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# Synthesis of new ionic liquids based on (5*Z*,9*Z*)-alkadienoic acids and choline

**Ilgiz I. Islamov, Adelya V. Yusupova, Vladimir A. D'yakonov and Usein M. Dzhemilev**

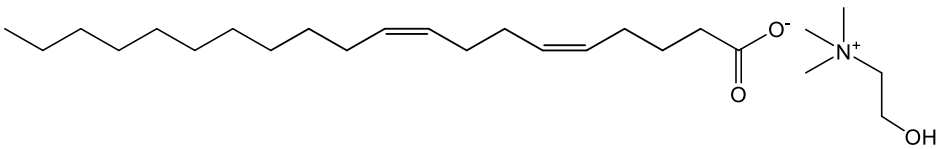
## Experimental section

### General methods

One- ($^{1}$H, $^{13}$C) and two-dimensional heteronuclear (HSQC, HMBC) NMR spectra were recorded in $CDCl_3$ on Bruker Avance-400 [(400.13 MHz ($^{1}$H), 100.62 MHz ($^{13}$C)] spectrometer. IR spectra were measured on a Bruker VERTEX 70V instrument using KBr discs over the range of 400–4000 $cm^{-1}$. High resolution mass spectra were recorded on a Bruker maXis spectrometer (tandem quadrupole/time-of-flight mass analyzer) equipped with an electrospray ionization source (ESI) and matrix-activated laser desorption/ionization (MALDI). Diethyl ether were dried over Na and freshly distilled before use. Cross-cyclomagnesiation reactions were carried out under a dry argon atmosphere. Commercially available choline chloride (Aldrich), $Cp_2TiCl_2$ (Aldrich) were used. (5*Z*,9*Z*)-Alka-5,9-dienoic acids **4a-d** were synthesized as described.[S1] Choline hydroxide was obtained from choline chloride according to procedure.[S2]

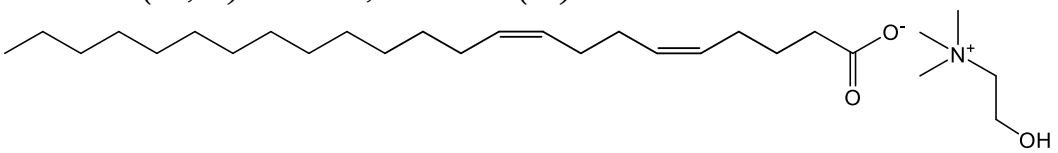
**General procedure for the synthesis of ILs 5a-d.** (5*Z*,9*Z*)-Alka-5,9-dienoic acid **4** (0.3 mmol, 1.0 equiv) and choline hydroxide (0.3 mmol, 1.0 equiv.) were dissolved in acetone or methanol (2.5 ml), and the reaction mixture was heated to 45 °C and stirred at this temperature for 24 h. After removal of the solvent by rotary evaporation, the remained ionic derivatives were were dried under vacuum at 60 °C for 48 h.

*Cholinium (5Z,9Z)-icosa-5,9-dienoate (**5a**).*



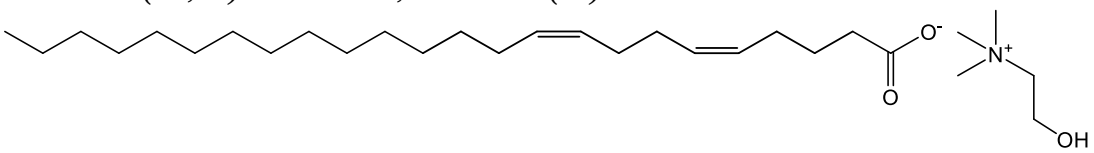

Yield: 96%, yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 5.41 – 5.31 (m, 4H), 4.03 – 3.94 (m, 2H), 3.73 – 3.53 (m, 2H), 3.29 (s, 9H), 2.14 – 1.96 (m, 10H), 1.62 – 1.52 (m, 2H), 1.43– 1.07 (m, 16H), 0.84 (t, *J* = 6.6 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 179.8, 130.3, 130.1, 129.3, 129.1, 68.3, 55.9, 54.4, 38.4, 31.9, 29.7, 29.6, 29.5, 29.3, 27.5, 27.4, 27.3, 27.2, 27.1, 22.6, 14.1. MS ES+ m/z (% rel. Intensity): 104 M+ (100). Calc. for $C_5H_{14}NO$ 104.1070, found 104.1072. MS ES- m/z (% rel. Intensity): 307 M- (100). Calc. for $C_{20}H_{47}O_2$ 307.2643, found 307.2647. IR (ν / $cm^{-1}$): 1566 (C–O), 1396 (C–O).

