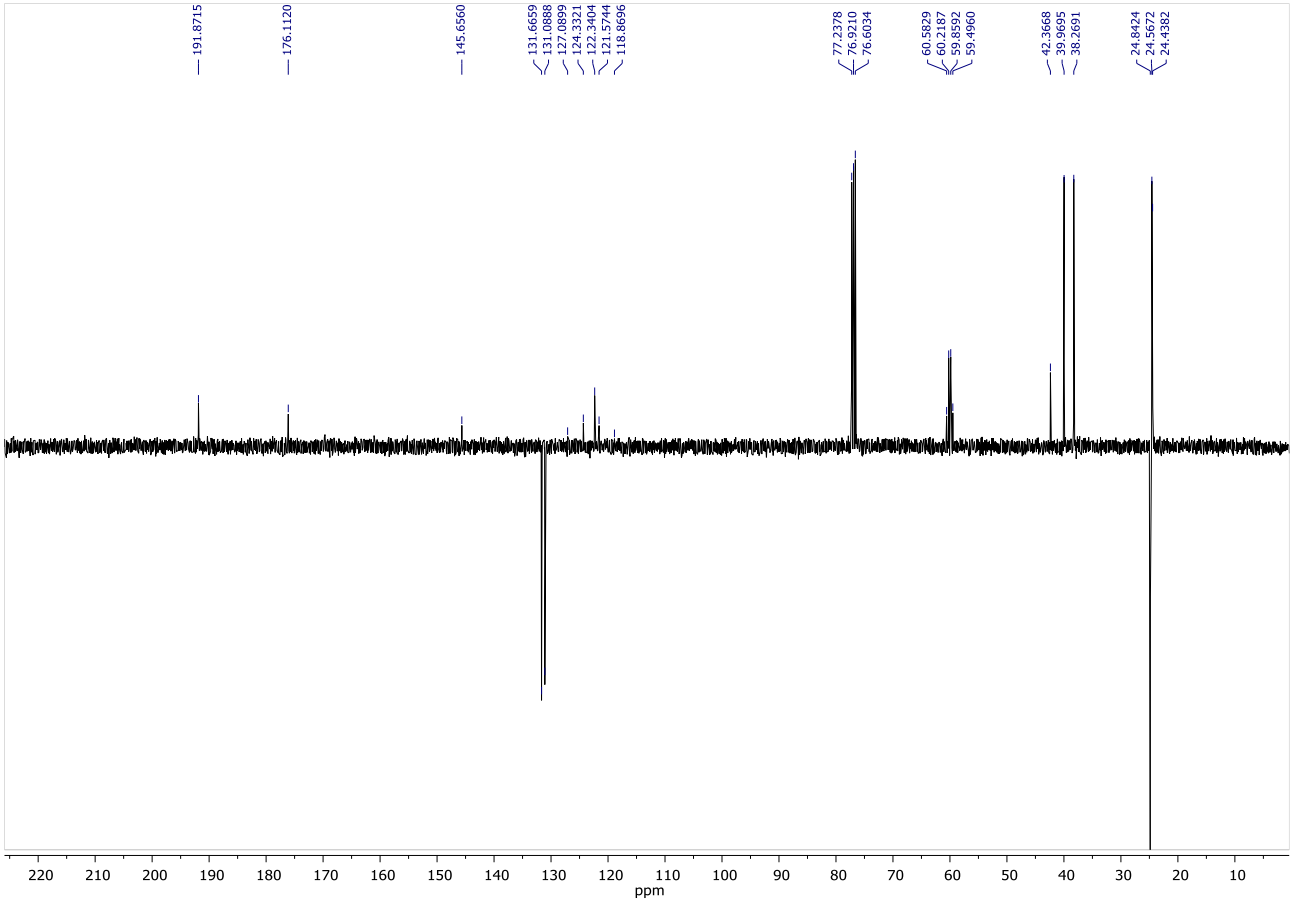


Figure S20. ^{13}C NMR spectrum of (**3f**) recorded in $CDCl_3$

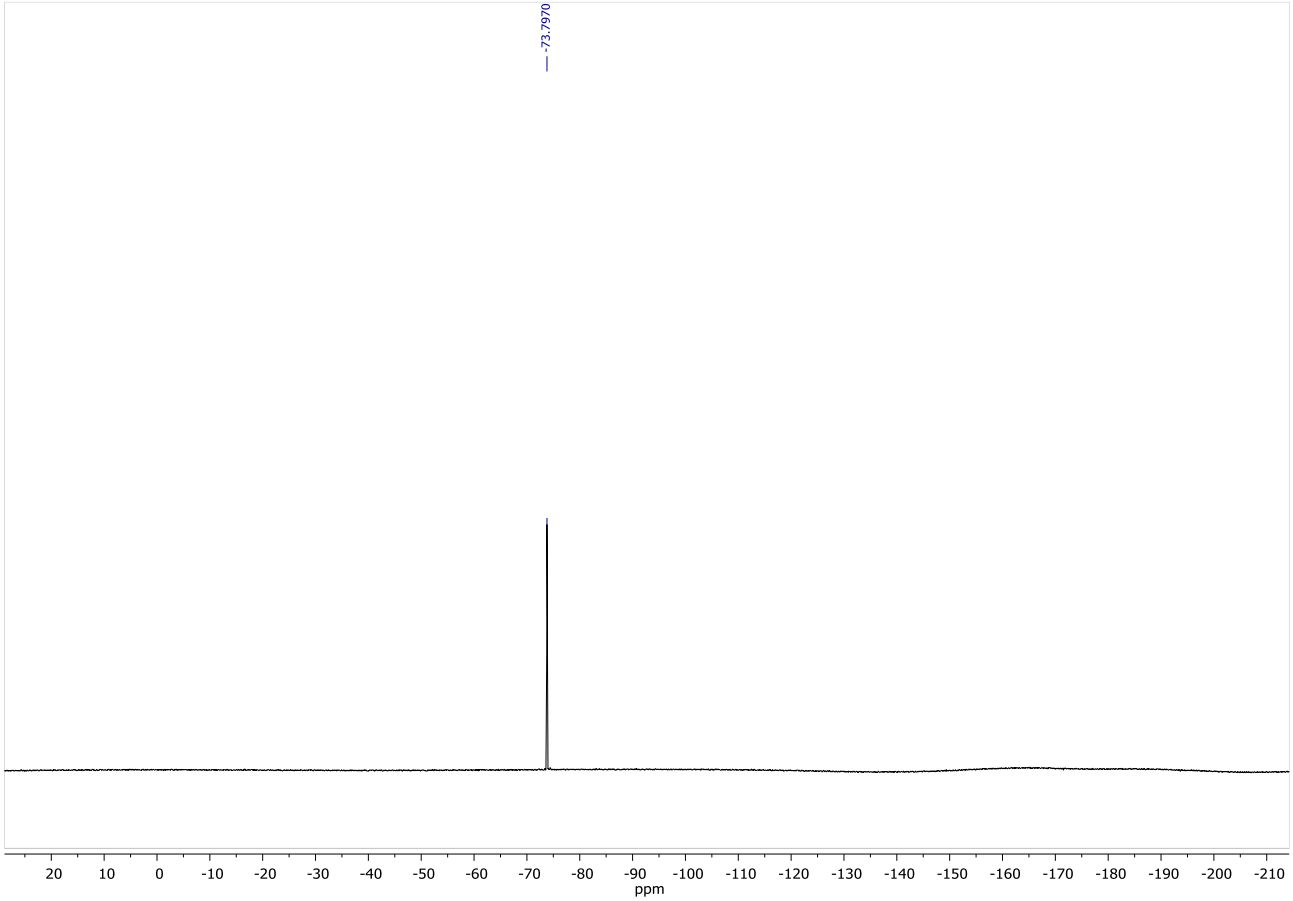


Figure S21. ^{19}F NMR spectrum of (**3f**) recorded in $CDCl_3$

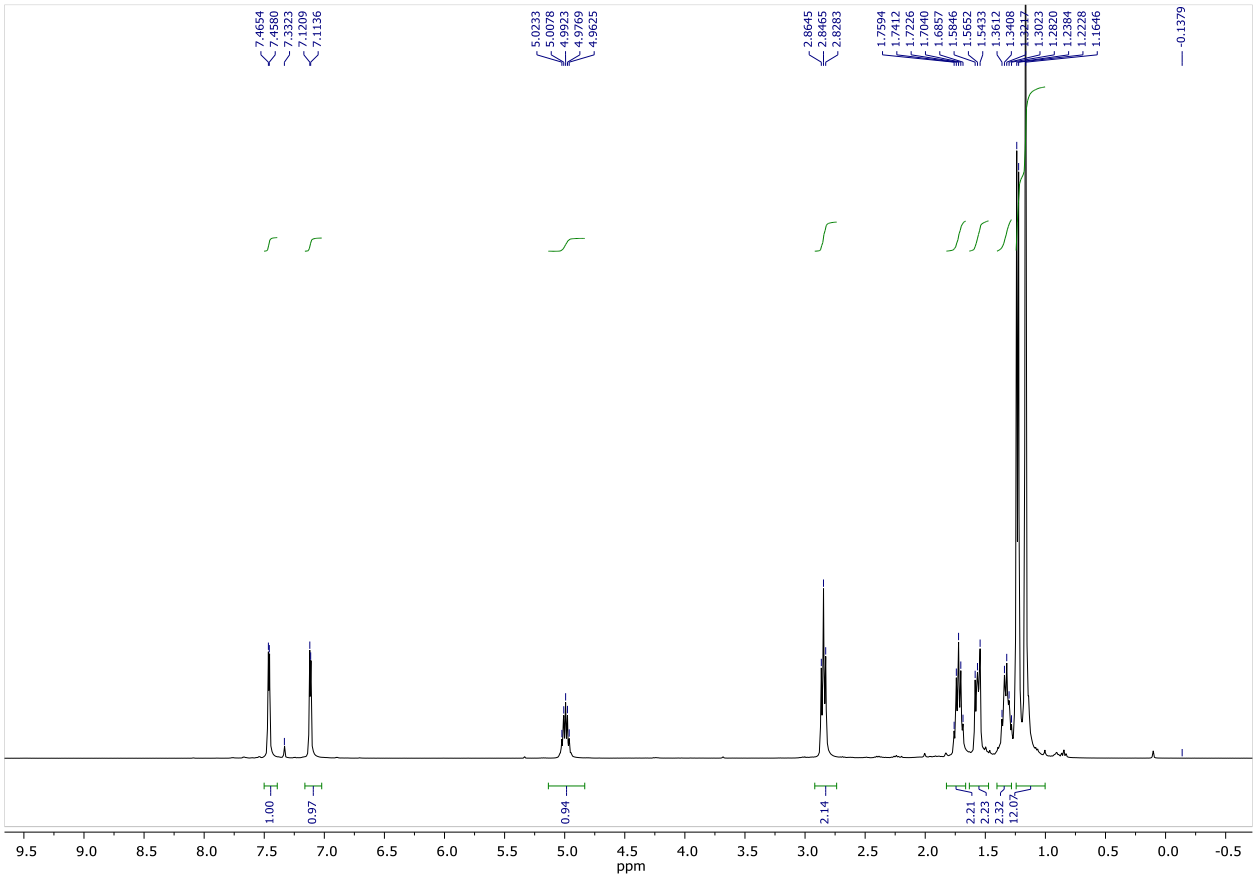


