Supporting Information

Doubly vinylogous and doubly rearomative functionalization of 2-alkyl-3-furfurals

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1. General Information

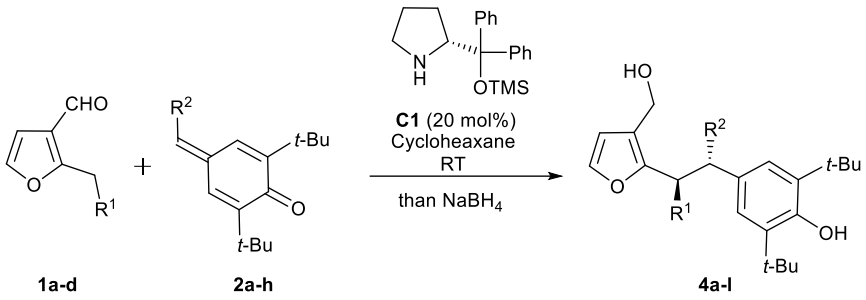
NMR spectra were acquired on a Bruker Ultra Shield 700 instrument, running at 700 MHz for ^{1}H and 176 MHz for ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$: 7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR). Mass spectra were recorded on a Bruker Maxis Impact spectrometer using electrospray (ES+) ionization (referenced to the mass of the charged species). Optical rotations were measured on a Perkin-Elmer 241 polarimeter and $[\alpha]_D$ values are given in deg•cm•g^{-1}•dm^{-1}; concentration *c* is listed in g•(100 mL)$^{-1}$. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminum-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation or phosphamolybdic acid stainer. The enantiomeric ratio (er) of the products was determined by chiral stationary phase HPLC (Daicel Chiralpak IA and IC). Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification. For flash chromatography (FC) silica gel (Silica gel 60, 230-400 mesh, Fluka) was used. 2-Alkyl-3-furfurals **1** were synthesized according to the literature procedure.[1] *para*-Quinone methides **2e**–**2g**[2] and **2a**–**d, 2h**[3] were synthesized according to the literature procedures.

1. J. Bojanowski, A. Skrzyńska and A. Albrecht, Dearomatizative and decarboxylative reaction cascade in the aminocatalytic synthesis of 3,4-dihydrocoumarins, *Asian J. Org. Chem.,* 2019, **8**, 844–848.

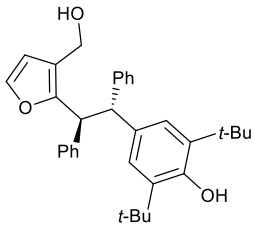
2. Y. Z. Lou, P. Cao, T. Jia, Y. Zhang, M. Wang and J. Lia, Copper-catalyzed enantioselective 1,6-boration of *para*-quinone methides and efficient transformation of *gem*-diarylmethine boronates to triarylmethanes, *Angew. Chem., Int. Ed.,* 2015, **54**, 12134–12138.

3. S. Gao, X. Xu, Z. Yuan, H. Zhou, H. Yao and A. Lin, 1,6-Addition arylation of *para*-quinone methides: an approach to unsymmetrical triarylmethanes, *Eur. J. Org. Chem*., 2016, **2016**, 3006–3012.

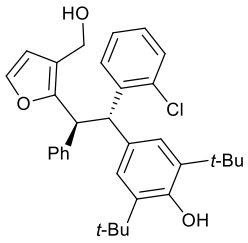
2.1 General procedure for dearomative functionalization of 2-alkyl-3-furfurals 1



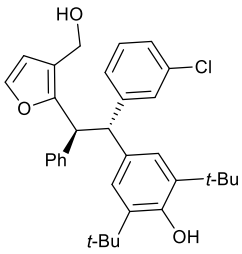
In an ordinary glass vial (4 mL), equipped with a teflon-coated magnetic stirring bar and a screw cap, the corresponding 2-alkyl-3-furfural **1** (0.2 mmol, 1 equiv) and *para*-quinone methide **2** (0.24 mmol, 1.2 equiv) were added followed by cyclohexane (0.4 mL, 0.5 M) and the catalyst **C1** (0.04 mmol, 0.2 equiv). The reaction mixture was stirred at 25 °C or 40 °C for 48 h to 120 h. After full conversion of the starting material **1** (as confirmed by ^{1}H NMR of a crude reaction mixture), MeOH (0.2 mL) was added and the reaction mixture was cooled to 0 °C. Subsequently, $NaBH_4$ (0.2 mmol, 1 equiv) was added in one portion. After 30 min, the reaction mixture was directly subjected to flash chromatography on silica gel (eluent: hexanes/ethyl acetate 4:1) to obtain pure product **4.**



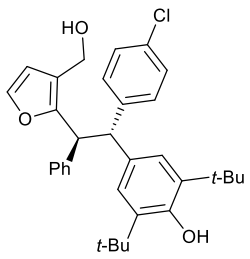
2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(3-(hydroxymethyl)furan-2-yl)-1,2-diphenylethyl)phenol 4a. Following the general procedure (reaction performed at 25 °C) product **4a** (6:1 dr in a crude reaction mixture) was isolated in 80% yield as light-yellow oil as a single diastereomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.25 – 7.23 (m, 3H), 7.21 – 7.19 (m, 4H), 7.15 – 7.12 (m, 2H), 7.11 – 7.08 (m, 1H), 7.06 – 7.03 (m, 1H), 6.87 (s, 2H), 6.14 (d, J = 1.9 Hz, 1H), 4.89 (s, 1H), 4.78 (d, J = 12.0 Hz, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.32 (d, J = 12.3 Hz, 1H), 4.26 (d, J = 12.3 Hz, 1H), 1.29 (s, 18H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 152.8, 151.9, 144.5, 141.2, 141.1, 135.3 (2C), 132.2, 128.8 (2C), 128.3 (2C), 128.2 (2C), 128.1 (2C), 126.4, 126.3, 125.6 (2C), 119.8, 110.9, 56.5, 55.5, 49.7, 34.4 (2C), 30.4 (6C). HRMS calcd for $C_{33}H_{38}O_3$ $[M+Na]^+$: 505.2714; found: 505.2717. The er was determined by HPLC using a chiral Chiralpack IC column [hexane:*i*-PrOH, 98:2]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 8.9 min, τ_{minor} = 8.0 min, (>99:1 er); $[\alpha]^D_{20}$ = +23.8 (c = 1.0, $CHCl_3$).



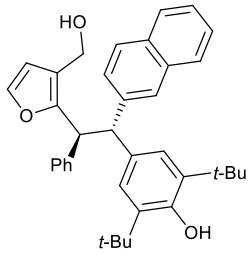
2,6-Di-*tert*-butyl-4-((1*S*,2*S*)-1-(2-chlorophenyl)-2-(3-(hydroxymethyl)furan-2-yl)-2-phenylethyl)phenol 4b. Following the general procedure (reaction performed at 40 °C) product **4b** (6:1 dr in a crude reaction mixture) was isolated in 58% yield as yellow oil as a single diastereomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.54 – 7.52 (m, 1H), 7.28 – 7.24 (m, 1H), 7.22 – 7.16 (m, 4H), 7.12 – 7.14 (m, 2H), 7.09 – 7.02 (m, 2H), 6.84 (s, 2H), 6.16 (d, J = 1.8 Hz, 1H), 5.35 (d, J = 12.0 Hz, 1H), 4.91 (s, 1H), 4.75 (d, J = 12.0 Hz, 1H), 4.41 (d, J = 3.4 Hz, 2H), 1.28 (s, 18H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 152.4, 152.0, 141.4, 141.3, 141.2, 135.3 (2C), 134.5, 131.3, 129.9, 128.7 (2C), 128.2 (2C), 127.3, 126.6, 126.5, 125.6 (2C), 125.0, 119.5, 110.8, 56.7, 50.8, 49.1, 34.3 (2C), 30.4 (6C). HRMS calcd for $C_{33}H_{37}O_3Cl$ $[M+Na]^+$: 539.2324; found: 539.2330. The er was determined by HPLC using a chiral Chiralpack IC column [hexane:*i*-PrOH, 98:2]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 7.7 min, τ_{minor} = 6.7 min, (>99:1 er); $[\alpha]^{D}_{20}$ = +30.4 (c = 1.0, $CHCl_3$).



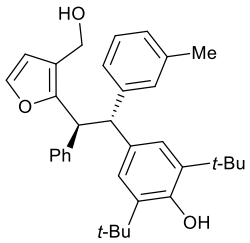
2,6-Di-*tert*-butyl-4-((1*S*,2*S*)-1-(3-chlorophenyl)-2-(3-(hydroxymethyl)furan-2-yl)-2-phenylethyl)phenol 4c. Following the general procedure (reaction performed at 25 °C) product **4c** (6:1 dr in a crude reaction mixture) was isolated in 80% yield as yellow oil as a single diastereomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.24 (d, J = 1.9 Hz, 1H), 7.23 – 7.21 (m, 1H), 7.20 – 7.18 (m, 2H), 7.15 – 7.11 (m, 4H), 7.09 – 7.04 (m, 2H), 6.80 (s, 2H), 6.16 (d, J = 1.9 Hz, 1H), 4.94 (d, J = 1.6 Hz, 1H), 4.74 (dd, J = 11.9, 1.4 Hz, 1H), 4.63 (dd, J = 12.0, 1.4 Hz, 1H), 4.41 – 4.30 (m, 2H), 1.28 (s, 18H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 152.4, 152.1, 146.1, 141.2, 140.9, 135.4 (2C), 134.0, 131.7, 129.5, 128.6 (2C), 128.5, 128.3 (2C), 126.5, 126.4, 126.1, 125.4 (2C), 119.9, 110.9, 56.6, 55.23, 49.4, 34.3 (2C), 30.3 (6C). HRMS calcd for $C_{33}H_{37}O_3Cl$ $[M+Na]^+$: 539.2324; found: 539.2332. The er was determined by HPLC using a chiral Chiralpack IC column [hexane:*i*-PrOH, 98:2]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 8.5 min, τ_{minor} = 7.8 min, (>99:1 er); $[\alpha]^{D}_{20}$ = +42.5 (c = 1.0, $CHCl_3$).



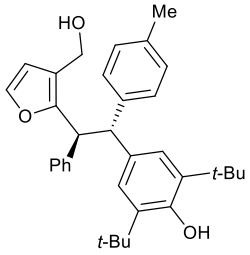
2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-1-(4-chlorophenyl)-2-(3-(hydroxymethyl)furan-2-yl)-2-phenylethyl)phenol 4d. Following the general procedure (reaction performed at 25 °C) product **4d** (3:1 dr in a crude reaction mixture) was isolated in 50% yield as yellow oil as a mixture of stereoisomers (3:1 dr). Major diastereoisomer: ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.23 (d, J = 1.9 Hz,, 1H), 7.19 – 7.15 (m, 6H), 7.12– 7.14 (m, 2H), 7.06 (s, 1H), 6.79 (s, 2H), 6.16 (d, J = 1.9 Hz, 1H), 4.91 (s, 1H), 4.75 (d, J = 11.9 Hz, 1H), 4.64 (d, J = 11.9 Hz, 1H), 4.39 – 4.31 (m, 2H), 1.28 (s, 18H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 152.6, 152.0, 142.67, 141.2, 135.4 (2C), 132.0, 131.9, 130.2, 129.4 (2C), 128.6 (2C), 128.4 (2C), 128.3 (2C), 126.5, 125.3 (2C), 119.8, 110.9, 56.6, 54.9, 49.5, 34.4 (2C), 30.4 (6C). Minor diastereoisomer diagnostic signals: ^{1}H NMR (700 MHz, $CDCl_3$) δ 4.80 (d, J=12.1, 1H), 4.60 (d, J= 12.2, 1H), 4.16 (d, J= 12.3, 1H), 4.10 (d, J= 12.3, 1H) 1.33 (s, 18H) ^{13}C NMR (176 MHz, $CDCl_3$) δ 56.2, 54.3, 49.4, 34.5 (2C), 30.3 (6C). HRMS calcd for $C_{33}H_{37}O_3Cl$ $[M+Na]^+$: 539.2324; found: 539.2329. The er was determined by HPLC using a chiral Chiralpack IC column [hexane:*i*-PrOH, 98:2]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 8.5 min, τ_{minor} = 7.8 min, (99:1 er); $[\alpha]^{D}_{20}$ = +25.5 (c = 1.0, $CHCl_3$).



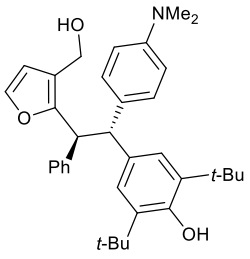
2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(3-(hydroxymethyl)furan-2-yl)-1-(naphthalen-2-yl)-2-phenylethyl)phenol 4e. Following the general procedure (reaction performed at 40 °C) product **4e** (6:1 dr in a crude reaction mixture) was isolated in 66% yield as orange oil as a single diastereomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.74– 7.76 (m, 2H), 7.73 – 7.70 (m, 2H), 7.46 – 7.37 (m, 3H), 7.30 – 7.27 (m, 2H), 7.21 (d, J = 1.8 Hz, 1H), 7.17– 7.16 (m, 2H), 7.08– 7.10 (m, 1H), 6.92 (s, 2H), 6.07 (d, J = 1.8 Hz, 1H), 4.97 (d, J = 12.0 Hz, 1H), 4.93 (s, 1H), 4.83 (d, J = 11.9 Hz, 1H), 4.37 (d, J = 12.3 Hz, 1H), 4.33 (s, 1H), 1.30 (s, 18H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 152.8, 151.9, 141.4, 141.3, 141.1, 135.3 (2C), 133.5, 132.3, 132.1, 128.7 (2C), 128.2 (2C), 127.8, 127.8, 127.6, 126.5, 126.4, 126.0, 125.5 (2C), 125.5 (2C), 119.7, 110.9, 56.5, 55.6, 49.4, 34.3 (2C), 30.4 (6C). HRMS calcd for $C_{37}H_{40}O_3$ $[M+Na]^+$: 555.2870; found: 555.2880. The er was determined by HPLC using a chiral Chiralpack IC column [hexane:*i*-PrOH, 98:2]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 10.0 min, τ_{minor} = 8.6 min, (>99:1 er); $[\alpha]^{D}_{20}$ = +22.6 (c = 1.0, $CHCl_3$).



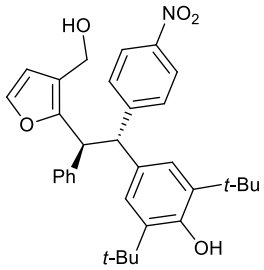
2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(3-(hydroxymethyl)furan-2-yl)-2-phenyl-1-(*m*-tolyl)ethyl)phenol 4f. Following the general procedure (reaction performed at 25 °C) product **4f** (8:1 dr in a crude reaction mixture) was isolated in 61% yield as brownish oil as a single diastereomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 1H), 7.18 (d, J = 1.9Hz, 1H), 7.17 – 7.11 (m, 5H), 7.08 – 7.00 (m, 3H), 6.79 (s, 2H), 6.17 (d, J = 1.9 Hz, 1H), 4.97 (d, J = 11.9 Hz, 1H), 4.88 (s, 1H), 4.71 (d, J = 11.9 Hz, 1H), 4.36 (d, J = 13.2 Hz, 2H), 2.33 (s, 3H), 1.27 (s, 18H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 152.9, 151.8, 142.2, 141.5, 141.1, 136.5, 135.2 (2C), 132.1, 130.6, 128.8 (2C), 128.1 (2C), 126.6, 126.3, 126.0, 125.8, 125.6 (2C), 119.5, 111.1, 56.6, 50.6, 49.7, 34.3 (2C), 30.4 (6C), 20.0. HRMS calcd for $C_{34}H_{40}O_3$ $[M+Na]^+$: 519.2870; found: 519.2876. The er was determined by HPLC using a chiral Chiralpack IC column [hexane:*i*-PrOH, 98:2]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 13.3 min, τ_{minor} = 14.4 min (99:1 er); $[\alpha]^{D}_{20}$ = +24.2 (c = 1.0, $CHCl_3$).



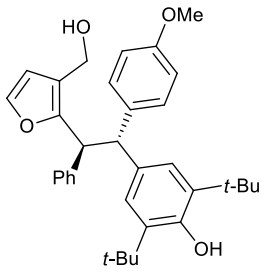
2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(3-(hydroxymethyl)furan-2-yl)-2-phenyl-1-(*p*-tolyl)ethyl)phenol 4g. Following the general procedure (reaction performed at 25 °C) product **4g** (5:1 dr in a crude reaction mixture) was isolated in 78% yield as brownish oil as a single diastereomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.25 (d, J = 1.8, 1H), 7.24 – 7.22 (m, 2H), 7.14 – 7.12 (m, 2H), 7.11 – 7.09 (m, 1H), 7.08 – 7.01 (m, 2H), 6.99 (d, J = 1.8 Hz, 1H), 6.92 (ddt, J = 7.5, 1.9, 1.0 Hz, 1H), 6.88 (s, 2H), 6.14 (d, J = 1.8 Hz, 1H), 4.89 (s, 1H), 4.73 (d, J = 11.9 Hz, 1H), 4.63 (d, J = 11.9 Hz, 1H), 4.33 (d, J = 12.3 Hz, 1H), 4.27 (d, J = 12.3 Hz, 1H), 2.25 (s, 3H), 1.30 (s, 18H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 152.9, 151.9, 144.3, 141.1 (2C), 137.8, 135.3 (2C), 132.3, 129.1 (2C), 128.8 (2C), 128.2 (2C), 127.0, 126.3, 125.5 (2C), 124.8, 119.8, 110.8, 56.5, 55.6, 53.6, 49.8, 34.3 (2C), 30.4 (6C). HRMS calcd for $C_{34}H_{40}O_3$ $[M+Na]^+$: 519.2870; found: 519.2879. The er was determined by HPLC using a chiral Chiralpack IC column [hexane:*i*-PrOH, 98:2]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 7.9 min, τ_{minor} = 7.3 min, (>99:1 er); $[\alpha]^{D}_{20}$ = +25.3 (c = 1.0, $CHCl_3$).



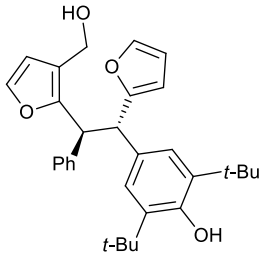
2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-1-(4-(dimethylamino)phenyl)-2-(3-(hydroxymethyl)furan-2-yl)-2-phenylethyl)phenol 4h. Following the general procedure (reaction performed at 25 °C) product **4h** (7:1 dr in a crude reaction mixture) was isolated in 50% yield as red oil as a single diastereomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.26 (d, J = 1.9 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.14 – 7.09 (m, 2H), 7.06 – 7.01 (m, 3H), 6.88 (s, 2H), 6.59 (s, 2H), 6.16 (d, J = 1.8 Hz, 1H), 4.85 (s, 1H), 4.67 (d, J = 11.9 Hz, 1H), 4.60 (d, J = 11.9 Hz, 1H), 4.35 (d, J = 12.2 Hz, 1H), 4.25 (d, J = 12.2 Hz, 1H), 2.86 (s, 6H), 1.29 (s, 18H).^{13}C NMR (176 MHz, $CDCl_3$) δ 153.3, 151.7, 141.4, 141.2, 141.0, 138.4, 135.1 (2C), 132.9, 128.9 (2C), 128.6 (2C), 128.1 (2C), 126.2, 125.4 (2C), 119.7, 112.5 (2C), 111.0, 56.5, 54.7, 50.1, 40.8 (2C), 34.3 (2C), 30.4 (6C). HRMS calcd for $C_{35}H_{43}NO_3$ $[M+Na]^+$: 548.3136; found: 548.3139. The er was determined by HPLC using a chiral Chiralpack IC column [hexane:*i*-PrOH, 98:2]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 11.0 min, τ_{minor} = 9.5 min, (99:1 er); $[\alpha]^{D}_{20}$ = +36.7 (c = 1.0, $CHCl_3$).



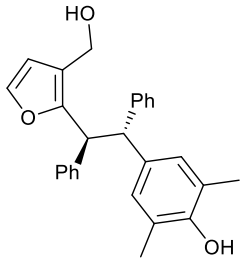
2,6-di-*tert*-butyl-4-((1R,2S)-2-(3-(hydroxymethyl)furan-2-yl)-1-(4-nitrophenyl)-2-phenylethyl)phenol 4i. Following the general procedure (reaction performed at 40 °C) product **4i** (5:1 dr in a crude reaction mixture) was isolated in 72% yield as a yellow oil as a mixture of diastereomers (4:1 dr). ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.11 – 7.96 (m, 2H), 7.48 – 7.42 (m, 2H), 7.25 – 7.12 (m, 5H), 7.11 – 7.06 (m, 1H), 6.76 (s, 2H), 6.15 (d, J = 1.9 Hz, 1H), 4.97 (s, 1H), 4.89 (d, J = 11.9 Hz, 1H), 4.74 (d, J = 11.9 Hz, 1H), 4.38 (s, 2H), 1.27 (s, 18H).^{13}C NMR (176 MHz, $CDCl_3$) Minor diastereoisomer diagnostic signals: ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.82 (s, 2H), 6.14 (d, J = 1.9 Hz, 1H), 5.09 (s, 1H), 4.17 (d, J = 12.4 Hz, 1H), 4.15 – 4.10 (m, 1H), 1.33 (s, 18H).^{13}C NMR (176 MHz, $CDCl_3$) δ 152.4, 152.2, 151.7, 146.4, 141.3, 140.8, 135.7 (2C), 128.9 (2C), 128.7, 128.5 (2C), 128.4 (2C), 126.7, 125.4 (2C), 123.5 (2C), 119.2, 111.0, 56.6, 55.4, 49.1, 34.4 (2C), 30.3 (6C). HRMS calcd for $C_{33}H_{37}NO_5$ $[M+Na]^+$: 535.2973; found: 535.26270. The er was determined by HPLC using a chiral Chiralpack IC column [hexane:*i*-PrOH, 95:5]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 19.38 min, τ_{minor} = 27.05 min, (>99:1 er); $[\alpha]^{D}_{20}$ = +44,5 (c = 1.0, $CHCl_3$).



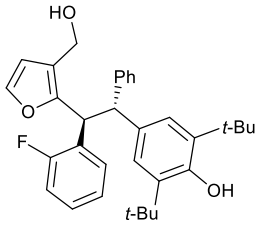
2,6-di-*tert*-butyl-4-((1R,2S)-2-(3-(hydroxymethyl)furan-2-yl)-1-(4-methoxyphenyl)-2-phenylethyl)phenol 4j. Following the general procedure (reaction performed at 40 °C) product **4j** (7:1 dr in a crude reaction mixture) was isolated in 81% yield as a yellow oil as a single diastereomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.24 (m, 1H), 7.24 – 7.20 (m, 2H), 7.17 – 7.09 (m, 4H), 7.09 – 7.01 (m, 1H), 6.84 (s, 2H), 6.74 (d, J = 8.7 Hz, 2H), 6.16 (d, J = 1.9 Hz, 1H), 4.88 (s, 1H), 4.72 (d, J = 12.2 Hz, 1H), 4.63 (d, J = 12.3 Hz, 1H), 4.35 (d, J = 12.2 Hz, 1H), 4.30 (d, J = 12.3 Hz, 1H), 3.72 (s, 3H), 1.29 (s, 18H).^{13}C NMR (176 MHz, Chloroform-*d*) δ 158.0, 153.0, 151.8, 141.2, 141.1, 136.5, 135.3 (2C), 132.7, 129.0, 128.8 (2C), 128.2 (2C), 126.3 (2C), 125.4 (2C), 119.7, 113.7 (2C), 110.9, 65.0, 55.3, 54.7, 49.9, 34.3(2C), 30.4 (6C). HRMS calcd for $C_{34}H_{40}O_4$ $[M+Na]^+$: 535.2973; found: 535.26270. The er was determined by HPLC using a chiral Chiralpack IG column [hexane:*i*-PrOH, 98:2]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 15.43 min, τ_{minor} = 14.06 min, (99:1 er); $[\alpha]^{D}_{20}$ = +27.4 (c = 1.0, $CHCl_3$).



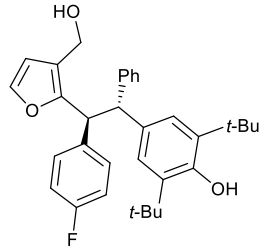
2,6-di-tert-butyl-4-((1S,2S)-1-(furan-2-yl)-2-(3-(hydroxymethyl)furan-2-yl)-2-phenylethyl)phenol 4k. Following the general procedure (reaction performed at 40 °C) product **4k** (3:1 dr in a crude reaction mixture) was isolated in 49% yield as a colorless oil as a single diastereomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.16 – 7.12 (m, 2H), 7.10 (m, 2H), 7.07 – 7.01 (m, 1H), 6.85 (s, 2H), 6.25 (d, J = 1.9 Hz, 1H), 6.21 (dd, J = 3.2, 1.8 Hz, 1H), 6.04 (dt, J = 3.2, 0.7 Hz, 1H), 4.93 (s, 1H), 4.73 (d, J = 11.5 Hz, 1H), 4.60 (d, J = 11.5 Hz, 1H), 4.46 (d, J = 12.3 Hz, 1H), 4.41 (d, J = 12.3 Hz, 1H), 1.29 (s, 18H).^{13}C NMR (176 MHz, $CDCl_3$) δ 156.5, 152.5, 152.3, 141.3, 141.2, 140.5, 135.4 (2C), 130.6, 128.8 (2C), 128.1 (2C), 126.5, 125.3 (2C), 119.9, 110.9, 110.5, 106.3, 56.6, 50.1, 49.3, 34.3 (2C), 30.3 (6C). HRMS calcd for $C_{31}H_{36}O_4$ $[M+Na]^+$: 495.2518; found: 495.2517. The er was determined by HPLC using a chiral Chiralpack IC column [hexane:*i*-PrOH, 95:5]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 5.82 min, τ_{minor} = 5.46 min, (>99:1 er); $[\alpha]^{D}_{20}$ = +57.3 (c = 1.0, $CHCl_3$).



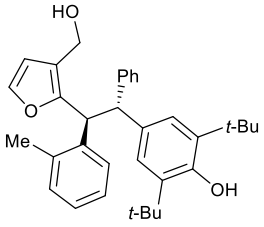
4-((1R,2S)-2-(3-(hydroxymethyl)furan-2-yl)-1,2-diphenylethyl)-2,6-dimethylphenol 4l. Following the general procedure (reaction performed at 40 °C) product **4l** (10:1 dr in a crude reaction mixture) was isolated in 66% yield as a colorless oil as a single diastereomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.23 (m, 1H), 7.21 – 7.12 (m, 6H), 7.11 – 7.05 (m, 2H), 6.85 – 6.82 (m, 2H), 6.10 (d, J = 1.9 Hz, 1H), 4.81 (d, J = 12.1 Hz, 1H), 4.73 (d, J = 12.2 Hz, 1H), 4.41 (s, 1H), 4.29 (d, J = 12.3 Hz, 1H), 4.22 (d, J = 12.3 Hz, 1H), 2.10 (s, 6H).^{13}C NMR (176 MHz, $CDCl_3$) δ 152.8, 150.5, 144.8, 141.2, 140.6, 133.2 (2C), 128.9 (2C), 128.7 (2C), 128.4 (4C), 127.9 (2C), 126.5, 126.3, 122.8, 119.8, 110.8, 56.4, 54.3, 48.7, 16.1 (2C). HRMS calcd for $C_{27}H_{26}O_3$ $[M+Na]^+$: 421.1882; found: 421.1920. The er was determined by HPLC using a chiral Chiralpack IC column [hexane:*i*-PrOH, 95:5]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 16.2 min, τ_{minor} = 15.3 min, (>99:1 er); $[\alpha]^{D}_{20}$ = +33.0 (c = 1.0, $CHCl_3$).



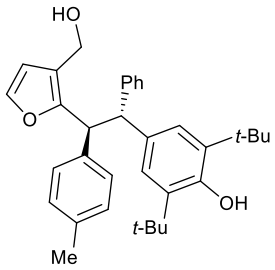
2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(2-fluorophenyl)-2-(3-(hydroxymethyl)furan-2-yl)-1-phenylethyl)phenol 4m. Following the general procedure (reaction performed at 40 °C) product **4m** (4:1 dr in a crude reaction mixture) was isolated in 78% yield as yellow oil as a single diastereomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.59 (d, J = 1.8 Hz, 1H), 7.27 (d, J = 1.9 Hz, 1H), 7.23 – 7.16 (m, 4H), 7.12 (s, 1H), 7.02 (dddd, J = 8.0, 7.1, 5.2, 1.8 Hz, 1H), 7.00 – 6.96 (m, 3H), 6.83 (s, 1H), 6.16 (d, J = 1.9 Hz, 1H), 5.14 (d, J = 12.2 Hz, 1H), 4.91 (s, 1H), 4.79 (d, J = 12.1 Hz, 1H), 4.30 (d, J = 12.4 Hz, 1H), 4.22 (d, J = 12.5 Hz, 1H), 1.31 (s, 18H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 160.1 (d, J = 244.0 Hz), 152.1, 151.4, 144.4, 141.4, 135.5 (2C), 131.8 , 130.0 (d, J = 3.7 Hz), 128.4 (2C), 128.0 (2C), 127.9, 127.86 (d, J = 21.3 Hz), 126.5, 125.2 (2C), 124.1 (d, J = 3.6 Hz), 120.5, 114.9 (d, J = 23.2 Hz), 110.90, 56.13, 54.95, 40.16, 34.37 (2C), 30.37 (6C). HRMS calcd for $C_{33}H_{37}O_3F$ $[M+Na]^+$: 523.2619; found: 523.2621. The er was determined by HPLC using a chiral Chiralpack IC column [hexane:*i*-PrOH, 98:2]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 8.6 min, τ_{minor} = 7.9 min, (>99:1 er); $[\alpha]^{D}_{20}$ = +32.9 (c = 1.0, $CHCl_3$).



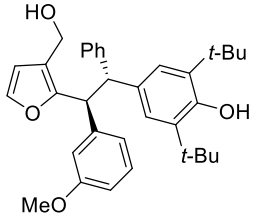
2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(4-fluorophenyl)-2-(3-(hydroxymethyl)furan-2-yl)-1-phenylethyl)phenol 4n. Following the general procedure (reaction performed at 40 °C) product **4n** (5:1 dr in a crude reaction mixture) was isolated in 70% yield as yellow oil as a single diastereomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 2H), 7.22 – 7.19 (m, 4H), 7.14 (dd, J = 8.4, 7.0 Hz, 2H), 7.11 (ddd, J = 8.5, 5.7, 2.6 Hz, 1H), 7.08 – 7.03 (m, 1H), 6.88 (s, 2H), 6.14 (d, J = 1.8 Hz, 1H), 4.90 (s, 1H), 4.78 (d, J = 12.0 Hz, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.32 (d, J = 12.3 Hz, 1H), 4.27 (d, J = 12.3 Hz, 1H), 1.30 (s, 18H).δ 7.59). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 160.0 (d, J=243 Hz) 152.8, 151.9, 144.5, 141.2, 141.1, 135.3 (2C), 132.2, 130.5, 128.8 (2C), 128.3 (d, J = 22.1 Hz, 2C), 128.1 (2C), 126.3 (d, J = 12.1 Hz, 2C), 125.5 (2C), 119.7, 110.84, 56.43, 55.48, 49.73, 34.34 (2C), 30.40 (6C). HRMS calcd for $C_{33}H_{37}O_3F$ [M+Na]+: 523.2619; found: 523.2612. The er was determined by HPLC using a chiral Chiralpack IC column [hexane:*i*-PrOH, 98:2]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 8.7 min, τ_{minor} = 7.9 min, (>99:1 er); $[\alpha]^{D}_{20}$ = +25.3 (c = 1.0, $CHCl_3$)



2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(3-(hydroxymethyl)furan-2-yl)-1-phenyl-2-(o-tolyl)ethyl)phenol 4o. Following the general procedure (reaction performed at 40 °C) product **4o** (5:1 dr in a crude reaction mixture) was isolated in 50% yield as yellow oil as a single diastereomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.59 (dd, J = 7.3, 1.0 Hz, 1H), 7.24 – 7.20 (m, 3H), 7.19 – 7.19 (m, 2H), 7.13 (s, 1H), 7.10 (s, 1H), 6.99 (m, 1H), 6.97 – 6.94 (m, 1H), 6.79 (s, 2H), 6.14 (d, J = 1.9 Hz, 1H), 4.91 (s, 1H), 4.89 (d, J = 11.9 Hz, 1H), 4.84 (d, J = 11.7 Hz, 1H), 4.28 (d, J = 3.0 Hz, 2H), 2.14 (d, J = 0.6 Hz, 3H), 1.27 (s, 18H).^{13}C NMR (176 MHz, $CDCl_3$) δ 152.0, 152.0, 144.5, 141.4, 139.1, 135.5, 135.4, 135.2, 132.1, 130.1, 128.6 (2C), 128.3, 128.3 (2C), 126.3 (2C), 126.2, 125.5 (2C), 119.8, 110.7, 56.5, 55.4, 44.3, 34.3 (2C), 30.3 (6C), 19.7. HRMS calcd for $C_{34}H_{40}O_3$ $[M+Na]^+$: 519.2870; found: 519.2879. The er was determined by HPLC using a chiral Chiralpack IC column [hexane:*i*-PrOH, 98:2]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 8.1 min, τ_{minor} = 10.4 min, (>99:1 er); $[\alpha]^{D}_{20}$ = +27.3 (c = 1.0, $CHCl_3$).



