Supplementary Information

Mitochondria-targeted liposomes decorated by amphiphilic 2-hydroxypropylphosphonium salts for hyperthermia-induced release and antitumor application

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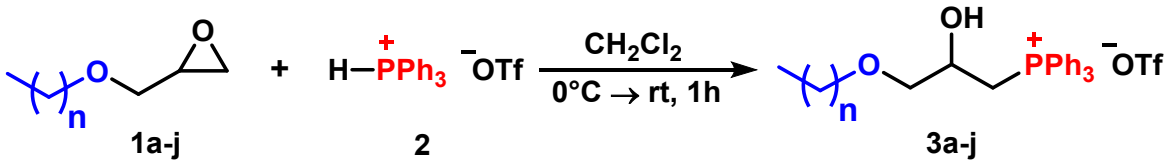

Scheme S1. Synthesis of amphiphilic **3a-h** with different alkyl chain lengths where n = 0 (**a**), 1 (**b**), 3 (**c**), 5 (**d**), 7 (**e**), 9 (**f**), 11 (**g**), 13 (**h**), 15 (**i**), 17 (**j**).

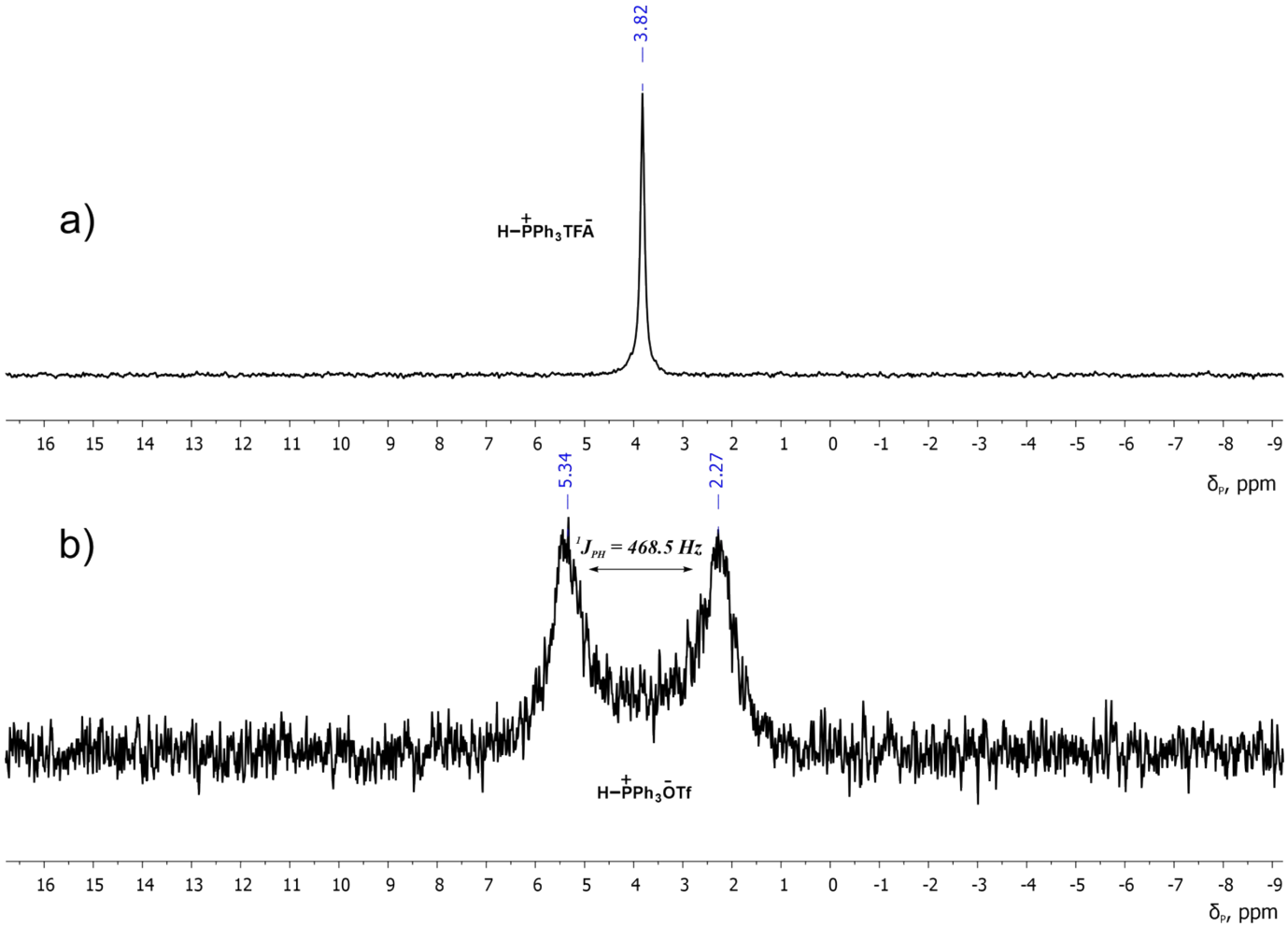

Figure S1. ^{31}P-{^{1}H} and ^{31}P NMR spectra (CH_2Cl_2, 162 MHz) of P–H-phosphonium salts: H–P^+Ph_3 $CF_3SO_3^-$ (a), H–P^+Ph_3 $CF_3CO_2^-$ (b).

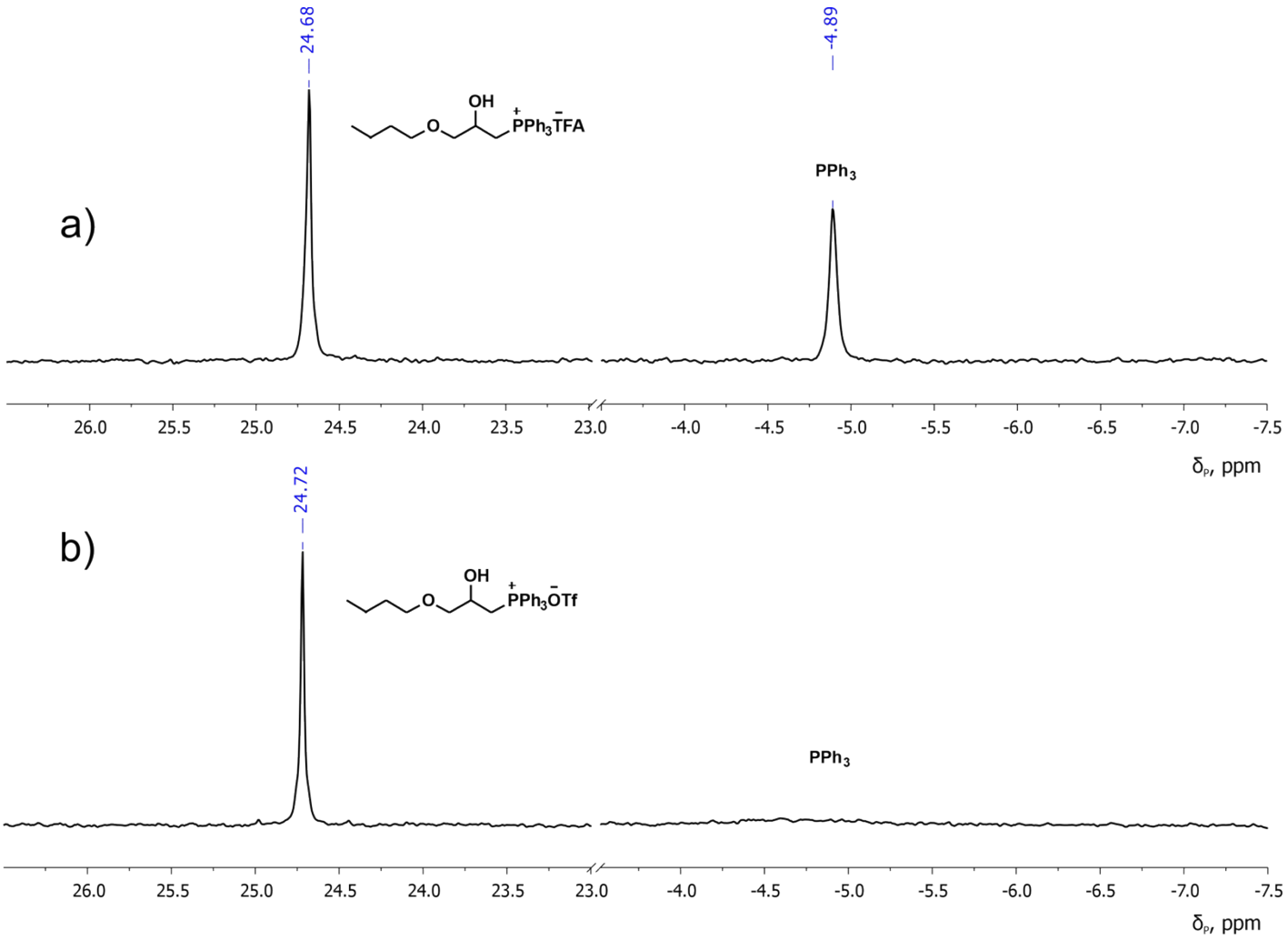

Figure S2. ^{31}P-{^{1}H} NMR spectra (CH_2Cl_2, 162 MHz) of reactions mixtures of compound **1c** with P–H-phosphonium salts: H–P^+Ph_3 $CF_3SO_3^-$ (a), H–P^+Ph_3 $CF_3CO_2^-$ (b).

Characteristics of precursors of compounds 1

1-Butoxy-3-chloropropan-2-ol. Colorless liquid, bp 100 °C (12 mmHg), yield was 3.730 g (84 %); IR (film): 3417, 2960, 2934, 2872, 2737, 1737, 1622, 1464, 1433, 1379, 1338, 1300, 1259, 1121, 1076, 1023, 996, 963, 944, 908, 843, 751, 708, 640, 625, 574, 512, 454, 417 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.97 (m, $^3J_{HH}$ = 5.3-5.4 Hz, $^3J_{HH}$ = 5.3-5.4 Hz, 1H, H^2), 3.64 (dd, $^2J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 5.4 Hz, 1H, $H^3{}_A$), 3.59 (dd, $^2J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 5.4 Hz, 1H, $H^3{}_B$), 3.53 (m, $^3J_{HH}$ = 5.1 Hz, 2H, H^1), 3.48 (ddd, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 0.9 Hz, 2H, $H^{1'}$), 2.26 (br. s, 1H, OH), 1.56 (m, $^3J_{HH}$ = 7.6-7.7 Hz, 2H, $H^{2'}$), 1.37 (m, $^3J_{HH}$ = 7.6-7.7 Hz, 2H, $H^{3'}$), 0.92 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $H^{4'}$); Calculated for $C_7H_{15}ClO_2$: C, 50.45; H, 9.07; Cl, 21.27; Found: C, 50.07; H, 9.36; Cl, 21.02.

3-Chloro-1-hexyloxypropan-2-ol. Colorless liquid, bp 121 °C (10 mmHg), yield was 6.388 g (82 %); IR (film): 3423, 2956, 2930, 2860, 2124, 1735, 1613, 1466, 1433, 1378, 1299, 1252, 1120, 1075, 946, 909, 843, 752, 709, 622, 573, 467 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.96 (m, H^2, 1H, $^3J_{HH}$ = 5.4, $^3J_{HH}$ = 5.4), 3.64 (dd, $^2J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 5.4 Hz, 1H, $H^3{}_A$), 3.58 (dd, $^2J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 5.4 Hz, 1H, $H^3{}_B$), 3.53 (m, $^3J_{HH}$ = 5.1 Hz, 2H, H^1), 3.47 (ddd, $^3J_{HH}$ = 6.6.6.8 Hz, $^4J_{HH}$ = 0.6-0.7 Hz, 2H, $H^{1'}$), 2.28 (br. s, 1H, OH), 1.57 (m, $^3J_{HH}$ = 6.6-6.8 Hz, $^3J_{HH}$ = 6.6-6.8 Hz, $H^{2'}$, 2H), 1.24-1.38 (m, 8H, $H^{3'}$-$H^{5'}$), 0.89 (t, $^3J_{HH}$ = 7.2 Hz, 3H, $H^{6'}$); Calculated for $C_9H_{19}ClO_2$: C, 55.52; H, 9.84; Cl, 18.21; Found: C, 55.29; H, 10.05; Cl, 18.09.

3-Chloro-1-octyloxypropan-2-ol. Colorless liquid, bp 145 °C (10 mmHg), yield was 7.484 g (84 %); IR (film): 3417, 2926, 2856, 1731, 1633, 1465, 1433, 1378, 1299, 1257, 1120, 1075, 947, 911, 843, 752, 723, 710, 622, 573 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.96 (m, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 5.4 Hz, 1H, H^2), 3.64 (dd, $^2J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 5.4 Hz, 1 H, $H^3{}_A$), 3.58 (dd, $^2J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 5.4 Hz, 1H, $H^3{}_B$), 3.52 (m, $^3J_{HH}$= 5.1 Hz, 2H, H^1), 3.47 (m, $^3J_{HH}$ = 6.6-6.8 Hz, $^4J_{HH}$ = 0.6-0.7 Hz, 2H, $H^{1'}$), 2.33 (br. s, 1H, OH), 1.56 (m, $^3J_{HH}$ = 6.6-6.8 Hz, $^3J_{HH}$ = 6.6-6.8 Hz, 2H, $H^{2'}$), 1.19-1.39 (m, 12H, $H^{3'}$-$H^{7'}$), 0.88 (t, $^3J_{HH}$ = 7.2 Hz, 3H, $H^{8'}$); Calculated for $C_{11}H_{23}ClO_2$: C, 59.31; H, 10.41; Cl, 15.92; Found: C, 59.12; H, 10.52; Cl, 15.65.

3-Chloro-1-decyloxypropan-2-ol. Colorless liquid, bp 130 °C (0.1 mmHg.), yield was 8.224 g (82 %); IR (film): 3418, 2954, 2925, 2855, 1598, 1465, 1430, 1378, 1299, 1260, 1120, 1074, 945, 910, 843, 753, 722, 624, 572 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.97 (m, $^3J_{HH}$ = 5.0-5.6 Hz, 1H, H^2), 3.60 (dd, $^2J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 5.7 Hz, 1H, $H^3{}_A$), 3.64 (dd, $^2J_{HH}$ = 11.1 Hz, $^3J_{HH}$ = 5.7 Hz, 1H, $H^3{}_B$), 3.53 (m, 2 H, $H^{1'}$), 3.48 (m, $^2J_{HH}$ = 10.4 Hz, 2H, H^1), 2.52 (br.s, 1H, OH), 1.57 (m, $^3J_{HH}$ = 6.6-6.8 Hz, $^3J_{HH}$ = 6.6-6.8 Hz, 2H, $H^{2'}$), 1.28-1.31 (m, 14H, $H^{3'}$-$H^{9'}$), 1.22 (t, $^3J_{HH}$ = 7.0 Hz, 3H, $H^{10'}$); Calculated for $C_{13}H_{27}ClO_2$: C, 62.25; H, 10.85; Cl, 14.13; Found: C, 61.91; H, 11.21; Cl, 14.0.

3-Chloro-1-dodecyloxypropan-2-ol. Colorless liquid, bp 145 °C (0.1 mmHg), yield was 9.034 g (81 %); IR (film): 3418, 2924, 2854, 2687, 1727, 1633, 1466, 1377, 1299, 1254, 1121, 1075, 947, 911, 844, 753, 722, 624, 573 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.96 (m, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, H^2), 3.64 (dd, $^2J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 5.5 Hz, $H^3{}_A$, 1H), 3.59 (dd, $^2J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, $H^3{}_B$), 3.53 (m, $^3J_{HH}$ = 5.5 Hz, 2H, H^1), 3.48 (m, $^3J_{HH}$ = 6.6-6.8 Hz, $^4J_{HH}$ = 1.6-1.7 Hz, 2H, $H^{1'}$), 2.36 (br. s, 1H, OH), 1.57

(m, $^{3}J_{HH}$ = 6.6-6.8 Hz, $^{3}J_{HH}$ = 6.6-6.8 Hz, 2H, $H^{2'}$), 1.22-1.36 (m, 18H, $H^{3'}$-$H^{11'}$), 0.88 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, $H^{12'}$); Calculated for $C_{15}H_{31}ClO_2$: C, 64.61; H, 11.21; Cl, 12.71; Found: C, 64.31; H, 11.43; Cl, 12.42.

3-Chloro-1-tetradecyloxypropan-2-ol. Colorless liquid, bp 174 °C (0.1 mmHg), yield was 9.947 g (81 %); IR (film): 3409, 2923, 2853, 2681, 1726, 1710, 1640, 1580, 1466, 1377, 1301, 1261, 1121, 1075, 946, 910, 844, 753, 722, 622, 573, 528, 513, 452 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.97 (m, $^{3}J_{HH}$ = 5.5 Hz, $^{3}J_{HH}$ = 5.5 Hz, 1H, H^{2}), 3.64 (dd, $^{2}J_{HH}$ = 11.0 Hz, $^{3}J_{HH}$ = 5.5 Hz, 1H, $H^{3}{}_{A}$), 3.59 (dd, $^{2}J_{HH}$ = 11.0 Hz, $^{3}J_{HH}$ = 5.5 Hz, 1H, $H^{3}{}_{B}$), 3.53 (m, $^{3}J_{HH}$ = 5.5 Hz, 2H, H^{1}), 3.47 (m, $^{3}J_{HH}$ = 6.6-6.8 Hz, $^{4}J_{HH}$ = 1.6-1.7 Hz, $H^{1'}$, 2 H), 2.13 (br. s, 1H, OH), 1.57 (m, $^{3}J_{HH}$ = 6.6-6.8 Hz, $^{3}J_{HH}$ = 6.6-6.8 Hz, 2 H, $H^{2'}$), 1.19-1.38 (m, 22H, $H^{3'}$-$H^{13'}$), 0.88 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, $H^{14'}$); Calculated for $C_{17}H_{35}ClO_2$: C, 66.53; H, 11.50; Cl, 11.55; Found: C, 66.16; H, 11.80; Cl, 11.35.

3-Chloro-1-hexadecyloxypropan-2-ol. Purified by column chromatography using a linear gradient elution system from 100 % to 10 % (by volume) hexane-diethyl ether. Colorless liquid, TLC R_f = 0.26 (hexanes/Et_2O = 7/ 3), yield was 11.826 g (89 %); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.97 (m, $^{3}J_{HH}$ = 5.5 Hz, $^{3}J_{HH}$ = 5.4 Hz, 1 H, , H^{2}), 3.64 (dd, $^{2}J_{HH}$ = 11.0 Hz, $^{3}J_{HH}$ = 5.5 Hz, 1 H, $H^{3}{}_{A}$), 3.59 (dd, $^{2}J_{HH}$ = 11.0 Hz, $^{3}J_{HH}$ = 5.5 Hz, 1 H, $H^{3}{}_{B}$), 3.53 (m, $^{3}J_{HH}$ = 5.1 Hz, 2 H, H^{1}), 3.47 (m, $^{3}J_{HH}$ = 6.6-6.8 Hz, $^{4}J_{HH}$ = 1.6-1.7 Hz, 2 H, $H^{1'}$), 2.16 (br. s, 1 H, OH), 1.57 (m, $^{3}J_{HH}$ = 6.6-6.8 Hz, $^{3}J_{HH}$ = 6.6-6.8 Hz, 2 H, $H^{2'}$), 1.20-1.38 (m, 26 H, $H^{3'}$-$H^{15'}$), 0.88 (t, $^{3}J_{HH}$ = 7.2 Hz, 3 H, $H^{16'}$); Calculated for $C_{19}H_{39}ClO_2$: C, 68.13; H, 11.74; Cl, 10.58; Found: C, 67.95; H, 11.91; Cl, 10.34.

3-Chloro-1-octadecyloxypropan-2-ol. Purified by column chromatography using a linear gradient elution system from 100 % to 10 % (by volume) hexane-diethyl ether. Colorless liquid, TLC R_f = 0.33 (haxanes/Et_2O = 7/3), yield was 12.923 g (89 %); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.97 (m, $^{3}J_{HH}$ = 5.5 Hz, $^{3}J_{HH}$ = 5.4 Hz, 1H, H^{2}), 3.64 (dd, $^{2}J_{HH}$ = 11.0 Hz, $^{3}J_{HH}$ = 5.5 Hz, 1H, $H^{3}{}_{A}$), 3.59 (dd, $^{2}J_{HH}$ = 11.0 Hz, $^{3}J_{HH}$ = 5.5 Hz, 1H, $H^{3}{}_{B}$), 3.53 (m, $^{3}J_{HH}$ = 5.1 Hz, 2H, H^{1}), 3.47 (m, $H^{1'}$, 2H, $^{3}J_{HH}$ = 6.6-6.8, $^{4}J_{HH}$ = 1.6-1.7 Hz), 2.16 (br. s, OH, 1H), 1.57 (m, $^{3}J_{HH}$ = 6.6-6.8 Hz, $^{3}J_{HH}$ = 6.6-6.8 Hz, 2H, $H^{2'}$), 1.41-1.20 (m, 30H, $H^{3'}$-$H^{15'}$), 0.88 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, $H^{18'}$); Calculated for $C_{21}H_{43}ClO_2$: C, 69.48; H, 11.94; Cl, 9.77; Found: C, 69.15; H, 12.19; Cl, 9.60.

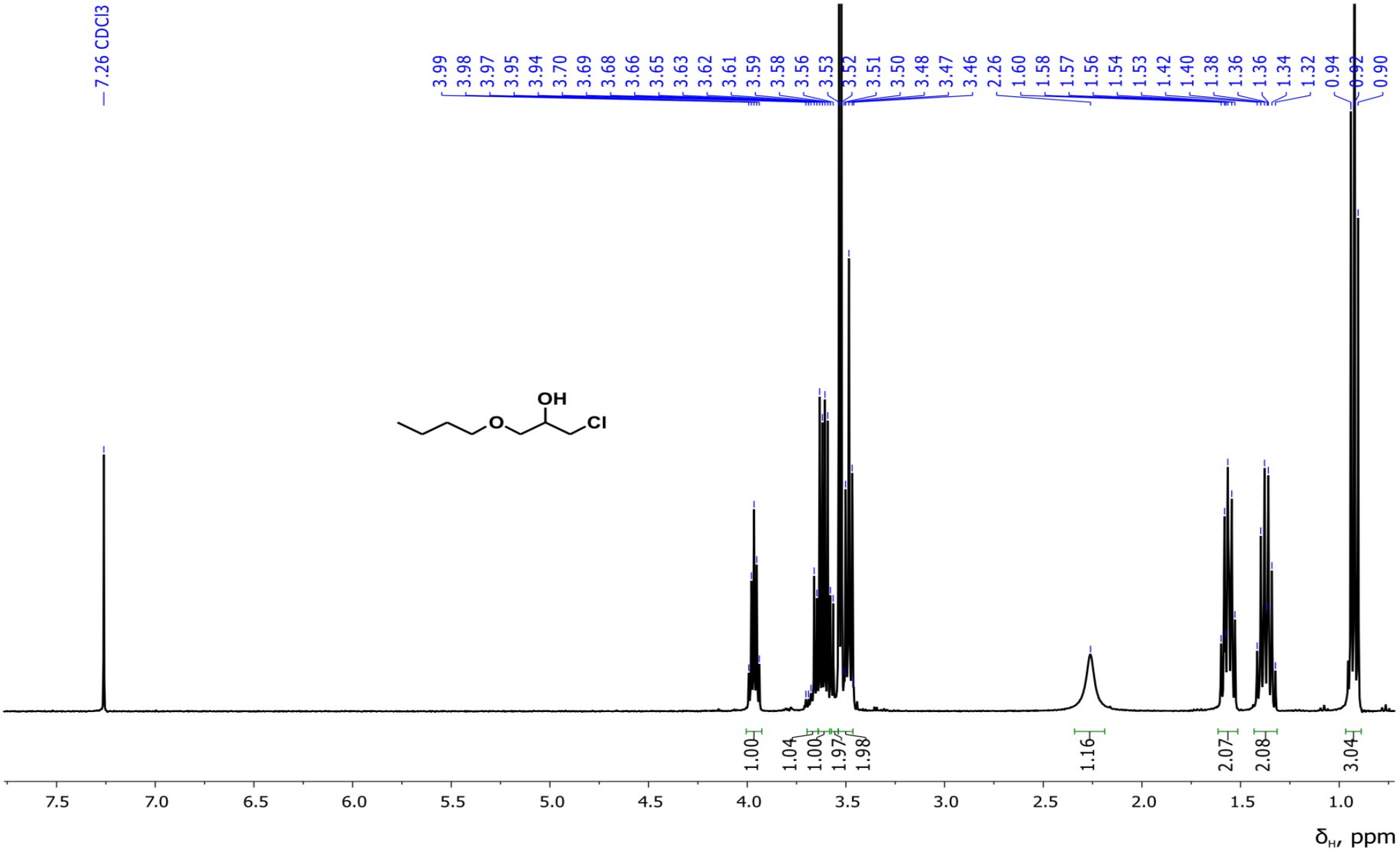

Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-chloro-1-butoxypropan-2-ol.

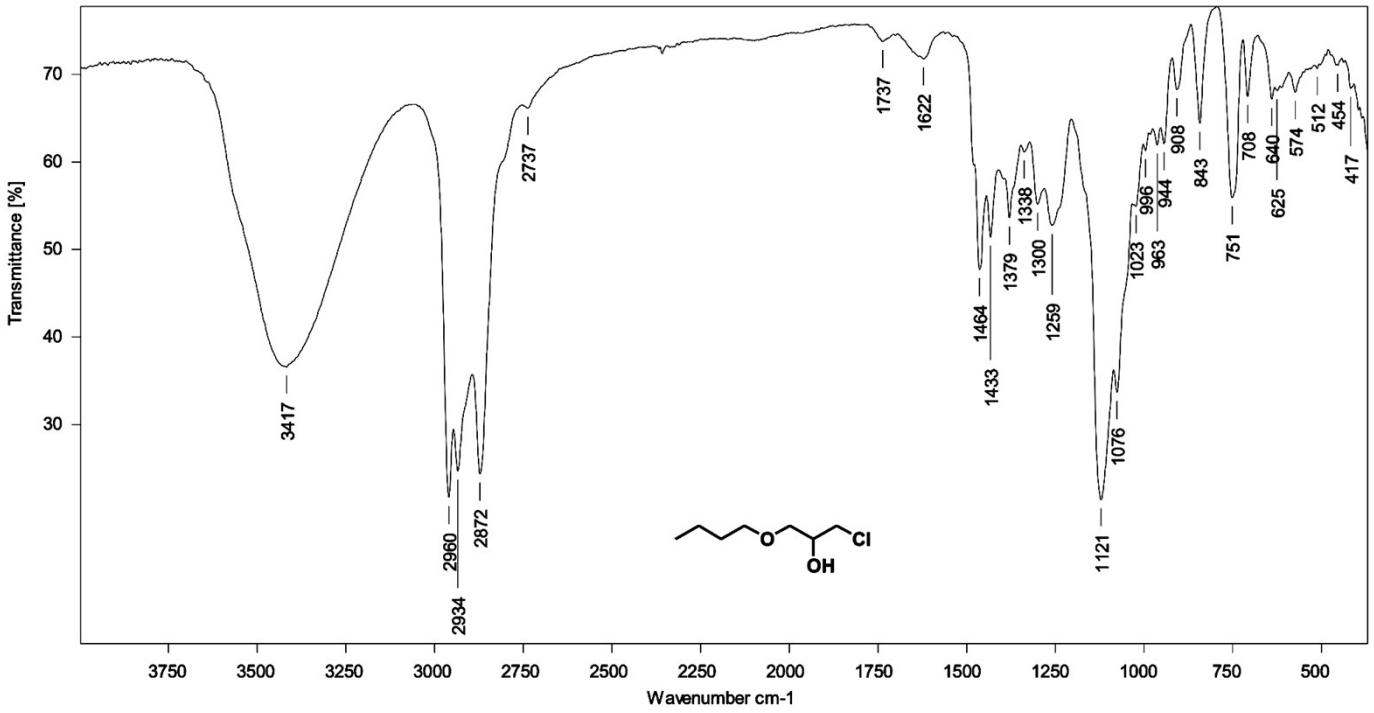

Figure S4. IR spectrum (film) of 3-chloro-1-butoxypropan-2-ol.

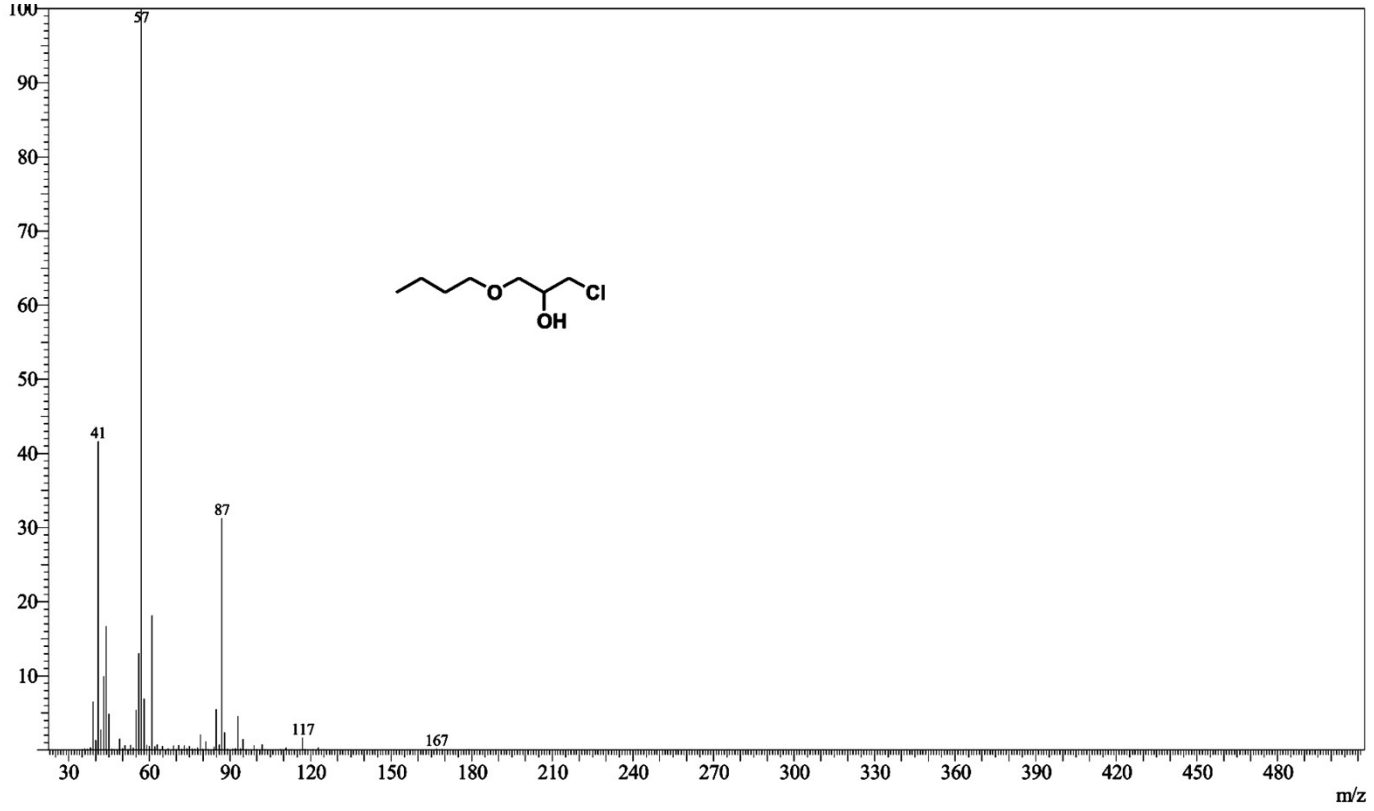

Figure S5. EI-MS spectrum of 3-chloro-1-butoxypropan-2-ol.

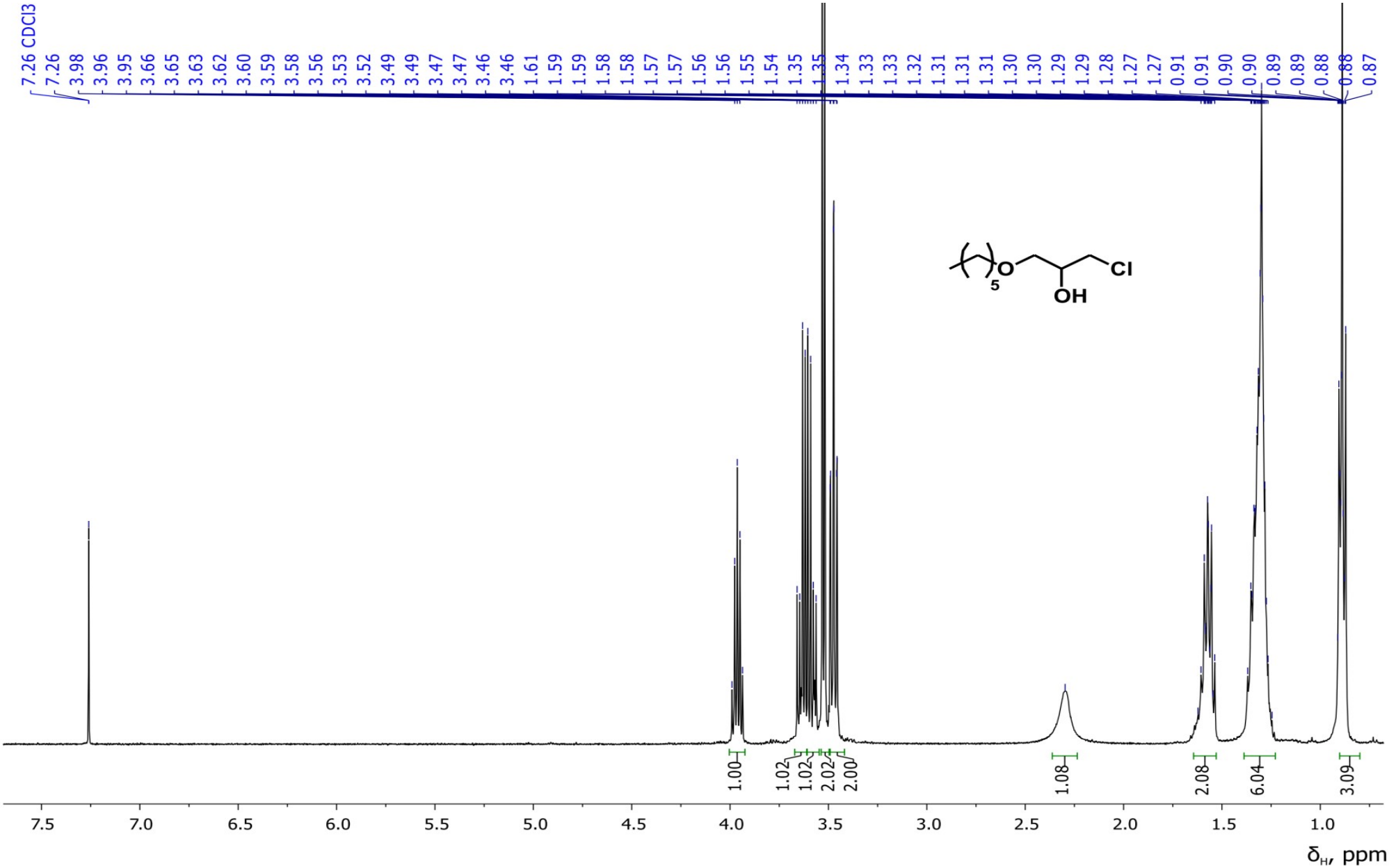

Figure S6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3-chloro-1-hexyloxypropan-2-ol.

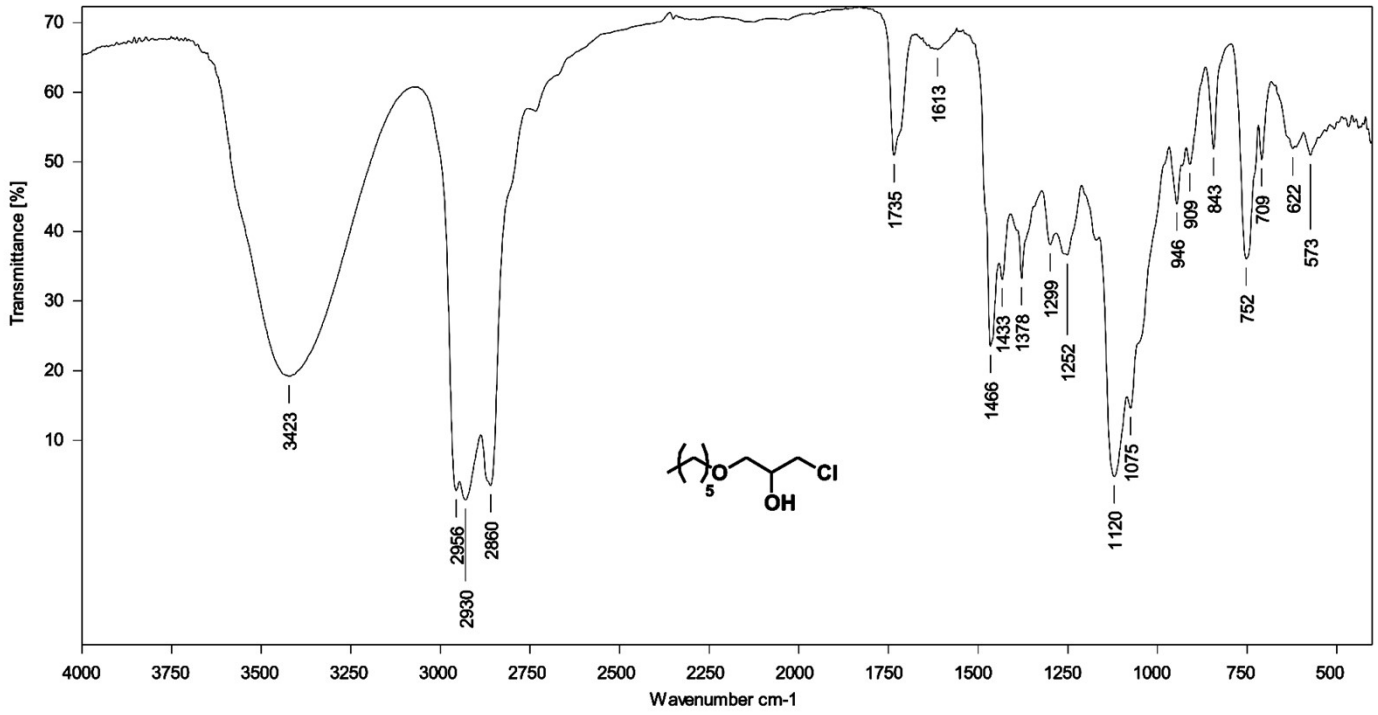

Figure S7. IR spectrum (film) of 3-chloro-1-hexyloxypropan-2-ol.

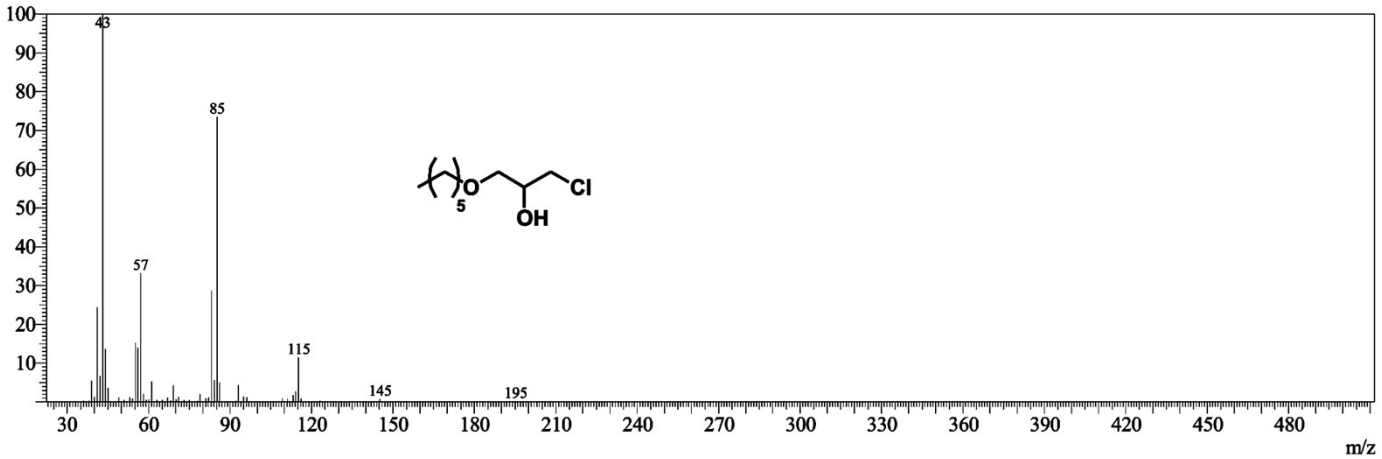

Figure S8. EI-MS spectrum of 3-chloro-1-hexyloxypropan-2-ol.

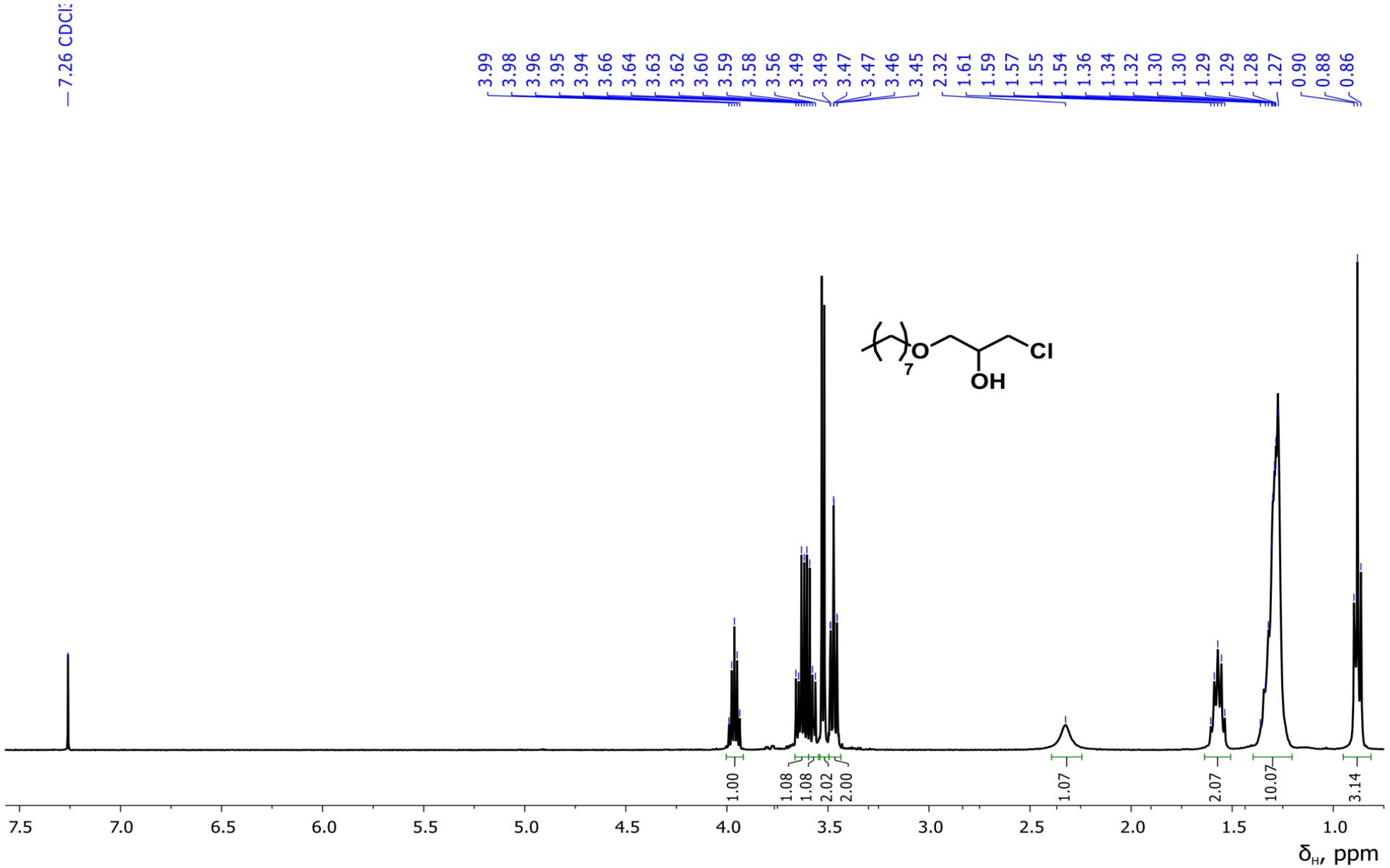

Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3-chloro-1-octyloxypropan-2-ol.

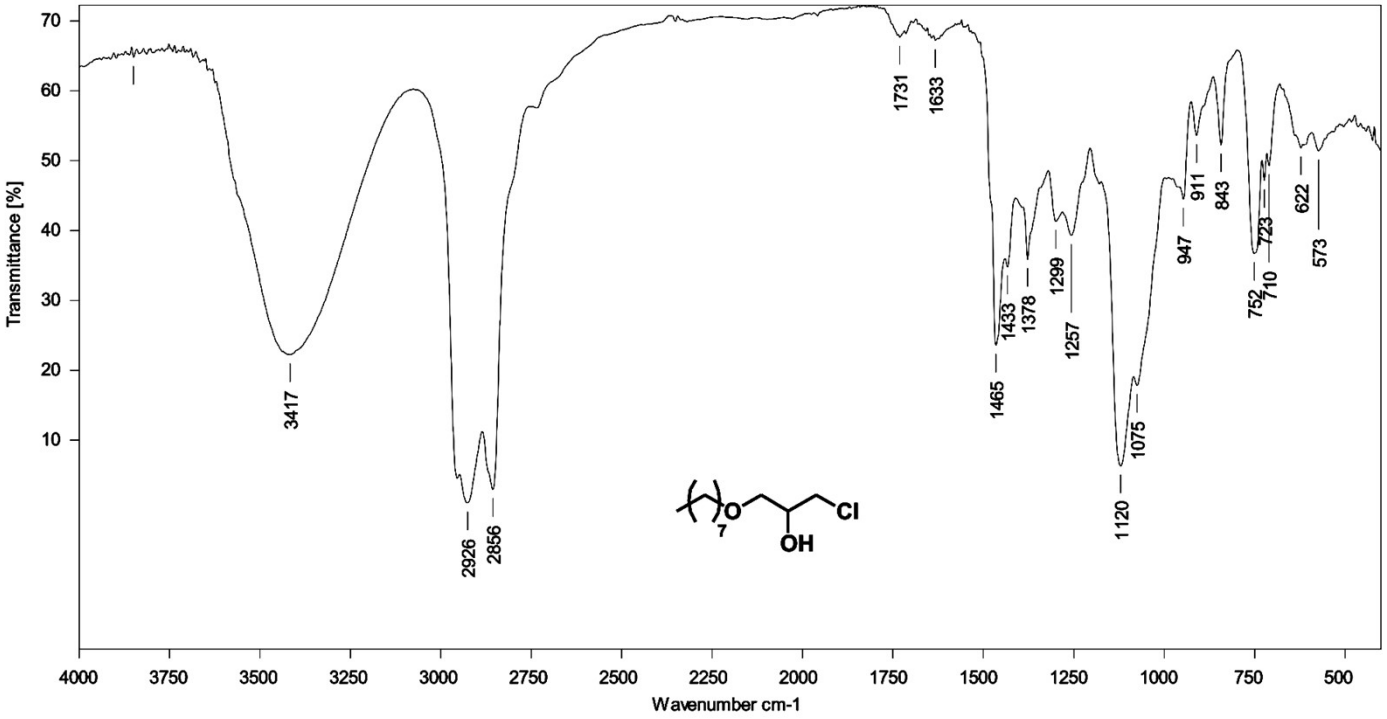

Figure S10. IR spectrum (film) of 3-chloro-1-octyloxypropan-2-ol.

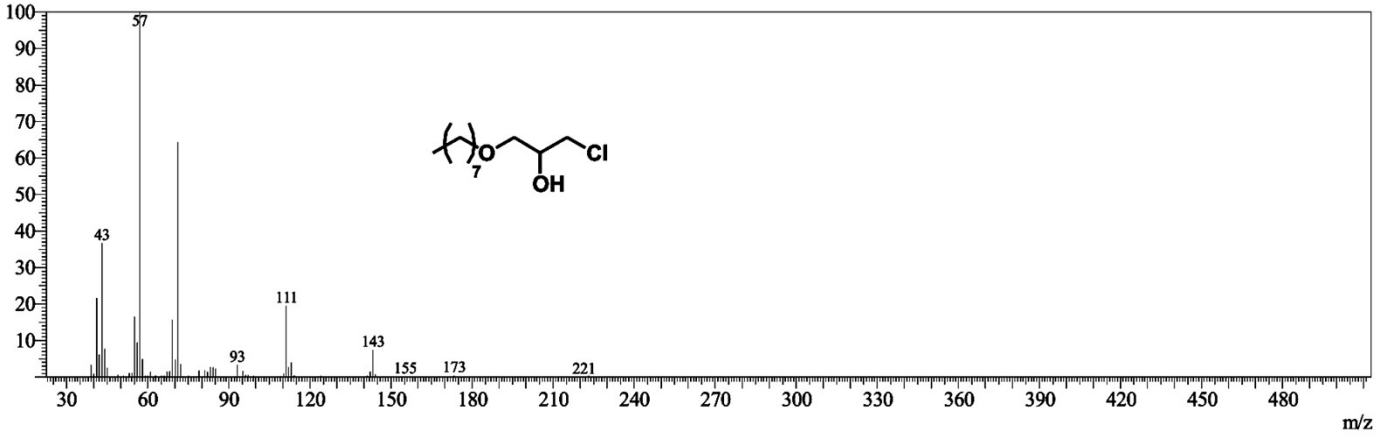

Figure S11. EI-MS spectrum of compound 3-chloro-1-octyloxypropan-2-ol.

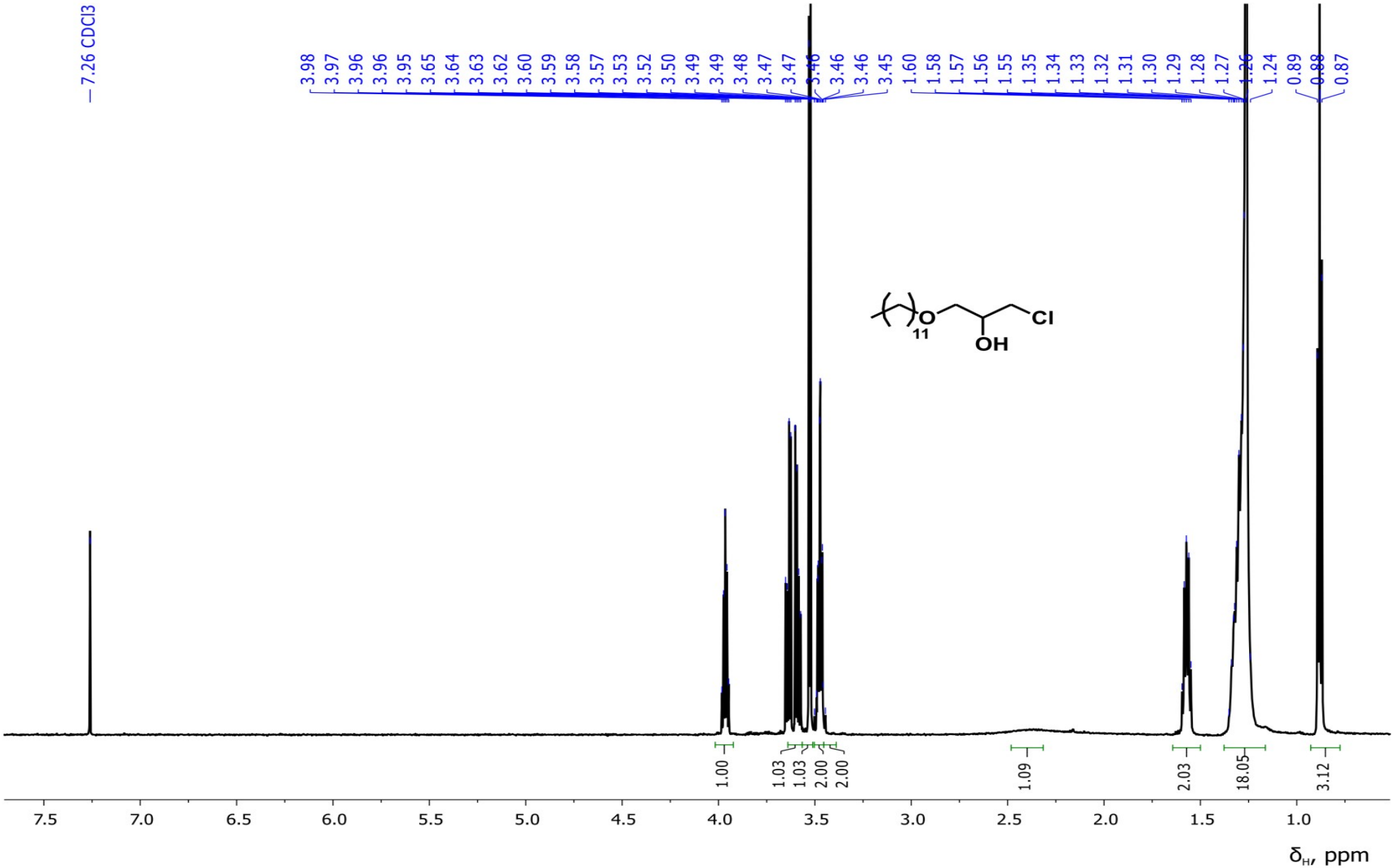

Figure S12. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3-chloro-1-dodecyloxypropan-2-ol.