Figure S22. ^{1}H NMR spectrum of (**3g**) recorded in $CDCl_3$

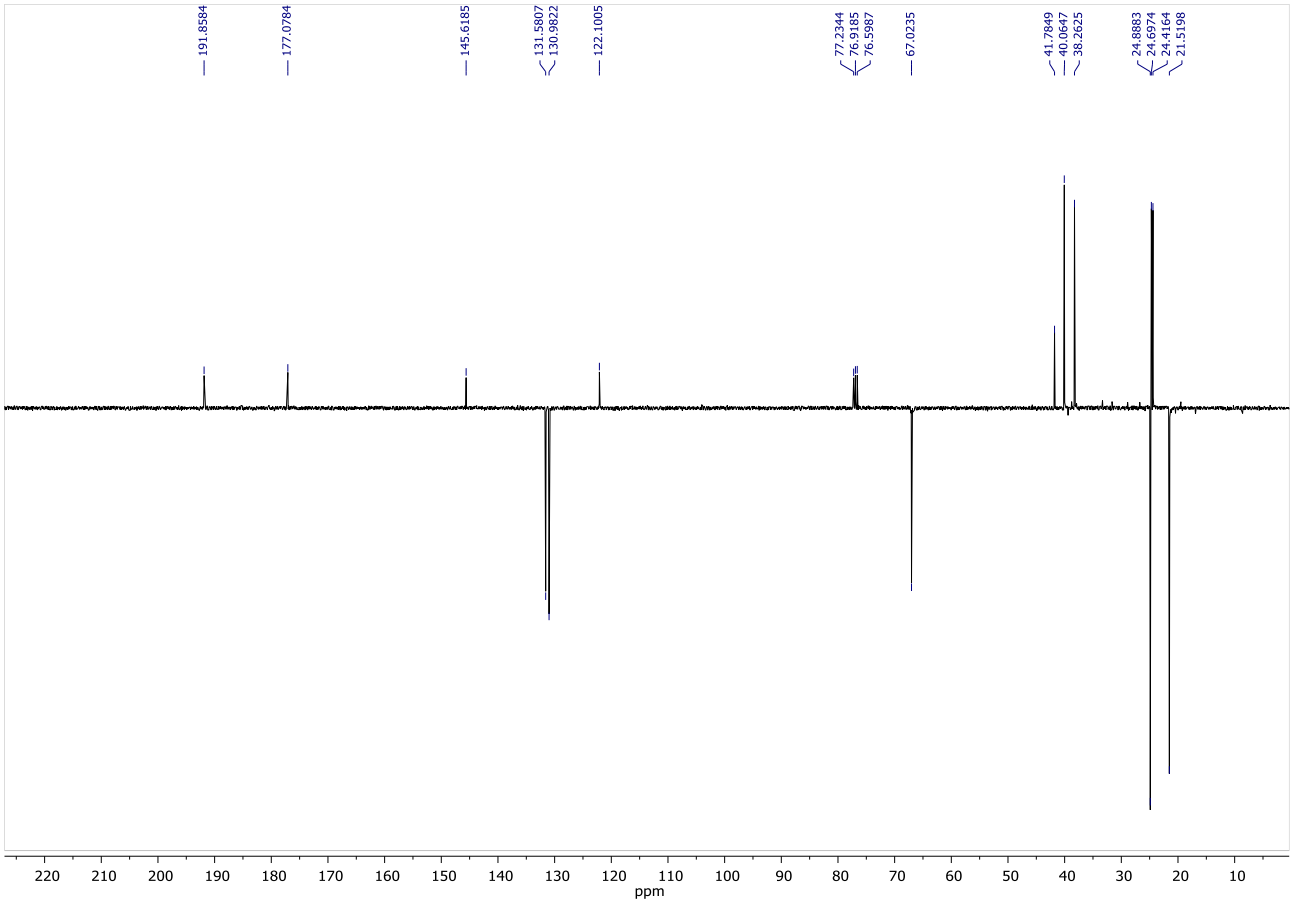


Figure S23. ^{13}C NMR spectrum of (**3g**) recorded in $CDCl_3$

5.3. Bifunctional products from nonanoyl chlorode