*Cholinium (5Z,9Z)-tricosa-5,9-dienoate (**5b**).*



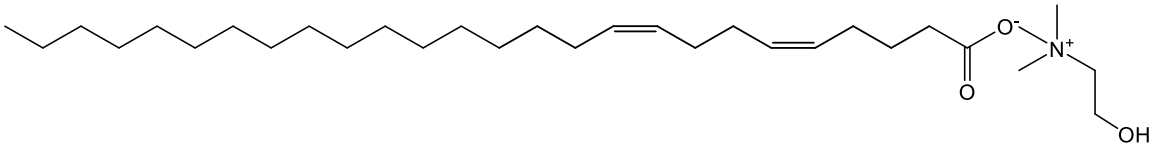
Yield: 95%, yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 5.41 – 5.26 (m, 4H), 4.04 – 3.89 (m, 2H), 3.66 – 3.48 (m, 2H), 3.22 (s, 9H), 2.25 – 1.92 (m, 10H), 1.60 – 1.51 (m, 2H), 1.38– 1.09 (m, 22H), 0.88 (t, *J* = 6.6 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 180.2, 130.4, 129.9, 129.5, 129.0, 67.9, 55.9, 54.2, 37.9, 31.9, 29.8, 29.7, 29.4, 27.4, 27.3, 26.7, 22.7, 14.1. MS ES+ m/z (% rel. Intensity): 104 M+ (100). Calc. for $C_5H_{14}NO$ 104.1070, found 104.1079. MS ES- m/z (% rel. Intensity): 349 M- (100). Calc. for $C_{23}H_{41}O_2$ 349.3112, found 349.3114. IR (ν / $cm^{-1}$): 1561 (C–O), 1403 (C–O).

*Cholinium (5Z,9Z)-tetracosa-5,9-dienoate (**5c**).*



Yield: 97%, yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 5.42 – 5.34 (m, 4H), 4.03 – 3.92 (m, 2H), 3.63 – 3.52 (m, 2H), 3.21 (s, 9H), 2.29 – 1.99 (m, 10H), 1.62 – 1.52 (m, 2H), 1.37– 1.09 (m, 24H), 0.88 (t, *J* = 6.6 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 179.8, 130.4, 129.7, 129.6, 129.0, 67.9, 55.9, 54.2, 31.9, 29.8, 29.7, 29.3, 27.4, 27.3, 26.4, 22.7, 14.1. MS ES+ m/z (% rel. Intensity): 104 M+ (100). Calc. for $C_5H_{14}NO$ 104.1070, found 104.1076. MS ES- m/z (% rel. Intensity): 363 M- (100). Calc. for $C_{24}H_{43}O_2$ 363.3268, found 363.3262. IR (ν / $cm^{-1}$): 1565 (C–O), 1399 (C–O).

*Cholinium (5Z,9Z)-hexacosa-5,9-dienoate (**5d**).*



Yield: 96%, yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 5.37 – 5.28 (m, 4H), 4.04 – 3.92 (m, 2H), 3.54– 3.39 (m, 2H), 3.23 (s, 9H), 2.21 – 1.91 (m, 10H), 1.58 – 1.43 (m, 2H), 1.43– 1.06 (m, 28H), 0.82 (t, *J* = 6.6 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 179.6, 130.3, 129.9, 129.4, 128.98, 68.1, 55.9, 54.3, 31.9, 29.6, 29.3, 27.4, 27.3, 27.3, 26.8, 22.6, 14.0. MS ES+ m/z (% rel. Intensity): 104 M+ (100). Calc. for $C_5H_{14}NO$ 104.1070, found 104.1079. MS ES- m/z (% rel. Intensity): 391 M- (100). Calc. for $C_{26}H_{47}O_2$ 391.3582, found 391.3585. IR (ν / $cm^{-1}$): 1566 (C–O), 1399 (C–O).