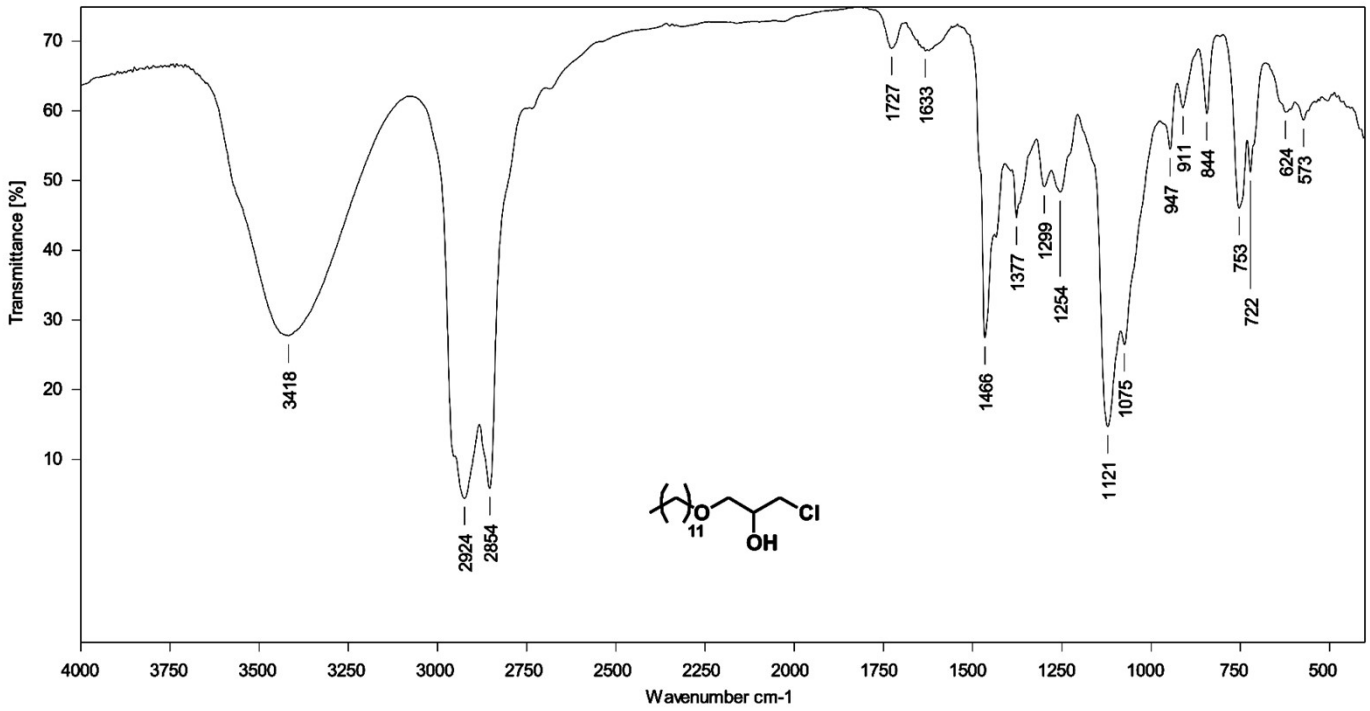

Figure S13. IR spectrum (film) of 3-chloro-1-dodecyloxypropan-2-ol.

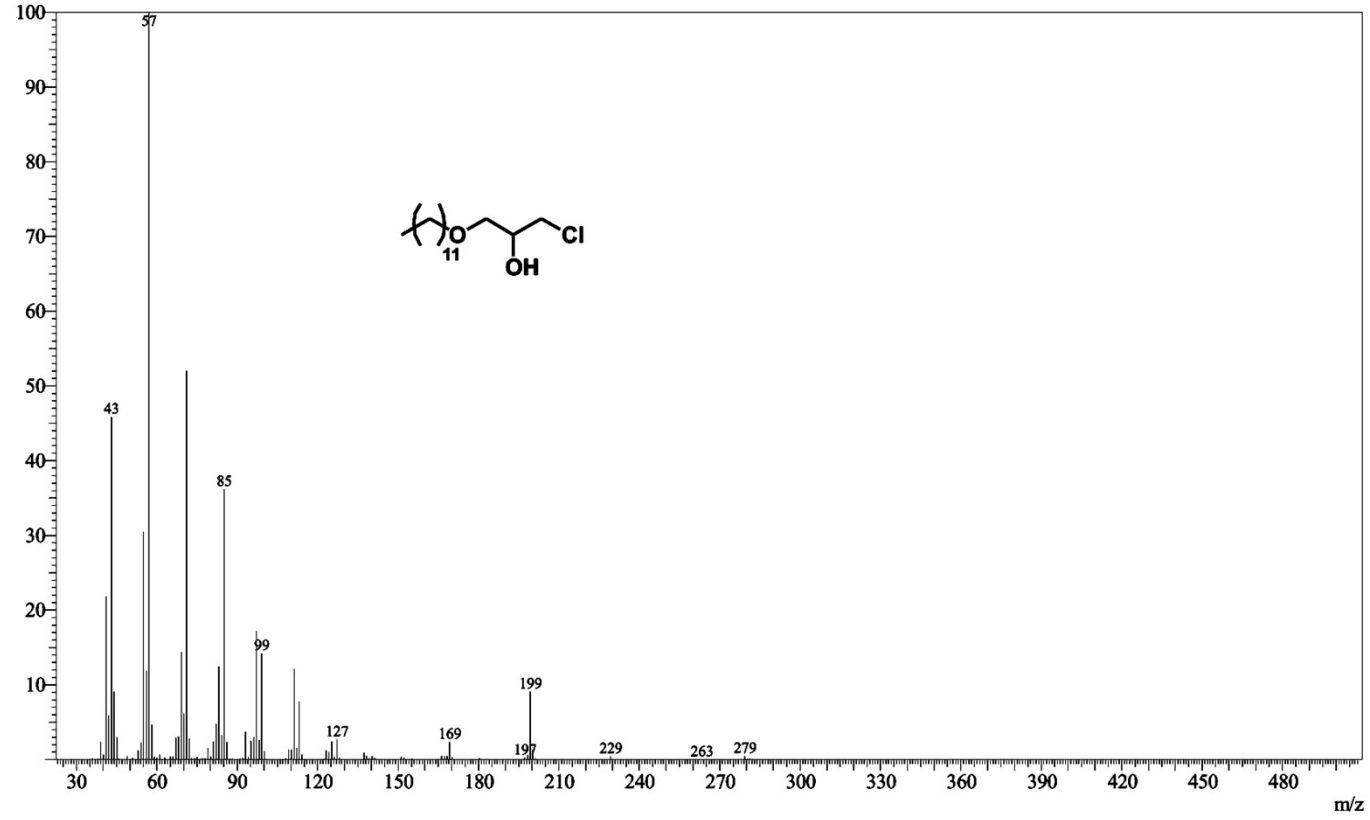

Figure S14. EI-MS spectrum of compound 3-chloro-1-dodecyloxypropan-2-ol.

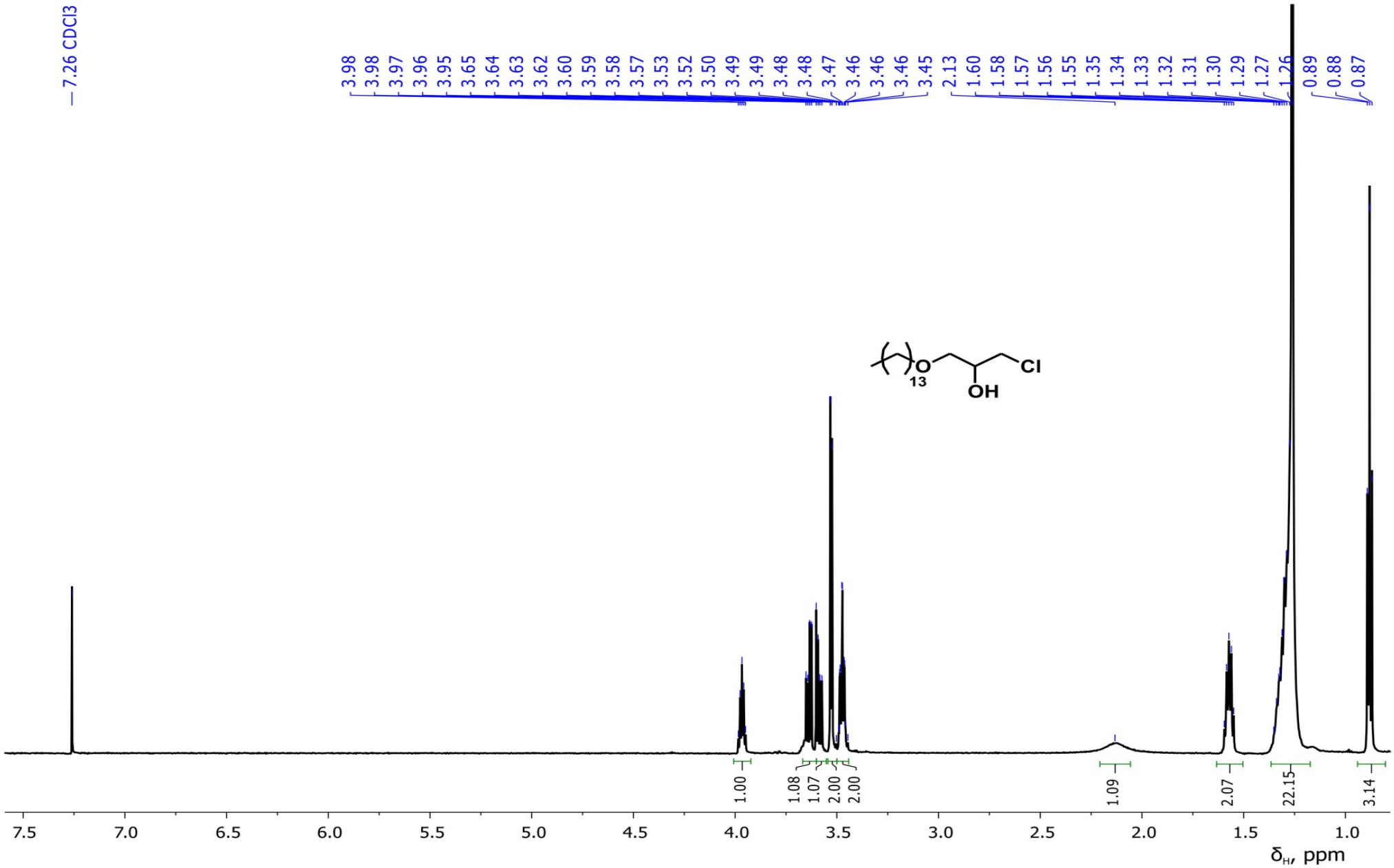

Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3-chloro-1-tetradecyloxypropan-2-ol.

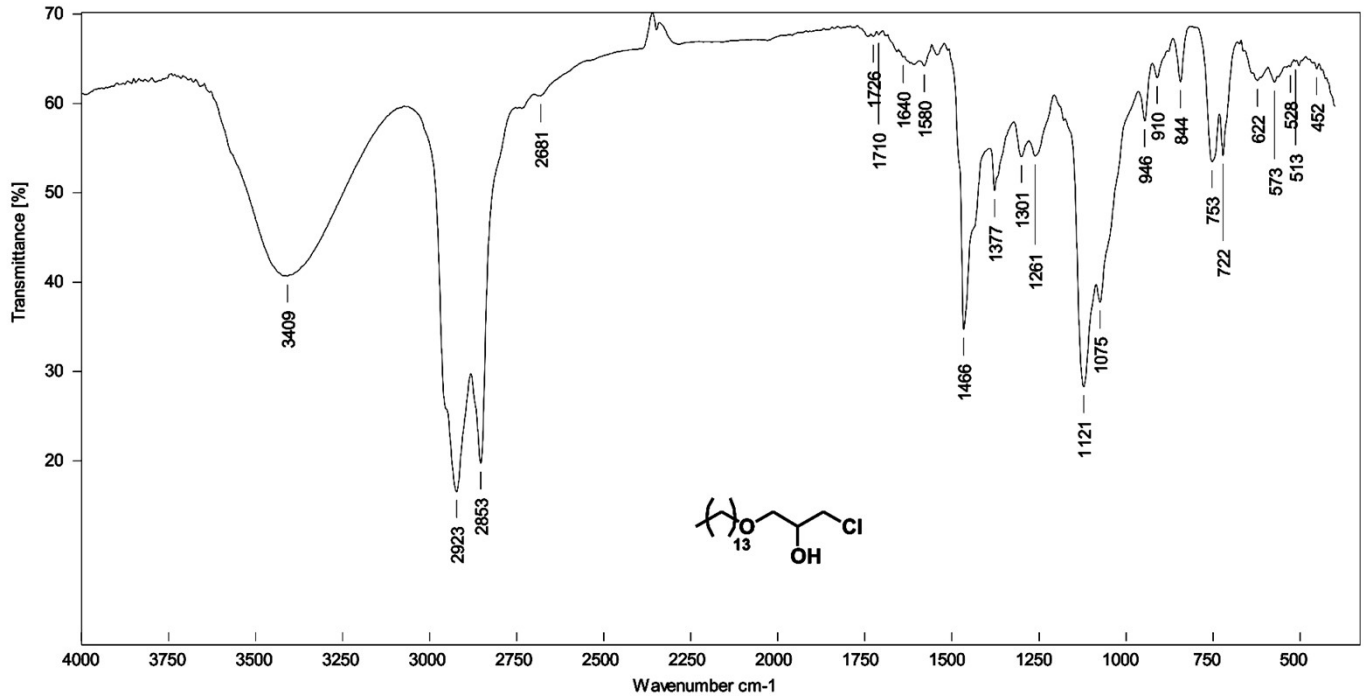

Figure S16. IR spectrum (film) of 3-chloro-1-tetradecyloxypropan-2-ol.

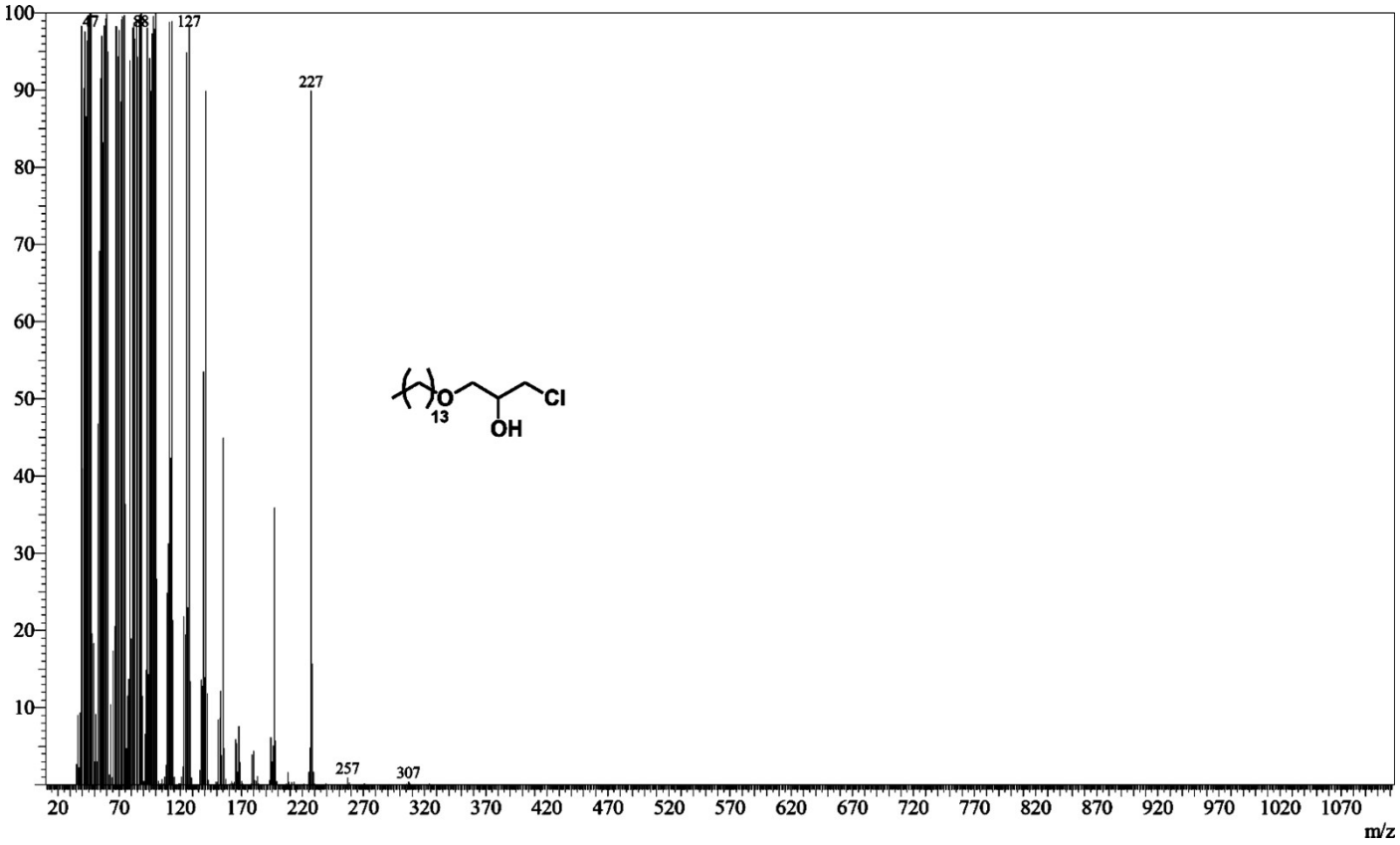

Figure S17. EI-MS spectrum of 3-chloro-1-tetradecyloxypropan-2-ol.

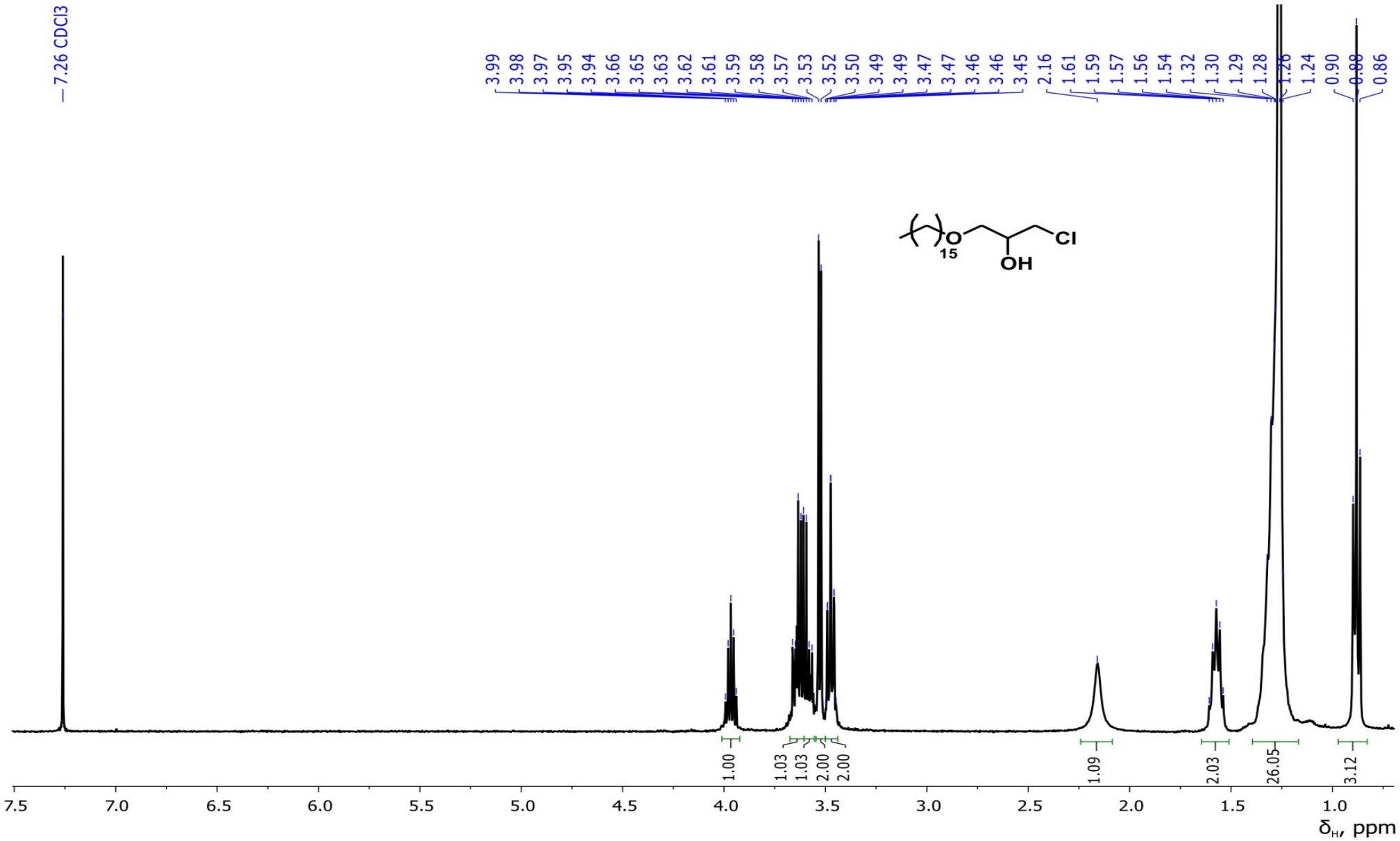

Figure S18. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3-chloro-1-hexadecyloxypropan-2-ol.

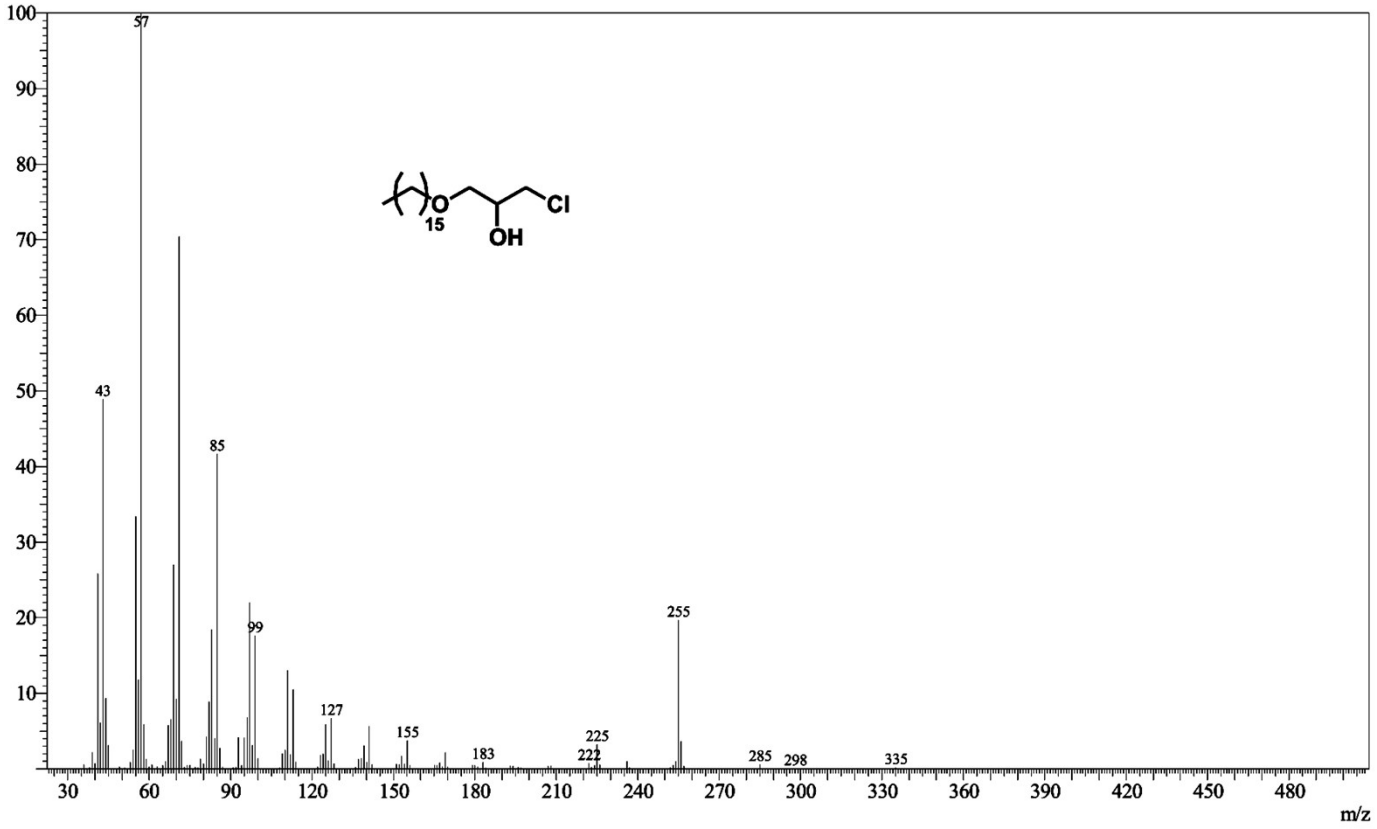

Figure S19. EI-MS spectrum of 3-chloro-1-hexadecyloxypropan-2-ol.

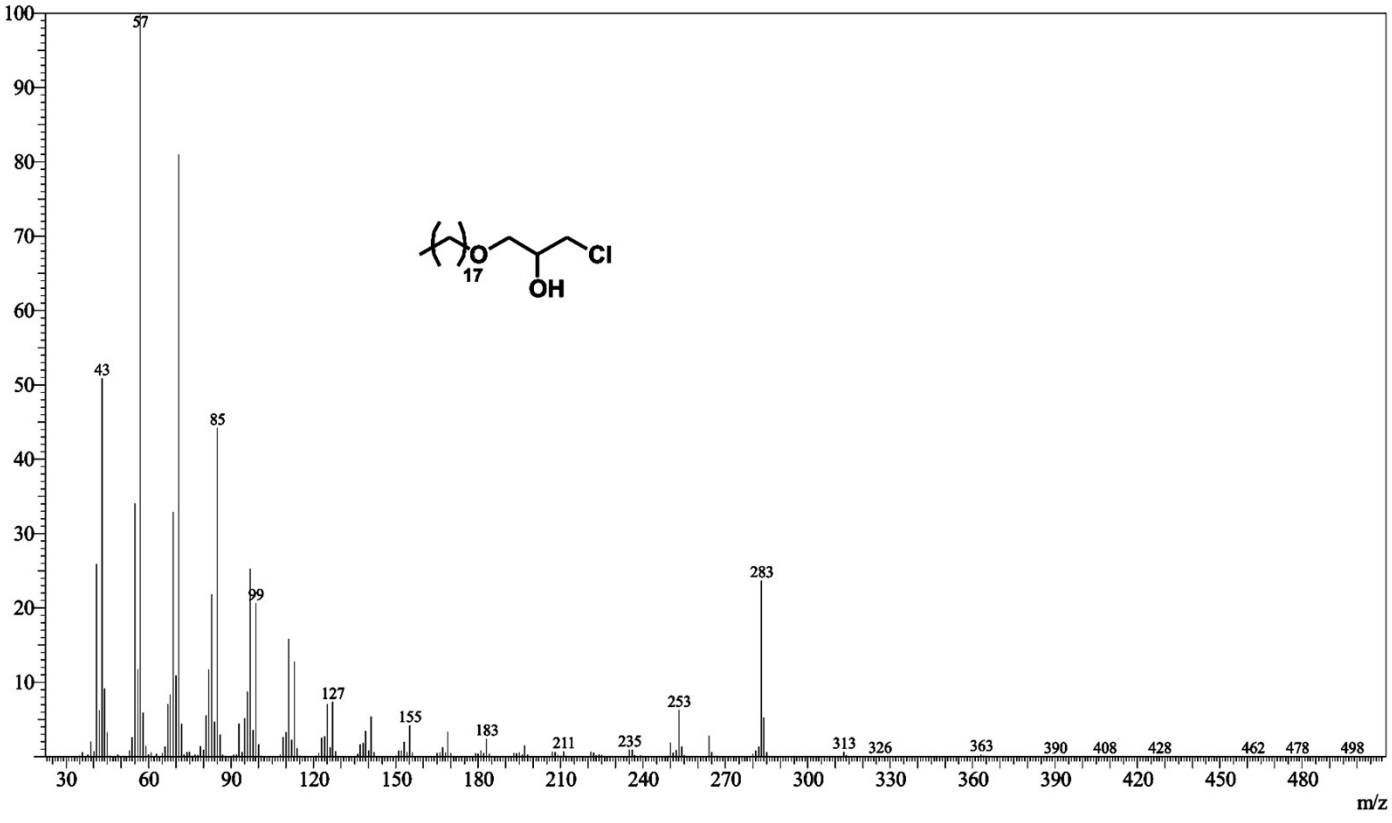

Figure S20. EI-MS spectrum of 3-chloro-1-hexadecyloxypropan-2-ol.

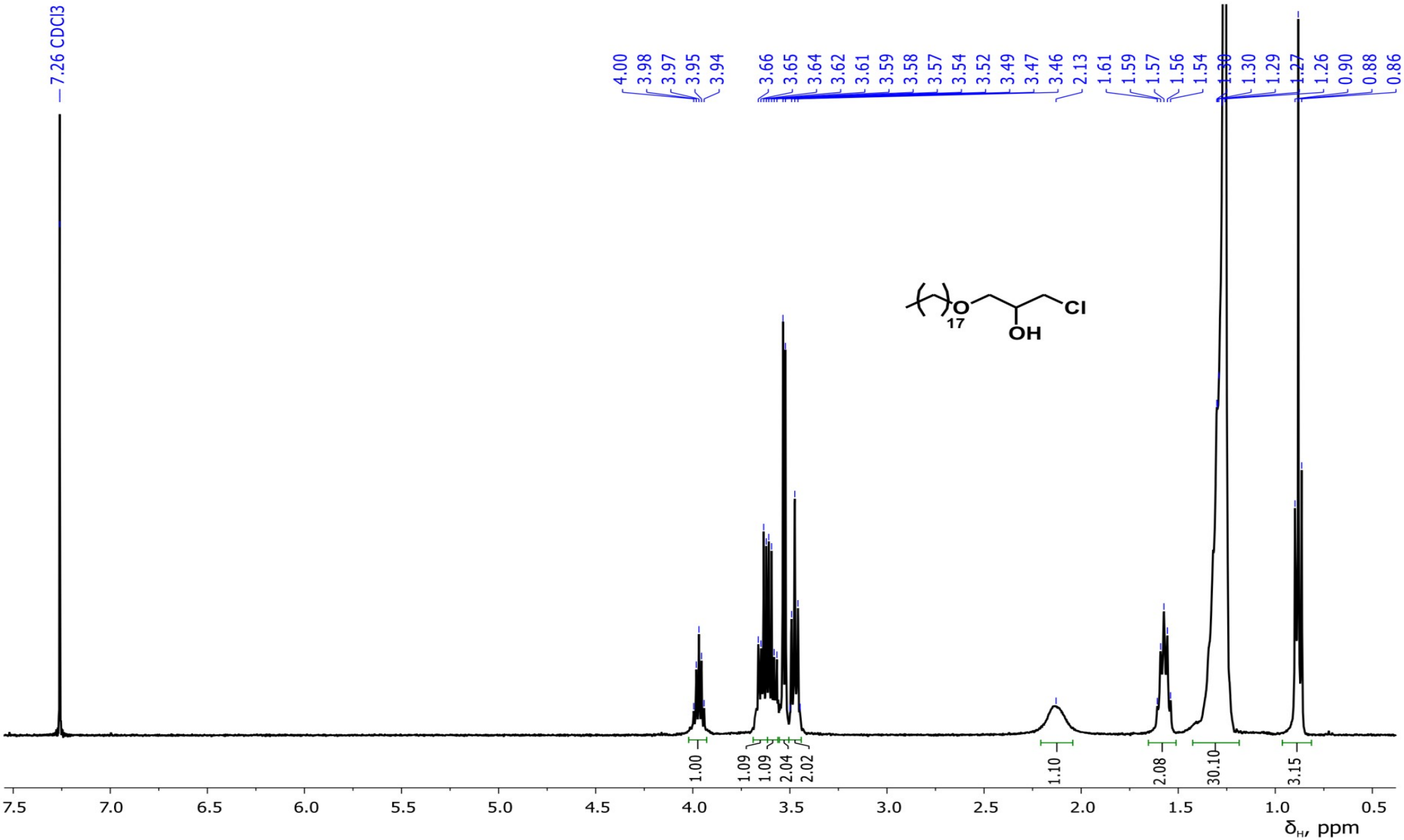

Figure S21. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3-chloro-1-octadecyloxypropan-2-ol.

Spectral data of compounds 1

*2-(Butoxymethyl)oxirane (**1c**)*. Colorless liquid, bp 62 °C (10 mmHg), yield was 1.716 g (88 %); IR (film): 3489, 3053, 2960, 2934, 2871, 1612, 1466, 1435, 1382, 1337, 1301, 1253, 1159, 1108, 999, 953, 938, 914, 844, 803, 762, 616, 547, 476, 457, 425 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.69 (dd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 3.1 Hz, 1H, $H^3{}_A$), 3.50 (ddd, $^2J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 6.6 Hz, , $^3J_{HH}$ = 6.6 Hz, 1 H, $H^{1'}{}_A$), 3.48 (ddd, $^2J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, $H^{1'}{}_B$), 3.39 (dd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 5.8 Hz, 1H, $H^3{}_B$), 3.14 (dddd, $^3J_{HH}$ = 5.8 Hz, $^3J_{HH}$ = 4.1 Hz, $^3J_{HH}$ = 2.9 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, H^2), 2.79 (dd, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 4.1 Hz, 1H, $H^1{}_A$), 2.60 (dd, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 2.7 Hz, 1H, $H^1{}_B$), 1.56 (m, $^3J_{HH}$ = 7.5 Hz, 2H, $H^{2'}$), 1.38 (m, $^3J_{HH}$ = 7.5 Hz, 2H, $H^{3'}$), 0.92 (t, $^3J_{HH}$ = 7.3 Hz, 3H, $H^{4'}$); ^{13}C-{^1H} NMR (100.6 MHz, $CDCl_3$): δ_C = 71.27 (s, $C^{1'}$), 71.06 (s, C^3), 50.58 (s, C^2), 43.85 (s, C^1), 31.59 (s, $C^{2'}$), 19.04 (s, $C^{3'}$), 13.59 (s, $C^{4'}$); Calculated for $C_7H_{14}O_2$: C, 64.58; H, 10.84; Found: C, 64.31; H, 11.07.

*2-((Hexyloxy)methyl)oxirane (**1d**)*. Colorless liquid, bp 88 °C (10 mmHg), yield was: 2.109 (89 %); IR (film): 3492, 3051, 2956, 2931, 2860, 1959, 1614, 1467, 1379, 1338, 1254, 1109, 977, 911, 849, 762, 727, 557, 532 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.69 (dd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ =3.0 Hz, 1H, $H^3{}_A$), 3.50 (dt, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, $H^{1'}{}_A$), 3.46 (dt, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, $H^{1'}{}_B$), 3.38 (dd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ =5.6-5.7 Hz, 1H, $H^3{}_B$), 3.13 (dddd, $^3J_{HH}$ = 5.8 Hz, $^3J_{HH}$ = 4.1 Hz, $^3J_{HH}$ = 2.9 Hz, $^3J_{HH}$ = 2.9 Hz, 1H, H^2), 2.78 (dd, $^2J_{HH}$ = 5.0 Hz, $H^1{}_A$, 1H), 2.60 (dd, $^2J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 2.6 Hz, 1H, $H^1{}_B$), 1.58 (m, $^3J_{HH}$ = 7.0-7.1 Hz, $^3J_{HH}$ = 7.0-7.1 Hz, 2H, $H^{2'}$), 1.37-1.24 (m, 8H, $H^{3'}$-$H^{5'}$), 0.88 (t, $^3J_{HH}$ = 6.9-7.0 Hz, 3H, $C^{6'}$); ^{13}C-{^1H} NMR (100.6 MHz, $CDCl_3$): δ_C = 70.84 (s, $C^{1'}$), 70.58 (s, C^3), 49.77 (s, C^2), 42.75 (s, C^1), 31.01 (s, $C^{2'}$), 29.02 (s, $C^{3'}$), 25.11 (s, $C^{4'}$), 21.89 (s, $C^{5'}$), 13.11 (s, $C^{6'}$); Calculated for $C_9H_{18}O_2$: C, 68.31; H, 11.47; Found: C, 68.05; H, 11.68.

*2-((Octyloxy)methyl)oxirane (**1e**)*. Colorless liquid, bp 125 °C (12 mmHg), yield was 2.427 g (87 %); IR (film): 3491, 3050, 2927, 2856, 1613, 1467, 1378, 1338, 1253, 1158, 1110, 976, 949, 912, 848, 807, 762, 617, 552 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.69 (dd, $^2J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 3.1 Hz, 1H, $H^3{}_A$), 3.50 (dt, $^2J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, $H^{1'}{}_A$), 3.45 (dt, $^2J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, $H^{1'}{}_B$), 3.38 (dd, $^2J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 5.6-5.7 Hz, 1H, $H^3{}_B$), 3.13 (dddd, $^3J_{HH}$ = 6.0 Hz, $^3J_{HH}$ = 4.4 Hz, $^3J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 3.3 Hz, 1H, H^2), 2.78 (dd, $^2J_{HH}$ = 5.0 Hz, 1H, $H^1{}_A$), 2.60 (dd, $^2J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 2.7 Hz, 1H, $H^1{}_B$), 1.58 (m, $^3J_{HH}$ = 7.0-7.1 Hz, $^3J_{HH}$ = 7.0-7.1 Hz, 2H, $H^{2'}$), 1.21-1.38 (m, 12H, $H^{3'}$-$H^{7'}$), 0.87 (t, $^3J_{HH}$ = 6.9-7.0 Hz, 3H, $C^{8'}$); ^{13}C-{^1H} NMR (100.6 MHz, $CDCl_3$): δ_C = 70.86 (s, $C^{1'}$), 70.65 (s, C^3), 49.81 (s, C^2), 42.79 (s, C^1), 31.21 (s, $C^{2'}$), 29.12 (s, $C^{5'}$), 28.82 (s, $C^{4'}$), 28.67 (s, $C^{3'}$), 25.49 (s, $C^{6'}$), 21.98 (s, $C^{7'}$), 13.23 (s, $C^{8'}$); Calculated for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90; Found: C, 70.63; H, 12.14.

*2-((Decyloxy)methyl)oxirane (**1f**)*. Colorless liquid, bp 87-90 °C (0.1 mmHg), yield was 2.898 g (90 %); IR (film): 3051, 2926, 2855, 1613, 1467, 1338, 1253, 1158, 1111, 913, 848, 762, 722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.47 (dd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 3.0 Hz, 1H, $H^3{}_A$), 3.13 (dd, $^2J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 5.8 Hz, 1H, $H^3{}_B$), 3.23-3.26 (m, $^2J_{HH}$ = 10.0-11.0 Hz, $^3J_{HH}$ = 6.7 Hz, $H^{1'}$), 2.90 (m, $^3J_{HH}$ = 3.0 Hz, 1H, H^2), 2.55 (dd, $^2J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 4.1 Hz, 1H, $H^1{}_A$), 2.36 (dd, $^2J_{HH}$ = 5.1 Hz, $^3J_{HH}$ = 2.7 Hz, 1H, $H^3{}_B$), 1.04-1.10

(m, 14H, $H^{3'}$-$H^{9'}$), 0.65 (t, $^3J_{HH}$ = 6.7 Hz, 3H, $H^{10'}$); ^{13}C-{^1H} NMR (100.6 MHz, $CDCl_3$): δ_C = 71.58 (s, $C^{1'}$), 71.40 (s, C^3), 50.75 (s, C^2), 44.06 (s, C^1), 31.86 (s, $C^{2'}$), 29.66 (s, $C^{3'}$), 29.56 (s, $C^{4'}$), 29.53 (s, $C^{5'}$), 9.44 (s, $C^{6'}$), 29.29 (s, $C^{7'}$), 26.05 (s, $C^{8'}$), 22.62 (s, $C^{9'}$), 14.01 (s, $C^{10'}$); Calculated for $C_{13}H_{26}O_2$: C, 72.85; H, 12.23; Found: C, 72.51; H, 12.50.

*2-((Dodecyloxy)methyl)oxirane (**1g**)*. Colorless liquid, bp 122 °C (0.1 mmHg), yield was 3.312 g (91 %); IR (film): 3049, 2925, 2854, 1725, 1612, 1466, 1378, 1338, 1253, 1158, 1112, 949, 913, 848, 807, 762, 722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.69 (dd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ =3.2 Hz, 1H, $H^3{}_A$), 3.50 (dt, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, $H^{1'}{}_A$), 3.46 (dt, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, $H^{1'}{}_B$), 3.39 (dd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 5.6-5.7 Hz, 1H, $H^3{}_B$), 3.14 (dddd, $^3J_{HH}$ = 5.7 Hz, $^3J_{HH}$ = 3.0 Hz, $^3J_{HH}$ = 2.6 Hz, $^3J_{HH}$ = 2.7 Hz, 1H, H^2), 2.79 (dd, $^2J_{HH}$ = 4.9, $^3J_{HH}$ =3.8 Hz, 1H, $H^1{}_A$), 2.60 (dd, $^2J_{HH}$ = 4.9 Hz, $^3J_{HH}$ = 2.7 Hz, 1H, $H^1{}_B$), 1.58 (m, $^3J_{HH}$ = 7.0-7.1 Hz, $^3J_{HH}$ = 7.0-7.1 Hz, 2H, $H^{2'}$), 1.20-1.39 (m, 18H, $H^{3'}$-$H^{11'}$), 0.88 (t, $^3J_{HH}$ = 7.1, 3H, $C^{12'}$); ^{13}C-{^1H} NMR (100.6 MHz, $CDCl_3$): δ_C = 71.34 (s, $C^{1'}$), 71.24 (s, C^3), 50.47 (s, C^2), 43.66 (s, $C^{2'}$), 29.53 (s, $C^{3'}$), 29.48 (s, $C^{4'}$), 29.45 (s, $C^{5'}$ overlapped with $C^{6'}$), 29.42 (s, $C^{7'}$), 29.29 (s, $C^{8'}$), 29.16 (s, $C^{9'}$), 25.91(s, $C^{10'}$), 22.45 (s, $C^{11'}$), 13.78 (s, $C^{12'}$); Calcd. for $C_{15}H_{30}O_2$: C, 74.32; H, 12.48; Found: C, 74.01; H, 12.72.

*2-((Tetradecyloxy)methyl)oxirane (**1h**)*. Colorless low-melting solid, bp 142 °C (0.1 mmHg), mp = 18-19 °C, yield was 3.816 g (94 %); IR (film): 3477, 3049, 2925, 2854, 2362, 1632, 1467, 1391, 1378, 1338, 1300, 1253, 1158, 1112, 973, 913, 847, 806, 762, 722, 618 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.69 (dd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 3.2 Hz, 1H, $H^3{}_A$), 3.50 (dt, J = 9.3 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, $H^{1'}{}_A$), 3.46 (dt, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, $H^{1'}{}_B$), 3.39 (dd, $^2J_{HH}$ = 11.3 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, $H^3{}_B$), 3.14 (dddd, $^3J_{HH}$ = 5.7 Hz, $^3J_{HH}$ = 3.0 Hz, $^3J_{HH}$ = 2.7 Hz, $^3J_{HH}$ = 2.7 Hz, 1H, H^2), 2.79 (dd, $^2J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 4.1 Hz, 1H, $H^1{}_A$), 2.60 (dd, $^2J_{HH}$ = 4.9 Hz, $^3J_{HH}$ = 2.7 Hz, 1H, $H^1{}_B$), 1.58 (m, $^3J_{HH}$ = 7.0-7.1 Hz, $^3J_{HH}$ = 7.0-7.1 Hz, 2H, $H^{2'}$), 1.21-1.37 (m, 22H, $H^{3'}$-$H^{13'}$), 0.88 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $C^{14'}$); ^{13}C-{^1H} NMR (100.6 MHz, $CDCl_3$): δ_C = 71.40 (s, $C^{1'}$), 71.28 (s, C^3), 50.55 (s, C^2), 43.77 (s, C^1), 31.80 (s, $C^{2'}$), 29.57 (s, $C^{3'}$ overlapped with $C^{4'}$-$C^{7'}$), 29.56 (s, $C^{8'}$), 29.49 (s, $C^{9'}$), 29.36 (s, $C^{10'}$), 29.25 (s, $C^{11'}$), 25.96 (s, $C^{12'}$), 22.53 (s, $C^{13'}$), 13.88 (s, $C^{14'}$); Calcd. for $C_{15}H_{30}O_2$: C, 74.32; H, 12.48; Found: C, 73.98; H, 12.80.

*2-((Hexadecyloxy)methyl)oxirane (**1i**)*. Purified by column chromatography using a linear gradient elution system from 100 % to 30 % (by volume) hexane-diethyl ether. Colorless low-melting solid, mp 28-31 °C, TLC R_f = 0.35 (hexane/Et_2O = 7/3), yield was 3.987 g (89 %); IR (film): 3439, 2956, 2919, 2851, 1736, 1637, 1468, 1396, 1378, 1340, 1256, 1162, 1122, 1026, 985, 968, 945, 909, 856, 800, 762, 722, 540, 494 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.69 (dd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ =3.2 Hz, 1H, $H^3{}_A$), 3.50 (dt, J = 9.3 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, $H^{1'}{}_A$), 3.46 (dt, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, $H^{1'}{}_B$), 3.39 (dd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ =5.7 Hz, 1H, $H^3{}_B$), 3.14 (dddd, $^3J_{HH}$ = 5.8 Hz, $^3J_{HH}$ = 3.1 Hz, $^3J_{HH}$ = 3.1 Hz, $^3J_{HH}$ = 3.1 Hz, 1H, H^2), 2.79 (dd, $^2J_{HH}$ = 4.6 Hz, $^3J_{HH}$ = 4.6 Hz, 1H, $H^1{}_A$), 2.60 (dd, $^2J_{HH}$ = 5.9 Hz, $^3J_{HH}$ = 2.7 Hz, 1H, $H^1{}_B$), 1.58 (m, $^3J_{HH}$ = 7.0-7.1 Hz, $^3J_{HH}$ = 7.0-7.1 Hz, 2H, $H^{2'}$), 1.21-1.37 (m, 26H, $H^{3'}$-$H^{15'}$), 0.88 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $C^{16'}$); ^{13}C-{^1H} NMR (100.6 MHz, $CDCl_3$): δ_C = 71.73 (s, $C^{1'}$), 71.50 (s, C^3), 50.87 (s, C^2), 44.23 (s, C^1), 31.98 (s, $C^{2'}$), 29.75 (s, $C^{3'}$ overlapped with $C^{4'}$-$C^{8'}$), 29.72 (s, $C^{9'}$), 29.66 (s, $C^{11'}$overlapped with $C^{10'}$),

29.53 (s, $C^{12'}$), 29.42 (s, $C^{13'}$), 26.15 (s, $C^{14'}$), 22.73 (s, $C^{15'}$), 14.11 (s, $C^{16'}$); Calcd. for $C_{19}H_{38}O_2$: C, 76.45; H, 12.83; Found: C, 76.12; H, 13.09.

*2-((Octadecyloxy)methyl)oxirane (**1j**)*. Purified by column chromatography using a linear gradient elution system from 100 % to 30 % (by volume) hexane-diethyl ether. Colorless low-melting solid, mp 38-39 °C, TLC R_f = 0.49 (hexane/Et_2O = 7/3), yield was 4.361 g (89 %); IR (film): 3447, 2956, 2918, 2850, 2772, 2634, 1465, 1396, 1378, 1340, 1251, 1209, 1125, 1033, 1009, 966, 945, 907, 853, 799, 762, 729, 720, 541, 510, 471, 456, 422 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.69 (dd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ =3.2 Hz, 1H, $H^3{}_A$), 3.50 (dt, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, $H^{1'}{}_A$), 3.46 (dt, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, $H^{1'}{}_B$), 3.39 (dd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 5.7 Hz, 1H, $H^3{}_B$), 3.14 (dddd, $^3J_{HH}$ = 5.7 Hz, $^3J_{HH}$ = 3.0 Hz, $^3J_{HH}$ = 2.7 Hz, 1H, H^2), 2.79 (dd, $^2J_{HH}$ = 4.7 Hz, $^3J_{HH}$ = 4.5 Hz, 1H, $H^1{}_A$), 2.60 (dd, $^2J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 2.7 Hz, 1H, $H^1{}_B$), 1.58 (m, $^3J_{HH}$ = 7.0-7.1 Hz, $^3J_{HH}$ = 7.0-7.1 Hz, 2H, $H^{2'}$), 1.21-1.37 (m, 30H, $H^{3'}$-$H^{17'}$), 0.88 (t, $^3J_{HH}$ = 7.1 Hz, 3H, $C^{18'}$); ^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ_C = 71.80 (s, $C^{1'}$), 71.54 (s, C^3), 50.93 (s, C^2), 44.31 (s, C^1), 32.02 (s, $C^{2'}$), 29.79 (s, $C^{3'}$ overlapped with $C^{4'}$-$C^{10'}$), 29.76 (s, $C^{11'}$), 29.70 (s, $C^{12'}$), 29.69 (s, $C^{13'}$), 29.57 (s, $C^{14'}$), 29.45 (s, $C^{15'}$), 26.19 (s, $C^{16'}$), 22.77 (s, $C^{17'}$), 14.16 (s, $C^{18'}$); Calcd. for $C_{21}H_{42}O_2$: C, 77.24; H, 12.96; Found: C, 76.91; H, 13.22.

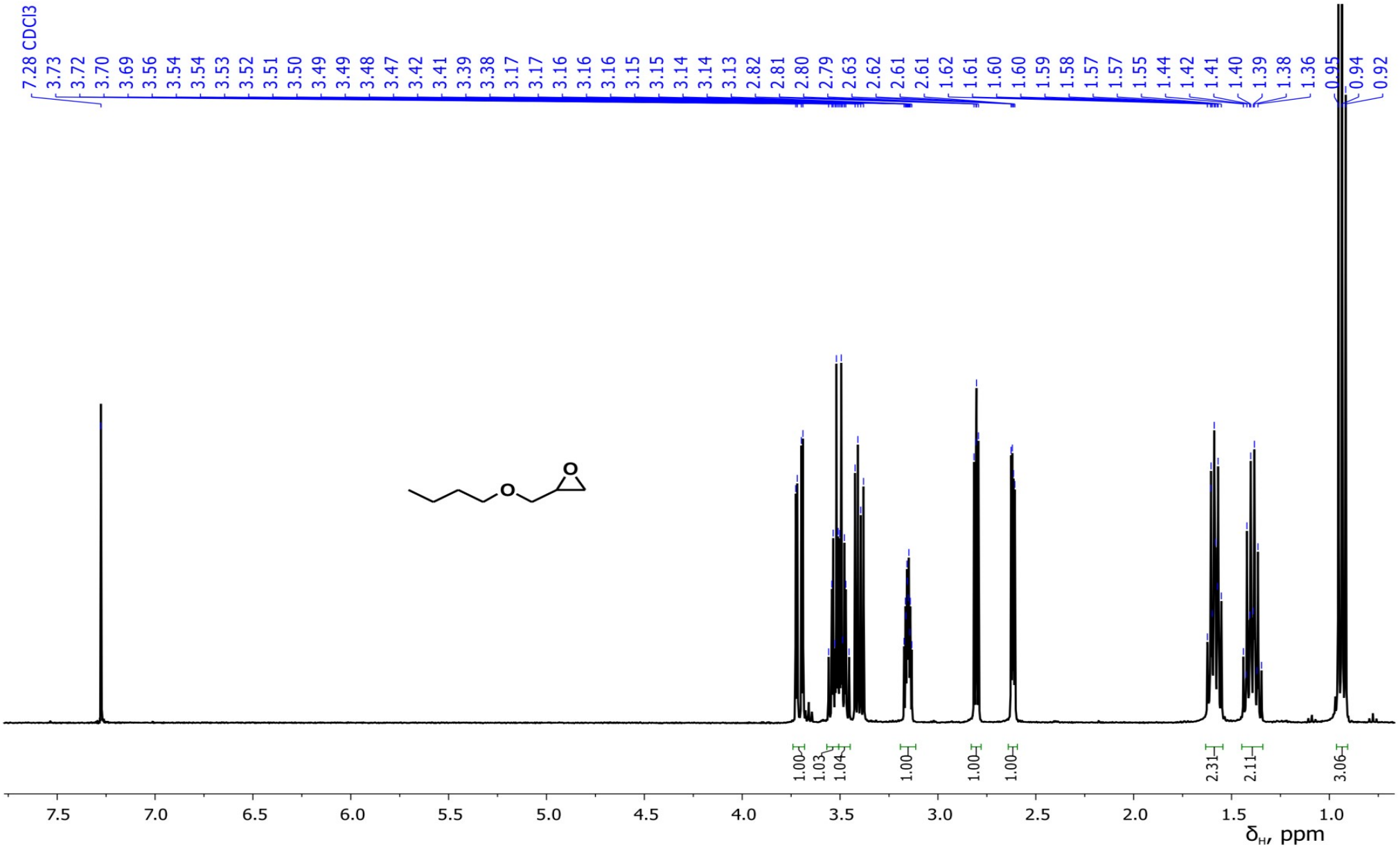

Figure S22. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1c**.

