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Supporting Information

Asymmetric Kulinkovich Hydroxycyclopropanation of Alkenes Mediated by Titanium(IV) TADDOLate Complexes

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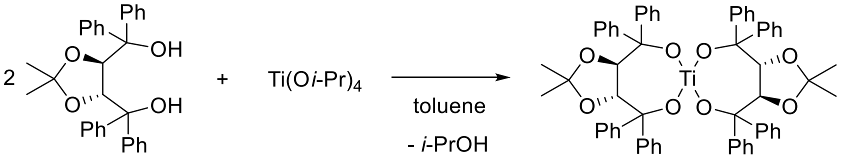
I. Preparation of the Starting Materials

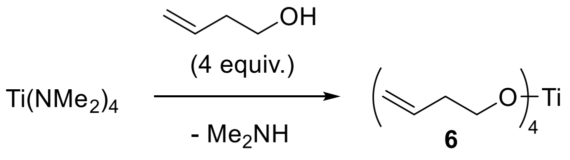
A. *Titanium complexes*

(TADDOL)$_2$Ti.[1]



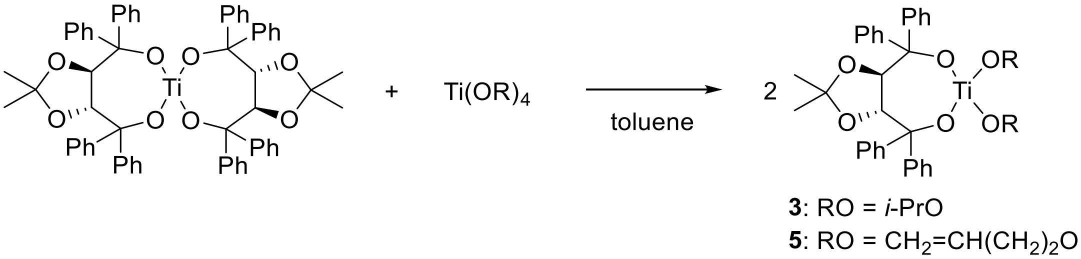
A flame dried 100 mL Schlenk flask equipped with a reflux condenser and a magnetic stirring bar was evacuated and backfilled with argon three times. The flask was charged with (*R*,*R*)-TADDOL (5.34 g, 11.4 mmol), dry toluene (15 mL), titanium(IV) isopropoxide (1.78 g, 6.3 mmol) and the mixture was refluxed under argon atmosphere for 1 h to give a clear solution. The reflux condenser was replaced with a distilling link and the solvent was slowly (approx. 40-60 min) evaporated under dynamic vacuum and condensed in a cold trap. The rate of evaporation was controlled by pressure (50–5 torr) and oil bath temperature. When evaporation was complete, the remaining yellowish solid was recrystallized from cyclohexane / toluene. Crystals of titanium bis-TADDOLate complex were filtered on a Schlenk frit, washed with small portions of dry hexane, transferred to a Schlenk flask and dried under reduced pressure overnight (0.5 torr, 80 °C) to afford pure complex as white crystalline solid (4.47 g, 80% yield). Additional portion of product can be obtained from the mother liquor. Solvent was evaporated under reduced pressure until formation of the first crystals, and then hexane was added to induce crystallization. The precipitate was filtered, washed and dried as described above to give additionally 0.78 g (14%) of Ti(TADDOL)$_2$. The title compound was stored in a Schlenk flask. It could be handled and weighed under air, however contact with atmospheric moisture must be minimized to avoid hydrolysis. ^{1}H NMR (400 MHz, toluene-*d*$_8$): δ = 7.82–7.75 (m, 8H, *o*-H$_{Ar}$), 7.69–7.61 (m, 8H, *o*-H$_{Ar}$), 07.11–6.90 (m, 24H, *m*,*p*-H$_{Ar}$), 5.46 (s, 4H, CH), 0.74 (s, 12H, CMe$_2$). ^{13}C NMR (100.6 MHz, toluene-*d*$_8$): δ = 147.68 (C$_{Ar}$), 142.87 (C$_{Ar}$), 129.54 (CH$_{Ar}$), 128.29 (CH$_{Ar}$), 127.61 (CH$_{Ar}$), 127.57 (CH$_{Ar}$), 127.56 (CH$_{Ar}$), 127.16 (CH$_{Ar}$), 111.52 ($\underline{\text{C}}$Me$_2$), 95.38 (CPh$_2$), 83.46 (CH), 27.52 (C$\underline{\text{Me}}_2$).

Titanium(IV) 3-buten-1-oxide 6.



A 10 mL round-bottom flask was charged with $Ti(NMe_2)_4$ (2.24 g, 10 mmol) and equipped with a two-neck adapter with a septum cap in one neck and a drying tube with solid NaOH in the second neck. Neat 3-buten-1-ol (3.05 g, 42 mmol) was slowly (2 h) added via syringe at stirring, causing vigorous evolution of dimethylamine. At the end of addition, the reaction mixture turns yellow. The flask was heated (60 °C) under argon flow for 1 h to give almost colorless viscous liquid. After cooling down to room temperature, the two-neck adapter was removed, replaced with a distilling link, and the residue was distilled under reduced pressure to afford the corresponding titanium alkoxide **6** as pale-yellow viscous liquid (2.05 g, 62%). ^{1}H NMR (400 MHz, toluene-d_8): δ = 5.90 (ddt, J = 17.1, 10.2, 7.0 Hz, 4H, 3-CH), 5.14 (dd, J = 17.1, 2.0 Hz, 4H, 4-CH_2), 5.06 (dd, J = 10.2, 2.0 Hz, 4H, 4-CH_2), 4.53 (br t, J = 7.2 Hz, 8H, 1-CH_2), 2.52 (br q, J = 7.2 Hz, 8H, 2-CH_2). ^{13}C NMR (100.6 MHz, toluene-d_8): δ = 135.87 (3-CH), 116.42 (4-CH_2), 75.19 (1-CH_2), 38.57 (2-CH_2).

Generation of TADDOLate complexes 3 and 5.



A 25 mL Schlenk tube, was charged with Ti(TADDOL)2 (254 mg, 0.26 mmol), closed with a septum cap and evacuated-backfilled with argon three times. Neat $Ti(OR)_4$ (0.25 mmol) was added via syringe. The tube was evacuated-backfilled with argon again, and content was dissolved in toluene (4 mL) to give a colorless solution containing ca. 0.5 mmol of (TADDOL)$Ti(OR)_2$, which was directly used for cyclopropanation reaction.

(TADDOL)Ti(O*i*-Pr)$_2$ (3): ^{1}H NMR (400 MHz, benzene-d_6): δ = 7.94–7.73 (m, 8H, *o*-H_{Ar}), 7.23–6.98 (m, 12H, *m*,*p*-H_{Ar}), 5.47 (s, 2H, CH), 4.50 (br s, 2H, $OCH_{i\text{-}Pr}$), 1.13 (d, J = 6.0 Hz, 6H, $Me_{i\text{-}Pr}$), 1.10 (d, J = 6.1 Hz, 6H, $Me_{i\text{-}Pr}$), 0.77 (s, 6H, CMe_2). ^{13}C NMR (100.6 MHz, benzene-d_6): δ = 148.97 (C_{Ar}), 143.70 (C_{Ar}), 130.10 (CH_{Ar}), 128.15 (CH_{Ar}), 127.52 (CH_{Ar}), 127.41 (CH_{Ar}), 127.22 (CH_{Ar}), 111.41 ($\underline{C}Me_2$), 94.29 (CPh_2), 82.42 (CH), 78.46 ($O\underline{C}HMe_2$), 27.78 ($C\underline{Me_2}$), 26.29 ($OCH\underline{Me_2}$), 26.22 ($OCH\underline{Me_2}$).

(TADDOL)Ti(OCH$_2$CH$_2$CH=CH$_2$)$_2$ (5): ^{1}H NMR (400 MHz, toluene-d_8): δ = 7.82–7.66 (m, 8H, *o*-H_{Ar}), 7.27–6.99 (m, 12H, *m*,*p*-H_{Ar}), 5.60 (ddt, J = 17.1, 10.2, 6.8 Hz, 2H, CH_{olef}), 5.34 (s, 2H, CH), 5.02–4.89 (m, 4H, $CH_{2\ olef}$), 4.40–3.90 (br m, 4H, OCH_2), 2.45–2.15 (br m, 4H, CH_2), 0.78 (s, 6H, CMe_2). ^{13}C NMR (100.6 MHz, toluene-d_8): δ = 148.99 (C_{Ar}), 144.21 (C_{Ar}), 135.01 (CH_{olef}), 130.12 (CH_{Ar}), 128.18 (CH_{Ar}), 128.16 (CH_{Ar}), 127.47 (CH_{Ar}), 127.40 (CH_{Ar}), 127.17 (CH_{Ar}), 116.71 ($CH_{2\ olef}$), 110.69 ($\underline{C}Me_2$), 95.20 (CPh_2), 81.55 (CH), 74.80 (br, CH_2O), 37.73 (CH_2), 27.68 ($C\underline{Me_2}$).

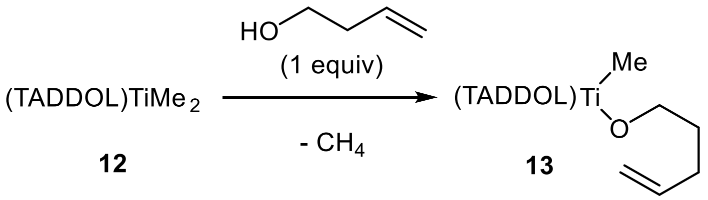
Generation of dimethyltitanium TADDOLate 12.

$$\mathrm{Ti(TADDOL)_2} \xrightarrow[\text{toluene}]{\mathrm{TiCl_4}} \underset{\mathbf{11}}{\mathrm{(TADDOL)TiCl_2}} \xrightarrow[\text{- LiCl}]{\text{2 MeLi}} \underset{\mathbf{12}}{\mathrm{(TADDOL)TiMe_2}}$$

$Ti(TADDOL)_2$ (245 mg, 0.25 mmol) was placed in a 25 mL Schlenk tube, evacuated-backfilled with argon three times and dissolved in toluene (3 mL). Titanium(IV) chloride (0.25 mmol, 0.25 mL, 1M solution in toluene) was added carefully via a syringe in dropwise manner at stirring. At the end of addition, almost colorless solution sharply attains pale-yellow color, indicating equivalence point. The obtained solution of dichlorotitanium TADDOLate complex **11** was cooled down to −15 °C with a salt/ice bath and then MeLi (1 mmol, 0.63 mL, 1.6M in ether) was added dropwise to afford a yellow solution of dimethyltitanium complex **12** and insoluble LiCl. At room temperature, yellow solution of complex **12** attains light-brown color, however no significant changes are noticeable in its NMR spectrum.

(TADDOL)TiMe$_2$ (12): ^{1}H NMR (400 MHz, toluene-d_8): δ = 7.89–7.72 (m, 4H, *o*-H_{Ar}), 7.62–7.58 (m, 4H, *o*-H_{Ar}), 7.20–7.00 (m, 12H, *m*,*p*-H_{Ar}), 5.14 (s, 2H, CH), 0.98 (s, 6H, $TiMe_2$), 0.69 (s, 6H, CMe_2). ^{13}C NMR (100.6 MHz, toluene-d_8): δ = 147.93 (C_{Ar}), 142.01 (C_{Ar}), 129.51 (CH_{Ar}), 128.34 (CH_{Ar}), 127.82 (CH_{Ar}), 127.73 (CH_{Ar}), 127.50 (CH_{Ar}), 127.45 (CH_{Ar}), 111.87 ($\underline{C}Me_2$), 95.67 (CPh_2), 82.75 (CH), 52.63 ($TiMe_2$), 27.54 ($C\underline{Me_2}$).

Generation of complex 13.



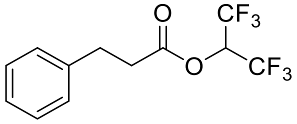
Dropwise addition (within 2-3 min) of 1 equiv. of homoallylic alcohol (18 mg, 0.25 mmol) in toluene (0.3 mL) to the solution of **12**, generated as described above (at -15°C), results in evolution of methane and formation of alkoxide complex **13**. Presence of **13** can be confirmed by ^{1}H NMR after removal of insoluble LiCl salt by filtration through a Schlenk frit.

For NMR characterization, complexes **12** and **13** were generated directly in toluene-d_8 as described above. Air-sensitive solutions were transferred from the Schlenk flask into NMR tubes by using a syringe. Prior to the transfer, NMR tube was placed into another Schlenk flask of appropriate length, and backfilled-evacuated with argon three times. NMR sample was securely closed with a rubber septum (Aldrich: Z553891-100EA) before removal from the Schlenk line.

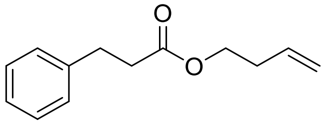
(TADDOL)TiMe(OCH$_2$CH$_2$CH=CH$_2$) (13): ^{1}H NMR (400 MHz, toluene-*d*$_8$): δ = 7.64 (d, *J* = 7.7 Hz, 2H, *o*-H$_{Ar}$), 7.60 (d, *J* = 7.7 Hz, 2H, *o*-H$_{Ar}$), 7.45 (d, *J* = 7.8 Hz, 2H, *o*-H$_{Ar}$), 7.28 (d, *J* = 7.8 Hz, 2H, *o*-H$_{Ar}$), 7.07 – 6.77 (m, 12H, *m*,*p*-H$_{Ar}$), 5.36 (d, *J* = 7.2 Hz, 1H, CH), 5.31 (m, 1H, CH$_{olef}$), 5.16 (d, *J* = 7.2 Hz, 1H, CH), 4.89–4.59 (m, 3H, CH$_{olef}$+OCH2), 4.49 (br s, 1H, OCH$_2$), 2.52 (br s, 1H, CH$_2$), 2.37 (br s, 1H, CH$_2$), 1.02 (s, 3H, MeTi), 0.66 (s, 3H, CMe$_2$), 0.51 (s, 3H, CMe$_2$).

B. *Carboxylic Esters*

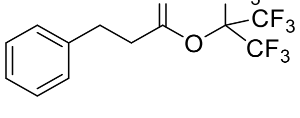
Preparation of esters, general procedure. A solution of acid chloride (18 mmol) in dichloromethane (5 mL) was added dropwise to the cooled (0°C) and stirred solution of alcohol (20 mmol) and pyridine (2.0 mL, 25 mmol) in dichloromethane (10 mL). The reaction mixture was stirred at room temperature for 2 h, and then was treated with water (10 mL) at vigorous stirring. The aqueous layer was separated, and the organic phase was washed with 1 M HCl (2×10 mL), water (10 mL), brine (10 mL) and dried (MgSO$_4$). The solution was filtered through silica gel plug (1.5 cm thick), washed with PE / DCM (1:2 v/v) and evaporated.



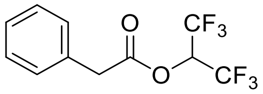
1,1,1,3,3,3-Hexafluoropropan-2-yl 3-phenylpropionate (4a). Colorless liquid, yield 5.19 g (96%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.41–7.26 (m, 2H, Ph), 7.26–7.06 (m, 3H, Ph), 5.76 (hept, *J*$_{HF}$ = 6.1 Hz, 1H, CH(CF$_3$)$_2$), 3.01 (t, *J* = 7.7 Hz, 2H, CH$_2$), 2.84 (m, 2H). ^{13}C NMR (100.6 MHz, CDCl$_3$): δ = 169.74 (CO), 139.25 (C$_{Ar}$), 128.82 (CH$_{Ar}$), 128.30 (CH$_{Ar}$), 126.84 (CH$_{Ar}$), 120.53 (qq, *J*$_{CF}$ = 282.1, 3.0 Hz, CF$_3$), 66.61 (hept, *J*$_{CF}$ = 34.7 Hz, $\underline{C}$H(CF$_3$)$_2$), 34.99 (CH$_2$), 30.58 (CH$_2$).



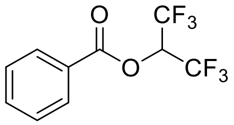
3-Buten-1-yl 3-phenylpropionate (7).[2] Colorless liquid, yield 0.92 g (90%, starting from 5 mmol of 3-phenylpropionyl chloride). ^{1}H NMR (400 MHz, CDCl$_3$): δ = δ 7.33–7.26 (m, 2H, Ph), 7.24–7.15 (m, 3H, Ph), 5.75 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 1H, CH$_{olef}$), 5.16–5.01 (m, 2H, CH$_2$=), 4.13 (t, *J* = 6.7 Hz, 2H, CH$_2$O), 2.95 (t, *J* = 7.8 Hz, 2H, CH$_2$), 2.63 (m, 2H, CH$_2$), 2.36 (qt, *J* = 6.7, 1.4 Hz, 2H, OCH$_2$C$\underline{H}_2$).



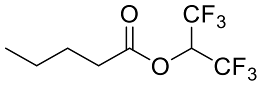
1,1,1,3,3,3-Hexafluoro-2-trifluoromethyl-2-propyl 3-phenylpropionate (9). Colorless liquid, solidifies upon standing into colorless solid with low melting point. Yield 6.15 g (93%).^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.27 (m, 2H, Ph), 7.27–7.13 (m, 3H, Ph), 3.01 (t, J = 7.6 Hz, 2H, CH_2), 2.86 (m, 2H, CH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 166.06 (CO), 138.99 (C_{Ar}), 128.85 (CH_{Ar}), 128.30 (CH_{Ar}), 126.91 (CH_{Ar}), 119.72 (q, J_{CF} = 291.4 Hz, CF_3), 80.04 (m, J_{CF} = 32.1 Hz, $\underline{C}(CF_3)_3$), 35.81 (CH_2), 30.56 (CH_2).



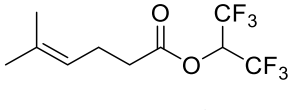
1,1,1,3,3,3-Hexafluoropropan-2-yl 3-phenylacetate (4b). Colorless liquid, yield 4.75 g (92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.30 (m, 3H, Ph), 7.30–7.26 (m, 2H, Ph), 5.75 (hept, J_{HF} = 6.1 Hz, 1H, $CH(CF_3)_2$), 3.81 (s, 2H, $PhCH_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 168.56 (CO), 131.89 (C_{Ar}), 129.31 (CH_{Ar}), 129.01 (CH_{Ar}), 127.96 (CH_{Ar}), 120.50 (qq, J_{CF} = 282.3, 3.0 Hz, CF_3), 66.87 (hept, J_{CF} = 34.6 Hz, $\underline{C}H(CF_3)_2$), 40.22 (CH_2).



1,1,1,3,3,3-Hexafluoropropan-2-yl benzoate (4c). Colorless liquid, yield 4.60 g (94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18–8.09 (m, 2H, Ph), 7.77–7.63 (m, 1H, Ph), 7.61–7.44 (m, 2H, Ph), 6.03 (hept, J_{HF} = 6.1 Hz, 1H, $CH(CF_3)_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 163.42 (CO), 134.92 (CH_{Ar}), 130.64 (CH_{Ar}), 129.02 (CH_{Ar}), 127.00 (C_{Ar}), 120.74 (qq, J_{CF} = 282.4, 2.6 Hz, CF_3), 67.08 (hept, J_{CF} = 34.8 Hz, $\underline{C}H(CF_3)_2$).



1,1,1,3,3,3-hexafluoropropan-2-yl pentanoate (4d). Colorless liquid, yield 3.76 g (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.77 (hept, J_{HF} = 6.2 Hz, 1H, $CH(CF_3)_2$), 2.52 (t, J = 7.5 Hz, 2H, CH_2CO), 1.76–1.61 (m, 2H, CH_2), 1.49 – 1.32 (m, 2H, CH_2), 0.94 (t, J = 7.4 Hz, 3H, Me). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 170.57 (CO), 120.60 (qq, J_{CF} = 282.7, 3.3 Hz, CF_3), 66.44 (hept, J_{CF} = 34.7 Hz, $\underline{C}H(CF_3)_2$), 33.17 (CH_2), 26.72 (CH_2), 22.10 (CH_2), 13.68 (CH_3).

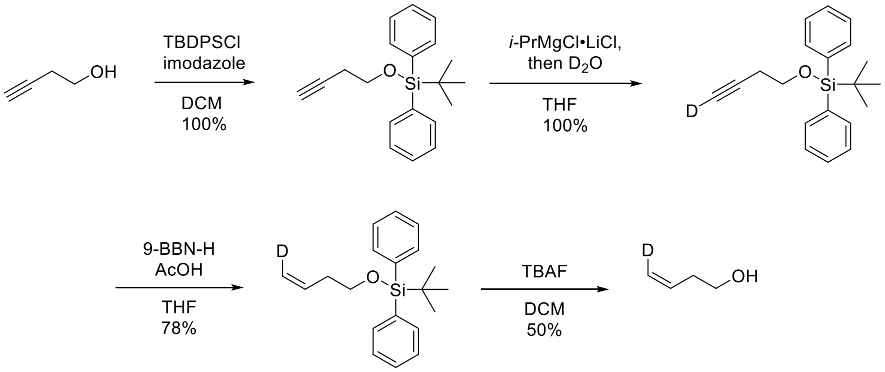


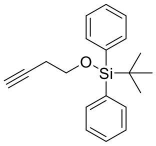
1,1,1,3,3,3-Hexafluoropropan-2-yl 5-methyl-4-hexenoate (4e). Colorless liquid, yield 0.23 g (83%, from 1 mmol of acid chloride). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.76 (hept, J_{HF} = 6.0 Hz, 1H, $CH(CF_3)_2$), 5.07 (m, 1H, CH_{olef}), 2.54 (t, J = 6.9 Hz, 2H, CH_2CO), 2.46–2.32 (m, 2H, $C\underline{H}_2CH=$), 1.69 (q, J = 1.3 Hz, 3H, Me), 1.62 (s, 3H, Me). ^{13}C NMR (100.6

MHz, $CDCl_3$): δ = 170.21 (CO), 134.44 (C_q), 121.13 (CH=), 120.58 (qq, J_{CF} = 282.0, 2.6 Hz, CF_3), 66.65 (hept, J_{CF} = 34.6 Hz, C̲H(CF_3)$_2$), 33.71, 25.77, 23.42, 17.79.

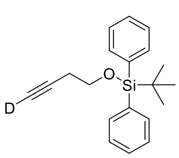
C. *Alkenes*

Preparation of deuterated homoallylic alcohol (14-*d*)

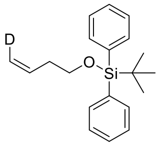




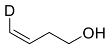
(But-3-yn-1-yloxy)(*tert*-butyl)diphenylsilane. To a solution of but-3-yn-1-ol (1.0 equiv., 16.2 mmol, 1.25 mL) and imidazole (1.3 equiv., 21.0 mmol, 1.43 g) in DCM (25 mL) was added TBDPSCl (1.1 equiv., 17.8 mmol, 4.72 mL) at 0 °C and stirred at rt for 30 min. The reaction mixture was quenched with water and extracted with DCM. The combined organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo to give a crude product, which was purified by silica gel column chromatography (petrol ether/DCM; DCM 0->25%) to afford the product in quantitative yield (5.09 g) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 4H, Ph), 7.48 – 7.33 (m, 6H, Ph), 3.79 (t, *J* = 7.1 Hz, 2H, CH_2O), 2.45 (td, *J* = 7.1, 2.6 Hz, 2H, C$\underline{H}_2$$CH_2O$), 1.95 (t, *J* = 2.6 Hz, 1H, HC≡), 1.06 (s, 9H, *t*Bu). ^{13}C NMR ($CDCl_3$, 101 MHz) δ 135.72 (CH_{Ar}), 133.70 (C_{Ar}), 129.84 (CH_{Ar}), 127.83 (CH_{Ar}), 81.63 (C≡), 69.46 (HC≡), 62.44 (CH_2O), 26.92 (CH_3), 22.73 (=CHC̲H_2), 19.35 (C).



((But-3-yn-1-yl-4-*d*)oxy)(*tert*-butyl)diphenylsilane. Turbo Grignard reagent (1 equiv., 8.1 mmol, 6.23 mL, 1.3 M in THF) was slowly added to the solution of alkyne (1 equiv., 8.1 mmol, 2.50 g) in dry THF (20 mL) at 0°C. Reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by addition of deuterium oxide (0.50 mL) at 0°C, diluted with diethyl ether and extracted form sat. NH_4Cl solution with diethyl ether (3 times), dried over MgSO4 and concentrated to provide pure product as a colorless liquid in quantitative yield (2.54 g, 96% deuterated). ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.64 (m, 4H, Ph), 7.50 – 7.34 (m, 6H, Ph), 3.79 (t, *J* = 7.1 Hz, 2H, CH_2O), 2.45 (t, *J* = 7.1 Hz, 2H, C$\underline{H}_2$$CH_2O$), 1.06 (s, 9H, *t*Bu). ^{13}C NMR ($CDCl_3$, 101 MHz) δ 135.72 (CH_{Ar}), 133.70 (C_{Ar}), 129.84 (CH_{Ar}), 127.83 (CH$_{Ar}$), 81.15 (t, J_{CD} = 7.6 Hz, C≡), 69.22 (t, J_{CD} = 38.2 Hz, DC≡), 62.45 (CH$_2$O), 26.92 (CH$_3$), 22.70 (=CH$\underline{\text{C}}$H$_2$), 19.35 (C).

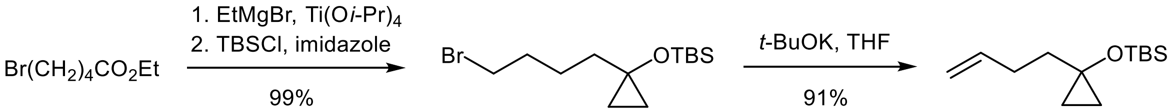


(*Z*)-((But-3-en-1-yl-4-*d*)oxy)(*tert*-butyl)diphenylsilane. 9-BBN-H (2 equiv., 16.2 mmol, 32.3 mL, 0.5 M in THF) was added to the soultion of alkyne (1 equiv., 8.1 mmol, 2.50 g) in THF (16.2 mL) at 0 °C under Ar. The mixture was allowed to warm to 25 °C and stirred for an additional 1 h. The mixture was heated at reflux temperature for an additional 2 h to ensure complete dihydroboration. The mixture was cooled to 0 °C, benzaldehyde (1 equiv., 8.1 mmol, 0.824 mL) was added dropwise, and the mixture was allowed to warm to 25 °C and stirred overnight. The reaction mixture was finally treated with acetic acid (4 equiv., 32.3 mmol, 1.85 mL) at 0°C and stirred at room temperature for 2 h. The mixture was diluted with DCM and extracted from conc. NaHCO$_3$ water solution with DCM, dried over MgSO4, filtered, concentrated. The crude product was purifed on Si-gel column using mixture of PE:DCM as eluent (DCM 0 -> 25%) to provide desired product as a colorless liquid in 78% yield (1.95 g). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 – 7.63 (m, 4H, Ph), 7.47 – 7.34 (m, 6H, Ph), 5.90 – 5.74 (m, 1H, =C$\underline{\text{H}}$CH$_2$), 5.01 (dt, *J* = 10.3, 1.3 Hz, 1H, DHC=), 3.72 (tt, *J* = 6.7, 1.5 Hz, 2H, CH$_2$O), 2.32 (qd, *J* = 6.7, 1.3 Hz, 2H, C$\underline{\text{H}_2}$CH$_2$O), 1.06 (s, 9H, *t*Bu). ^{13}C NMR (CDCl$_3$, 101 MHz) δ 135.59 (CH$_{Ar}$), 135.34 (=$\underline{\text{C}}$HCH$_2$), 133.98 (C$_{Ar}$), 129.54 (CH$_{Ar}$), 127.59 (CH$_{Ar}$), (t, J_{CD} = 23.7 Hz, DHC=), 63.50 (CH$_2$O), 37.14 (=CH$\underline{\text{C}}$H$_2$), 26.84 (CH$_3$), 19.23 (C).



(*Z*)-But-3-en-4-*d*-1-ol (14-*d*). A TBAF (2 equiv., 12.4 mmol, 12.4 mL, 1 M) solution in THF was added to a round-bottom flask and THF was evaporated under reduced pressure. Deuterated silyl ether (1 equiv., 6.20 mmol, 1.93 g) was dissolved in DCM (12.4 mL) and transferred to the reaction flask containing TBAF. After stirring overnight at room temperature, 2 mL of toluene were added to the reaction mixture and the product was distilled of with DCM and toluene as a one fraction. The product solution was transferred to a silica gel column and solvents were washed out with pentane (3 CV). The product was washed out with pentane:Et$_2$O mixture 1:1 (4 CV) and concentrated carefully at reduced pressure. The product was obtained in 50% yield (0.34 g, contains 66% Et$_2$O). ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.84 – 5.75 (m, 1H, =C$\underline{\text{H}}$CH$_2$), 5.11 (dt, *J* = 10.3, 1.0 Hz, 1H, DHC=), 3.68 (q, *J* = 5.9 Hz, 2H, CH$_2$O), 2.33 (qd, *J* = 6.4, 1.0 Hz, 2H, C$\underline{\text{H}_2}$CH$_2$O), 1.43 (s, 1H, OH). ^{13}C NMR (CDCl$_3$, 101 MHz) δ 134.85 (=$\underline{\text{C}}$HCH$_2$), 117.60 (t, J_{CD} = 23.6 Hz, DHC=), 61.74 (CH$_2$O), 37.21 (=CH$\underline{\text{C}}$H$_2$). HRMS (ESI): m/z [M+H]$^+$ calcd for C_4H_7OD: 74.0711; found: 74.0714.

Preparation of TBS-protected alkenol 24.

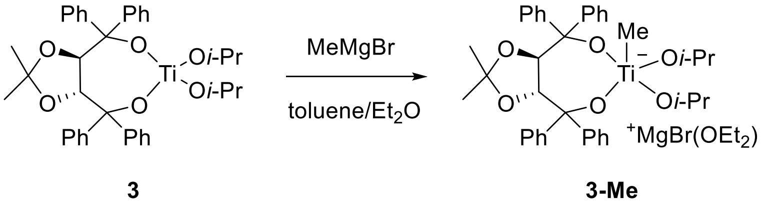


TBS-Protected 1-(4-bromobutyl)cyclopropan-1-ol. The Kulinkovich method was used to synthesize the corresponding cyclopropanol from ethyl 5-bromopentanoate (20 mmol, 4.18 g) by slow addition (3 h) of EtMgBr (3 equiv, 60 mmol) in the presence of catalytic amount of Ti(*i*-PrO)$_4$ (20 mol%, 4 mmol, 1.2 mL) in anhydrous diethyl ether. After addition of the Grignard reagent, the mixture was put into an ice bath, cooled and hydrolysis was performed with small amount of water (2 mL). After filtration through celite and evaporation of the solvent, crude reaction mixture was dissolved in 40 mL of anhydrous THF, imidazole (60 mmol, 4.05 g) was added, and the resulting mixture was cooled with an ice bath. Solid TBS-Cl (26 mmol, 3.9 g) was added in small portions. Mixture was stirred until completion of the reaction (TLC control, ca. 22 h), then quenched with water (20 mL), and extracted with DCM (3×10 mL), dried over MgSO$_4$ and purified with flash chromatography (eluent = petroleum ether) to obtain the silylated cyclopropanol as a yellow oil (6.04 g, 99 %). ^{1}H NMR (400 MHz, CDCl3) δ 3.41 (t, *J* = 6.8 Hz, 2H), 1.98–1.81 (m, 2H), 1.74–1.59 (m, 2H), 1.52–1.43 (m, 2H), 0.85 (s, 9H), 0.71 – 0.66 (m, 2H), 0.42–0.39 (m, 2H), 0.09 (s, 6H); ^{13}C NMR (100.6 MHz, CDCl3) δ 56.72, 38.47, 34.02, 32.98, 25.88, 24.93, 17.94, 13.23, -3.27.

(1-(But-3-en-1-yl)cyclopopoxy)(*tert*-butyl)dimethylsilane (24). An ice bath cooled and stirred solution of bromocyclopropane (6.1 g, 19.9 mmol) in anhydrous THF (15 mL) was treated dropwise with a solution of potassium *tert*-butoxide (3.36 g, 30 mmol, 1.5 equiv.) in anhydrous THF (15 mL). The white suspension was then heated at 60 °C for additional 2 hours. After quenching with saturated aq. NH$_4$Cl (10 mL), the mixture was extracted with petroleum ether (3×5 mL). The organic layer was separated and dried (MgSO$_4$). The mixture was filtered and the solvent was evaporated to give the crude mixture which was purified by flash column chromatography (eluent = petroleum ether). Title compound obtained as colorless liquid (4.09 g, 91%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.87 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.04–4.92 (m, 2H), 2.30–2.24 (m, 2H), 1.64–1.52 (m, 2H), 0.85 (s, 9H), 0.70–0.67 (m, 2H), 0.44–0.41 (m, 2H), 0.09 (s, 6H); ^{13}C NMR (100.6 MHz, CDCl$_3$) δ 139.10, 114.28, 56.80, 38.85, 30.53, 25.88, 17.95, 13.24, -3.31. HRMS (AJSESI) calcd. for $C_{13}H_{27}OSi^+$ [M+H]$^+$ 227.1831, found m/z 227.1826.

II. NMR Experiments with Titanium Ate Complexes

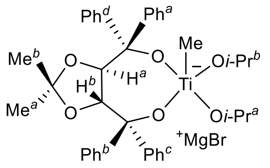
A. *Generation and NMR characterization of methyltitanium ate complexes*



Scheme S1.

Addition of MeMgBr (1 equiv., solution in toluene/ether) to the toluene solution of titanium TADDOLate complex **3** affords a pale-yellow solution, which according to NMR contains a single TADDOLate complex as the reaction product. The species is C_1-symmetric, which is evidenced by two separate resonances observed for methine and methyl protons of the C_2-symmetric TADDOL ligand, as well as by four distinct signals for ortho-protons of phenyl rings in ^{1}H NMR. The signal of organometallic methyl group is observed at 1.12 ppm in ^{1}H NMR and 53.54 ppm in ^{13}C NMR. Two isopropoxyde ligands give a single broad resonance of methine protons at 5.11 ppm in ^{1}H NMR at room temperature that splits into two distinct signals below 260 K, revealing their non-equivalence and rapid mutual exchange at ambient conditions. All these data support the formation of pentacoordinated methyltitanium ate complex **3-Me** as a result of Grignard reagent addition to tetracoordinated alkoxide complex **3** as depicted on Scheme S1. It is worth noting that the signals of methylene protons of diethyl ether, which was used as a co-solvent for the Grignard reagent, display complex multiplet signals in ^{1}H NMR instead of the conventional quartet (see Fig. S1). This supports the argument that ether molecules are complexed to the chiral complex **3-Me**. On the other hand, no complexation can be seen upon addition of diethyl ether to titanium TADDOLate **3**. This observation indicates that the coordination of ether molecules to complexes **3-Me** likely occurs through the more Lewis acidic magnesium that is linked to the titanium atom via μ-oxo bridges, although the exact location of coordinated magnesium is difficult to define on the basis of NMR data alone. Key NMR data for ate complex **3-Me** are given in the Table S1 below. Similar ate complexes can be also generated (although with a bit lower yields) by addition of EtMgBr and *i*-PrMgBr to the toluene solution of TADDOLate complex **3**, however these results will not be presented here; NMR data for the ethyl complex was presented in the preceding work.[3]

Table S1. Key NMR data for ate complex **3-Me**

		^{1}H ^{a} δ (m, $^{2}J_{\mathrm{HH}}$)	^{13}C {^{1}H} ^{b} δ
TADDOL	Me(*a*)	0.68 (s)	26.63
	Me(*b*)	0.79 (s)	27.32
	CH(*a*)	5.24 (d, 7.3 Hz)	80.65
	CH(*b*)	5.45 (d, 7.3 Hz)	81.55
	o-CH Ph(*a*)	7.83 (d, 7.2 Hz)	128.06
	o-CH Ph(*b*)	7.73 (d, 7.0 Hz)	130.30
	o-CH Ph(*c*)	7.59 (d, 7.0 Hz)	128.56
	o-CH Ph(*d*)	7.48 (d, 7.1 Hz)	130.09
i-PrO	CH(*a*)	5.11 (br s, 2H)^{c}	71.53 (2C)^{c}
	CH(*b*)		
CH_3-Ti		1.12 (s, 3H)	53.54

^{a} 800 MHz, 298 K in toluene-d_8; ^{b} at 100.6 MHz, 288 K in C_6D_6; ^{c} splits into two signals below 260 K.

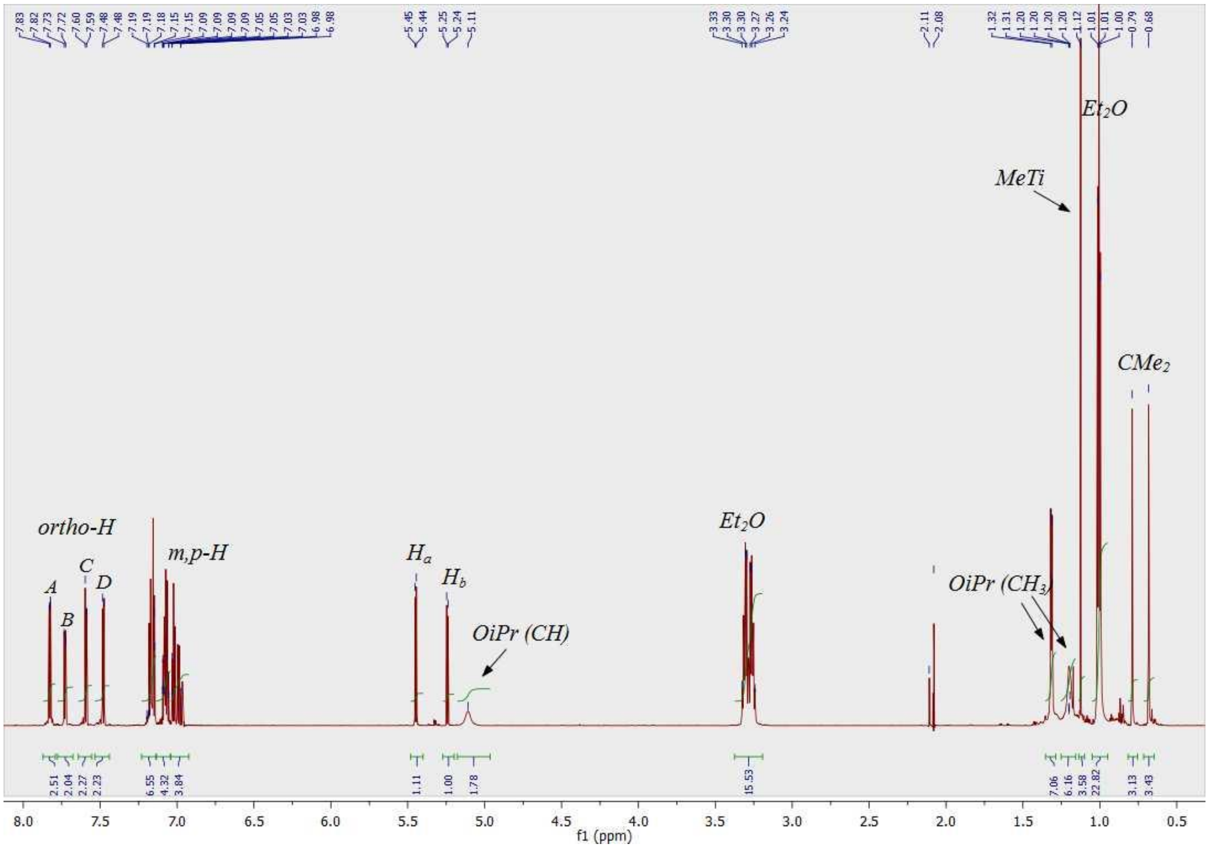
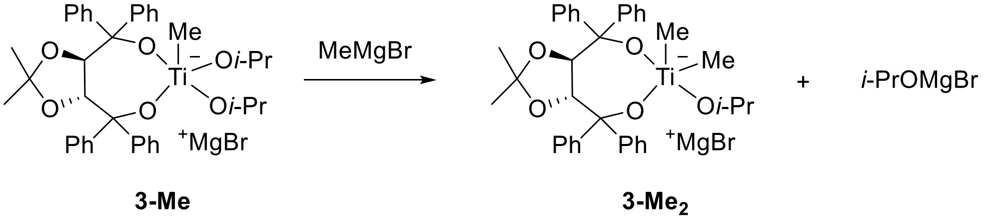


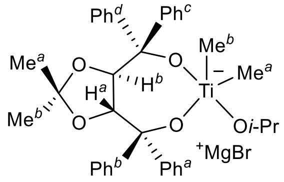
Fig. S1. ^{1}H NMR spectrum of ate complex **3-Me** (800 MHz, 298 K, toluene-d8).

