Supplementary Information (SI) for Catalysis Science & Technology.

Supporting Information

Aluminosilicate-Mediated $C(sp^2)$-H Alkylation of Furans using Allylic Alcohols

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1. General Experimental

1.1 General Considerations

Chemicals and solvents were purchased from the following suppliers and used as received: furan (Sigma Aldrich); 2-methylfuran (Merck); 2-ethylfuran (Sigma Aldrich); 2,5-dimethylfuran (Sigma Aldrich); 2,3-dimethylfuran (Sigma Aldrich); methyl-2-furoate (TCI); furfural (TCI); 2-acetylfuran (TCI); benzofuran (TCI); allyl alcohol (Thermo Scientific); cinnamyl alcohol (Acros Organics); prenol (sigma Aldrich); geraniol (Sigma Aldrich); phytol (Sigma Aldrich); tetrahydrofuran (Sigma Aldrich); 1,2-dimethoxyethane (Beantown Chemical); toluene (Thermo Scientific); 1,2-dichloroethane (Acros Organics); ethyl acetate (Sigma Aldrich); hexane (Honeywell); 1,3,5-trimethoxybenzene (Thermo Scientific); Amberlyst 15 (Sigma Aldrich); Perlkat 46-10 (BASF); zeolites (Zeolyst, except mordenite-type CBV90A purchased from PQ).

1.2 Chromatography

Flash column chromatography was carried out using Thermo Scientific silica gel 60 (0.036-0.071 mm). TLC was carried out using Merck silica gel 60 F_{254} aluminum-backed plates and visualized using a combination of UV light at 254 nm and iodine.

1.3 NMR Spectroscopy

All spectra were recorded on a Bruker Ascend™ 400 MHz spectrometer and obtained at room temperature. CDCl3 with 1% tetramethylsilane (TMS) was purchased from Beantown Chemical. The chemical shifts (δ) are recorded in parts per million (ppm). Coupling constants (*J*) are recorded in hertz (Hz). Multiplicities (reported using the standard nomenclature s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, sex. = sextet, hept. = heptet, non. = nonet, m = multiplet, br. s = broad singlet, app. = apparent and coupling constants are reported where applicable.^{1}H- and ^{13}C{^{1}H}-NMR spectra were referenced relative to TMS.

1.4 Gas Chromatography Mass Spectrometry

Carried out using an Agilent 8890 GC system equipped with an Agilent 5977B MSD detector and a Polyarc system. The Polyarc system is a catalytic microreactor that converts all organic compounds to methane after chromatographic separation and prior to detection by FID and provides a universal and uniform carbon response with a 7-order of magnitude linear range. No internal or external standard is needed with the Polyarc system. As such, percentages of each component in products are based on the area percent of FID signals. The column used was an Agilent CP-Sil 5 CB (30 m; 0.25 mm; 0.25 µm). Samples were diluted in ethyl acetate for analysis. Details of method used: 0.5 µl injection; injection temperature 300 °C; 45 °C (5 minute hold), ramp rate of 40 °C/min to an end temperature of 300 °C (5 or 30 minute hold); 4 minute solvent delay for MS.

2. Experimental Procedures

2.1 Optimization of Reaction Conditions for Coupling of Furan and Phytol

Phytol (0.59 ml; 0.50 g; 1.7 mmol) added to a 20 mL scintillation vial containing the solid catalyst and a magnetic stirrer bar, followed immediately by the addition of furan (1.2 mL; 16.5 mmol). The vial was subsequently sealed and placed to stir at 25 °C for 16 h, after which time 1,3,5-trimethoxybene (95 mg; 0.56 mmol; 33 mol%) was added and stirred to dissolve. An aliquot was removed, diluted with $CDCl_3$ and filtered for analysis by ^1H-NMR spectroscopy. Reported yields were determined by ^1H-NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Catalyst	Loading (wt%)	Residual Phytol (%)	Allylic Furan product (%)
CBV720CY	50	-	92
CBV720CY	25	9	81
CBV760	50	-	93
CBV90A	50	25	62
CBV8014CY	50	101	-
CBV3024E	50	100	-
Perlkat 46-10	50	66	26
SiO_2	50	98	-
Al_2O_3	50	100	-
$NbOPO_4.xH_2O$	50	73	15
Amberlyst-15	50	-	78

2.2 Optimization of Reaction Conditions for Coupling of 2-Methylfuran and Phytol

Phytol (0.59 ml; 0.50 g; 1.7 mmol) added to a 20 mL scintillation vial containing the solid catalyst and a magnetic stirrer bar, followed immediately by the addition of 2-methylfuran (1.5 mL; 16.6 mmol). The vial was subsequently sealed and placed to stir at the relevant temperature for 16 h, after which time it was allowed to cool to room temperature before adding 1,3,5-trimethoxybene (95 mg; 0.56 mmol; 33 mol%) and stirred to dissolve. An aliquot was removed, diluted with $CDCl_3$ and filtered for analysis by ^1H-NMR spectroscopy. Reported yields were determined by ^1H-NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Catalyst	Loading (wt%)	Temperature (°C)	Residual Phytol (%)	3-Allyl Furan product (%)	5-Allyl Furan product (%)
CBV720CY	50	25	95	-	3
CBV760	50	25	97	-	2
CBV90A	50	25	80	5	7
Perlkat 46-10	50	25	85	3	6
$NbOPO_4.xH_2O$	50	25	73	3	7
Amberlyst-15	50	25	-	9	35
Amberlyst-15	25	25	23	8	30
Amberlyst-15	10	25	47	6	15

Amberlyst-15	5	25	71	3	8
CBV720CY	50	40	91	-	5
CBV760	50	40	85	-	8
CBV90A	50	40	44	11	18
Perlkat 46-10	50	40	34	9	30
$NbOPO_4.xH_2O$	50	40	58	6	14
Amberlyst-15	25	40	9	11	39
CBV720CY	50	60	75	4	9
CBV760	50	60	19	8	30
CBV90A	50	60	11	19	35
Perlkat 46-10	50	60	-	14	51
Perlkat 46-10	25	60	-	14	50
Perlkat 46-10	10	60	21	9	36
$NbOPO_4.xH_2O$	50	60	11	10	33
Amberlyst-15	10	60	-	12	41

2.3 Solvent Optimization for Coupling of 2-Methylfuran and Phytol

Phytol (0.59 ml; 0.50 g; 1.7 mmol) added to a 20 mL scintillation vial containing Perlkat 46-10 (125 mg; 73.5 mg/mmol) and a magnetic stirrer bar, followed immediately by the addition of solvent (0.5-2.0 mL) and then 2-methylfuran (1.5 mL; 16.6 mmol). The vial was subsequently sealed and placed to stir at 60 °C for 18 h, after which time it was allowed to cool to room temperature before adding 1,3,5-trimethoxybene (95 mg; 0.56 mmol; 33 mol%) and stirred to dissolve. An aliquot was removed, diluted with $CDCl_3$ and filtered for analysis by ^{1}H-NMR spectroscopy. Reported yields were determined by ^{1}H-NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

Solvent	Equivalents 2-Methylfuran	Solvent Volume (mL)	Residual Phytol (%)	3-Allyl Furan product (%)	5-Allyl Furan product (%)
THF	10	2	66	6	15
DME	10	2	66	5	15
Toluene	10	2	-	13	48
DCE	10	2	-	15	50
DCE	5	2	-	12	44
DCE	3	2	-	10	42
DCE	3	1	-	10	40
DCE	3	0.5	-	9	39
DCE	1.5	2	-	10	33

2.4 General Procedures

General procedure A: Coupling with furan

Relevant alcohol (1.7 mmol) was added to a 20 mL scintillation vial containing HSY zeolite (250 mg; 147 mg/mmol) and a magnetic stirrer bar, followed immediately by the addition of furan (1.2 mL; 17 mmol). The resulting suspension was stirred at 25 °C for 16 hours after which time it was concentrated in vacuo.

To the crude reaction mixture was then added hexane (circa 5 ml) and celite. The suspension was concentrated in vacuo and the resulting solid dry-loaded for flash column chromatography.

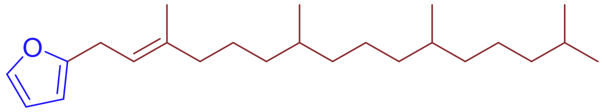
General procedure B: Coupling with furan-derivatives

1,2-dichloroethane (2 ml) was added to a vial containing Perlkat 46-10 (125 mg; 73.5 mg/mmol) and a magnetic stirrer bar, followed immediately by the addition of the relevant alcohol (1.7 mmol) and furan-derivative (17 mmol). The resulting suspension was stirred at 60 °C for 16 hours after which time it was allowed to cool to room temperature with stirring. Once cooled, stirring was ceased and the reaction allowed to settle, the mother-liquor siphoned off and residual solids washed with hexanes (2 × 1.5 ml). The combined 1,2-dichloroethane and hexanes fractions were concentrated in vacuo and the crude reaction mixture purified by flash column chromatography.

3. Characterization of Reaction Products

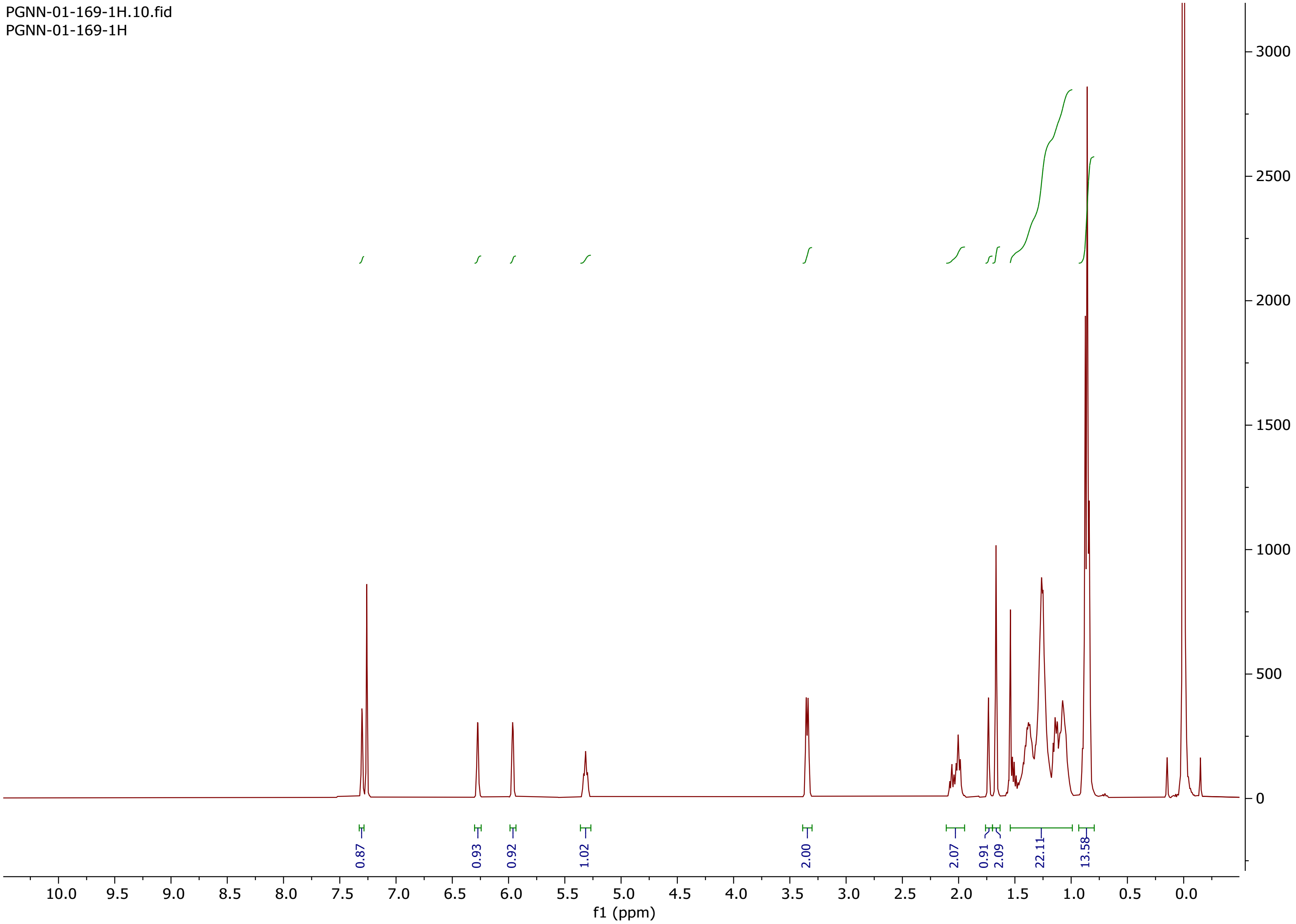
Phytol-furan product **3**

IUPAC name: (E)-2-(3,7,11,15-tetramethylhexadec-2-en-1-yl)furan

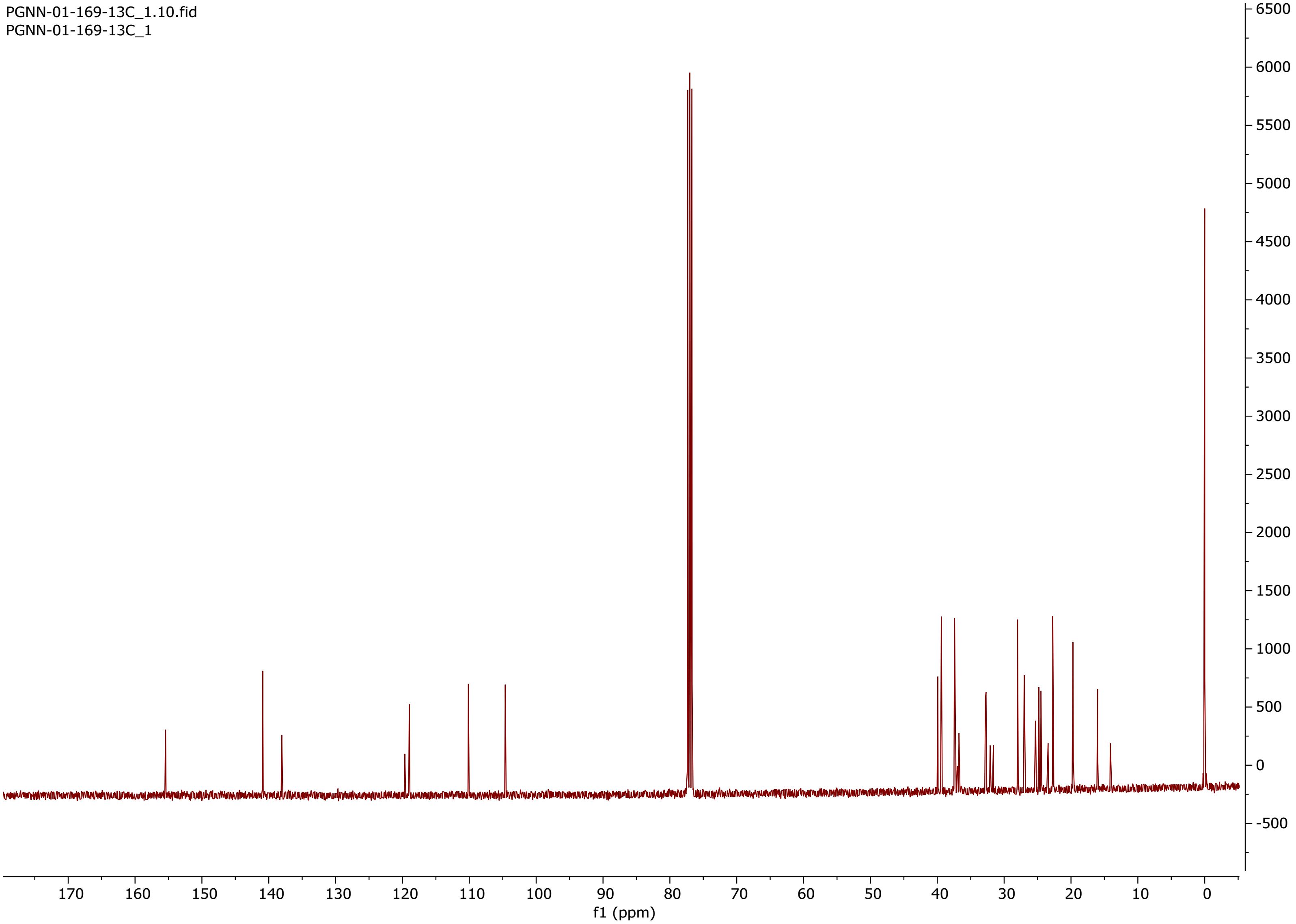


According to General Procedure A, phytol (0.59 mL; 1.7 mmol) was reacted with furan (1.2 mL; 16.5 mmol) in the presence of CBV720CY (250 mg). The crude reaction mixture was purified by flash column chromatography (circa 100 mL silica gel; hexanes) to give the product as a colorless oil (444 mg; 75%).

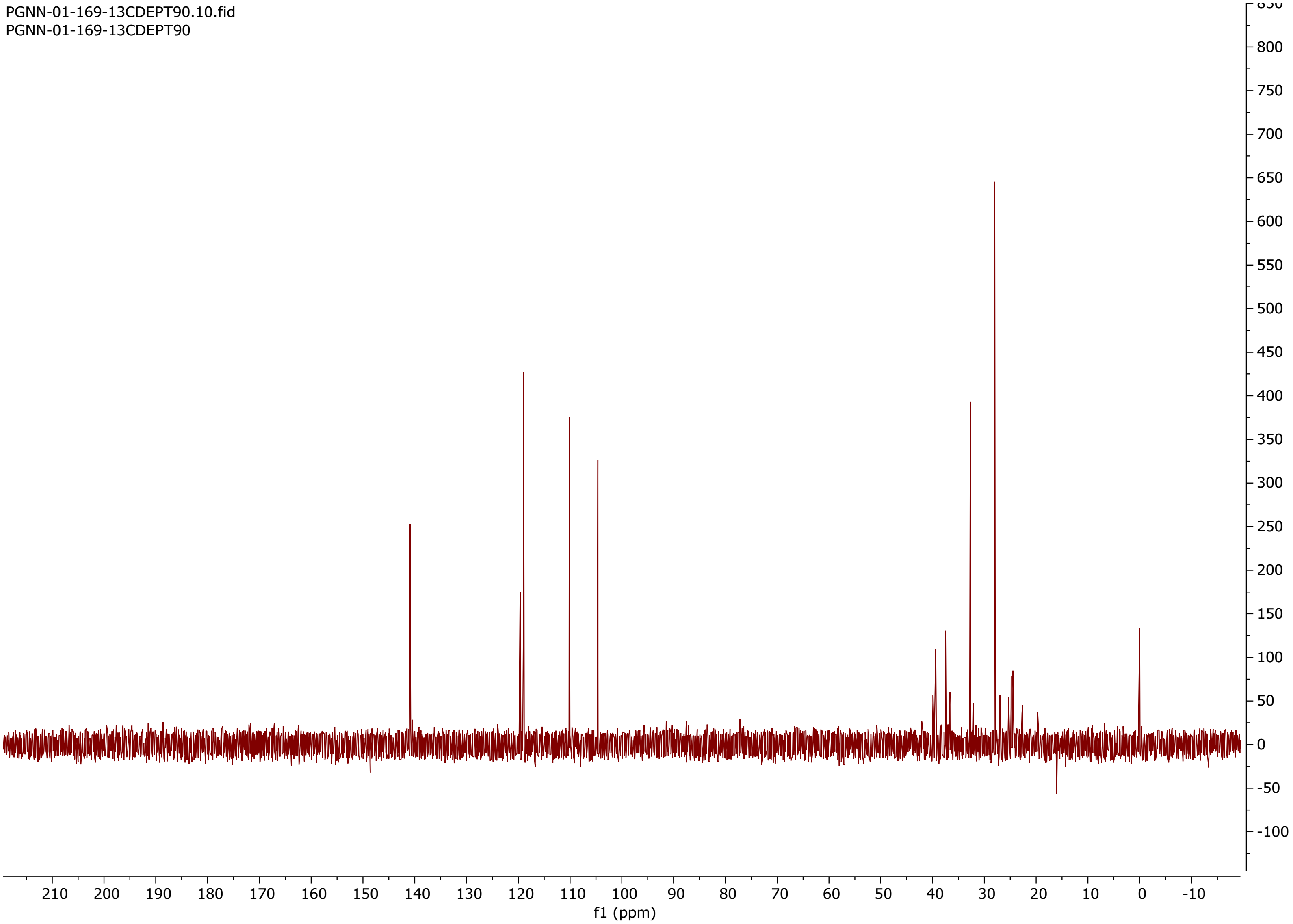
TLC:	Rf = 0.43 (hexane) [I_2]
^{1}H-NMR:	(400 MHz, $CDCl_3$)
	7.30 (app. s, 1H), 6.27 (app. s, 1H), 5.97 (app. s, 1H), 5.32 (t, *J* = 7.2 Hz, 1H), 3.35 (d, *J* = 7.2 Hz, 2H), 2.10 – 1.95 (m, 2H), 1.73 (s, 1H), 1.67 (s, 2H), 1.54 – 0.96 (m, 22H), 0. 92 – 0.81 (m, 12H).
^{13}C{^{1}H}-NMR:	(101 MHz, $CDCl_3$)
	155.44, 140.90, 138.05, 118.97, 110.14, 104.63, 39.91, 39.39, 37.41, 37.32, 37.01, 36.75, 32.73, 32.10, 31.61, 28.00, 27.00, 25.29, 24.82, 24.49, 23.43, 19.70, 16.02, 14.13.
GCMS:	14.531 min (29%; m/z 346.30); 14.668 (71%; m/z 346.31).



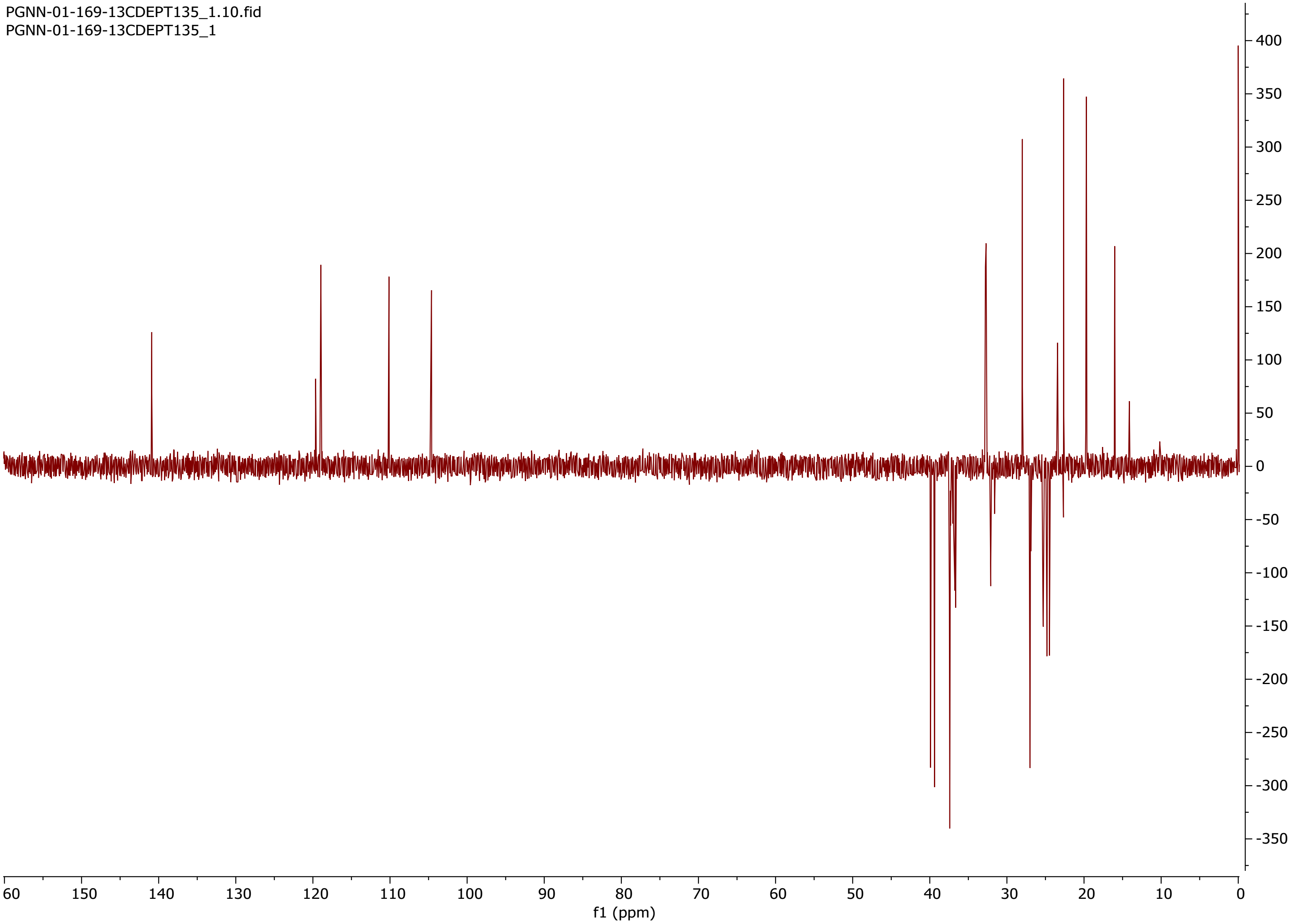
^{1}H-NMR spectrum of phytol-furan coupled product **3**.



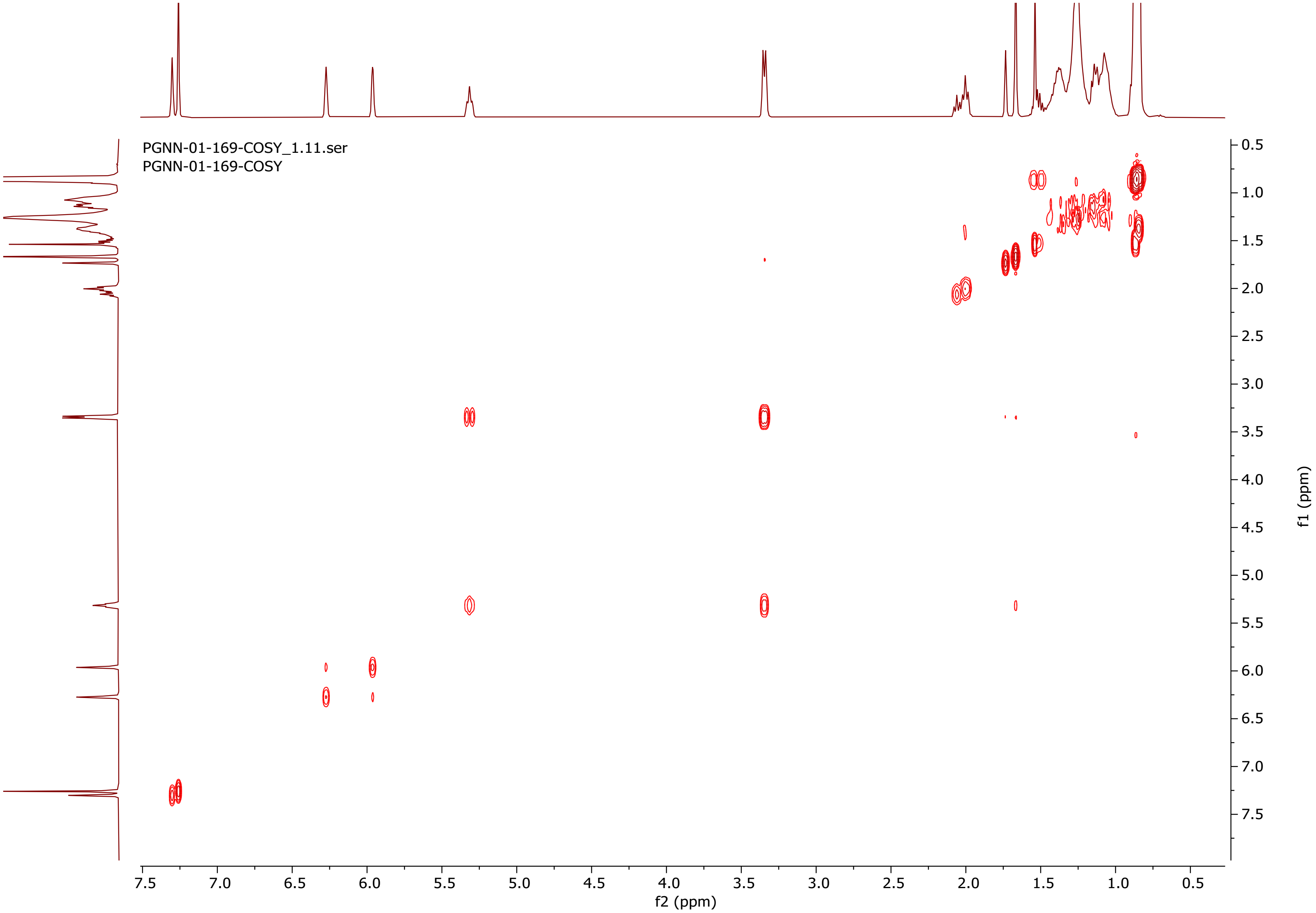
^{13}C-NMR spectrum of phytol-furan coupled product **3**.



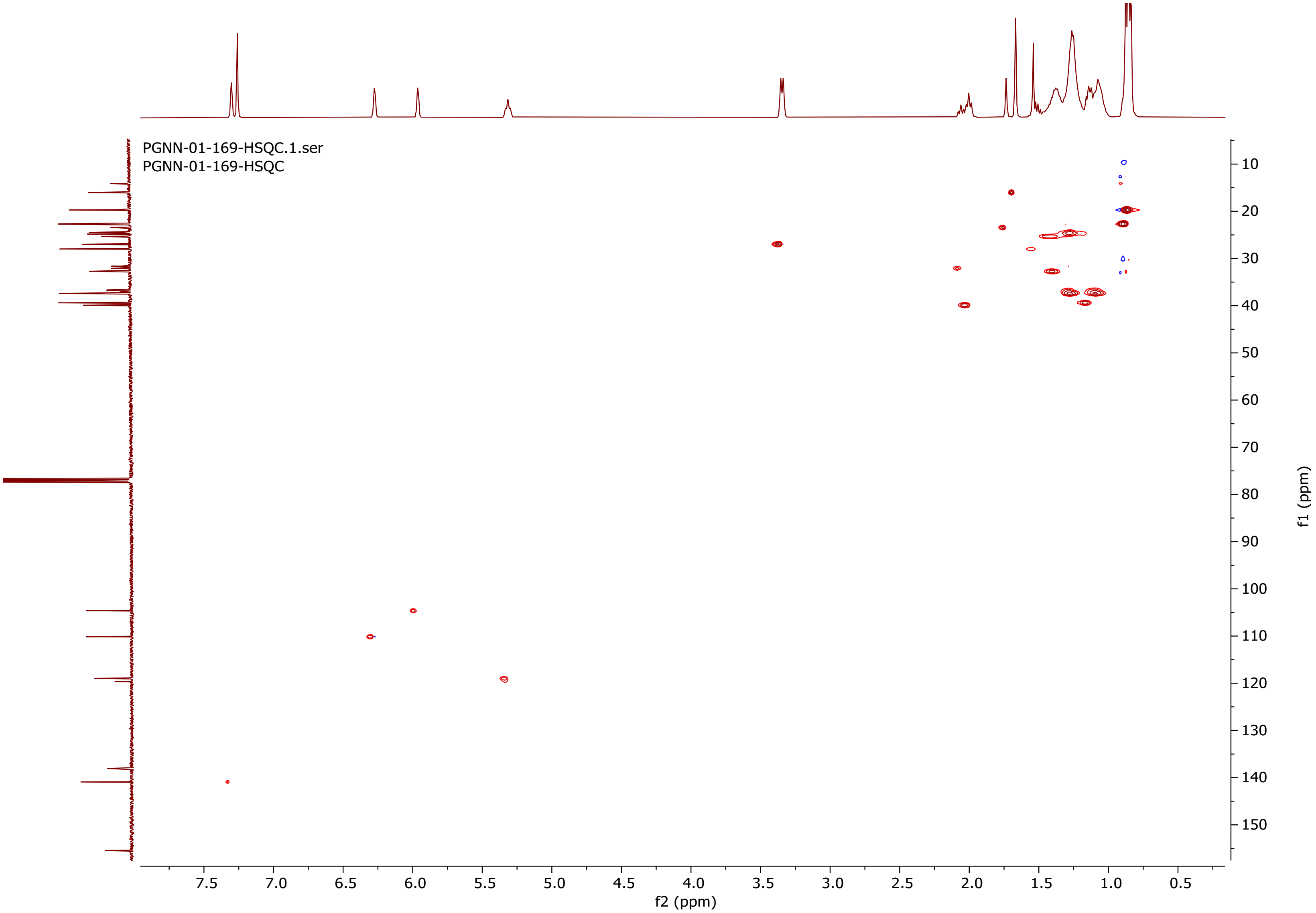
^{13}C-DEPT90-NMR spectrum of phytol-furan coupled product **3**.



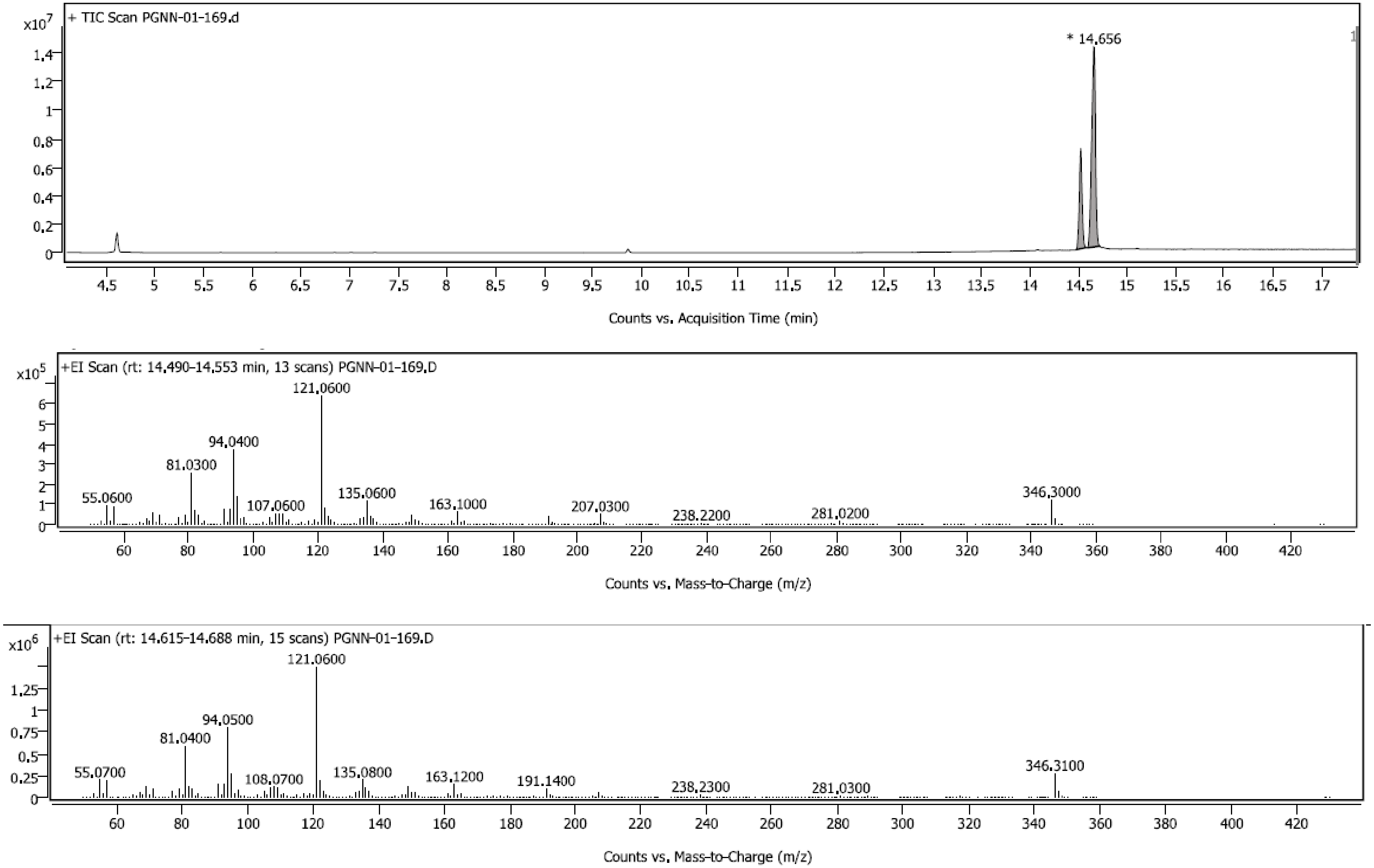
^{13}C-DEPT135-NMR spectrum of phytol-furan coupled product **3**.



COSY-NMR spectrum of phytol-furan coupled product **3**.



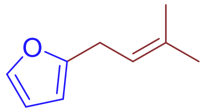
HSQC-NMR spectrum of phytol-furan coupled product **3**.



GCMS data of phytol-furan coupled product **3**.

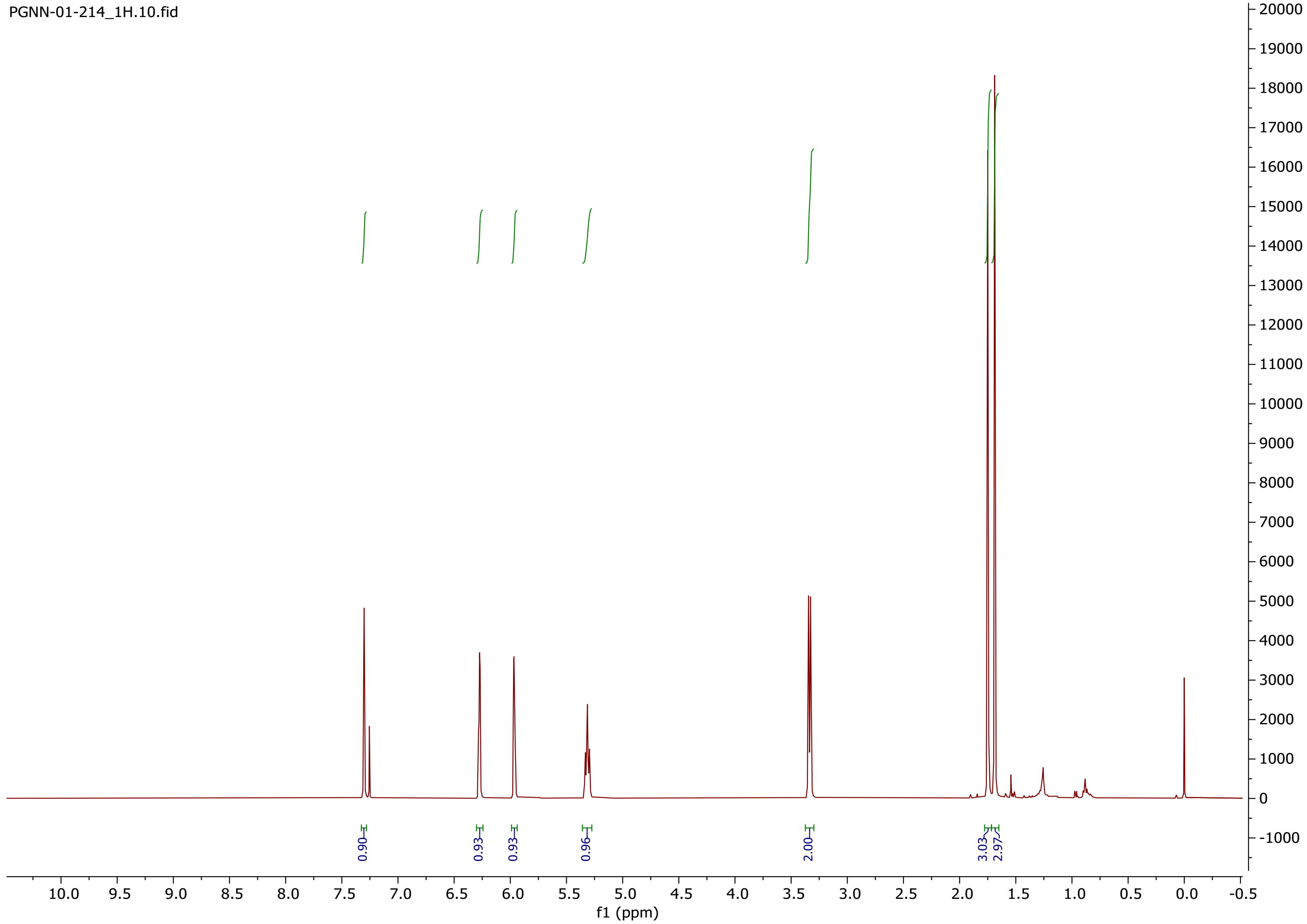
Prenol-furan product **4**

IUPAC name: 2-(3-methylbut-2-en-1-yl)furan

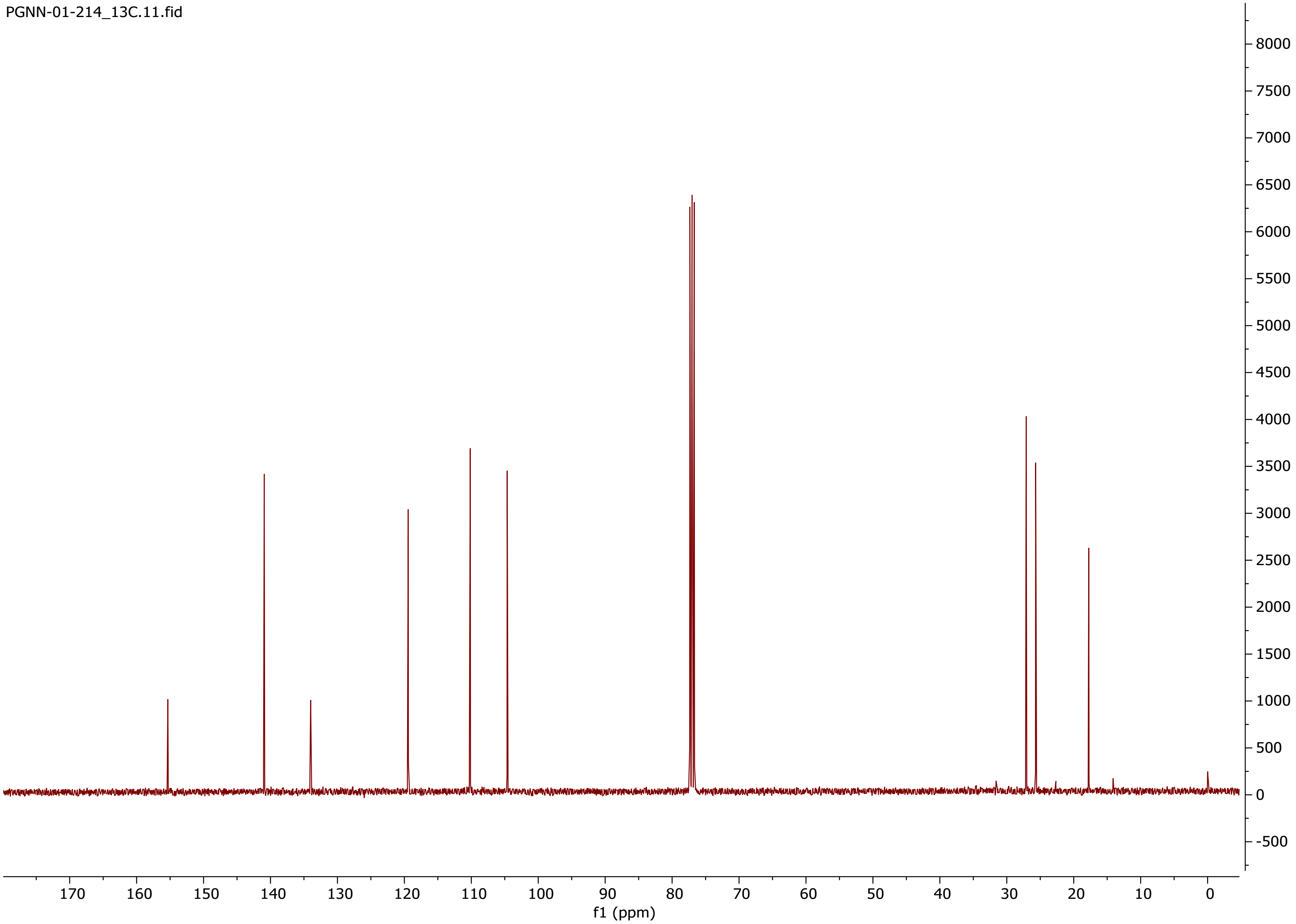


According to General Procedure A, prenol (0.17 mL; 1.7 mmol) was reacted with furan (1.2 mL; 16.5 mmol) in the presence of CBV720CY (250 mg). The crude reaction mixture was purified by flash column chromatography (circa 170 mL silica gel; hexanes) to give the product as a colorless oil (113 mg; 50%).