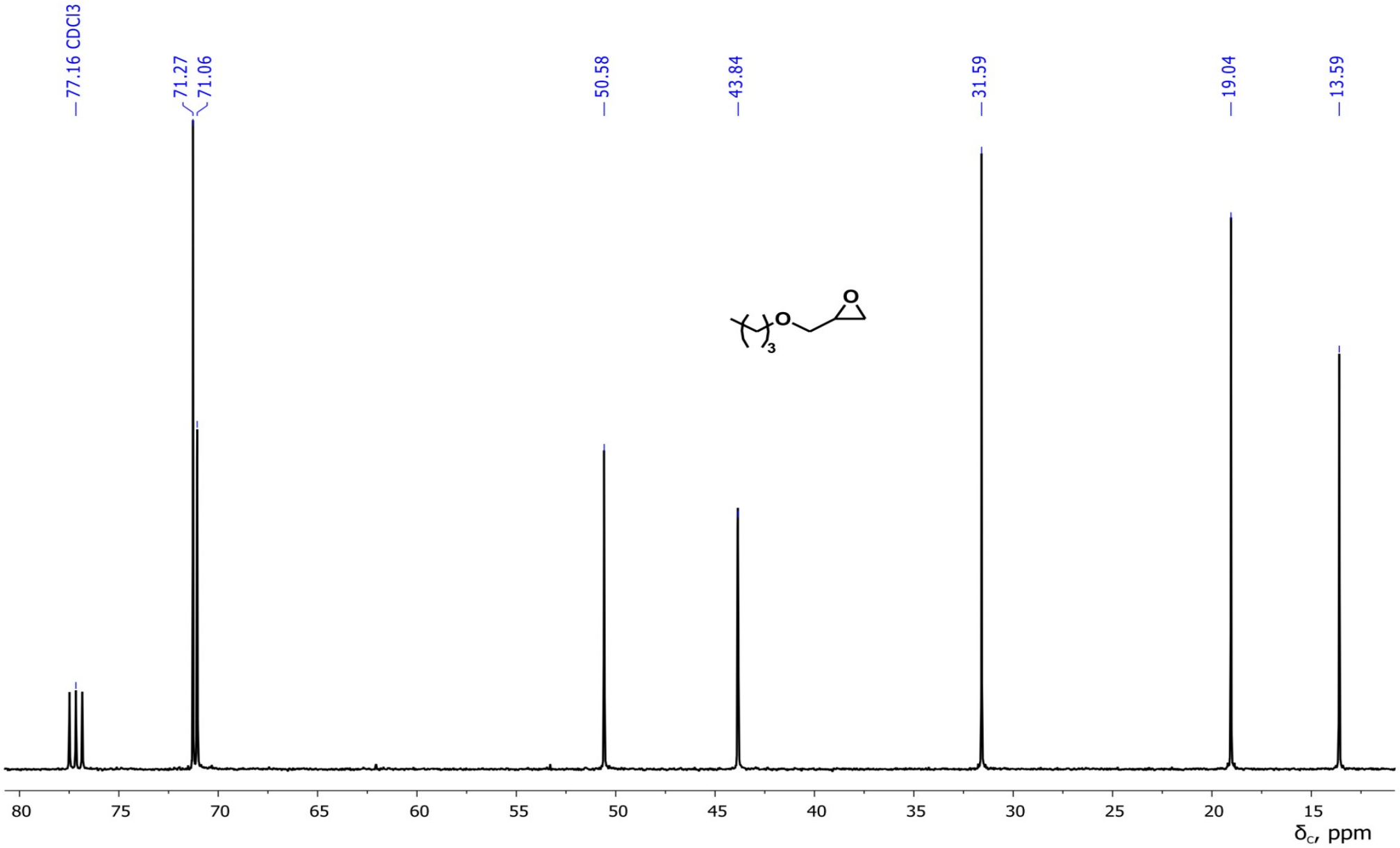

Figure S23. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of compound **1c**.

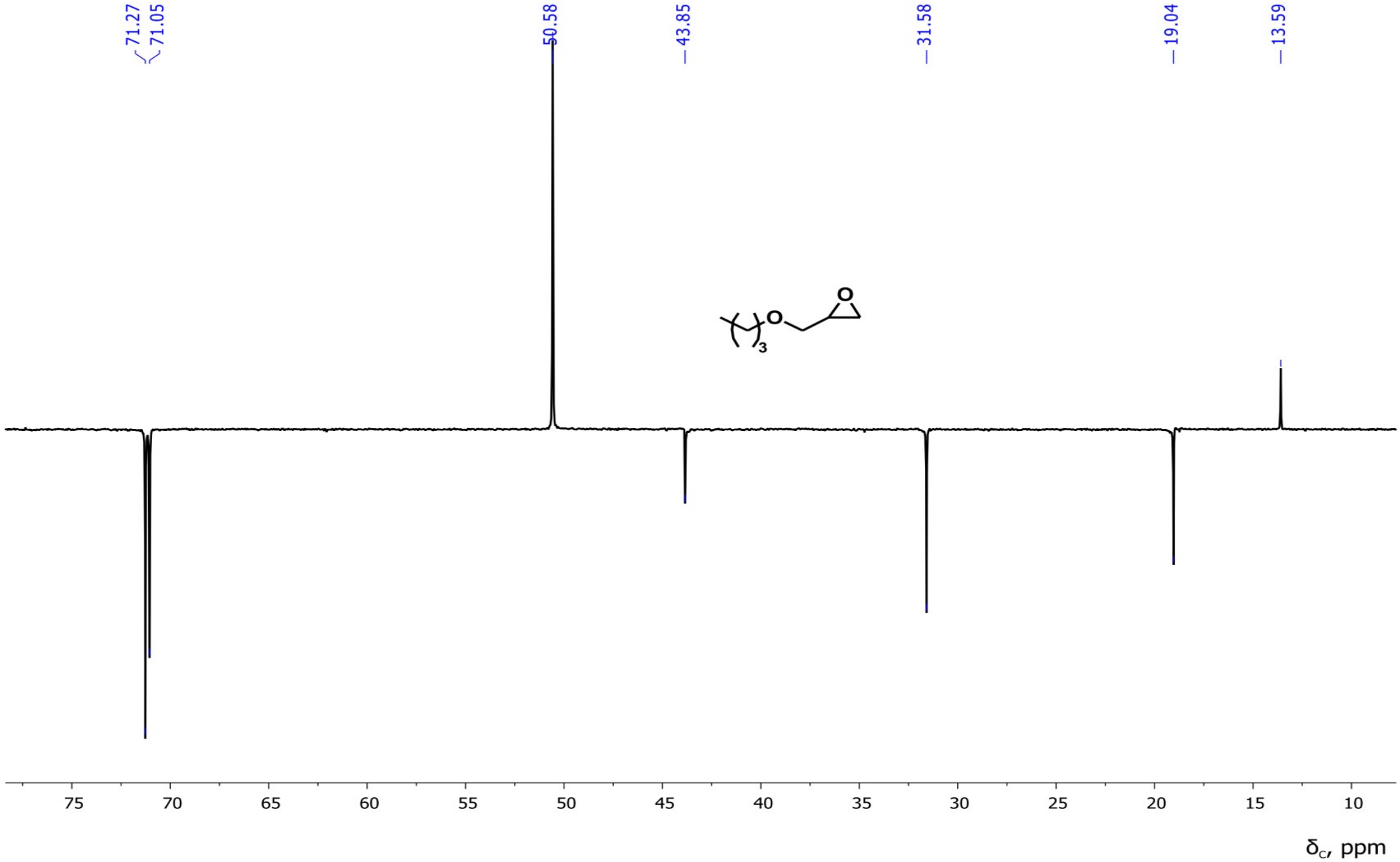

Figure S24. ^{13}C-{^{1}H} APT NMR spectrum (100.6 MHz, $CDCl_3$) of compound **1c**.

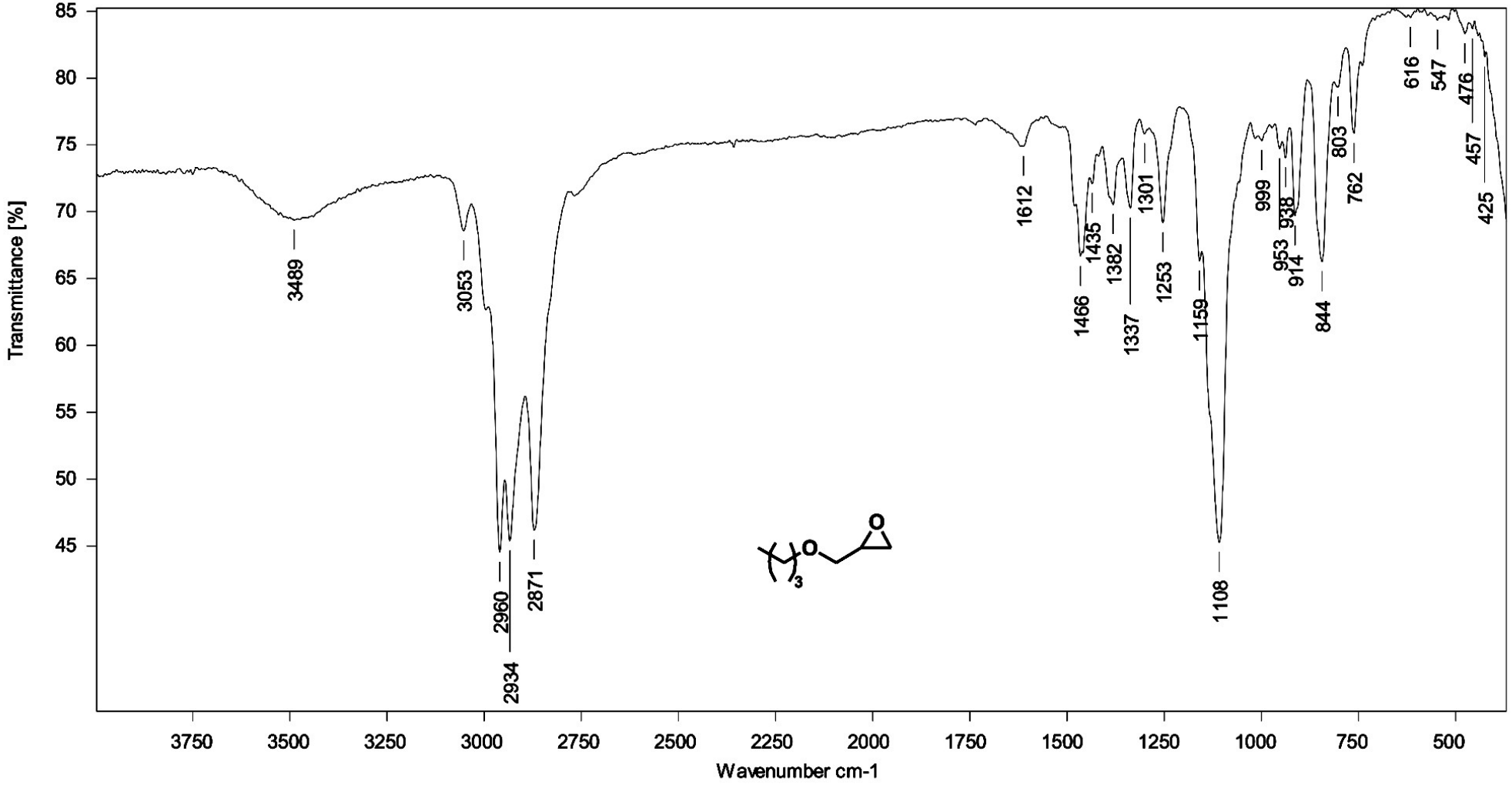

Figure S25. IR spectrum (film) of compound **1c**.

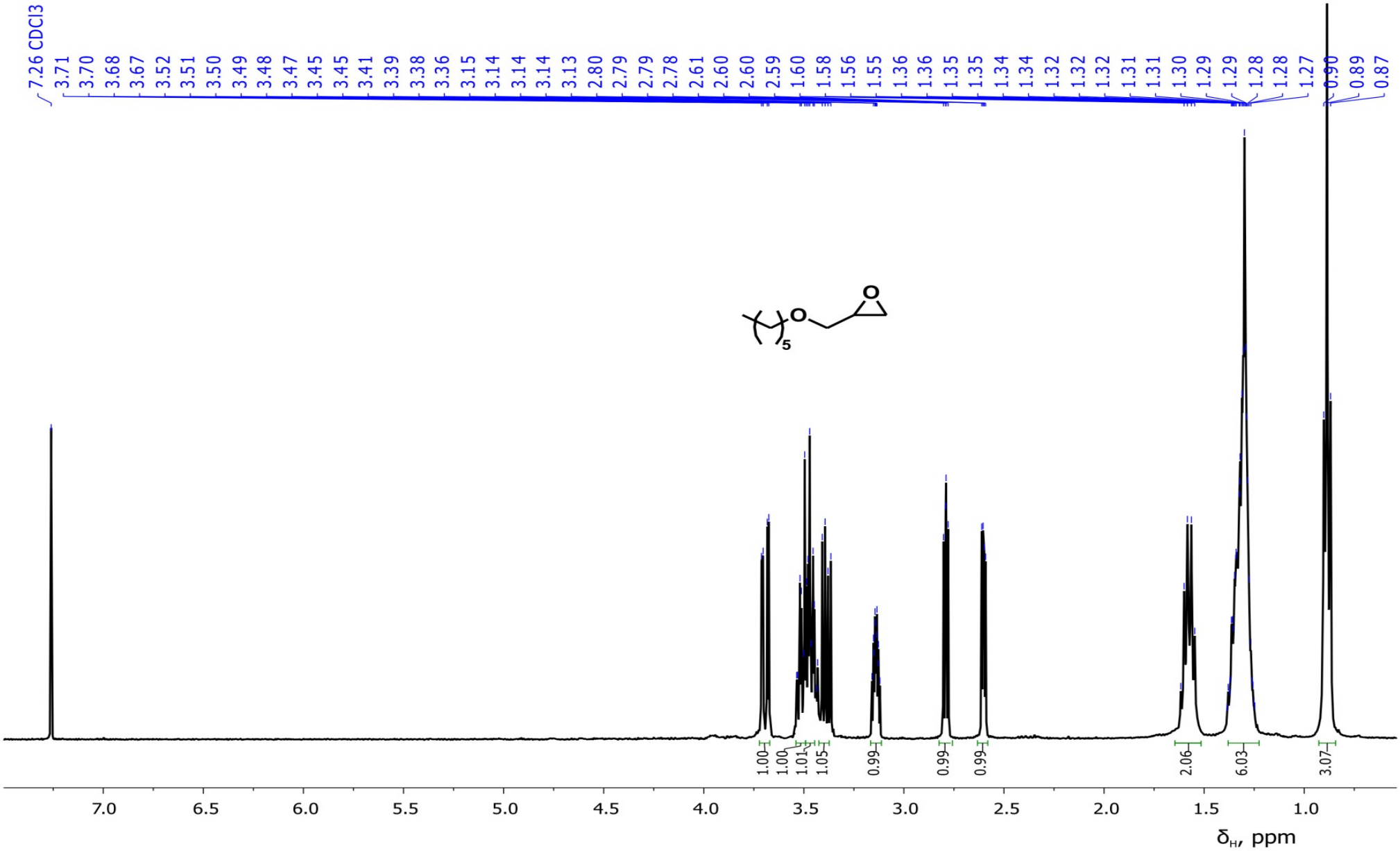

Figure S26. ^{1}H NMR spectrum(400 MHz, $CDCl_3$) of compound **1d**.

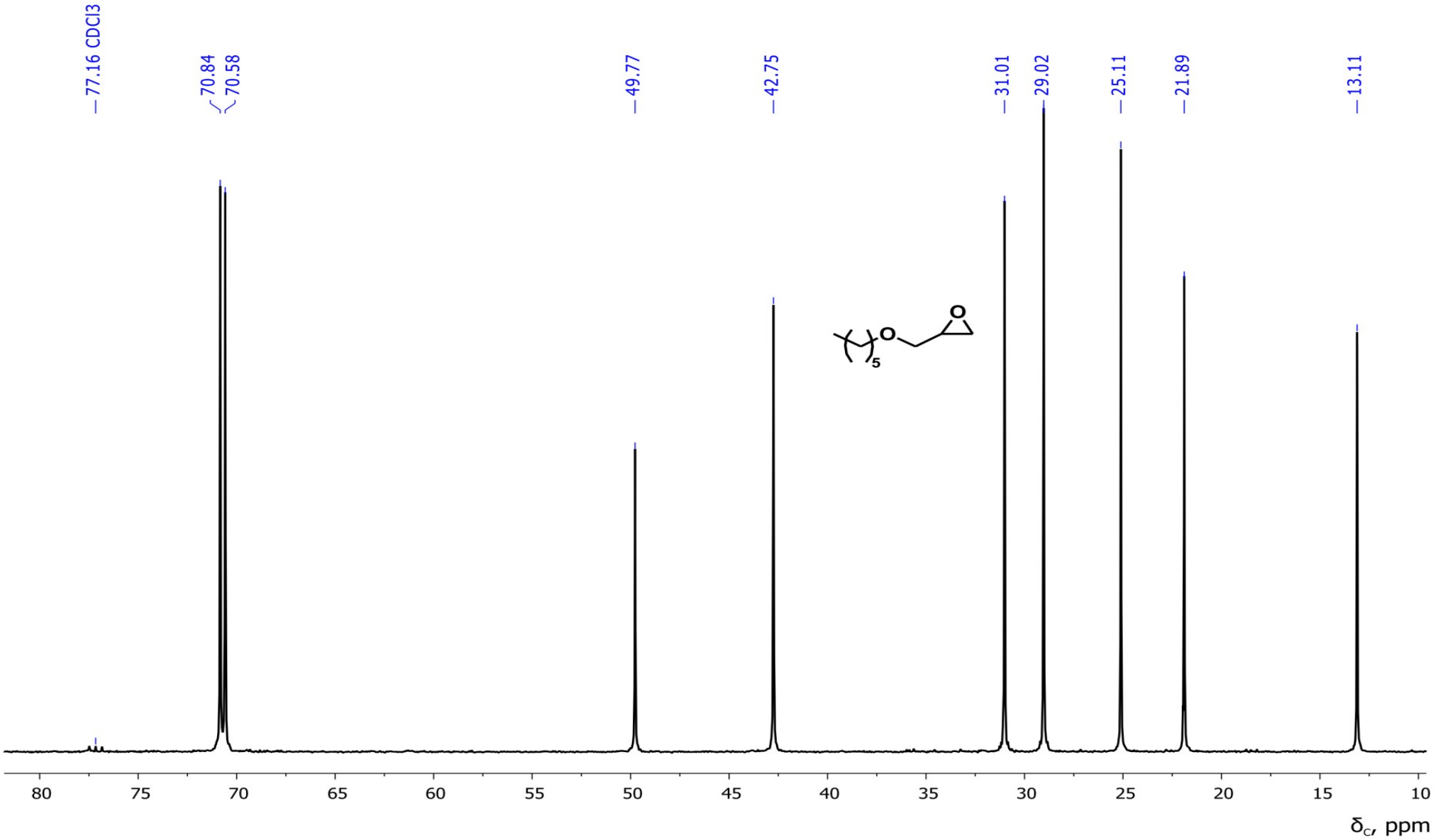

Figure S27. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of compound **1d**.

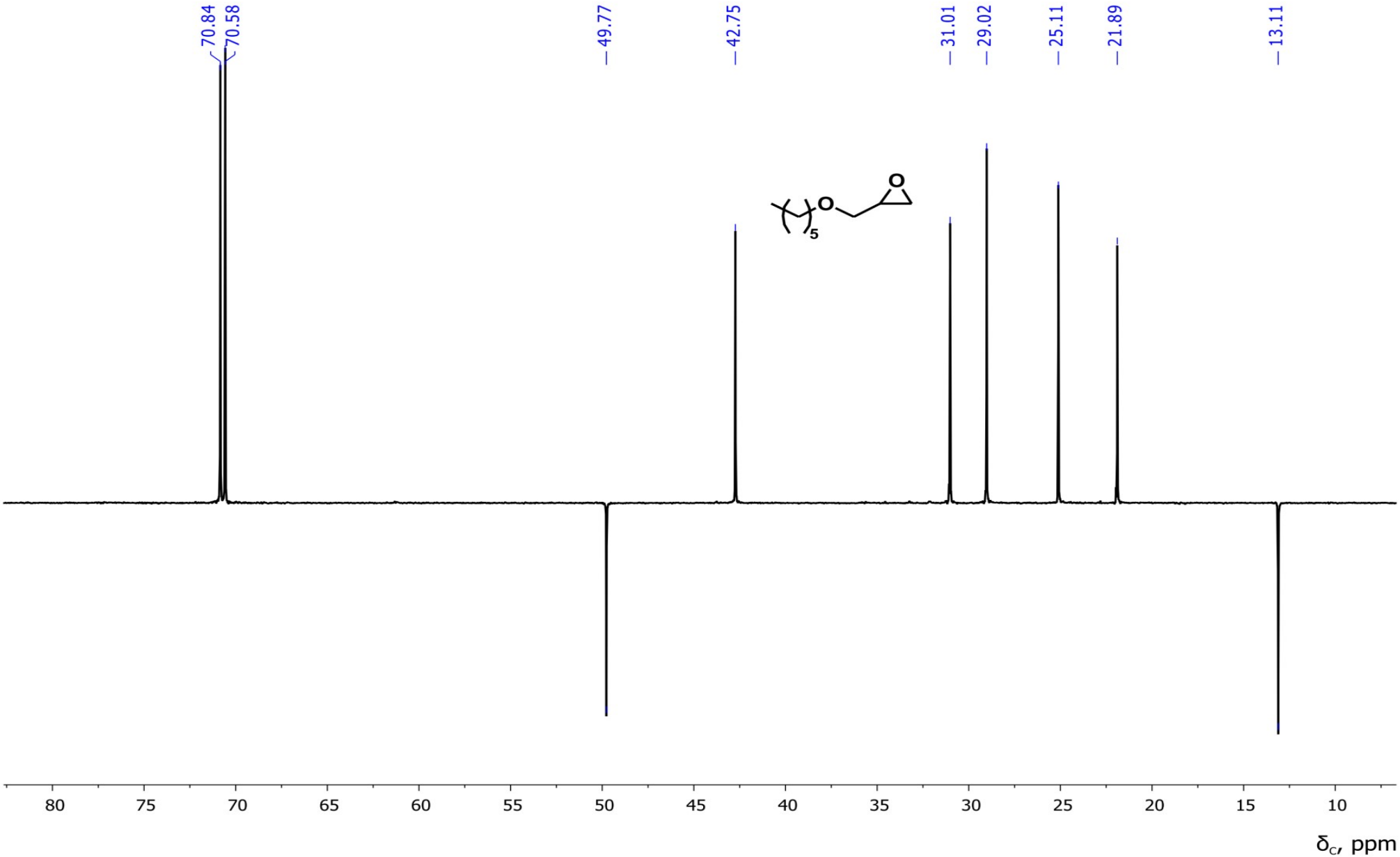

Figure S28. ^{13}C-{^{1}H} APT NMR spectrum (100.6 MHz, $CDCl_3$) of compound **1d**.

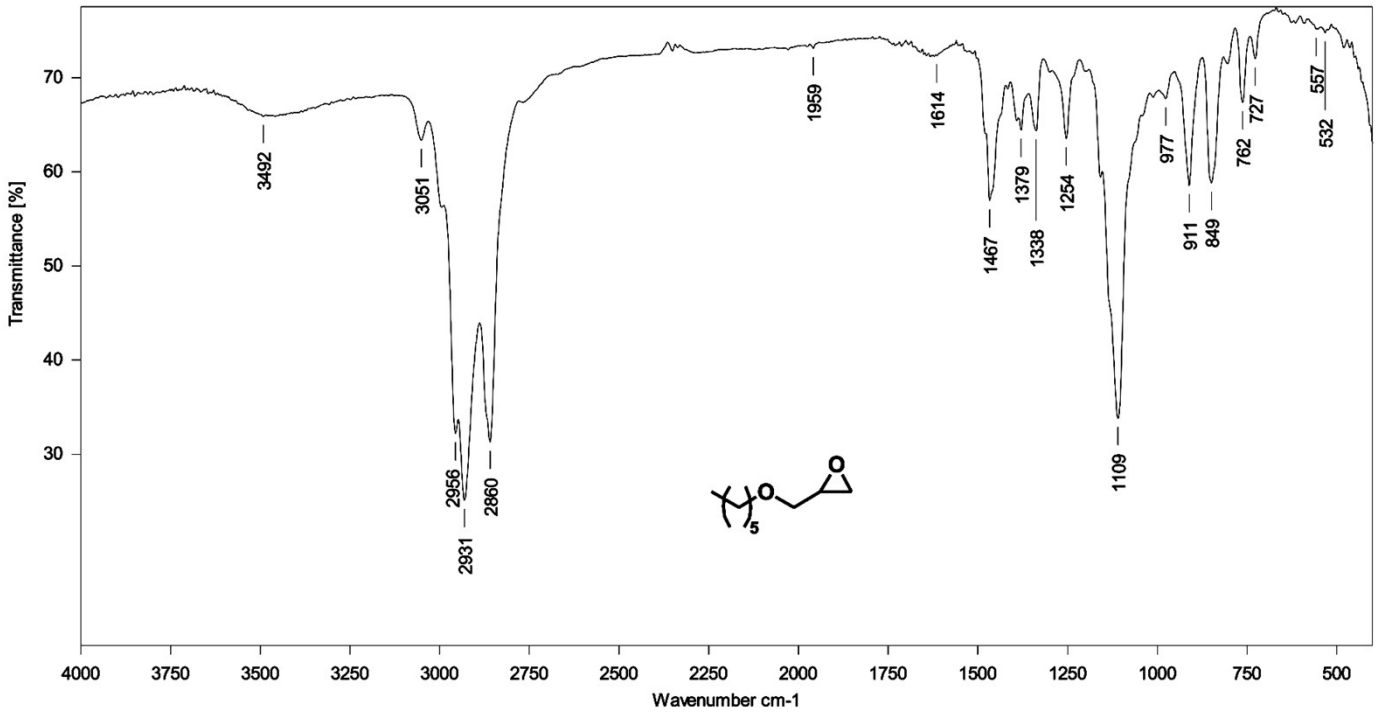

Figure S29. IR spectrum (film) of compound **1d**.

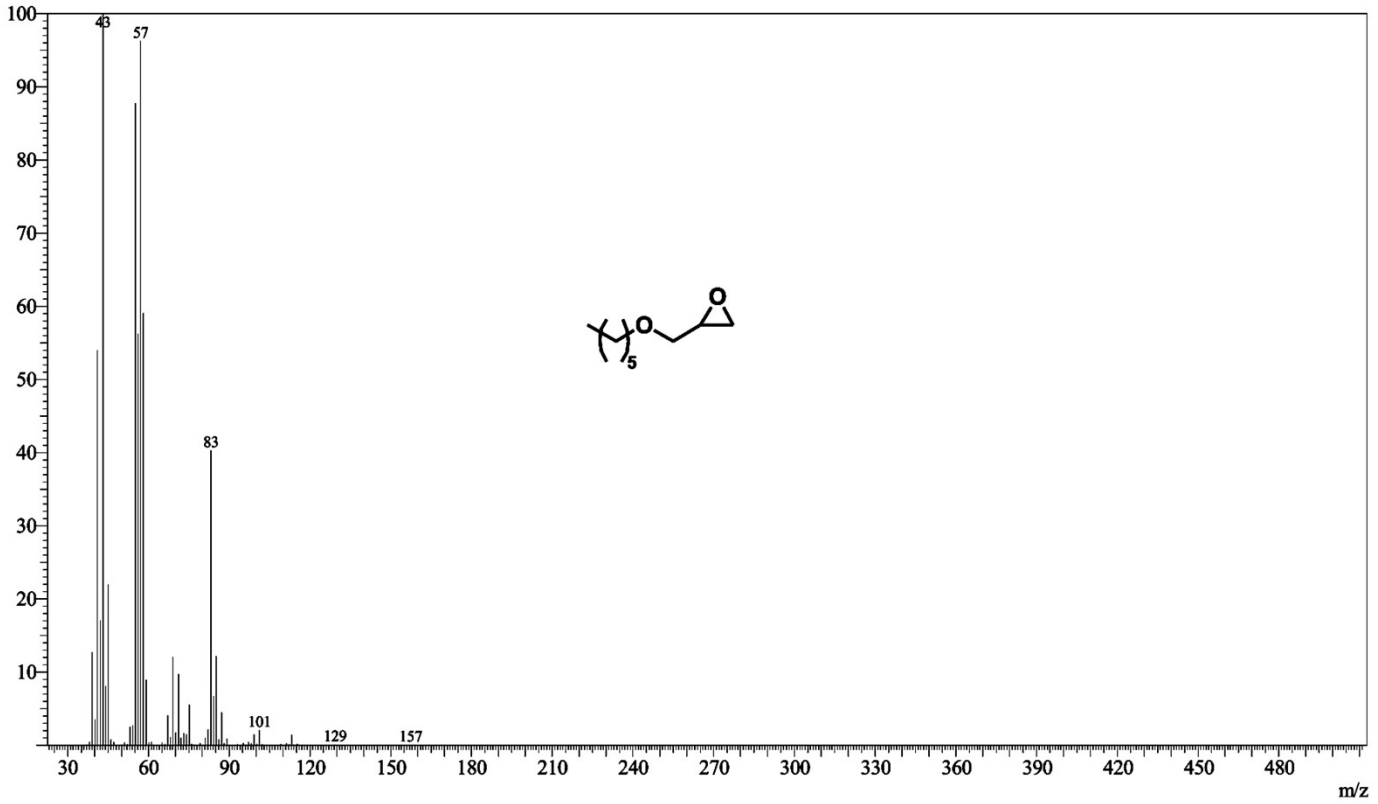

Figure S30. EI-MS spectrum of compound **1d**.

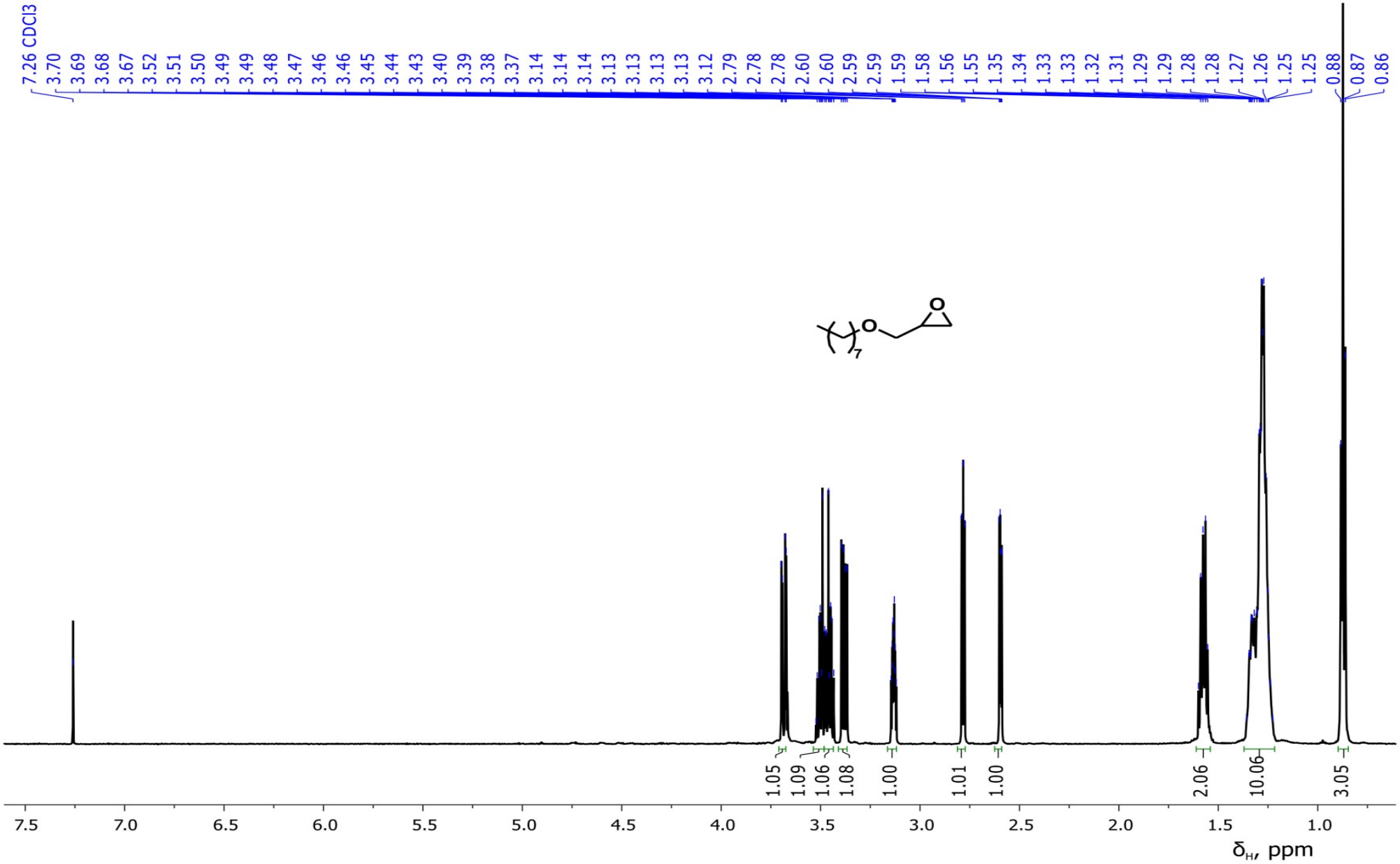

Figure S31. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1e**.

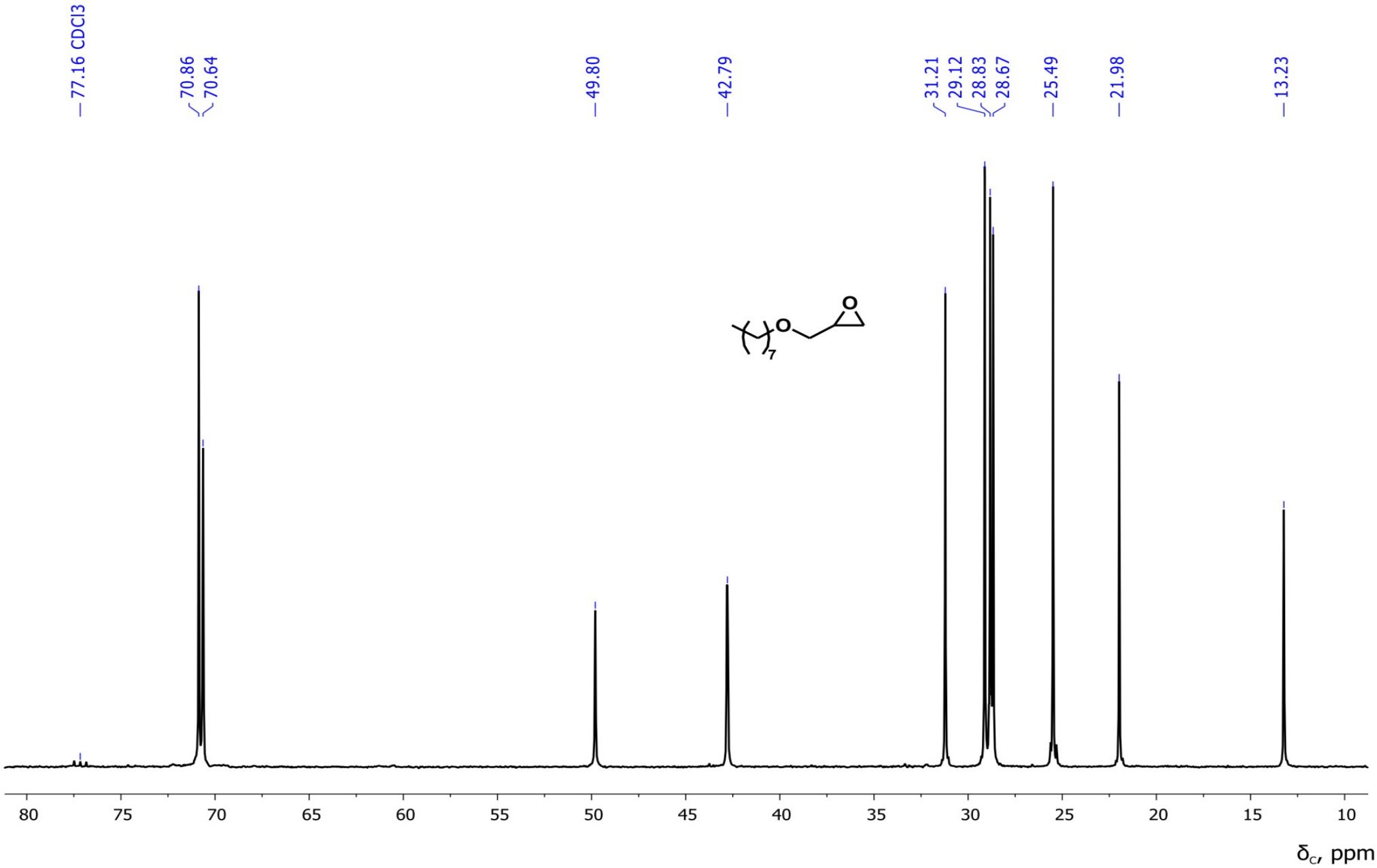

Figure S32. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of compound **1e**.

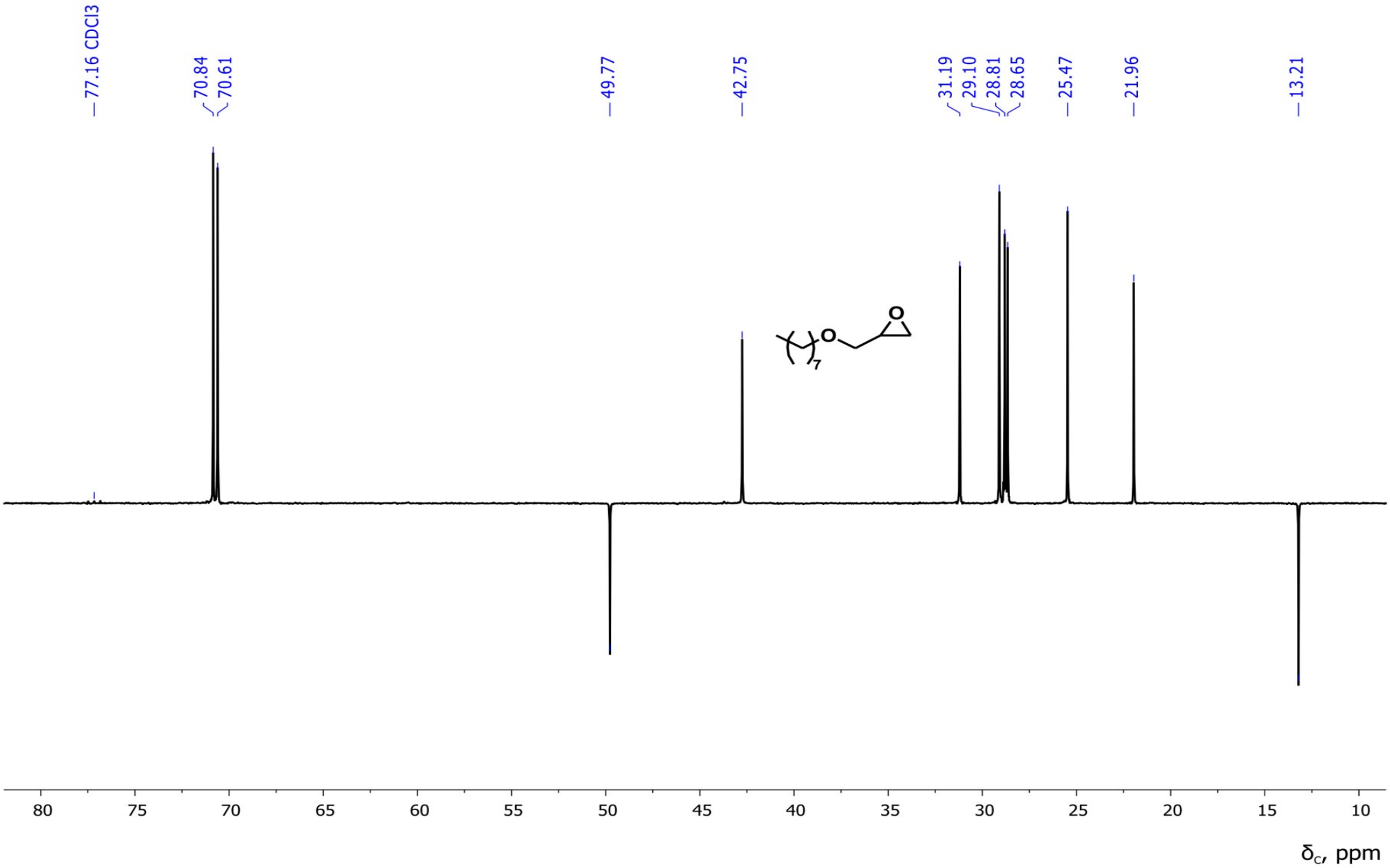

Figure S33. ^{13}C-{^{1}H} APT NMR spectrum (100.6 MHz, $CDCl_3$) of compound **1e**.

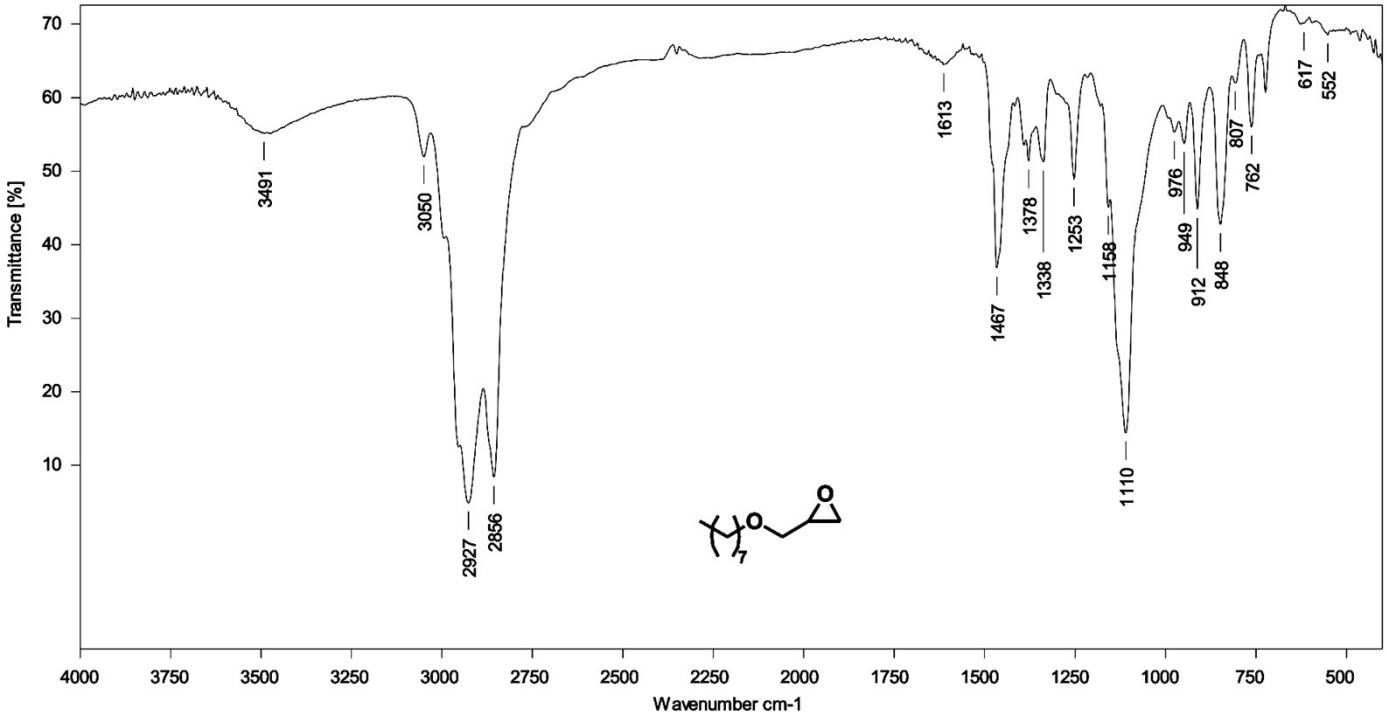

Figure S34. IR spectrum (film) of compound **1e**.

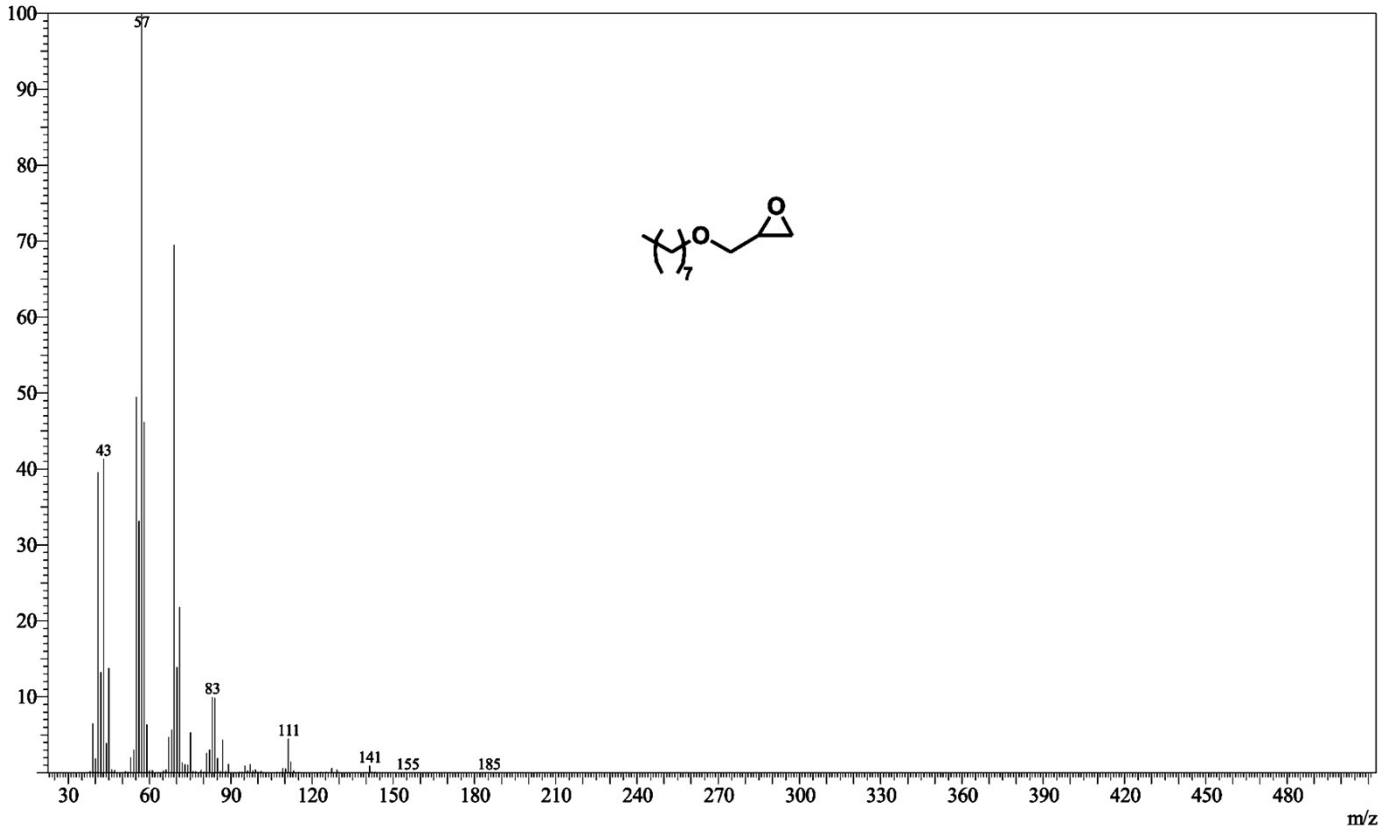

Figure S35. EI-MS spectrum of compound **1e**.

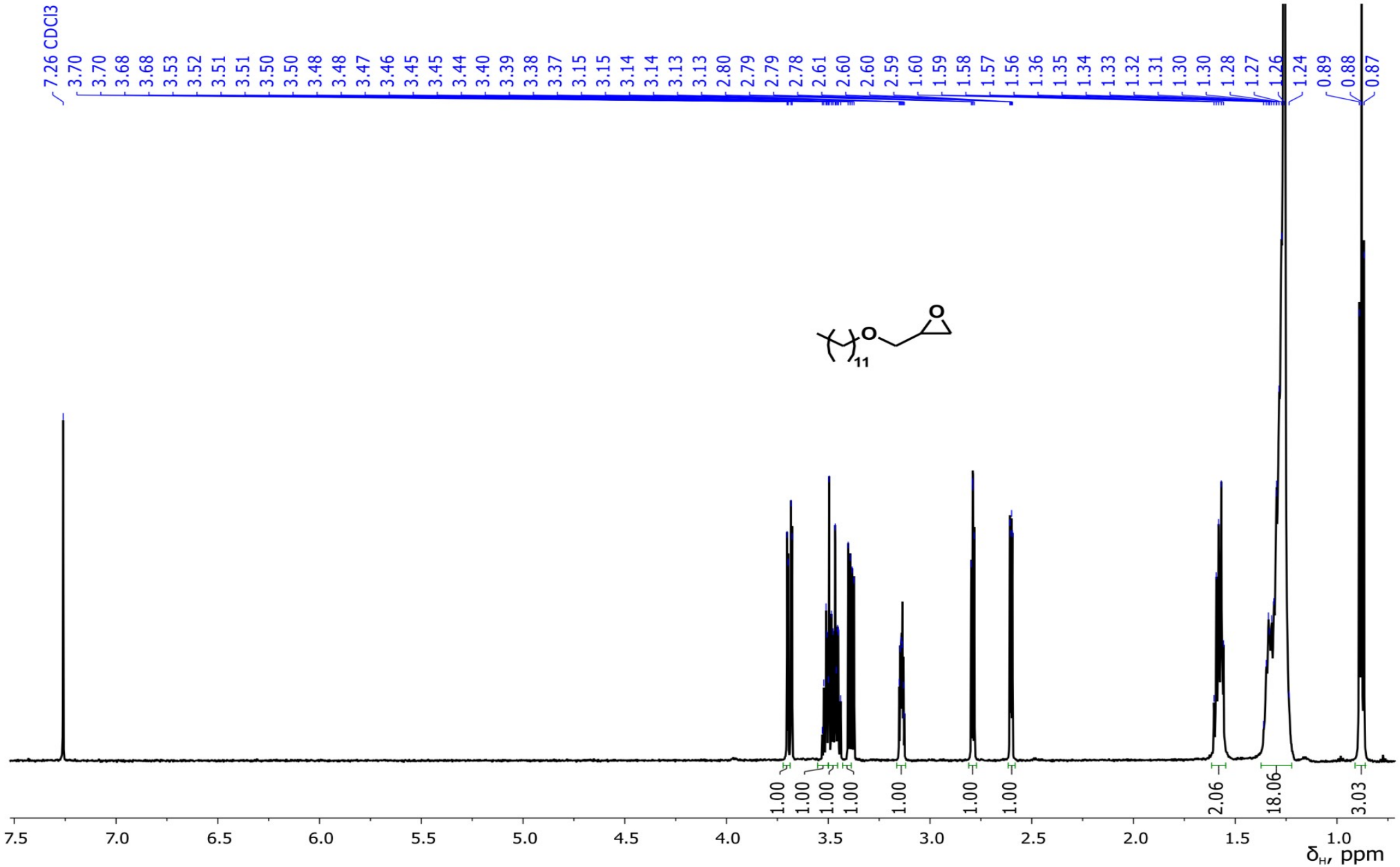

Figure S36. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1g**.

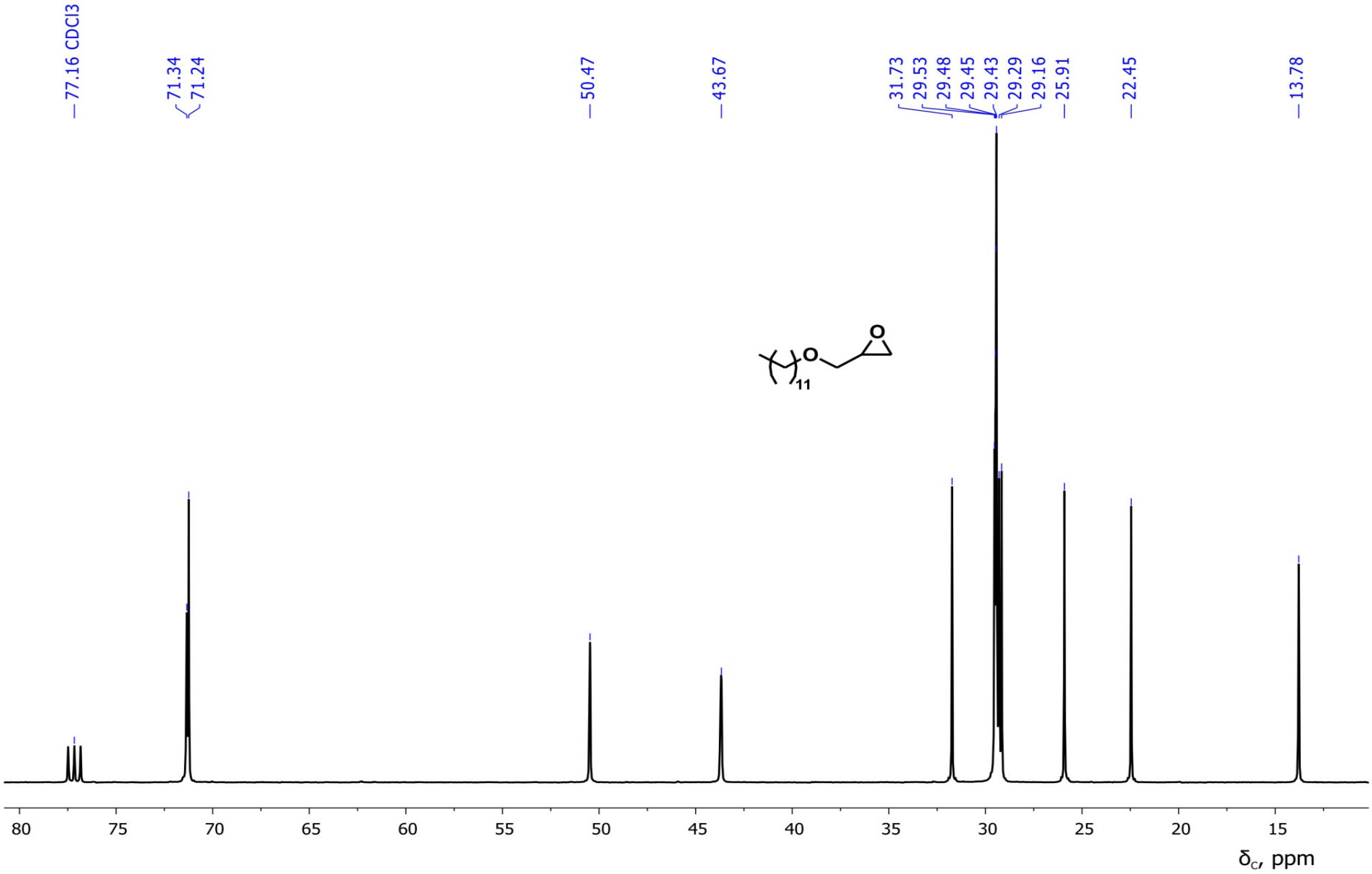

Figure S37. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of compound **1g**.