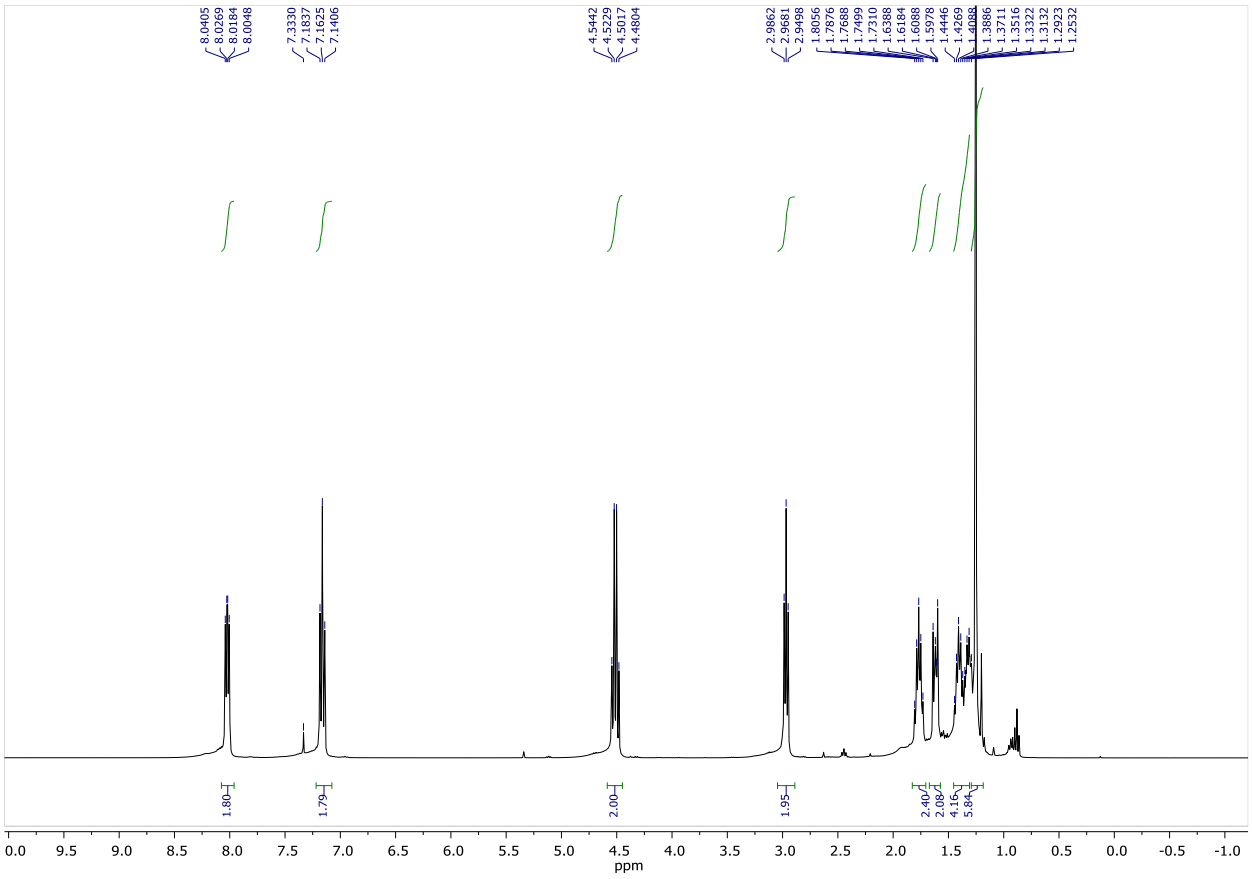


Figure S24. ^{1}H NMR spectrum of (**4a**) recorded in $CDCl_3$

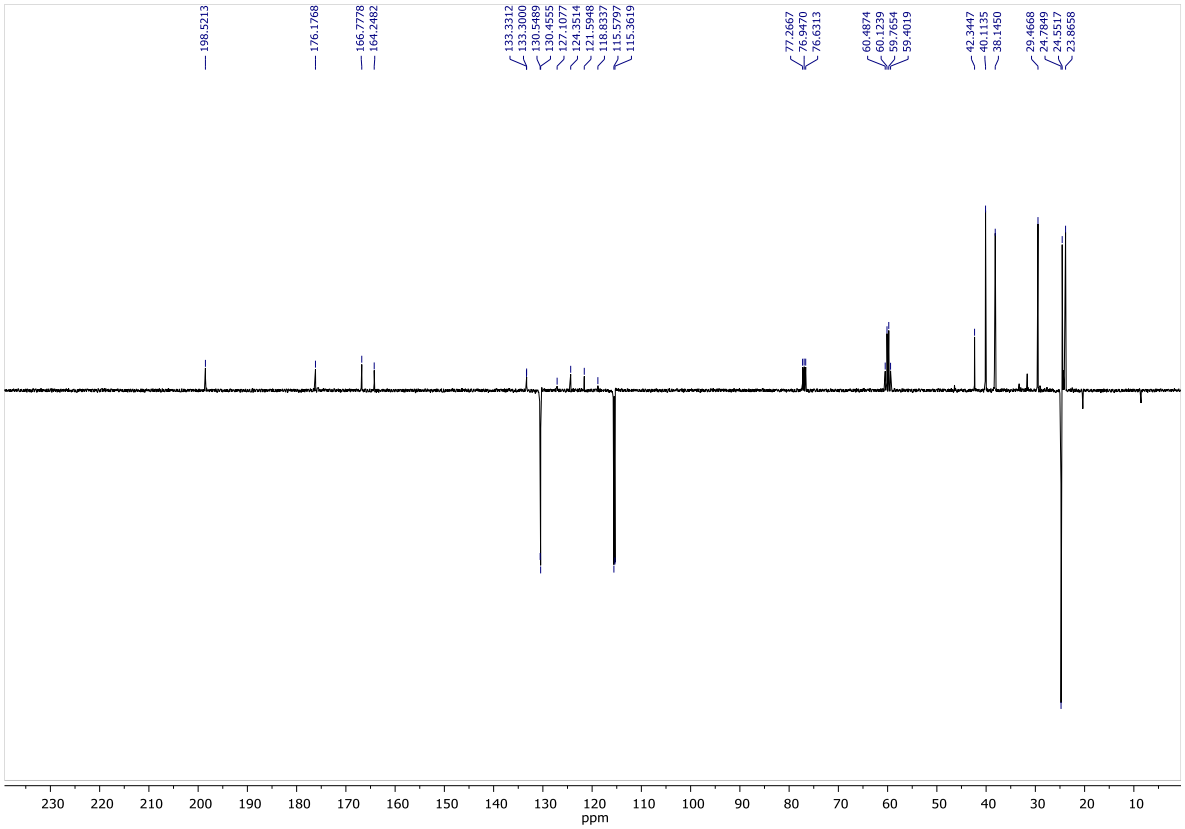


Figure S25. ^{13}C NMR spectrum of (**4a**) recorded in $CDCl_3$

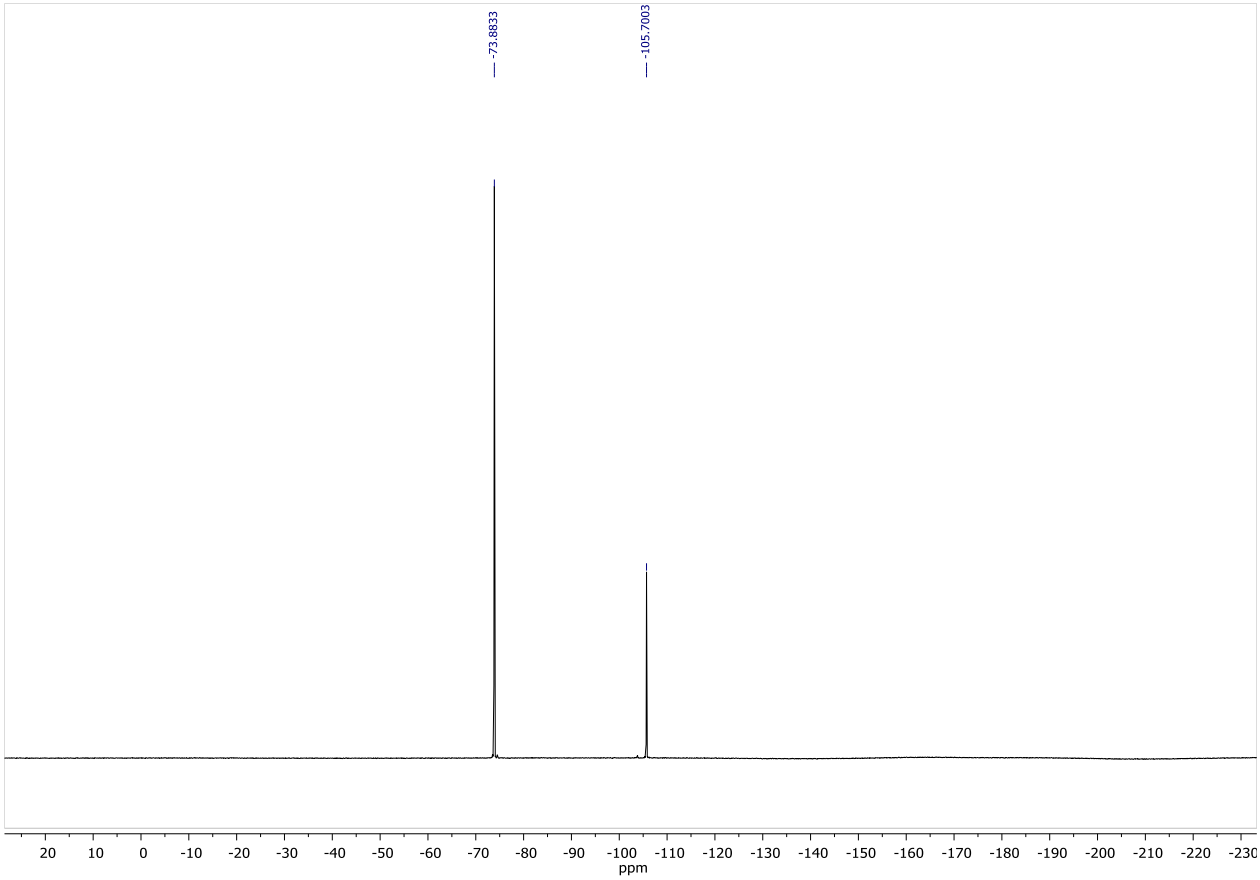