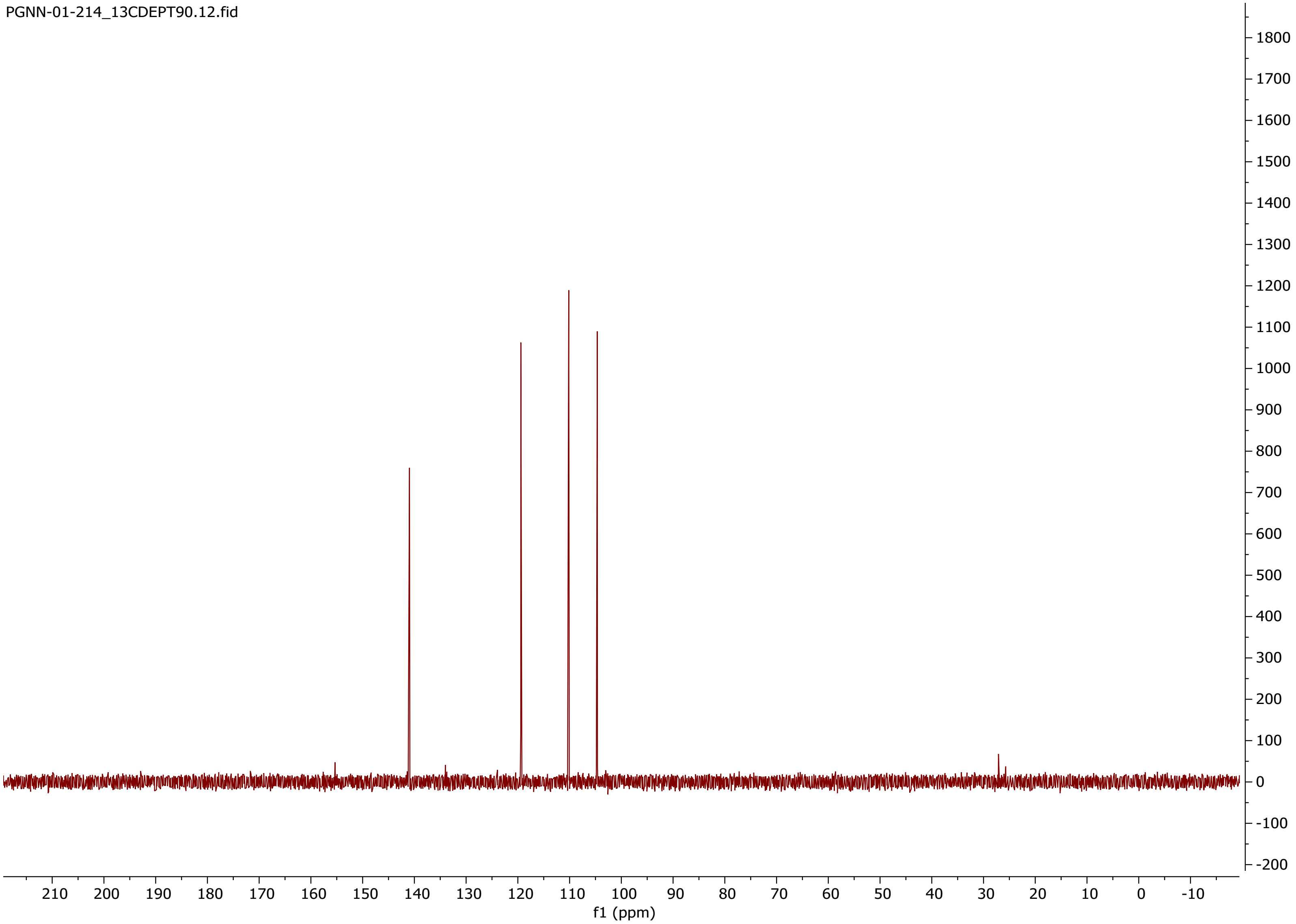
TLC:	Rf = 0.21 (hexane) [I_2]
^{1}H-NMR:	(400 MHz, $CDCl_3$)
	7.30 (d, *J* = 1.2 Hz, 1H), 6.27 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.00 – 5.93 (m, 1H), 5.31 (tp, *J* = 7.2, 1.5 Hz, 1H), 3.34 (d, *J* = 7.2 Hz, 2H), 1.75 (s, 3H), 1.69 (s, 3H).
^{13}C{^{1}H}-NMR:	(101 MHz, $CDCl_3$)
	155.33, 140.93, 134.00, 119.42, 110.15, 104.64, 27.10, 25.68, 17.75.
GCMS:	8.749 min (m/z 136.10).



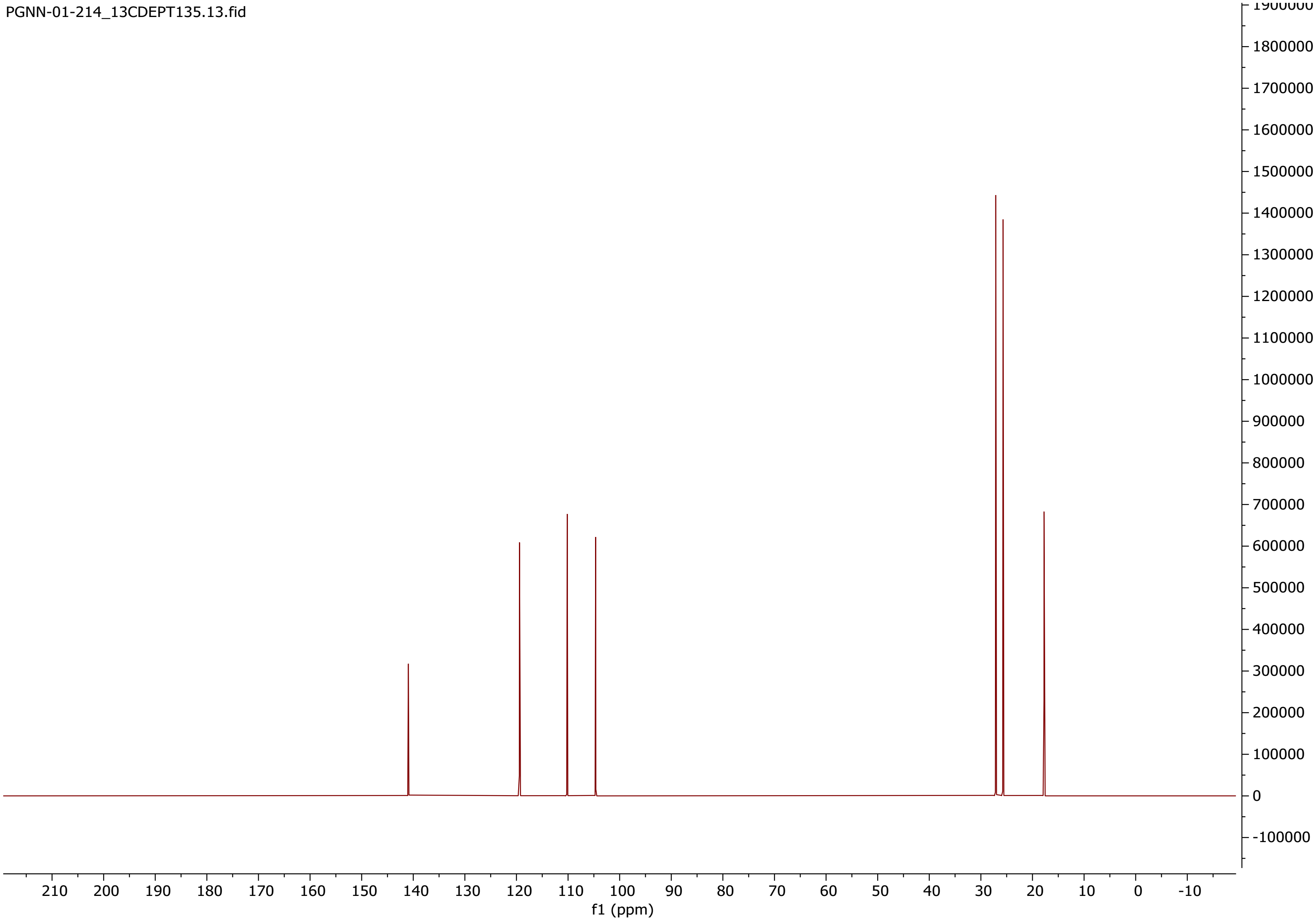
^{1}H-NMR spectrum of prenol-furan coupled product **4**.



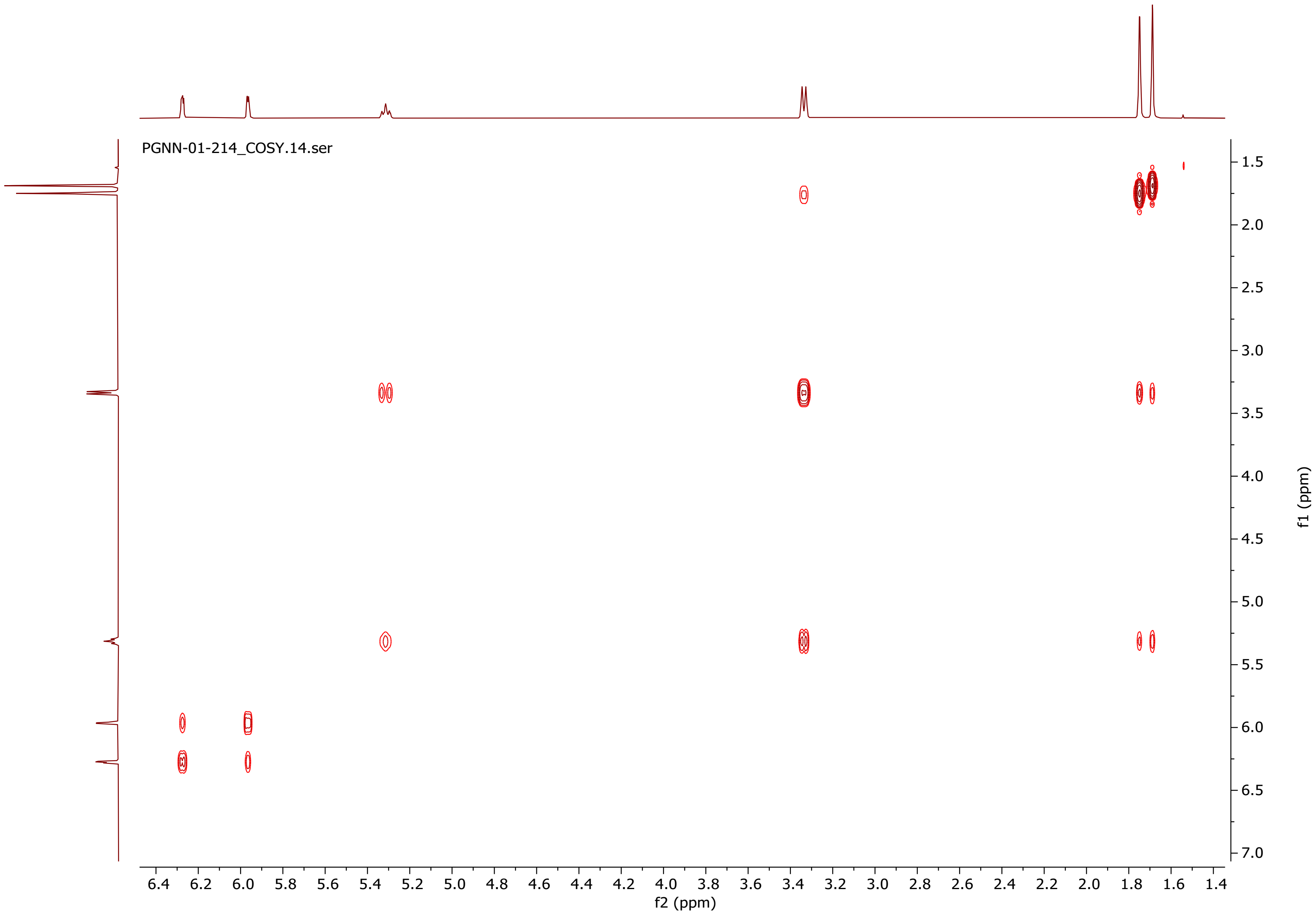
^{13}C-NMR spectrum of prenol-furan coupled product **4**.



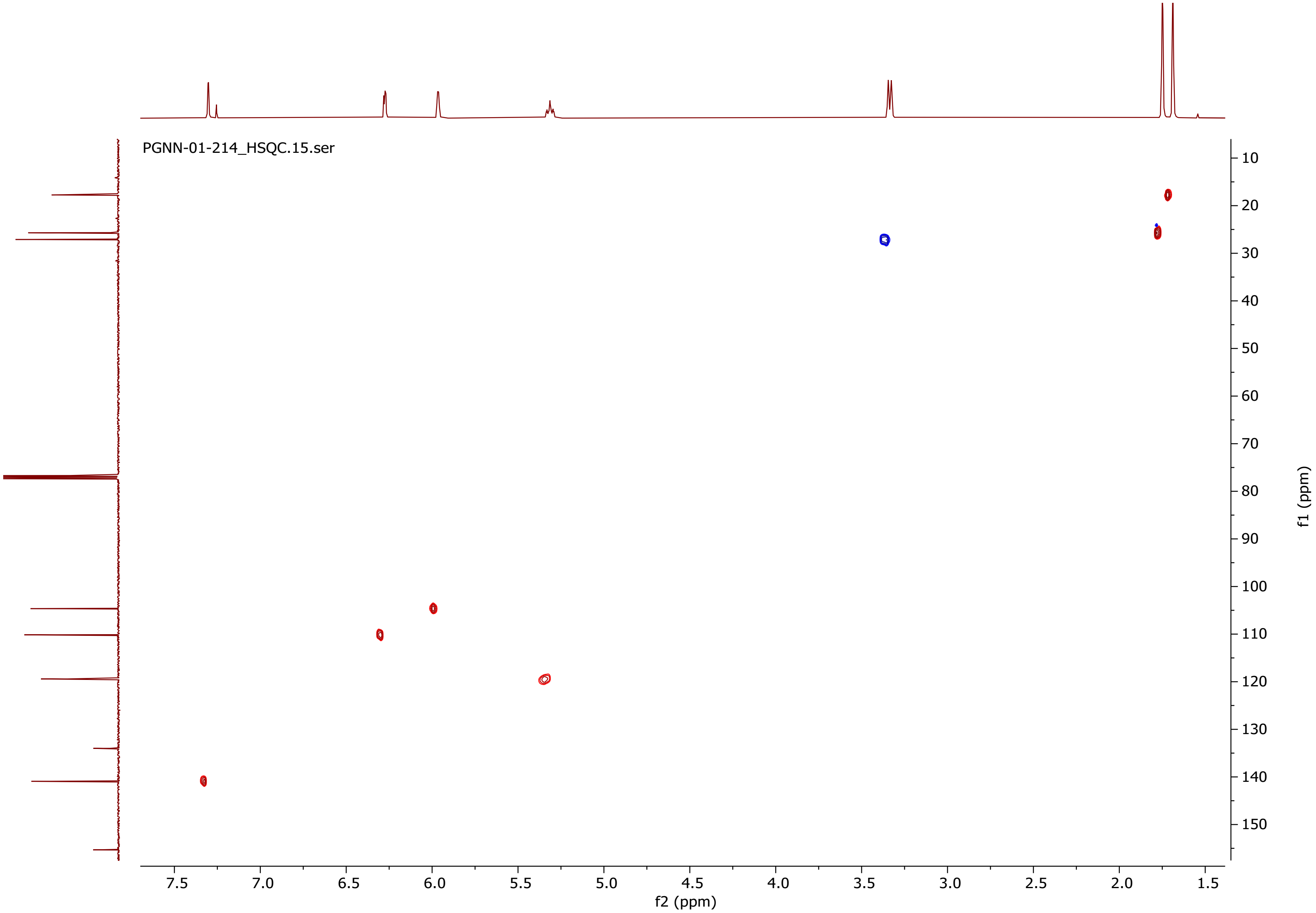
^{13}C-DEPT90-NMR spectrum of prenol-furan coupled product **4**.



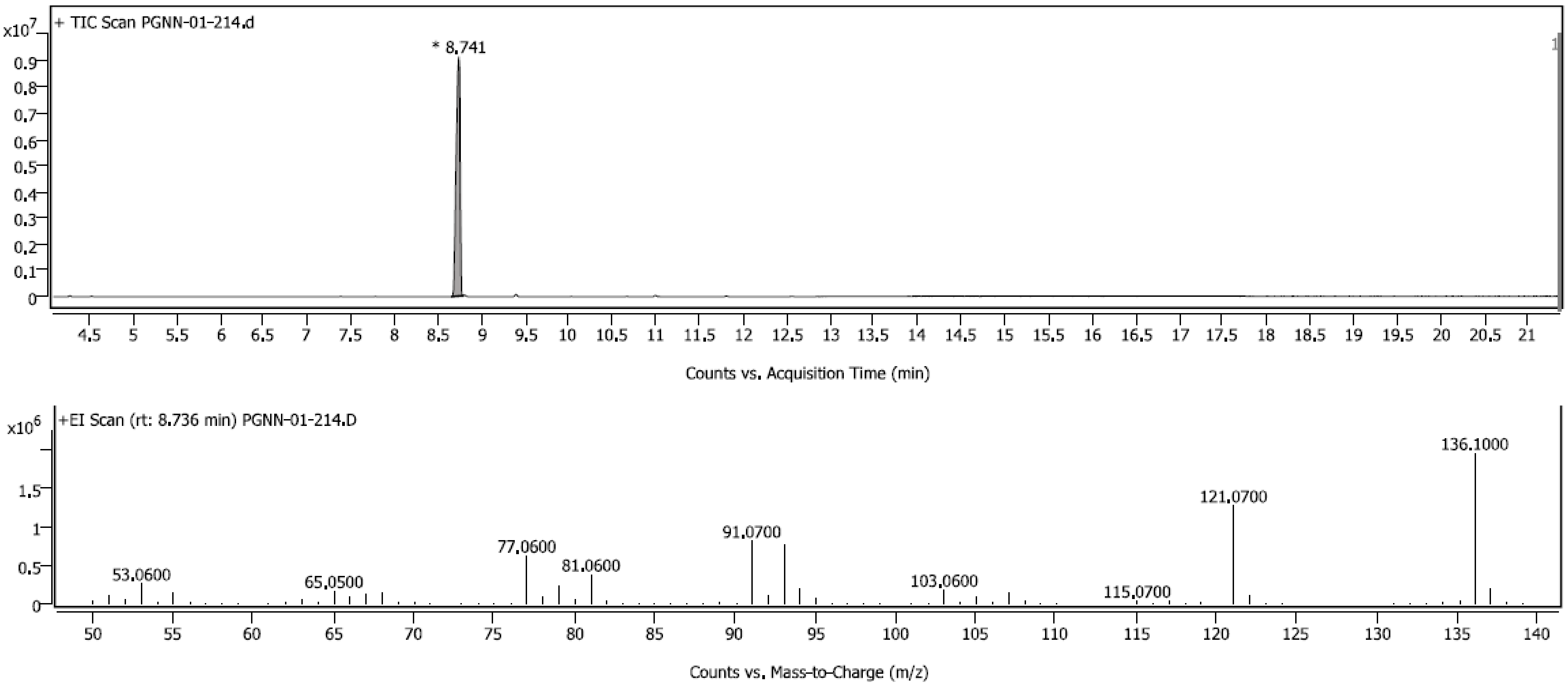
^{13}C-DEPT135-NMR spectrum of prenol-furan coupled product **4**.



COSY-NMR spectrum of prenol-furan coupled product **4**.



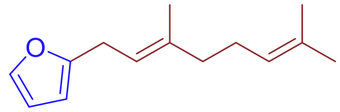
HSQC-NMR spectrum of prenol-furan coupled product **4**.



GCMS data of prenol-furan coupled product **4**.

Geraniol-furan product **5**

IUPAC name: (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)furan



According to General Procedure A, geraniol (0.30 mL; 1.7 mmol) was reacted with furan (1.2 mL; 16.5 mmol) in the presence of CBV720CY (250 mg). The crude reaction mixture was purified by flash column chromatography (circa 100 mL silica gel; hexanes) to give the product as a colorless oil (225 mg; 65%).

TLC: Rf = 0.44 (hexane) [I_2]

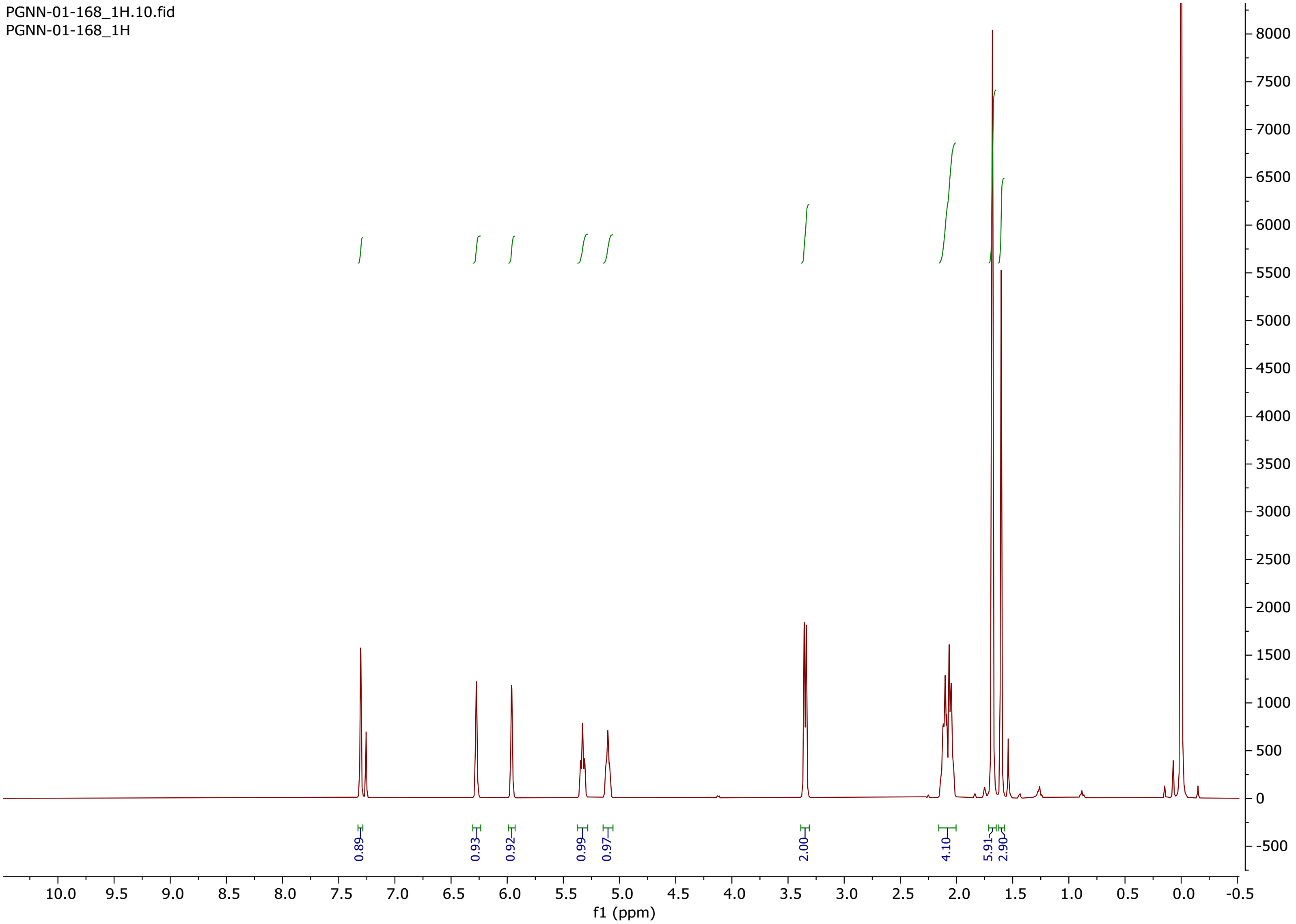
^{1}H-NMR: (400 MHz, $CDCl_3$)

7.30 (app. s, 1H), 6.28 (app. s, 1H), 5.96 (app. s, 1H), 5.33 (t, *J* = 6.9 Hz, 1H), 5.10 (t, *J* = 6.8 Hz, 1H), 3.35 (d, *J* = 7.2 Hz, 2H), 2.17 – 1.98 (m, 4H), 1.68 (s, 6H), 1.60 (s, 3H).

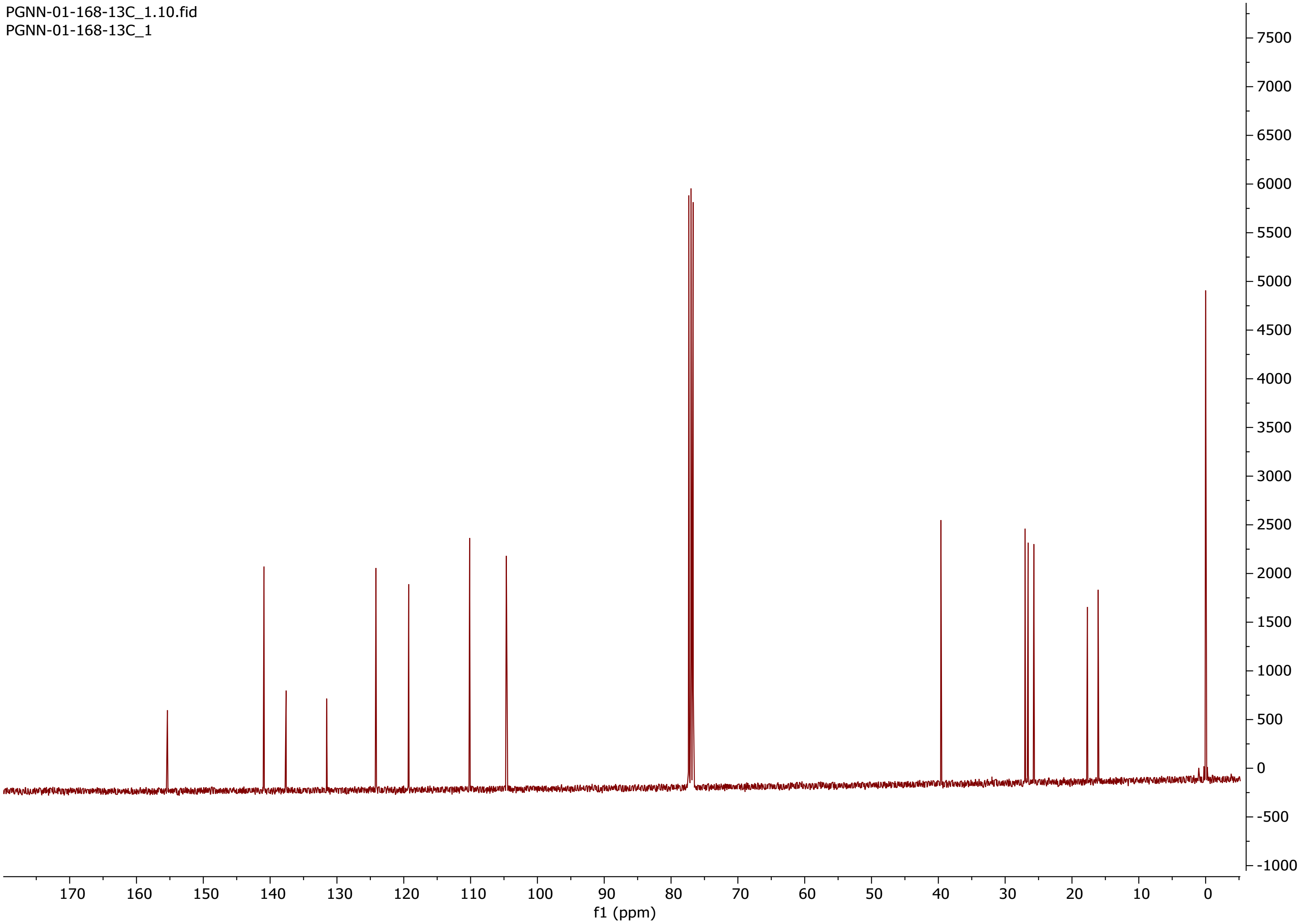
^{13}C{^{1}H}-NMR: (101 MHz, $CDCl_3$)

155.37, 140.92, 137.61, 131.54, 124.16, 119.26, 110.14, 104.65, 39.61, 27.01, 26.56, 26.51, 25.71, 17.69, 16.08.

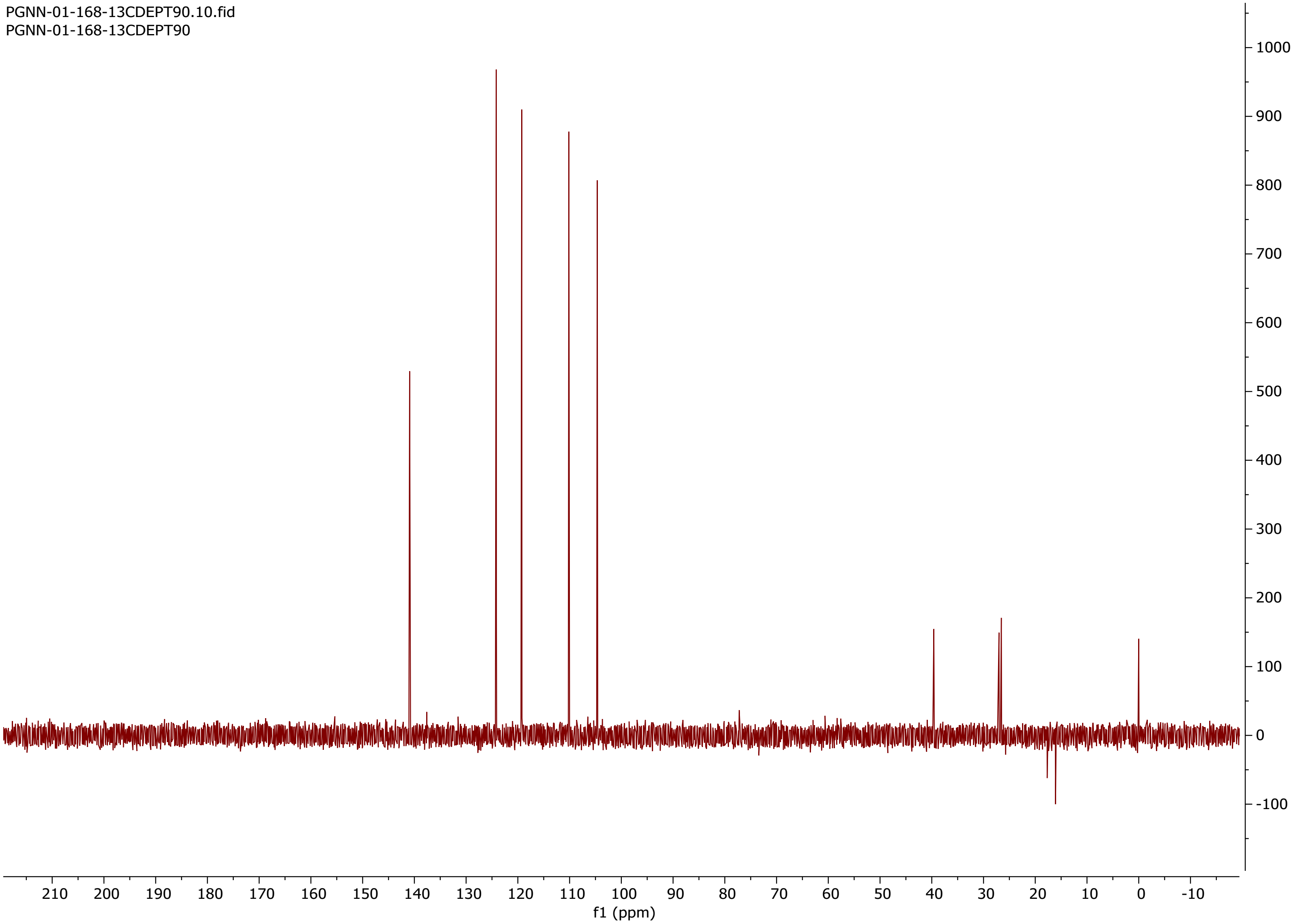
GCMS: 11.348 min (m/z 204.11).



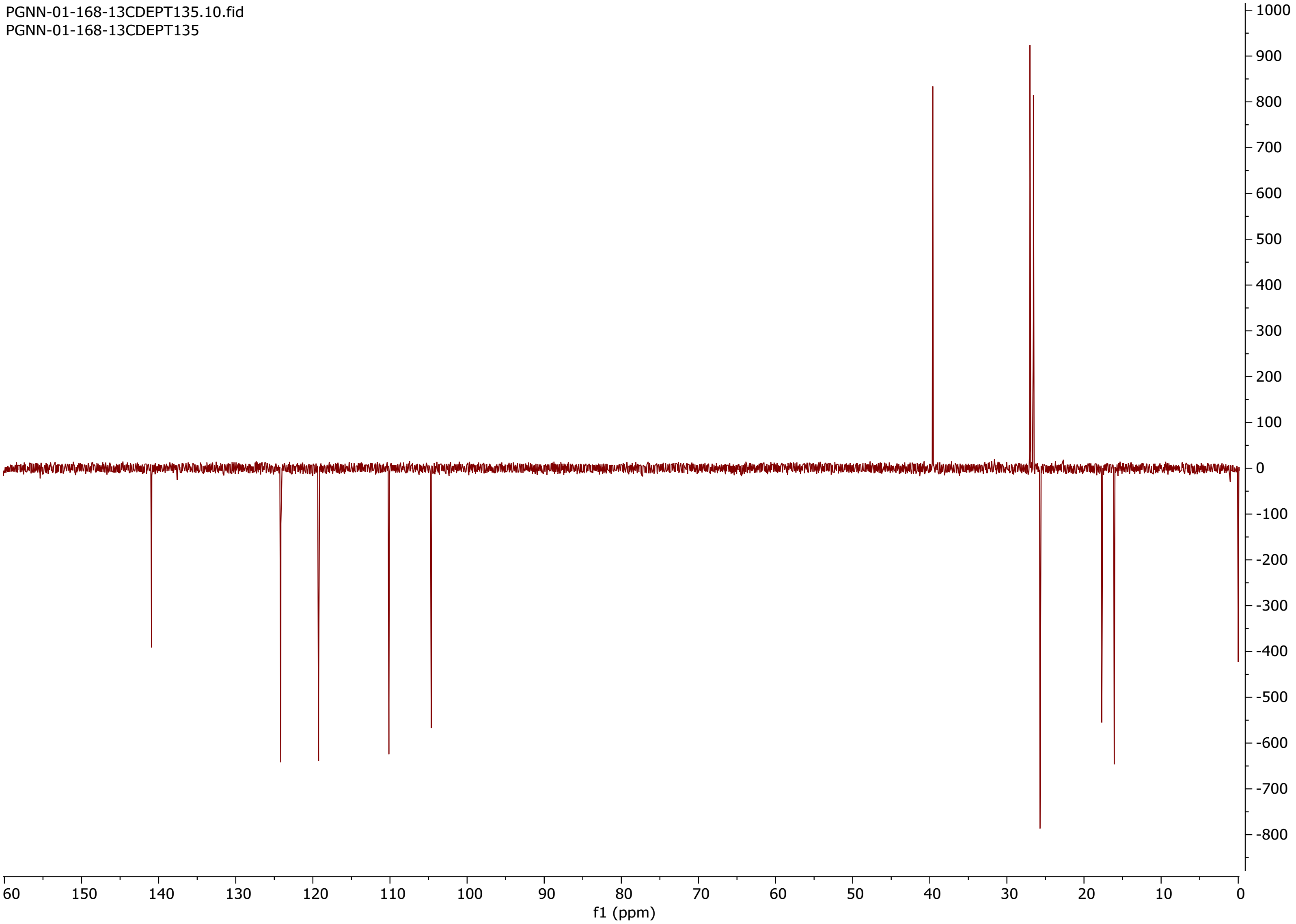
^{1}H-NMR spectrum of geraniol-furan coupled product **5**.



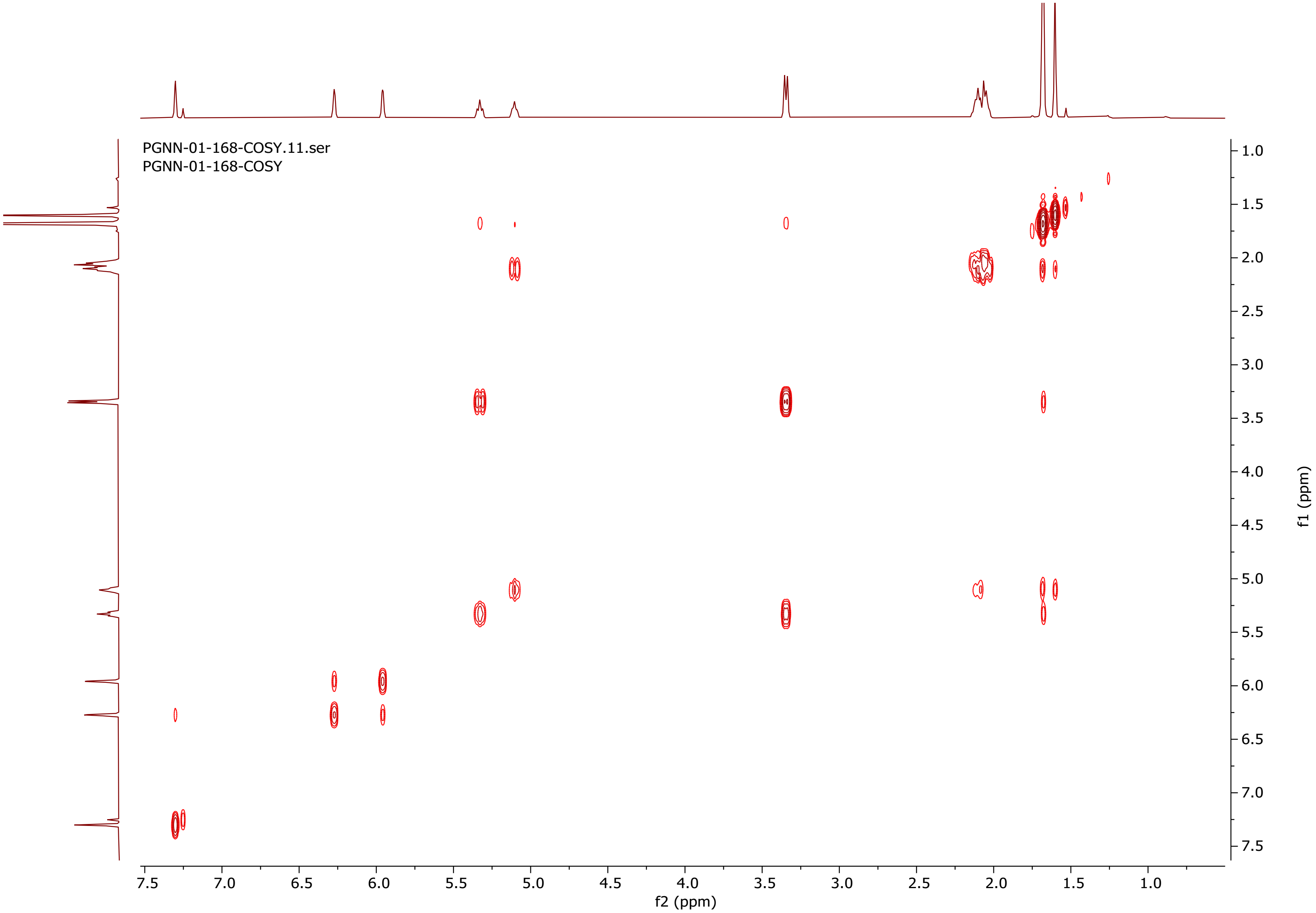
^{13}C-NMR spectrum of geraniol-furan coupled product **5**.



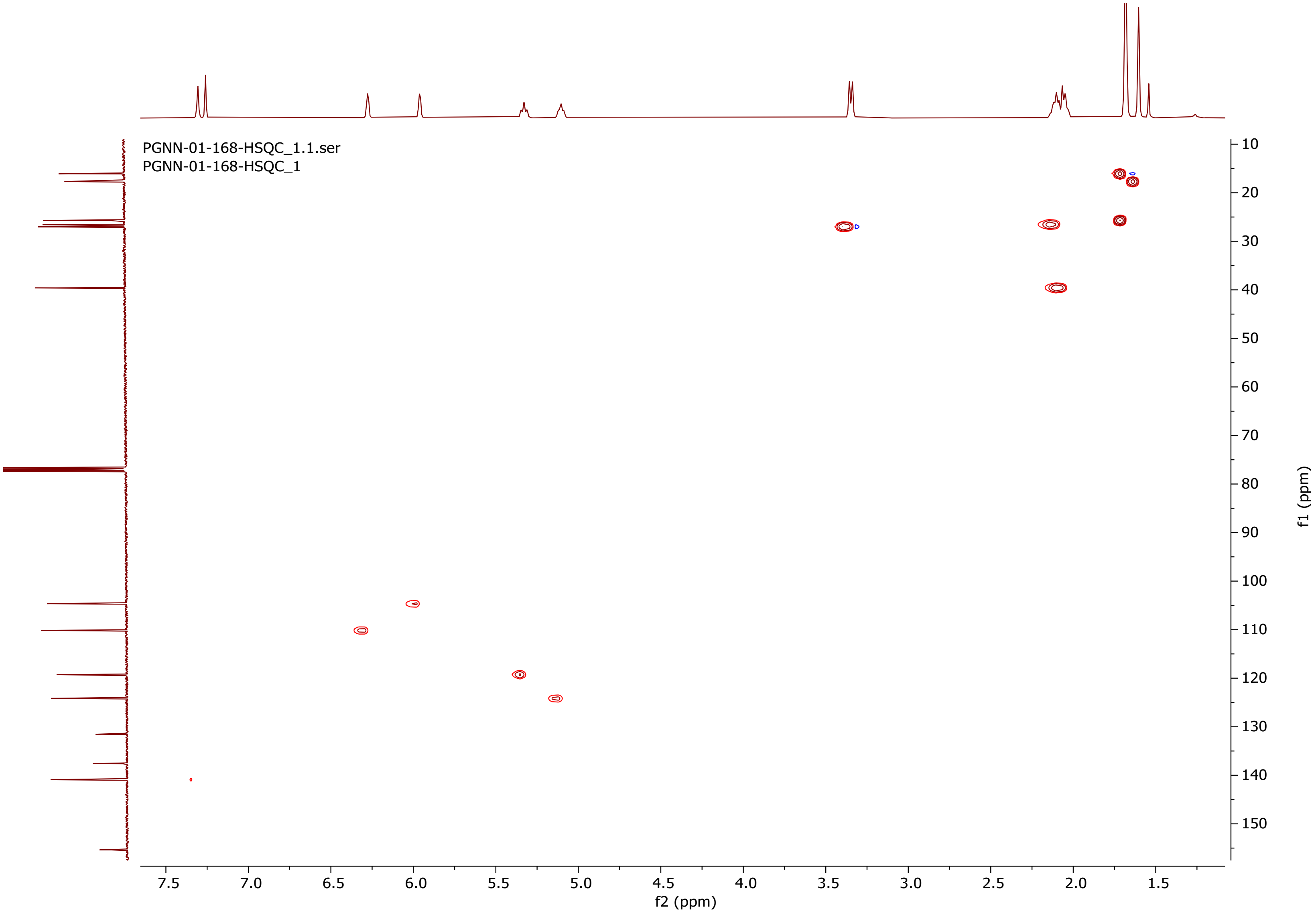
^{13}C-DEPT90-NMR spectrum of geraniol-furan coupled product **5**.



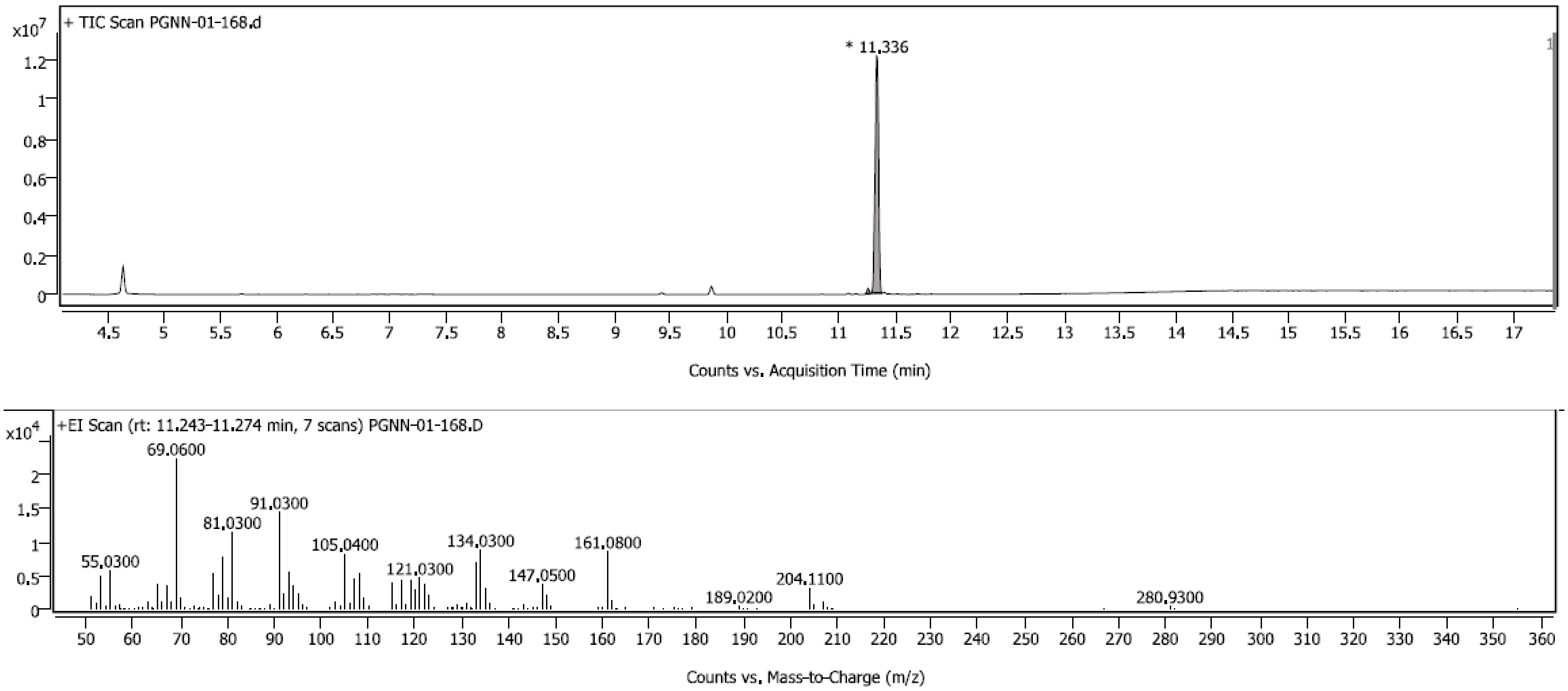
^{13}C-DEPT135-NMR spectrum of geraniol-furan coupled product **5**.



