Electronic Supplementary Material (ESI) for ChemComm.

Contents

1 General Information

All reactions were carried out in flame dried glassware under a nitrogen atmosphere using standard Schlenk techniques. Glassware and stir bars contaminated with transition metals were treated with *aqua regia* (conc. HCl/conc. HNO_3 3:1) prior to cleaning. For cleaning, glassware and stir bars were kept in a *iso*-PrOH/KOH bath overnight, rinsed with H_2O, kept in a citric acid/H_2O bath overnight and finally rinsed with deionized H_2O and dried at 120 °C. Solutions and reagents were added with nitrogen-flushed disposable syringes/needles. Solvents were added using glass syringes and stainless steel needles (stored at 120 °C). Analytical thin layer chromatography (TLC) was performed on silica gel 60 G/UV_{254} aluminium sheets (*Macherey-Nagel*). Flash column chromatography was performed on silica gel Davisil LC60A (40-63 µm, pore size 60 Å, *Grace*) using the indicated solvents. NMR spectra were recorded on AV400, AV500 or AV700 instruments (*Bruker*) at the Institut für Chemie of *Technische Universität Berlin*. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard according to the standard literature.[1] Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, m_c = centrosymmetric multiplet), coupling constants (Hz), integration and – if possible – atom assignment. The assignment refers to the atom number shown in the corresponding molecule figure and was achieved by analysis of DEPT (DEPT 135) and 2D-NMR spectra (COSY, HMQC, HSQC, HMBC, NOESY). If a distinct assignment was not possible, atoms were marked with "*" and are interchangeable. Designation "*Ar*" refers to atoms of an aromatic system where a distinct assignment was not possible. Melting points (m.p.) were determined using a Leica Galen III melting point apparatus (*Wagner & Munz*). Infrared (IR) spectra were recorded on a Cary 630 FT-IR spectrometer equipped with an ATR unit (*Agilent Technologies).* Mass spectra (HRMS) were obtained from the Analytical Facility at the Institut für Chemie at *Technische Universität Berlin* (ESI/APCI: LTQ Orbitrap XL, *Thermo Scientific*; EI: GC-system 5975C, HP-5MS, *Agilent Technologies*). Analytical gas chromatography (GC) of reaction mixtures and pure substances was performed using a gas chromatograph 430-GC (*Varian Inc*.). The instrument was equipped with a FactorFour VF-WAXms capillary column (*Varian Inc., length*: 30 m, inner diameter: 0.25 mm, film thickness of the stationary phase: 0.25 µm). The following temperature program was used for the analysis: carrier gas N_2; injection temperature 270 °C; detector temperature 270 °C; flow rate 4.0 mL/min; temperature program: 40 °C start temperature, 20 °C/min heating rate to 250 °C for 10 min, then 20 °C/min heating rate to final temperature 260 °C for 5 min. The data was recorded with the program Galaxie 1.9.302.952 (*Varian Inc*.). Enantiomeric excesses were determined by analytical high performance liquid chromatography (HPLC) analysis on an

Agilent Technologies 1290 Infinity instrument with a chiral stationary phase using a Daicel Chiralcel OD-H column (*n*-heptane/iso-propanol = 98:2, 0.5 mL/min, 20 °C, 30 bar).

1.1 Solvents

THF and 1,4-dioxane were dried over sodium/benzophenone and distilled under N_2 atmosphere prior to use. Et_3N and CH_2Cl_2 were dried over CaH_2 and distilled under N_2 atmosphere prior to use. Acetone and EtOH were destilled under reduced pressure prior to use. Solvents (technical grade) for extraction/chromatography (*n*-pentane, cyclohexane, CH_2Cl_2, *tert*-butyl methyl ether, EtOAc) were distilled under reduced pressure prior to use. Liquid substrates for hydrogenation reactions were degassed prior to use.

1.2 Reactions under H_2 pressure

All reactions under H_2 pressure were carried out in glass vials (50 x 14 mm, *Schütt*), equipped with a magnetic stir bar and a rubber septum in autoclaves BR-100 or Br-300 (including the appropriate heating blocks, *Berghof*). The autoclave was purged with N_2 (3 x 10 bar) before the vials were placed in the autoclave and the septum was pierced under a counter flow of N_2. The autoclave was purged with N_2 (1 x 1 bar, 3 x 10 bar) and H_2 (3 x 10 bar) or D_2 (2 x 5 bar) before the appropriate H_2 or D_2 pressure was applied (pressure is given as initial pressure before heating). The heating block was pre-heated before the autoclave was placed inside. After the respective reaction time the autoclave was allowed to cool to rt and H_2 or D_2 was released. The autoclave was purged with N_2 (3 x 10 bar) before the vials were taken out.

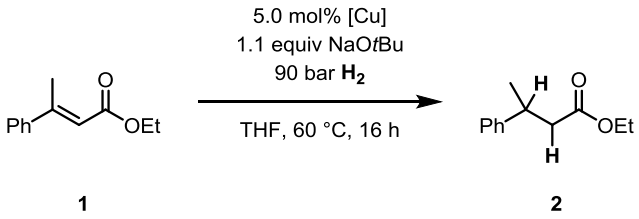
1.3 Chemicals

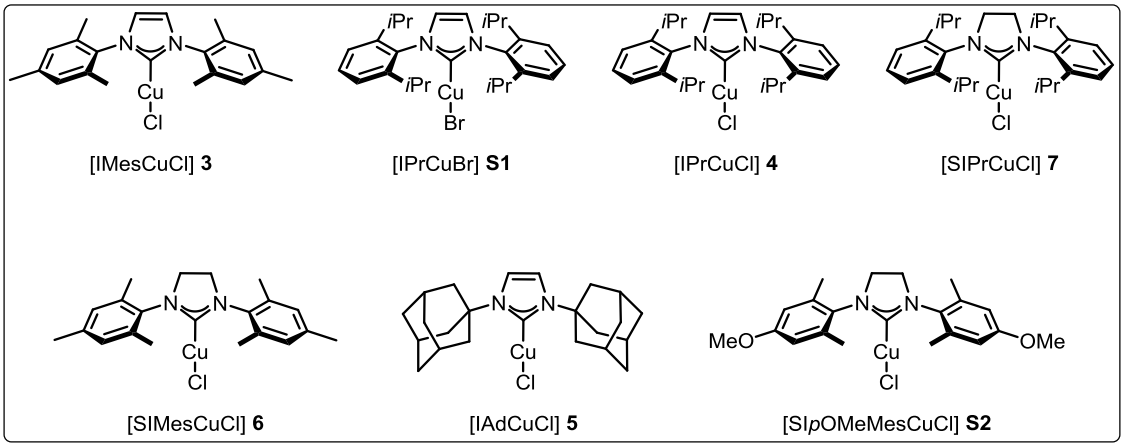
All reagents were purchased from established commercial suppliers (*Sigma-Aldrich, Alfa Aesar, TCI, Acros, Strem,, Merck, ABCR, Fluka, Fisher Scientrific*) and used without further purification. H_2 (99.999%) and D_2 (99.8%) was purchased from *Air Liquide*. (1*E*,2*E*)-N^1,N^2-dimesitylethane-1,2-diimine,[2] diethyl 3,3'-(1,4-phenylene)(2*E*,2'*E*)-bis(but-2-enoate) (**8r**),[3] ethyl (*E*)-2-methyl-3-phenylbut-2-enoate (**8l**),[4] ethyl 3-propylhex-2-enoate (**8v**),[3] ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate (**12**)[5], ethyl (*E*)-3-(4-(dimethylamino)phenyl)but-2-enoate (**8n**),[6] 1-(4-((*tert*-butyldiphenylsilyl)oxy)phenyl)ethan-1-one[7] and (*E*)-3-phenylbut-2-enoic acid[8] were synthesized following known procedures.

2 Additional optimization data

2.1 Influence of catalyst, base, solvent, pressure and temperature

Table S1: Influence of Cu-catalyst.[a]

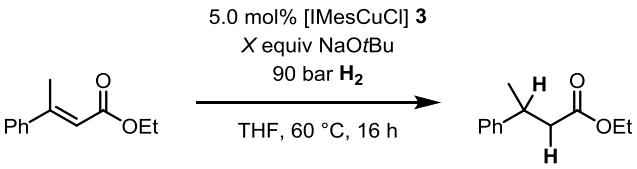




Entry	[Cu]	Conv.[b] [%]
1	[IMesCuCl] **3**	>95
2	[IPrCuBr] **S1**	67
3	[IPrCuCl] **4**	94
4	[SIPrCuCl] **7**	41
5	[SIMesCuCl] **6**	>95
6	[IAdCuCl] **5**	17
7	[SI*p*OMeMesCuCl] **S2**	>95

[a] All reactions with 4.6 µmol [Cu] in 1.1 mL solvent. [b] Determined by ^{1}H NMR spectroscopy.

Table S2: Influence of base.[a]

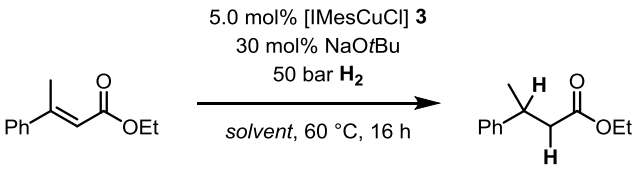


1 2

Entry	Conditions	Conv.[b] [%]
1	no [IMesCuCl] **3** 1.1 equiv NaO*t*Bu	0
2	no NaO*t*Bu	0
3	no [IMesCuCl] **3** no NaO*t*Bu	0
4	10 mol% NaO*t*Bu	6
5	30 mol% NaO*t*Bu	>95
6	50 mol% NaO*t*Bu	>95
7	80 mol% NaO*t*Bu	>95

[a] All reactions with 4.6 µmol [Cu] in 1.1 mL solvent. [b] Determined by ^{1}H NMR spectroscopy.

Table S3: Influence of solvent.[a]



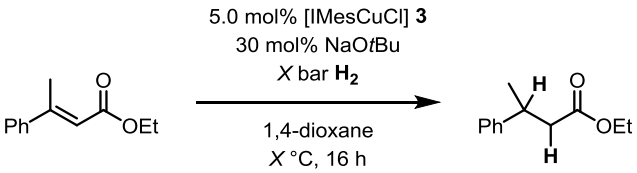
1 2

Entry	solvent	Conv.[b] [%]
1	THF	32
2	1,4-dioxane	>95
3	2-Me-THF	8
4	DMF	0
5	MeCN	6
6	cyclohexane	27

Entry	solvent	Conv.[b] [%]
7	*n*-hexane	27
8	benzene	18
9	chlorobenzene	5
10	1,2-dichlorobenzene	16
11	toluene	44

[a] All reactions with 4.6 µmol [Cu] in 1.1 mL solvent. [b] Determined by ^{1}H NMR spectroscopy.

Table S4: Influence of H_2-pressure and temperature.[a]

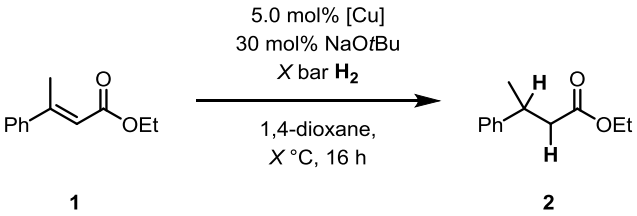


1 **2**

Entry	H_2 pressure [bar]	Temperature [°C]	Conv.[b] [%]
1	50	60	>95
2	10	60	5
3	10	100	>95
4	1[c]	100	0
5	1[c]	120	0
6	5	120	0

[a] All reactions with 5.5 µmol [Cu] in 1 mL solvent. [b] Determined by ^{1}H NMR spectroscopy. [c] Reaction was performed in an H_2-purged pressure tube.

Table S5: Performance of Cu catalysts at low H_2 pressure.[a]

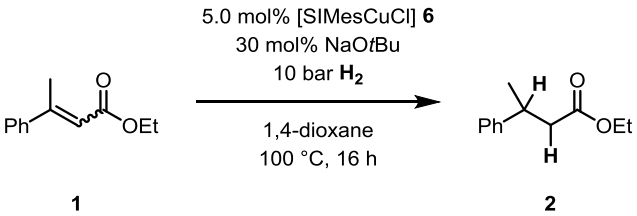


1 **2**

Entry	[Cu]	H_2 pressure [bar]	Temperature [°C]	Conv.[b] [%]
1	[IMesCuCl] **3**	10	60	5
2	[SIpOMeMesCuCl] **S2**	10	60	10
3	[SIMesCuCl] **6**	10	60	79
4	[SIMesCuCl] **6**	1[c]	100	32
5	[SIMesCuCl] **6**	10	100	>95 (71%)[d]

[a] All reactions with 5.5 µmol [Cu] in 1 mL solvent. [b] Determined by ^{1}H NMR spectroscopy. [c] Reaction was performed in an H_2-purged pressure tube. [d] Isolated yield.

Table S6: Investigation of *E*- and *Z*-enoates.[a]



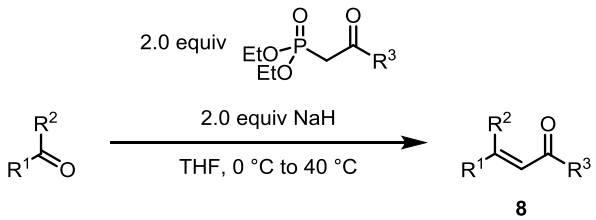
1 **2**

Entry	Enoate	Conv.[b] [%]
1	*E*-**1**	>99
2	*Z*-**1**	>99

[a] All reactions with 5.5 µmol [Cu] in 1 mL solvent. [b] Determined by GC analysis

3 General procedures

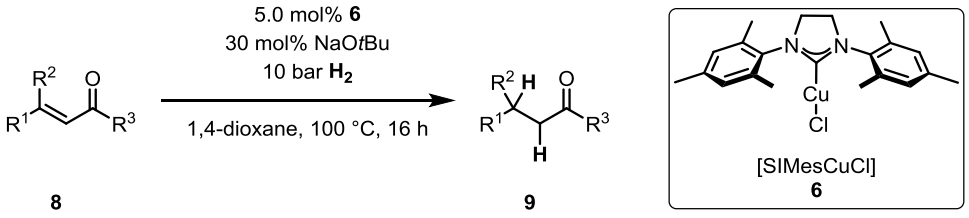
3.1 General procedure 1 – synthesis of α,β-unsaturated esters 8 *via* Horner-Wadsworth-Emmons reaction (GP1)



8

According to a literature procedure[3] NaH (60 wt% in mineral oil, 2.00 equiv) is suspended in THF (0.5M) and cooled to 0 °C. The corresponding phosphonate (2.00 equiv) is added dropwise and the reaction mixture is stirred at 0 °C for 30 min. The corresponding ketone (1.00 equiv) is added (neat for liquids, in solution in THF for solids 0.1 mL/mmol). The cooling bath is removed and the mixture is stirred at 40 °C until full conversion was detected (conversion monitored *via* TLC). After quenching the reaction by addition of H_2O (2 mL/mmol ketone) the aqueous phase is extracted with *tert*-butyl methyl ether (3 x 3 mL/mmol) and the combined organic layers are dried over Na_2SO_4 and filtered. All volatiles are removed under reduced pressure and the obtained crude product **8** is purified by flash column chromatography on silica gel.

3.2 General procedure 2 – H_2-mediated conjugate reduction (GP2)



8 **9**

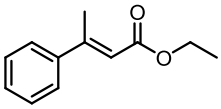
In a 5 mL glass vial equipped with a septum, [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) is placed and the vial is transferred into a N_2-filled glovebox. NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) is added and the solids are dissolved in 1,4-dioxane (1 mL). The mixture is stirred for 5 min at 40 °C. The degassed α,β-unsaturated ester **8** (0.25 mmol, 1.0 equiv) is dissolved in 1,4-dioxane (0.5 mL) and transferred to the reaction vial. The vial is placed in an autoclave and the septum is pierced with a needle under N_2-counterflow. The autoclave is purged with H_2 (3 x 10 bar). The reaction mixture is stirred for 16 h at 100 °C under H_2-atmosphere (10 bar). The crude reaction mixture is filtered over a small plug silica (eluant: CH_2Cl_2,

0.5 x 3 cm, 10 mL) and all volatiles are removed under reduced pressure. The crude product **9** is purified by flash column chromatography on silica gel.

4 Experimental Details

4.1 Syntheses of α,β-unsaturated esters and amides

4.1.1 Ethyl (*E*)-3-phenylbut-2-enoate (1)

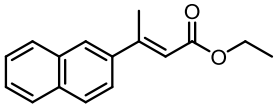


1
$C_{12}H_{14}O_2$
Mw = 190.24

Prepared according to **GP1** from acetophenone (2.3 mL, 20.0 mmol, 1.00 equiv), NaH (60 wt% in mineral oil, 1.60 g, 40.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (7.9 mL, 40 mmol, 2.0 equiv) in THF (40 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 100:1) yielded **1** as a colorless oil (2.59 g, 13.6 mmol, 68%).

R_f = 0.35 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).
^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.1 Hz, 3H), 2.58 (d, *J* = 1.4 Hz, 3H), 4.22 (q, *J* = 7.1 Hz, 2H), 6.13 (q, *J* = 1.3 Hz, 1H), 7.33–7.39 (m, 3H), 7.45–7.50 (m, 2H) ppm.
^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 14.4, 18.0, 59.9, 117.3, 126.4, 128.6, 129.0, 142.3, 155.5, 166.9 ppm.
HRMS (APCI) for $C_{12}H_{15}O_2^+$ [$(M+H)^+$] calculated: 191.1067, found: 191.1070.
The data is in accordance with literature.[9]

4.1.2 Ethyl (*E*)-3-(naphthalen-2-yl)but-2-enoate (8a)



8a
$C_{16}H_{16}O_2$
Mw = 240.30

Prepared according to **GP1** from 2-acetonaphthone (5.11 g, 30.0 mmol, 1.00 equiv), NaH (60 wt% in mineral oil, 2.40 g, 60.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (11.9 mL, 60.0 mmol, 2.00 equiv) in THF (60 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 100:1) yielded **8a** as a colorless oil (4.93 g, 20.5 mmol, 68%).

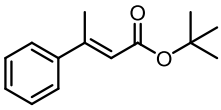
R_f = 0.59 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 4:1).
^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 1.35 (m_c, 3H), 2.70 (m, 3H), 4.26 (m_c, 2H), 6.29–6.31 (m, 1H), 7.50 (m_c, 2H), 7.60 (dd, *J* = 8.6 Hz, *J* = 1.9 Hz, 1H), 7.81–7.88 (m, 3H), 7.95 (d, *J* = 1.7 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.5, 18.0, 60.0, 117.6, 124.0, 126.0, 126.6, 126.8, 127.7, 128. 2, 128.6, 133.2, 133.6, 139.5, 155.3, 167.0 ppm.

HRMS (APCI) for $C_{16}H_{17}O_2^+$ [$(M+H)^+$] calculated: 241.1223, found: 241.1228.

The data is in accordance with literature.[10]

4.1.3 *tert*-Butyl (*E*)-3-phenylbut-2-enoate (8b)



8b
$C_{14}H_{18}O_2$
Mw = 218.30

Prepared according to **GP1** from acetophenone (2.1 mL, 18.6 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 1.48 g, 37.1 mmol, 2.00 equiv) and *tert*-butyl 2-(diethoxyphosphoryl)acetate (**S4**, 9.36 g, 37.1 mmol, 2.0 equiv) in THF (35 mL). The reaction mixture was stirred for 7 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 20:1) yielded **8b** as a colorless oil (2.10 g, 9.76 mmol, 65%).

R_f = 0.80 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

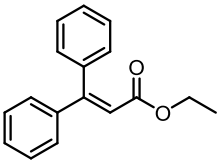
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.52 (s, 9H), 2.53 (d, *J* = 1.3 Hz, 3H), 6.05 (q, *J* = 1.3 Hz, 1H), 7.31–7.37 (m, 3H), 7.43–7.48 (m, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 17.9, 28.4, 80.1, 119.2, 126.4, 128.5, 128.8, 142.7, 154.1, 166.5 ppm.

HRMS (APCI) for $C_{14}H_{19}O_2^+$ [$(M+H)^+$] calculated: 219.1380, found: 219.1375.

IR (ATR): $\tilde{\upsilon}$ = 2975 (w), 1703 (s), 1625 (s), 1445 (m), 1365 (m), 1273 (m), 1203 (w), 1138 (s), 1011 (m), 915 (w), 871 (m), 758 (m), 692 (s) cm^{-1}.

4.1.4 Ethyl 3,3-diphenylacrylate (8c)



8c
$C_{17}H_{16}O_2$
Mw = 252.31

Prepared according to **GP1** from benzophenone (3.64 g, 20.0 mmol, 1.00 equiv), NaH (60 wt% in mineral oil, 1.60 g, 40.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (7.9 mL, 40 mmol, 2.0 equiv) in THF (40 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 50:1) yielded **8c** as a colorless oil (2.87 g, 11.4 mmol, 57%).

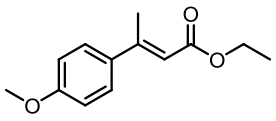
R_f = 0.46 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.11 (t, *J* = 7.1 Hz, 3H), 4.05 (q, *J* = 7.1 Hz, 2H), 6.37 (s, 1H), 7.19–7.24 (m, 2H), 7.28–7.42 (m, 8H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1, 60.1, 117.6, 127.9, 128.2, 128.4, 128.4, 129.2, 129.4, 139.1, 140.9, 156.5, 166.2 ppm.

HRMS (APCI) for $C_{17}H_{17}O_2^+$ [(M+H)$^+$] calculated: 253.1223, found: 253.1217.
The data is in accordance with literature.[3]

4.1.5 Ethyl (*E*)-3-(4-methoxyphenyl)but-2-enoate (8d)

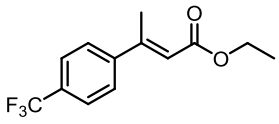


8d
$C_{13}H_{16}O_3$
Mw = 220.27

Prepared according to **GP1** from 4-methoxy acetophenone (3.00 g, 20.0 mmol, 1.00 equiv), NaH (60 wt% in mineral oil, 1.60 g, 40.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (7.9 mL, 40 mmol, 2.0 equiv) in THF (40 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 50:1) yielded **8d** as a yellow oil (2.87 g, 13.0 mmol, 65%).

R_f = 0.36 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).
^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.2 Hz, 3H), 2.56 (d, *J* = 1.3 Hz, 3H), 3.83 (s, 3H), 4.21 (q, *J* = 7.1 Hz, 2H), 6.11 (q, *J* = 1.3 Hz, 1H), 6.89 (m_c, 2H), 7.45 (m_c, 2H) ppm.
^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 14.4, 17.7, 55.4, 59.8, 113.9, 115.4, 127.7, 134.4, 154.9, 160.5, 167.1 ppm.
HRMS (APCI) for $C_{13}H_{17}O_3^+$ [(M+H)$^+$] calculated: 221.1172, found: 221.1165.
The data is in accordance with the literature.[3]

4.1.6 Ethyl (*E*)-3-(4-(trifluoromethyl)phenyl)but-2-enoate (8e)

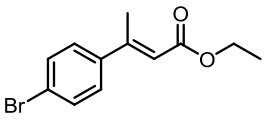


8e
$C_{13}H_{13}F_3O_2$
Mw = 258.24

Prepared according to **GP1** from 4-trifluoroacetophenone (3.76 g, 20.0 mmol, 1.00 equiv), NaH (60 wt% in mineral oil, 1.60 g, 40.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (7.9 mL, 40 mmol, 2.0 equiv) in THF (40 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 50:1) yielded **8e** as a colorless oil (3.31 g, 12.8 mmol, 65%).

R_f = 0.46 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).
^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.1 Hz, 3H), 2.57 (d, *J* = 1.3 Hz, 3H), 4.23 (q, *J* = 7.1 Hz, 2H), 6.14 (q, *J* = 1.3 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H) ppm.
^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 14.4, 18.0, 60.2, 119.1, 124.1 (q, *J* = 272.2 Hz), 125.6 (q, *J* = 3.8 Hz), 126.7, 130.9 (q, *J* = 32.7 Hz), 145.9, 153.8, 166.5 ppm.
^{19}**F NMR** (659 MHz, $CDCl_3$): δ = –62.7 ppm.
HRMS (APCI) for $C_{13}H_{14}F_3O_2^+$ [(M+H)$^+$] calculated: 259.0940, found: 259.0935.
The data is in accordance with literature.[9]

4.1.7 Ethyl (*E*)-3-(4-bromophenyl)but-2-enoate (8f)



8f
$C_{12}H_{13}BrO_2$
Mw = 269.14

Prepared according to **GP1** from 1-(4-bromophenyl)ethan-1-one (2.99 g, 15 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.0 equiv) in THF (30 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 50:1) yielded **8f** as a colorless oil (2.54 g, 9.44 mmol, 63%).

$\mathbf{R_f}$ = 0.44 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

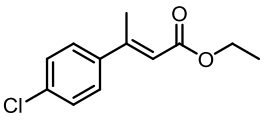
^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.1 Hz, 3H), 2.54 (d, *J* = 1.2 Hz, 3H), 4.21 (q, *J* = 7.1 Hz, 2H), 6.11 (m_c, 1H), 7.33 (m_c, 2H), 7.49 (m_c, 2H) ppm.

^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 14.4, 17.9, 60.1, 117.7, 123.3, 128.0, 131.8, 141.2, 154.1, 166.7 ppm.

HRMS (APCI) for $C_{12}H_{14}{}^{79}BrO_2^+$ [$(M+H)^+$] calculated: 269.0172, found: 269.0168.

The data is in accordance with literature.[9]

4.1.8 Ethyl (*E*)-3-(4-chlorophenyl)but-2-enoate (8g)



8g
$C_{12}H_{13}ClO_2$
Mw = 224.68

Prepared according to **GP1** from 1-(4-chlorophenyl)ethan-1-one (2.0 mL, 15 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.0 equiv) in THF (30 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 50:1) yielded **8g** as a colorless oil (2.15 g, 10.0 mmol, 67%).

$\mathbf{R_f}$ = 0.48 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

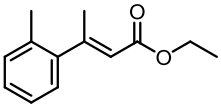
^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.1 Hz, 3H), 2.54 (d, *J* = 1.3 Hz, 3H), 4.21 (q, *J* = 7.1 Hz, 2H), 6.10 (d, *J* = 1.3 Hz, 1H), 7.33 (m_c, 2H), 7.40 (m_c, 2H) ppm.

^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 14.4, 17.9, 60.0, 117.7, 127.7, 128.8, 135.1, 140.7, 154.1, 166.7 ppm.

HRMS (APCI) for $C_{12}H_{14}{}^{35}ClO_2^+$ [$(M+H)^+$] calculated: 225.0677, found: 225.0672.

The data is in accordance with literature.[9]

4.1.9 Ethyl (*E*)-3-(o-tolyl)but-2-enoate (8h)



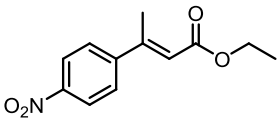
8h
$C_{13}H_{16}O_2$
Mw = 204.27

Prepared according to **GP1** from 1-(*o*-tolyl)ethan-1-one (2.0 mL, 15 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and

triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.0 equiv) in THF (30 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 50:1) yielded **8h** as a colorless oil (1.97 g, 9.66 mmol, 64%).

R_f = 0.55 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 10:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.1 Hz, 3H), 2.29 (s, 3H), 2.44 (d, *J* = 1.4 Hz, 3H), 4.21 (q, *J* = 7.1 Hz, 2H), 5.76 (q, *J* = 1.4 Hz, 1H), 7.05–7.08 (m, 1H), 7.14–7.23 (m, 3H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.4, 19.8, 20.9, 59.9, 119.5, 125.8, 127.2, 127.8, 130.5, 134.0, 144.0, 158.3, 166.8 ppm.
HRMS (APCI) for $C_{13}H_{17}O_2^+$ [$(M+H)^+$] calculated: 205.1223, found: 205.1218.
The data is in accordance with literature.[11]

4.1.10 Ethyl (*E*)-3-(4-nitrophenyl)but-2-enoate (8i)

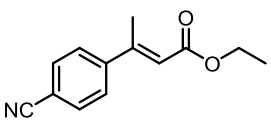


8i
$C_{12}H_{13}NO_4$
Mw = 235.23

Prepared according to **GP1** from 4-nitroacetophenone (2.48 g, 15.0 mmol, 1.00 equiv), NaH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 6.78 g, 30.0 mmol, 2.00 equiv) in THF (40 mL). The reaction mixture was stirred for 24 h at 40 °C. Purification by flash column chromatography on silica gel cyclohexane/*tert*-butyl methyl ether = 20:1) yielded **8i** as a colorless oil (*E/Z* = 88:12, 1.20 g, 5.12 mmol, 34%).

R_f = 0.37 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.2 Hz, 3H), 2.58 (d, *J* = 1.2 Hz, 3H), 4.24 (q, *J* = 7.2 Hz, 2H), 6.18 (m_c, 1H), 7.61 (m_c, 2H), 8.21 (m_c, 2H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.4, 18.0, 60.4, 120.3, 123.9, 127.4, 148.1, 148.7, 152.8, 166.2 ppm.
HRMS (APCI) for $C_{14}H_{18}N_2O_3^+$ [$(M+H+MeCN)^+$] calculated: 262.1306, found: 262.1158.
IR (ATR): $\tilde{\upsilon}$ = 2986 (w), 2907 (w), 2114 (w), 1709 (s), 1594 (m), 1511 (s), 1339 (s), 1274 (m), 1177 (s), 1039 (m), 846 (s).

4.1.11 Ethyl (*E*)-3-(4-cyanophenyl)but-2-enoate (8j)



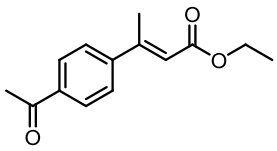
8j
$C_{13}H_{13}NO_2$
Mw = 215.25

Prepared according to **GP1** from 4-acetylbenzonitrile (2.17 g, 15 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.0 equiv) in THF (30 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel

cyclohexane/*tert*-butyl methyl ether = 20:1) yielded **8j** as a colorless oil (2.10 g, 9.76 mmol, 65%).

R_f = 0.21 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).
^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.1 Hz, 3H), 2.55 (d, *J* = 1.3 Hz, 3H), 4.22 (q, *J* = 7.1 Hz, 2H), 6.13 (q, *J* = 1.3 Hz, 1H), 7.54 (m_c, 2H), 7.66 (m_c, 2H) ppm.
^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 14.4, 17.8, 60.3, 112.6, 118.5, 119.8, 127.1, 132.4, 146.8, 153.1, 166.2 ppm.
HRMS (APCI) for $C_{13}H_{14}NO_2^+$ [$(M+H)^+$] calculated: 216.1019, found: 216.1020.
The data is in accordance with literature.[9]

4.1.12 Ethyl (*E*)-3-(4-acetylphenyl)but-2-enoate (8k)

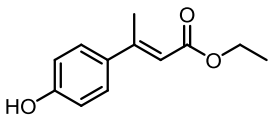


8k
$C_{14}H_{16}O_3$
Mw = 232.27

Prepared according to **GP1** from 1,1'-(1,4-phenylene)bis(ethan-1-one) (2.43 g, 15.0 mmol, 1.00 equiv), NaH (60 wt% in mineral oil, 0.670 g, 16.5 mmol, 1.1 equiv) and triethyl phosphonoacetate (3.3 mL, 17 mmol, 1.1 equiv) in THF (40 mL). The reaction mixture was stirred for 24 h at 40 °C. Purification by flash column chromatography on silica gel cyclohexane/*tert*-butyl methyl ether = 10:1) yielded **8k** as a colorless oil (*E/Z* = 87:13, 1.29 g, 5.54 mmol, 37%).

R_f = 0.23 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).
^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.2 Hz, 3H), 2.58 (d, *J* = 1.4 Hz, 3H), 2.61 (s, 3H), 4.23 (q, *J* = 7.2 Hz, 2H), 6.17 (q, *J* = 1.3 Hz, 1H), 7.55 (m_c, 2H), 7.95 (m_c, 2H) ppm.
Indicative signals for the *Z*-isomer are at δ = 1.10, 4.00, 5.95, 7.28.
^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 14.5 (C-2''), 18.0 (C-4), 26.8 (C-6'), 60.2 (C-1''), 119.0 (C-2), 126.7 (C-2'), 128.7 (C-3'), 137.3 (C-4'), 146.9 (C-1'), 154.1 (C-3), 166.6 (C-1), 197.6 (C-5') ppm.
HRMS (APCI) for $C_{14}H_{17}O_3^+$ [$(M+H)^+$] calculated: 233.1172, found: 233.1169.
IR (ATR): $\tilde{\upsilon}$ = 2975 (w), 1681 (m), 1626 (m), 1358 (m), 1261 (s), 1159 (s), 1039 (m), 829 (m).
The data is in accordance with literature.[12]

4.1.13 Ethyl (*E*)-3-(4-hydroxyphenyl)but-2-enoate (8l)



XXX
$C_{12}H_{16}O_3$
Mw = 206.24

In a 10 mL-schlenkflask ethyl (*E*)-3-(4-((*tert*-butyldiphenylsilyl)oxy)phenyl)but-2-enoate (**8m**, 204 mg, 1.24 mmol, 1.00 equiv) was desolved in THF (5 mL). Tetrabutylammonium fluoride solution (1M, 1.4 mL, 1.4 mmol, 1.1 equiv) was added. The resulting solution was stirred for 1 h at rt until full conversion

(conversion monitored *via* TLC). After quenching the reaction by addition of saturated aqueous NH_4Cl solution (10 mL) the aqueous phase was extracted with *tert*-butyl methyl ether (3 x 10 mL) and the combined organic layers are dried over $MgSO_4$ and filtered. All volatiles were removed and the obtained crude product **8l** was purified by flash column chromatography on silica gel (cyclohexane/ *tert*-butyl methyl ether = 10:1). The product **8l** was obtained as a white solid (150 mg, 0.728 mmol, 59%).

R_f = 0.57 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 2:1).

^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.1 Hz, 3H), 2.55 (d, *J* = 1.3 Hz, 3H), 4.21 (q, *J* = 7.1 Hz, 2H), 5.15 (br s, 1H), 6.09 (q, *J* = 1.3 Hz, 1H), 6.83 (m_c, 2H), 7.40 (m_c, 2H) ppm.

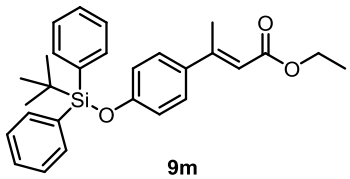
^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 14.4, 17.8, 59.9, 115.4, 115.5, 128.0, 134.7, 155.0, 156.7, 167.3 ppm.

HRMS (APCI) for $C_{13}H_{14}NO_2^+$ [$(M+H)^+$] calculated: 207.1016, found: 207.1011.

IR (ATR): $\tilde{\upsilon}$ = 3340 (m), 1676 (m), 1595 (m), 1509 (w), 1435 (w), 1274 (m), 1171 (m), 1041 (w), 869 (w), 835 (m) cm^{-1}.

M.p.: T = 94 °C.

4.1.14 Ethyl (*E*)-3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)but-2-enoate (9m)



9m
$C_{28}H_{32}O_3Si$
Mw = 444.64

Prepared according to **GP1** from 1-(4-((*tert*-butyldiphenylsilyl)oxy)phenyl)ethan-1-one (1.7 g, 4.6 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 0.40 g, 10.0 mmol, 2.2 equiv) and triethyl phosphonoacetate (2.0 mL, 10 mmol, 2.2 equiv) in THF (10 mL). The reaction mixture was stirred for 20 h at 40 °C. Purification by flash column chromatography on silica gel cyclohexane/*tert*-butyl methyl ether = 100:1) yielded **9m** as a white solid (E/Z = 93:7, 0.550 g, 1.24 mmol, 27%).

R_f = 0.69 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 1.10 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H), 2.49 (d, *J* = 1.2 Hz, 3H), 4.18 (q, *J* = 7.1 Hz, 2H), 6.03 (q, *J* = 1.2 Hz, 1H), 6.74 (m_c, 2H), 7.25 (m_c, 2H), 7.34–7.40 (m, 4H), 7.41–7.46 (m, 2H), 7.69–7.73 (m, 4H) ppm.

^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 14.4, 17.6, 19.6, 26.6, 59.7, 115.4, 119.7, 127.5, 127.9, 130.1, 132.7, 134.7, 135.6, 155.0, 156.7, 167.2 ppm.

The NMR spectra contain 7% of the *Z*-Isomer, indicative signals in ^{1}H NMR are at 1.20, 3.74, 5.29 and 7.68 ppm.

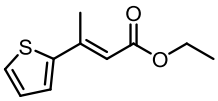
^{29}**SI DEPT NMR** (99MHz, *J* = 20 Hz, $CDCl_3$): δ = –5.6 ppm.

HRMS (APCI) for $C_{28}H_{33}O_3Si^+$ [$(M+H)^+$] calculated: 445.2193, found: 445.2184.

IR (ATR): $\tilde{\upsilon}$ = 2930 (w), 2892 (w), 2857 (w), 1703 (m), 1598 (m), 1507 (m), 1424 (w), 1372 (w), 1258 (s), 1112 (s), 1044 (m), 1007 (w), 916 (s), 819 (s), 696 (s) cm^{-1}.

M.p.: T = 69 °C.

4.1.10 Ethyl (*E*)-3-(thiophen-2-yl)but-2-enoate (8o)



8o
$C_{10}H_{12}O_2S$
Mw = 196.26

Prepared according to **GP1** from 1-(thiophen-2-yl)ethan-1-one (1.6 mL, 15 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.0 equiv) in THF (30 mL). The reaction mixture was stirred for 36 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 50:1) yielded **8o** as a colorless oil (1.64 g, 8.33 mmol, 56%).

R_f = 0.43 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 10:1).

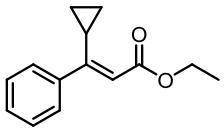
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.1 Hz, 3H), 2.60 (d, *J* = 1.2 Hz, 3H), 4.20 (q, *J* = 7.1 Hz, 2H), 6.25 (q, *J* = 1.2 Hz, 1H), 7.04 (m_c, 1H), 7.30–7.32 (m, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.4, 17.4, 59.9, 114.4, 126.7, 127.1, 128.0, 145.7, 147.8, 166.8 ppm.

HRMS (APCI) for $C_{10}H_{13}O_2S^+$ [$(M+H)^+$] calculated: 197.0631, found: 197.0626.

The data is in accordance with literature.[9]

4.1.15 Ethyl (*E*)-3-cyclopropyl-3-phenylacrylate (8p)



8p
$C_{14}H_{16}O_2$
Mw = 216.28

Prepared according to **GP1** from cyclopropyl(phenyl)methanone (2.1 mL, 15 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.0 equiv) in THF (30 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 50:1) yielded **8p** as a colorless oil (0.64 g, 3.0 mmol, 35%).

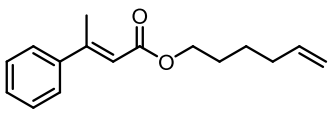
R_f = 0.5 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.47 (m_c, 2H), 0.89 (m_c, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 3.12 (m_c, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 5.79 (d, *J* = 0.8 Hz, 1H), 7.11–7.15 (m, 2H), 7.27–7.33 (m, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 7.0, 13.6, 14.4, 59.8, 118.9, 127.8, 127.8, 128.1, 138.9, 163.2, 167.0 ppm.

HRMS (APCI) for $C_{14}H_{17}O_2^+$ [$(M+H)^+$] calculated: 217.1223, found: 217.1215.
The data is in accordance with literature.[9]

4.1.16 Hex-5-en-1-yl (*E*)-3-phenylbut-2-enoate (8q)

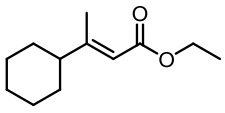


8q
$C_{16}H_{20}O_2$
Mw = 244.33

Following a literature procedure,[13] in a 25 mL-schlenk tube, (E)-3-phenylbut-2-enoic acid (0.50 g, 3.1 mmol, 1.00 equiv) was dissolved in CH_2Cl_2 (10 mL). DMAP (452 mg, 3.70 mmol, 1.20 equiv) and hex-5-en-1-ol (0.73 mL, 6.2 mmol, 2.0 equiv) were added. The resulting solution was cooled to 0 °C and DCC (954 mg, 4.62 mmol, 1.50 equiv) was added. The solution was stirred for 5 min at 0 °C and 18 h at rt until full conversion was detected (conversion monitored *via* TLC). Precipitated urea was filtered off over a plug of silica gel (3 x 3 cm, eluent: CH_2Cl_2, 30 mL). The filtrate was evaporated and the obtained crude product **8q** was purified by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 100:1). Remaining urea residues were removed by dissolving the product **8q** in Et_2O (10 mL) and washing the organic layer with aqueous HCl (2M, 3 x 10 mL). The organic layer was dried over $MgSO_4$, filtered and all volatiles were removed. The product **8q** was obtained as a yellow oil (330 mg, 1.35 mmol, 44%).

R_f = 0.73 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.46–1.55 (m, 2H), 1.66–1.74 (m, 2H), 2.11 (m_c, 2H), 2.57 (d, *J* = 1.3 Hz, 3H), 4.16 (t, *J* = 6.6 Hz, 2H), 4.97 (m_c, 1H), 5.02 (m_c, 1H), 5.81 (m_c, 1H), 6.13 (q, *J* = 1.3 Hz, 1H), 7.34–7.40 (m, 3H), 7.45–7.50 (m, 2H) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ = 18.0, 25.4, 28.3, 33.4, 63.9, 114.9, 117.3, 126.4, 128.6, 129.0, 138.5, 142.3, 155.6, 167.0 ppm.
HRMS (APCI) for $C_{16}H_{21}O_2^+$ [$(M+H)^+$] calculated: 245.1536, found: 245.1532.
IR (ATR): $\tilde{\upsilon}$ = 2934 (w), 1709 (s), 1626 (m), 1575 (w), 1445 (w), 1379 (w), 1343 (m), 1270 (m), 1154 (s), 1023 (m), 909 (m), 870 (m), 764 (s), 692 (m) cm^{-1}.

4.1.17 Ethyl (*E*)-3-cyclohexylbut-2-enoate (8t)



8t
$C_{12}H_{20}O_2$
Mw = 196.29

Prepared according to **GP1** from 1-cyclohexylethan-1-one (2.1 mL, 15 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.0 equiv) in THF (30 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 50:1) yielded **8t** as a colorless oil (*E*/*Z* = 90:10, 2.22 g, 11.3 mmol, 75%).

R_f = 0.56 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 10:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.11–1.39 (m, 8H), 1.55–1.82 (m, 5H), 1.96 (tt, *J* = 1.9 Hz, *J* = 2.8 Hz, 1H), 2.13 (d, *J* = 1.2 Hz, 3H), 4.13 (q, *J* = 7.1 Hz, 2H), 5.64 (m_c, 1H) ppm.

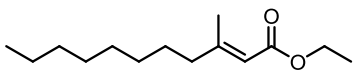
The sample contains 10% of the *Z*-isomer (detected *via* ^{1}H NMR and ^{1}H-^{1}H NOESY). Therefore, the value of the integration for the cyclohexyl substituent is too high (see the attached spectra).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.4, 17.5, 26.2, 26.5, 31.5, 48.8, 59.5, 114.0, 164.9, 167.4 ppm.

HRMS (APCI) for $C_{12}H_{21}O_2^+$ [$(M+H)^+$] calculated: 197.1536, found: 197.1531.

The data is in accordance with literature.[14]

4.1.18 Ethyl (*E*)-3-methylundec-2-enoate (8u)



8u
$C_{14}H_{26}O_2$
Mw = 226.36

Prepared according to **GP1** from decan-2-one (2.8 mL, 15 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 1.20 g, 30.0 mmol, 2.00 equiv) and triethyl phosphonoacetate (6.0 mL, 30 mmol, 2.0 equiv) in THF (30 mL). The reaction mixture was stirred for 48 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 50:1) yielded **8u** as a colorless oil (*E*/*Z* = 77:23, 3.17 g, 14.0 mmol, 93%).

R_f = 0.59 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

E-isomer:

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.9 Hz, 3H), 1.16–1.36 (m, 13H), 1.41–1.49 (m, 2H), 2.12 (m_c, 2H), 2.14 (d, *J* = 1.3 Hz, 3H), 4.14 (q, *J* = 7.1 Hz, 2H), 5.65 (q, *J* = 1.2 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2, 14.4, 18.9, 22.7, 27.5, 29.3, 29.3, 29.5, 31.9, 41.0, 59.5, 115.5, 160.4, 167.0 ppm.

Z-isomer:

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.0 Hz, 3H), 2.54 (d, *J* = 1.3 Hz, 3H), 4.21 (q, *J* = 7.1 Hz, 2H), 6.10 (d, *J* = 1.3 Hz, 1H), 1.87 (d, *J* = 1.3 Hz, 3H), 4.13 (q, *J* = 7.1 Hz, 2H), 5.63 (m_c, 1H) ppm.

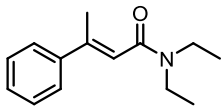
^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2, 14.4, 25.2, 28.3, 29.3, 29.5, 29.8, 33.5, 59.4, 116.0, 160.8 ppm.

E- and *Z*-Isomer could be identified *via* ^{1}H-^{1}H NOESY.

Not all signals for the *Z*-isomer could be detected in ^{1}H and ^{13}C NMR due to low concentration and overlay with signals of the *E*-isomer.

HRMS (APCI) for $C_{14}H_{27}O_2^+$ [$(M+H)^+$] calculated: 227.2006, found: 227.1997.
The data is in accordance with literature.[14]

4.1.19 (*E*)-*N*,*N*-diethyl-3-phenylbut-2-enamide (10)

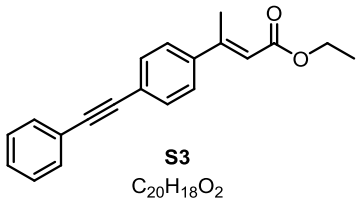


10
$C_{14}H_{19}NO$
Mw = 217.31

Prepared according to **GP1** from acetophenone (0.47 mL, 4.0 mmol, 1.0 equiv), NaH (60 wt% in mineral oil, 316 mg, 7.96 mmol, 2.00 equiv) and diethyl (2-(diethylamino)-2-oxoethyl)phosphonate (**S6**, 1.8 mL, 8.0 mmol, 2.0 equiv) in THF (8 mL). The reaction mixture was stirred for 24 h at 40 °C. Purification by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 4:1) yielded **10** as a colorless oil (589 mg, 2.71 mmol, 68%).

R_f = 0.16 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).
^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 1.18 (t, *J* = 7.0 Hz, 6H), 2.30 (d, *J* = 1.2 Hz, 3H), 3.43 (m_c, 4H), 6.29 (d, *J* = 1.2 Hz, 1H), 7.29–7.38 (m, 3H), 7.42–7.46 (m, 2H) ppm.
^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 13.3, 14.5, 18.0, 39.7, 42.7, 120.3, 126.1, 128.2, 128.5, 142.3, 145.6, 167.7 ppm.
HRMS (APCI) for $C_{14}H_{20}NO^+$ [$(M+H)^+$] calculated: 218.1539, found: 218.1531.
The data is in accordance with literature.[15]

4.1.20 Ethyl (*E*)-3-(4-(phenylethynyl)phenyl)but-2-enoate (S3)



S3
$C_{20}H_{18}O_2$
Mw = 290.36

Prepared according to **GP1** from 1-(4-(phenylethynyl)phenyl)ethan-1-one (1.65 g, 7.50 mmol, 1.00 equiv), NaH (60 wt% in mineral oil, 0.60 g, 15 mmol, 2.0 equiv) and triethyl phosphonoacetate (3.0 mL, 3.4 g, 15 mmol, 2.0 equiv) in THF (20 mL). The reaction mixture was stirred for 24 h at 40 °C. Purification by flash column chromatography on silica gel cyclohexane/*tert*-butyl methyl ether = 70:1) yielded **S3** as a colorless oil (1.36 g, 4.96 mmol, 66%).

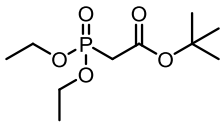
R_f = 0.46 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).
^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.0 Hz, 3H), 2.58 (d, *J* = 1.3 Hz, 3H), 4.23 (q, *J* = 7.3 Hz, 2H), 6.17 (d, *J* = 1.3 Hz, 1H), 7.34–7.38 (m, 2H), 7.45–7.49 (m, 2H), 7.51–7.56 (m, 5H) ppm.
^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 14.4, 17.7, 60.0, 89.1, 90.9, 117.7, 123.2, 124.1, 126.4, 128.5, 128.5, 131.7, 131.8, 141.9, 154.5, 166.8 ppm.

HRMS (APCI) for $C_{20}H_{19}O_2^+$ [$(M+H)^+$] calculated: 291.1380, found: 291.1383.

IR (ATR): $\tilde{\upsilon}$ = 2978 (w), 2908 (w), 2117 (w), 1705 (m), 1619 (m), 1440 (m), 1342 (m), 1272 (m), 1167 (s), 1039 (m), 879 (m), 831 (s), 756 (s).

4.2 Syntheses of alkyl phosphonates

4.2.1 *tert*-Butyl 2-(diethoxyphosphoryl)acetate (S4)



S4
$C_{10}H_{21}O_5P$
Mw = 252.25

According to a literature procedure[16] a 25 mL two neck flask with reflux condenser was charged with *tert*-butyl bromoacetate (7.2 mL, 50 mmol, 1.0 equiv) and triethylphosphite (8.6 mL, 50 mmol, 1.0 equiv) was added. The reaction mixture was stirred for 1 h at 100 °C and heated to reflux for 14 h until full conversion was detected (conversion monitored *via* TLC). The obtained crude product **S4** was purified by fractional distillation (106 °C, $8.6 \cdot 10^{-1}$ mbar) and yielded **S4** as a colorless oil (10.8 g, 43.0 mmol, 86%).

$\mathbf{R_f}$ = 0.56 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 1.34 (t, *J* = 7.1 Hz, 6H), 1.46 (s, 9H), 2.87 (d, *J* = 21.4 Hz, 2H), 4.15 (m_c, 4H) ppm.

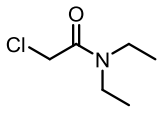
^{13}**C NMR** (126 MHz, $CDCl_3$): δ = 16.4 (d, *J* = 6.1 Hz), 28.0, 35.7 (d, *J* = 133.1 Hz), 62.5 (d, *J* = 6.0 Hz), 82.1, 165.0 (d, *J* = 6.3 Hz) ppm.

^{31}**P NMR** (202 MHz, $CDCl_3$): δ = 20.5 (m_c) ppm.

HRMS (APCI) for $C_{10}H_{22}O_5P^+$ [$(M-H)^+$] calculated: 253.1199, found: 253.1191.

The data is in accordance with literature.[16,17]

4.2.2 2-Chloro-N,N-diethylacetamide (S5)



S5
$C_6H_{12}ClNO$
Mw = 149.62

According to a literature procedure[18] diethylamine (3.1 mL, 30 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 (150 mL). Triethylamine (4.8 mL, 38 mmol, 1.3 equiv) was added and chloroacetylchloride (2.6 mL, 33 mmol, 1.1 equiv) was added dropwise over 15 min. The reaction mixture was stirred for 16 h at rt until full conversion (conversion monitored *via* TLC). The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with aqueous HCl (1M, 3 x 40 mL). The organic layer was dried over $MgSO_4$ and filtered. The obtained crude product **S5** was purified by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 2:1) and yielded **S5** as a orange oil (3.18 g, 21.3 mmol, 71%).

$\mathbf{R_f}$ = 0.28 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 1:1).

^{1}**H NMR** (500 MHz, $CDCl_3$): δ = 1.13 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 3.37 (m_c,

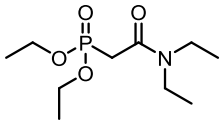
4H), 4.04 (s, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 12.7, 14.4, 40.6, 41.3, 42.5, 165.8 ppm.

HRMS (APCI) for $C_6H_{13}ClNO^+$ [$(M+H)^+$] calculated: 150.0680, found: 150.0677.

IR (ATR): $\tilde{\upsilon}$ = 2973 (w), 1639 (s), 1429 (m), 1380 (m), 1315 (w), 1253 (m), 1218 (m), 1120 (m), 1098 (m), 1016 (w), 950 (w), 788 (m), 721 (w) cm^{-1}.

4.2.3 Diethyl (2-(diethylamino)-2-oxoethyl)phosphonate (S6)



S6
$C_{10}H_{22}NO_4P$
Mw = 251.26

According to a literature procedure[15] a 25 mL two neck flask with reflux condenser was charged with 2-chloro-N,N-diethylacetamide (**S6**, 3.00 g, 20.0 mmol, 1.00 equiv) and triethylphosphite (3.6 mL, 21.1 mmol, 1.15 equiv) was added. The reaction mixture was stirred for 8 h at 180 °C. The obtained crude product **S6** was purified by fractional distillation (125 °C, $1.2 \cdot 10^{-1}$ mbar) and yielded **S6** as a colorless oil (4.01 g, 15.9 mmol, 80%).

Bp = 125 °C ($1.2 \cdot 10^{-1}$ mbar).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.0 Hz, 6H), 3.00 (d, *J* = 22.0 Hz, 2H), 3.40 (m_c, 4H), 4.16 (m_c, 4H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.0, 14.2, 16.4 (d, *J* = 6.3 Hz), 33.5 (d, *J* = 134.0 Hz), 40.6, 43.1, 62.6 (d, *J* = 6.5 Hz), 164.0 (d, *J* = 5.6 Hz) ppm.

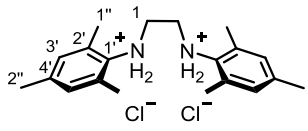
^{31}P NMR (202 MHz, $CDCl_3$): δ = 21.4 (m_c) ppm.

HRMS (APCI) for $C_{10}H_{23}NO_4P^+$ [$(M+H)^+$] calculated: 252.1359, found: 252.1351.

The data is in accordance with literature.[15]

4.3 Synthesis of [SIMesCuCl] 6

4.3.1 Synthesis of *N*^{1},*N*^{2}-dimesitylethane-1,2-diaminium chloride (S7)



S7
$C_{20}H_{30}Cl_2N_2$
Mw = 369.37

Following a literature procedure,[2] in a 250 mL-schlenk flask, *N*^{1},*N*^{2}-dimesitylethane-1,2-diimine (5.00 g, 17.1 mmol, 1.00 equiv) was dissolved in THF (80 mL) and and the solution was cooled to 0 °C. $NaBH_4$ (2.59 g, 68.4 mmol, 4.00 equiv) was added and the suspension was stirred for 15 min at 0 °C. Concentrated aqueous HCl (2.9 ml, 34 mmol, 2.0 equiv) was added dropwise over 30 min. The suspension was stirred for 1 h at 0 °C. Aqueous HCl (3M, 130 mL) was added and the suspension was stirred for 16 h at rt. The precipitate was collected on a sintered funnel and washed with H_2O (100 mL). The obtained product was dried under reduced pressure ($2 \cdot 10^{-2}$ mbar) and used without further purification. The product **S7** (4.88 g, 13.2 mmol, 77%) was obtained as a white solid.

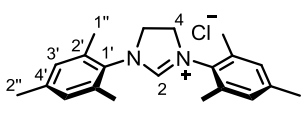
^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.22 (s, 6H, H-2‘‘), 2.31–2.40 (m, 12H, H-1’’), 3.34–3.49 (m, 4H, H-1), 6.91 (s, 4H, H-3’) ppm.

^{13}C NMR (126 MHz, DMSO-d_6): δ = 18.0 (C-1‘‘), 20.2 (C-2‘‘), 46.9 (C-4), 129.8 (C-3‘), 130.9 (C-1’), 135.8 (C-4’) ppm. C-2’ could not be detected in ^{13}C NMR.

HRMS (APCI) for $C_{20}H_{29}N_2^+$ [(M–2Cl–H)$^+$]: calculated: 297.2325, found: 297.2320.

The data is in accordance with literature.[19]

4.3.2 Synthesis of 1,3-dimesityl-4,5-dihydro-1H-imidazol-3-ium chloride (S8)



S8
$C_{21}H_{27}ClN_2$
Mw = 342.91

Following a literature procedure[20], in a 100 mL-two-necked flask, N^1,N^2-dimesitylethane-1,2-diaminium chloride (**S7**, 4.80 g, 13.0 mmol, 1.00 equiv) was suspended in triethylorthoformate (65 mL) and formic acid (3 drops) was added. The resulting suspension was stirred for 48 h at 120 °C. The precipitate was filtered off and washed with Et_2O (30 mL). The obtained crude product was purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH = 50:1) and yielded **S8** (3.09 mg, 9.01 mmol, 69%) as yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.25 (s, 6H, H-2‘‘), 2.32–2.39 (m, 12H, H-1’’), 4.50–4.59 (m, 4H, H-4), 6.88–6.94 (m, 4H, H-3’), 9.41 (m_c, 1H, H-2) ppm.

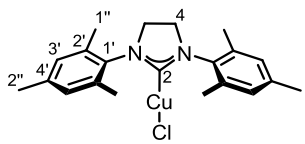
^{13}C NMR (126 MHz, $CDCl_3$): δ = 18.0 (C-1‘‘), 21.1 (C-2‘‘), 52.0 (C-4), 130.1 (C-3‘), 130.3 (C-1’), 135.0 (C-2’’), 140.5 (C-4’), 160.0 (C-2) ppm.

HRMS (APCI) for $C_{21}H_{27}N_2^+$ [(M–Cl)$^+$]: calculated: 307.2169, found: 442.1559.

IR (ATR): $\tilde{\upsilon}$ = 3242 (w), 2953 (w), 2914 (w), 2830 (w), 1620 (s), 1481 (m), 1450 (m), 1376 (w), 1266 (s), 1216 (s), 1151 (w), 1042 (m), 984 (w), 936 (w), 845 (m), 819 (m), 731 (s) cm^{-1}.

The data is in accordance with literature.[20]

4.3.3 Synthesis of (1,3-dimesitylimidazolidin-2-yliden)copper(I) chloride (6)



6
$C_{21}H_{26}ClCuN_2$
Mw = 405.44

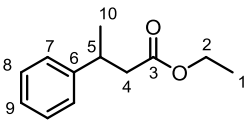
Following a literature procedure,[21] a 25 mL-two-necked flask was charged with copper(I) chloride (99.99%, 289 mg, 2.92 mmol, 1.00 equiv), 1,3-dimesityl-4,5-dihydro-1*H*-imidazol-3-ium chloride (**S8**, 1.00 g, 2.92 mmol, 1.00 equiv) and K_2CO_3 (806 mg, 5.83 mmol, 2.00 equiv). The flask was evacuated and backfilled with nitrogen (2 x). Acetone (12 mL) was added and the resulting yellow suspension was

stirred for 24 h at 60 °C. The reaction mixture was filtered over a plug of silica (3 x 2 cm, eluent: CH_2Cl_2, 2 x 30 mL) and the yellow filtrate was concentrated under reduced pressure to ~5 mL. *n*-Pentane (50 mL) was added rapidly to precipitate the crude product, which was collected on a funnel and washed with *n*-pentane (2 x 20 mL). The resulting yellow crystals were dried under reduced pressure. Copper(I)/NHC complex **6** (845 mg, 2.09 mmol, 72%) was obtained as yellow crystals.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.29 (s, 6H, H-2‘‘), 2.31 (s, 12H, H-1’’), 3.94 (br s, 4H, H-4), 6.95 (s, 4H, H-3’) ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ = 18.1 (C-1‘‘), 21.1 (C-2‘‘), 51.1 (C-4), 129.9 (C-3‘), 135.1 (C-4’), 135.5 (C-1‘), 138.8 (C-2‘) ppm. The ^{13}C-NMR resonance of C-2 could not be detected.
HRMS (APCI) for $C_{23}H_{29}CuN_3^+$ [((M–Cl)MeCN)$^+$]: calculated: 410.1657, found: 410.1649.
IR (ATR): $\tilde{\upsilon}$ = 2909 (w), 1607 (w), 1485 (s), 1438 (m), 1315 (w), 1270 (s), 1189 (w), 1020 (w), 849 (s), 802 (w), 731 (w) cm^{-1}.
M.p.: T = 205 °C.
The data is in accordance with literature.[21]

4.4 Conjugate reduction products

4.4.1 Ethyl 3-phenylbutanoate (2)

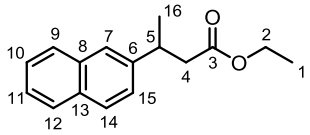


2
$C_{12}H_{16}O_2$
Mw = 192.26

Prepared according to **GP2** from ethyl (*E*)-3-phenylbut-2-enoate (**1**, 95 mg, 0.50 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 10 mg, 25 µmol, 5.0 mol%) and NaO*t*Bu (14 mg, 0.15 mmol, 30 mol%) in 1,4-dioxane (2.0 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether = 30:1) yielded **2** as a colorless oil (68 mg, 0.35 mmol, 71%).

R_f = 0.33 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 20:1).
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 (m_c, 3H, H-1), 1.31 (d, $^3J_{10,5}$ = 7.0 Hz, 3H, H-10), 2.58 (m_c, 2H, H-4), 3.28 (m_c, 1H, H-5), 4.08 (q, $^3J_{2,1}$ = 7.1 Hz, 2H, H-2), 7.18–7.24 (m, 3H, H-7, H-9), 7.28–7.33 (m, 2H, H-8)ppm.
^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (C-1), 21.9 (C-10), 36.6 (C-5), 43.1 (C-4), 60.3 (C-2), 126.4 (C-7)*, 126.8 (C-9)*, 128.5 (C-8), 145.8 (C-6), 172.5 (C-3) ppm.
HRMS (APCI) for $C_{12}H_{17}O_2^+$ [(M+H)$^+$] calculated: 193.1223, found: 193.1222.
The data is in accordance with literature.[22]

4.4.2 Ethyl 3-(naphthalen-2-yl)butanoate (9a)



9a
$C_{16}H_{18}O_2$
Mw = 242.32

Prepared according to **GP2** from ethyl (*E*)-3-(naphthalen-2-yl)but-2-enoate (**8a**, 60 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 50:1) yielded **9a** as a colorless oil (41.1 mg, 0.170 mmol, 68%).

R_f = 0.45 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

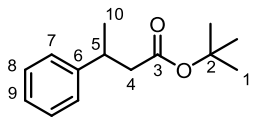
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.39 (d, $^3J_{16,5}$ = 6.9 Hz, 3H, H-16), 2.67 (m_c, 2H, H-4), 3.46 (m_c, 1H, H-5) 4.07 (m_c, 2H, H-2), 7.38 (dd, $^3J_{15,14}$ = 8.4 Hz, $^4J_{15,7}$ = 1.8 Hz, 1H, H-15), 7.44 (m_c, 2H, H-10/H-11)*, 7.65 (m_c, 1H, H-7), 7.77–7.82 (m, 3H, H-9/H-12/H-14)* ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (C-1), 21.9 (C-16), 36.7 (C-5), 43.0 (C-4), 60.4 (C-2), 125.0 (C-7), 125.4 (C-10)*, 125.6 (C-15), 126.0 (C-11)*, 127.6 (C-9)*, 127.7 (C-12)*, 128.2 (C-14)*, 132.4 (C-13), 133.6 (C-8), 143.3 (C-6), 172.4 (C-3) ppm.

HRMS (APCI) for $C_{16}H_{19}O_2^+$ [$(M+H)^+$] calculated: 243.1380, found: 243.1374.

The data is in accordance with literature.[23]

4.4.3 *tert*-Butyl 3-phenylbutanoate (9b)



9b
$C_{14}H_{20}O_2$
Mw = 220.31

Prepared according to **GP2** from tert-butyl (*E*)-3-phenylbut-2-enoate (**8b**, 55 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 50:1) yielded **9b** as a colorless oil (46 mg, 0.21 mmol, 84%).

R_f = 0.65 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

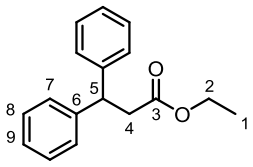
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.28 (d, $^3J_{10,5}$ = 7.0 Hz, 3H, H-10), 1.35 (s, 9H, H-1), 2.49 (m_c, 2H, H-4), 3.22 (m_c, 1H, H-5), 7.00–7.23 (m, 3H, H-7/H-9), 7.26–7.31 (m, 2H, H-8) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.0 (C-10), 28.1 (C-1), 36.9 (C-5), 44.3 (C-4), 80.3 (C-2), 126.3 (C-9), 126.9 (C-7), 128.4 (C-8), 146.0 (C-6), 171.8 (C-3) ppm.

HRMS (EI) for $C_{14}H_{20}O_2^{\bullet+}$ [$(M)^{\bullet+}$] calculated: 220.1457, found: 220.1467.

IR (ATR): $\tilde{\upsilon}$ = 2969 (w), 1724 (s), 1603 (w), 1452 (w), 1365 (m), 1255 (w), 1144 (s), 1082 (w), 1018 (m), 956 (m), 907 (w), 843 (m), 754 (m), 697 (s) cm^{-1}.

4.4.4 Ethyl 3,3-diphenylpropanoate (9c)



9c
$C_{17}H_{18}O_2$
Mw = 254.33

Prepared according to **GP2** from ethyl 3,3-diphenylacrylate (**8c**, 63 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 50:1) yielded **9c** as a colorless oil (50.1 mg, 0.197 mmol, 79%).

R_f = 0.45 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

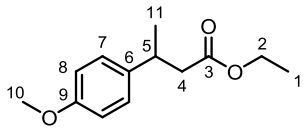
^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.11 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 3.04 (d, $^3J_{4,5}$ = 8.0 Hz, 2H, H-4), 4.01 (q, $^3J_{2,1}$ = 7.1 Hz, 2H, H-2), 4.52 (t, $^3J_{5,4}$ = 8.0 Hz, 1H, H-5), 7.16–7.21 (m, 2H, H-9), 7.22–7.31 (m, 8H, H-7/H-8) ppm.

^{13}C NMR (126 MHz, CD_2Cl_2): δ = 14.2 (C-1), 40.9 (C-4), 47.4 (C-5), 60.7 (C-2), 126.8 (C-9), 128.0 (C-7), 128.9 (C-8), 144.2 (C-6), 171.9 (C-3) ppm.

HRMS (APCI) for $C_{17}H_{19}O_2^+$ [$(M+H)^+$] calculated: 255.1380, found: 255.1374.

The data is in accordance with literature.[24]

4.4.5 Ethyl 3-(4-methoxyphenyl)butanoate (9d)



9d
$C_{13}H_{18}O_3$
Mw = 222.28

Prepared according to **GP2** from ethyl (*E*)-3-(4-methoxyphenyl)but-2-enoate (**8d**, 55 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 30:1) yielded **9d** as a colorless oil (42.4 mg, 0.191 mmol, 76%).

R_f = 0.30 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

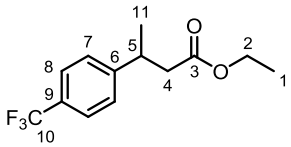
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.27 (d, $^3J_{11,5}$ = 7.0 Hz, 3H, H-11), 2.53 (m_c, 2H, H-4), 3.23 (m_c, 1H, H-5), 3.78 (s, 3H, H-10), 4.07 (m_c, 2H, H-2), 6.83 (m_c, 2H, H-8), 7.14 (m_c, 2H, H-7) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.3 (C-1), 22.1 (C-11), 35.8 (C-5), 43.3 (C-4), 55.3 (C-10), 60.3 (C-2), 113.9 (C-8), 127.7 (C-7), 138.0 (C-6), 158.2 (C-9), 172.5 (C-3) ppm.

HRMS (APCI) for $C_{13}H_{19}O_3^+$ [$(M+H)^+$] calculated: 223.1329, found: 223.1324.

The data is in accordance with literature.[25,26]

4.4.6 Ethyl 3-(4-(trifluoromethyl)phenyl)butanoate (9e)



9e
$C_{13}H_{15}F_3O_2$
Mw = 260.26

Prepared according to **GP2** from ethyl (*E*)-3-(4-(trifluoromethyl)phenyl)but-2-enoate (**8e**, 64 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 50:1) yielded **9e** as a colorless oil (41.4 mg, 0.159 mmol, 64%).

R_f = 0.45 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.17 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.31 (d, $^3J_{10,5}$ = 7.0 Hz, 3H, H-10), 2.59 (m_c, 2H, H-4), 3.34 (m_c, 1H, H-5), 4.07 (m_c, 2H, H-2), 7.33 (d, $^3J_{7,8}$ = 8.2 Hz, 2H, H-7), 7.41 (d, $^3J_{8,7}$ = 8.3 Hz, 2H, H-8) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (C-1), 21.8 (C-11), 36.5 (C-5), 42.6 (C-4), 60.5 (C-2), 124.4 (q, $^1J_{10,F}$ = 271.5 Hz, C-10), 125.5 (q, $^3J_{8,F}$ = 3.6 Hz, C-8), 127.3 (C-7), 128.8 (q, $^2J_{9,F}$ = 32.2 Hz, C-9), 149.8 (C-6), 172.0 (C-3) ppm.

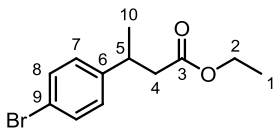
^{19}F NMR (659 MHz, $CDCl_3$): δ = –62.4 ppm.

HRMS (APCI) for $C_{13}H_{16}F_3O_2^+$ [$(M+H)^+$] calculated: 261.1097, found: 261.1090.

IR (ATR): $\tilde{\upsilon}$ = 2970 (w), 1731 (s), 1618 (m), 1457 (w), 1419 (w), 1371 (w), 1322 (s), 1268 (w), 1160 (s), 1112 (s), 1066 (s), 1015 (m), 953 (w), 838 (s), 712 (w) cm^{-1}.

The ^{1}H and ^{13}C NMR data is in accordance with literature.[27]

4.4.7 Ethyl 3-(4-bromophenyl)butanoate (9f)



9f
$C_{12}H_{15}BrO_2$
Mw = 271.15

Prepared according to **GP2** from ethyl (*E*)-3-(4-bromophenyl)but-2-enoate (**8f**, 67 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 50:1) yielded **9f** as a colorless oil (57.9 mg, 0.214 mmol, 85%).

R_f = 0.48 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.27 (d, $^3J_{10,5}$ = 6.9 Hz, 3H, H-10), 2.54 (m_c, 2H, H-4), 3.24 (m_c, 1H, H-5), 4.07 (m_c, 2H, H-2), 7.09 (m_c, 2H, H-7), 7.41 (m_c, 2H, H-8) ppm.

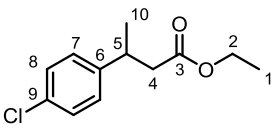
^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (C-1), 21.9 (C-10), 36.1 (C-5), 42.8 (C-4), 60.4 (C-2), 120.1 (C-9), 128.7 (C-7), 131.6 (C-8), 144.8 (C-6), 172.1 (C-3) ppm.

HRMS (APCI) for $C_{12}H_{16}{}^{79}BrO_2^+$ [(M+H)$^+$] calculated: 271.0328, found: 271.0323.

IR (ATR): $\tilde{\upsilon}$ = 2966 (w), 1729 (s), 1488 (m), 1455 (w), 1406 (w), 1369 (m), 1260 (m), 1160 (s), 1071 (m), 1031 (m), 949 (w), 821 (s), 762 (w), 716 (w) cm^{-1}.

The ^{1}H and ^{13}C NMR data is in accordance with literature.[28]

4.4.8 Ethyl 3-(4-chlorophenyl)butanoate (9g)



9g
$C_{12}H_{15}ClO_2$
Mw = 226.70

Prepared according to **GP2** from ethyl (*E*)-3-(4-chlorophenyl)but-2-enoate (**8g**, 56 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 50:1) yielded **9g** as a colorless oil (37 mg, 0.16 mmol, 65%).

R$_f$ = 0.52 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

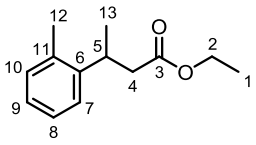
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.17 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.27 (d, $^3J_{10,5}$ = 7.0 Hz, 3H, H-10), 2.54 (m$_c$, 2H, H-4), 3.25 (m$_c$, 1H, H-5), 4.06 (m$_c$, 2H, H-2), 7.15 (m$_c$, 2H, H-7), 7.25 (m$_c$, 2H, H-8) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (C-1), 21.9 (C-10), 36.0 (C-5), 42.9 (C-4), 60.4 (C-2), 128.3 (C-7), 128.7 (C-8), 132.1 (C-9), 144.3 (C-6), 172.2 (C-3) ppm.

HRMS (APCI) for $C_{12}H_{16}{}^{35}ClO_2^+$ [(M+H)$^+$] calculated: 227.0833, found: 227.0828.

IR (ATR): $\tilde{\upsilon}$ = 2965 (w), 2115 (w), 1729 (s), 1492 (m), 1457 (w), 1410 (w), 1369 (m), 1259 (m), 1161 (s), 1093 (s), 1032 (s), 950 (w), 825 (s), 732 (w) cm^{-1}.

4.4.9 Ethyl 3-(*o*-tolyl)butanoate (9h)



9h
$C_{13}H_{18}O_2$
Mw = 206.28

Prepared according to **GP2** from ethyl (*E*)-3-(*o*-tolyl)but-2-enoate (**8h**, 51 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 10.2 mg, 25.0 µmol, 10.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 50:1) yielded **9h** as a colorless oil (90% conversion, 28.6 mg, 0.138 mmol, 55%).

R$_f$ = 0.60 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

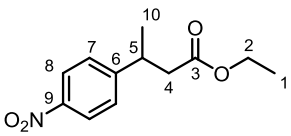
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{1,2}$ = 6.9 Hz, 3H, H-1), 1.25 (d, $^3J_{13,4}$ = 6.9 Hz, 3H, H-13), 2.37 (s, 3H, H-12), 2.57 (m$_c$, 2H, H-4), 3.53 (m$_c$, 1H, H-5), 4.08 (q, $^3J_{2,1}$ = 7.1 Hz, 2H, H-2), 7.06–7.21 (m, 4H, H-7/H-8/H-9/H-10) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (C-1), 19.5 (C-12), 21.4 (C-13), 31.6 (C-5), 42.3 (C-4), 60.3 (C-2), 125.1 (C-7), 126.1 (C-8)*, 126.3 (C-9)*, 130.5 (C-10), 135.4 (C-11), 144.0 (C-6), 172.6 (C-3) ppm.

HRMS (APCI) for $C_{13}H_{19}O_2^+$ [$(M+H)^+$] calculated: 207.1380, found: 207.1379.

The data is in accordance with literature.[26]

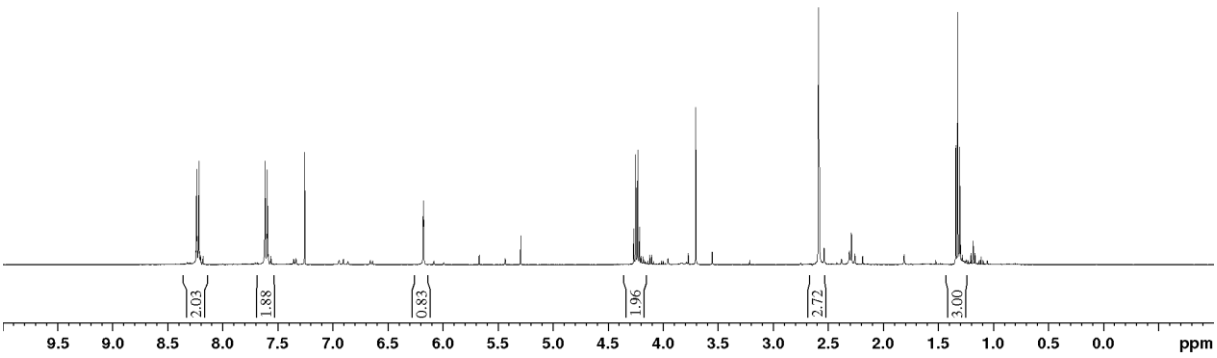
4.4.10 Ethyl 3-(4-nitrophenyl)butanoate (9i)



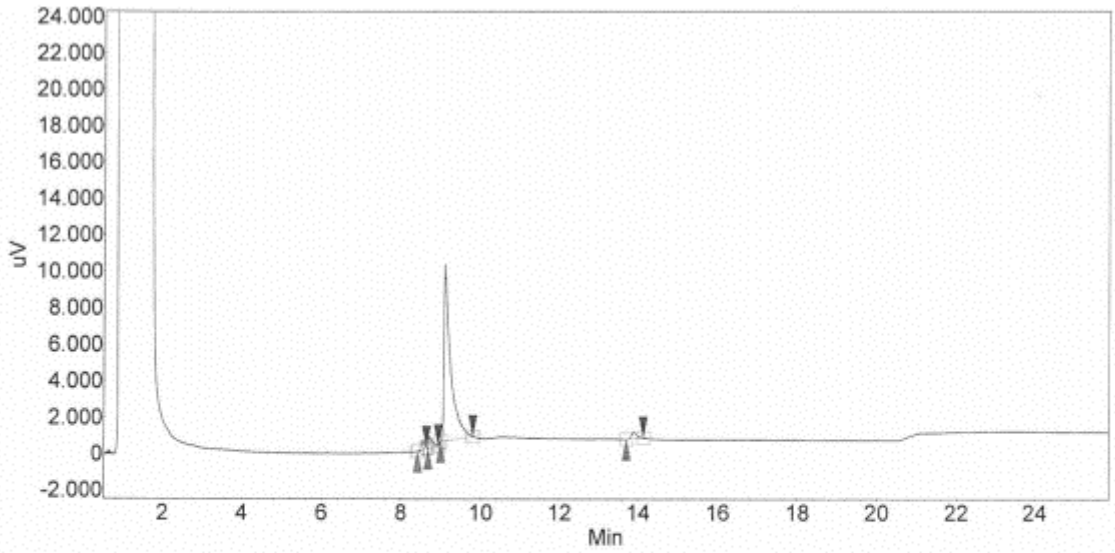
9i
$C_{12}H_{15}NO_4$
Mw = 237.25

Prepared according to **GP2** from ethyl (*E*)-3-(4-nitrophenyl)but-2-enoate (**8i**, 58 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. No conversion could be observed in ^{1}H NMR, GC and GC-MS.

Crude ^{1}H NMR of conjugate reduction of 8i



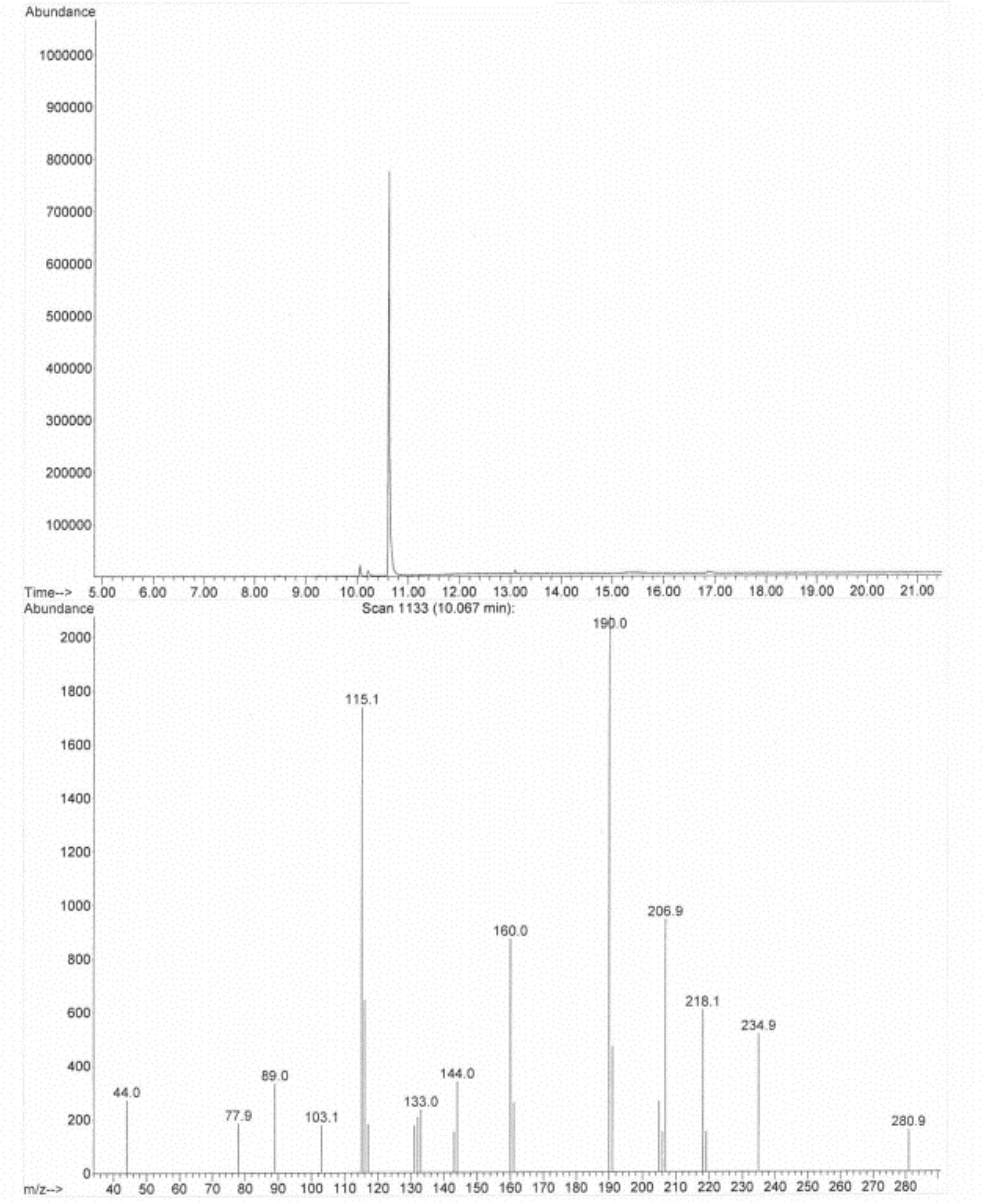
GC of conjugate reduction of 8i

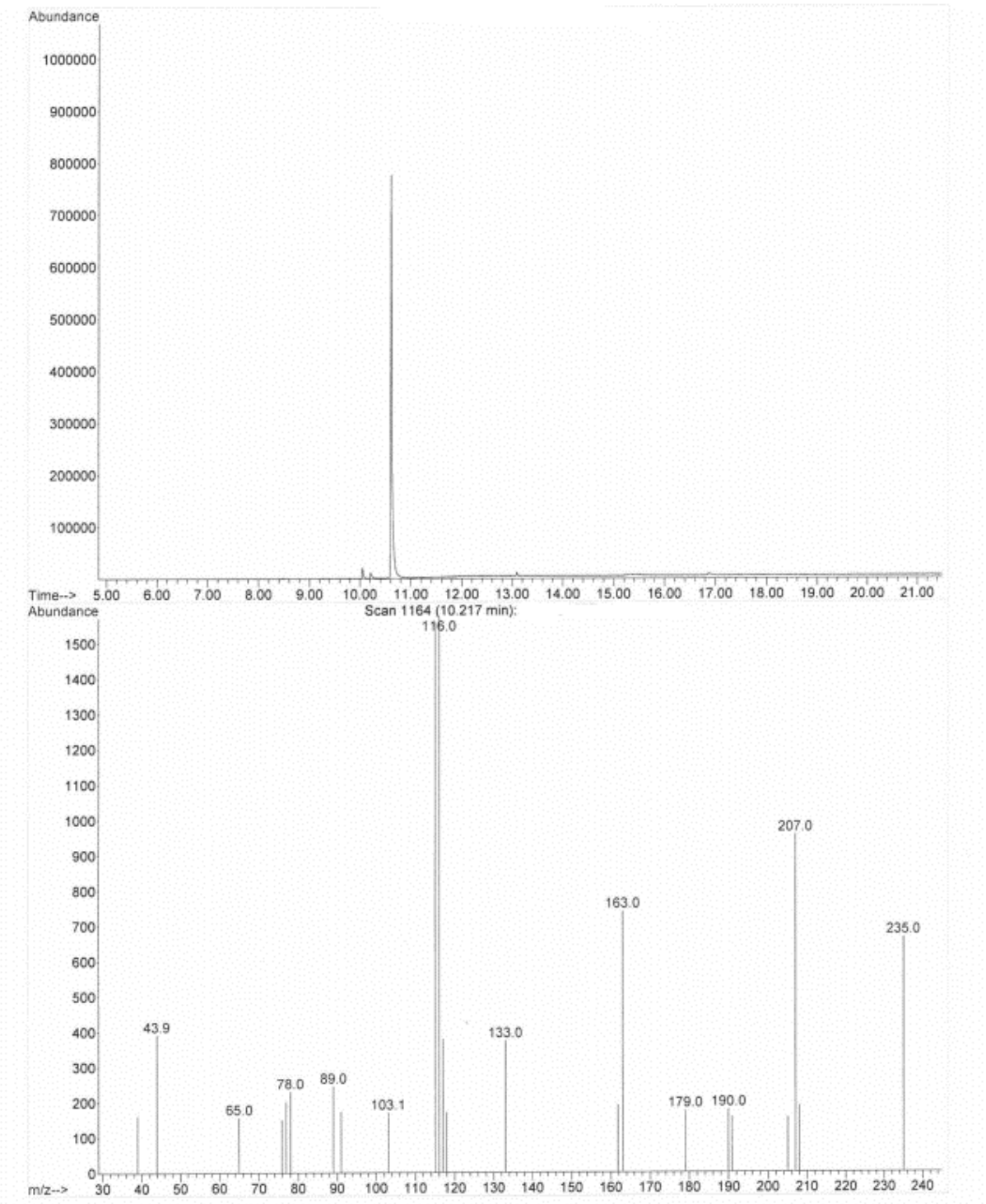


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	8.55	1.41	501.9	27.9	1.414
2	UNKNOWN	8.72	3.43	603.6	67.6	3.429
3	UNKNOWN	9.09	92.05	9660.2	1814.8	92.054
4	UNKNOWN	13.88	3.10	368.0	61.2	3.104
Total			100.00	11133.7	1971.5	100.000

GC/ MS of conjugate reduction of 8i




Abundance
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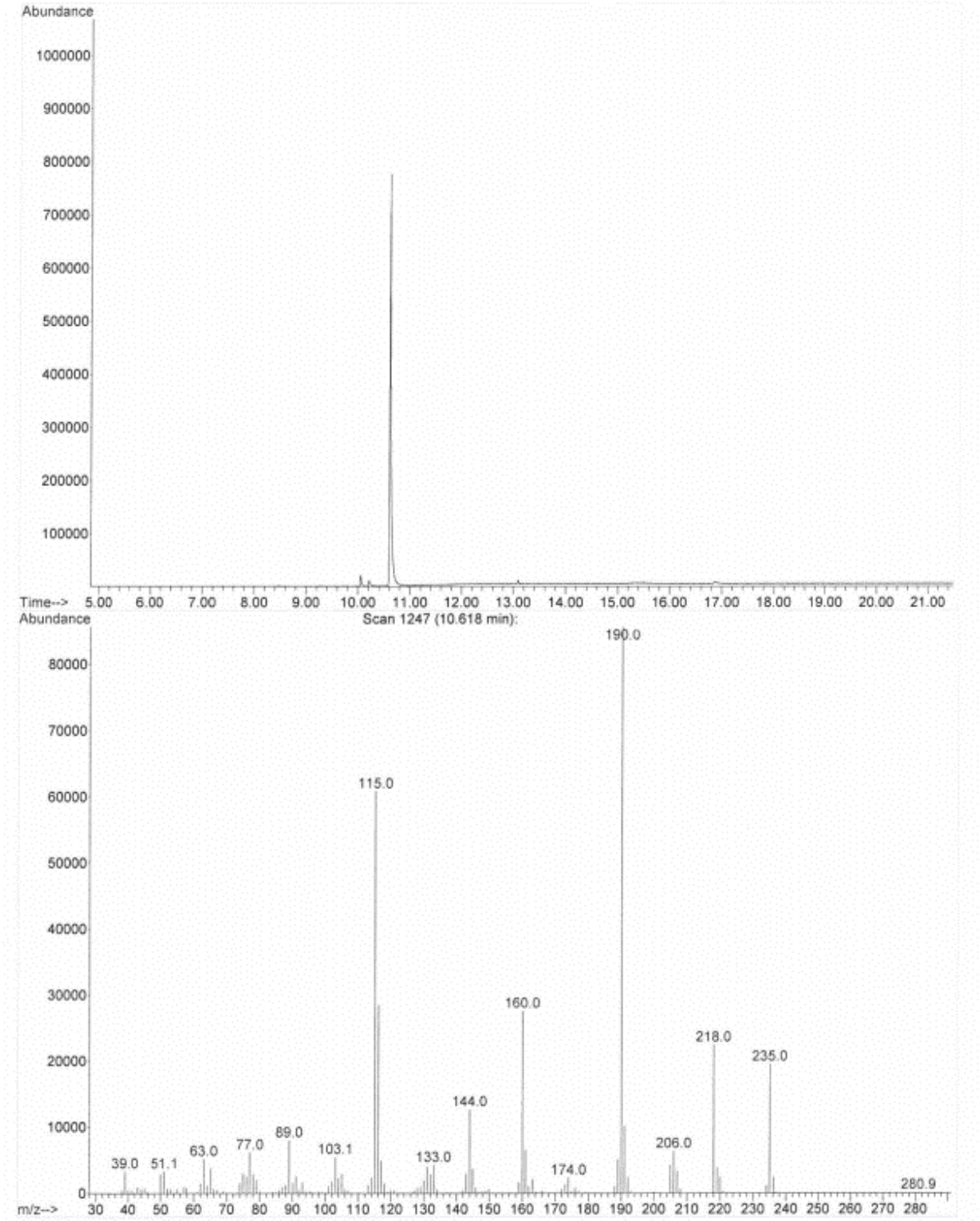
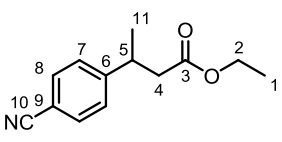
800000
700000
600000
500000
400000
300000
200000
100000
Time--> 5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00
Abundance
Scan 1164 (10.217 min):
116.0
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
207.0
163.0
235.0
43.9
133.0
78.0
89.0
65.0
103.1
179.0
190.0
m/z--> 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240



4.4.11 Ethyl 3-(4-cyanophenyl)butanoate (9j)



9j
$C_{13}H_{15}NO_2$
Mw = 217.26

Prepared according to **GP2** from ethyl (*E*)-3-(4-cyanophenyl)but-2-enoate (**8j**, 54 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-

pentane/*tert*-butyl methyl ether = 15:1) yielded **9j** as a colorless oil (9.8 mg, 45 µmol, 5%).

R_f = 0.30 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 4:1).

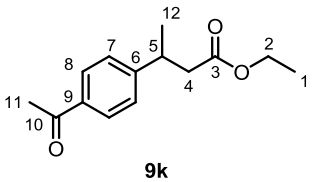
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.17 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.30 (d, $^3J_{11,5}$ = 7.0 Hz, 3H, H-11), 2.58 (m_c, 2H, H-4), 3.33 (m_c, 1H, H-5), 4.06 (m_c, 2H, H-2), 7.33 (m_c, 2H, H-7), 7.59 (m_c, 2H, H-8) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (C-1), 21.7 (C-11), 36.7 (C-5), 42.4 (C-4), 60.6 (C-2), 110.5 (C-9), 119.0 (C-10), 127.8 (C-7), 132.5 (C-8), 151.3 (C-6), 171.8 (C-3) ppm.

HRMS (APCI) for $C_{13}H_{15}NO_2^+$ [$(M+H)^+$] calculated: 218.1176, found: 218.1182.

IR (ATR): $\tilde{\nu}$ = 2972 (w), 2227 (m), 1732 (s), 1608 (w), 1505 (w), 1457 (w), 1416 (w), 1371 (w), 1266 (w), 1174 (m), 1116 (w), 1033 (w), 838 (w) cm^{-1}.

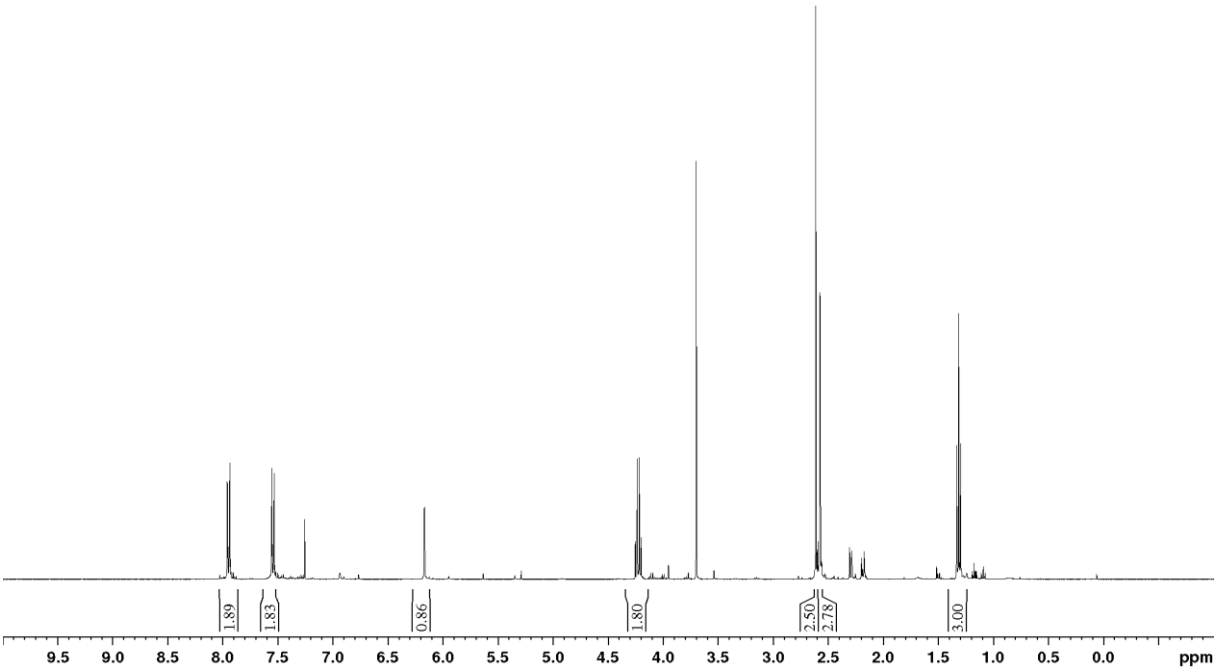
4.4.12 Ethyl 3-(4-acetylphenyl)butanoate (9k)



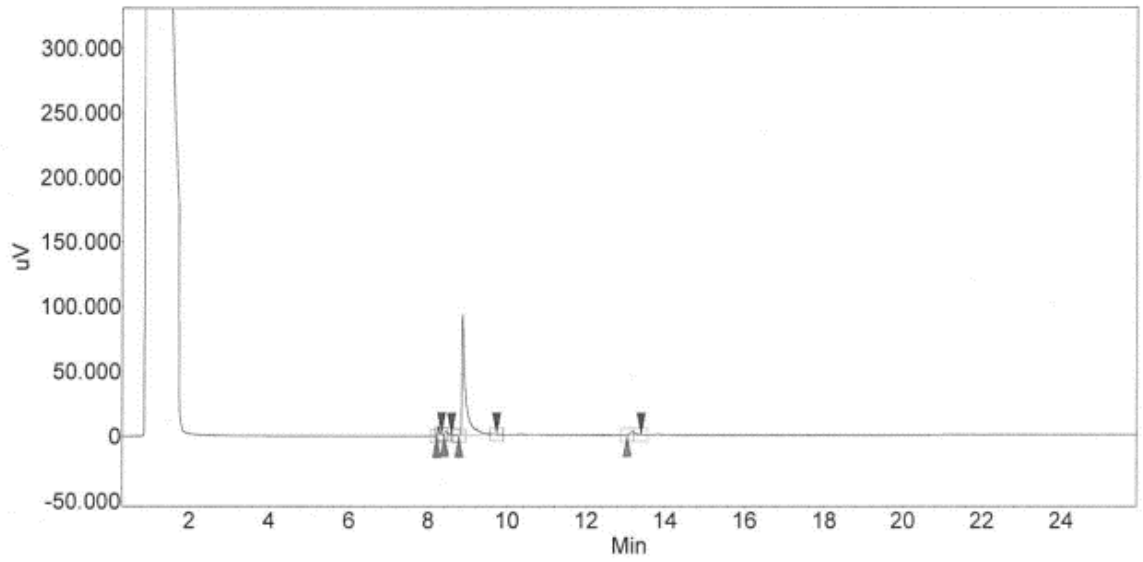
9k
$C_{14}H_{18}O_3$
Mw = 234.29

Prepared according to **GP2** from ethyl (*E*)-3-(4-acetylphenyl)but-2-enoate (**8k**, 58 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. No conversion could be observed in ^{1}H NMR, GC and GC-MS.

Crude ^{1}H NMR of conjugate reduction of 8k



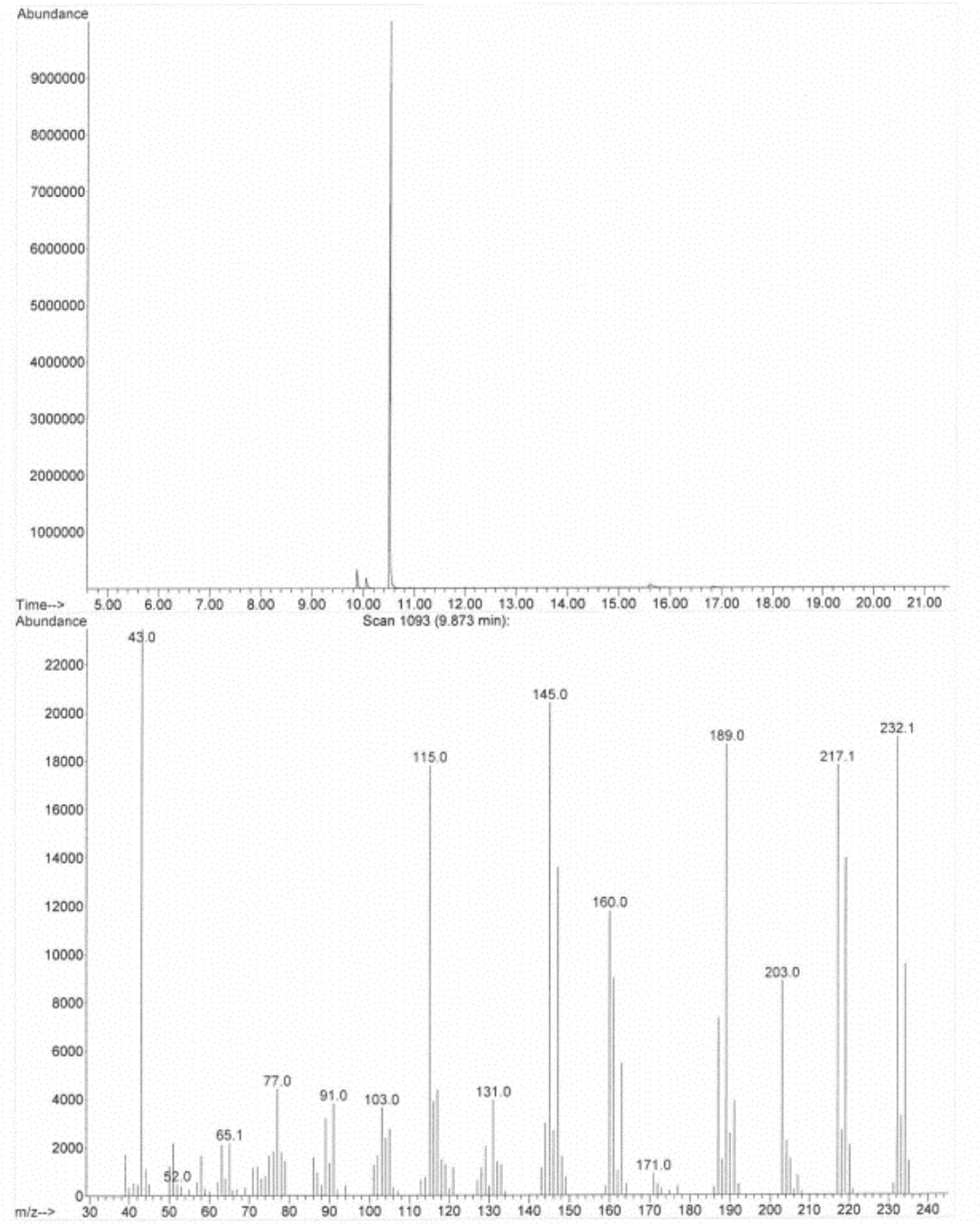
GC of conjugate reduction of 8k

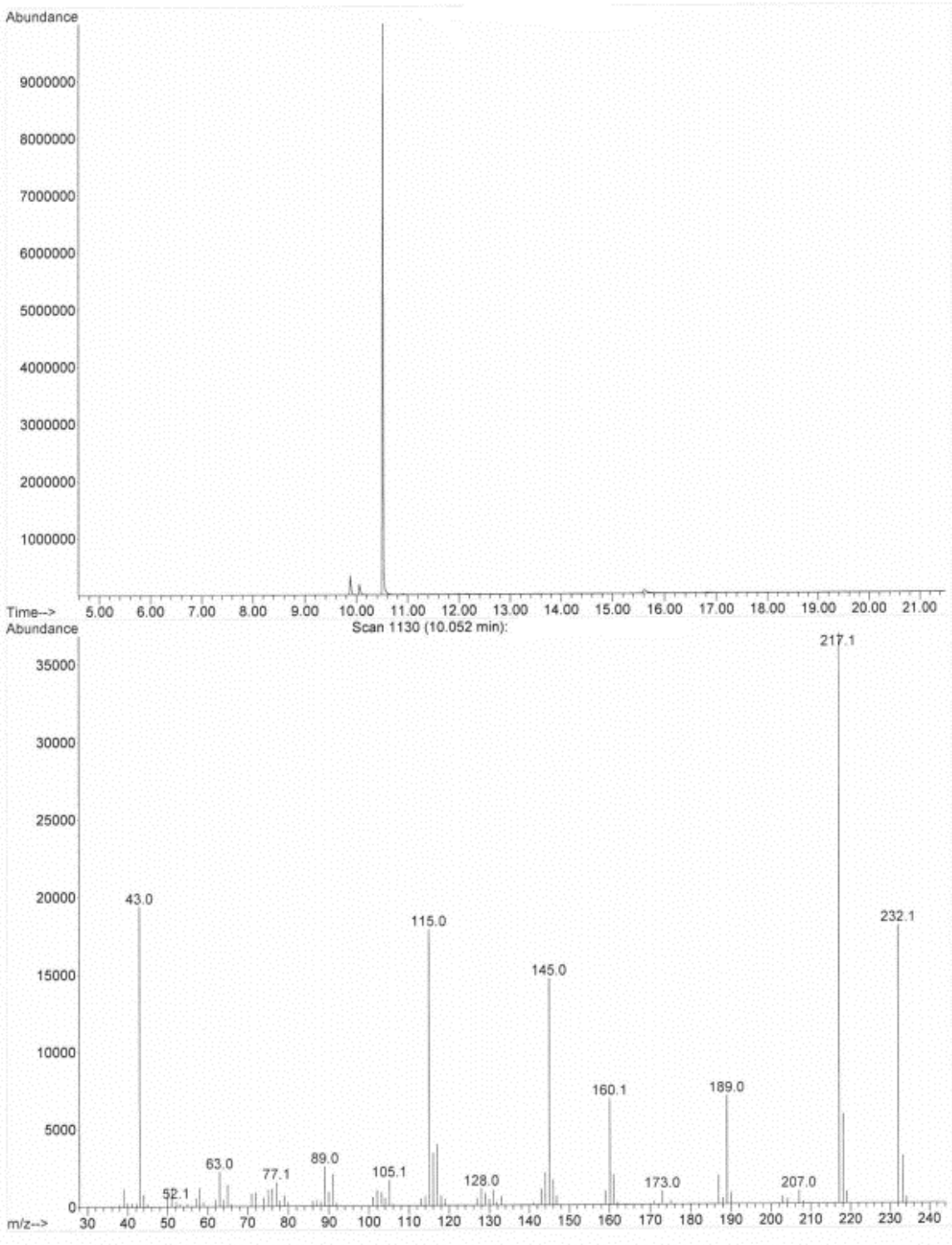


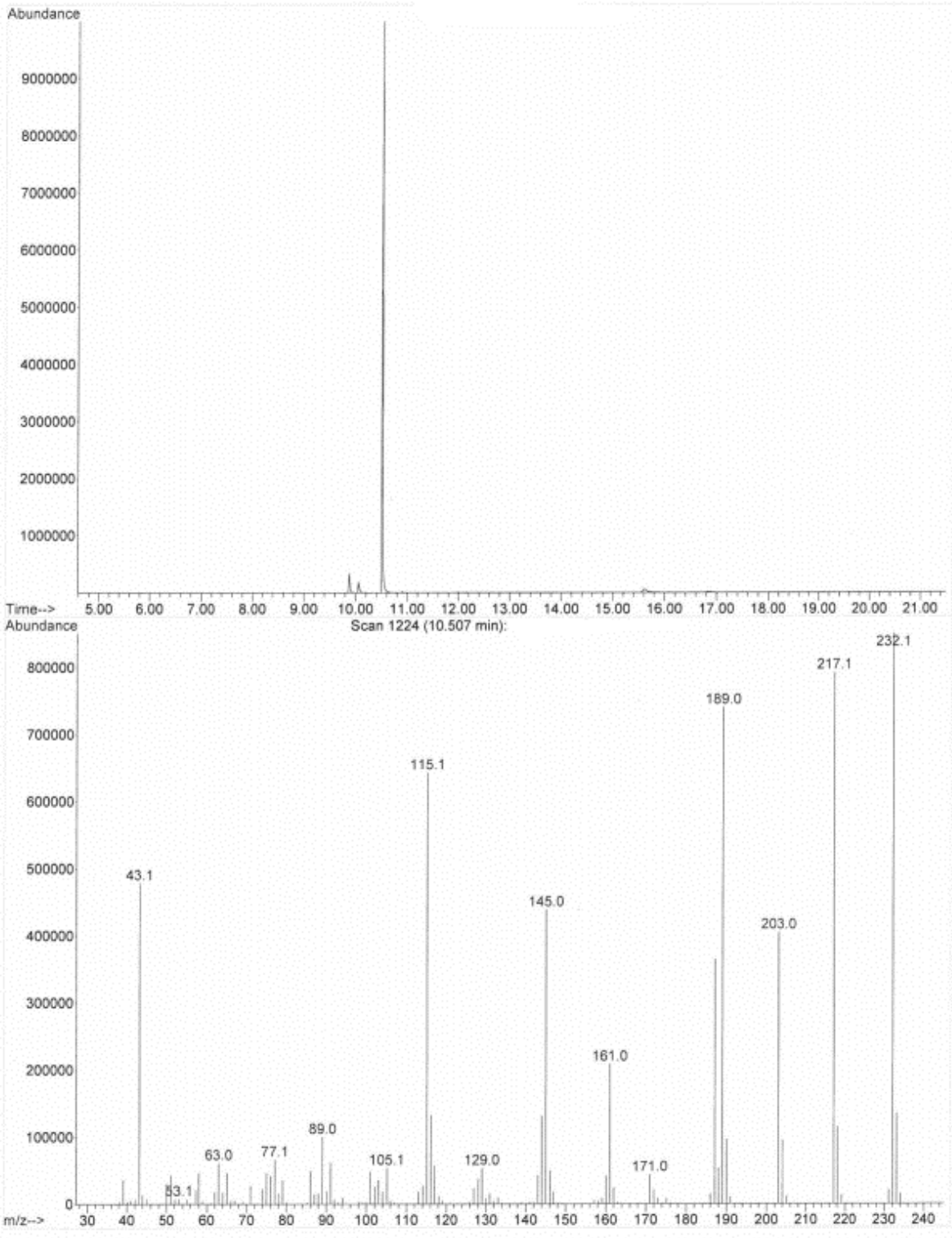
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
4	UNKNOWN	8,25	3,52	7526,1	391,2	3,524
3	UNKNOWN	8,44	2,05	3136,5	227,9	2,053
2	UNKNOWN	8,87	90,95	92915,4	10097,6	90,953
1	UNKNOWN	13,16	3,47	2677,6	385,3	3,470
Total			100,00	106255,6	11101,9	100,000

GC/MS data of conjugate reduction of 8k




Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00
Abundance
Scan 1130 (10.052 min):
35000
30000
25000
20000
15000
10000
5000
0
m/z-->
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240
43.0
52.1
63.0
77.1
89.0
105.1
115.0
128.0
145.0
160.1
173.0
189.0
207.0
217.1
232.1


Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00
Abundance
Scan 1224 (10.507 min):
800000
700000
600000
500000
400000
300000
200000
100000
0
m/z-->
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240
232.1
217.1
189.0
115.1
43.1
145.0
203.0
161.0
89.0
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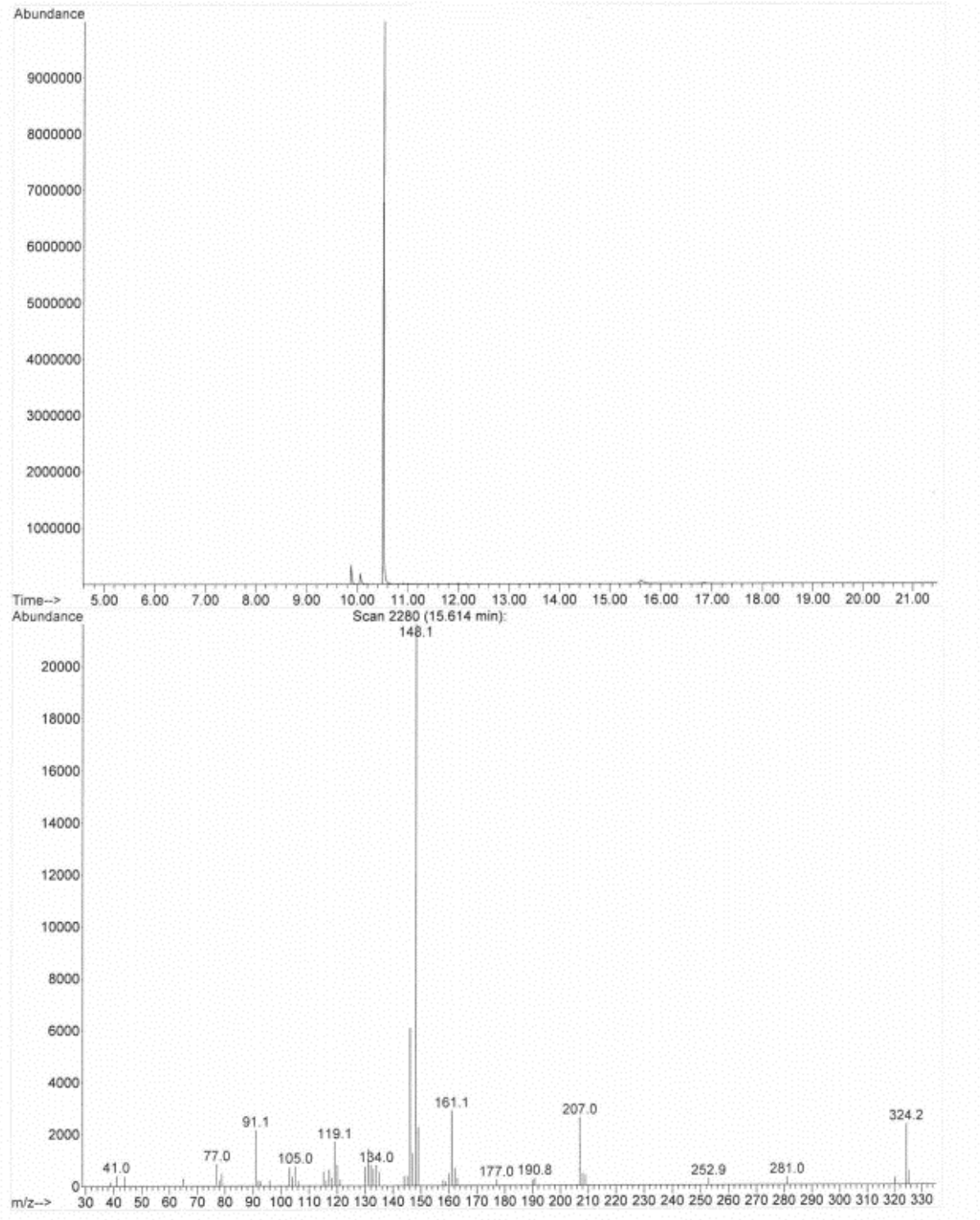
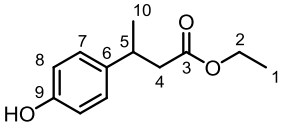
77.1
105.1
129.0
171.0
53.1



4.4.13 Ethyl 3-(4-hydroxyphenyl)butanoate (9l)



9l
$C_{12}H_{16}O_3$
Mw = 208.25

Prepared according to **GP2** from ethyl (*E*)-3-(4-hydroxyphenyl)but-2-enoate (**8l**, 45 mg, 0.22 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 6.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 34 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-

pentane/*tert*-butyl methyl ether = 10:1) yielded **9l** as a colorless oil (conv. 81%, 21.3 mg, 0.102 mmol, 47%).

R_f = 0.44 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.26 (d, $^3J_{11,5}$ = 6.9 Hz, 3H, H-11), 2.53 (m_c, 2H, H-4), 3.22 (m_c, 1H, H-5), 4.07 (m_c, 2H, H-2), 4.82 (s, 1H,O*H*), 6.74 (m_c, 2H, H-8), 7.08 (m_c, 2H, H-7) ppm.

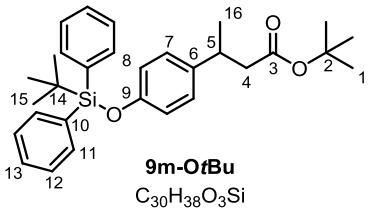
The ^{1}H NMR spectra still contains 9% of the starting material.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.3 (C-1), 22.1 (C-10), 35.9 (C-5), 43.4 (C-4), 60.4 (C-2), 115.3 (C-8), 128.0 (C-7), 138.0 (C-6), 154.1 (C-9), 172.7 (C-3) ppm.

HRMS (APCI) for $C_{12}H_{17}O_3^+$ [$(M+H)^+$] calculated: 209.1172, found: 209.1169.

IR (ATR): $\tilde{\upsilon}$ = 3349 (m), 2965 (w), 1704 (s), 1613 (m), 1515 (s), 1444 (m), 1371 (m), 1266 (m), 1219 (m), 1174 (m), 1109 (w), 1032 (m), 833 (s) cm^{-1}.

4.4.14 Ethyl 3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)butanoate (9m-OEt) and *tert*-butyl 3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)butanoate (9m-O*t*Bu)

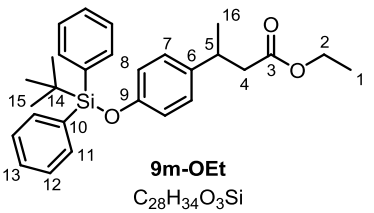


9m-O*t*Bu
$C_{30}H_{38}O_3Si$
Mw = 474.72

Prepared according to **GP2** from diethyl ethyl (*E*)-3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)but-2-enoate (104 mg, 0.250 mmol, 1.00 equiv), [SIMesCuCl] (**6**, 10.2 mg, 25.0 µmol, 10.0 mol%) and NaO*t*Bu (14 mg, 0.15 mmol, 60 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. A crude reaction mixture of the product **9m-OEt** and *tert*-butyl 3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)butanoate (**9m-O*t*Bu**) as a side product (**9m-OEt/9m-O*t*Bu** = 83:17) was obtained. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 100:1) yielded **9m-OEt** as a colorless oil (44.9 mg, 0.101 mmol, 40%) and **9m-O*t*Bu** as a colorless oil (8.6 mg, 0.018 mmol, 7%).

Ethyl 3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)butanoate (9m-OEt):

R_f = 0.37 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).



9m-OEt
$C_{28}H_{34}O_3Si$
Mw = 446.66

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.08 (s, 9H, H-15), 1.39 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.21 (d, $^3J_{16,5}$ = 6.9 Hz, 3H, H-16), 2.46 (m_c, 2H, H-4), 3.14 (m_c, 1H, H-5), 4.03 (q, $^3J_{2,1}$ = 7.1 Hz, 2H, H-2), 6.68 (m_c, 2H, H-8), 6.92 (m_c, 2H, H-7), 7.32–7.37 (m, 4H, H-12), 7.39–7.43 (m, 2H, H-13), 7.67–7.73 (m, 4H, H-11) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.3 (C-1), 19.6 (C-14), 21.9 (C-16), 26.6 (C-15), 35.9 (C-5), 43.4 (C-4), 60.2 (C-2), 119.6 (C-8), 127.5 (C-7). 127.8 (C-12), 129.9 (C-13), 133.2 (C-10), 135.6 (C-11), 138.3 (C-6), 154.0 (C-9), 172.6 (C-3) ppm.

^{29}SI DEPT NMR (99MHz, *J* = 20 Hz, $CDCl_3$): δ = –6.6 ppm.

HRMS (APCI) for $C_{18}H_{27}O_4^+$ [$(M+H)^+$] calculated: 447.2350, found: 447.2343.

IR (ATR): $\tilde{\nu}$ = 2930 (m), 2856 (w), 1731 (s), 1606 (m), 1509 (s), 1471 (w), 1427 (m), 1367 (w), 1252 (s), 1160 (m), 1107 (s), 1032 (w), 916 (s), 832 (m), 779 (w), 740 (m), 698 (s) cm^{-1}.

***tert*-Butyl 3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)butanoate (9m-O*t*Bu):**

R_f = 0.47 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.08 (s, 9H, H-15), 1.19 (d, $^3J_{16,5}$ = 7.0 Hz, 3H, H-16), 1.31 (s, 9H, H-1), 2.38 (m_c, 2H, H-4), 3.09 (m_c, 1H, H-5), 6.68 (m_c, 2H, H-8), 6.93 (m_c, 2H, H-7), 7.32–7.38 (m, 4H, H-12), 7.38–7.44 (m, 2H, H-13), 7.69–7.72 (m, 4H, H-11) ppm.

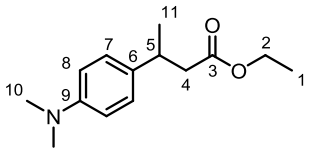
^{13}C NMR (126 MHz, $CDCl_3$): δ = 19.6 (C-14), 22.1 (C-16), 26.6 (C-15), 28.1 (C-1), 36.1 (C-5), 44.5 (C-4), 80.1 (C-2), 119.5 (C-8), 127.6 (C-7), 127.8 (C-12), 129.9 (C-13), 133.2 (C-10), 135.6 (C-11), 138.4 (C-6), 154.0 (C-9), 171.9 (C-1) ppm.

^{29}SI DEPT NMR (99MHz, *J* = 20 Hz, $CDCl_3$): δ = –6.7 ppm.

HRMS (APCI) for $C_{20}H_{25}O_3^+$ [$(M+H–Ph–t\text{Bu})^+$] calculated: 341.1567, found: 341.1569.

IR (ATR): $\tilde{\nu}$ 2960 (m), 2857 (w), 1727 (s), 1607 (w), 1509 (s), 1472 (w), 1427 (w), 1365 (w), 1255 (s), 1148 (m), 1110 (m), 1011 (w), 920 (m), 834 (m), 779 (w), 741 (w), 701 (s) cm^{-1}.

4.4.15 Ethyl 3-(4-(dimethylamino)phenyl)butanoate (9n)



9n
$C_{14}H_{21}NO_2$
Mw = 235.32

Prepared according to **GP2** from ethyl (*1*)-3-(4-(dimethylamino)phenyl)but-2-enoate (**8n**, 61 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 50:1) yielded **9n** as a colorless oil (38.1 mg, 0.162 mmol, 65%).

R_f = 0.16 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

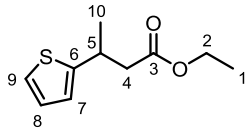
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.20 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.26 (d, $^3J_{11,5}$ = 6.9 Hz, 2H, H-11), 2.52 (m_c, 2H, H-4), 2.91 (s, 6H, H-10), 3.19 (m_c, 1H, H-5), 4.08 (m_c, 2H, H-2), 6.69 (m_c, 2H, H-8), 7.10 (m_c, 2H, H-7) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.3 (C-1), 22.0 (C-11), 35.6 (C-5), 40.9 (C-10), 43.5 (C-4), 60.2 (C-2), 113.0 (C-8), 127.4 (C-7), 134.0 (C-6), 149.4 (C-9), 172.8 (C-3) ppm.

HRMS (APCI) for $C_{14}H_{22}NO_2^+$ [$(M+H)^+$] calculated: 236.1645, found: 236.1640.

The data is in accordance with literature.[6]

4.4.16 Ethyl 3-(thiophen-2-yl)butanoate (9o)



9o
$C_{10}H_{14}O_2S$
Mw = 198.28

Prepared according to **GP2** from ethyl (*E*)-3-(thiophen-2-yl)but-2-enoate (**8o**, 49 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 30:1) yielded **9o** as a colorless oil (38.8 mg, 0.196 mmol, 78%).

R_f = 0.55 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.22 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.38 (d, $^3J_{10,5}$ = 6.9 Hz, 3H, H-10), 2.61 (m_c, 2H, H-4), 3.59 (m_c, 1H, H-5), 4.12 (q, $^3J_{2,1}$ = 7.1 Hz, 2H, H-2), 6.83 (m_c, 1H, H-7), 6.91 (dd, $^3J_{8,7}$ = 5.1 Hz, $^3J_{8,9}$ = 5.1 Hz, 1H, H-8), 7.13 (dd, $^3J_{9,8}$ = 5.1 Hz, $^4J_{9,7}$ = 1.1 Hz, 1H, H-9) ppm.

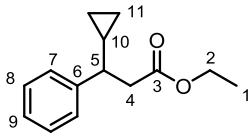
^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.3 (C-1), 22.7 (C-10), 32.1 (C-5), 44.0 (C-4), 60.5 (C-2), 123.0 (C-7), 123.0 (C-8), 126.7 (C-9), 149.8 (C-6), 172.0 (C-3) ppm.

HRMS (APCI) for $C_{10}H_{15}O_2S^+$ [$(M+H)^+$] calculated: 199.0787, found: 199.0782.

IR (ATR): $\tilde{\nu}$ = 2971 (w), 1729 (s), 1456 (w), 1369 (m), 1344 (w), 1280 (m), 1248 (m), 1160 (m), 1071 (w), 1028 (m), 947 (w), 848 (m), 691 (s) cm^{-1}.

The ^{1}H NMR data is in accordance with literature.[29]

4.4.17 Ethyl 3-cyclopropyl-3-phenylpropanoate (9p)



9p
$C_{14}H_{18}O_2$
Mw = 218.30

Prepared according to **GP2** from ethyl (*E*)-3-cyclopropyl-3-phenylacrylate (**8p**, 54 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 50:1) yielded **9p** as a colorless oil (52.0 mg, 0.238 mmol, 95%).

R_f = 0.52 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.14 (m_c, 1H, H-11_α)*, 0.27 (m_c, 1H, H-$11'_\alpha$)*, 0.41 (m_c, 1H, H-11_β)*, 0.57 (m_c, 1H, H-$11'_\beta$), 1.03 (m_c, 1H, H-10), 1.15 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 2.37 (m_c,

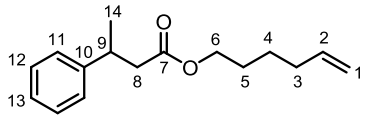
1H, H-5), 2.73 (m_c, 2H, H-4), 4.04 (m_c, 2H, H-2), 7.18–7.25 (m, 3H, H-7/H-9), 7.26–7.32 (m, 2H, H-8) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 4.1 (C-11)*, 5.4 (C-11')*, 14.2 (C-1), 17.2 (C-10), 41.9 (C-4), 47.3 (C-5), 60.3 (C-2), 126.5 (C-9), 127.4 (C-7), 128.4 (C-8), 144.2 (C-6), 172.5 (C-3) ppm.

HRMS (APCI) for $C_{14}H_{19}O_2^+$ [$(M+H)^+$] calculated: 219.1380, found: 219.1372.

The data is in accordance with literature.[30]

4.4.18 Hex-5-en-1-yl 3-phenylbutanoate (9q)



9q
$C_{16}H_{22}O_2$
Mw = 246.35

Prepared according to **GP2** from hex-5-en-1-yl (*E*)-3-phenylbut-2-enoate (**8q**, 61 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 50:1) yielded **9q** as a colorless oil (40.9 mg, 0.166 mmol, 66%).

R_f = 0.53 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

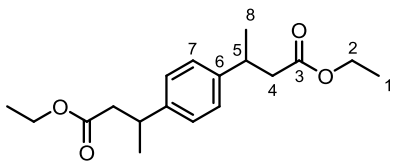
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.17 (d, $^3J_{14,9}$ = 7.0 Hz, 3H, H-14), 1.19–1.27 (m, 2H, H-4), 1.38–1.46 (m, 2H, H-5), 1.90 (m_c, 2H, H-3), 2.45 (m_c, 2H, H-8), 3.14 (m_c, 1H, H-9), 3.88 (d, $^3J_{6,5}$ = 6.6 Hz, 2H, H-6), 4.82 (m_c, 1H, H-1*Z*), 4.86 (m_c, 1H, H-1*E*), 5.63 (m_c, 1H, H-2), 7.03–7.11 (m, 3H,H-11/H-13), 7.13–7.19 (m, 2H, H-12) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 22.0 (C-14), 25.7 (C-4), 28.1 (C-5), 33.3 (C-3), 36.7 (C-9), 43.1 (C-8), 64.3 (C-6), 114.9 (C-1), 126.5 (C-13), 126.8 (C-11), 128.6 (C-12), 138.4 (C-2), 145.8 (C-10), 172.6 (C-3) ppm.

HRMS (APCI) for $C_{16}H_{13}O_2^+$ [$(M+H)^+$] calculated: 247.1693, found: 247.1690.

IR (ATR): $\tilde{\upsilon}$ = 2930 (w), 1730 (s), 1639 (w), 1602 (w), 1452 (w), 1265 (m), 1162 (m), 1082 (m), 993 (m), 909 (m), 760 (m), 698 (s) cm^{-1}.

4.4.19 Diethyl 3,3'-(1,4-phenylene)dibutyrate (9r)



9r
$C_{18}H_{26}O_4$
Mw = 306.40

Prepared according to **GP2** from diethyl 3,3'-(1,4-phenylene)(2*E*,2'*E*)-bis(but-2-enoate) (**8k**, 76 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 10.2 mg, 25.0 µmol, 10.0 mol%) and NaO*t*Bu (14 mg, 0.15 mmol, 60 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 25:2) yielded **9r** as a colorless oil (47.9 mg, 0.156 mmol, 62%).

$\mathbf{R_f}$ = 0.31 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

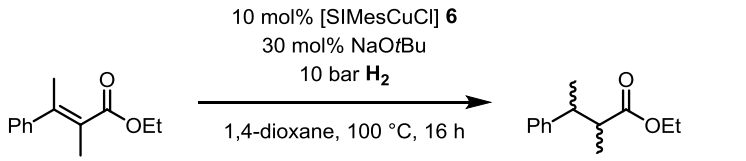
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.17 (t, $^3J_{1,2}$ = 7.1 Hz, 6H, H-1), 1.27 (d, $^3J_{8,4}$ = 6.9 Hz, 6H, H-8), 2.54 (m_c, 4H, H-4), 3.24 (m_c, 2H, H-5), 4.07 (q, $^3J_{2,1}$ = 7.1 Hz, 4H, H-2), 7.14 (s, 4H, H-7) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.3 (C-1), 21.8 (C-8), 36.2 (C-5), 43.1 (C-4), 60.3 (C-2), 126.9 (C-7), 143.8 (C-6), 172.5 (C-3) ppm.

HRMS (APCI) for $C_{18}H_{27}O_4^+$ [$(M+H)^+$] calculated: 307.1904, found: 307.1903.

IR (ATR): $\tilde{\upsilon}$ = 2964 (w), 1729 (s), 1510 (w), 1456 (w), 1369 (m), 1264 (m), 1158 (s), 1095 (w), 1032 (s), 949 (w), 831 (m), 721 (w) cm^{-1}.

4.4.20 Ethyl 2-methyl-3-phenylbutanoate (9s)

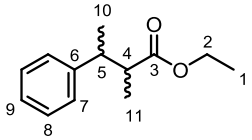


8s
66% conversion

9s
mixture of two diastereomers
59:41

Prepared according to **GP2** from ethyl (*E*)-2-methyl-3-phenylbut-2-enoate (**8s**, 51 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 10.2 mg, 25.0 µmol, 10.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/Et_2O = 50:1) yielded **9** as a colorless oil (66% conversion, 37 mg combined yield of ***E*-8s**, ***Z*-8s**, ***syn*-9s** and ***anti*-9s**).

$\mathbf{R_f}$ = 0.59 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).



9s
$C_{13}H_{18}O_2$
Mw = 206.28

Major diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (d, $^3J_{11,4}$ = 6.9 Hz, 3H, H-11), 1.23–1.27 (m, 2H, H-10), 1.28 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 2.57 (m_c, 1H, H-4), 2.89 (m_c, 1H, H-5), 4.18 (m_c, 2H, H-2), 7.11–7.23 (m, 3H, H-7/H-9)*, 7.26–7.41 (m, 2H, H-8)* ppm.

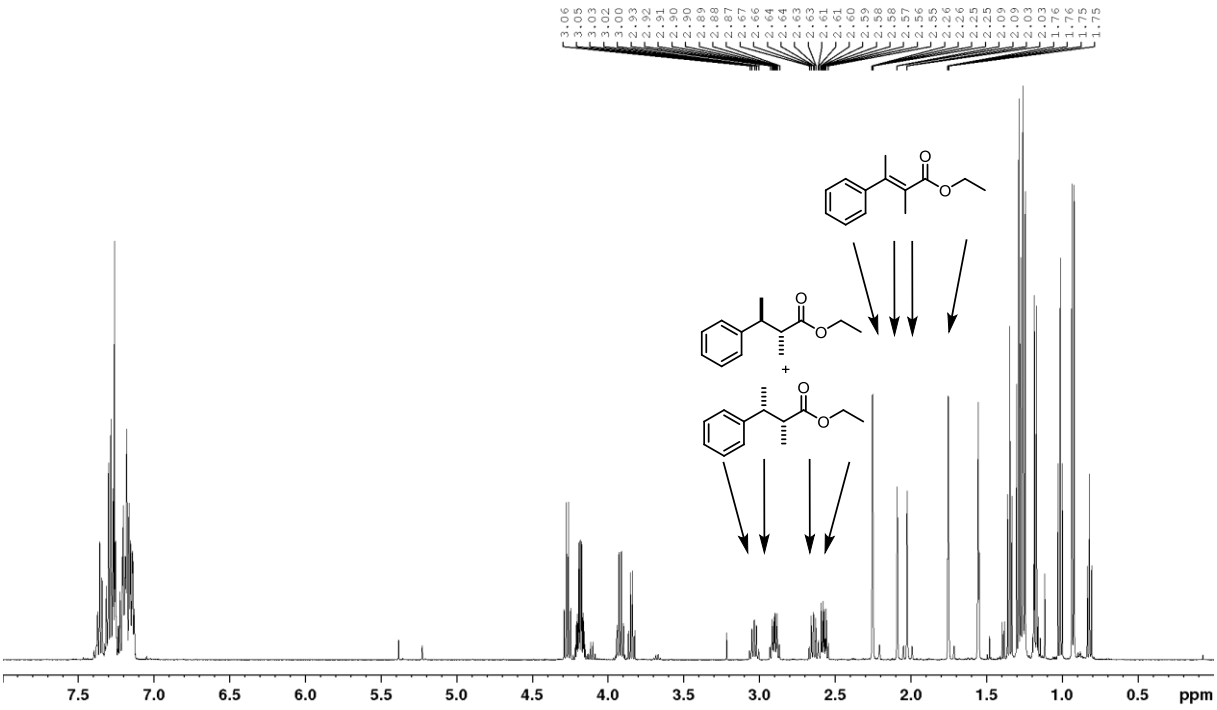
Minor diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.01 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.17 (d, $^3J_{11,4}$ = 6.9 Hz, 3H, H-11), 1.23–1.27 (m, 2H, H-10), 2.64 (m_c, 1H, H-4), 3.03 (m_c, 1H, H-5), 3.91 (m_c, 2H, H-2), 7.11–7.23 (m, 3H, H-7/H-9)*, 7.26–7.41 (m, 2H, H-8)* ppm.

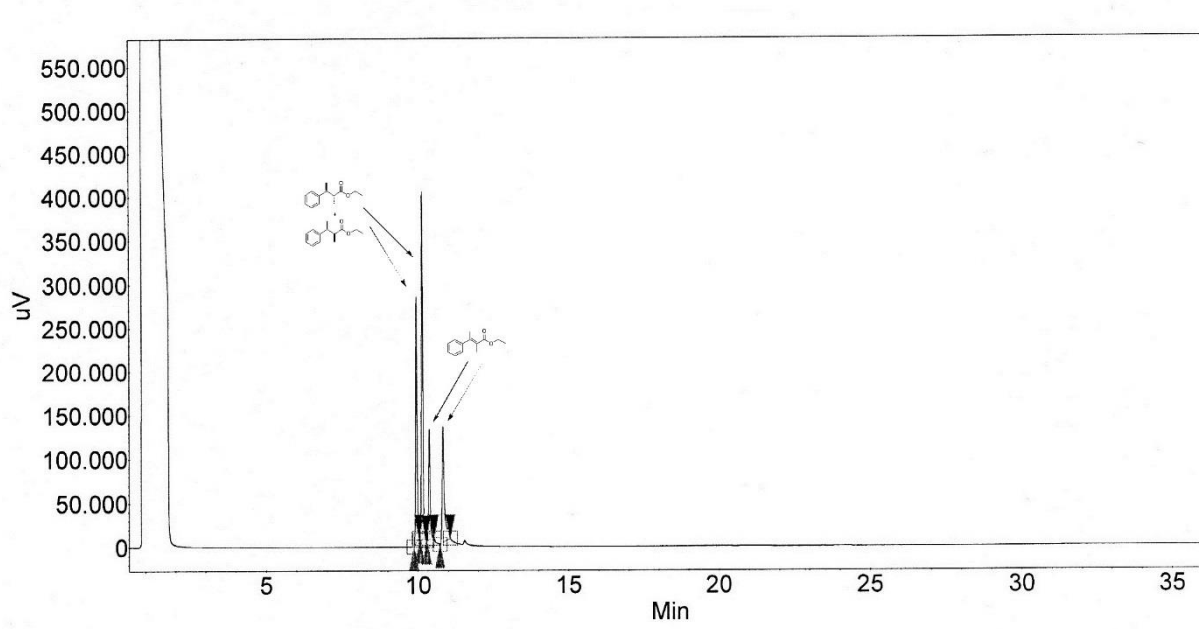
Integrated signals in ^{1}H NMR which are not further listed belong to the starting material (***E*-8s**) and its isomer (***Z*-8s**). Due to overlaying signals, ^{13}C signals have not been correlated.

For **MS** see following GC/MS data.

^{1}H NMR of 9s



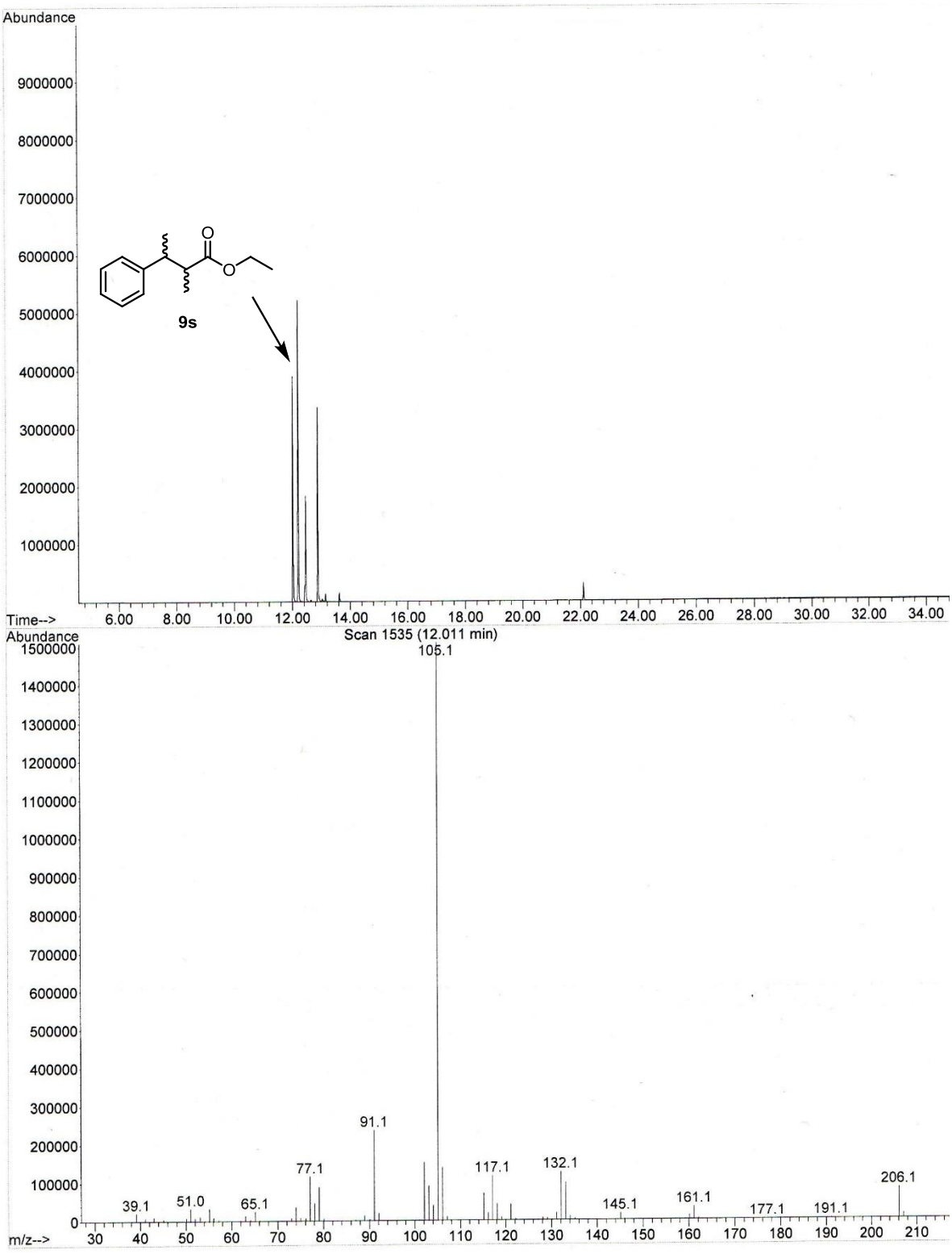
GC of 9s



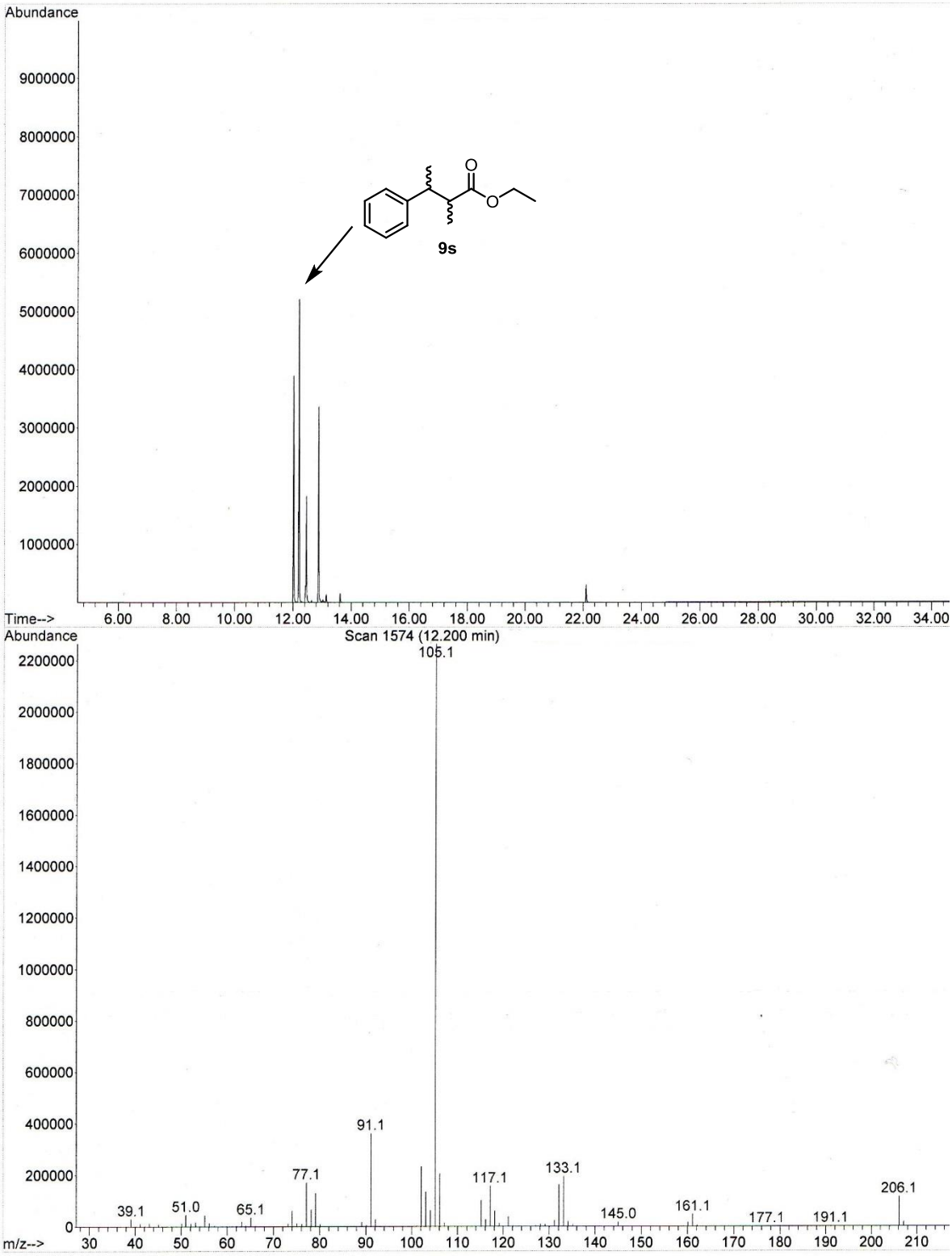
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	9,96	26,83	281221,8	14658,6	26,832
2	UNKNOWN	10,15	39,25	397480,1	21441,8	39,249
3	UNKNOWN	10,37	13,46	125736,1	7354,0	13,461
4	UNKNOWN	10,83	20,46	131657,1	11175,8	20,457
Total			100,00	936095,0	54630,3	100,000

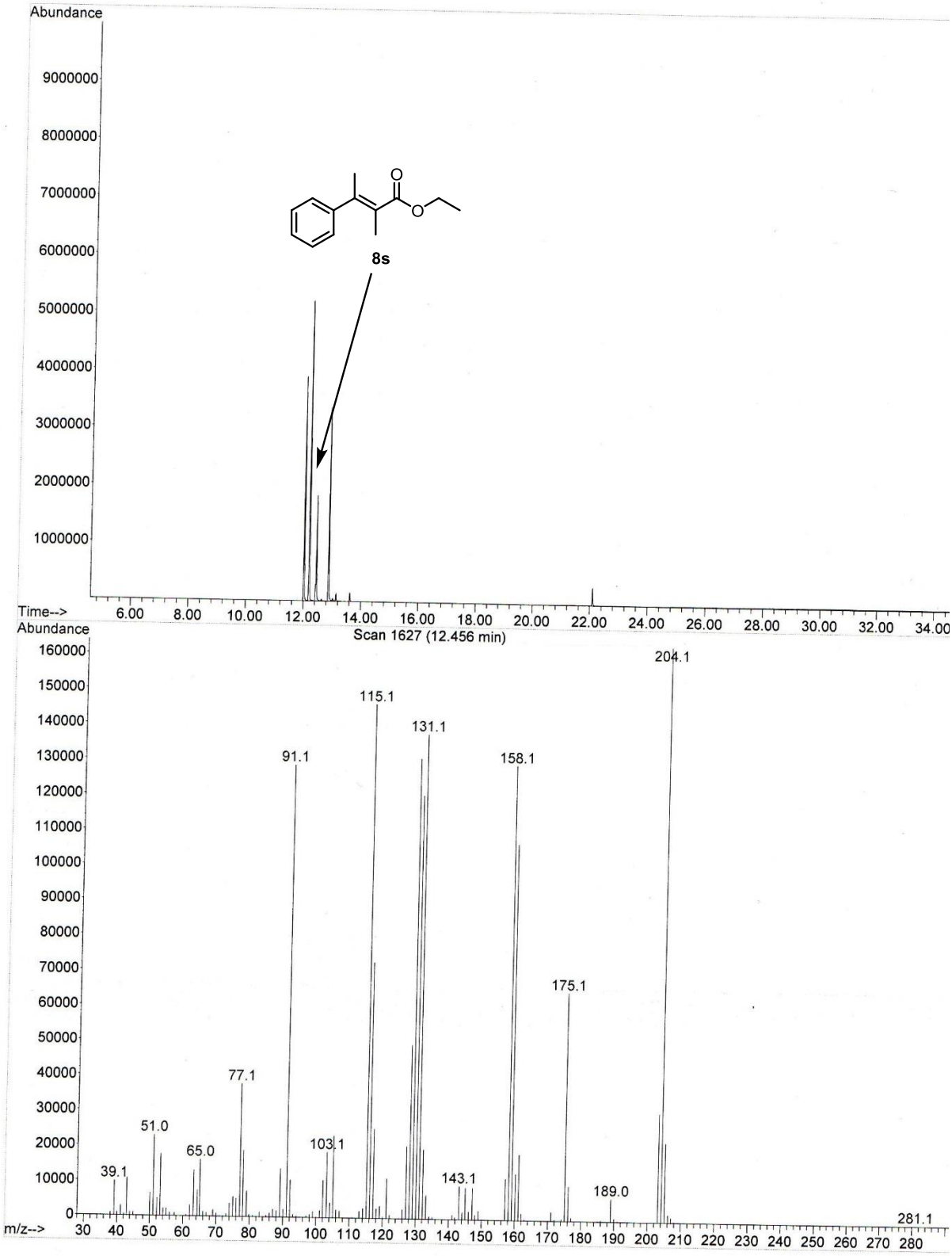
GC/MS of 9s minor diastereomer



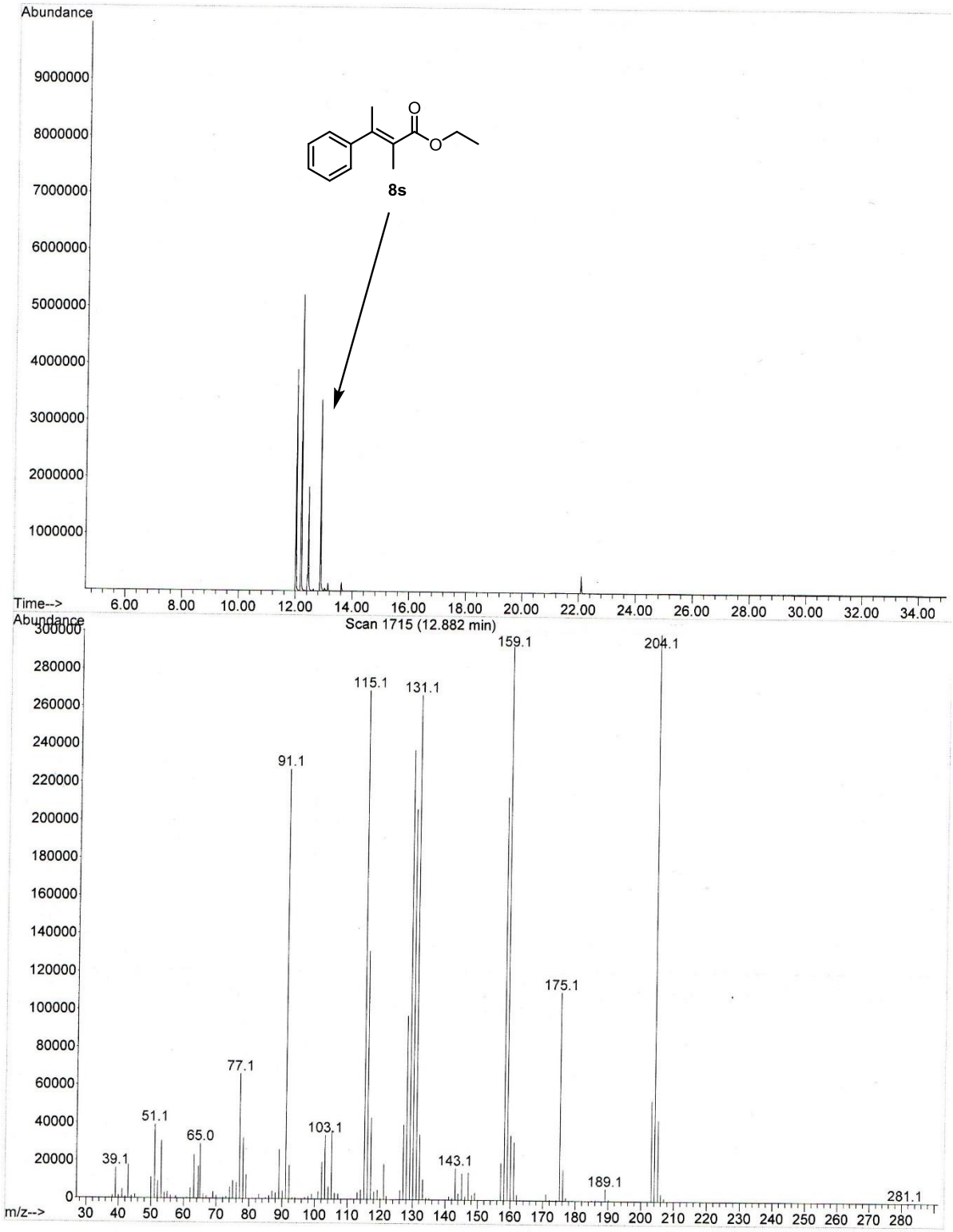
GC/MS of 9s major diasteromer



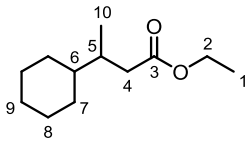
GC/MS of *E*-8s


Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
8s
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
Abundance
Scan 1627 (12.456 min)
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
204.1
115.1
131.1
91.1
158.1
175.1
77.1
51.0
65.0
103.1
39.1
143.1
189.0
281.1
m/z-->
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280

GC/MS of *Z*-8s


Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
O
O
8s
Abundance
Scan 1715 (12.882 min)
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
m/z-->
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280
159.1
204.1
115.1
131.1
91.1
175.1
77.1
51.1
65.0
103.1
39.1
143.1
189.1
281.1

4.4.21 Ethyl 3-cyclohexylbutanoate (9t)



9t
$C_{12}H_{22}O_2$
Mw = 198.31

Prepared according to **GP2** from ethyl (*E*)-3-cyclohexylbut-2-enoate (**8t**, 49 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 50:1) yielded **9t** as a colorless oil (41 mg, 0.21 mmol, 83%).

R_f = 0.63 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

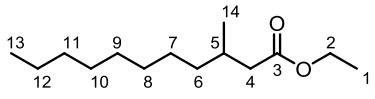
^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (d, $^3J_{10,5}$ = 6.8 Hz 3H, H-10), 0.91–1.04 (m, 2H, H-9*), 1.05–1.23 (m, 4H, H-6/H-7*/H-7'*), 1.25 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.59–1.68 (m, 3H, H-9'*/H-8*), 1.69–1.78 (m, 2H, H-8'*), 1.85 (m_c, 1H, H-5), 2.21 (m_c, 2H, H-4), 4.12 (q, $^3J_{2,1}$ = 7.1 Hz, 2H, H-2) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.4 (C-1), 16.6 (C-10), 26.7 (C-7)*, 26.8 (C-8)*, 26.8 (C-9)*, 29.0 (C-7')*, 30.4 (C-8')*, 35.5 (C-5), 39.4 (C-4), 42.7 (C-6), 60.2 (C-2), 174.0 (C-3) ppm.

HRMS (APCI) for $C_{12}H_{23}O_2^+$ [$(M+H)^+$] calculated: 199.1693, found: 199.1689.

The data is in accordance with literature.[31]

4.4.22 Ethyl 3-methylundecanoate (9u)



9u
$C_{14}H_{28}O_2$
Mw = 228.38

Prepared according to **GP2** from ethyl (*E*)-3-methylundec-2-enoate (**8u**, 57 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 50:1) yielded **9u** as a colorless oil (52.7 mg, 0.231 mmol, 92%).

R_f = 0.78 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

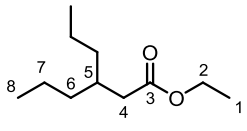
^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, $^3J_{13,12}$ = 13.9 Hz, 3H, H-13), 0.92 (d, $^3J_{14,5}$ = 6.6 Hz, 3H, H-14), 1.12–1.34 (m, 17H, H-1/H-6/H-7/H-8/H-9/H-10/H-11/H-12), 1.94 (m_c, 1H, H-5), 2.18 (m_c, 2H, H-4), 4.12 (q, $^3J_{2,1}$ = 7.1, 2H, H-7) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (C-13), 14.4 (C-1), 19.8 (C-14), 22.8 (C-12)*, 27.0 (C-10)*, 29.4 (C-9)*, 29.7 (C-8)*, 29.9 (C-7)*, 30.5 (C-5), 32.0 (C-11)*, 36.8 (C-6), 42.1 (C-4), 60.1 (C-2), 173.5 (C-3) ppm.

HRMS (APCI) for $C_{14}H_{29}O_2^+$ [$(M+H)^+$] calculated: 229.2162, found: 229.2157.

IR (ATR): $\tilde{\upsilon}$ = 2923 (m), 2853 (m), 1735 (s), 1461 (m), 1371 (m), 1250 (m), 1159 (m), 1032 (m), 954 (w), 844 (w), 722 (w) cm^{-1}.

4.4.23 Ethyl 3-propylhexanoate (9v)



9v
$C_{11}H_{22}O_2$
Mw = 186.29

Prepared according to **GP2** from ethyl 3-propylhex-2-enoate (46 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/Et_2O = 50:1) yielded **9v** as a colorless oil (100% conversion, due to volatility of the product the yield could not be determined).

$\mathbf{R_f}$ = 0.78 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.88 (t, $^3J_{8,7}$ = 7.0 Hz, 6H, H-8), 1.19–1.33 (m, 11H, H-1/H-6/H-7), 1.84 (m_c, 1H, H-5), 2.19 (d, $^3J_{4,5}$ = 6.8 Hz, 2H, H-4), 4.08 (q, $^3J_{2,1}$ = 7.1 Hz, 2H, H-2) ppm.

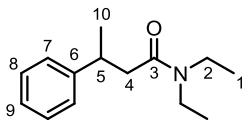
Due to volatility of the product, the sample contains *n*-pentane residues. Therefore, the value of the integration for H-8 and H1/H-6/H-7 is too high (see the attached spectra).

^{13}C NMR (126 MHz, CD_2Cl_2): δ = 14.4 (C-1/C-8), 20.0 (C-7), 35.0 (C-5), 36.6 (C-6), 39.6 (C-4), 60.3 (C-2), 173.7 (C-3) ppm.

HRMS (APCI) for $C_{11}H_{23}O_2^+$ [$(M+H)^+$] calculated: 187.1693, found: 187.1692.

IR (ATR): $\tilde{\upsilon}$ = 2957 (s), 2929 (m), 2871 (m), 2358 (w), 1735 (s), 1641 (w), 1462 (m), 1374 (w), 1302 (w), 1247 (m), 1173 (m), 1106 (w), 1036 (m), 854 (w), 739 (w) cm^{-1}.

4.4.24 *N*,*N*-diethyl-3-phenylbutanamide (11)



11
$C_{14}H_{21}NO$
Mw = 219.32

Prepared according to **GP2** from (*E*)-*N*,*N*-diethyl-3-phenylbut-2-enamide (**10**, 46 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 5.1 mg, 13 µmol, 5.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by preparative TLC (Al_2O_3, cyclohexane/ *tert*-butyl methyl ether = 5:1, Et_3N 2%) yielded **11** as a colorless oil (60% conversion (average of 3 runs), 9.5 mg, 43 µmol, 17%).

$\mathbf{R_f}$ = 0.28 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 2:1).

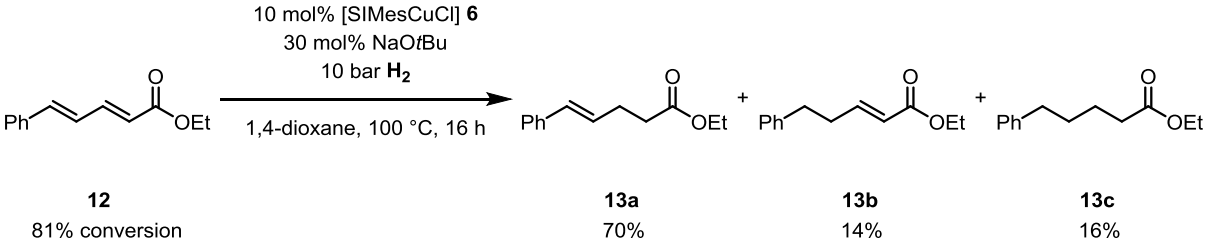
^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.02 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1)*, 1.07 (t, $^3J_{1',2'}$ = 7.1 Hz, 3H, H-1')*, 1.28 (d, $^3J_{10,5}$ = 7.0 Hz, 3H, H-10), 2.51 (m_c, 2H, H-4), 3.19 (t, $^3J_{2,1}$ = 7.1 Hz, 2H, H-2), 3.23–3.38 (m, 3H, H-5/H-2'), 7.14–7.20 (m, 1H, H-9), 7.21–7.31 (m, 4H, H-7/H-8) ppm.

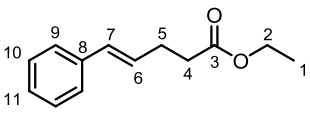
^{13}C NMR (126 MHz, CD_2Cl_2): δ = 13.2 (C-1)*, 14.5 (C-1')*, 21.8 (C-10), 36.9 (C-5), 40.39 (C-2)**, 41.8 (C-4), 42.2 (C-2')**, 126.4 (C-9), 127.3 (C-7), 128.6 (C-8), 147.3 (C-6), 170.7 (C-3) ppm.

HRMS (APCI) for $C_{14}H_{22}NO^+$ [$(M+H)^+$] calculated: 220.1696, found: 220.1694.

IR (ATR): $\tilde{\upsilon}$ = 2968 (m), 2931 (w), 2359 (w), 1638 (s), 1454 (m), 1278 (w), 11276 (w), 1222 (w), 1142 (w), 1085 (w), 1021 (w), 761 (w), 701 (m) cm^{-1}.

4.4.25 Ethyl (*E*)-5-phenylpent-4-enoate (13a)





13a
$C_{13}H_{16}O_2$
Mw = 204.26

Prepared according to **GP2** from ethyl (2*E*,4*E*)-5-phenylpenta-2,4-dienoate (**12**, 51 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 10.2 mg, 25.0 µmol, 10.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/Et_2O = 50:1) yielded **13** as a colorless oil (81% conversion, 35 mg combined yield of **12**¸ **13a**, **13b** and **13c**).

R_f = 0.61 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 2.45–2.57 (m, 4H, H4/H-5), 4.15 (q, $^3J_{2,1}$ = 7.1 Hz, 2H, H-2), 6.21 (dt, $^3J_{6,7}$ = 15.8 Hz, $^3J_{6,5}$ = 6.6 Hz, 1H, H-6), 6.43 (d, $^3J_{7,6}$ = 15.8 Hz, 1H, H-7), 7.15–7.23 (m, 1H, H-11)*, 7.26–7.37 (m, 4H, H-9/H-10)* ppm.

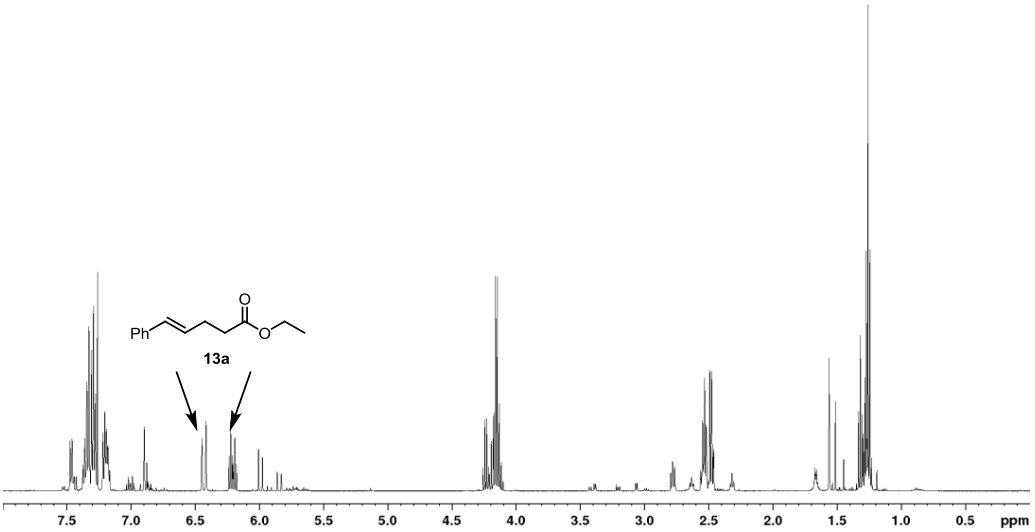
^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.4 (C-1), 28.4 (C-5), 34.2 (C-4), 60.5 (C-2), 126.1 (C-9),127.2 (C-11)*, 127.3 (C-10)*, 128.6 (C-6), 131.0 (C-7), 137.5 (C-8), 173.1 (C-3) ppm.

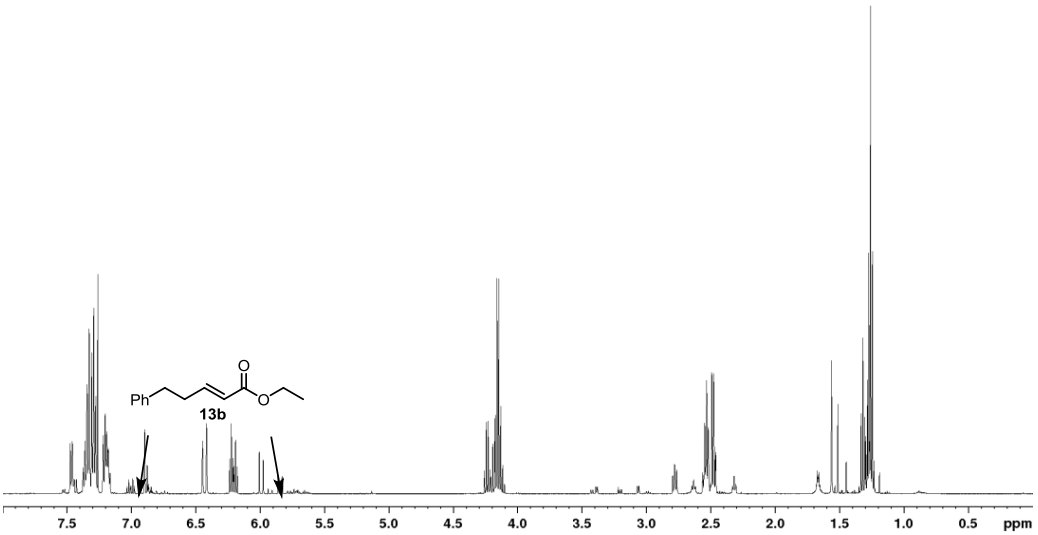
Other unpicked and not integrated signals belong to the starting material or the other products.

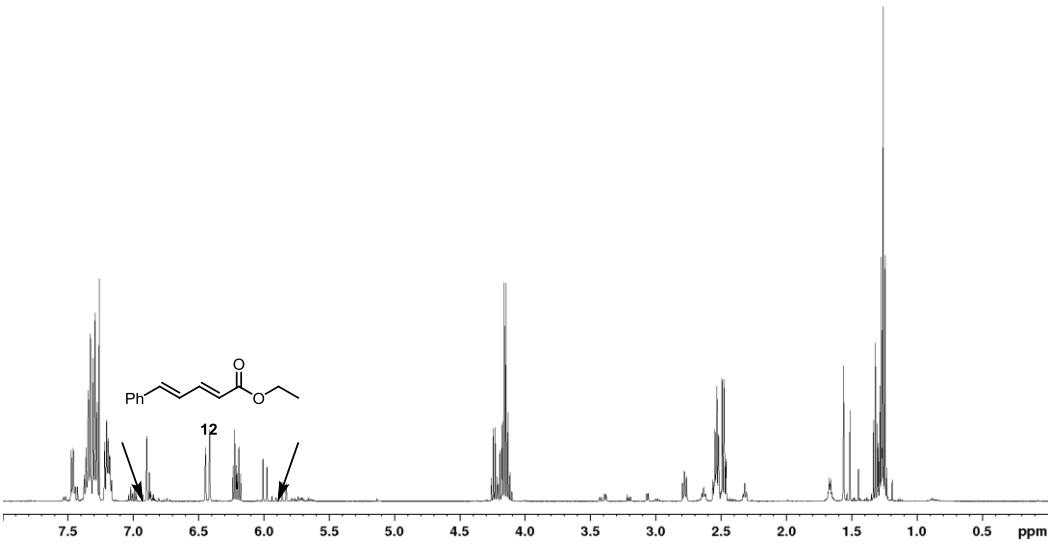
Indicative signals for the starting material **12** in the ^{1}H NMR are at δ = 5.84, 5.99 and 6.89 ppm. Indicative for the 1,6-conjugate reduction product **13b** are the signals at δ = 5.82 and 7.00 ppm.

HRMS (APCI) for $C_{13}H_{17}O_2^+$ [$(M+H)^+$] calculated: 205.1223, found: 205.1221.

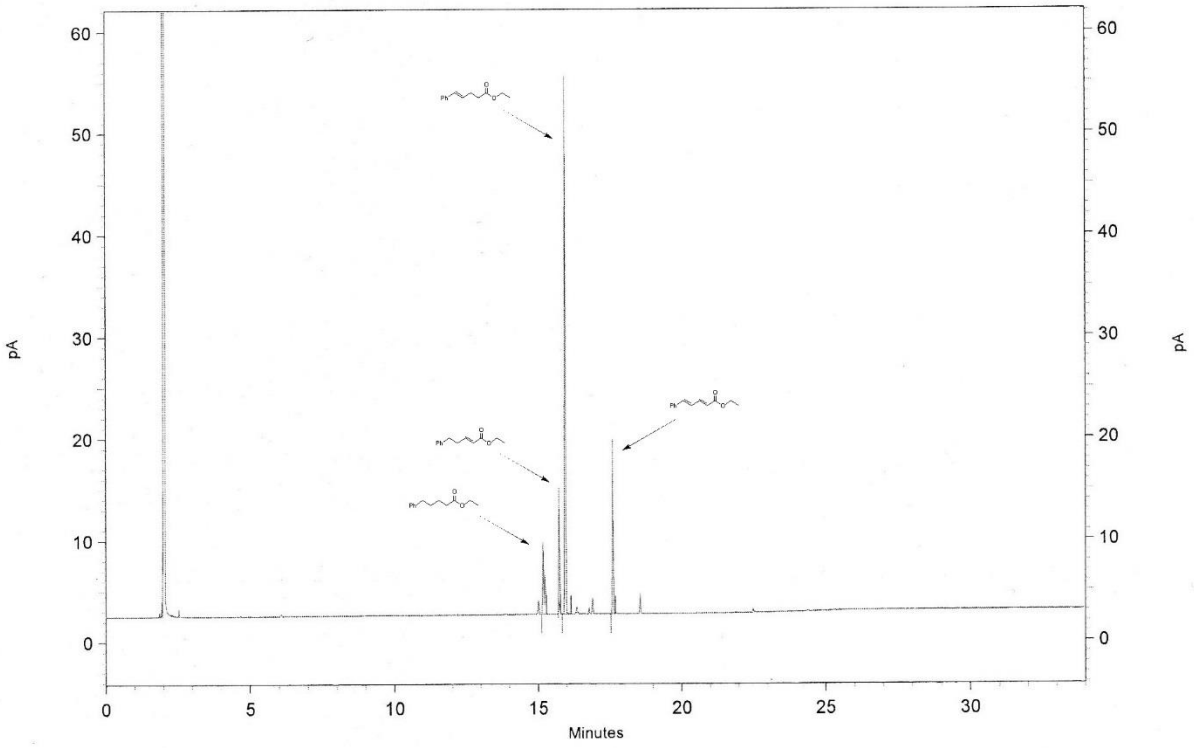
^{1}H NMR of 13a, 13b, 12







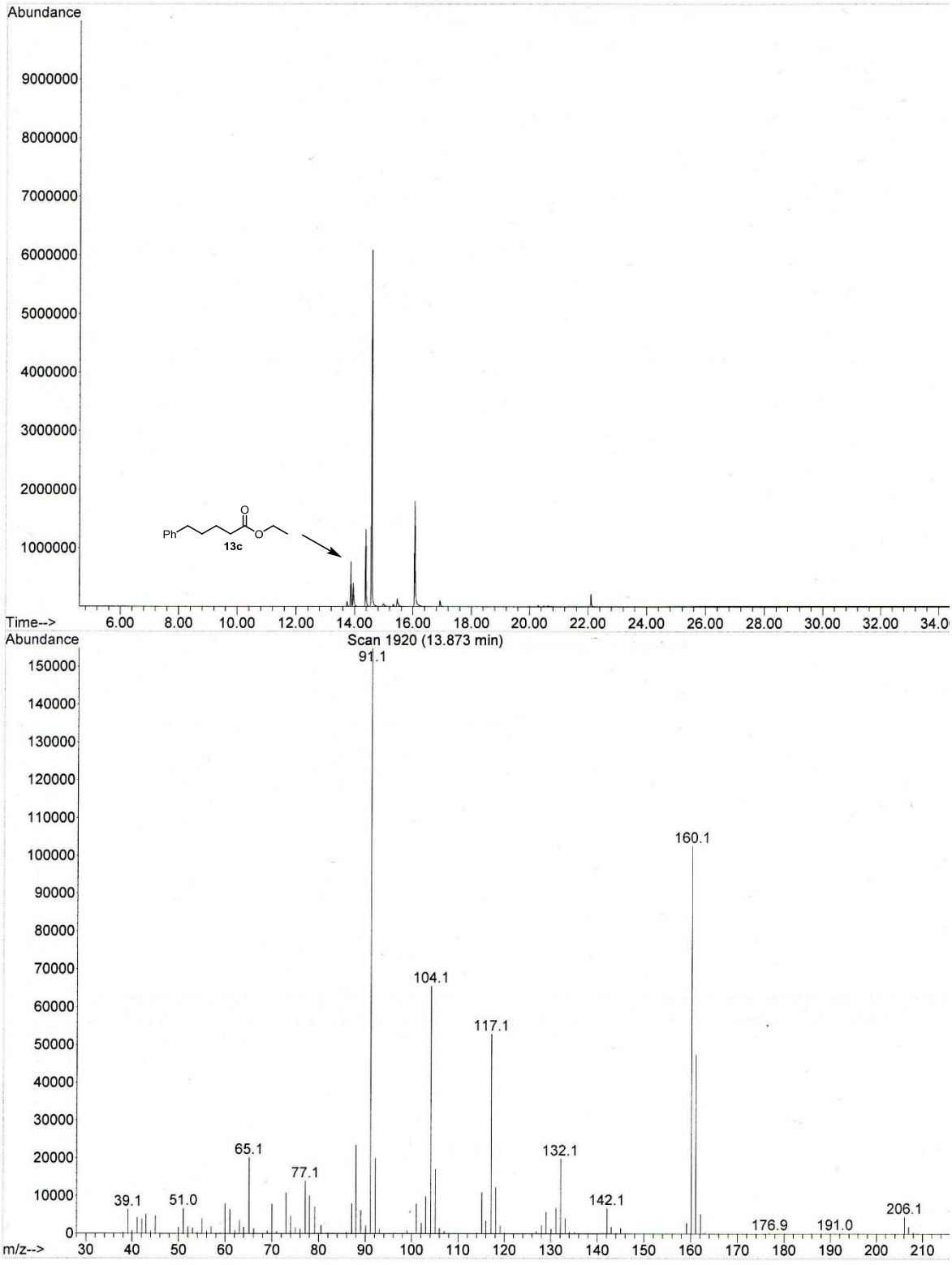
GC of 13



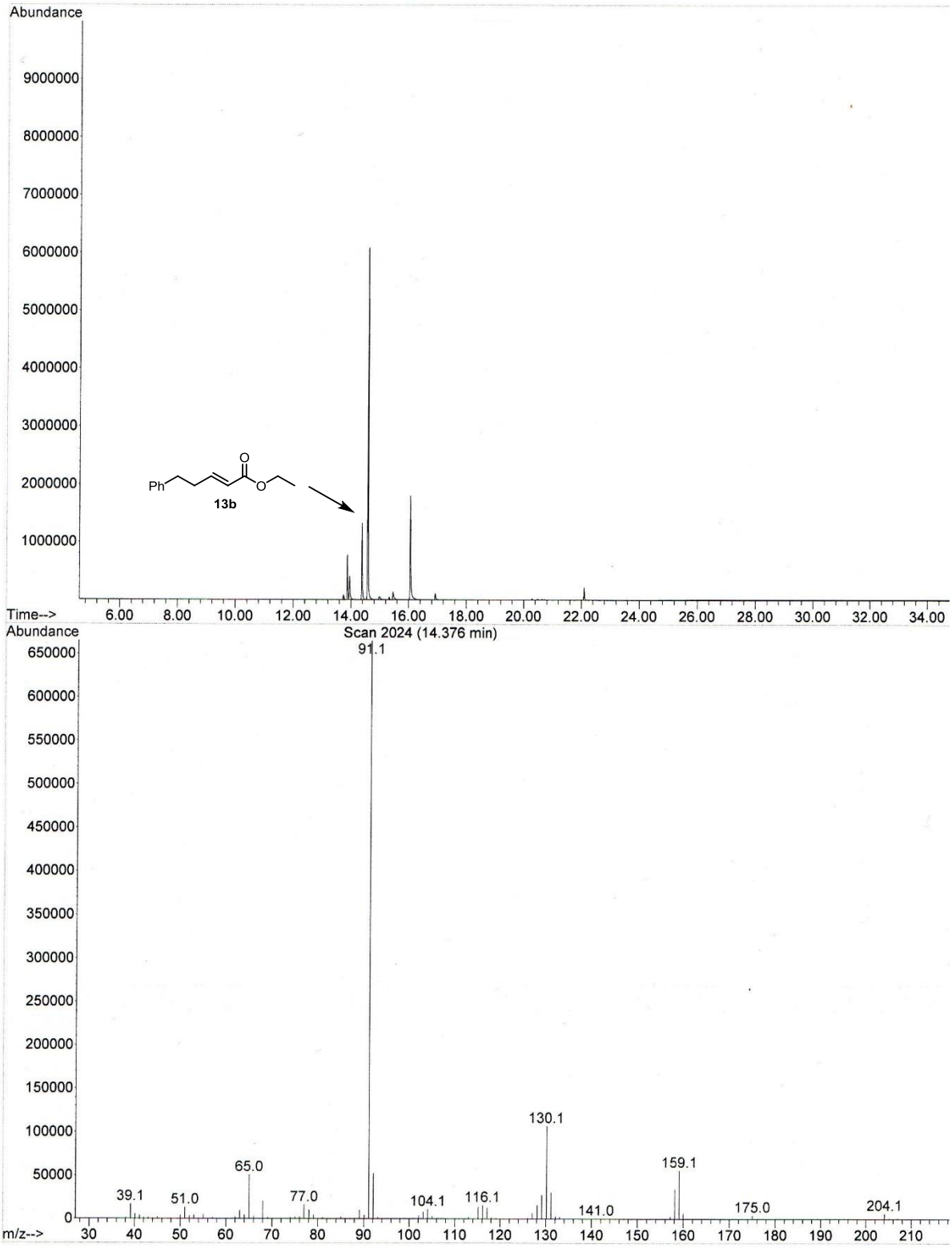
Back
Signal
Results

Peak #	Retention Time	Height	Height Percent	Area	Area Percent
1	15,1697	54197	7,9615	195890	13,2092
2	15,7293	88192	12,9553	166022	11,1952
3	15,9453	406108	59,6567	845219	56,9947
4	17,6103	132245	19,4266	275846	18,6008
Totals		680742	100,0000	1482977	100,0000

GC/MS of 13c


Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Ph
O
O
13c
Time-->
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00
30.00
32.00
34.0
Abundance
Scan 1920 (13.873 min)
91.1
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
160.1
104.1
117.1
65.1
77.1
132.1
39.1
51.0
142.1
176.9
191.0
206.1
m/z-->
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

GC/MS of 13b


Abundance
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8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Ph
O
O
13b
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
Abundance
Scan 2024 (14.376 min)
91.1
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
130.1
65.0
159.1
39.1
51.0
77.0
104.1
116.1
141.0
175.0
204.1
m/z-->
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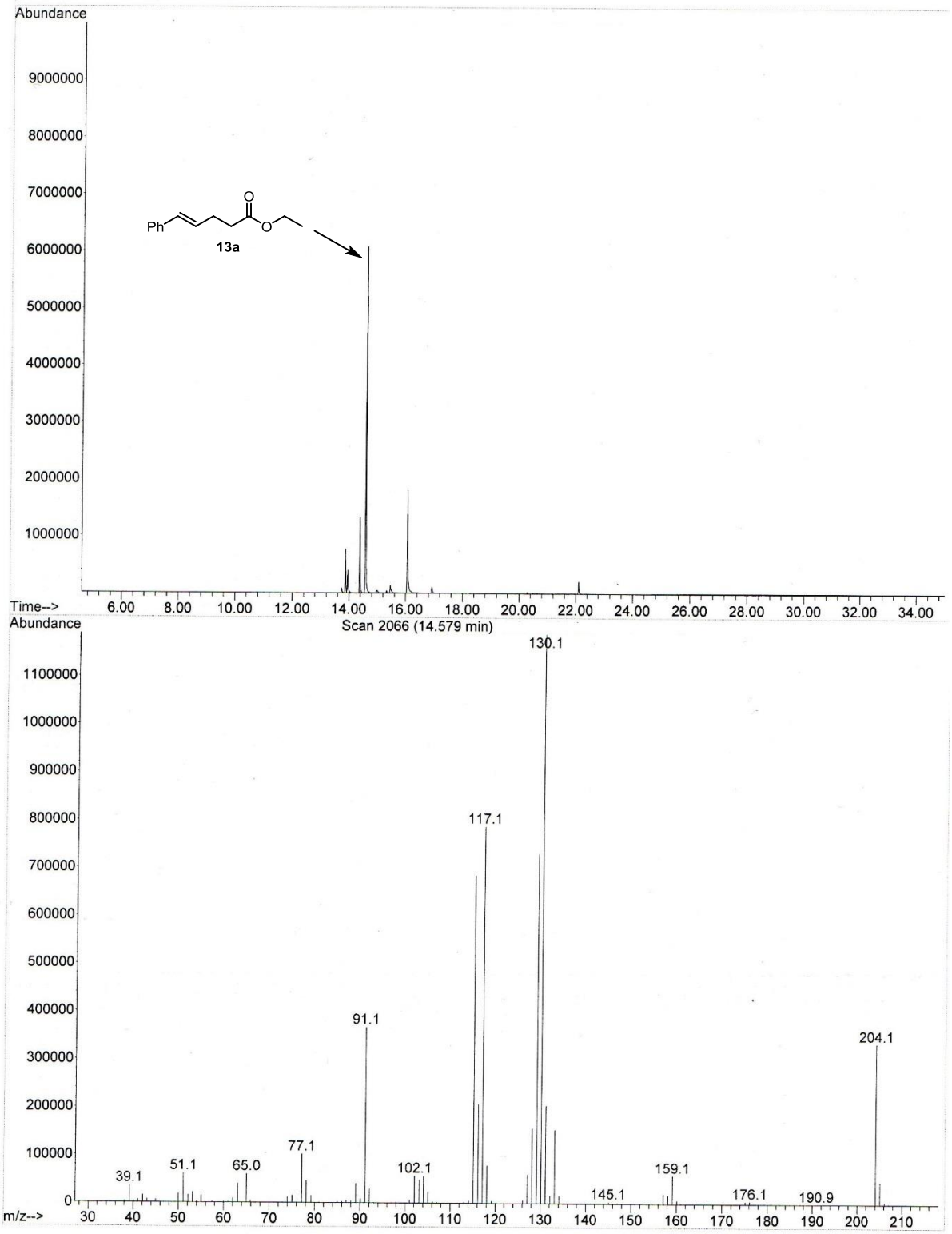
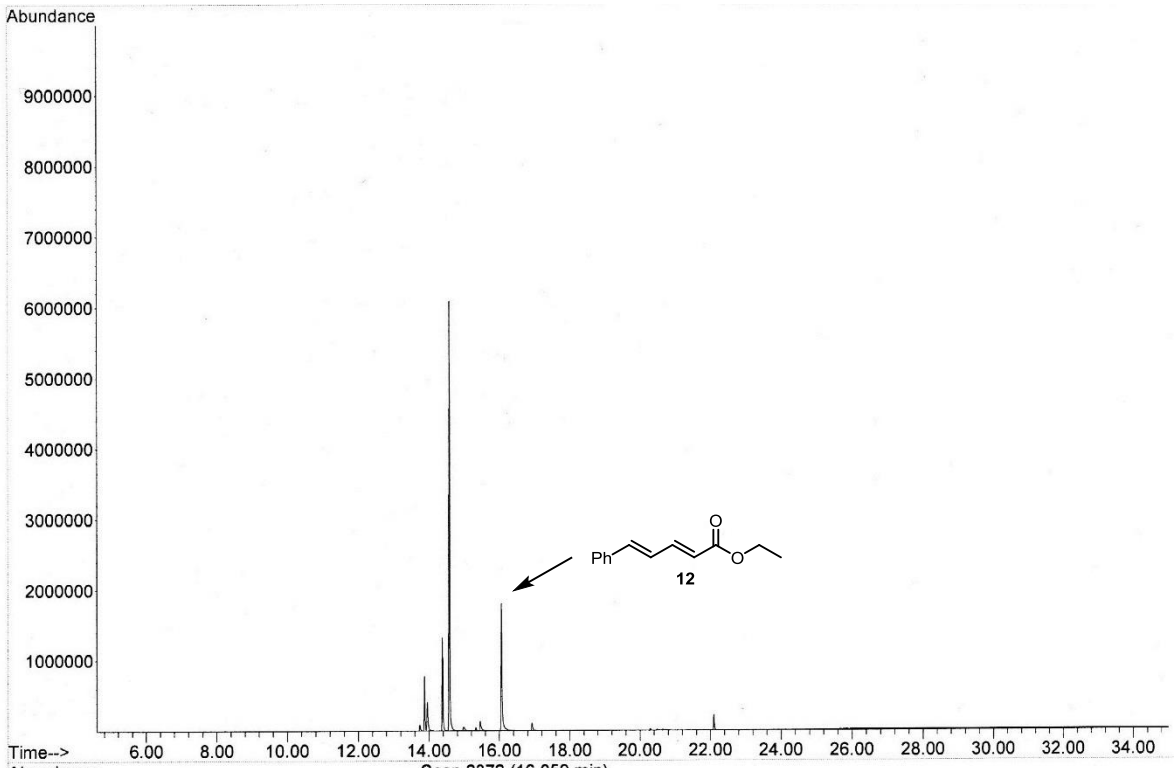
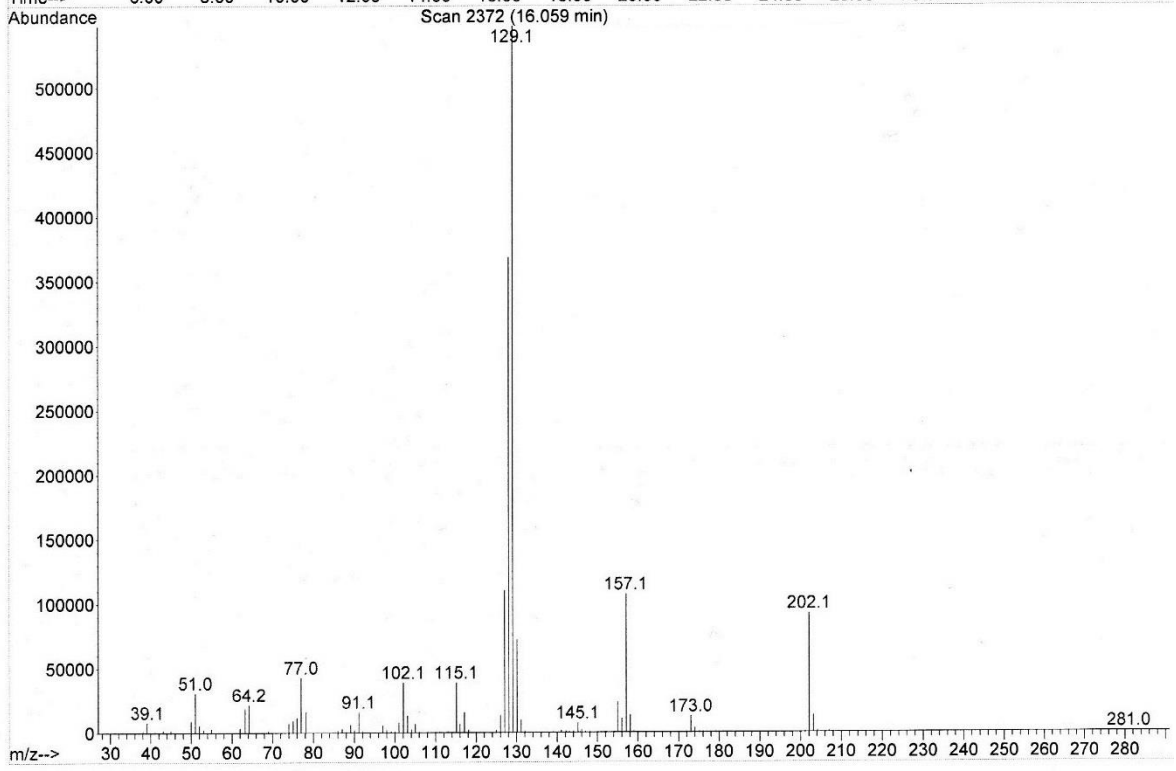
GC/MS of 13a


Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Ph
O
O
13a
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
Abundance
Scan 2066 (14.579 min)
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
m/z-->
130.1
117.1
91.1
204.1
77.1
51.1
65.0
39.1
102.1
159.1
145.1
176.1
190.9
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210

GC/MS of 12


Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
Ph
O
O
12


Abundance
Scan 2372 (16.059 min)
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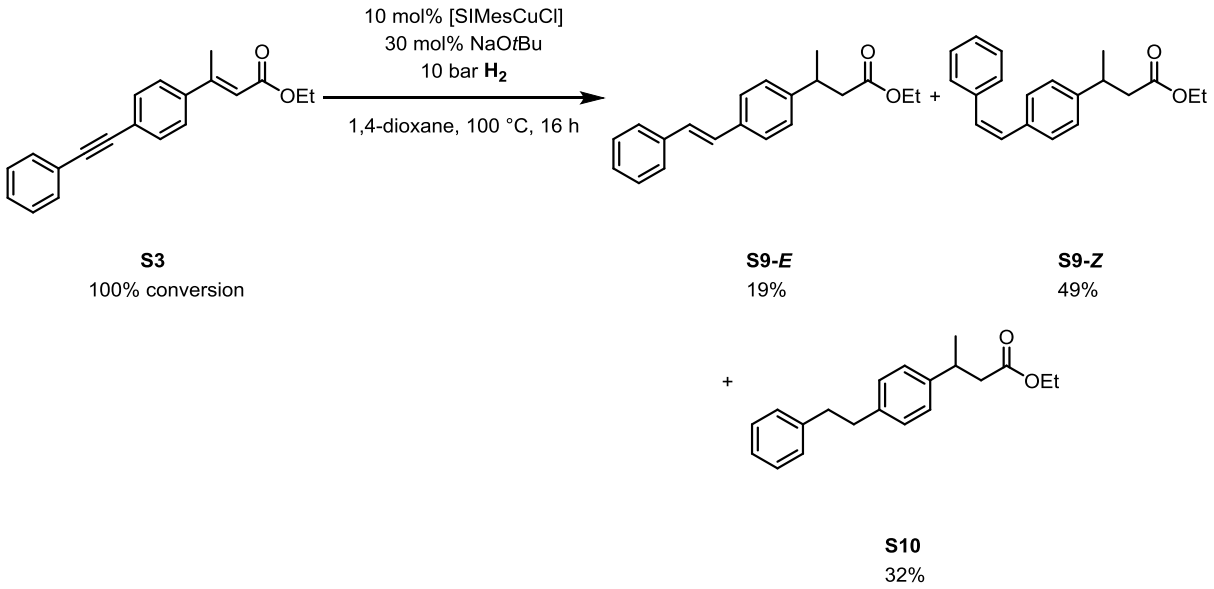
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
157.1
202.1
77.0
102.1
115.1
51.0
64.2
91.1
39.1
145.1
173.0
281.0
m/z-->
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280

4.4.26 Ethyl 3-(4-styrylphenyl)butanoate (S9)



S3
100% conversion

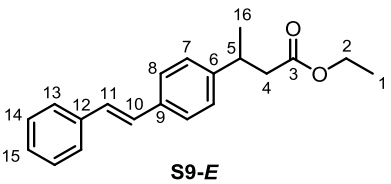
S9-*E*
19%

S9-*Z*
49%

S10
32%

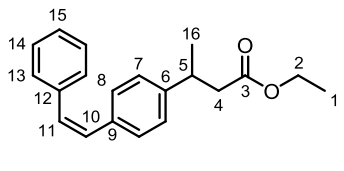
Prepared according to **GP2** from ethyl (*E*)-3-(4-(phenylethynyl)phenyl)but-2-enoate (**S3**, 69 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 10.2 mg, 25.0 µmol, 10.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/Et_2O = 50:1) yielded a mixture of **S9-*E***, **S9-*Z*** and **S10** as a colorless oil (full conversion, 44.6 mg combined yield of **S9-*E***, **S9-*Z*** and **S10**).

R_f = 0.16 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 50:1).



S9-*E*
$C_{20}H_{22}O_2$
Mw = 249.39

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.19 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.25–1.32 (m, 3H, H-16), 2.45–2.66 (m, 2H, H-4), 3.19–3.34 (m, 1H, H-5), 4.03–4.13 (m, 2H, H-2), 6.55 (m_c, 2H, H-10/H-11), 7.05–7.53 (m, 9H, H-7/H-8/H-13/H-14/H-15) ppm.



S9-*Z*
$C_{20}H_{22}O_2$
Mw = 249.39

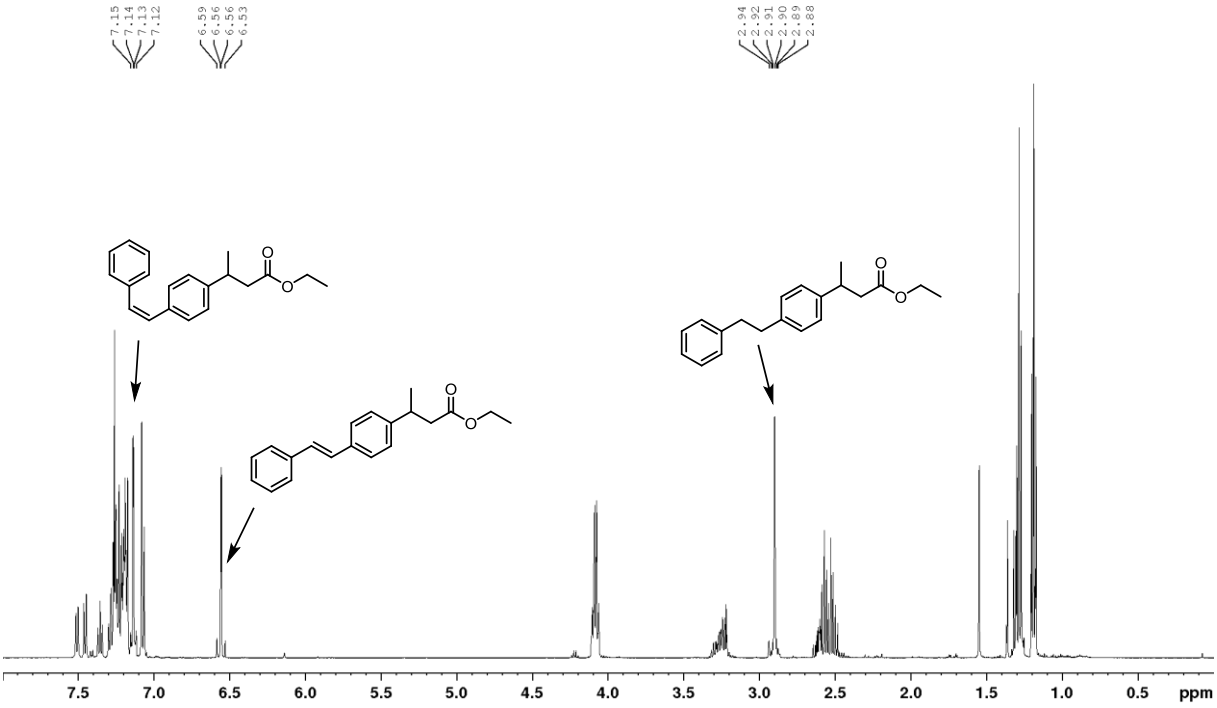
^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.18 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.25–1.32 (m, 3H, H-16), 2.45–2.66 (m, 2H, H-4), 3.19–3.34 (m, 1H, H-5), 4.03–4.13 (m, 2H, H-2), 7.13 (m_c, 2H, H-10/H-11), 7.05–7.53 (m, 9H, H-7/H-8/H-13/H-14/H-15) ppm.

Due to overlaying signals, ^{13}C signals have not been correlated.

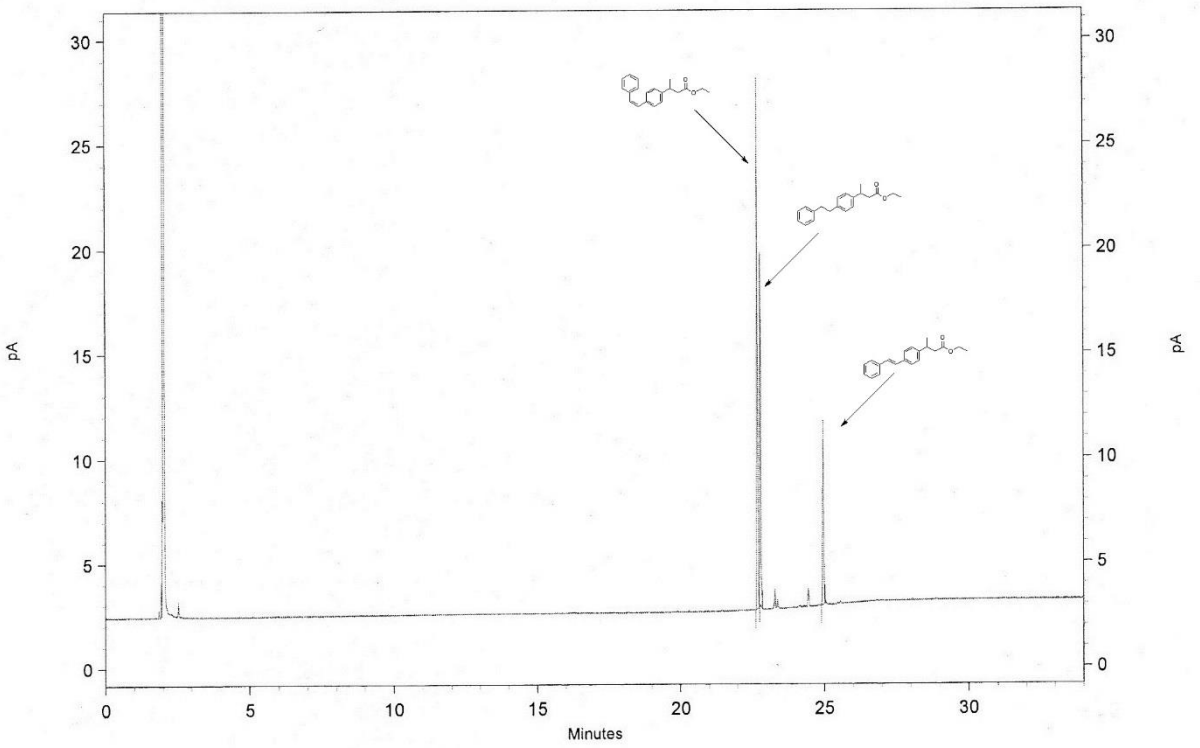
Indicative signals for the alkane product **S10** in the ^{1}H NMR are at δ = 2.89 ppm.

HRMS (APCI) for $C_{20}H_{23}O_2^+$ [$(M+H)^+$] calculated: 295.1693, found: 295.1691.

^{1}H NMR of S9


7.15
7.14
7.13
7.12
6.59
6.56
6.56
6.53
2.94
2.92
2.91
2.90
2.89
2.88
O
O
O
O
O
O
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
ppm

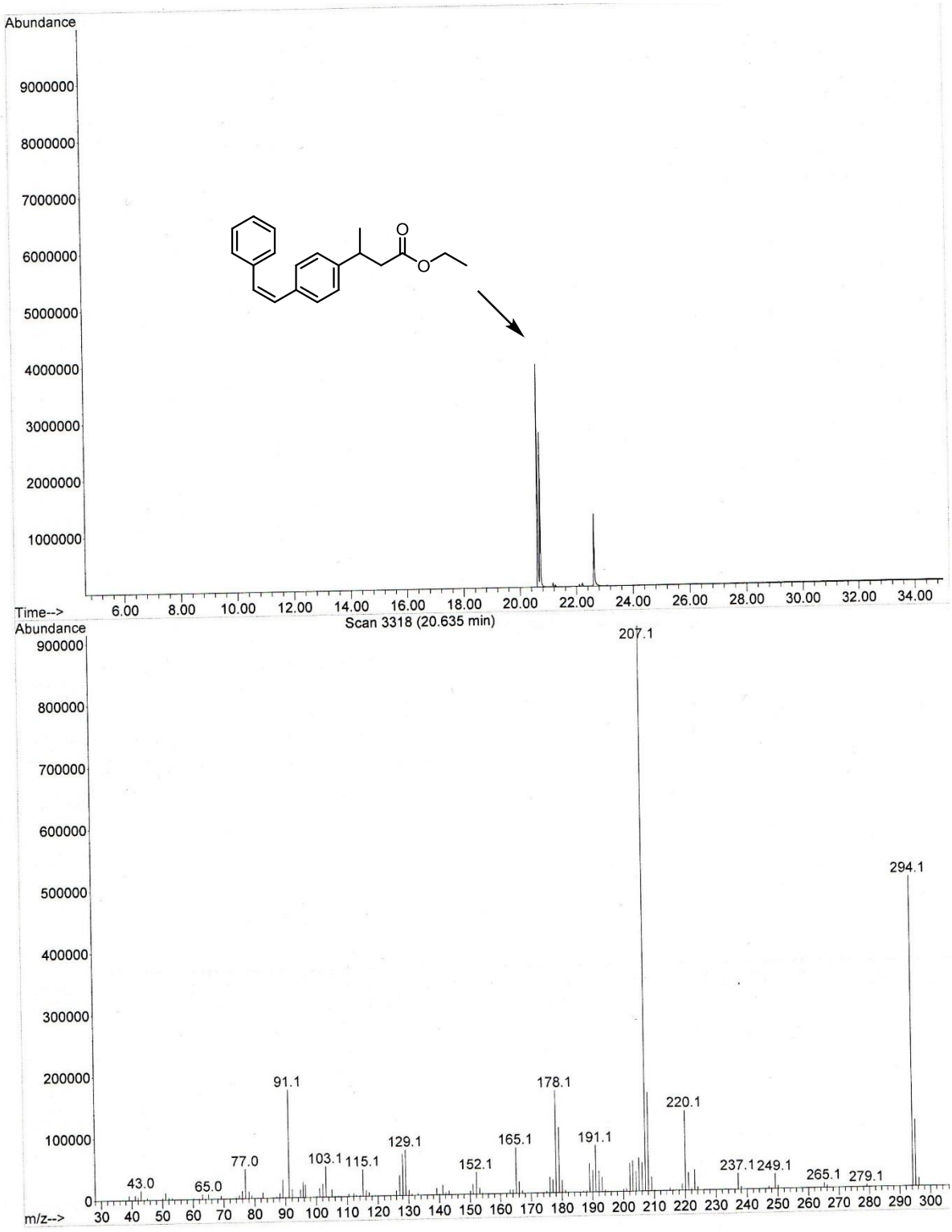
GC of S9



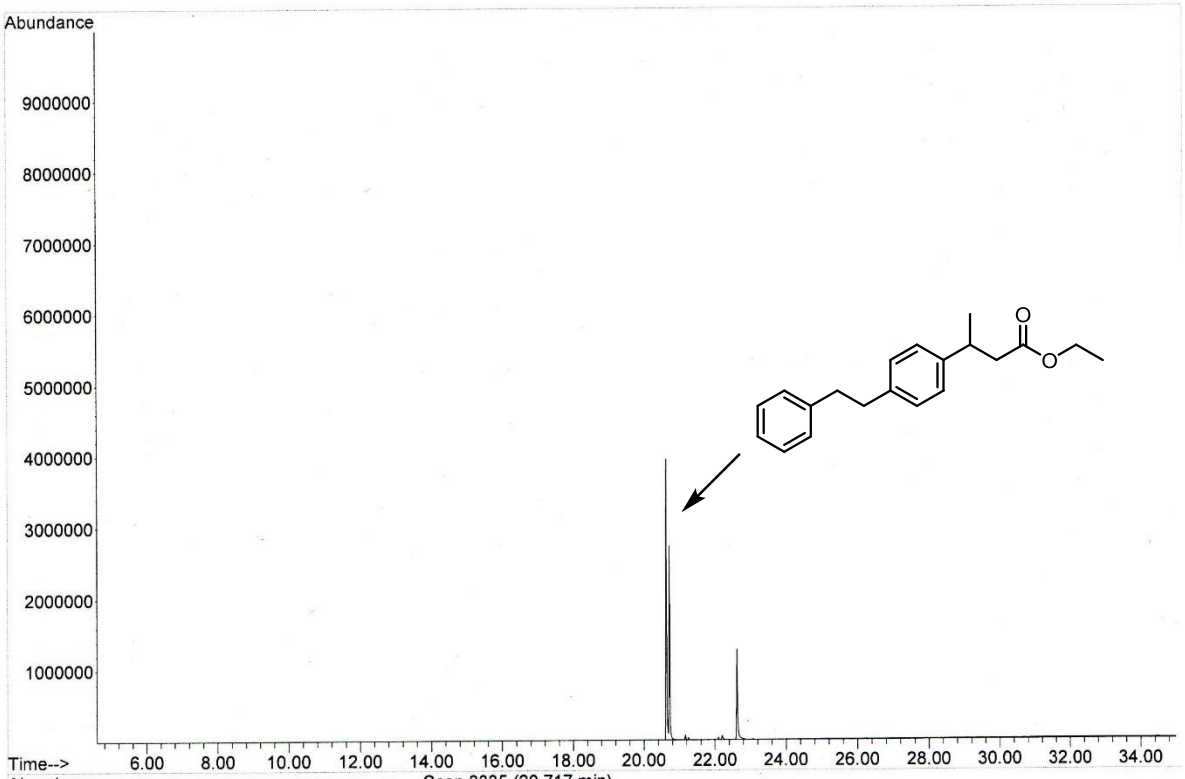
Back
Signal
Results

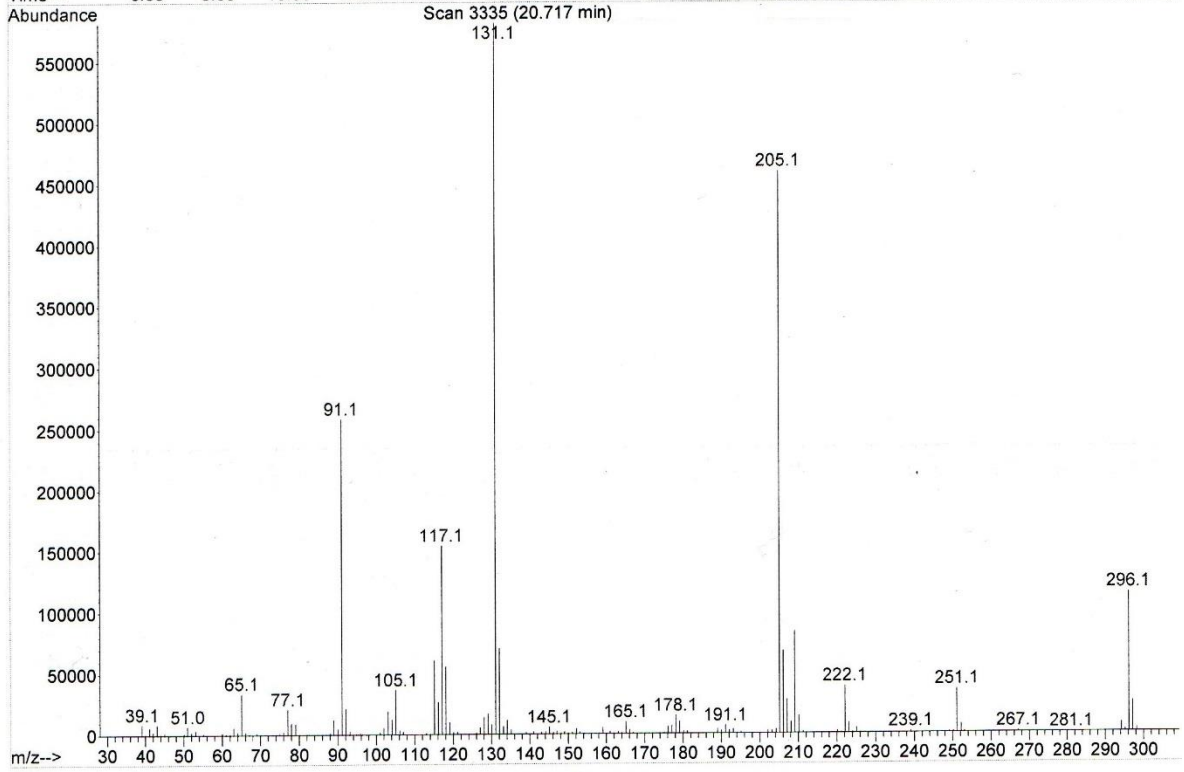
Peak #	Retention Time	Height	Height Percent	Area	Area Percent
1	22,6897	195053	49,7130	429181	49,0139
2	22,8000	129937	33,1170	278477	31,8030
3	24,9660	67368	17,1700	167974	19,1832
Totals		392358	100,0000	875632	100,0000

GC/MS of S9-*Z*

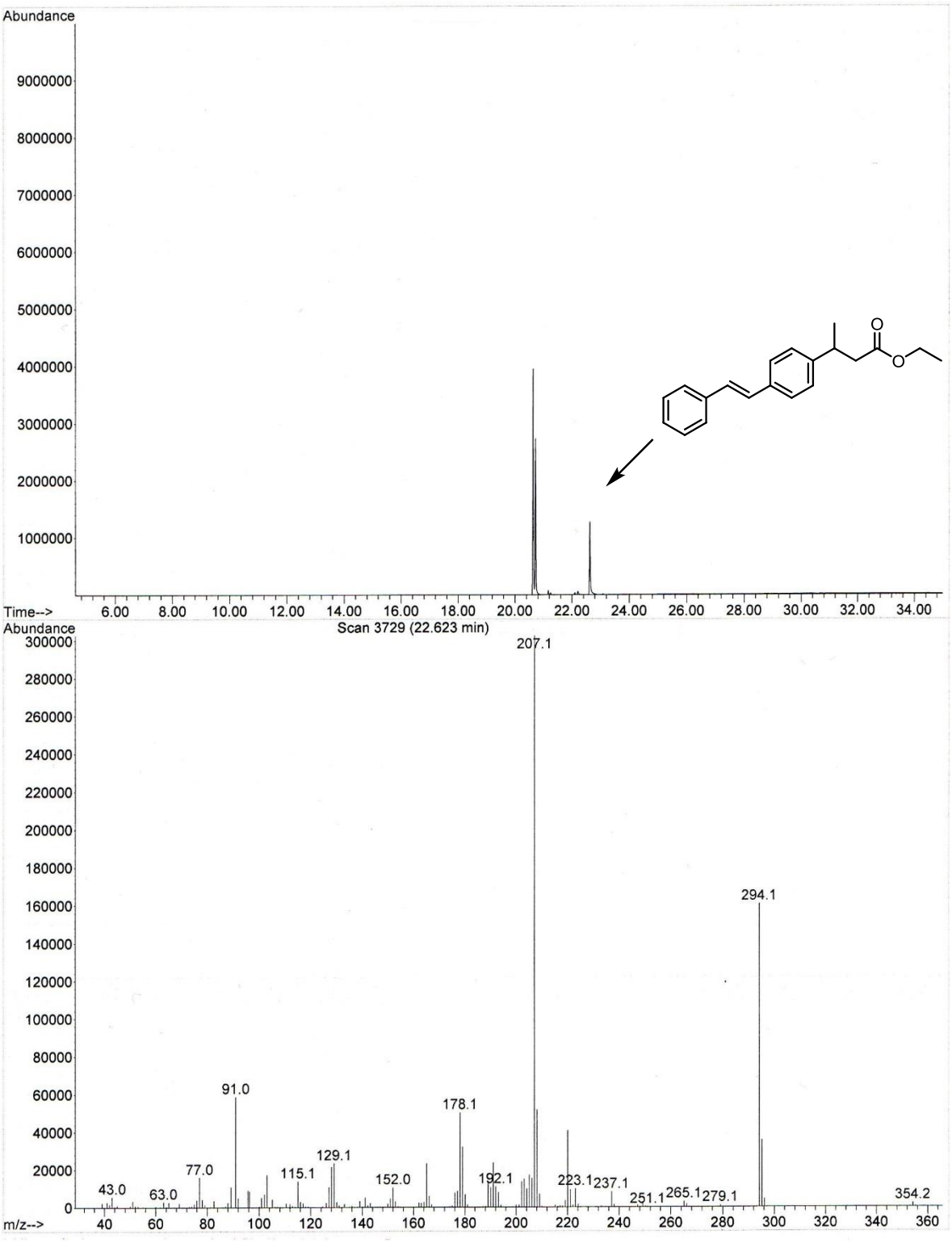

Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
Scan 3318 (20.635 min)
Abundance
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
m/z-->
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300
207.1
294.1
91.1
178.1
220.1
129.1
165.1
191.1
77.0
103.1
115.1
152.1
237.1
249.1
265.1
279.1
43.0
65.0

GC/MS of S10


Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
O
O


Abundance
Scan 3335 (20.717 min)
131.1
205.1
91.1
117.1
296.1
222.1
251.1
65.1
77.1
105.1
39.1
51.0
145.1
165.1
178.1
191.1
239.1
267.1
281.1
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
m/z-->
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300

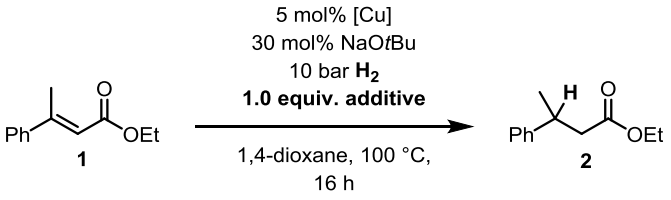
GC/MS of S9-*E*

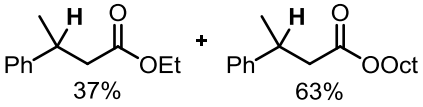
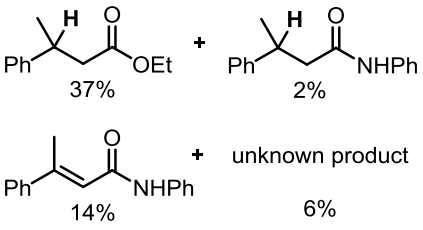

Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
O
O
Abundance
Scan 3729 (22.623 min)
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
207.1
294.1
91.0
178.1
129.1
77.0
115.1
152.0
192.1
223.1
237.1
251.1
265.1
279.1
43.0
63.0
354.2
m/z-->
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360

4.5 Additives tested in the conjugate reduction

In order to further probe the functional group tolerance of the present protocol, we have added three protic additives (1.0 equivalents with respect to the enoate **1**) to the standard conditions, namely *n*-octanol, benzoic acid and aniline. Robustness and functional group tolerance screening experiments[32] were following **GP 2**. Additionally to the substrate 1.00 equiv of an additiv was added to the reaction mixture together with the starting material.

Table S7: Influence of additives on the catalytic conjugate reduction.[a]



Entry	Additive	Conv.[b] [%]	Comments
1	1-octanol	100%	
2	benzoic acid	-	-
3	anilin	62%	

[a] All reactions with 5.5 µmol [Cu] in 1 mL solvent. [b] Determined by ^{1}H NMR spectroscopy or GC analysis. [c] Reaction was performed in an H_2-purged pressure tube. [d] Isolated yield.

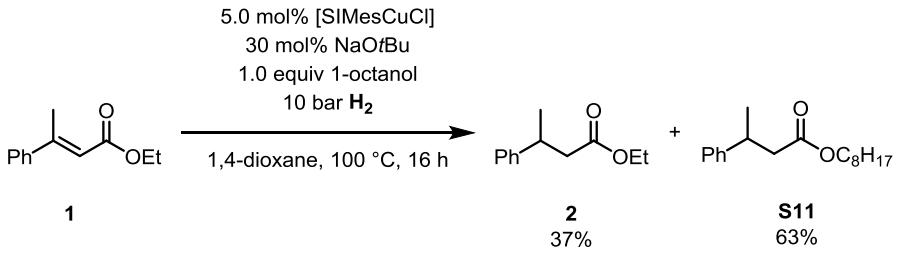
As can be seen from the table, the copper-catalyzed conjugate reduction tolerates the alcohol additive, with full conversion reached, however, we detect 63% of transesterification product (octyl ester).

Addition of the significantly more acidic benzoic acid led to a complete halt of the reaction, most probably due to protonation of the key *tert*-butoxide additive.

The addition of 1.0 equivalents aniline led to significantly lower conversion (only 62% reached), displaying the limits of the present catalyst. A mixture of products was found, including the corresponding reduced and not reduced amides derived from anilin.

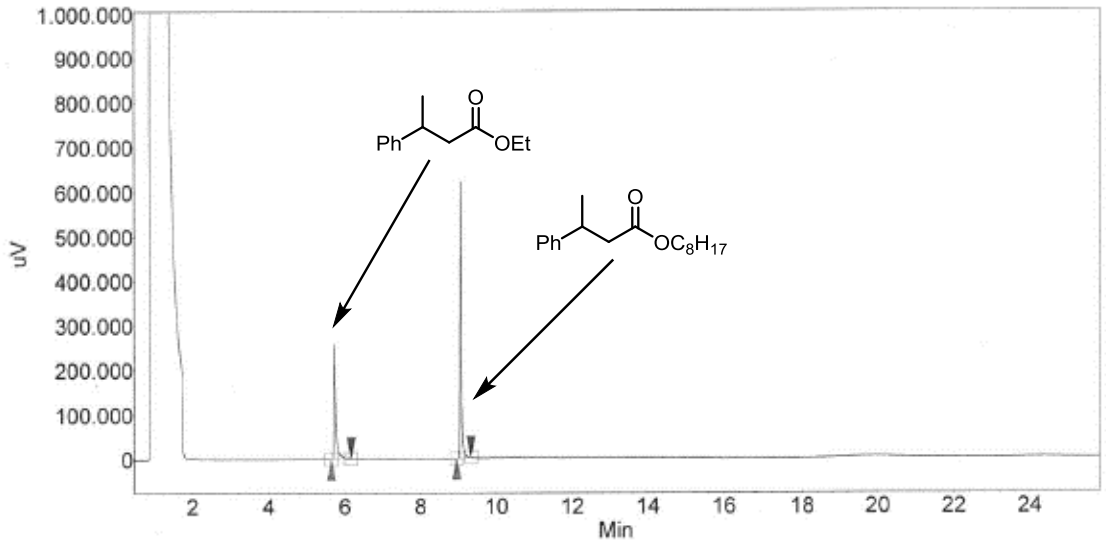
4.5.1 Analytical data for the additives tested:

4.5.1.1 1-Ocantol as additive



1 | **2** 37% | **S11** 63%

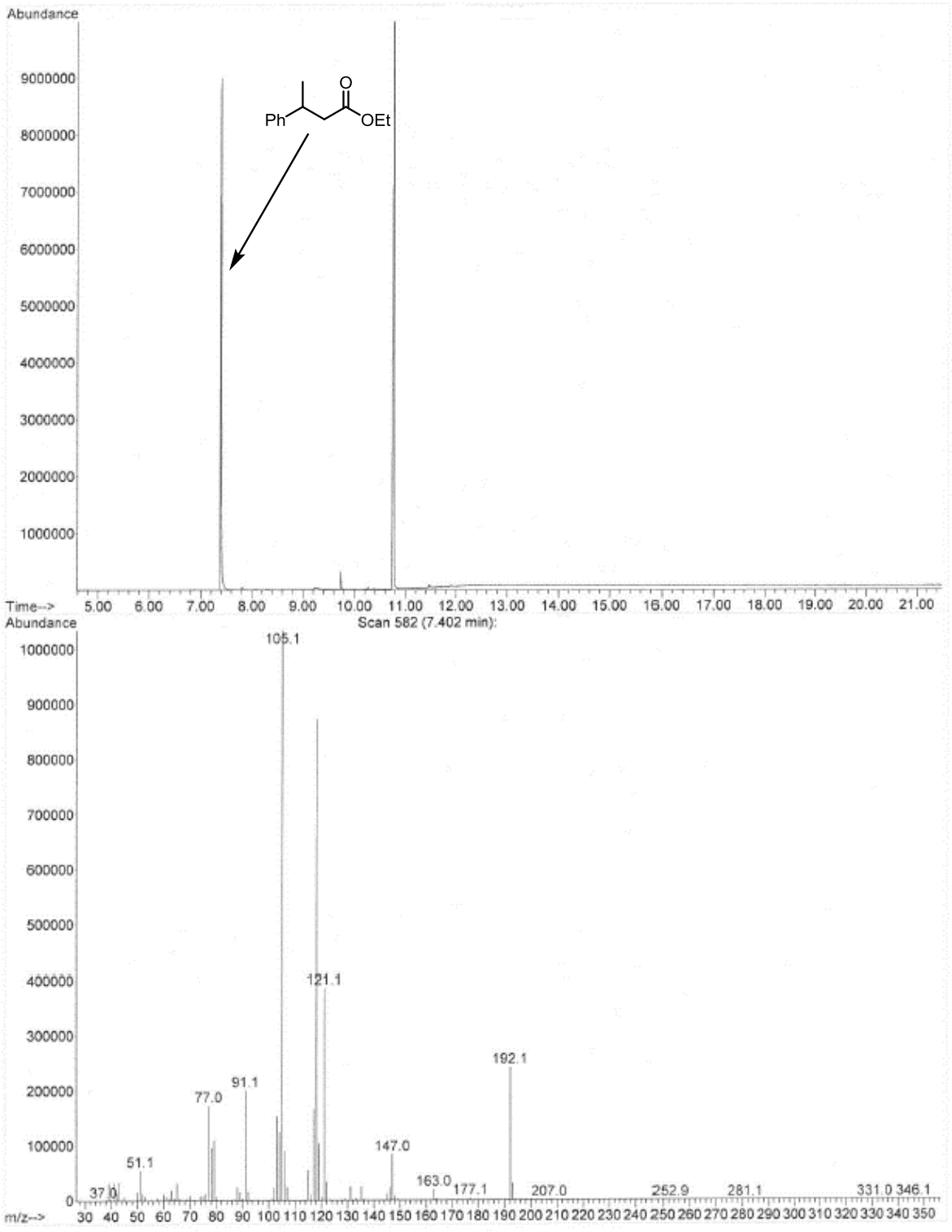
GC-data

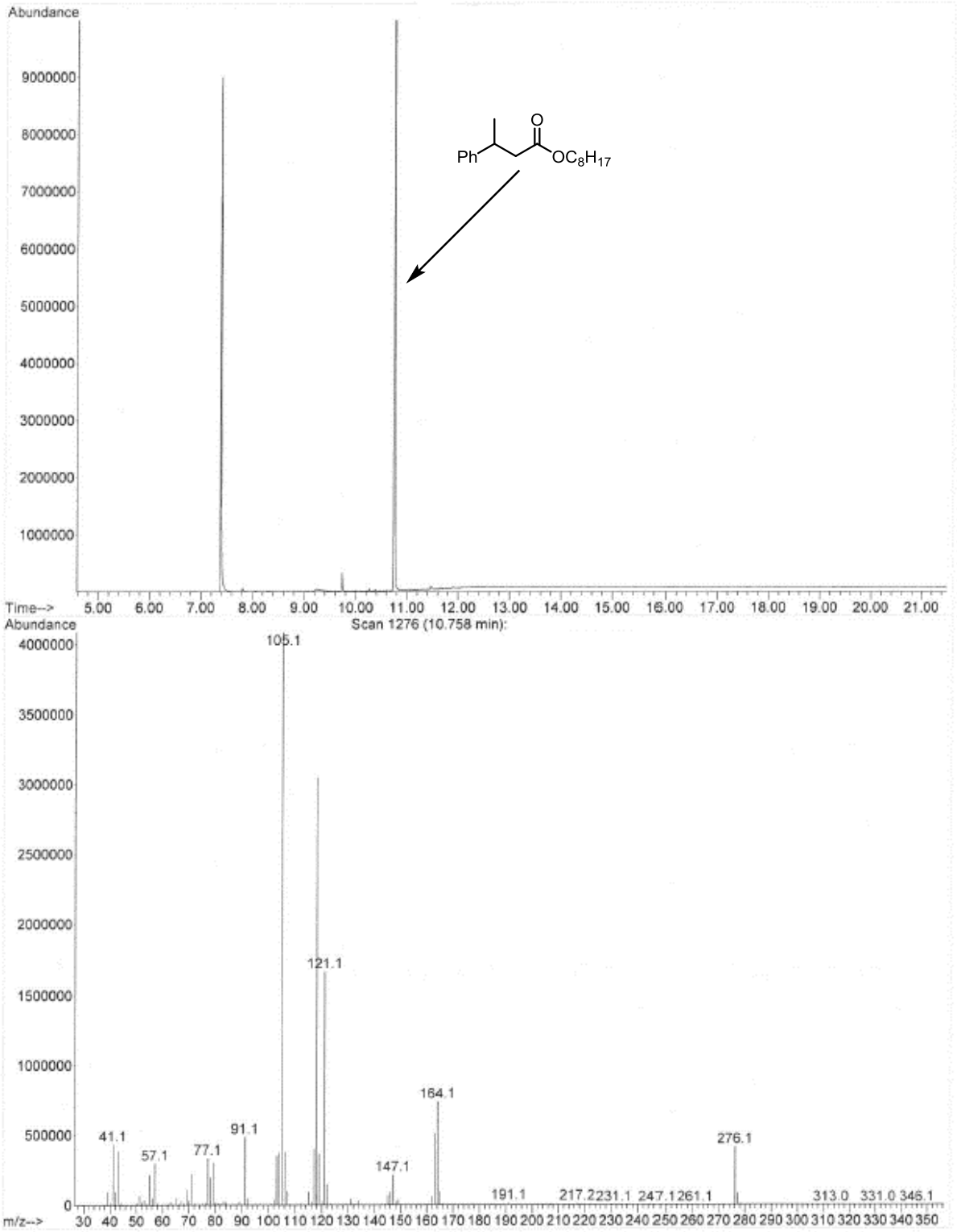


Peak results :

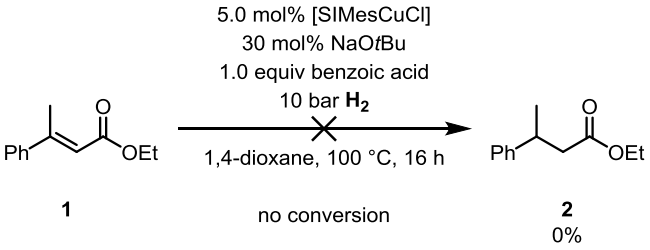
Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	5.71	36.52	259180.5	15184.1	36.518
2	UNKNOWN	9.06	63.48	621326.4	26395.8	63.482
Total			100.00	880506.9	41579.9	100.000

GC/MS-data


Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Ph
O
OEt
Time-->
5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00
Abundance
Scan 582 (7.402 min):
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
105.1
121.1
192.1
91.1
77.0
147.0
51.1
37.0
163.0
177.1
207.0
252.9
281.1
331.0 346.1
m/z-->
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350

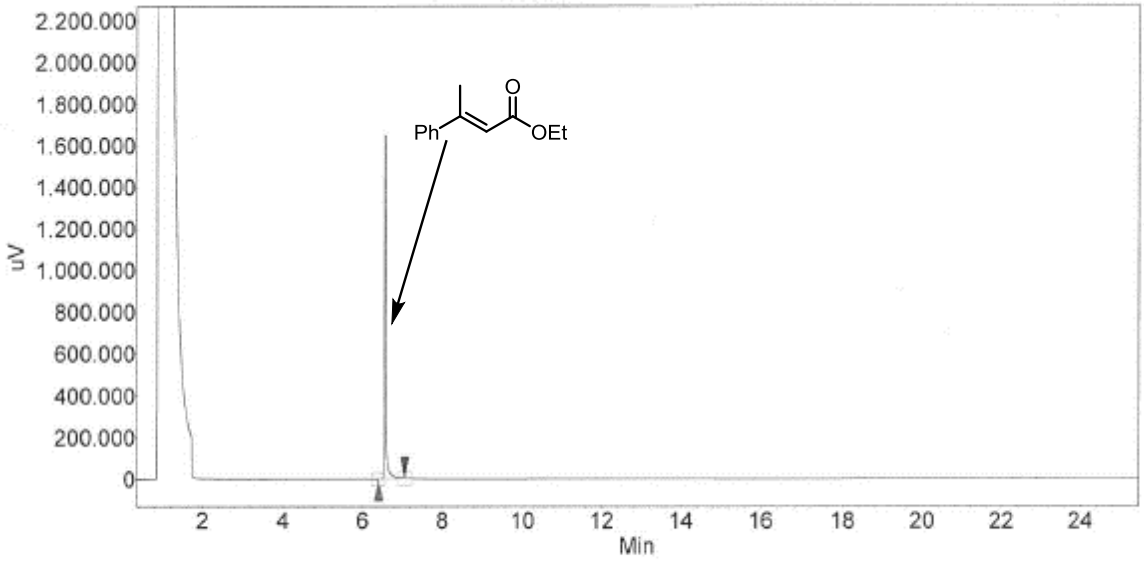

Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00
Ph
O
OC8H17
Abundance
Scan 1276 (10.758 min):
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
105.1
121.1
164.1
91.1
41.1
57.1
77.1
147.1
276.1
191.1
217.2
231.1
247.1
261.1
313.0
331.0
346.1
m/z-->
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350

4.5.1.2 Benzoic acid as additive



1 | no conversion | **2** 0%

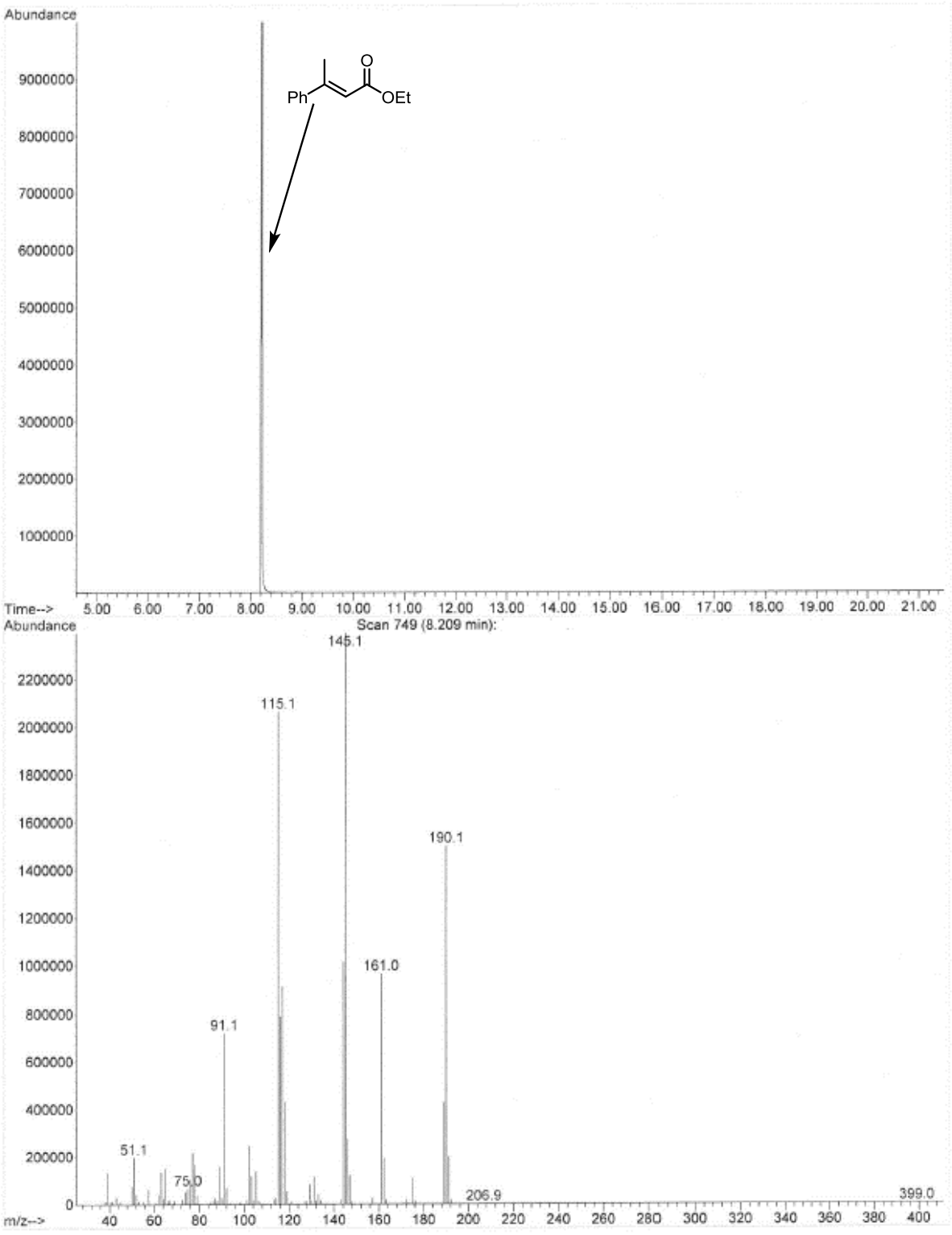
GC-data



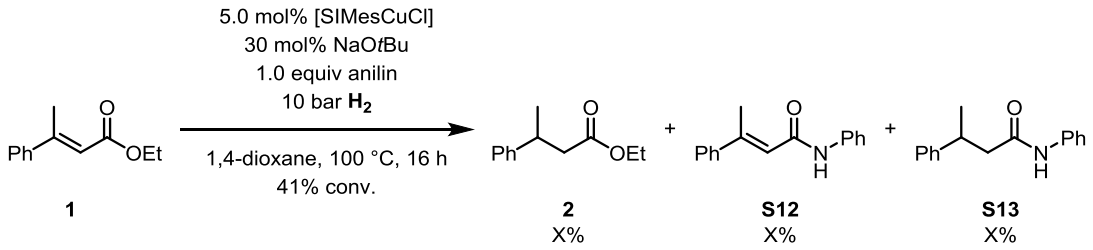
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	6.56	100.00	1649337.9	66134.0	100.000
Total			100.00	1649337.9	66134.0	100.000

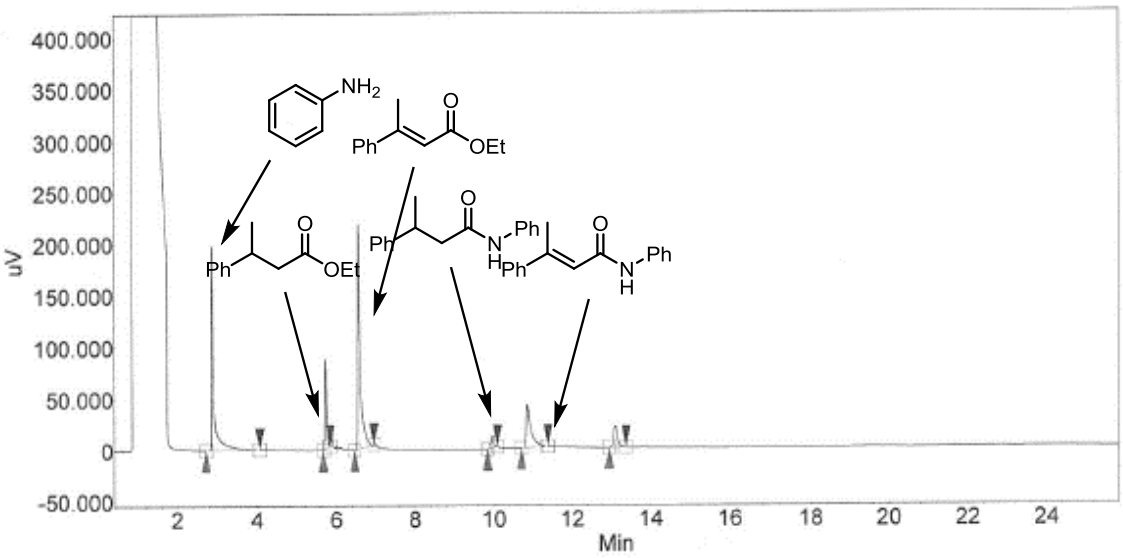
GC/MS-data


Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Ph
O
OEt
Time-->
5.00 6.00 7.00 8.00 9.00 10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00
Abundance
Scan 749 (8.209 min):
145.1
115.1
190.1
161.0
91.1
51.1
75.0
206.9
399.0
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
m/z-->
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400

4.5.1.3 Anilin as additive



GC-data



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	2.88	29.90	198626.2	12051.3	29.902
5	UNKNOWN	5.73	9.59	86987.7	3865.8	9.592
4	UNKNOWN	6.56	38.24	218050.0	15413.5	38.244
6	UNKNOWN	9.96	2.49	12578.6	1001.6	2.485
3	UNKNOWN	10.85	13.69	42289.7	5518.3	13.692
2	UNKNOWN	13.09	6.09	21185.8	2452.6	6.085
Total			100.00	579718.1	40303.1	100.000

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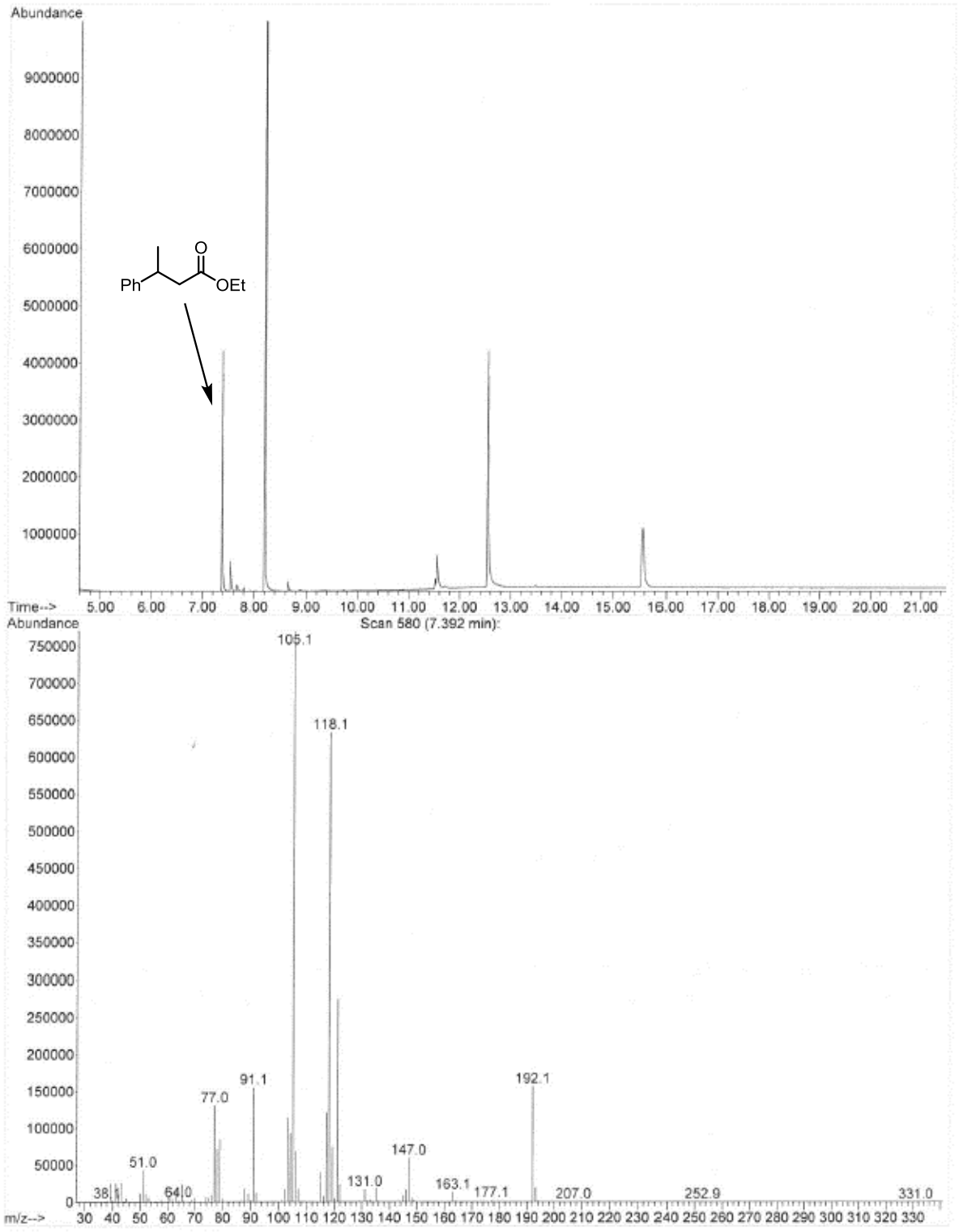
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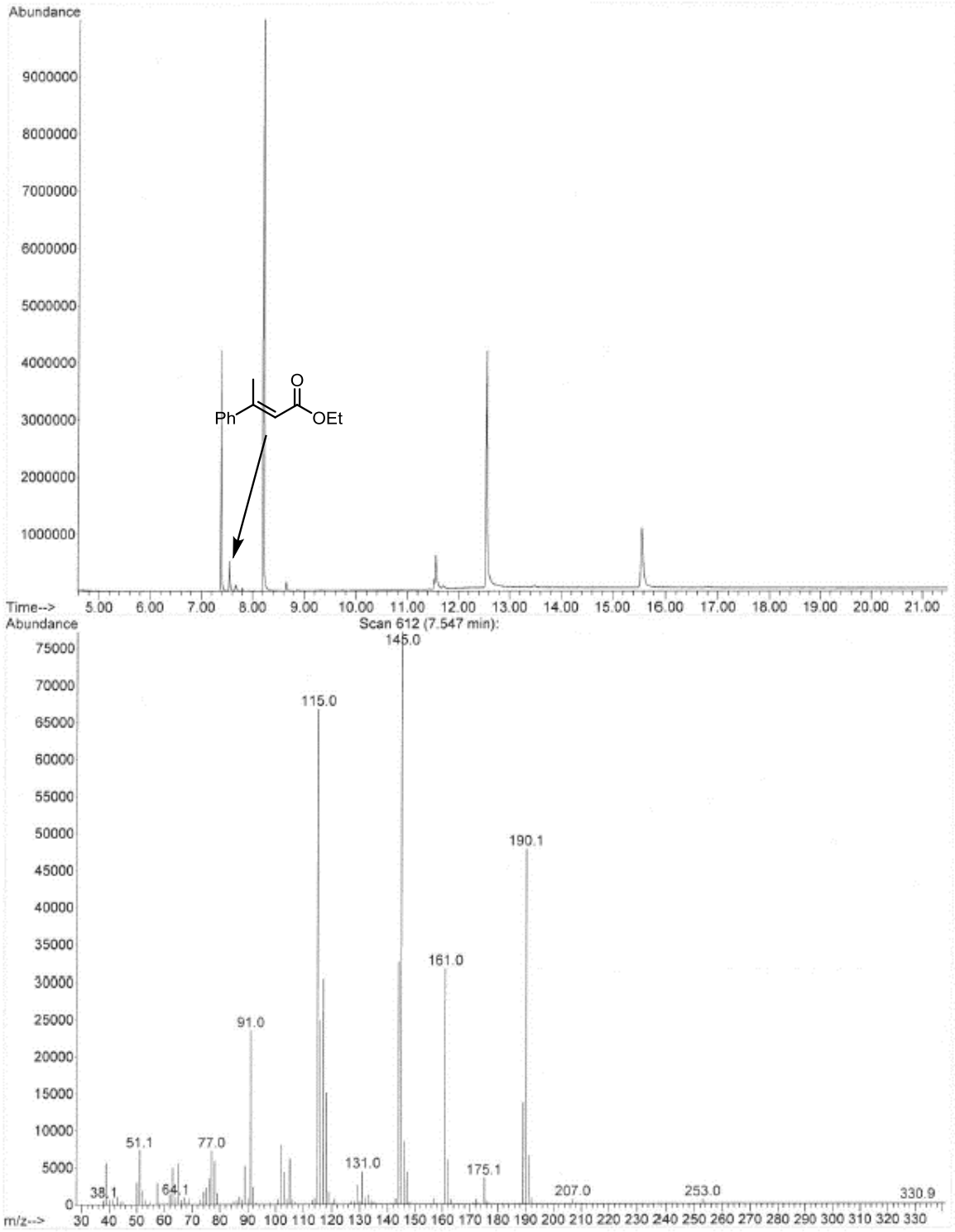
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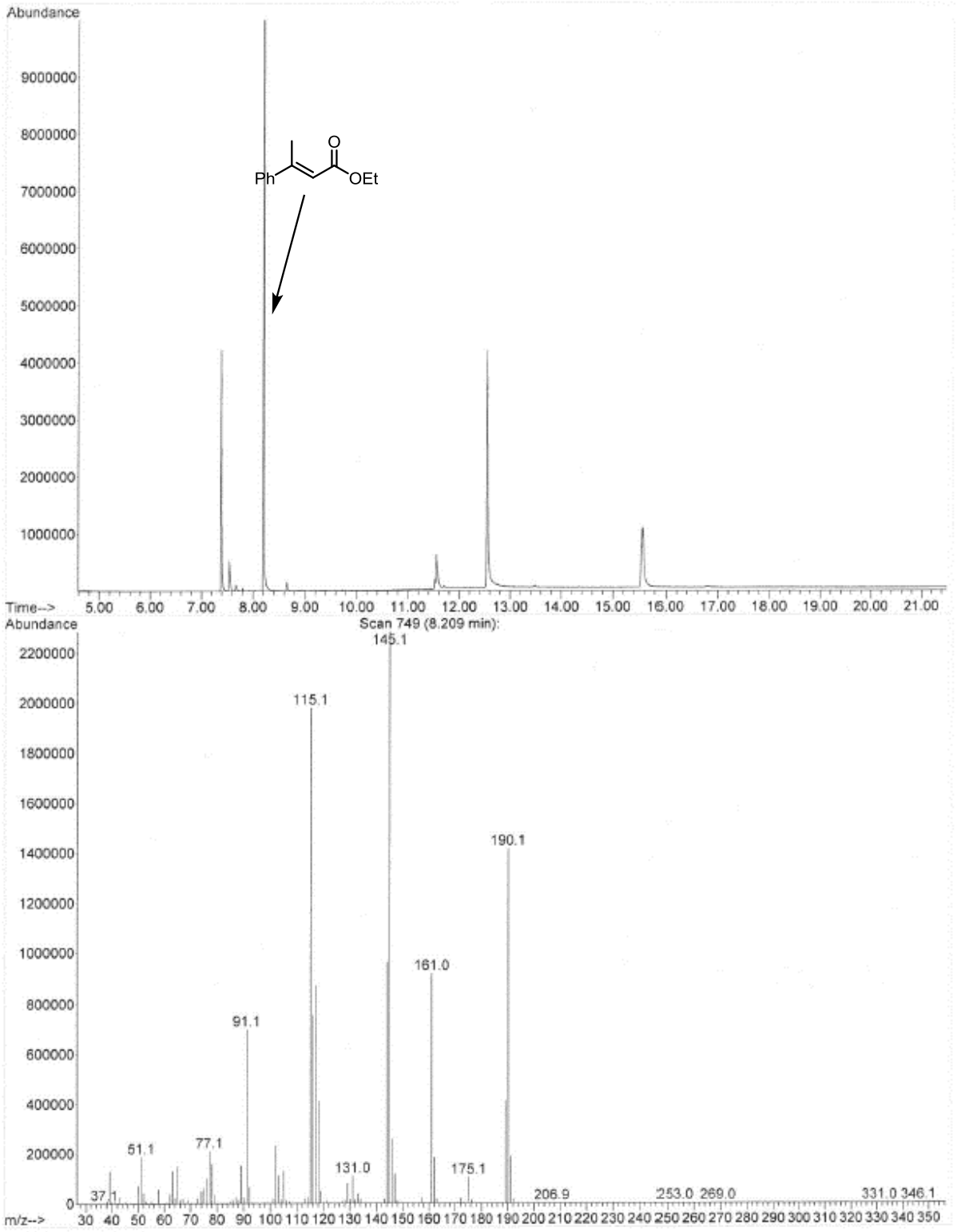
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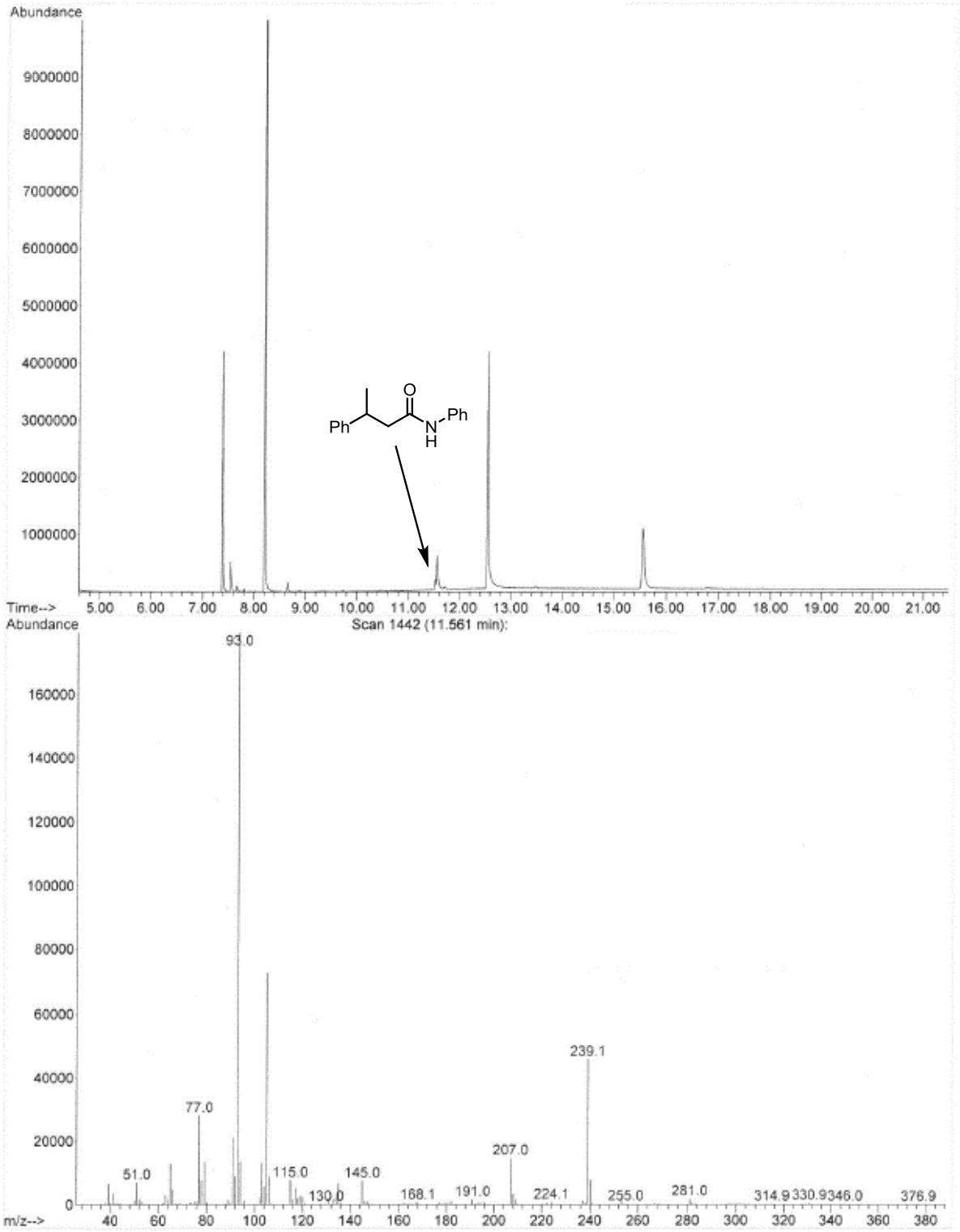
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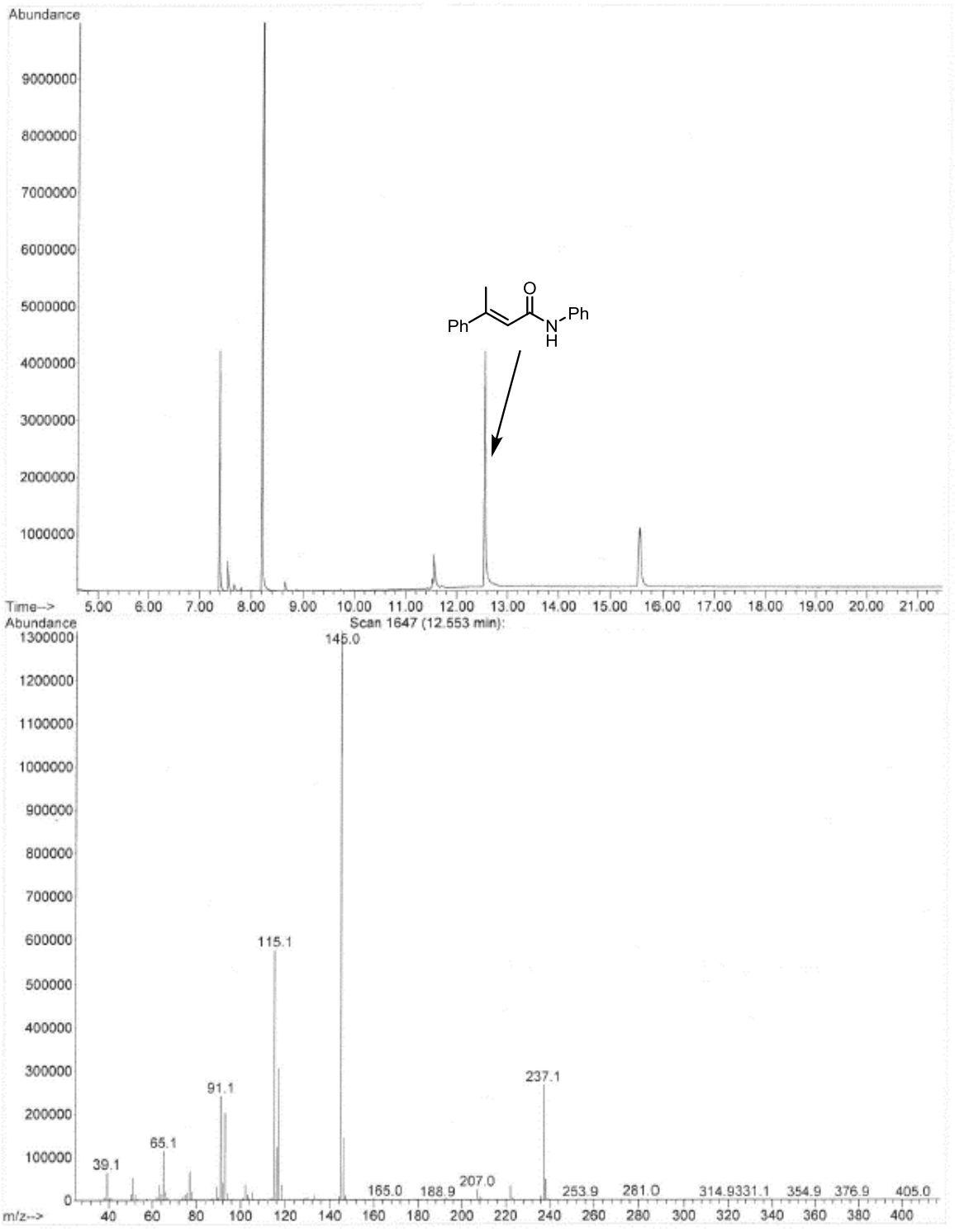
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Ph
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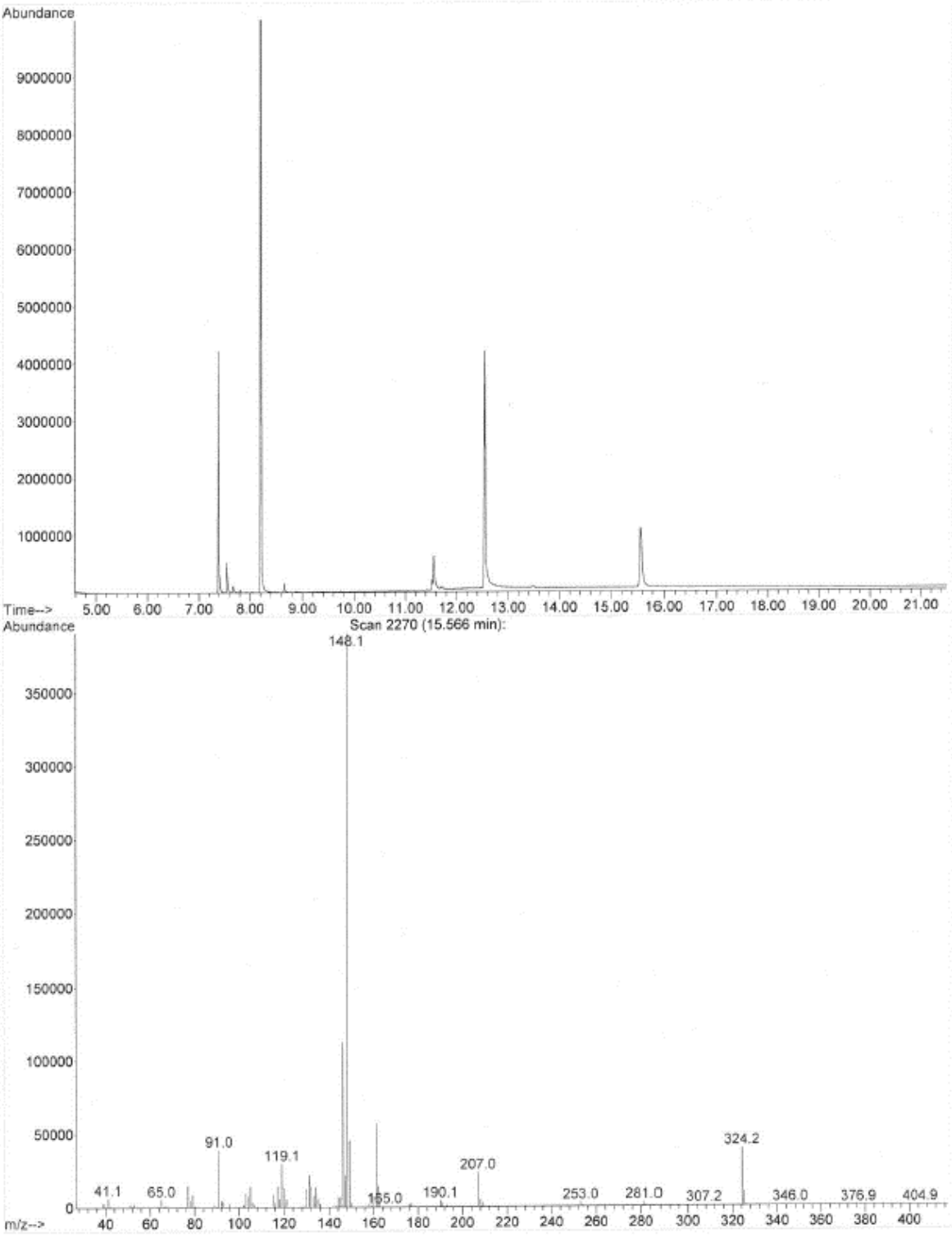
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404.9
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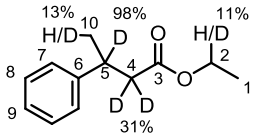
4.6 Deuteration experiments

Deuteration experiments were following **GP 2** using D_2 instead of H_2.

