Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Using alcohols as simple H_2-equivalents for copper-catalysed transfer semihydrogenations of alkynes

Contents

1 General Information

All reactions were carried out in flame dried glassware under a nitrogen atmosphere using standard Schlenk techniques. Glassware and stirring bars contaminated with transition metals were treated with *aqua regia* (conc. HCl/conc. HNO_3 3:1) prior to cleaning. For cleaning, glassware and stirring bars were kept in a *i*PrOH/KOH bath overnight, rinsed with H_2O, kept in a citric acid/H_2O bath overnight and finally rinsed with dest. 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 AVII 400, AVIII 500 or AVIII 700 NMR instruments (*Bruker*) at the Institut für Chemie of *Technische Universität Berlin*. Chemical shifts are reported in parts per million (ppm) relative to TMS or CCl_3F. For the calibration of the chemical shift the residual solvent resonance was used as the internal standard according to the standard literature.[1,2] ^{19}F chemical shifts were calibrated using the unified scale.[2] Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, 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 and was achieved by analysis of DEPT (DEPT 135) and 2D-NMR spectra (COSY, HSQC, HMQC, HMBC, NOESY). If a distinct assignment was not possible, atoms were marked with "*" and can be interchanged. Melting points (m.p.) were determined using a Leica Galen III melting point apparatus (*Wagner & Munz*) and are reported as the meniscus melting point.[3] 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*). All transfer hydrogenation reactions were carried out in pressure tubes, equipped with a magnetic stirring bar.

1.1 Solvents

THF and 1,4-dioxane were dried over sodium/benzophenone and distilled under a N_2 atmosphere prior to use. HPLC grade *i*PrOH, 2-pentanol and 2-hexanol were dried over CaH_2 and distilled under a N_2 atmosphere prior to use. Solvents (technical grade) for extraction/chromatography

(cyclohexane, CH_2Cl_2, *tert*-butyl methyl ether and *n*-pentane) were distilled under reduced pressure prior to use.

1.2 Chemicals

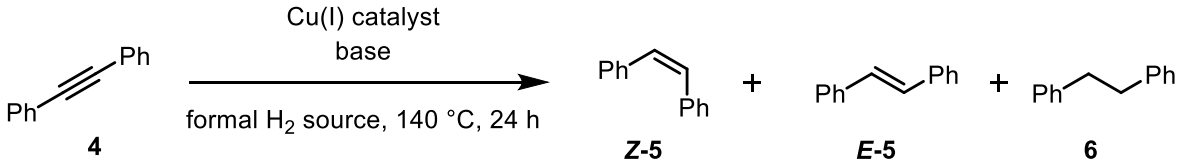
The following chemicals were purchased and used without further purification: tolane (*Sigma-Aldrich*), copper(I) chloride (99.99% Cu, Strem), dodec-6-yne (*TCI*),sodium *tert*-butoxide (*Acros*), lithium *tert*-butoxide (*ABCR*), acetophenone (*Sigma-Aldrich*), 4-chlorobenzaldehyde (*Sigma-Aldrich*).

The Cu-complexes [IPrCuCl], [IMesCuCl] and [SIMesCuCl] were prepared according to a literature procedure[4] from the corresponding imidazolium salts.[5]

BnOH-D_2 (**2**-*d*$_2$) was prepared following a literature procedure.[6] Alkynes 1,2-di-*p*-tolylethyne (**7b**),[7] 1,2-di-*o*-tolylethyne (**7c**),[7] 1,2-bis(4-methoxyphenyl)ethyne (**7d**),[7] 1-methoxy-4-(phenylethynyl)benzene (**7e**),[8] 1-chloro-4-(phenylethynyl)benzene (**7f**),[8] 1-(phenylethynyl)-4-(trifluoromethyl)benzene (**7g**),[8] (5-(benzyloxy)pent-1-yn-1-yl)benzene (**7h**),[9] (cyclohexylethynyl)benzene (**7i**)[10] and (cyclopropylethynyl)benzene (**7j**)[11] were synthesized following literature procedures.

2 Optimization

Table: Optimization of the reaction conditions[a]



4 ***Z*-5** ***E*-5** **6**

Entry	Catalyst	Base	H_2 Source	Conversion	*Z*/*E*[b]	Alkane
1	5 mol% [SIMesCuCl]	1.1 equiv NaO*t*Bu	*i*PrOH (1 ml)	49%	90:10	<1
2	10 mol% [SIMesCuCl]	1.1 equiv NaO*t*Bu	*i*PrOH (1 ml)	100%	92:8	<1
3	10 mol% [IPrCuCl]	1.1 equiv NaO*t*Bu	*i*PrOH (1ml)	90%	92:8	<1%

Entry	Catalyst	Base	H_2 Source	Conversion	*Z*/*E*[b]	Alkane
4	10 mol% [IMesCuCl]	1.1 equiv NaO*t*Bu	*i*PrOH (1ml)	100%	90:10	<1%
5[c]	10 mol% [SIMesCuCl]	1.1 equiv NaO*t*Bu	*i*PrOH (1ml)	100%	95:05	<1%
6	10 mol% [SIMesCuCl]	50 mol% NaO*t*Bu	*i*PrOH (1ml)	100%	84:16	<1%
7[d]	10 mol% [SIMesCuCl]	1.1 equiv NaO*t*Bu	*i*PrOH (1ml)	2%	20:80	0%
8	10 mol% [SIMesCuCl]	1.1 equiv NaO*t*Bu	2.0 equiv. BnOH in dioxane (1ml)	100%	70:30	<1%
9	10 mol% [SIMesCuCl]	1.1 equiv NaO*t*Bu	1:10 (1 ml) (glycerol:dioxane)	69%	64:05	<1%
10	10 mol% [SIMesCuCl]	1.1 equiv NaO*t*Bu	EtOH (1ml)	29%	93:7	<1%
11	10 mol% [SIMesCuCl]	1.1 equiv NaO*t*Bu	2-pentanol (1 mL)	56%	88:12	0%
12	10 mol% [SIMesCuCl]	1.1 equiv NaO*t*Bu	2-hexanol (1 mL)	100%	<1%	100%
13	20 mol% CuCl	1.1 equiv NaO*t*Bu	*i*PrOH (1ml)	100%	80:20	6%
14	20 mol% CuCl	1.0 equiv LiO*t*Bu	*i*PrOH (1ml)	100%	<1%	100%

[a] Reactions were conducted on a 0.2 mmol scale in *i*PrOH (1 mL). [b] Determined by GC and ^{1}H NMR Analysis. [c] recation performed in microwave at 120 °C for 16h. [d] Reaction was performed at 85 °C.