COSY-NMR spectrum of geraniol-furan coupled product **5**.



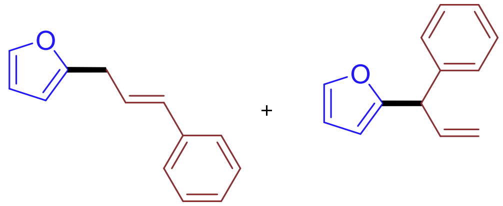
HSQC-NMR spectrum of geraniol-furan coupled product **5**.



GCMS data of geraniol-furan coupled product **5**.

Cinnamyl alcohol-furan product **6/7**

IUPAC name: 2-cinnamylfuran, and (R)-2-(1-phenylallyl)furan



According to General Procedure A, cinnamyl alcohol (228 mg; 1.7 mmol) was reacted with furan (1.2 mL; 16.5 mmol) in the presence of CBV720CY (250 mg). The crude reaction mixture was purified by flash column chromatography (circa 50 mL silica gel; hexanes) to give the product as a colorless oil (236 mg; 75%).

TLC: Rf = 0.20 (hexane) [UV/I_2]

^{1}H-NMR: (400 MHz, $CDCl_3$)

Major isomer: 7.39 – 7.33 (m, 3H), 7.30 (t, J = 7.7 Hz, 2H), 7.25 – 7.19 (m, 1H), 6.49 (d, J = 15.8 Hz, 1H), 6.36 – 6.26 (m, 2H), 6.07 (d, J = 3.2 Hz, 1H), 3.56 (d, J = 6.7 Hz, 2H).

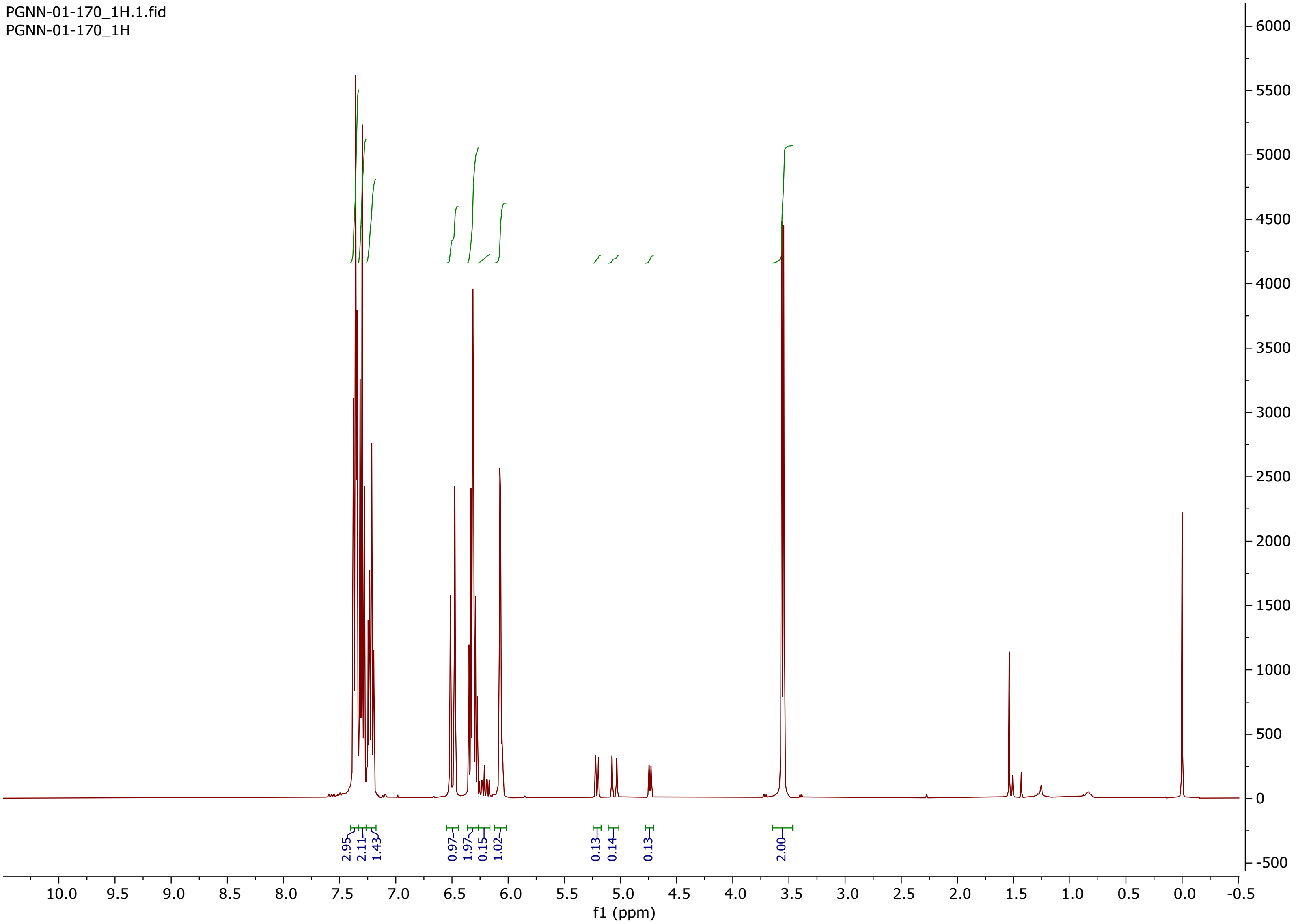
Distinct peaks corresponding to minor isomer: 6.21 (ddd, J = 17.2, 10.1, 7.1 Hz, 2H), 6.05 (d, J = 3.0 Hz, 2H), 5.21 (d, J = 10.1 Hz, 1H), 5.05 (d, J = 17.1 Hz, 1H), 4.74 (d, J = 7.2 Hz, 2H).

^{13}C{^{1}H}-NMR: (101 MHz, $CDCl_3$)

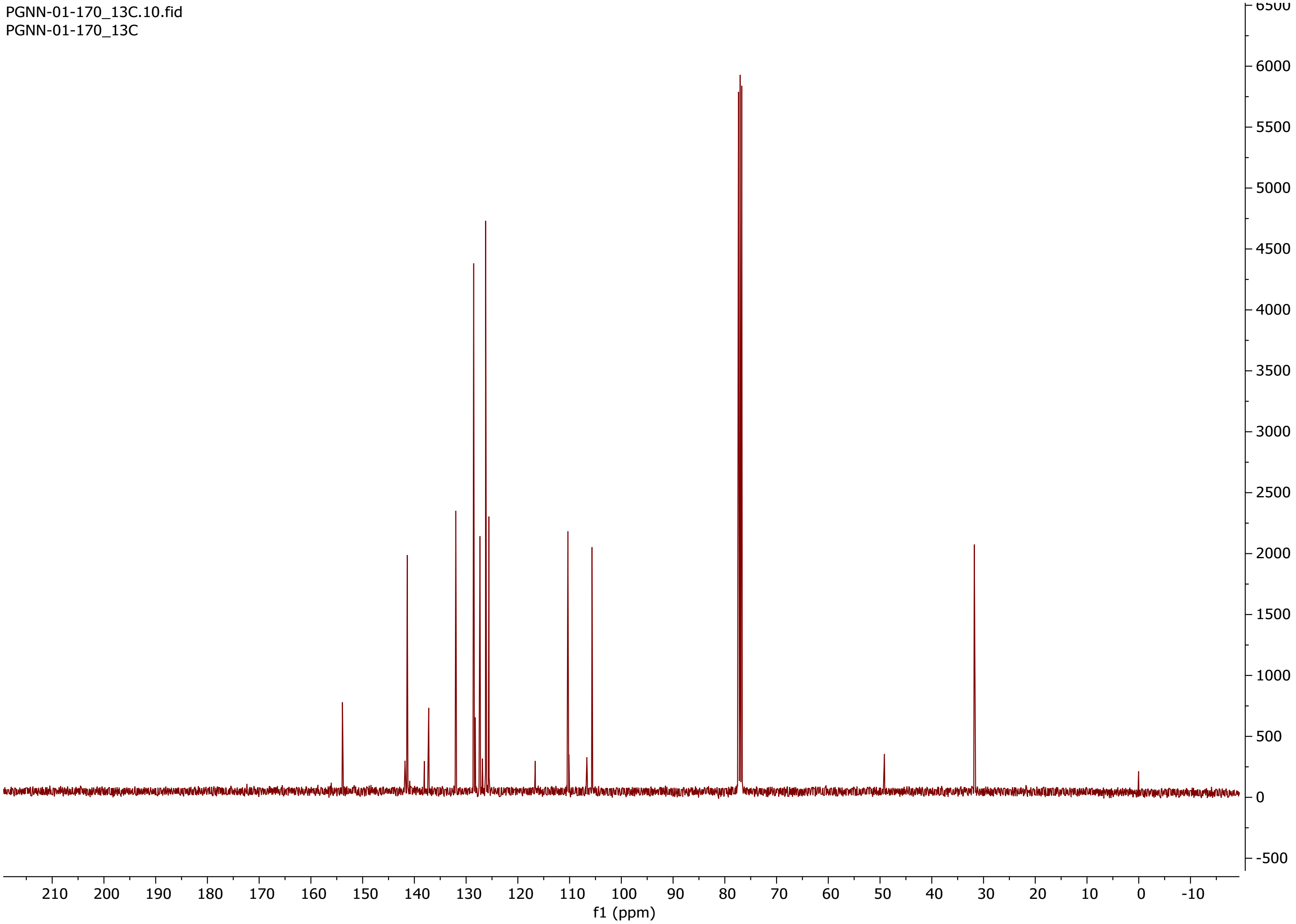
Major isomer: 153.90, 141.39, 137.23, 131.99, 128.54, 127.32, 126.22, 125.59, 110.33, 105.66, 31.79.

Distinct peaks corresponding to minor isomer: 141.80, 138.08, 128.23, 126.85, 116.63, 110.12, 106.66, 49.15.

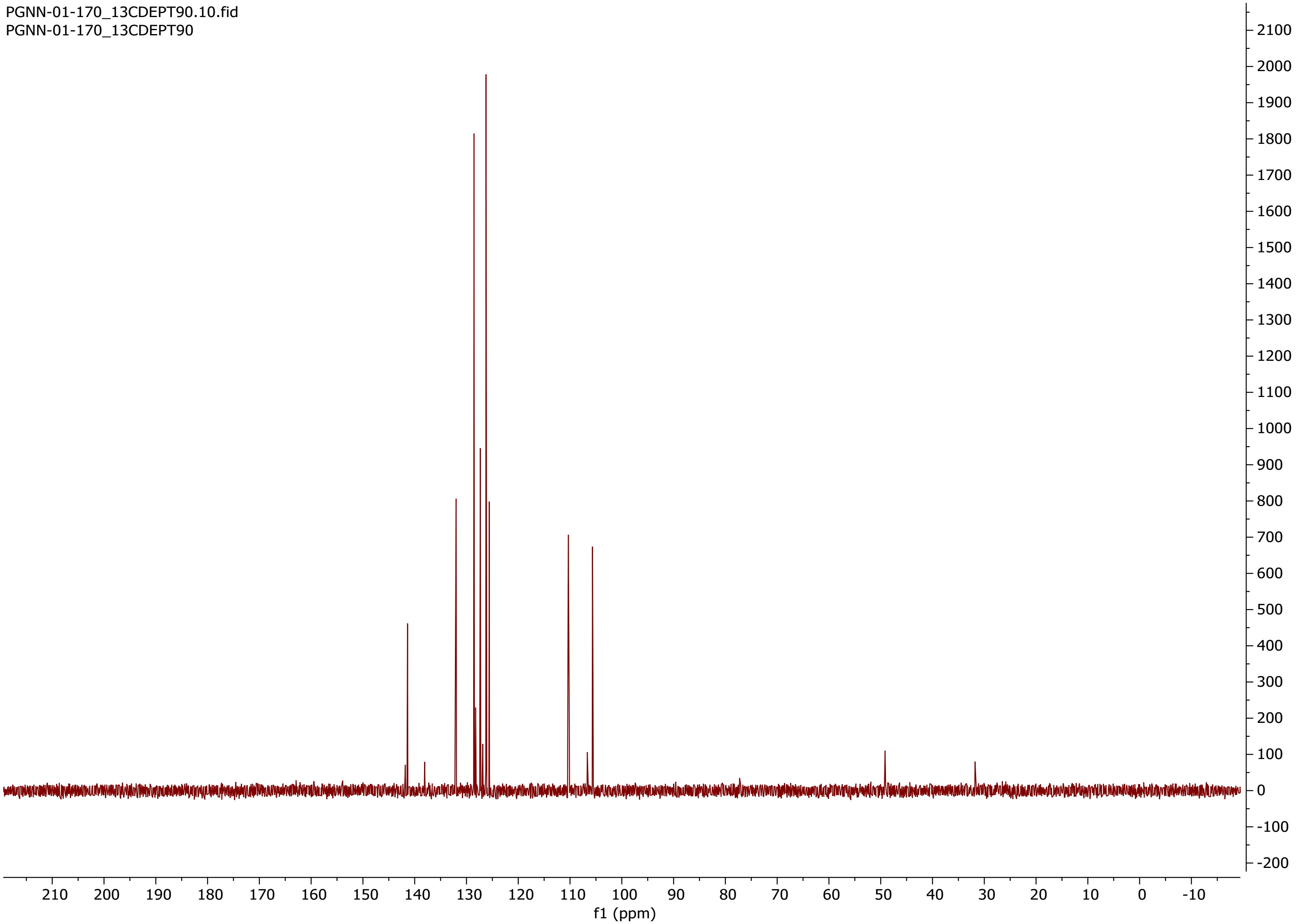
GCMS: 10.906 min (12%; m/z 184.07); 11.642 (88%; m/z 184.08).



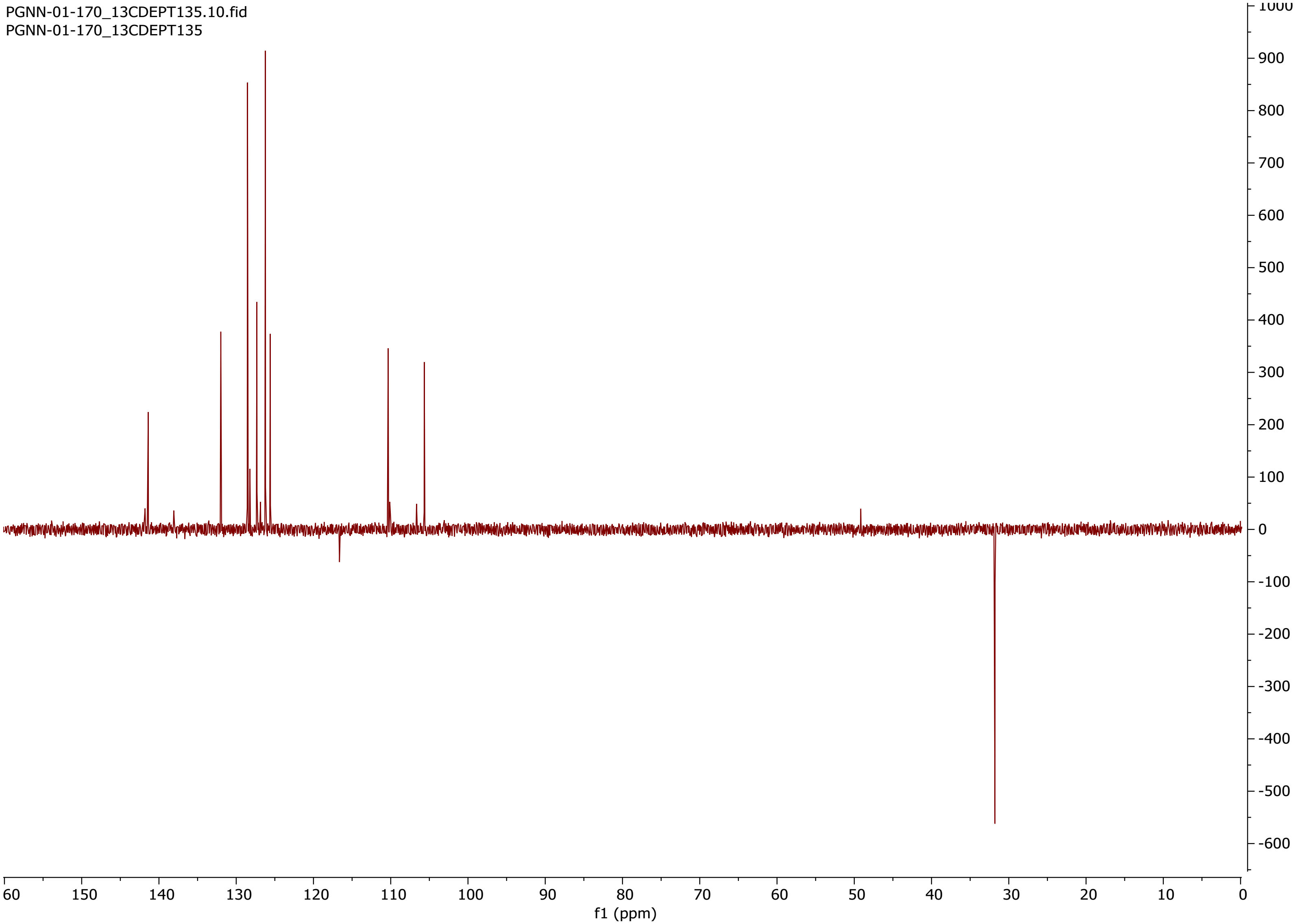
^{1}H-NMR spectrum of cinnamyl alcohol-furan coupled product **6**/**7**.



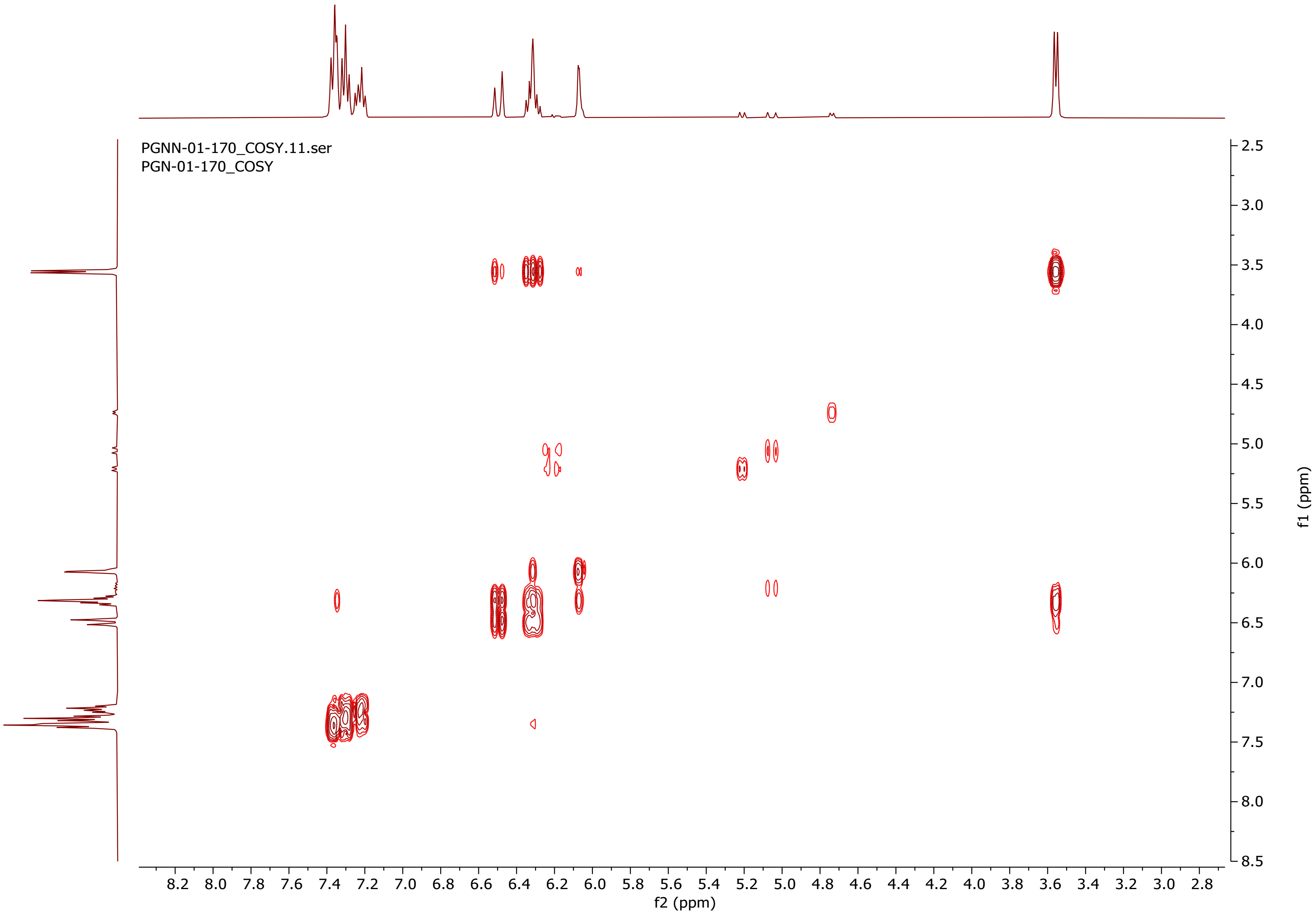
^{13}C-NMR spectrum of cinnamyl alcohol-furan coupled product **6**/**7**.



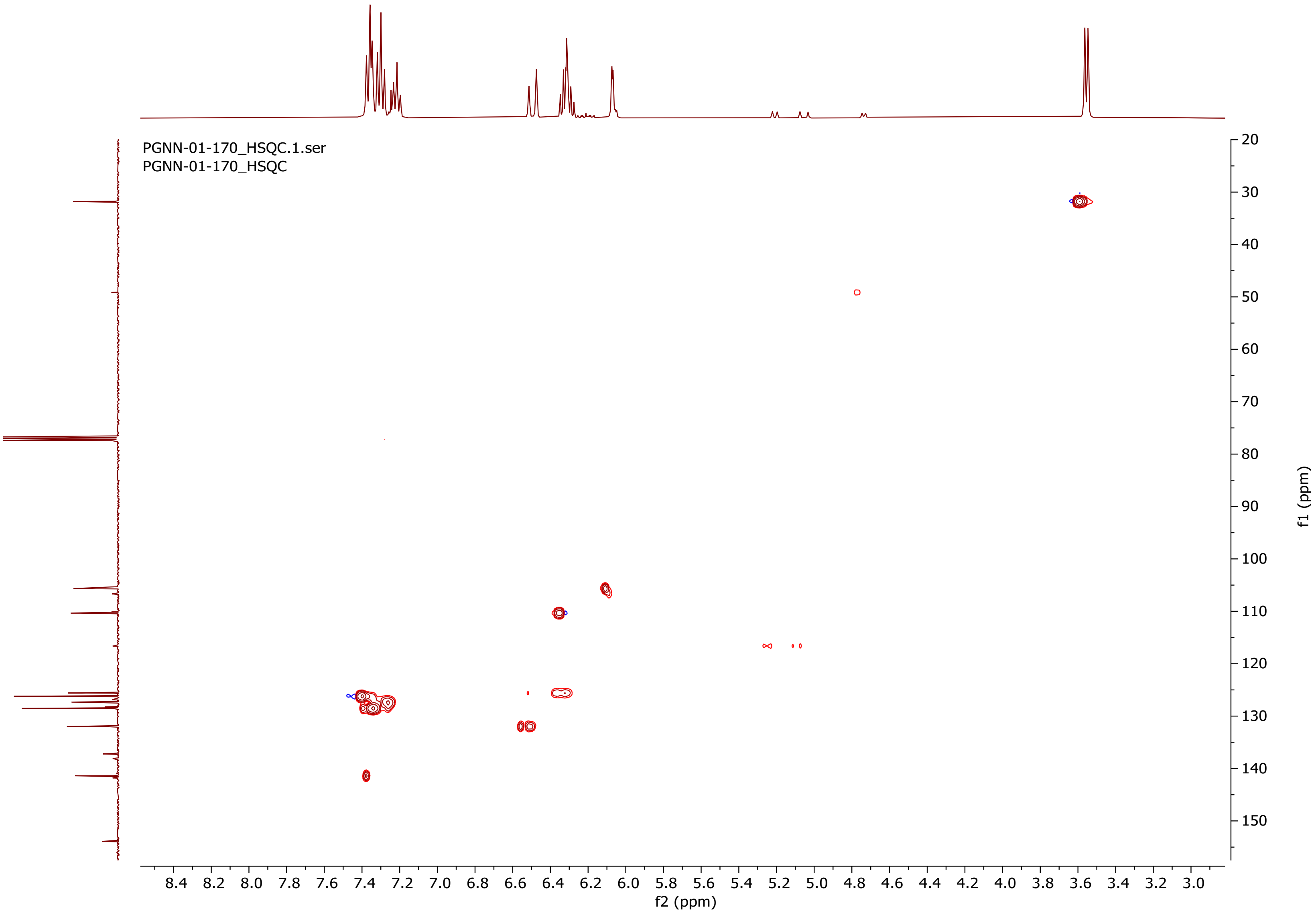
^{13}C-DEPT90-NMR spectrum of cinnamyl alcohol-furan coupled product **6**/**7**.



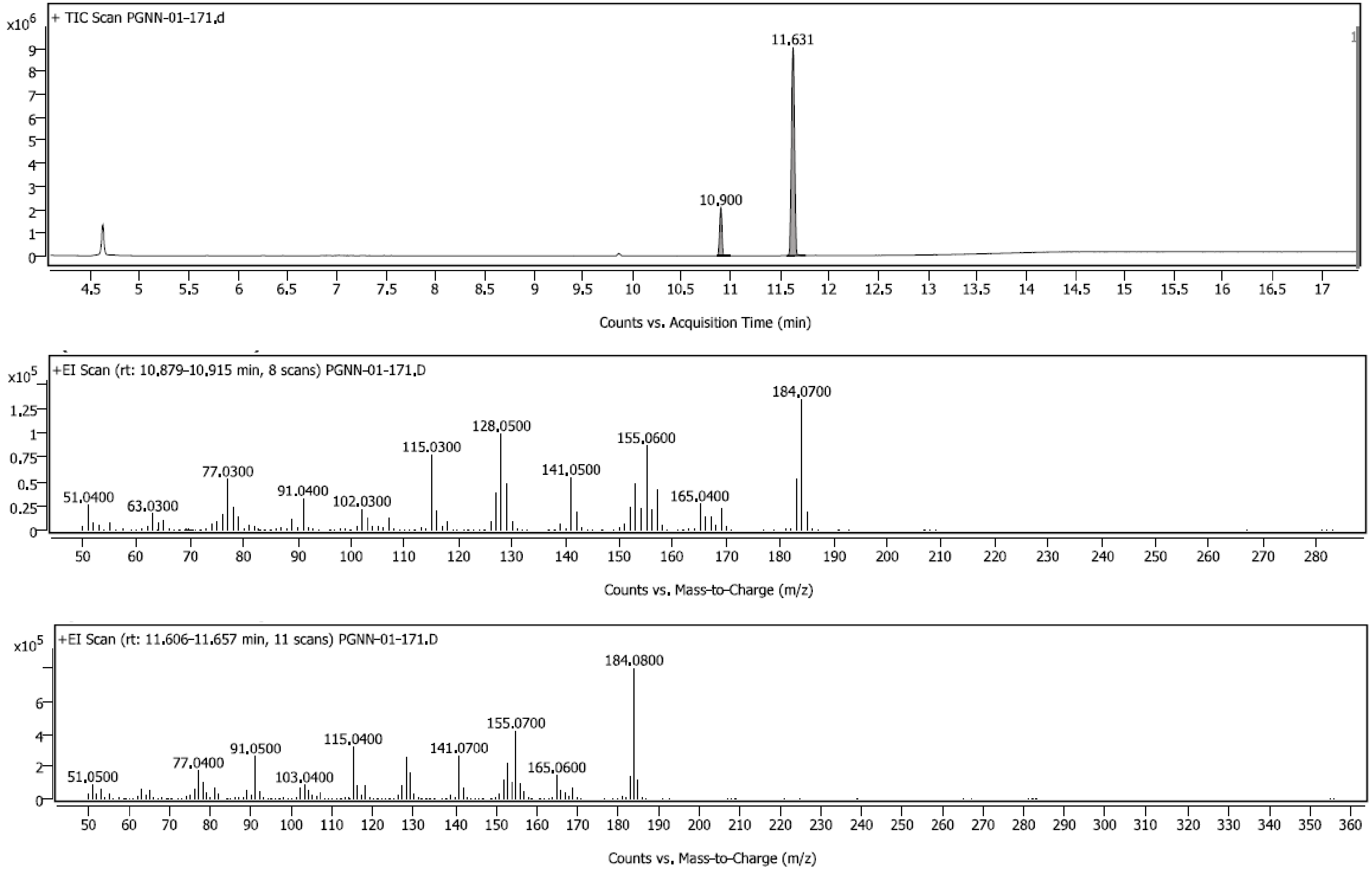
^{13}C-DEPT135-NMR spectrum of cinnamyl alcohol-furan coupled product **6**/**7**.



COSY-NMR spectrum of cinnamyl alcohol-furan coupled product **6**/**7**.



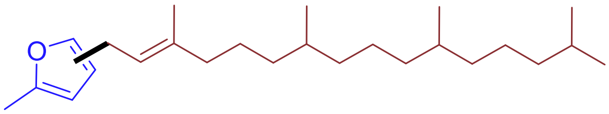
HSQC-NMR spectrum of cinnamyl alcohol-furan coupled product **6**/**7**.



GCMS data of cinnamyl alcohol-furan coupled product **6**/**7**.

2-methylfuran-phytol **9/10**

IUPAC name: (E)-2-methyl-5-(3,7,11,15-tetramethylhexadec-2-en-1-yl)furan, and (E)-2-methyl-4-(3,7,11,15-tetramethylhexadec-2-en-1-yl)furan



According to General Procedure B, phytol (0.59 mL; 1.7 mmol) was reacted with 2-methylfuran (1.5 mL; 16.6 mmol) in the presence of Perlkat 46-10 (125 mg) and 1,2-dichloroethane (2 mL) at 60 °C. The crude reaction mixture was purified by flash column chromatography (circa 300 mL silica gel; hexanes) to give the product as a colorless oil (260 mg; 42%).

TLC: Rf = 0.61 (hexane) [I_2]

^{1}H-NMR: (400 MHz, $CDCl_3$)

Major isomer (2, 5-substituted furan): 5.83 (s, 1.56H), 5.30 (t, *J* = 7.1 Hz, 0.82H), 3.29 (d, *J* = 6.8 Hz, 1.63H), 2.25 (s, 2.36H), 2.10 – 1.93 (m, 2H), 1.73 (s, 1H), 1.65 (s, 2H), 1.55 – 0.99 (m, 20H), 0.85 (dd, *J* = 9.5, 6.6 Hz, 12H).

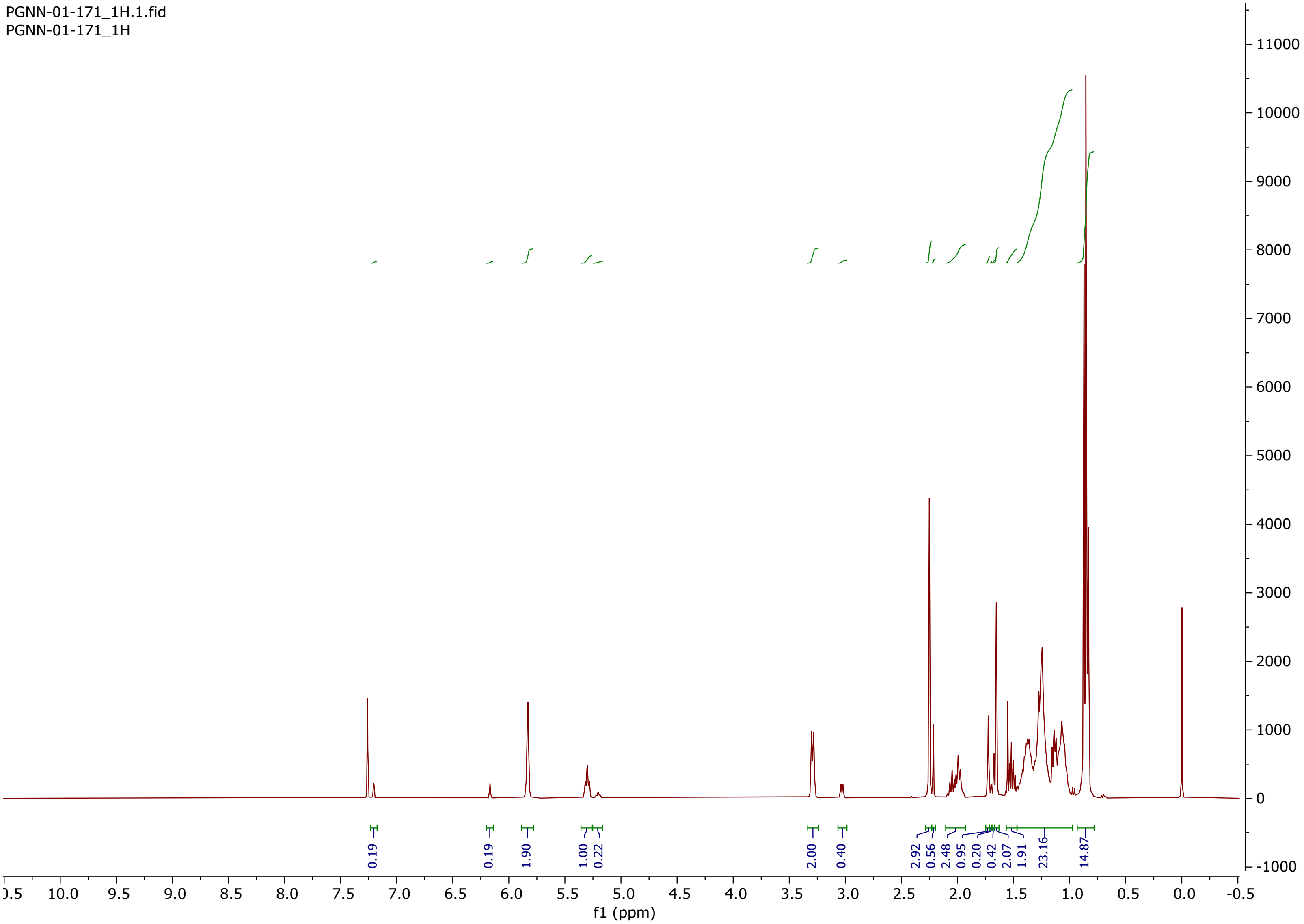
Distinct peaks corresponding to minor isomer (2, 3-substituted furan): 7.20 (d, J = 1.9 Hz, 1H), 6.17 (d, J = 1.9 Hz, 1H), 5.20 (t, J = 7.5 Hz, 1H), 3.03 (d, J = 7.2 Hz, 2H), 2.22 (s, 3H), 1.70 (s, 1H), 1.67 (s, 2H).

^{13}C{^{1}H}-NMR: (101 MHz, $CDCl_3$)

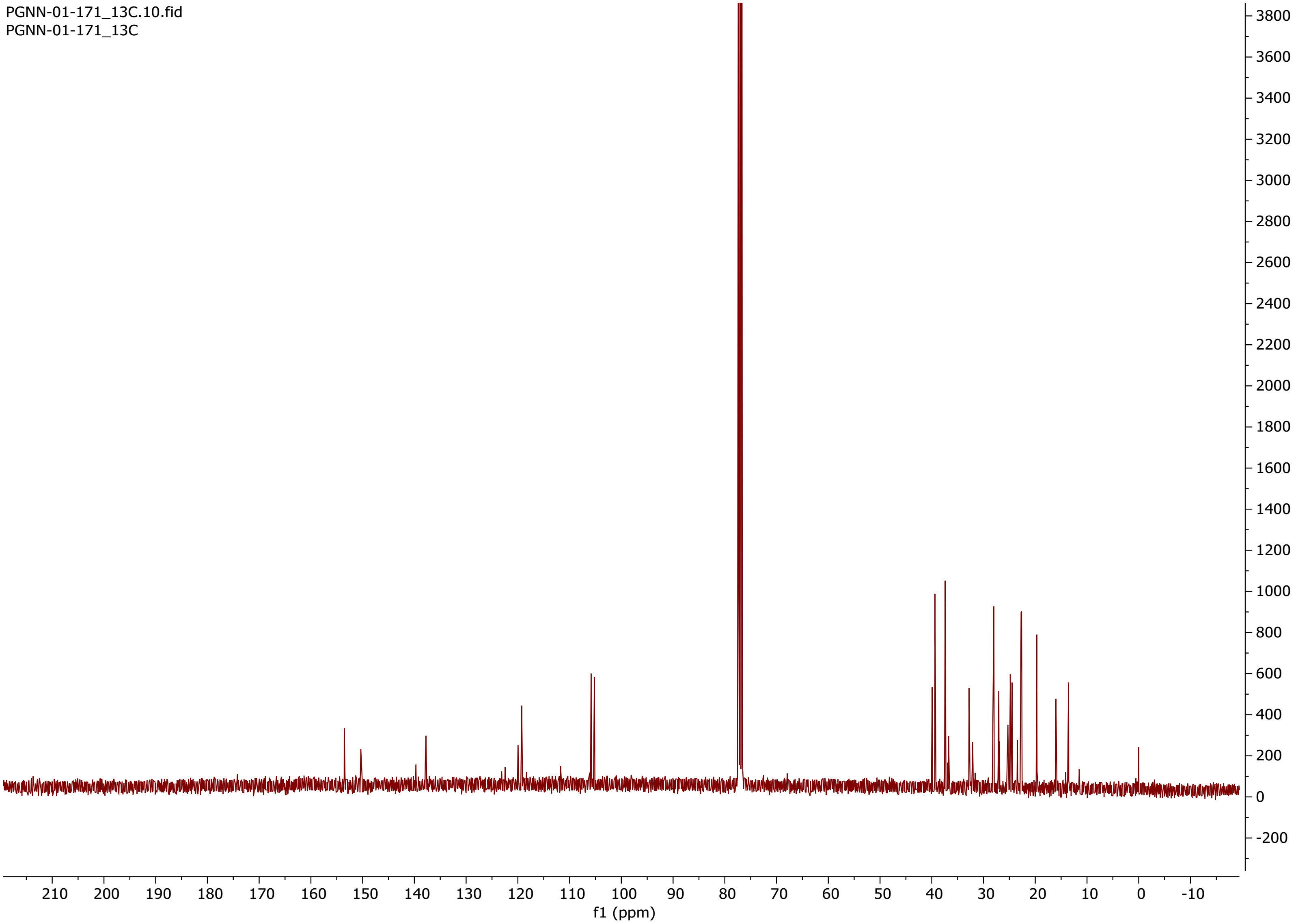
Major isomer (2, 5-substituted furan): 153.55, 150.35, 137.76, 119.62, 105.53, 39.92, 39.38, 37.41, 37.31, 36.65, 32.75, 32.69, 32.09, 28.00, 27.04, 26.94, 25.41, 25.29, 24.83, 24.49, 23.45, 22.69, 19.74, 16.01, 13.56.

Distinct peaks corresponding to minor isomer (2, 3-substituted furan): 137.88. 122.70, 111.63, 23.49, 11.47.

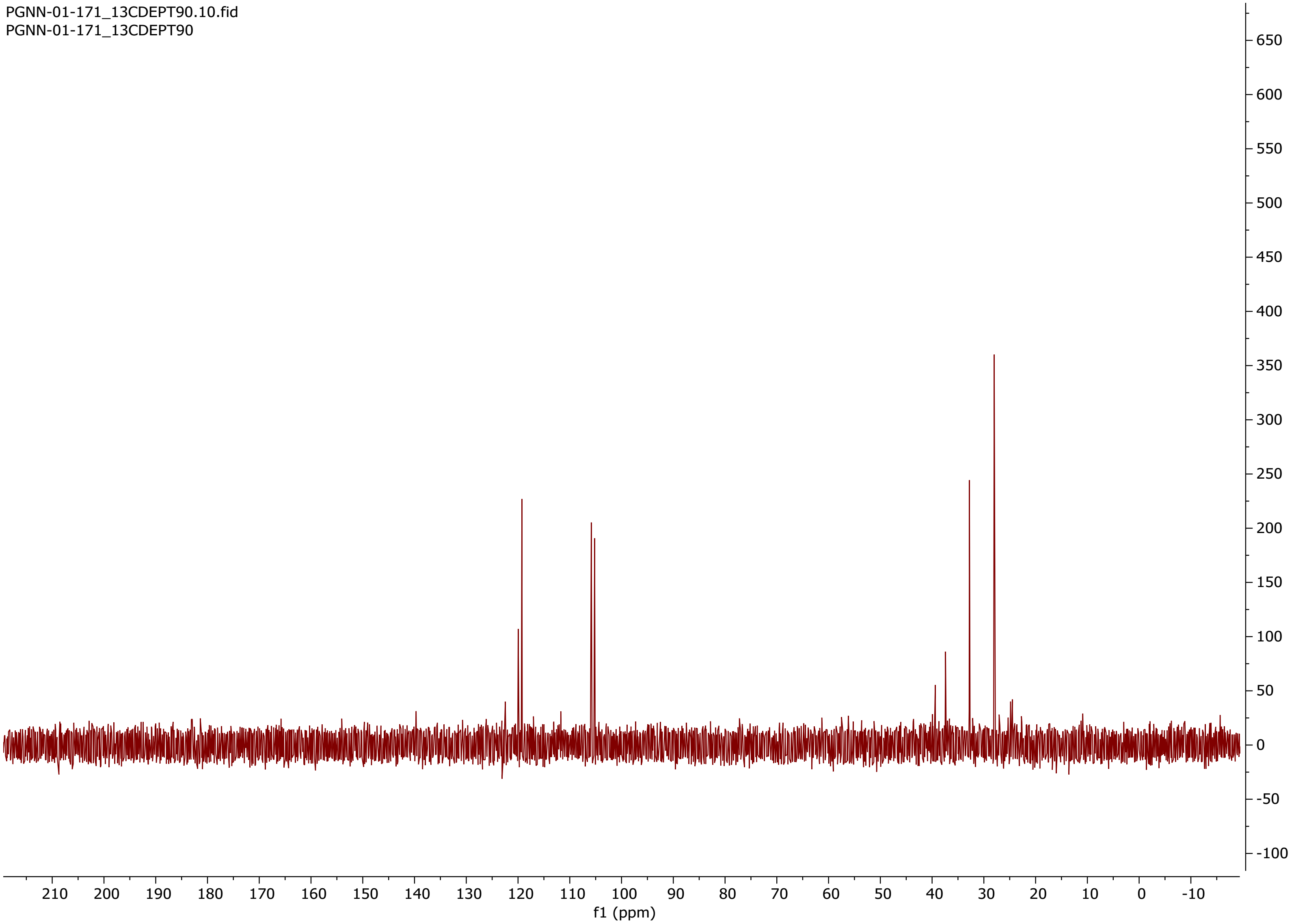
GCMS: 14.823 min (27%; m/z 360.32); 14.978 (61%; m/z 360.31); 15.087 (12%; m/z 360.30).