Deuterium incorporation was determined *via* quantitative ^{1}H NMR and comparison of two selected ^{1}H NMR signals (relaxation delay (d_1), and selected ^{1}H NMR signals with the respective substrates).

4.6.1 Ethyl 3-phenylbutanoate-d_n (2-d_n)



2-d_n
$C_{12}H_{14}D_2O_2$
Mw = 194.27

Prepared according to **GP2** from ethyl (*E*)-3-phenylbut-2-enoate (**1**, 48 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 10 mg, 25 µmol, 10 mol%) and NaO*t*Bu (14 mg, 0.15 mmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 48 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 50:1) yielded **2-d_n** as a colorless oil (38.6 mg, 0.198 mmol, 79%).

R_f = 0.48 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.15–1.20 (m, 2.9H, H-1), 1.26–1.30 (m, 2.6H, H-10), 2.49–2.63 (m, 1.4H, H-4), 4.07 (m_c, 1.8H, H-2), 7.17–7.24 (m, 3H, H-7, H-9), 7.27–7.32 (m, 2H, H-8) ppm.

^{2}H NMR (77 MHz, $CDCl_3$): δ = 1.30 (s, D-10), 2.55 (m_c, D-4), 3.25 (s, D-5), 4.07 (s, D-2) ppm.

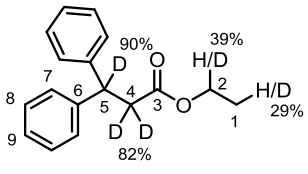
^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.3 (C-1), 21.8 (C-10), 36.6 (C-5), 43.1 (C-4), 60.3 (C-2), 126.4 (C-7)*, 126.8 (C-9)*, 128.5 (C-8), 145.8 (C-6), 172.5 (C-3) ppm. Due to low concentration C-5 could not be detected in ^{13}C NMR but was identified *via* coupling in HMBC.

HRMS (APCI) for $C_{12}H_{15}D_2O_2^+$ [(M–D+2H)$^+$] calculated: 195.1349, found: 195.1344.

IR (ATR): $\tilde{\nu}$ = 2974 (w), 1729 (s), 1603 (w), 1493 (w), 1446 (m), 1367 (m), 1324 (m), 1246 (m), 1178 (s), 1094 (m), 1031 (s), 909 (w), 849 (w), 755 (m), 697 (s) cm^{-1}.

The deuterium incorporation was determined by comparing the integrals of the corresponding ^{1}H NMR signal H-2 (δ = 4.07 ppm), H-4 (δ = 2.49–2.63 ppm), H-5 (δ = 3.27 ppm) and H-10 (δ = 1.26–1.30 ppm) with H-7/H-9 (δ = 7.17–7.24 ppm) [^{1}H NMR (700 MHz, $CDCl_3$), d_1 = 23 s].

4.6.2 Ethyl 3,3-diphenylpropanoate-d_n (9c-d_n)



9c-d_n
$C_{17}H_{15}D_3O_2$
Mw = 257.14

Prepared according to **GP2** from ethyl ethyl 3,3-diphenylacrylate (**8c**, 63 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 10 mg, 25 µmol, 10 mol%) and NaO*t*Bu (14 mg, 0.15 mmol, 30 mol%) in

1,4-dioxane (1.5 mL). The reaction mixture was stirred for 48 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 50:1) yielded **9c-*d*$_n$** as a colorless oil (48.5 mg, 0.188 mmol, 75%).

R$_f$ = 0.40 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.03–1.13 (m, 2.1H, H-1), 3.01–3.05 (m, 0.4H, H-4), 3.98–4.05 (m, 1.2H, H-2), 7.16–7.20 (m, 2H, H-9), 7.22–7.25 (m, 4H, H-7)*, 7.26–7.29 (m, 4H, H-8)* ppm.

^{2}H NMR (77 MHz, $CDCl_3$): δ = 1.15 (s, D-1), 1.27 (s, D-11), 2.51 (m_c, D-4), 3.21 (s, D-5), 4.07 (s, D-2) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.5 (C-1), 41.0 (C-4), 46.7 (C-5), 60.5 (C-2), 126.6 (C-9), 127.8 (C-7), 128.6 (C-8), 128.9 (C-6), 143.5 (C-6), 171.9 (C-3) ppm.

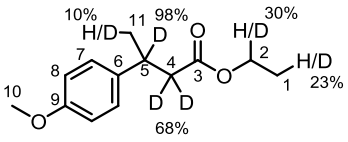
Due to low concentration C-1, C-4, C-5 and C-2 could not be detected in ^{13}C NMR but were identified *via* coupling in HMQC and HMBC.

HRMS (APCI) for $C_{17}H_{16}D_3O_2^+$ [$(M+H)^+$] calculated: 258.1568, found: 258.1562.

IR (ATR): $\tilde{\upsilon}$ = 3024 (w), 2978 (w), 2127 (w), 1726 (s), 1599 (w), 1492 (m), 1446 (m), 1351 (w), 1259 (s), 1174 (w), 1122 (m), 1024 (m), 909 (w), 741 (m), 696 (s) cm^{-1}.

The deuterium incorporation was determined by comparing the integrals of the corresponding ^{1}H NMR signal H-1 (δ = 1.03–1.13 ppm), H-2 (δ = 3.98–4.05 ppm), H-4 (δ = 3.01–3.05 ppm) and H-5 (δ = 4.53–4.55 ppm) with H-9 (δ = 7.16–7.20 ppm) [^{1}H NMR (700 MHz, $CDCl_3$), d_1 = 21 s].

4.6.3 Ethyl 3-(4-methoxyphenyl)butanoate-2,2,3-*d*$_3$ (9d-*d*$_n$)



9d-*d*$_n$
$C_{13}H_{15}D_3O_3$
Mw = 225.14

Prepared according to **GP2** from ethyl (*E*)-3-(4-methoxyphenyl)but-2-enoate (**8d**, 55 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 10 mg, 25 µmol, 10 mol%) and NaO*t*Bu (14 mg, 0.15 mmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 48 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 30:1) yielded **9d-*d*$_n$** as a colorless oil (41.4 mg, 0.184 mmol, 74%).

R$_f$ = 0.26 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.14–1.20 (m, 2.3H, H-1), 1.23–1.28 (m, 2.7H, H-11), 2.45–2.57 (m, 0.6H, H-4), 3.78 (s, 3H, H-10), 4.01–4.10 (m, 1.4H, H-2), 6.83 (m_c, 2H, H-8), 7.13 (m_c, 2H, H-7) ppm.

^{13}C NMR (125 MHz, CD_2Cl_2): δ = 13.2–14.5 (m, C-1), 21.4–22.3 (m, C-11), 35.2–36.0 (m, C-5), 42.3–43.4 (m, C-4), 55.5 (C-10), 59.7–60.7 (m, C-2), 114.1 (C-8), 128.0 (C-7), 138.3 (C-6), 158.5 (C-9), 172.5 (C-3) ppm.

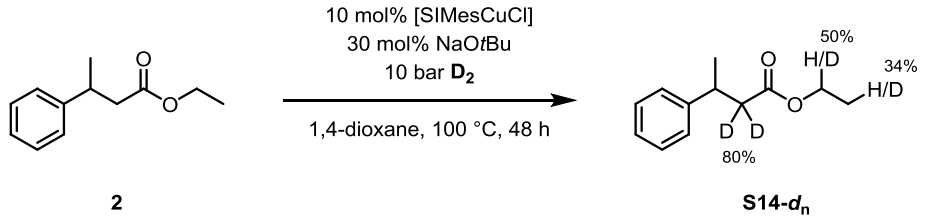
^{2}H NMR (77 MHz, $CDCl_3$): δ = 1.15 (s, D-1), 1.27 (s, D-11), 2.51 (m_c, 0.7D, D-4), 3.21 (s, D-5), 4.07 (s, D-2) ppm.

HRMS (APCI) for $C_{13}H_{16}D_3O_3^+$ [$(M+H)^+$] calculated: 226.1517, found: 226.1508.

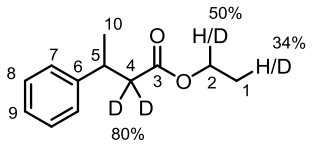
IR (ATR): $\tilde{\upsilon}$ = 2956 (w), 2835 (w), 2133 (w), 1725 (s), 1611 (m), 1511 (s), 1459 (m), 1362 (w), 1241 (s), 1176 (s), 1095 (m), 1031 (s), 829 (s) 725 (w), 633 (w) cm^{-1}.

The deuterium incorporation was determined by comparing the integrals of the corresponding ^{1}H NMR signal H-1 (δ = 1.14–1.20 ppm), H-2 (δ = 4.01–4.10 ppm), H-4 (δ = 2.45–2.57 ppm), H-5 (δ = 3.21 ppm) and H-11 (δ = 1.23–1.28 ppm) with H-10 (δ = 3.78 ppm) [^{1}H NMR (700 MHz, $CDCl_3$), d_1 = 18 s].

4.6.4 Ethyl 3-phenylbutanoate-2,2-d_2 (S14-d_n)



2 **S14-d_n**



S14-d_n
$C_{12}H_{14}D_2O_2$
Mw = 194.27

Prepared according to **GP2** from ethyl 3-phenylbutanoate (**3**, 48 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 10 mg, 25 µmol, 10 mol%) and NaO*t*Bu (14 mg, 0.15 mmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 48 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/*tert*-butyl methyl ether = 100:1) yielded **S14-d_n** as a colorless oil (26.8 mg, 0.198 mmol, 79%).

R_f = 0.48 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 9:1).

^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.12–1.19 (m, 2.0H, H-1), 1.30 (d, $^3J_{10,5}$ = 7.0 Hz, 3H, H-10), 2.48–2.63 (m, 0.4H, H-4), 3.26 (m_c, 1H, H-5), 4.02–4.10 (m, 1.0H, H-2), 7.17–7.23 (m, 3H, H-7, H-9), 7.27–7.31 (m, 2H, H-8) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.9–14.4 (m, C-1), 21.8–21.9 (m, C-10), 36.4–36.7 (m, C-5), 42.2–43.3 (m, C-4), 59.7–60.4 (m, C-2), 126.5 (C-9), 126.9 (C-7), 128.6 (C-8), 145.8 (C-6), 172.5 (C-3) ppm.

^{2}H NMR (77 MHz, $CDCl_3$): δ = 1.14 (s, D-1), 2.55 (m_c, D-4), 4.06 (s, D-2) ppm.

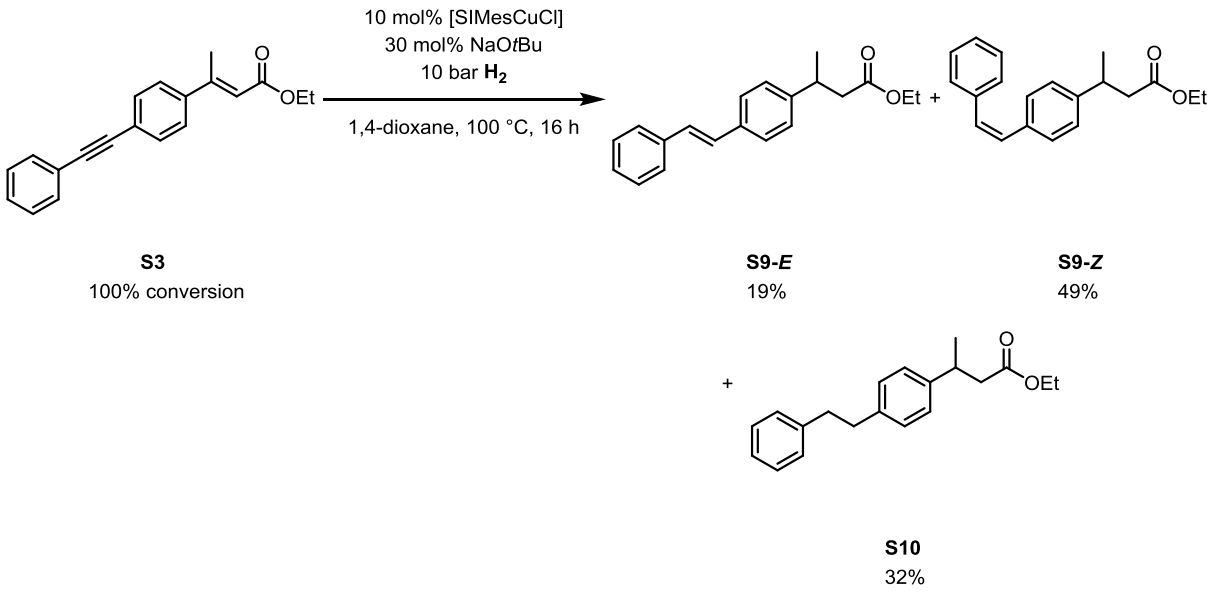
HRMS (APCI) for $C_{12}H_{14}D_3O_2^+$ [$(M+D+H)^+$] calculated: 196.1409, found: 196.1411.

IR (ATR): $\tilde{\nu}$ = 2962 (w), 2927 (w), 1731 (s), 1603 (w), 1494 (w), 1453 (w), 1376 (w), 1255 (m), 1173 (w), 802 (w), 759 (w), 700 (m) cm^{-1}.

The deuterium incorporation was determined by comparing the integrals of the corresponding ^{1}H NMR signal H-2 (δ = 4.02–4.10 ppm), H-4 (δ = 2.48–2.63 ppm) and H-1 (δ = 1.12–1.19 ppm) with H-7/H-9 (δ = 7.17–7.23 ppm) [^{1}H NMR (700 MHz, $CDCl_3$), d_1 = 23 s].

4.7 Competition with alkyne semihydrogenation

4.7.1 Ethyl 3-(4-styrylphenyl)butanoate (S9)



S3
100% conversion

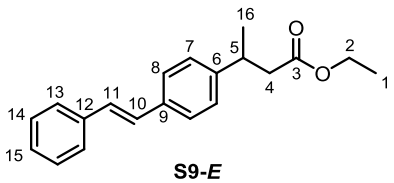
S9-*E*
19%

S9-*Z*
49%

S10
32%

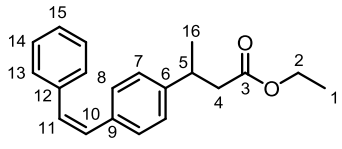
Prepared according to **GP2** from ethyl (*E*)-3-(4-(phenylethynyl)phenyl)but-2-enoate (**S3**, 69 mg, 0.25 mmol, 1.0 equiv), [SIMesCuCl] (**6**, 10.2 mg, 25.0 µmol, 10.0 mol%) and NaO*t*Bu (7.2 mg, 75 µmol, 30 mol%) in 1,4-dioxane (1.5 mL). The reaction mixture was stirred for 16 h at 100 °C. Purification by flash column chromatography on silica gel (*n*-pentane/Et_2O = 50:1) yielded a mixture of **S9-*E***, **S9-*Z*** and **S10** as a colorless oil (full conversion, 44.6 mg combined yield of **S9-*E***, **S9-*Z*** and **S10**).

$\mathbf{R_f}$ = 0.16 (SiO_2, cyclohexane/*tert*-butyl methyl ether = 50:1).



S9-*E*
$C_{20}H_{22}O_2$
Mw = 249.39

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.19 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.25–1.32 (m, 3H, H-16), 2.45–2.66 (m, 2H, H-4), 3.19–3.34 (m, 1H, H-5), 4.03–4.13 (m, 2H, H-2), 6.55 (m_c, 2H, H-10/H-11), 7.05–7.53 (m, 9H, H-7/H-8/H-13/H-14/H-15) ppm.



S9-*Z*
$C_{20}H_{22}O_2$
Mw = 249.39

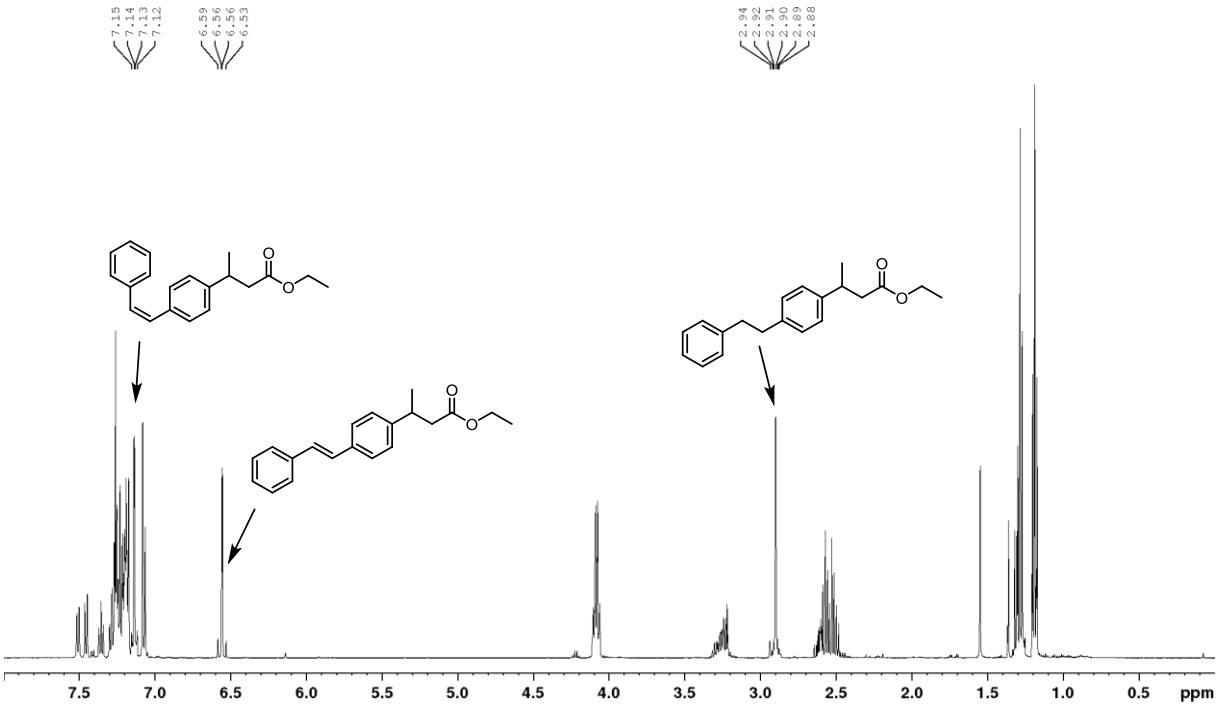
^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.18 (t, $^3J_{1,2}$ = 7.1 Hz, 3H, H-1), 1.25–1.32 (m, 3H, H-16), 2.45–2.66 (m, 2H, H-4), 3.19–3.34 (m, 1H, H-5), 4.03–4.13 (m, 2H, H-2), 7.13 (m_c, 2H, H-10/H-11), 7.05–7.53 (m, 9H, H-7/H-8/H-13/H-14/H-15) ppm.

Due to overlaying signals, ^{13}C signals have not been correlated.

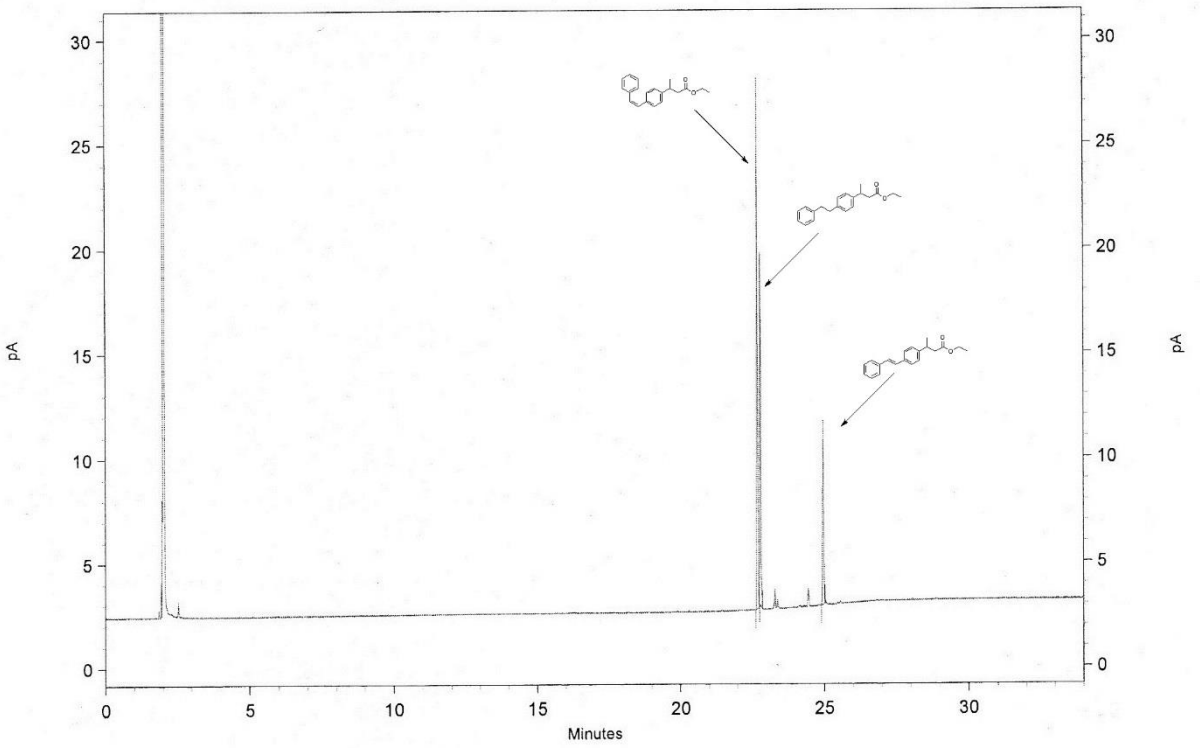
Indicative signals for the alkane product **S10** in the ^{1}H NMR are at δ = 2.89 ppm.

HRMS (APCI) for $C_{20}H_{23}O_2^+$ [$(M+H)^+$] calculated: 295.1693, found: 295.1691.

^{1}H NMR of S9


7.15
7.14
7.13
7.12
6.59
6.56
6.56
6.53
2.94
2.92
2.91
2.90
2.89
2.88
O
O
O
O
O
O
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
ppm

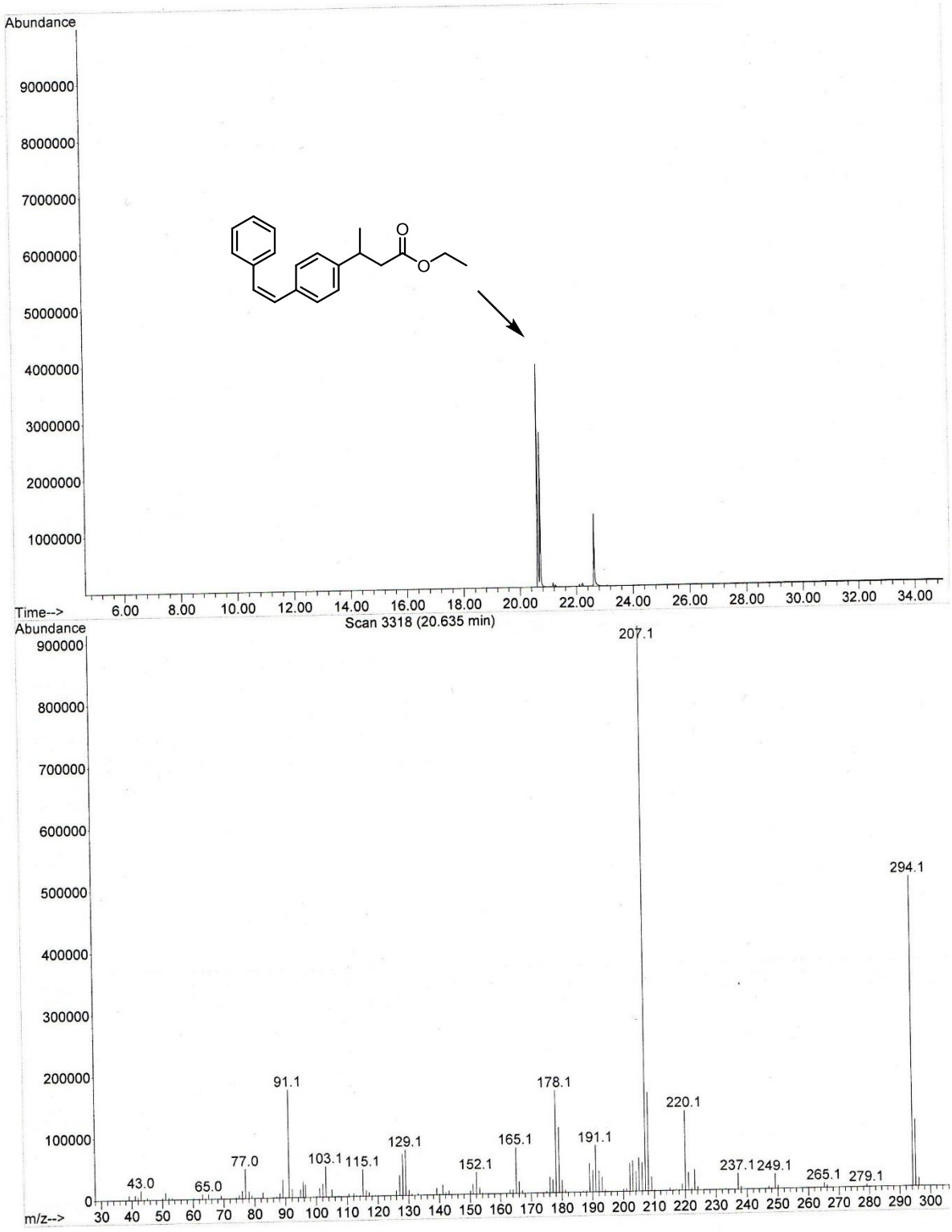
GC of S9



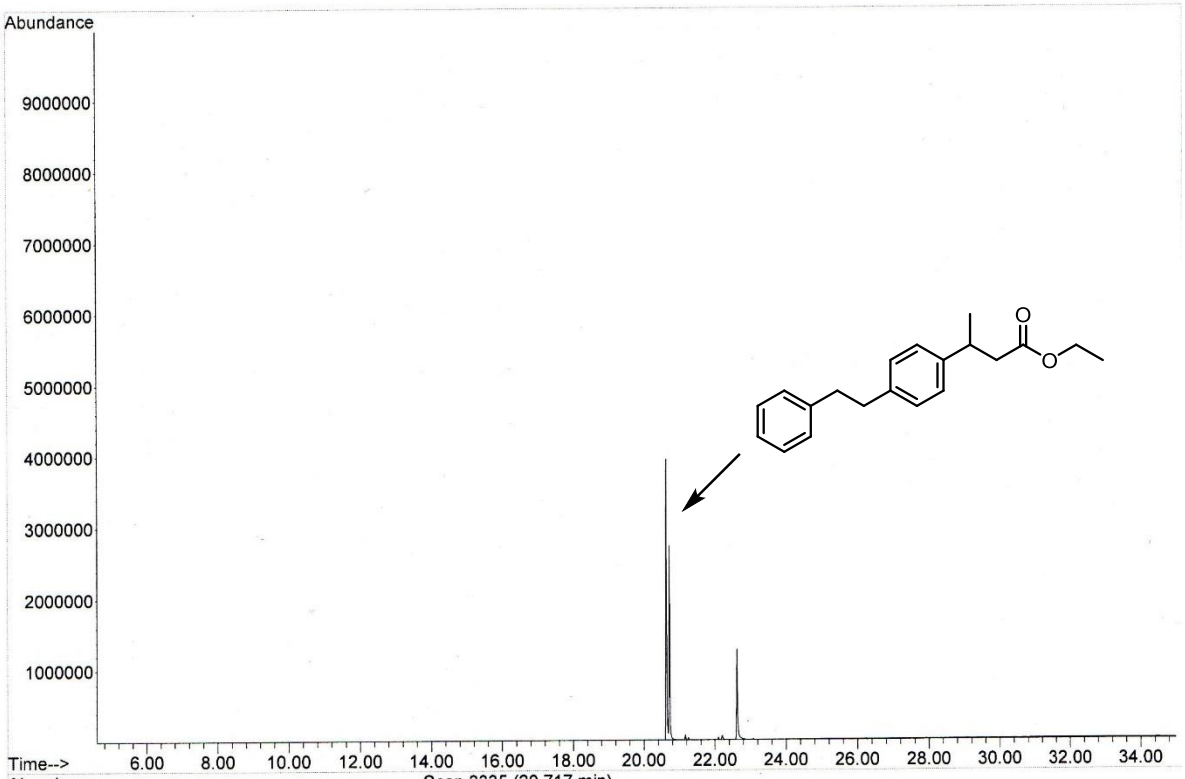
Back
Signal
Results

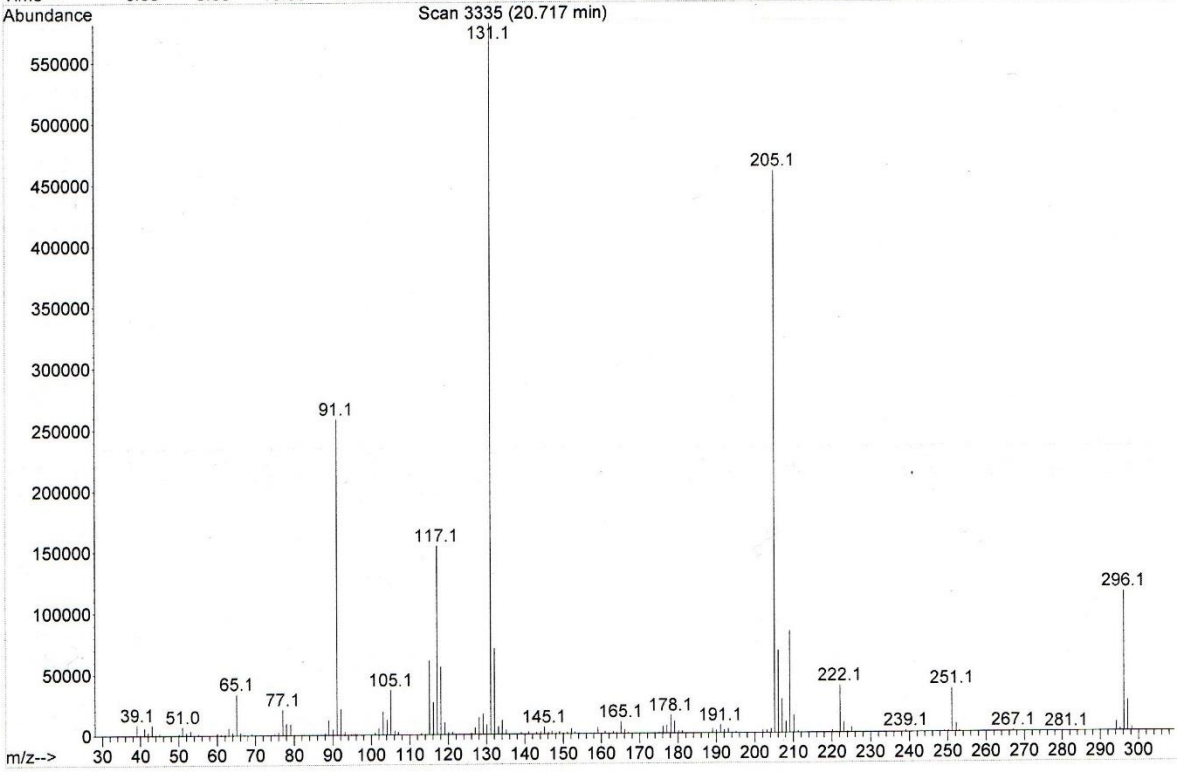
Peak #	Retention Time	Height	Height Percent	Area	Area Percent
1	22,6897	195053	49,7130	429181	49,0139
2	22,8000	129937	33,1170	278477	31,8030
3	24,9660	67368	17,1700	167974	19,1832
Totals		392358	100,0000	875632	100,0000

GC/MS of S9-*Z*

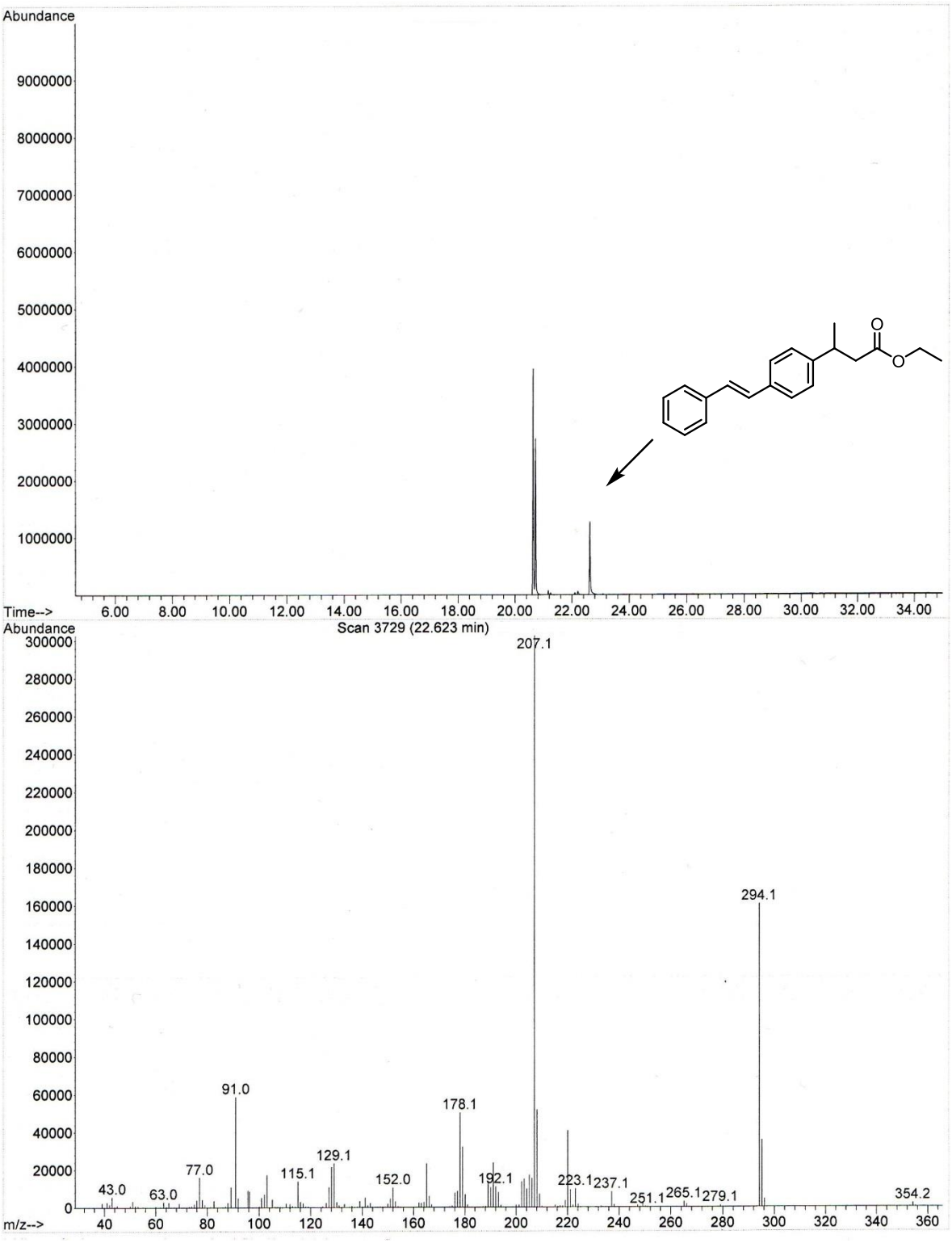

Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
Scan 3318 (20.635 min)
Abundance
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
m/z-->
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300
207.1
294.1
91.1
178.1
220.1
129.1
165.1
191.1
77.0
103.1
115.1
152.1
237.1
249.1
265.1
279.1
43.0
65.0

GC/MS of S10


Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
O
O

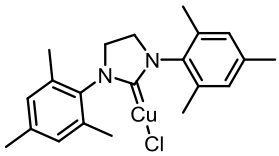

Abundance
Scan 3335 (20.717 min)
131.1
205.1
91.1
117.1
296.1
222.1
251.1
65.1
77.1
105.1
39.1
51.0
145.1
165.1
178.1
191.1
239.1
267.1
281.1
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
m/z-->
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300

GC/MS of S9-*E*


Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
O
O
Abundance
Scan 3729 (22.623 min)
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
207.1
294.1
91.0
178.1
129.1
77.0
115.1
152.0
192.1
223.1
237.1
251.1
265.1
279.1
43.0
63.0
354.2
m/z-->
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360

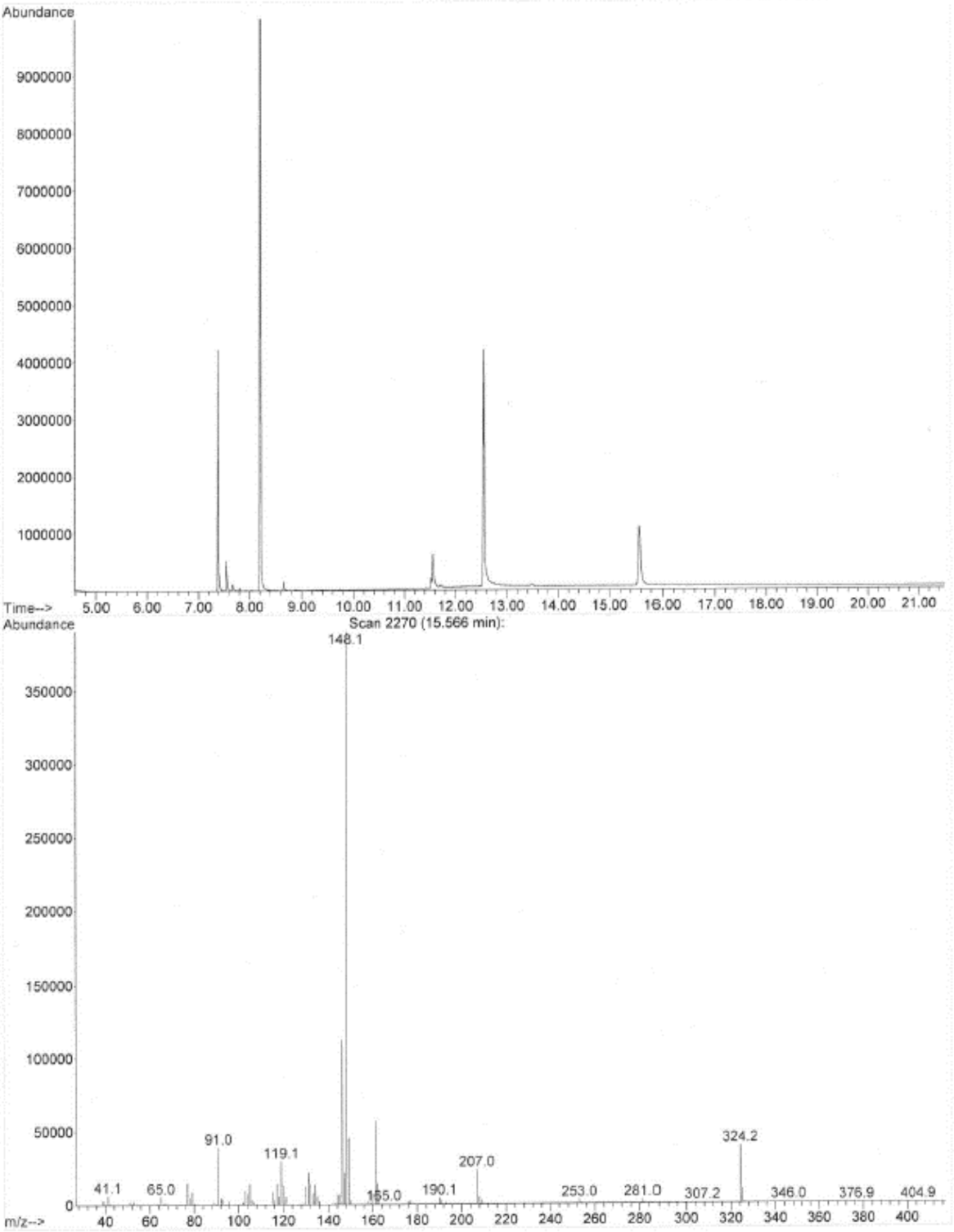
4.8 Circumstantial evidence for possible recycling and re-isolation of the catalyst [SIMesCuCl] (6)

To address the issue of the homogeneous or hetergenous nature of the catalyst, attempts have been carried out to re-isolate the catalyst (**6**), by quenching the standard conjugate reduction reaction with HCl in Et_2O. These experiments have failed to deliver the desired complex **6**. However, in various catalytic conjugate reductions of enoates employing compound **6** as catalyst, we have identified the corresponding mass (Mw = 404) by GC/MS analysis. (see below for a representative GC/MS trace).



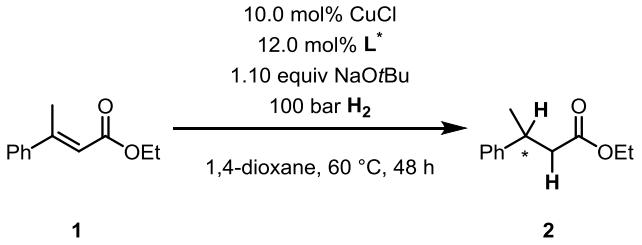
[SiMesCuCl] (**6**)
$C_{21}H_{26}ClCuN_2$
Mw: 404,11

From the reaction of **1** with anilin as additive (see section 4.5.1.3): Note the peak at 15.56 min.

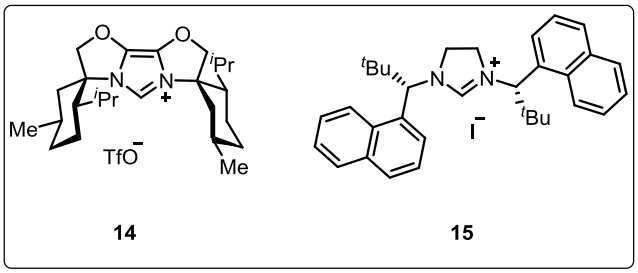


5 Asymmetric conjugate reduction of α,β-unsaturated esters

5.1 General procedure 3 – asymmetric conjugate reduction (GP3)



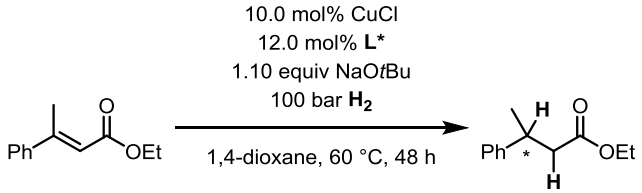
1 **2**



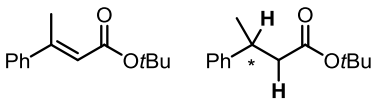
14 **15**

In a glass vial equipped with a septum, CuCl (99.99%, 2.0 mg, 20 µmol, 10 mol%) and L* (24 µmol, 12 mol%) are placed and the vial is transferred into a glovebox. Dried NaO*t*Bu (21.4 mg, 0.222 mmol, 1.10 equiv) is added and the solids are dissolved in 1,4-dioxane (1 mL). The mixture is stirred for 10 min at 40 °C. The degassed α,β-unsaturated ester **1** (38.4 mg, 0.202 mmol, 1.00 equiv) is dissolved in 1,4-dioxane (0.2 mL) and transferred to the reaction vial. The vial is placed in an autoclave and the septum is pierced with a needle under N_2-counterflow. The autoclave is purged with H_2 (3 x 10 bar). The reaction mixture is stirred for 48 h at 60 °C under H_2-atmosphere (100 bar). The crude reaction mixture is filtered over a small plug silica (eluent: CH_2Cl_2, 0.5 x 3 cm, 10 mL) and all volatiles are removed under reduced pressure. The crude product **2** is purified by flash column chromatography on silica gel.

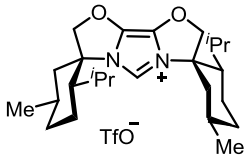
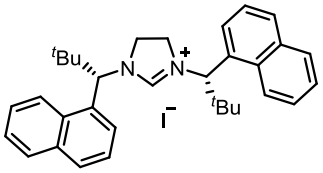
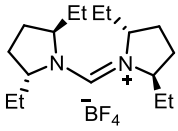
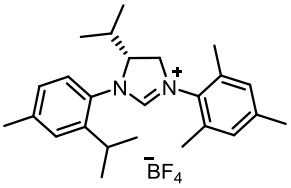
Table S7: Asymmetric conjugate reduction – Ligand screening.[a]



1 **2**

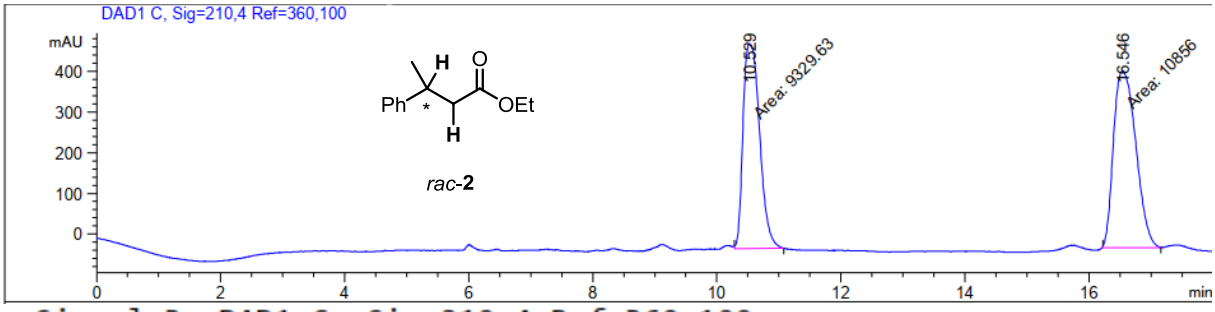


8b **9b**

Entry	Ligand L*	Conv [%][b]	comment	e.r. of 2[c]
1	 **14**	71%	67% **2** 23% **9b** 10% **8b**	82:18
2	 **15**	100%	81% **2** 19% **9b**	78:22
3	 **S15**	89%	69% **2** 27% **9b** 4% **8b**	63:37
4	 **S16**	100%	74% **2** 26% **9b**	53:47

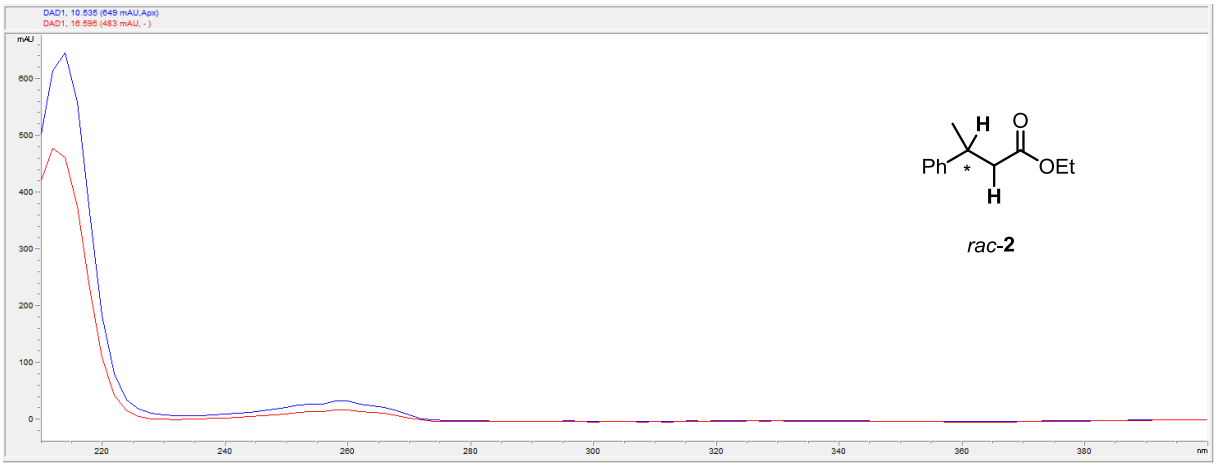
[a] All reactions with 2.0 µmol [Cu] in 1.2 mL solvent.. [b] Determined by GC analysis. [c] Determined by HPLC, OD-H, *n*-heptane/*i*PrOH = 98:2, 0.5 mL/min, 20 °C, 30 bar.

HPLC data for racemic mixture

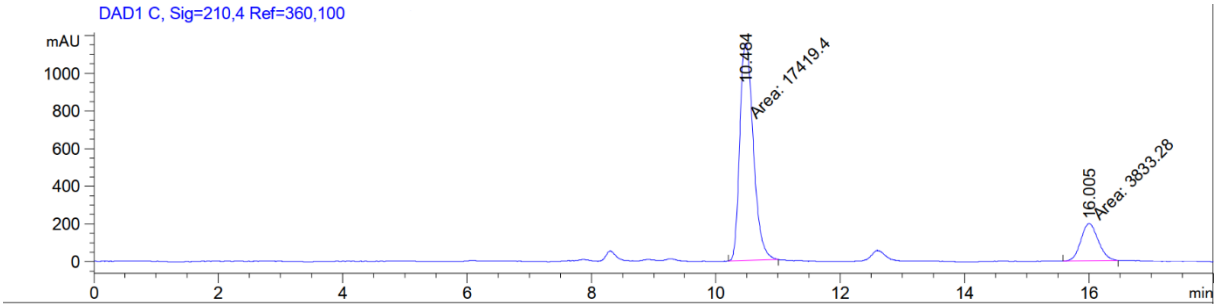


Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.529	MM	0.3088	9329.62891	503.57388	46.2191
2	16.546	MM	0.4167	1.08560e4	434.18994	53.7809
Totals :				2.01857e4	937.76382	

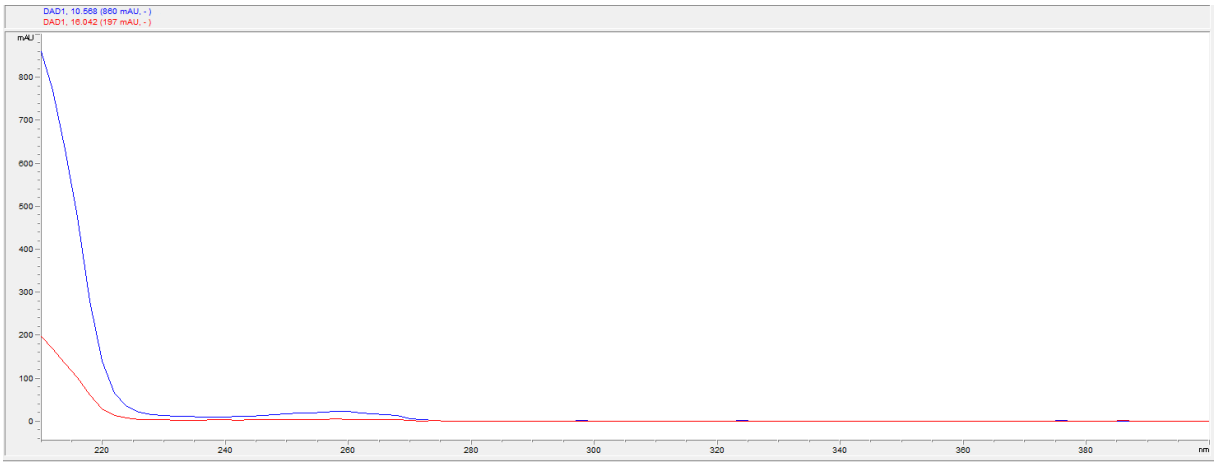


HPLC data for 2 with 14, table S7, entry 1

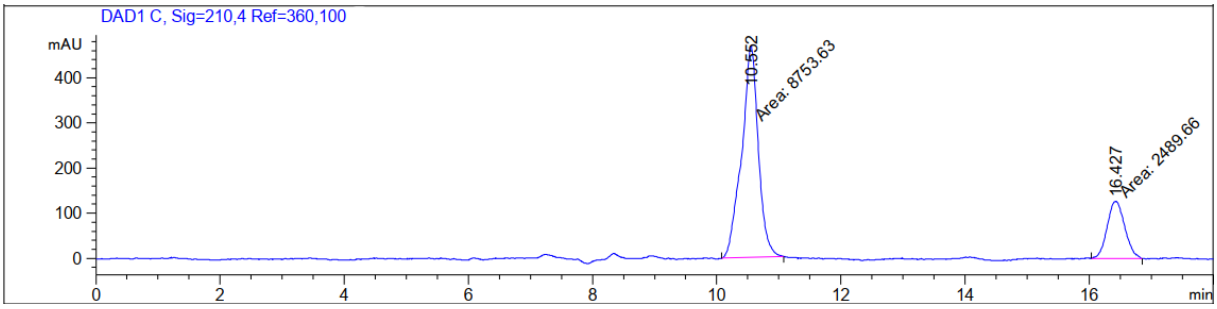


Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.484	MM	0.2518	1.74194e4	1152.90198	81.9633
2	16.005	MM	0.3233	3833.27954	197.61829	18.0367
Totals :				2.12527e4	1350.52026	

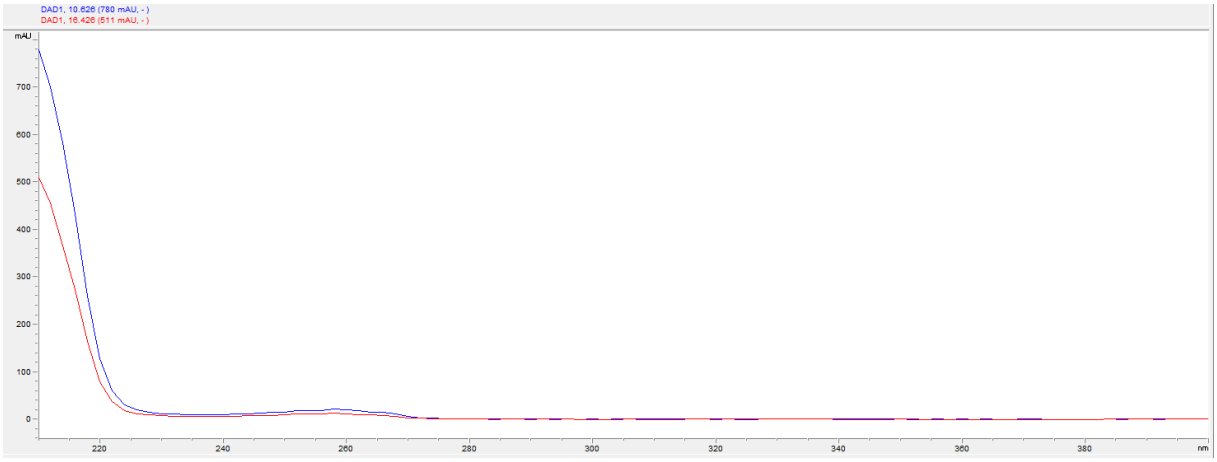


HPLC data for 2 with 15, table S7, entry 2:

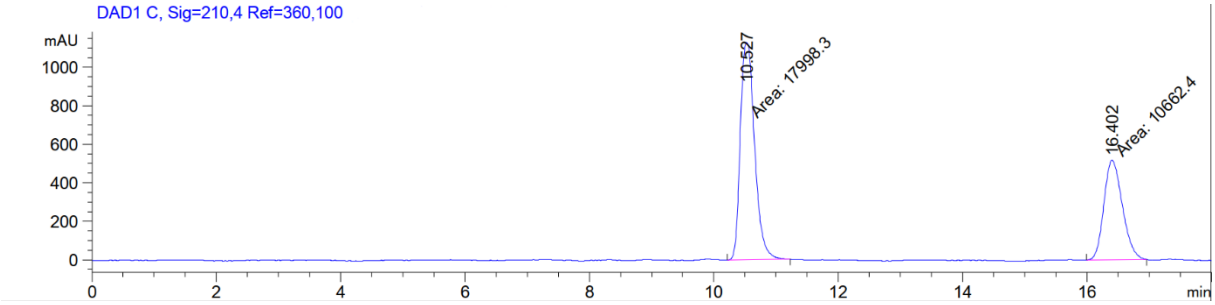


Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.552	MM	0.3109	8753.63086	469.27487	77.8565
2	16.427	MM	0.3289	2489.65576	126.16525	22.1435
Totals :				1.12433e4	595.44012	

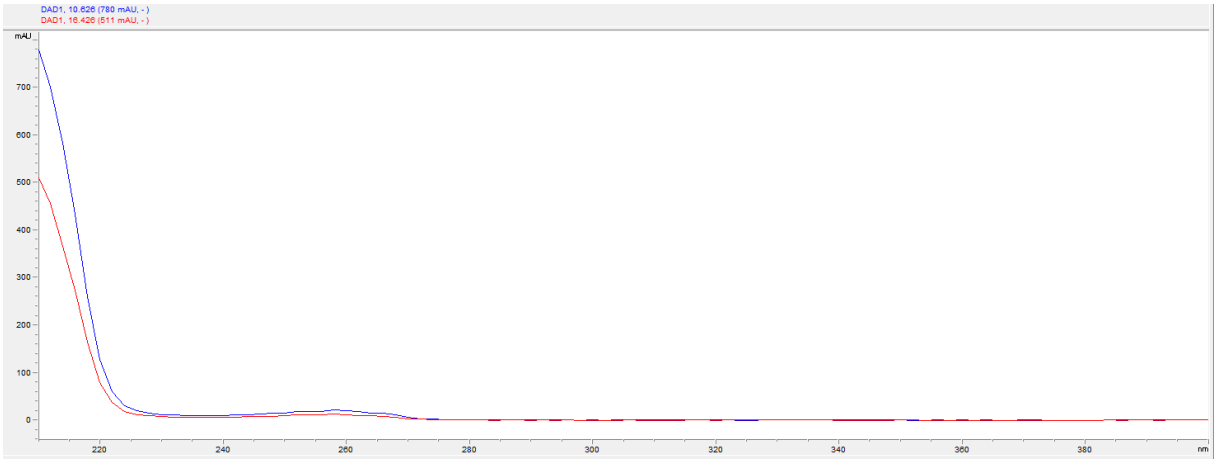


HPLC data for 2 with S15, table S7, entry 3:

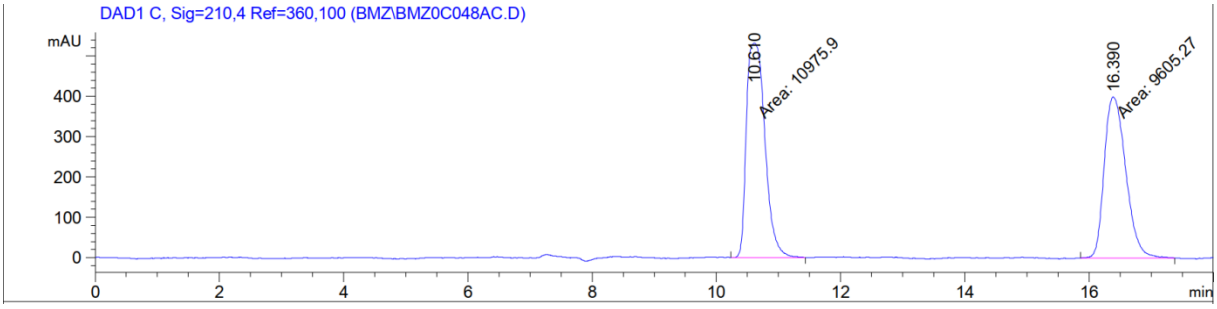


Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.527	MM	0.2658	1.79983e4	1128.76367	62.7978
2	16.402	MM	0.3433	1.06624e4	517.70624	37.2022

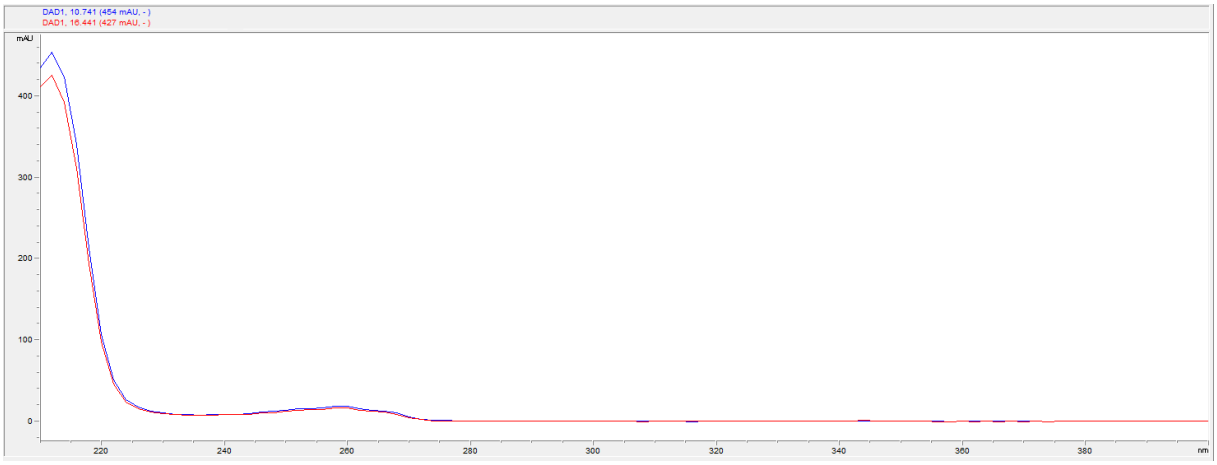


HPLC data for 2 with S16, table S7, entry 4:



Signal 3: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.610	MM	0.3442	1.09759e4	531.48633	53.3297
2	16.390	MM	0.4014	9605.26758	398.84921	46.6703
Totals :				2.05811e4	930.33554	



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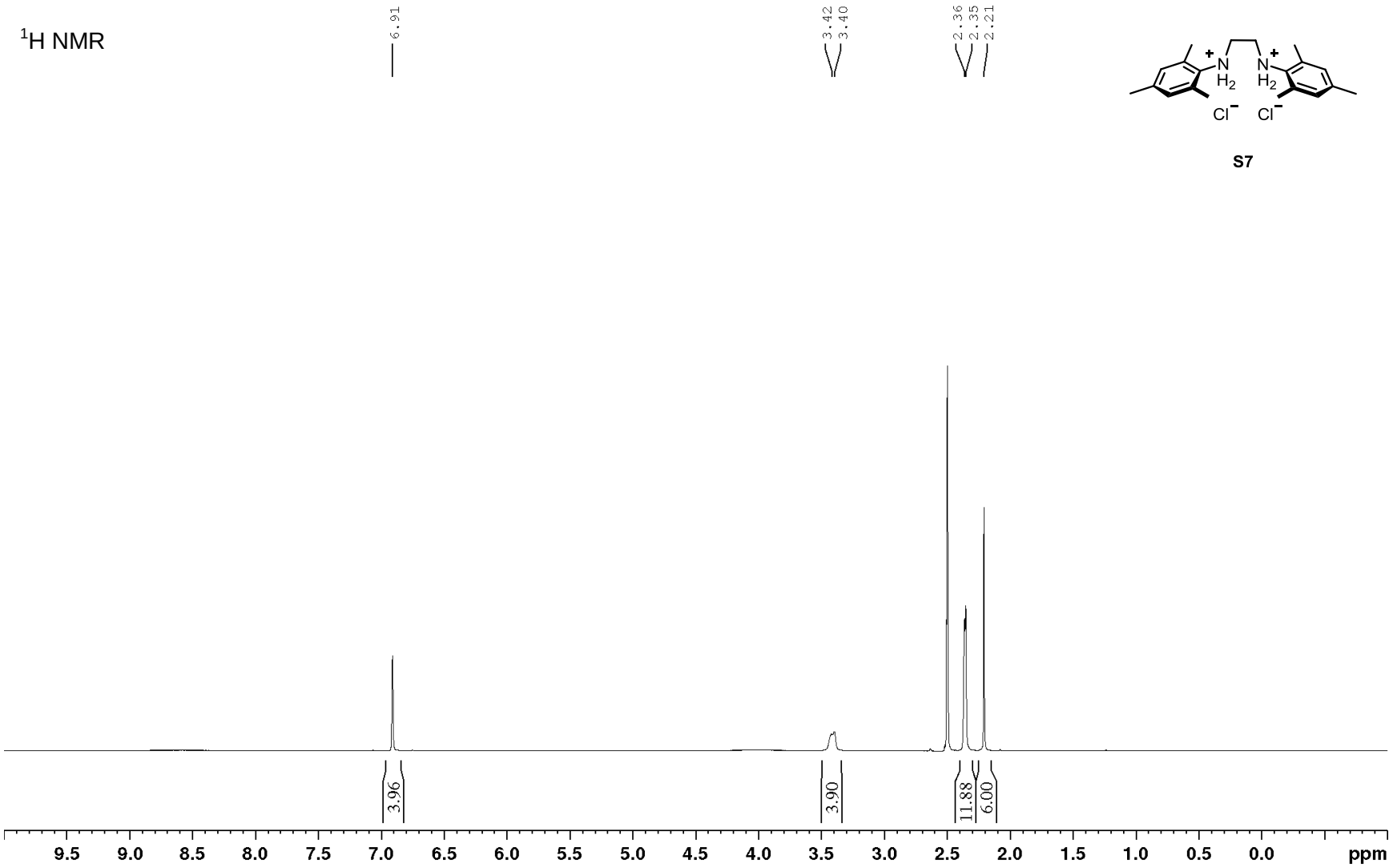
7 Spectra

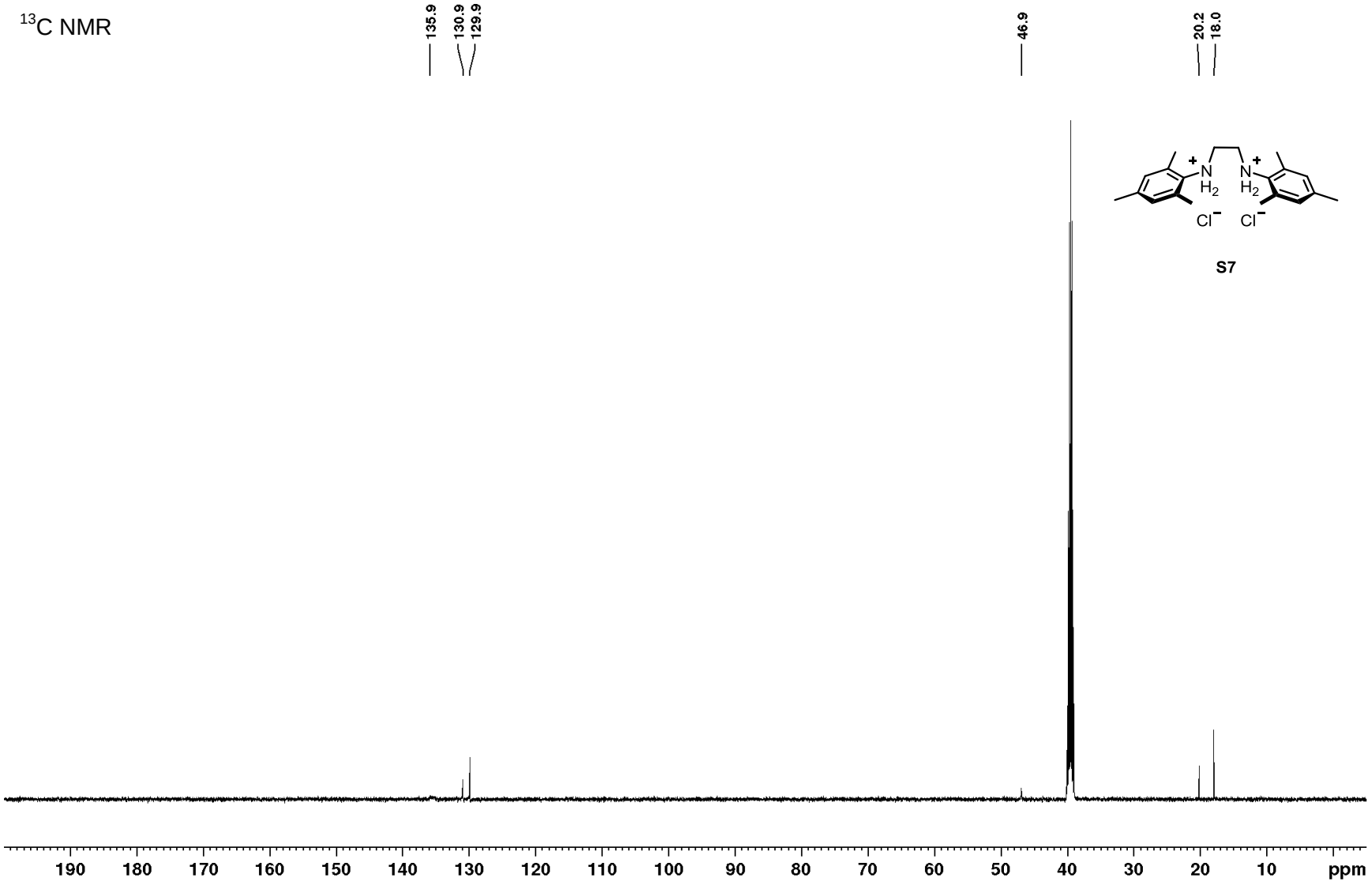
***N*[1],*N*[2]-dimesitylethane-1,2-diaminium chloride (S7)**

^{1}H NMR



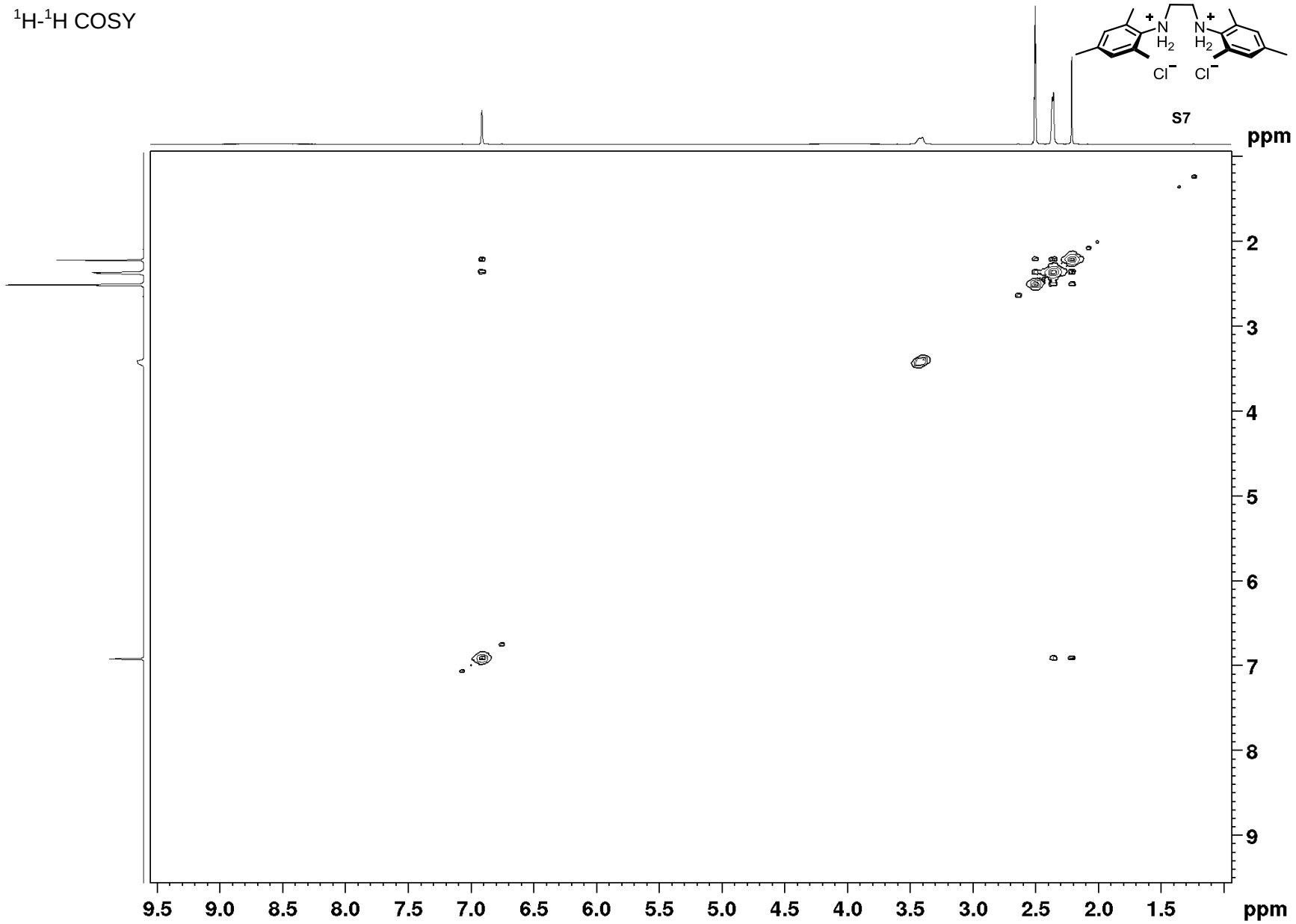
S7

^{13}C NMR

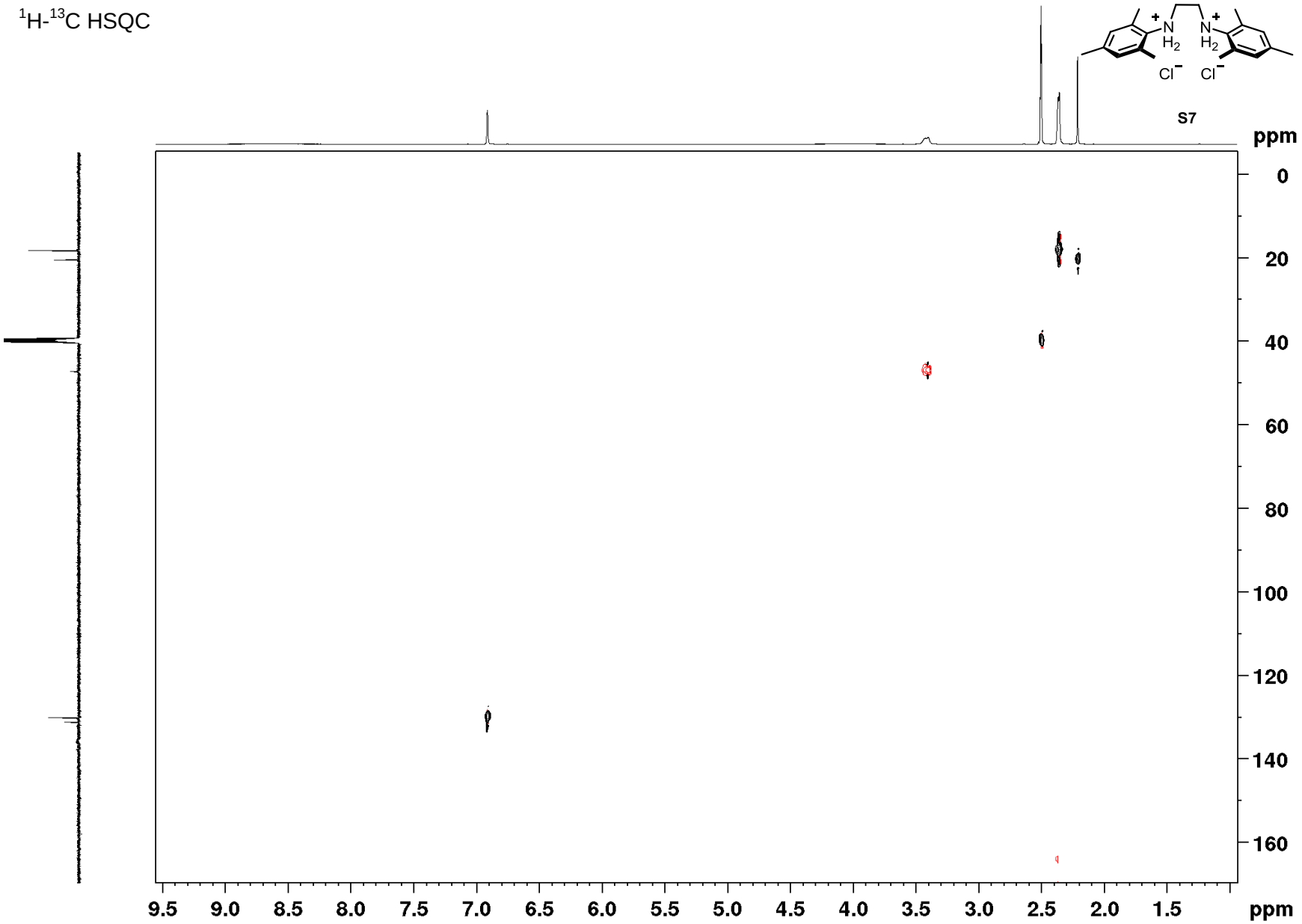

135.9
130.9
129.9
46.9
20.2
18.0
N
H2
N
H2
Cl−
Cl−
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

S7

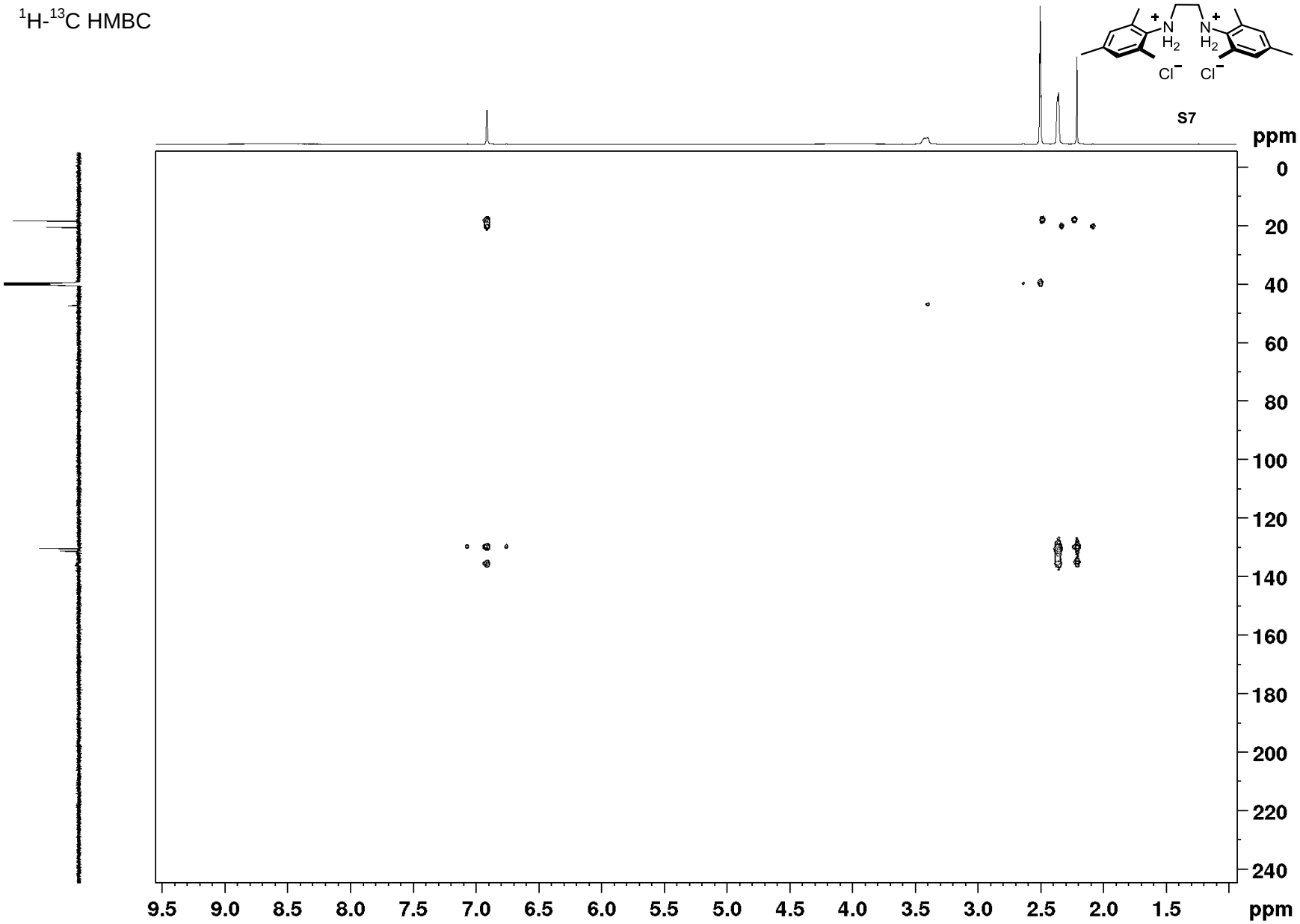
^{1}H-^{1}H COSY

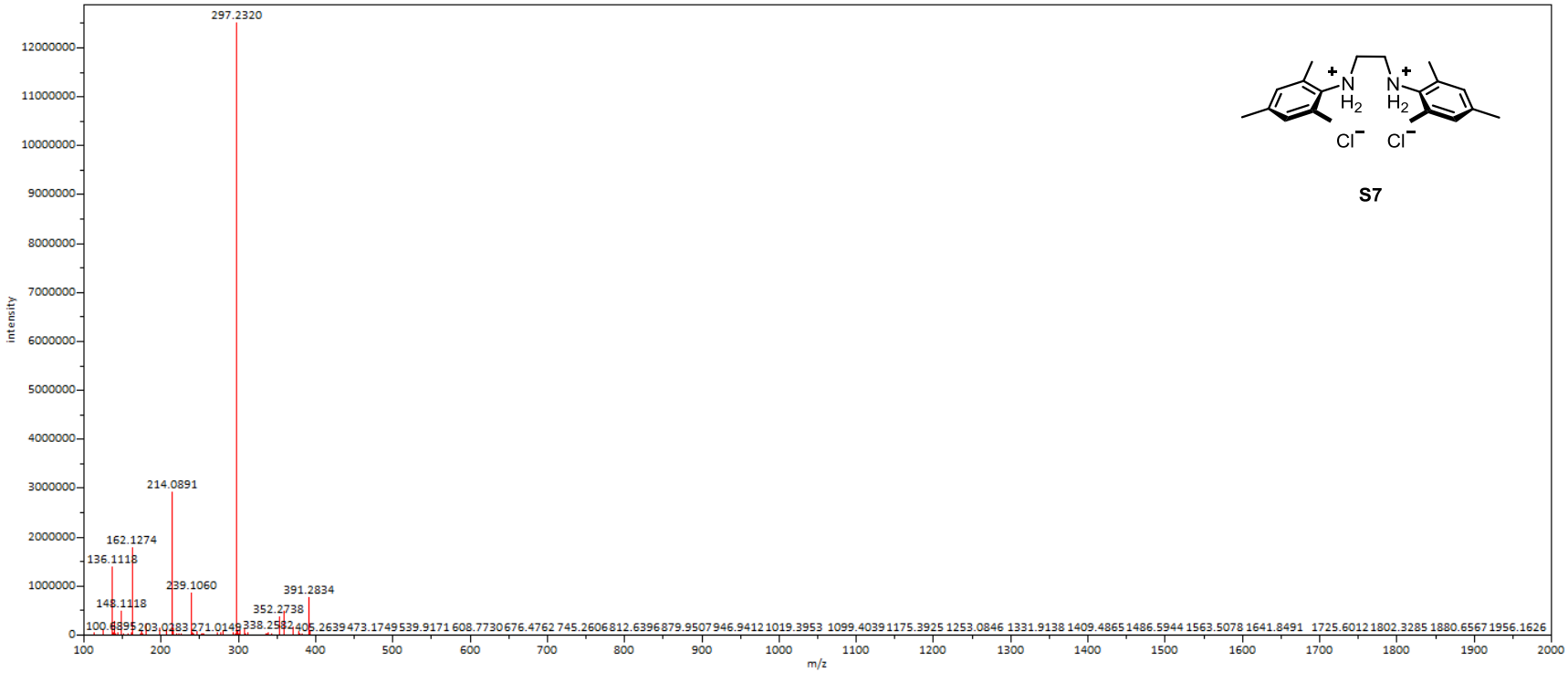

S7
ppm
2
3
4
5
6
7
8
9
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

^{1}H-^{13}C HSQC


S7
ppm
0
20
40
60
80
100
120
140
160
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

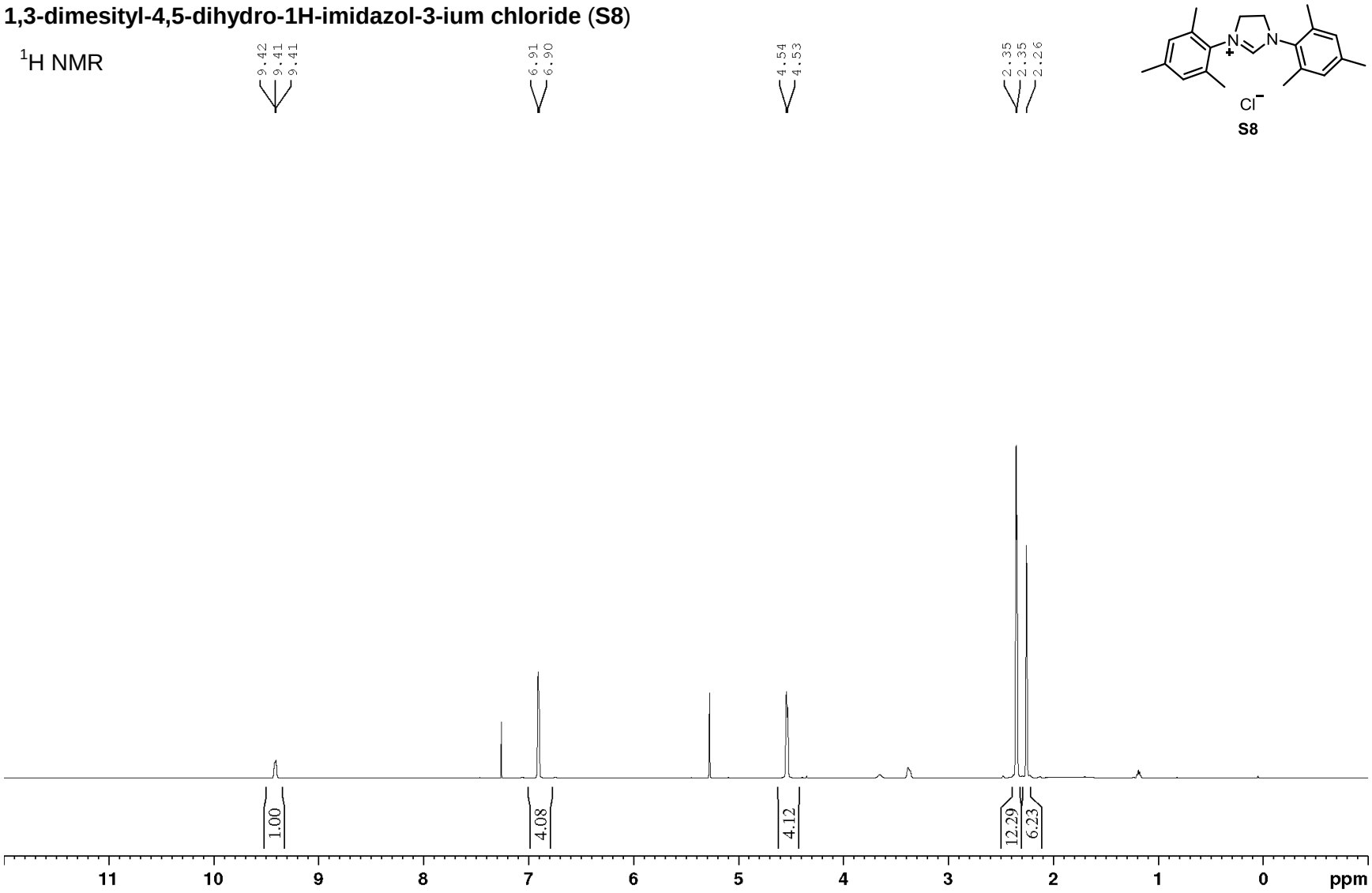
^{1}H-^{13}C HMBC


S7
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

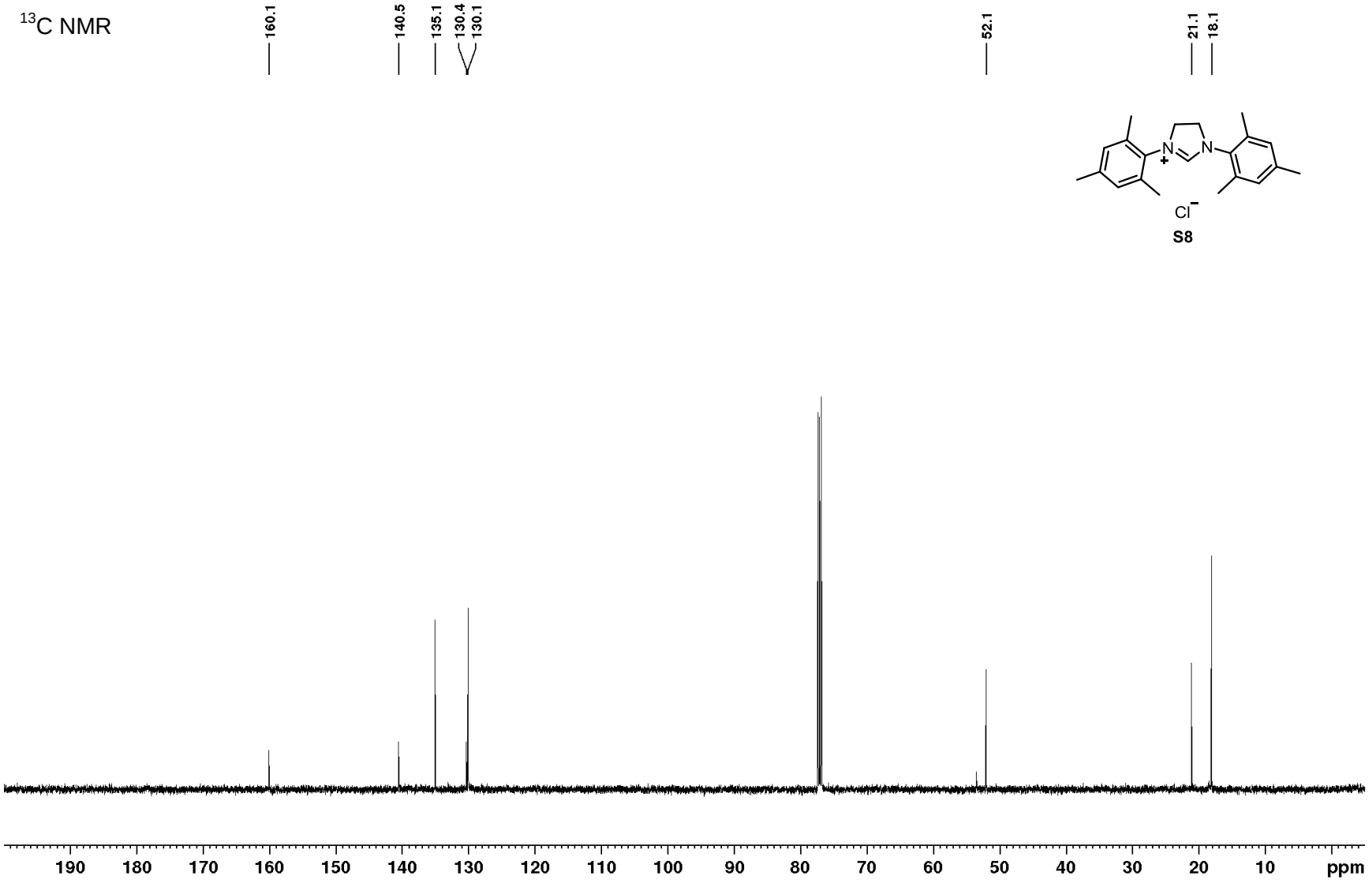

297.2320
214.0891
162.1274
136.1118
239.1060
148.1118
391.2834
352.2738
intensity
m/z
S7

1,3-dimesityl-4,5-dihydro-1H-imidazol-3-ium chloride (S8)

^{1}H NMR



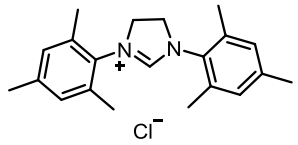
^{13}C NMR


160.1
140.5
135.1
130.4
130.1
52.1
21.1
18.1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

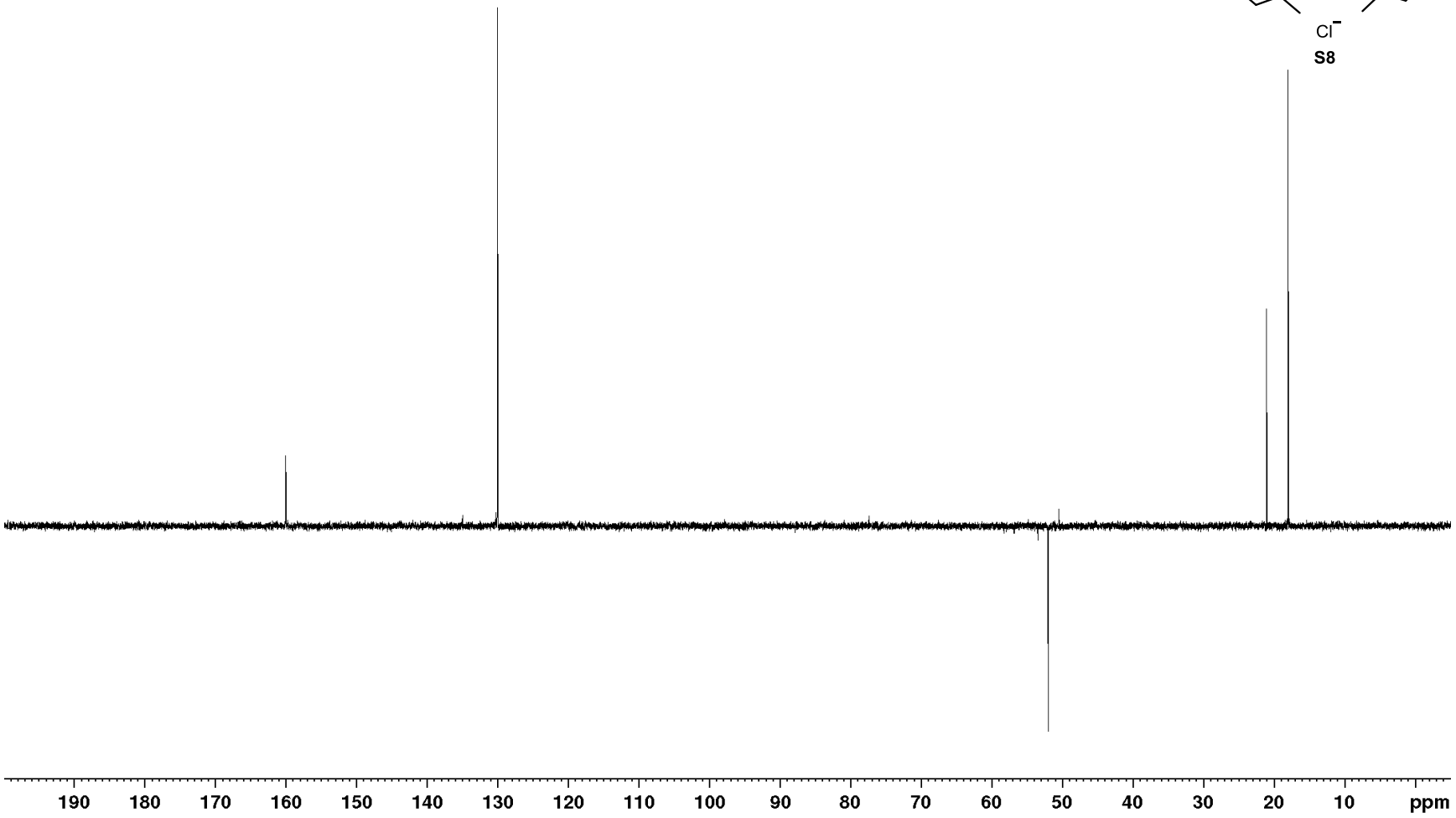
N
N
Cl

S8

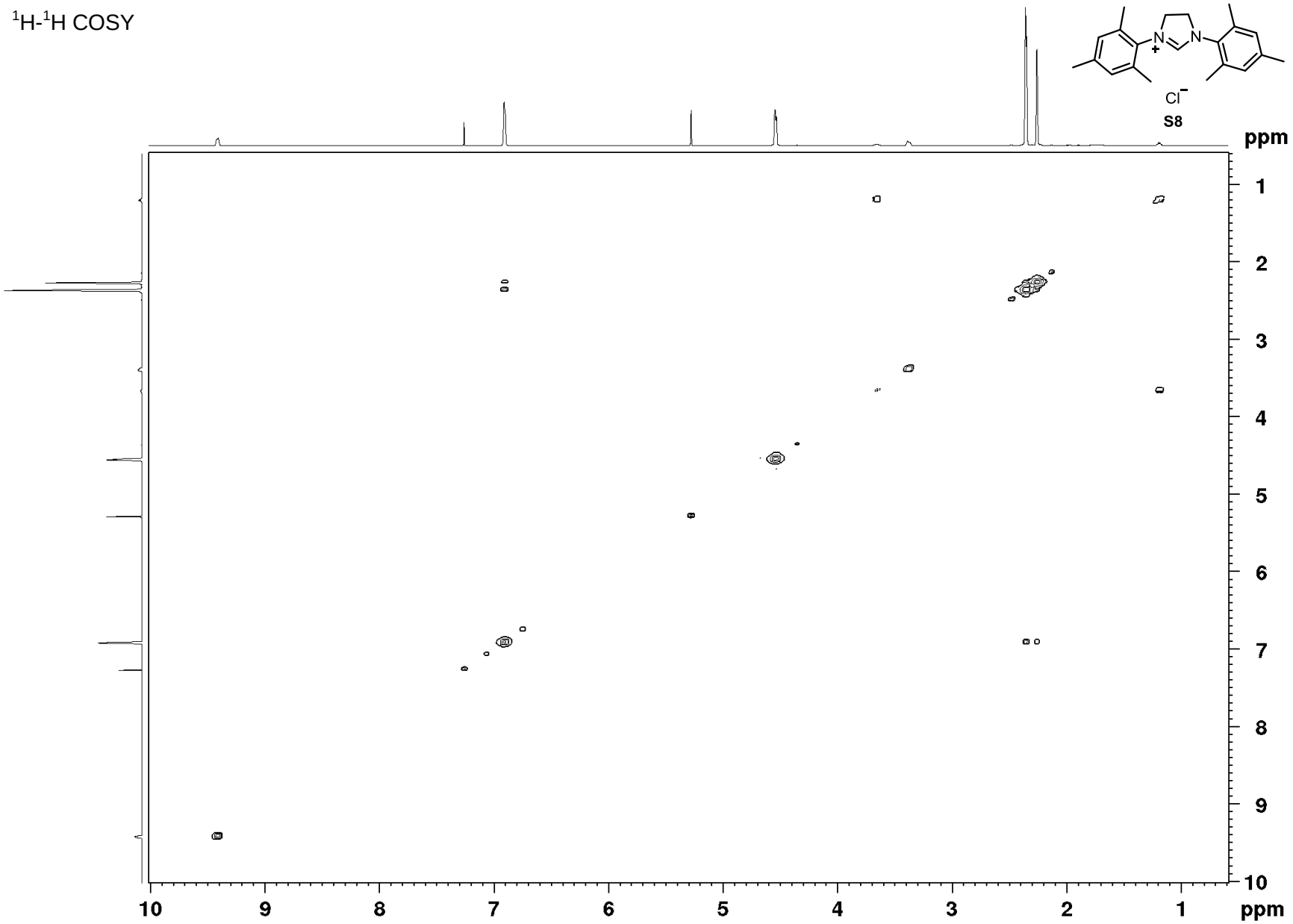
^{13}C DEPT NMR



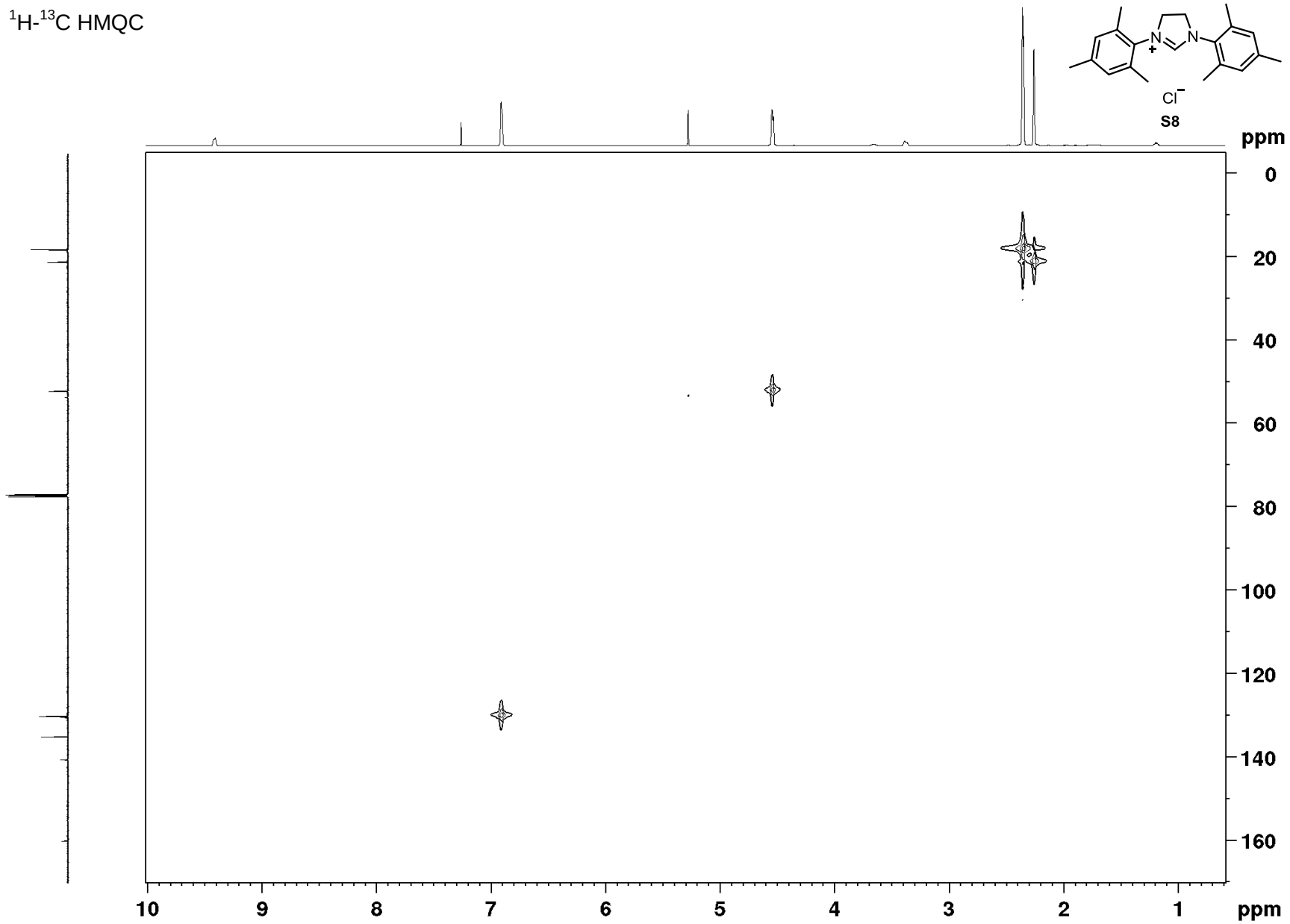
S8



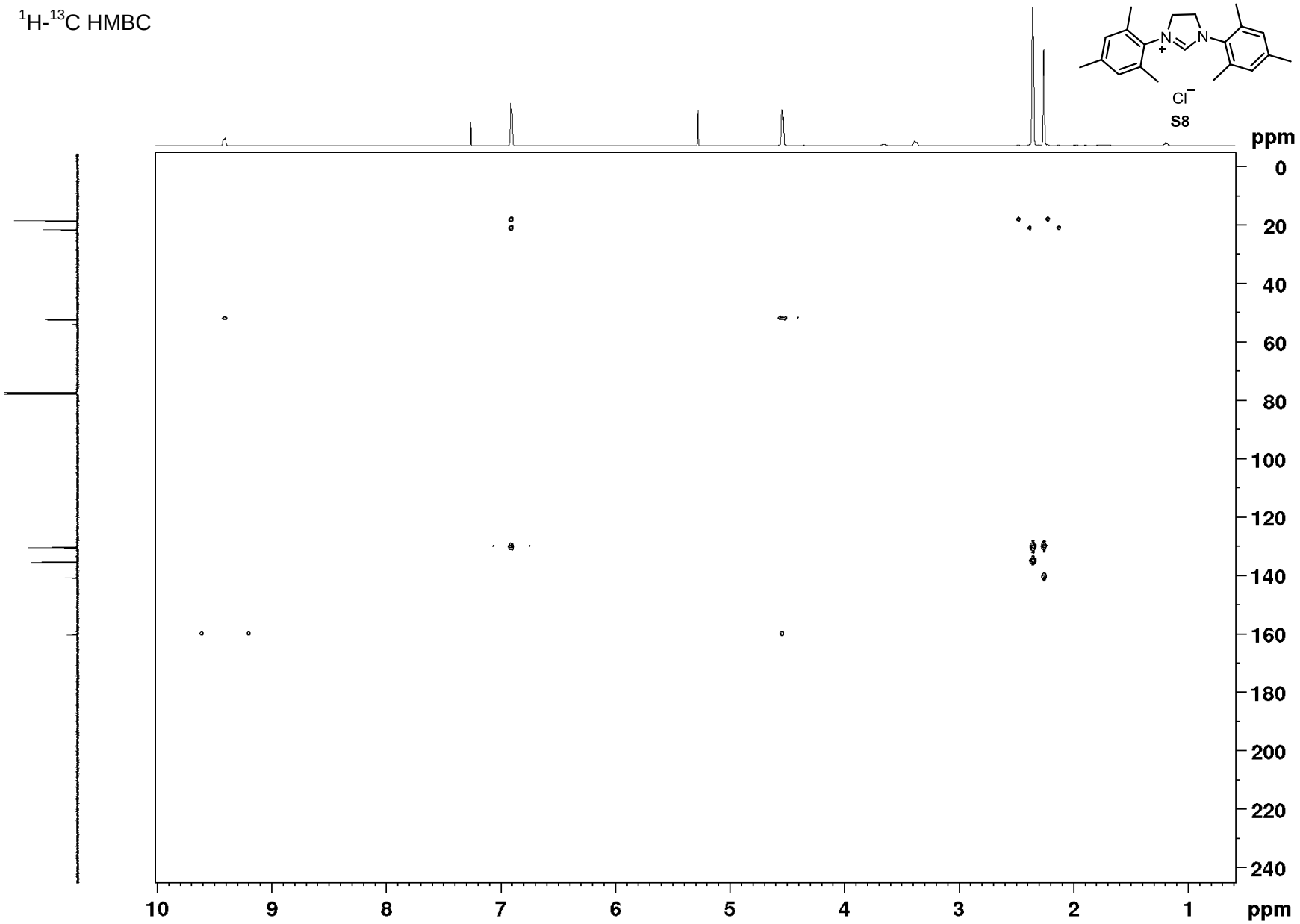
^{1}H-^{1}H COSY

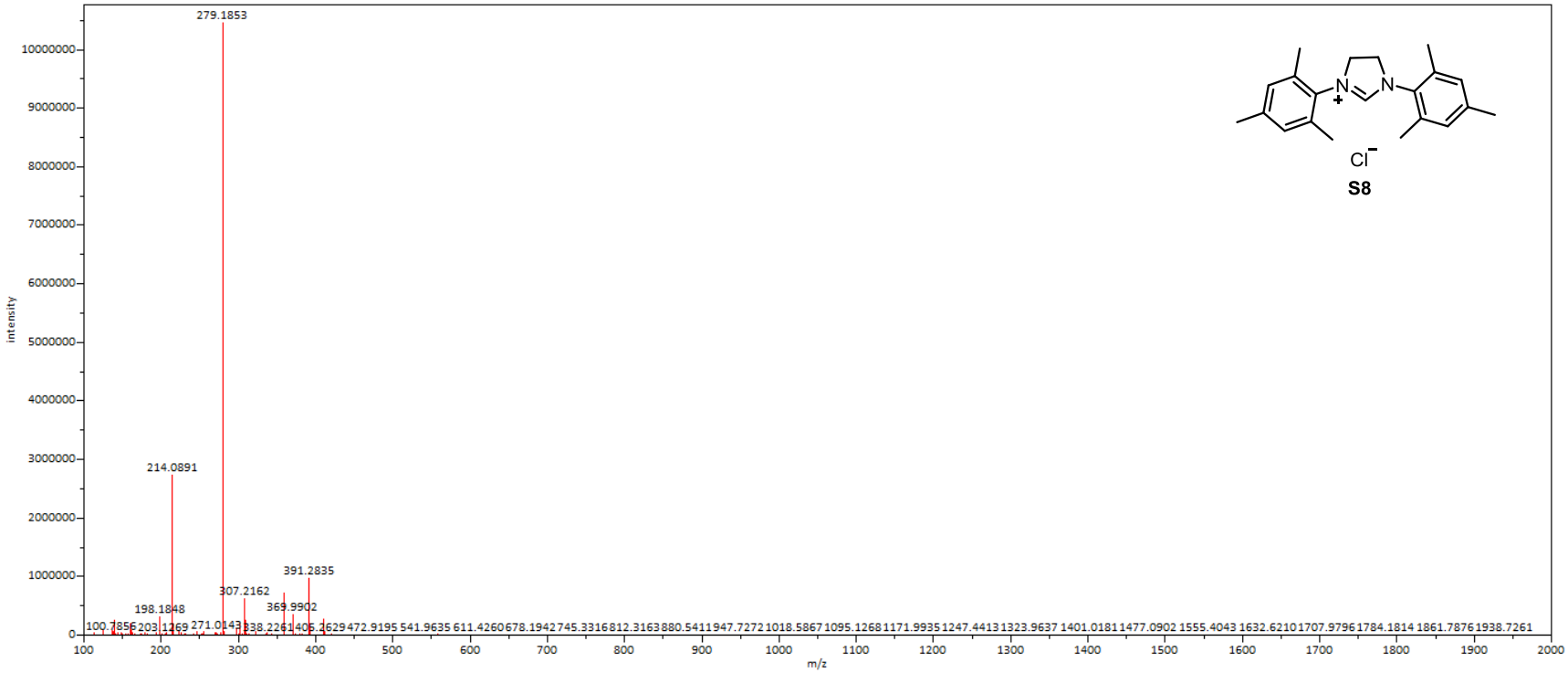


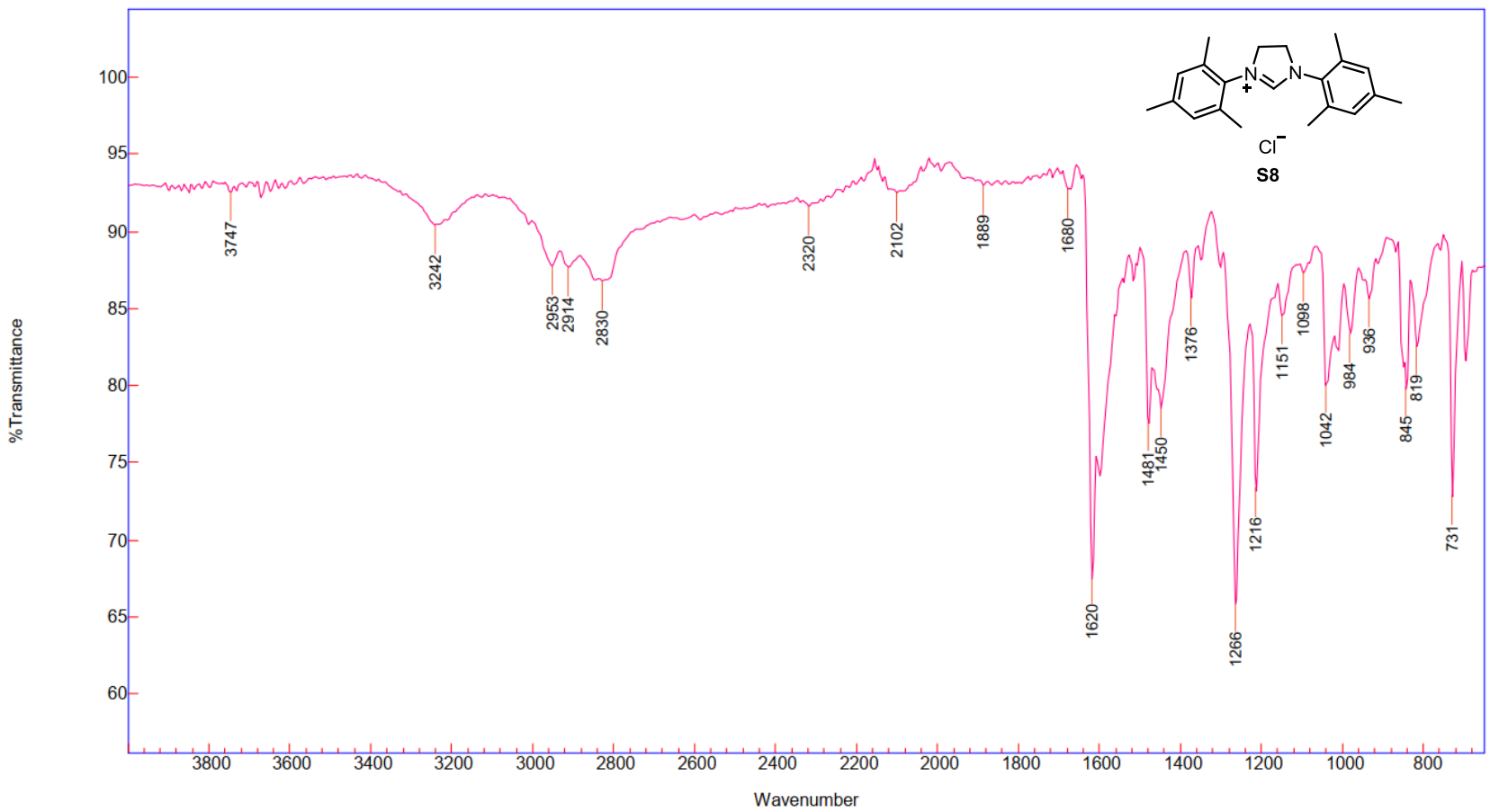
^{1}H-^{13}C HMQC



^{1}H-^{13}C HMBC

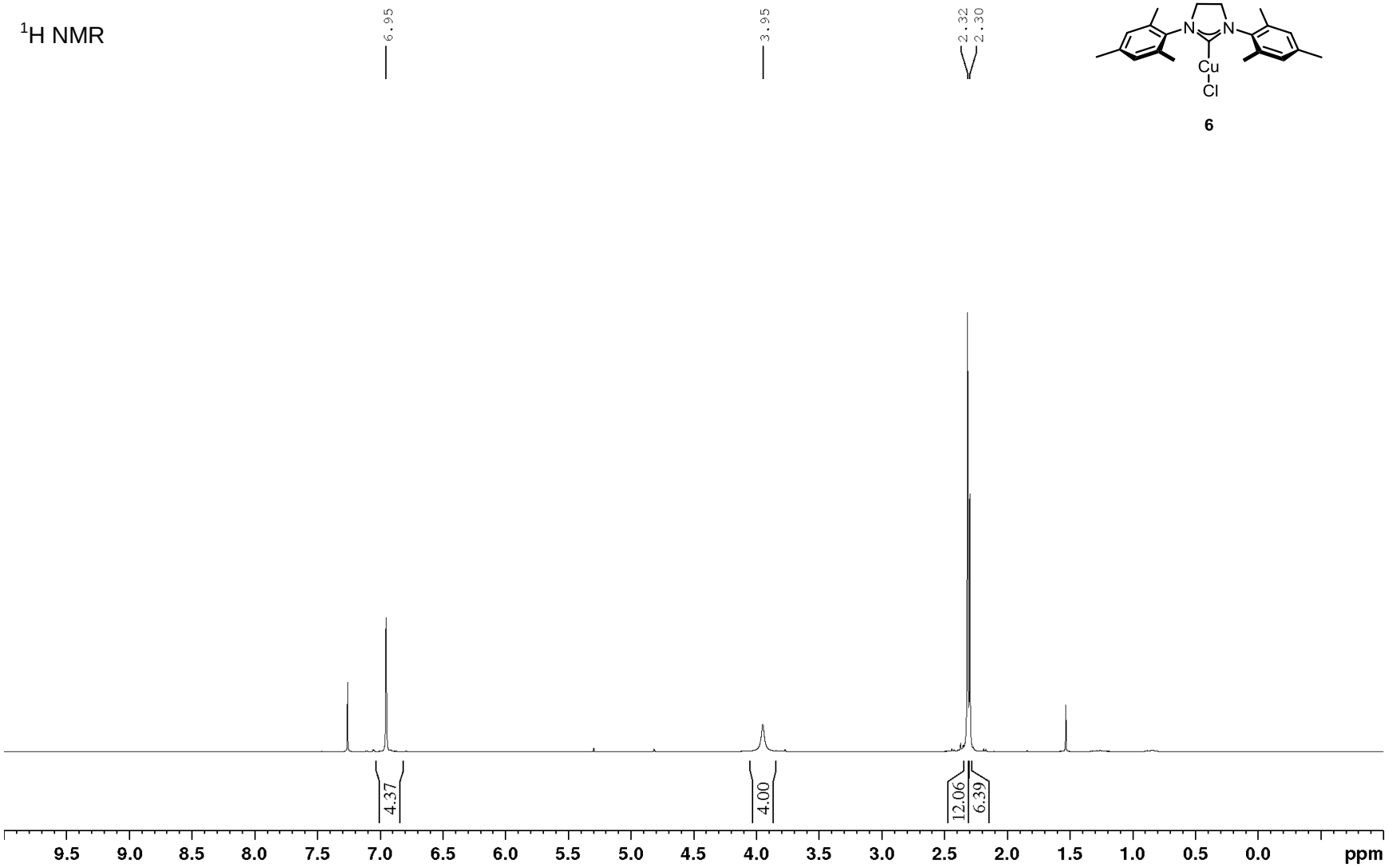

Cl⁻
S8
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
10
9
8
7
6
5
4
3
2
1
ppm


279.1853
214.0891
391.2835
307.2162
369.9902
198.1848
intensity
m/z
Cl⁻
S8


%Transmittance
100
95
90
85
80
75
70
65
60
3747
3242
2953
2914
2830
2320
2102
1889
1680
1620
1481
1450
1376
1266
1216
1151
1098
1042
984
936
845
819
731
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber
Cl⁻
S8

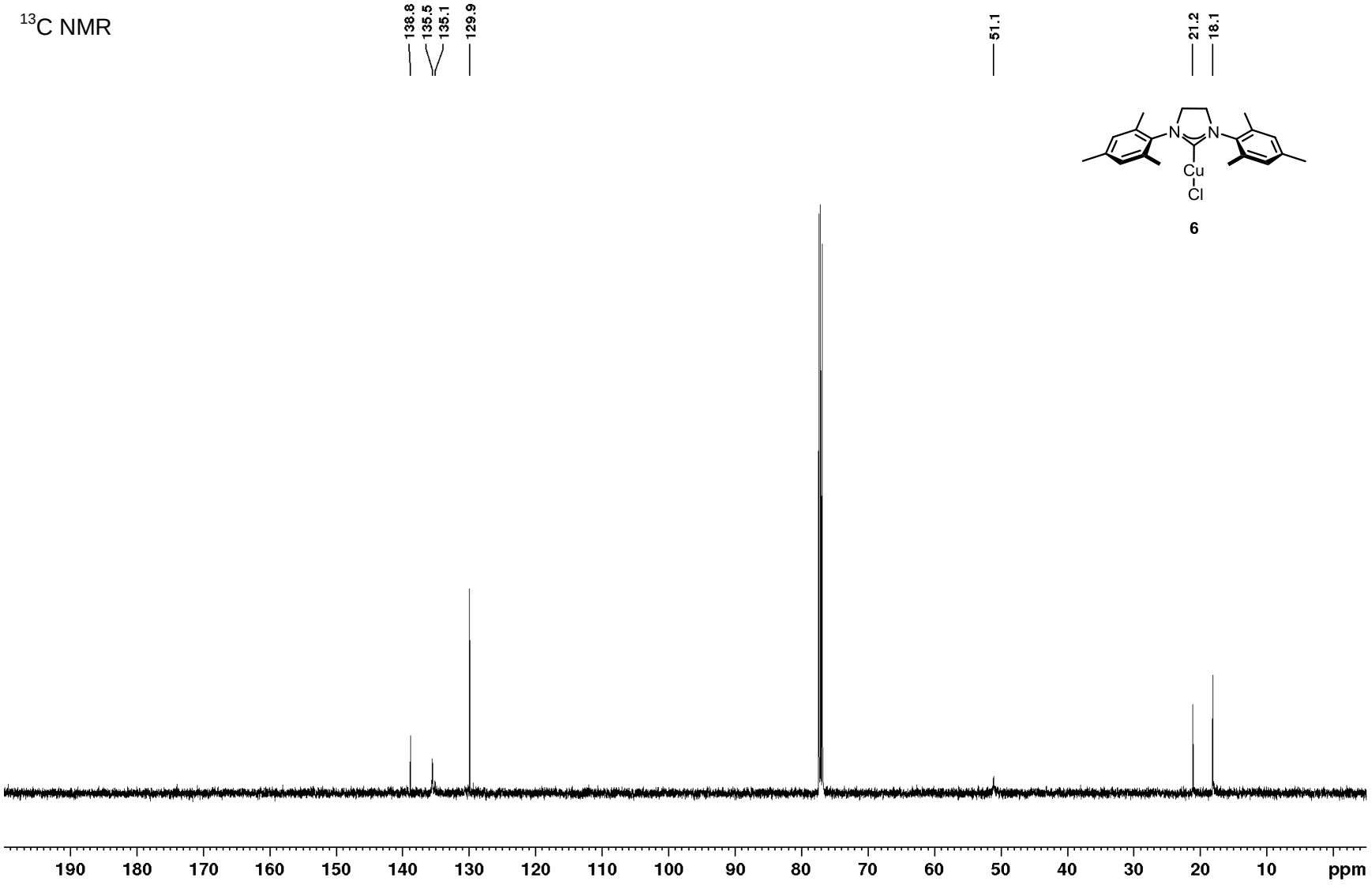
(1,3-dimesitylimidazolidin-2-yliden)copper(I) chloride (**6**)

^{1}H NMR

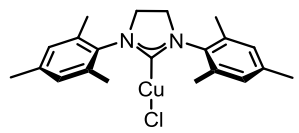


6

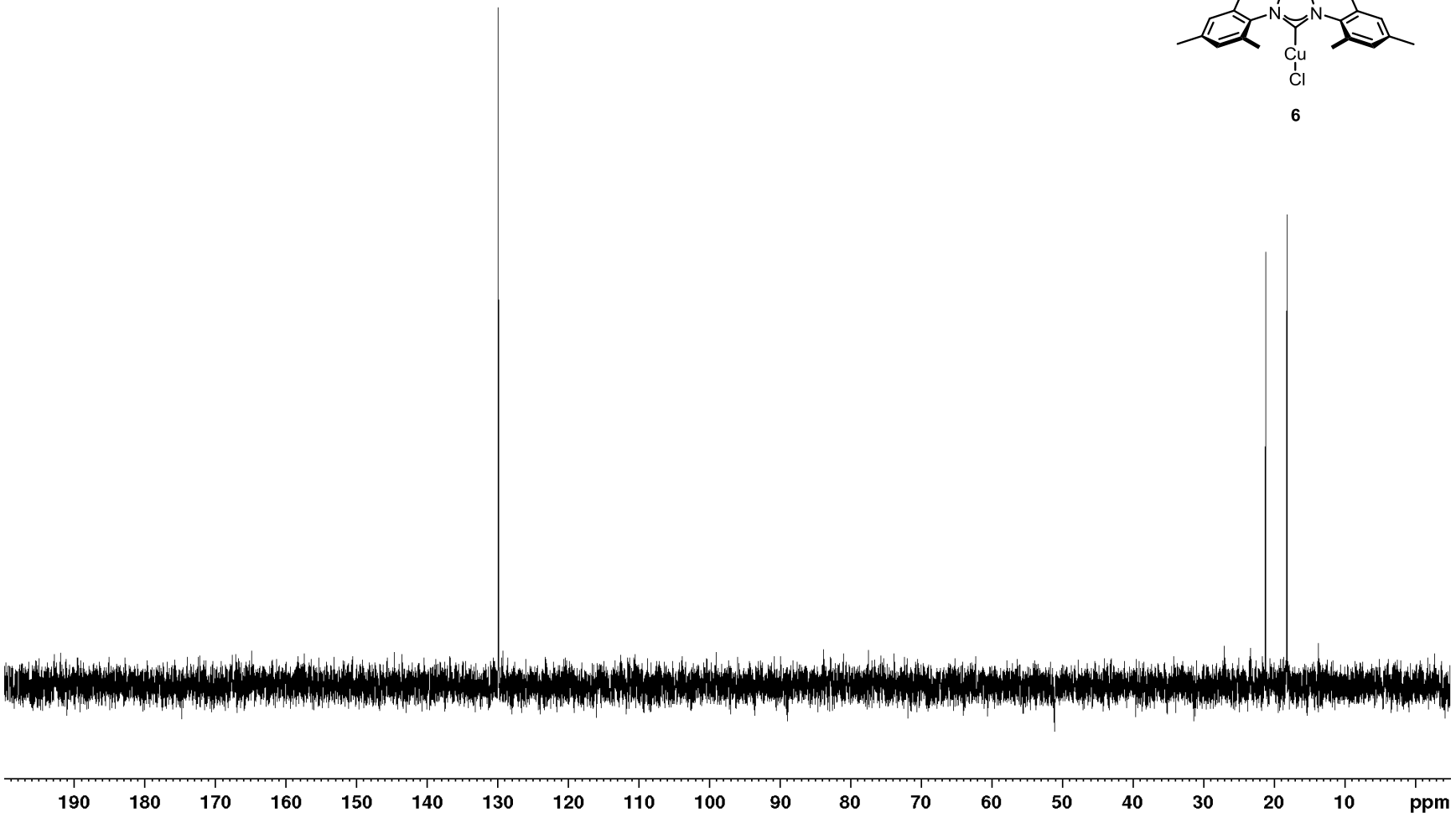
^{13}C NMR


138.8
135.5
135.1
129.9
51.1
21.2
18.1
N
N
Cu
Cl
6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{13}C DEPT NMR

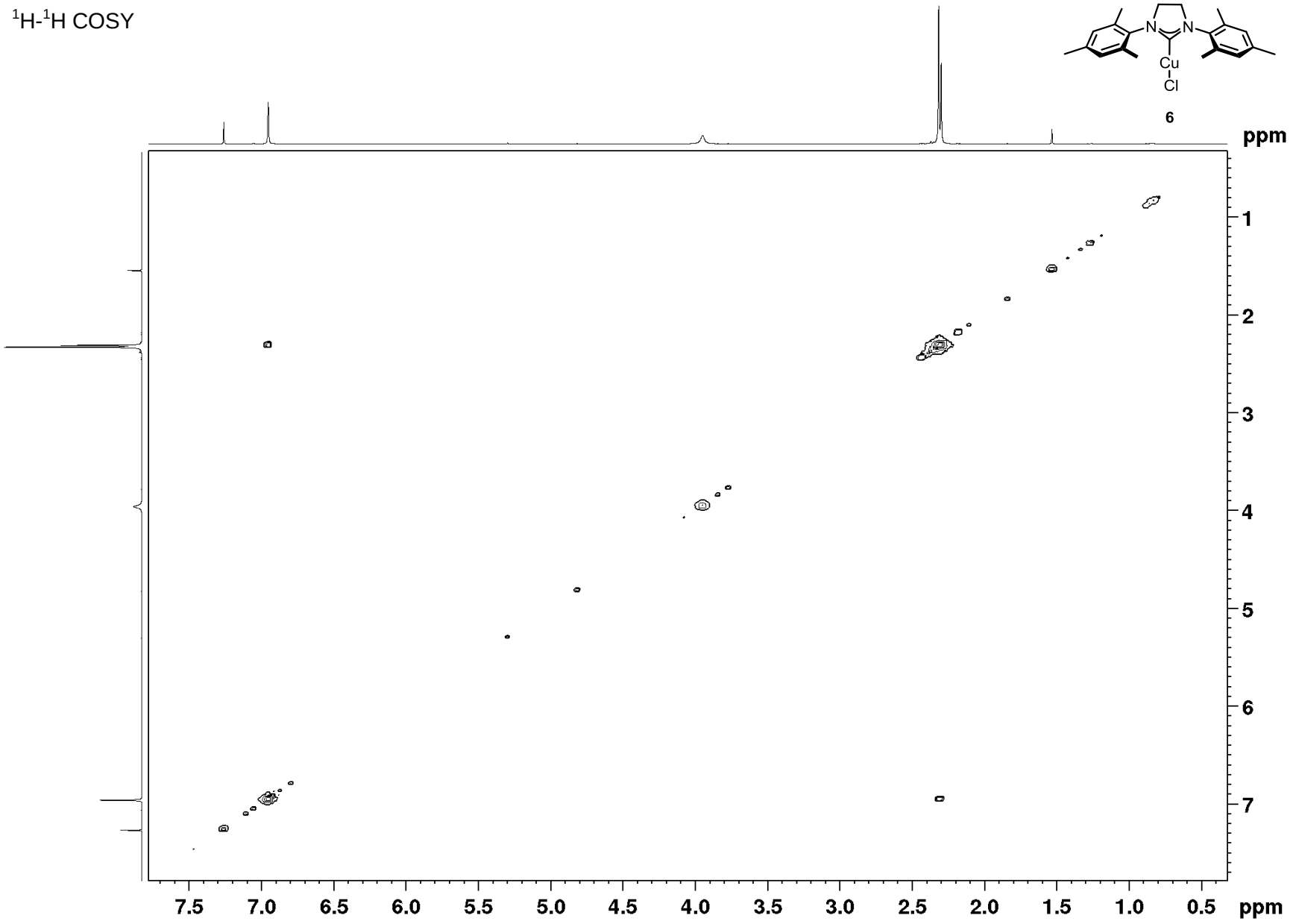


6

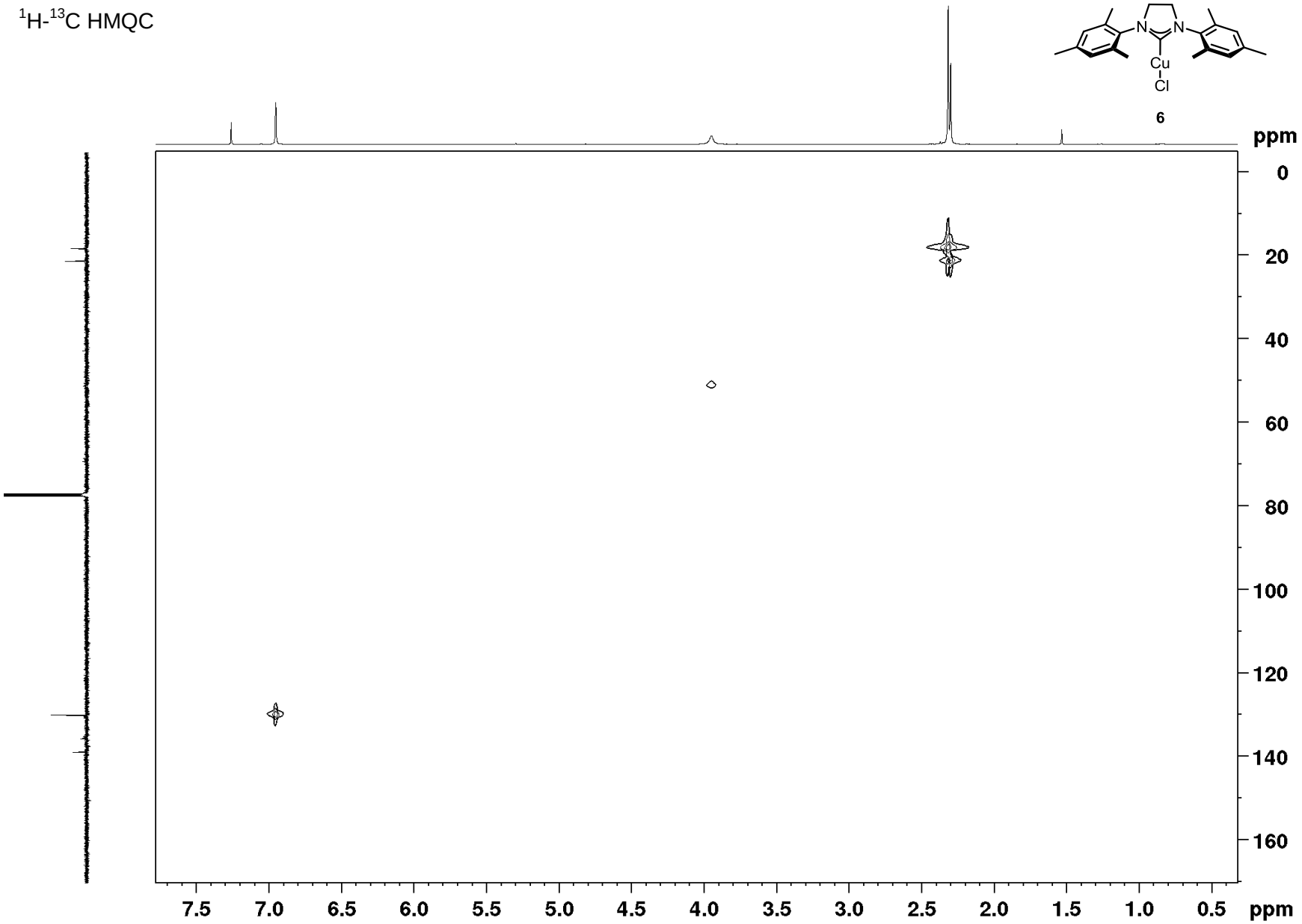


^{1}H-^{1}H COSY

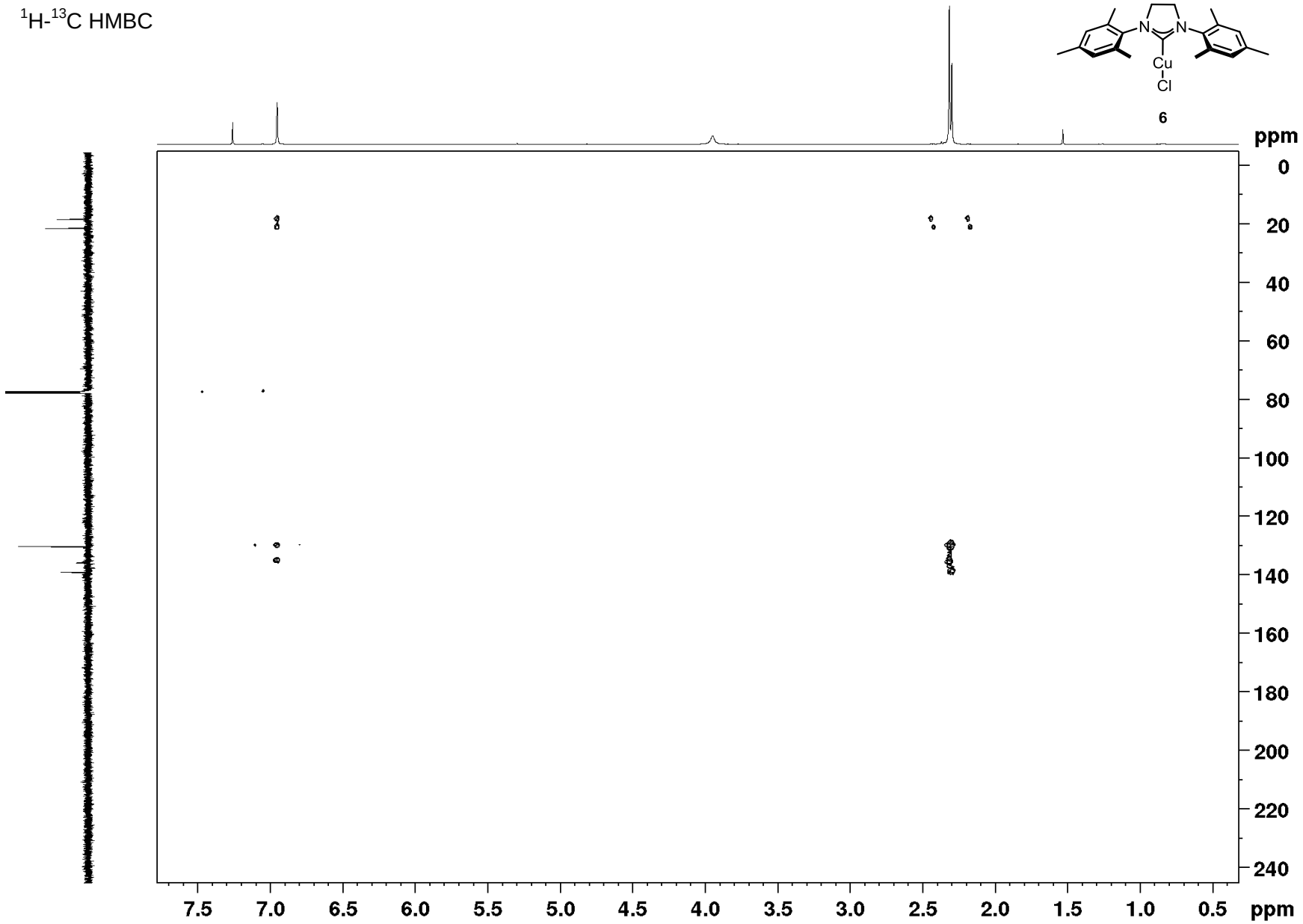
6

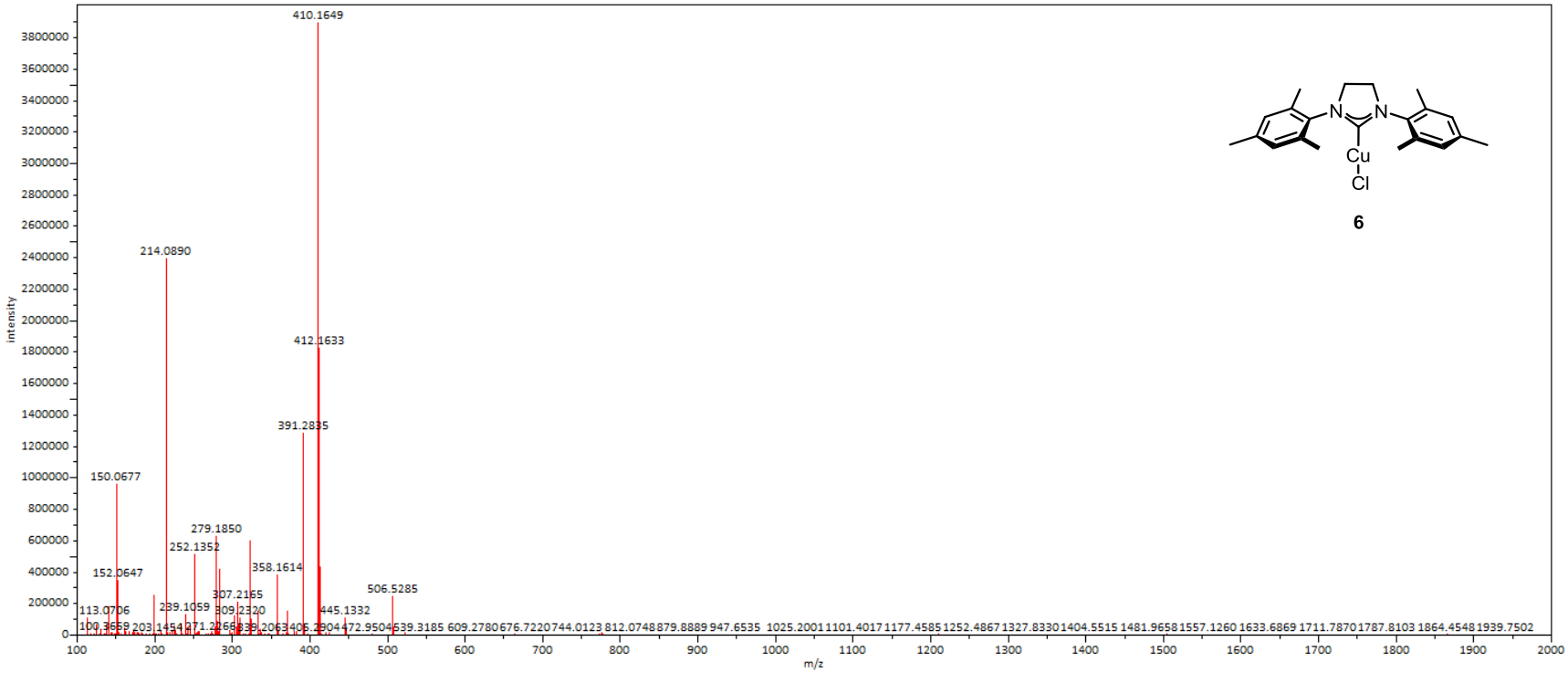


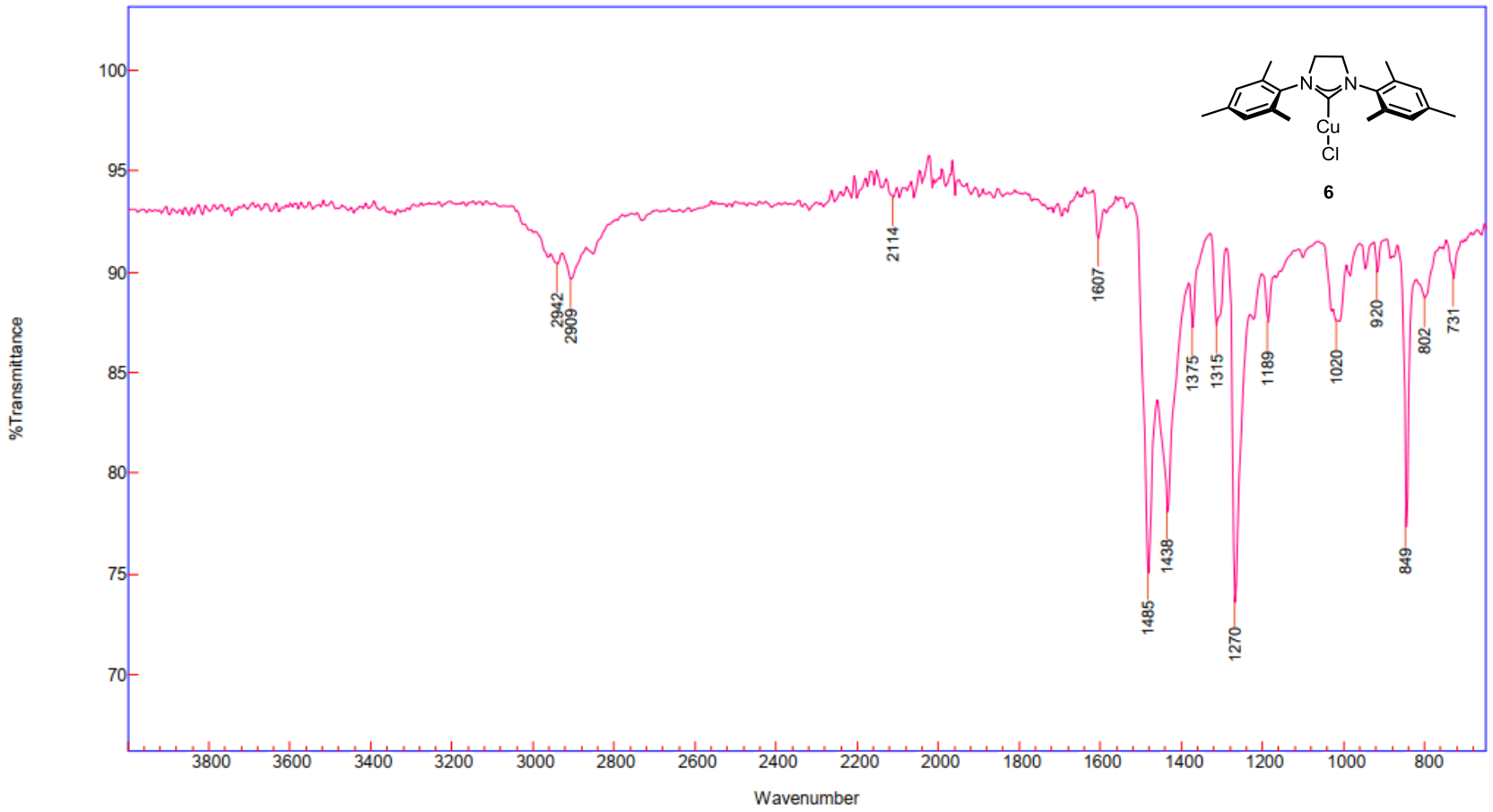
^{1}H-^{13}C HMQC


N
N
Cu
Cl
6
ppm
0
20
40
60
80
100
120
140
160
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
ppm

^{1}H-^{13}C HMBC

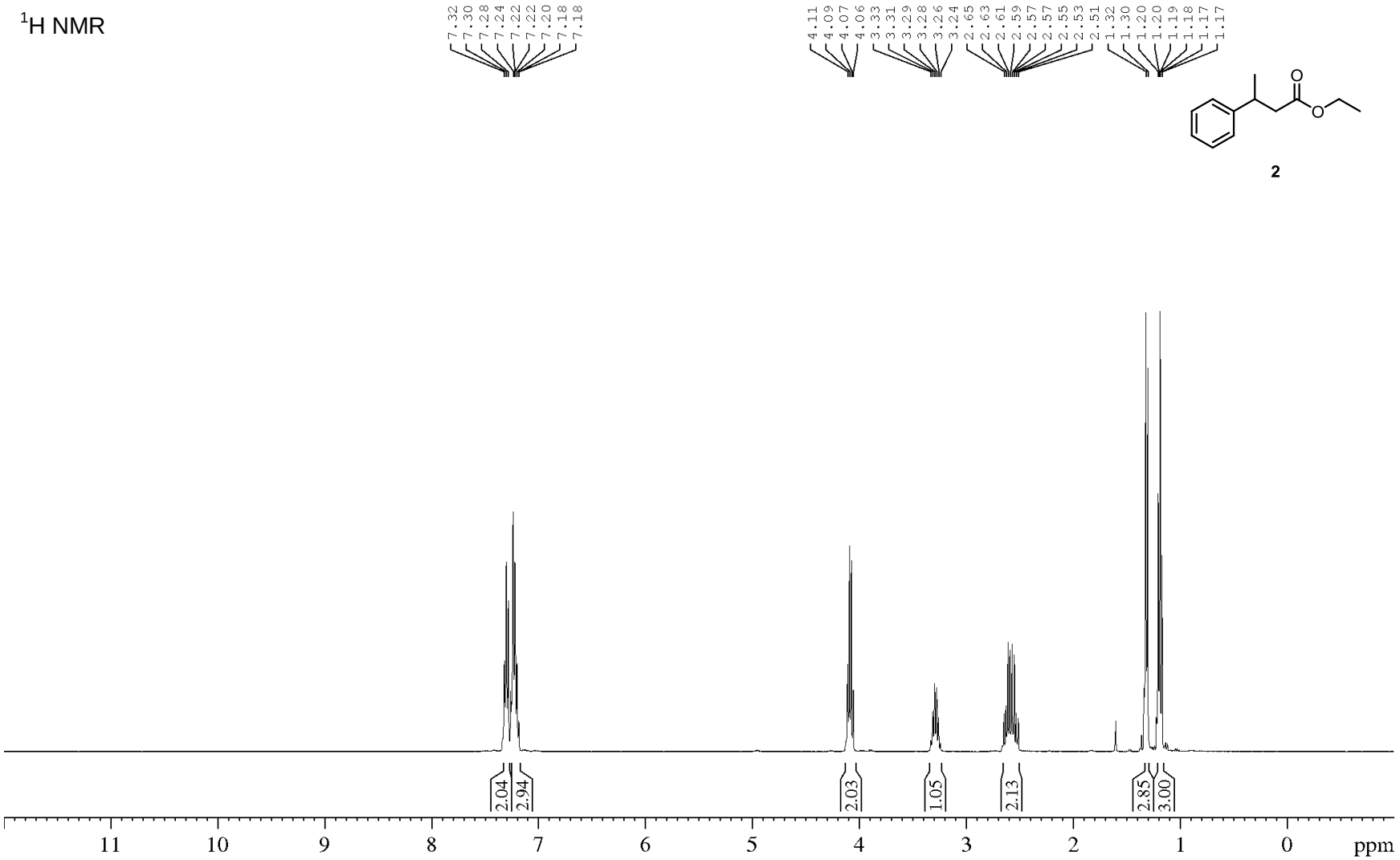

N
N
Cu
Cl
6
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


410.1649
214.0890
412.1633
391.2835
150.0677
279.1850
252.1352
358.1614
152.0647
307.2165
506.5285
intensity
m/z
Cu
Cl
6

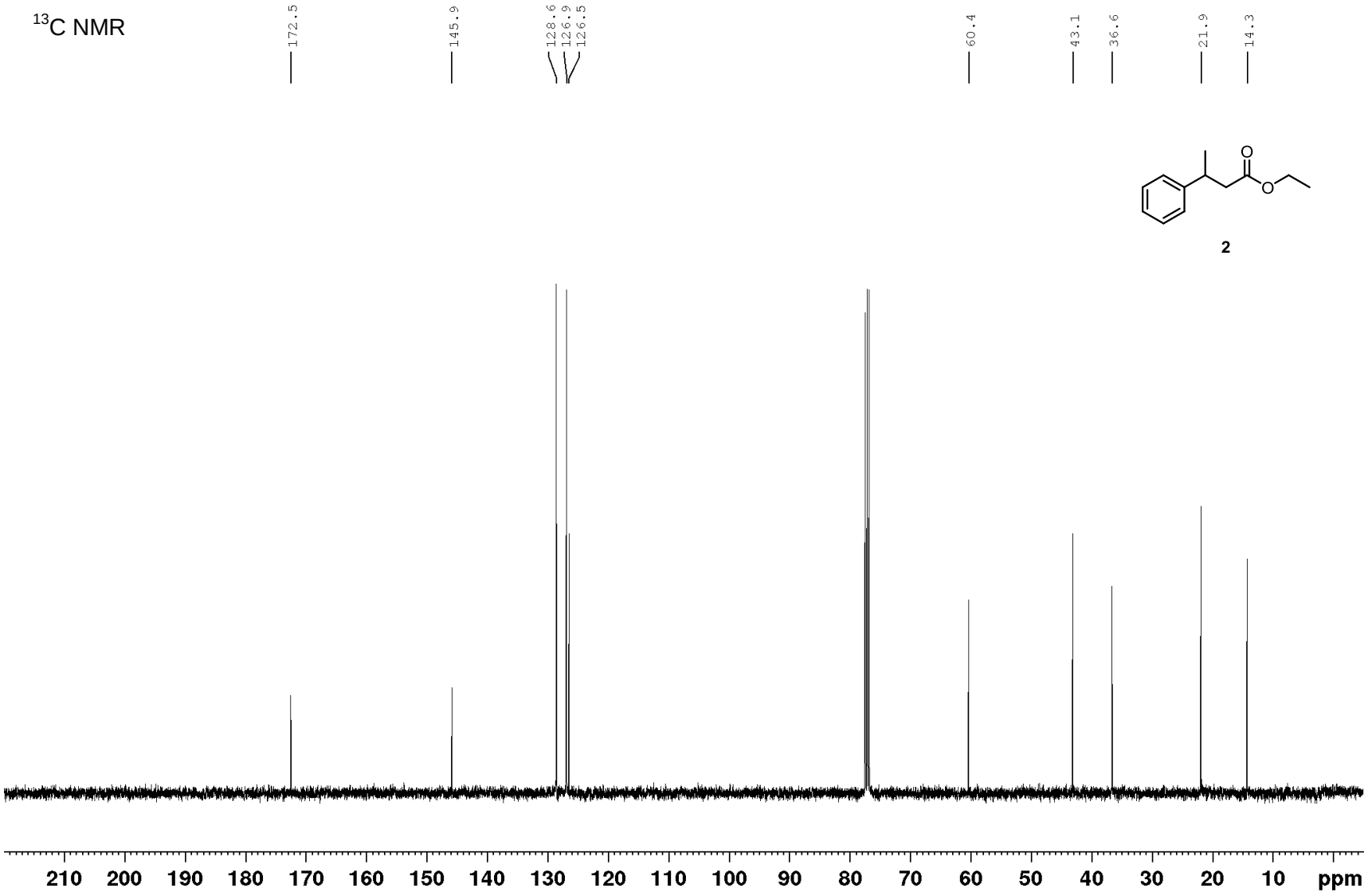

%Transmittance
100
95
90
85
80
75
70
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber
2942
2909
2114
1607
1485
1438
1375
1315
1270
1189
1020
920
849
802
731
N
N
Cu
Cl
6

Ethyl 3-phenylbutanoate (2)

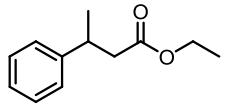
^{1}H NMR



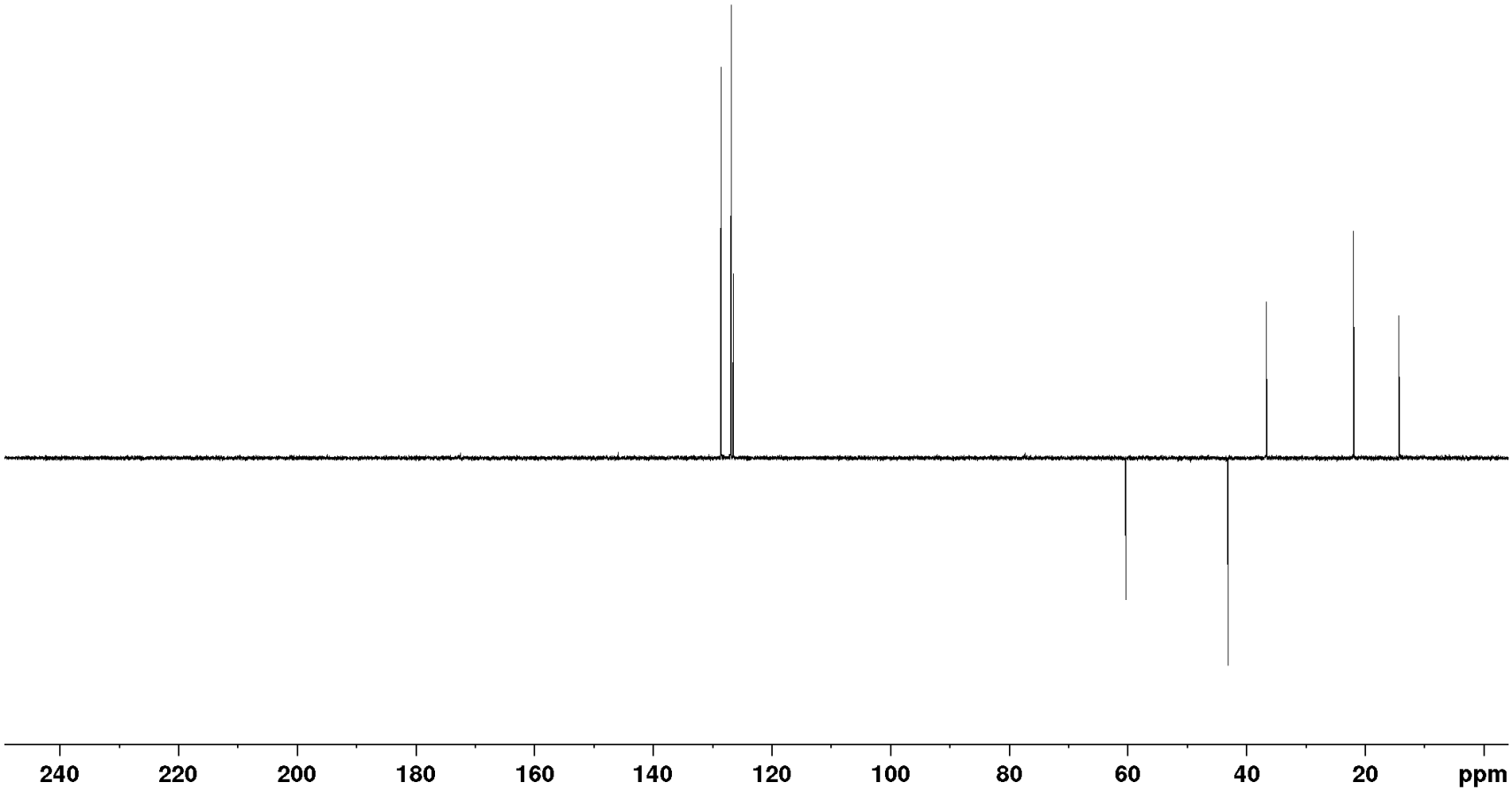
^{13}C NMR


172.5
145.9
128.6
126.9
126.5
60.4
43.1
36.6
21.9
14.3
O
O
2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

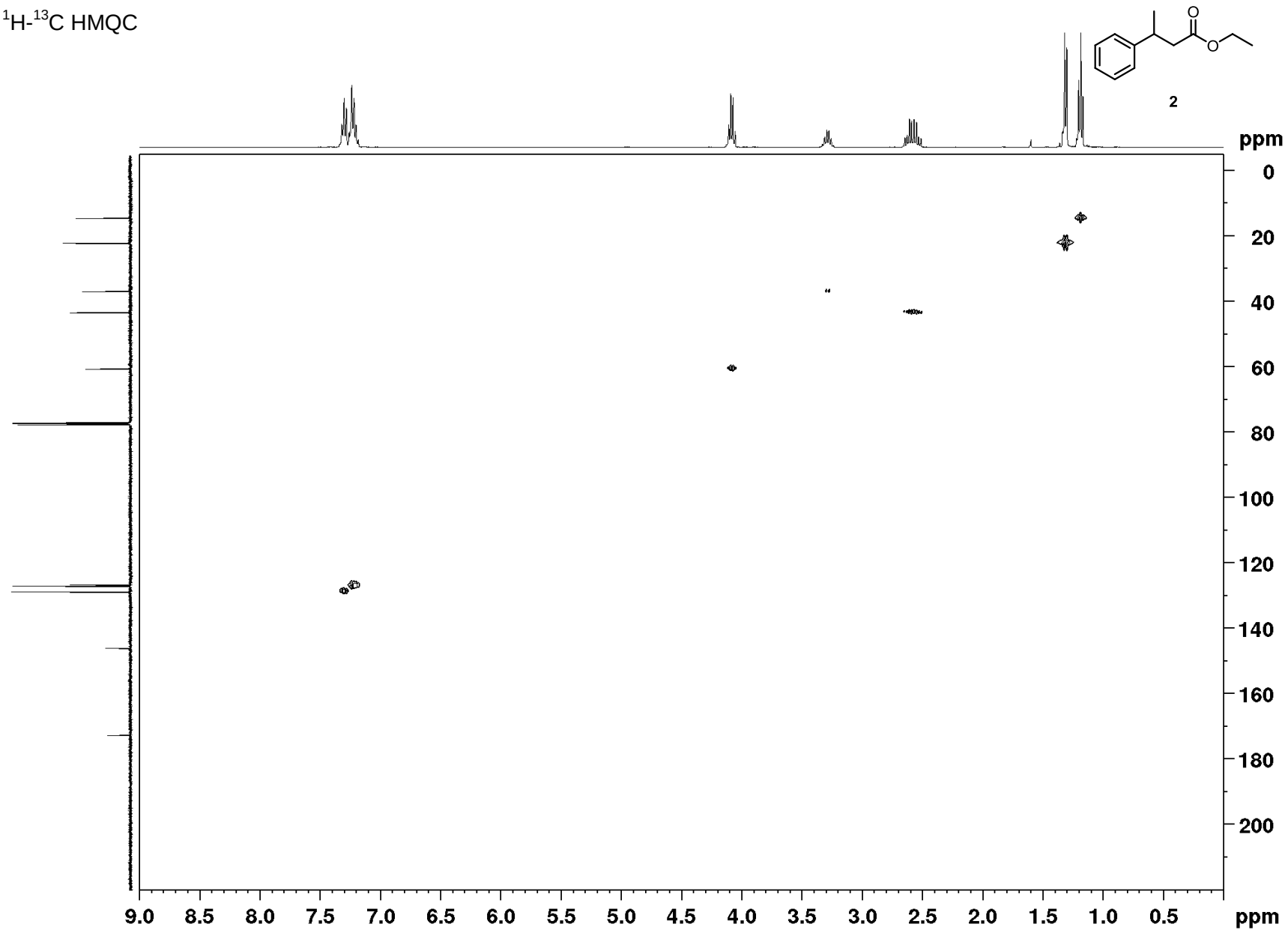
^{13}C DEPT NMR

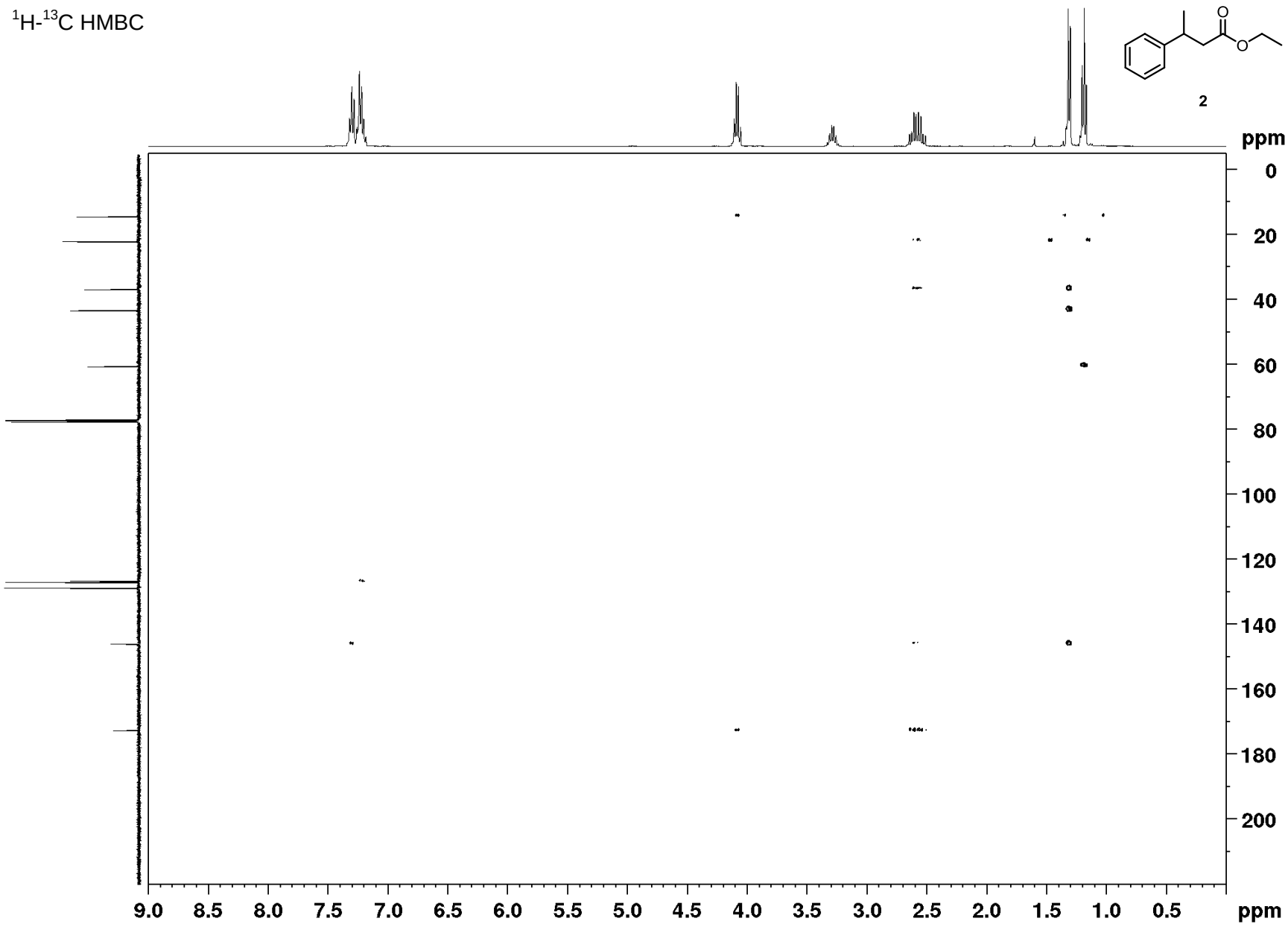


2

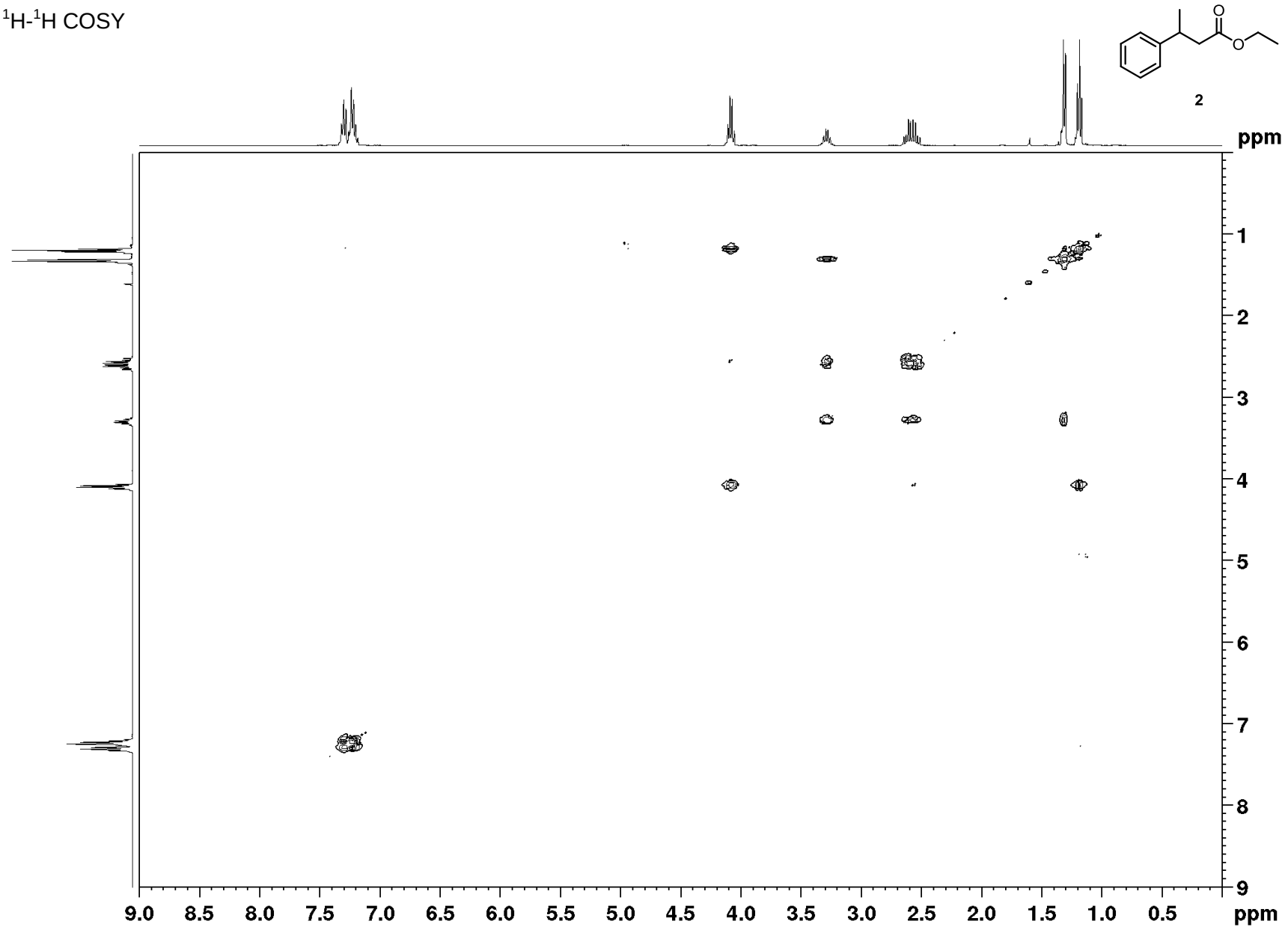


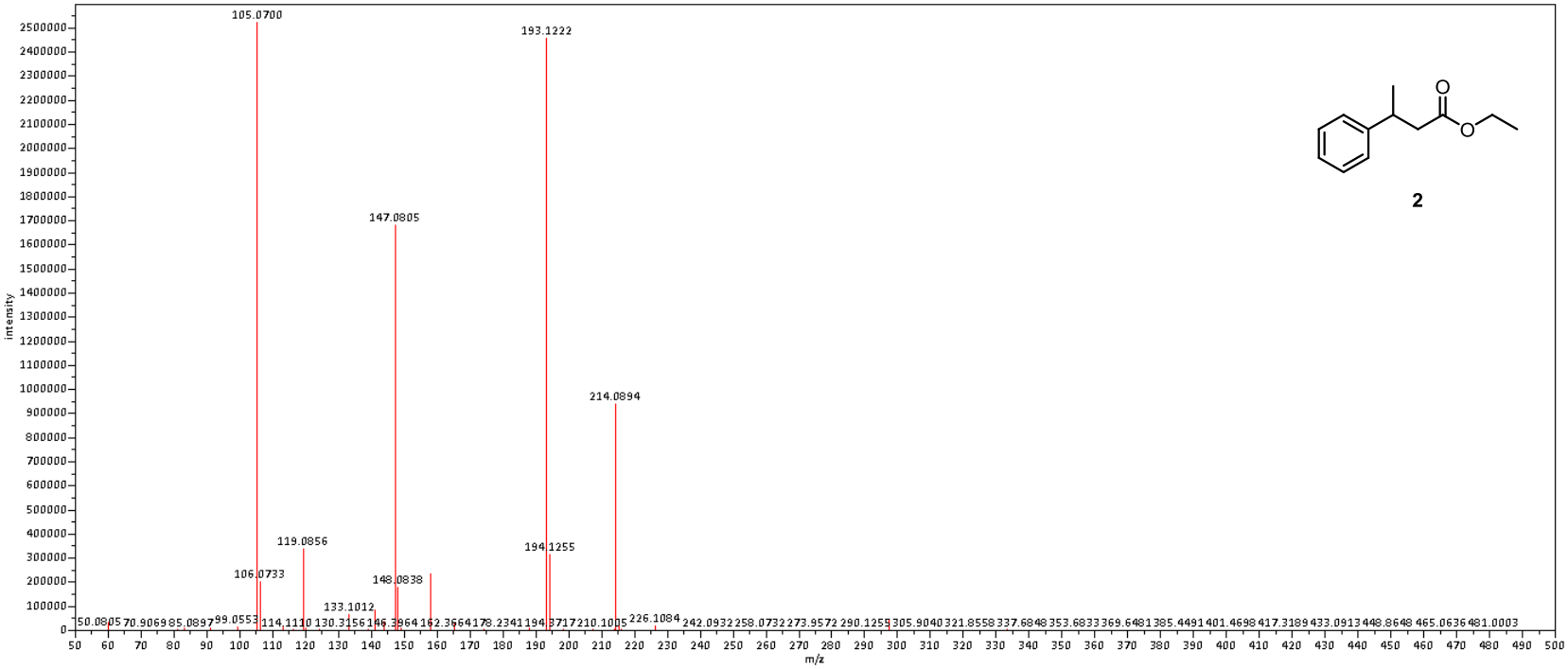
^{1}H-^{13}C HMQC


O
O
2
ppm
0
20
40
60
80
100
120
140
160
180
200
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


^{1}H-^{13}C HMBC
O
O
2
ppm
0
20
40
60
80
100
120
140
160
180
200
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

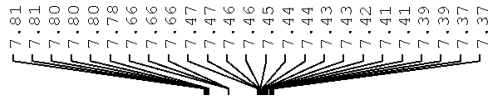
^{1}H-^{1}H COSY

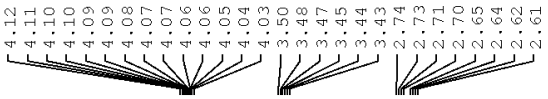

O
O
2
ppm
1
2
3
4
5
6
7
8
9
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

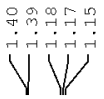

105.0700
193.1222
147.0805
214.0894
119.0856
194.1255
106.0733
148.0838
133.1012
intensity
m/z
2

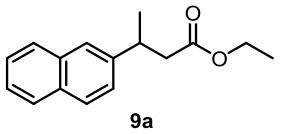
Ethyl 3-(naphthalen-2-yl)butanoate (9a)

^{1}H NMR

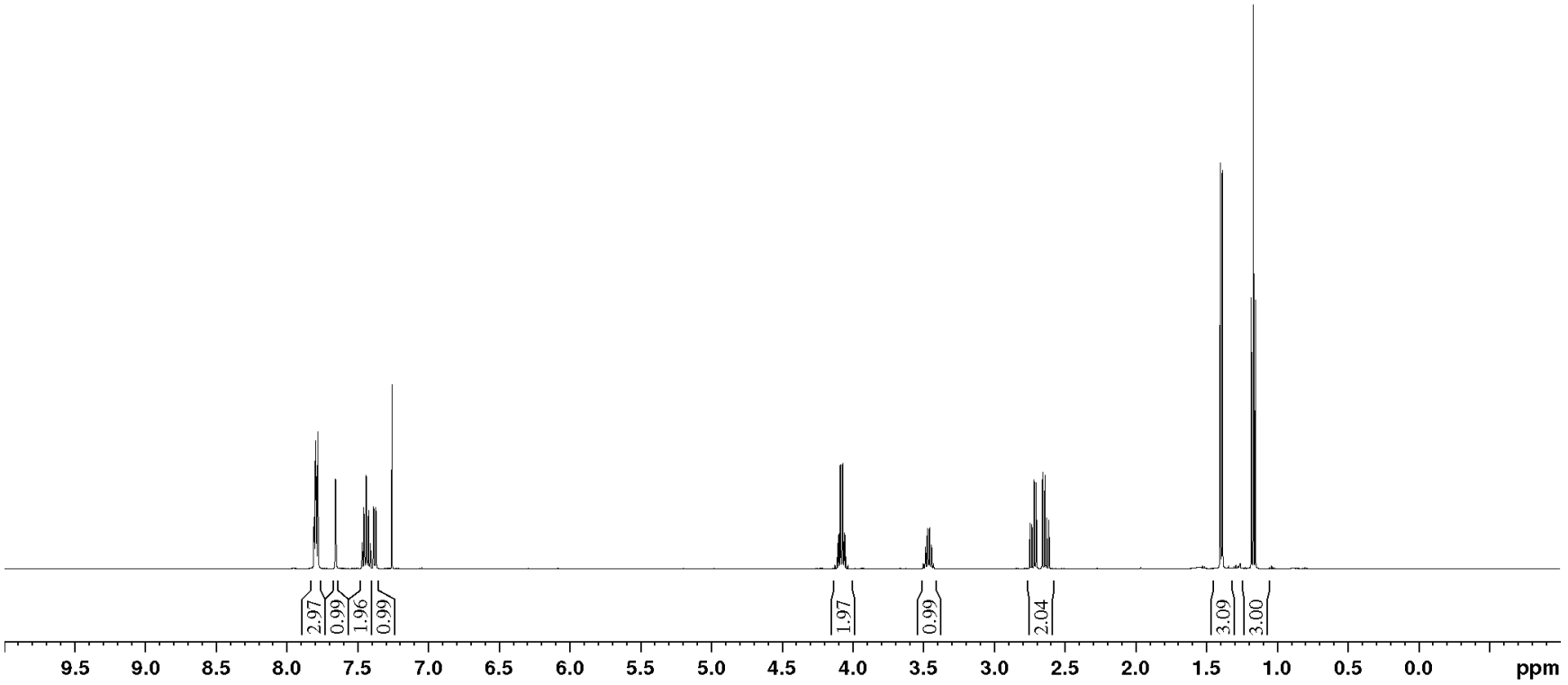


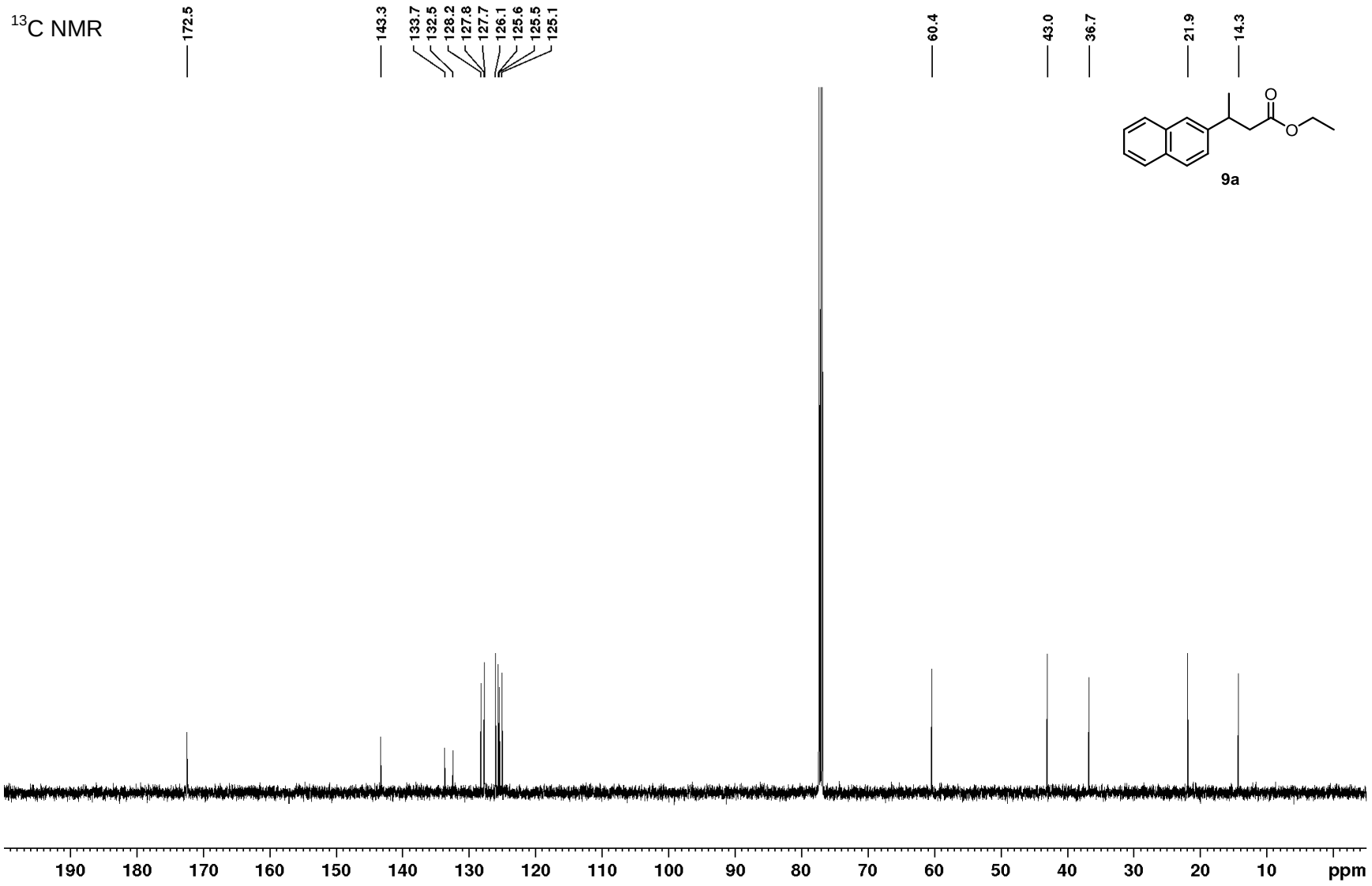




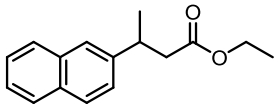


9a

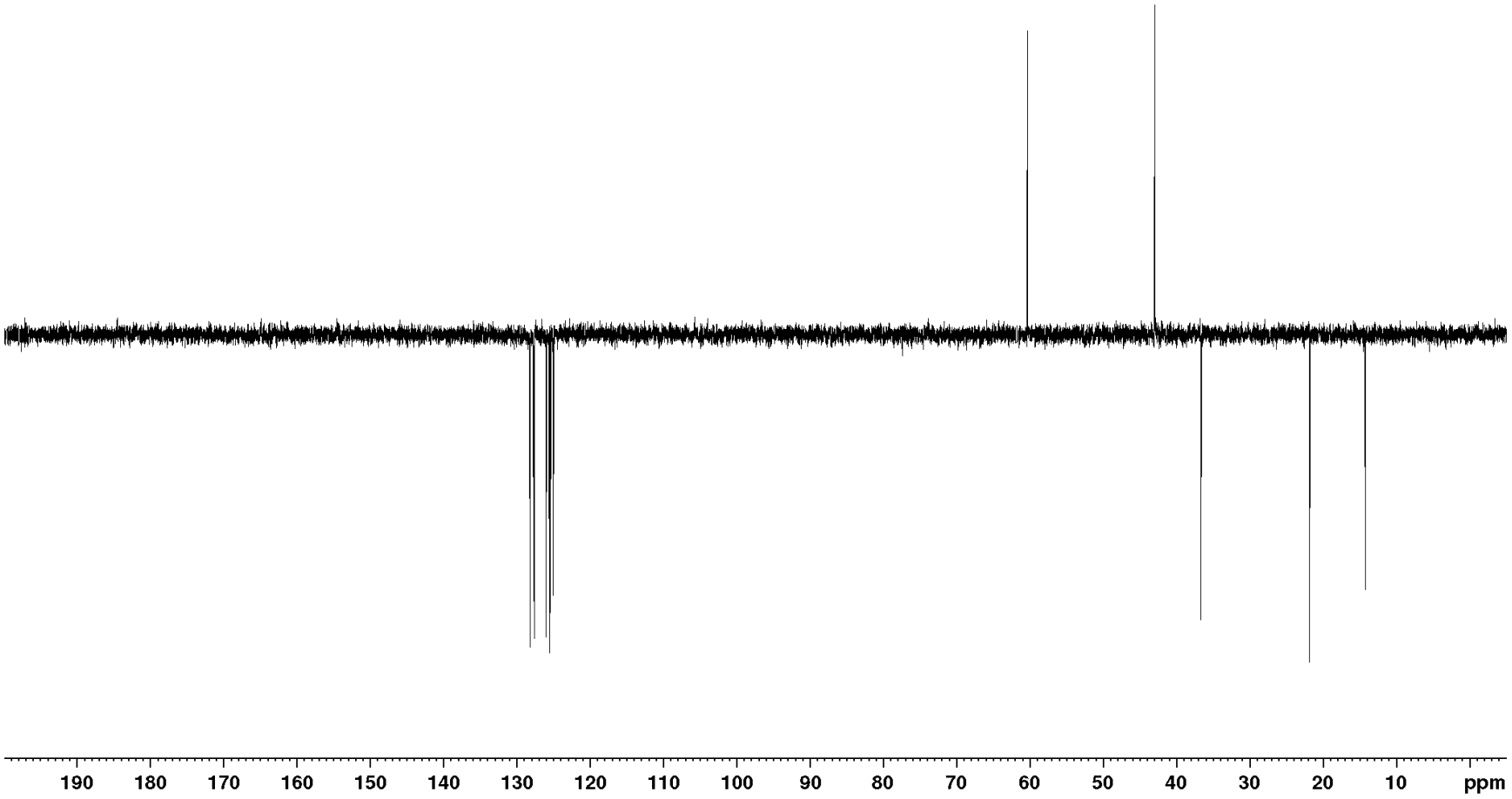



^{13}C NMR
172.5
143.3
133.7
132.5
128.2
127.8
127.7
126.1
125.6
125.5
125.1
60.4
43.0
36.7
21.9
14.3
O
O
9a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

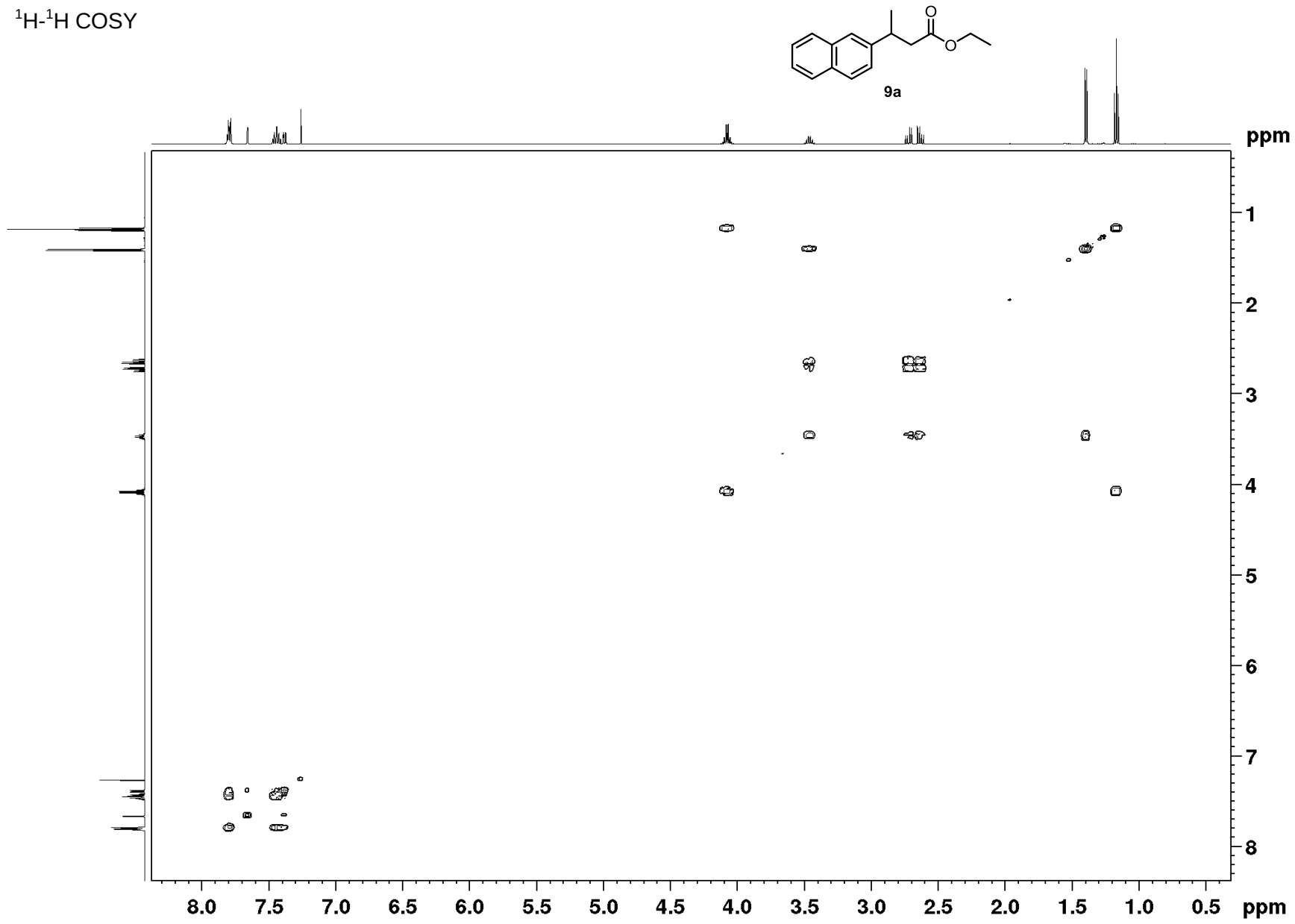
^{13}C DEPT NMR



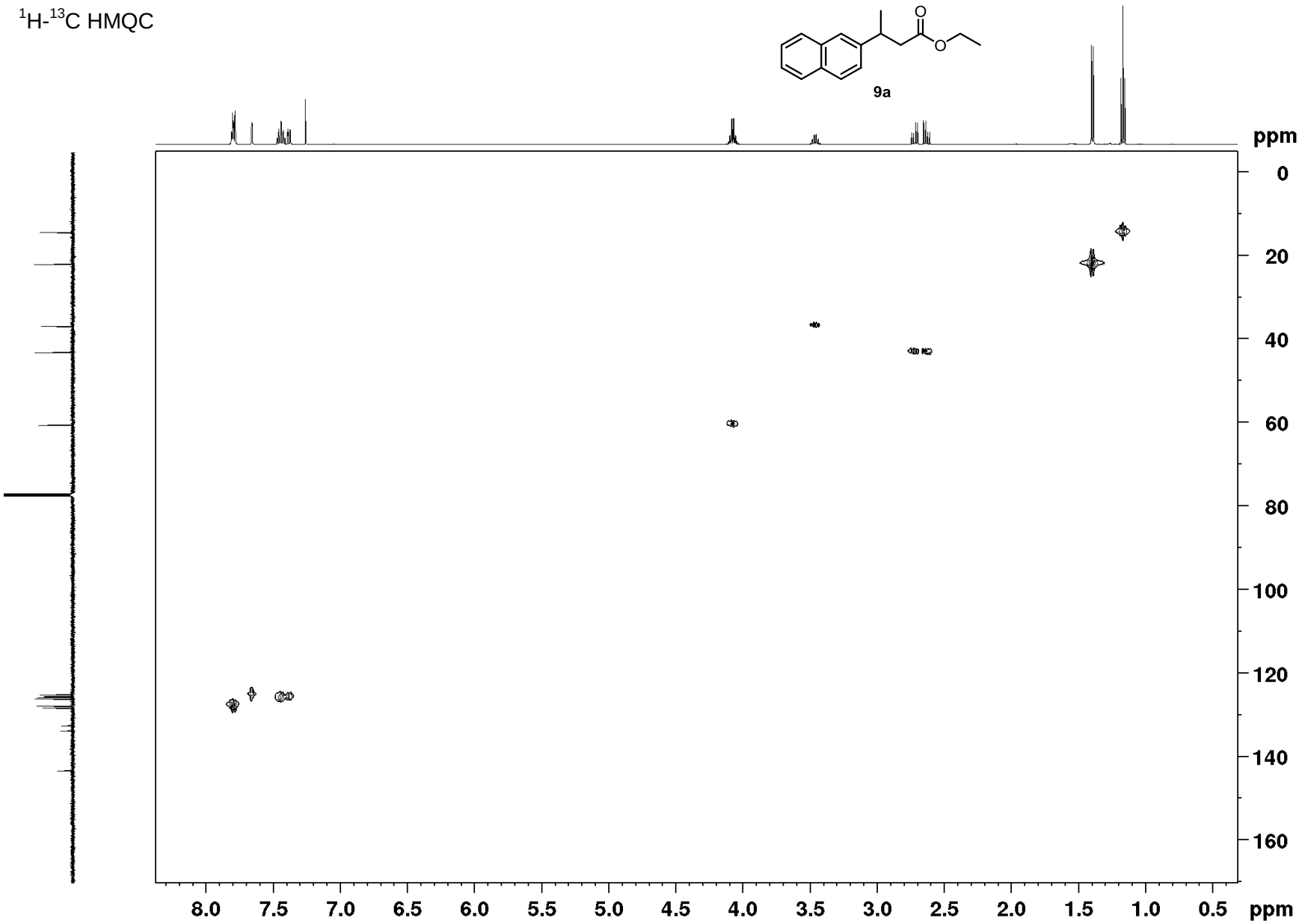
9a



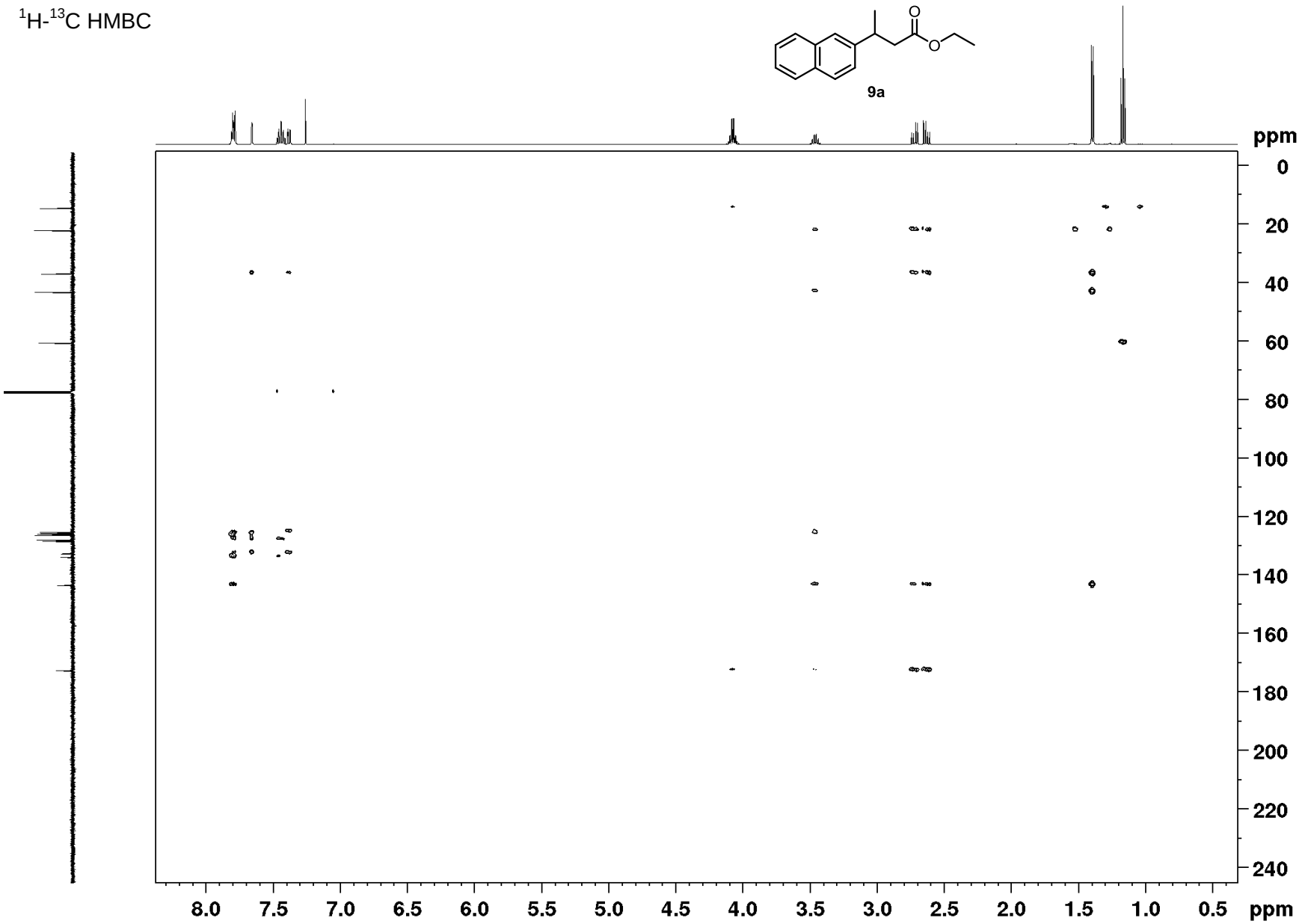
^{1}H-^{1}H COSY

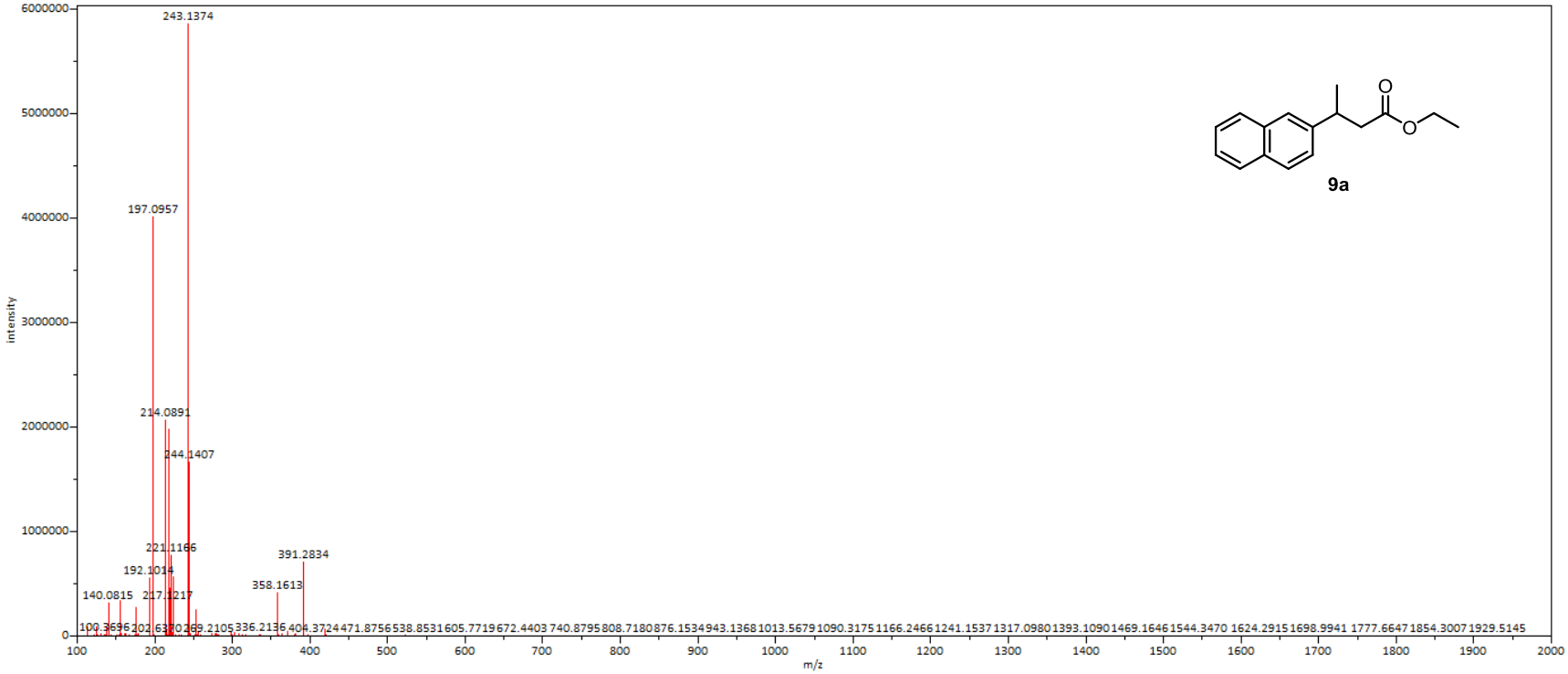


^{1}H-^{13}C HMQC


9a
ppm
0
20
40
60
80
100
120
140
160
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
ppm

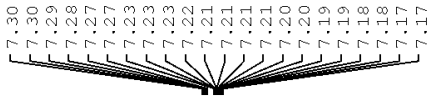
^{1}H-^{13}C HMBC

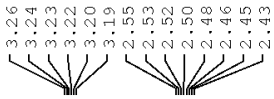

O
O
9a
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

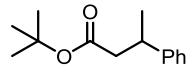

243.1374
197.0957
214.0891
244.1407
221.1166
192.1014
391.2834
358.1613
140.0815
217.1217
intensity
m/z
9a

***tert*-Butyl 3-phenylbutanoate (9b)**

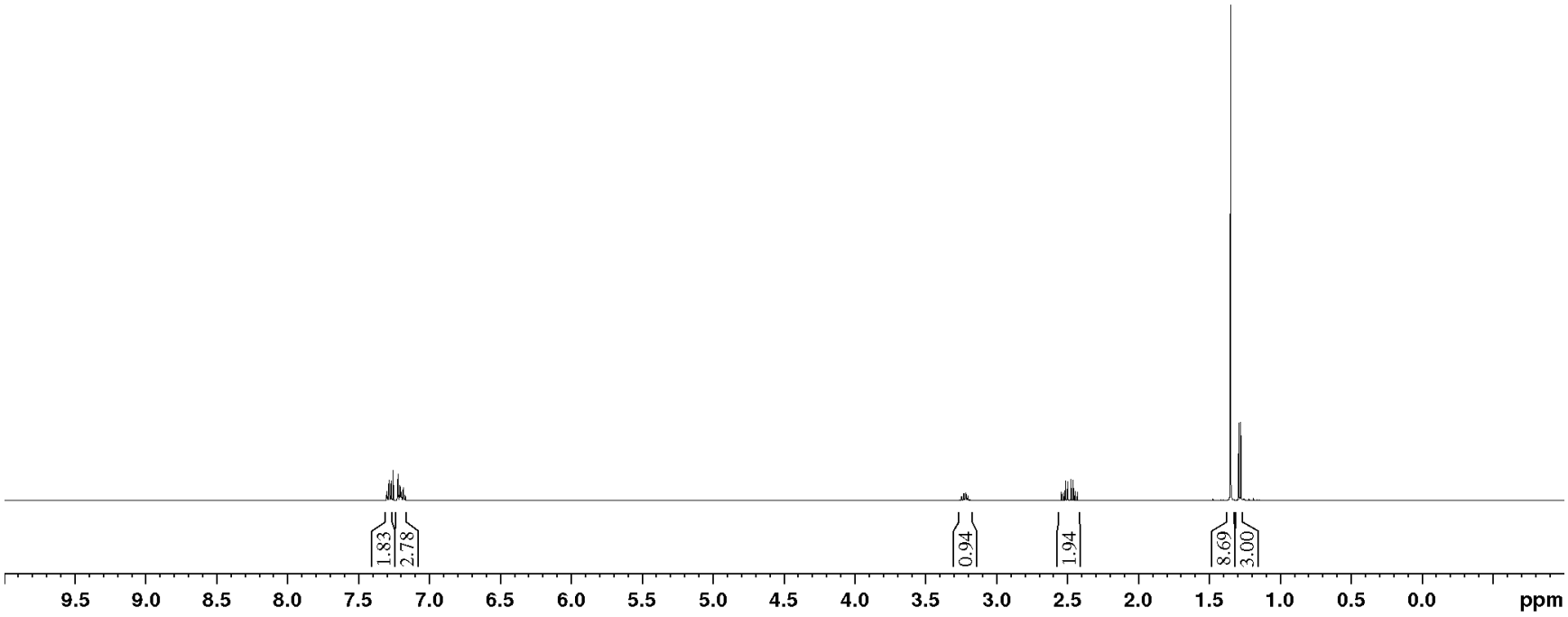
^{1}H NMR

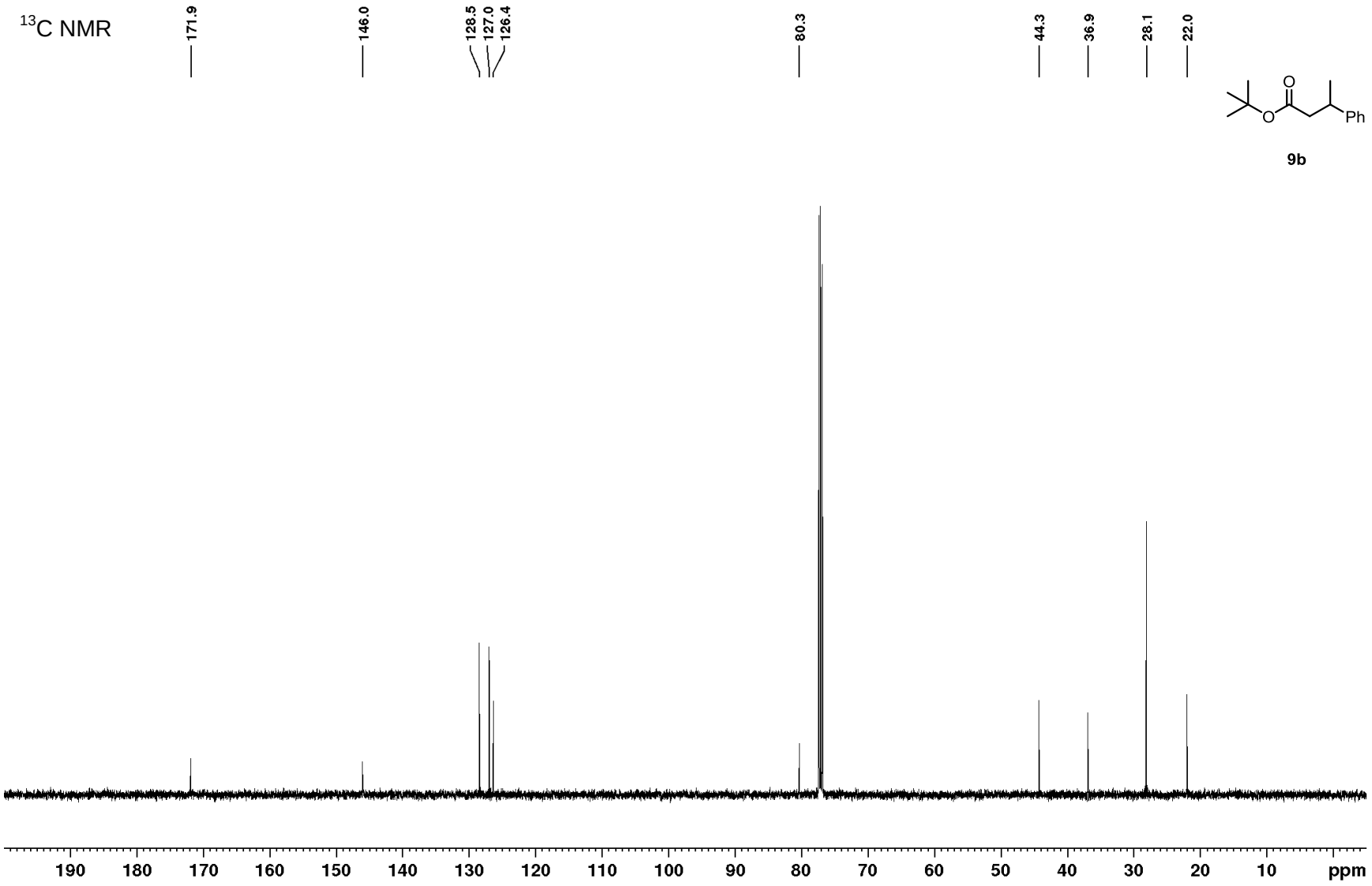




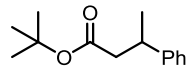


9b

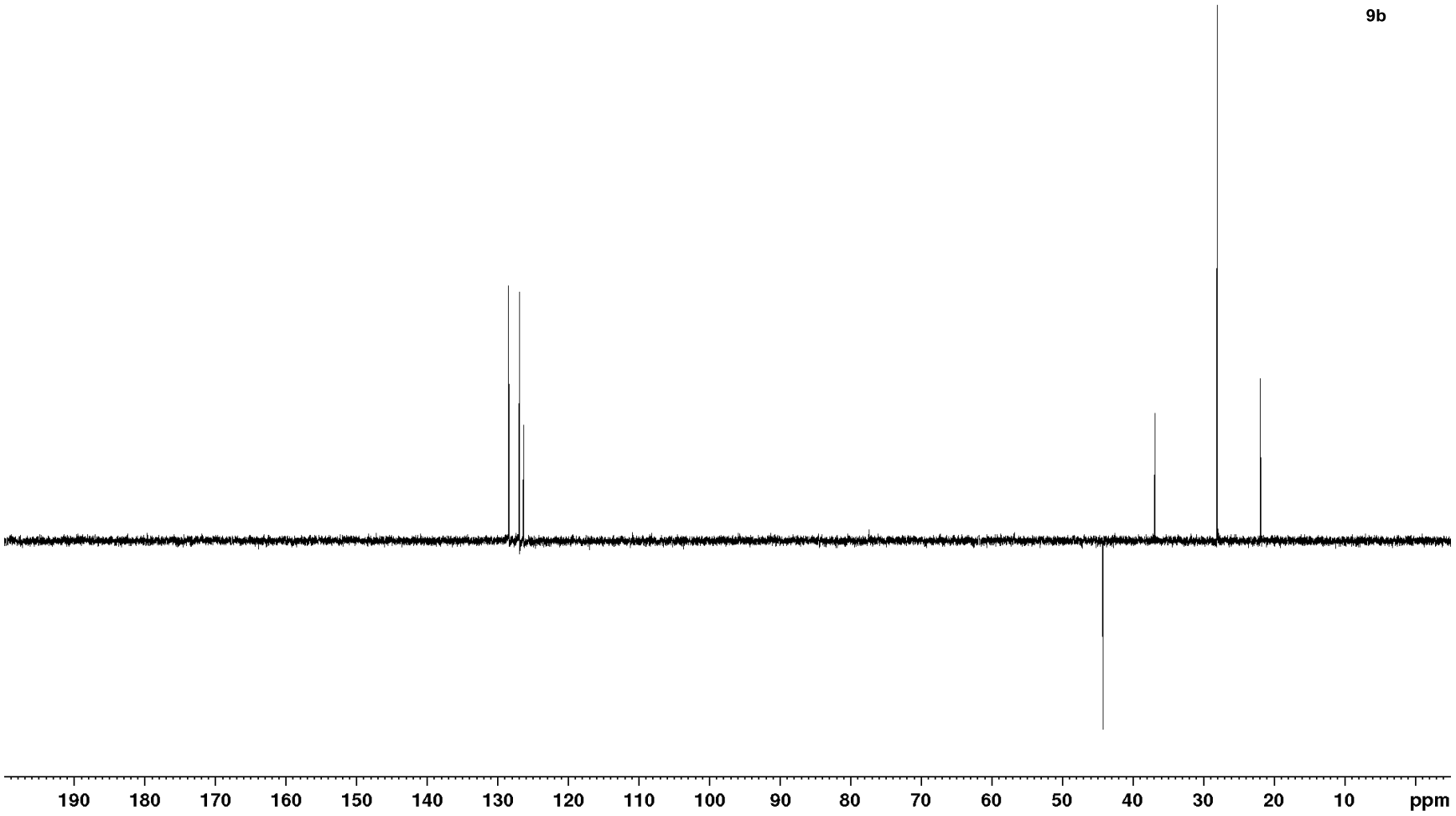



^{13}C NMR
171.9
146.0
128.5
127.0
126.4
80.3
44.3
36.9
28.1
22.0
O
O
Ph
9b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

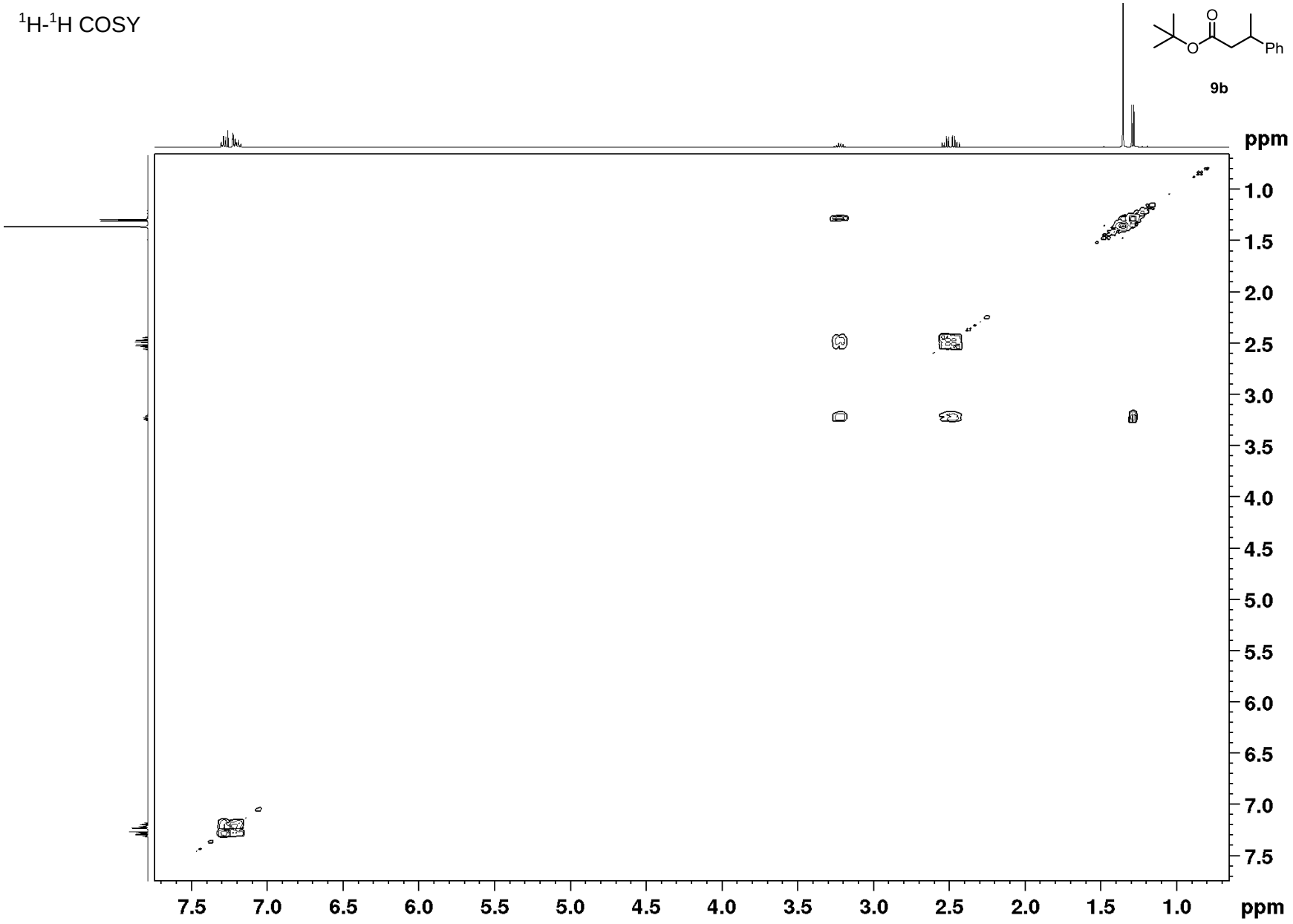
^{13}C DEPT NMR



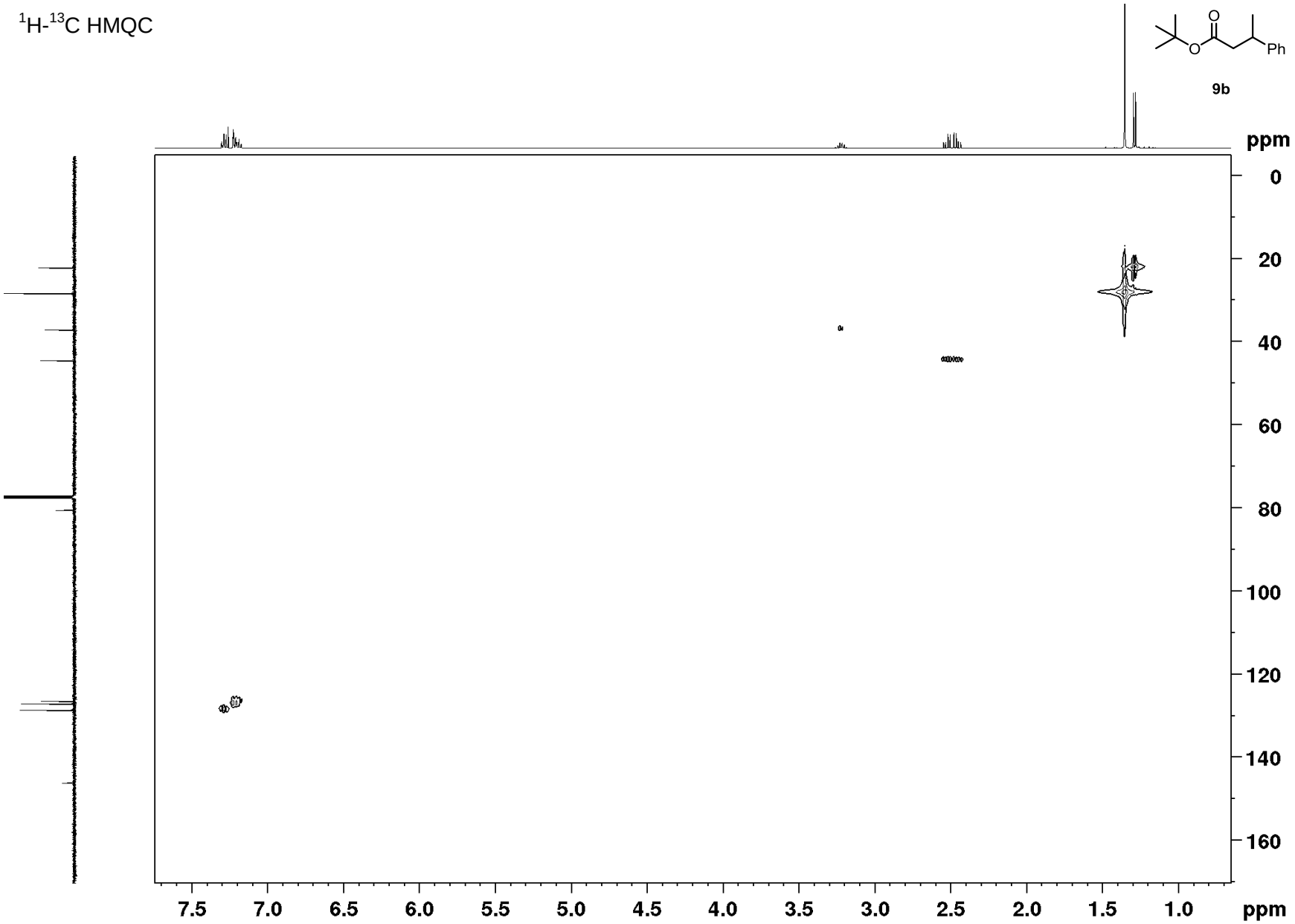
9b



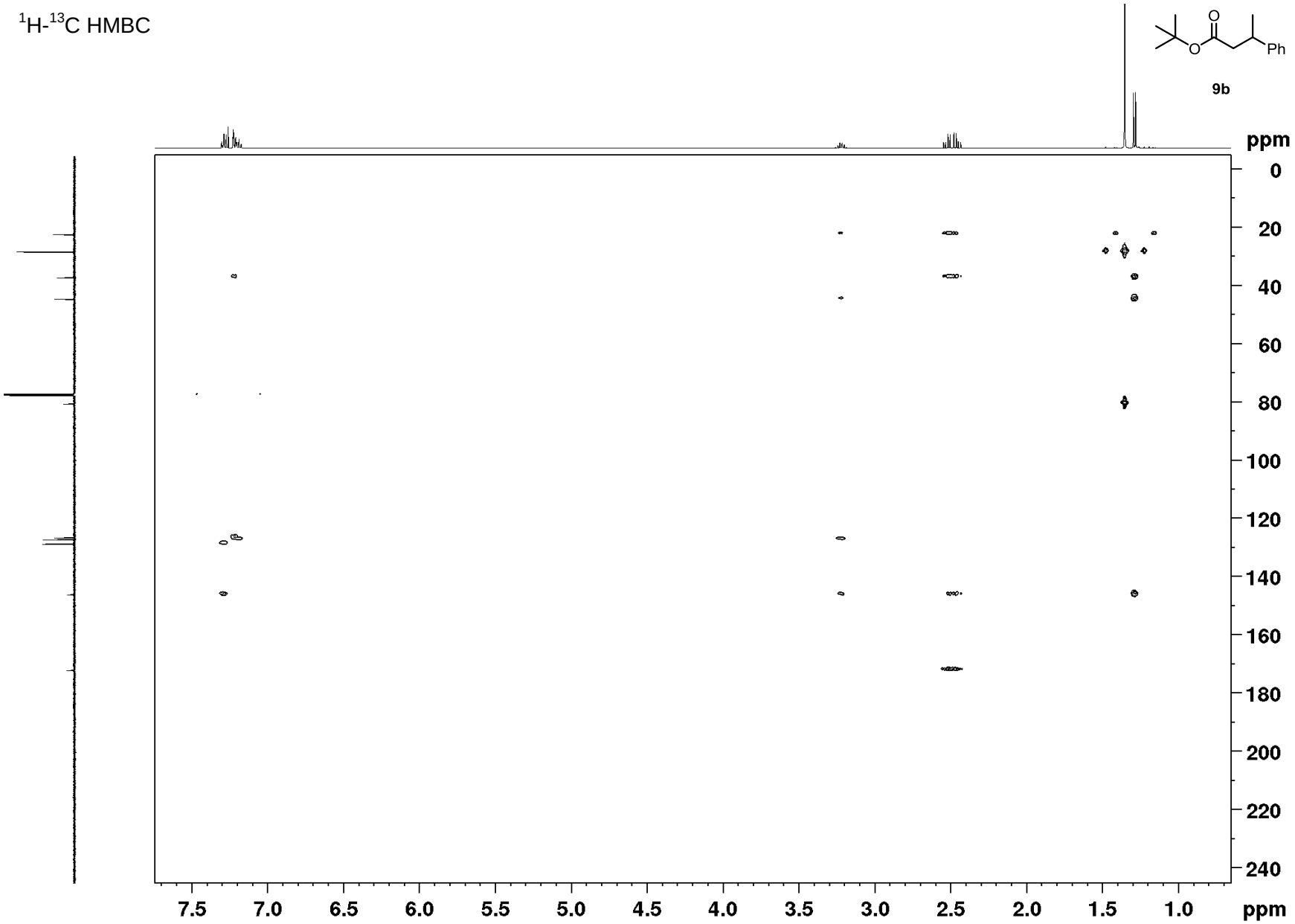
^{1}H-^{1}H COSY

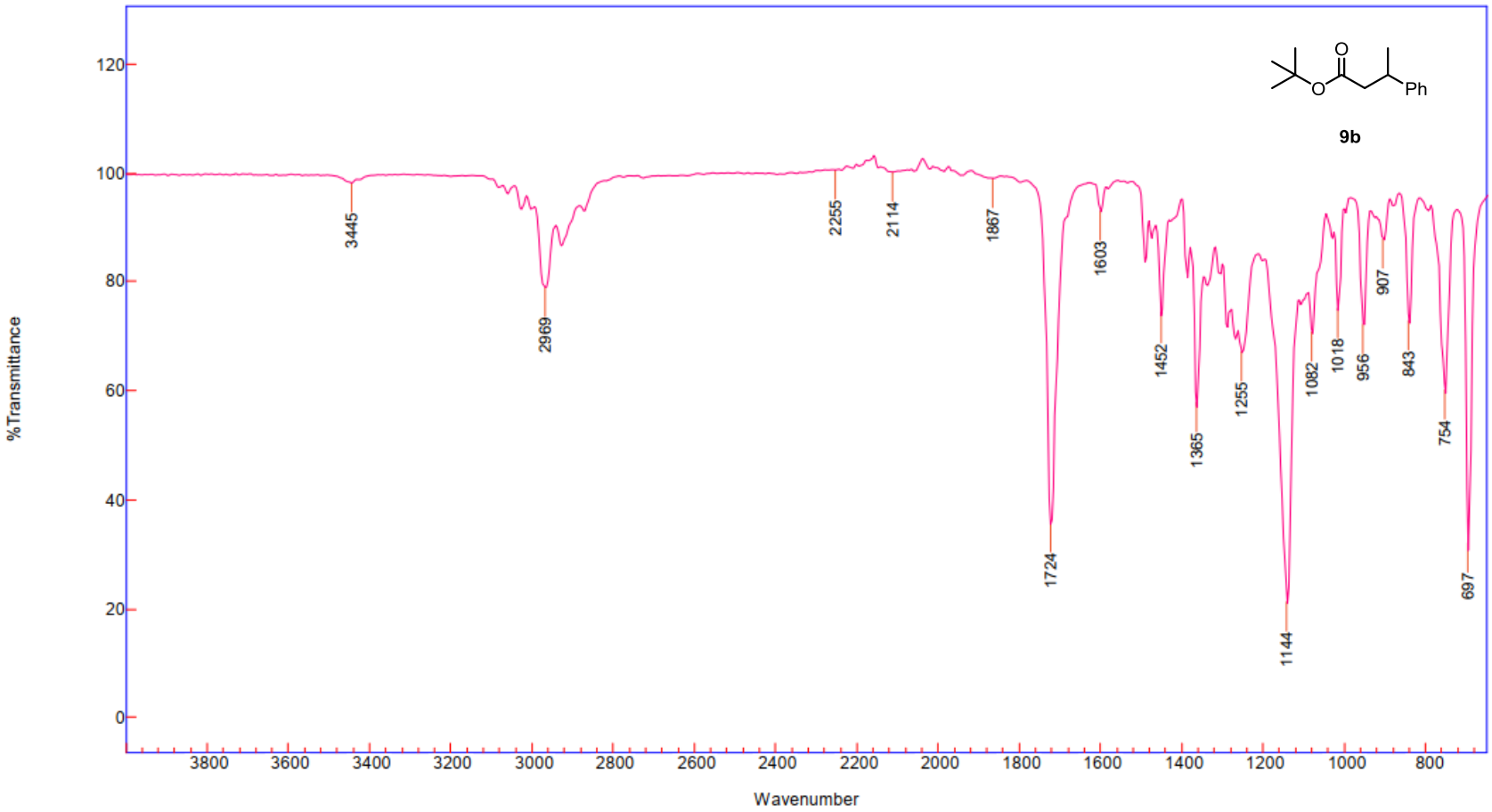


^{1}H-^{13}C HMQC


O
O
Ph
9b
ppm
0
20
40
60
80
100
120
140
160
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
ppm

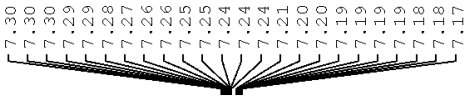
^{1}H-^{13}C HMBC

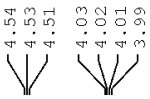

O
O
Ph
9b
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

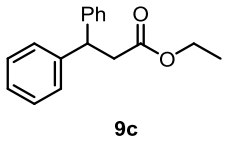

%Transmittance
120
100
80
60
40
20
0
3445
2969
2255
2114
1867
1724
1603
1452
1365
1255
1144
1082
1018
956
907
843
754
697
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber
O
O
Ph
9b

Ethyl 3,3-diphenylpropanoate (9c)

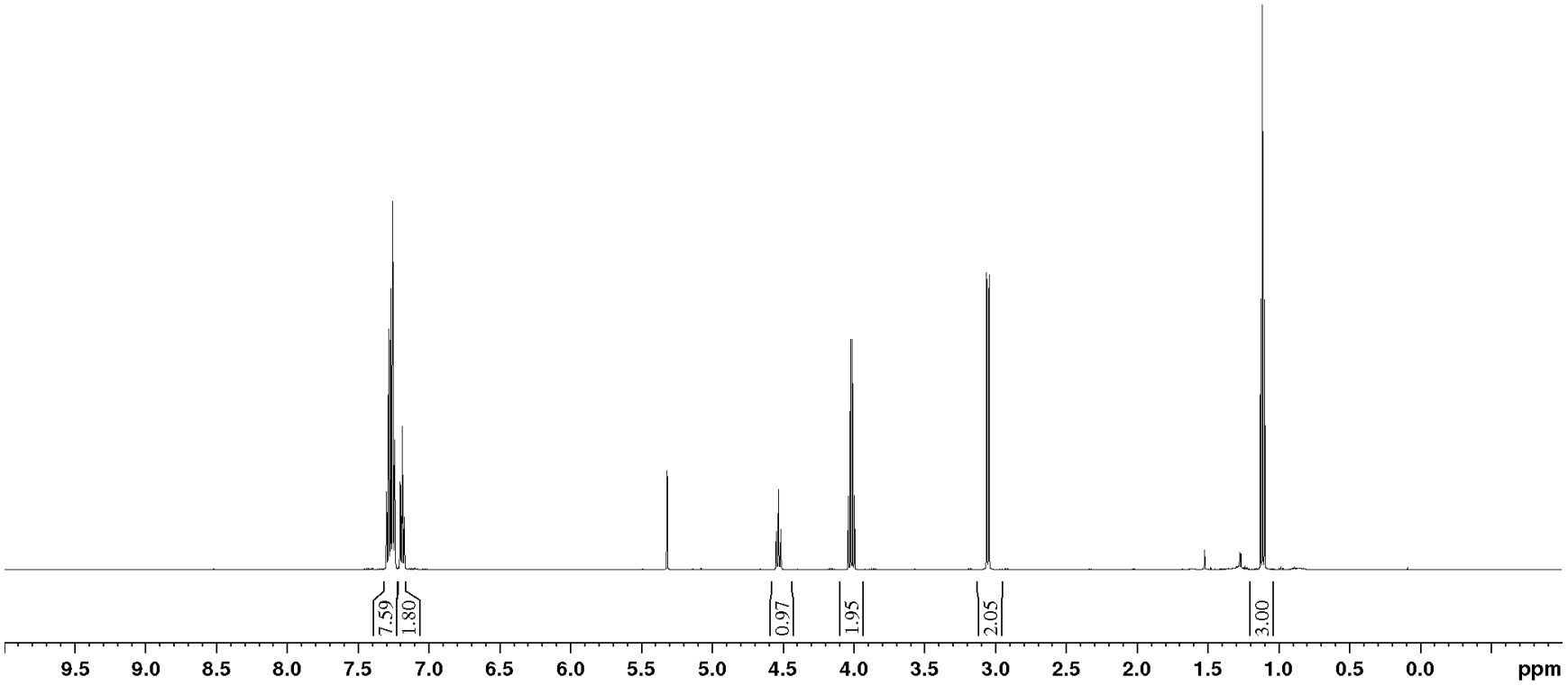
^{1}H NMR

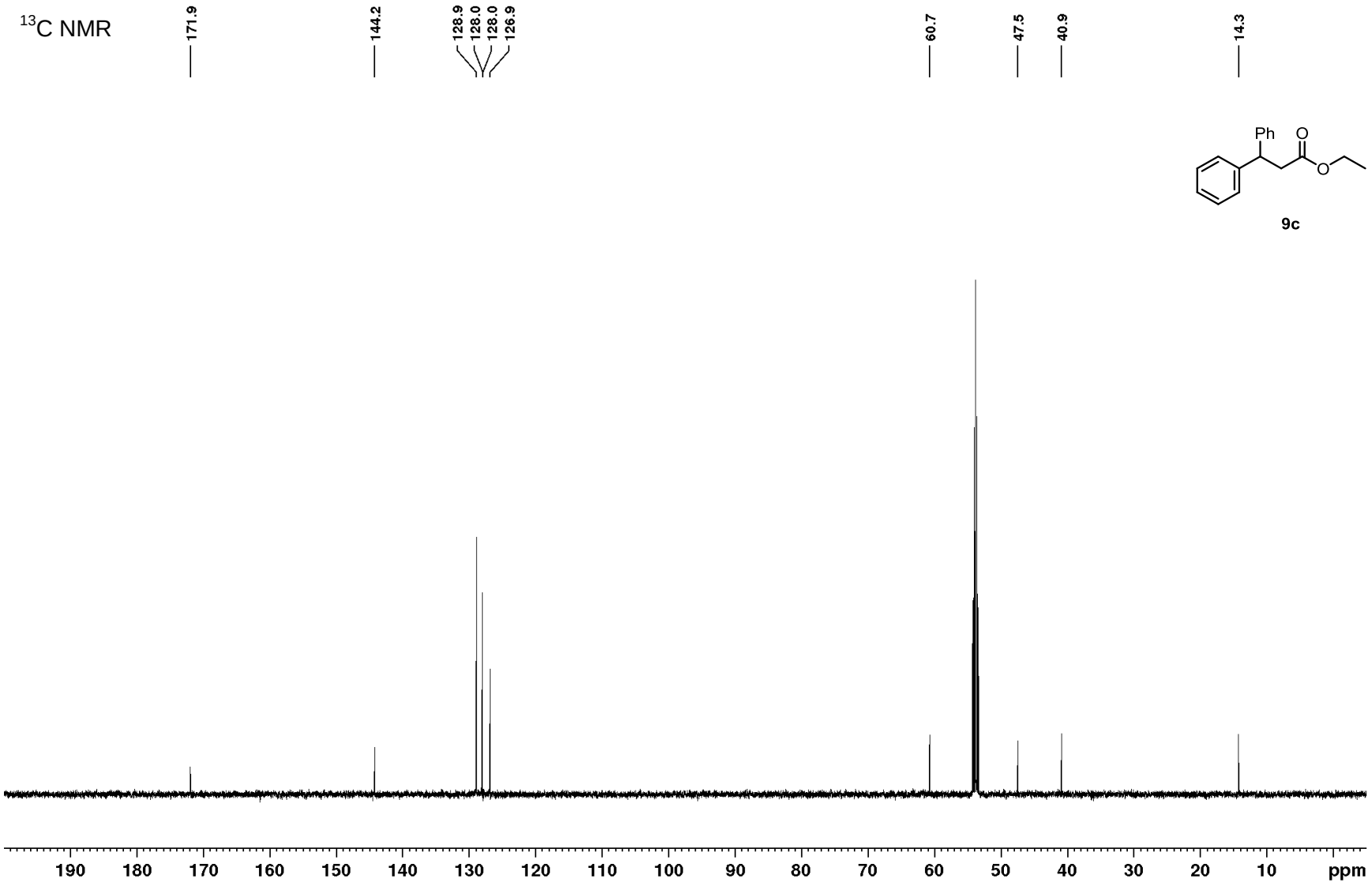




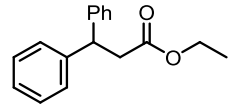


9c

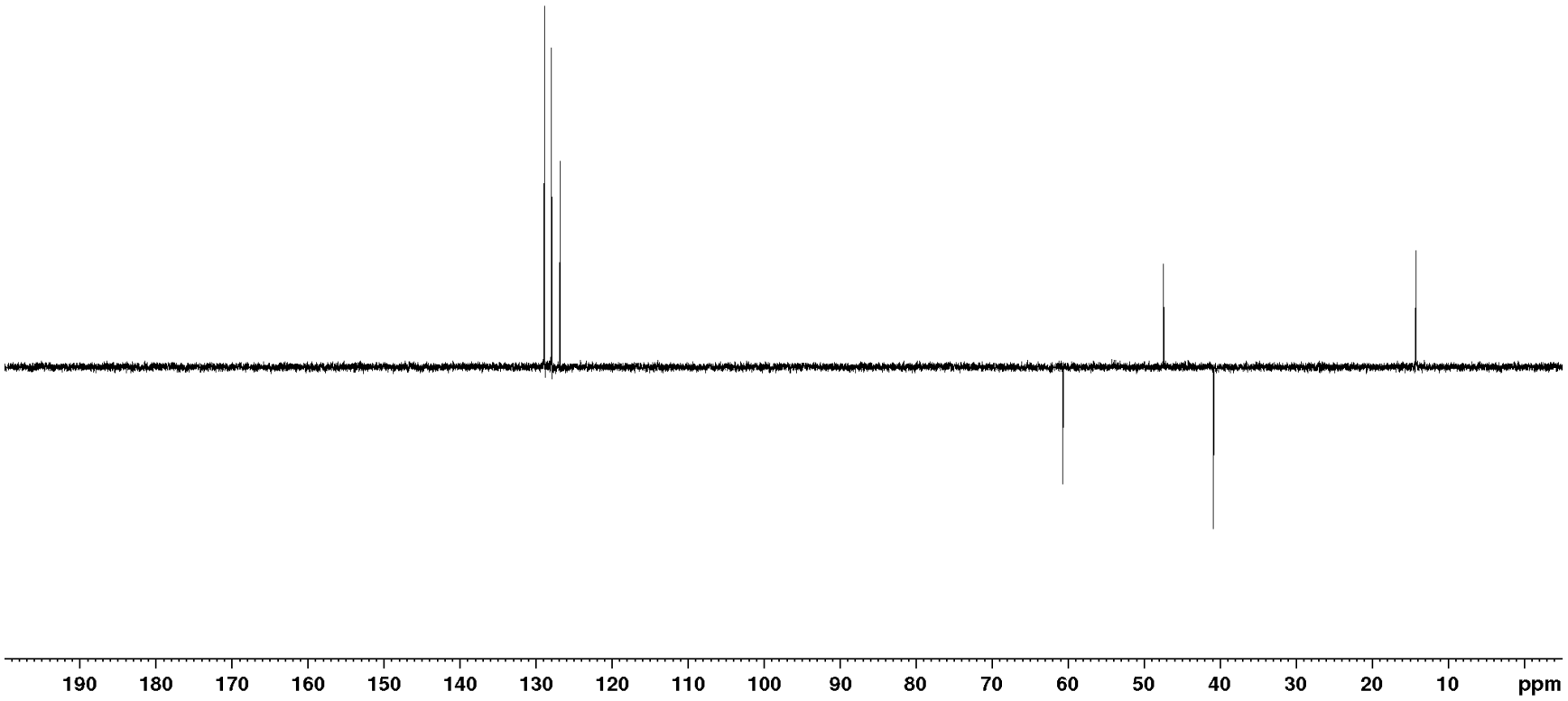



^{13}C NMR
171.9
144.2
128.9
128.0
128.0
126.9
60.7
47.5
40.9
14.3
Ph
O
O
9c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