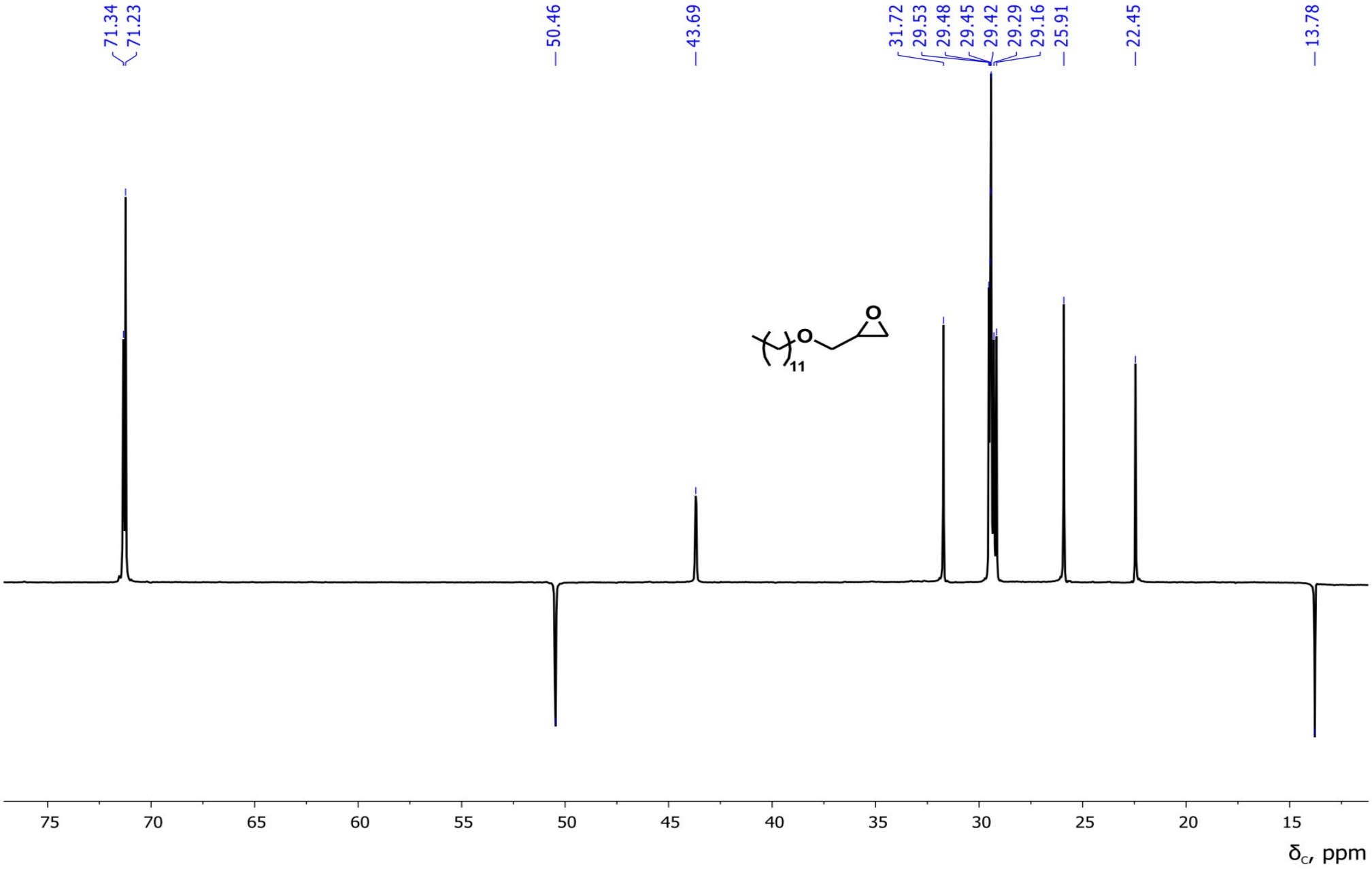

Figure S38. ^{13}C-{^{1}H} APT NMR (100.6 MHz, $CDCl_3$) spectrum of compound **1g**.

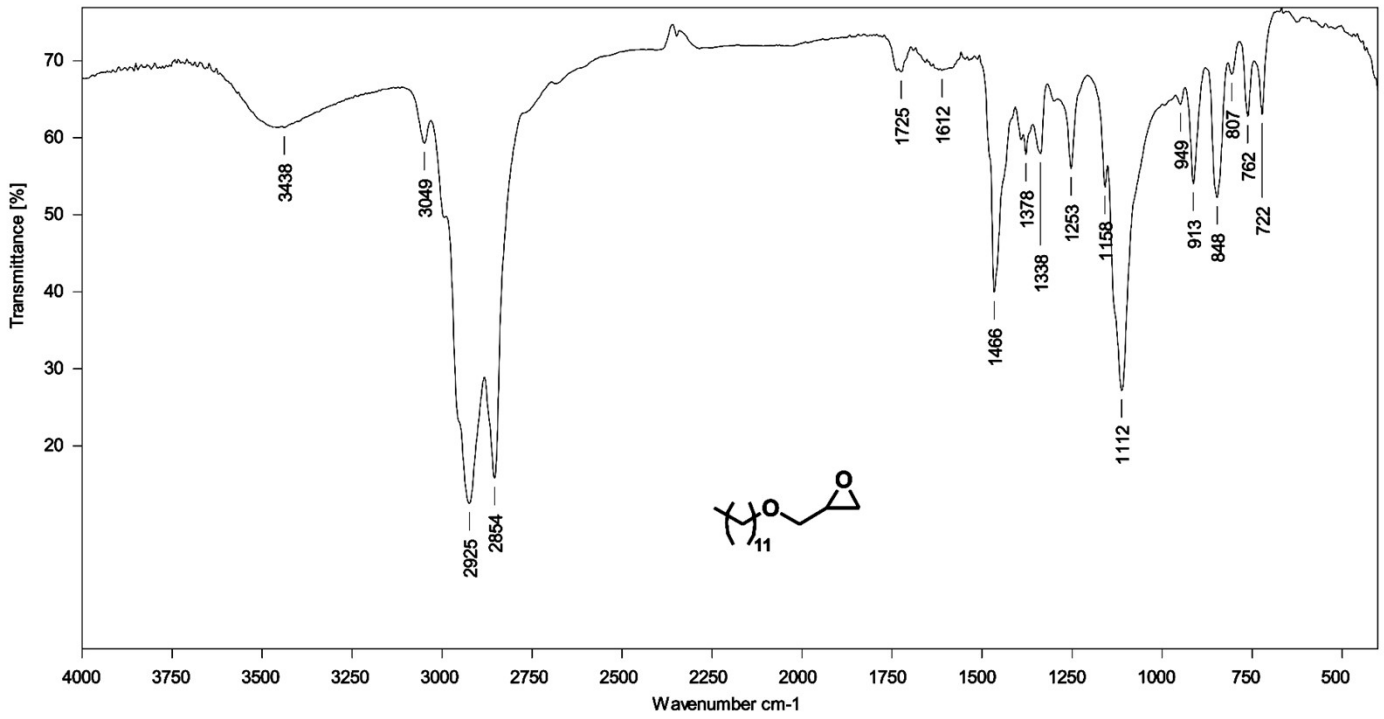

Figure S39. IR spectrum (film) of compound **1g**.

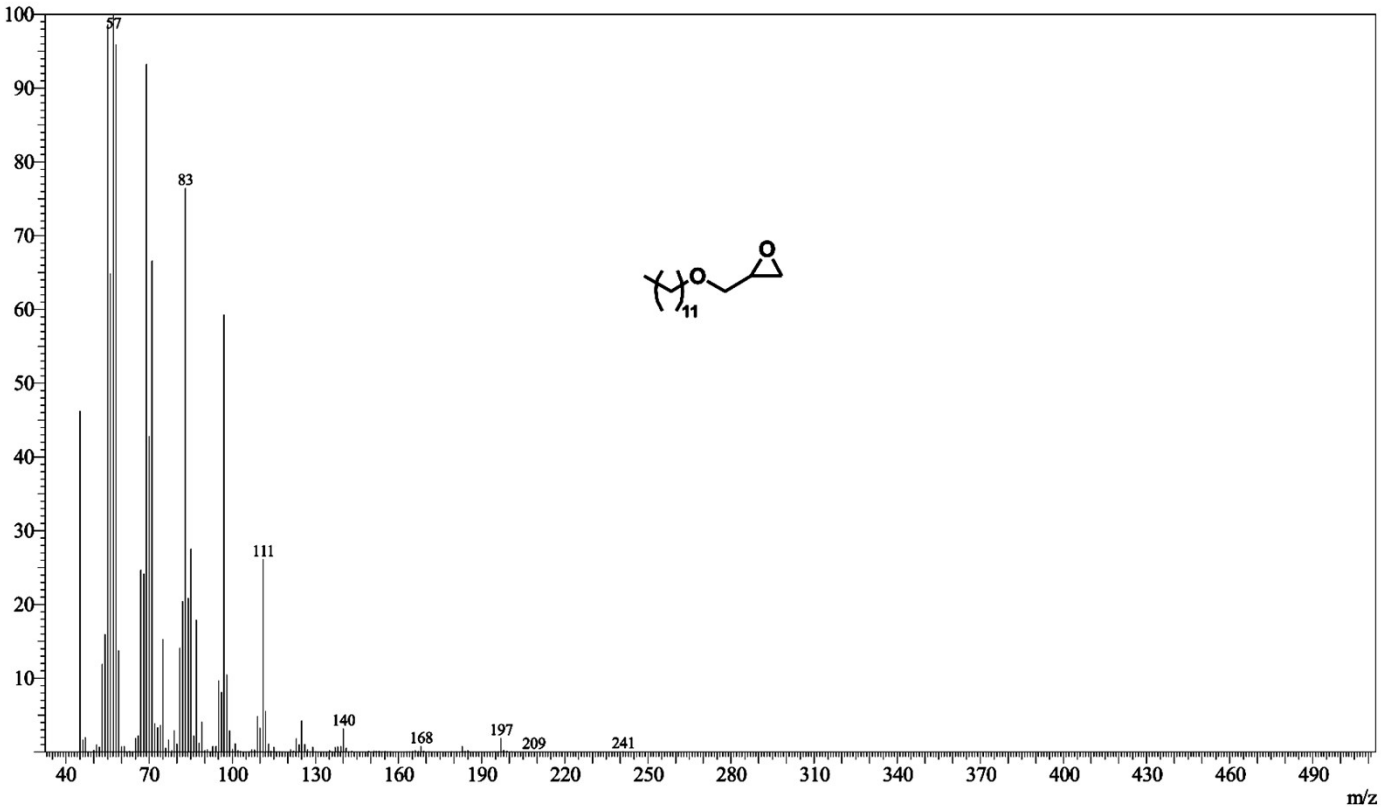

Figure S40. EI-MS spectrum of compound **1g**.

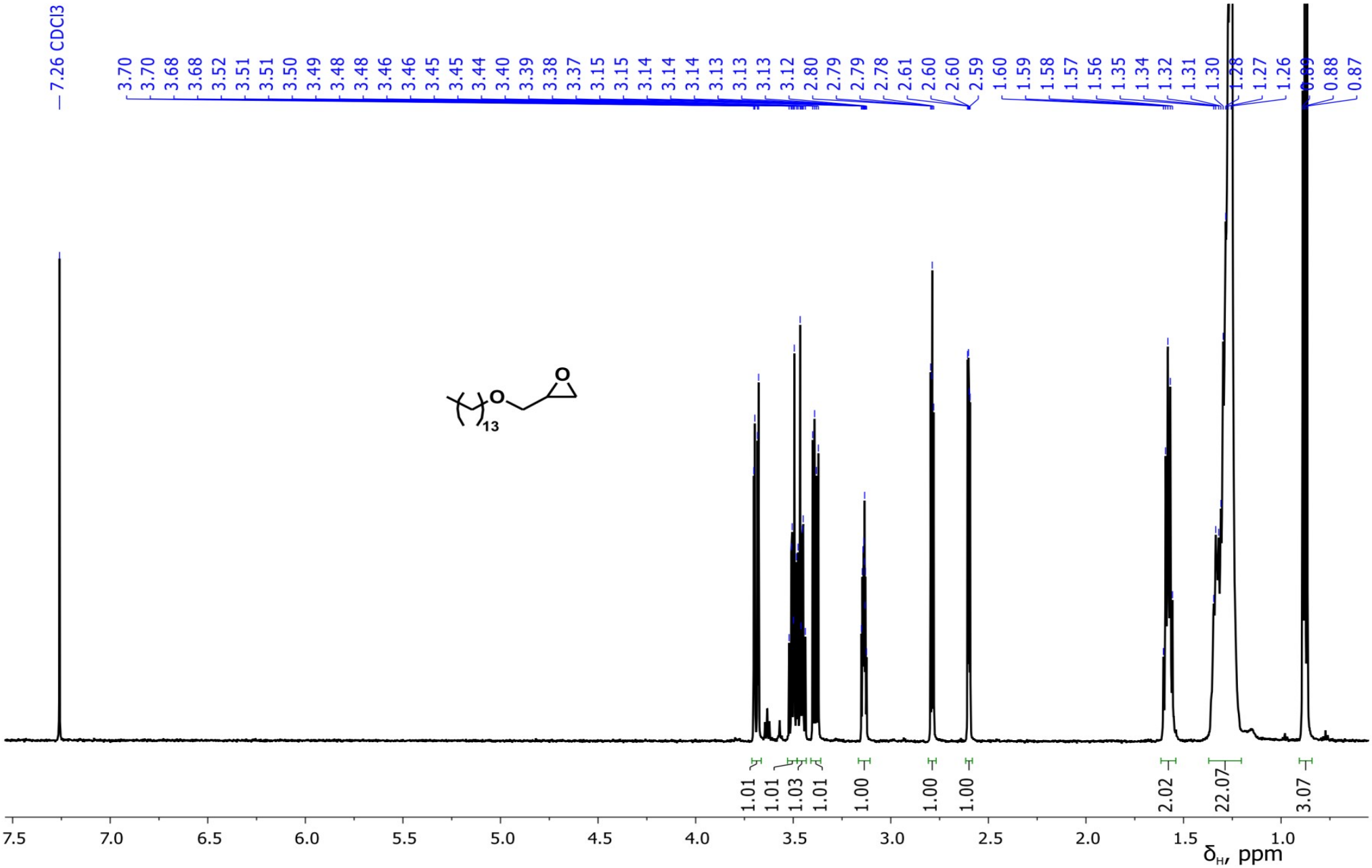

Figure S41. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1h**.

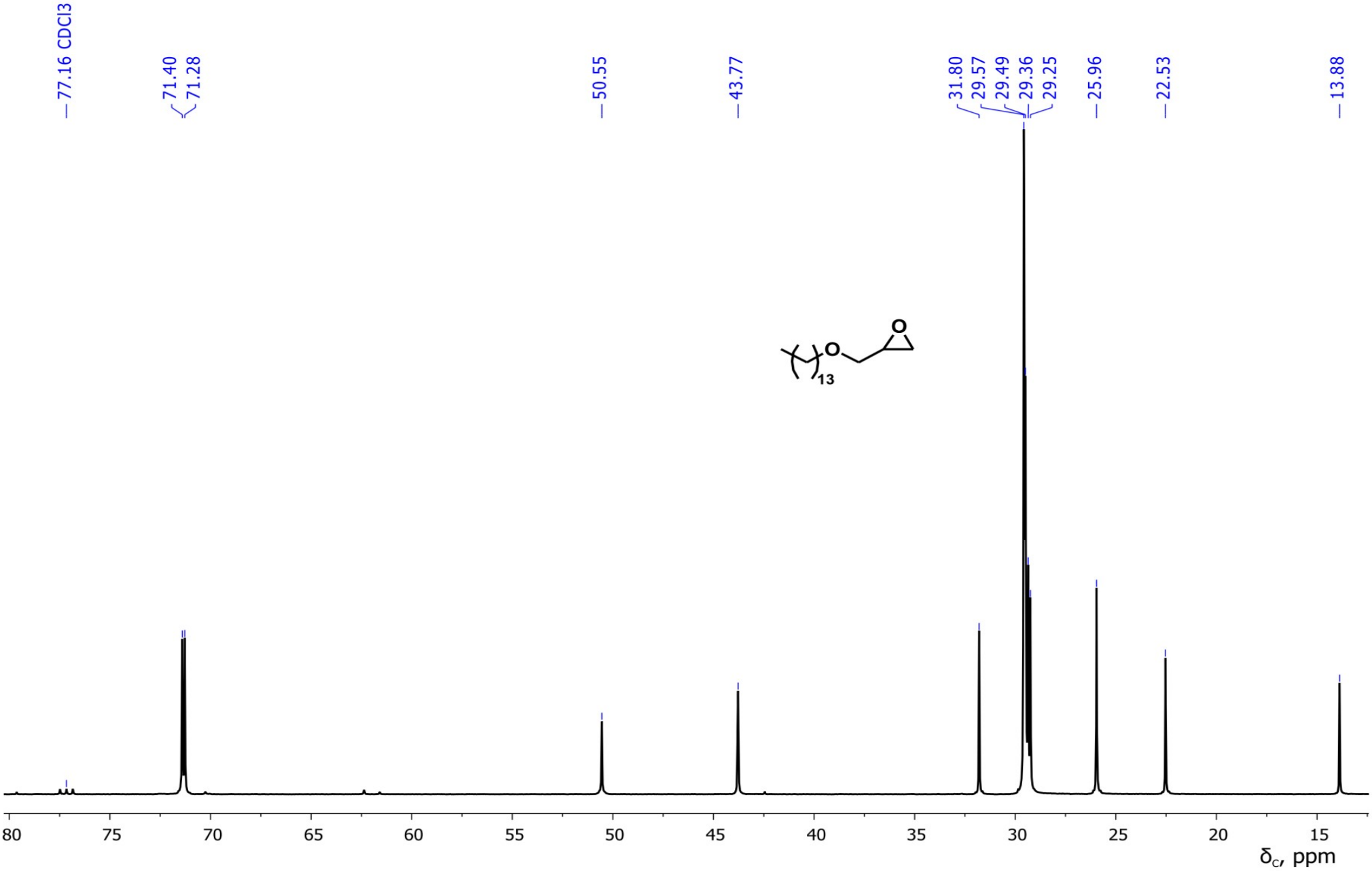

Figure S42. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of compound **1h**.

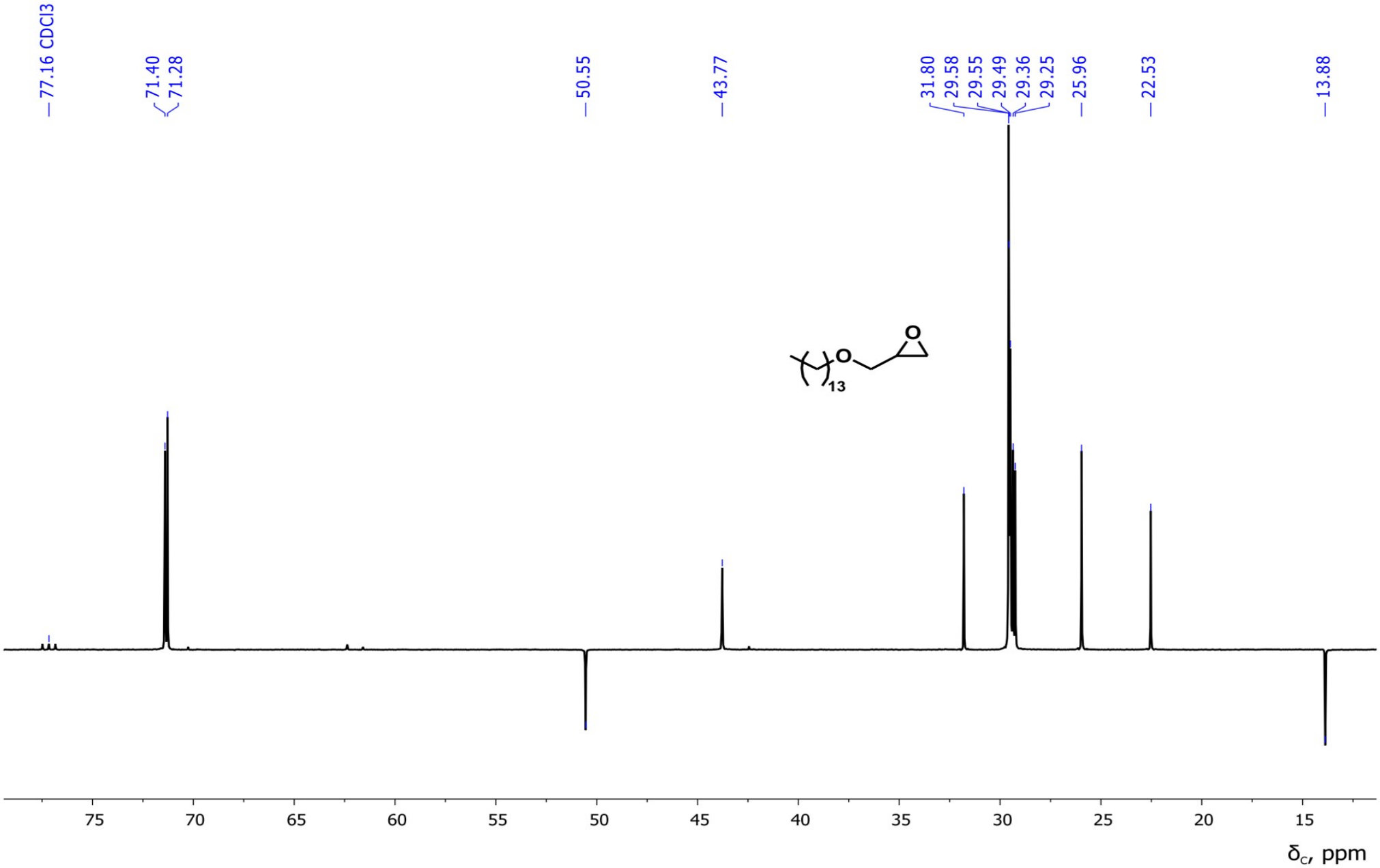

Figure S43. ^{13}C-{^{1}H} APT NMR spectrum (100.6 MHz, $CDCl_3$) of compound **1h**.

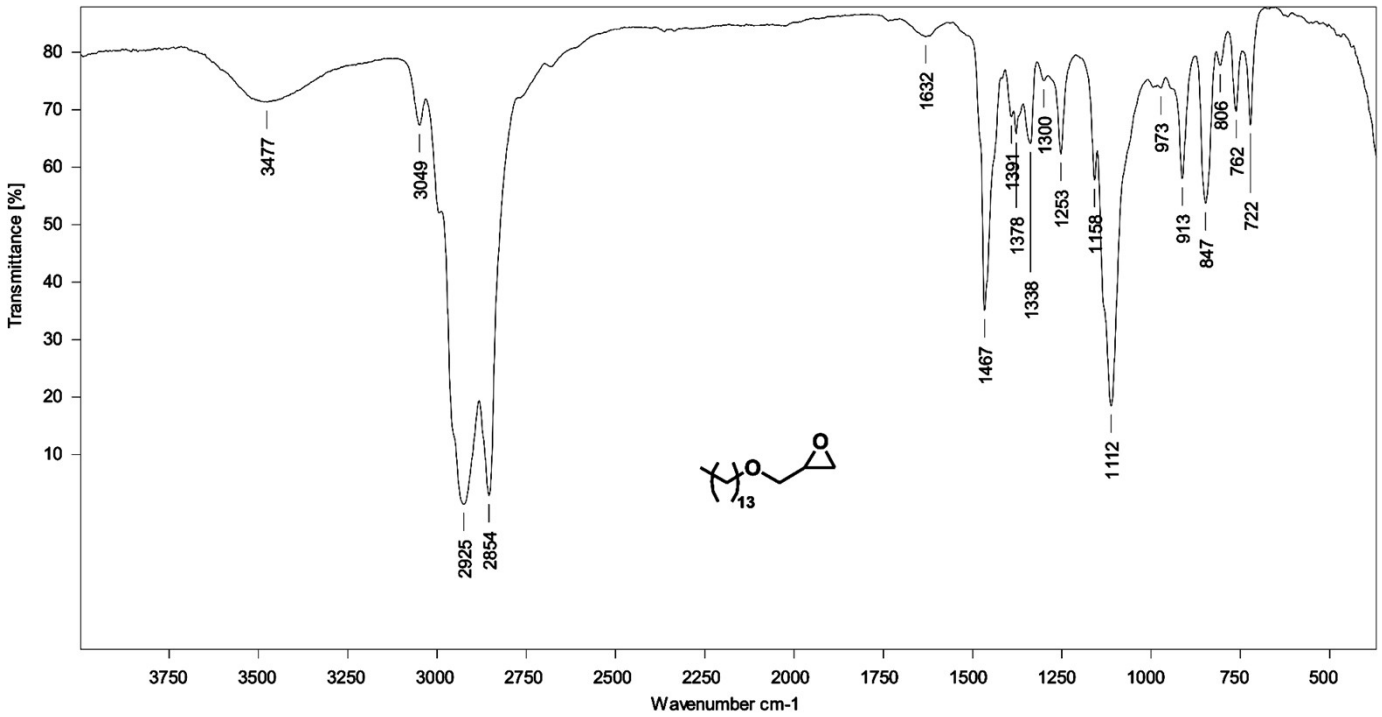

Figure S44. IR spectrum (film) of compound **1h**.

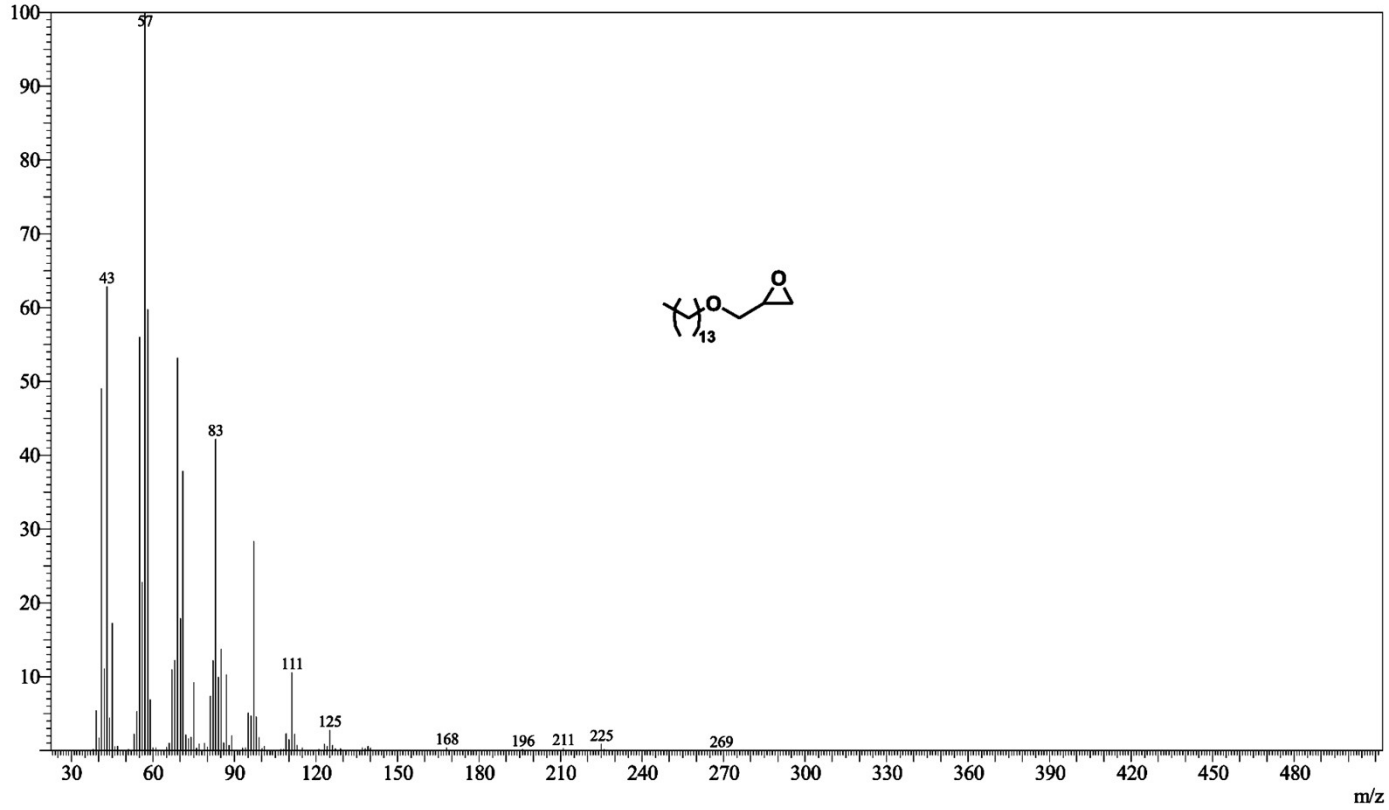

Figure S45. EI-MS spectrum of compound **1h**.

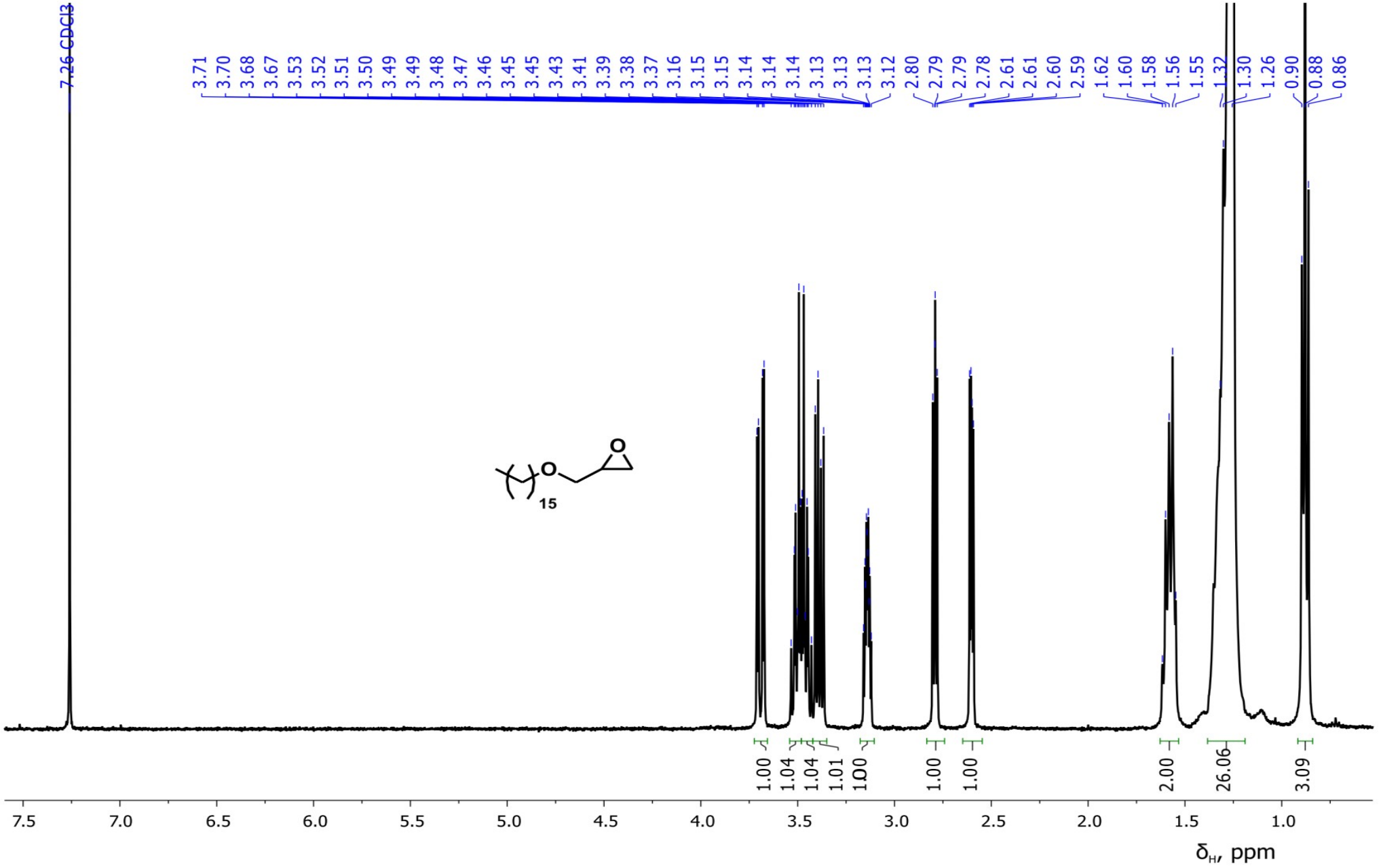

Figure S46. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1i**.

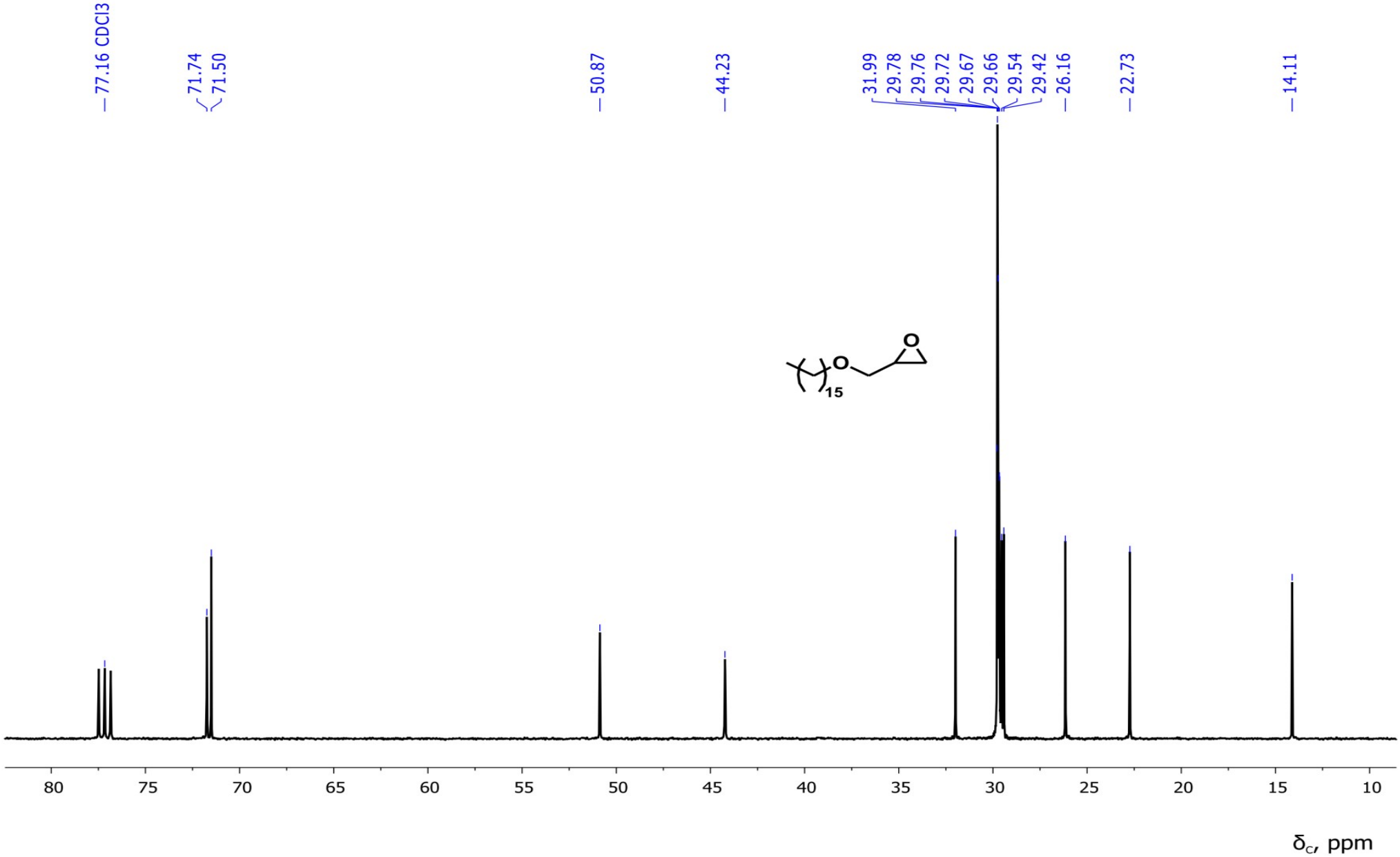

Figure S47. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of compound **1i**.

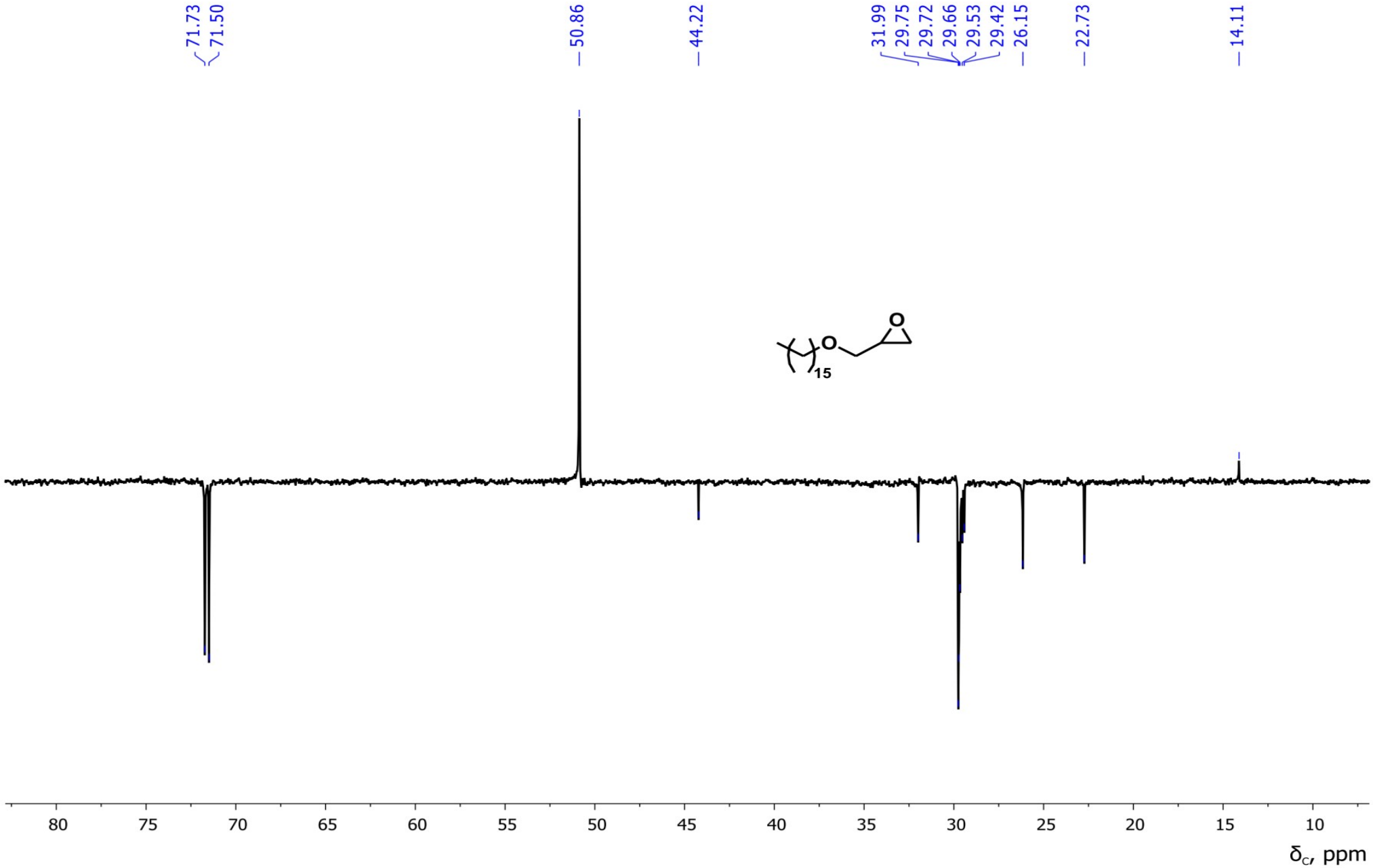

Figure S48. ^{13}C-{^{1}H} APT NMR spectrum (100.6 MHz, $CDCl_3$) of compound **1i**.

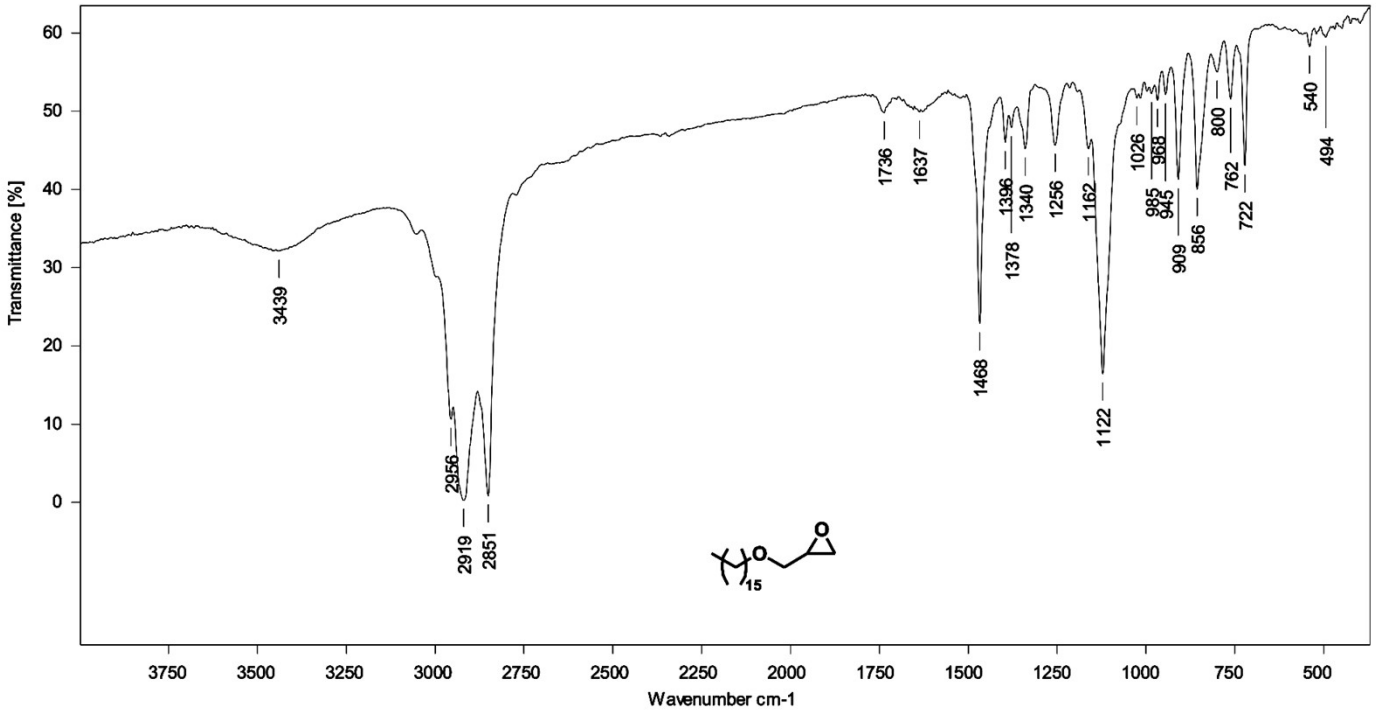

Figure S49. IR spectrum (KBr) of compound **1i**.

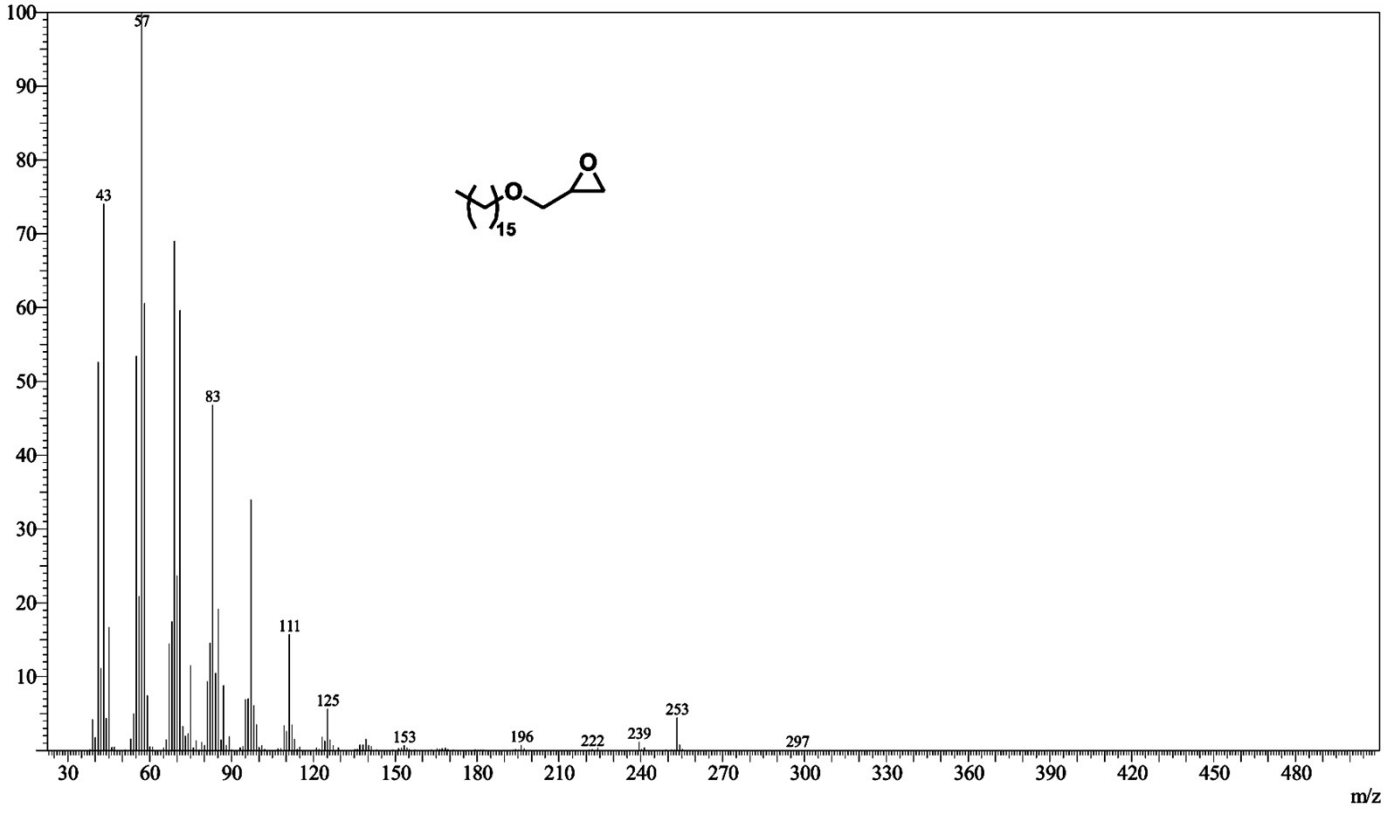

Figure S50. EI-MS spectrum of compound **1i**.

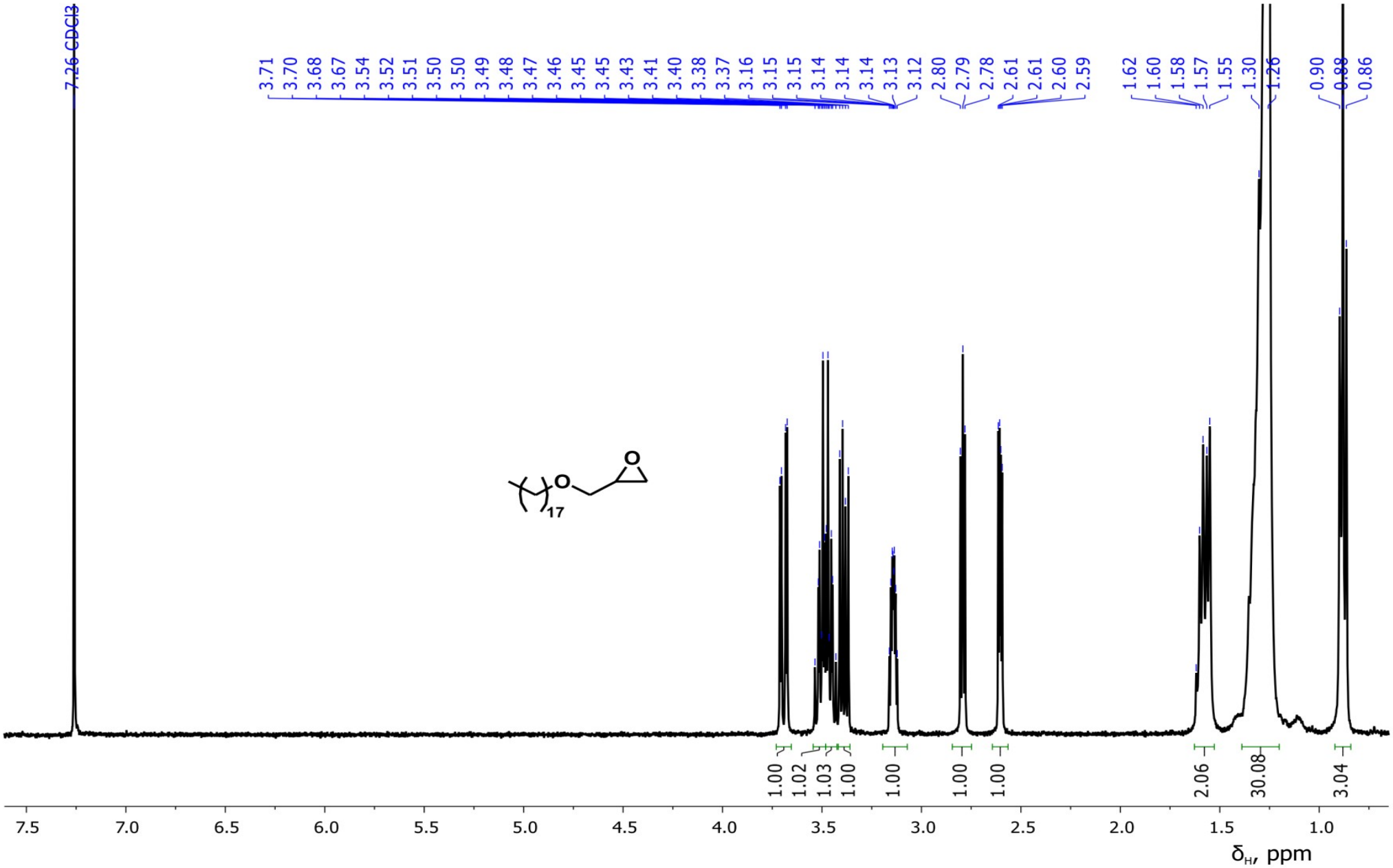

Figure S51. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **1j**.

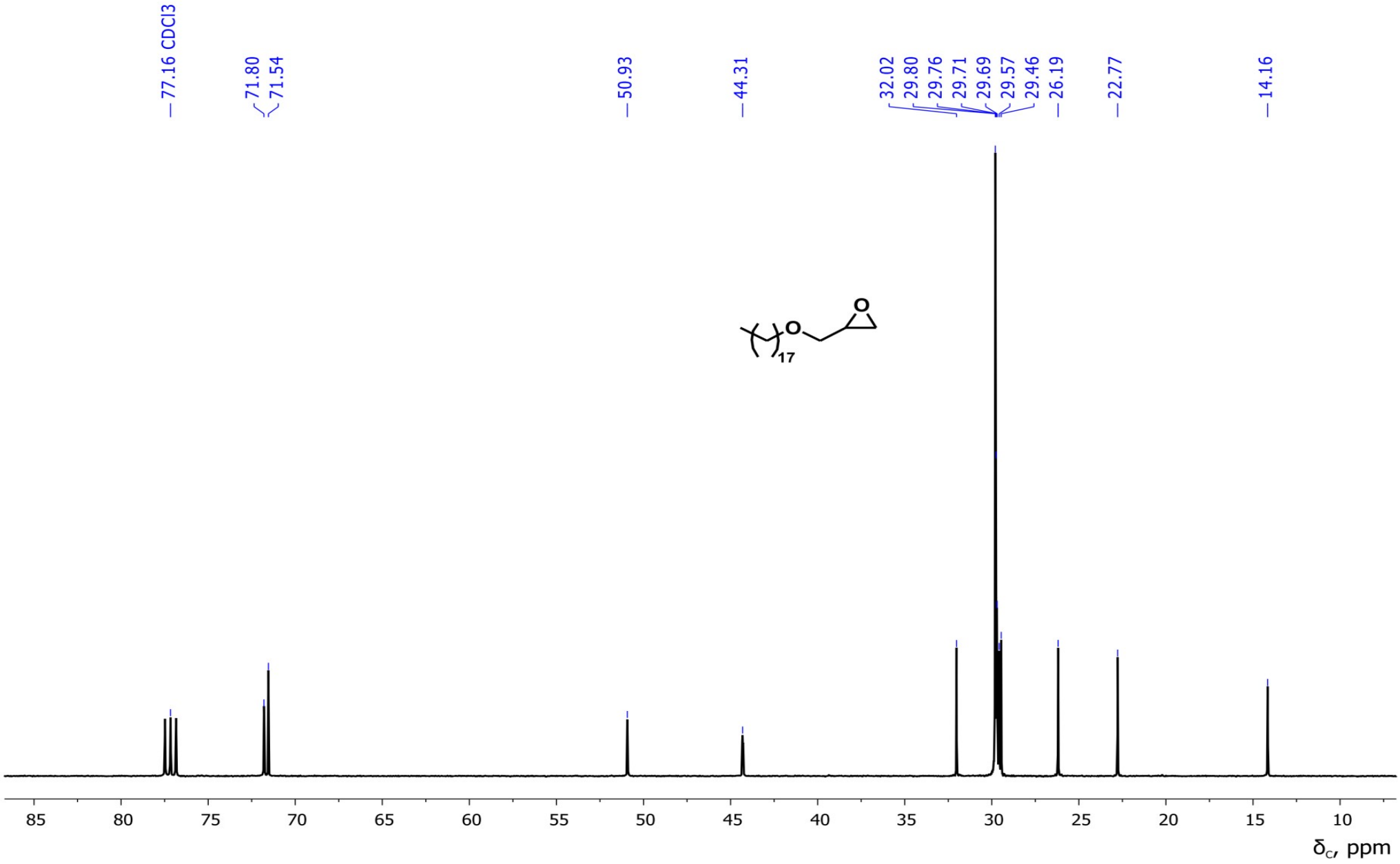

Figure S52. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of compound **1j**.