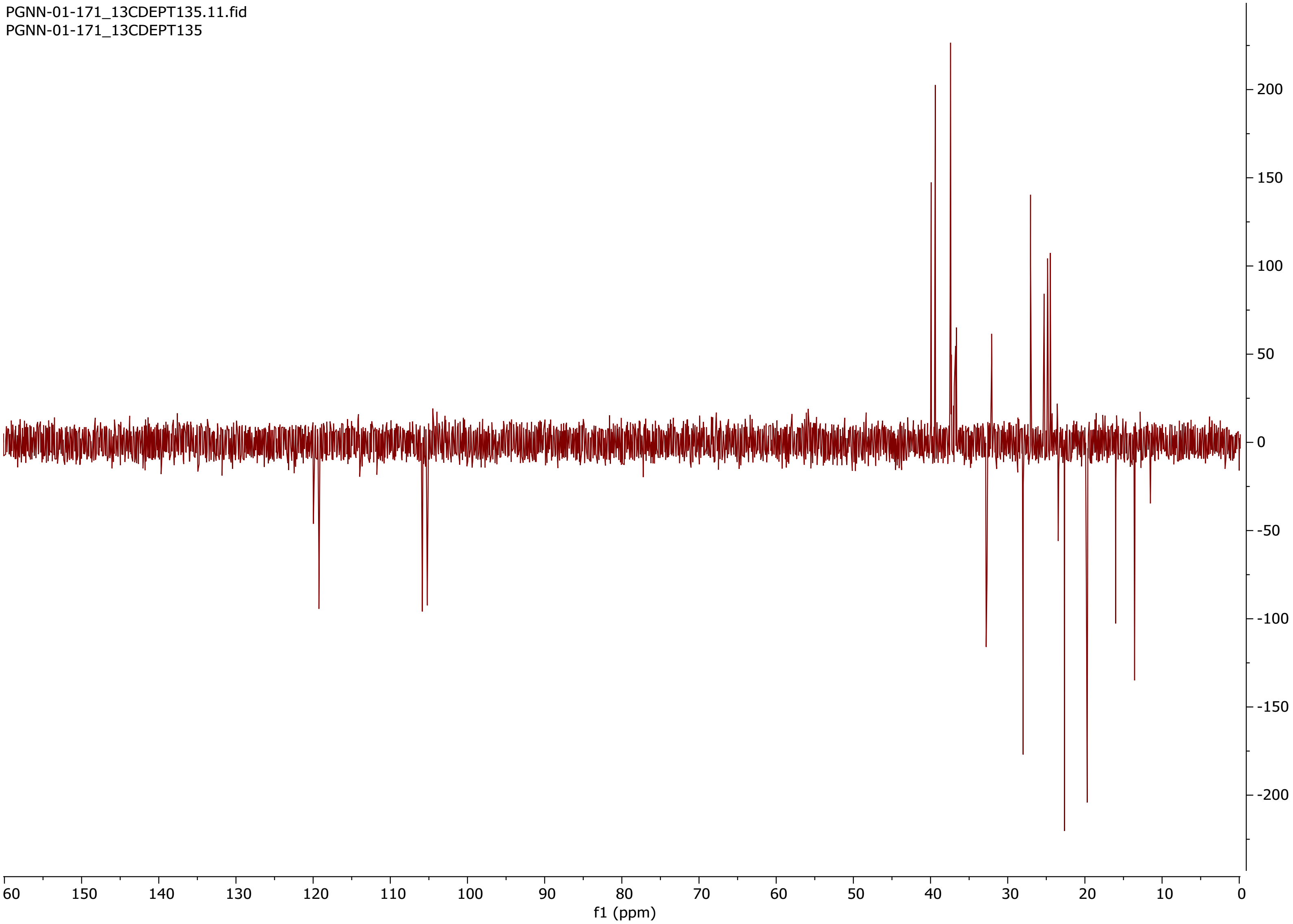
^{1}H-NMR spectrum of phytol-2-methylfuran coupled product **9**/**10**.



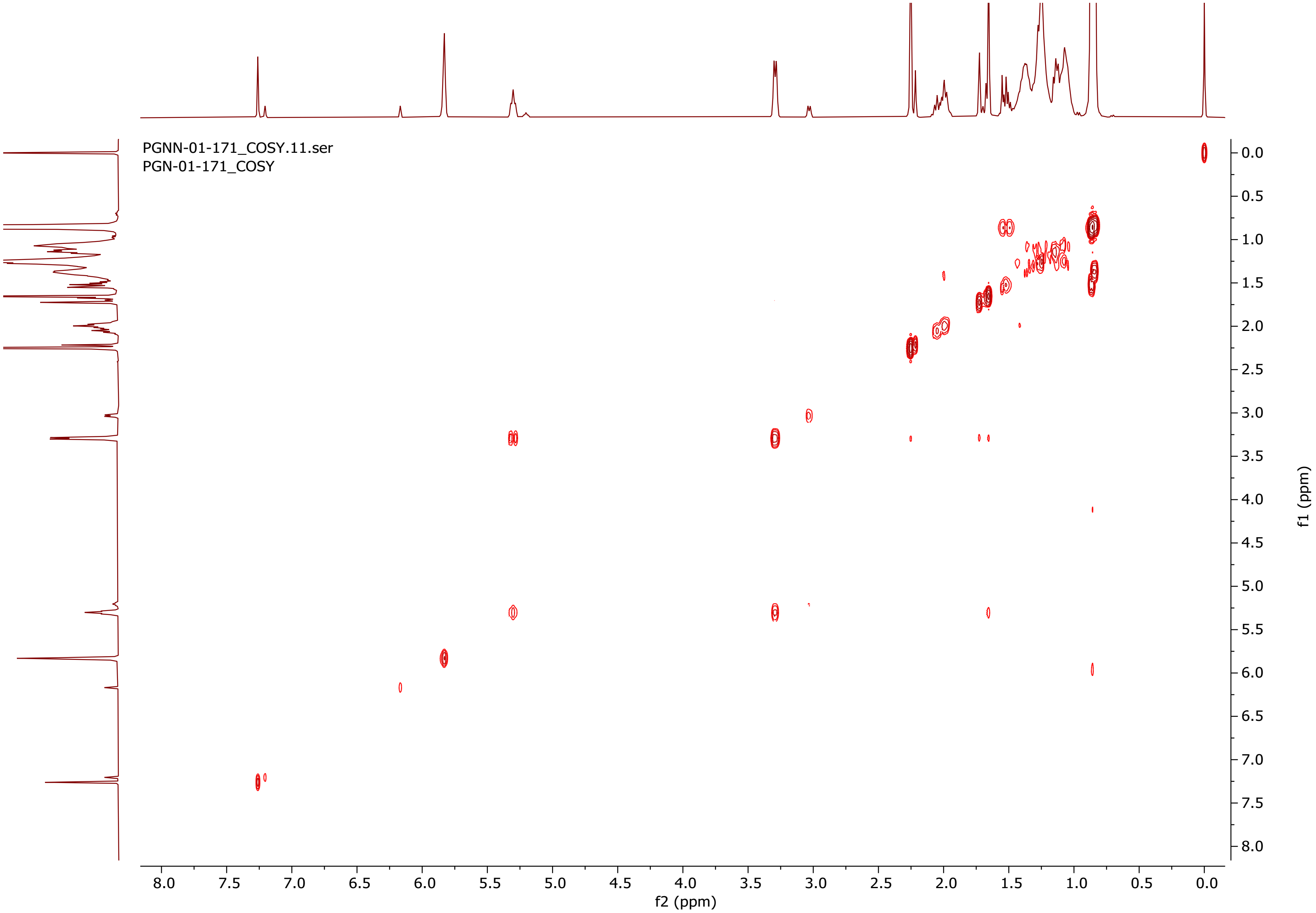
^{13}C-NMR spectrum of phytol-2-methylfuran coupled product **9**/**10**.



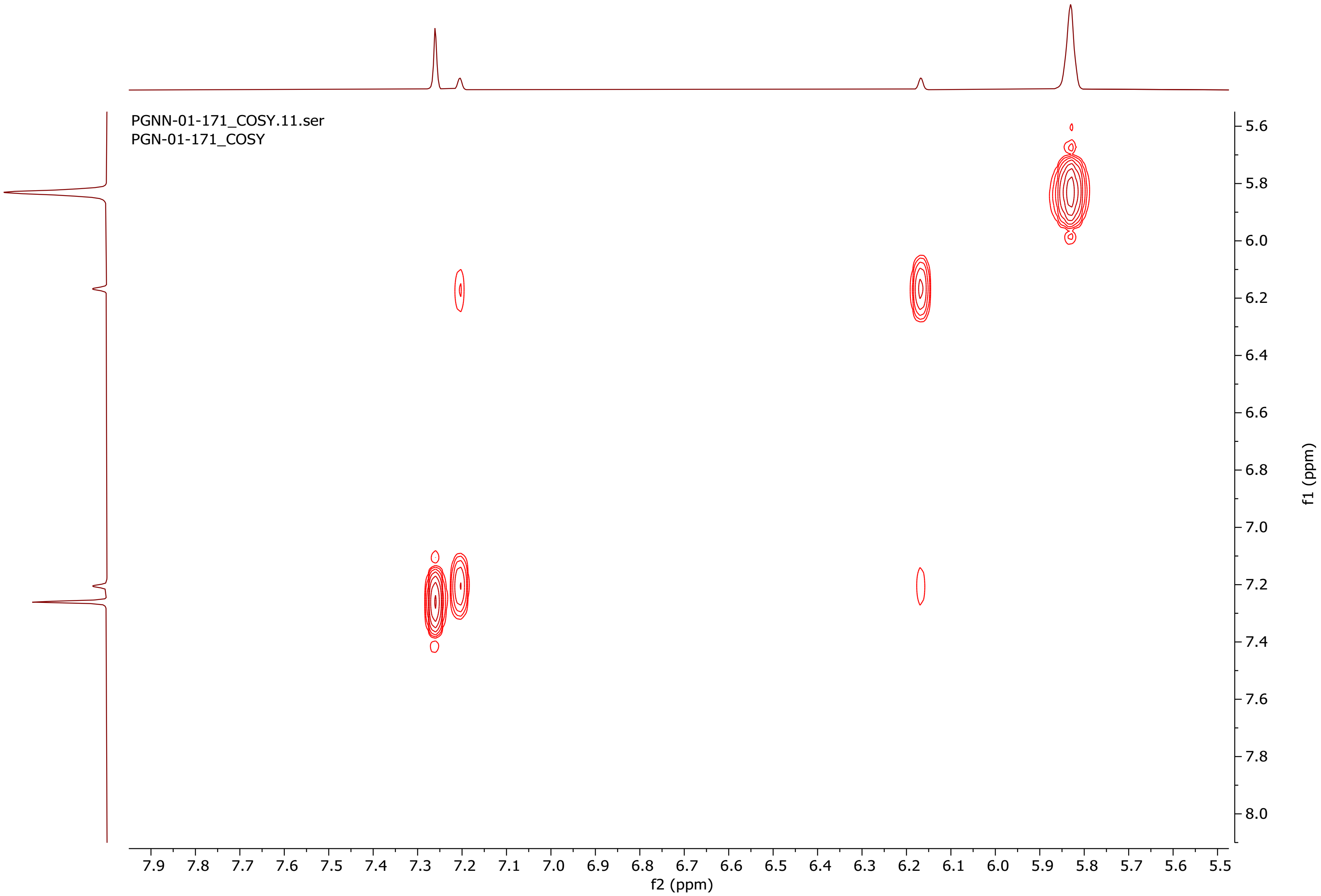
^{13}C-DEPT90-NMR spectrum of phytol-2-methylfuran coupled product **9**/**10**.



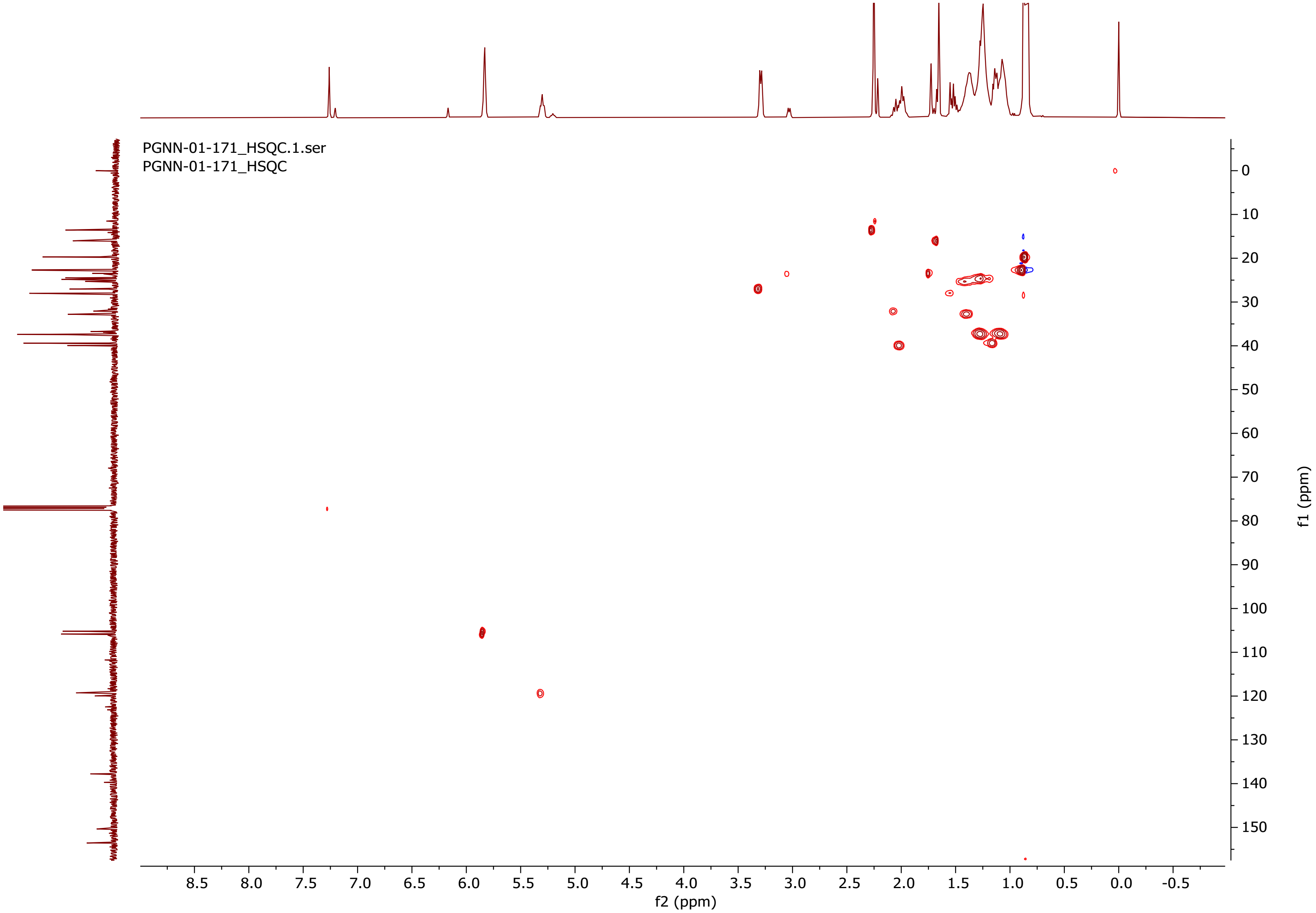
^{13}C-DEPT135-NMR spectrum of phytol-2-methylfuran coupled product **9**/**10**.



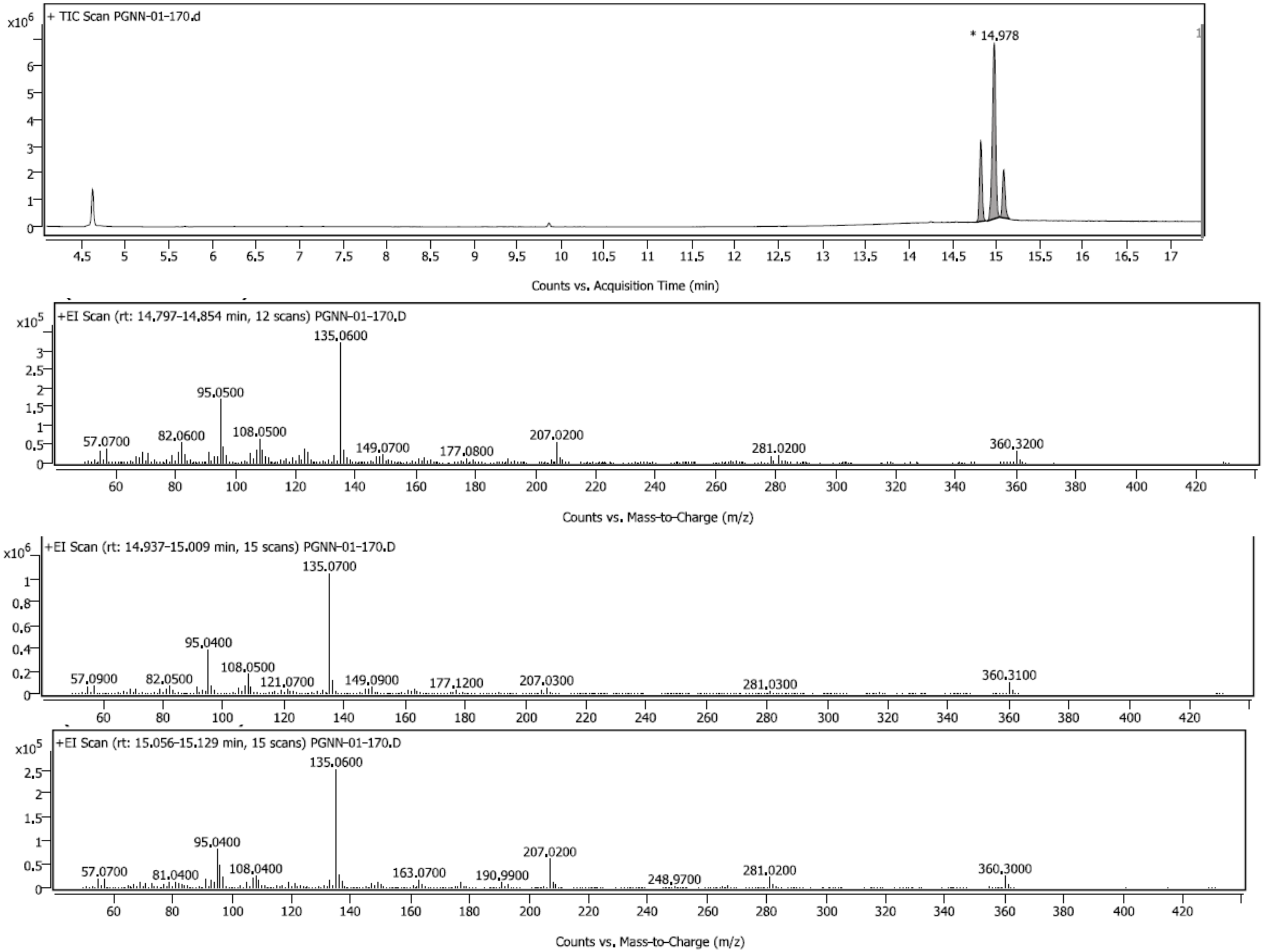
COSY-NMR spectrum of phytol-2-methylfuran coupled product **9**/**10**.



COSY-NMR spectrum of phytol-2-methylfuran coupled product zoomed to show furan signal cross-peaks **9**/**10**.



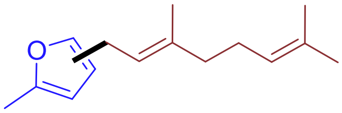
HSQC-NMR spectrum of phytol-2-methylfuran coupled product **9**/**10**.



GCMS data of phytol-2-methylfuran coupled product **9**/**10**.

2-methylfuran-geraniol **11**

IUPAC name: (E)-2-(3,7-dimethylocta-2,6-dien-1-yl)-5-methylfuran, and (E)-3-(3,7-dimethylocta-2,6-dien-1-yl)-2-methylfuran



According to General Procedure B, geraniol (0.30 mL; 1.7 mmol) was reacted with 2-methylfuran (1.5 mL; 16.6 mmol) in the presence of Perlkat 46-10 (125 mg) and 1,2-dichloroethane (2 mL) at 60 °C. The crude reaction mixture was purified by flash column chromatography (circa 300 mL silica gel; hexanes) to give the product as a colorless oil (260 mg; 34%).

TLC: Rf = 0.30 (hexane) [I_2]

^{1}H-NMR: (400 MHz, $CDCl_3$)

Major isomer (2, 5-substituted furan): 5.83 (app. d, J = 3.5 Hz, 2H), 5.32 (app. td, J = 7.1, 1.3 Hz, 1H), 5.11 (app. tt, J = 7.0, 1.5 Hz, 1H), 3.29 (d, J = 7.2 Hz, 2H), 2.25 (s, 3H), 2.15 – 1.98 (m, 4H), 1.68 (d, J = 7.2 Hz, 6H), 1.60 (s, 3H).

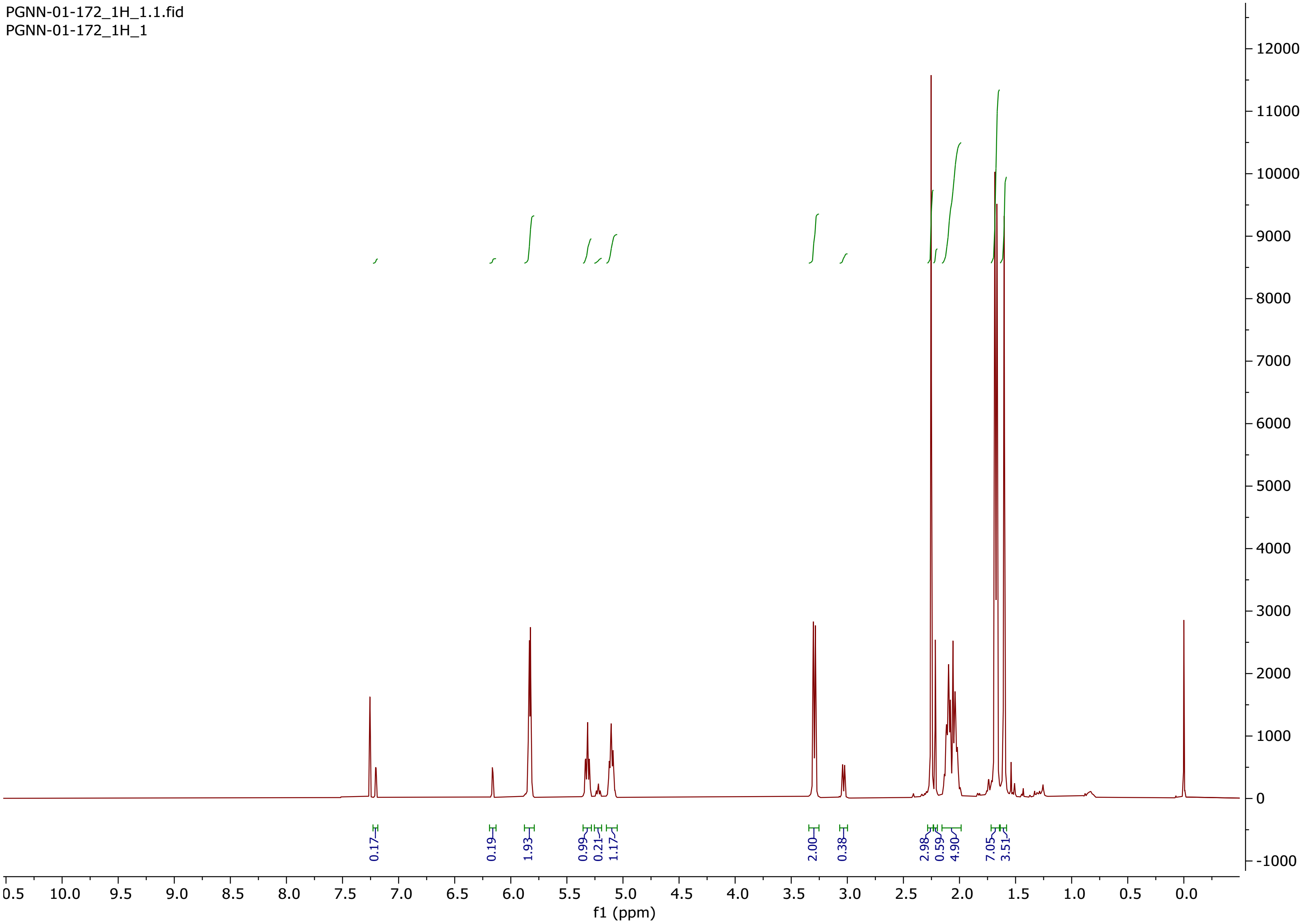
Distinct peaks corresponding to minor isomer (2, 3-substituted furan): 7.20 (d, J = 1.8 Hz, 1H), 6.16 (d, J = 1.8 Hz, 1H), 5.22 (tq, J = 7.2, 1.3 Hz, 1H), 3.03 (d, J = 7.2 Hz, 2H), 2.22 (s, 3H).

^{13}C{^{1}H}-NMR: (101 MHz, $CDCl_3$)

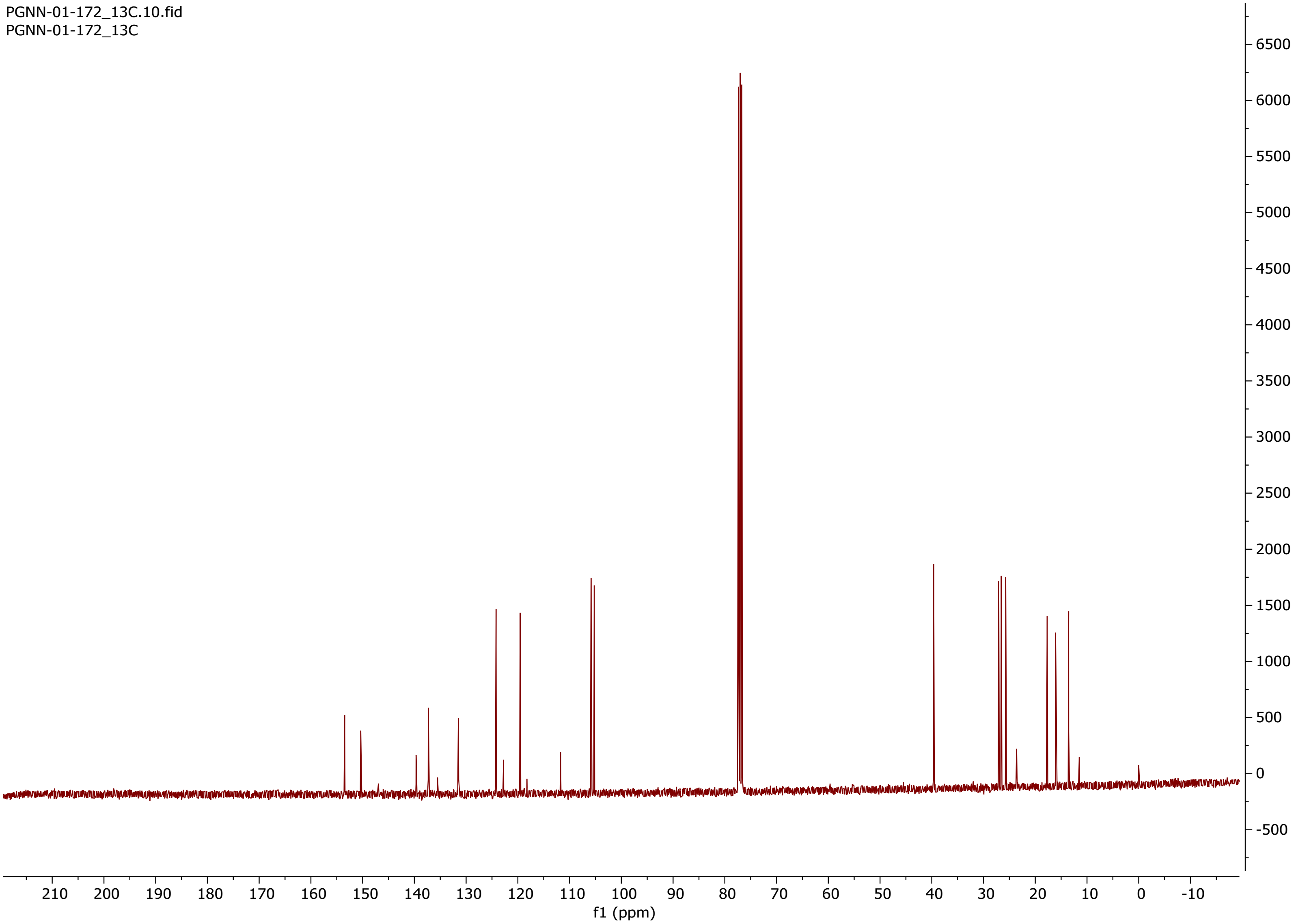
Major isomer (2, 5-substituted furan): 153.47, 150.36, 139.67, 137.31, 131.49, 124.21, 119.56, 105.55, 39.62, 27.05, 26.57, 25.71, 17.70, 16.07, 13.54.

Distinct peaks corresponding to minor isomer (2, 3-substituted furan): 146.95, 135.52, 122.75, 118.25, 111.75, 23.60, 11.49.

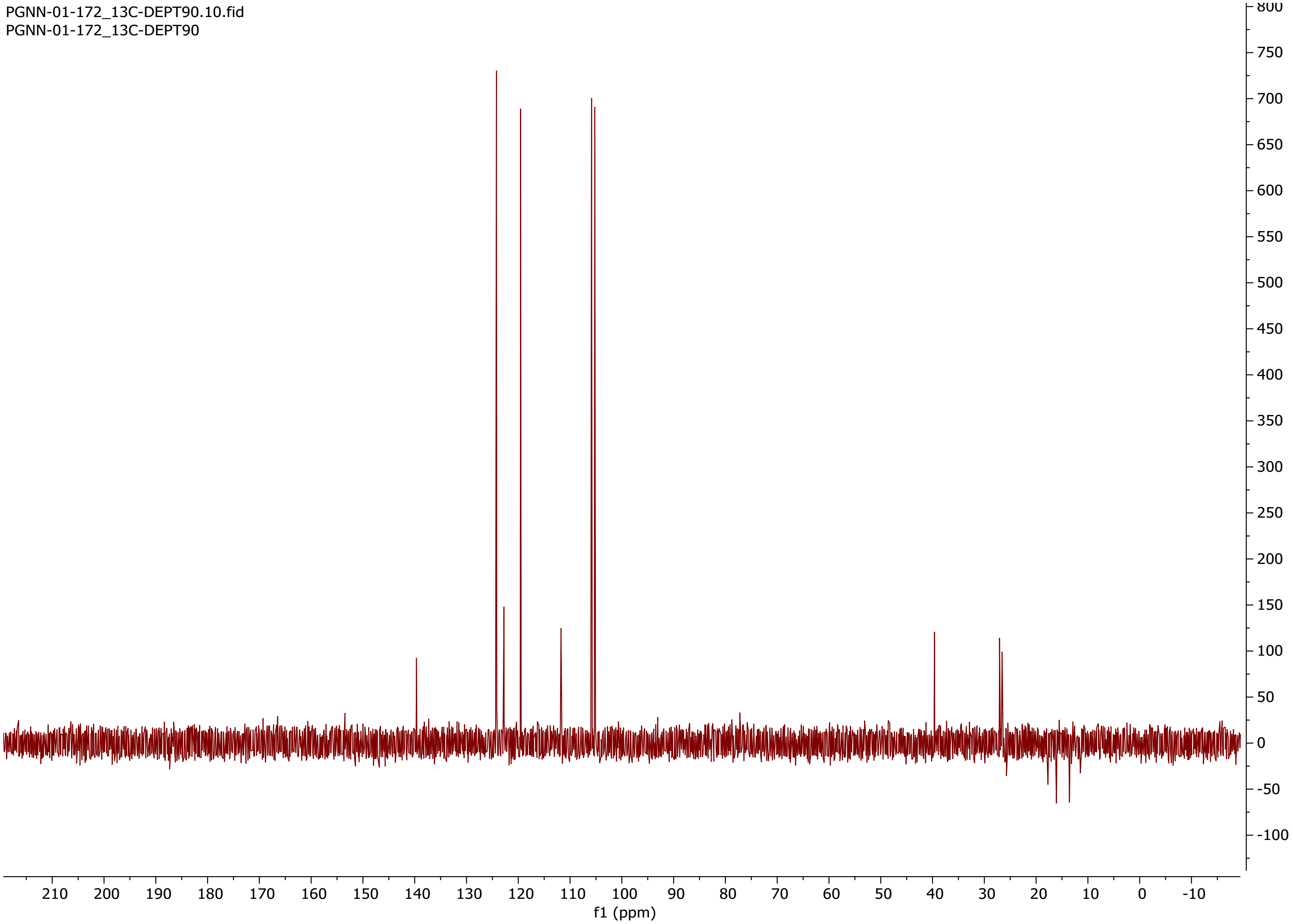
GCMS: 11.685 min (shouldered peak; m/z 218.14).



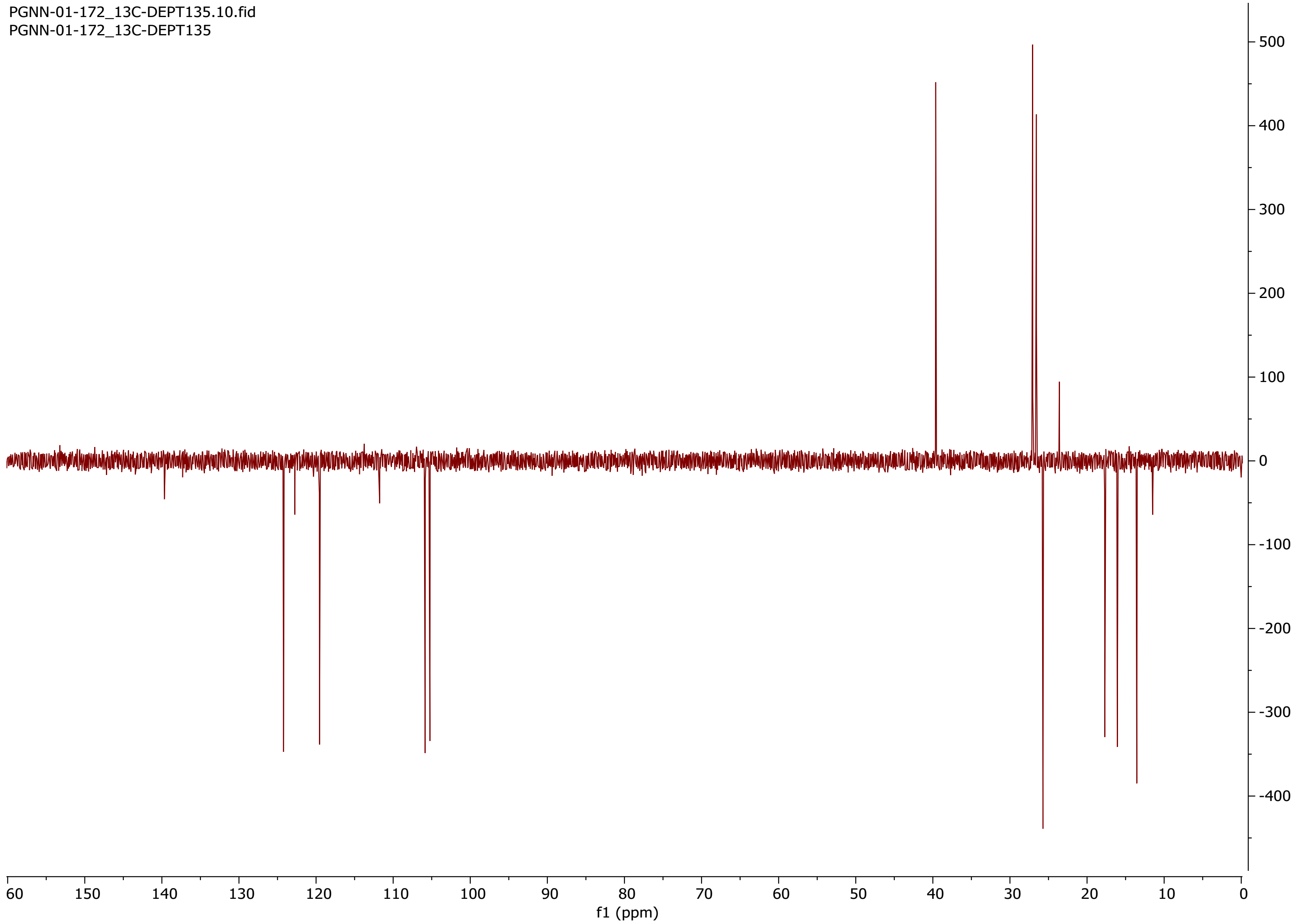
^{1}H-NMR spectrum of geraniol-2-methylfuran coupled product **11**.



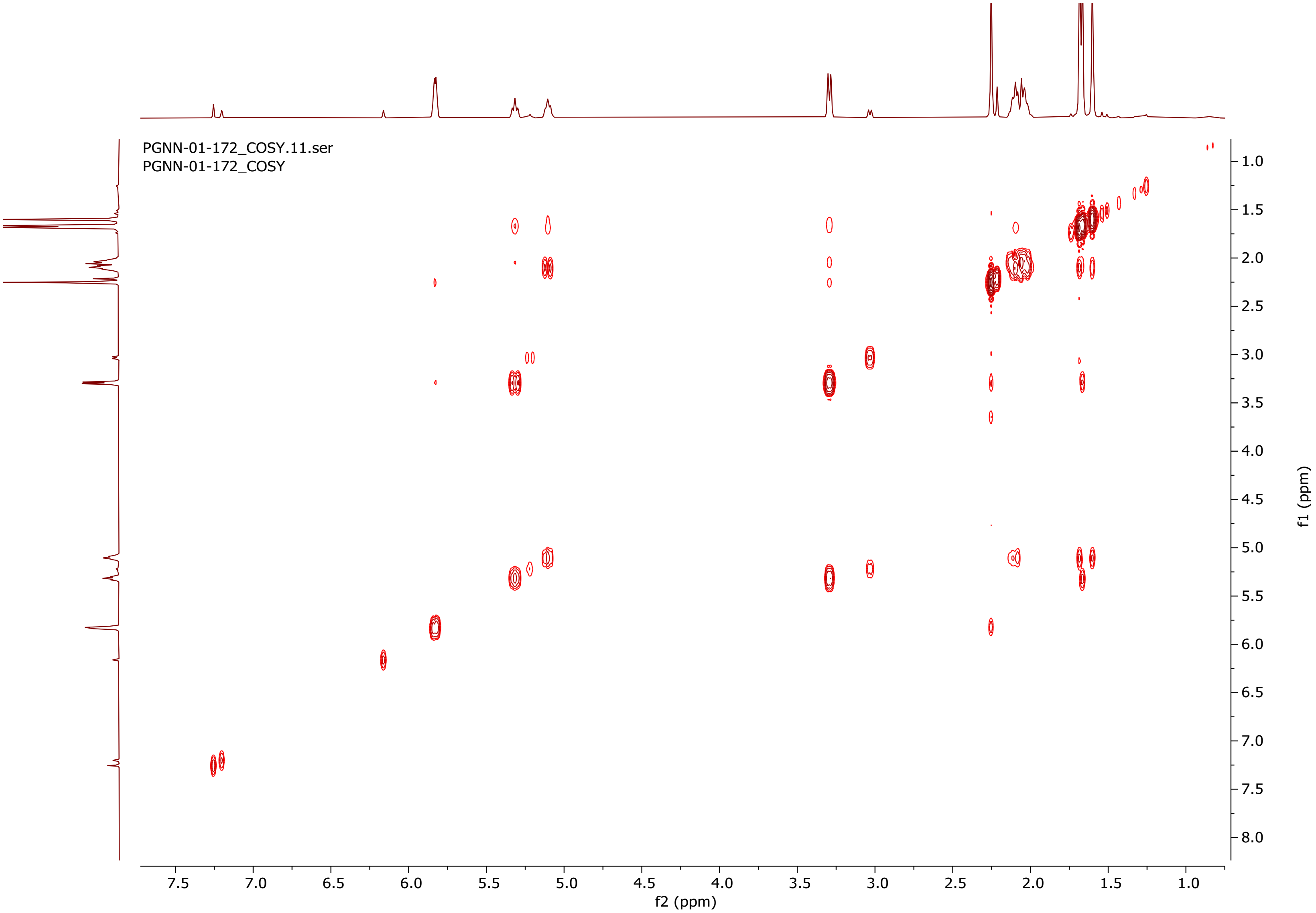
^{13}C-NMR spectrum of geraniol-2-methylfuran coupled product **11**.



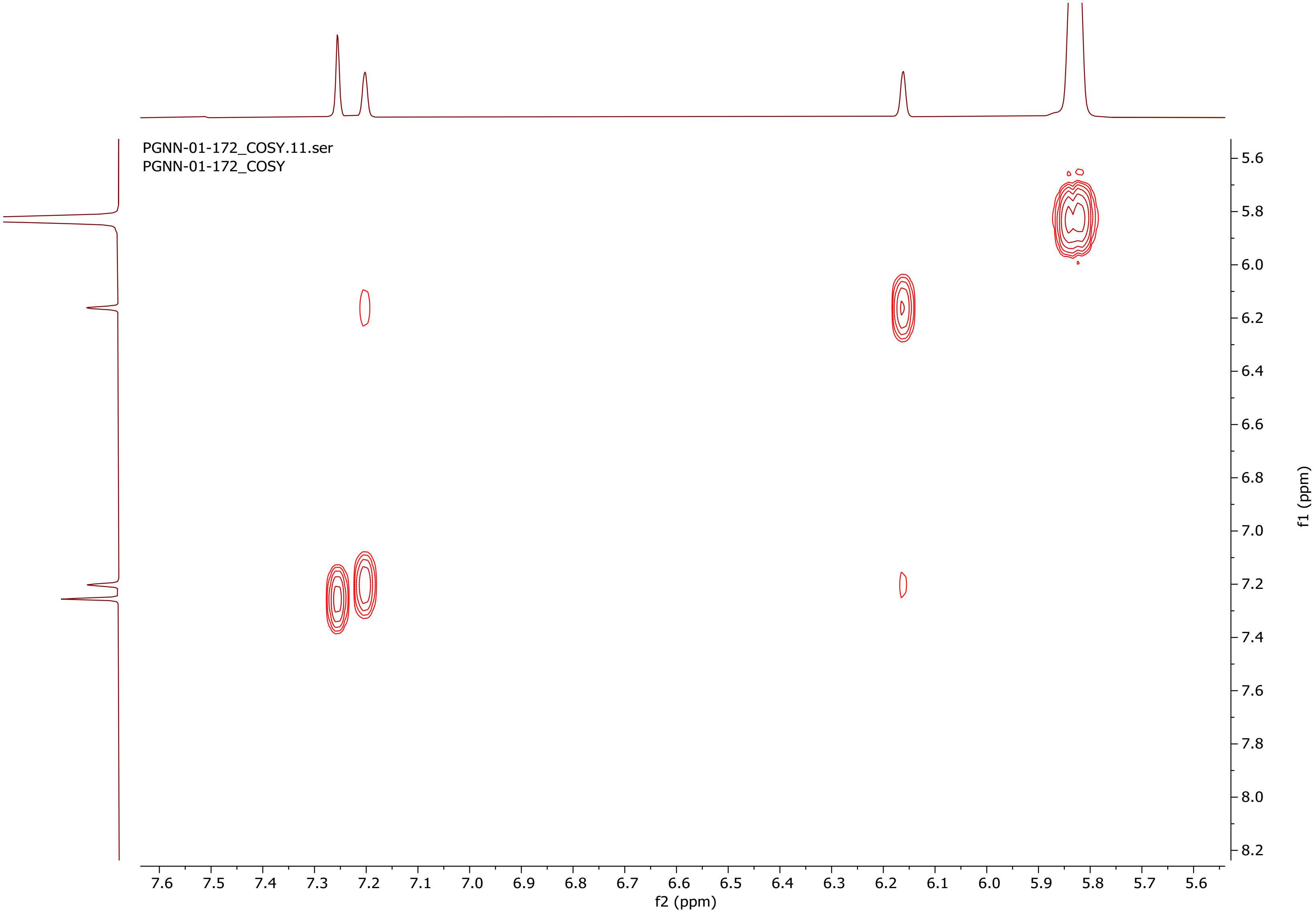
^{13}C-DEPT90-NMR spectrum of geraniol-2-methylfuran coupled product **11**.



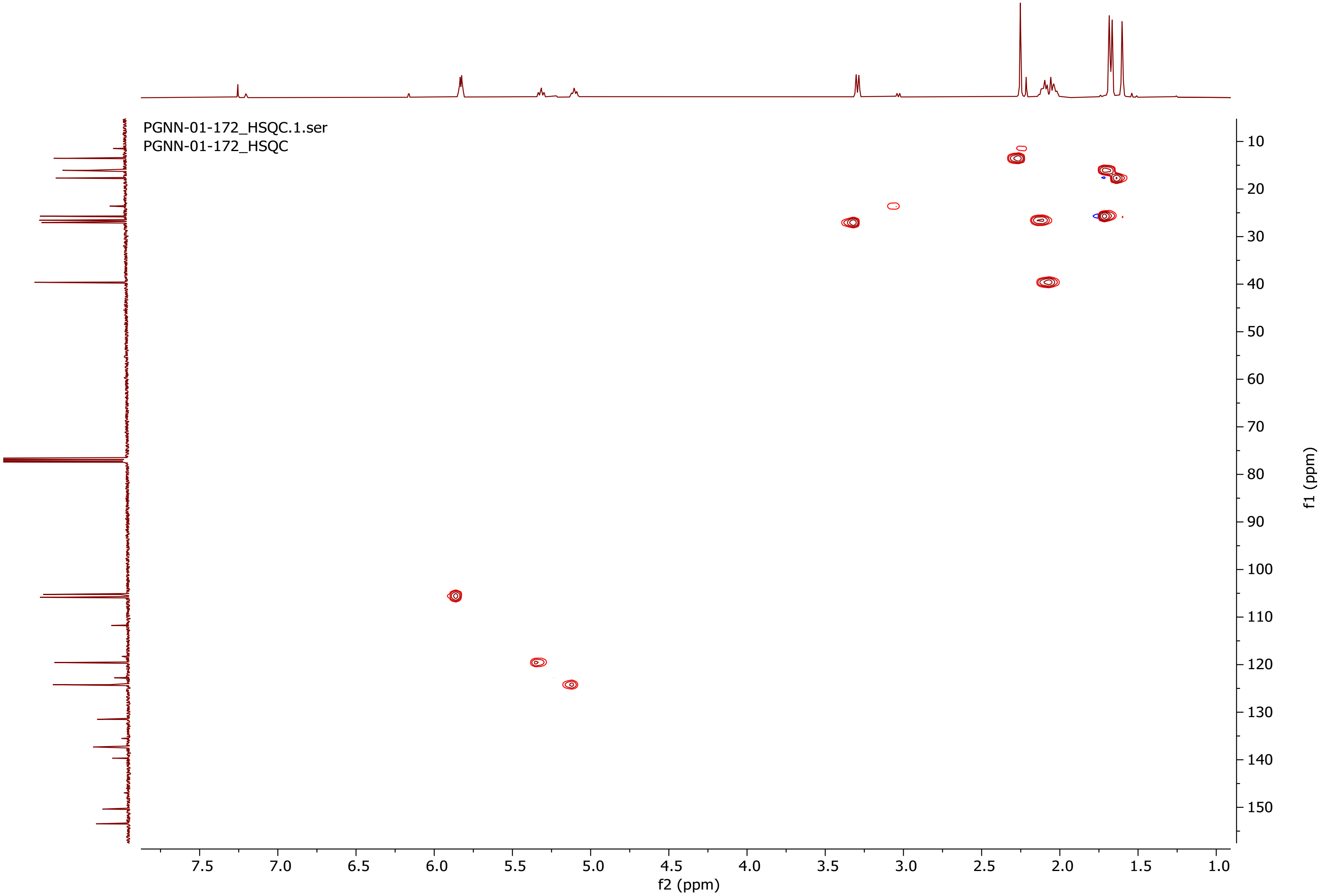
^{13}C-DEPT135-NMR spectrum of geraniol-2-methylfuran coupled product **11**.