Addition of the second equivalent of MeMgBr to the solution of **3-Me** results in substitution of one of the isopropoxide ligands (as evidenced by generation of free *i*-PrOMgBr) and formation of pentacoordianted dimethyltitanium ate complex **3-Me$_2$** (Scheme S2 and Table S2). Complex **3-Me$_2$** is five-coordinated and C_1-symmetric as is obvious from the appearance of TADDOL ligand signals, presence of one isopropoxide ligand with diastereotopic methyls, and two non-equivalent methyl groups bonded to titanium (δ = 1.00 and 1.28 ppm in ^{1}H and 64.14 and 55.08 ppm in ^{13}C NMR respectively).



Scheme S2.

Table S2. Key NMR data for dimethyltitanium ate complex **3-Me$_2$**.[a]

		^{1}H δ (m, $^2J_{HH}$)	^{13}C {^{1}H} δ
TADDOL	Me(*a*)	0.48 (s)	26.57
	Me(*b*)	1.15 (s)	27.72
	CH(*b*)	4.65 (d, 7.6 Hz)	82.84
	CH(*a*)	5.44 (d, 7.6 Hz)	82.50
	o-CH Ph(*a*)	7.87 (d, 7.7 Hz)	nd[b]
	o-CH Ph(*b*)	7.77 (d, 7.6 Hz)	nd[b]
	o-CH Ph(*c*)	7.68 (d, 7.8 Hz)	nd[b]
	o-CH Ph(*d*)	7.51 (br s)	nd[b]
***i*-PrOTi**	OCH	5.33 (sept, 6.2 Hz)	71.02
	Me	1.42 and 1.89 (d, 6.2 Hz)	26.35 and 26.50
Me-Ti	Me(*a*)	1.00 (s)	64.14
	Me(*b*)	1.28 (s)	55.08

[a] 800 MHz for ^{1}H, 201.2 MHz for ^{13}C, at 295 K in toluene-d_8 / Et$_2$O-d_{10}; [b] not determined due to overlapping with solvent signals.

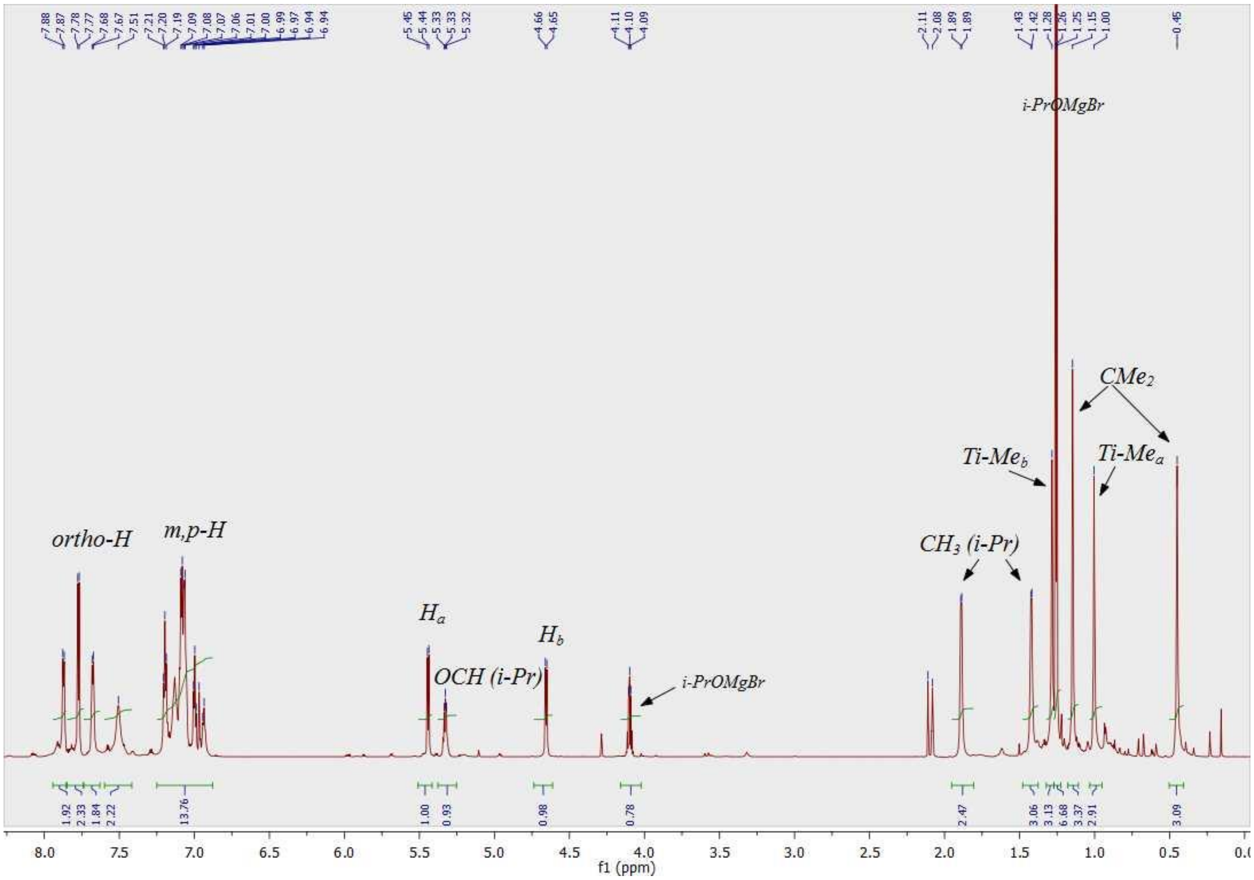
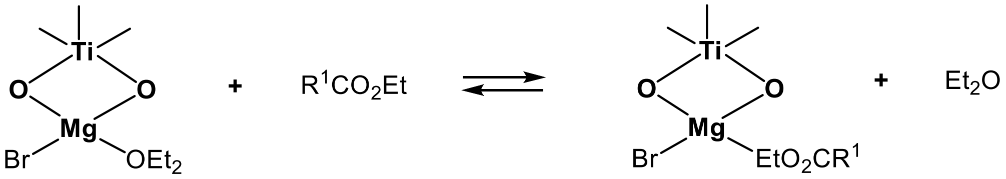


Fig. S2. ^{1}H NMR spectrum of ate complex **3-Me$_2$** (800 MHz, 298 K, toluene-d$_8$ / Et$_2$O-d$_{10}$).

Analogous monoalkyl and dimethyl titanium ate species can also be generated by reaction of other alkoxide complexes, e.g. (TADDOL)Ti(OEt)$_2$, with MeMgBr and other Grignard reagents.

B. *Complexation of ethyl 3-phenylpropionate with ate complex* 3-Me

Illustrative example of ester complexation with methyl titanium ate complex **3-Me** as evidenced by ^{1}H NMR spectroscopy (400 MHz, toluene-d_8). Addition of ethyl 3-phenylpropionate **8** (3 equiv) causes substitution of diethyl ether ligand in complex **3-Me** with a carboxylic ester (Fig. S3, C), what can be concluded from ester's signals shift / broadening and appearance of Et_2O methylene signal as a "normal" quartet. On the other hand, addition of less basic hexafluoroisopropyl 3-phenylpropionate (3 equiv) introduces only a minor change in spectrum appearance, thus evidencing weak coordination to ate complex **3-Me** (Fig. S3, D).



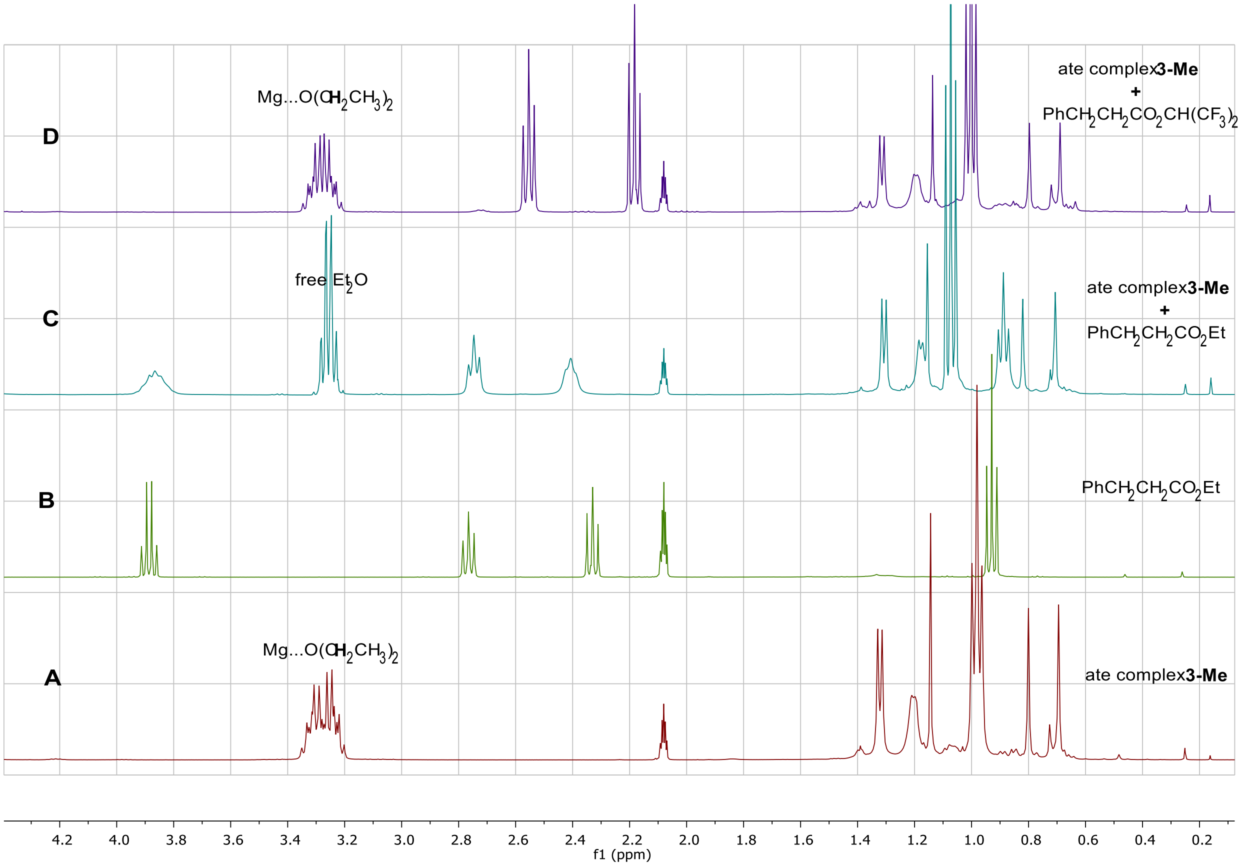
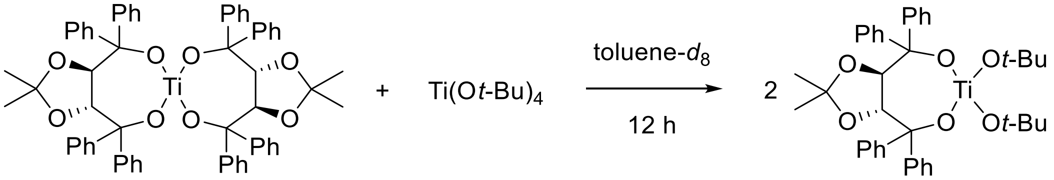


Fig. S3. A) ^{1}H NMR spectrum (400 MHz, toluene-d_8) of methyl titanium ate complex **3-Me** (see above for signal assignment); diethyl ether shows complex multiplet signal for the diastereotopic CH_2 protons due to inclusion into a chiral ate complex; **B)** Reference spectrum of ethyl 3-phenylpropionate; **C)** Ethyl 3-phenylpropionate (3 equiv) is added to ate complex **3-Me**; **D)** Hexafluoroisopropyl 3-phenylpropionate (3 equiv) is added to ate complex **3-Me**.

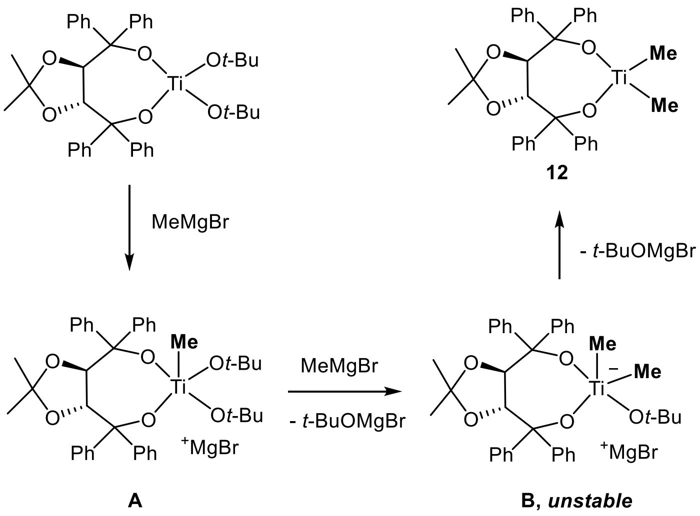
C. ***Reaction of (TADDOL)Ti(Ot-Bu)$_2$ with MeMgBr***

Starting TADDOLate complex complex can be conveniently prepared by mixing equimolecular amount of Ti(TADDOL)$_2$ and Ti(O*t*-Bu)$_4$ in toluene-*d*$_8$, following general procedure described on page S3. In contrast to reaction of primary and secondary alkoxides, ligand exchange with bulkier *tert*-butoxide takes several hours to complete (^{1}H NMR monitoring).



(TADDOL)Ti(O*t*-Bu)$_2$: ^{1}H NMR (400 MHz, toluene-*d*$_8$): δ = 7.80–7.44 (m, 8H, *o*-H$_{Ar}$), 7.26–6.98 (m, 12H, *m*,*p*-H$_{Ar}$), 5.41 (s, 2H, CH), 1.17 (s, 18H, *t*-BuO), 0.72 (s, 6H, CMe$_2$). ^{13}C NMR (100.6 MHz, toluene-*d*$_8$): δ = 149.06 (C$_{Ar}$), 143.79 (C$_{Ar}$), 129.93 (CH$_{Ar}$), 128.01 (CH$_{Ar}$), 127.90 (CH$_{Ar}$), 127.32 (CH$_{Ar}$), 127.27 (CH$_{Ar}$), 127.14 (CH$_{Ar}$), 111.89 ($\underline{C}$Me$_2$), 94.53 (CPh$_2$), 82.57 (CH), 82.56 (O$\underline{C}$Me$_3$), 32.15 (OC$\underline{Me_3}$), 27.83 (C$\underline{Me_2}$).

Progress of the reaction between *tert*-butoxide complex and MeMgBr can be conveniently tracked by ^{1}H NMR spectroscopy (Fig. S4). Different TADDOLate species are easily distinguishable in a characteristic region of the TADDOL ligand methine protons (δ 5.0-5.7 ppm). As in the case of previously tested titanium TADDOLates (see above), treatment of (TADDOL)Ti(O*t*-Bu)$_2$ with MeMgBr results in formation of pentacoordinated methyltitanium ate complex **A**, although with a noticeably slower rate (Scheme S3, Fig. S4, B). Addition of the next equivalent of MeMgBr results in formation of a further *C*$_1$-symmetric species, presumably ate complex **B** (Fig. S4, C). The latter is unstable and undergoes gradual decomposition with release of *C*$_2$-symmetric TADDOLate complex (Fig. S4, C-E), with spectral characteristics identical to (TADDOL)TiMe$_2$ (**12**, Fig. S4, F). (The minor discrepancy of chemical shifts with the reference sample of complex **12** is likely caused by presence of diethyl ether as co-solvent).



Scheme S3.

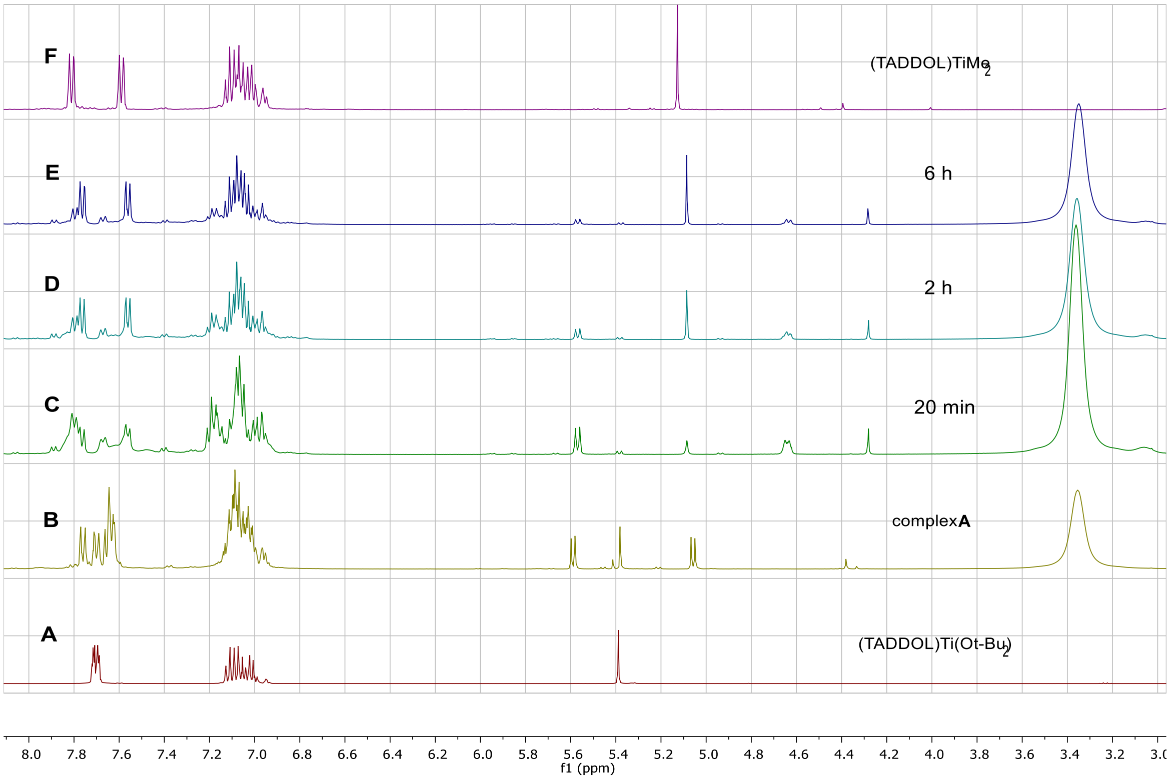
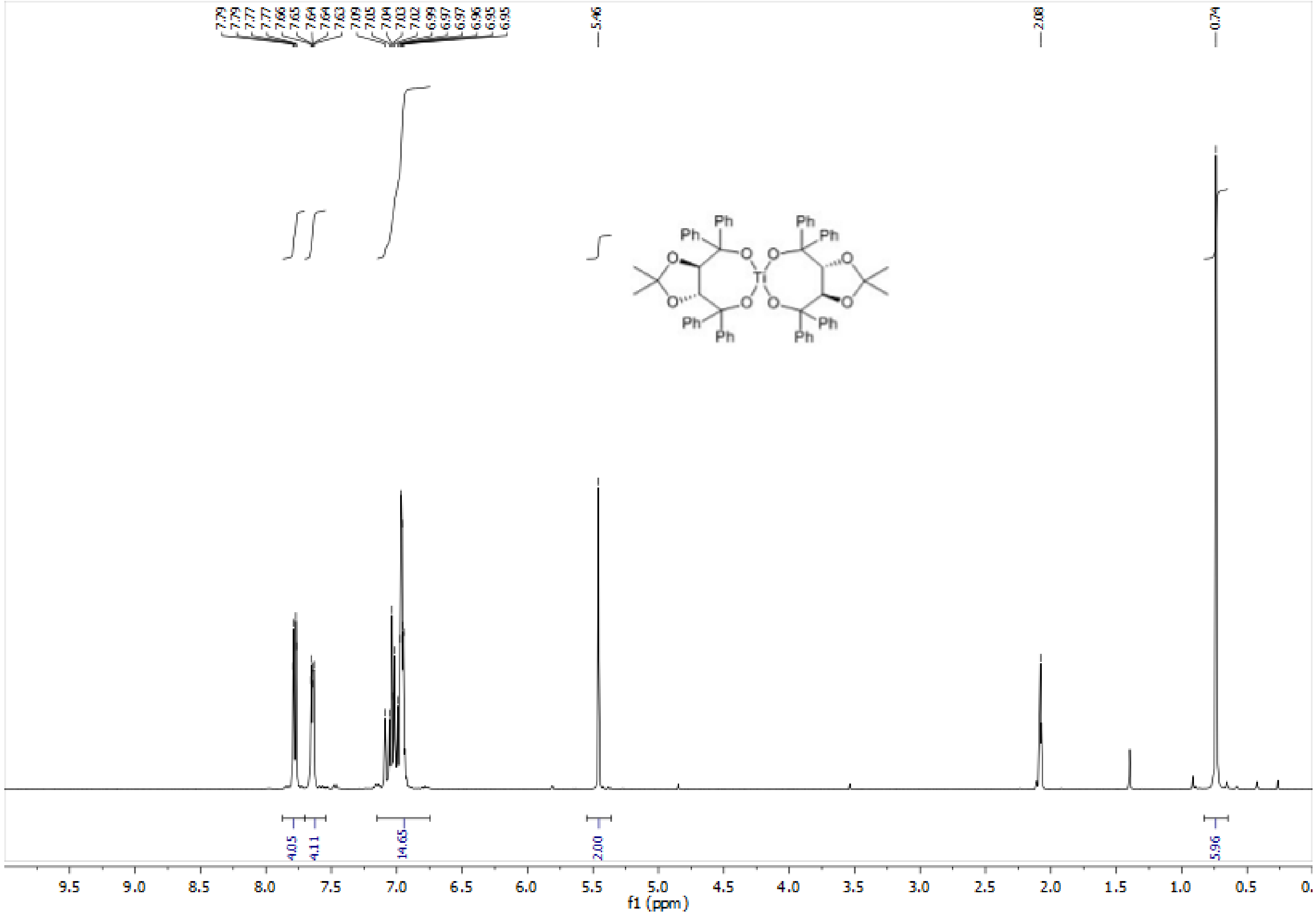
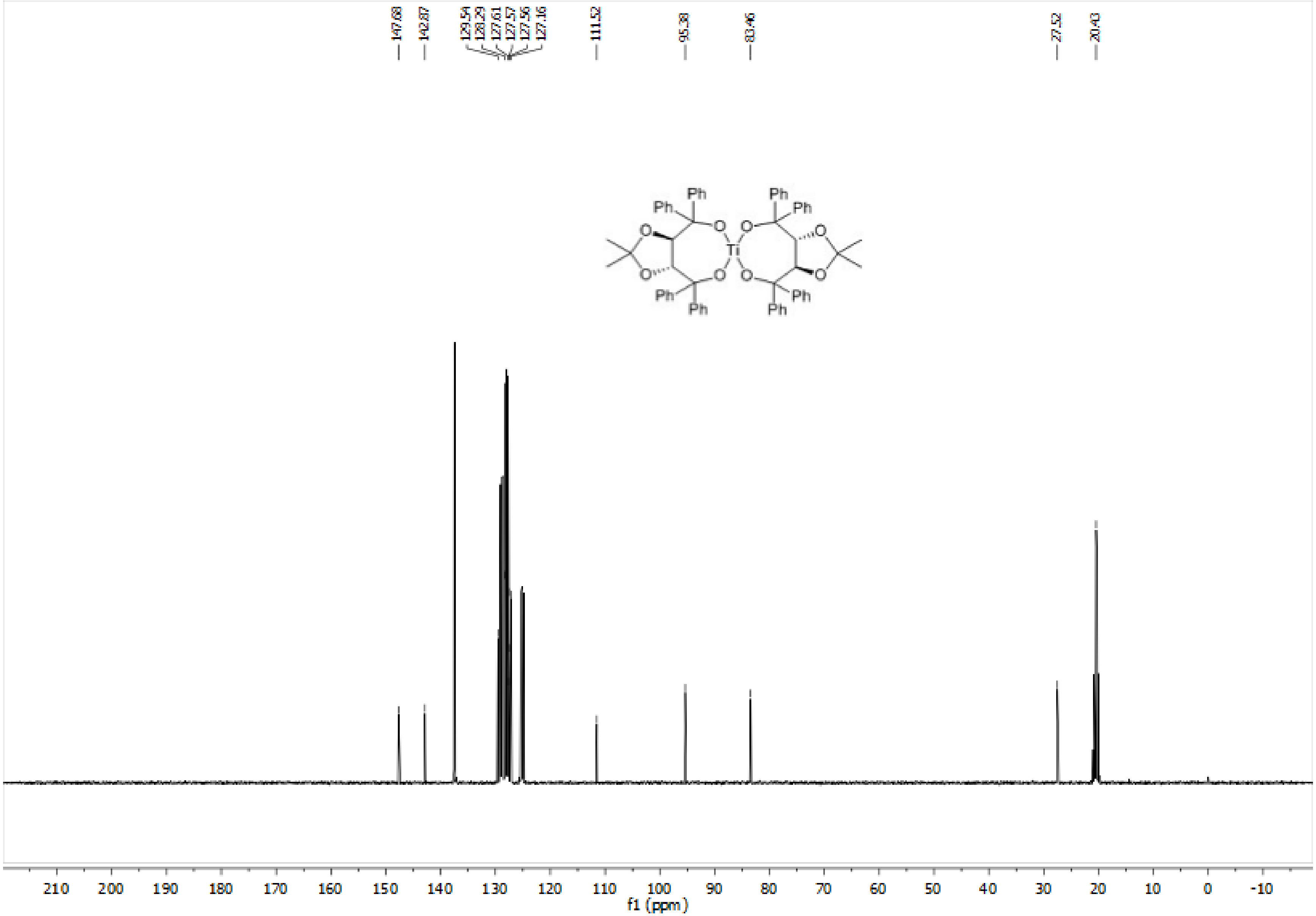


Fig. S4. A) ^{1}H NMR spectrum (400 MHz, toluene-d_8) of (TADDOL)Ti(O*t*-Bu)$_2$; **B)** After addition of MeMgBr (ca. 1 equiv), signals of C_1-symmetric ate complex **A** appeared, along with residual starting material; **C)** Addition of the second equivalent of MeMgBr results in formation of ate complex **B**, and some amounts of (TADDOL)TiMe$_2$ (spectrum recorded 20 min after addition of the Grignard reagent); **D)** Same reaction mixture after 2 h; **E)** Same reaction mixture after 6 h; **F)** Reference spectrum of (TADDOL)TiMe$_2$.

III. Copies of ^{1}H NMR and ^{13}C NMR spectra

A. *Titanium Complexes*

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95.38
83.46
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Ph
Ph
O
O
Ti
O
O
Ph
Ph
Ph
Ph
O
O
O
O
Ph
Ph
Ph
Ph
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200
190
180
170
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140
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120
110
100
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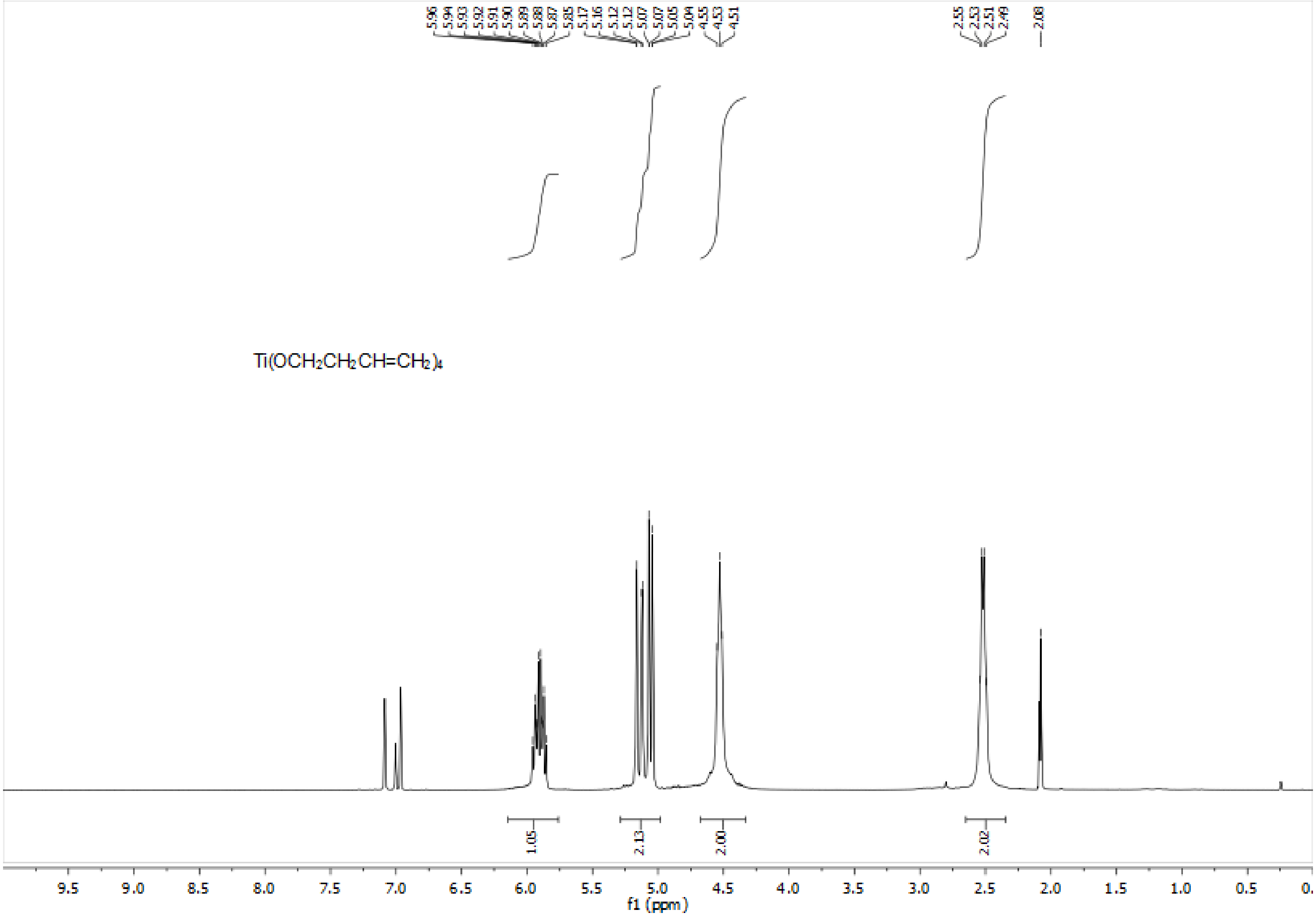
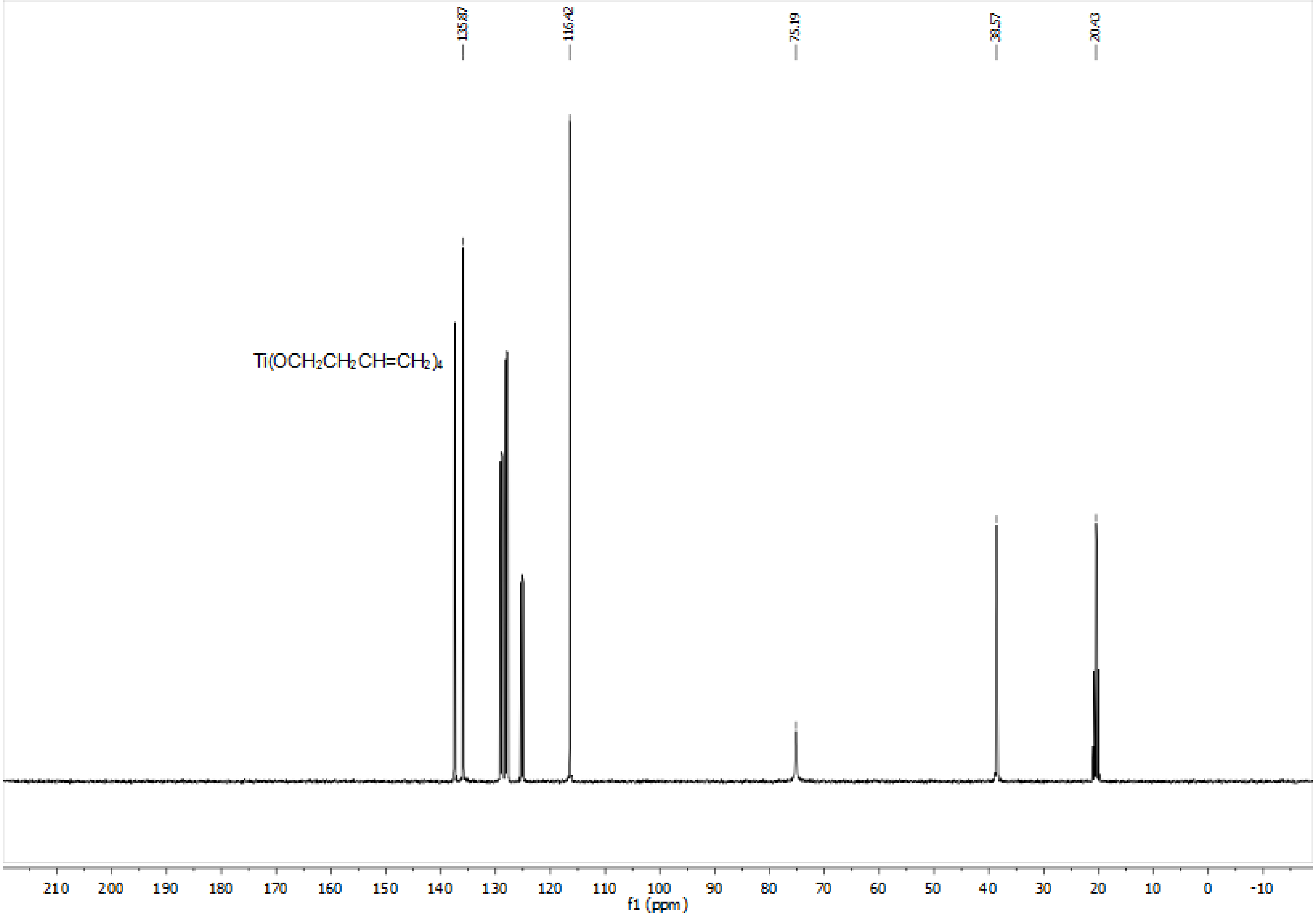
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