2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(3-(hydroxymethyl)furan-2-yl)-1-phenyl-2-(*p*-tolyl)ethyl)phenol 4p. Following the general procedure (reaction performed at 25 °C) product **4p** (5:1 dr in a crude reaction mixture) was isolated in 70% yield as yellow oil as a single diastereomer. ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.28 (d, J = 1.9 Hz, 1H), 7.26 – 7.23 (m, 3H), 7.18 – 7.17 (m, 2H), 7.16 – 7.14 (m, 1H), 7.03 – 6.99 (m, 2H), 6.92 (s, 2H), 6.18 (d, J = 1.9 Hz, 1H), 4.96 (s, 1H), 4.81 (d, J = 11.9 Hz, 1H), 4.67 (d, J = 12.0 Hz, 1H), 4.37 (d, J = 12.3 Hz, 1H), 4.32 (d, J = 12.3 Hz, 1H), 2.27 (s, 3H), 1.35 (s, 18H).^{13}C NMR (176 MHz, $CDCl_3$) δ 153.1, 151.9, 144.5, 141.1, 138.1, 135.8, 135.2 (2C), 132.4, 128.9 (2C), 128.6 (2C), 128.3 (2C), 128.1 (2C), 126.2, 125.6 (2C), 119.6, 110.8, 56.5, 55.5, 49.3, 34.3 (2C), 30.4 (6C), 21.0. HRMS calcd for $C_{34}H_{40}O_3$ $[M+Na]^+$: 519.2870; found: 519.2872. The er was determined by HPLC using a chiral Chiralpack IA column [hexane:*i*-PrOH, 98:2]; column temperature 30 °C; flow rate 1.0 mL/min; τ_{major} = 10.5 min, τ_{minor} = 11.6 min, (>99:1 er); $[\alpha]^{D}_{20}$ = +39.2 (c = 1.0, $CHCl_3$).



2,6-Di-tert-butyl-4-((1R,2S)-2-(3-(hydroxymethyl)furan-2-yl)-2-(3-methoxyphenyl)-1-phenylethyl)phenol 4q. Following the general procedure (reaction performed at 40 °C) product **4q** (1.6:1 dr in a crude reaction mixture) was isolated in 77% (48%/29%) yield as orange oil. **Major diastereomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.16 (m, 5H), 7.13–7.02 (m, 2H), 6.91–6.81 (m, 3H), 6.71 (t, *J* = 2.2 Hz, 1H), 6.60 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.14 (d, *J* = 2.0 Hz, 1H), 4.92 (s, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.29 (q, *J* = 12.0 Hz, 2H), 3.65 (s, 3H), 1.29 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 152.5, 144.1, 142.5, 141.1, 135.2, 132.2, 129.0, 128.2 (2C), 127.9 (2C), 126.2, 125.4 (2C), 121.1, 119.7, 114.23, 112.1, 110.7, 56.3, 55.4, 55.1, 49.6, 34.2 (2C), 30.3 (6C). HRMS calcd for $C_{34}H_{40}O_4$ $[M+Na]^+$: 535.2819; found: 535.2815. The er was determined by HPLC using a chiral Chiralpack IF column [hexane:*i*-PrOH, 95:5]; column temperature 35 °C; flow rate 1.0 mL/min; t_{minor}= 9.28 min, t_{major} = 7.67 min (>99:1 er). $[\alpha]_D^{20}$= +47.4 (c = 1.0, $CHCl_3$). **Minor diastereomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 2.0 Hz, 1H), 7.24–7.10 (m, 7H), 6.96 (s, 2H), 6.50 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.17 (d, *J* = 2.0 Hz, 1H), 5.21 (d, *J* = 12.0 Hz, 1H), 4.94 (s, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.38–4.18 (m, 2H), 3.72 (s, 3H), 1.32 (s, 18H). 13C NMR (100 MHz, $CDCl_3$) δ 158.8, 152.0, 150.2, 144.1, 141.6, 140.2, 135.4, 132.6, 131.5, 128.3(2C), 127.9(2C), 126.4, 125.3(2C), 120.9, 115.9,

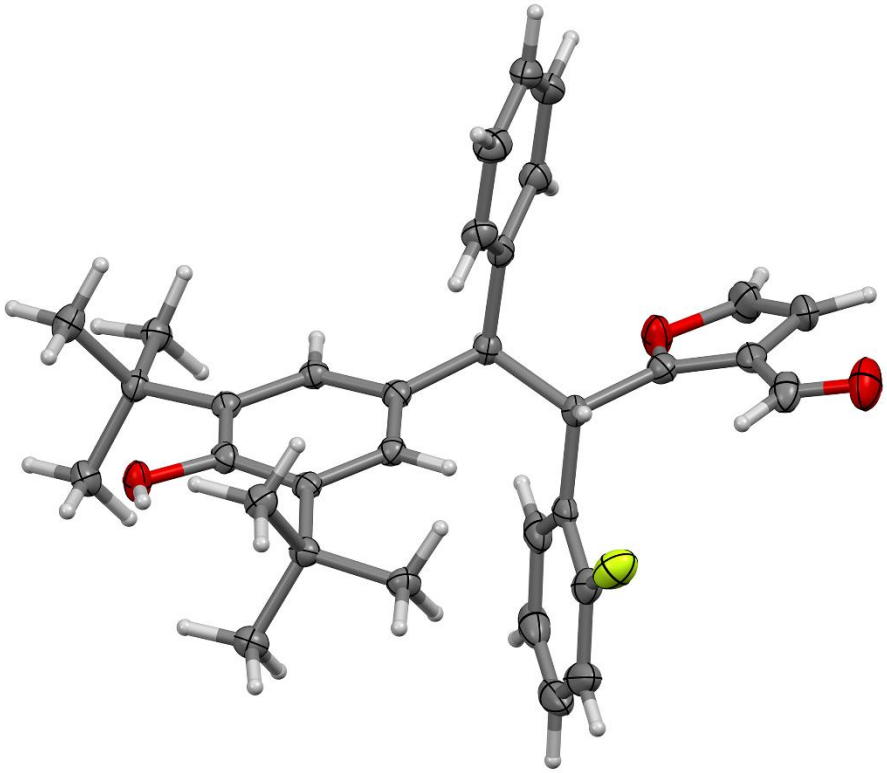
115.4, 114.2, 110.8, 56.2, 55.5, 55.4, 47.5, 34.3(2C), 30.3(6C). The er was determined by HPLC using a chiral Chiralpack IC column [hexane:*i*-PrOH, 95:5]; column temperature 35 °C; flow rate 1.0 mL/min; t_{minor}= 7.71 min, t_{major} = 6.90 min (>99:1 er). $[\alpha]_D^{20}$= -35.4 (c= 0.5, $CHCl_3$).

2.2 Procedure for dearomative functionalization of 2-benzyl-3-furfural 1a in a gram scale

To the solution of 2-benzyl-3-furfural **1a** (1 g, 5.4 mmol, 1 equiv) in cyclohexane (11 mL, 0.5 M) *para*-quinone methide **2a** (1.9 g, 6.5 mmol, 1.2 equiv) was added followed by the addition of the catalyst (325 mg, 1 mmol, 0.2 equiv). The reaction mixture was stirred for 48 h at 25°C. After full conversion of the starting material **1a** (as confirmed by ^{1}H NMR of a crude reaction mixture, 6:1 dr), MeOH (2 mL) was added, the reaction mixture was cooled to 0 °C and $NaBH_4$ (184 mg, 5.4 mmol, 1 equiv) was slowly added in portions. After 30 min. the reaction mixture was warmed up to rt and quenched with 5 mL of 1M $HCl_{(aq.)}$. Phases were separated, the aqueous phase was washed with diethyl ether (2 x 10 mL), and the combined organic phases were dried over anhydrous Na_2SO4, filtered and concentrated *in vacuo*. The residue was subjected to flash column chromatography on silica gel (eluent: hexanes/ethyl acetate 4:1) to obtain pure product **4a** in 78 % yield as single diastereomer. NMR and UPC^2 data were in accordance with previously obtained results.

3. Crystal and X-ray data for 2,6-di-*tert*-butyl-4-((1*R*,2*S*)-2-(2-fluorophenyl)-2-(3-(hydroxymethyl)furan-2-yl)-1-phenylethyl)phenol (4m)

The single crystal X-ray diffraction study at 100 K revealed that compound 2,6-di-*tert*-butyl-4-(2-(2-fluorophenyl)-2-(3-(hydroxymethyl)furan-2-yl)-1-phenylethyl)phenol **4m** ($C_{33}H_{35}FO_3$) crystallizes in the non-centrosymmetric monoclinic space group $P2_1$ (Z = 4) and the crystal structure consists of one crystallographically independent formula unit in the unit cell.



The molecular structure of the compound **4m** at 100 K, showing 50% probability displacement ellipsoids. Hydrogen atoms are drawn with an arbitrary radius.

Single crystal X-ray diffraction data were collected at 100 K by the ω-scan technique using a RIGAKU XtaLAB Synergy, Dualflex, Pilatus 300K diffractometer[4] with PhotonJet micro-focus X-ray Source Cu-Kα (λ = 1.54184 Å). Data collection, cell refinement, data reduction and absorption correction were performed using CrysAlis PRO software.[4] The crystal structure was solved by using direct methods with the SHELXT 2018/2 program.[5] Atomic scattering factors were taken from the International Tables for X-ray Crystallography. Positional parameters of non-H-atoms were refined by a full-matrix least-squares method on F^2 with anisotropic

thermal parameters by using the SHELXL 2018/3 program.[6] All hydrogen atoms were found from the difference Fourier maps and for further calculations they were positioned geometrically in calculated positions (C–H = 0.95–1.00 Å) and constrained to ride on their parent atoms with isotropic displacement parameters set to 1.2-1.5 times the U_{eq} of the parent atom. Hydrogen atom of hydroxyl group was refined freely.

4m: Formula $C_{33}H_{35}FO_3$, monoclinic, space group $P2_1$, Z = 4, unit cell constants a = 9.2914(1), b = 14.7113(2), c = 9.9029(1) Å, β = 94.550(1)°, V = 1349.35(3) Å^3. The integration of the data yielded a total of 33987 reflections with θ angles in the range of 4.47 to 78.83°, of which 5050 were independent (R_{int} = 2.98%), and 4950 were greater than 2σ(F^2). The final anisotropic full-matrix least-squares refinement on F^2 with 344 parameters converged at R_1 = 3.13% and wR_2 = 9.31% for all data. The largest peak in the final difference electron density synthesis was 0.276 e Å^{-3} and the largest hole was -0.157 e Å^{-3}. The goodness-of-fit was 1.079. The absolute configuration was unambiguously determined from anomalous scattering, by calculating the *x* Flack parameter[7] of 0.02(4) using 2299 quotients.

CCDC 1963935 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

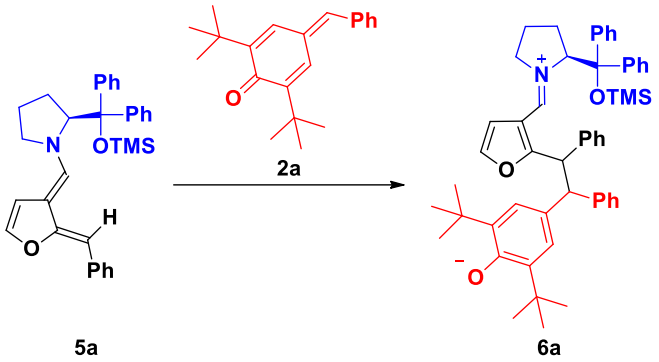
4. Rigaku OD. CrysAlis PRO. Rigaku Oxford Diffraction Ltd, Yarnton, Oxfordshire, England, 2019.

5. G. M. Sheldrick, SHELXT - integrated space-group and crystal-structure determination, *Acta Cryst.* 2015, **A71**, 3-8.

6. G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Cryst.* 2015, **C71**, 3-8.

7. S. Parsons, H.D. Flack, T. Wagner, Use of intensity quotients and differences in absolute structure refinement, *Acta Cryst.* 2013, **B69**, 249-259.

4. Methodology and computational data



Stereoselective addition Michael dienamine **5a** to dienone **2a**

The calculations were performer with Gaussian 09 rev.A software.[8] Density functional theory (DFT) hybrid functional M06-2X with the 6-31G(d,p) basis set was used for optimization of the geometry of dienamine **5a** and quinone derivative **2a** in gas phase.[9,10] Then, potential energy scan (PES) relative to the distance between reacting carbon atoms was applied. The data was utilized as inputs (reactants) for computing transition state structures. The transition states for the addition of dienamine **5a** to quinone derivative **2a** were located in the gas phase. Obtained transition state had one imaginary frequency, which indicated the path of reaction in further calculations. In order to determine the correctness of calculations, the transition state intrinsic reaction coordinate (IRC) analysis was used.[11] Resultant substrates and products geometries were re-optimized. Corresponding energies of substrates, products and transition states were re-calculated using M06-2X/6-31G+(d,p) PCM(cyclohexane) (Table 1). The output files are available online under DOI: 10.5281/zenodo.3923615.

Table 1 Calculated energies for reactants (RC), transition states (TS) and products (RC) for the evaluated approaches. Values shown in kcal/mol.

	R,S		***S,S***	
	1	2	1	2
RC	-1647448	-1647443	-1647444	-1647442
TS	-1647441	-1647430	-1647439	-1647430
PC	-1647453	-1647440	-1647455	-1647438

Table 2 Energy differences for reactants (RC), transition states (TS) and products (RC)) for the evaluated approaches in regard to the lowest RC energy. Values shown in kcal/mol.

	R,S		***S,S***	
	1	2	1	2
RC	0.0	5.5	4.0	6.0
TS	7.20	18.3	9.4	18.5
PC	-5.0	8.7	-7.0	10.8

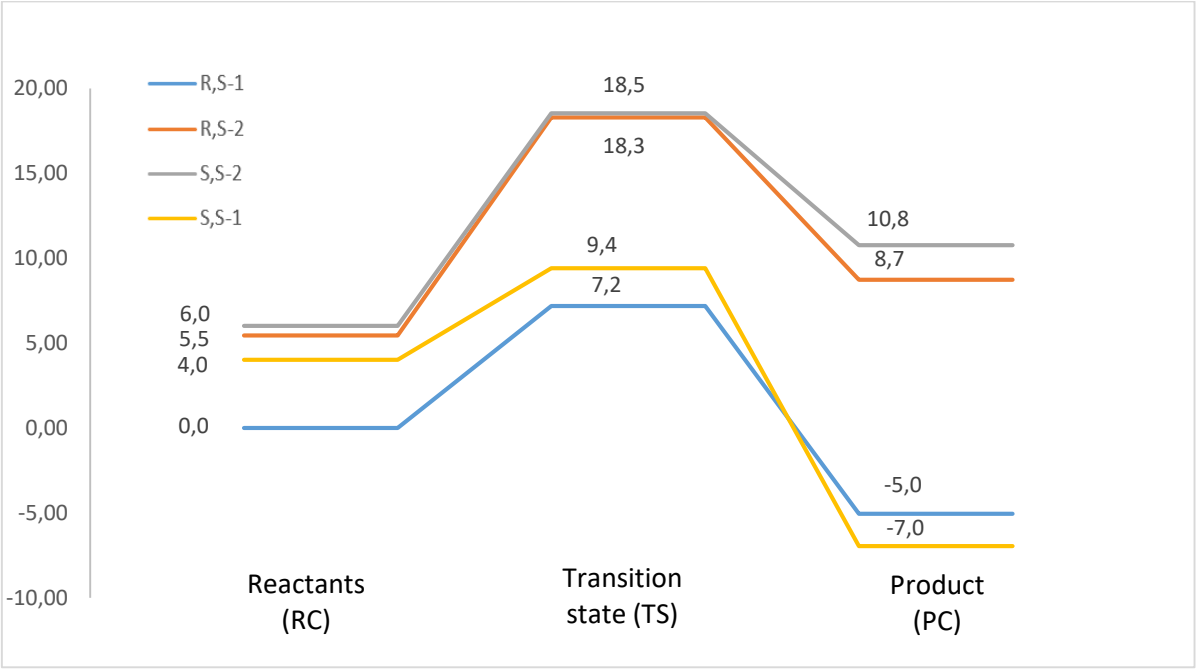


Figure 1 Reaction progress for the evaluated approaches. Values shown in kcal/mol.

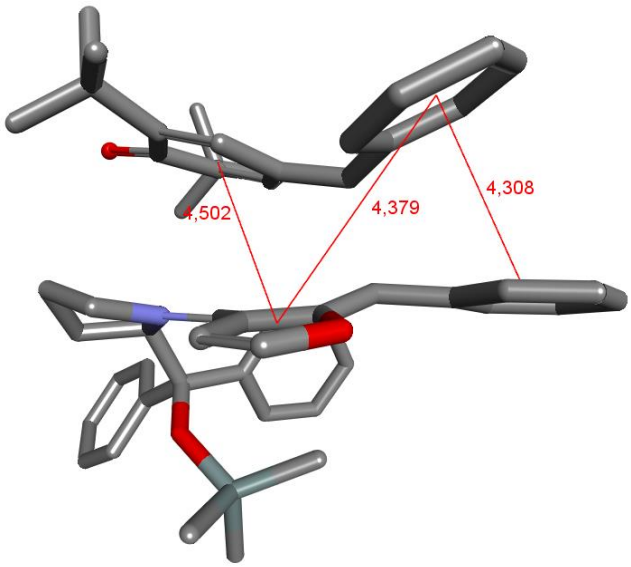


Figure 2. Geometry of the Transition state calculated for pro-*R,S*-TS1. Distances between centroids of aromatic rings indicated with the red line. Values in Ångstroms.

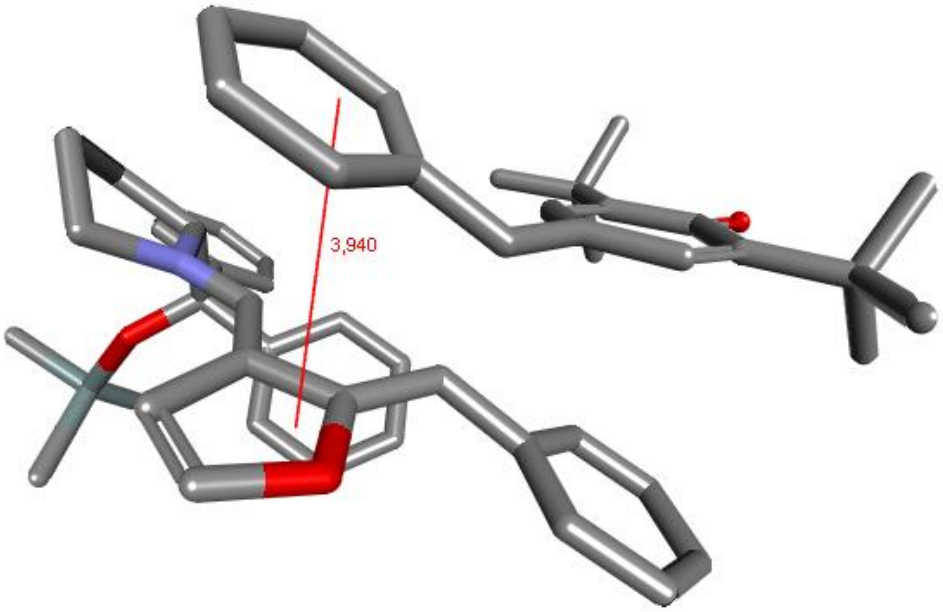


Figure 3. Geometry of the Transition state calculated for pro-*R,S*-TS2. Distances between centroids of aromatic rings indicated with the red line. Values in Ångstroms.

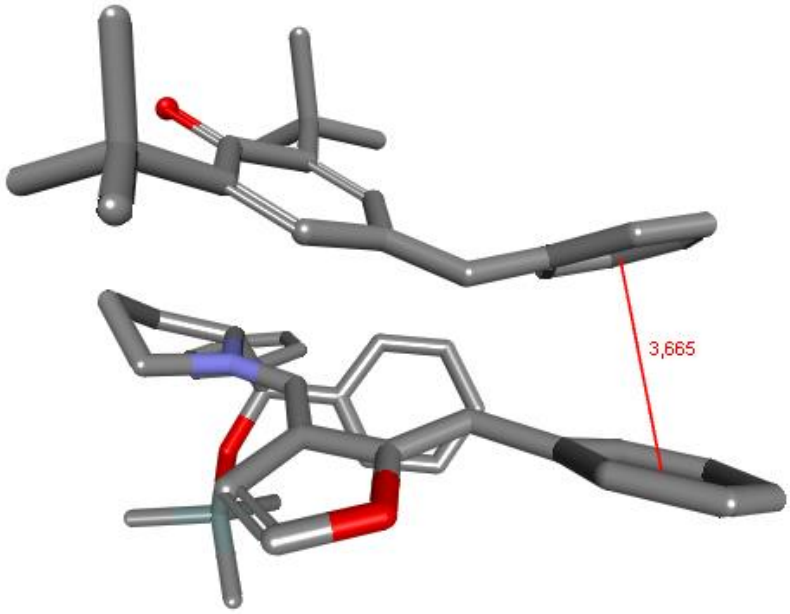


Figure 4. Geometry of the Transition state calculated for pro-*S,S*-TS1. Distances between centroids of aromatic rings indicated with the red line. Values in Ångstroms.

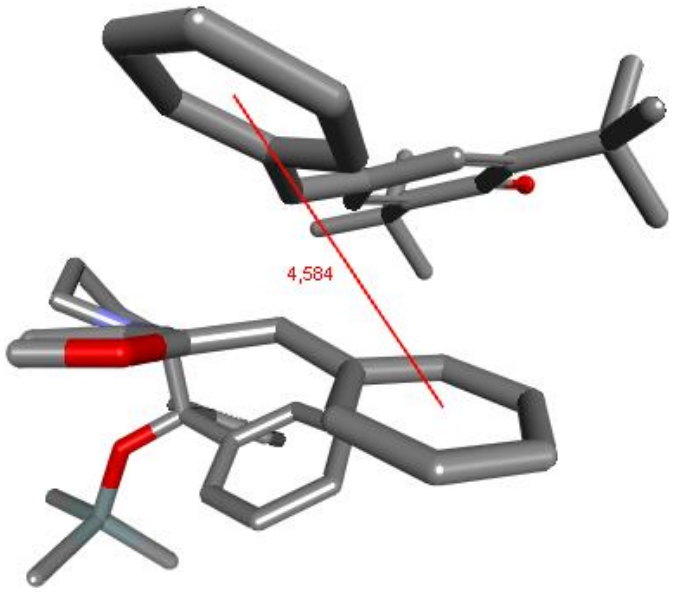


Figure 5. Geometry of the Transition state calculated for pro-*S,S*-TS2. Distances between centroids of aromatic rings indicated with the red line. Values in Ångstroms.

8. M. J. Frisch, G.W. Trucks, H. B. Schlegel, G. E. Scuseria, M.A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, M. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, revision A.01; Gaussian, Inc.: Wallingford, CT, 2009.

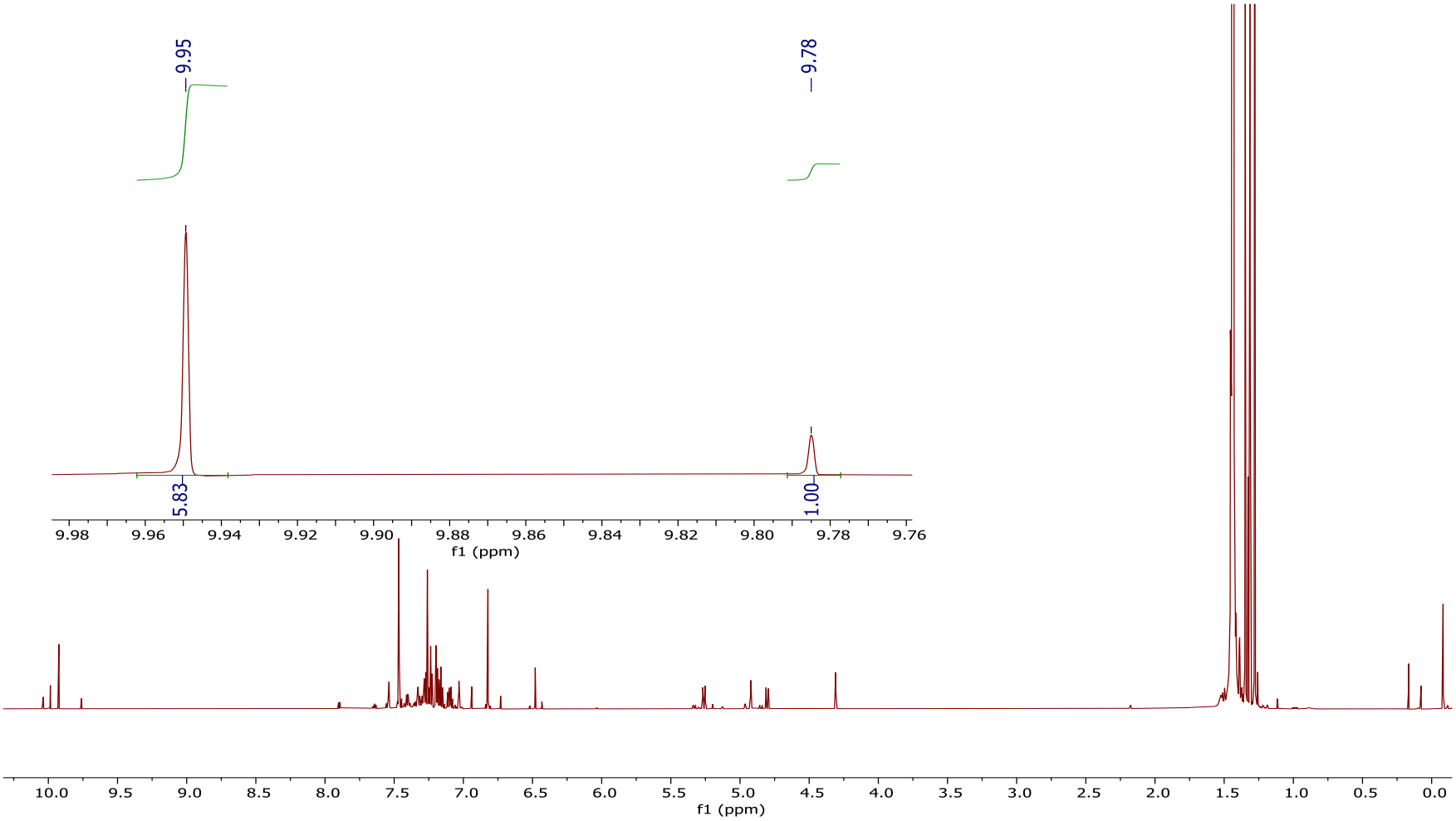
9. (a) Y. Zhao and D. G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theor. Chem. Acc.* 2008, **120**, 215. (b) Y. Zhao and D. G. Truhlar, Density functionals with broad applicability in chemistry, *Acc. Chem. Res.* 2008, **41**, 157.

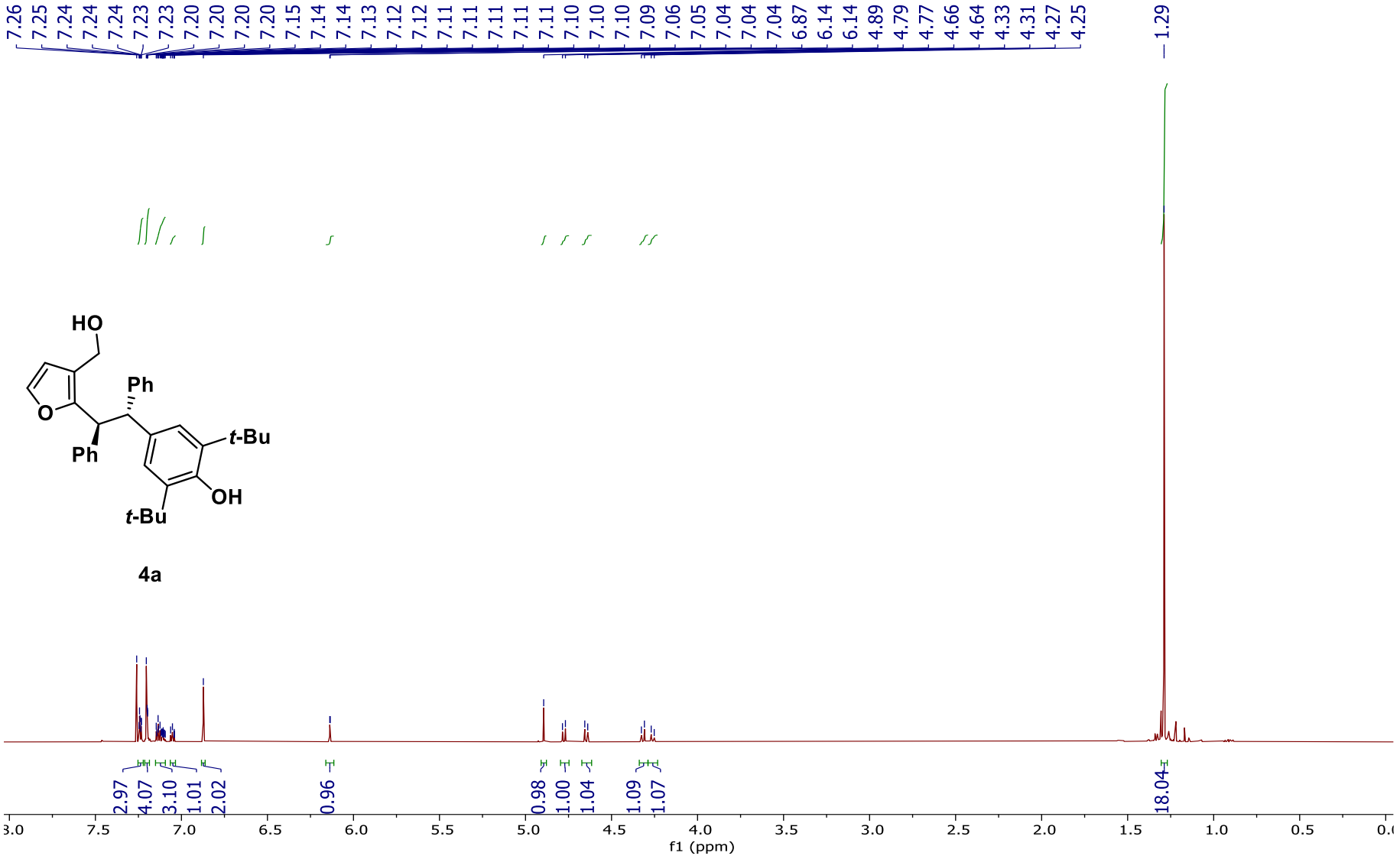
10. (a) W. J. Hehre, R. Ditchfield and J. A. Pople, J., Self—Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules, *Chem. Phys.* 1972, **56**, 2257. (b) P. C. Hariharan and J. A. Pople, The influence of polarization functions on molecular orbital hydrogenation energies, *Theor. Chim. Acta* 1973, **28**, 213.

11. A. Ratkiewicz, L. K. Huynh and T. N. Troung, Performance of first-principles-based reaction class transition state theory, *J. Phys. Chem. B* 2016, **120** , 1871.