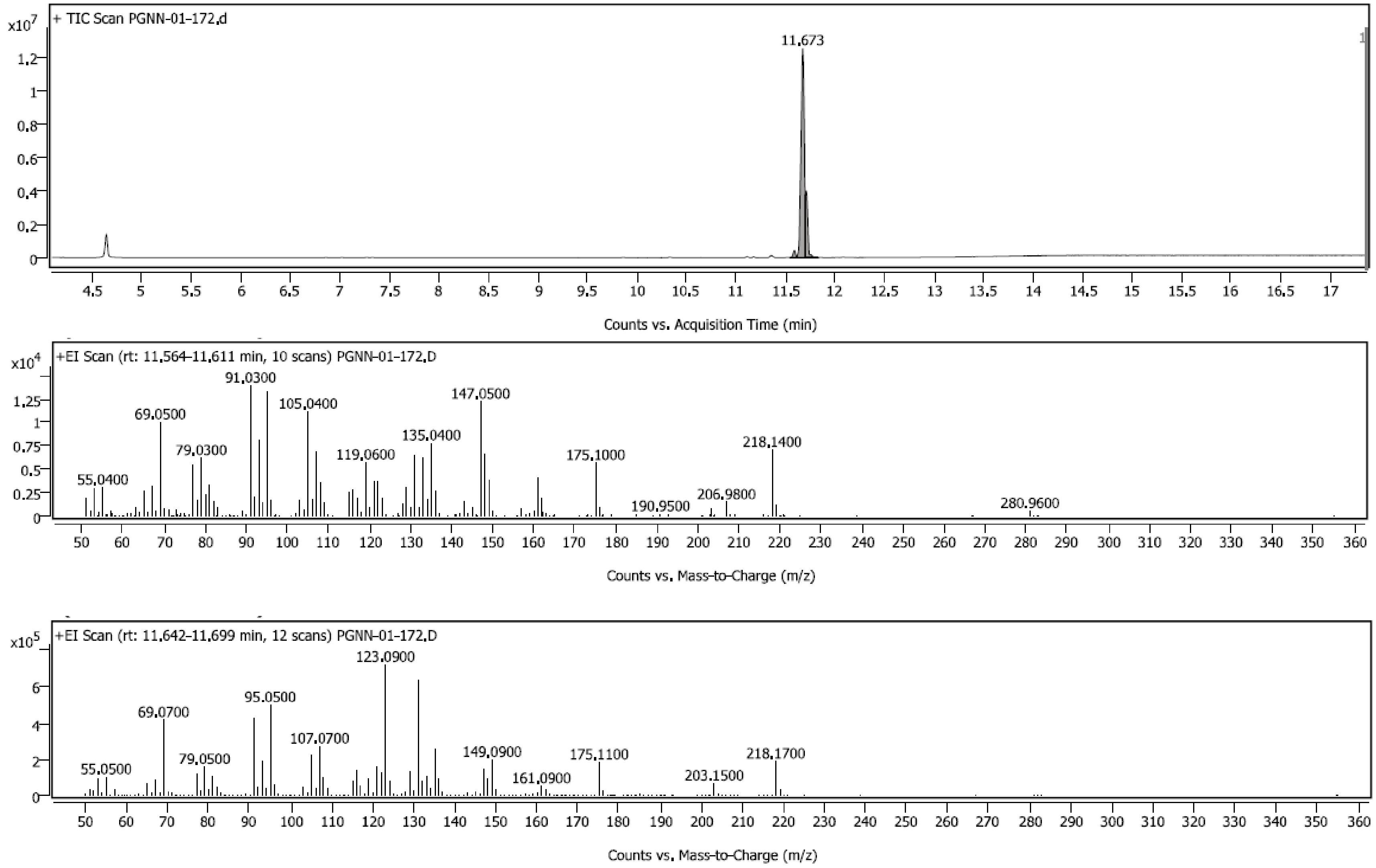
COSY-NMR spectrum of geraniol-2-methylfuran coupled product **11**.



COSY-NMR spectrum of geraniol-2-methylfuran coupled product zoomed to show furan signal cross-peaks **11**.



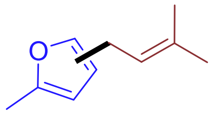
HSQC-NMR spectrum of geraniol-2-methylfuran coupled product **11**.



GCMS data of geraniol-2-methylfuran coupled product **11**.

2-methylfuran-prenol **12**

IUPAC name: 2-methyl-5-(3-methylbut-2-en-1-yl)furan, and 2-methyl-3-(3-methylbut-2-en-1-yl)furan



According to General Procedure B, prenol (0.17 mL; 1.7 mmol) was reacted with 2-methylfuran (1.5 mL; 16.6 mmol) in the presence of Perlkat 46-10 (125 mg) and 1,2-dichloroethane (2 mL) at 60 °C. The crude reaction mixture was purified by flash column chromatography (circa 250 mL silica gel; hexanes) to give the product as a colorless oil (105 mg; 41%).

TLC: Rf = 0.24 (hexane) [I_2]

^{1}H-NMR: (400 MHz, $CDCl_3$)

Major isomer (2, 5-substituted furan): 5.87 – 5.80 (m, 2H), 5.30 (ddq, J = 8.6, 5.8, 1.5 Hz, 1H), 3.28 (d, J = 7.1 Hz, 2H), 2.25 (s, 3H), 1.74 (s, 3H), 1.68 (s, 3H).

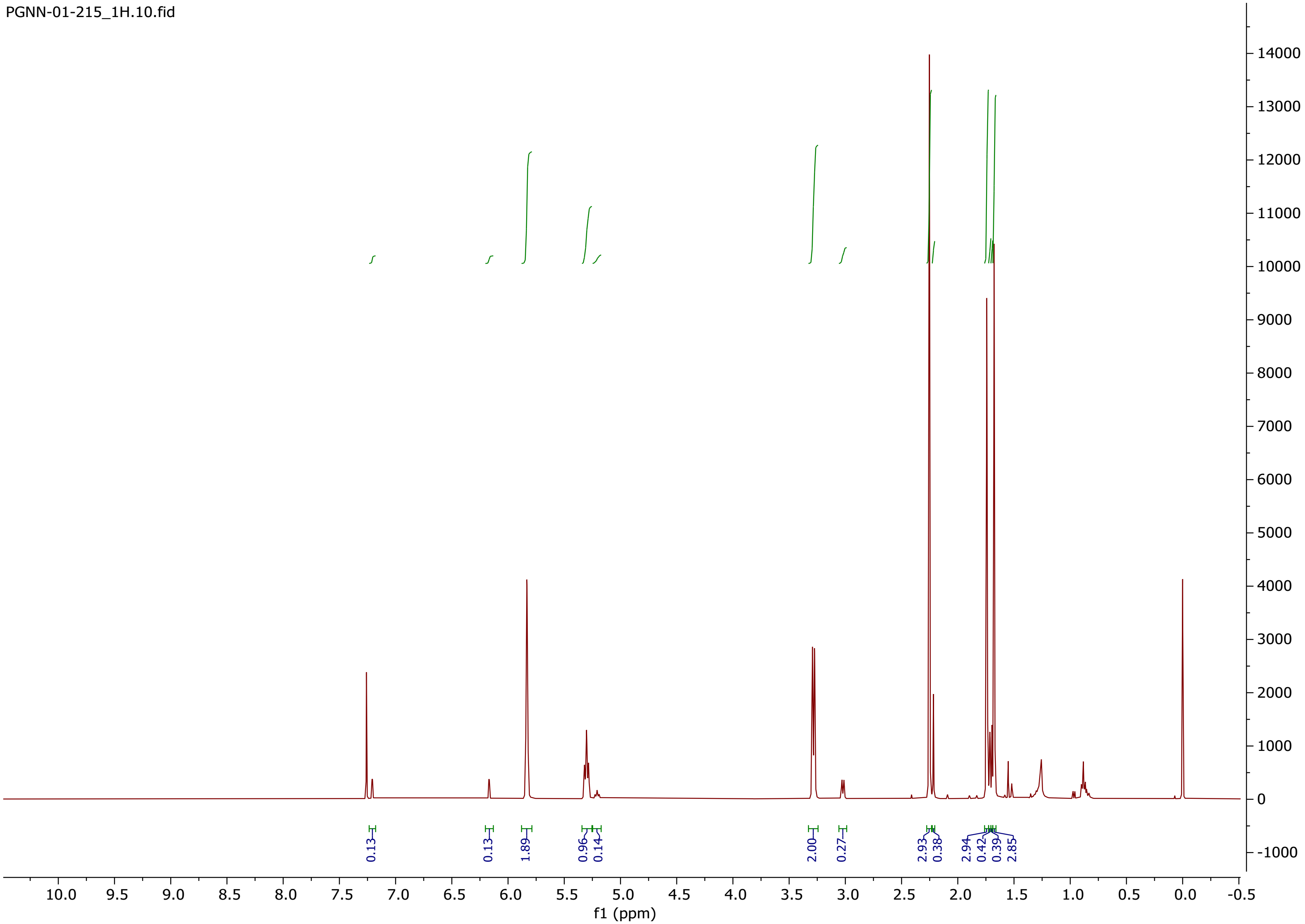
Distinct peaks corresponding to minor isomer (2, 3-substituted furan): 7.21 (d, J = 1.9 Hz, 1H), 6.17 (d, J = 1.8 Hz, 1H), 5.21 (ddq, J = 8.8, 5.8, 1.5 Hz, 1H), 3.02 (d, J = 7.2 Hz, 2H), 2.22 (s, 3H), 1.71 (s, 3H), 1.70 (s, 3H).

^{13}C{^{1}H}-NMR: (101 MHz, $CDCl_3$)

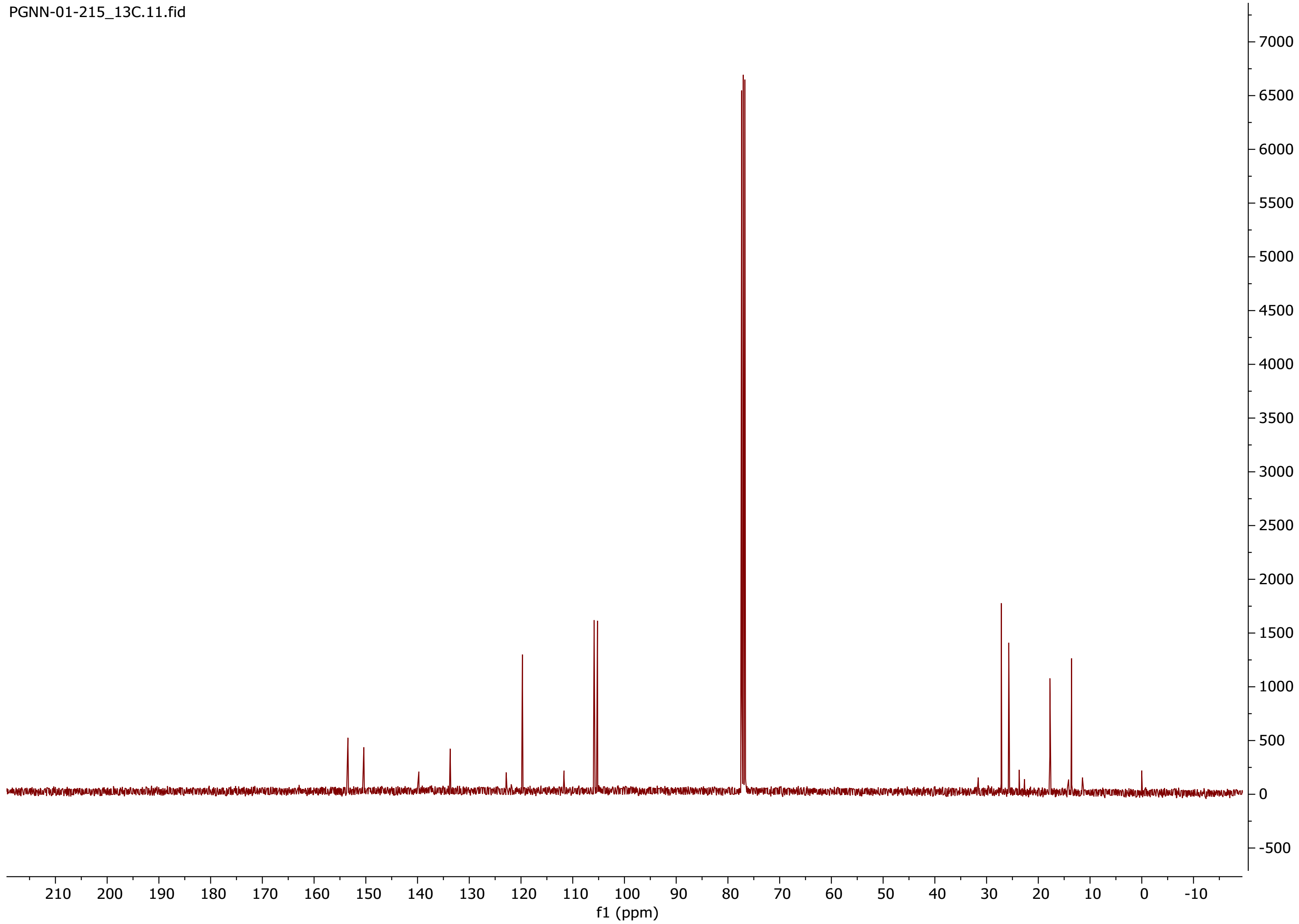
Major isomer (2, 5-substituted furan): 153.45, 150.37, 133.68, 119.72, 105.85, 105.21, 27.15, 25.69, 17.75, 13.55.

Distinct peaks corresponding to minor isomer (2, 3-substituted furan): 139.74, 122.86, 111.67, 31.60, 23.69, 22.67, 14.13, 11.46.

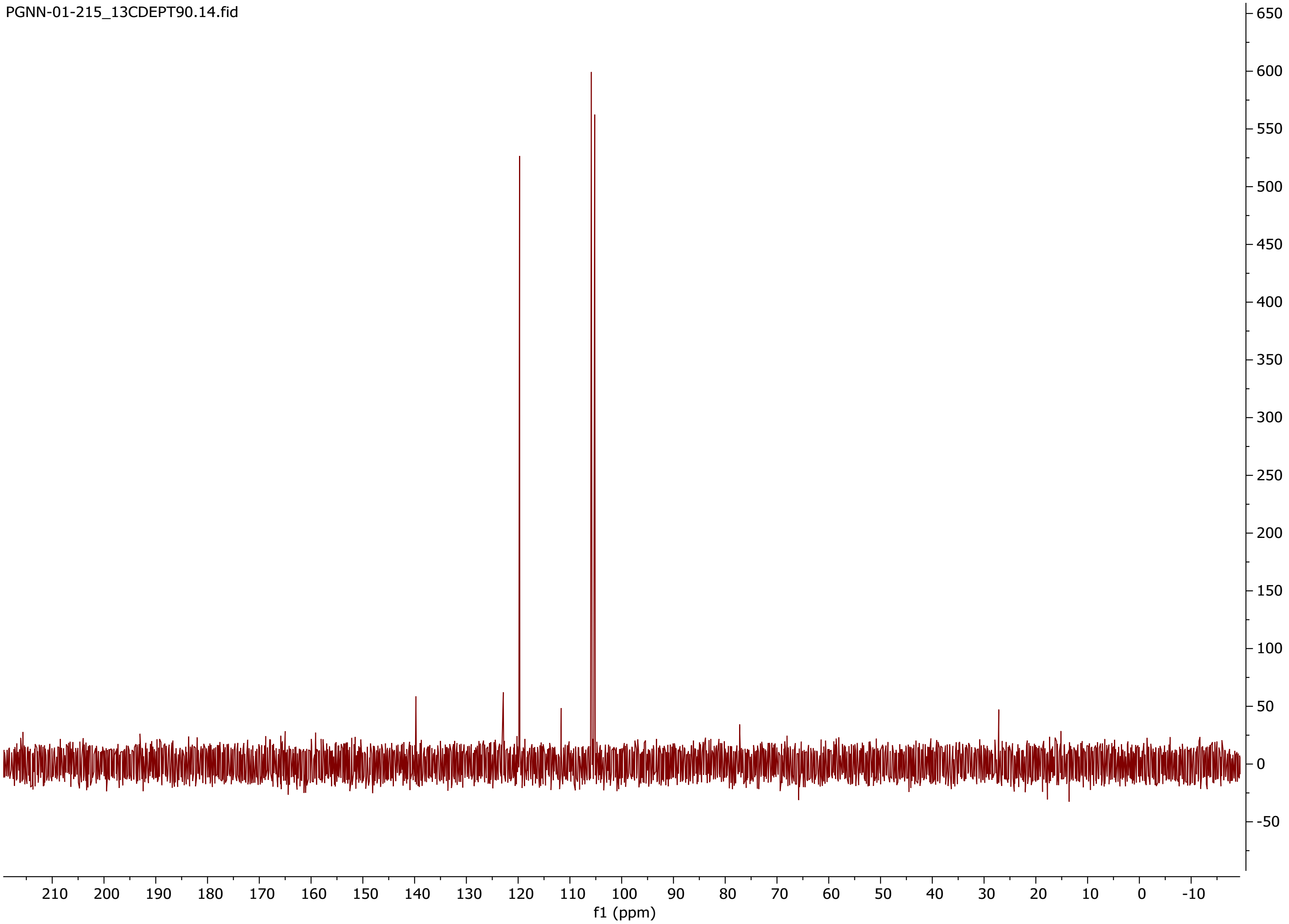
GCMS: 9.447 min (m/z 150.15).



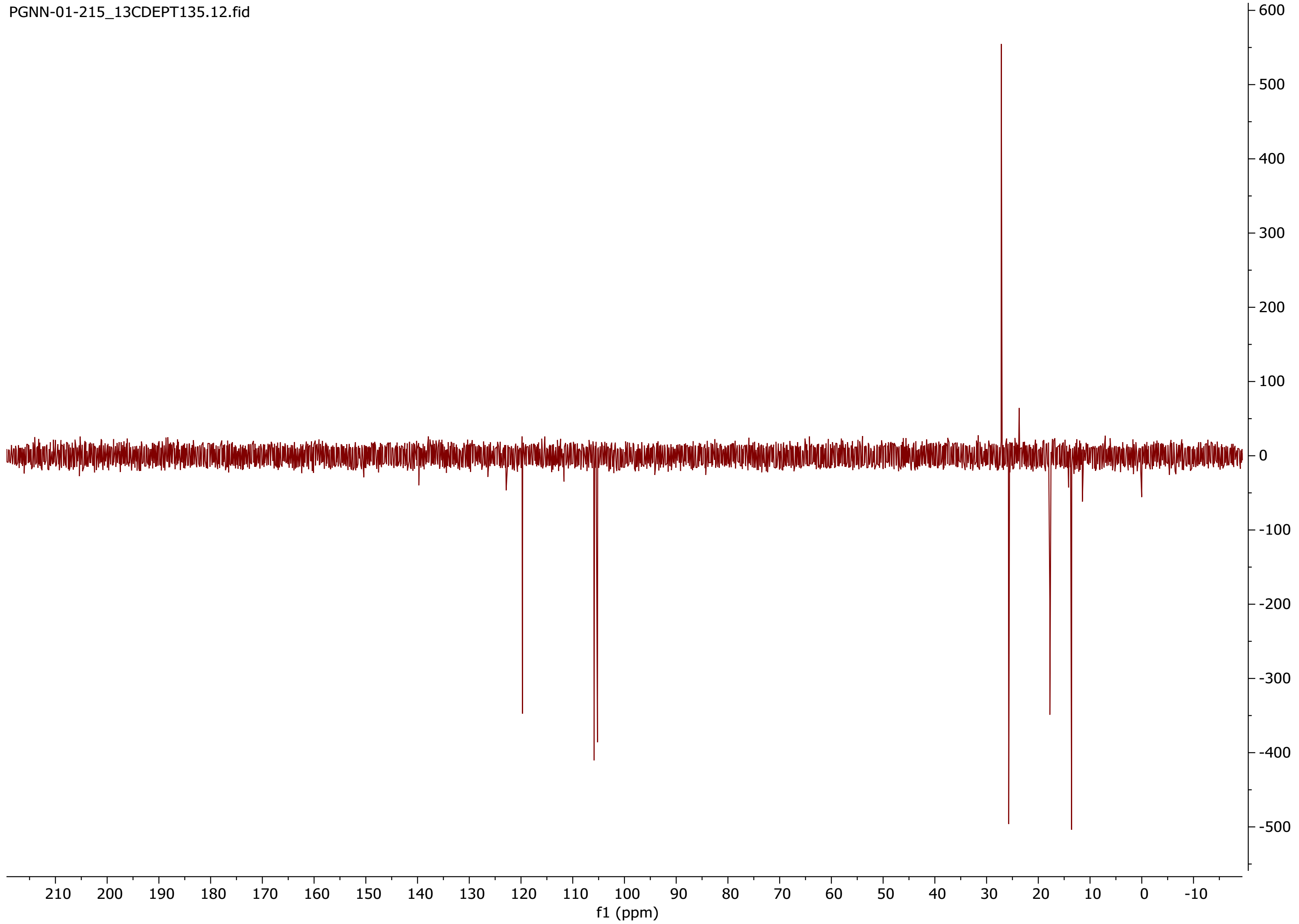
^{1}H-NMR spectrum of prenol-2-methylfuran coupled product **12**.



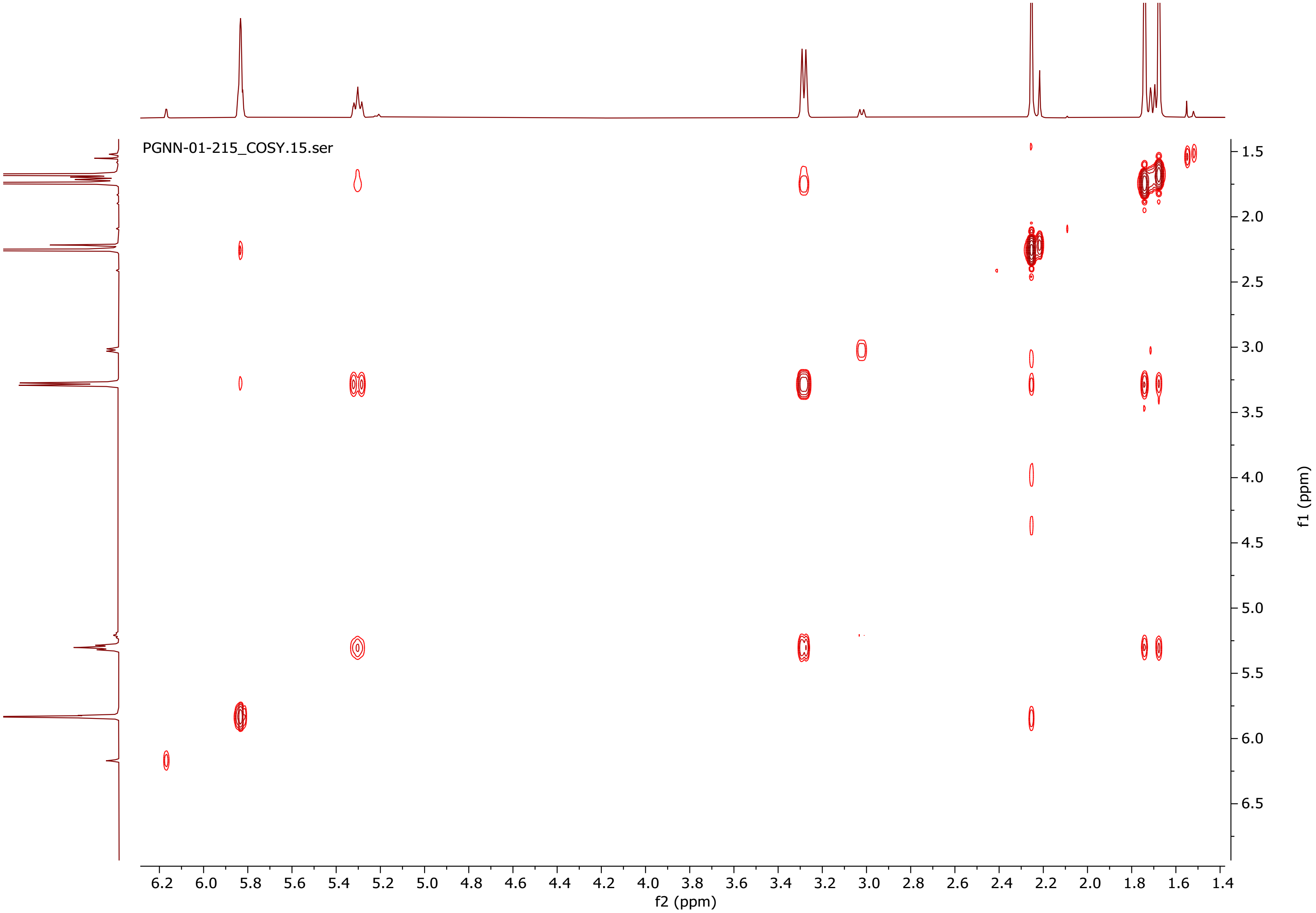
^{13}C-NMR spectrum of prenol-2-methylfuran coupled product **12**.



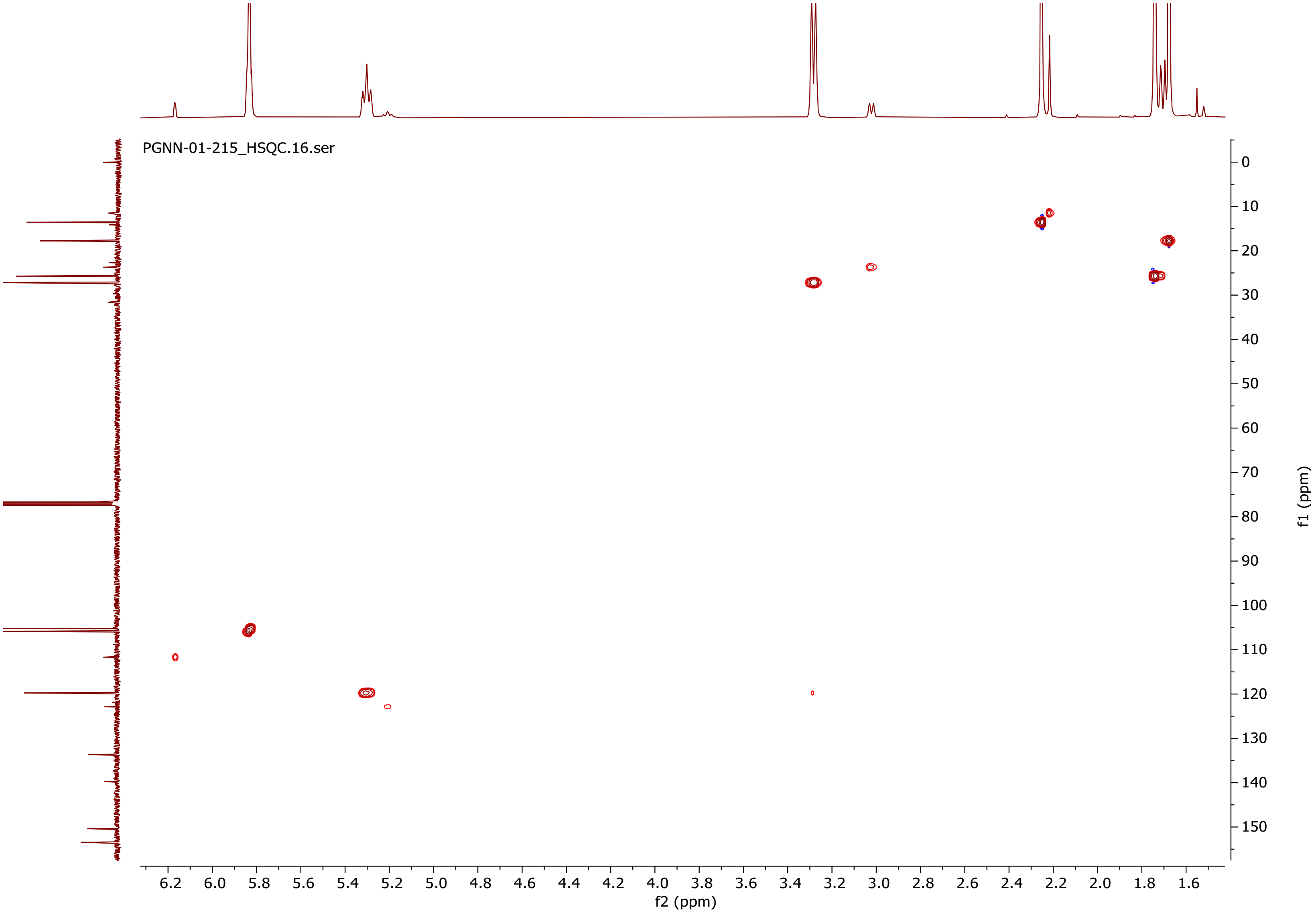
^{13}C-DEPT90-NMR spectrum of prenol-2-methylfuran coupled product **12**.



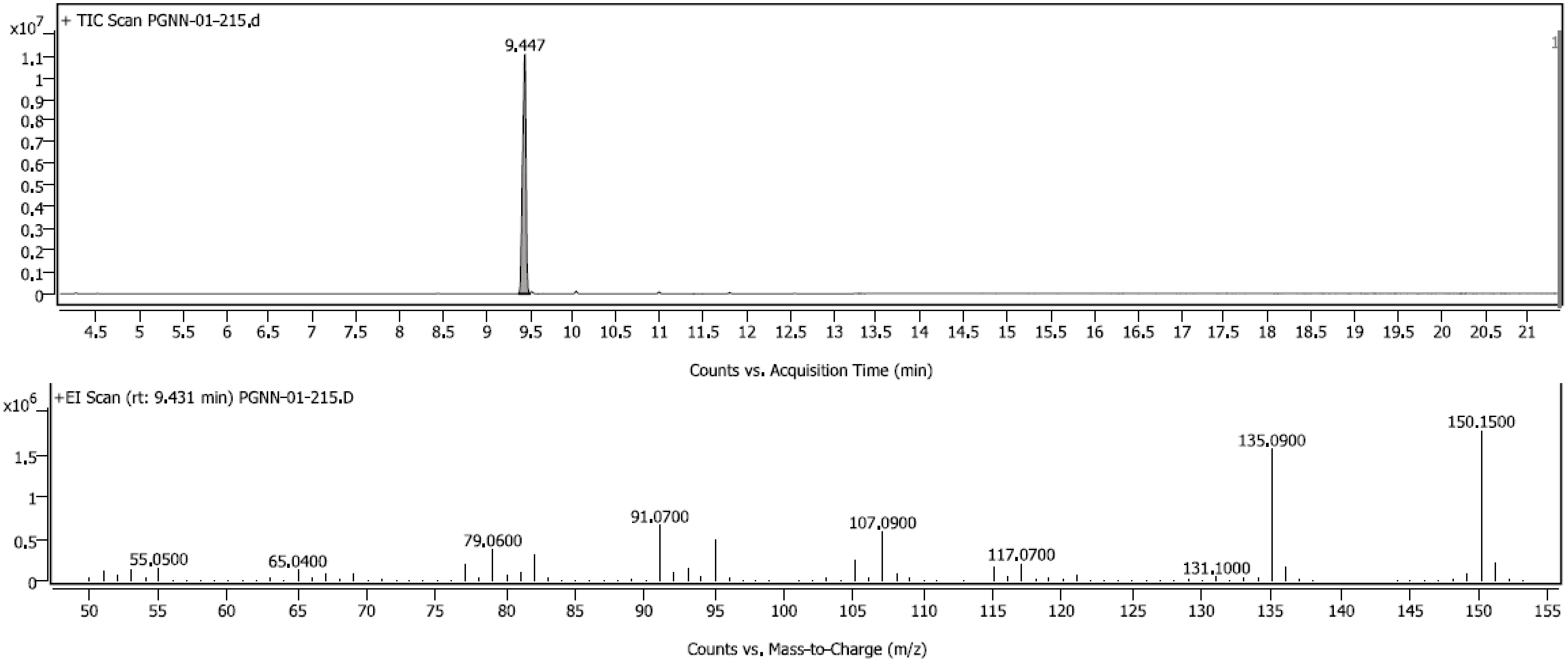
^{13}C-DEPT135-NMR spectrum of prenol-2-methylfuran coupled product **12**.



COSY-NMR spectrum of prenol-2-methylfuran coupled product **12**.



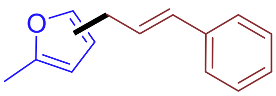
HSQC-NMR spectrum of prenol-2-methylfuran coupled product **12**.



GCMS data of prenol-2-methylfuran coupled product **12**.

2-methylfuran-cinnamyl alcohol **13**

IUPAC name: 2-cinnamyl-5-methylfuran, and 3-cinnamyl-2-methylfuran



According to General Procedure B, cinnamyl alcohol (228 mg; 1.7 mmol) was reacted with 2-methylfuran (1.5 mL; 16.6 mmol) in the presence of Perlkat 46-10 (125 mg) and 1,2-dichloroethane (2 mL) at 60 °C. The crude reaction mixture was purified by flash column chromatography (circa 100 mL silica gel; hexanes) to give the product as a yellow oil (194 mg; 58%).

TLC: Rf = 0.28 (hexane) [I_2]

^{1}H-NMR: (400 MHz, $CDCl_3$)

Major isomer (2, 5-substituted furan): 7.40 – 7.26 (m, 5H), 7.24 – 7.17 (m, 2H), 6.49 (d, J = 15.8 Hz, 1H), 6.30 (dt, J = 15.7, 6.7 Hz, 1H), 5.93 (d, J = 2.9 Hz, 1H), 5.88 (dt, J = 3.1, 1.2 Hz, 1H), 3.50 (d, J = 6.7 Hz, 2H), 2.27 (s, 3H).

Distinct peaks corresponding to secondary isomer (α-aryl furan): 6.25 – 6.15 (m, 1H), 5.91 (app. d, J = 2.0 Hz, 1H), 5.18 (dt, J = 10.2, 1.3 Hz, 1H), 5.04 (dt, J = 17.1, 1.4 Hz, 1H), 4.68 (d, J = 7.2 Hz, 1H), 2.24 (s, 3H).

Distinct peaks corresponding to tertiary isomer (2, 3-substituted furan): 6.40 (d, J = 15.8 Hz, 1H), 3.25 (d, J = 6.4 Hz, 2H), 2.24 (s, 3H).

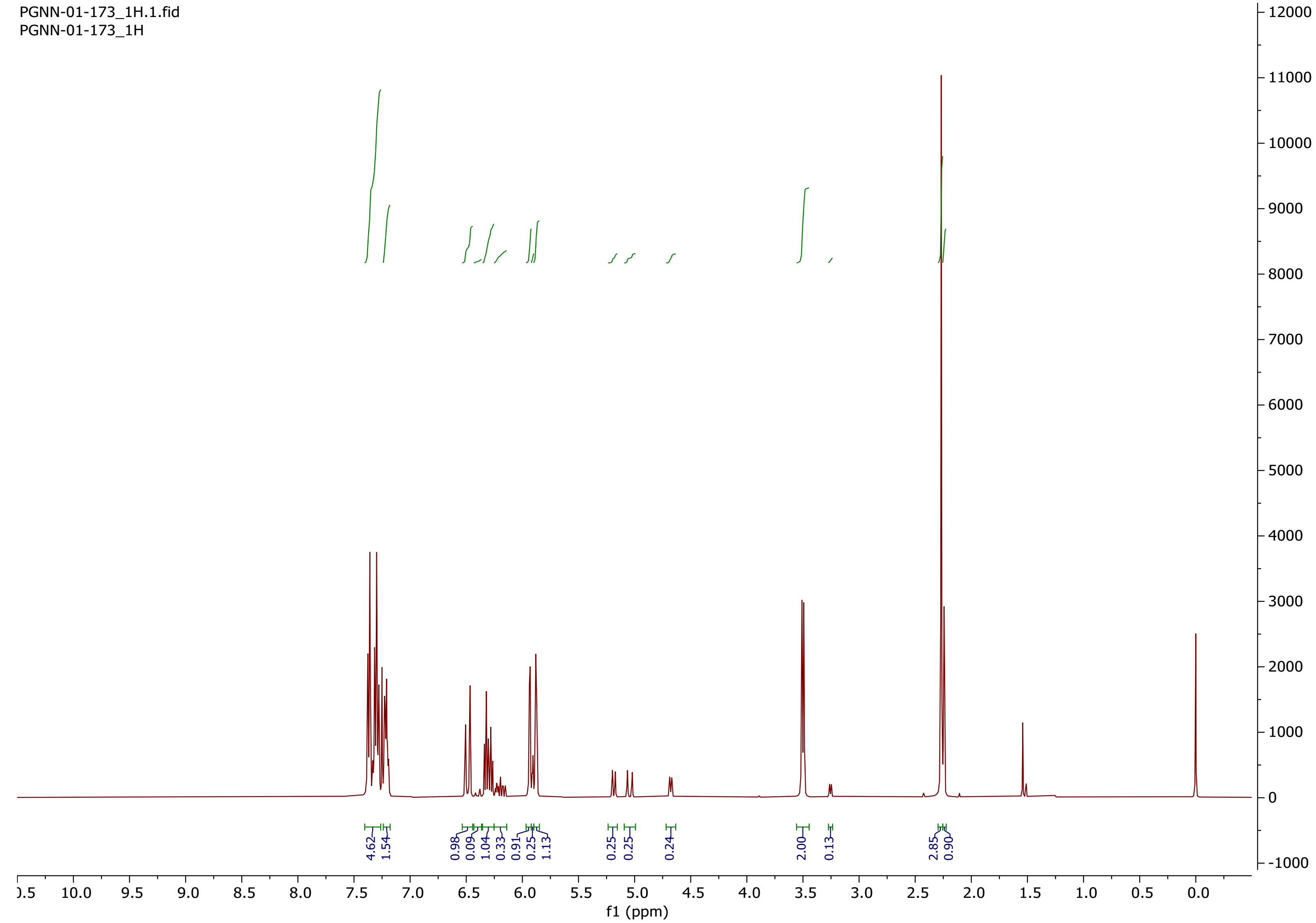
^{13}C{^{1}H}-NMR: (101 MHz, $CDCl_3$)

Major isomer (2, 5-substituted furan): 152.01, 150.89, 138.40, 137.36, 131.71, 128.51, 127.23, 126.20, 126.02, 106.27, 106.06, 31.88, 13.57.

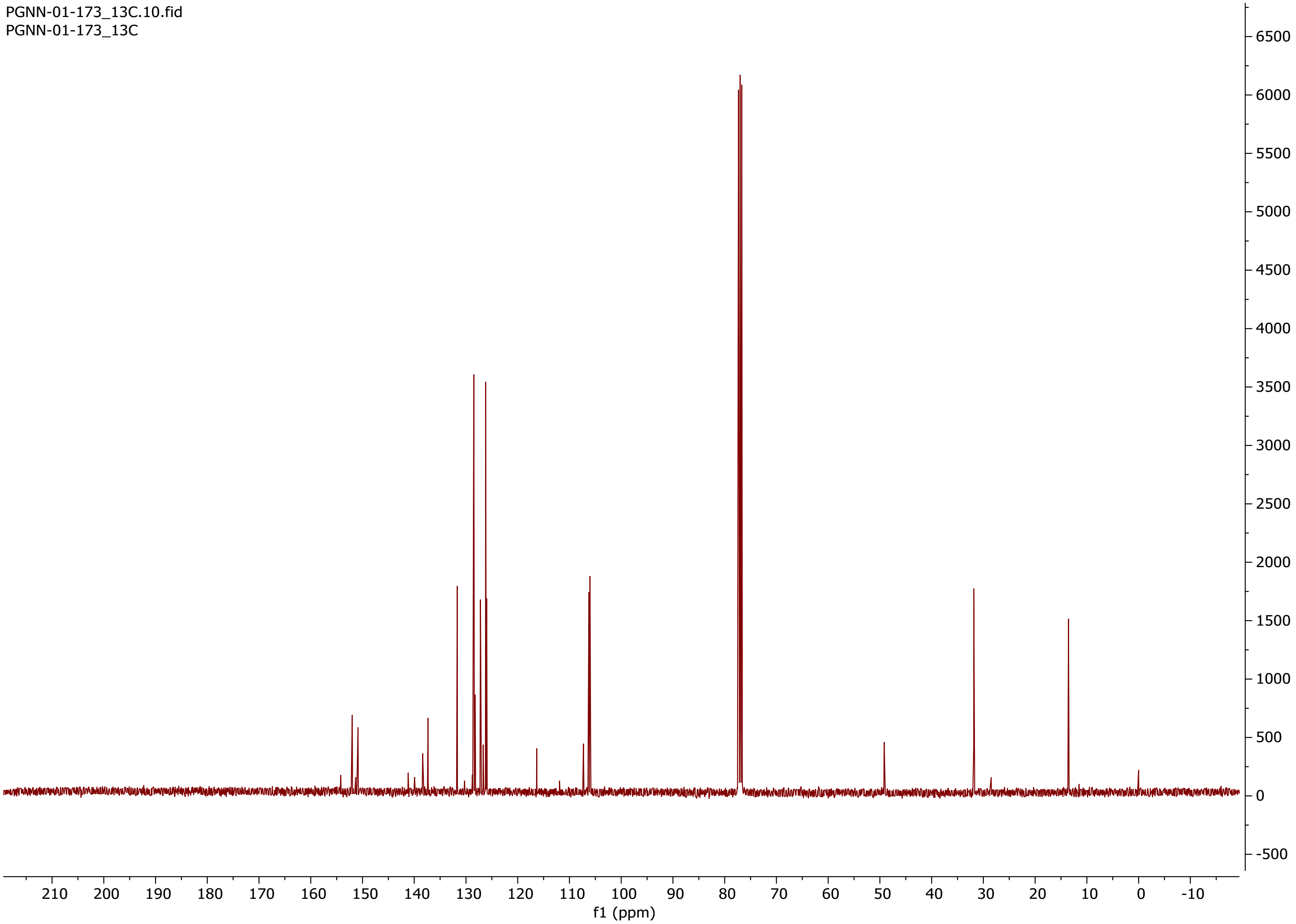
Distinct peaks corresponding to secondary isomer (α-aryl furan): 154.22, 151.35, 141.19, 139.96, 116.36, 111.95, 107.33, 49.21, 28.51.

Distinct peaks corresponding to tertiary isomer (2, 3-substituted furan): not observed owing to very low concentrations in sample.