3 General Procedures

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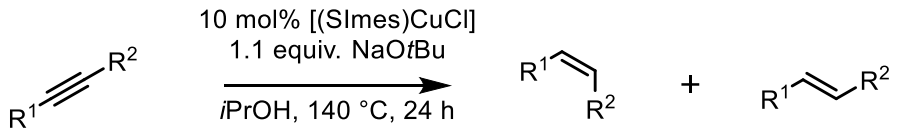
3.1 General procedure for the Cu(I)-Catalyzed Transfer Semihydrogenation of Alkynes (**GP1**)

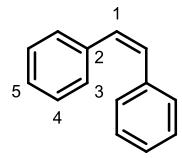


7 ***Z*-8** ***E*-8**

A flame dried 5 ml pressure tube equipped with a magnetic stir bar is charged with [SIMesCuCl] (10 mol%), NaO*t*Bu (1.1 equiv). The corresponding alkyne substrate (1.0 equiv) is added to the reaction mixture followed by the addition of *i*PrOH (5.0 mL/mmol) under N_2 atmosphere. The reaction mixture is placed in a pre-heated heating block at 140 °C for 24 h. The reaction mixture is allowed to cool down to room temperature and diluted with *tert*-butyl methyl ether, filtered over a pad of silica (2.5 x 2.5 cm) and eluted with *tert*-butyl methyl ether (30 mL/mmol). Reactions were subsequently analyzed either by GC or ^{1}H NMR. All volatiles are removed under reduced pressure and the residue is purified via flash column chromatography to afford the corresponding alkenes.

4 Preparation of Z-Alkenes

4.1 (*Z*)-1,2-diphenylethene (**8a**)



8a
$C_{14}H_{12}$
Mw = 180.25 g/mol

Following the general procedure **GP1,** 1,2-diphenylethyne **3a** (36 mg, 0.2 mmol, 1.0 equiv), [SIMesCuCl] (8.1 mg, 0.02 mmol, 10 mol%), NaO*t*Bu (69 mg, 0.22 mmol, 1.1 equiv) was allowed to react in *i*PrOH at 140 °C for 24 h. Then, the reaction mixture was filtered through a plug of silica (1 cm), eluted with *tert*-butyl methyl ether (5 mL) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded **8a** (34 mg, 0.19 mmol, 94%, 92:8 = *Z*:*E*) as a colorless oil.

R_f = 0.62 (cyclohexane).

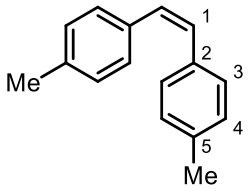
^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.64 (s, 2H, H-1), 7.30-7.20 (m, 10H, H-3, H-4, H-5) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 127.2 (C-5), 128.3 (C-4), 129.0 (C-3), 130.4 (C-1), 137.4 (C-2) ppm.

HRMS (APCI) calcd for $C_{14}H_{12}^{\bullet+}$ [$(M)^{\bullet+}$]: 180.0934, found 180.0928.

The analytical data is in accordance with the literature.[9]

4.2 (*Z*)-1,2-di-*p*-tolylethene (**8b**)



8b

$C_{16}H_{16}$

Mw = 208.30 g/mol

Following the general procedure **GP3**, 1,2-di-*p*-tolylethyne (**7b,** 41 mg, 0.20 mmol, 1.0 equiv) with [SIMesCuCl] (8.1 mg, 0.02 mmol, 10 mol%), NaO*t*Bu (21.1 mg, 0.22 mmol, 1.1 equiv) was allowed to react in *i*PrOH (1.0 ml) at 140 °C for 24 h. Then, the reaction mixture was filtered through a plug of silica (2.5 cm), eluted with *tert*-butyl methyl ether (5 mL) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded **8b** (40 mg, 0.19 mmol, 96%, 98:2 = *Z*:*E*) as a colorless oil.

R$_f$ = 0.43 (cyclohexane)

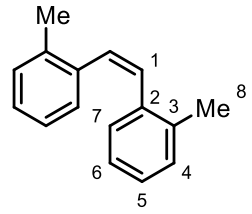
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.34 (s, 6H, H-6), 6.55 (s, 2H, H-1), 7.06 (d, $^3J_{3,4}$ = 7.9 Hz, 4H, H-3), 7.19 (d, $^3J_{4,3}$ = 8.1 Hz, 4H, H-4) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.4 (C-6), 128.9 (C-3), 129.0 (C-4), 129.7 (C-1), 134.7(C- 2), 136.8 (C-5).

HRMS (APCI) calcd for $C_{16}H_{16}^{\bullet+}$ [$(M)^{\bullet+}$]: 208.1252, found 208.1244.

The analytical data is in accordance with the literature.[12]

4.3 (*Z*)-1,2-di-*o*-tolylethene (**8c**)



8c

$C_{16}H_{16}$

Mw = 208.30 g/mol

Following the general procedure **GP1**, 1,2-di-*o*-tolylethyne (**7c**, 41.3 mg, 0.2 mmol, 1.0 equiv) with [SIMesCuCl] (8.1 mg, 0.02 mmol, 10 mol%), NaO*t*Bu (21.1 mg, 0.22 mmol, 1.1 equiv) was allowed to react in *i*PrOH (1.1 ml) at 140 °C for 24 h. Then, the reaction mixture was filtered through a plug of silica, eluted with *tert*-butyl methyl ether (5 mL) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded **8c** (39 mg, 0.19 mmol, 94%, 91:9 = *Z*:*E*) as a colorless oil which solidified slowly upon standing.

R$_f$ = 0.40 (cyclohexane).

M.p. = 53 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.31 (s, 6H, H-8), 6.75 (s, 2H, H-1), 6.98-6.93 (m, 4H, H-4, H-5), 7.11 (td, ^3J = 6.9 Hz, ^4J = 1.9 Hz, 2H, H-7), 7.16 (d, ^3J = 7.2 Hz, 2H, H-6) ppm.

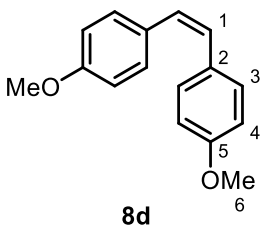
^{13}C NMR (126 MHz, $CDCl_3$): δ = 20.0 (C-8), 125.5 (C-6), 127.1 (C-5), 129.2 (C-7), 129.5 (C-1), 130.1(C-4),136.3 (C-3),136.7 (C-2).