$Ti(OCH_2CH_2CH{=}CH_2)_4$


135.87
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20.43
Ti(OCH2CH2CH=CH2)4
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120
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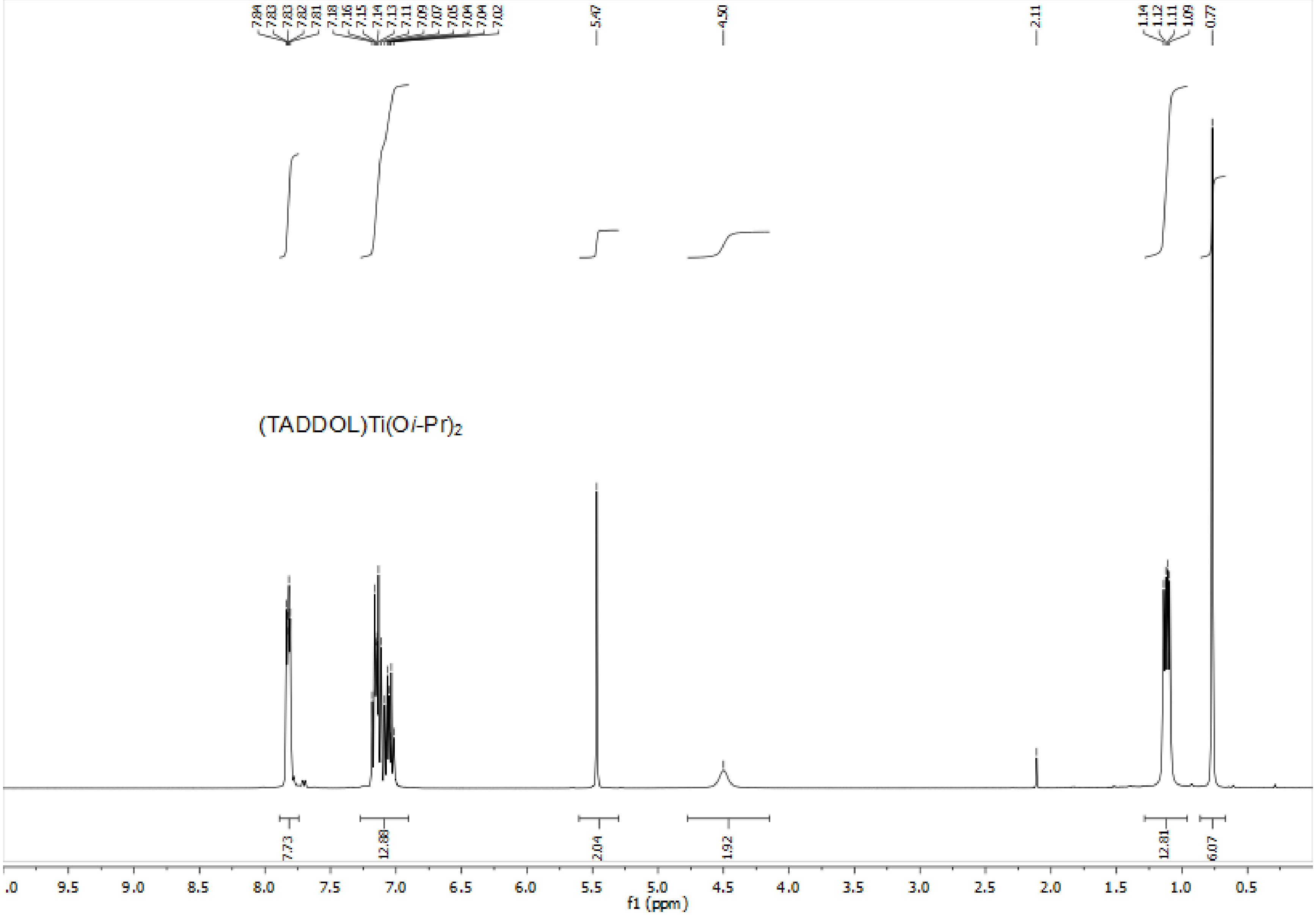
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.81
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7.07
7.05
7.04
7.04
7.02
5.47
4.50
2.11
1.14
1.12
1.11
1.09
0.77
(TADDOL)Ti(O*i*-Pr)$_2$
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2.04
1.92
12.81
6.07
.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
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3.0
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2.0
1.5
1.0
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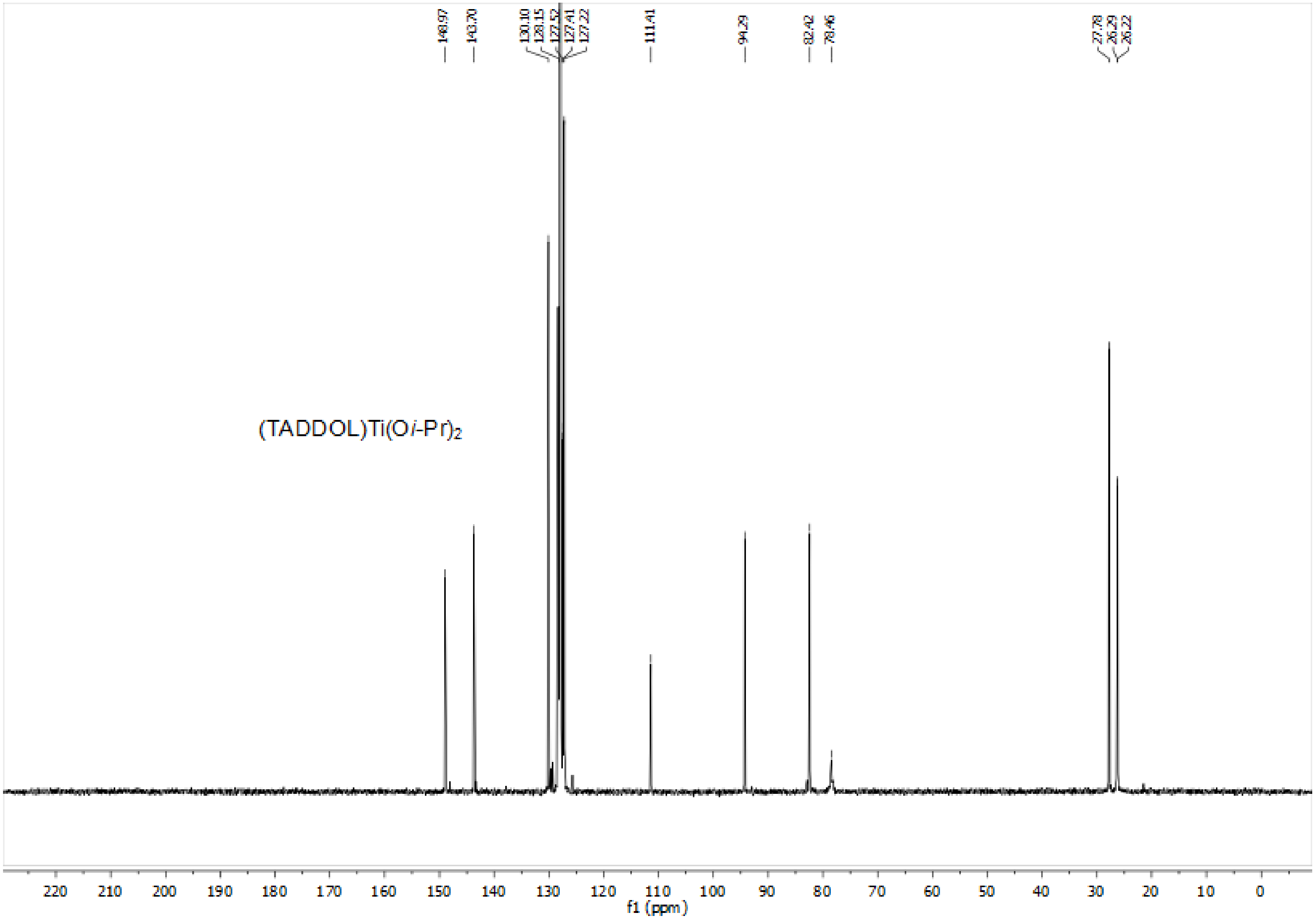
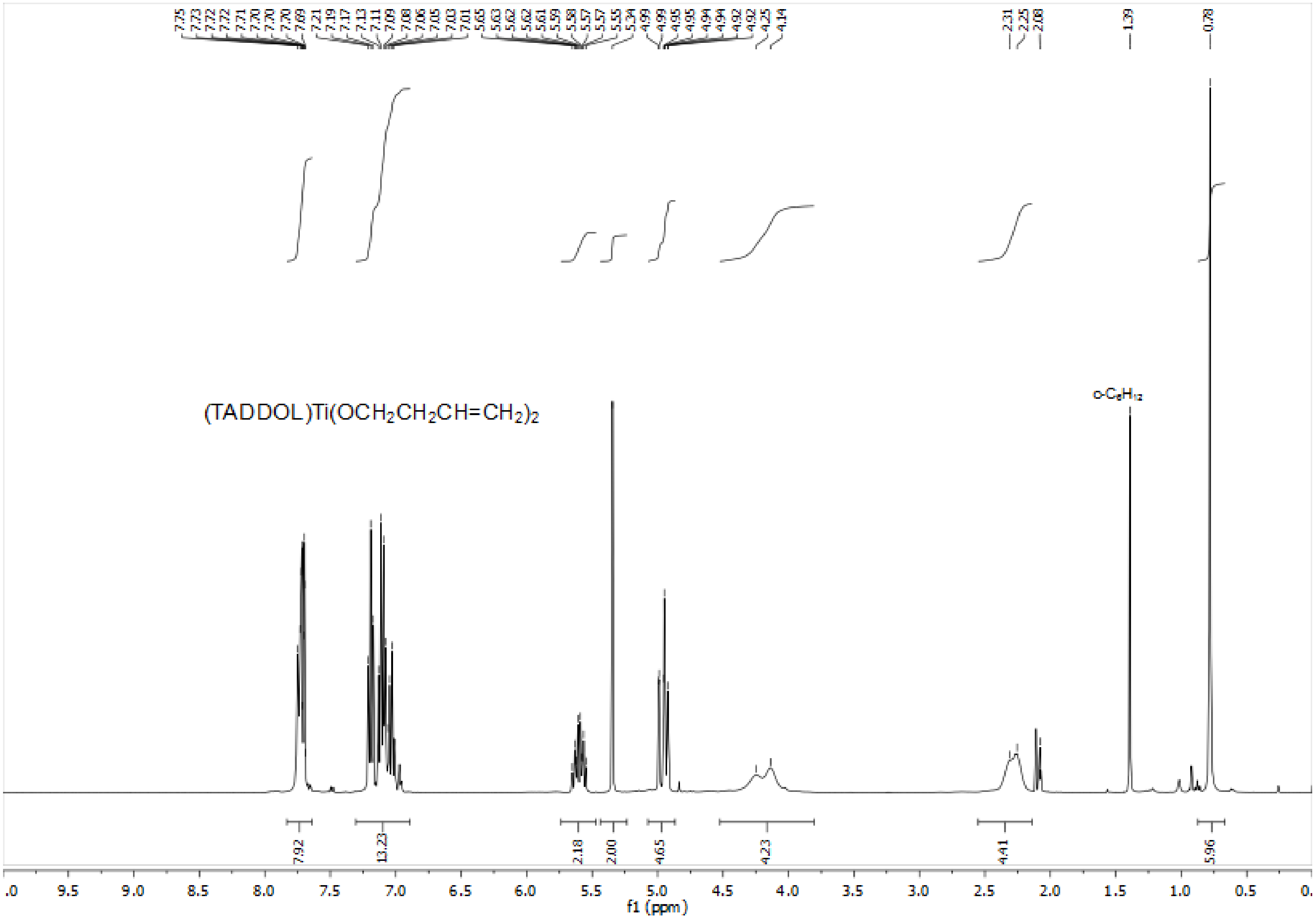
f1 (ppm)



(TADDOL)Ti(O*i*-Pr)$_2$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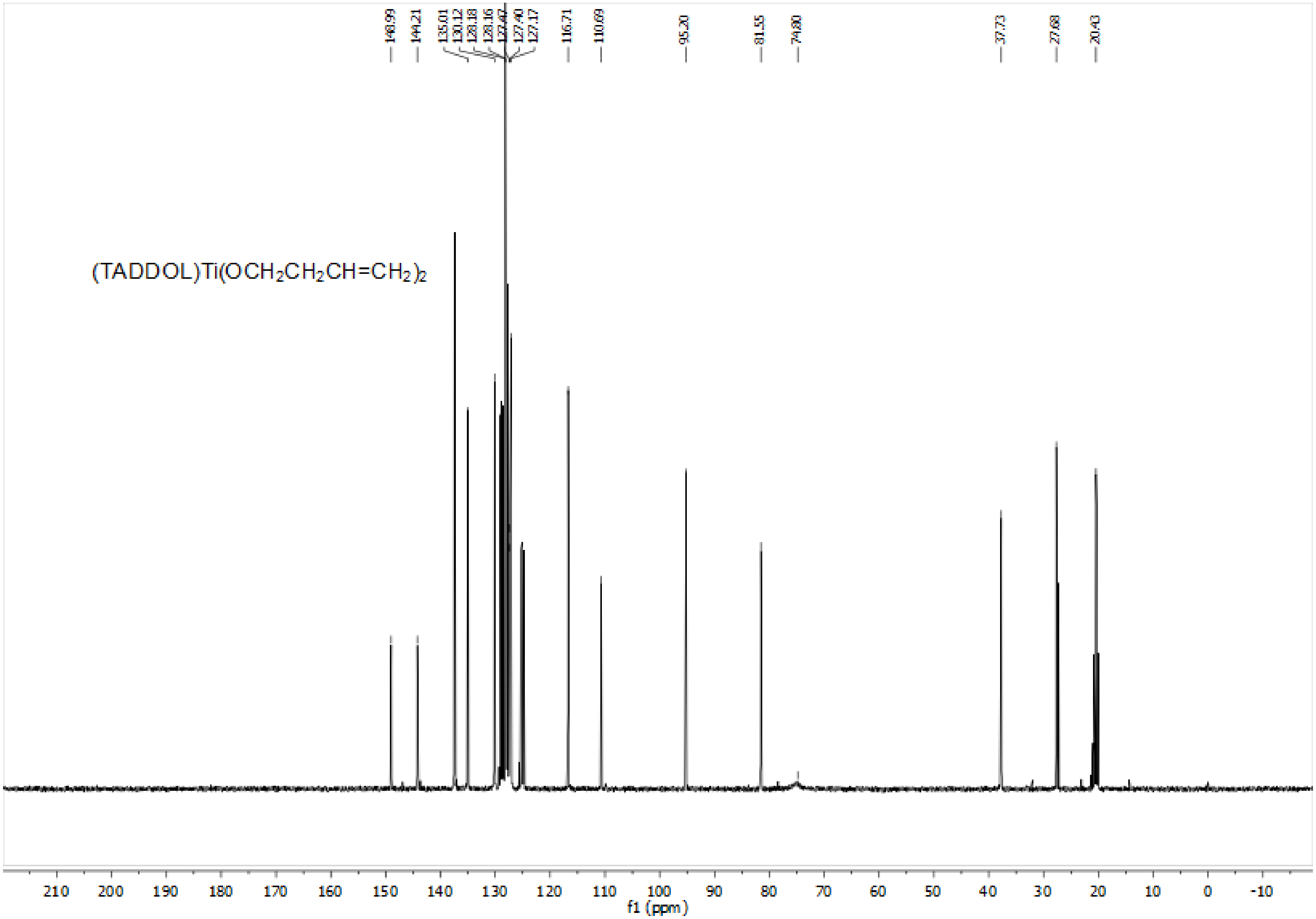
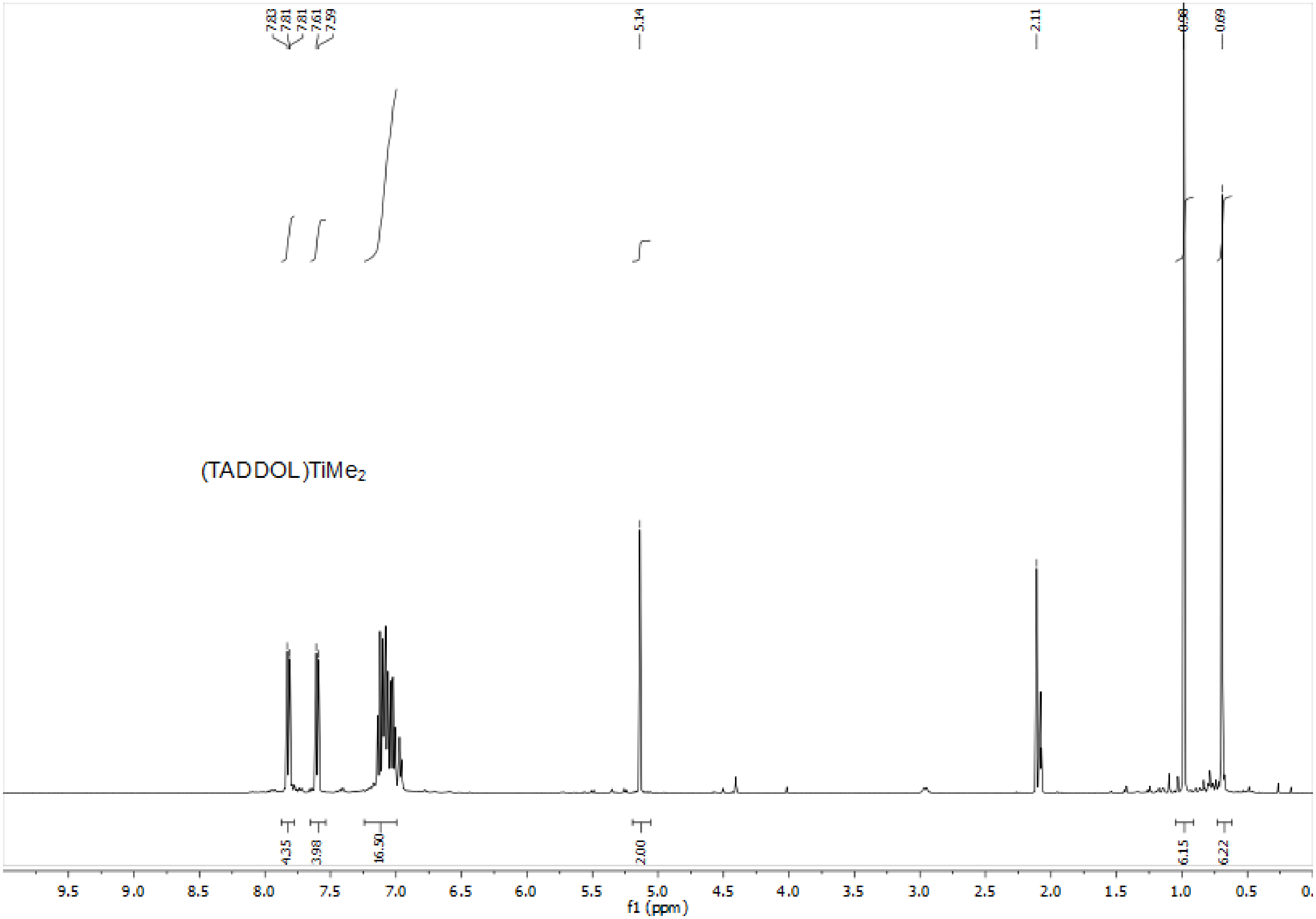
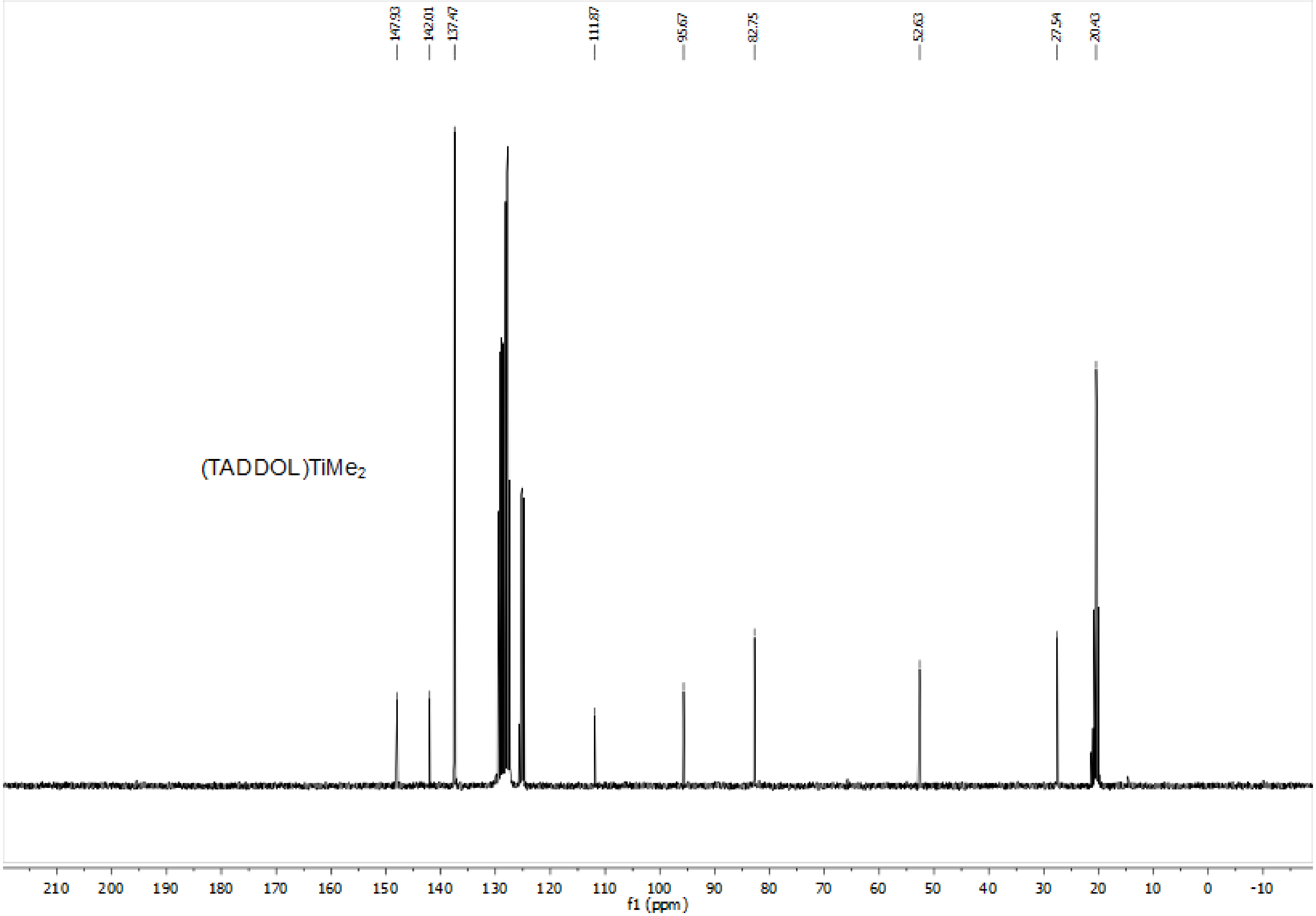
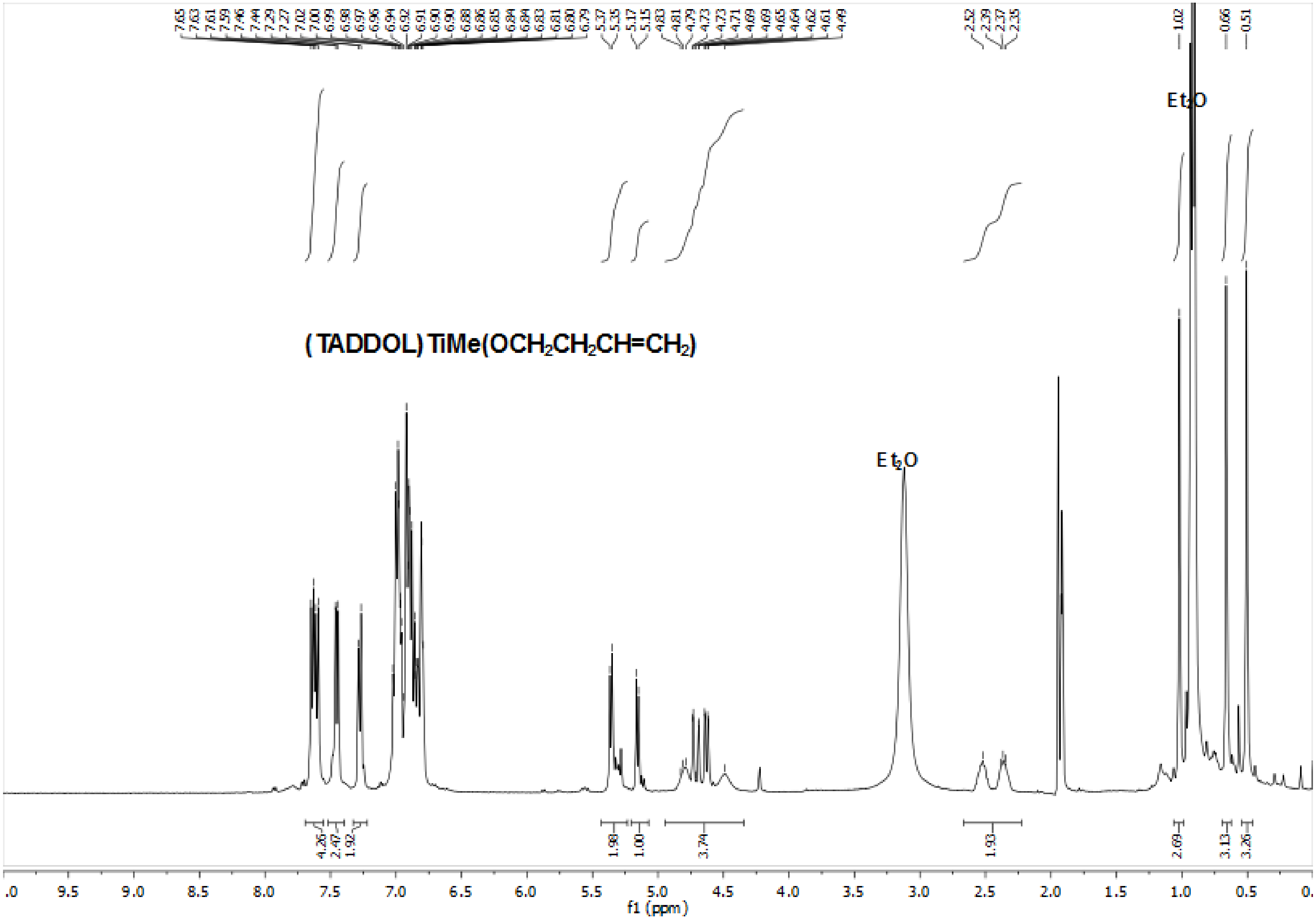
5.58
5.57
5.57
5.55
5.34
4.99
4.99
4.95
4.95
4.94
4.94
4.92
4.92
4.25
4.14
2.31
2.25
2.08
1.39
0.78
(TADDOL)Ti(OCH$_2$CH$_2$CH=CH$_2$)$_2$
o-C$_6$H$_{12}$
7.92
13.23
2.18
2.00
4.65
4.23
4.41
5.96
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

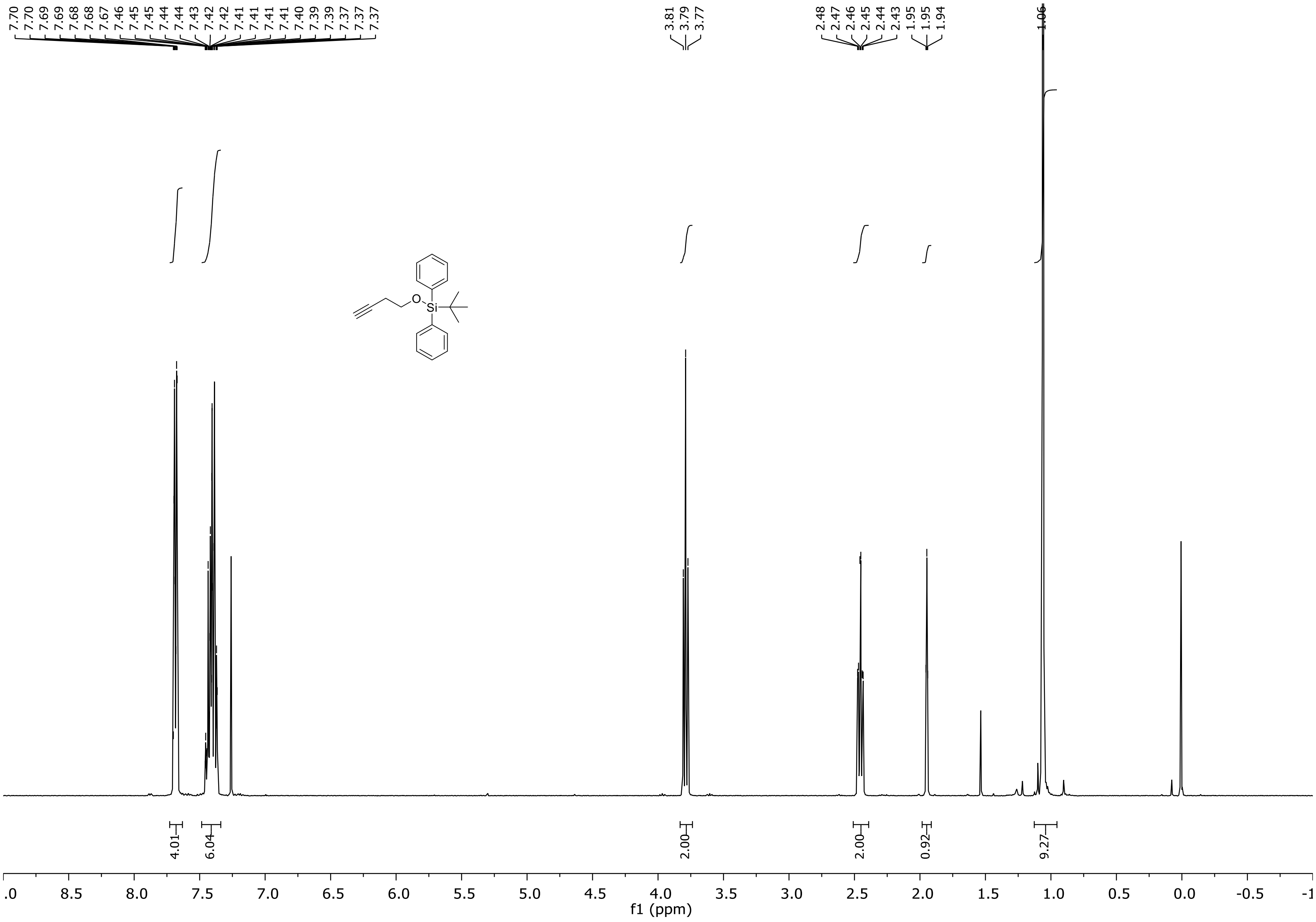

(TADDOL)Ti$(OCH_2CH_2CH=CH_2)_2$
148.99
144.21
135.01
130.12
128.18
128.16
127.47
127.40
127.17
116.71
110.69
95.20
81.55
74.80
37.73
27.68
20.43
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

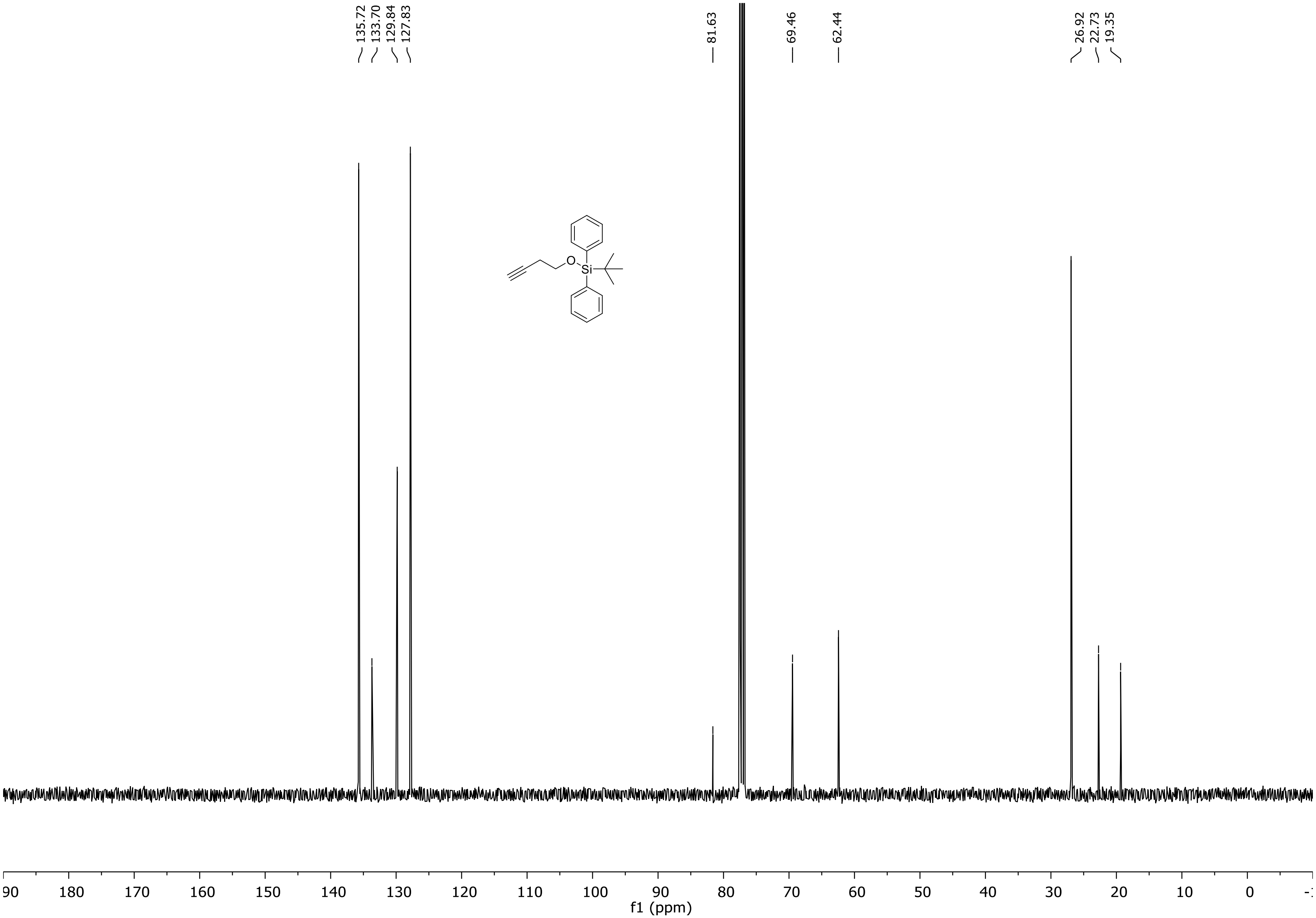

7.83
7.81
7.81
7.61
7.59
5.14
2.11
0.98
0.69
(TADDOL)TiMe₂
4.35
3.98
16.50
2.00
6.15
6.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

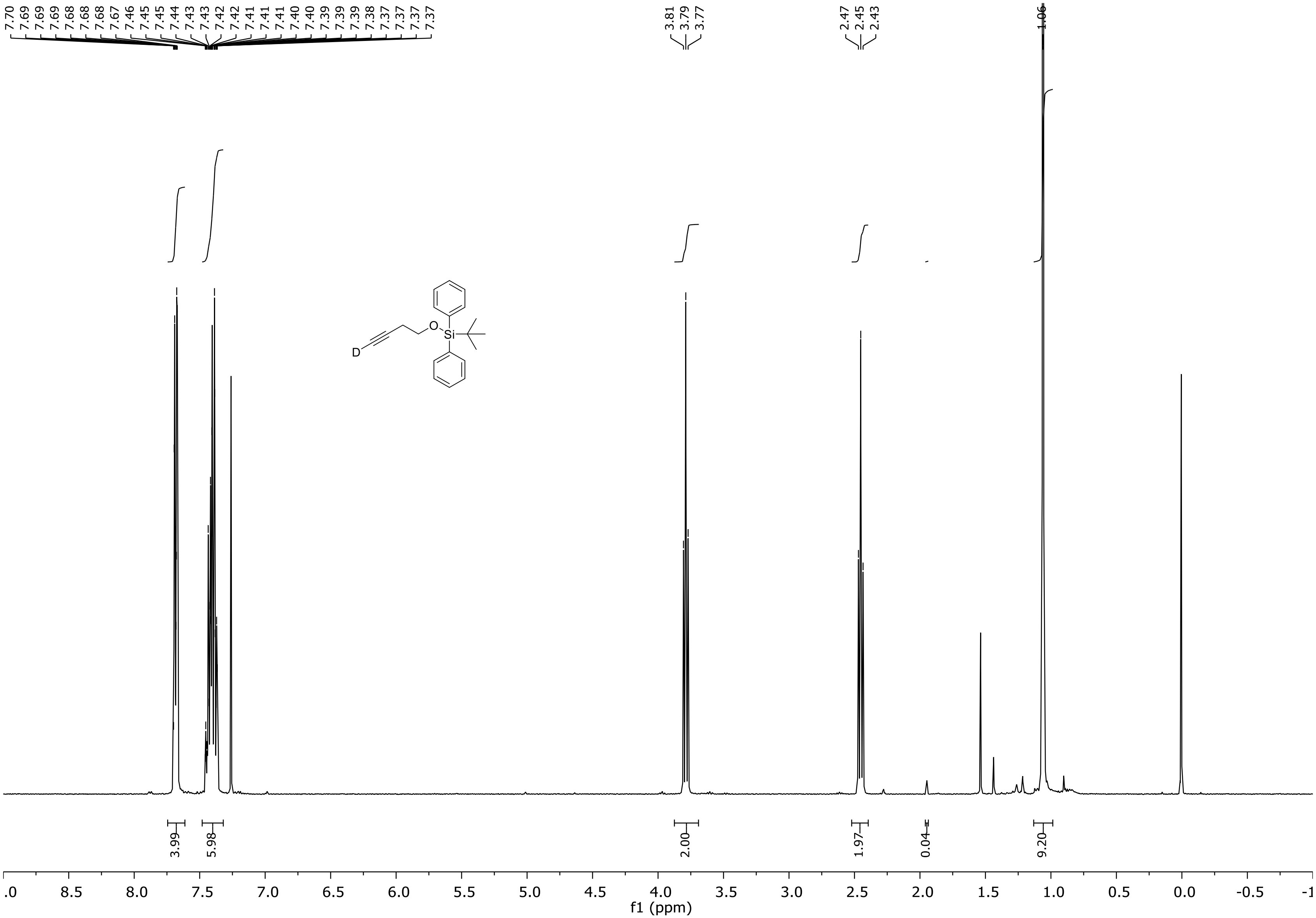

(TADDOL)TiMe$_2$

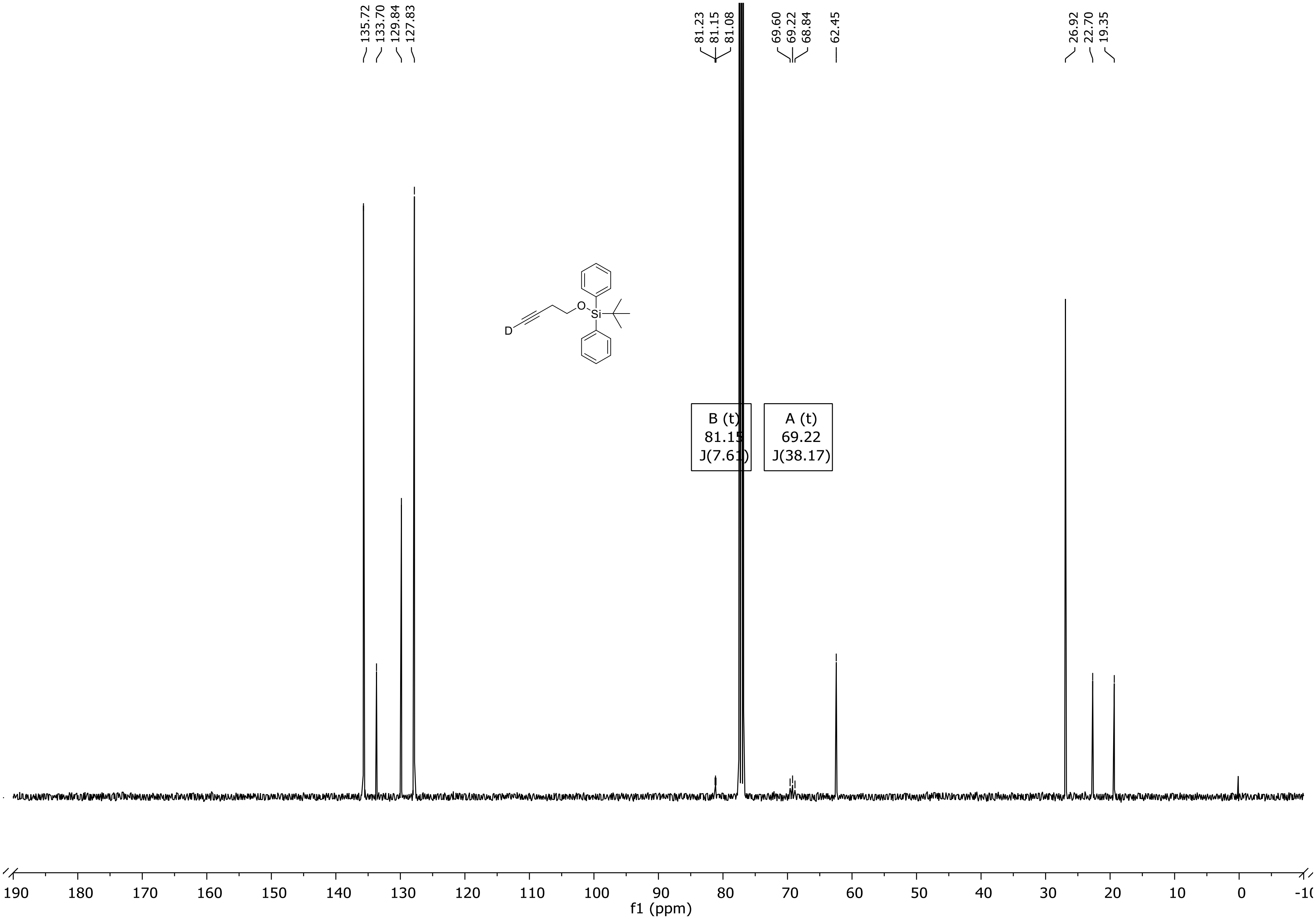

7.65
7.63
7.61
7.59
7.46
7.44
7.29
7.27
7.02
7.00
6.99
6.98
6.97
6.96
6.94
6.92
6.91
6.90
6.90
6.88
6.86
6.85
6.84
6.84
6.83
6.81
6.80
6.79
5.37
5.35
5.17
5.15
4.83
4.81
4.79
4.73
4.73
4.71
4.69
4.69
4.65
4.64
4.62
4.61
4.49
2.52
2.39
2.37
2.35
1.02
0.66
0.51
Et$_2$O
(TADDOL) TiMe(OCH$_2$CH$_2$CH=CH$_2$)
Et$_2$O
4.26
2.47
1.92
1.98
1.00
3.74
1.93
2.69
3.13
3.26
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

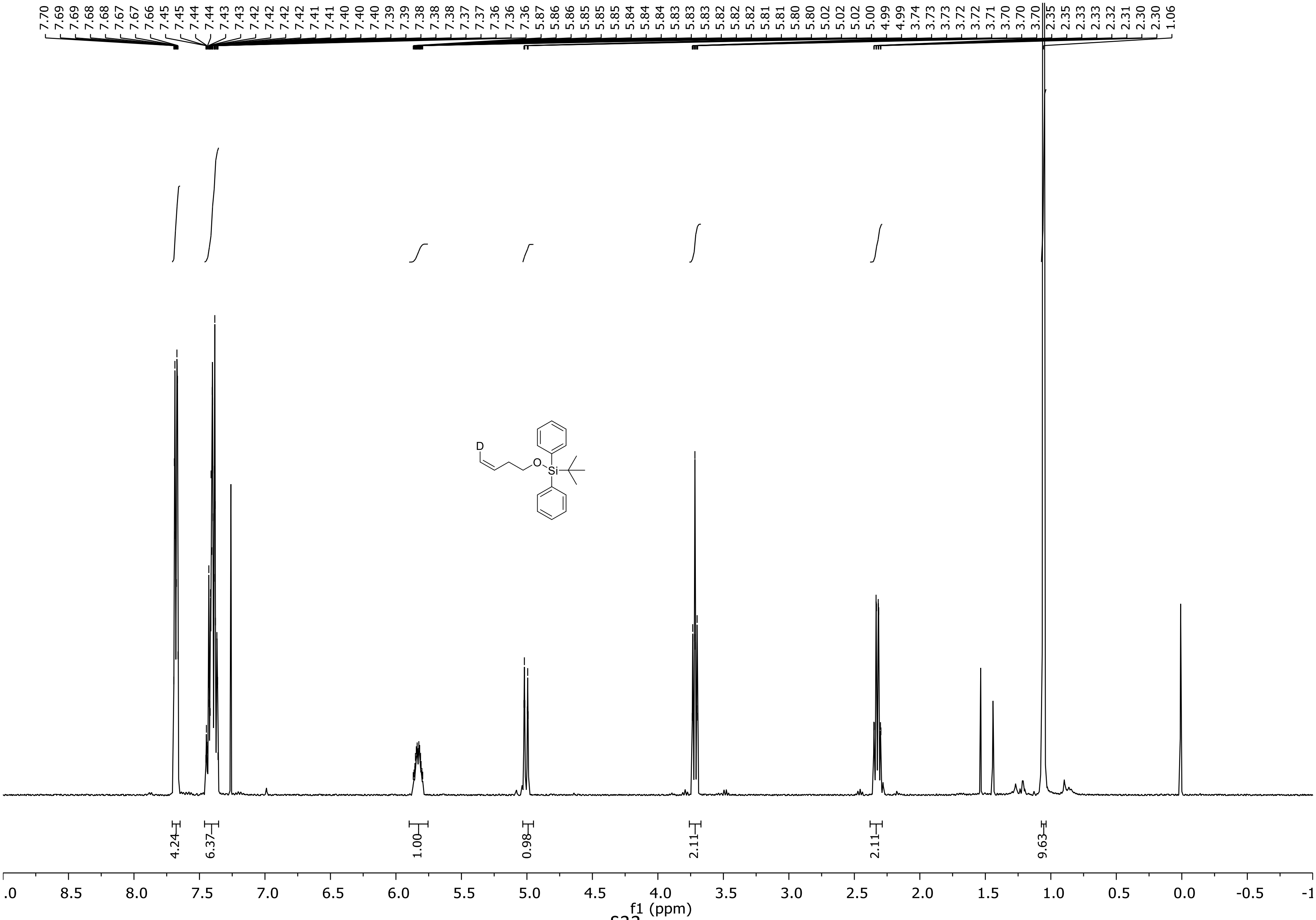
B. *Alkenes and synthetic intermediates*