## References

S1 V. A. D'yakonov, A. A. Makarov, L. U. Dzhemileva, E. Kh. Makarova, E. K. Khusnutdinova and U. M. Dzhemilev, *Chem. Commun.*, 2013, **49**, 8401.

S2 M. R. Chowdhury, R. M. Moshikur, R. Wakabayashi, Y. Tahara, N. Kamiya, M. Moniruzzaman and M. Goto, *Mol. Pharm.*, 2018, **15**, 2484.

## NMR data

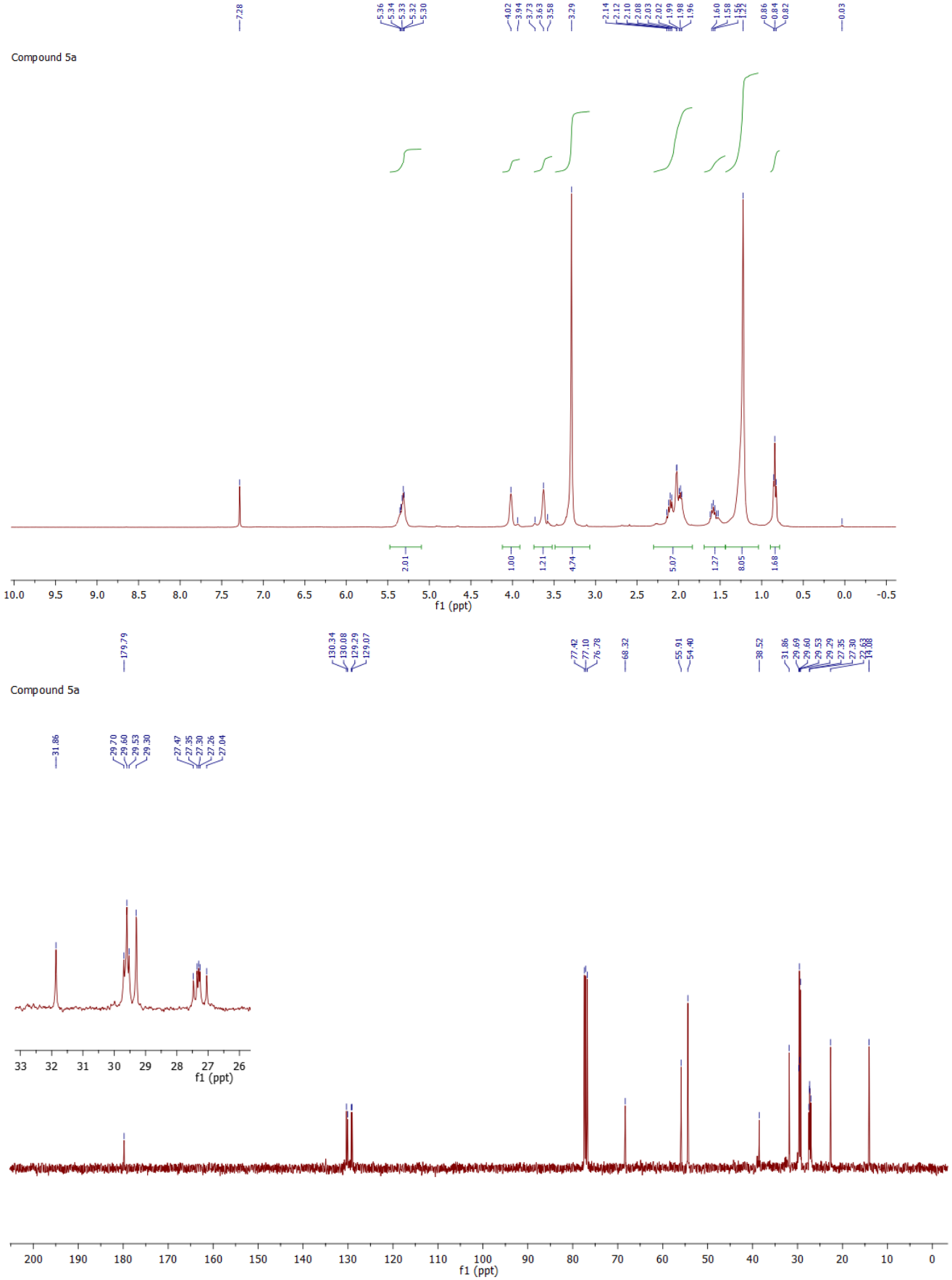



**Figure S1.** $^{1}H$ and $^{13}C$ NMR spectra