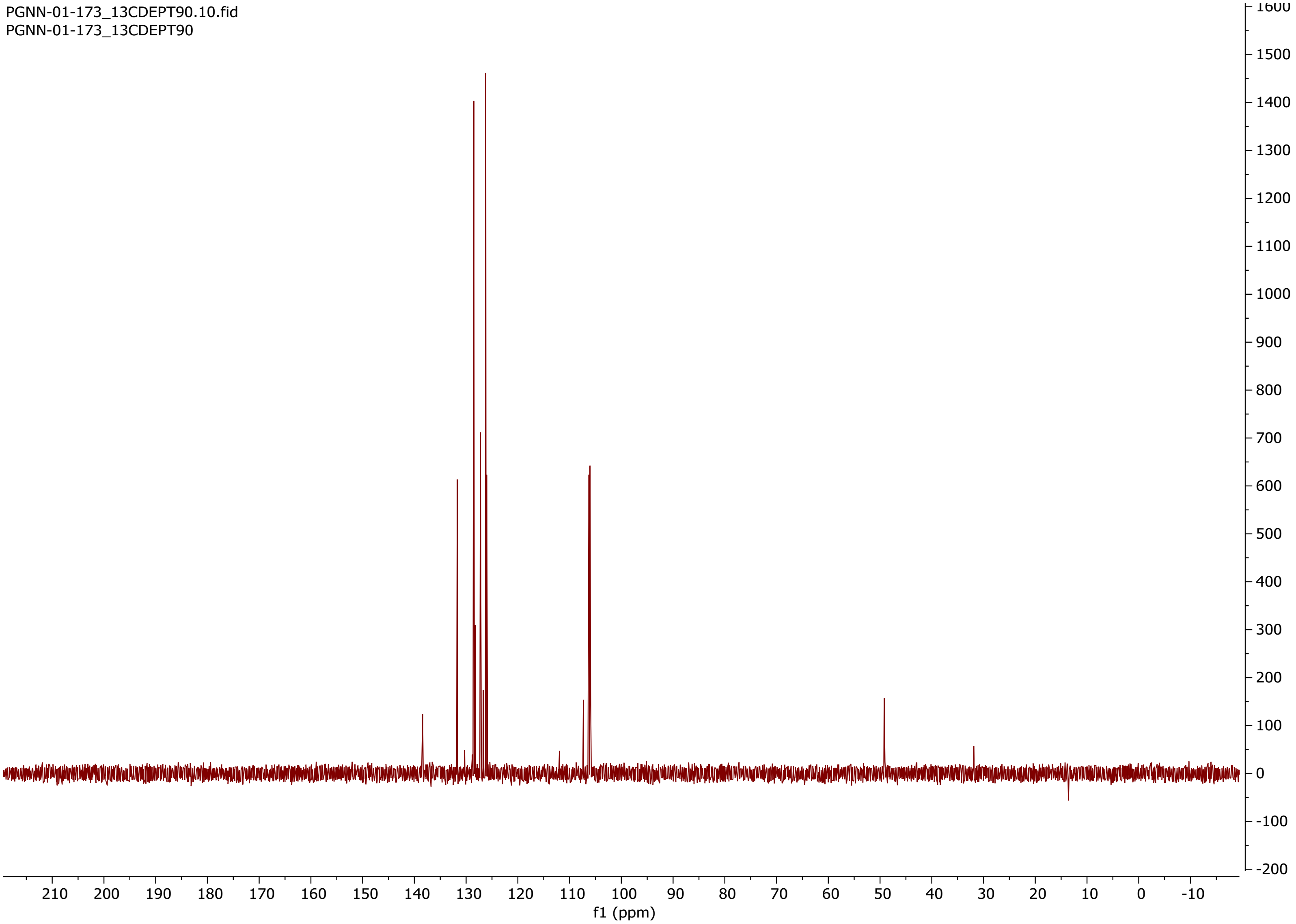
GCMS: 11.216 min (20%; m/z 198.12); 11.979 (80%; m/z 198.12).



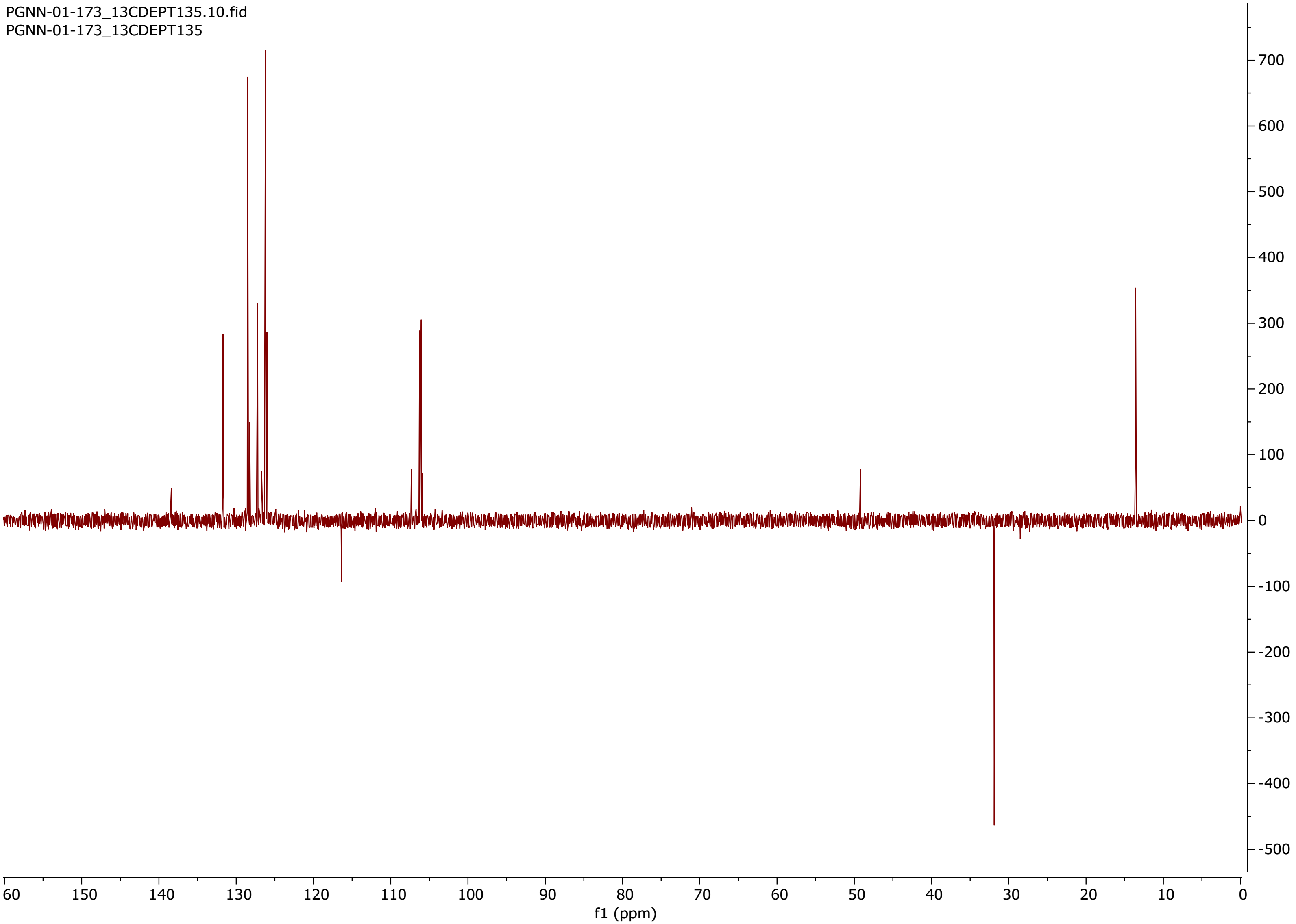
^{1}H-NMR spectrum of cinnamyl alcohol-2-methylfuran coupled product **13**.



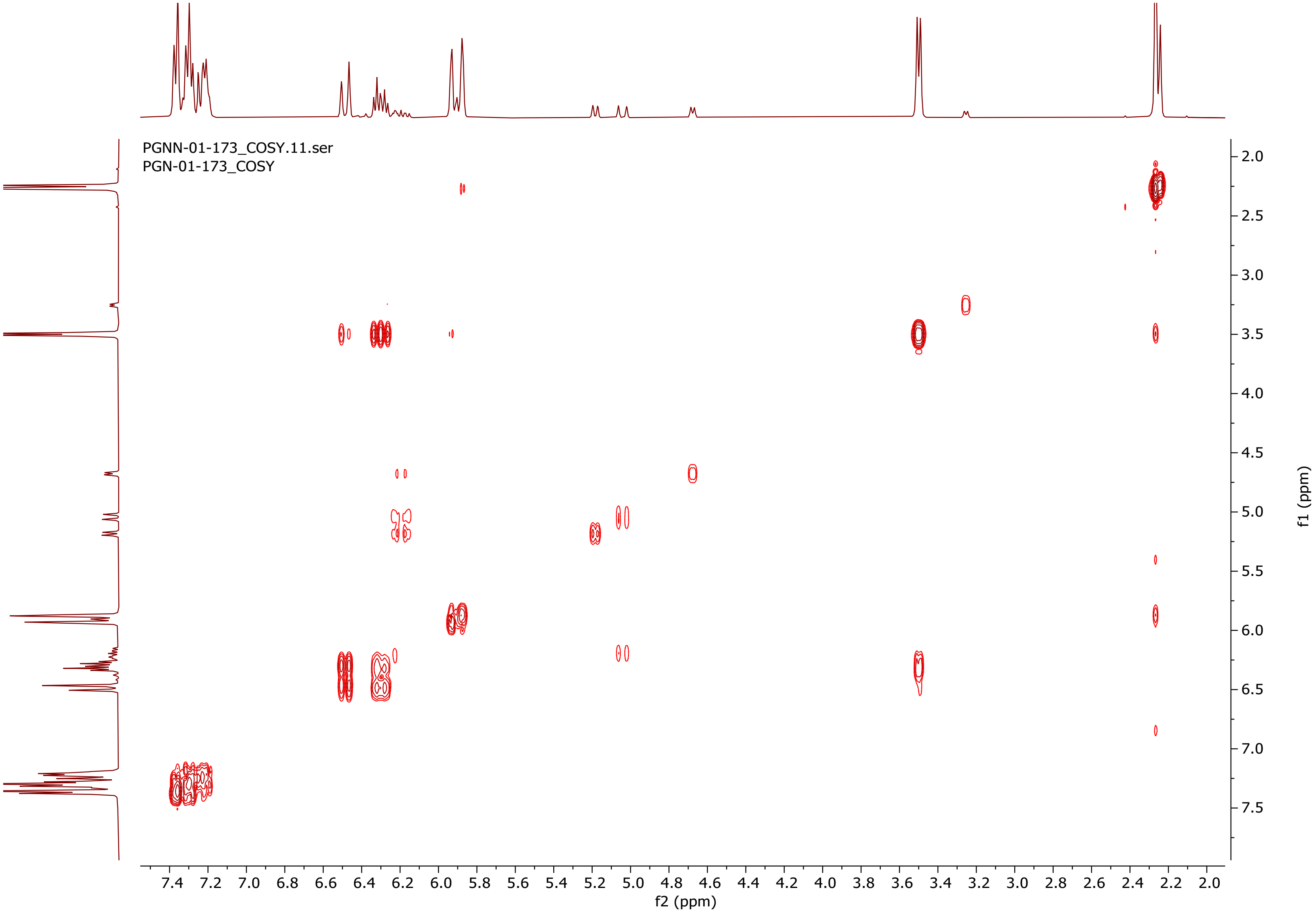
^{13}C-NMR spectrum of cinnamyl alcohol-2-methylfuran coupled product **13**.



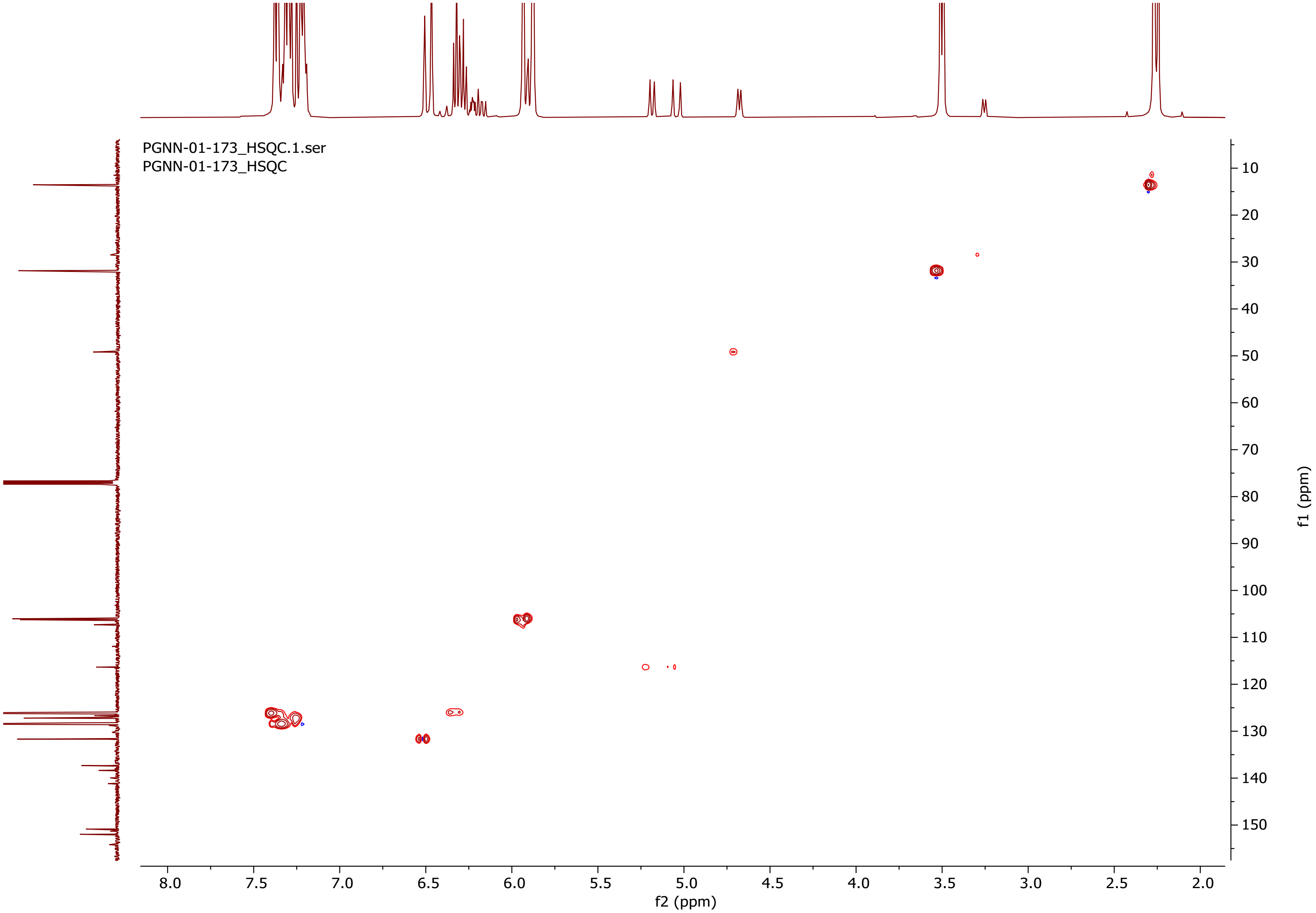
^{13}C-DEPT90-NMR spectrum of cinnamyl alcohol-2-methylfuran coupled product **13**.



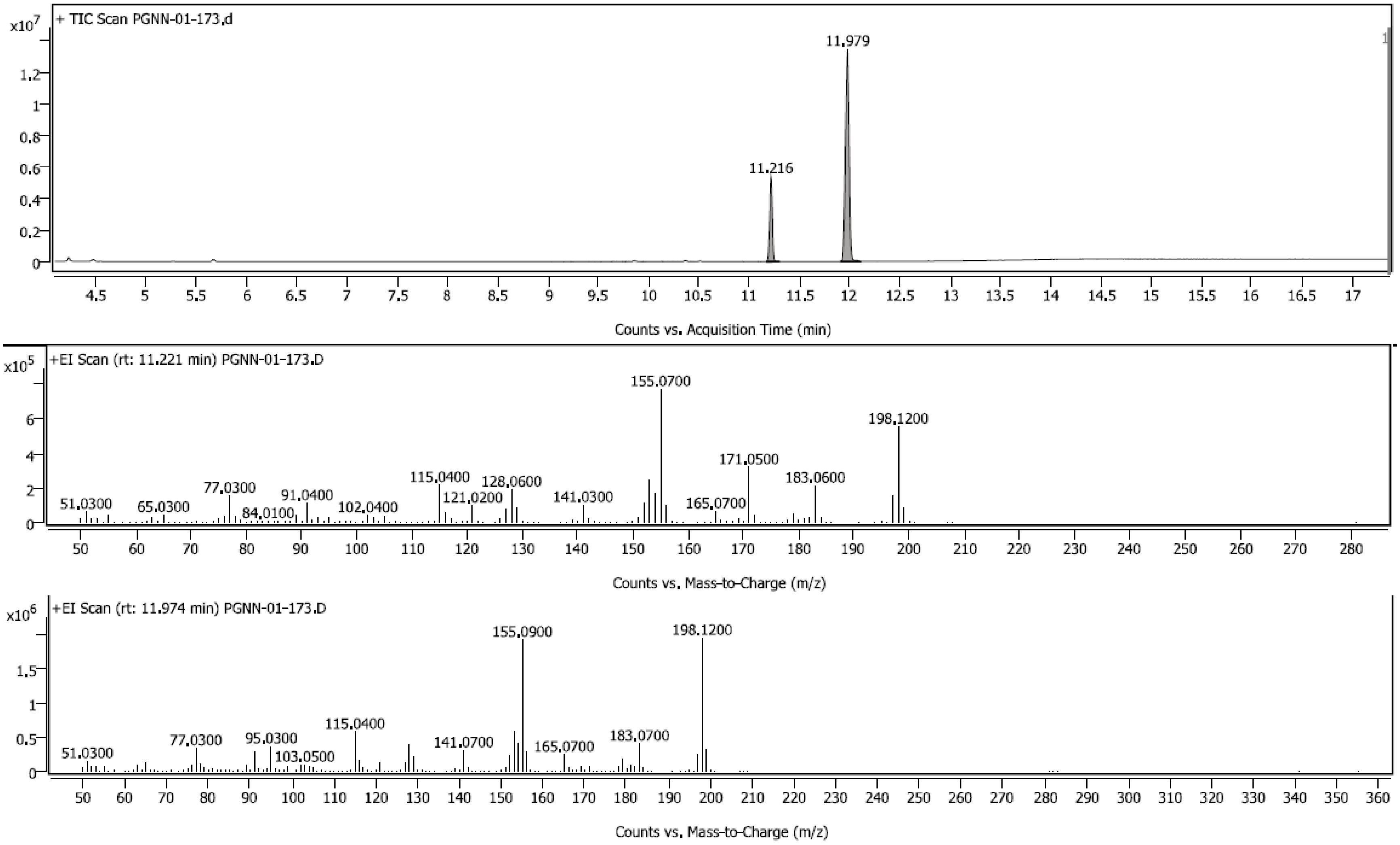
^{13}C-DEPT135-NMR spectrum of cinnamyl alcohol-2-methylfuran coupled product **13**.



COSY-NMR spectrum of cinnamyl alcohol-2-methylfuran coupled product **13**.



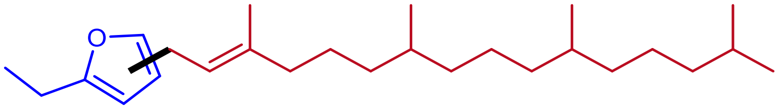
HSQC-NMR spectrum of cinnamyl alcohol-2-methylfuran coupled product **13**.



GCMS data of cinnamyl alcohol-2-methylfuran coupled product **13**.

2-ethylfuran-phytol **14**

IUPAC name: (E)-2-ethyl-5-(3,7,11,15-tetramethylhexadec-2-en-1-yl)furan, and (E)-2-ethyl-4-(3,7,11,15-tetramethylhexadec-2-en-1-yl)furan



According to General Procedure B, phytol (0.59 mL; 1.7 mmol) was reacted with 2-ethylfuran (1.8 mL; 16.6 mmol) in the presence of Perlkat 46-10 (125 mg) and 1,2-dichloroethane (2 mL) at 60 °C. The crude reaction mixture was purified by flash column chromatography (circa 250 mL silica gel; hexanes) to give the product as a colorless oil (277 mg; 43%).

TLC: Rf = 0.32 (hexane) [I_2]

^{1}H-NMR: (400 MHz, $CDCl_3$)

Major isomer (2, 5-substituted furan): 5.84 (s, 2H), 5.35 – 5.27 (m, 1H), 3.30 (d, J = 7.1 Hz, 2H), 2.60 (q, J = 7.6 Hz, 2H), 2.02 (dt, J = 21.2, 7.8 Hz, 2H), 1.73 (d, J = 1.5 Hz, 1H), 1.66 (s, 2H), 1.54 – 1.01 (m, 24H), 0.91 – 0.80 (m, 12H).

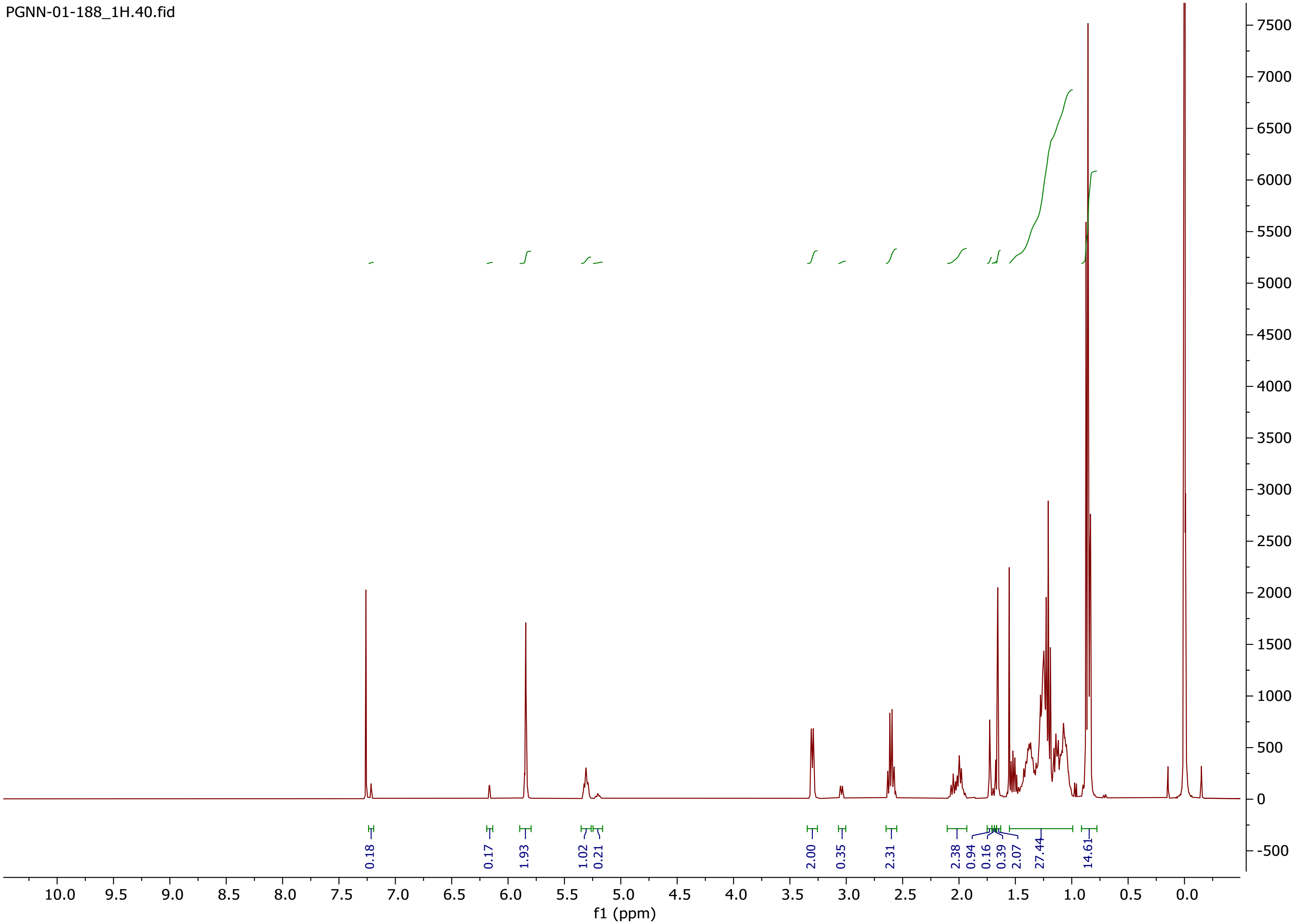
Distinct peaks corresponding to minor isomer (2, 3-substituted furan): 7.22 (d, J = 1.8 Hz, 1H), 6.17 (d, J = 2.0 Hz, 1H), 5.24 – 5.17 (m, 1H), 3.04 (d, J = 7.3 Hz, 2H), 1.70 (app. d, J = 1.3 Hz, 1H), 1.68 (s, 2H).

^{13}C{^{1}H}-NMR: (101 MHz, $CDCl_3$)

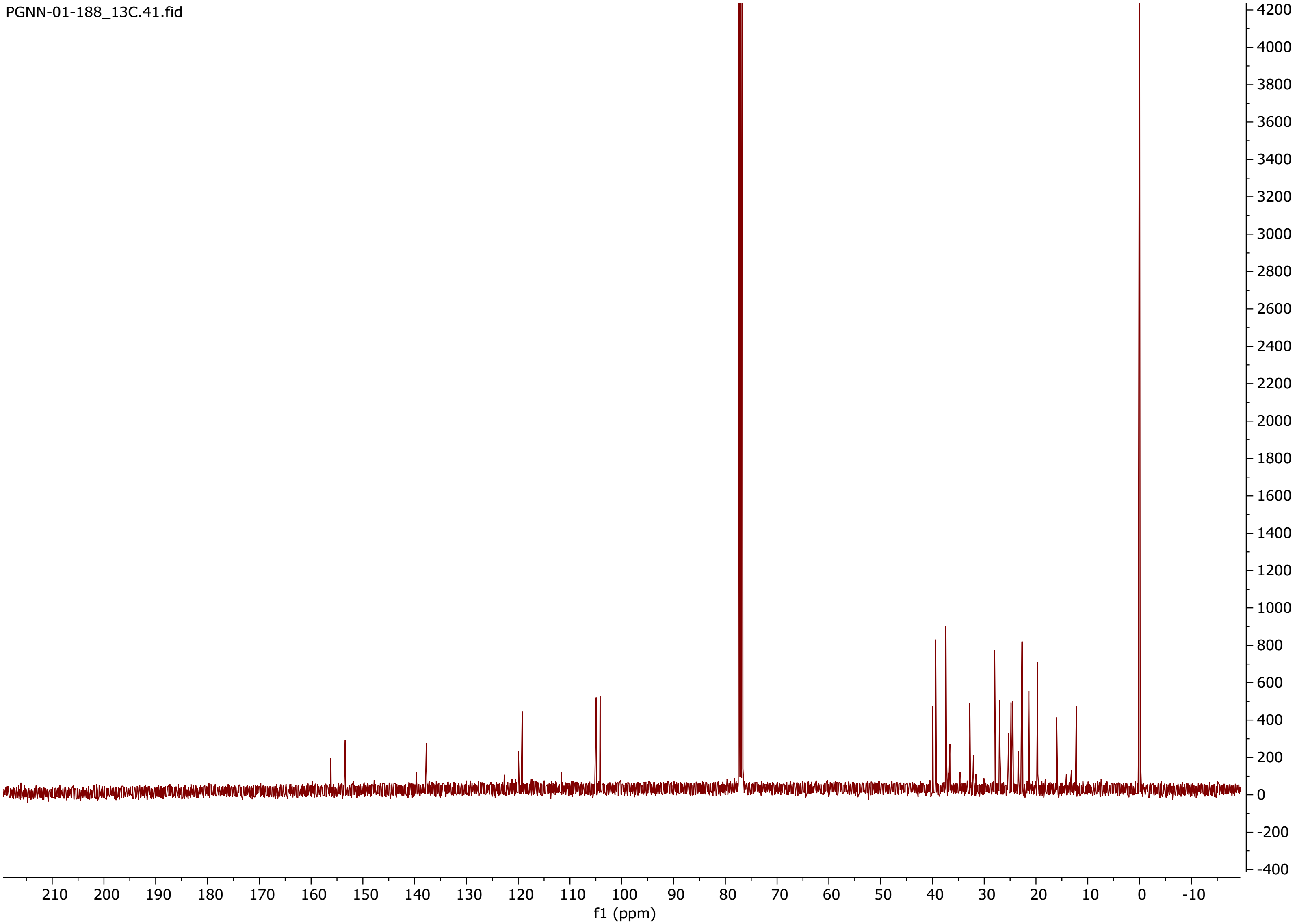
Major isomer (2, 5-substituted furan): 153.42, 137.74, 119.95, 119.23, 104.94, 104.19, 39.92, 39.37, 37.40, 36.74, 36.64, 32.78, 27.99, 27.04, 25.28, 24.81, 24.48, 23.44, 22.73, 22.64, 21.37, 19.76, 19.69, 16.00, 12.21.

Distinct peaks corresponding to minor isomer (2, 3-substituted furan): 139.72, 122.69, 111.66, 34.67, 32.08, 23.44, 14.13, 13.15.

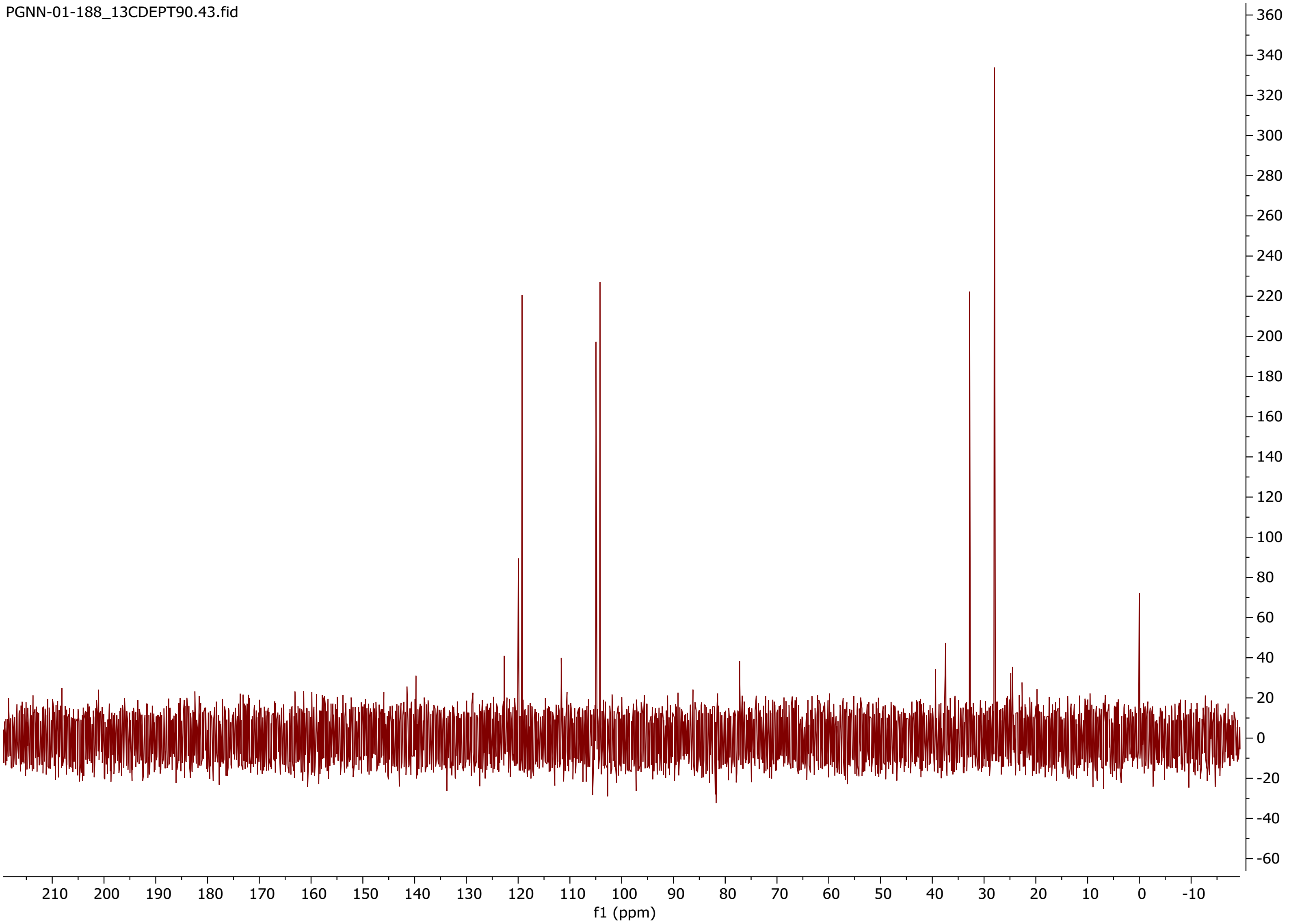
GCMS: 15.155 min (22%; m/z 374.30); 15.362 (78%; m/z 374.34).



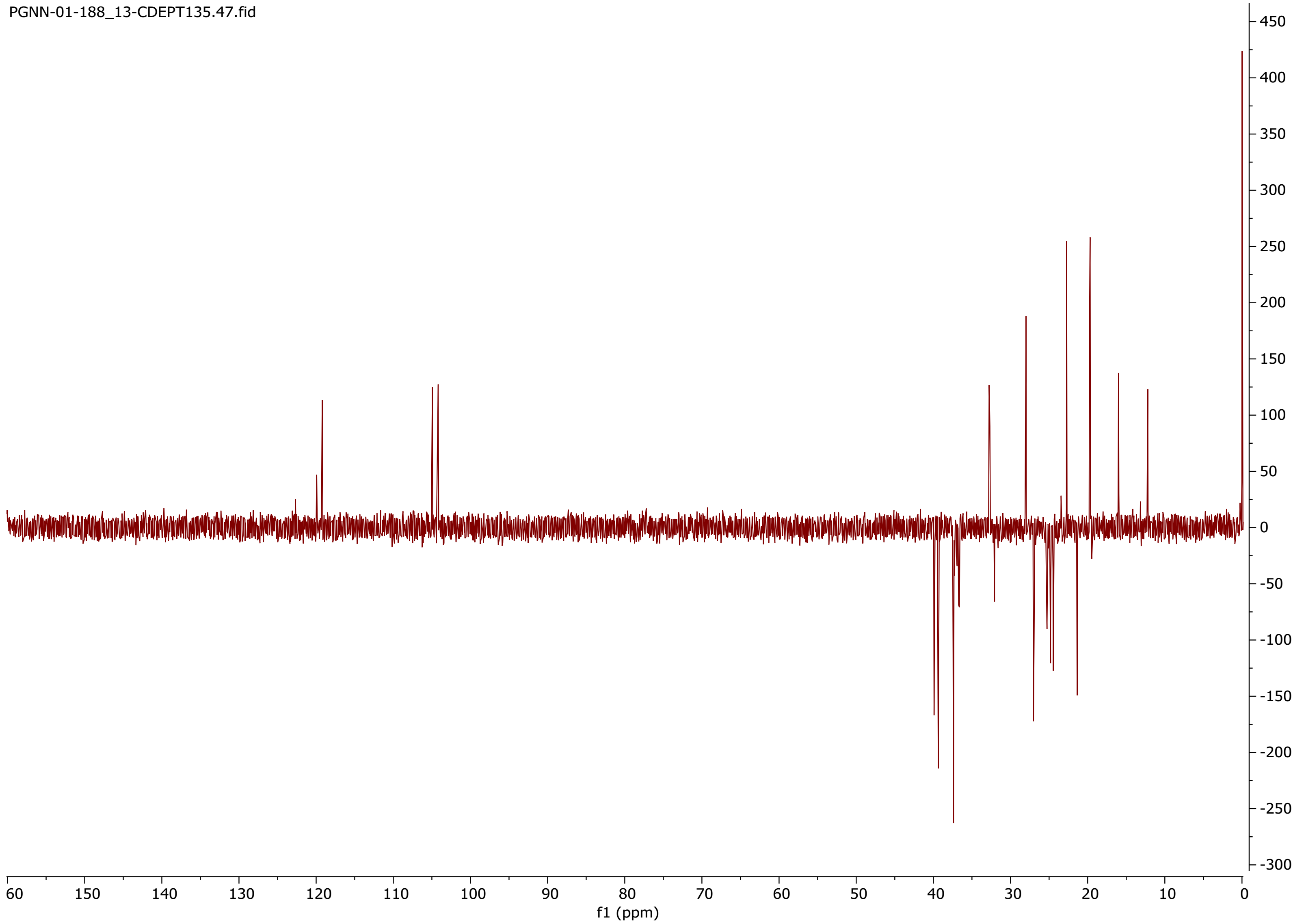
^{1}H-NMR spectrum of phytol-2-ethylfuran coupled product **14**.



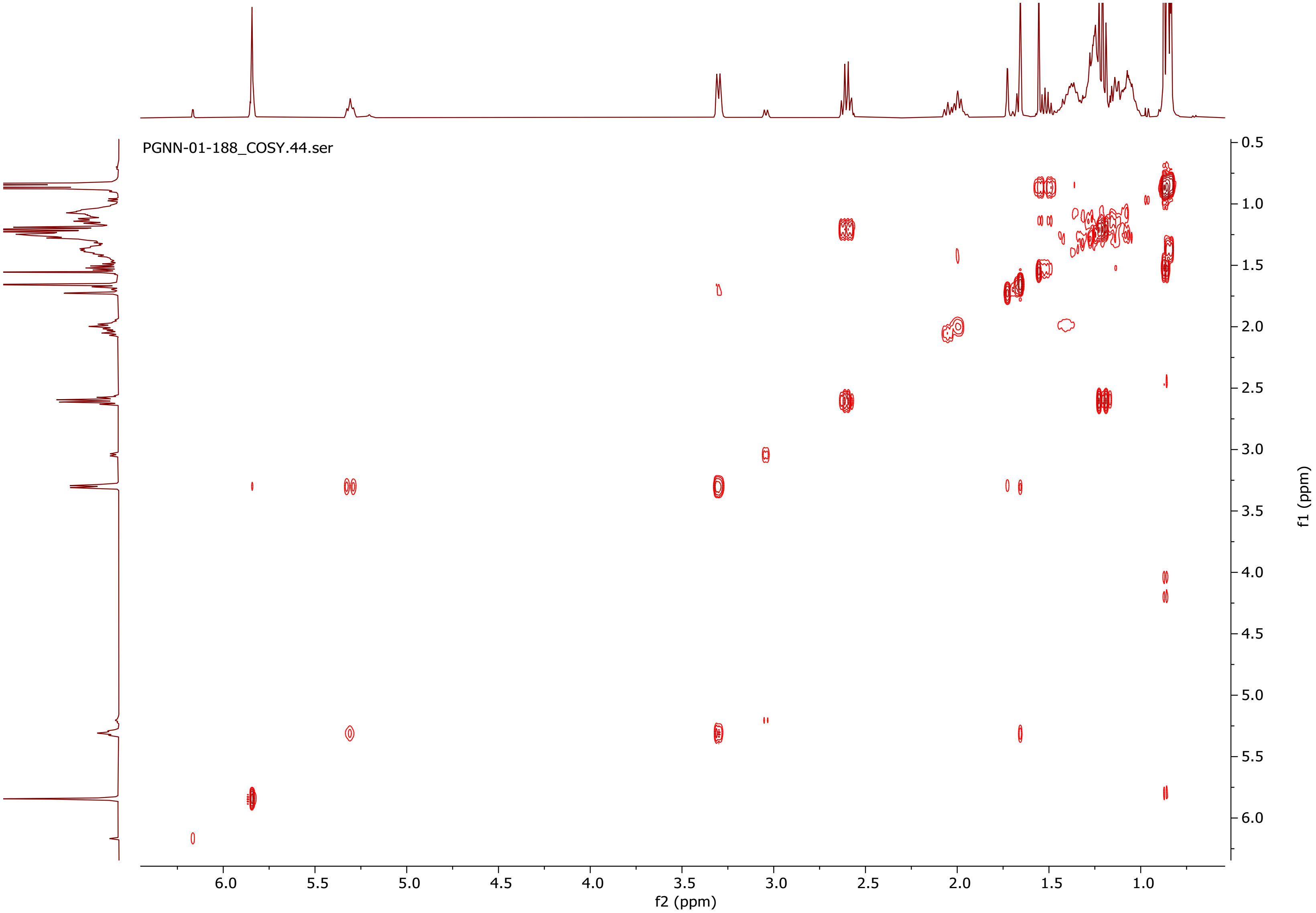
^{13}C-NMR spectrum of phytol-2-ethylfuran coupled product **14**.



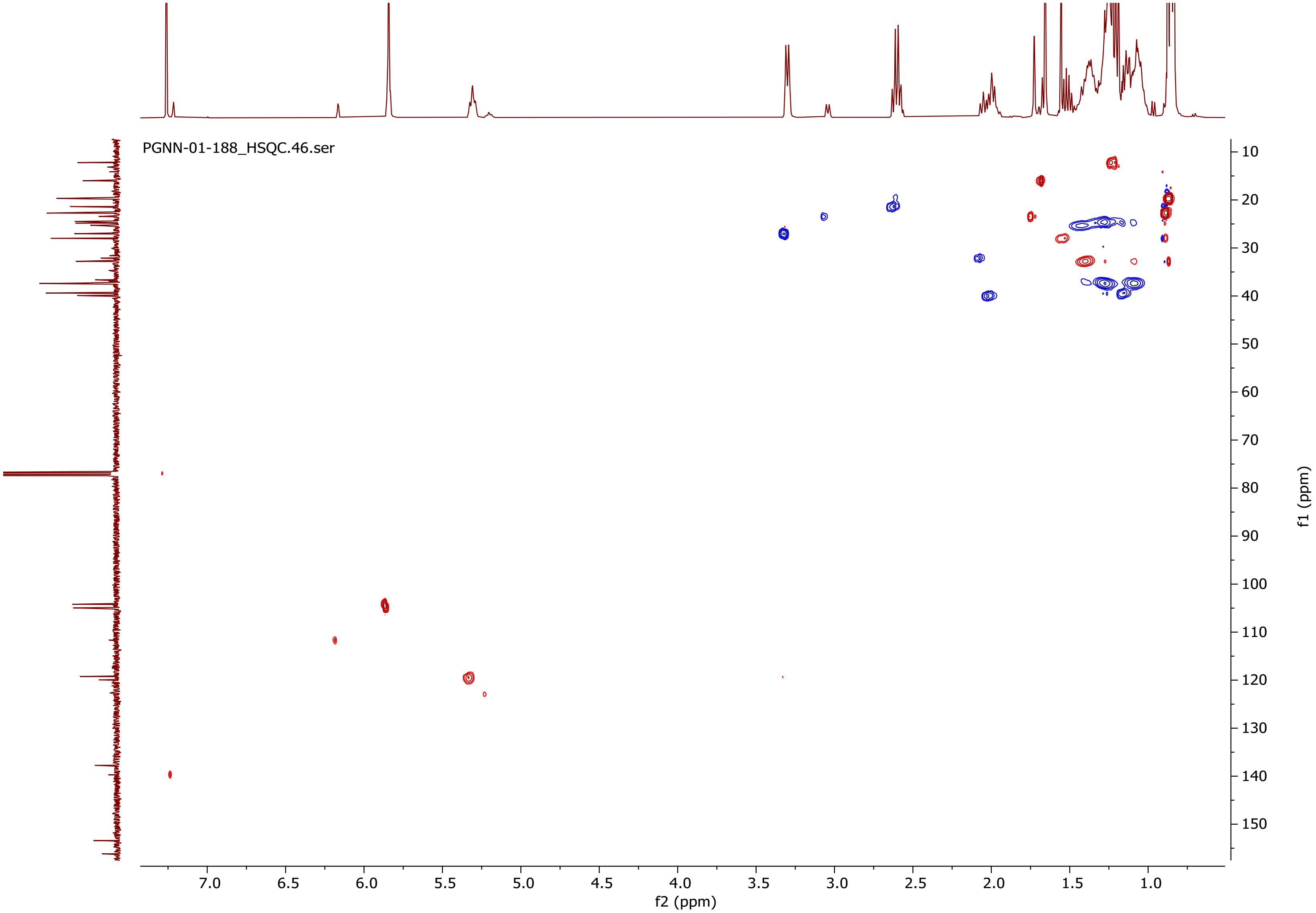
^{13}C-DEPT90-NMR spectrum of phytol-2-ethylfuran coupled product **14**.



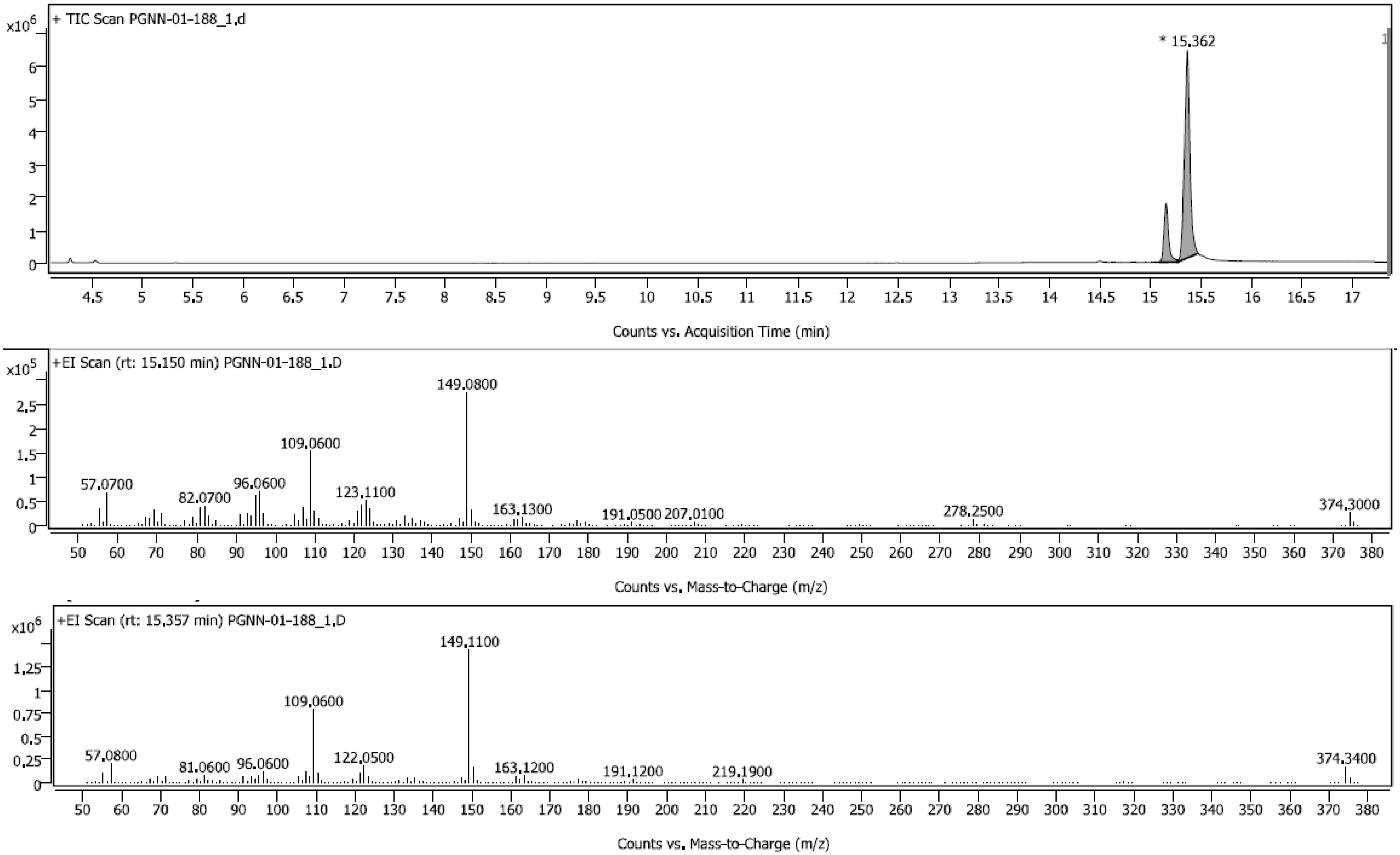
^{13}C-DEPT135-NMR spectrum of phytol-2-ethylfuran coupled product **14**.