Figure S26. ^{19}F NMR spectrum of (**4a**) recorded in $CDCl_3$

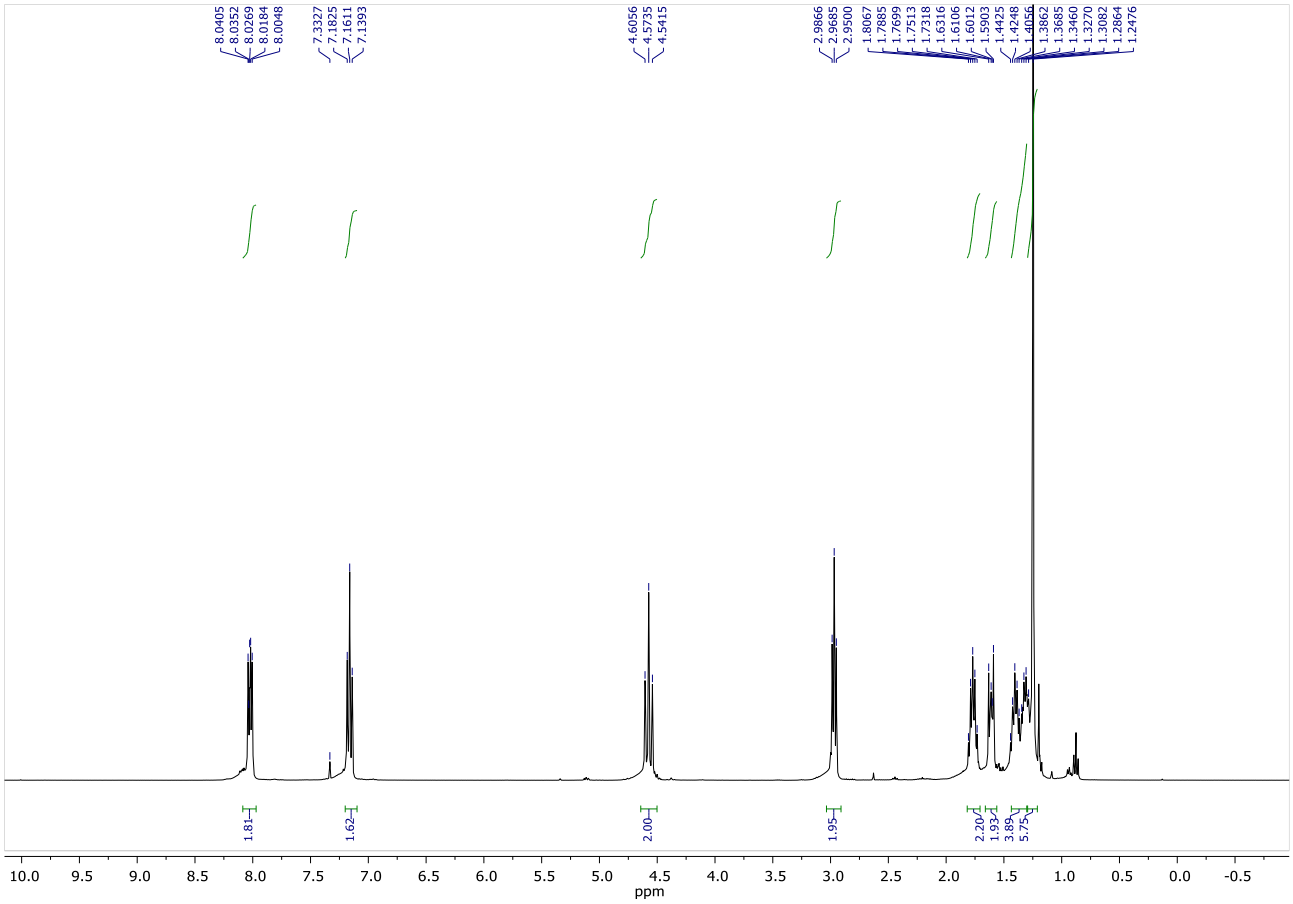


Figure S27. ^{1}H NMR spectrum of (**4b**) recorded in $CDCl_3$

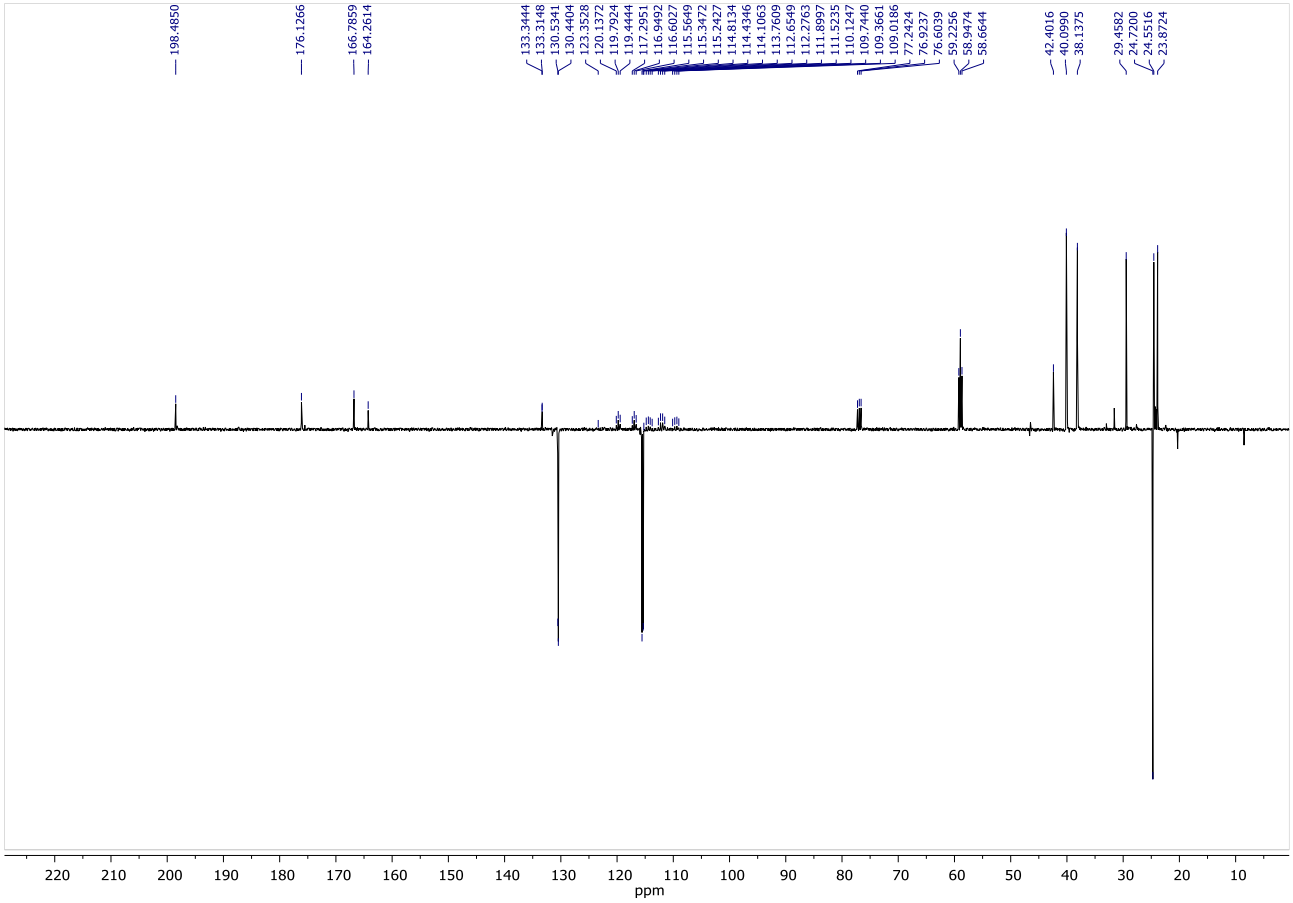


Figure S28. ^{13}C NMR spectrum of (**4b**) recorded in $CDCl_3$