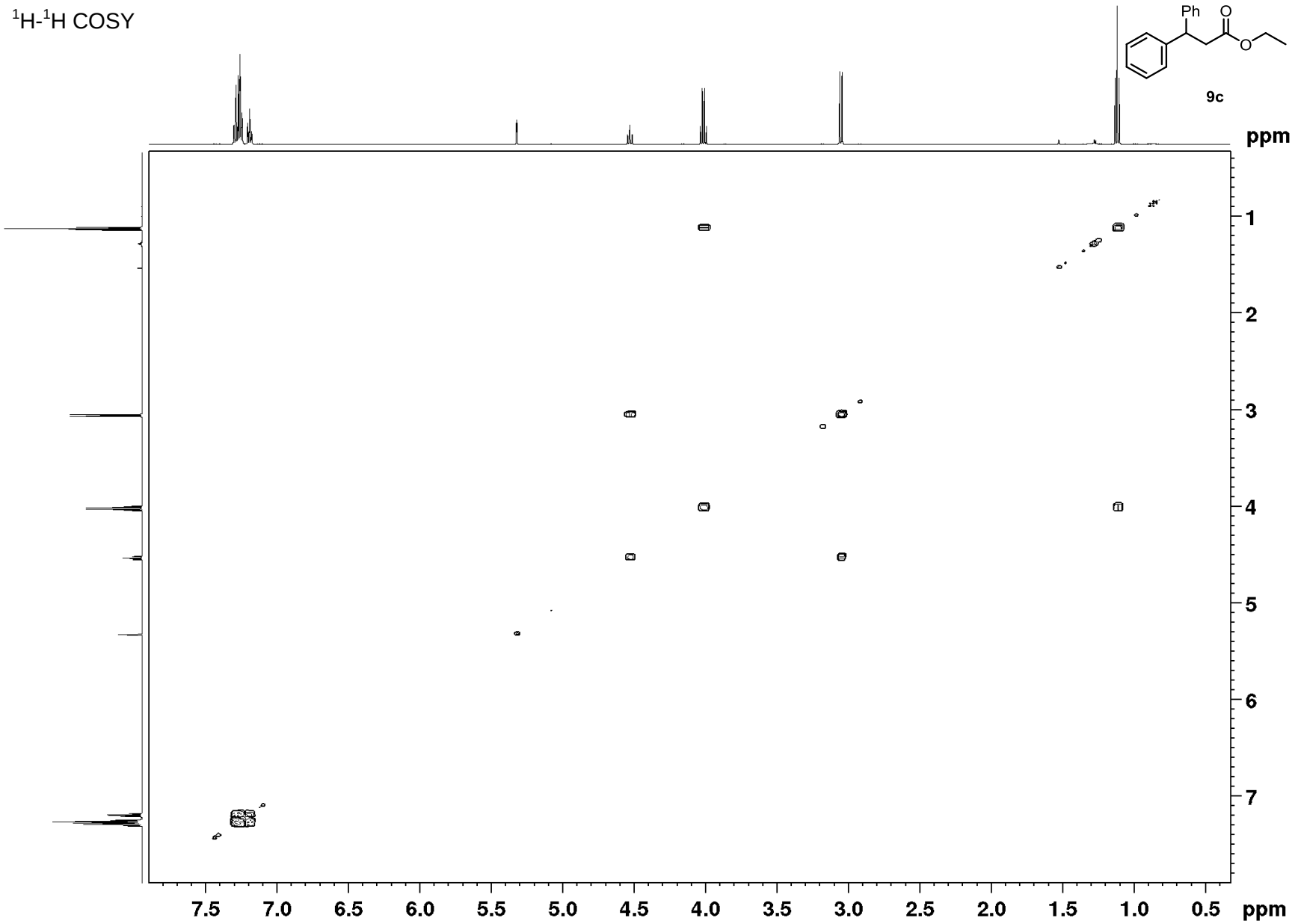
^{13}C DEPT NMR

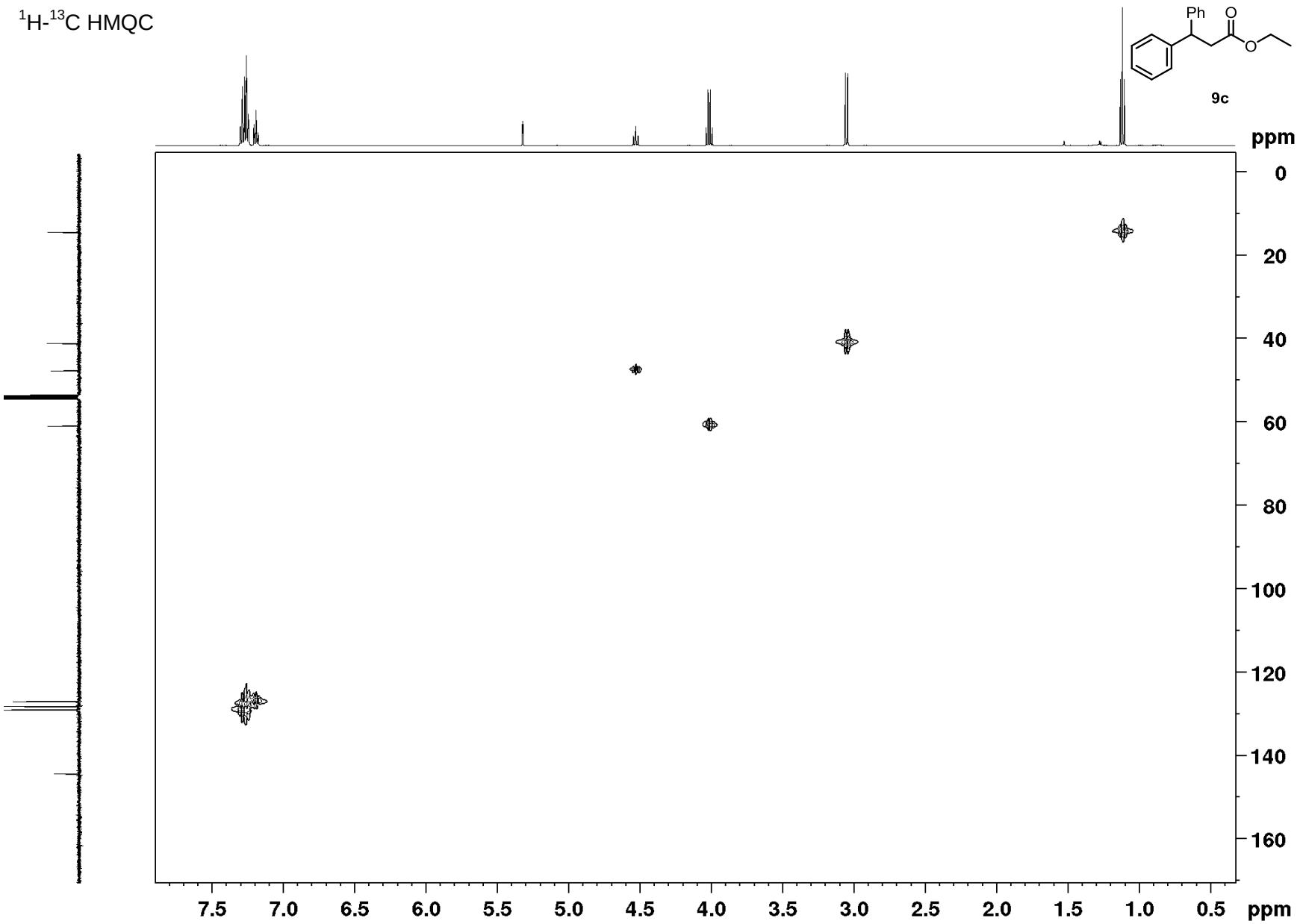


9c

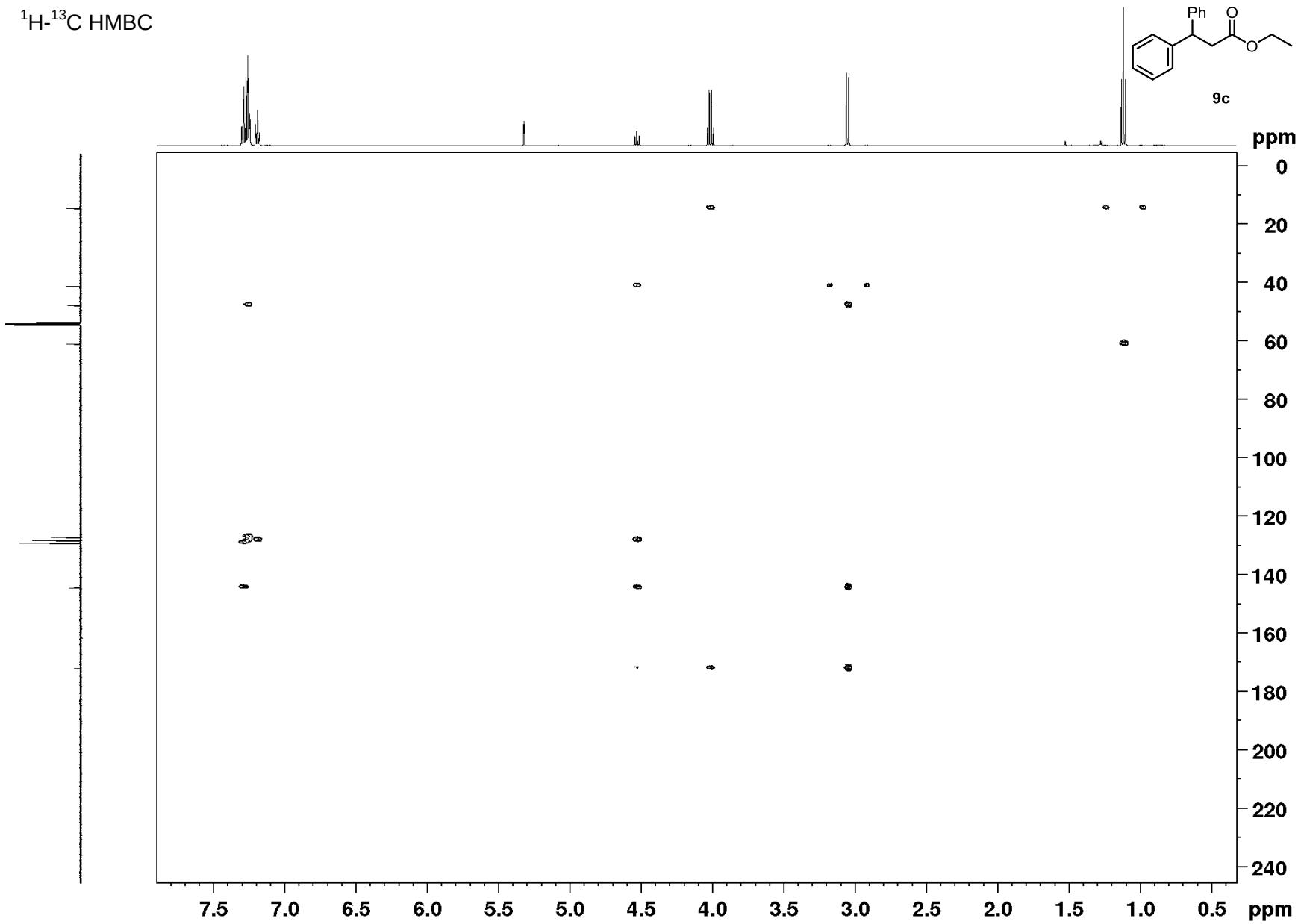


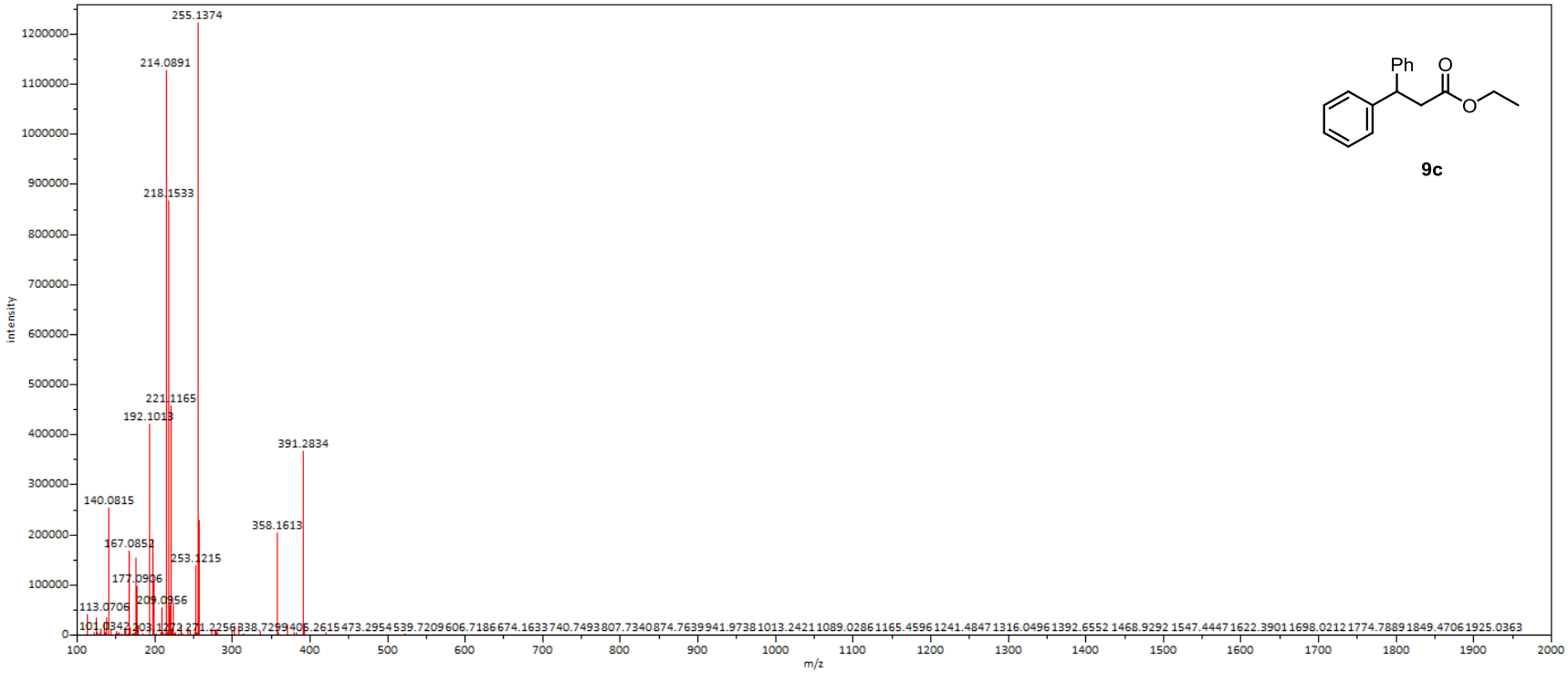
^{1}H-^{1}H COSY




^{1}H-^{13}C HMQC
Ph
O
O
9c
ppm
0
20
40
60
80
100
120
140
160
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
ppm

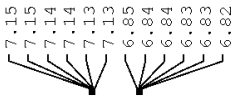
^{1}H-^{13}C HMBC

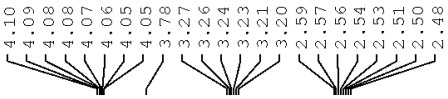

Ph
O
O
9c
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

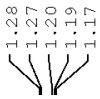

255.1374
214.0891
218.1533
221.1165
192.1013
391.2834
140.0815
358.1613
167.0852
253.1215
177.0906
209.0956
113.0706
intensity
m/z
Ph
O
O
9c

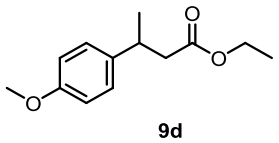
Ethyl 3-(4-methoxyphenyl)butanoate (9d)

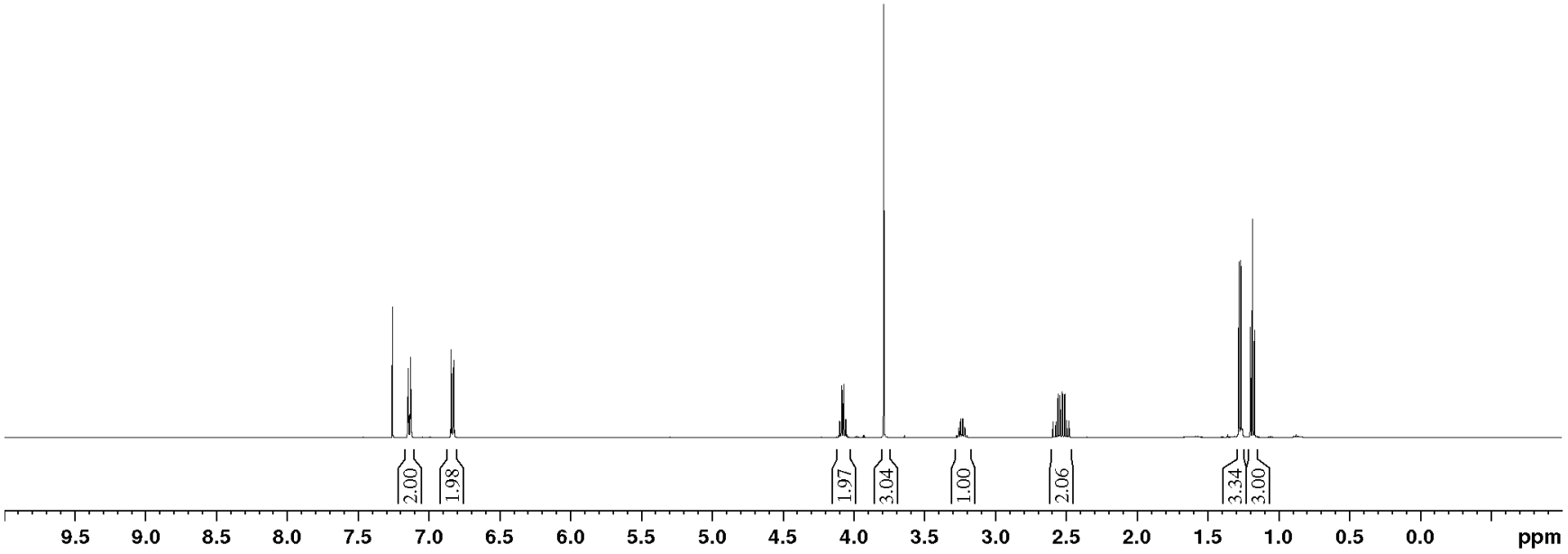
^{1}H NMR

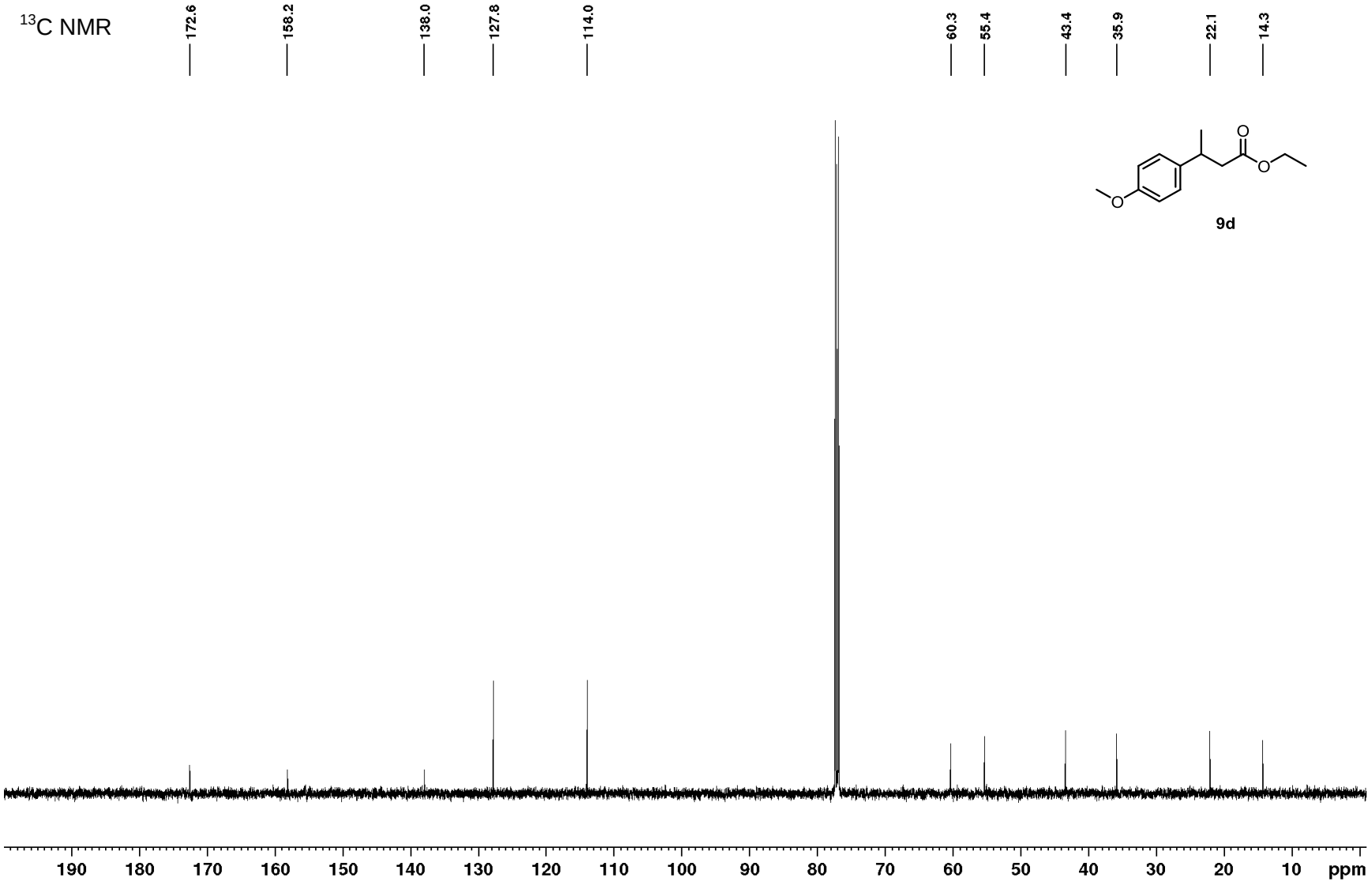




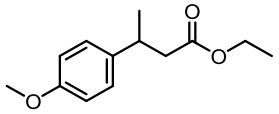




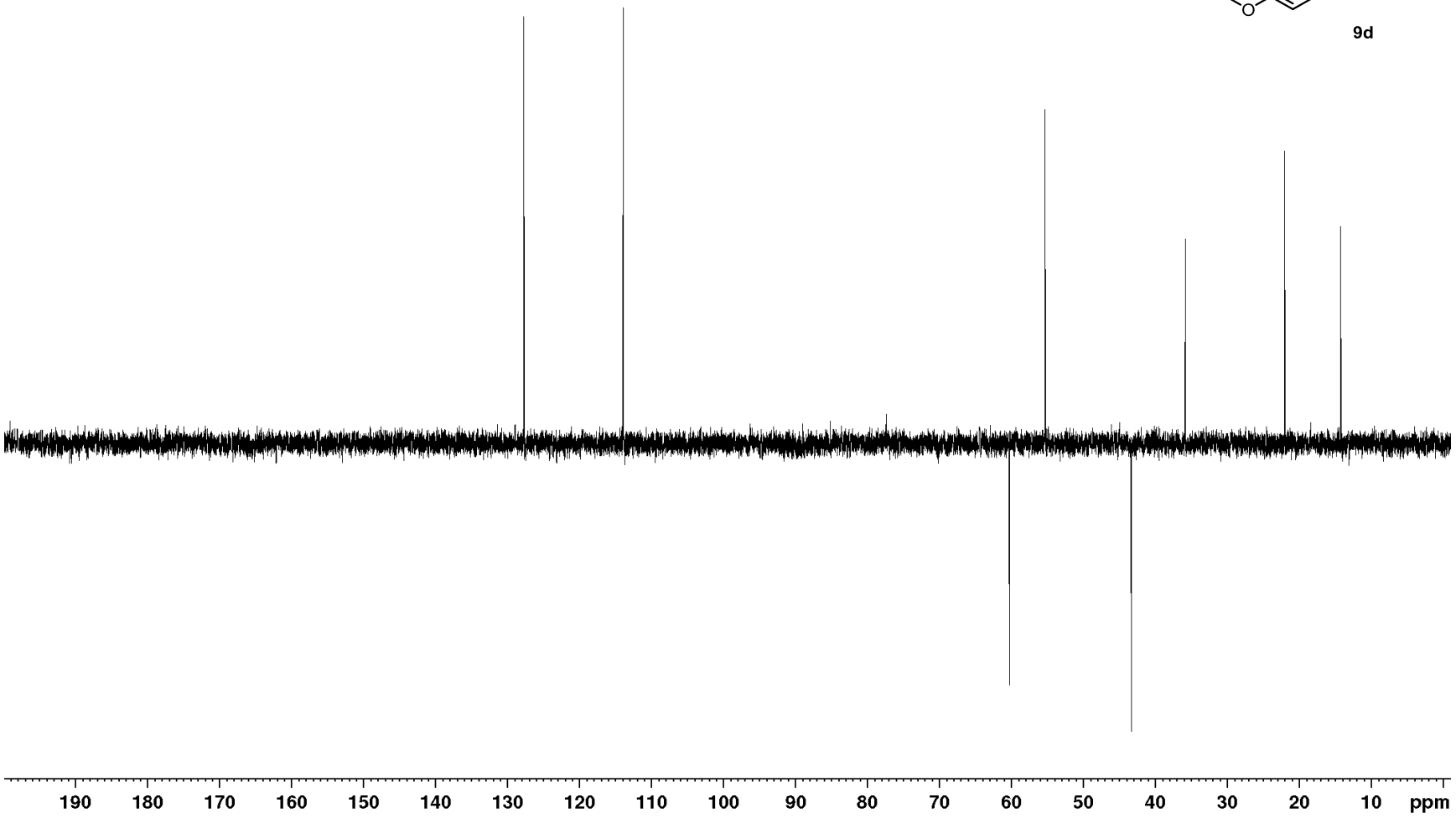



^{13}C NMR
172.6
158.2
138.0
127.8
114.0
60.3
55.4
43.4
35.9
22.1
14.3
O
O
O
9d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

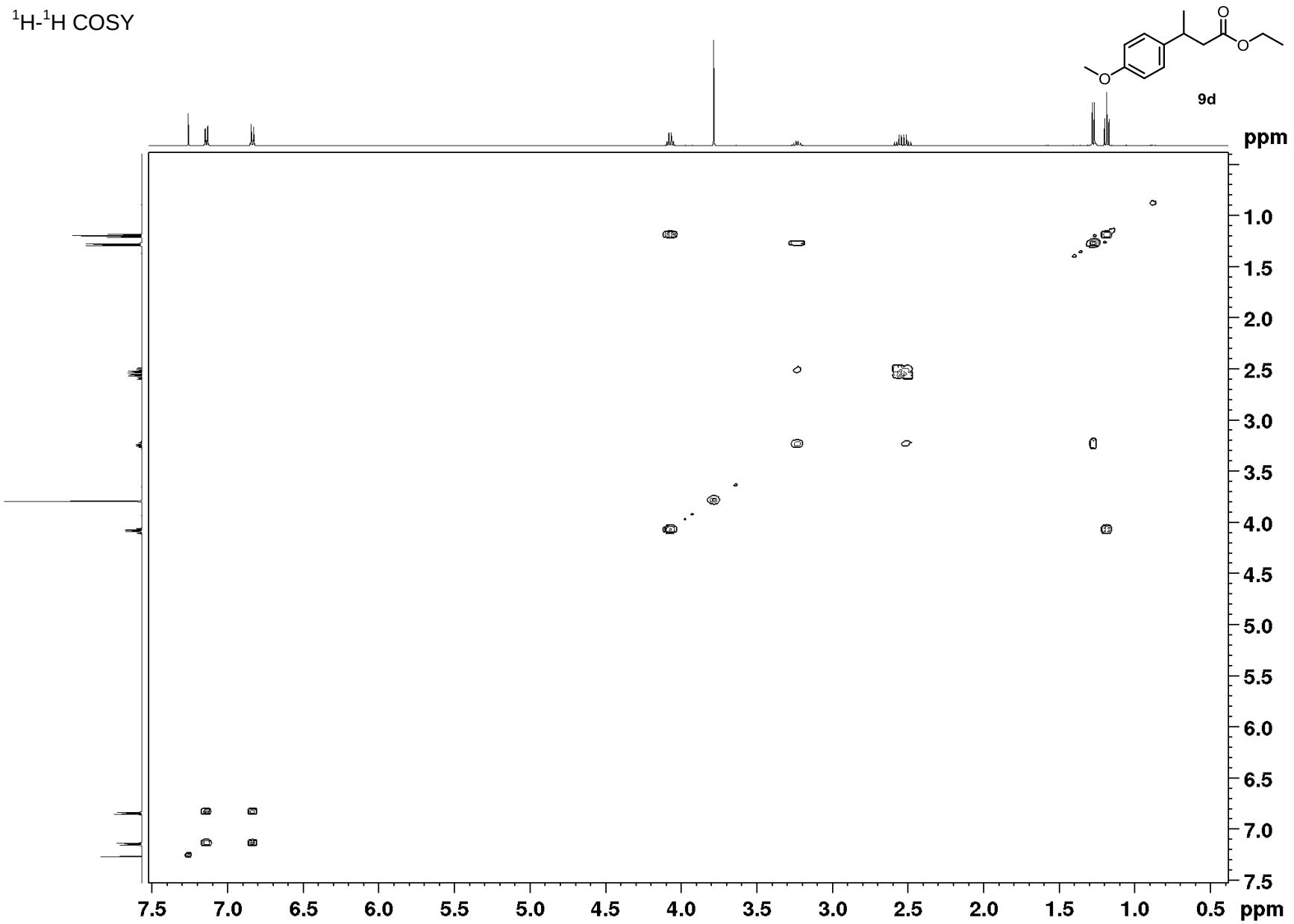
^{13}C DEPT NMR

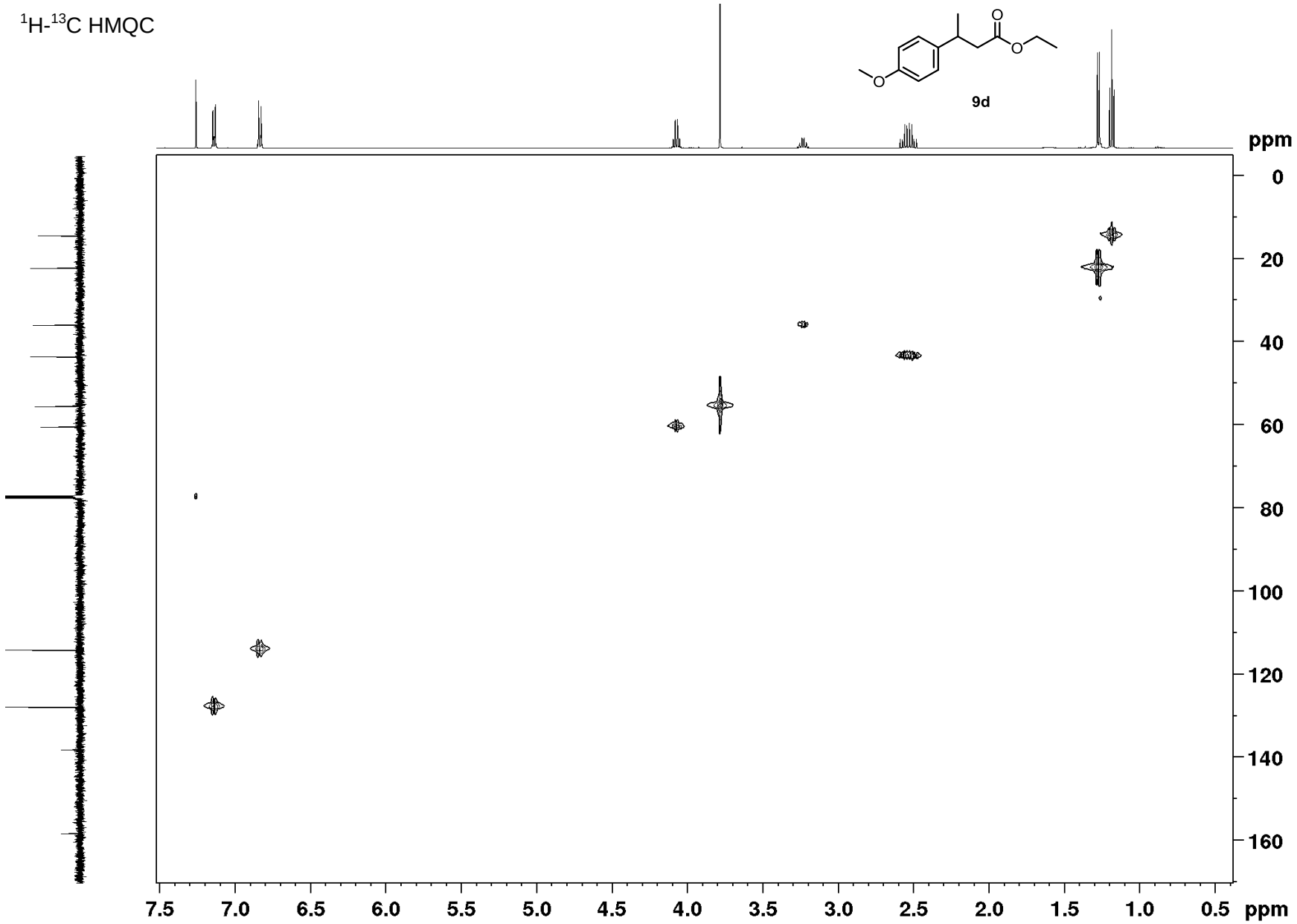


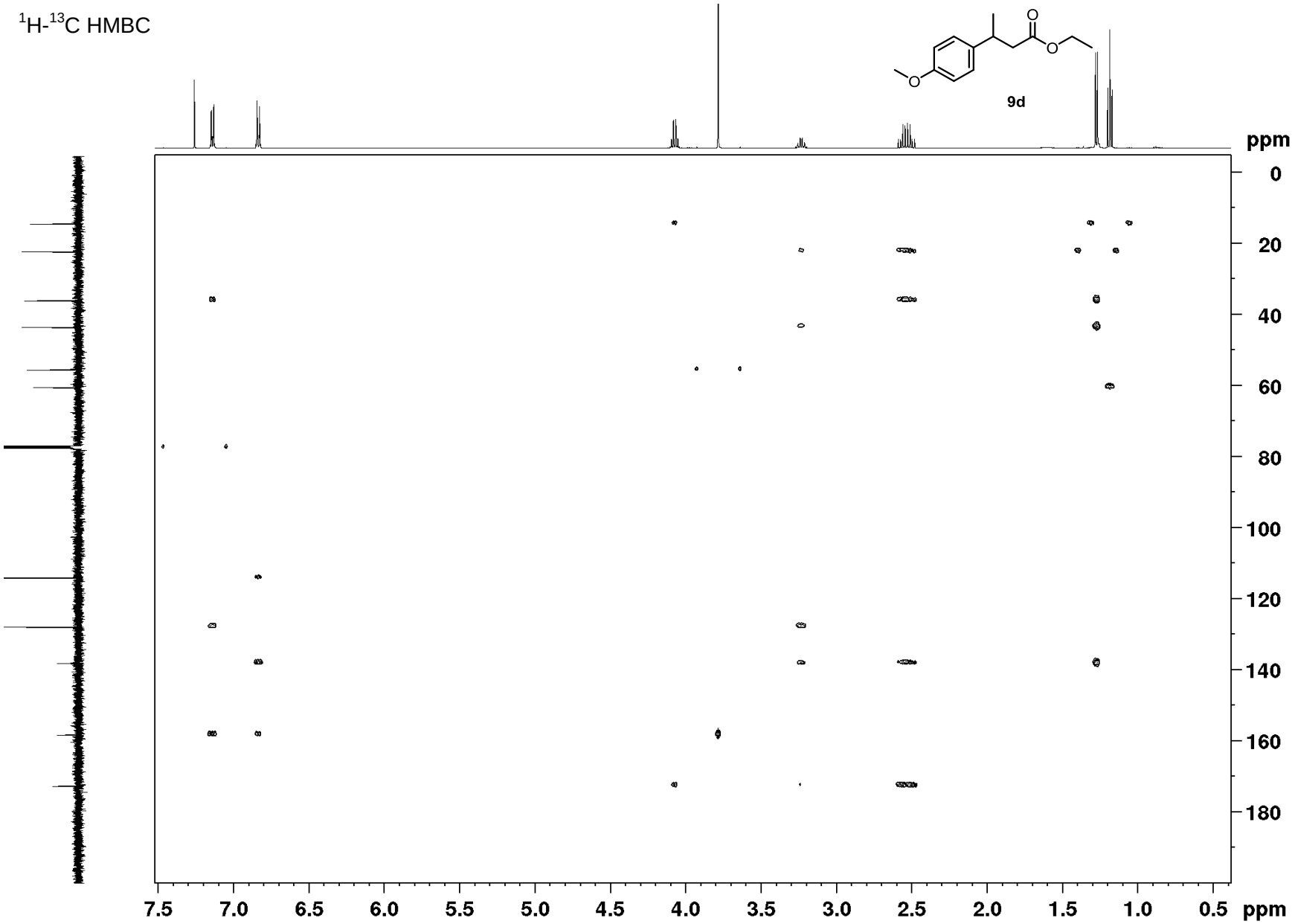
9d

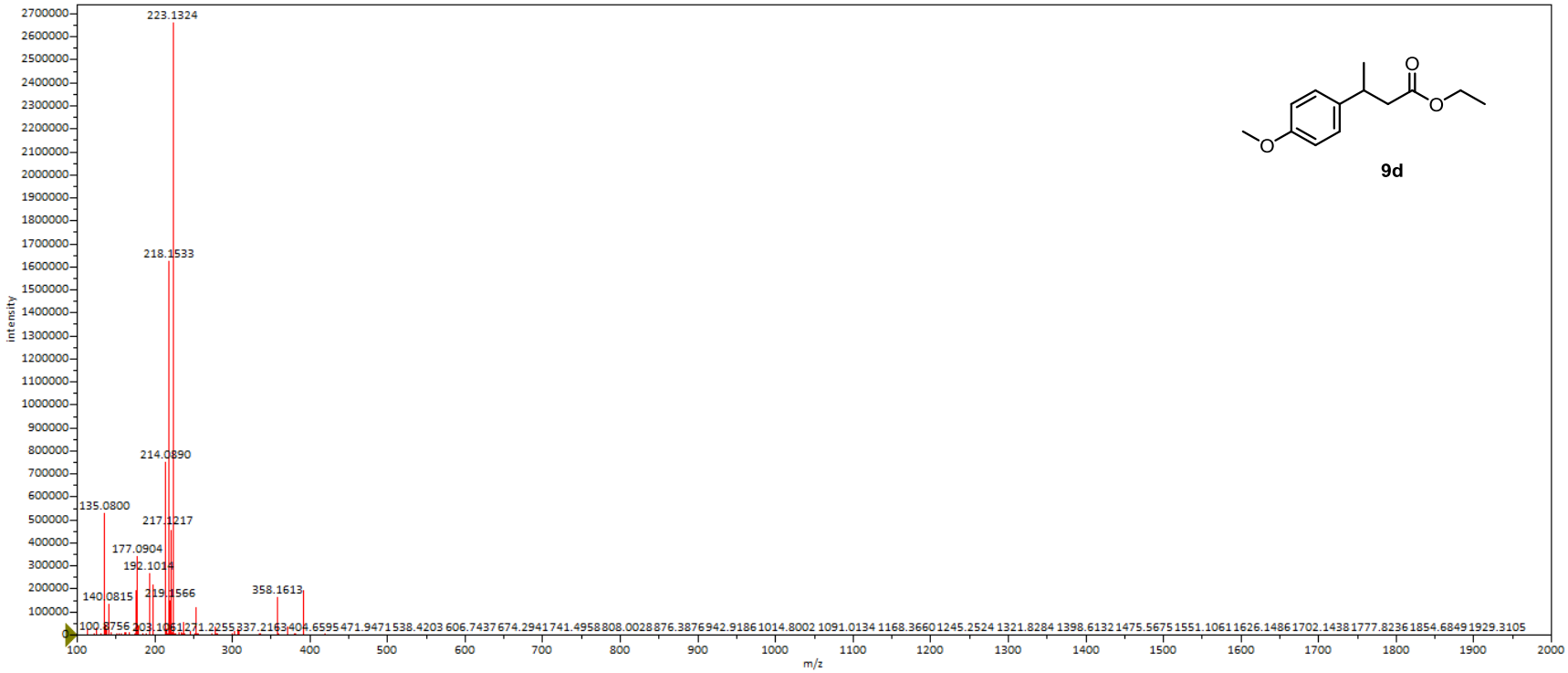


^{1}H-^{1}H COSY


9d
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
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
ppm

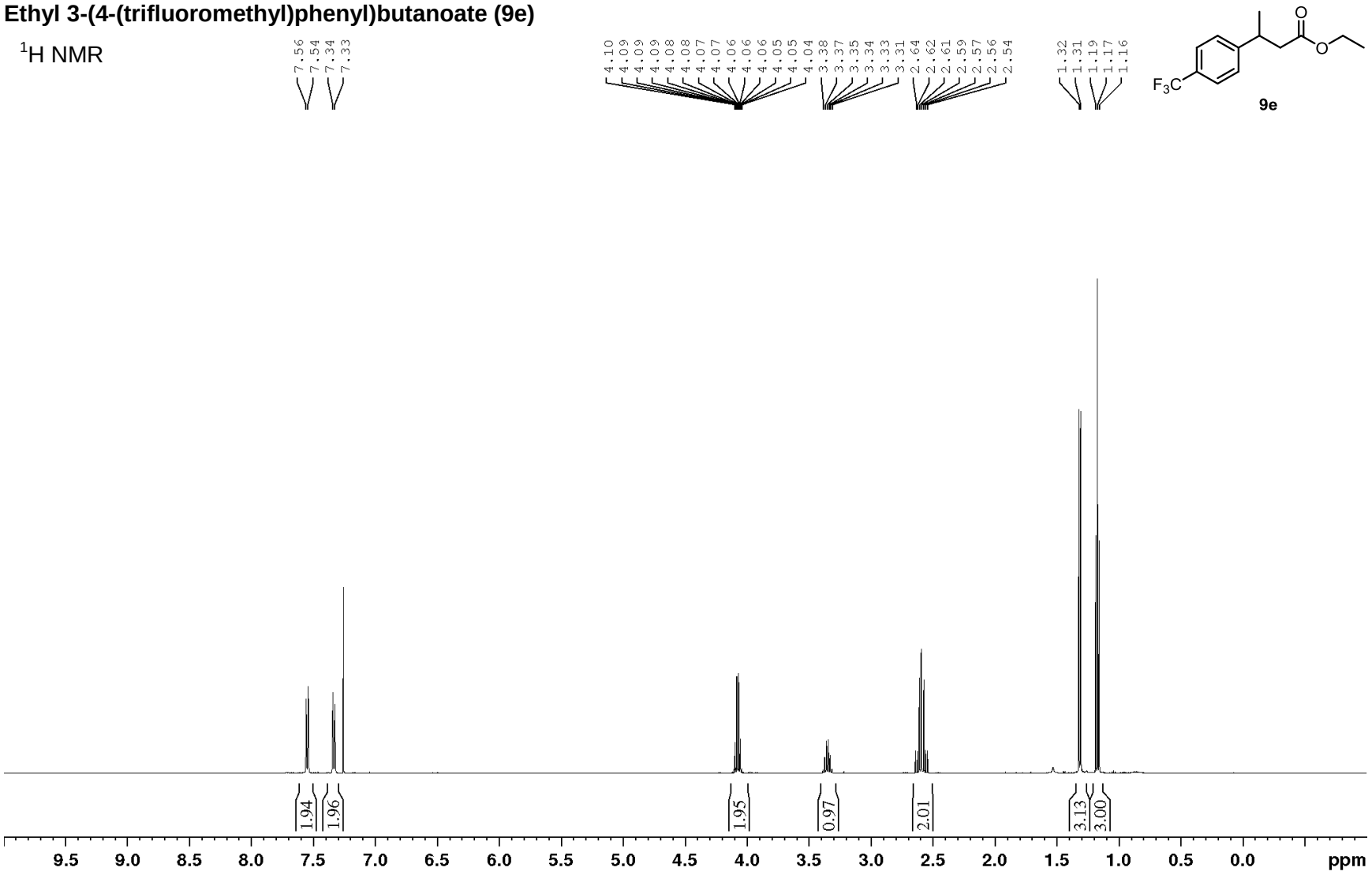

^{1}H-^{13}C HMQC
9d
ppm
0
20
40
60
80
100
120
140
160
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

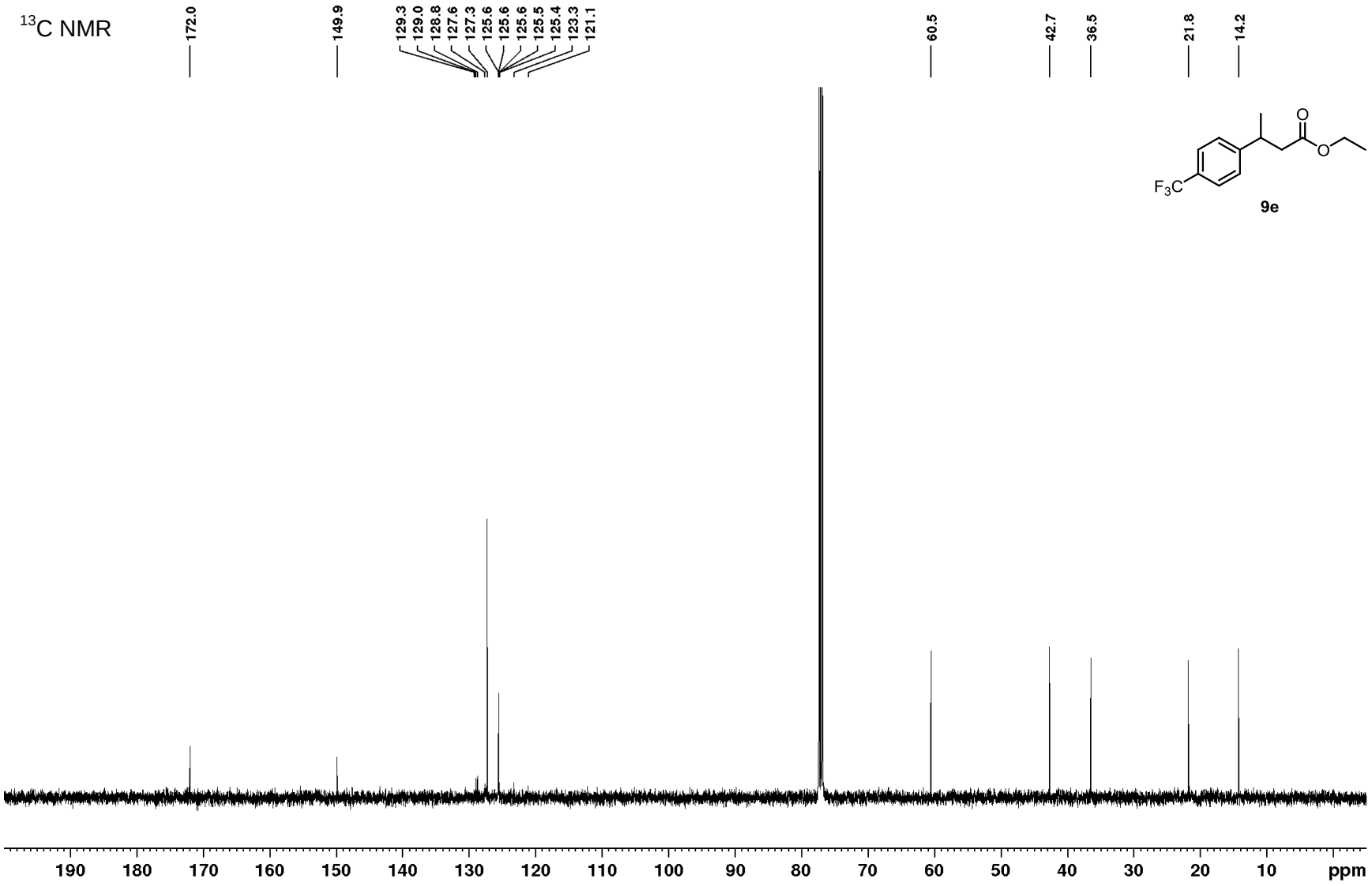

^{1}H-^{13}C HMBC
9d
ppm
0
20
40
60
80
100
120
140
160
180
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


223.1324
218.1533
214.0890
135.0800
217.1217
177.0904
192.1014
219.1566
140.0815
358.1613
intensity
m/z
9d

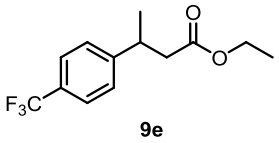
Ethyl 3-(4-(trifluoromethyl)phenyl)butanoate (9e)

^{1}H NMR

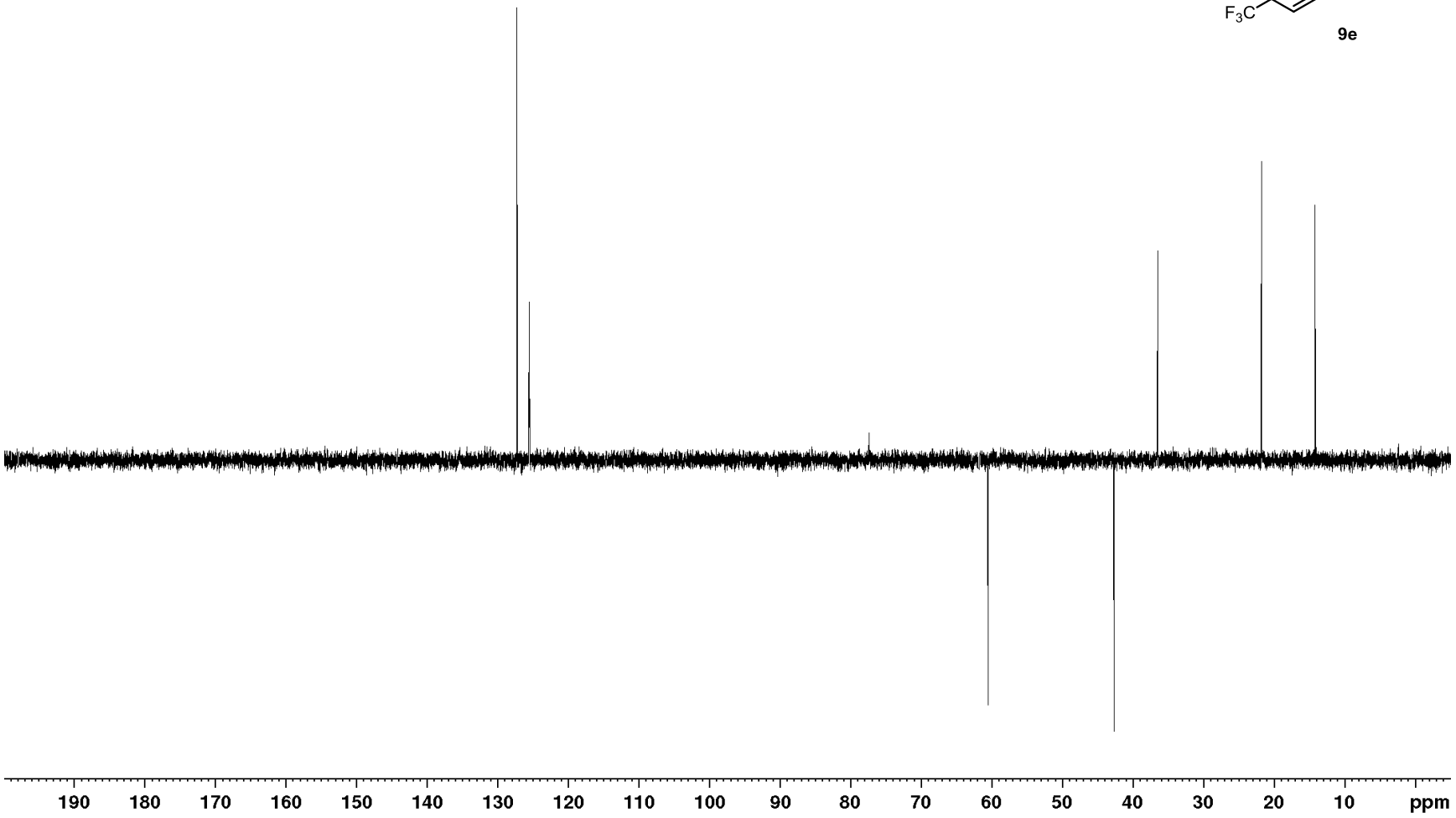



^{13}C NMR
172.0
149.9
129.3
129.0
128.8
127.6
127.3
125.6
125.6
125.6
125.5
125.4
123.3
121.1
60.5
42.7
36.5
21.8
14.2
O
O
F3C
9e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

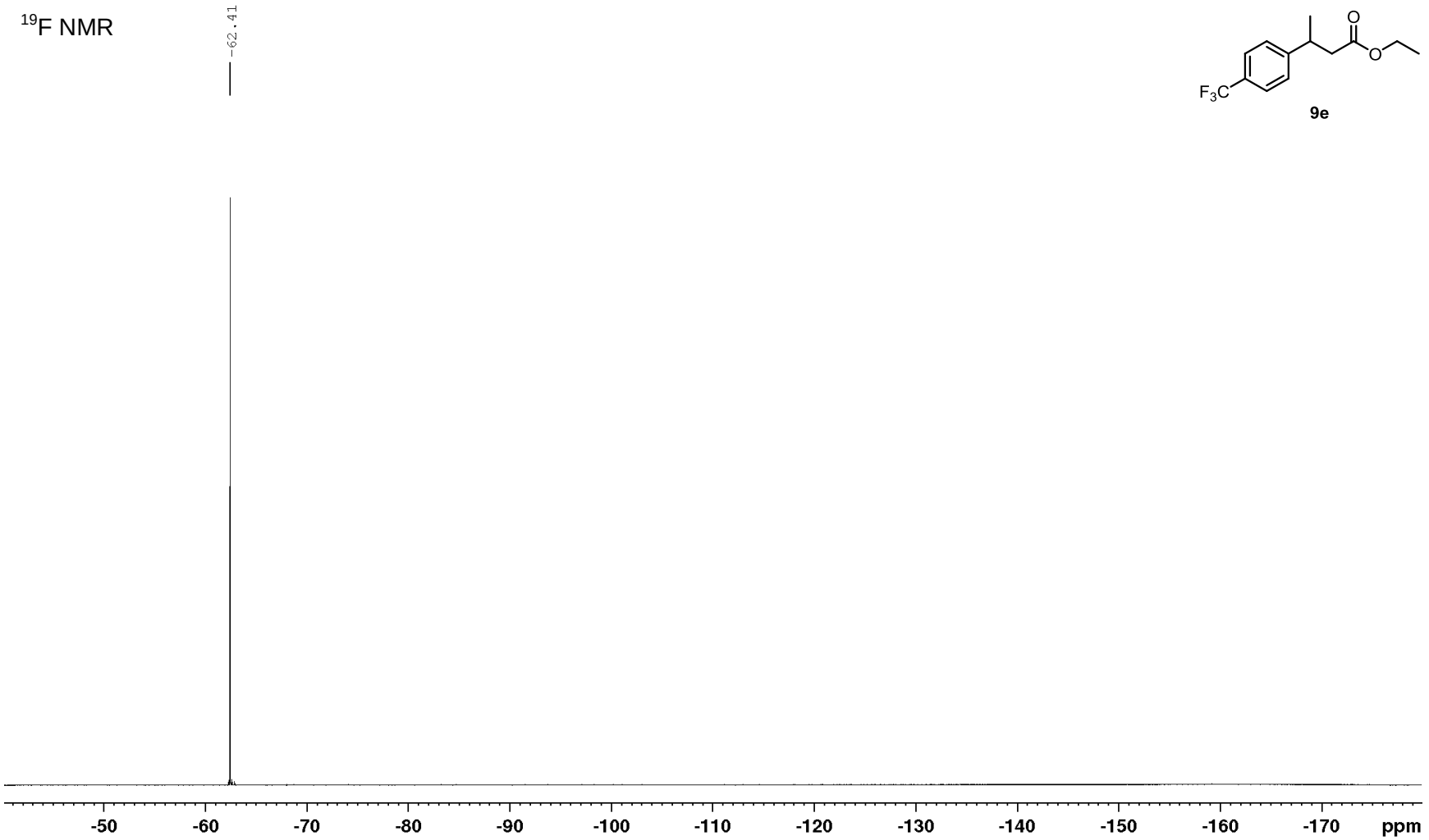
^{13}C DEPT NMR



9e

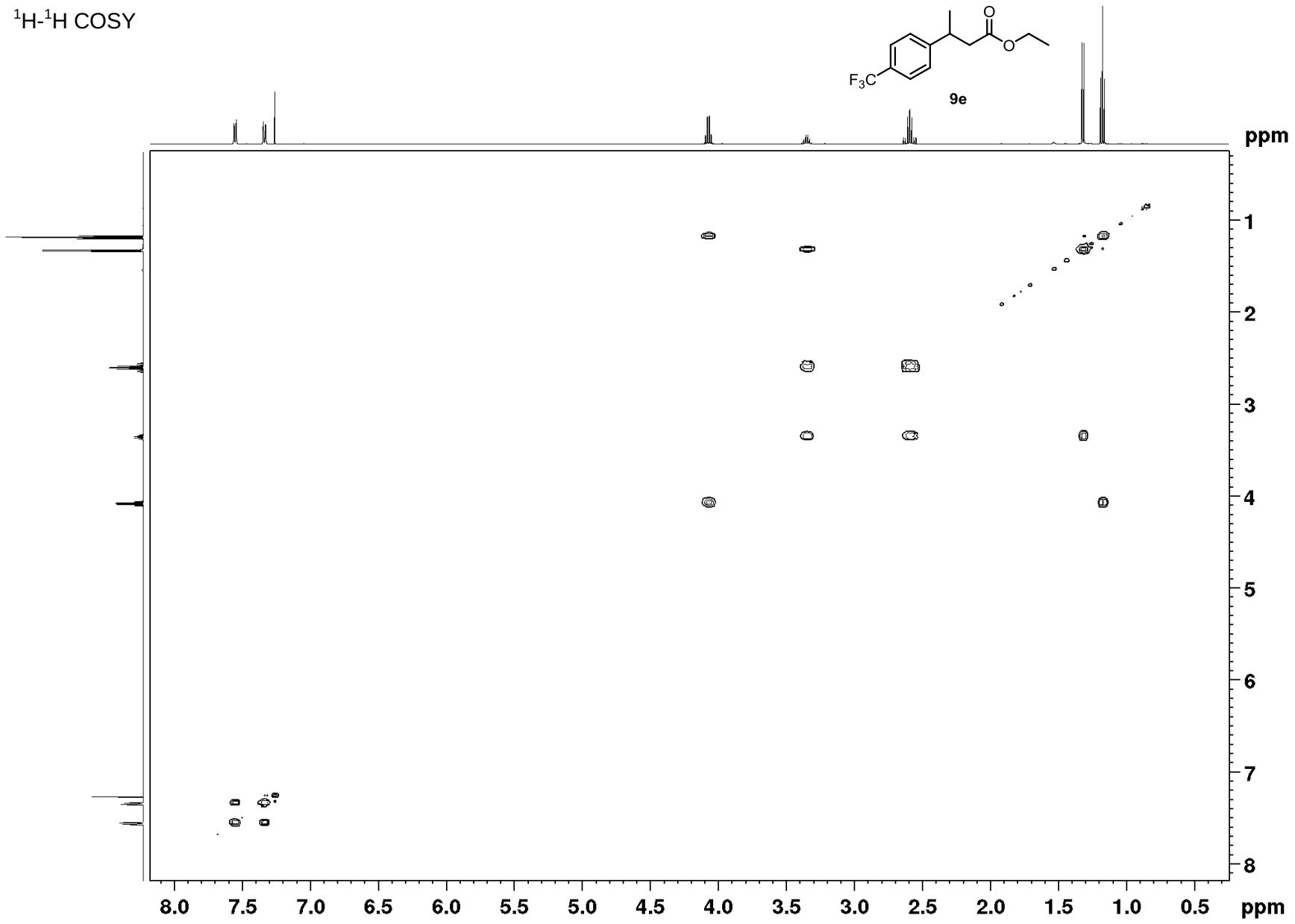


^{19}F NMR

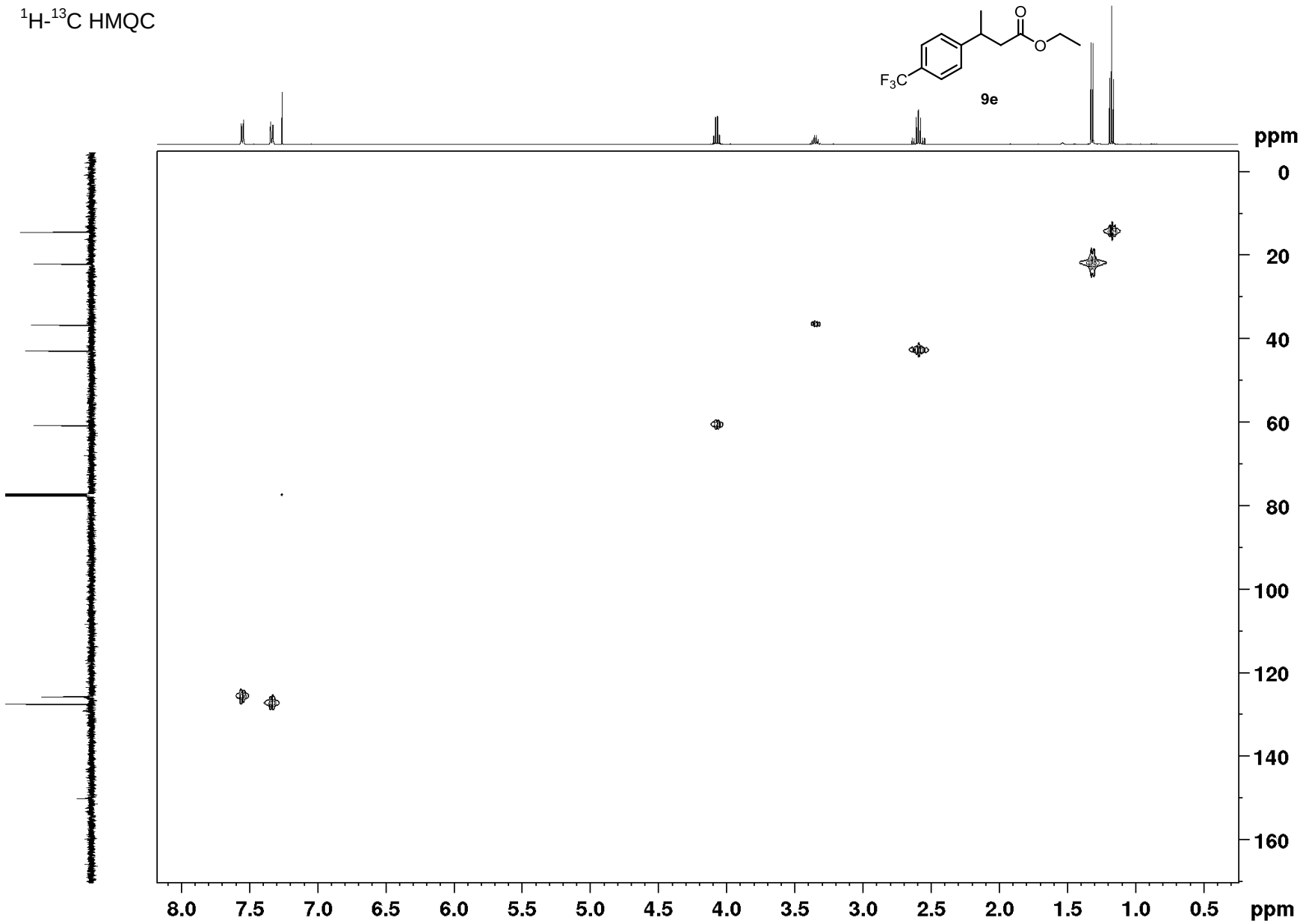


9e

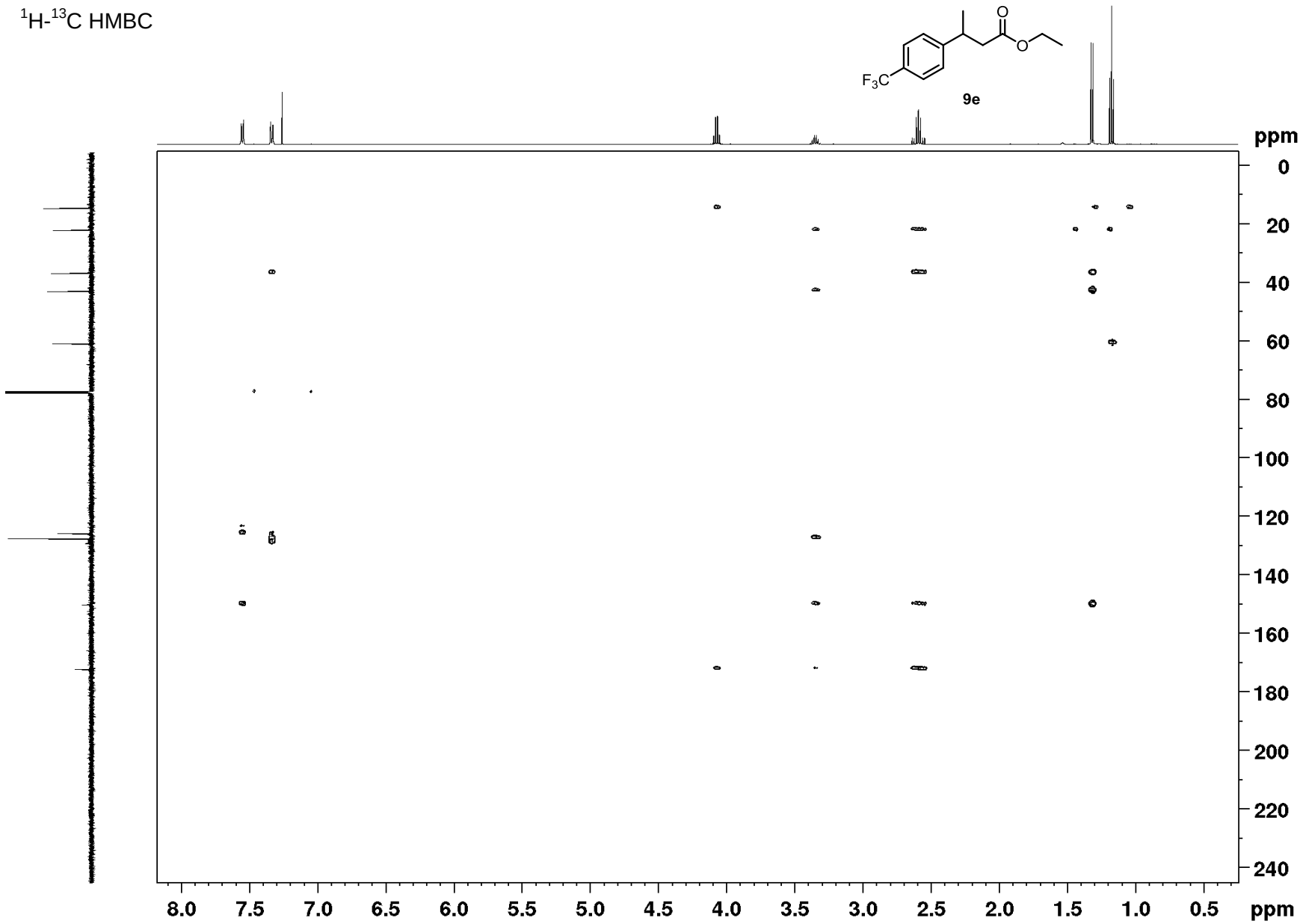
^{1}H-^{1}H COSY

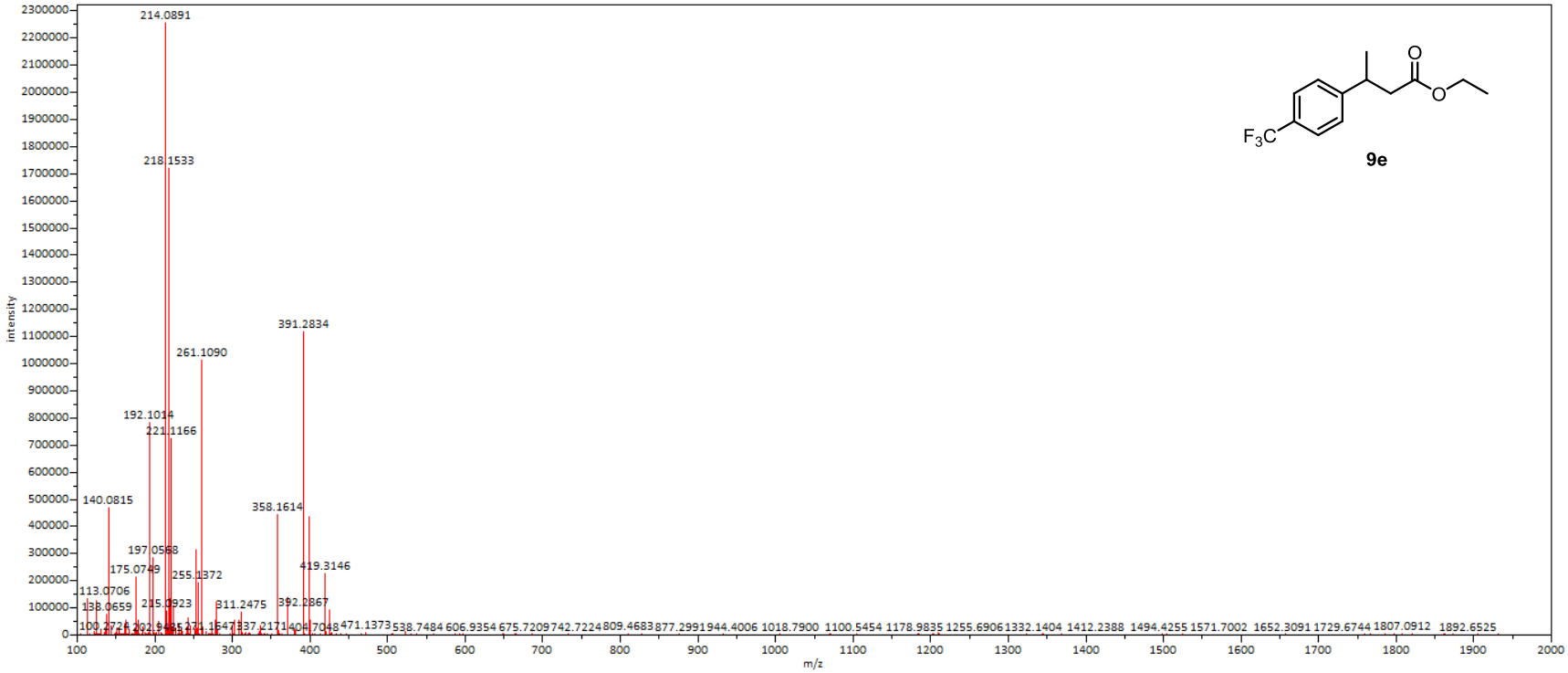

O
O
F3C
9e
ppm
1
2
3
4
5
6
7
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{1}H-^{13}C HMQC


O
O
F3C
9e
ppm
0
20
40
60
80
100
120
140
160
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
ppm

^{1}H-^{13}C HMBC

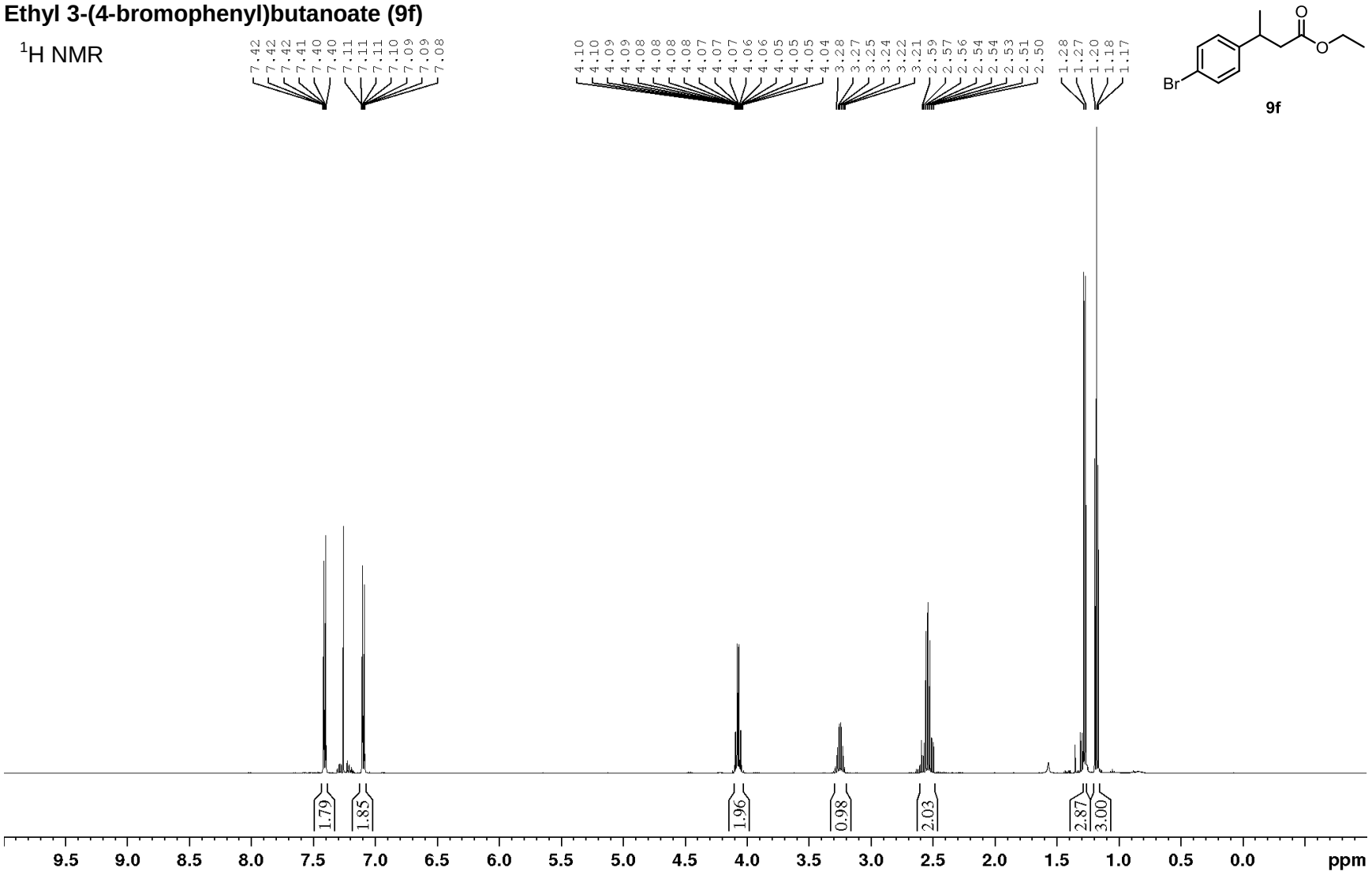

O
O
F3C
9e
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

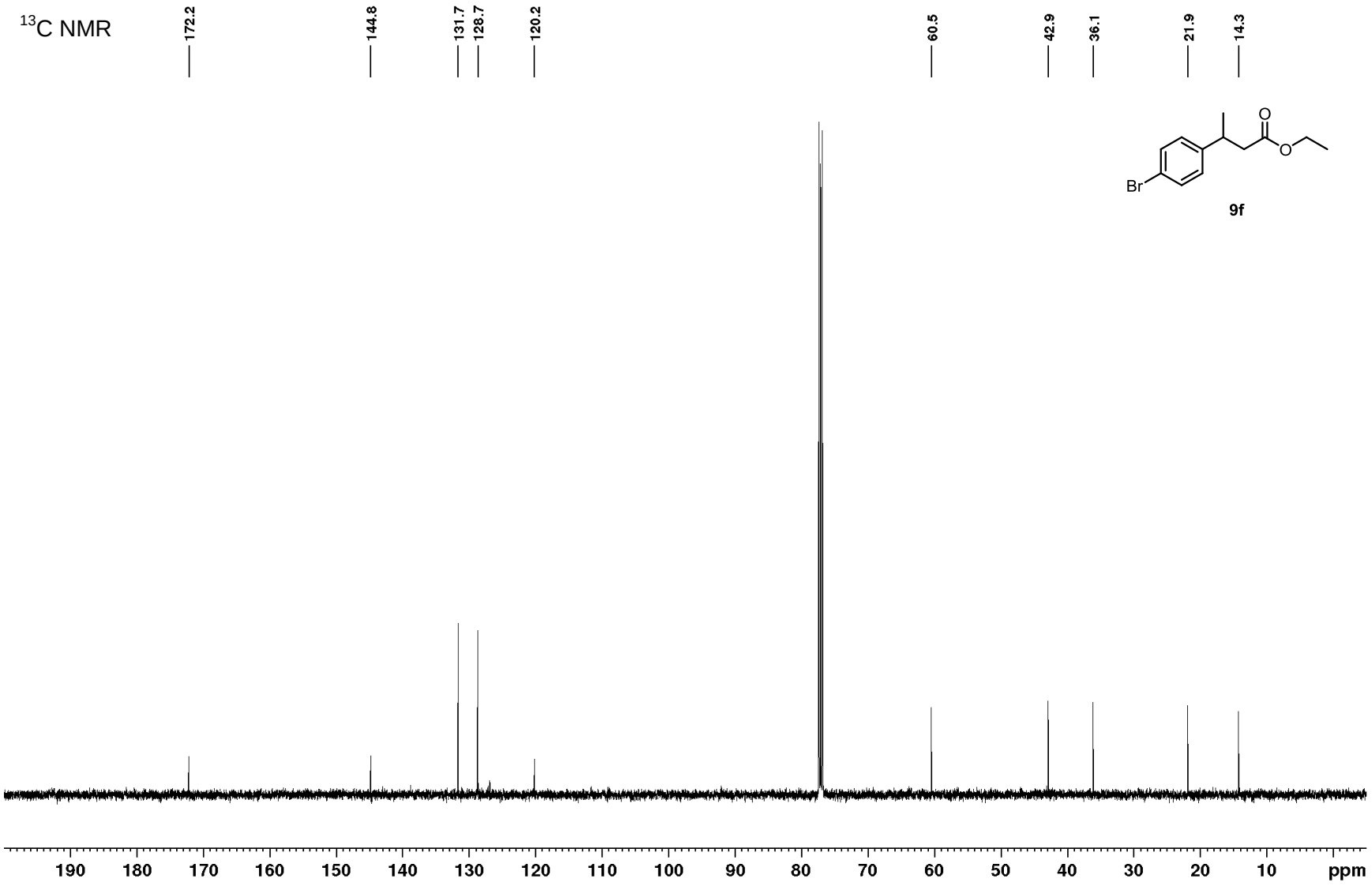

214.0891
218.1533
391.2834
261.1090
192.1014
221.1166
140.0815
358.1614
197.0568
175.0749
255.1372
419.3146
113.0706
138.0659
215.0923
311.2475
392.2867
intensity
m/z
O
O
F3C
9e


%Transmittance
120
100
80
60
40
20
0
3459
2970
2306
2115
2003
1920
1731
1618
1457
1419
1371
1322
1268
1160
1112
1066
1015
953
838
712
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber
O
O
F3C
9e

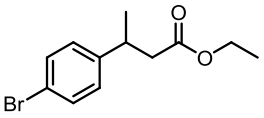
Ethyl 3-(4-bromophenyl)butanoate (9f)

^{1}H NMR

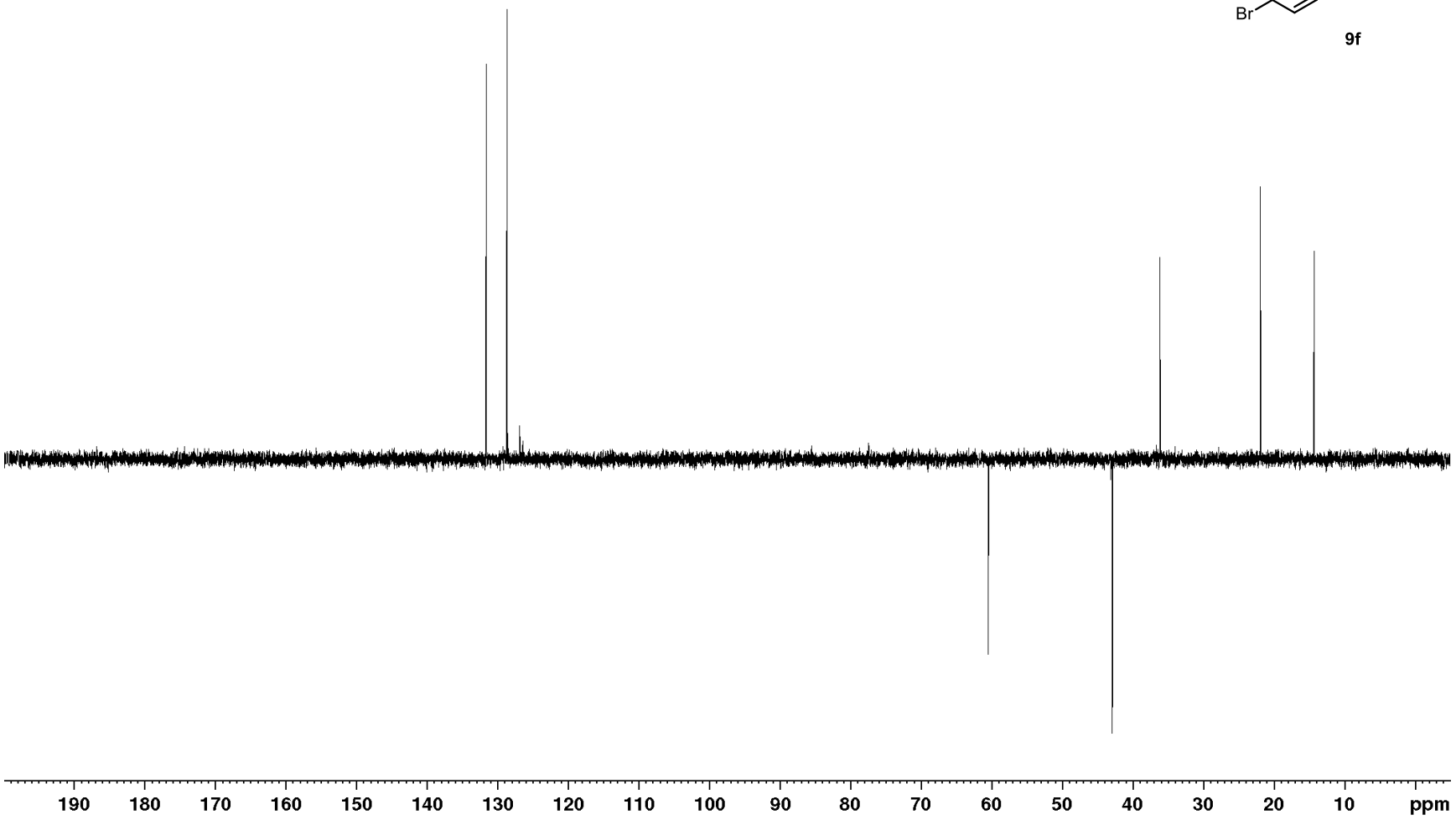



^{13}C NMR
172.2
144.8
131.7
128.7
120.2
60.5
42.9
36.1
21.9
14.3
O
O
Br
9f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

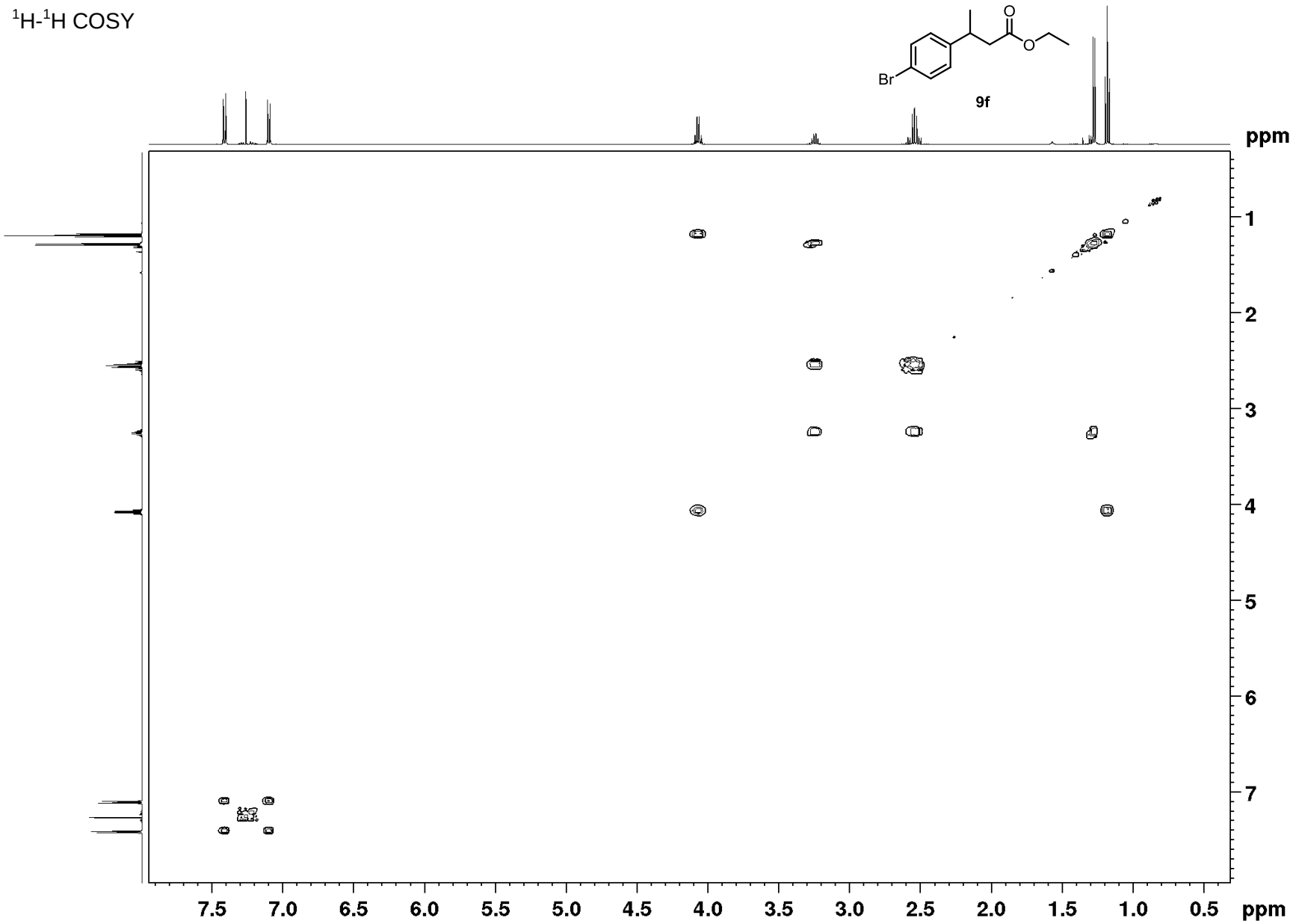
^{13}C DEPT NMR



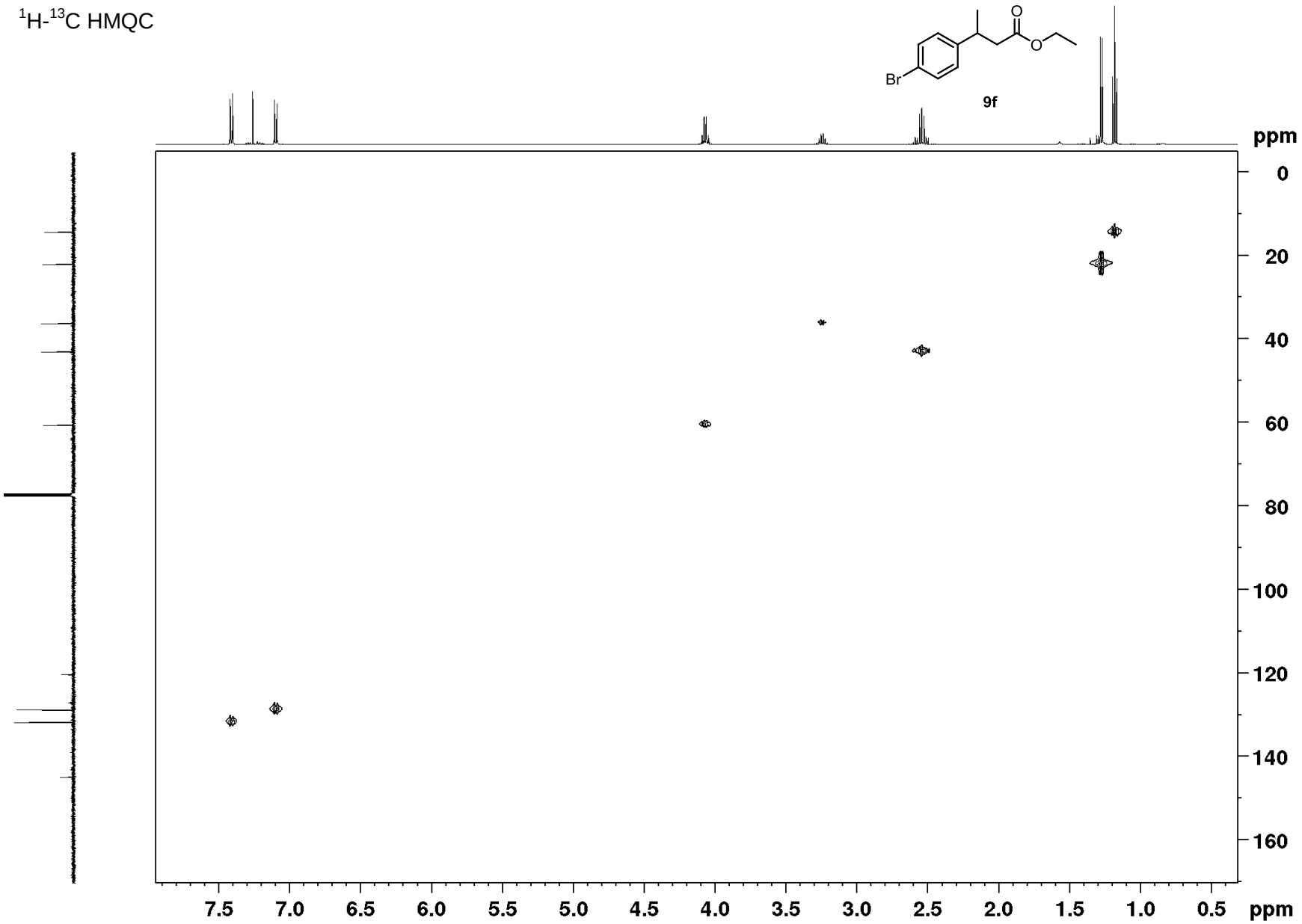
9f



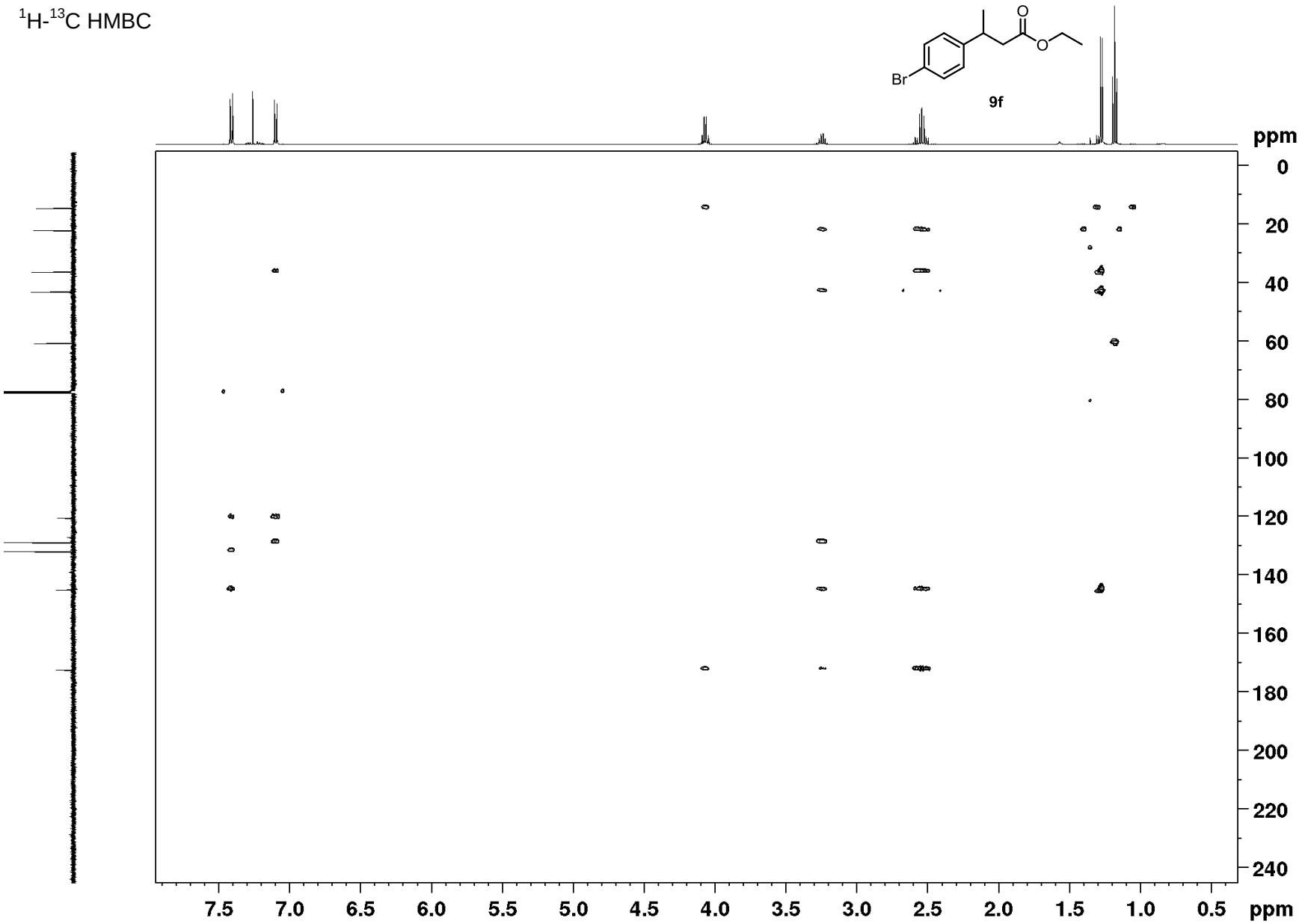
^{1}H-^{1}H COSY

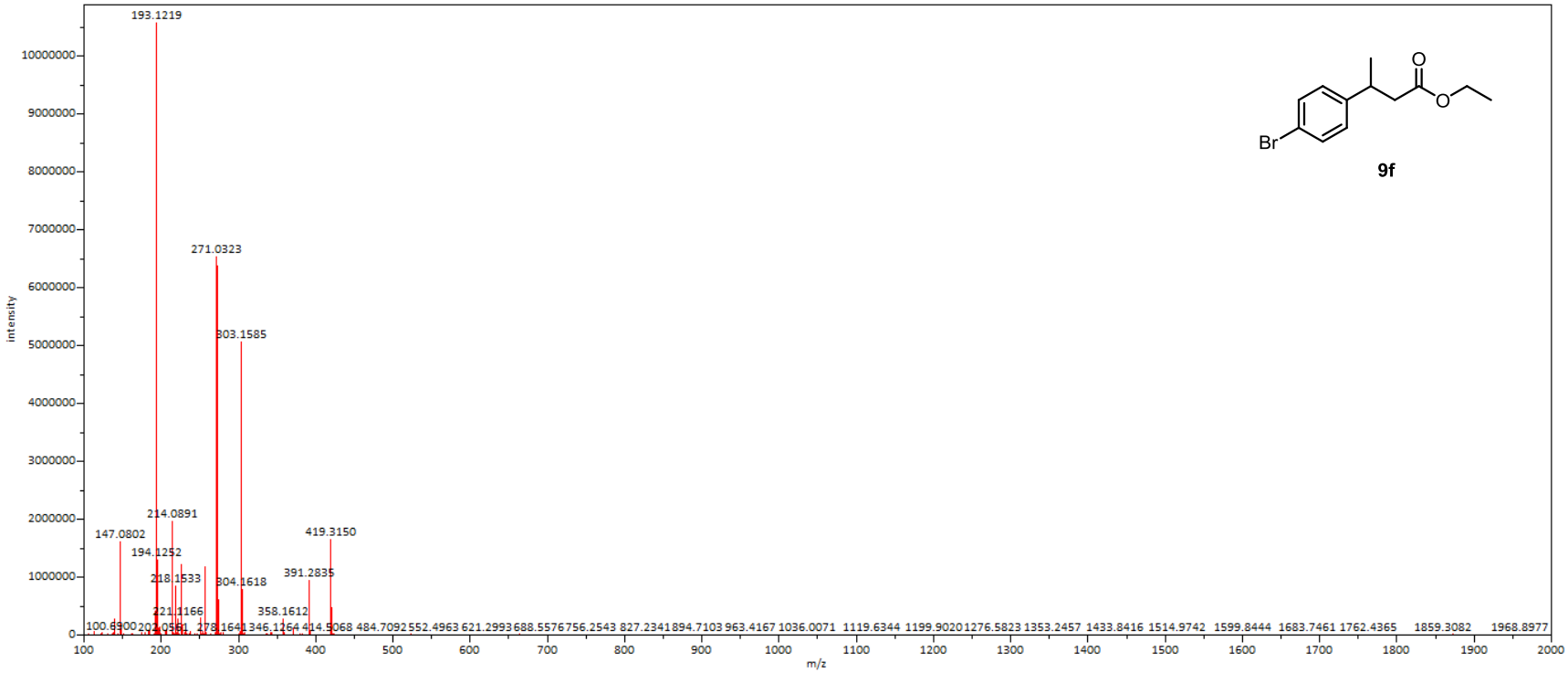


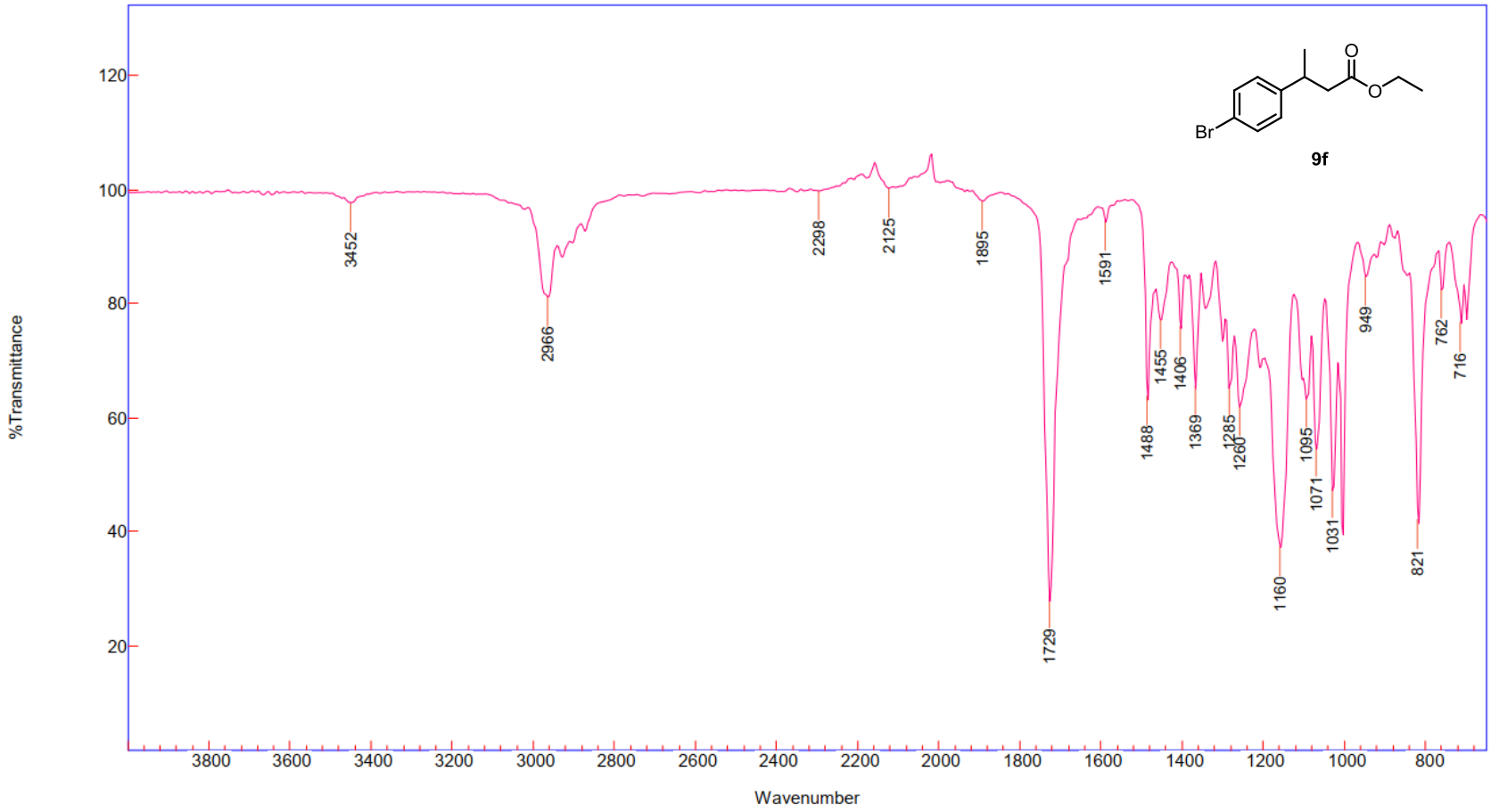
^{1}H-^{13}C HMQC


Br
O
O
9f
ppm
0
20
40
60
80
100
120
140
160
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
ppm

^{1}H-^{13}C HMBC

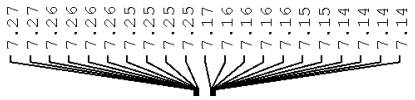

Br
O
O
9f
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

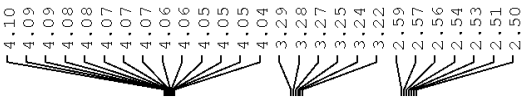

193.1219
271.0323
303.1585
214.0891
147.0802
194.1252
218.1533
304.1618
419.3150
391.2835
358.1612
221.1166
intensity
m/z
Br
O
O
9f

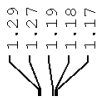

%Transmittance
120
100
80
60
40
20
3452
2966
2298
2125
1895
1729
1591
1488
1455
1406
1369
1285
1260
1160
1095
1071
1031
949
821
762
716
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber
Br
O
O
9f

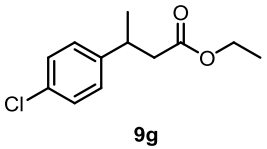
Ethyl 3-(4-chlorophenyl)butanoate (9g)

^{1}H NMR

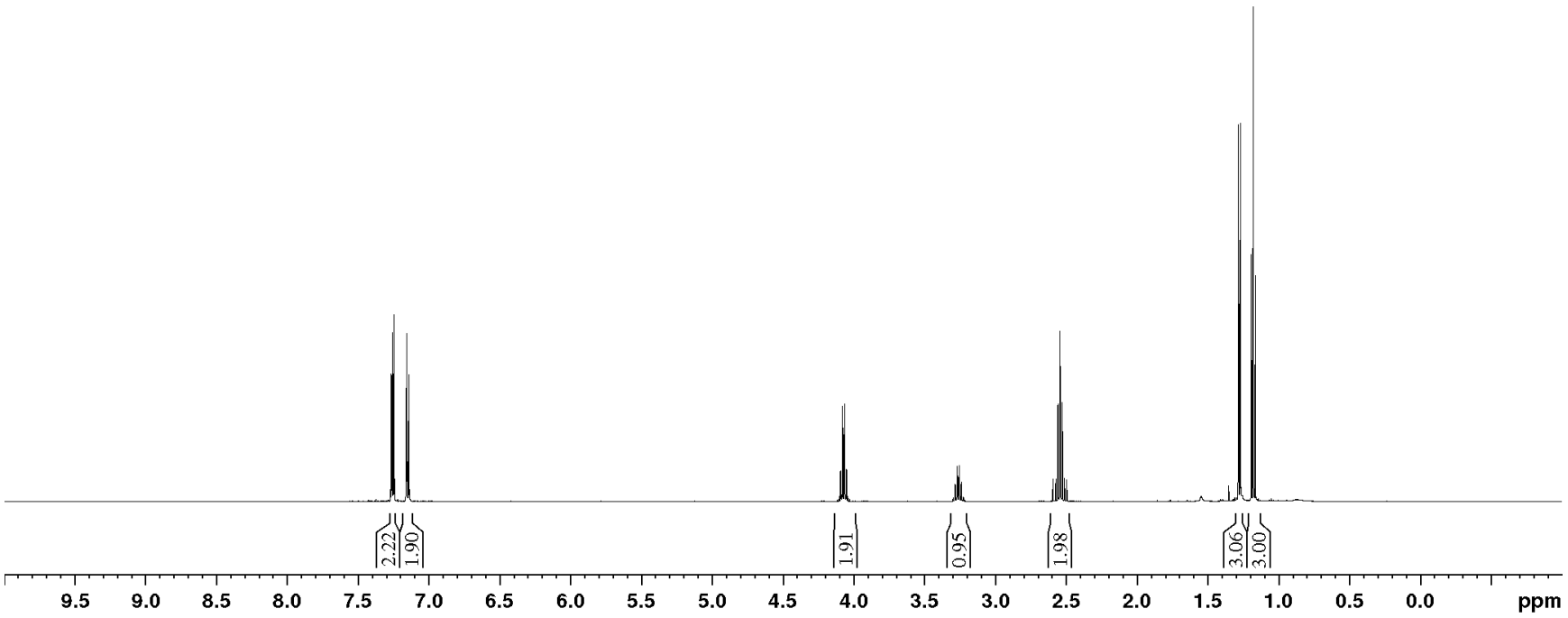


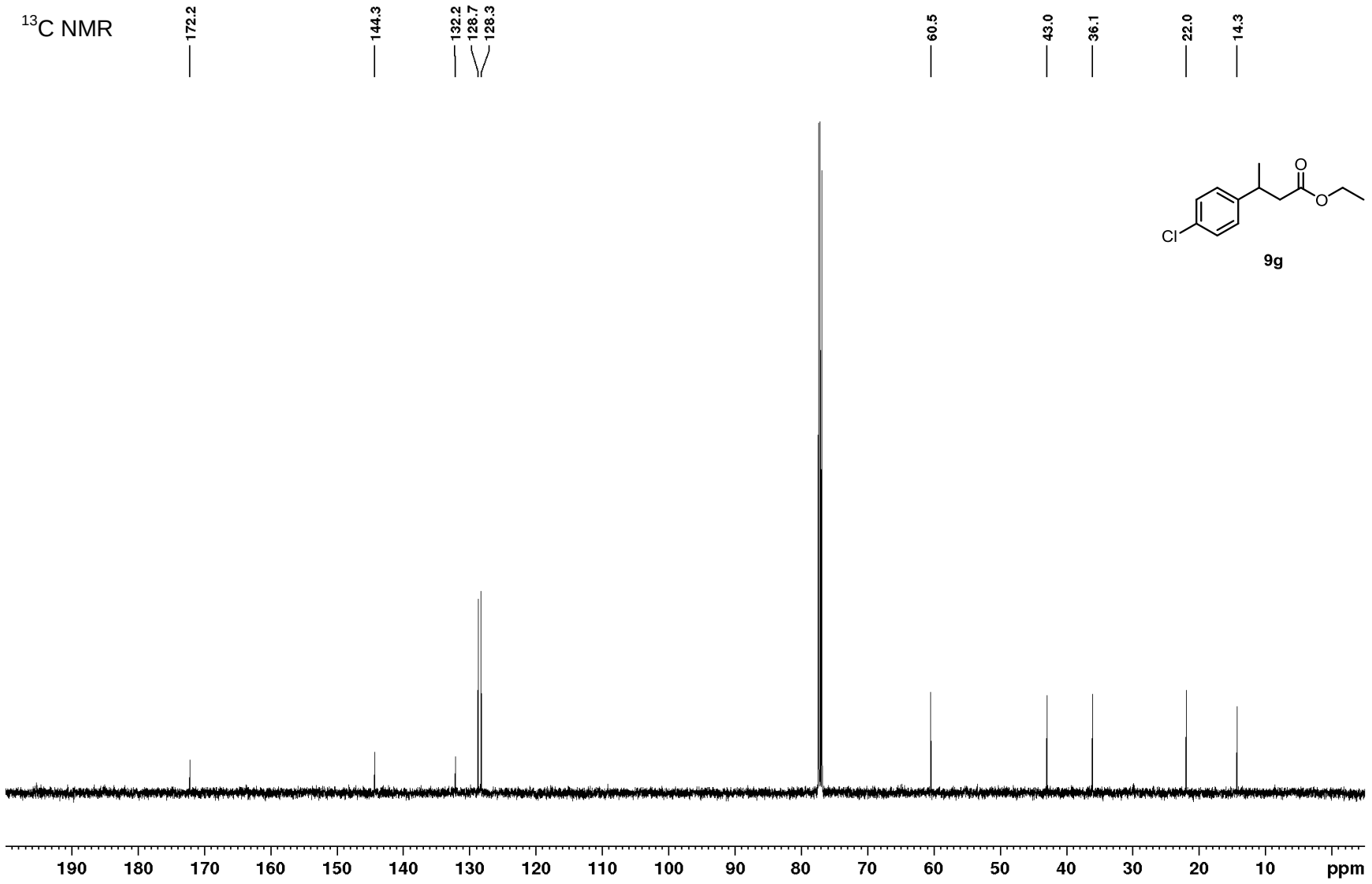




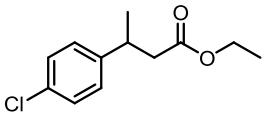


9g

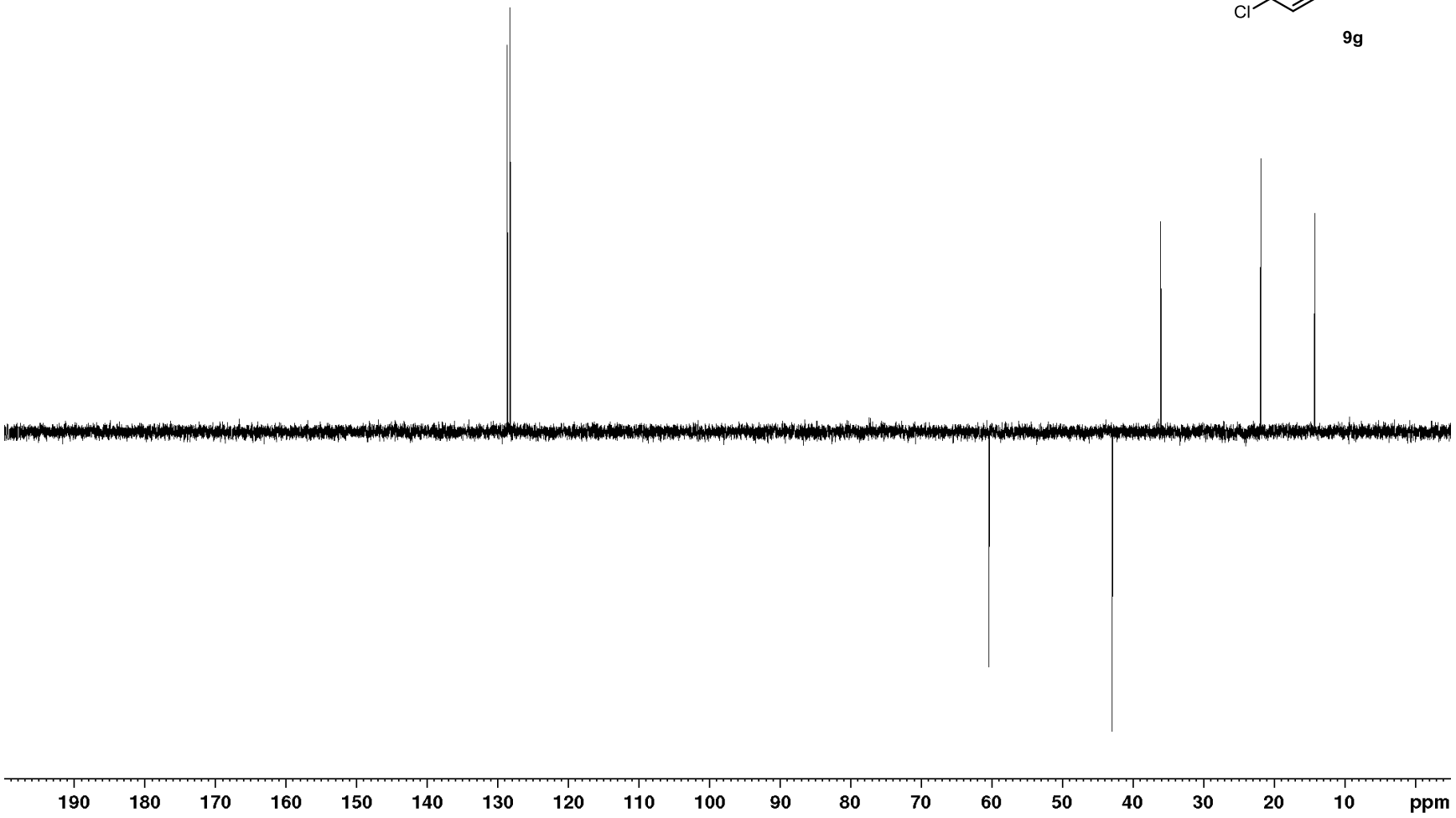



^{13}C NMR
172.2
144.3
132.2
128.7
128.3
60.5
43.0
36.1
22.0
14.3
Cl
O
O
9g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

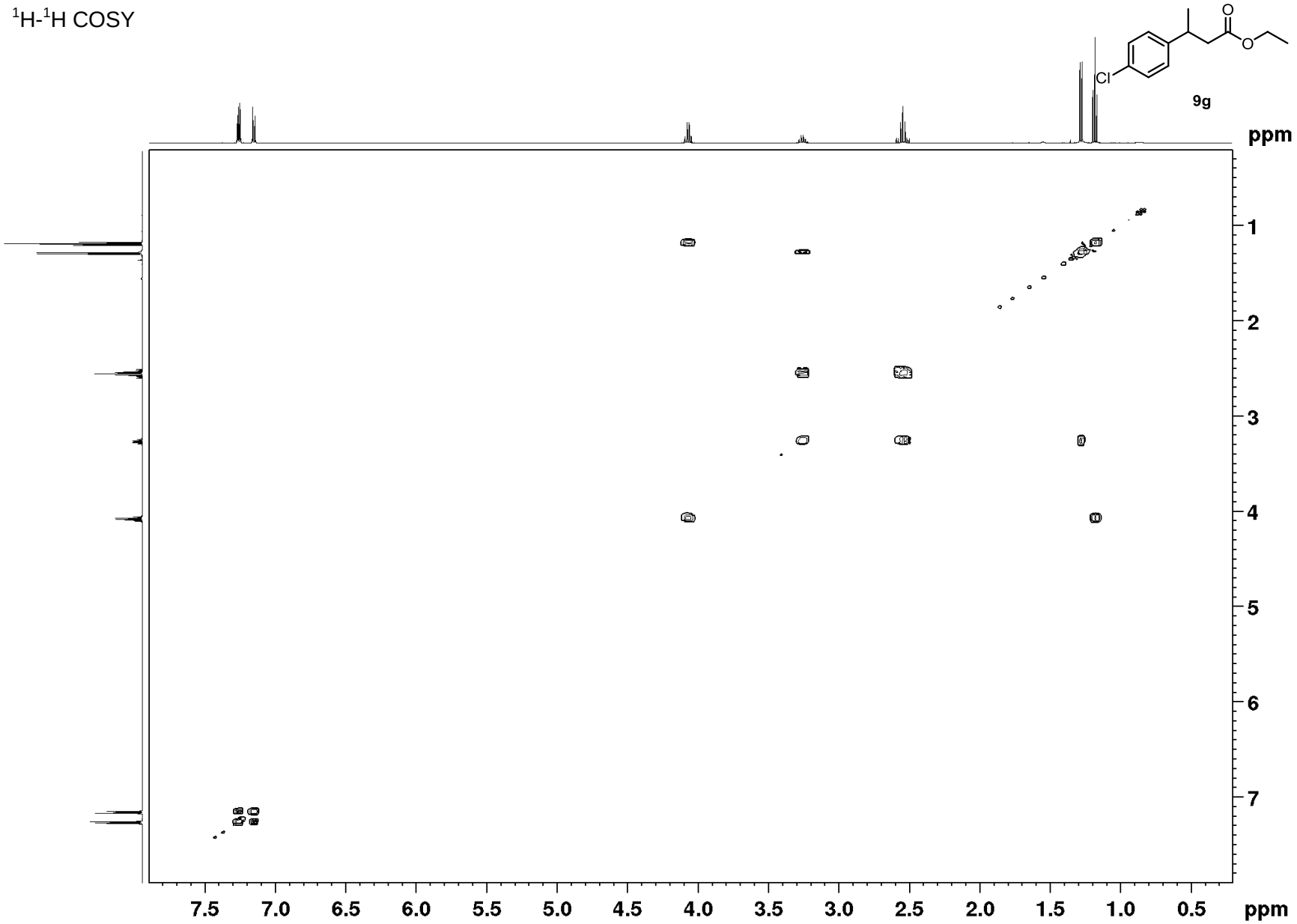
^{13}C DEPT NMR



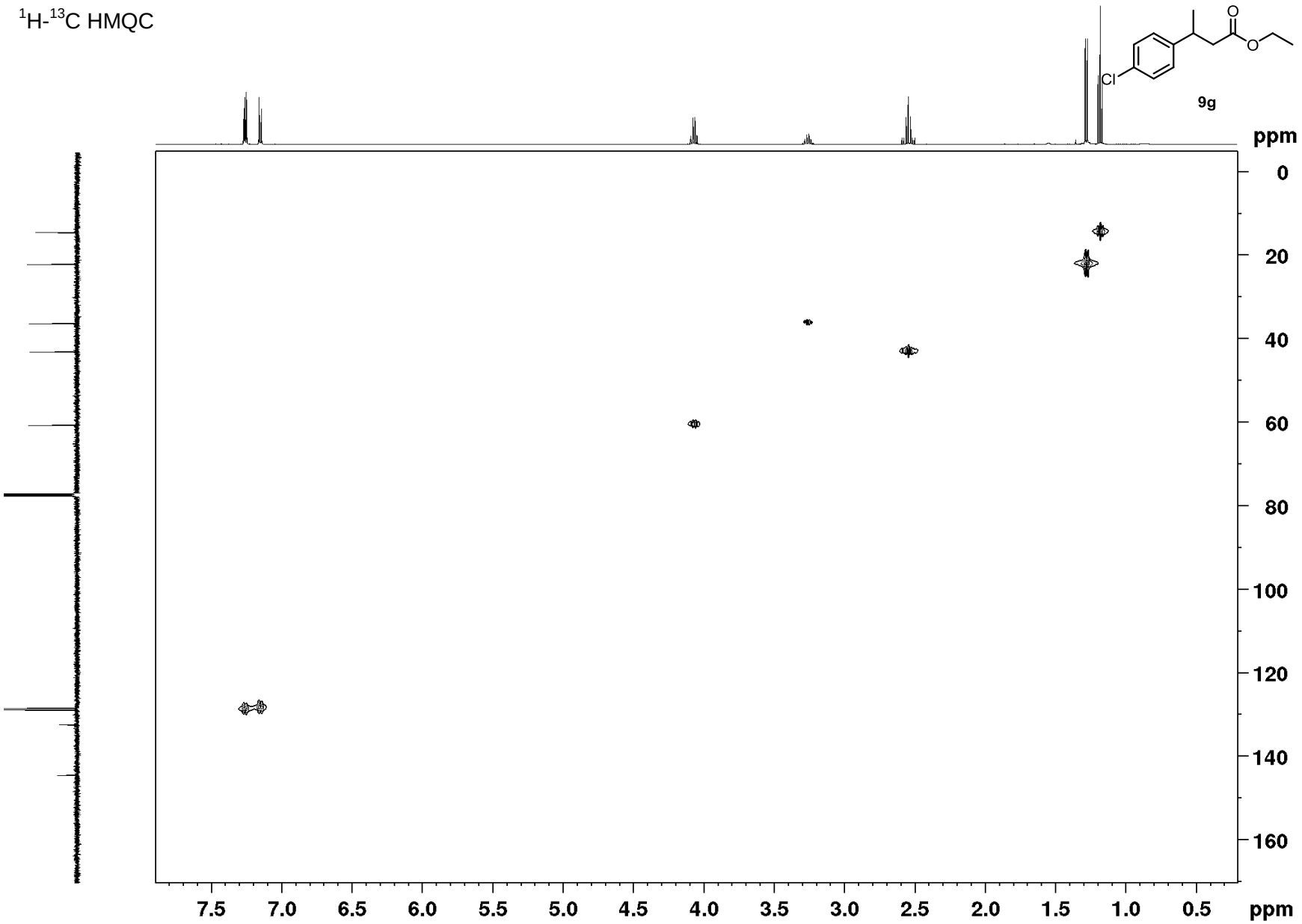
9g



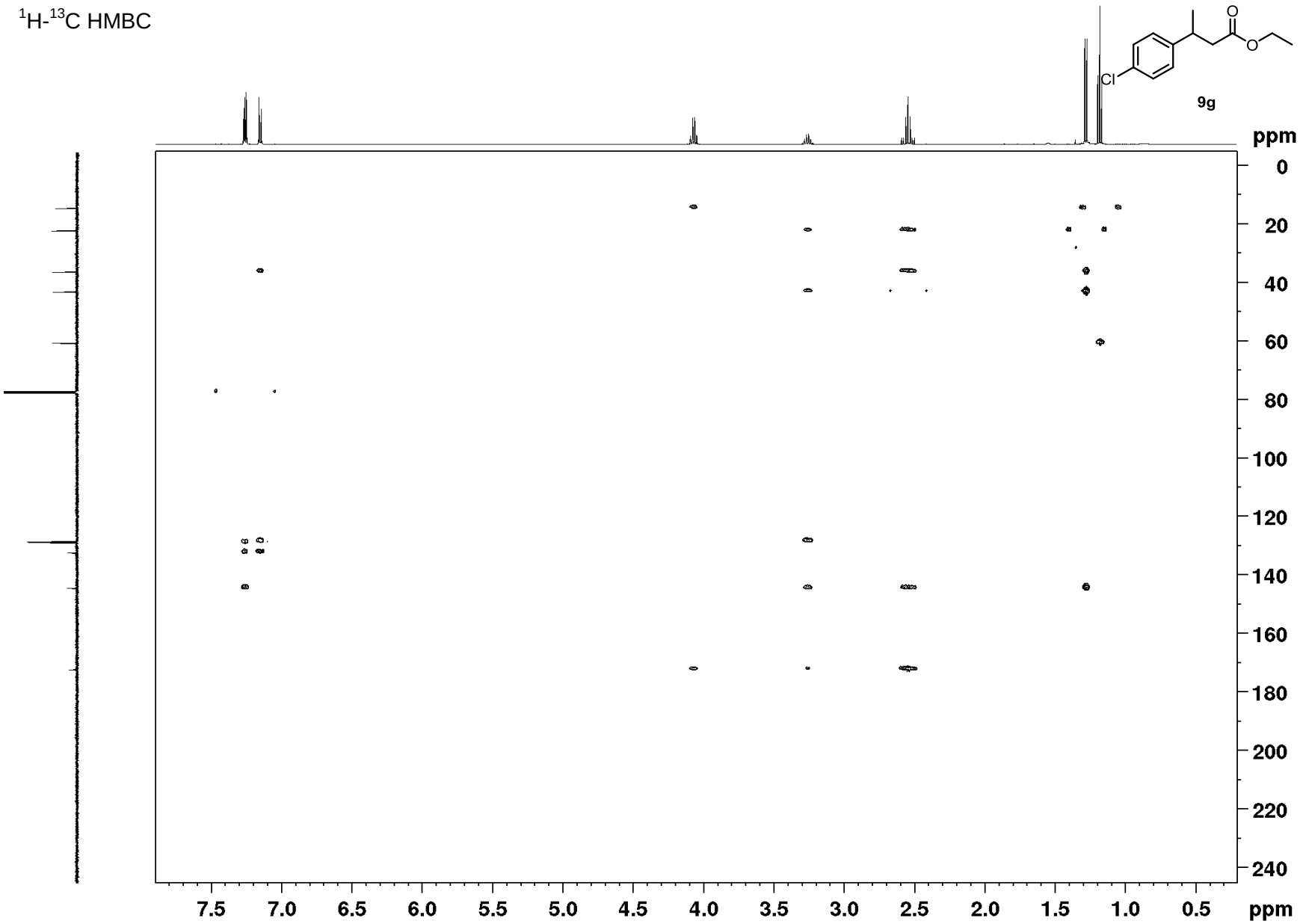
^{1}H-^{1}H COSY

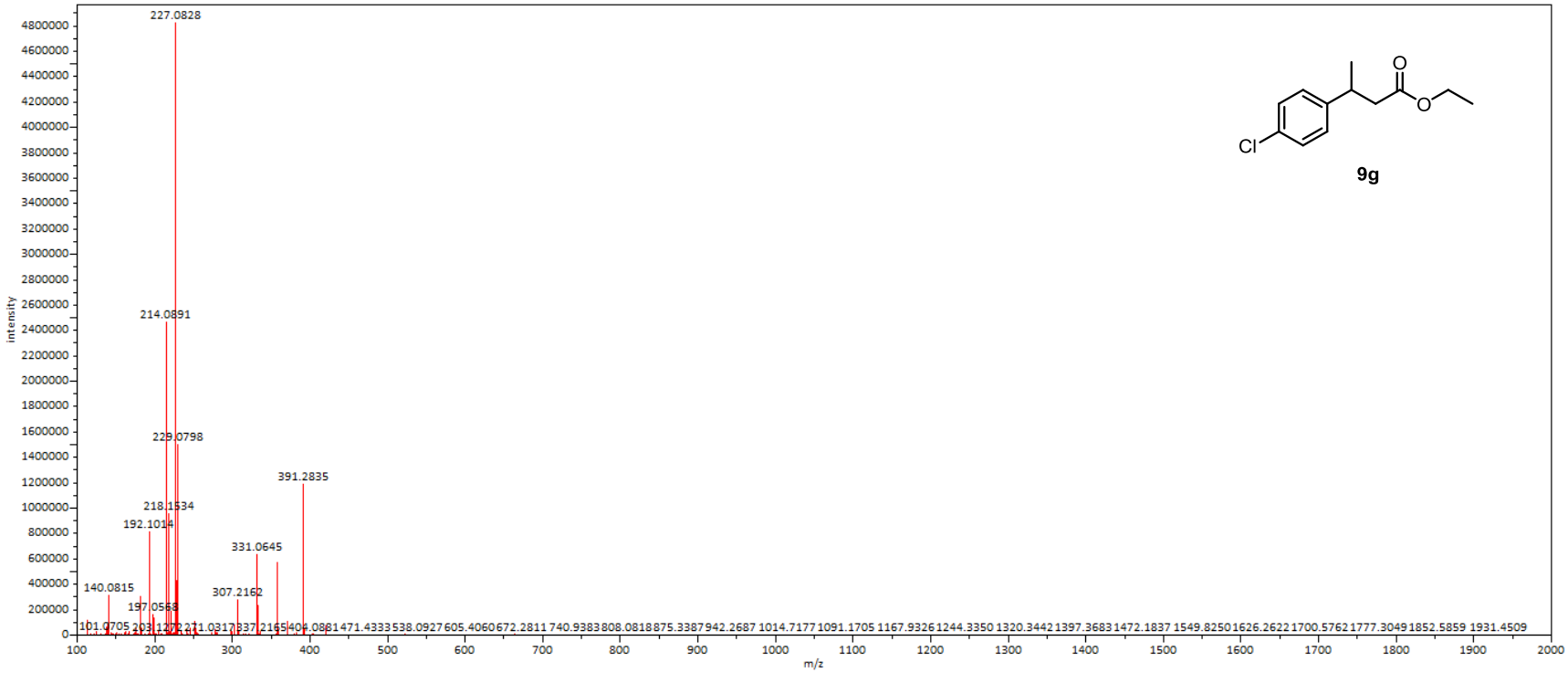


^{1}H-^{13}C HMQC


Cl
O
O
9g
ppm
0
20
40
60
80
100
120
140
160
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
ppm

^{1}H-^{13}C HMBC

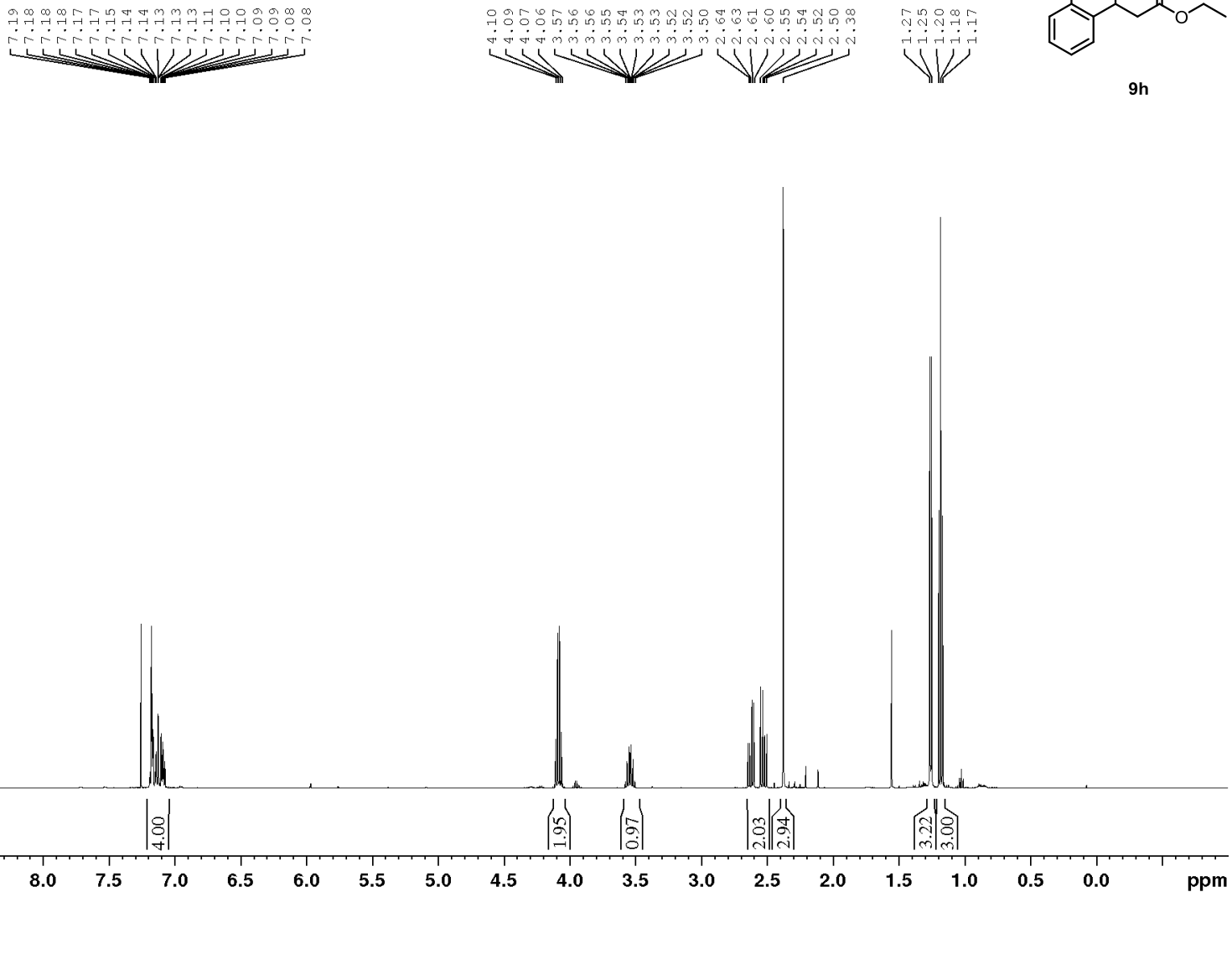

Cl
O
O
9g
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

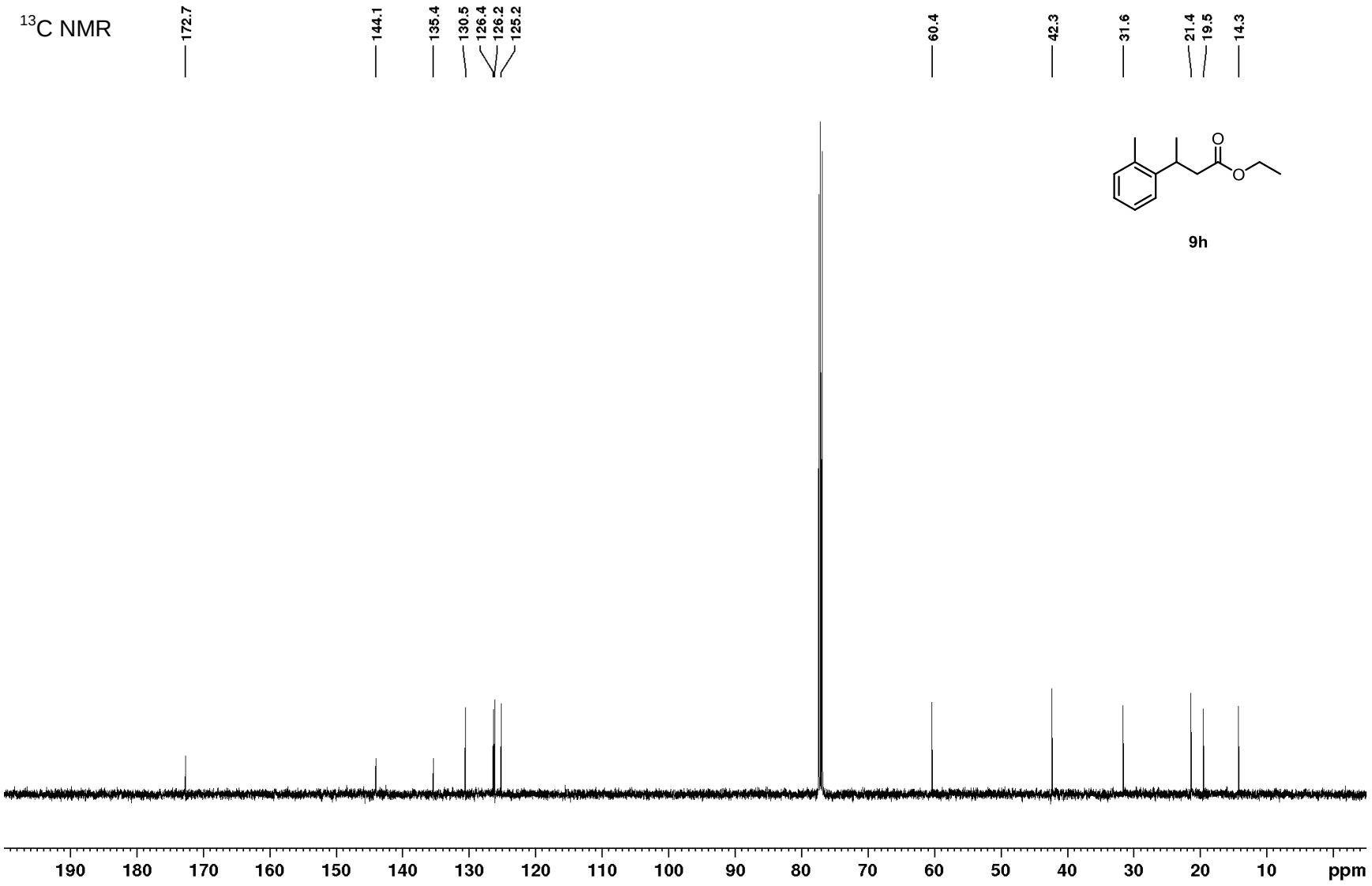

227.0828
214.0891
229.0798
391.2835
218.1534
192.1014
331.0645
140.0815
307.2162
197.0563
intensity
m/z
Cl
O
O
9g


%Transmittance
120
100
80
60
40
20
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber
3447
2965
2290
2115
2003
1895
1729
1596
1492
1457
1410
1369
1286
1259
1161
1093
1032
950
825
732
Cl
O
O
9g

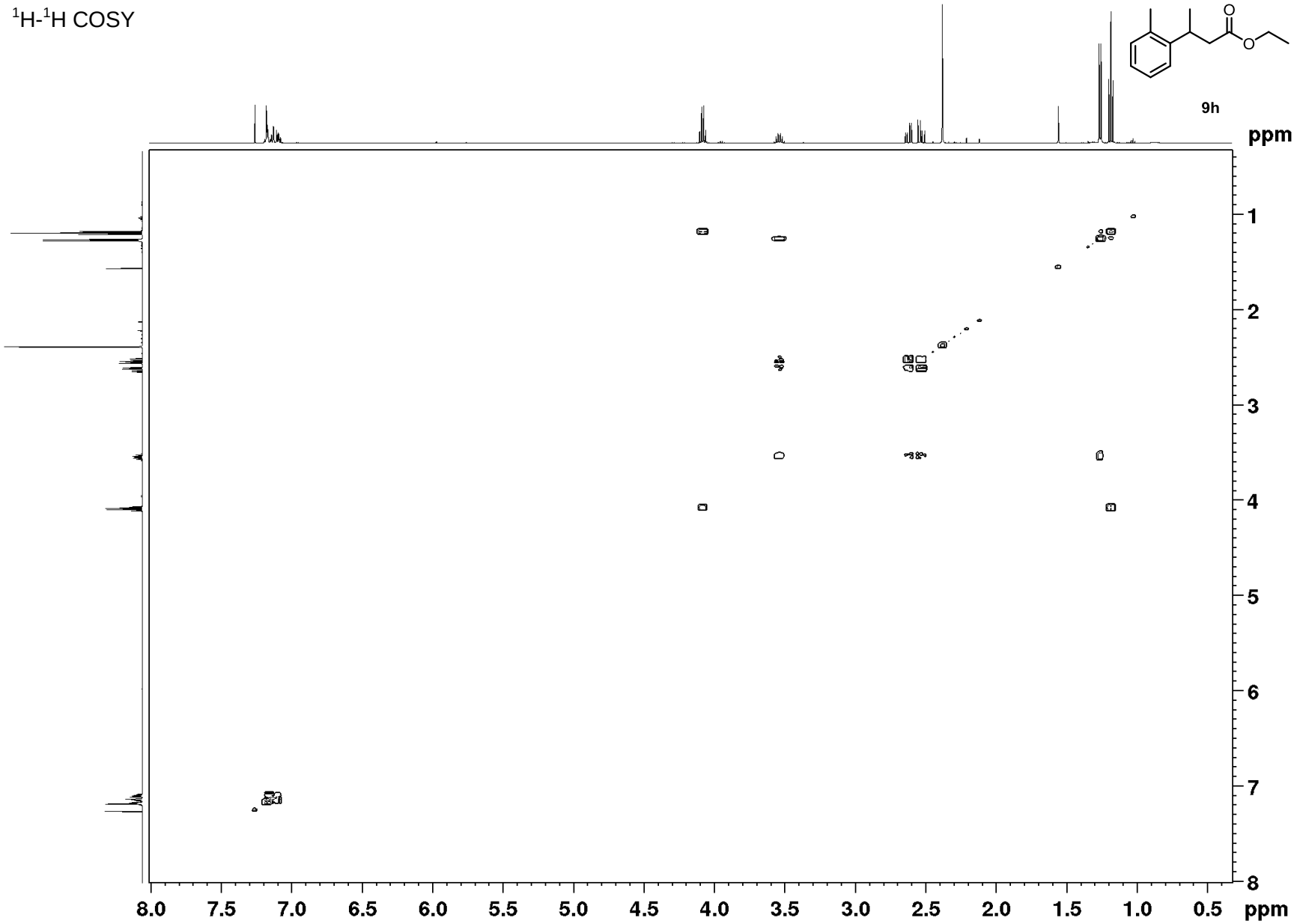
Ethyl 3-(*o*-tolyl)butanoate (9h)

^{1}H NMR

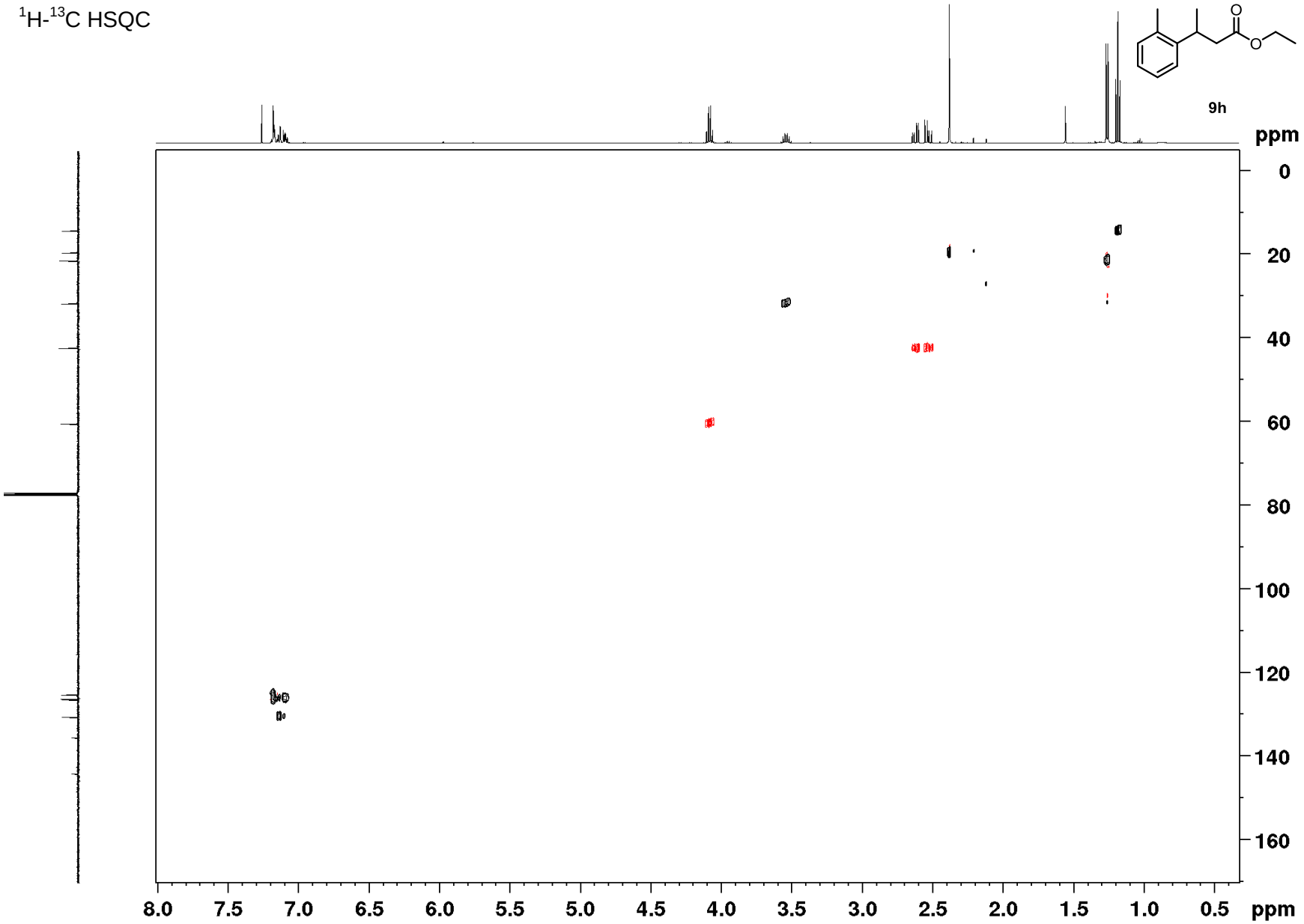



^{13}C NMR
172.7
144.1
135.4
130.5
126.4
126.2
125.2
60.4
42.3
31.6
21.4
19.5
14.3
O
O
9h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

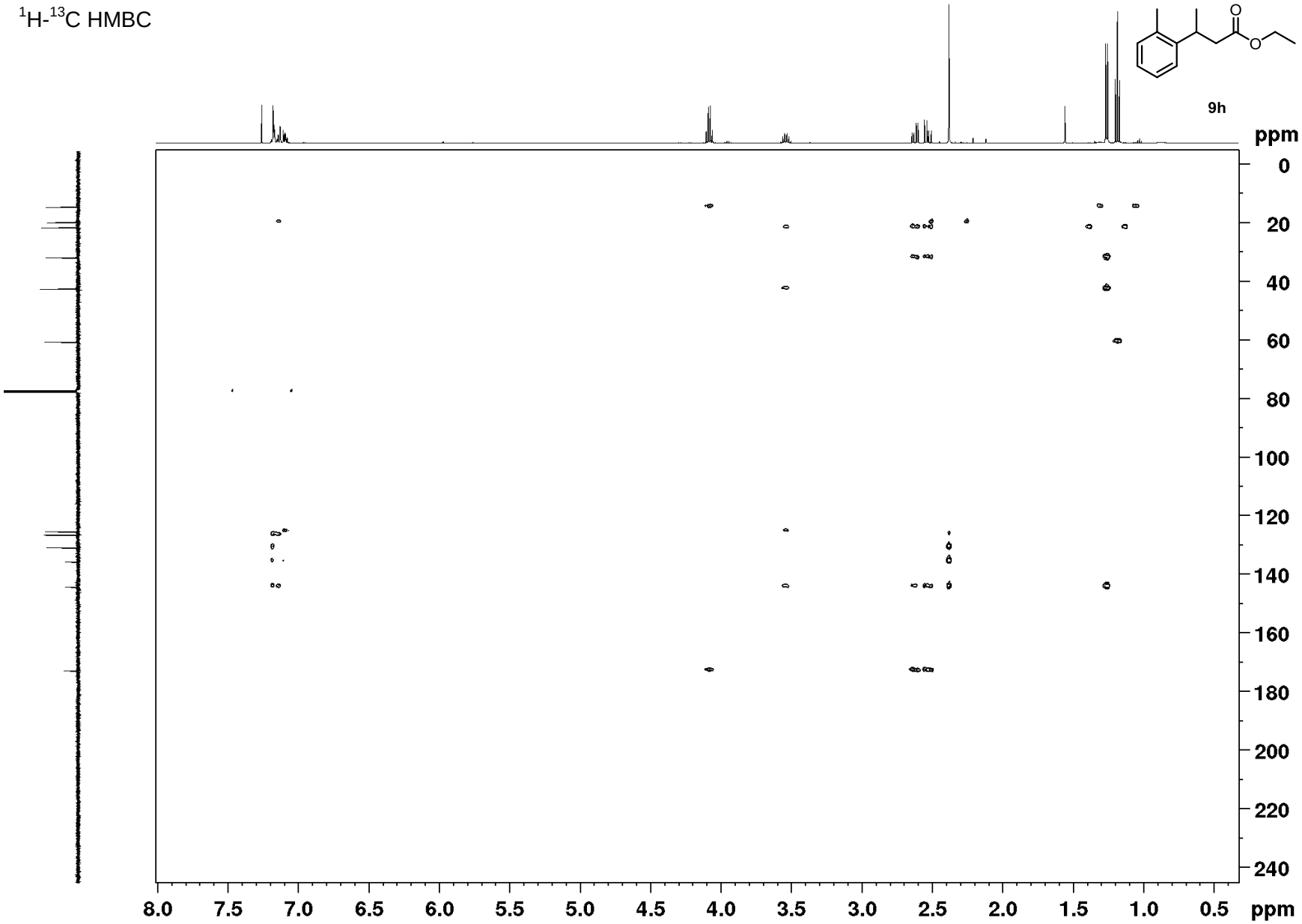
^{1}H-^{1}H COSY

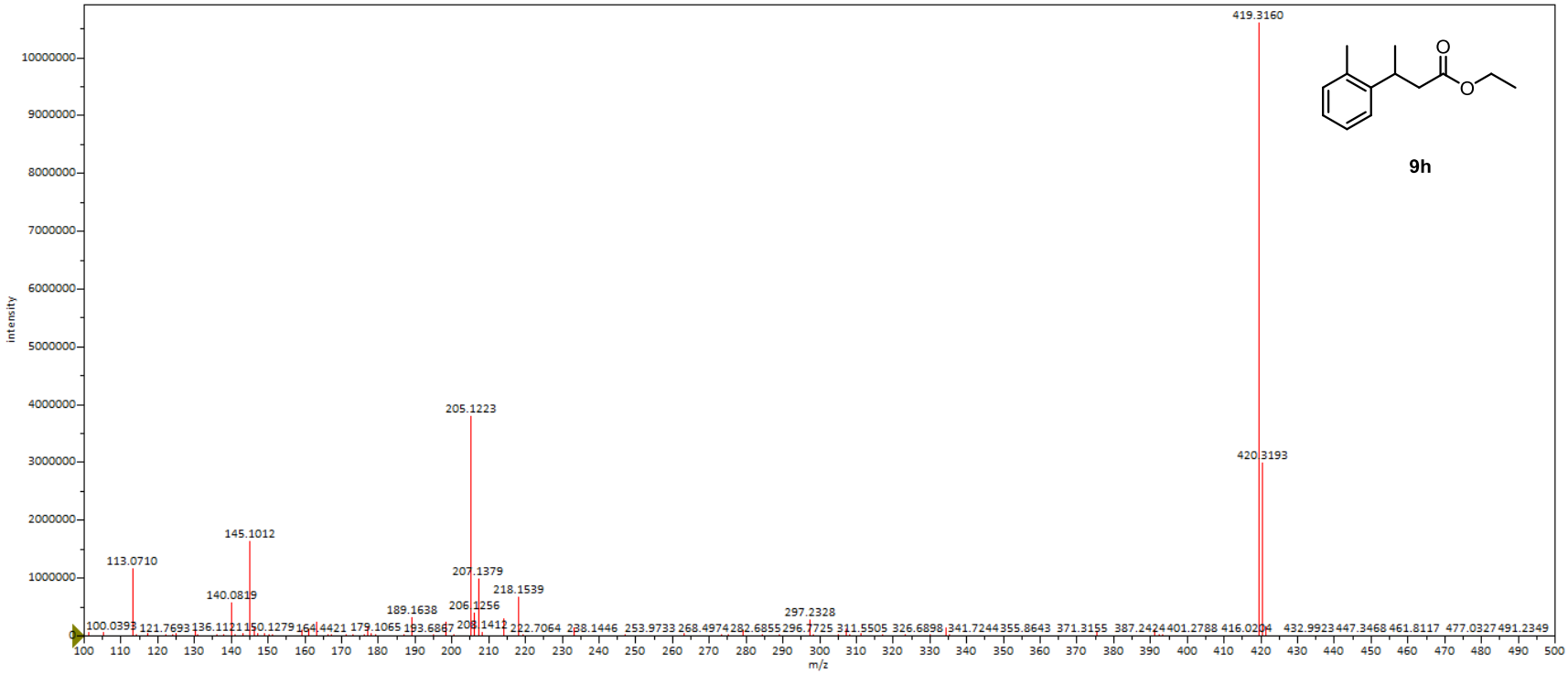


^{1}H-^{13}C HSQC


9h
ppm
0
20
40
60
80
100
120
140
160
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
ppm

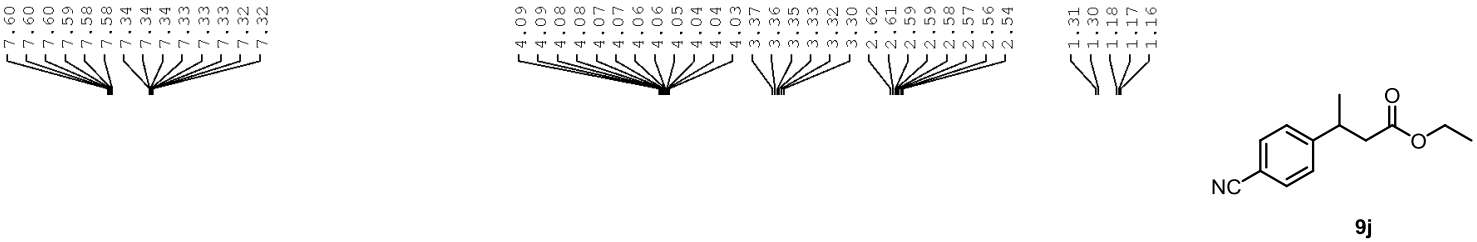
^{1}H-^{13}C HMBC


9h
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

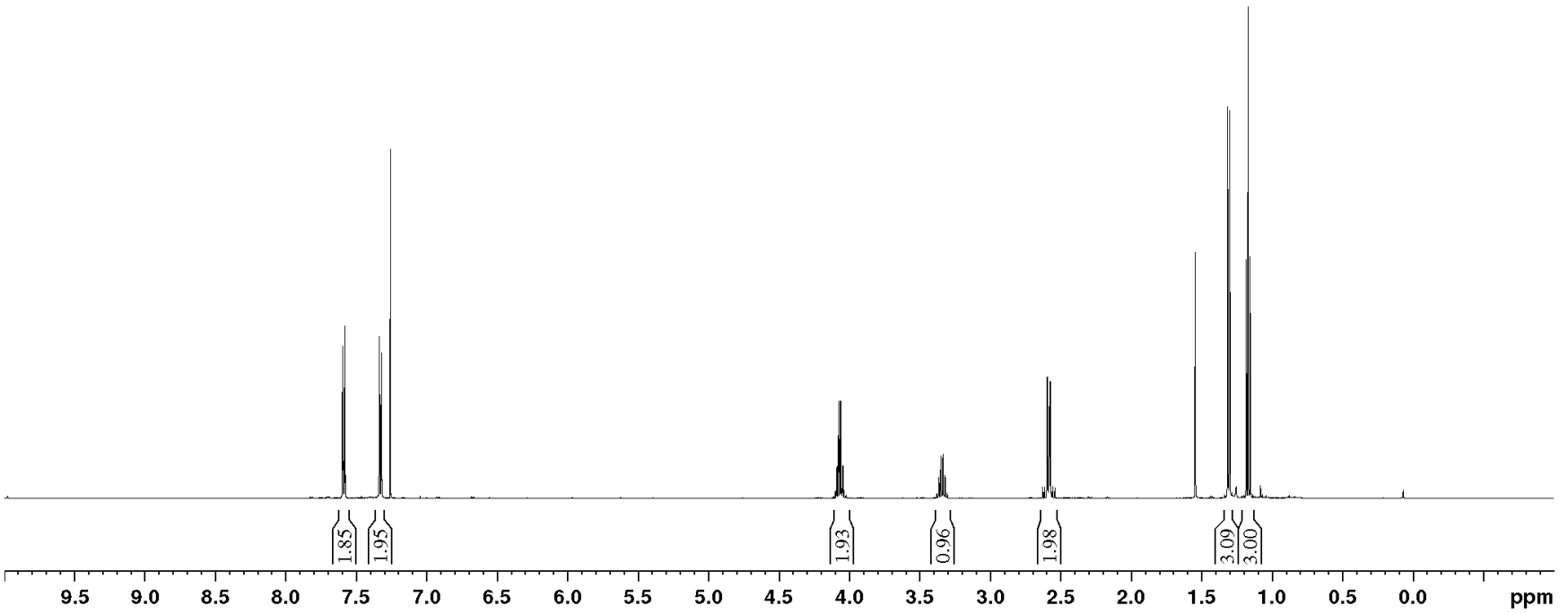

419.3160
420.3193
205.1223
145.1012
113.0710
140.0819
207.1379
218.1539
189.1638
206.1256
297.2328
intensity
m/z
9h

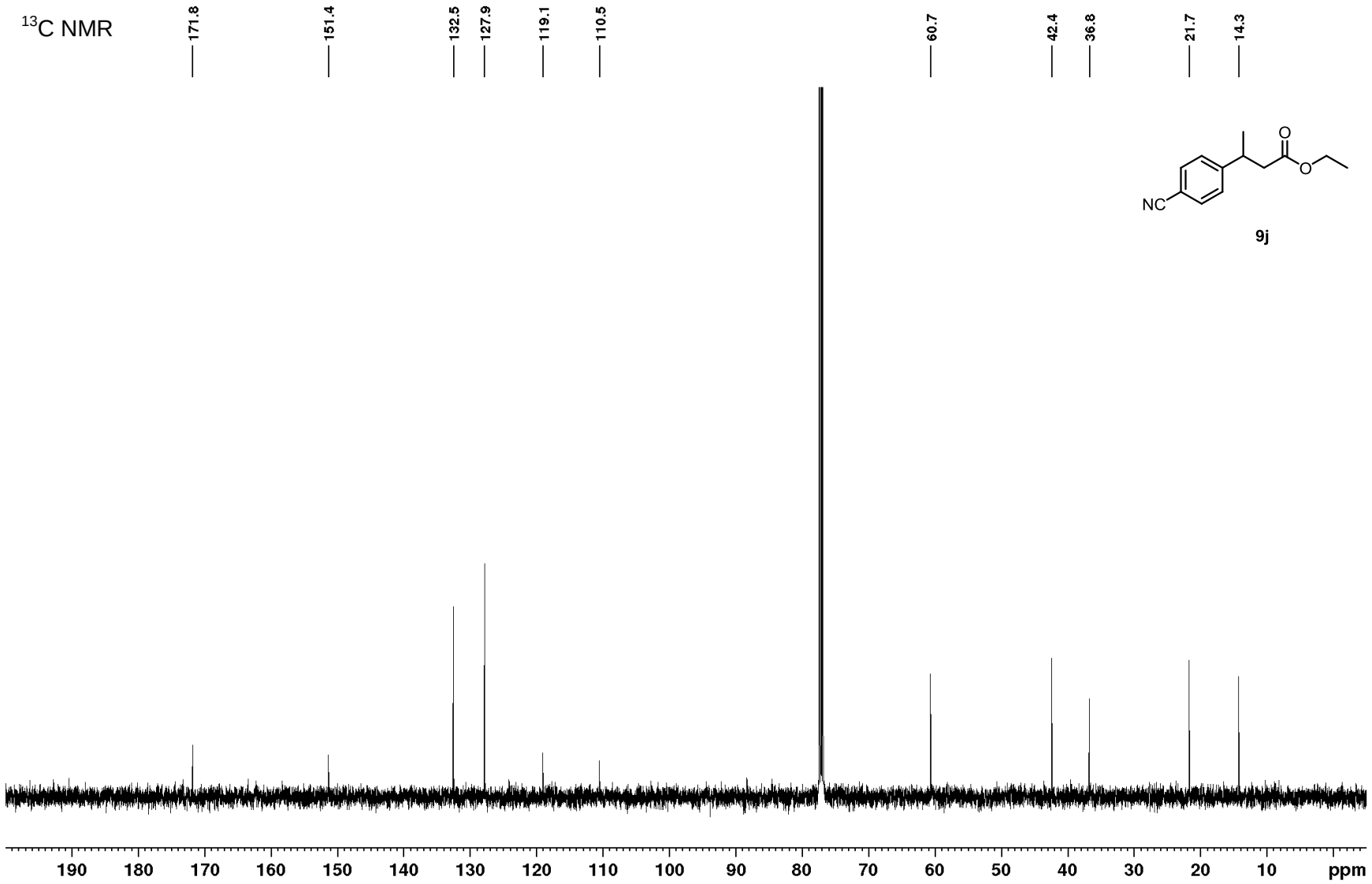
Ethyl 3-(4-cyanophenyl)butanoate (9j)

^{1}H NMR

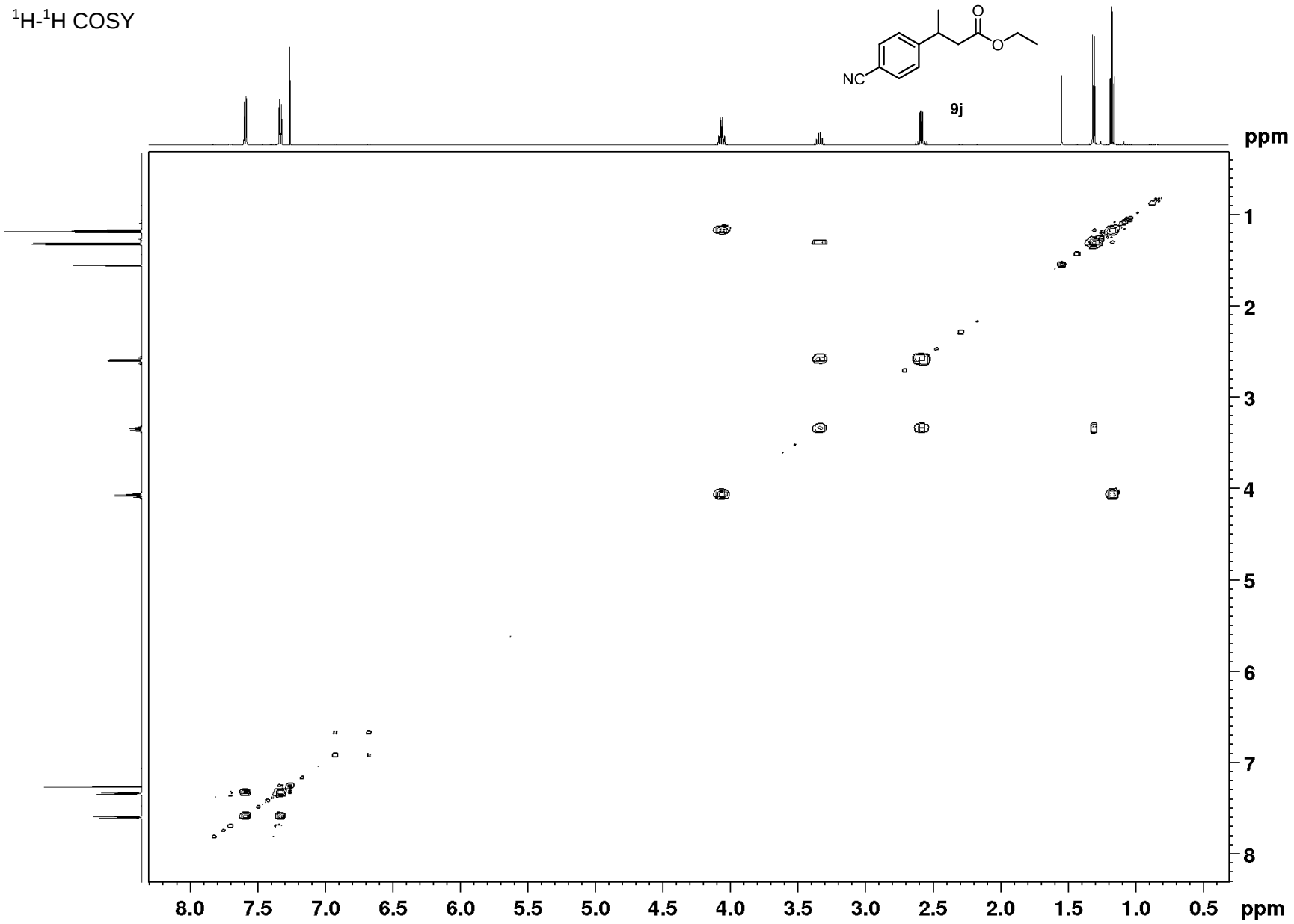


9j

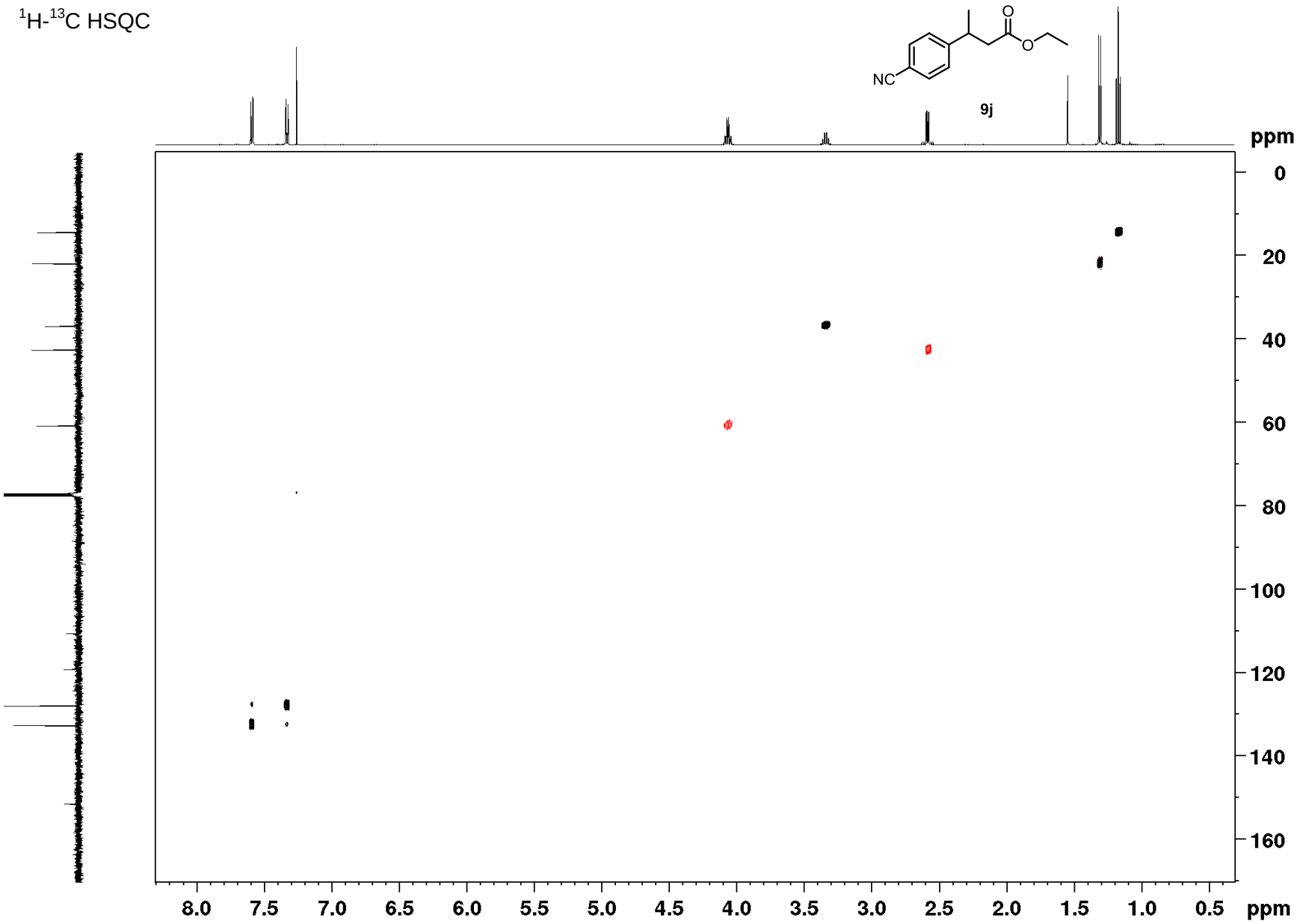



^{13}C NMR
171.8
151.4
132.5
127.9
119.1
110.5
60.7
42.4
36.8
21.7
14.3
NC
O
O
9j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

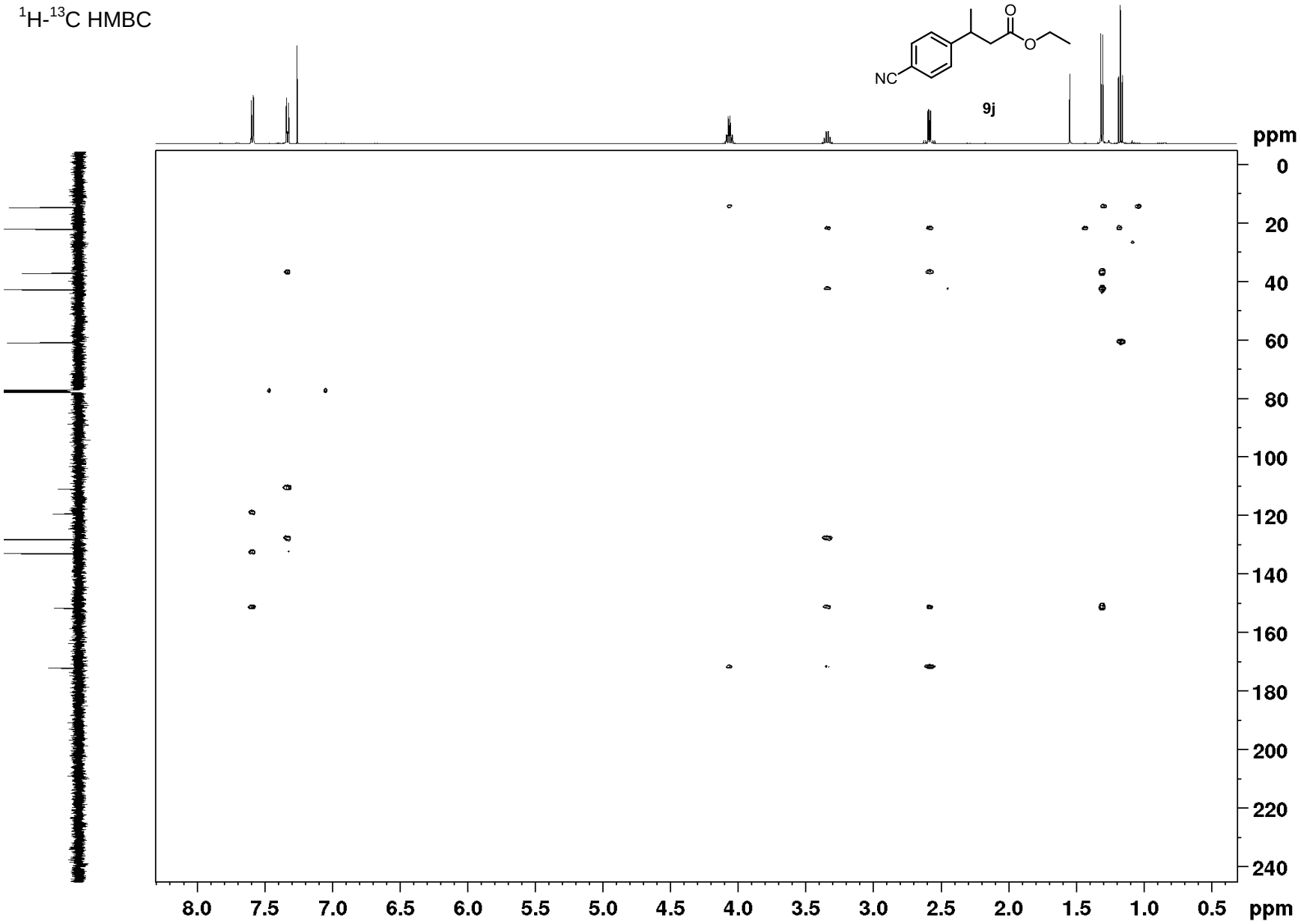
^{1}H-^{1}H COSY

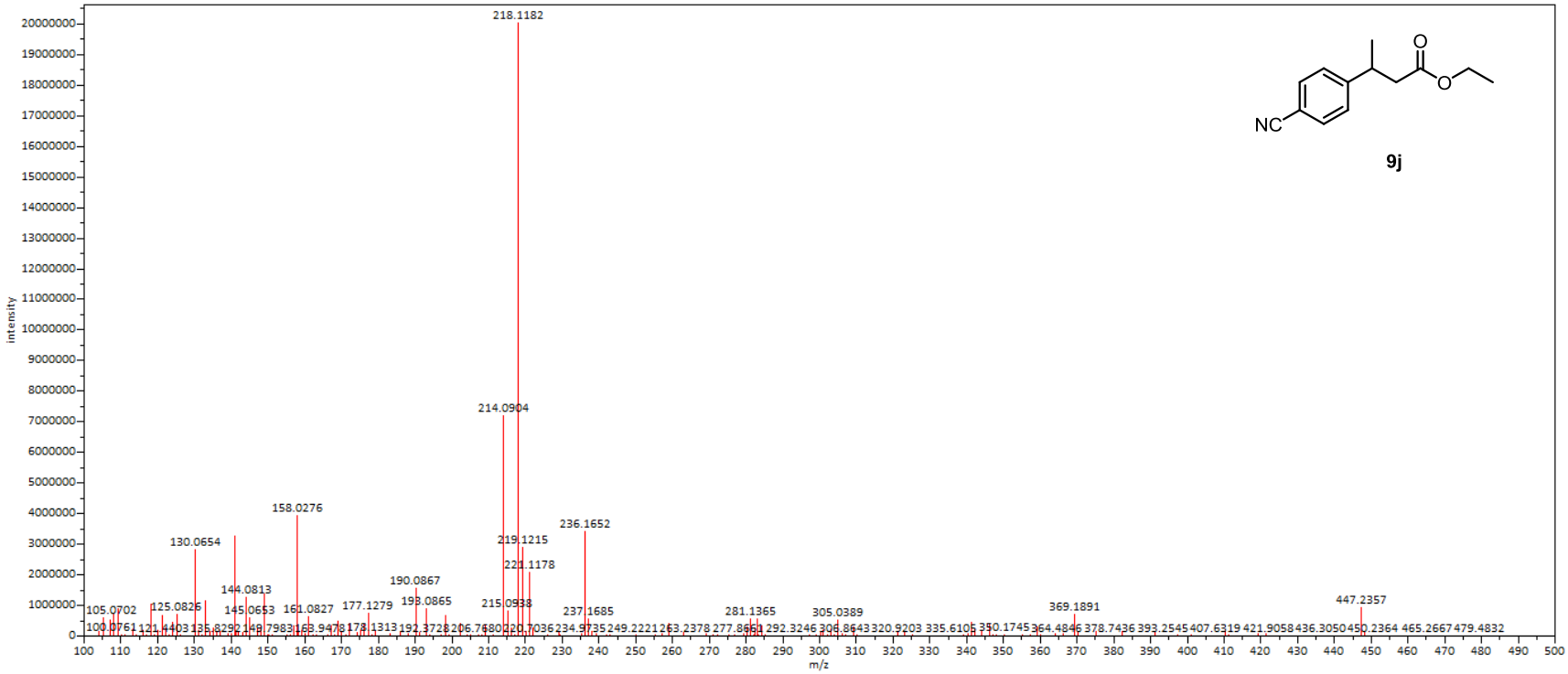

NC
O
O
9j
ppm
1
2
3
4
5
6
7
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

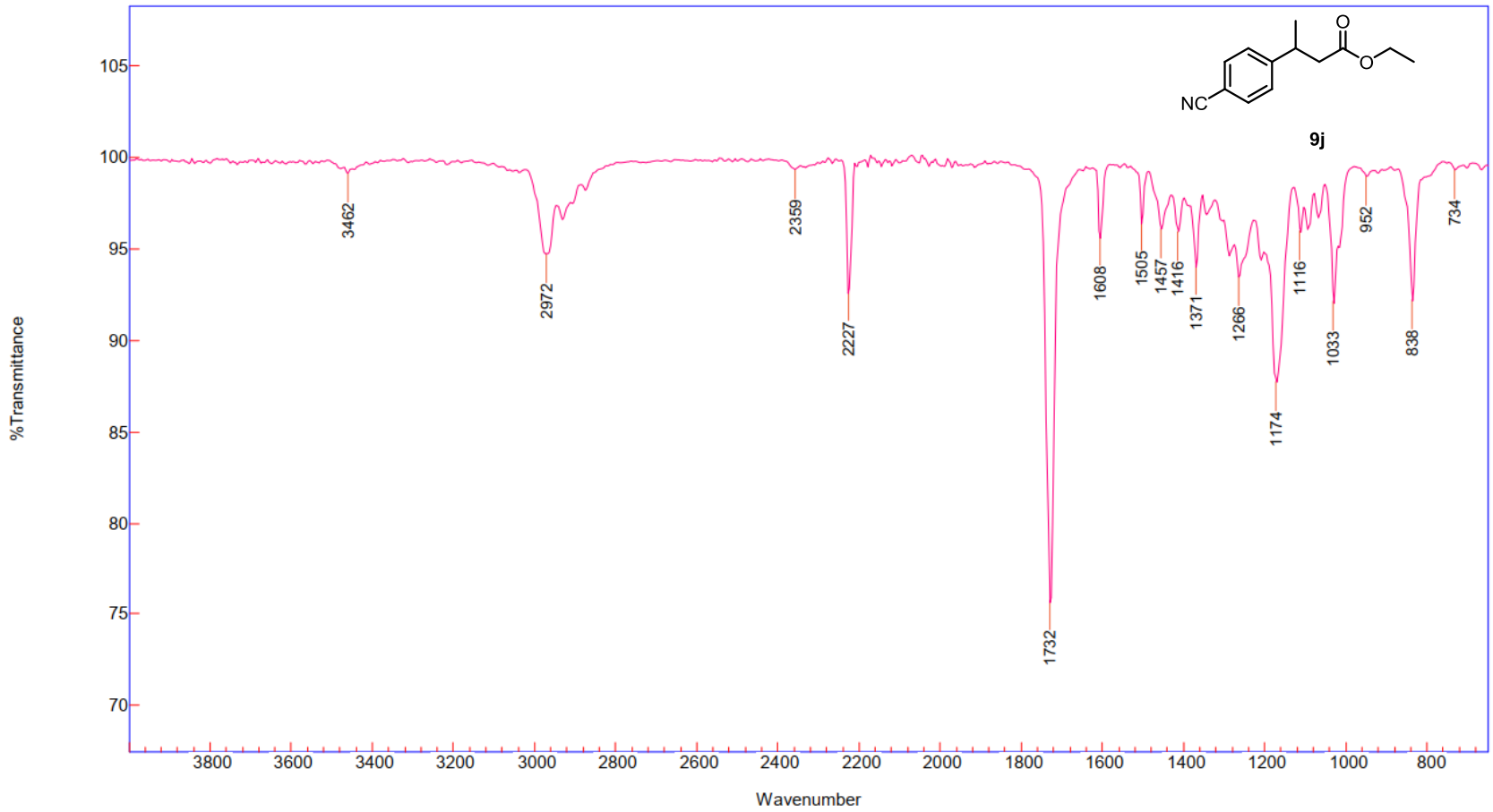
^{1}H-^{13}C HSQC


NC
O
O
9j
ppm
0
20
40
60
80
100
120
140
160
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
ppm

^{1}H-^{13}C HMBC

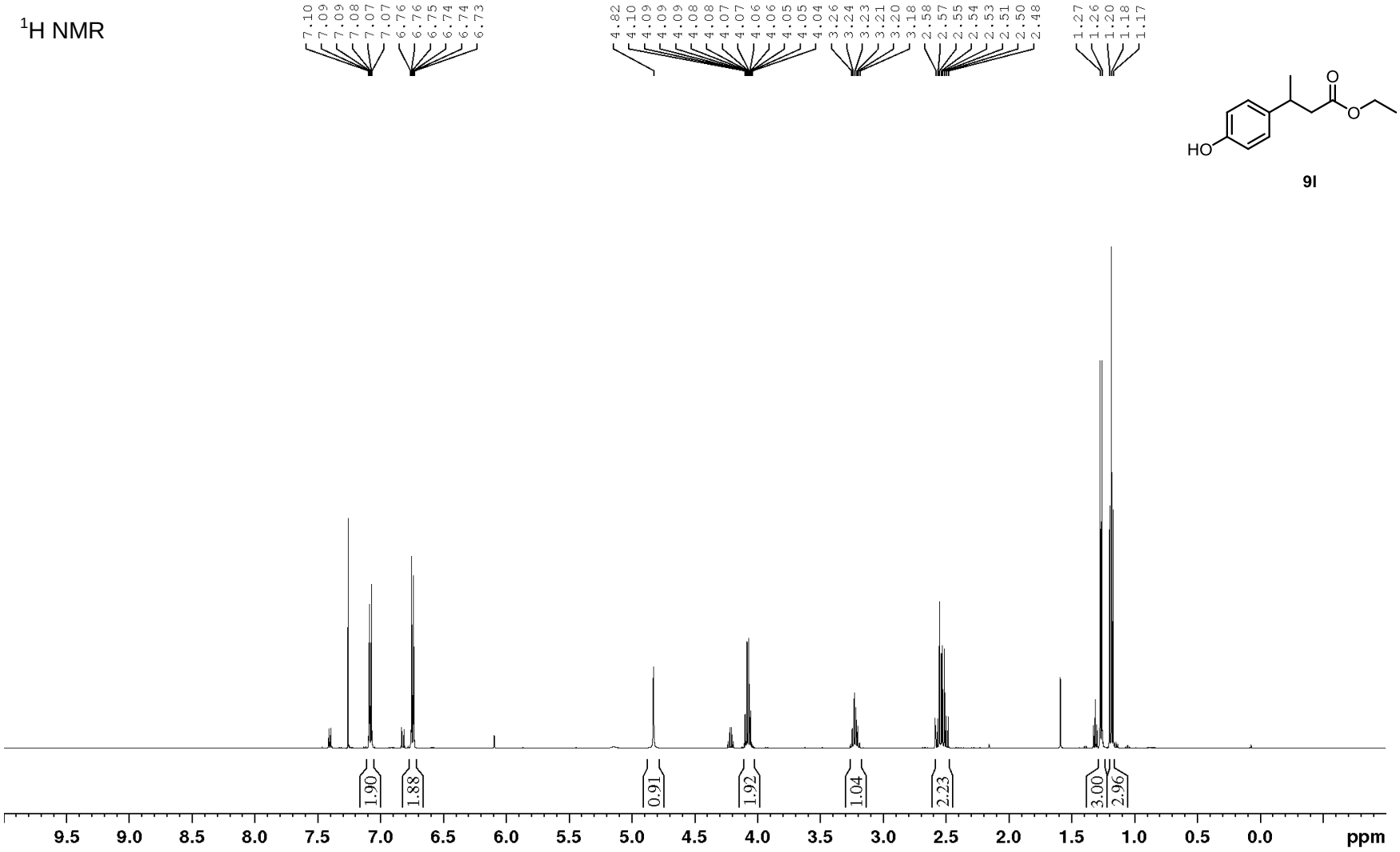

NC
O
O
9j
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

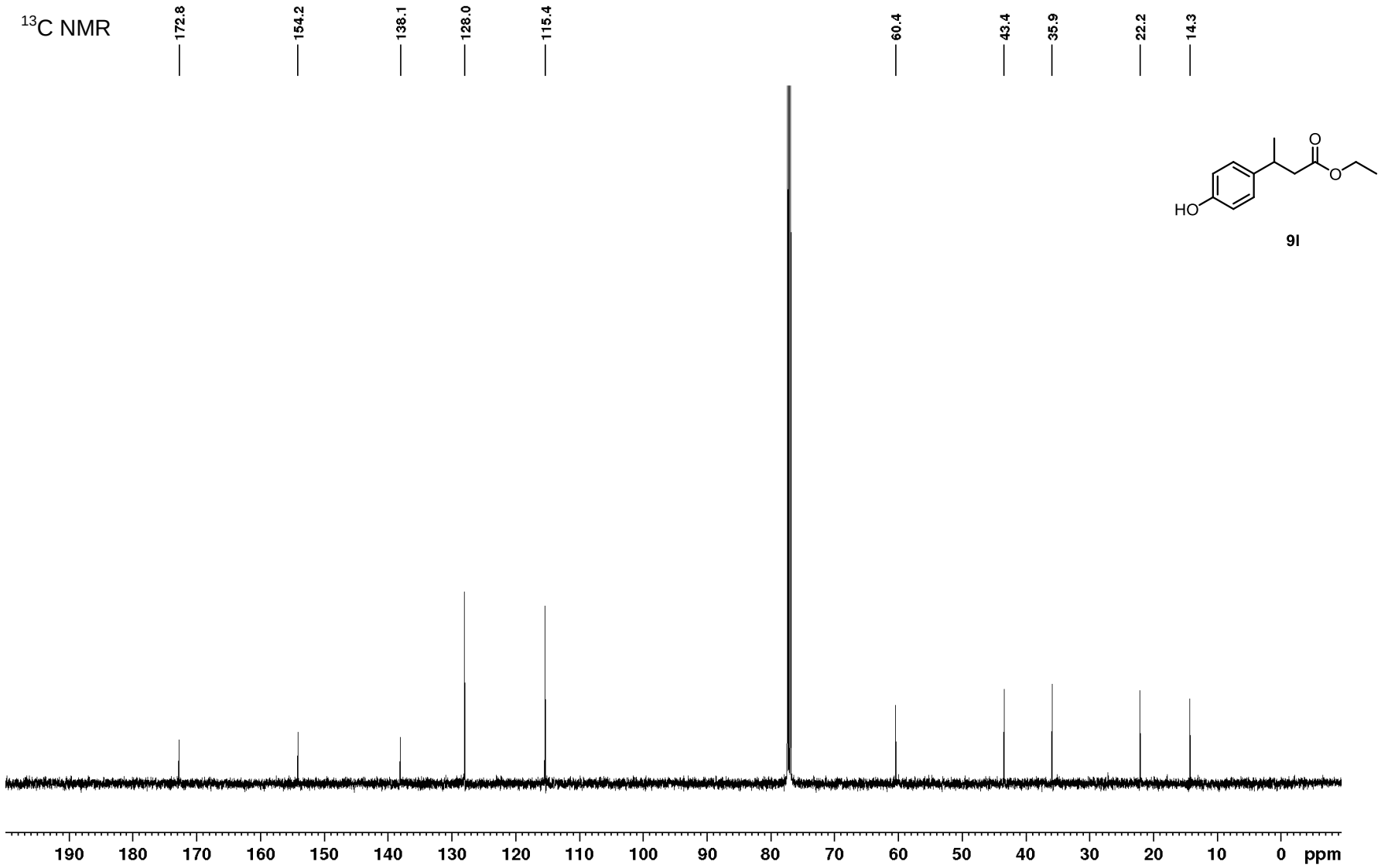

218.1182
214.0904
158.0276
130.0654
236.1652
219.1215
221.1178
144.0813
190.0867
193.0865
105.0702
125.0826
161.0827
177.1279
215.0938
237.1685
281.1365
305.0389
369.1891
447.2357
intensity
m/z
NC
O
O
9j


%Transmittance
105
100
95
90
85
80
75
70
3462
2972
2359
2227
1732
1608
1505
1457
1416
1371
1266
1174
1116
1033
952
838
734
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber
NC
O
O
9j

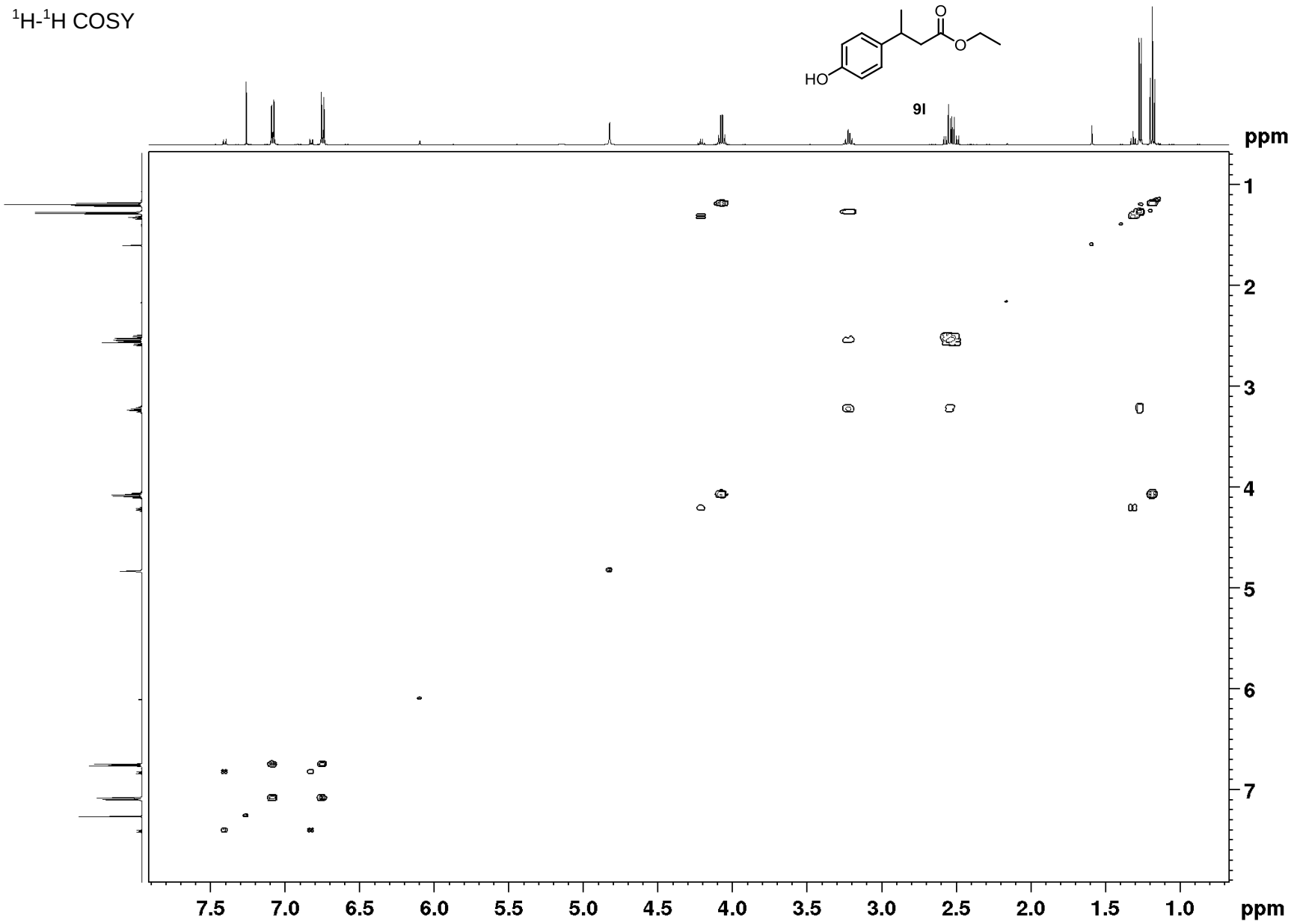
Ethyl 3-(4-hydroxyphenyl)butanoate (9l)

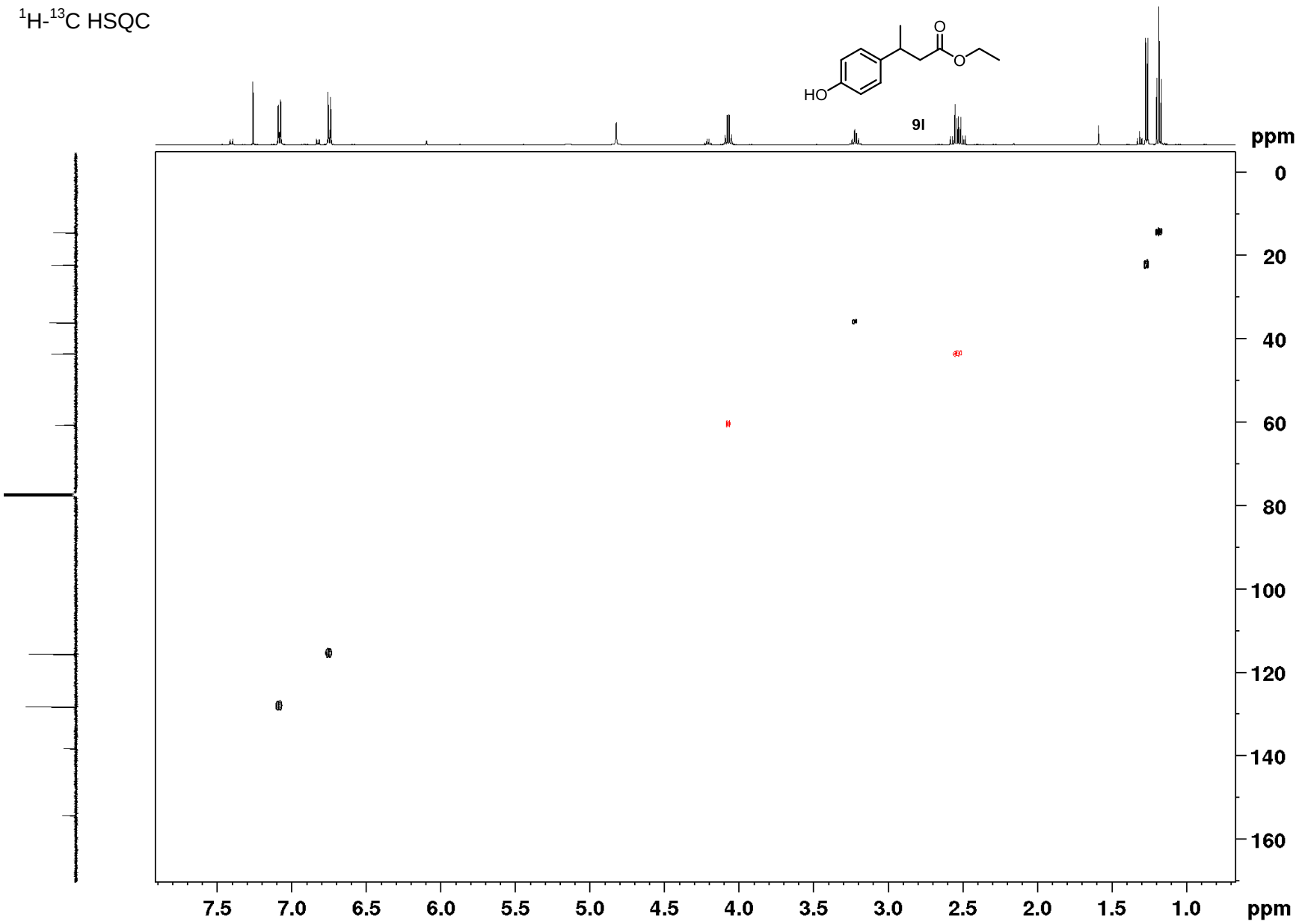
^{1}H NMR



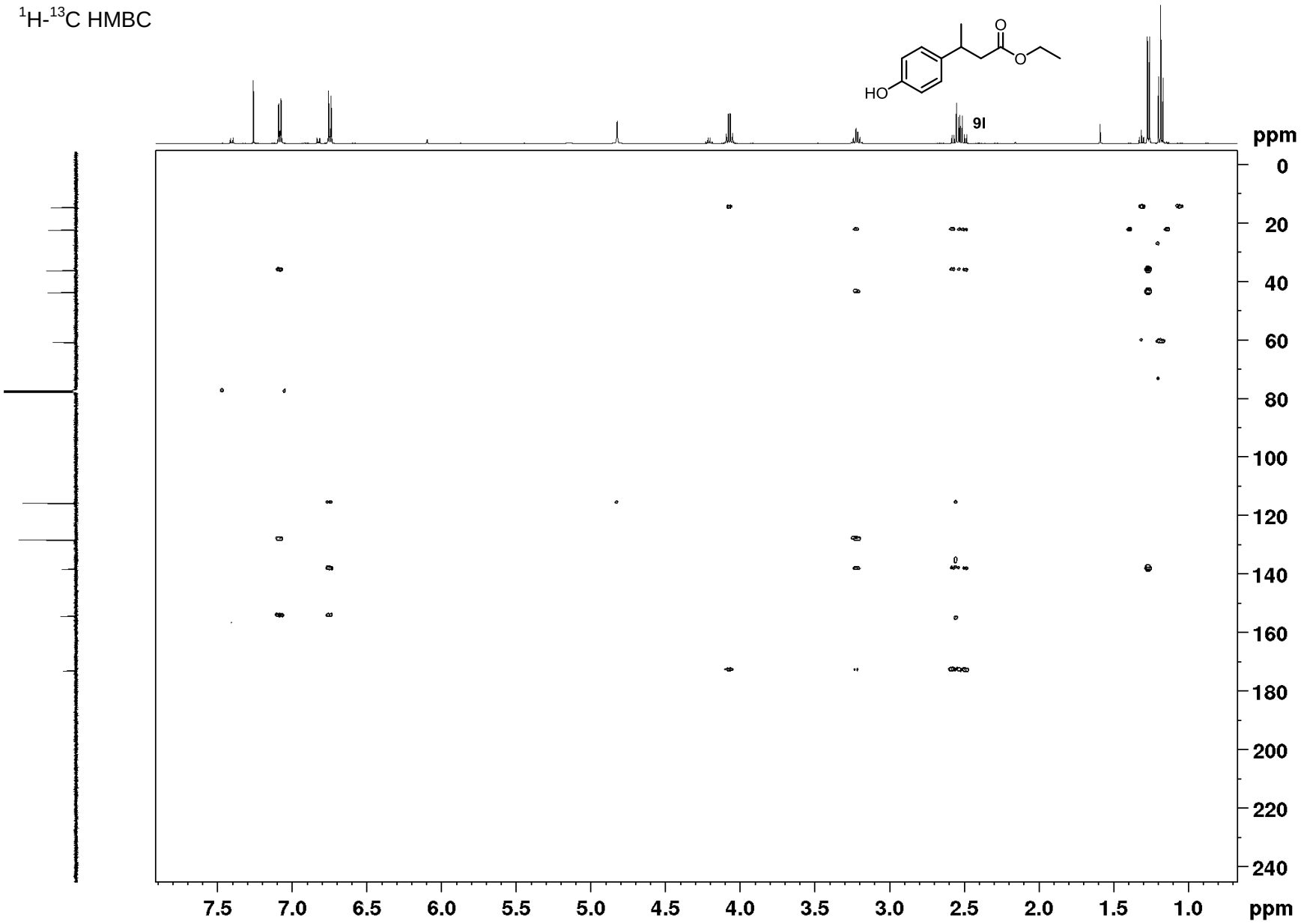

^{13}C NMR
172.8
154.2
138.1
128.0
115.4
60.4
43.4
35.9
22.2
14.3
HO
O
O
9l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

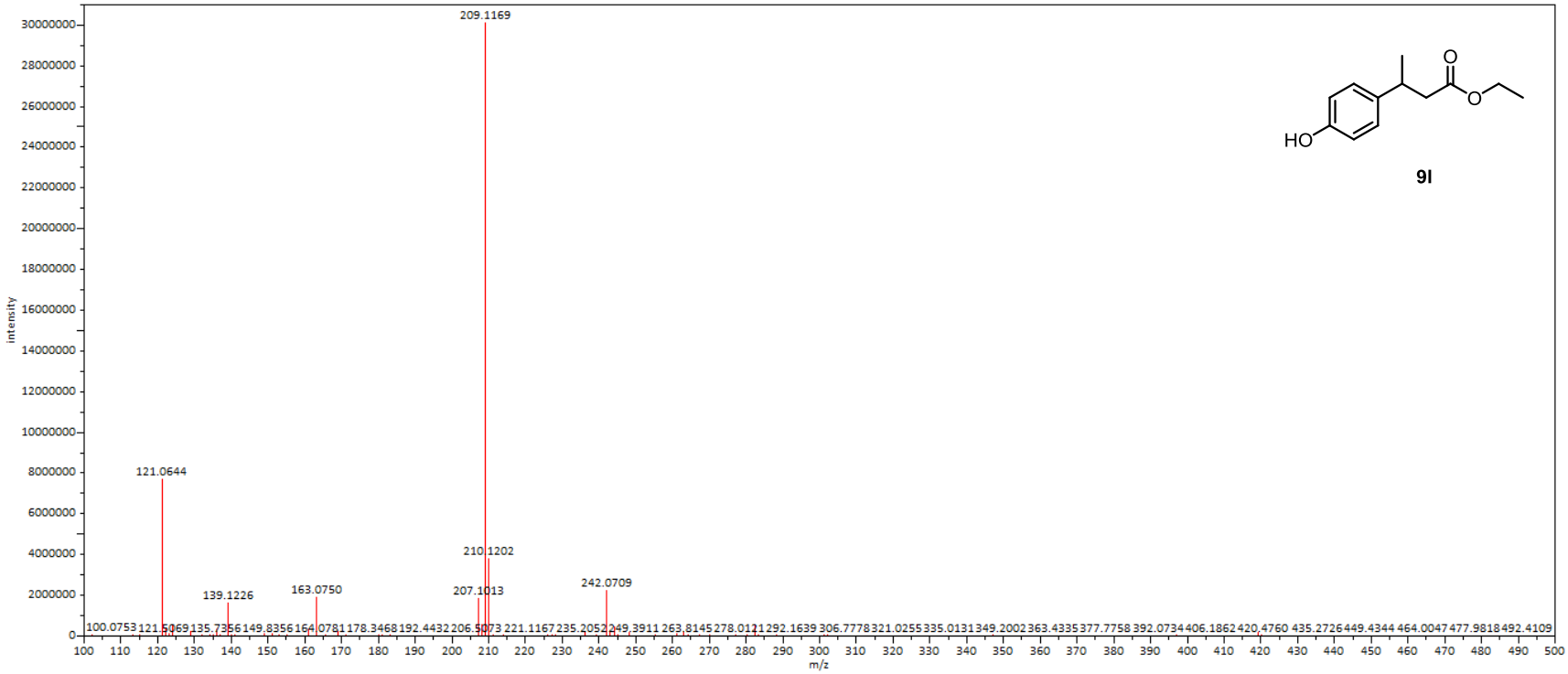
^{1}H-^{1}H COSY

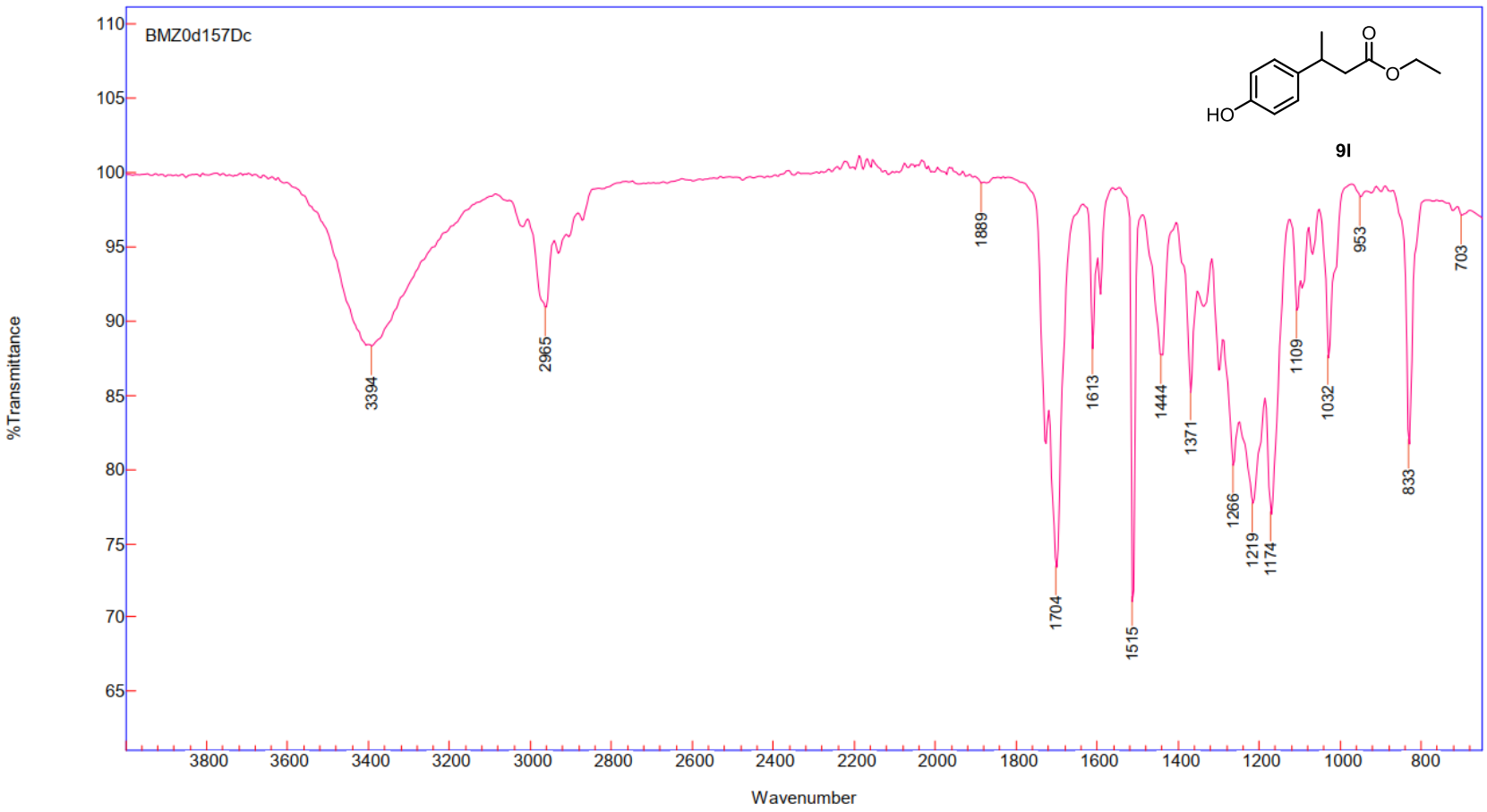



^{1}H-^{13}C HSQC
HO
O
O
9l
ppm
0
20
40
60
80
100
120
140
160
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

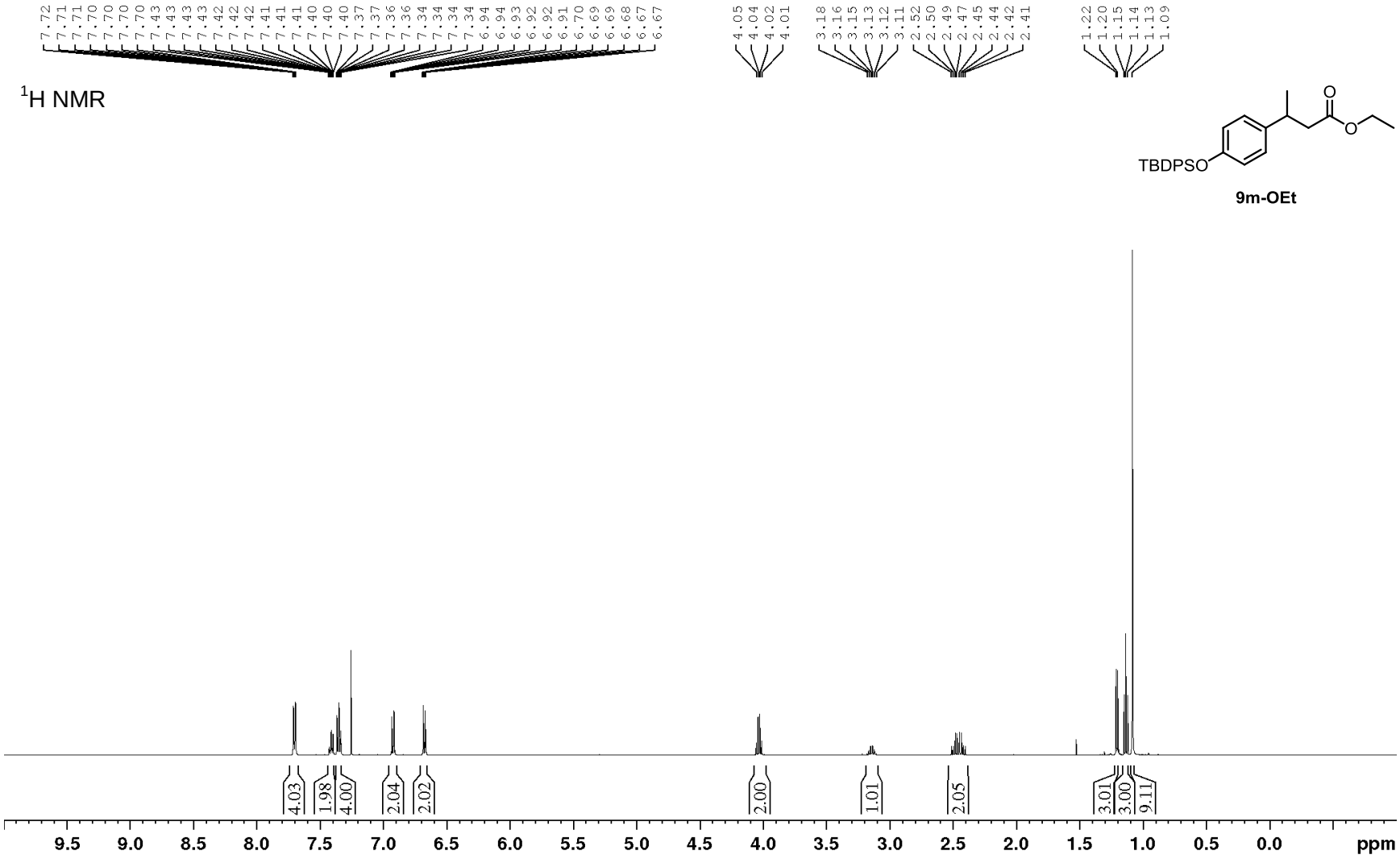
^{1}H-^{13}C HMBC

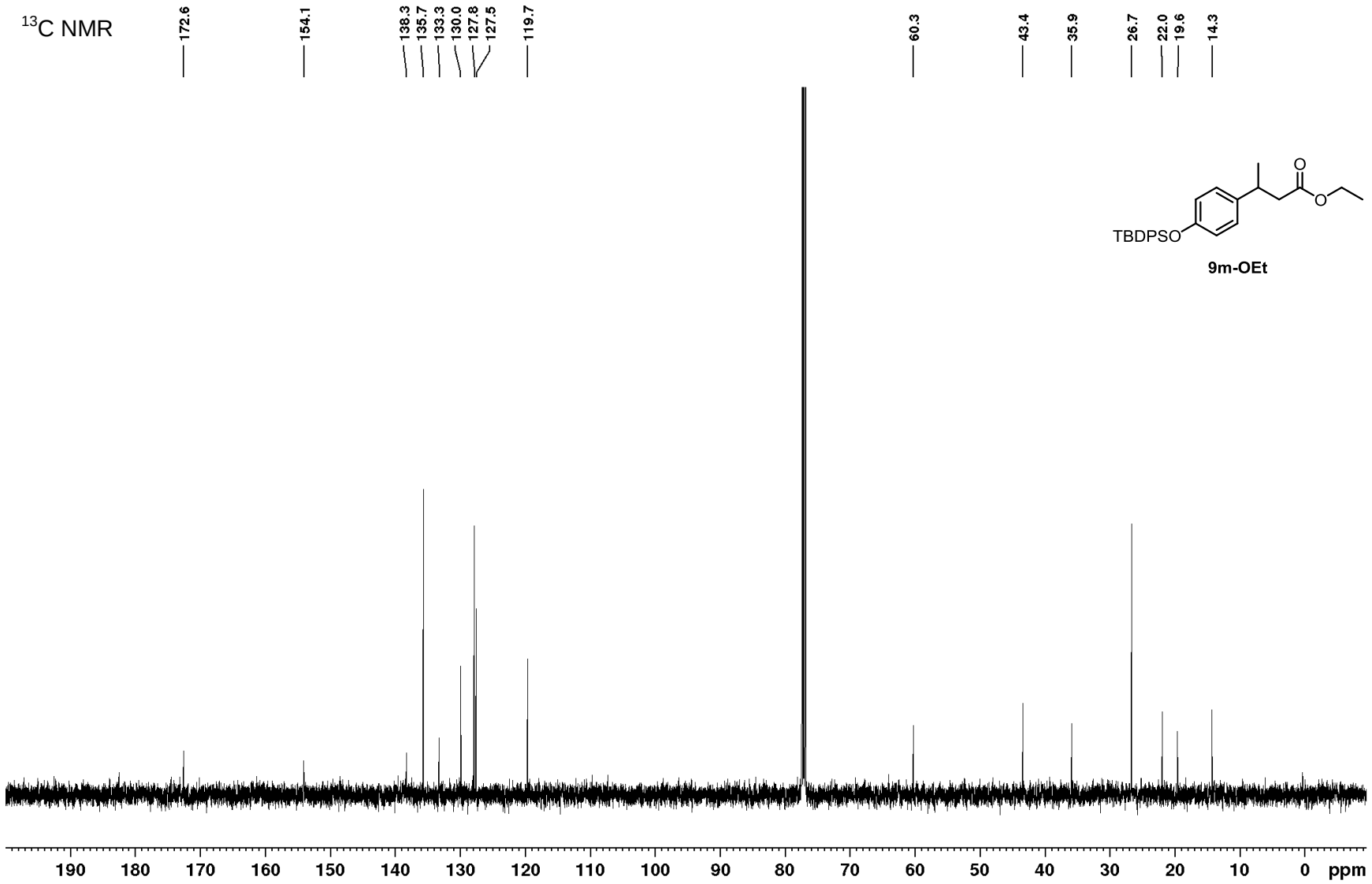

HO
O
O
9l
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


209.1169
121.0644
210.1202
139.1226
163.0750
207.1013
242.0709
intensity
m/z
HO
O
O
9l

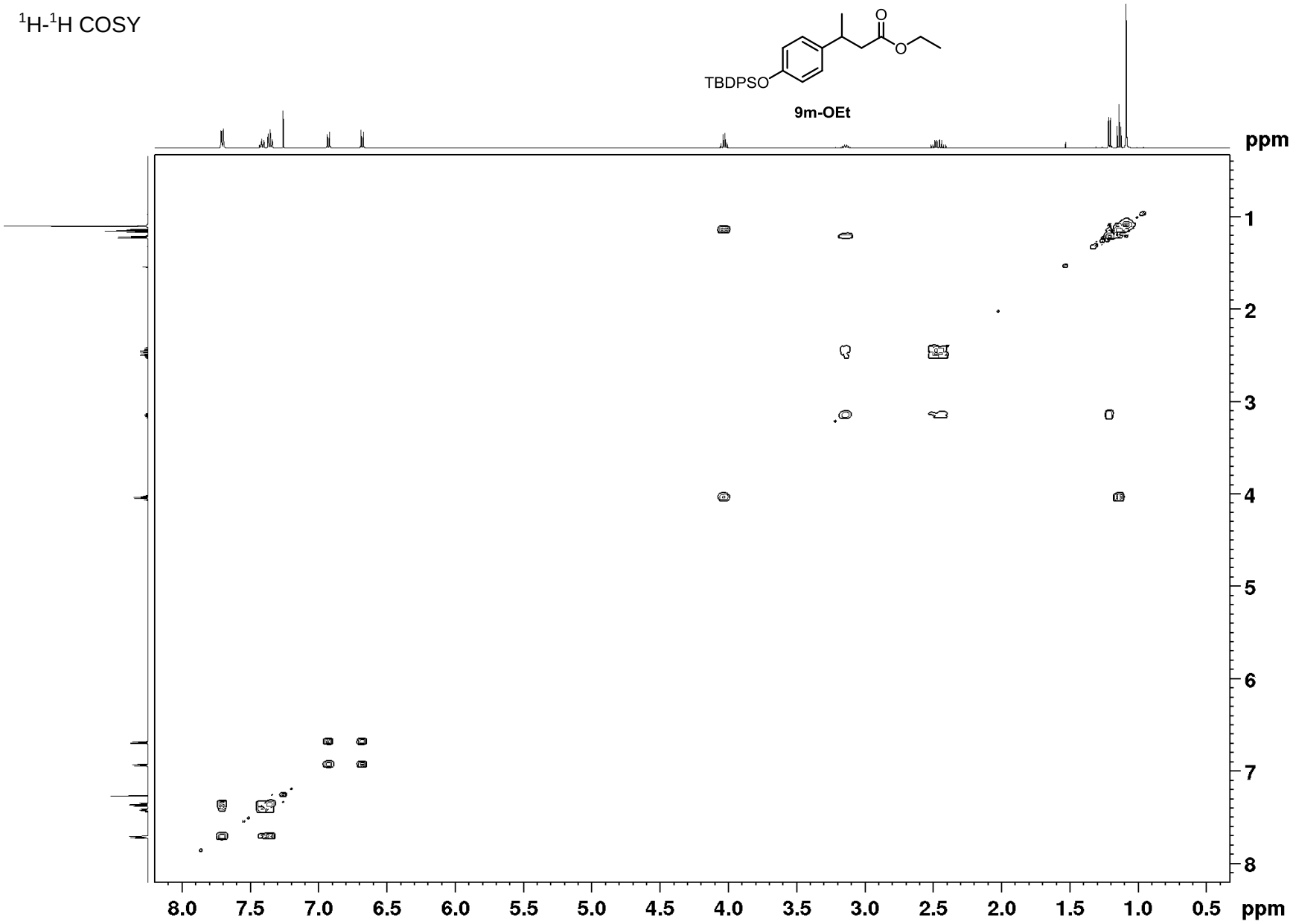

BMZ0d157Dc
%Transmittance
Wavenumber
110
105
100
95
90
85
80
75
70
65
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
3394
2965
1889
1704
1613
1515
1444
1371
1266
1219
1174
1109
1032
953
833
703
HO
O
O
9l

Ethyl 3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)butanoate (9m-OEt)

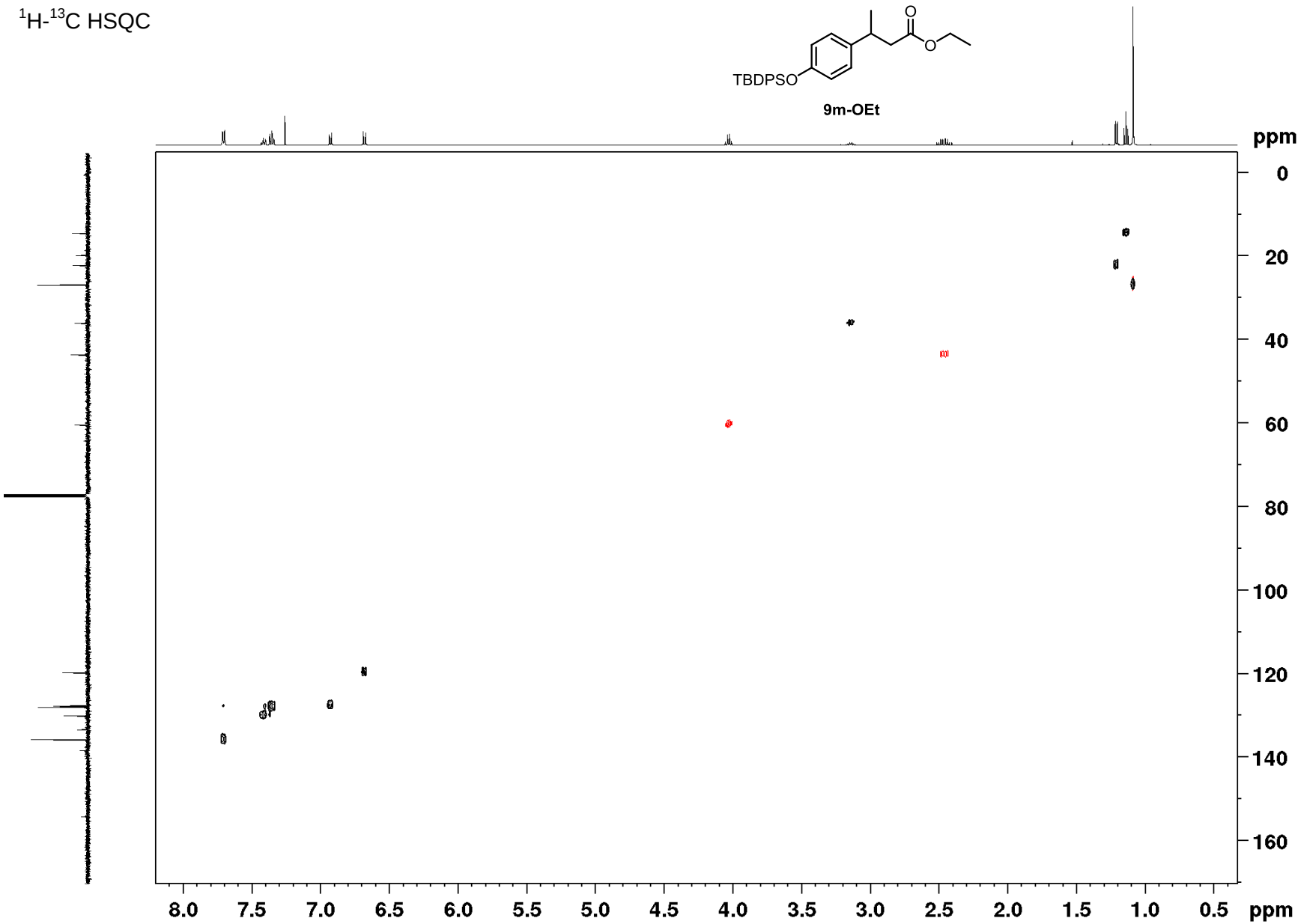



^{13}C NMR
172.6
154.1
138.3
135.7
133.3
130.0
127.8
127.5
119.7
60.3
43.4
35.9
26.7
22.0
19.6
14.3
TBDPSO
O
O
9m-OEt
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

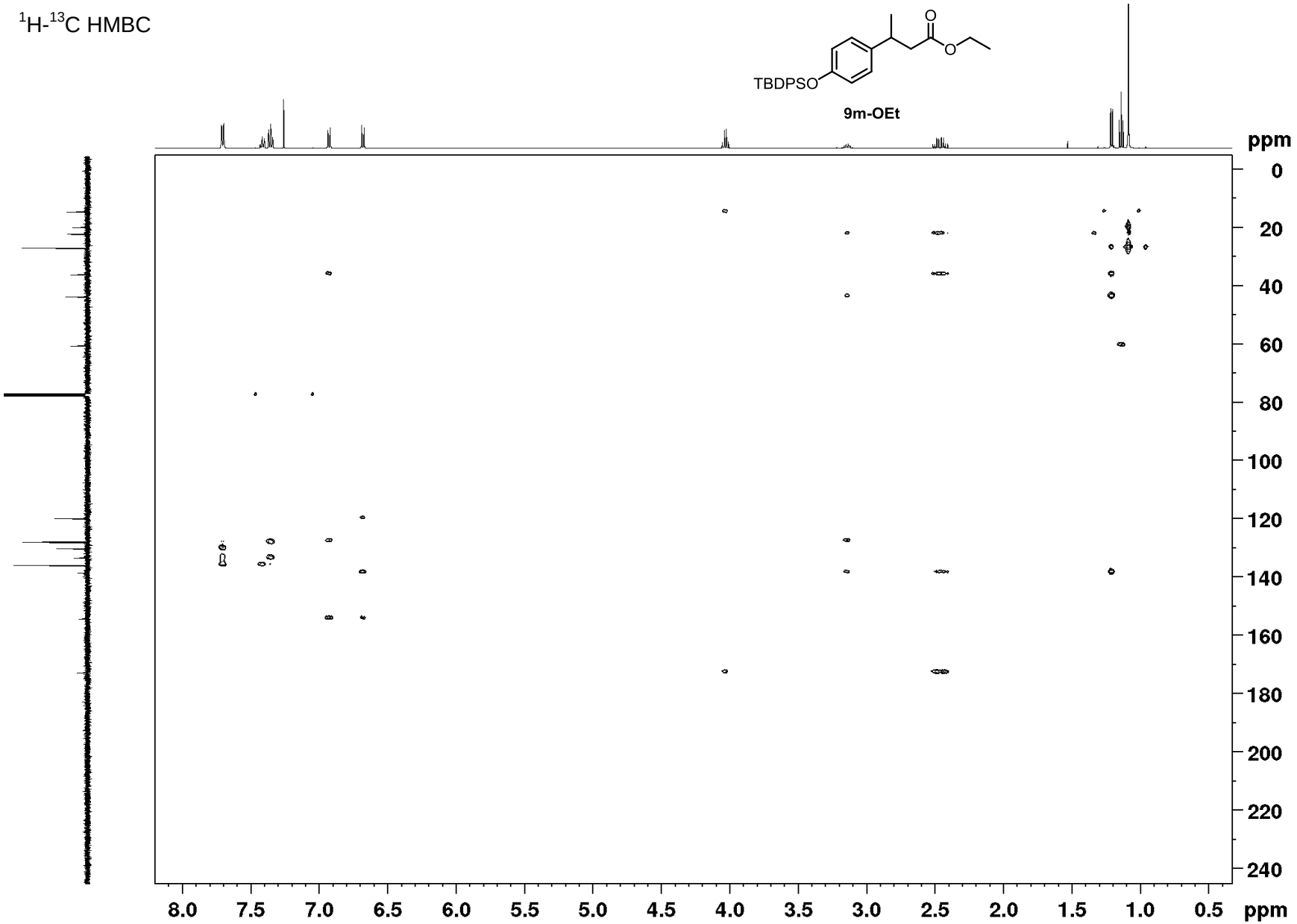
^{1}H-^{1}H COSY


TBDPSO
O
O
9m-OEt
ppm
1
2
3
4
5
6
7
8
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
ppm

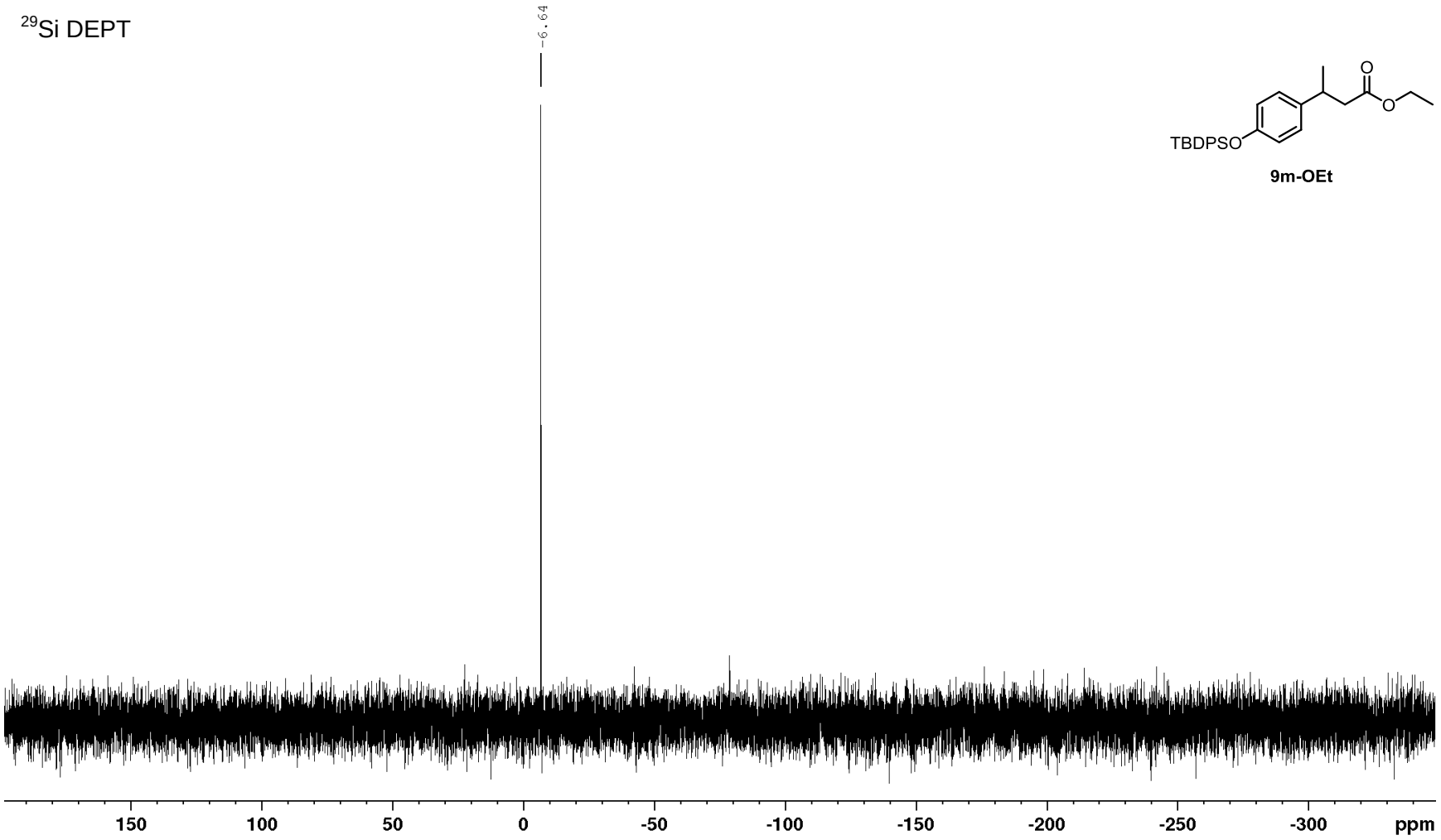
^{1}H-^{13}C HSQC


TBDPSO
O
O
9m-OEt
ppm
0
20
40
60
80
100
120
140
160
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
ppm

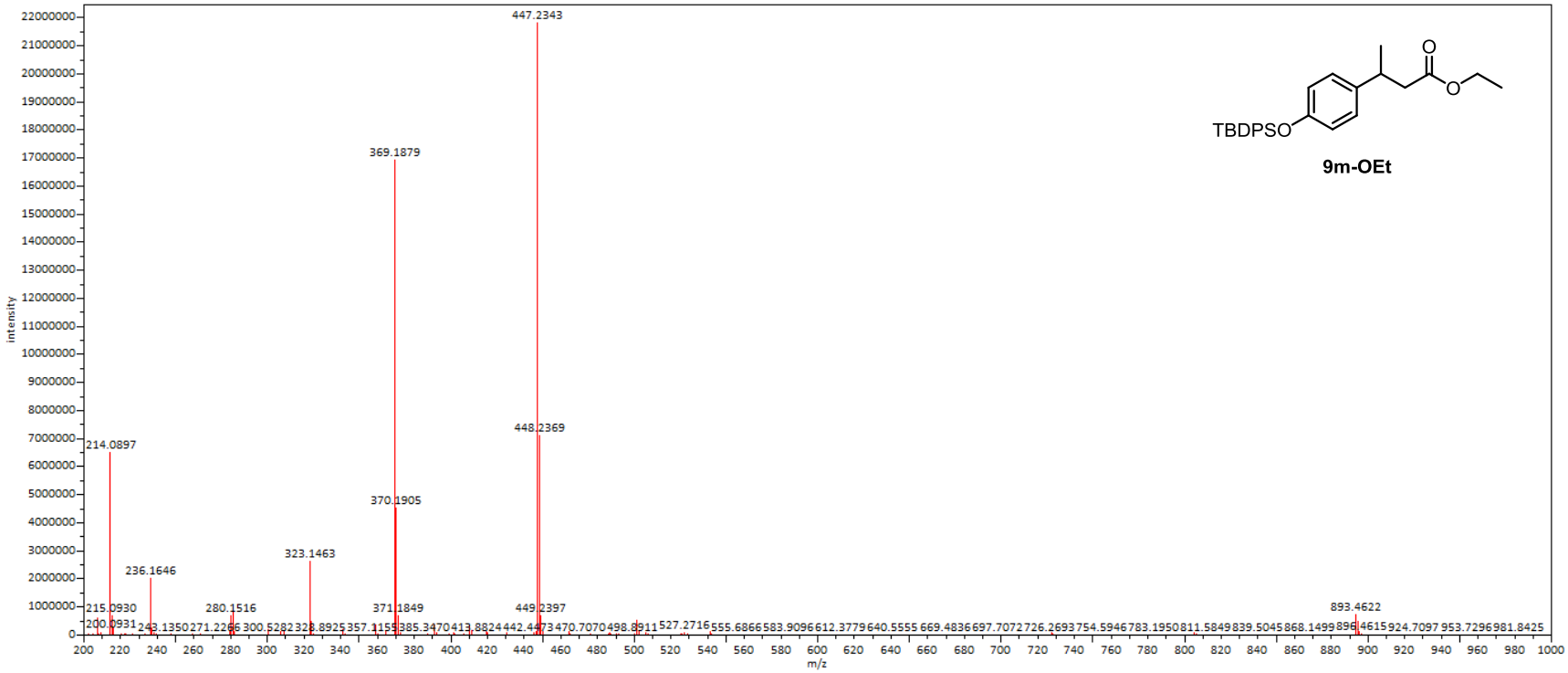
^{1}H-^{13}C HMBC


TBDPSO
O
O
9m-OEt
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

^{29}Si DEPT

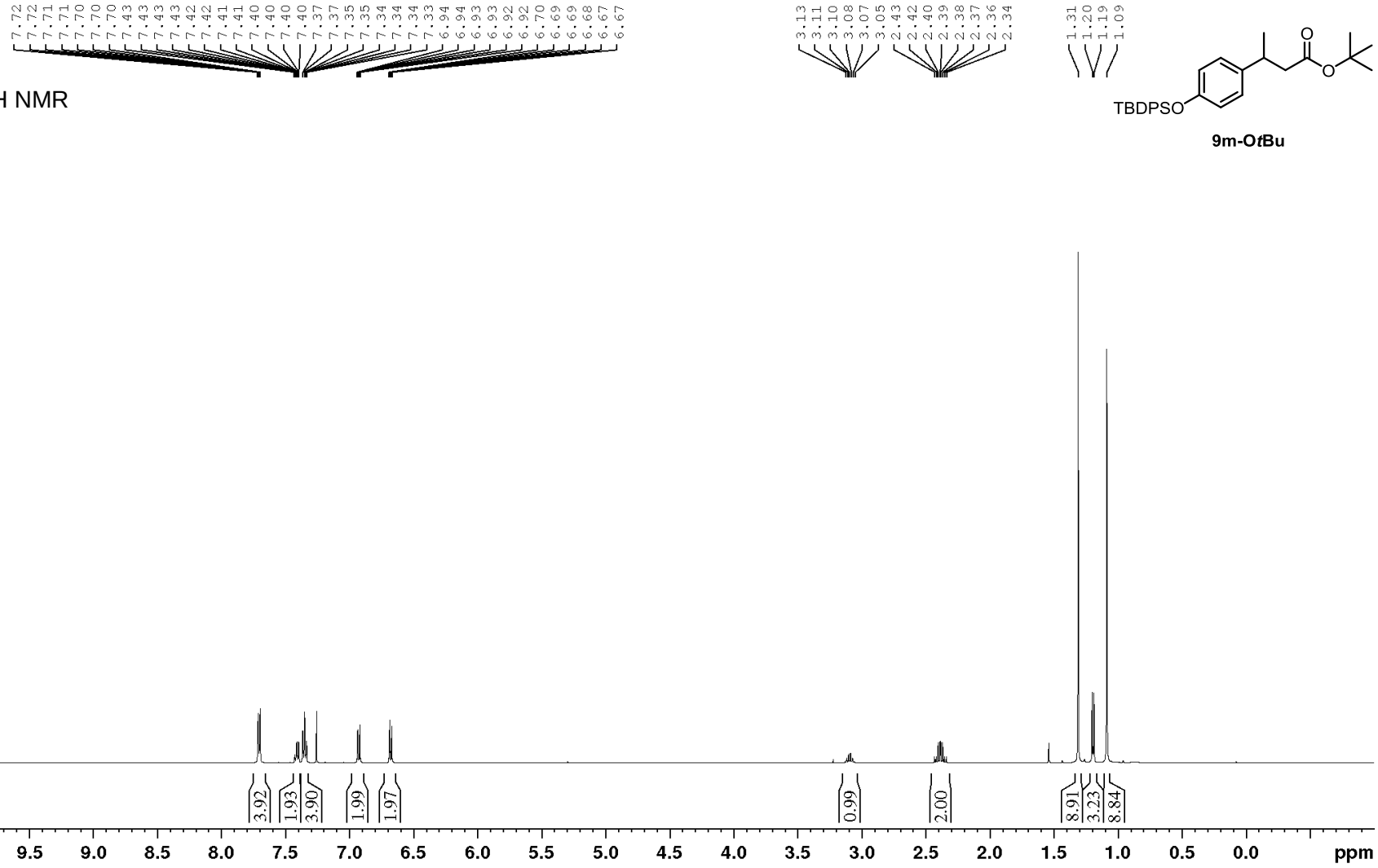


9m-OEt


447.2343
369.1879
448.2369
214.0897
370.1905
323.1463
236.1646
280.1516
371.1849
449.2397
893.4622
intensity
m/z
TBDPSO
O
O
9m-OEt

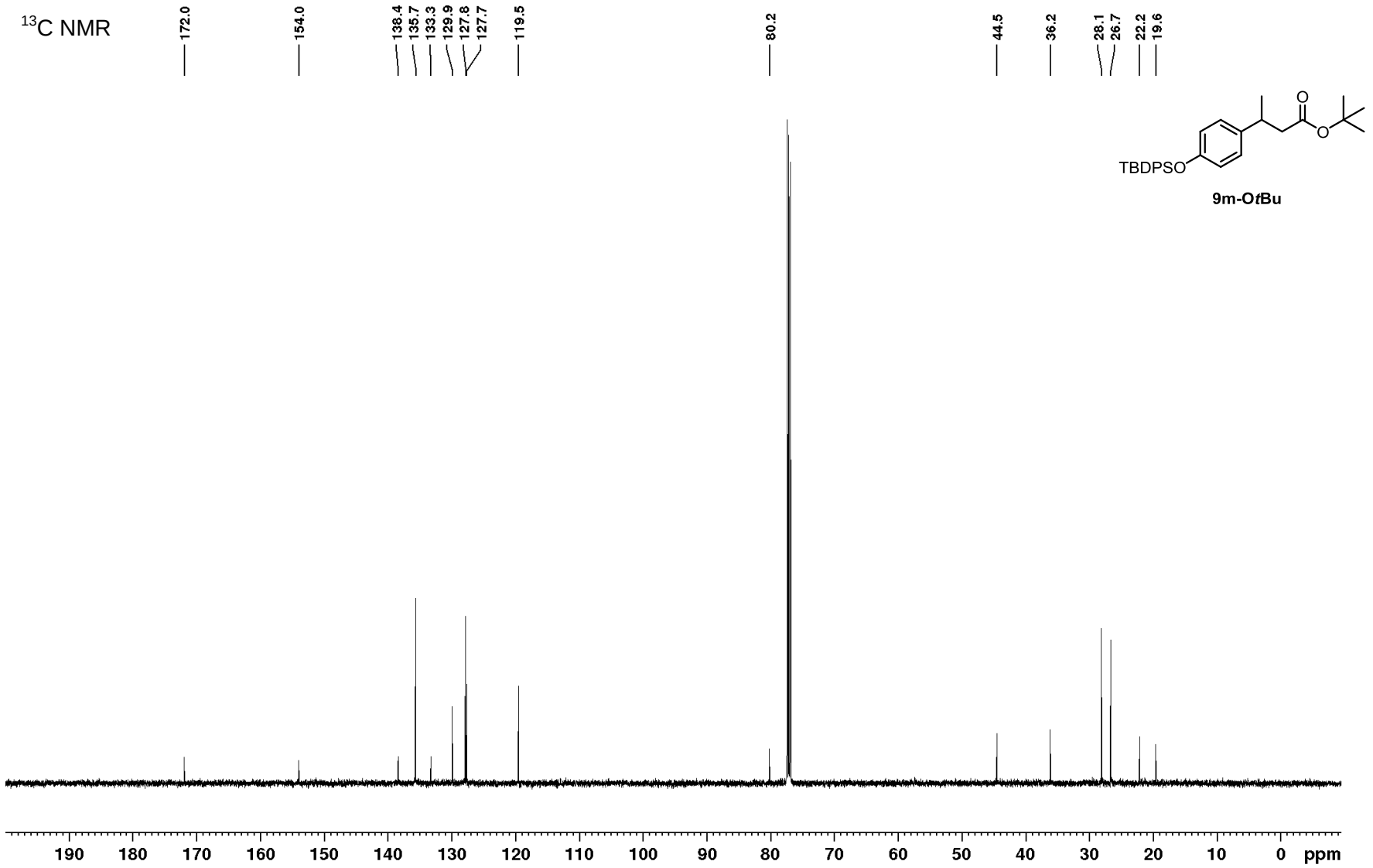

%Transmittance
Wavenumber
120
100
80
60
40
20
0
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
3455
2930
2856
2287
2109
1960
1886
1731
1606
1509
1471
1427
1367
1252
1160
1107
1032
916
832
779
740
698
TBDPSO
O
O
9m-OEt