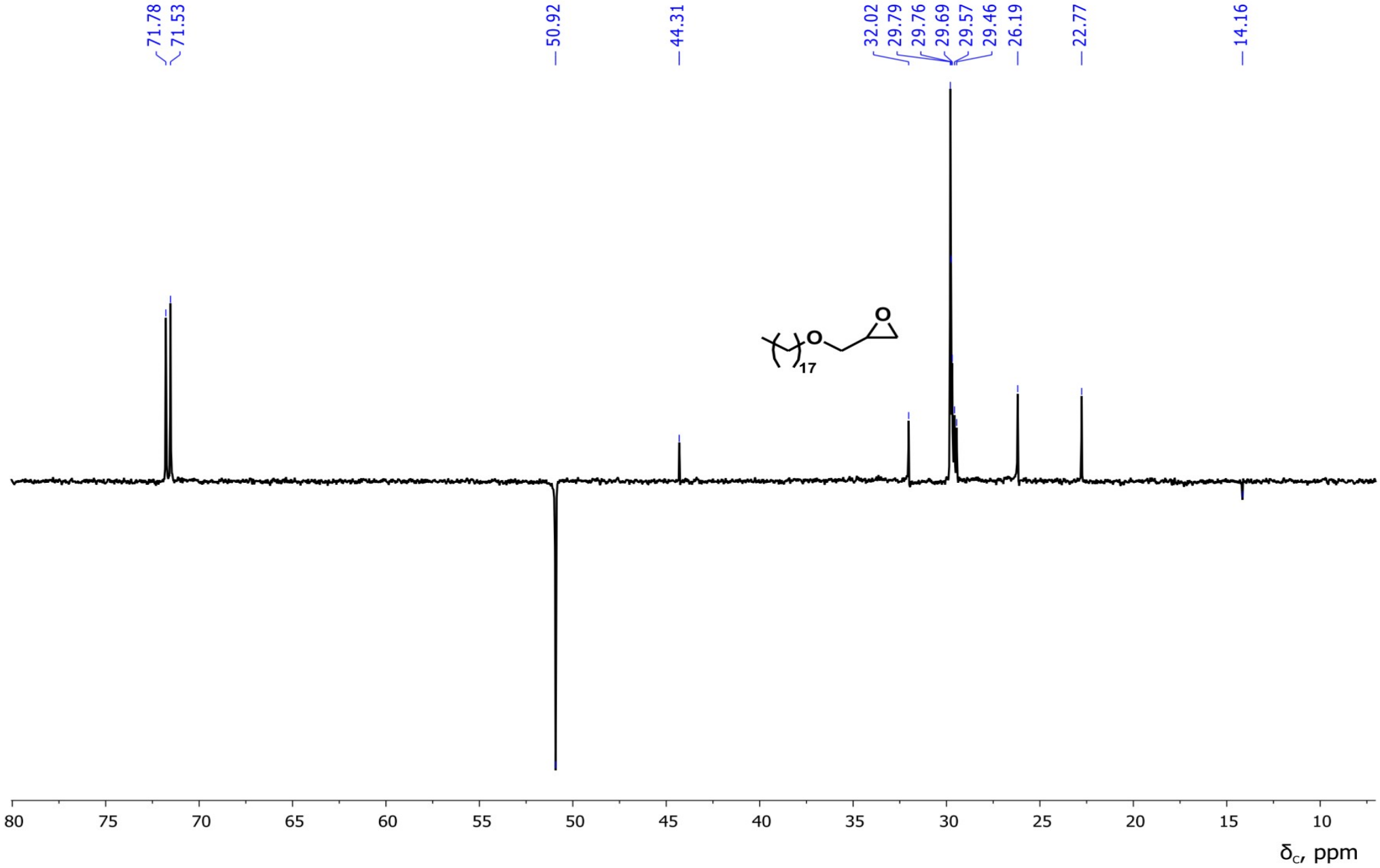

Figure S53. ^{13}C-{^{1}H} APT NMR spectrum (100.6 MHz, $CDCl_3$) of compound **1j**.

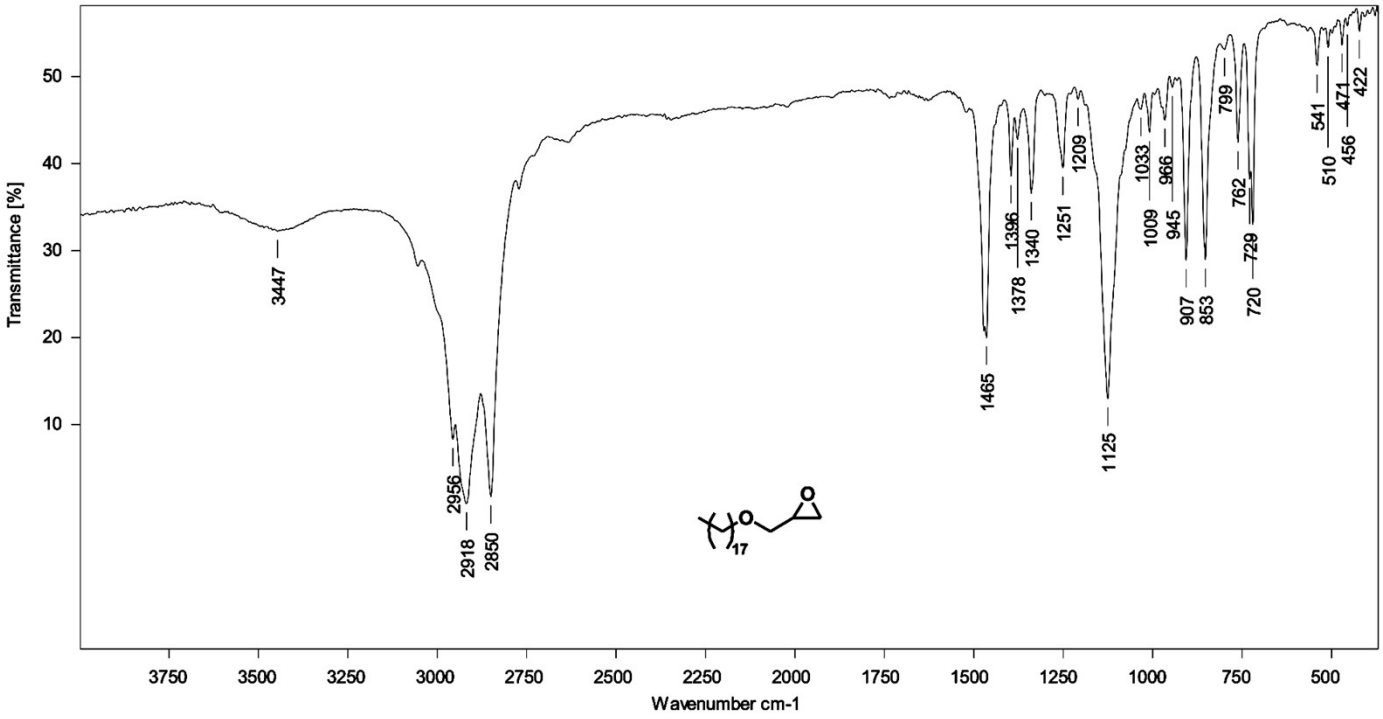

Figure S54. IR spectrum (KBr) of compound **1j**.

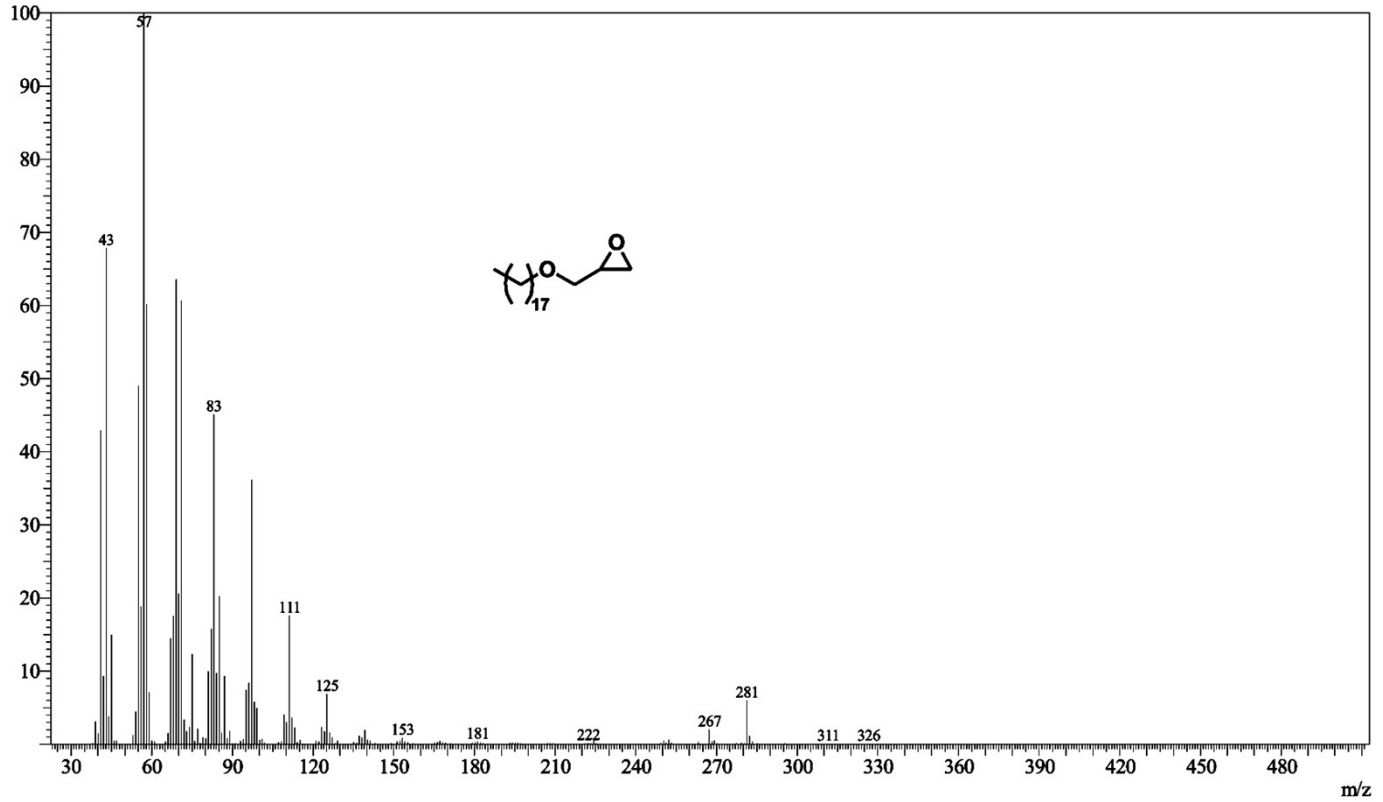

Figure S55. EI-MS spectrum of compound **1j**.

Spectral data of compounds 3.

*(3-Butoxy-2-hydroxypropyl)triphenylphosphonium trifluoromethanesulfonate (**3c**)*. Colorless solid, mp 91-93 °C, yield was 150 mg (81 %); TLC R_f = 0.62 (benzene/acetonitrile = 3/2); IR (KBr): 3413, 3065, 2959, 2930, 2872, 1818, 1773, 1710, 1620, 1589, 1486, 1465, 1440, 1384, 1280, 1258, 1225, 1160, 1112, 1030, 998, 897, 825, 783, 748, 723, 691, 638, 573, 539, 513, 443 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (m, $^3J_{HH}$ = 6.9 Hz, $^5J_{PH}$ = 1.8 Hz, $^4J_{HH}$ = 1.2 Hz, 3H, $H^{Ar}{}_p$), 7.73 (m, $^3J_{PH}$ = 12.6 Hz, $^3J_{HH}$ = 7.3–7.4 Hz, 6H, $H^{Ar}{}_o$), 7.67 (m, $^3J_{HH}$ = 7.3 Hz, $^4J_{PH}$ = 4.0 Hz, 6H, $H^{Ar}{}_m$), 4.13 (s, 1H, H^2), 3.64 (m, 3H, $H^1{}_B$ overlapped with H^3), 3.47 (m, 3H, $H^1{}_A$ overlapped with $H^{1'}$), 2.78 (br. s, 1H, OH), 1.52 (m, $^3J_{HH}$ = 7.5, 2H, $H^{2'}$), 1.32 (m, $^3J_{HH}$ = 7.5, 2H, $H^{3'}$), 0.90 (t, $^3J_{HH}$ = 7.4 Hz, 3H, $H^{4'}$); ^{13}C-{^1H} NMR (100.6 MHz, $CDCl_3$): δ_C = 135.03 (d, $^4J_{PC}$ = 2.5 Hz, $C^{Ar}{}_p$), 133.97 (d, $^2J_{PC}$ = 10.1 Hz, $C^{Ar}{}_o$), 130.37 (d, $^3J_{PC}$ = 12.7 Hz, $C^{Ar}{}_m$), 120.40 (q, $^1J_{FC}$ = 320.0 Hz, CF_3), 118.95 (d, $^1J_{PC}$ = 87.1 Hz, $C^{Ar}{}_i$), 73.96 (d, $^3J_{PC}$ = 15.1 Hz, C^3), 71.54 (s, $C^{1'}$), 65.56 (d, $^2J_{PC}$ = 5.6 Hz, C^2), 31.73 (s, $C^{2'}$), 28.50 (d, $^1J_{PC}$ = 54.4 Hz, C^1), 19.36 (s, $C^{3'}$), 14.01 (s, $C^{4'}$); ^{31}P-{^1H} NMR (162MHz, $CDCl_3$): δ_P = 24.3 (s); MALDI-MS, *m/z* 393.0 $[M - CF_3SO_3]^+$. Calculated for $C_{26}H_{32}O_2P^+$: 393.2; Calculated for $C_{26}H_{30}F_3O_5PS$: C, 57.56; H, 5.57; Found: C, 57.28; H, 5.81.

*(3-(Hexyloxy)-2-hydroxypropyl)triphenylphosphonium trifluoromethanesulfonate (**3d**)*. Colorless solid, mp 84-85 °C, yield was 143 mg (73 %); TLC R_f = 0.62 (benzene/acetonitrile = 3/2); IR (KBr): 3406, 3064, 3031, 2930, 2860, 2694, 2588, 2306, 2214, 1979, 1913, 1825, 1782, 1723, 1589, 1538, 1486, 1466, 1440, 1395, 1379, 1338, 1255, 1225, 1159, 1112, 1031, 998, 929, 882, 824, 783, 748, 722, 691, 638, 573, 536, 514, 445, 409 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.78 (m, $^3J_{HH}$ = 7.3 Hz, 3H, $H^{Ar}{}_p$), 7.72 (m, $^3J_{PH}$ = 12.8 Hz, $^3J_{HH}$ = 7.8 Hz, 6H, $H^{Ar}{}_o$), 7.66 (m, $^3J_{HH}$ = 7.8 Hz, $^4J_{PH}$ = 3.5 Hz, 6H, $H^{Ar}{}_m$), 4.11 (br. m, 1H, H^2), 3.64 (m, 3H, $H^1{}_B$ overlapped with H^3), 3.45 (m, 3H, $H^1{}_A$ overlapped with $H^{1'}$), 2.81 (br. s, 1H, OH), 1.52 (m, $^3J_{HH}$ = 7.0 Hz, 2H, $H^{2'}$), 1.18-1.36 (m, 6H, $H^{3'-5'}$), 0.86 (t, $^3J_{HH}$ = 6.8 Hz, 3H, $H^{6'}$); ^{13}C-{^1H} NMR (100.6 MHz, $CDCl_3$): δ_C = 134.81 (d, $^4J_{PC}$ = 2.5 Hz, $C^{Ar}{}_p$), 133.59 (d, $^2J_{PC}$ = 10.2 Hz, $C^{Ar}{}_o$), 130.11 (d, $^3J_{PC}$ = 12.8 Hz, $C^{Ar}{}_m$), 120.40 (q, $^1J_{FC}$ = 320.0 Hz, CF_3), 118.53 (d, $^1J_{PC}$ = 87.1 Hz, $C^{Ar}{}_i$), 73.74 (d, $^3J_{PC}$ = 14.6 Hz, C^3), 71.49 (s, $C^{1'}$), 65.13 (d, $^2J_{PC}$ = 5.5 Hz, C^2), 31.44 (s, $C^{2'}$), 29.31 (s, $C^{3'}$), 28.04 (d, $^1J_{PC}$ = 54.8 Hz, C^1), 25.57 (s, $C^{4'}$), 22.44 (s, $C^{5'}$), 13.89 (s, $C^{6'}$); ^{31}P-{^1H} NMR (162 MHz, $CDCl_3$): δ_P = 24.6 (s); MALDI-MS, *m/z* 421.1 $[M - CF_3SO_3]^+$. Calculated for $C_{28}H_{36}O_2P^+$: 421.2; Calculated for $C_{28}H_{34}F_3O_5PS$: C, 58.94; H, 6.01; Found: C, 58.63; H, 6.28.

*(2-Hydroxy-3-(octyloxy)propyl)triphenylphosphonium trifluoromethanesulfonate (**3e**)*. Colorless solid, yield was 163 mg (80 %); mp 79-80 °C; TLC R_f = 0.62 (benzene/acetonitrile = 3/2); IR (KBr): 3407, 3064, 2927, 2857, 2307, 2214, 1979, 1913, 1825, 1723, 1614, 1589, 1538, 1486, 1466, 1440, 1395, 1378, 1338, 1257, 1225, 1157, 1112, 1030, 998, 881, 824, 783, 748, 722, 691, 638, 573, 541, 513, 444, 413 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (m, $^3J_{HH}$ = 7.3 Hz, $^5J_{PH}$ = 1.8 Hz, $^4J_{HH}$ = 1.2 Hz, 3H, $H^{Ar}{}_p$), 7.72 (m, $^3J_{PH}$ = 12.6 Hz, $^3J_{HH}$ = 7.8 Hz, 6H, $H^{Ar}{}_o$), 7.67 (m, $^3J_{HH}$ = 7.8 Hz, $^4J_{PH}$ = 4.0 Hz, 6H, $H^{Ar}{}_m$), 4.11 (br. s, 1H, H^2), 3.72-3.56 (m, 3H, $H^1{}_B$ overlapped with H^3), 3.52-3.37 (m, 3H, $H^1{}_A$ overlapped with $H^{1'}$), 1.51 (m, $^3J_{HH}$

= 6.7 Hz, 2H, $H^{2'}$) 1.17-1.34 (m, 10 H, $H^{3'-7'}$), 0.86 (t, $^3J_{HH}$ = 6.7 Hz, 3H, $H^{8'}$); ^{13}C-{^1H} NMR (100.6 MHz, $CDCl_3$): δ_C = 134.94 (d, $^4J_{PC}$ = 3.0 Hz, $C^{Ar}{}_p$), 133.78 (d, $^2J_{PC}$ = 10.1 Hz, $C^{Ar}{}_o$), 130.26 (d, $^3J_{PC}$ = 12.8 Hz, $C^{Ar}{}_m$), 120.58 (κ, $^1J_{FC}$ = 320.2 Hz, CF_3), 118.70 (d, $^1J_{PC}$ = 87.1 Hz, $C^{Ar}{}_i$), 73.80 (d, $^3J_{PC}$ = 14.7 Hz, C^3), 71.68 (s, $C^{1'}$), 65.34 (d, $^2J_{PC}$ = 5.6 Hz, C^2), 31.80 (s, $C^{2'}$), 29.54 (s, $C^{3'}$), 29.41 (s, $C^{4'}$), 29.28 (s, $C^{5'}$), 28.26 (d, $^1J_{PC}$ = 54.8 Hz, C^1), 26.09 (s, $C^{6'}$), 22.65 (s, $C^{7'}$), 14.12 (s, $C^{8'}$); ^{31}P-{^1H} NMR (162MHz, $CDCl_3$): δ_P = 24.3 (s); MALDI-MS, *m/z* 449.3 $[M - CF_3SO_3]^+$. Calculated for: $C_{30}H_{40}O_2P^+$: 449.3; Calculated for: $C_{30}H_{38}F_3O_5PS$: C, 60.19; H, 6.40; Found: C, 59.87; H, 6.65.

*(3-(Decyloxy)-2-hydroxypropyl)triphenylphosphonium trifluoromethanesulfonate (**3f**)*. Colorless solid, mp 78-79 °C, yield was 171 mg (80 %); IR (KBr): C: 3381, 3066, 2927, 2856, 2795, 1486, 1467, 1459, 1440, 1406, 1363, 1287, 1246, 1227, 1162, 1111, 1031, 997, 950, 879, 838, 791, 748, 724, 715, 689, 640, 573, 530, 510, 497, 465 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.75 (m, $^3J_{HH}$ = 7.2 Hz, $^5J_{PH}$ = 2.0 Hz, $^4J_{HH}$ 1.5 Hz, 3H, $H^{Ar}{}_p$), 7.68 (m, $^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.5 Hz, 6H, $H^{Ar}{}_o$), 7.64 (m, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ =7.2 Hz, $^4J_{PH}$ = 3.6 Hz, 6H, $H^{Ar}{}_m$), 4.08 (m, 1H, H^2), 3.98 (br. s, 1H, OH), 3.54-3.55 (m, 3H, $H^1{}_A$ overlapped with H^3), 3.37-3.40 (m, 3H, $H^1{}_B$ overlapped with $H^{1'}$), 1.49 (m, $^3J_{HH}$ = 7.0 Hz, 2 H, $H^{2'}$), 1.20-1.23 (m, 14H, $H^{3'}$-$H^{9'}$), 0.84 (t, $^3J_{HH}$ = 7.0 Hz, 3H, $H^{10'}$); ^{13}C-{^1H} NMR (100.6 MHz, $CDCl_3$): δ_C = 134.91 (d, $^4J_{PC}$ = 3.0 Hz, $C^{Ar}{}_p$), 133.71 (d, $^2J_{PC}$ = 10.3 Hz, $C^{Ar}{}_o$), 130.22 (d, $^3J_{PC}$ = 7.2 Hz, $C^{Ar}{}_m$), 120.58 (q, $^1J_{FC}$ = 320.4 Hz, CF_3), 118.63 (d, $^1J_{PC}$ = 87.1 Hz, $C^{Ar}{}_i$), 73.79 (d, $^3J_{PC}$ = 14.6 Hz, C^3), 71.61 (s, $C^{1'}$), 65.26 (d, $^2J_{PC}$ = 5.7 Hz, C^2), 32.84 (s, $C^{2'}$), 29.58 (s, $C^{3'}$), 29.51 (s, $C^{4'-5'}$), 29.41 (s, $C^{6'}$), 29.27 (s, $C^{7'}$), 28.15 (d, $^1J_{PC}$ = 54.6 Hz, C^1), 26.05 (s, $C^{8'}$), 22.63 (s, $C^{9'}$), 14.10 (s, $C^{10'}$); ^{31}P-{^1H} NMR (162MHz, $CDCl_3$): δ_P = 24.2 (s); MALDI-MS, *m/z* 477.4 $[M - CF_3SO_3]^+$. Calculated for $C_{32}H_{44}O_2P^+$: 477.3; Calculated for $C_{32}H_{42}F_3O_5PS$: C, 61.33; H, 6.76; Found: C, 61.02; H, 7.01.

*(3-(Dodecyloxy)-2-hydroxypropyl)triphenylphosphonium trifluoromethanesulfonate (**3g**)*

Colorless solid, mp 73-74 °C, yield was 197 mg (84 %); TLC R_f = 0.62 (benzene/acetonitrile = 3/2); IR (KBr): 3399, 3064, 2925, 2855, 1825, 1773, 1719, 1637, 1590, 1542, 1485, 1468, 1440, 1408, 1368, 1338, 1288, 1244, 1226, 1163, 1112, 1030, 997, 840, 749, 725, 716, 690, 640, 573 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.75 (m, $^3J_{HH}$ = 7.2 Hz, $^5J_{PH}$ = 2.0 Hz, $^4J_{HH}$ 1.5 Hz, 3H, $H^{Ar}{}_p$), 7.68 (m, $^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ =7.2 Hz, $^4J_{HH}$ = 1.5 Hz, 6H, $H^{Ar}{}_o$), 7.64 (m, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{PH}$ = 3.6 Hz, 6H, $H^{Ar}{}_m$), 4.08 (m, 1H, H^2), 3.98 (br. s, 1H, OH), 3.54-3.55 (m, 3H, $H^1{}_A$ overlapped with H^3), 3.37-3.40 (m, 3H, $H^1{}_B$ overlapped with $H^{1'}$), 1.49 (m, $^3J_{HH}$ =7.0 Hz, 2H, $H^{2'}$), 1.20-1.23 (m, 18H, $H^{3'}$-$H^{11'}$), 0.84 (t, $^3J_{HH}$ = 7.0 Hz, 3H, $H^{12'}$); ^{13}C-{^1H} NMR (100.6 MHz, $CDCl_3$): δ_C = 135.0 (d, $^4J_{PC}$ = 2.9 Hz, $C^{Ar}{}_p$), 133.87 (d, $^2J_{PC}$ = 10.3 Hz, $C^{Ar}{}_o$), 130.33 (d, $^3J_{PC}$ = 12.8 Hz, $C^{Ar}{}_m$), 120.64 (κ, $^1J_{FC}$ = 320.4 Hz, CF_3), 118.77 (d, $^1J_{PC}$ = 87.3 Hz, $C^{Ar}{}_i$), 73.88 (d, $^3J_{PC}$ = 14.8 Hz, C^3), 71.76 (s, $C^{1'}$), 65.42 (d, $^2J_{PC}$ = 5.9 Hz, C^2), 31.99 (s, $C^{2'}$), 29.74 (s, $C^{3'}$), 29.71 (s, $C^{4'}$overlapped with $C^{5'}$), 29.69 (s, $C^{6'}$), 29.63 (s, $C^{7'}$), 29.54 (6s, $C^{8'}$), 29.43 (s, $C^{9'}$), 28.38 (d, $^1J_{PC}$ = 54.7 Hz, C^1), 26.17 (s, $C^{10'}$), 22.76 (s, $C^{11'}$), 14.22 (s, $C^{12'}$); ^{31}P-{^1H} NMR (162 MHz, $CDCl_3$): δ_P = 25.1 (s); ESI-MS, *m/z* 505.29 $[M - CF_3SO_3]^+$. Calculated for $C_{34}H_{48}O_2P^+$: 505.32; Calculated for $C_{34}H_{46}F_3O_5PS$: C, 62.37; H, 7.08; Found: C, 62.05; H, 7.33.

*(2-Hydroxy-3-(tetradecyloxy)propyl)triphenylphosphonium trifluoromethanesulfonate (**3h**)*. Colorless solid, mp 70-72 °C, yield was 203 mg (87 %); TLC R_f = 0.62 (benzene/acetonitrile = 3/2); IR (KBr): 3405, 2925, 2854, 1637, 1486, 1468, 1440, 1369, 1287, 1244, 1225, 1163, 1112, 1030, 997, 884, 840, 794, 749, 725, 716, 691, 640, 573 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (m, $^3J_{HH}$ = 7.2 Hz, $^5J_{PH}$ = 2.0 Hz, $^4J_{HH}$ 1.5 Hz, 3H, $H^{Ar}{}_p$), 7.68 (m, $^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ =7.2 Hz, $^4J_{HH}$ = 1.5 Hz, 6H, $H^{Ar}{}_o$), 7.64 (m, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{PH}$ = 3.6 Hz, 6H, $H^{Ar}{}_m$), 4.08 (m, 1H, H^2), 3.98 (br. s, 1H, OH), 3.54-3.55 (m, 3H, $H^1{}_A$ overlapped with H^3), 3.37-3.40 (m, 3H, $H^1{}_B$ overlapped with $H^{1'}$), 1.49 (m, $^3J_{HH}$ = 7.0 Hz, 2H, $H^{2'}$), 1.20-1.23 (m, 22H, $H^{3'}$-$H^{13'}$), 0.84 (t, $^3J_{HH}$ =7.0 Hz, 3H, $H^{14'}$); ^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ_C = 135.0 (d, $^4J_{PC}$ = 3.2 Hz, $C^{Ar}{}_p$), 133.89 (d, $^2J_{PC}$ = 10.2 Hz, $C^{Ar}{}_o$), 130.33 (d, $^3J_{PC}$ = 12.7 Hz, $C^{Ar}{}_m$), 120.64 (q, $^1J_{FC}$ = 320.1 Hz, CF_3), 118.85 (d, $^1J_{PC}$ = 87.0 Hz, $C^{Ar}{}_i$), 73.92 (d, $^3J_{PC}$ = 14.4 Hz, C^3), 71.80 (s, $C^{1'}$), 65.45 (d, $^2J_{PC}$ = 5.2 Hz, C^2), 32.01 (s, $C^{3'}$), 29.78 (s, $C^{4'}$ overlapped with $C^{5'}$), 29.75 (s, $C^{6'}$), 29.73 (s, $C^{7'}$), 29.72 (s, $C^{8'}$), 29.65 (s, $C^{9'}$), 29.57 (s, $C^{10'}$), 29.45 (s, $C^{11'}$), 28.39 (d, $^1J_{PC}$ = 54.6 Hz, C^1), 26.19 (s, $C^{12'}$), 22.78 (s, $C^{13'}$), 14.22 (s, $C^{14'}$); ^{31}P-{^{1}H} NMR (162 MHz, $CDCl_3$): δ_P = 25.1 (s); ESI-MS, *m/z* 533.33 $[M - CF_3SO_3]^+$. Calculated for $C_{36}H_{52}O_2P^+$: 533.35; Calculated for $C_{36}H_{50}F_3O_5PS$: C, 63.33; H, 7.38; Found: C, 63.01; H, 7.62.

*(3-(Hexadecyloxy)-2-hydroxypropyl)triphenylphosphonium trifluoromethanesulfonate (**3i**)*. Colorless solid, mp 67 °C, yield was 193 mg (52 %); TLC R_f = 0.62 (benzene/acetonitrile = 3/2); IR (KBr): 3396, 3063, 2924, 2854, 1982, 1912, 1825, 1779, 1589, 1486, 1466, 1440, 1384, 1340, 1278, 1259, 1225, 1159, 1113, 1031, 998, 895, 825, 783, 748, 722, 691, 639, 573, 542, 514, 439 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 7.75 (m, $^3J_{HH}$ = 7.2 Hz, $^5J_{PH}$ = 2.0 Hz, $^4J_{HH}$ = 1.5 Hz, 3H, $H^{Ar}{}_p$), 7.68 (m, $^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.5 Hz, 6H, $H^{Ar}{}_o$), 7.64 (m, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{PH}$ = 3.6 Hz, 6H, $H^{Ar}{}_m$), 4.08 (m, 1H, H^2), 3.98 (br. s, 1H, OH), 3.54-3.55 (m, 3H, $H^1{}_A$ overlapped with H^3), 3.37-3.40 (m, 3H, $H^1{}_B$ overlapped with $H^{1'}$), 1.49 (m, $^3J_{HH}$ = 7.0 Hz, 2H, $H^{2'}$), 1.20-1.23 (m, 26H, $H^{3'}$-$H^{15'}$), 0.84 (t, $^3J_{HH}$ = 7.0 Hz, 3H, $H^{16'}$); ^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ_C = 135.02 (d, $^4J_{PC}$ = 3.0 Hz, $C^{Ar}{}_p$), 133.95 (d, $^2J_{PC}$ = 10.3 Hz, $C^{Ar}{}_o$), 130.36 (d, $^3J_{PC}$ = 12.8 Hz, $C^{Ar}{}_m$), 123.90 (q, $^1J_{CF}$ = 320.1 Hz, CF_3), 118.94 (d, $^1J_{PC}$ = 86.9 Hz, $C^{Ar}{}_i$), 73.94 (d, $^3J_{PC}$ = 14.8 Hz, C^3), 71.84 (s, $C^{1'}$), 65.53 (d, $^2J_{PC}$ = 5.7 Hz, C^2), 32.03 (s, $C^{3'}$), 29.80 (s, $C^{4'}$ overlapped with $C^{5'\text{-}9'}$), 29.77 (s, $C^{10'}$), 29.69 (s, $C^{11'}$), 29.59 (s, $C^{12'}$), 29.46 (s, $C^{13'}$), 28.49 (d, $^1J_{PC}$ = 54.9 Hz, C^1), 26.22 (s, $C^{14'}$), 22.79 (s, $C^{15'}$), 14.21 (s, $C^{16'}$); ^{31}P-{^{1}H} NMR (162MHz, $CDCl_3$): δ_P = 24.5 (s.); MALDI-MS, *m/z* 561.3 $[M - CF_3SO_3]^+$. Calculated for $C_{38}H_{56}O_2P^+$: 561.4; Calculated for $C_{38}H_{54}F_3O_5PS$: C, 64.21; H, 7.66; Found: C, 63.89; H, 7.92.

*(2-Hydroxy-3-(octadecyloxy)propyl)triphenylphosphonium trifluoromethanesulfonate (**3j**)*. Colorless solid, mp 64-65 °C, yield was 197 mg (78 %); TLC R_f = 0.62 (benzene/acetonitrile = 3/2); IR (KBr): 3406, 3064, 3000, 2924, 2854, 1983, 1913, 1712, 1589, 1486, 1466, 1440, 1363, 1278, 1260, 1224, 1158, 1113, 1031, 998, 902, 826, 784, 750, 723, 692, 639, 573, 531, 514, 439 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (m, $^3J_{HH}$ = 7.2 Hz, $^5J_{PH}$ = 2.0 Hz, $^4J_{HH}$ 1.5 Hz, 3H, $H^{Ar}{}_p$), 7.68 (m, $^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.5 Hz, 6H, $H^{Ar}{}_o$), 7.64 (m, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{PH}$ = 3.6 Hz, 6H, $H^{Ar}{}_m$), 4.08 (m, 1H, H^2), 3.98

(br. s, 1H, OH), 3.54-3.55 (m, 3H, $H^1{}_A$ overlapped with H^3), 3.37-3.40 (m, 3H, $H^1{}_B$ overlapped with $H^{1'}$), 1.49 (m, $^3J_{HH}$ =7.0 Hz, 2 H, $H^{2'}$), 1.20-1.23 (m, 30 H, $H^{3'}$-$H^{17'}$), 0.84 (t, $^3J_{HH}$ =7.0 Hz, 3 H, $H^{18'}$); ^{13}C-{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ_C = 135.02 (d, $^4J_{PC}$ = 3.1 Hz, $C^{Ar}{}_p$), 133.98 (d, $^2J_{PC}$ = 10.2 Hz, $C^{Ar}{}_o$), 130.37 (d, $^3J_{PC}$ = 12.7 Hz, $C^{Ar}{}_m$), 121.24 (κ, $^1J_{FC}$ = 320.0 Hz, CF_3), 118.96 (d, $^1J_{PC}$ = 87.1 Hz, $C^{Ar}{}_i$), 73.97 (d, $^3J_{PC}$ = 14.9 Hz, C^3), 71.85 (s, $C^{1'}$), 65.56 (d, $^2J_{PC}$ = 5.7, C^2 Hz), 29.82 (s, $C^{3'}$), 29.77 (s, $C^{4'}$ overlapped with $C^{5'\text{-}10'}$), 29.70 (s, $C^{12'}$ overlapped with $C^{11'}$), 29.60 (s, $C^{13'}$), 29.47 (s, $C^{14'}$), 28.55 (d, $^1J_{PC}$ = 54.7 Hz, C^1), 26.23 (s, $C^{15'}$), 22.80 (s, $C^{17'}$), 14.22 (s, $C^{18'}$); ^{31}P-{^{1}H} NMR (162 MHz, $CDCl_3$): δ_P = 24.91 (s); MALDI-MS, *m/z* 589.3 $[M - CF_3SO_3]^+$. Calculated for $C_{40}H_{60}O_2P^+$: 589.4; Calculated for $C_{40}H_{58}F_3O_5PS$: C, 65.02; H, 7.91; Found: C, 64.71; H, 8.16.

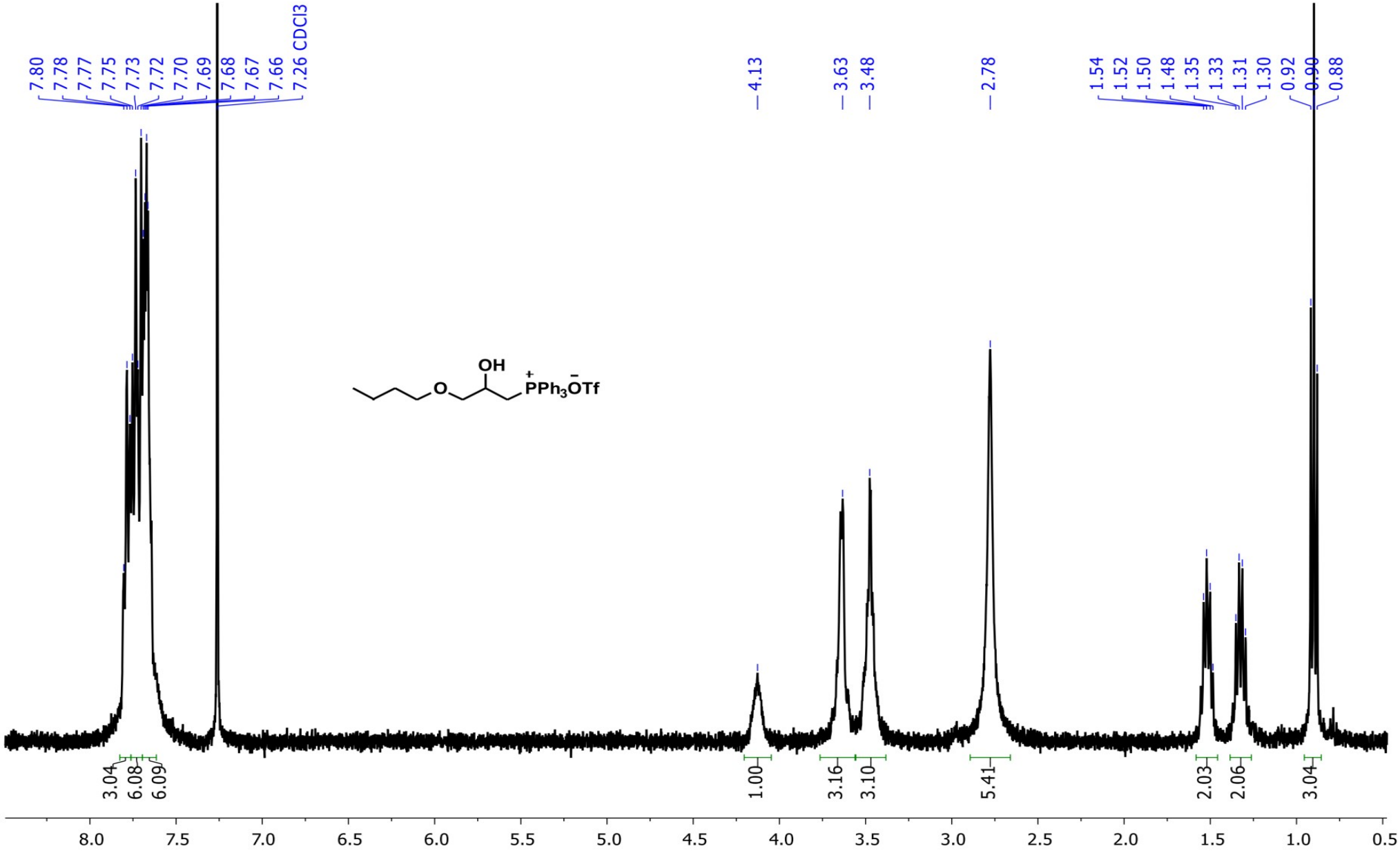

Figure S56. [1]H NMR spectrum (400 MHz, CDCl3) of compound **3c**.

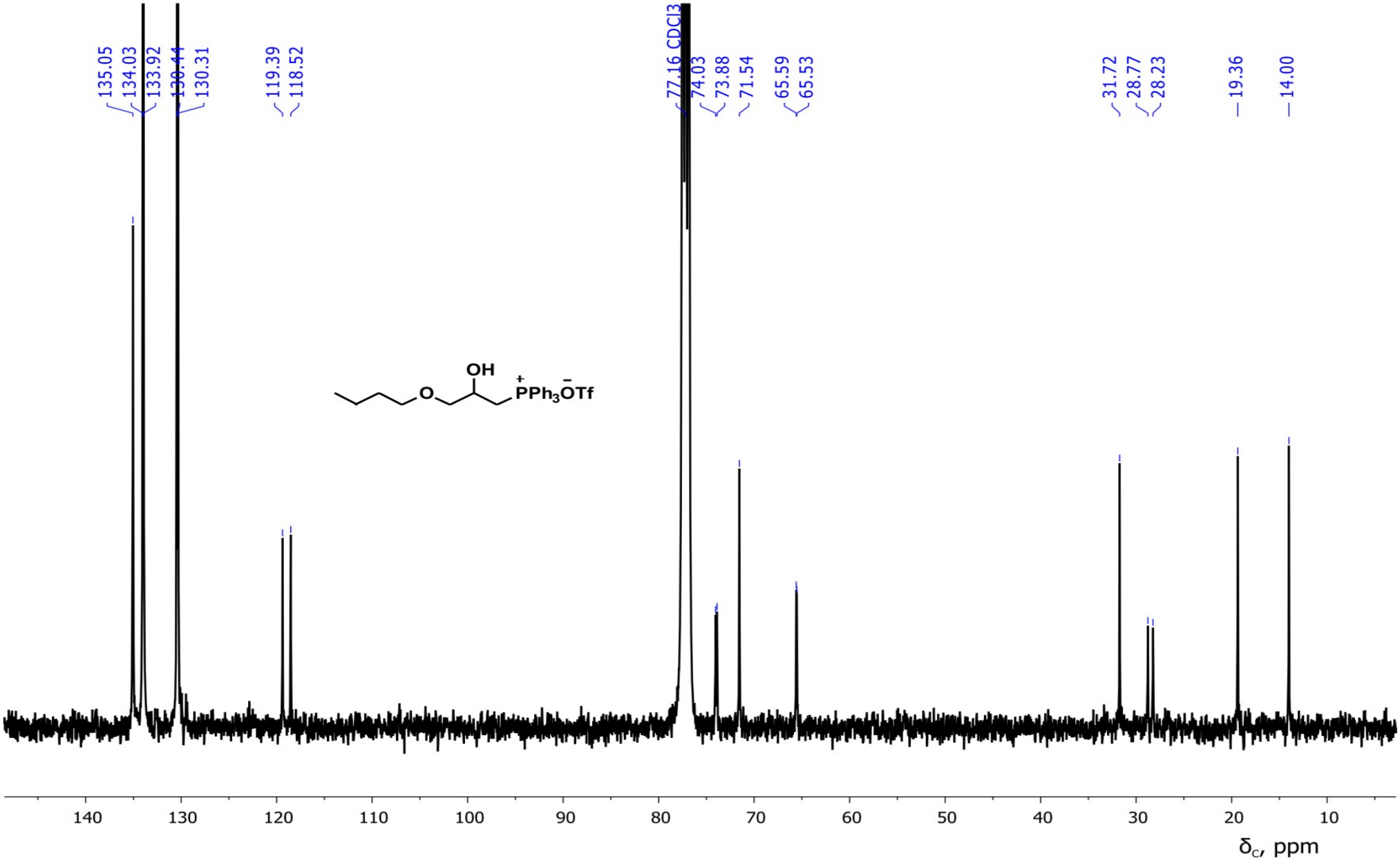

Figure S57. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of compound **3c**.

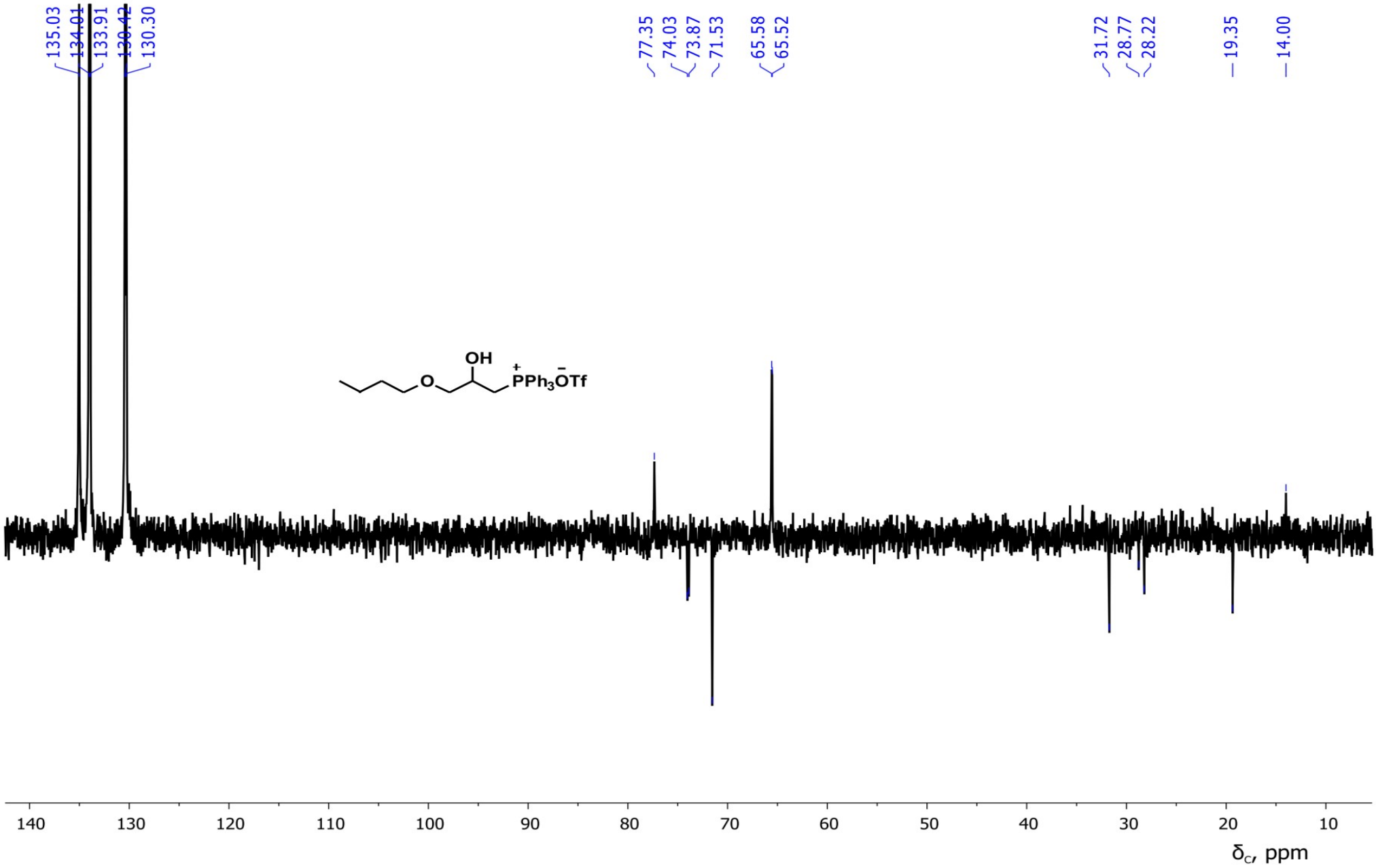

Figure S58. ^{13}C-{^{1}H} APT NMR spectrum (100.6 MHz, $CDCl_3$) of compound **3c**.

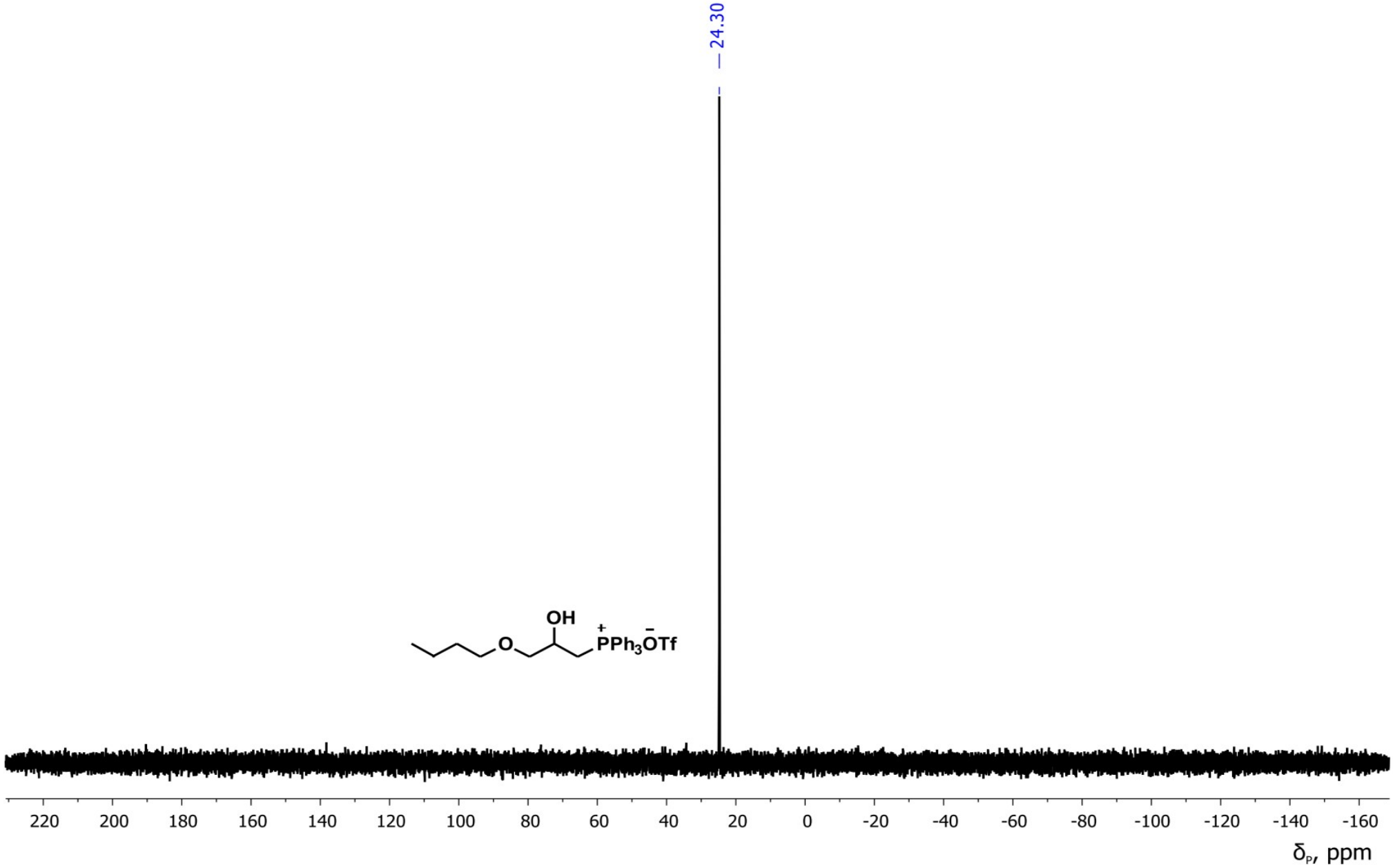

Figure S59. ^{31}P-{^{1}H} NMR spectrum (162 MHz, $CDCl_3$) of compound **3c**.

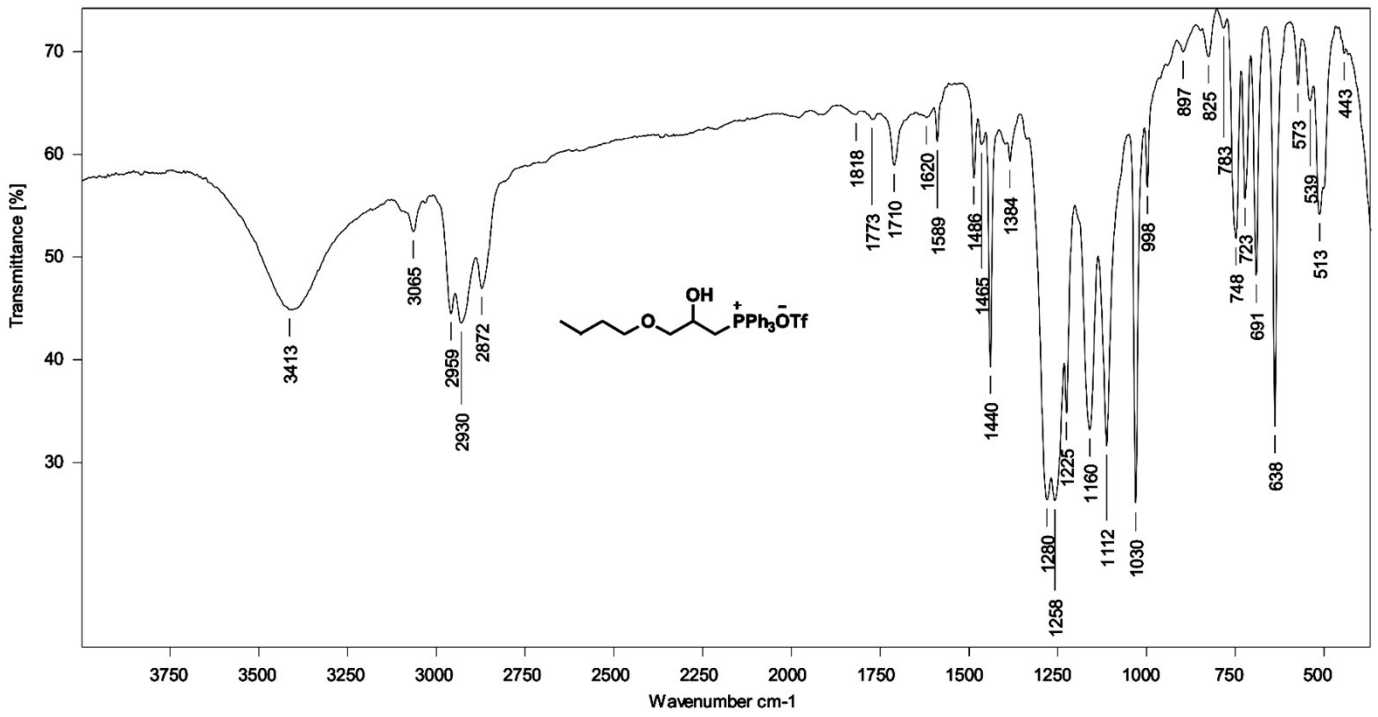

Figure S60. IR spectrum (KBr) of compound **3c**.