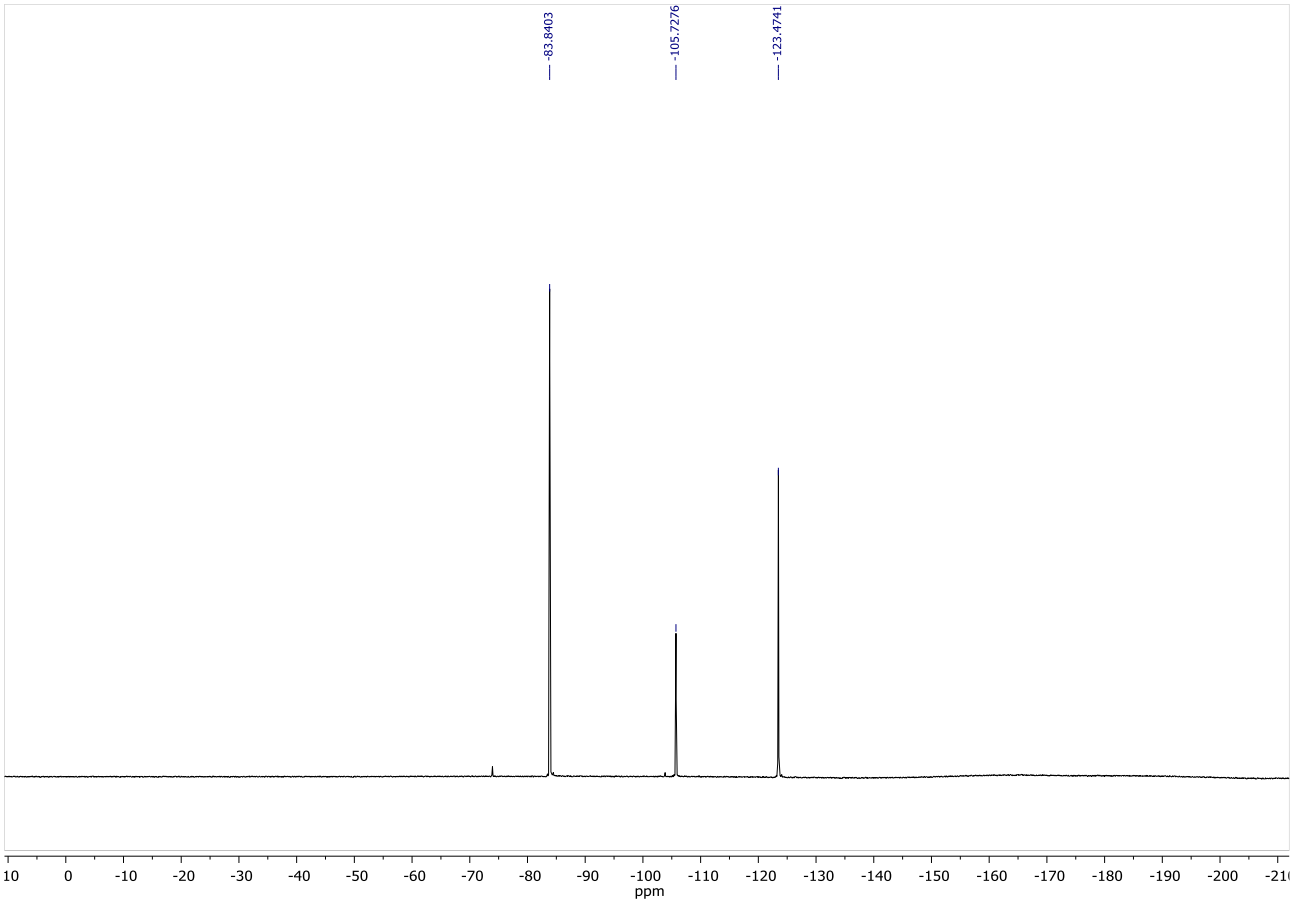


Figure S29. ^{19}F NMR spectrum of (**4b**) recorded in $CDCl_3$

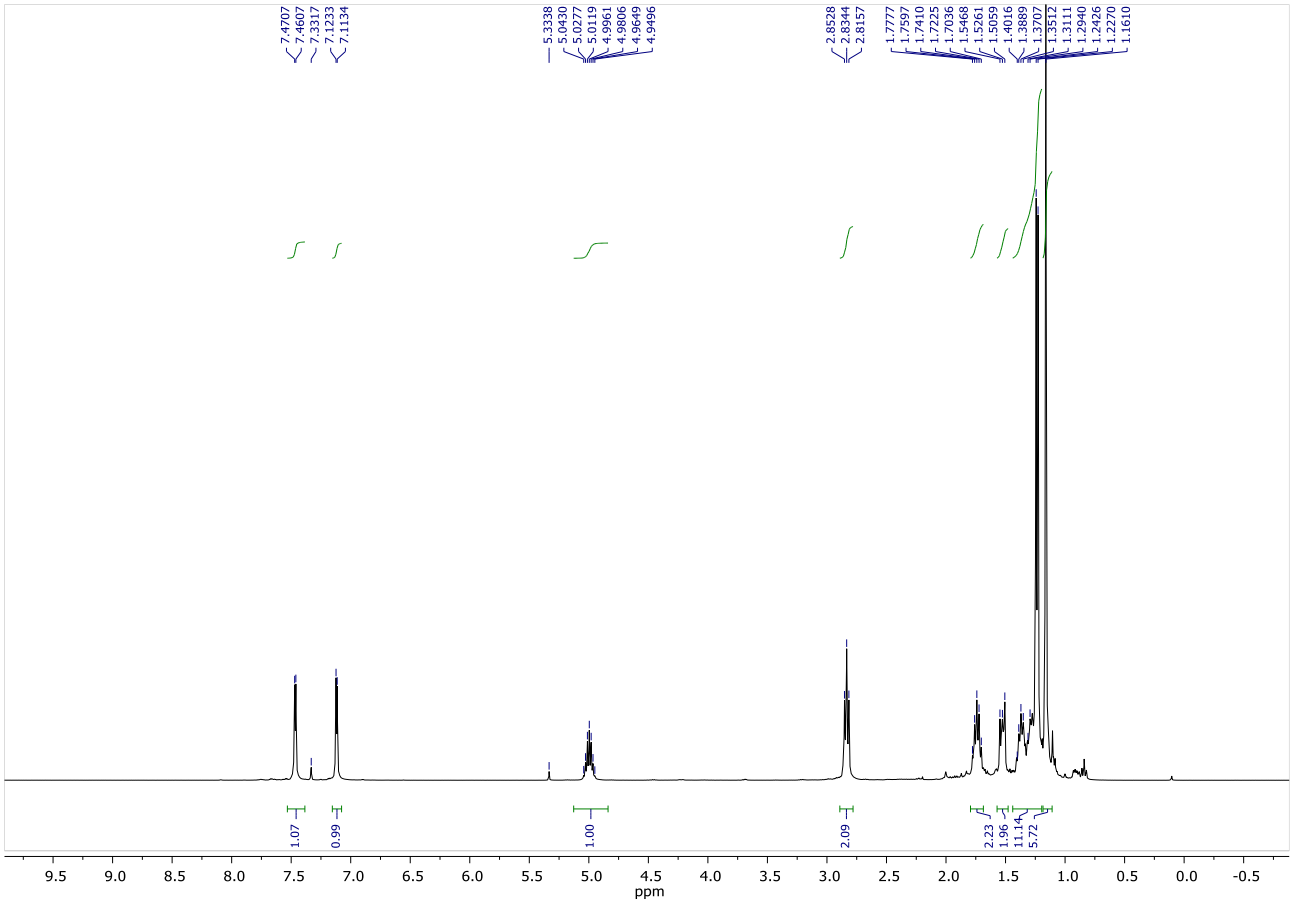


Figure S30. ^{1}H NMR spectrum of (**4c**) recorded in $CDCl_3$