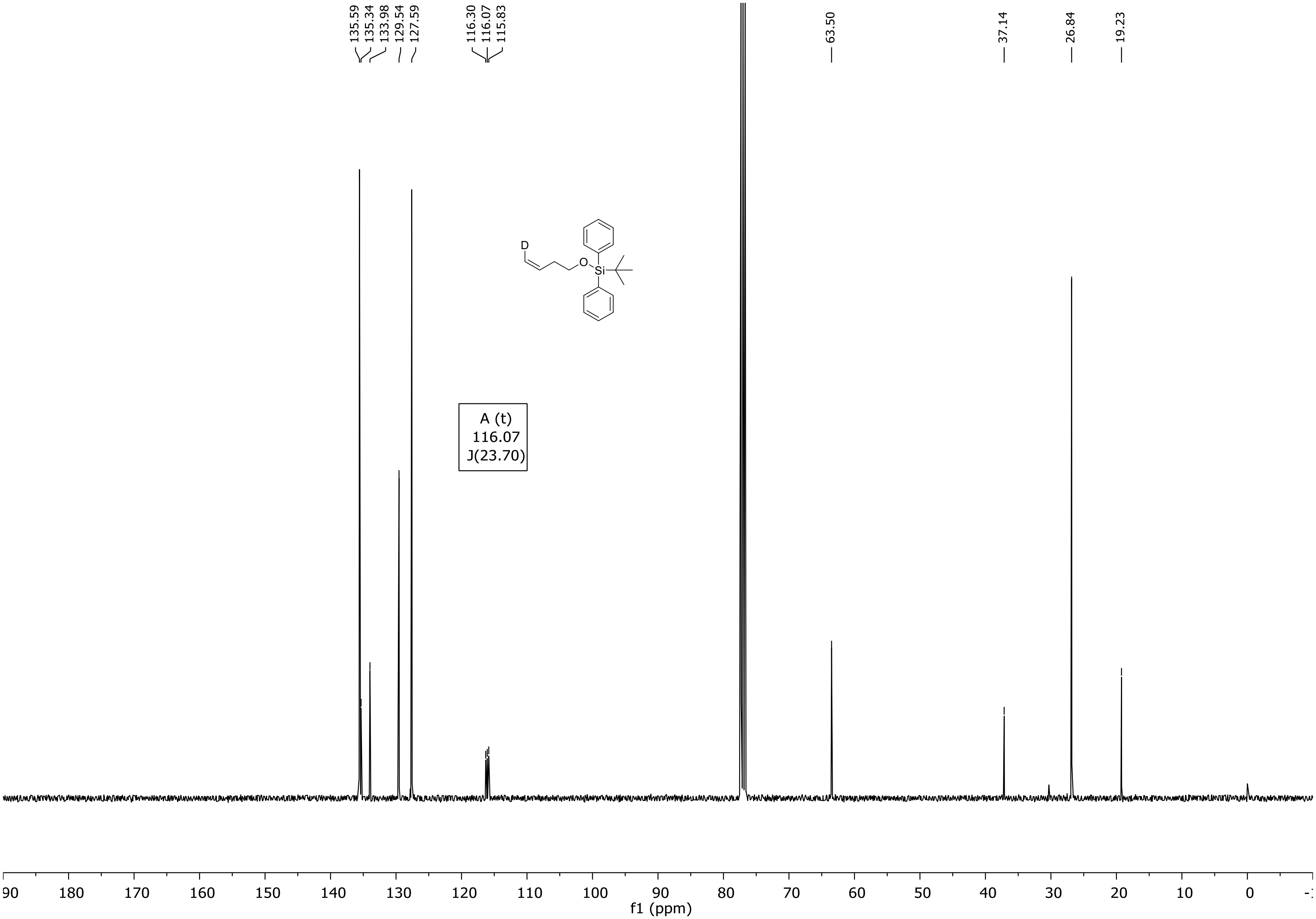


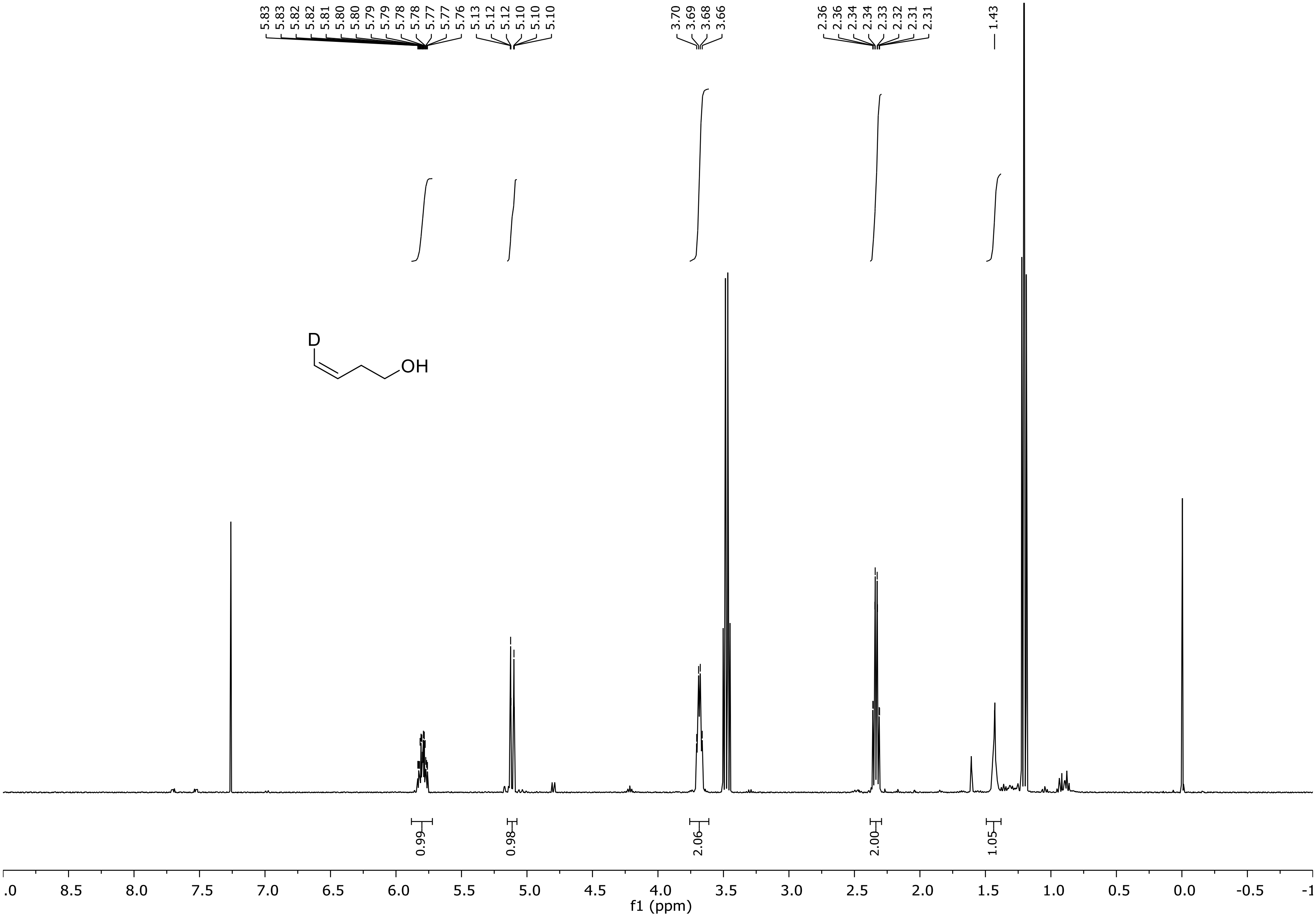

135.72
133.70
129.84
127.83
81.63
69.46
62.44
26.92
22.73
19.35
O
Si
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)

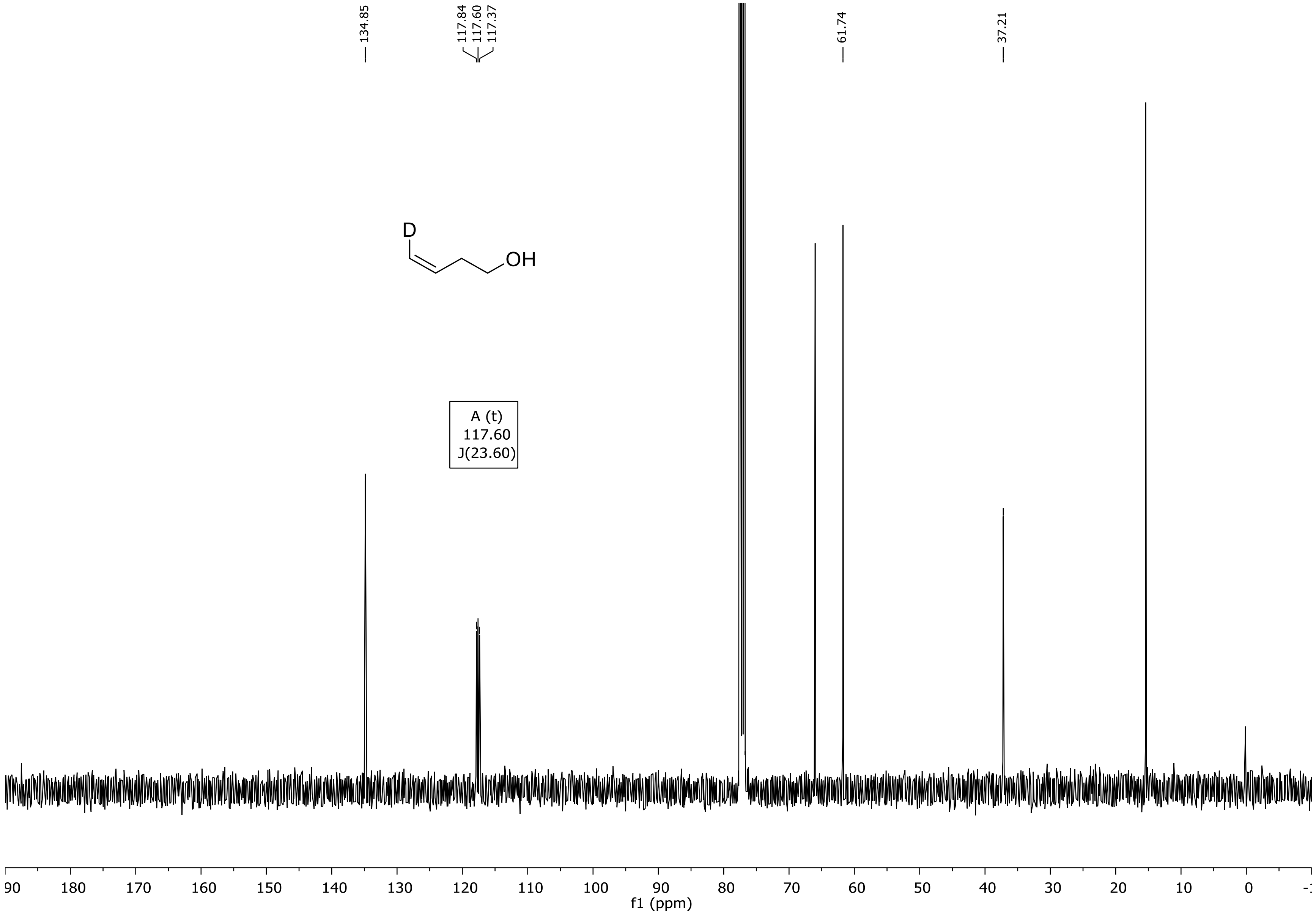

7.70
7.69
7.69
7.68
7.68
7.68
7.67
7.46
7.45
7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.37
7.37
3.81
3.79
3.77
2.47
2.45
2.43
1.06
D
O
Si
3.99
5.98
2.00
1.97
0.04
9.20
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

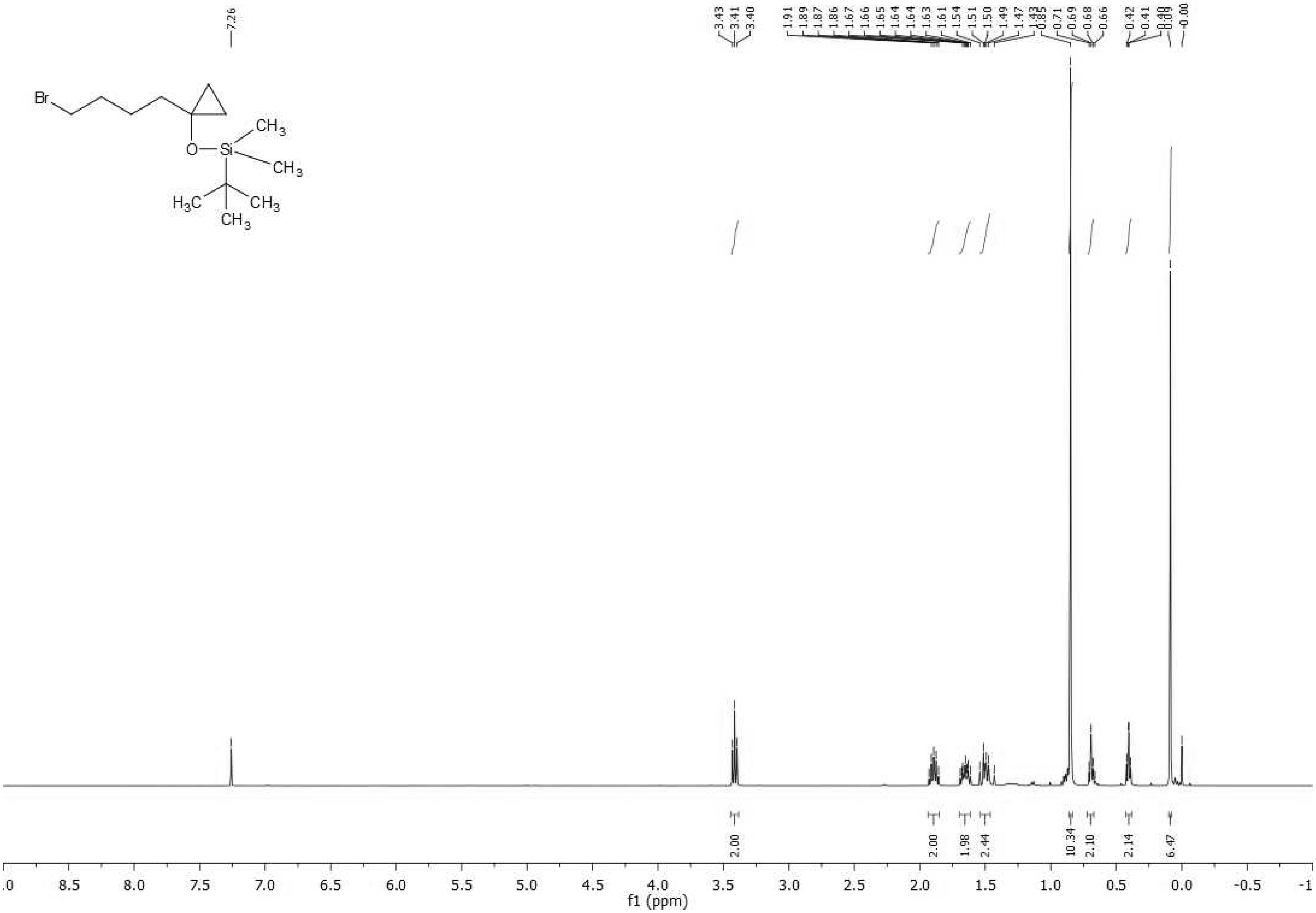

135.72
133.70
129.84
127.83
81.23
81.15
81.08
69.60
69.22
68.84
62.45
26.92
22.70
19.35
D
O
Si
B (t)
81.15
J(7.61)
A (t)
69.22
J(38.17)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.70 7.69 7.69 7.68 7.68 7.67 7.67 7.66 7.45 7.45 7.44 7.44 7.43 7.43 7.42 7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.36 5.87 5.86 5.86 5.85 5.85 5.84 5.84 5.84 5.83 5.83 5.83 5.82 5.82 5.81 5.81 5.80 5.80 5.02 5.02 5.02 5.00 4.99 4.99 3.74 3.73 3.73 3.72 3.72 3.71 3.70 3.70 3.70 2.35 2.35 2.33 2.33 2.32 2.31 2.30 2.30 1.06
D
O
Si
4.24
6.37
1.00
0.98
2.11
2.11
9.63
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

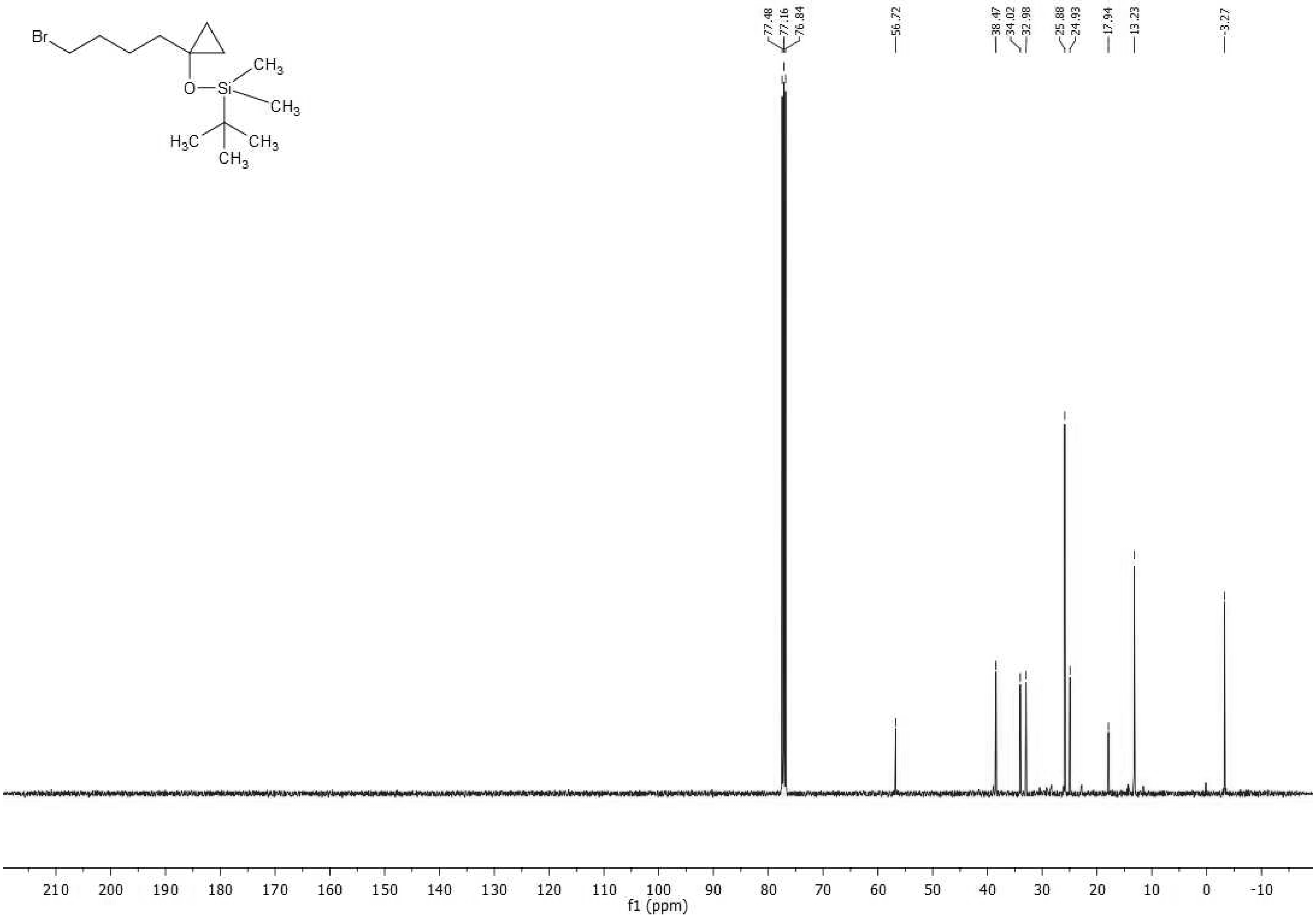

135.59
135.34
133.98
129.54
127.59
116.30
116.07
115.83
63.50
37.14
26.84
19.23
D
O
Si
A (t)
116.07
J(23.70)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

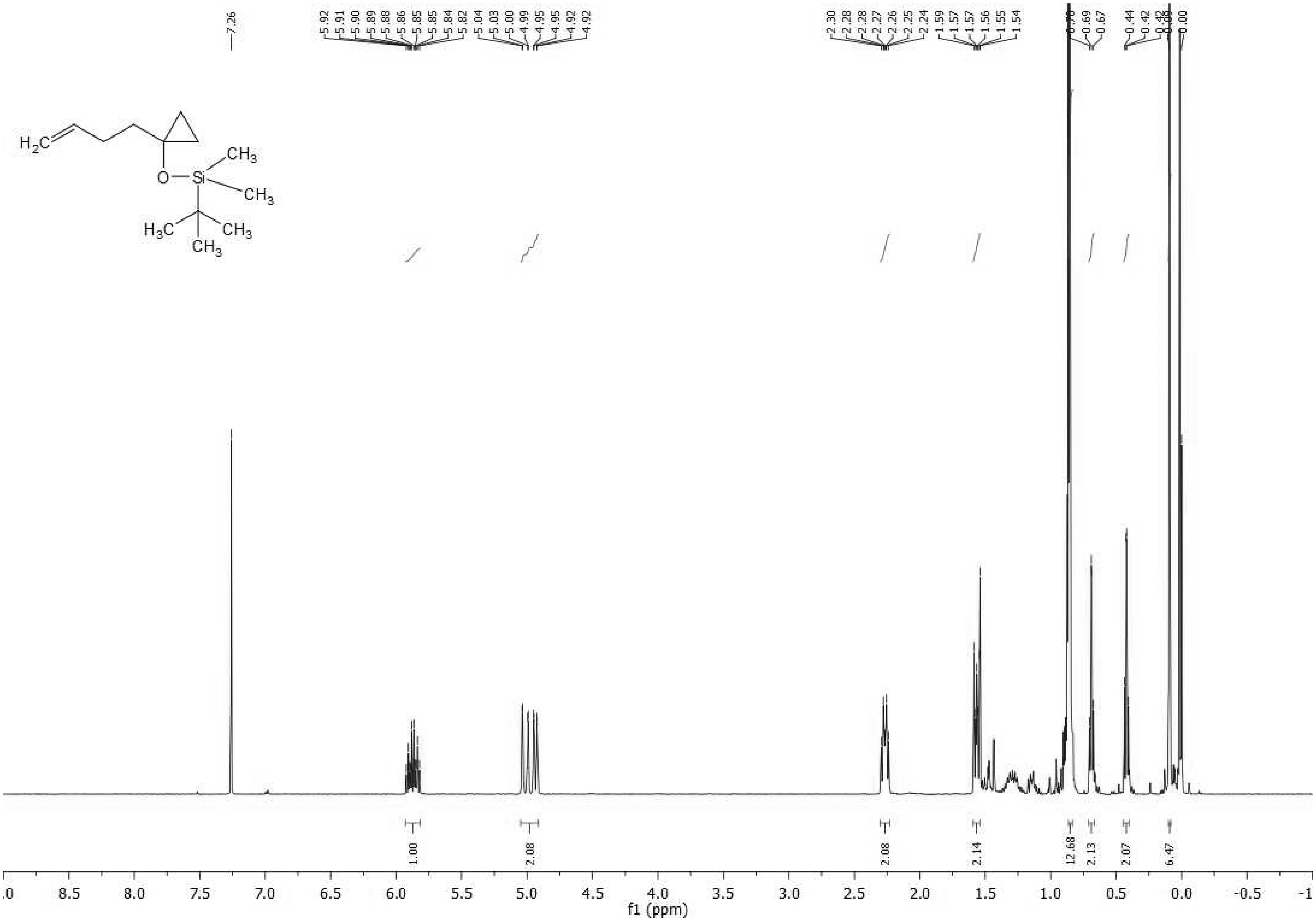

5.83
5.83
5.82
5.82
5.81
5.80
5.80
5.79
5.79
5.78
5.78
5.77
5.77
5.76
5.13
5.12
5.12
5.10
5.10
5.10
3.70
3.69
3.68
3.66
2.36
2.36
2.34
2.34
2.33
2.32
2.31
2.31
1.43
D
OH
0.99
0.98
2.06
2.00
1.05
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

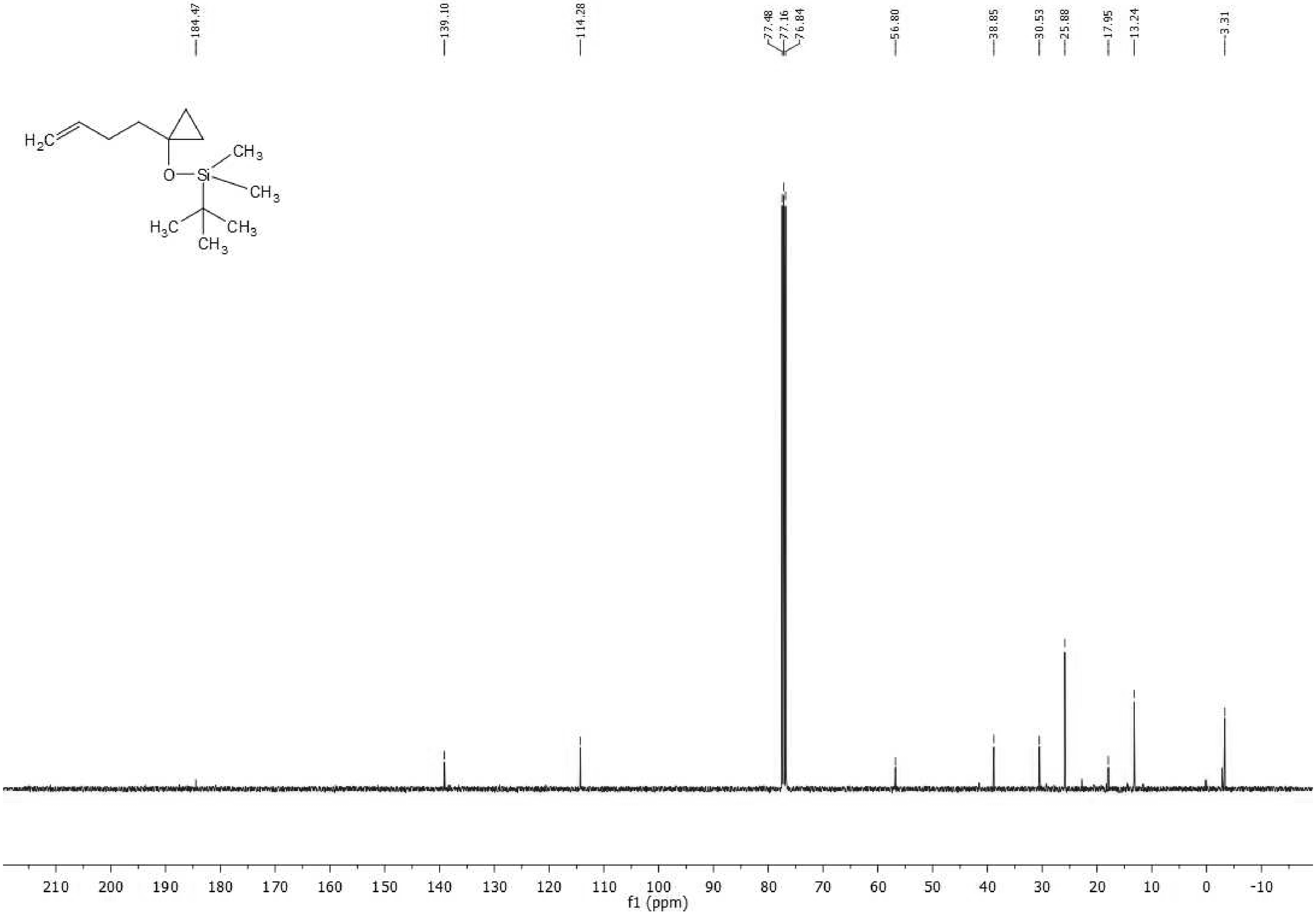

134.85
117.84
117.60
117.37
61.74
37.21
D
OH
A (t)
117.60
J(23.60)
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-
f1 (ppm)



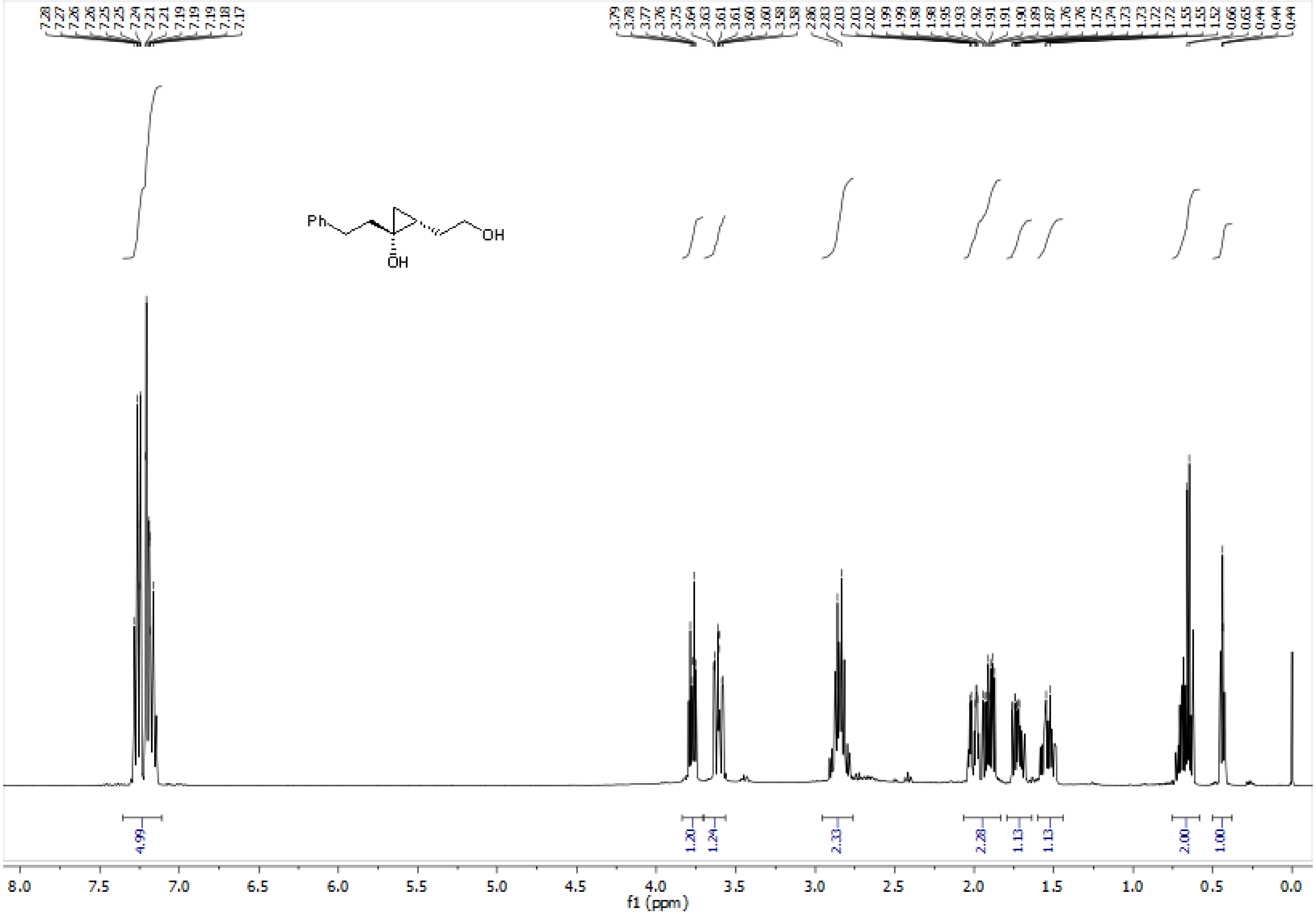
Br
O
Si
CH3
CH3
H3C
CH3
CH3
7.26
3.43
3.41
3.40
1.91
1.89
1.87
1.86
1.67
1.66
1.65
1.64
1.64
1.63
1.61
1.54
1.51
1.50
1.49
1.47
1.43
0.85
0.71
0.69
0.68
0.66
0.42
0.41
0.40
0.09
-0.00
2.00
2.00
1.98
2.44
10.34
2.10
2.14
6.47
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

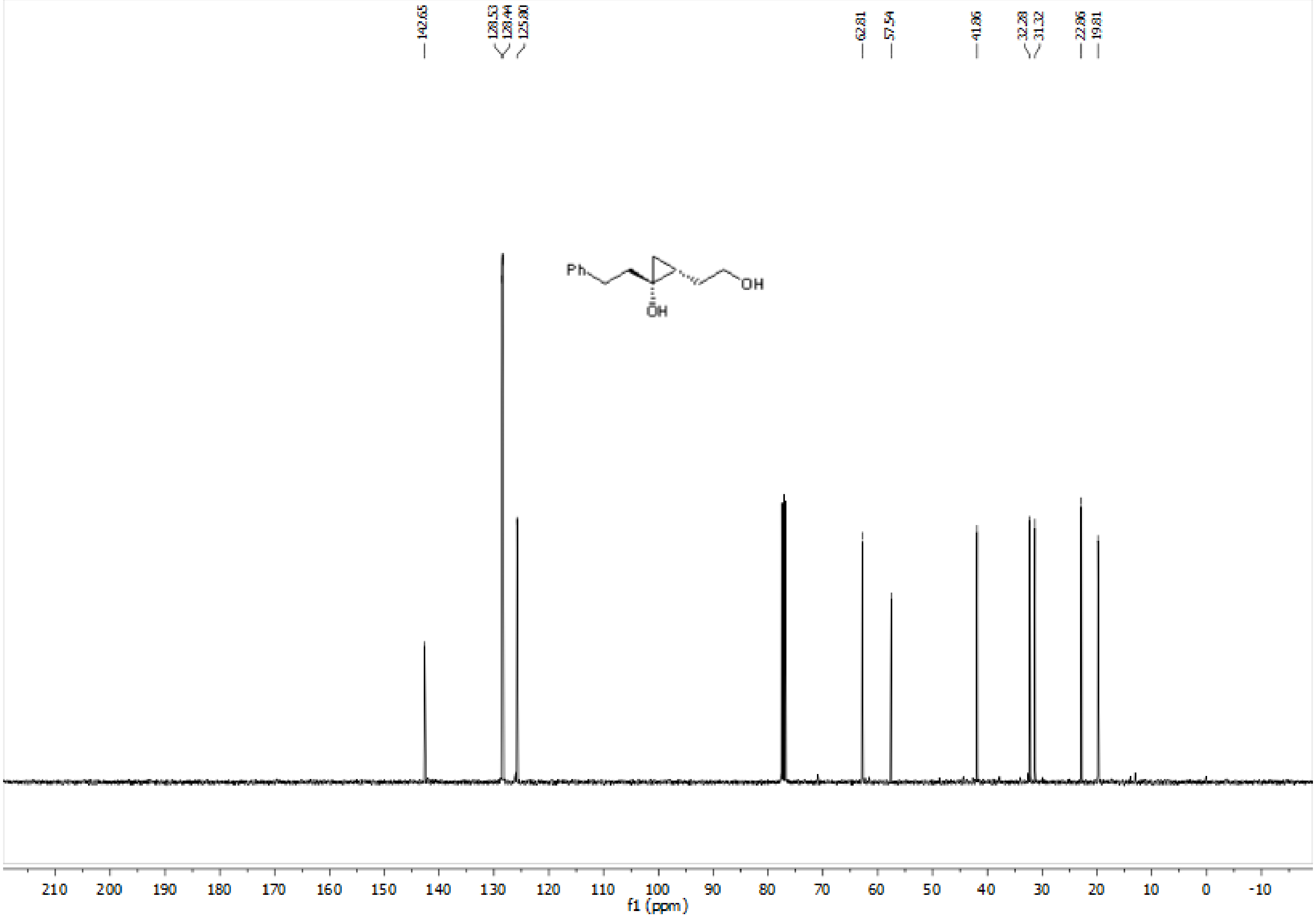

Br
O
Si
CH3
CH3
H3C
CH3
CH3
77.48
77.16
76.84
56.72
38.47
34.02
32.98
25.88
24.93
17.94
13.23
-3.27
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

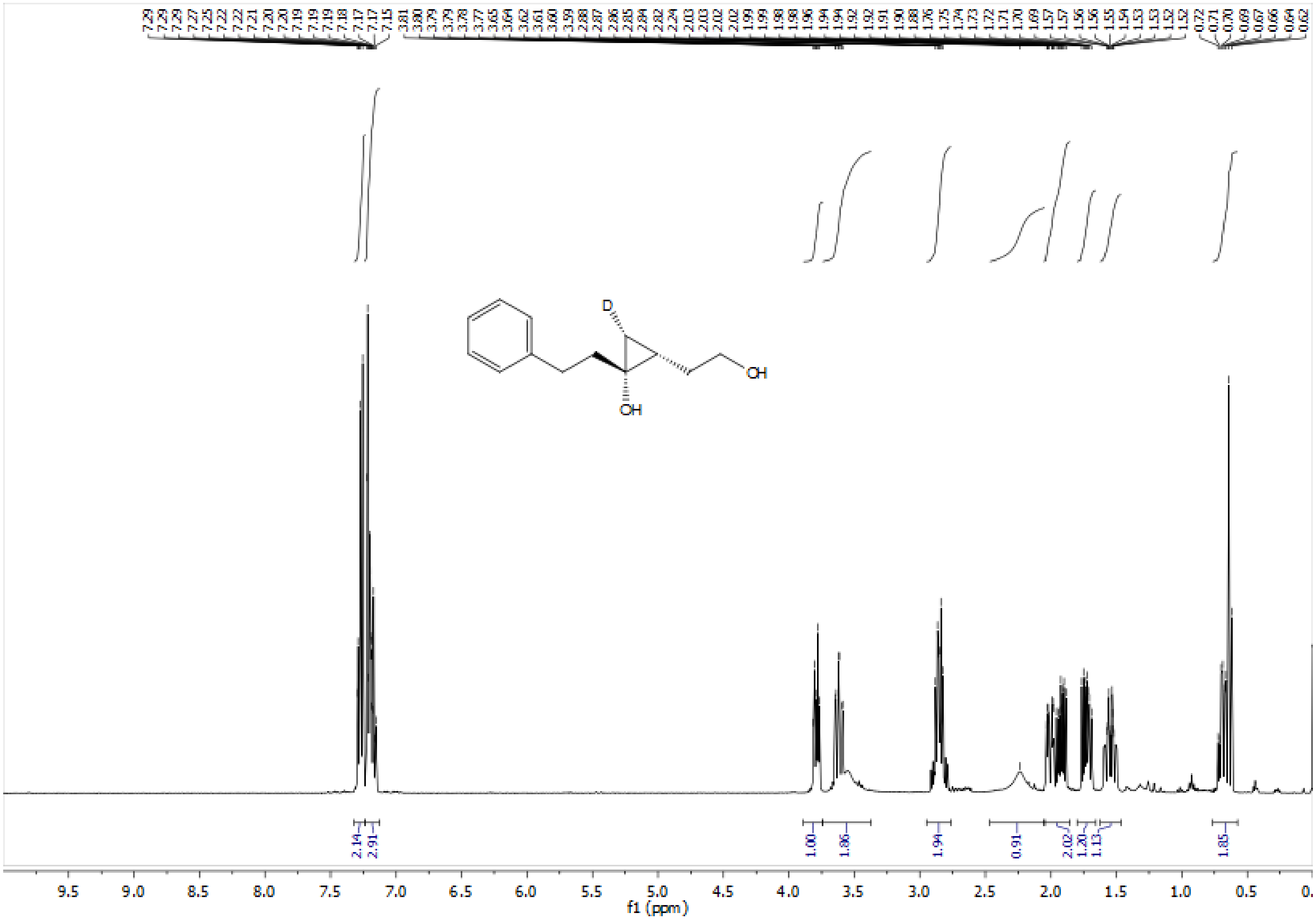
H2C
O
Si
CH3
CH3
H3C
CH3
CH3
7.26
5.92
5.91
5.90
5.89
5.88
5.86
5.85
5.85
5.84
5.82
5.04
5.03
5.00
4.99
4.95
4.95
4.92
4.92
2.30
2.28
2.28
2.27
2.26
2.25
2.24
1.59
1.57
1.57
1.56
1.55
1.54
0.69
0.67
0.44
0.42
0.00
1.00
2.08
2.08
2.14
12.68
2.13
2.07
6.47
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