5. NMR data

Spectrum of the crude reaction mixture for 3a

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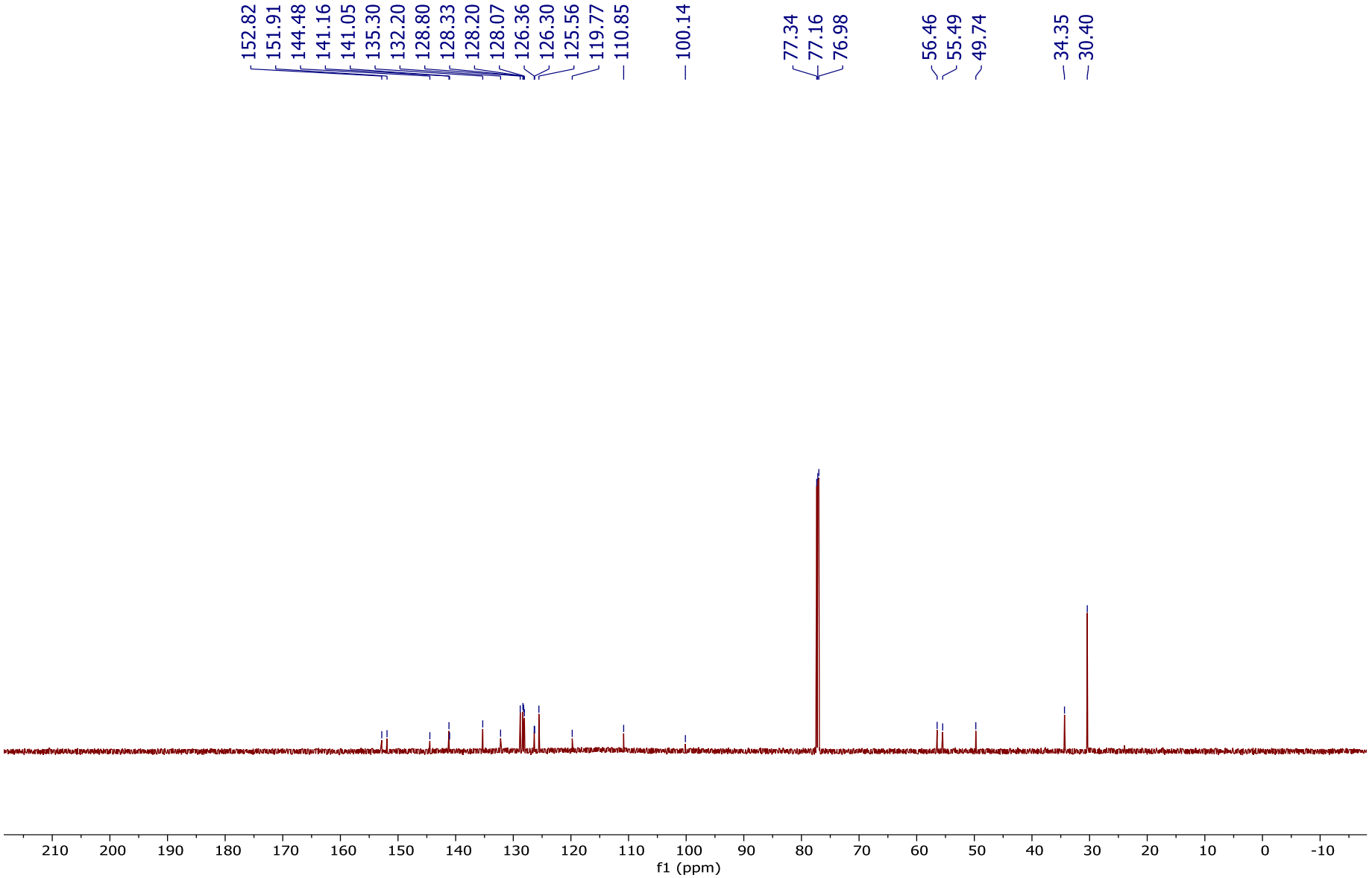
4a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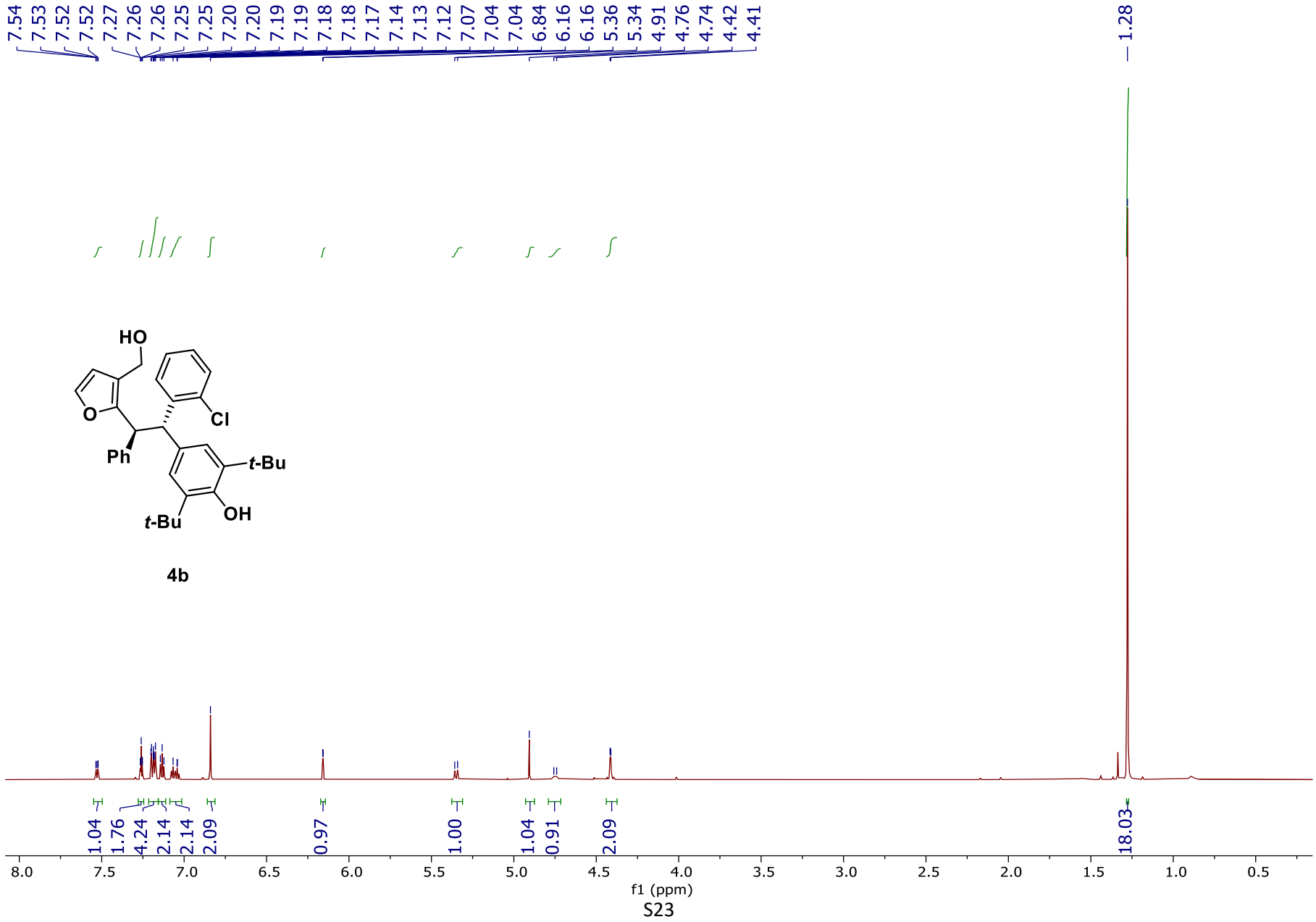
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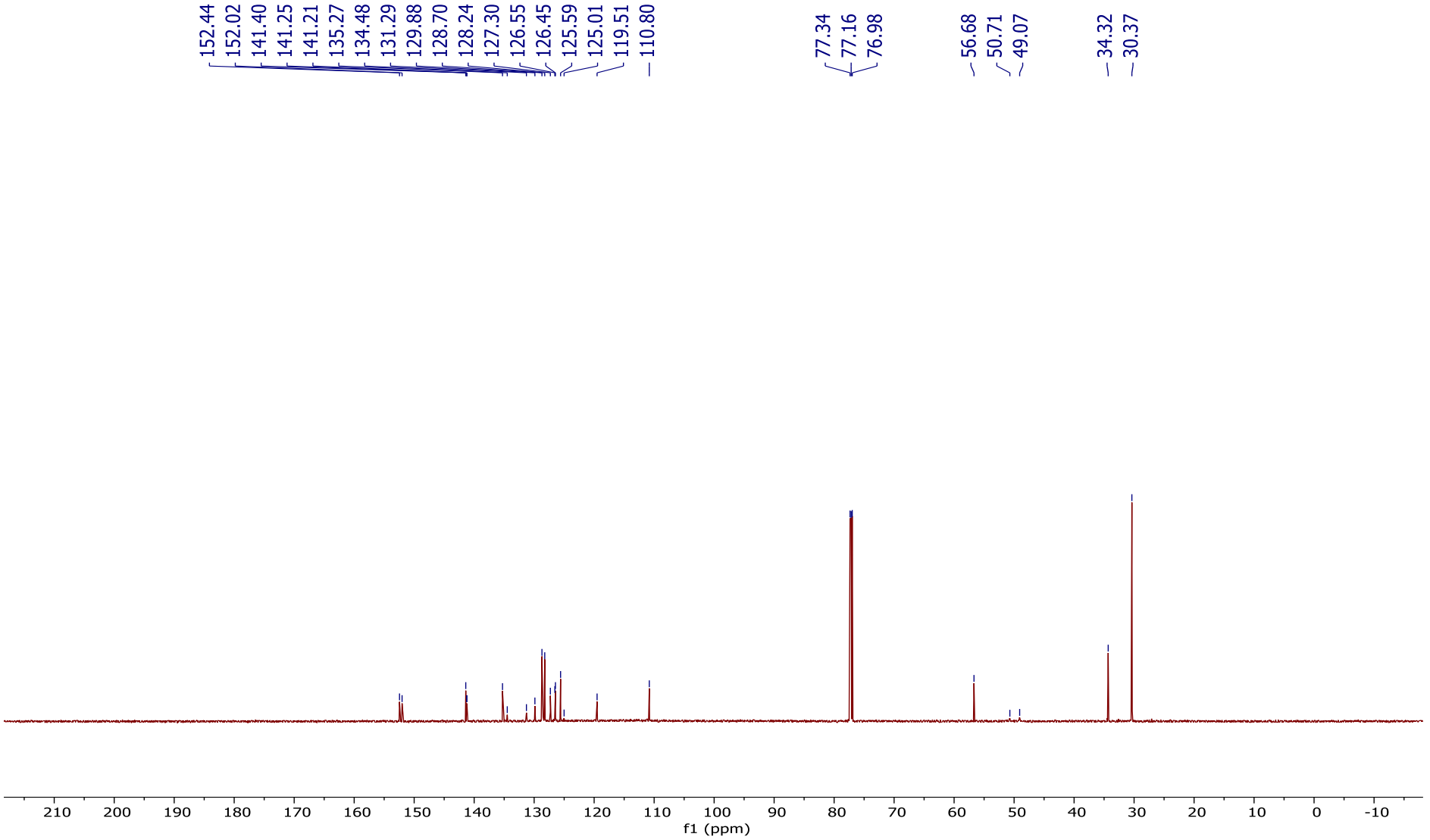
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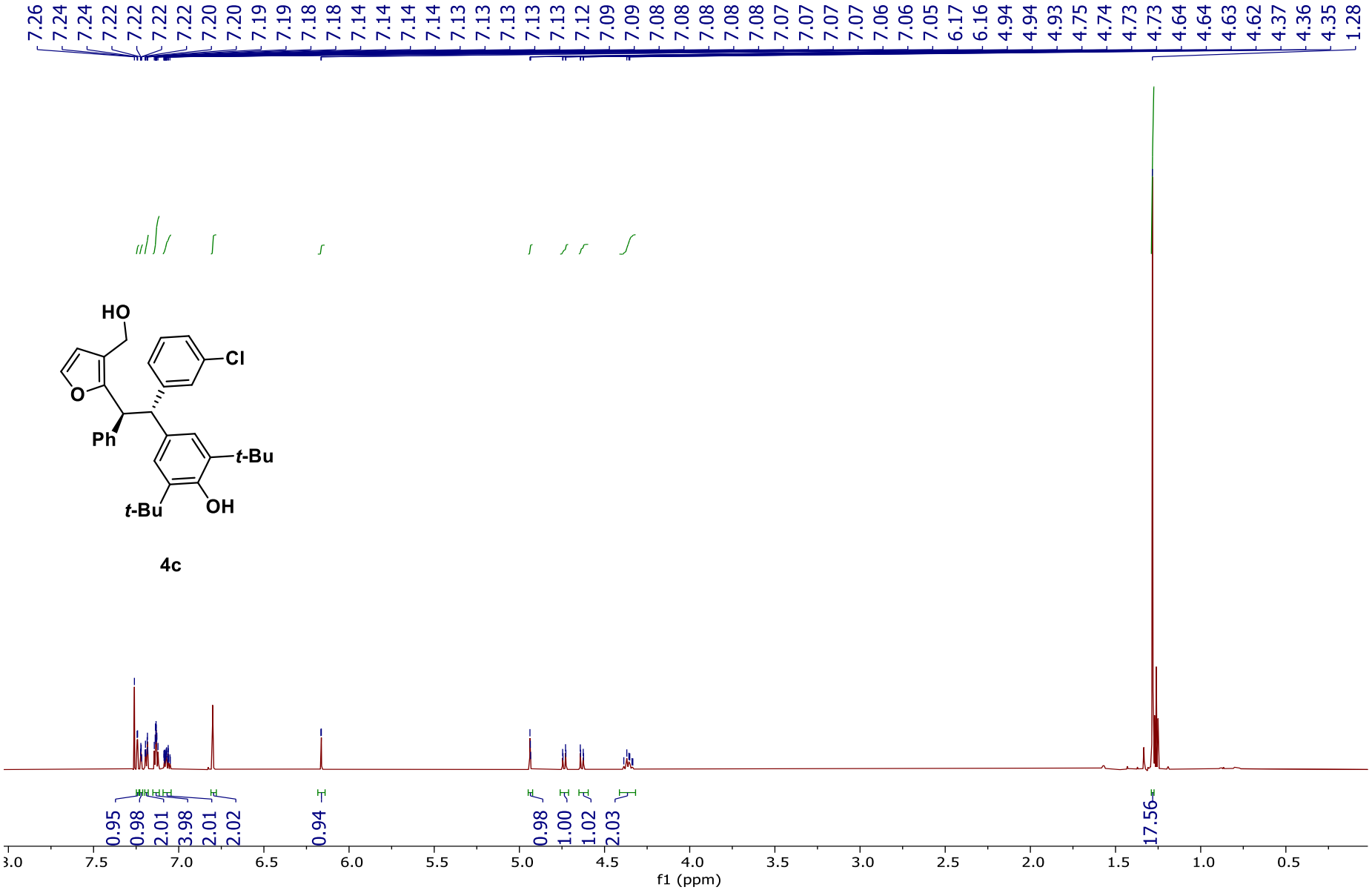
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Ph
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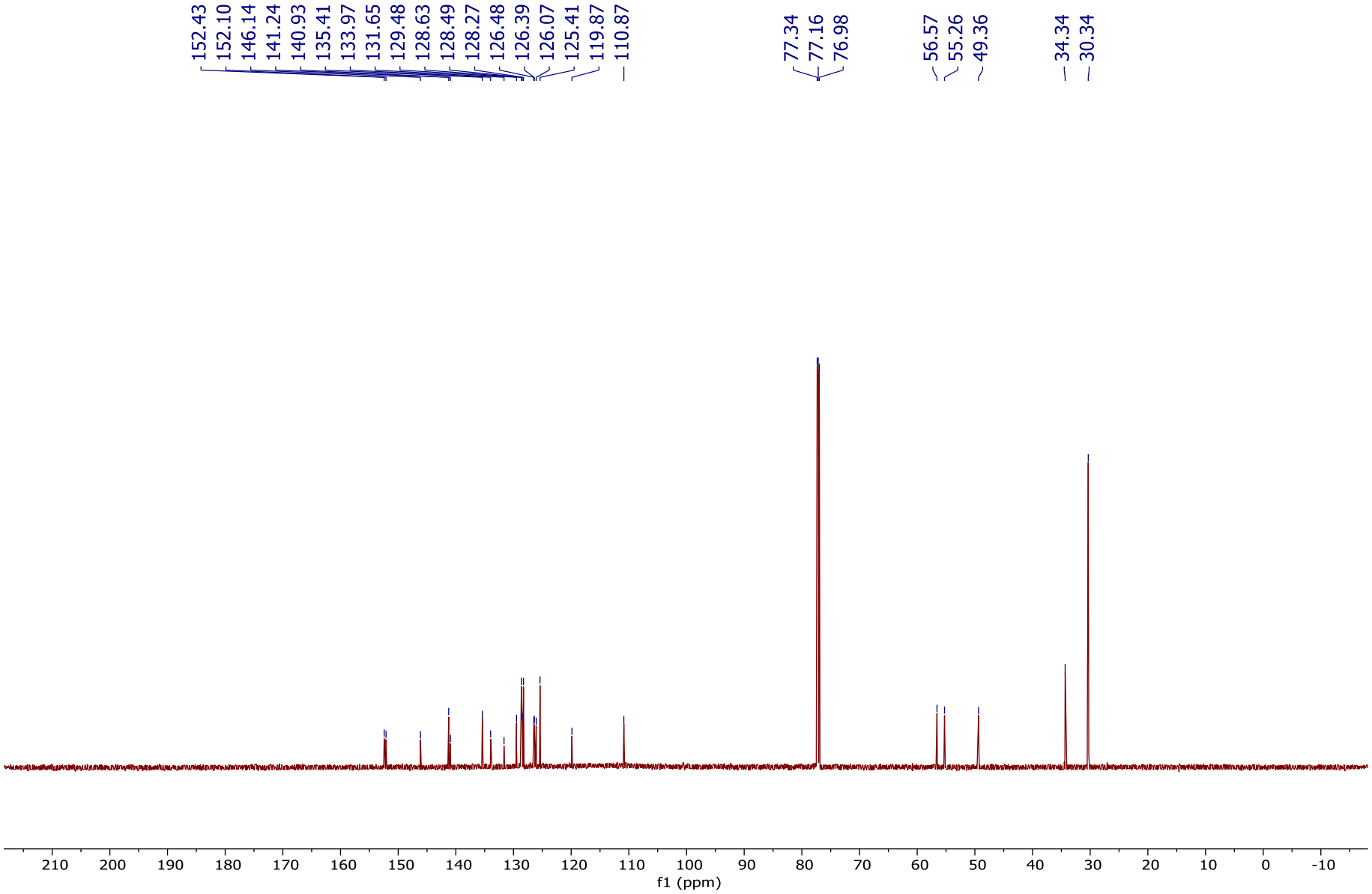
4c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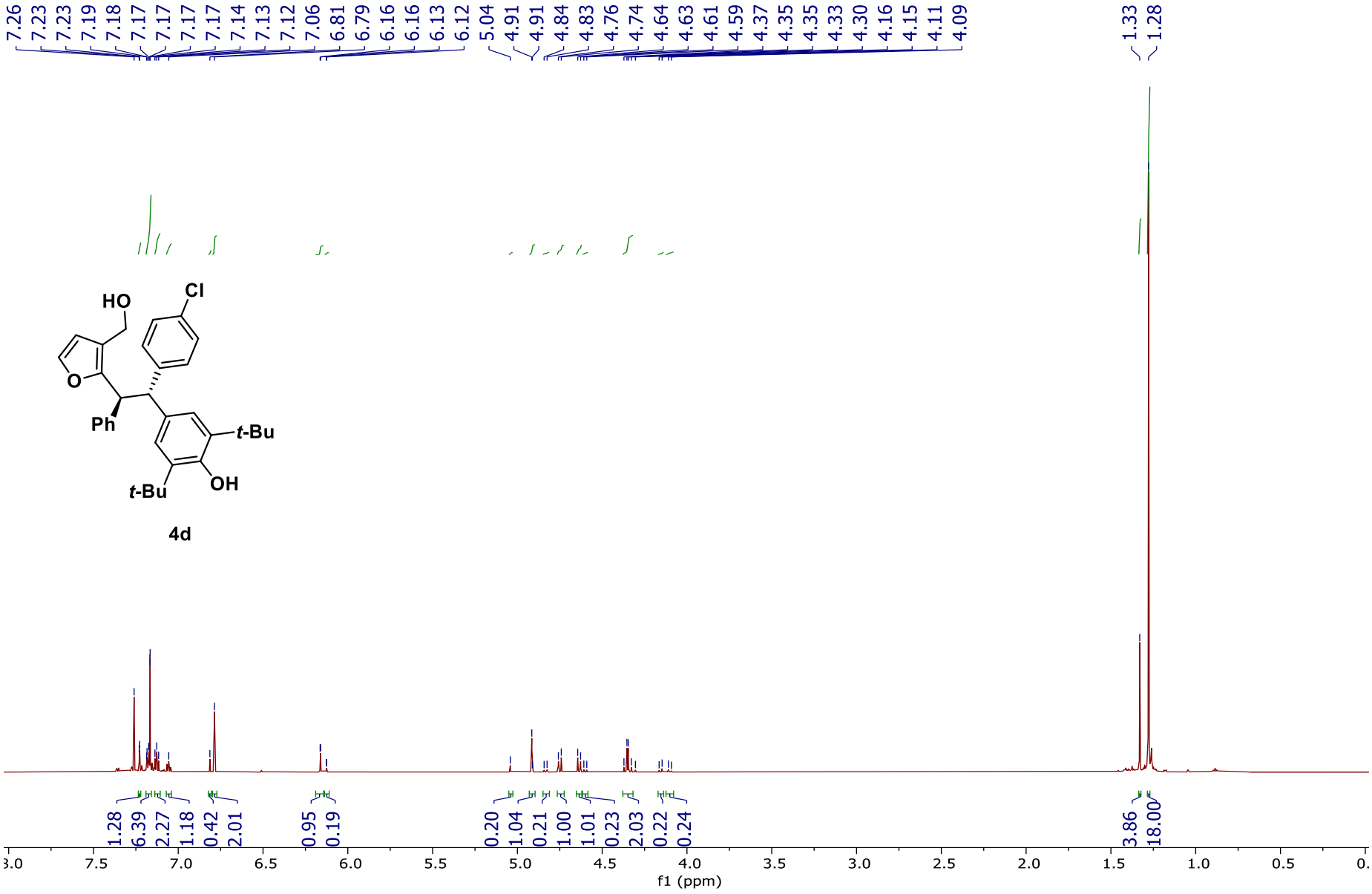
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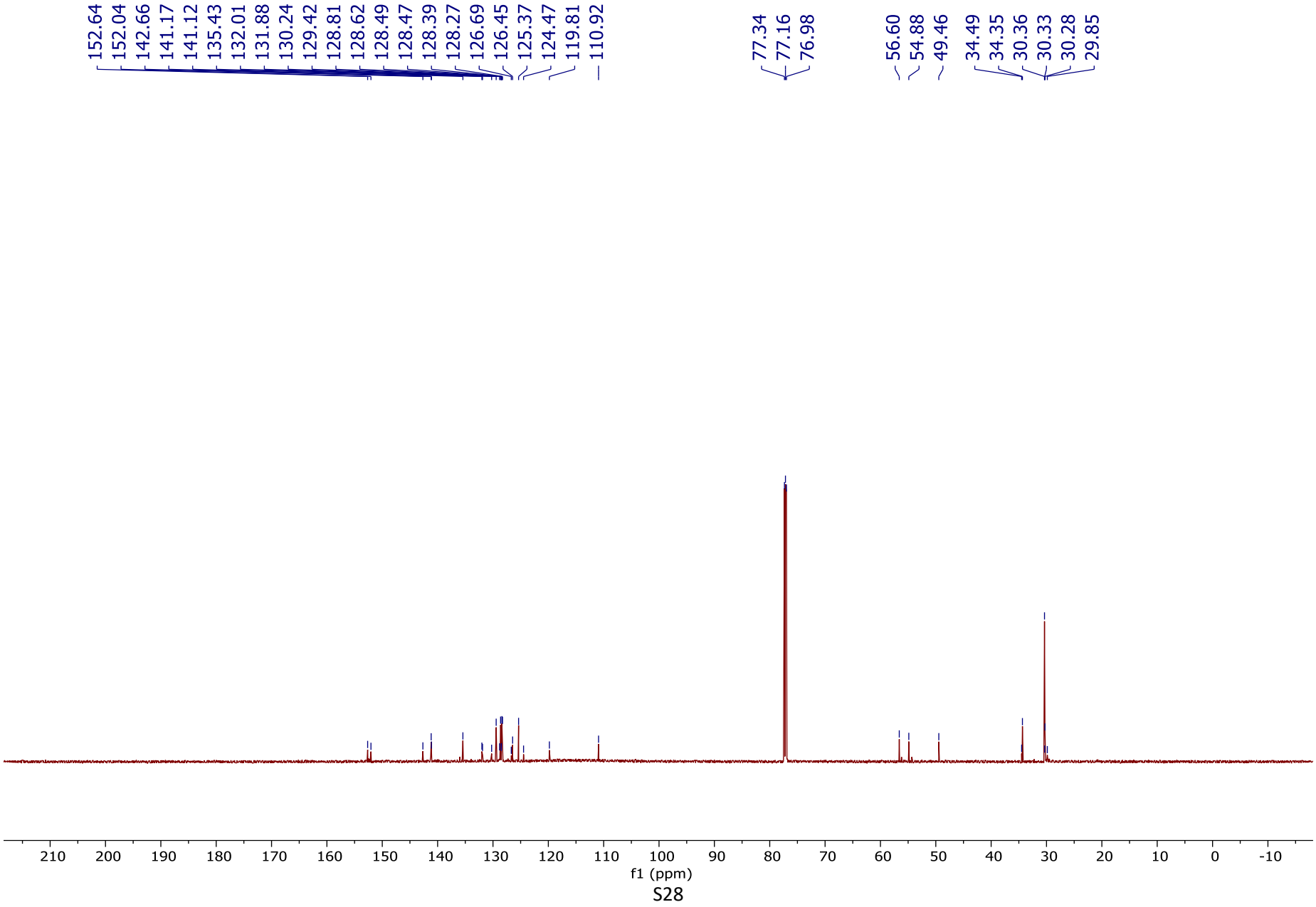
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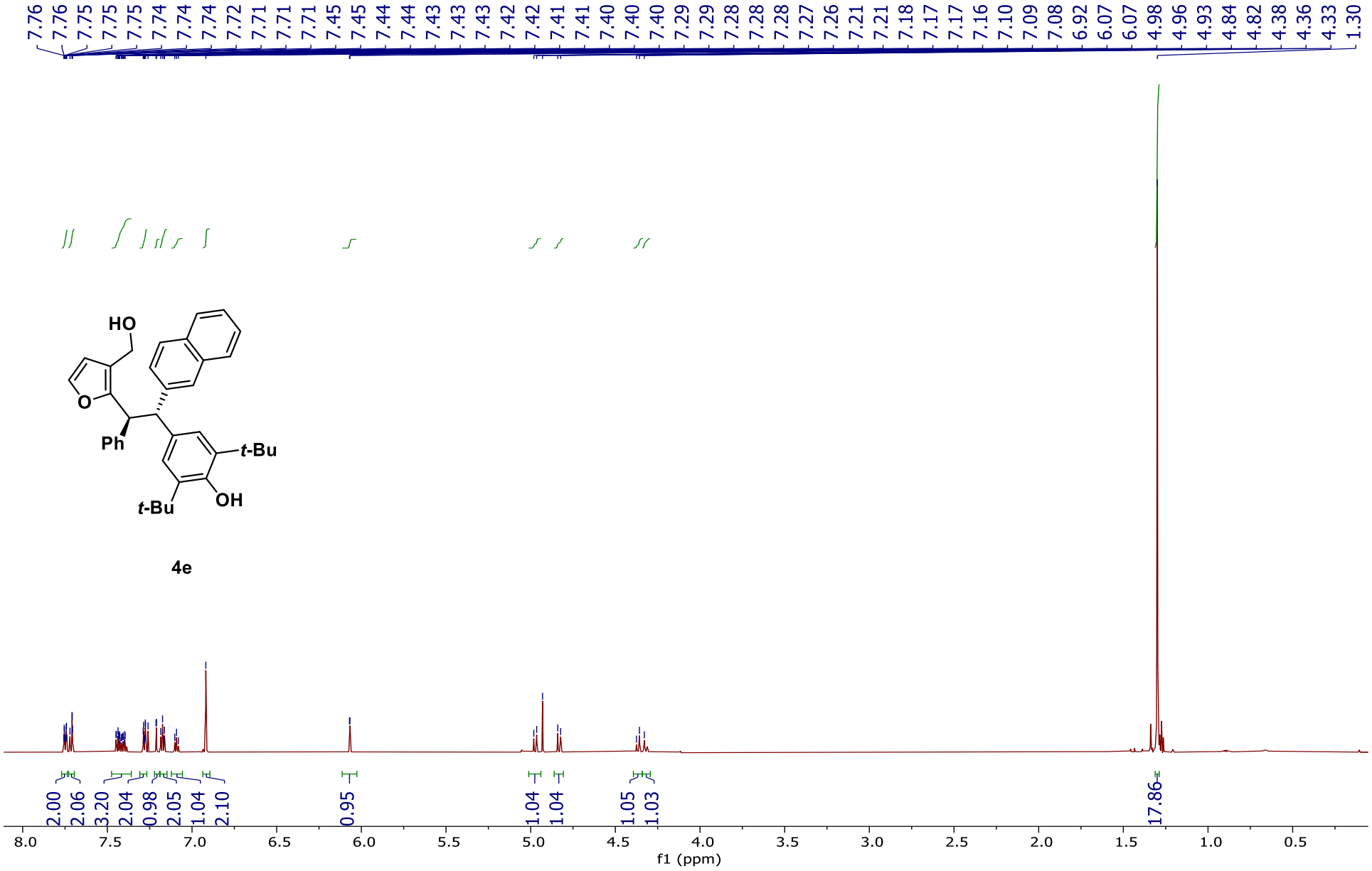
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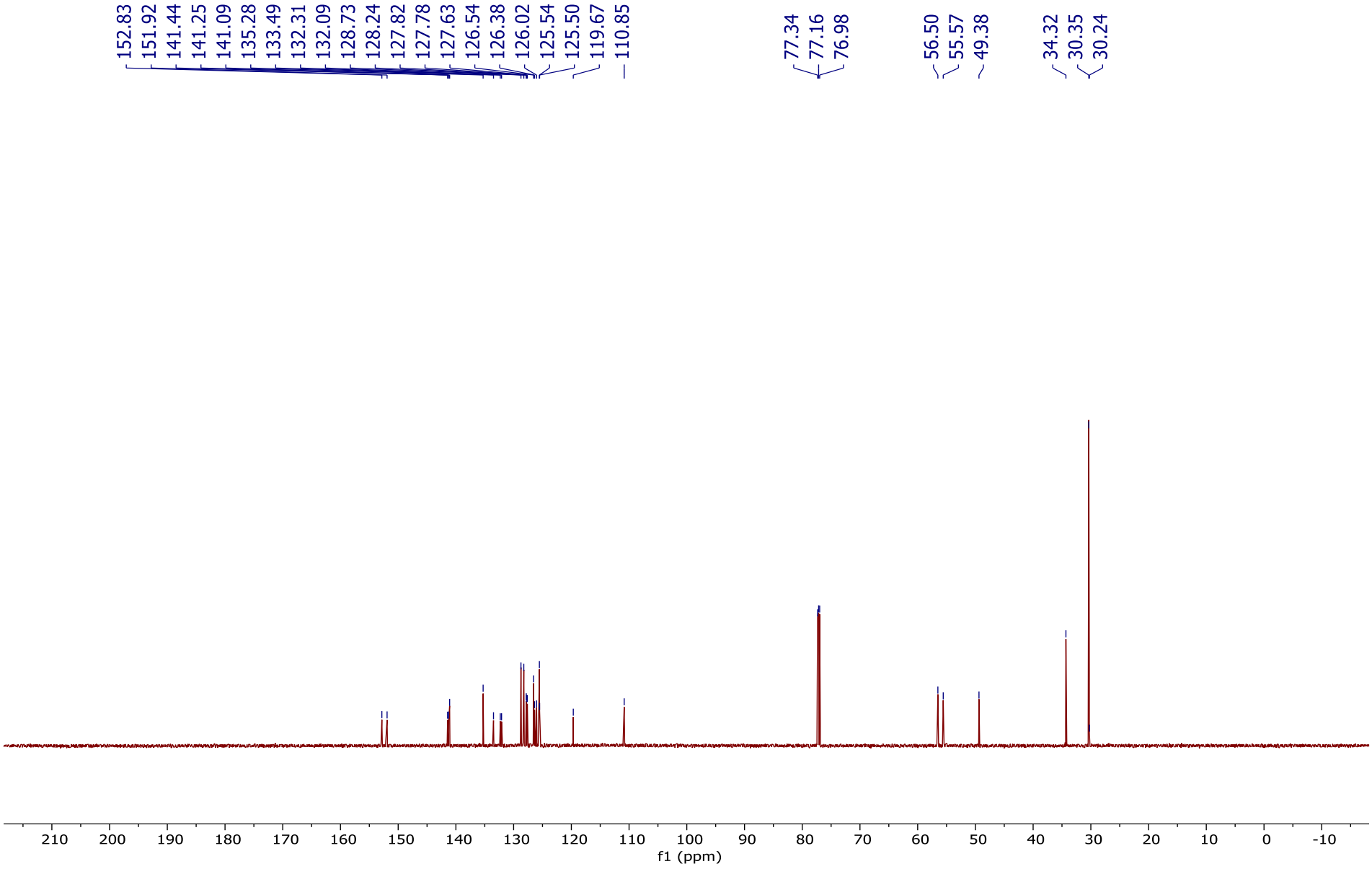
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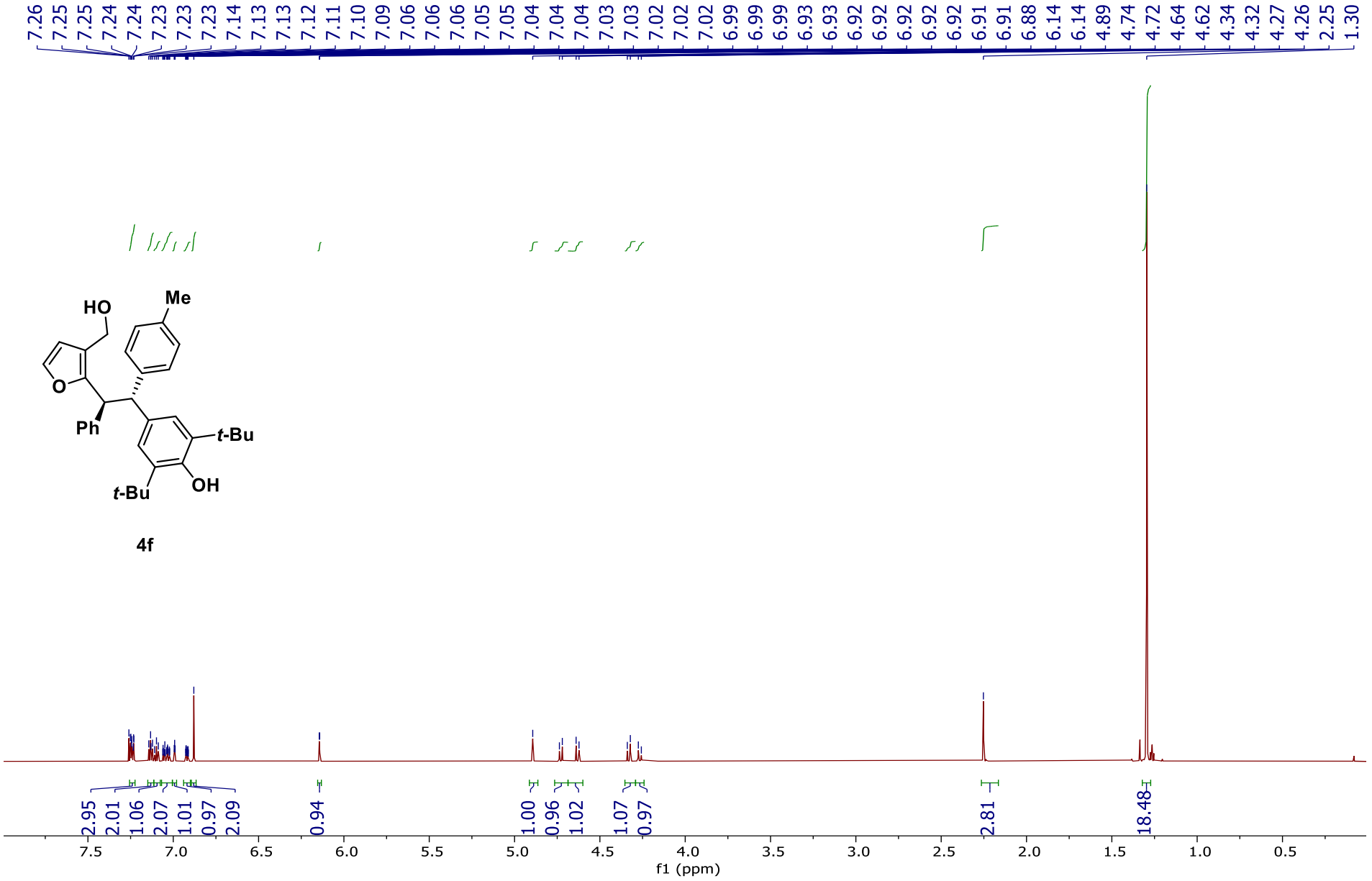
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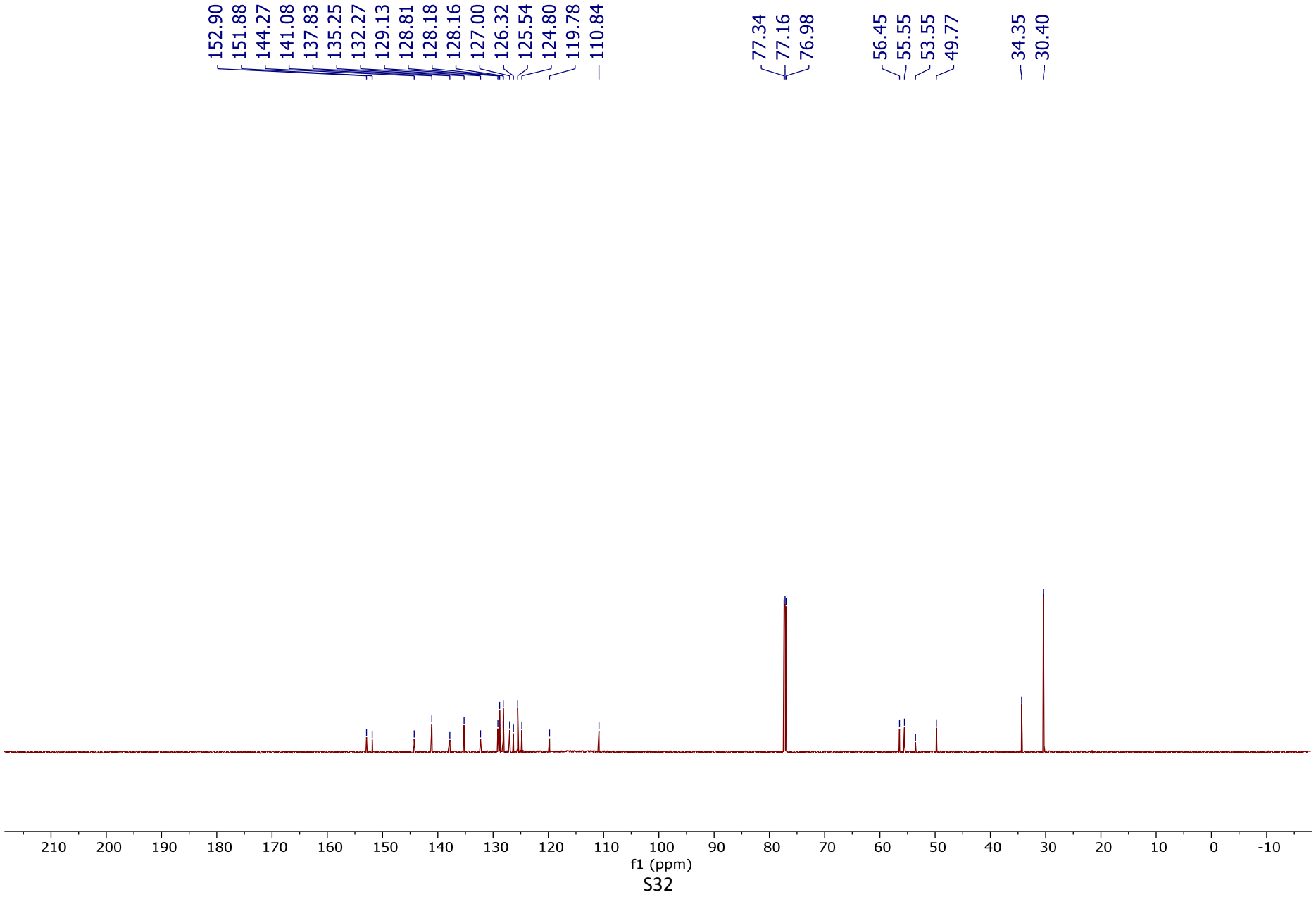
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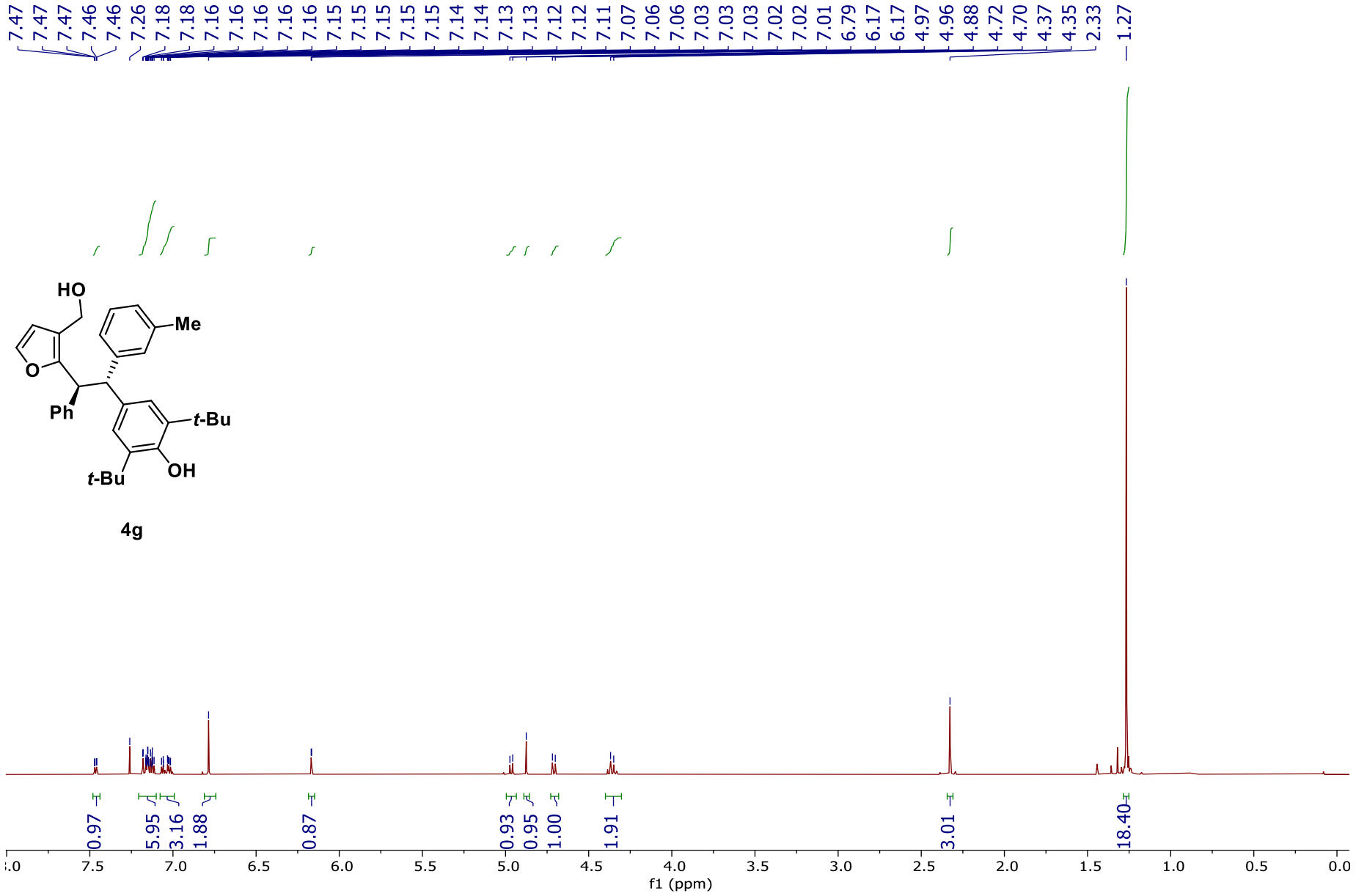
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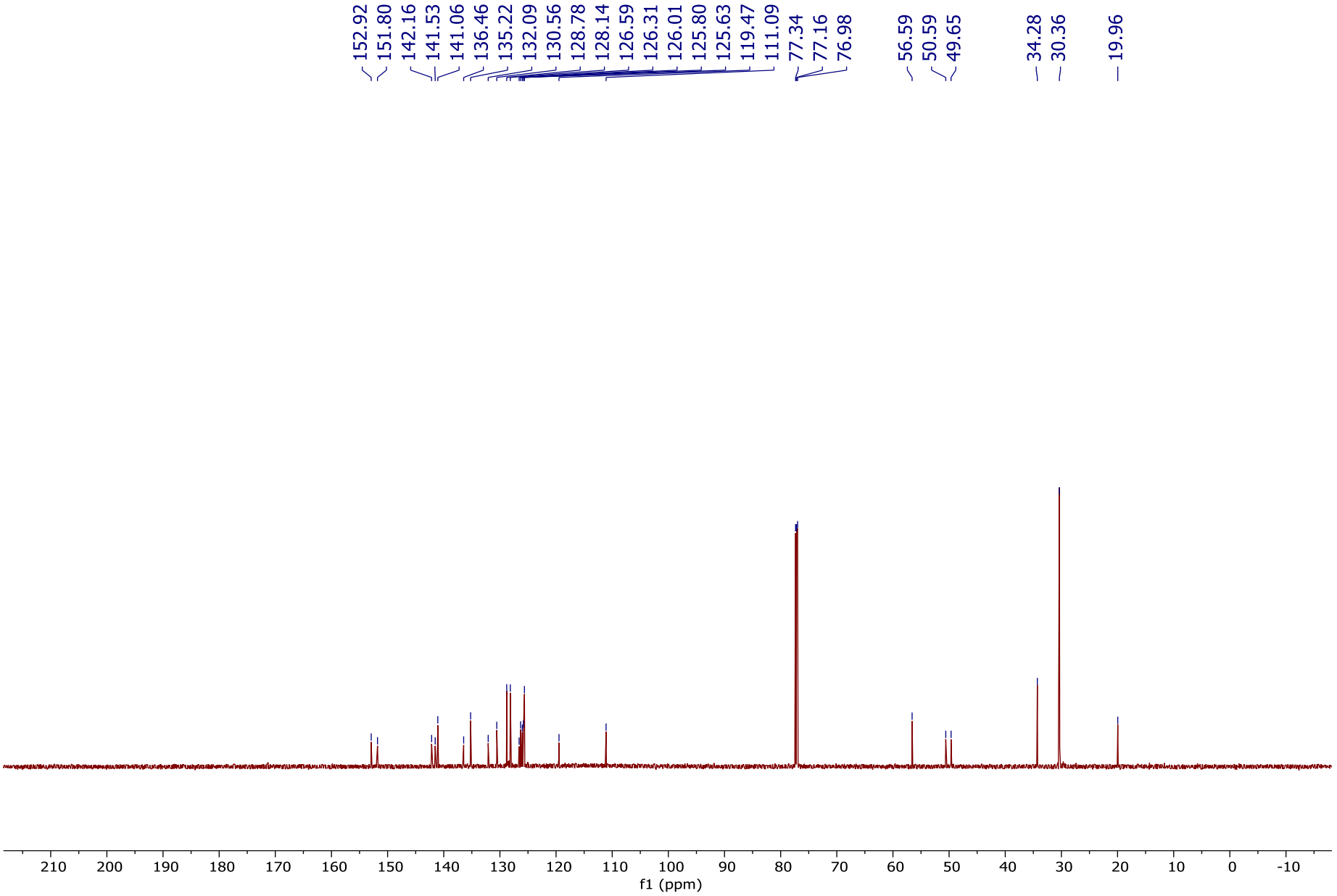
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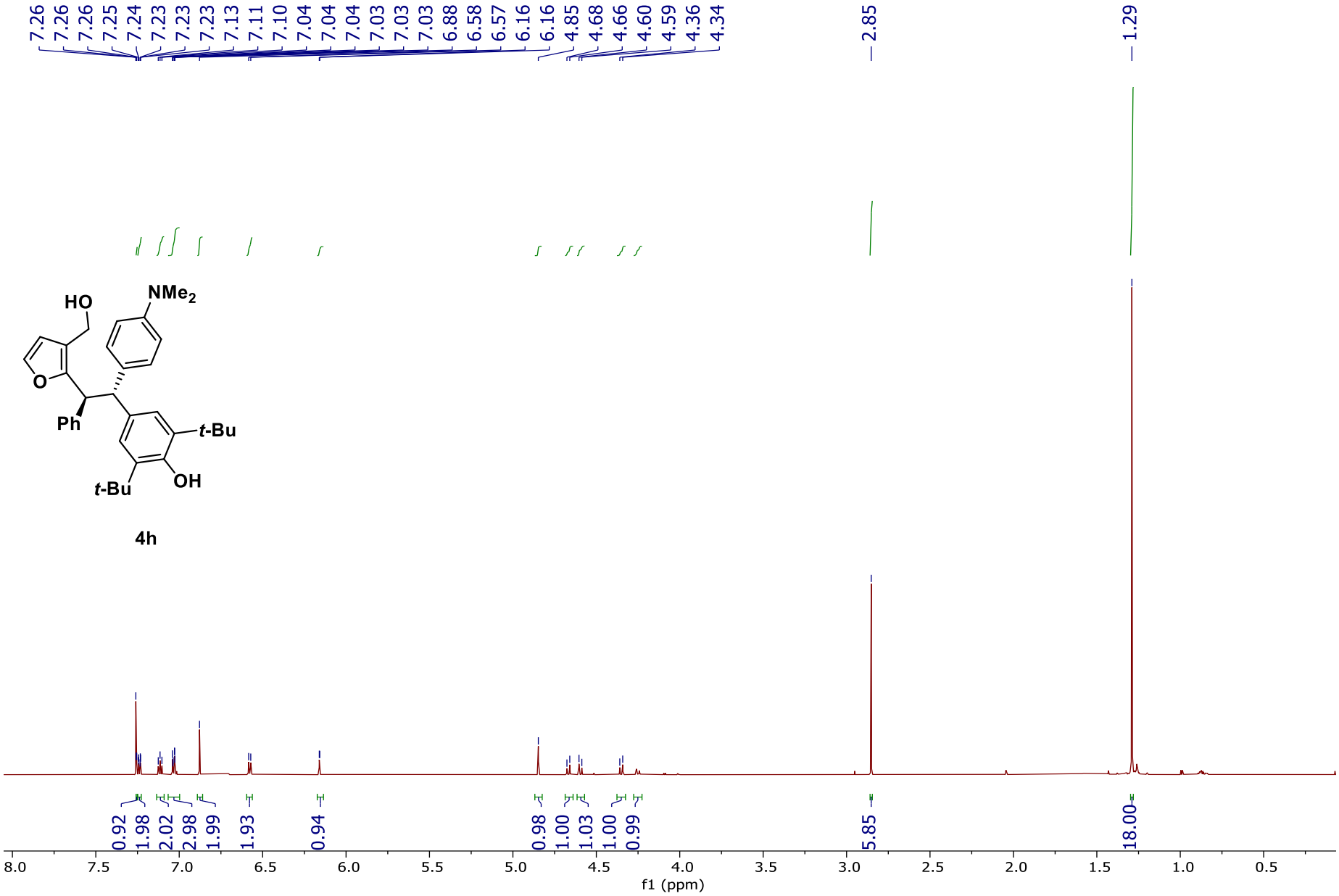
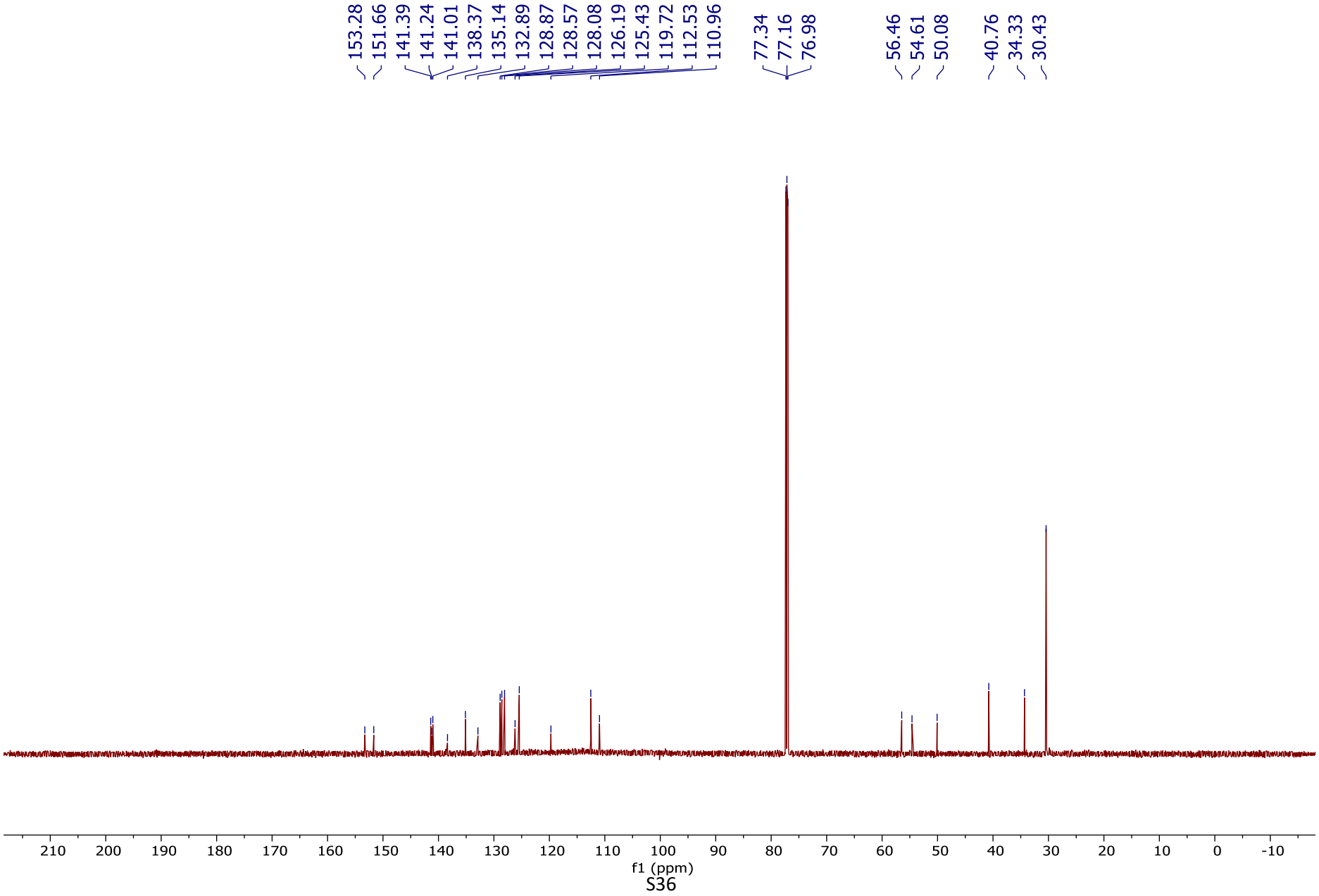
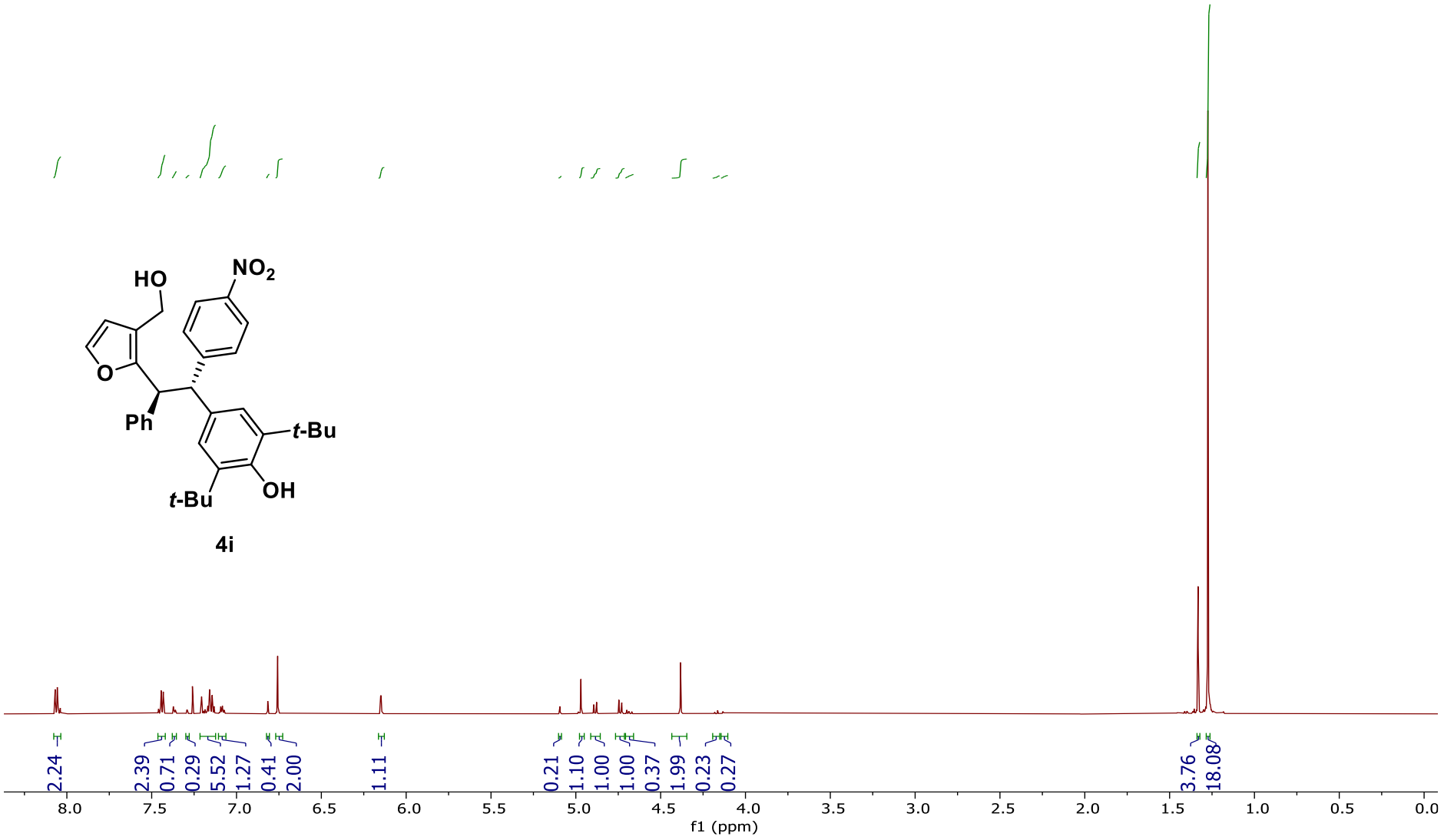
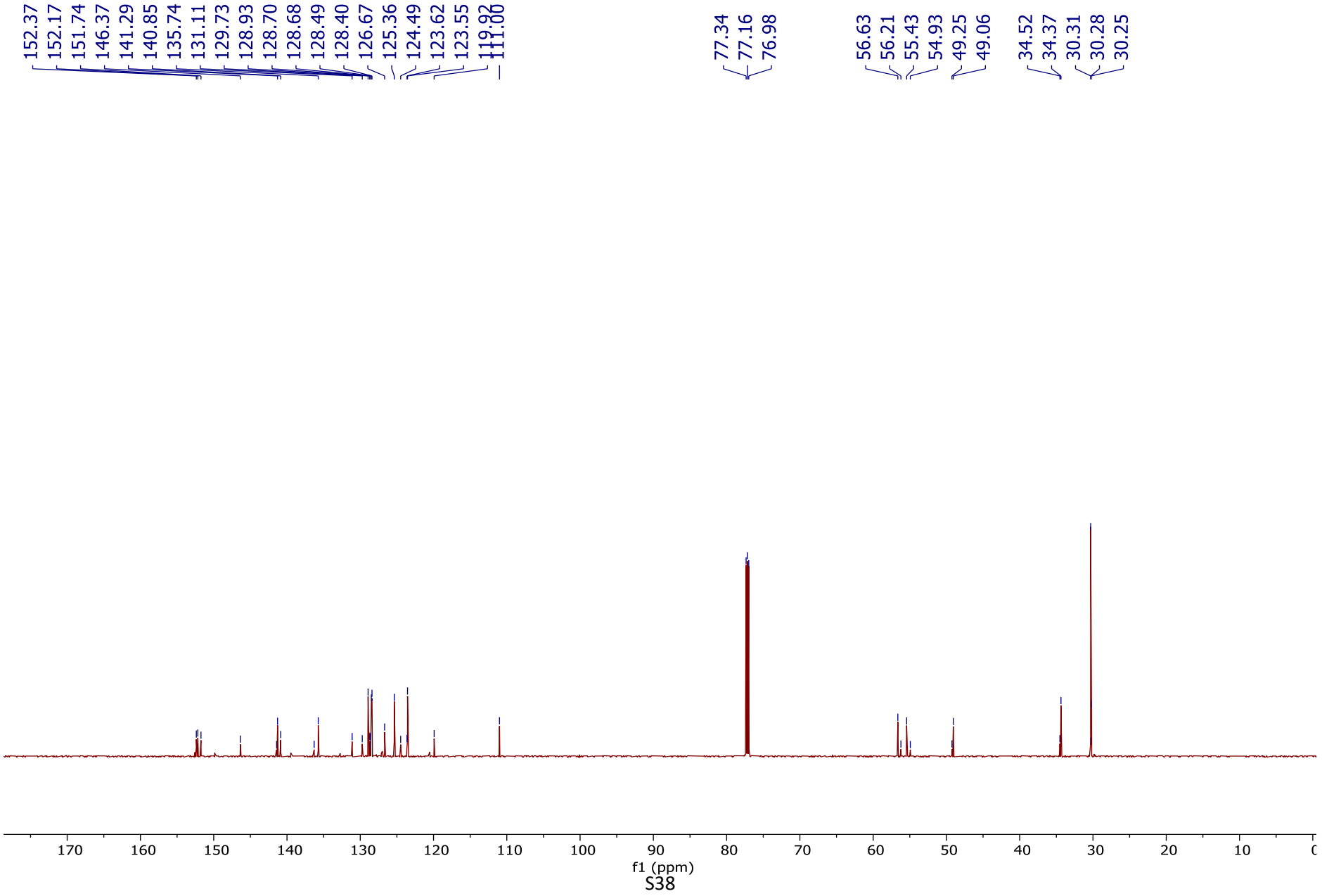
-10
f1 (ppm)