***tert*-Butyl 3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)butanoate (9m-O*t*Bu)**

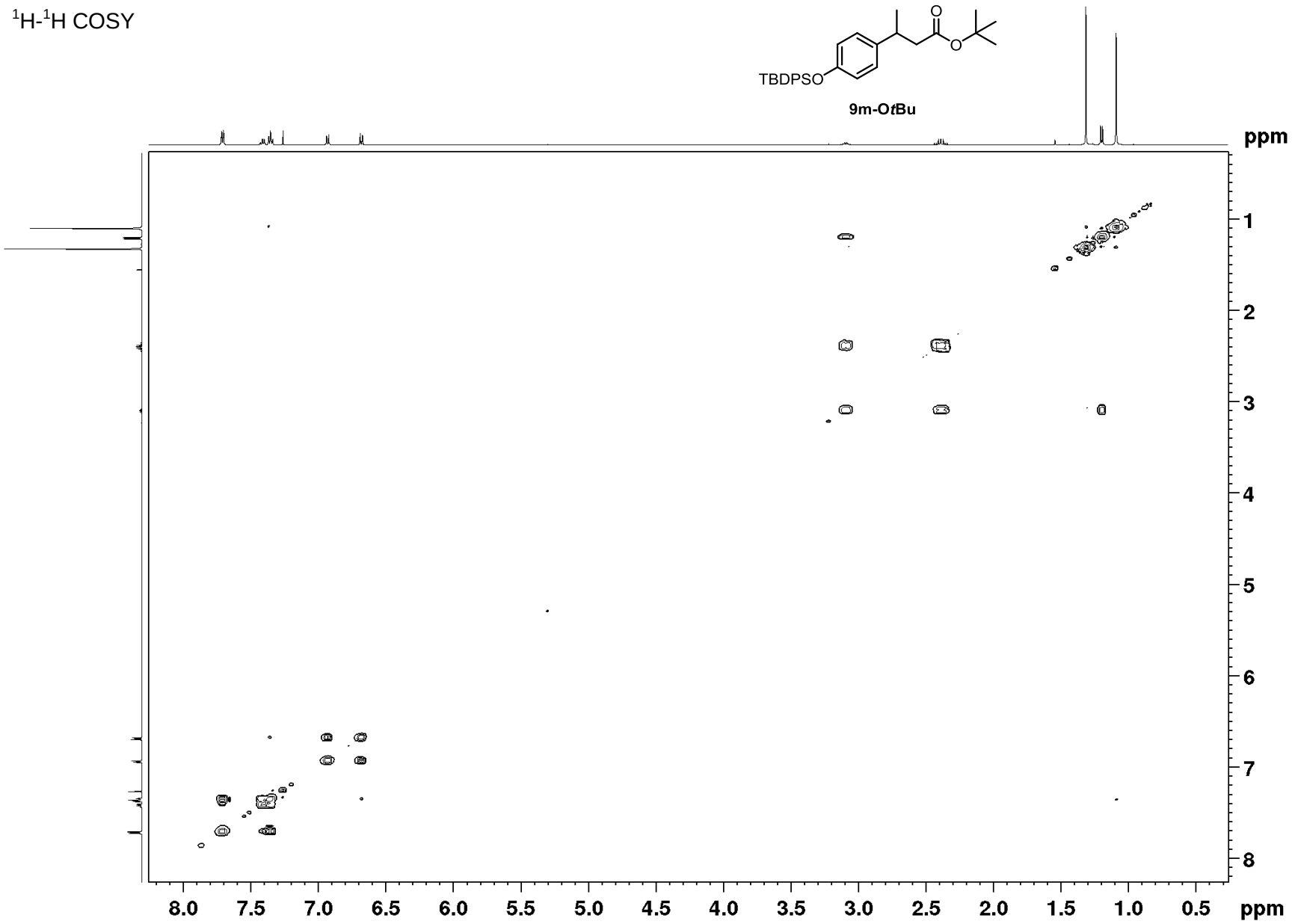


^{1}H NMR

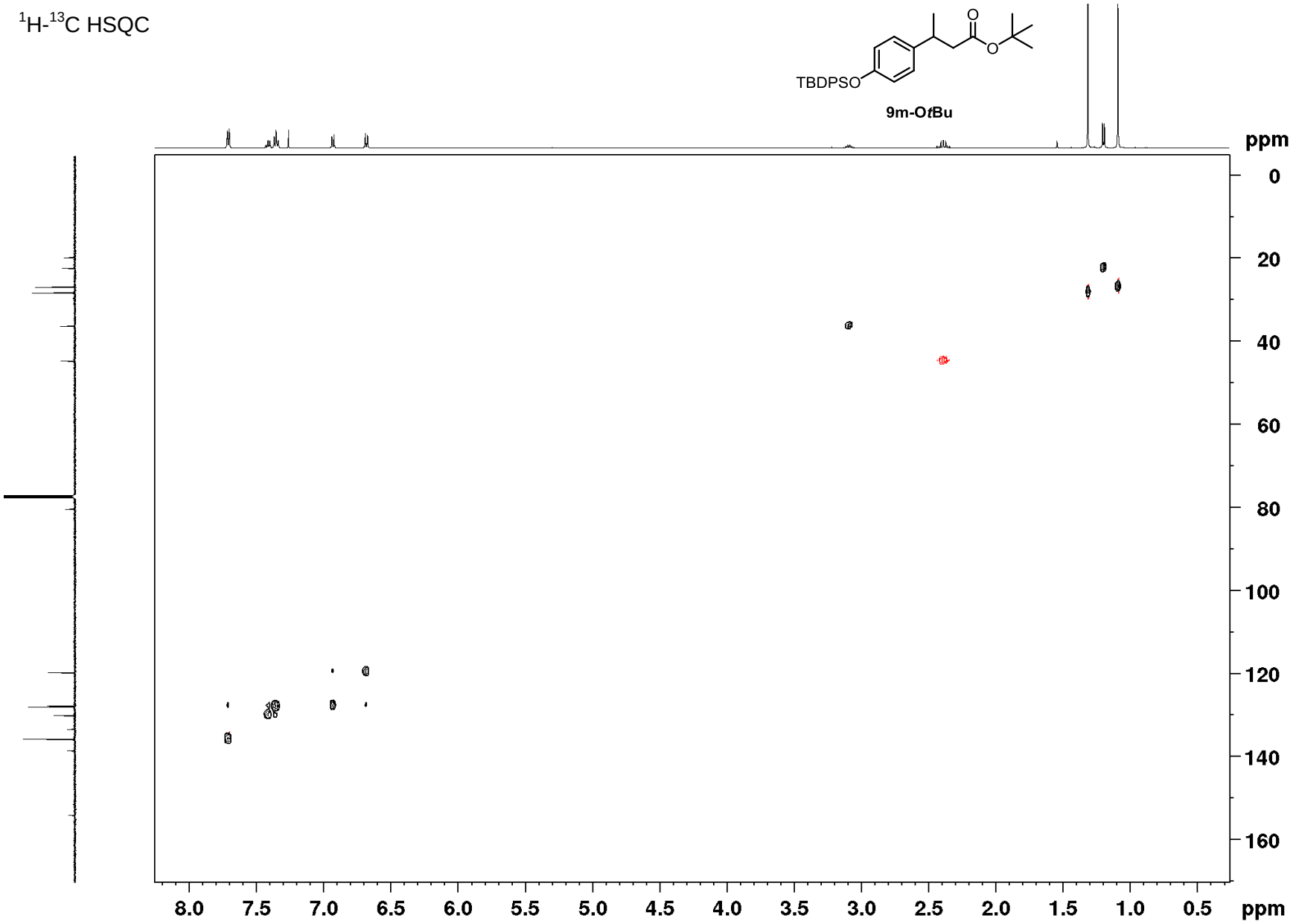
9m-O*t*Bu


^{13}C NMR
172.0
154.0
138.4
135.7
133.3
129.9
127.8
127.7
119.5
80.2
44.5
36.2
28.1
26.7
22.2
19.6
TBDPSO
O
O
9m-O*t*Bu
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

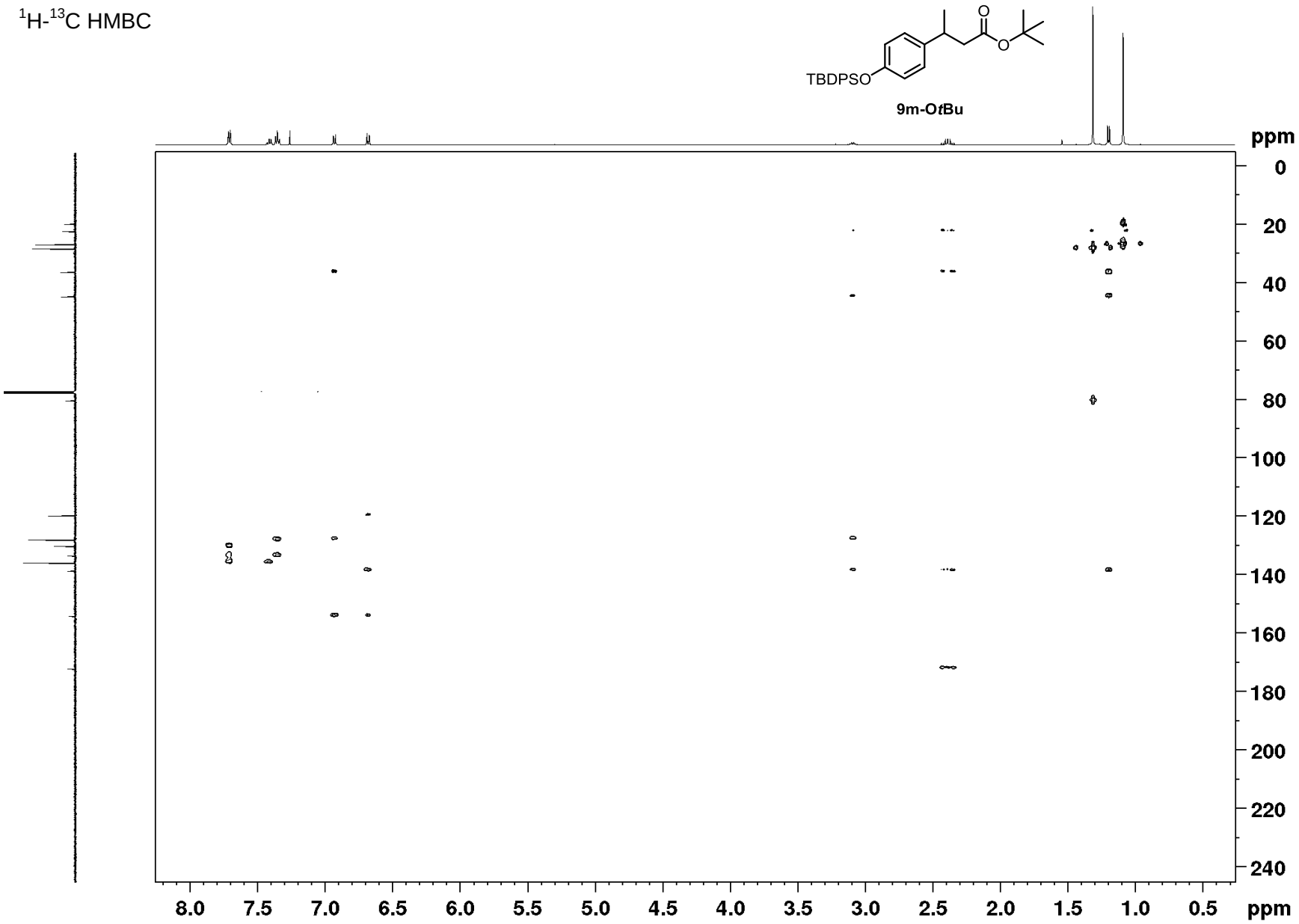
^{1}H-^{1}H COSY


TBDPSO
O
O
9m-O*t*Bu
ppm
1
2
3
4
5
6
7
8
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
ppm

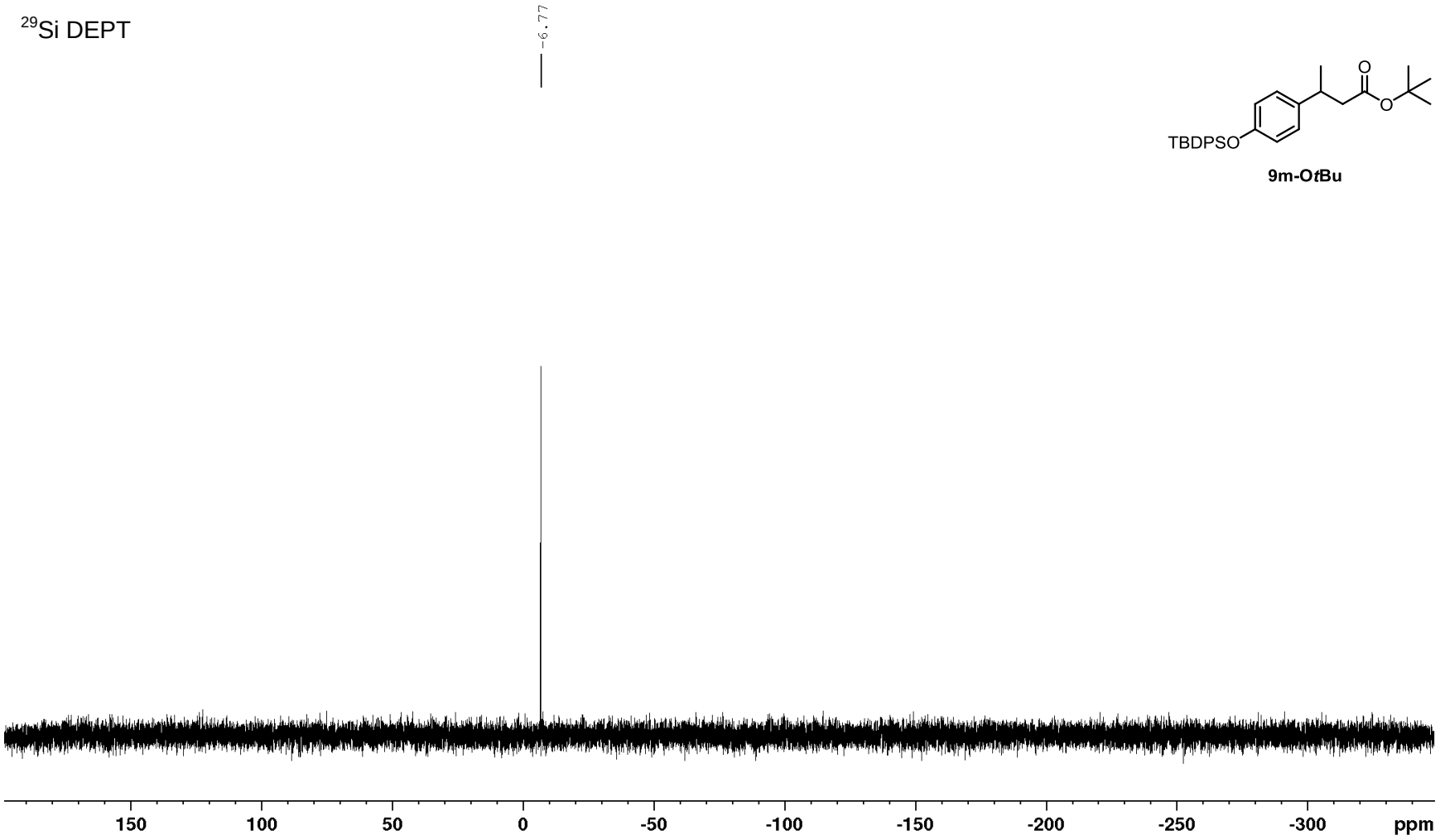
^{1}H-^{13}C HSQC


TBDPSO
O
O
9m-O*t*Bu
ppm
0
20
40
60
80
100
120
140
160
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
ppm

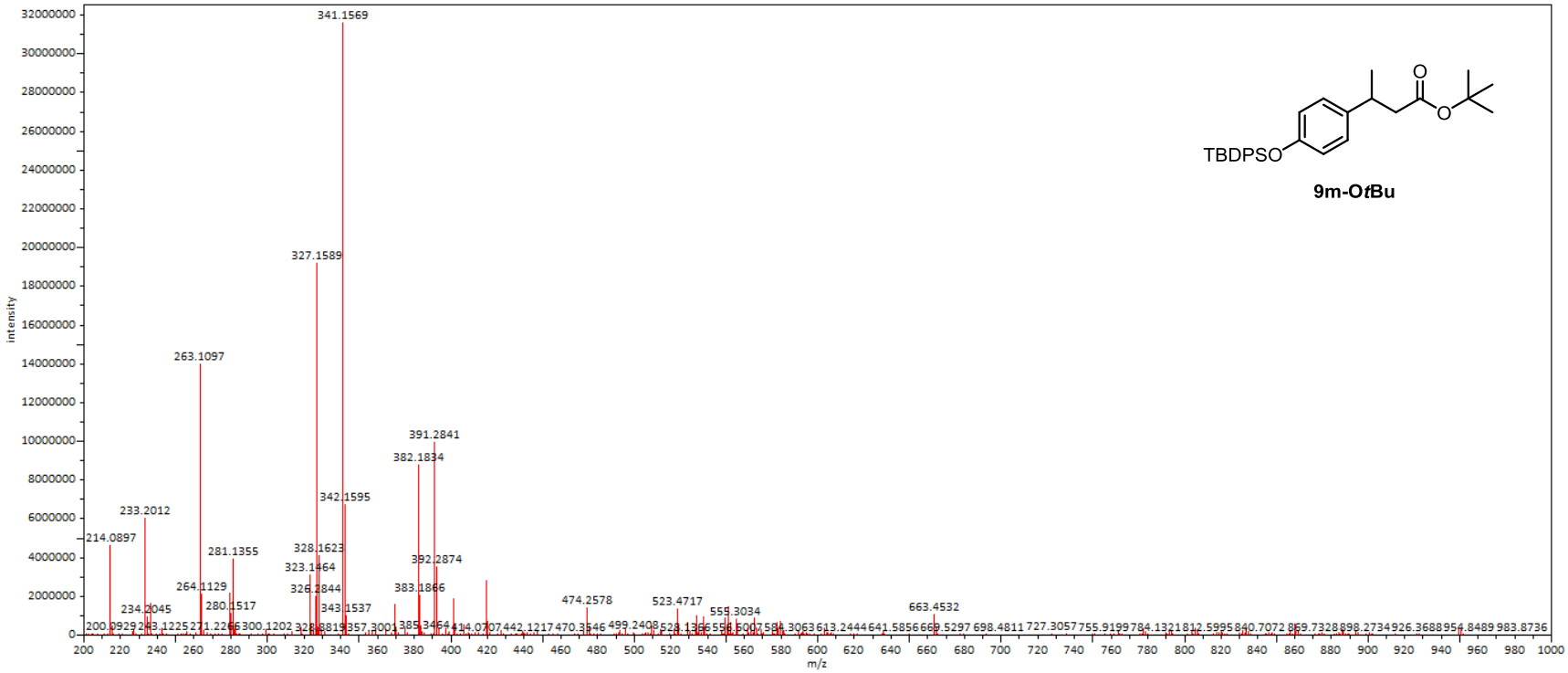
^{1}H-^{13}C HMBC

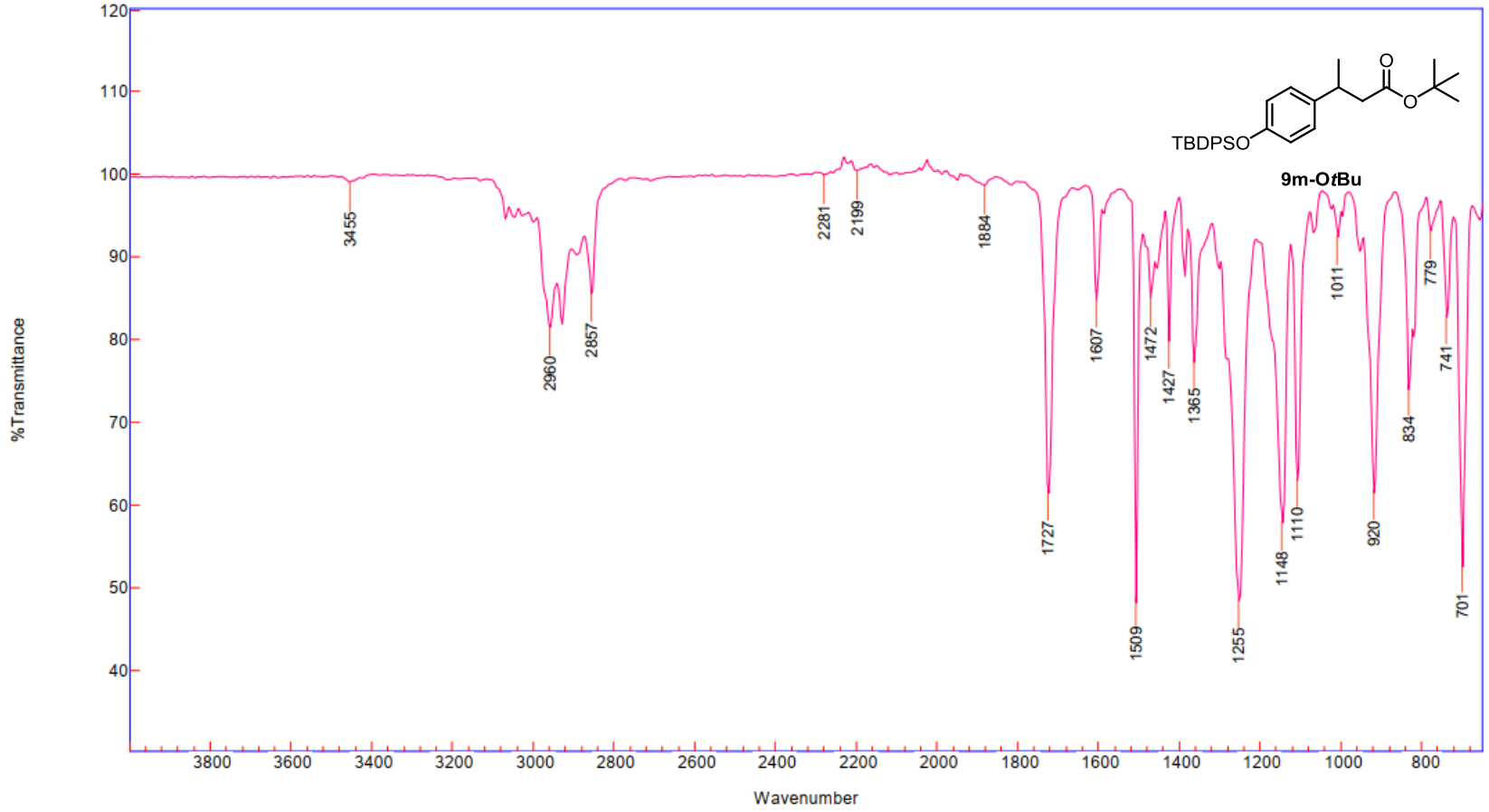

TBDPSO
O
O
9m-OtBu
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{29}Si DEPT



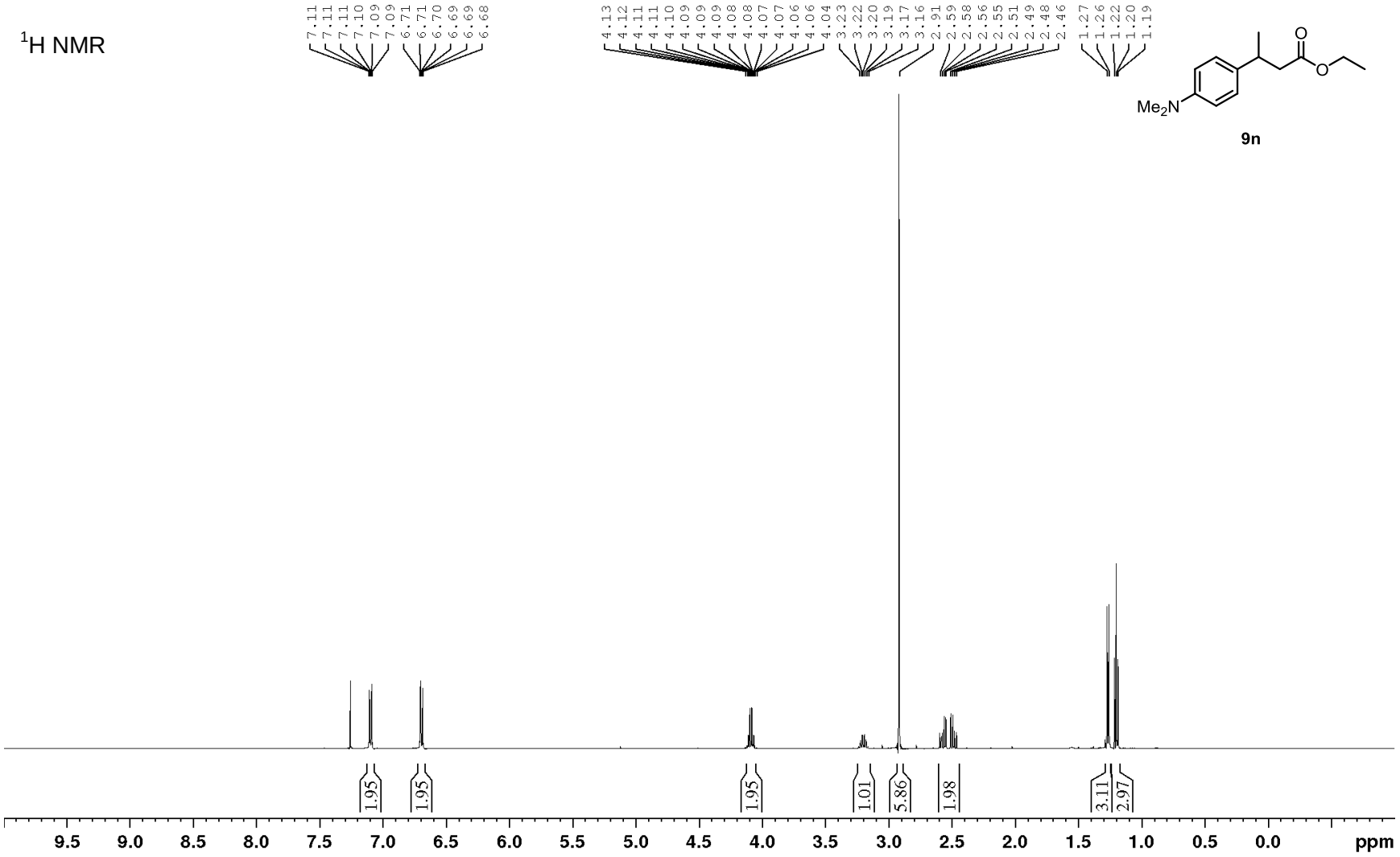
9m-O*t*Bu

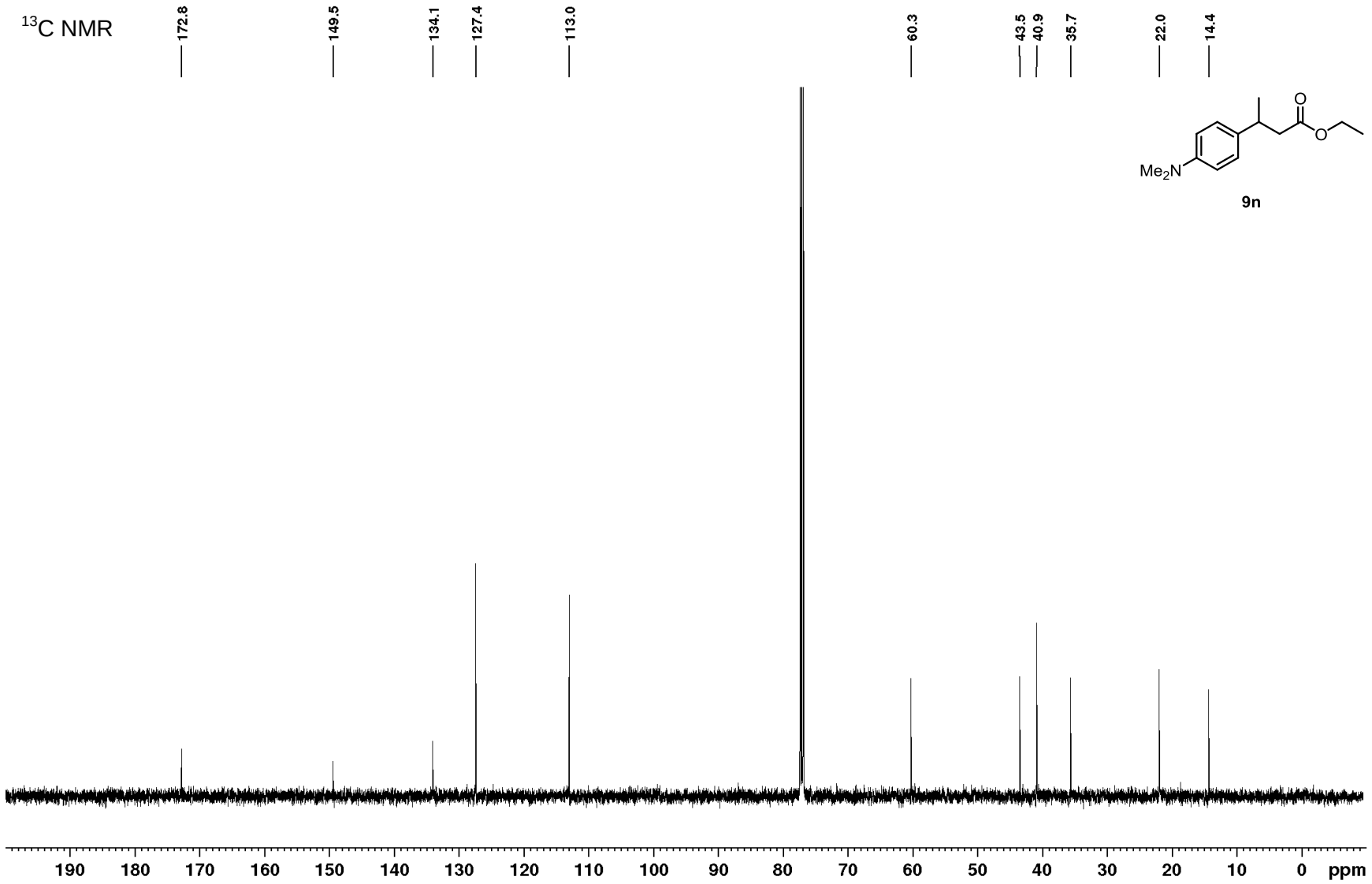

TBDPSO
O
O
9m-OtBu
intensity
m/z
341.1569
327.1589
263.1097
391.2841
382.1834
342.1595
233.2012
214.0897
281.1355
328.1623
323.1464
392.2874
264.1129
326.2844
383.1866
280.1517
343.1537
234.2045
474.2578
523.4717
559.3034
663.4532


%Transmittance
Wavenumber
TBDPSO
O
O
9m-OtBu
3455
2960
2857
2281
2199
1884
1727
1607
1509
1472
1427
1365
1255
1148
1110
1011
920
834
779
741
701

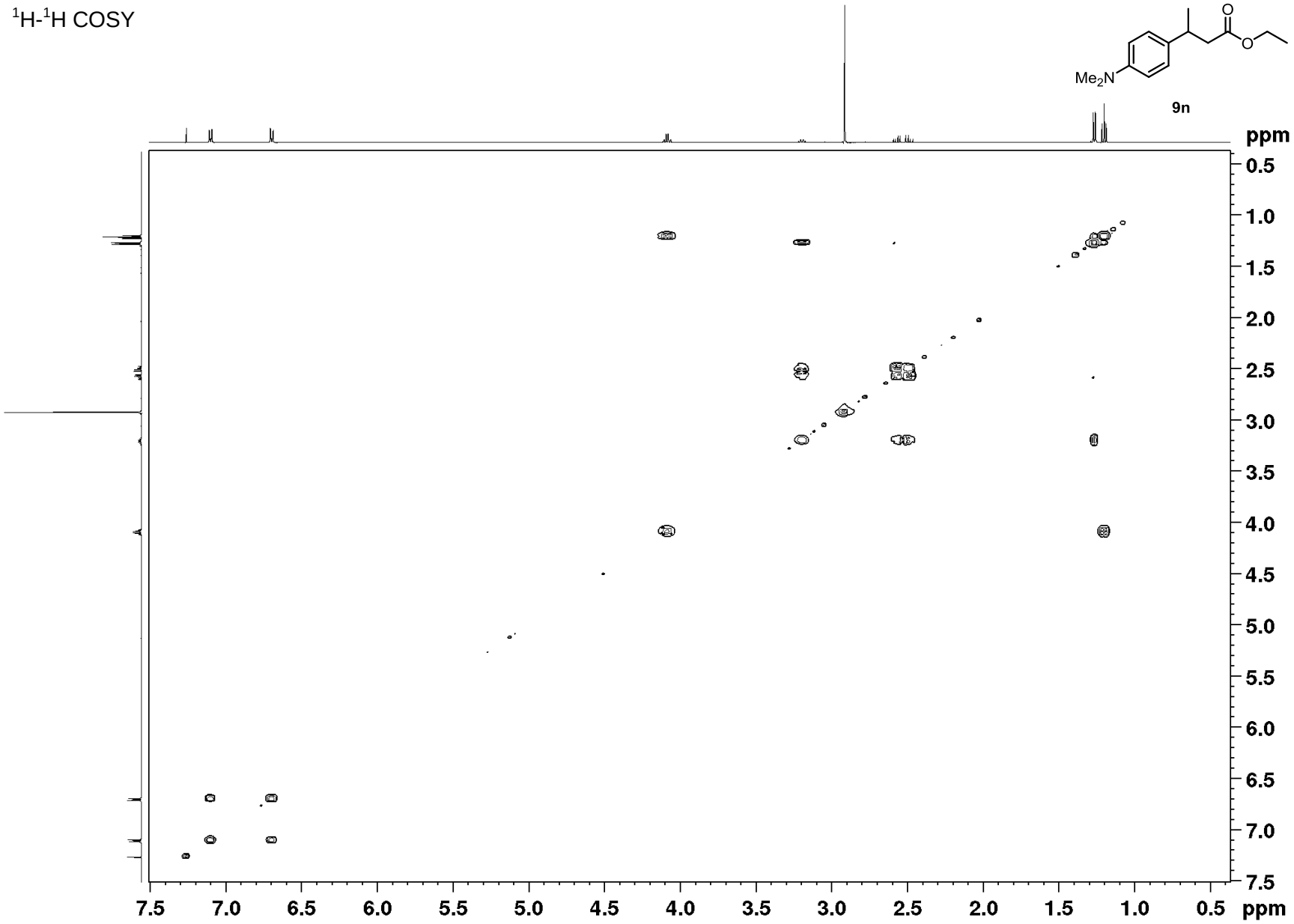
Ethyl 3-(4-(dimethylamino)phenyl)butanoate (9n)

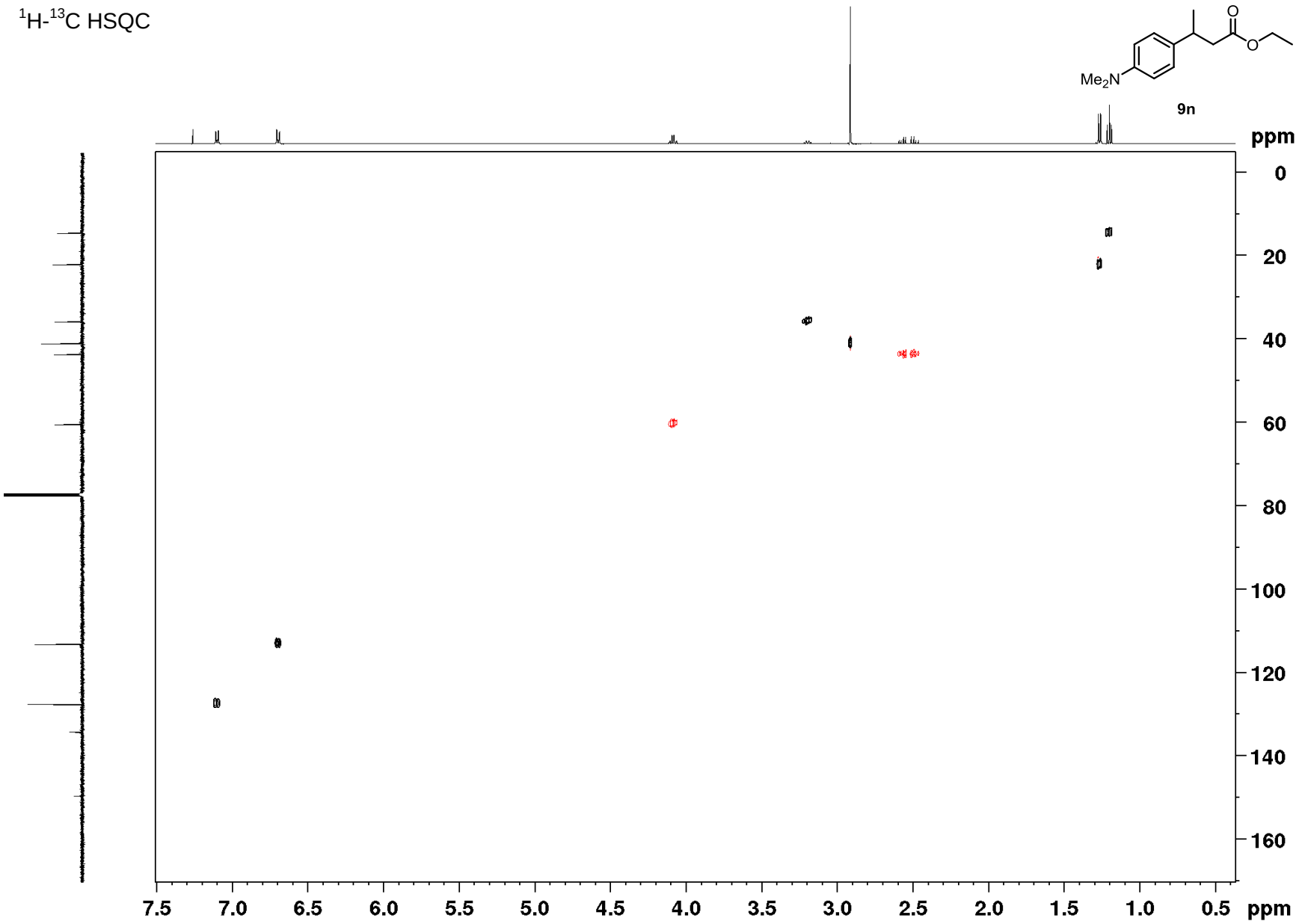
^{1}H NMR



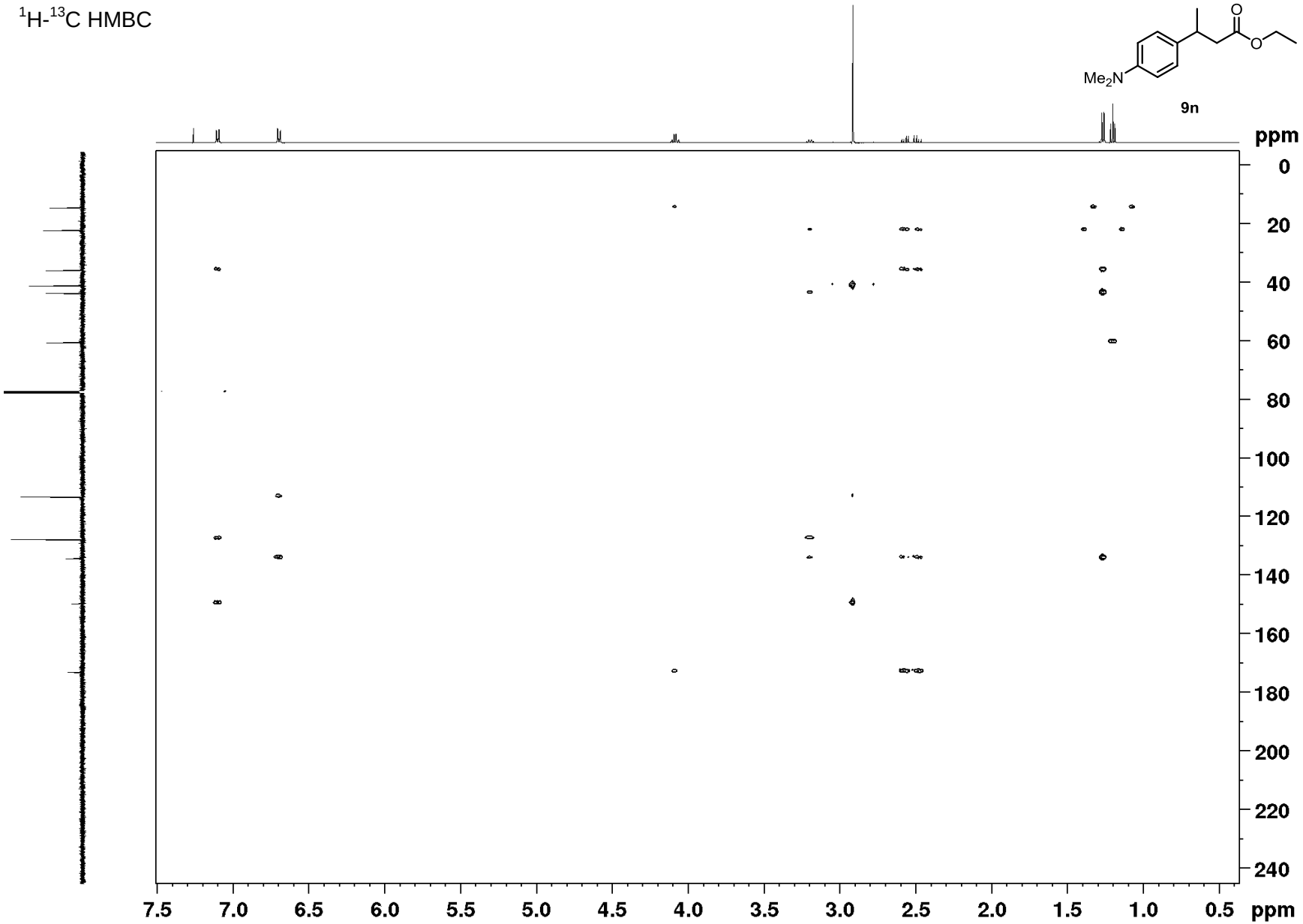

^{13}C NMR
172.8
149.5
134.1
127.4
113.0
60.3
43.5
40.9
35.7
22.0
14.4
Me2N
O
O
9n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

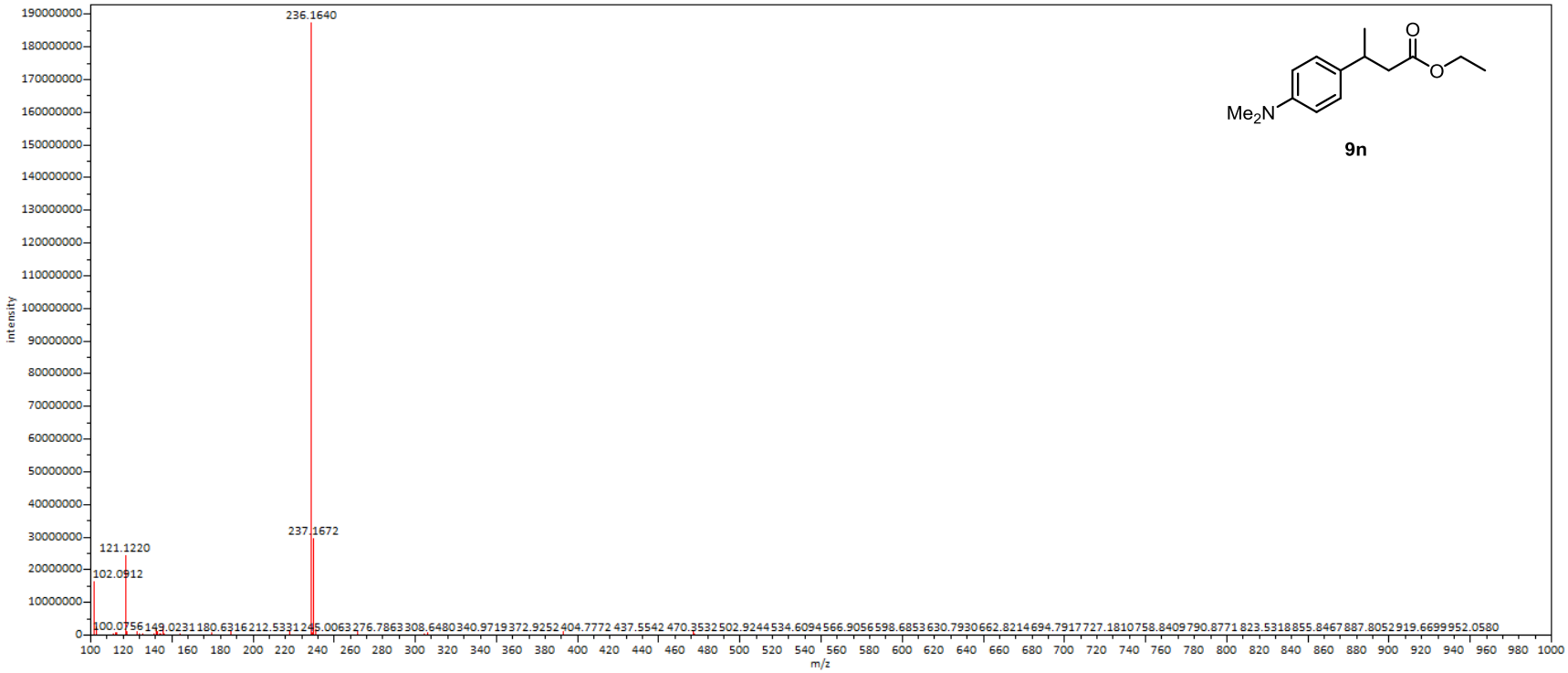
^{1}H-^{1}H COSY


Me2N
O
O
9n
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
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
ppm


^{1}H-^{13}C HSQC
Me$_2$N
O
O
9n
ppm
0
20
40
60
80
100
120
140
160
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
ppm

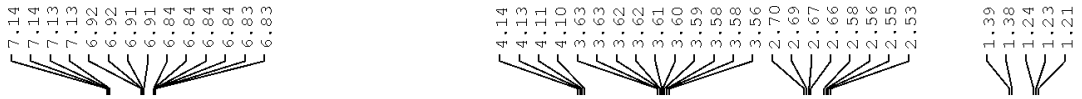
^{1}H-^{13}C HMBC

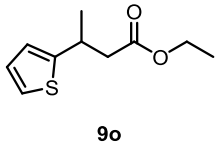

Me2N
O
O
9n
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


236.1640
237.1672
121.1220
102.0912
100.0756
intensity
m/z
Me2N
O
O
9n

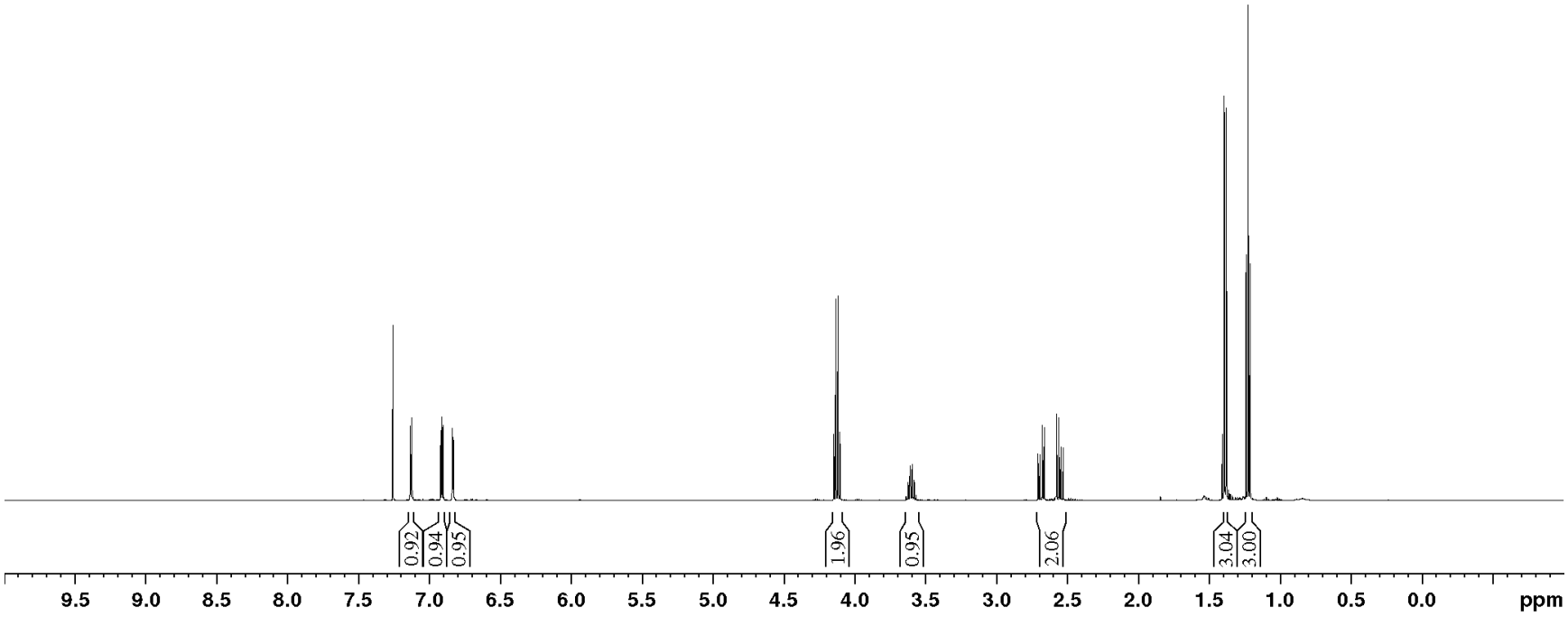
Ethyl 3-(thiophen-2-yl)butanoate (9o)

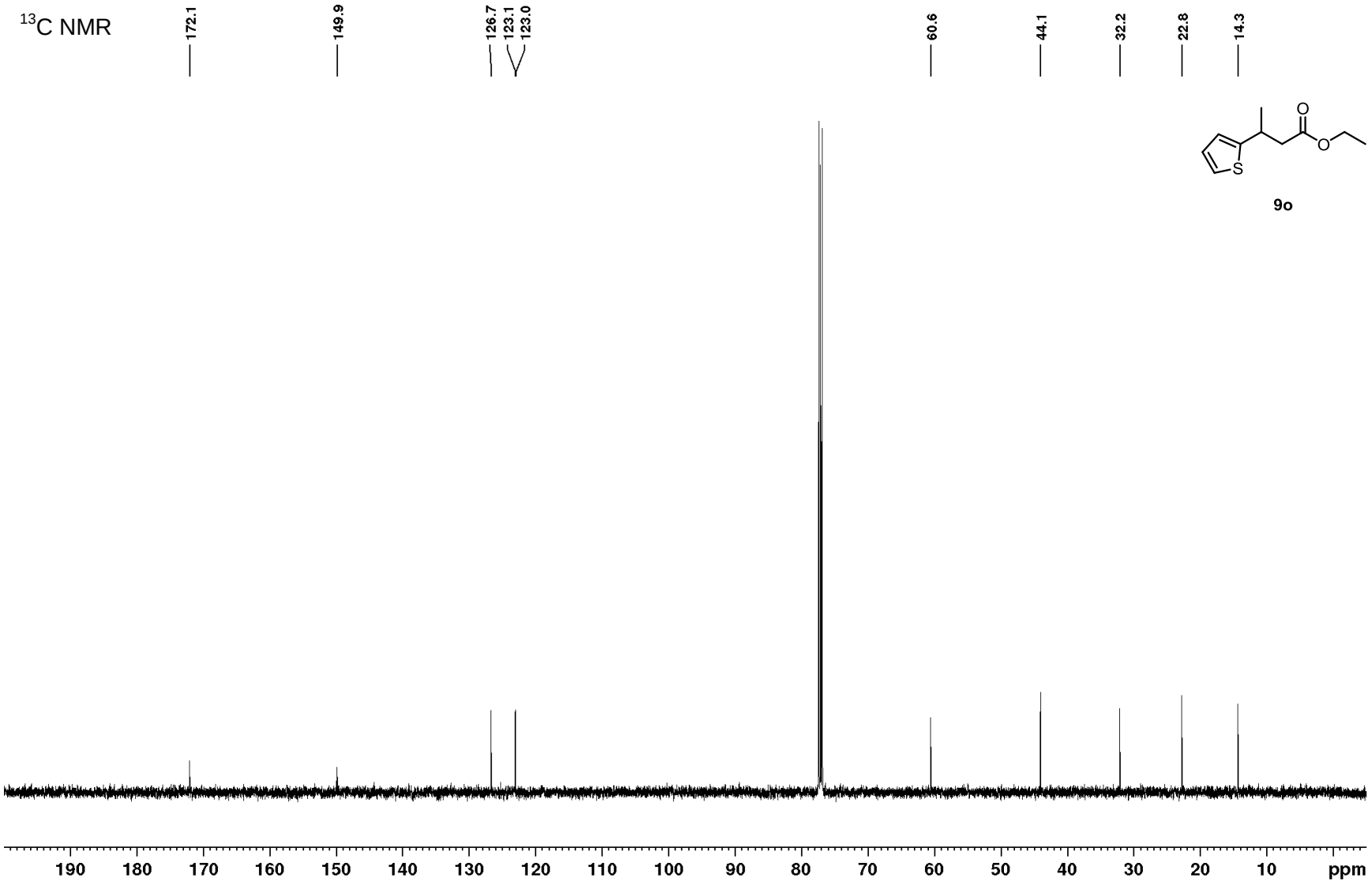
^{1}H NMR



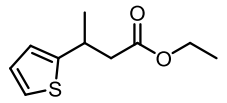


9o

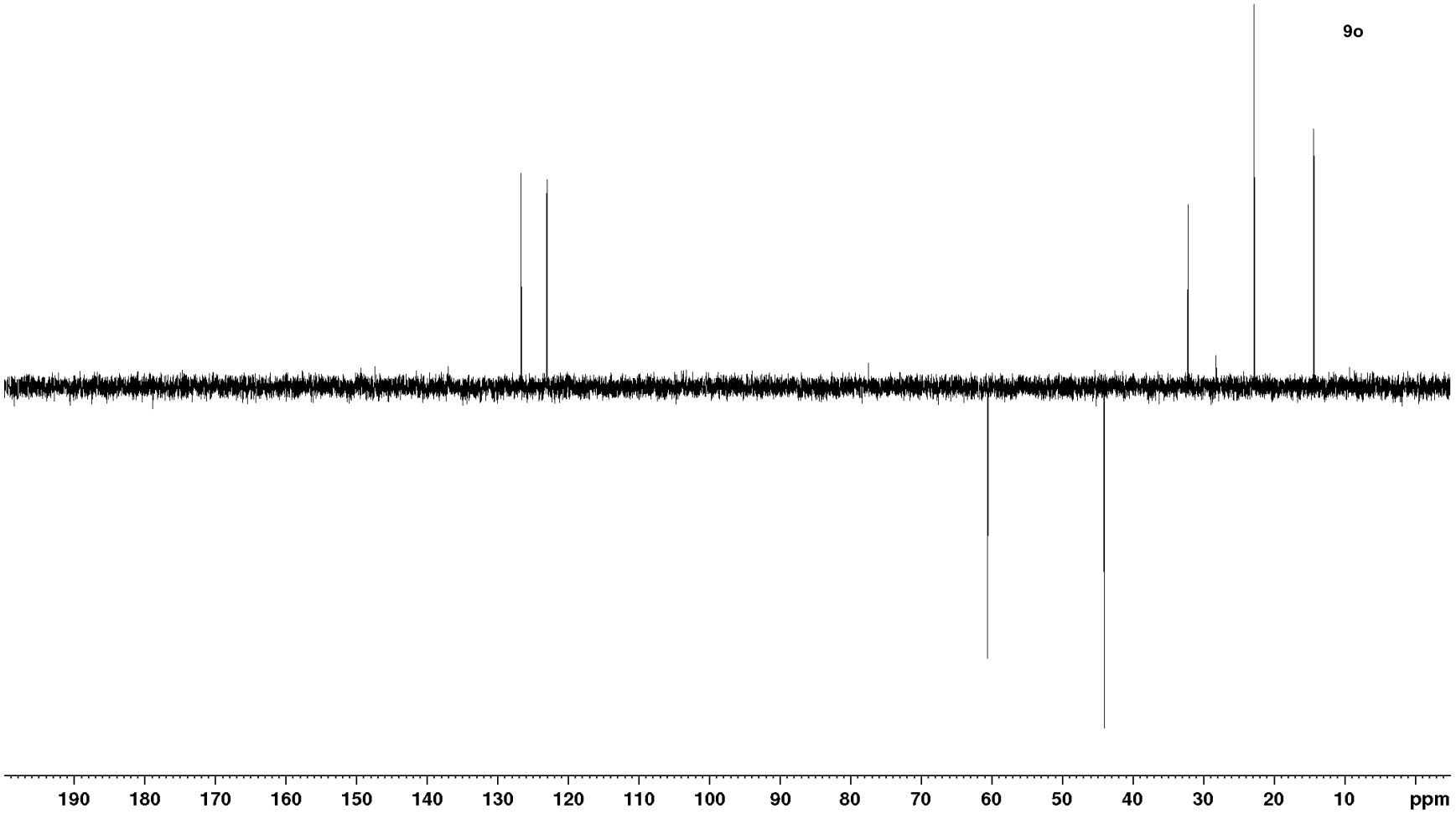



13C NMR
172.1
149.9
126.7
123.1
123.0
60.6
44.1
32.2
22.8
14.3
O
O
S
9o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

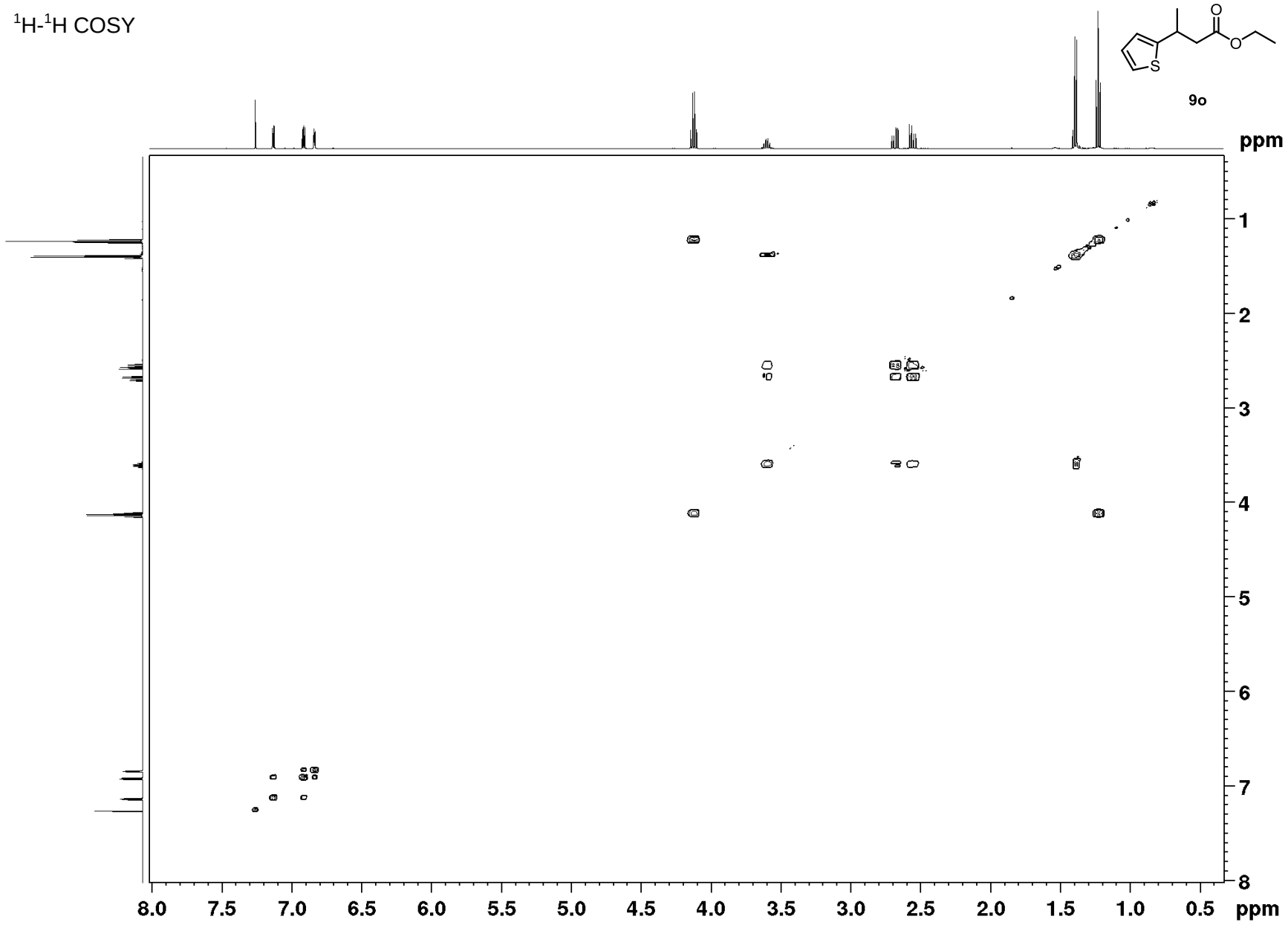
^{13}C DEPT NMR



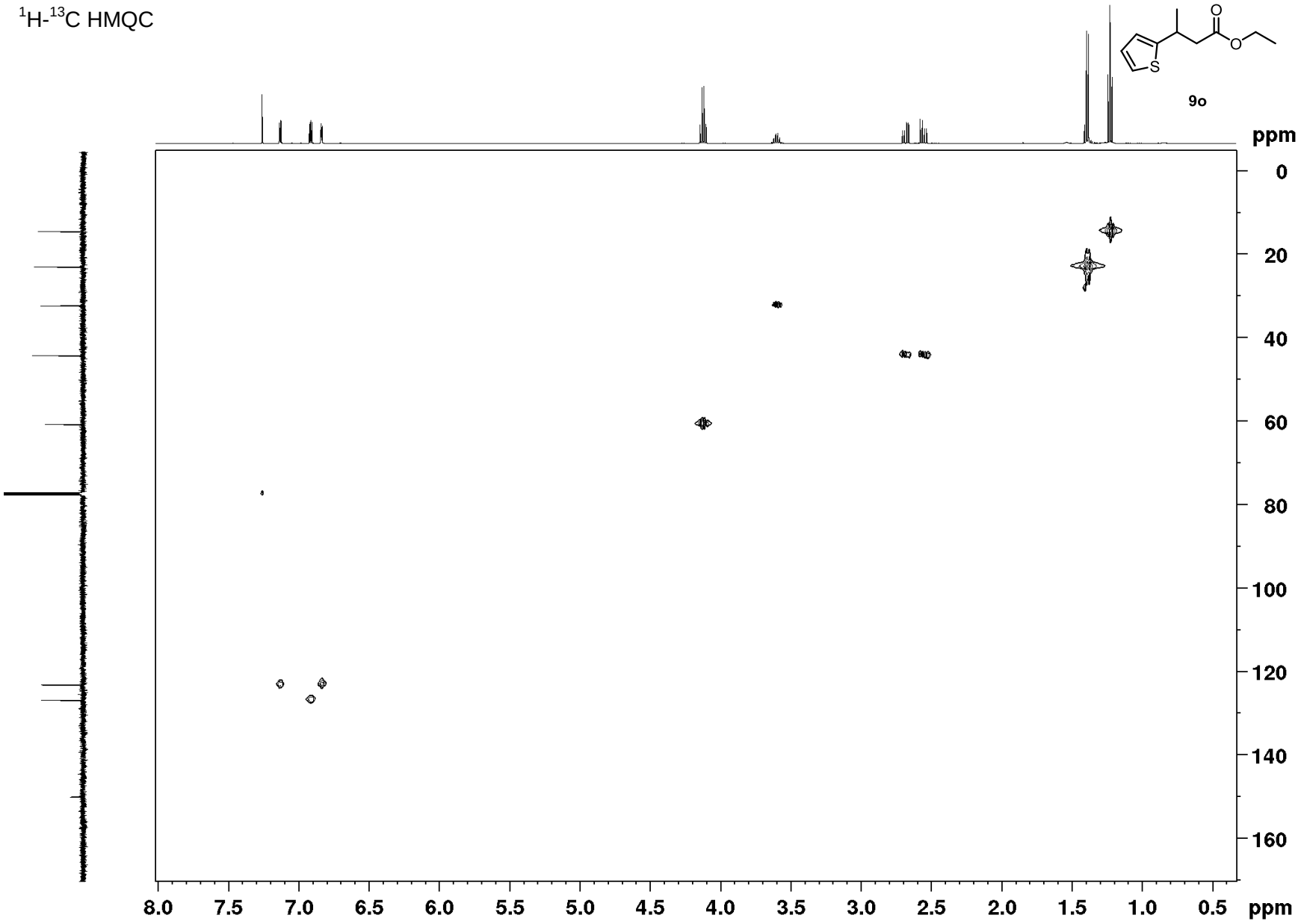
9o



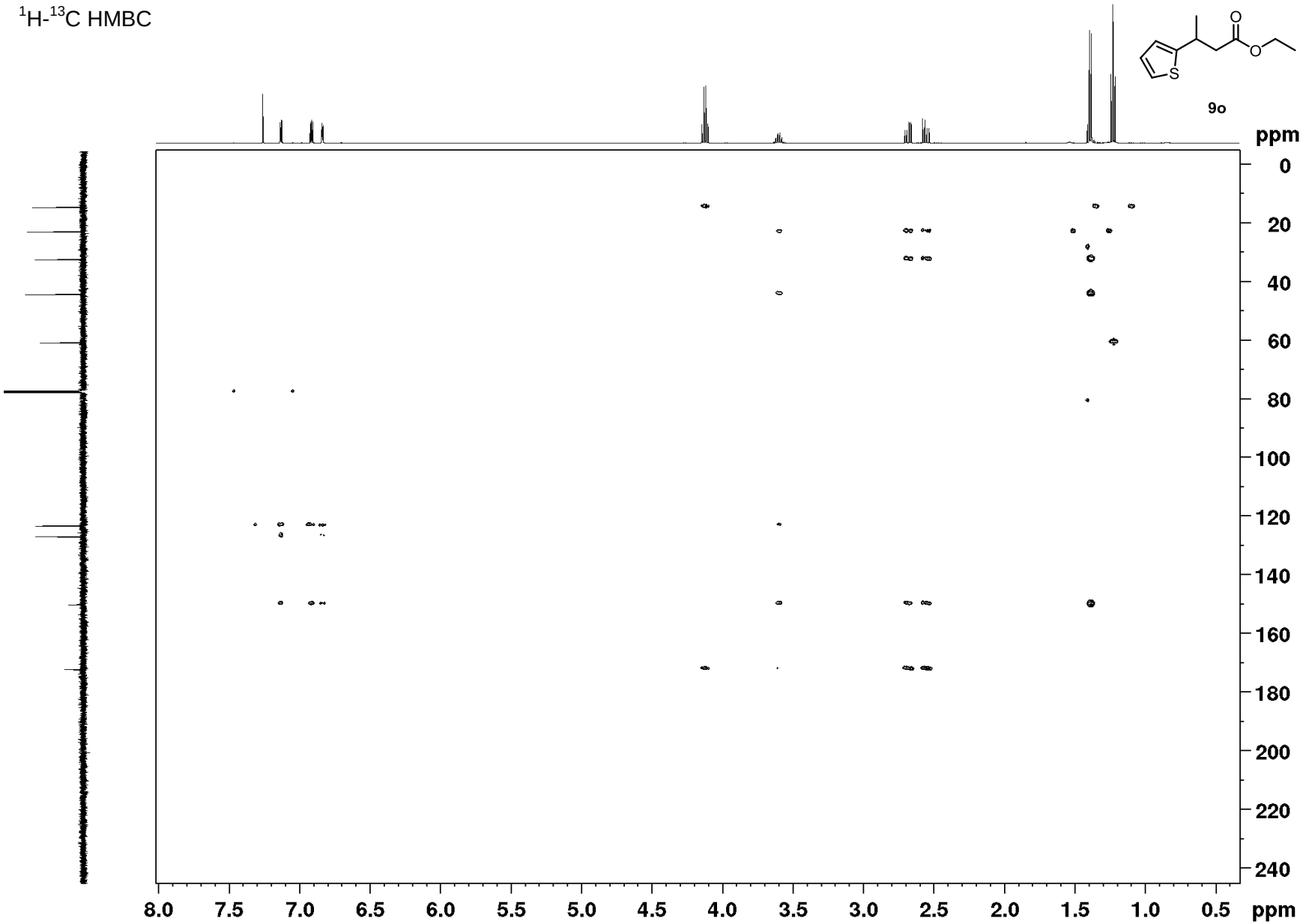
^{1}H-^{1}H COSY

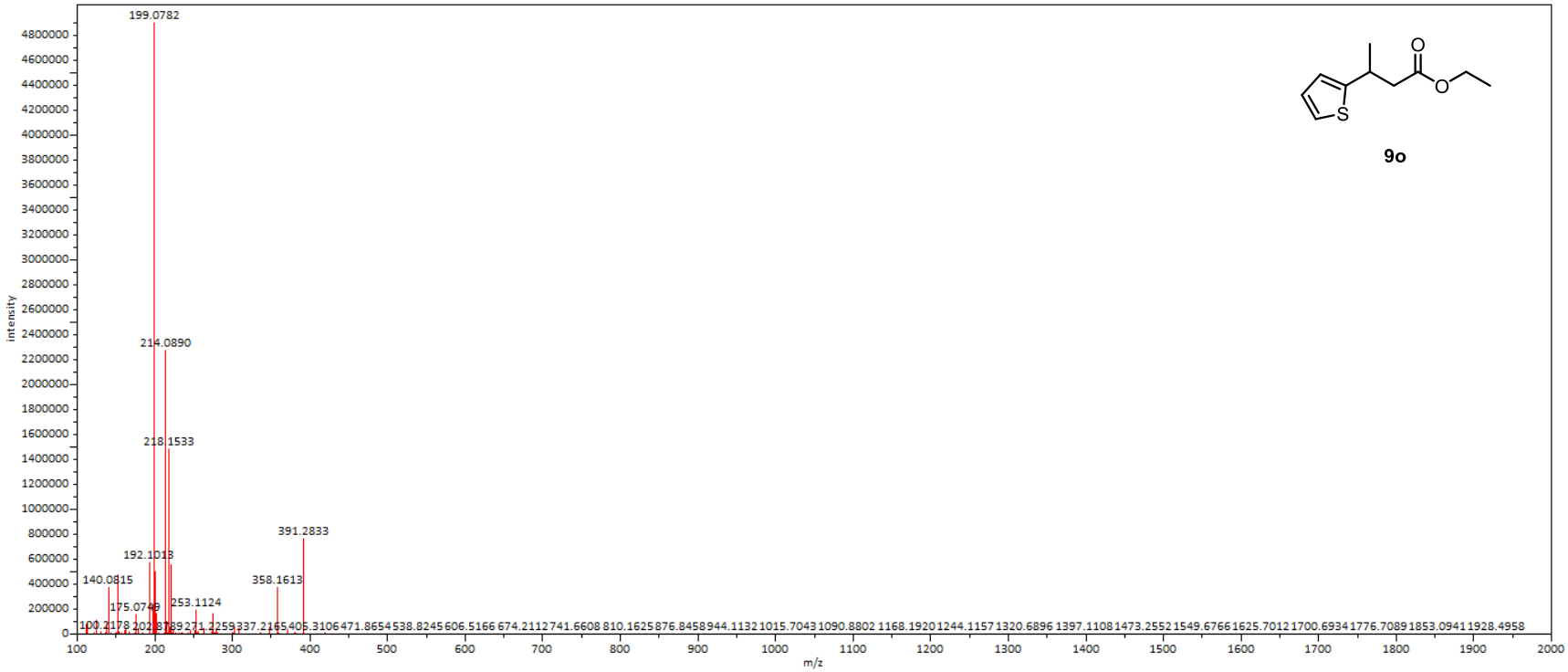

O
O
S
9o
ppm
1
2
3
4
5
6
7
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

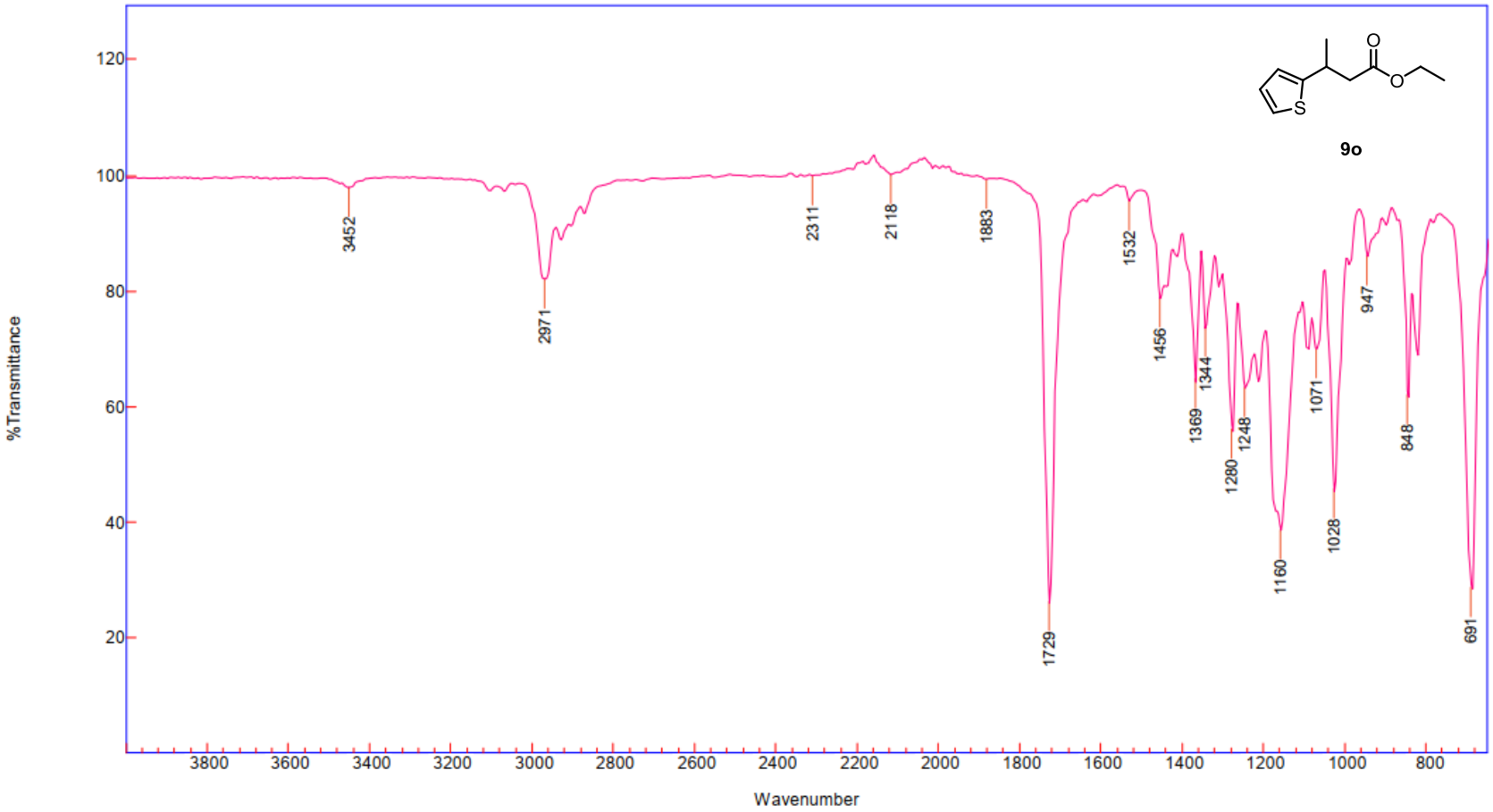
^{1}H-^{13}C HMQC


O
O
S
9o
ppm
0
20
40
60
80
100
120
140
160
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
ppm

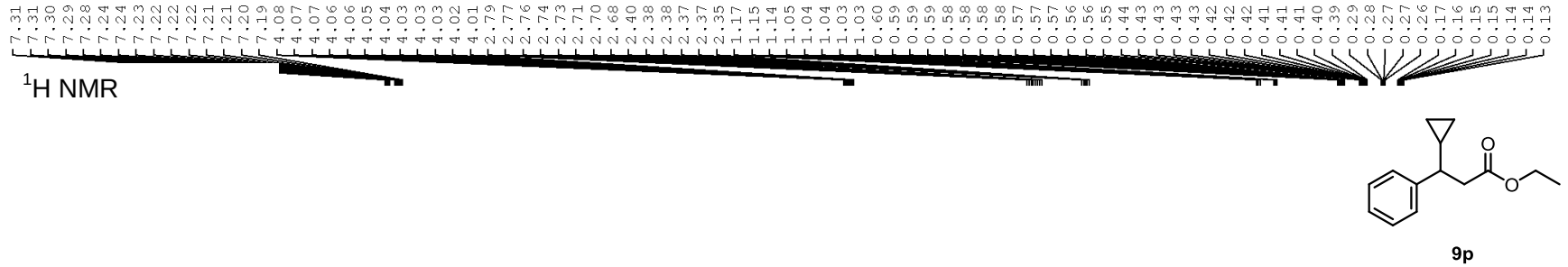
^{1}H-^{13}C HMBC


O
O
S
9o
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm


199.0782
214.0890
218.1533
391.2833
192.1013
140.0815
358.1613
175.0749
253.1124
intensity
m/z
9o

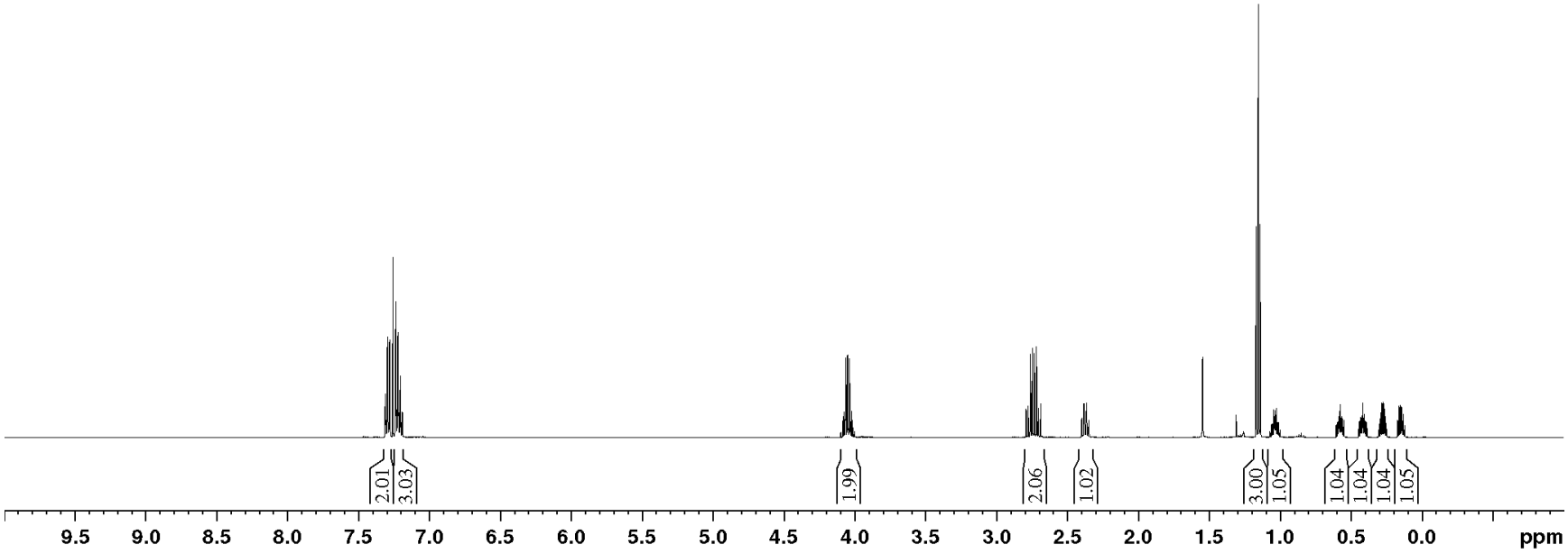

%Transmittance
120
100
80
60
40
20
3452
2971
2311
2118
1883
1729
1532
1456
1369
1344
1280
1248
1160
1071
1028
947
848
691
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber
O
O
S
9o

Ethyl 3-cyclopropyl-3-phenylpropanoate (9p)

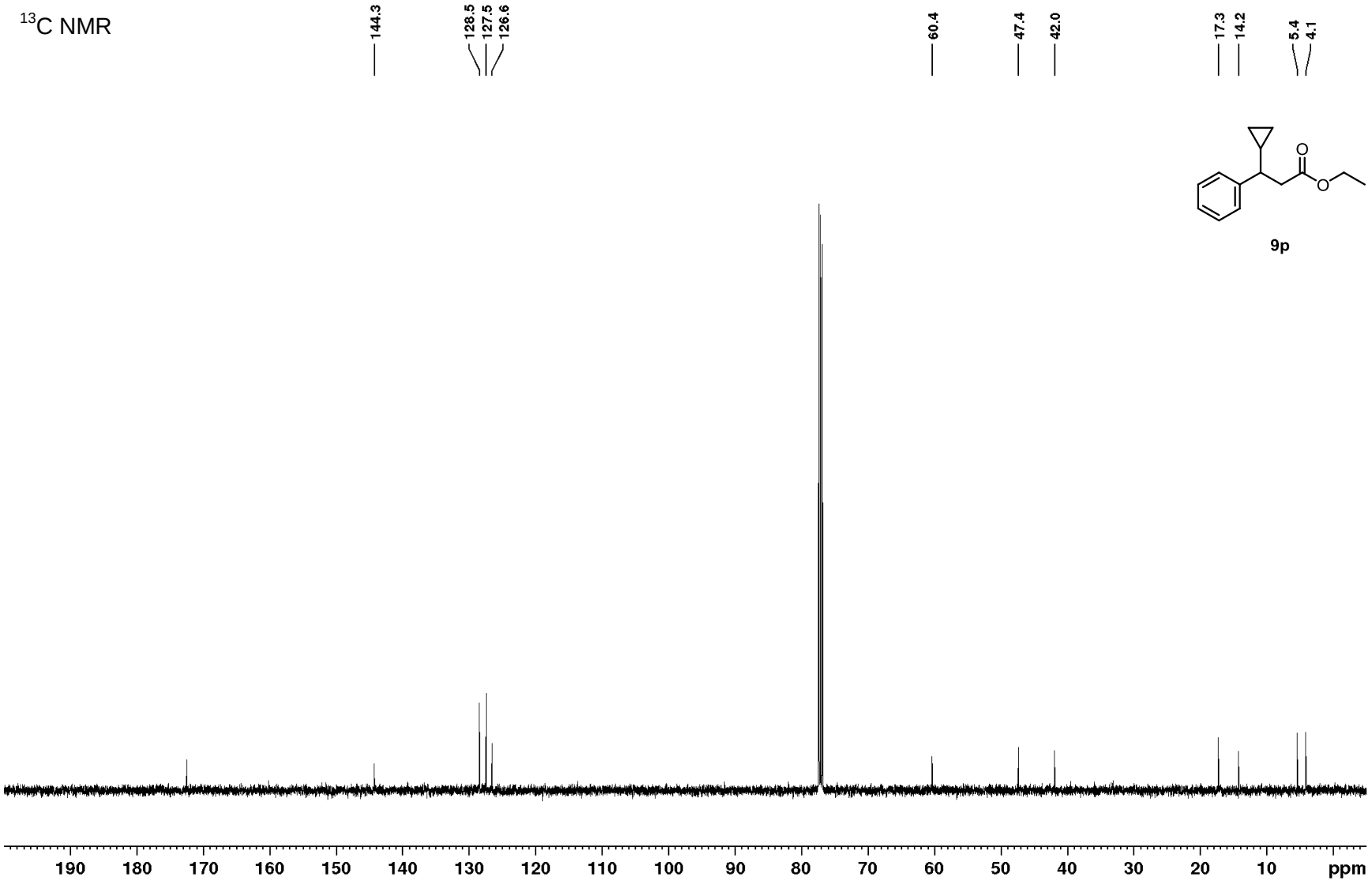


^{1}H NMR

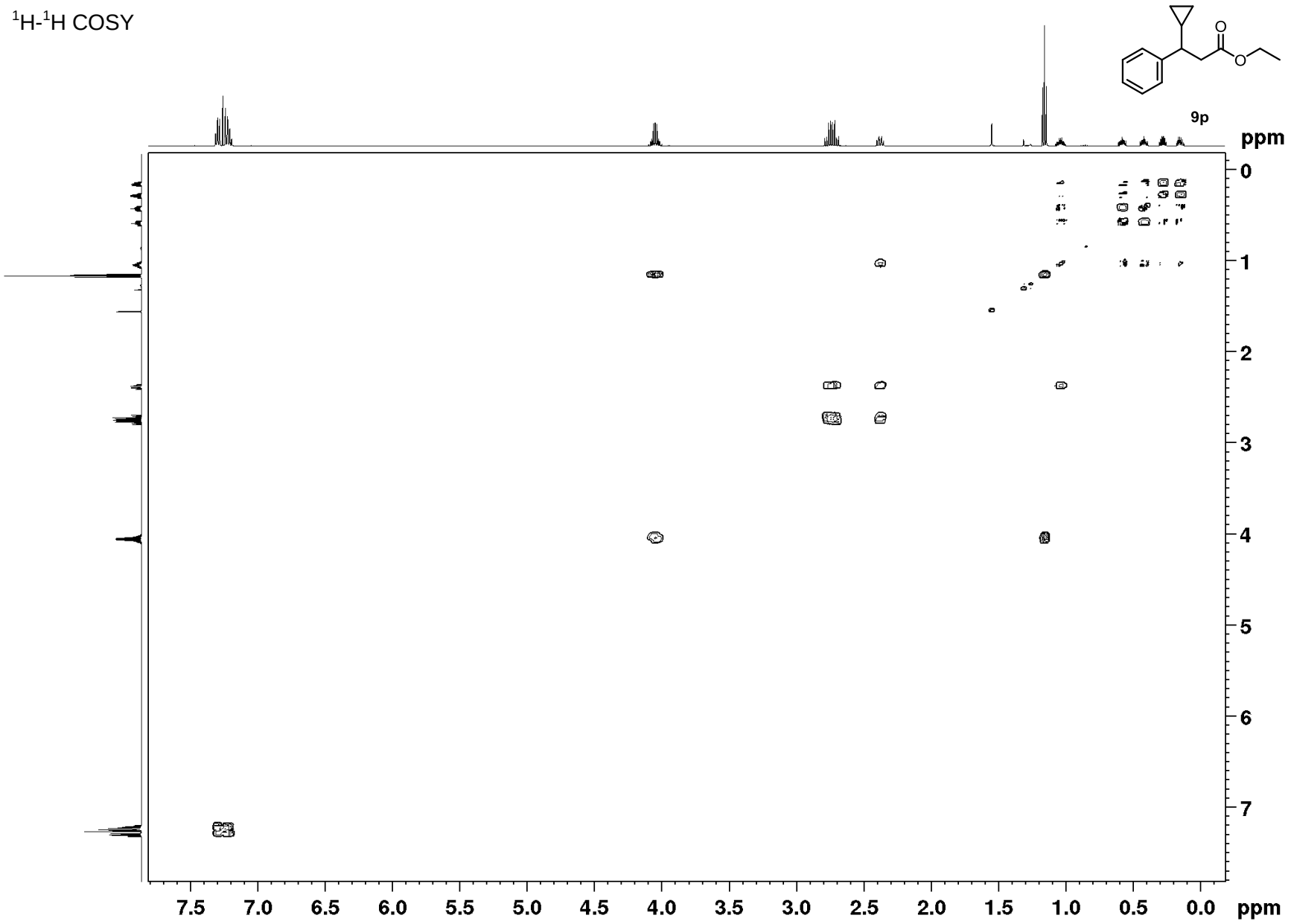
9p



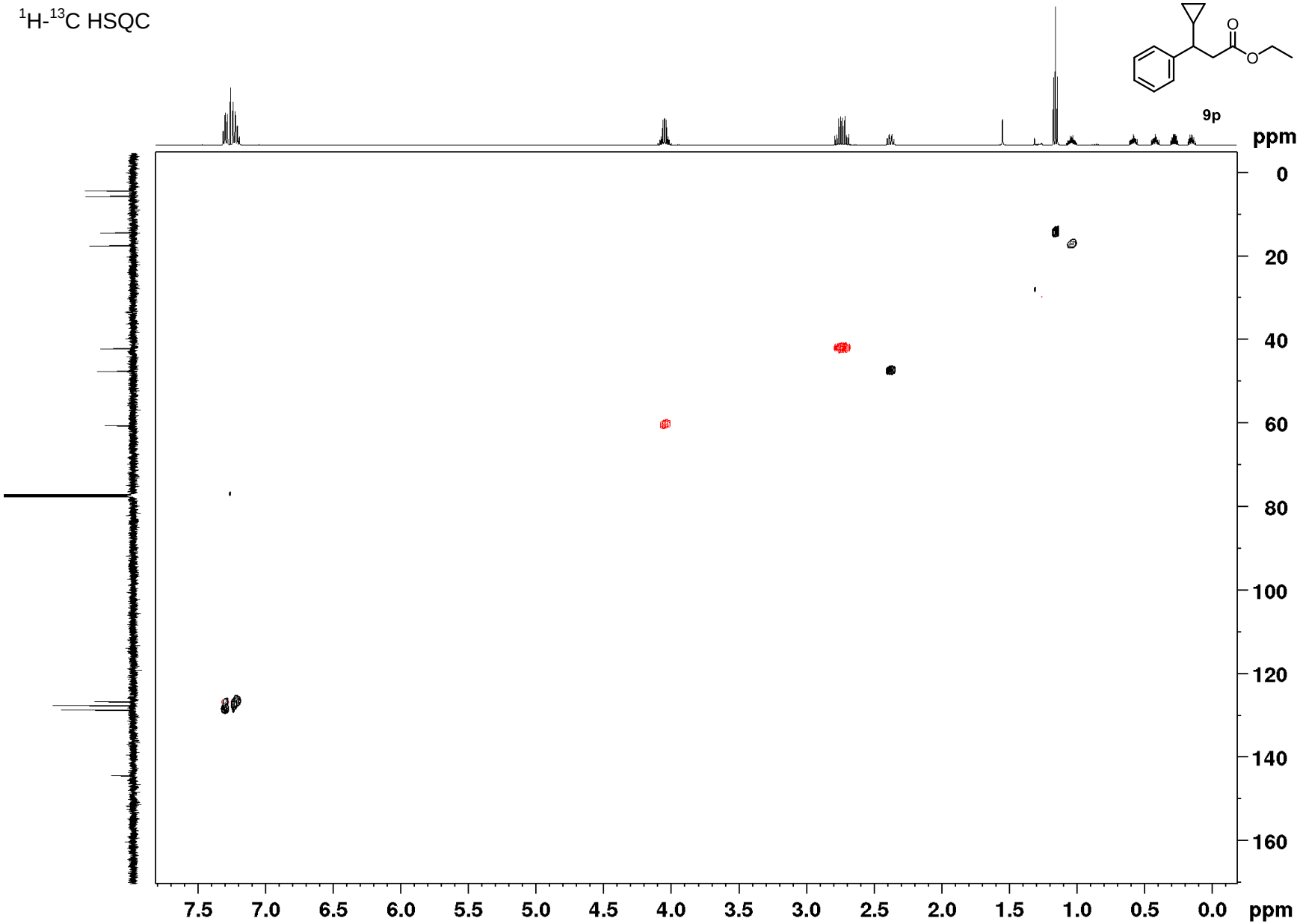
^{13}C NMR


144.3
128.5
127.5
126.6
60.4
47.4
42.0
17.3
14.2
5.4
4.1
O
O
9p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

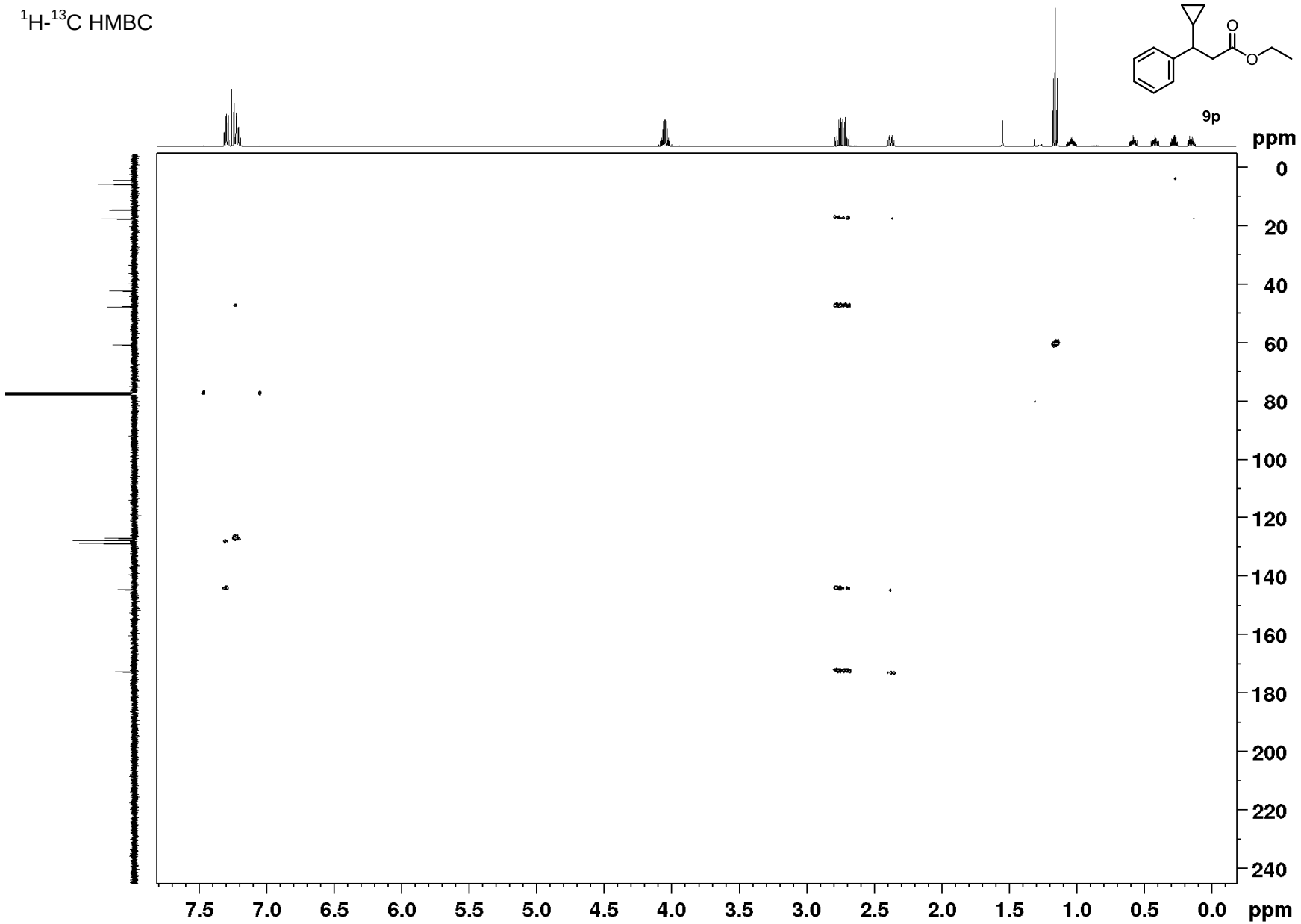
^{1}H-^{1}H COSY

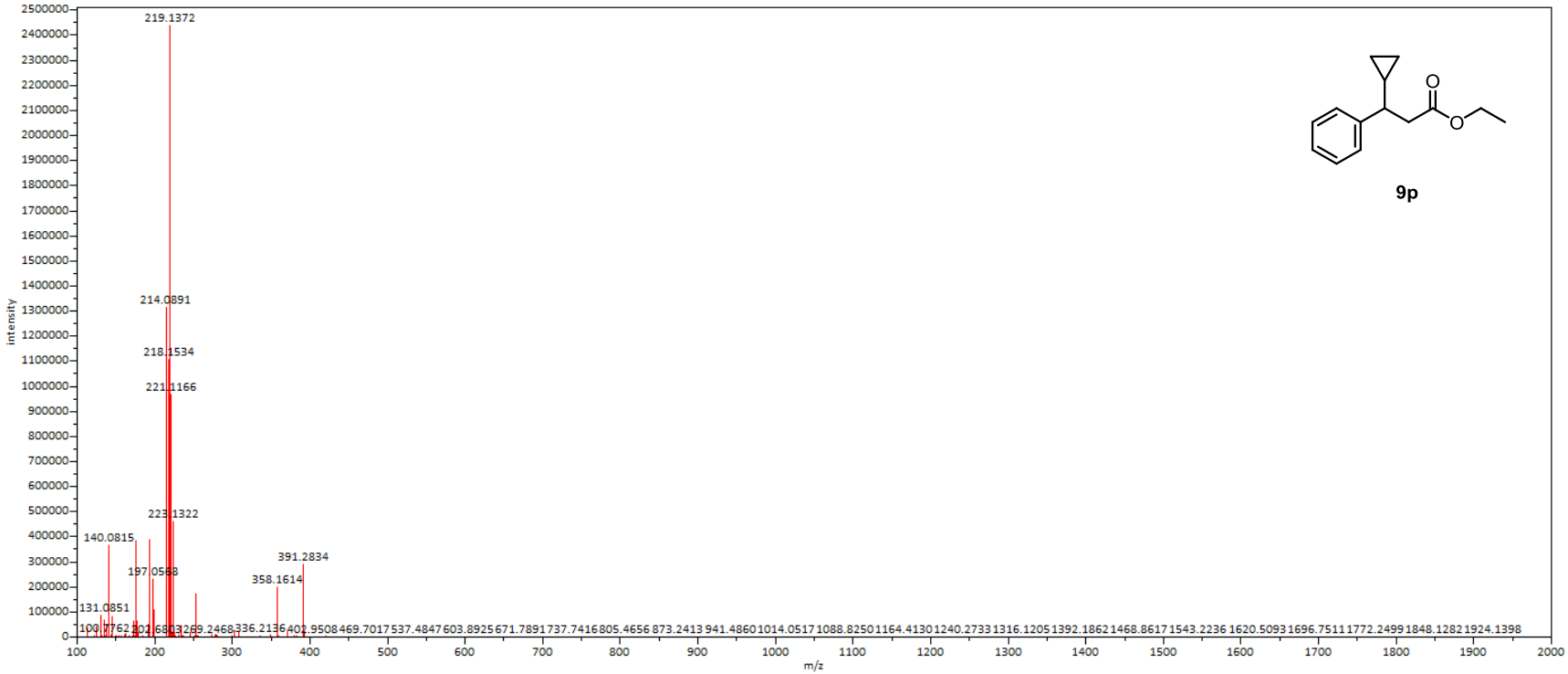


^{1}H-^{13}C HSQC

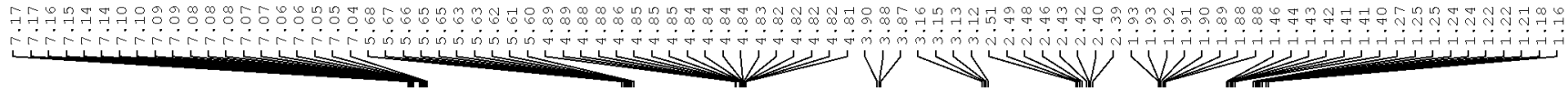

9p
ppm
0
20
40
60
80
100
120
140
160
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

^{1}H-^{13}C HMBC

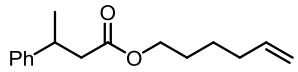

9p
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


219.1372
214.0891
218.1534
221.1166
223.1322
140.0815
391.2834
197.0588
358.1614
131.0851
intensity
m/z
9p

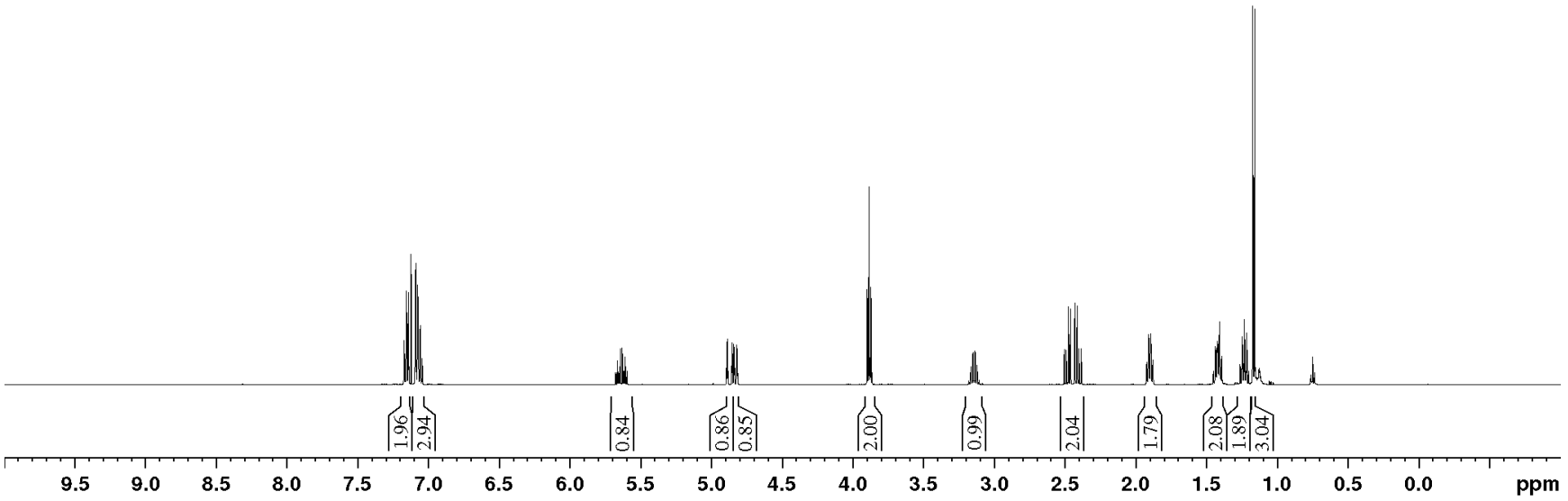
Hex-5-en-1-yl 3-phenylbutanoate (9q)

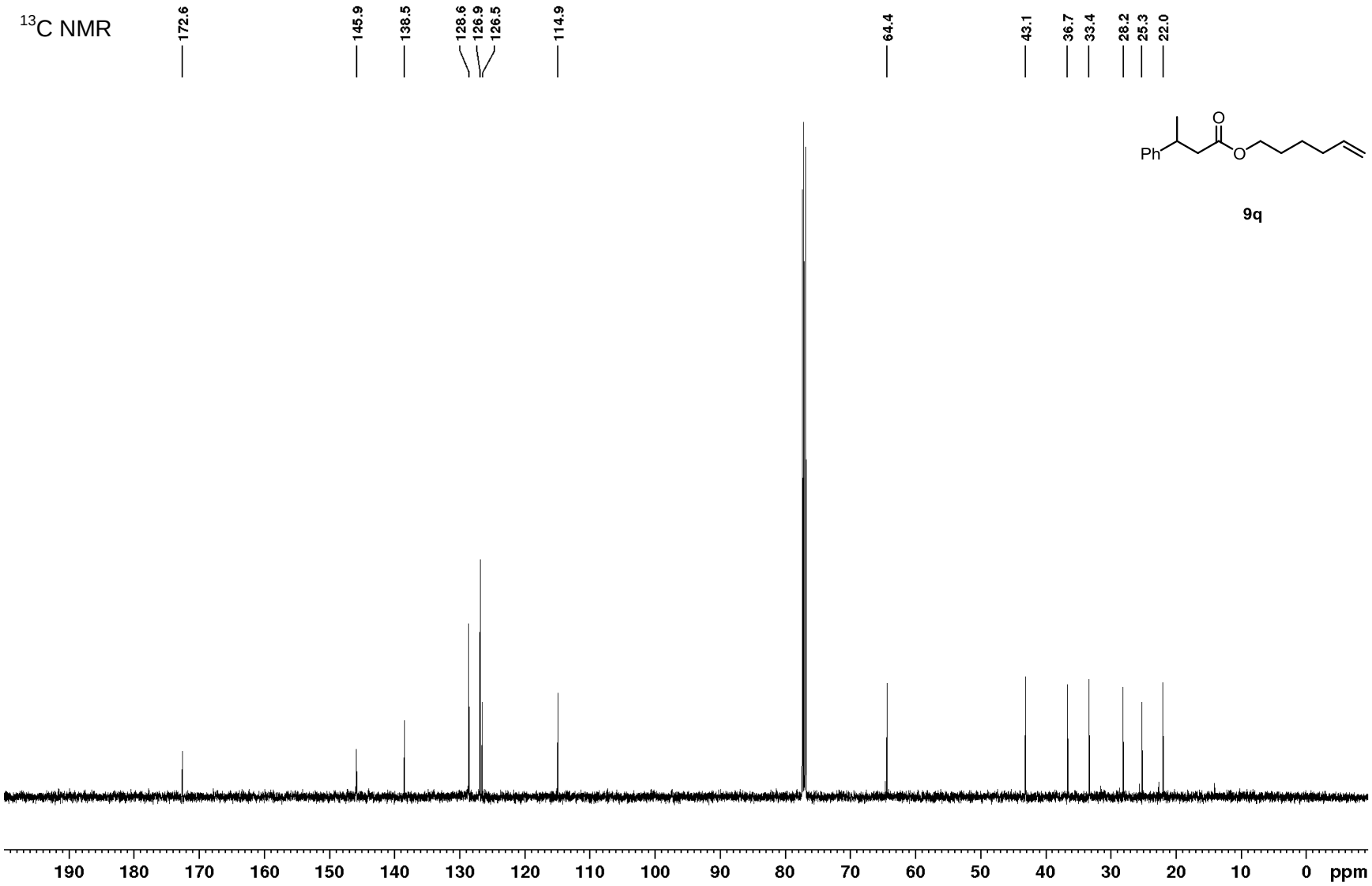


^{1}H NMR

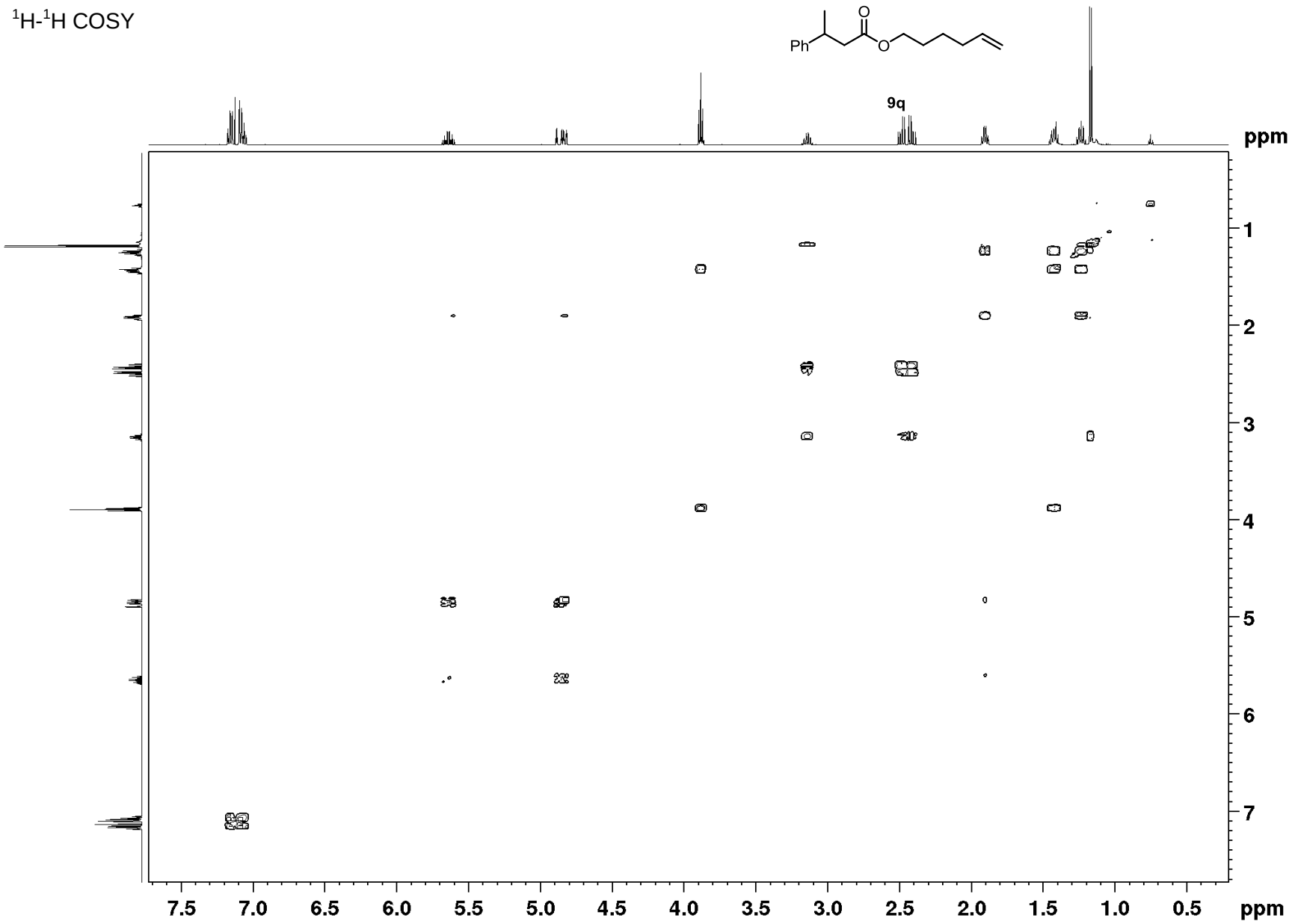


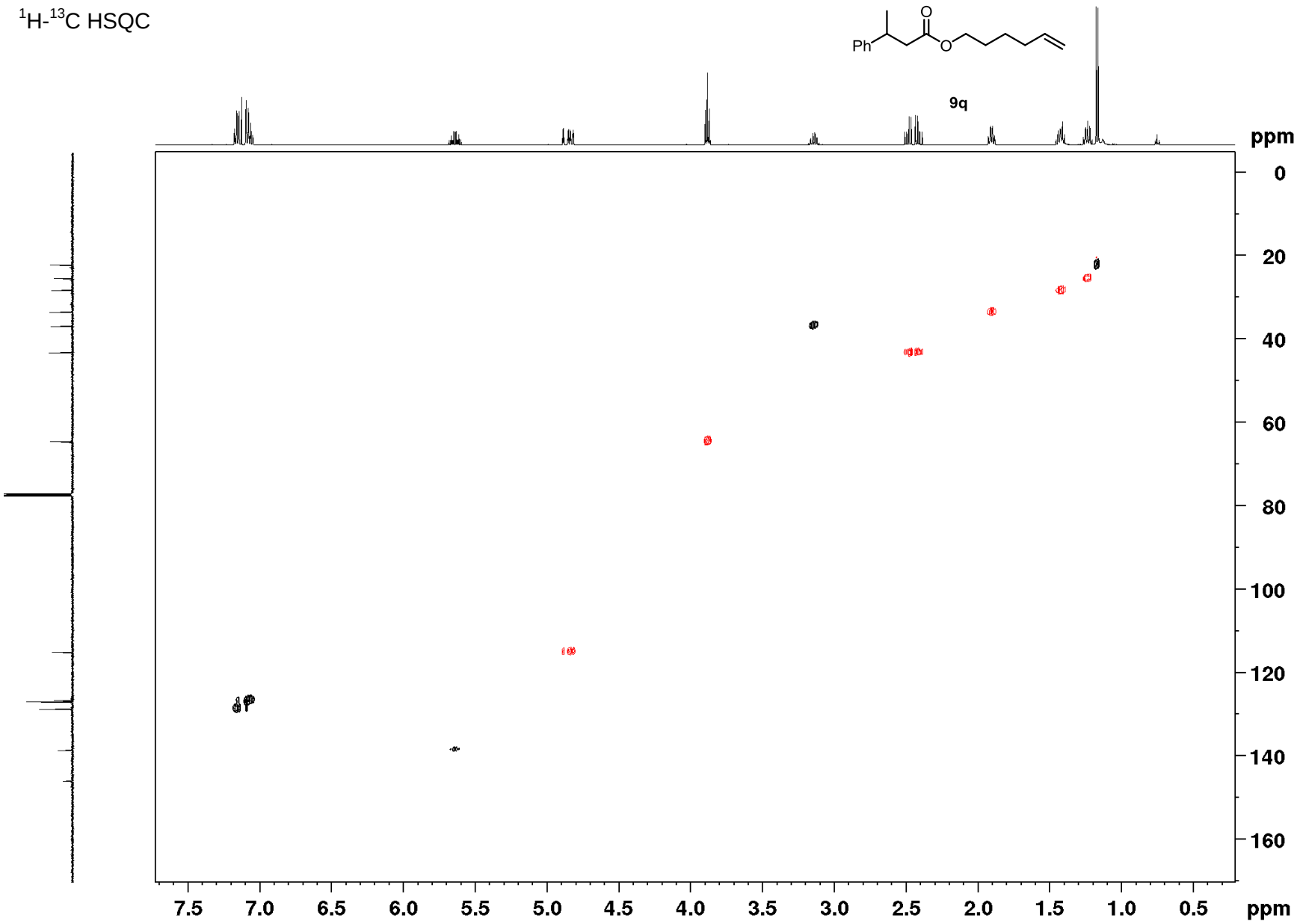
9q

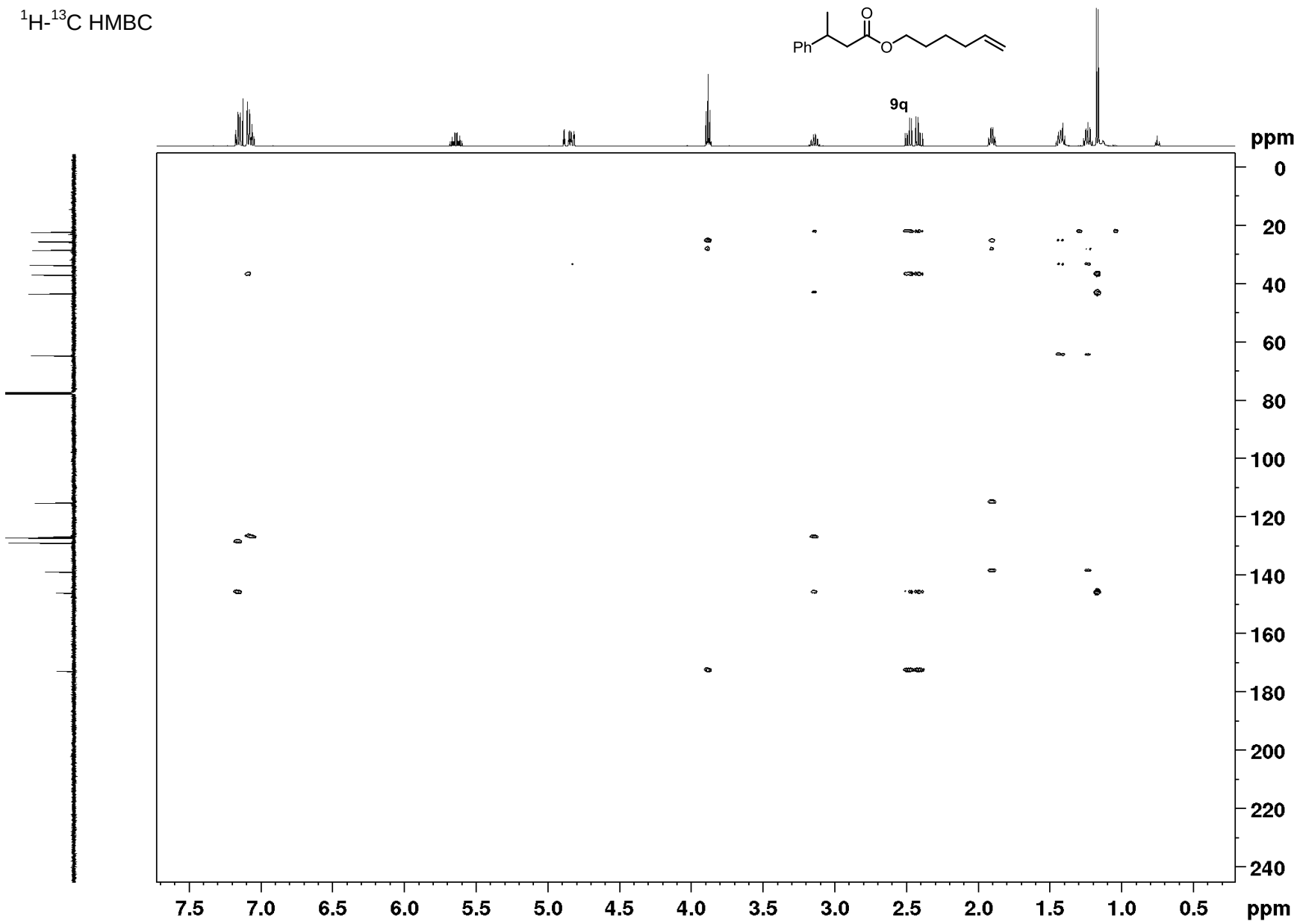


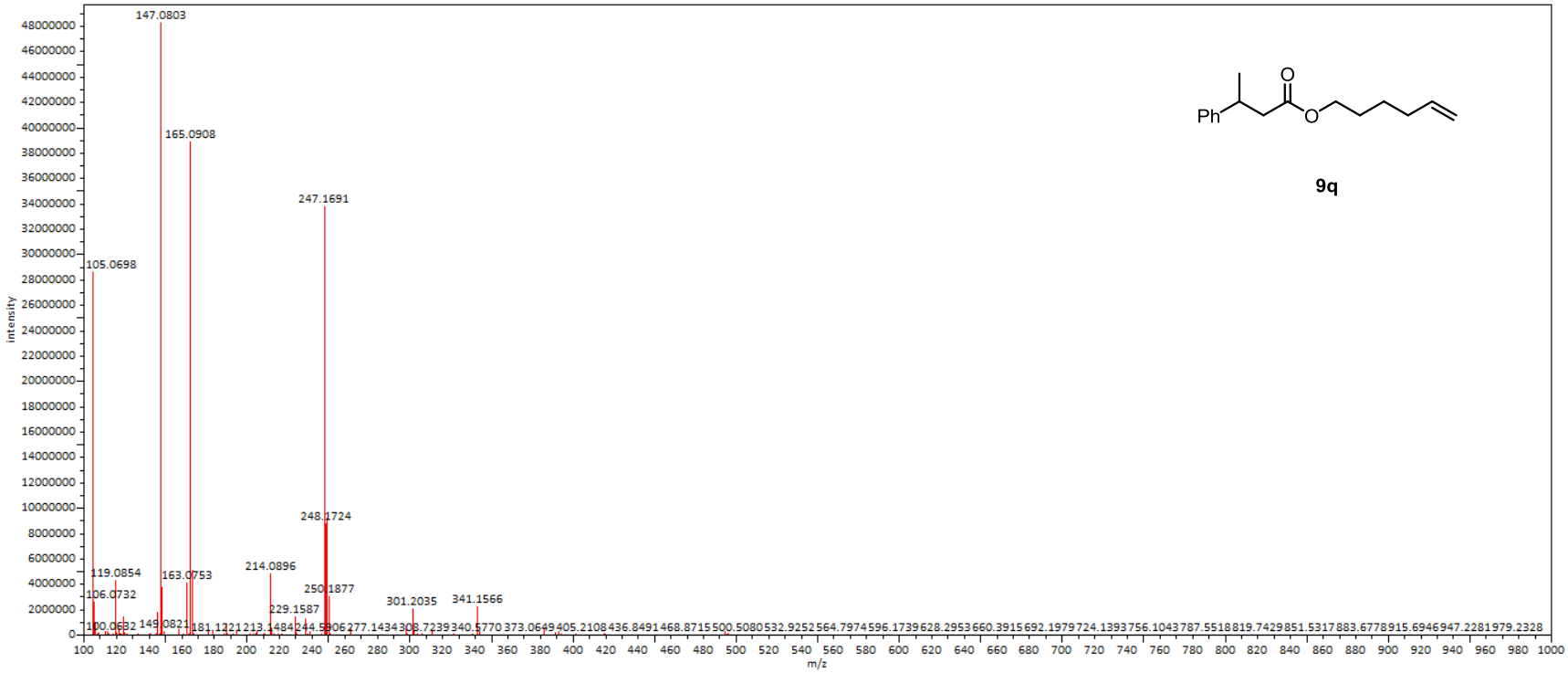

13C NMR
172.6
145.9
138.5
128.6
126.9
126.5
114.9
64.4
43.1
36.7
33.4
28.2
25.3
22.0
Ph
O
O
9q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

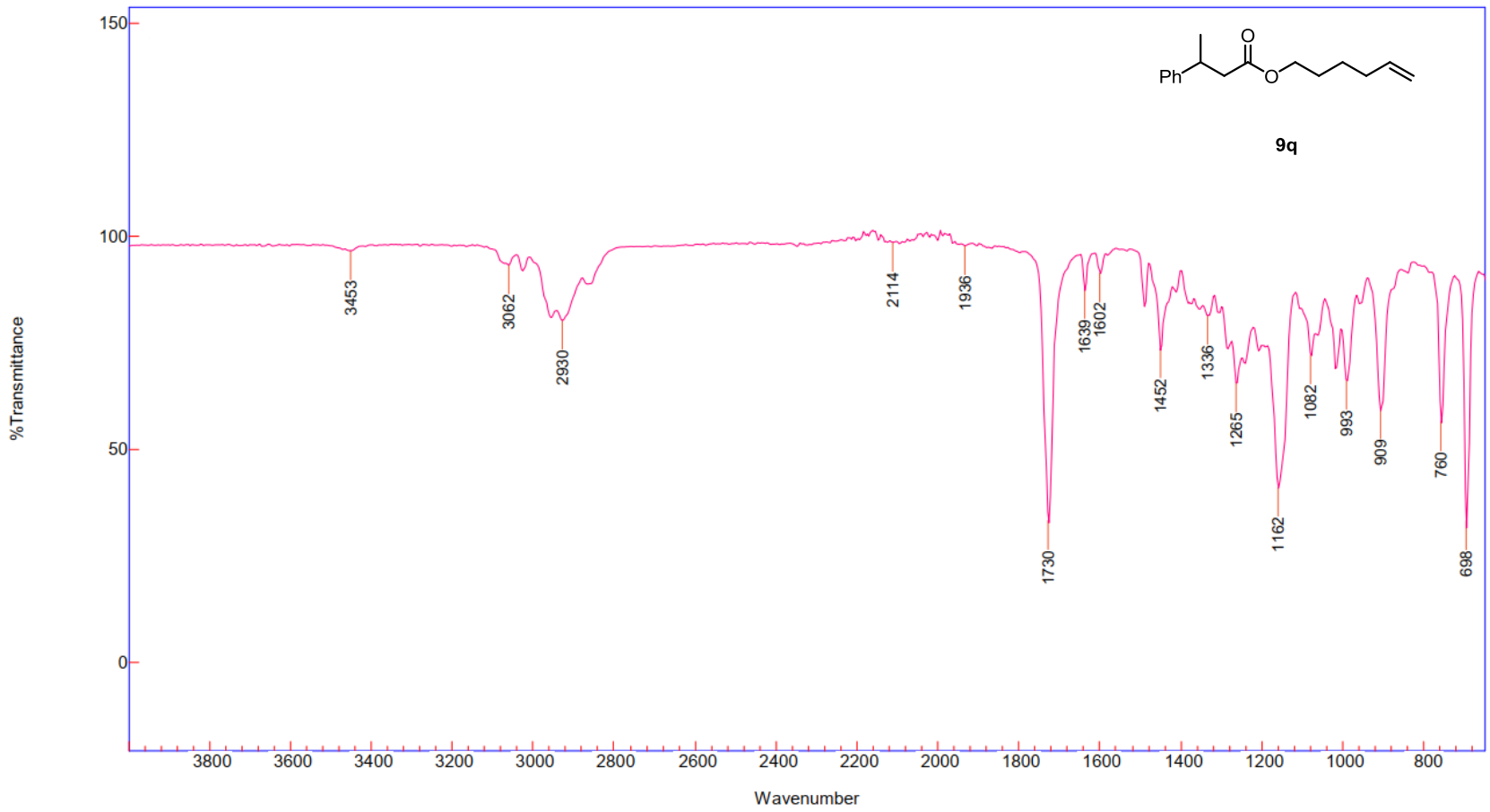
^{1}H-^{1}H COSY




^{1}H-^{13}C HSQC
Ph
O
O
9q
ppm
0
20
40
60
80
100
120
140
160
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
ppm

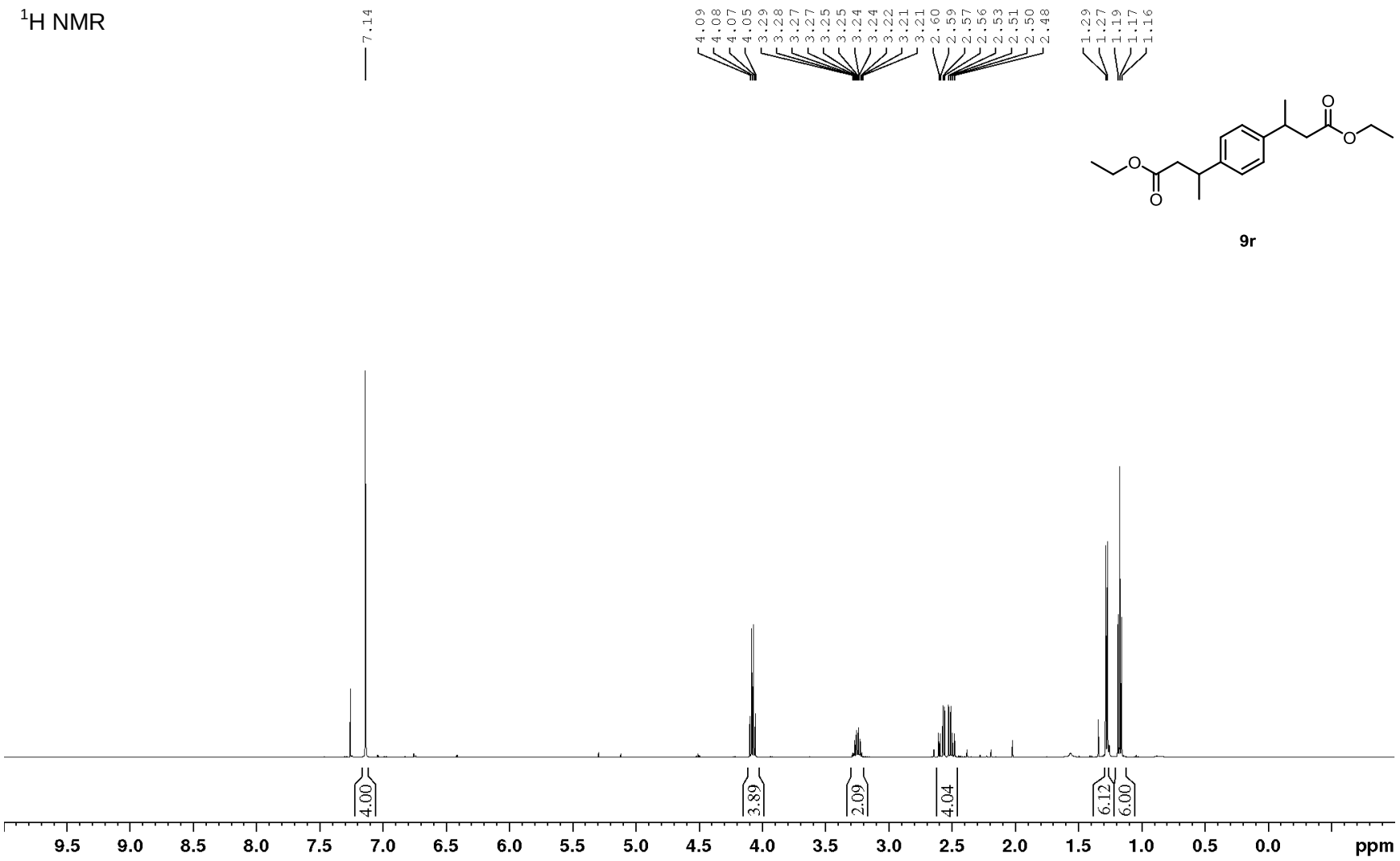

^{1}H-^{13}C HMBC
Ph
O
O
9q
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

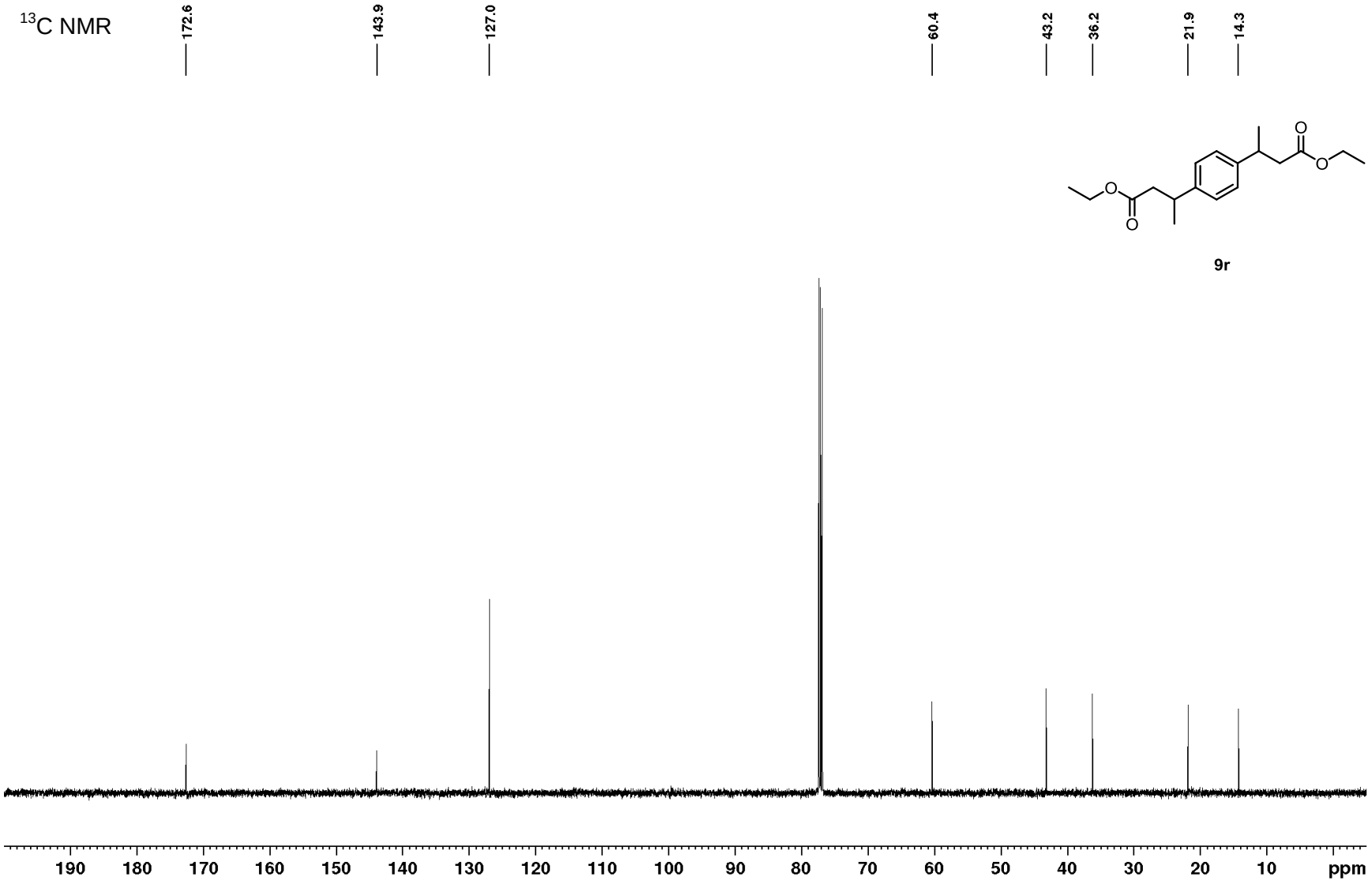

147.0803
165.0908
247.1691
105.0698
248.1724
214.0896
119.0854
163.0753
106.0732
250.1877
301.2035
341.1566
229.1587
intensity
m/z
9q

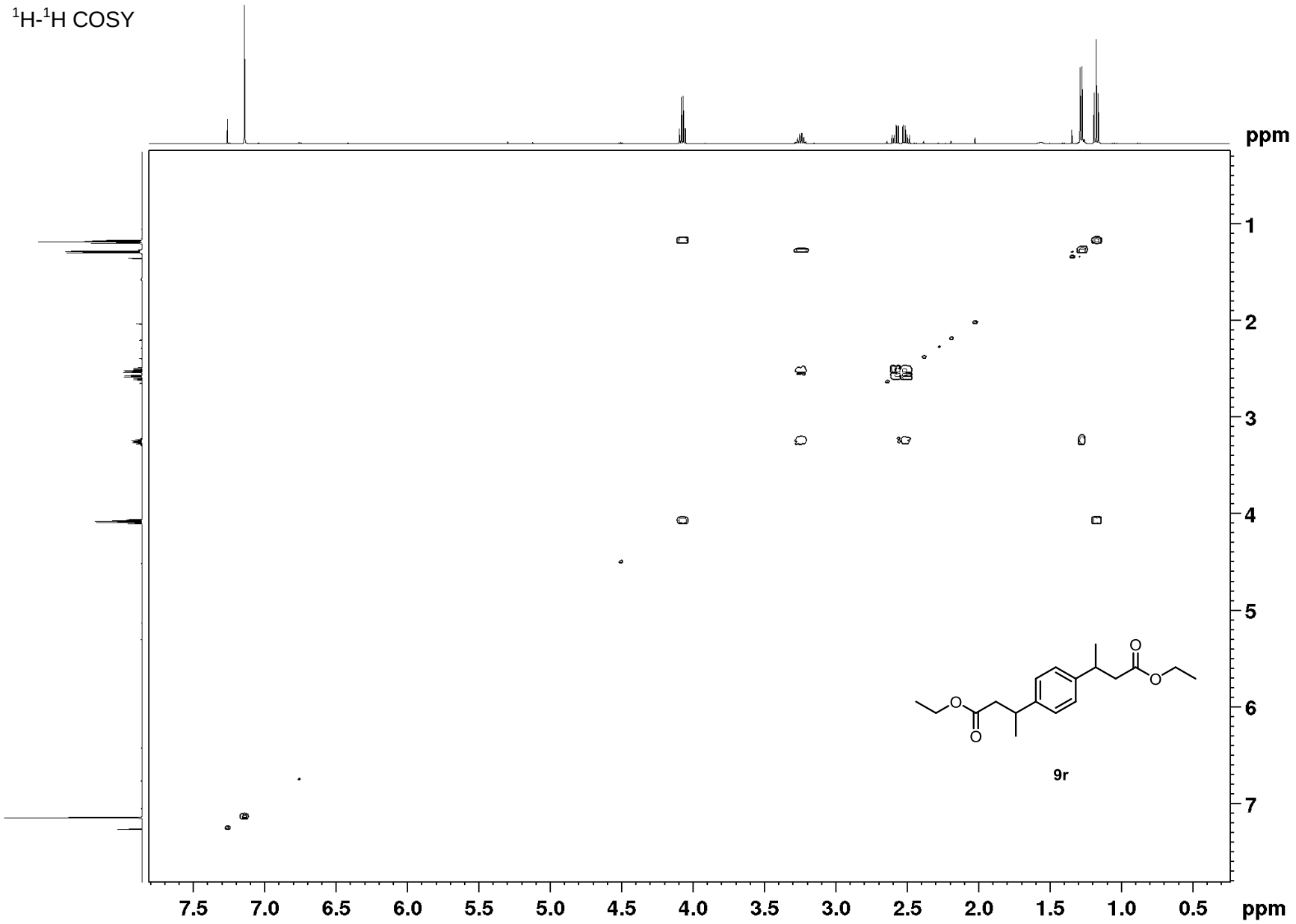

9q
%Transmittance
Wavenumber
150
100
50
0
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
3453
3062
2930
2114
1936
1730
1639
1602
1452
1336
1265
1162
1082
993
909
760
698

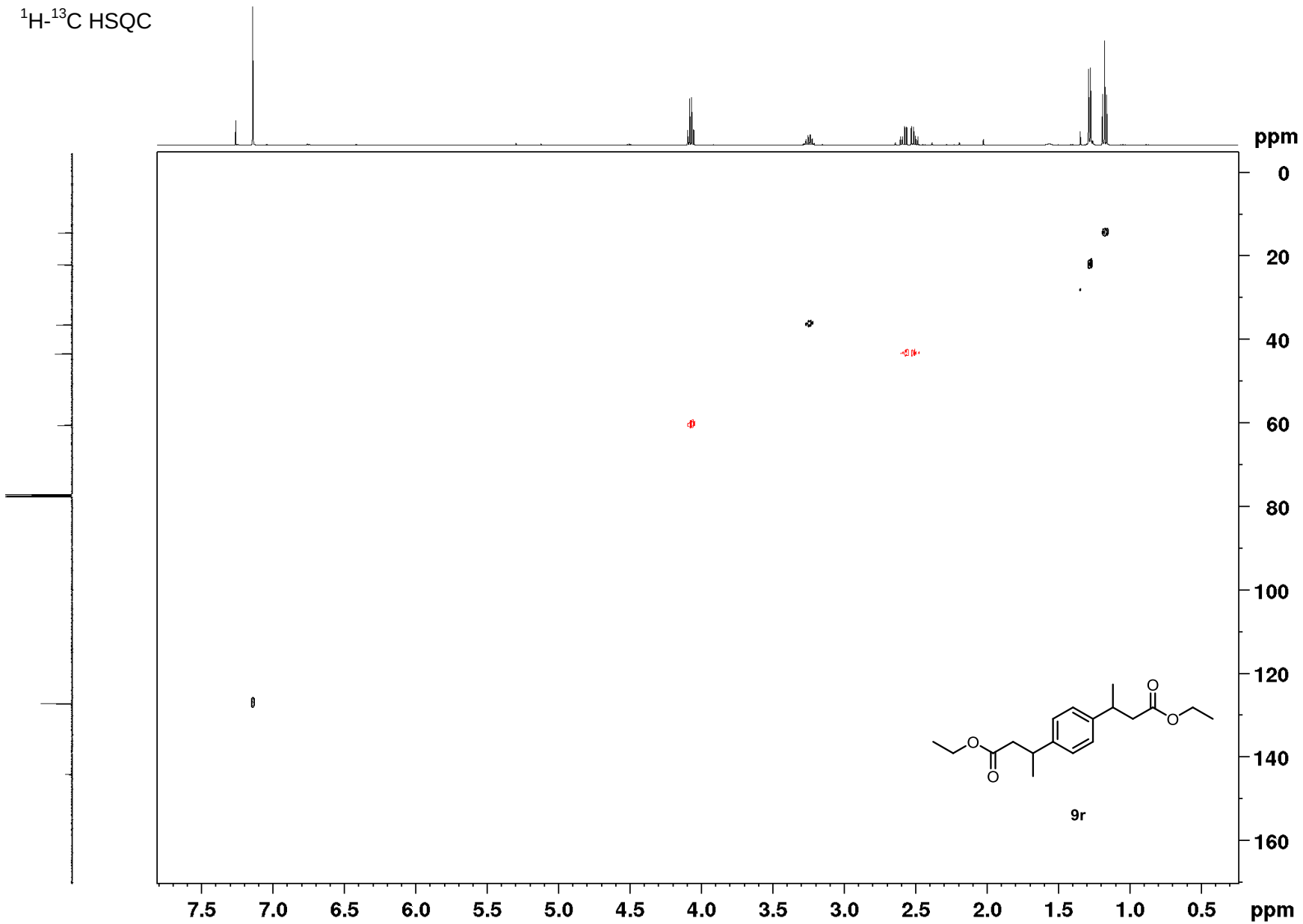
Diethyl 3,3'-(1,4-phenylene)dibutyrate (9r)

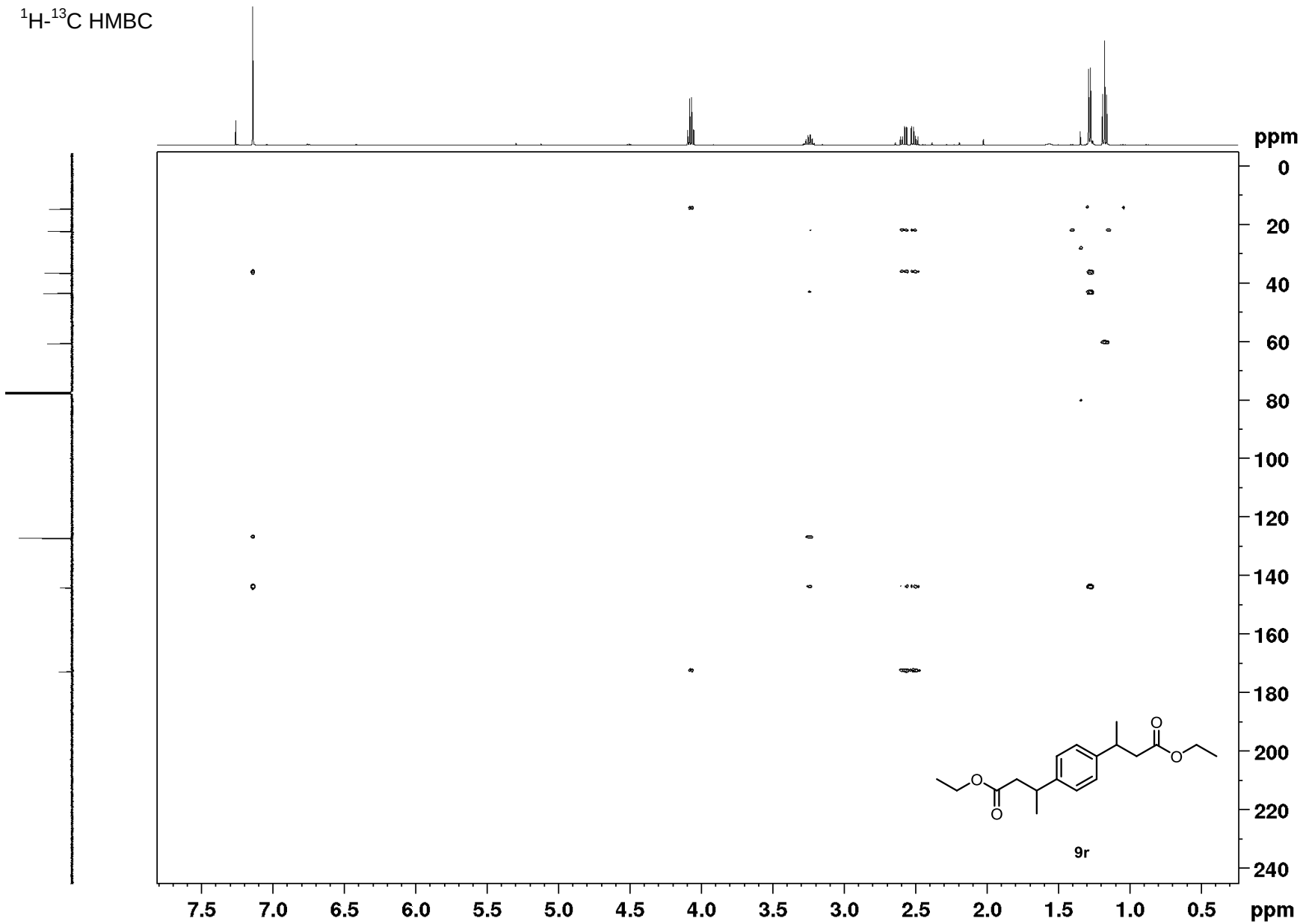
^{1}H NMR

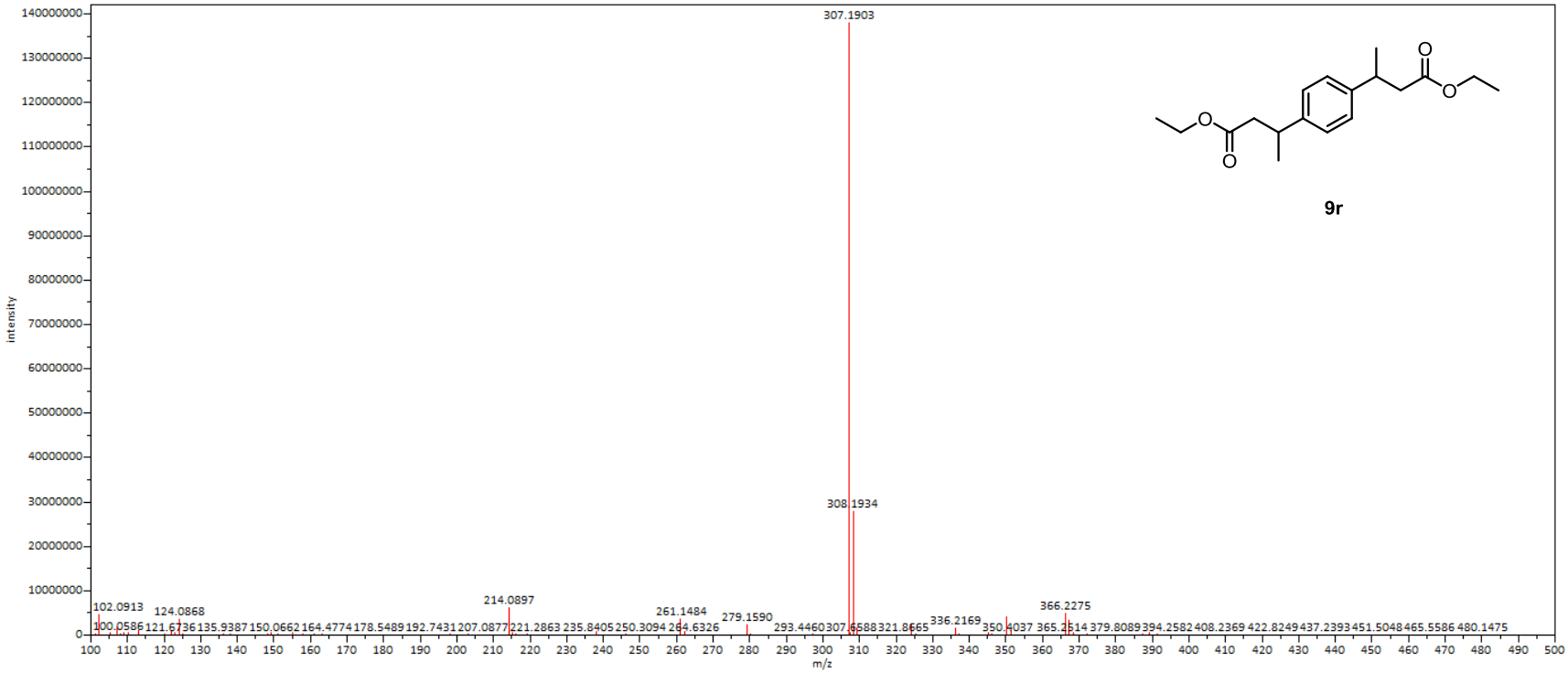


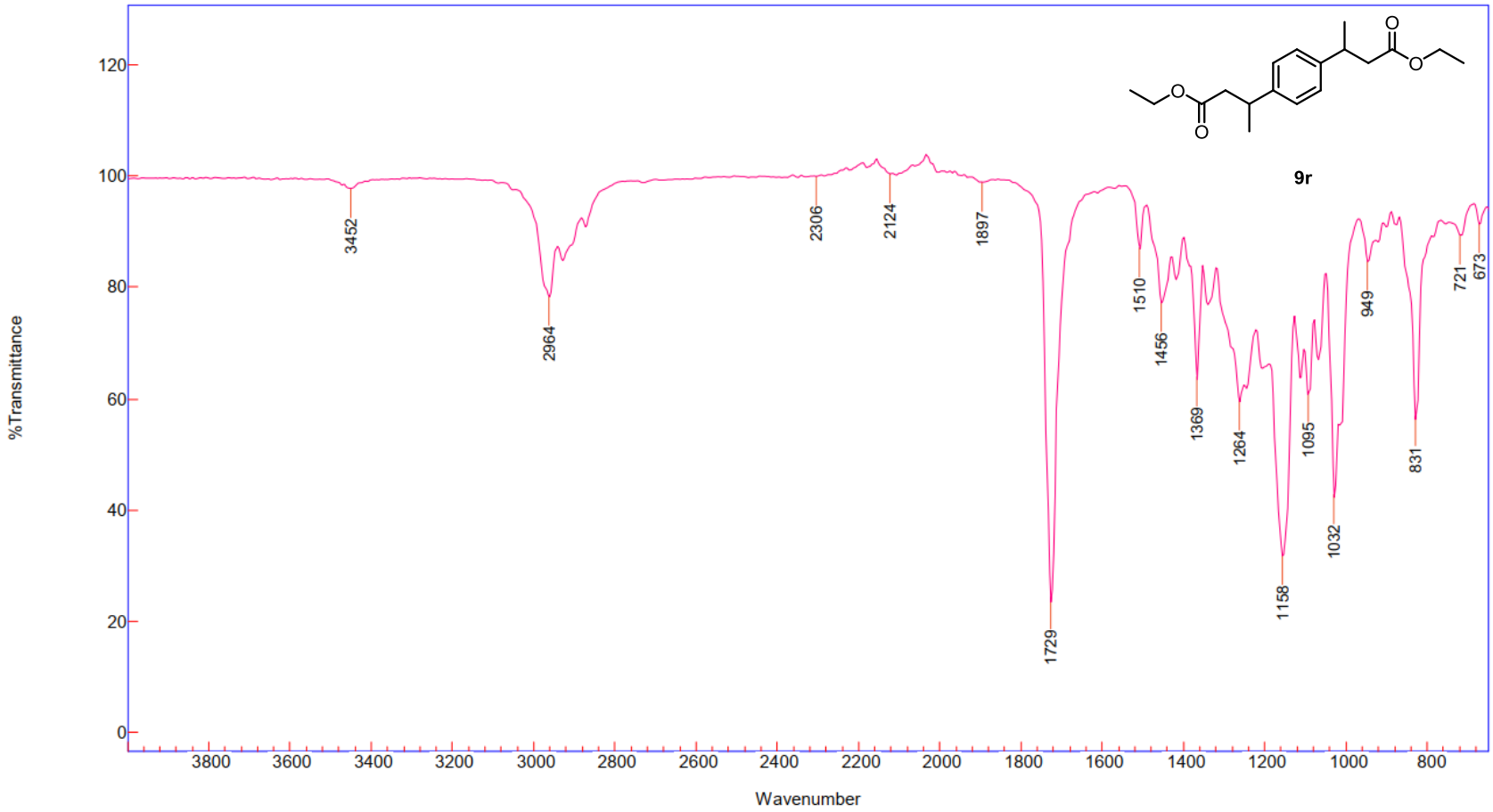

^{13}C NMR
172.6
143.9
127.0
60.4
43.2
36.2
21.9
14.3
O
O
O
O
9r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


^{1}H-^{1}H COSY
ppm
1
2
3
4
5
6
7
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
ppm
O
O
O
O
9r

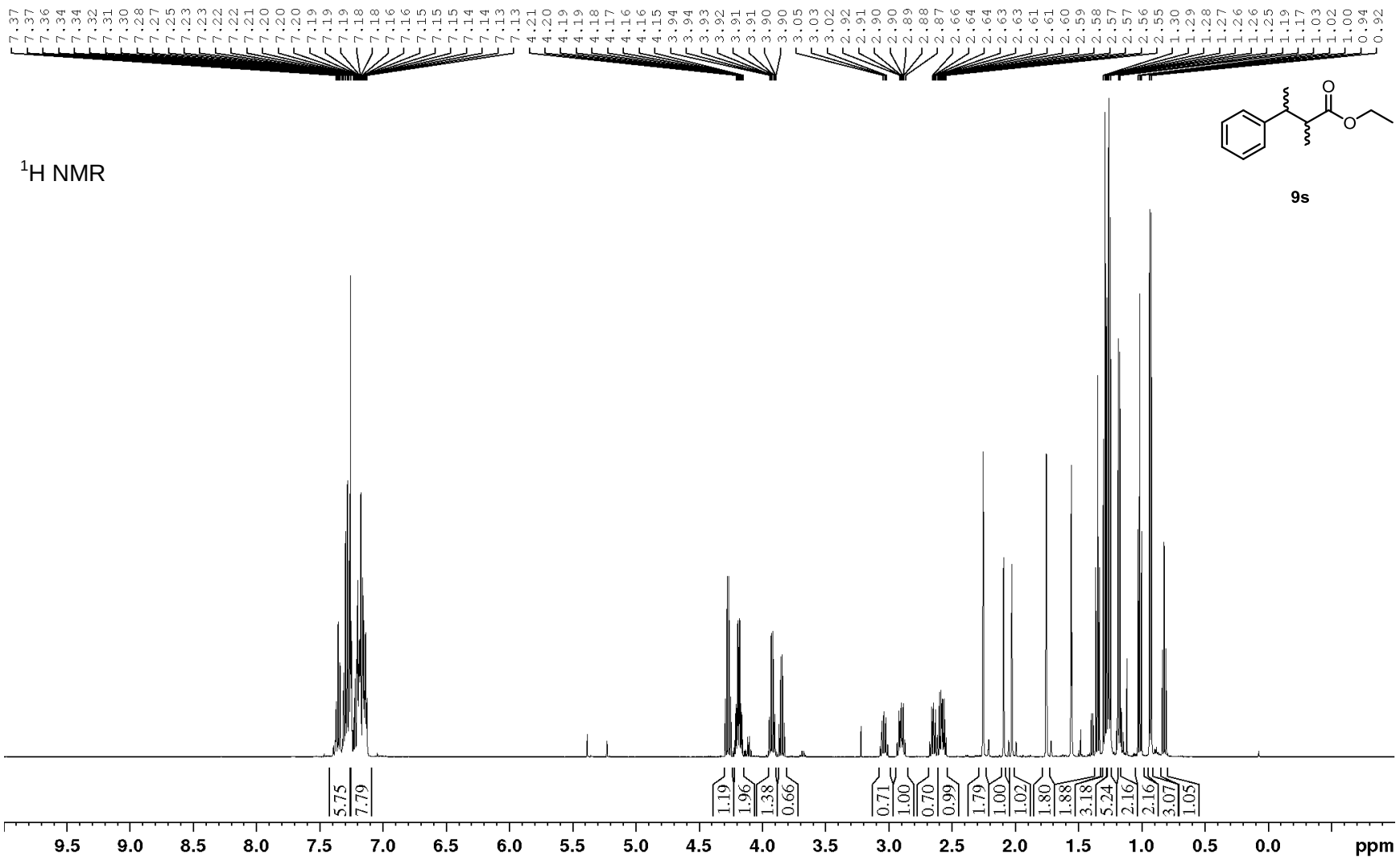

^{1}H-^{13}C HSQC
ppm
0
20
40
60
80
100
120
140
160
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
9r


^{1}H-^{13}C HMBC
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm
O
O
O
O
9r

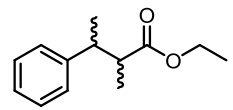

307.1903
308.1934
214.0897
261.1484
279.1590
336.2169
366.2275
102.0913
124.0868
intensity
m/z
9r


9r
%Transmittance
Wavenumber
120
100
80
60
40
20
0
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
3452
2964
2306
2124
1897
1729
1510
1456
1369
1264
1158
1095
1032
949
831
721
673

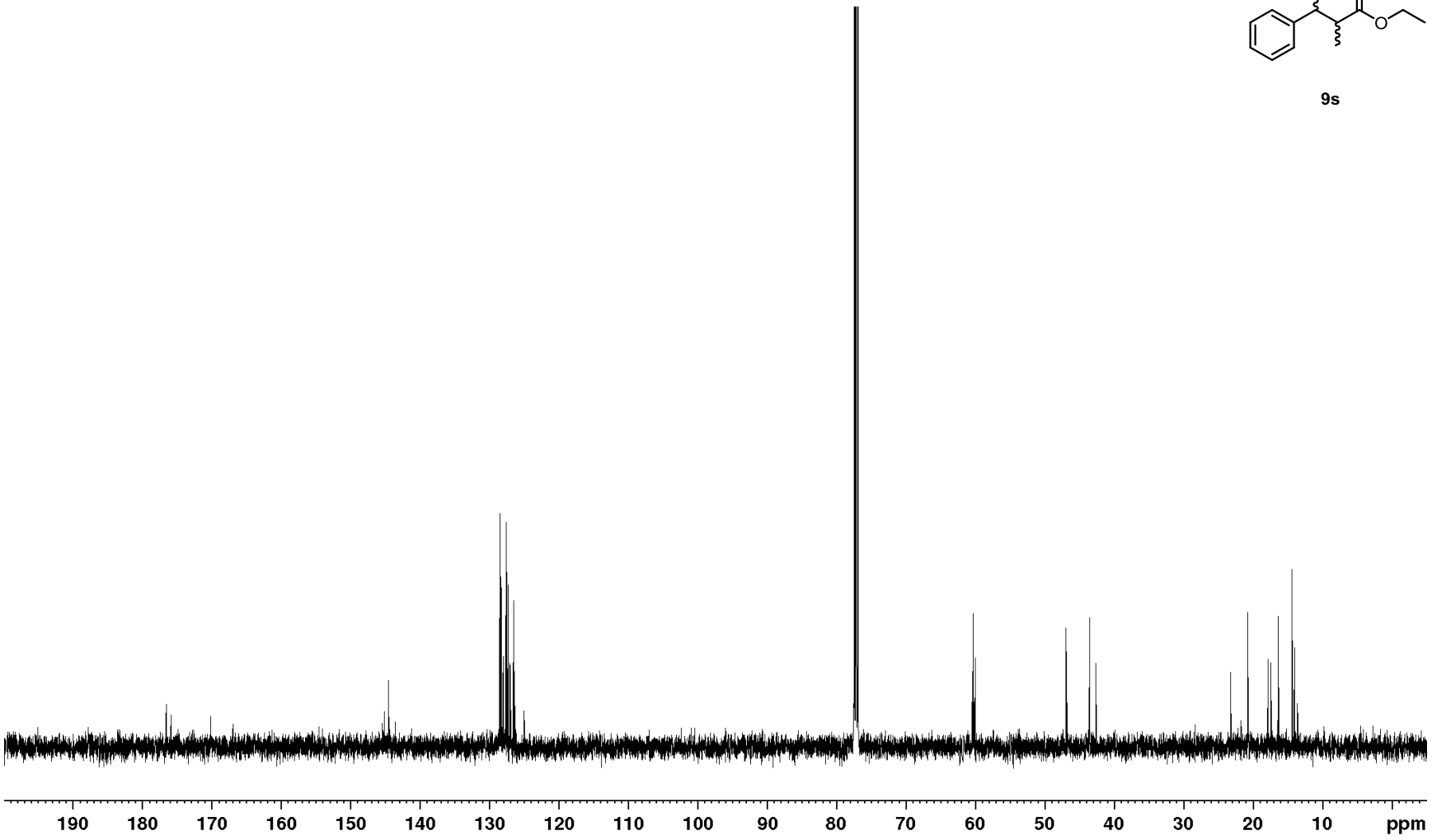
Ethyl-2-methyl-3-phenylbutanoate (9s)

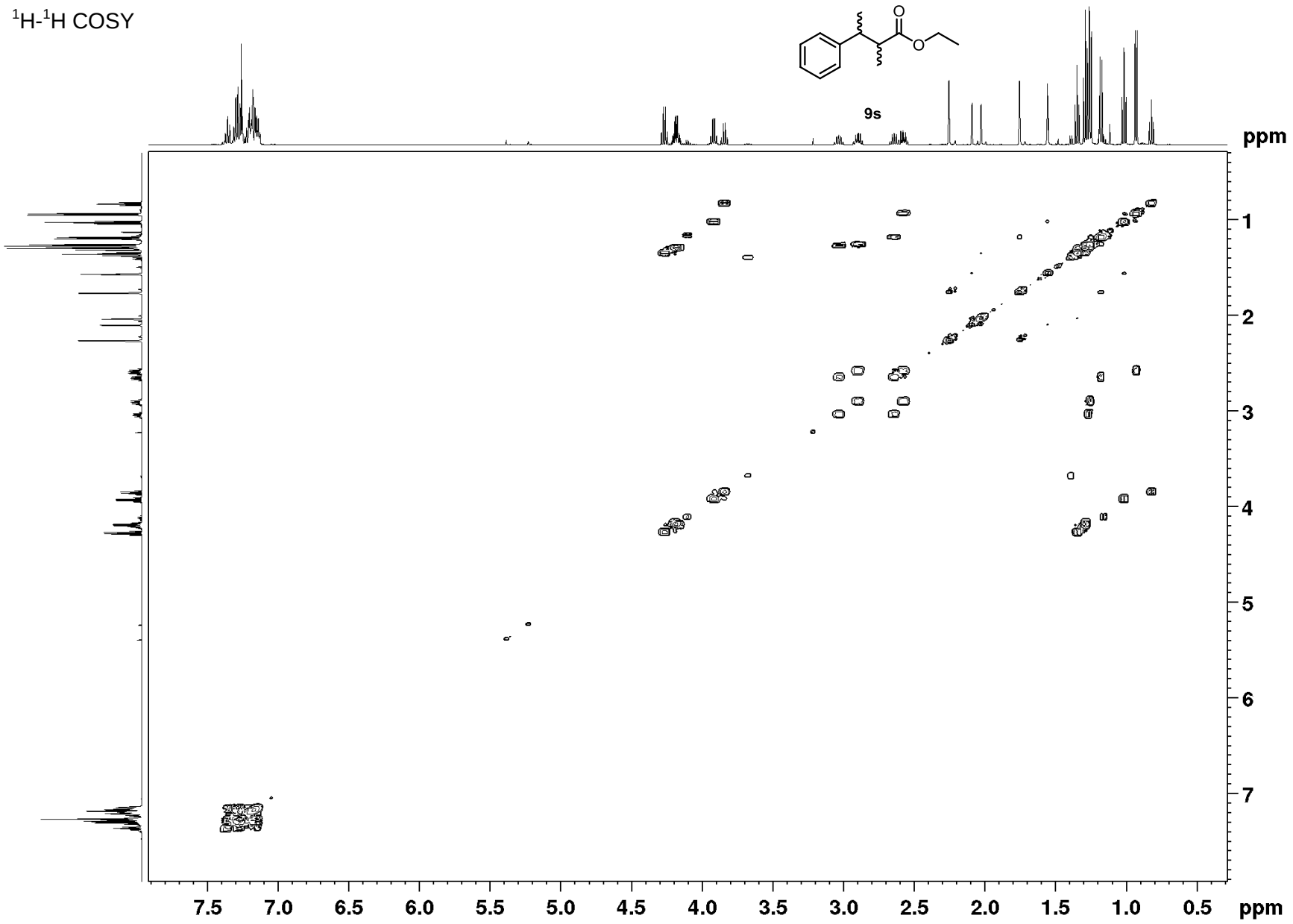


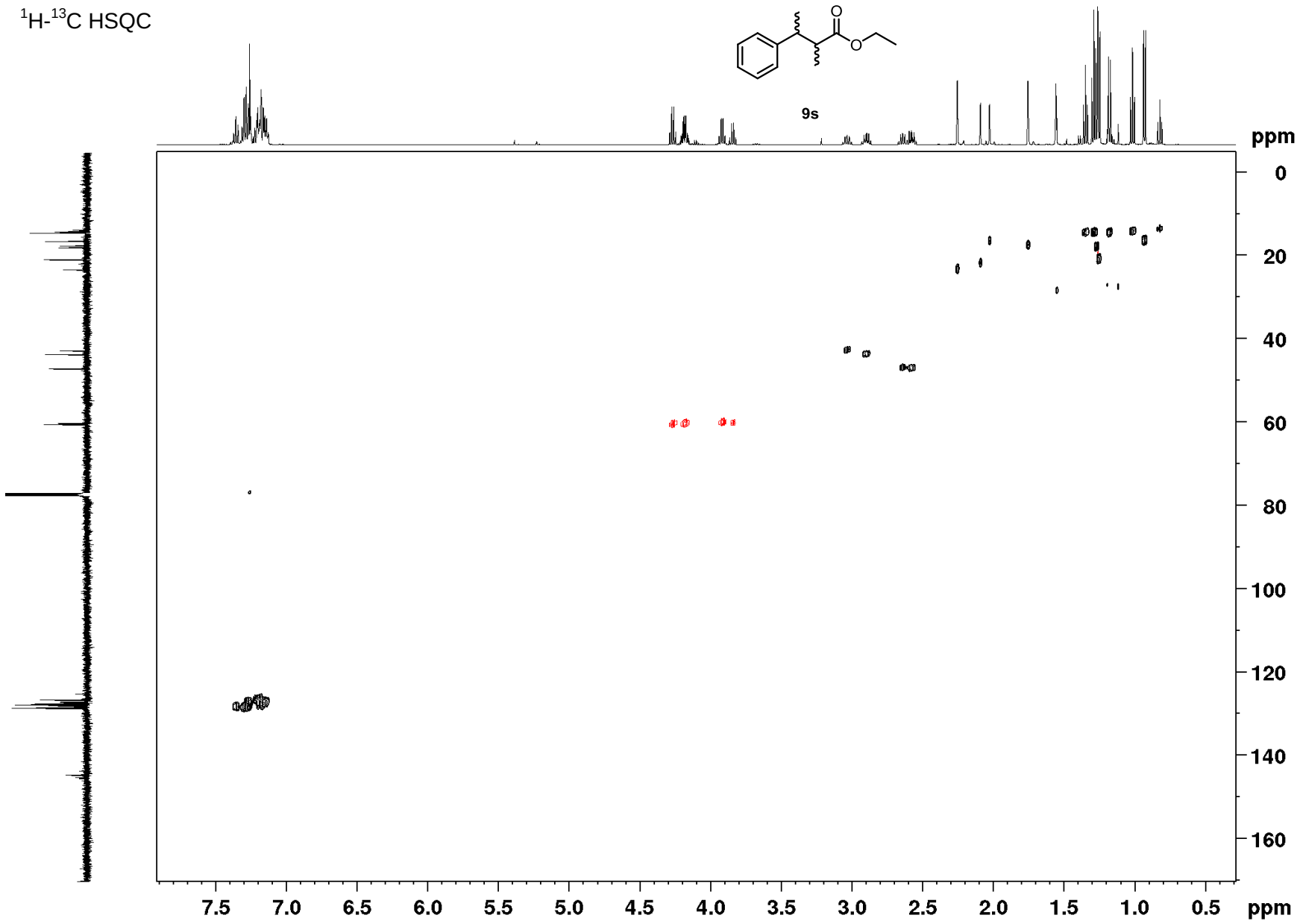
^{13}C NMR



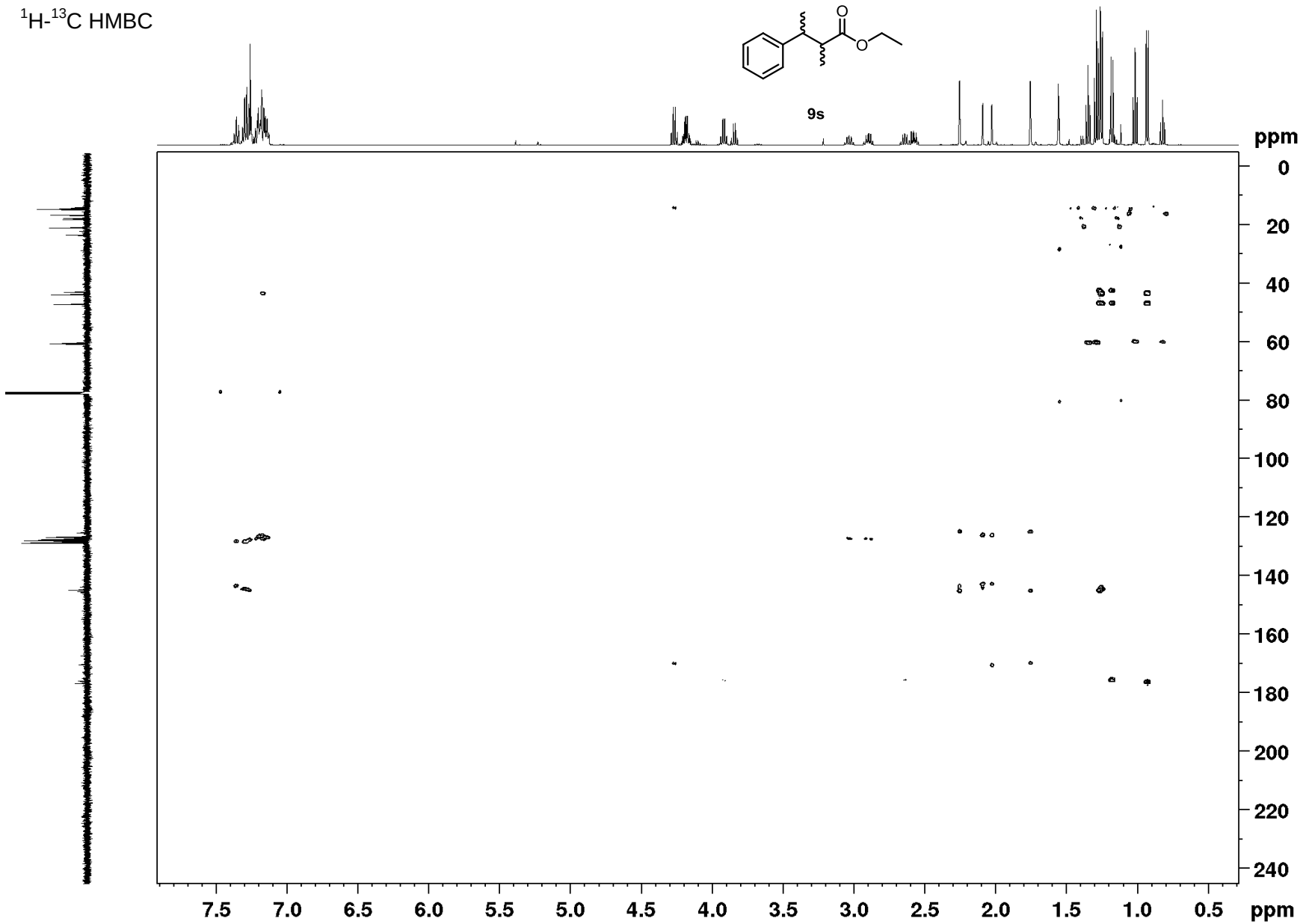
9s

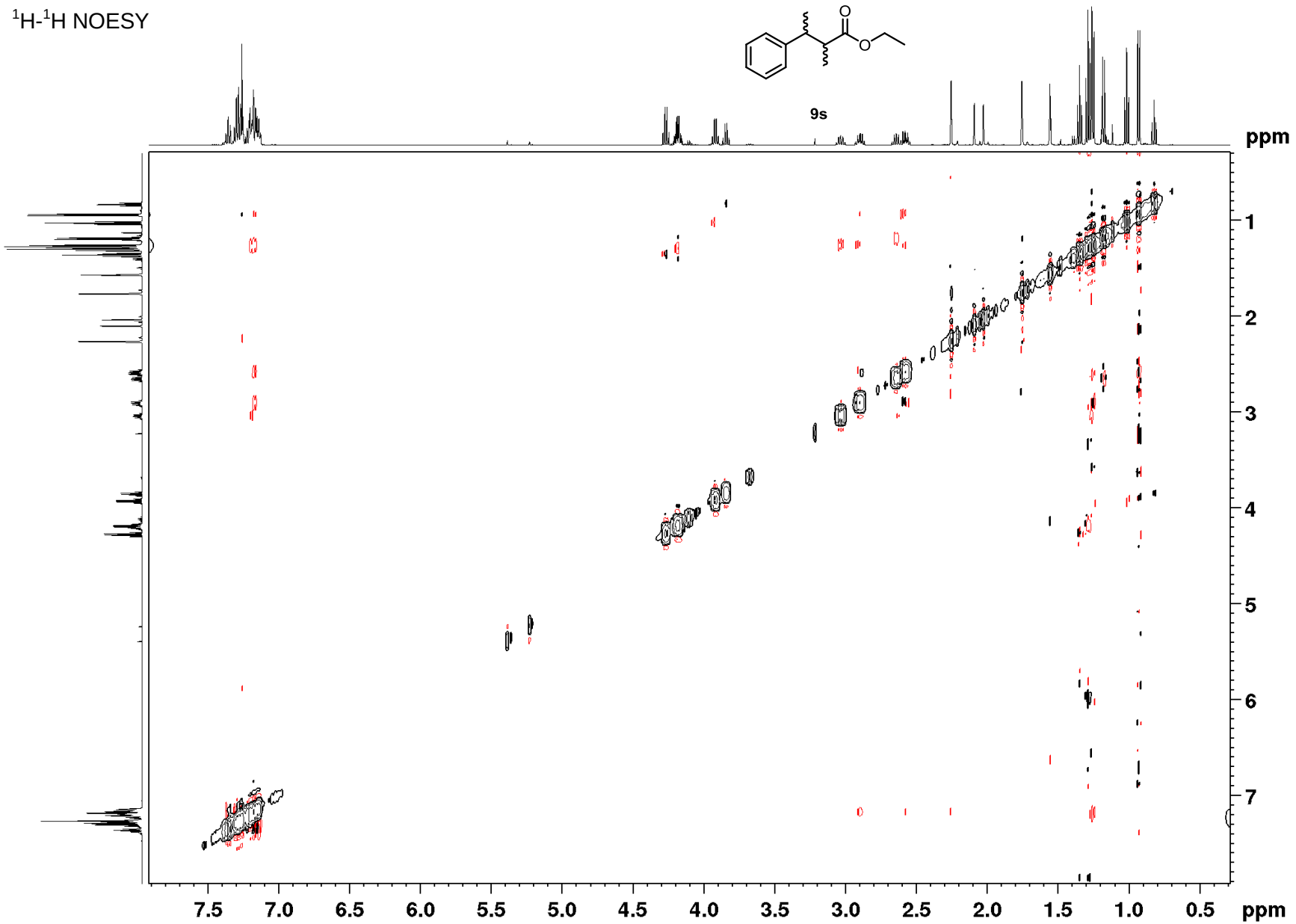

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


^{1}H-^{1}H COSY
9s
ppm
1
2
3
4
5
6
7
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
ppm


^{1}H-^{13}C HSQC
9s
ppm
0
20
40
60
80
100
120
140
160
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
ppm

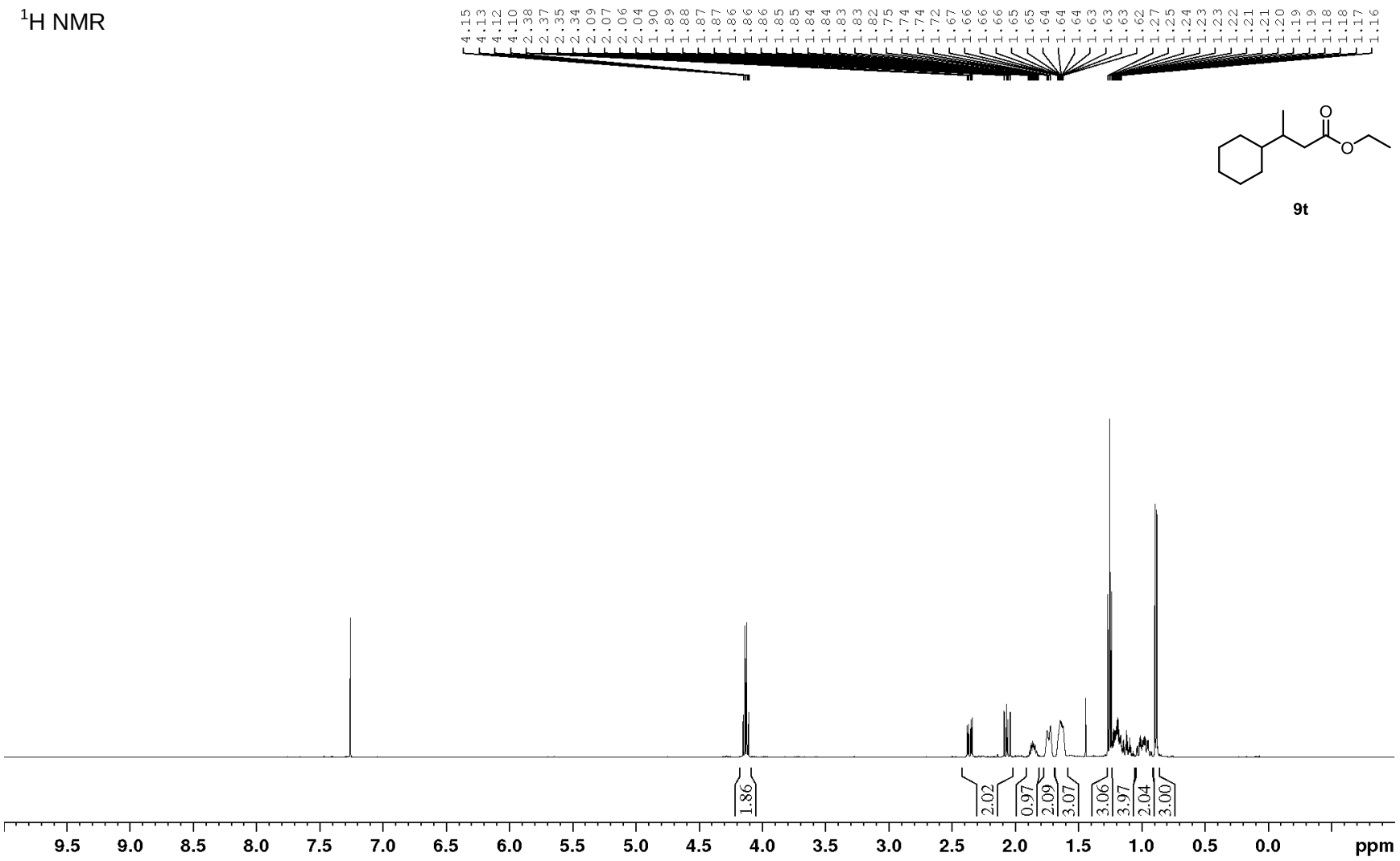
^{1}H-^{13}C HMBC

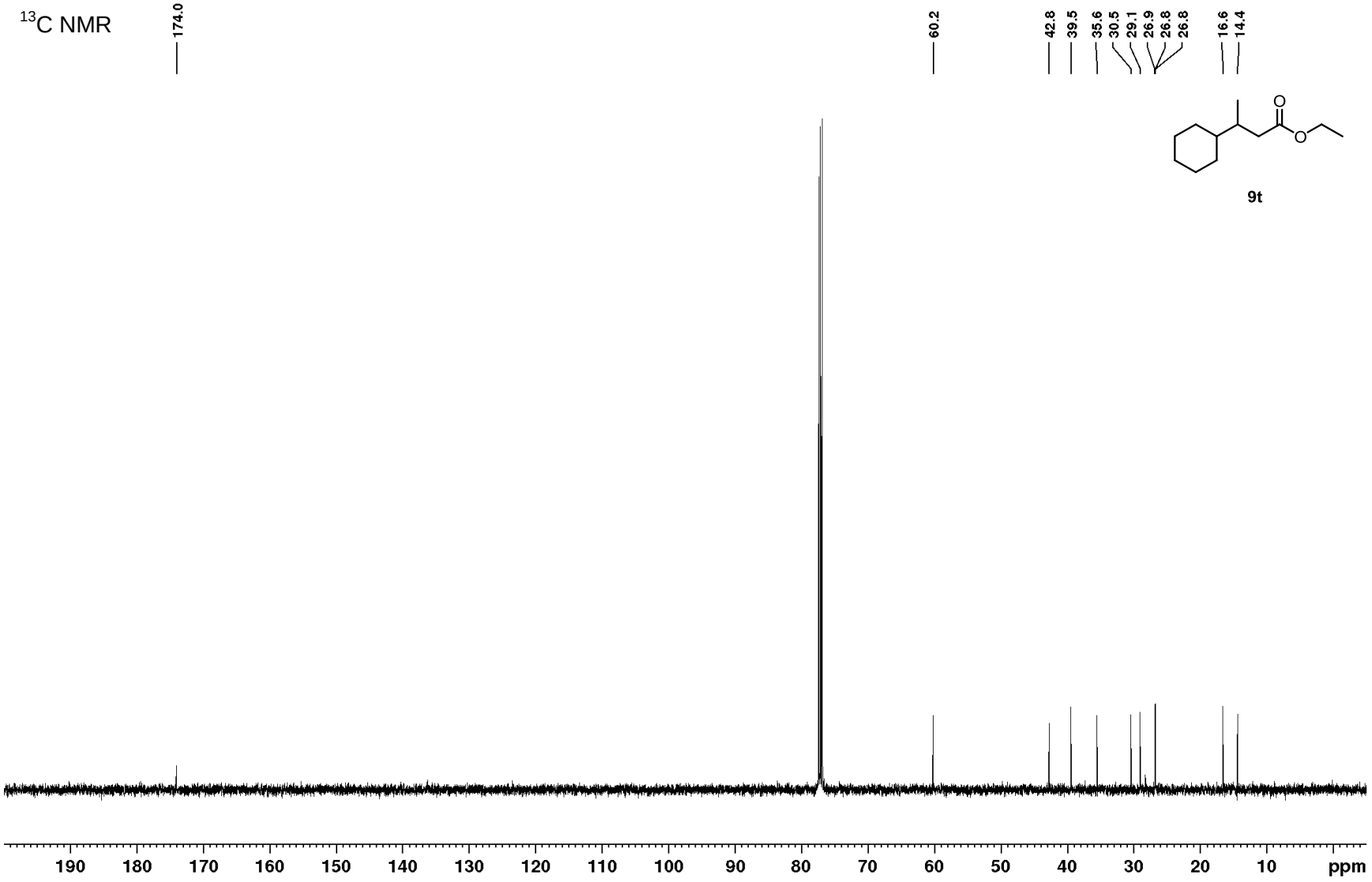

O
O
9s
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


^{1}H-^{1}H NOESY
9s
ppm
1
2
3
4
5
6
7
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
ppm

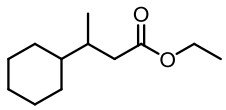
Ethyl 3-cyclohexylbutanoate (9t)

^{1}H NMR

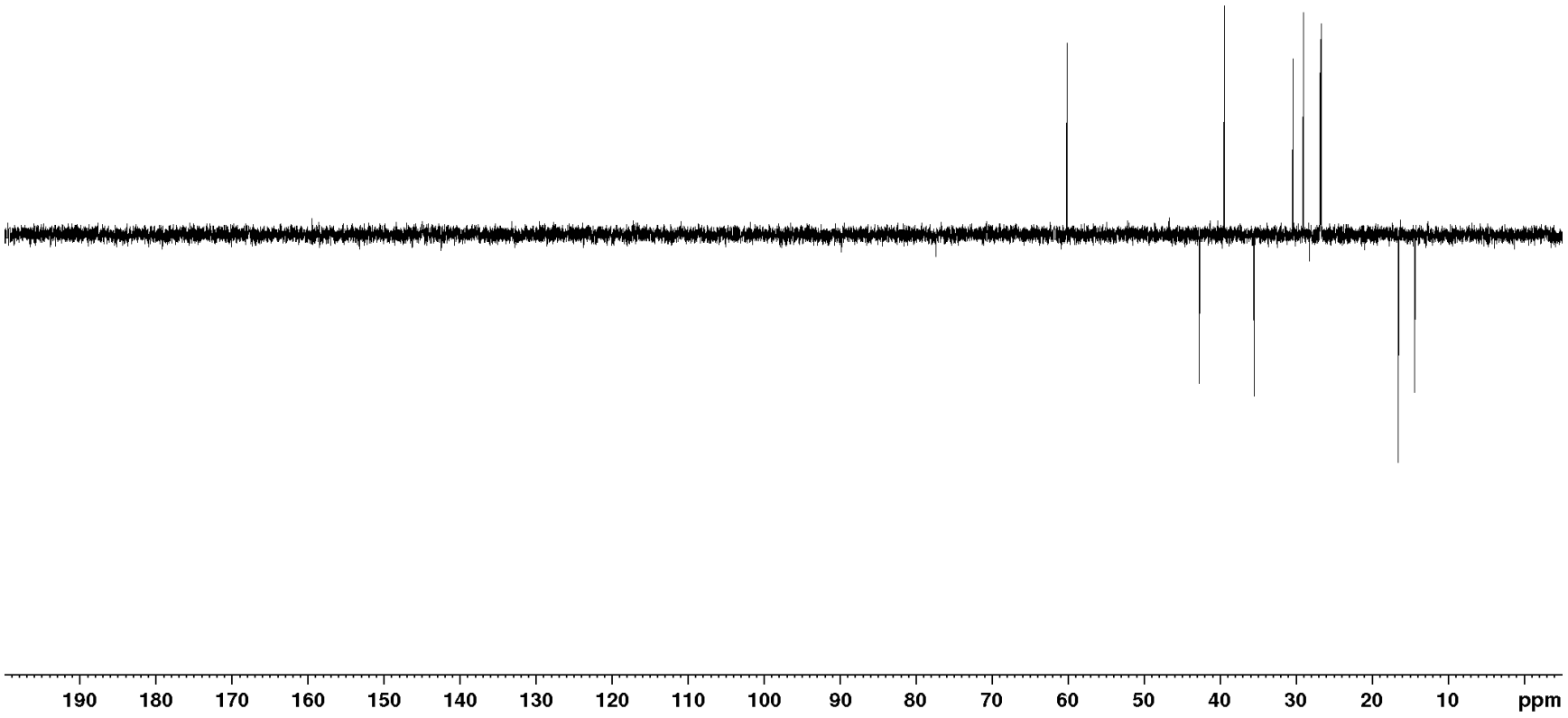



^{13}C NMR
174.0
60.2
42.8
39.5
35.6
30.5
29.1
26.9
26.8
26.8
16.6
14.4
O
O
9t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

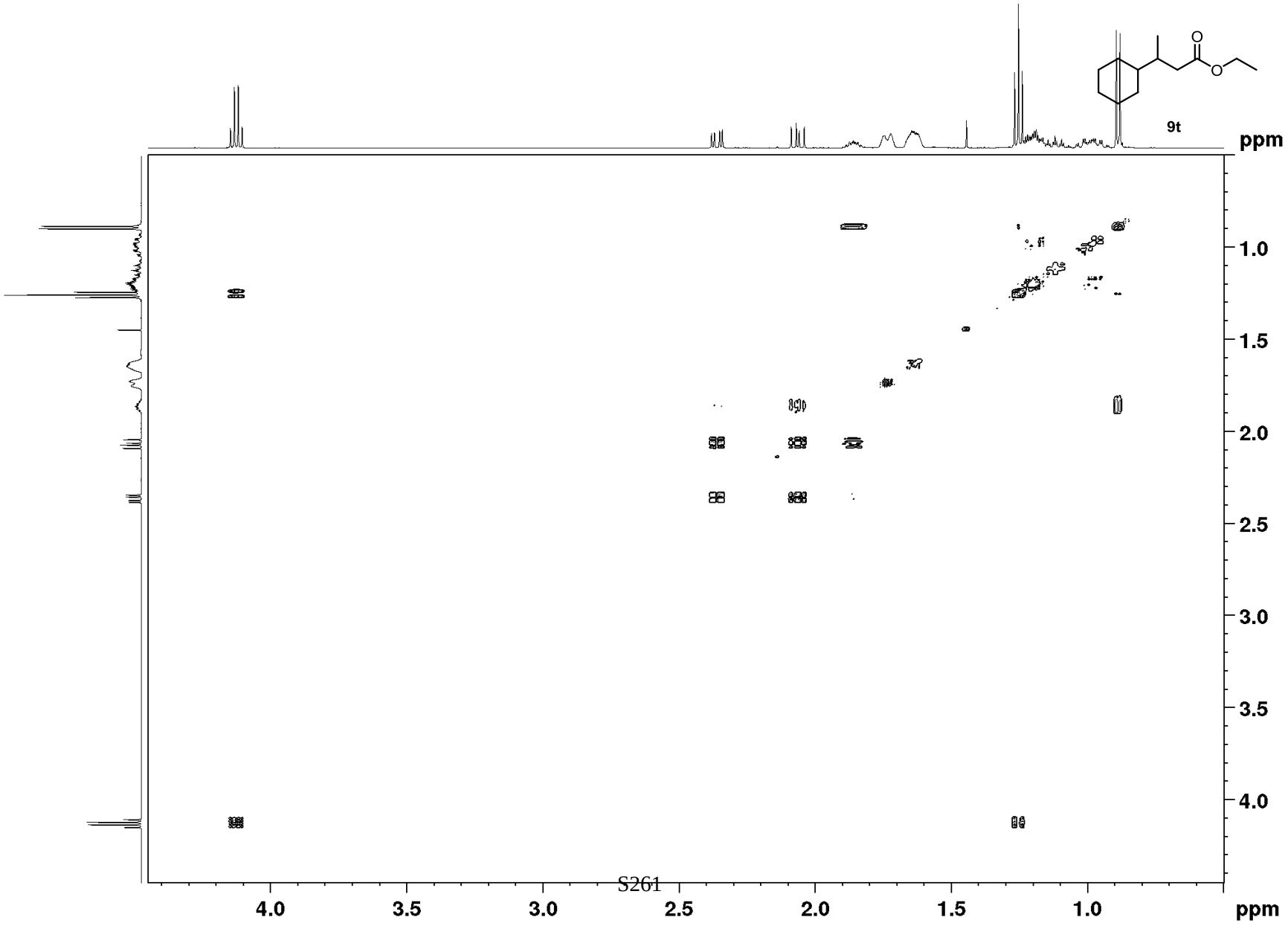
^{13}C DEPT NMR



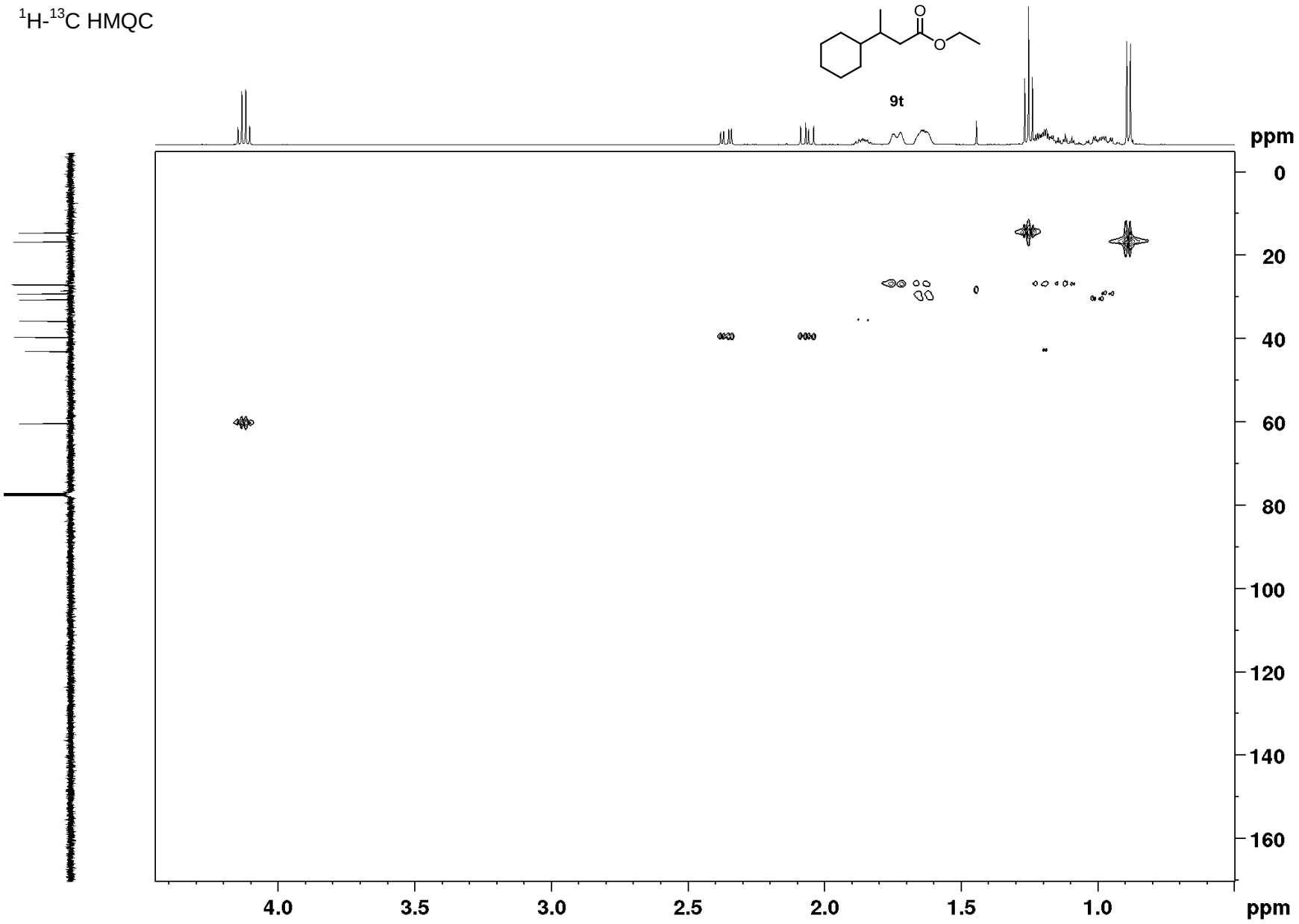
9t



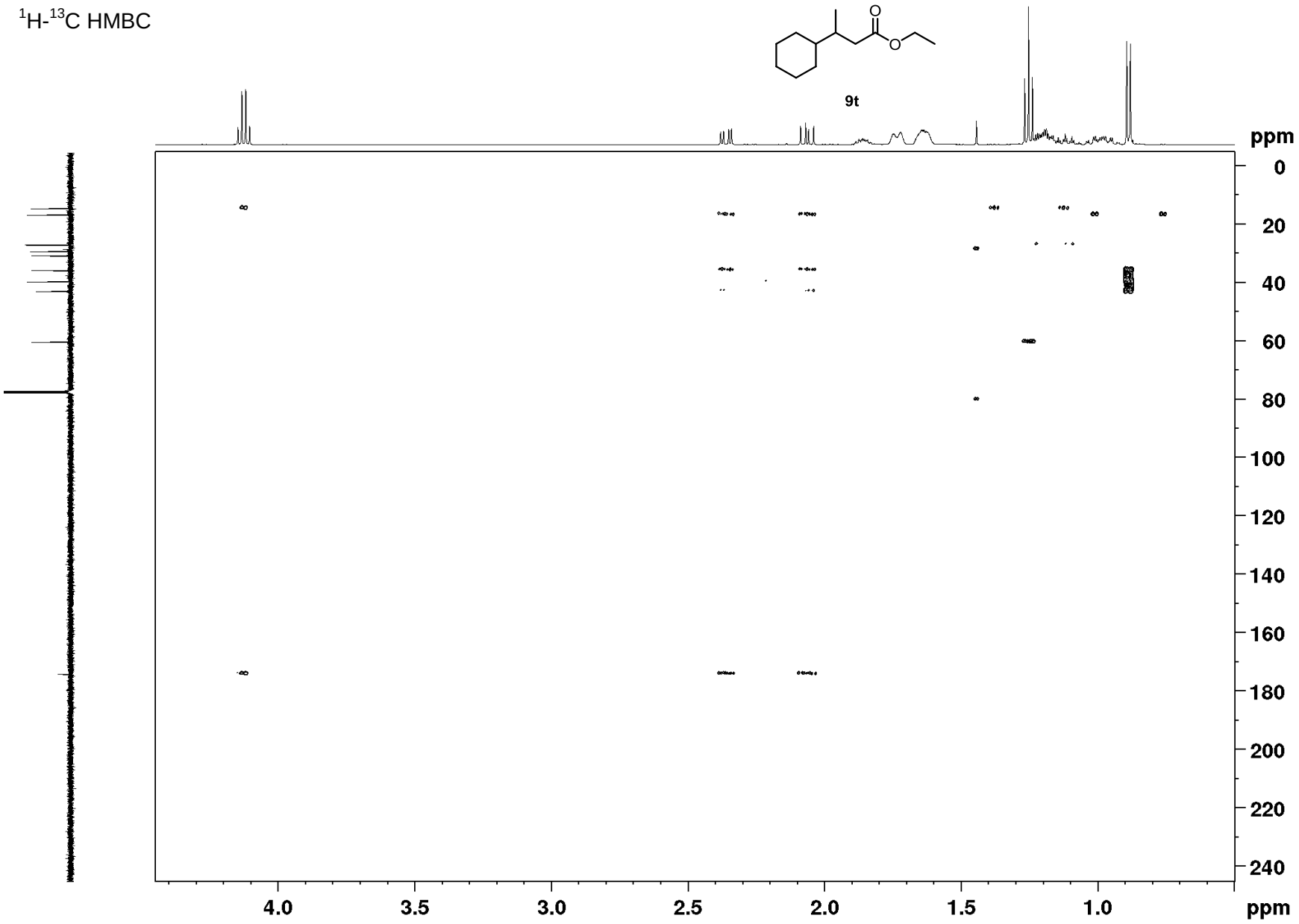
^{1}H-^{1}H COSY

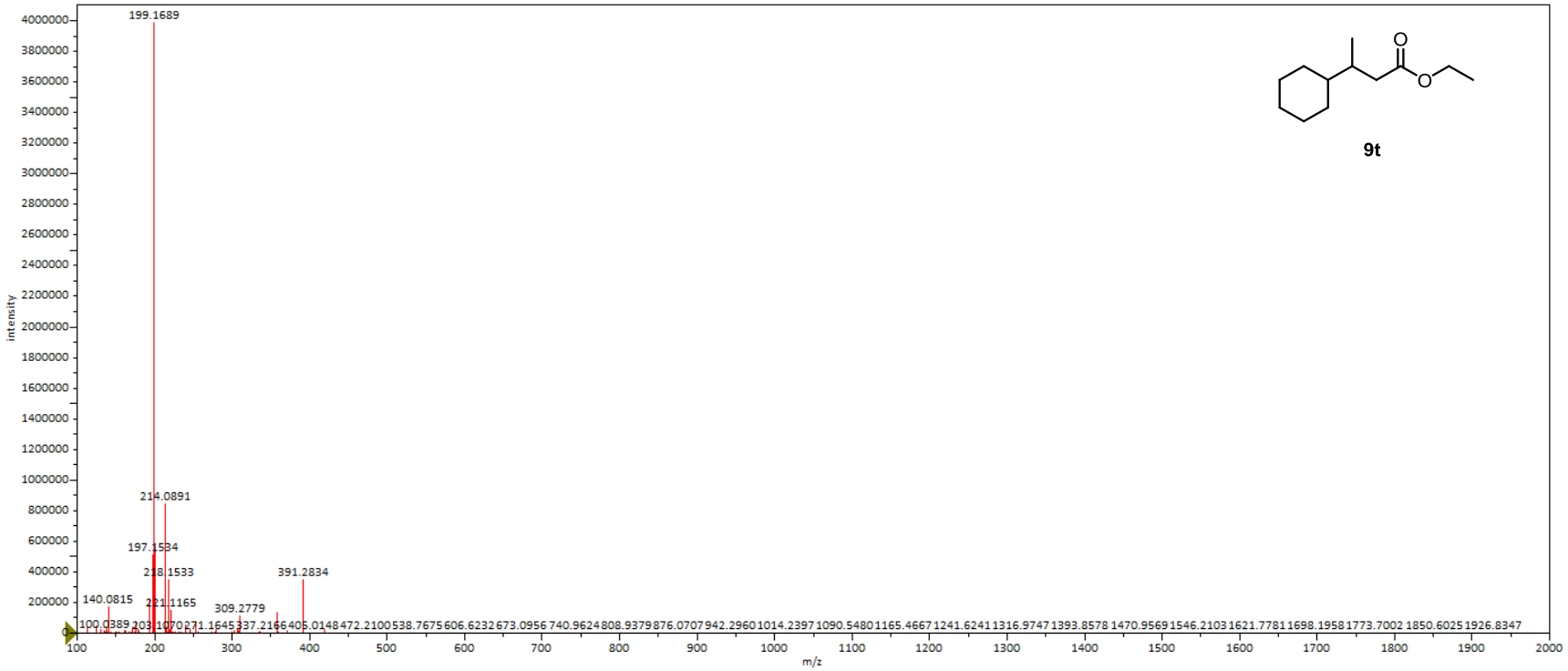


^{1}H-^{13}C HMQC



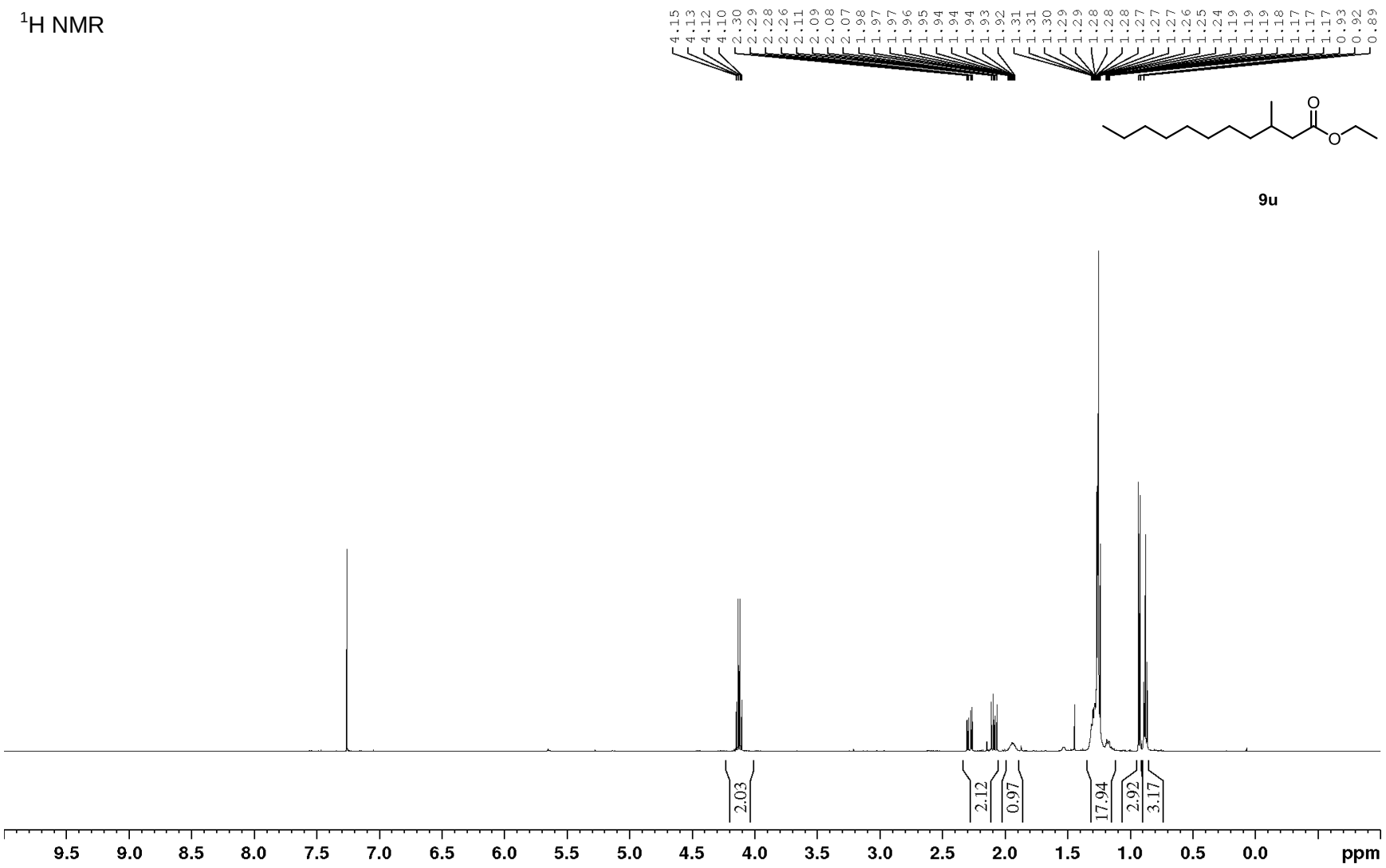
^{1}H-^{13}C HMBC

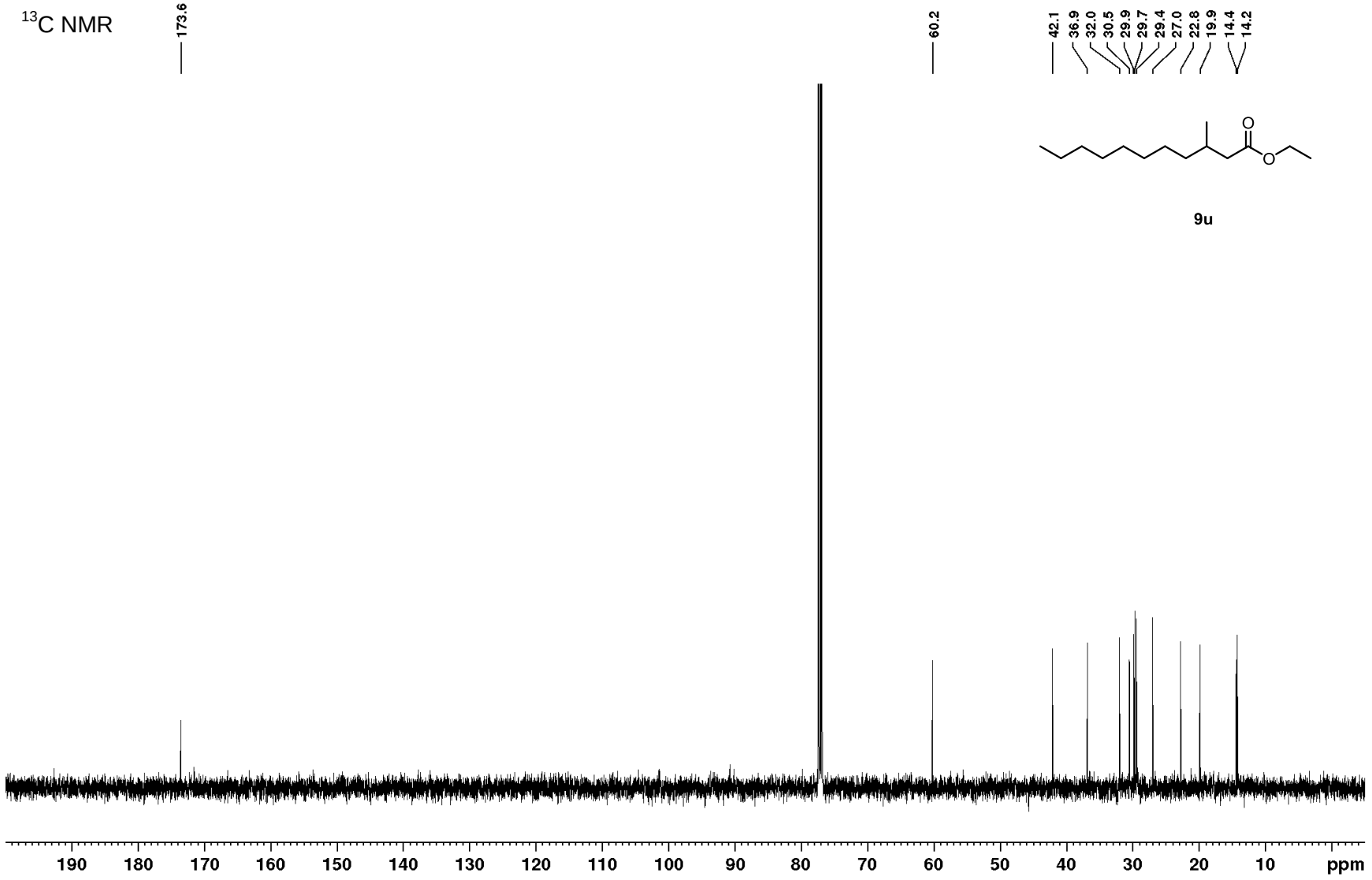

9t
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


199.1689
214.0891
197.1534
218.1533
391.2834
140.0815
221.1165
309.2779
intensity
m/z
9t

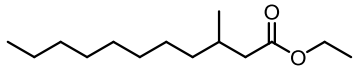
Ethyl 3-methylundecanoate (9u)

^{1}H NMR

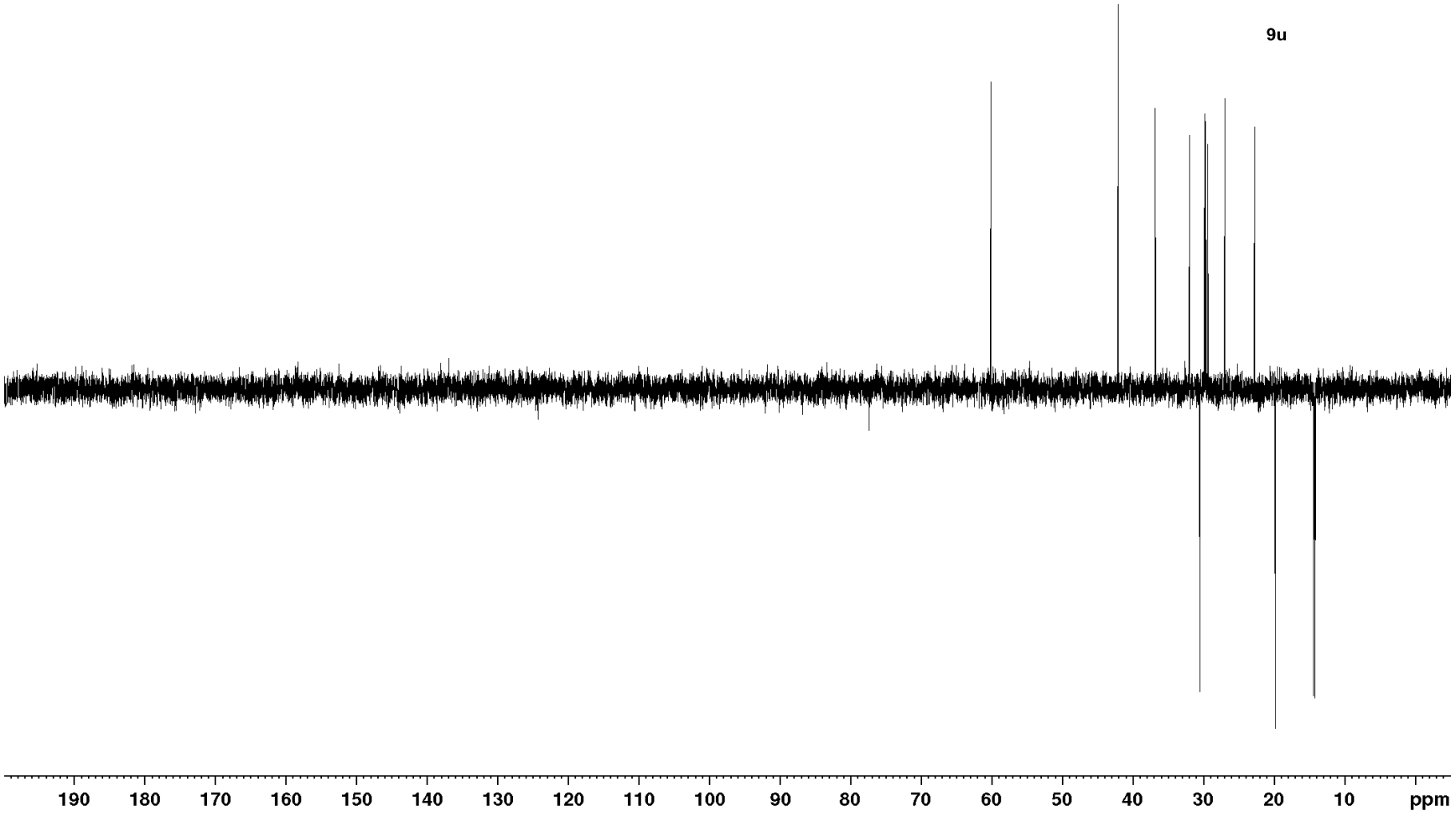



^{13}C NMR
173.6
60.2
42.1
36.9
32.0
30.5
29.9
29.7
29.4
27.0
22.8
19.9
14.4
14.2
O
O
9u
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

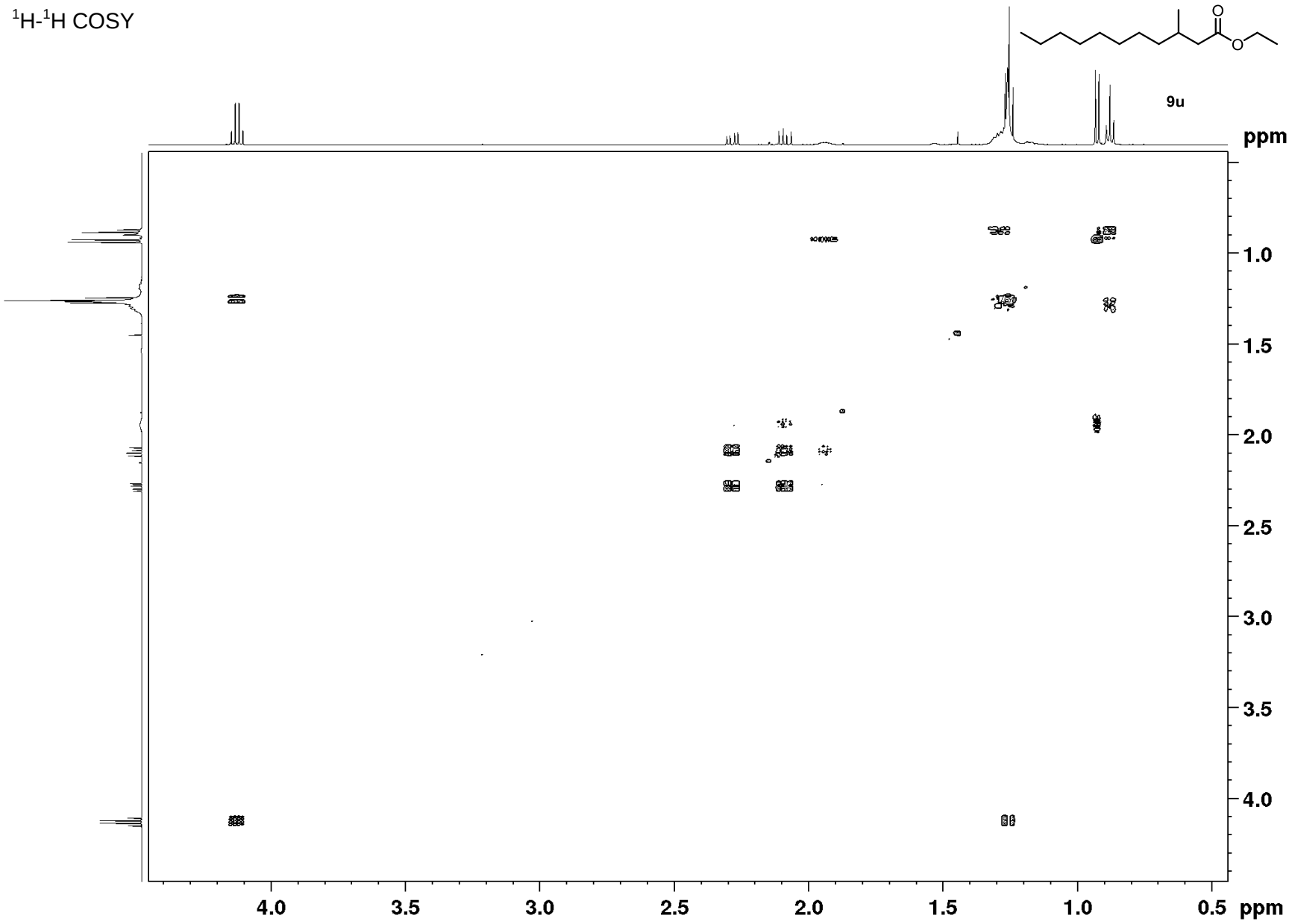
^{13}C DEPT NMR

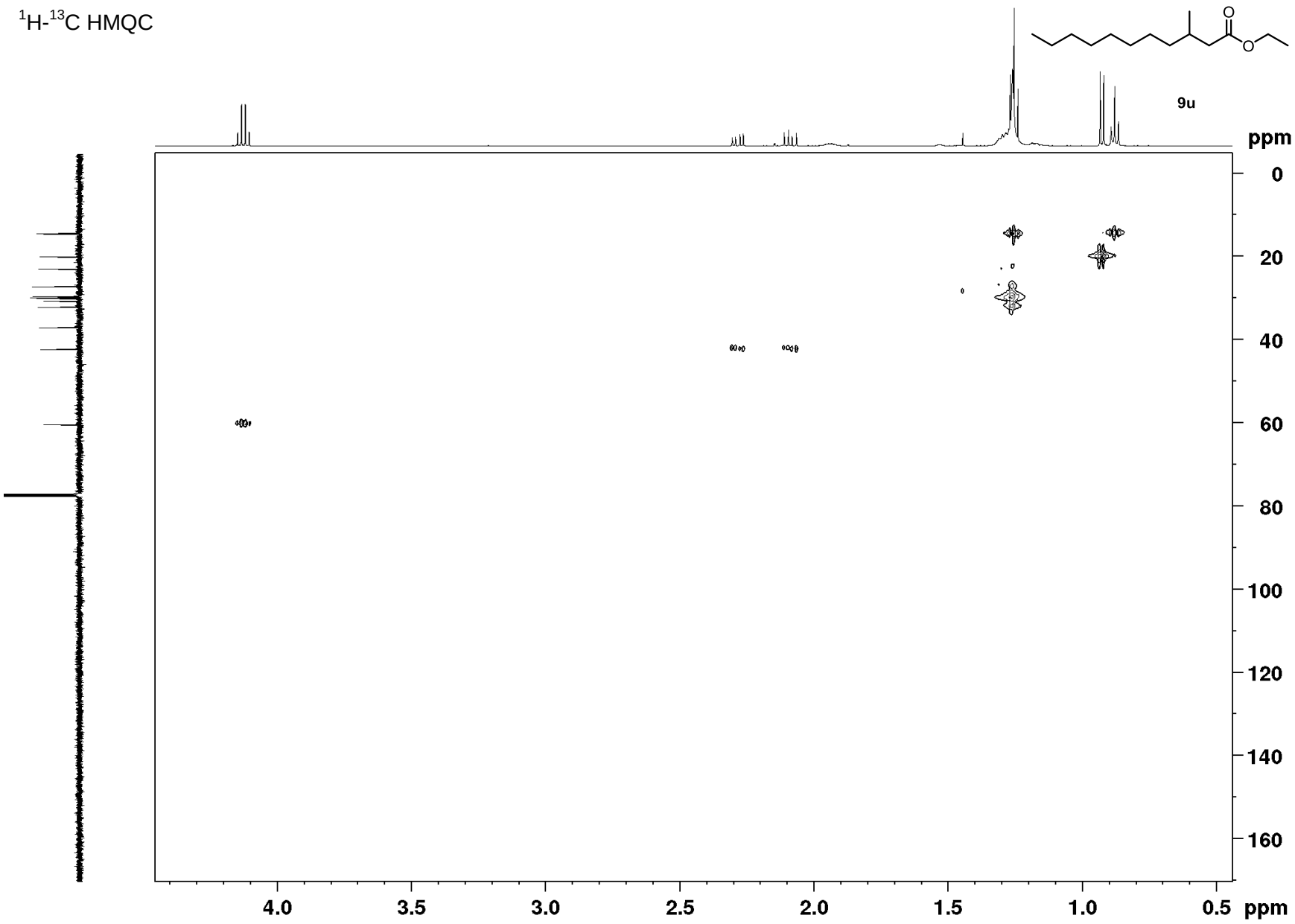


9u

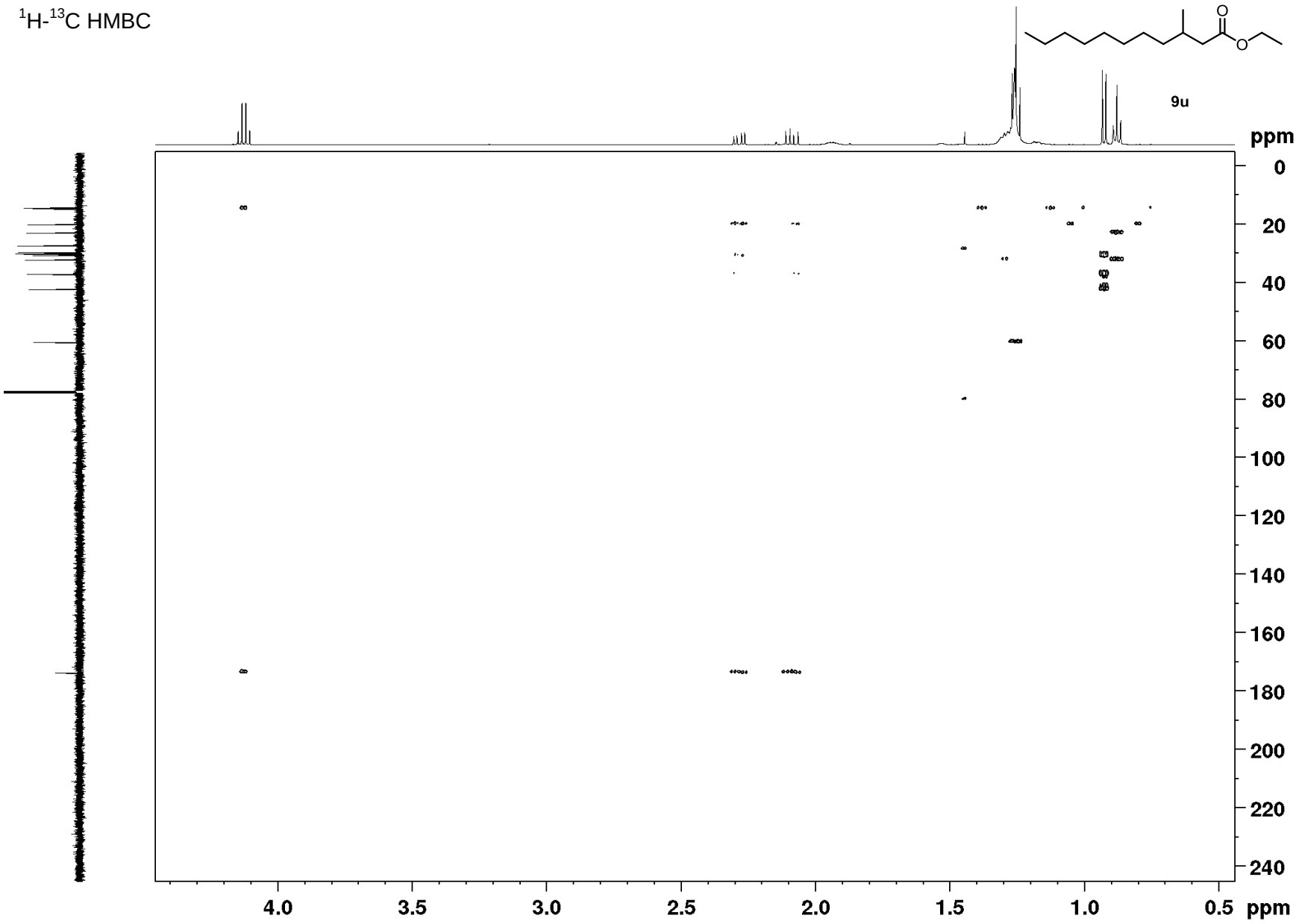


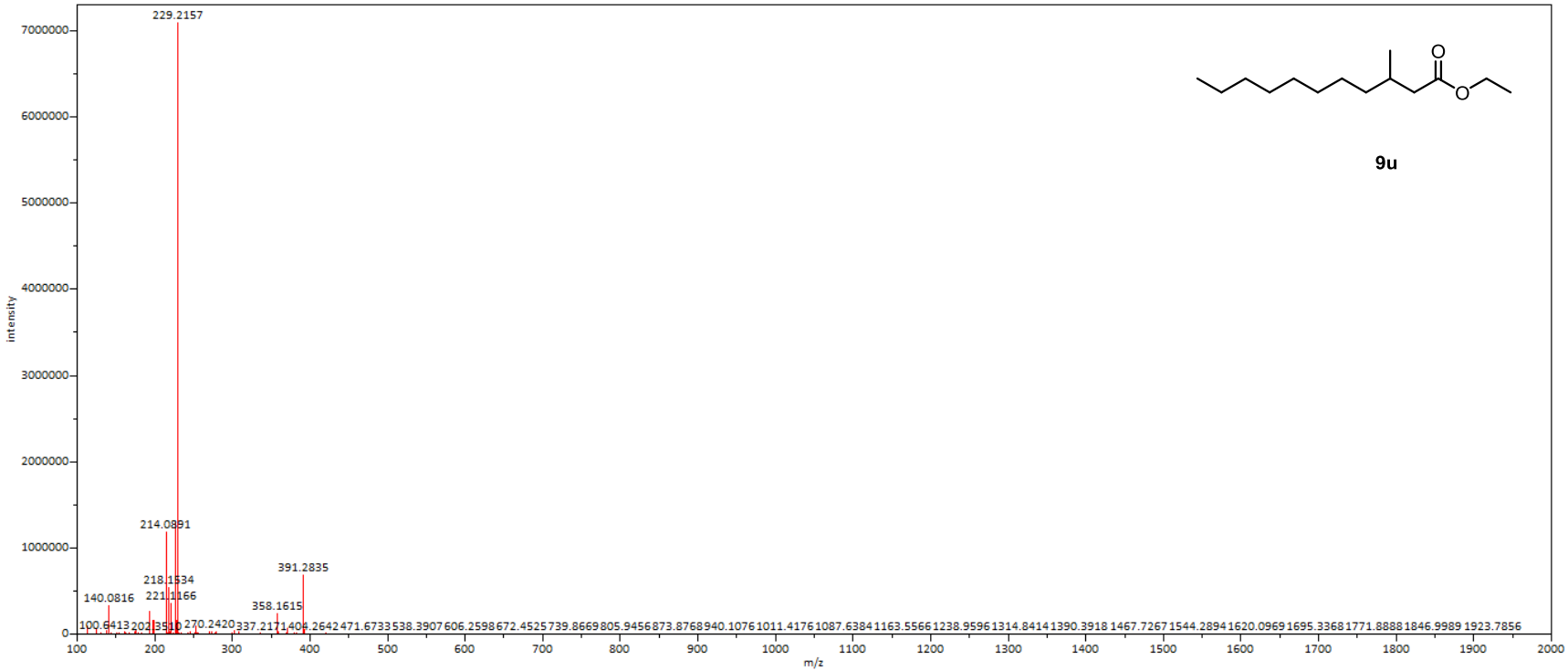
^{1}H-^{1}H COSY

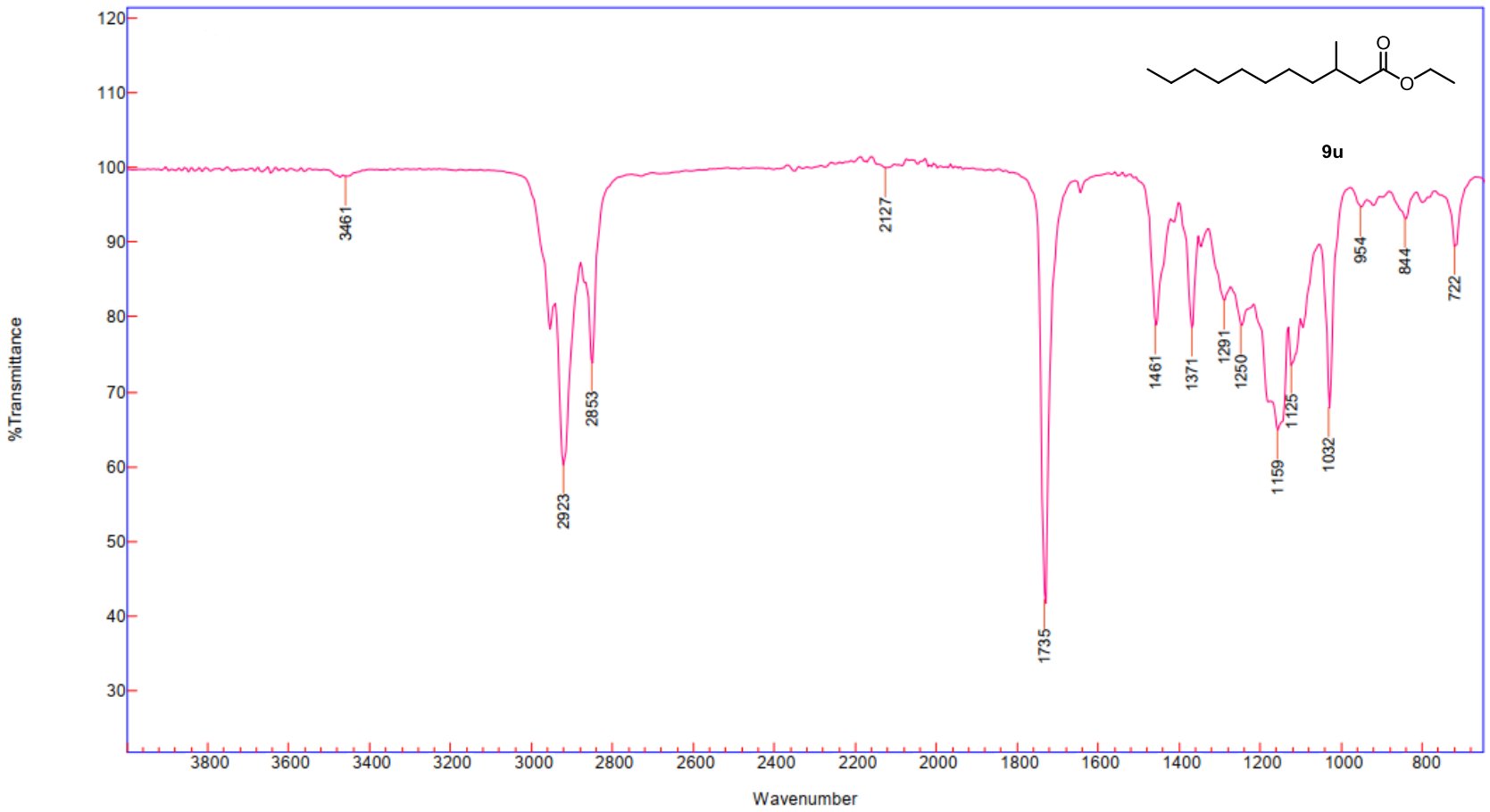



^{1}H-^{13}C HMQC
9u
ppm
0
20
40
60
80
100
120
140
160
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{1}H-^{13}C HMBC

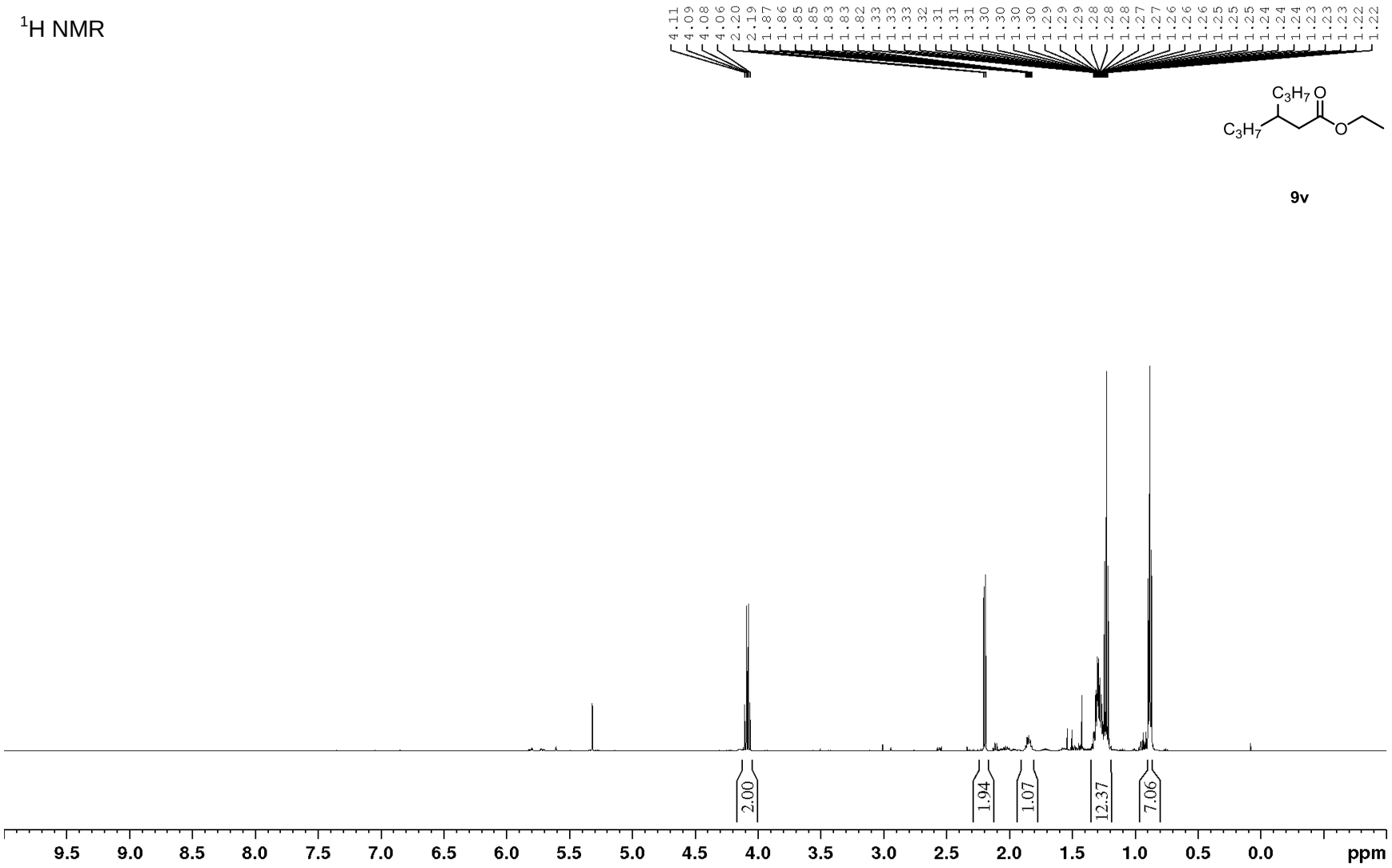

9u
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

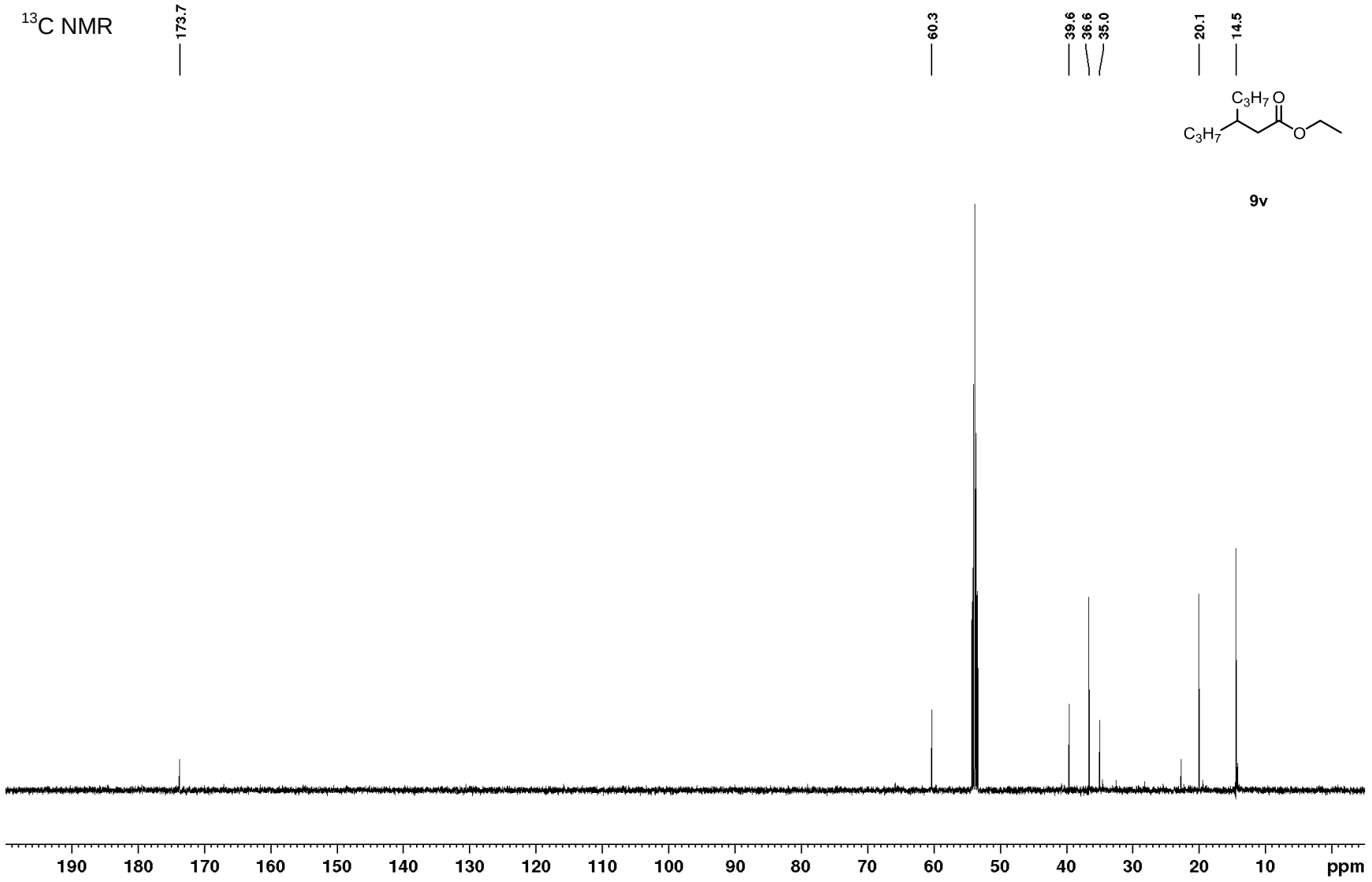

229.2157
214.0891
218.1534
221.1166
140.0816
391.2835
358.1615
intensity
m/z
9u


9u
%Transmittance
Wavenumber
120
110
100
90
80
70
60
50
40
30
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
3461
2923
2853
2127
1735
1461
1371
1291
1250
1159
1125
1032
954
844
722

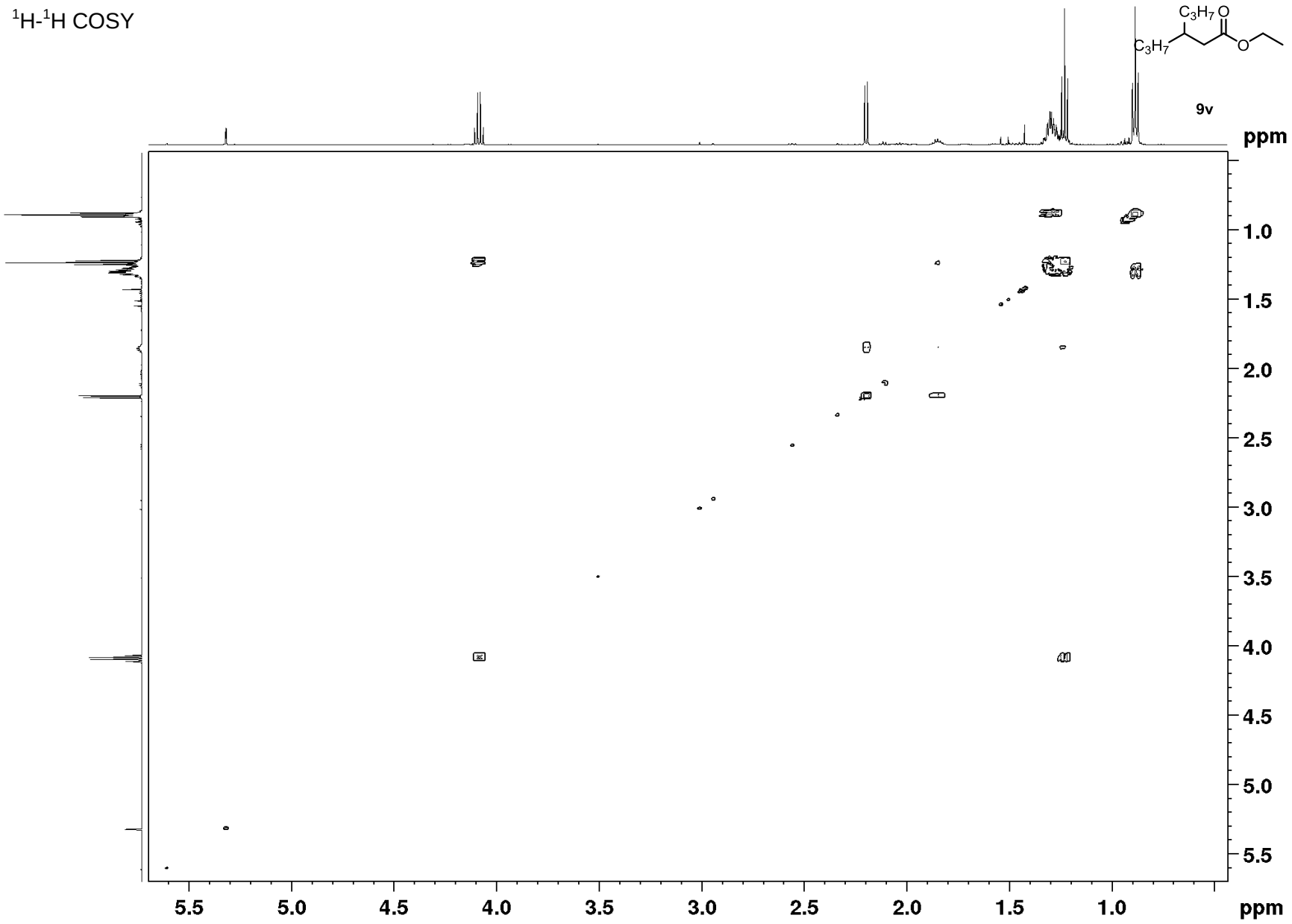
Ethyl 3-propylhexanoate (9v)