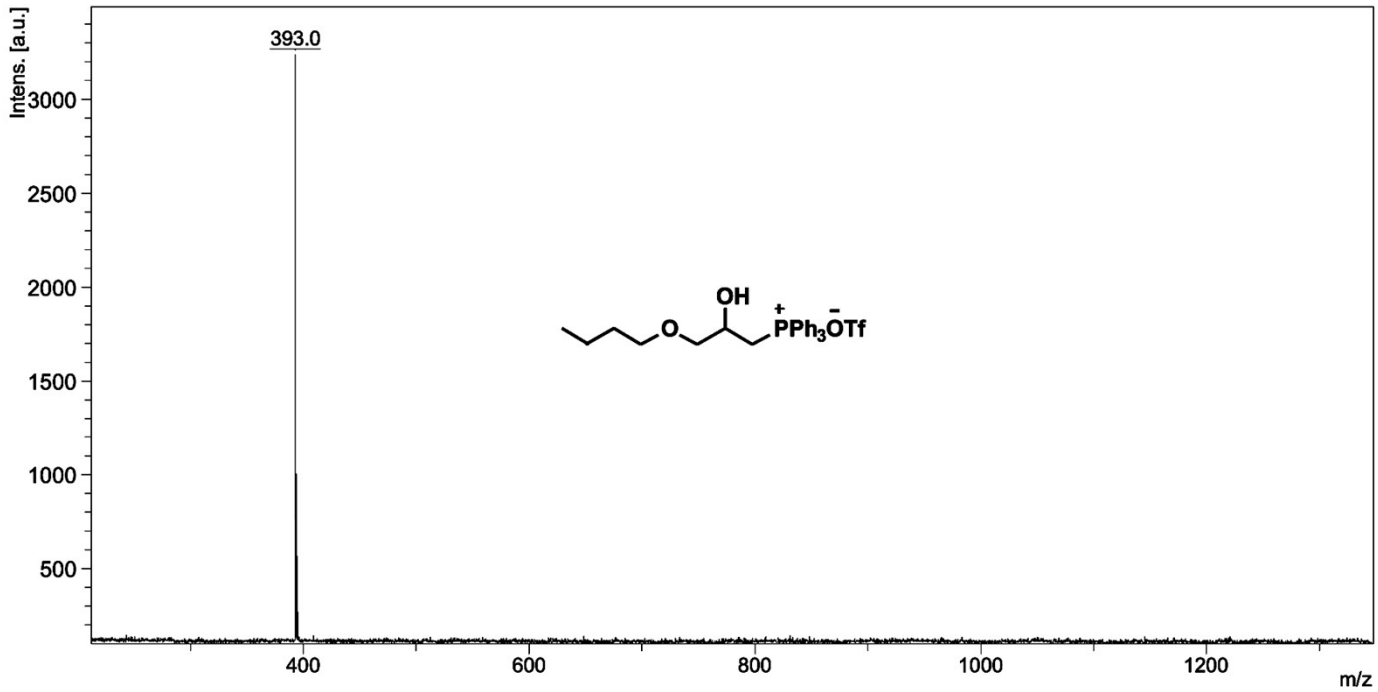

Figure S61. MALDI-MS spectrum of compound **3c**.

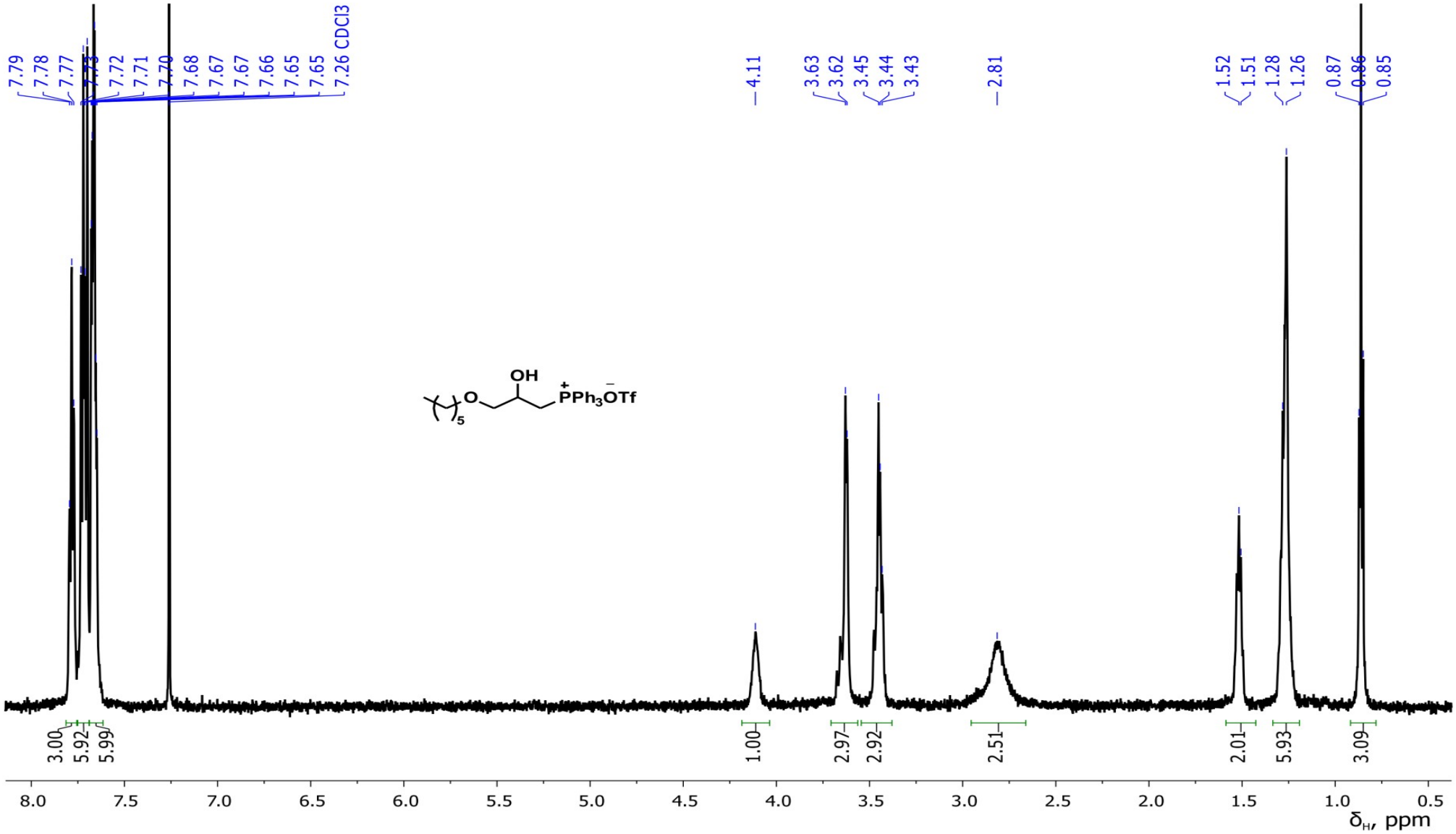

Figure S62. ^{1}H NMRspectrum (600 MHz, $CDCl_3$) of compound **3d**.

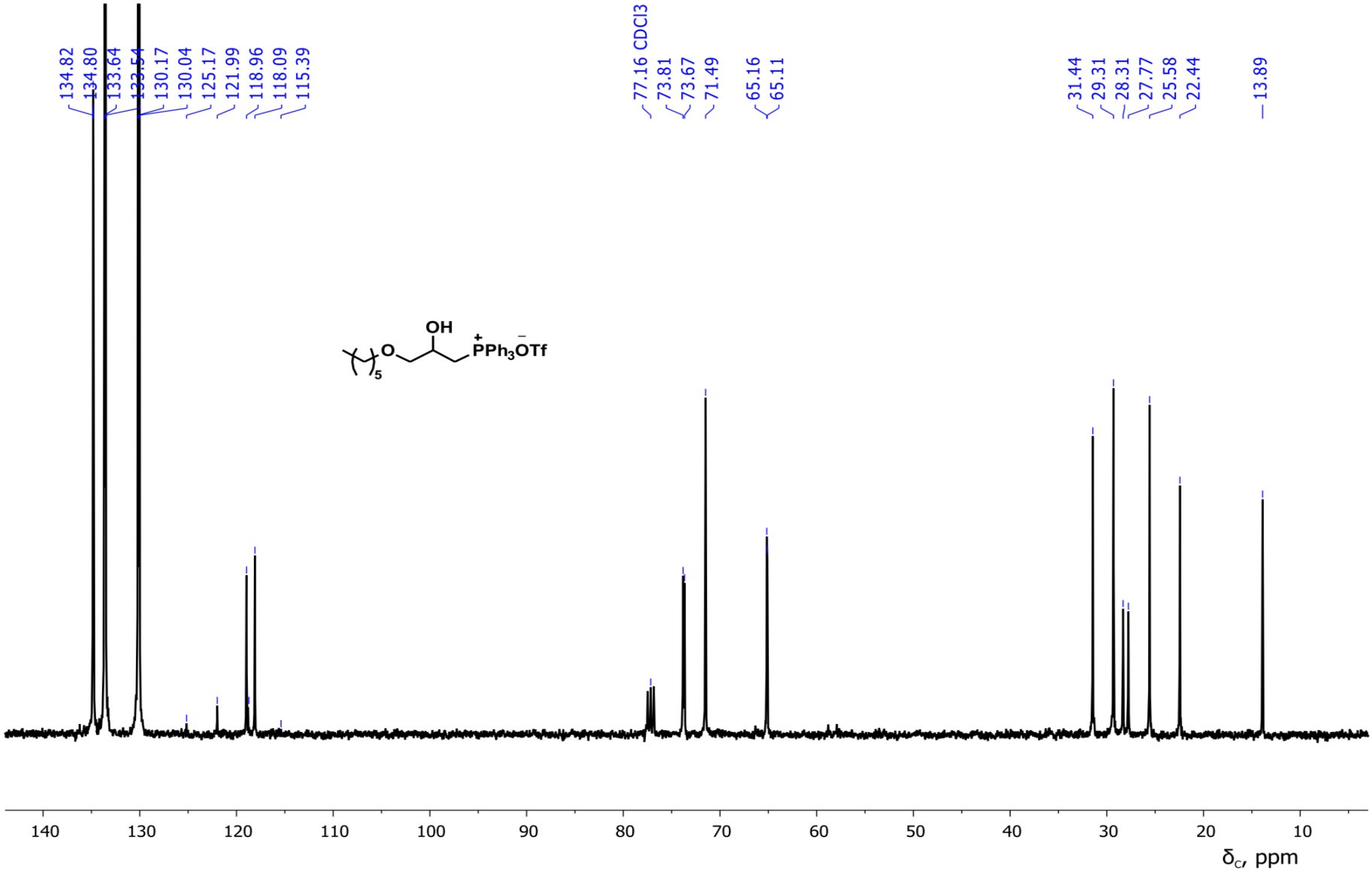

Figure S63. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of compound **3d**.

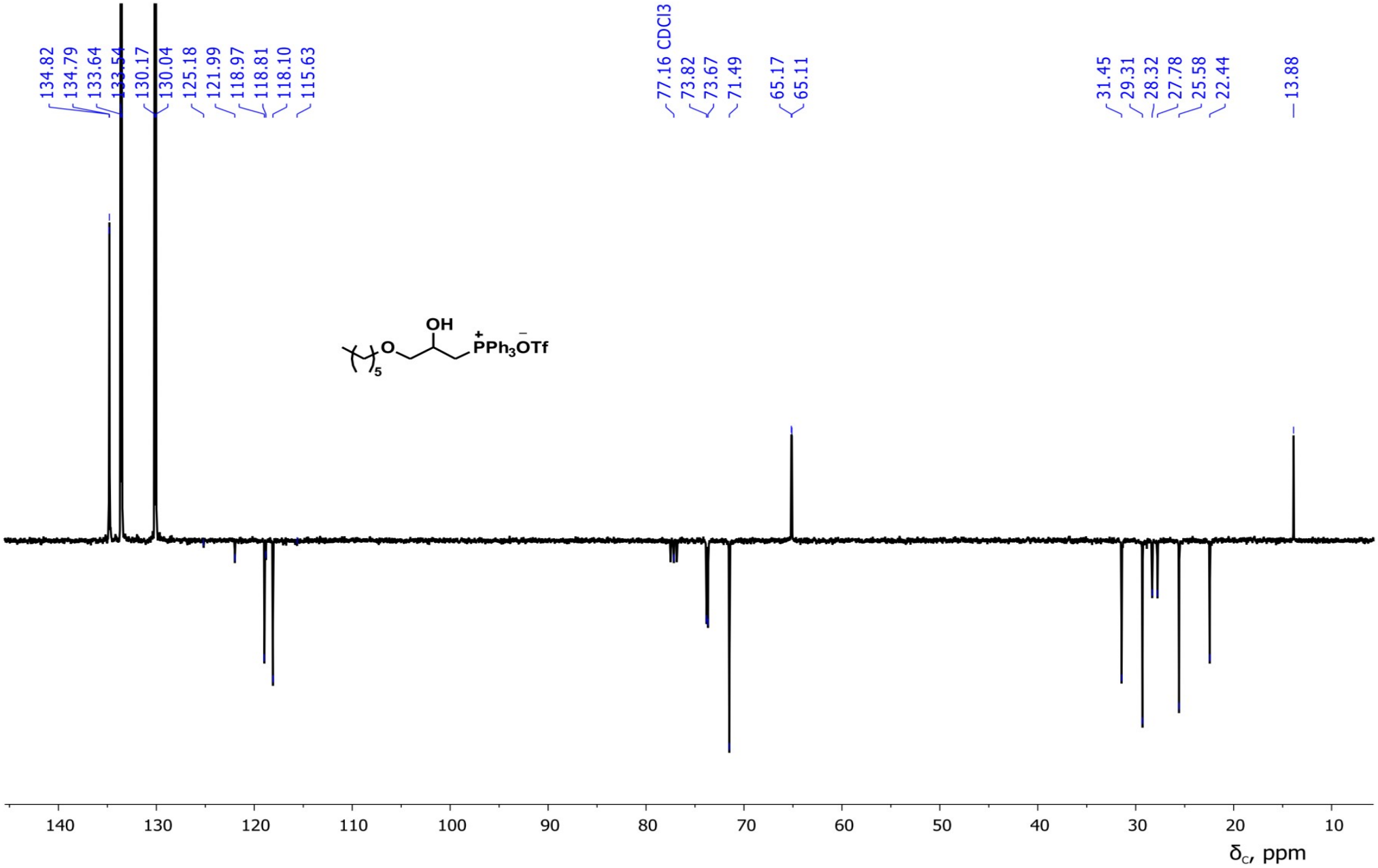

Figure S64. ^{13}C-{^{1}H} APT NMR spectrum (100.6 MHz, $CDCl_3$) of compound **3d**.

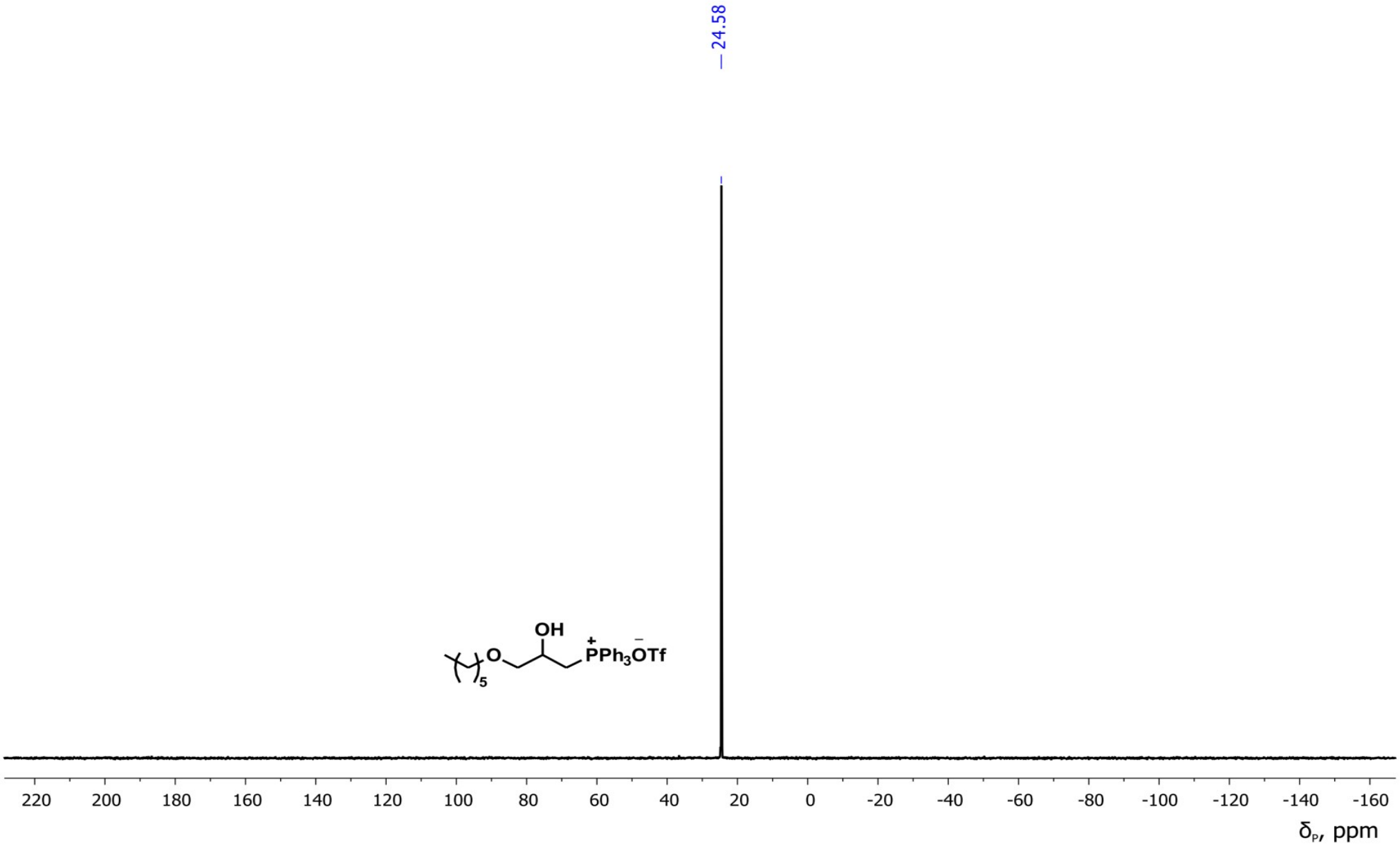

Figure S65. ^{31}P-{^{1}H} NMR spectrum (162 MHz, $CDCl_3$) of compound **3d**.

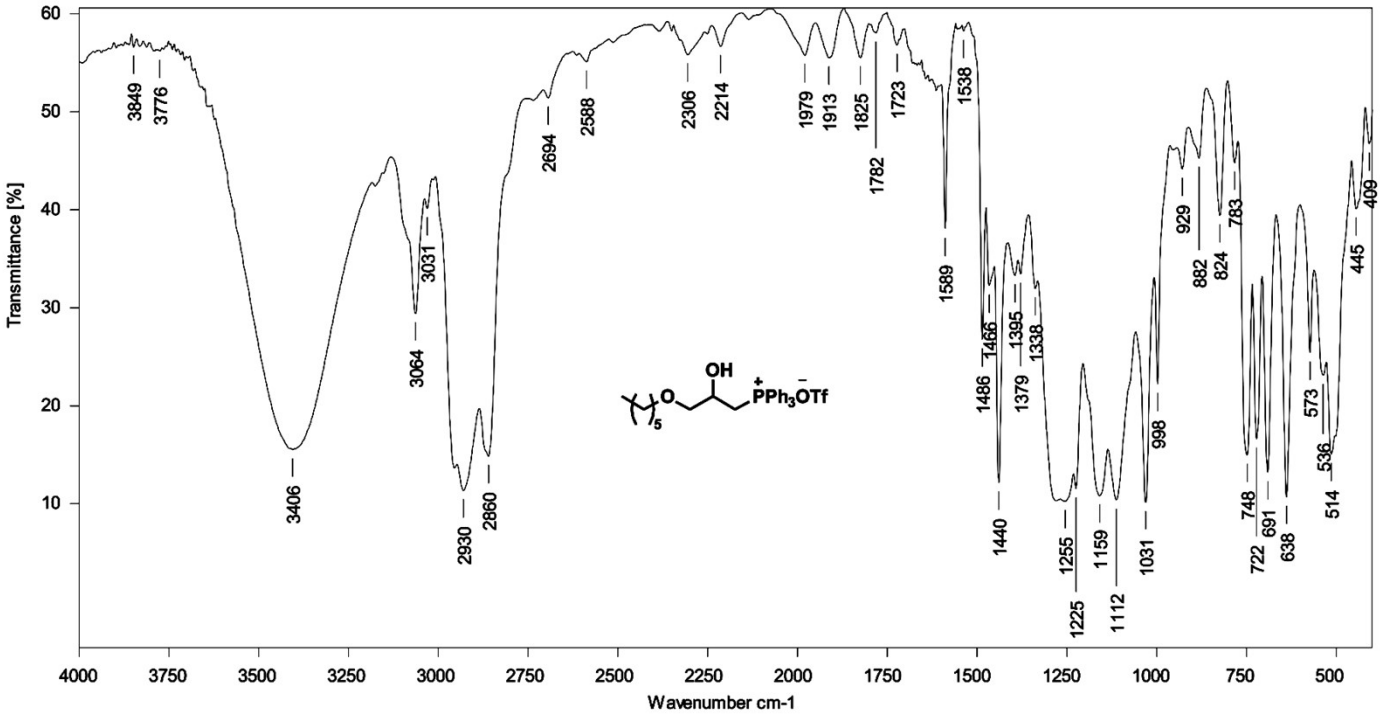

Figure S66. IR spectrum (KBr) of compound **3d**.

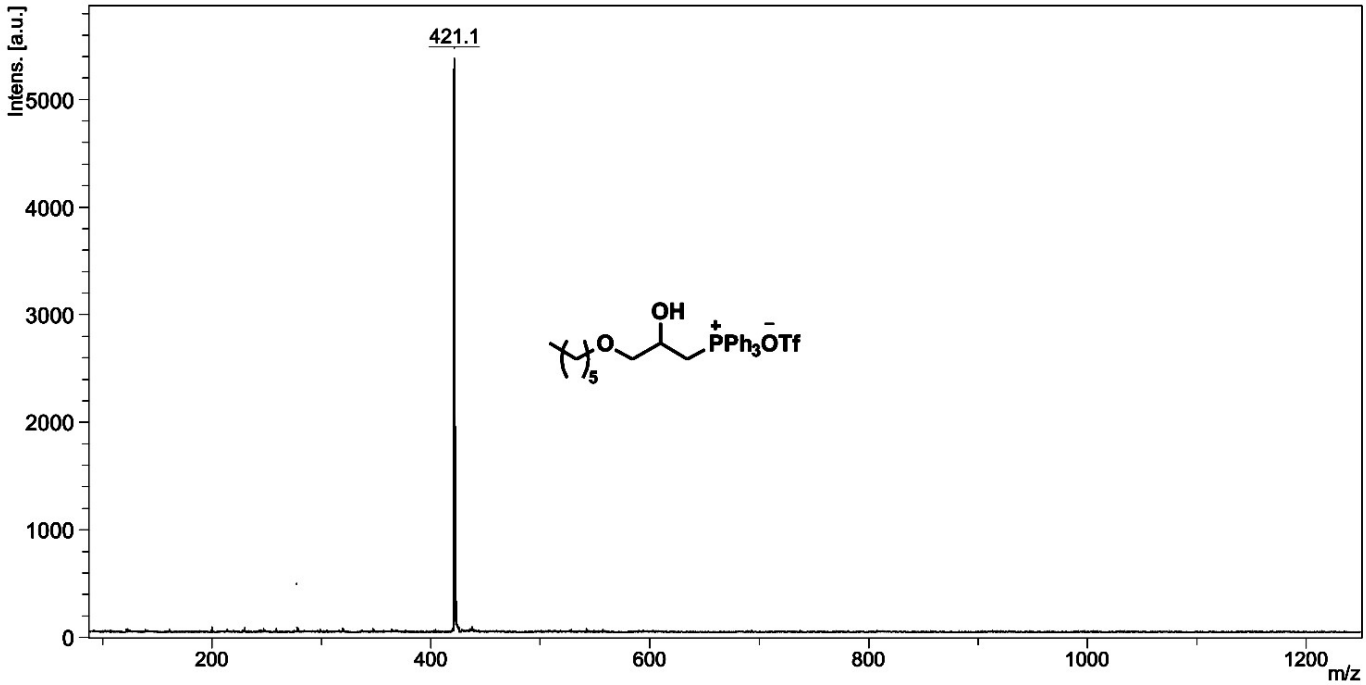

Figure S67. MALDI-MS spectrum of compound **3d**.

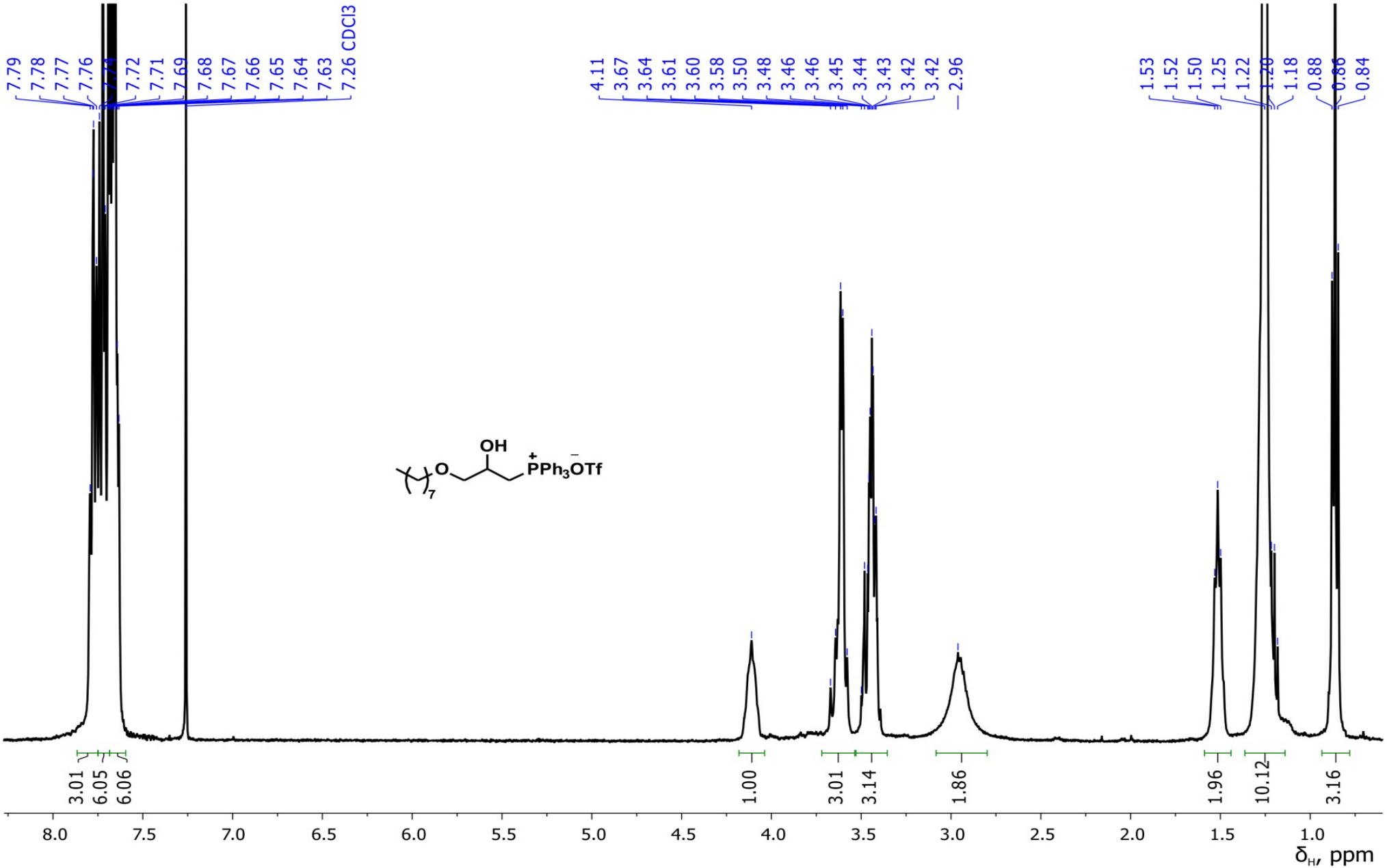

Figure S68. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3e.**

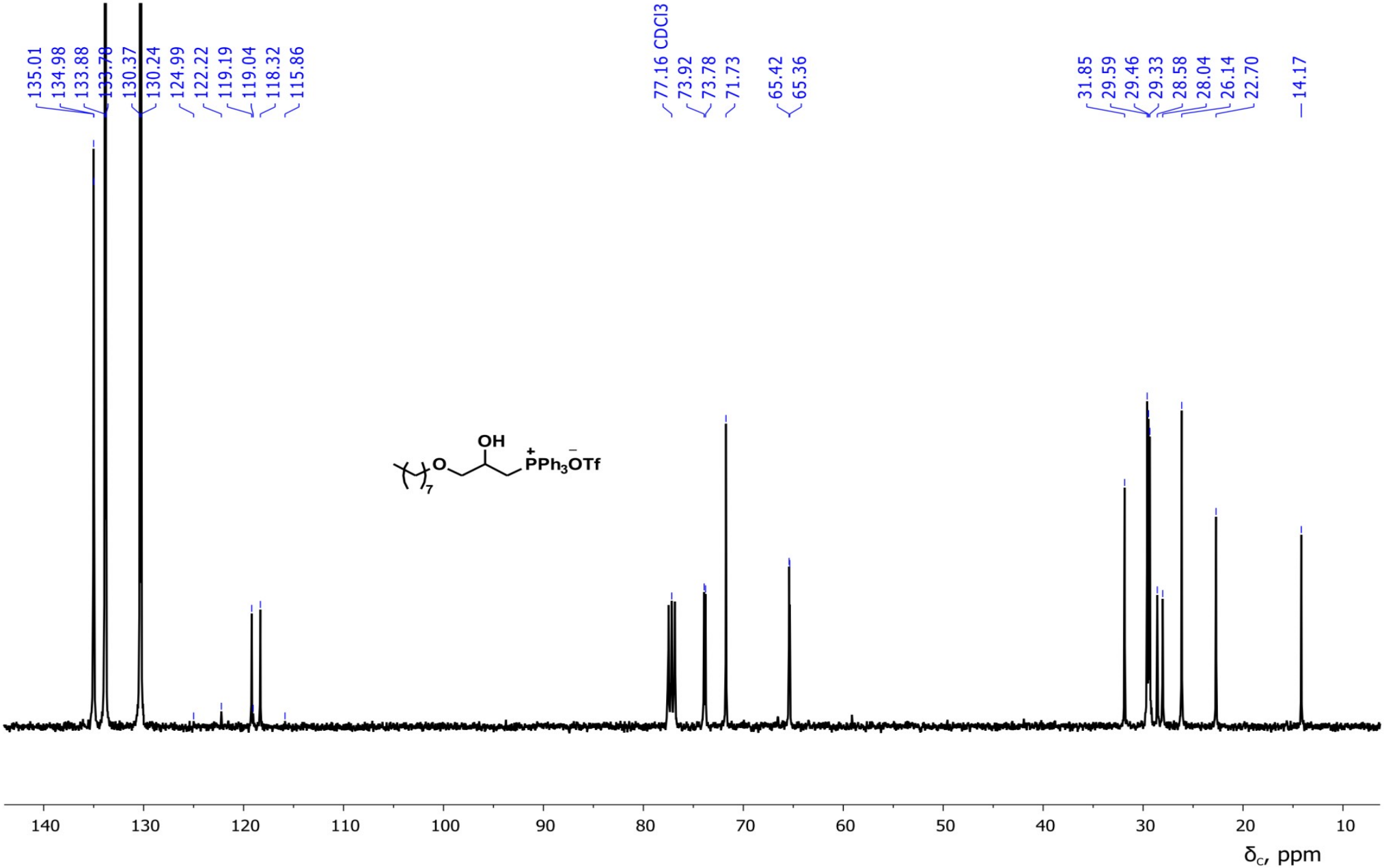

Figure S69. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of compound **3e**.

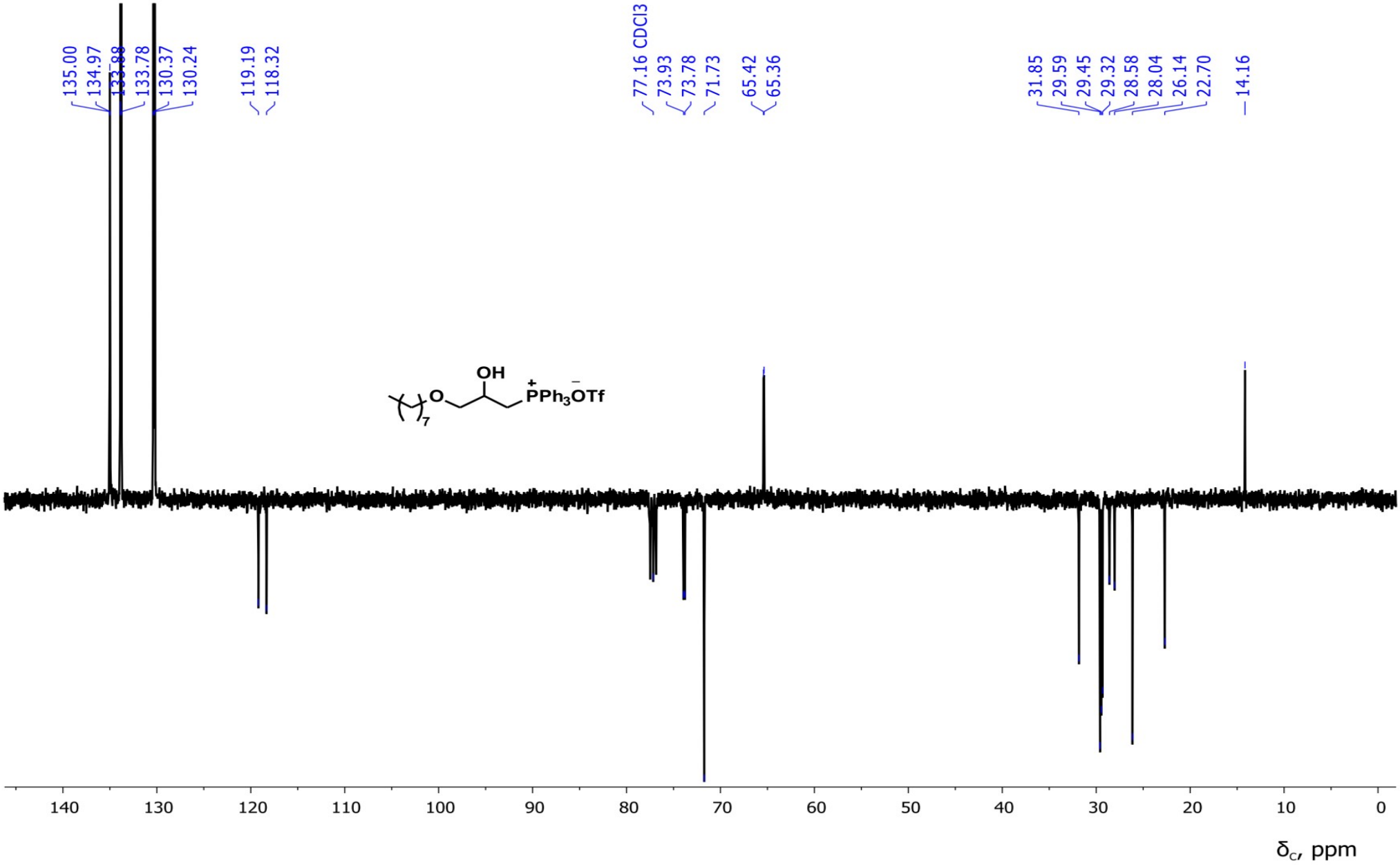

Figure S70. ^{13}C-{^{1}H} APT NMR spectrum (100.6 MHz, $CDCl_3$) of compound **3e**.

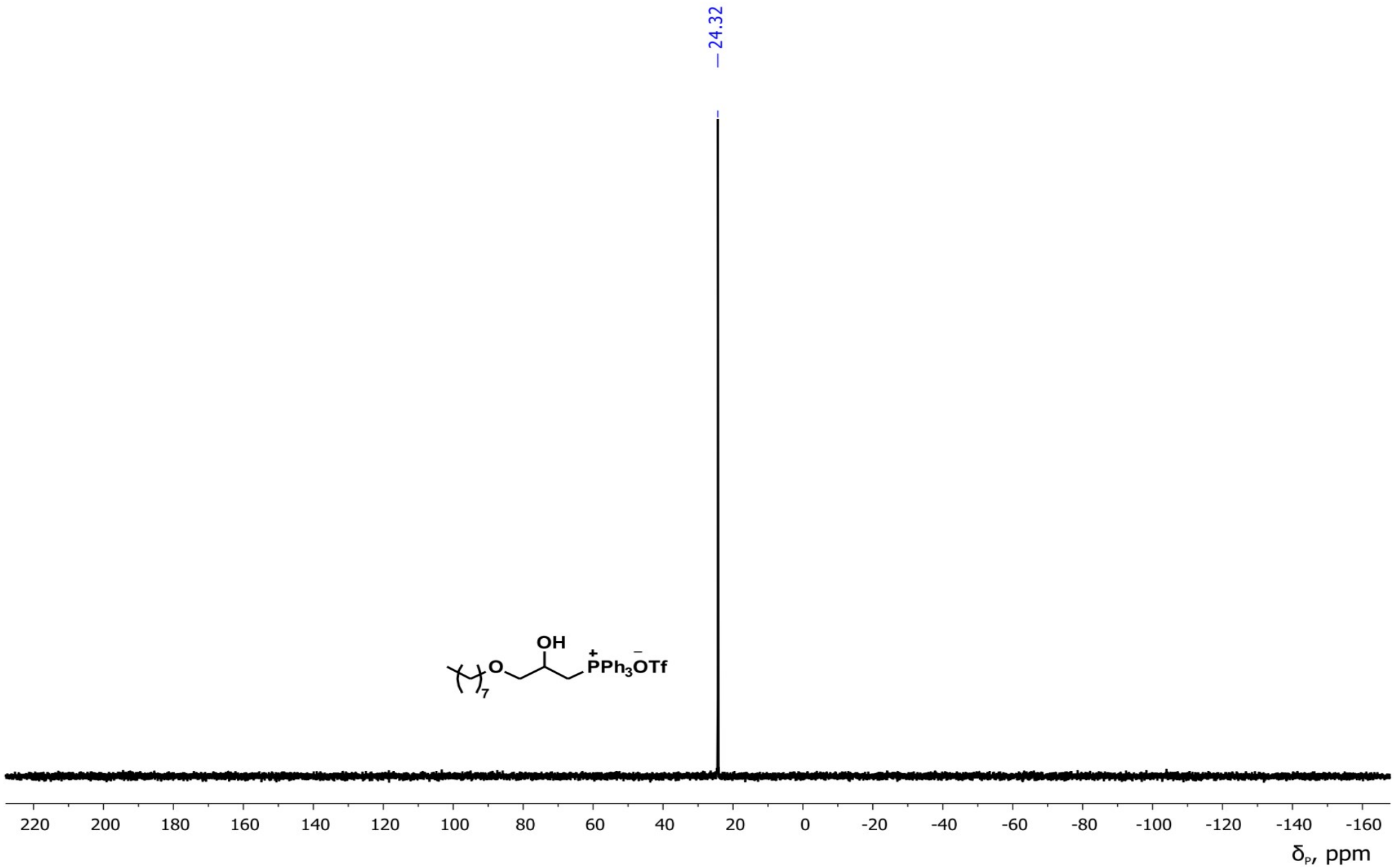

Figure S71. ^{31}P-{^{1}H} NMR spectrum (162 MHz, $CDCl_3$) of compound **3e**.

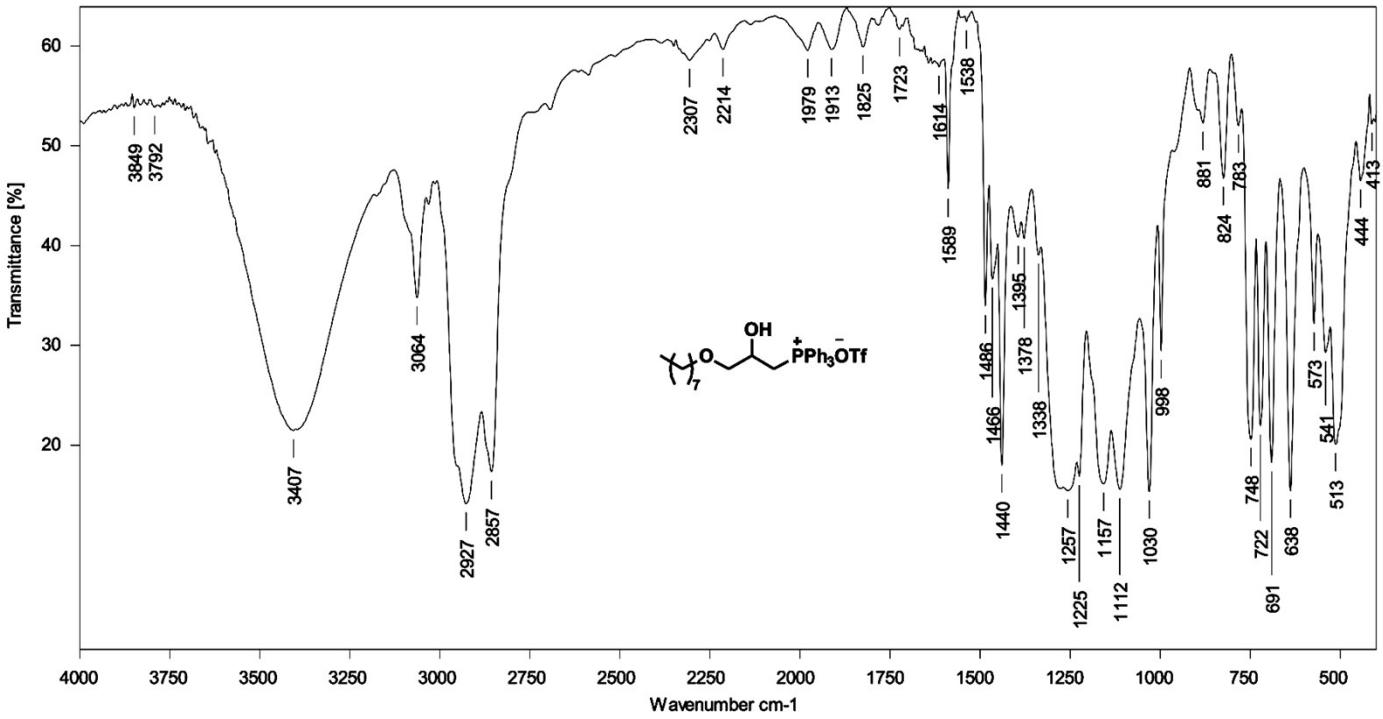

Figure S72. IR spectrum (KBr) of compound **3e**.

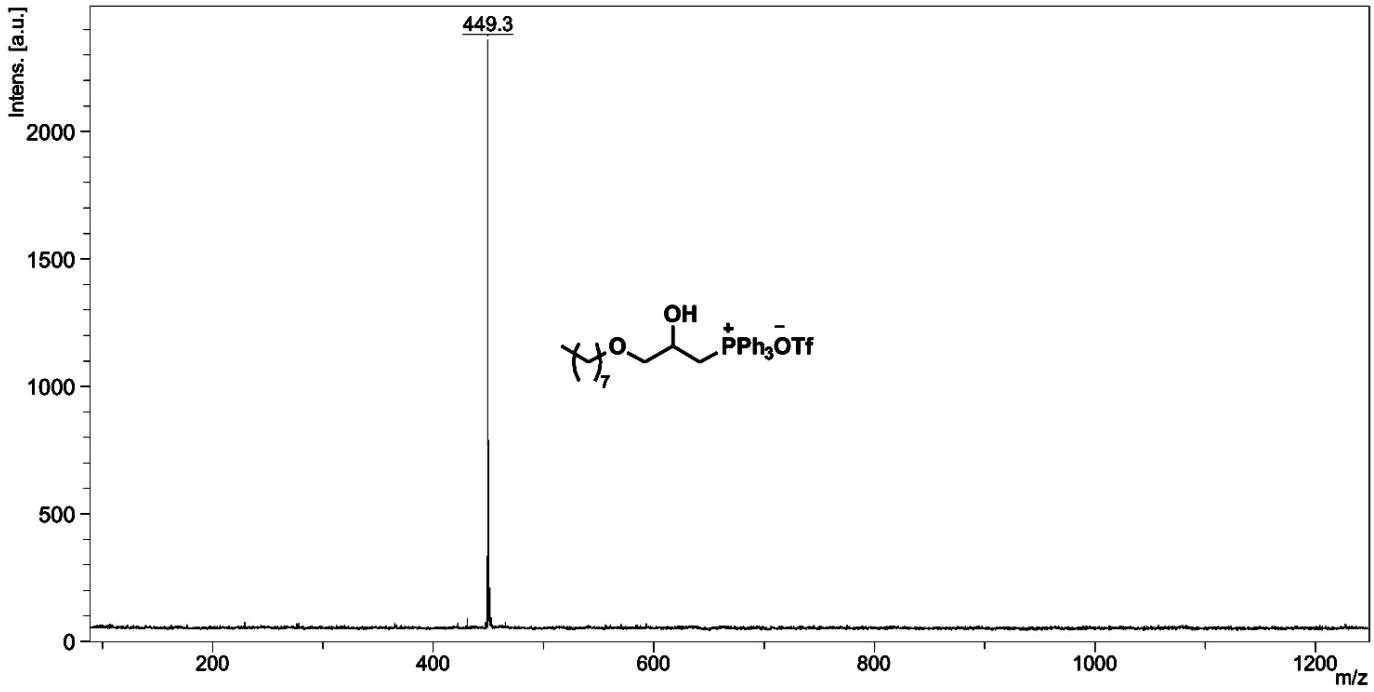

Figure S73. MALDI-MS spectrum of compound **3e**.

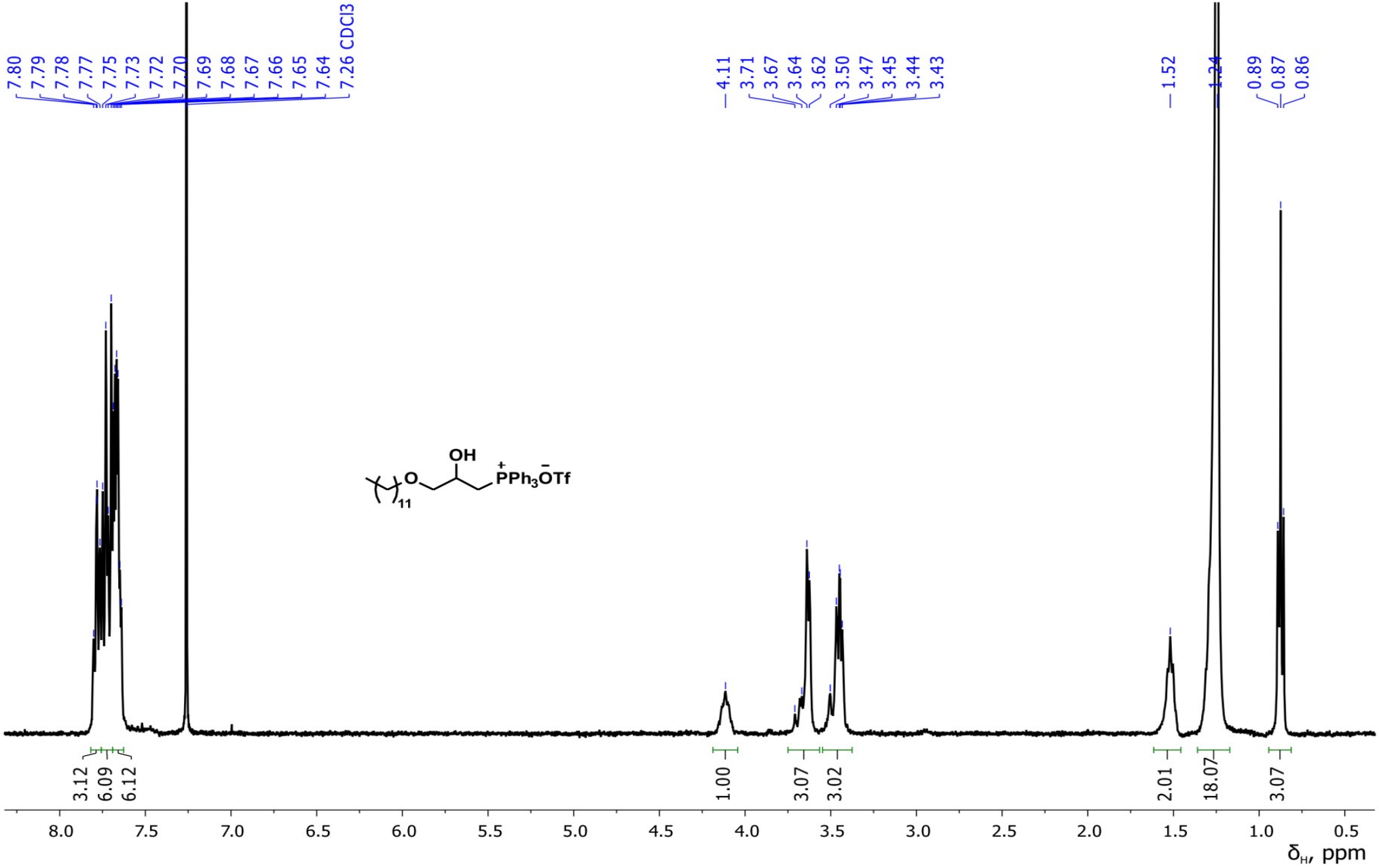

Figure S74. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3g**.

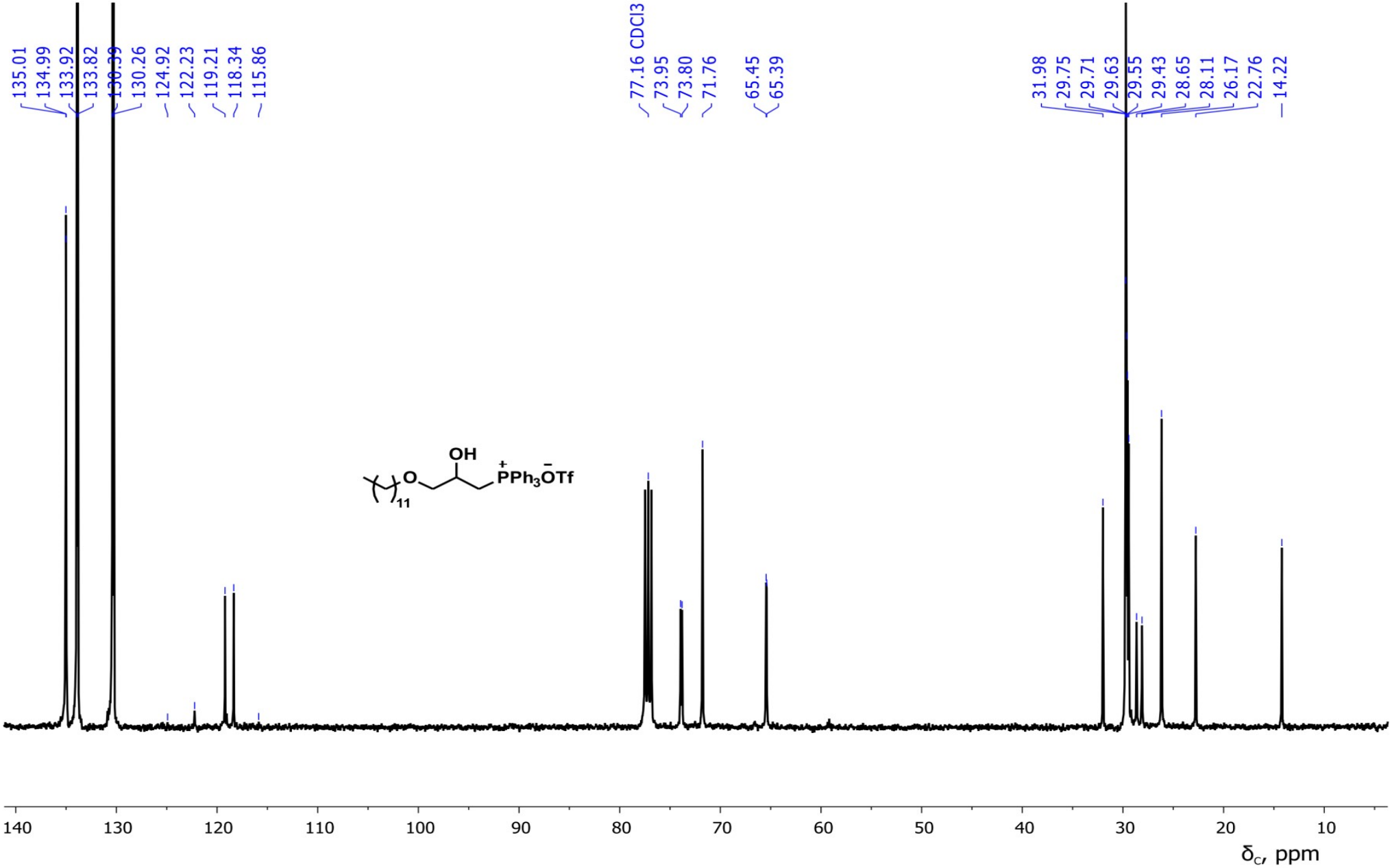

Figure S75. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of compound **3g**.