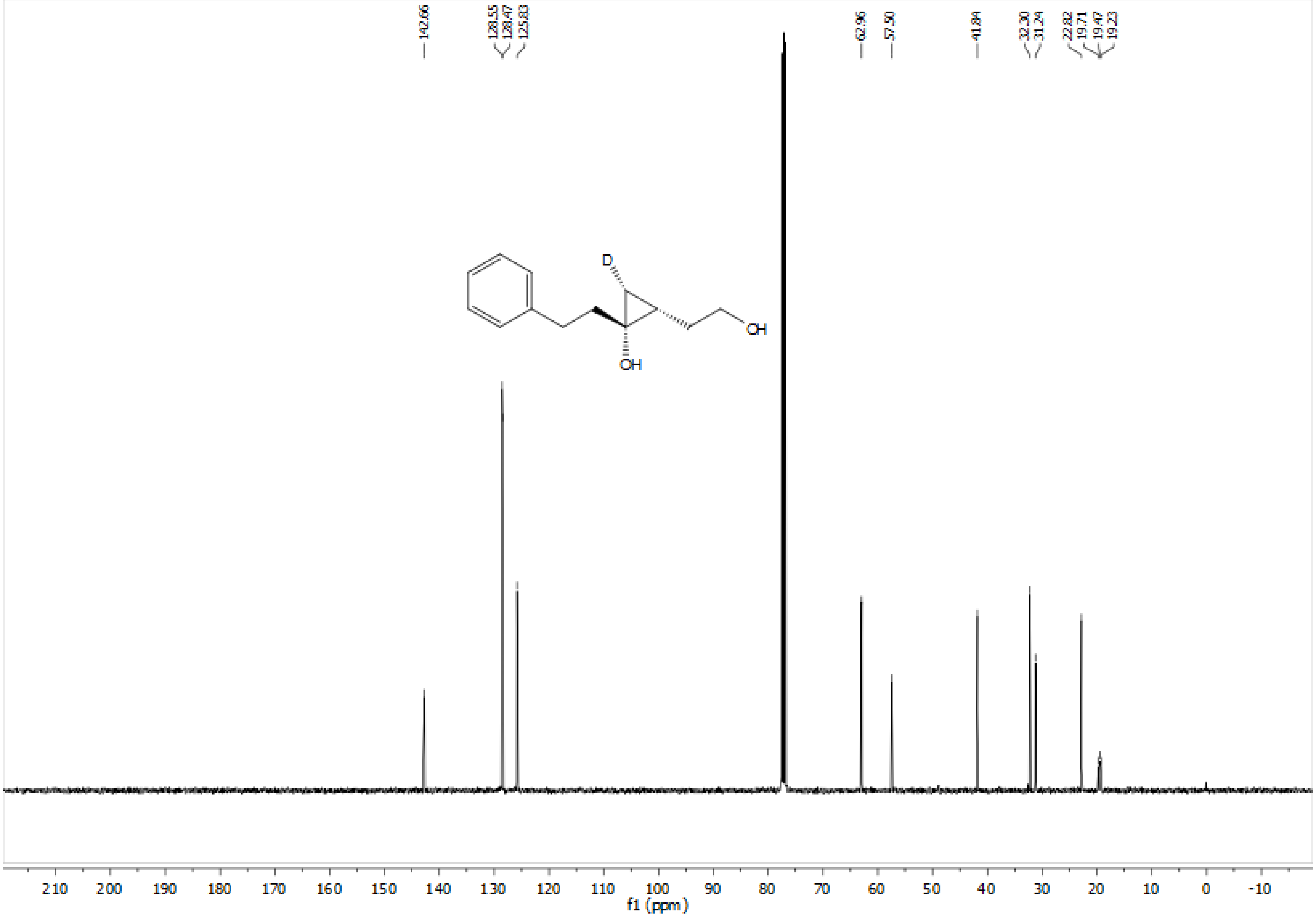

184.47
139.10
114.28
77.48
77.16
76.84
56.80
38.85
30.53
25.88
17.95
13.24
-3.31
H2C
O
Si
CH3
CH3
H3C
CH3
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

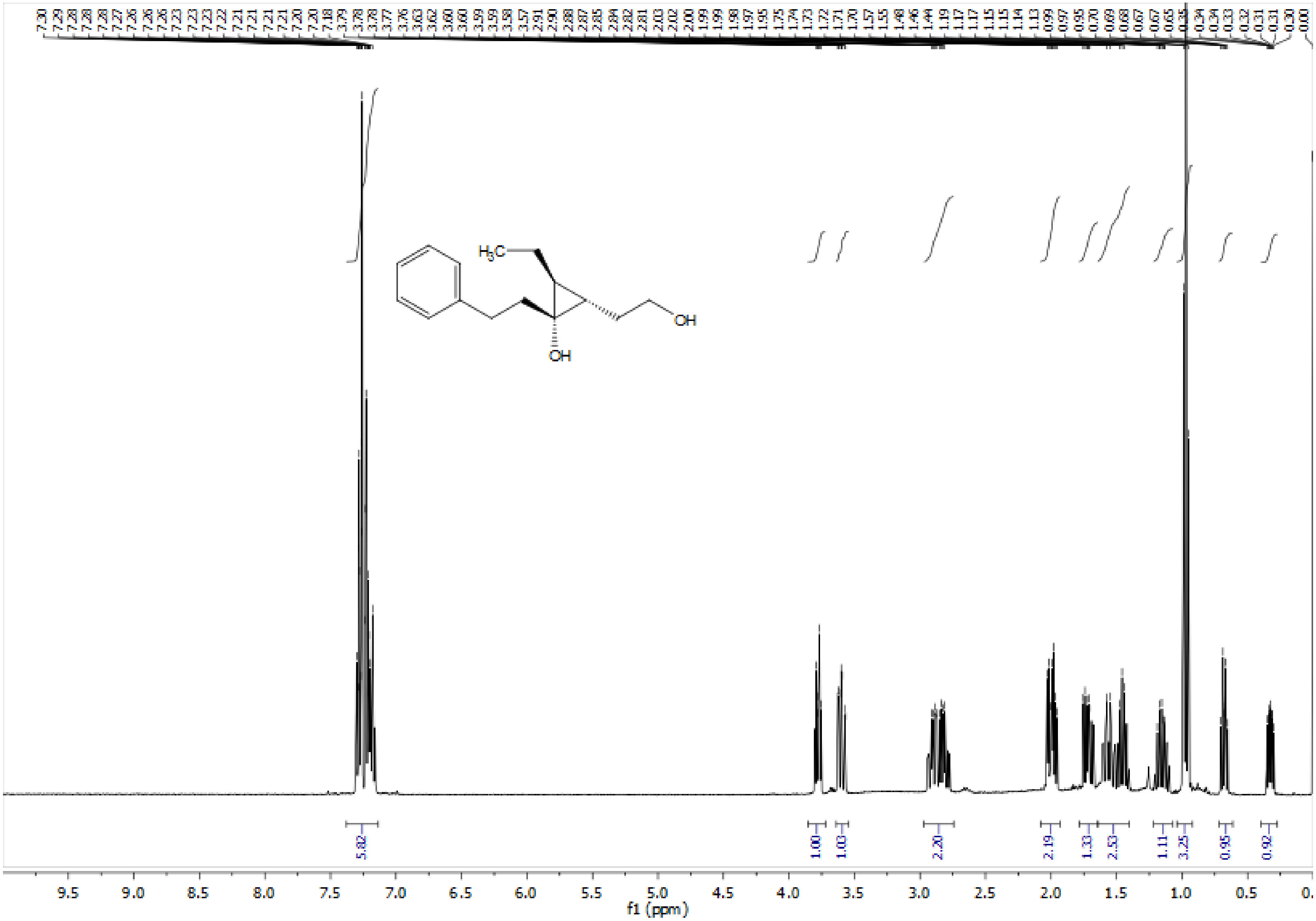
C. *Cyclopropanols*

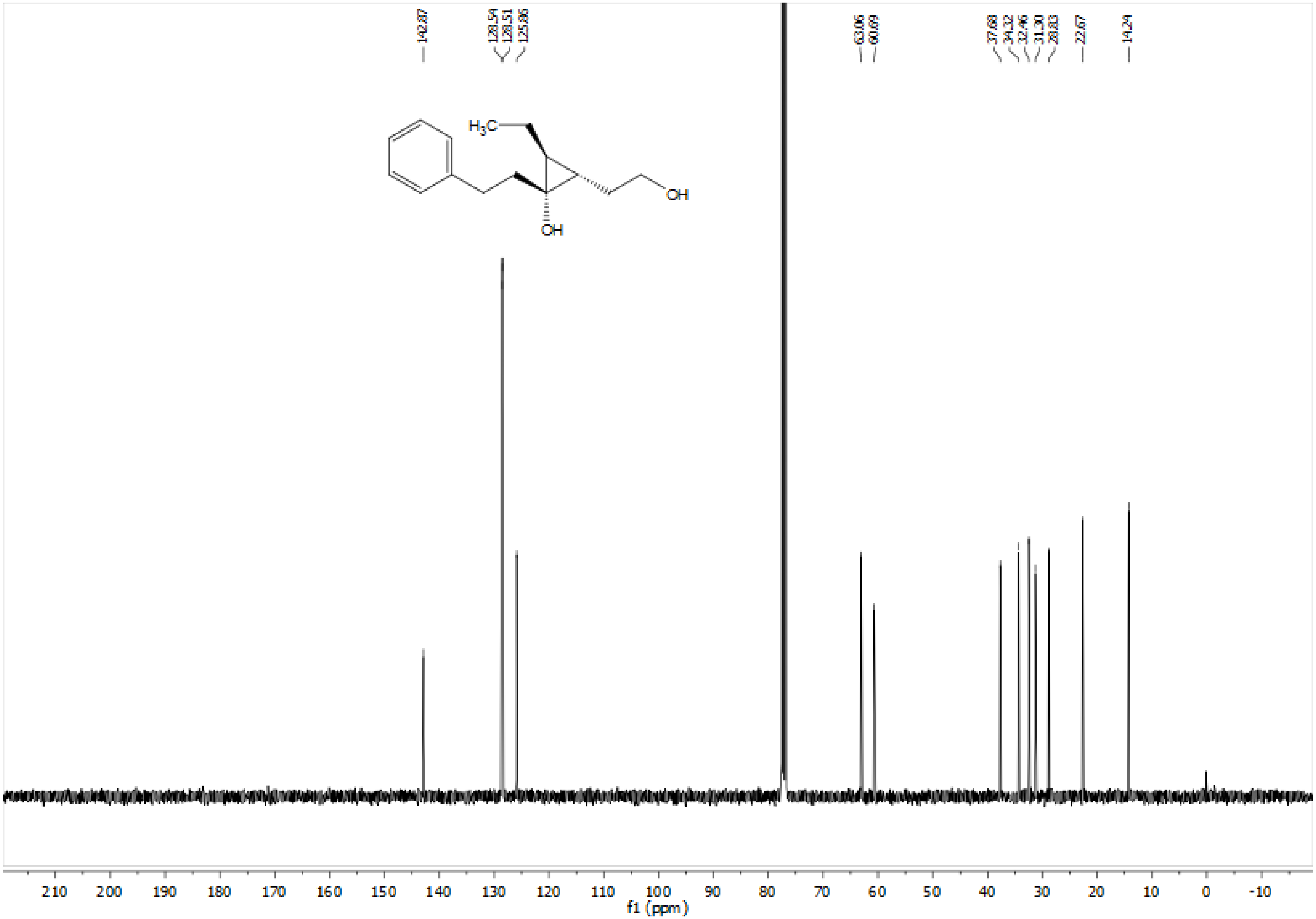


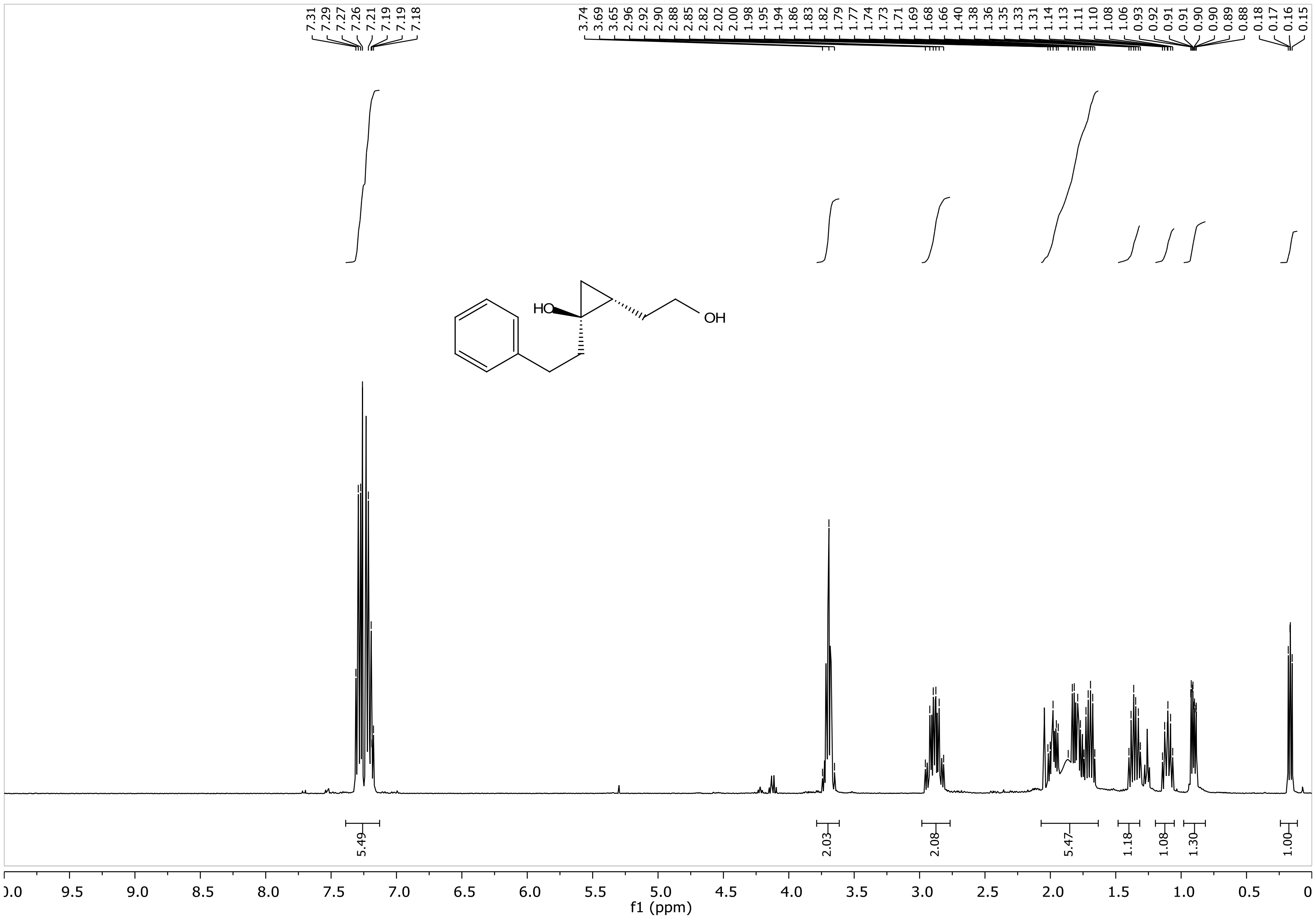

142.65
128.53
128.44
125.80
62.81
57.54
41.86
32.28
31.32
22.86
19.81
Ph
OH
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.29
7.29
7.29
7.27
7.25
7.22
7.22
7.21
7.20
7.20
7.19
7.19
7.19
7.18
7.17
7.17
7.15
3.81
3.80
3.79
3.79
3.78
3.77
3.65
3.64
3.62
3.61
3.60
3.59
2.88
2.87
2.86
2.85
2.84
2.82
2.24
2.03
2.03
2.02
2.02
1.99
1.99
1.98
1.98
1.96
1.94
1.94
1.92
1.92
1.91
1.90
1.88
1.76
1.75
1.74
1.73
1.72
1.71
1.70
1.69
1.57
1.57
1.56
1.56
1.55
1.54
1.53
1.53
1.52
1.52
0.72
0.71
0.70
0.69
0.67
0.66
0.64
0.62
D
OH
OH
2.14
2.91
1.00
1.86
1.94
0.91
2.02
1.20
1.13
1.85
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


142.66
128.55
128.47
125.83
62.96
57.50
41.84
32.30
31.24
22.82
19.71
19.47
19.23
D
OH
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.30
7.29
7.28
7.28
7.28
7.27
7.26
7.26
7.26
7.23
7.23
7.23
7.22
7.21
7.21
7.21
7.21
7.20
7.20
7.18
3.79
3.78
3.78
3.77
3.76
3.63
3.62
3.60
3.60
3.59
3.59
3.58
3.57
2.91
2.90
2.88
2.87
2.85
2.84
2.82
2.81
2.03
2.02
2.00
1.99
1.99
1.98
1.97
1.95
1.75
1.74
1.73
1.72
1.71
1.70
1.57
1.55
1.48
1.46
1.44
1.19
1.17
1.17
1.15
1.15
1.14
1.13
0.99
0.97
0.95
0.70
0.70
0.69
0.68
0.67
0.67
0.65
0.35
0.34
0.34
0.33
0.32
0.31
0.31
0.30
0.00
H_3C
OH
OH
5.82
1.00
1.03
2.20
2.19
1.33
2.53
1.11
3.25
0.95
0.92
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


142.87
128.59
128.51
125.86
63.06
60.69
37.68
34.32
32.46
31.30
28.83
22.67
14.24
H3C
OH
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.31
7.29
7.27
7.26
7.21
7.19
7.19
7.18
3.74
3.69
3.65
2.96
2.92
2.90
2.88
2.85
2.82
2.02
2.00
1.98
1.95
1.94
1.86
1.83
1.82
1.79
1.77
1.74
1.73
1.71
1.69
1.68
1.66
1.40
1.38
1.36
1.35
1.33
1.31
1.14
1.13
1.11
1.10
1.08
1.06
0.93
0.92
0.91
0.91
0.90
0.90
0.89
0.88
0.18
0.17
0.16
0.15
HO
OH
5.49
2.03
2.08
5.47
1.18
1.08
1.30
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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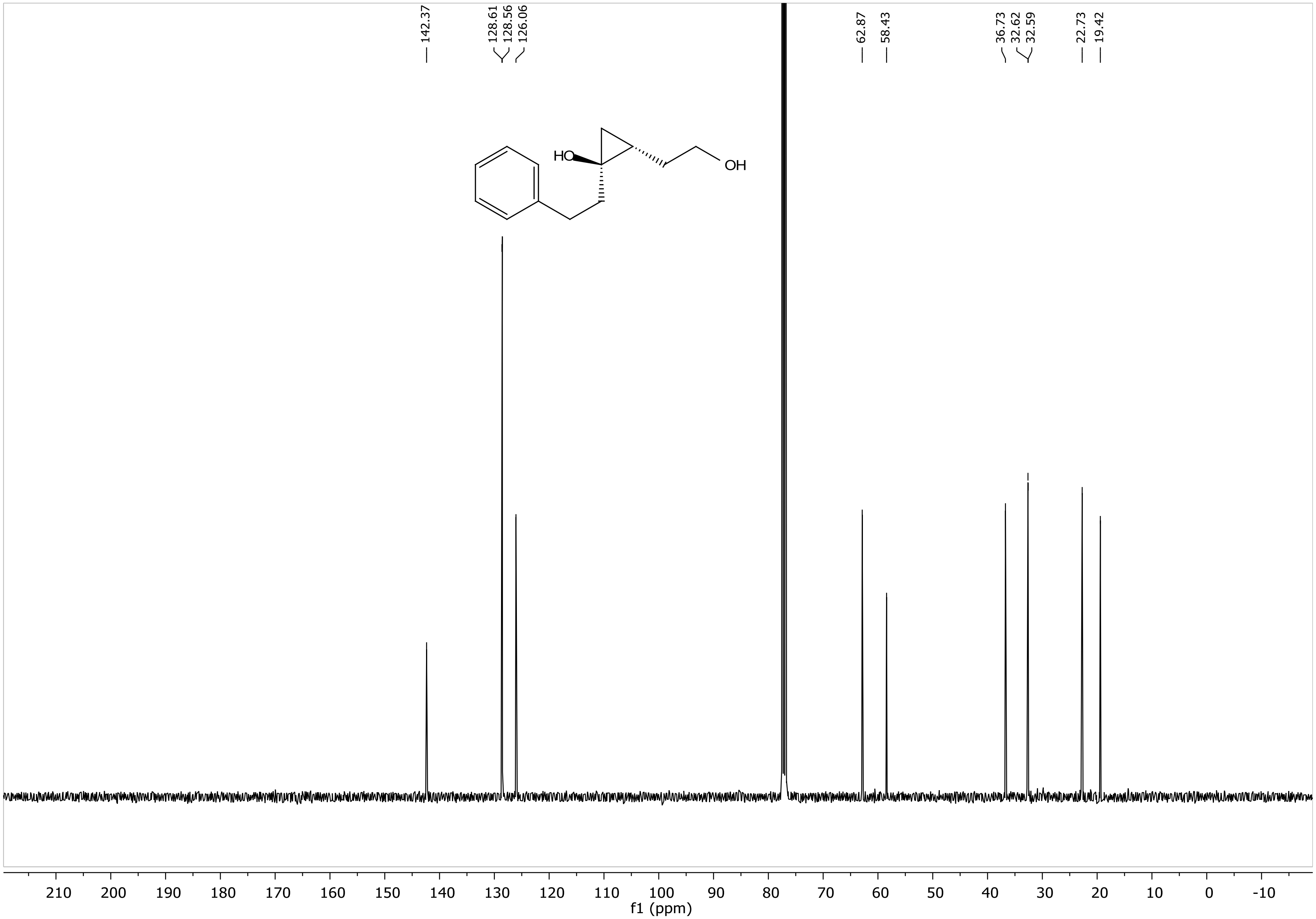
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OH
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200
190
180
170
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100
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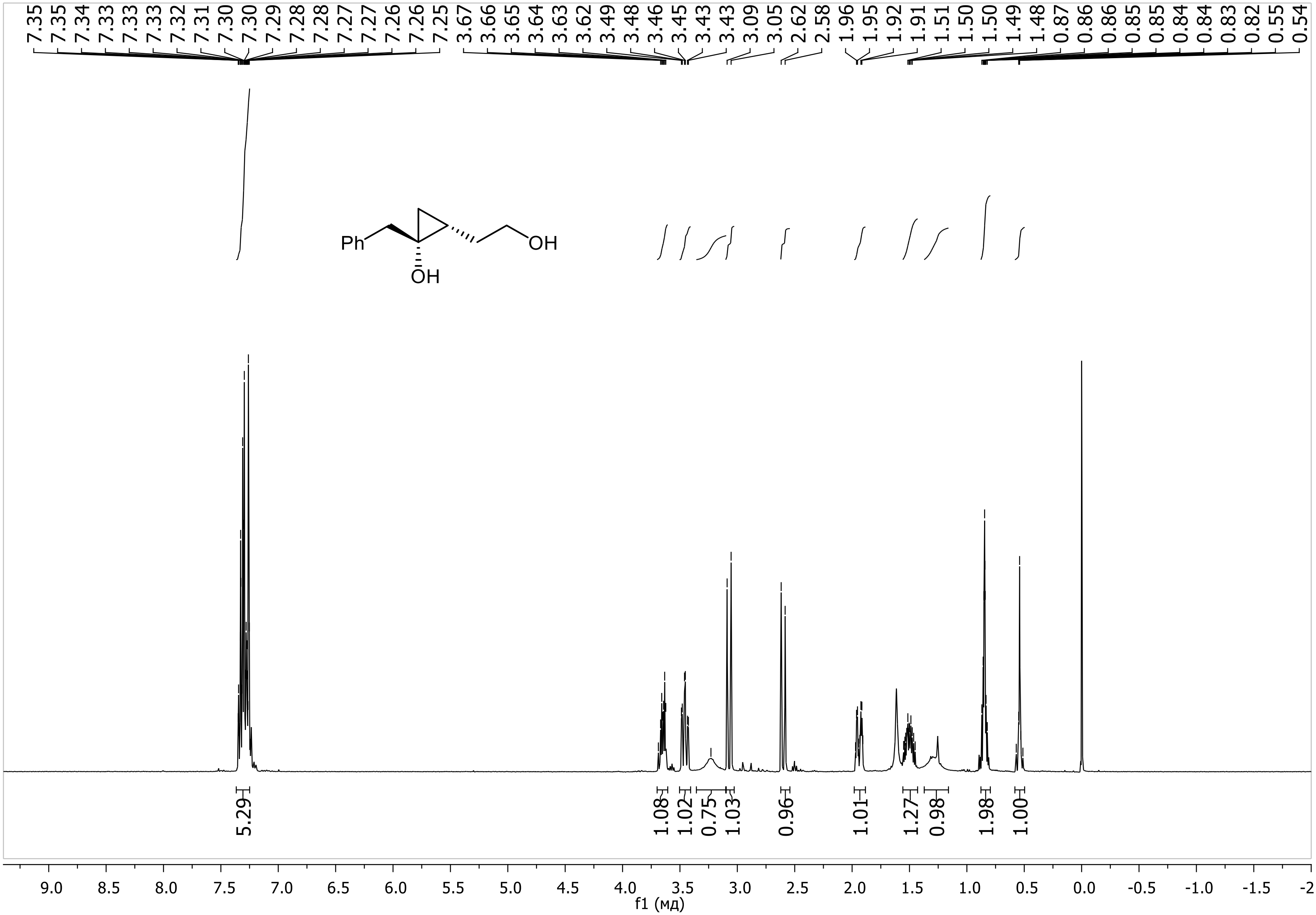
f1 (ppm)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7.27
7.26
7.26
7.25
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3.66
3.65
3.64
3.63
3.62
3.49
3.48
3.46
3.45
3.43
3.43
3.09
3.05
2.62
2.58
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1.95
1.92
1.91
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1.50
1.50
1.49
1.48
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0.86
0.86
0.85
0.85
0.84
0.84
0.83
0.82
0.55
0.54
Ph
OH
OH
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1.08
1.02
0.75
1.03
0.96
1.01
1.27
0.98
1.98
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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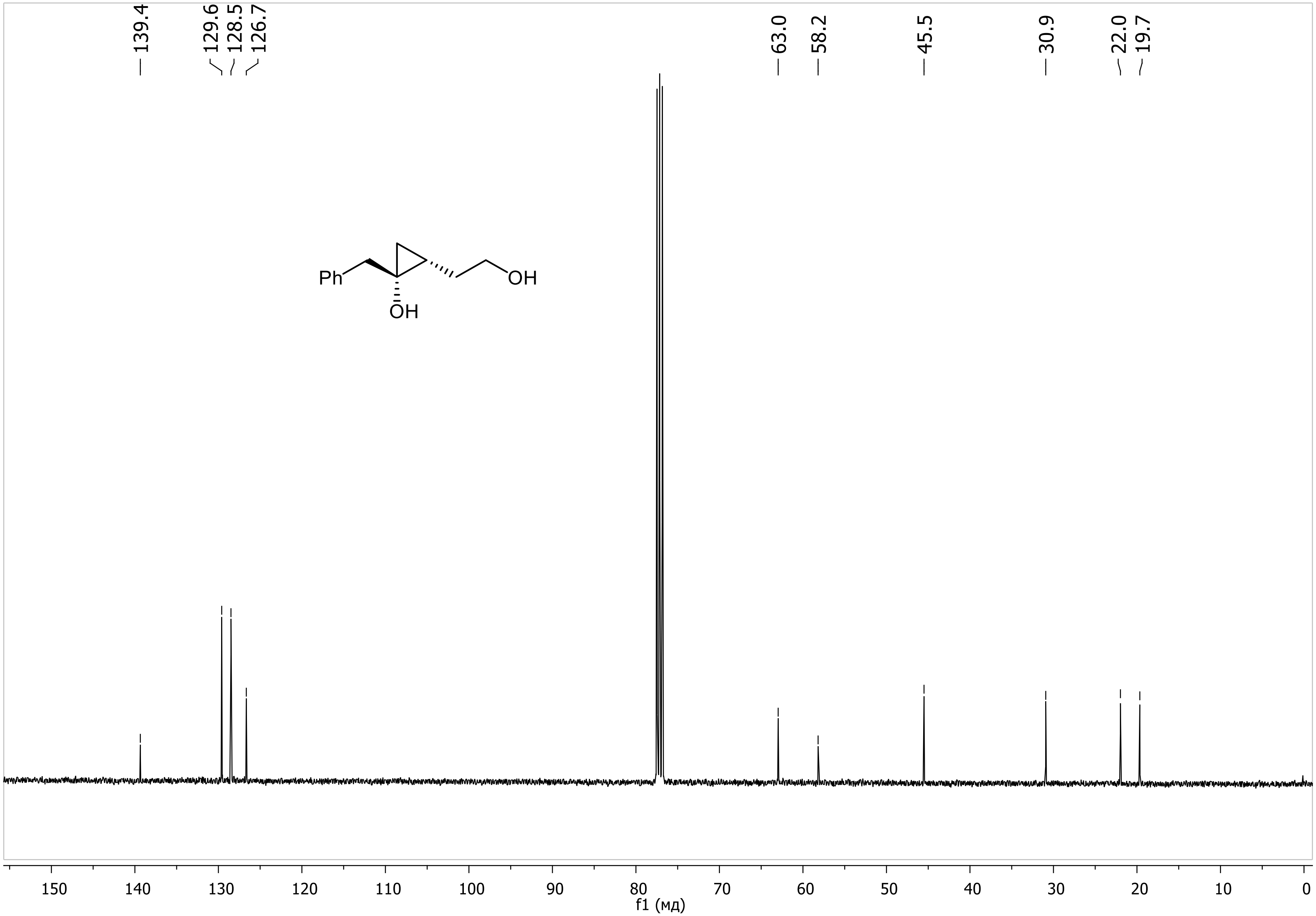
-1.0
-1.5
-2.(
f1 (мд)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120
110
100
90
80
70
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50
40
30
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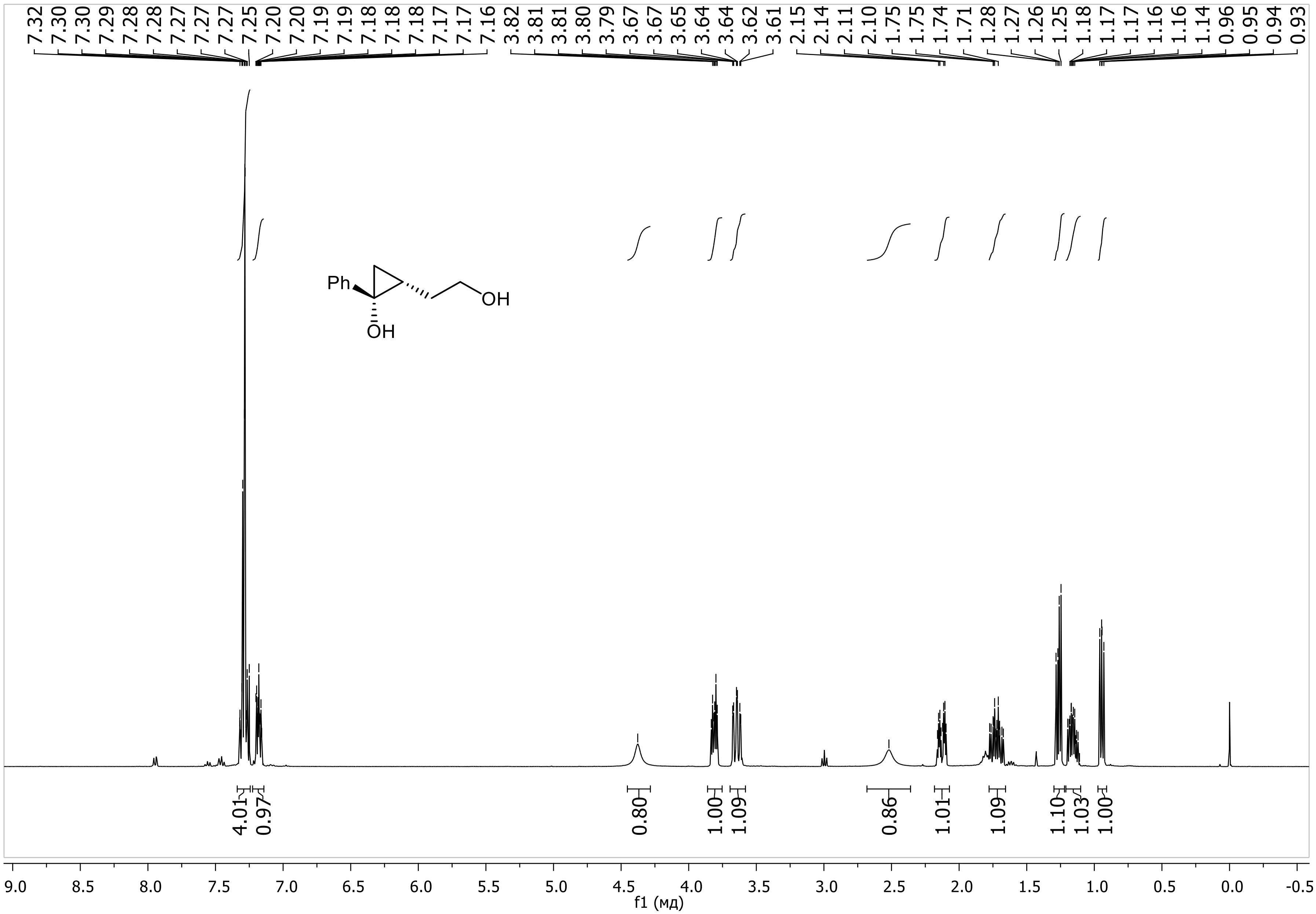
10
0
f1 (мд)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7.19
7.18
7.18
7.18
7.17
7.17
7.16
3.82
3.81
3.81
3.80
3.79
3.67
3.67
3.65
3.64
3.64
3.62
3.61
2.15
2.14
2.11
2.10
1.75
1.75
1.74
1.71
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1.27
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1.25
1.18
1.17
1.17
1.16
1.16
1.14
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0.95
0.94
0.93
Ph
OH
OH
4.01
0.97
0.80
1.00
1.09
0.86
1.01
1.09
1.10
1.03
1.00
9.0
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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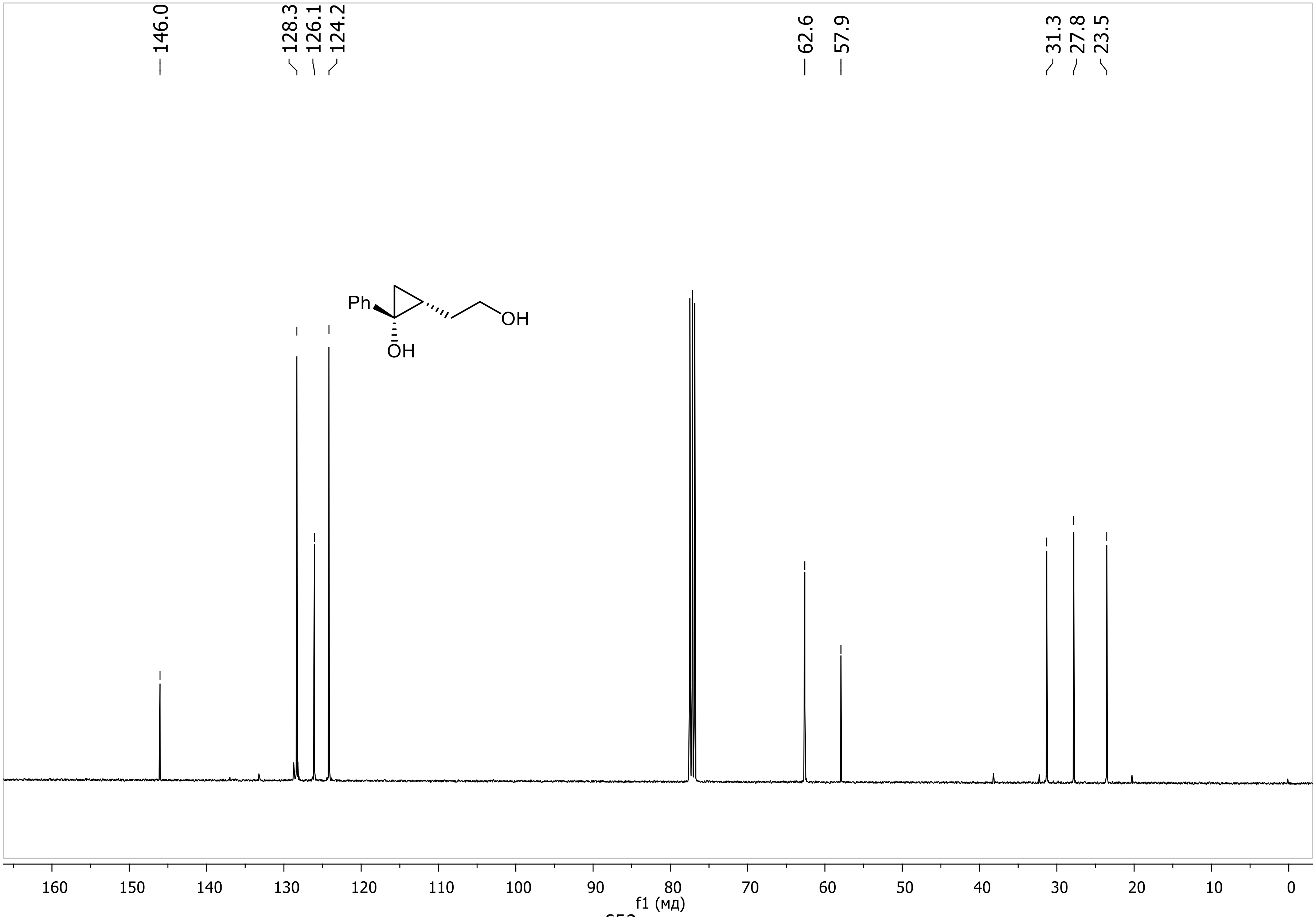
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (мд)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23.5
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OH
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120
110
100
90
80
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40
30
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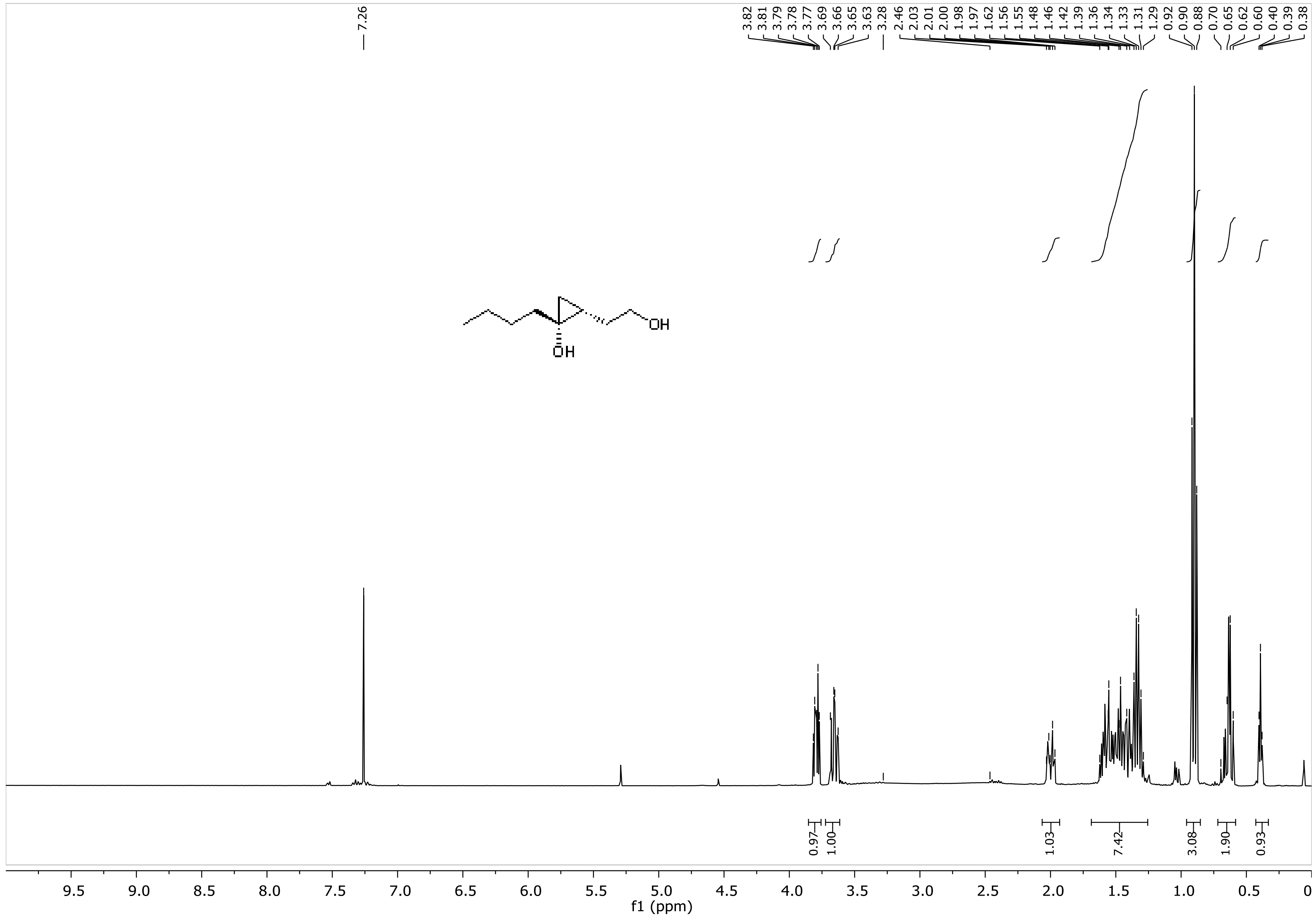
0
f1 (мд)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3.82
3.81
3.79
3.78
3.77
3.69
3.66
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3.63
3.28
2.46
2.03
2.01
2.00
1.98
1.97
1.62
1.56
1.55
1.48
1.46
1.42
1.39
1.36
1.34
1.33
1.31
1.29
0.92
0.90
0.88
0.70
0.65
0.62
0.60
0.40
0.39
0.38
OH
OH
0.97
1.00
1.03
7.42
3.08
1.90
0.93
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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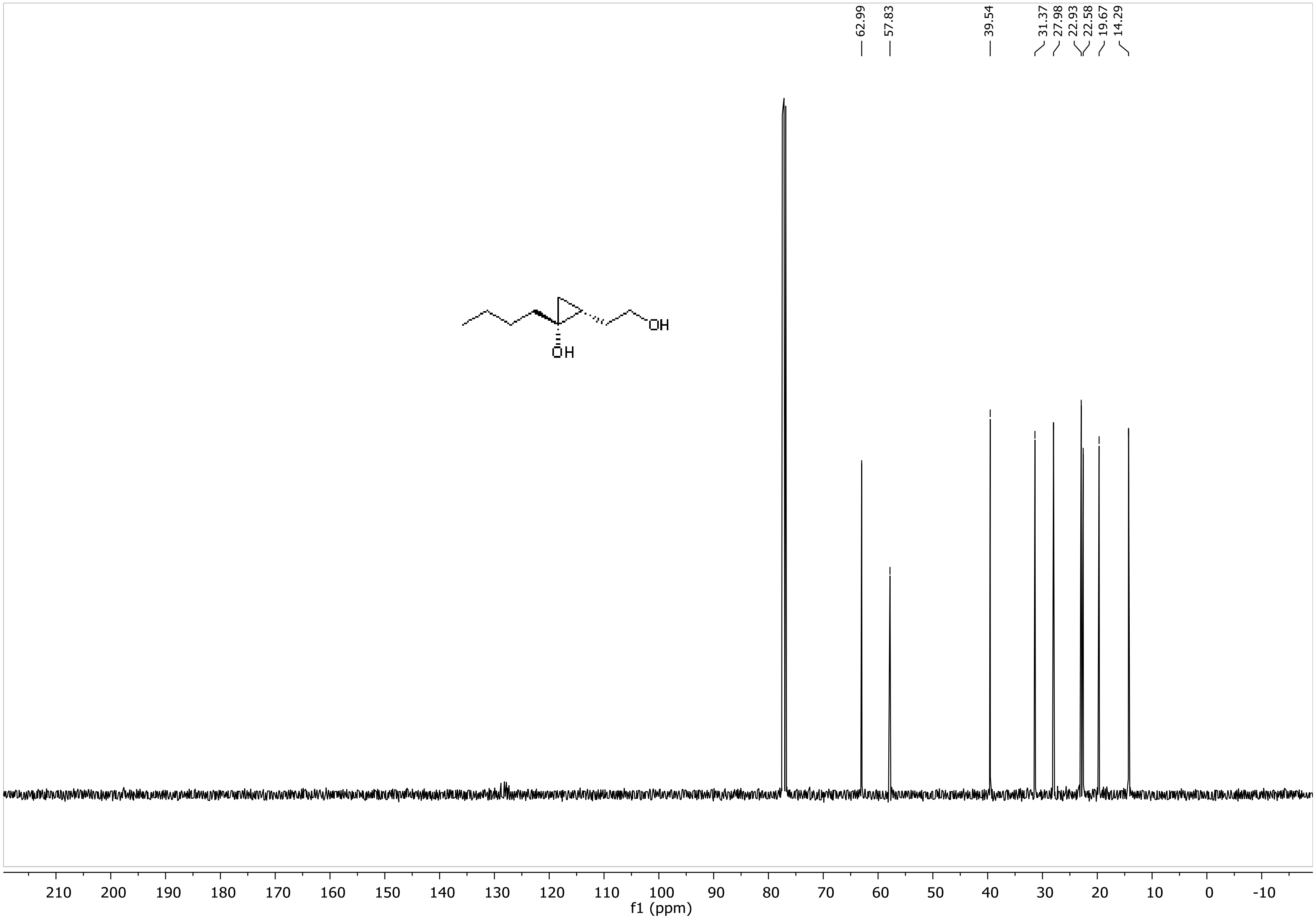
f1 (ppm)