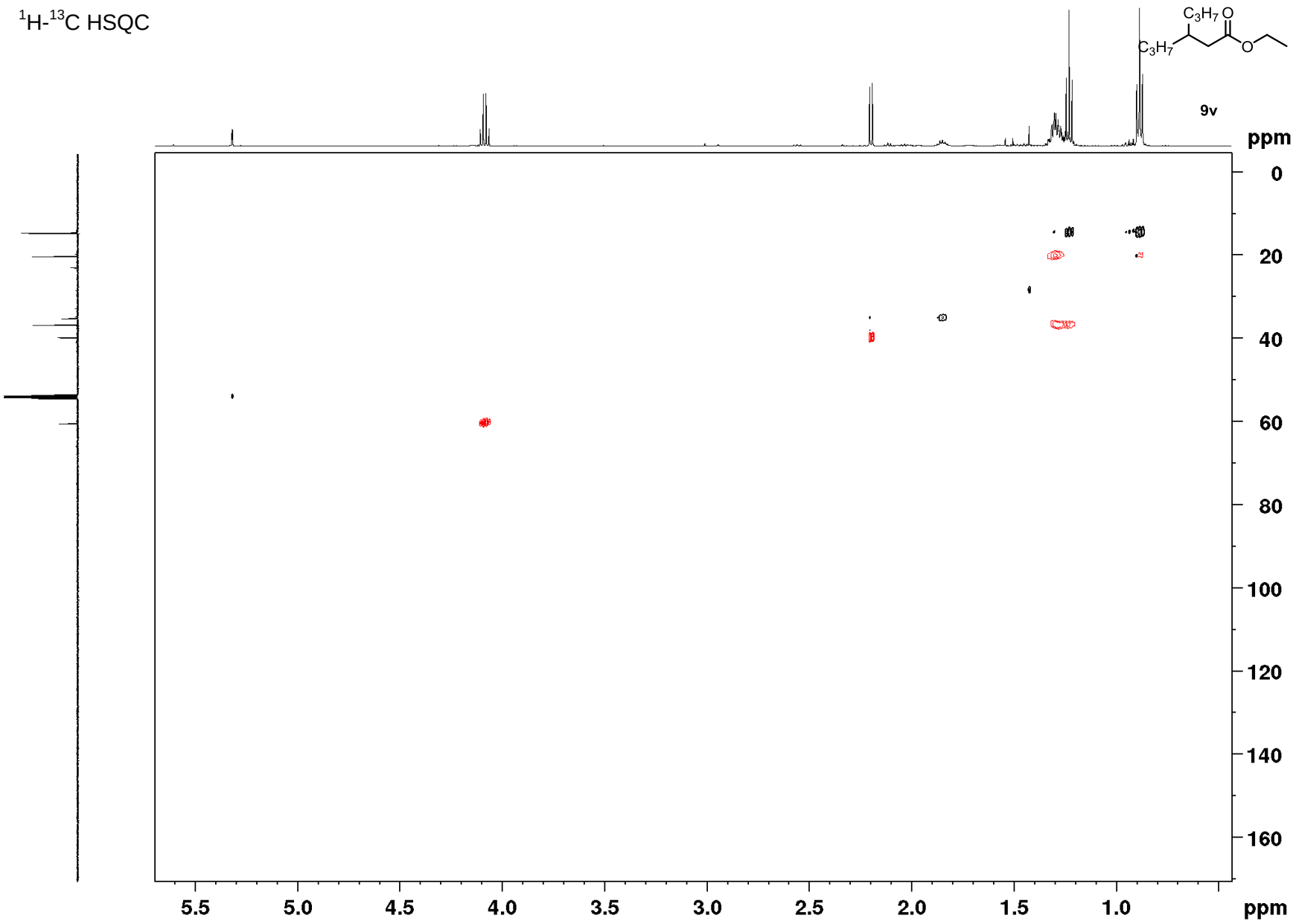
^{1}H NMR



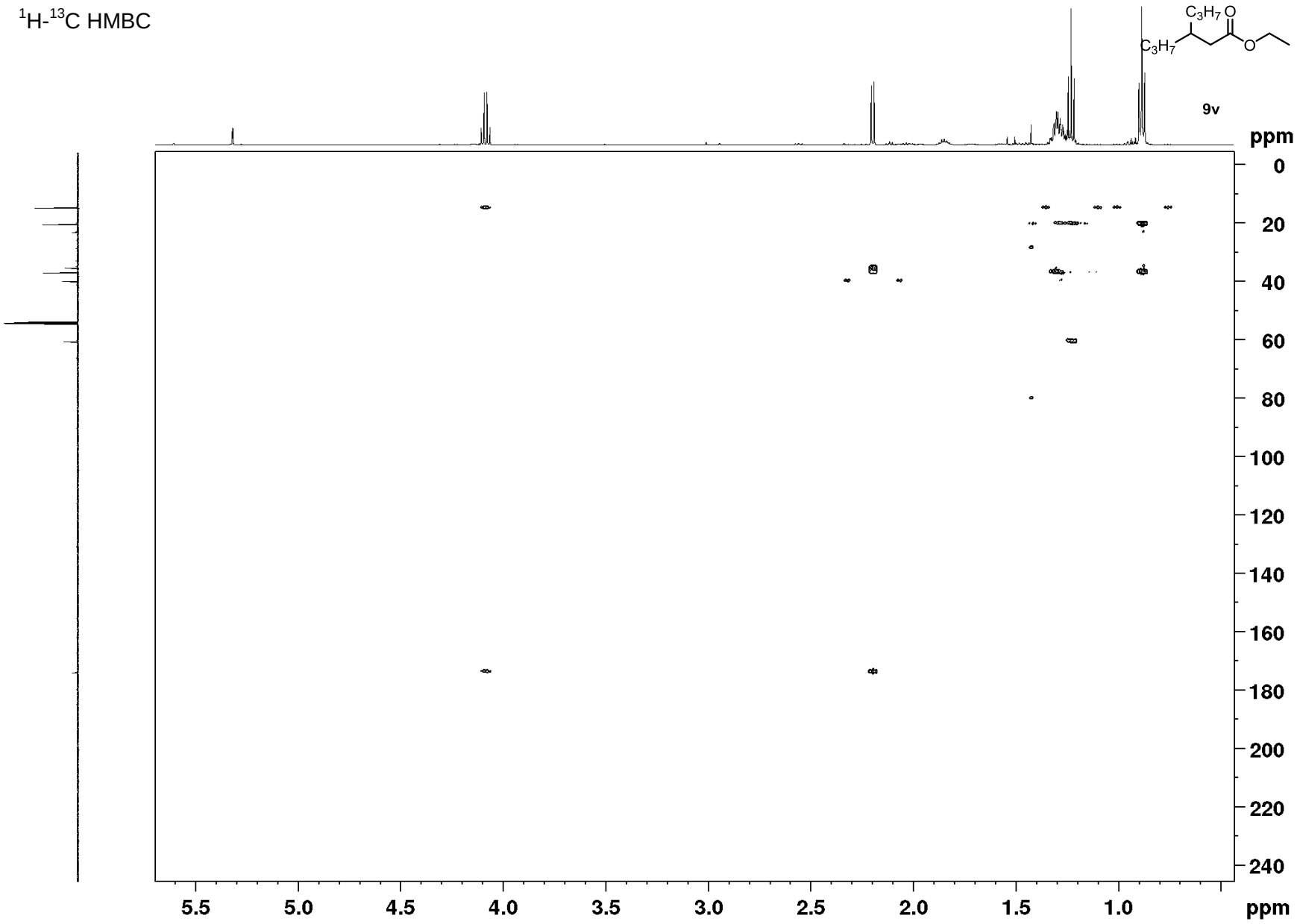

^{13}C NMR
173.7
60.3
39.6
36.6
35.0
20.1
14.5
C_3H_7 O
C_3H_7
O
9v
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

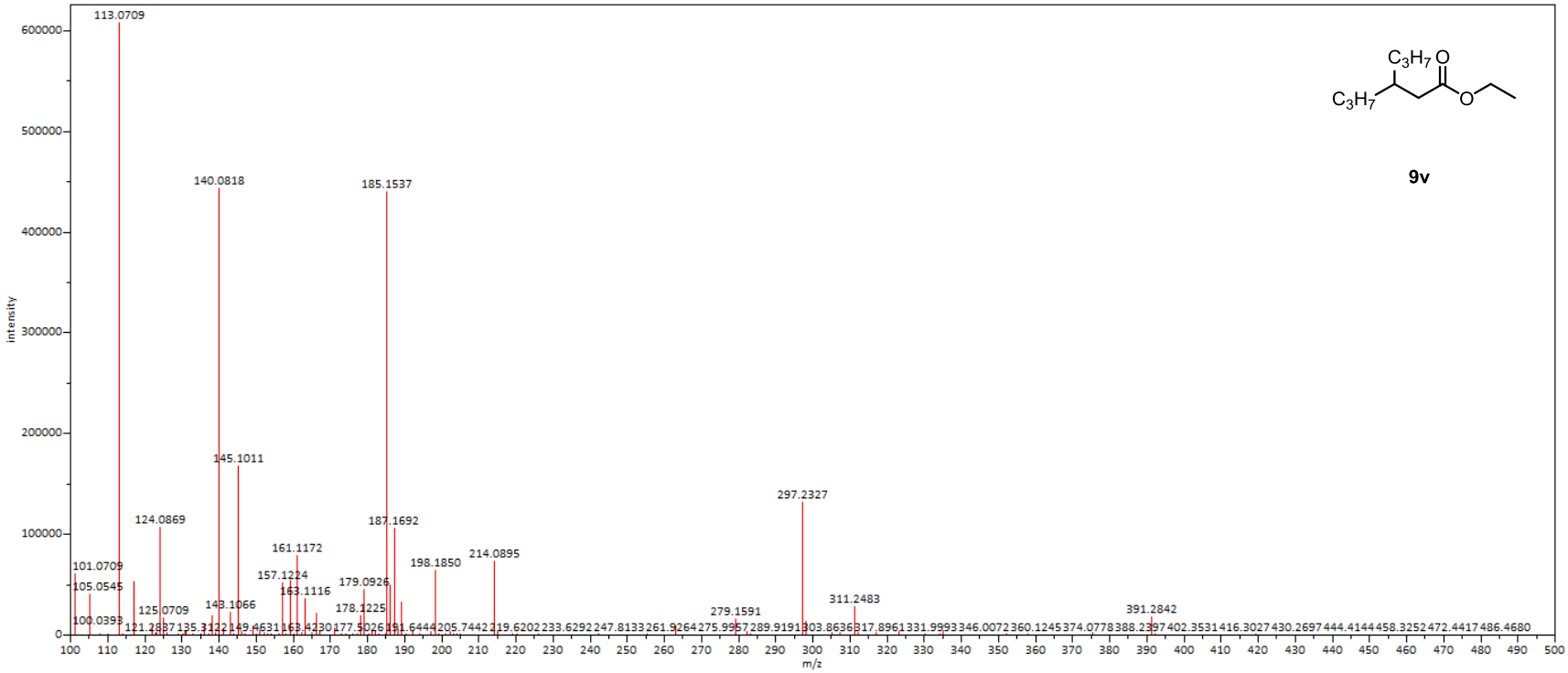
^{1}H-^{1}H COSY



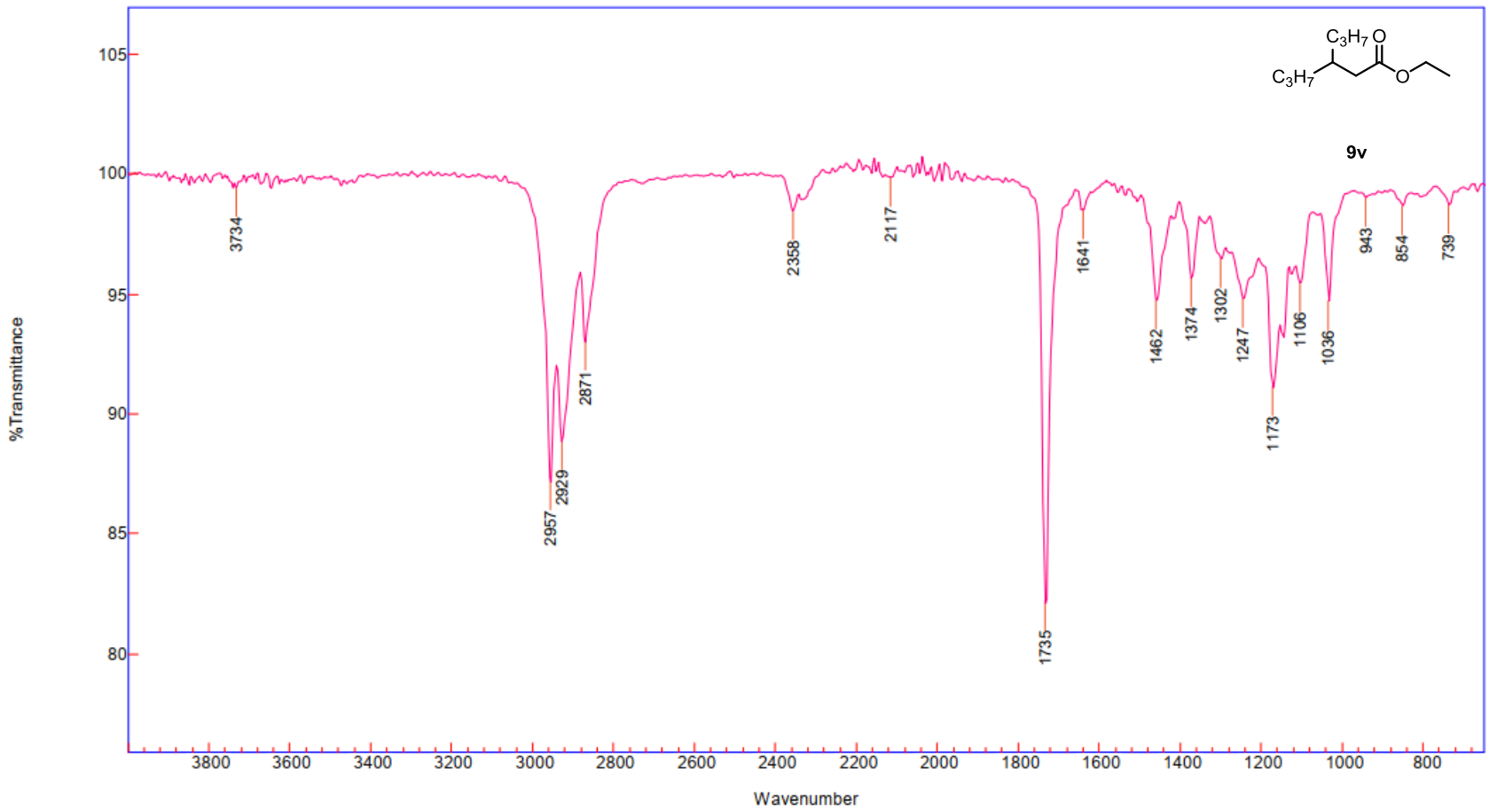

^{1}H-^{13}C HSQC
C_3H_7 O
C_3H_7
O
9v
ppm
0
20
40
60
80
100
120
140
160
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

^{1}H-^{13}C HMBC


C3H7 O
C3H7
O
9v
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

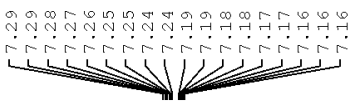

113.0709
140.0818
185.1537
145.1011
124.0869
297.2327
187.1692
161.1172
214.0895
198.1850
101.0709
105.0545
157.1224
163.1116
179.0926
143.1066
178.1225
125.0709
311.2483
279.1591
391.2842
100.0393
intensity
m/z
C_3H_7 O
C_3H_7
O

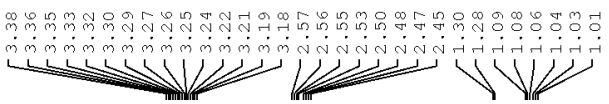
9v

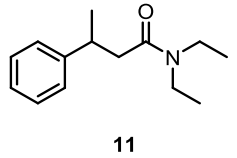

9v
%Transmittance
Wavenumber
105
100
95
90
85
80
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
3734
2957
2929
2871
2358
2117
1735
1641
1462
1374
1302
1247
1173
1106
1036
943
854
739

***N*,*N*-diethyl-3-phenylbutanamide (11)**

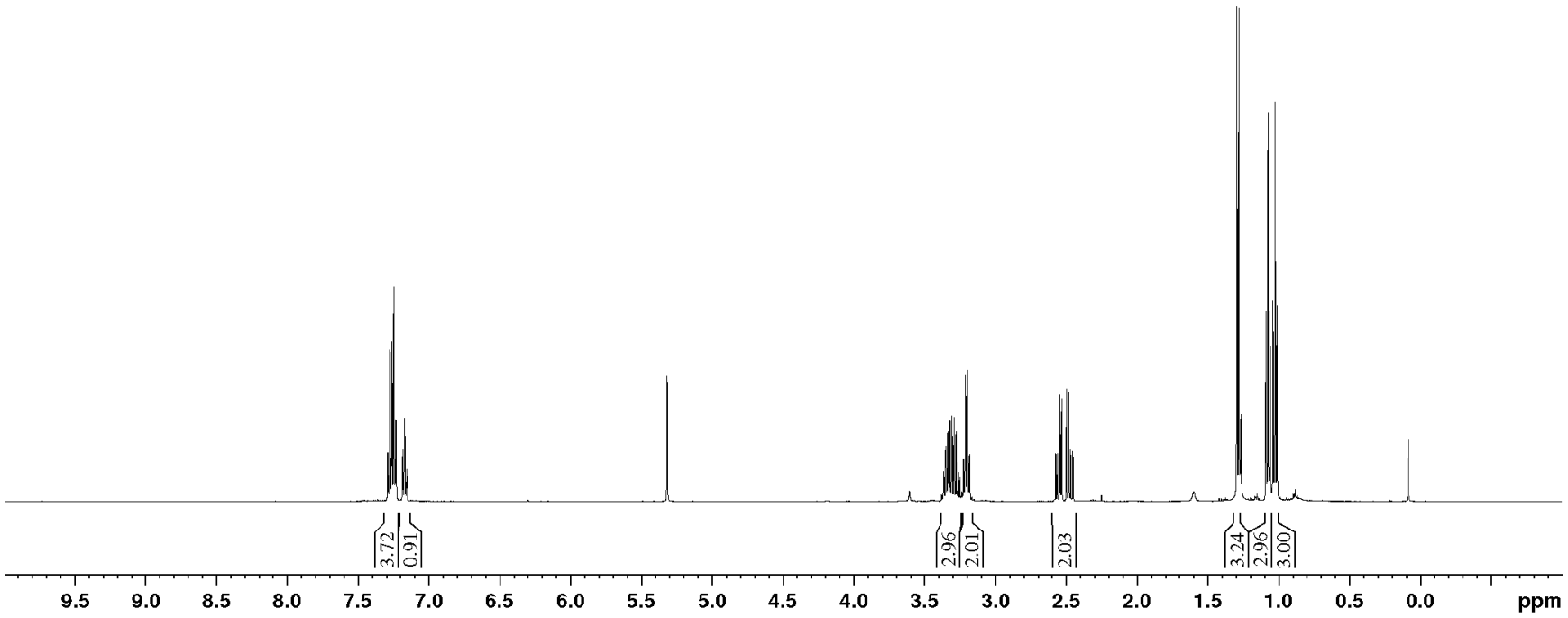
^{1}H NMR



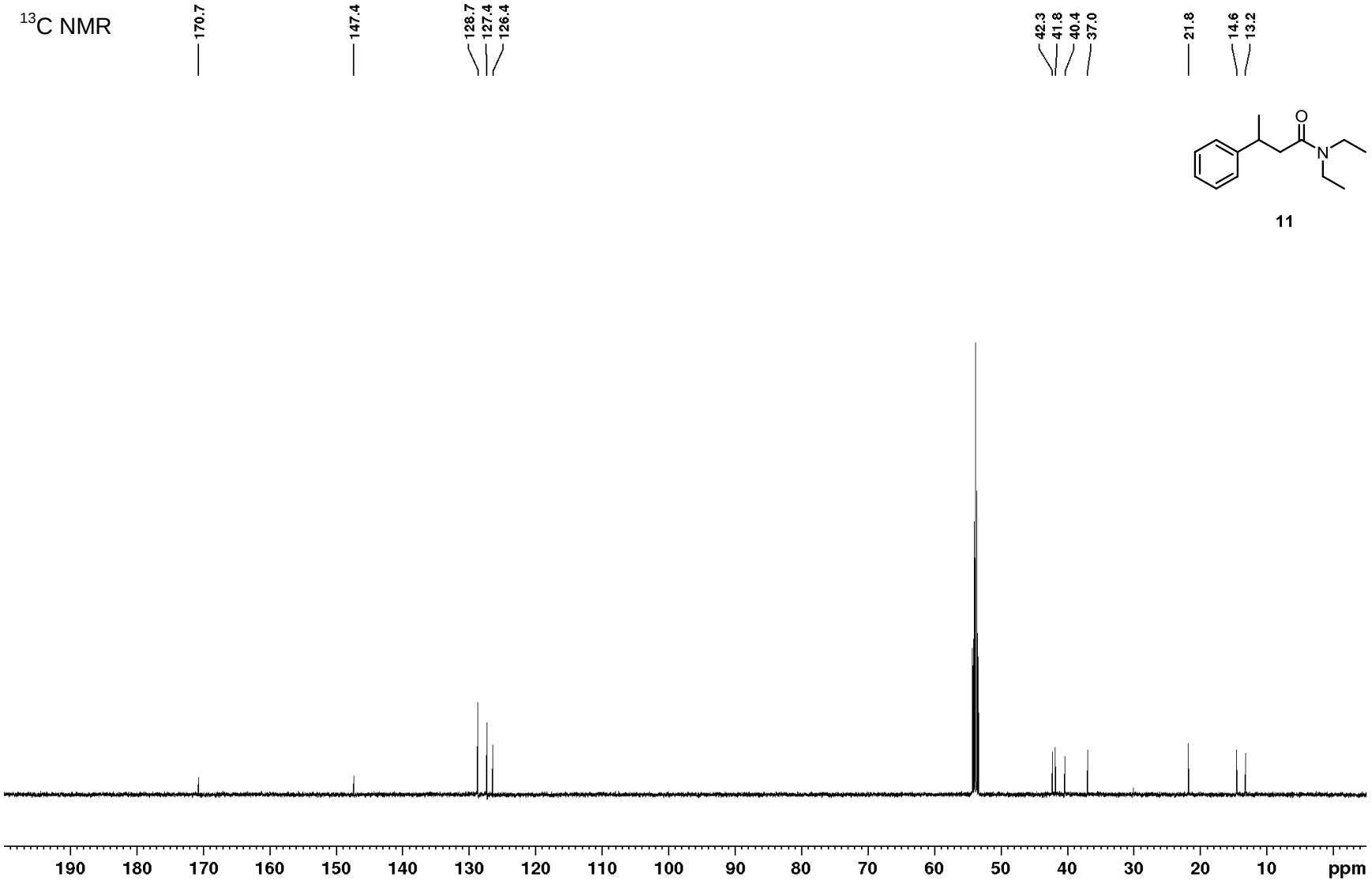




11

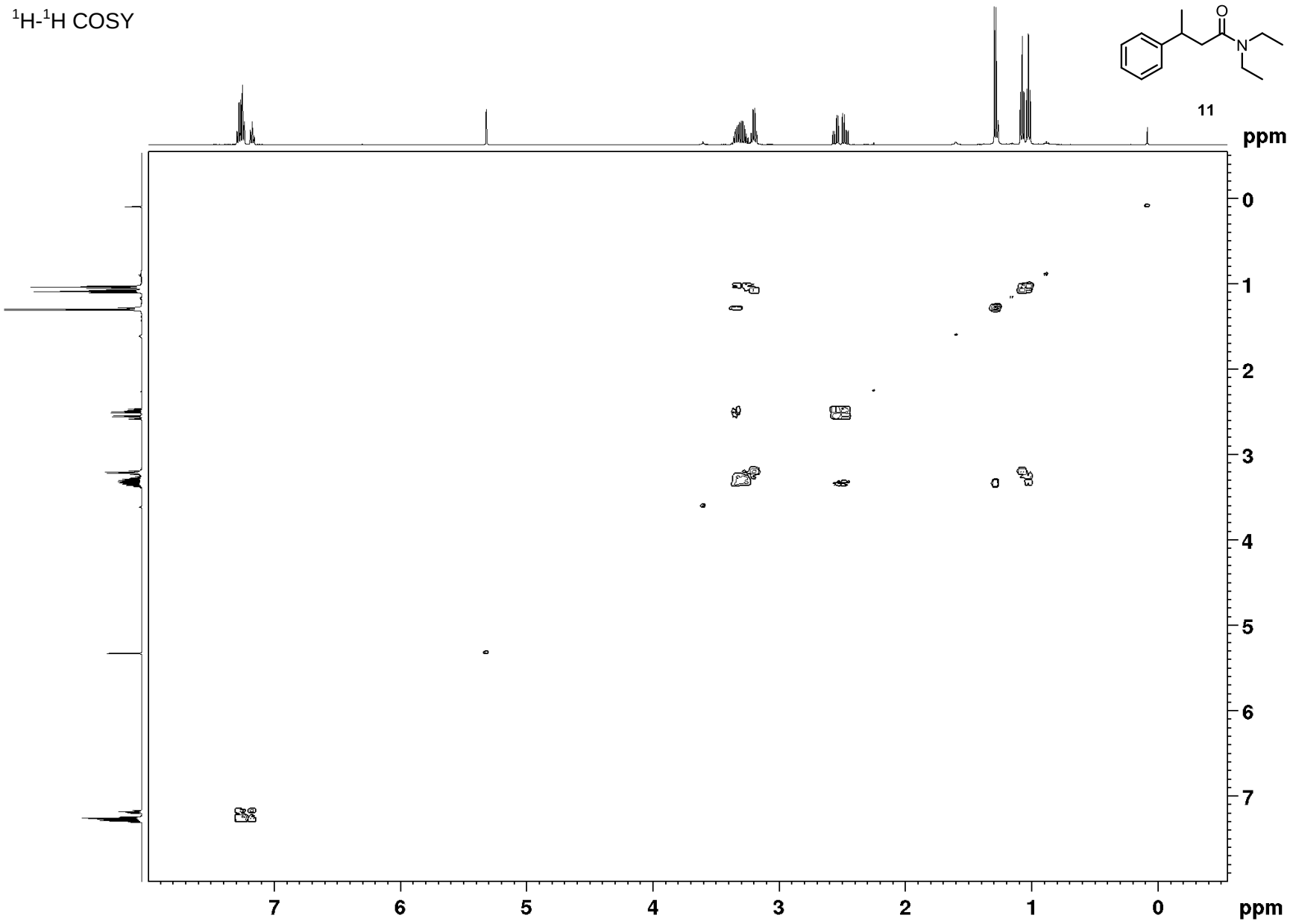


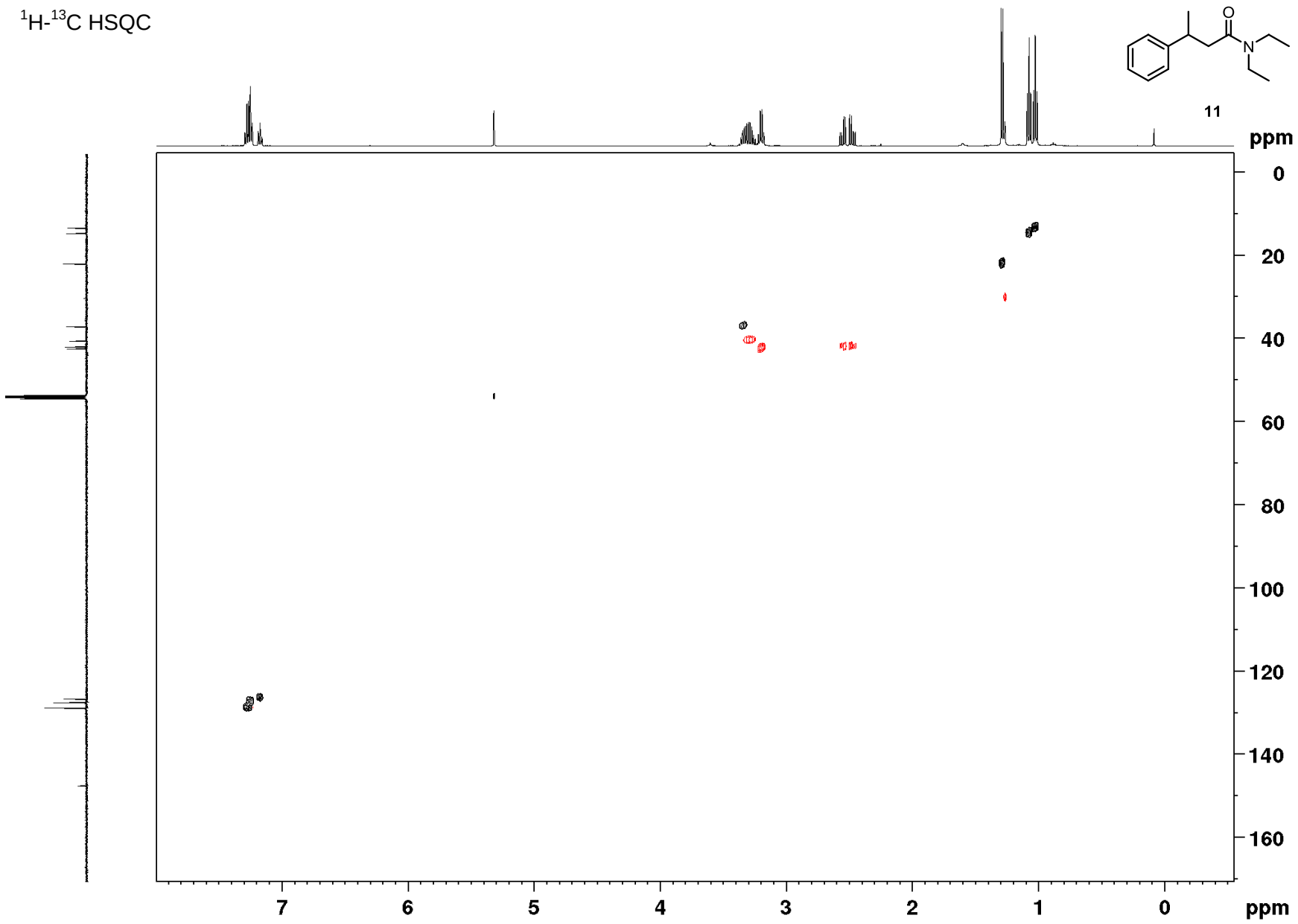
^{13}C NMR


170.7
147.4
128.7
127.4
126.4
42.3
41.8
40.4
37.0
21.8
14.6
13.2
O
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

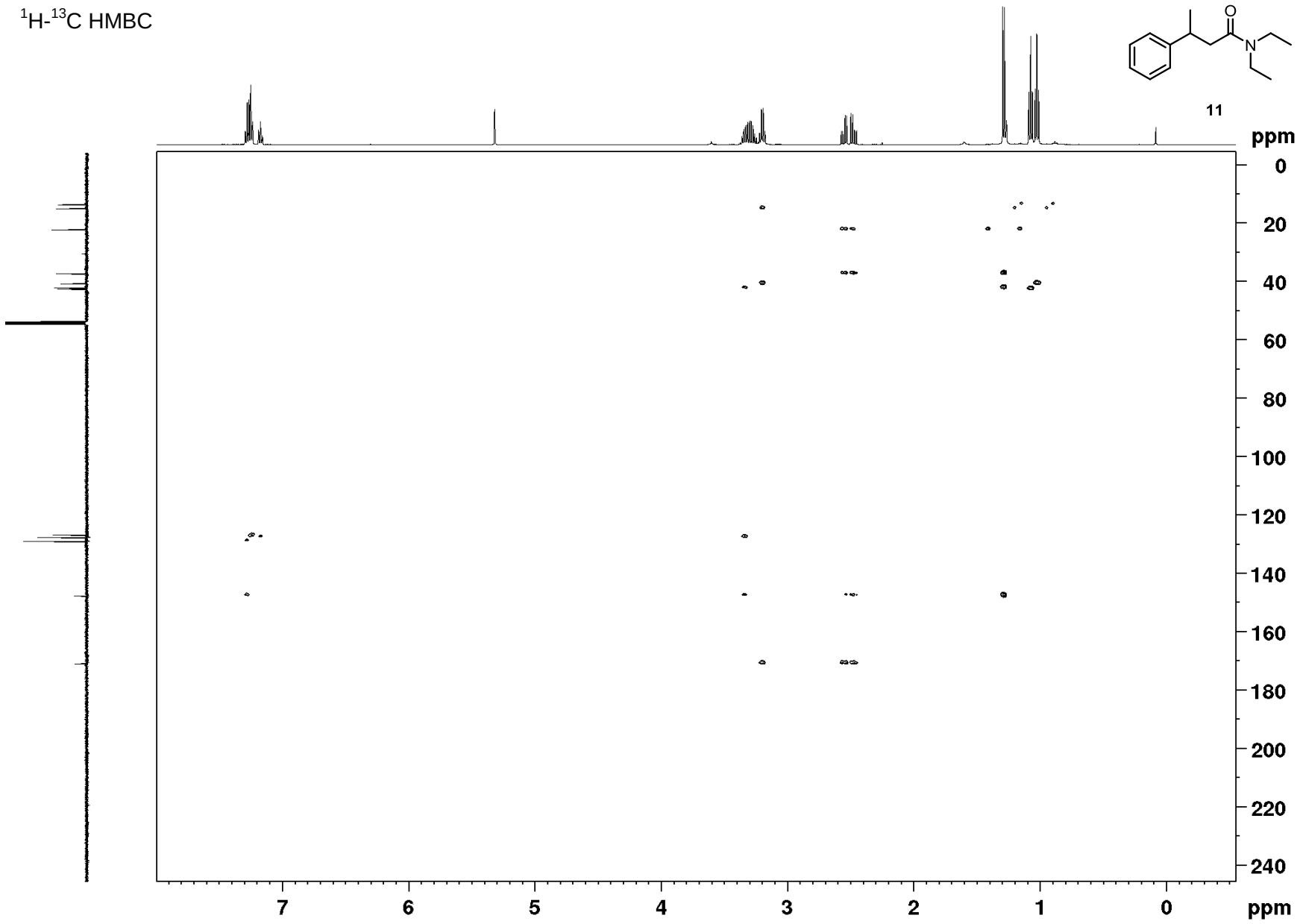
11

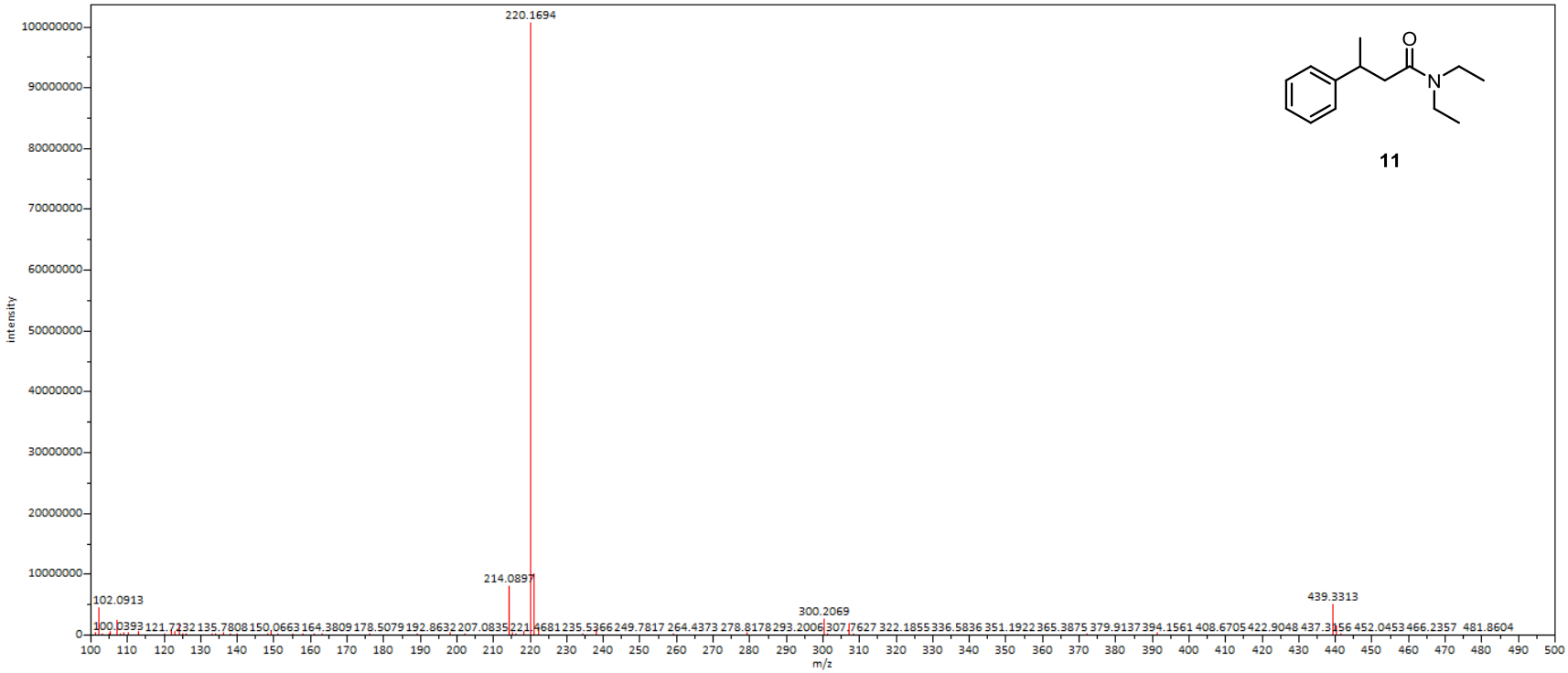
^{1}H-^{1}H COSY




^{1}H-^{13}C HSQC
O
N
11
ppm
0
20
40
60
80
100
120
140
160
7
6
5
4
3
2
1
0
ppm

^{1}H-^{13}C HMBC

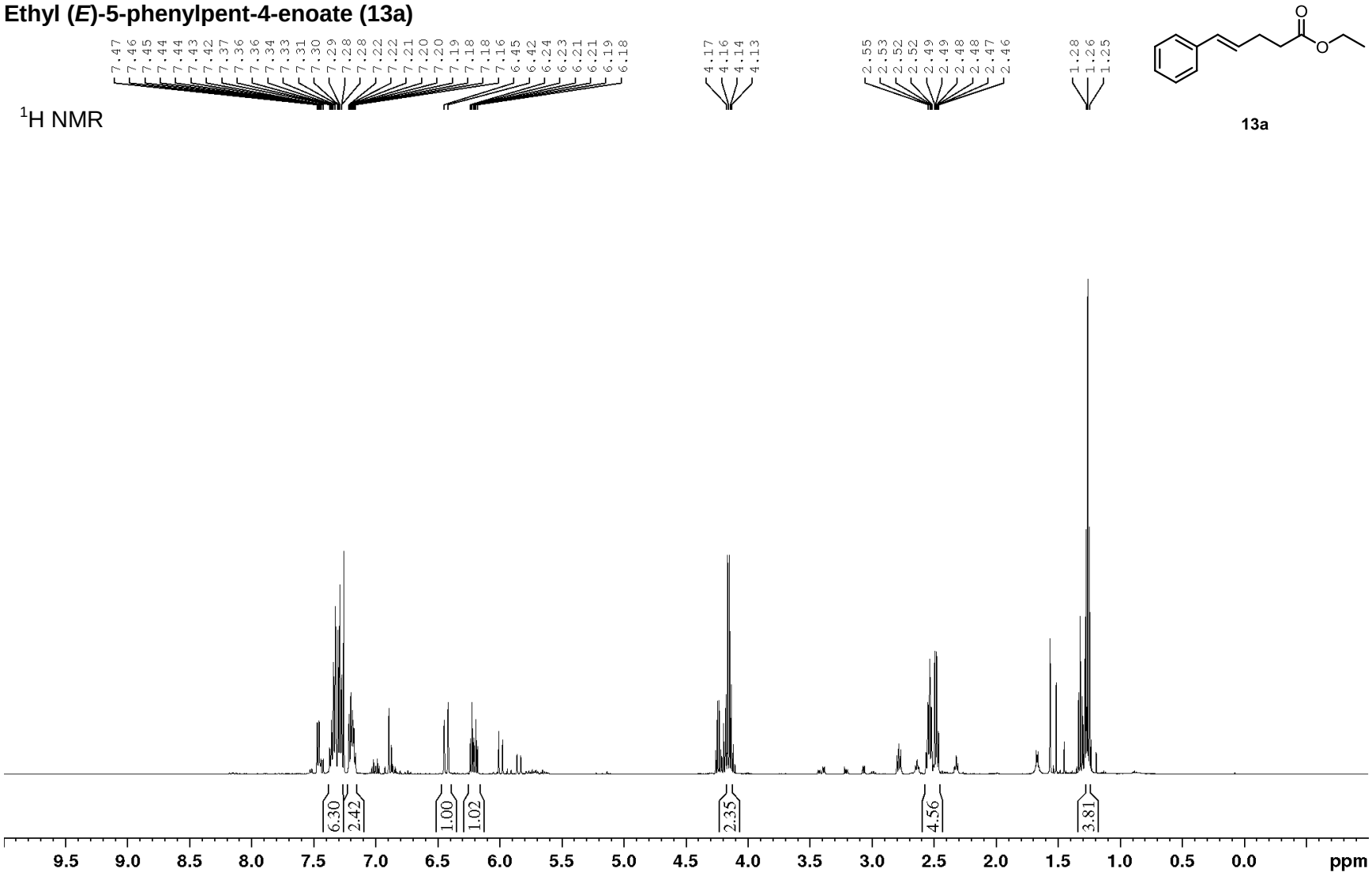

O
N
11
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7
6
5
4
3
2
1
0
ppm

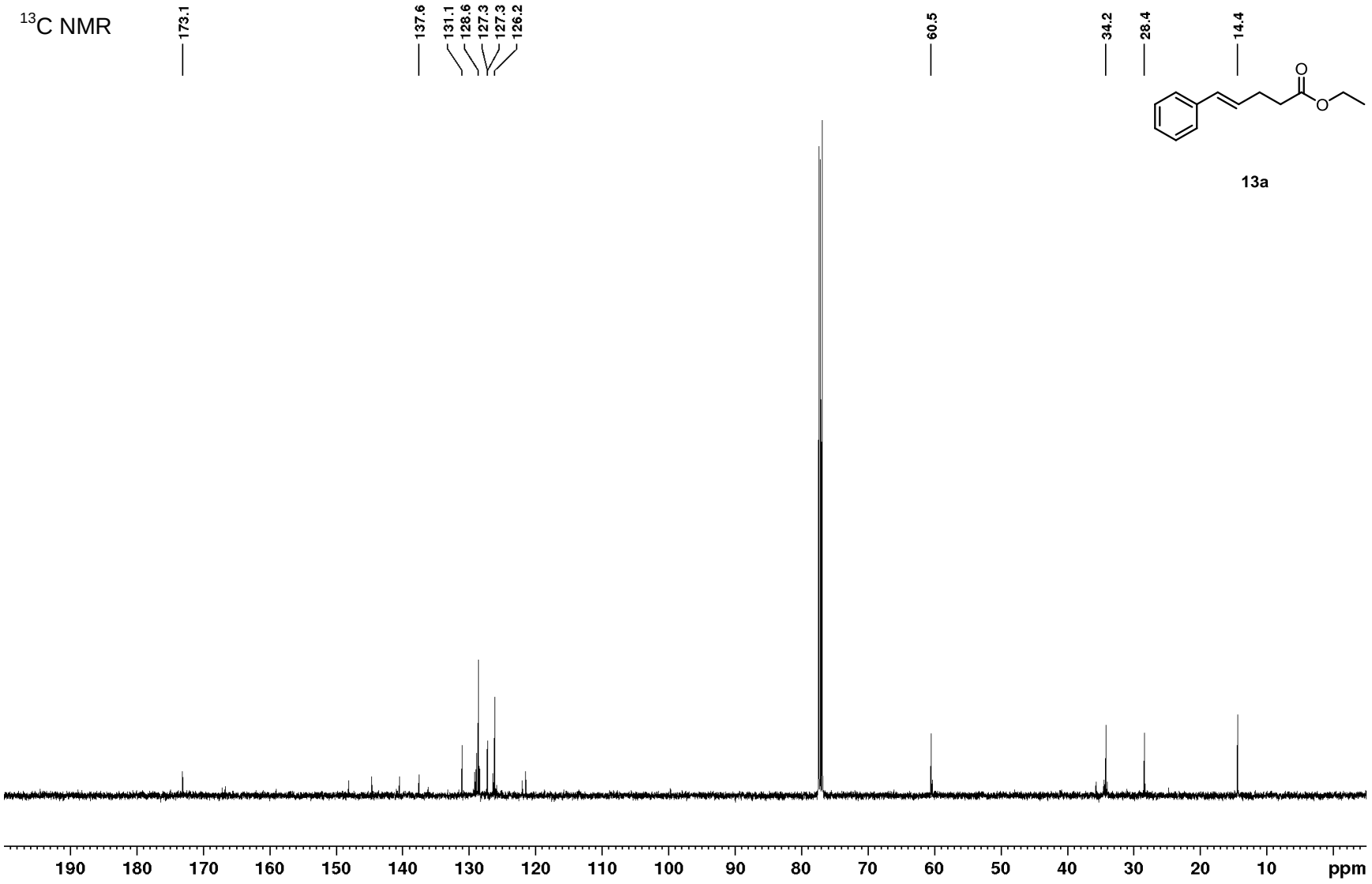

220.1694
214.0897
102.0913
300.2069
439.3313
intensity
m/z
11


11
%Transmittance
Wavenumber
105
100
95
90
85
80
75
70
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
2968
2931
2359
2235
2147
1972
1638
1454
1378
1276
1222
1142
1085
1021
909
761
701

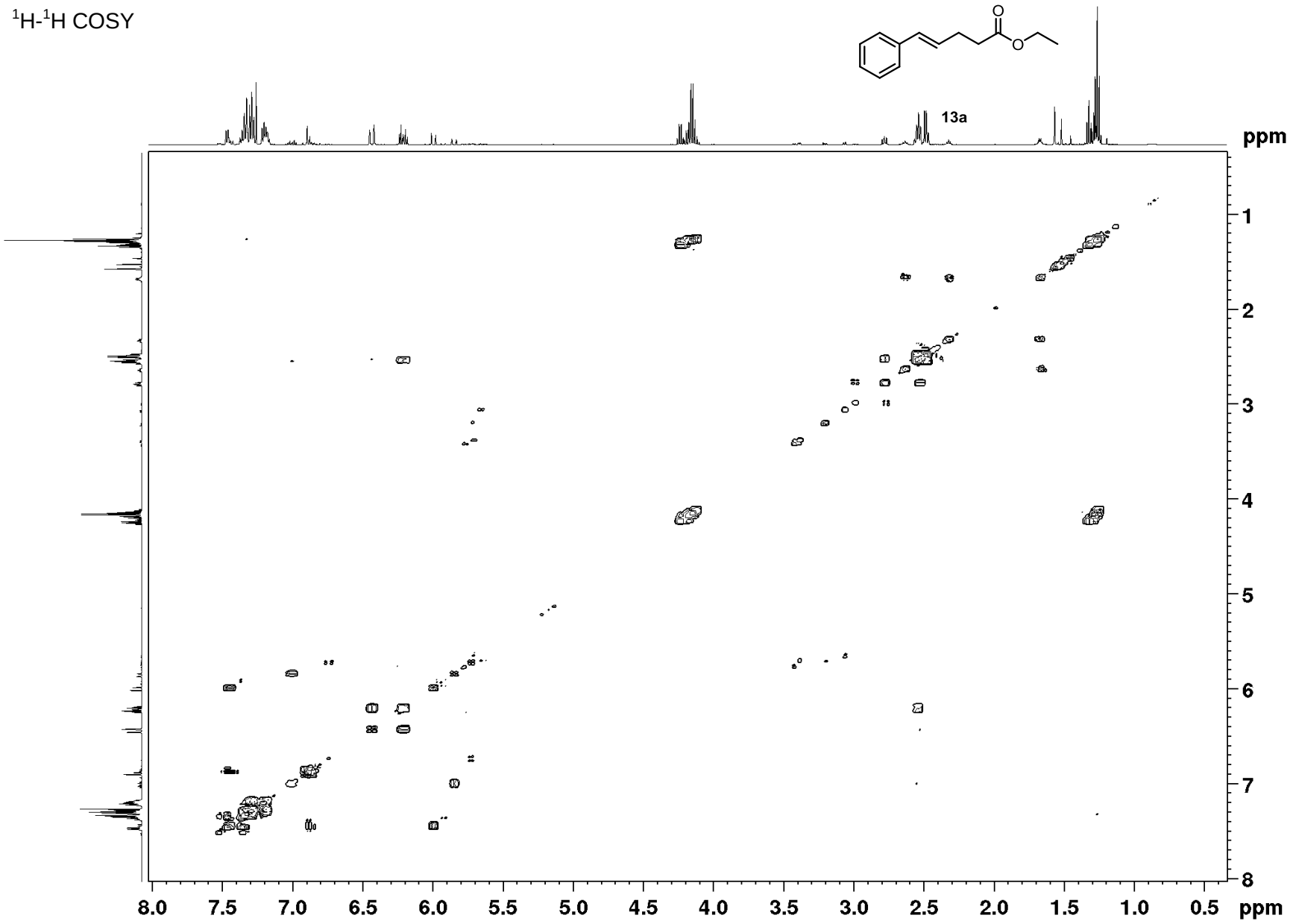
Ethyl (*E*)-5-phenylpent-4-enoate (13a)

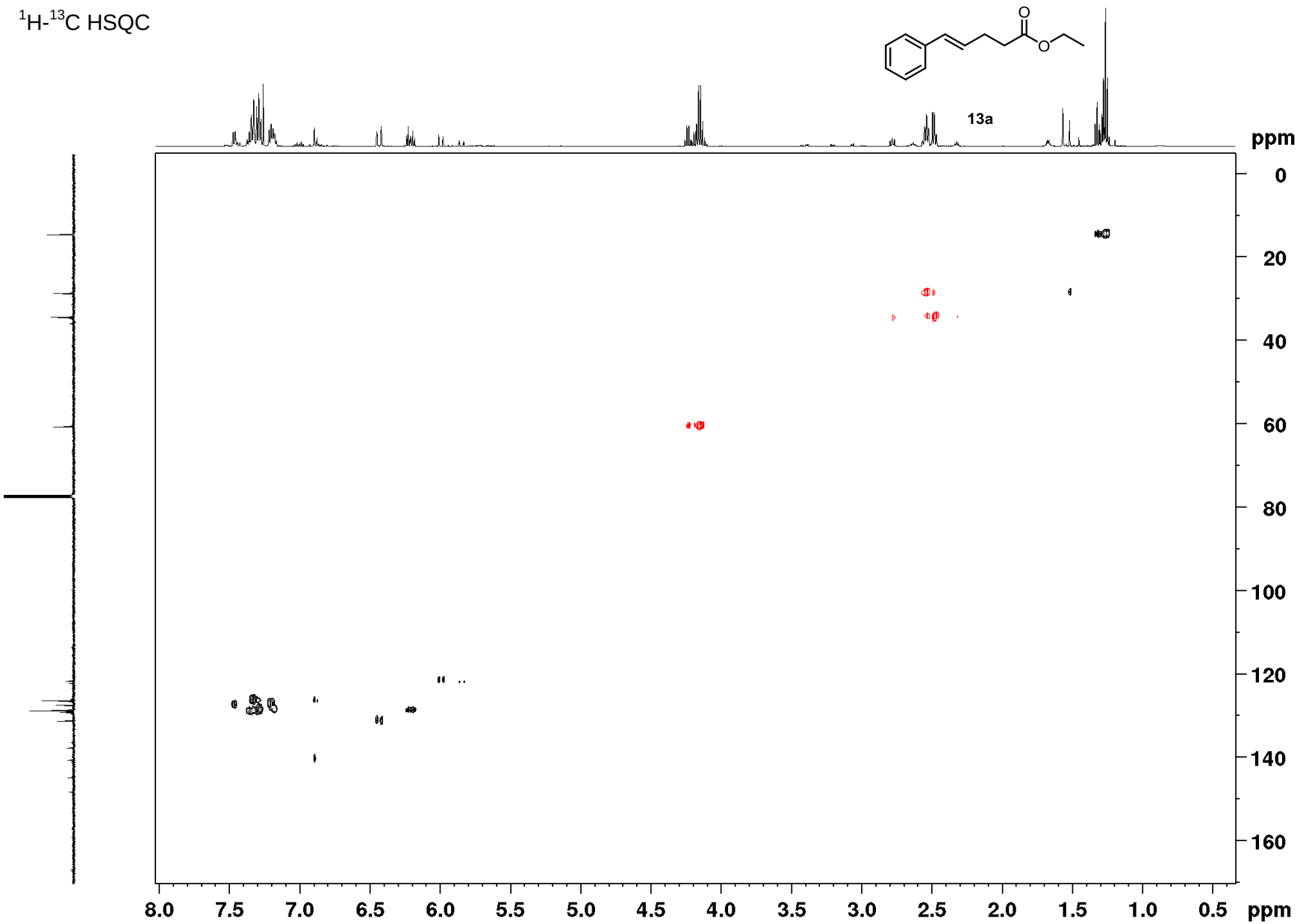
^{1}H NMR



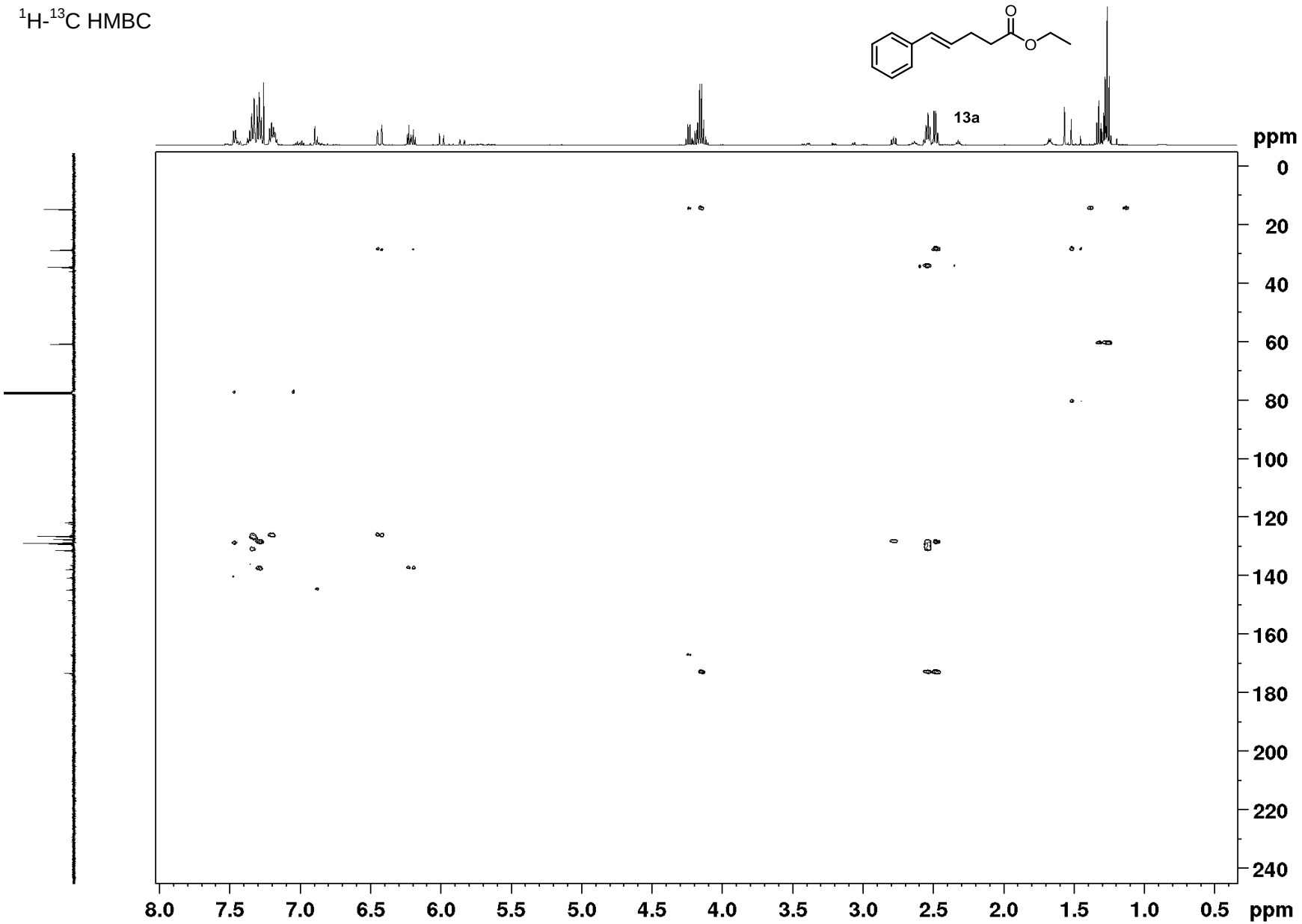

^{13}C NMR
173.1
137.6
131.1
128.6
127.3
127.3
126.2
60.5
34.2
28.4
14.4
O
O
13a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

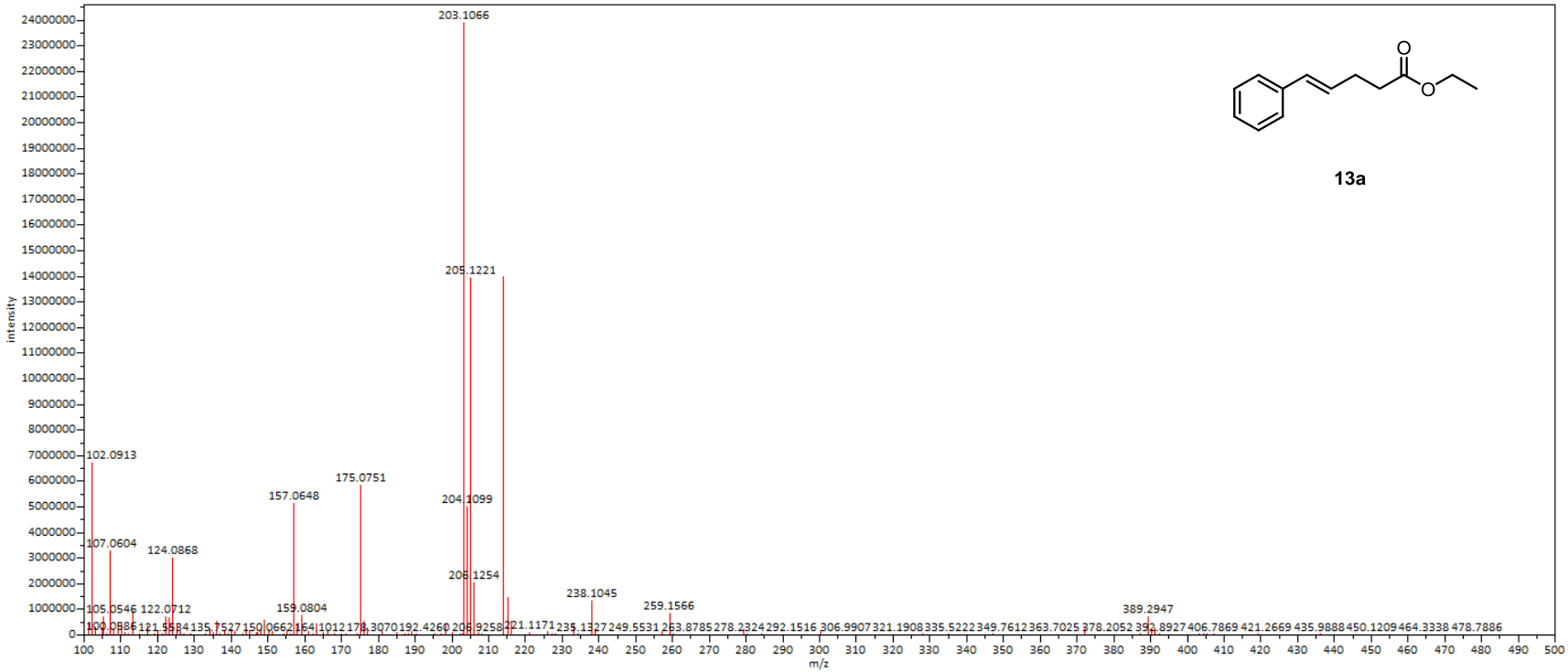
^{1}H-^{1}H COSY



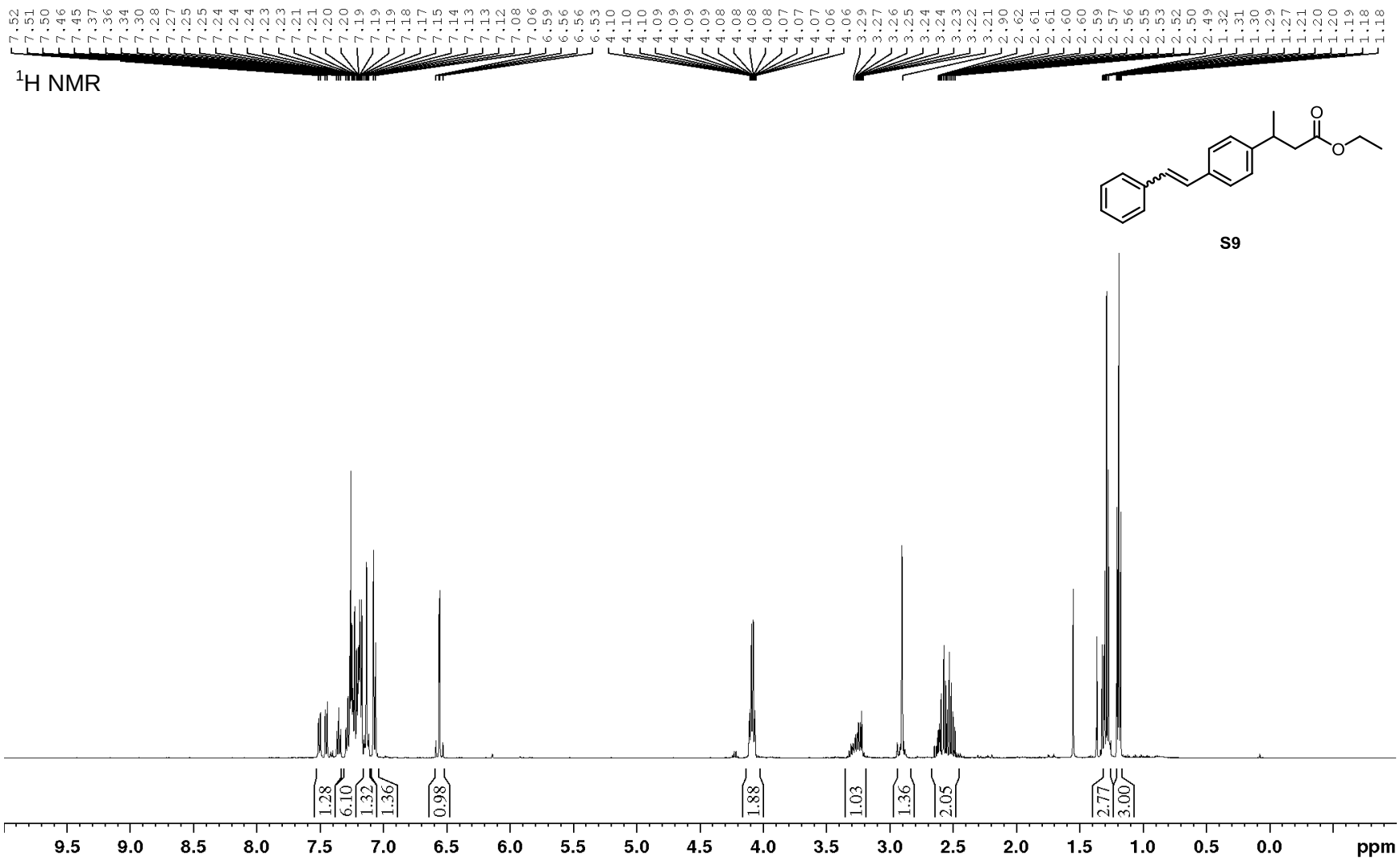

^{1}H-^{13}C HSQC
13a
ppm
0
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{1}H-^{13}C HMBC


13a
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

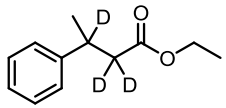

203.1066
205.1221
204.1099
206.1254
102.0913
175.0751
157.0648
107.0604
124.0868
238.1045
259.1566
389.2947
intensity
m/z
13a

Ethyl 3-(4-styrylphenyl)butanoate (S9)

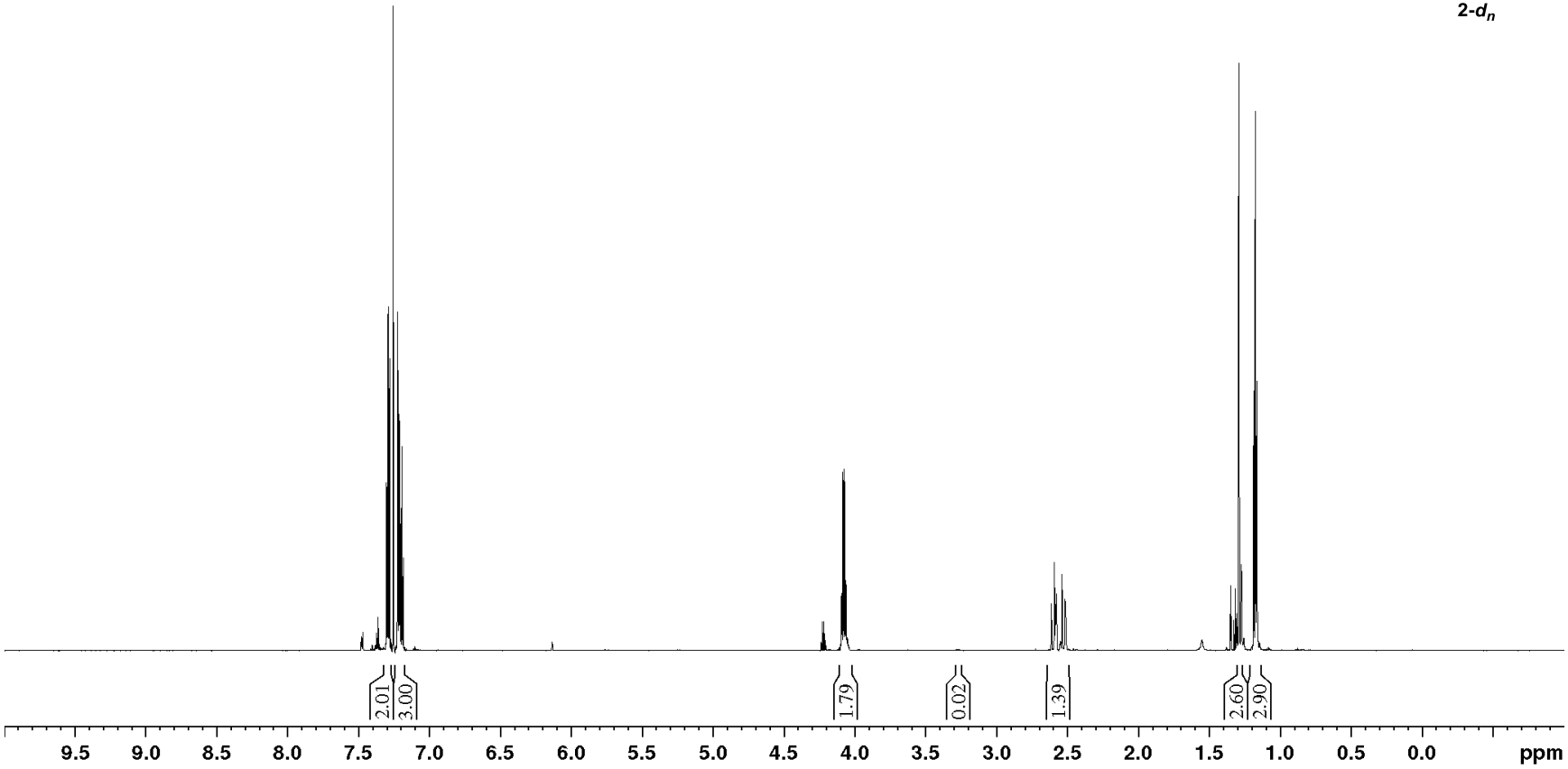


Ethyl 3-phenylbutanoate-2,3-d_n (2-d_n)

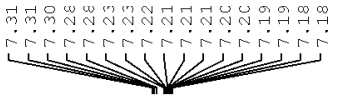
quant. ^{1}H NMR



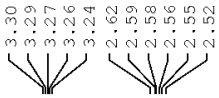
2-d_n

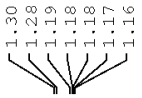


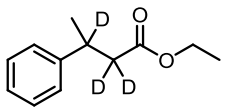
^{1}H NMR


7.31
7.31
7.30
7.26
7.26
7.23
7.23
7.22
7.21
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.18

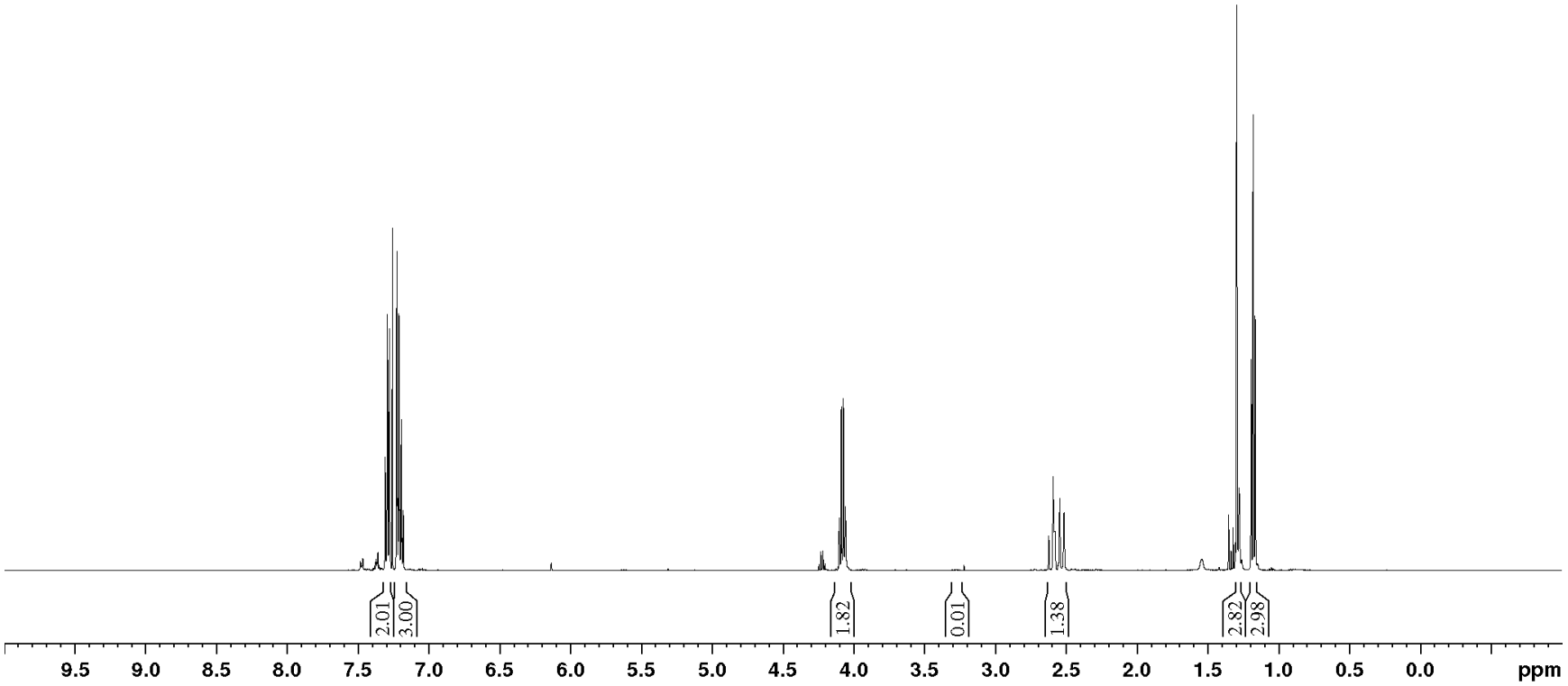

4.10
4.08
4.07
4.06

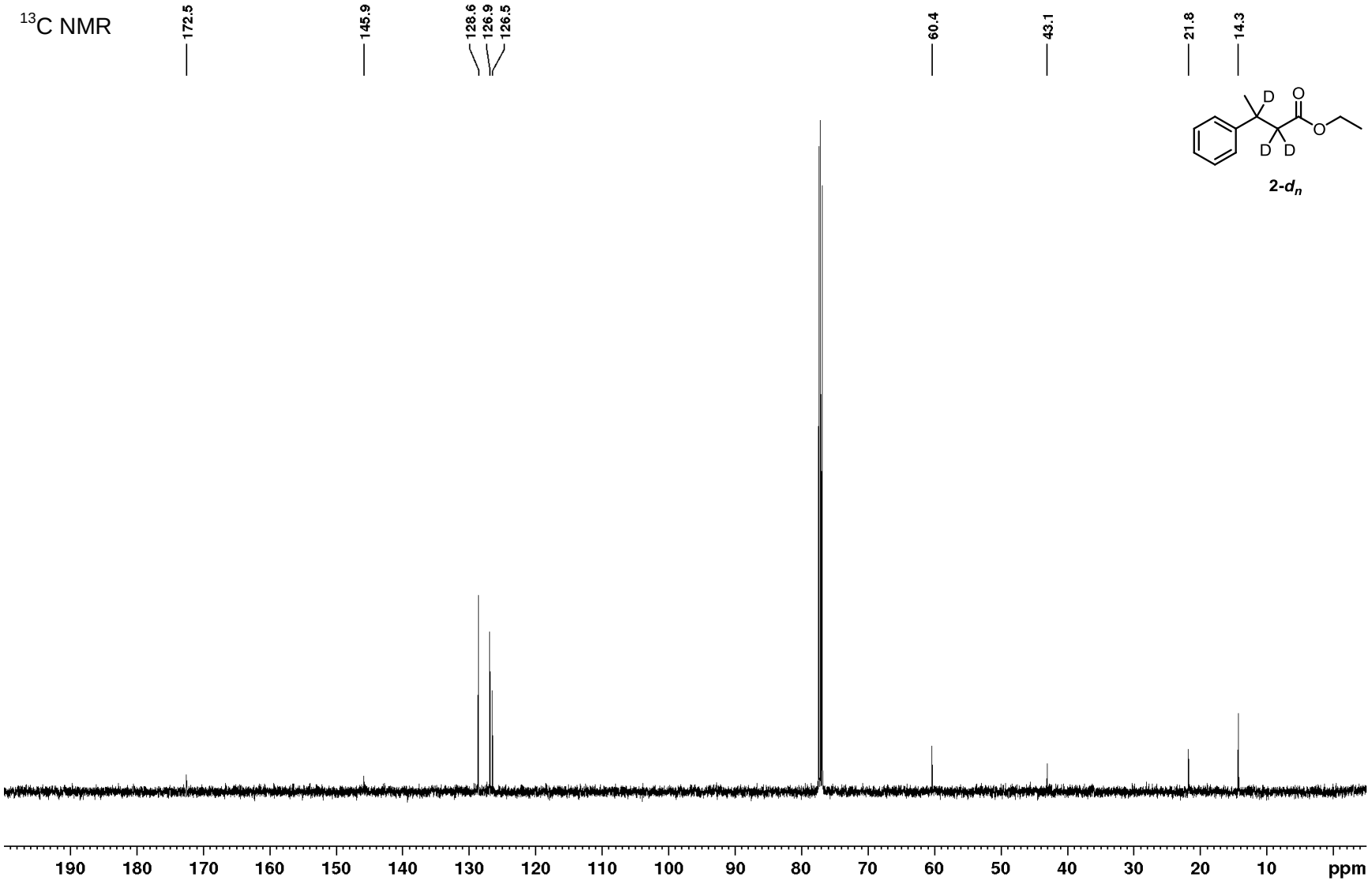

3.30
3.29
3.27
3.26
3.24
2.62
2.59
2.58
2.56
2.55
2.52


1.30
1.28
1.19
1.18
1.18
1.17
1.16

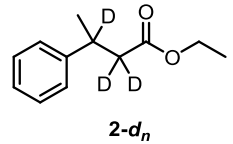

D
O
O
D
D

2-d_n

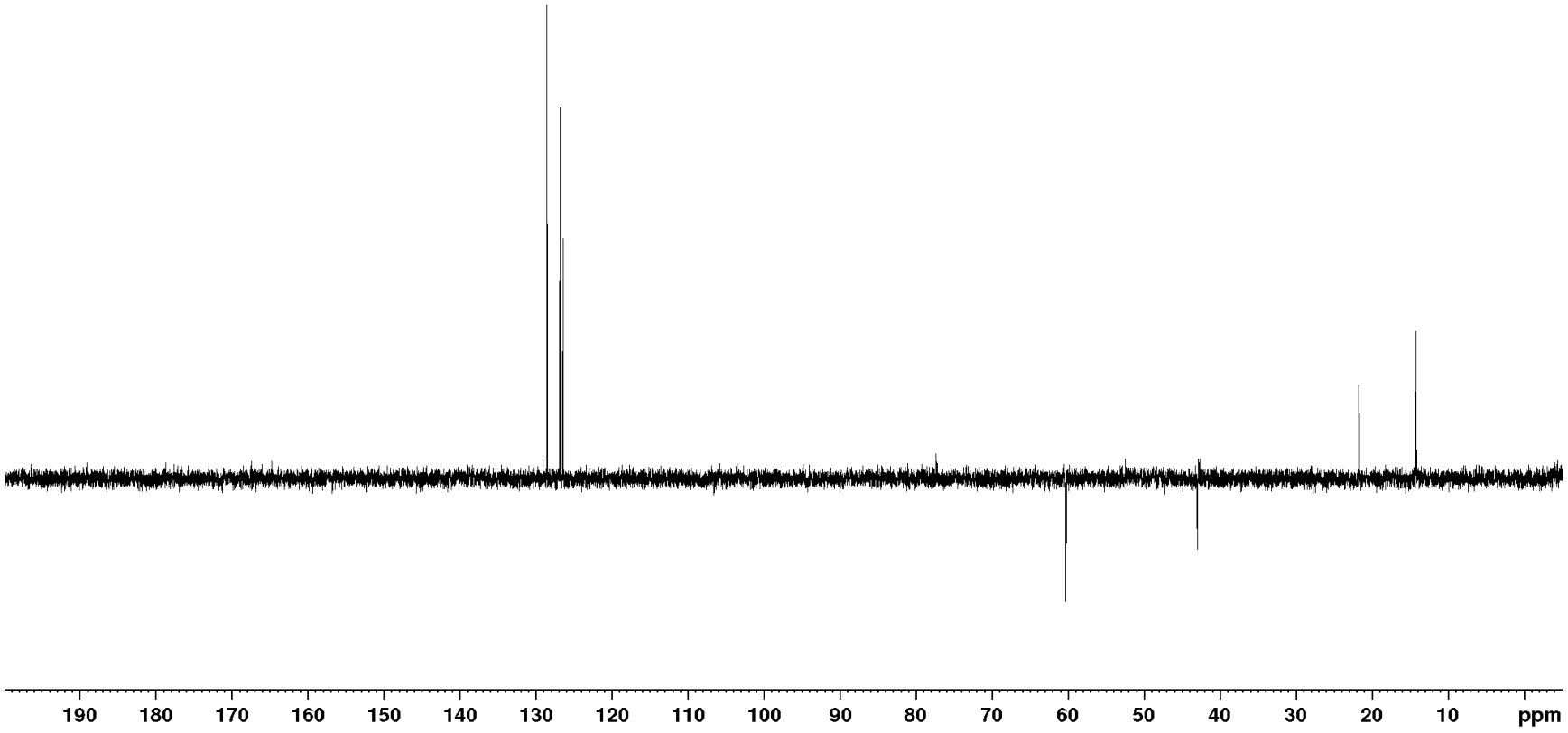

2.01
3.00
1.82
0.01
1.38
2.82
2.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


^{13}C NMR
172.5
145.9
128.6
126.9
126.5
60.4
43.1
21.8
14.3
D
O
O
D
D
2-d_n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

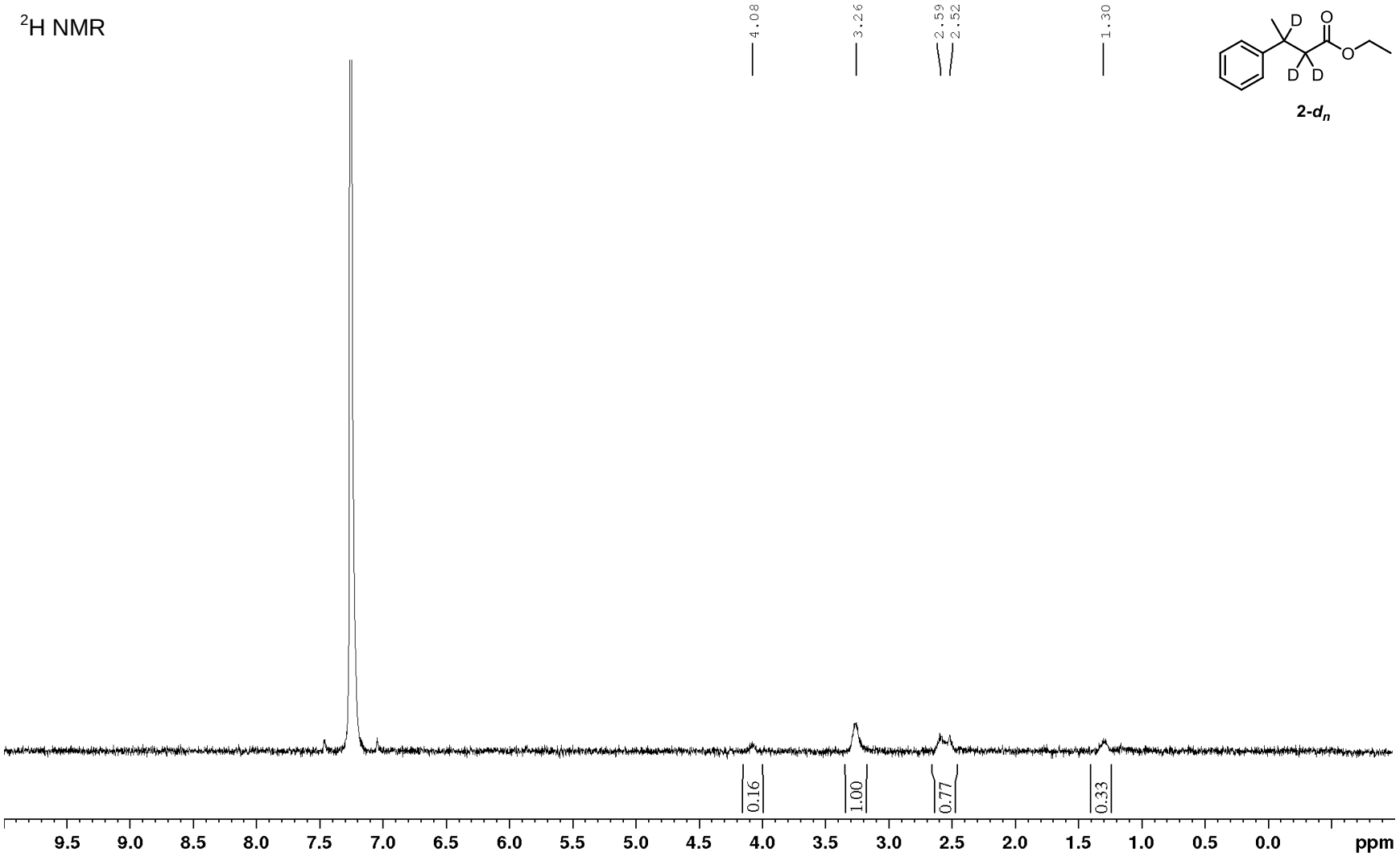
^{13}C DEPT NMR



2-d_n

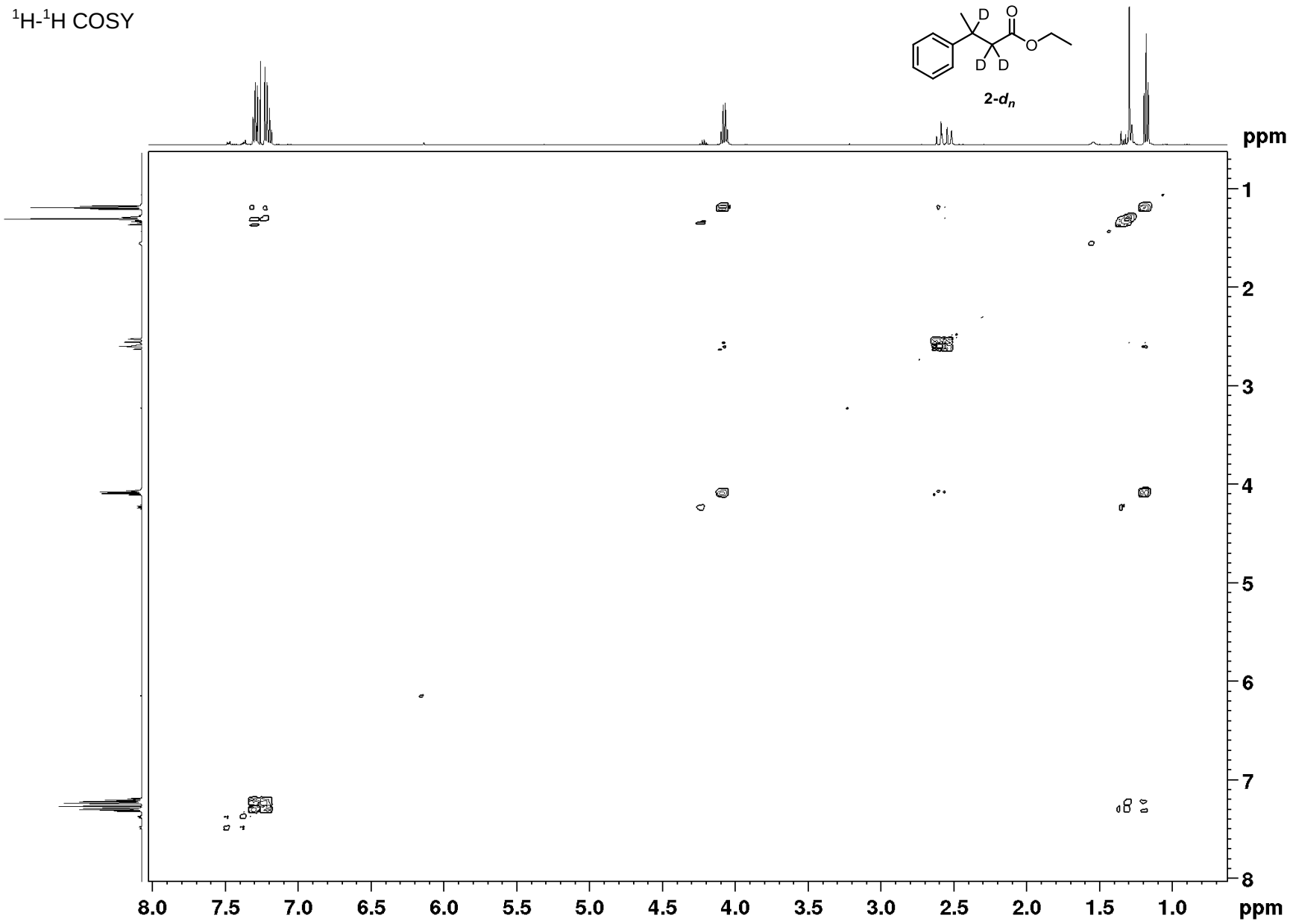


^{2}H NMR

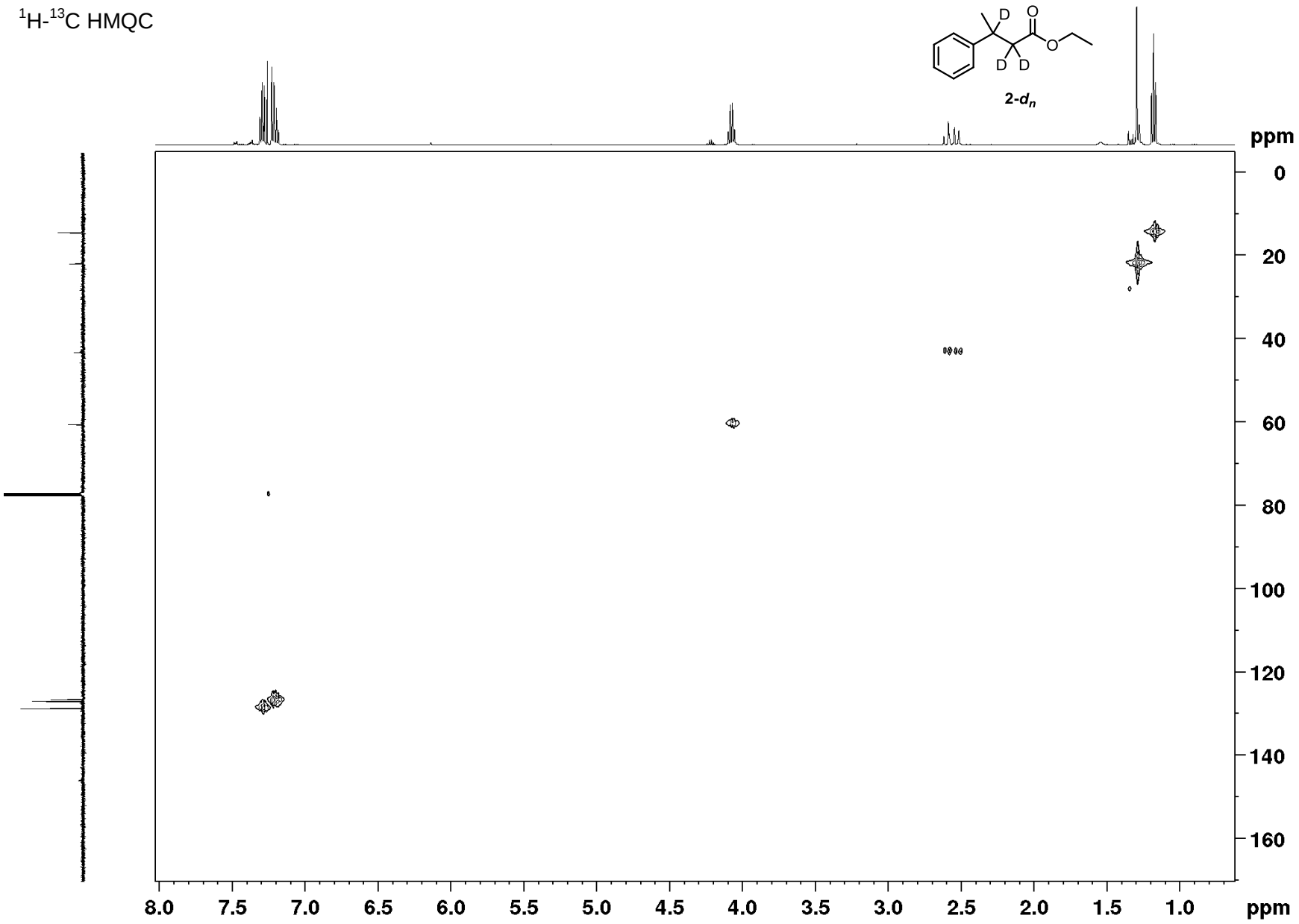

4.08
3.26
2.59
2.52
1.30
D
O
D
D
O
0.16
1.00
0.77
0.33
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

2-d_n

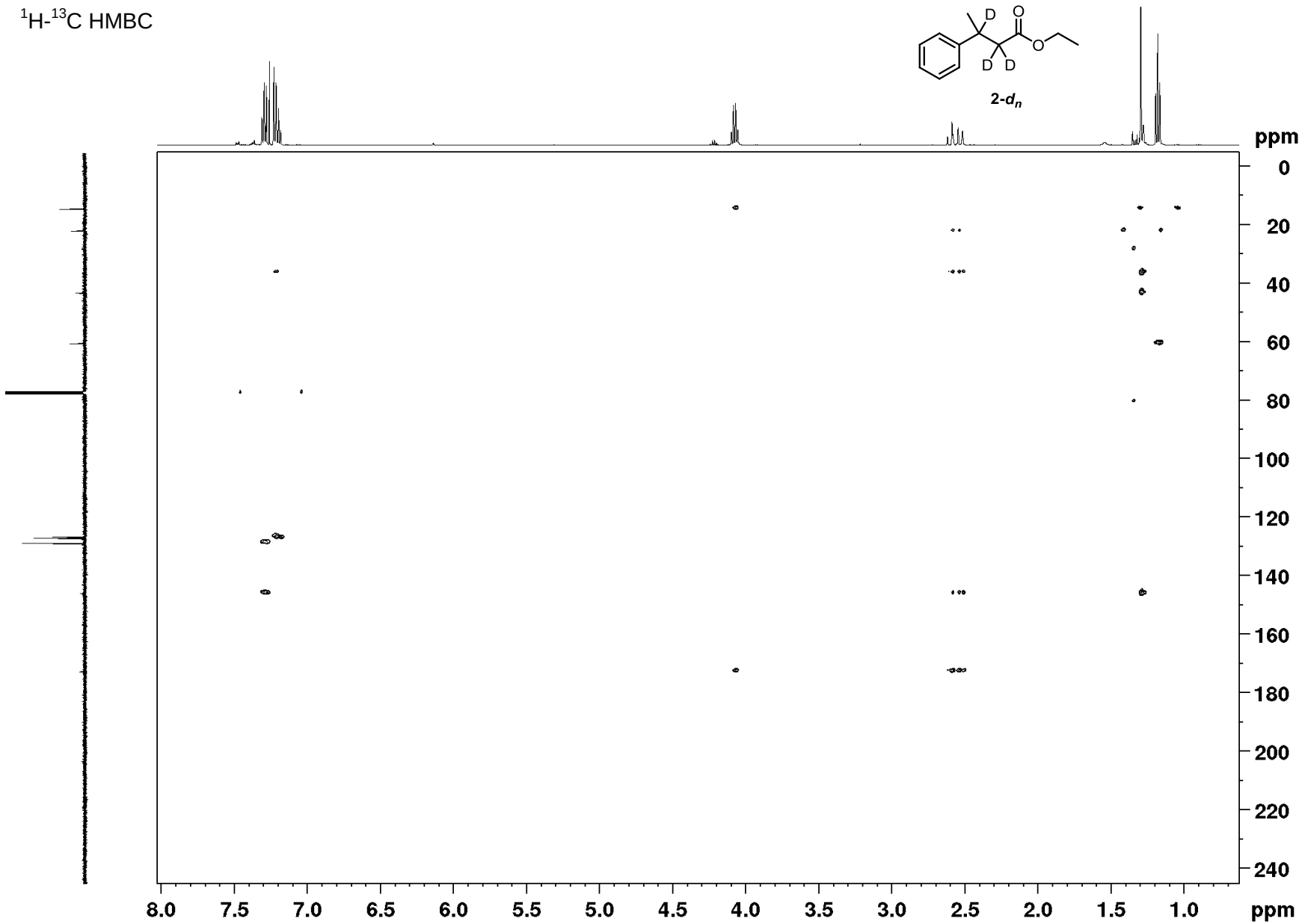
^{1}H-^{1}H COSY

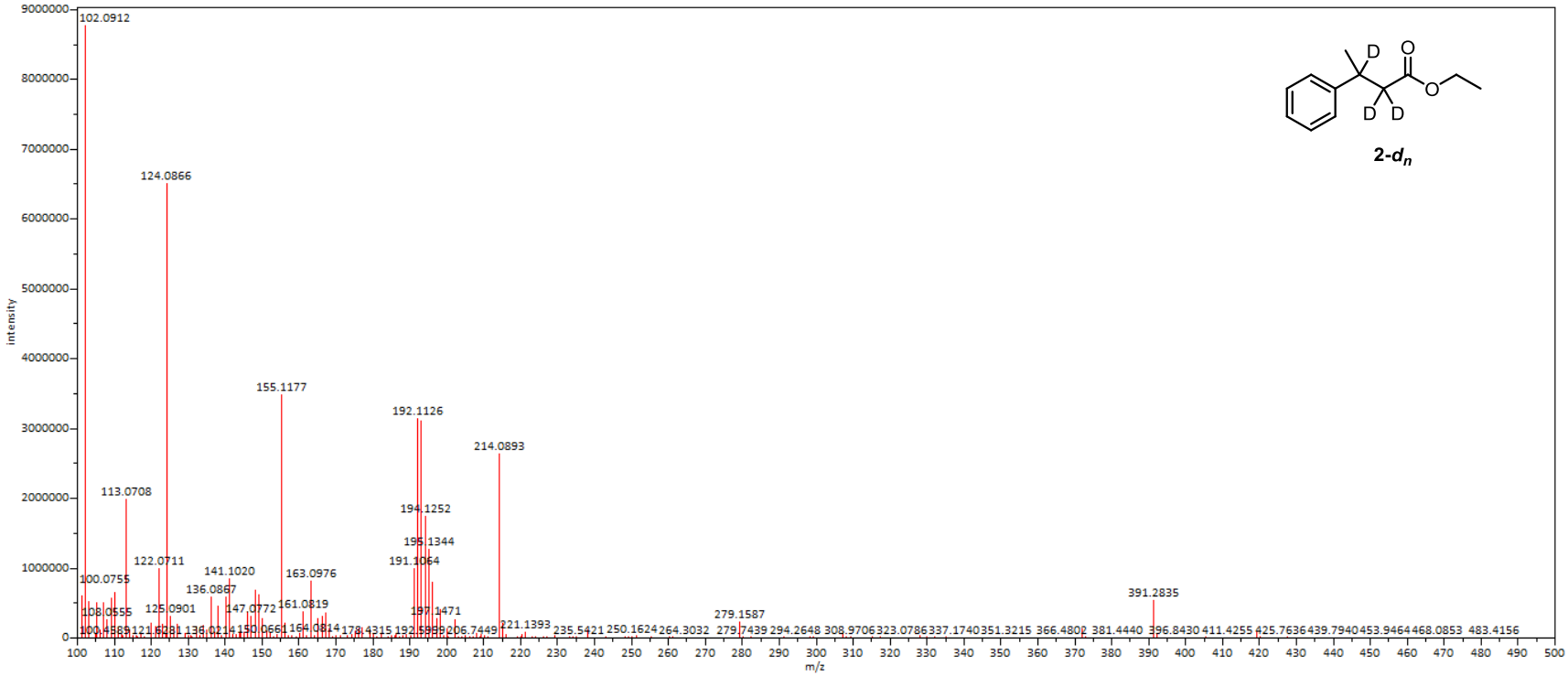

D
O
O
D D
2-d_n
ppm
1
2
3
4
5
6
7
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

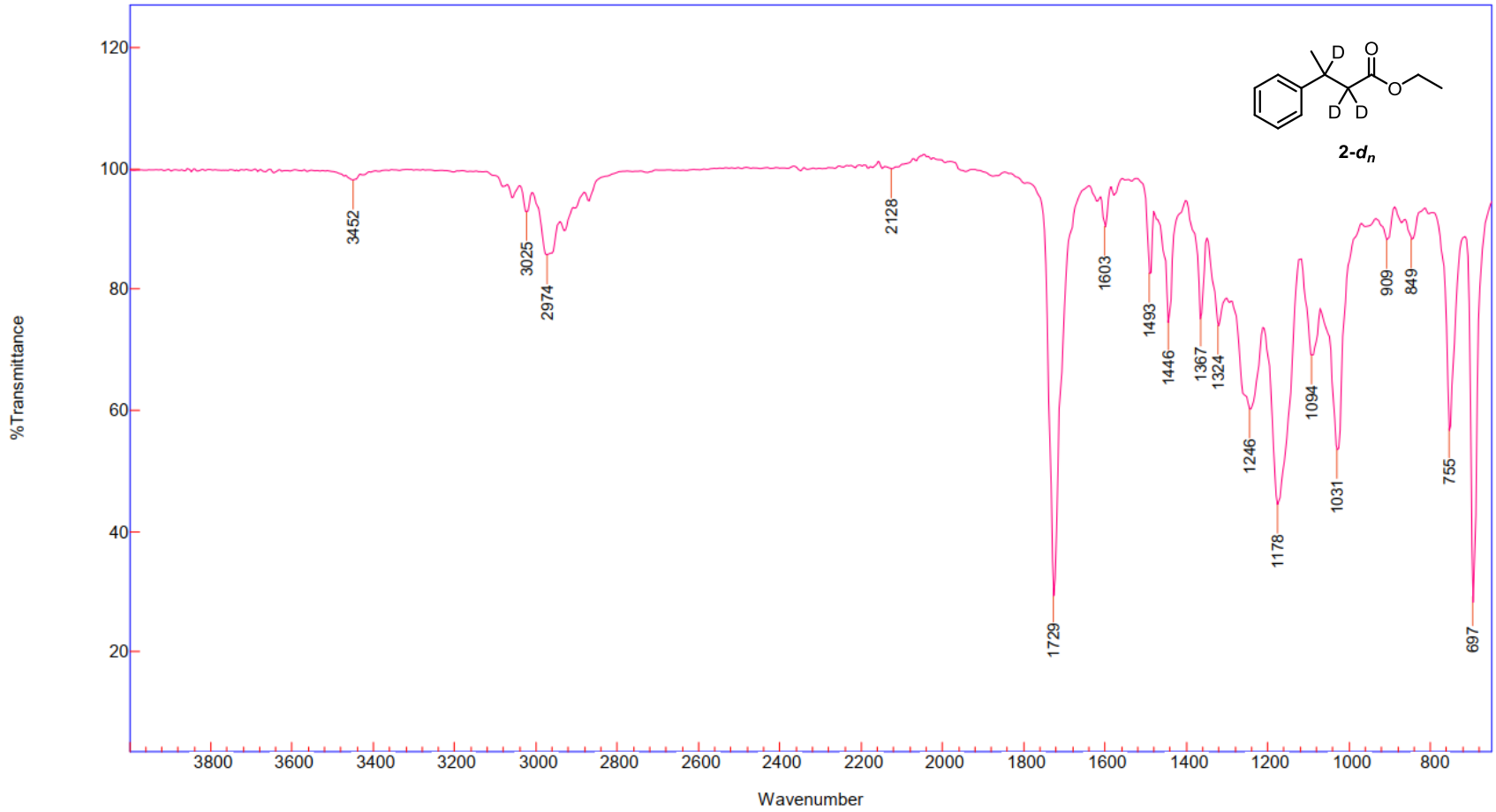
^{1}H-^{13}C HMQC


D
O
O
D
D
2-d_n
ppm
0
20
40
60
80
100
120
140
160
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
ppm

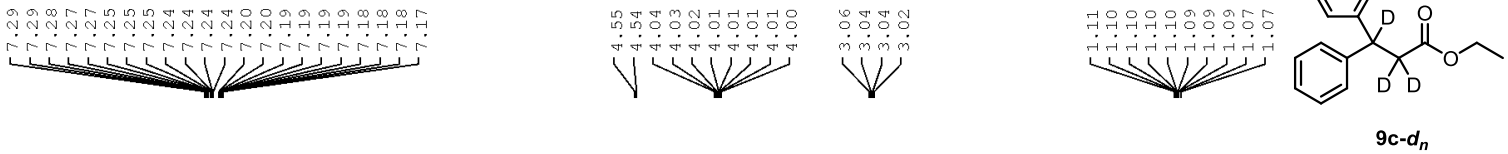
^{1}H-^{13}C HMBC


D
O
D
D
O
2-d_n
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm


intensity
m/z
102.0912
124.0866
155.1177
192.1126
214.0893
113.0708
194.1252
195.1344
191.1064
122.0711
141.1020
163.0976
100.0755
136.0867
161.0819
125.0901
147.0772
197.1471
279.1587
391.2835
D
O
O
D
D
2-d_n

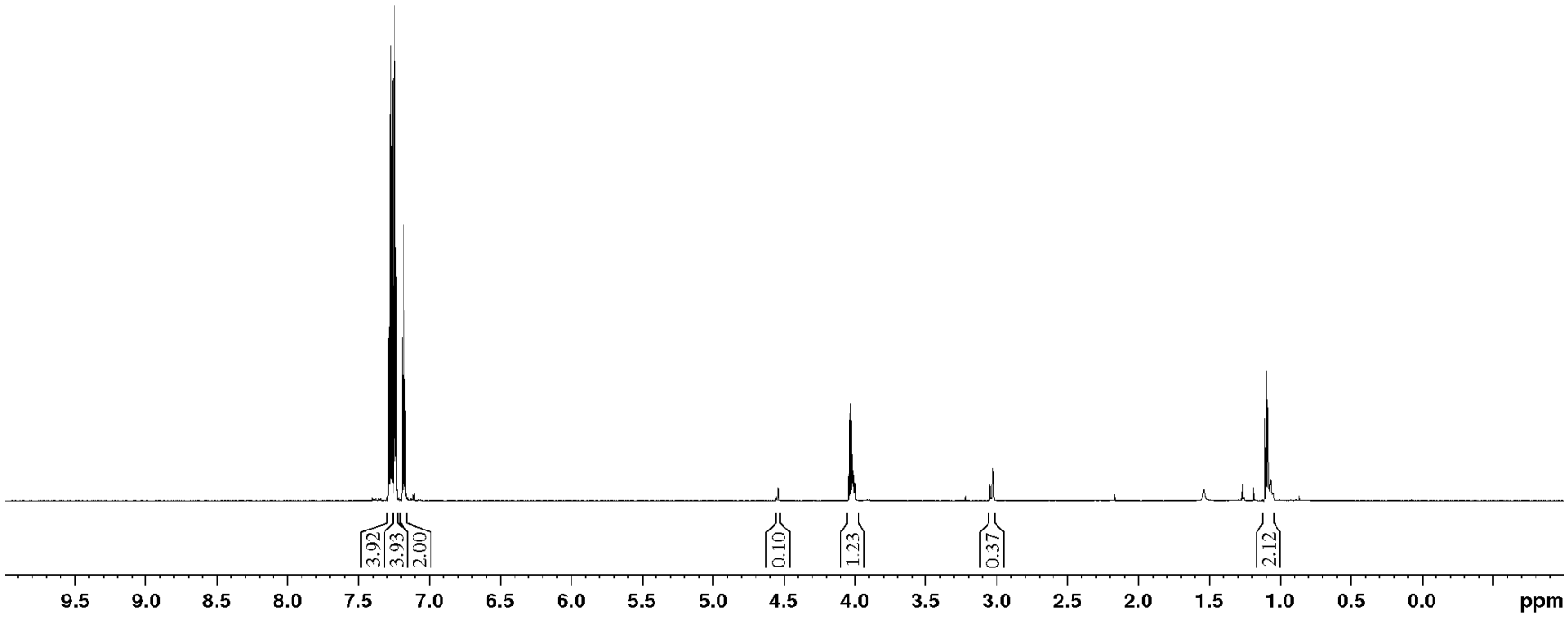

%Transmittance
120
100
80
60
40
20
3452
3025
2974
2128
1729
1603
1493
1446
1367
1324
1246
1178
1094
1031
909
849
755
697
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber
D
O
D
D
O
2-d_n

Ethyl 3,3-diphenylpropanoate-2,2,3-d_n (9c-d_n)

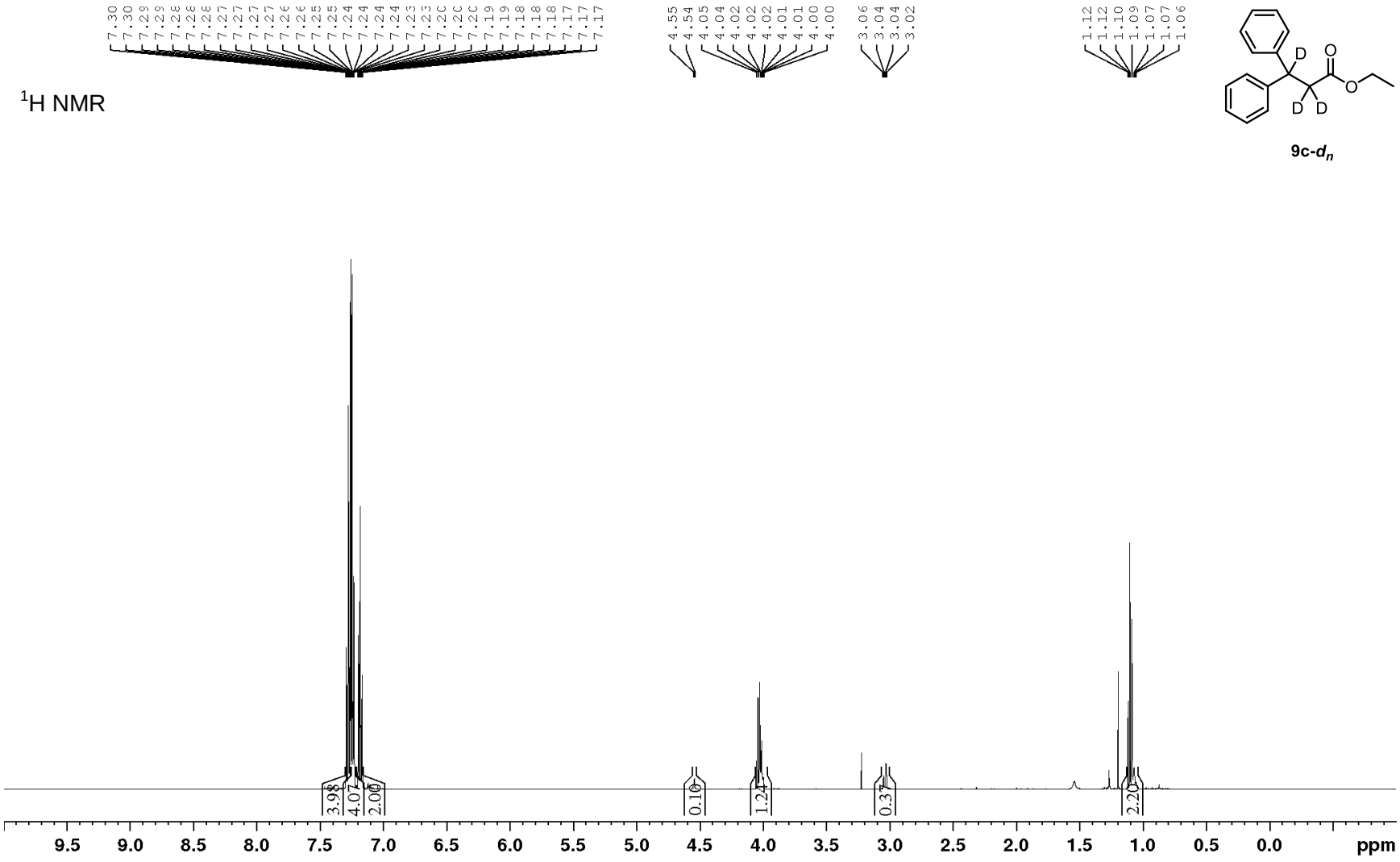


9c-d_n

quant. ^{1}H NMR

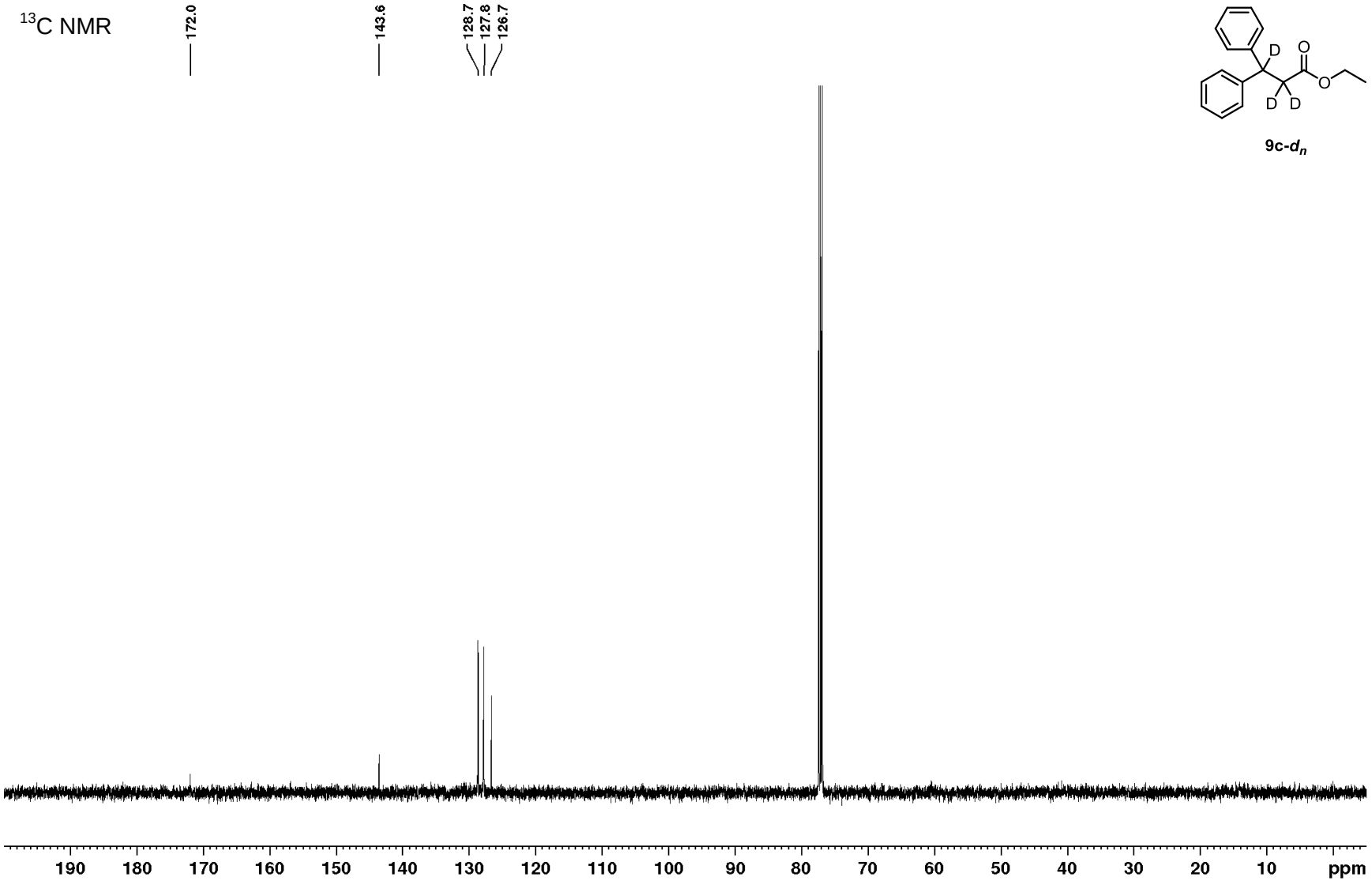


^{1}H NMR

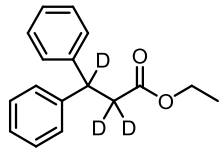

7.30 7.30 7.29 7.29 7.26 7.26 7.26 7.27 7.27 7.27 7.27 7.26 7.26 7.25 7.25 7.24 7.24 7.24 7.24 7.23 7.23 7.20 7.20 7.20 7.19 7.19 7.18 7.18 7.18 7.17 7.17 7.17
4.55 4.54 4.05 4.04 4.02 4.02 4.02 4.01 4.01 4.00 4.00
3.06 3.04 3.04 3.02
1.12 1.12 1.10 1.09 1.07 1.07 1.07 1.06
D
O
O
D
D
3.98
4.07
2.06
0.10
1.24
0.37
2.20
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

9c-d_n

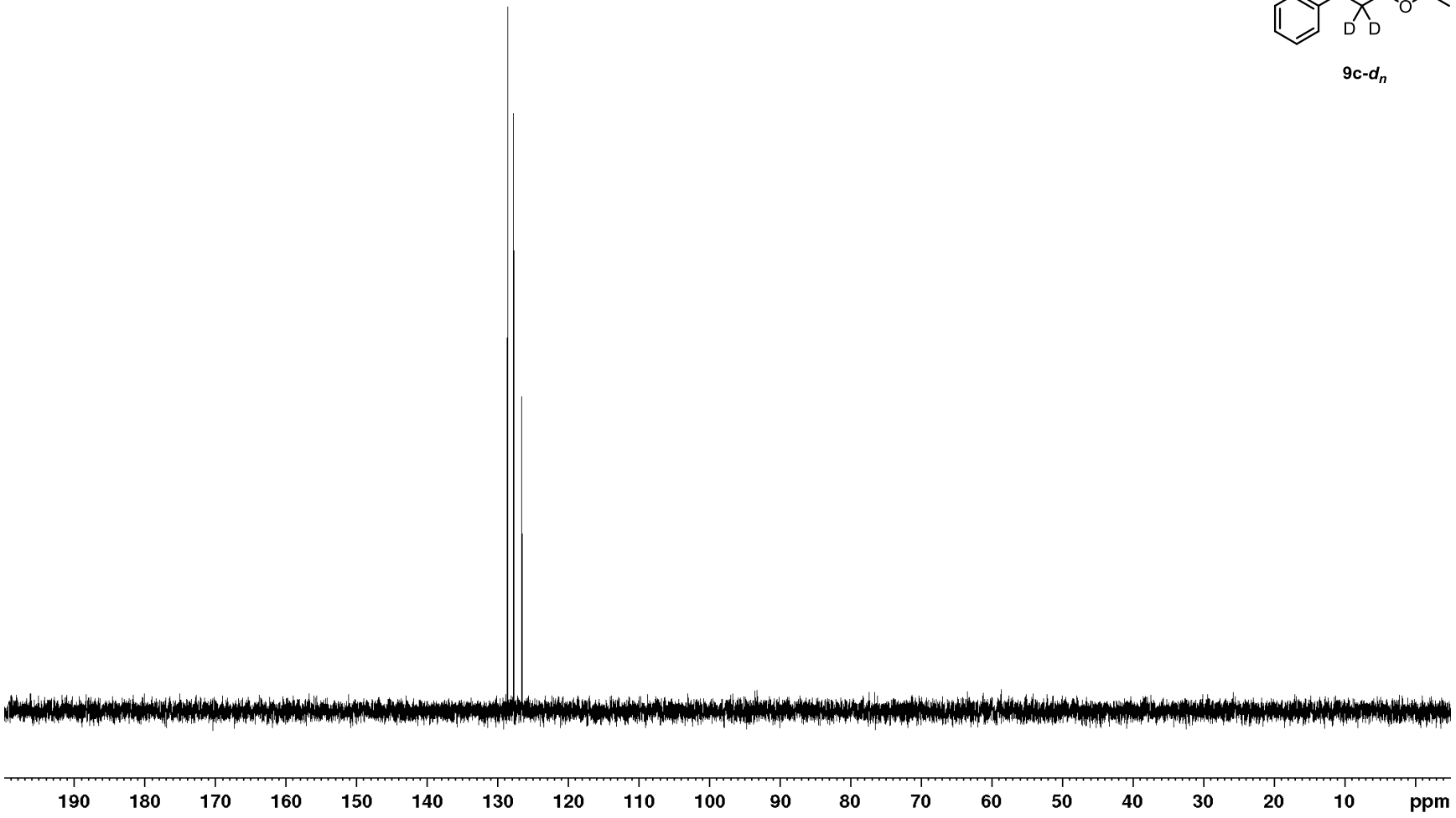
^{13}C NMR


172.0
143.6
128.7
127.8
126.7
D
O
O
D
D
D
9c-d_n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

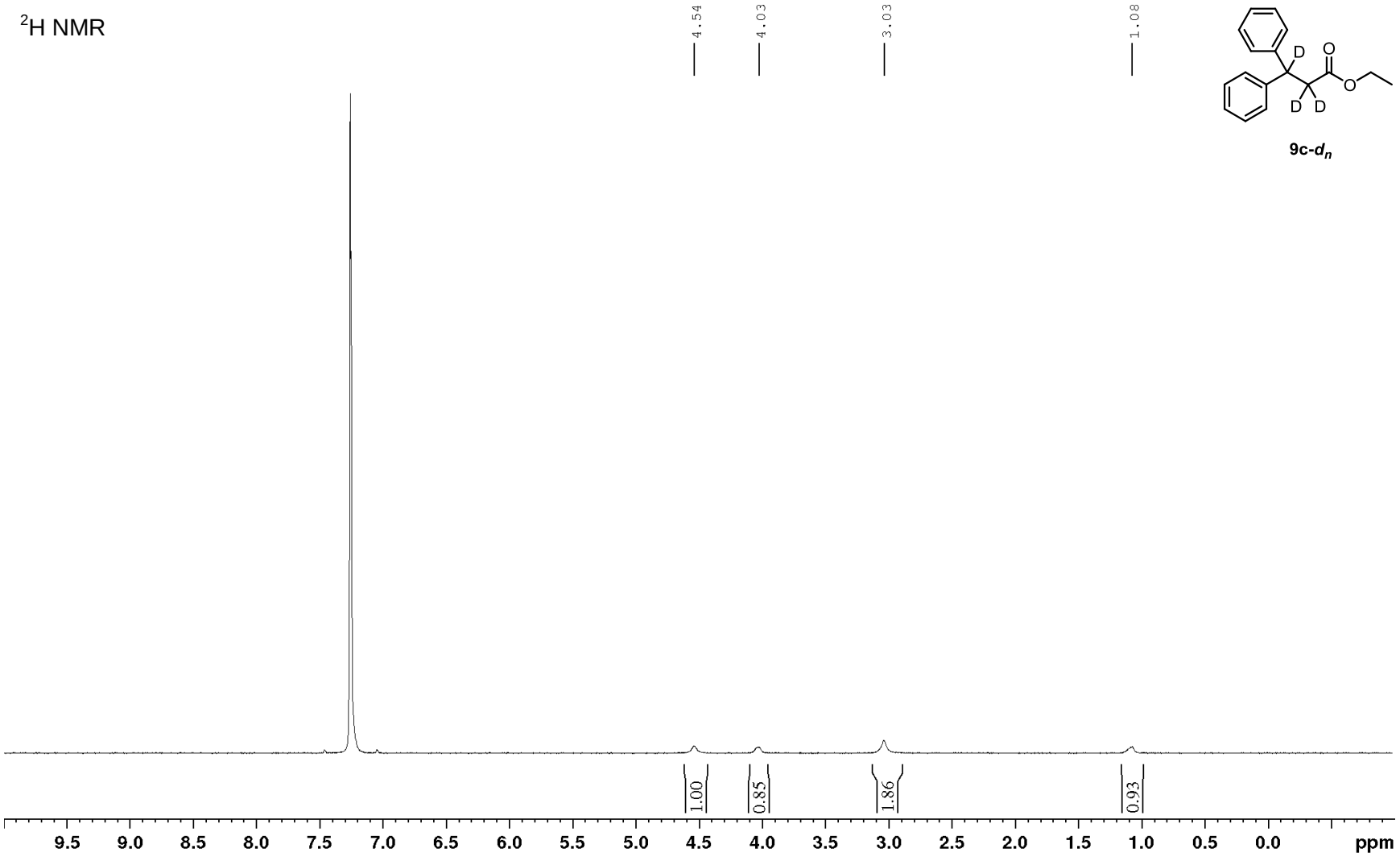
^{13}C DEPT NMR



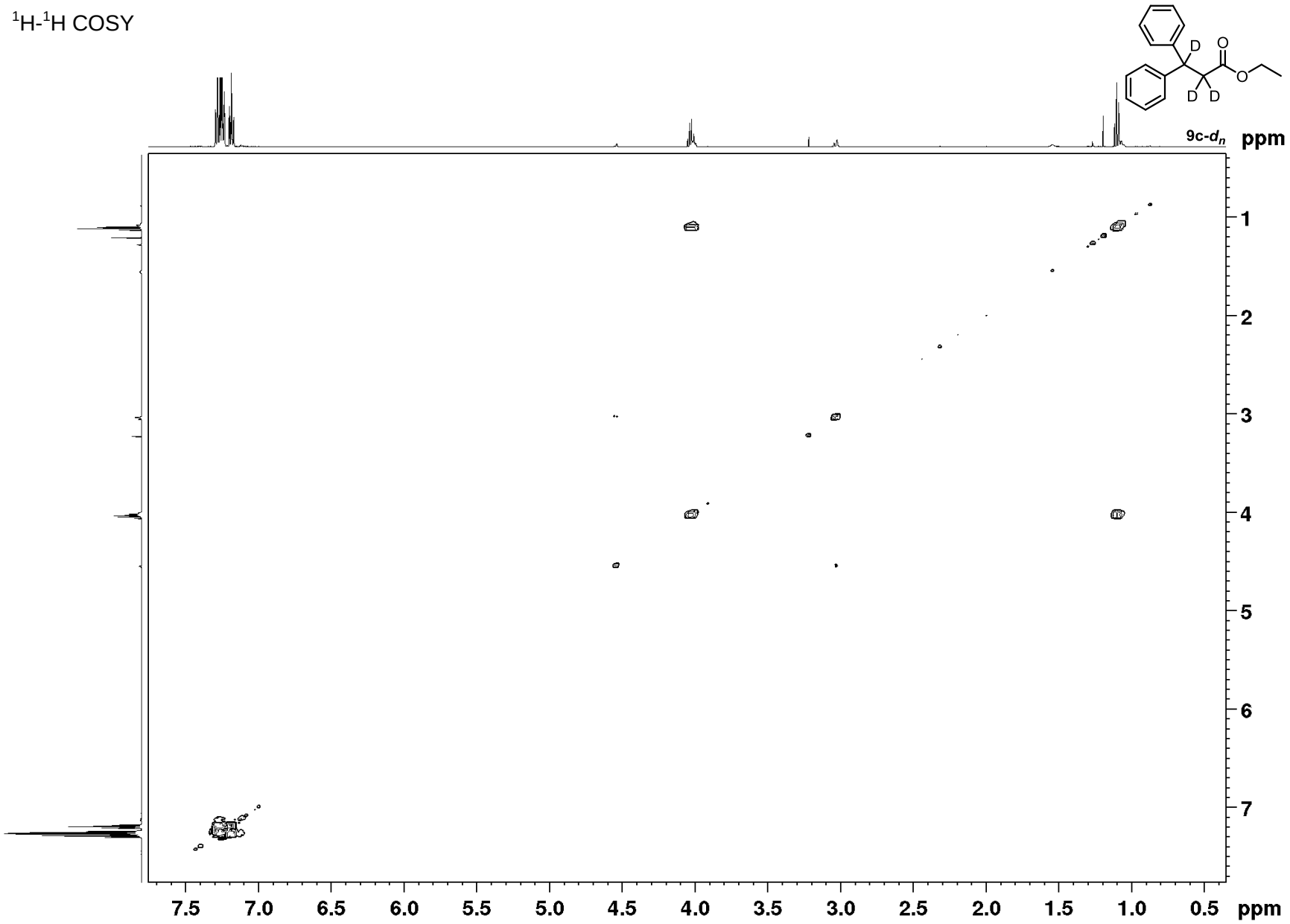
9c-d_n



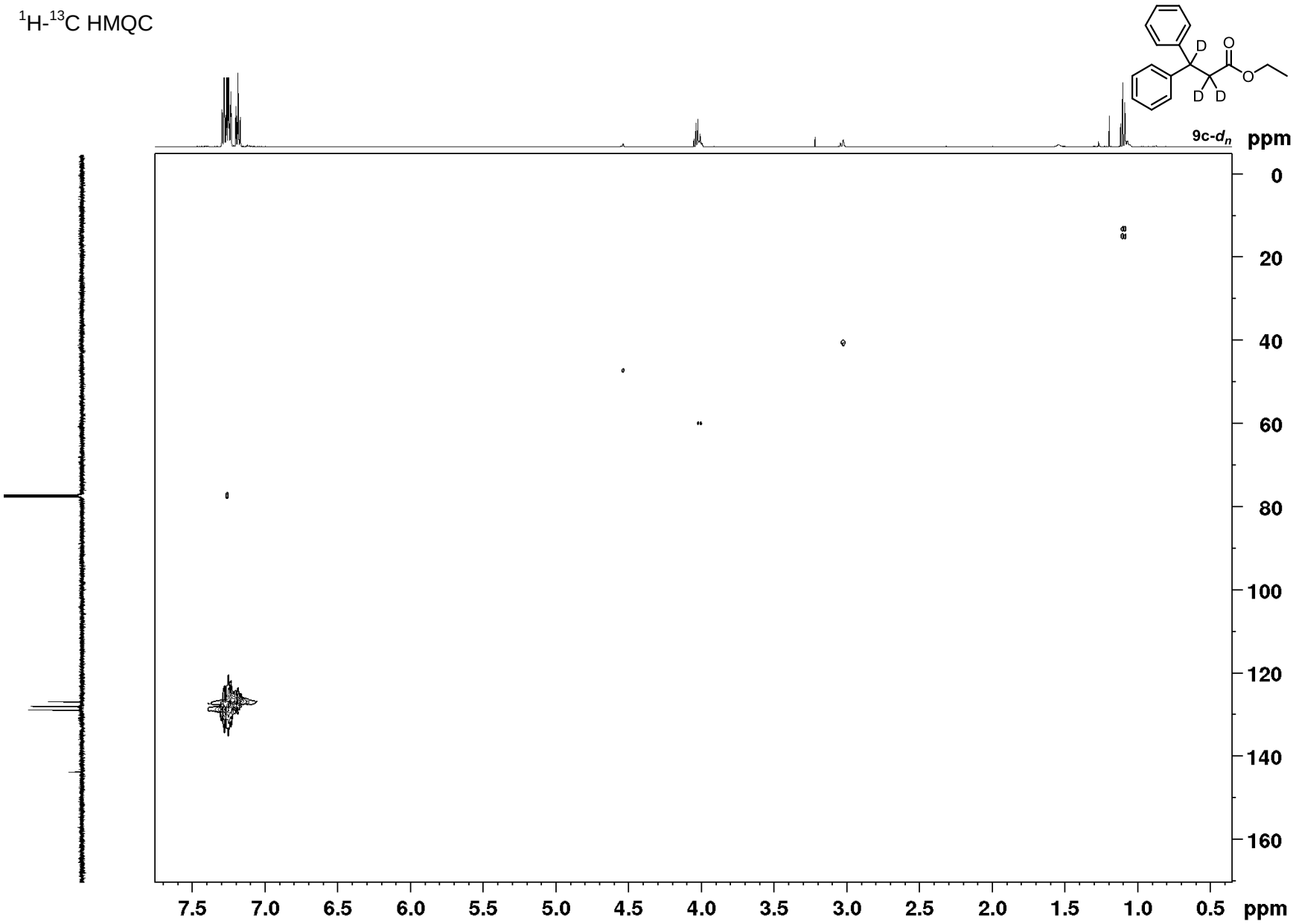
^{2}H NMR


4.54
4.03
3.03
1.08
D
O
O
D
D
D
9c-d_n
1.00
0.85
1.86
0.93
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

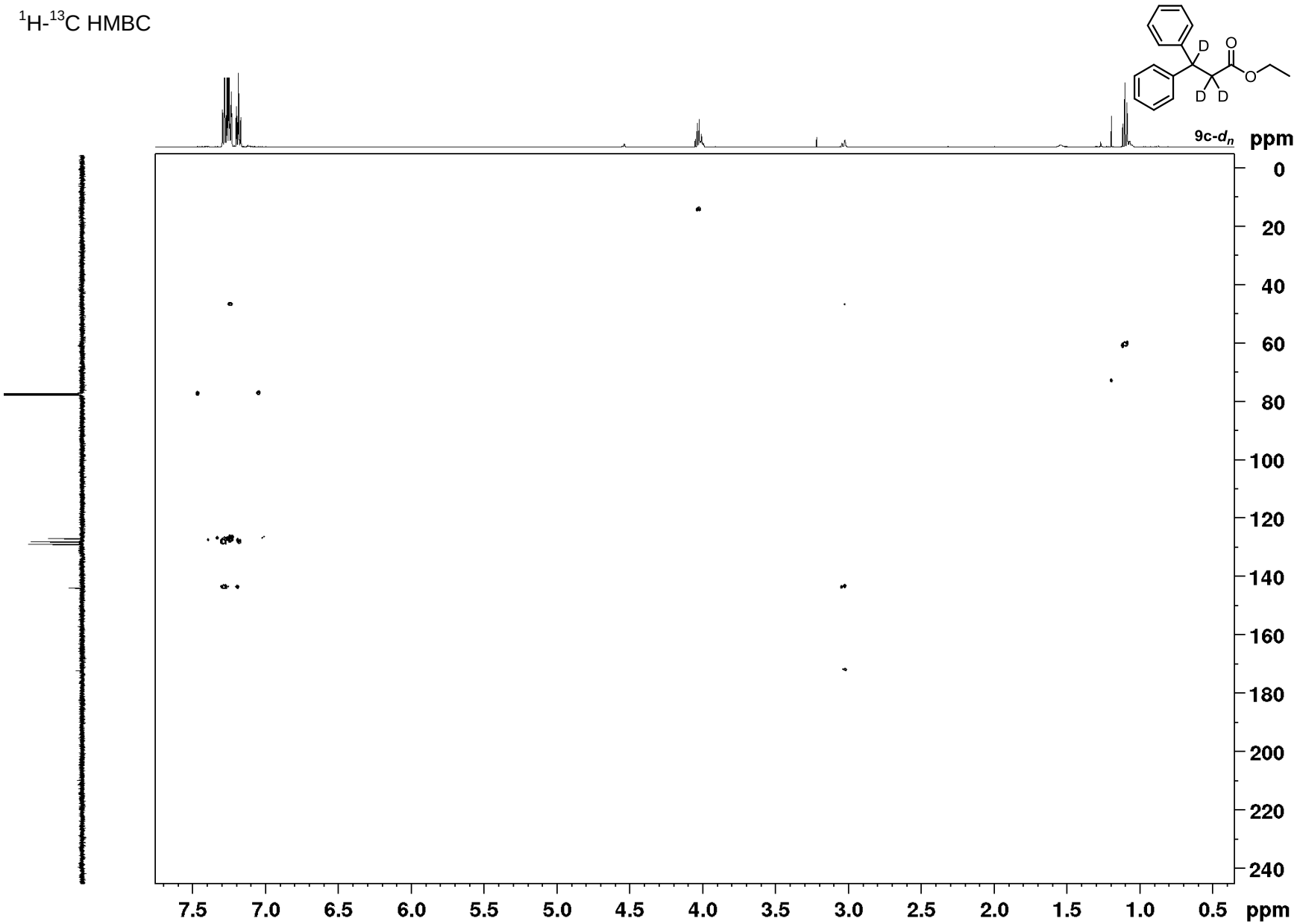
^{1}H-^{1}H COSY

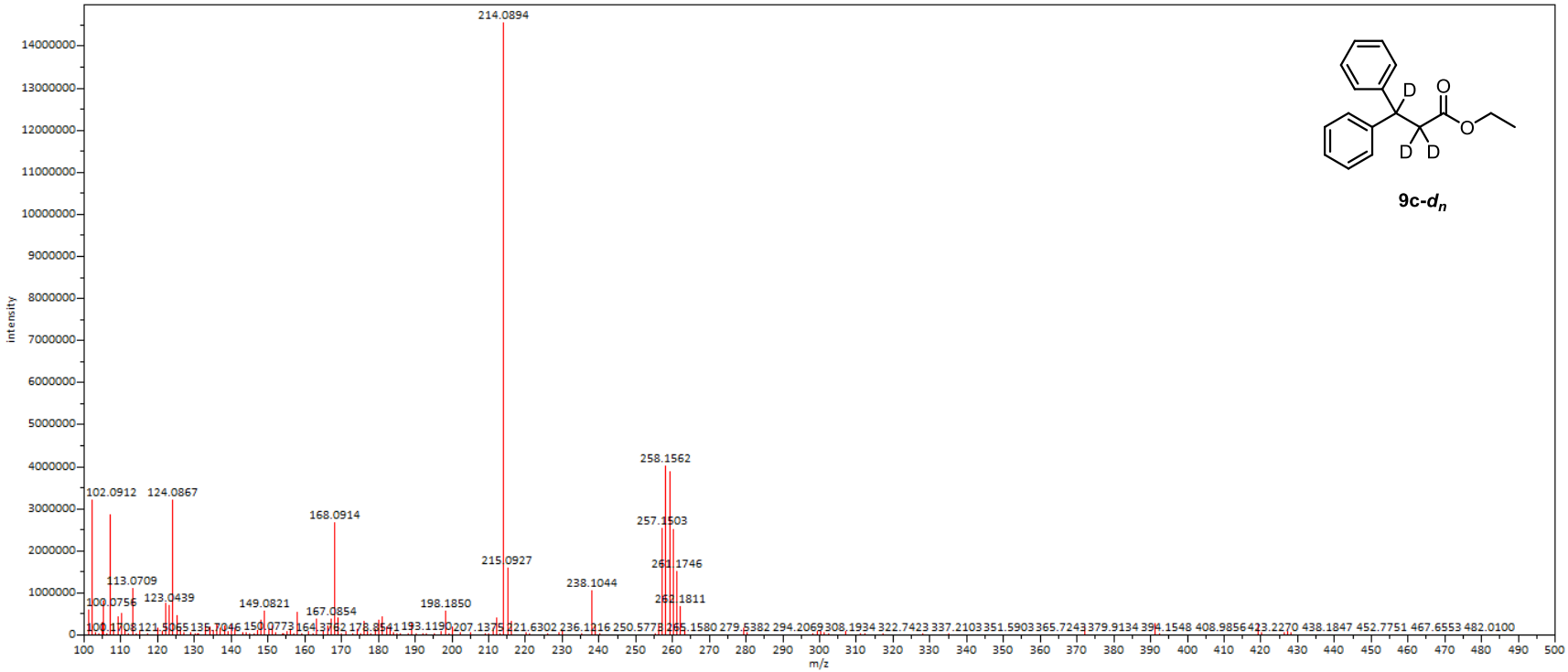

D
O
O
D
D
D
9c-d_n
ppm
1
2
3
4
5
6
7
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

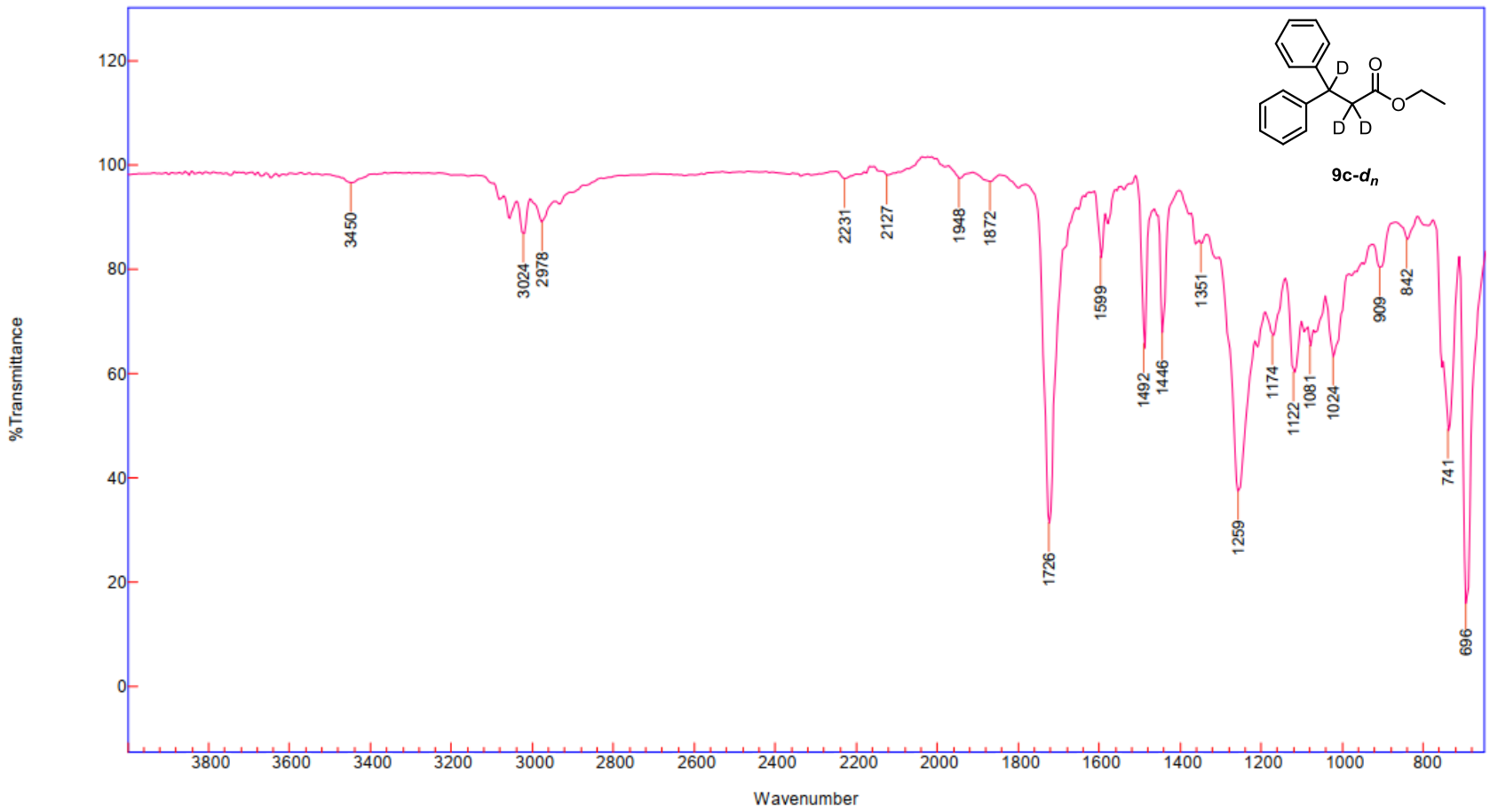
^{1}H-^{13}C HMQC


D
O
O
D
D
9c-d_n
ppm
0
20
40
60
80
100
120
140
160
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
ppm

^{1}H-^{13}C HMBC

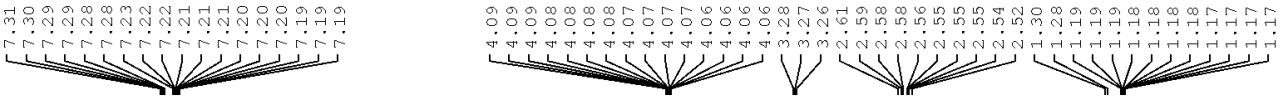

D
O
O
D
D
9c-d_n
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

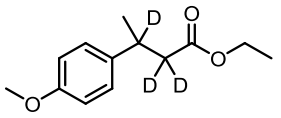

214.0894
258.1562
102.0912
124.0867
168.0914
257.1503
215.0927
261.1746
113.0709
238.1044
123.0439
262.1811
109.0756
149.0821
167.0854
198.1850
intensity
m/z
D
O
O
D
D
9c-d_n


%Transmittance
Wavenumber
120
100
80
60
40
20
0
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
3450
3024
2978
2231
2127
1948
1872
1726
1599
1492
1446
1351
1259
1174
1122
1081
1024
909
842
741
696
D
O
O
D
D
9c-d_n

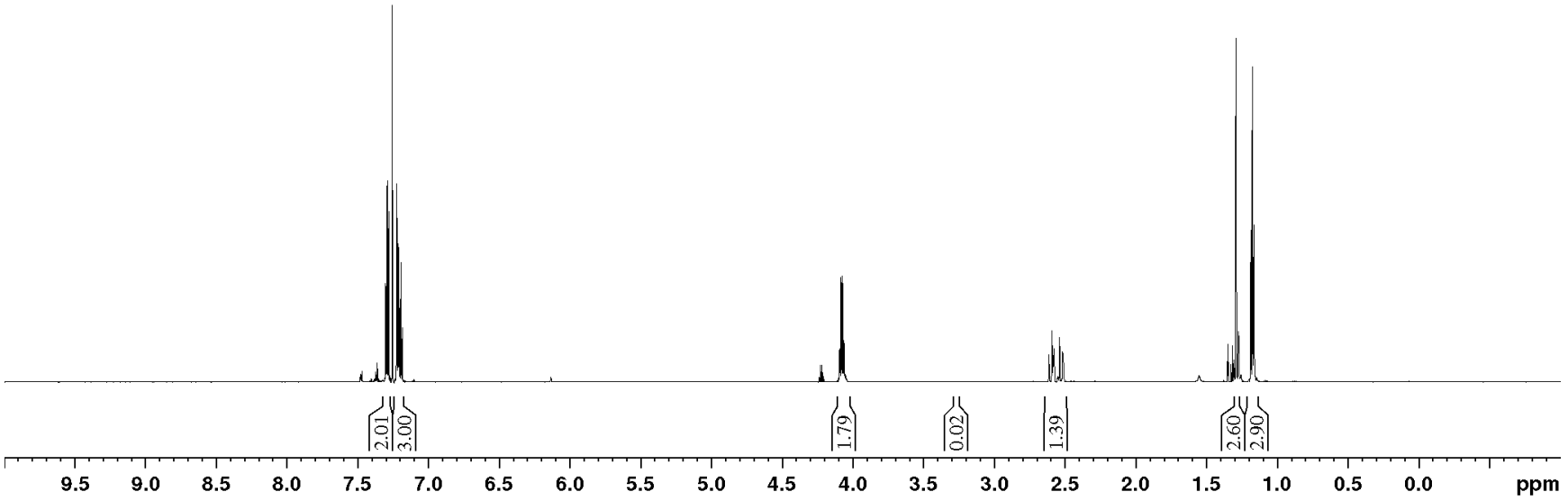
Ethyl 3-(4-methoxyphenyl)butanoate-2,2,3-d_n (9d-d_n)

quant. ^{1}H NMR

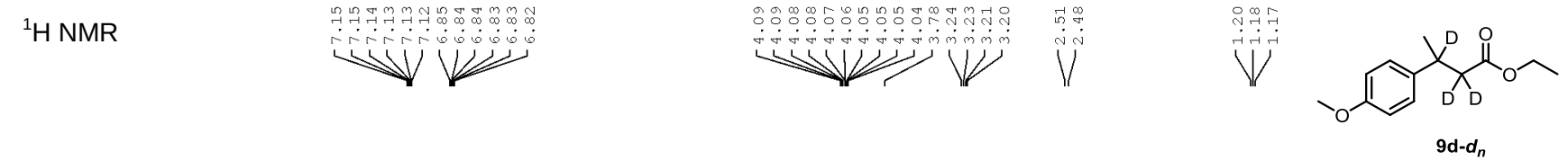


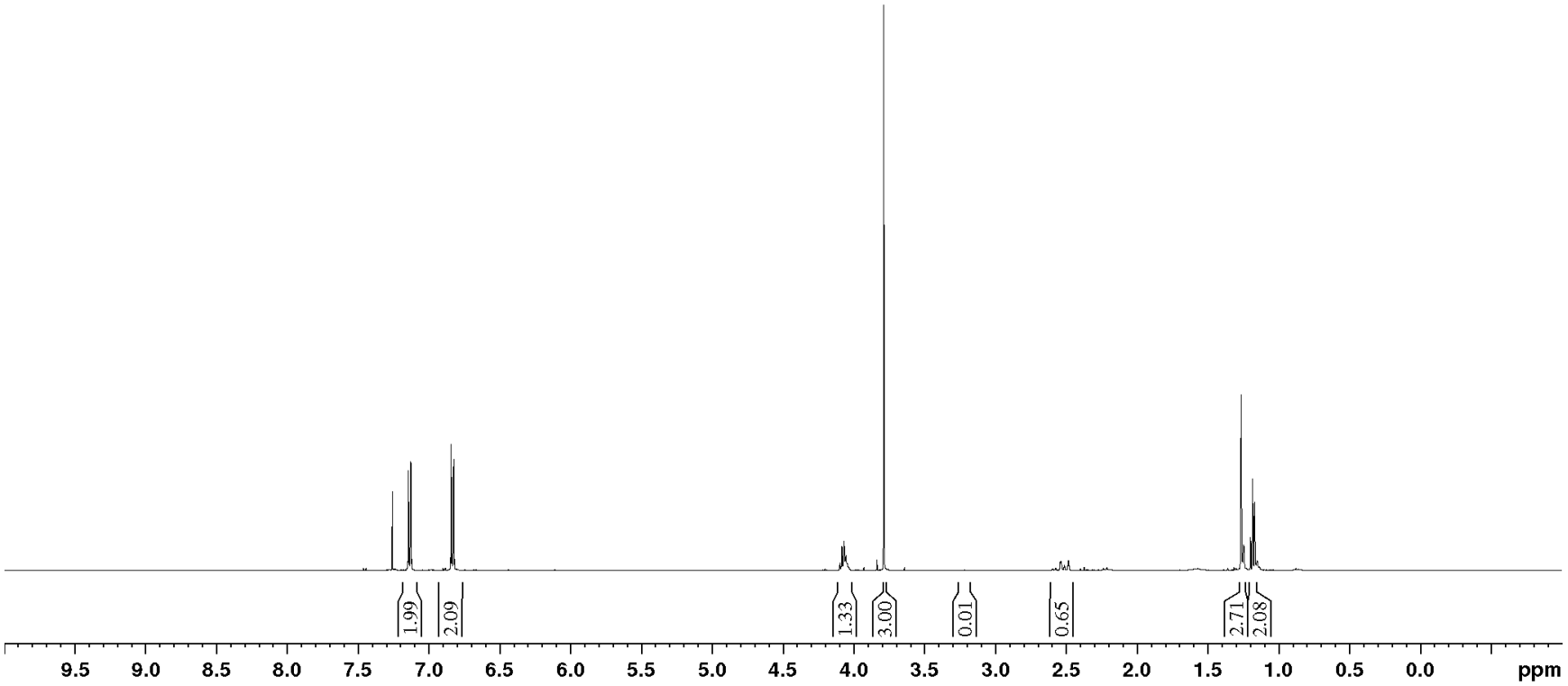


9d-d_n

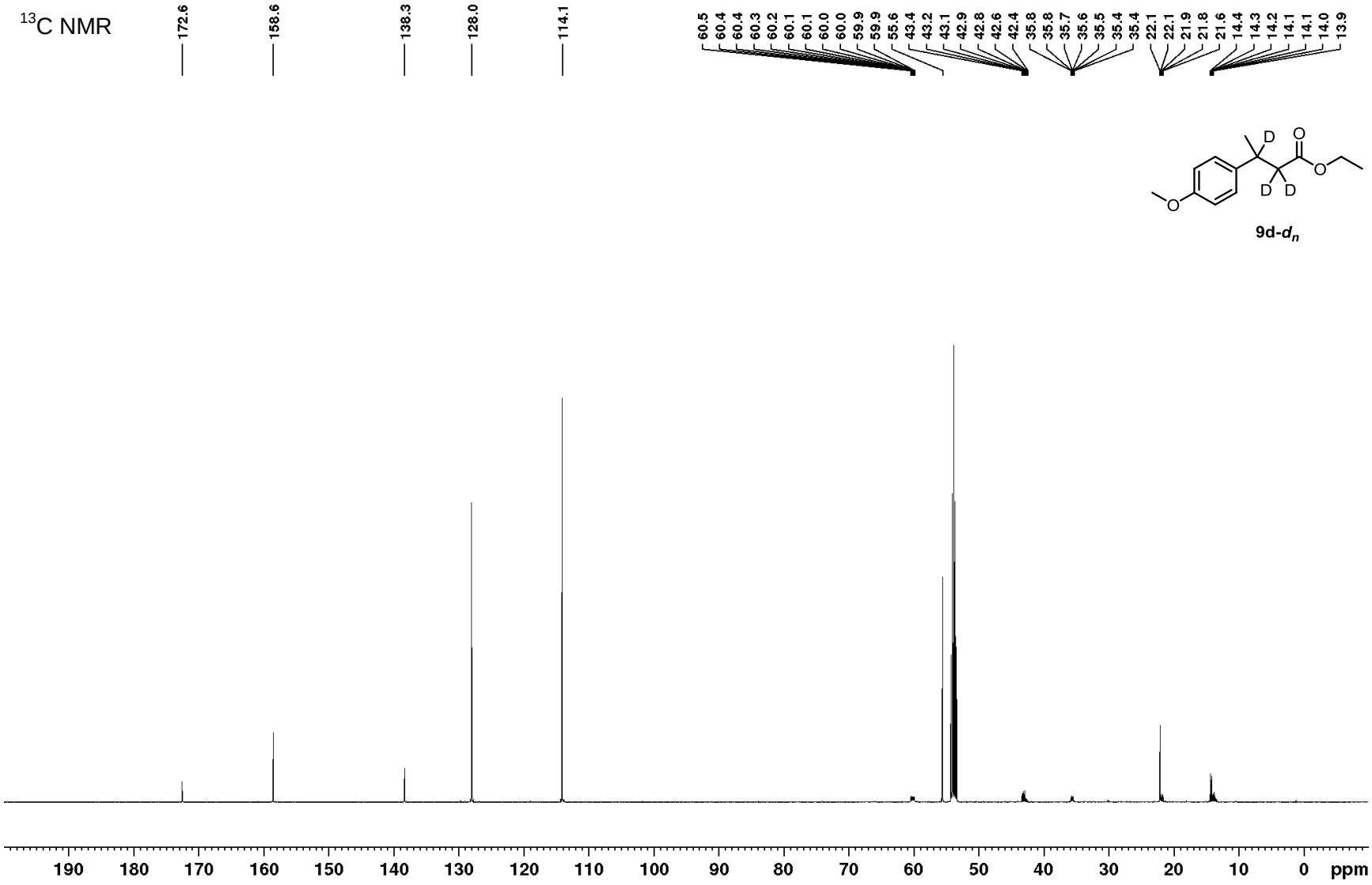


^{1}H NMR


7.15
7.15
7.14
7.13
7.13
7.12
6.85
6.84
6.84
6.83
6.83
6.82
4.09
4.09
4.08
4.08
4.07
4.06
4.05
4.05
4.05
4.04
3.78
3.24
3.23
3.21
3.20
2.51
2.48
1.20
1.18
1.17
D
O
O
D
D
O
9d-d_n

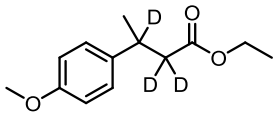

1.99
2.09
1.33
3.00
0.01
0.65
2.71
2.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

^{13}C NMR

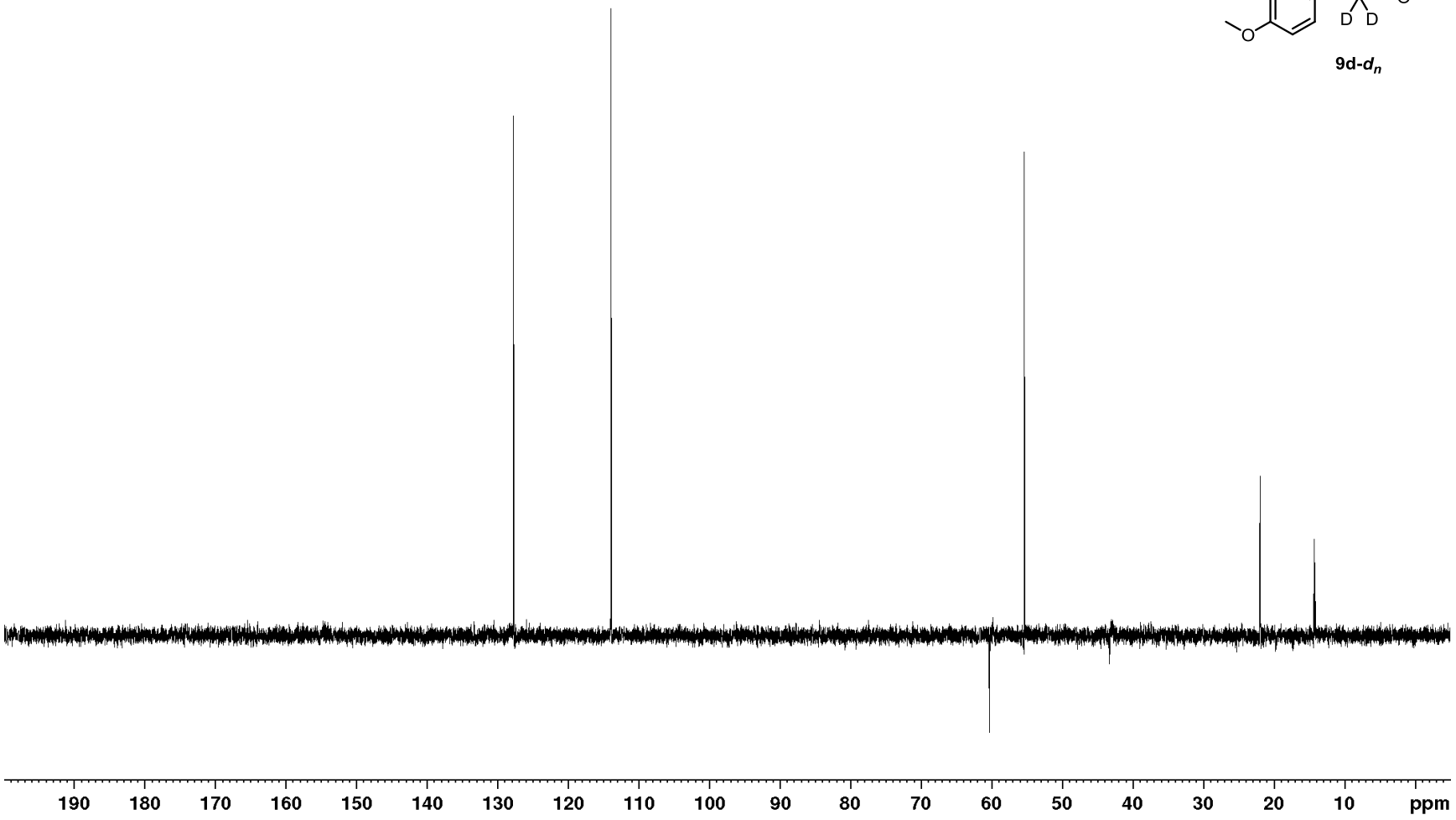

172.6
158.6
138.3
128.0
114.1
60.5
60.4
60.4
60.3
60.2
60.1
60.1
60.0
60.0
59.9
59.9
55.6
43.4
43.2
43.1
42.9
42.8
42.6
42.4
35.8
35.8
35.7
35.6
35.5
35.4
35.4
22.1
22.1
21.9
21.8
21.6
14.4
14.3
14.2
14.1
14.1
14.0
13.9
D
O
O
D
D
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

9d-d_n

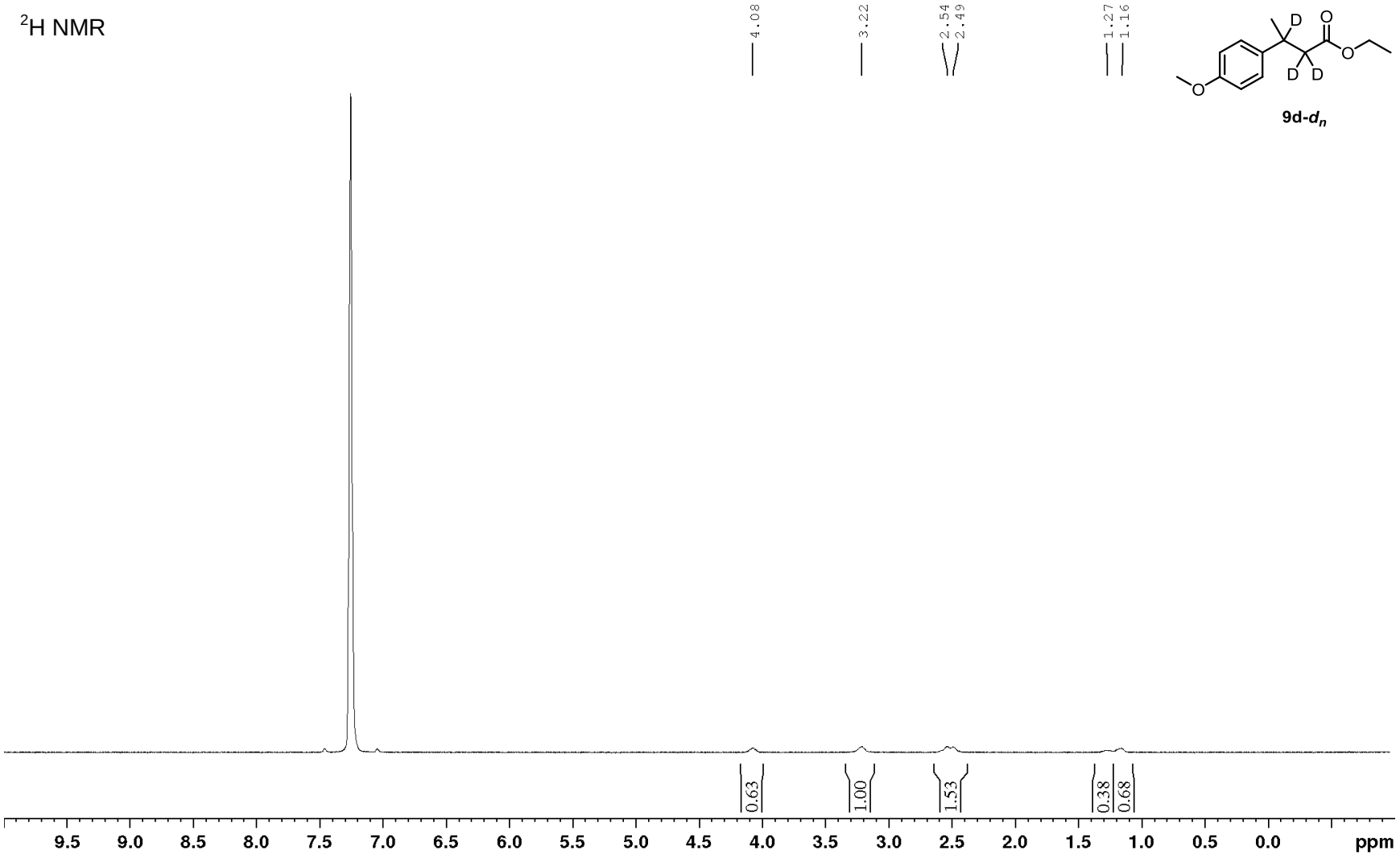
^{13}C DEPT NMR



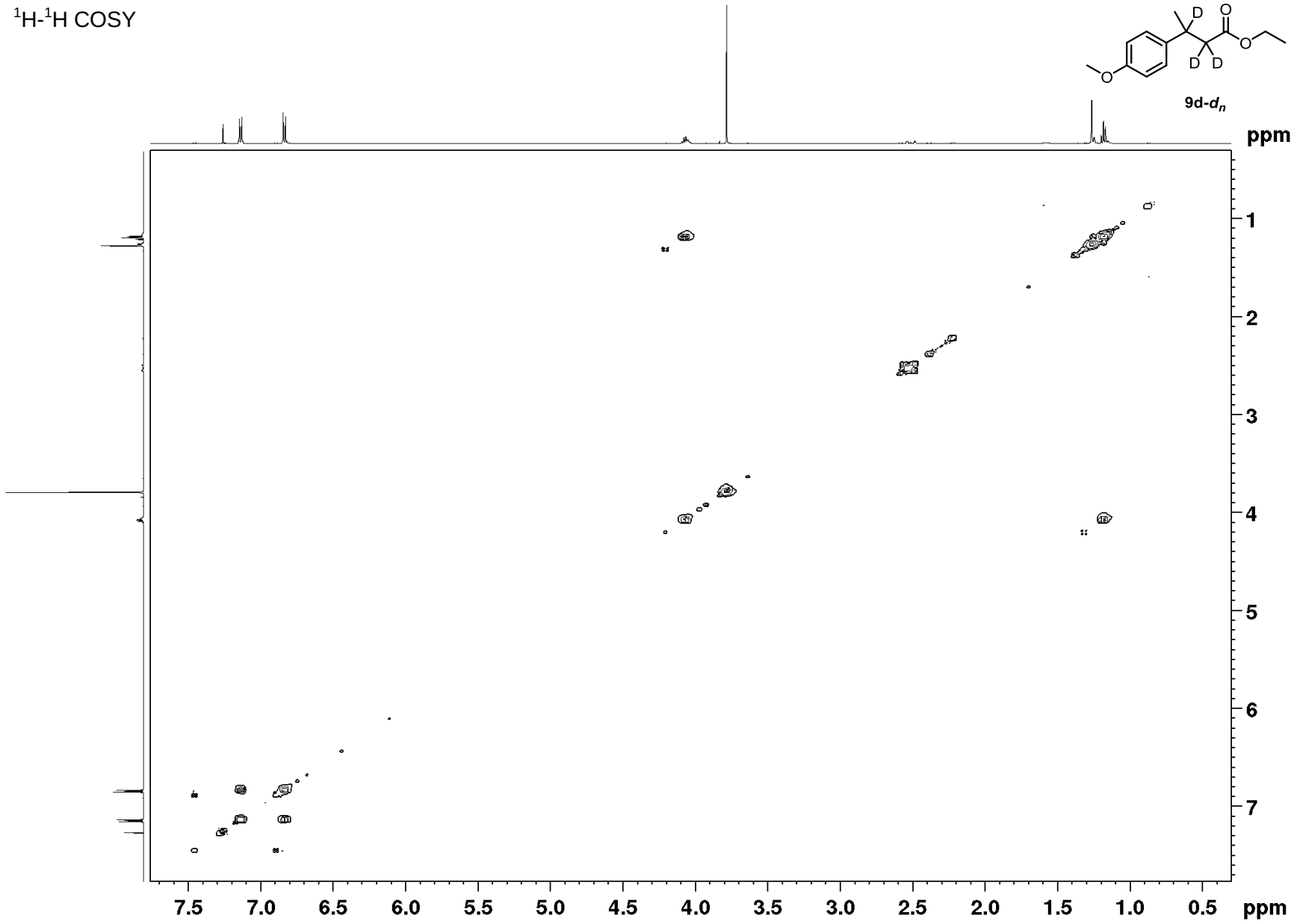
9d-d_n

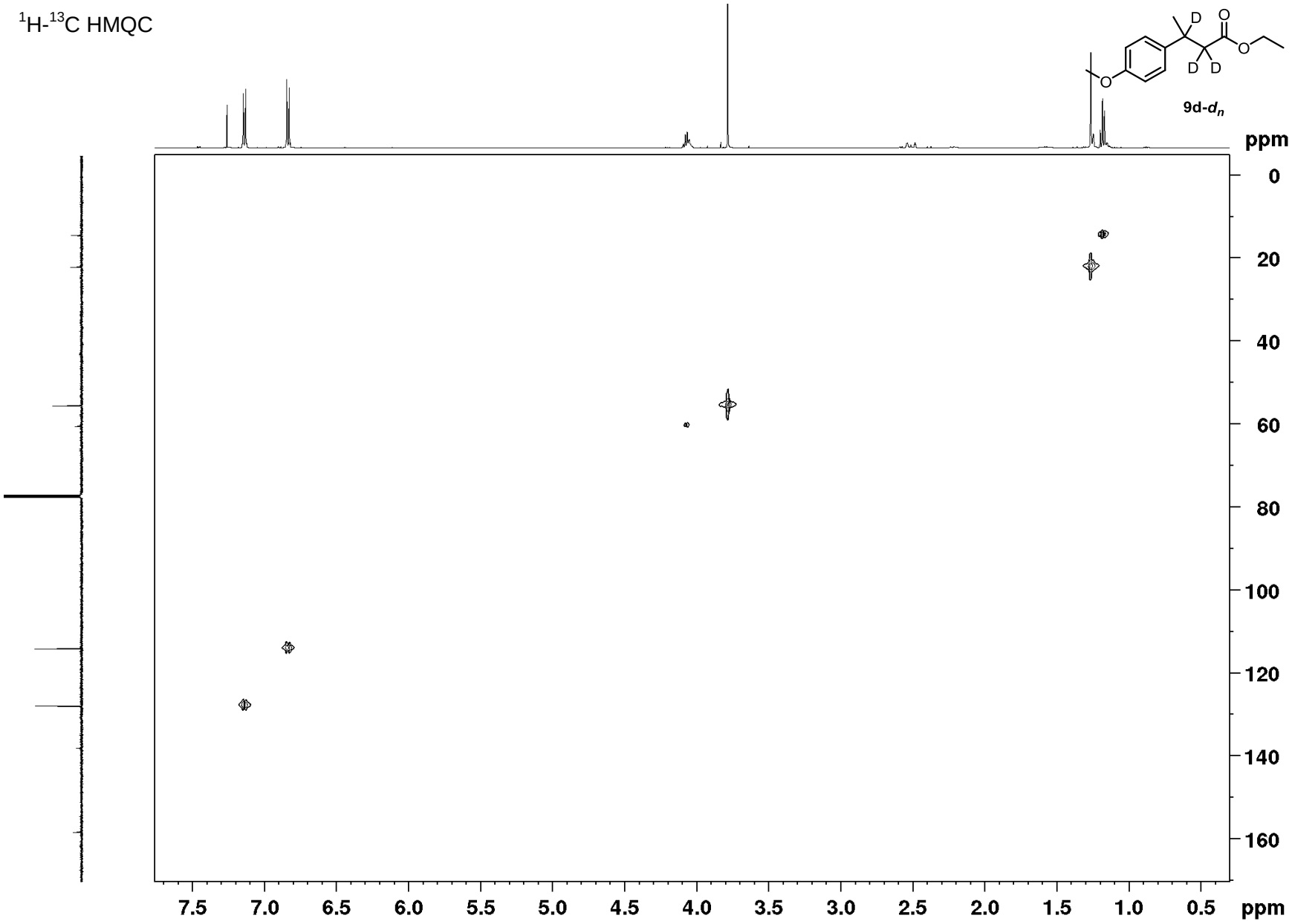


^{2}H NMR

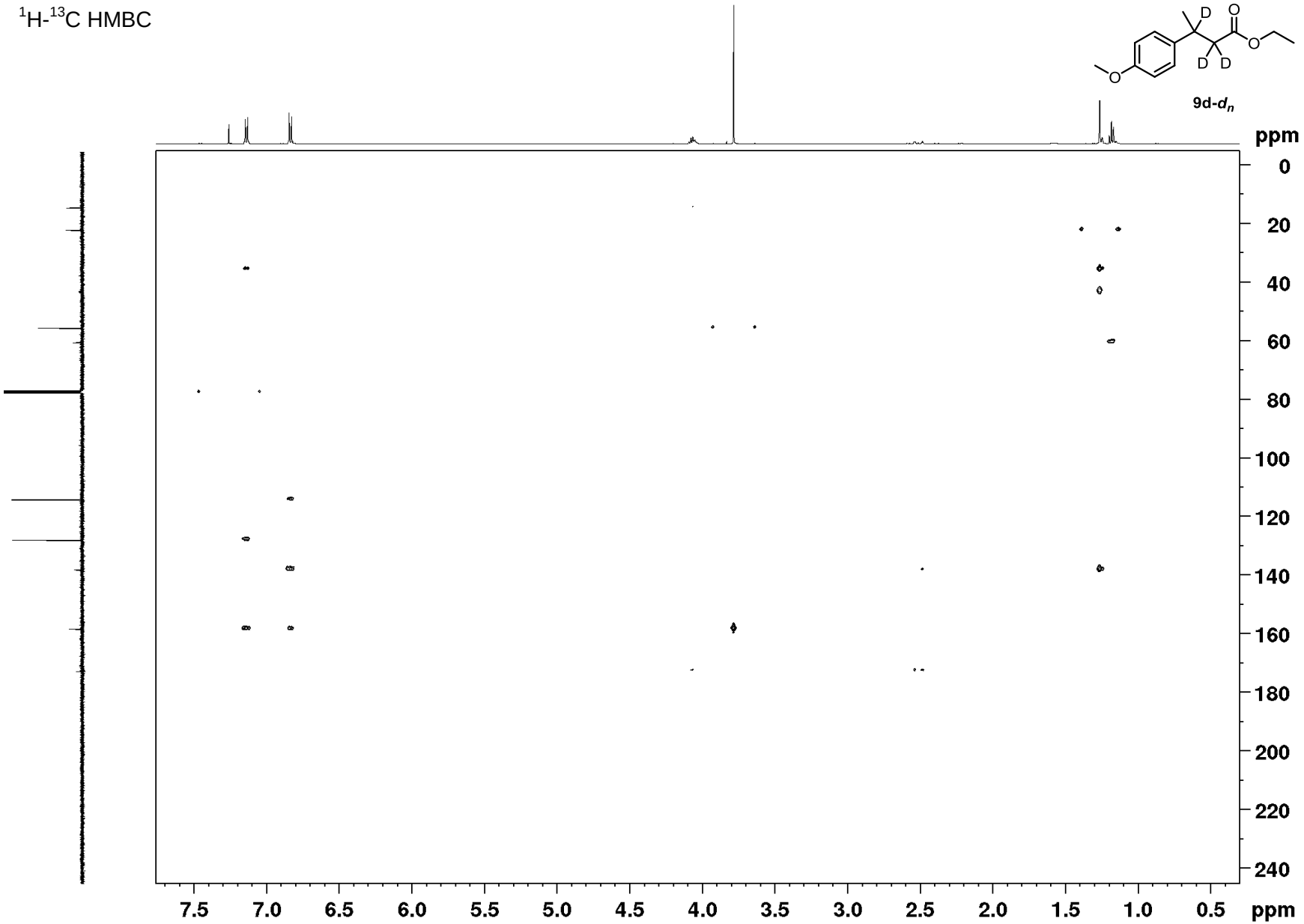

4.08
3.22
2.54
2.49
1.27
1.16
D
O
O
D
D
O
9d-d_n
0.63
1.00
1.53
0.38
0.68
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

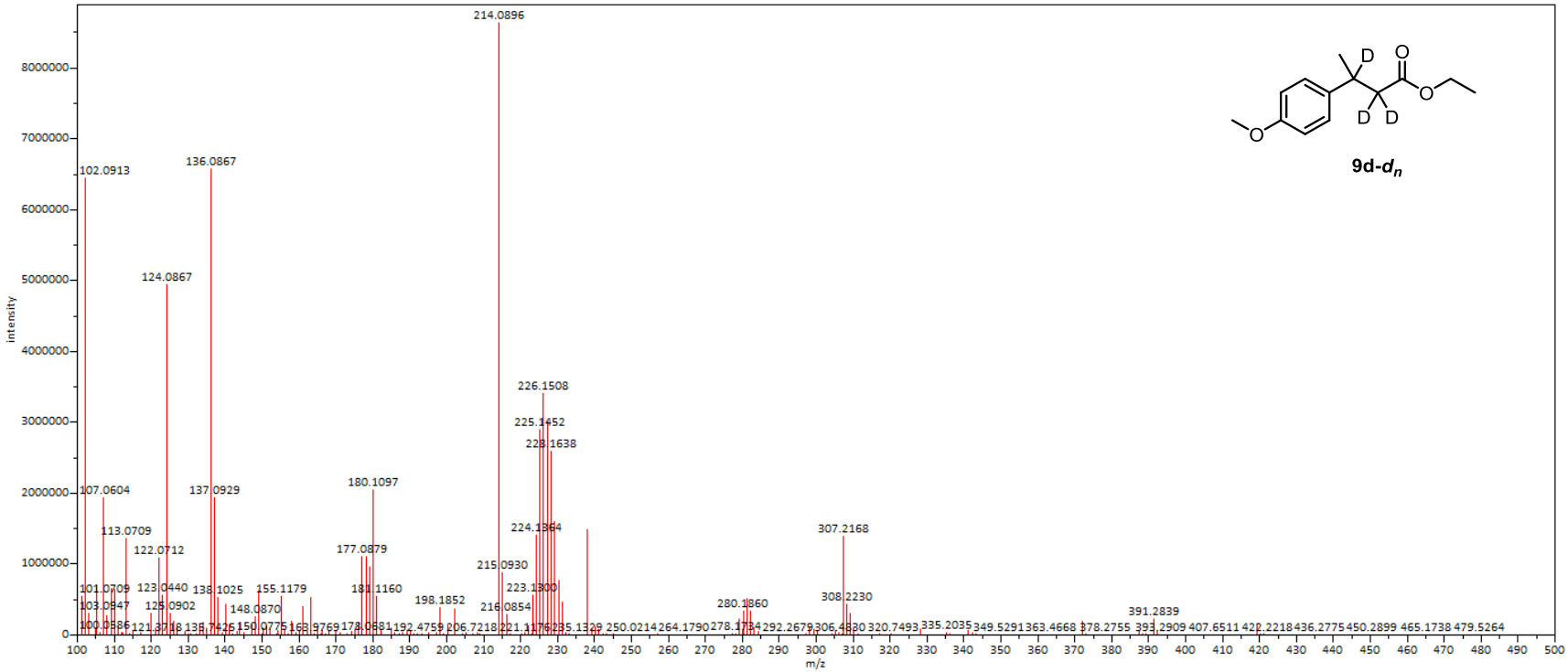
^{1}H-^{1}H COSY

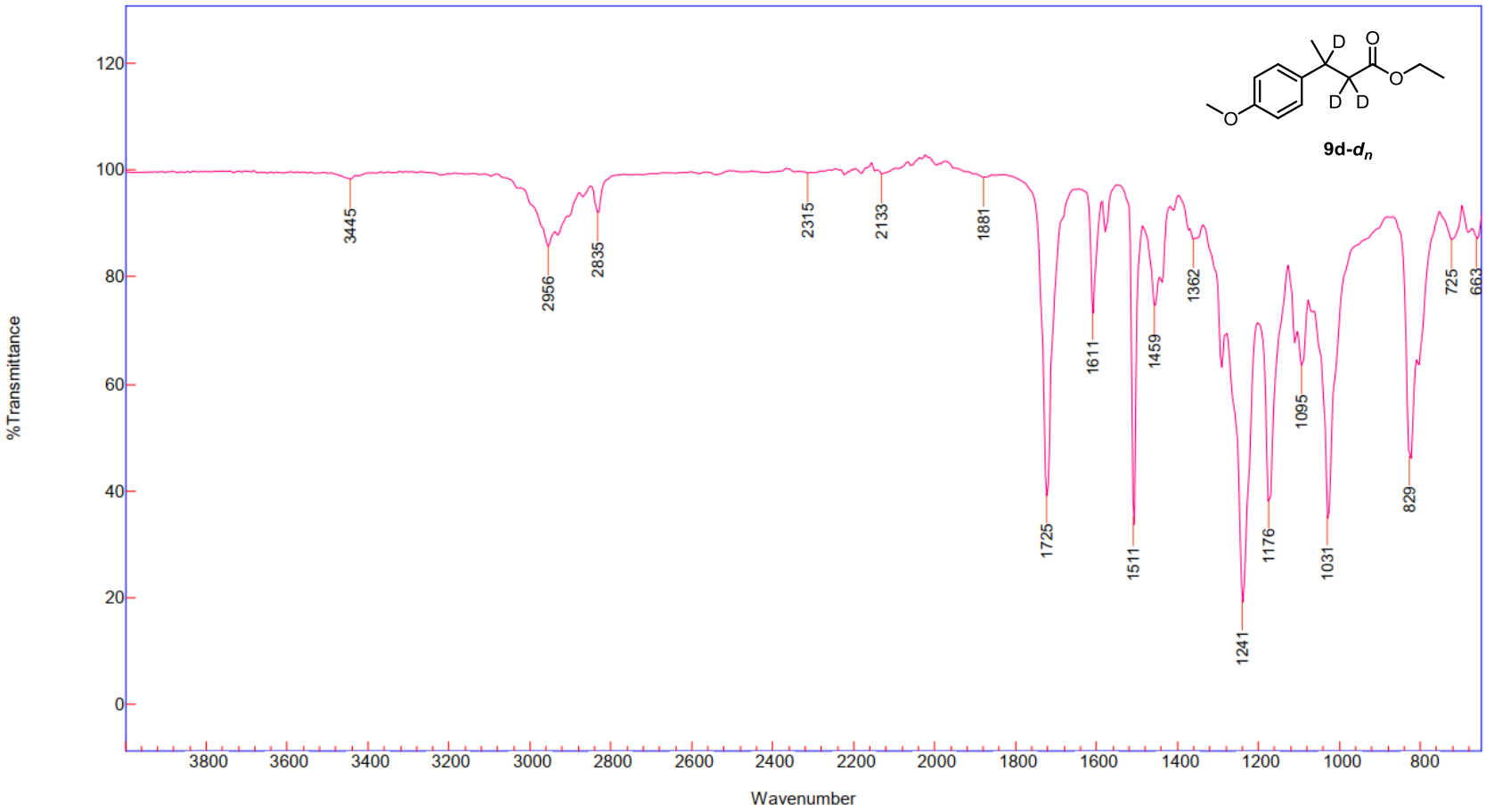

D
O
O
D
D
D
O
9d-d_n
ppm
1
2
3
4
5
6
7
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


^{1}H-^{13}C HMQC
D
O
O
D
D
O
9d-d_n
ppm
0
20
40
60
80
100
120
140
160
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
ppm

^{1}H-^{13}C HMBC

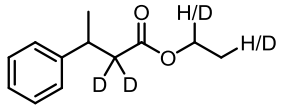

D
O
O
D
D
O
9d-d_n
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


214.0896
136.0867
102.0913
124.0867
226.1508
225.1452
228.1638
180.1097
107.0604
137.0929
113.0709
122.0712
224.1364
307.2168
177.0879
215.0930
223.1300
308.2230
280.1860
198.1852
391.2839
intensity
m/z
D
O
D
D
O
O
9d-d_n

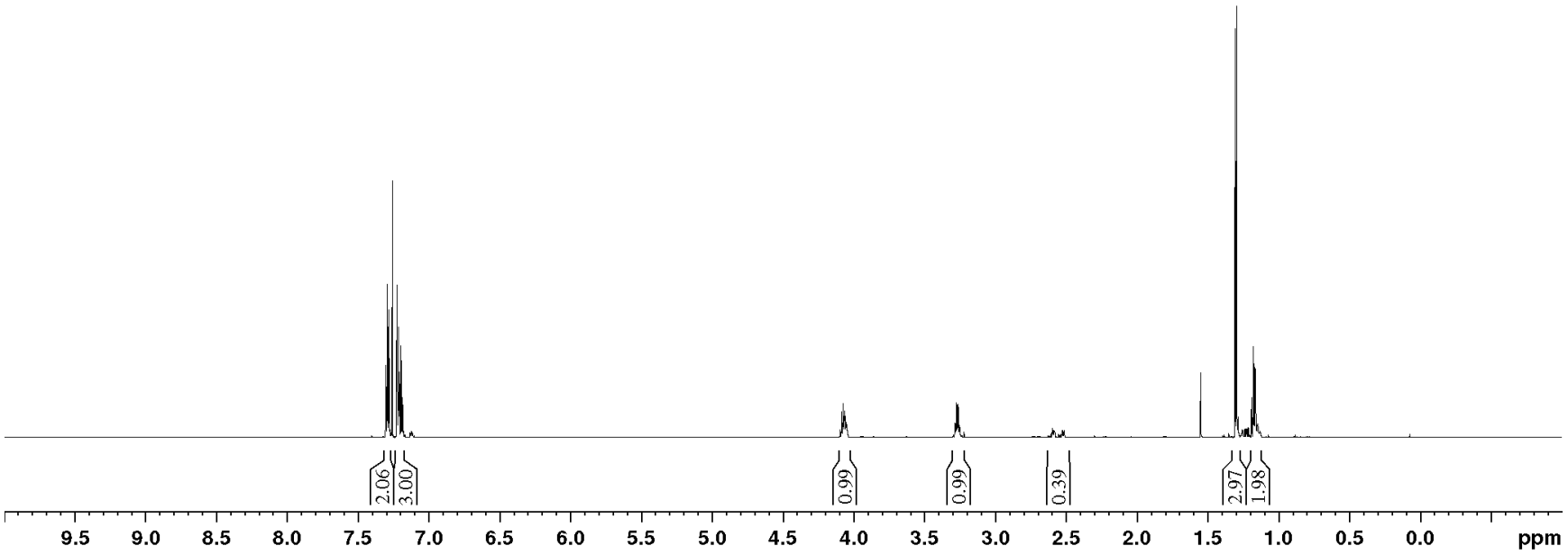

%Transmittance
Wavenumber
120
100
80
60
40
20
0
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
3445
2956
2835
2315
2133
1881
1725
1611
1511
1459
1362
1241
1176
1095
1031
829
725
663
D
O
D
O
D
D
O
9d-d_n

Ethyl 3-phenylbutanoate-2,2-d_2 (9d-d_n)

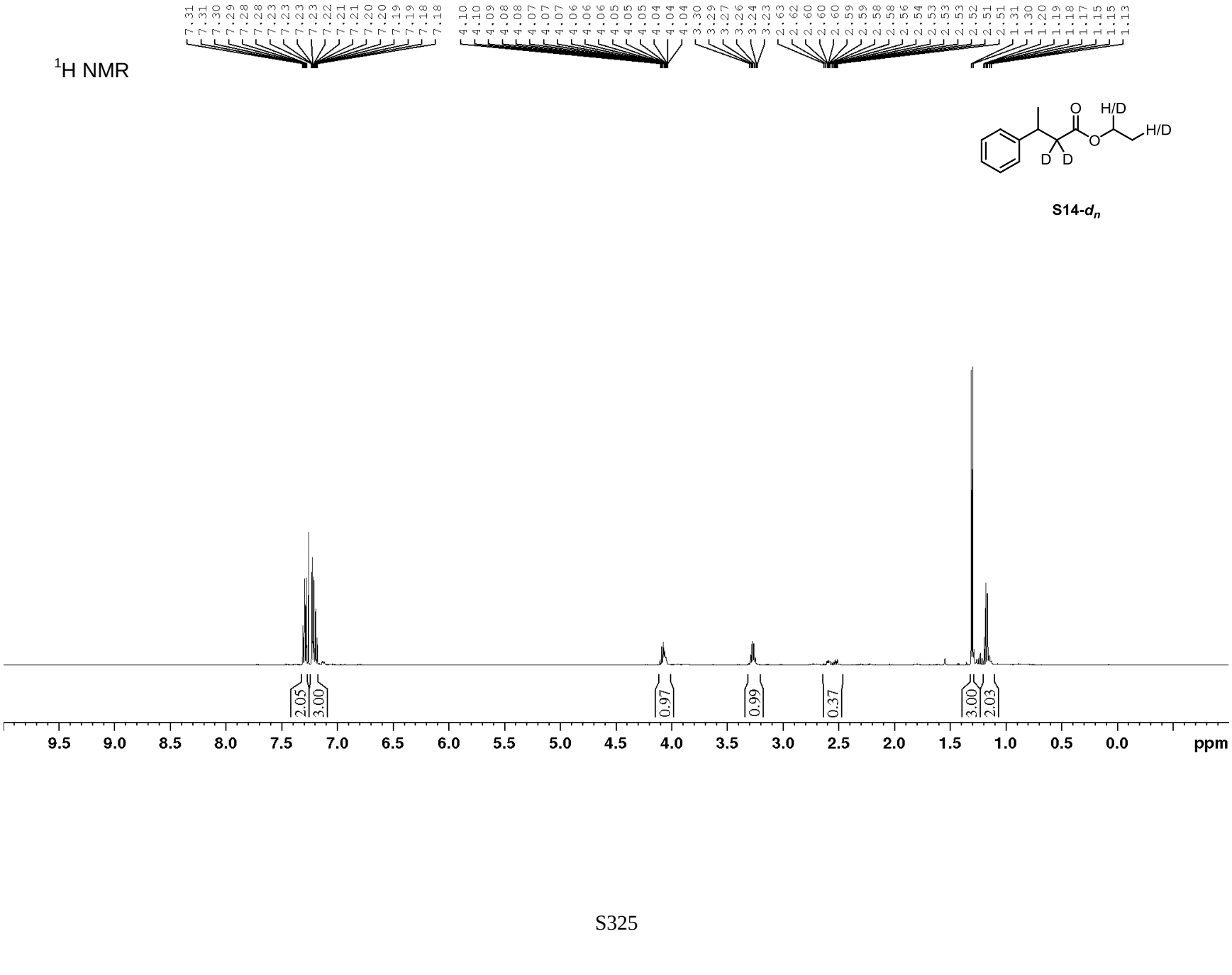
quant. ^{1}H NMR



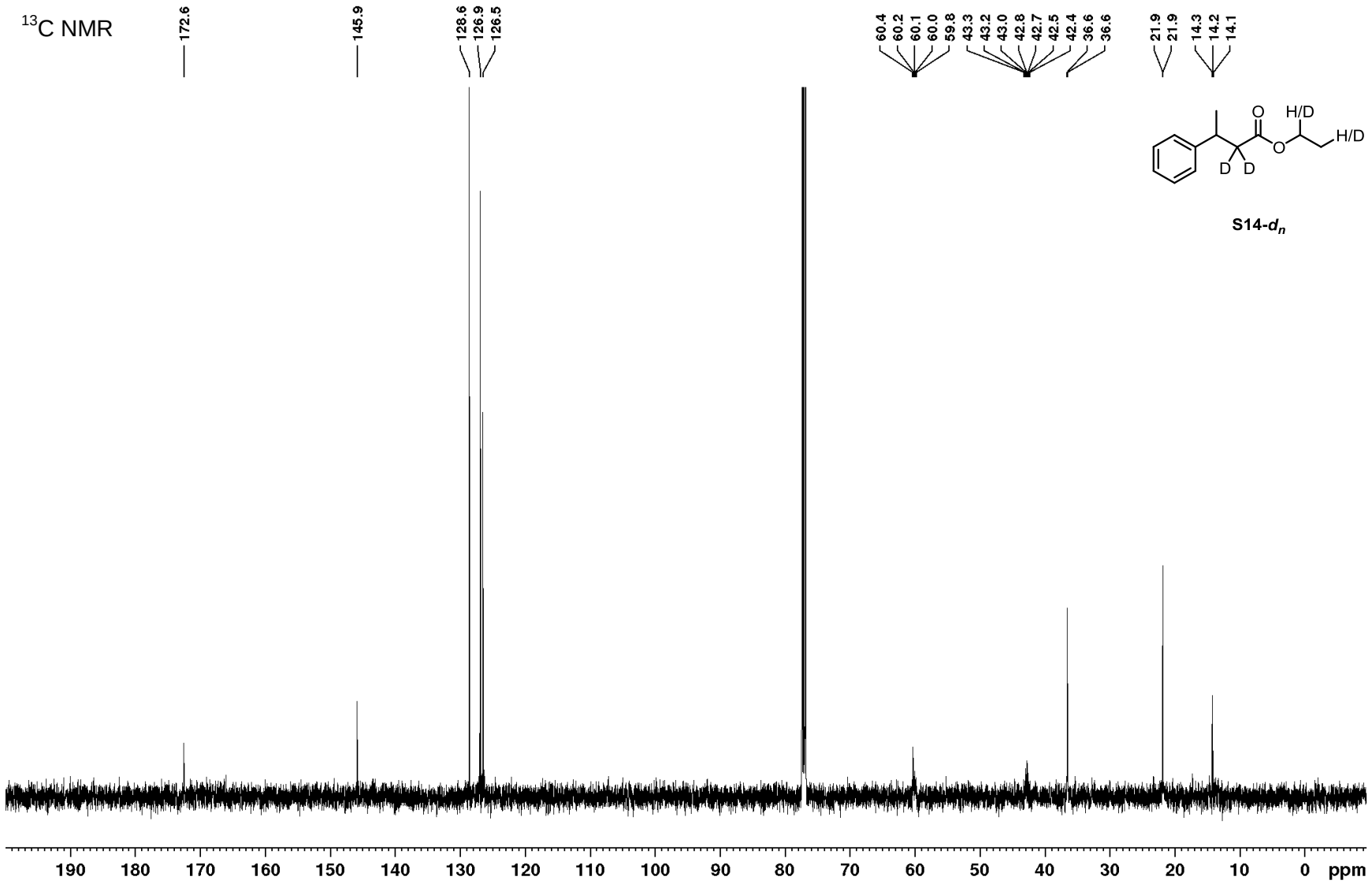
S14-d_n



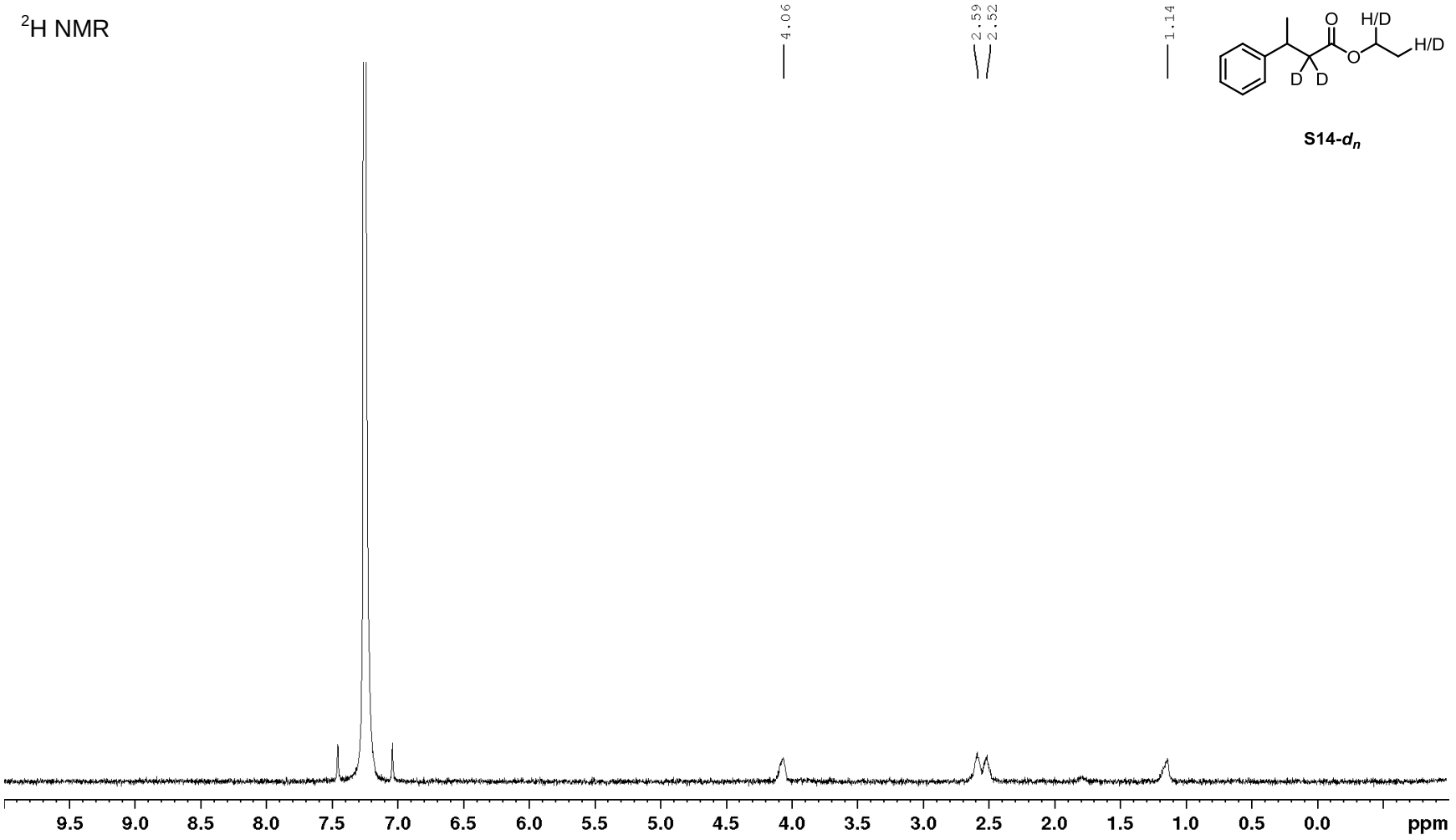
^{1}H NMR


7.31
7.31
7.30
7.29
7.28
7.28
7.23
7.23
7.23
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.18
4.10
4.10
4.09
4.08
4.08
4.07
4.07
4.07
4.06
4.06
4.06
4.05
4.05
4.05
4.04
4.04
4.04
3.30
3.29
3.27
3.26
3.24
3.23
2.63
2.62
2.60
2.60
2.60
2.59
2.59
2.58
2.58
2.56
2.54
2.53
2.53
2.53
2.52
2.51
2.51
1.31
1.30
1.20
1.19
1.18
1.17
1.15
1.15
1.13
O
H/D
H/D
O
D
D
2.05
3.00
0.97
0.99
0.37
3.00
2.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

S14-d_n

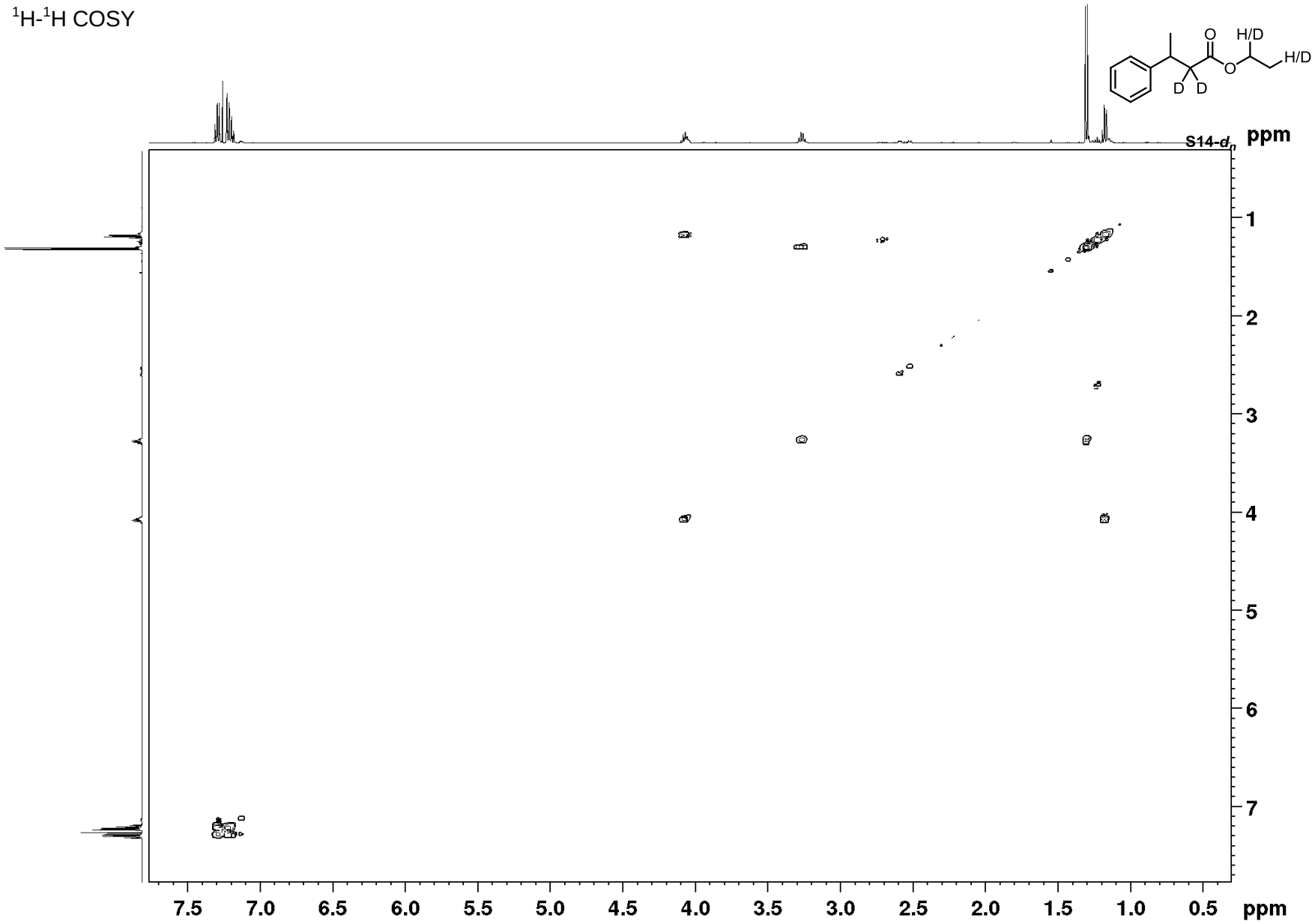

^{13}C NMR
172.6
145.9
128.6
126.9
126.5
60.4
60.2
60.1
60.0
59.8
43.3
43.2
43.0
42.8
42.7
42.5
42.4
36.6
36.6
21.9
21.9
14.3
14.2
14.1
O
H/D
H/D
O
D
D
S14-d_n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

^{2}H NMR

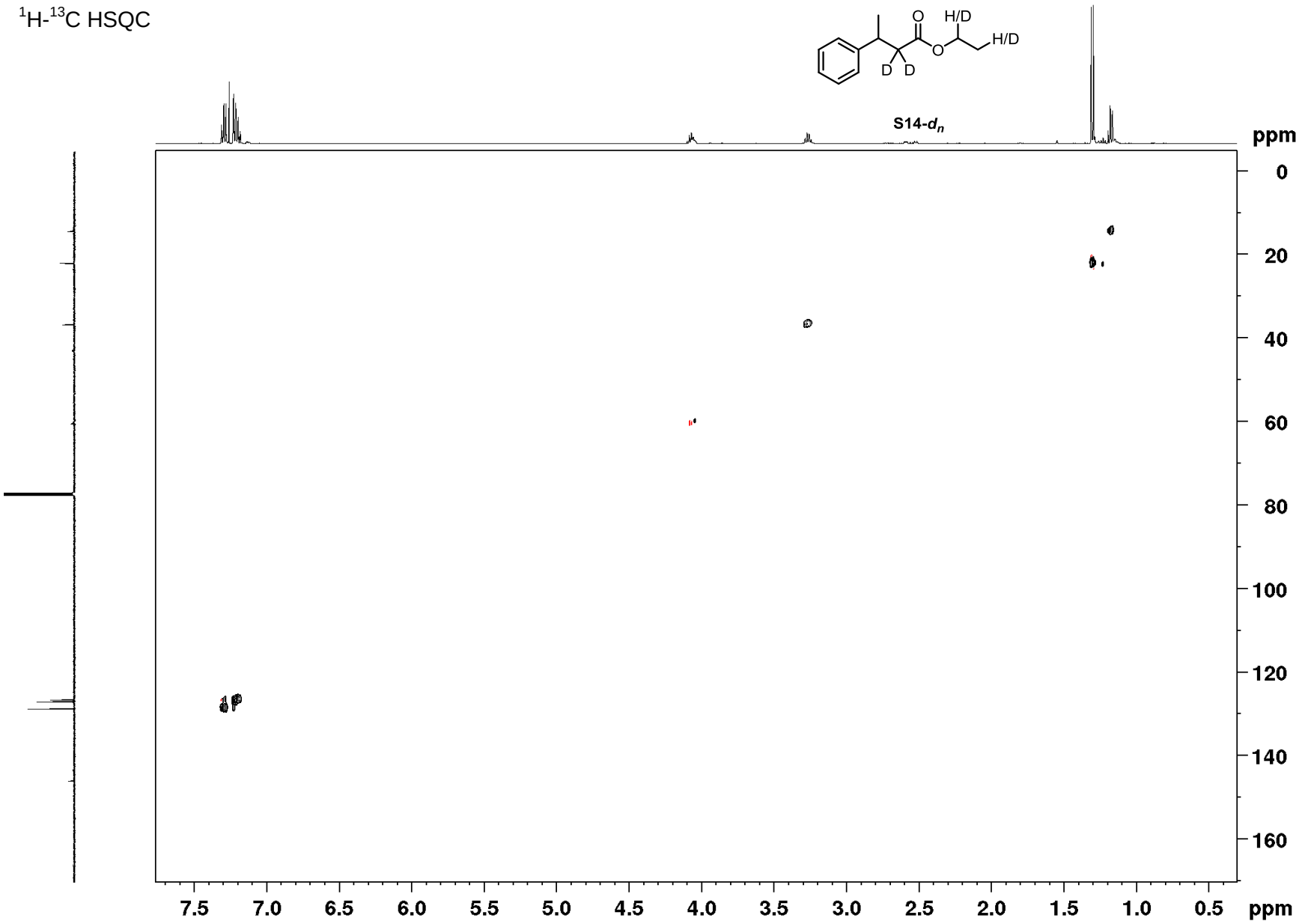

4.06
2.59
2.52
1.14
O
H/D
H/D
O
D
D
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

S14-d_n

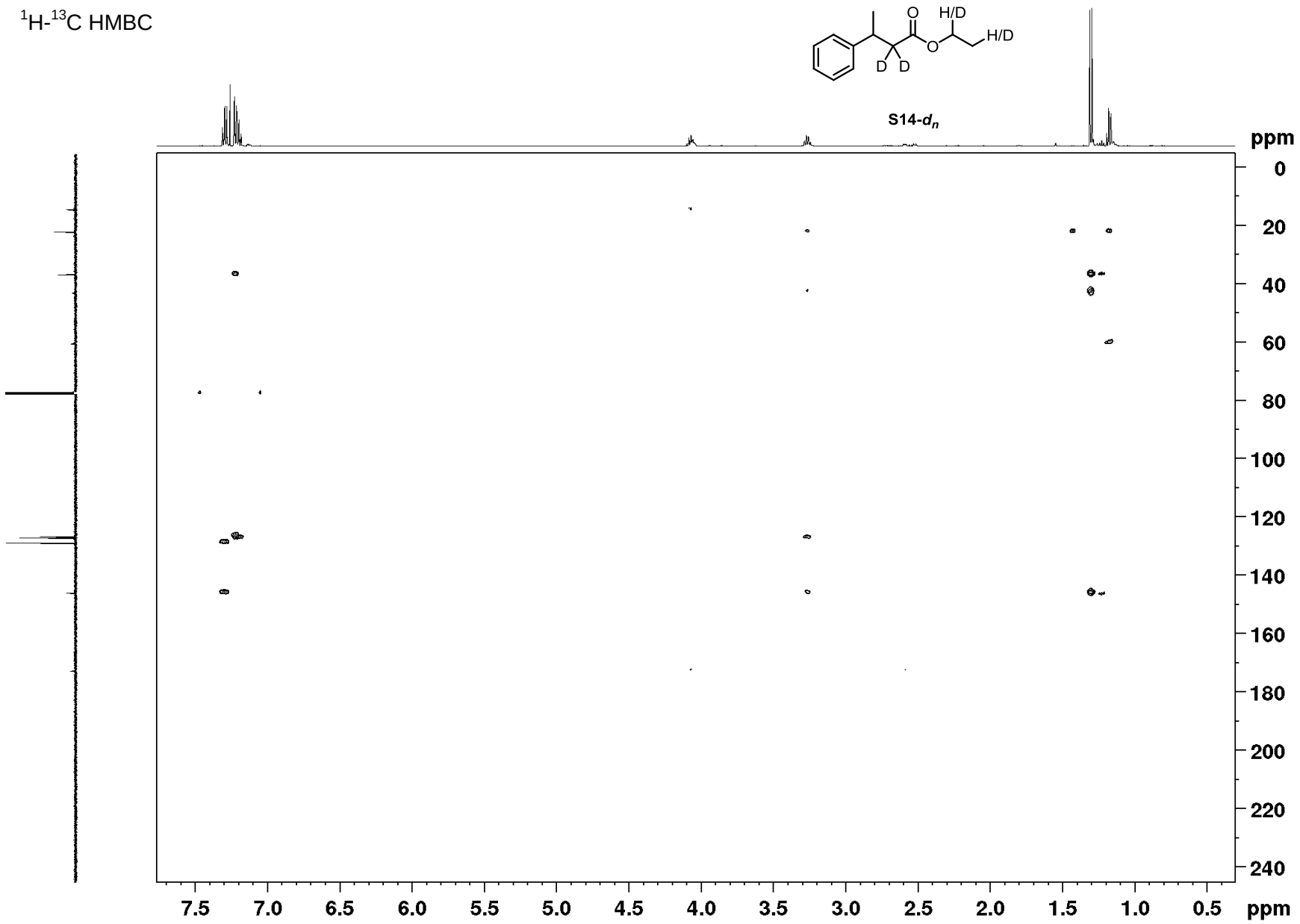
^{1}H-^{1}H COSY

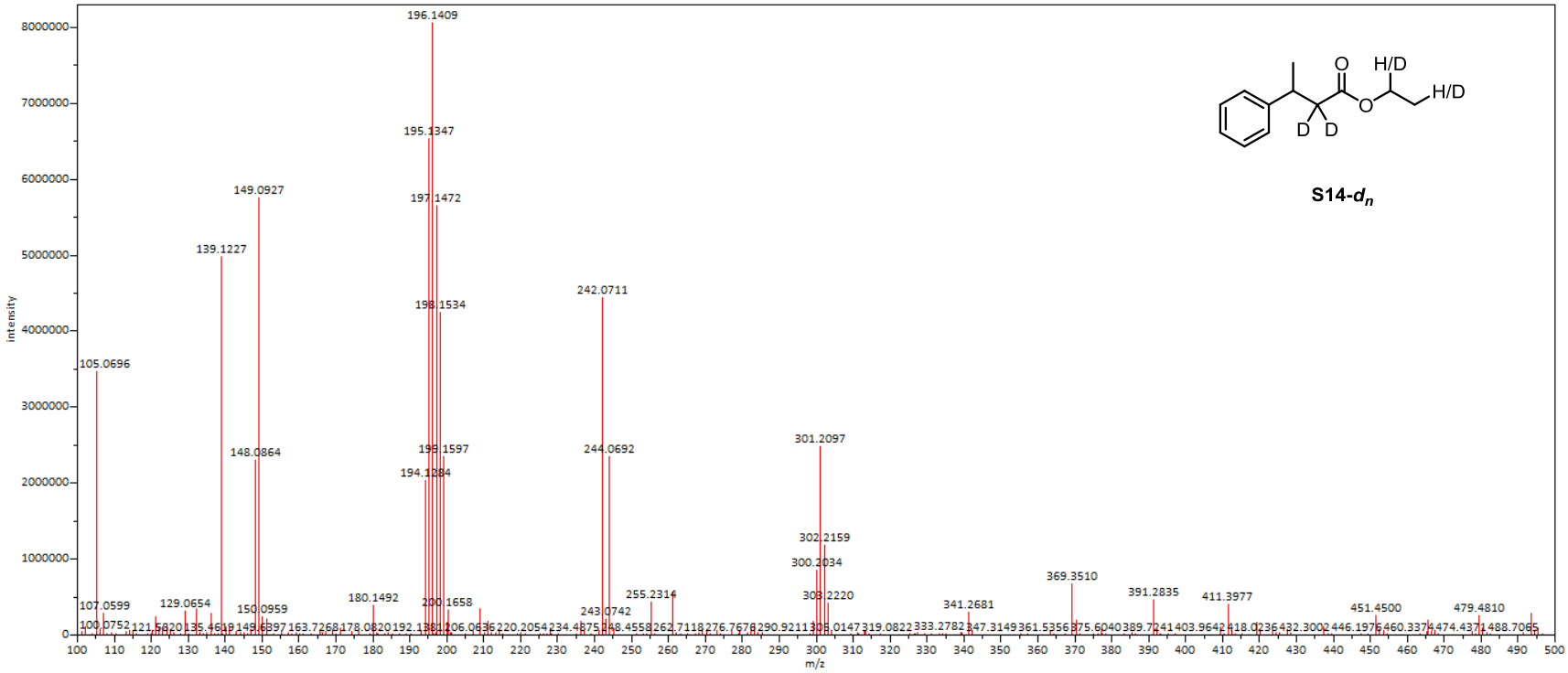

O
H/D
O
H/D
D D
S14-d_n
ppm
1
2
3
4
5
6
7
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

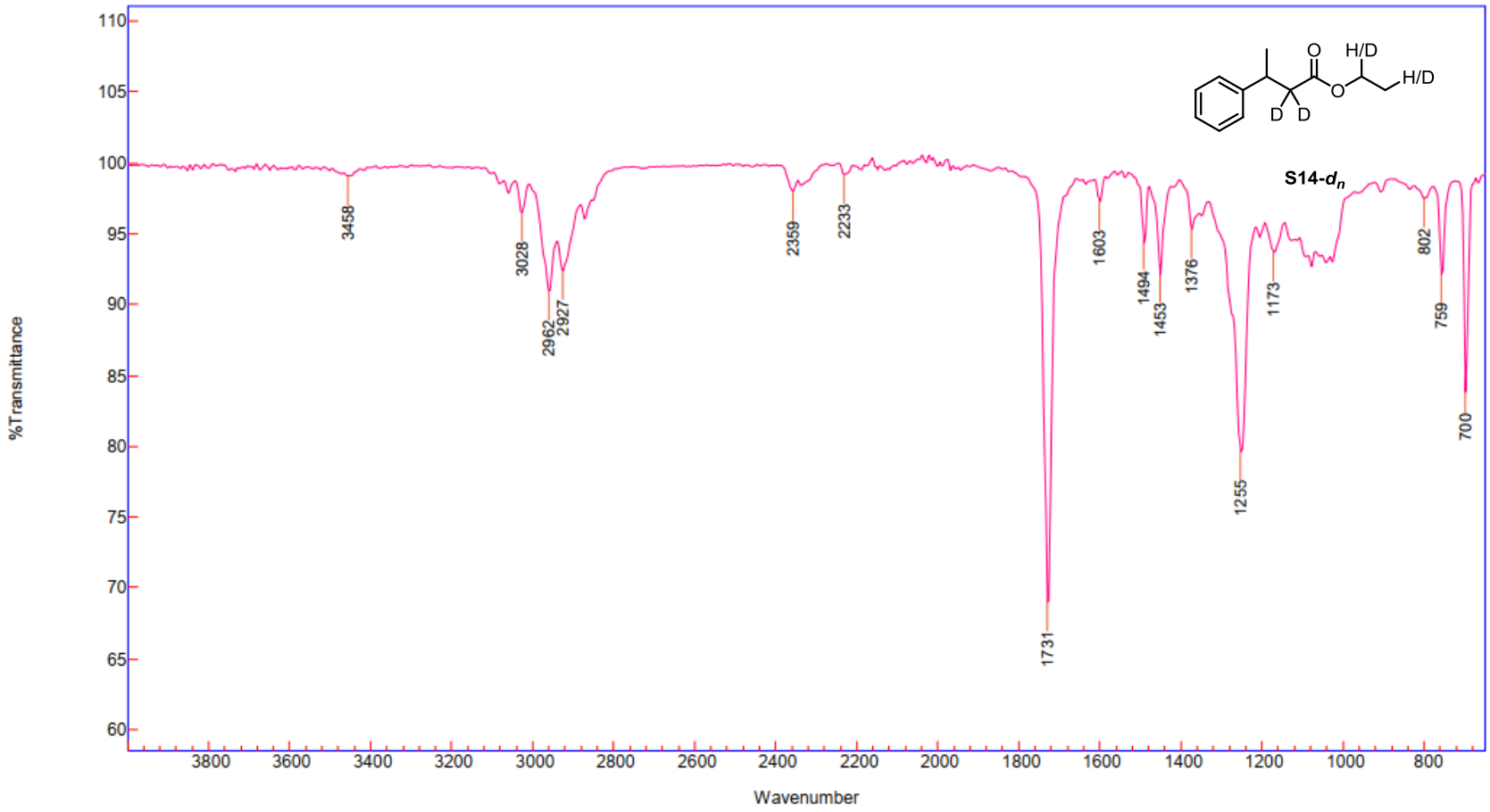
^{1}H-^{13}C HSQC


O
H/D
H/D
O
D D
S14-d_n
ppm
0
20
40
60
80
100
120
140
160
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
ppm

^{1}H-^{13}C HMBC

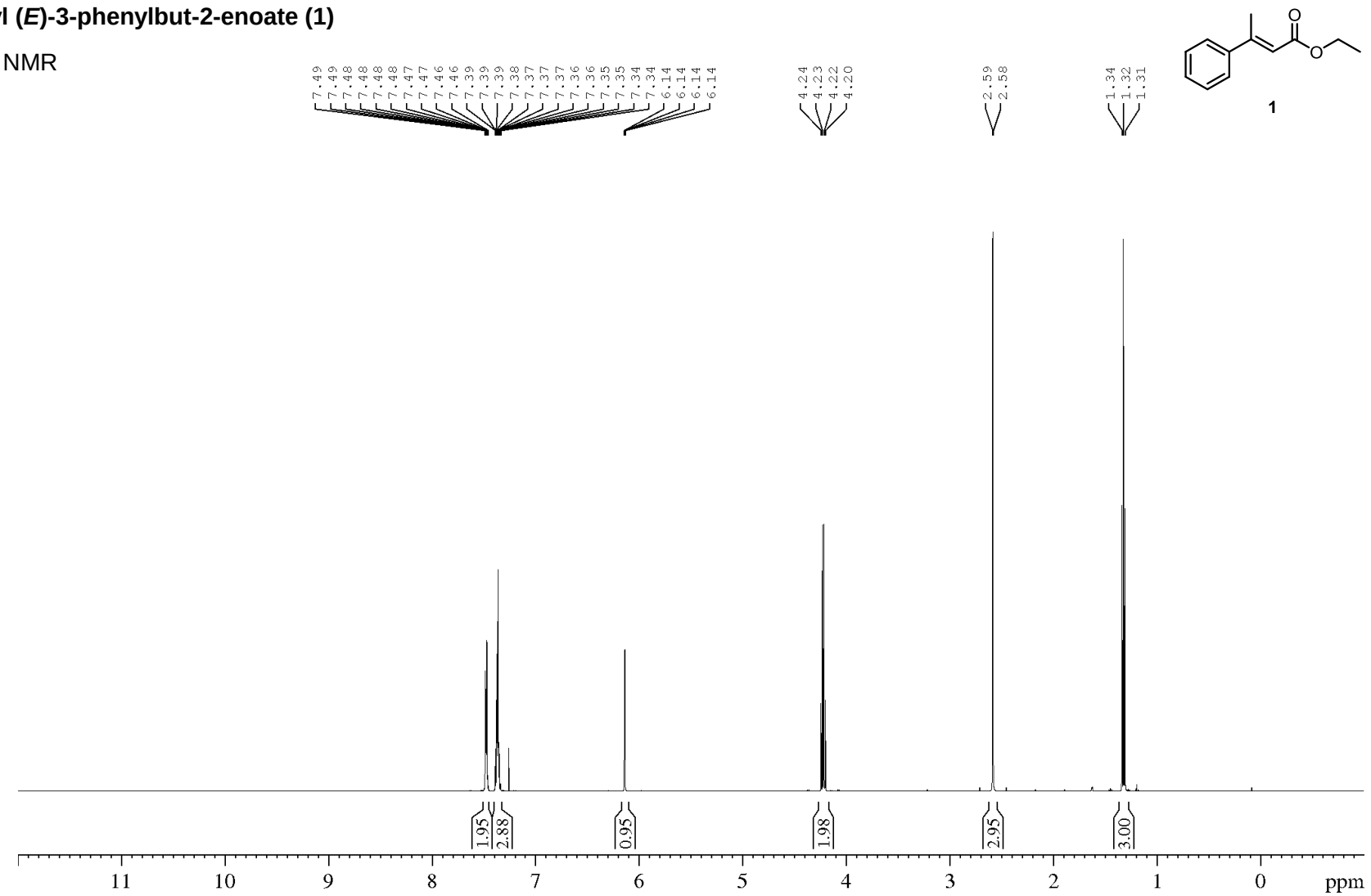

O
H/D
O
H/D
D D
S14-d_n
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


196.1409
195.1347
197.1472
149.0927
139.1227
198.1534
242.0711
105.0696
148.0864
199.1597
194.1284
244.0692
301.2097
302.2159
300.2034
303.2220
369.3510
391.2835
411.3977
180.1492
200.1658
255.2314
243.0742
341.2681
451.4500
479.4810
intensity
m/z
O
H/D
H/D
O
D
D
S14-d_n

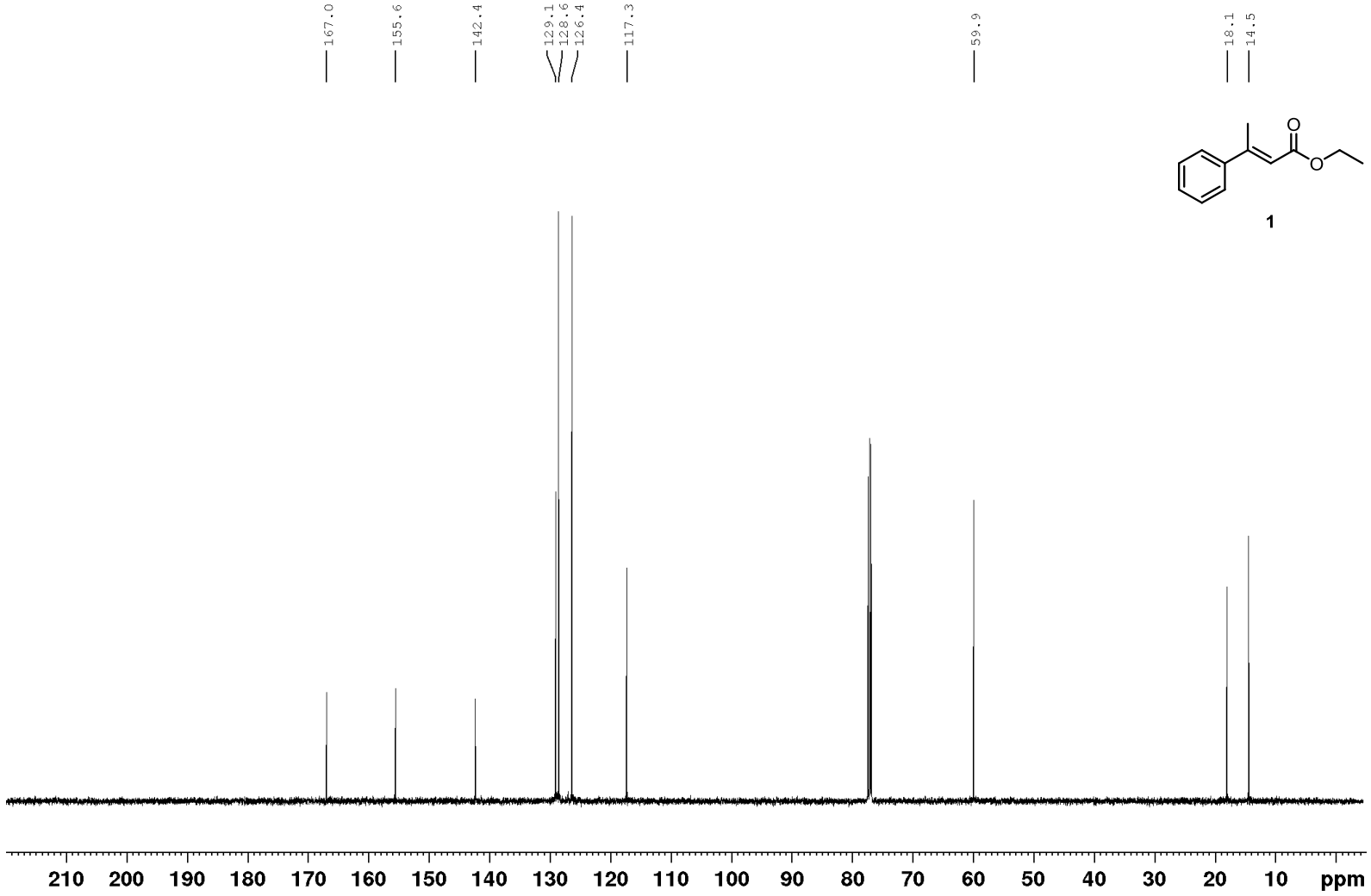

%Transmittance
Wavenumber
S14-d_n
H/D
H/D
O
O
D
D
3458
3028
2962
2927
2359
2233
1731
1603
1494
1453
1376
1255
1173
802
759
700

Ethyl (*E*)-3-phenylbut-2-enoate (1)

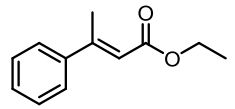
^{1}H NMR



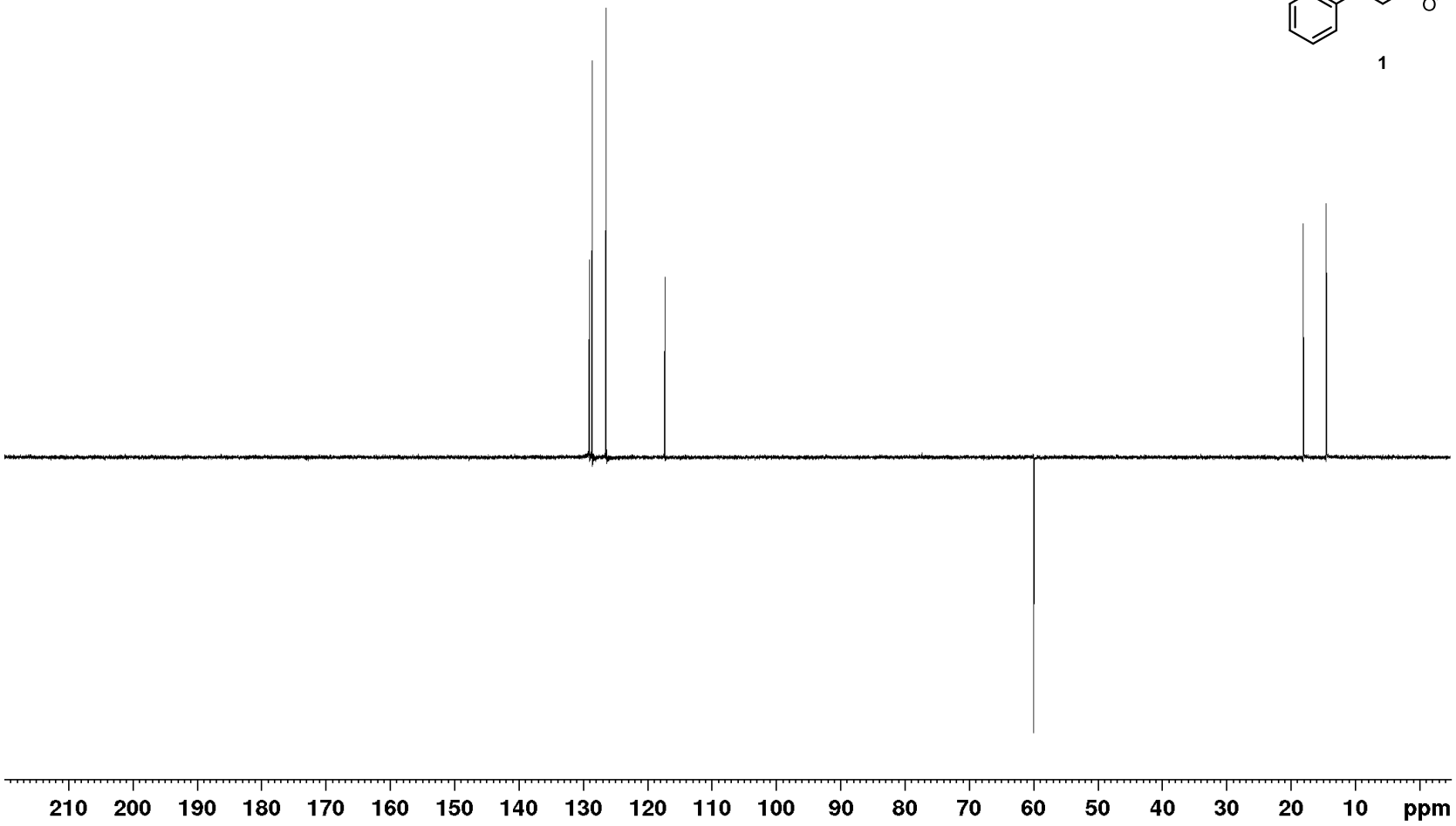
^{13}C NMR

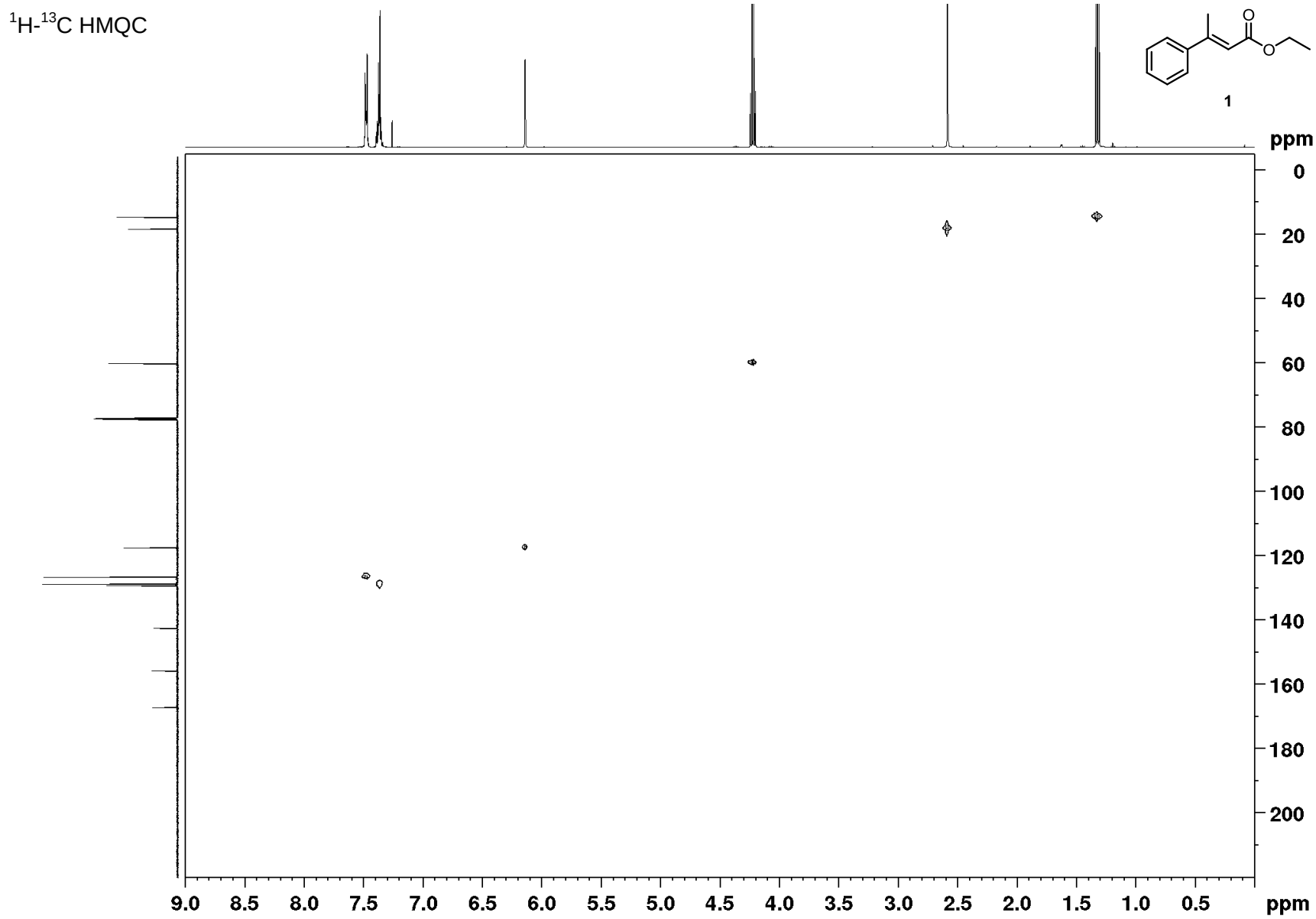

167.0
155.6
142.4
129.1
128.6
126.4
117.3
59.9
18.1
14.5
O
O
1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{13}C DEPT NMR

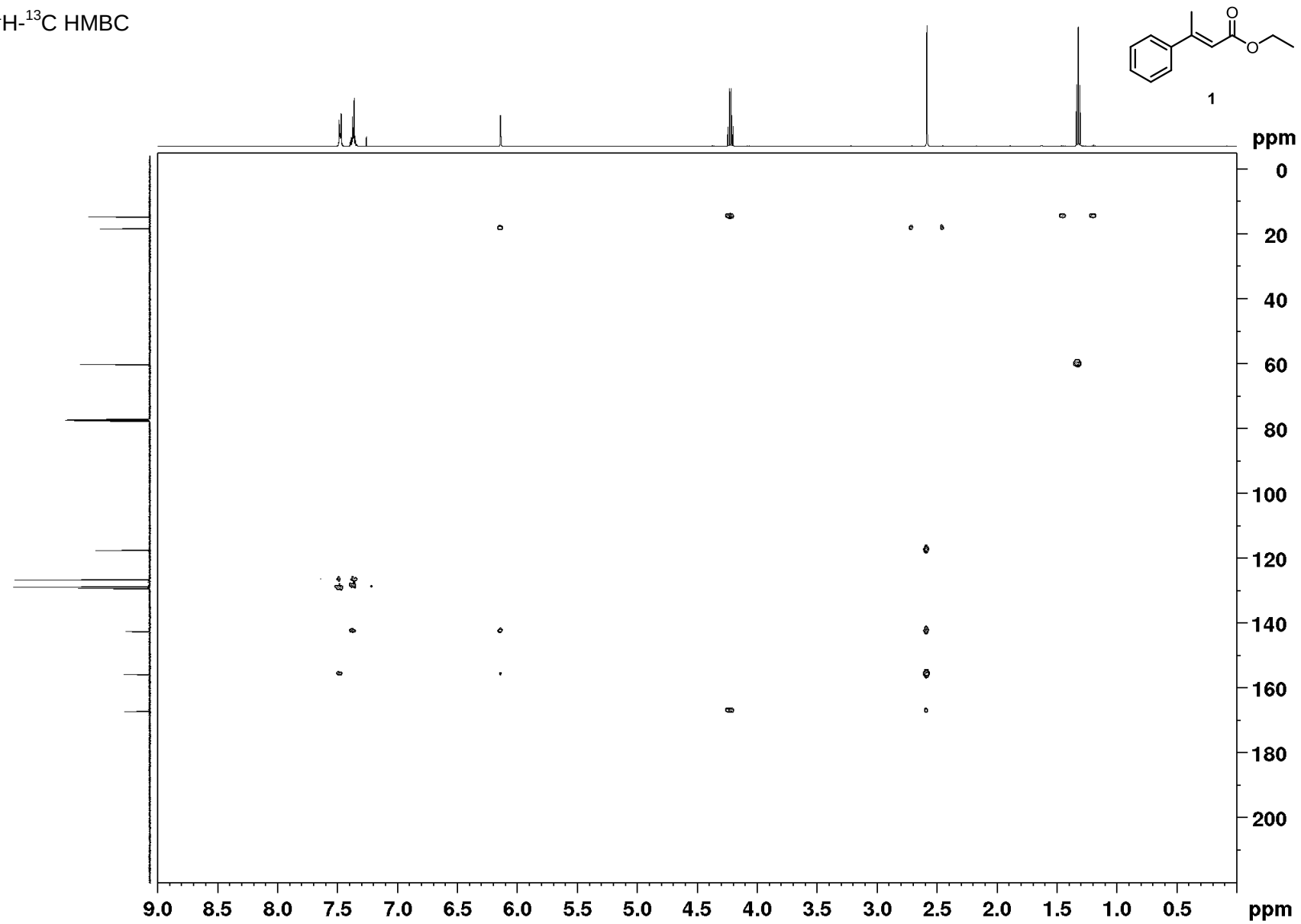


1

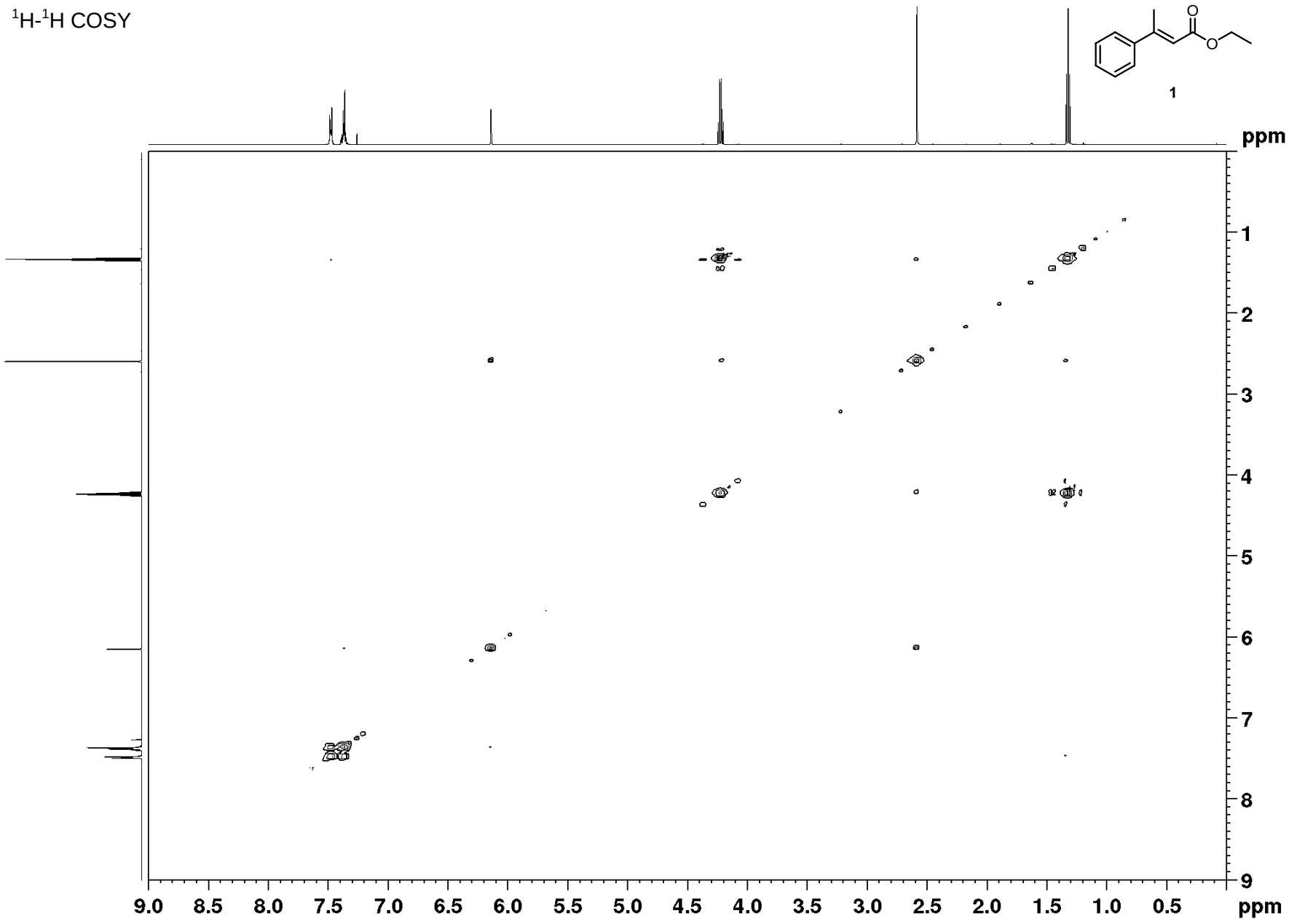



^{1}H-^{13}C HMQC
O
O
1
ppm
0
20
40
60
80
100
120
140
160
180
200
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

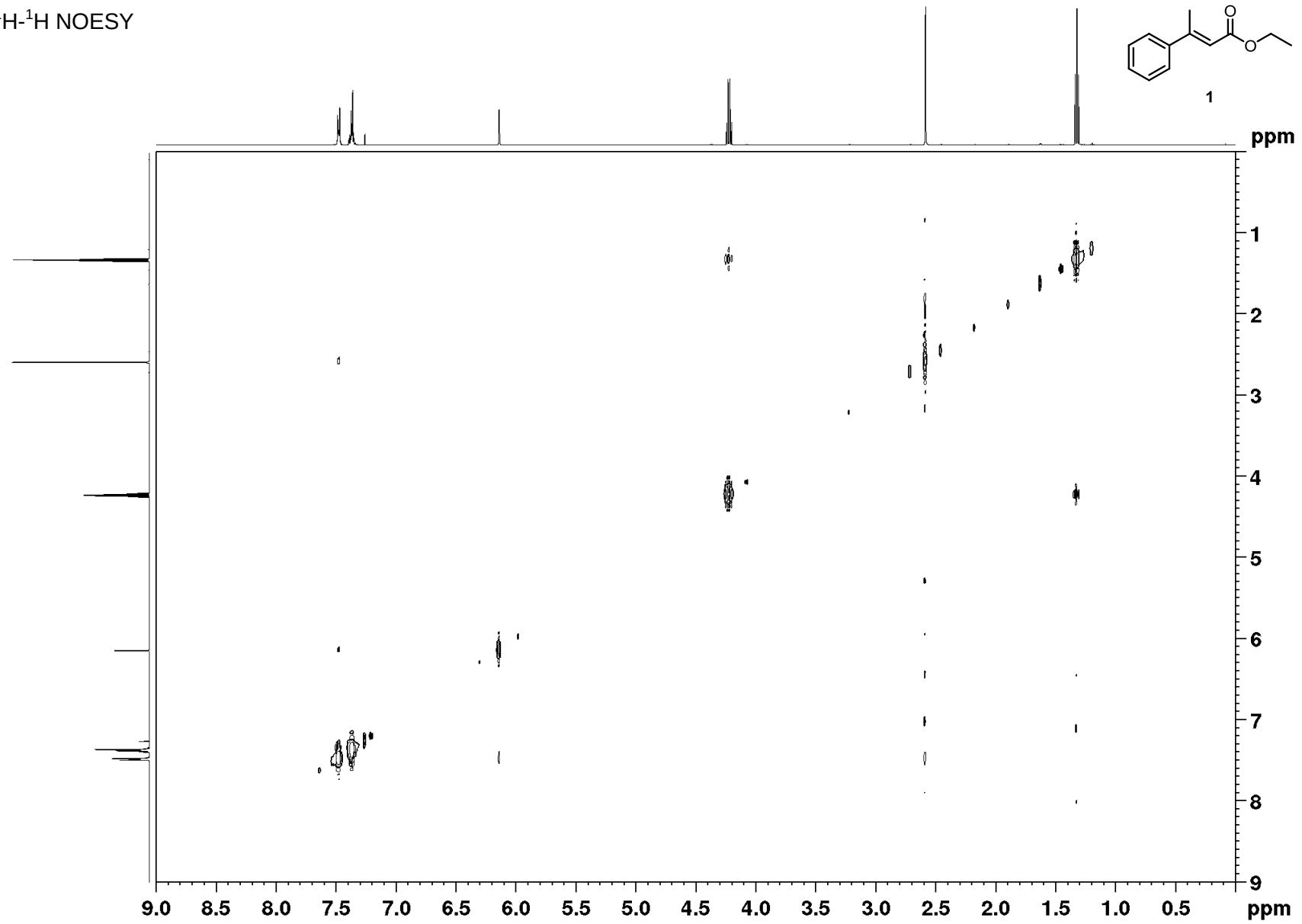
^{1}H-^{13}C HMBC

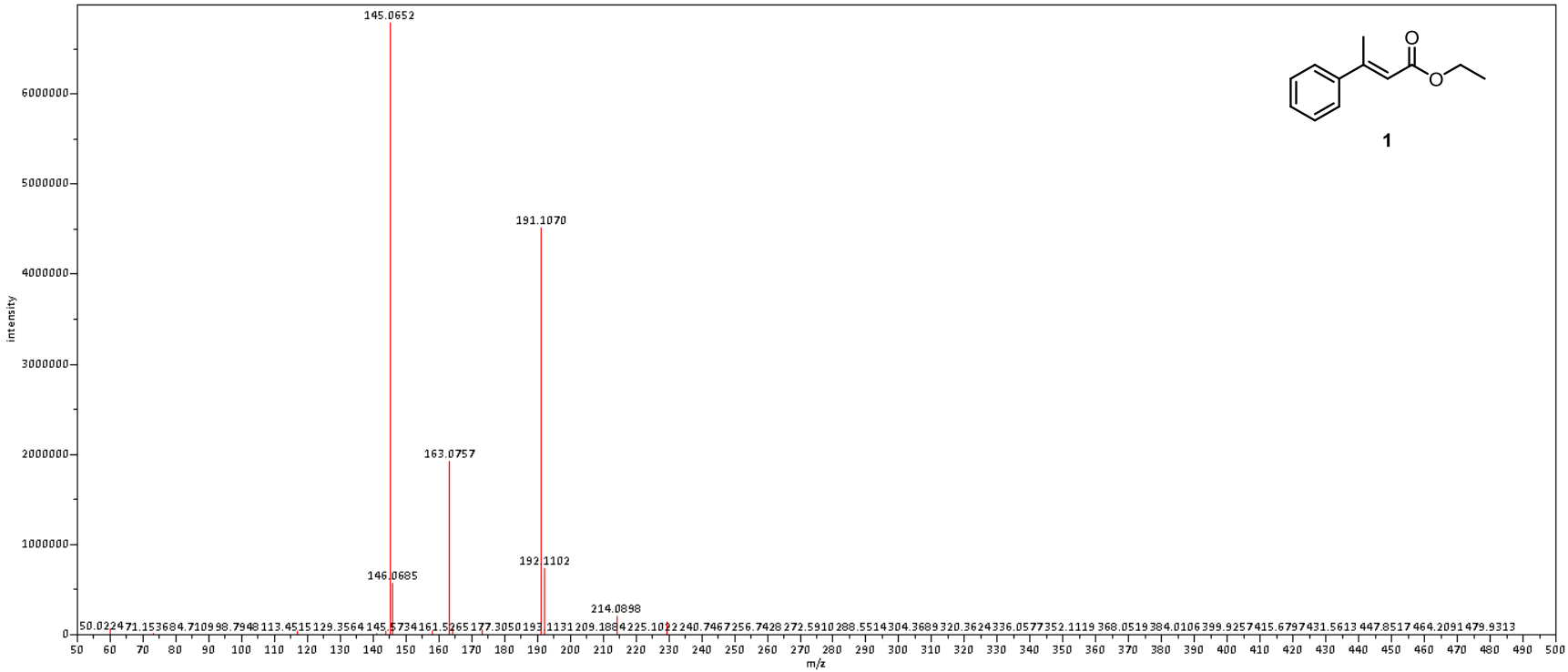

O
O
1
ppm
0
20
40
60
80
100
120
140
160
180
200
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{1}H-^{1}H COSY