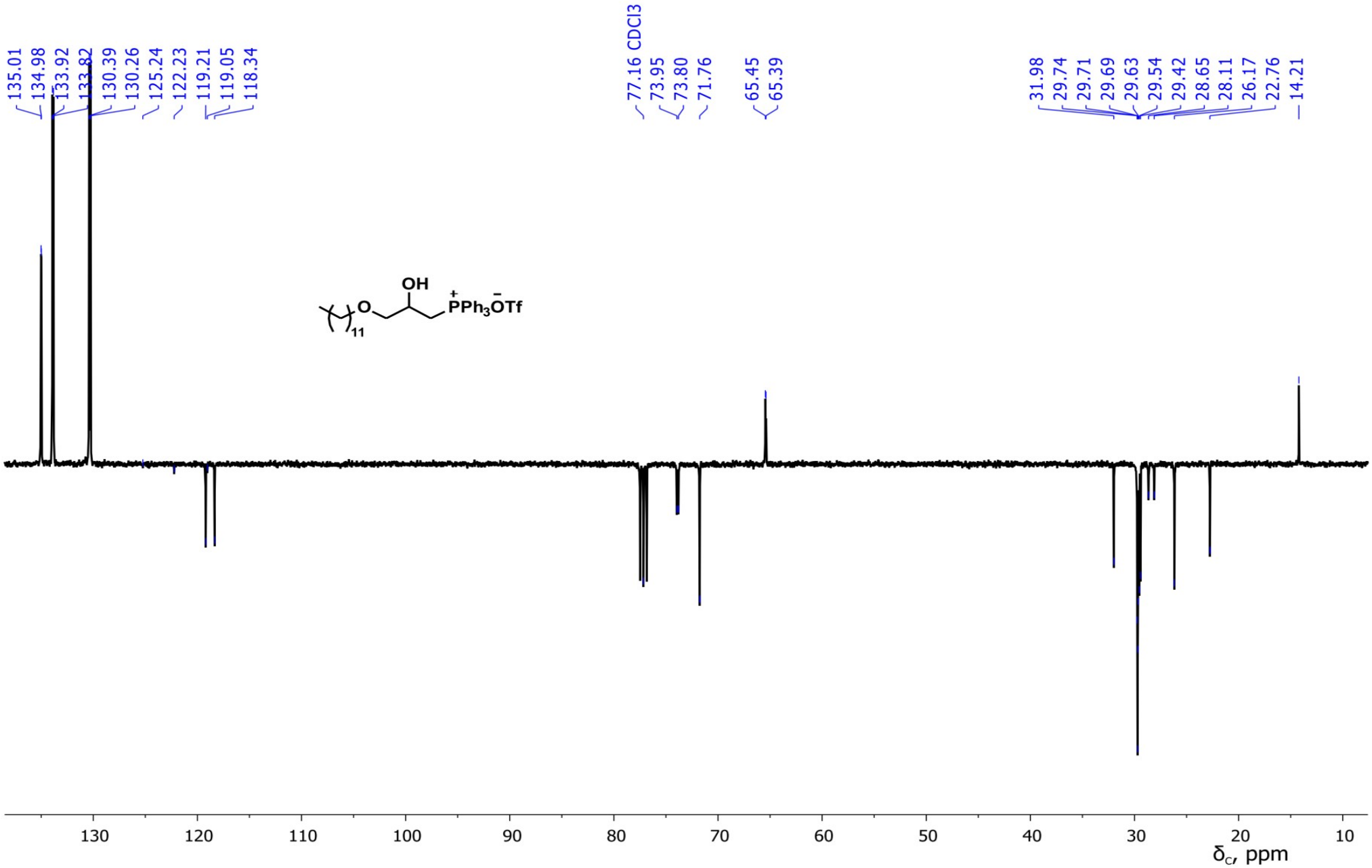

Figure S76. ^{13}C-{^{1}H} APT NMR spectrum (100.6 MHz, $CDCl_3$) of compound **3g**.

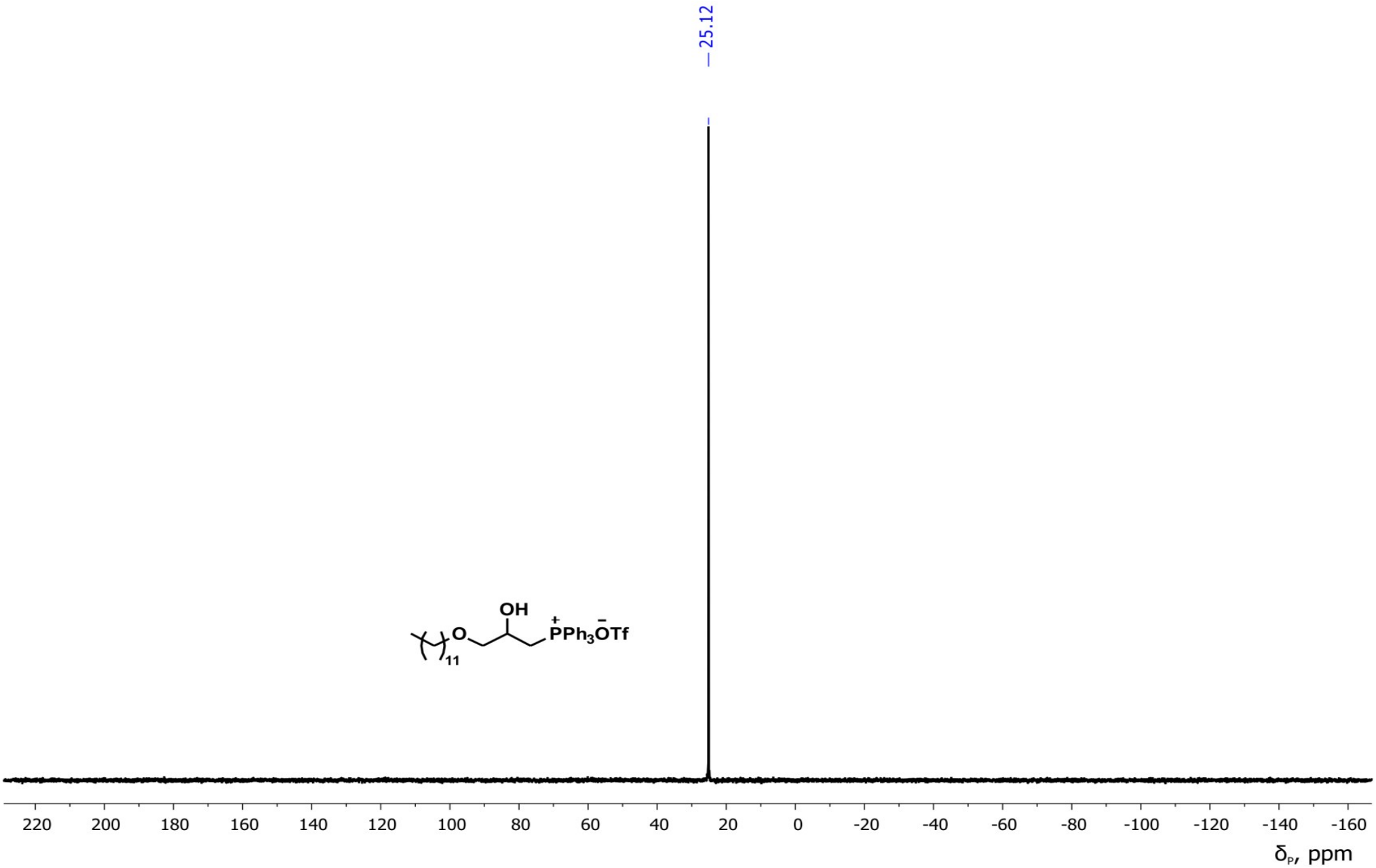

Figure S77. ^{31}P-{^{1}H} NMR spectrum (162 MHz, $CDCl_3$) of compound **3g**.

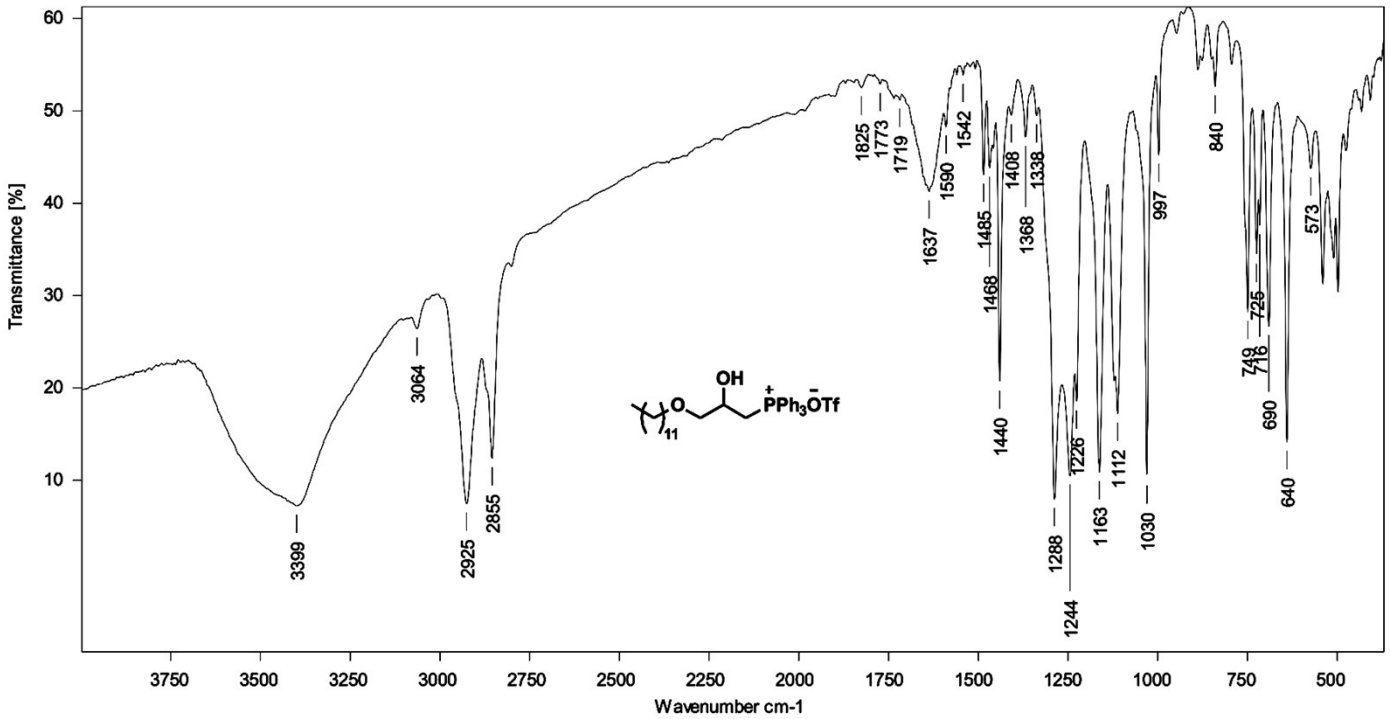

Figure S78. IR spectrum (KBr) of compound **3g**.

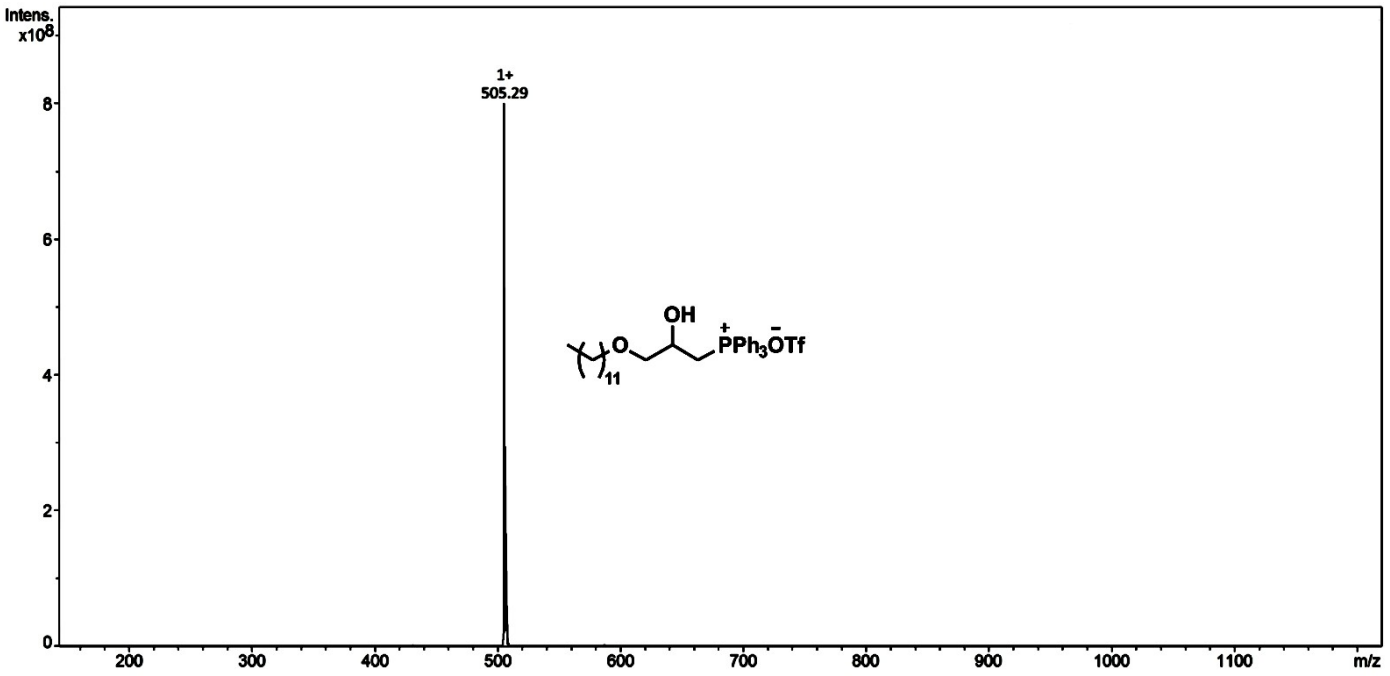

Figure S79. ESI-MS spectrum of compound **3g**.

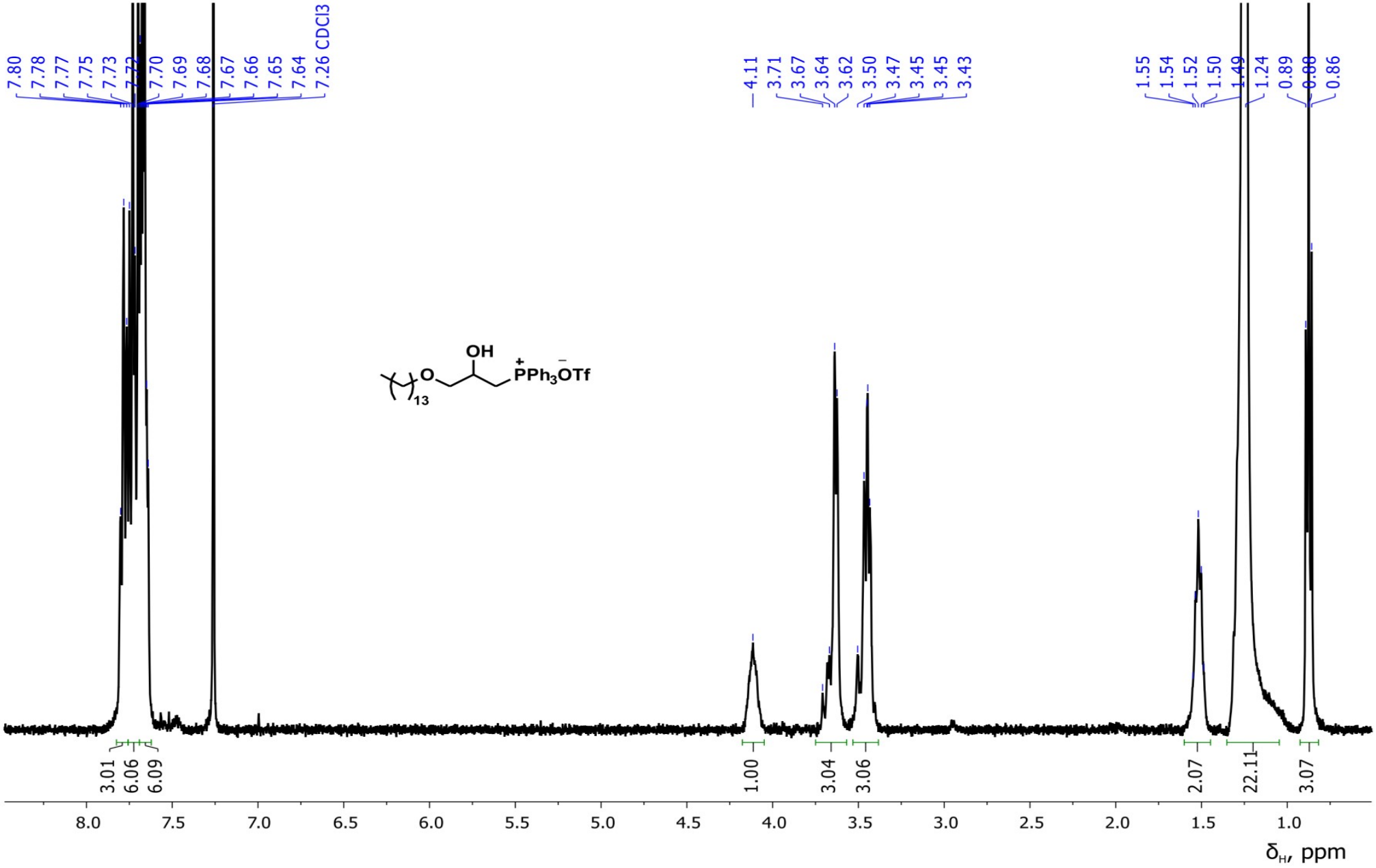

Figure S80. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3h**.

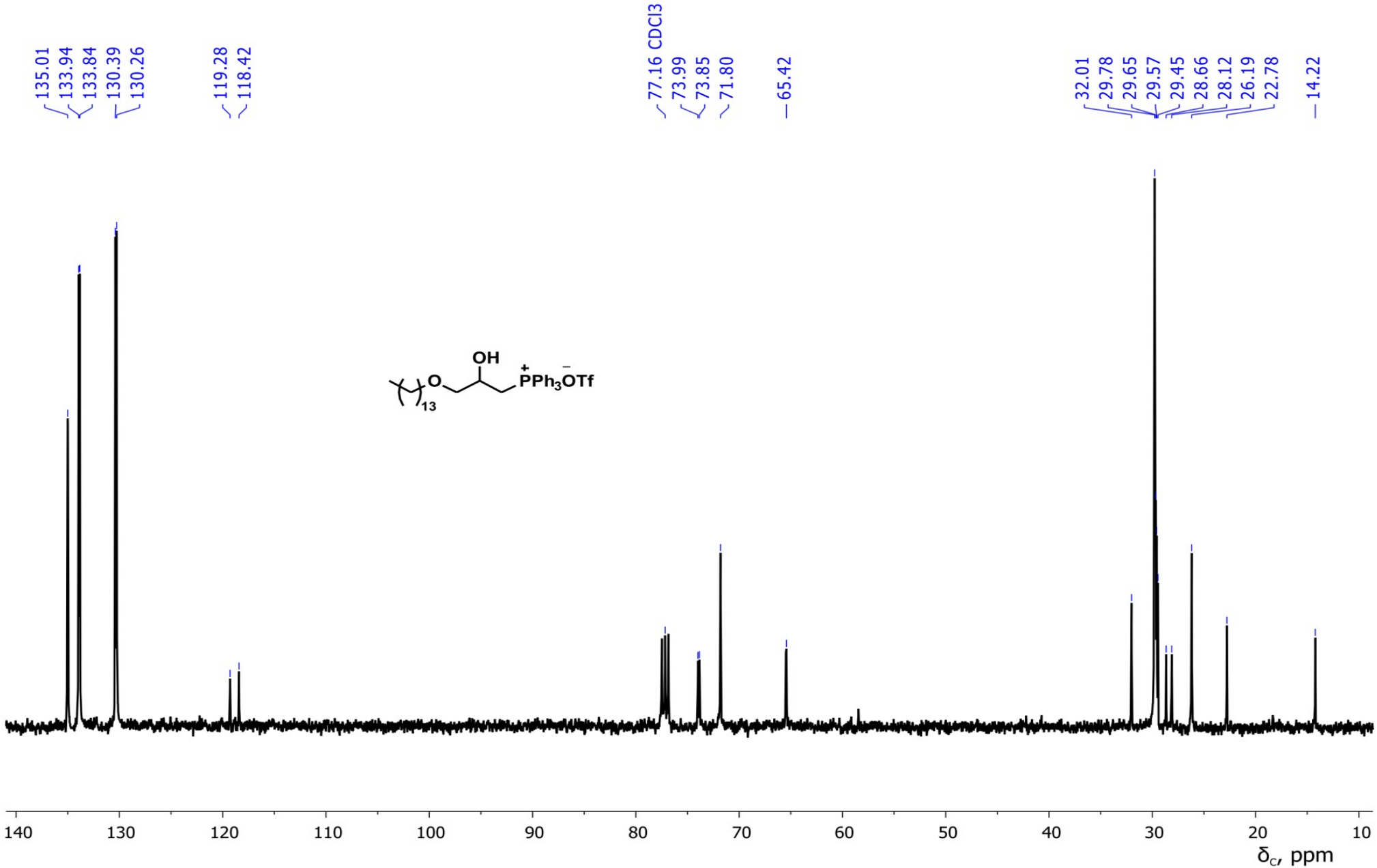

Figure S81. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of compound **3h**.

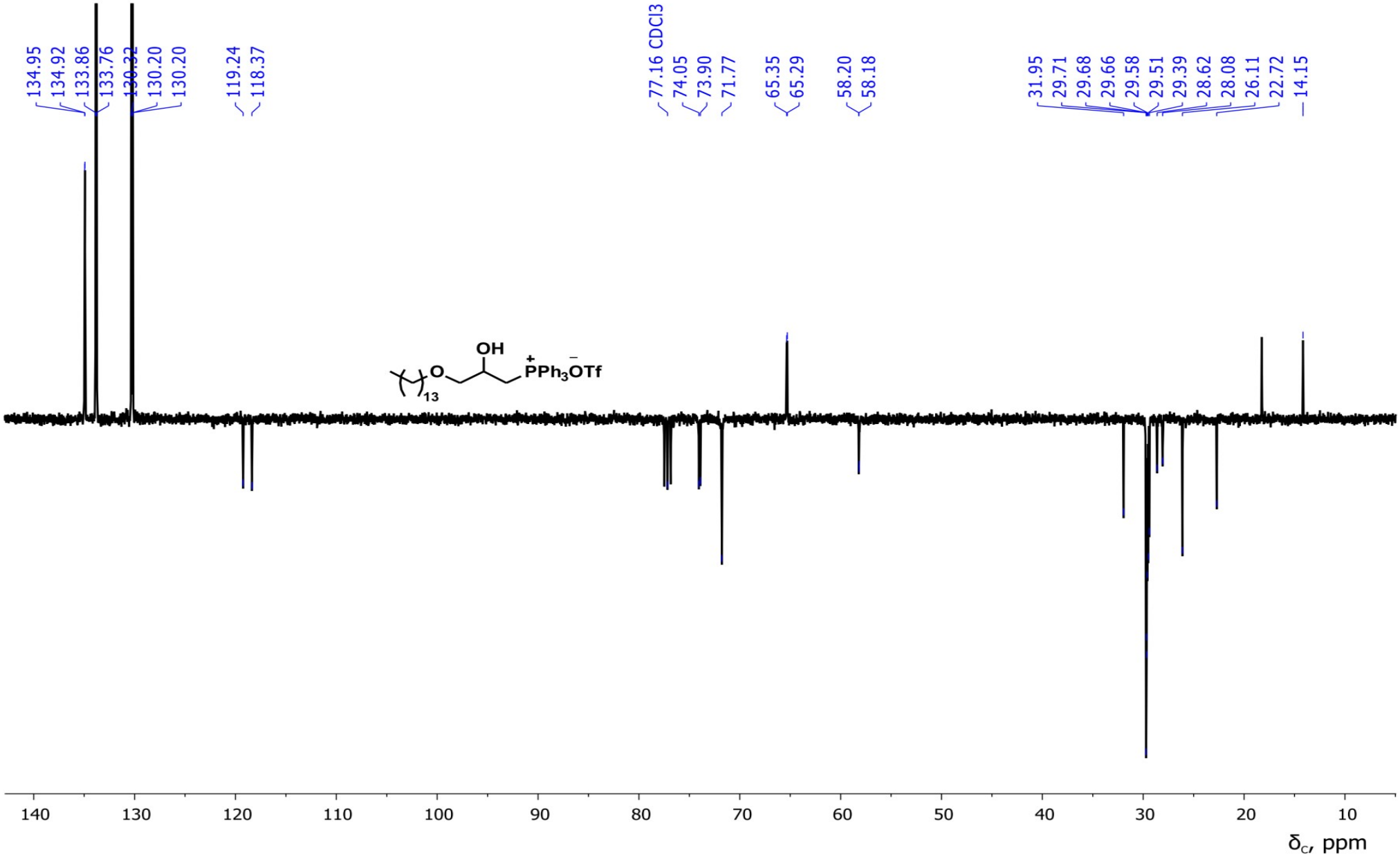

Figure S82. ^{13}C-{^{1}H} APT NMR spectrum (100.6 MHz, $CDCl_3$) of compound **3h**.

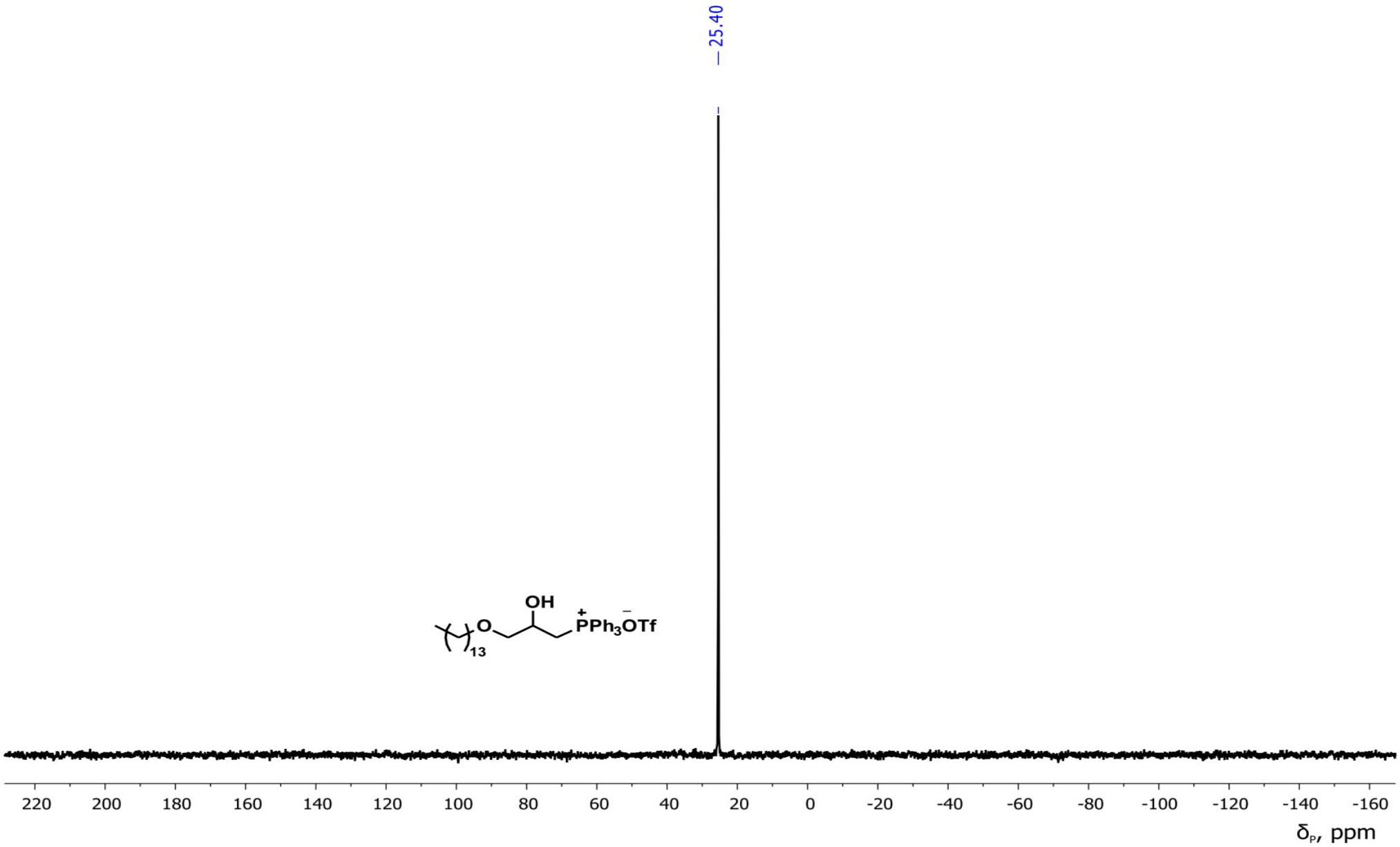

Figure S83. ^{31}P-{^{1}H} NMR spectrum (162 MHz, $CDCl_3$) of compound **3h**.

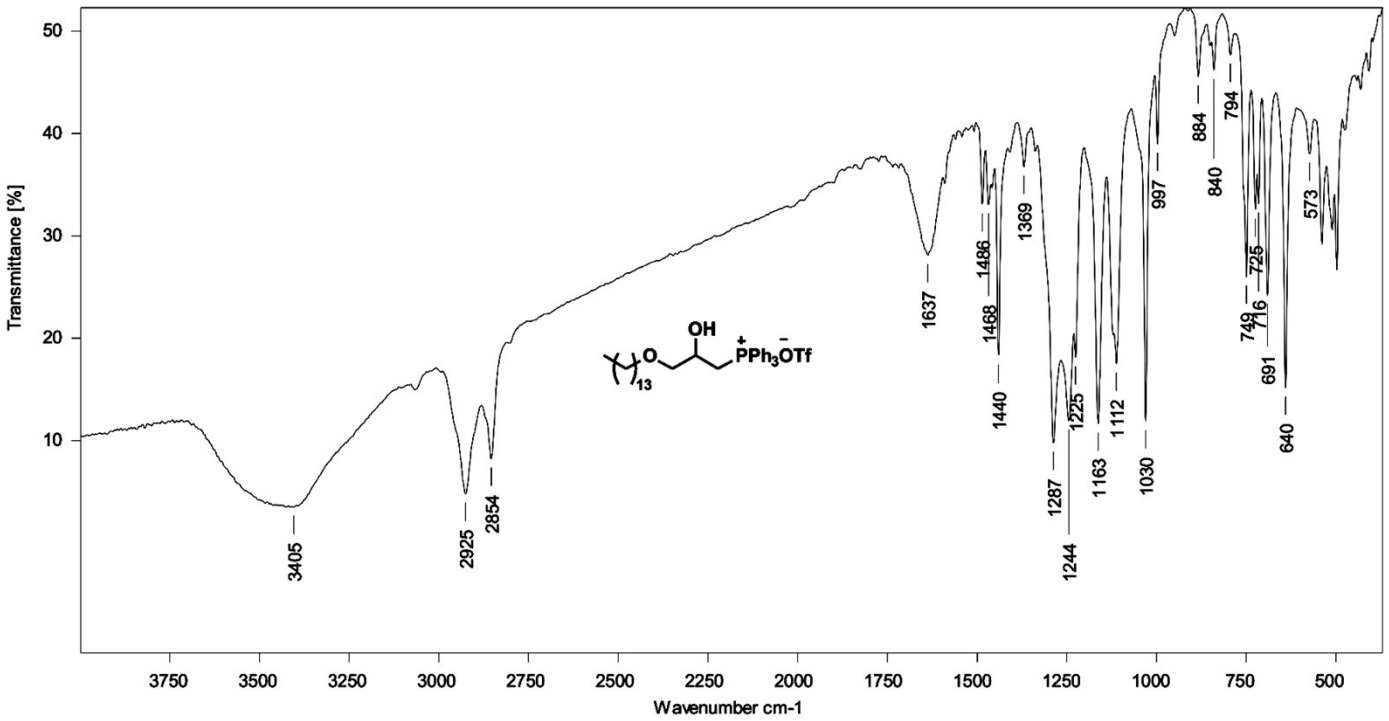

Figure S84. IR spectrum (KBr) of compound **3h**.

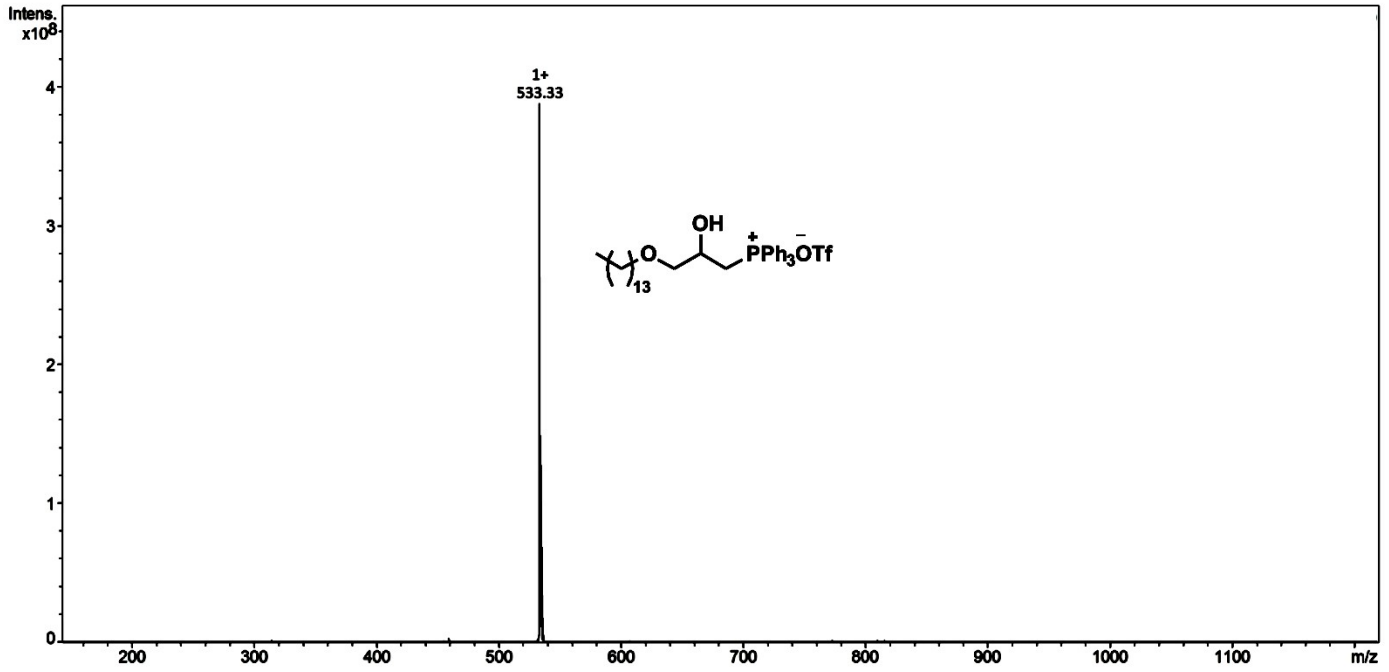

Figure S85. ESI-MS spectrum of compound **3h**.

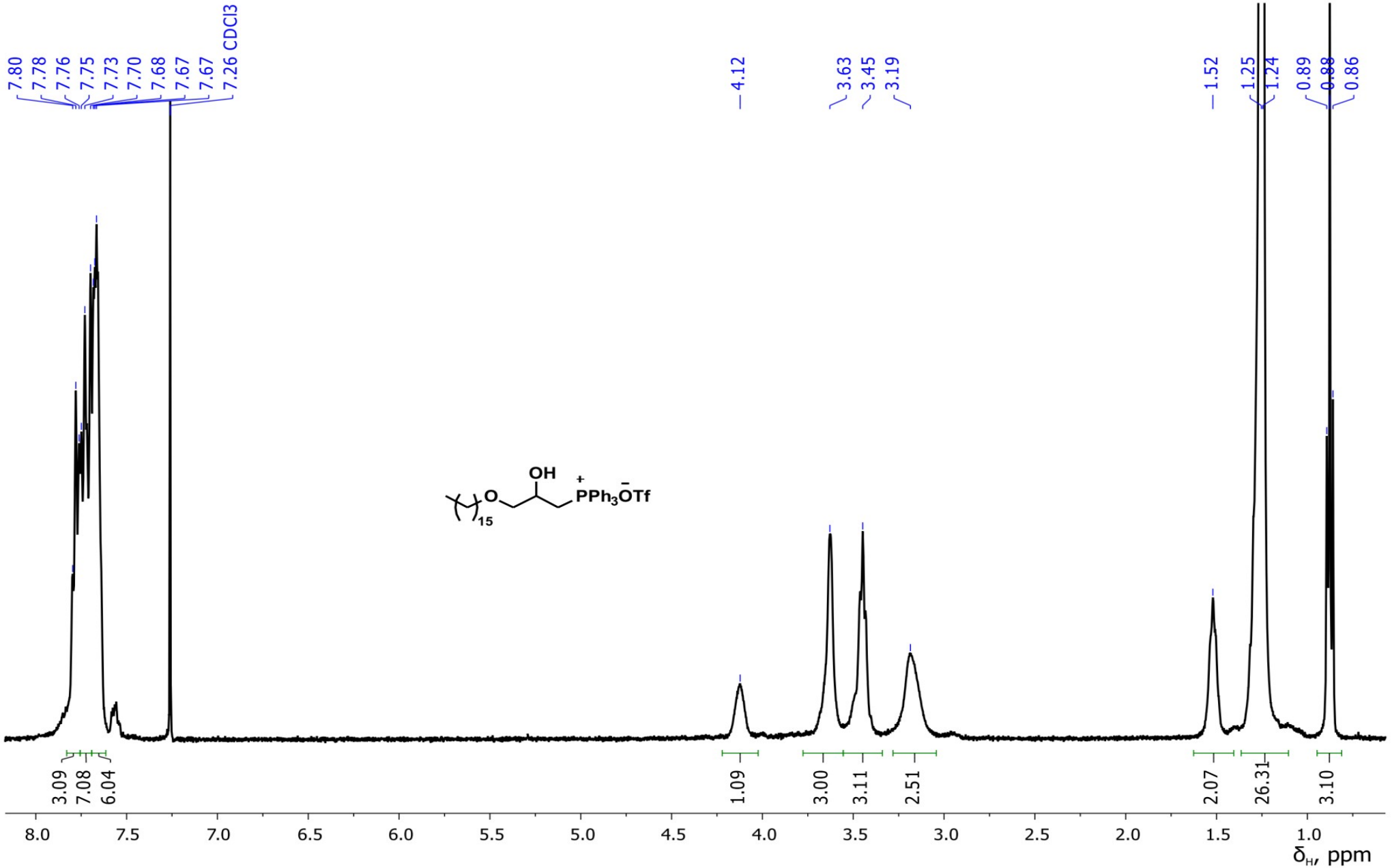

Figure S86. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3i**.

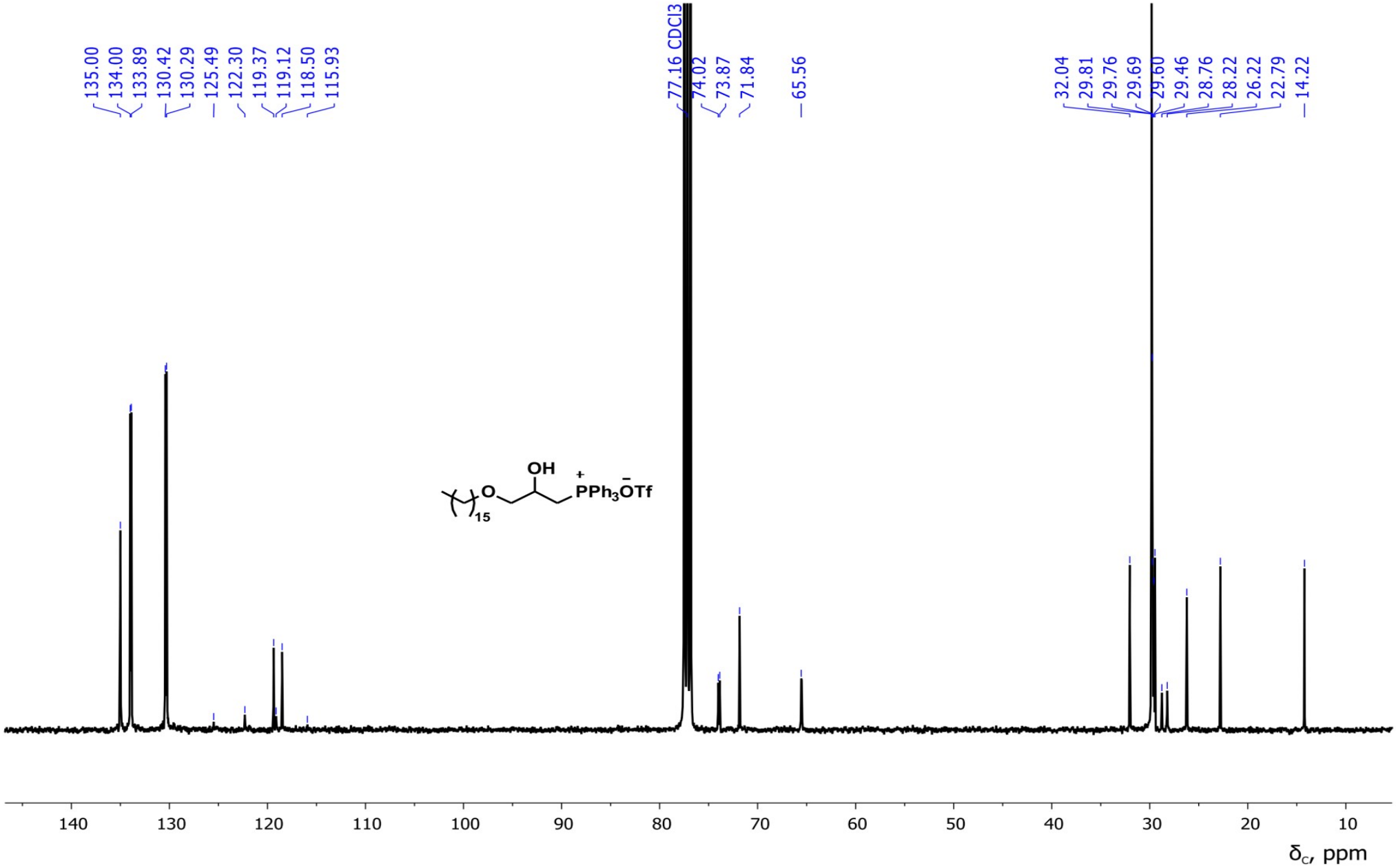

Figure S87. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of compound **3i**.

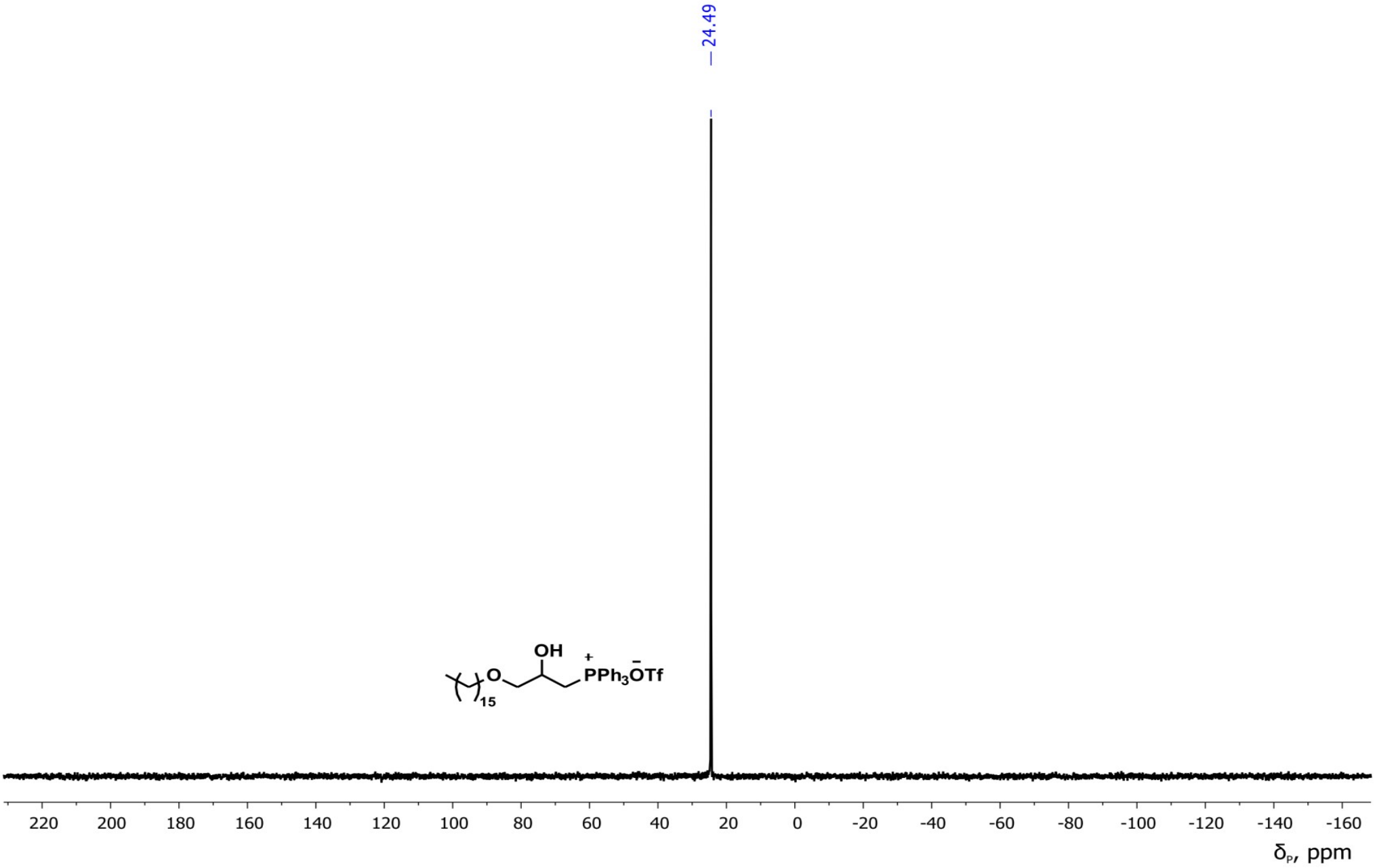

Figure S88. ^{31}P-{^{1}H} NMR spectrum (162 MHz, $CDCl_3$) of compound **3i**.

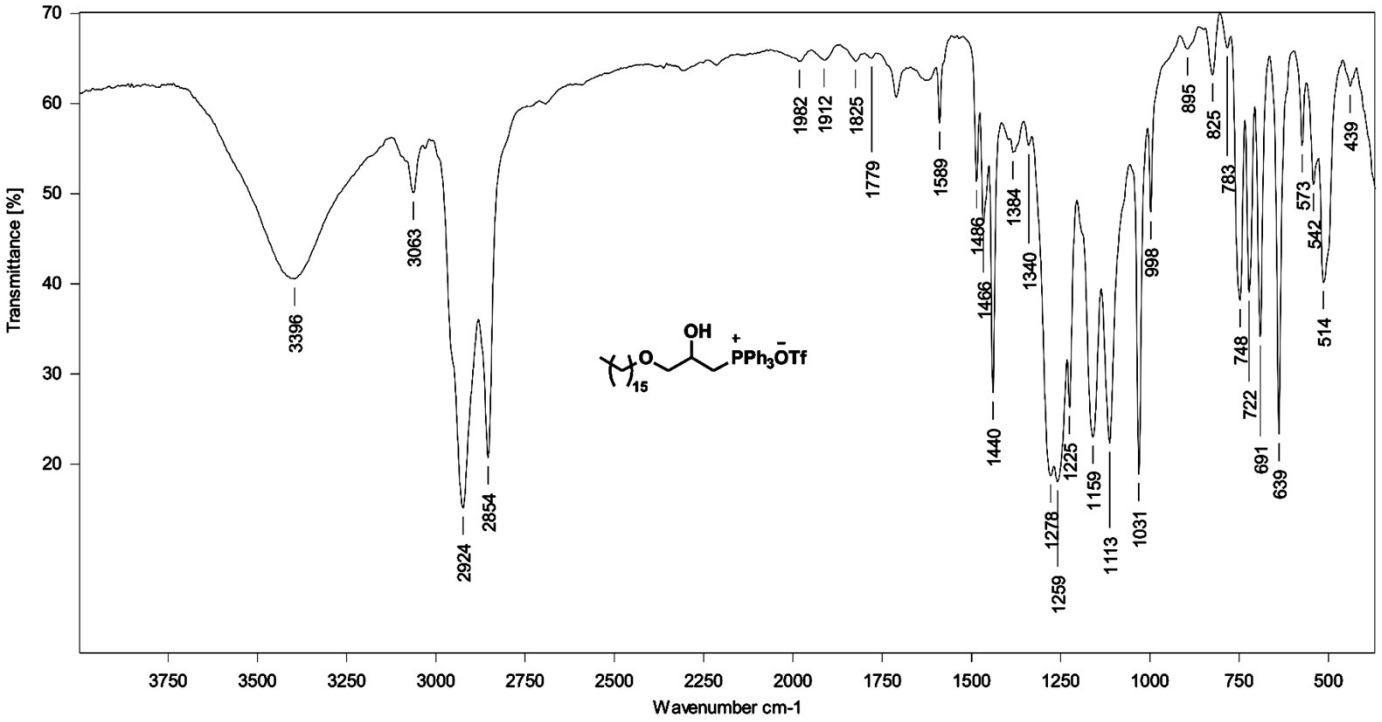

Figure S89. IR spectrum (KBr) of compound **3i**.

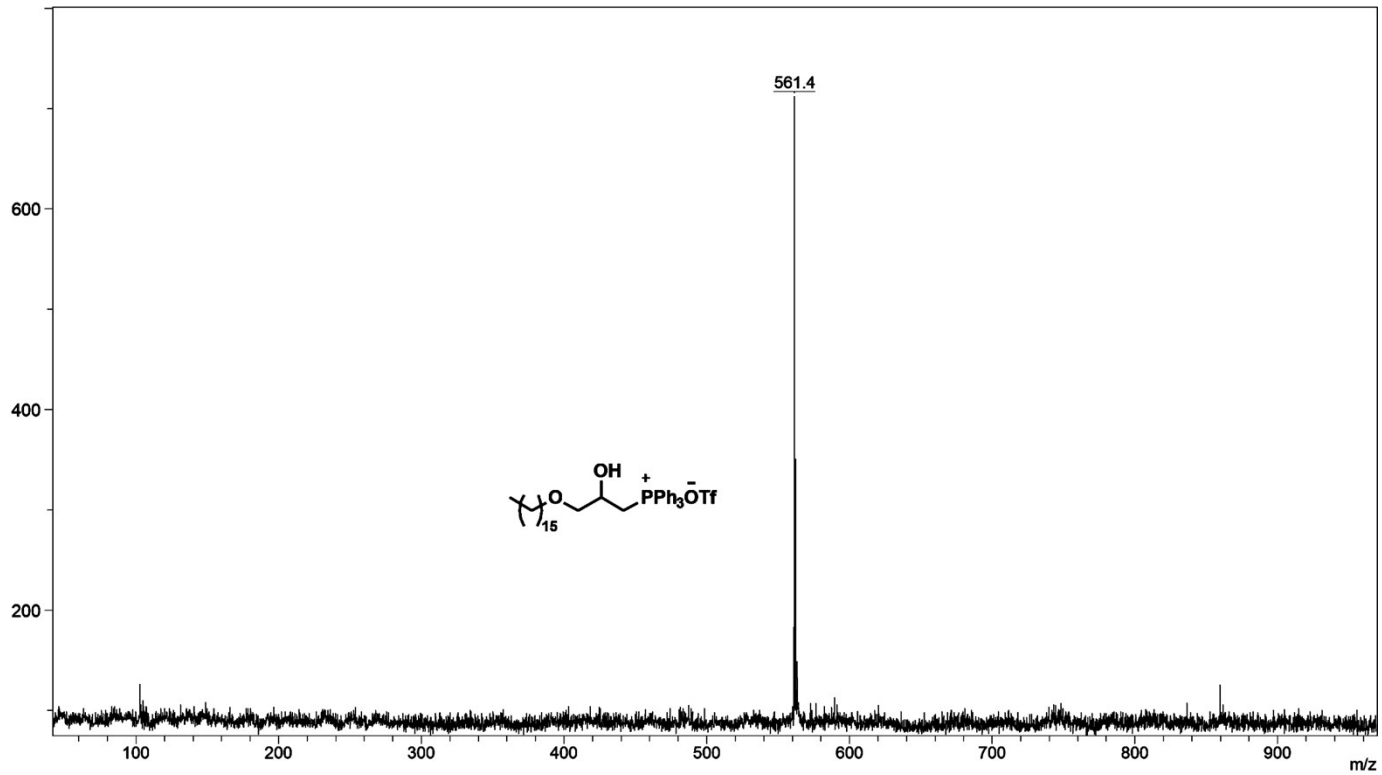

Figure S90. MALDI-MS spectrum of compound **3i**.