62.99
57.83
39.54
31.37
27.98
22.93
22.58
19.67
14.29
OH
OH
210
200
190
180
170
160
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140
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120
110
100
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80
70
60
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40
30
20
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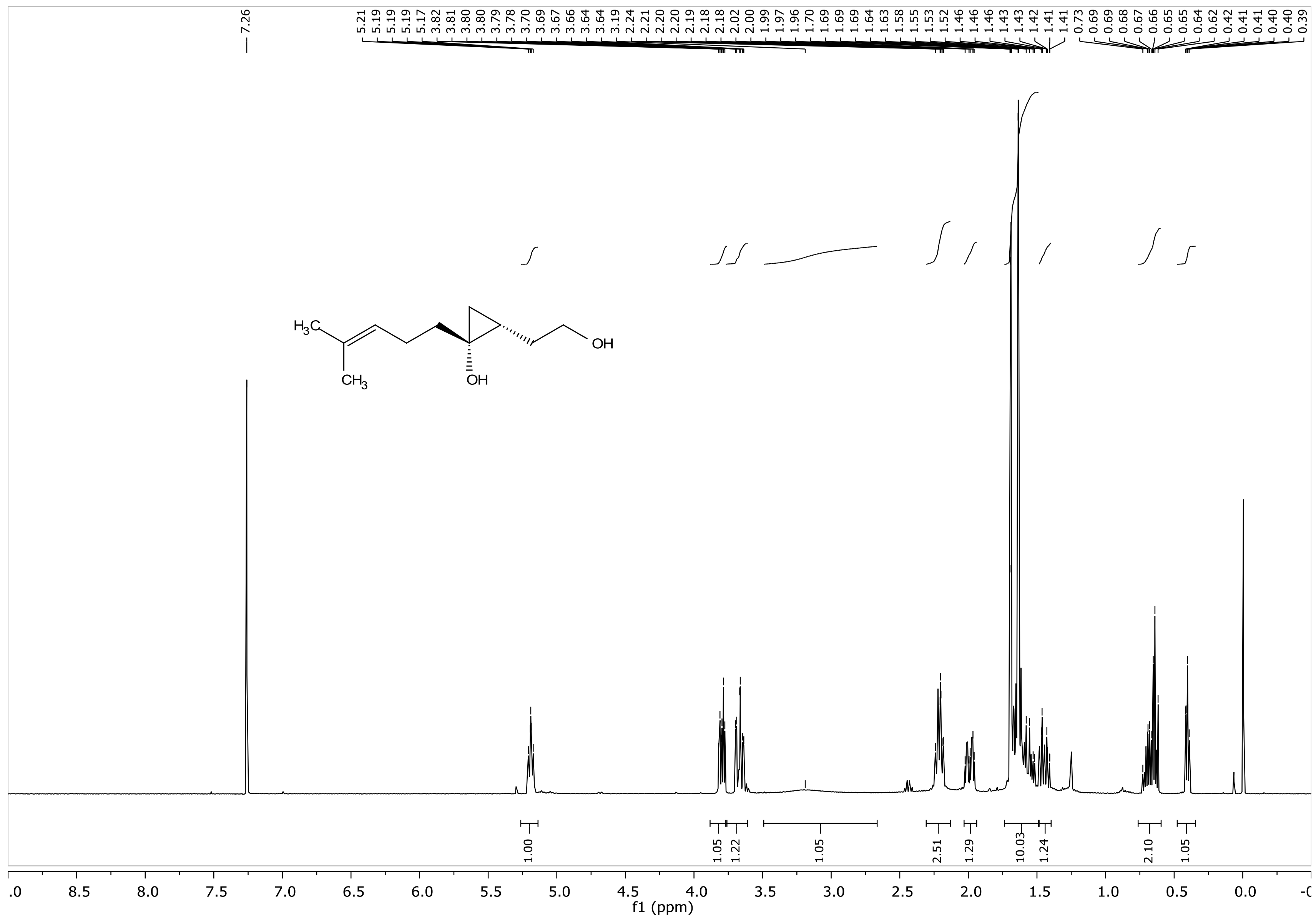
0
-10
f1 (ppm)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5.17
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3.80
3.79
3.78
3.70
3.69
3.67
3.66
3.64
3.64
3.19
2.24
2.21
2.20
2.20
2.19
2.18
2.02
2.00
1.99
1.97
1.96
1.70
1.69
1.69
1.69
1.64
1.63
1.58
1.55
1.53
1.52
1.46
1.46
1.43
1.43
1.42
1.41
1.41
0.73
0.69
0.69
0.68
0.67
0.66
0.65
0.65
0.64
0.62
0.42
0.41
0.41
0.40
0.40
0.39
H_3C
CH_3
OH
OH
1.00
1.05
1.22
1.05
2.51
1.29
10.03
1.24
2.10
1.05
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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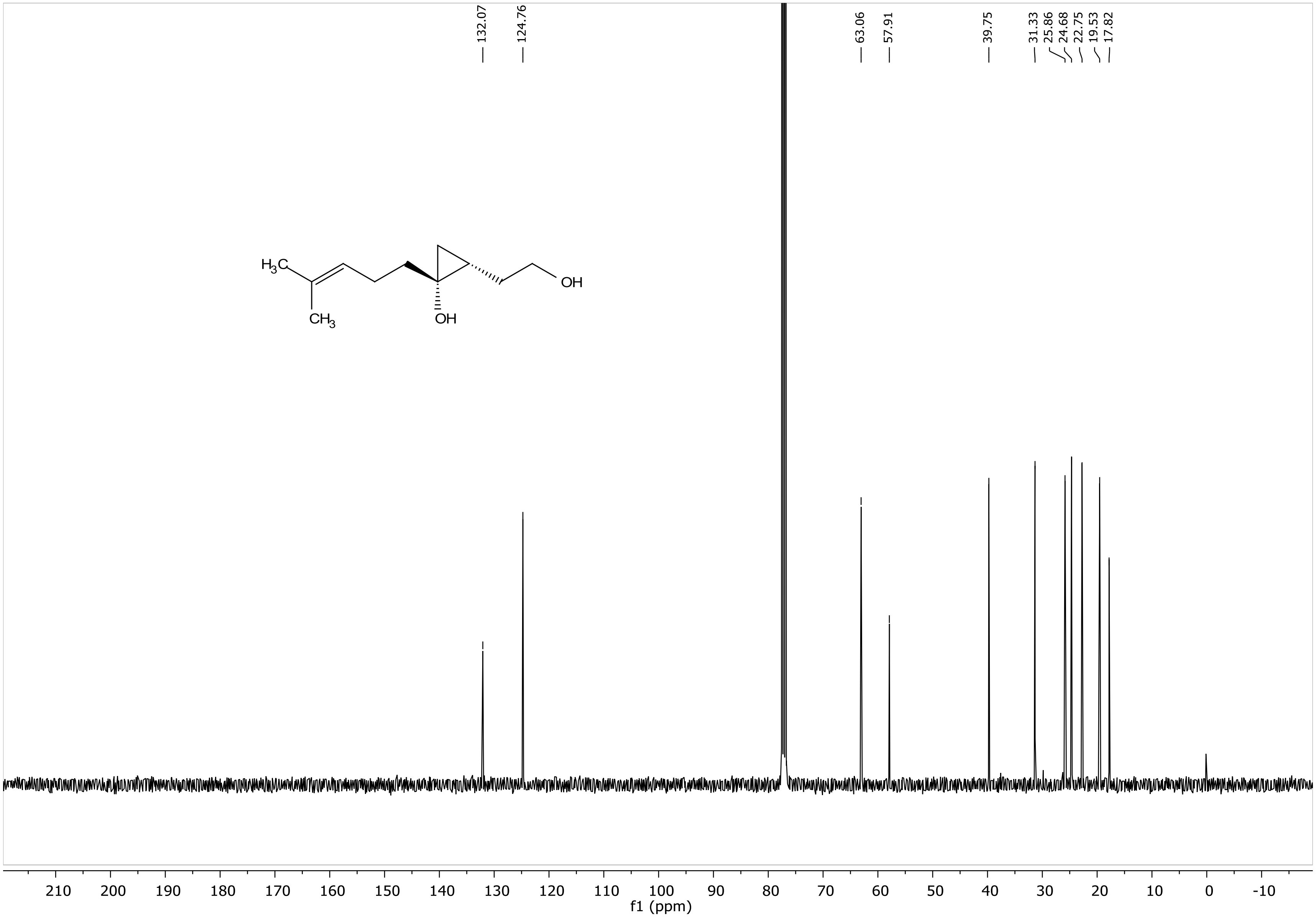
f1 (ppm)



132.07
124.76
63.06
57.91
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31.33
25.86
24.68
22.75
19.53
17.82
H3C
CH3
OH
OH
210
200
190
180
170
160
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140
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120
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100
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80
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60
50
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30
20
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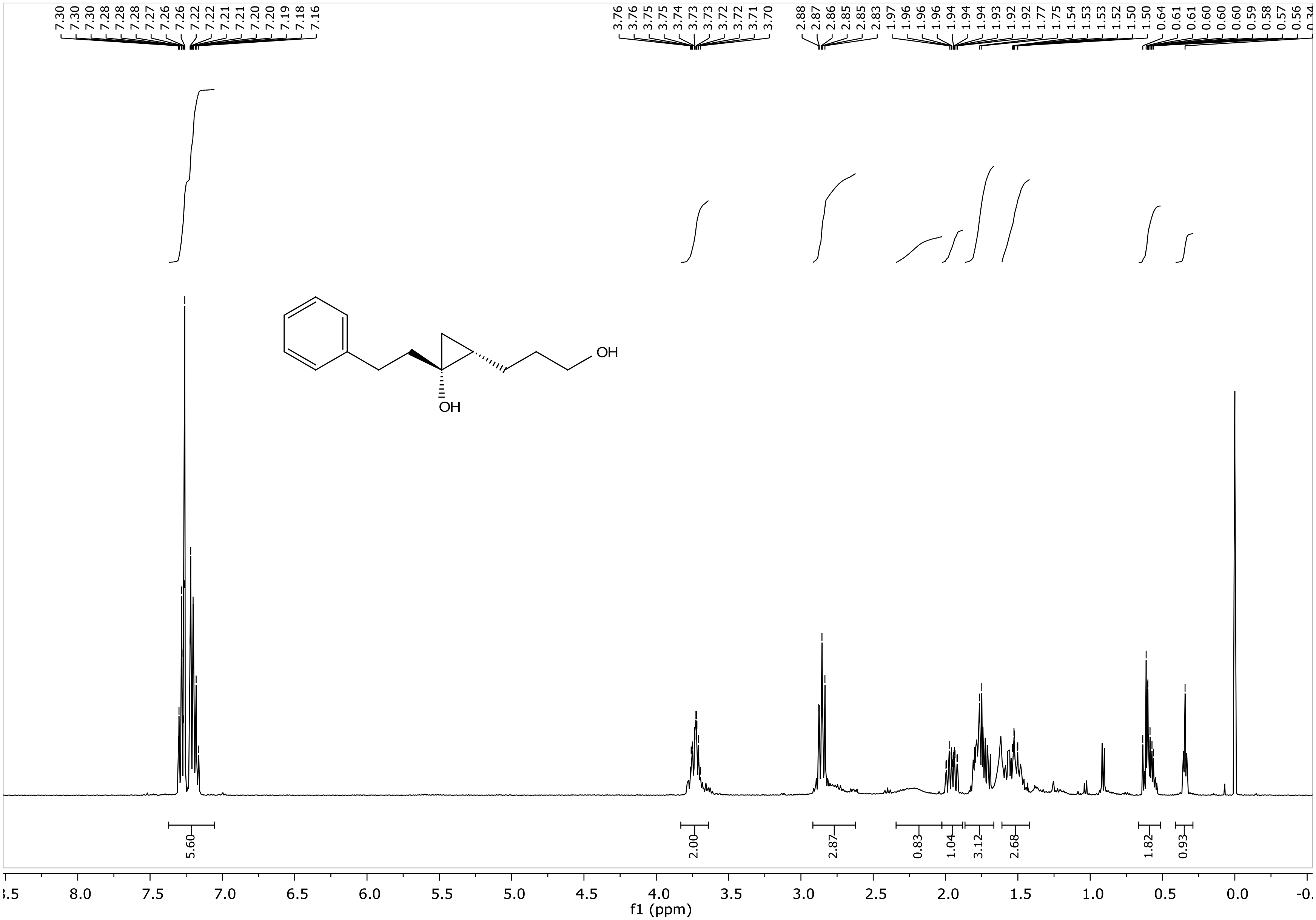
-10
f1 (ppm)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7.21
7.20
7.20
7.19
7.18
7.16
3.76
3.76
3.75
3.75
3.74
3.73
3.73
3.72
3.72
3.71
3.70
2.88
2.87
2.86
2.85
2.85
2.83
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1.96
1.96
1.96
1.94
1.94
1.94
1.93
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1.92
1.77
1.75
1.54
1.53
1.53
1.52
1.50
1.50
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0.61
0.60
0.60
0.60
0.59
0.58
0.57
0.56
OH
OH
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1.04
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2.68
1.82
0.93
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
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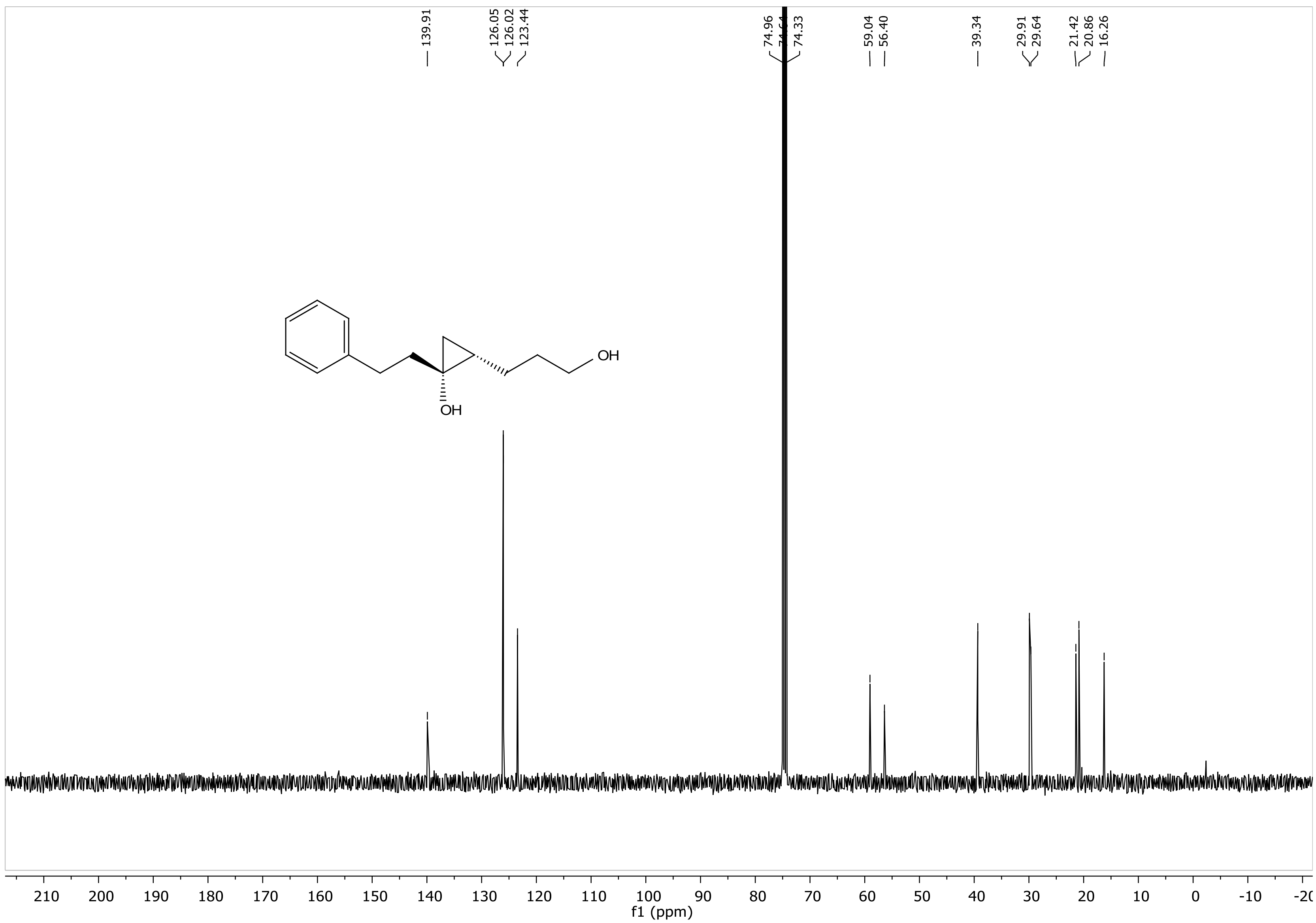
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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74.64
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29.91
29.64
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20.86
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OH
OH
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200
190
180
170
160
150
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130
120
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100
90
80
70
60
50
40
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20
10
0
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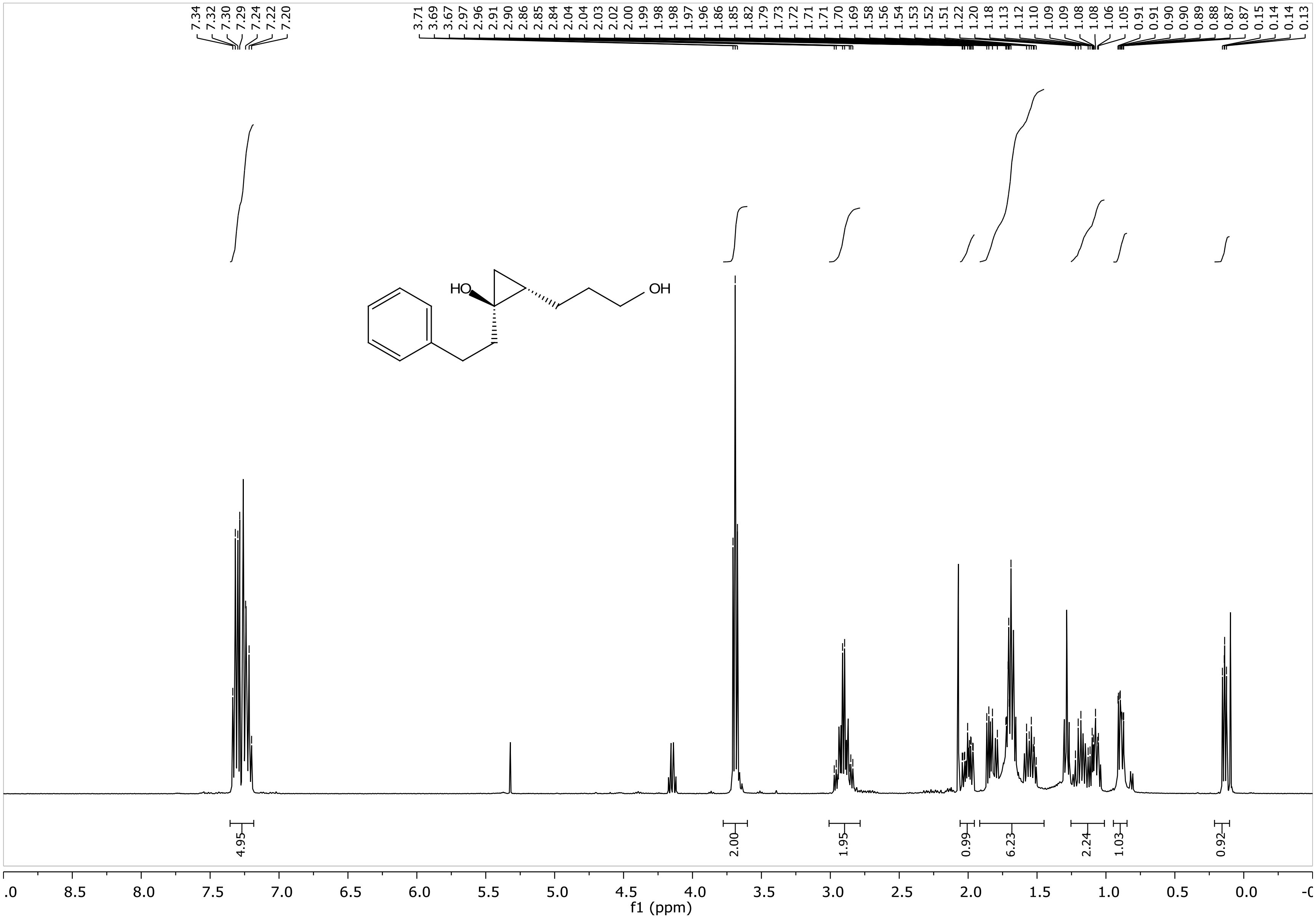
-2
f1 (ppm)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2.91
2.90
2.86
2.85
2.84
2.04
2.04
2.03
2.02
2.00
1.99
1.98
1.98
1.97
1.96
1.86
1.85
1.82
1.79
1.73
1.72
1.71
1.71
1.70
1.69
1.58
1.56
1.54
1.53
1.52
1.51
1.22
1.20
1.18
1.13
1.12
1.10
1.09
1.09
1.08
1.08
1.06
1.05
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0.91
0.90
0.90
0.89
0.88
0.87
0.15
0.14
0.14
0.13
HO
OH
4.95
2.00
1.95
0.99
6.23
2.24
1.03
0.92
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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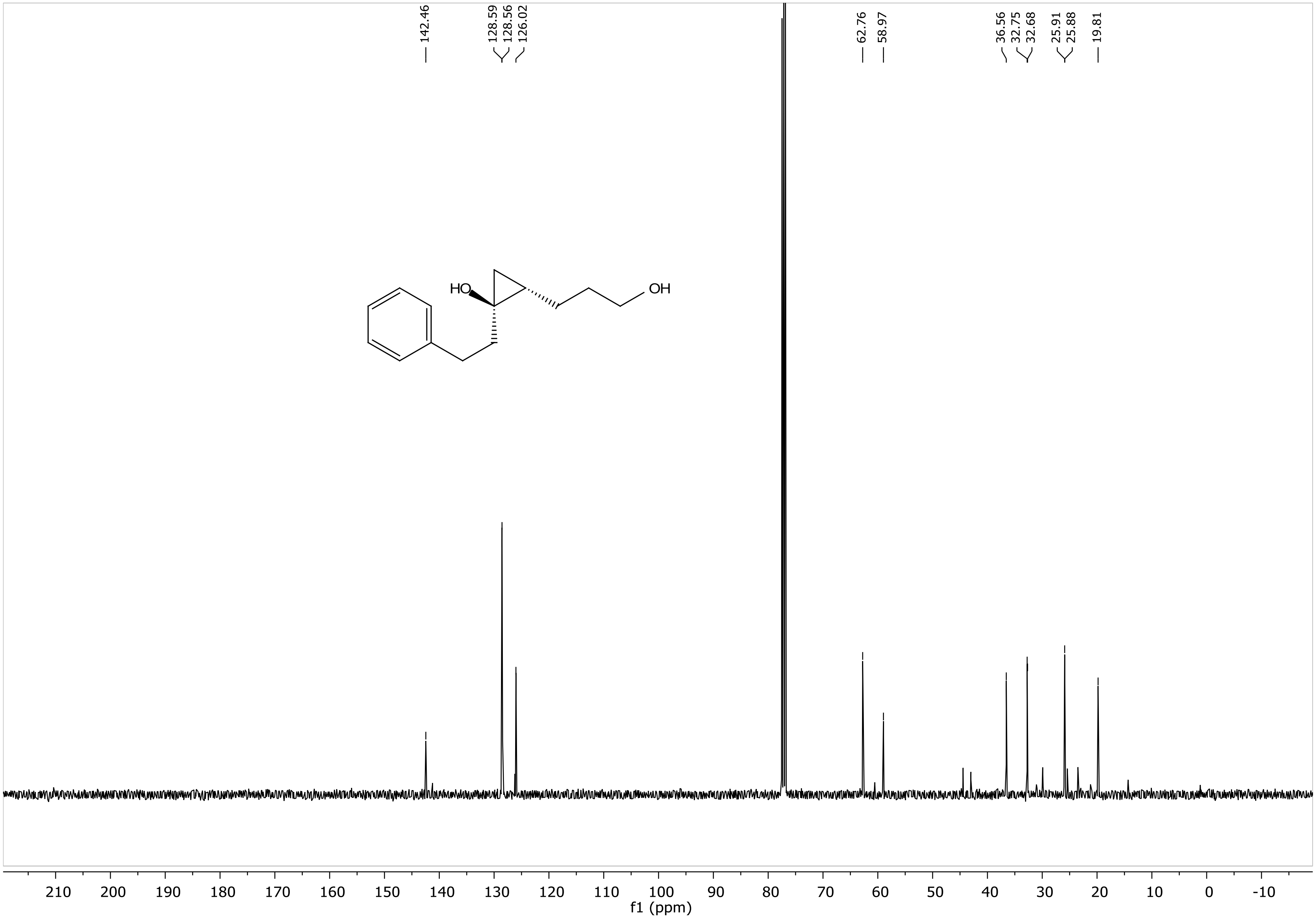
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)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OH
210
200
190
180
170
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120
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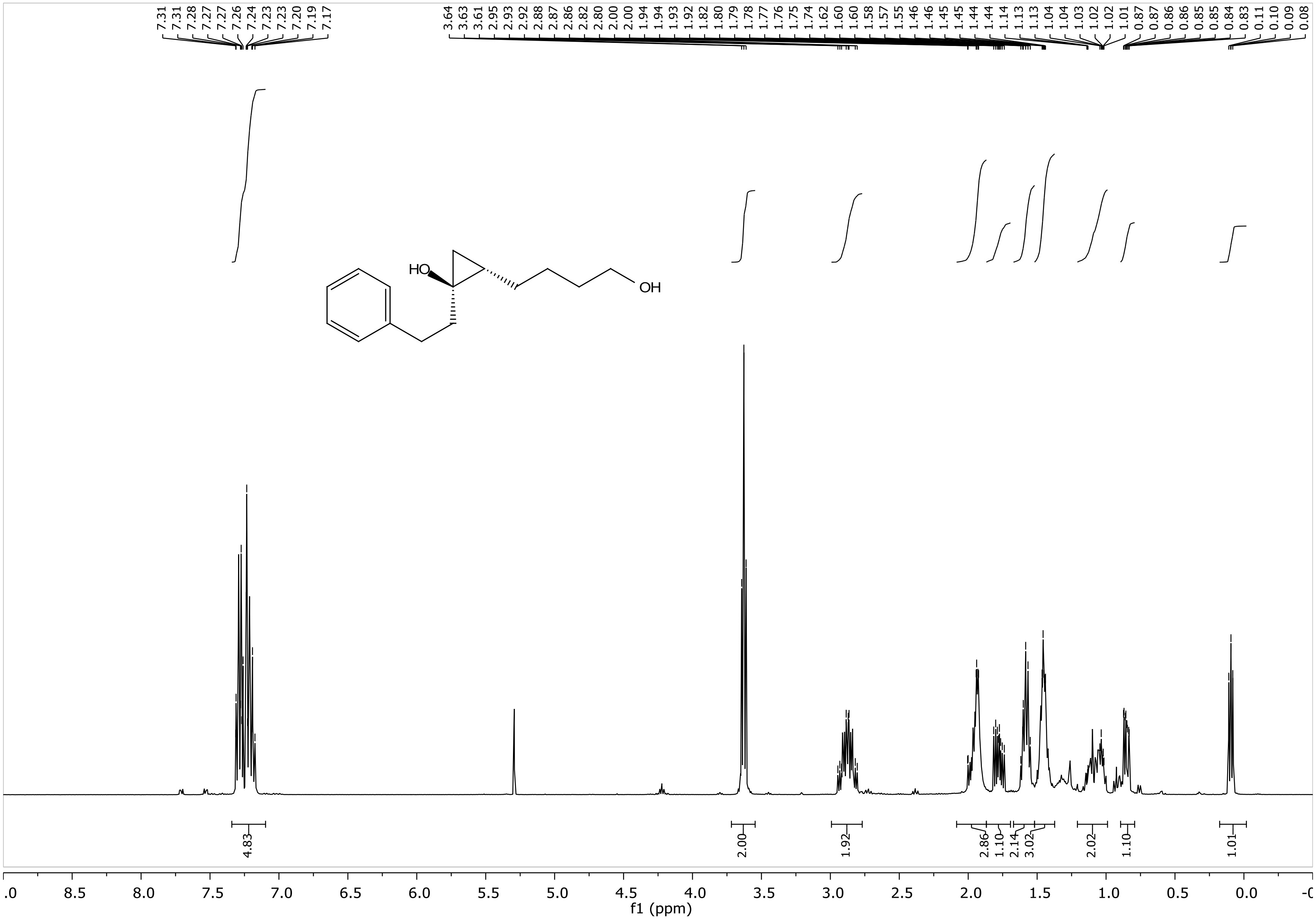
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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2.93
2.92
2.88
2.87
2.86
2.82
2.80
2.00
2.00
1.94
1.94
1.93
1.92
1.82
1.80
1.79
1.78
1.77
1.76
1.75
1.74
1.62
1.60
1.58
1.57
1.55
1.46
1.46
1.45
1.45
1.44
1.44
1.14
1.13
1.13
1.04
1.04
1.03
1.02
1.02
1.01
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0.87
0.86
0.86
0.85
0.85
0.84
0.83
0.11
0.10
0.09
0.08
HO
OH
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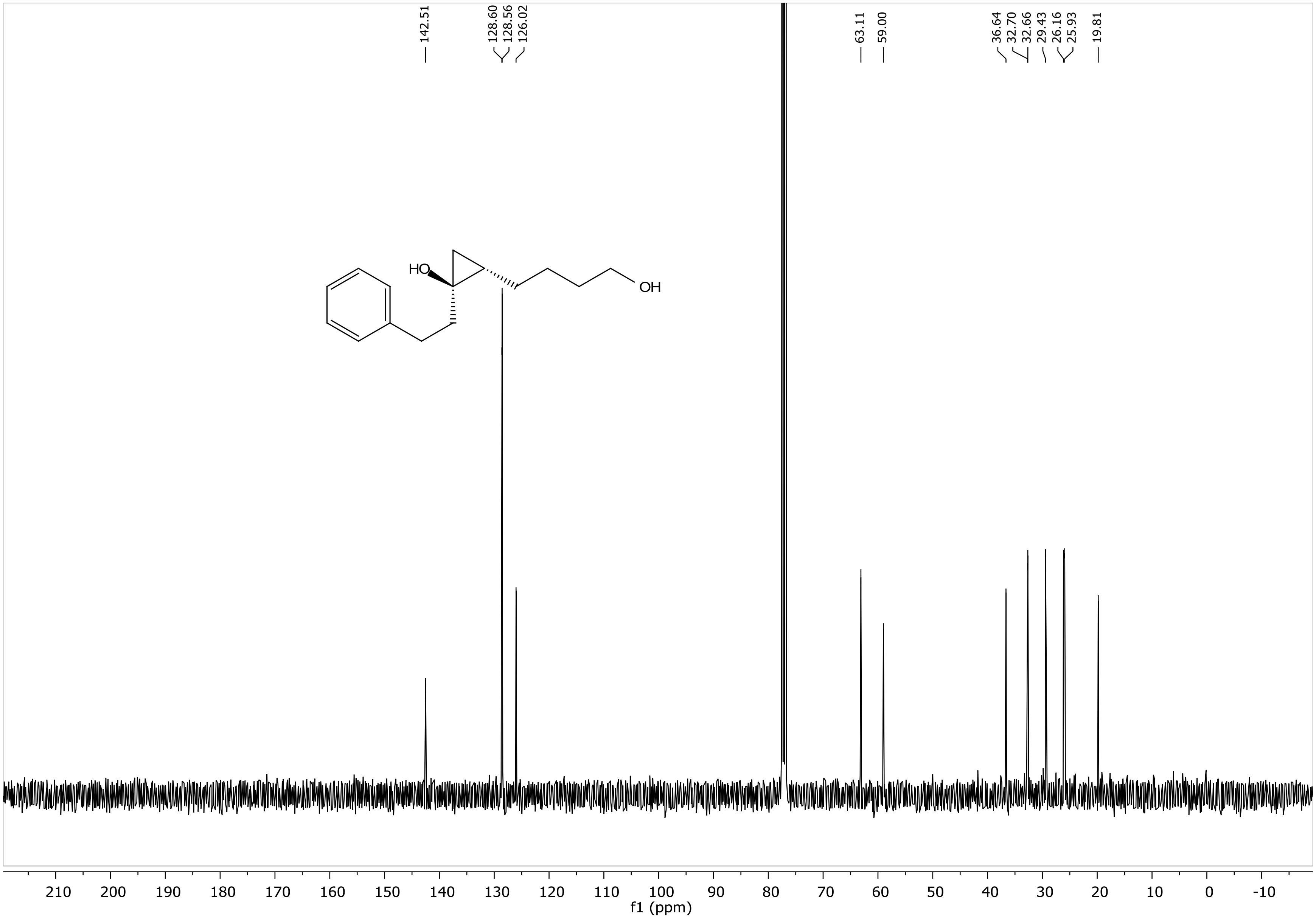
1.92
2.86
1.10
2.14
3.02
2.02
1.10
1.01
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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19.81
HO
OH
210
200
190
180
170
160
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140
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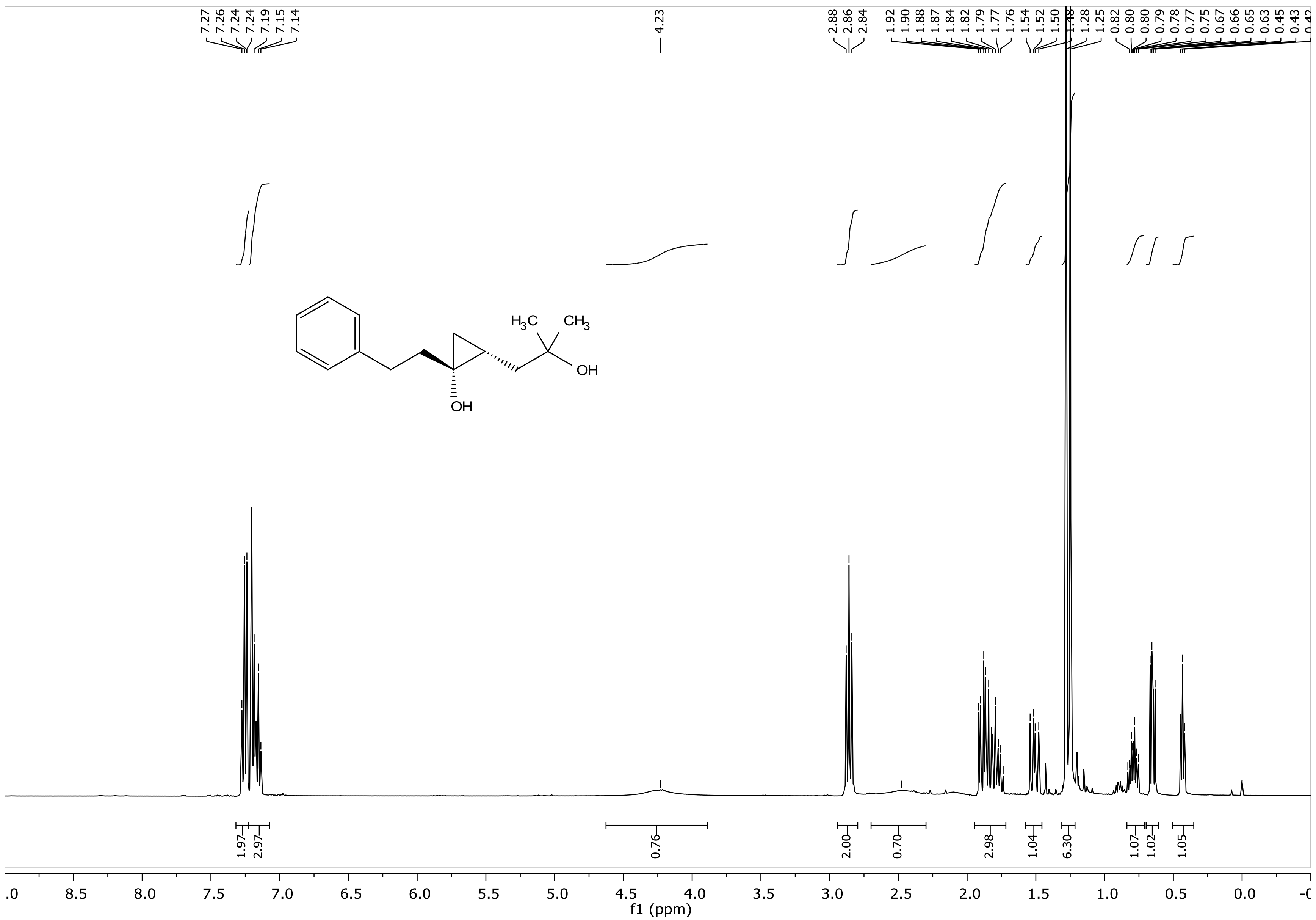
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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2.86
2.84
1.92
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1.88
1.87
1.84
1.82
1.79
1.77
1.76
1.54
1.52
1.50
1.48
1.28
1.25
0.82
0.80
0.80
0.79
0.78
0.77
0.75
0.67
0.66
0.65
0.63
0.45
0.43
0.42
H3C
CH3
OH
OH
1.97
2.97
0.76
2.00
0.70
2.98
1.04
6.30
1.07
1.02
1.05
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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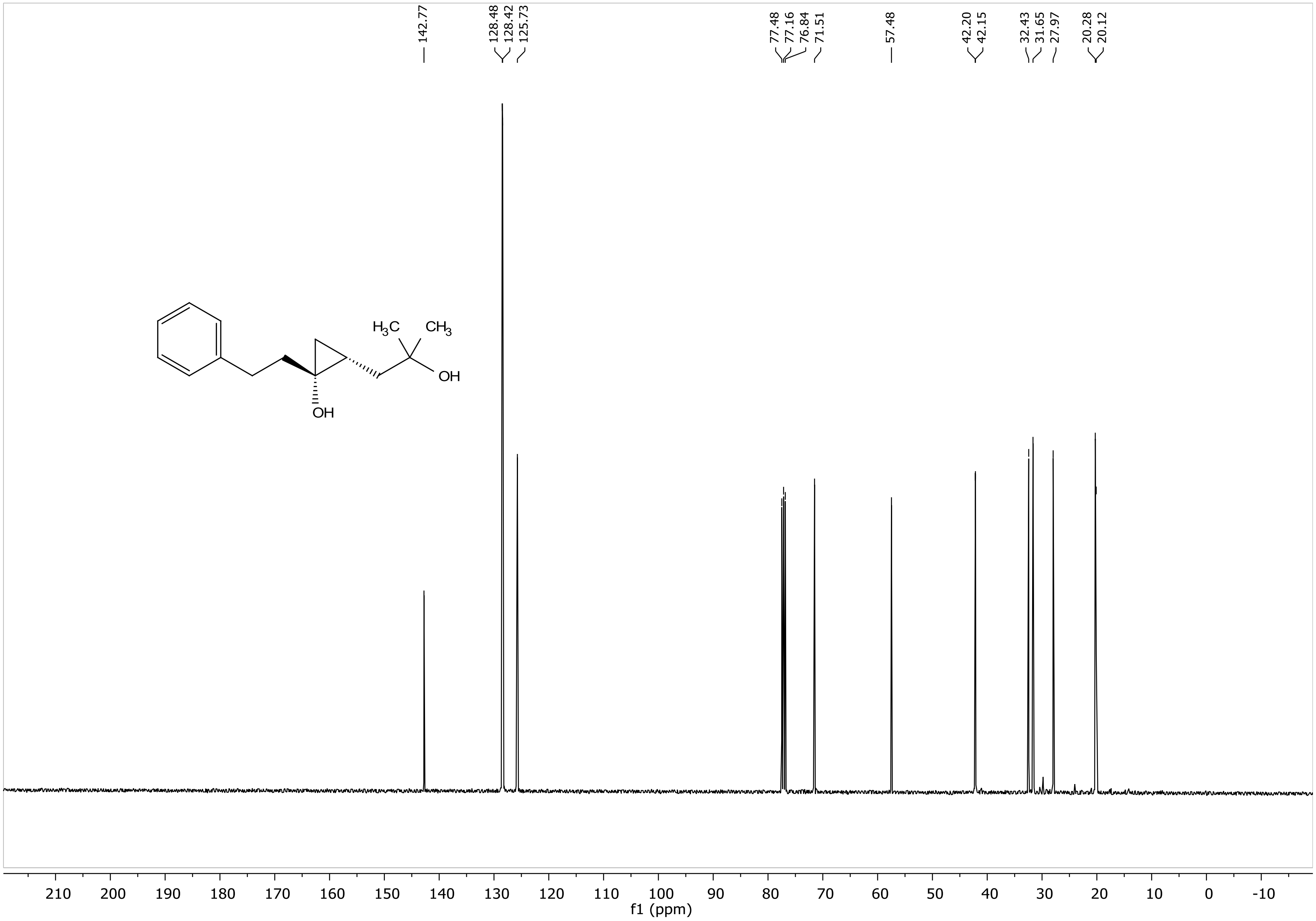
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