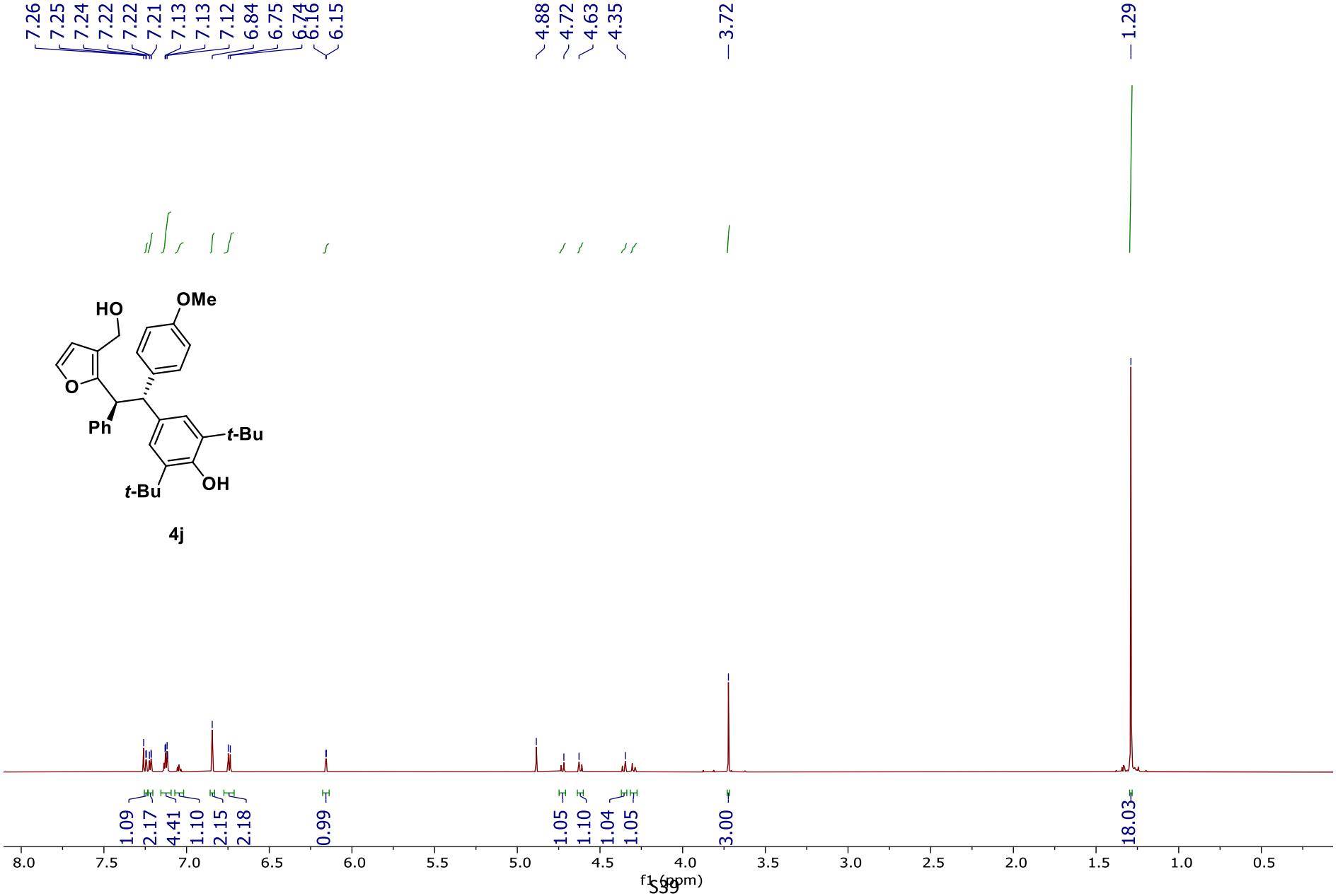

7.26
7.26
7.26
7.25
7.24
7.23
7.23
7.23
7.13
7.11
7.10
7.04
7.04
7.04
7.03
7.03
7.03
6.88
6.58
6.57
6.16
6.16
4.85
4.68
4.66
4.60
4.59
4.36
4.34
2.85
1.29
HO
NMe2
O
Ph
t-Bu
t-Bu
OH
0.92
1.98
2.02
2.98
1.99
1.93
0.94
0.98
1.00
1.03
1.00
0.99
5.85
18.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

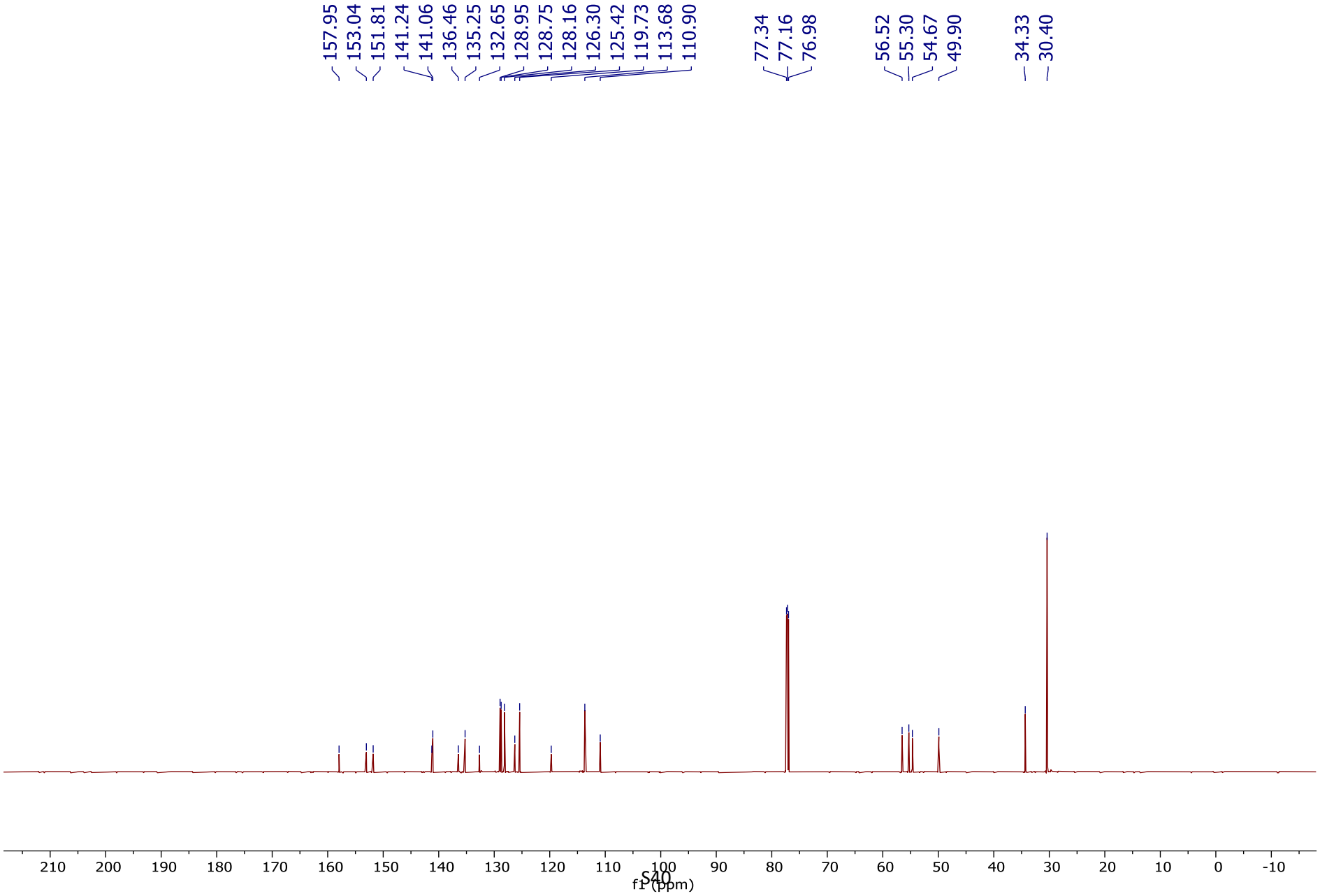
4h

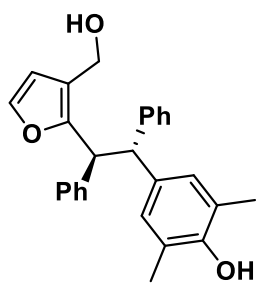

153.28
151.66
141.39
141.24
141.01
138.37
135.14
132.89
128.87
128.57
128.08
126.19
125.43
119.72
112.53
110.96
77.34
77.16
76.98
56.46
54.61
50.08
40.76
34.33
30.43
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