O
O
1
ppm
1
2
3
4
5
6
7
8
9
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

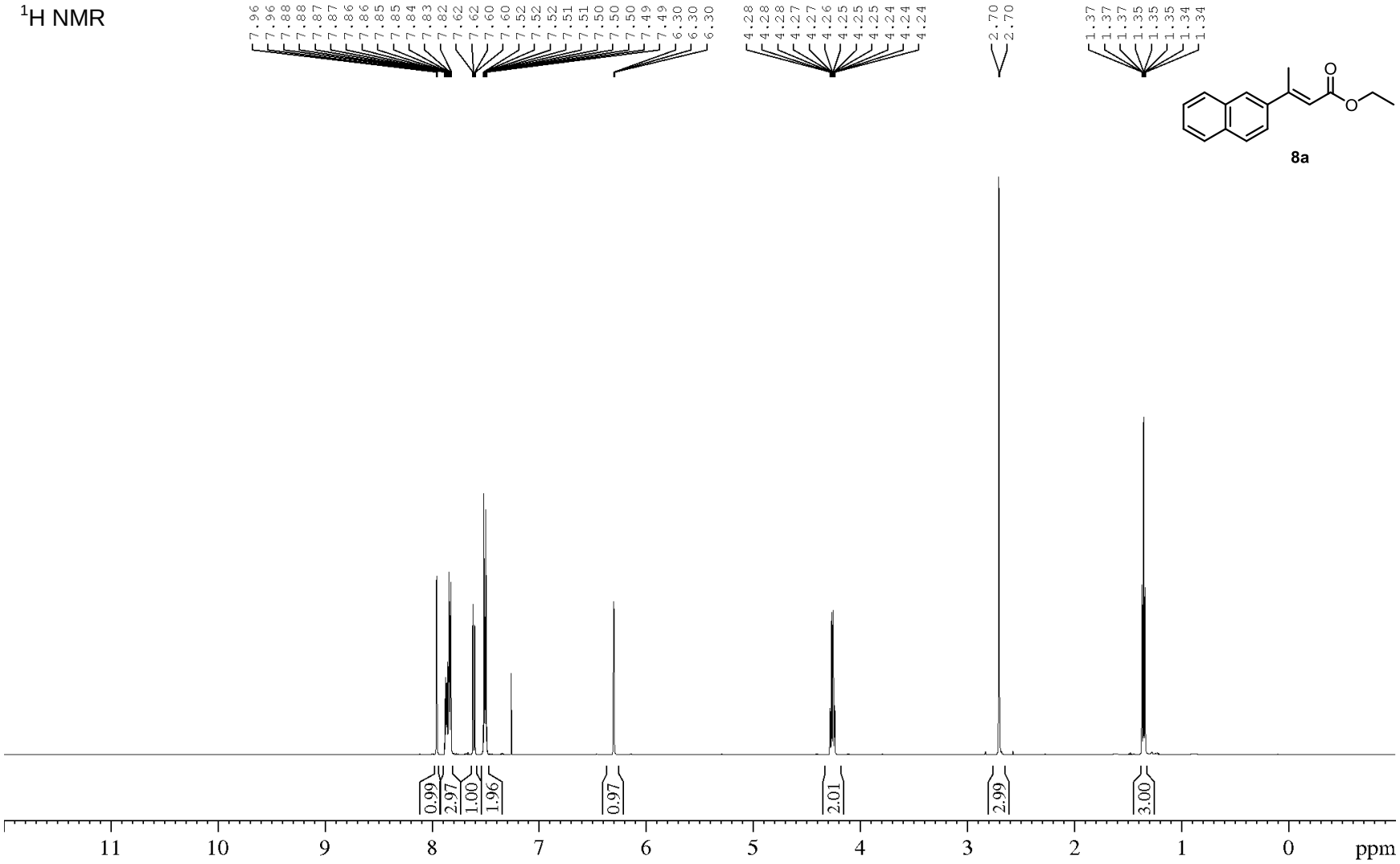
^{1}H-^{1}H NOESY


O
O
1
ppm
1
2
3
4
5
6
7
8
9
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

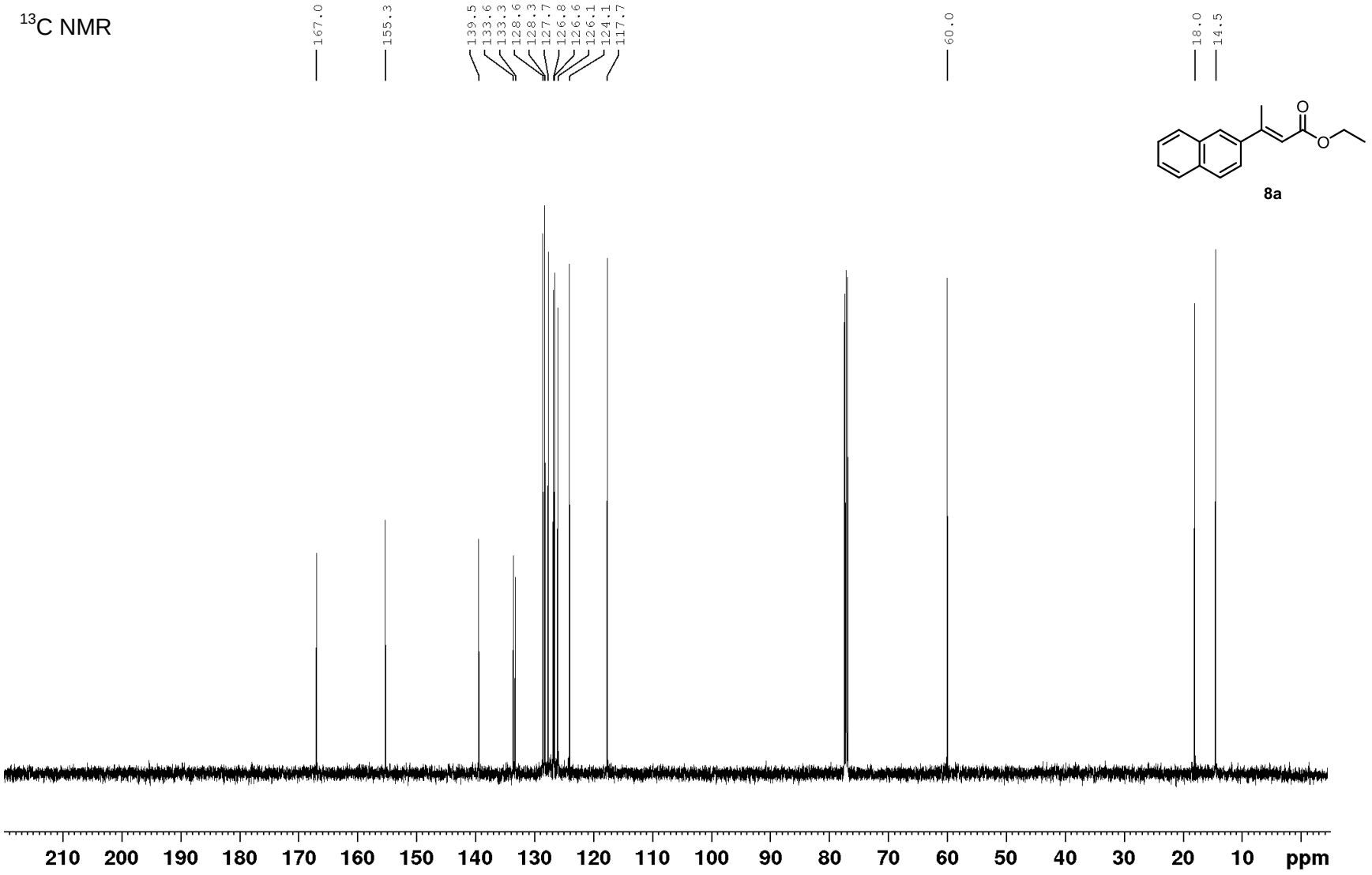

145.0652
191.1070
163.0757
192.1102
146.0685
214.0898
intensity
m/z
1

Ethyl (*E*)-3-(naphthalen-2-yl)but-2-enoate (8a)

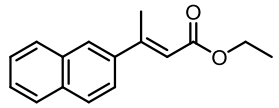
^{1}H NMR



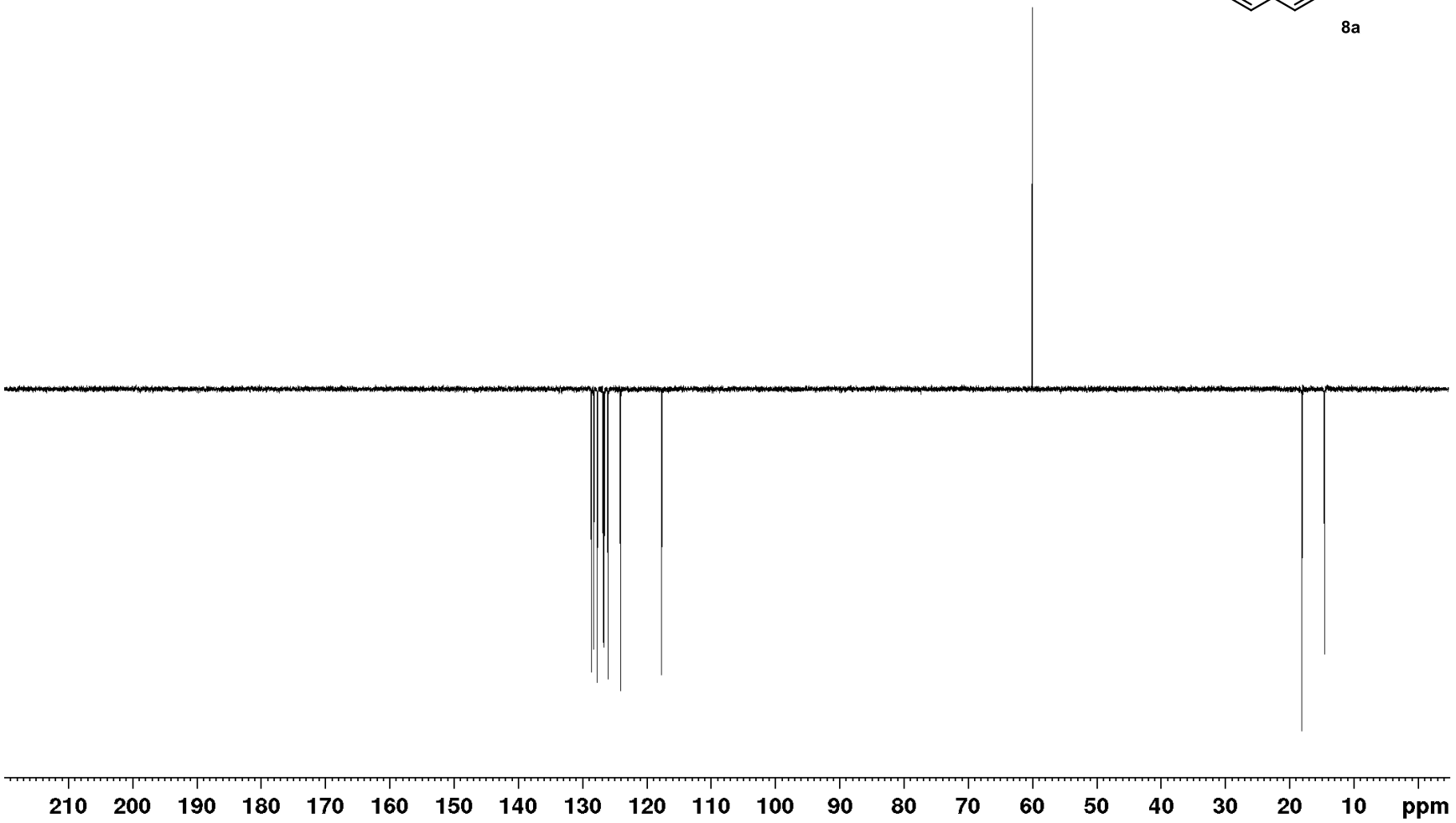
^{13}C NMR

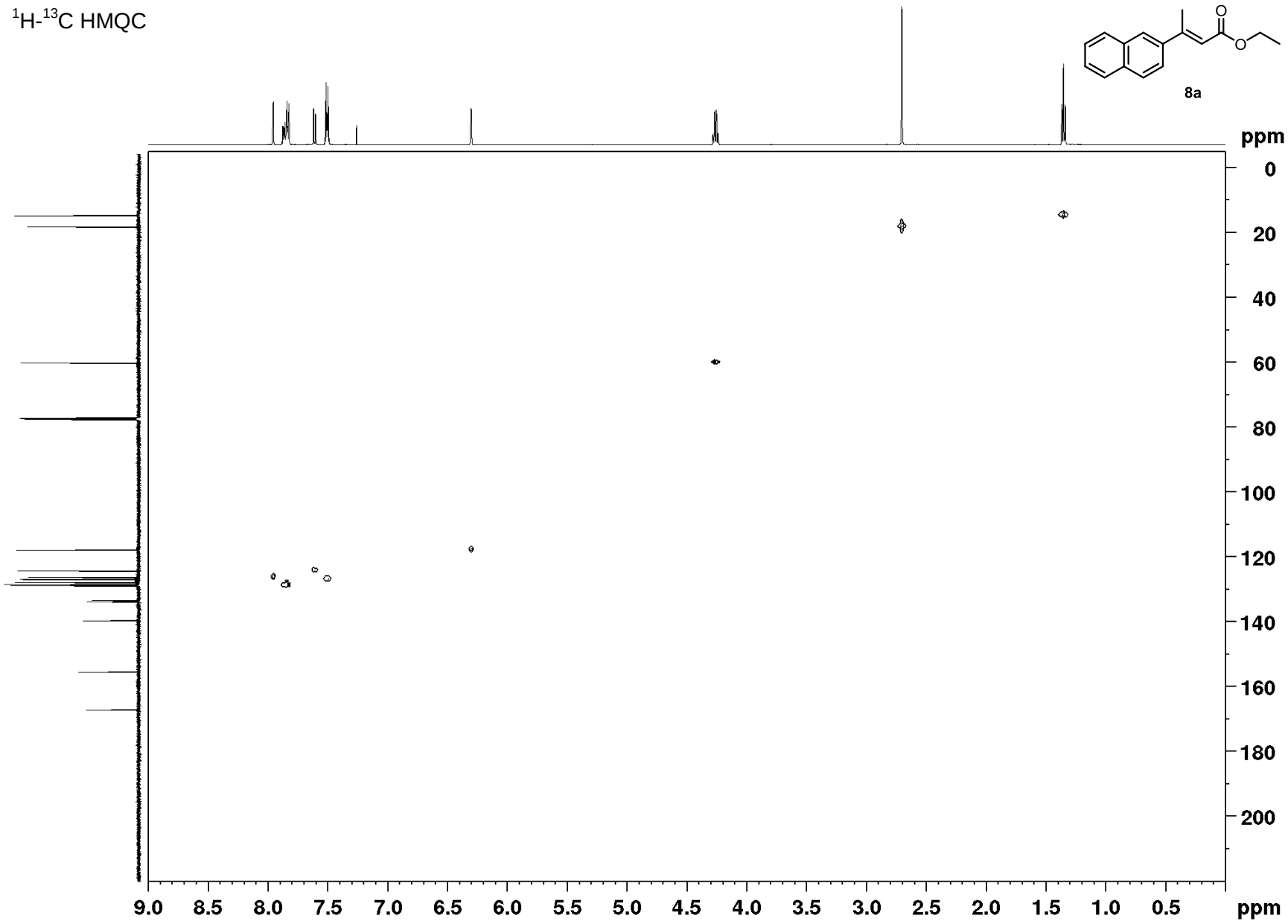

167.0
155.3
139.5
133.6
133.3
128.6
128.3
127.7
126.8
126.6
126.1
124.1
117.7
60.0
18.0
14.5
O
O
8a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{13}C DEPT NMR

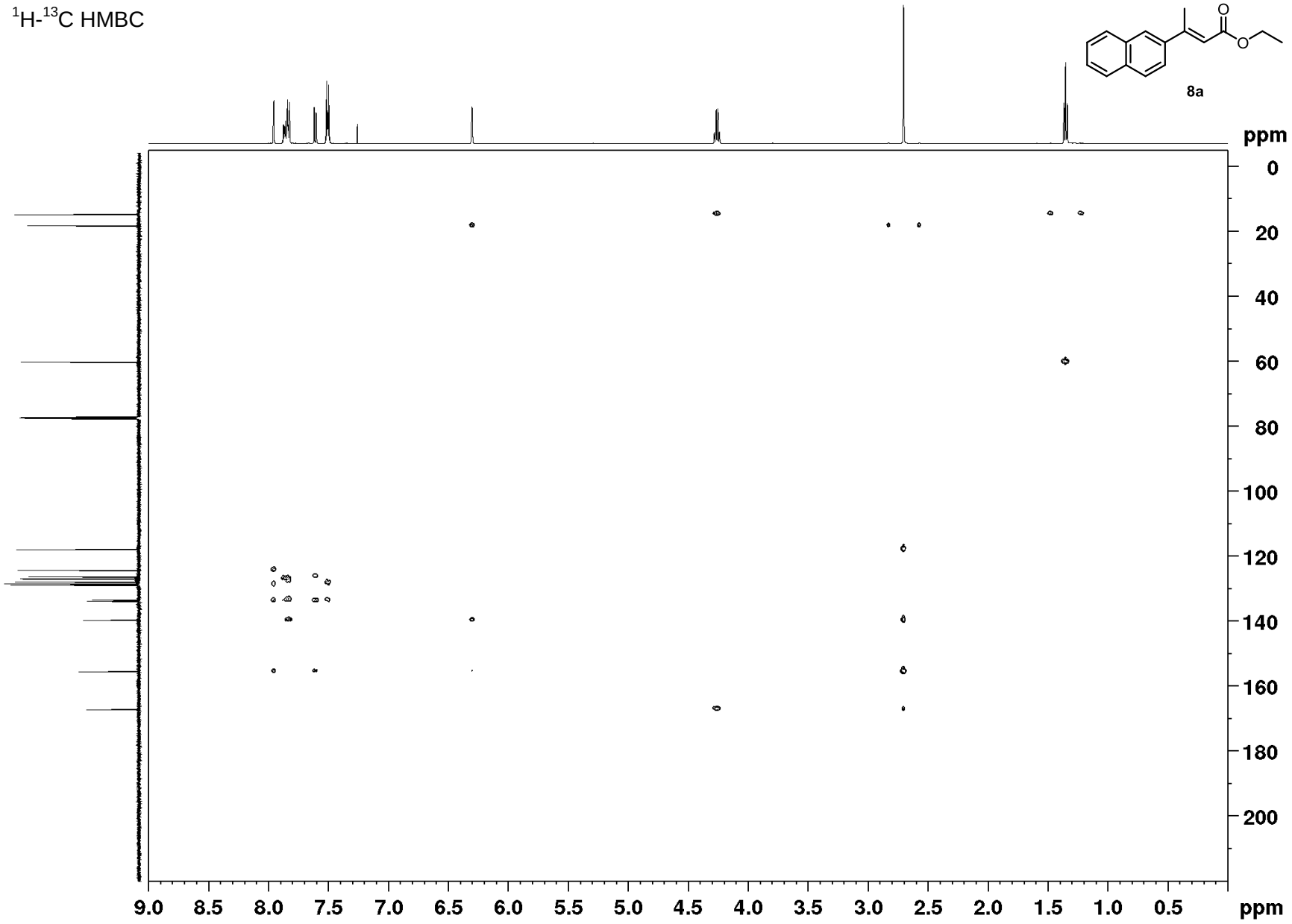


8a




^{1}H-^{13}C HMQC
8a
ppm
0
20
40
60
80
100
120
140
160
180
200
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

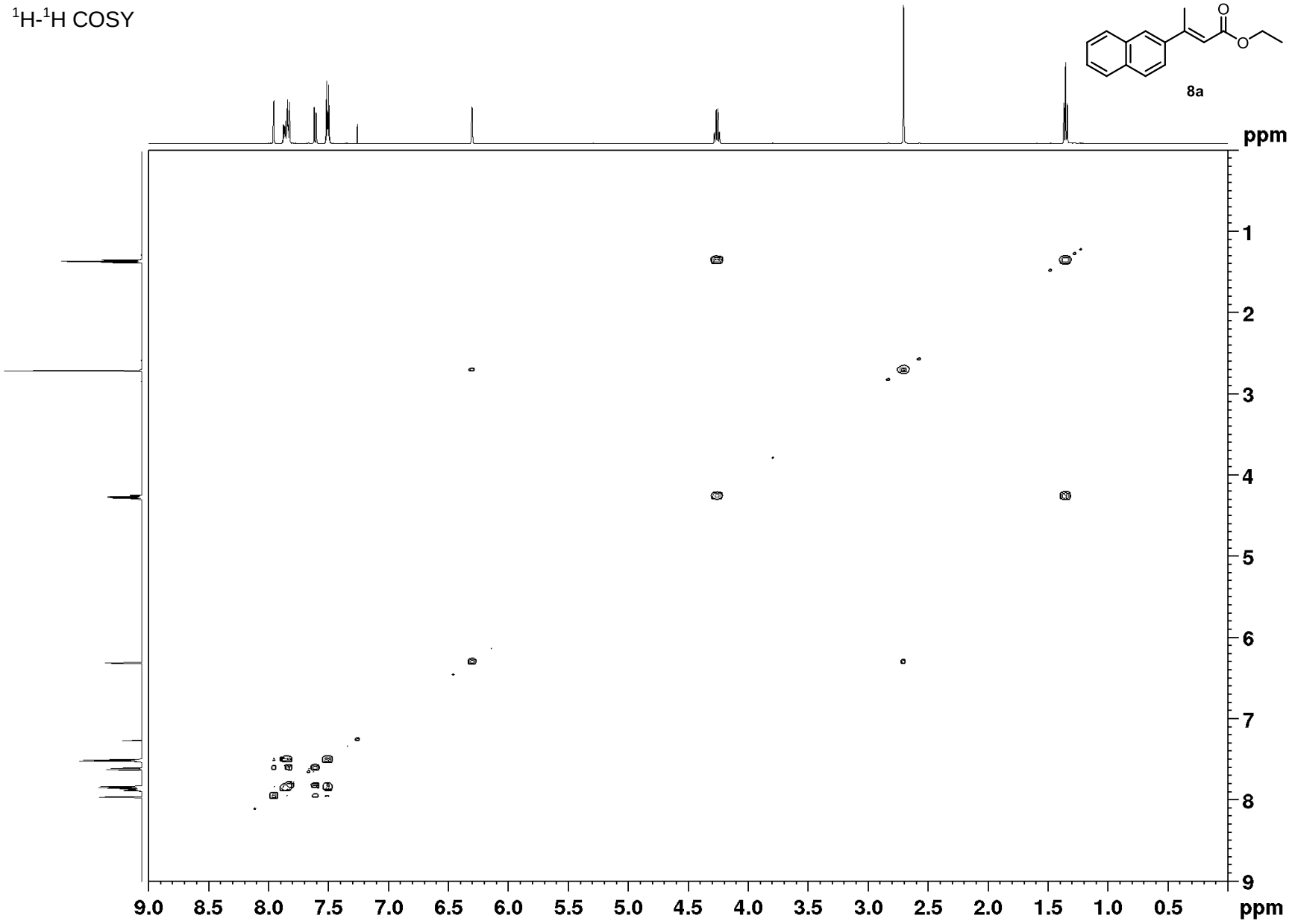
^{1}H-^{13}C HMBC


8a
ppm
0
20
40
60
80
100
120
140
160
180
200
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

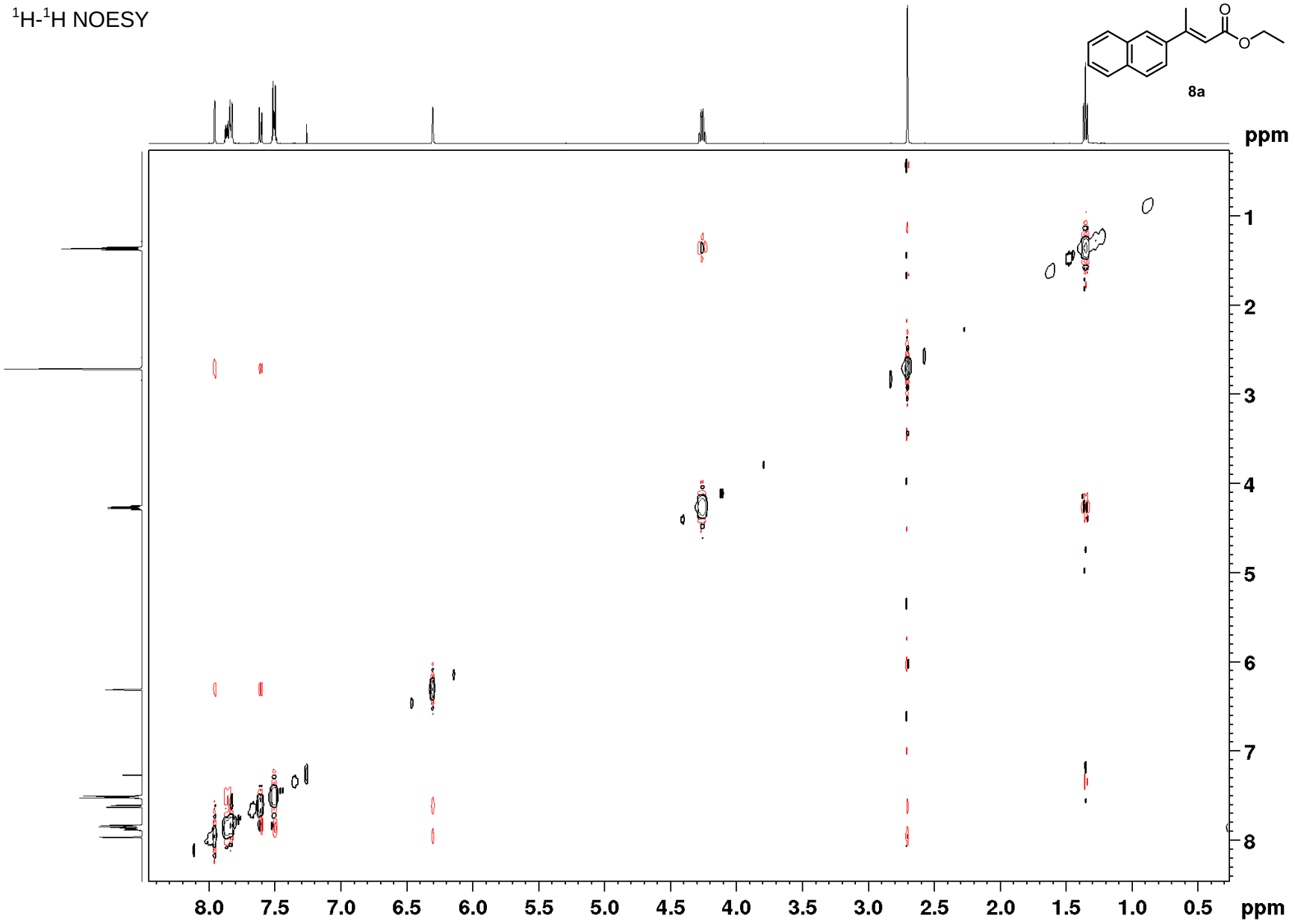
^{1}H-^{1}H COSY

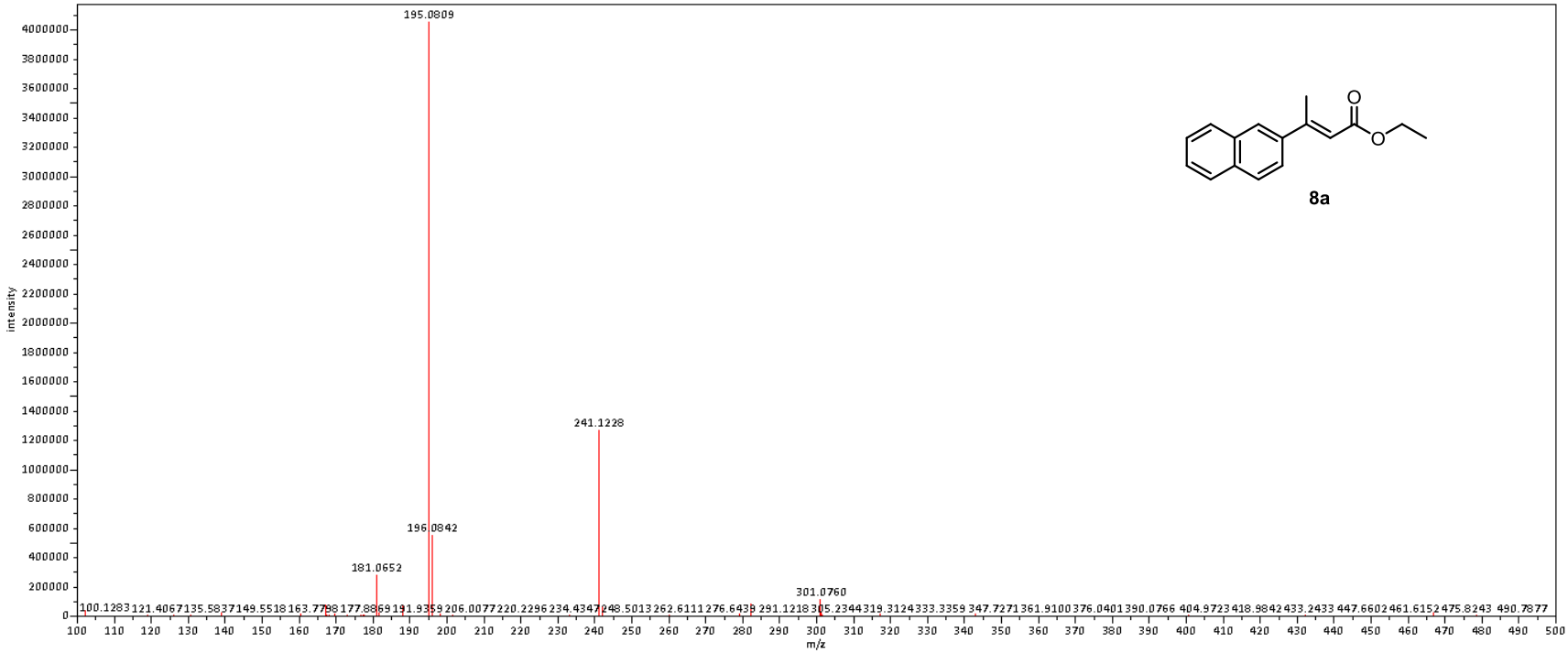
O
O

8a


ppm
1
2
3
4
5
6
7
8
9
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

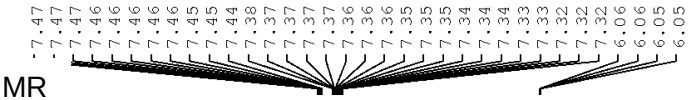
^{1}H-^{1}H NOESY

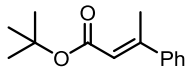



195.0809
241.1228
196.0842
181.0652
301.0760
intensity
m/z
8a

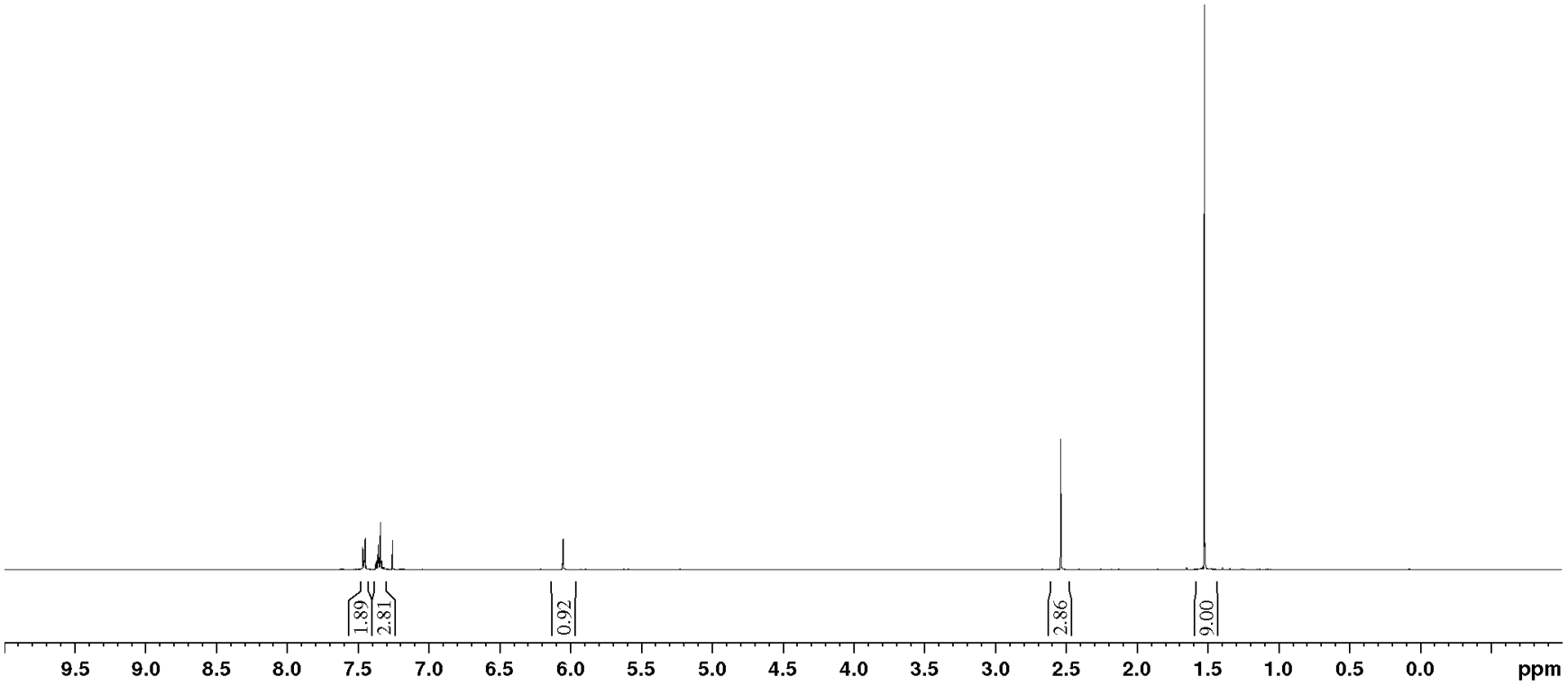
***tert*-Butyl (*E*)-3-phenylbut-2-enoate (8b)**

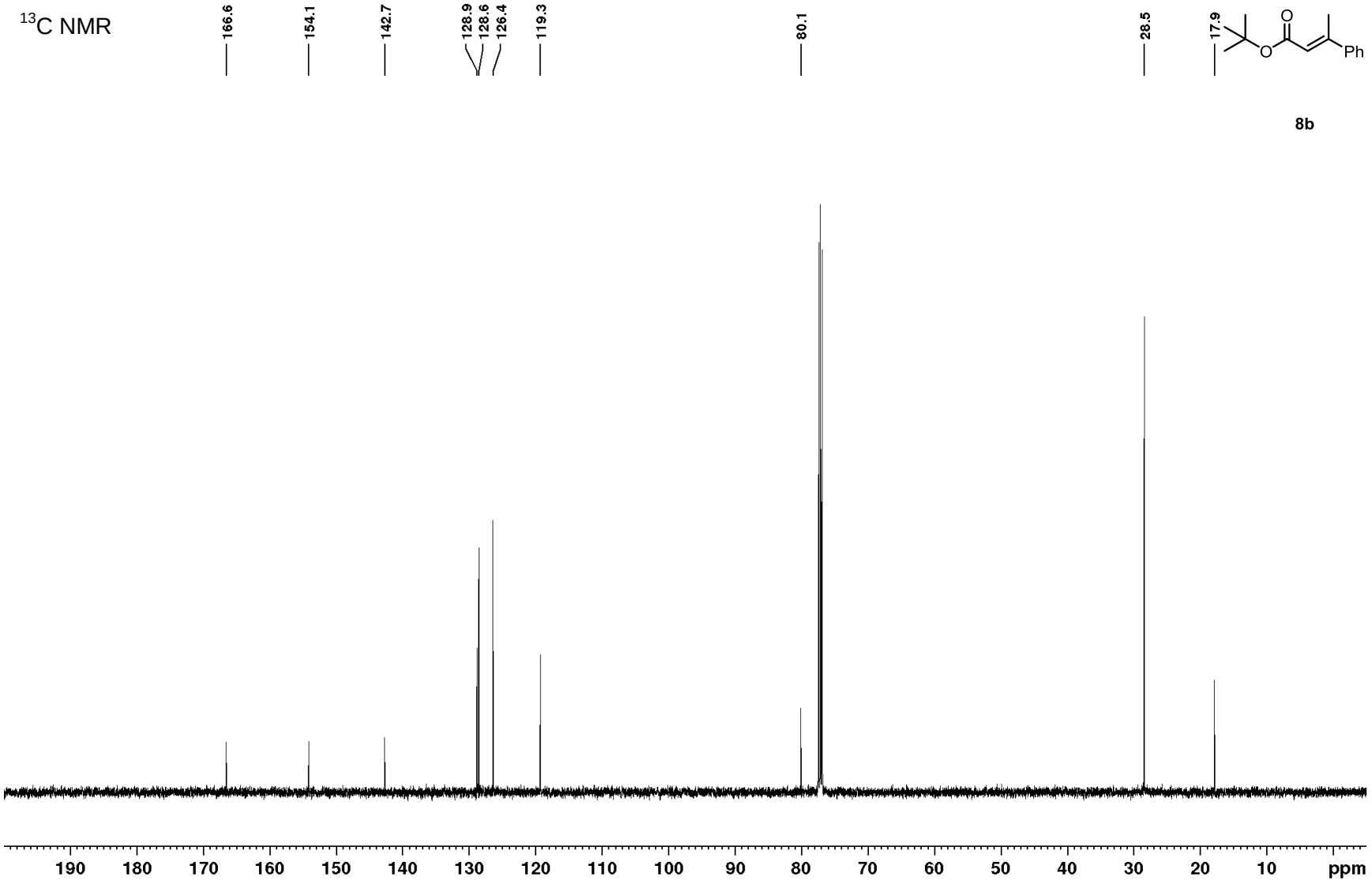
^{1}H NMR



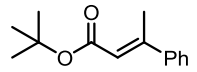


8b

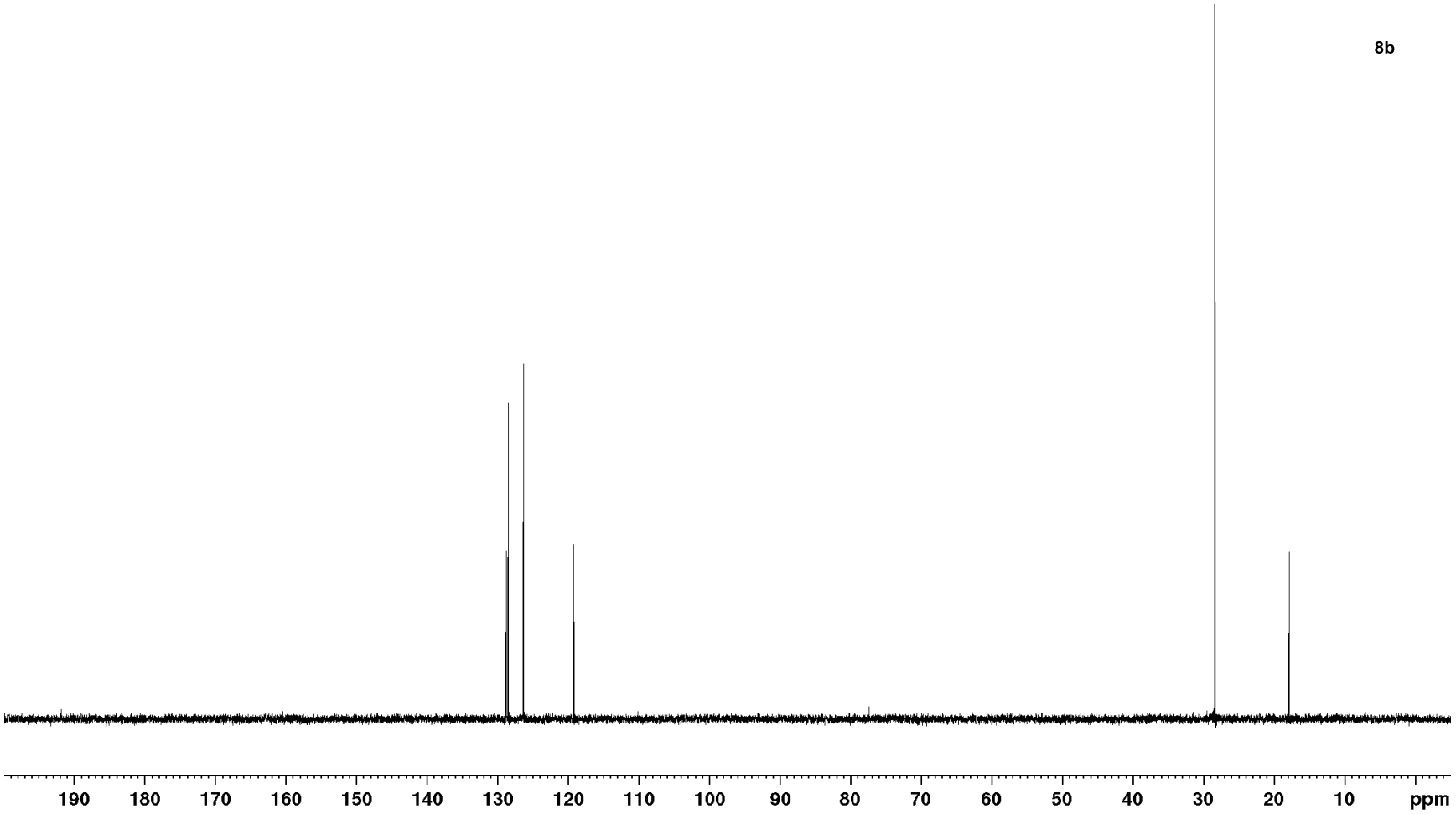



^{13}C NMR
166.6
154.1
142.7
128.9
128.6
126.4
119.3
80.1
28.5
17.9
O
O
Ph
8b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

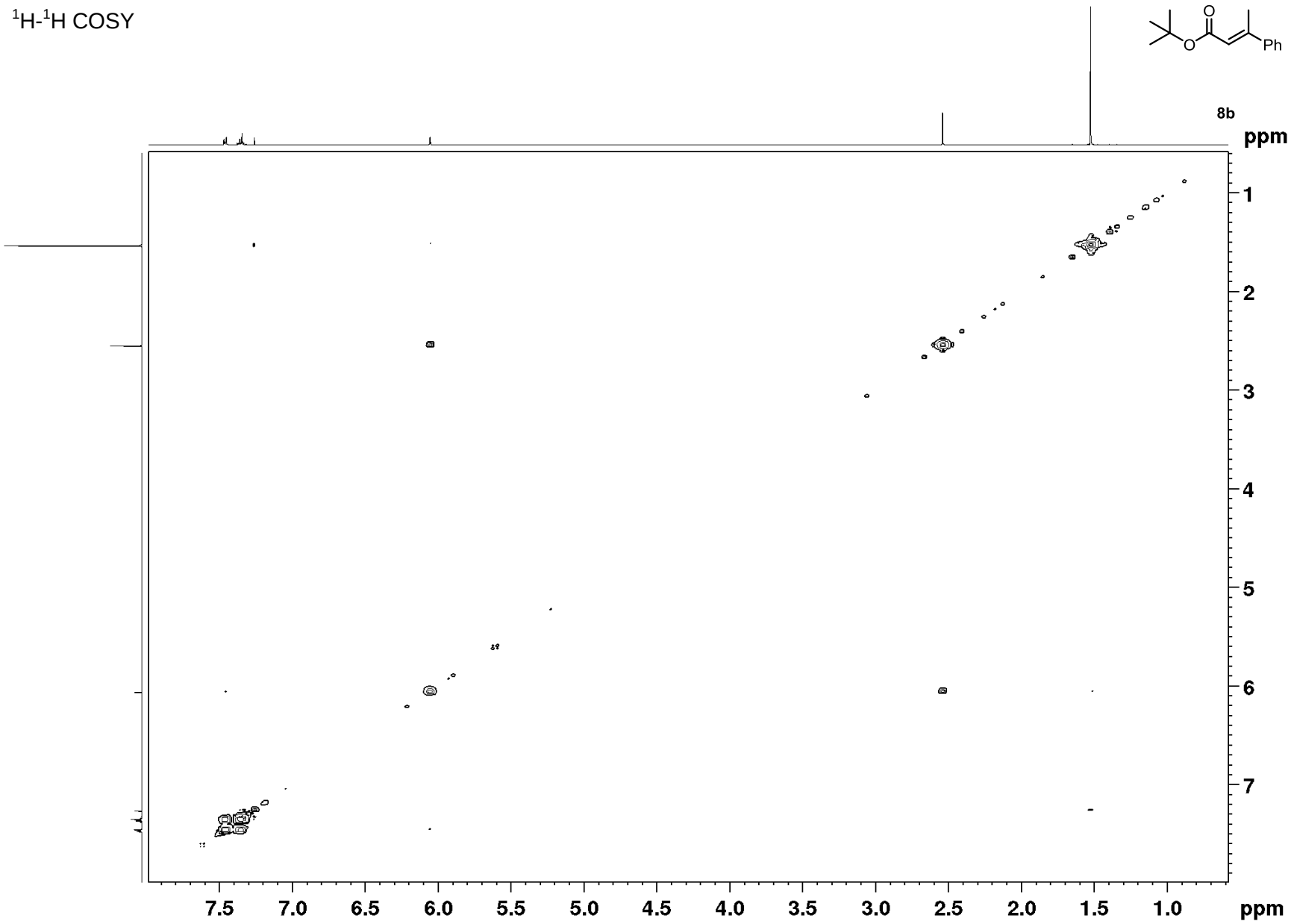
^{13}C DEPT NMR



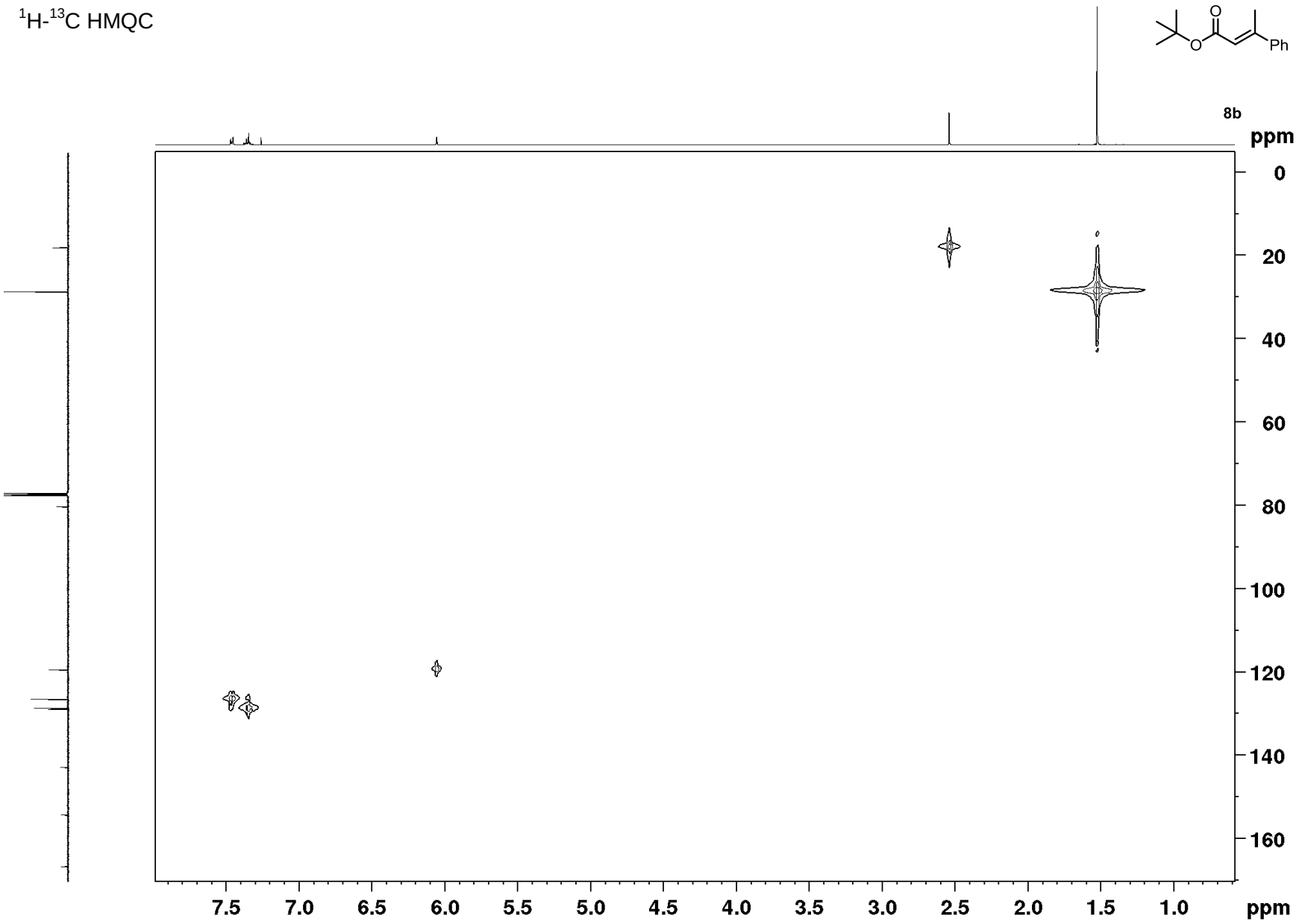
8b



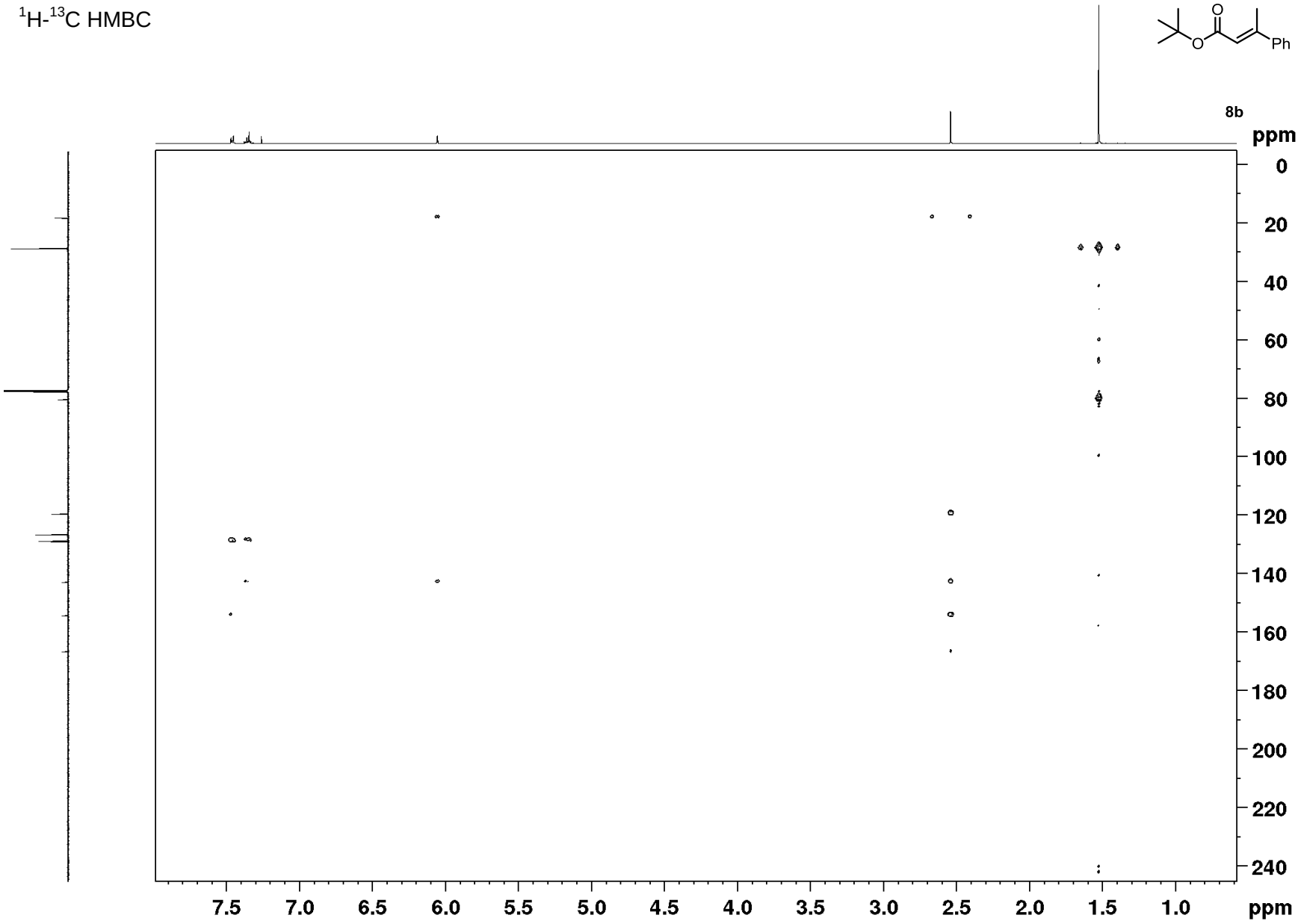
^{1}H-^{1}H COSY



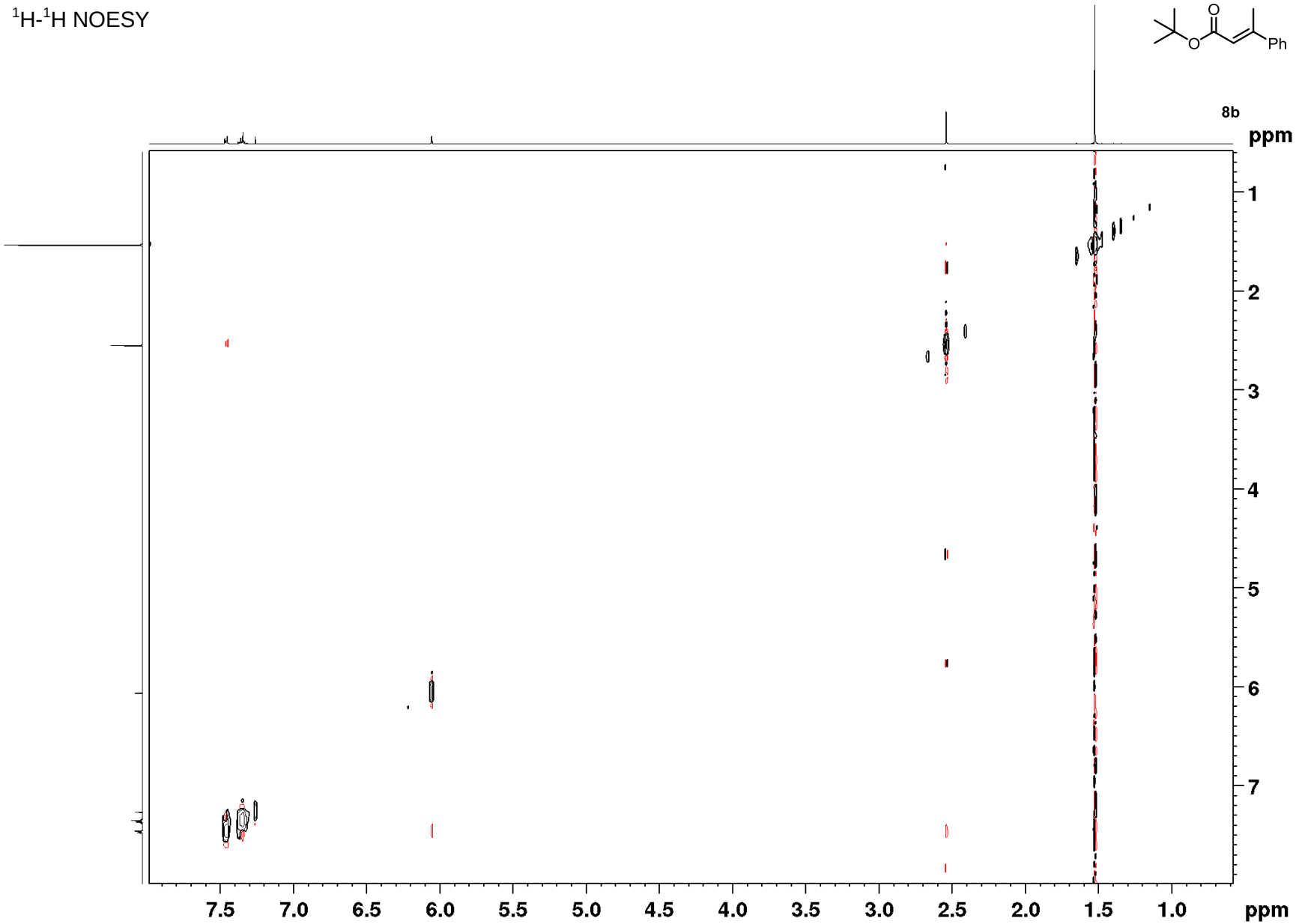
^{1}H-^{13}C HMQC


O
O
Ph
8b
ppm
0
20
40
60
80
100
120
140
160
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
ppm

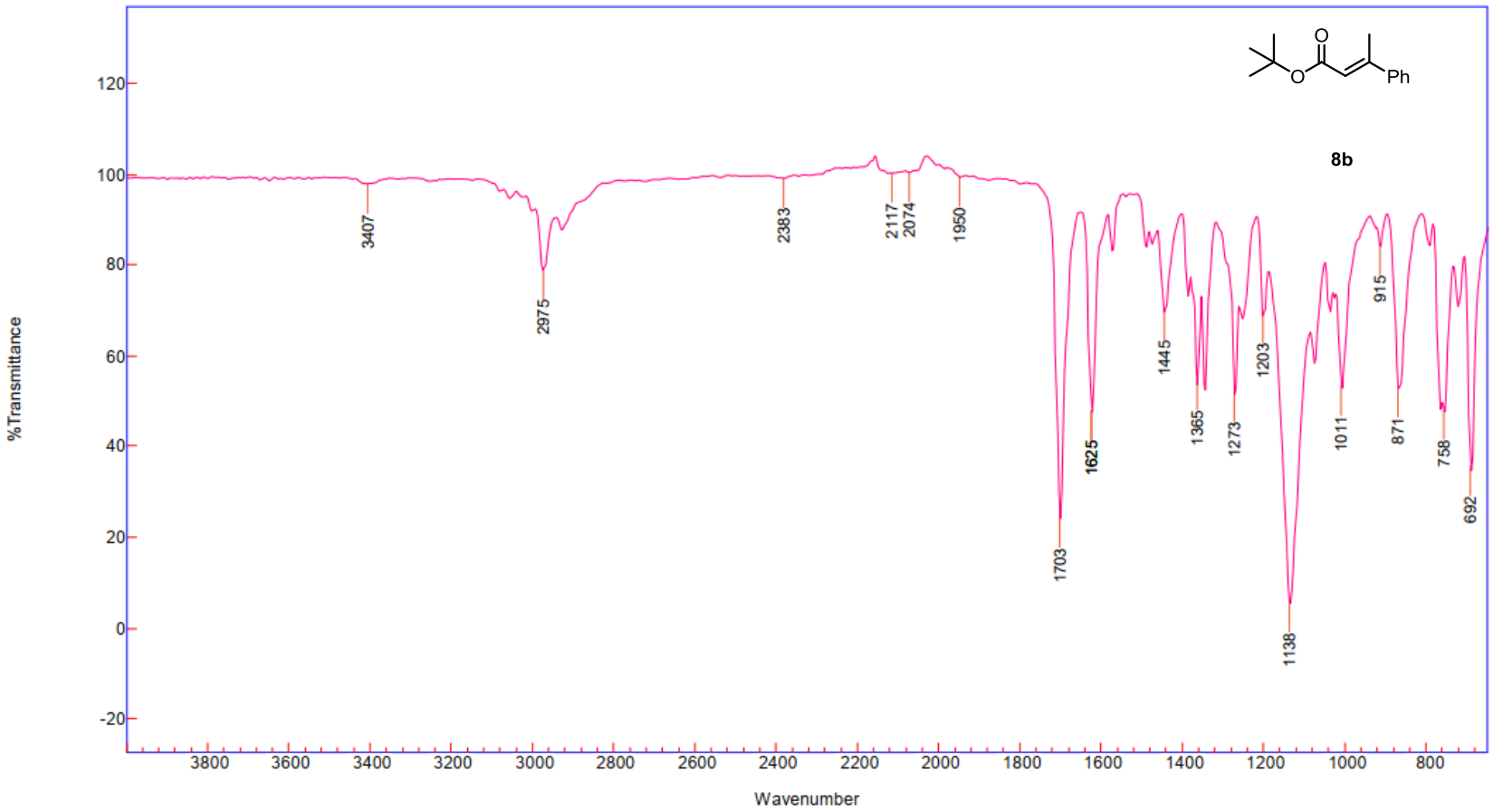
^{1}H-^{13}C HMBC


O
O
Ph
8b
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

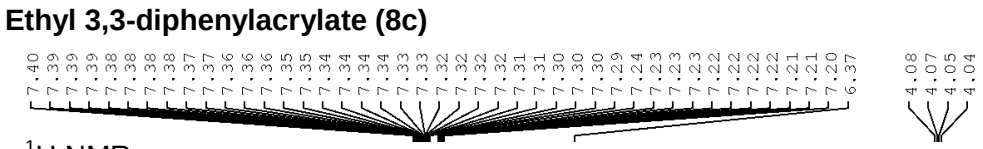
^{1}H-^{1}H NOESY



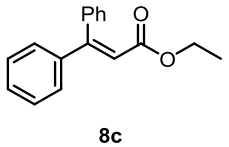

163.0752
145.0646
164.0784
219.1375
intensity
m/z
O
O
Ph
8b


8b
%Transmittance
Wavenumber
120
100
80
60
40
20
0
-20
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
3407
2975
2383
2117
2074
1950
1703
1625
1445
1365
1273
1203
1138
1011
915
871
758
692
O
O
Ph

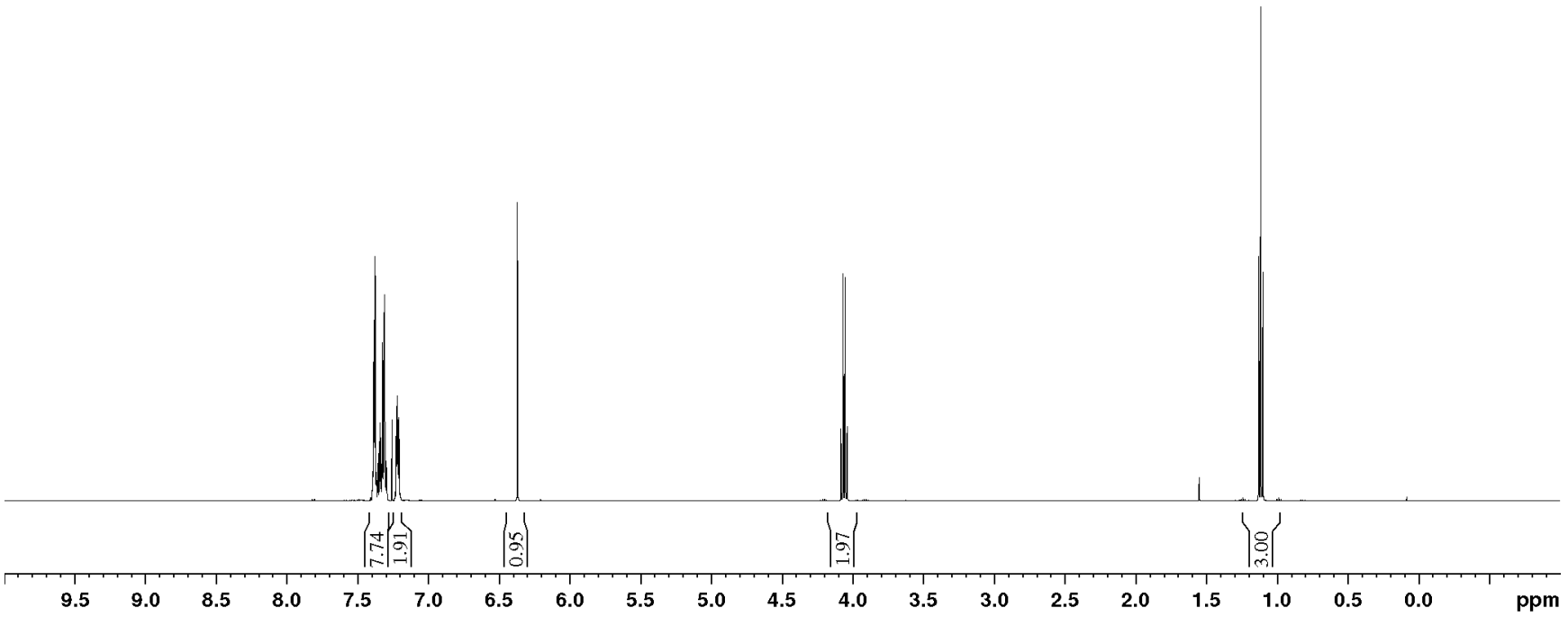
Ethyl 3,3-diphenylacrylate (8c)



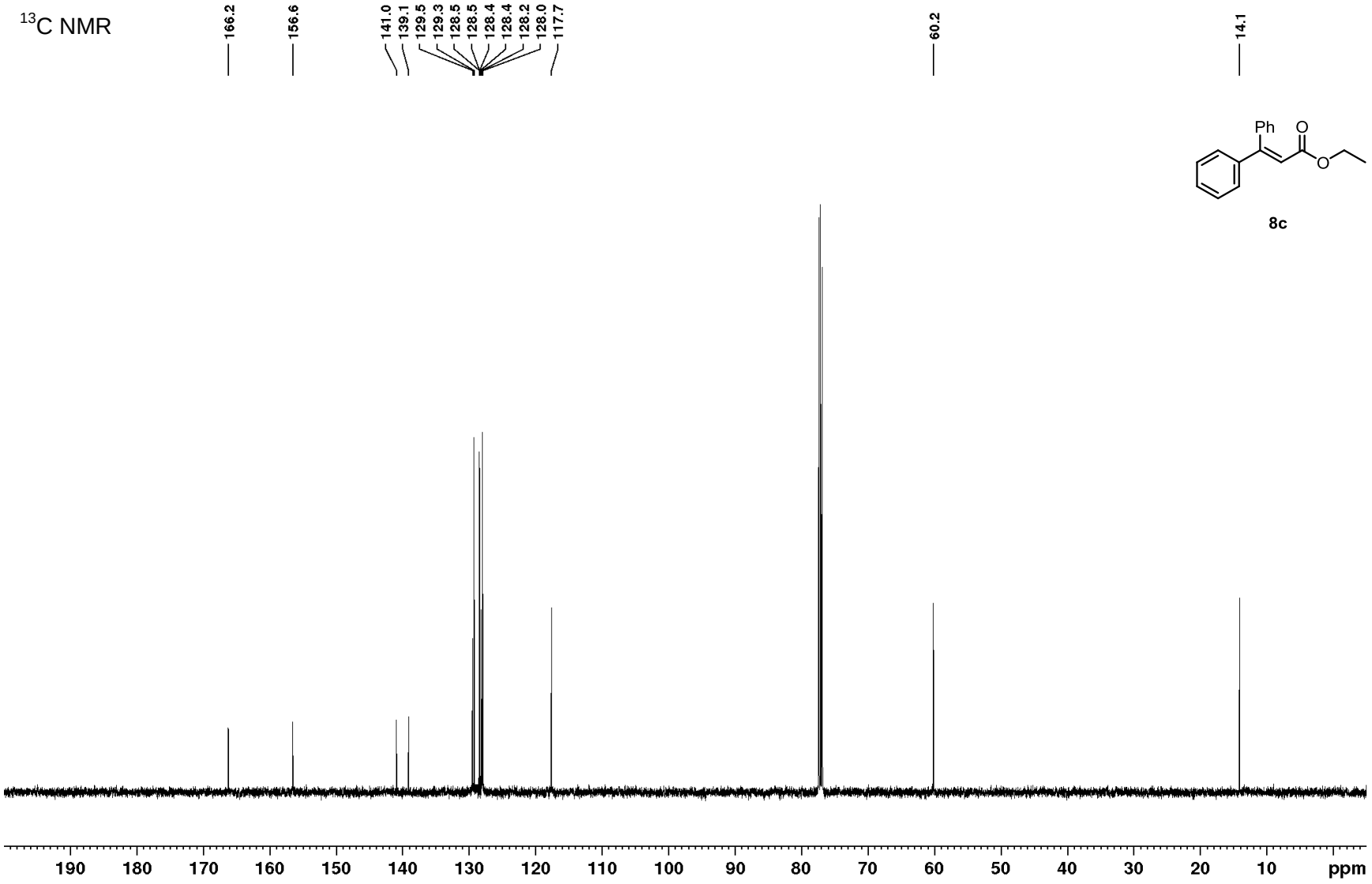
^{1}H NMR



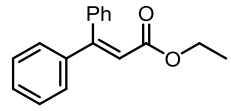
8c



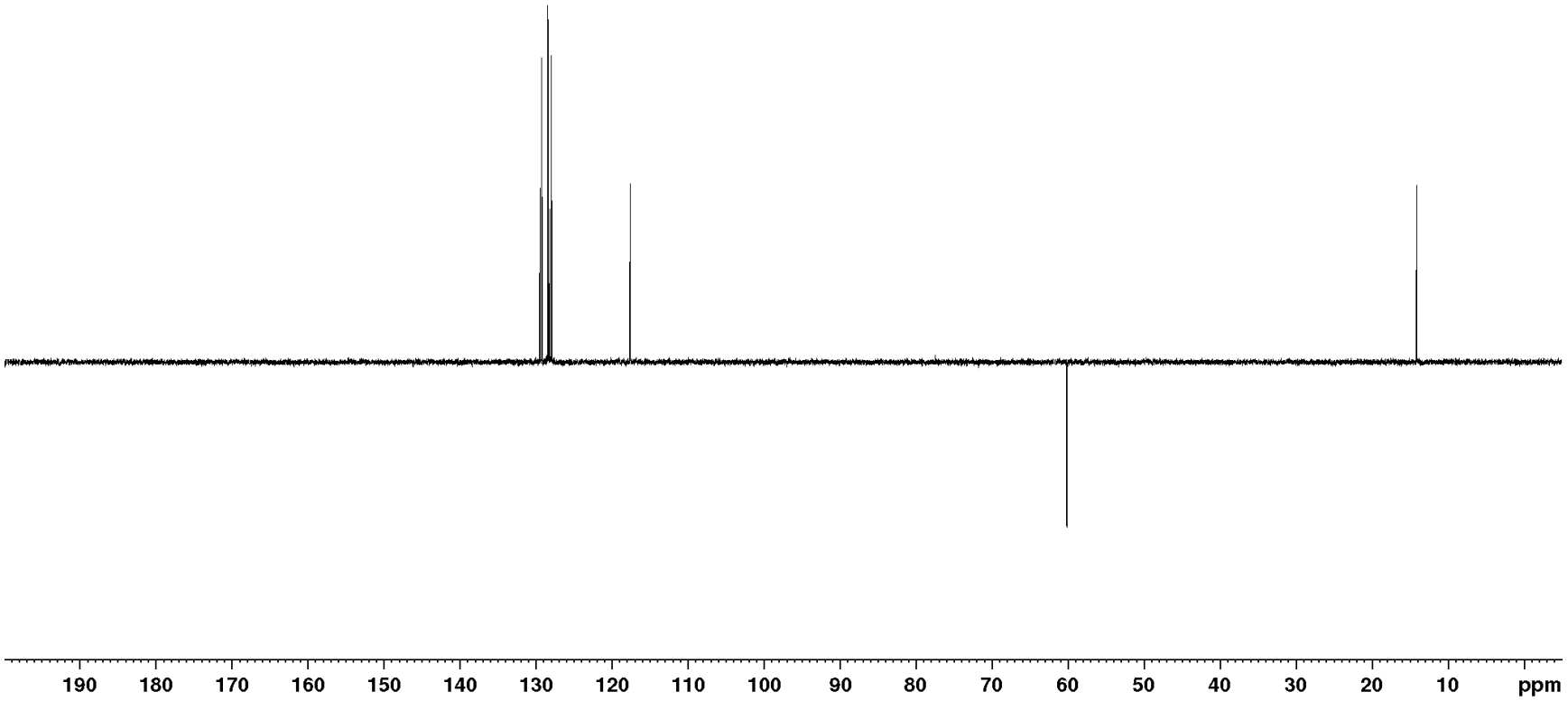
^{13}C NMR


166.2
156.6
141.0
139.1
129.5
129.3
128.5
128.5
128.4
128.4
128.2
128.0
117.7
60.2
14.1
Ph
O
O
8c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

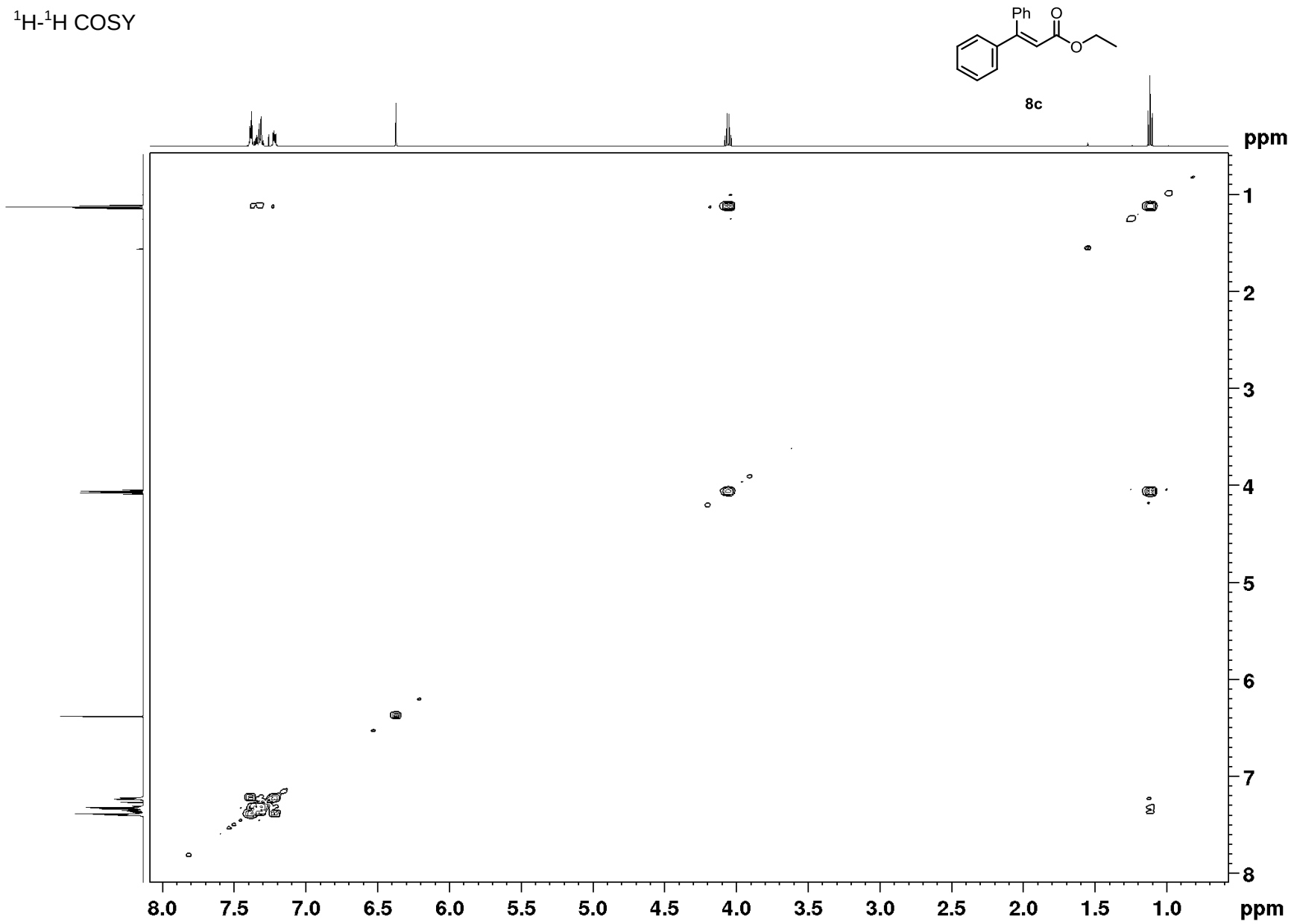
^{13}C DEPT NMR



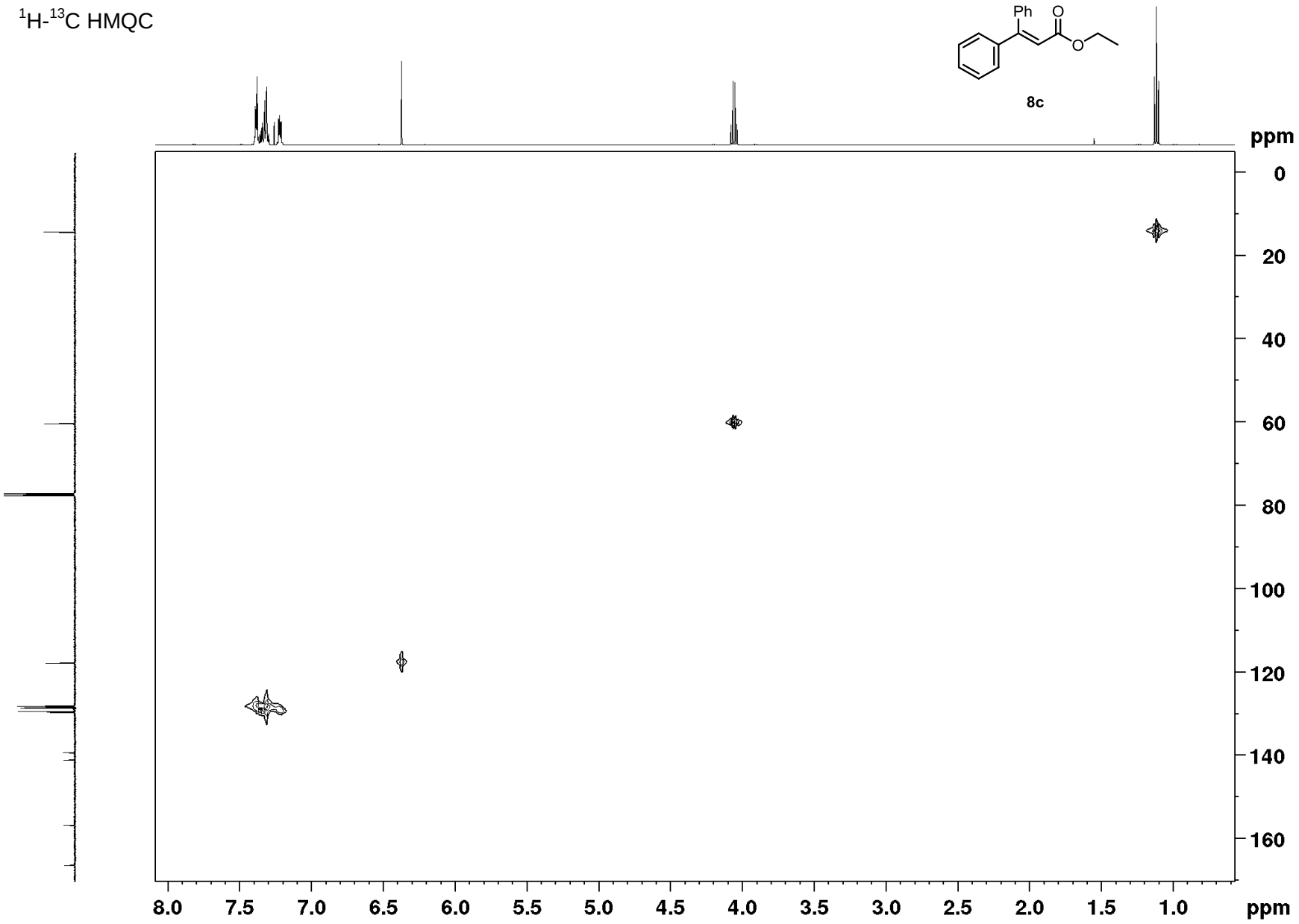
8c



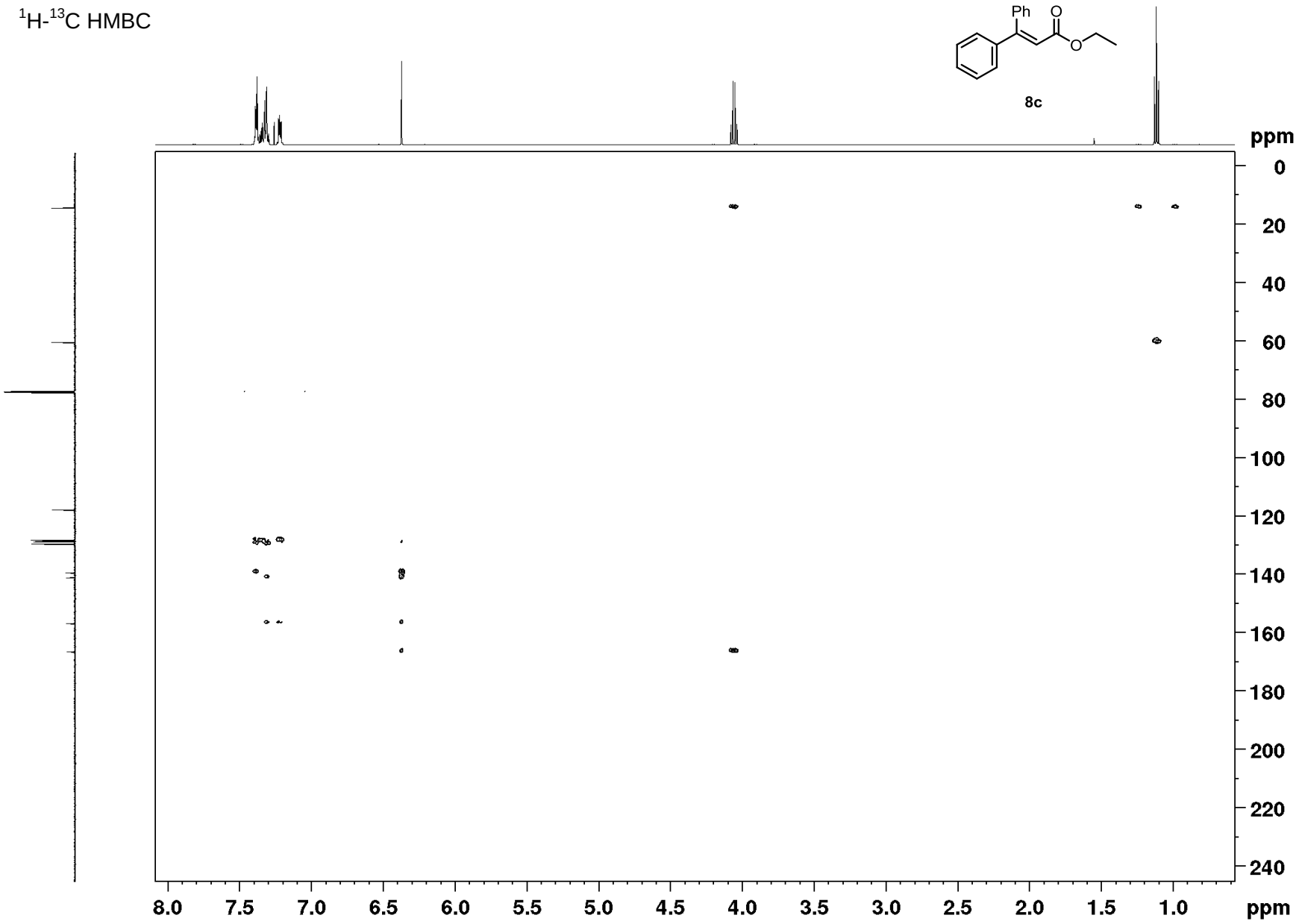
^{1}H-^{1}H COSY

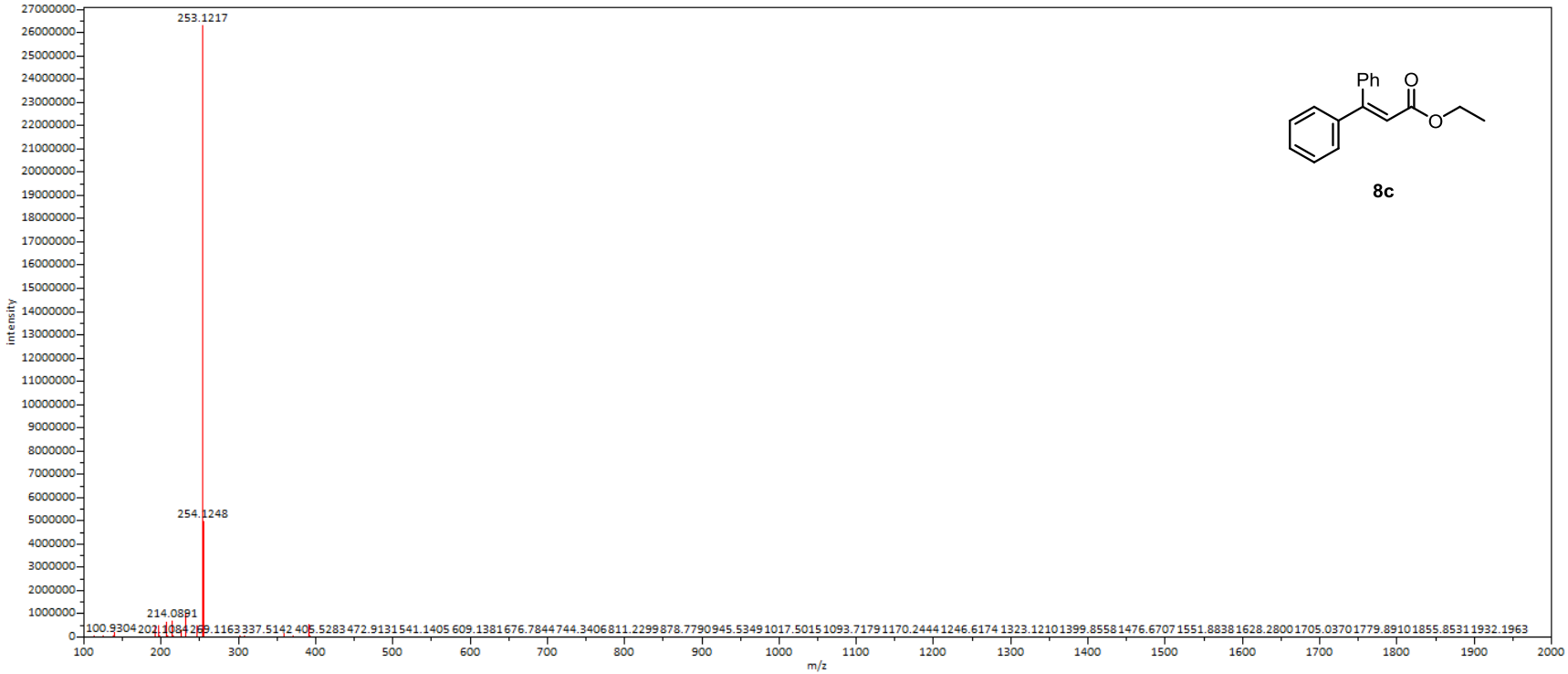

Ph
O
O
8c
ppm
1
2
3
4
5
6
7
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

^{1}H-^{13}C HMQC


Ph
O
O
8c
ppm
0
20
40
60
80
100
120
140
160
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
ppm

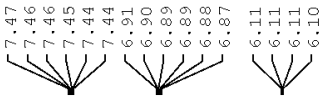
^{1}H-^{13}C HMBC

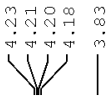

Ph
O
O
8c
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

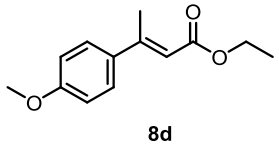

253.1217
254.1248
214.0891
Ph
O
O
8c
intensity
m/z

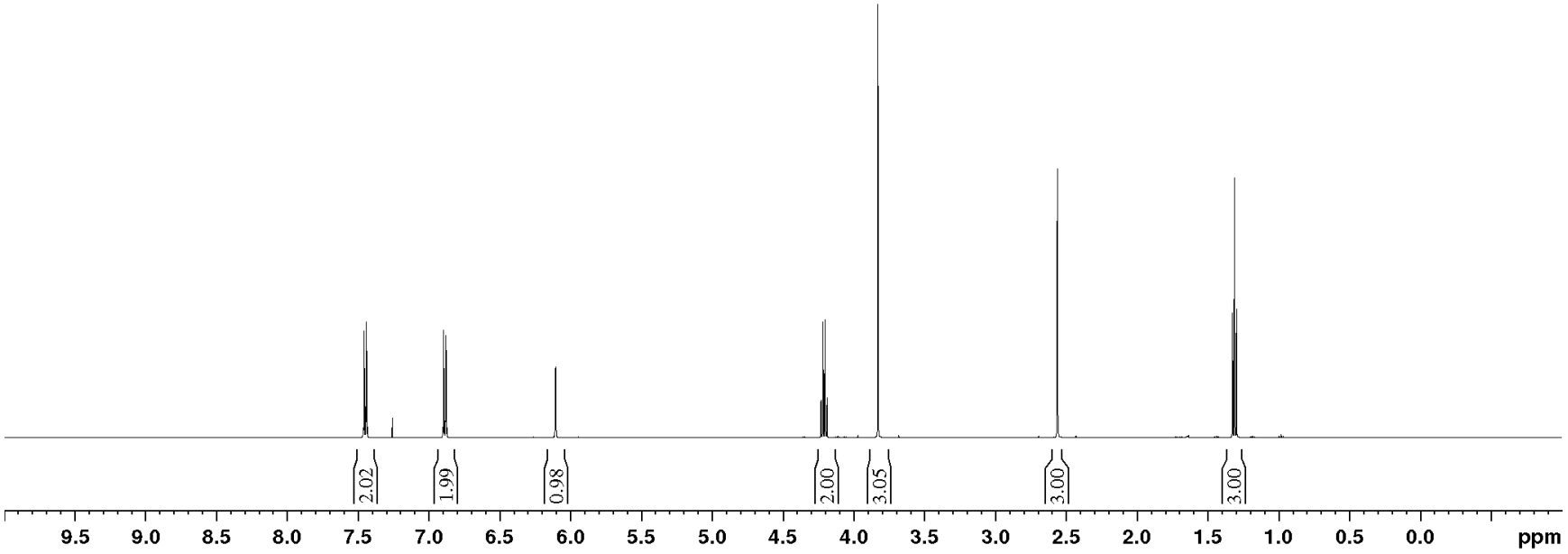
Ethyl (*E*)-3-(4-methoxyphenyl)but-2-enoate (8d)

^{1}H NMR

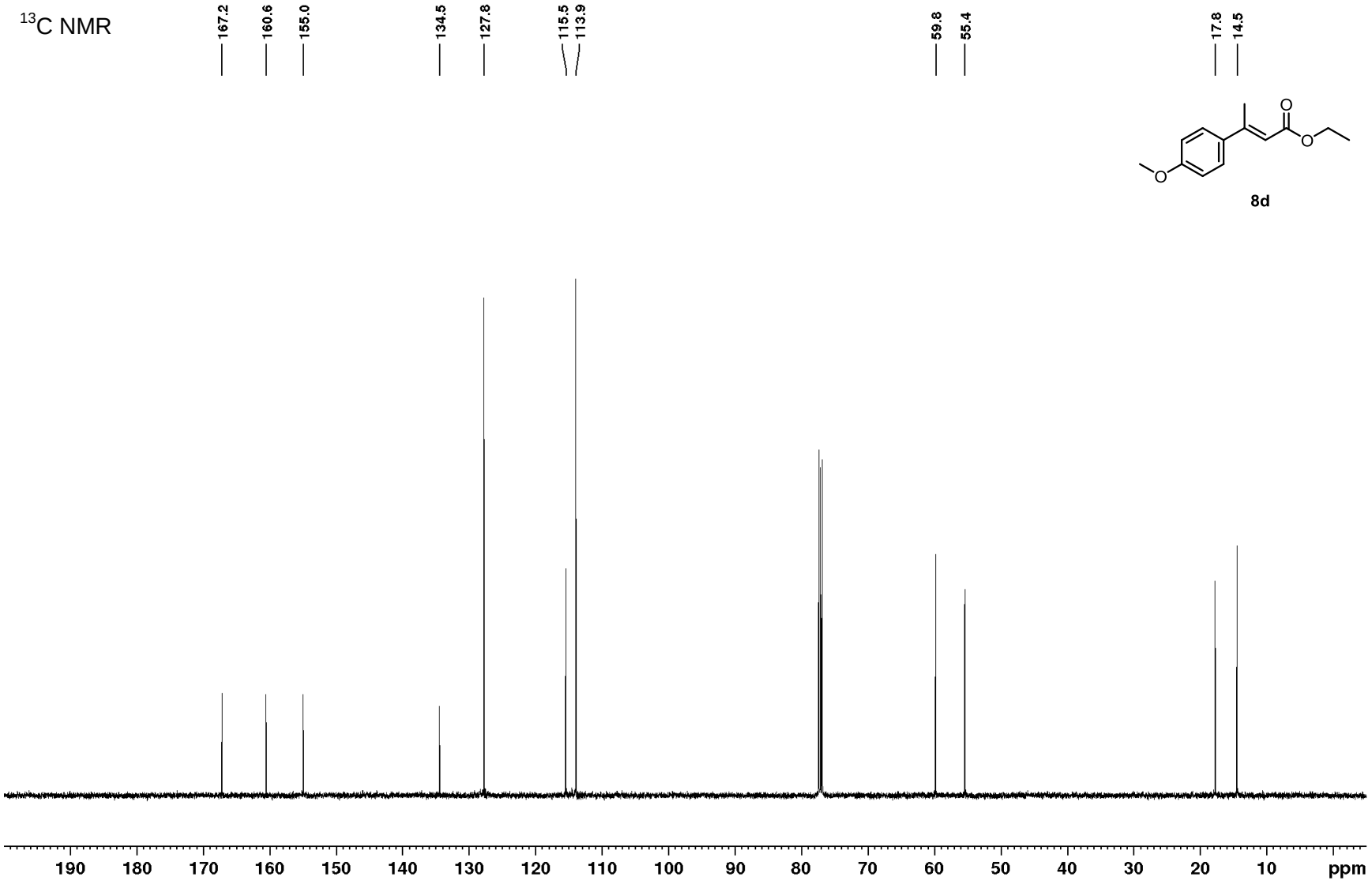




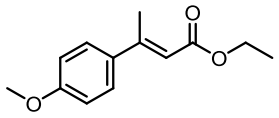




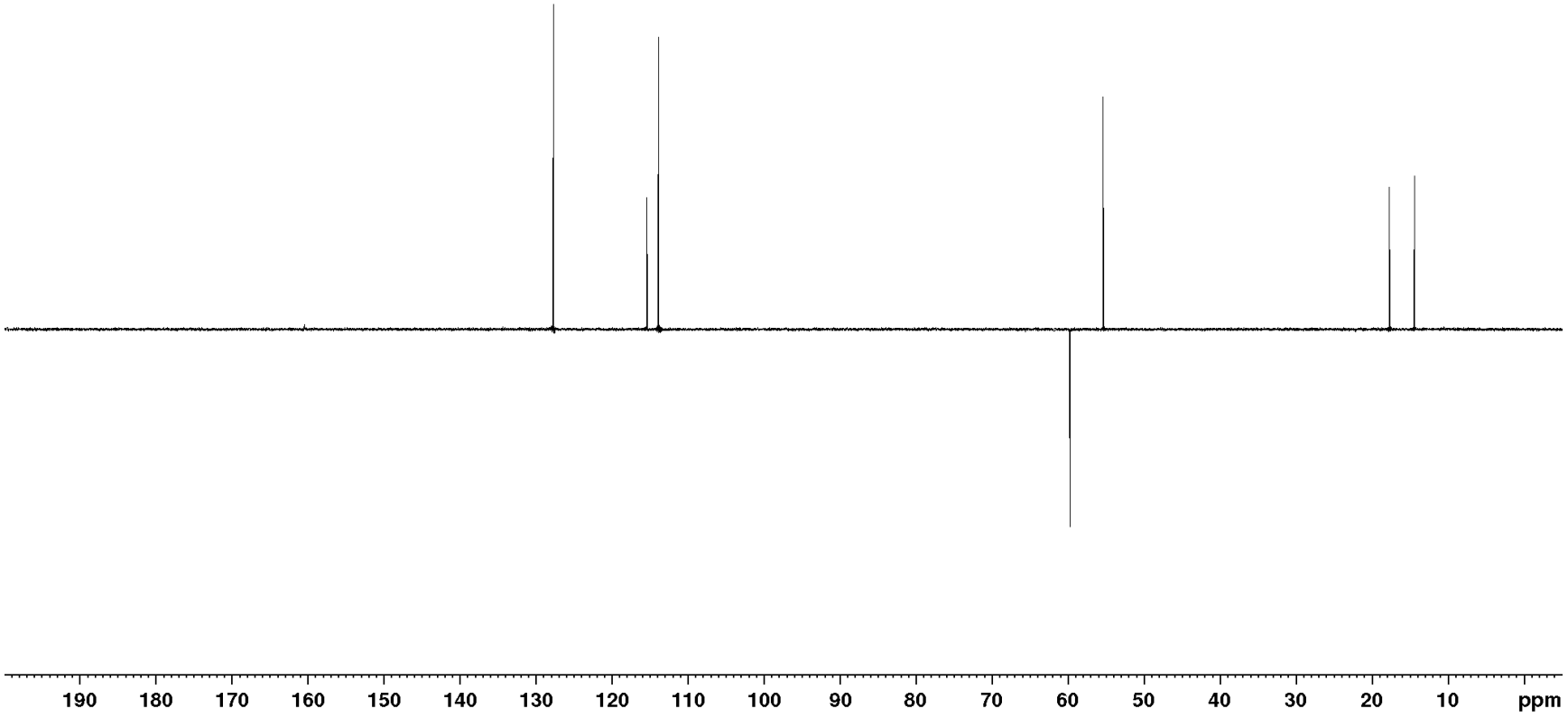
^{13}C NMR


167.2
160.6
155.0
134.5
127.8
115.5
113.9
59.8
55.4
17.8
14.5
O
O
O
8d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

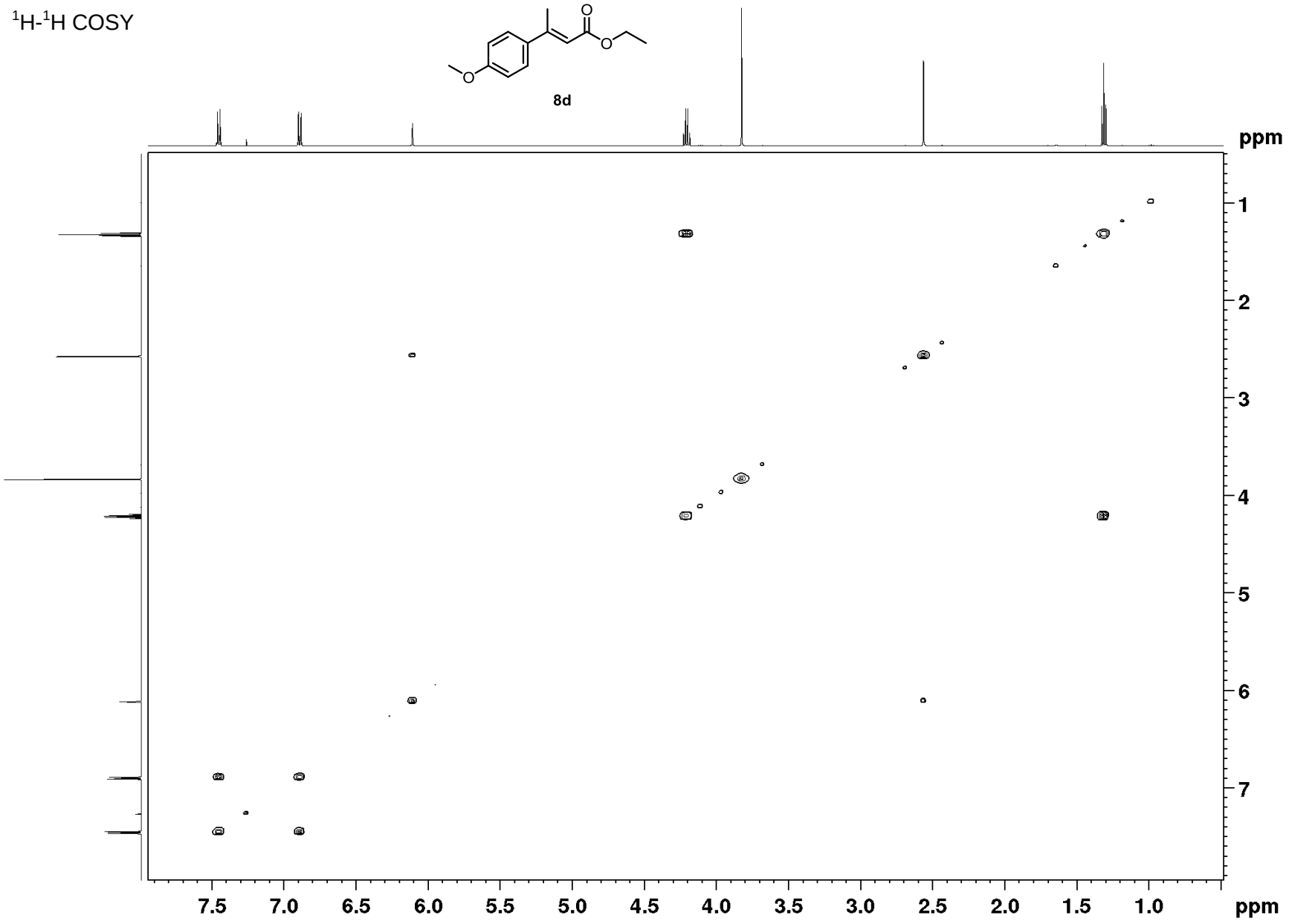
^{13}C DEPT NMR



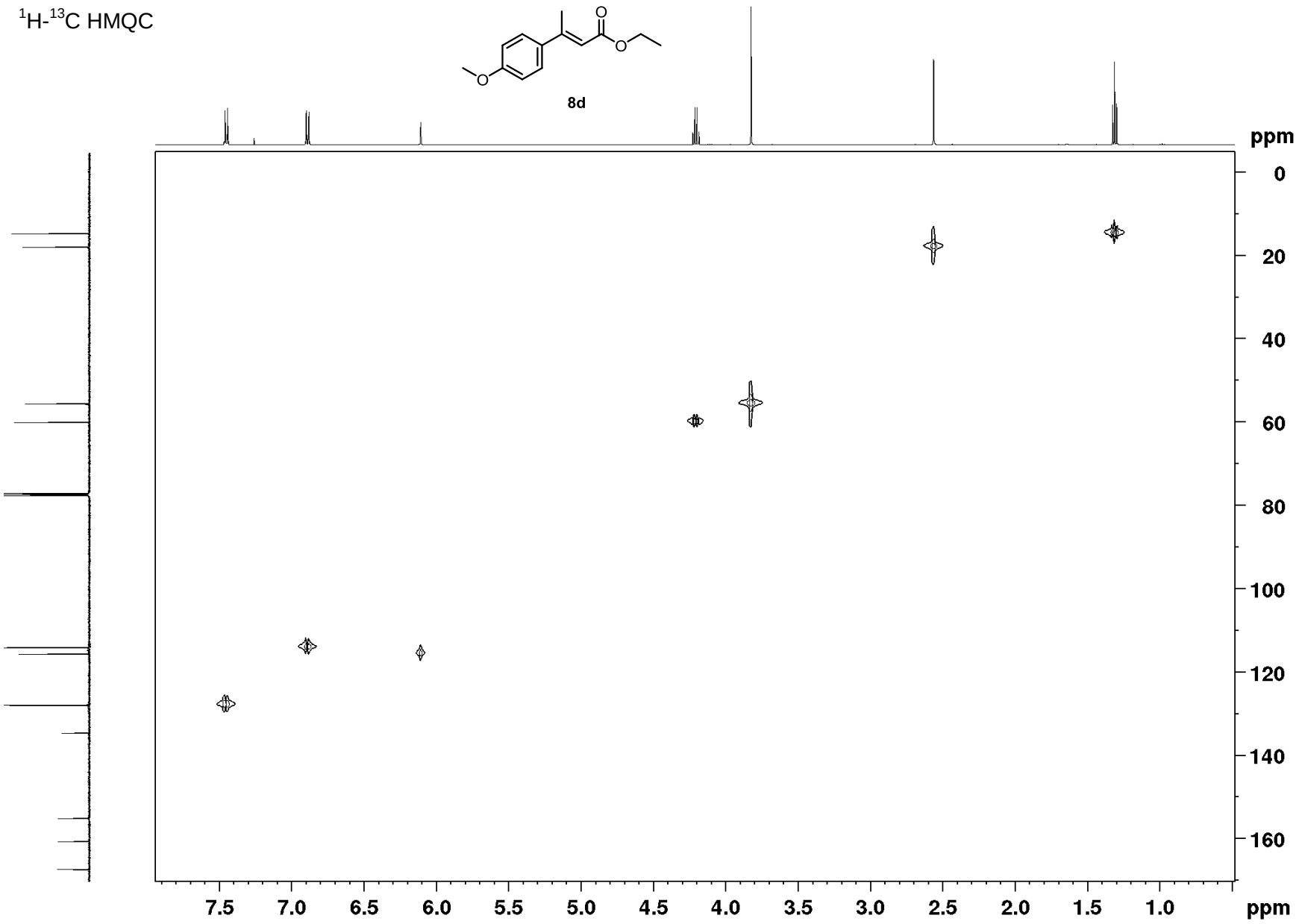
8d



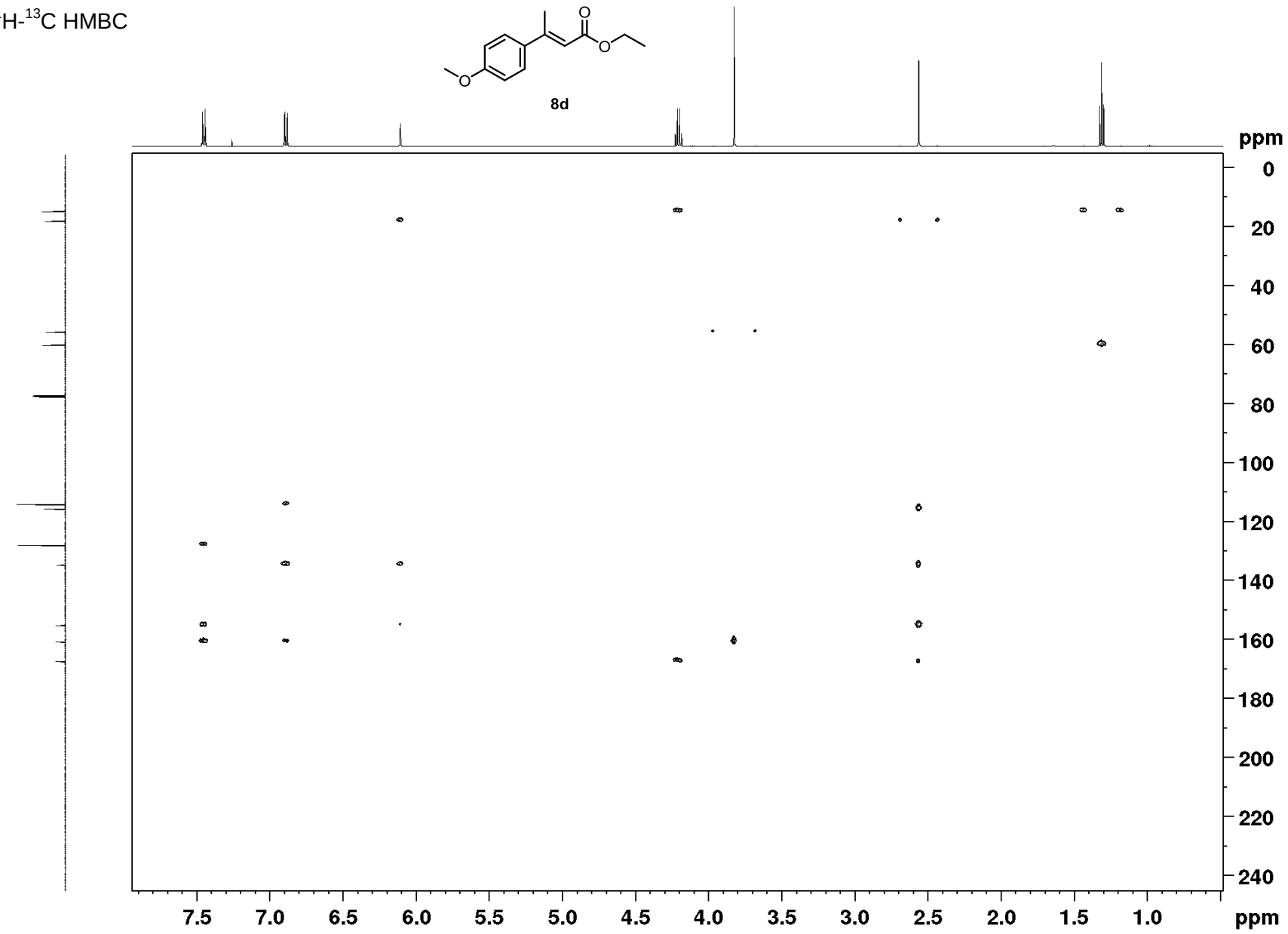
^{1}H-^{1}H COSY



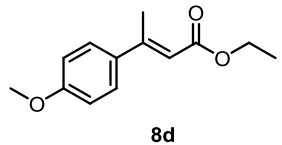
^{1}H-^{13}C HMQC


O
O
O
8d
ppm
0
20
40
60
80
100
120
140
160
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
ppm

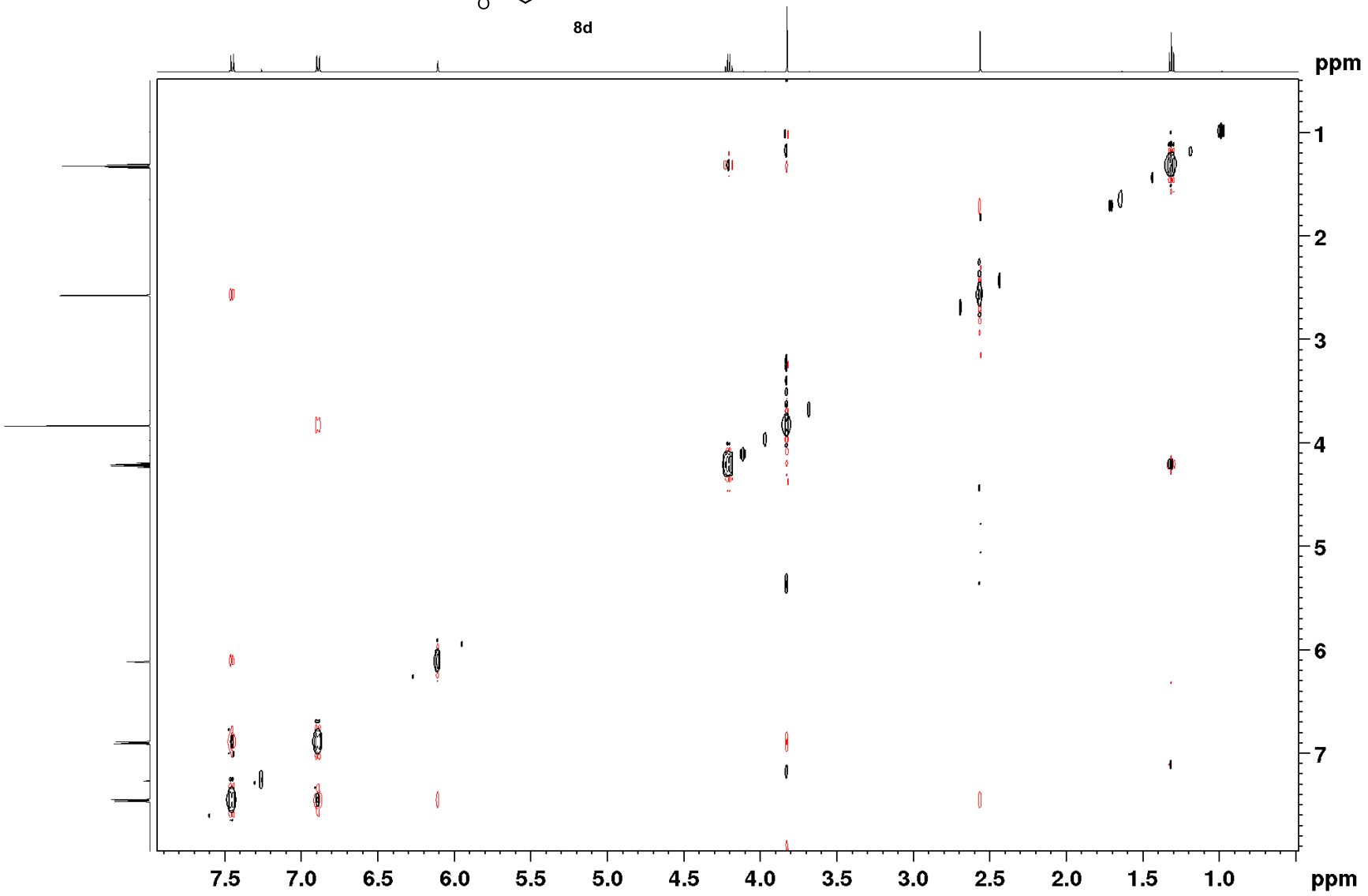
^{1}H-^{13}C HMBC

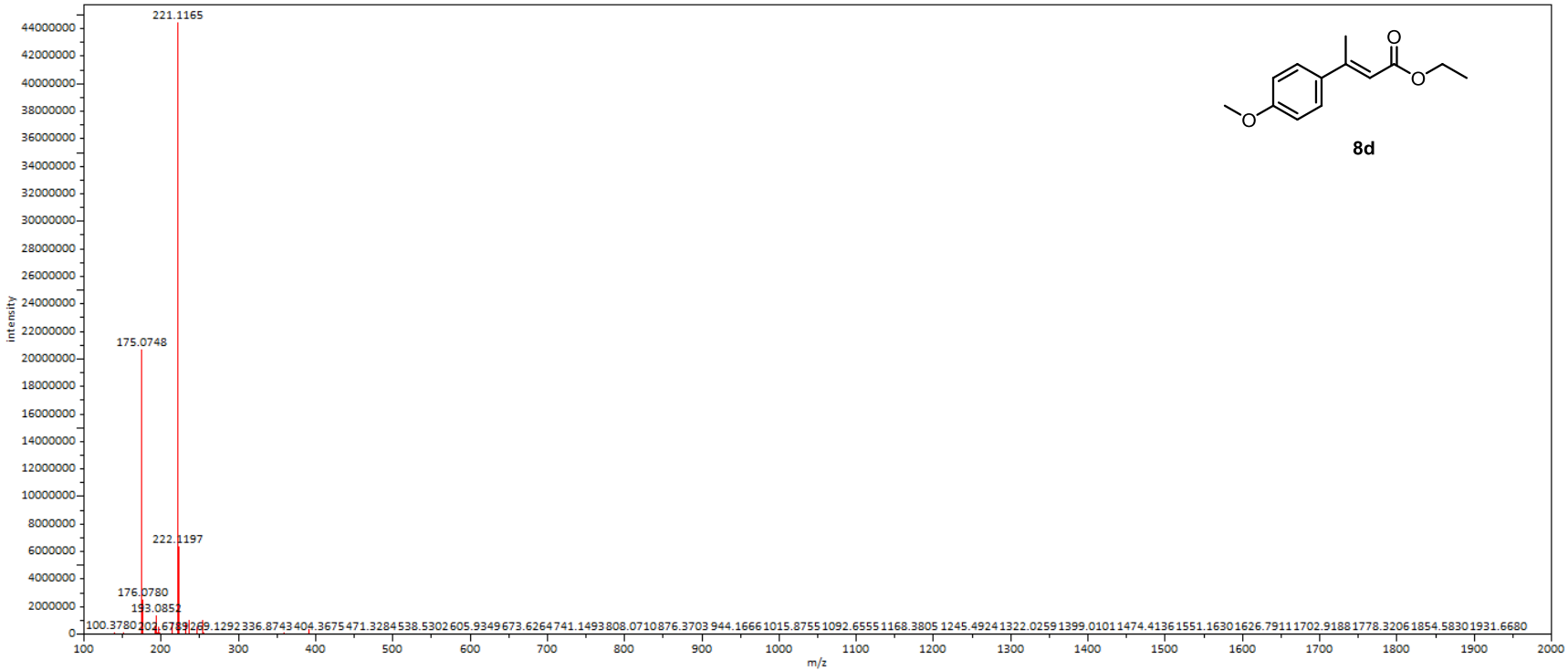

8d
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

^{1}H-^{1}H NOESY



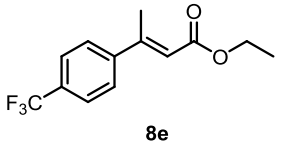
8d



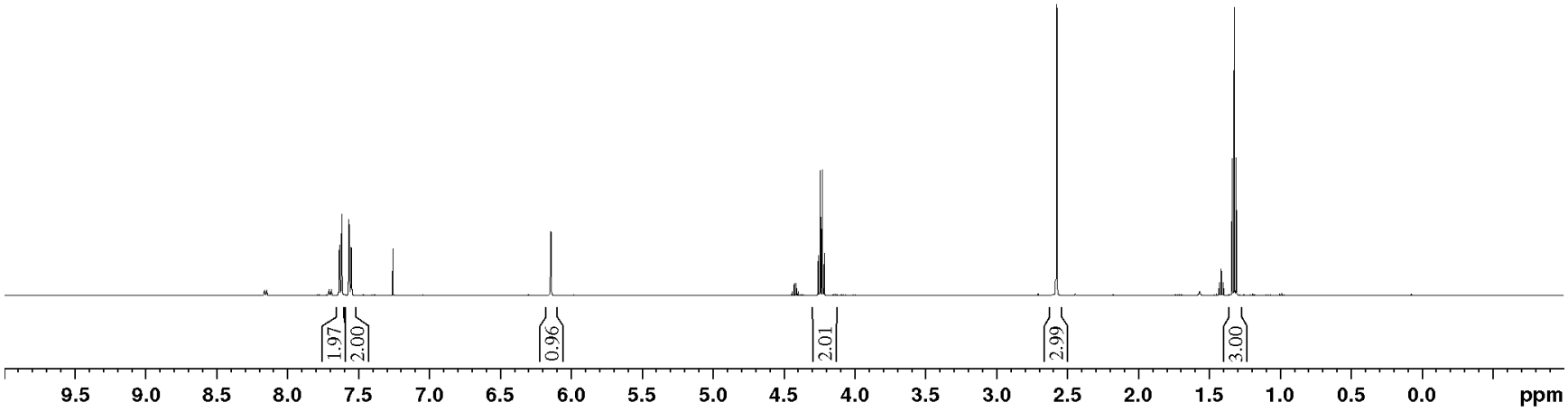

221.1165
175.0748
222.1197
176.0780
193.0852
intensity
m/z
8d

Ethyl (*E*)-3-(4-(trifluoromethyl)phenyl)but-2-enoate (8e)

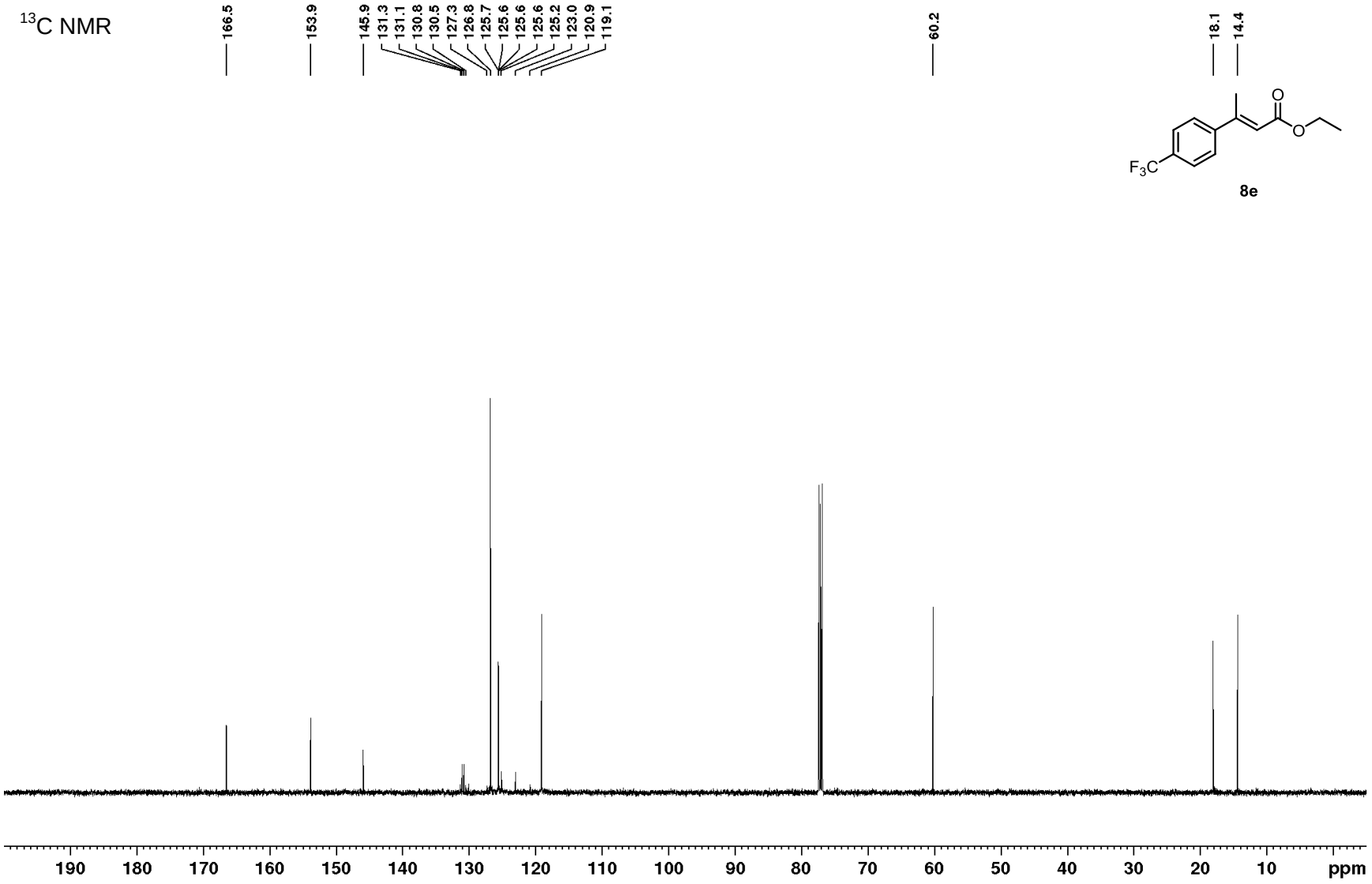
^{1}H NMR



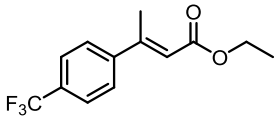
8e



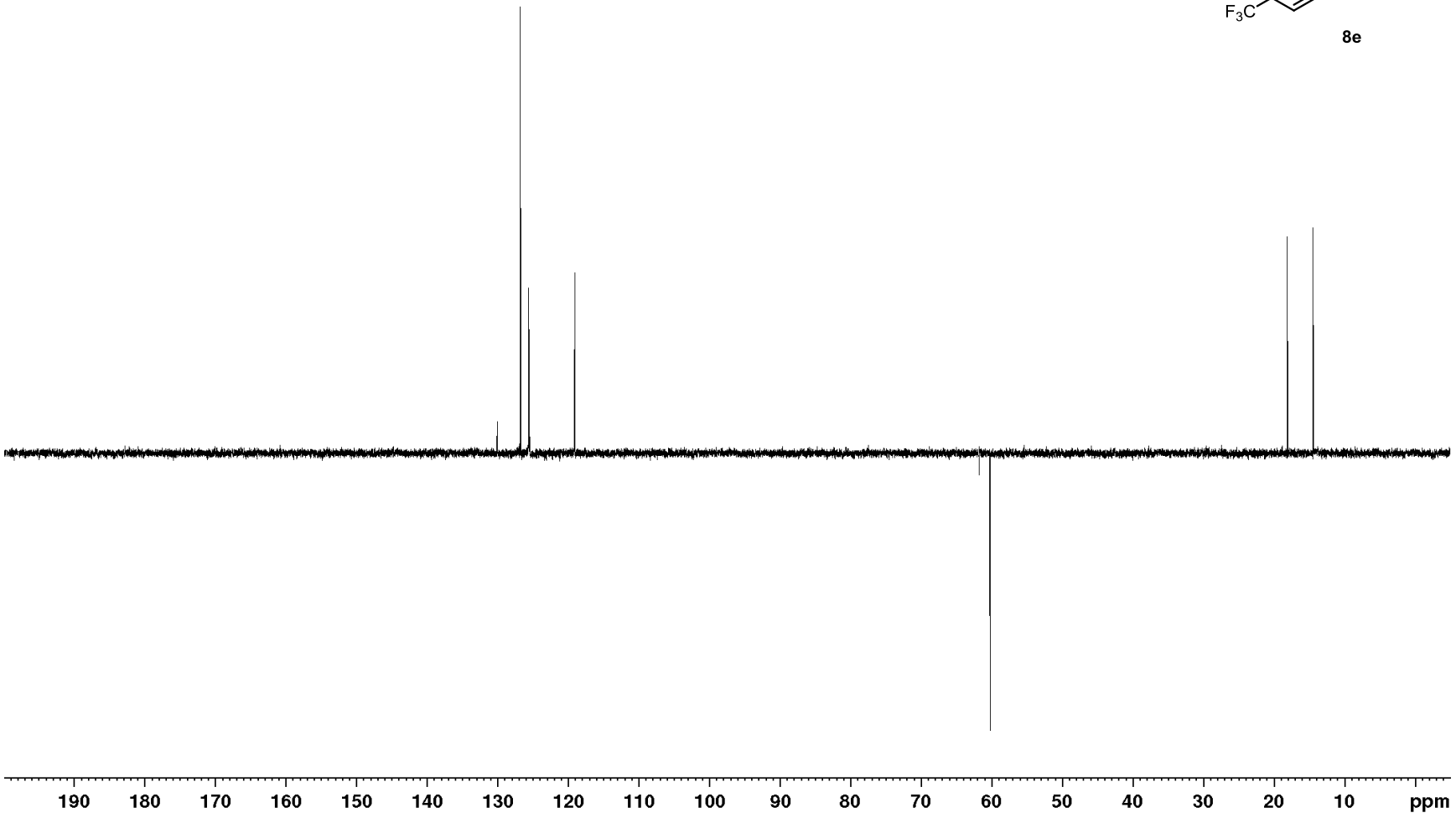
^{13}C NMR


166.5
153.9
145.9
131.3
131.1
130.8
130.5
127.3
126.8
125.7
125.6
125.6
125.6
125.2
123.0
120.9
119.1
60.2
18.1
14.4
O
O
F3C
8e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

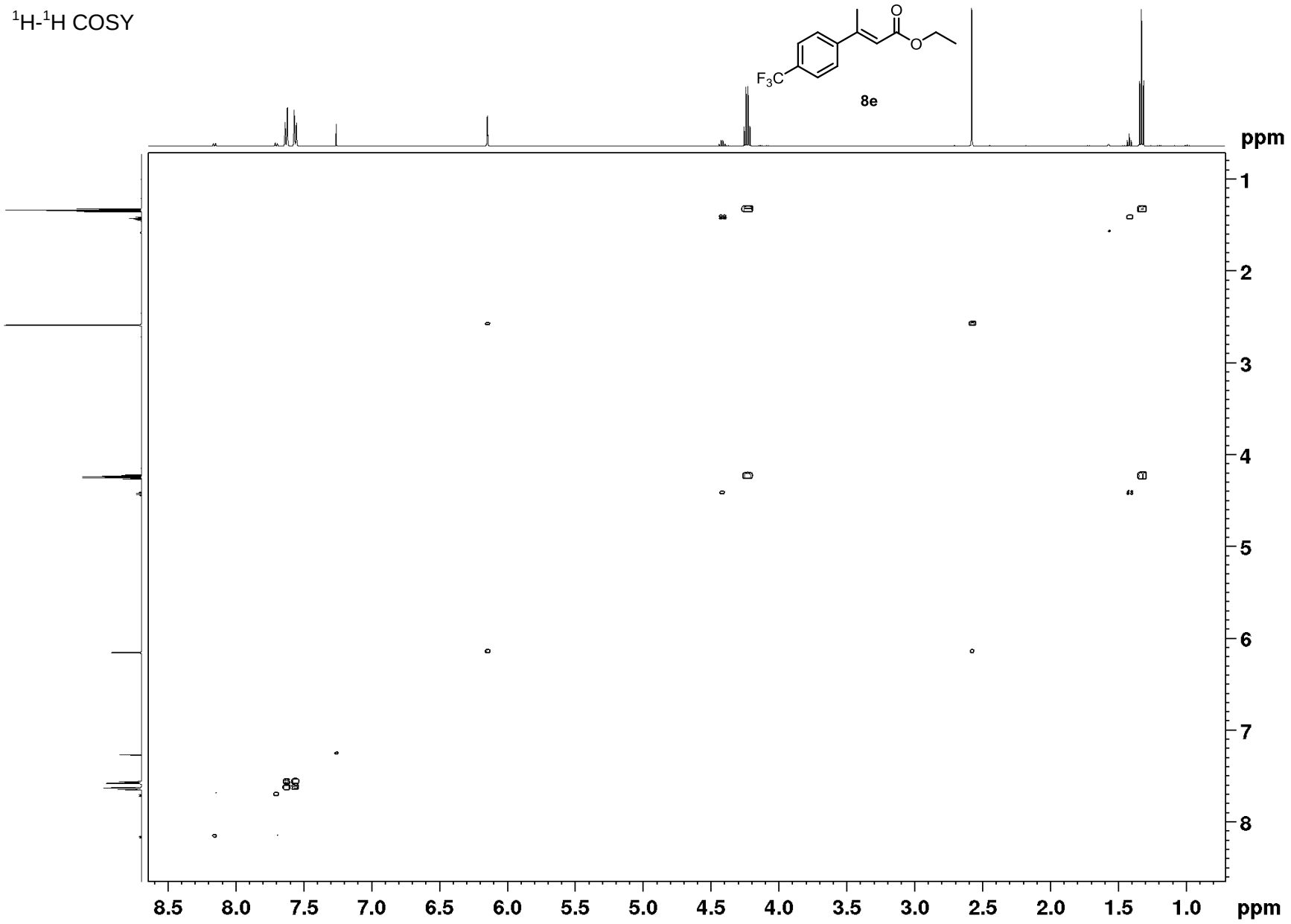
^{13}C DEPT NMR



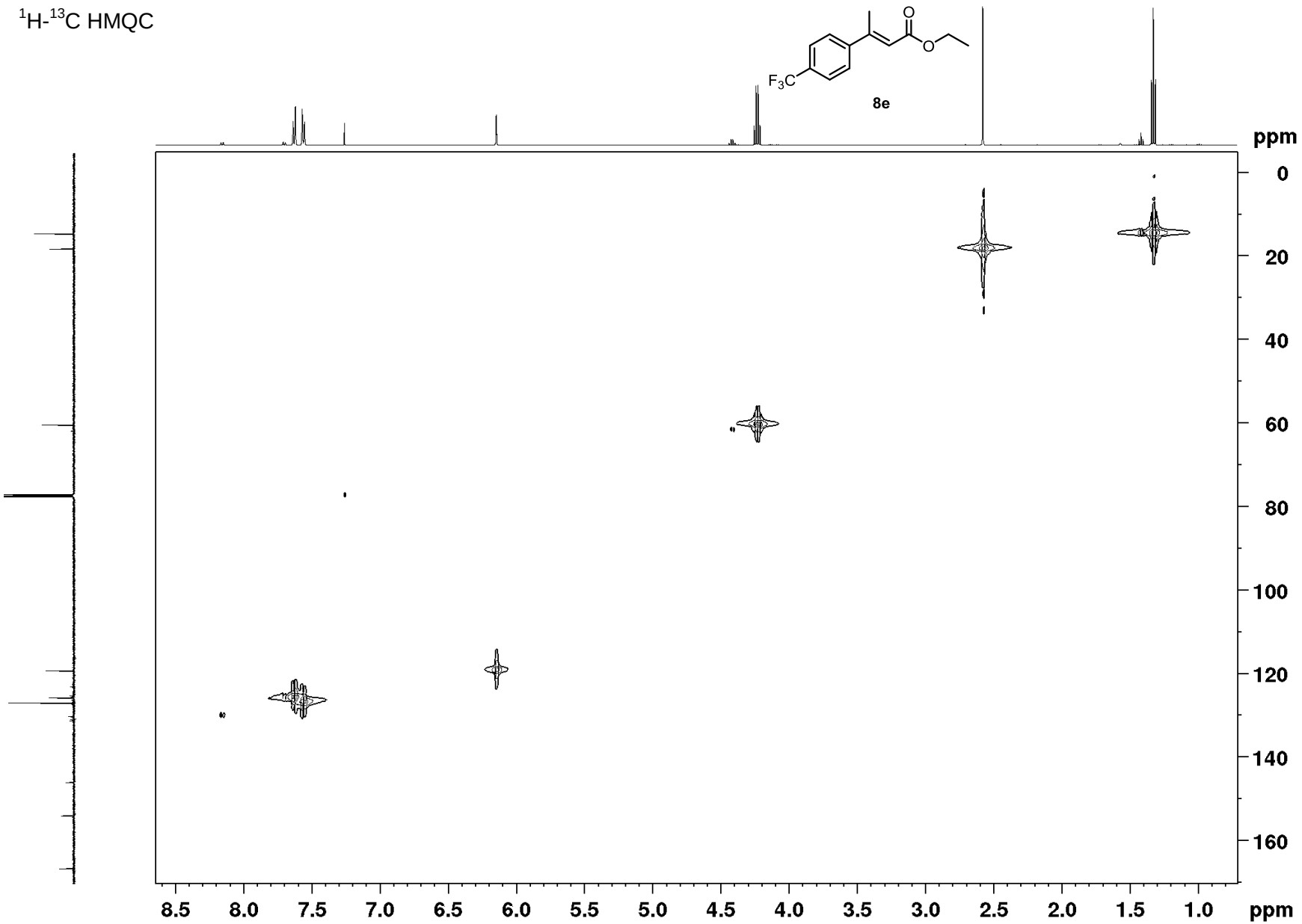
8e



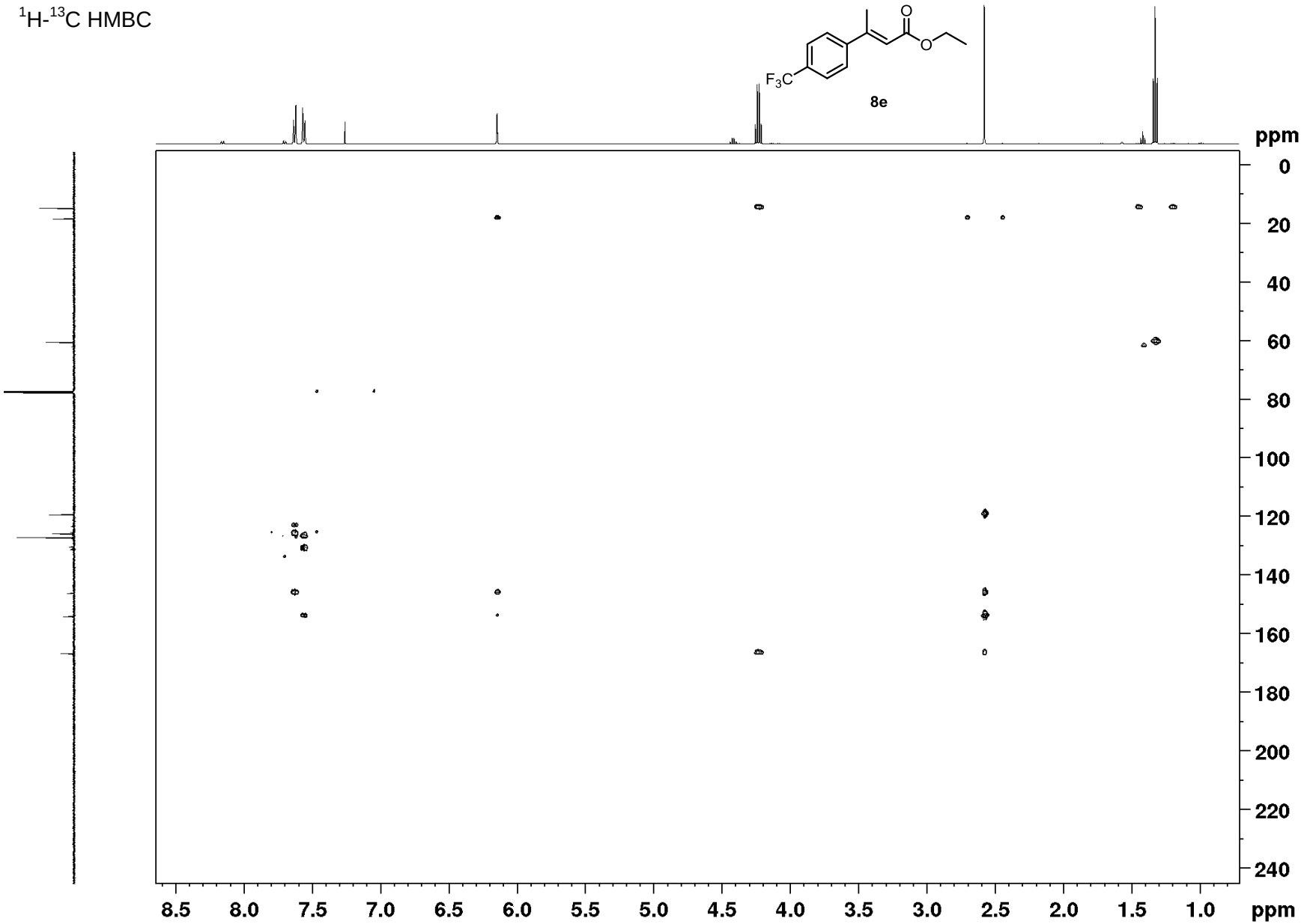
^{1}H-^{1}H COSY


F3C
O
O
8e
ppm
1
2
3
4
5
6
7
8
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

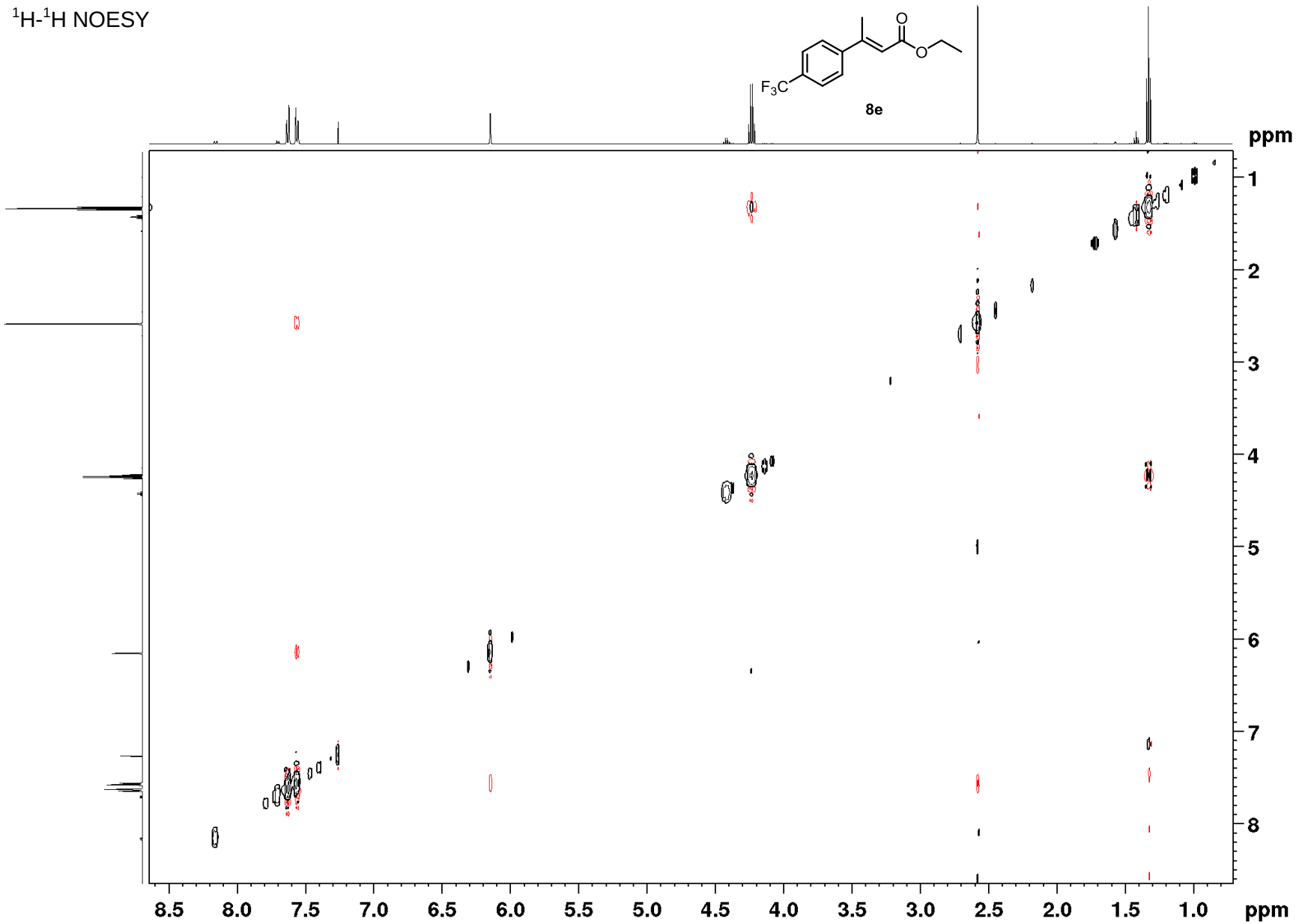
^{1}H-^{13}C HMQC


F3C
O
O
8e
ppm
0
20
40
60
80
100
120
140
160
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

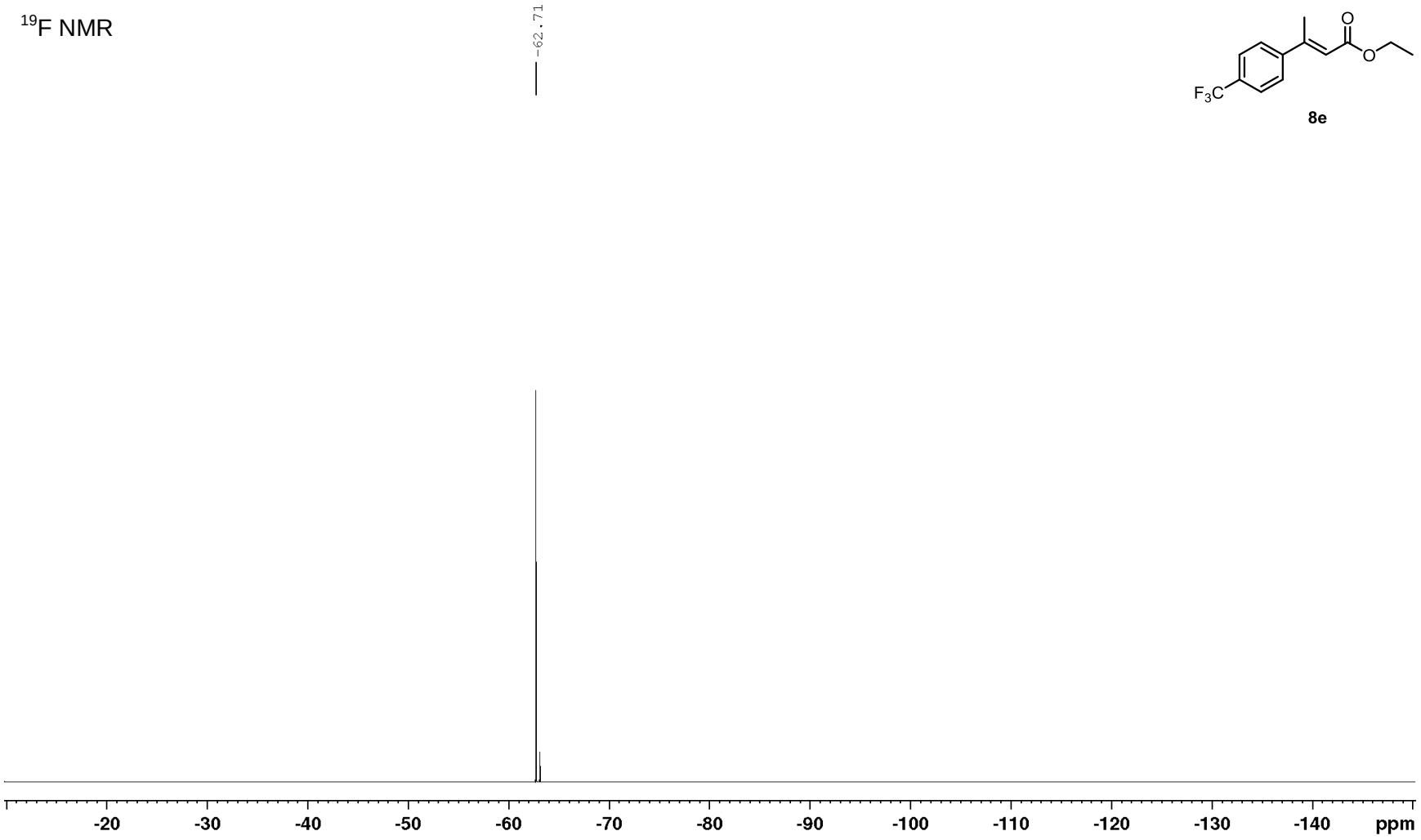
^{1}H-^{13}C HMBC

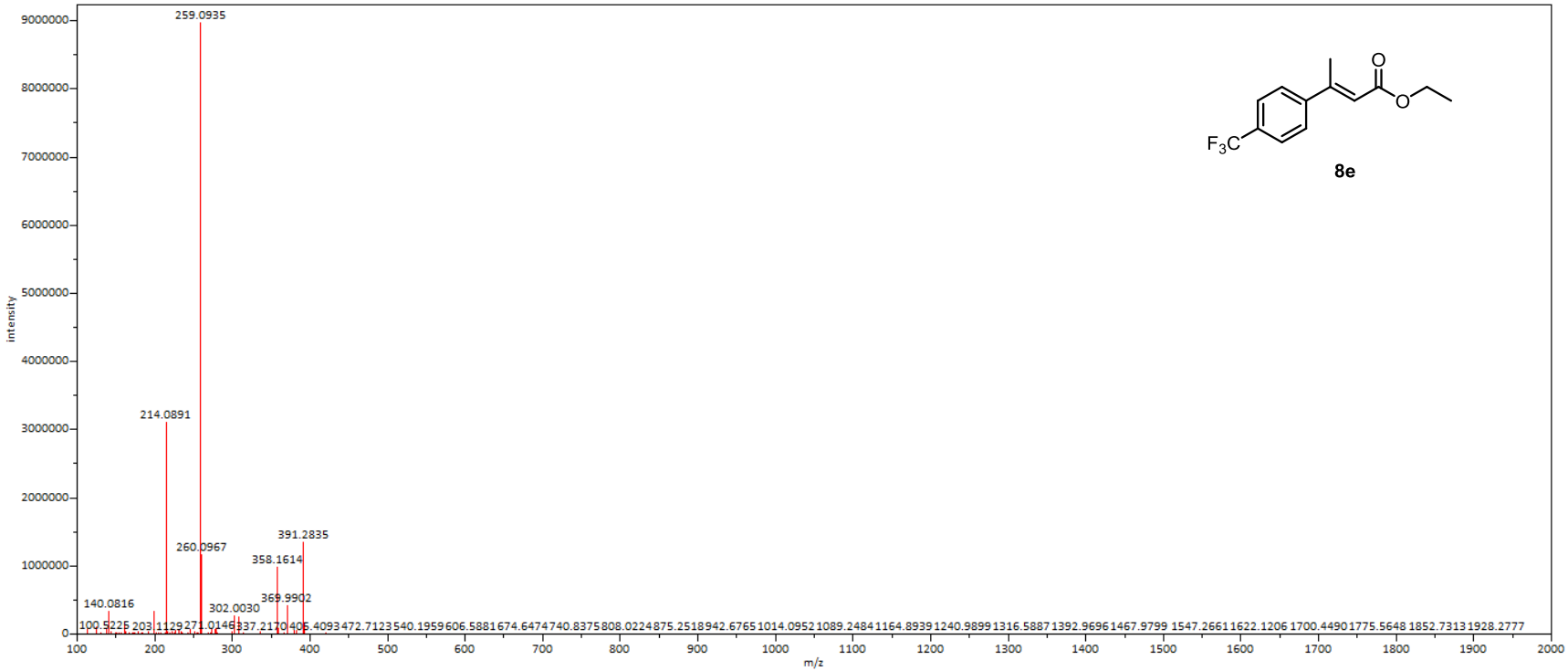

O
O
F3C
8e
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

^{1}H-^{1}H NOESY


F3C
O
O
8e
ppm
1
2
3
4
5
6
7
8
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

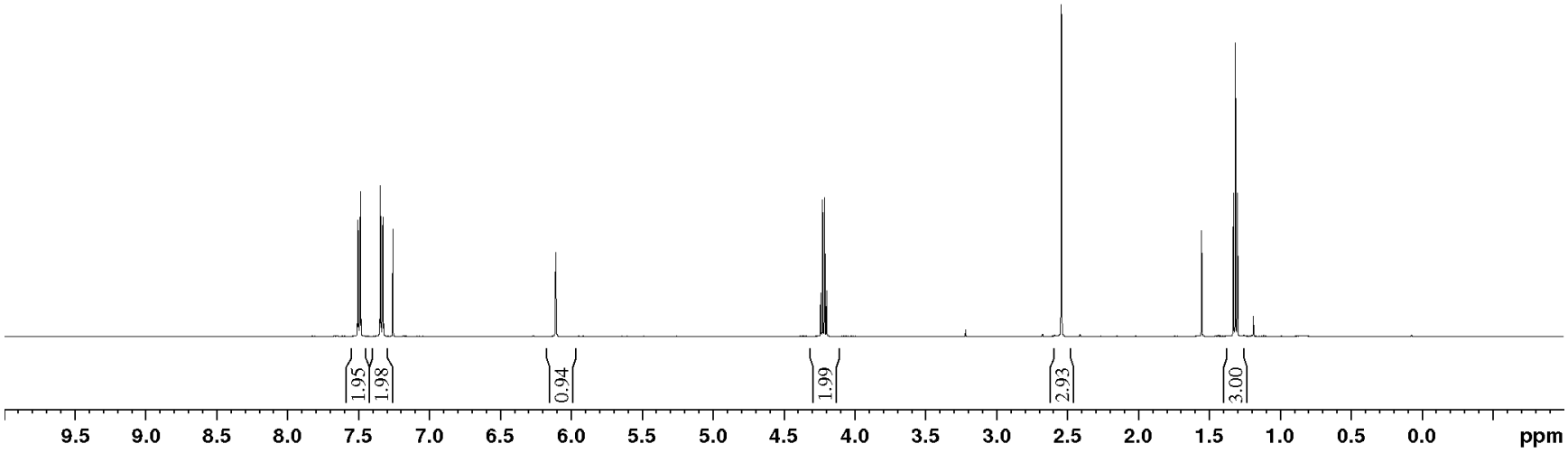
^{19}F NMR



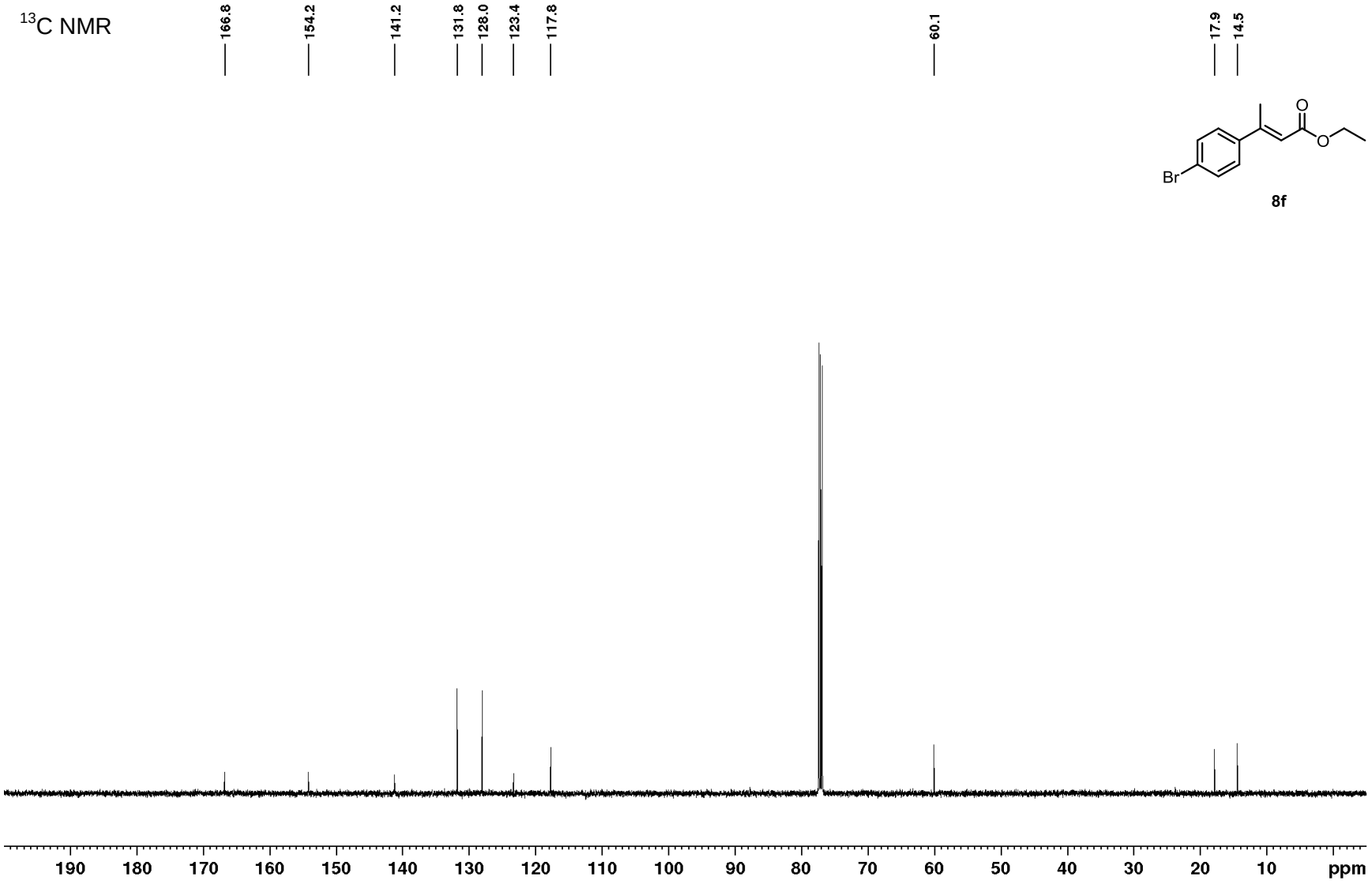

259.0935
214.0891
260.0967
391.2835
358.1614
369.9902
302.0030
140.0816
intensity
m/z
8e

Ethyl (*E*)-3-(4-bromophenyl)but-2-enoate (8f)

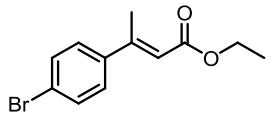
^{1}H NMR



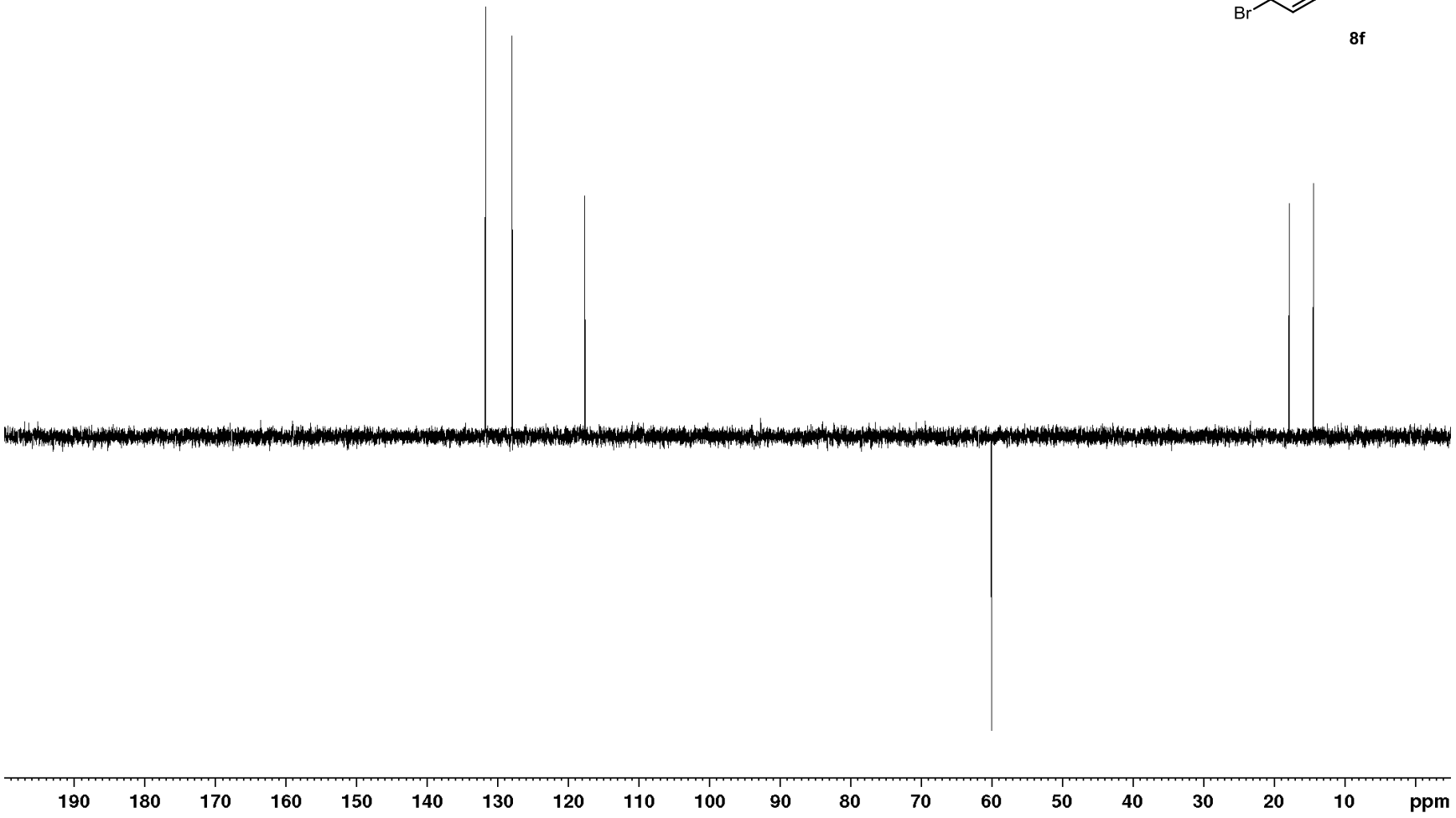
^{13}C NMR


166.8
154.2
141.2
131.8
128.0
123.4
117.8
60.1
17.9
14.5
O
O
Br
8f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

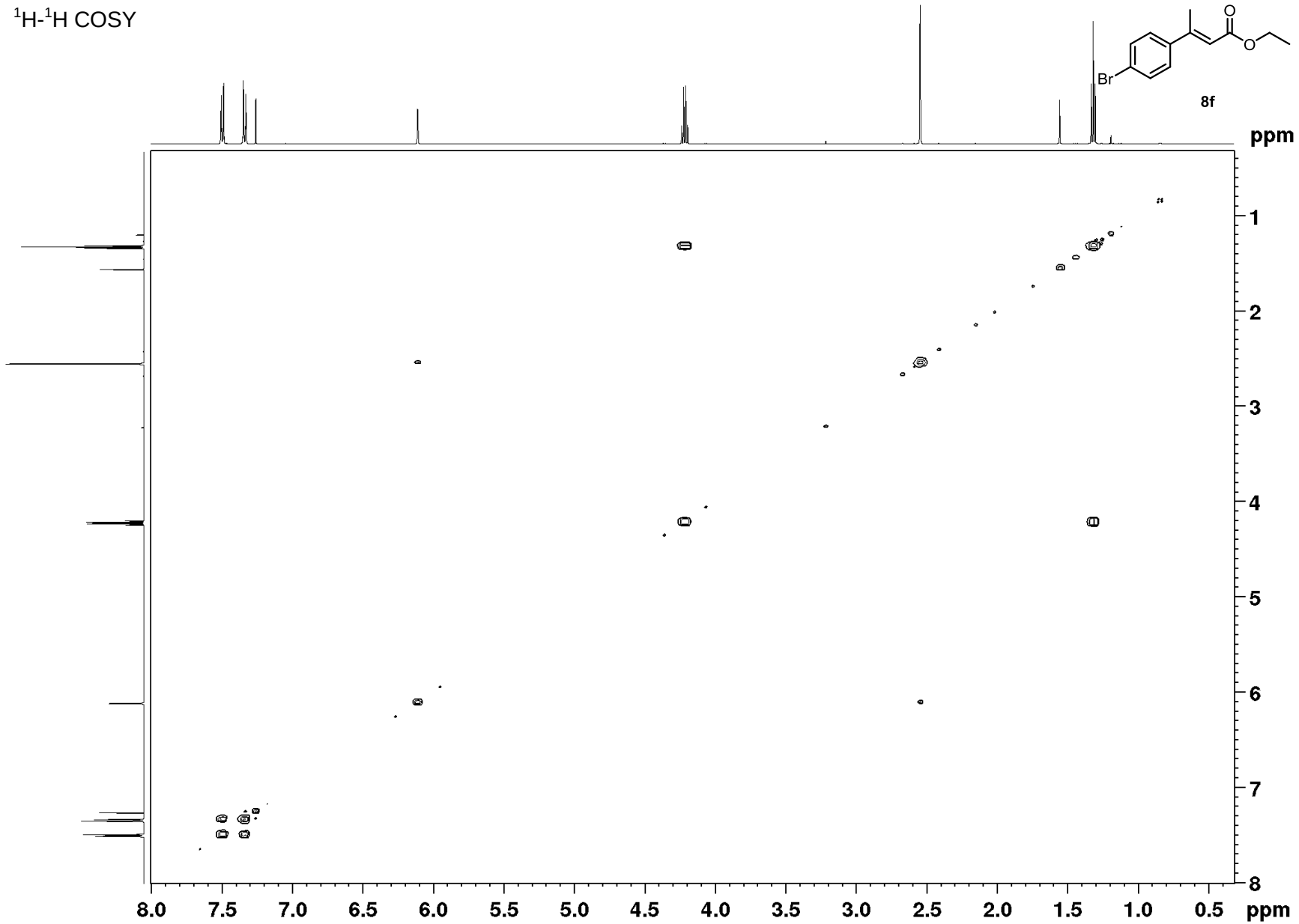
^{13}C DEPT NMR



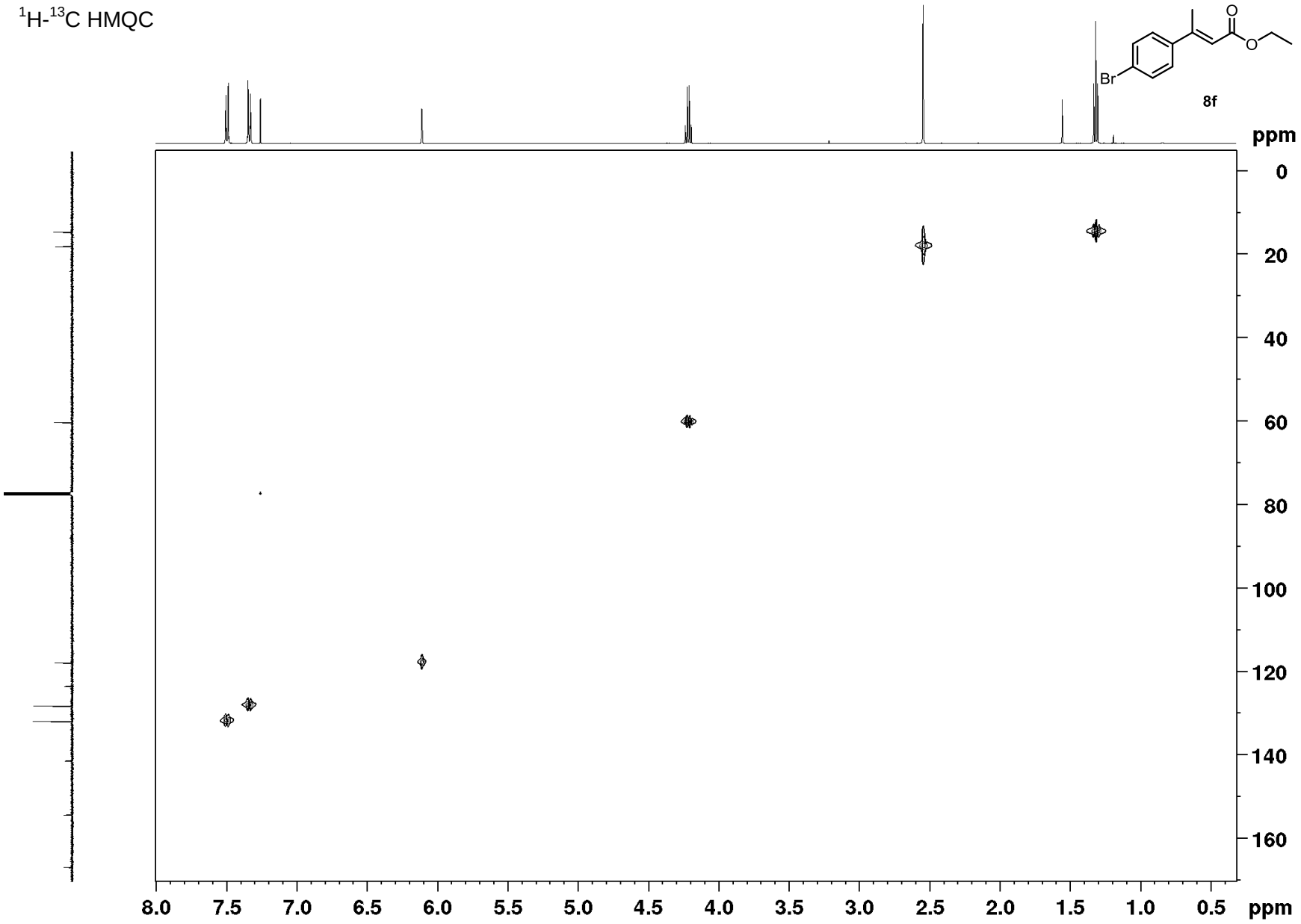
8f



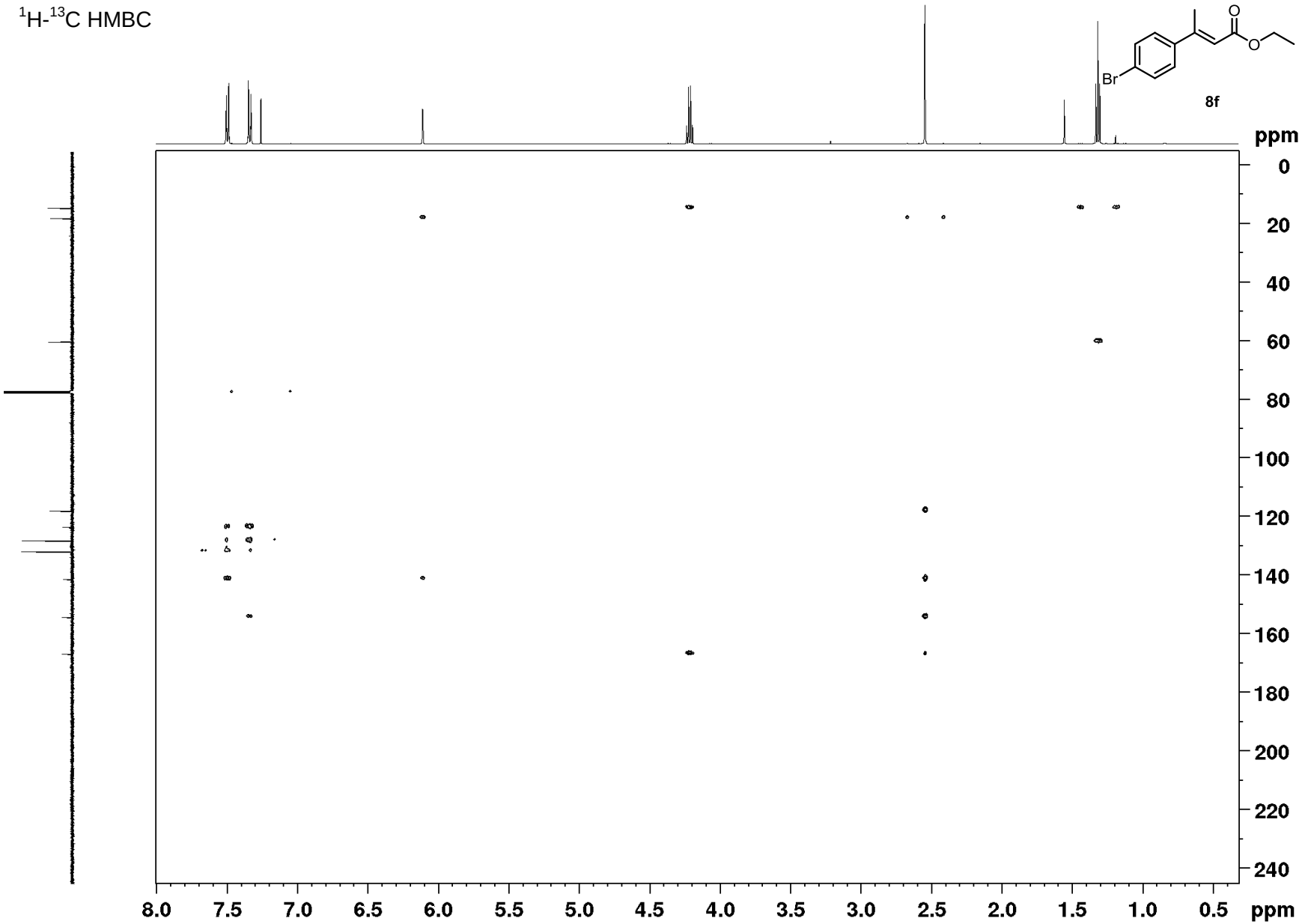
^{1}H-^{1}H COSY


Br
O
O
8f
ppm
1
2
3
4
5
6
7
8
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
ppm

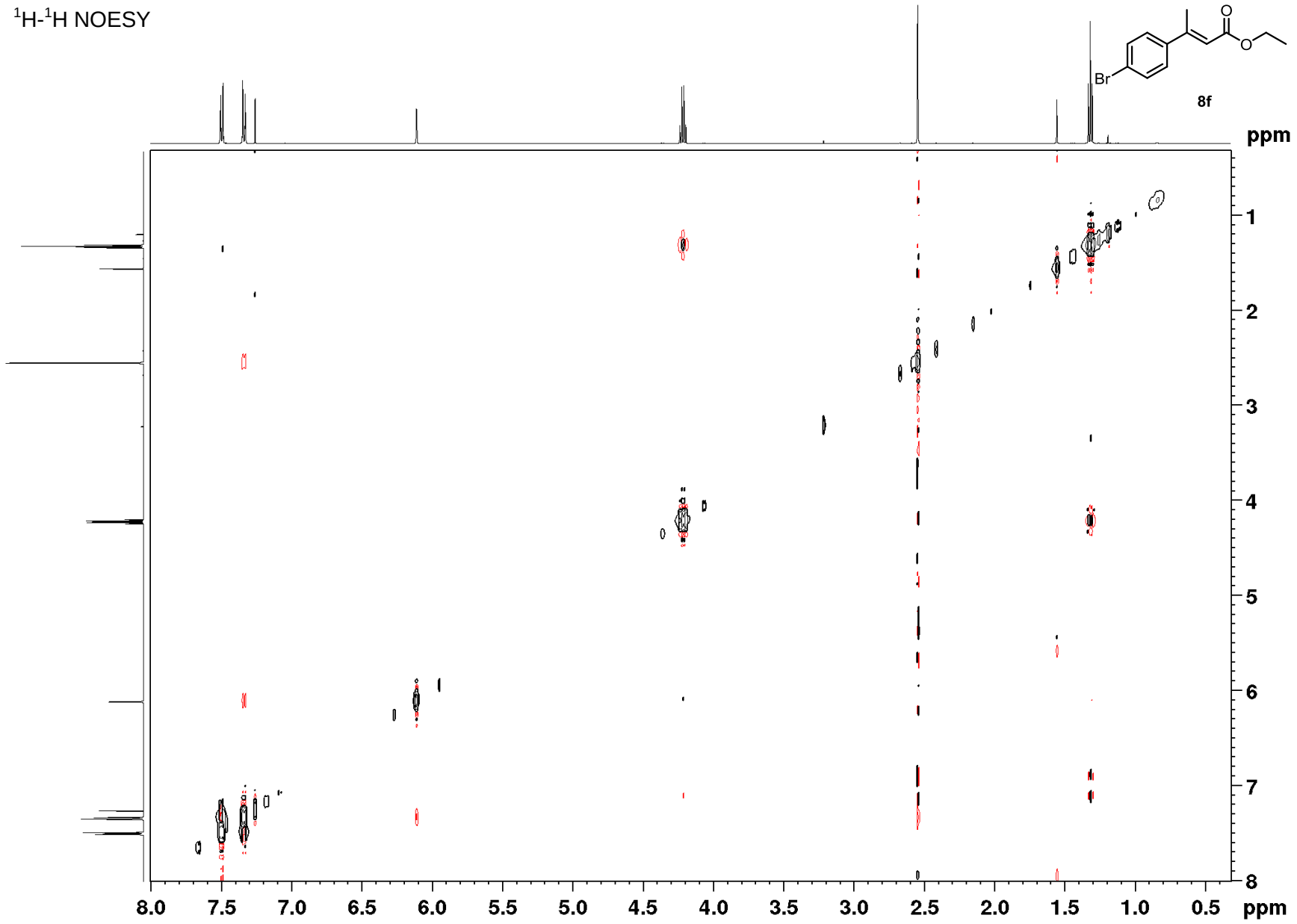
^{1}H-^{13}C HMQC

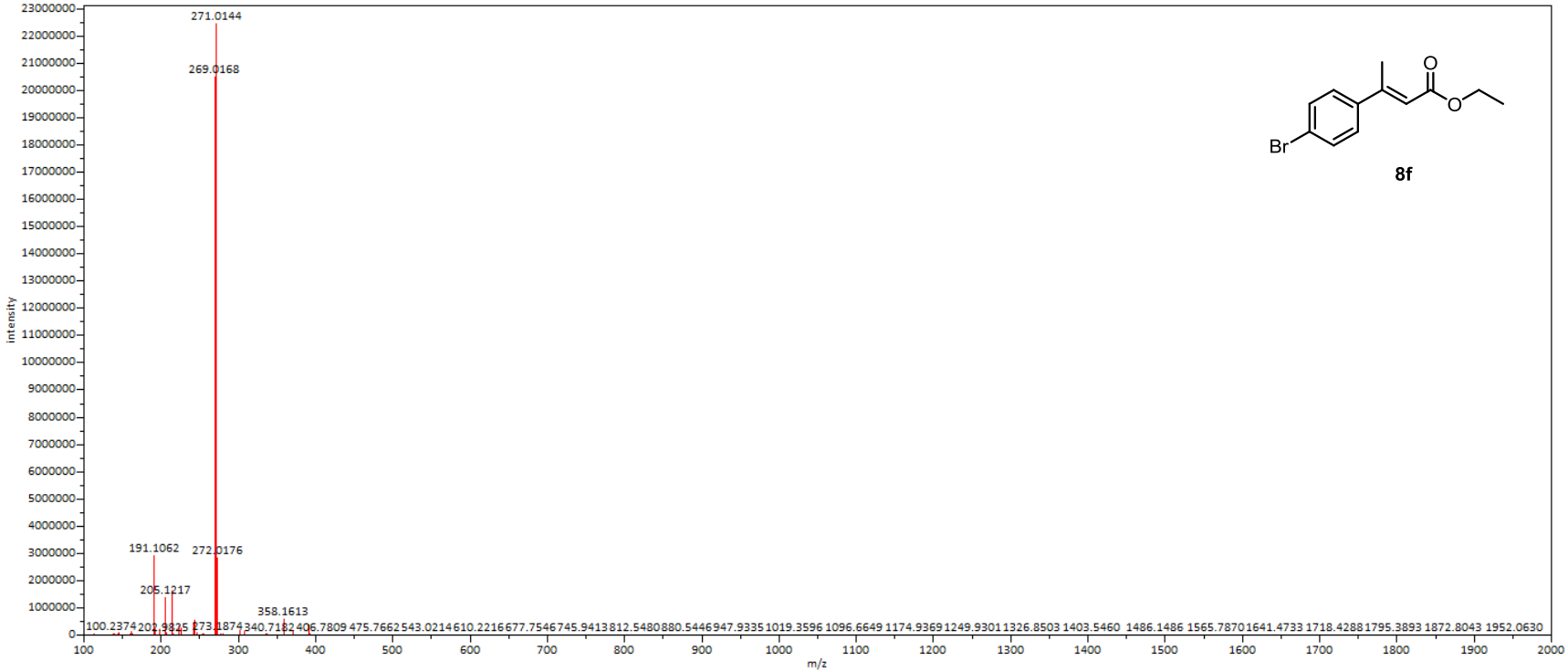

O
O
Br
8f
ppm
0
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{1}H-^{13}C HMBC


Br
O
O
8f
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

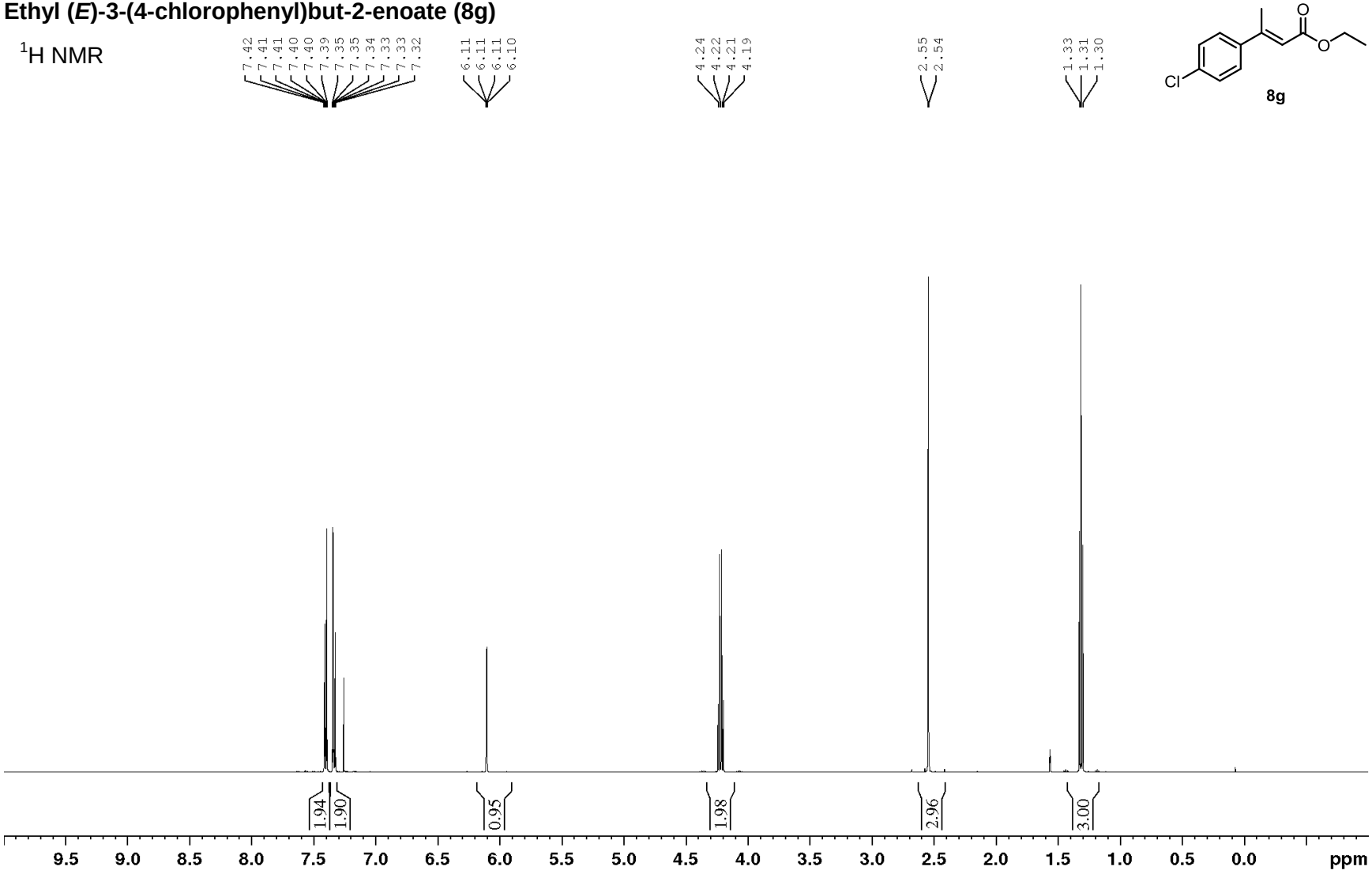
^{1}H-^{1}H NOESY


Br
O
O
8f
ppm
1
2
3
4
5
6
7
8
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
ppm

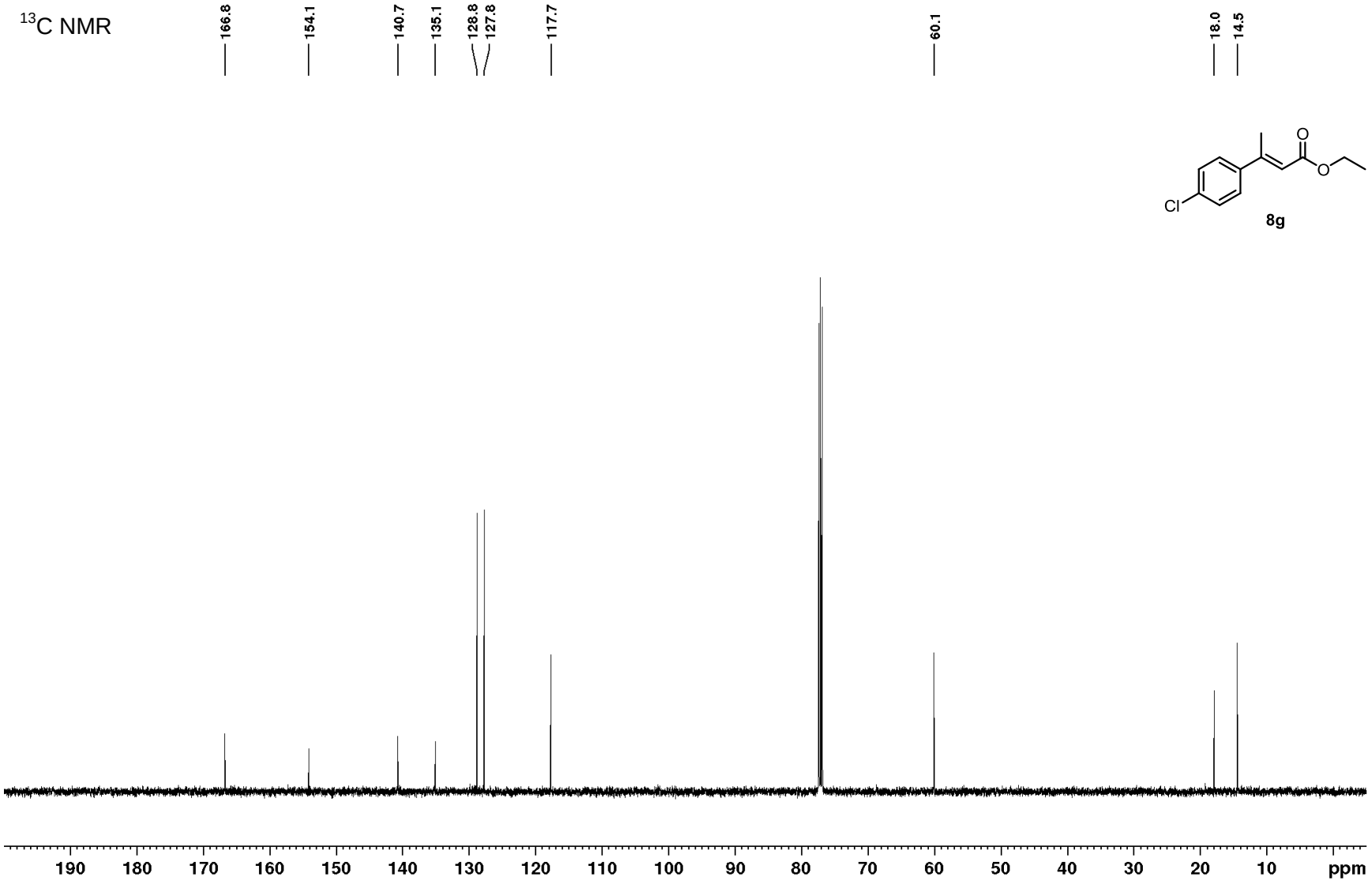

271.0144
269.0168
191.1062
272.0176
205.1217
358.1613
intensity
m/z
Br
O
O
8f

Ethyl (*E*)-3-(4-chlorophenyl)but-2-enoate (8g)

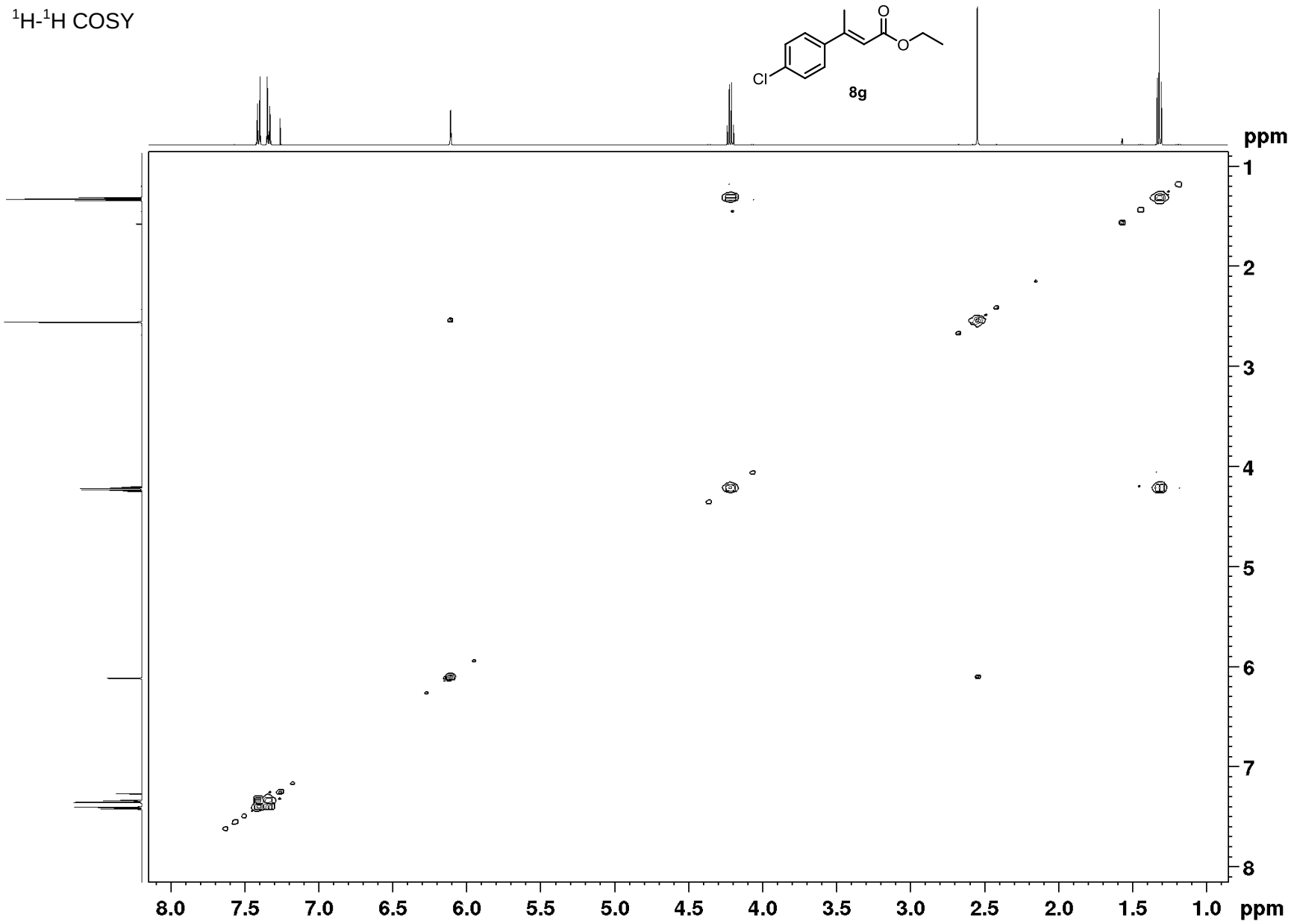
^{1}H NMR

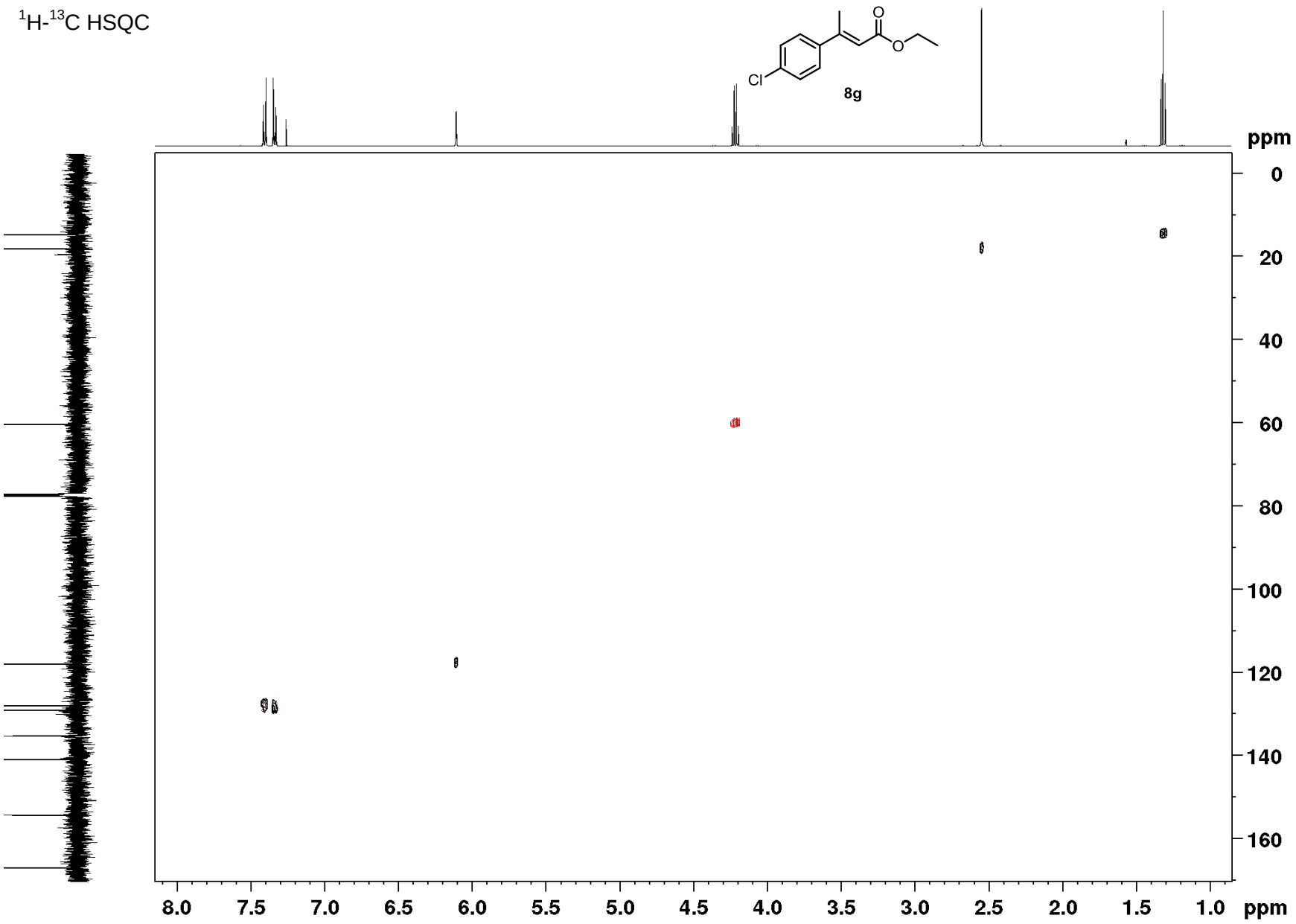


^{13}C NMR

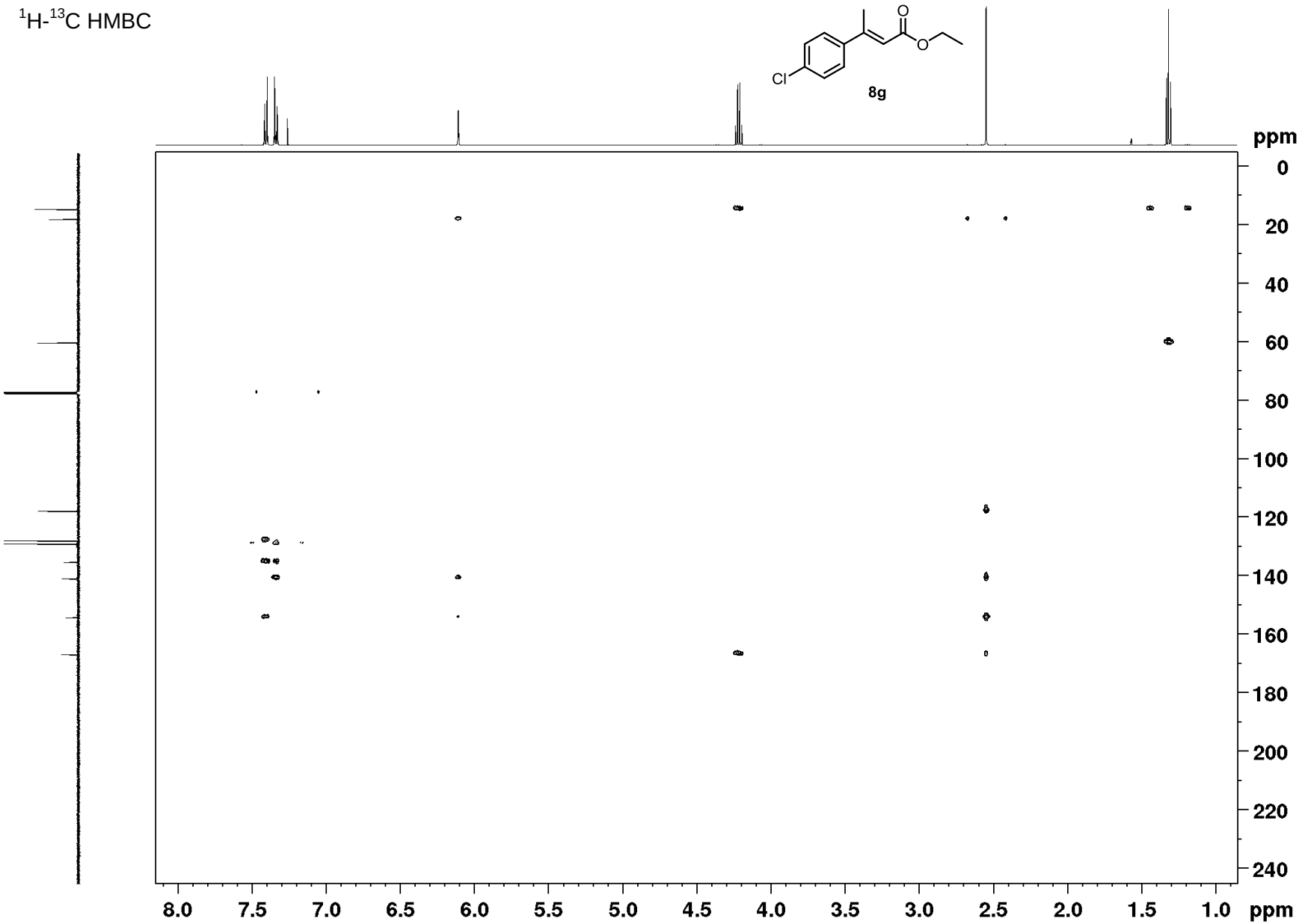

166.8
154.1
140.7
135.1
128.8
127.8
117.7
60.1
18.0
14.5
O
O
Cl
8g
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{1}H-^{1}H COSY

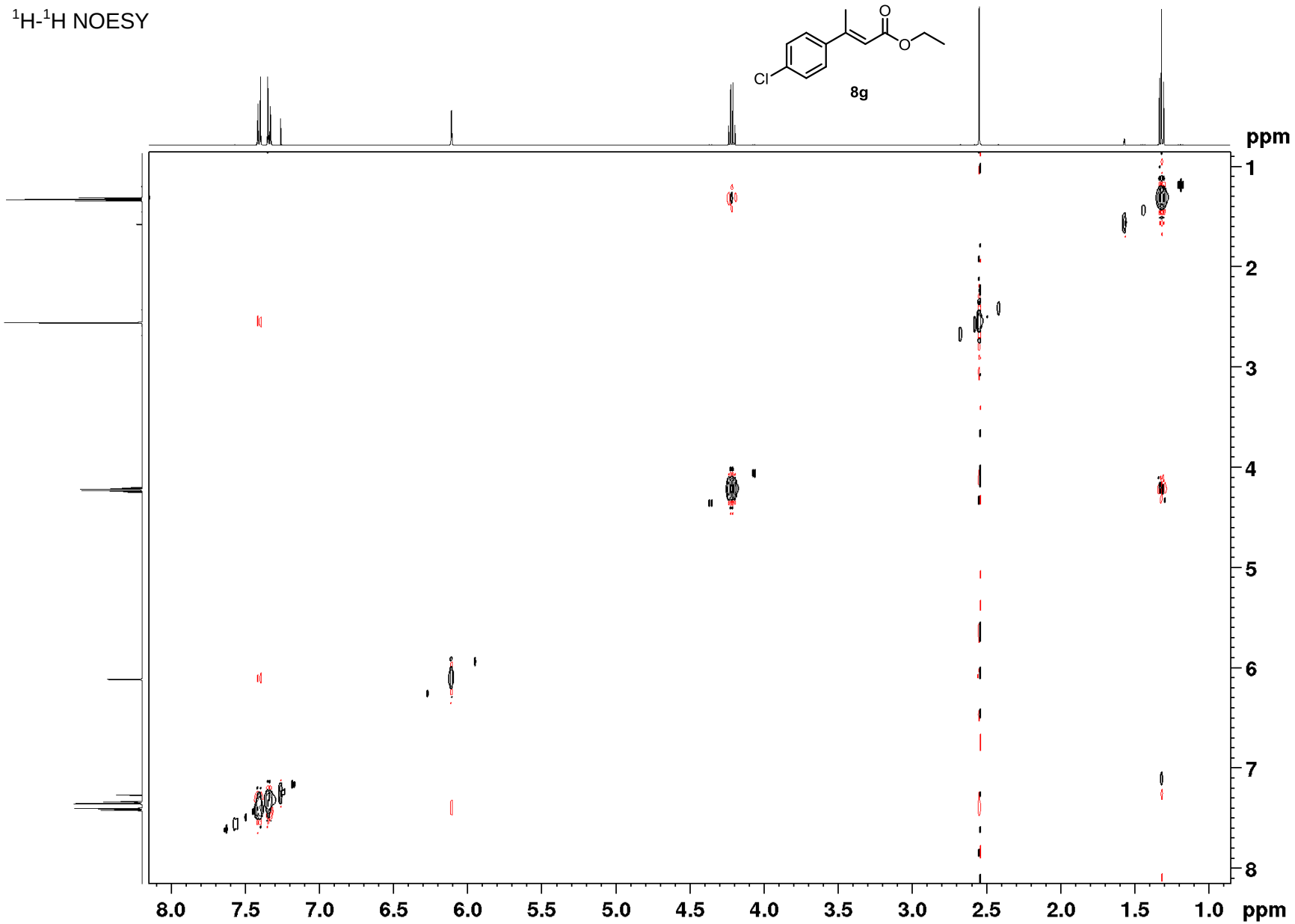

Cl
O
O
8g
ppm
1
2
3
4
5
6
7
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

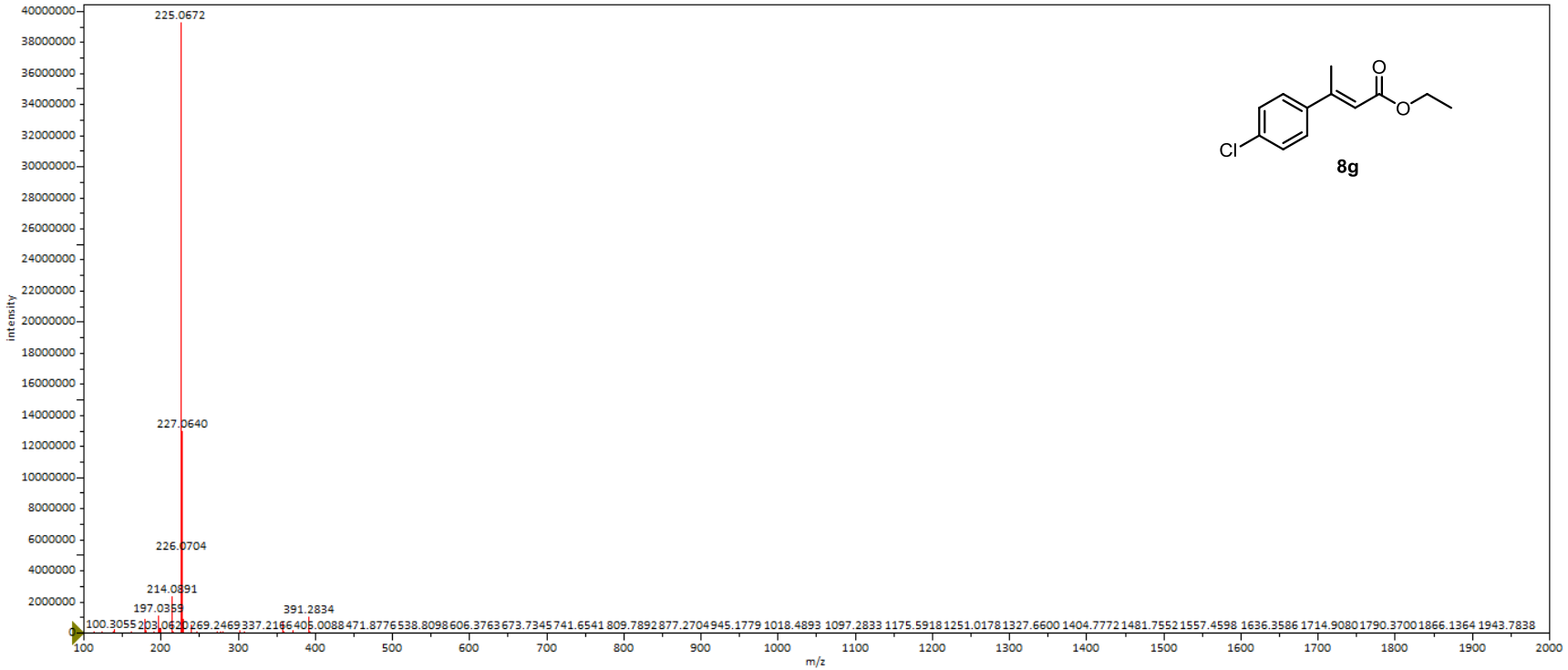

^{1}H-^{13}C HSQC
Cl
O
O
8g
ppm
0
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

^{1}H-^{13}C HMBC


Cl
O
O
8g
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

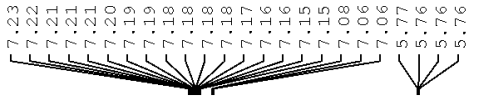
^{1}H-^{1}H NOESY

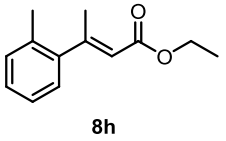

Cl
O
O
8g
ppm
1
2
3
4
5
6
7
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


225.0672
227.0640
226.0704
214.0891
197.0359
391.2834
intensity
m/z
Cl
O
O
8g

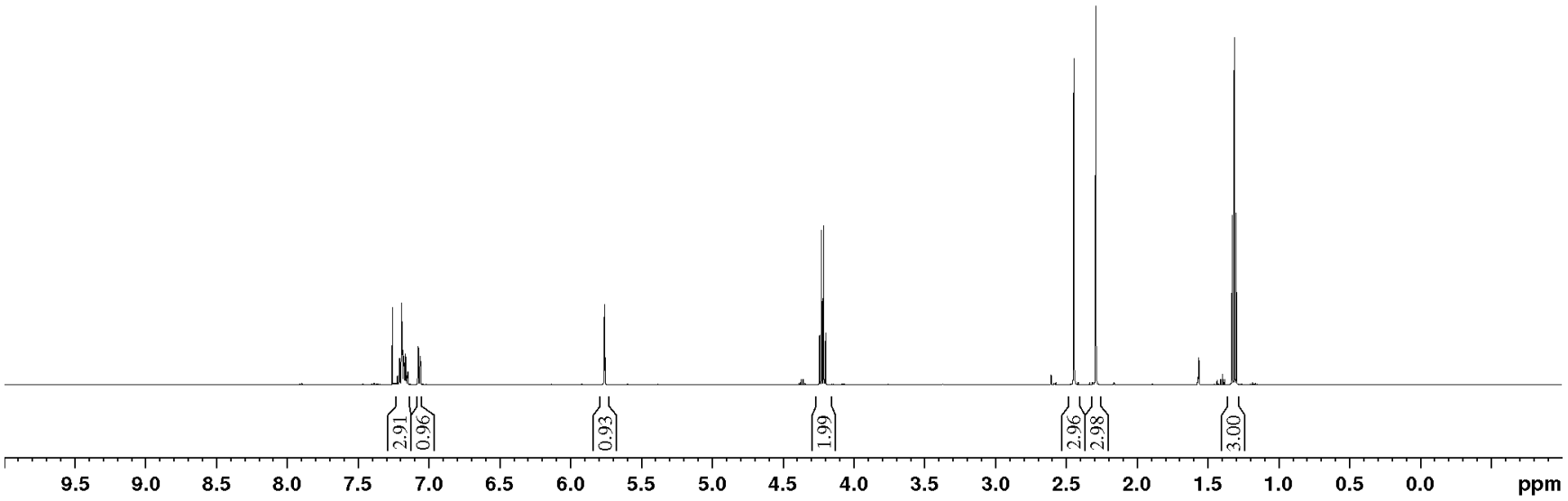
Ethyl (*E*)-3-(o-tolyl)but-2-enoate (8h)

^{1}H NMR

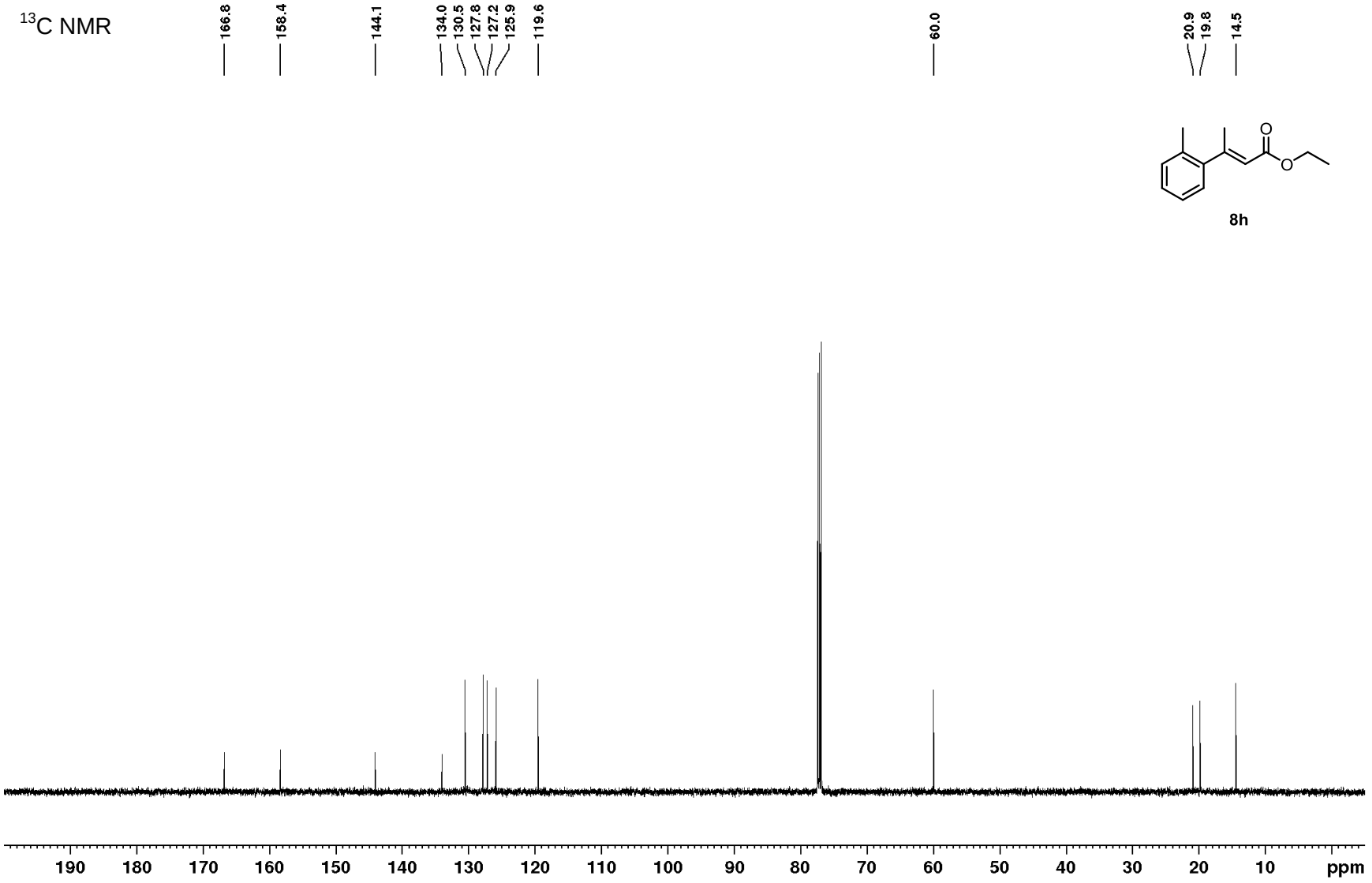




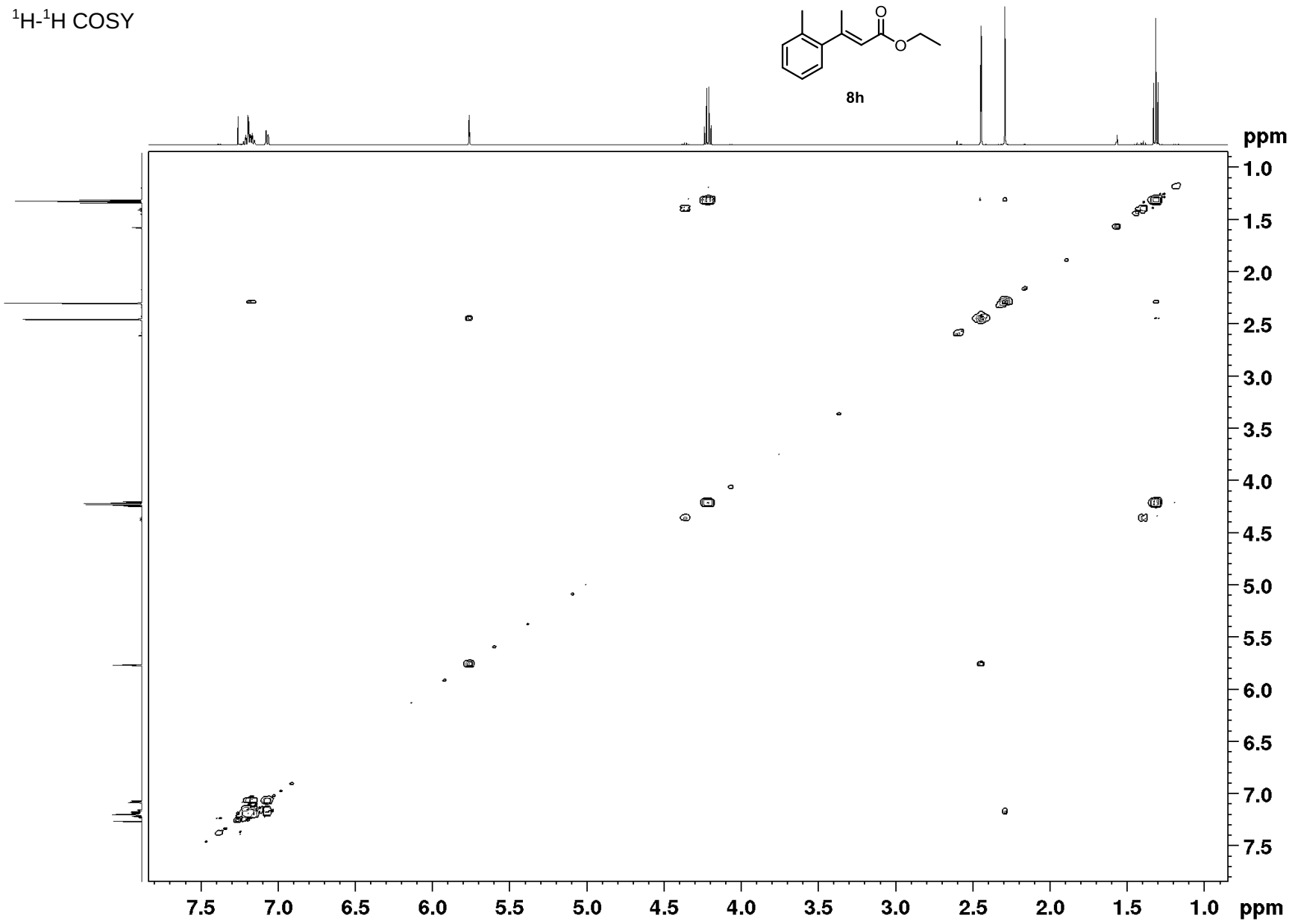
8h



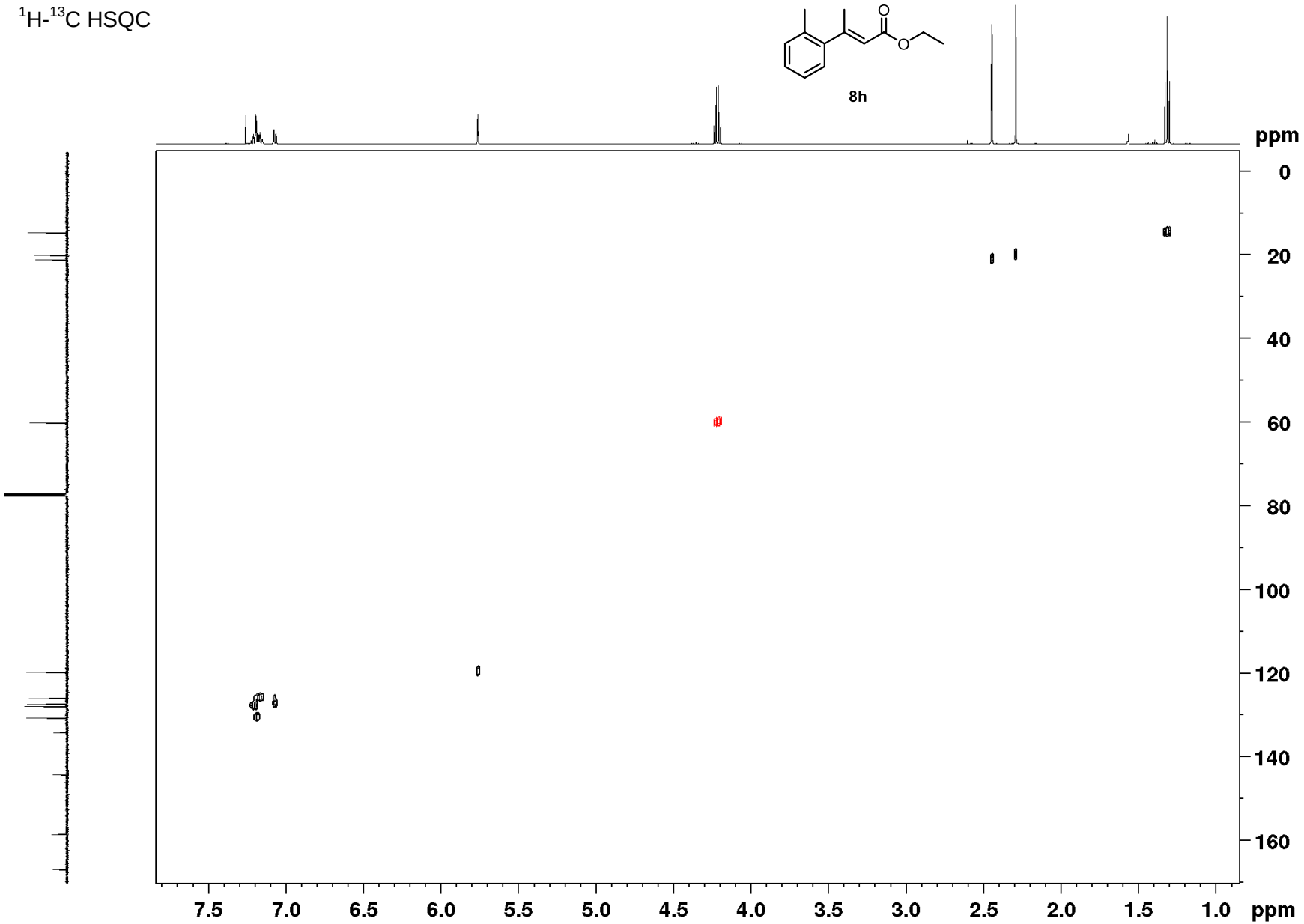
^{13}C NMR


166.8
158.4
144.1
134.0
130.5
127.8
127.2
125.9
119.6
60.0
20.9
19.8
14.5
O
O
8h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

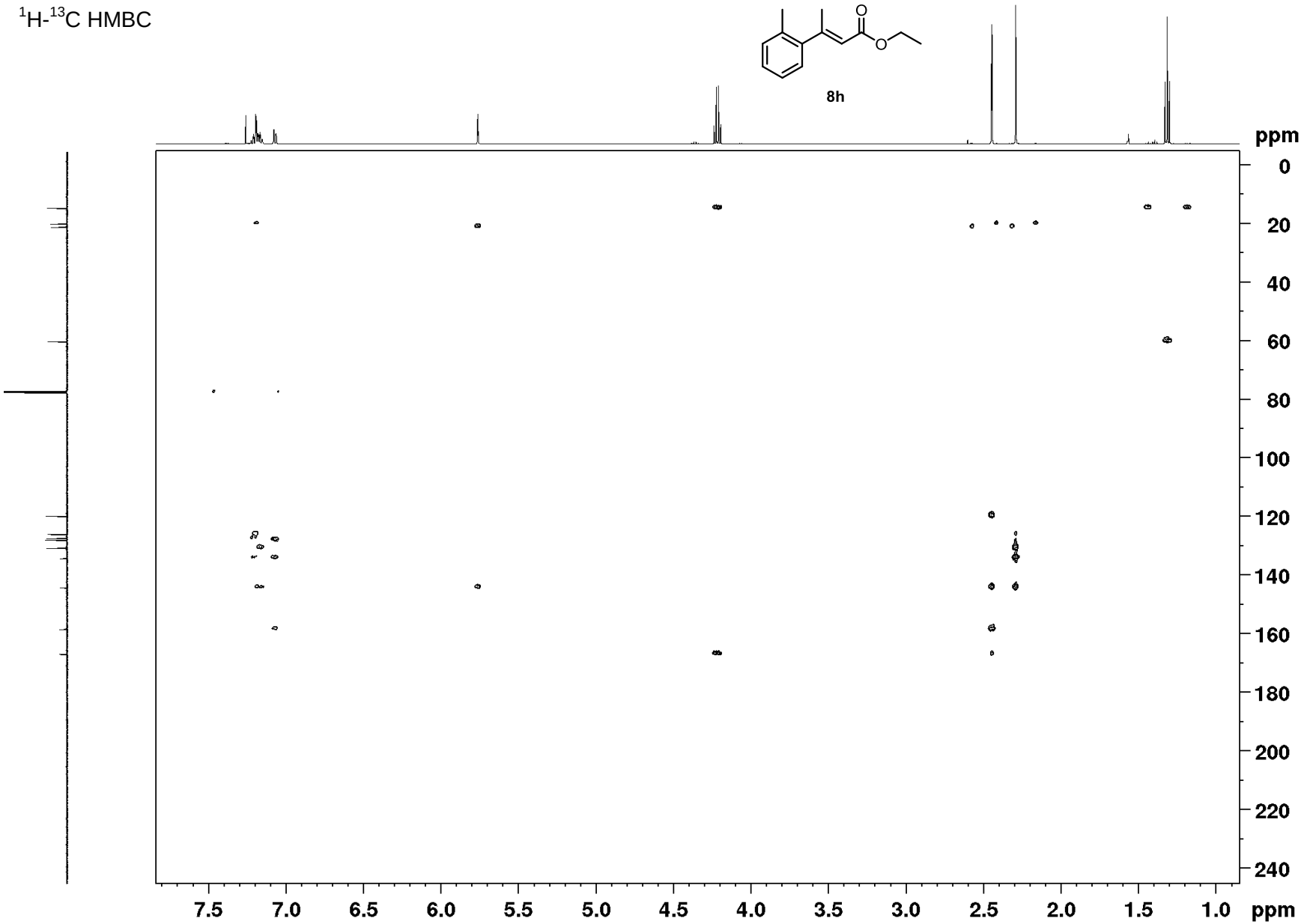
^{1}H-^{1}H COSY



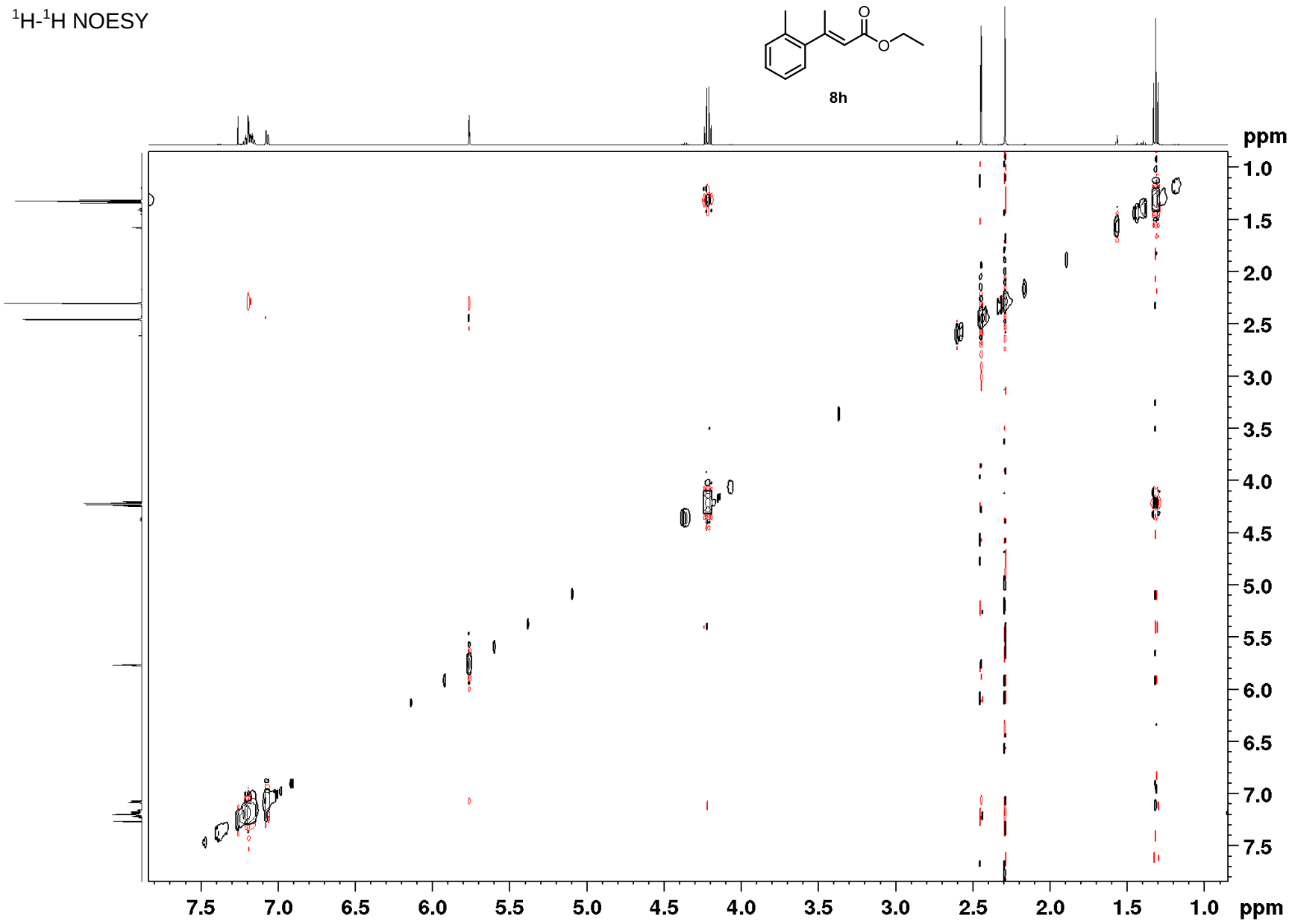
^{1}H-^{13}C HSQC


8h
ppm
0
20
40
60
80
100
120
140
160
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
ppm

^{1}H-^{13}C HMBC


8h
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

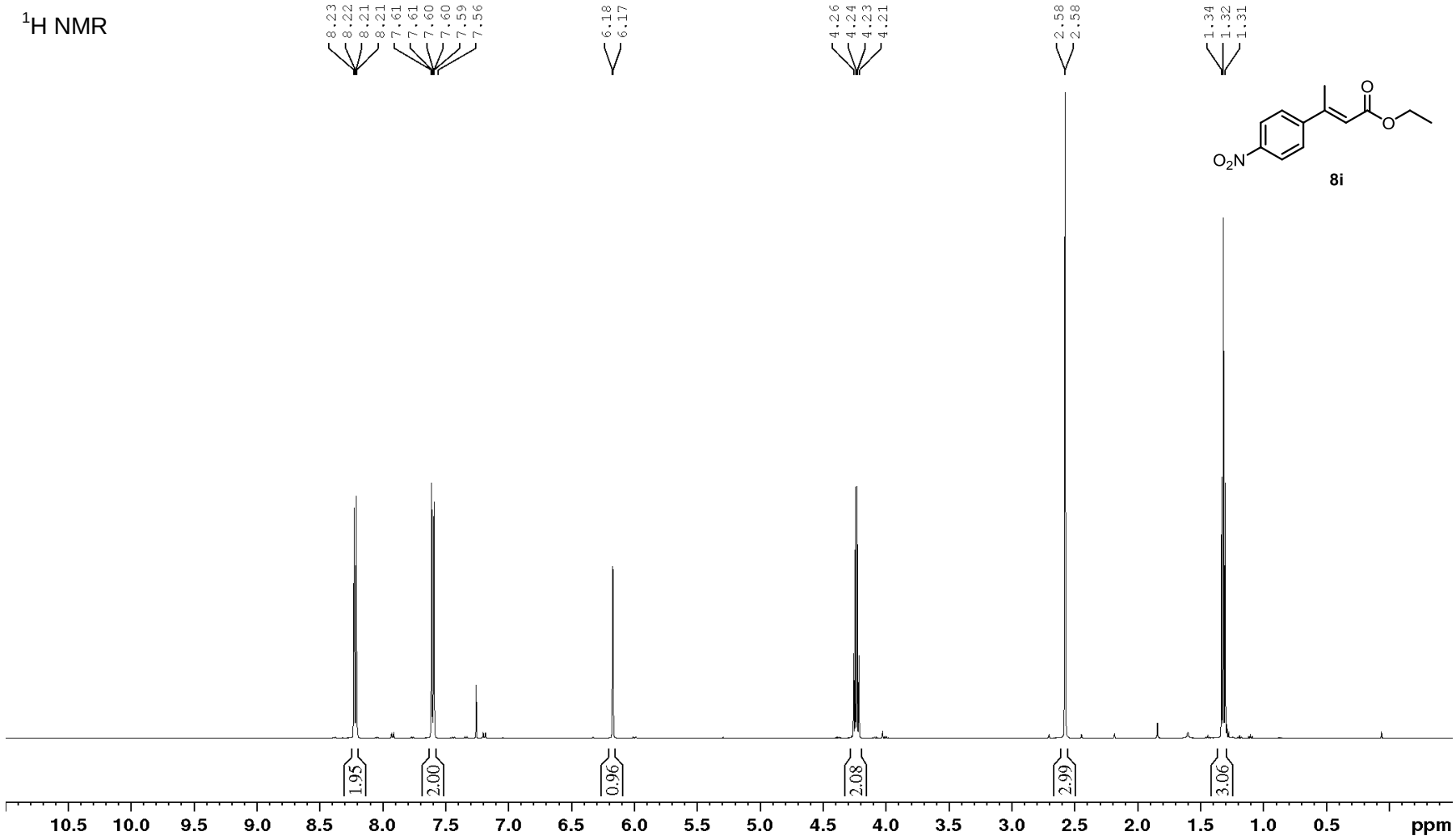
^{1}H-^{1}H NOESY


8h
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
ppm
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

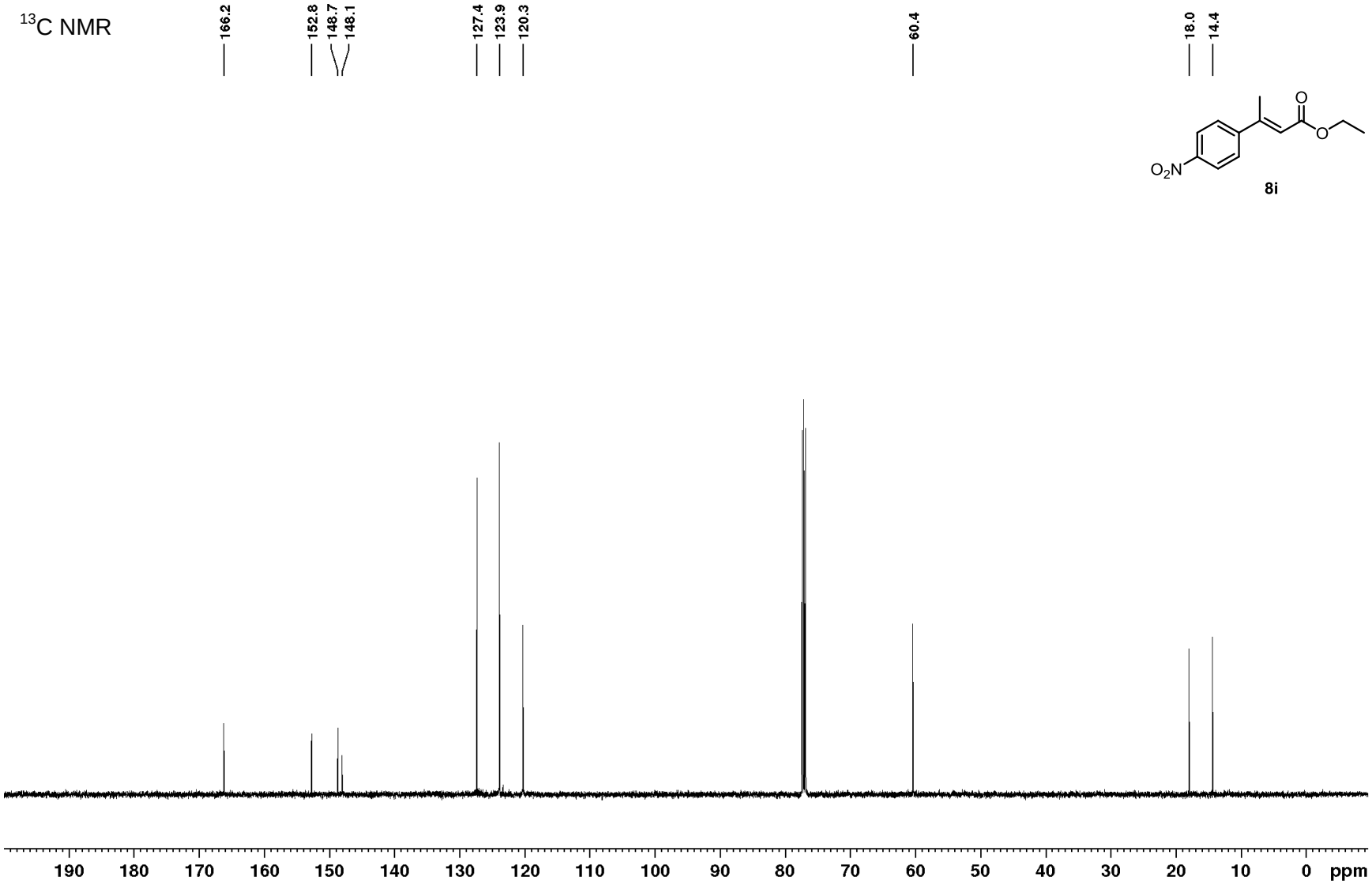

205.1218
159.0801
177.0906
intensity
m/z
8h

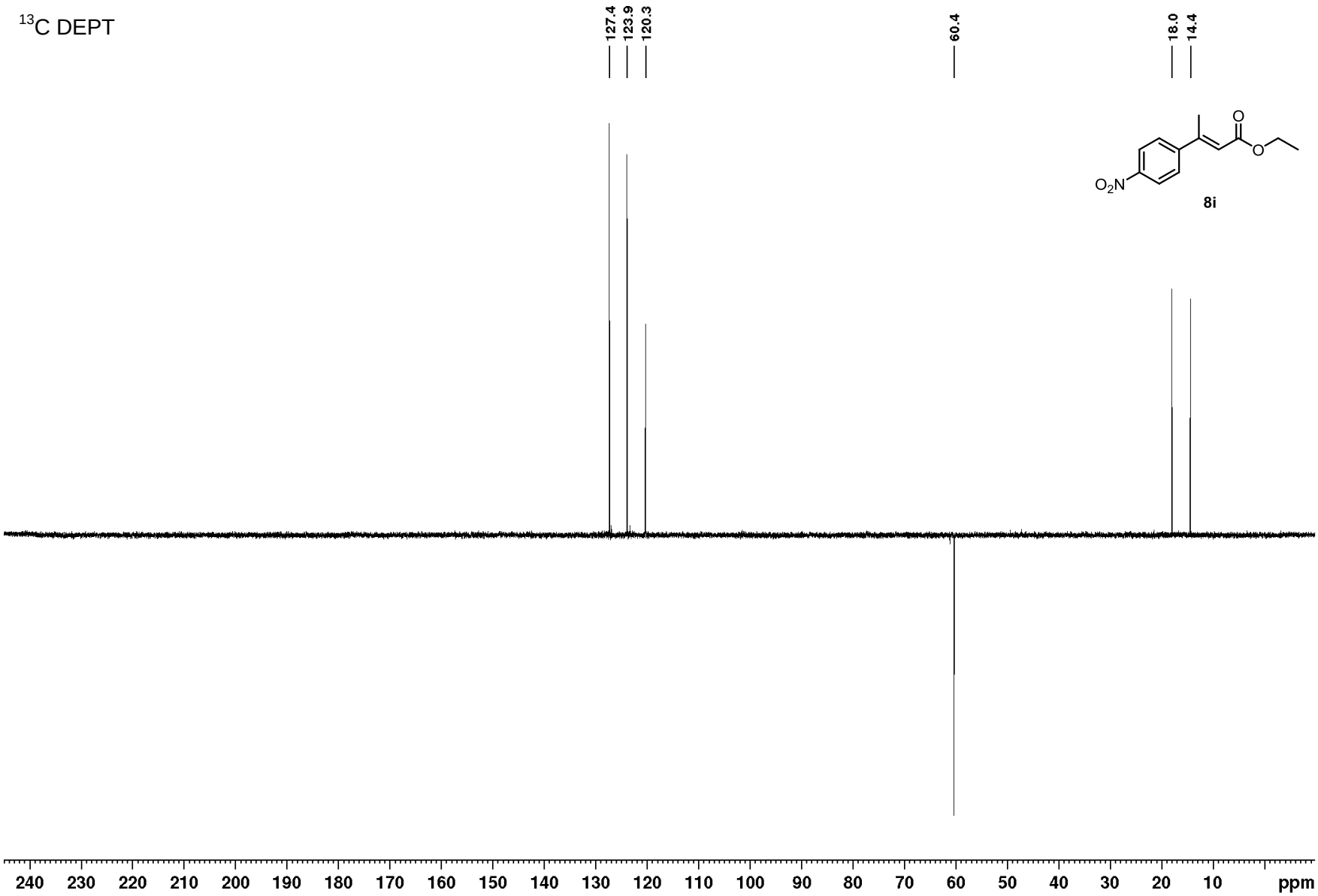
Ethyl (*E*)-3-(4-nitrophenyl)but-2-enoate (8i)

^{1}H NMR

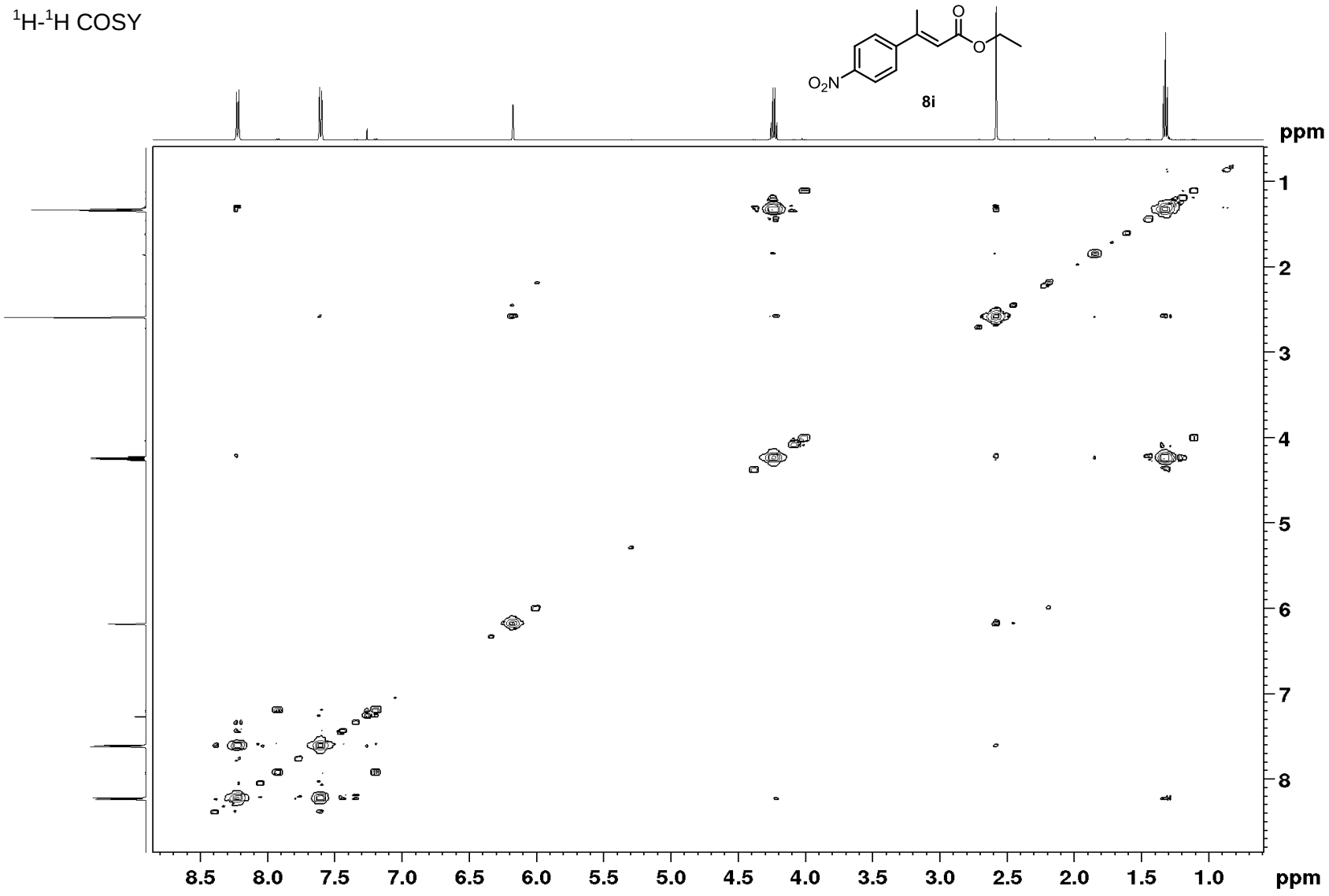


^{13}C NMR

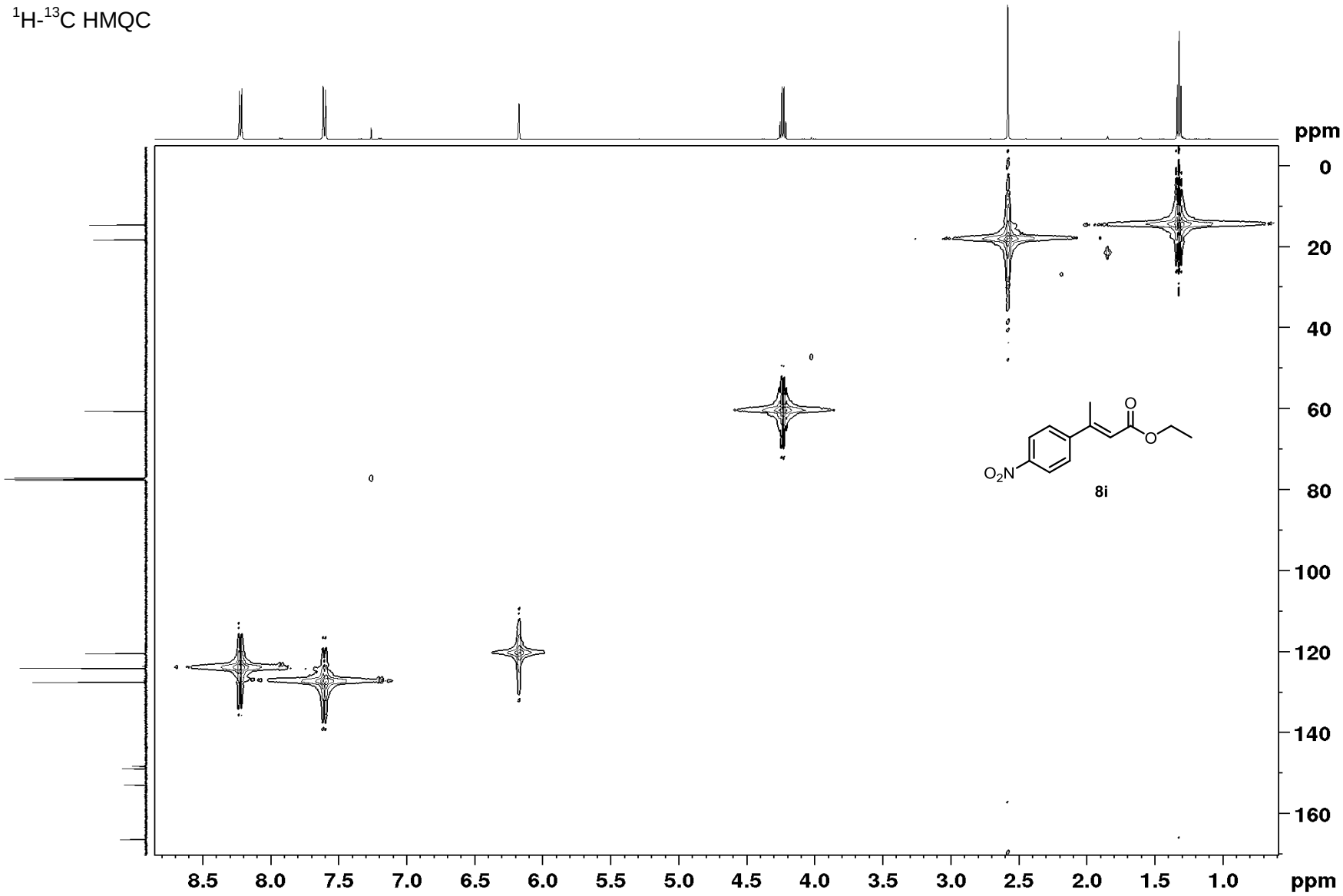

166.2
152.8
148.7
148.1
127.4
123.9
120.3
60.4
18.0
14.4
O
O
O2N
8i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