of compound **5a** in $CDCl_3$.

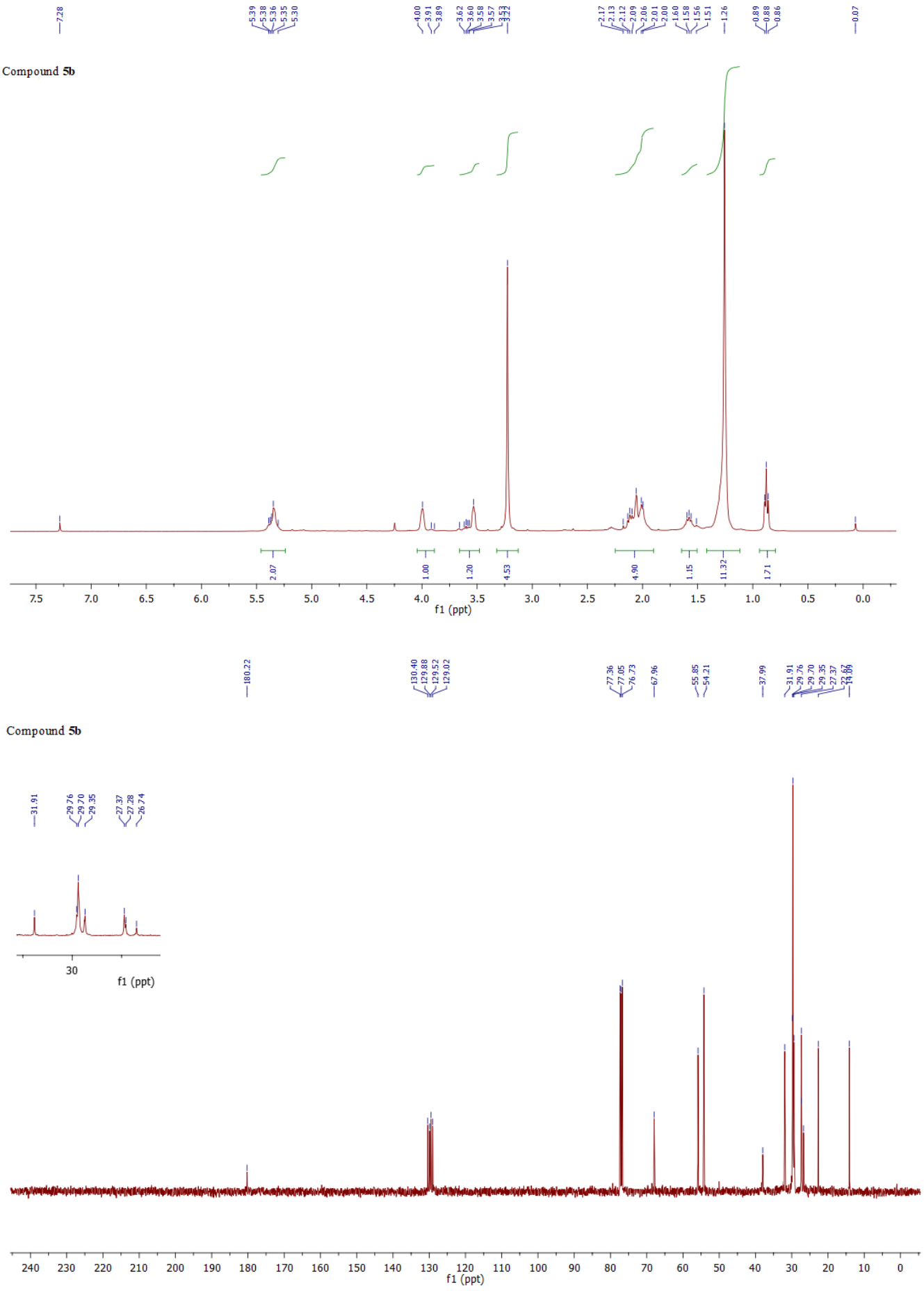



**Figure S2**. $^{1}H$ and $^{13}C$ NMR spectra of compound **5b** in $CDCl_3$.

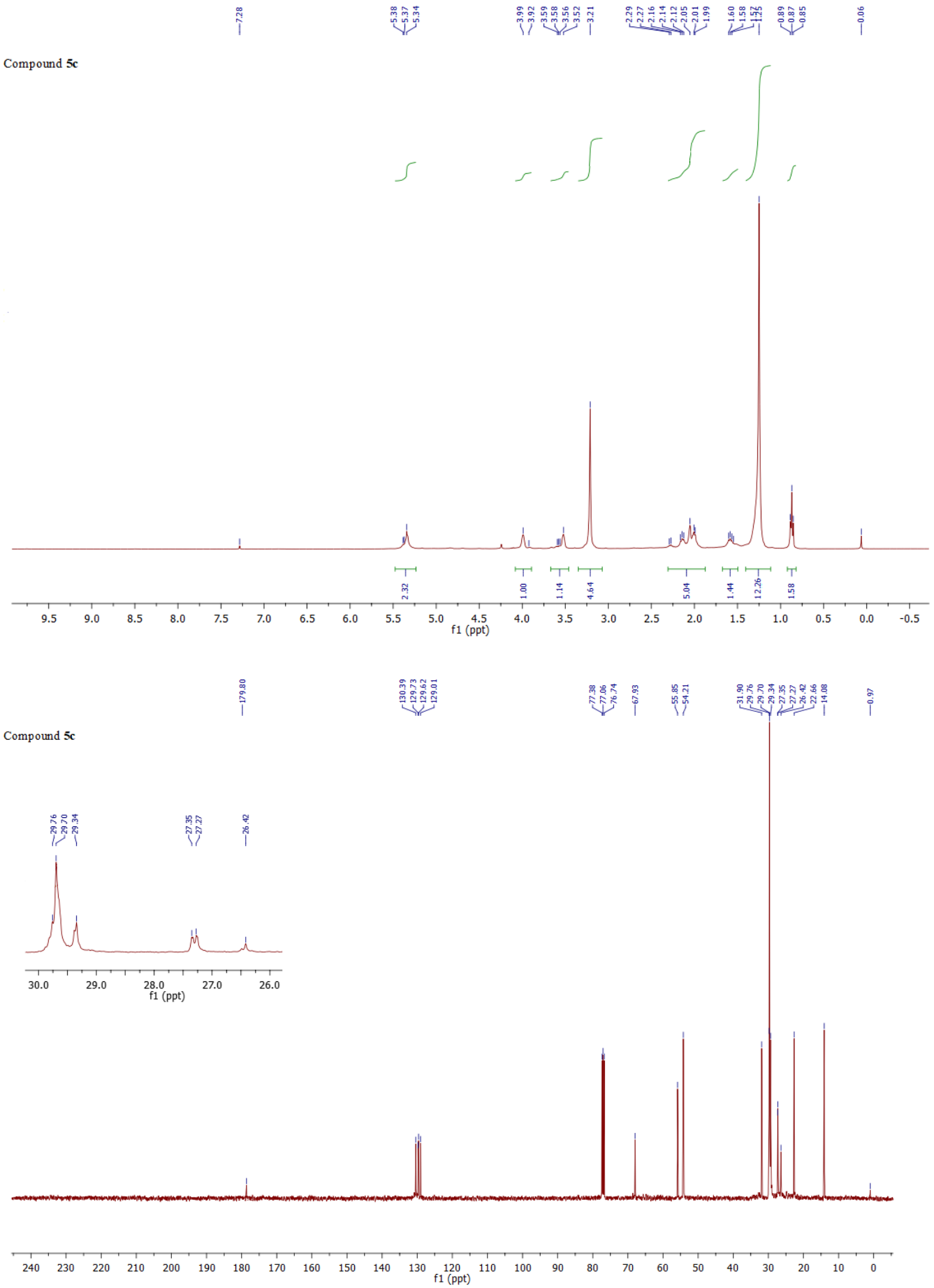