COSY-NMR spectrum of phytol-2-ethylfuran coupled product **14**.



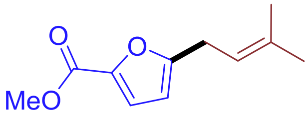
HSQC-NMR spectrum of phytol-2-ethylfuran coupled product **14**.



GCMS data of phytol-2-ethylfuran coupled product **14**.

Methyl-2-furoate-prenol **15**

IUPAC name: methyl 5-(3-methylbut-2-en-1-yl)furan-2-carboxylate



According to General Procedure B, prenol (0.17 mL; 1.7 mmol) was reacted with 2-methylfuran (1.8 mL; 16.8 mmol) in the presence of Perlkat 46-10 (125 mg) and 1,2-dichloroethane (2 mL) at 60 °C. After removal of excess furan under vacuum on a Schlenk line at 70 °C, the crude reaction mixture was purified by flash column chromatography (circa 250 mL silica gel; 10% ethyl acetate in hexanes) to give the product as a pale yellow oil (116 mg; 35%).

TLC: Rf = 0.54 (10% EtOAC in hexane) [UV/I_2]

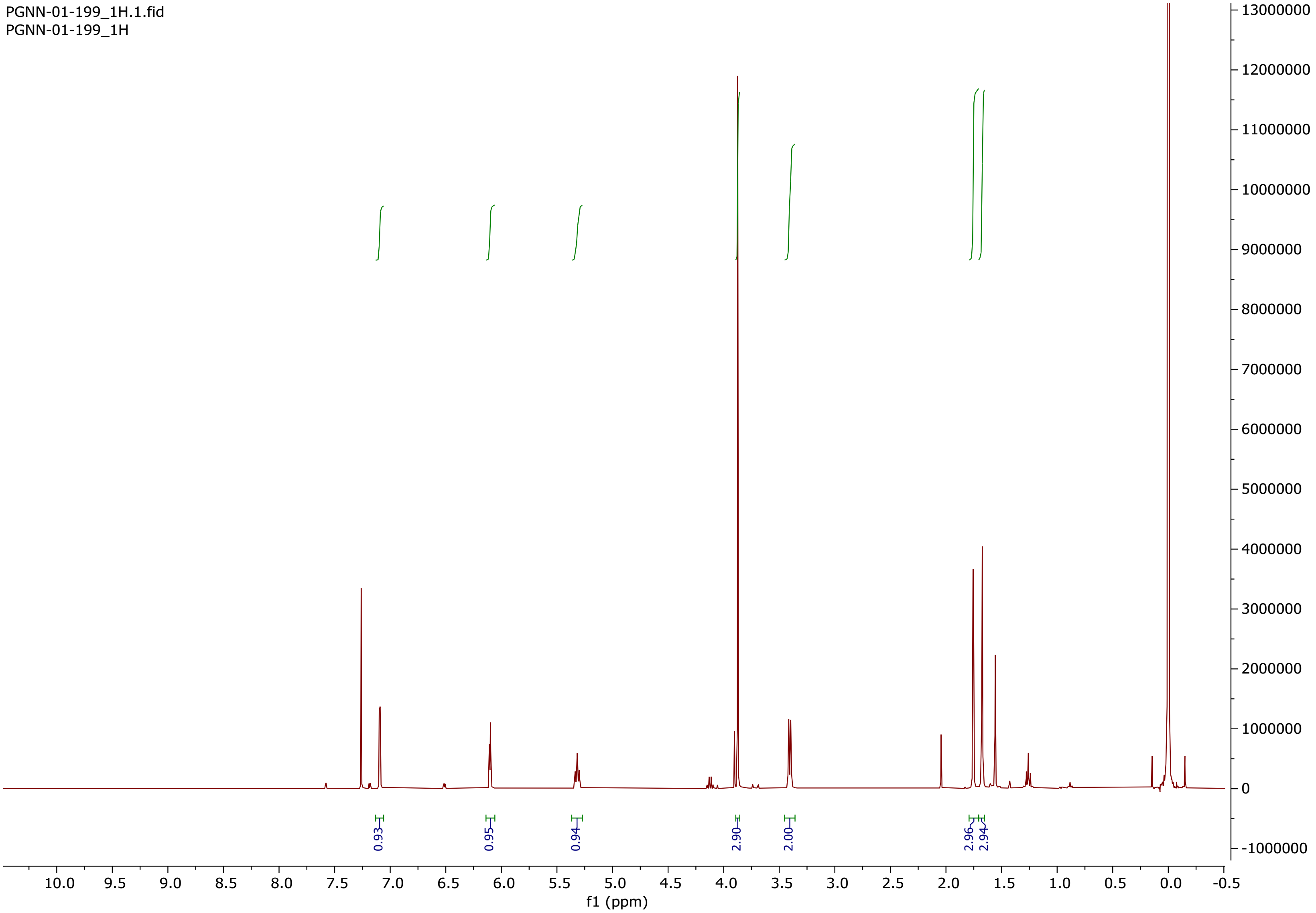
^{1}H-NMR: (400 MHz, $CDCl_3$)

7.09 (d, *J* = 3.4 Hz, 1H), 6.10 (dt, *J* = 3.4, 1.0 Hz, 1H), 5.31 (tdt, *J* = 5.8, 2.9, 1.4 Hz, 1H), 3.87 (s, 3H), 3.41 (d, *J* = 7.2 Hz, 2H), 1.76 (d, *J* = 1.4 Hz, 3H), 1.67 (s, 3H).

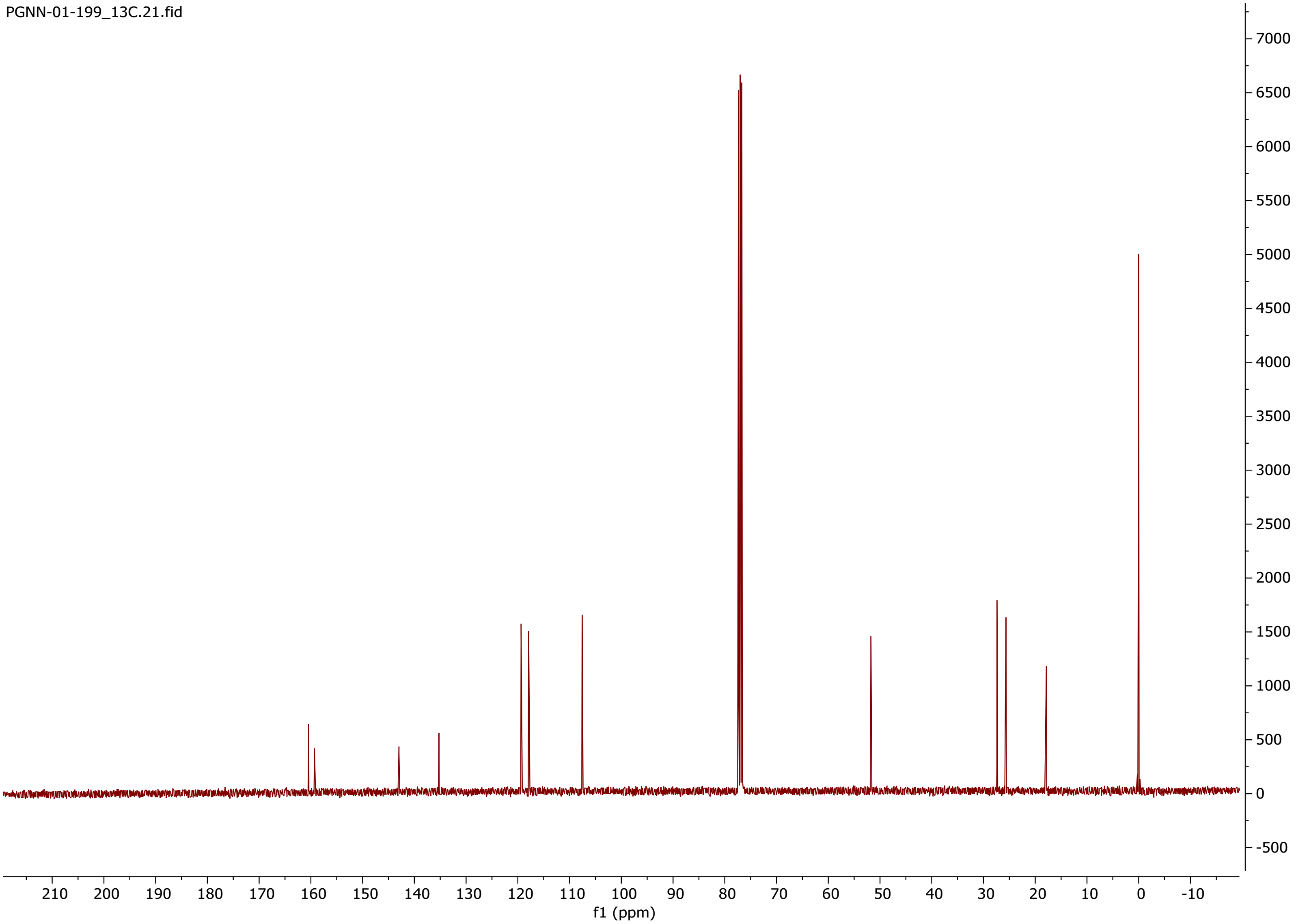
^{13}C{^{1}H}-NMR: (101 MHz, $CDCl_3$)

160.42, 159.31, 142.97, 135.25, 119.37, 117.91, 107.57, 51.75, 27.40, 25.65, 17.84.

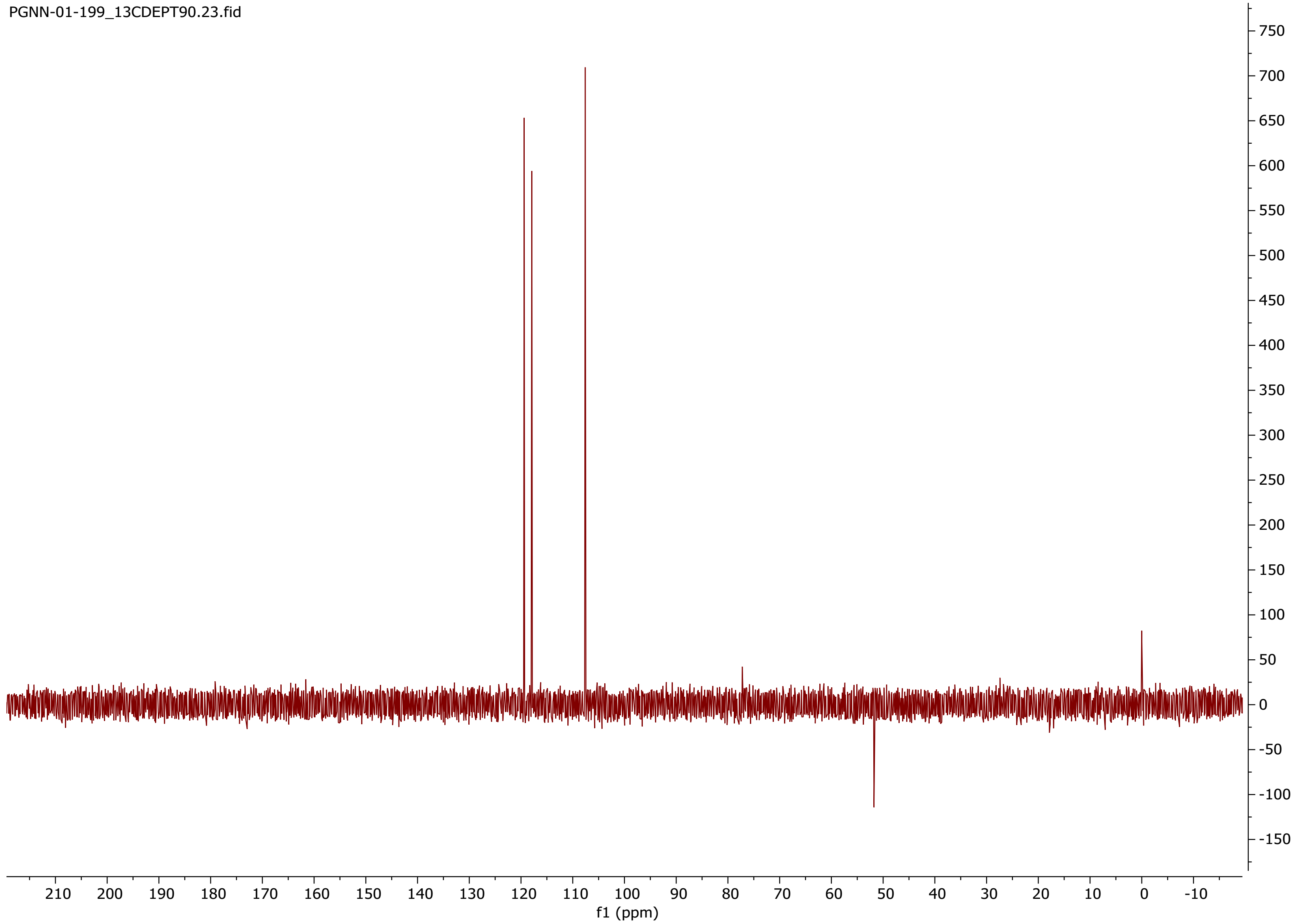
GCMS: 11.273 min (m/z 194.12).



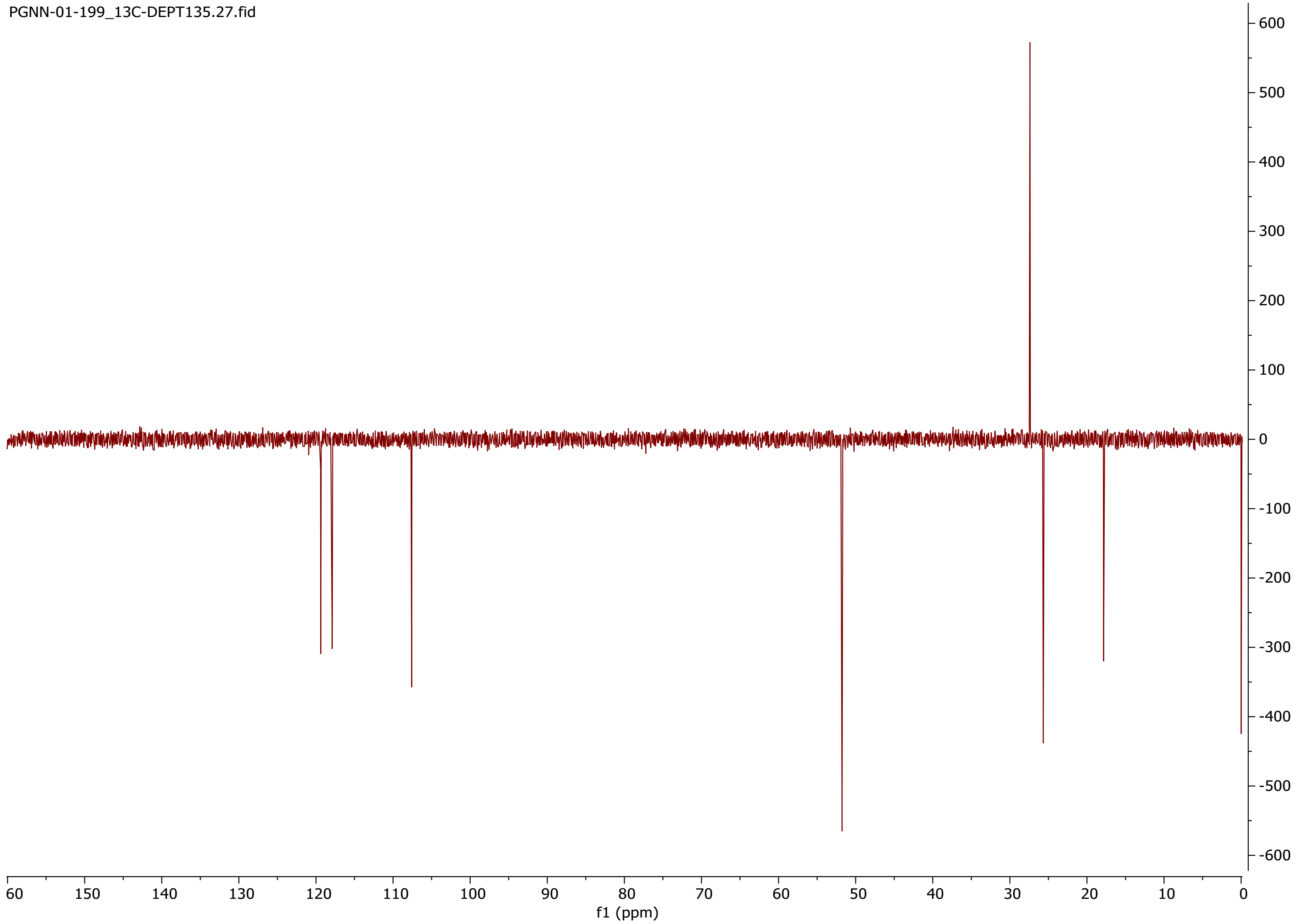
^{1}H-NMR spectrum of prenol-methyl-2-furoate coupled product **15**.



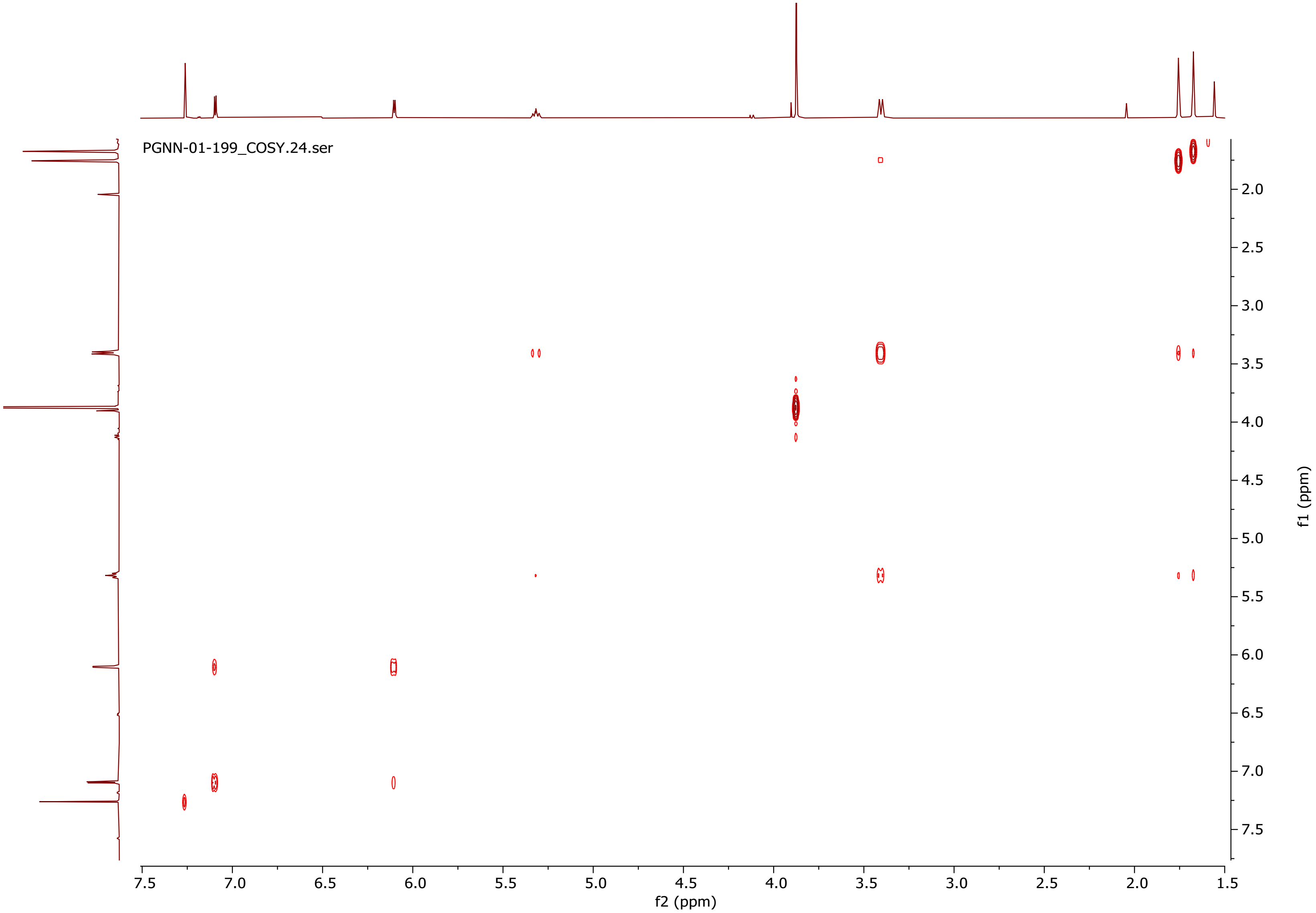
^{13}C-NMR spectrum of prenol-methyl-2-furoate coupled product **15**.



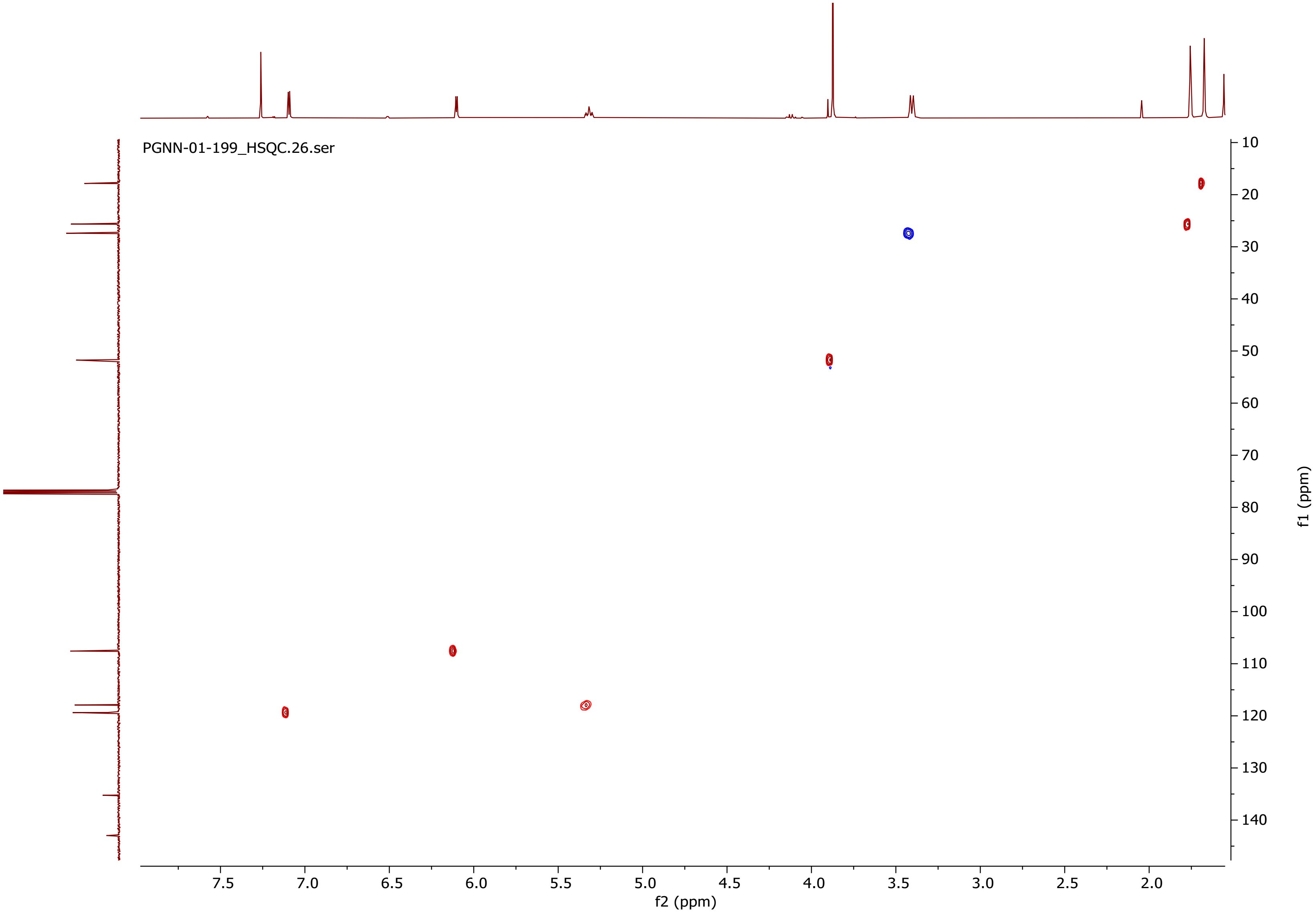
^{13}C-DEPT90-NMR spectrum of prenol-methyl-2-furoate coupled product **15**.



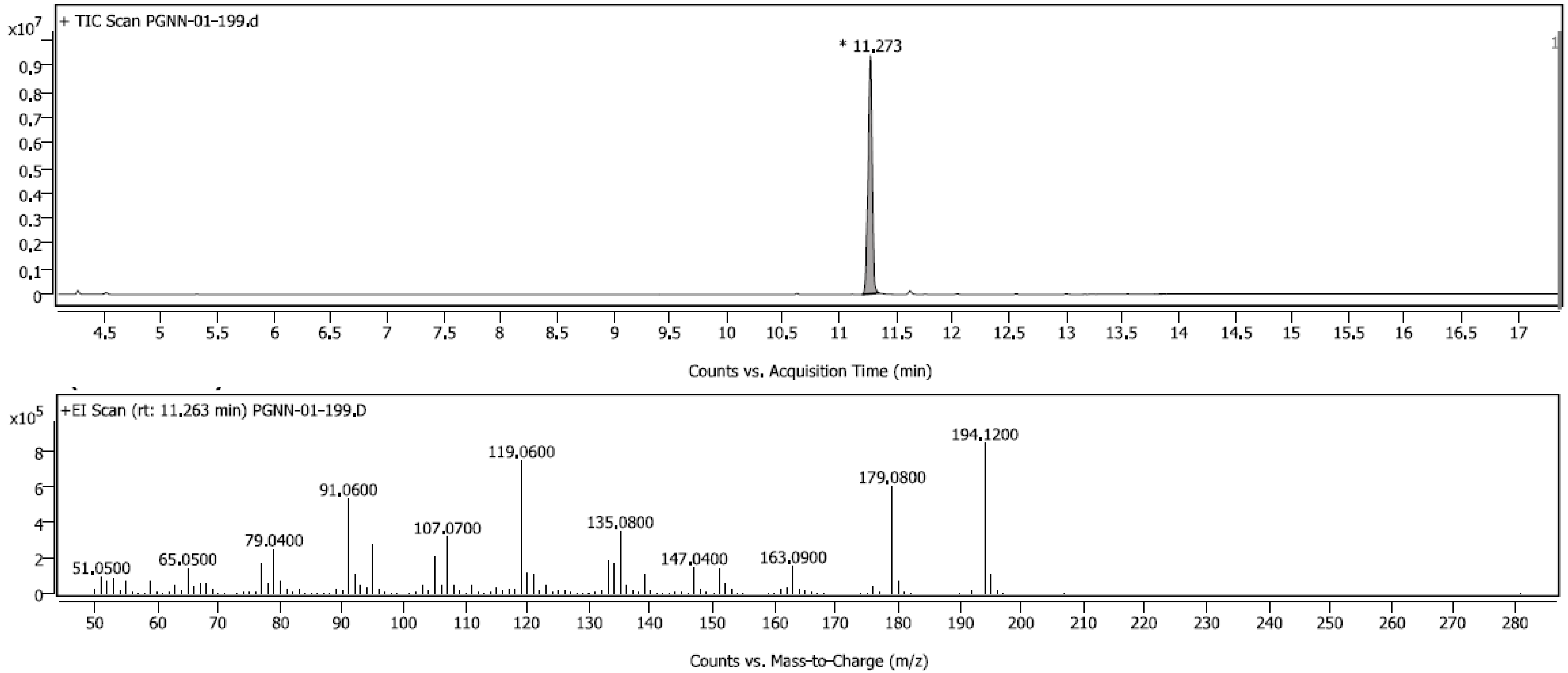
^{13}C-DEPT135-NMR spectrum of prenol-methyl-2-furoate coupled product **15**.



COSY-NMR spectrum of prenol-methyl-2-furoate coupled product **15**.



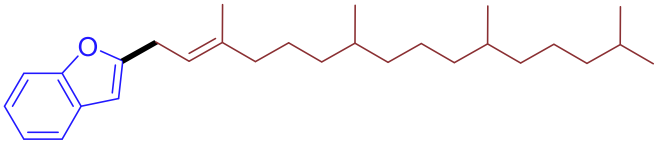
HSQC-NMR spectrum of prenol-methyl-2-furoate coupled product **15**.



GCMS data of prenol-methyl-2-furoate coupled product **15**.

Benzofuran-phytol **16**

IUPAC name: (E)-2-(3,7,11,15-tetramethylhexadec-2-en-1-yl)benzofuran



According to General Procedure B, phytol (0.59 mL; 1.7 mmol) was reacted with 2,3-benzofuran (1.9 mL; 17.2 mmol) in the presence of Perlkat 46-10 (125 mg) and 1,2-dichloroethane (2 mL) at 60 °C. After removal of excess furan under vacuum on a Schlenk line at 70 °C, the crude reaction mixture was purified by flash column chromatography (circa 270 mL silica gel; hexanes) to give the product as a colorless oil (449 mg; 66%).

TLC: Rf = 0.34 (hexane) [UV/I_2]

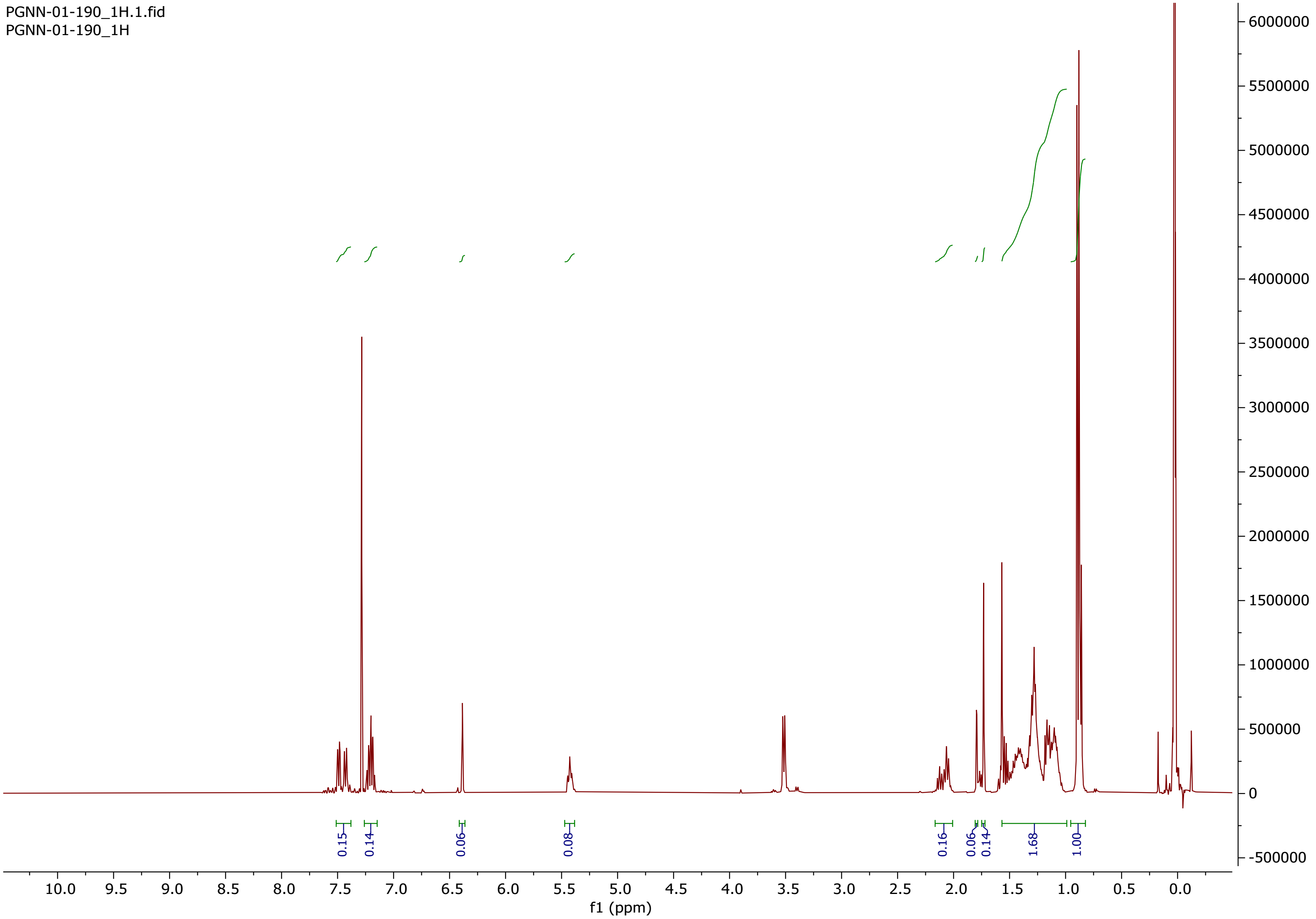
^{1}H-NMR: (400 MHz, $CDCl_3$)

7.48 – 7.44 (m, 1H), 7.40 (dtd, J = 7.1, 1.9, 0.9 Hz, 1H), 7.22 – 7.13 (m, 2H), 6.38 – 6.34 (m, 1H), 5.40 (tdt, J = 7.3, 2.8, 1.4 Hz, 1H), 3.49 (d, J = 6.1 Hz, 2H), 2.07 (dt, J = 24.2, 7.7 Hz, 2H), 1.77 (q, J = 1.3 Hz, 1H), 1.71 (s, 2H), 1.58 – 0.99 (m, 24H), 0.90 – 0.80 (m, 12H).

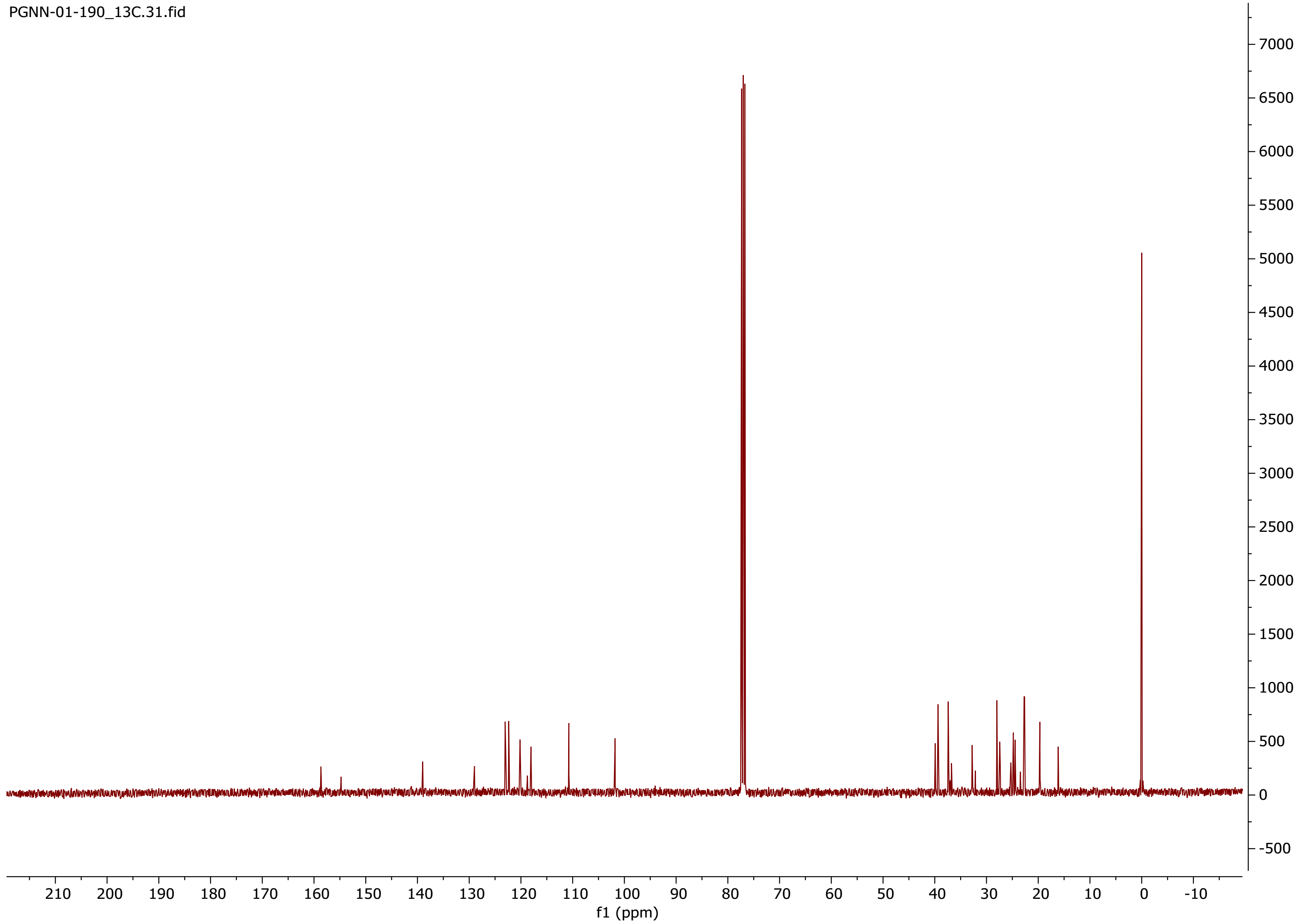
^{13}C{^{1}H}-NMR: (101 MHz, $CDCl_3$)

158.65, 154.77, 138.98, 128.99, 123.05, 122.36, 120.18, 118.74, 118.06, 110.73, 101.79, 39.92, 39.37, 37.39, 37.02, 36.76, 32.80, 32.17, 27.99, 27.43, 25.30, 24.82, 24.48, 23.47, 22.73, 19.76, 16.14.

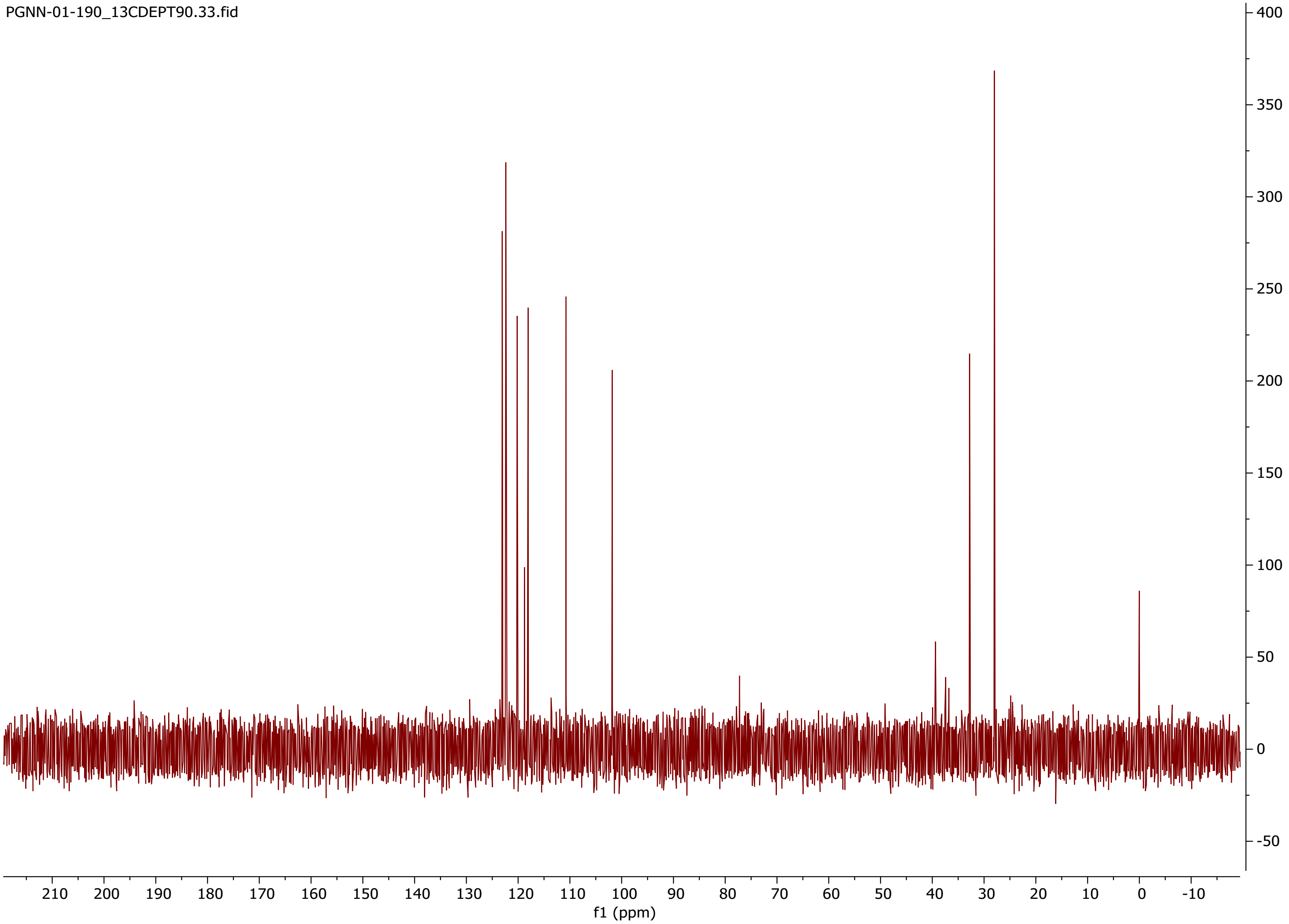
GCMS: 18.112 min (19%; m/z 396.23); 18.626 (81%; m/z 396.30).



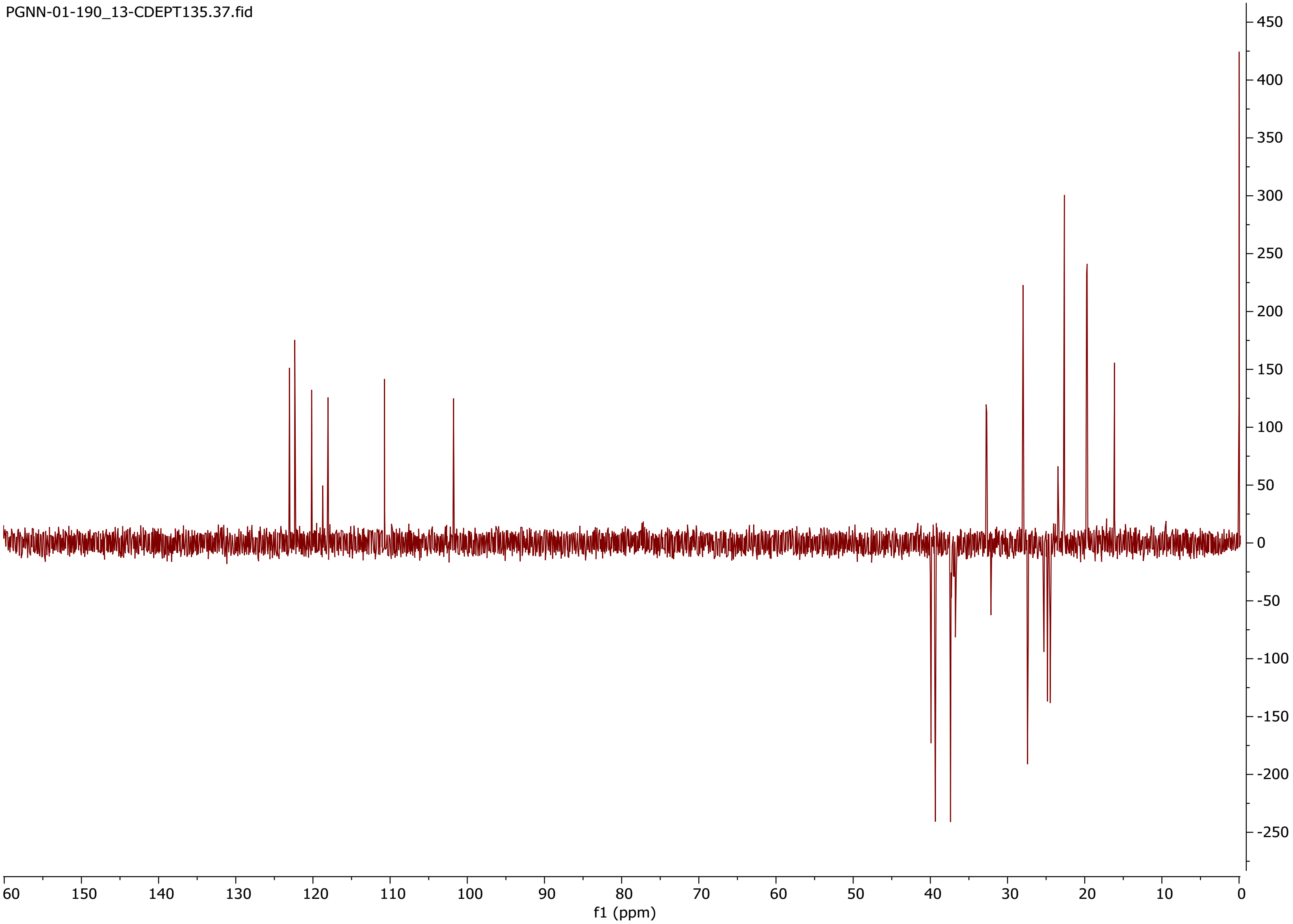
^{1}H-NMR spectrum of phytol-benzofuran coupled product **16**.