HRMS (APCI) calcd for $C_{16}H_{16}^{\bullet+}$ [$(M)^{\bullet+}$]: 208.1247, found 208.1244.

The analytical data is in accordance with the literature.[13]

Not integrated signals belong to the minor *E*-isomer.

4.4 (*Z*)-1,2-bis(4-methoxyphenyl)ethene (**8d**)



8d

$C_{16}H_{16}O_2$

Mw = 240.30 g/mol

Following the general procedure **GP1,** 1-methoxy-4-(p-tolylethynyl)benzene (**7d,** 47.7 mg, 0.2 mmol, 1.0 equiv) with [SIMesCuCl] (8.1 mg, 0.02 mmol, 10 mol%), NaO*t*Bu (21.1 mg, 0.22 mmol, 1.1 equiv) was allowed to react in *i*PrOH (1.0 ml) at 140 °C for 24 h. Then, the reaction mixture was filtered through a plug of silica, eluted with *tert*-butyl methyl ether (5 mL) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using (2 × 15 cm, cyclohexane/*t*BME = 50:1 as eluent afforded **8d** (43 mg, 0.18 mmol, 89%, 92:8 = *Z*:*E*) as a slight yellow oil.

R_f = 0.52 (cyclohexane/*tert*-butyl methyl ether = 10:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.79 (s, 6H, H-6), 6.46 (s, 2H, H-1), 6.77 (d, $^3J_{3,4}$ = 8.9 Hz, 4H, H-3), 7.19 (d, $^3J_{4,3}$ = 8.1 Hz, 4H, H-4) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 55.3 (C-6), 113.7 (C-4), 128.5 (C-2), 130.1 (C-1), 130.2(C- 3), 158.65 (C-5).

HRMS (APCI) calcd for $C_{16}H_{16}O_2^{\bullet+}$ [$(M)^{\bullet+}$]: 240.1145, found 240.1141.

The analytical data is in accordance with the literature.[14]

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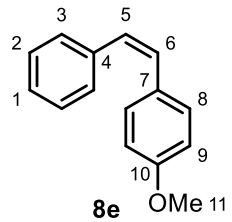
4.5 (*Z*)-1-methoxy-4-styrylbenzene (**8e**)



8e

$C_{15}H_{14}O$

Mw = 210.28 g/mol

Following the general procedure **GP1**, 1-methoxy-4-(phenylethynyl)benzene (**7e**, 41.7 mg, 0.2 mmol, 1.0 equiv) with [SIMesCuCl] (8.1 mg, 0.02 mmol, 10 mol%), NaO*t*Bu (21.1 mg, 0.22 mmol, 1.0 equiv) was allowed to react in *i*PrOH (1.1 ml) at 140 °C for 24 h. Then, the reaction mixture was filtered through a plug of silica, eluted with *tert*-butyl methyl ether (5 mL) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (2 × 15 cm) using cyclohexane/*t*BME = 50:1 as eluent afforded **8e** (39 mg, 0.19 mmol, 93%, 88:12 = *Z*:*E*) as a pale yellow oil.

R_f = 0.64 (cyclohexane/*tert*-butyl methyl ether = 10:1).

^{1}H NMR (500 MHz, $CDCl_3$): 3.79 (s, 3H, H-11), 6.47-6.56 (m, 2H, H-5, H-6), 6.70-6.79 (m, 2H, H-9), 1.11-7.3 (m, 7H, H-8, H-1, H-2, H-3) ppm.

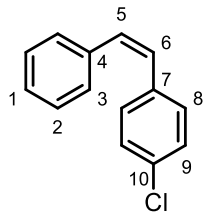
^{13}C NMR (126 MHz, $CDCl_3$): δ = 55.3 (C-11), 113.7 (C-9), 127.0 (C-1), 128.3 (C-2), 128.9 (C-5), 128.9 (C-3), 129.8 (C-7), 129.9 (C-6), 130.2 (C-8), 137.7 (C-4), 158.8 (C-10) ppm.

HRMS (APCI) calcd for $C_{15}H_{15}O^+$ [$(M+H)^+$]: 211.1116, found 211.1117.

Minor *E*-isomer corresponding resonances: ^{1}H NMR (500 MHz, $CDCl_3$): 3.83 (s, 3H), 6.90 (m_c, 2H), 6.97 (d, *J* = 16.3 Hz, 1H), 7.07 (d, *J* = 16.3 Hz, 1H), 7.20-7.25 (m, 1H), 7.34 (m_c, 2H), 7.43-7.51 (m, 4H) ppm.

The analytical data is in accordance with the literature.[9]

4.6 (*Z*)-1-chloro-4-styrylbenzene (**8f**)



8f

$C_{14}H_{11}Cl$

Mw = 214.69 g/mol

Following the general procedure **GP1** 1-chloro-4-(phenylethynyl)benzene (**7f**, 42.9 mg, 0.2 mmol, 1.0 equiv) with [SIMesCuCl] (8.1 mg, 0.02 mmol, 10 mol%), NaO*t*Bu (21.1 mg, 0.22 mmol, 1.1 equiv) was allowed to react in *i*PrOH at 140 °C for 24 h. Then, the reaction mixture was filtered through a plug of silica, eluted with *tert*-butyl methyl ether (5 mL) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded **8f** (39 mg, 0.18 mmol, 91%, 94:6 = *Z*:*E*) as a colorless oil.

R_f = 0.50 (cyclohexane).

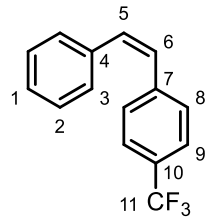
^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.55 (d, $^3J_{6,5}$ = 12.2 Hz, 1H, H-6), 6.64 (d, $^3J_{5,6}$ = 12.2 Hz, 1H, H-5), 7.18-7.22 (mc, 4H, H-8, H-9), 7.25-7.28 (m, 5H, H-1, H-2, H-3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 127.5 (C-1), 128.4 (C-2), 128.5 (C-9), 128.9 (C-3), 129.1 (C- 6), 130.3 (C-8), 131.1 (C-5), 132.9 (C-10), 135.8 (C-7), 137.0 (C-4) ppm.

HRMS (APCI) calcd for $C_{14}H_{14}Cl^{\bullet+}$ [$(M)^{\bullet+}$]: 214.0544, found 214.0543.