**Figure S3**. $^{1}H$ and $^{13}C$ NMR spectra of compound **5c** in $CDCl_3$.

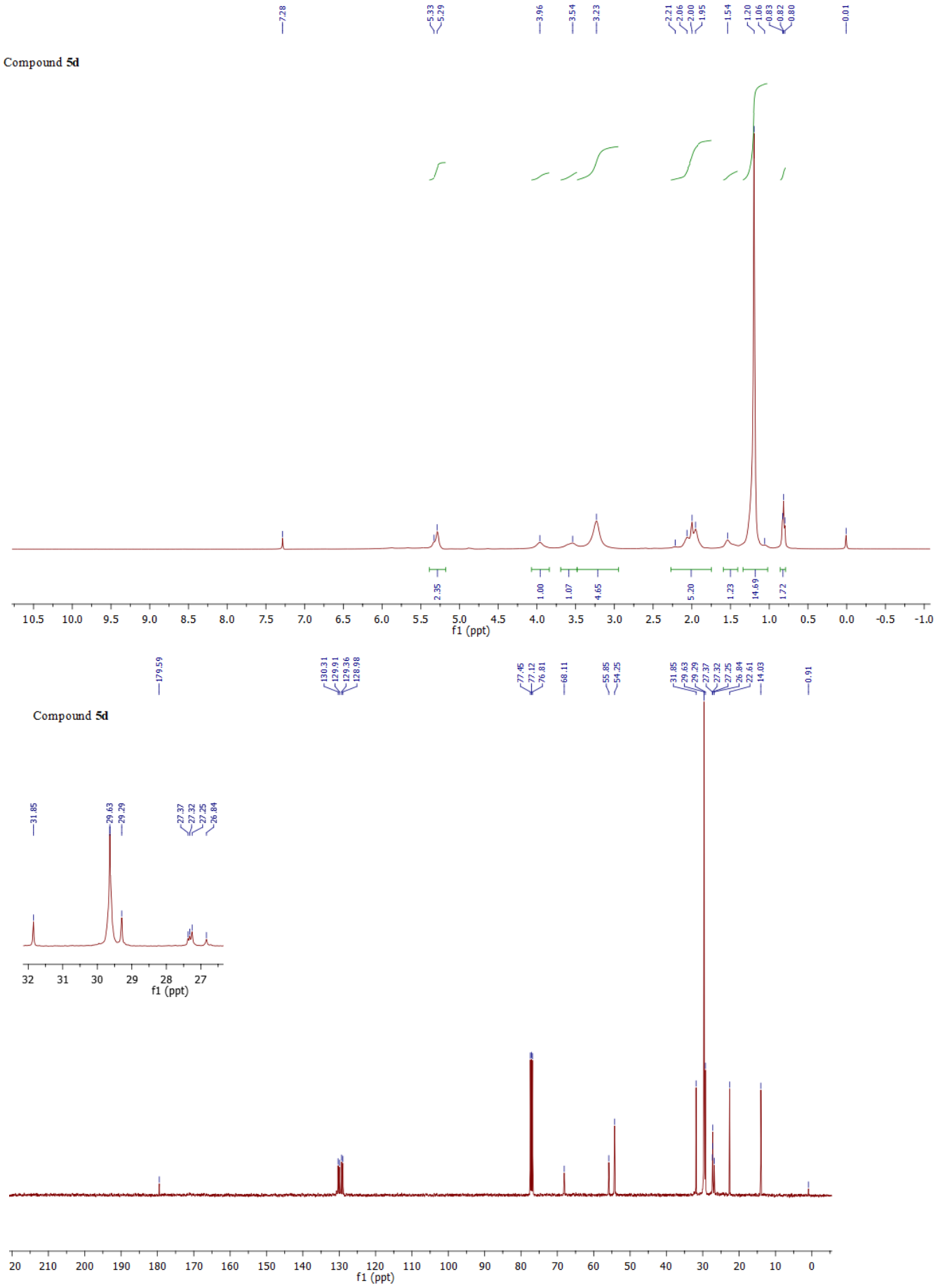



**Figure S4.** $^{1}H$ and $^{13}C$ NMR spectra of compound **5d** in $CDCl_3$.