HO
NO2
O
Ph
t-Bu
t-Bu
OH
4i
2.24
2.39
0.71
0.29
5.52
1.27
0.41
2.00
1.11
0.21
1.10
1.00
1.00
0.37
1.99
0.23
0.27
3.76
18.08
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)


152.37
152.17
151.74
146.37
141.29
140.85
135.74
131.11
129.73
128.93
128.70
128.68
128.49
128.40
126.67
125.36
124.49
123.62
123.55
119.92
111.00
77.34
77.16
76.98
56.63
56.21
55.43
54.93
49.25
49.06
34.52
34.37
30.31
30.28
30.25
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

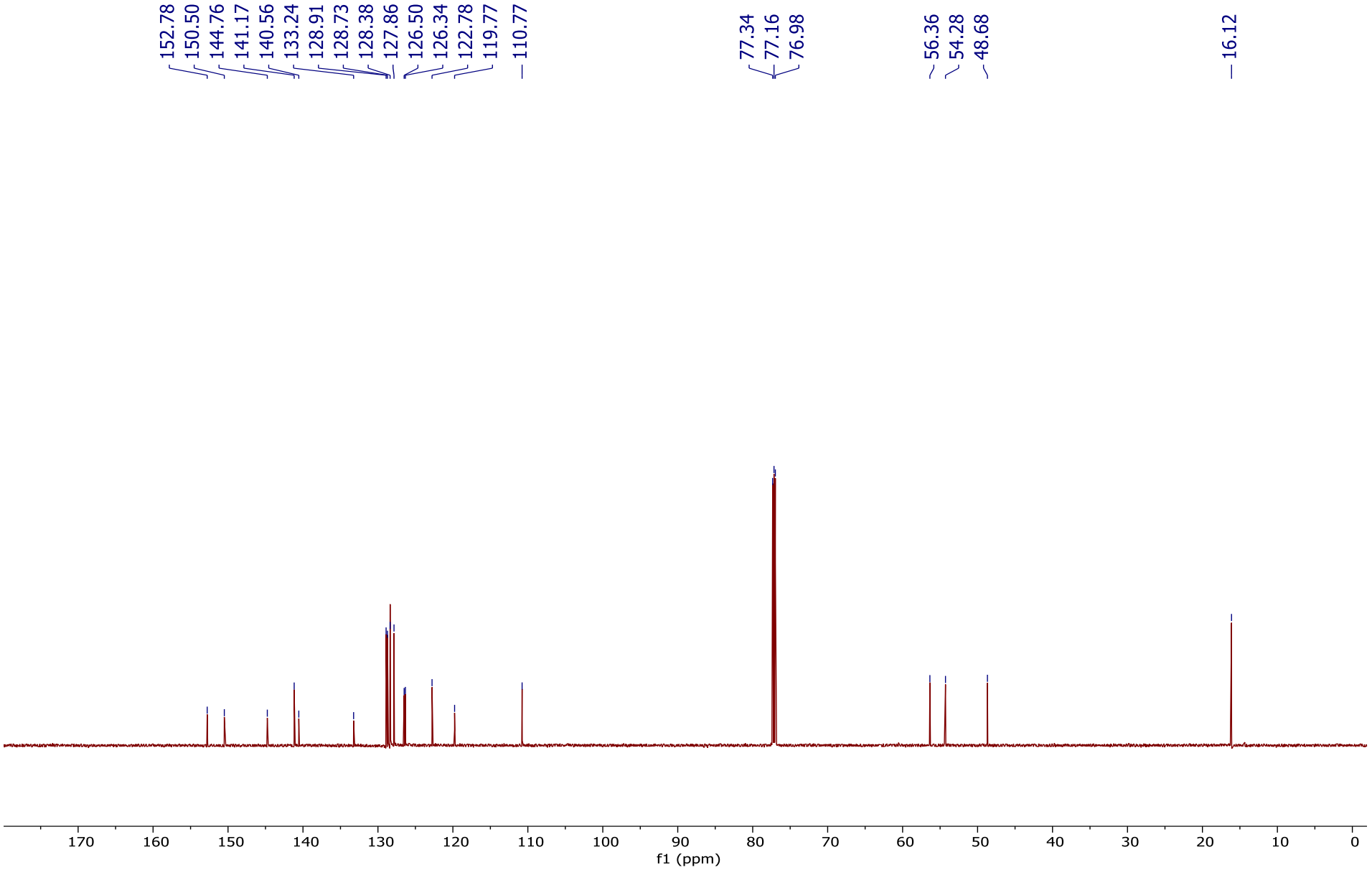

7.26
7.25
7.24
7.22
7.22
7.21
7.13
7.13
7.12
6.84
6.75
6.74
6.16
6.15
4.88
4.72
4.63
4.35
3.72
1.29
HO
OMe
O
Ph
t-Bu
t-Bu
OH
4j
1.09
2.17
4.41
1.10
2.15
2.18
0.99
1.05
1.10
1.04
1.05
3.00
18.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

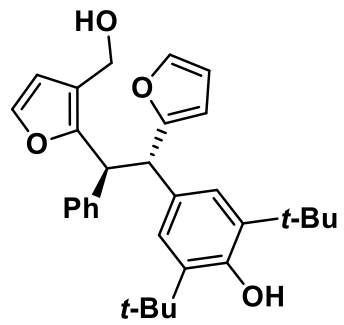

157.95
153.04
151.81
141.24
141.06
136.46
135.25
132.65
128.95
128.75
128.16
126.30
125.42
119.73
113.68
110.90
77.34
77.16
76.98
56.52
55.30
54.67
49.90
34.33
30.40
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


HO
O
Ph
Ph
OH

4k

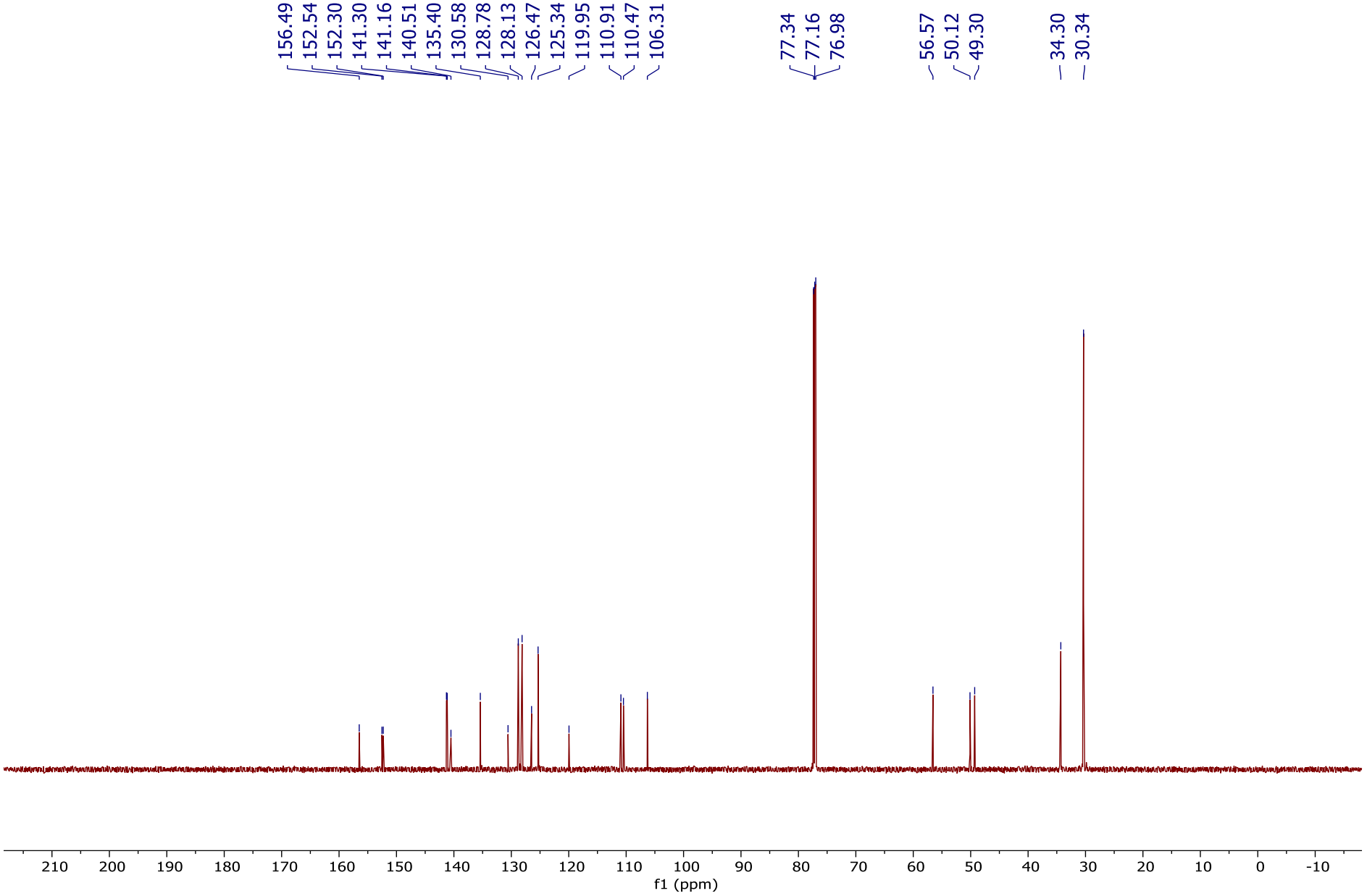
2.00
1.04
5.94
1.93
1.96
0.89
1.00
0.99
0.89
1.00
1.00
5.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

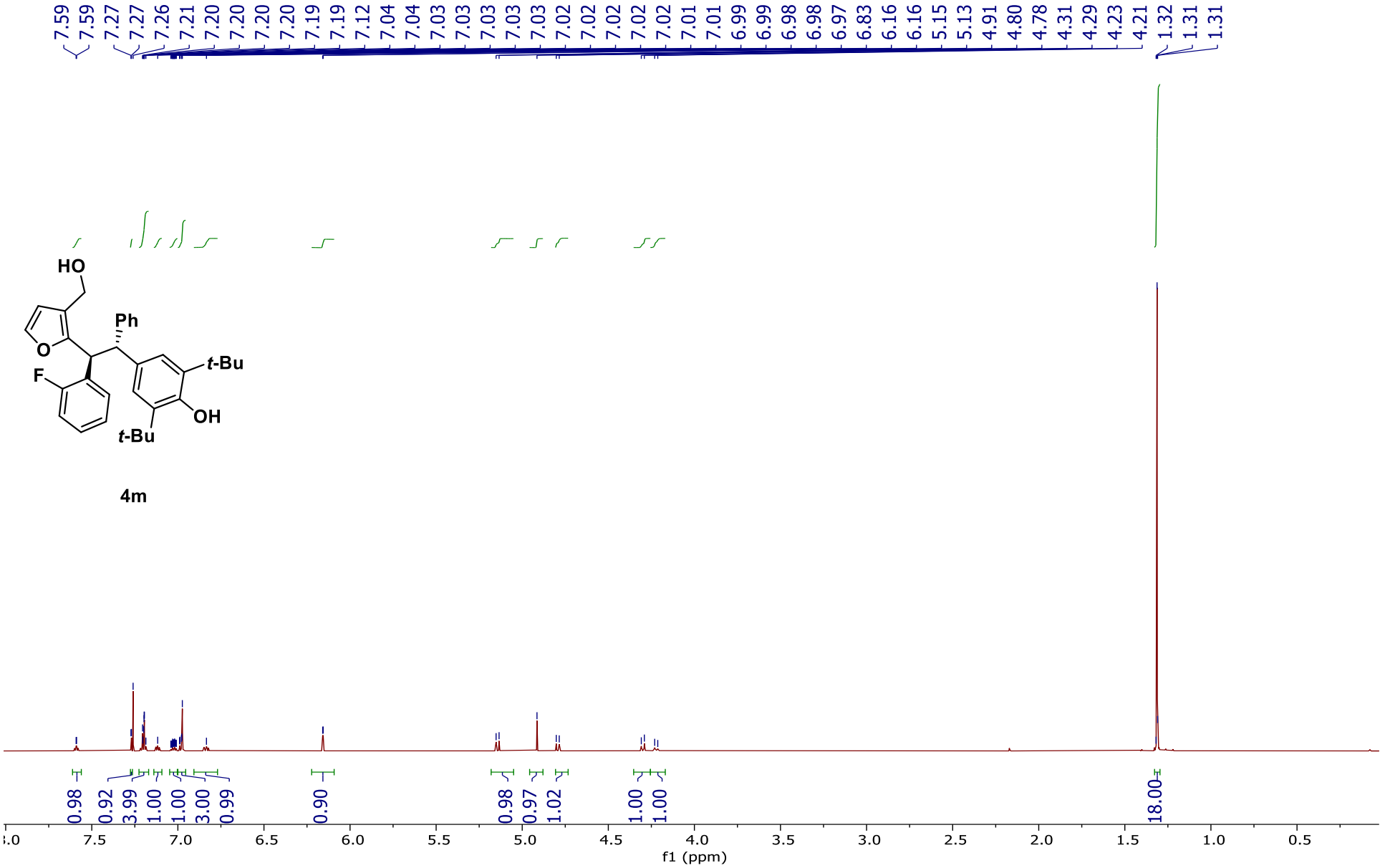

152.78
150.50
144.76
141.17
140.56
133.24
128.91
128.73
128.38
127.86
126.50
126.34
122.78
119.77
110.77
77.34
77.16
76.98
56.36
54.28
48.68
16.12
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HO
O
O
Ph
t-Bu
t-Bu
OH

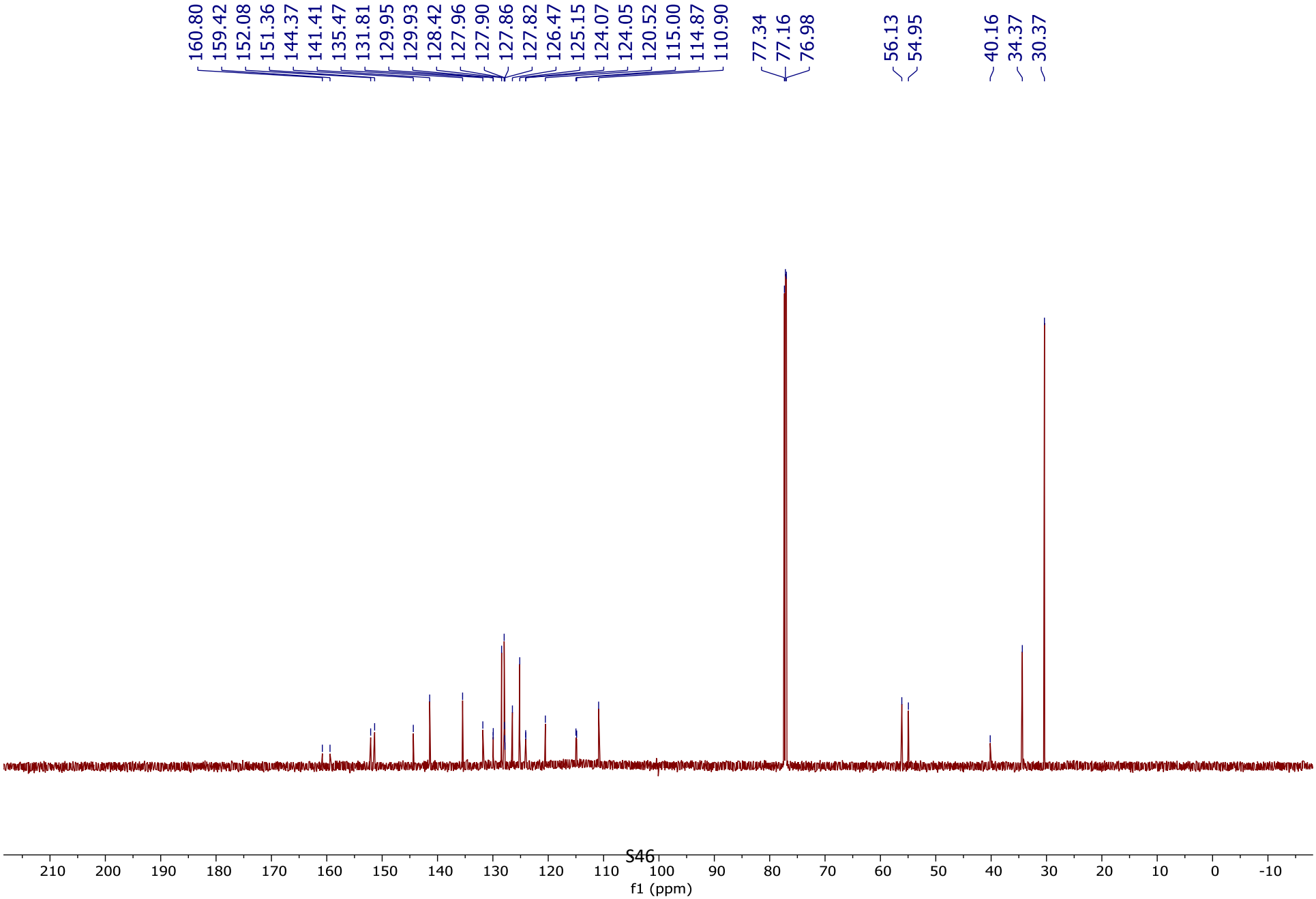
4l

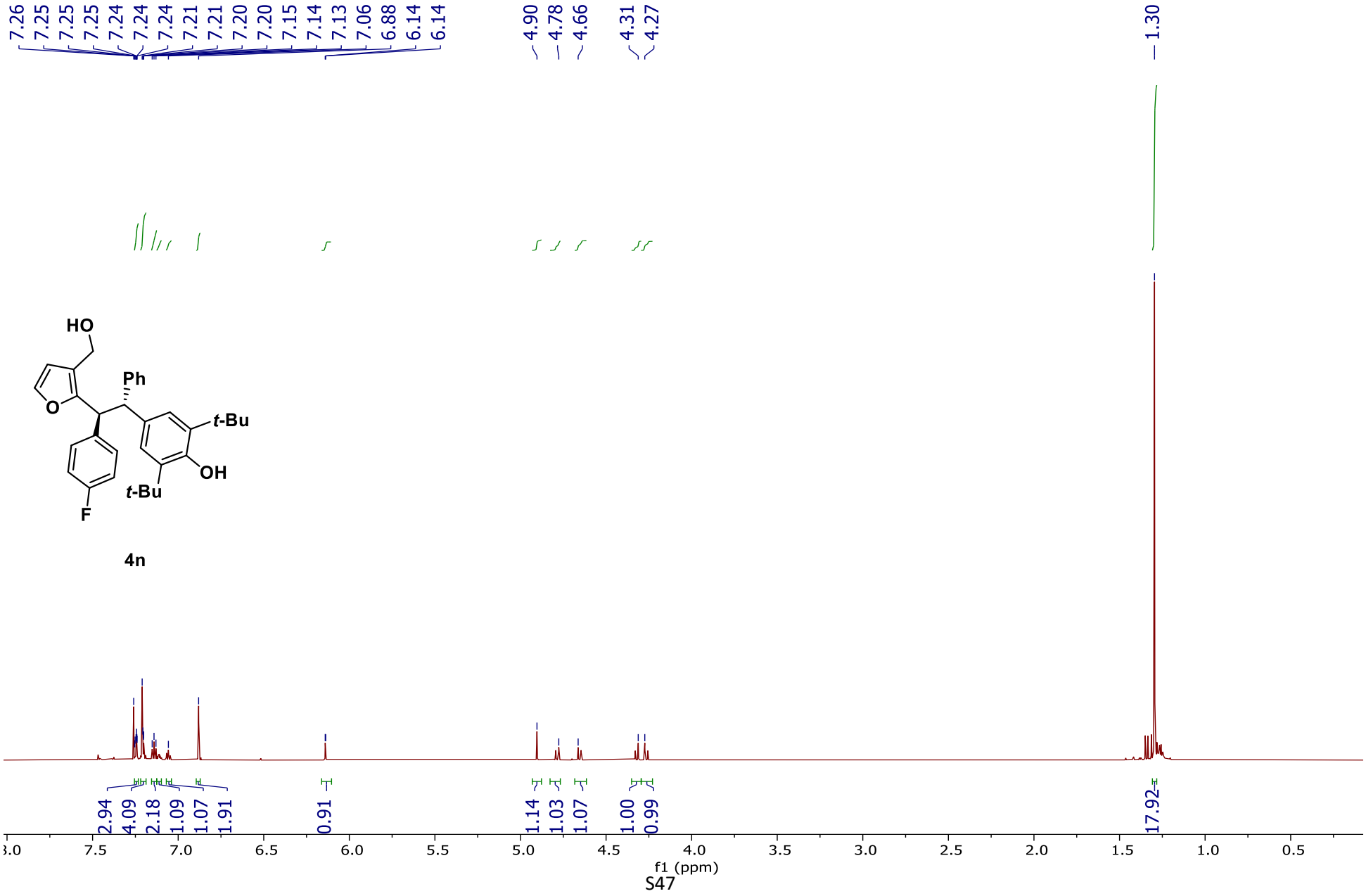
2.02
1.99
1.98
1.02
1.95
0.87
0.88
0.94
1.00
1.02
1.00
1.00
0.99
18.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


156.49
152.54
152.30
141.30
141.16
140.51
135.40
130.58
128.78
128.13
126.47
125.34
119.95
110.91
110.47
106.31
77.34
77.16
76.98
56.57
50.12
49.30
34.30
30.34
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)

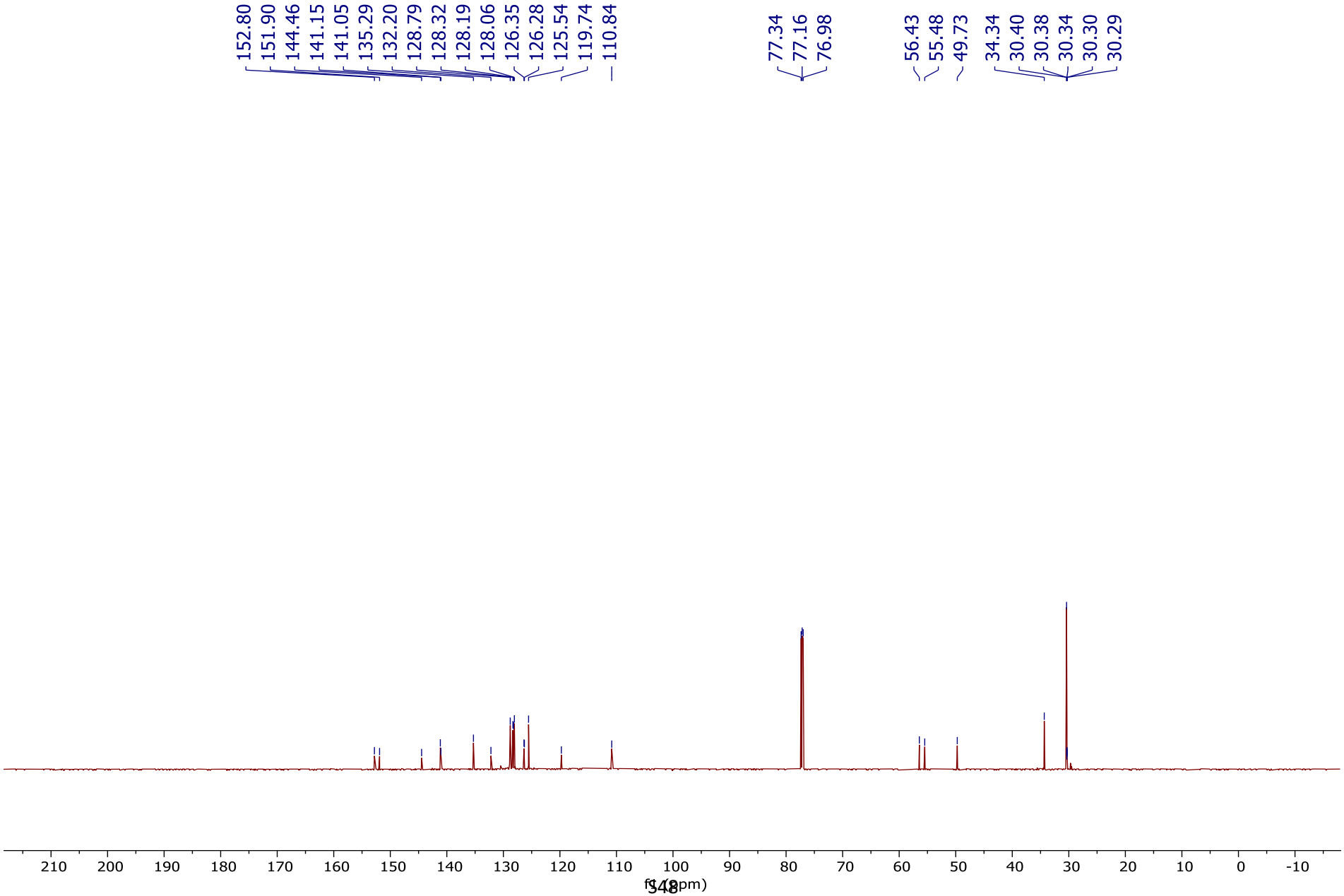

7.59 7.59 7.27 7.27 7.26 7.21 7.20 7.20 7.20 7.20 7.19 7.19 7.12 7.04 7.04 7.03 7.03 7.03 7.03 7.03 7.02 7.02 7.02 7.02 7.02 7.01 7.01 6.99 6.99 6.98 6.98 6.97 6.83 6.16 6.16 5.15 5.13 4.91 4.80 4.78 4.31 4.29 4.23 4.21 1.32 1.31 1.31
HO
Ph
O
F
t-Bu
OH
t-Bu
0.98 0.92 3.99 1.00 1.00 3.00 0.99 0.90 0.98 0.97 1.02 1.00 1.00 18.00
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
f1 (ppm)

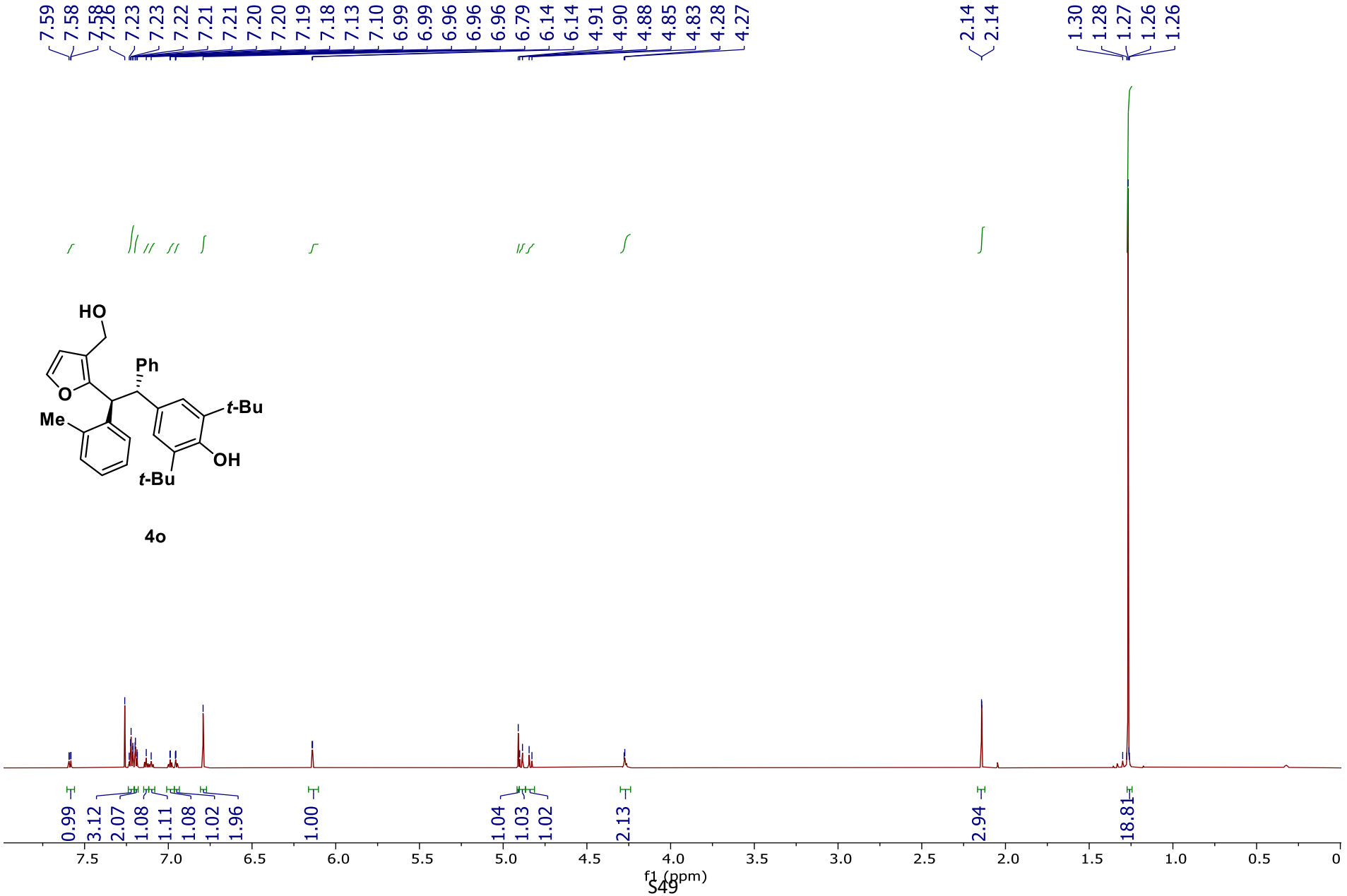
4m


160.80
159.42
152.08
151.36
144.37
141.41
135.47
131.81
129.95
129.93
128.42
127.96
127.90
127.86
127.82
126.47
125.15
124.07
124.05
120.52
115.00
114.87
110.90
77.34
77.16
76.98
56.13
54.95
40.16
34.37
30.37
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)

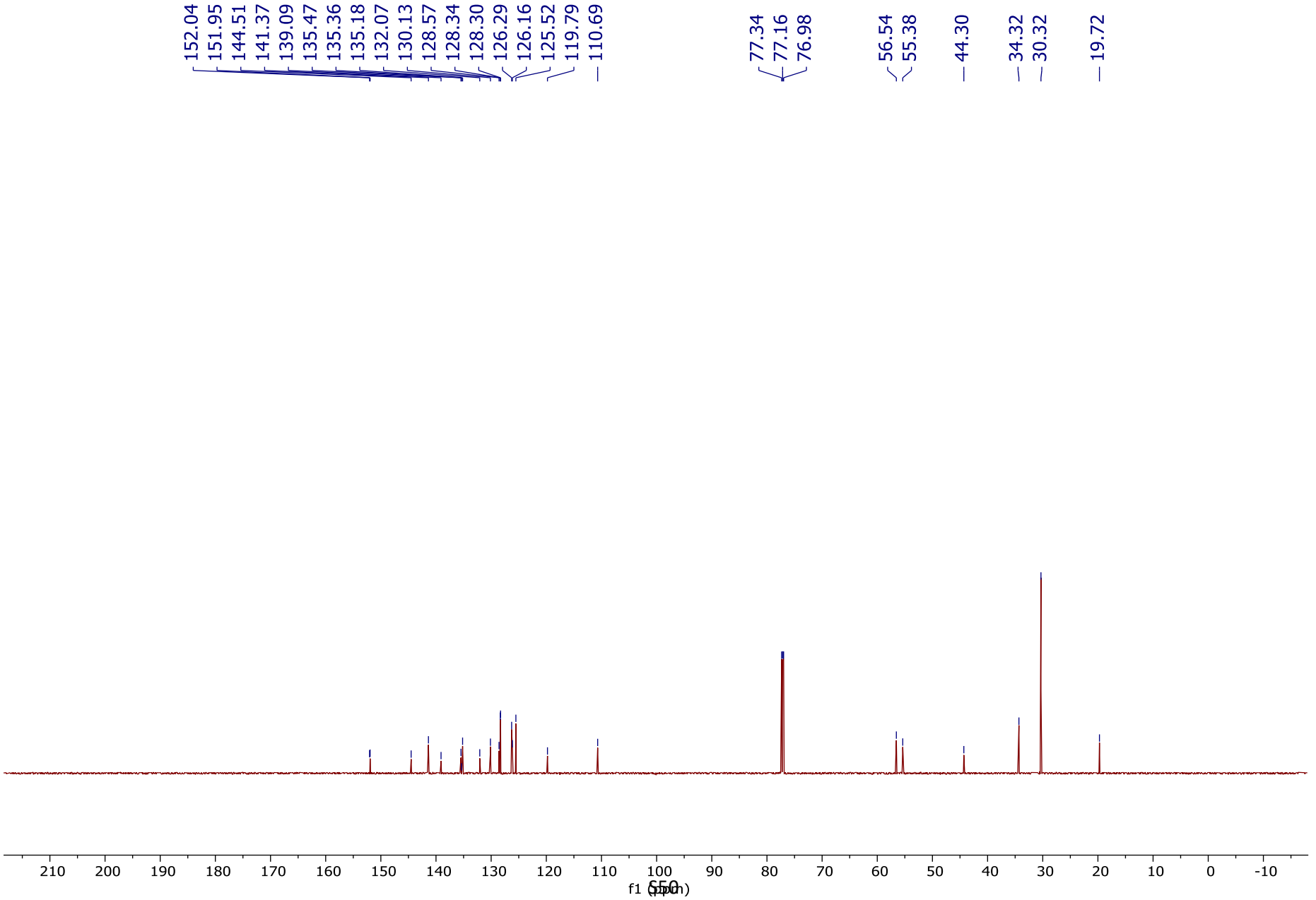

7.26
7.25
7.25
7.25
7.24
7.24
7.24
7.21
7.21
7.20
7.20
7.15
7.14
7.13
7.06
6.88
6.14
6.14
4.90
4.78
4.66
4.31
4.27
1.30
HO
Ph
O
t-Bu
OH
t-Bu
F
2.94
4.09
2.18
1.09
1.07
1.91
0.91
1.14
1.03
1.07
1.00
0.99
17.92
f1 (ppm)