The analytical data is in accordance with the literature.[15]

4.7 (*Z*)-1-styryl-4-(trifluoromethyl)benzene (**8g**)



8g

$C_{15}H_{11}F_3$

Mw = 248.25 g/mol

Following the general procedure **GP1,** 1-(phenylethynyl)-4-(trifluoromethyl)benzene (**7g**, 49.3 mg, 0.2 mmol, 1.0 equiv) with [SIMesCuCl] (8.1 mg, 0.02 mmol, 10 mol%), NaO*t*Bu (21.1 mg, 0.22 mmol, 1.1 equiv) was allowed to react in *i*PrOH (1.0 ml) at 140 °C for 24 h. Then, the reaction mixture was filtered through a plug of silica, eluted with *tert*-butyl methyl ether (5 mL) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded **8g** (33 mg, 0.13 mmol, 66%, 96:4 = *Z*:*E*) as a colorless oil.

R$_f$ = 0.52 (cyclohexane/*tert*-butyl methyl ether = 10:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.52 (d, $^3J_{6,5}$ = 12.3 Hz, 1H, H-6), 6.65 (d, $^3J_{5,6}$ = 12.2 Hz, 1H, H-5), 7.18-7.11 (m, 5H, H-1, H-2, H-3), 7.26 (d, $^3J_{8,9}$ = 8.15 Hz, 2H, H-8), 7.38 (d, $^3J_{9,8}$ = 8.20 Hz, 2H, H-9)ppm.

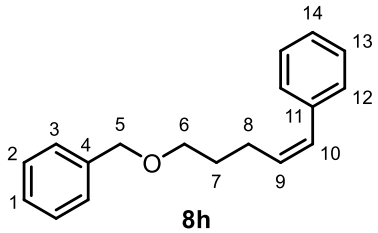
^{13}C NMR (126 MHz, $CDCl_3$): δ = 124.3 (d, ^1J = 272.5 Hz, C-11), 125.3 (q, $^3J_{9F}$ = 3.7 Hz, C-9), 127.7 (C-1), 127.6 (C-2), 128.6 (C-10), 128.8 (C-6), 128.9 (C-3), 129.3 (C-8), 132.5 (C-5), 136.7 (C-4), 141.1 (C-7).

^{19}F NMR (471 MHz, $CDCl_3$): δ = –62.5 ppm.

HRMS (APCI) calcd for $C_{15}H_{11}F_3^{\bullet+}$ [$(M)^{\bullet+}$]: 248.0807, found 248.0804.

The analytical data is in accordance with the literature.[8]

4.8 (*Z*)-(5-(benzyloxy)pent-1-en-1-yl)benzene (**8h**)



8h

$C_{18}H_{20}O$

Mw = 252.36 g/mol

Following the general procedure **GP1,** (5-(benzyloxy)pent-1-yn-1-yl)benzene (**7h**, 41.3 mg, 0.2 mmol, 1.0 equiv) with [SIMesCuCl] (8.1 mg, 0.02 mmol, 10 mol%), NaO*t*Bu (21.1 mg, 0.22 mmol, 1.0 equiv) was allowed to react in *i*PrOH (1.0 ml) at 140 °C for 24 h. Then, the reaction mixture was filtered through a plug of silica, eluted with *tert*-butyl methyl ether (5 mL) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using 2 × 15 cm, cyclohexane/*t*BME = 50:1 as eluent afforded **8h** (46 mg, 0.19 mmol, 90%, 82:18 = *Z*:*E*) as a colorless oil.

R$_f$ = 0.72 (cyclohexane/*tert*-butyl methyl ether = 10:1.)

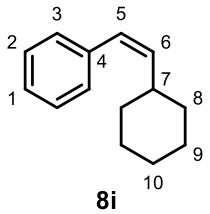
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.66-1.72 (m, 2H, H-7), 2.36 (m_c, 2H, H-8), 3.41 (t, $^3J_{6,7}$ = 7.1 Hz, 2H, H-6), 4.38 (s, 2H, H-5), 5.58 (dt, $^3J_{9,10}$ = 11.6 Hz, $^3J_{9,8}$ = 7.4 Hz, 1H, H-9), 6.35 (d, $^3J_{10,9}$ = 11.6 Hz, 1H, H-10), 7.12-7.26 (m, 10H, H-Ar) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): 25.4 (C-7), 30.0 (C-8), 69.7 (C-6), 72.9 (C-5),126.6 (C-14), 127.6 (C-1), 127.7 (C-3), 128.2 (C-13), 128.5 (C- 2), 128.9 (C-12), 129.5 (C-10), 132.4 (C- 9), 137.7 (C-11), 138.7 (C-4) ppm.

HRMS (APCI) calcd for $C_{18}H_{21}O^+$ [$(M+H)^+$]: 253.1587, found 253.1579.

The analytical data is in accordance with the literature.[8]

4.9 (*Z*)-(2-cyclohexylvinyl)benzene (**8i**)



8i

$C_{14}H_{18}$

Mw = 186.30 g/mol

Following the general procedure **GP3** (cyclohexylethynyl)benzene (**7i**, 36.8 mg, 0.2 mmol, 1.0 equiv) with [SIMesCuCl] (8.1 mg, 0.02 mmol, 10 mol%), NaO*t*Bu (21.1 mg, 0.22 mmol, 1.0 equiv) was allowed to react in *i*PrOH (1.1 ml) at 140 °C for 24 h. Then, the reaction mixture was filtered through a plug of silica, eluted with *tert*-butyl methyl ether (5 mL) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded **8i** (18 mg, 0.10 mmol, 48%, 93:4 = *Z*:*E*) as a colorless oil containing 4% of the corresponding alkane.

R$_f$ = 0.38 (cyclohexane).

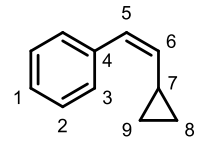
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.17-1.31 (m, 6H, H-9, H-10), 1.71-1.76 (m, 4H, H-8), 2.59 (m_c, 1H, H-7), 5.50 (dd, $^3J_{6,5}$ = 11.7 Hz, ^4J = 10.2 Hz, 1H, H-6), 6.33 (d, $^3J_{5,6}$ = 11.6 Hz, 1H, H-5), 7.28-7.21 (m, 3H, H-1,H-3), 7.35-7.33 (m, 2H, H-2) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 25.8 (C-9), 26.2 (C-10), 33.4 (C-8), 37.0 (C-7), 126.5 (C-6), 127.0 (C-5), 128.3 (C-2), 128.7(C-3), 138.1 (C-4), 139.1 (C-1) ppm.

HRMS (APCI) calcd for $C_{14}H_{18}^{\bullet+}$ [$(M)^{\bullet+}$]: 186.1403, found 186.1401.