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42.20
42.15
32.43
31.65
27.97
20.28
20.12
H3C
CH3
OH
OH
210
200
190
180
170
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100
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80
70
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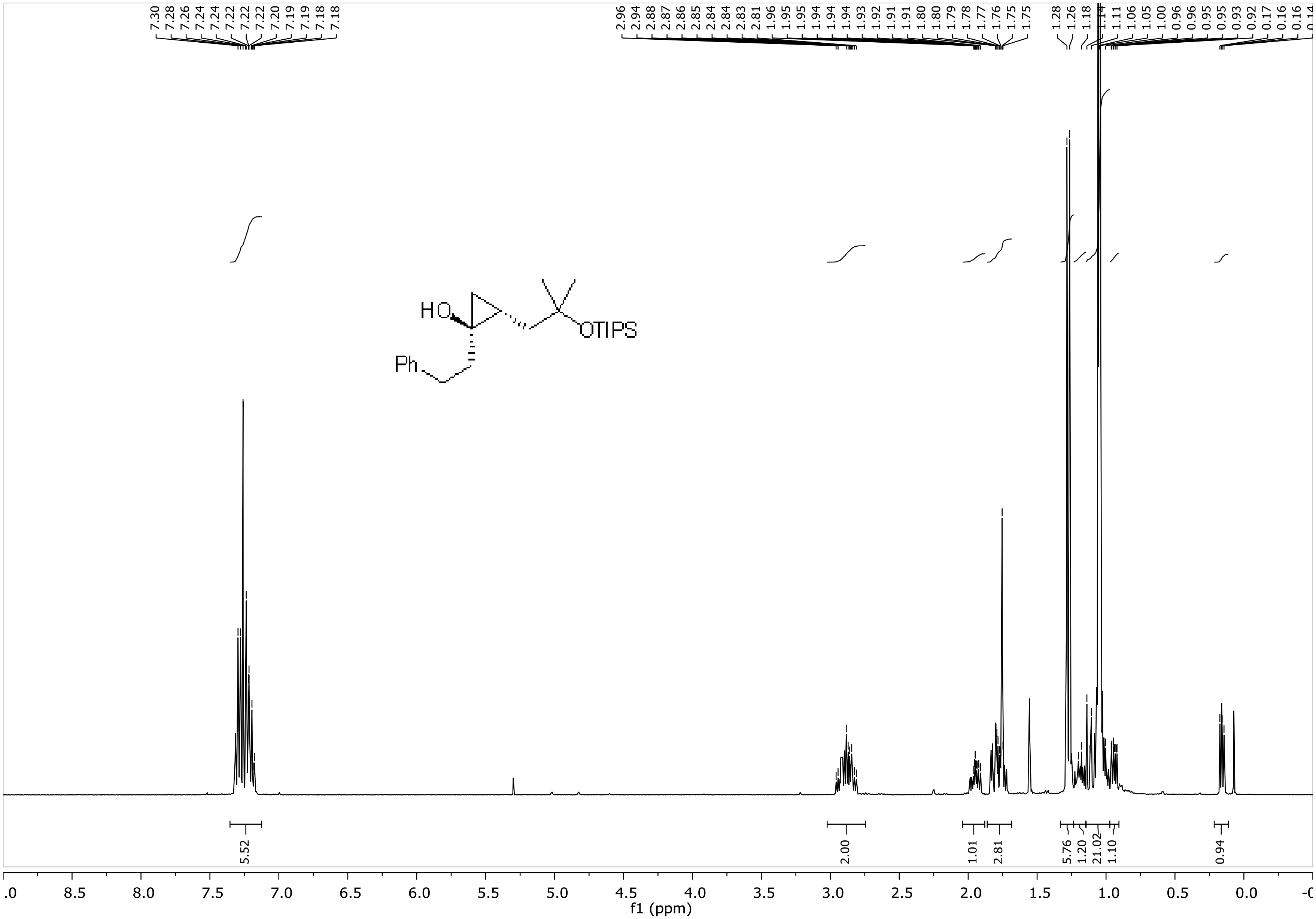
50
40
30
20
10
0
-10
f1 (ppm)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2.84
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1.95
1.95
1.94
1.94
1.94
1.93
1.92
1.91
1.91
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1.77
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1.75
1.75
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1.26
1.18
1.14
1.11
1.06
1.05
1.00
0.96
0.96
0.95
0.95
0.93
0.92
0.17
0.16
0.16
HO
OTIPS
Ph
5.52
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21.02
1.10
0.94
.0
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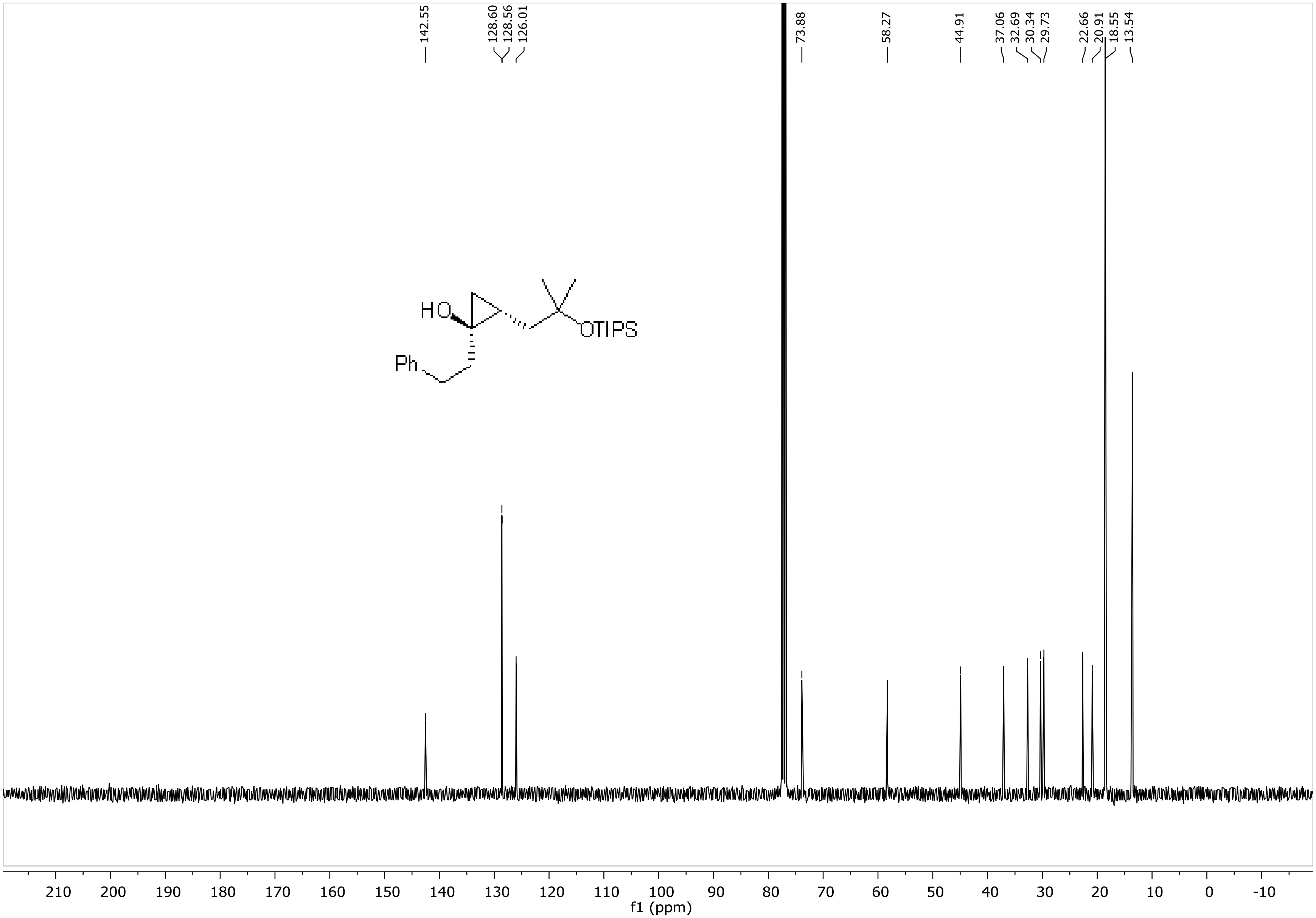
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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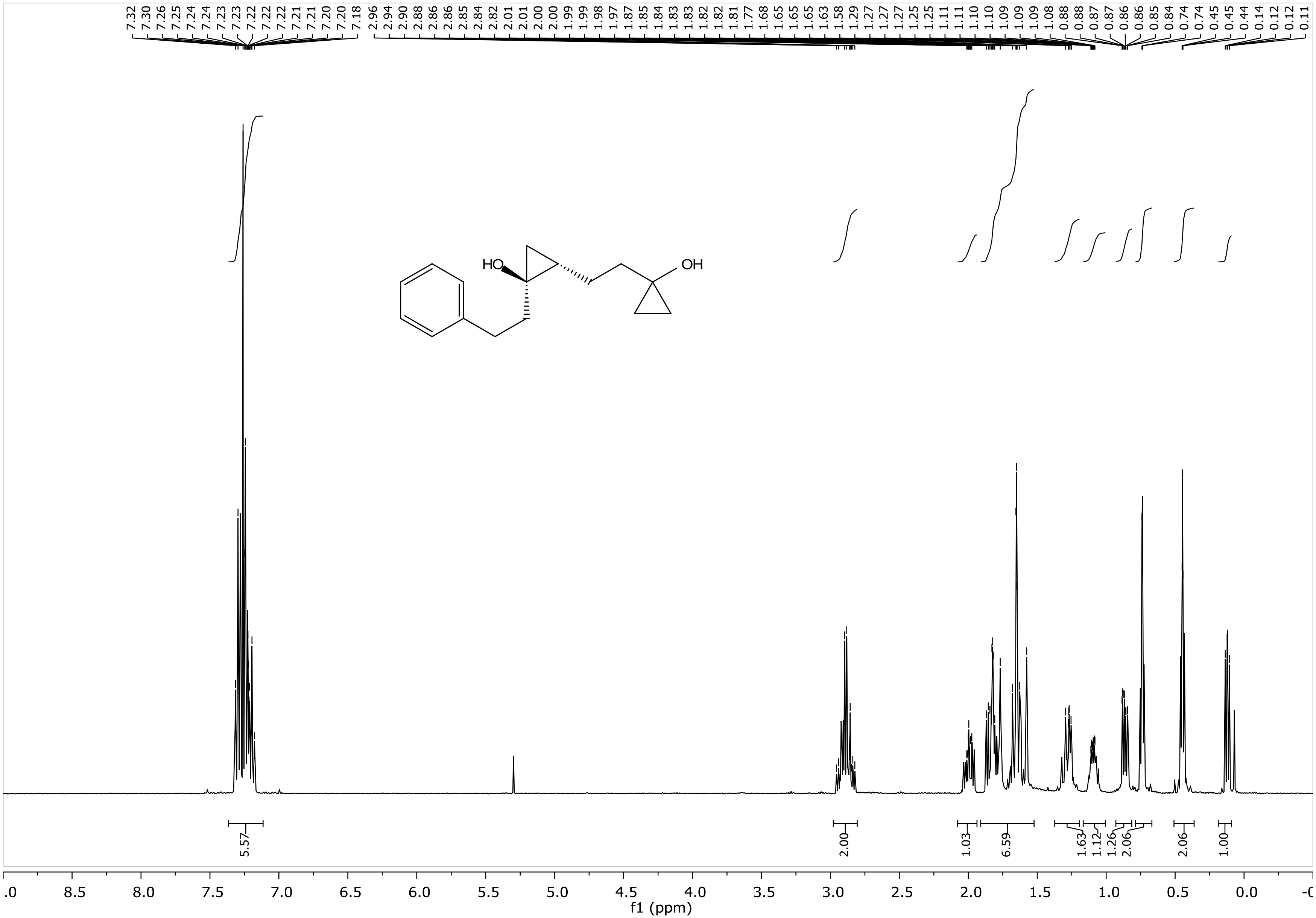
29.73
22.66
20.91
18.55
13.54
HO
OTIPS
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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2.90
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2.82
2.82
2.01
2.00
2.00
1.99
1.99
1.98
1.97
1.87
1.85
1.84
1.83
1.83
1.82
1.82
1.81
1.77
1.68
1.65
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1.65
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1.25
1.25
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1.11
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1.09
1.09
1.08
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0.88
0.87
0.87
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0.86
0.85
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0.74
0.45
0.45
0.44
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0.12
0.12
0.11
HO
OH
5.57
2.00
1.03
6.59
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1.26
2.06
2.06
1.00
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7.5
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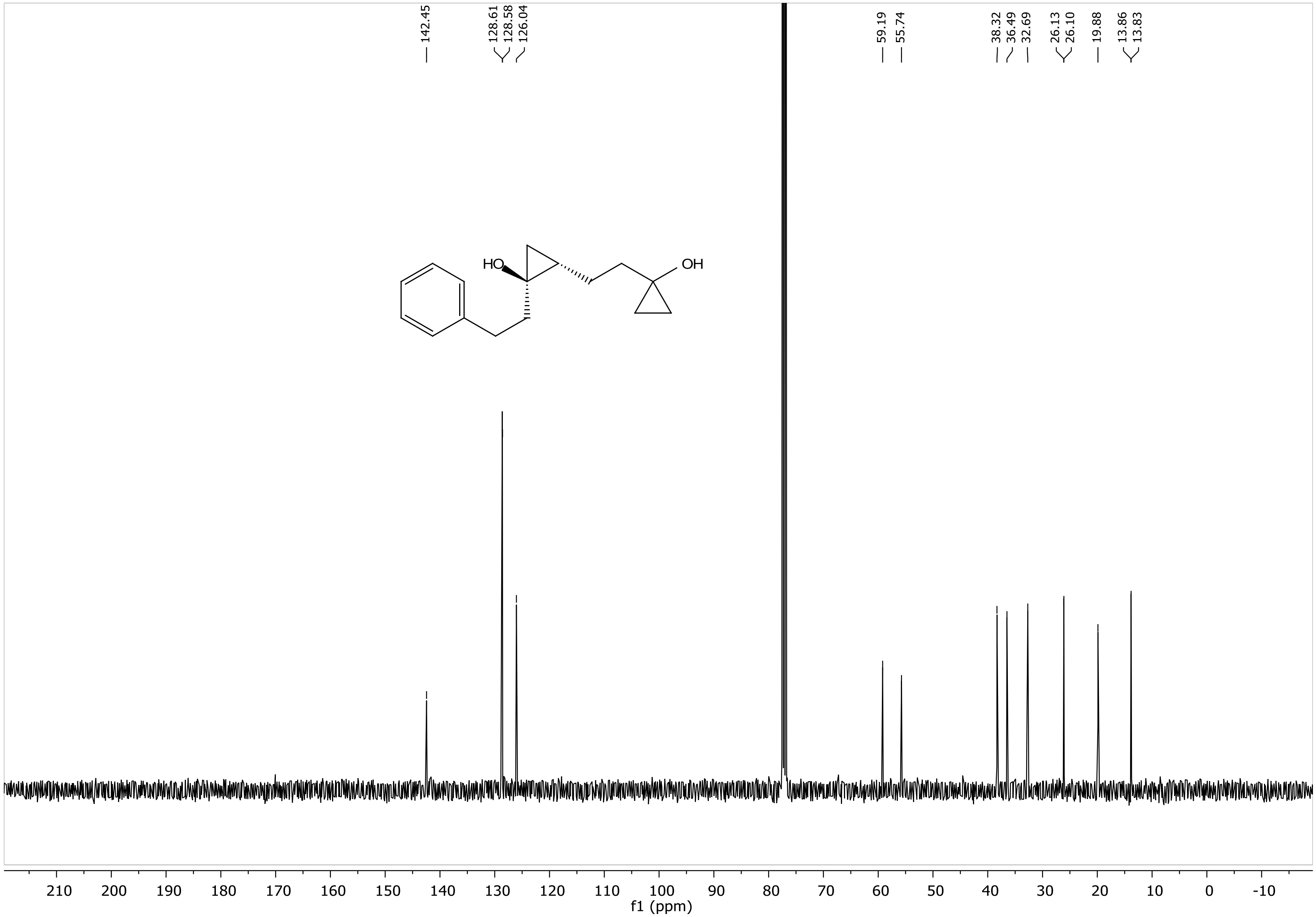
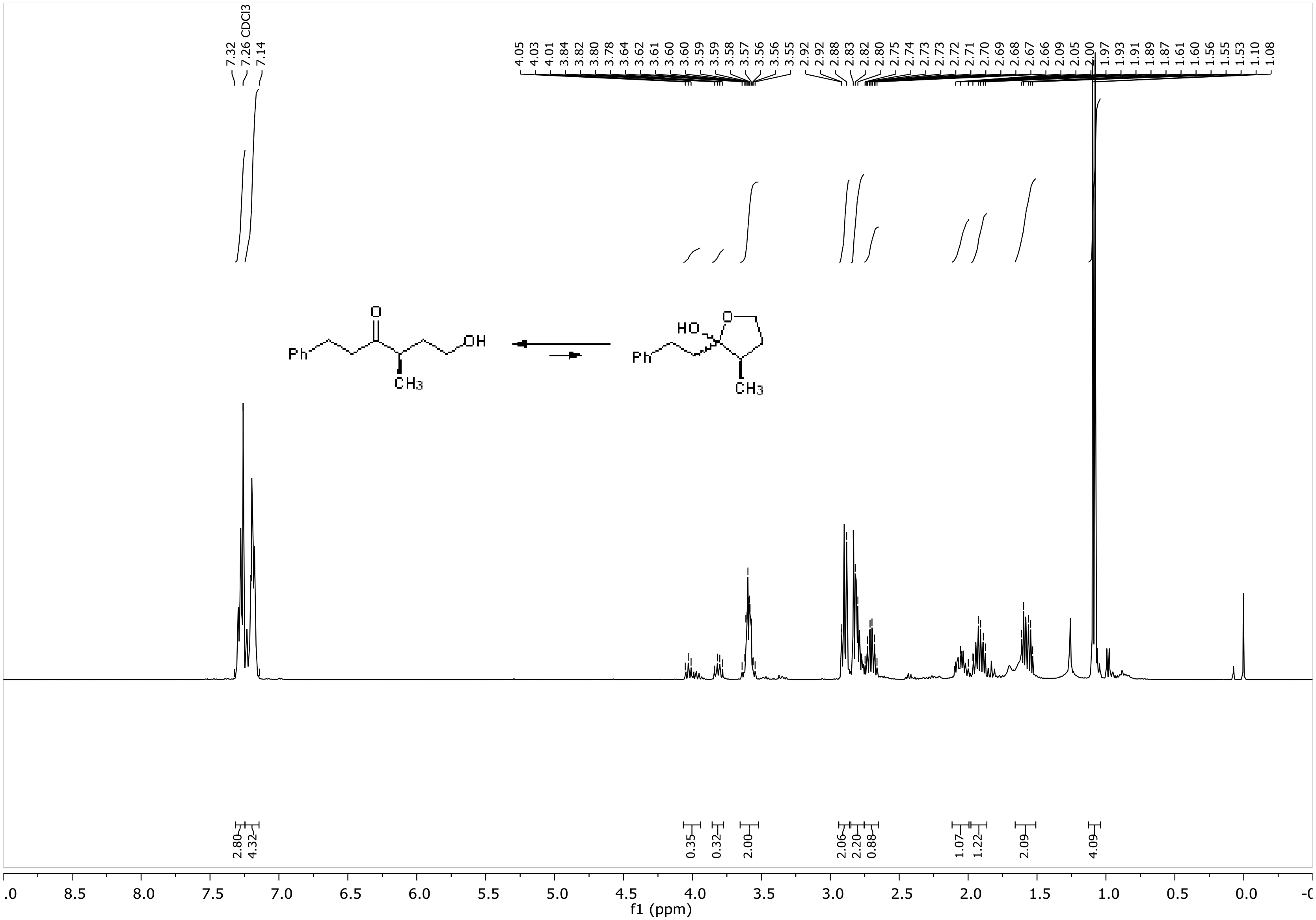
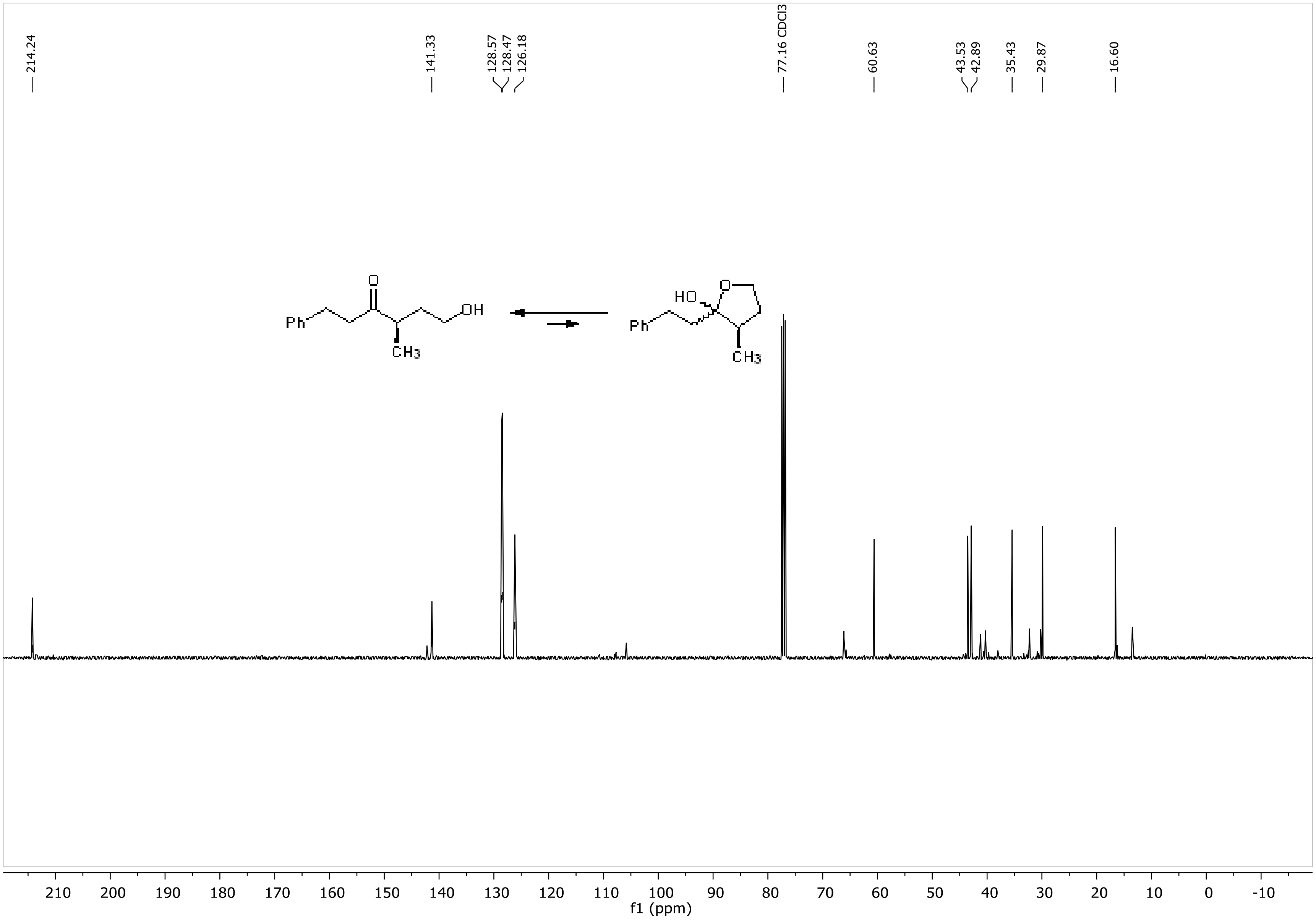
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


142.45
128.61
128.58
126.04
59.19
55.74
38.32
36.49
32.69
26.13
26.10
19.88
13.86
13.83
HO
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

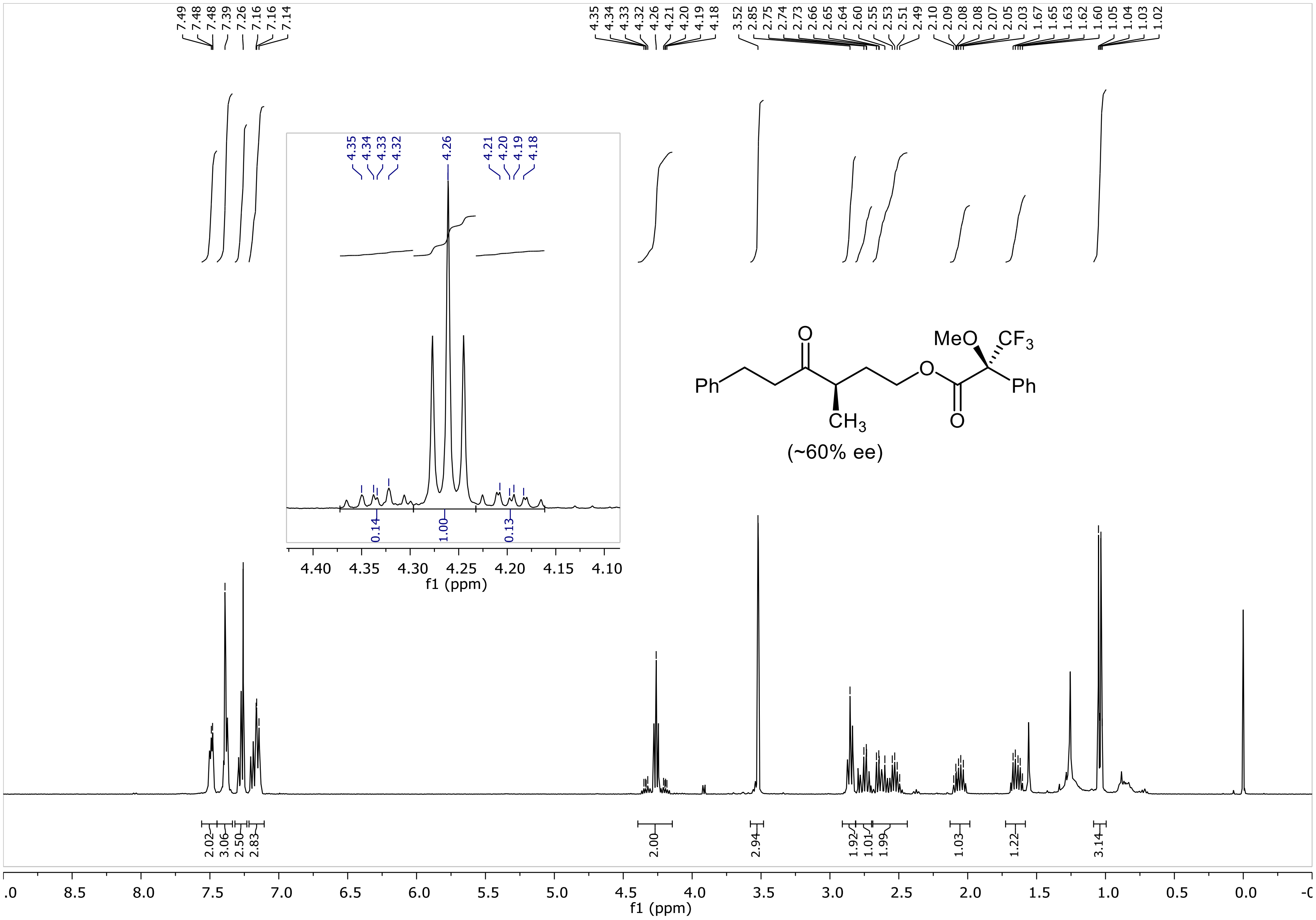
Ketone 25



7.32
7.26 CDCl3
7.14
4.05
4.03
4.01
3.84
3.82
3.80
3.78
3.64
3.62
3.61
3.60
3.60
3.59
3.59
3.58
3.57
3.56
3.56
3.55
2.92
2.92
2.88
2.83
2.82
2.80
2.75
2.74
2.73
2.73
2.72
2.71
2.70
2.69
2.68
2.67
2.66
2.09
2.05
2.00
1.97
1.93
1.91
1.89
1.87
1.61
1.60
1.56
1.55
1.53
1.10
1.08
O
Ph
OH
CH3
HO
O
Ph
CH3
2.80
4.32
0.35
0.32
2.00
2.06
2.20
0.88
1.07
1.22
2.09
4.09
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-(
f1 (ppm)

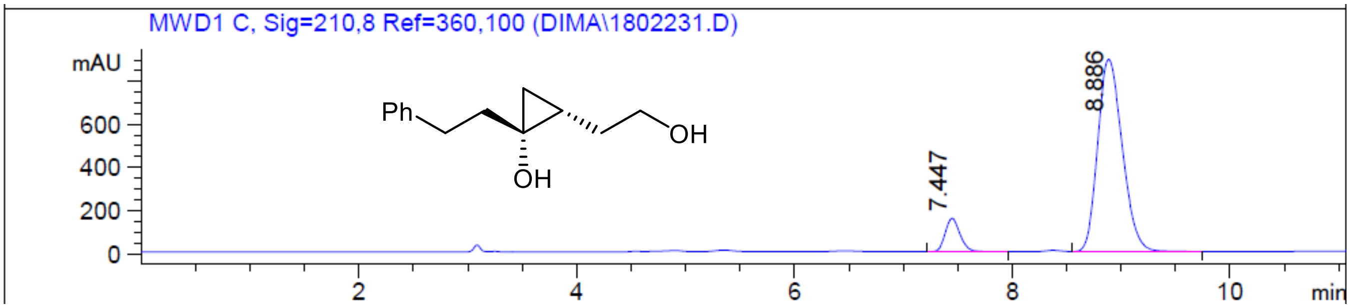

214.24
141.33
128.57
128.47
126.18
77.16 CDCl3
60.63
43.53
42.89
35.43
29.87
16.60
O
Ph
OH
CH3
HO
O
Ph
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

(*S*)-MTPA ester of ketone **25** (ca. 60% ee)

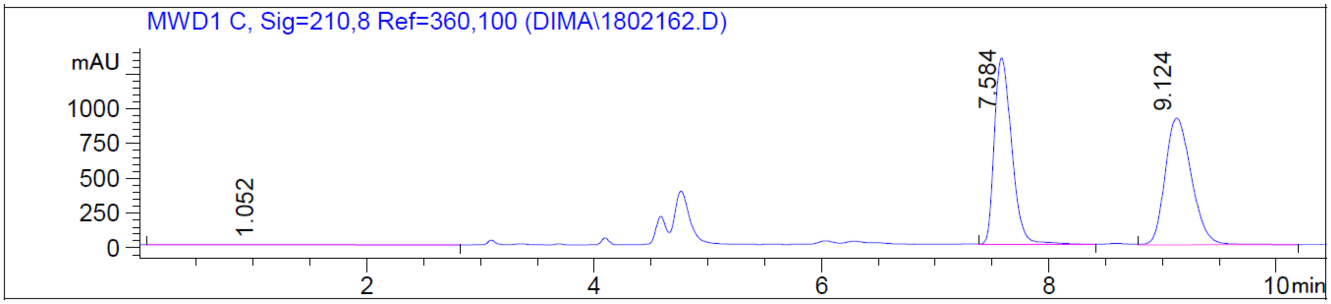


IV. Copies of HPLC Chromatograms

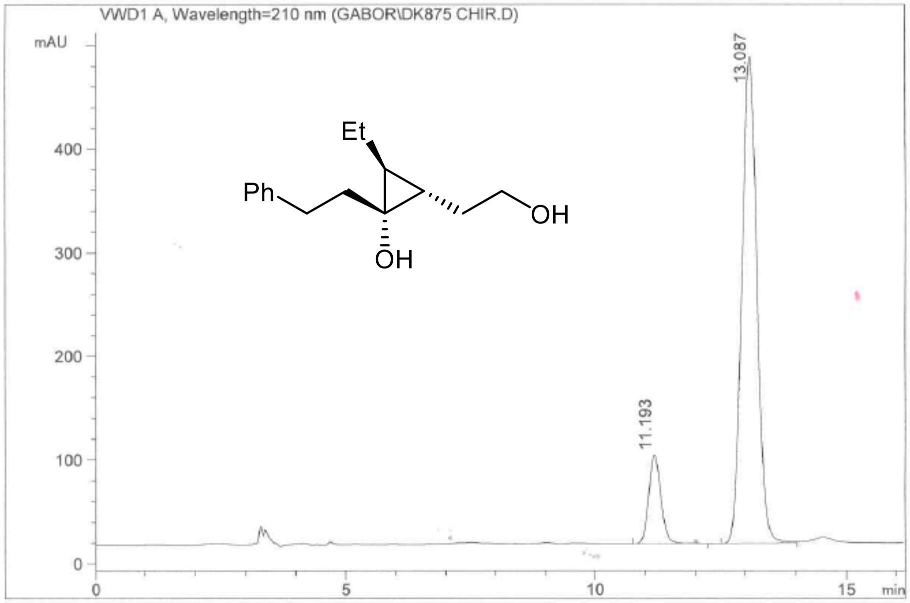
(chiral product and racemic reference)