^{13}C DEPT
127.4
123.9
120.3
60.4
18.0
14.4
O
O
O_2N
8i
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

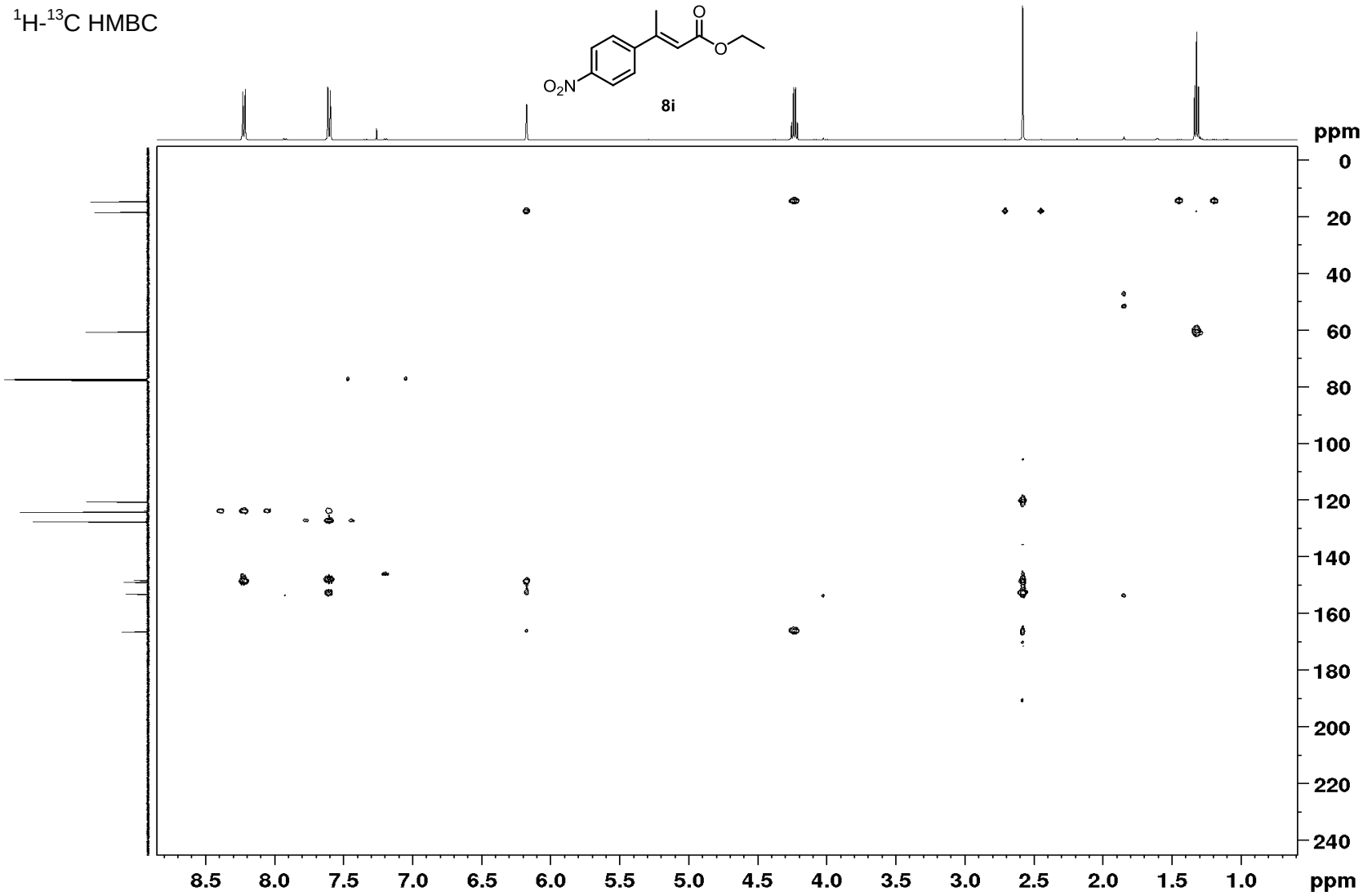
^{1}H-^{1}H COSY


O
O
O2N
8i
ppm
1
2
3
4
5
6
7
8
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

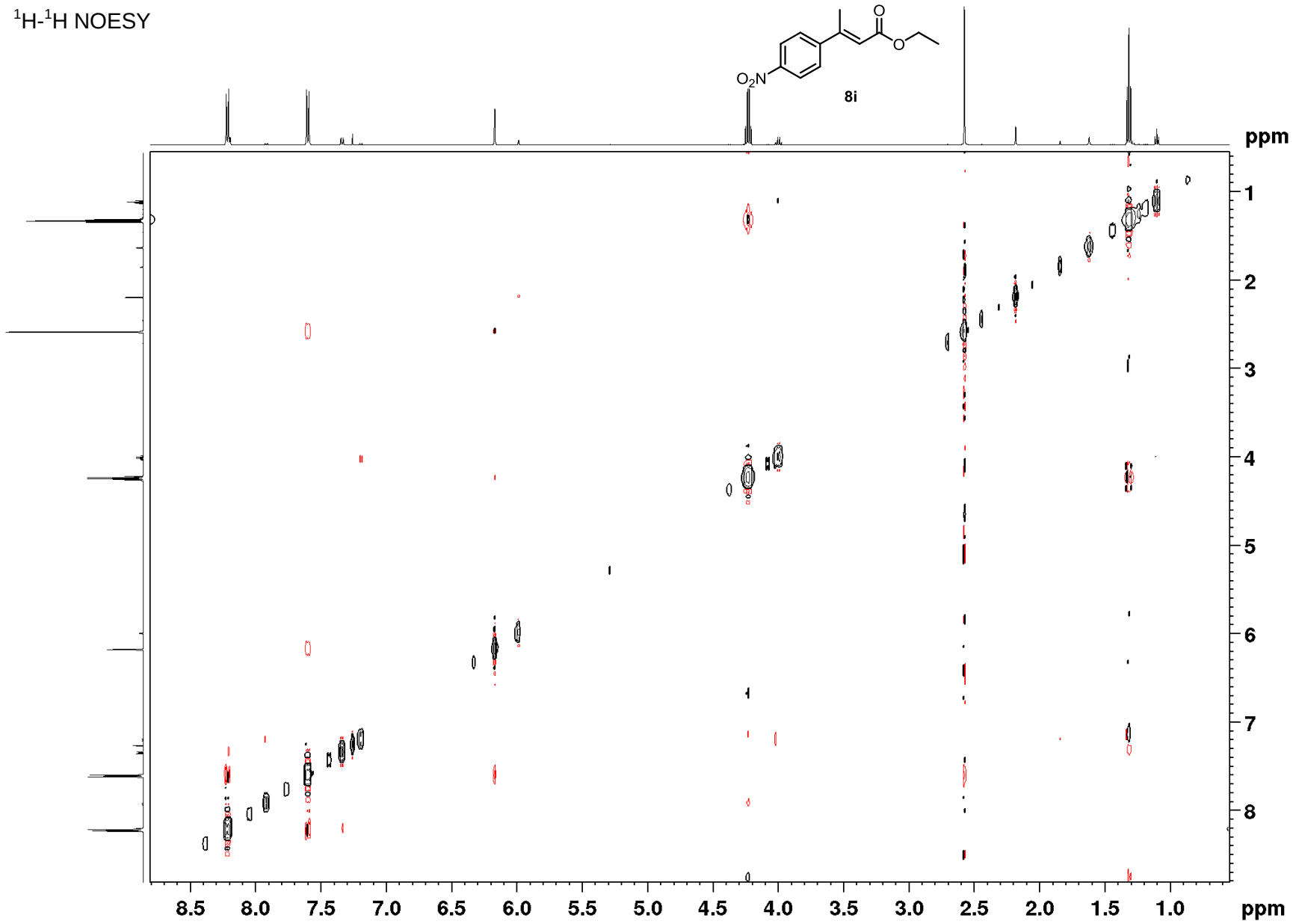
^{1}H-^{13}C HMQC

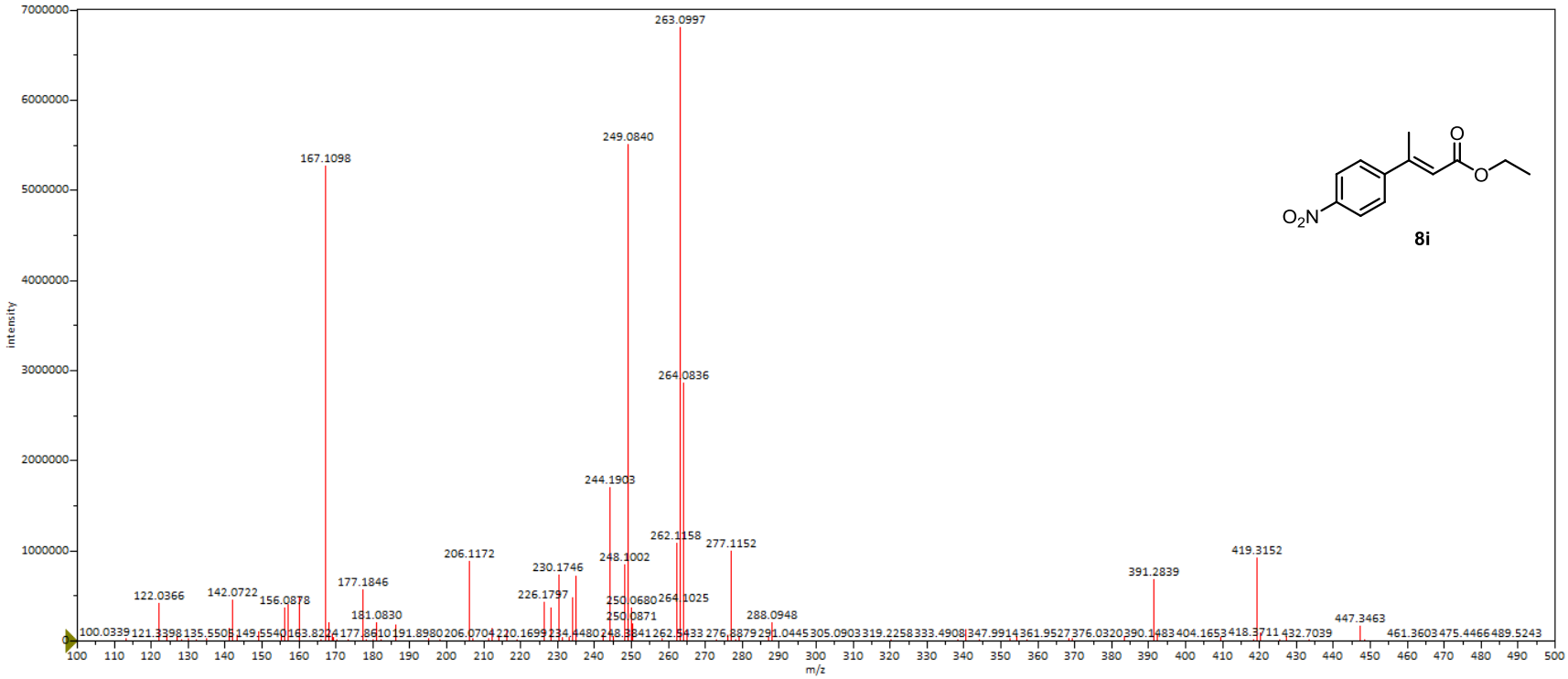

ppm
0
20
40
60
80
100
120
140
160
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
O2N
O
O
8i

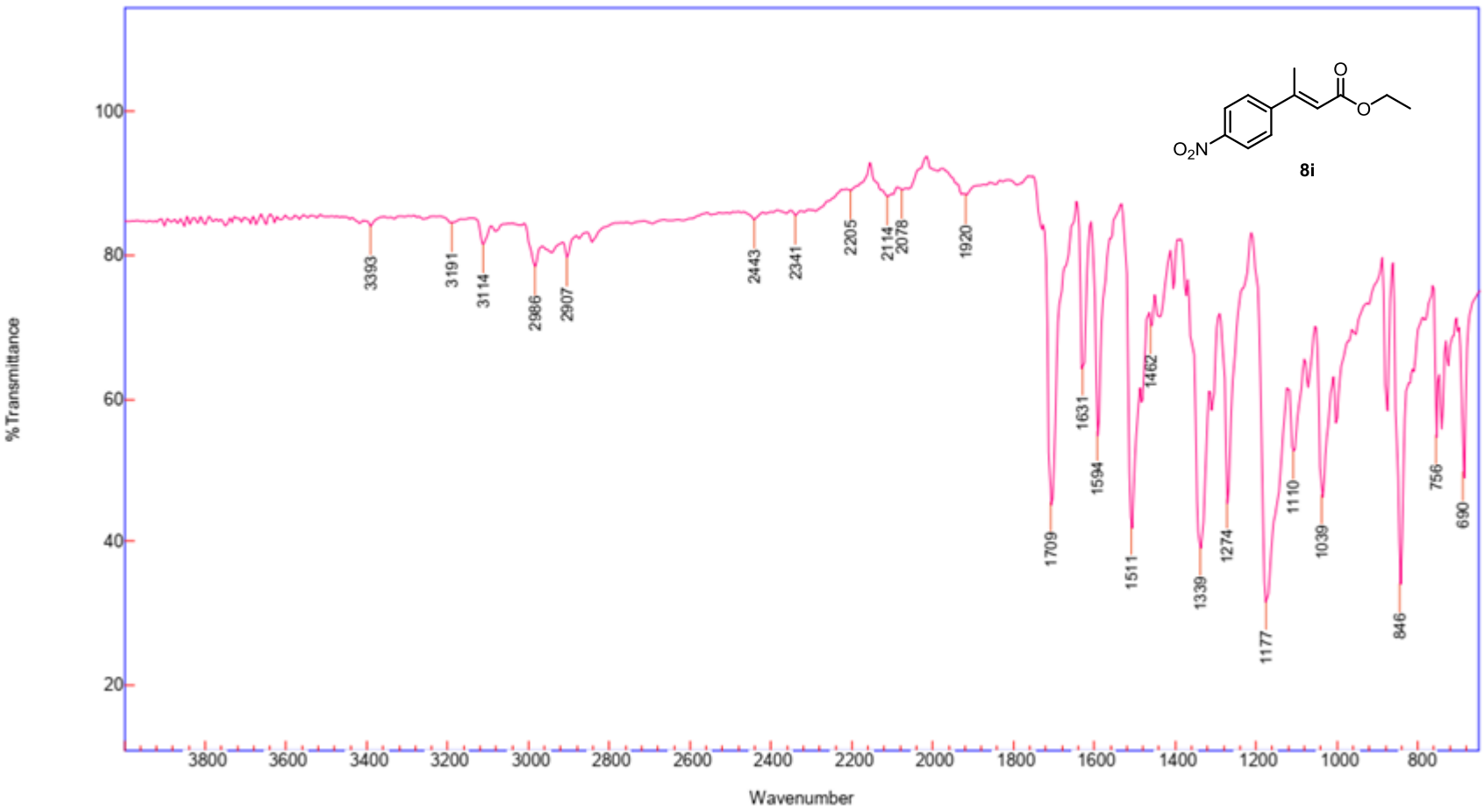
^{1}H-^{13}C HMBC


O
O
O2N
8i
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

^{1}H-^{1}H NOESY

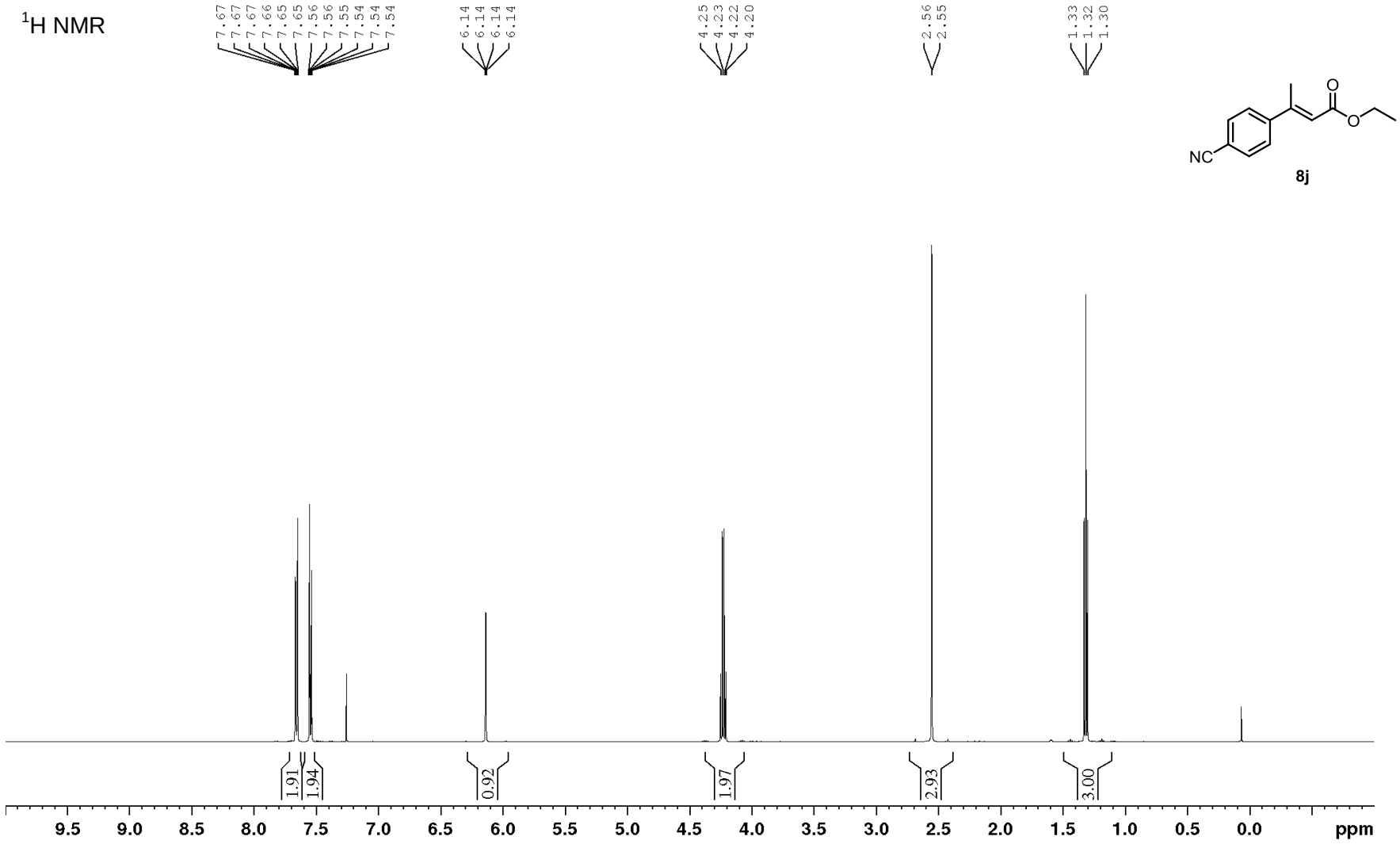

O2N
O
O
8i
ppm
1
2
3
4
5
6
7
8
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


intensity
m/z
263.0997
249.0840
167.1098
264.0836
244.1903
262.1158
277.1152
248.1002
206.1172
230.1746
177.1846
122.0366
142.0722
156.0878
226.1797
250.0680
264.1025
181.0830
288.0948
391.2839
419.3152
447.3463
O2N
O
O
8i

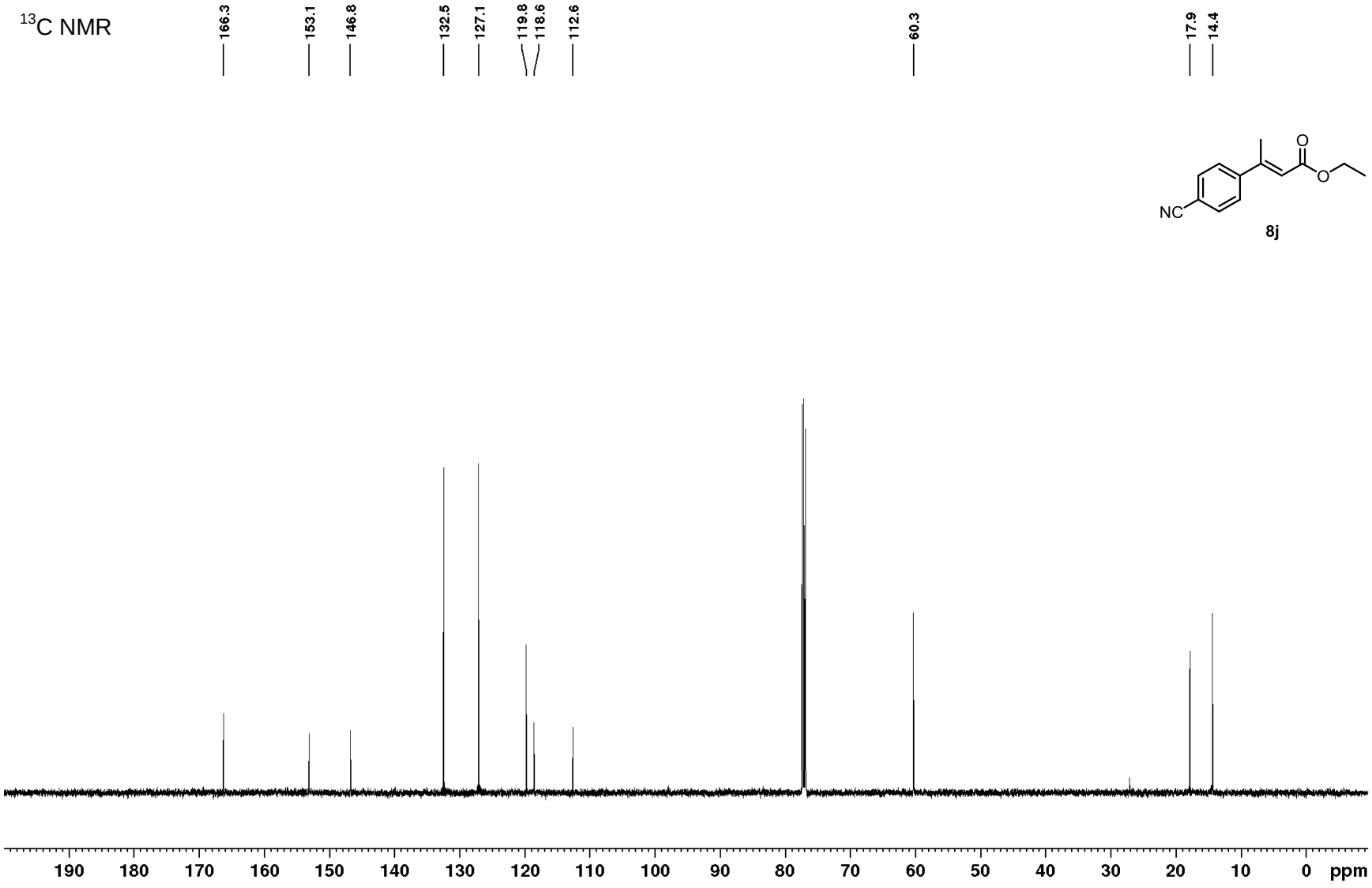

% Transmittance
100
80
60
40
20
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber
3393
3191
3114
2986
2907
2443
2341
2205
2114
2078
1920
1709
1631
1594
1511
1462
1339
1274
1177
1110
1039
846
756
690
O
O
O2N
8i

Ethyl (*E*)-3-(4-cyanophenyl)but-2-enoate (8j)

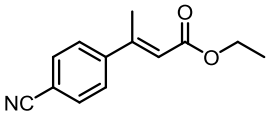
^{1}H NMR



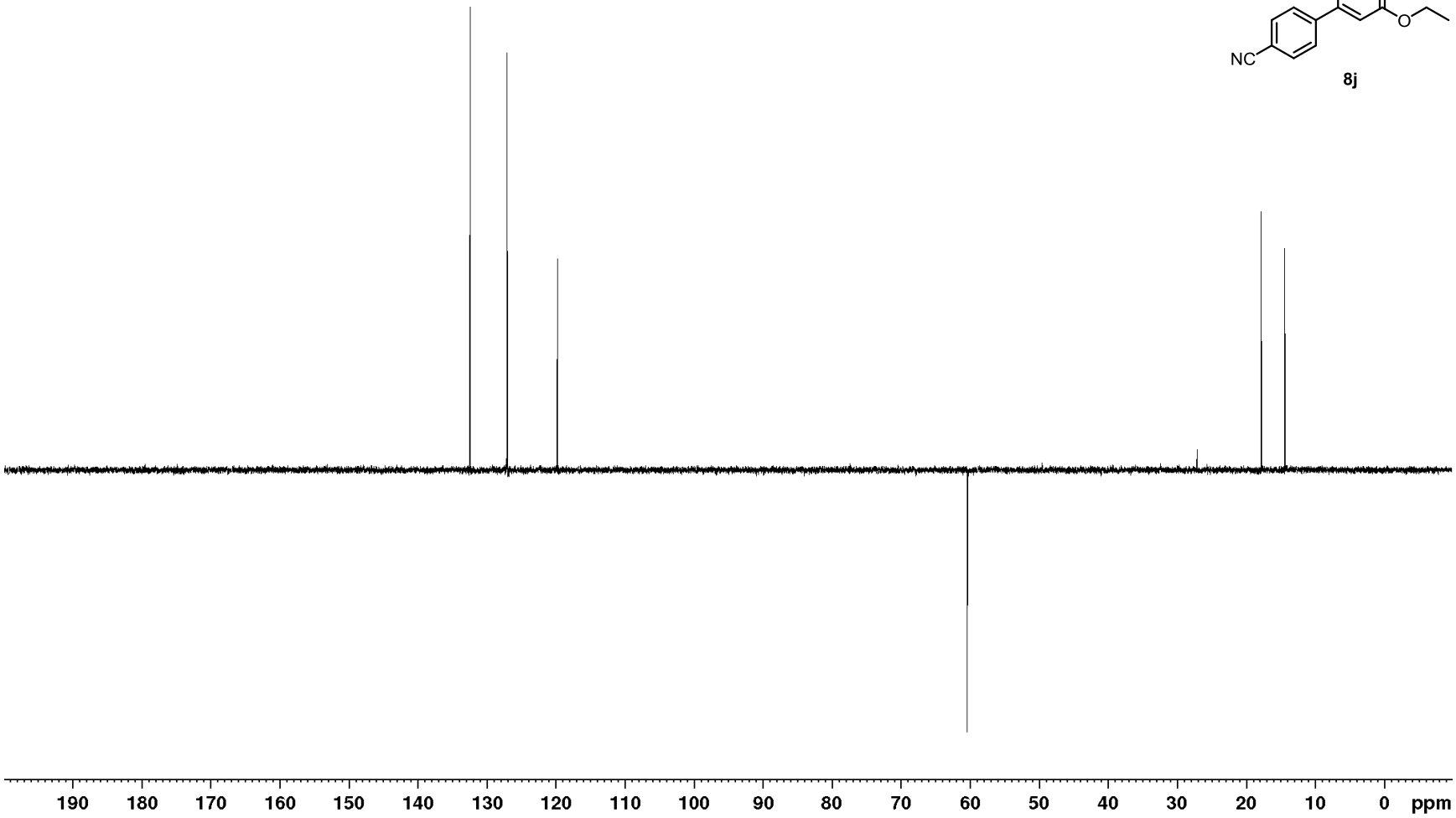
^{13}C NMR


166.3
153.1
146.8
132.5
127.1
119.8
118.6
112.6
60.3
17.9
14.4
O
O
NC
8j
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

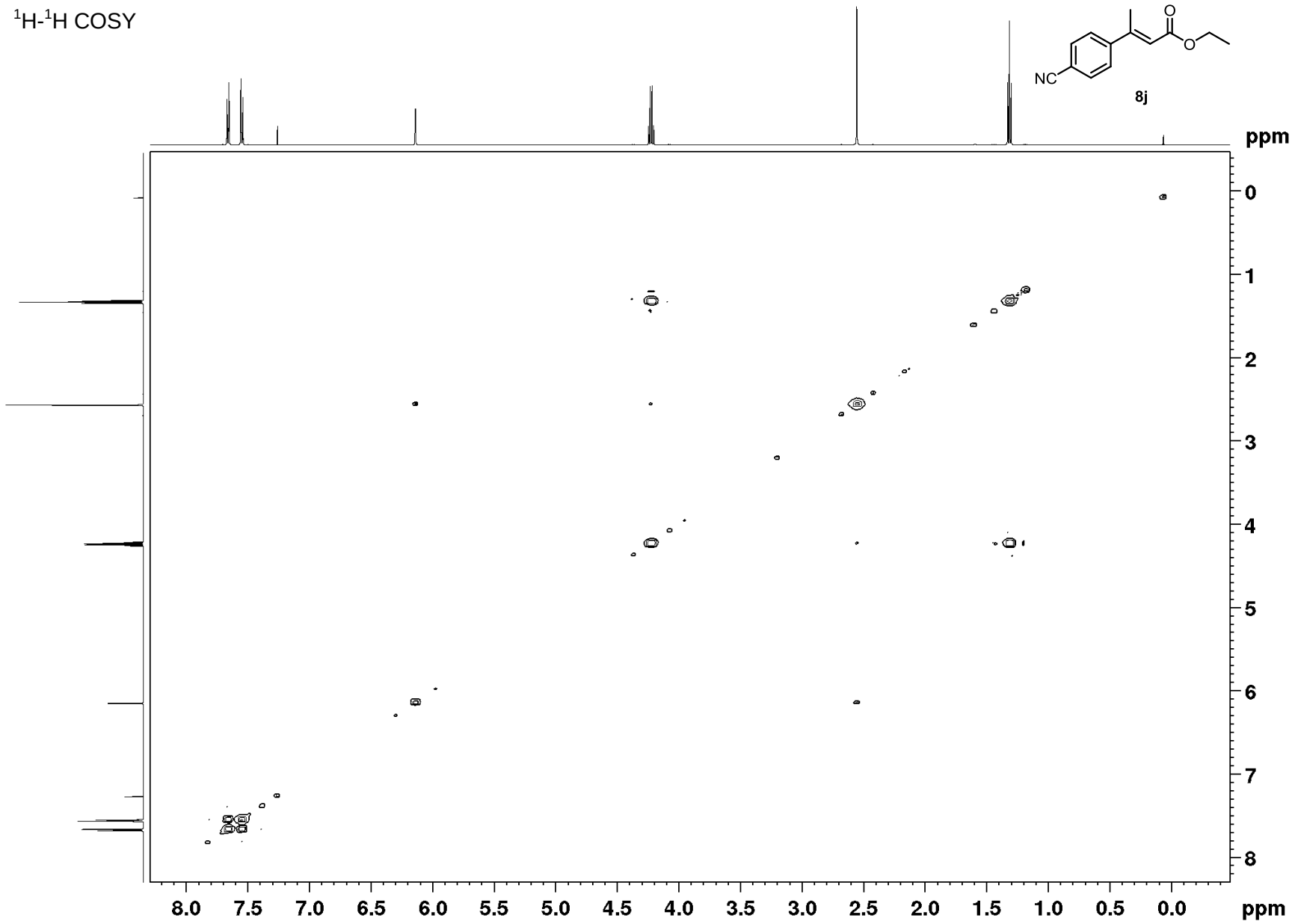
^{13}C DEPT


O
O
NC

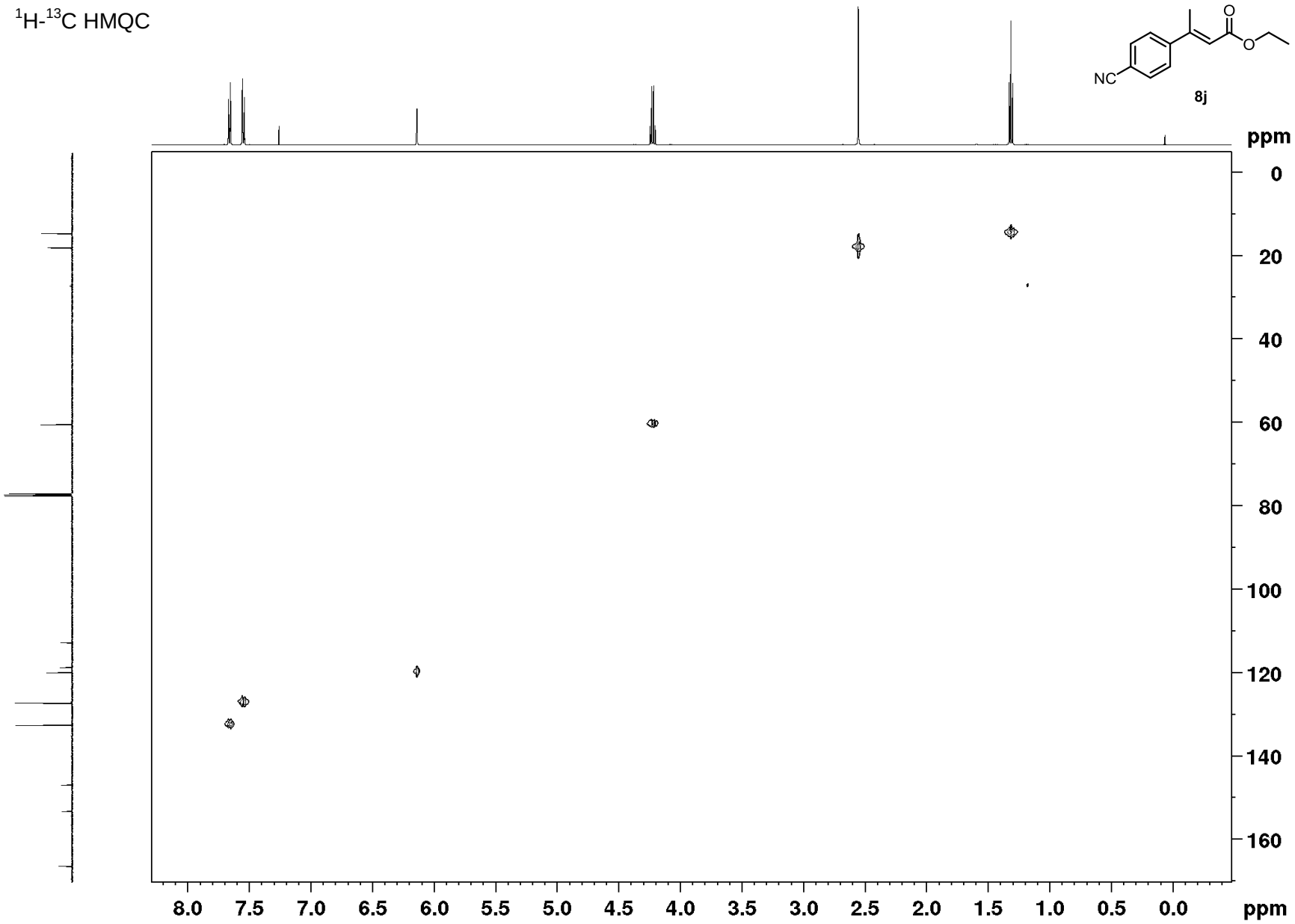
8j


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

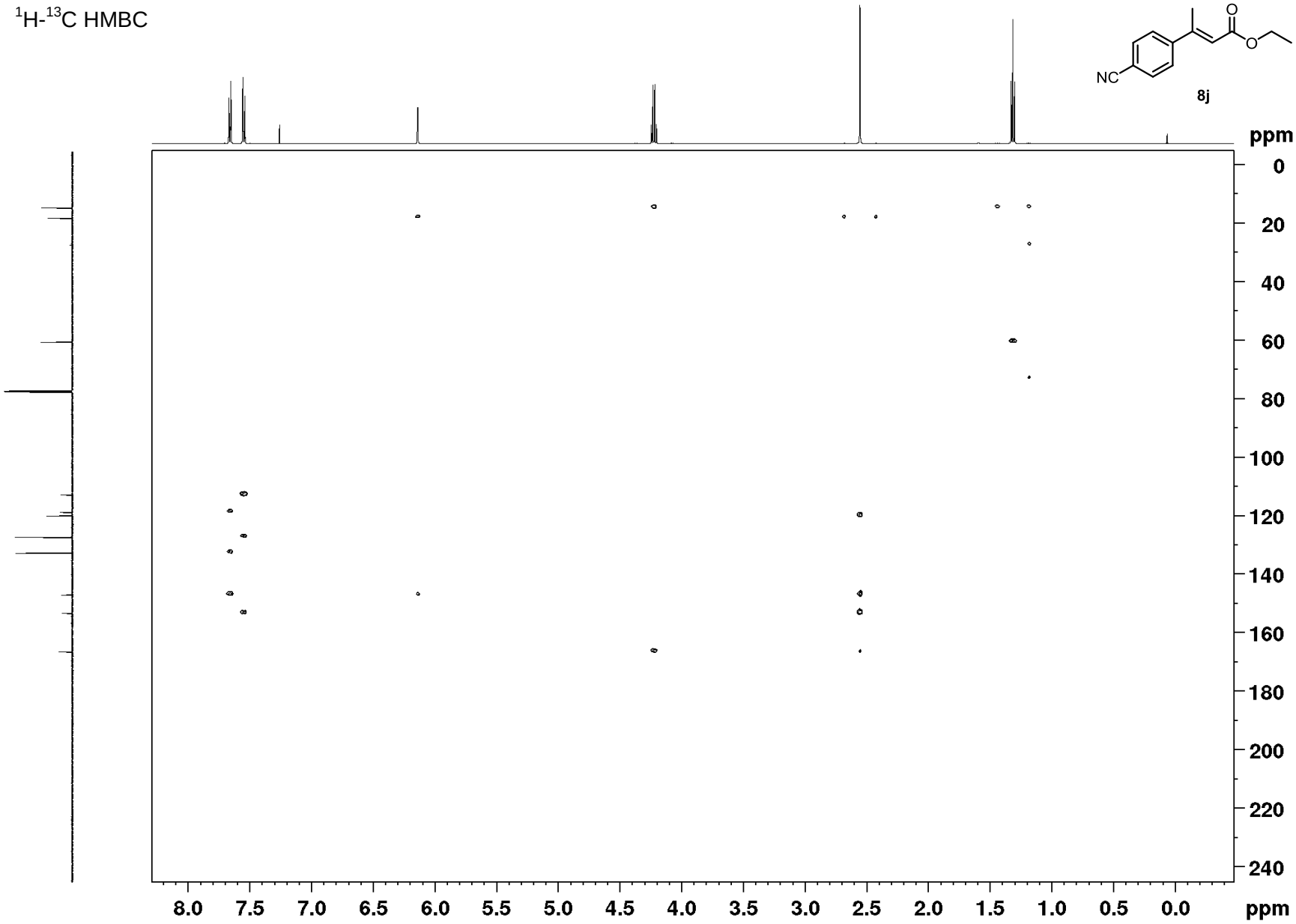
^{1}H-^{1}H COSY


NC
O
O
8j
ppm
0
1
2
3
4
5
6
7
8
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
ppm

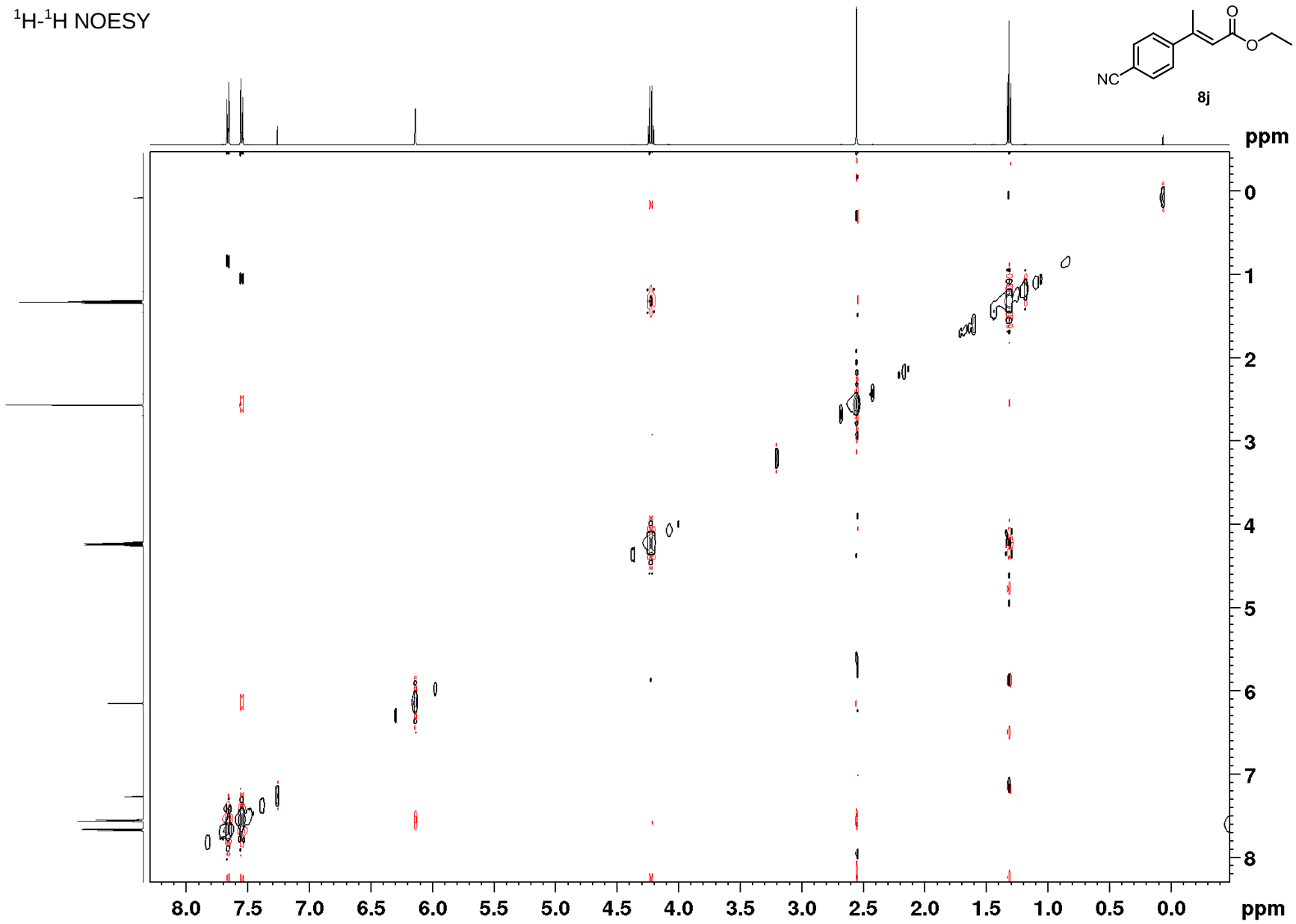
^{1}H-^{13}C HMQC

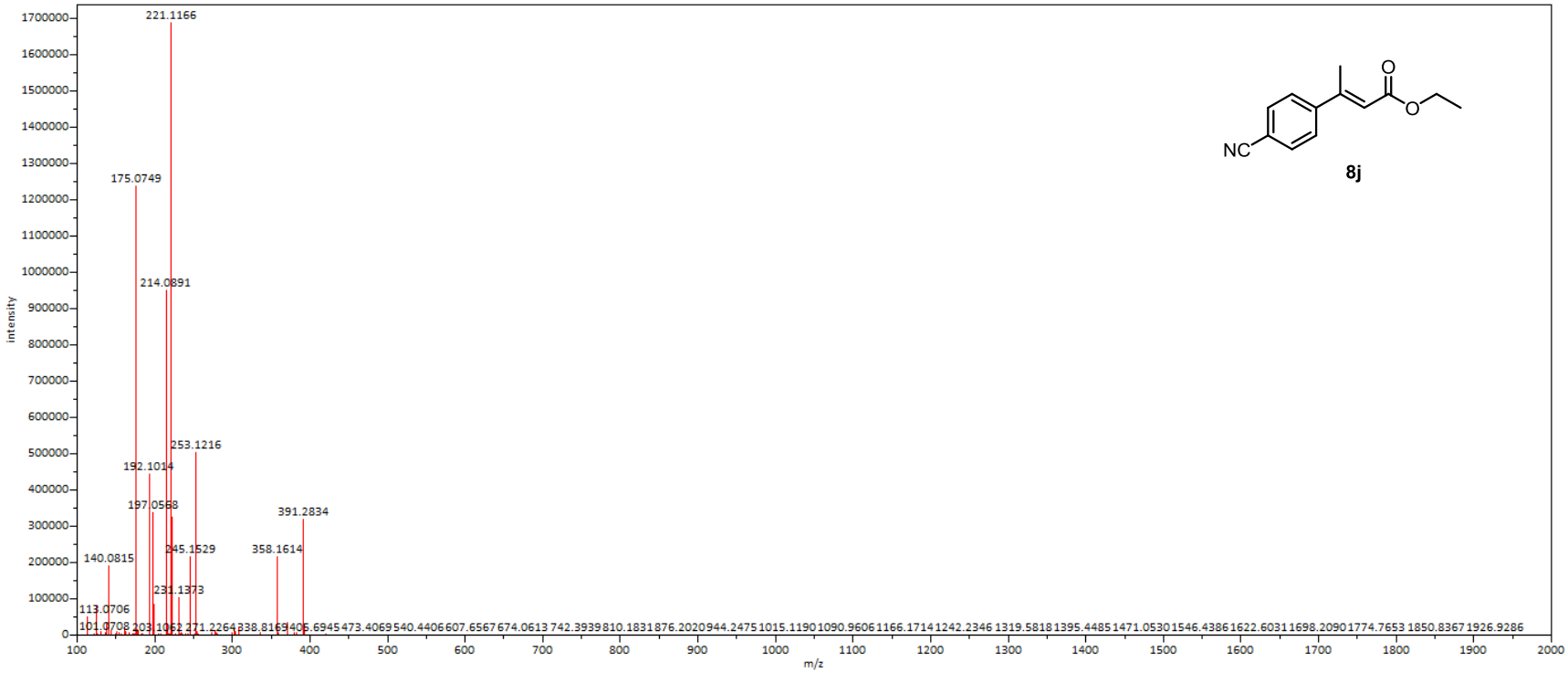

NC
O
O
8j
ppm
0
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

^{1}H-^{13}C HMBC


NC
O
O
8j
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

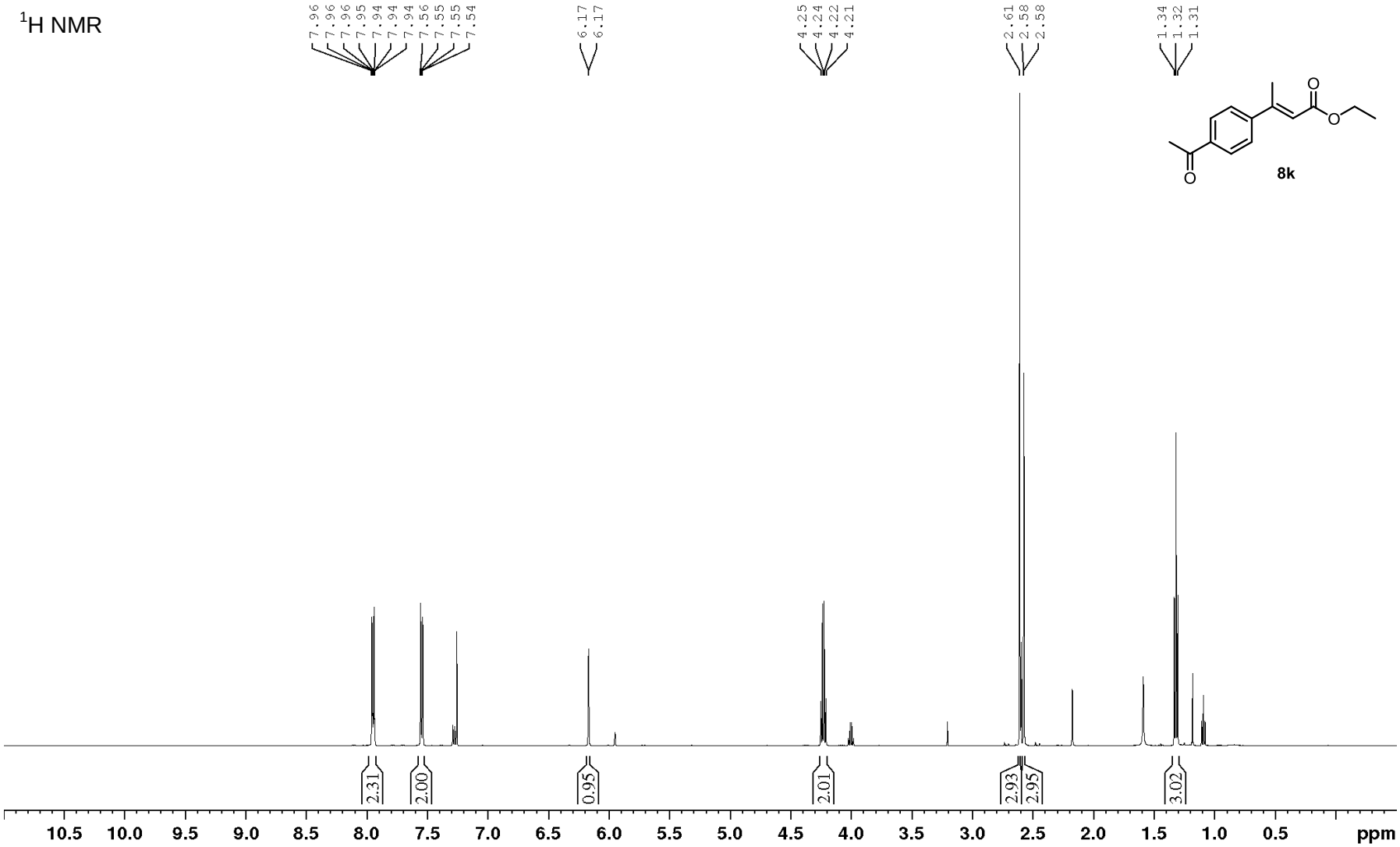
^{1}H-^{1}H NOESY

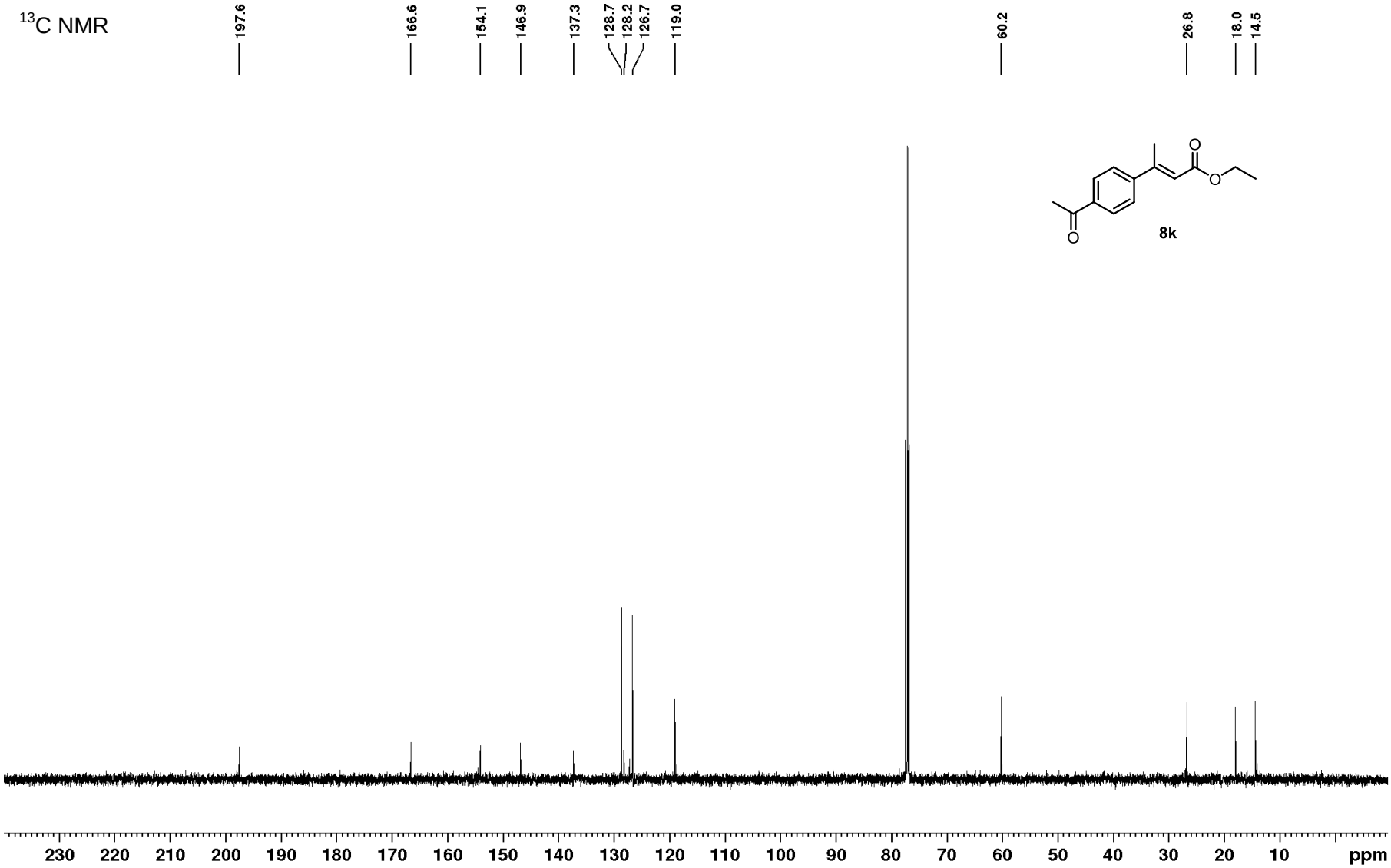

NC
O
O
8j
ppm
0
1
2
3
4
5
6
7
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

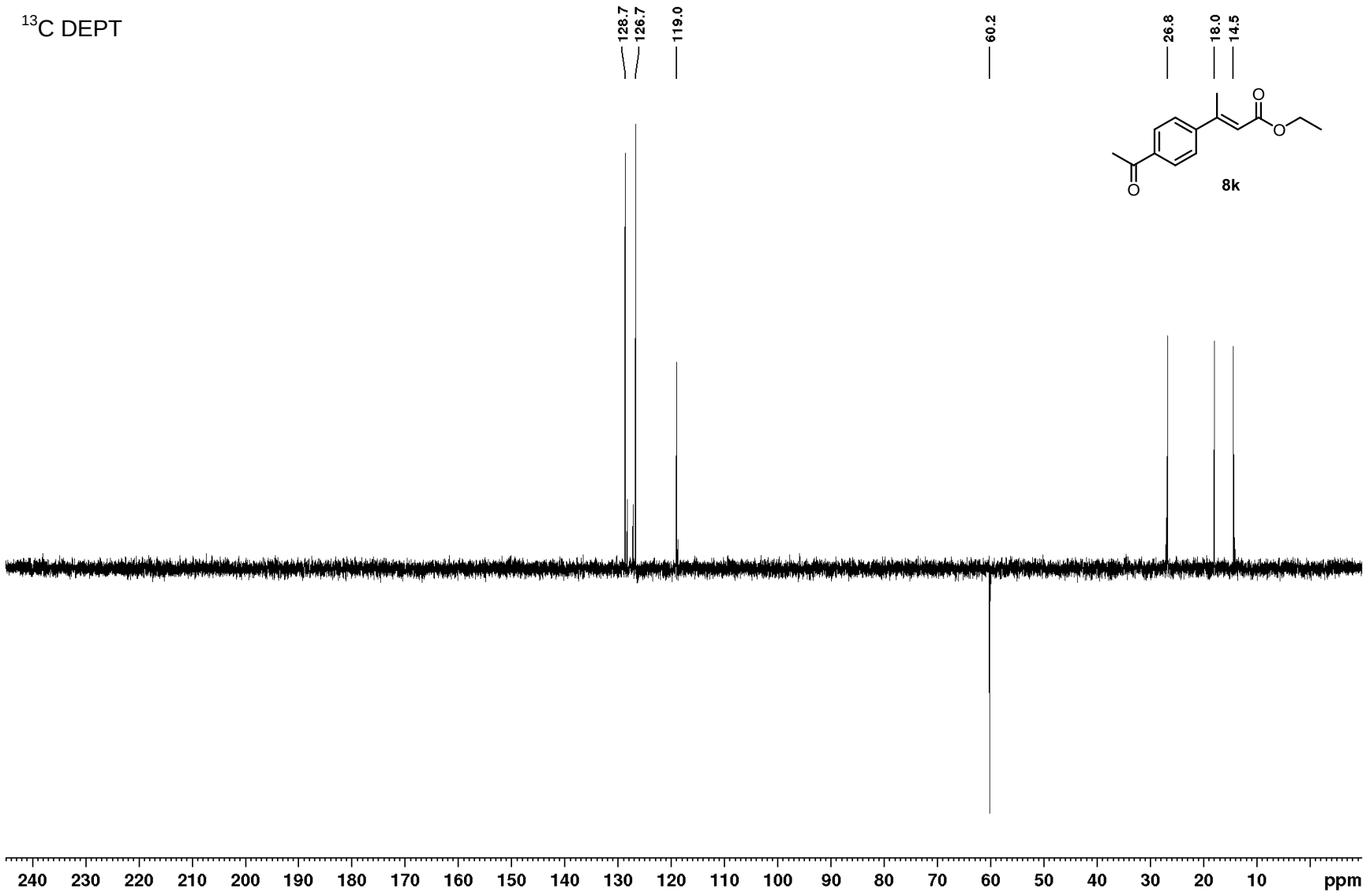

221.1166
175.0749
214.0891
253.1216
192.1014
197.0568
391.2834
140.0815
245.1529
358.1614
231.1373
113.0706
intensity
m/z
NC
O
O
8j

Ethyl (*E*)-3-(4-acetylphenyl)but-2-enoate (8k)

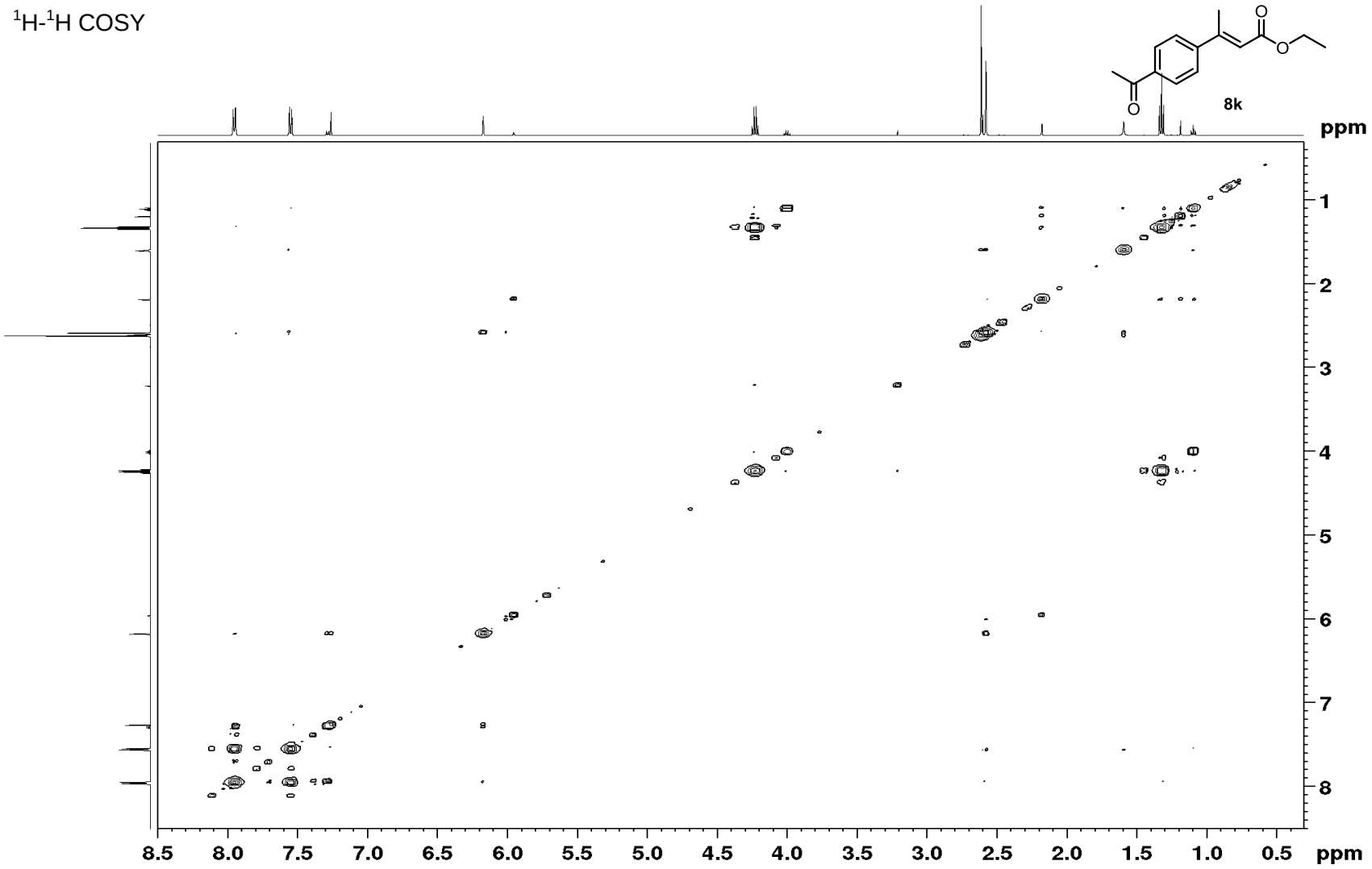
^{1}H NMR

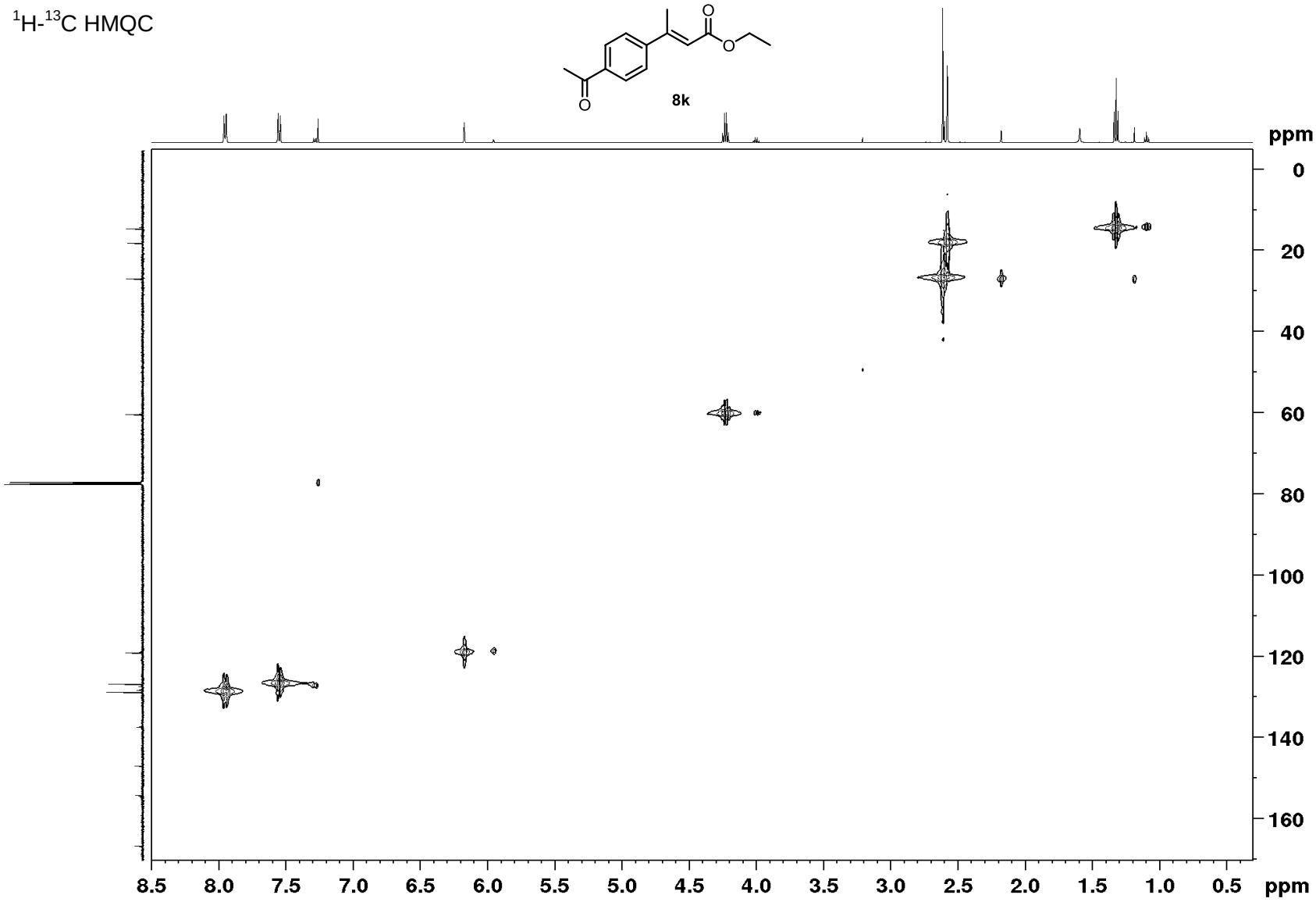



^{13}C NMR
197.6
166.6
154.1
146.9
137.3
128.7
128.2
126.7
119.0
60.2
26.8
18.0
14.5
8k
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

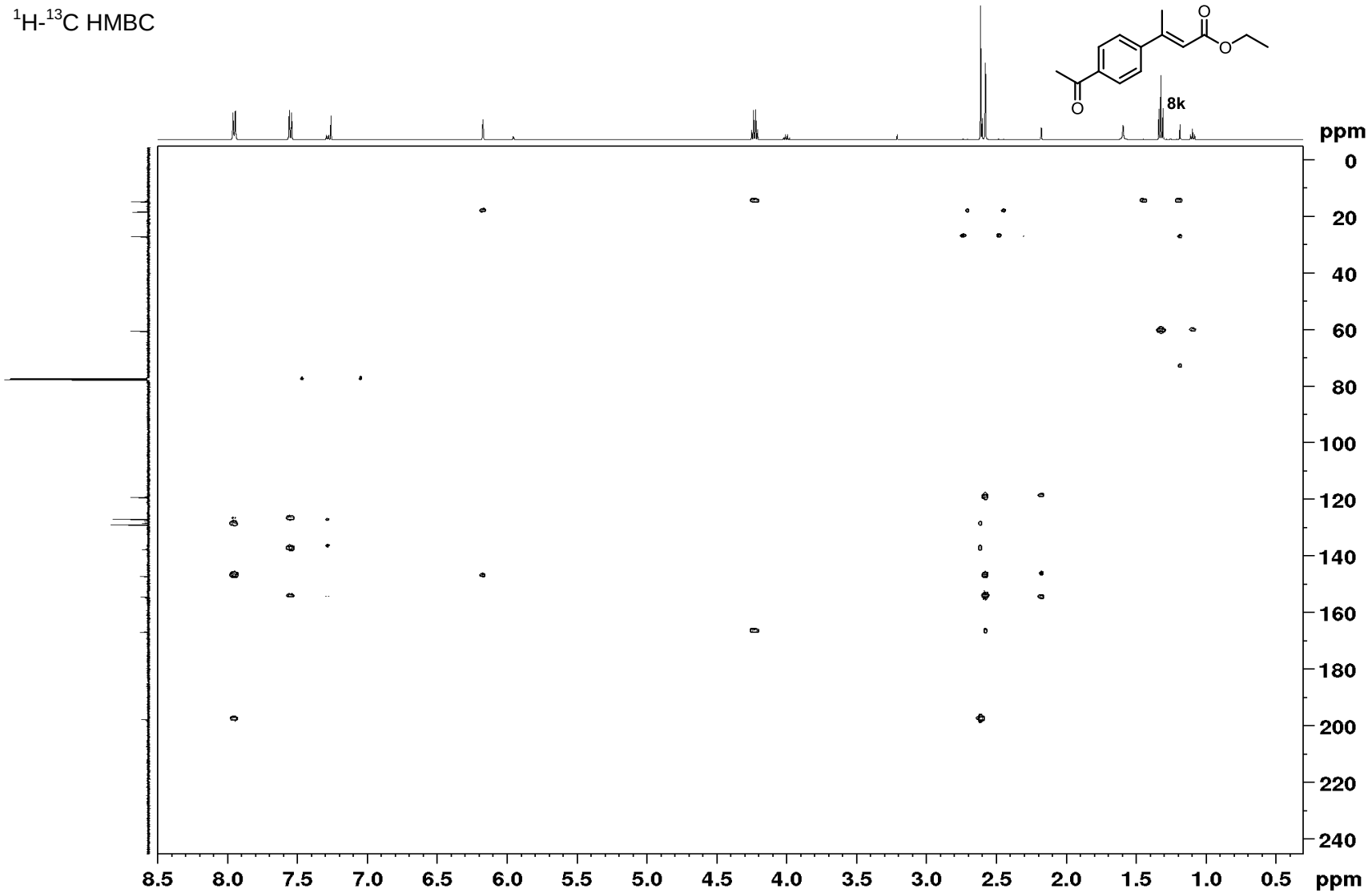

^{13}C DEPT
128.7
126.7
119.0
60.2
26.8
18.0
14.5
O
O
O
8k
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{1}H-^{1}H COSY

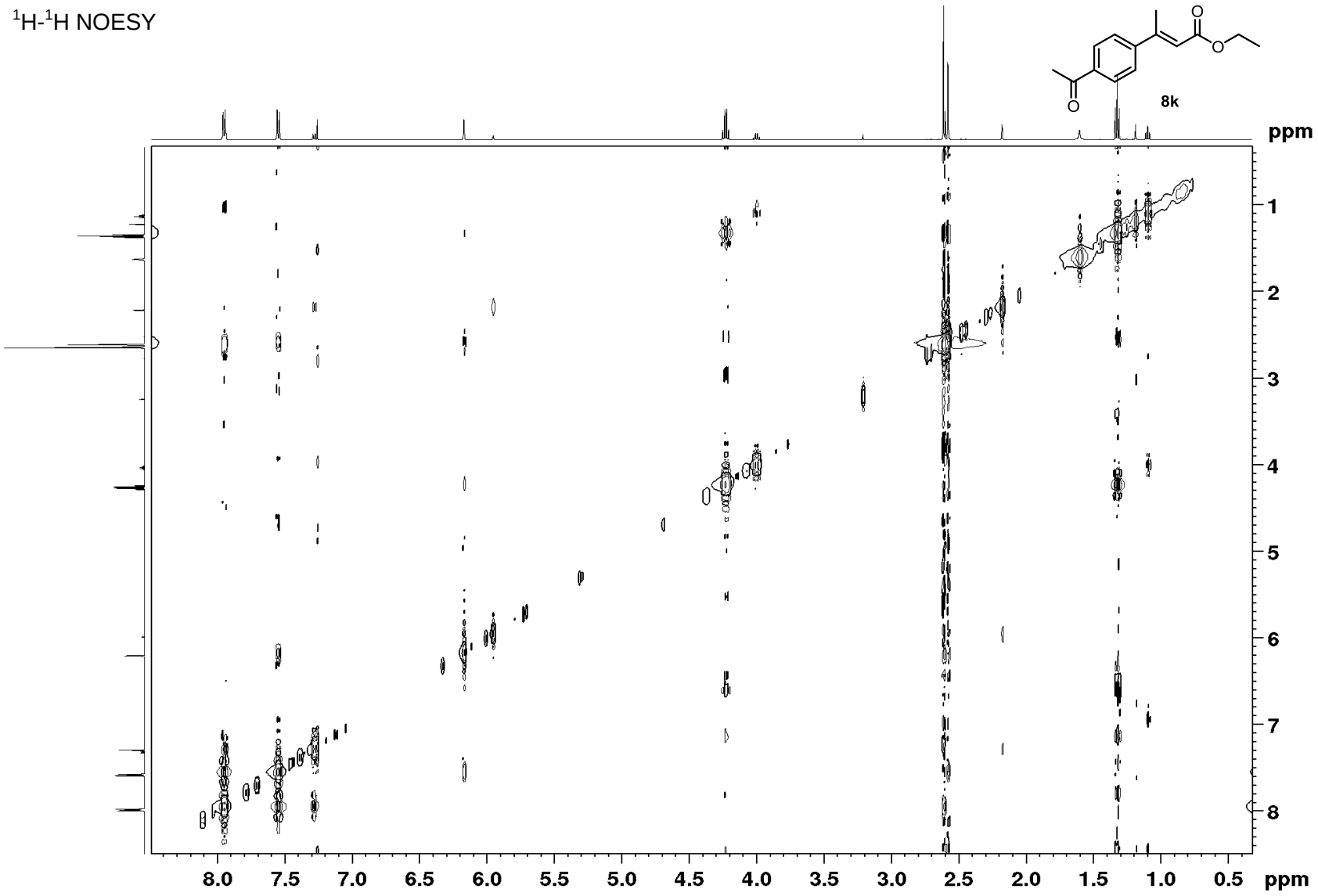

8k
ppm
1
2
3
4
5
6
7
8
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

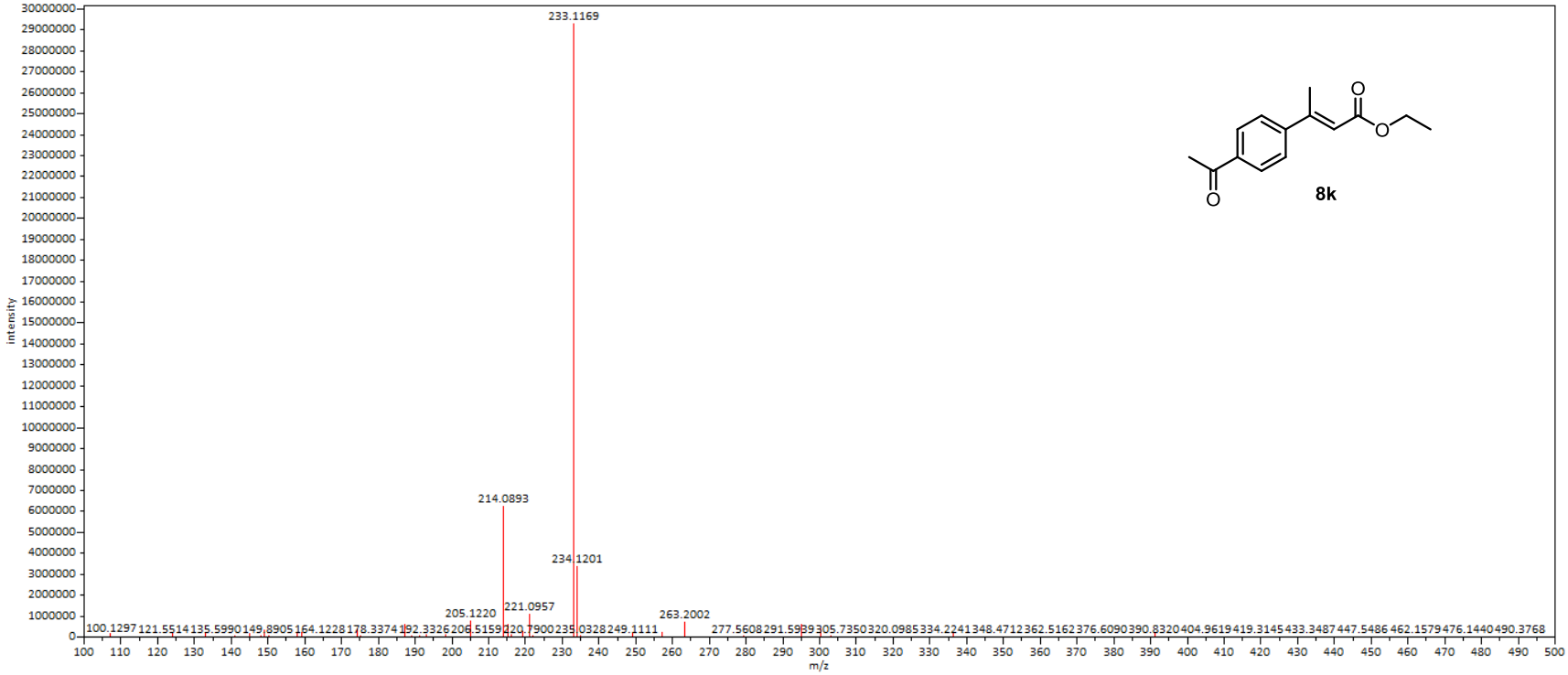

^{1}H-^{13}C HMQC
O
O
O
8k
ppm
0
20
40
60
80
100
120
140
160
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

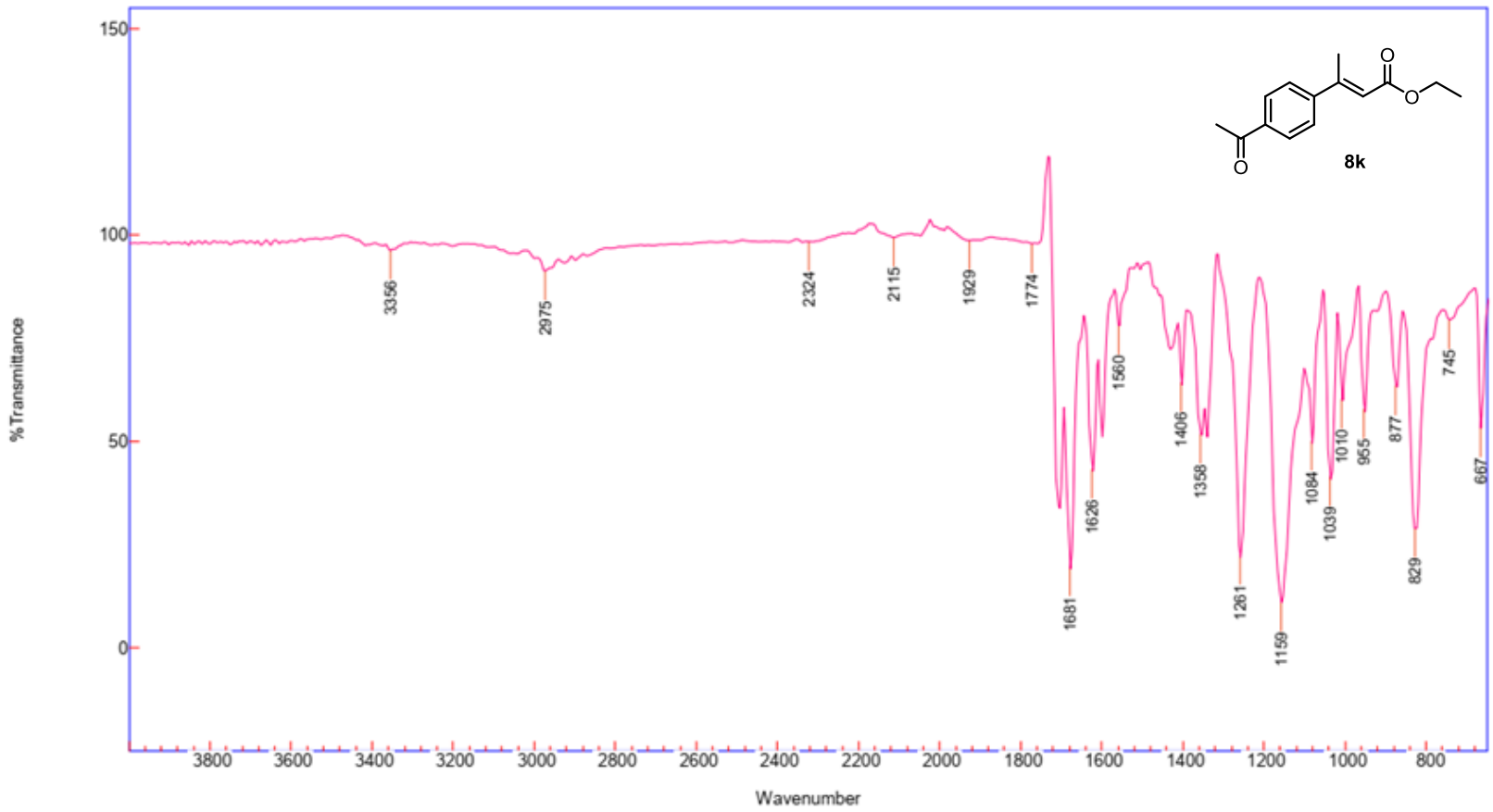
^{1}H-^{13}C HMBC


8k
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{1}H-^{1}H NOESY

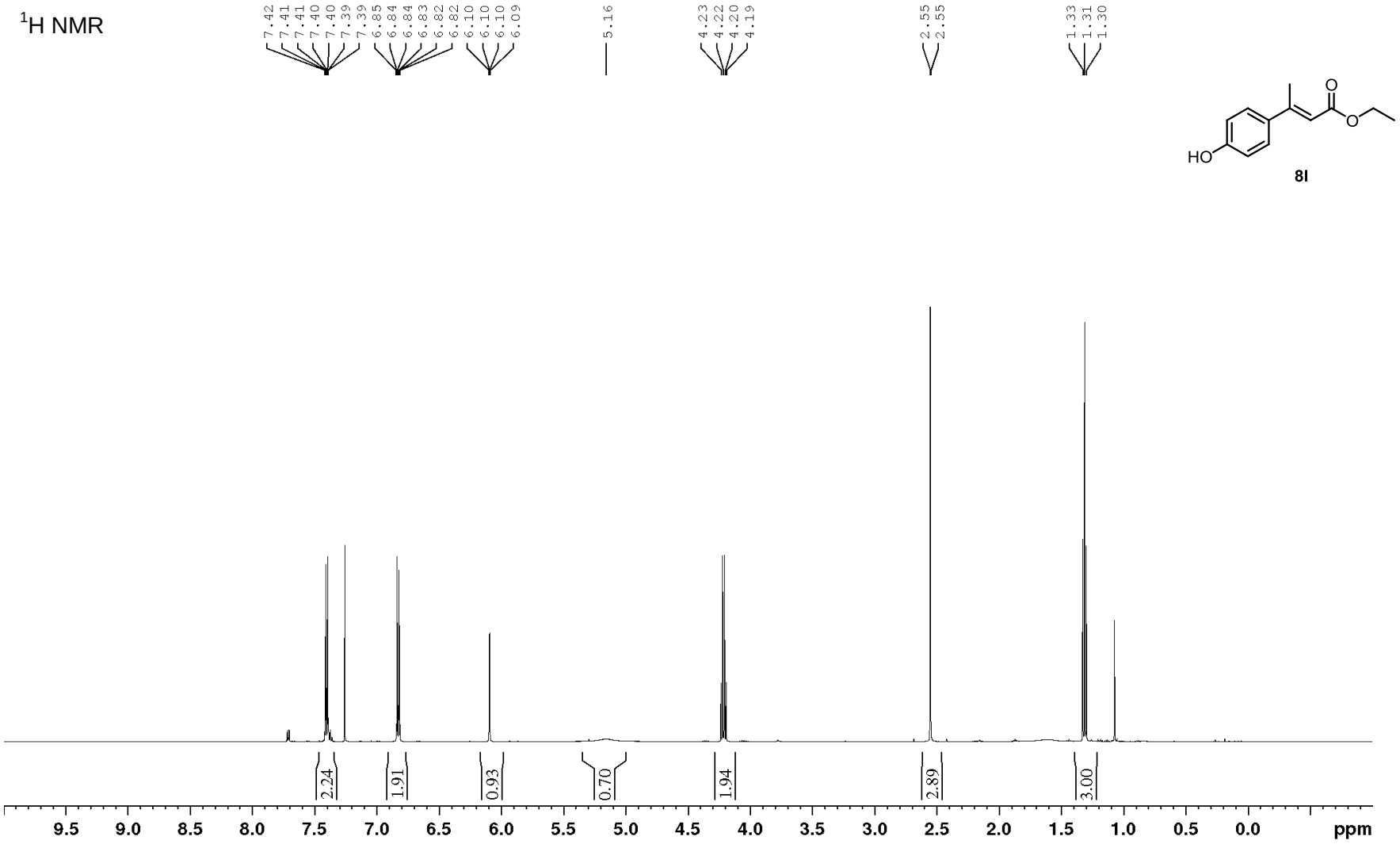


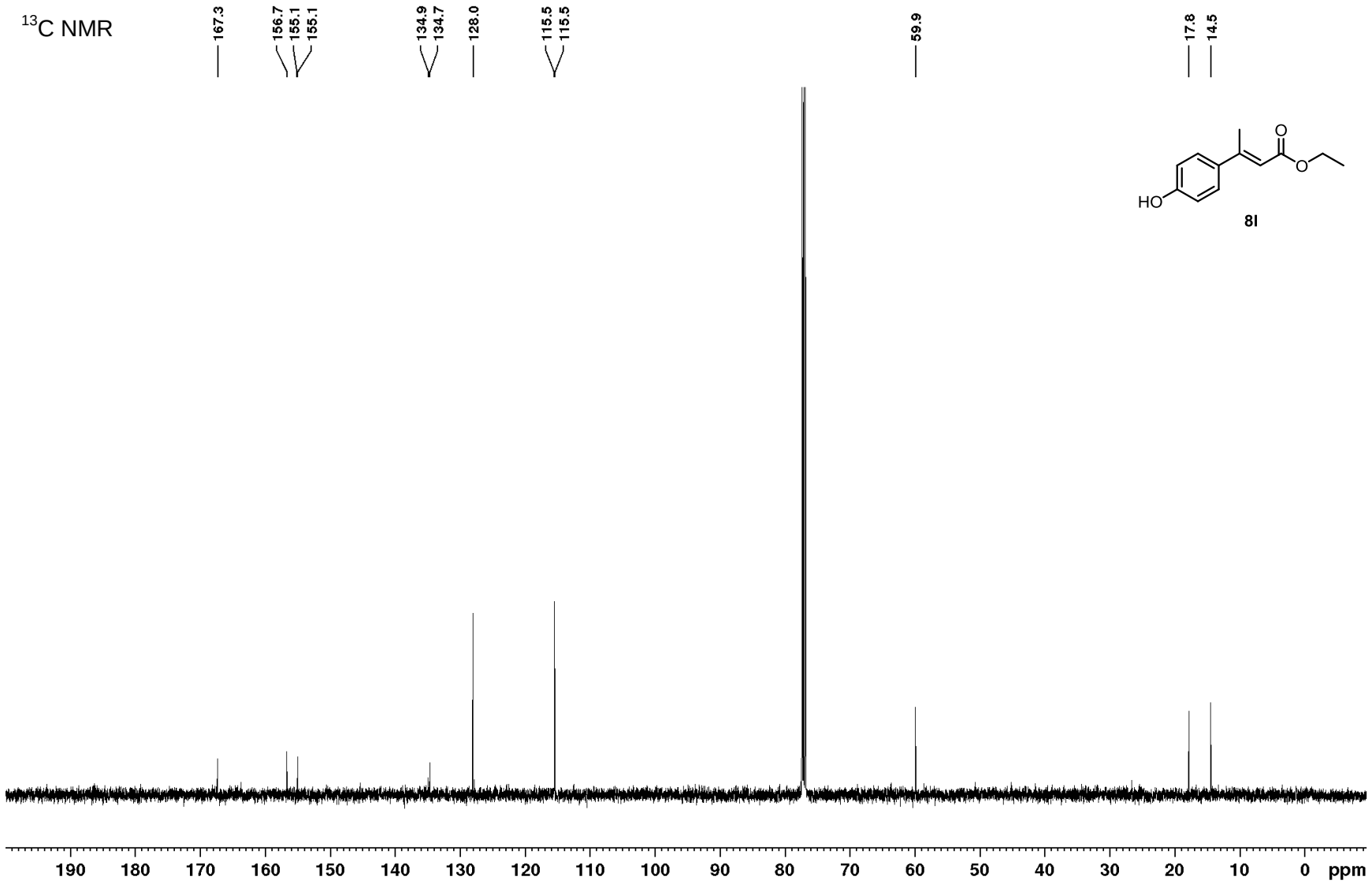

233.1169
214.0893
234.1201
221.0957
205.1220
263.2002
intensity
m/z
8k


8k
% Transmittance
Wavenumber
150
100
50
0
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
3356
2975
2324
2115
1929
1774
1681
1626
1560
1406
1358
1261
1159
1084
1039
1010
955
877
829
745
667

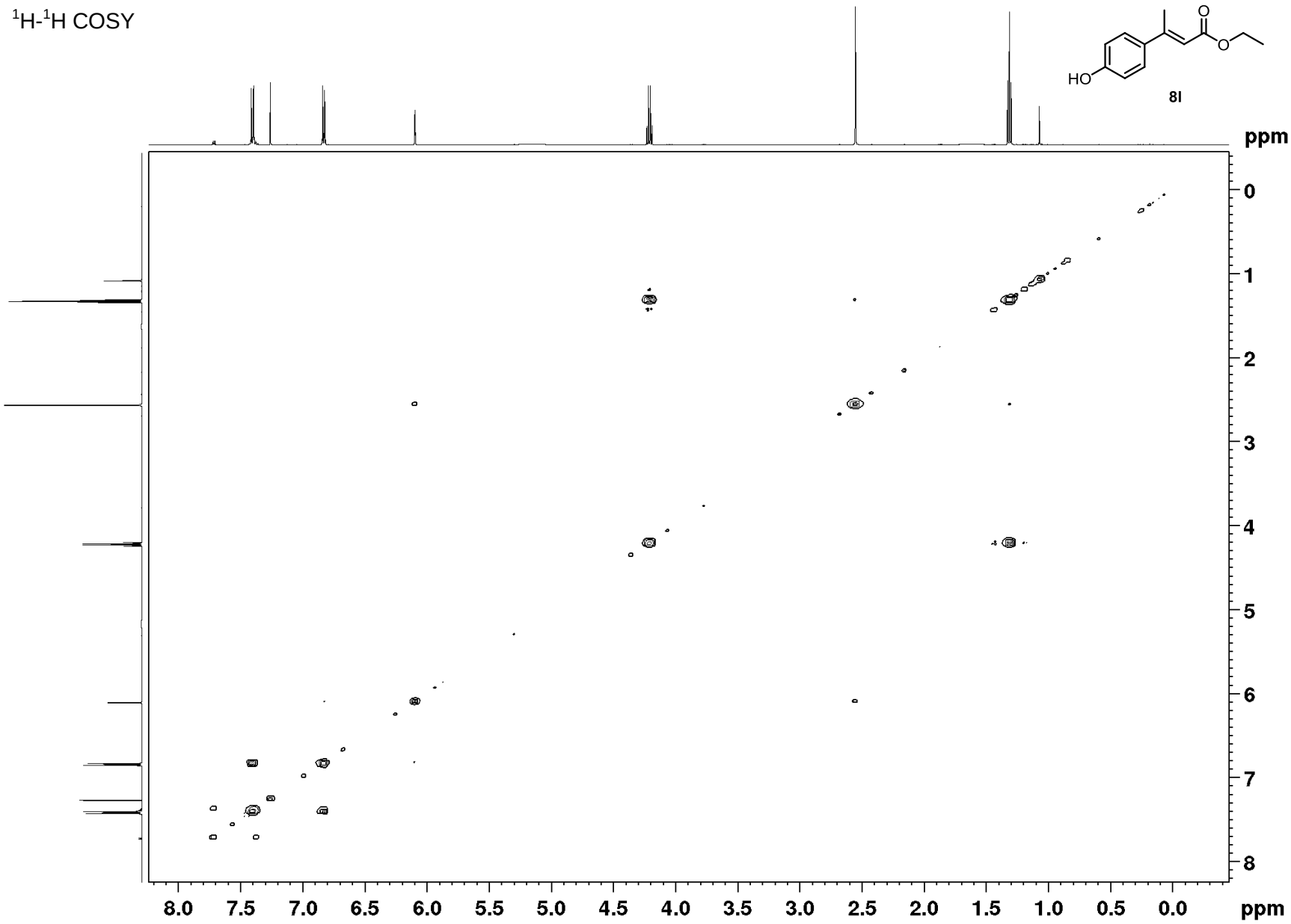
Ethyl (*E*)-3-(4-hydroxyphenyl)but-2-enoate (8l)

^{1}H NMR

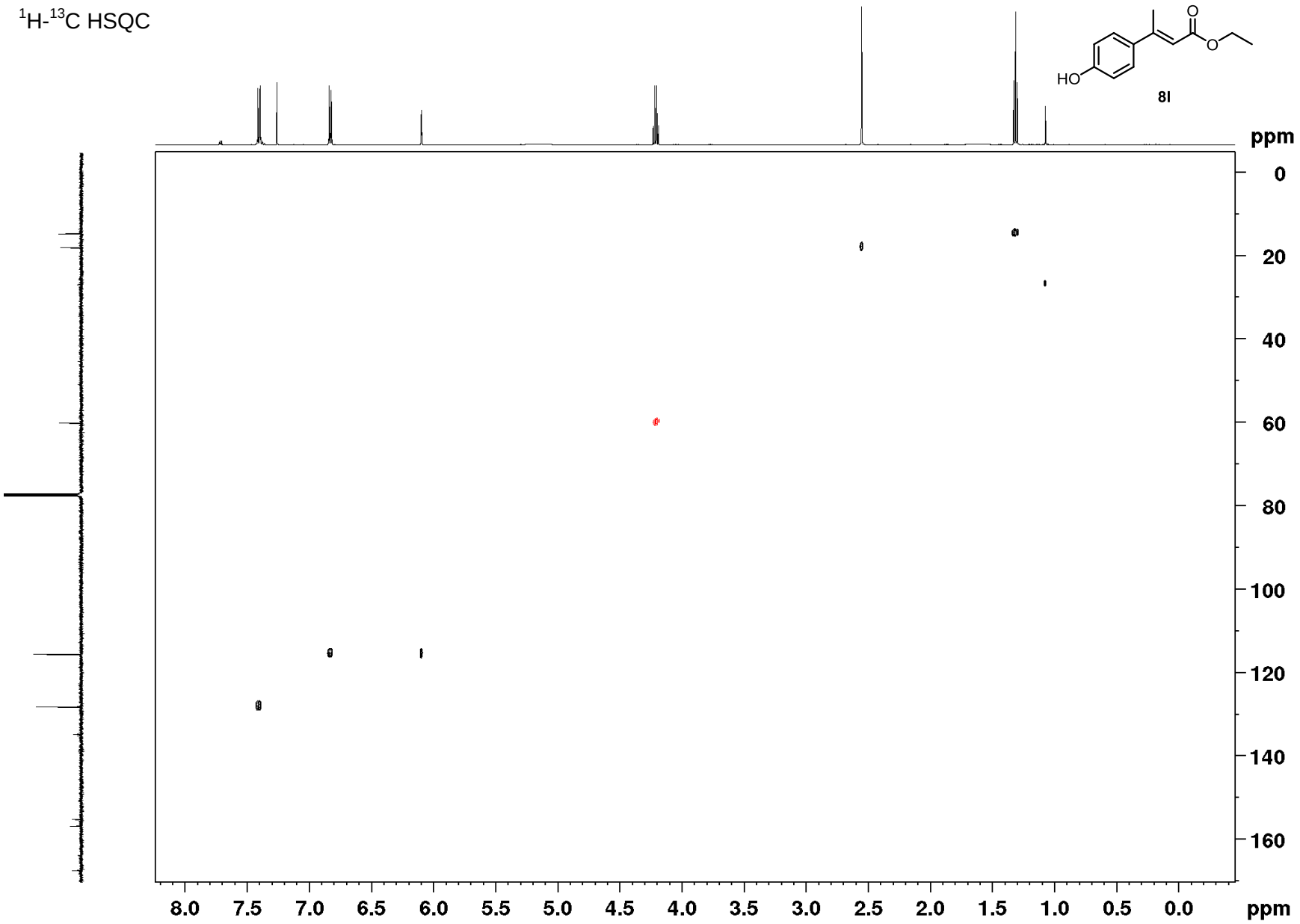



13C NMR
167.3
156.7
155.1
155.1
134.9
134.7
128.0
115.5
115.5
59.9
17.8
14.5
HO
O
O
8l
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

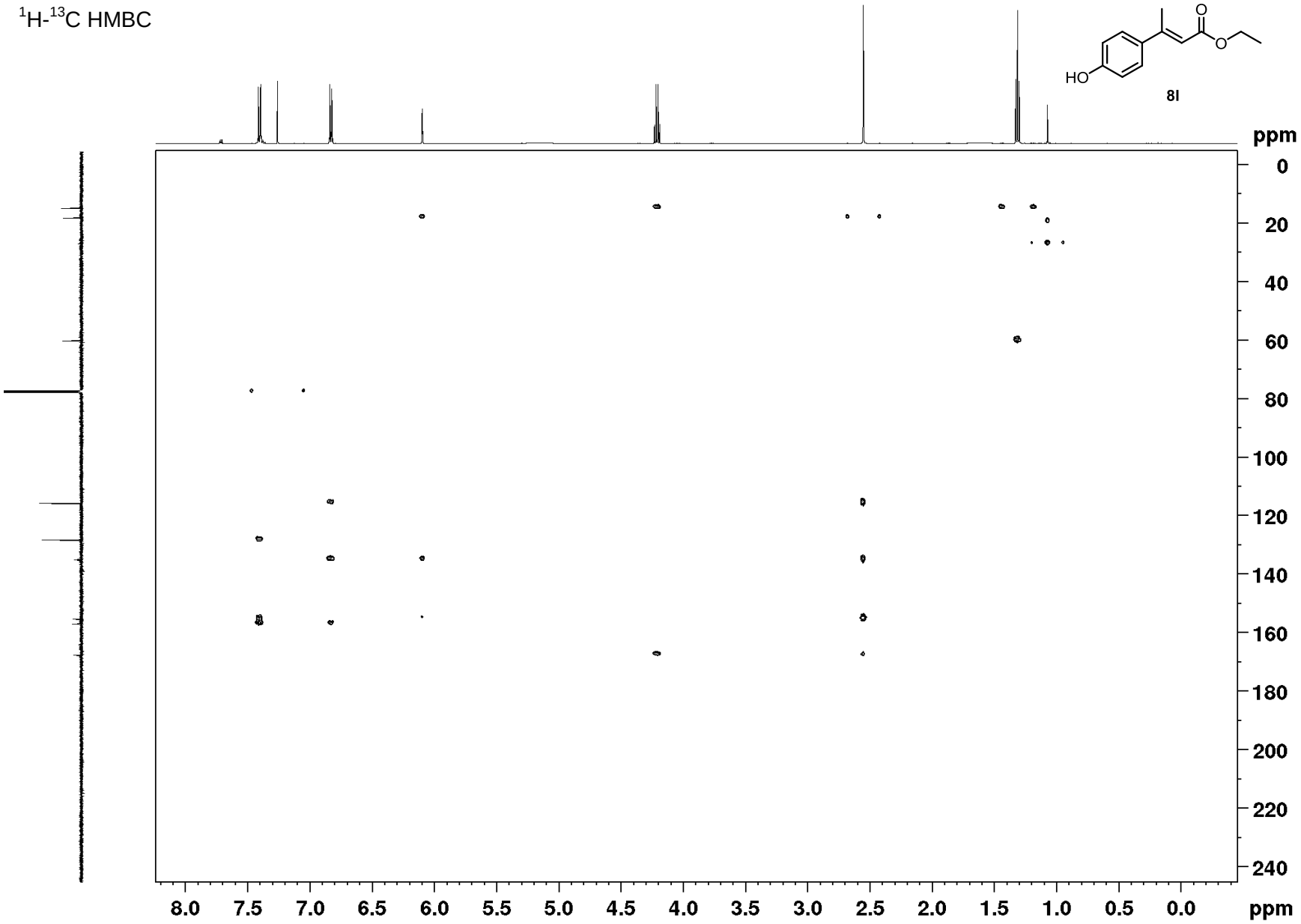
^{1}H-^{1}H COSY


HO
O
O
8l
ppm
0
1
2
3
4
5
6
7
8
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
ppm

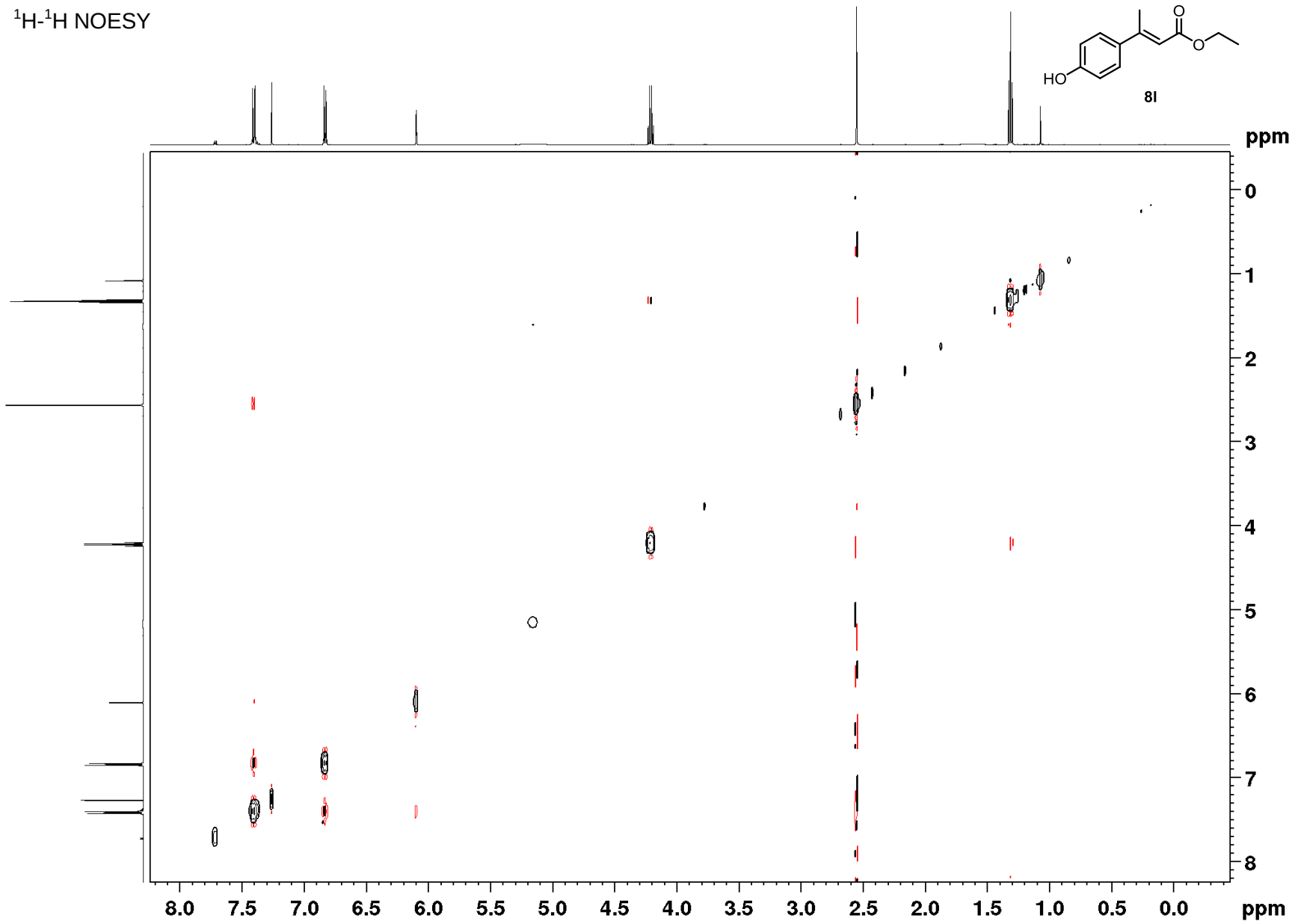
^{1}H-^{13}C HSQC


HO
O
O
8l
ppm
0
20
40
60
80
100
120
140
160
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
ppm

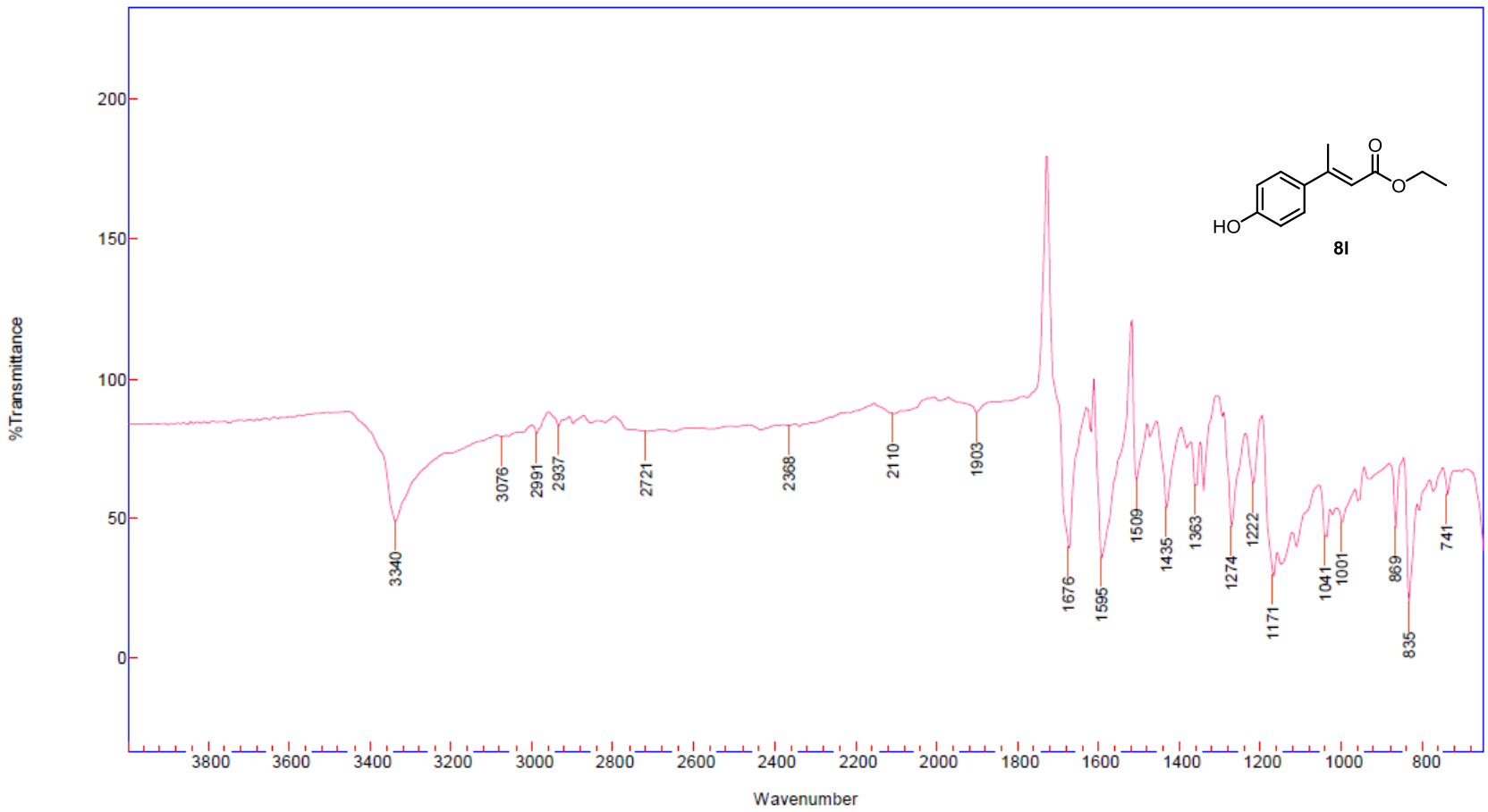
^{1}H-^{13}C HMBC


HO
O
O
8l
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

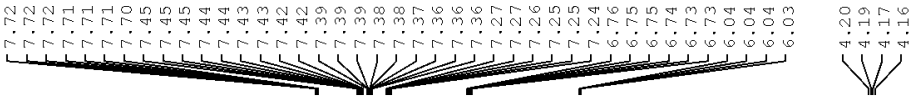
^{1}H-^{1}H NOESY

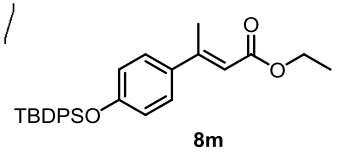

HO
O
O
8l
ppm
0
1
2
3
4
5
6
7
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


207.1011
102.0911
161.0593
214.0892
208.1043
107.0602
236.1641
162.0626
149.0820
intensity
m/z
HO
O
O
8l


%Transmittance
200
150
100
50
0
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber
3340
3076
2991
2937
2721
2368
2110
1903
1676
1595
1509
1435
1363
1274
1222
1171
1041
1001
869
835
741
HO
O
O
8l

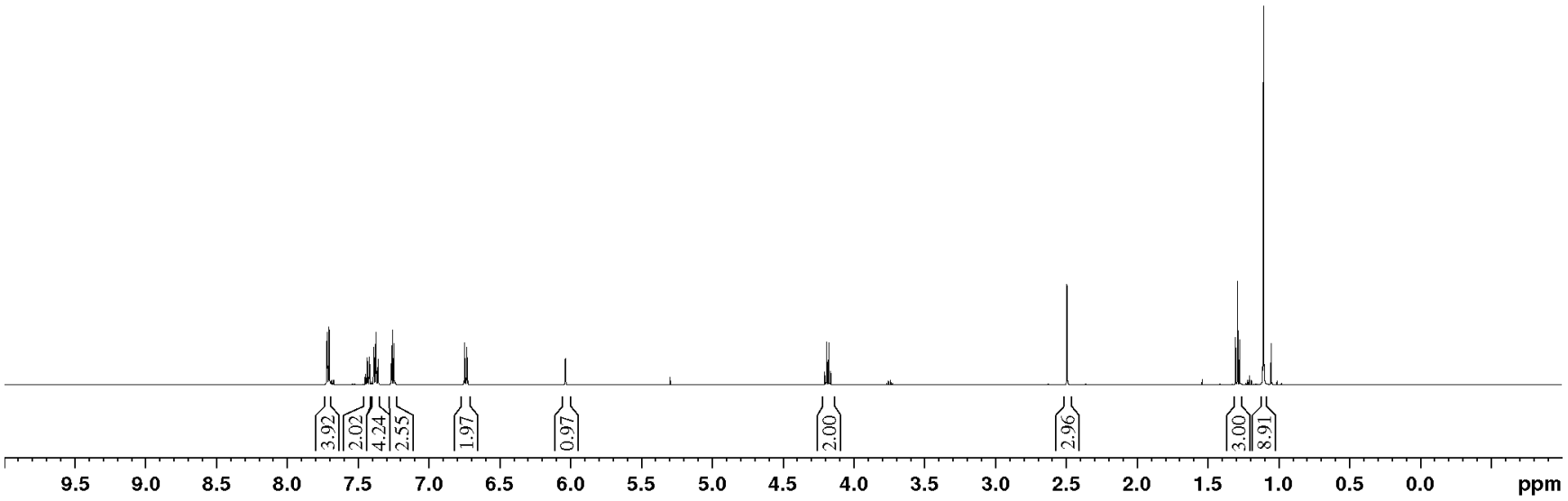
Ethyl (*E*)-3-(4-((tert-butyldiphenylsilyl)oxy)phenyl)but-2-enoate (8m)



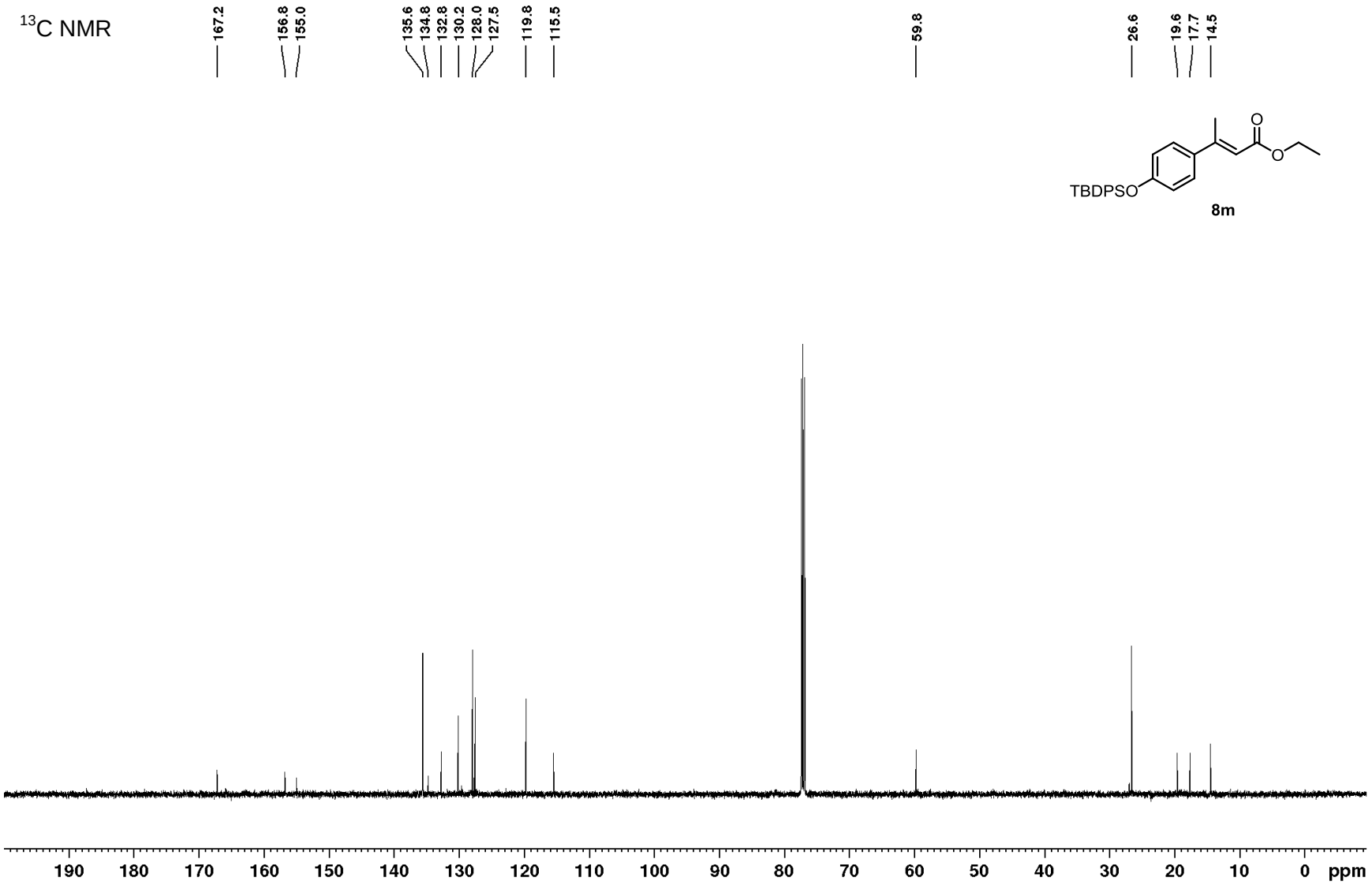


8m

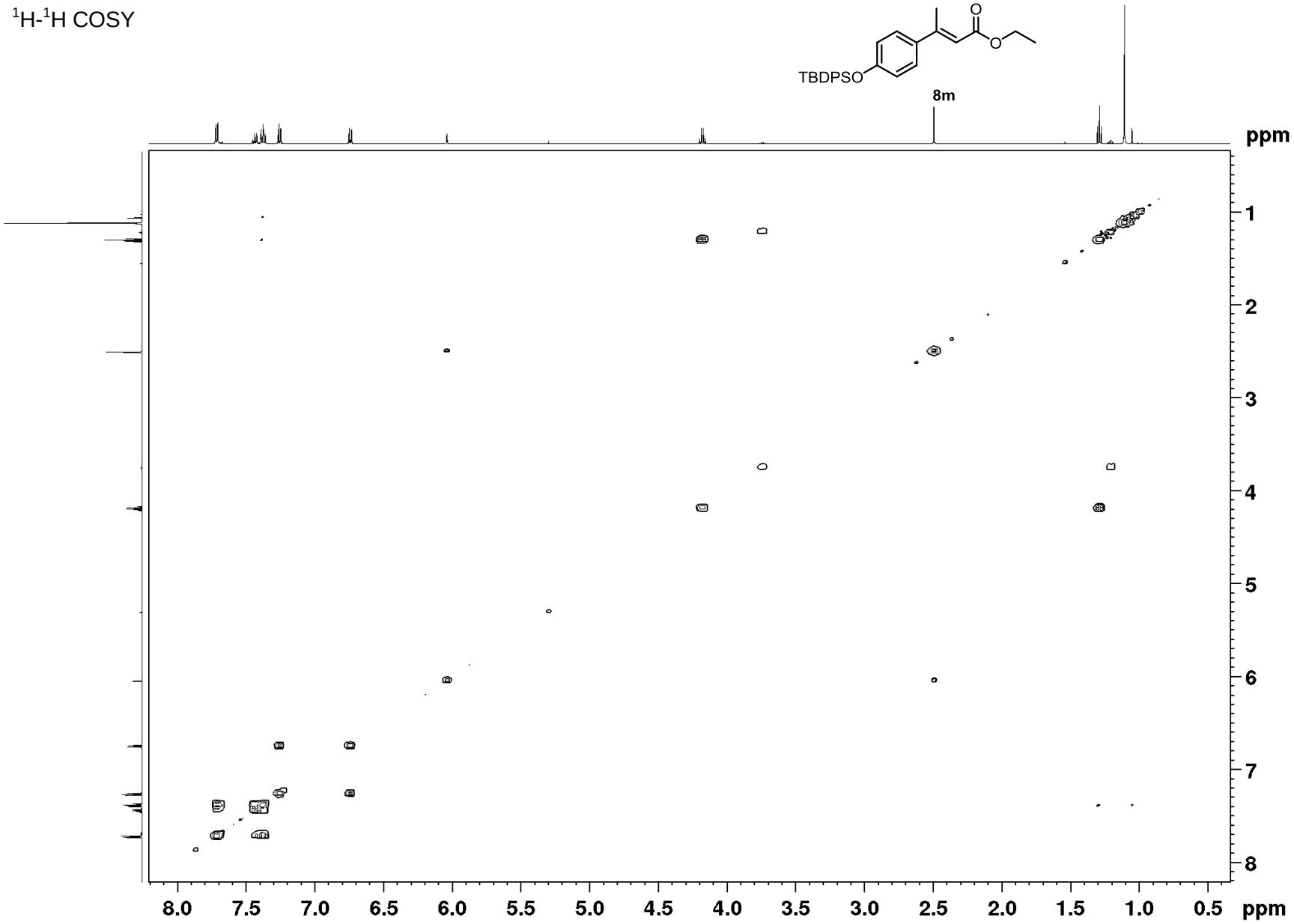
^{1}H NMR



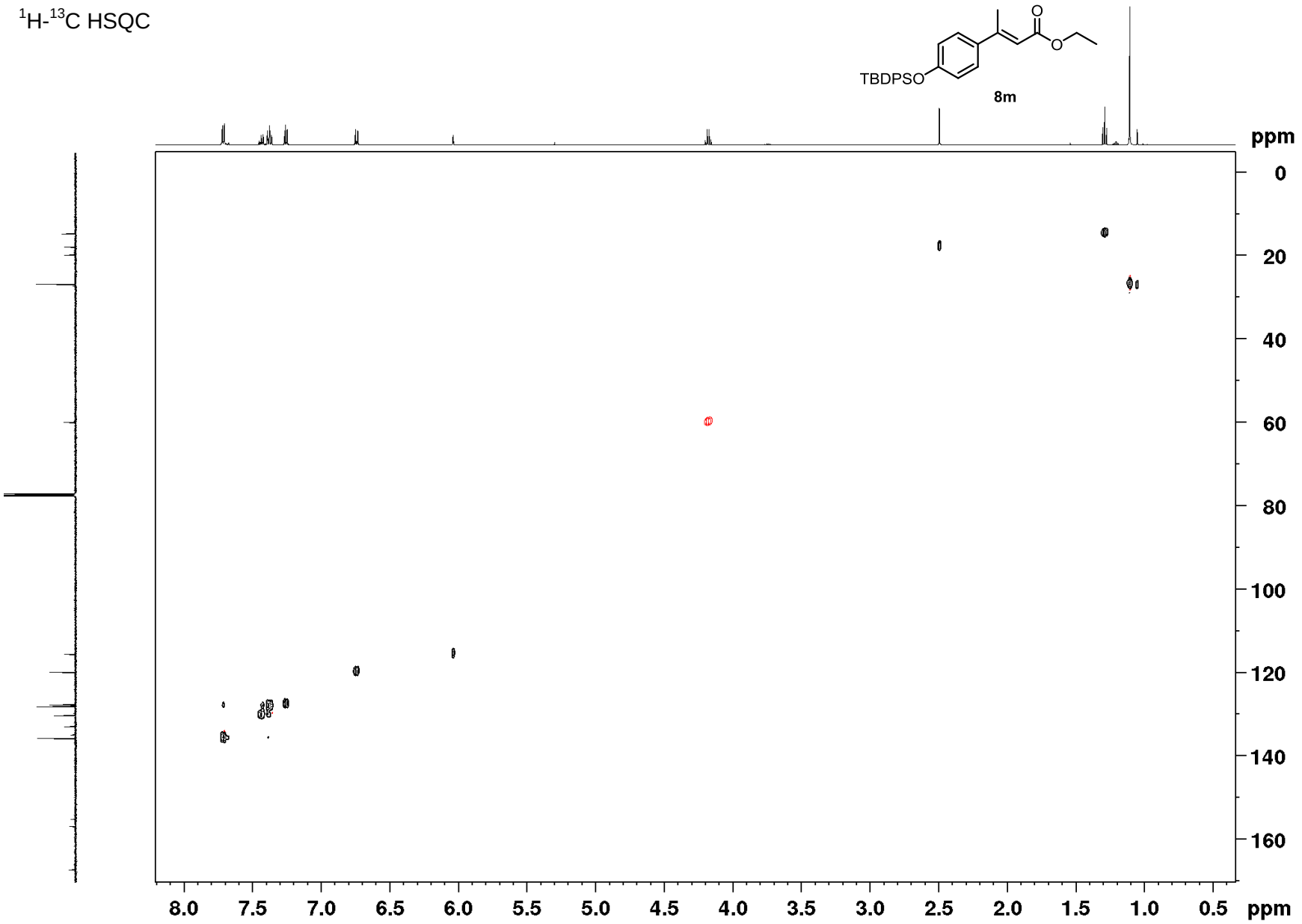
^{13}C NMR


167.2
156.8
155.0
135.6
134.8
132.8
130.2
128.0
127.5
119.8
115.5
59.8
26.6
19.6
17.7
14.5
TBDPSO
O
O
8m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

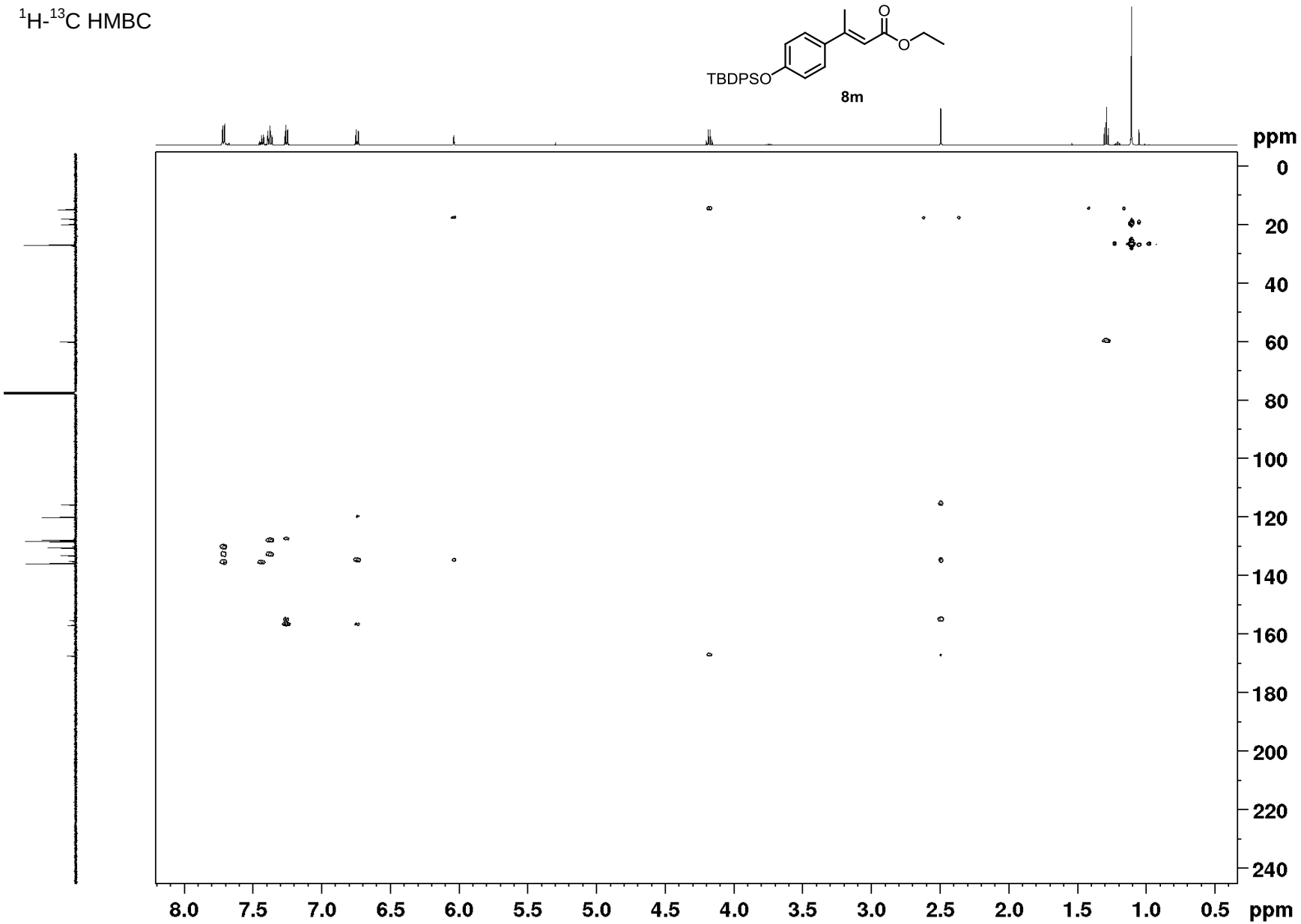
^{1}H-^{1}H COSY


TBDPSO
O
O
8m
ppm
1
2
3
4
5
6
7
8
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
ppm

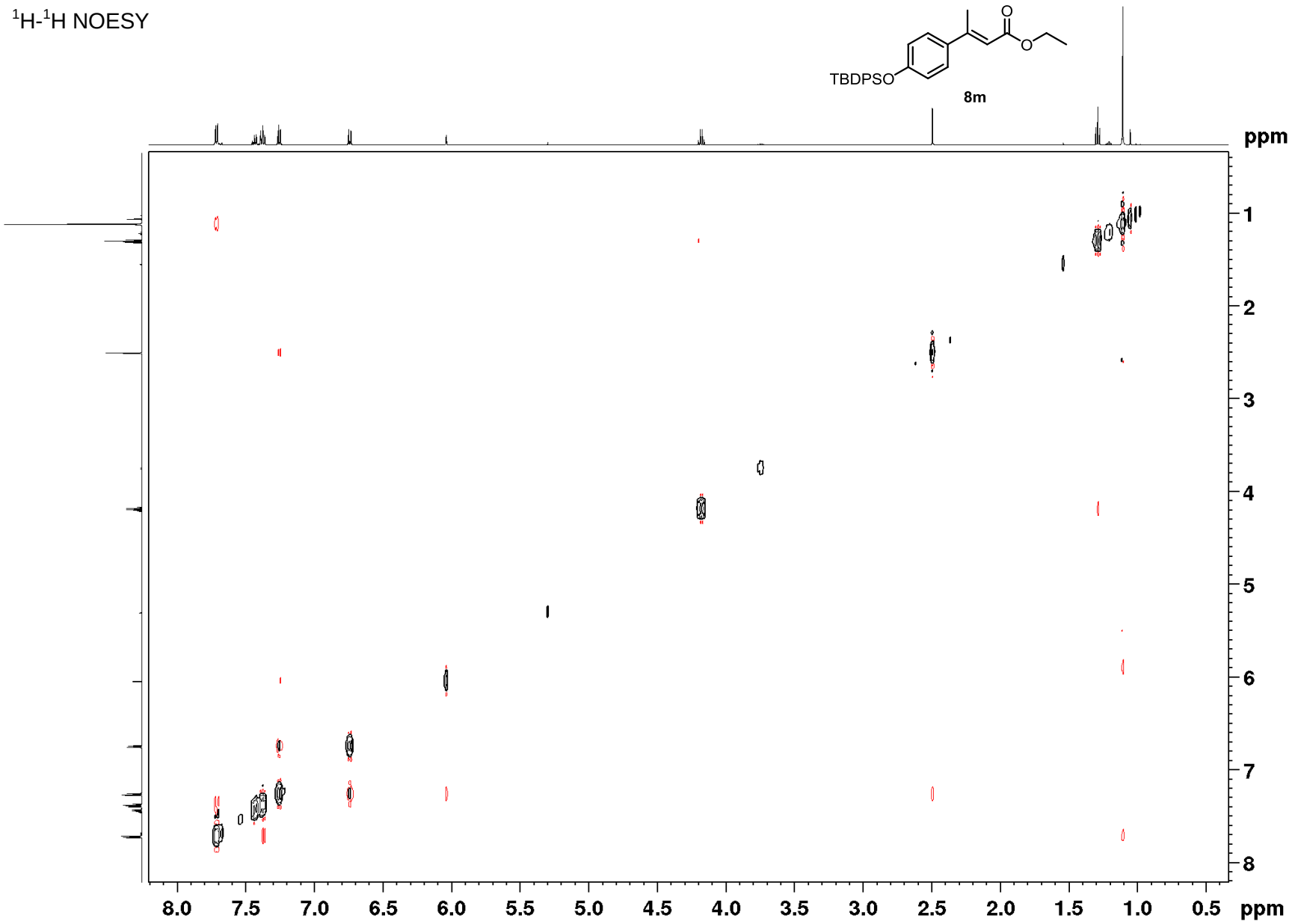
^{1}H-^{13}C HSQC


TBDPSO
O
O
8m
ppm
0
20
40
60
80
100
120
140
160
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
ppm

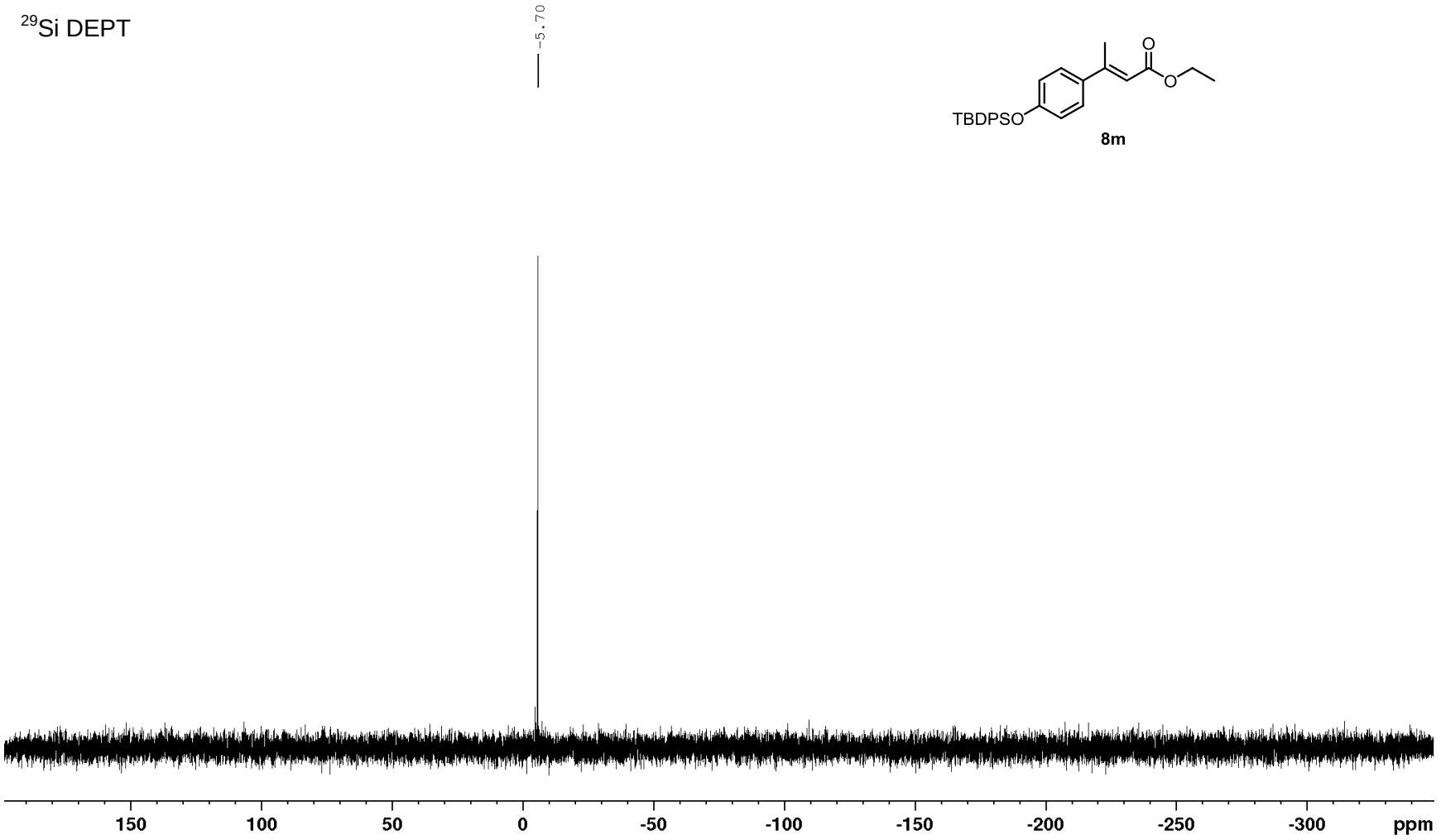
^{1}H-^{13}C HMBC

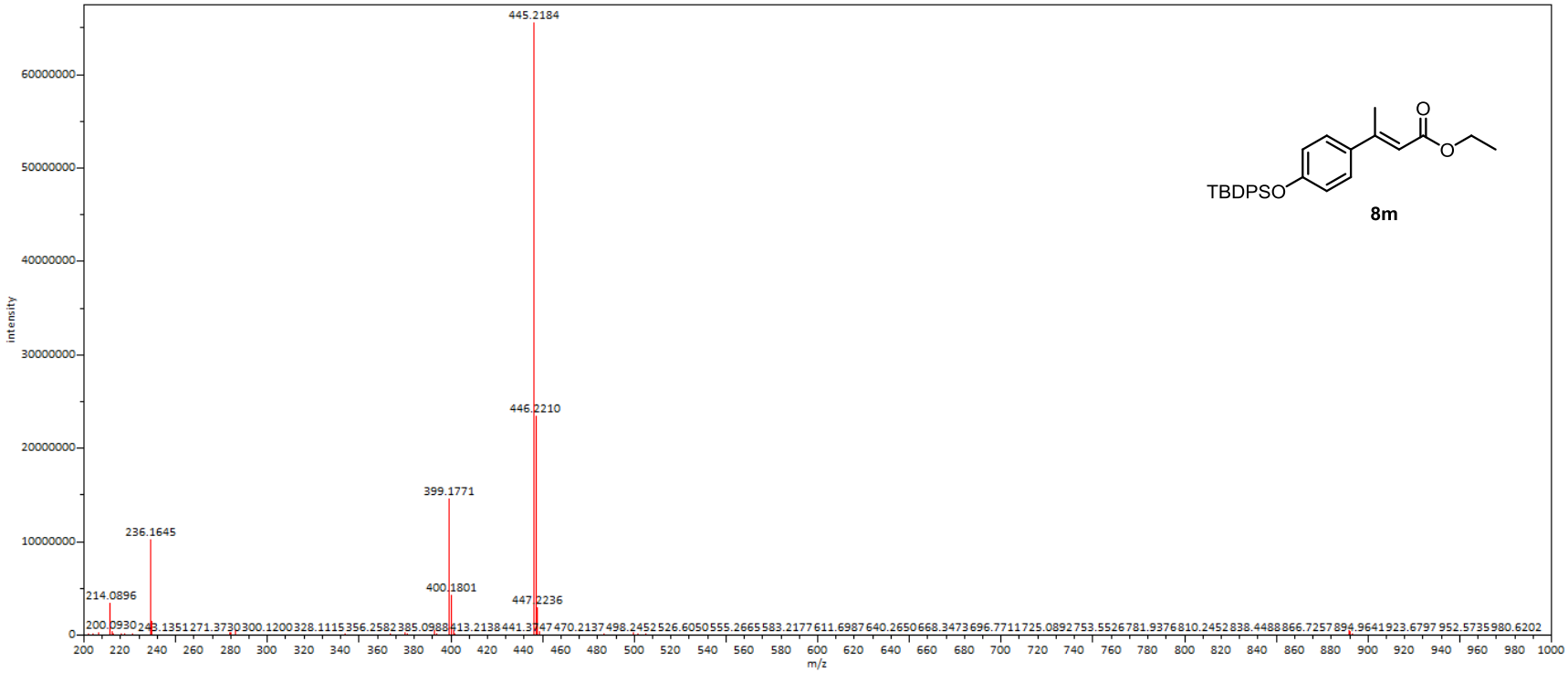

TBDPSO
O
O
8m
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

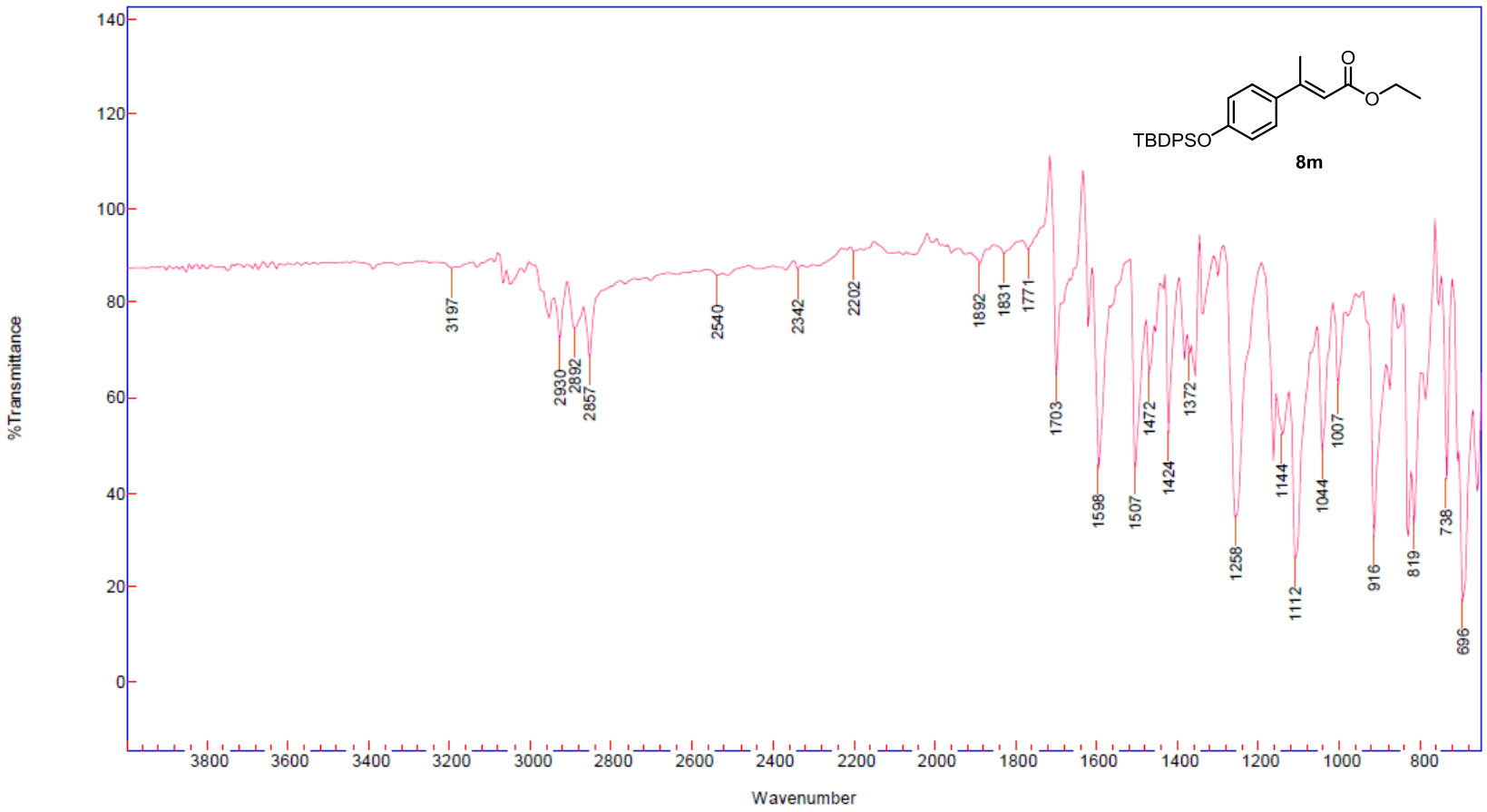
^{1}H-^{1}H NOESY


TBDPSO
O
O
8m
ppm
1
2
3
4
5
6
7
8
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
ppm

^{29}Si DEPT

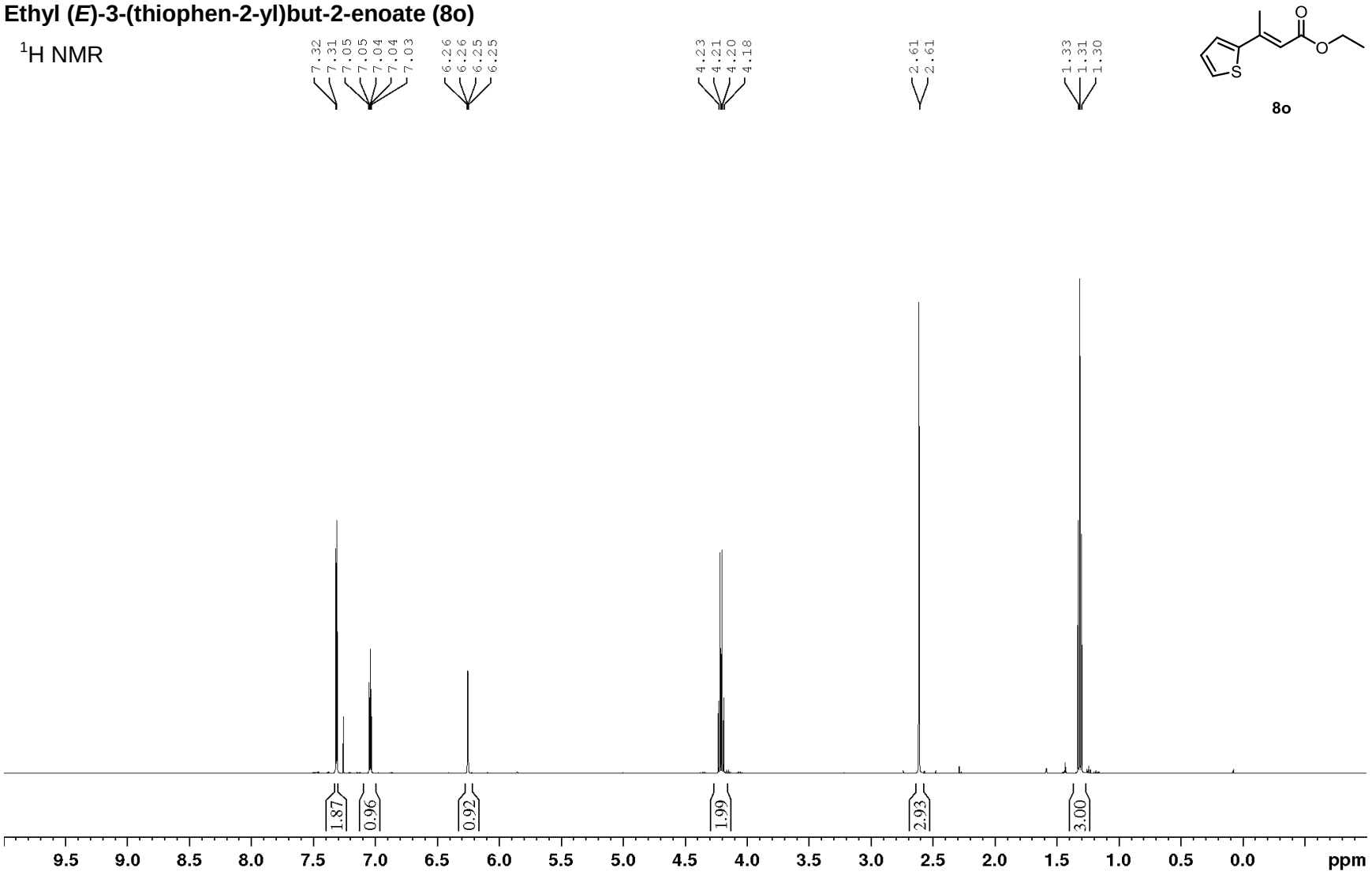



445.2184
446.2210
399.1771
236.1645
214.0896
400.1801
447.2236
200.0930
intensity
m/z
TBDPSO
O
O
8m

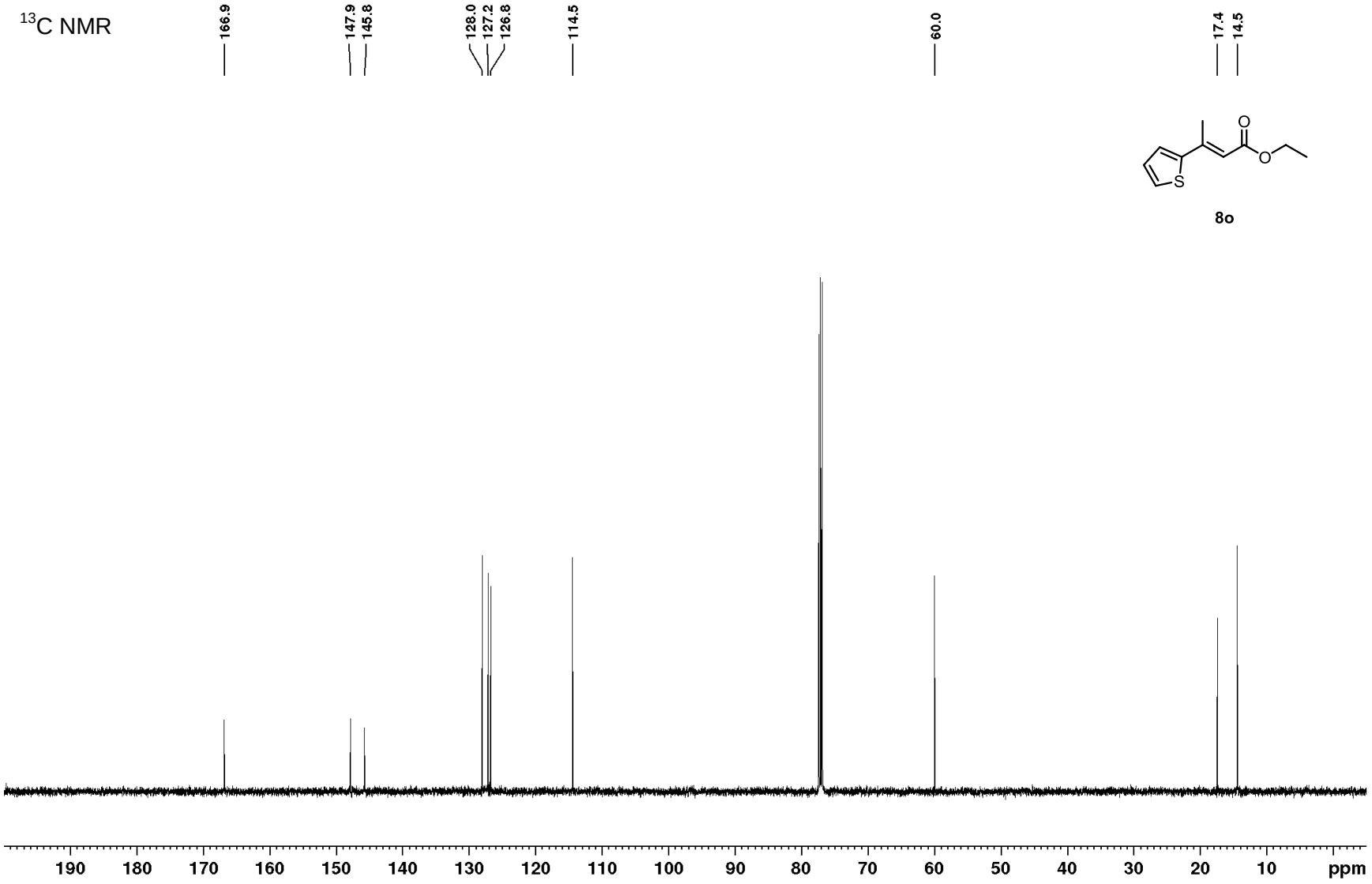

%Transmittance
Wavenumber
TBDPSO
O
O
8m
3197
2930
2892
2857
2540
2342
2202
1892
1831
1771
1703
1598
1507
1472
1424
1372
1258
1144
1112
1044
1007
916
819
738
696

Ethyl (*E*)-3-(thiophen-2-yl)but-2-enoate (8o)

^{1}H NMR

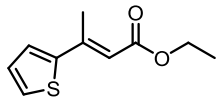


^{13}C NMR

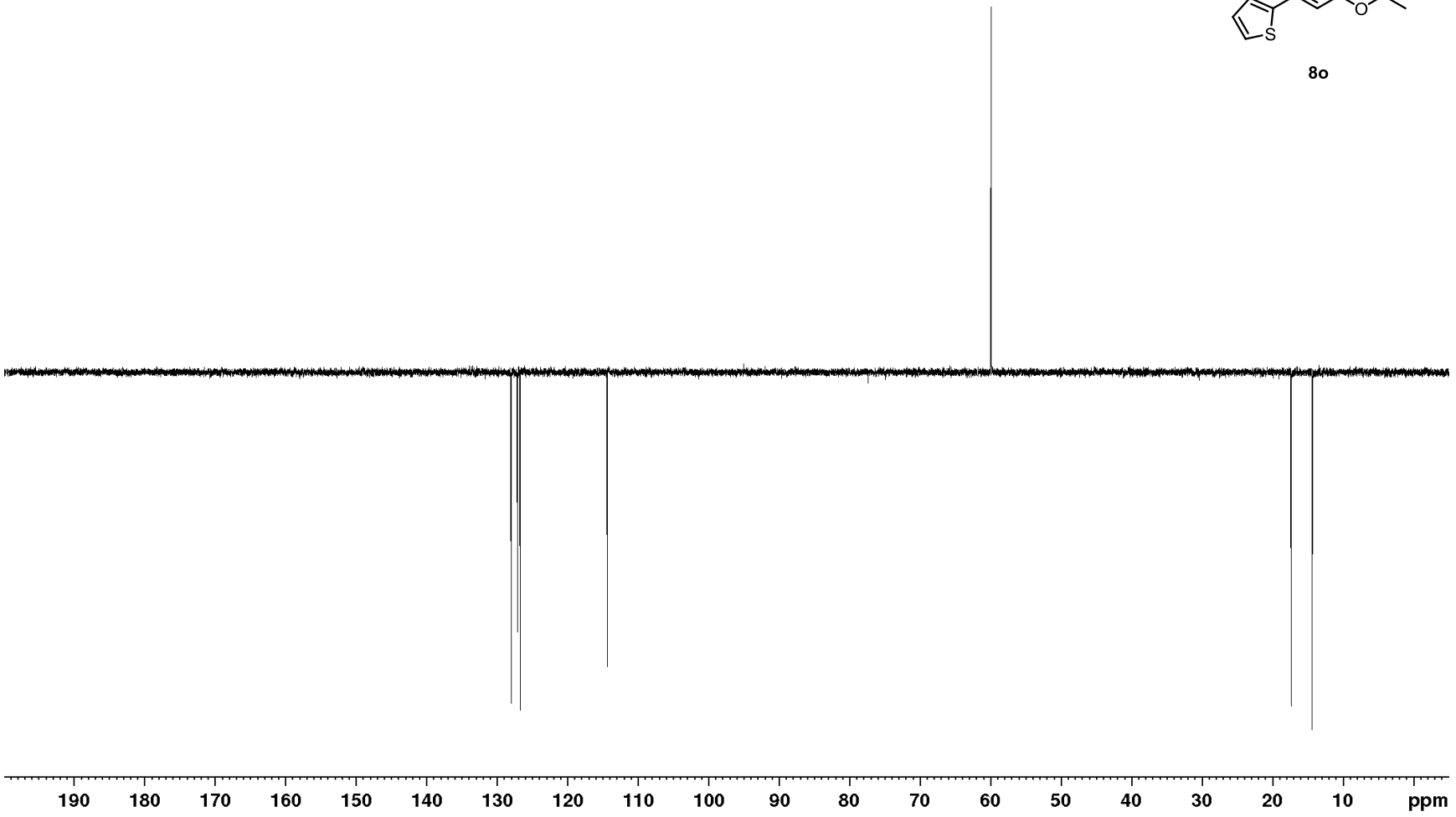

166.9
147.9
145.8
128.0
127.2
126.8
114.5
60.0
17.4
14.5
O
O
S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

8o

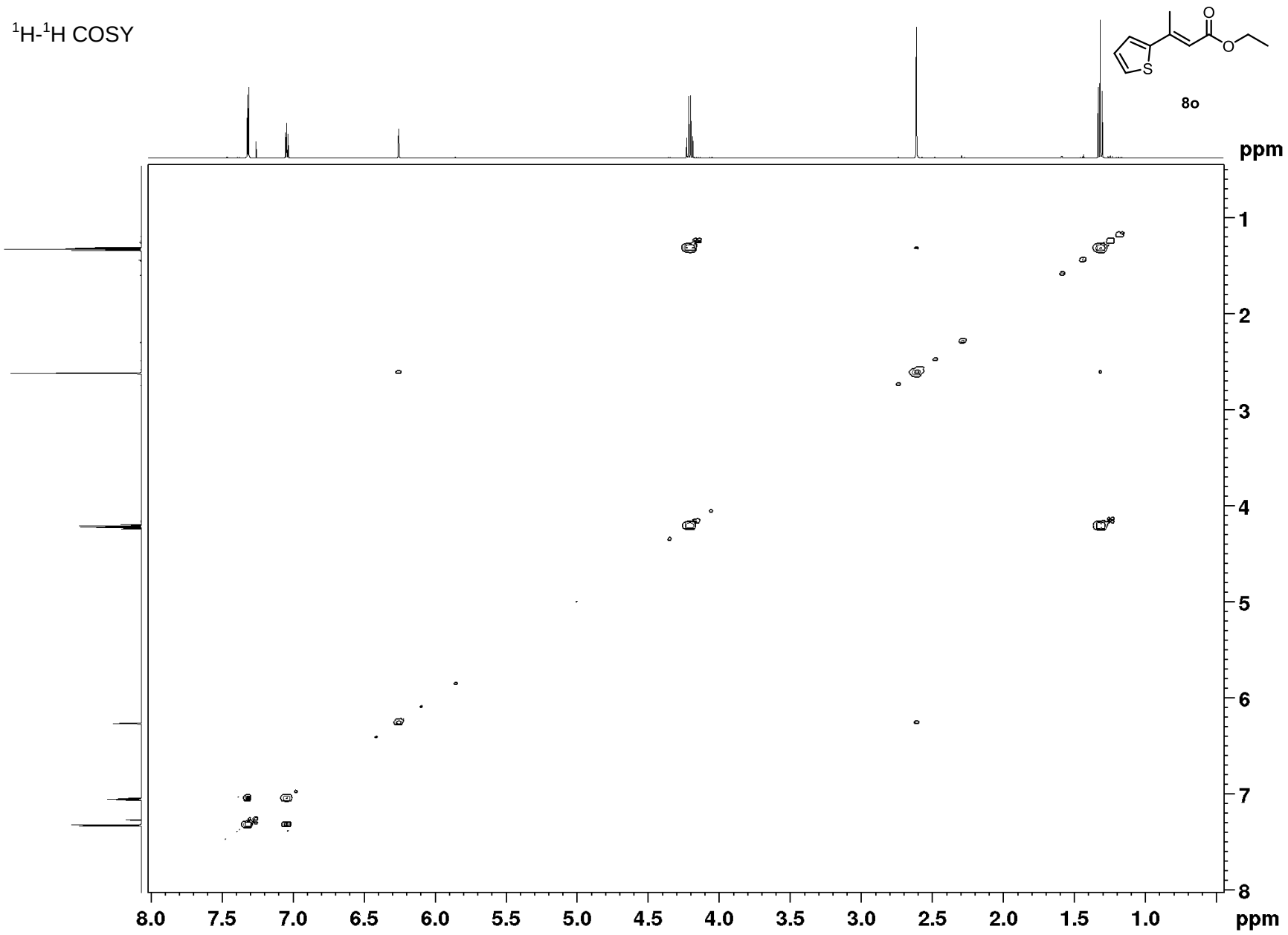
^{13}C DEPT NMR



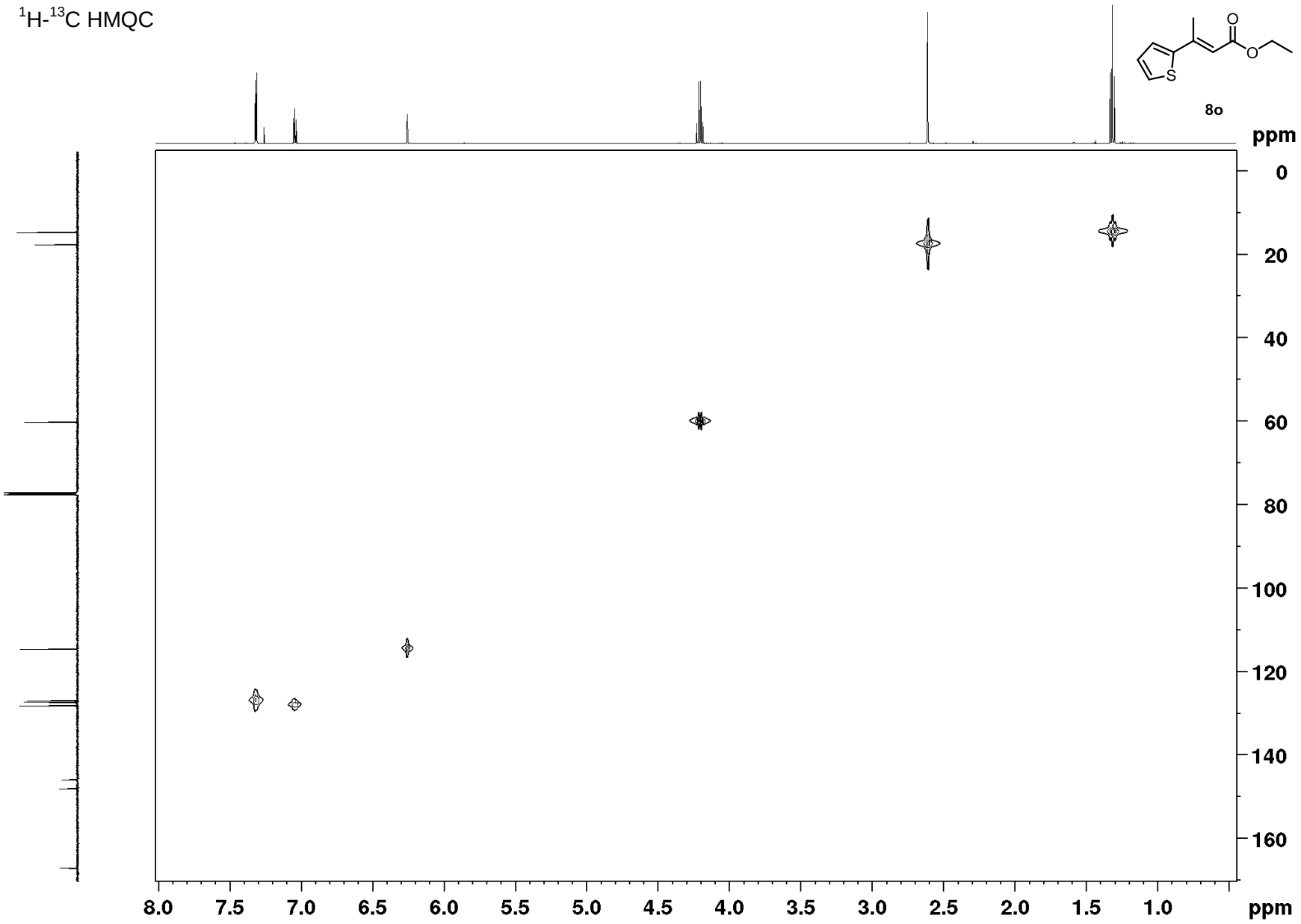
8o



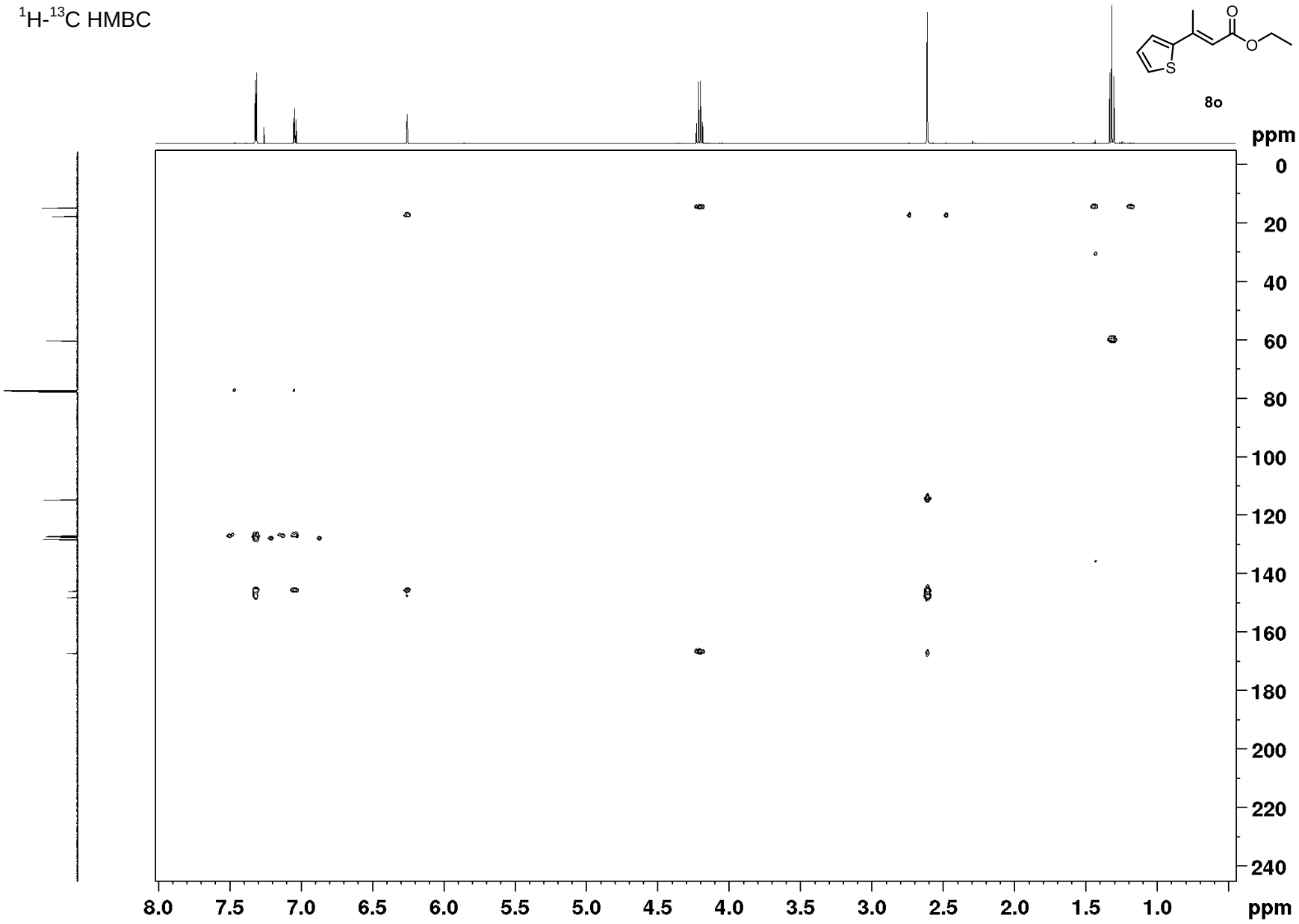
^{1}H-^{1}H COSY



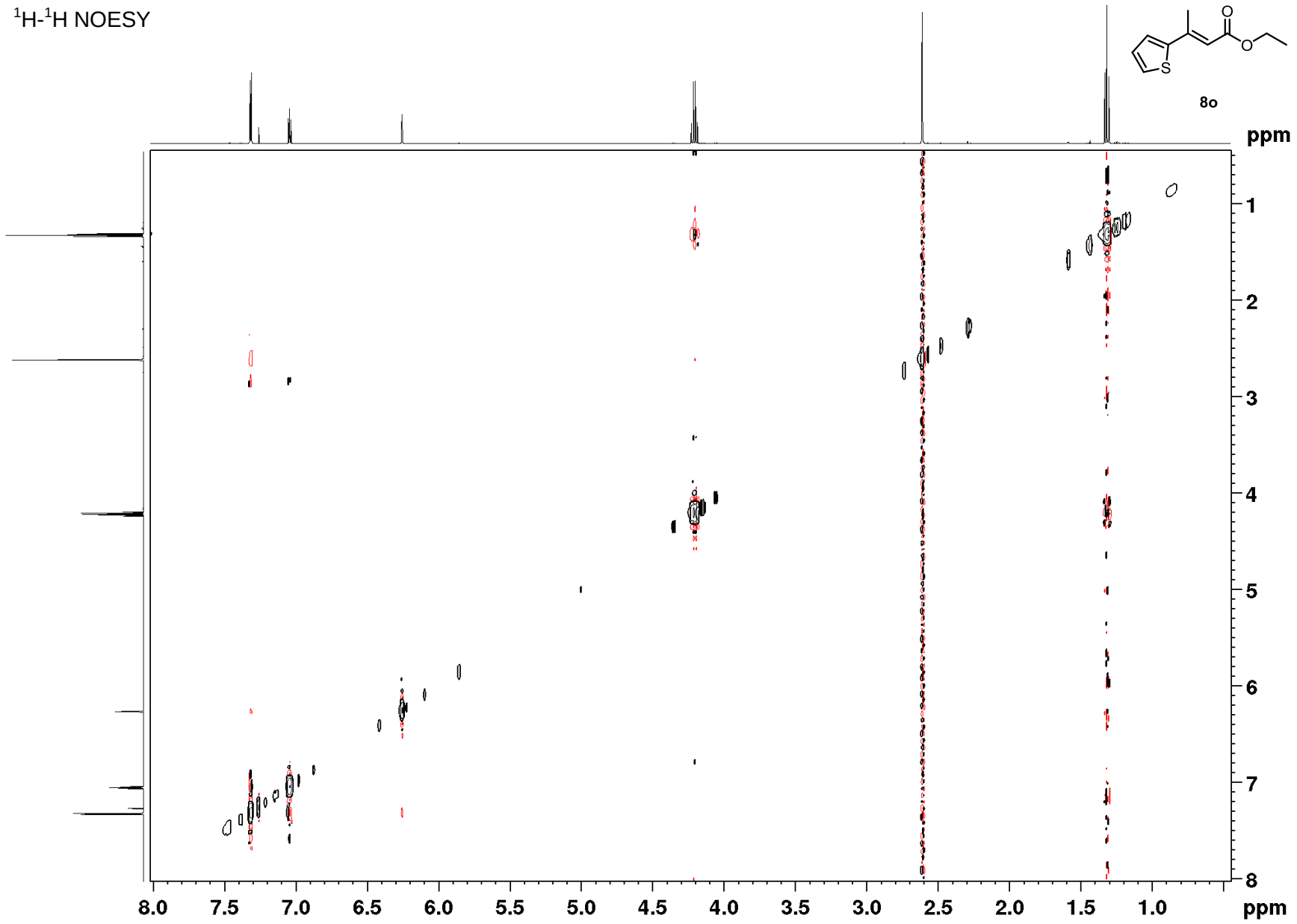
^{1}H-^{13}C HMQC

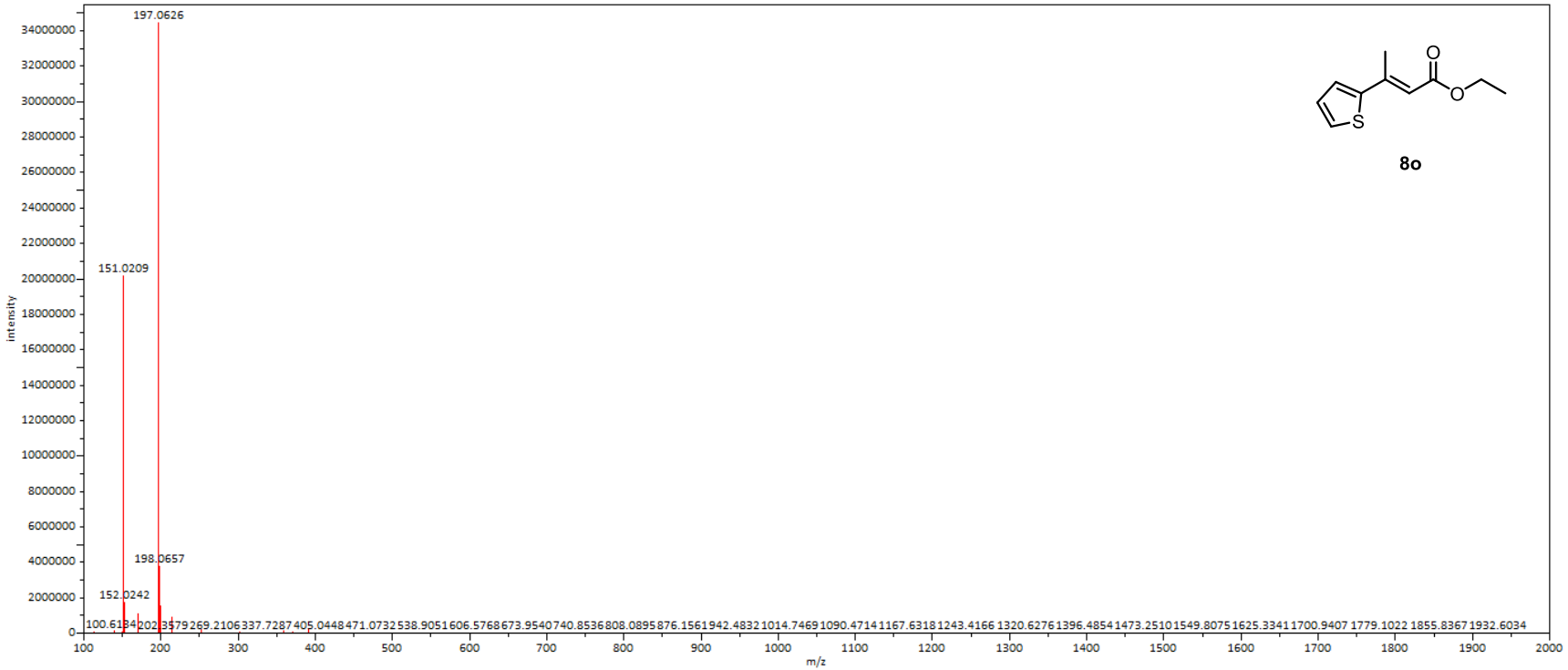

O
O
S
8o
ppm
0
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

^{1}H-^{13}C HMBC


O
O
S
8o
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

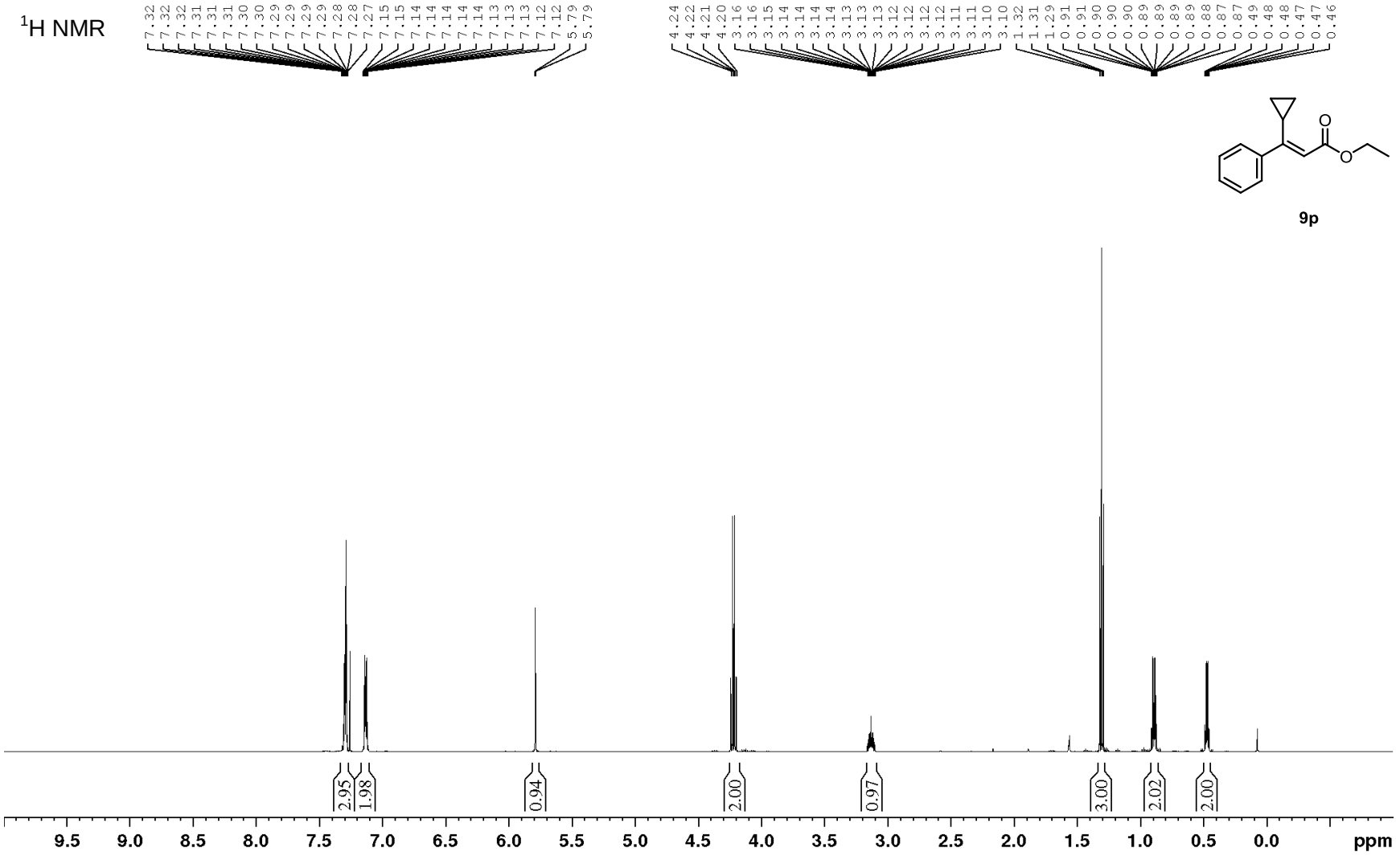
^{1}H-^{1}H NOESY

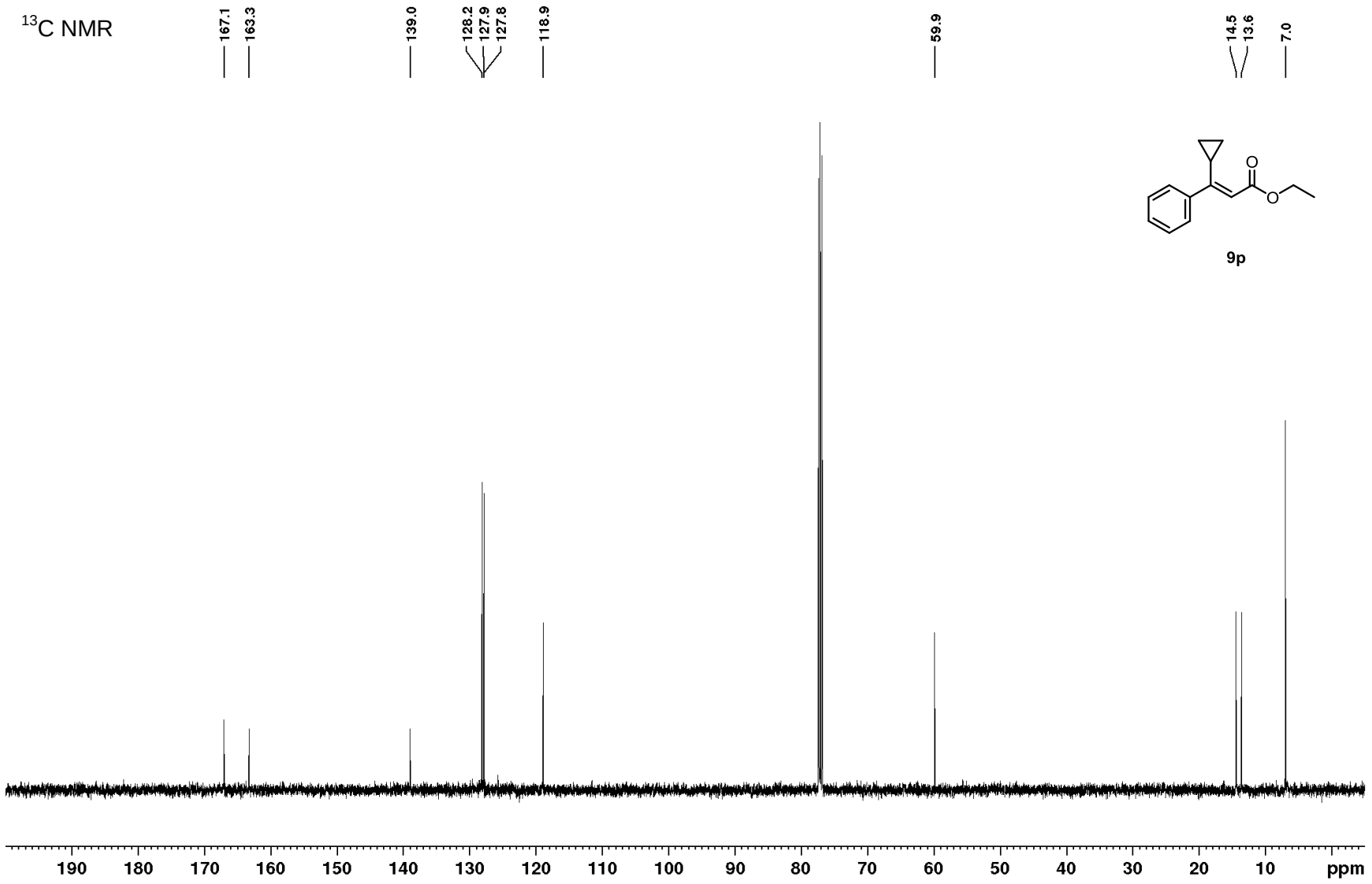



197.0626
151.0209
198.0657
152.0242
intensity
m/z
8o

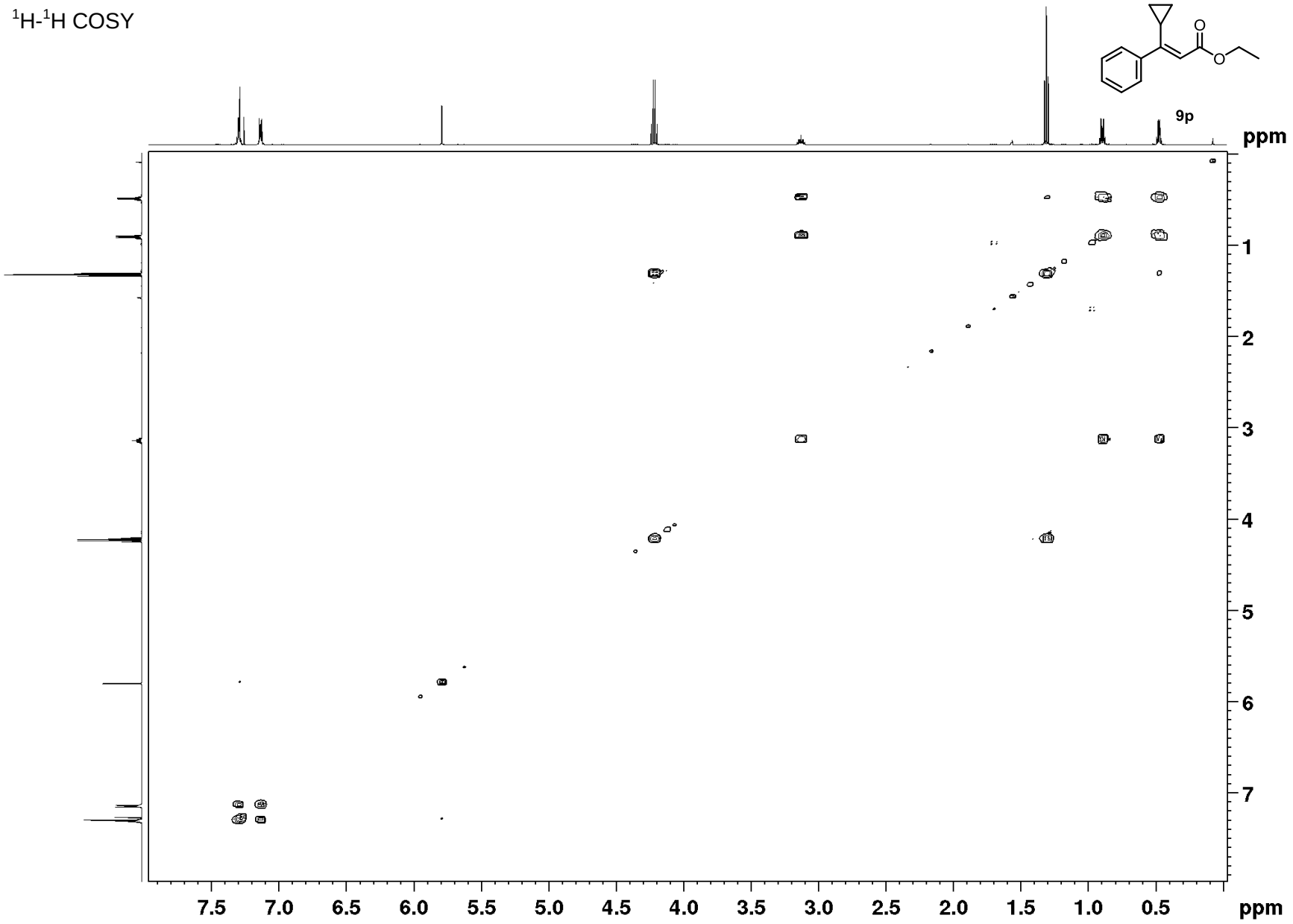
Ethyl (*E*)-3-cyclopropyl-3-phenylacrylate (9p)

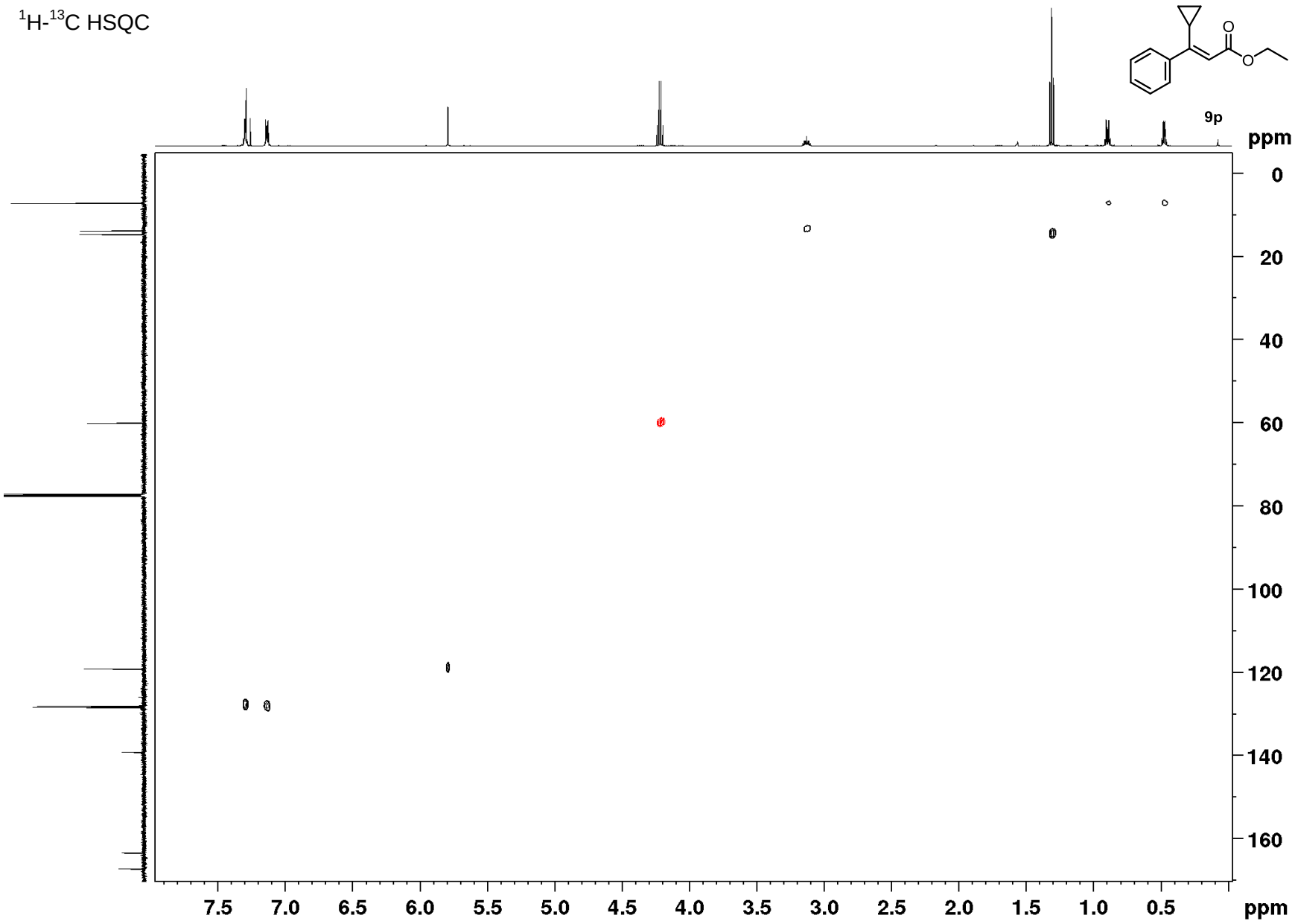
^{1}H NMR



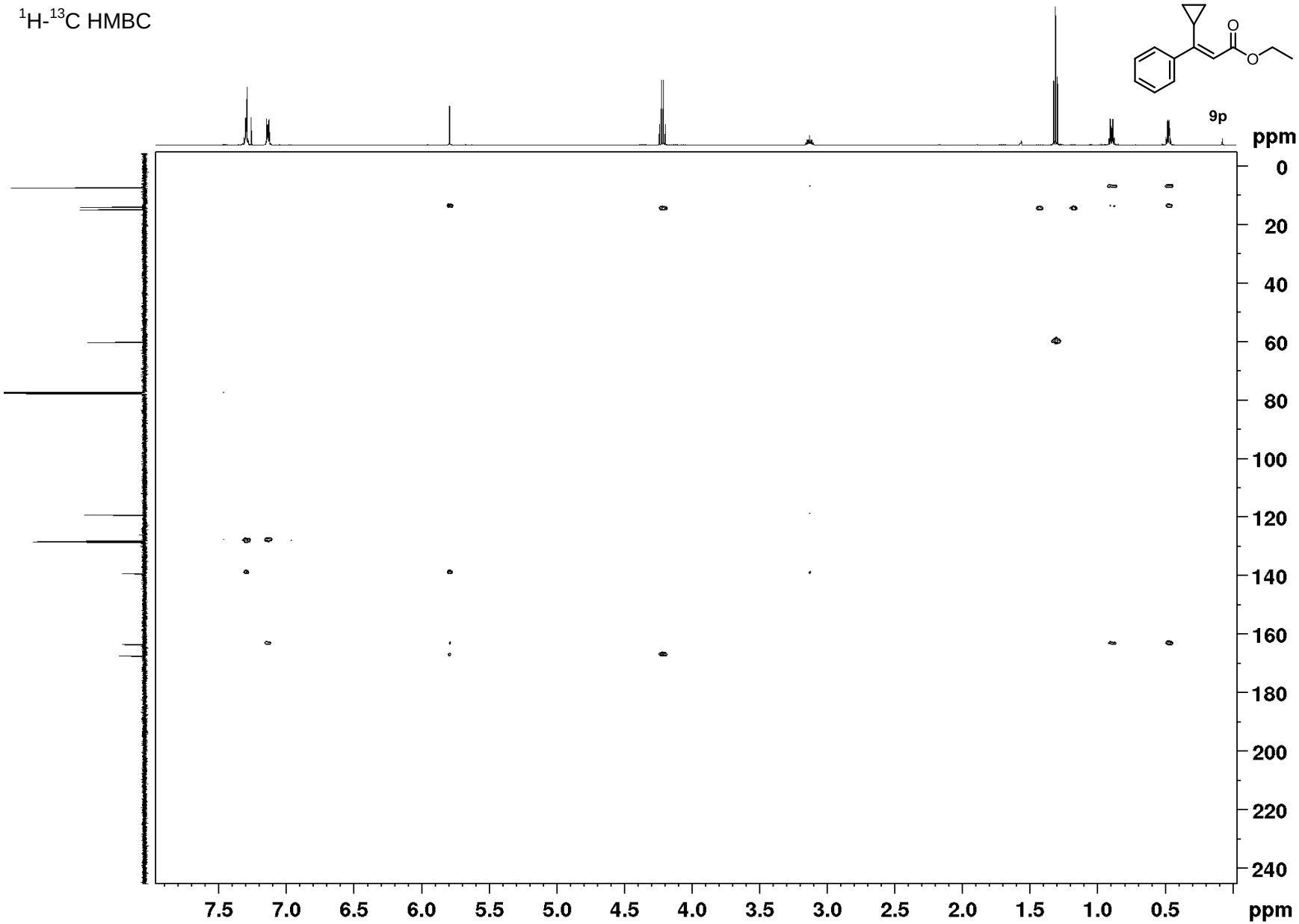

13C NMR
167.1
163.3
139.0
128.2
127.9
127.8
118.9
59.9
14.5
13.6
7.0
O
O
9p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{1}H-^{1}H COSY

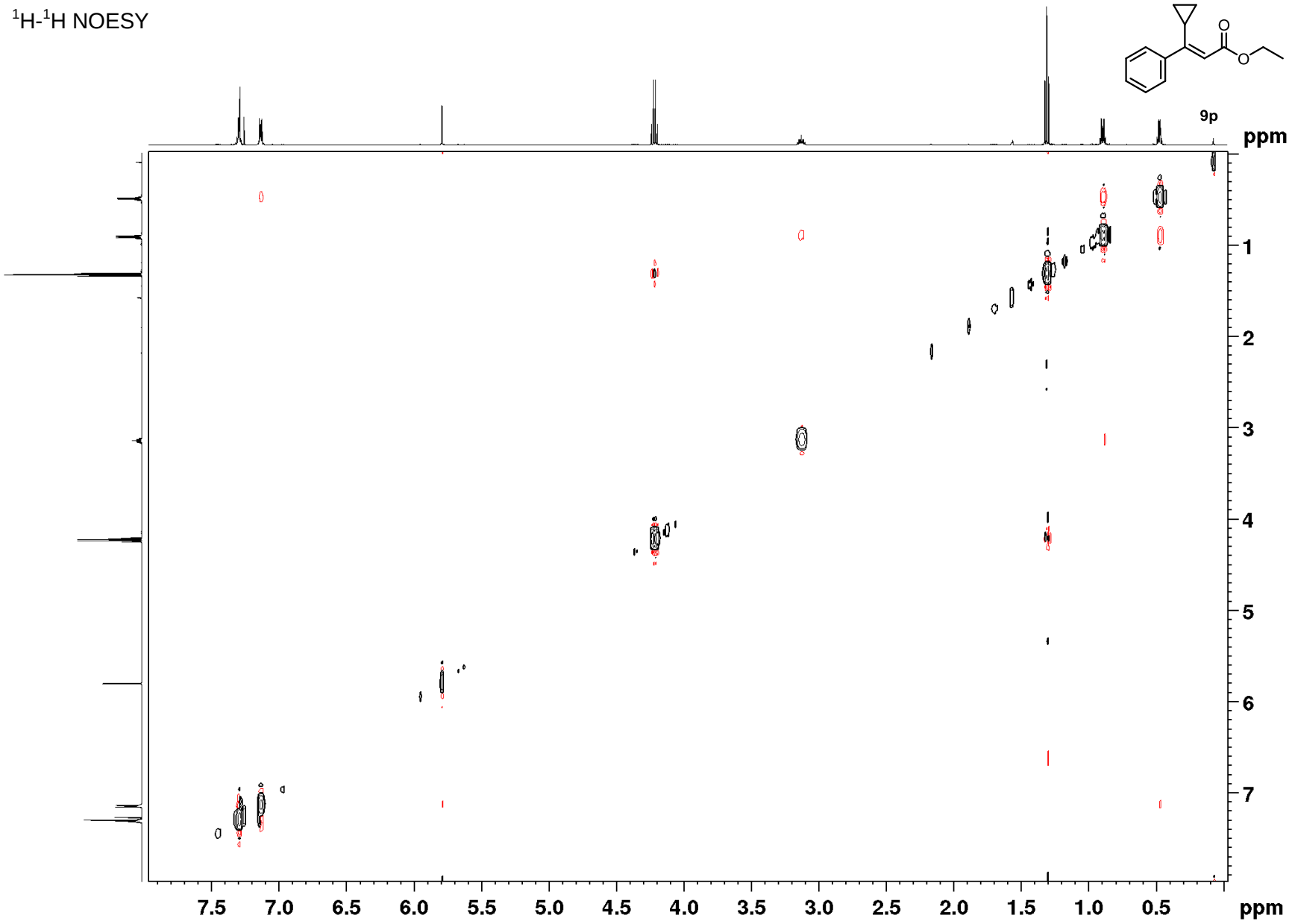


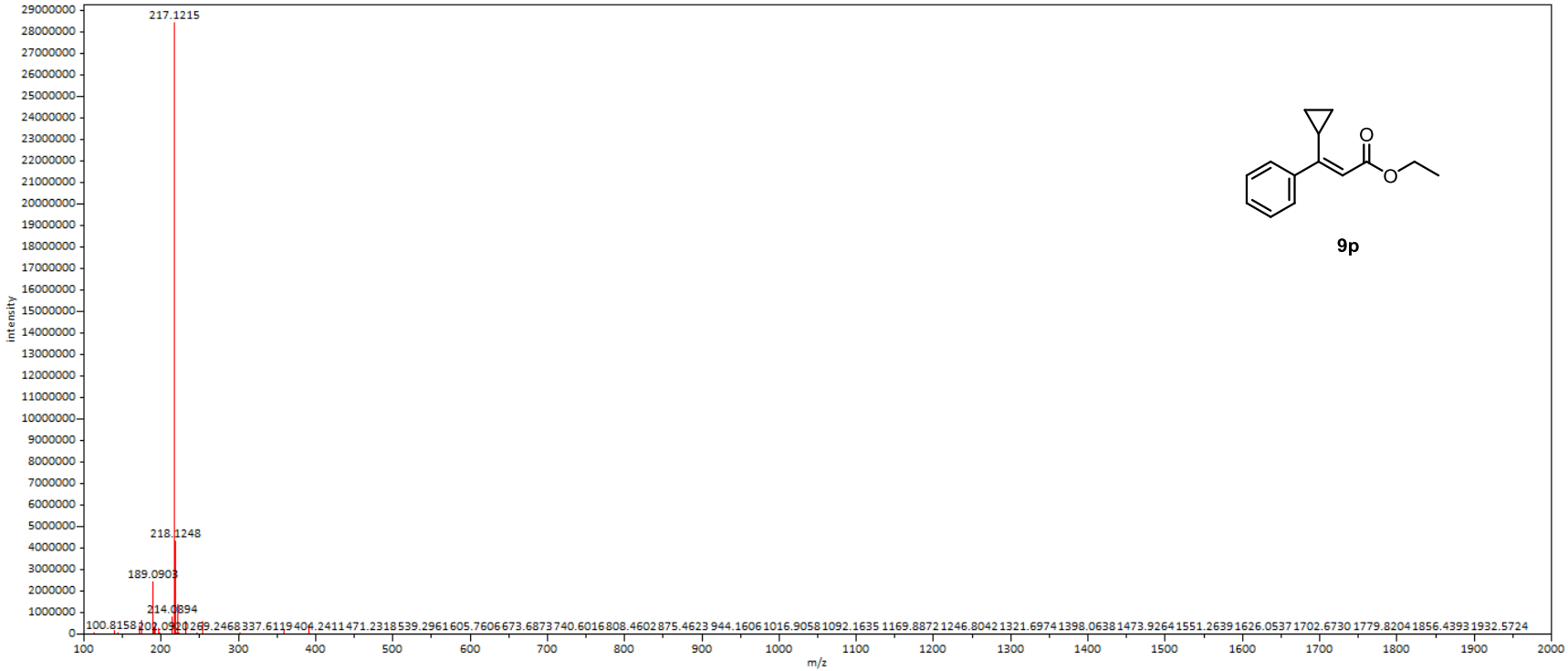

^{1}H-^{13}C HSQC
9p
ppm
0
20
40
60
80
100
120
140
160
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{1}H-^{13}C HMBC


9p
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

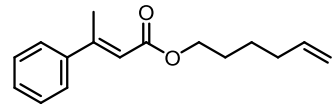
^{1}H-^{1}H NOESY



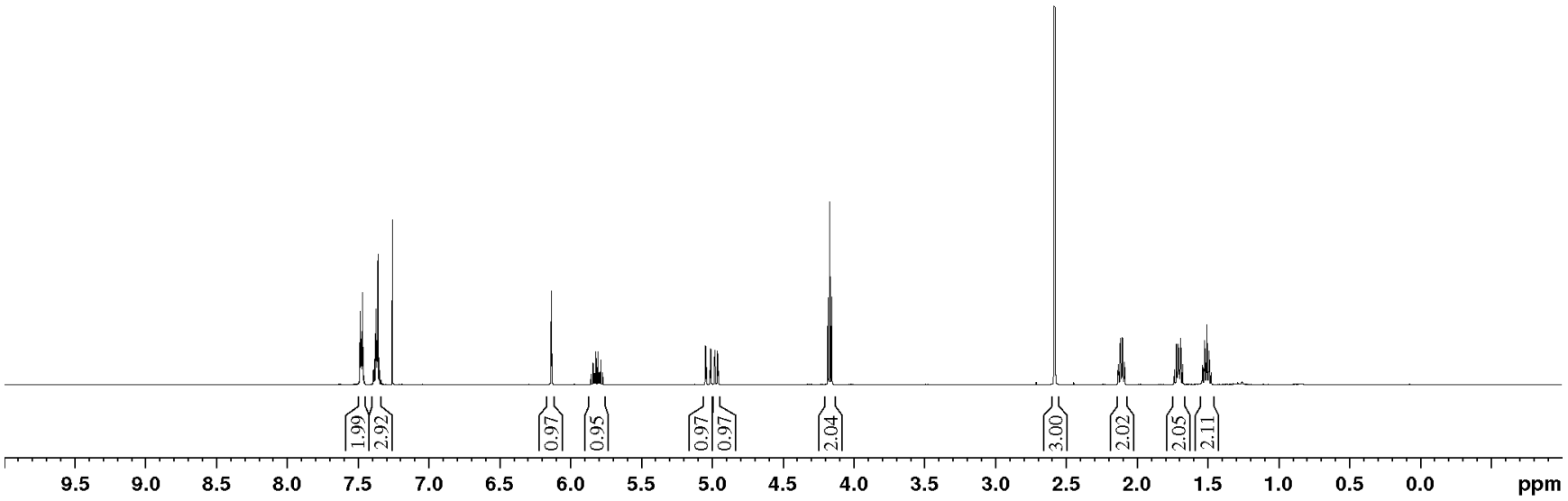

217.1215
218.1248
189.0903
214.0894
intensity
m/z
9p

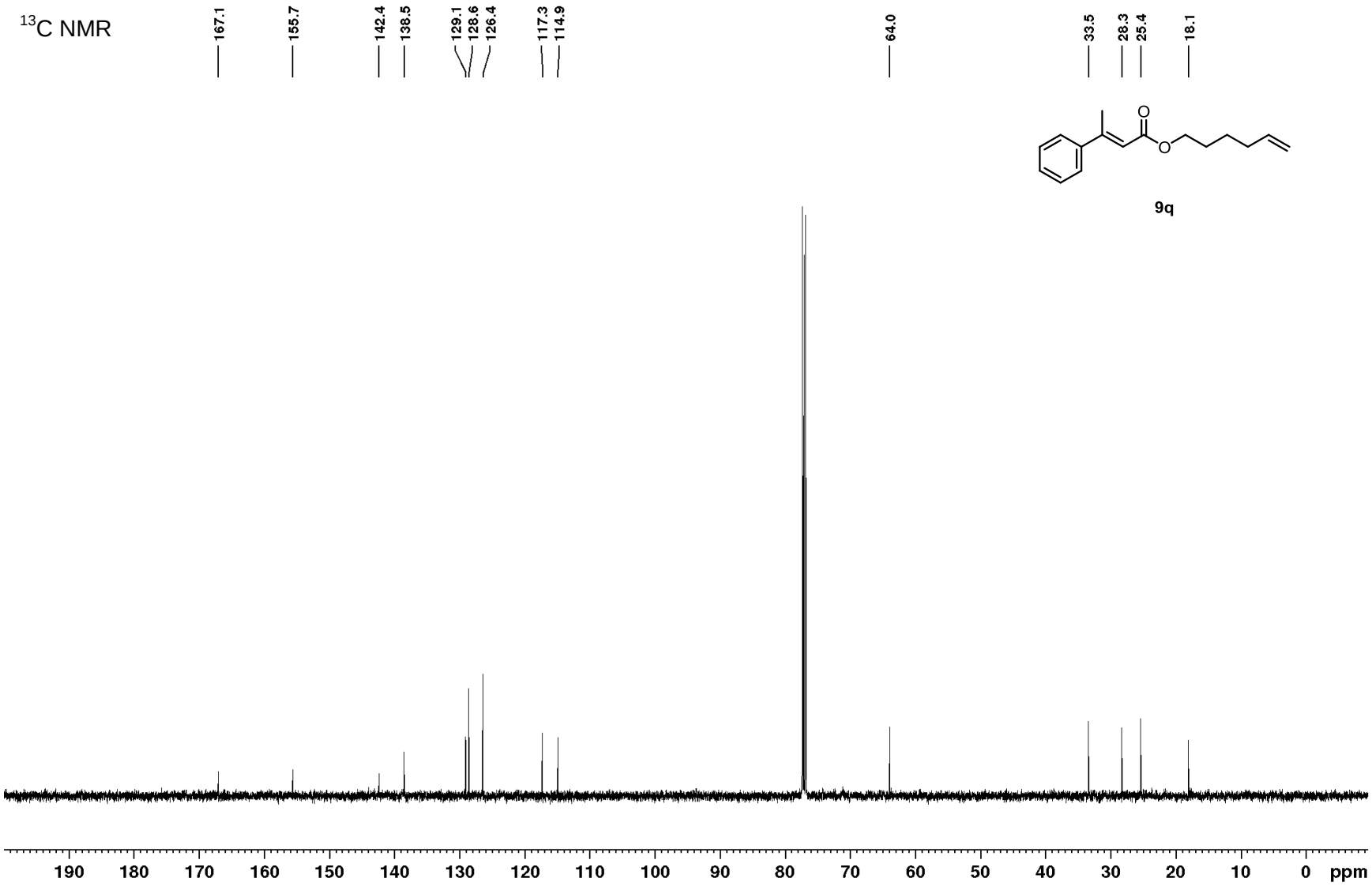
Hex-5-en-1-yl (*E*)-3-phenylbut-2-enoate (9q)

^{1}H NMR

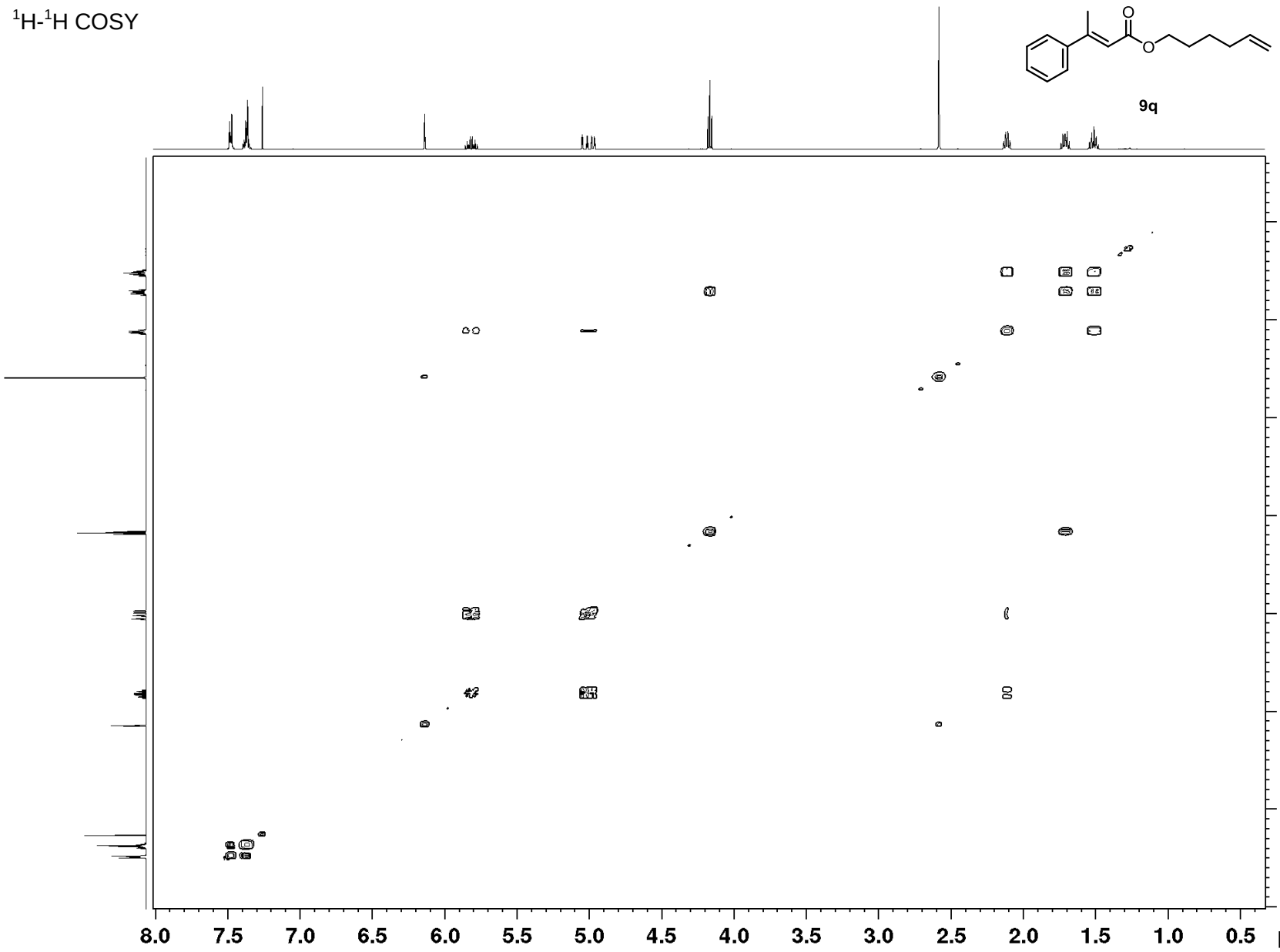


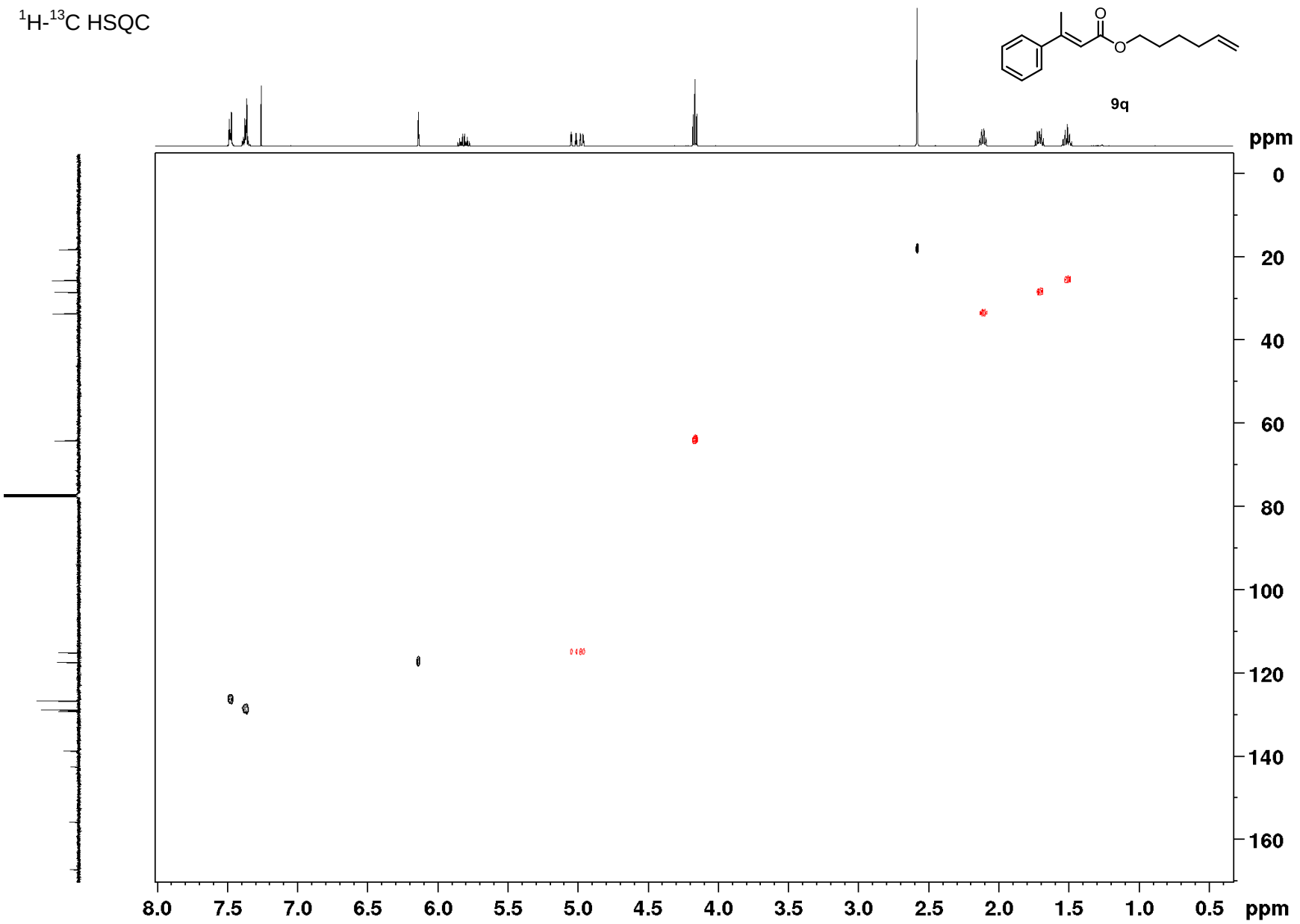
9q



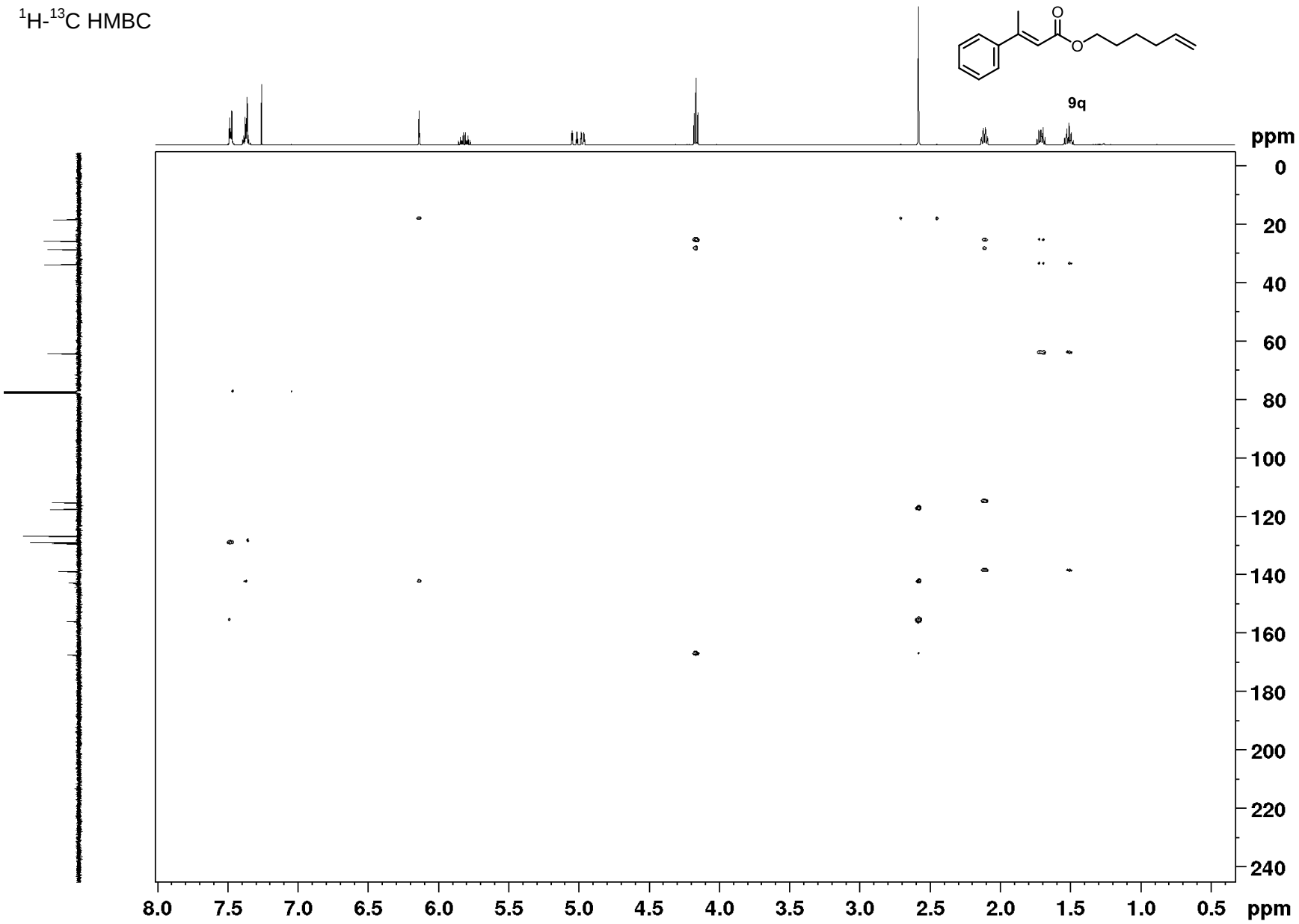

^{13}C NMR
167.1
155.7
142.4
138.5
129.1
128.6
126.4
117.3
114.9
64.0
33.5
28.3
25.4
18.1
O
O
9q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

^{1}H-^{1}H COSY

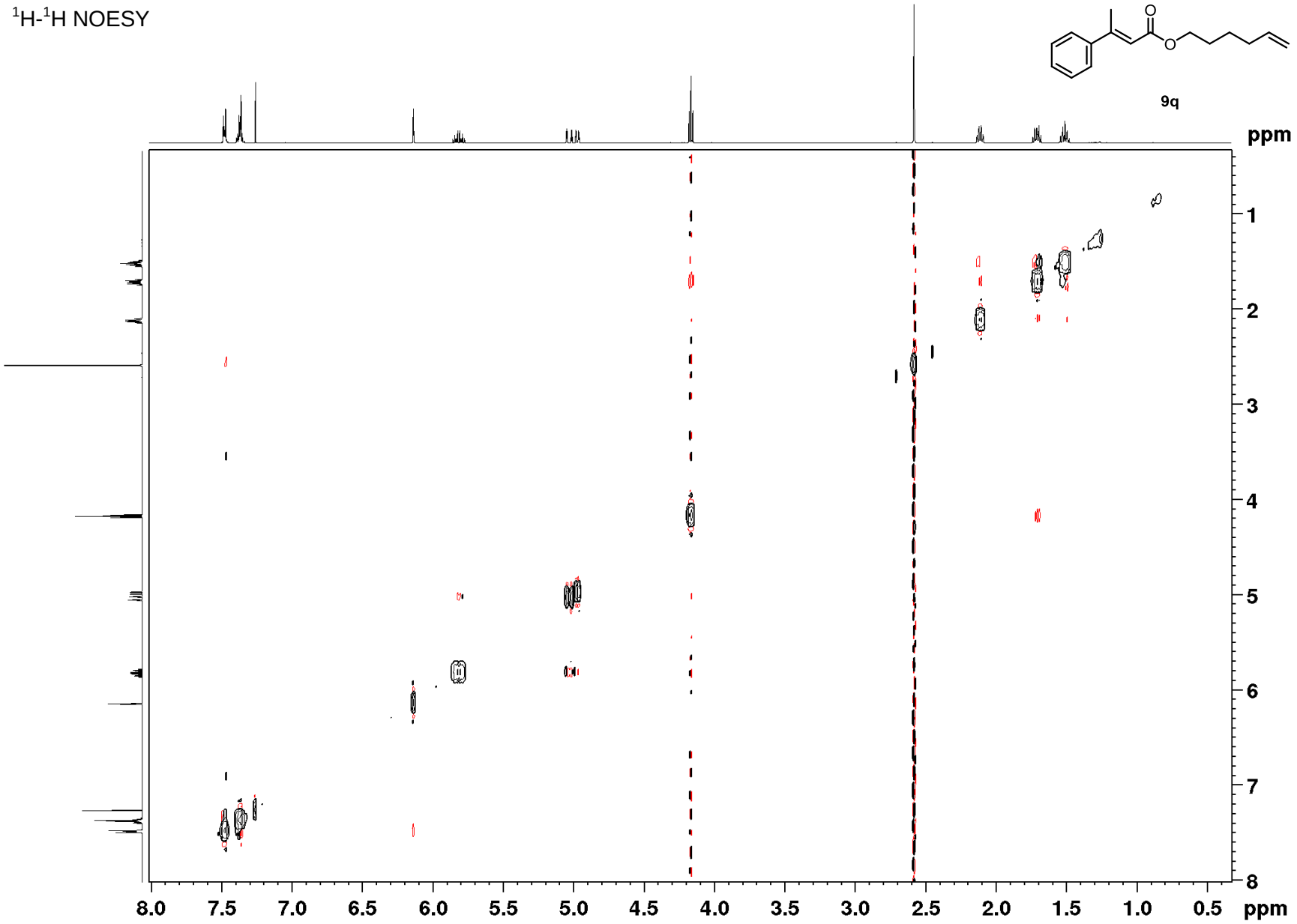



^{1}H-^{13}C HSQC
9q
ppm
0
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

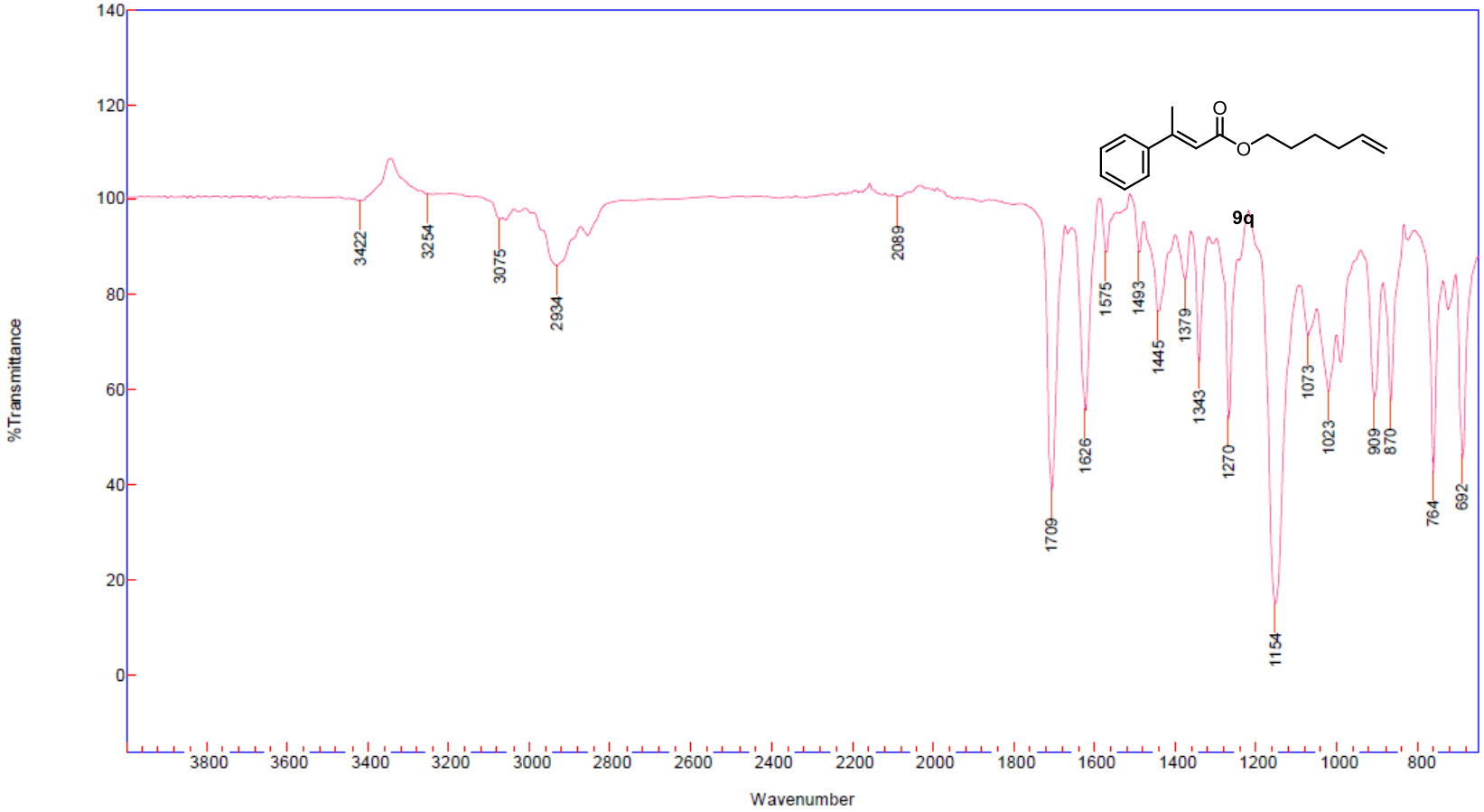
^{1}H-^{13}C HMBC


9q
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

^{1}H-^{1}H NOESY

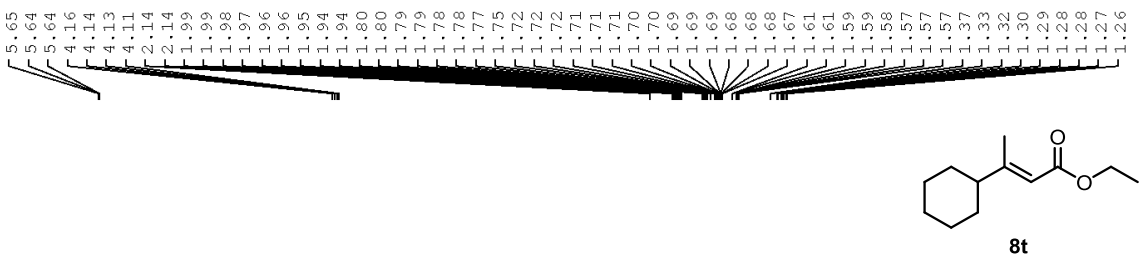



245.1532
163.0750
145.0646
246.1563
164.0782
102.0911
214.0893
intensity
m/z
9q

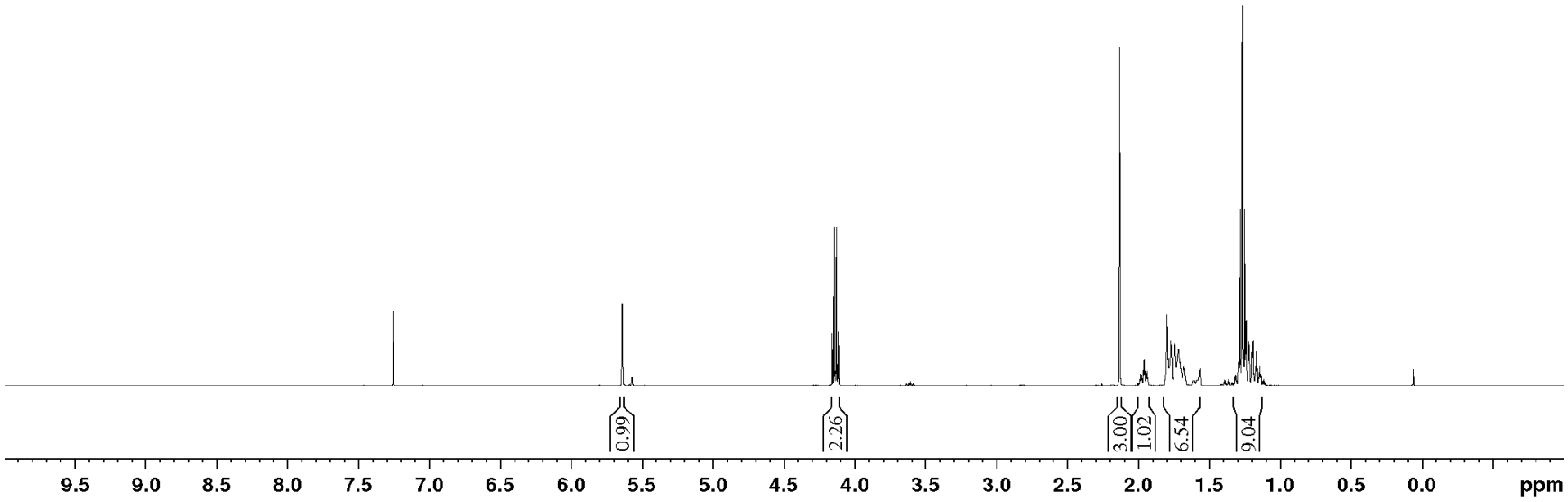

%Transmittance
Wavenumber
9q
3422
3254
3075
2934
2089
1709
1626
1575
1493
1445
1379
1343
1270
1154
1073
1023
909
870
764
692

Ethyl (*E*)-3-cyclohexylbut-2-enoate (8t)

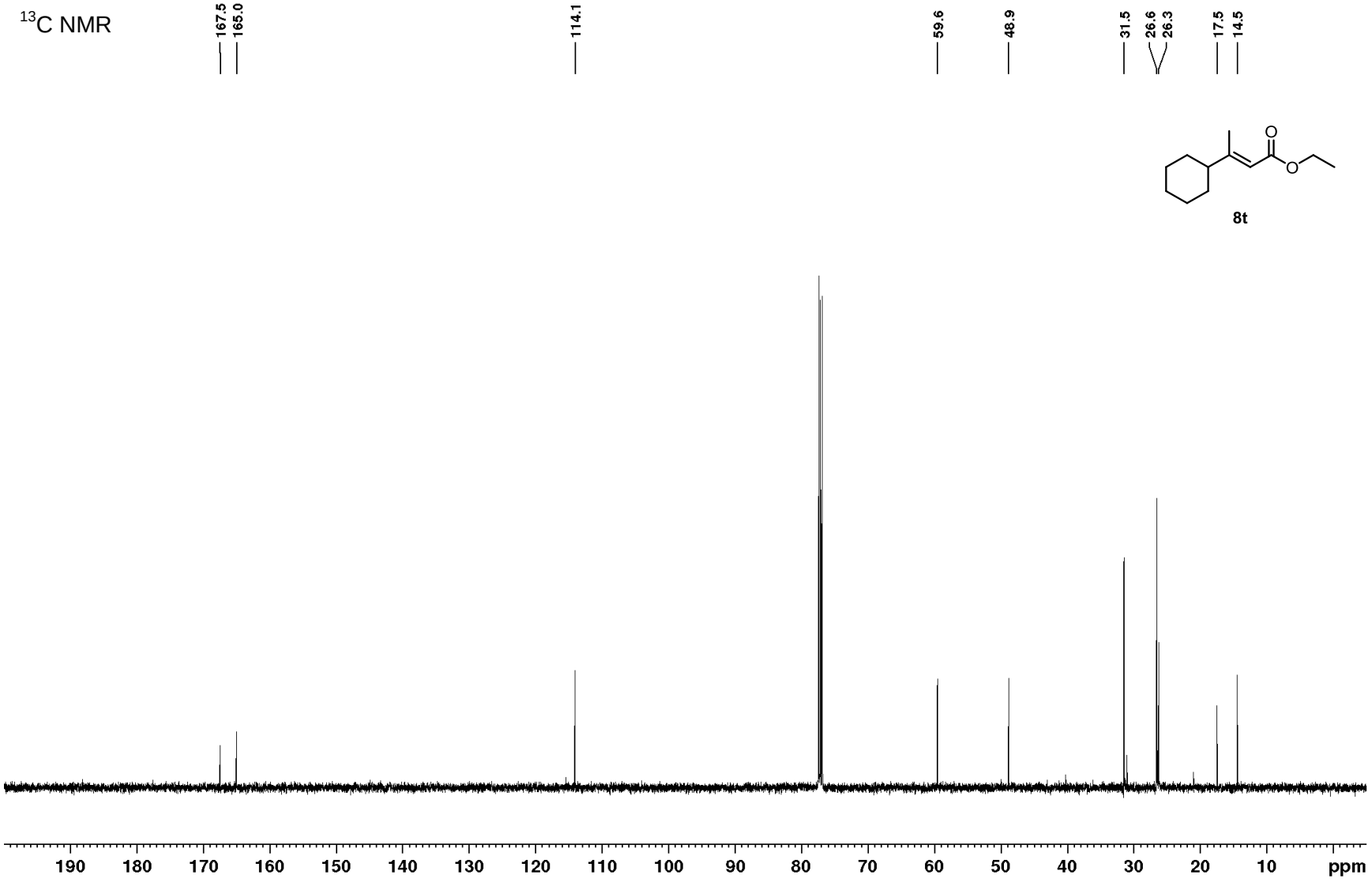
^{1}H NMR



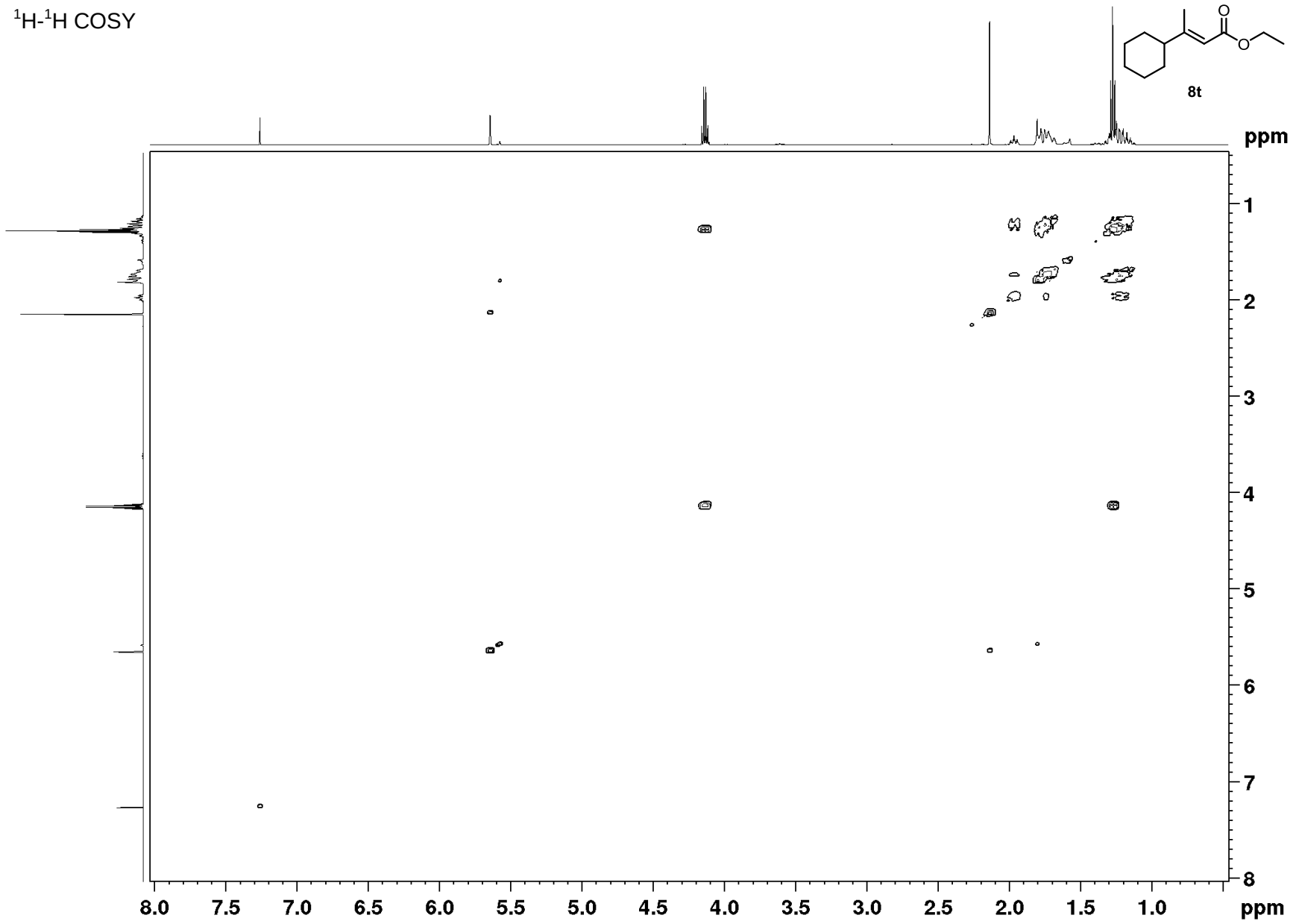
8t



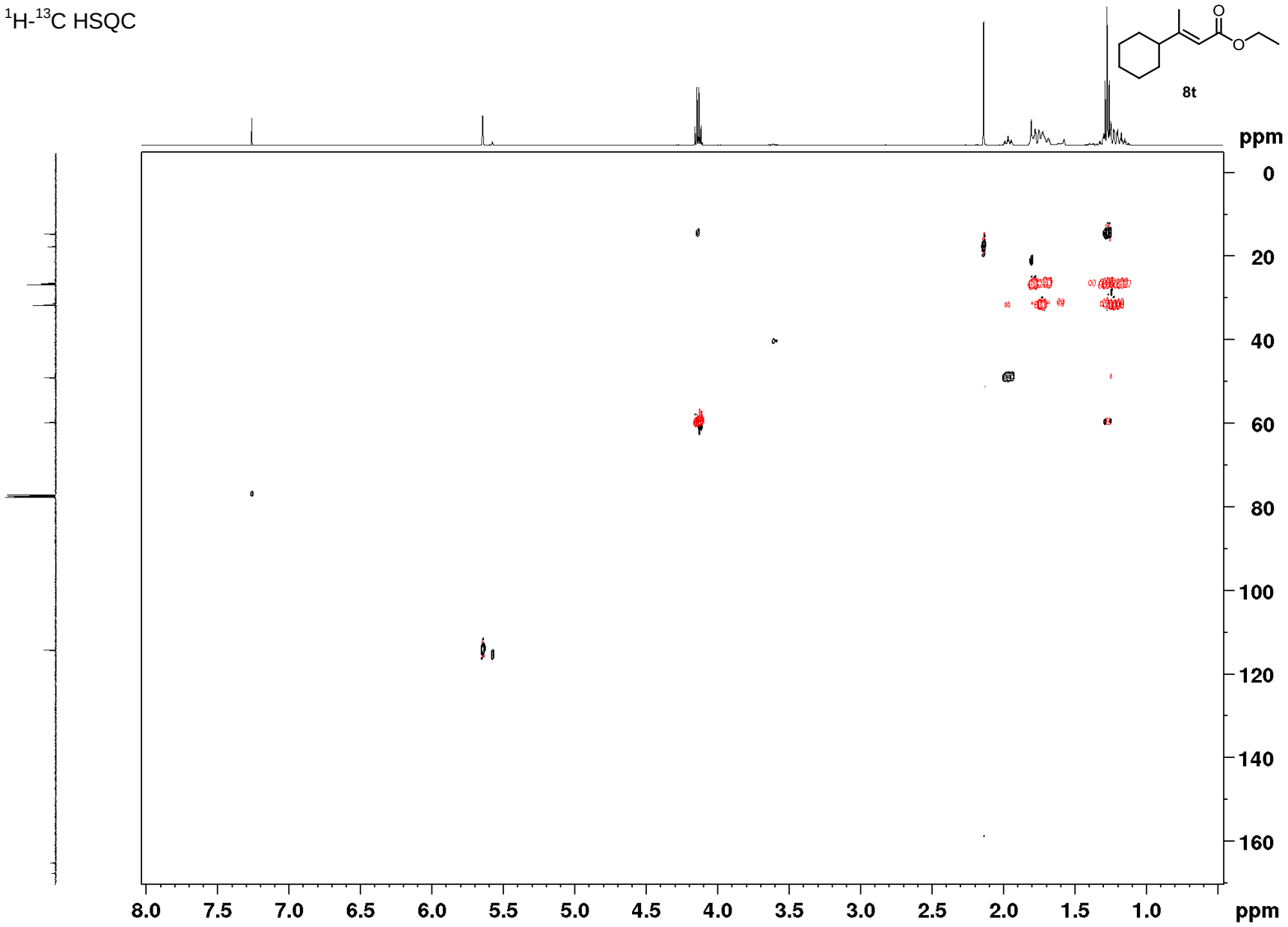
^{13}C NMR


167.5
165.0
114.1
59.6
48.9
31.5
26.6
26.3
17.5
14.5
O
O
8t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