The analytical data is in accordance with the literature.[16]

4.10 (*Z*)-(2-cyclopropylvinyl)benzene (**8j**)



8j

$C_{11}H_{12}$

Mw = 144.22 g/mol

Following the general procedure **GP1** (cyclopropylethynyl)benzene (**7j**, 42.7 mg, 0.3 mmol, 1.0 equiv) with [SIMesCuCl] (12.1 mg, 0.03 mmol, 10 mol%), NaO*t*Bu (31.7 mg, 0.33 mmol, 1.1 equiv) was allowed to react in *i*PrOH (1.5 ml) at 140 °C for 24 h. Then, the reaction mixture was filtered through a plug of silica, eluted with *tert*-butyl methyl ether (5 mL) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded **8j** (36 mg, 0.25 mmol, 84%, 97:3 = *Z*:*E*) as a colorless oil.

R$_f$ = 0.63 (cyclohexane).

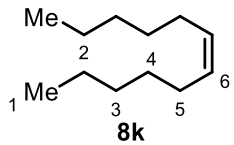
^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.49 (m_c, 2H, H-9), 0.84 (m_c, 2H, H-8), 1.90 (m_c, 1H, H-7), 5.08 (dd, $^3J_{6,5}$ = 11.5 Hz, ^4J = 10.0 Hz, 1H, H-6), 6.37 (d, $^3J_{5,6}$ = 11.5, 1H Hz, H-5), 7.29 (t, ^3J = 7.4 Hz, 1H, H-1), 7.35 (t, ^3J = 7.9 Hz, 2H, H-2), 7.44 (d, ^3J = 7.8 Hz, 2H, H-3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 8.2 (C-9, C-8), 11.2 (C-7), 126.5 (C-1), 127.5 (C-5), 128.3 (C-3), 128.8 (C-2), 136.9 (C-6), 138.1 (C-4) ppm.

HRMS (APCI) calcd for $C_{11}H_{12}^{\bullet+}$ [$(M)^{\bullet+}$]: 144.0934, found 144.0932.

The analytical data is in accordance with the literature.[17]

4.11 (*Z*)-dodec-6-ene (**8k**)



8k

$C_{12}H_{24}$

Mw = 168.32 g/mol

Following the general procedure **GP1,** dodec-6-yne (**7k**, 49.9 mg, 0.3 mmol, 1.0 equiv) with [SIMesCuCl] (12.1 mg, 0.03 mmol, 10 mol%), NaO*t*Bu (31.7 mg, 0.33 mmol, 1.1 equiv) was allowed to react in *i*PrOH (1.5 ml) at 140 °C for 24 h. Then, the reaction mixture was filtered through a plug of silica, eluted with *tert*-butyl methyl ether (5 mL) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded **8k** (31 mg, 0.18 mmol, 61%, 99:1 = *Z*:*E*) as a colorless oil.

R_f = 0.62 (cyclohexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, ^3J = 6.9 Hz, 6H, H-1), 1.36-1.26 (m, 12H, H-2, H-3, H-4), 2.00-2.04 (m, 4H, H-5), 5.36 (m_c, 2H, H-6) ppm.

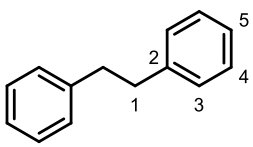
^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (C-1); 22.7 (C-2), 27.3 (C-5), 29.6 (C-4), 31.7 (C-3), 130.1 (C-6) ppm.

HRMS (APCI) calcd for $C_{12}H_{23}^{+}$ [$(M-H)^{+}$]: 167.1794, found 167.1795.

The analytical data is in accordance with the literature.[18]

5 CuCl-catalyzed transfer hydrogenation of internal alkynes to alkanes

5.1 1,2-diphenylethane (**9**)



9

$C_{14}H_{14}$

Mw = 182.27 g/mol

To a flame dried 5 ml pressure tube equipped with a magnetic stir bar was added 1,2-diphenylethyne (**7a**, 35.6 mg, 0.2 mmol, 1.0 equiv) CuCl (4.0 mg, 0.04 mmol, 20 mol%) and LiO*t*Bu (16.0 mg, 0.20 mmol, 1.0 equiv) was allowed to react in *i*PrOH (1.0 ml). Then the reaction mixture was placed in a pre-heated heating block at 140 °C for 24 h. Then, the reaction was stopped and the reaction mixture was allowed cool to room

temperature. Then, the reaction mixture was filtered through a plug of silica (2.5 cm), eluted with *tert*-butyl methyl ether (5 mL) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded 1,2-diphenylethane **9** (34 mg, 0.19 mmol, 93%) as a white solid.

R_f = 0.61 (cyclohexane).

M.p. = 55 °C.

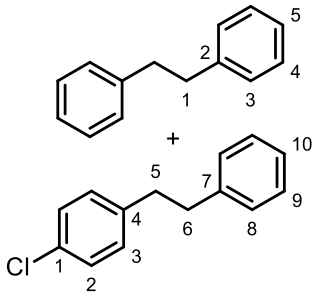
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.95 (s, 4H, H-1), 7.23-7.20 (m, 6H, H-3, H-5), 7.29-7.32 (m, 4H, H-4) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 38.1 (C-1), 126.04 (C-5), 128.5 (C-3)*, 128.6 (C-4)*, 141.9 (C-2) ppm.

HRMS (APCI) calcd for $C_{14}H_{14}^{\bullet+}$ [$(M)^{\bullet+}$]: 182.1090, found 182.1089.

The analytical data is in accordance with the literature.[19]

5.2 1,2-diphenylethane (**9**) and 1-chloro-4-phenethylbenzene (**10**)



9
$C_{14}H_{14}$
Mw = 182.27 g/mol

10
$C_{14}H_{13}Cl$
Mw = 216.70 g/mol

To a flame dried 5 ml pressure tube equipped with a magnetic stir bar was added 1-chloro-4-(phenylethynyl)benzene (**7f**, 42.9 mg, 0.2 mmol, 1.0 equiv) CuCl (4.0 mg, 0.04 mmol, 20 mol%) and base (0.30 mmol, 1.5 equiv) in *i*PrOH (1.0 ml). Then, the reaction mixture was placed in a pre-heated heating block at 140 °C for 24 h. Then, the reaction was stopped and the reaction mixture was allowed to cool to room temperature. Then, the reaction mixture was filtered through a plug of silica (2.5 cm), eluted with *tert*-butyl methyl ether (5 mL) and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane as eluent afforded as a mixture of **9** and **10**.