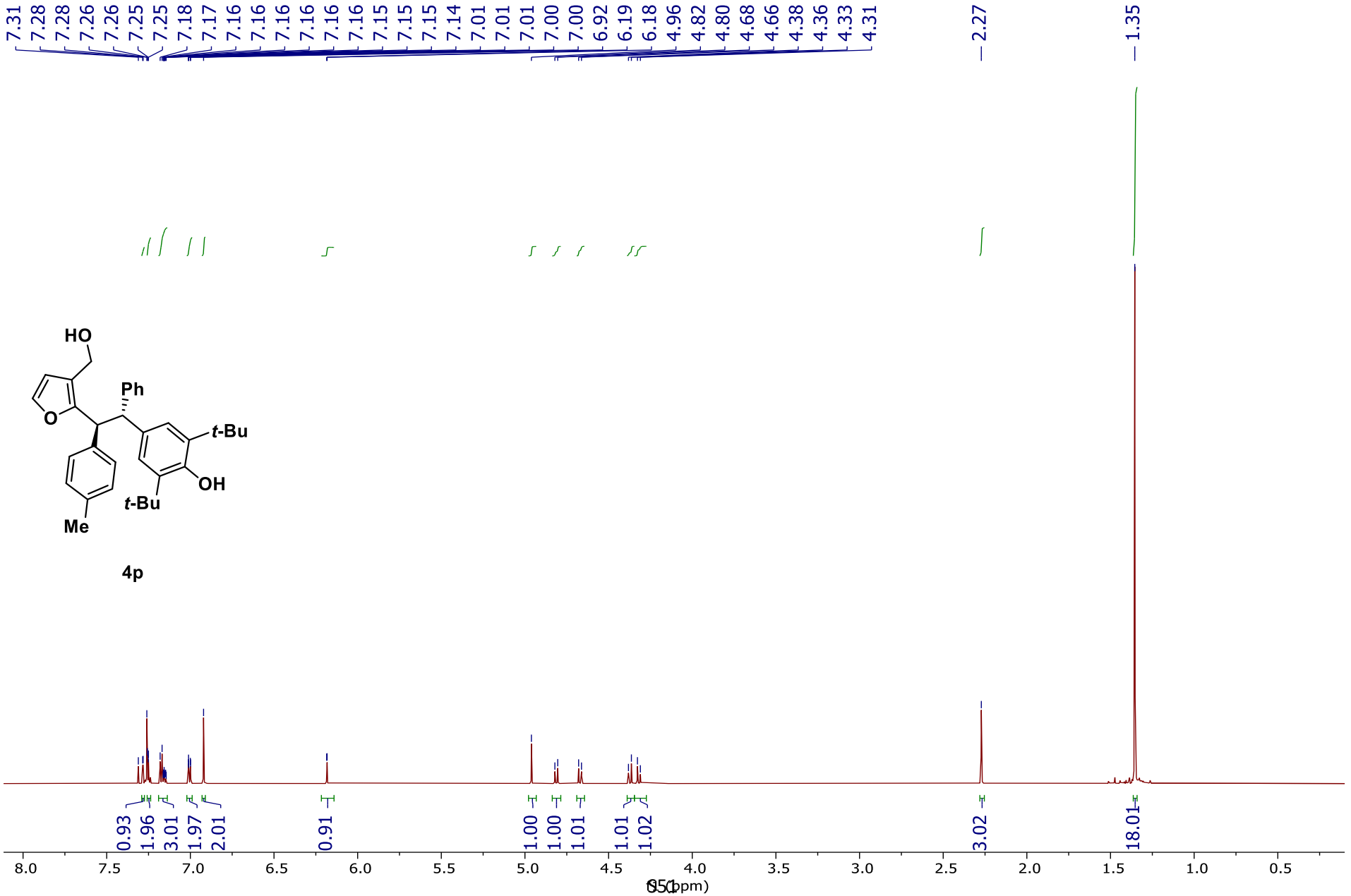
4n


152.80
151.90
144.46
141.15
141.05
135.29
132.20
128.79
128.32
128.19
128.06
126.35
126.28
125.54
119.74
110.84
77.34
77.16
76.98
56.43
55.48
49.73
34.34
30.40
30.38
30.34
30.30
30.29
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)

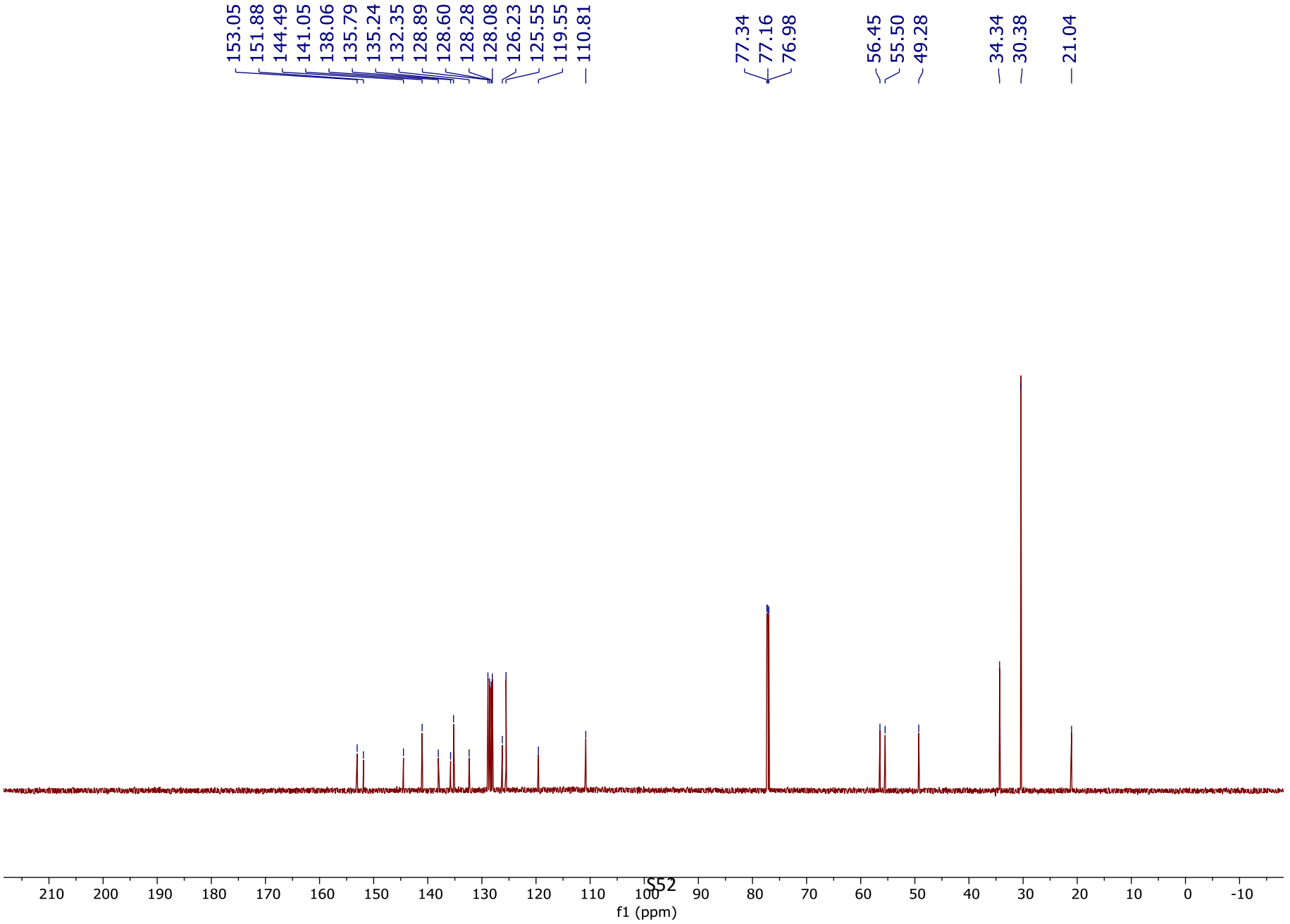

7.59
7.58
7.58
7.26
7.23
7.23
7.22
7.21
7.21
7.20
7.20
7.19
7.18
7.13
7.10
6.99
6.99
6.96
6.96
6.96
6.79
6.14
6.14
4.91
4.90
4.88
4.85
4.83
4.28
4.27
2.14
2.14
1.30
1.28
1.27
1.26
1.26
HO
Ph
O
Me
t-Bu
OH
t-Bu
0.99
3.12
2.07
1.08
1.11
1.08
1.02
1.96
1.00
1.04
1.03
1.02
2.13
2.94
18.81
7.5
7.0
6.5
6.0
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)

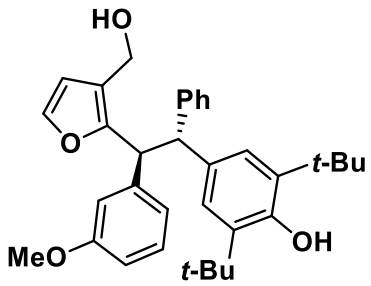
4o


152.04
151.95
144.51
141.37
139.09
135.47
135.36
135.18
132.07
130.13
128.57
128.34
128.30
126.29
126.16
125.52
119.79
110.69
77.34
77.16
76.98
56.54
55.38
44.30
34.32
30.32
19.72
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)

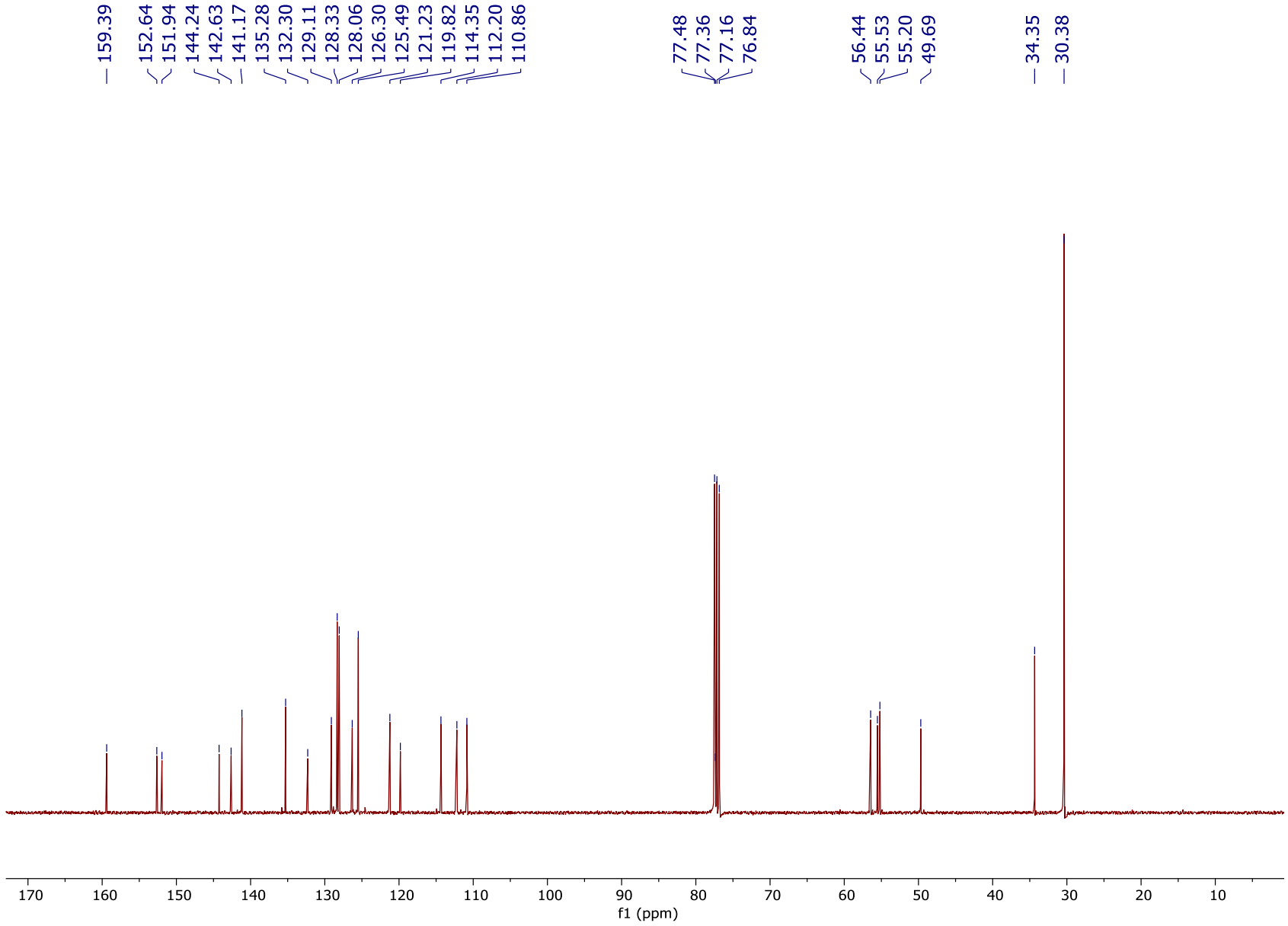

7.31
7.28
7.28
7.26
7.26
7.25
7.25
7.18
7.17
7.16
7.16
7.16
7.16
7.16
7.16
7.15
7.15
7.15
7.14
7.01
7.01
7.01
7.00
7.00
6.92
6.19
6.18
4.96
4.82
4.80
4.68
4.66
4.38
4.36
4.33
4.31
2.27
1.35
HO
Ph
O
t-Bu
OH
t-Bu
Me
0.93
1.96
3.01
1.97
2.01
0.91
1.00
1.00
1.01
1.01
1.02
3.02
18.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

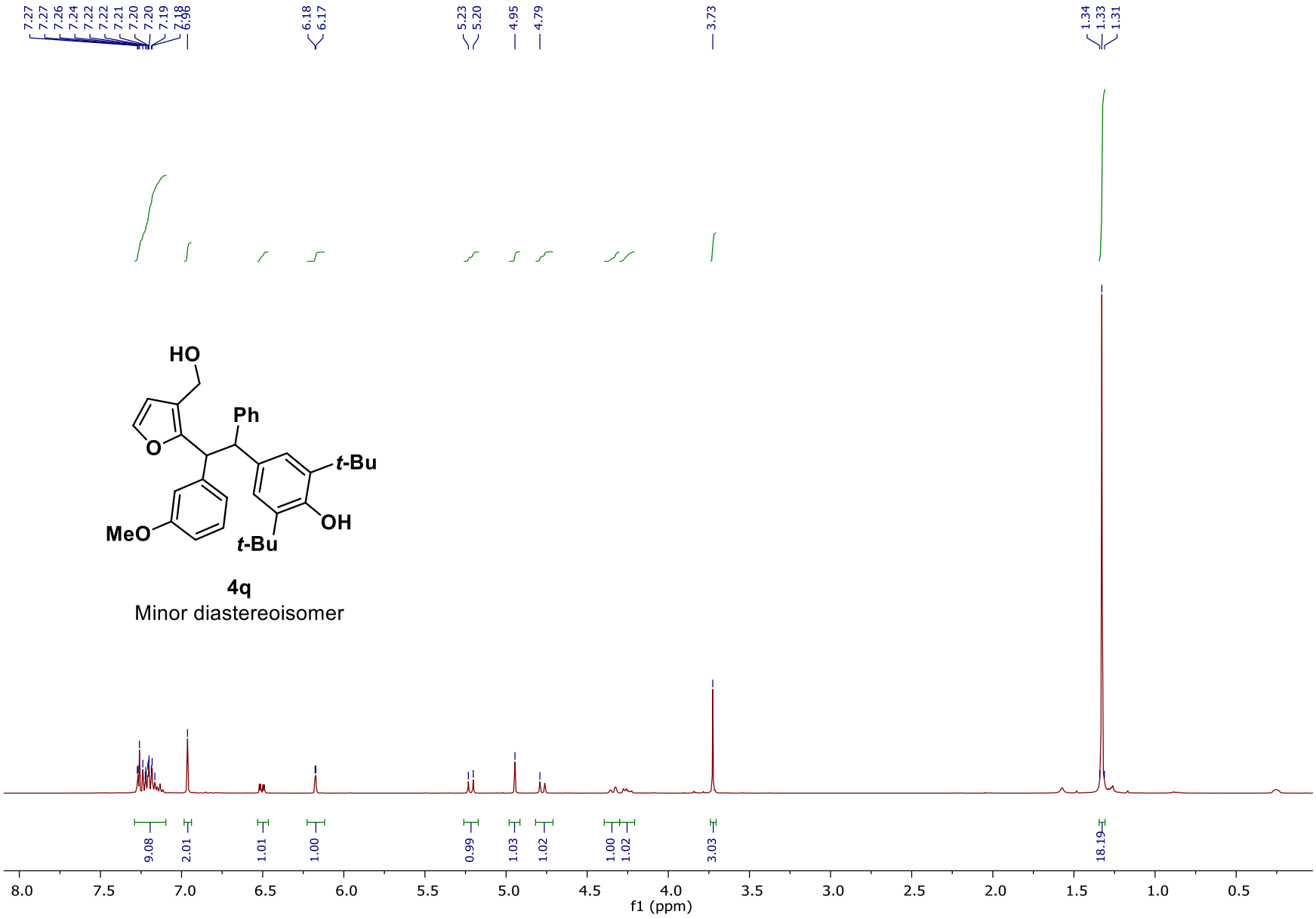
4p


153.05
151.88
144.49
141.05
138.06
135.79
135.24
132.35
128.89
128.60
128.28
128.08
126.23
125.55
119.55
110.81
77.34
77.16
76.98
56.45
55.50
49.28
34.34
30.38
21.04
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)

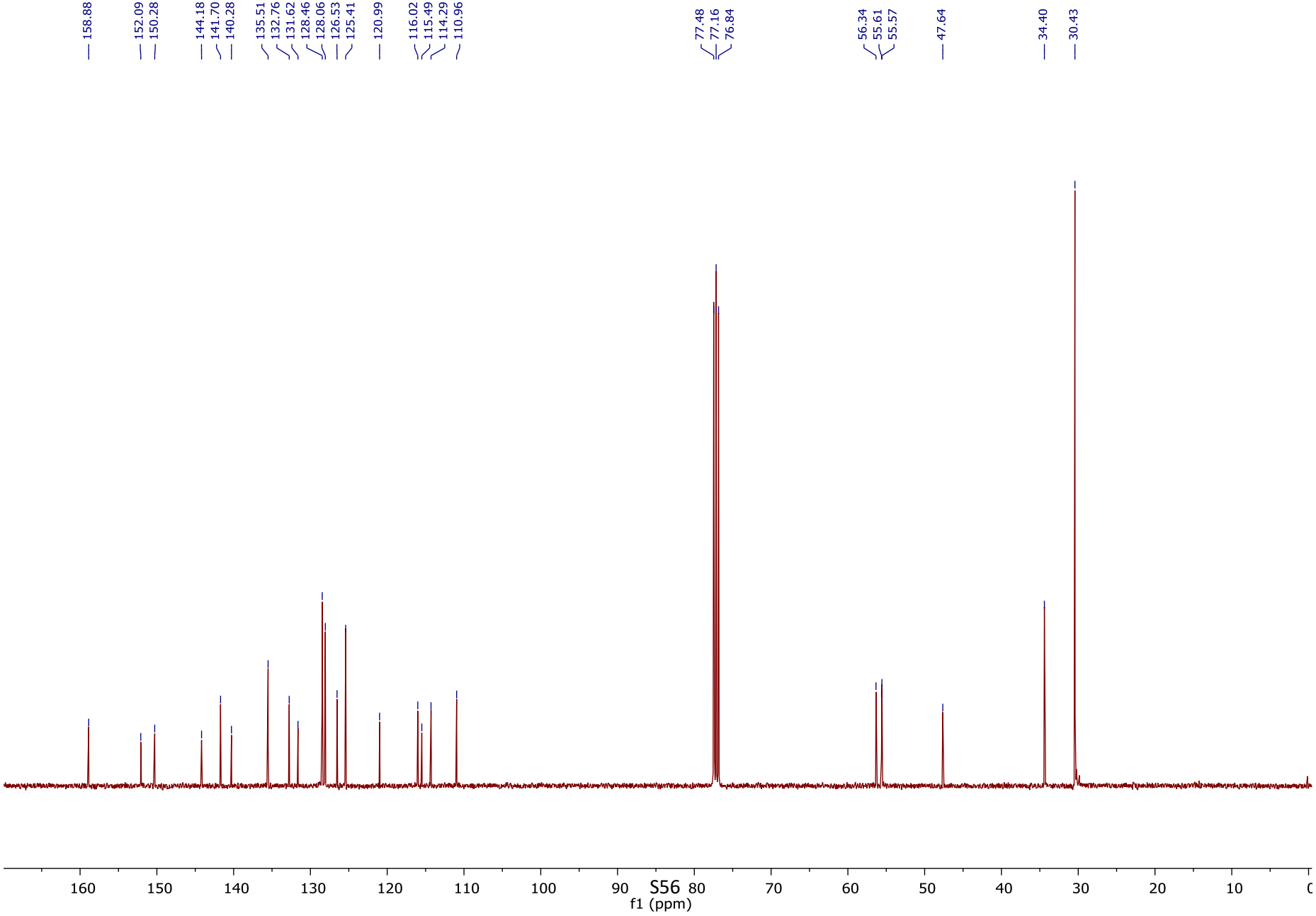


4q
Major diastereoisomer


159.39
152.64
151.94
144.24
142.63
141.17
135.28
132.30
129.11
128.33
128.06
126.30
125.49
121.23
119.82
114.35
112.20
110.86
77.48
77.36
77.16
76.84
56.44
55.53
55.20
49.69
34.35
30.38
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



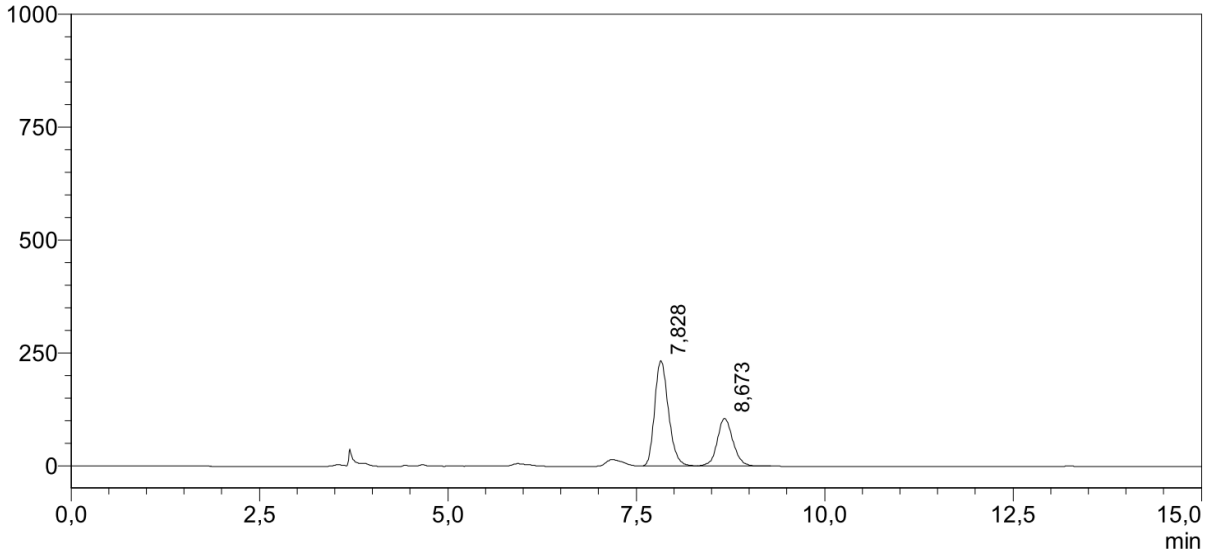
4q
Minor diastereoisomer


158.88
152.09
150.28
144.18
141.70
140.28
135.51
132.76
131.62
128.46
128.06
126.53
125.41
120.99
116.02
115.49
114.29
110.96
77.48
77.16
76.84
56.34
55.61
55.57
47.64
34.40
30.43
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

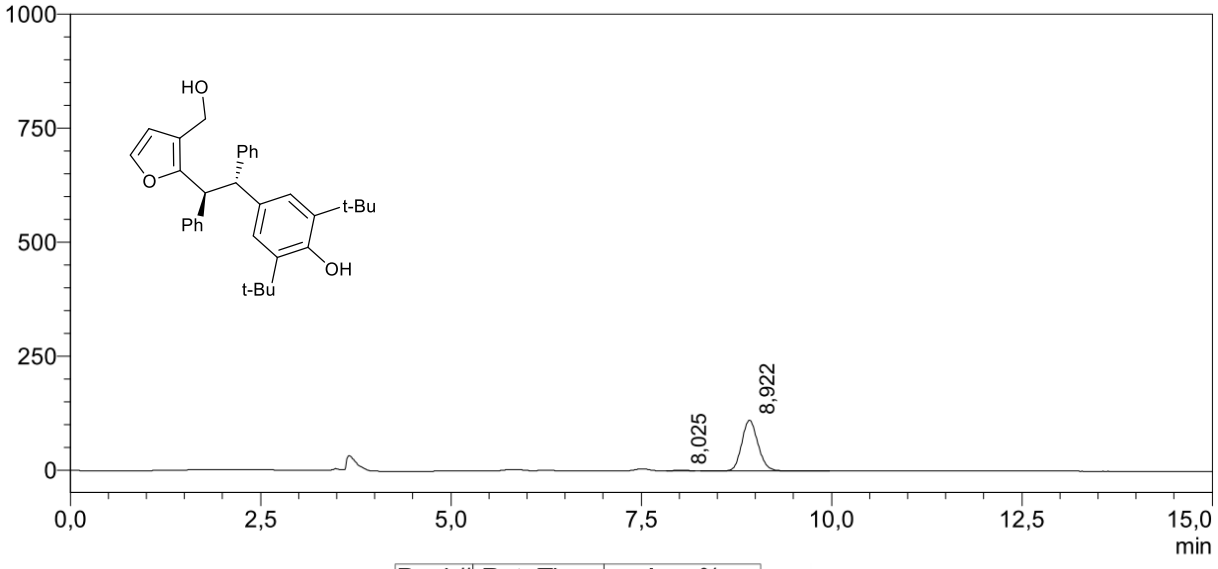
6. HPLC Traces

2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(3-(hydroxymethyl)furan-2-yl)-1,2-diphenylethyl)phenol (4a)

Racemic sample



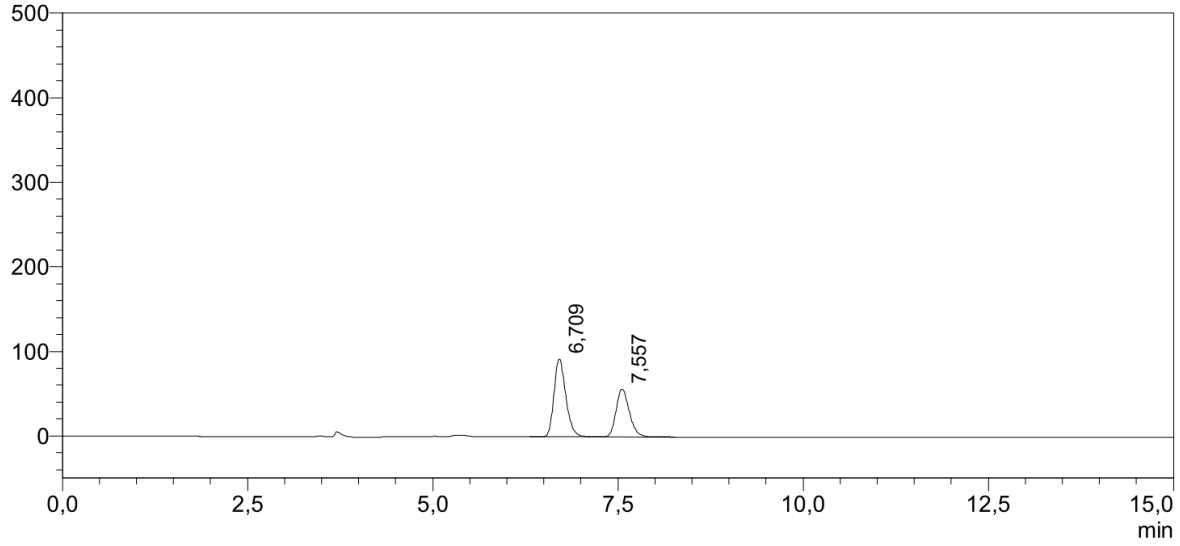
Enantiomerically enriched sample



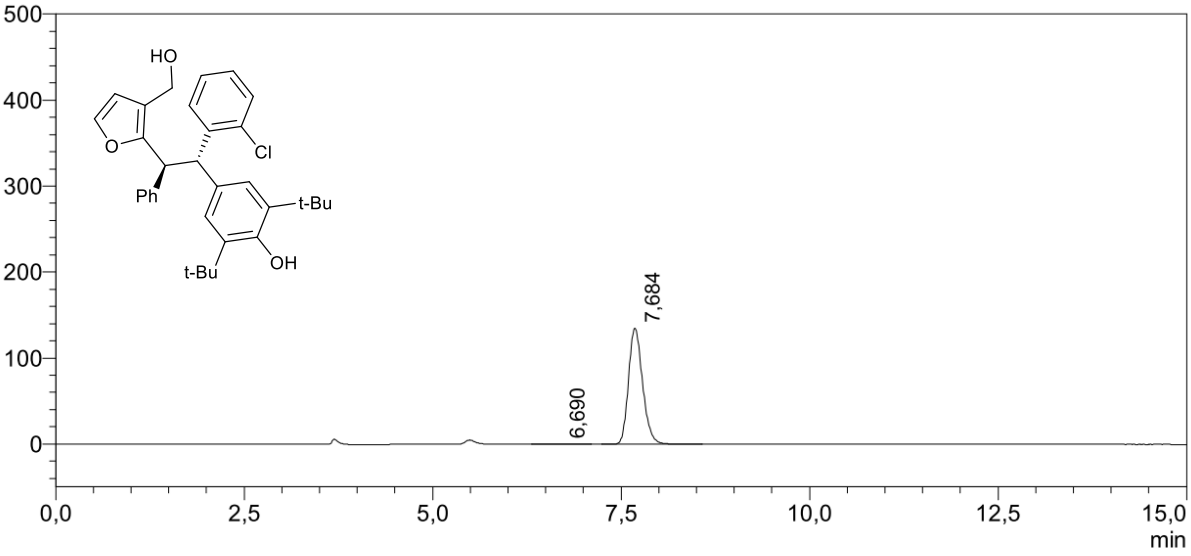
Peak#	Ret. Time	Area%
1	8,025	0,941
2	8,922	99,059
Total		100,000

2,6-Di-*tert*-butyl-4-((1*S*,2*S*)-1-(2-chlorophenyl)-2-(3-(hydroxymethyl)furan-2-yl)-2-phenylethyl)phenol (4b)

Racemic sample



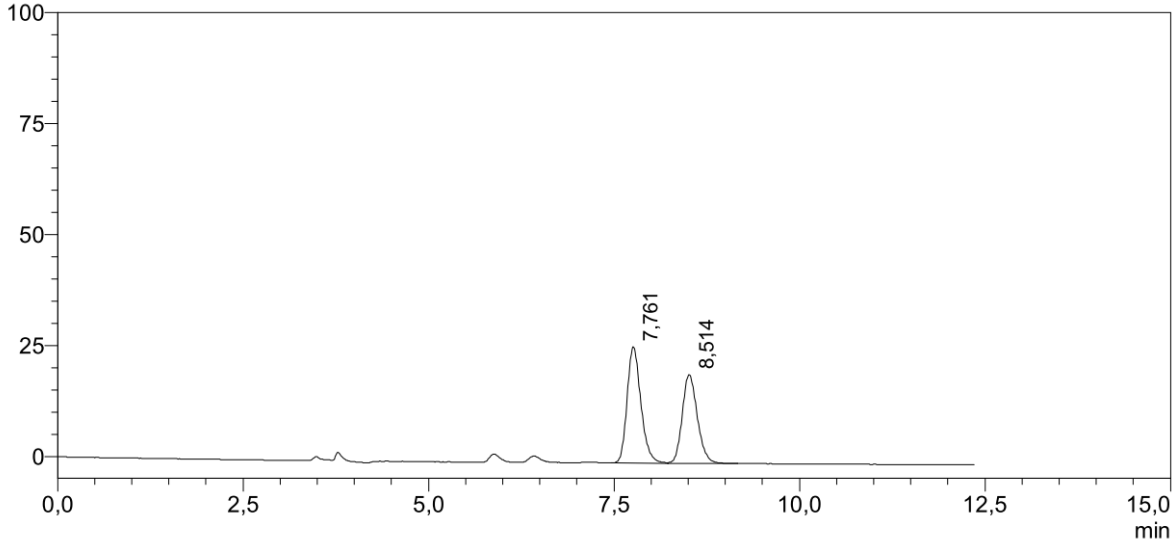
Enantiomerically enriched sample



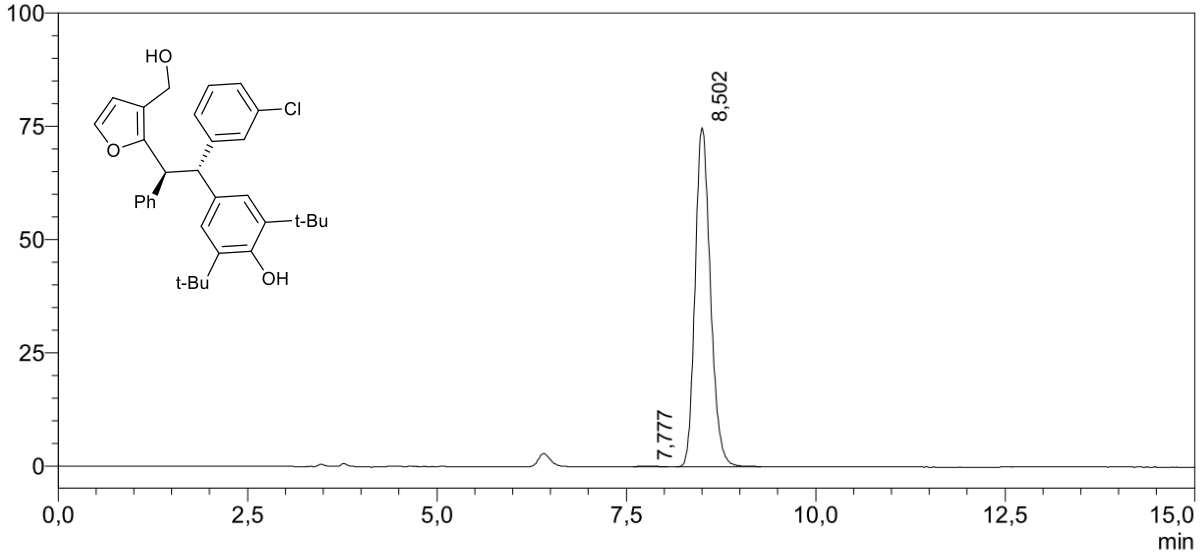
Peak#	Ret. Time	Area%
1	6,690	0,136
2	7,684	99,864
Total		100,000