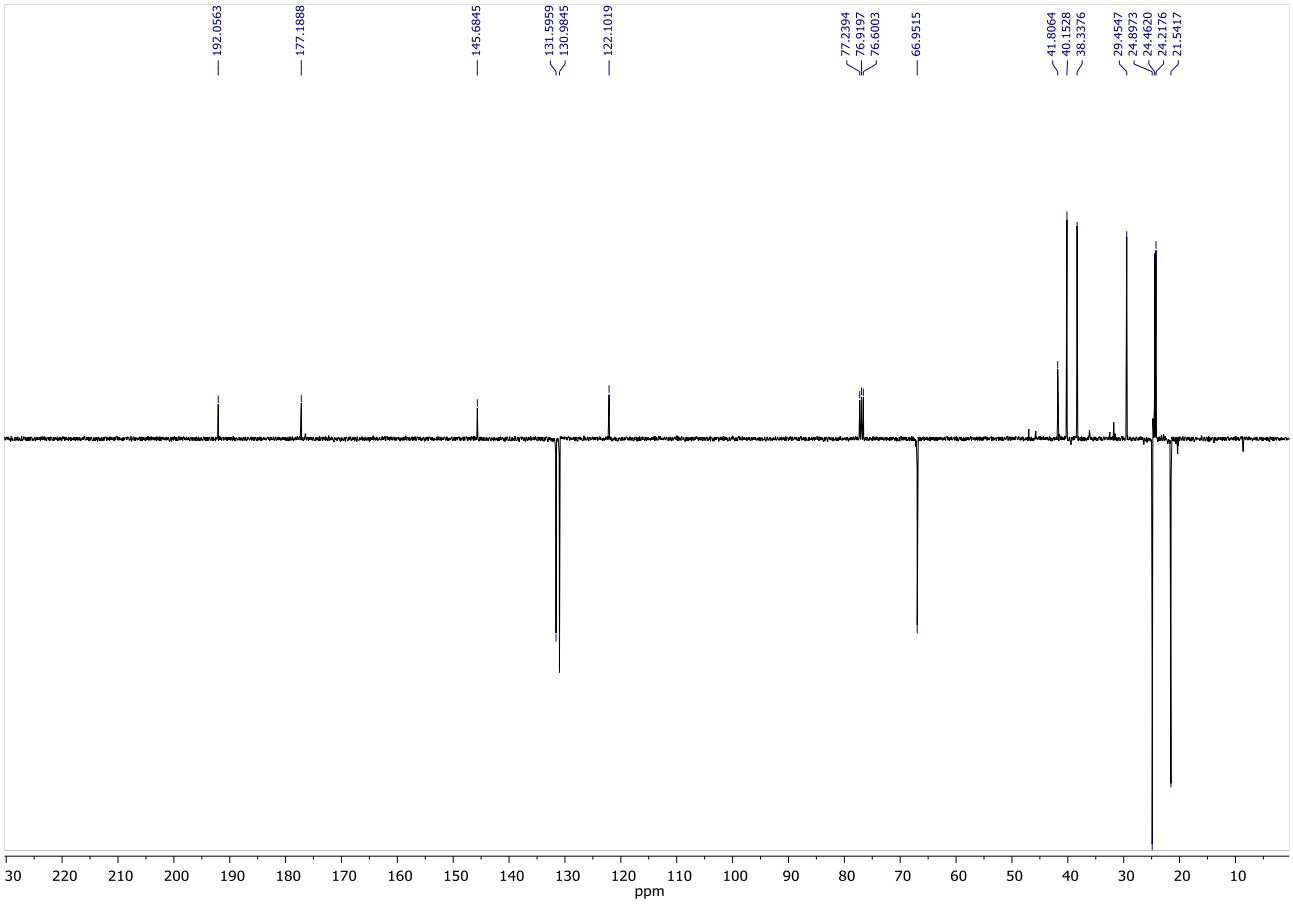


Figure S31. ^{13}C NMR spectrum of (**4c**) recorded in $CDCl_3$

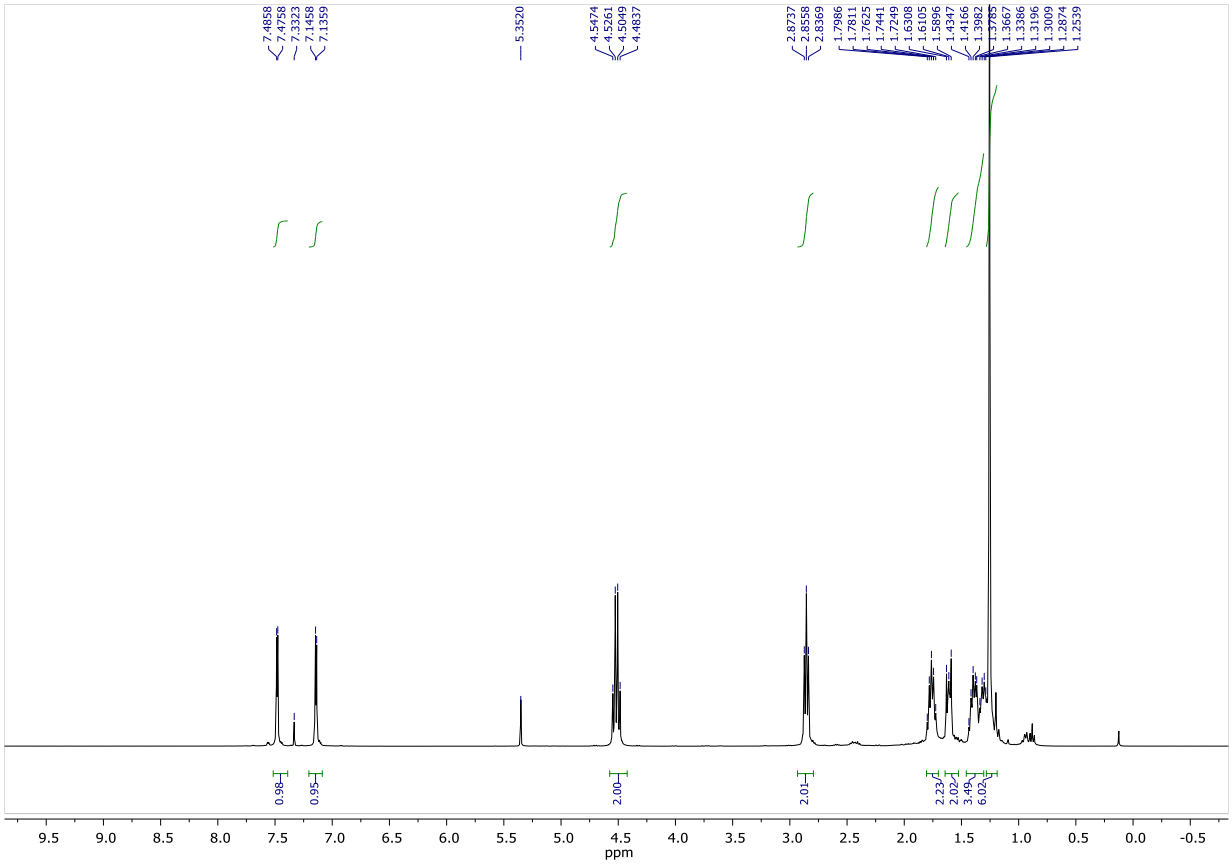


Figure S32. ^{1}H NMR spectrum of (**4d**) recorded in $CDCl_3$

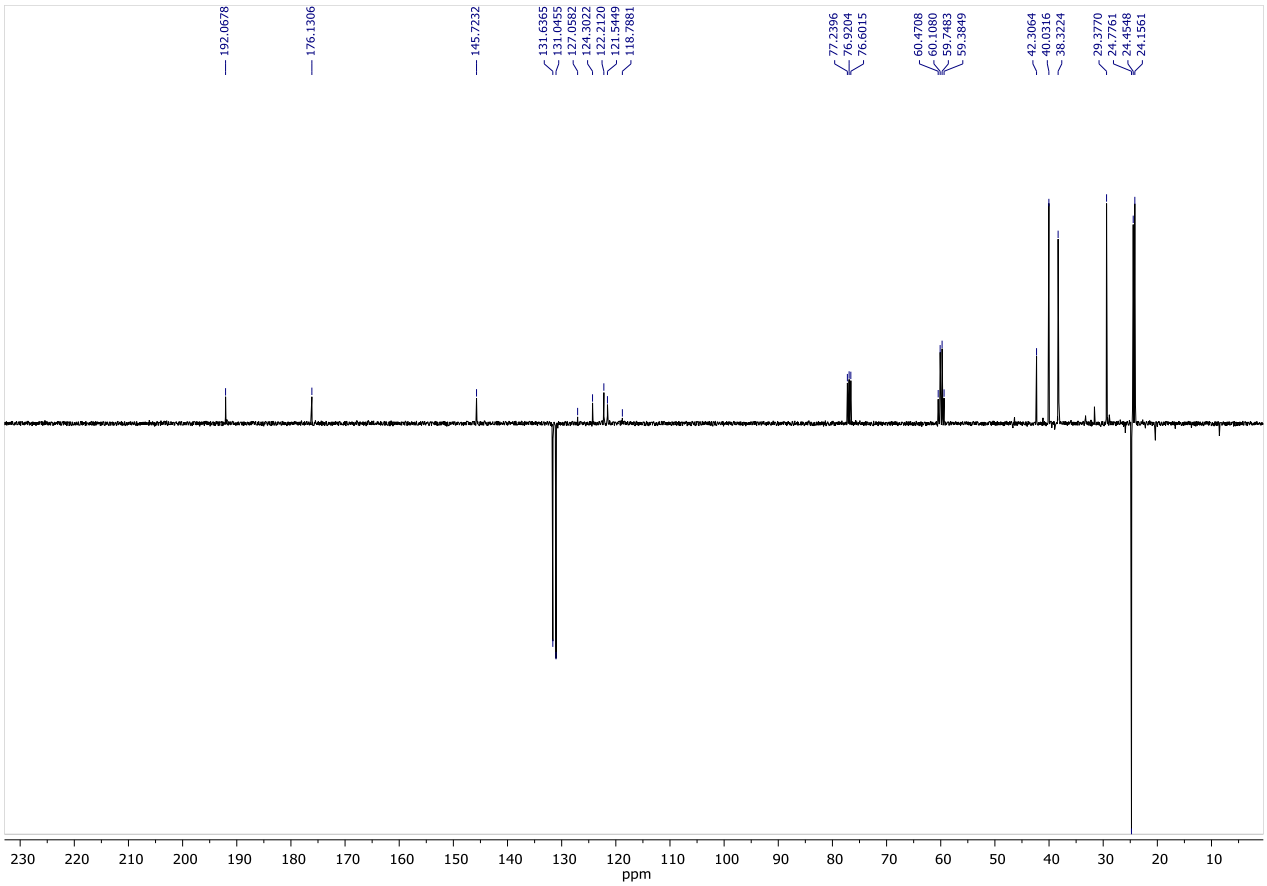