Entry	Base	Conversion[a]	9/10[a]
1	LiO*t*Bu	full	66:34
2	NaO*t*Bu	full	20:80

[a] Determined by GC.

R_f = 0.61 (cyclohexane).

9: 1,2-diphenylethane representative peaks

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.99 (s, 4H, H-1).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 38.1 (C-1), 126.04, 128.5, 128.6, 141.9 ppm.

HRMS (APCI) calcd for $C_{14}H_{13}^+$ [(M-H)$^+$]: 181.1012, found 181.1011.

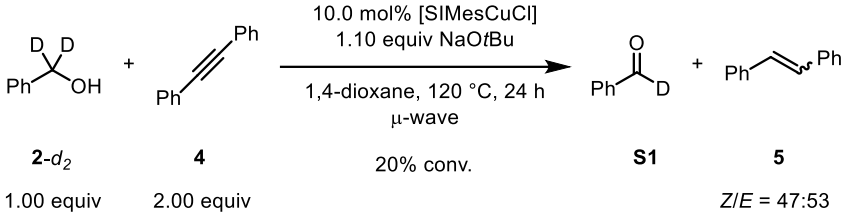
10: 1-chloro-4-phenethylbenzene representative peaks

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.96 (s, 4H, H-5, H-5).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 37.3 (C-5)*, 37.9 (C-6)*, 126.2, 128.5, 130.0, 131.8, 140.2, 141.4.

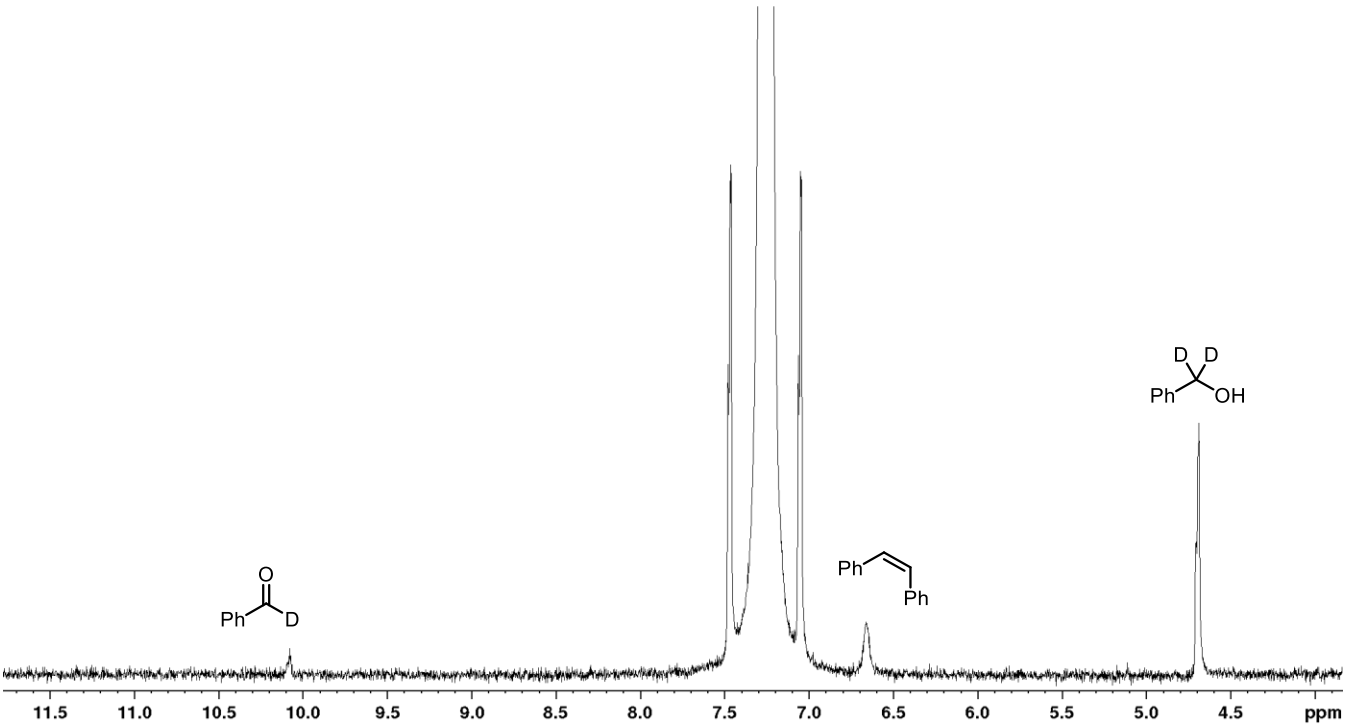
HRMS (APCI) calcd for $C_{14}H_{12}Cl^+$ [(M-H)$^+$]: 215.0622, found 215.0625.

6 Deuteration experiment with BnOH-D_2

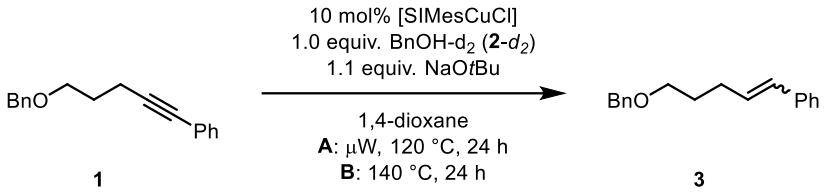


A flame dried 2 ml microwave vial was charged with [SIMesCuCl] (3.6 mg, 8.5 µmol, 10 mol%), NaO*t*Bu (11 mg, 9.4 µmol, 1.1 equiv). The mixture was suspended in 1,4-dioxane (1 mL), stirred for 5 min at 40 °C. Then first a solution of 1,2-diphenylethyne (**4**, 32 mg, 0.17 mmol, 2.0 equiv) in 1,4-dioxane (0.1 mL) and second a solution of BnOH-D_2 (**2**-*d_2*, 12 mg, 8.5 µmol, 1.0 equiv) in 1,4-dioxane (0.1 mL) were added to the reaction mixture. The reaction was heated for 24 h at 120 °C under microwave reaction conditions. The reaction mixture was cooled down to RT, diluted with CH_2Cl_2 (2 mL) and filtered over a pad of silica (2.5 x 0.5 cm, CH_2Cl_2, 20 mL). All volatiles are removed under reduced pressure and the crude reaction mixture was obtained and analyzed by NMR spectroscopy and GC analysis.

^{2}H NMR show circumstantial evidence for the presence of benzaldehyde-*d_1* (**S1**).