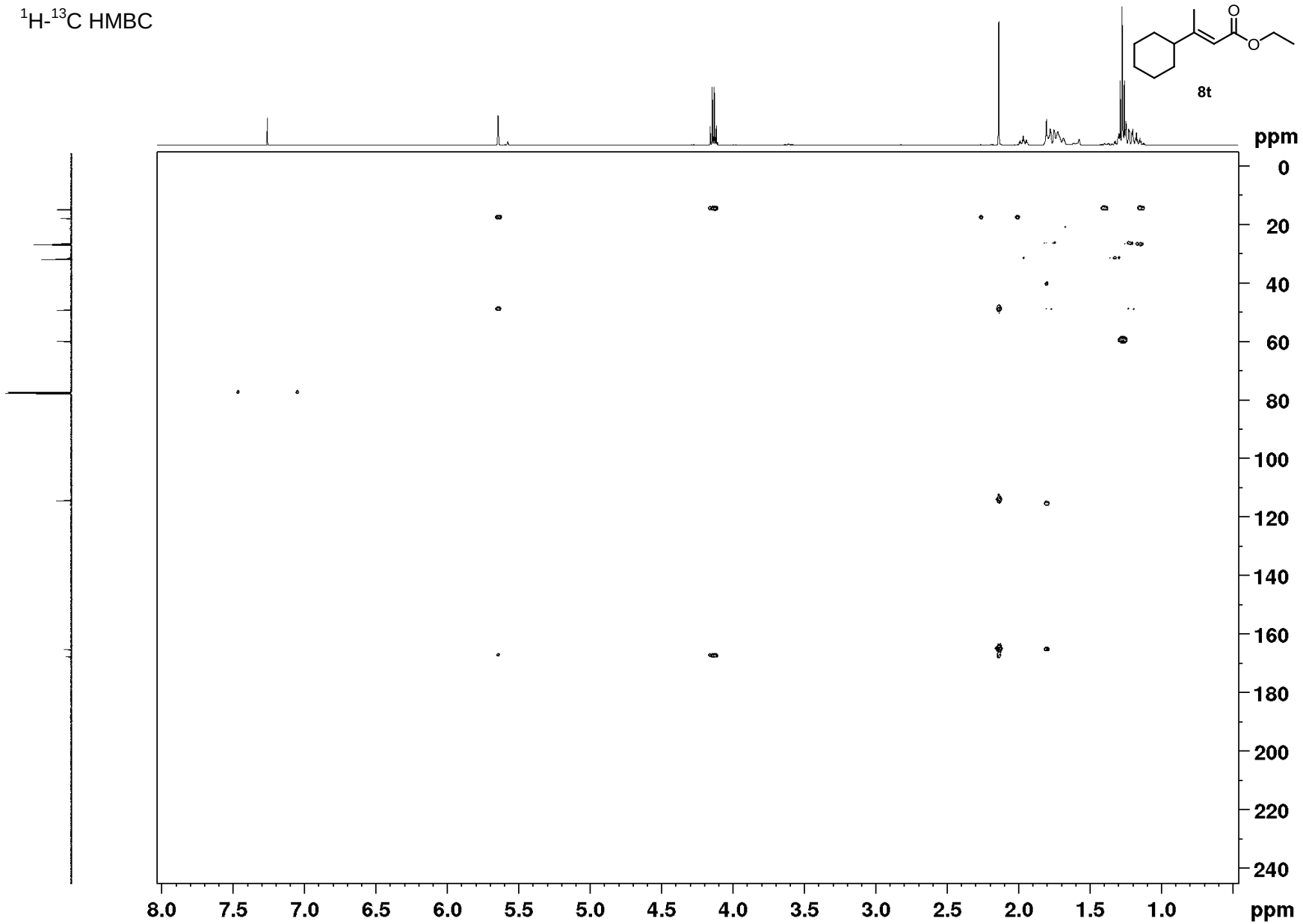
^{1}H-^{1}H COSY



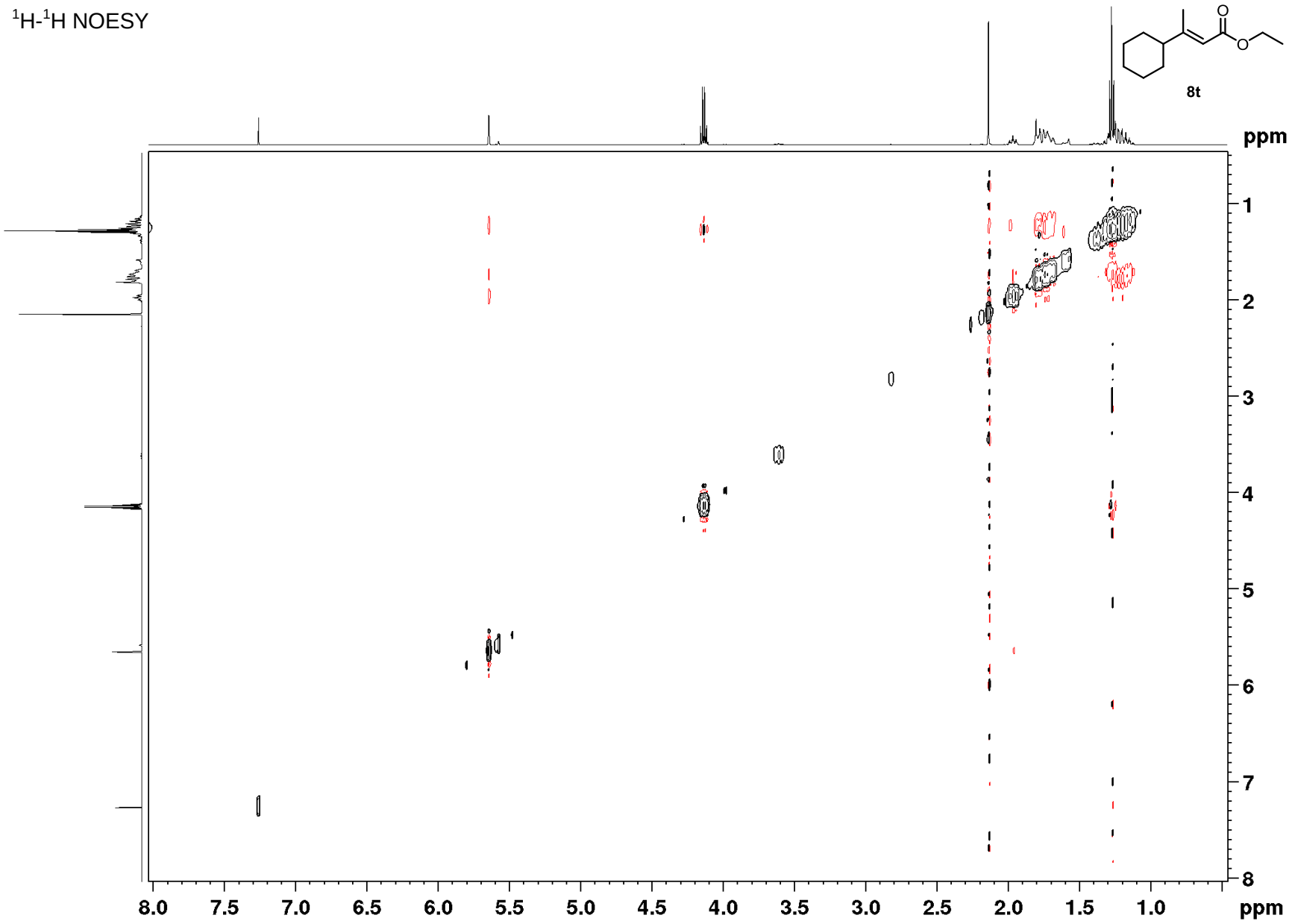
^{1}H-^{13}C HSQC

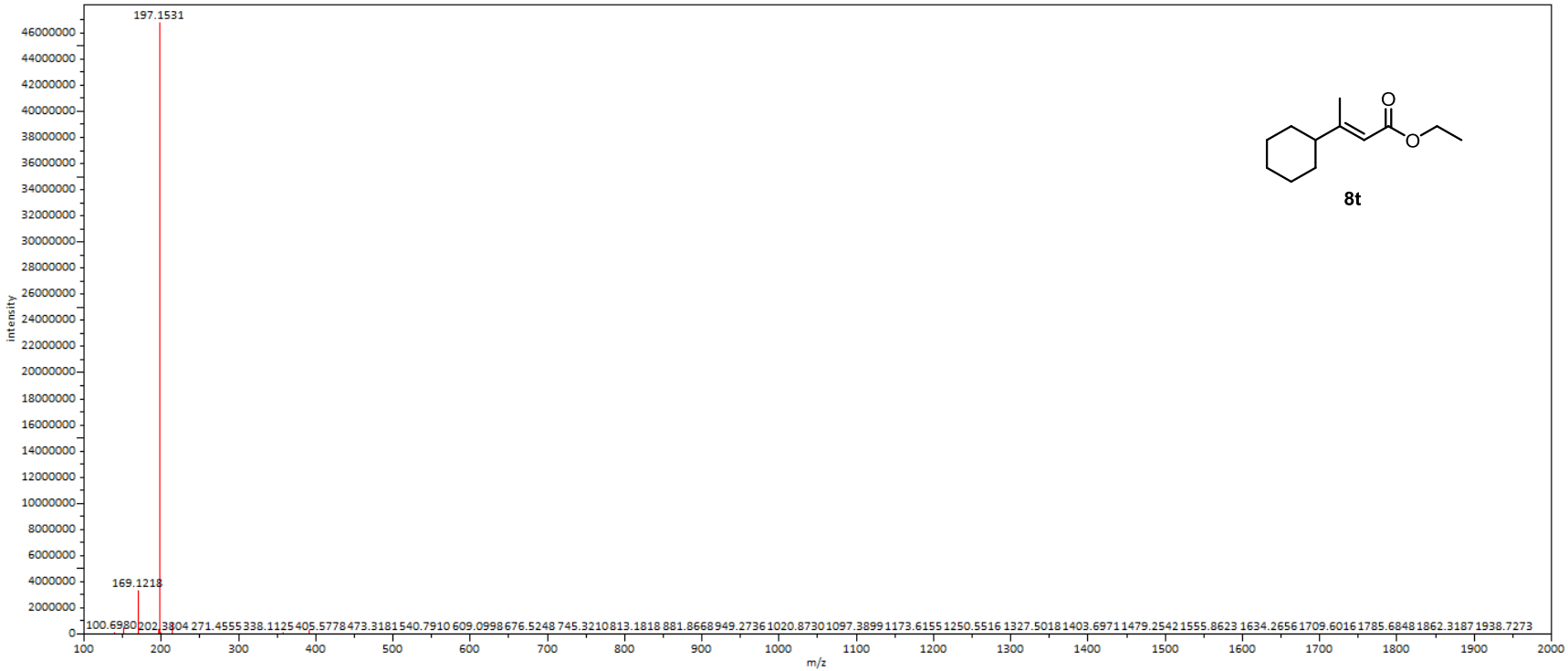

8t
ppm
0
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

^{1}H-^{13}C HMBC


8t
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

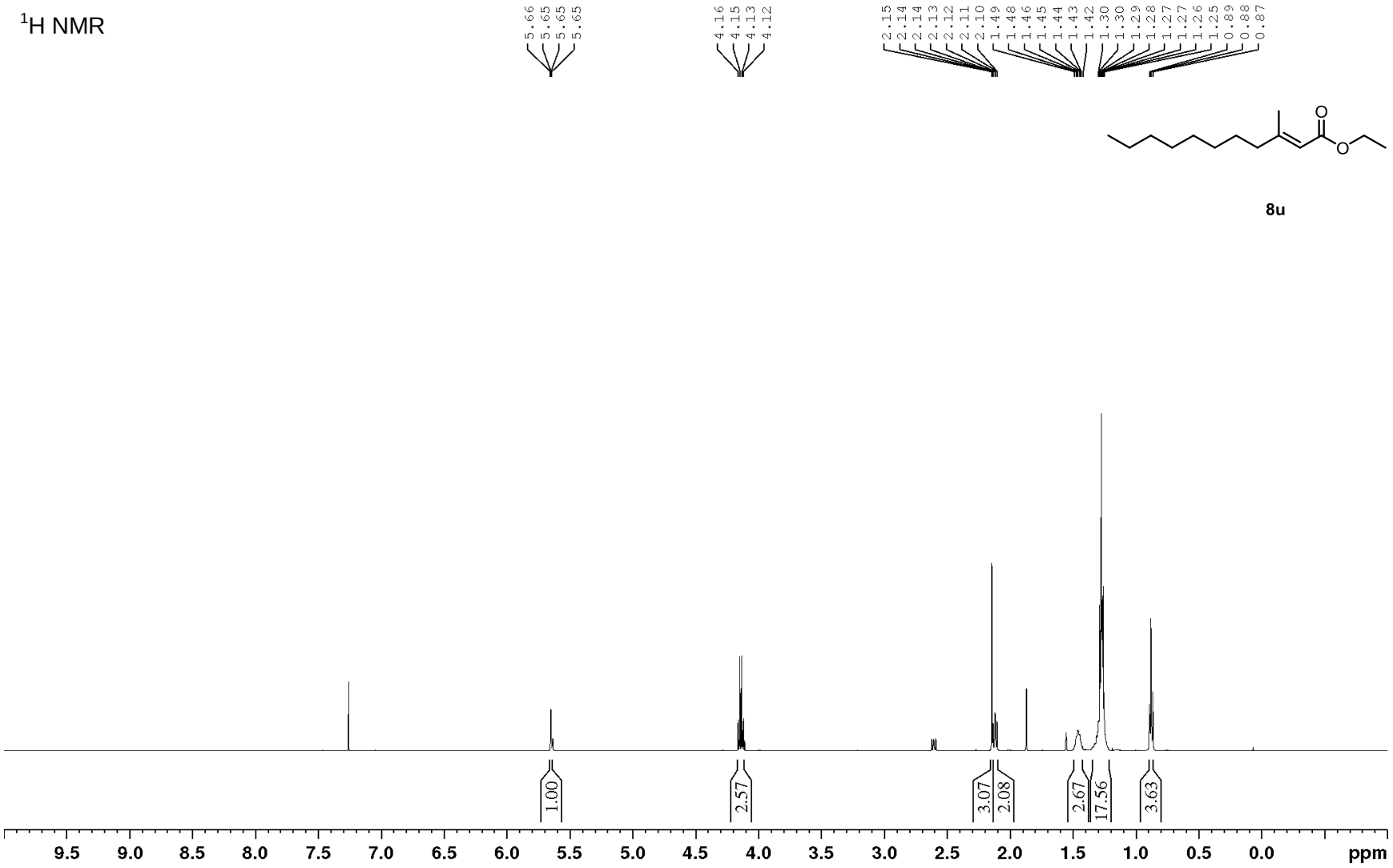
^{1}H-^{1}H NOESY



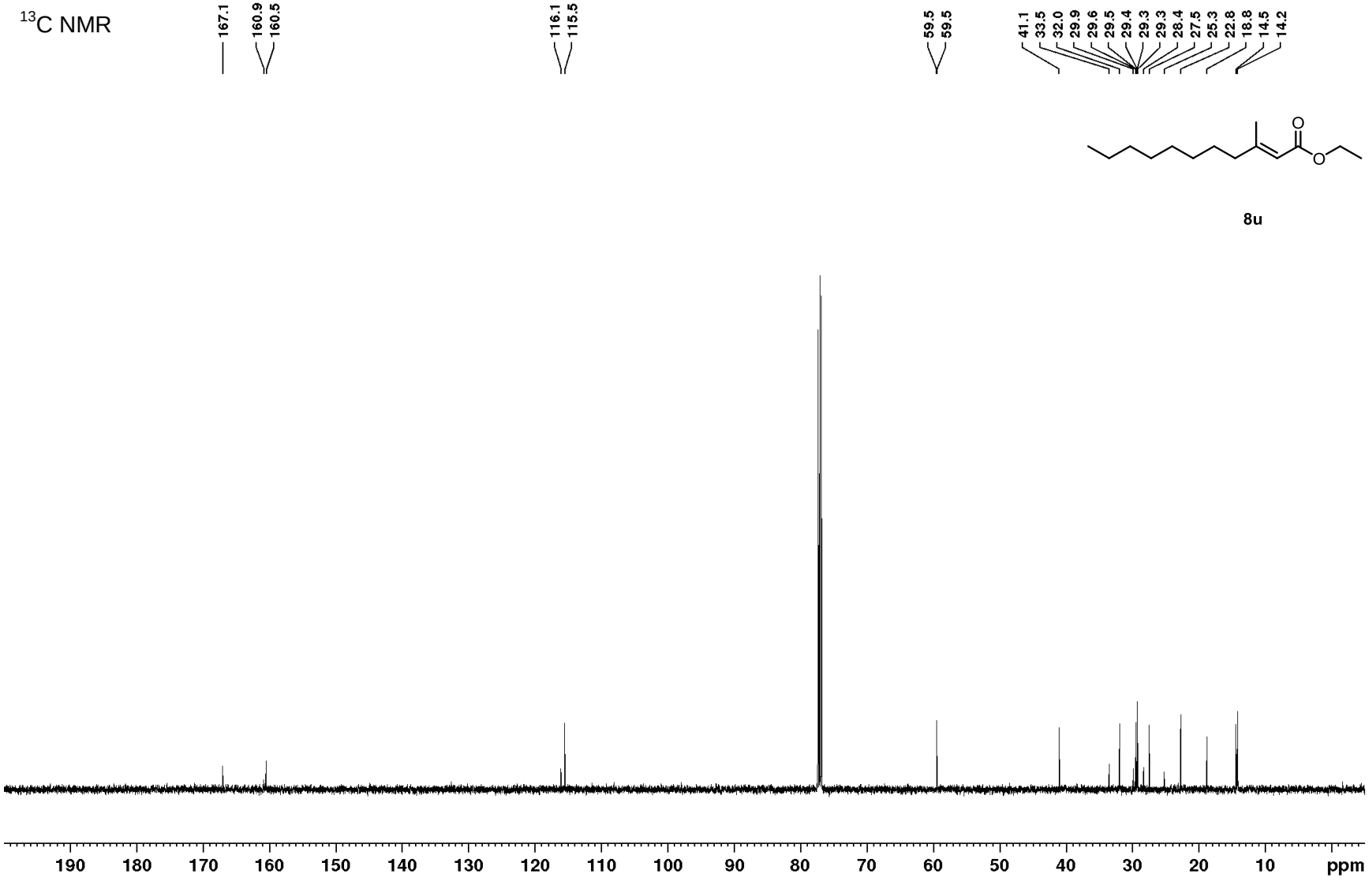

197.1531
169.1218
intensity
m/z
8t

Ethyl (*E*)-3-methylundec-2-enoate (8u)

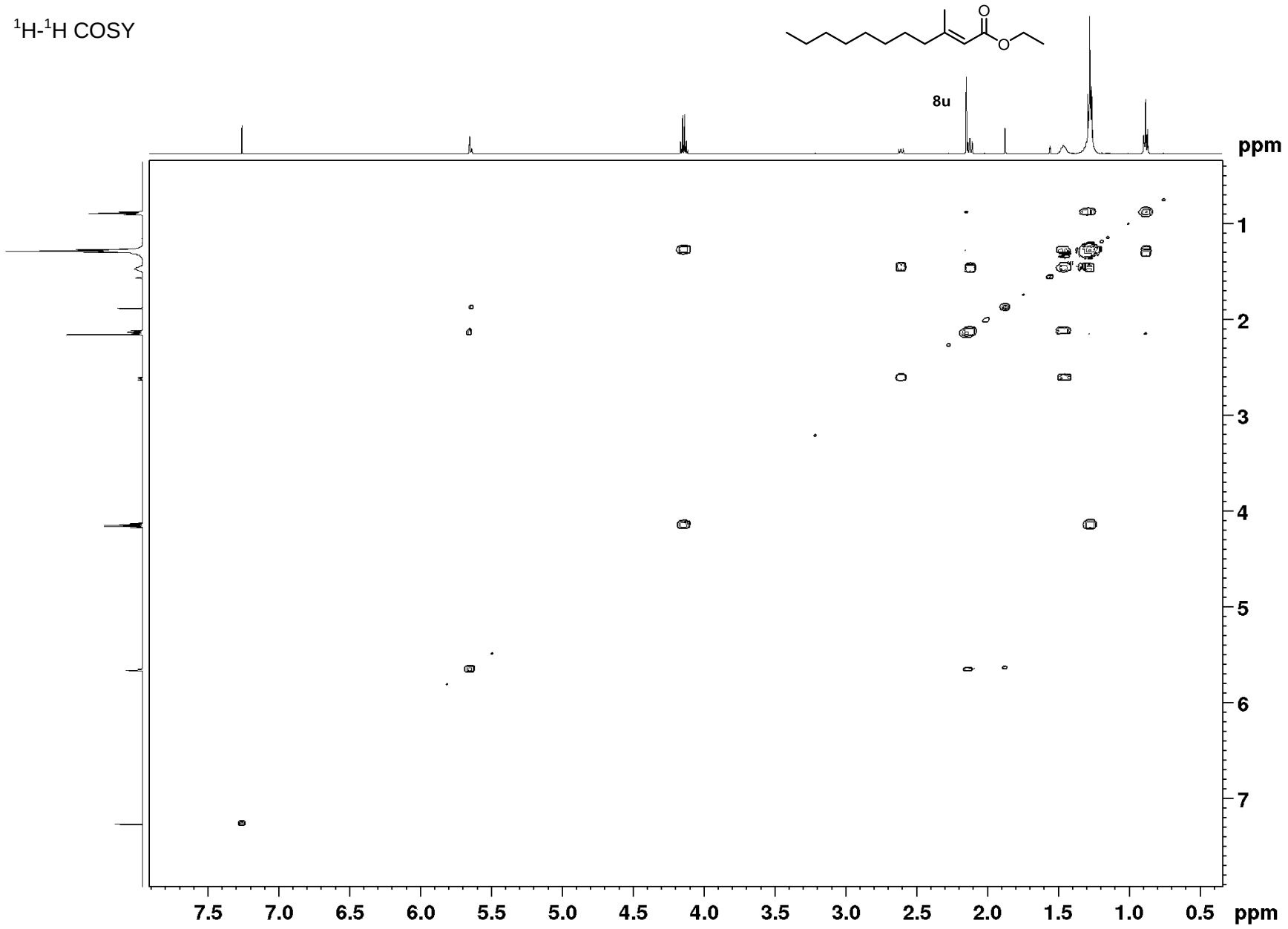
^{1}H NMR

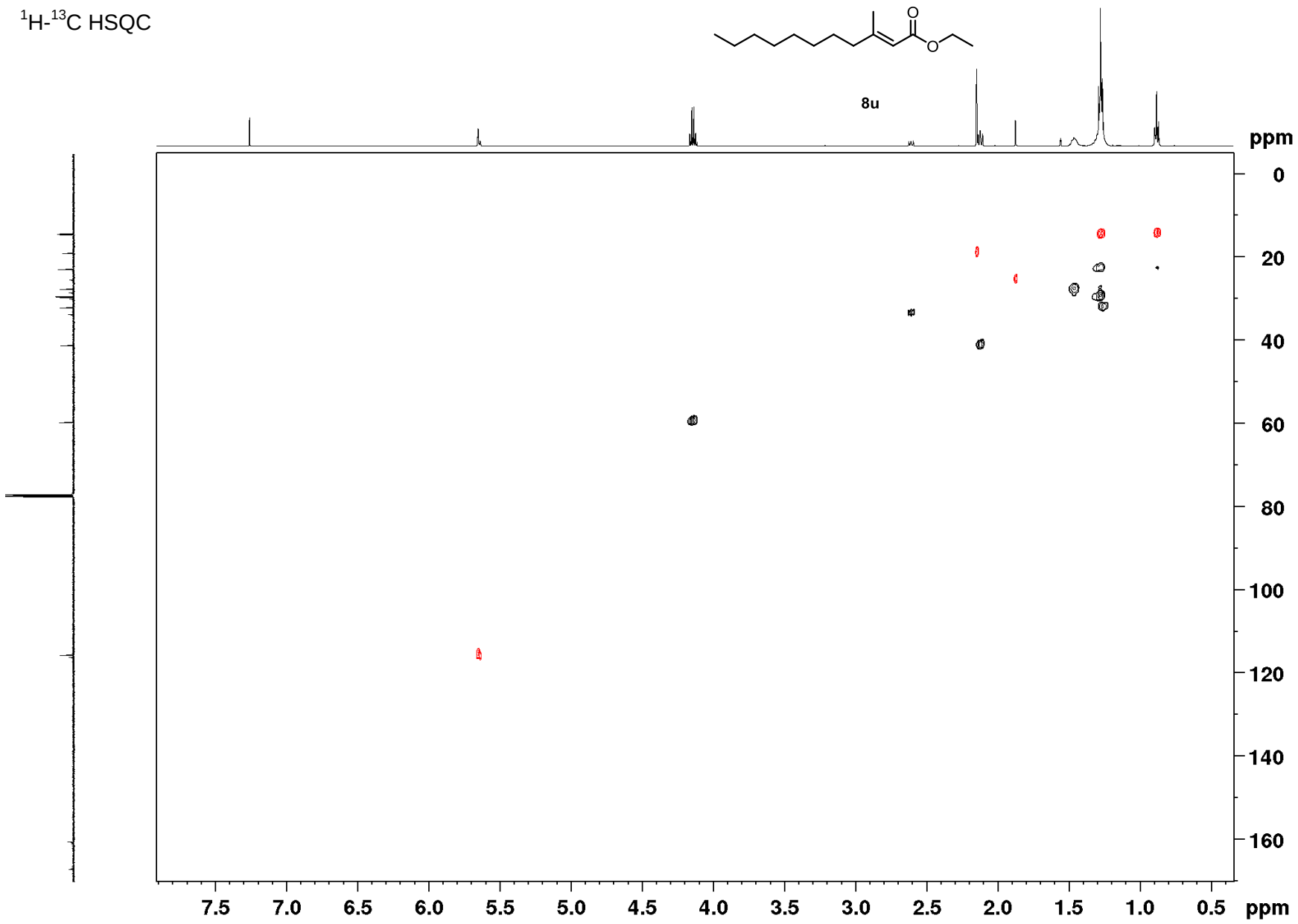


^{13}C NMR

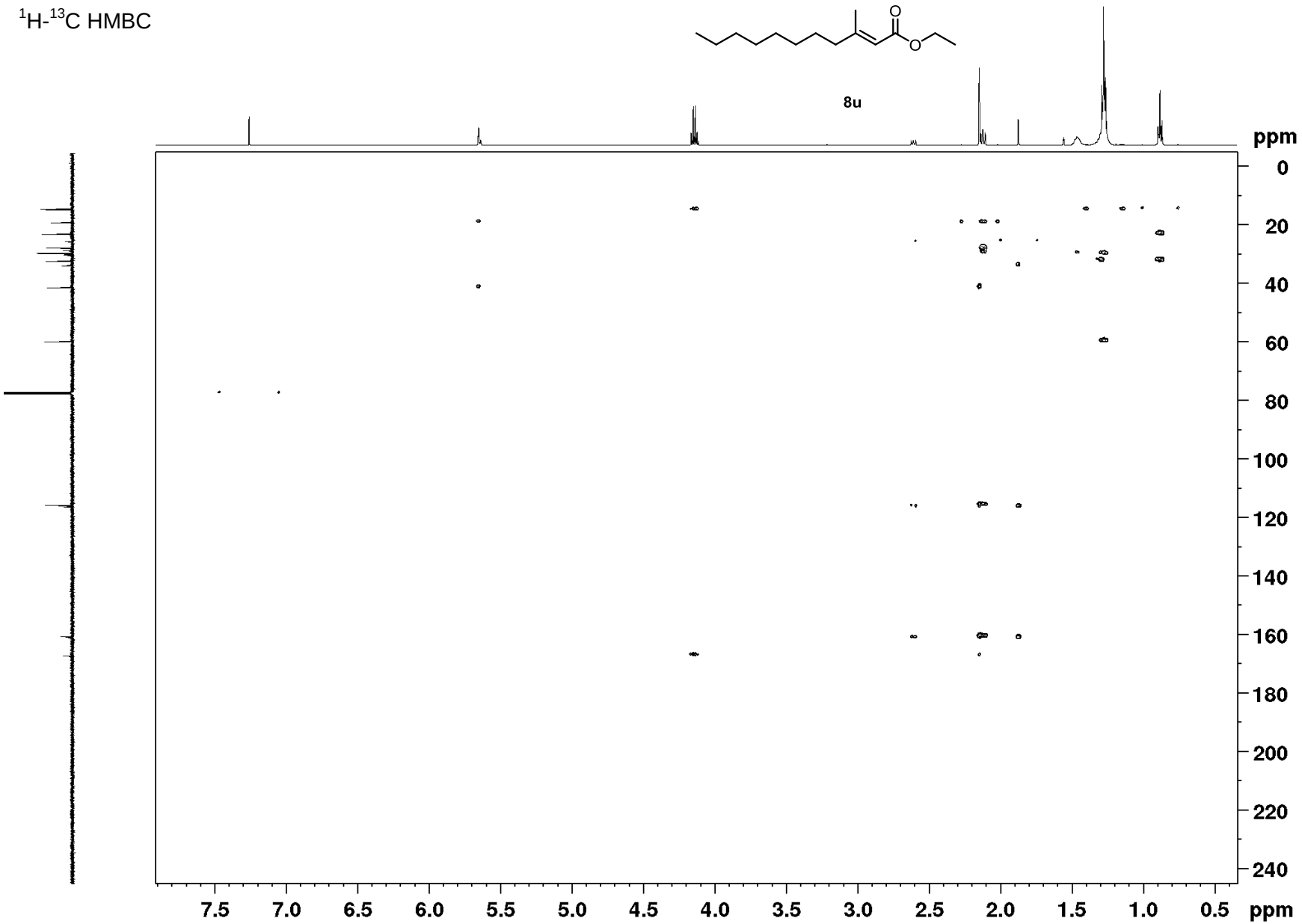

167.1
160.9
160.5
116.1
115.5
59.5
59.5
41.1
33.5
32.0
29.9
29.6
29.5
29.4
29.3
29.3
28.4
27.5
25.3
22.8
18.8
14.5
14.2
O
O
8u
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

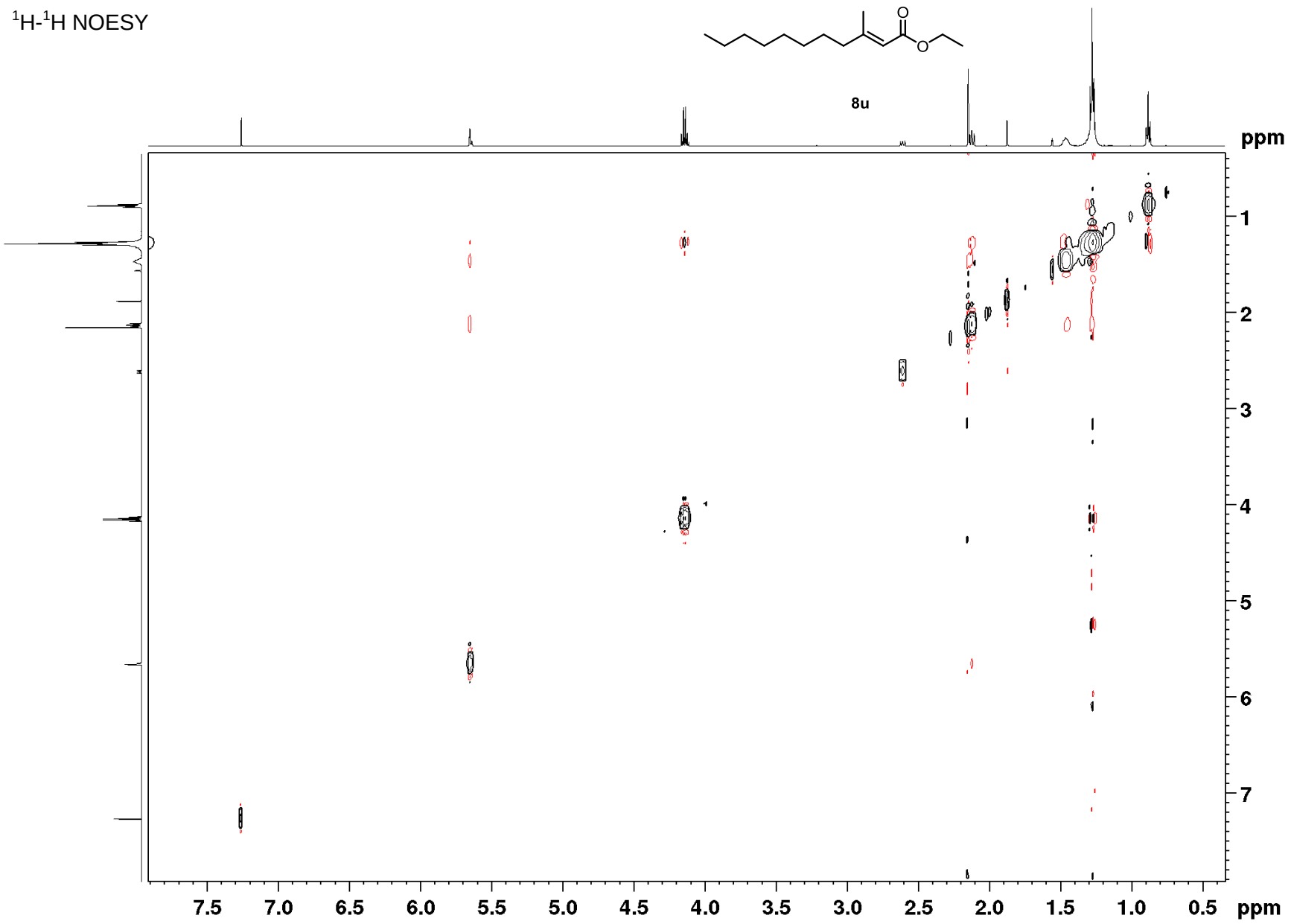
^{1}H-^{1}H COSY

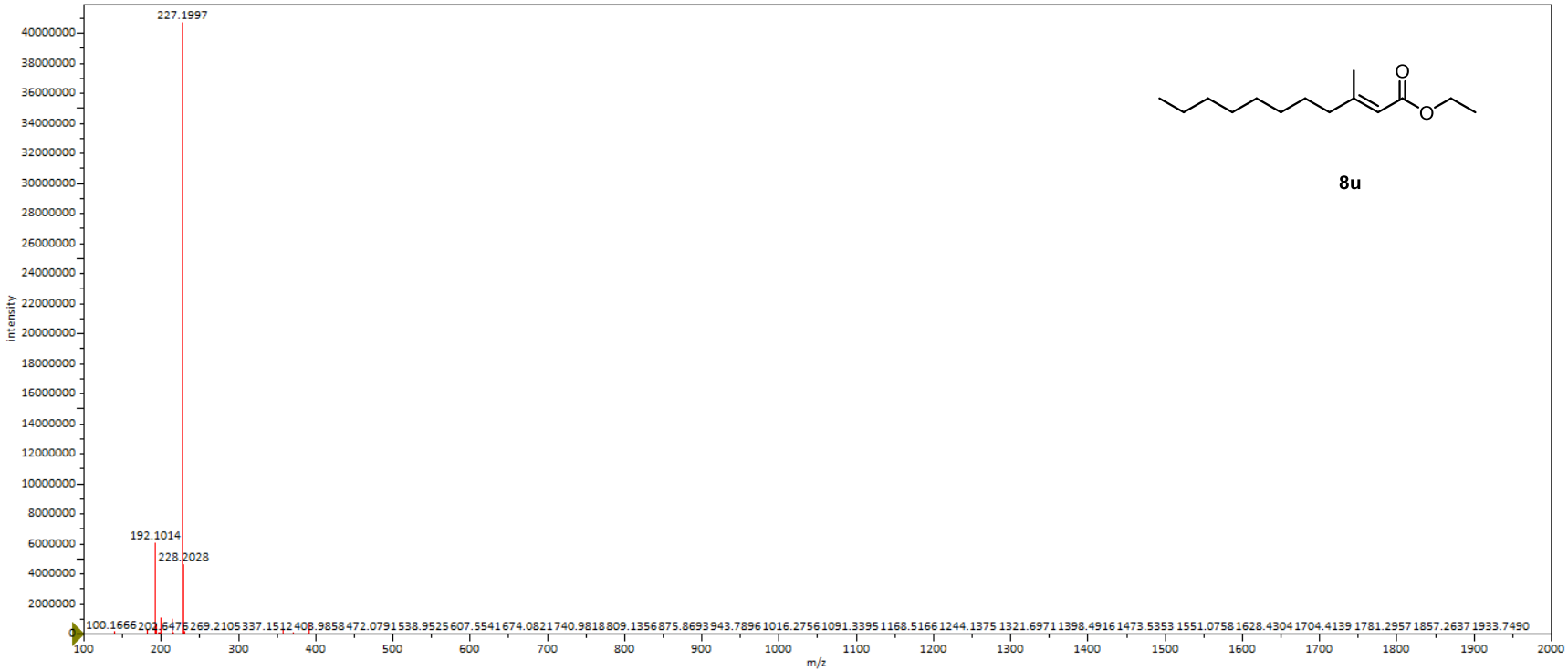



^{1}H-^{13}C HSQC
O
O
8u
ppm
0
20
40
60
80
100
120
140
160
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{1}H-^{13}C HMBC

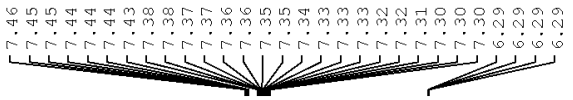

8u
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

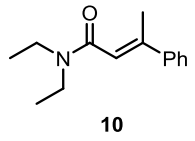

^{1}H-^{1}H NOESY
8u
ppm
1
2
3
4
5
6
7
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


227.1997
192.1014
228.2028
intensity
m/z
8u

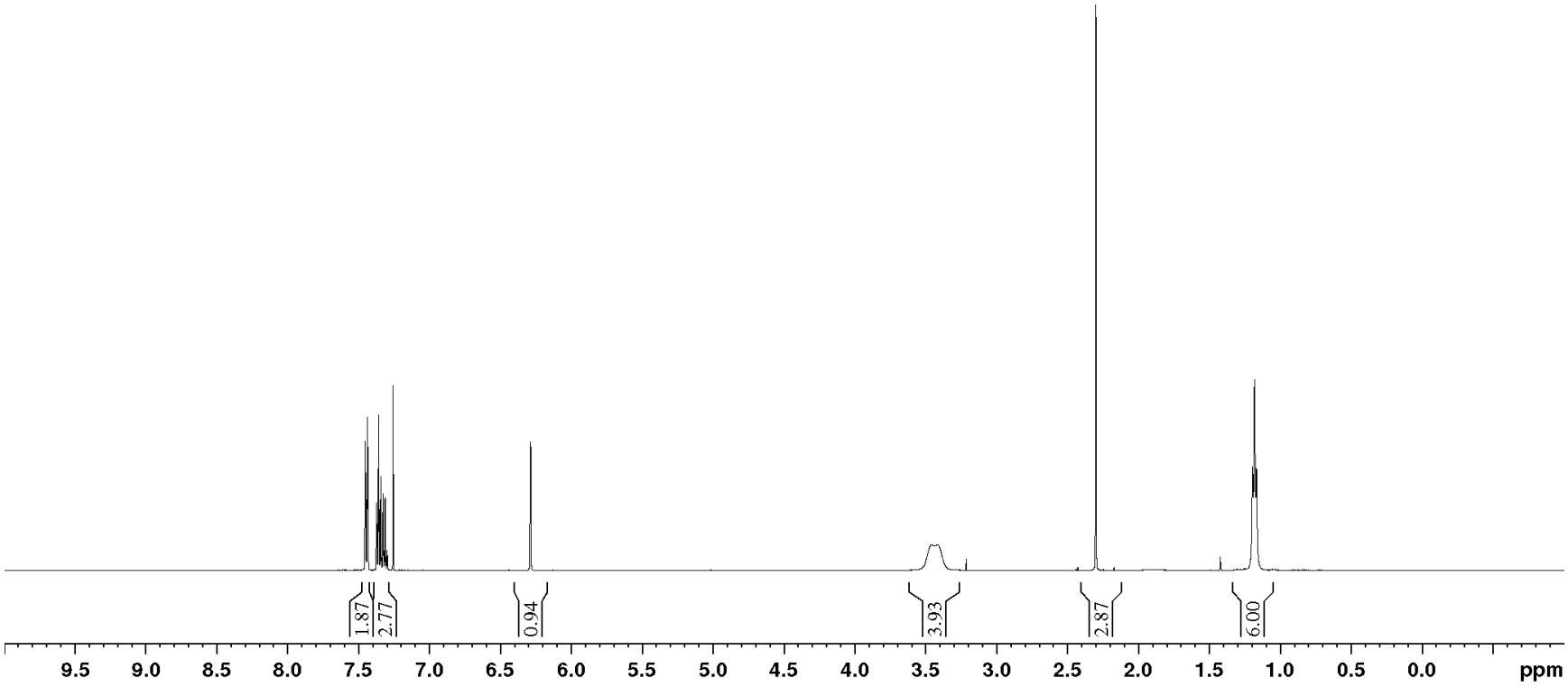
(*E*)-N,N-diethyl-3-phenylbut-2-enamide (10)

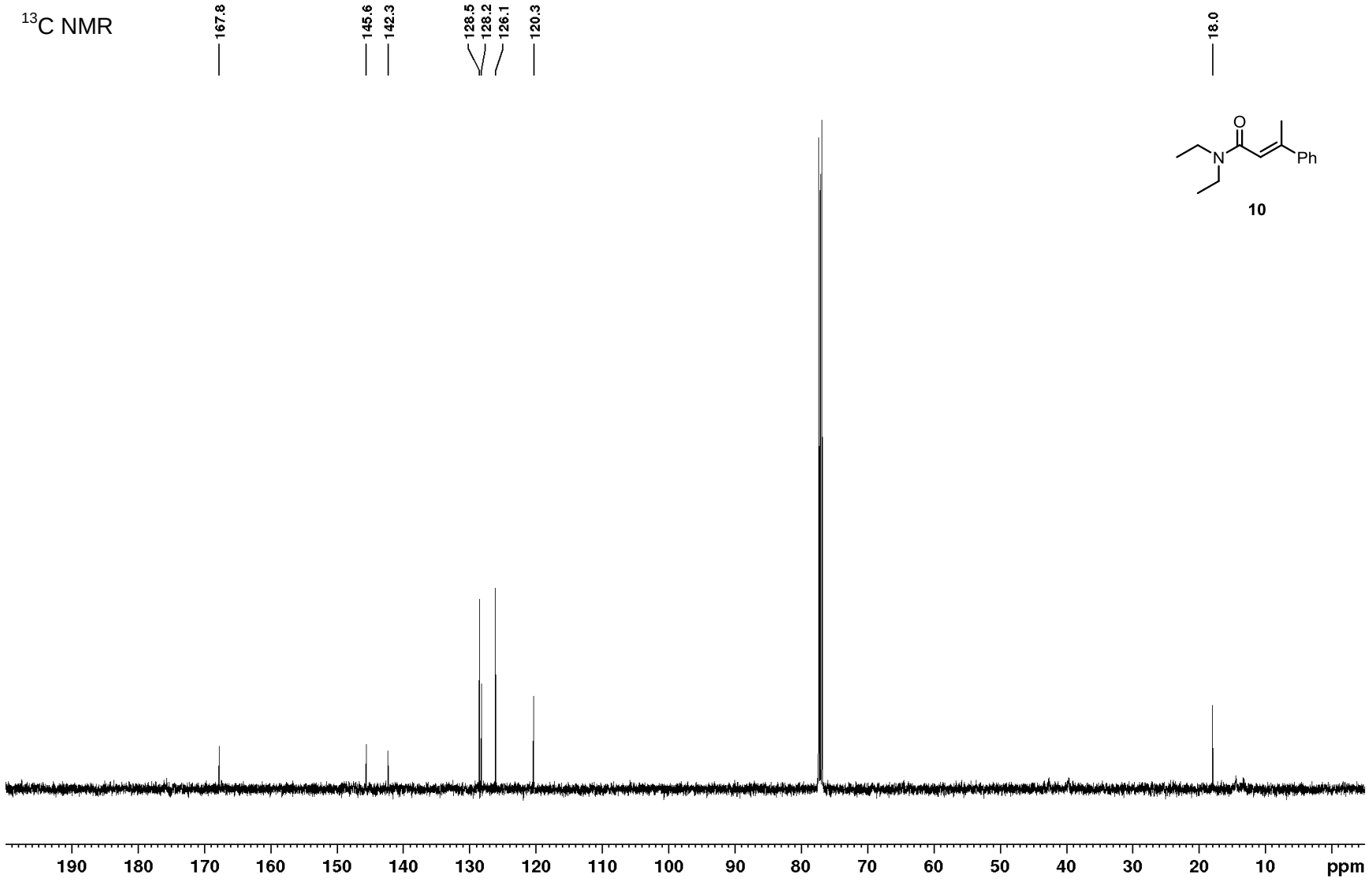
^{1}H NMR



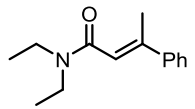


10

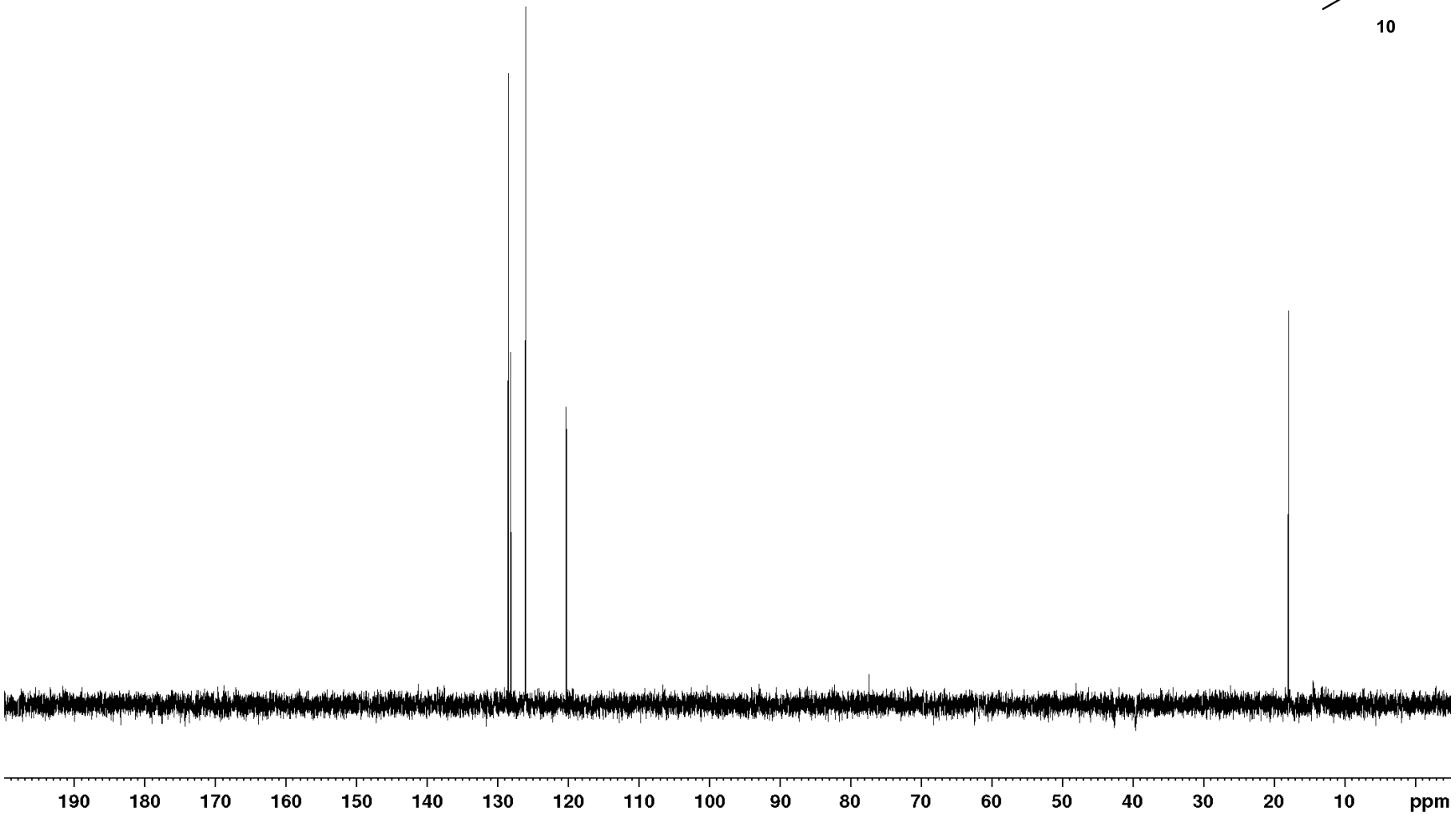



^{13}C NMR
167.8
145.6
142.3
128.5
128.2
126.1
120.3
18.0
O
N
Ph
10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

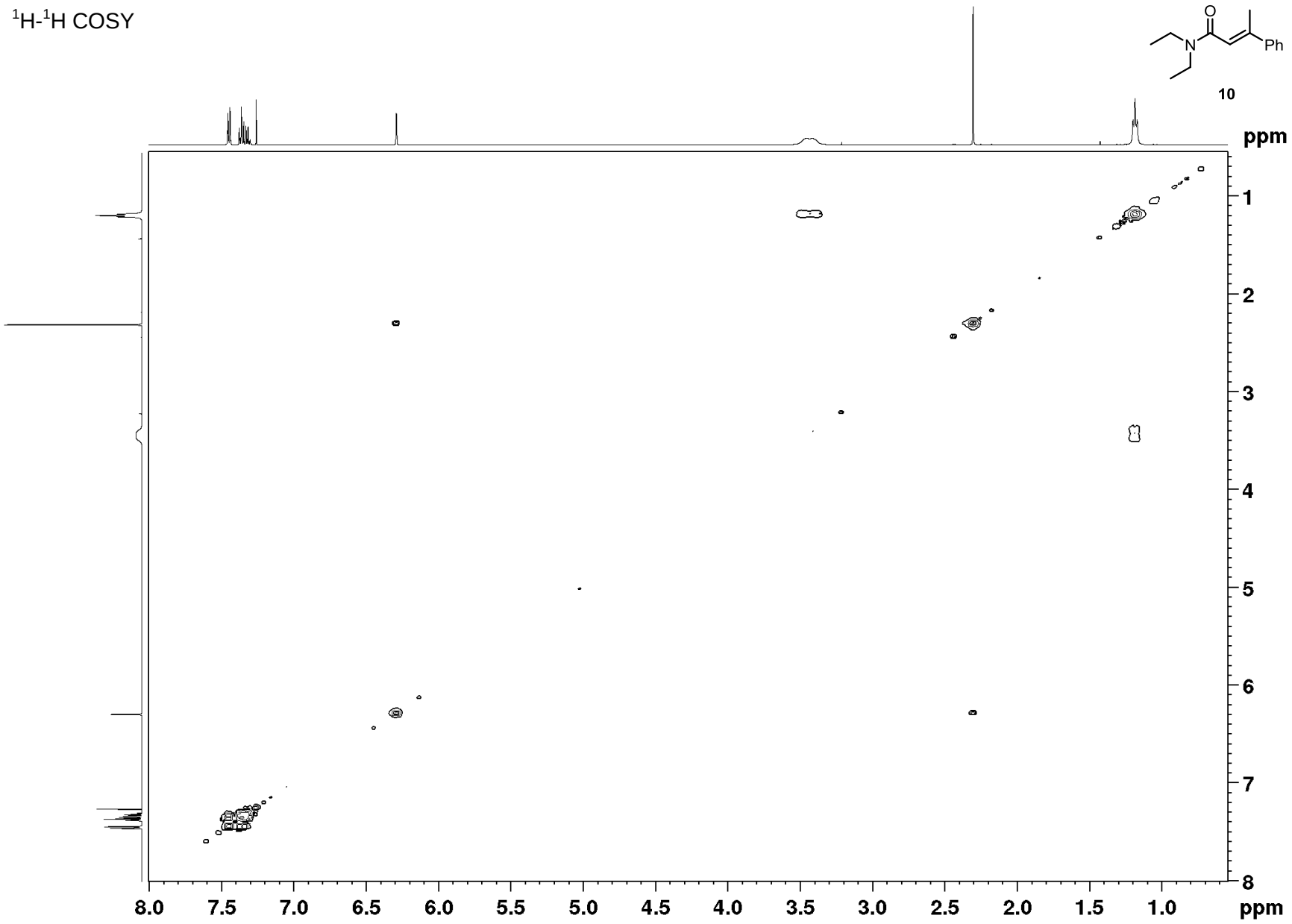
^{13}C DEPT NMR



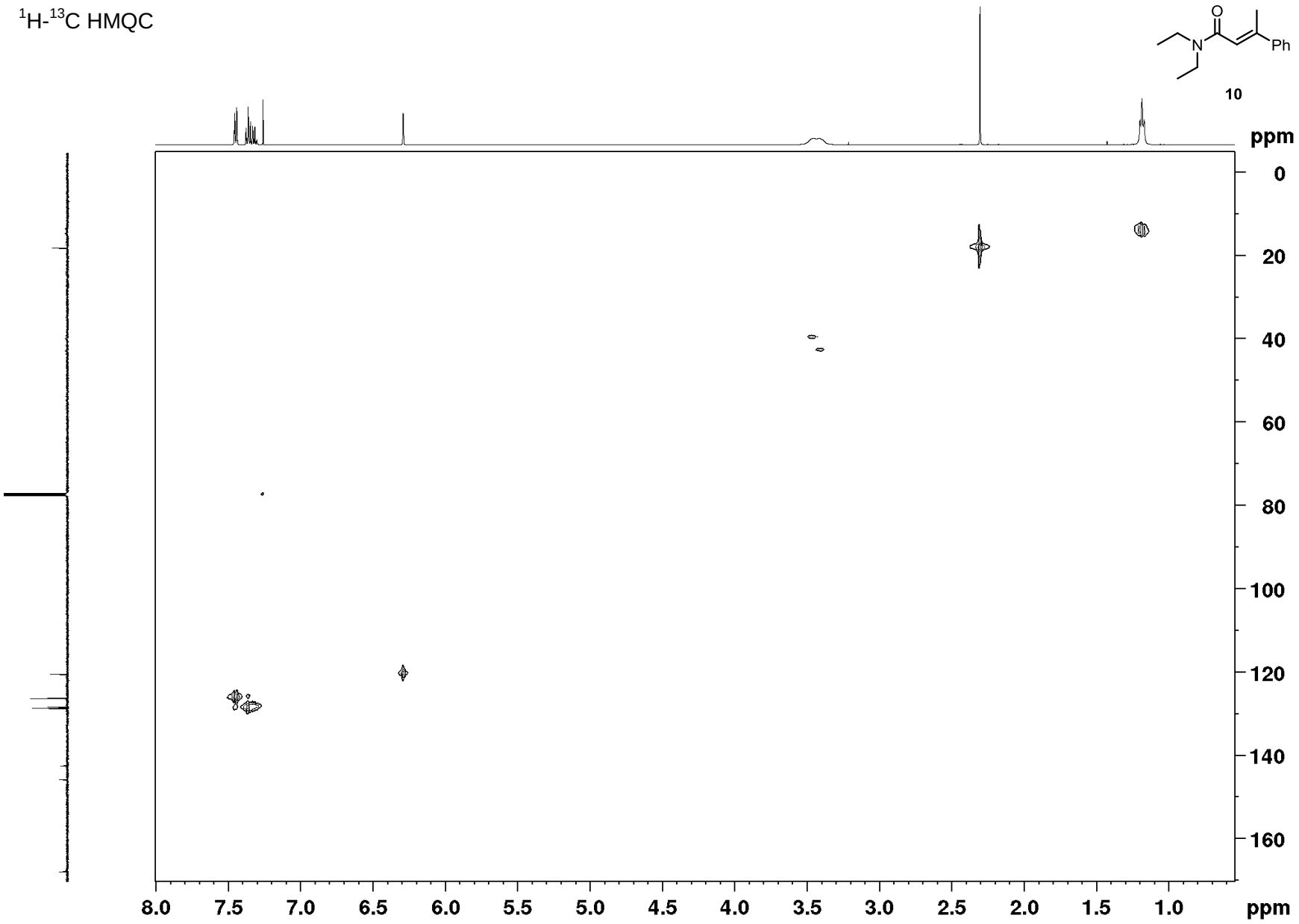
10



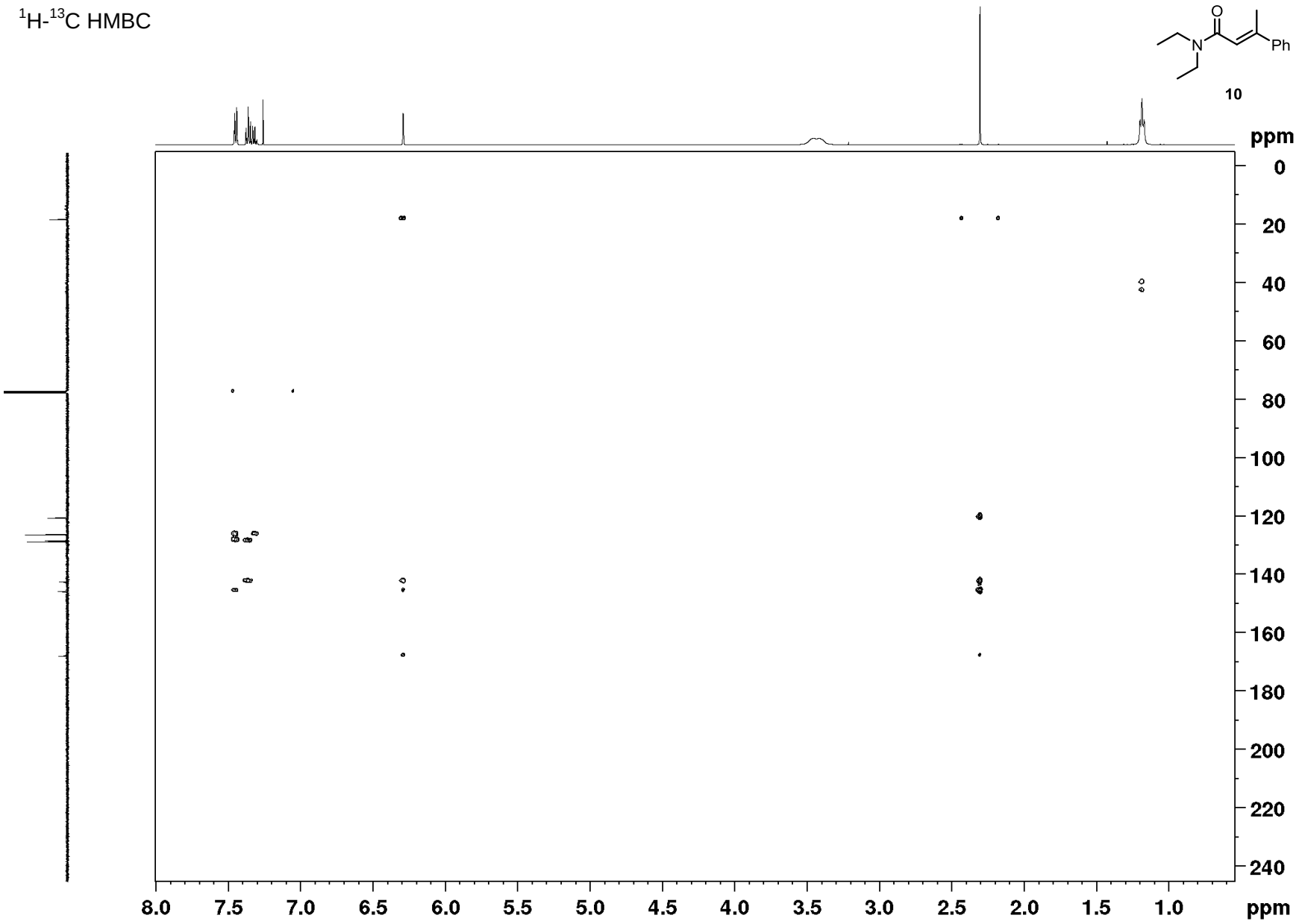
^{1}H-^{1}H COSY


O
N
Ph
10
ppm
1
2
3
4
5
6
7
8
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
ppm

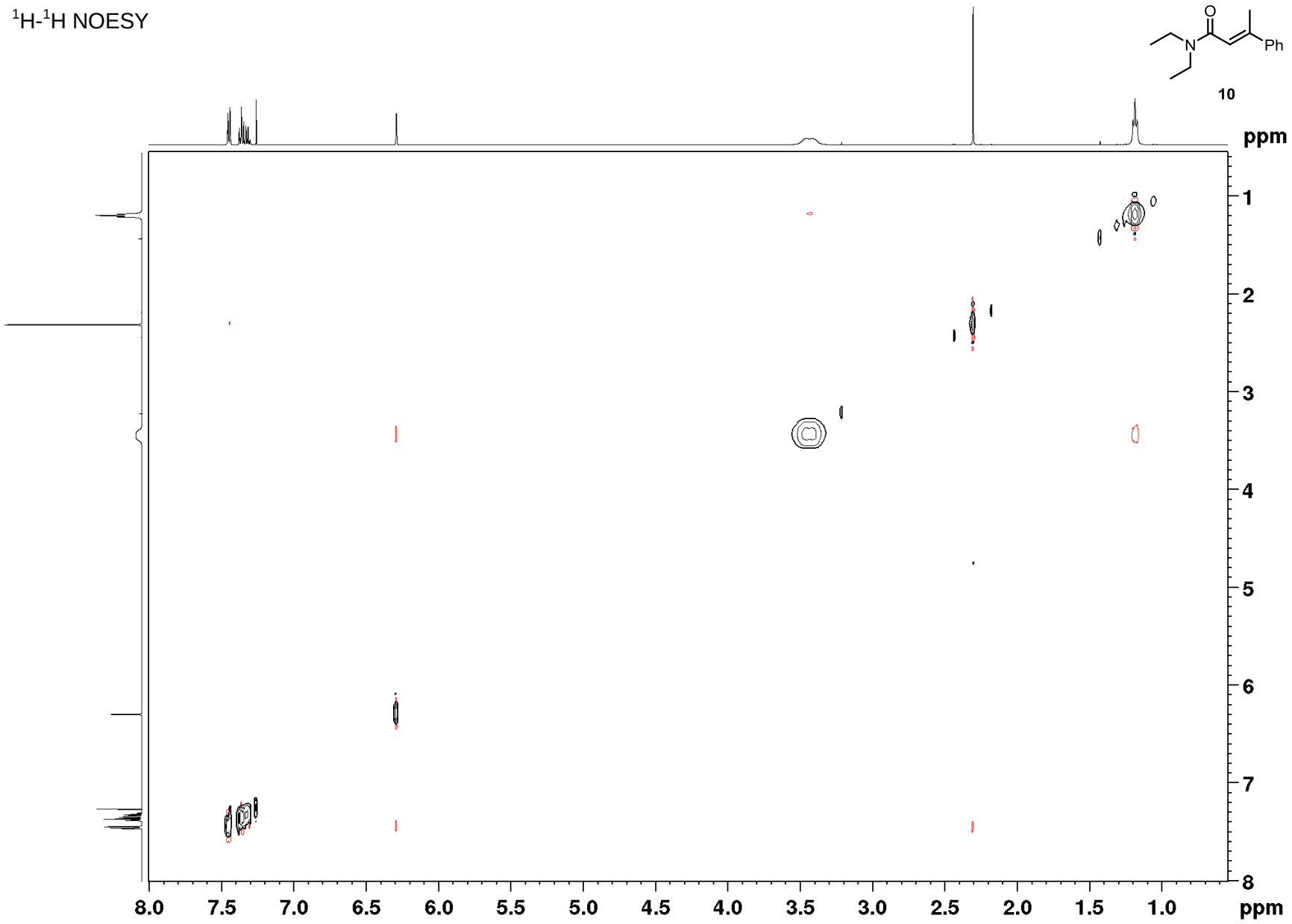
^{1}H-^{13}C HMQC

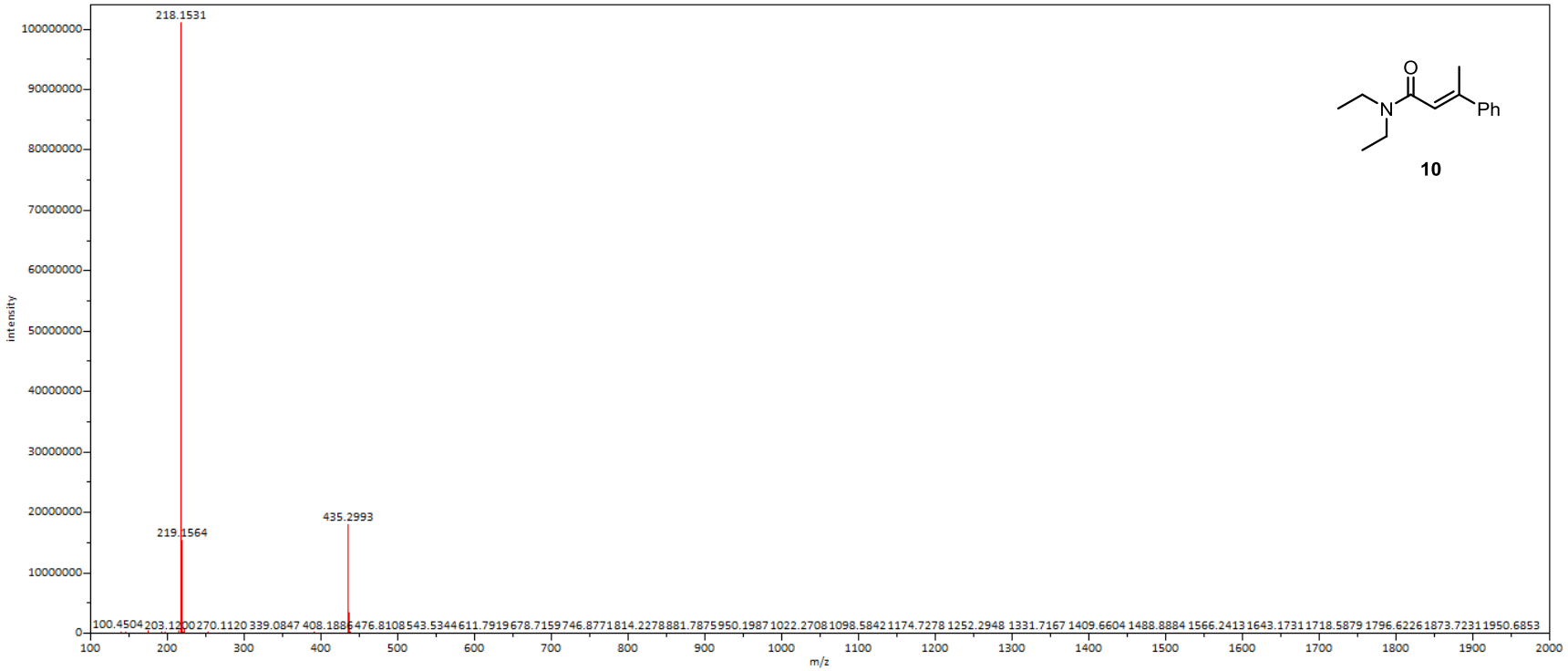

O
N
Ph
10
ppm
0
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

^{1}H-^{13}C HMBC


O
N
Ph
10
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

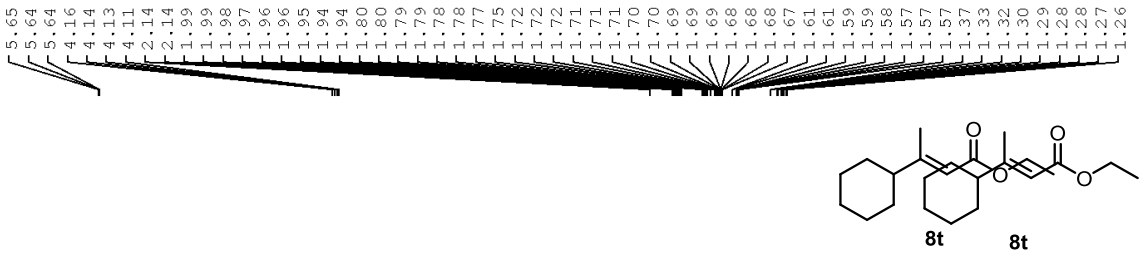
^{1}H-^{1}H NOESY

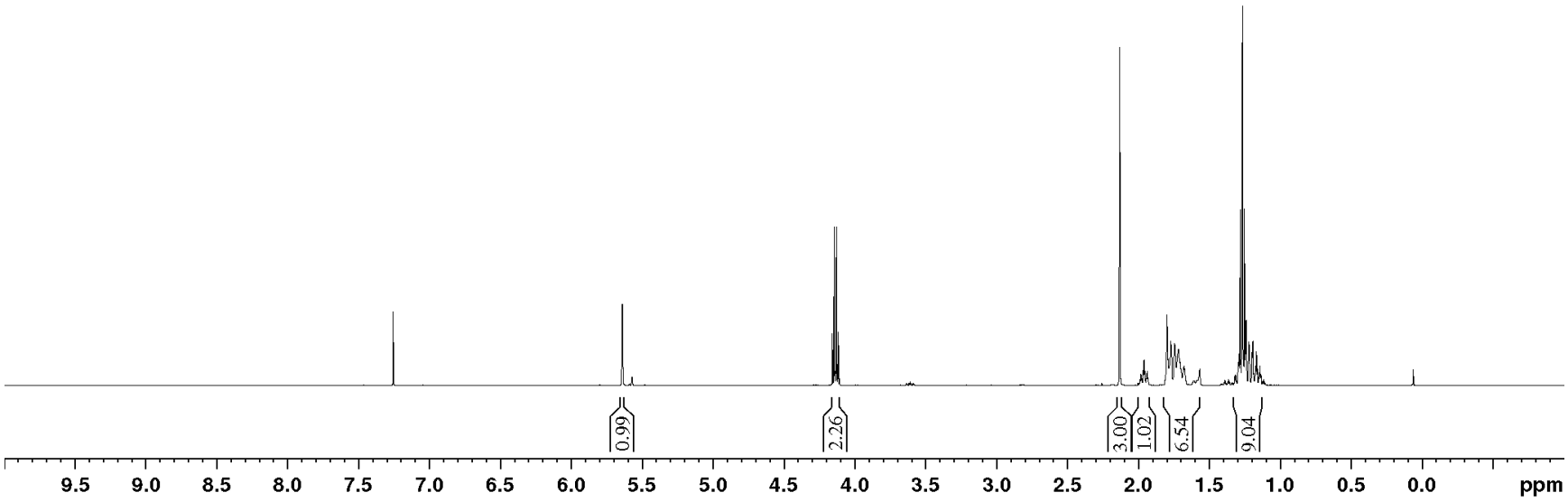

O
N
Ph
10
ppm
1
2
3
4
5
6
7
8
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


218.1531
219.1564
435.2993
intensity
m/z
10

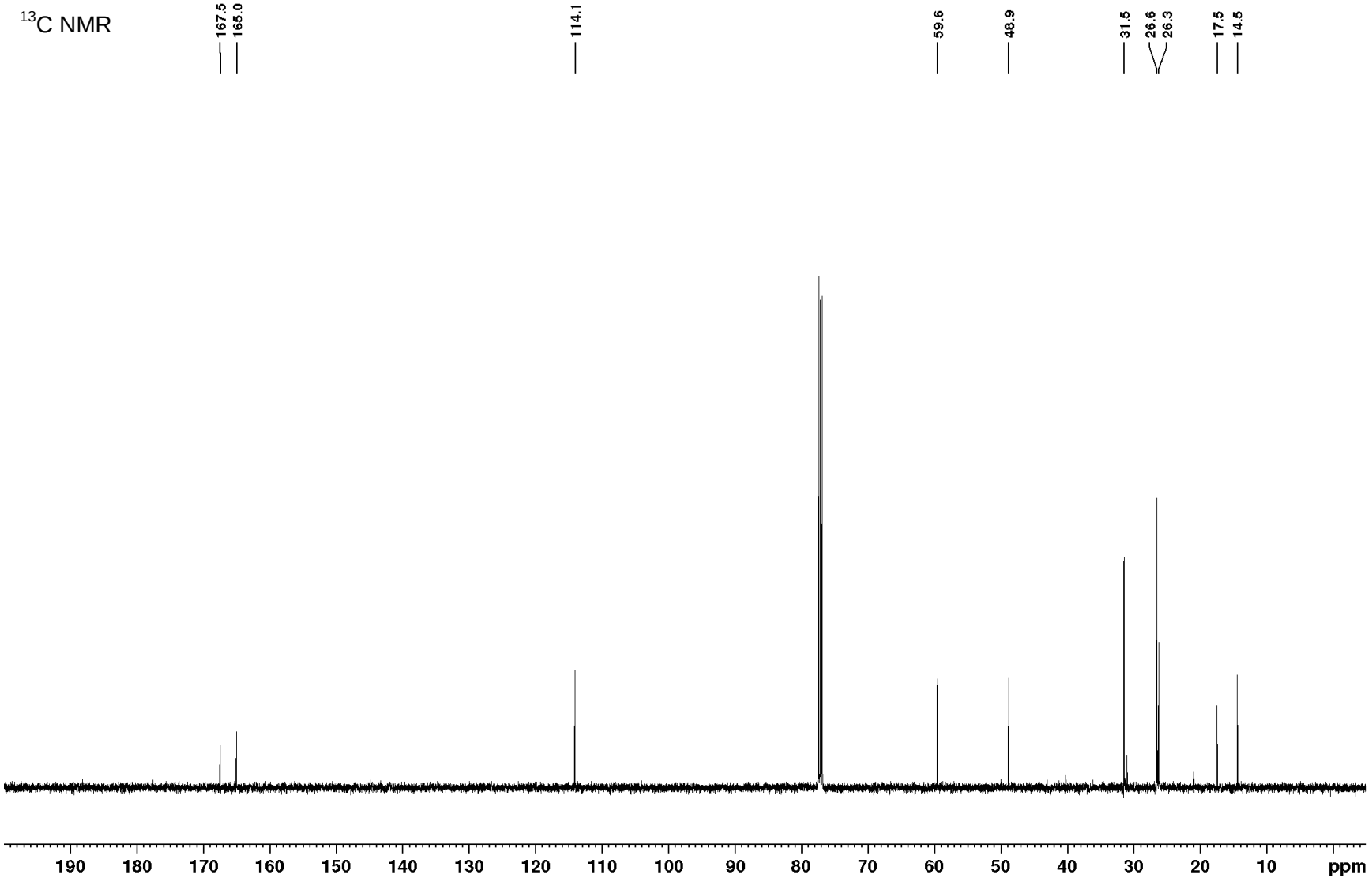
Ethyl (*E*)-3-cyclohexylbut-2-enoate (8t)

^{1}H NMR

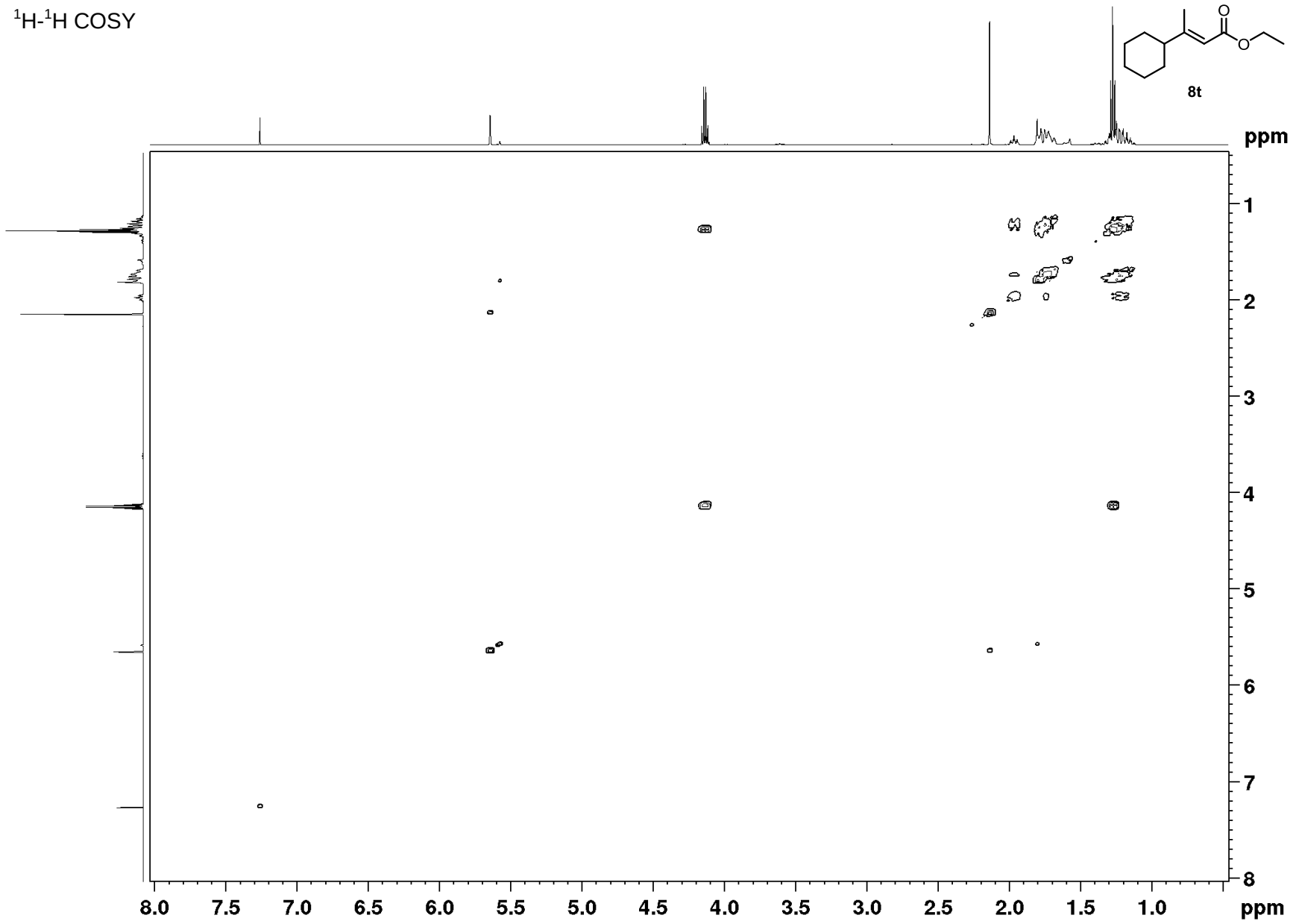




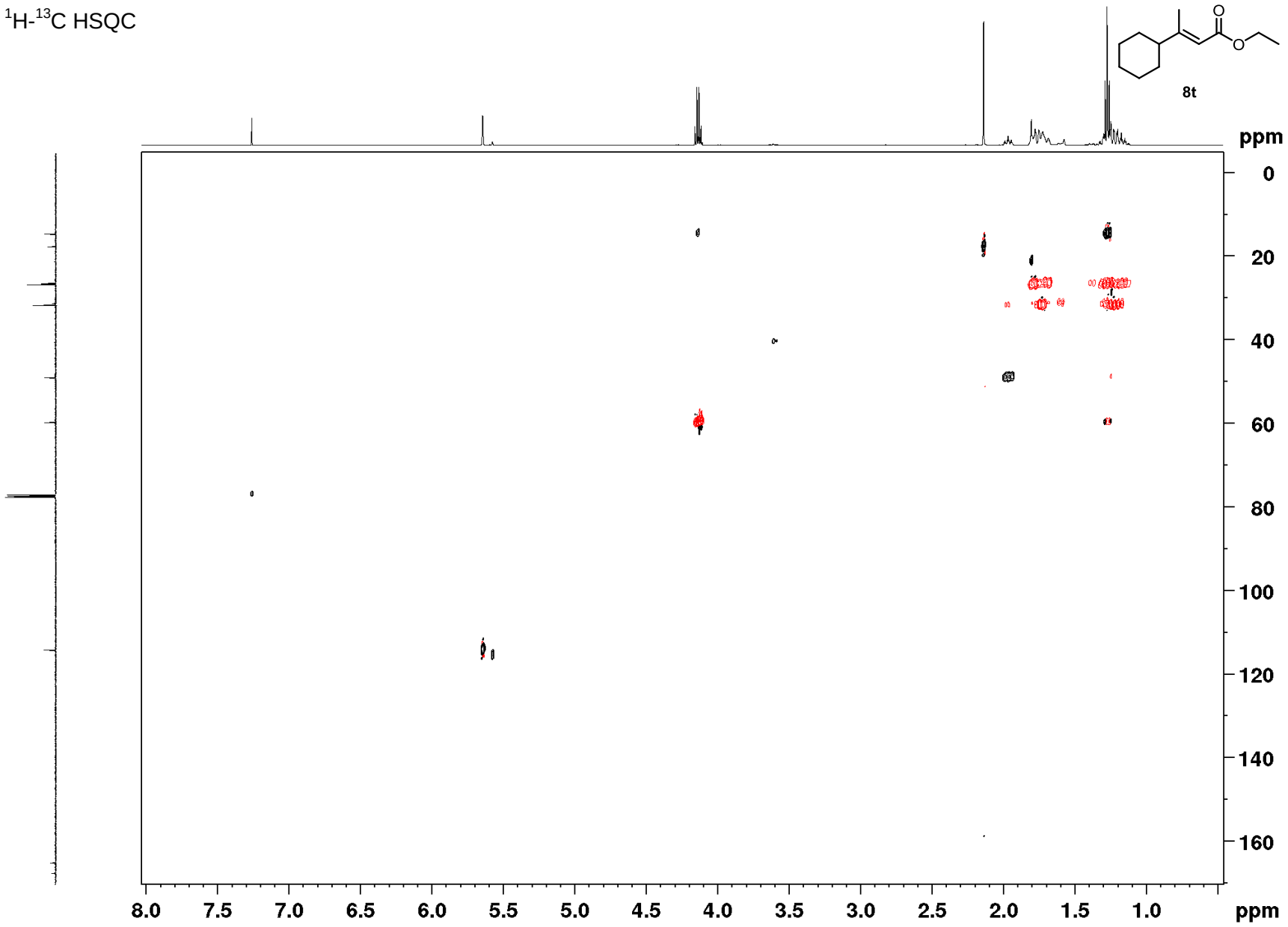
^{13}C NMR


167.5
165.0
114.1
59.6
48.9
31.5
26.6
26.3
17.5
14.5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

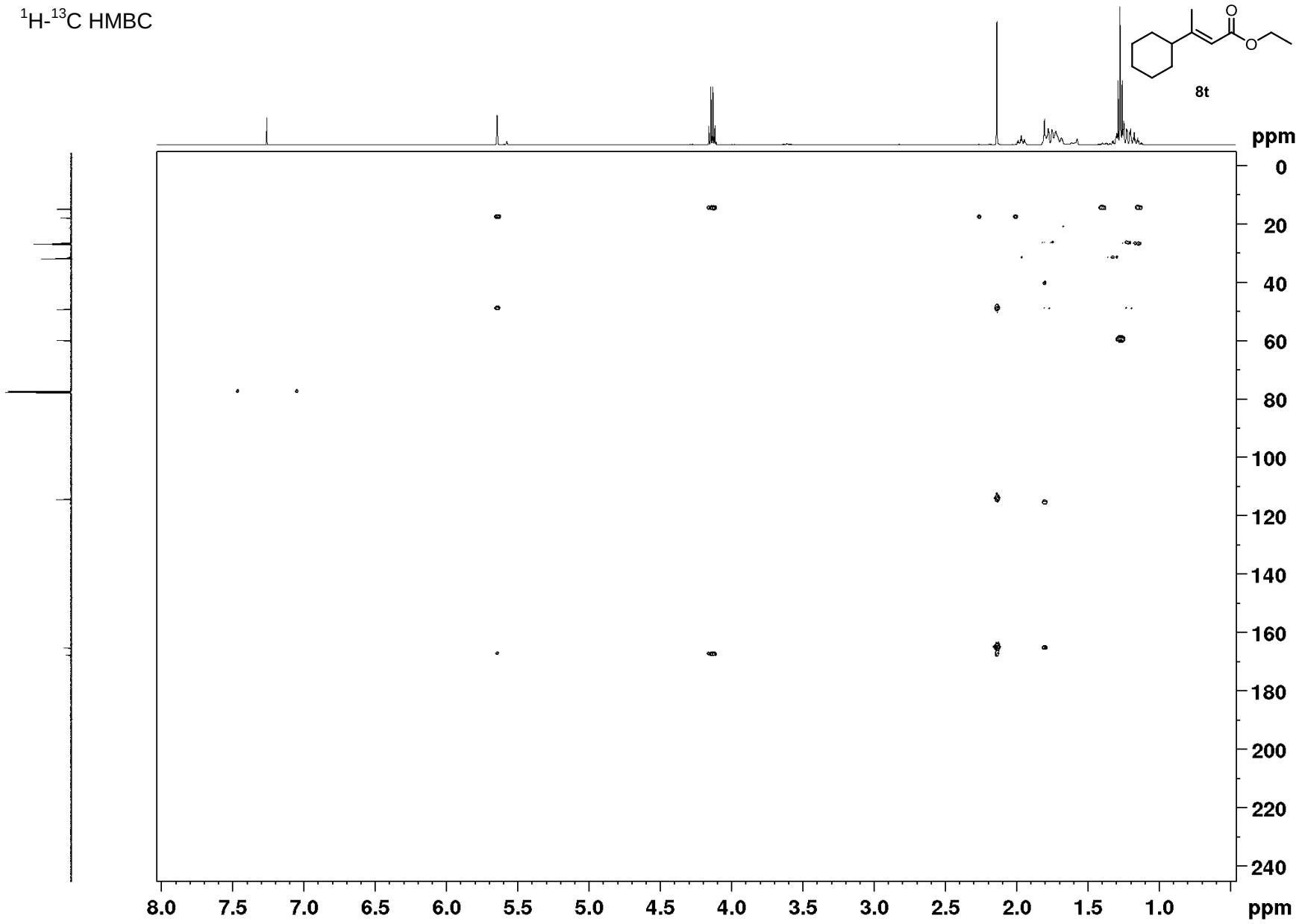
^{1}H-^{1}H COSY



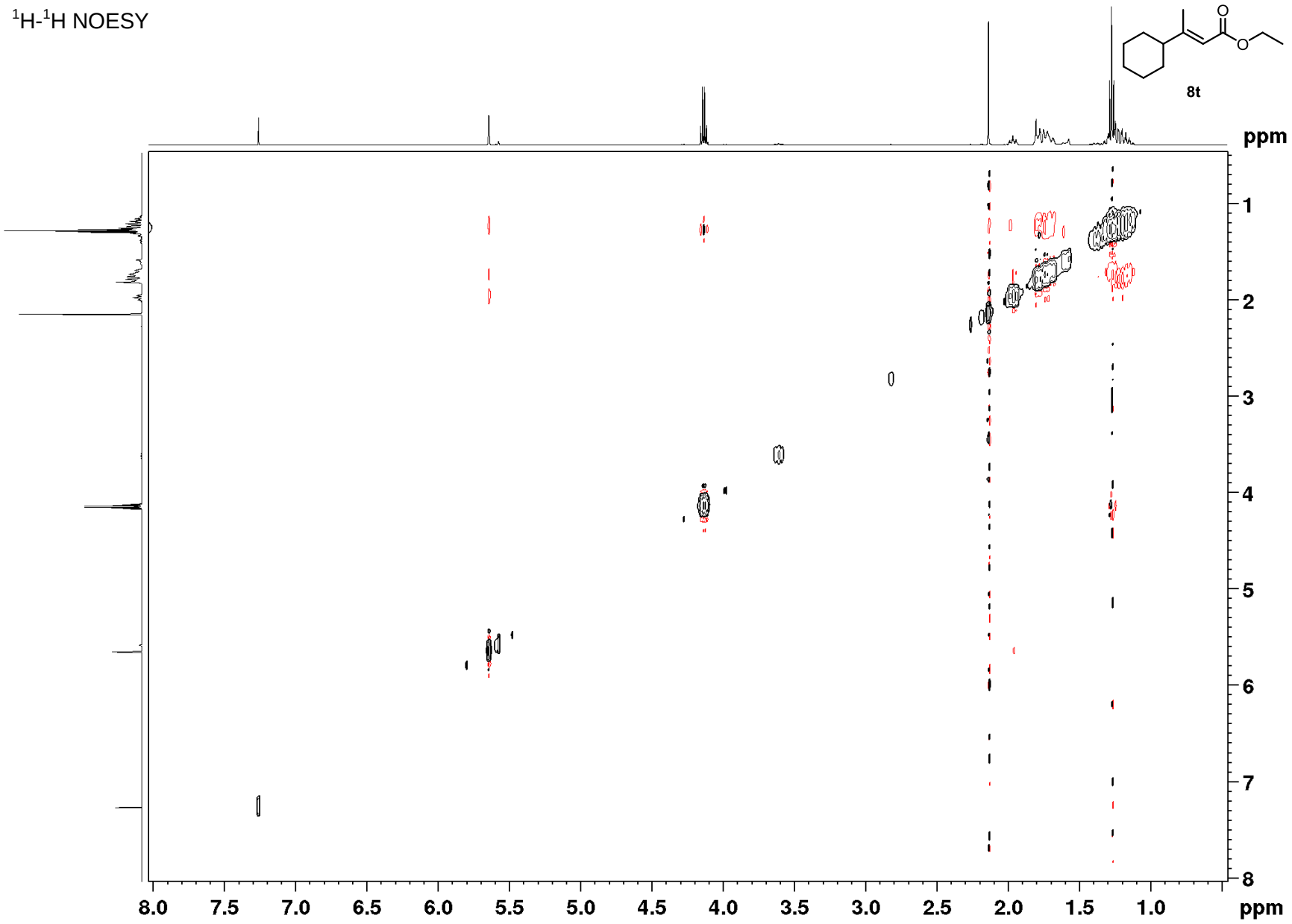
^{1}H-^{13}C HSQC

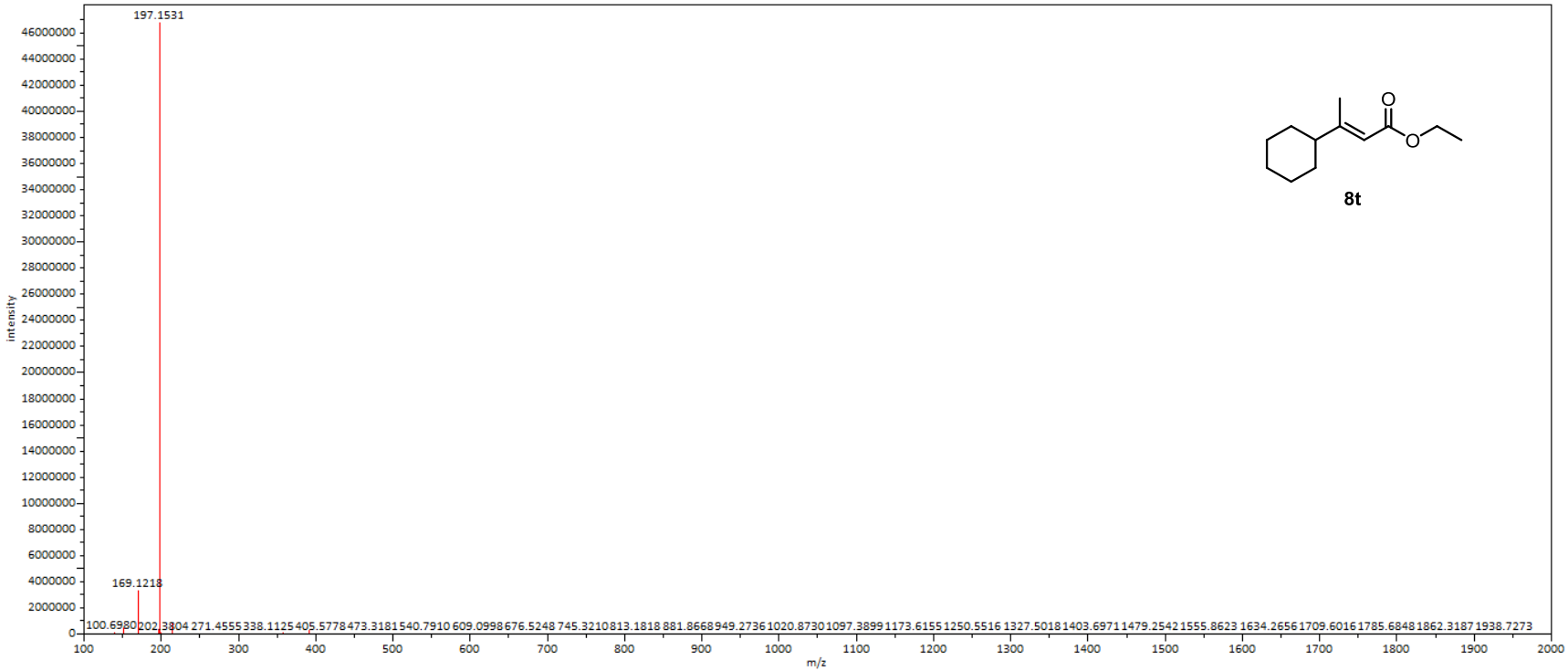

8t
ppm
0
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

^{1}H-^{13}C HMBC


8t
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

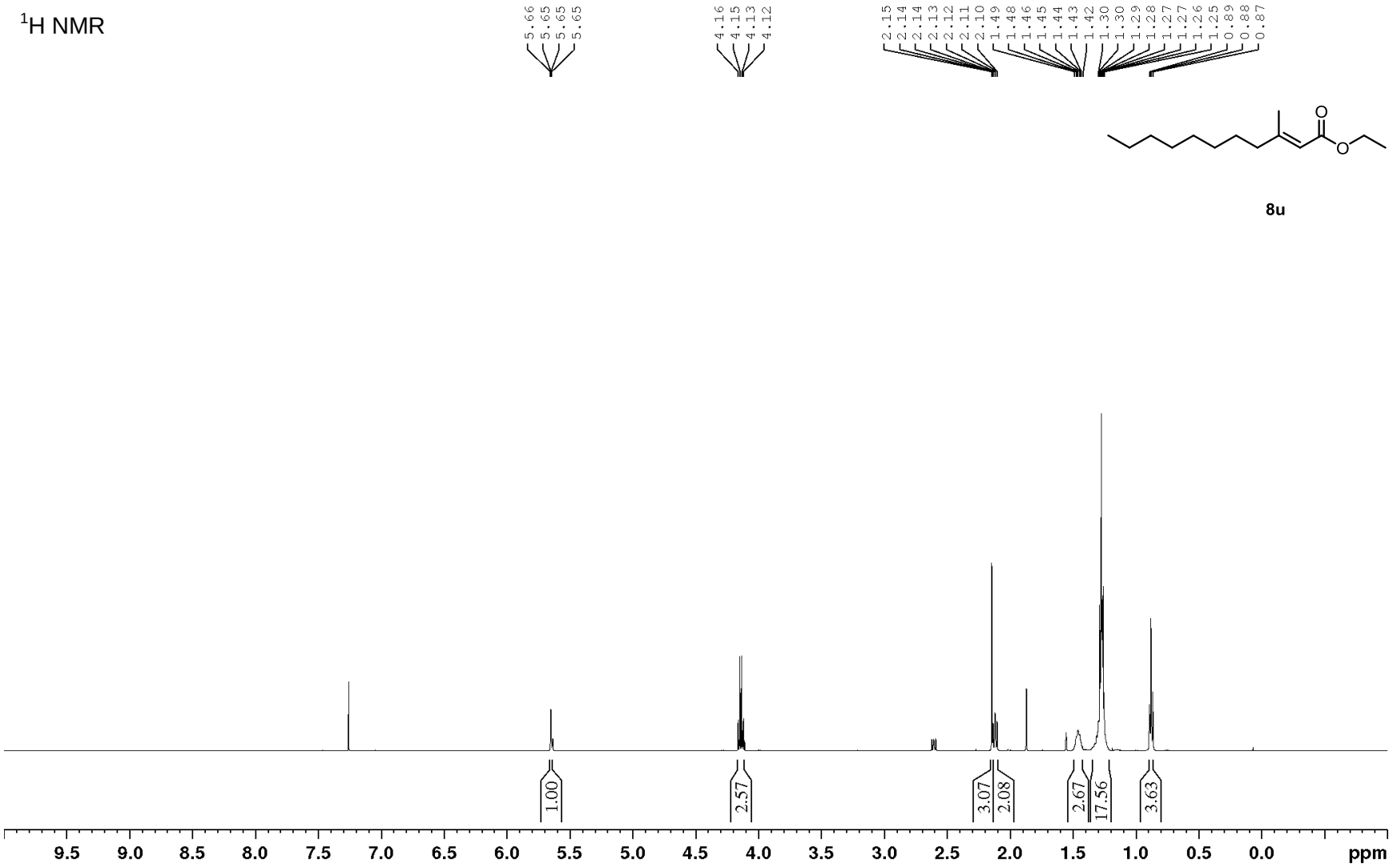
^{1}H-^{1}H NOESY



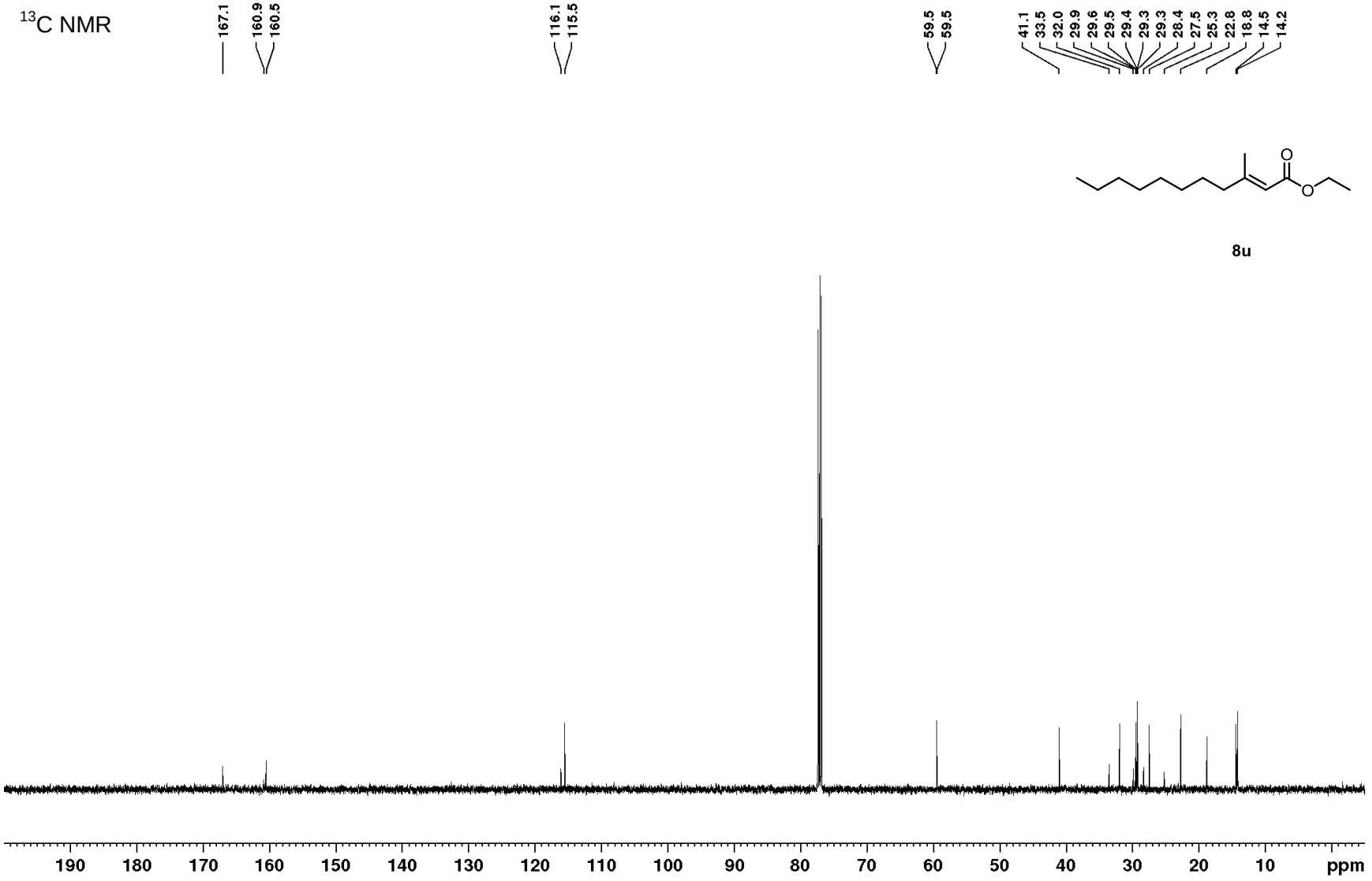

197.1531
169.1218
intensity
m/z
8t

Ethyl (*E*)-3-methylundec-2-enoate (8u)

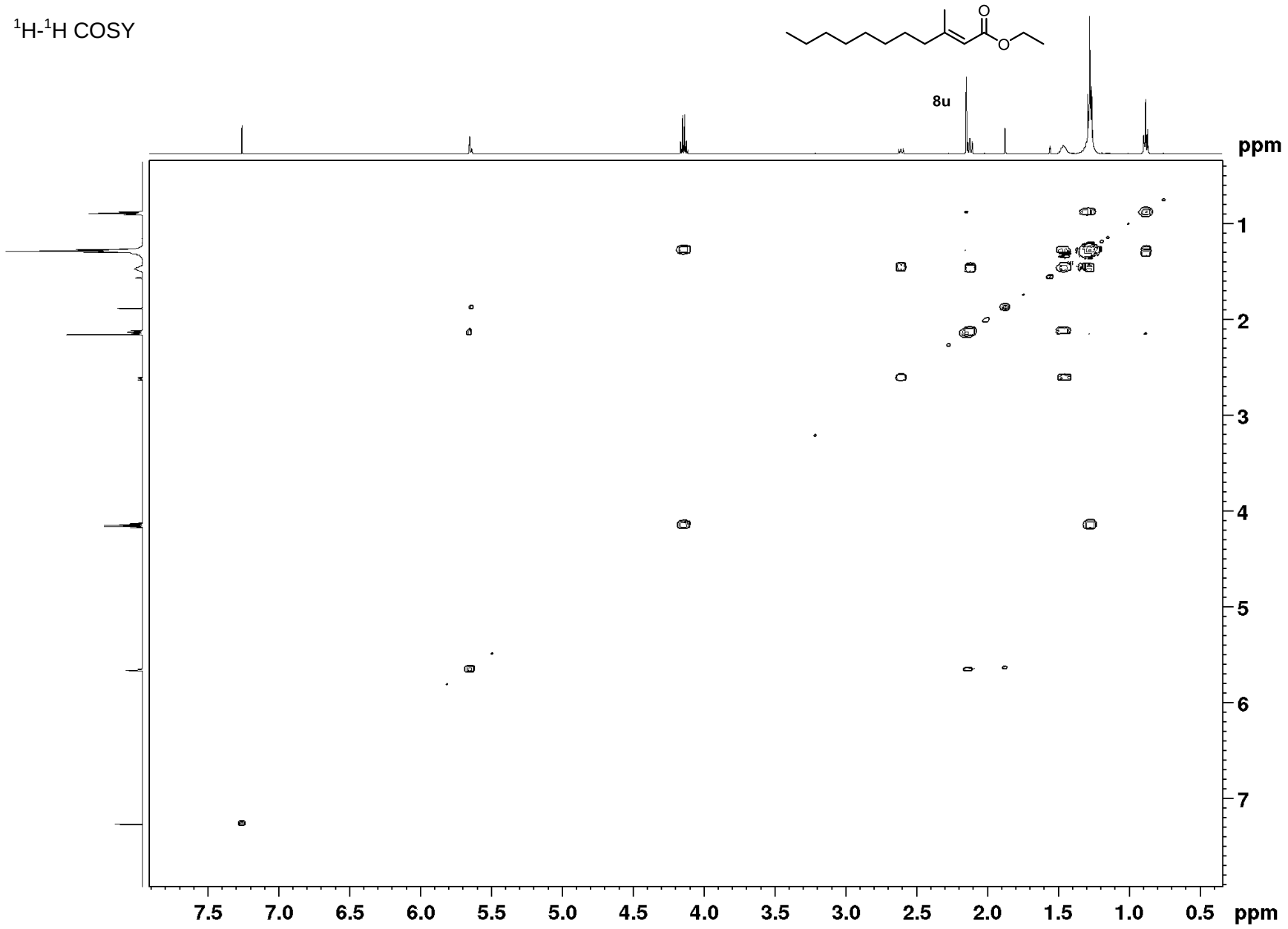
^{1}H NMR

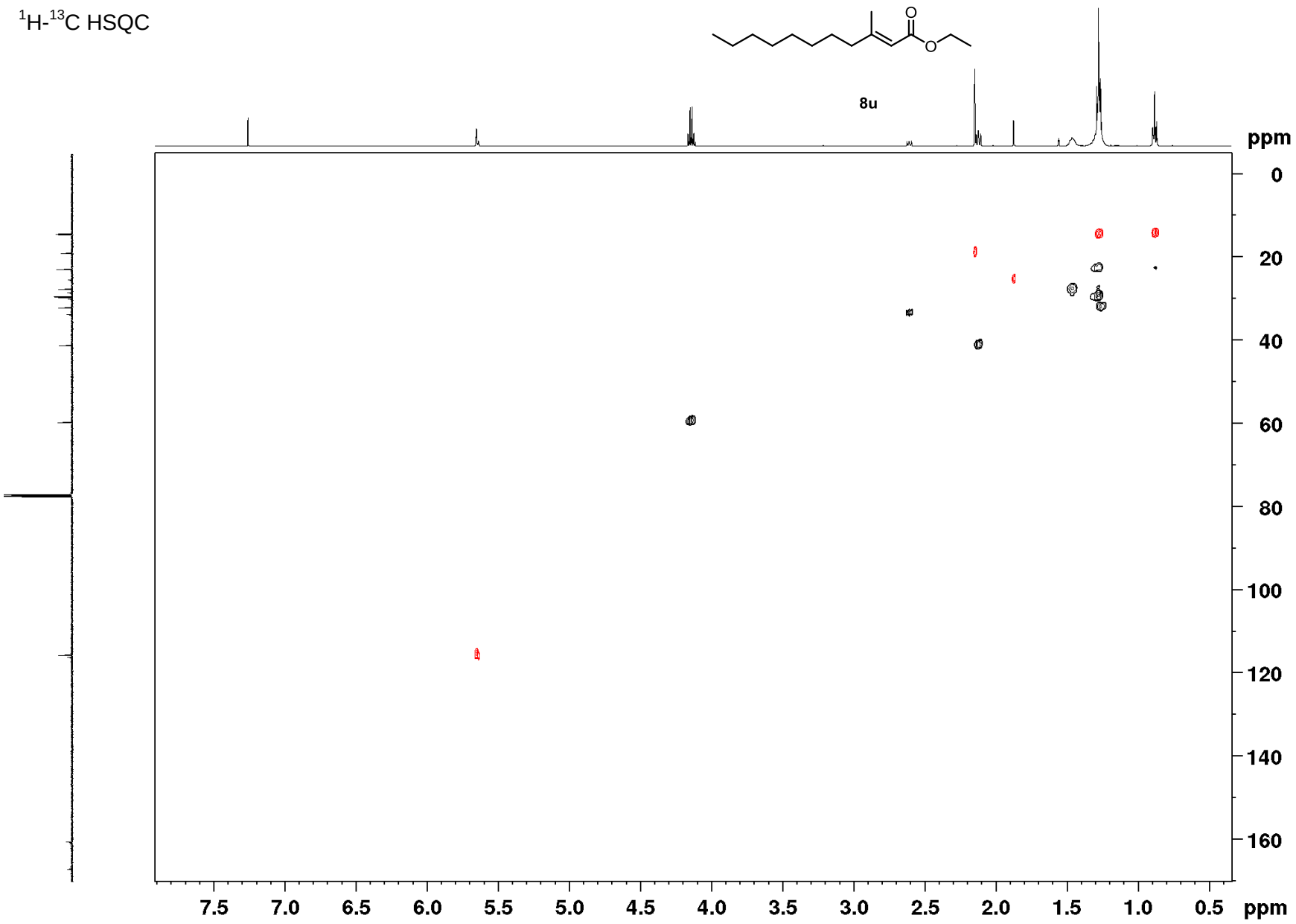


^{13}C NMR

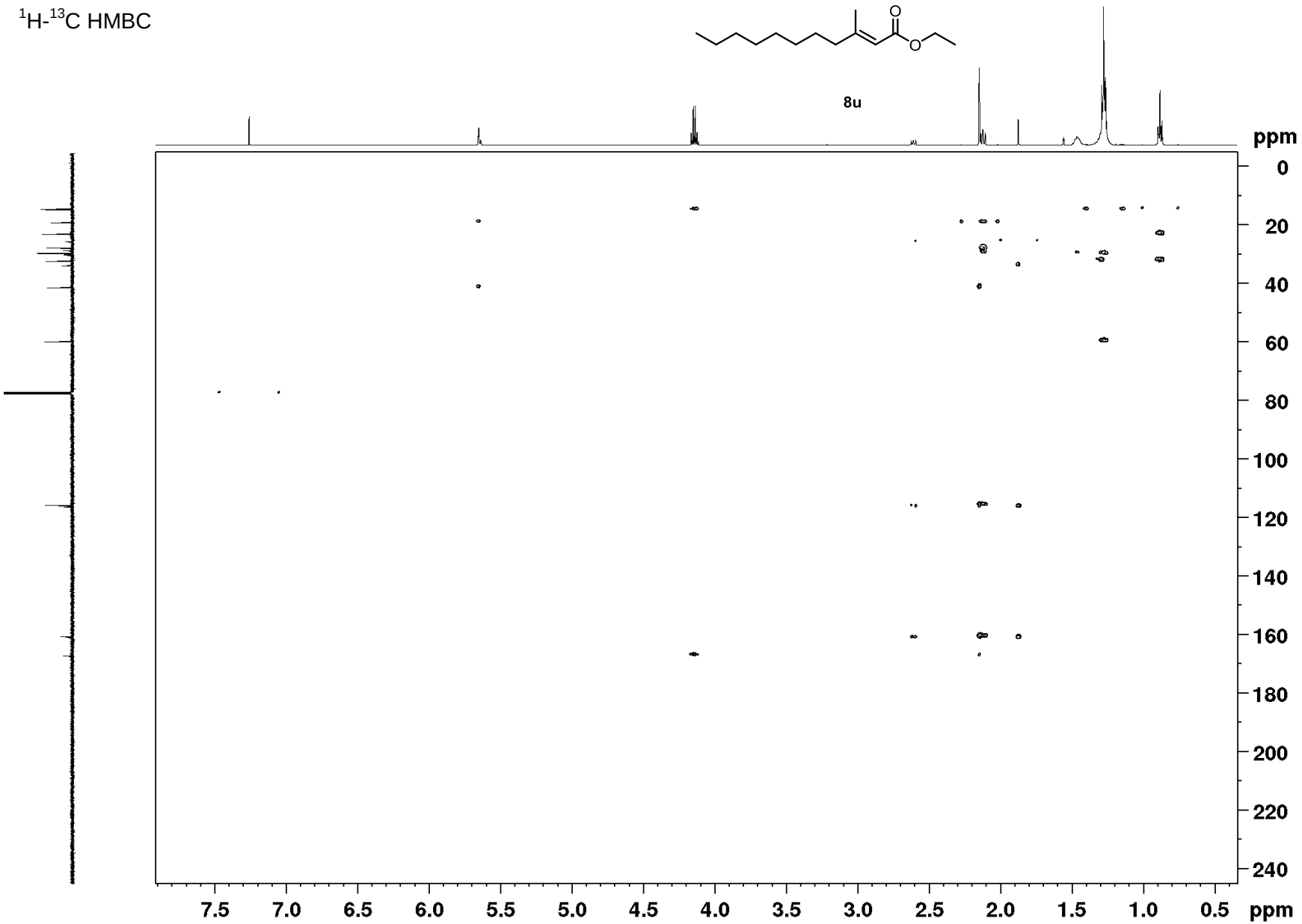

167.1
160.9
160.5
116.1
115.5
59.5
59.5
41.1
33.5
32.0
29.9
29.6
29.5
29.4
29.3
29.3
28.4
27.5
25.3
22.8
18.8
14.5
14.2
O
O
8u
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{1}H-^{1}H COSY

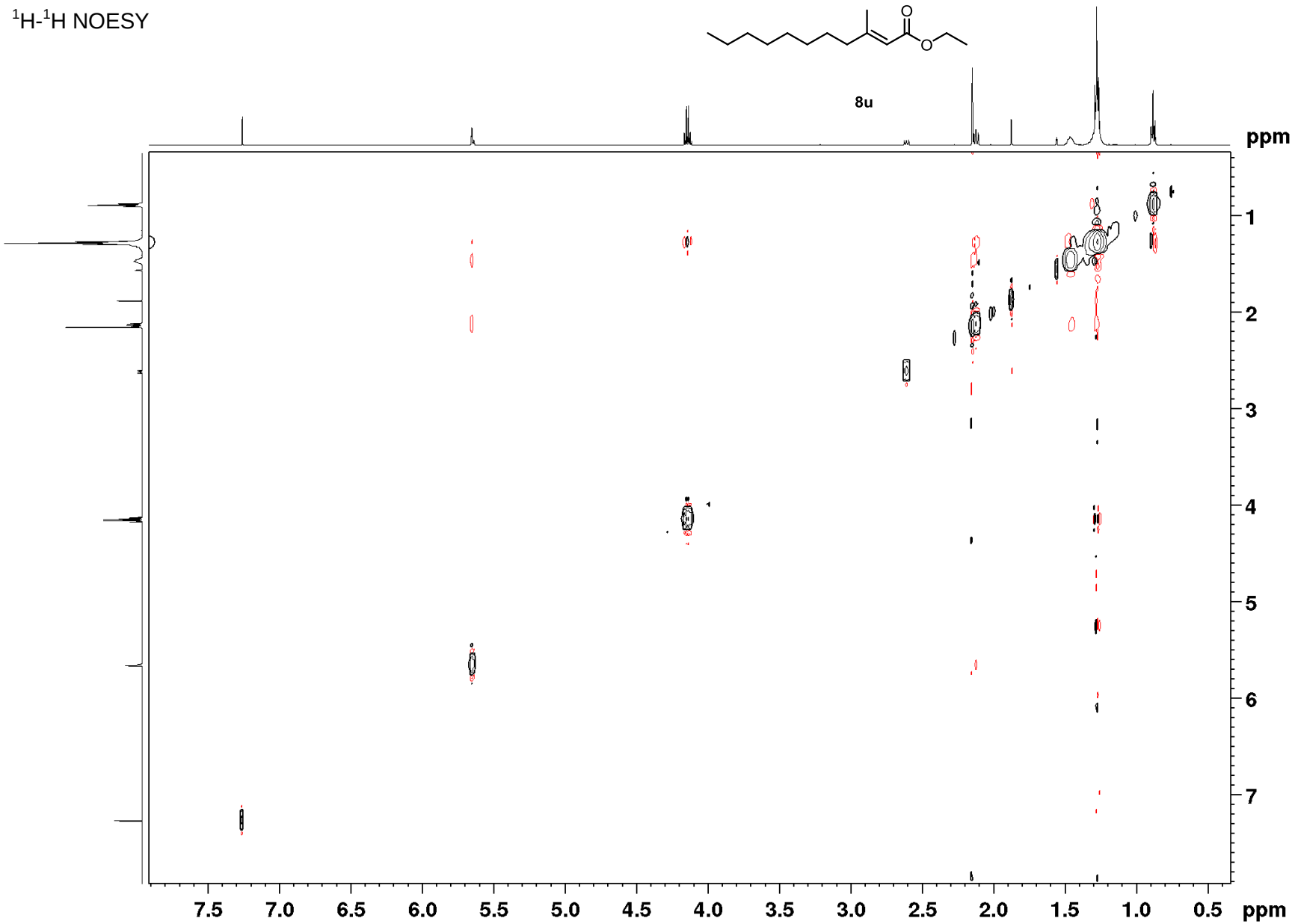


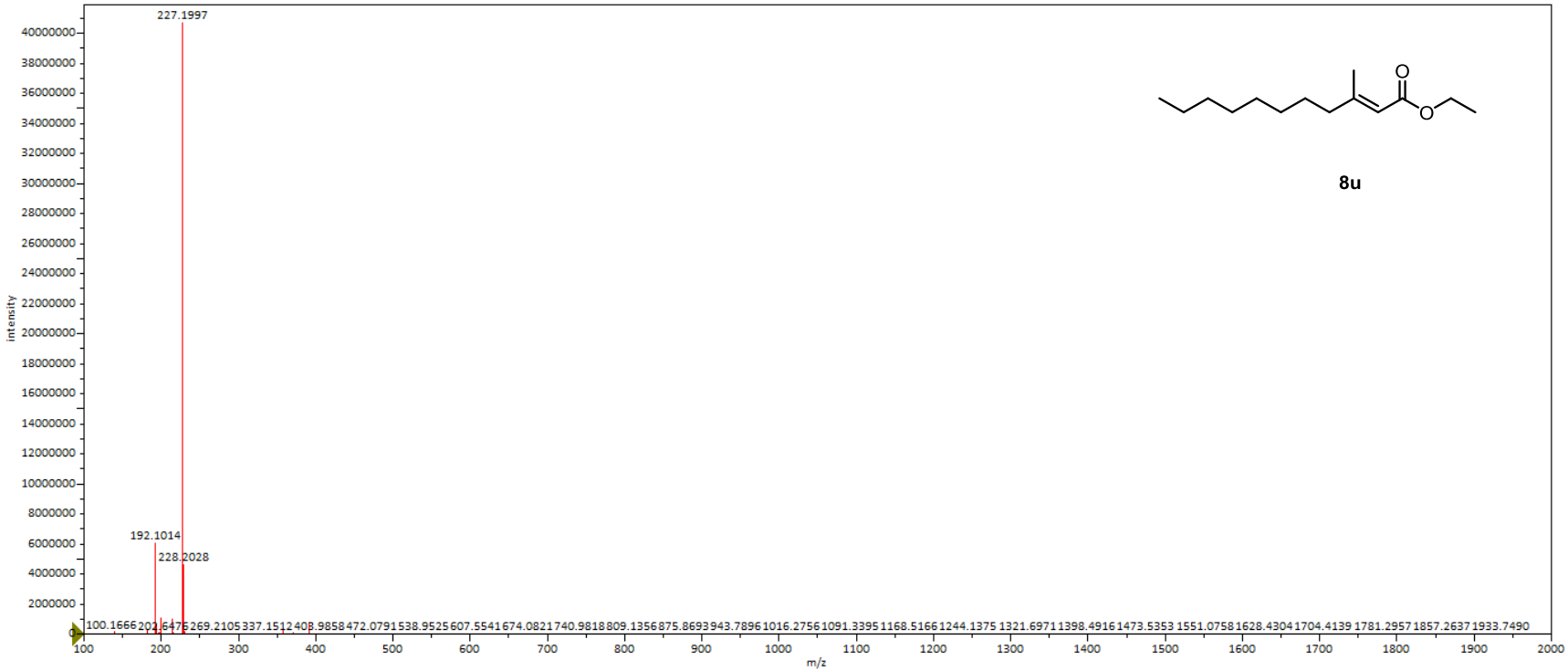

^{1}H-^{13}C HSQC
O
O
8u
ppm
0
20
40
60
80
100
120
140
160
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

^{1}H-^{13}C HMBC


8u
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
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
ppm

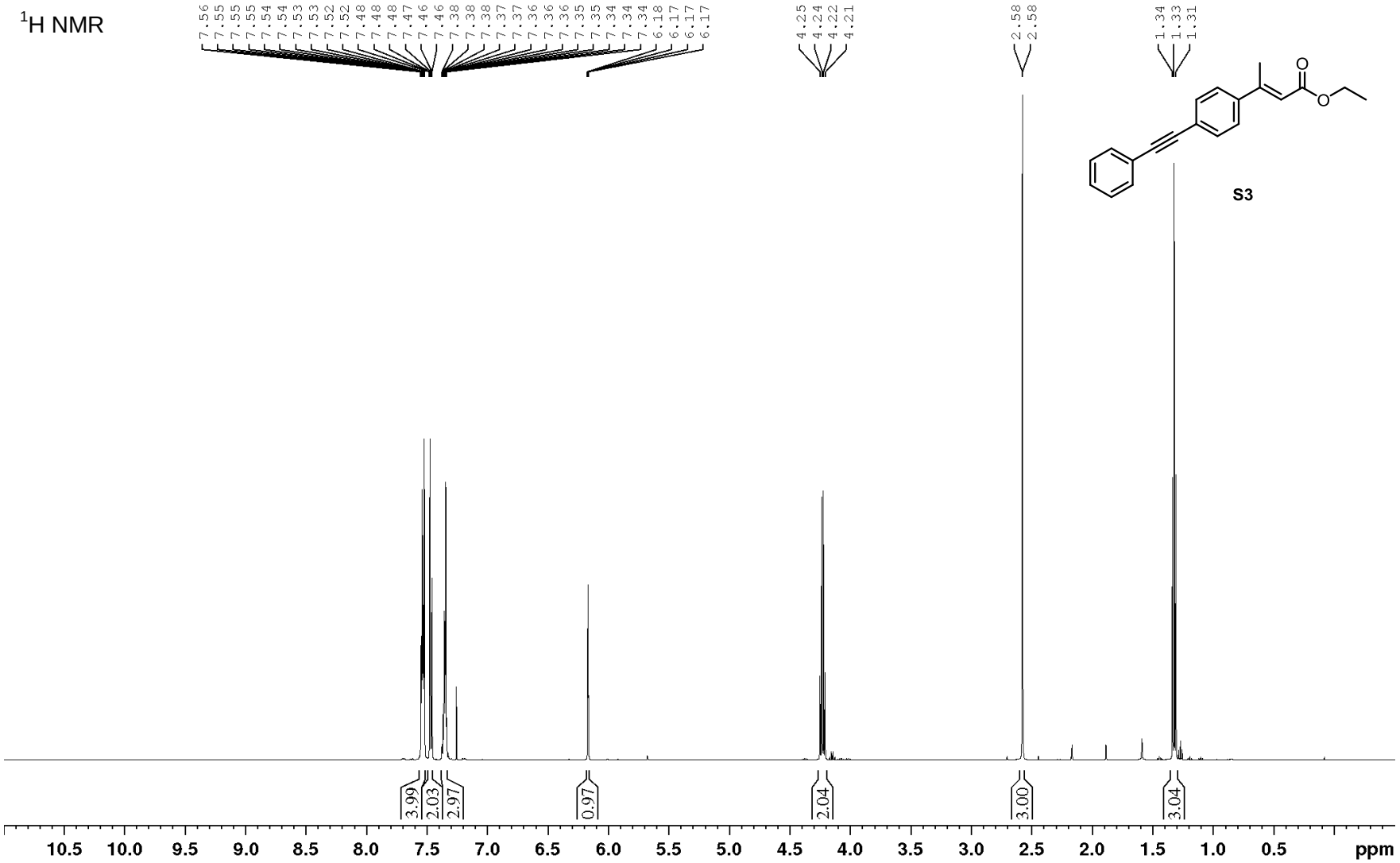
^{1}H-^{1}H NOESY



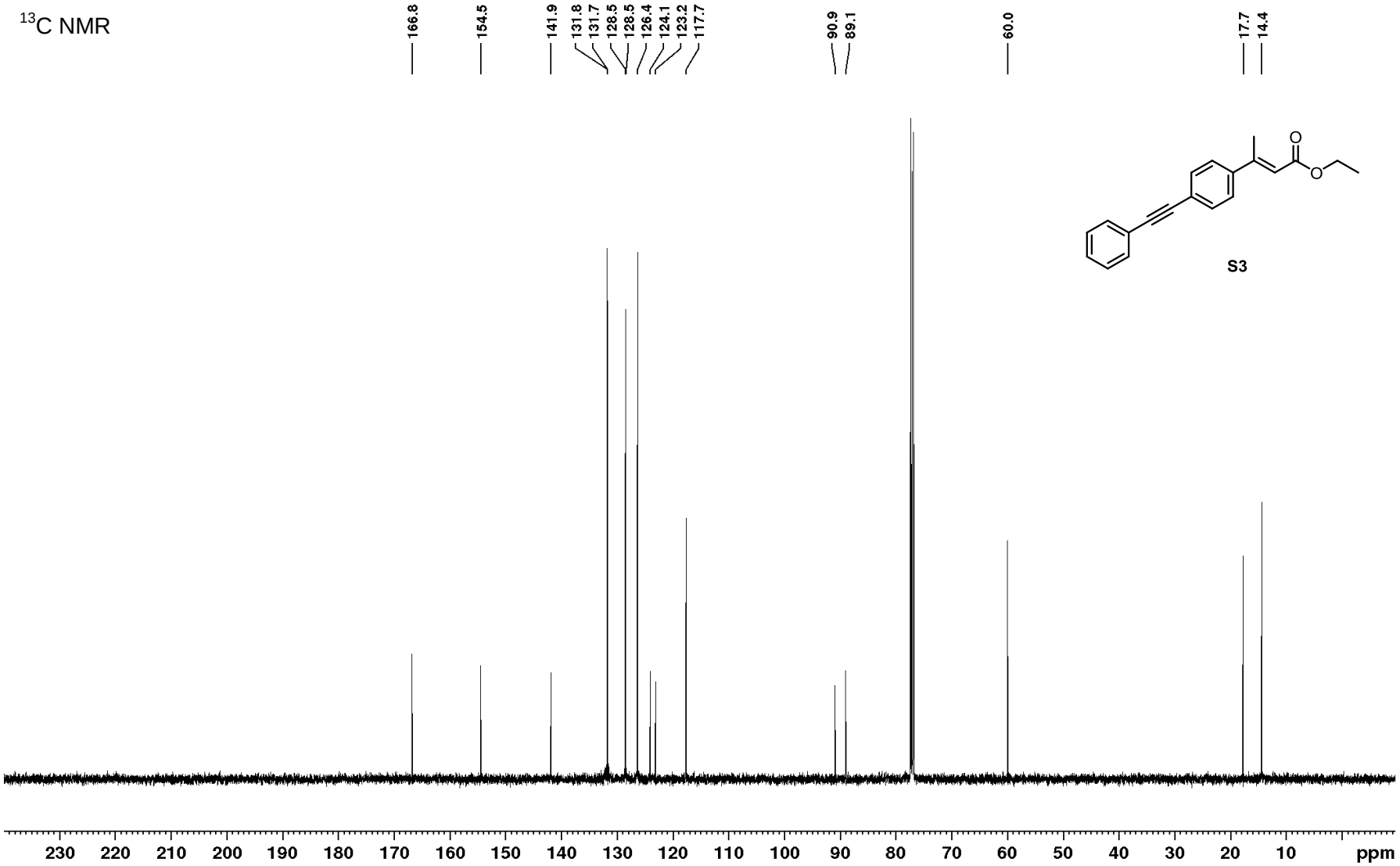

227.1997
192.1014
228.2028
intensity
m/z
8u

Ethyl (*E*)-3-(4-(phenylethynyl)phenyl)but-2-enoate (S3)

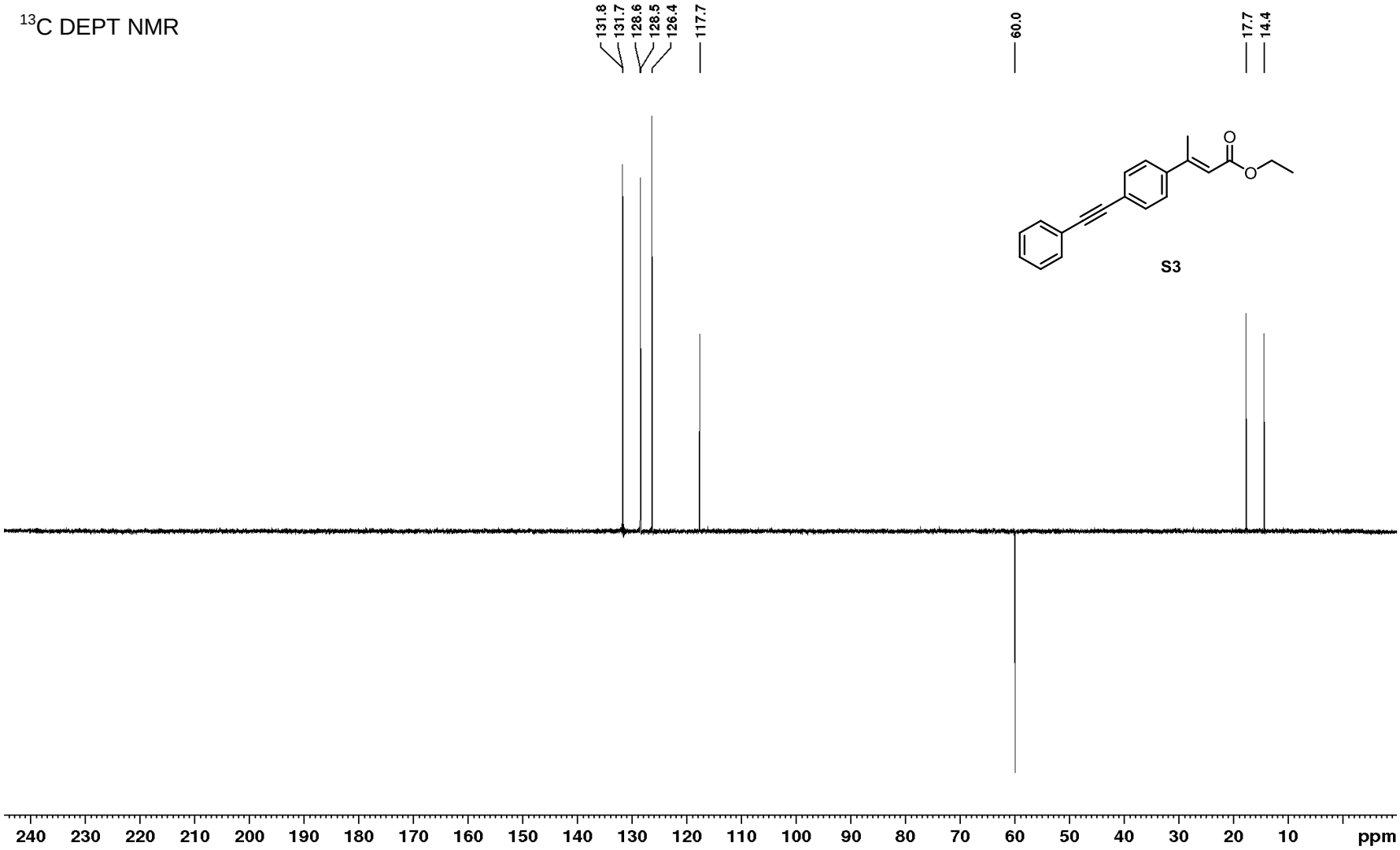
^{1}H NMR



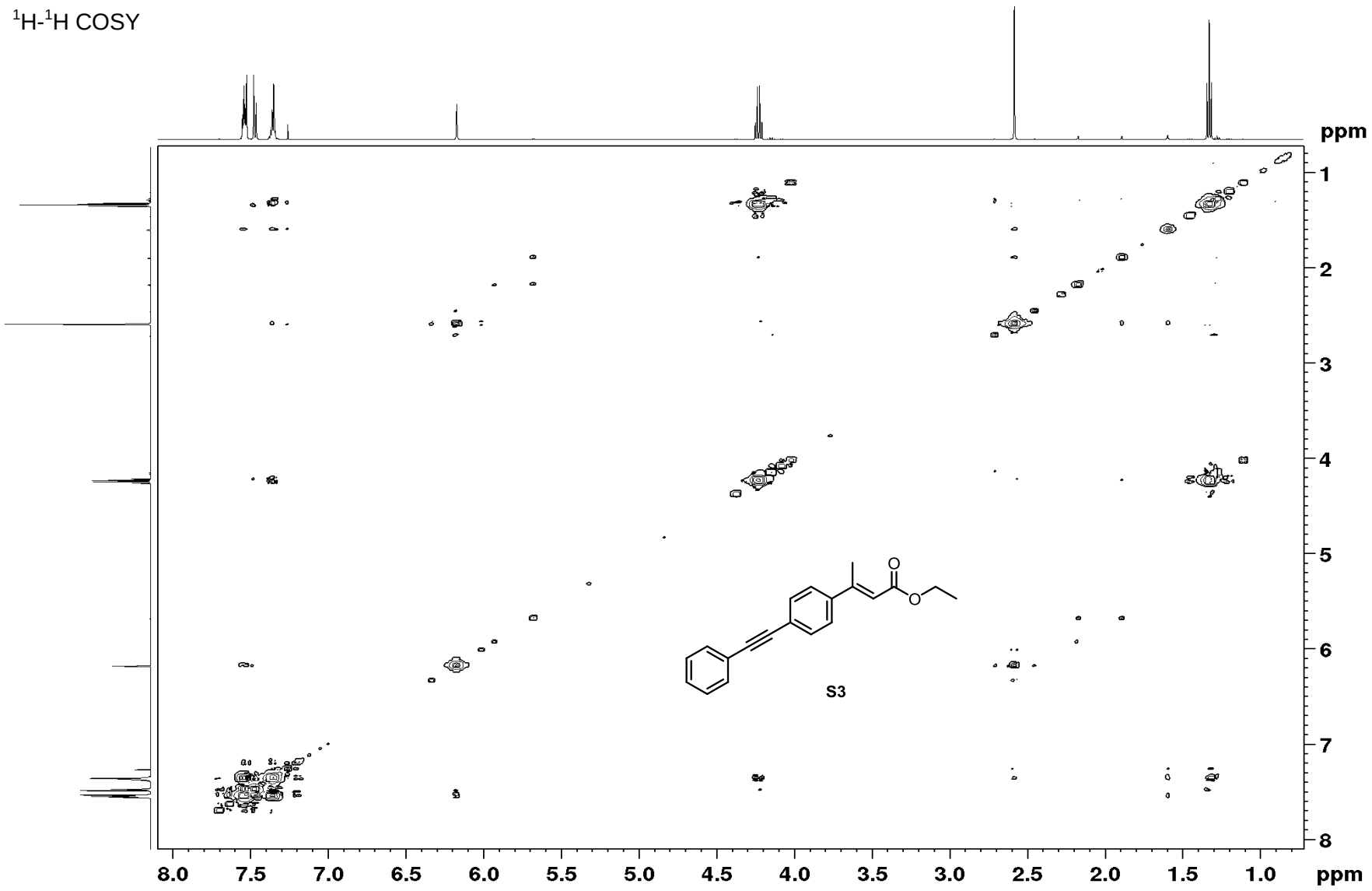
^{13}C NMR


166.8
154.5
141.9
131.8
131.7
128.5
128.5
126.4
124.1
123.2
117.7
90.9
89.1
60.0
17.7
14.4
O
O
S3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

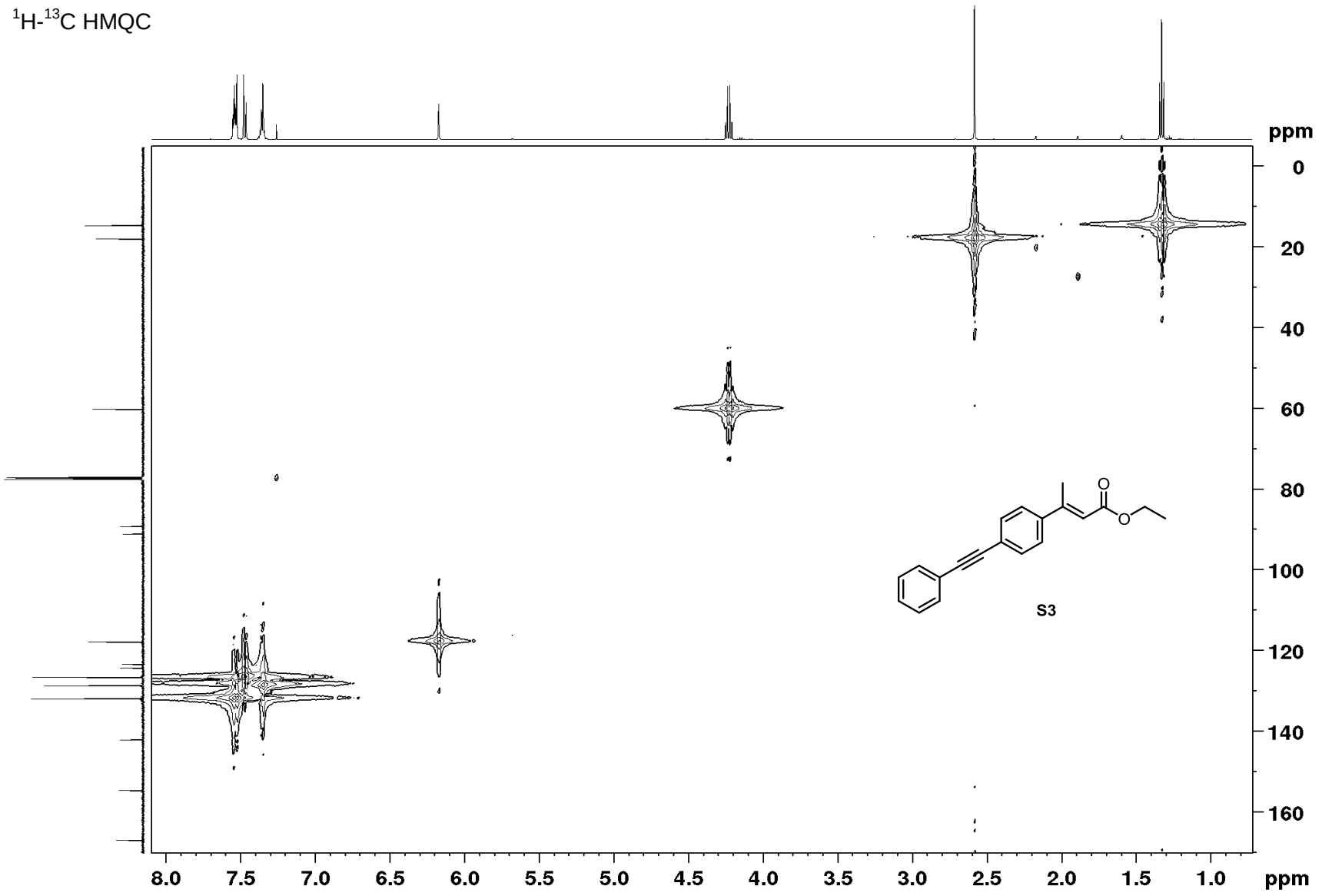
^{13}C DEPT NMR


131.8
131.7
128.6
128.5
126.4
117.7
60.0
17.7
14.4
O
O
S3
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

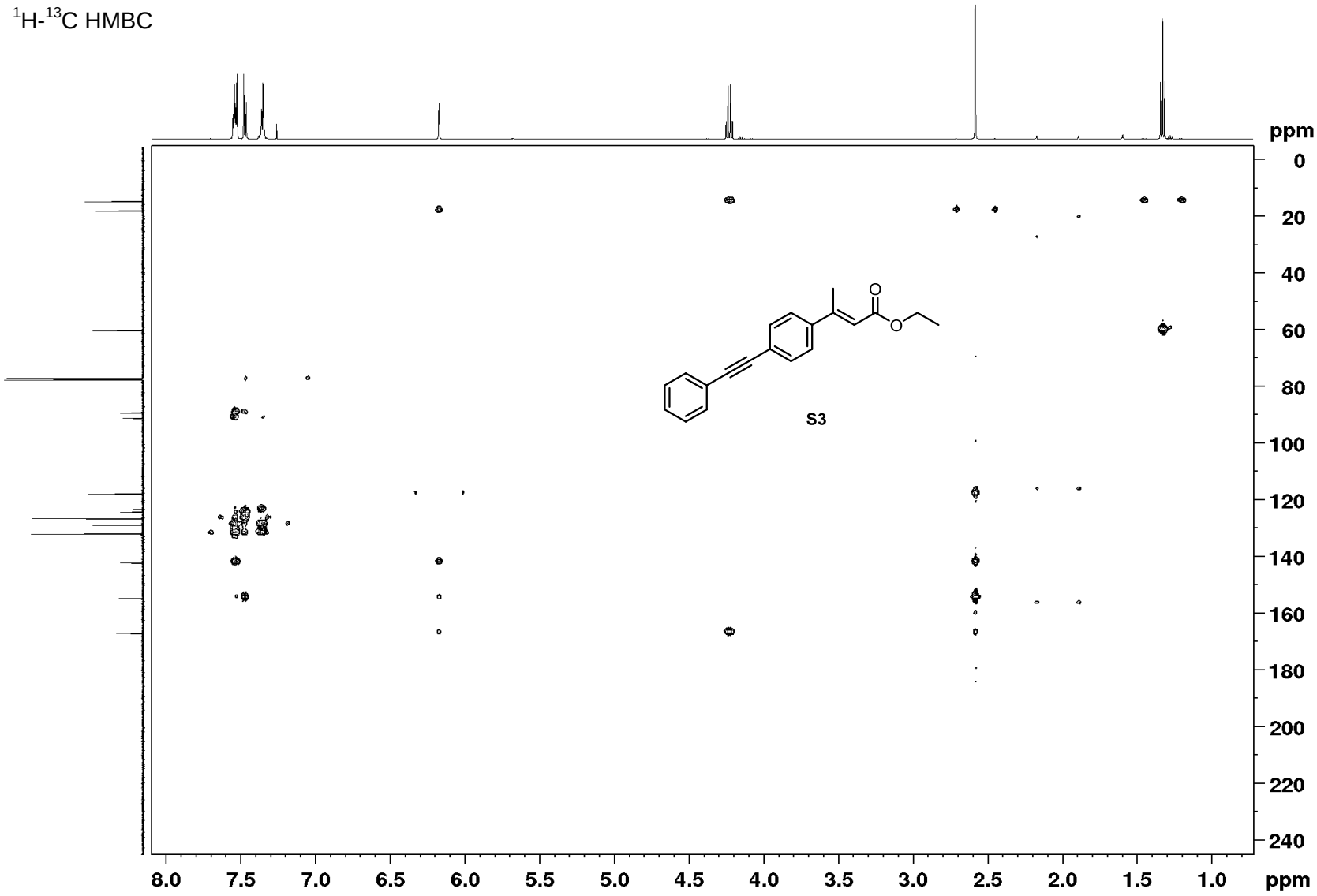
^{1}H-^{1}H COSY



^{1}H-^{13}C HMQC

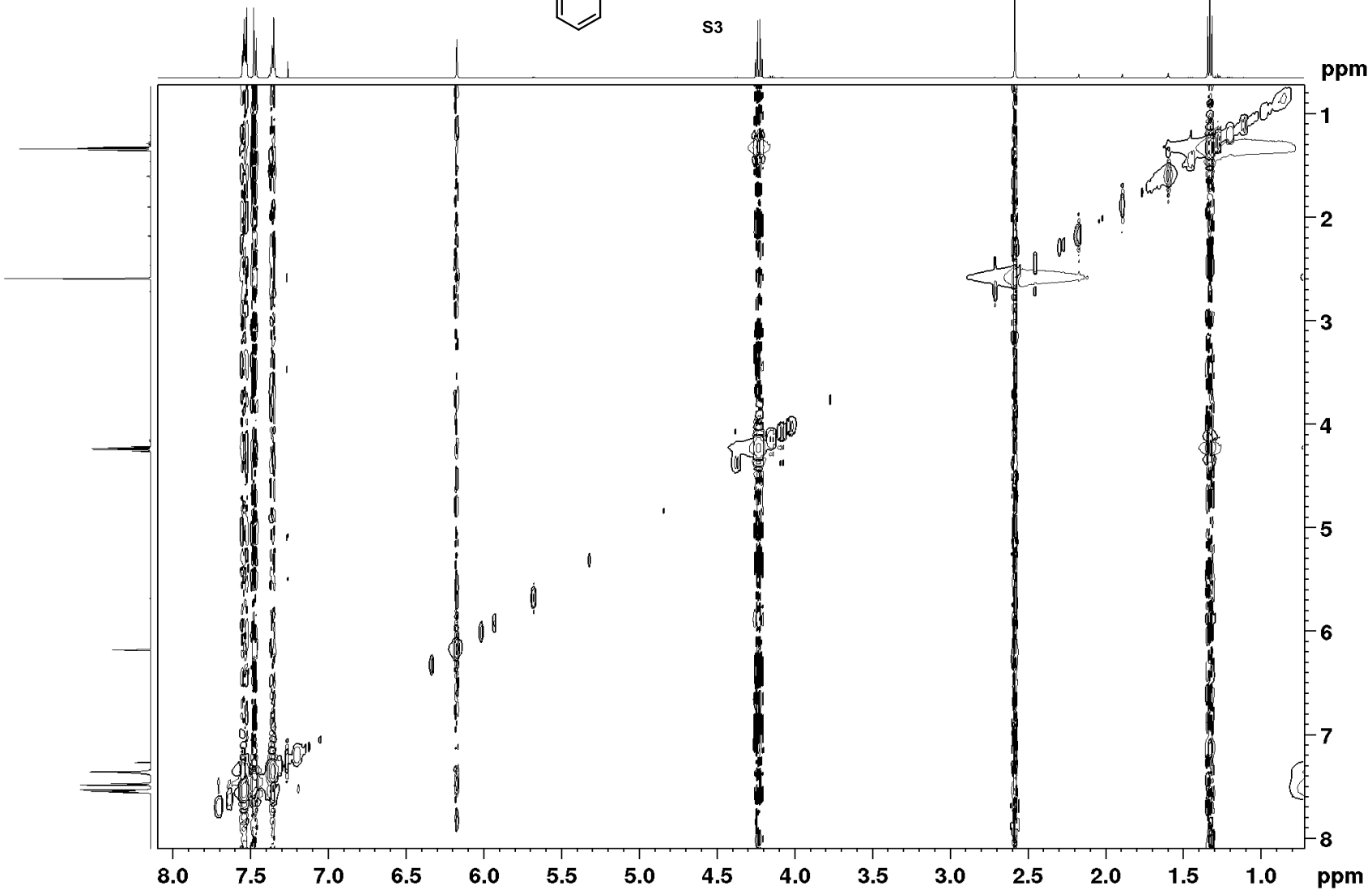

ppm
0
20
40
60
80
100
120
140
160
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
O
O
S3

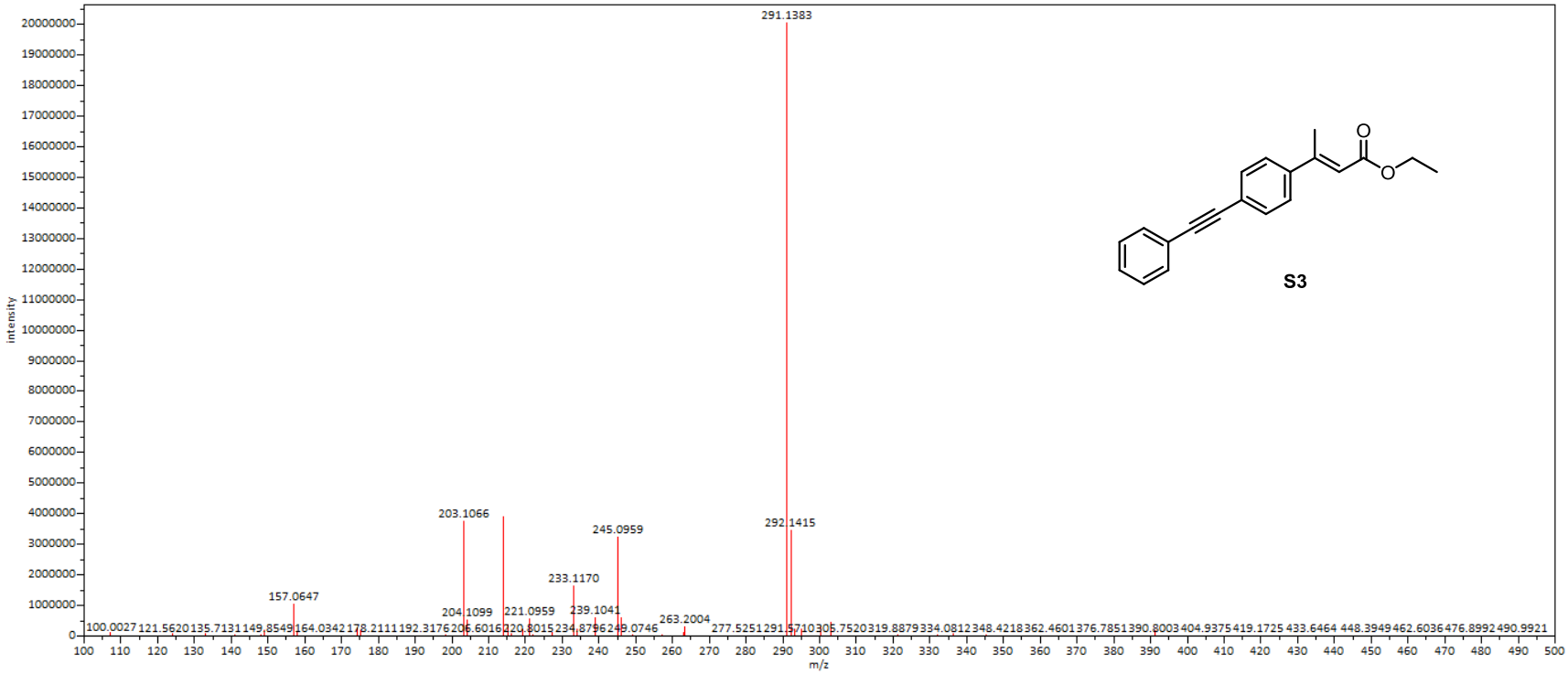
^{1}H-^{13}C HMBC

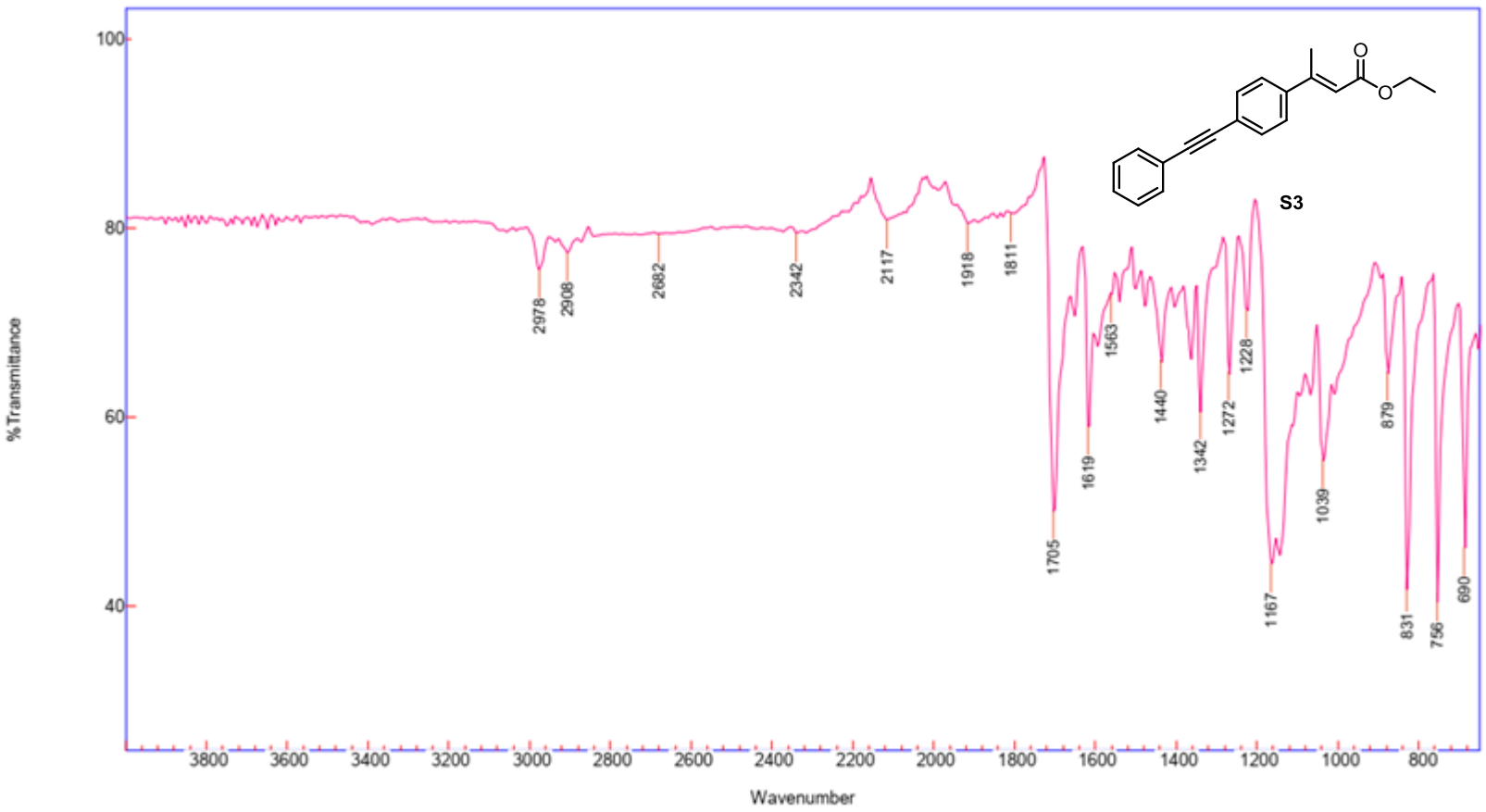

ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
O
O
S3

^{1}H-^{1}H NOESY

S3

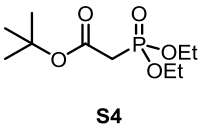



291.1383
203.1066
245.0959
292.1415
233.1170
157.0647
204.1099
221.0959
239.1041
263.2004
intensity
m/z
S3

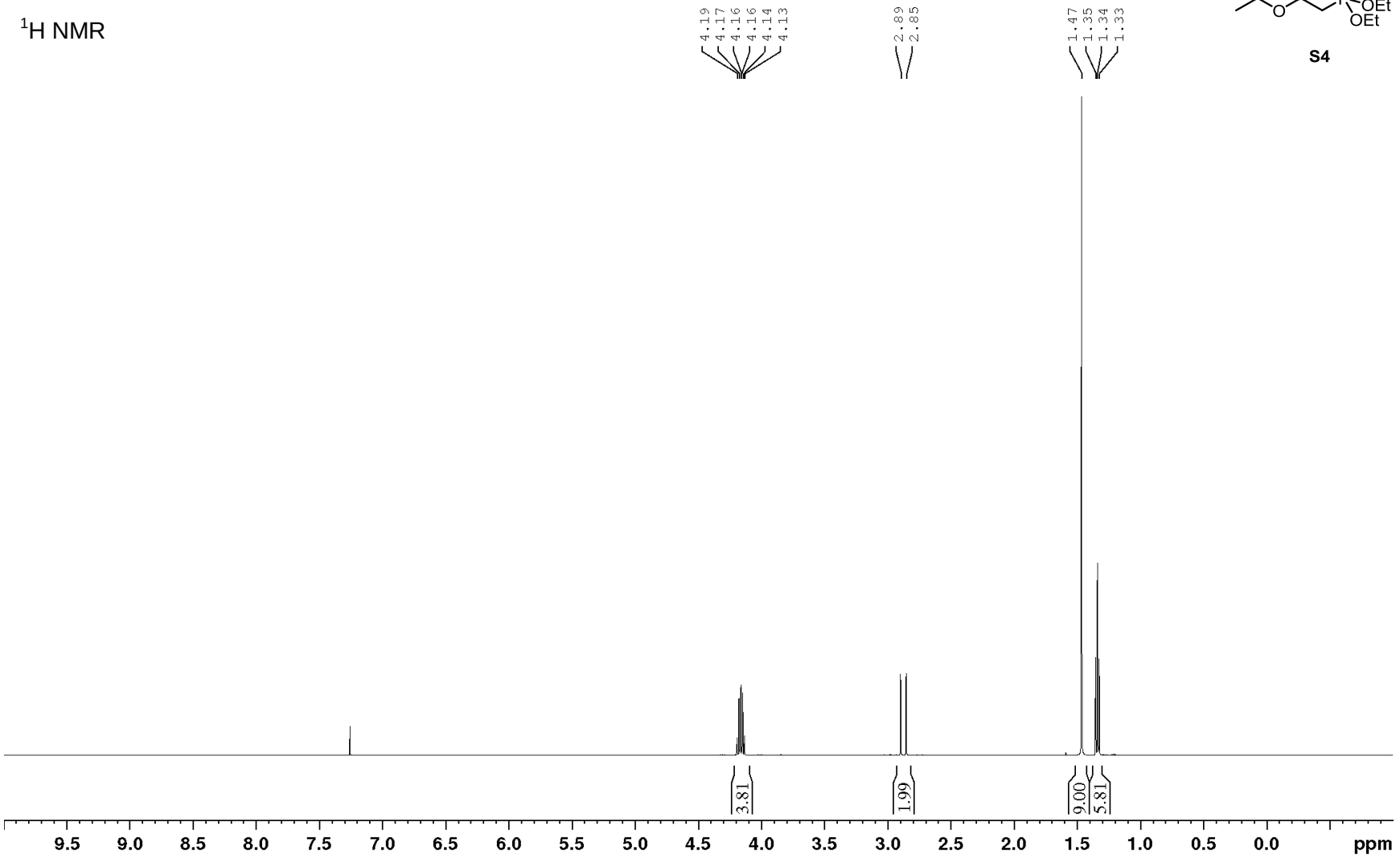

100
80
60
40
% Transmittance
2978
2908
2682
2342
2117
1918
1811
1705
1619
1563
1440
1342
1272
1228
1167
1039
879
831
756
690
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber
O
O
S3

***tert*-Butyl 2-(diethoxyphosphoryl)acetate (S4)**

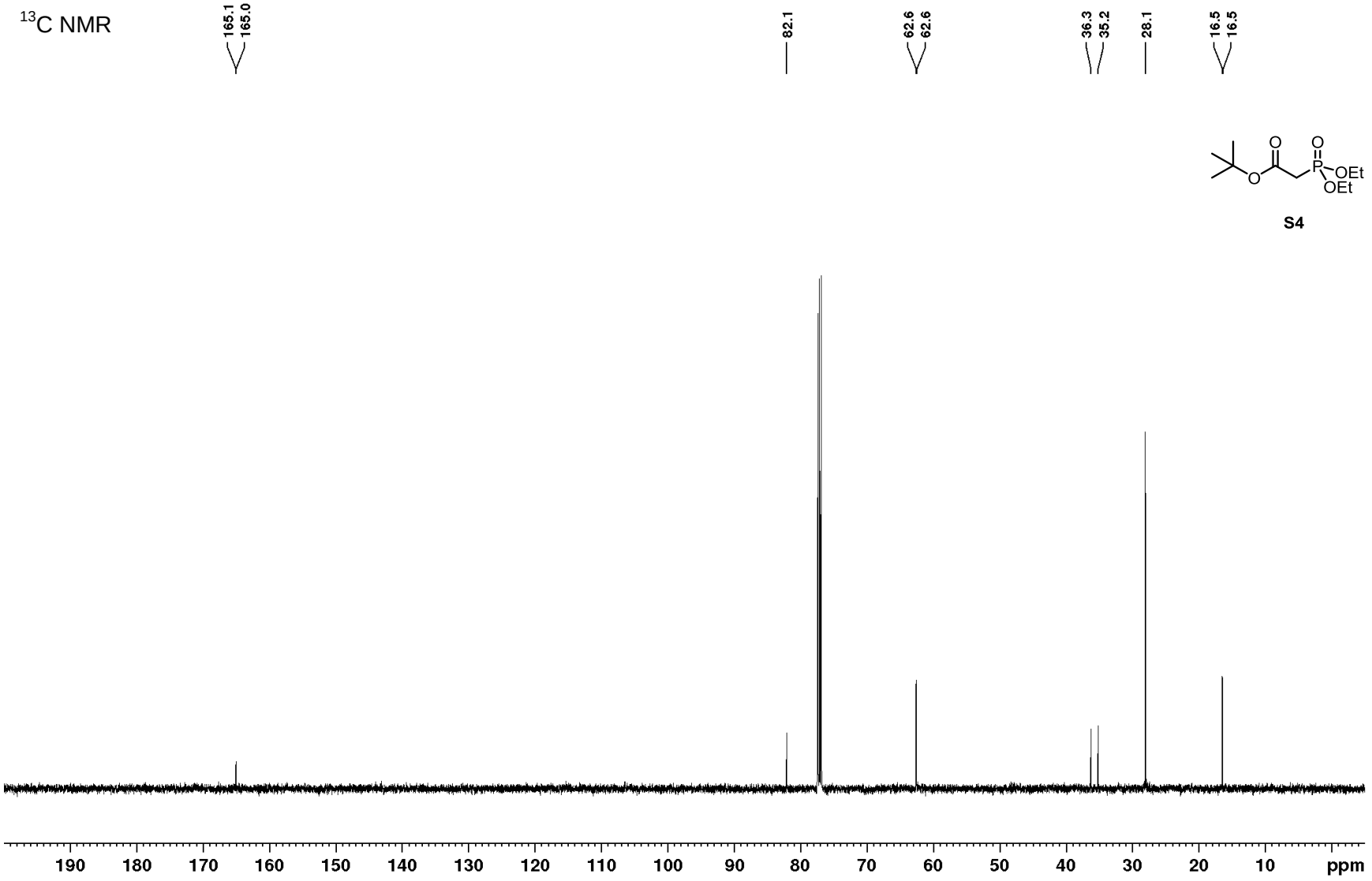
^{1}H NMR



S4

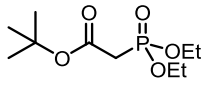


^{13}C NMR

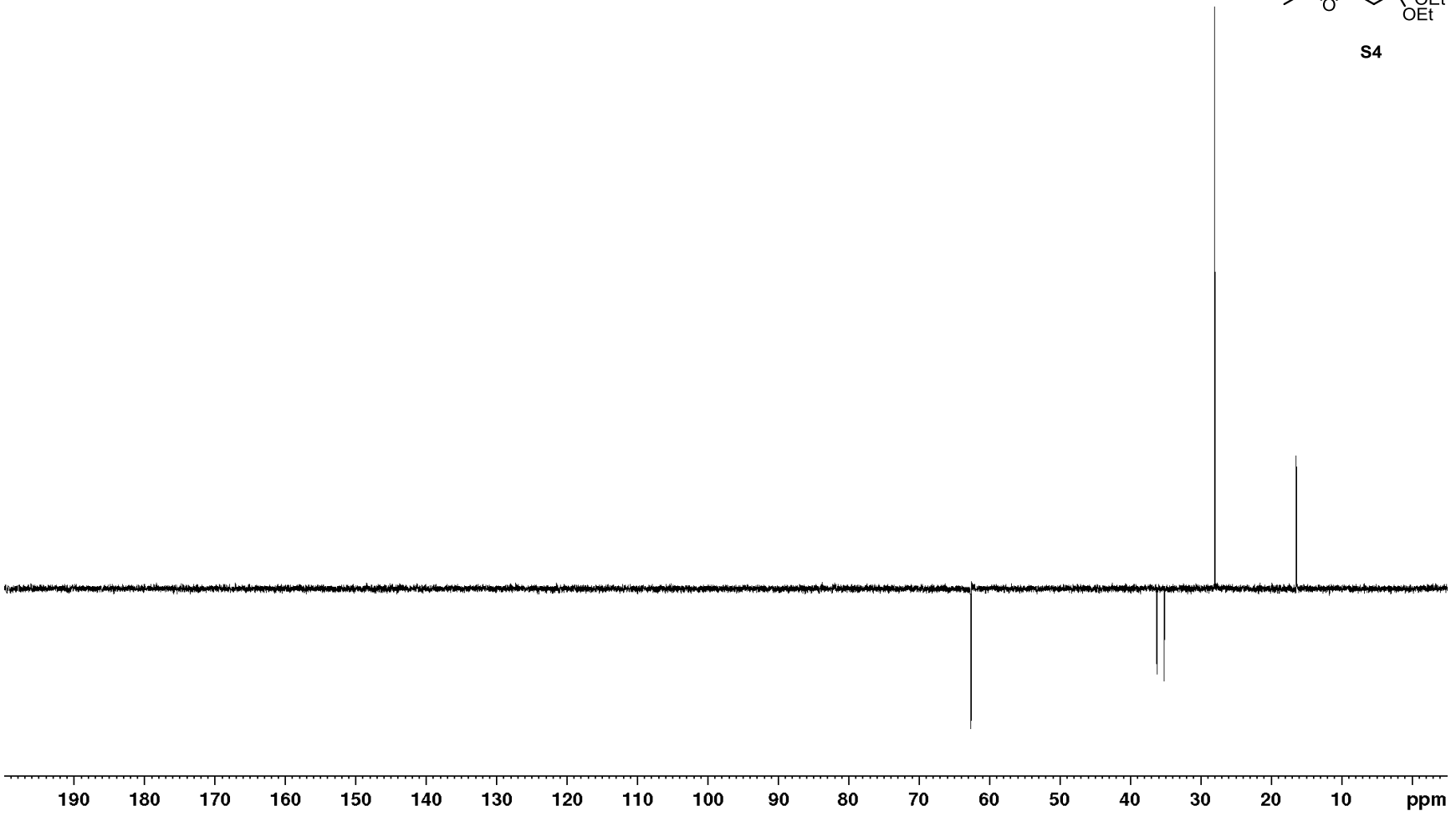

165.1
165.0
82.1
62.6
62.6
36.3
35.2
28.1
16.5
16.5
O
O
O
P
OEt
OEt
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

S4

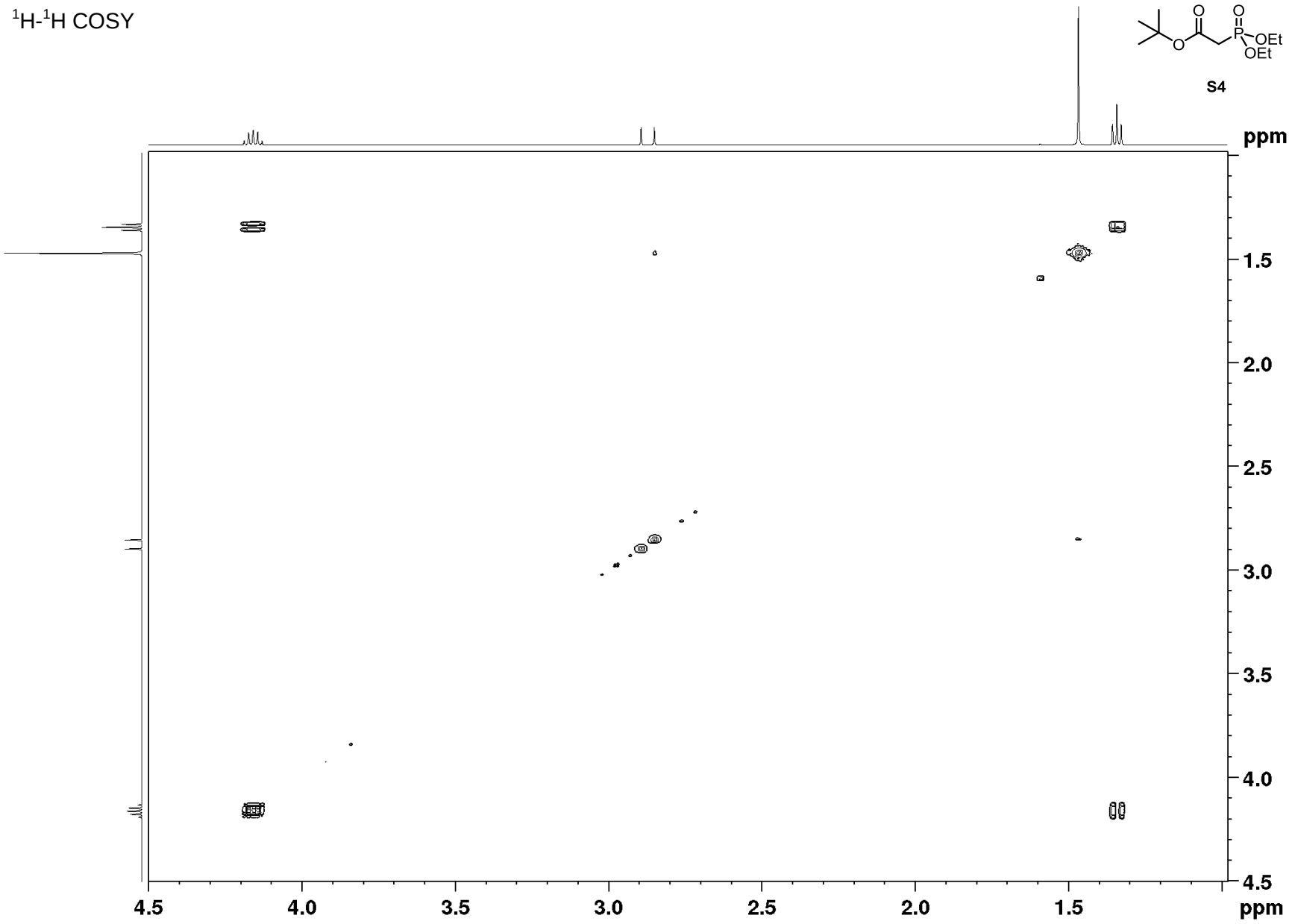
^{13}C DEPT NMR



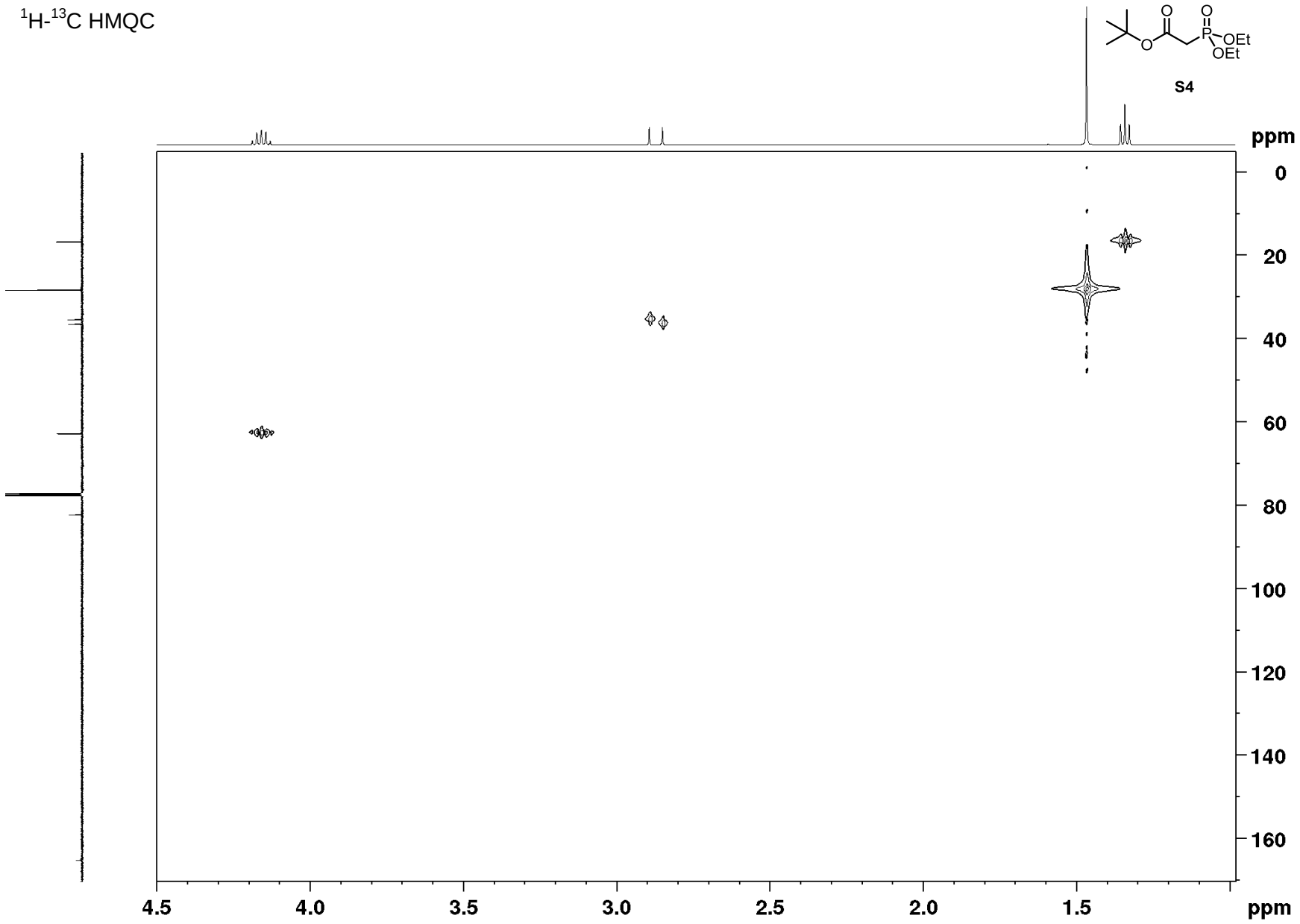
S4



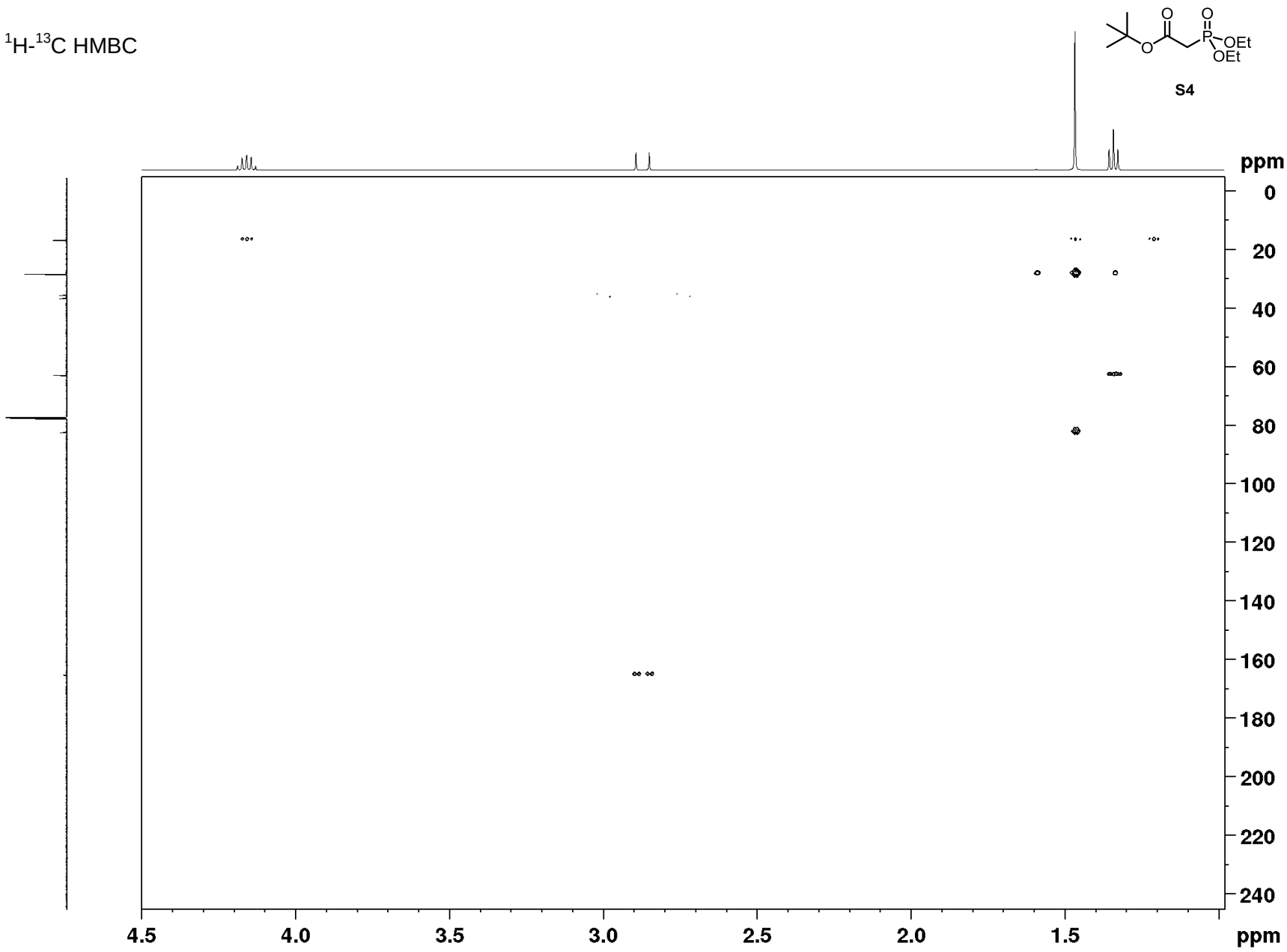
^{1}H-^{1}H COSY



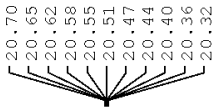
^{1}H-^{13}C HMQC

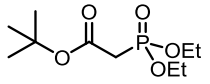


^{1}H-^{13}C HMBC

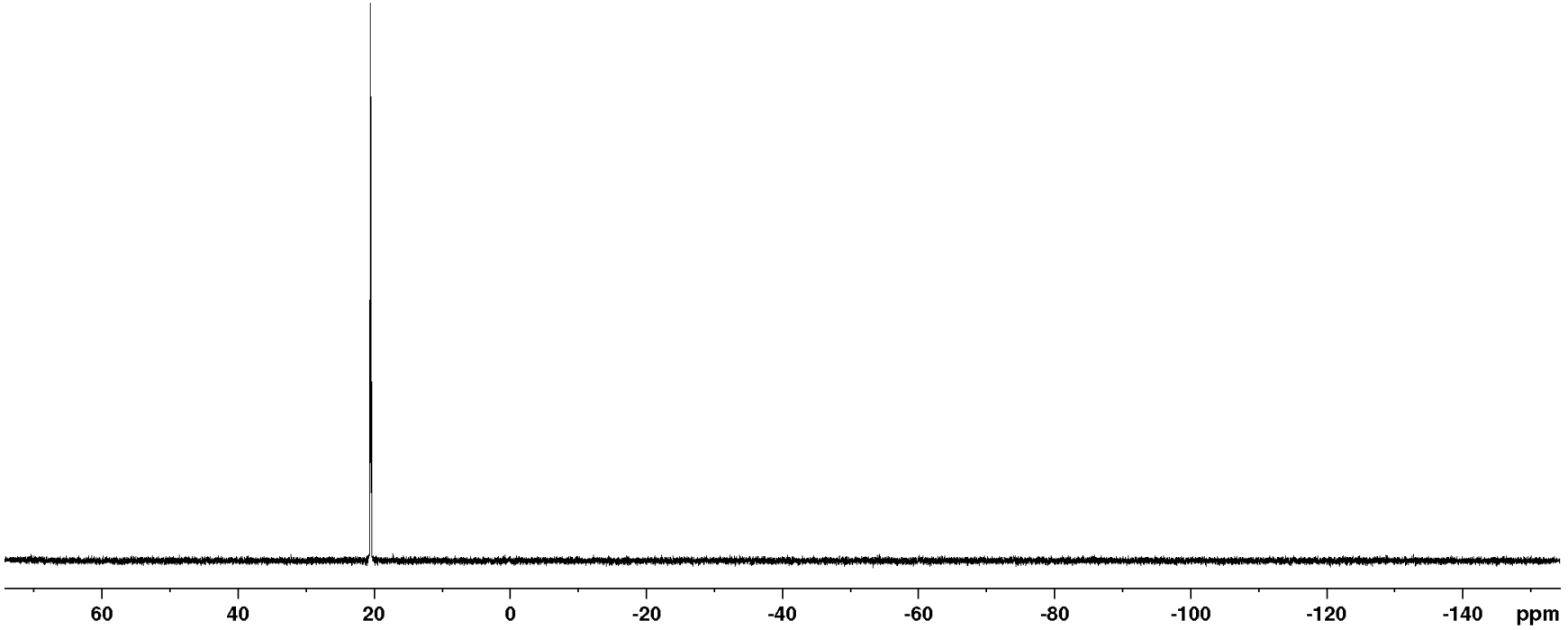

O
O
O
OEt
OEt
S4
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

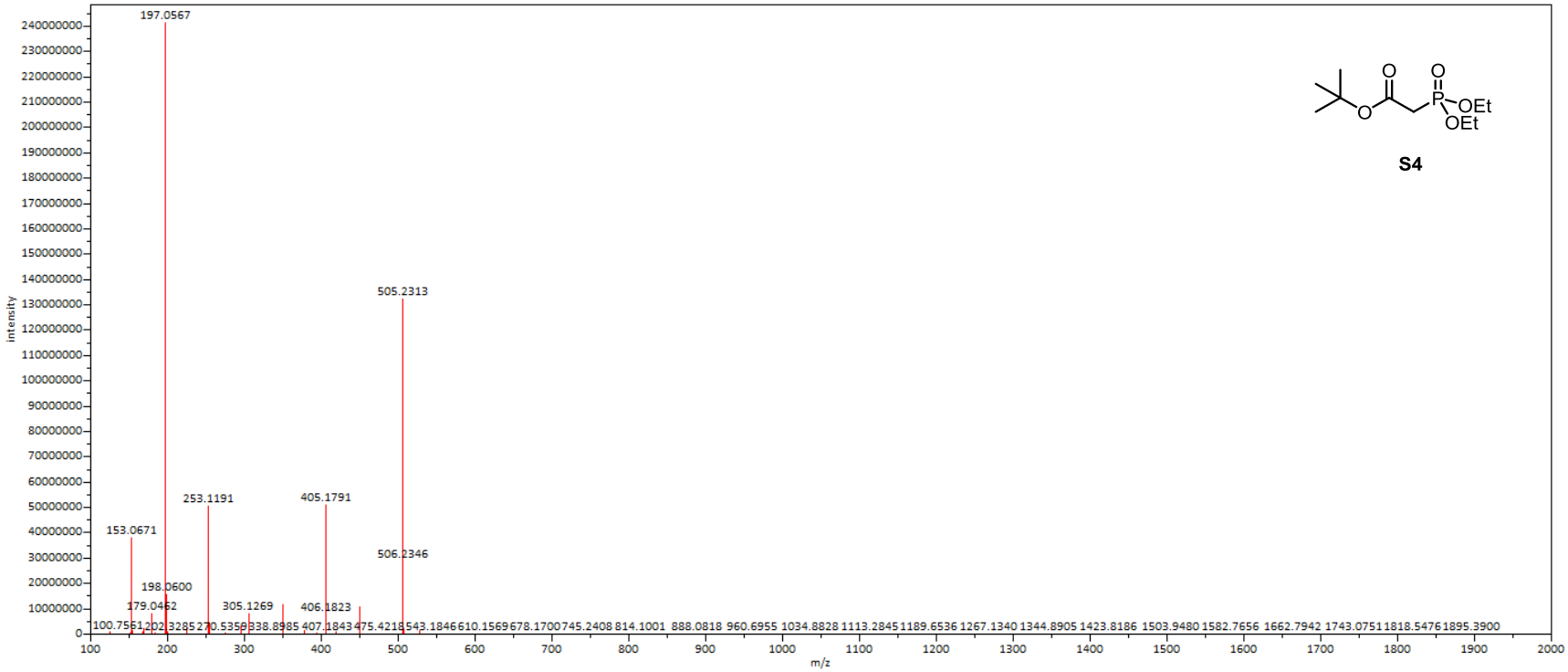
^{31}P NMR

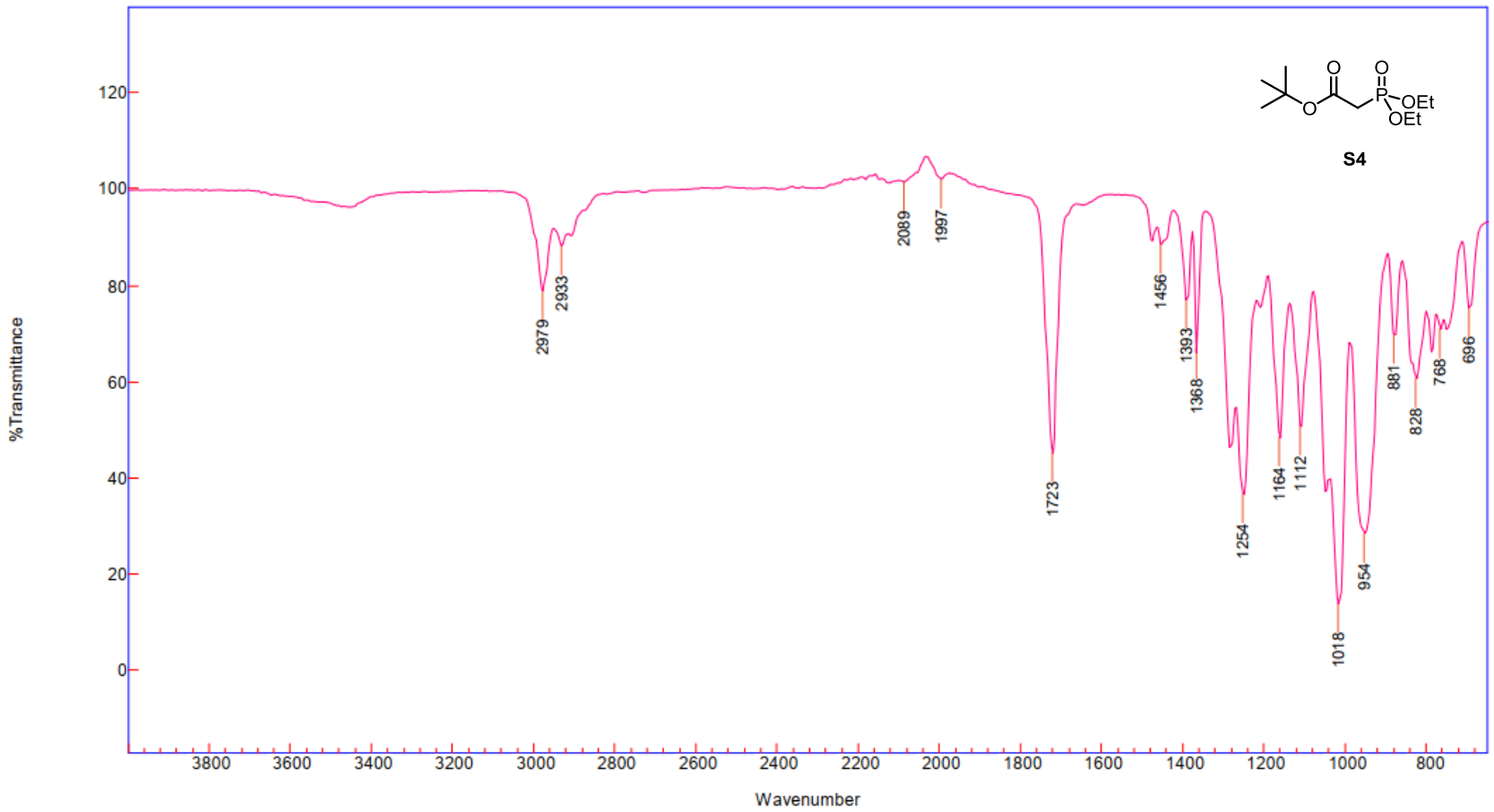

20.70
20.65
20.62
20.58
20.55
20.51
20.47
20.44
20.40
20.36
20.32


O
O
O
P
OEt
OEt

S4

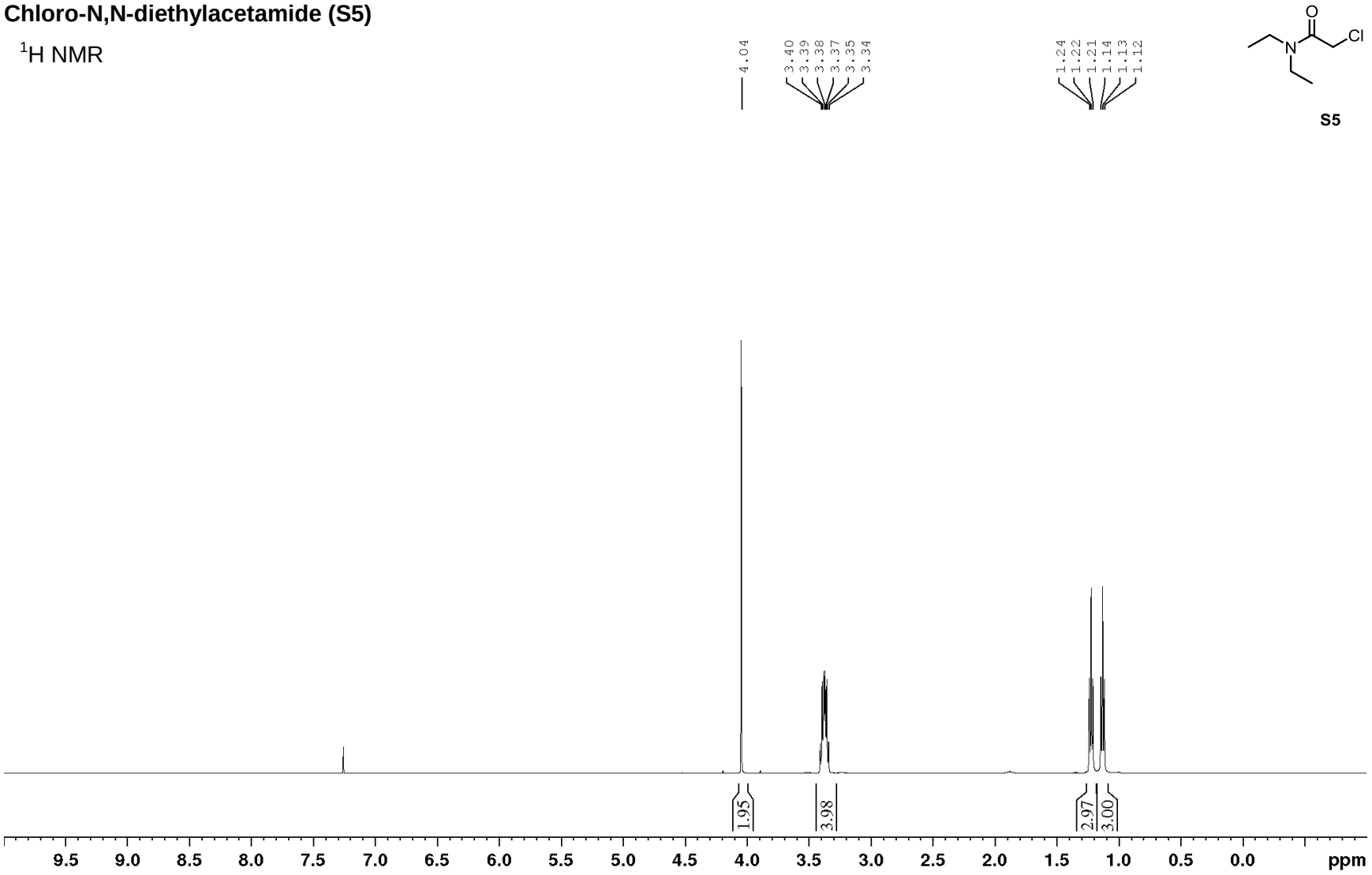

60
40
20
0
-20
-40
-60
-80
-100
-120
-140
ppm


197.0567
505.2313
253.1191
405.1791
153.0671
506.2346
198.0600
179.0462
305.1269
406.1823
intensity
m/z
S4

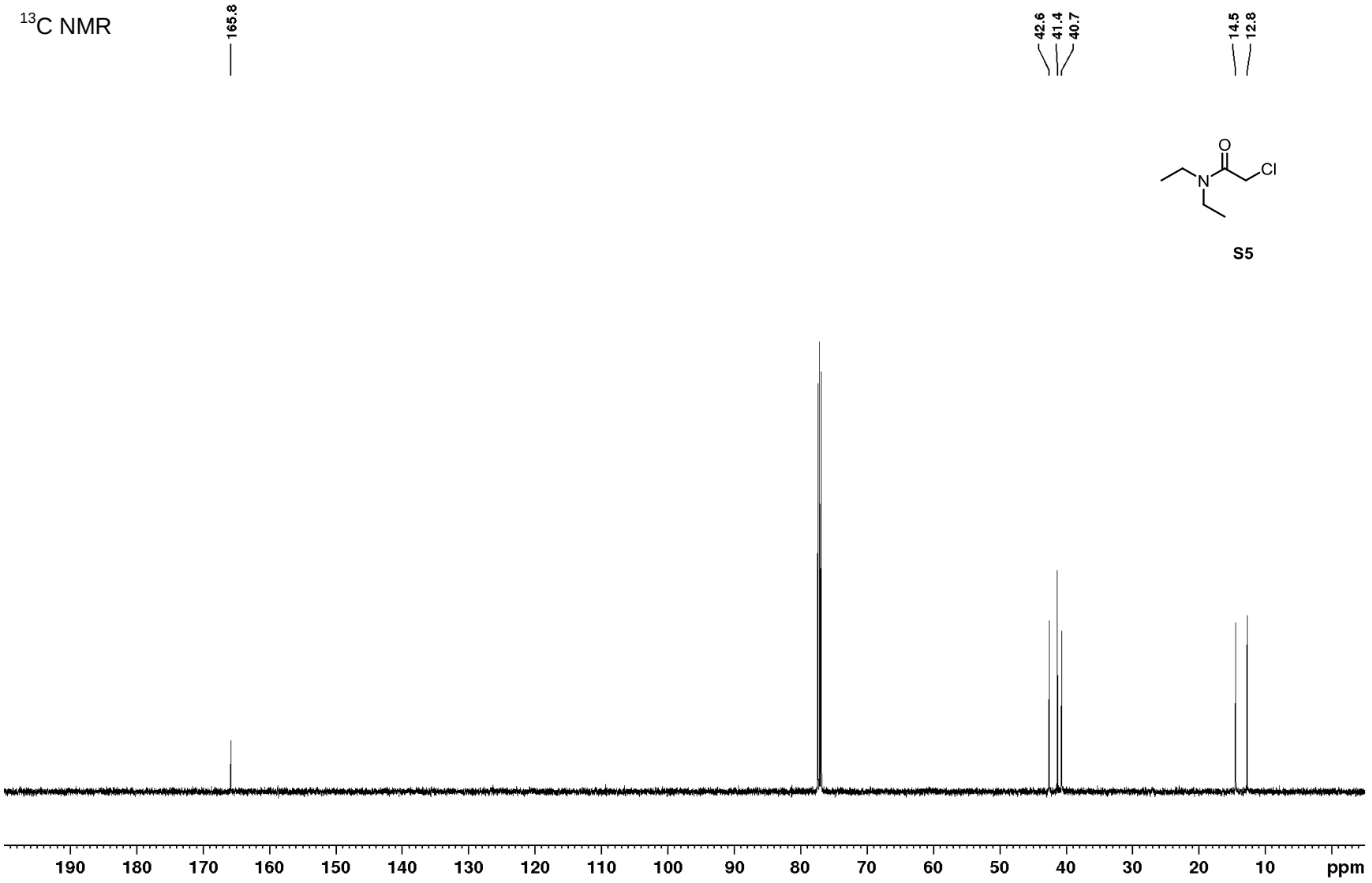

S4
%Transmittance
Wavenumber
120
100
80
60
40
20
0
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
2979
2933
2089
1997
1723
1456
1393
1368
1254
1164
1112
1018
954
881
828
768
696

Chloro-N,N-diethylacetamide (S5)

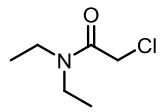
^{1}H NMR



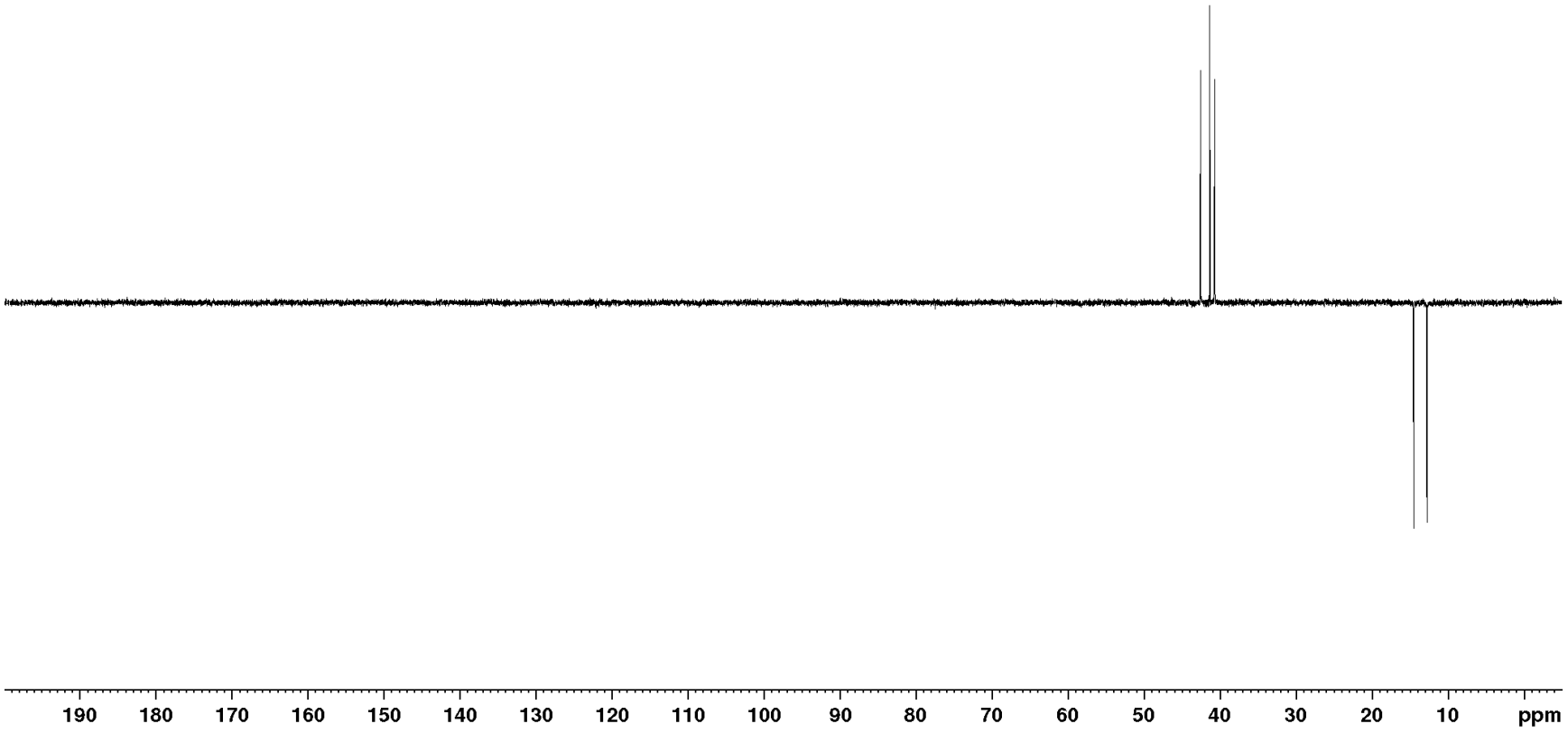
^{13}C NMR


165.8
42.6
41.4
40.7
14.5
12.8
O
N
Cl
S5
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

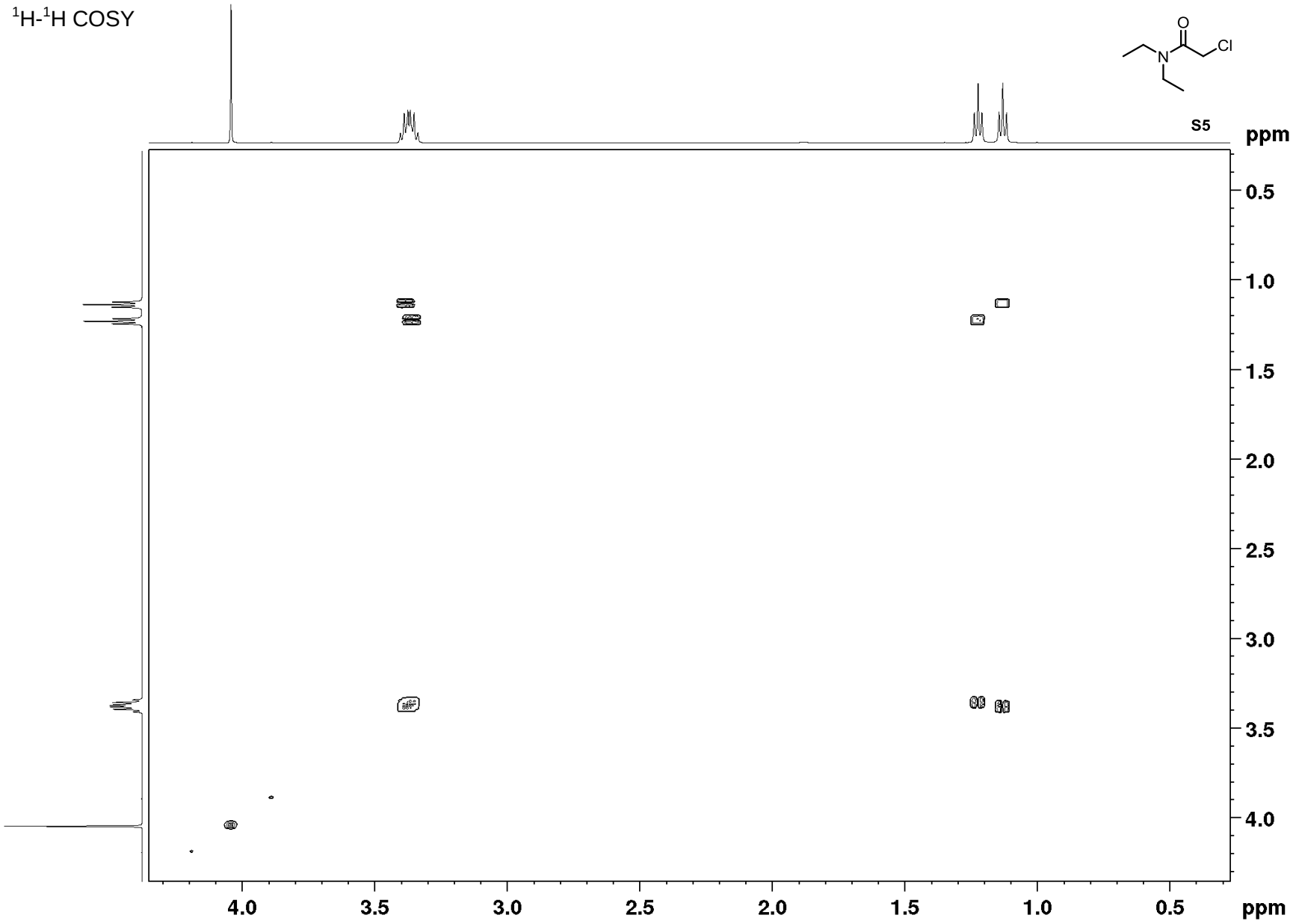
^{13}C DEPT NMR

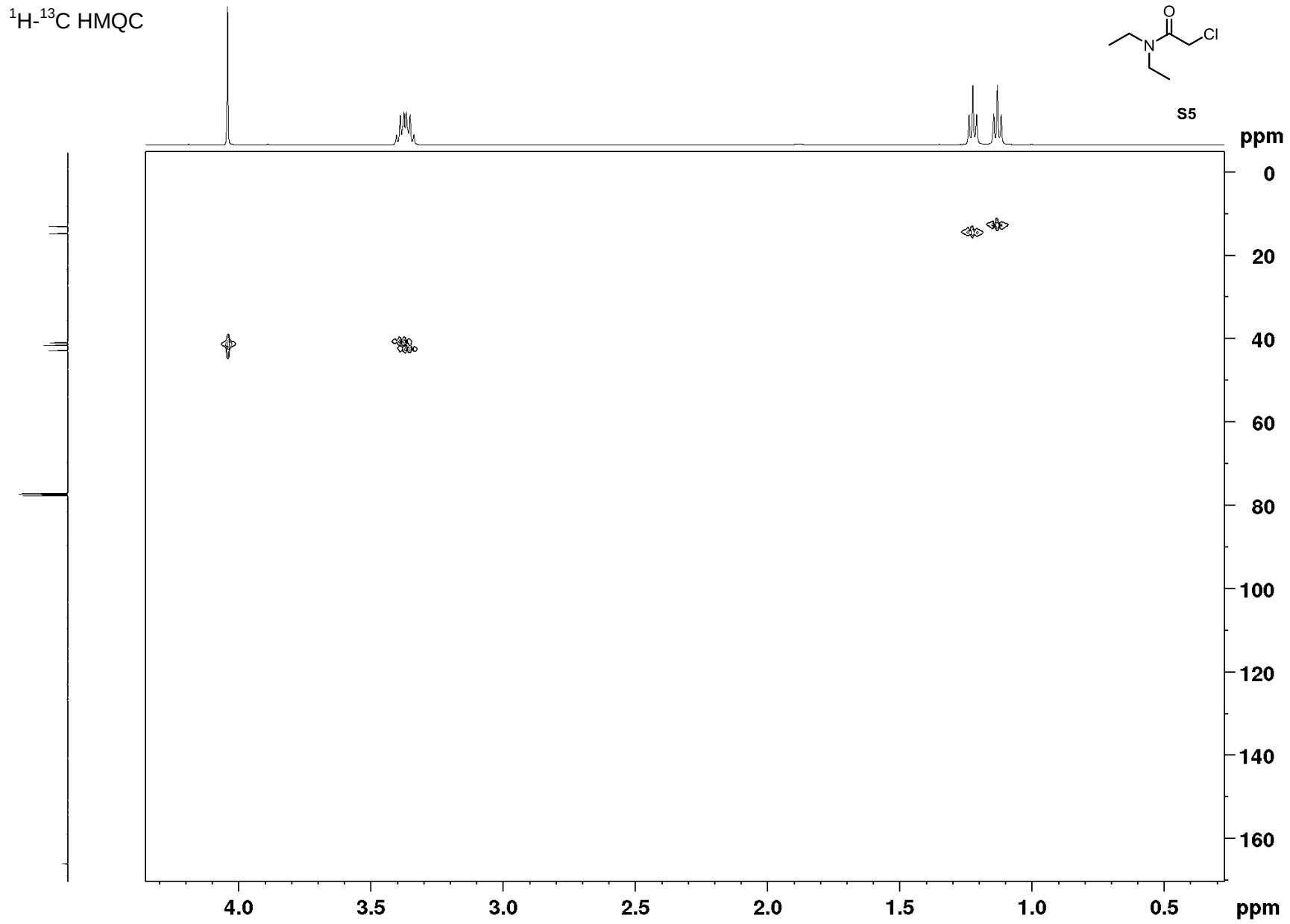


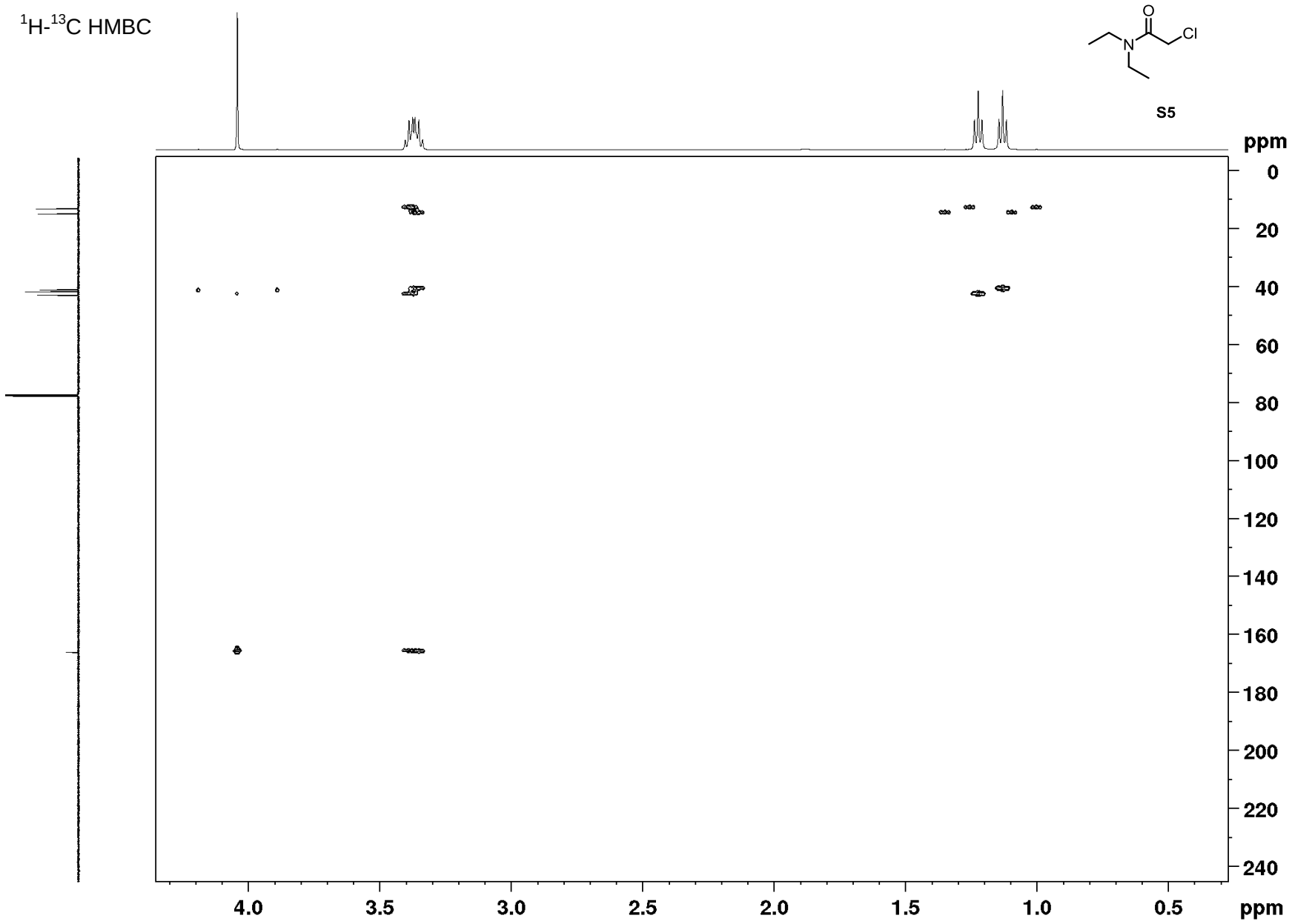
S5

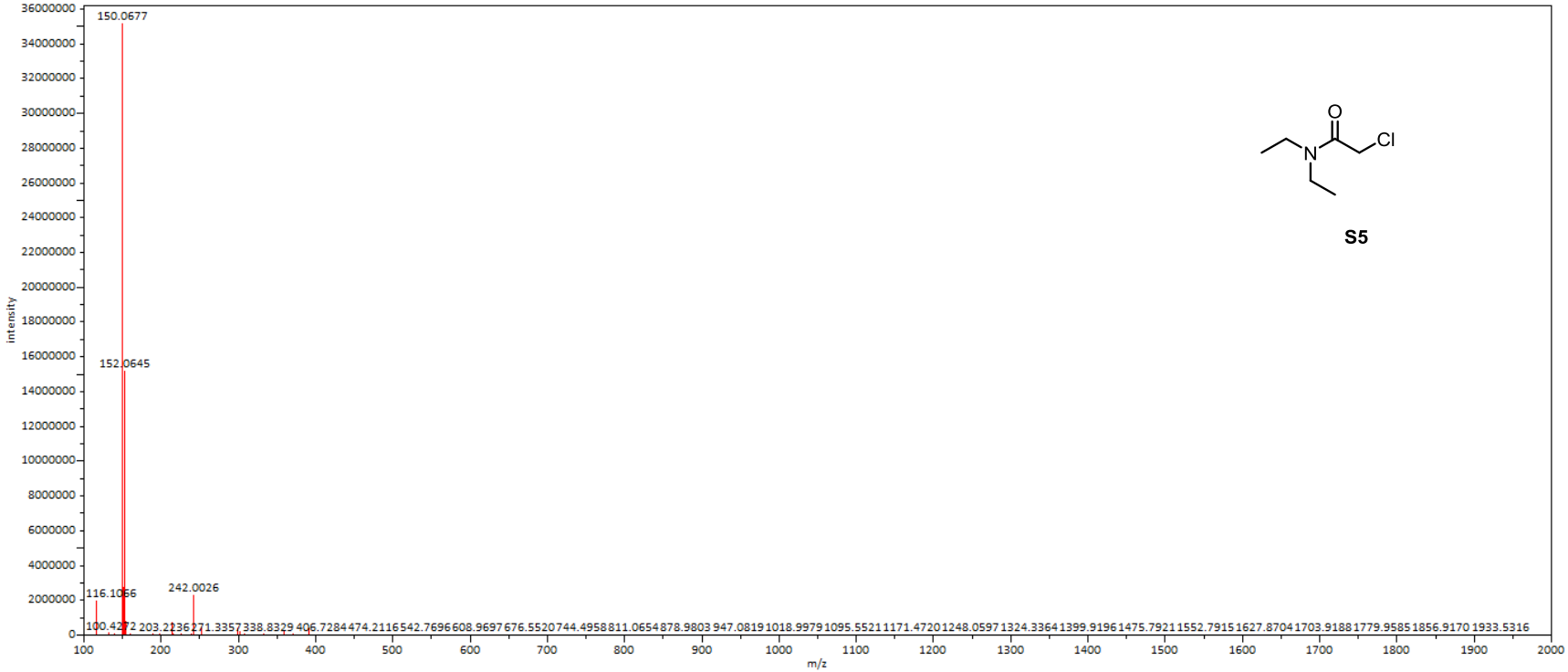


^{1}H-^{1}H COSY

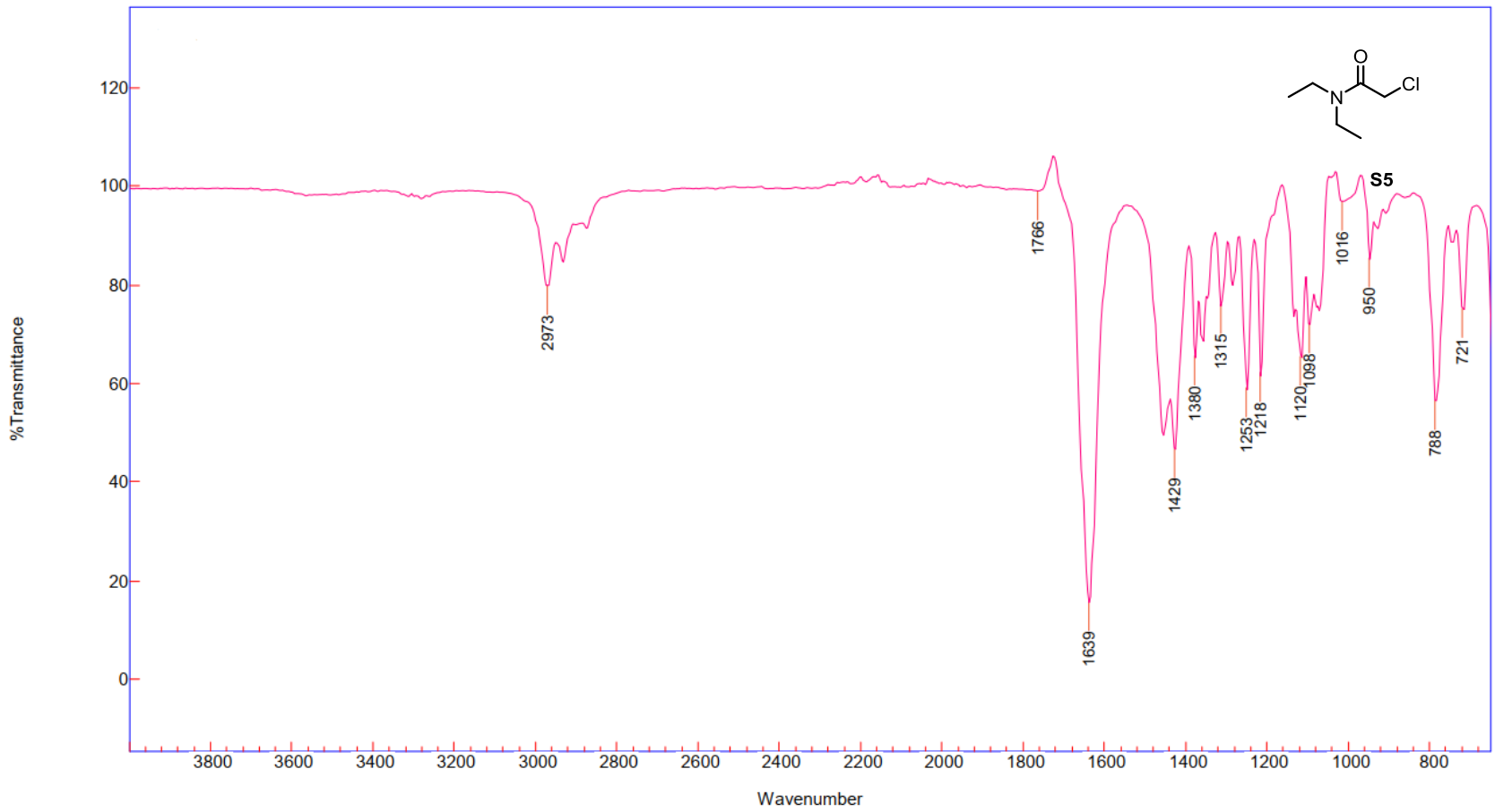



^{1}H-^{13}C HMQC
O
N
Cl
S5
ppm
0
20
40
60
80
100
120
140
160
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


^{1}H-^{13}C HMBC
O
N
Cl
S5
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

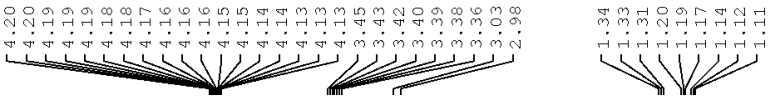


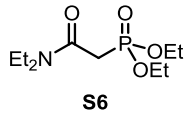
S5


S5
%Transmittance
Wavenumber
120
100
80
60
40
20
0
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
2973
1766
1639
1429
1380
1315
1253
1218
1120
1098
1016
950
788
721
O
N
Cl

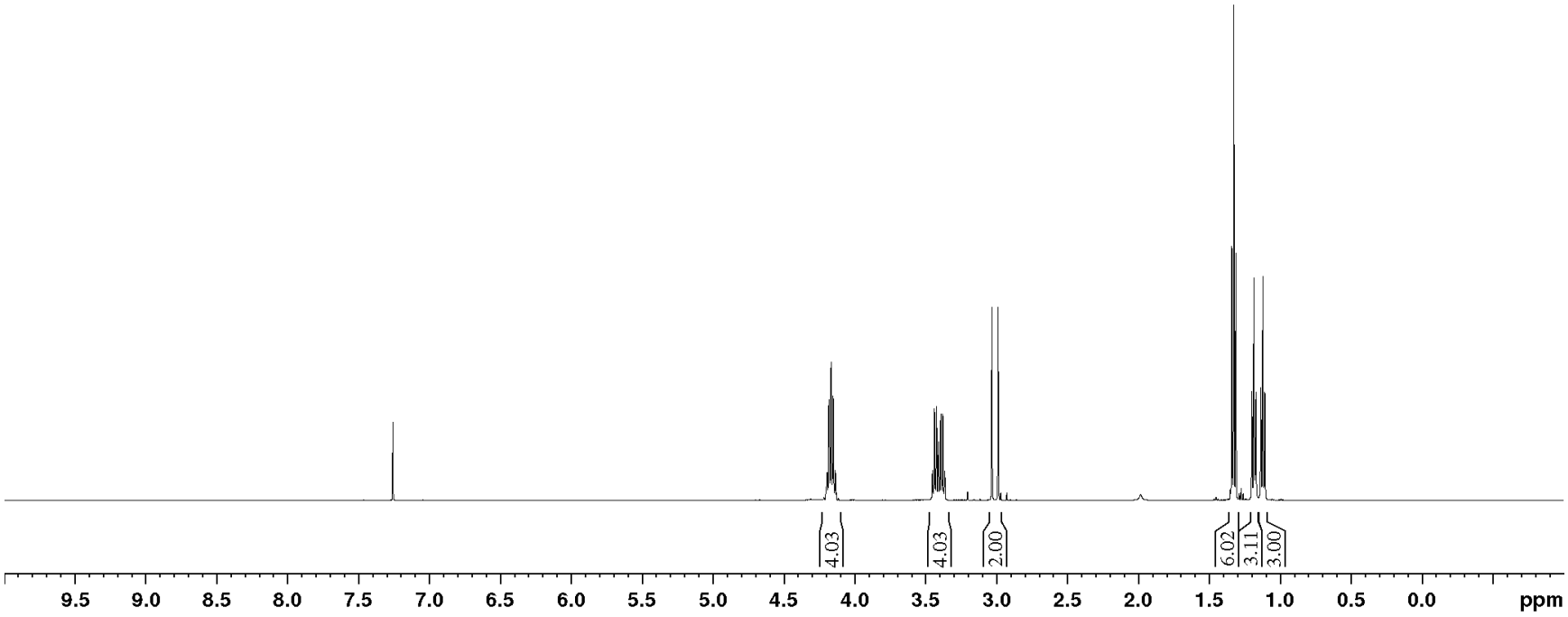
Diethyl (2-(diethylamino)-2-oxoethyl)phosphonate (S6)

^{1}H NMR

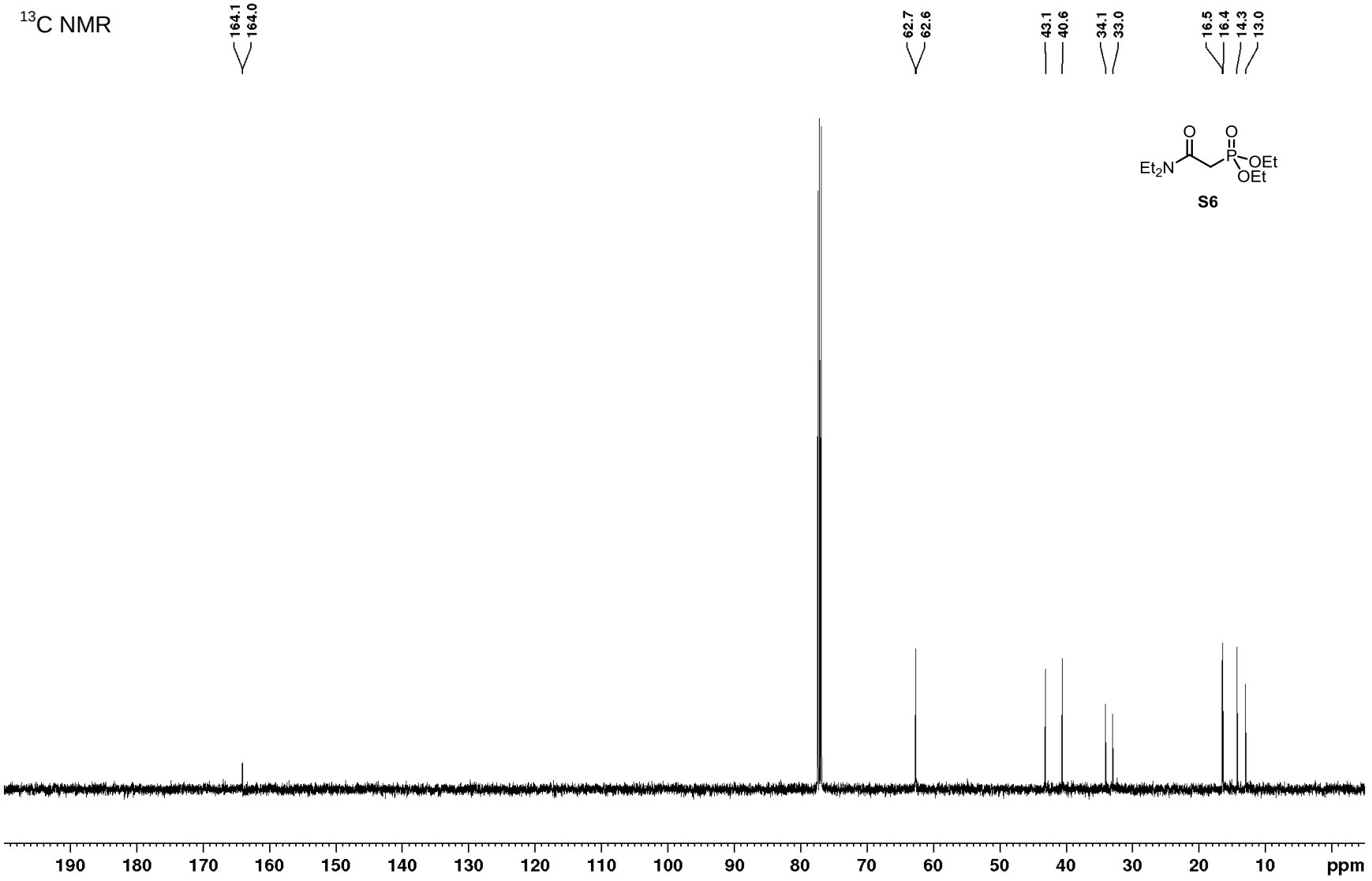




S6

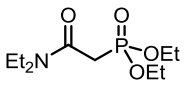


^{13}C NMR

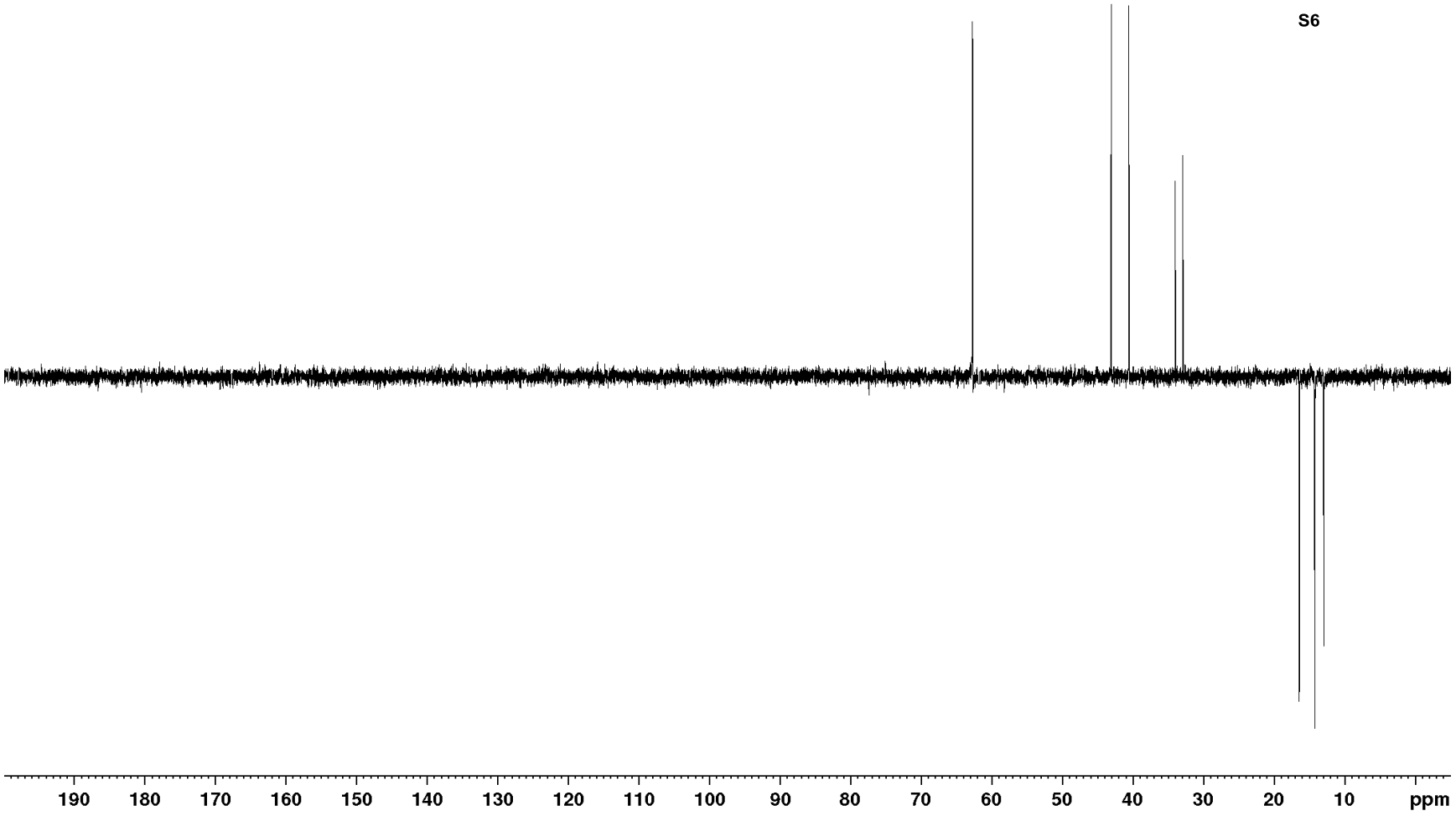

164.1
164.0
62.7
62.6
43.1
40.6
34.1
33.0
16.5
16.4
14.3
13.0
O
O
Et2N
P
OEt
OEt
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

S6

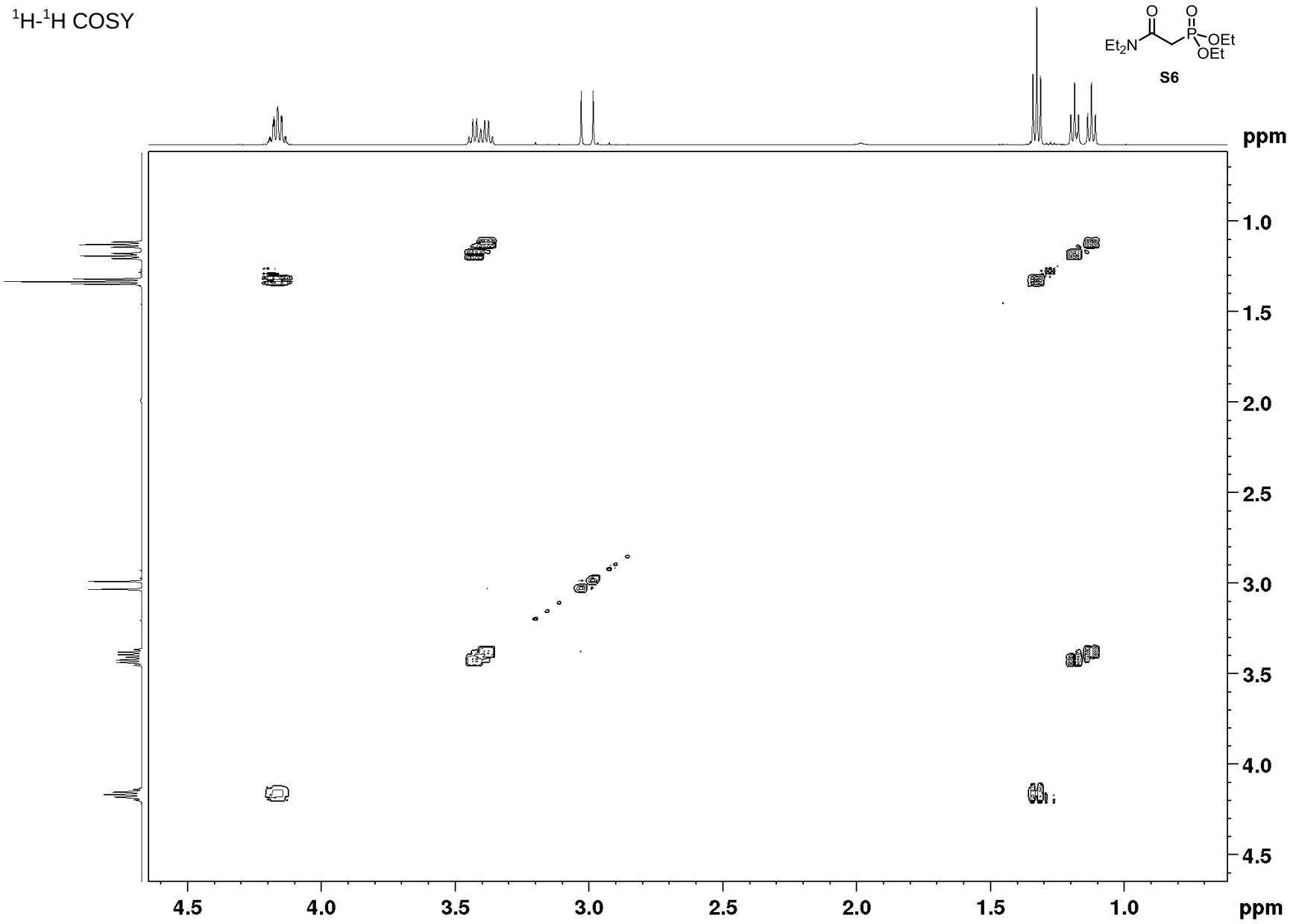
^{13}C DEPT NMR



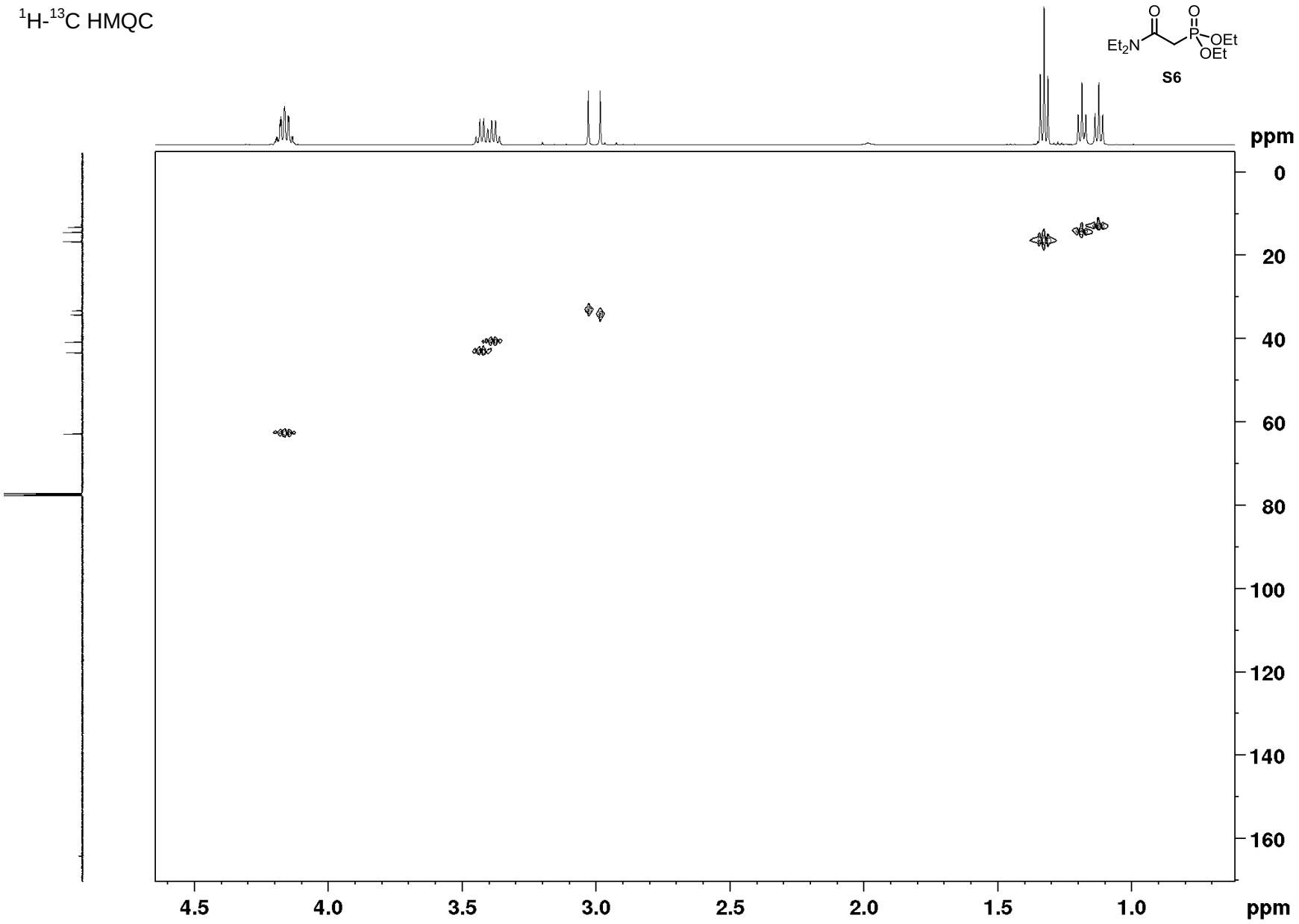
S6



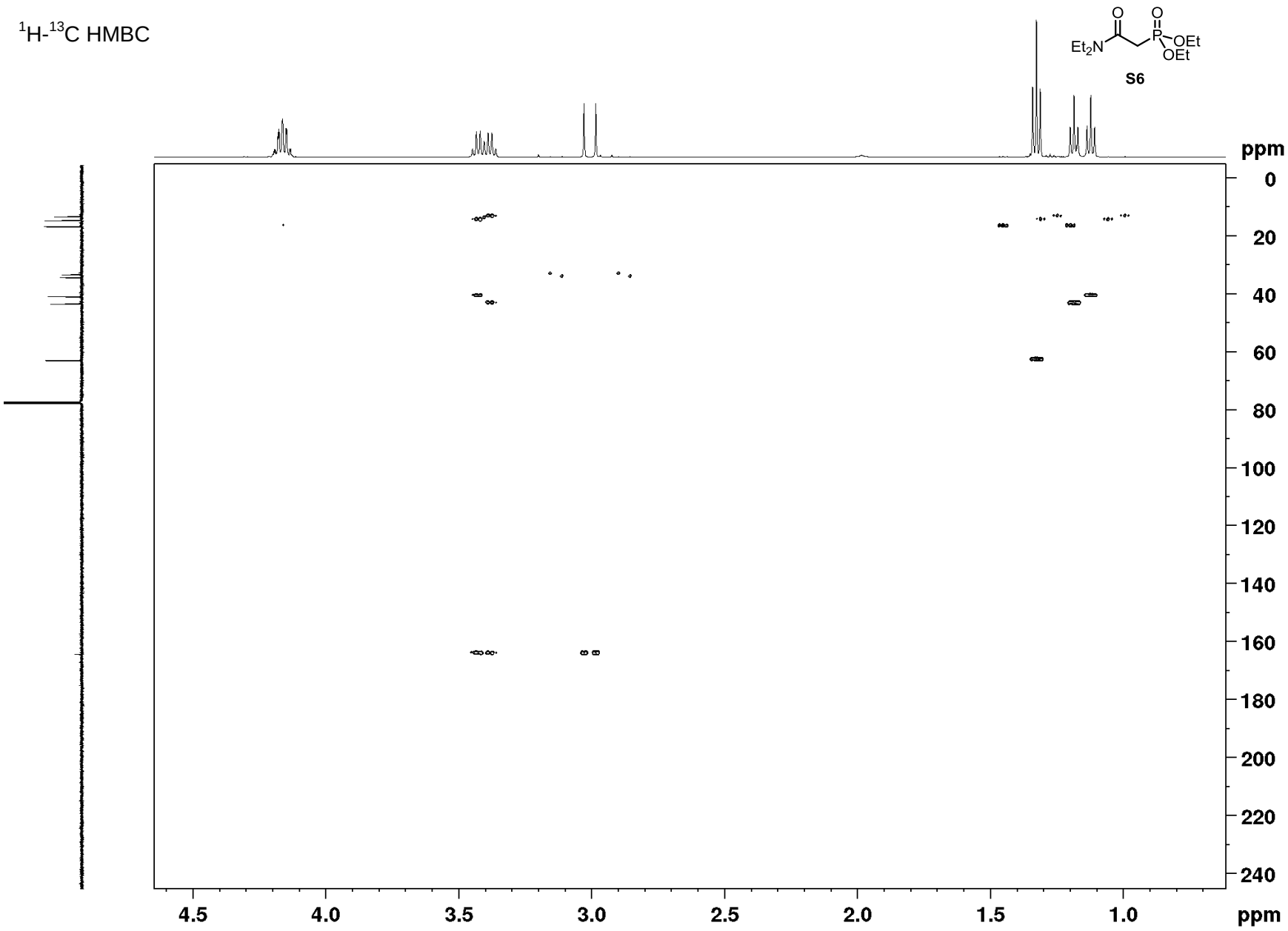
^{1}H-^{1}H COSY


Et2N
O
O
P
OEt
OEt
S6
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

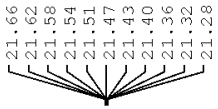
^{1}H-^{13}C HMQC

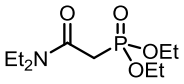

Et2N
O
O
P
OEt
OEt
S6
ppm
0
20
40
60
80
100
120
140
160
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

^{1}H-^{13}C HMBC

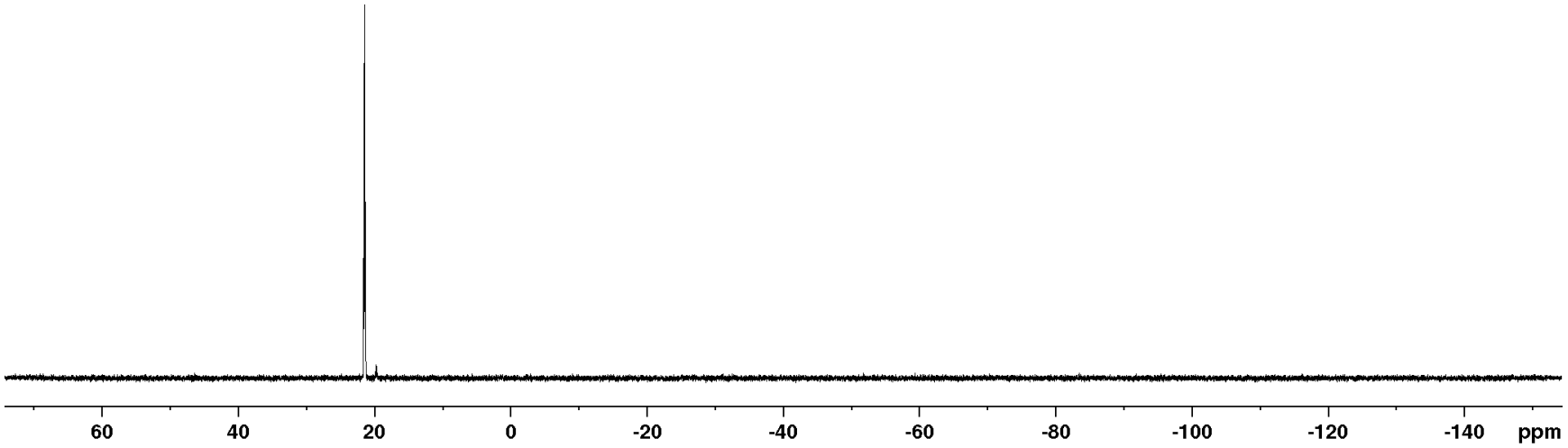

Et2N
O
O
P
OEt
OEt
S6
ppm
0
20
40
60
80
100
120
140
160
180
200
220
240
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

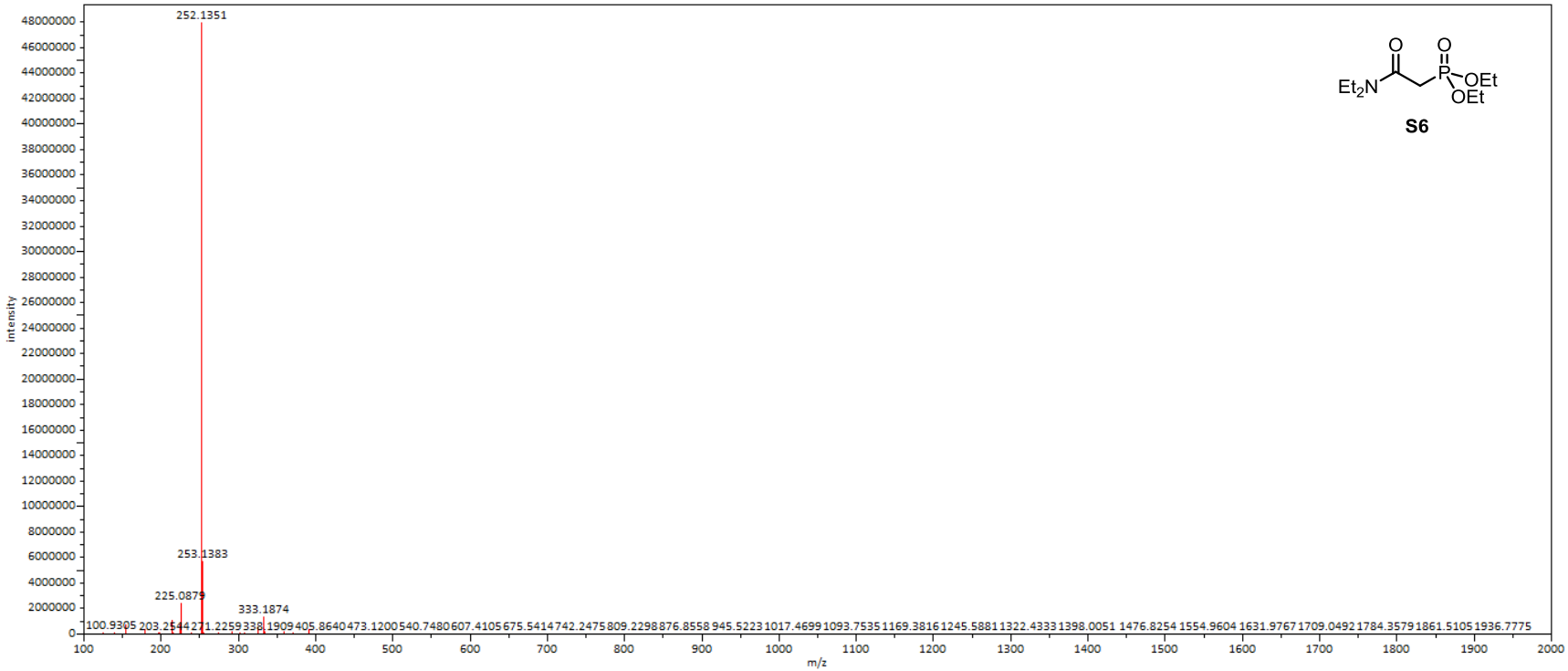
^{31}P NMR


21.66
21.62
21.58
21.54
21.51
21.47
21.43
21.40
21.36
21.32
21.28


O
O
Et2N
P
OEt
OEt

S6


60
40
20
0
-20
-40
-60
-80
-100
-120
-140
ppm


252.1351
253.1383
225.0879
333.1874
intensity
m/z
S6