Figure S33. ^{13}C NMR spectrum of (**4d**) recorded in $CDCl_3$

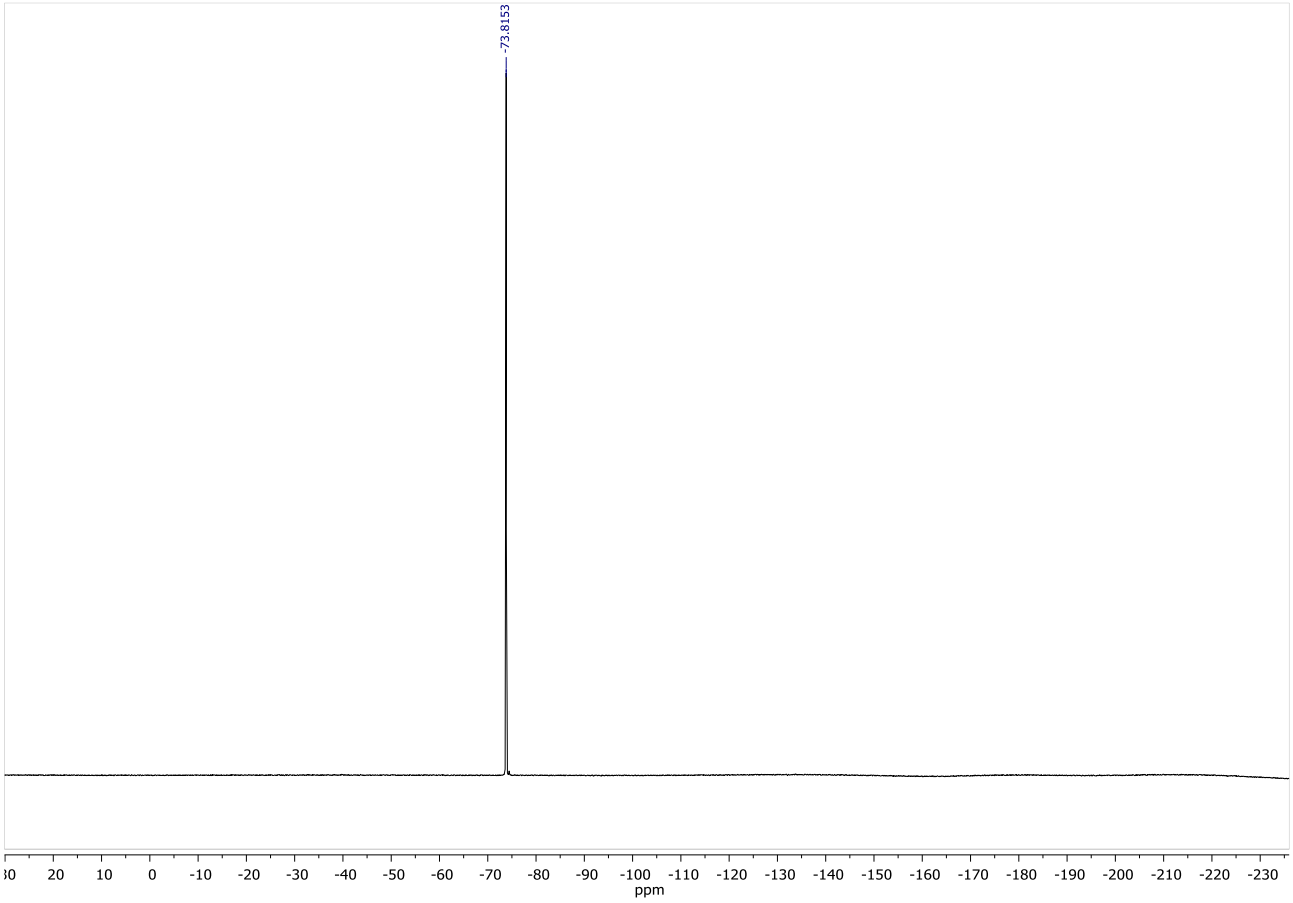


Figure S34. ^{19}F NMR spectrum of (**4d**) recorded in $CDCl_3$

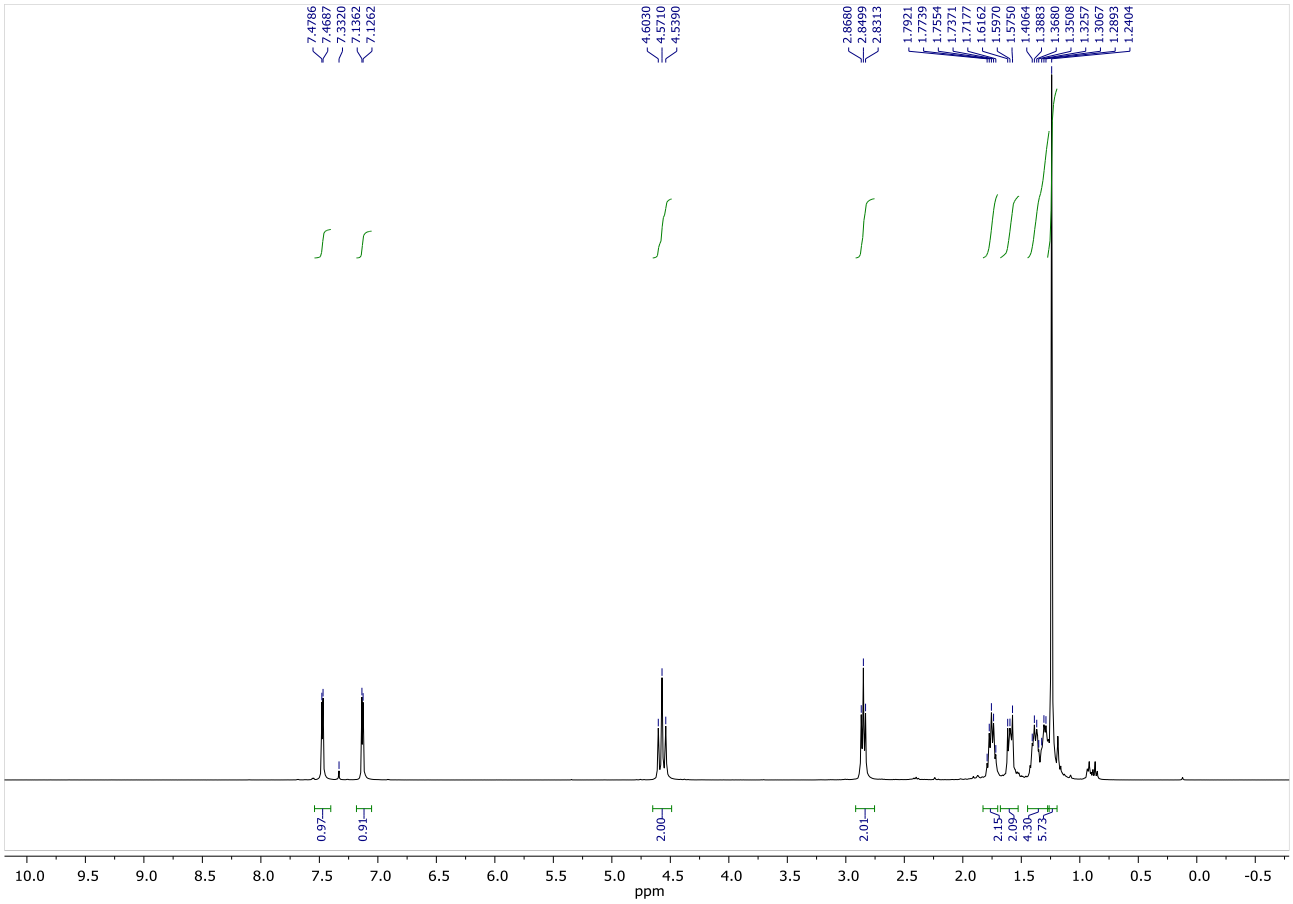