2,6-Di-*tert*-butyl-4-((1*S*,2*S*)-1-(3-chlorophenyl)-2-(3-(hydroxymethyl)furan-2-yl)-2-phenylethyl)phenol (4c)

Racemic sample



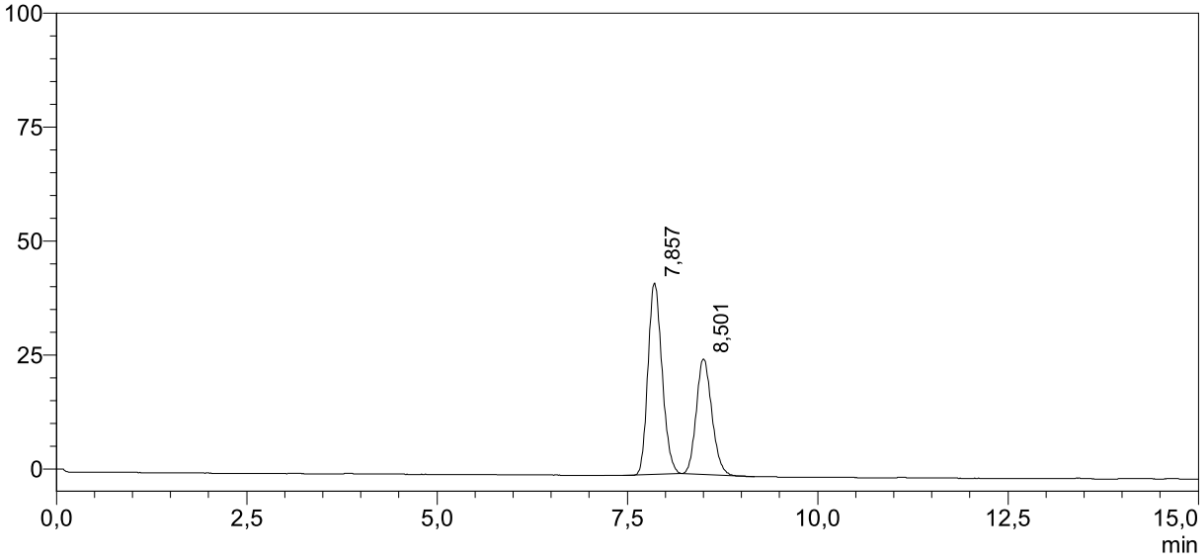
Enantiomerically enriched sample



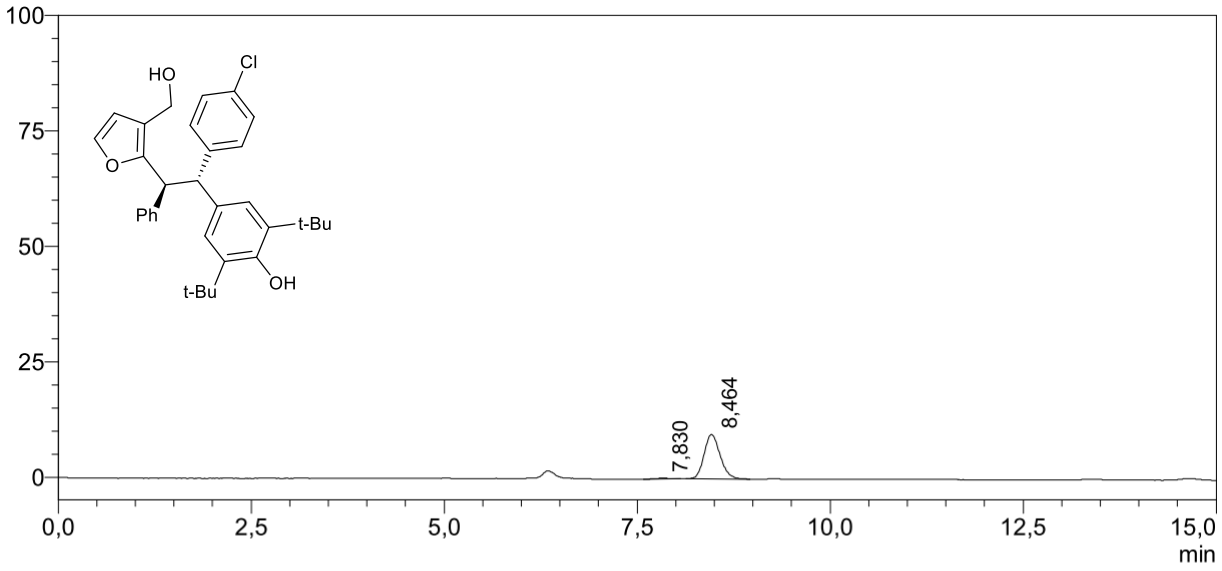
Peak#	Ret. Time	Area%
1	7,777	0,177
2	8,502	99,823
Total		100,000

2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-1-(4-chlorophenyl)-2-(3-(hydroxymethyl)furan-2-yl)-2-phenylethyl)phenol (4d)

Racemic sample



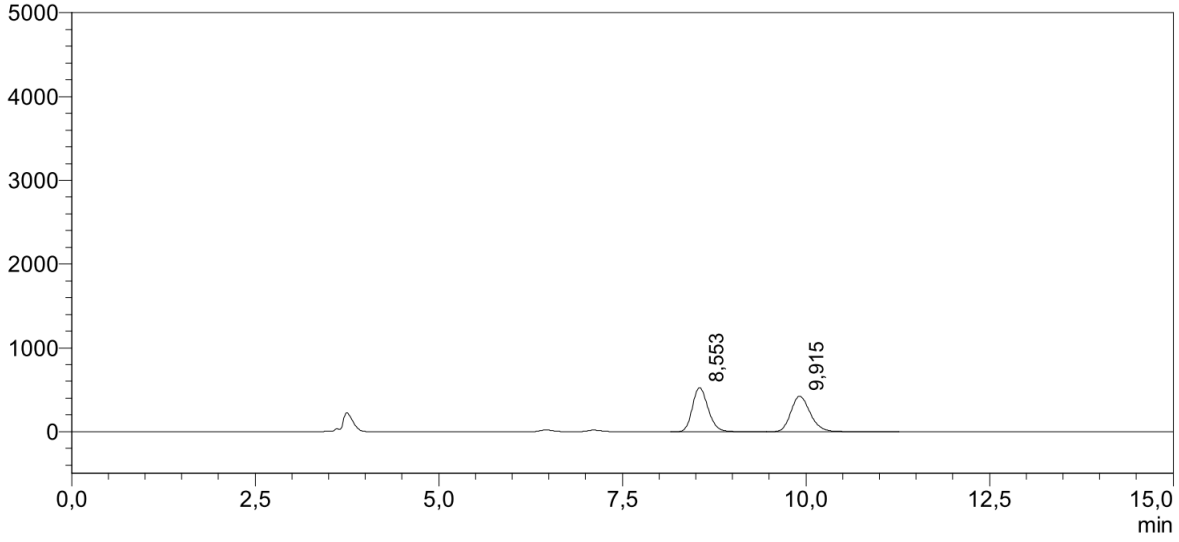
Enantiomerically enriched sample



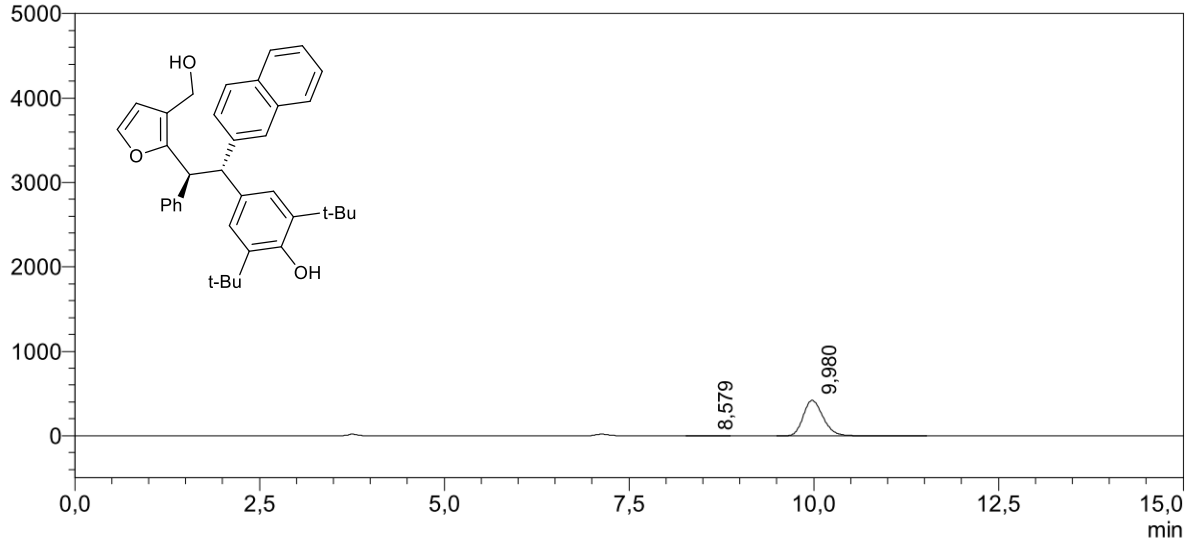
Peak#	Ret. Time	Area%
1	7,830	1,071
2	8,464	98,929
Total		100,000

2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(3-(hydroxymethyl)furan-2-yl)-1-(naphthalen-2-yl)-2-phenylethyl)phenol (4e)

Racemic sample



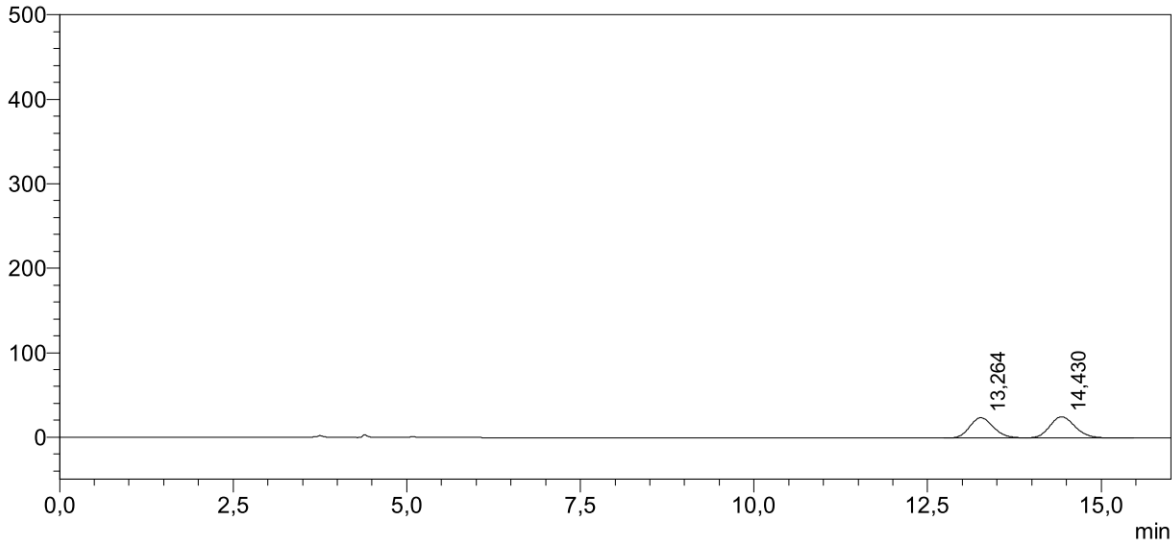
Enantiomerically enriched sample



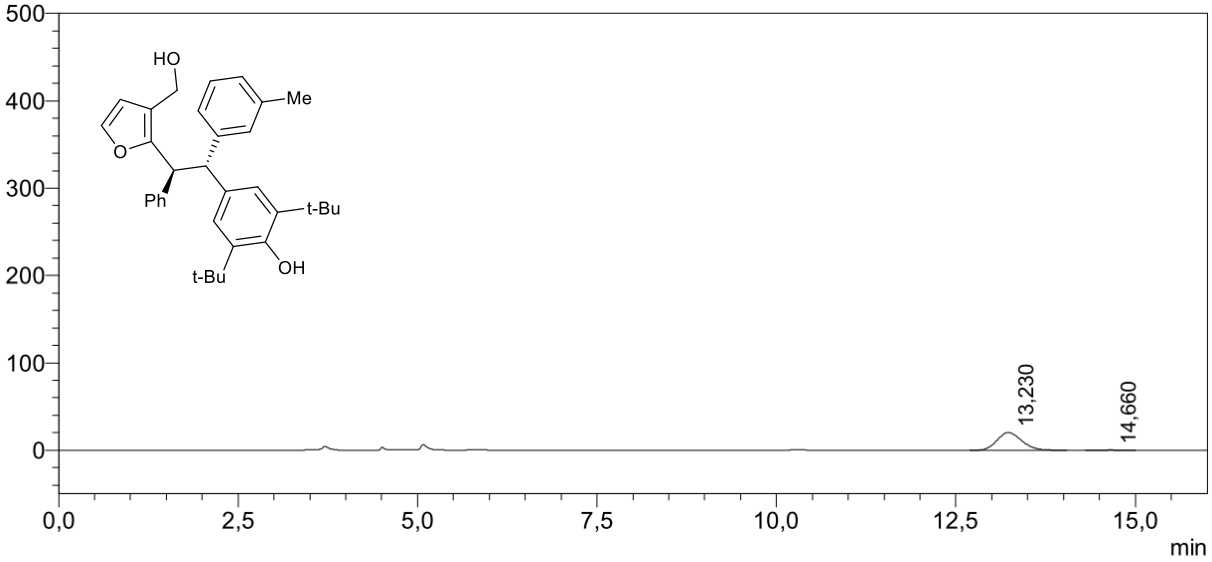
Peak#	Ret. Time	Area%
1	8,579	0,187
2	9,980	99,813
Total		100,000

2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(3-(hydroxymethyl)furan-2-yl)-2-phenyl-1-(m-tolyl)ethyl)phenol (4f)

Racemic sample



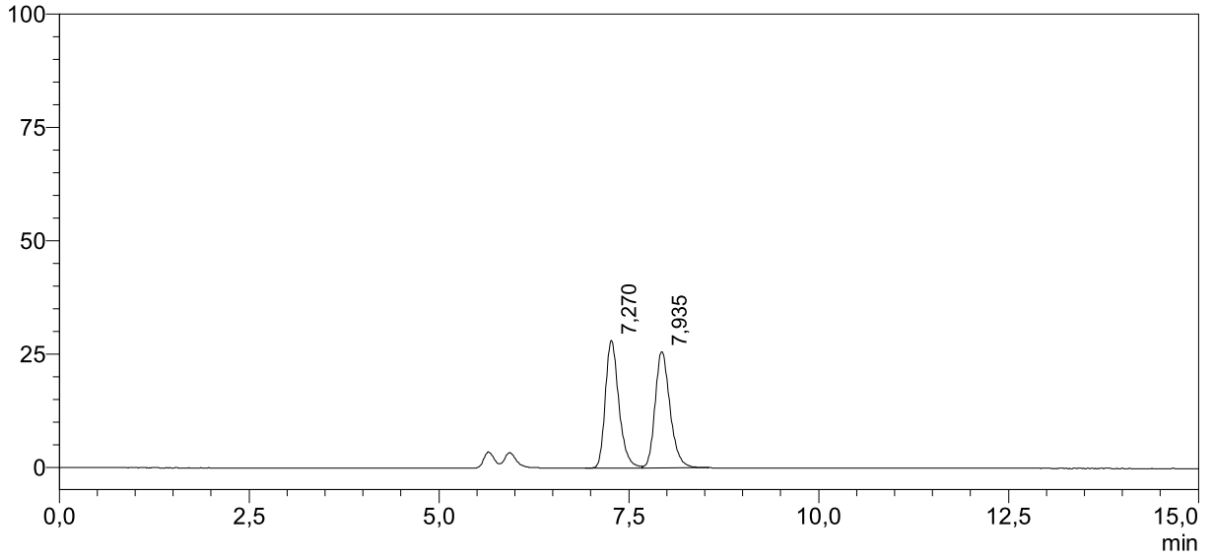
Enantiomerically enriched sample



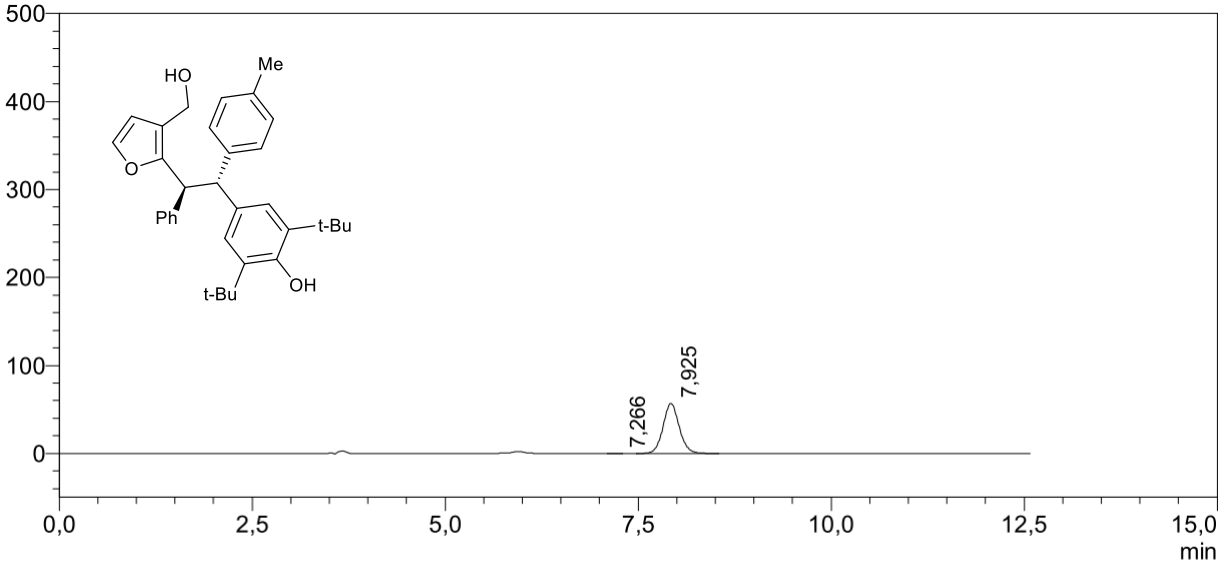
Peak#	Ret. Time	Area%
1	13,230	98,810
2	14,660	1,190
Total		100,000

2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(3-(hydroxymethyl)furan-2-yl)-2-phenyl-1-(*p*-tolyl)ethyl)phenol (4g)

Racemic sample



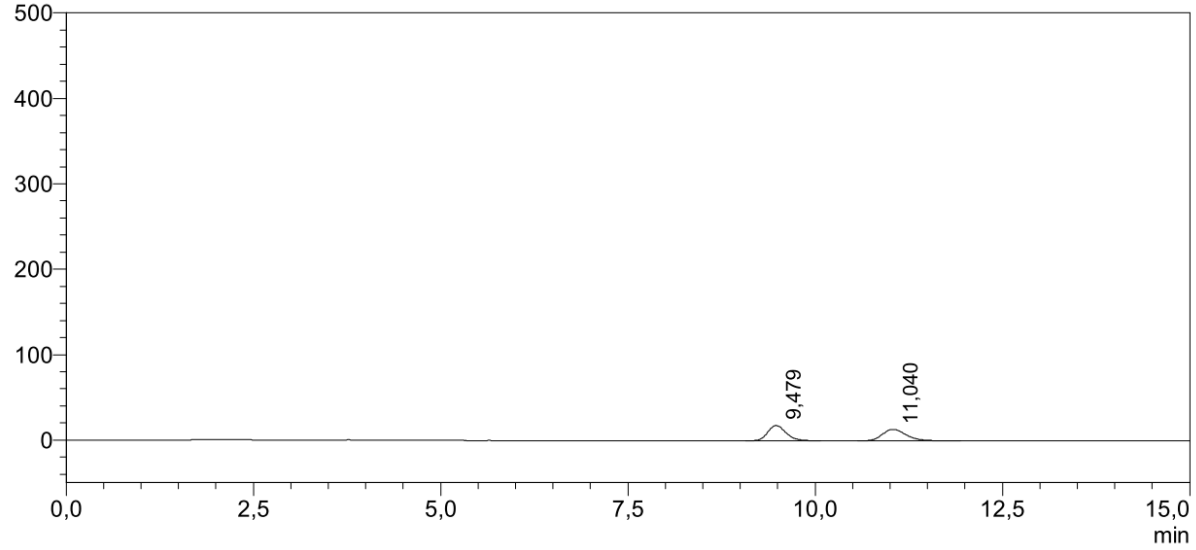
Enantiomerically enriched sample



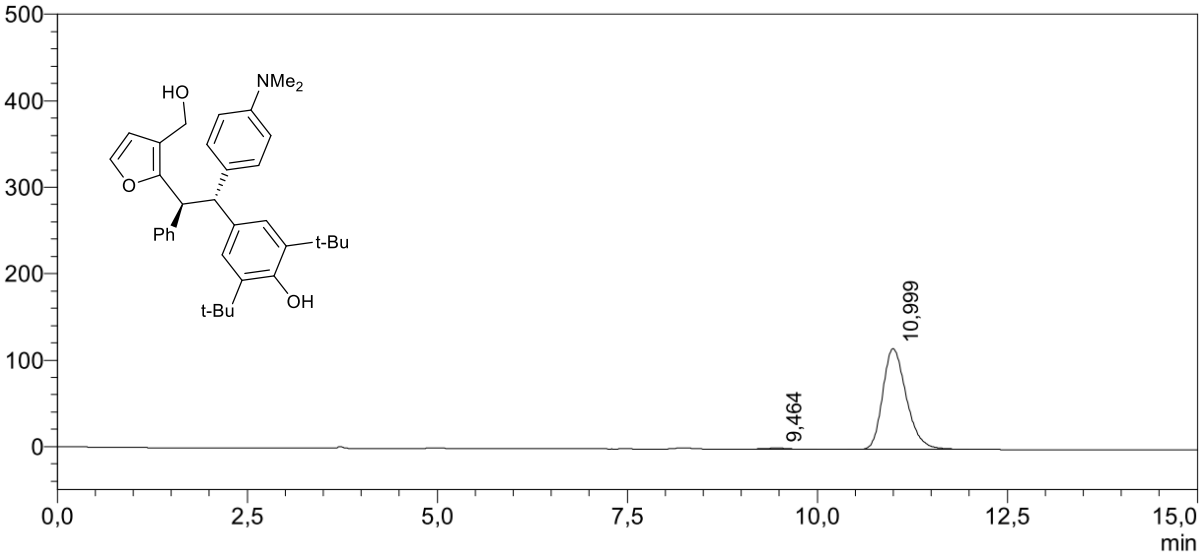
Peak#	Ret. Time	Area%
1	7,266	0,009
2	7,925	99,991
Total		100,000

2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-1-(4-(dimethylamino)phenyl)-2-(3-(hydroxymethyl)furan-2-yl)-2-phenylethyl)phenol (4h)

Racemic sample



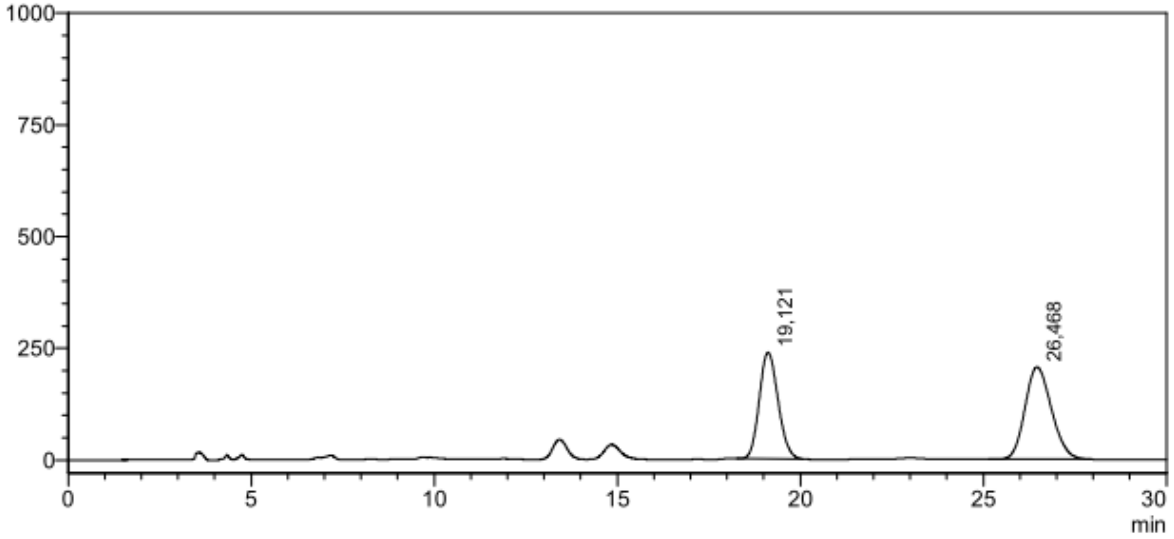
Enantiomerically enriched sample



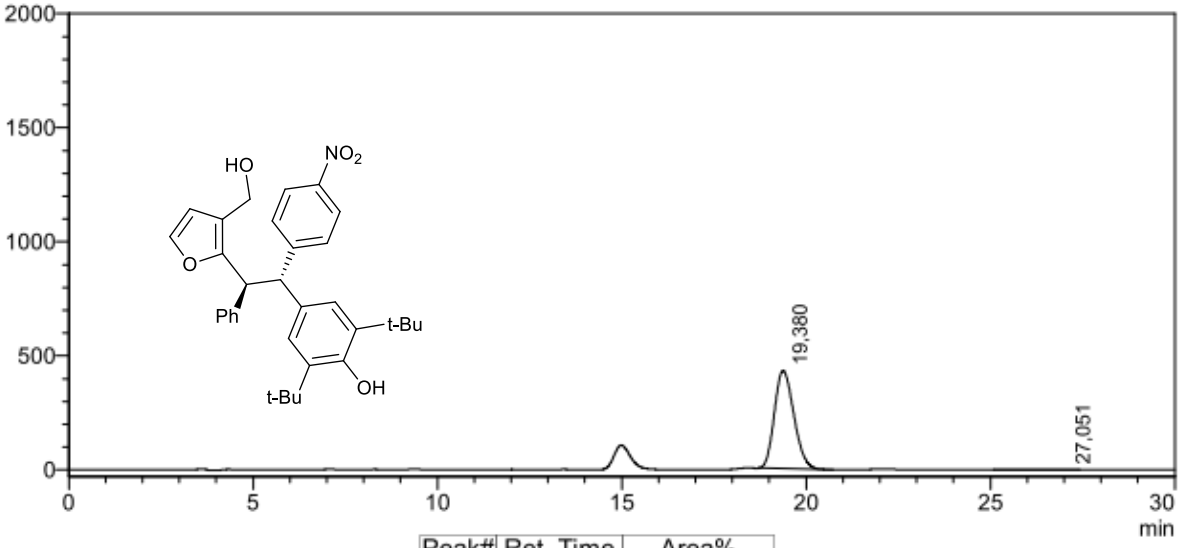
Peak#	Ret. Time	Area%
1	9,464	0,871
2	10,999	99,129
Total		100,000

2,6-di-tert-butyl-4-((1R,2S)-2-(3-(hydroxymethyl)furan-2-yl)-1-(4-nitrophenyl)-2-phenylethyl)phenol (4i)

Racemic sample



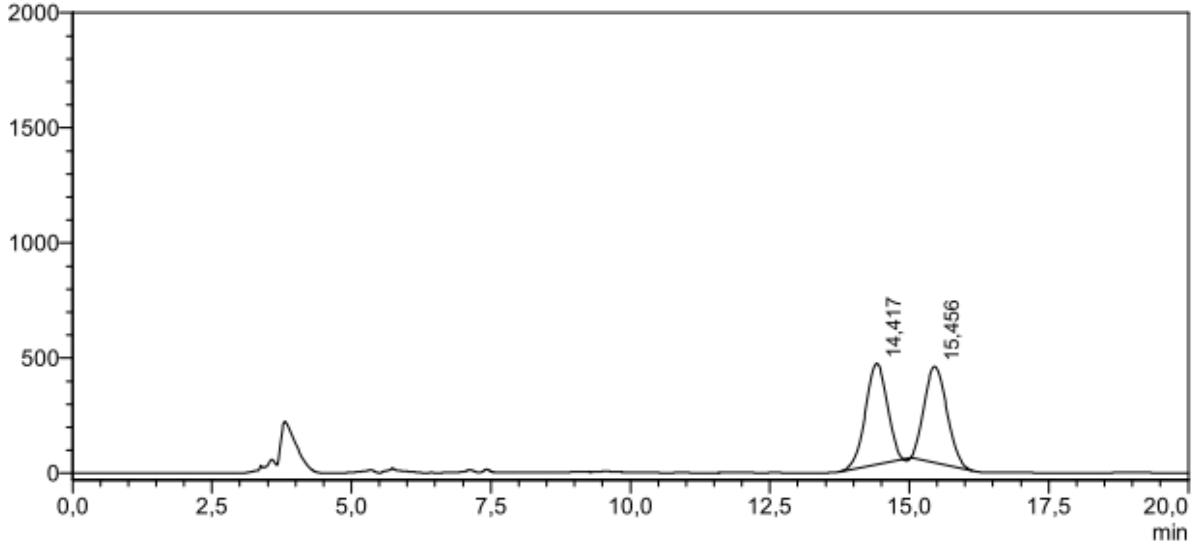
Enantiomerically enriched sample



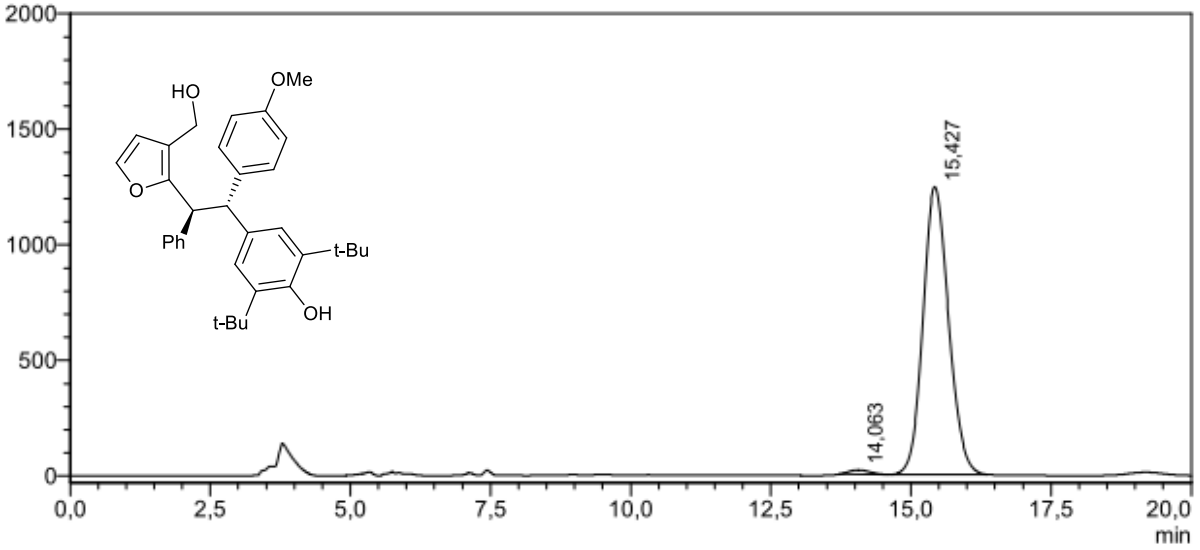
Peak#	Ret. Time	Area%
1	19,380	99,988
2	27,051	0,012
Total		100,000

2,6-di-tert-butyl-4-((1R,2S)-2-(3-(hydroxymethyl)furan-2-yl)-1-(4-methoxyphenyl)-2-phenylethyl)phenol (4j)