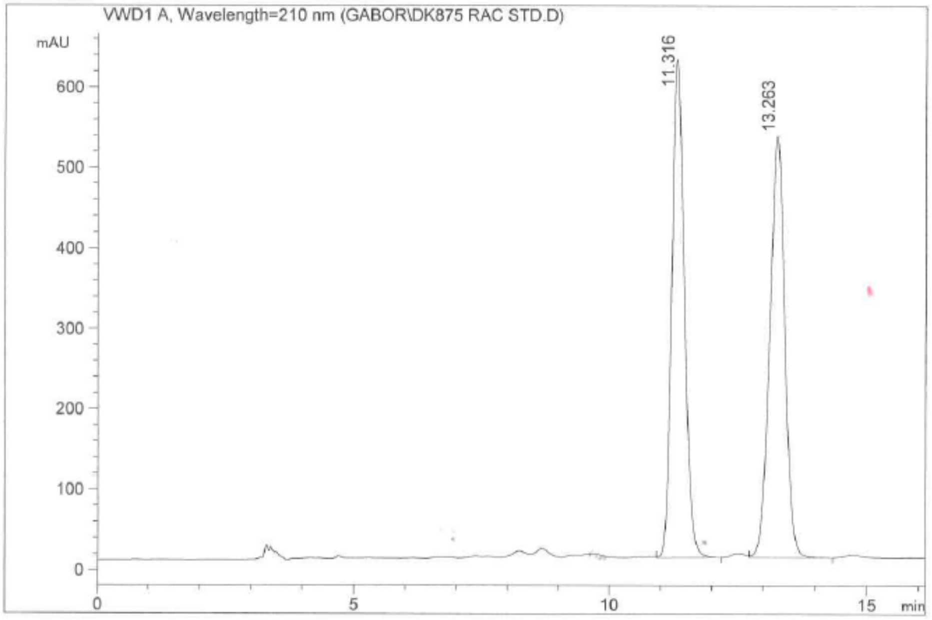
```
Signal  2: MWD1 C, Sig=210,8 Ref=360,100

|Peak|    RT    | Type  | Width |   Area    | Area %  |      Name      |
| #  |  [min]   |       | [min] |           |         |                |
|----|----------|-------|-------|-----------|---------|----------------|
|   1|     7.447|VB     |  0.147|  1473.074|    9.498|                |
|   2|     8.886|VB     |  0.247| 14036.102|   90.502|                |
------------------------------------------------------------------------
```



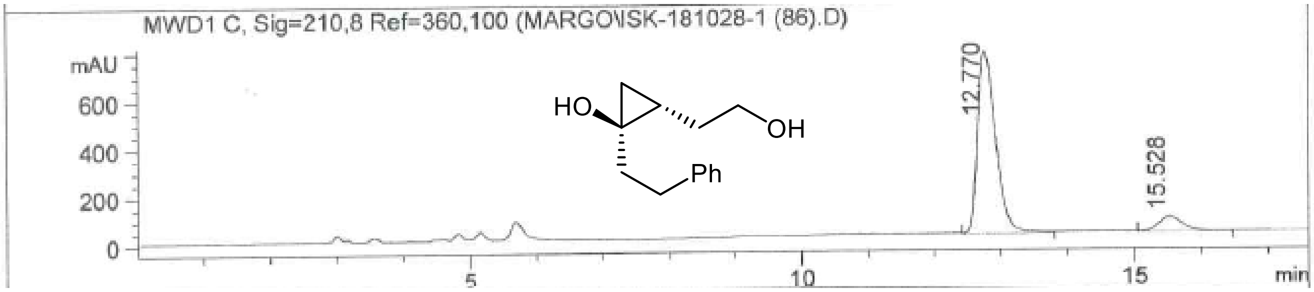
```
Signal  2: MWD1 C, Sig=210,8 Ref=360,100

|Peak|    RT    | Type  | Width |   Area    | Area %  |      Name      |
| #  |  [min]   |       | [min] |           |         |                |
|----|----------|-------|-------|-----------|---------|----------------|
|   1|     1.052|BV     |  0.963|   155.988|    0.533|                |
|   2|     7.584|VV     |  0.168| 14464.388|   49.427|                |
|   3|     9.124|VV     |  0.252| 14643.512|   50.040|                |
------------------------------------------------------------------------
```



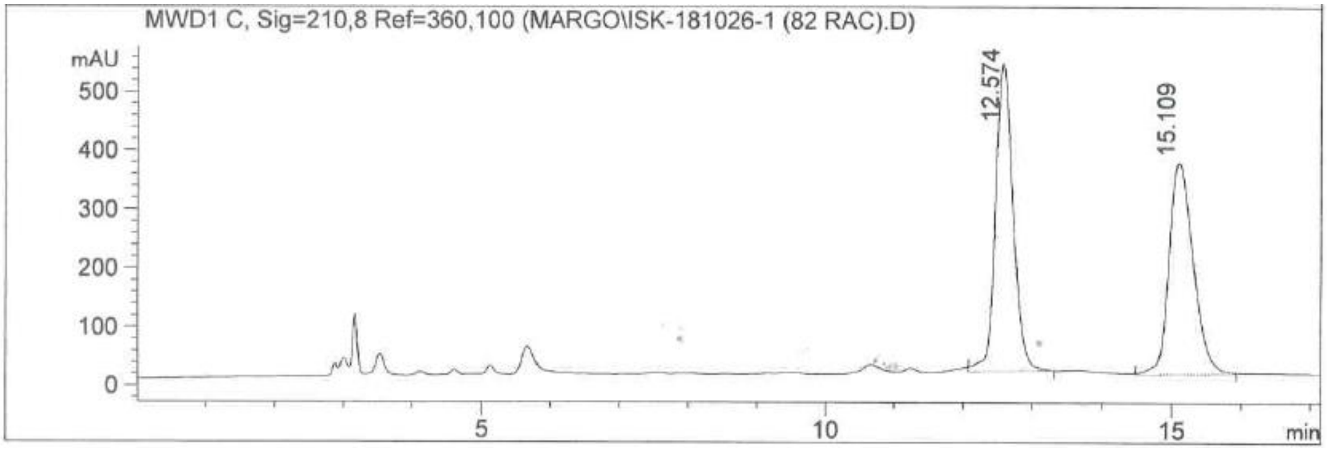
```
Signal 1: VWD1 A, Wavelength=210 nm

|Peak|    RT    | Type  | Width |   Area    | Area %  |     Name      |
| #  |  [min]   |       | [min] |           |         |               |
|----|----------|-------|-------|-----------|---------|---------------|
|   1|    11.193|BB     |  0.260|  1439.498|  12.866|               |
|   2|    13.087|BV     |  0.321|  9748.488|  87.134|               |
-----------------------------------------------------------------------
```



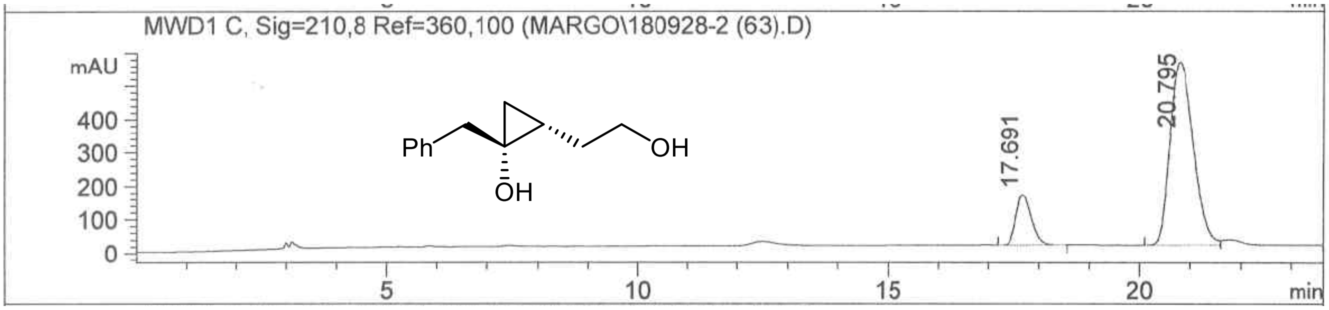
```
Signal 1: VWD1 A, Wavelength=210 nm

|Peak|    RT    | Type  | Width |   Area    | Area %  |     Name      |
| #  |  [min]   |       | [min] |           |         |               |
|----|----------|-------|-------|-----------|---------|---------------|
|   1|    11.316|VB     |  0.262| 10517.276|  49.766|               |
|   2|    13.263|VV     |  0.308| 10616.085|  50.234|               |
-----------------------------------------------------------------------
```



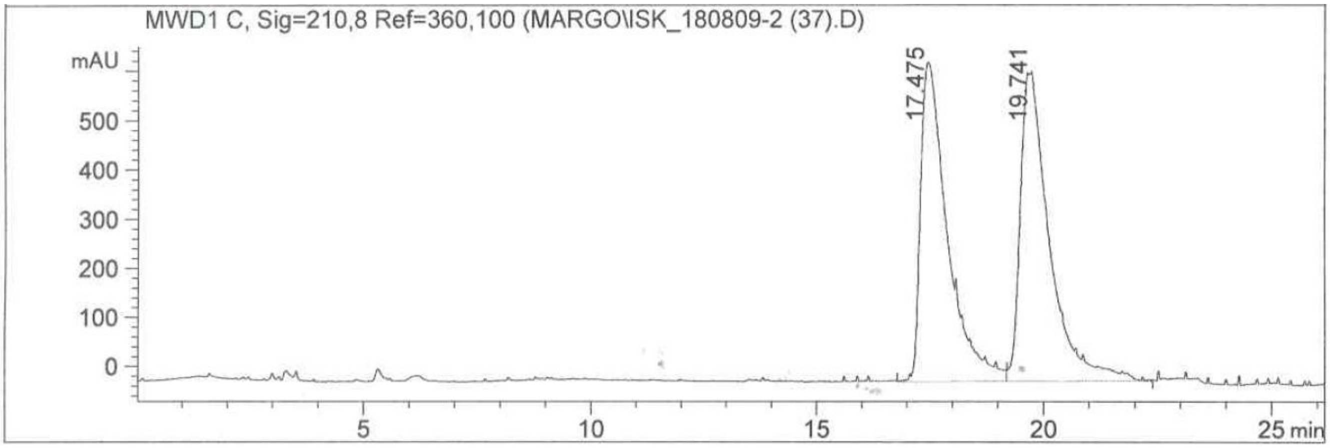
```
|Peak|    RT     | Type   | Width |    Area    | Area %  |      Name       |
| #  |  [min]    |        | [min] |            |         |                 |
|----|-----------|--------|-------|------------|---------|-----------------|
|   1|    12.770|MM      |  0.316| 14344.414|  90.071|                 |
|   2|    15.528|MM      |  0.439|  1581.273|   9.929|                 |
------------------------------------------------------------------------------
```



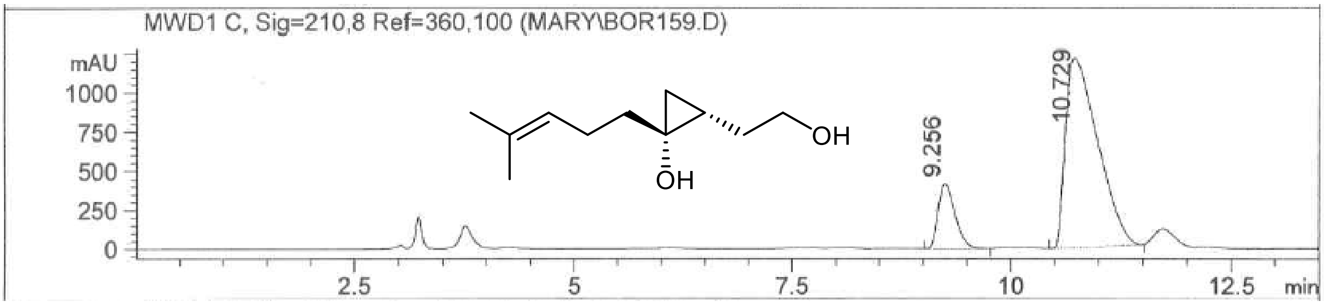
```
|Peak|    RT     | Type   | Width |    Area    | Area %  |      Name       |
| #  |  [min]    |        | [min] |            |         |                 |
|----|-----------|--------|-------|------------|---------|-----------------|
|   1|    12.574|MM      |  0.296|  9292.315|  51.463|                 |
|   2|    15.109|MM      |  0.406|  8764.151|  48.537|                 |
------------------------------------------------------------------------------
```



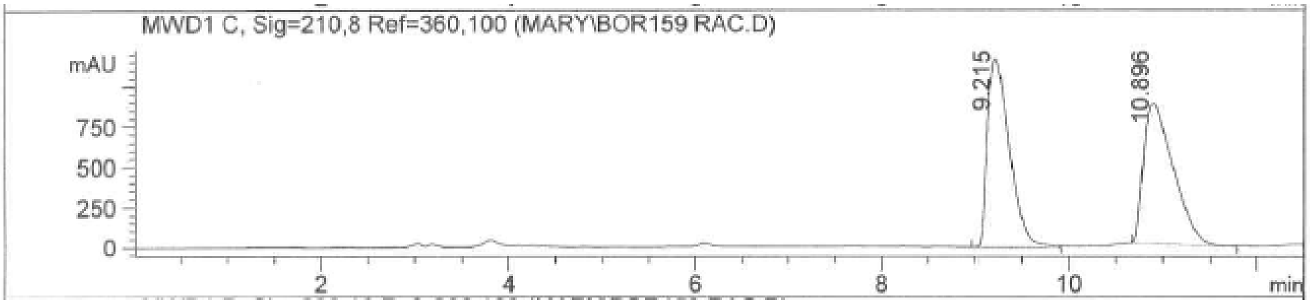
```
|Peak|    RT     | Type   | Width  |   Area     | Area %  |      Name      |
| #  |   [min]   |        | [min]  |            |         |                |
|----|-----------|--------|--------|------------|---------|----------------|
|   1|    17.691 |VB      |  0.326 |  3138.060  |  14.992 |                |
|   2|    20.795 |VV      |  0.516 | 17793.945  |  85.008 |                |
--------------------------------------------------------------------------
```



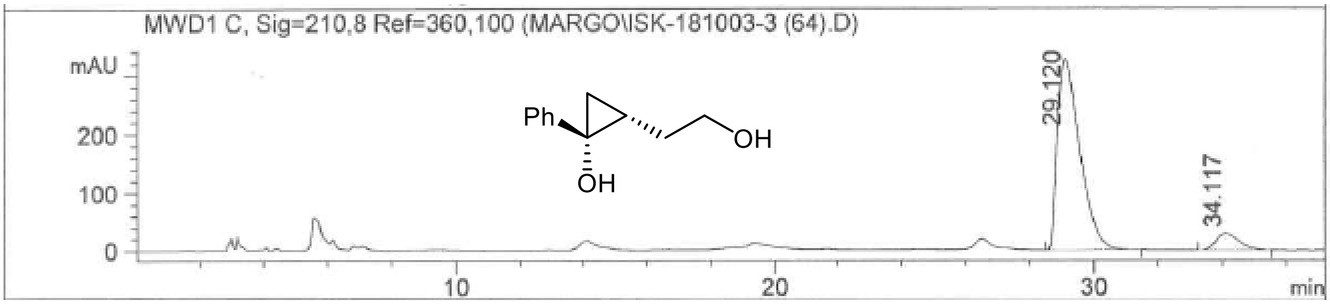
```
|Peak|    RT     | Type   | Width  |   Area     | Area %  |      Name      |
| #  |   [min]   |        | [min]  |            |         |                |
|----|-----------|--------|--------|------------|---------|----------------|
|   1|    17.475 |MF      |  0.689 | 26780.561  |  48.883 |                |
|   2|    19.741 |FM      |  0.742 | 28003.984  |  51.117 |                |
--------------------------------------------------------------------------
```



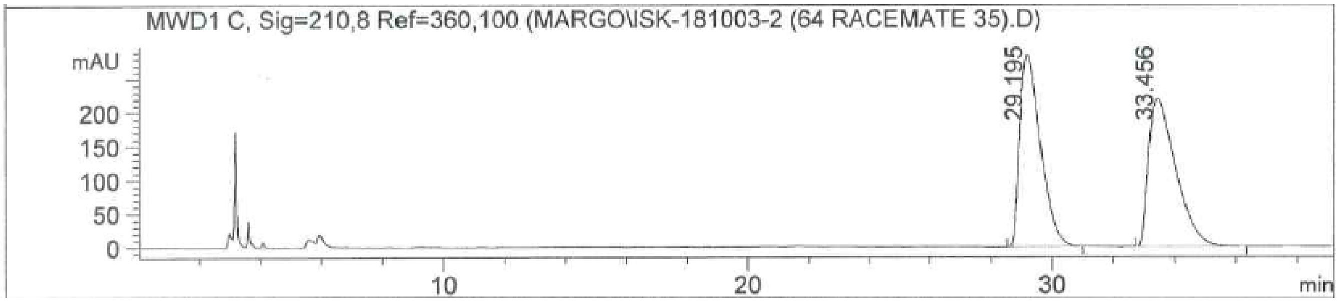
```
|Peak|   RT    | Type  | Width |   Area    | Area % |      Name      |
| #  |  [min]  |       | [min] |           |        |                |
|----|---------|-------|-------|-----------|--------|----------------|
|   1|    9.256|VV     |  0.212|  5655.788|  15.415|                |
|   2|   10.729|MM     |  0.427| 31035.225|  84.585|                |
----------------------------------------------------------------------
```



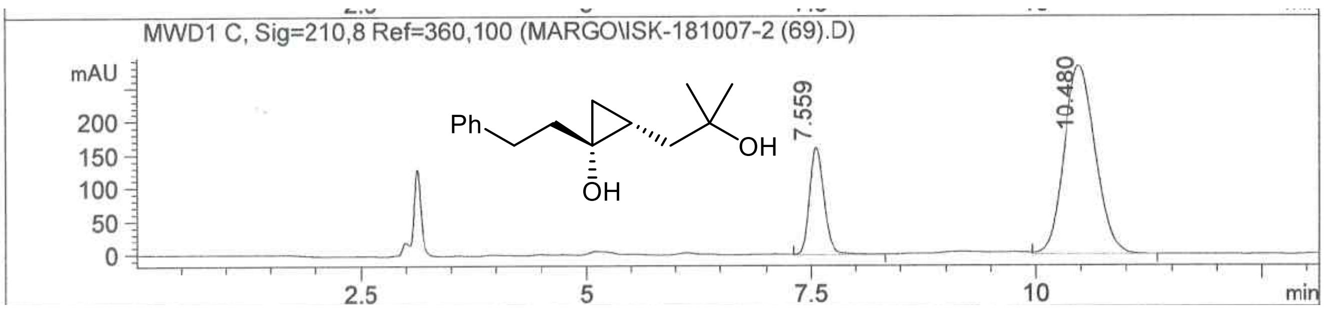
```
|Peak|   RT    | Type  | Width |   Area    | Area % |      Name      |
| #  |  [min]  |       | [min] |           |        |                |
|----|---------|-------|-------|-----------|--------|----------------|
|   1|    9.215|VV     |  0.257| 19127.672|  49.926|                |
|   2|   10.896|MM     |  0.368| 19184.215|  50.074|                |
----------------------------------------------------------------------
```



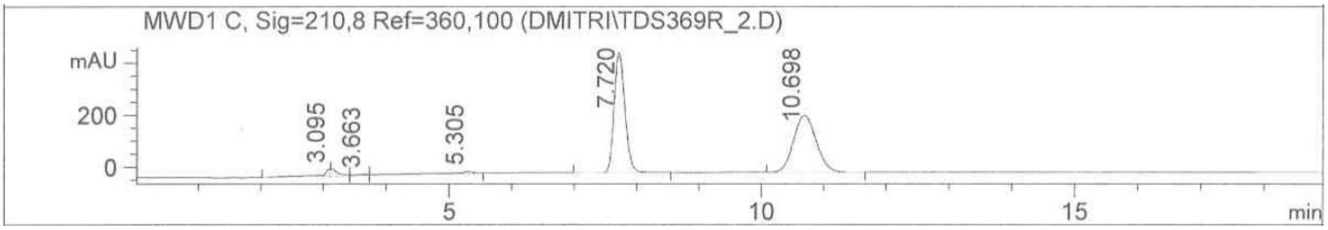
```
|Peak|    RT     | Type  | Width |   Area    | Area % |      Name      |
| #  |   [min]   |       | [min] |           |        |                |
|----|-----------|-------|-------|-----------|--------|----------------|
|   1|    29.120|BB     |  0.744| 15982.054|  92.002|                |
|   2|    34.117|BB     |  0.753|  1389.435|   7.998|                |
--------------------------------------------------------------------------
```



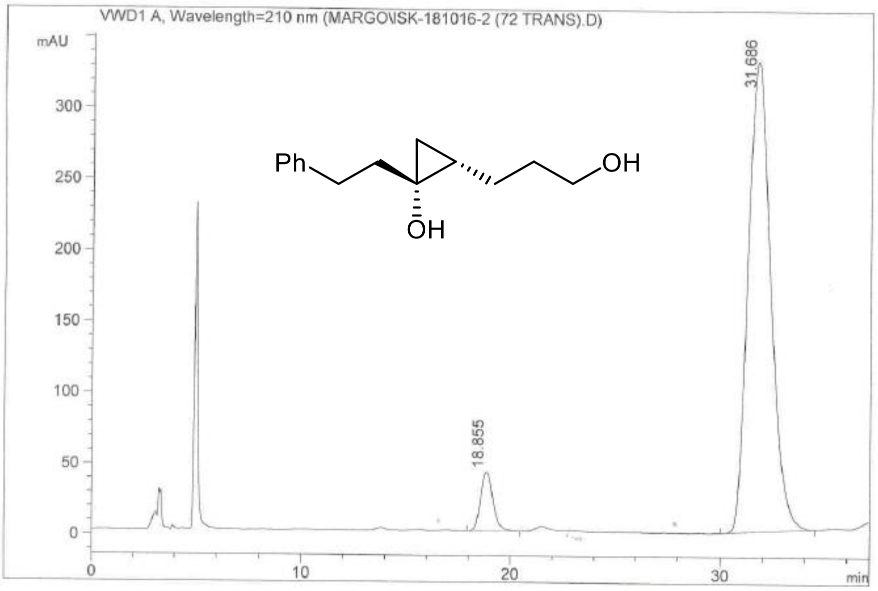
```
|Peak|    RT     | Type  | Width |   Area    | Area % |      Name      |
| #  |   [min]   |       | [min] |           |        |                |
|----|-----------|-------|-------|-----------|--------|----------------|
|   1|    29.195|BB     |  0.733| 13450.270|  49.885|                |
|   2|    33.456|BB     |  0.947| 13512.279|  50.115|                |
--------------------------------------------------------------------------
```



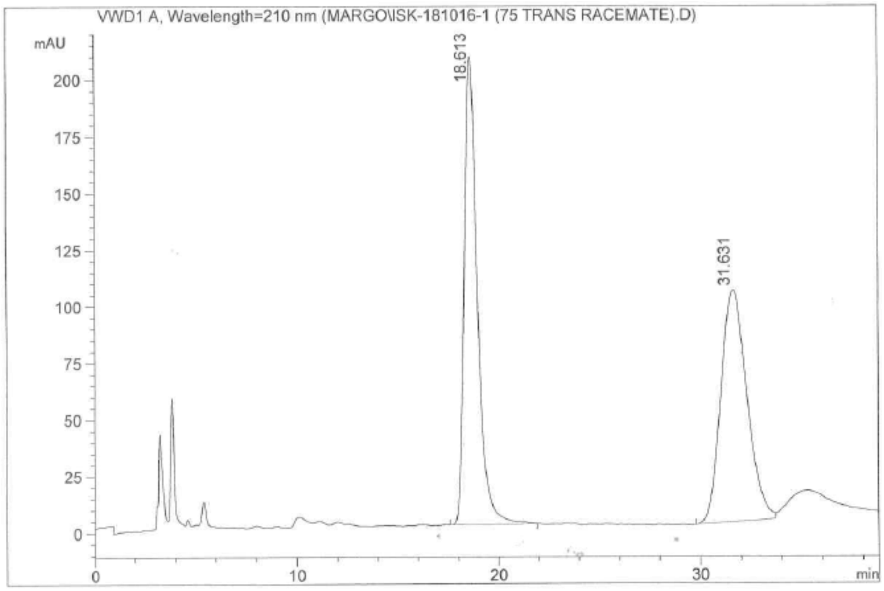
Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	7.559	VB	0.173	1814.720	21.084	
2	10.480	VB	0.377	6792.184	78.916	



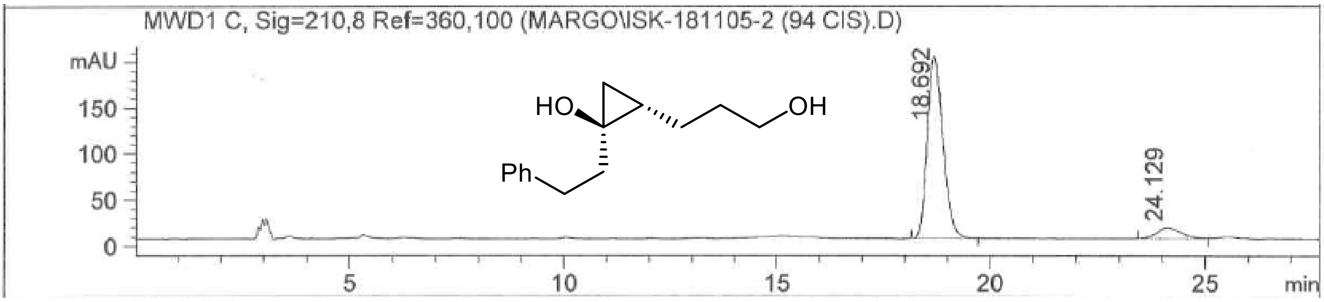
Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	7.720	BB	0.185	117.875	50.068	
2	10.699	BB	0.392	117.556	49.932	



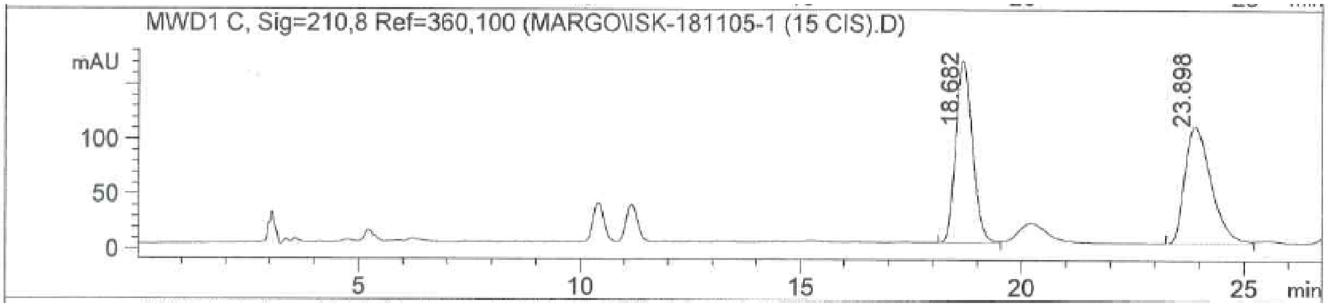
```
Signal   1: VWD1 A, Wavelength=210 nm

|Peak|   RT     | Type  | Width |    Area    | Area % |     Name       |
| #  |  [min]   |       | [min] |            |        |                |
|----|----------|-------|-------|------------|--------|----------------|
|   1|   18.855|BB      |  0.642|  1738.982|   6.578|                 |
|   2|   31.686|BB      |  1.127| 24698.756|  93.422|                 |
------------------------------------------------------------------------
```



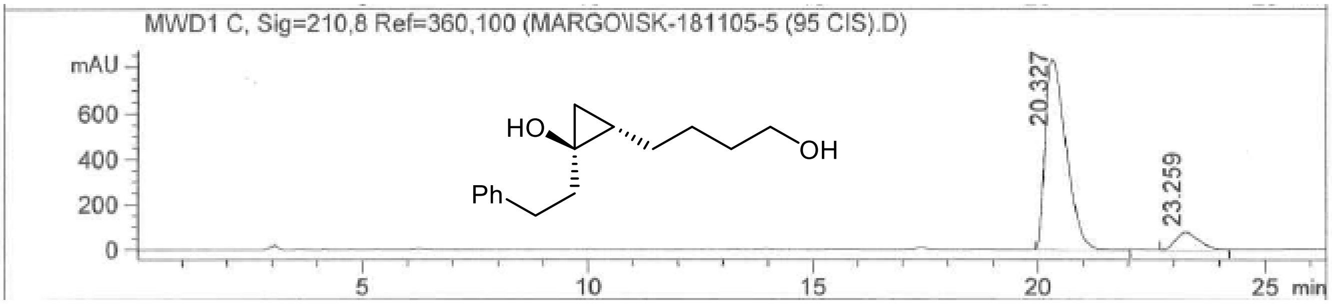
```
Signal   1: VWD1 A, Wavelength=210 nm

|Peak|   RT     | Type  | Width |    Area    | Area % |     Name       |
| #  |  [min]   |       | [min] |            |        |                |
|----|----------|-------|-------|------------|--------|----------------|
|   1|   18.613|BB      |  0.694|  9375.072|  50.762|                 |
|   2|   31.631|BV      |  1.343|  9093.718|  49.238|                 |
------------------------------------------------------------------------
```



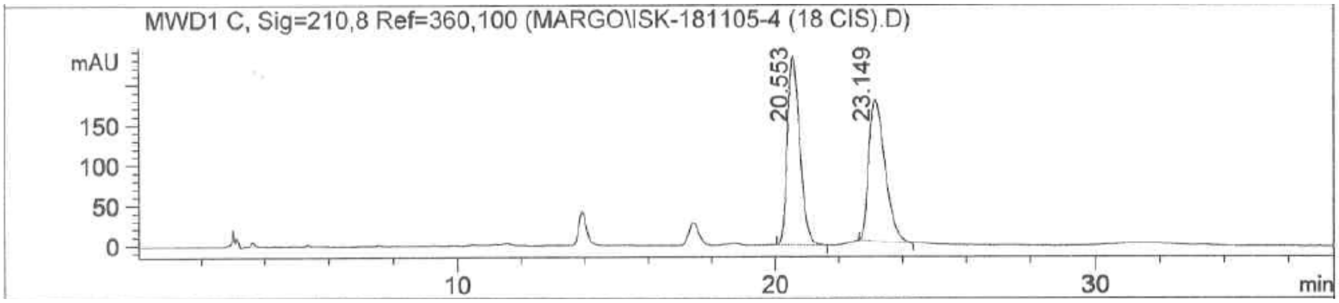
```
|Peak|   RT     | Type  | Width |   Area    | Area % |      Name      |
| #  |  [min]   |       | [min] |           |        |                |
|----|----------|-------|-------|-----------|--------|----------------|
|   1|   18.692|BB     |  0.396|  5062.664|  91.811|                |
|   2|   24.129|BV     |  0.584|   451.561|   8.189|                |
--------------------------------------------------------------------------
```



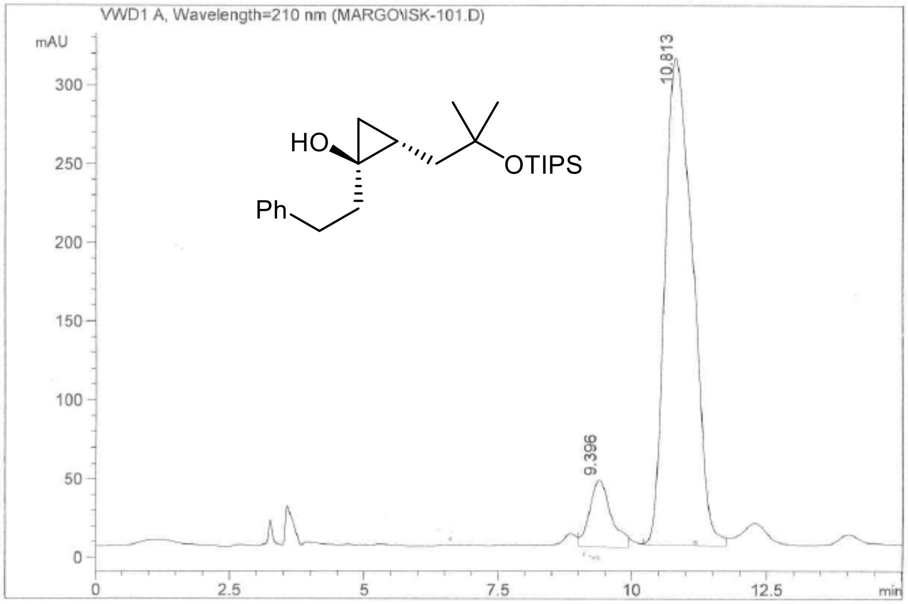
```
|Peak|   RT     | Type  | Width |   Area    | Area % |      Name      |
| #  |  [min]   |       | [min] |           |        |                |
|----|----------|-------|-------|-----------|--------|----------------|
|   1|   18.682|BB     |  0.408|  4336.587|  49.724|                |
|   2|   23.898|BB     |  0.633|  4384.690|  50.276|                |
--------------------------------------------------------------------------
```



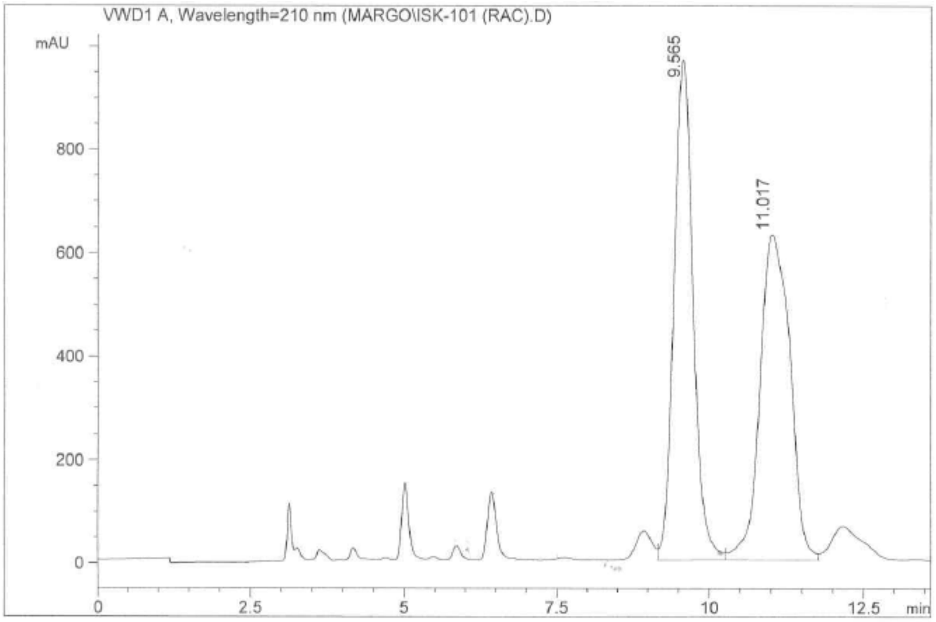
Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	20.327	MM	0.542	27151.287	90.260	
2	23.259	MM	0.617	2929.814	9.740	



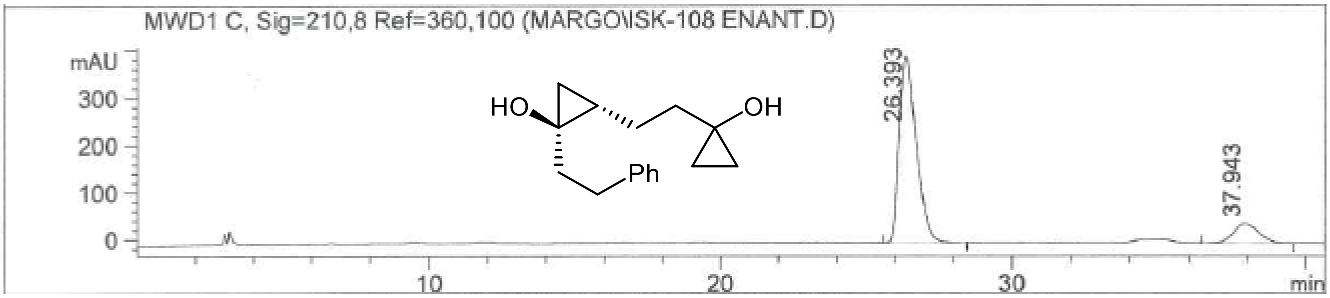
Peak #	RT [min]	Type	Width [min]	Area	Area %	Name
1	20.553	MM	0.452	6357.242	50.346	
2	23.149	MM	0.595	6269.857	49.654	



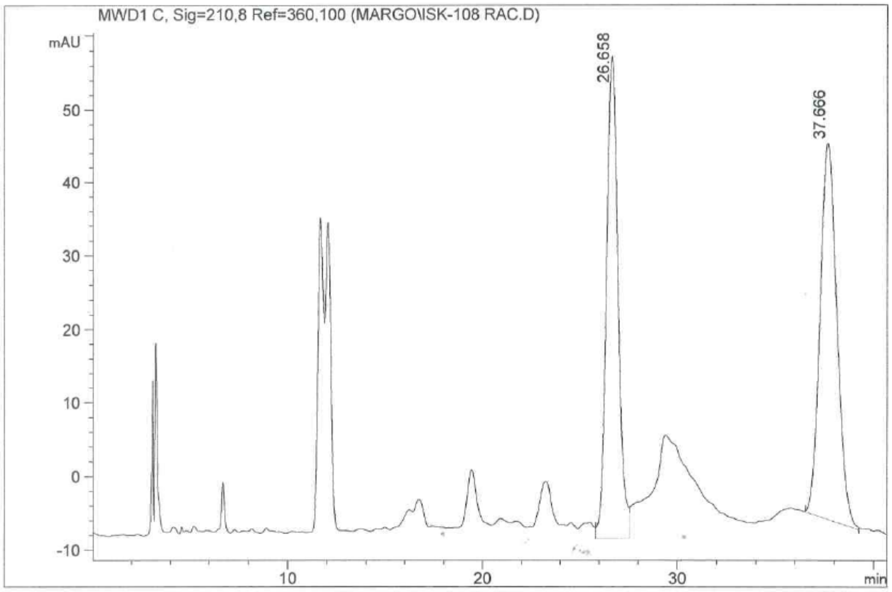
```
Signal   1: VWD1 A, Wavelength=210 nm

|Peak|    RT     | Type   | Width  |   Area    | Area %  |      Name       |
| #  |  [min]    |        | [min]  |           |         |                 |
|----|-----------|--------|--------|-----------|---------|-----------------|
|   1|     9.396|MM       |  0.470|  1203.144|    9.832|                 |
|   2|    10.813|MM       |  0.595| 11033.966|   90.168|                 |
-----------------------------------------------------------------------
```



```
Signal   1: VWD1 A, Wavelength=210 nm

|Peak|    RT     | Type   | Width  |   Area    | Area %  |      Name       |
| #  |  [min]    |        | [min]  |           |         |                 |
|----|-----------|--------|--------|-----------|---------|-----------------|
|   1|     9.565|VV       |  0.336| 21145.084|   49.679|                 |
|   2|    11.017|VV       |  0.483| 21418.750|   50.321|                 |
-----------------------------------------------------------------------
```



```
|Peak|   RT     | Type  | Width |   Area    | Area % |      Name      |
| #  |  [min]   |       | [min] |           |        |                |
|----|----------|-------|-------|-----------|--------|----------------|
|   1|   26.393 |VB     |  0.622| 16246.863|  86.725|                |
|   2|   37.943 |VB     |  0.917|  2486.937|  13.275|                |
-------------------------------------------------------------------------
```



```
Signal  1: MWD1 C, Sig=210,8 Ref=360,100

|Peak|   RT     | Type  | Width |   Area    | Area % |      Name      |
| #  |  [min]   |       | [min] |           |        |                |
|----|----------|-------|-------|-----------|--------|----------------|
|   1|   26.658 |MM     |  0.690|  2715.008|  47.207|                |
|   2|   37.666 |MM     |  0.989|  3036.317|  52.793|                |
-------------------------------------------------------------------------
```

V. References

1. B. Weber, D. Seebach, *Tetrahedron* **1994**, *50*, 7473.

2. S. Kiyooka, Y. Wada, M. Ueno, T. Yokoyama, *Tetrahedron* **2007**, *63*, 12695.

3. Kulinkovich, O. G.; Kananovich, D. G.; Lopp, M.; Snieckus, V. *Adv. Synth. Catal*. **2014**, *356*, 3615.