Figure S35. ^{1}H NMR spectrum of (**4e**) recorded in $CDCl_3$

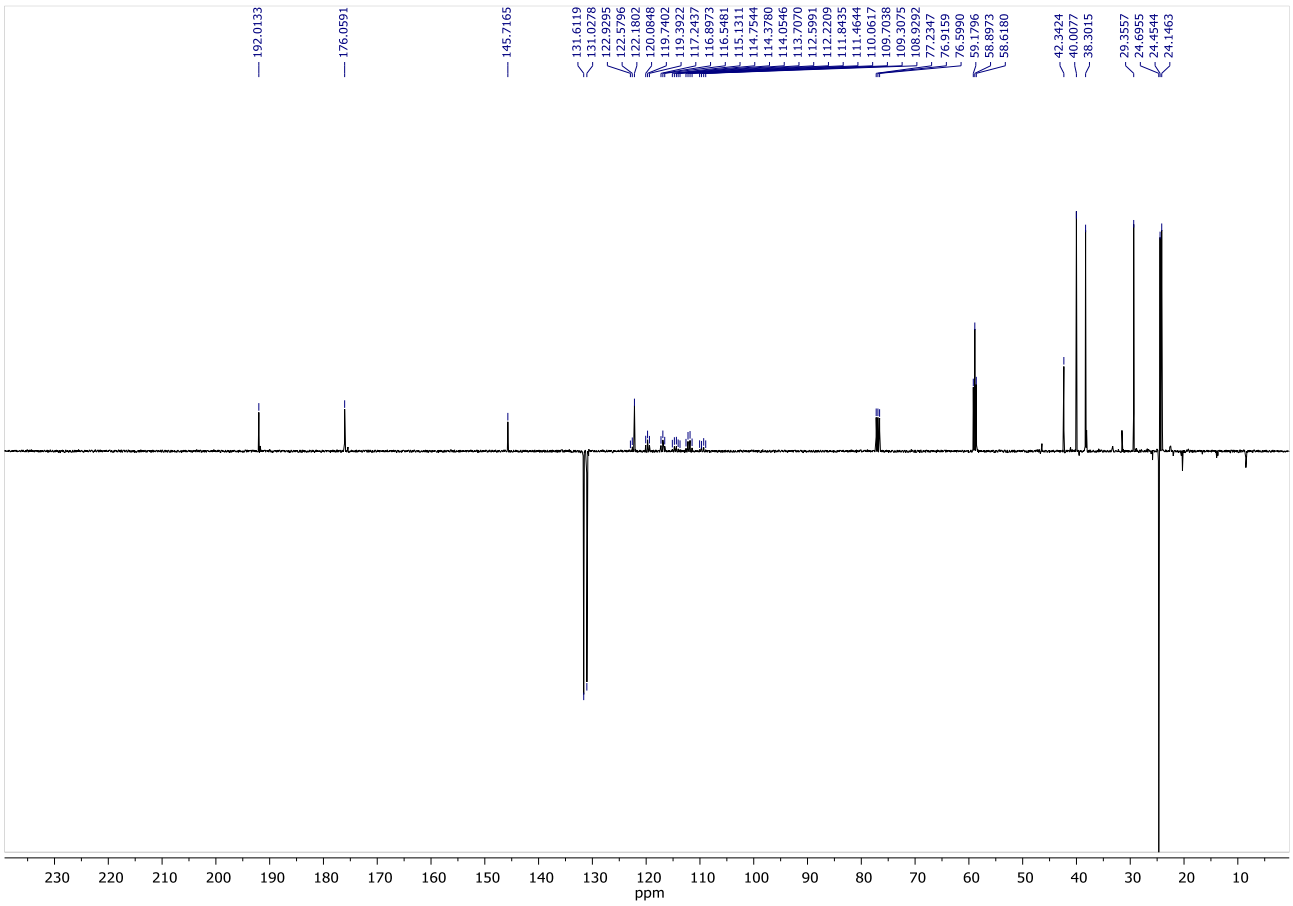


Figure S36. ^{13}C NMR spectrum of (**4e**) recorded in $CDCl_3$

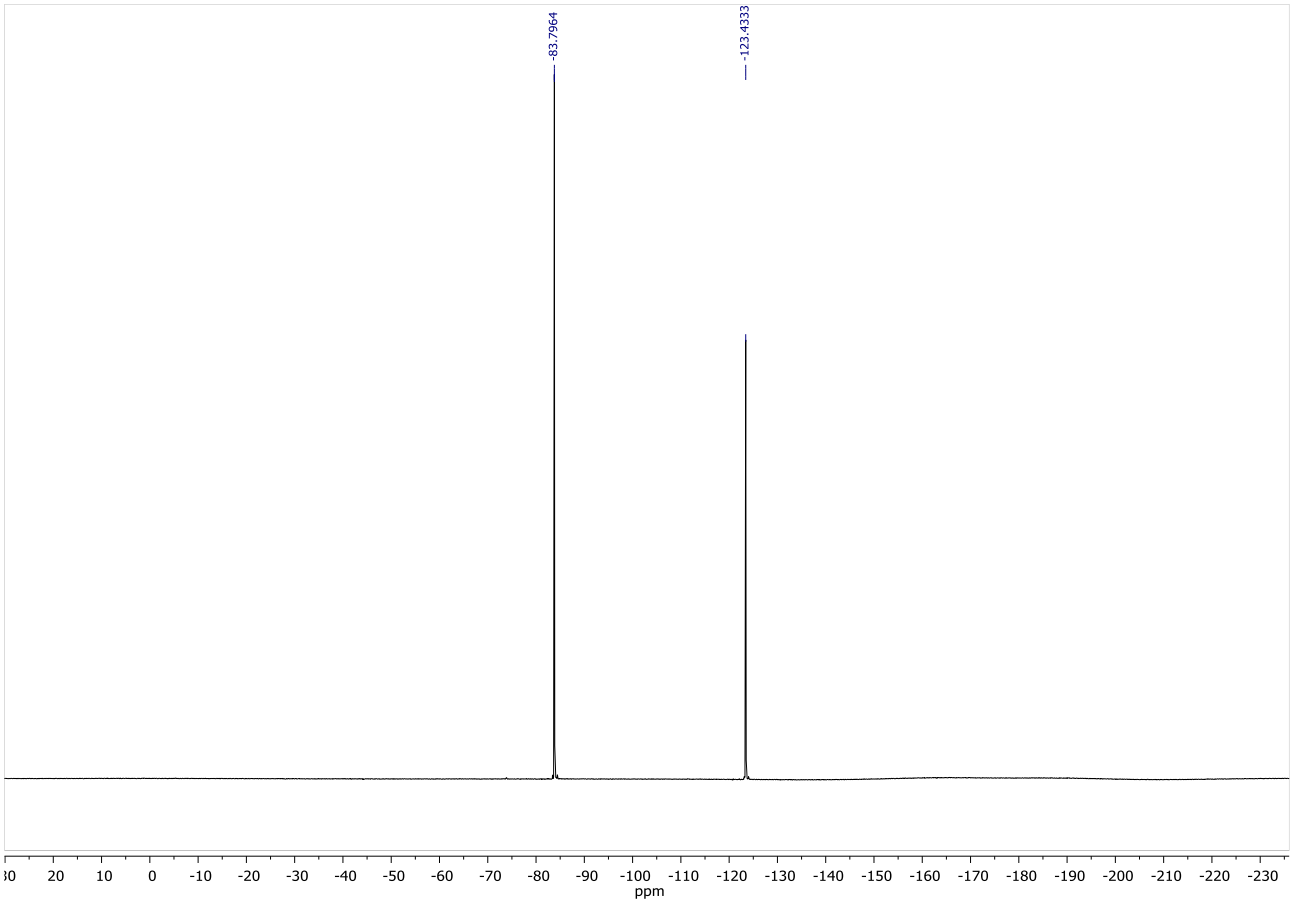


Figure S37. ^{19}F NMR spectrum of (**4e**) recorded in $CDCl_3$