Racemic sample



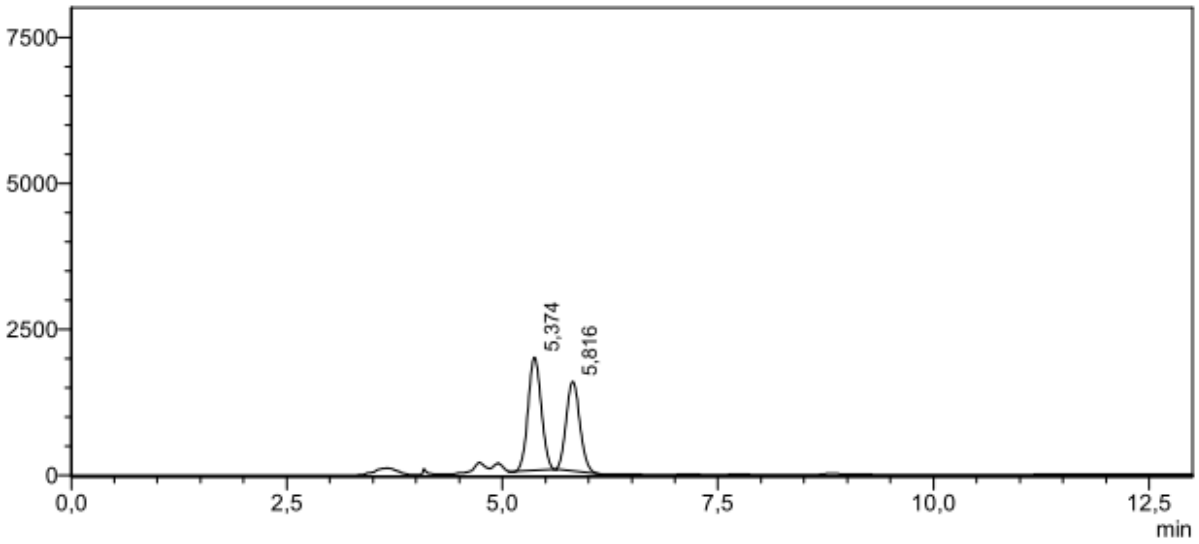
Enantiomerically enriched sample



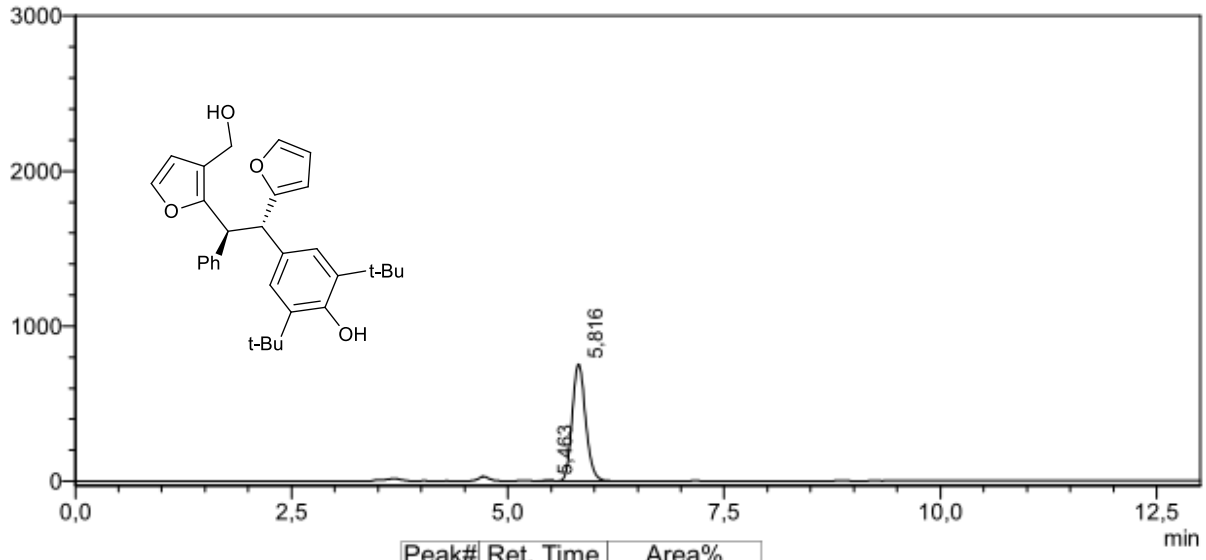
Peak#	Ret. Time	Area%
1	14,063	1,210
2	15,427	98,790
Total		100,000

2,6-di-tert-butyl-4-((1S,2S)-1-(furan-2-yl)-2-(3-(hydroxymethyl)furan-2-yl)-2-phenylethyl)phenol (4k)

Racemic sample



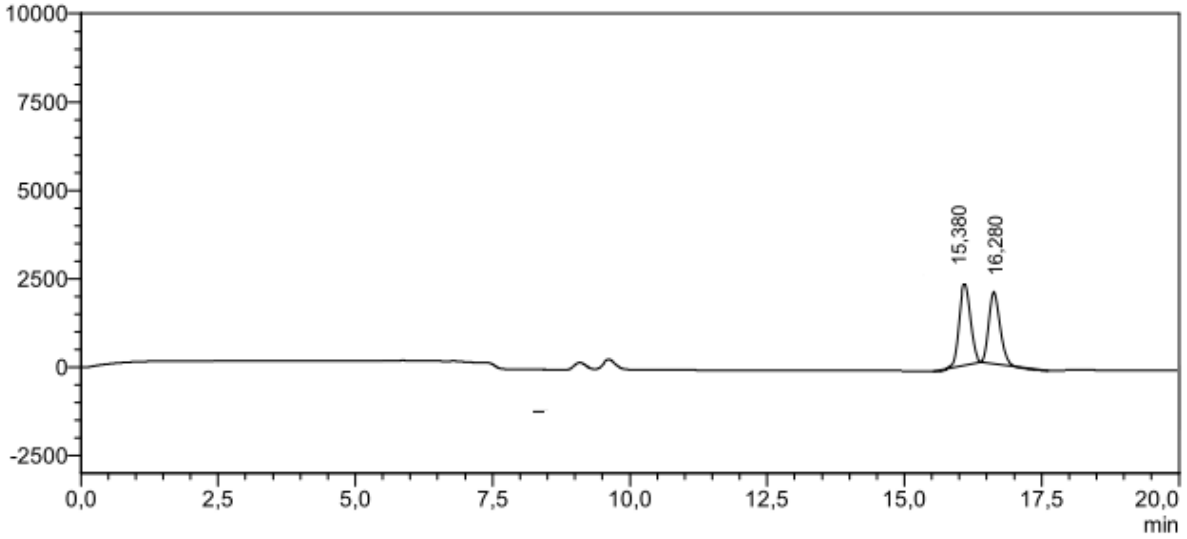
Enantiomerically enriched sample



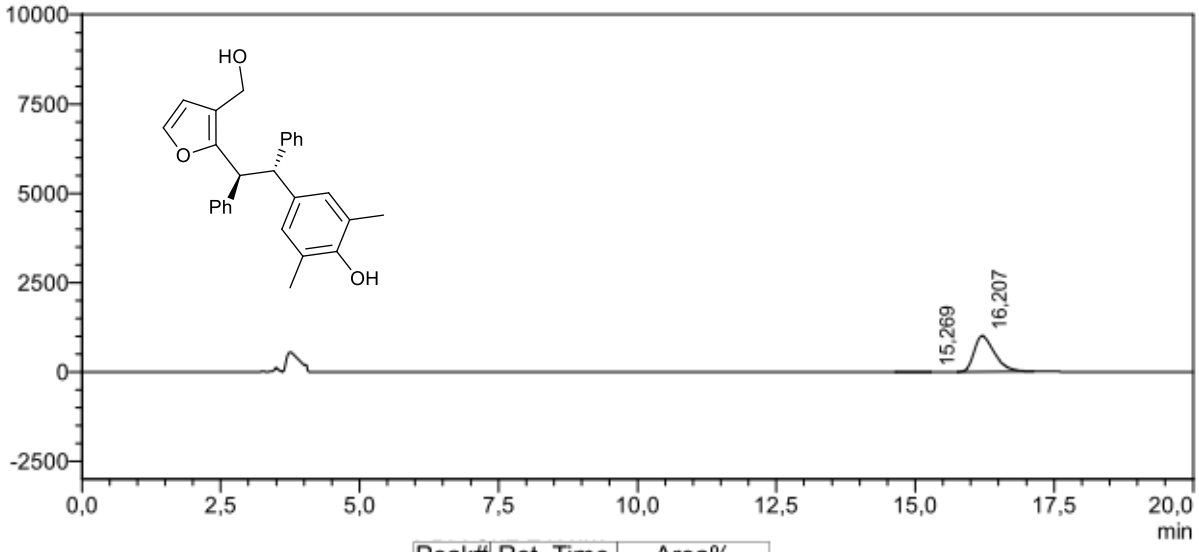
Peak#	Ret. Time	Area%
1	5,463	0,053
2	5,816	99,947
Total		100,000

4-((1R,2S)-2-(3-(hydroxymethyl)furan-2-yl)-1,2-diphenylethyl)-2,6-dimethylphenol (4l)

Racemic sample



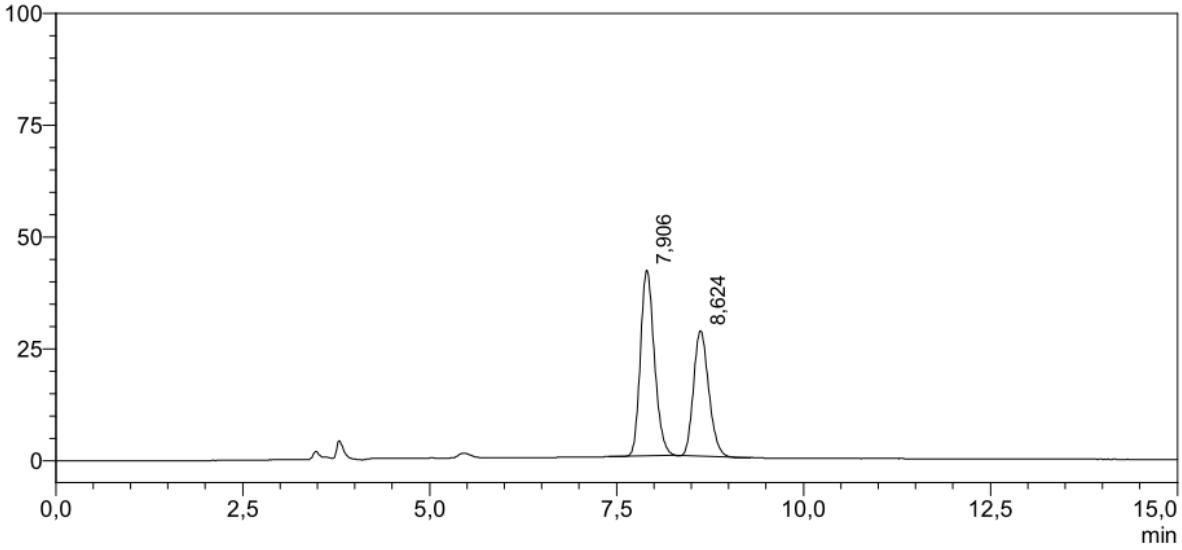
Enantiomerically enriched sample



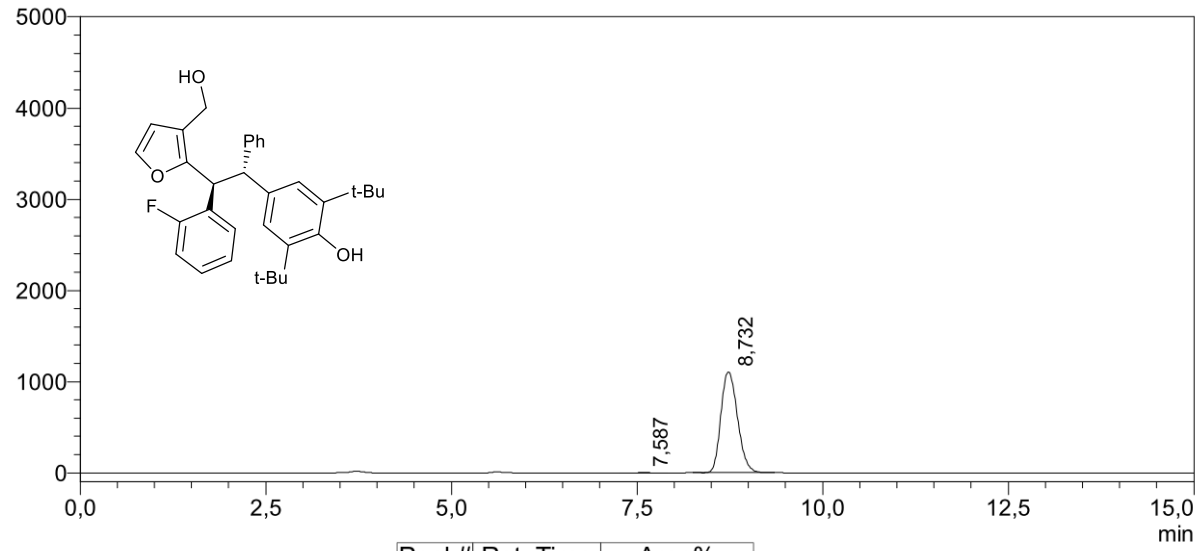
Peak#	Ret. Time	Area%
1	15,269	0,305
2	16,207	99,695
Total		100,000

2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(2-fluorophenyl)-2-(3-(hydroxymethyl)furan-2-yl)-1-phenylethyl)phenol (4m)

Racemic sample



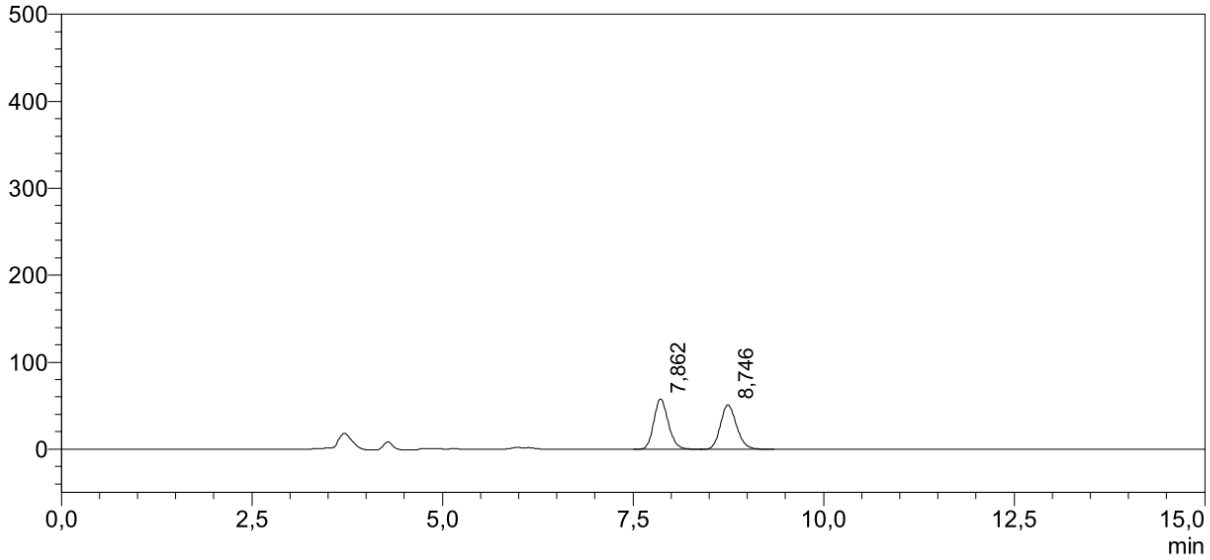
Enantiomerically enriched sample



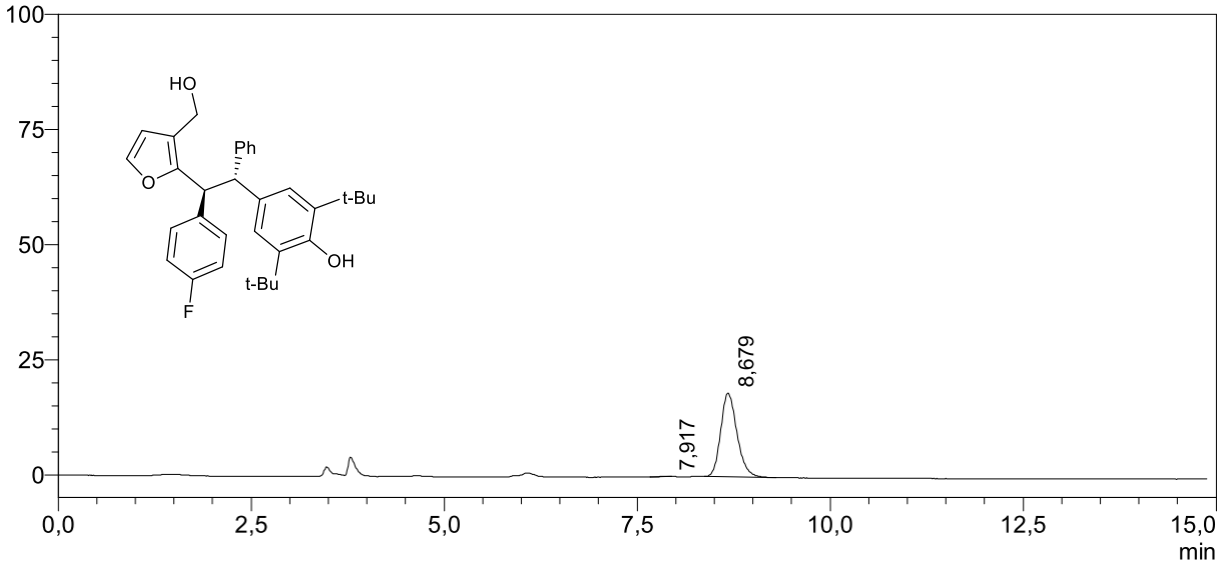
Peak#	Ret. Time	Area%
1	7,587	0,097
2	8,732	99,903
Total		100,000

2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(4-fluorophenyl)-2-(3-(hydroxymethyl)furan-2-yl)-1-phenylethyl)phenol (4n)

Racemic sample



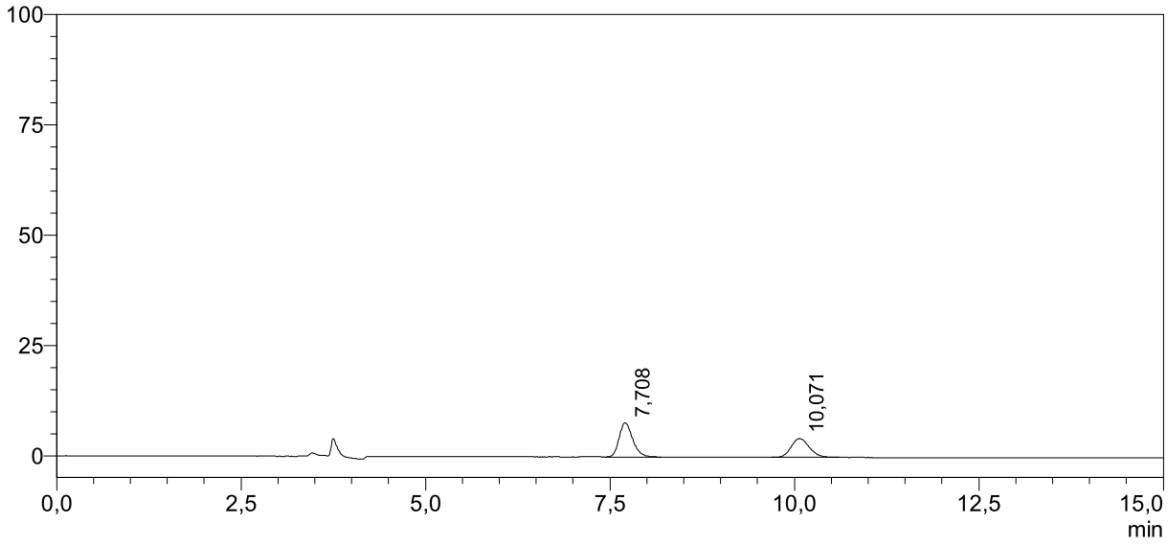
Enantiomerically enriched sample



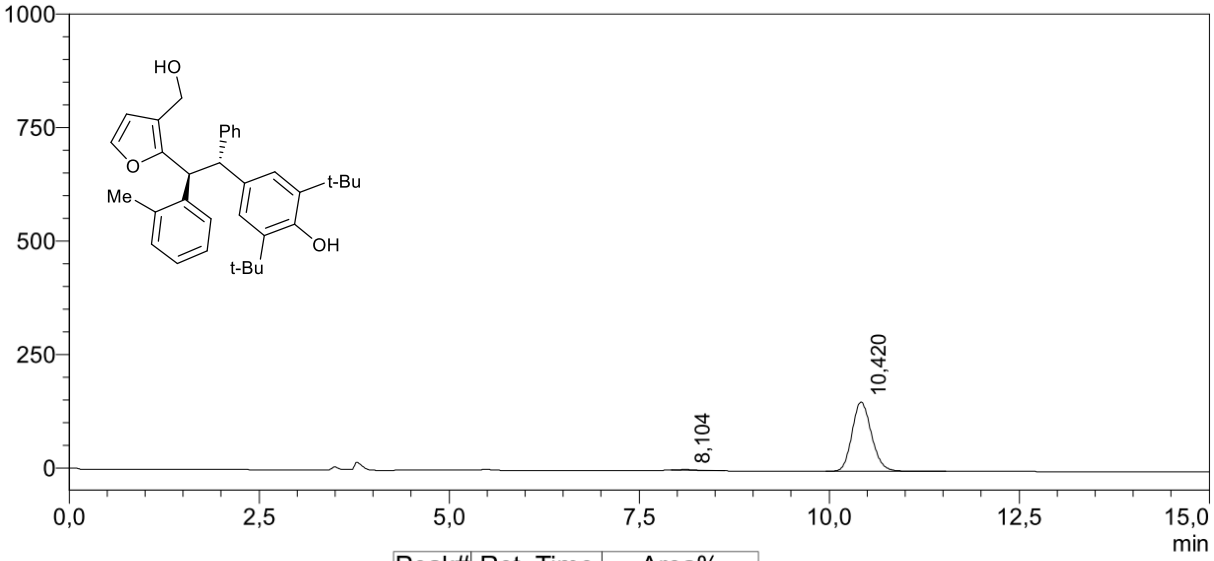
Peak#	Ret. Time	Area%
1	7,886	0,569
2	8,679	99,431
Total		100,000

2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(3-(hydroxymethyl)furan-2-yl)-1-phenyl-2-(o-tolyl)ethyl)phenol (4o)

Racemic sample



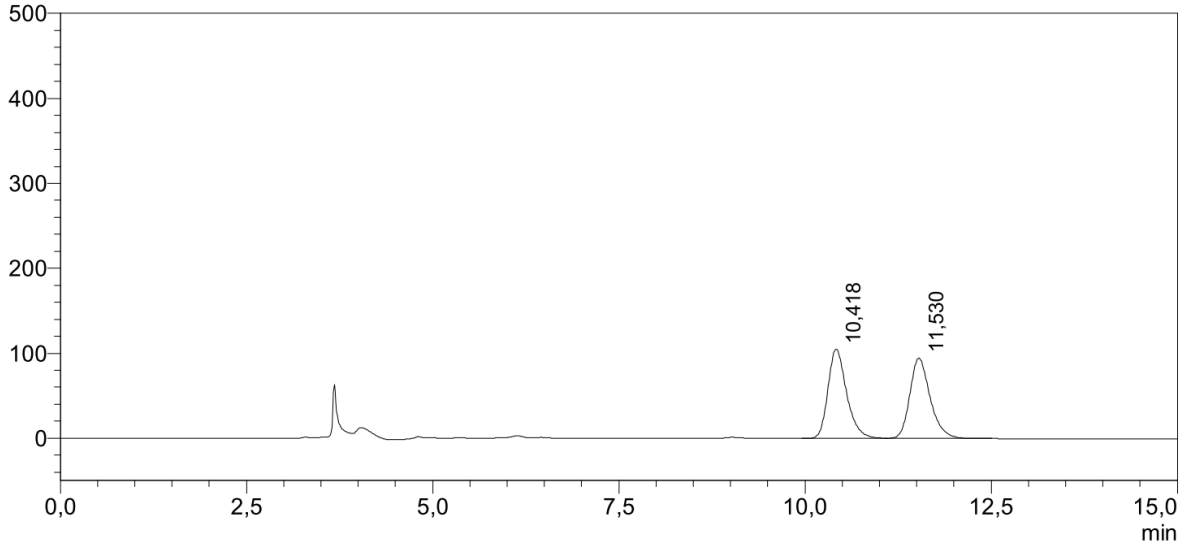
Enantiomerically enriched sample



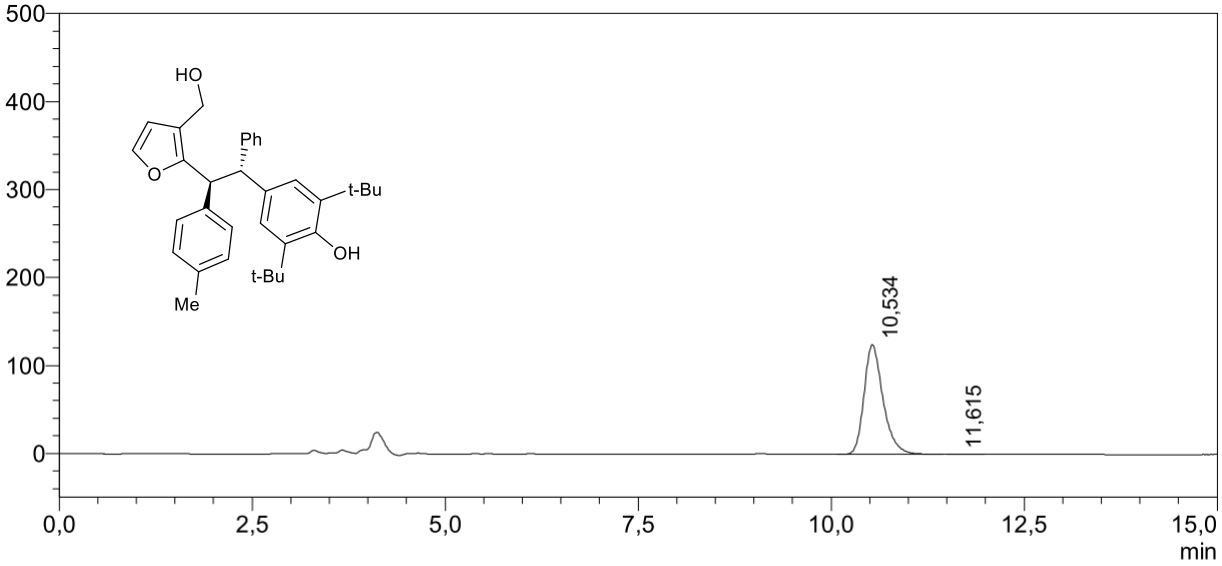
Peak#	Ret. Time	Area%
1	8,104	0,559
2	10,420	99,441
Total		100,000

2,6-Di-*tert*-butyl-4-((1*R*,2*S*)-2-(3-(hydroxymethyl)furan-2-yl)-1-phenyl-2-(*p*-tolyl)ethyl)phenol (4p)

Racemic sample



Enantiomerically enriched sample

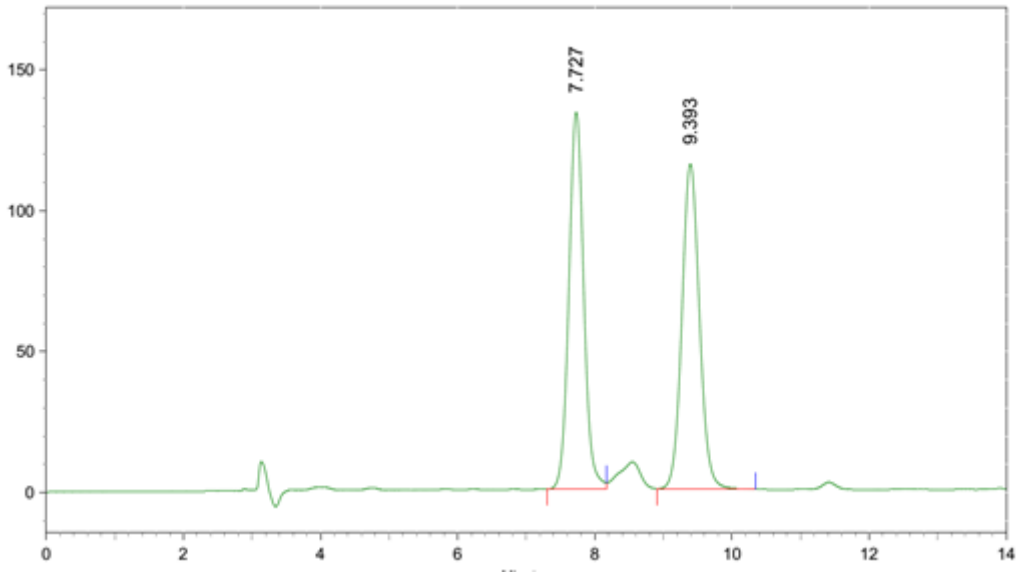


Peak#	Ret. Time	Area%
1	10,534	99,973
2	11,615	0,027
Total		100,000

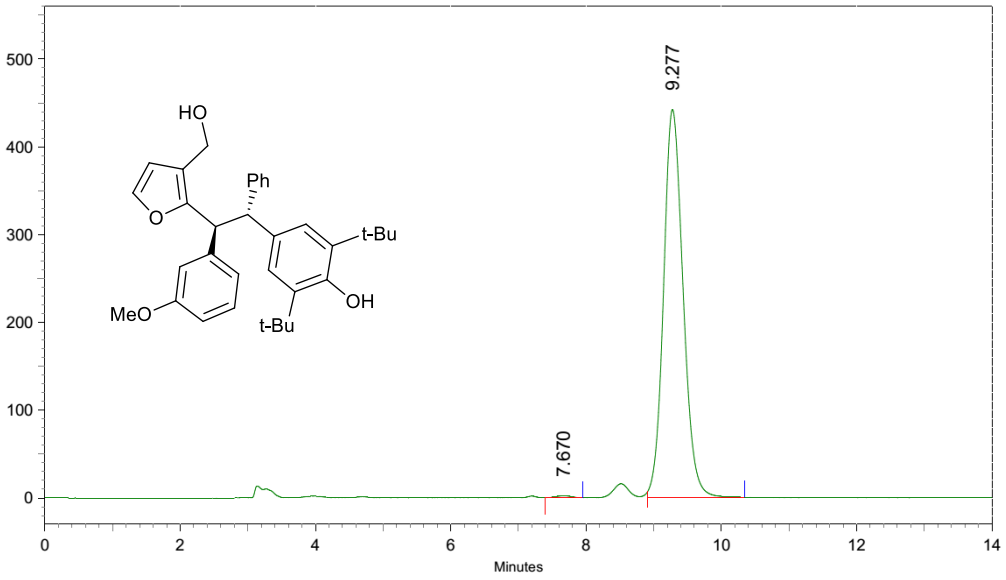
2,6-Di-*tert*-butyl-4-((1R,2S)-2-(3-(hydroxymethyl)furan-2-yl)-2-(3-methoxyphenyl)-1-phenylethyl)phenol (4q)

Major diastereoisomer

Racemic sample



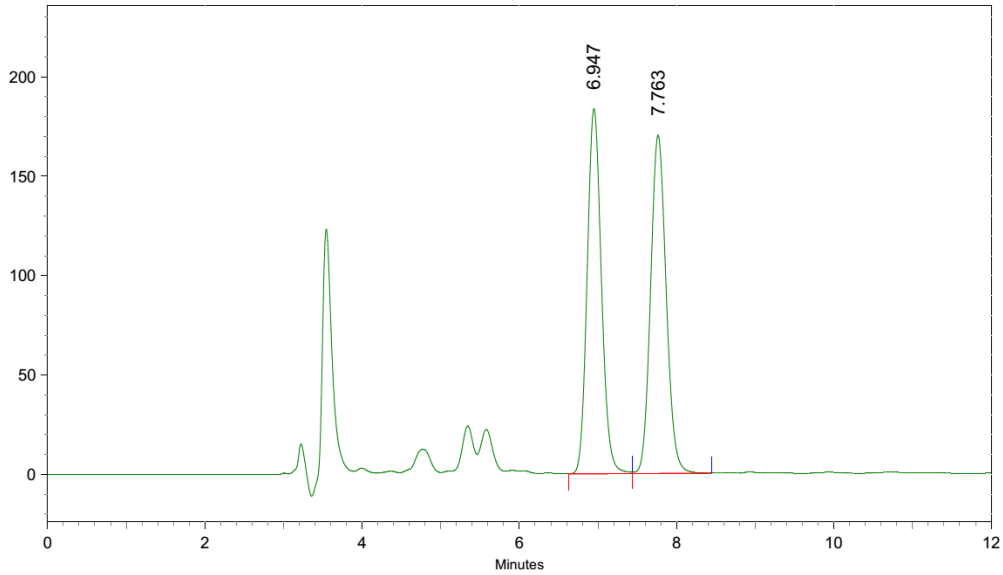
Enantiomerically enriched sample



Peak No.	Ret Time	Width	Height	Area	Area [%]
1	7.670	0.563	37588	570918	0.3833
2	9.277	1.427	7412651	148370240	99.6167

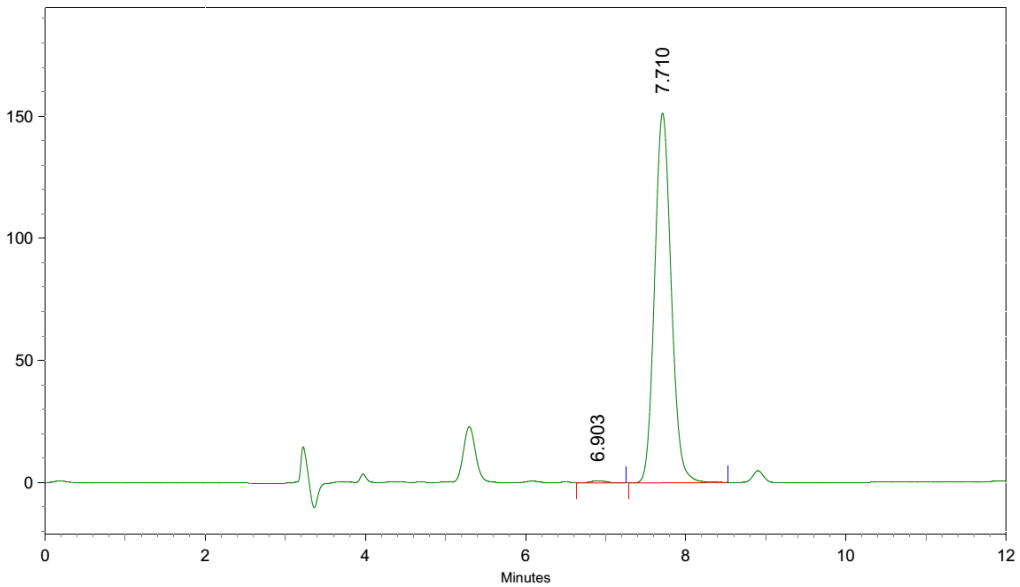
Minor diastereoisomers

Racemic sample



Peak No.	Ret Time	Width	Height	Area	Area [%]
1	6.947	0.813	3082708	38682219	49.5614
2	7.763	1.000	2856862	39366811	50.4386

Enantiomerically enriched sample



Peak No.	Ret Time	Width	Height	Area	Area [%]
1	6.903	0.617	14910	202173	0.5508
2	7.710	1.233	2539217	36499886	99.4492