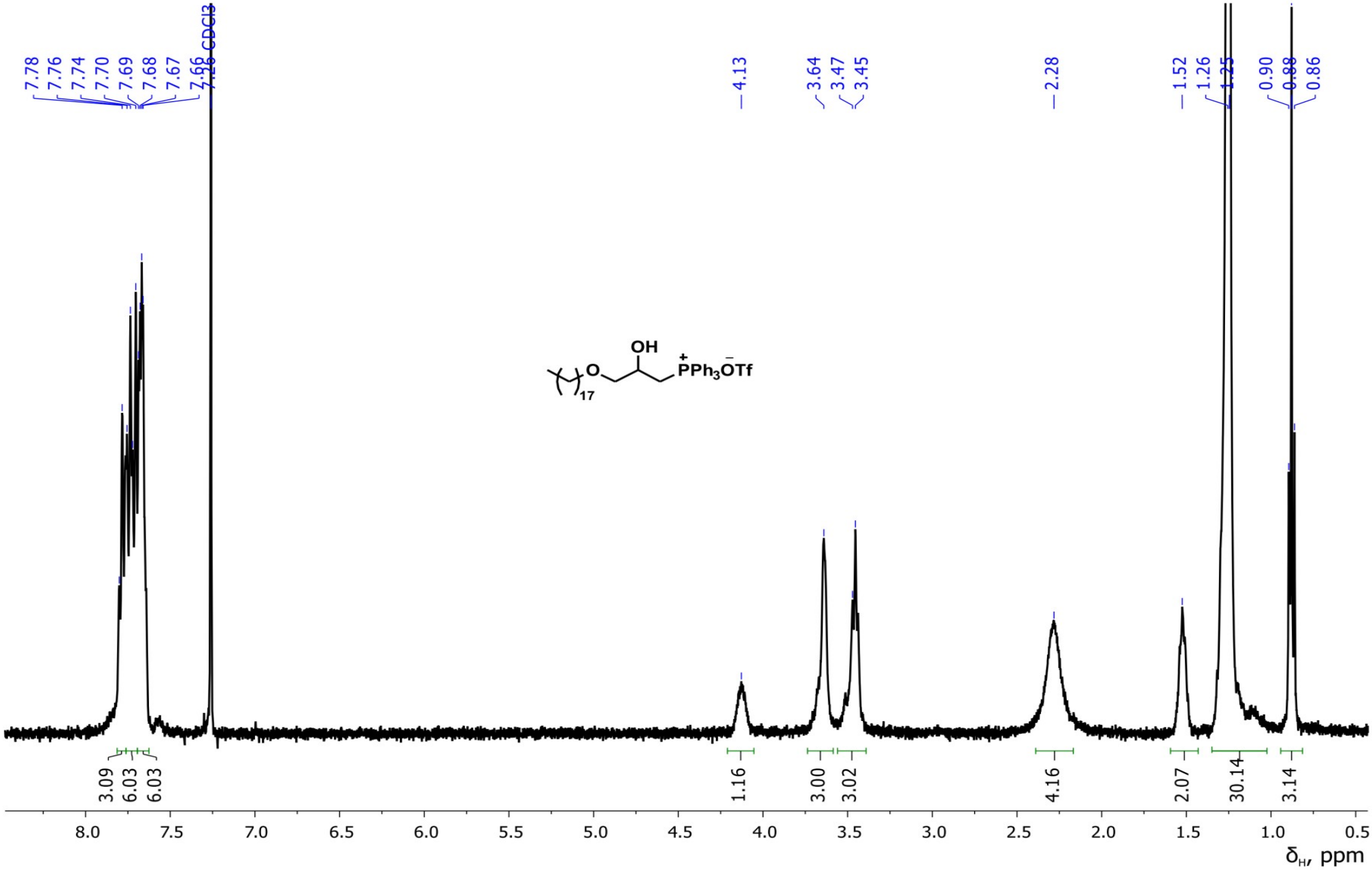

Figure S91. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3j**.

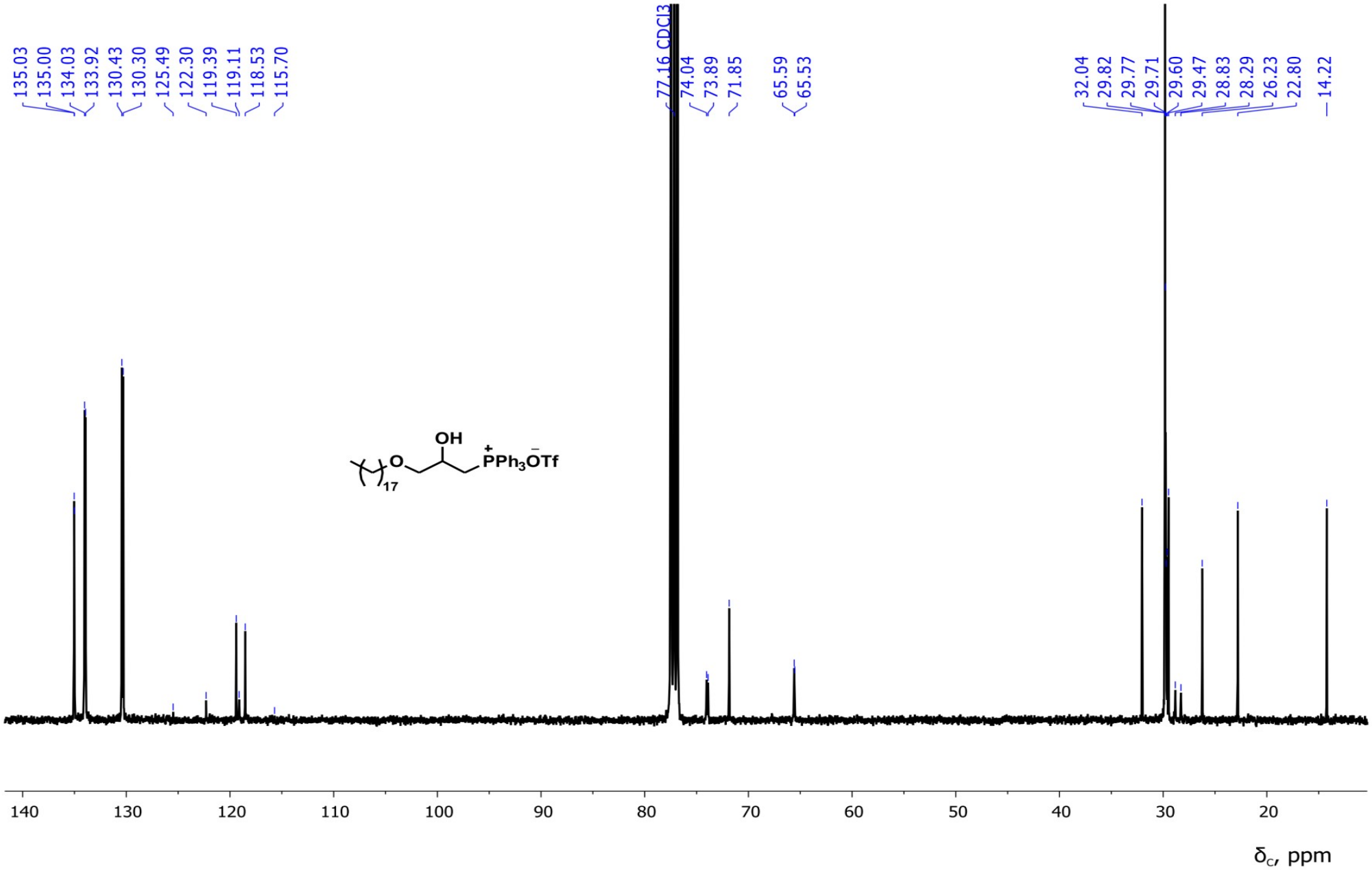

Figure S92. ^{13}C-{^{1}H} NMR spectrum (100.6 MHz, $CDCl_3$) of compound **3j.**

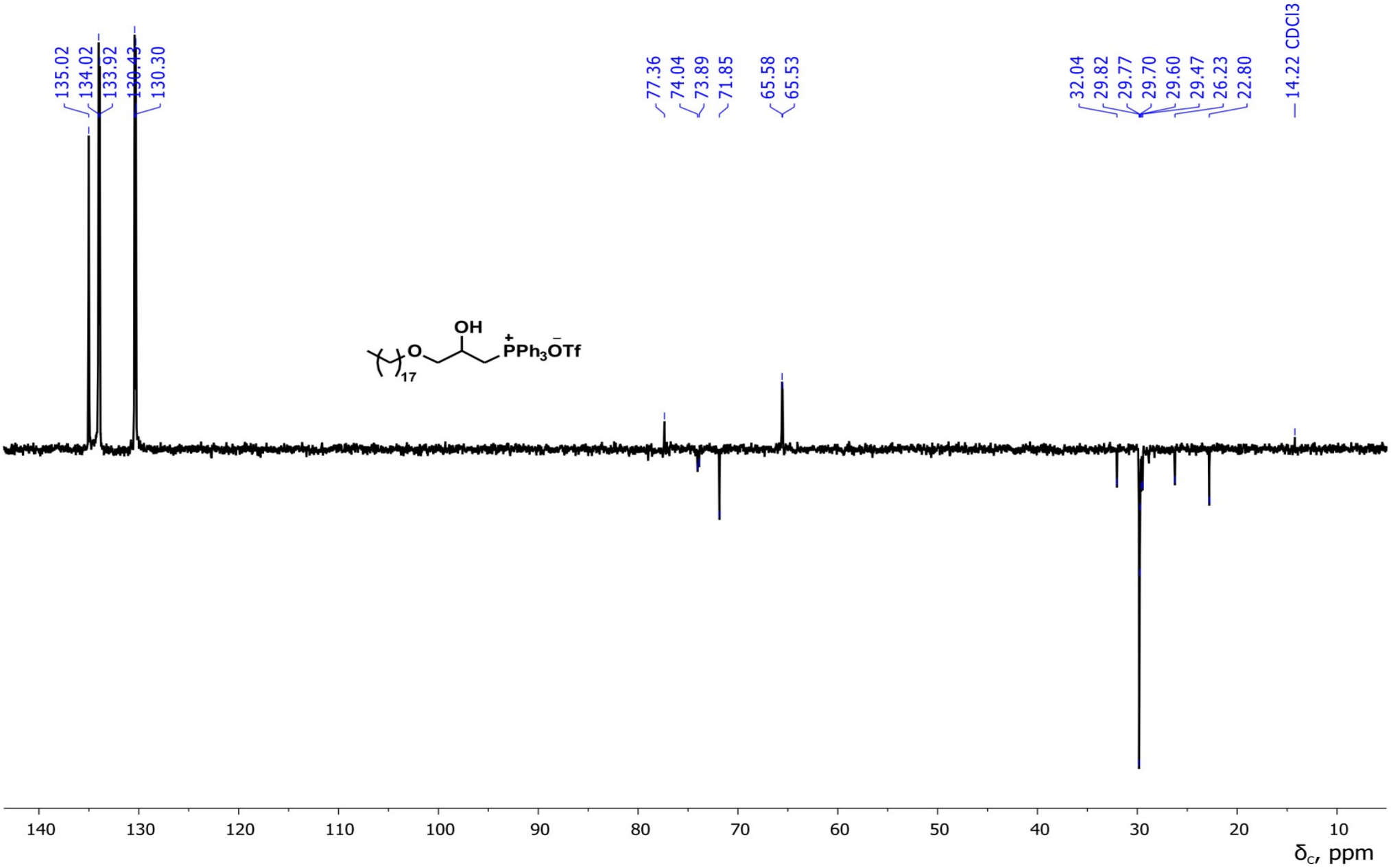

Figure S93. ^{13}C-{^{1}H} APT NMR spectrum (100.6 MHz, $CDCl_3$) of compound **3j**.

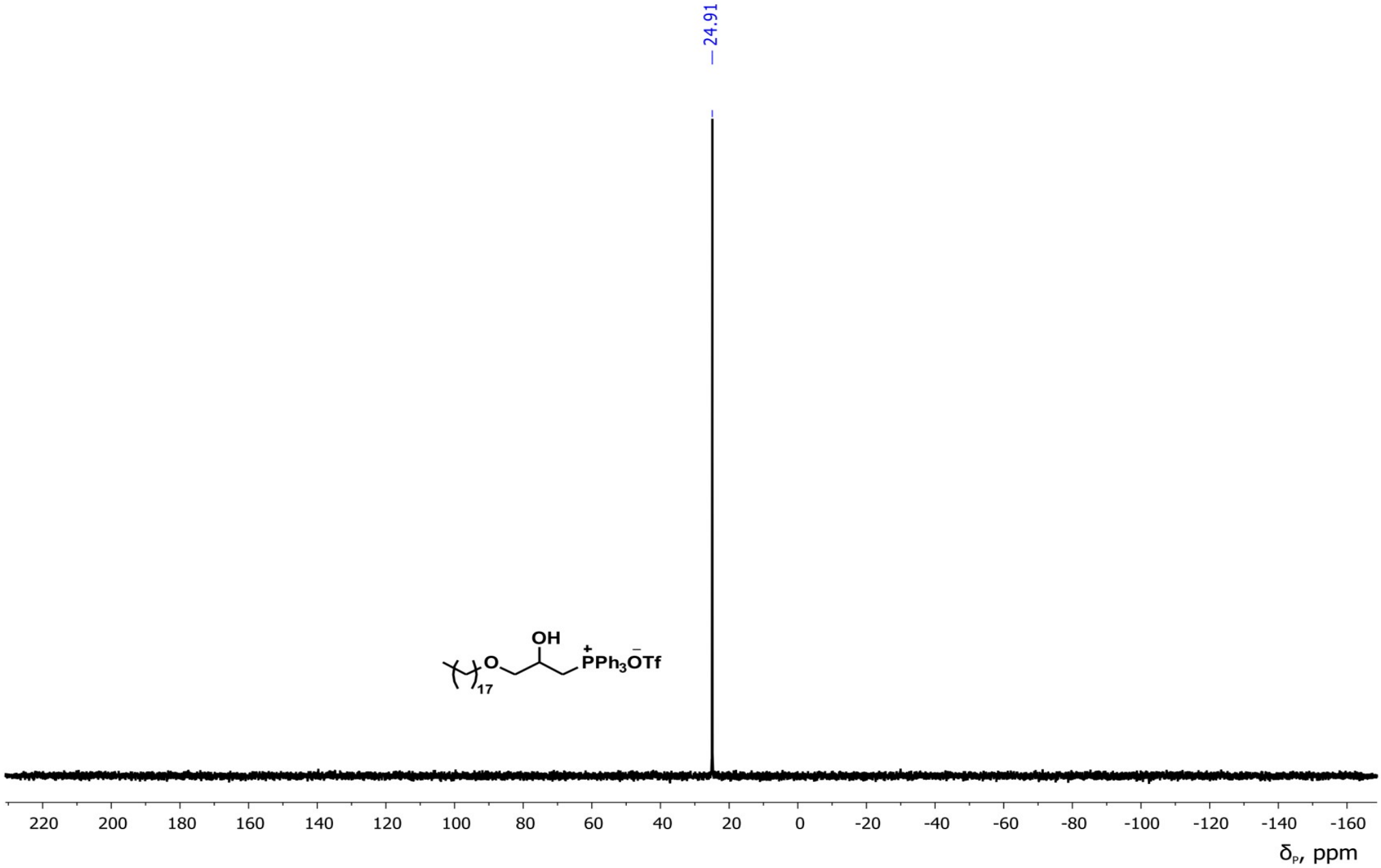

Figure S94. ^{31}P-{^{1}H} NMR spectrum (162 MHz, $CDCl_3$) of compound **3j**.

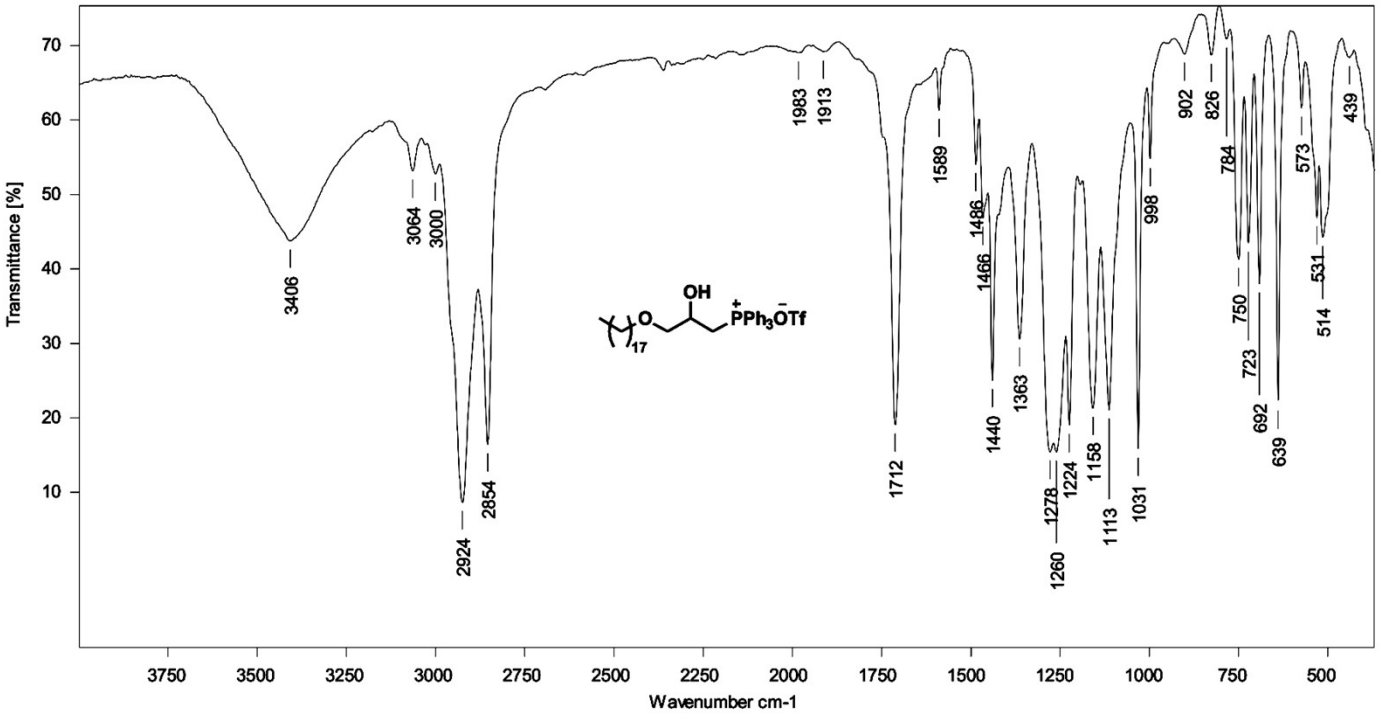

Figure S95. IR spectrum (KBr) of compound **3j**.

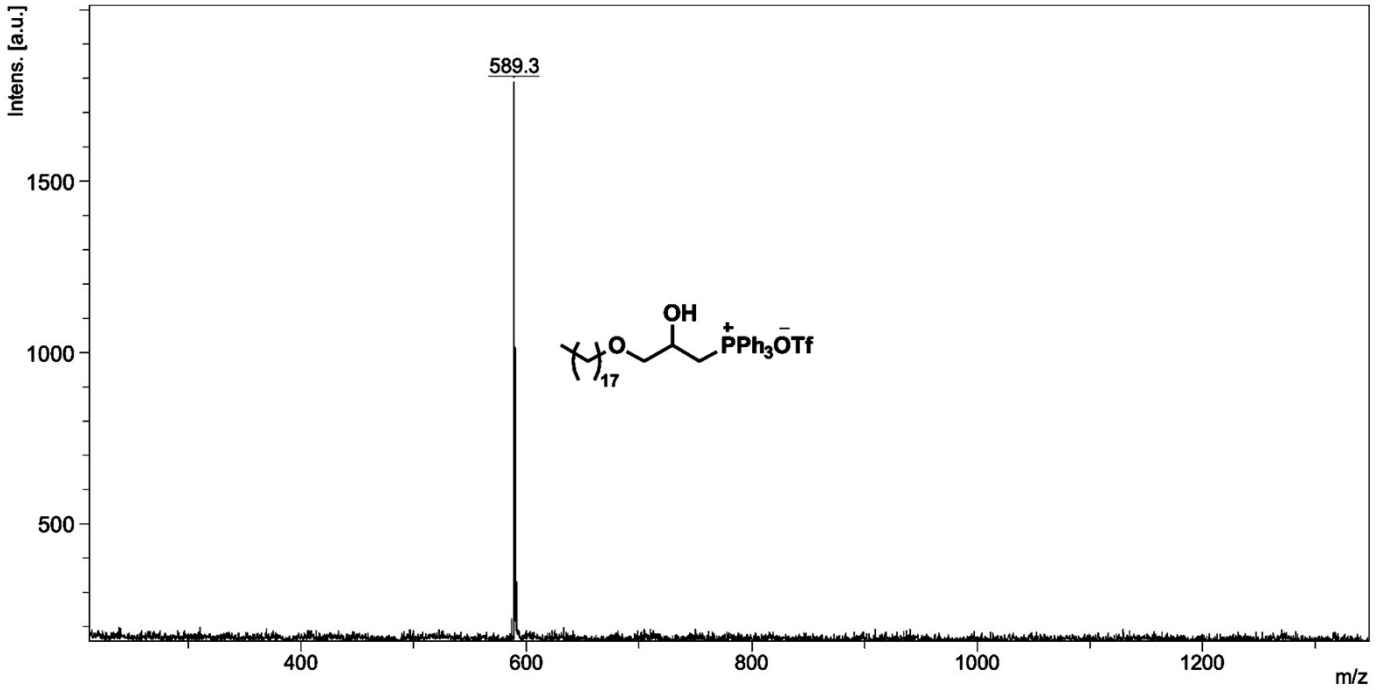

Figure S96. MALDI-MS spectrum of compound **3j**.

Table S1

Synthesis 2-hydroxyphosphonium salts by epoxy ring-opening reaction

Compound	R	Yield, %	Melting point (Tm), °C	Krafft temperature, °C
3a[21]	CH_3	78[21]	122–124[21]	–
3b[21]	C_2H_5	77[21]	99–101[21]	–
3c	n-C_4H_9	89	109	–
3d	n-C_6H_{13}	73	90	–
3e	n-C_8H_{17}	80	79–80	–
3f[21]	n-$C_{10}H_{21}$	75[21]	78–79[21]	70
3g	n-$C_{12}H_{25}$	84	73–74	36
3h	n-$C_{14}H_{29}$	87	70–72	58
3i	n-$C_{16}H_{33}$	79	67	68
3j	n-$C_{18}H_{37}$	78	69–70	68
4[21]	n-$C_{10}H_{21}$	–	75–77[21]	73
5	n-$C_{10}H_{21}$	–	<20	76

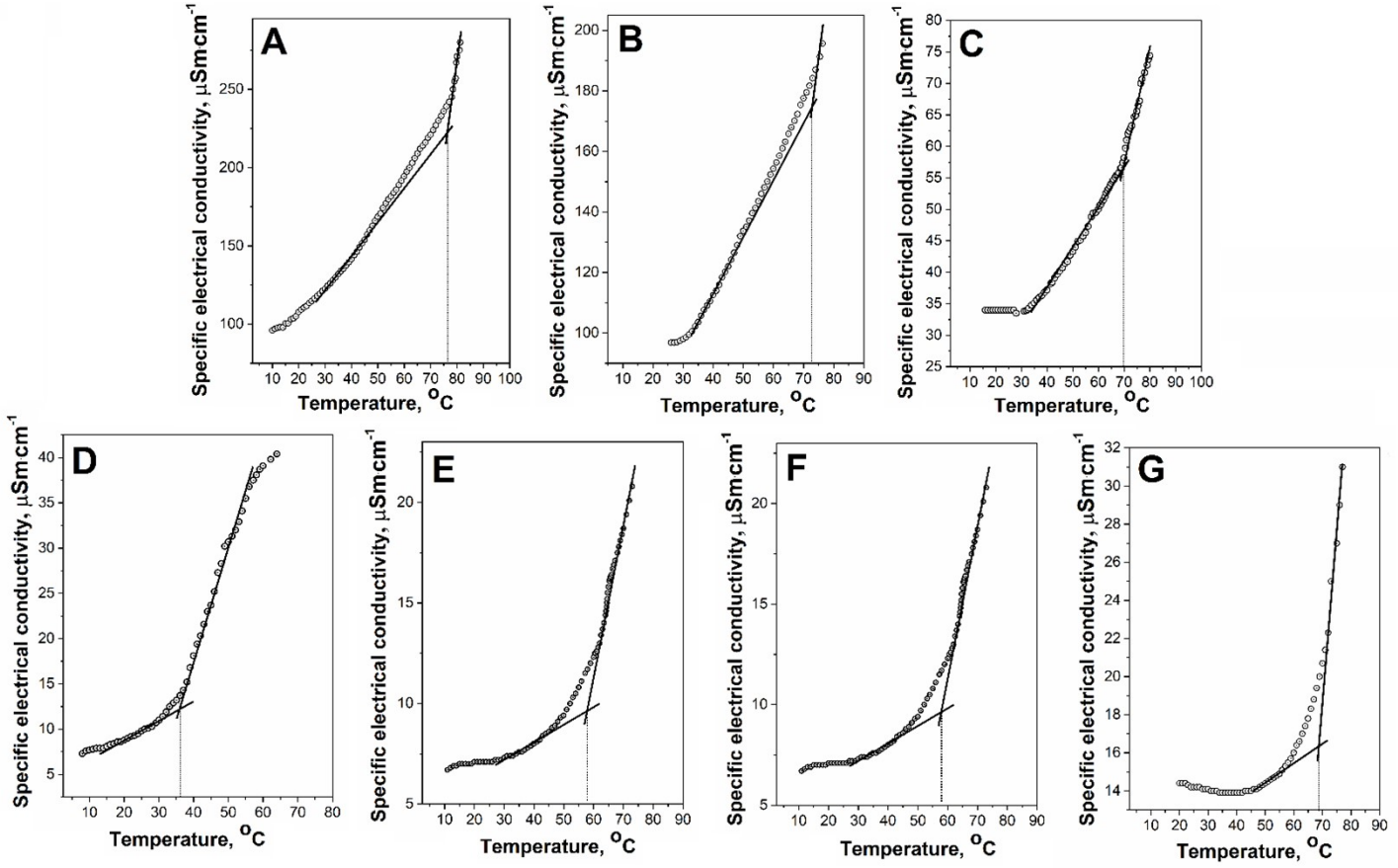

Figure S97. Specific electroconductivity of water solutions of **5** (A), **4** (B), **3f** (C), **3g** (D), **3h** (E), **3i** (F), **3j** (G) as a function of temperature.

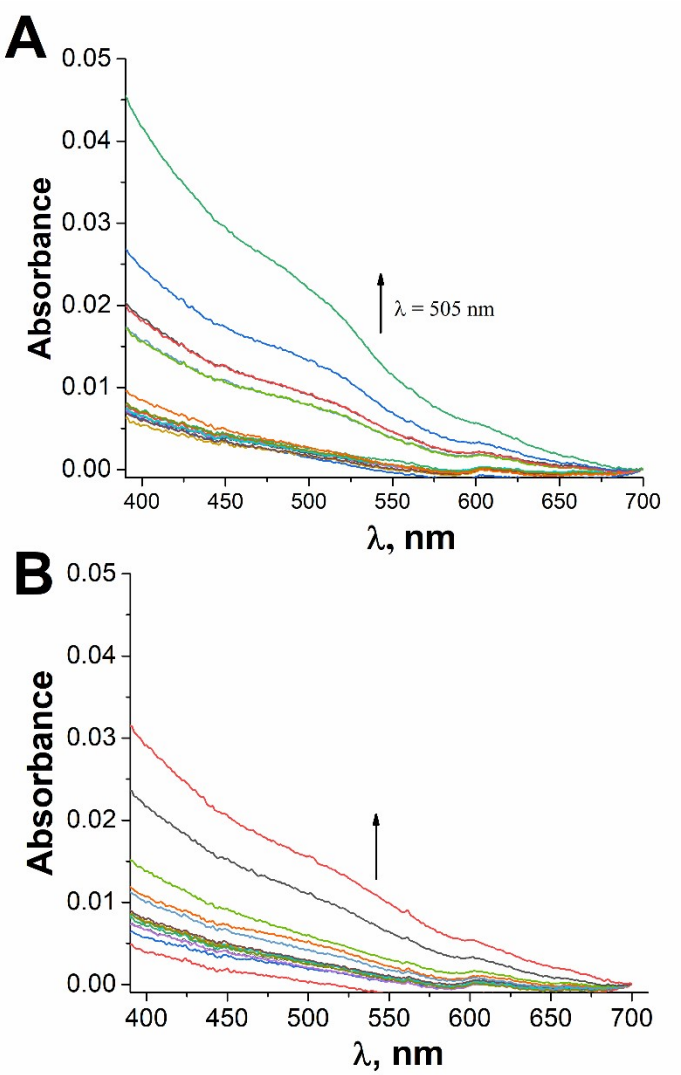

Figure S98. Absorption profile of Sudan I in solutions of **3g** (A), **3h** (B) with increasing their concentrations, L=1cm.

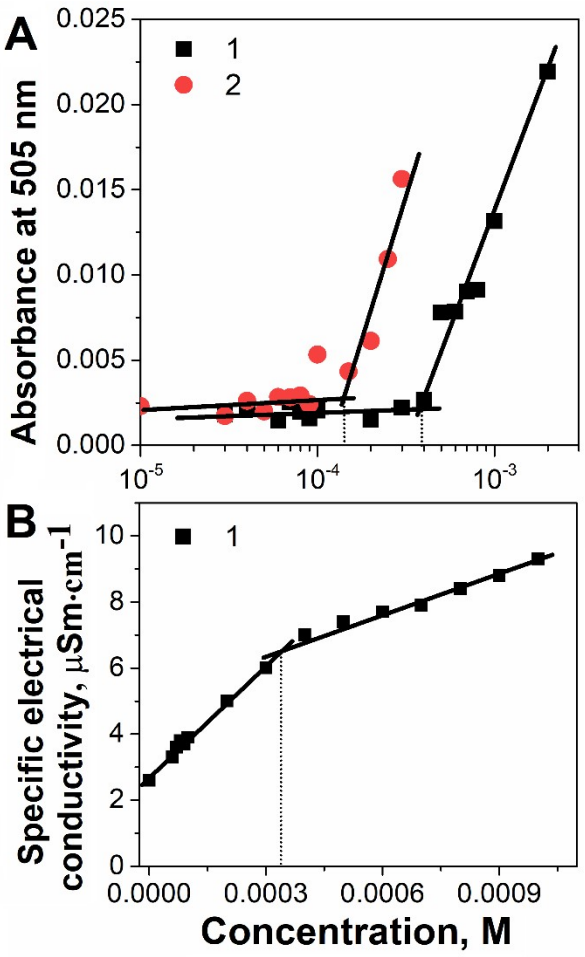

Figure S99. (A) Absorbance of Sudan I in solutions of **3g** (1) and **3h** (2) L = 1cm, λ =505 nm; (B) Change in specific electrical conductivity of **3g** solutions (1), 45 ºC (1) and 60 ºC (2).

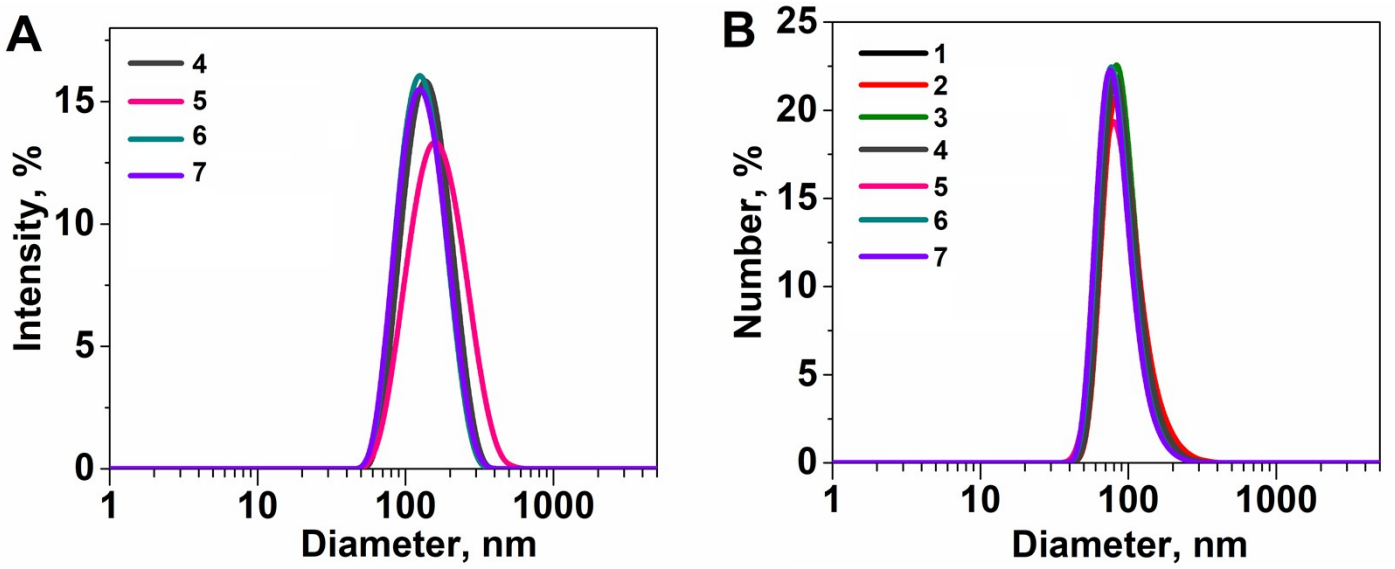

Figure S100. Particle size distribution using the intensity (A) and the number parameters (B) of PC/**3g**-liposomes (1, 4), RhB-loaded PC/**3g**-liposomes (2, 5), 3 – SPC/Ch/PEG/**3g**-liposomes (3, 6, 7), where 1, 2, 3 are samples measured on the first day of preparation and 4, 5, 6, 7 are samples after 5 months of storage, a stock diluted 20 times by water and 7 is diluted 20 times in 10 mM Tris buffer, pH = 7.4, $C_{\mathbf{3g,\ 3h}}$ = 0.05 % (w/w), 25°C.

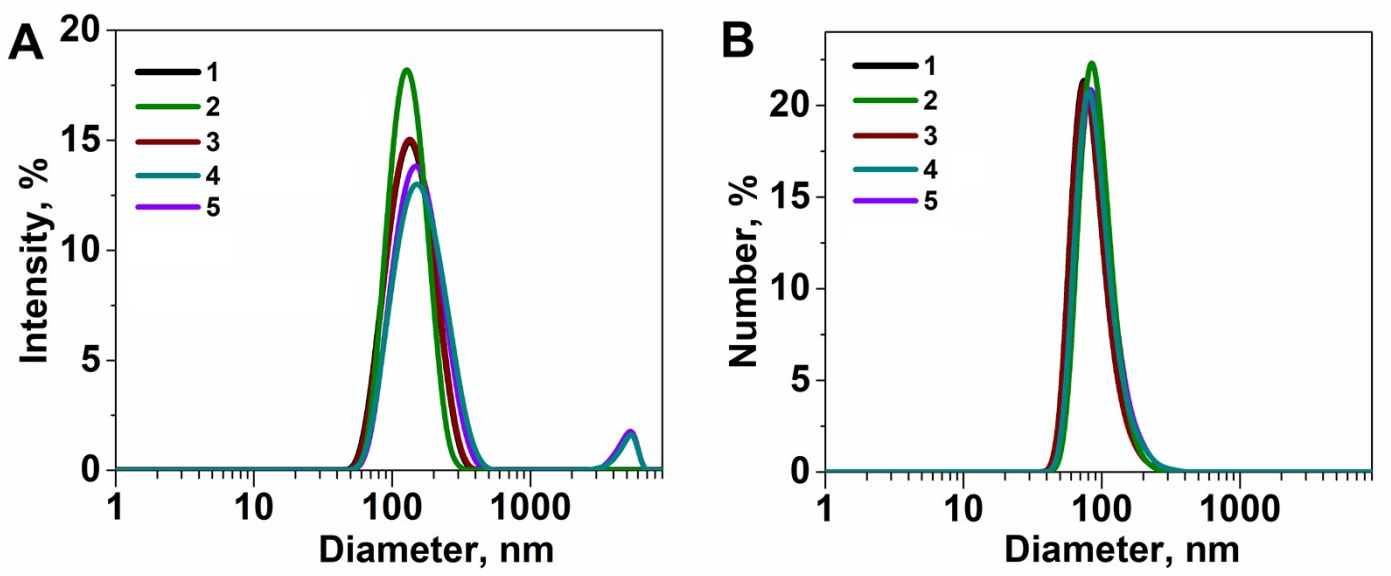

Figure S101. Particle size distribution using the intensity (A) and the number parameters (B) of PC/**3h**-liposomes (1, 3), SPC/Ch/PEG/**3h**-liposomes (2, 4, 5), where 1, 2 are samples measured on the first day of preparation and 3, 4, 5 are samples after 5 months of storage, a stock diluted 20 times by water and 5 is diluted 20 times in 10 mM Tris buffer, pH = 7.4, $C_{\mathbf{3g,\ 3h}}$ = 0.05 % (w/w), 25 ºC.

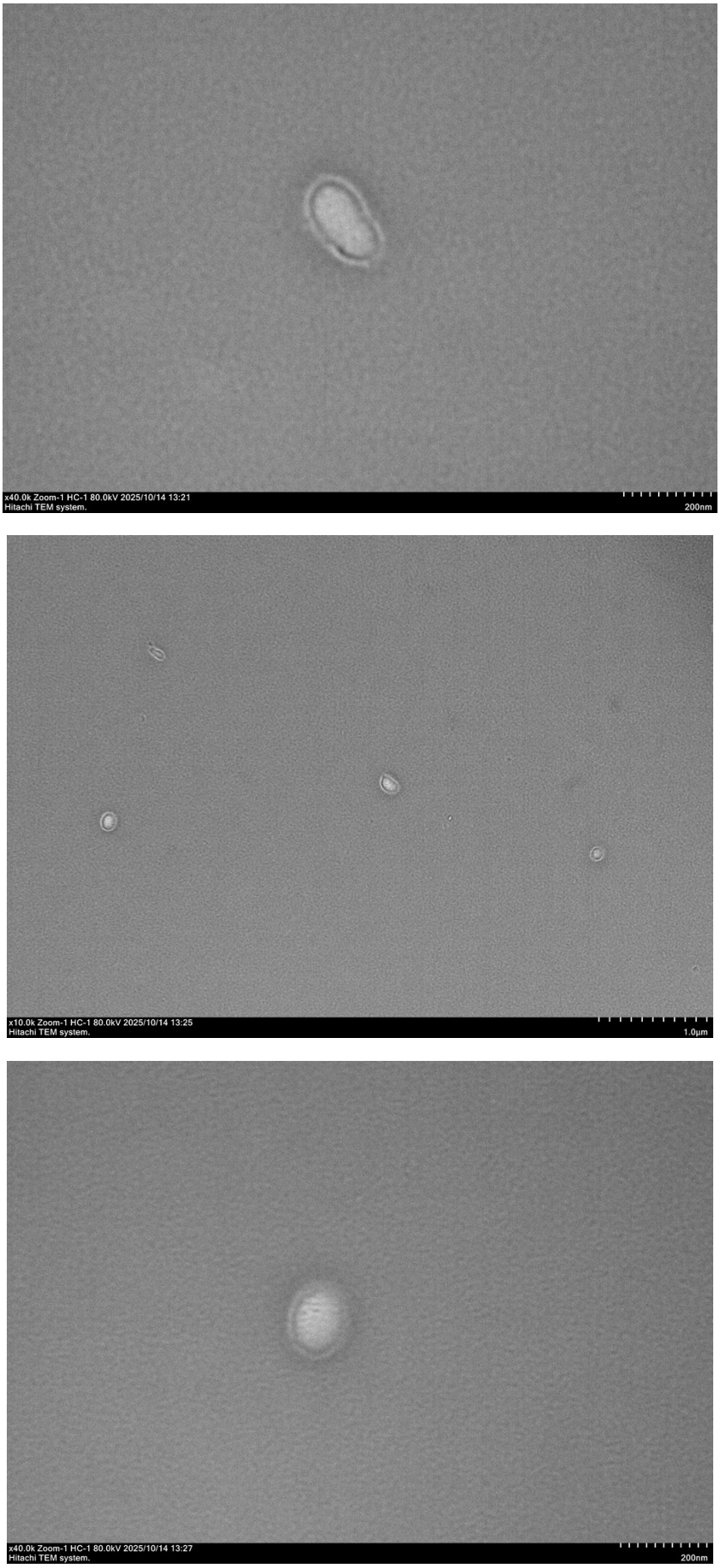

Figure S102. TEM imaging of SPC/Ch/PEG/**3g**-liposomes, a stock diluted 1000 times in 10 mM Tris buffer, pH = 7.4.

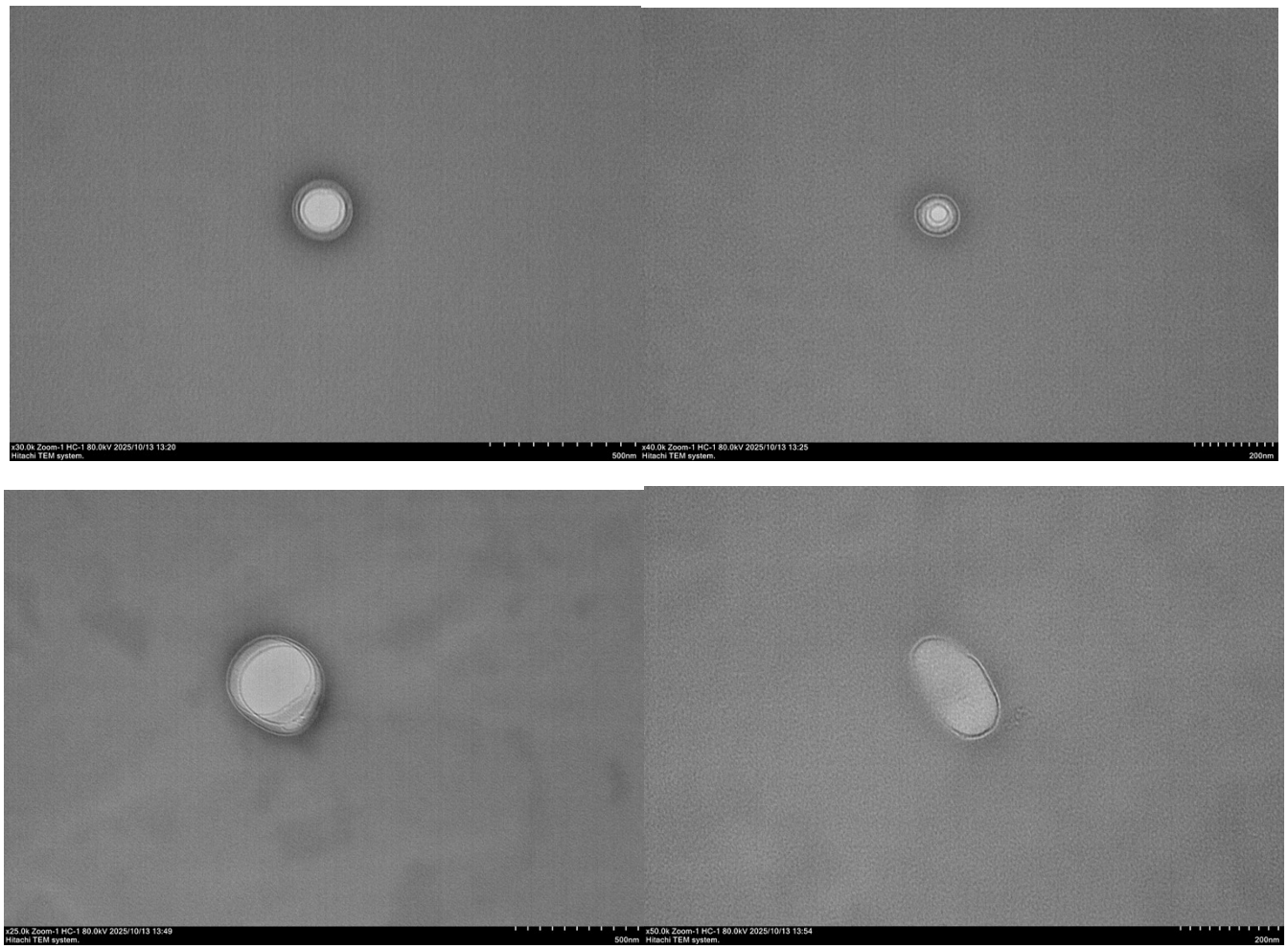

Figure S103. TEM imaging of SPC/Ch/PEG/**3h**-liposomes, a stock diluted 1000 times in 10 mM Tris buffer, pH = 7.4.

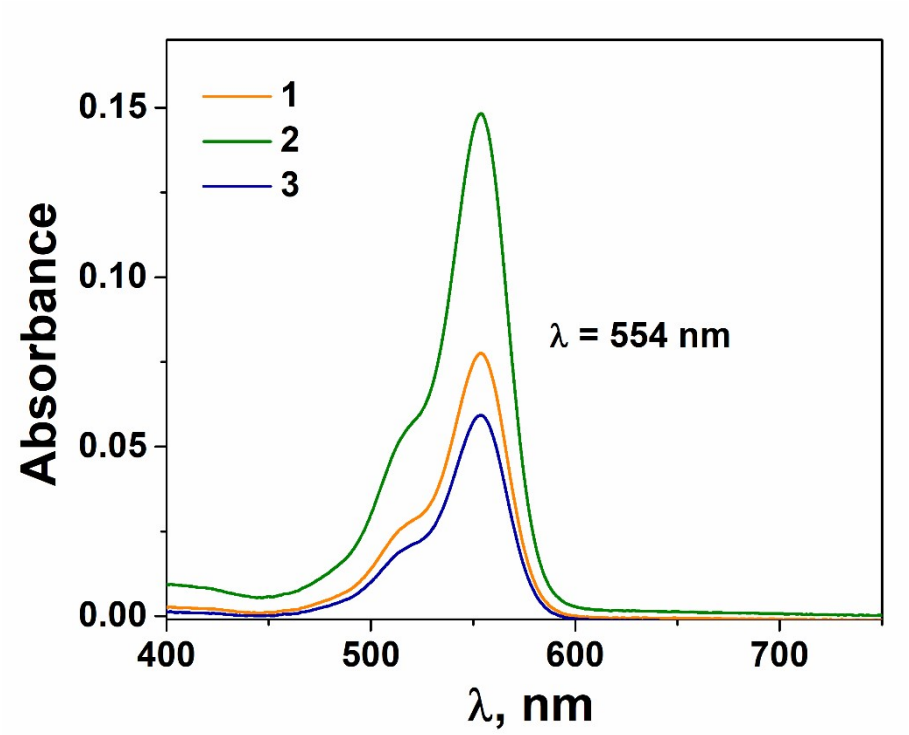

Figure S104. Absorbance spectra of RhB after ultracentrifugation of RhB-loaded PC/**3g**-liposomes in 0.025 phosphate buffer, pH=7.4, L=1cm, 25°C.

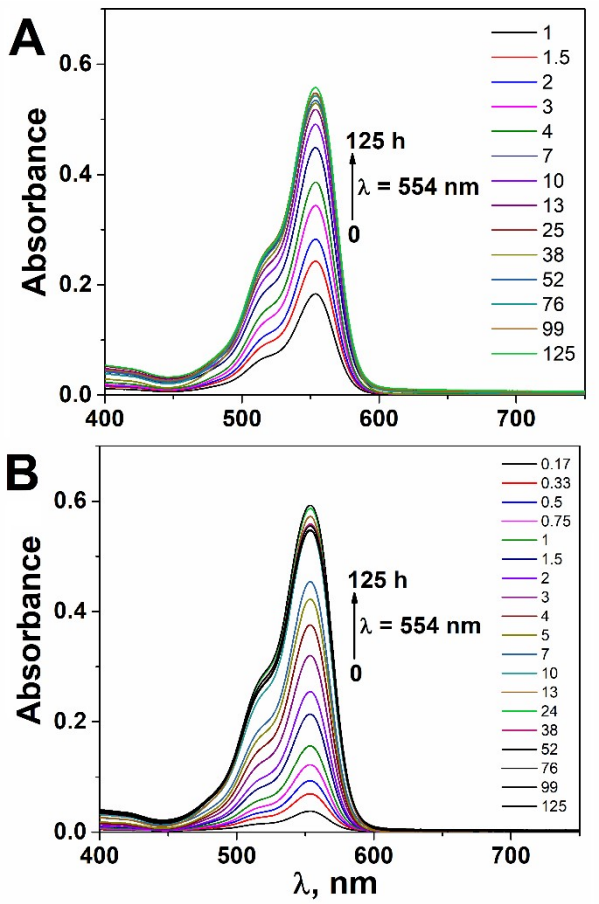

Figure S105. UV Absorbance spectra of Rhodamine B released from PC/**3g** -liposomes monitored by dialysis method during time, 0.025 M phosphate buffer, pH=7.4, 37°C (A), 45°C (B), L=1 cm.

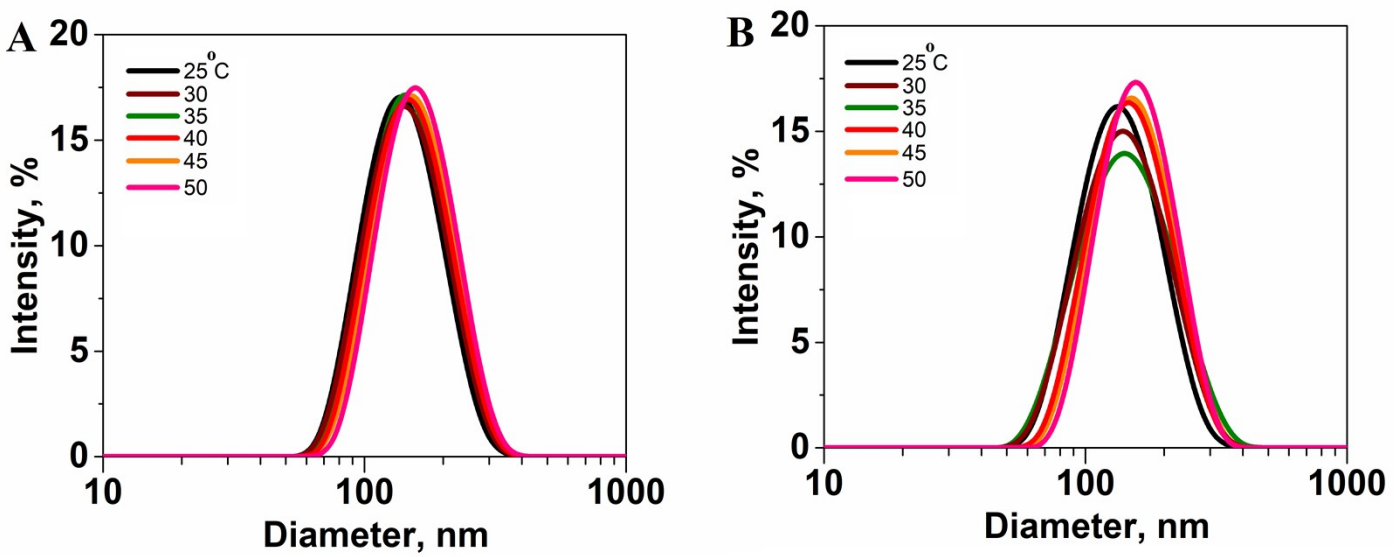

Figure S106. Particle size distribution using the intensity parameter of PC-liposomes (A) and of PC/**3g**-liposomes (B) at different temperatures 25°C, 30°C, 35°C, 40°C, 45°C, 50°C, C_{3g}=0.05 % (w/w) in water.

Table S2. Cytotoxic effects (μM) and selectivity index values (SI) of phosphonium salts **3a-j** and decorated liposomes

Test compounds	IC_{50} (μM)			
	Cancer cell lines			Normal cell lines
	MCF-7	A 549	T98G	WI38
3a[25]	61±5	39±3	60±4	36±3
3b[25]	67±5	42±3	63±5	30±2
3c	19±2	72.0±0.7	17±1	4.4±0.05
3d	3.6±0.3	5.4±0.4	41±3	2.7±0.2
3e	2.2±0.1	2.9±0.2	11.0±0.9	0.7±0.05
3f[25]	2.9±0.2	3.7±0.3	1.7±0.1	3.1±0.2
3g	0.7±0.06	1.3±0.1	6.5±0.5	0.3±0.02
PC/**3g**	–	–	–	1.4±0.3
SPC/Ch/PEG/**3g**	–	–	–	1.8±0.2
3h	0.5±0.03	1.6±0.1	4.1±0.3	0.2±0.01
PC/**3h**	–	–	–	1.6±0.06
SPC/Ch/PEG/**3h**	–	–	–	2.8±0.4
3i	16±1	56±6	22±1	8±1
3j	10±2	4.5±0.1	4.0±0.03	0.7±0.04
doxorubicin	0.4±0.04	0.7±0.05	1.0±0.08	0.4±0.05

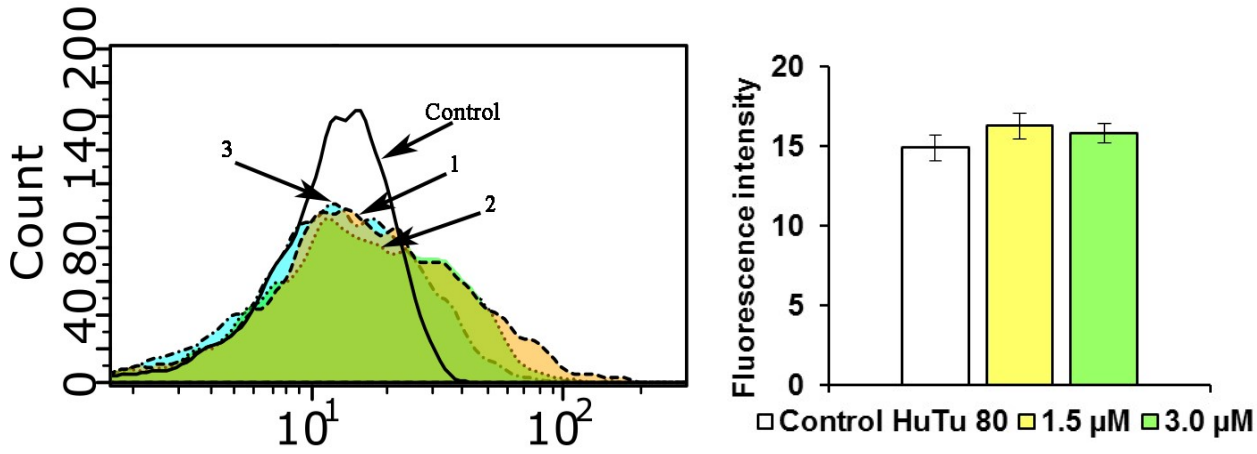

Figure S107. Effects on ROS level on HuTu 80 cell line by compound **3g** at concentration 1-1.5 μM; 2-3.0 μM; 3-6 μM.