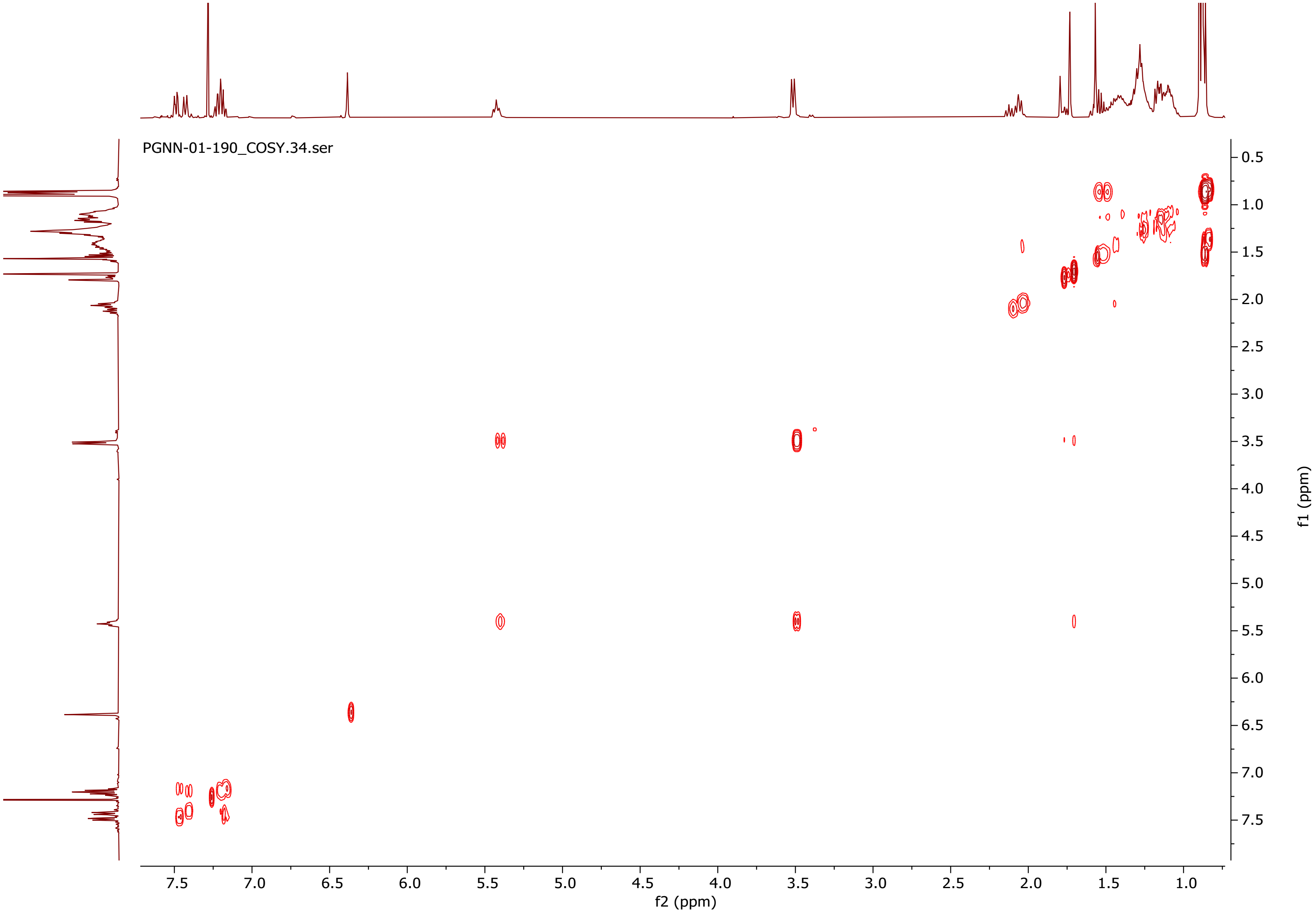
^{13}C-NMR spectrum of phytol-benzofuran coupled product **16**.



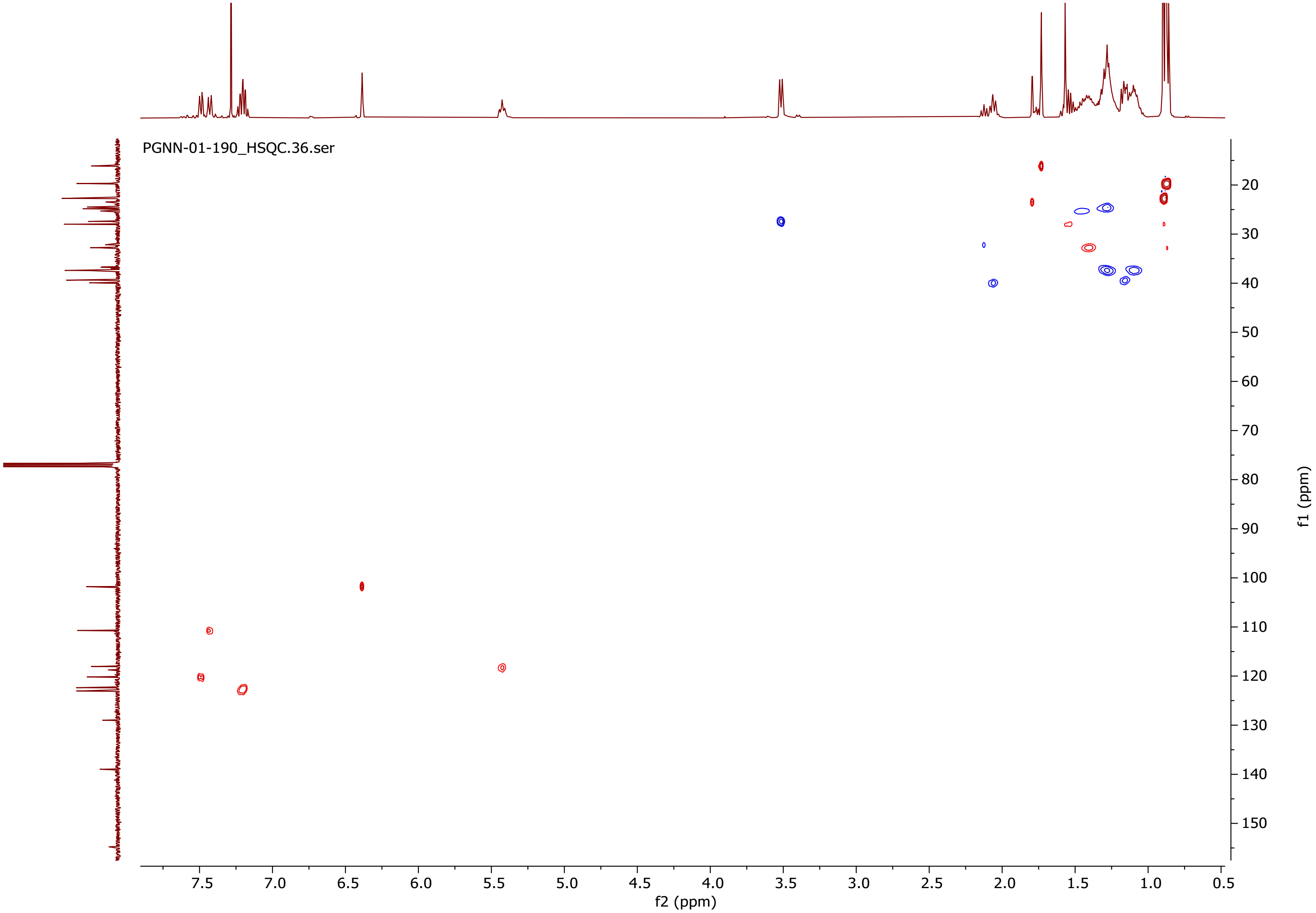
^{13}C-DEPT90-NMR spectrum of phytol-benzofuran coupled product **16**.



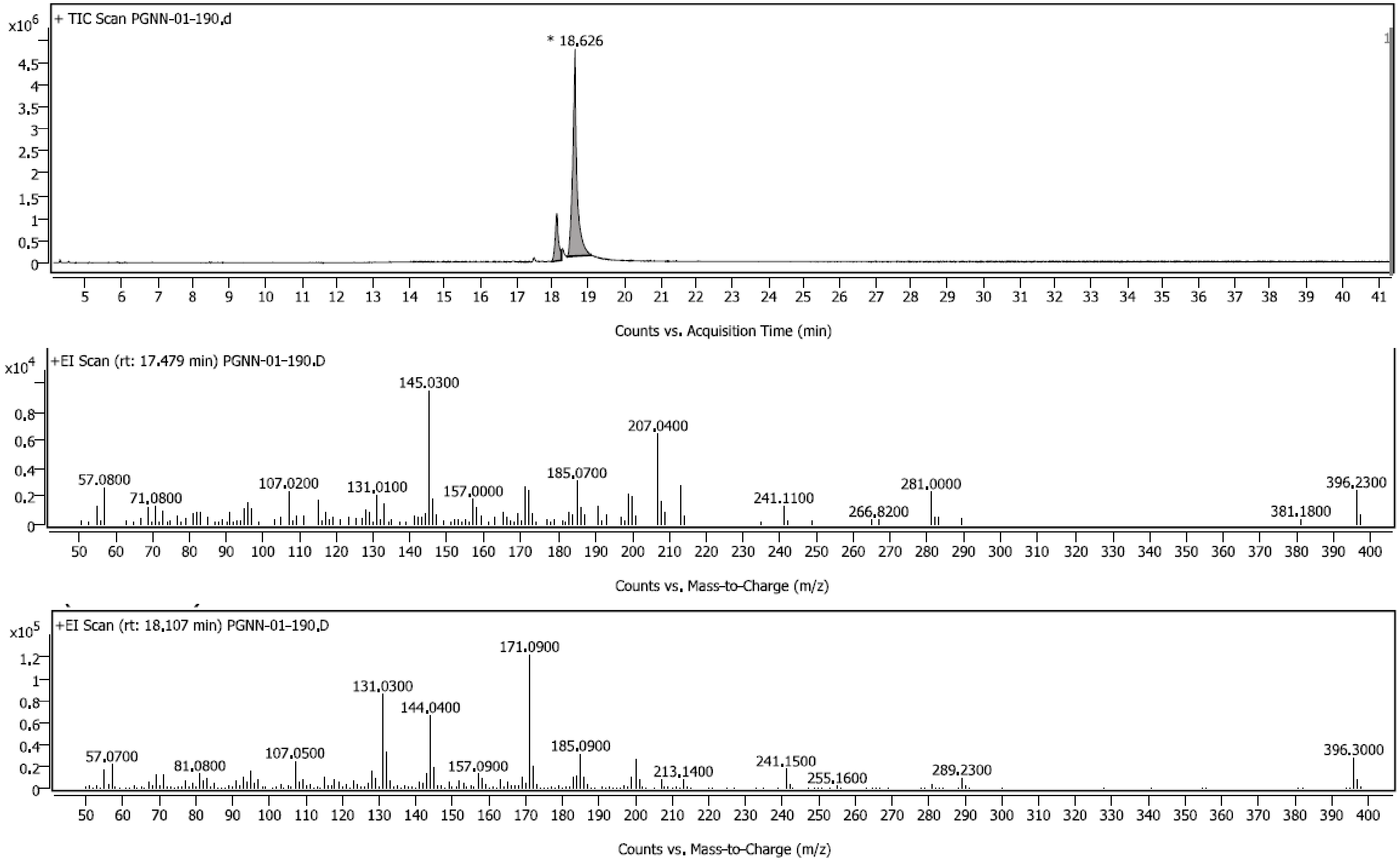
^{13}C-DEPT135-NMR spectrum of phytol-benzofuran coupled product **16**.



COSY-NMR spectrum of phytol-benzofuran coupled product **16**.



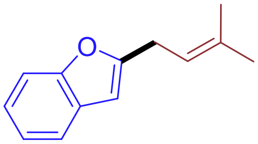
HSQC-NMR spectrum of phytol-benzofuran coupled product **16**.



GCMS data of phytol-benzofuran coupled product **16**.

Benzofuran-prenol **17**

IUPAC name: 2-(3-methylbut-2-en-1-yl)benzofuran



According to General Procedure B, prenol (0.17 mL; 1.7 mmol) was reacted with 2,3-benzofuran (1.9 mL; 17.2 mmol) in the presence of Perlkat 46-10 (125 mg) and 1,2-dichloroethane (2 mL) at 60 °C. After removal of excess furan under vacuum on a Schlenk line at 70 °C, the crude reaction mixture was purified by flash column chromatography (circa 250 mL silica gel; hexanes) to give the product as a colorless oil (142 mg; 45%).

TLC: Rf = 0.26 (hexane) [UV/I_2]

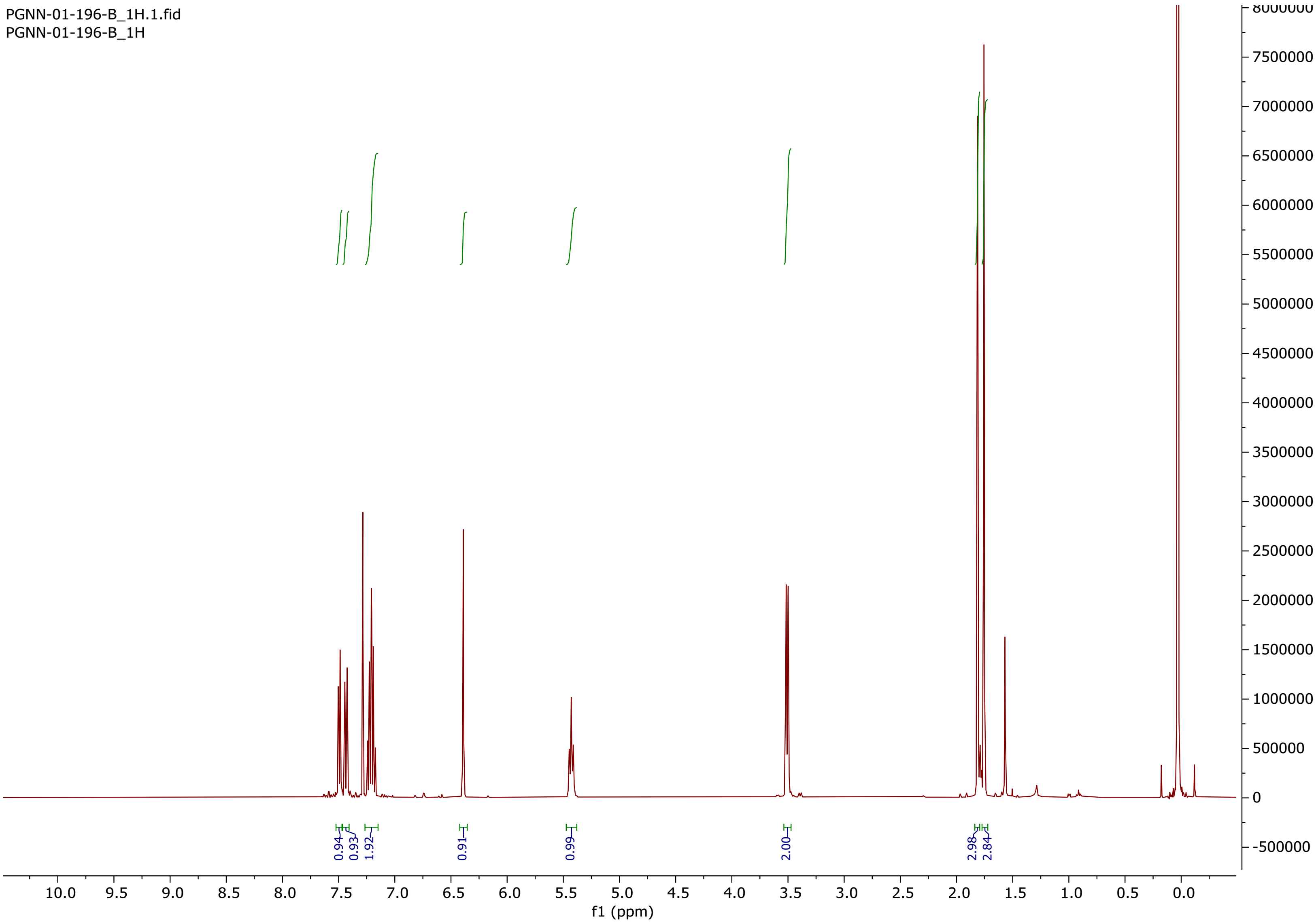
^{1}H-NMR: (400 MHz, $CDCl_3$)

7.48 – 7.44 (m, 1H), 7.43 – 7.38 (m, 1H), 7.18 (pd, J = 7.3, 1.5 Hz, 2H), 6.36 (app. d, J = 1.0 Hz, 1H), 5.40 (tp, J = 7.3, 1.5 Hz, 1H), 3.48 (d, J = 6.3 Hz, 2H), 1.78 (s, 3H), 1.72 (s, 3H).

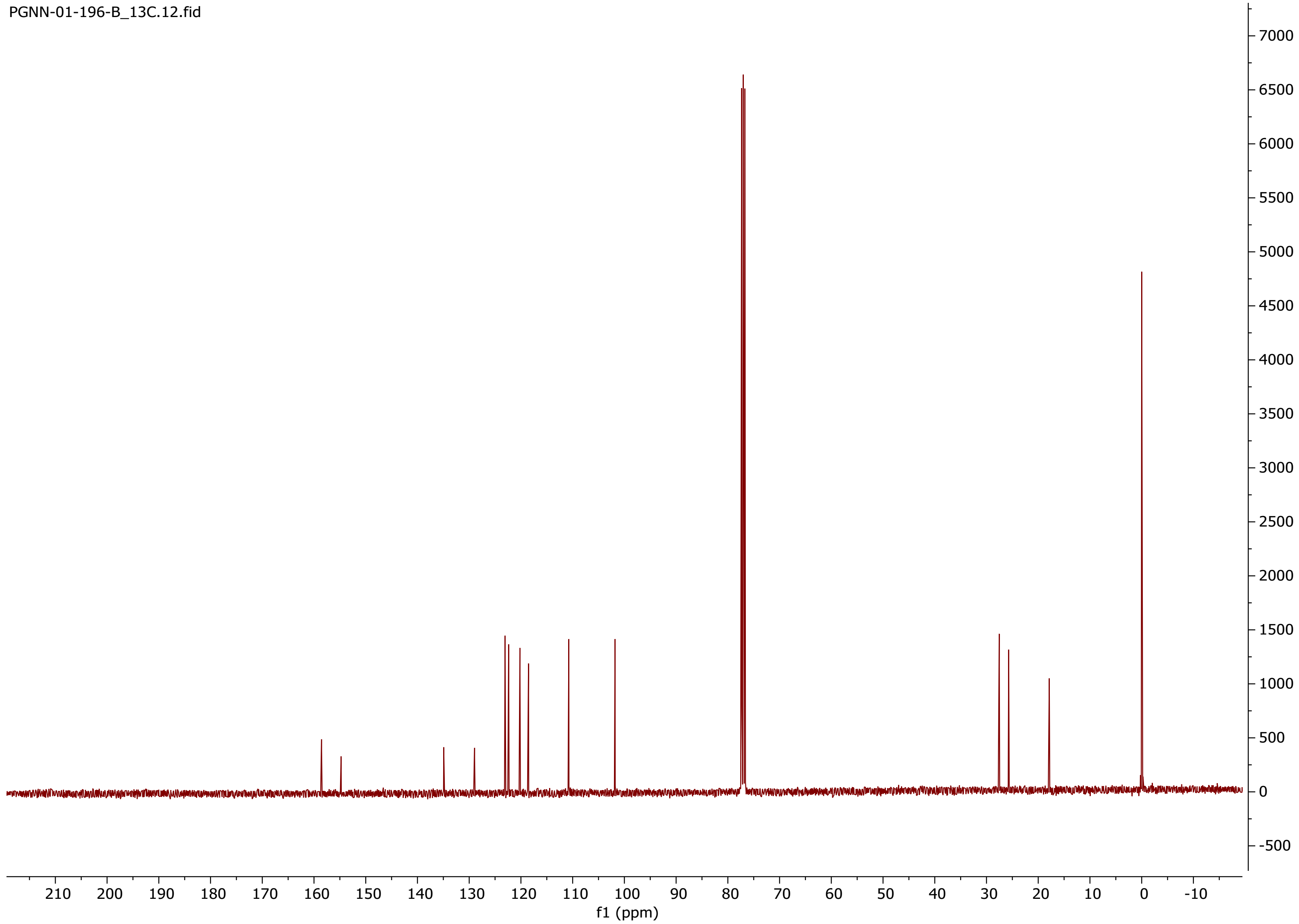
^{13}C{^{1}H}-NMR: (101 MHz, $CDCl_3$)

158.55, 154.76, 134.92, 128.98, 123.07, 122.37, 120.20, 118.53, 110.74, 101.81, 27.54, 25.71, 17.86.

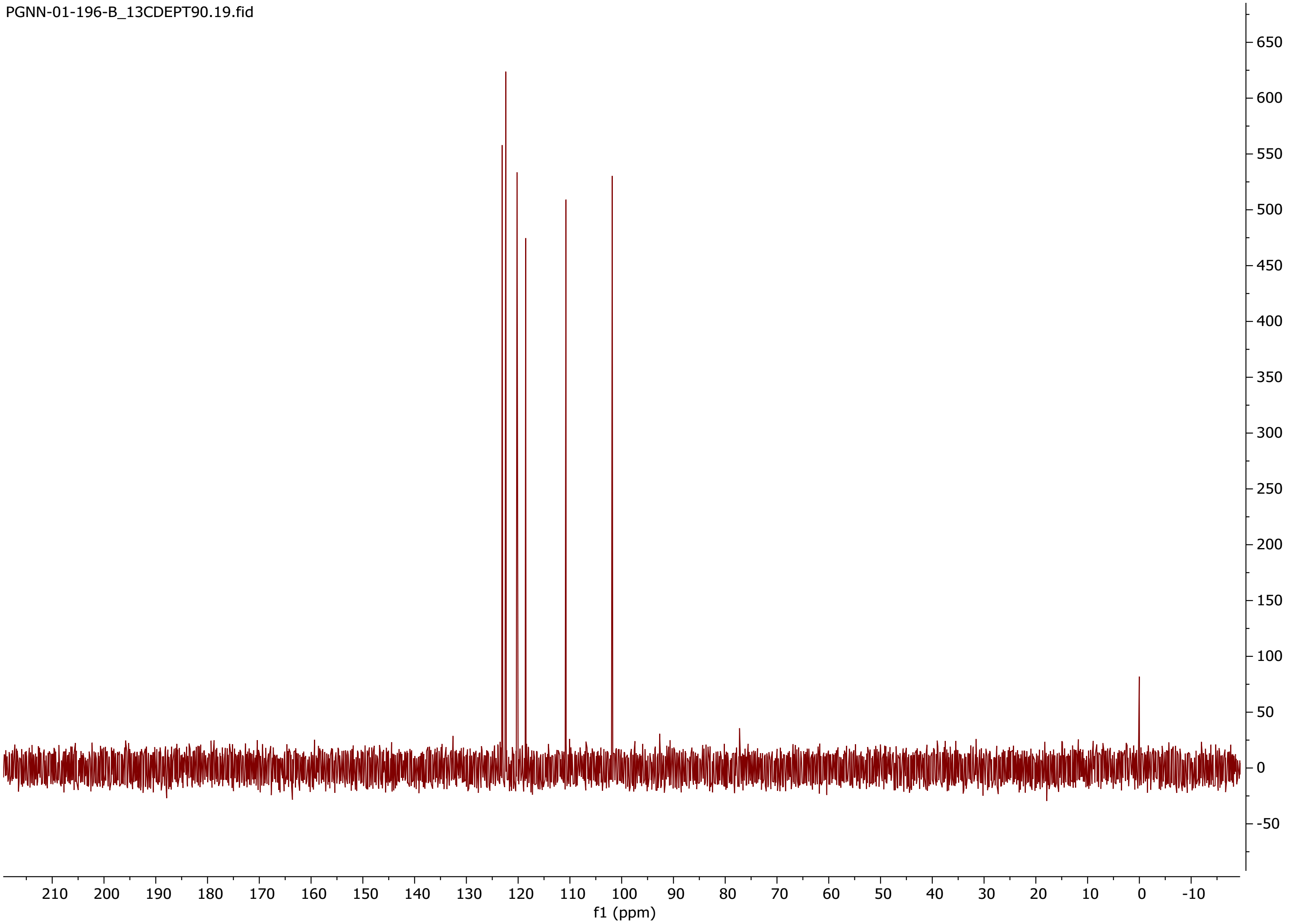
GCMS: 11.580 min (m/z 186.07).



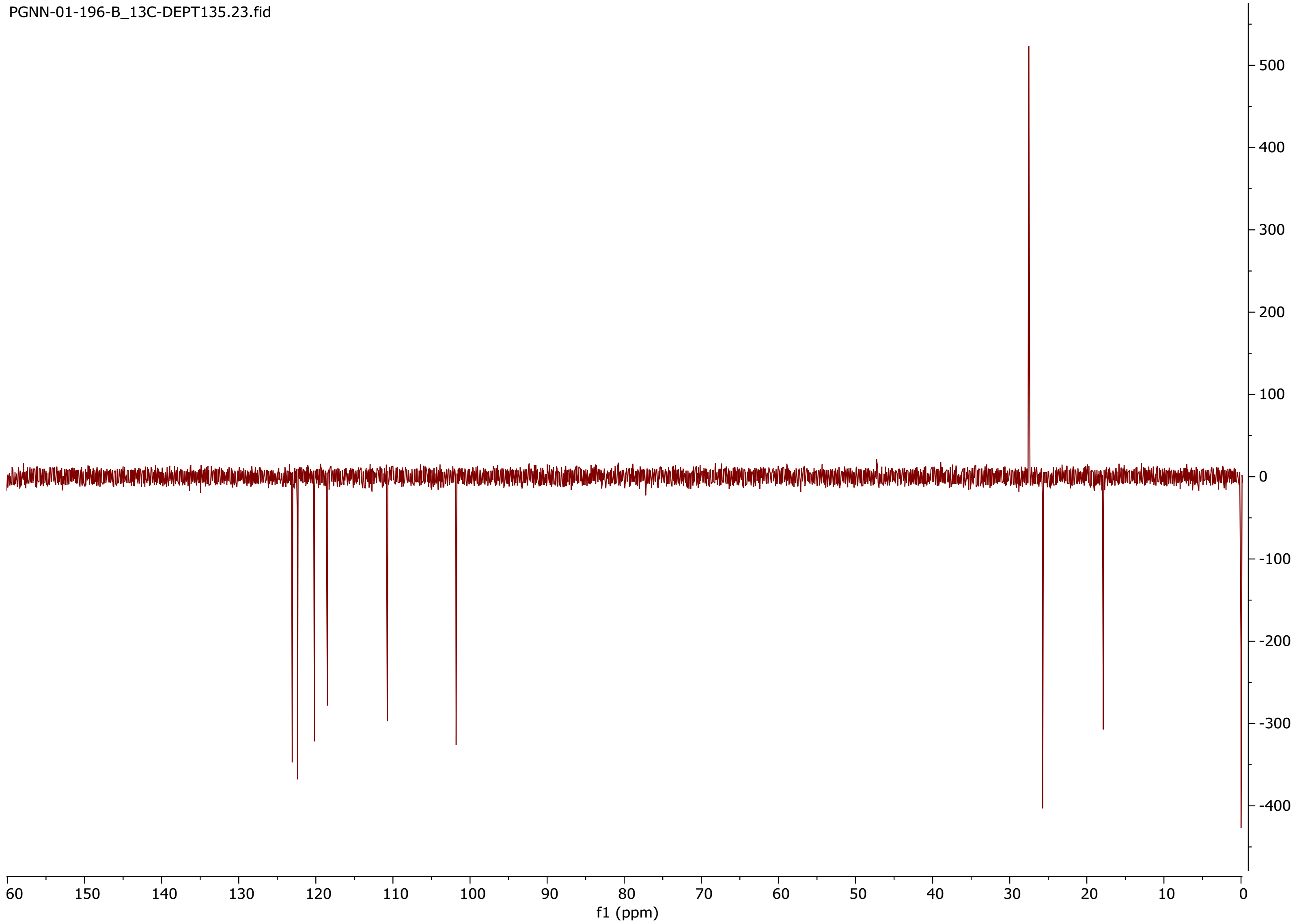
^{1}H-NMR spectrum of prenol-benzofuran coupled product **17**.



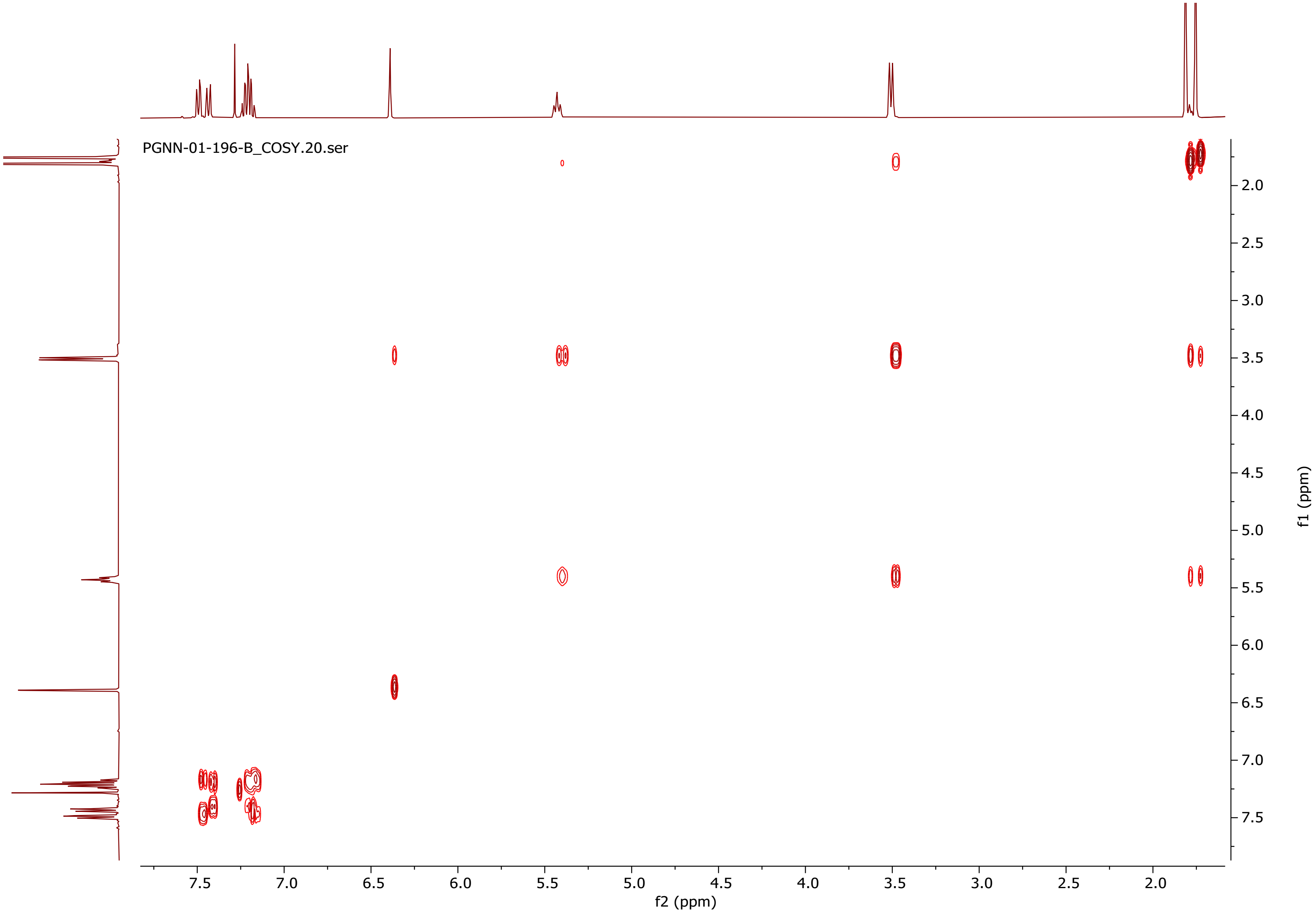
^{13}C-NMR spectrum of prenol-benzofuran coupled product **17**.



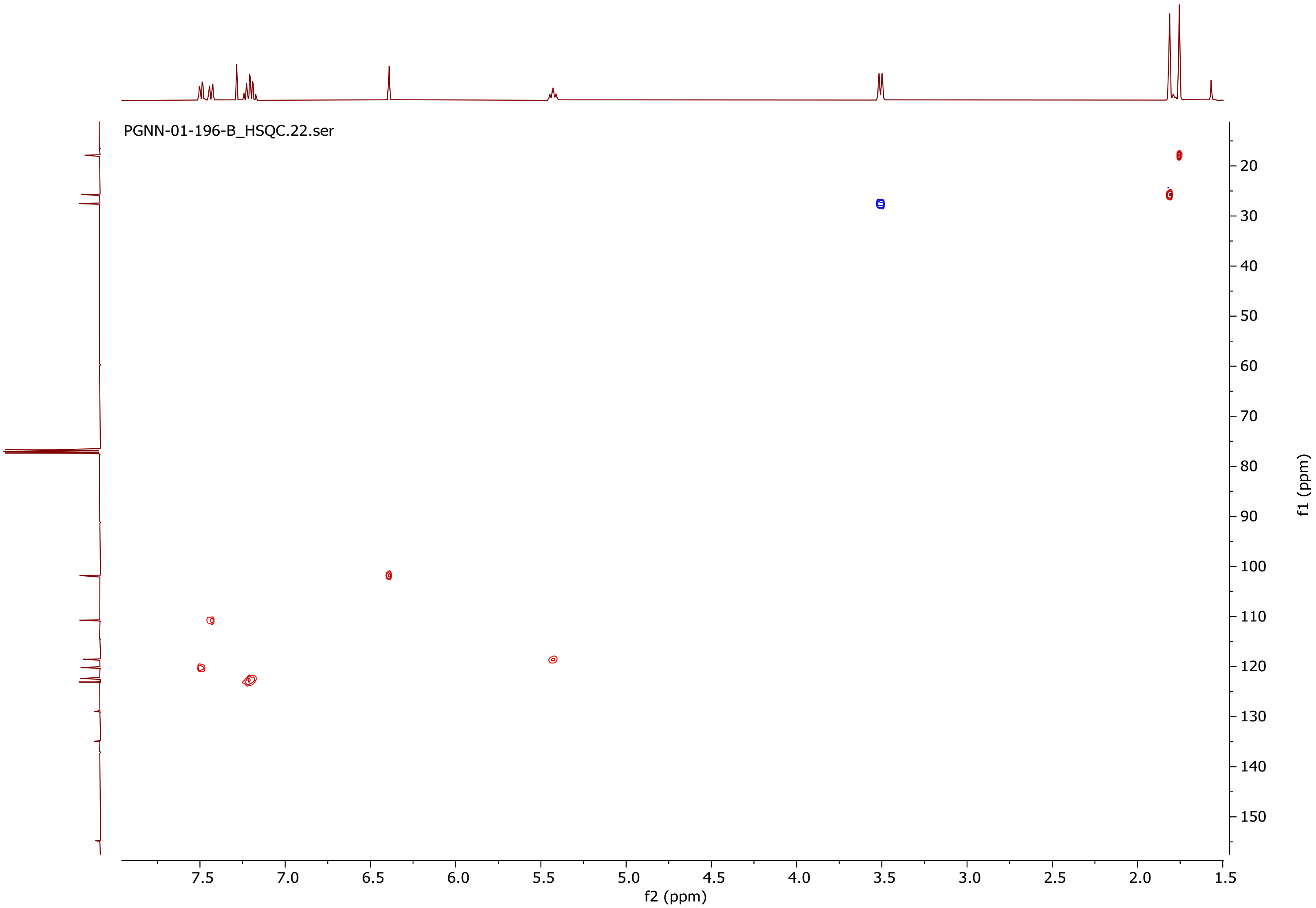
^{13}C-DEPT90-NMR spectrum of prenol-benzofuran coupled product **17**.



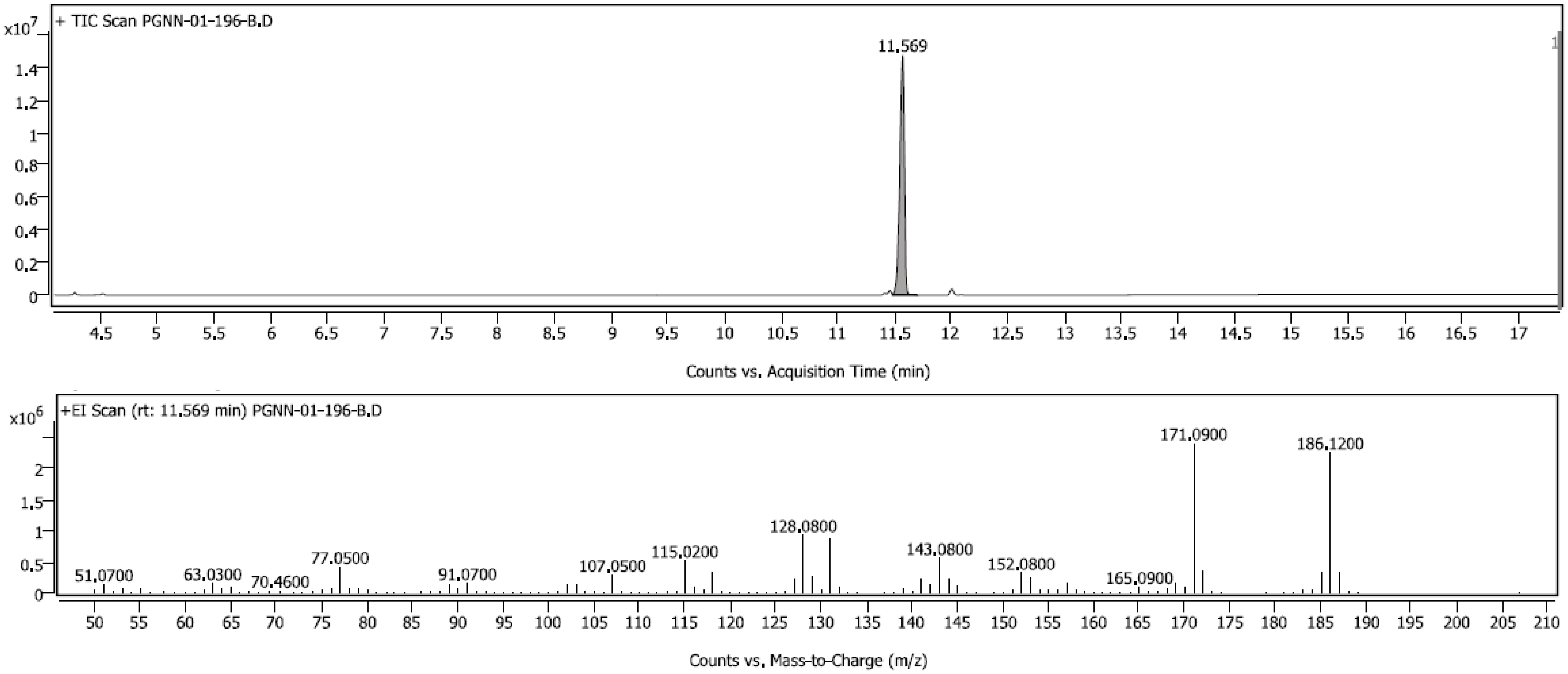
^{13}C-DEPT135-NMR spectrum of prenol-benzofuran coupled product **17**.



COSY-NMR spectrum of prenol-benzofuran coupled product **17**.



HSQC-NMR spectrum of prenol-benzofuran coupled product **17**.



GCMS data of prenol-benzofuran coupled product **17**.

4. Computational Methods and Details

Structural coordinates for Faujasite (FAU), Mordenite (MOR), and ZSM-5 (MFI) were obtained from the International Zeolite Association (IZA) database[1]. The zeolite frameworks were modeled as fully siliceous due to high experimental Si/Al ratios, thus minimizing the influence of extra-framework cations and electrostatic interactions. All computational analyses were performed using BIOVIA Materials Studio 2024[2]. Calculations involved modules including Adsorption Locator for identifying favorable adsorption sites, Sorption module for adsorption isotherms, and Forcite for geometry optimization and molecular dynamics simulations. The consistent valence force field (CVFF) was used to describe the interactions between zeolite frameworks and adsorbed furans as shown in Table 3. Zeolite structures were geometry-optimized under periodic boundary conditions using the CVFF force field until convergence criteria were met at energy tolerance of 2.0×10^{-5} kcal/mol, force tolerance of 0.001 kcal/mol·Å^{-1}.

Zero-coverage adsorption energies were determined using the Adsorption Locator module. A Monte Carlo approach with 100,000 random configurations was performed, from which the 10 lowest-energy adsorption poses were selected and subsequently optimized. Adsorption energies (E_{ads}) were calculated by:

$$E_{ads} = E_{complex} - \left(E_{zeolite} + E_{adsorbate}\right)$$

where $E_{complex}$, $E_{zeolite}$, and $E_{adsorbate}$ are the total energies of the adsorbate-zeolite complex, isolated zeolite framework, and isolated adsorbate molecule, respectively. Gas-phase adsorbate structures were optimized through simulated annealing from 300 K to 1000 K and back, ensuring global minima identification.

Adsorption isotherms were simulated at a constant temperature of 298 K, covering a wide pressure range from 0.01 Pa to 100 kPa using the Grand Canonical Monte Carlo (GCMC) technique implemented within the Sorption module. Initially, simulations included an equilibration phase consisting of 2 million Monte Carlo (MC) steps, followed by a production phase of 3 million MC steps to achieve accurate equilibrium conditions. Move probability ratios were carefully selected, comprising insertion/deletion (regrowth), translation, rotation, and torsion moves in proportions of 2:1:1:1, respectively. Amplitudes of these moves were dynamically adjusted to maintain an acceptance ratio around 50%, ensuring efficient sampling of the configurational space. Simulation convergence was thoroughly assessed by performing duplicate runs using distinct random seeds and deviations between these duplicates remained consistently below 5%, demonstrating statistical reliability of the isotherm calculations.

For molecular dynamics (MD) and diffusion analyses, the self-diffusion coefficients of reactants within Faujasite pores were determined through MD simulations conducted in the canonical NVT ensemble. Each simulation spanned a total duration of 10 nanoseconds, comprising an initial 7 ns equilibration period and a subsequent 3 ns production phase, with a timestep of 1 femtosecond. Temperature was maintained rigorously at 298 K using the Nosé-Hoover thermostat, and self-diffusion coefficients were extracted based on Einstein's relation, utilizing mean-square displacement data accumulated over the 7-10 ns interval of the simulation trajectories. Interactions between zeolite frameworks and adsorbates were modeled using the consistent valence force field (CVFF), employing Lennard-Jones potentials parameterized via Lorentz-Berthelot mixing rules. Electrostatic interactions within the systems were calculated using Ewald summation methods, applying a cutoff radius of 14 Å.

In addition, to validate and ensure robustness of force field parameters, comparative single-point calculations using alternative force fields (UFF and PCFF) were executed, confirming the consistency of adsorption energy trends observed with CVFF. Furthermore, periodic density functional theory (DFT) calculations using the DMol^3 module[3] with the PBE functional[4] and Grimme's D3 dispersion correction[5] were conducted, affirming the qualitative consistency of binding energy trends obtained from classical force field calculations. Collectively, these validation procedures confirmed the reliability and accuracy of the computational protocols employed in this work.

Reference

(1) Database of Zeolite Structures (access in April 2025): http://www.iza-structure.org/databases/

(2) BIOVIA Materials Studio 2024: https://www.3ds.com/products/biovia/materials-studio

(3) B. Delley, "From Molecules to Solids with the DMol^3 Approach", Journal of Chemical Physics, 2000, 113, 7756-7764.

(4) J. P. Perdew, K. Burke, M. Ernzerhof, "Generalized Gradient Approximation Made Simple", Physical Review Letter, 1996, 77, 3865.

(5) S. Grimme, "Semiempirical GGA-type Density Functional Constructed with a Long-range Dispersion Correction", Journal of Computational Chemistry, 2006, 27(15), 1787-1799.