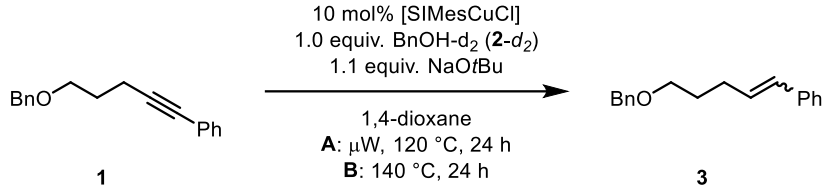


7 Extended Deuteration experiments with BnOH-D_2 (**2**-d_2) and isomerization studies

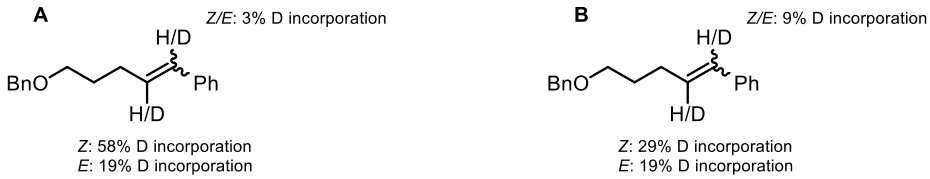


To a flame dried 2 ml microwave vial was charged with [SIMesCuCl] (8.1 mg, 0.02 mmol, 10 mol%) and NaO*t*Bu (21 mg, 0.22 mmol, 1.1 equiv). The mixture was suspended in 1,4-dioxane (0.4 mL), stirred for 5 min at 40 °C. In two separate vials, a solution of 1(5-(benzyloxy)pent-1-yn-1-yl)benzene (**1**, 50 mg, 0.20 mmol, 1.0 equiv) in 1,4-dioxane (0.2 mL), and BnOH-D_2 (**2**-d_2, 22 mg, 0.20 mmol, 1.0 equiv) in 1,4-dioxane (0.2 mL) are prepared under nitrogen atmosphere. The alkyne solution was added first and the alcohol solution afterwards. The reaction mixture was heated for 24 h at 120 °C in a microwave (conditions **A**) or for 2 h at 140 °C using conventional heating. The reaction mixture was cooled down to RT, diluted with CH_2Cl_2 (2 mL) and filtered over

a pad of silica (2.5 x 0.5 cm, CH_2Cl_2, 20 mL). All volatiles are removed under reduced pressure and crude product **3** was obtained.

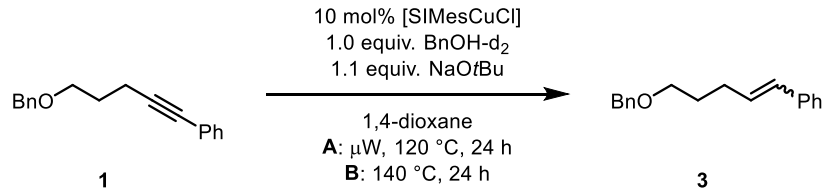


A: full conv., *Z*/*E* = 30:70
B: full conv., *Z*/*E* = 21:79

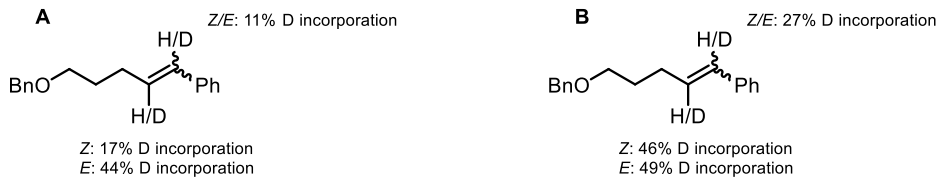


To increase the deuterium incorporation further, the glassware was treated with D_2O before flame drying. (To do this, the high pressure tube was washed several times with D_2O at room tempereature and D_2O was left within the glassware for 2 h.)Finally, the D_2O was removed and the glassware was commonly dried and degassed using standard Schlenck technique. The overall D incorporation did indeed rise (see below), indicating that there is significant exchange with the OH groups of the glassware.

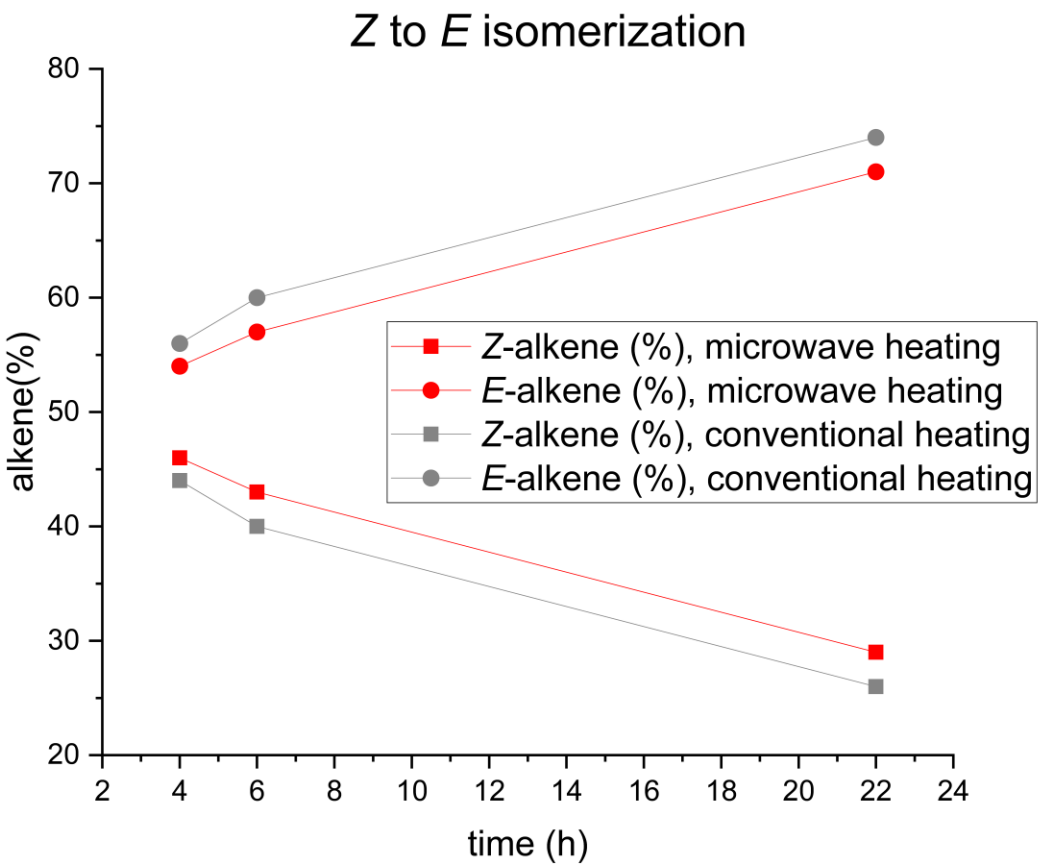
D_2O treatment:



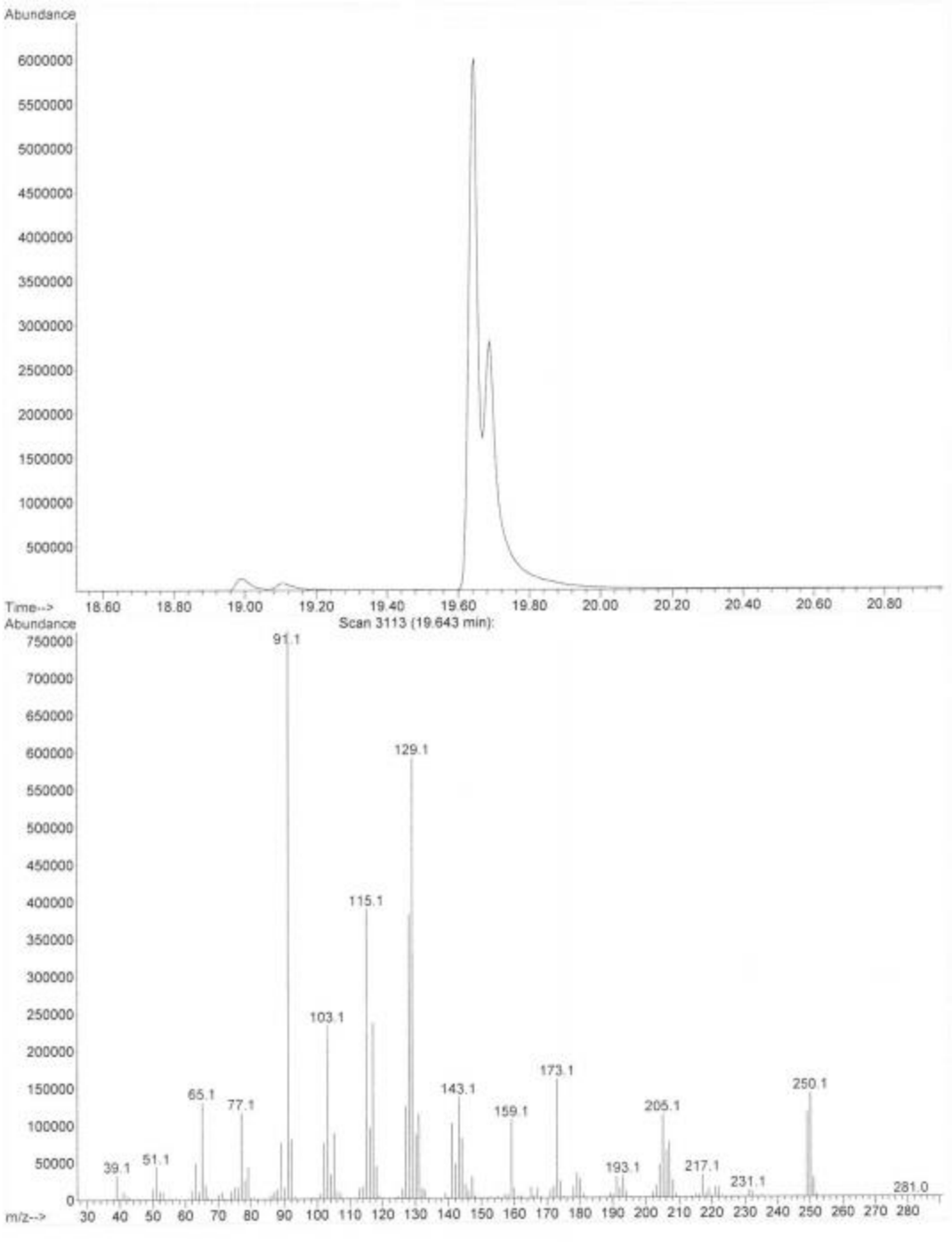
A: full conv., *Z*/*E* = 23:77
B: full conv., *Z*/*E* = 45:55



For isomerization studies a GC sample (0.05 mL of the crude mixture, filtered over a plug of silica 0.5 x 2 cm, CH_2Cl) was taken at different reaction times.

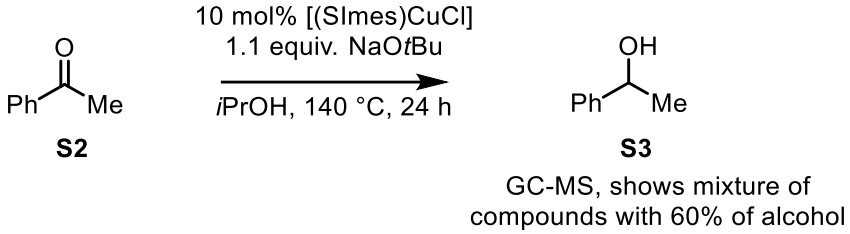


In these experiments, full conversion of the starting materials was reached after 4 h reaction times. This indicates that a secondary Z to E isomerization process is taking place after the actual alkyne semihydrogenation. This eludes to the fact that careful reaction control should be extert with an alkyne of interest, as it is possible to attain higher Z/E ratios if the reaction is stopped early enough.



For further spectra see additional spectral data.

8 Cu(I)-Catalyzed Transfer Semihydrogenation of Ketones

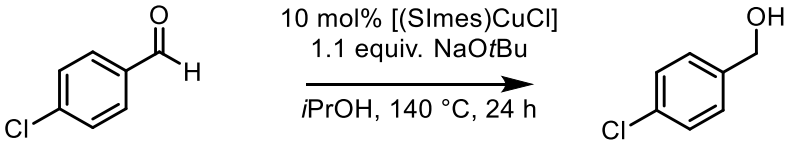


S2 **S3**

GC-MS, shows mixture of compounds with 60% of alcohol

To a flame dried 5 ml pressure tube was equipped with a magnetic stir bar was added acetophenone (**S2**, 24.0 mg, 0.2 mmol, 1.0 equiv) with [SIMesCuCl] (8.1 mg, 0.02 mmol, 10 mol%), NaO*t*Bu (21.1 mg, 0.22 mmol, 1.0 equiv) followed by the addition of *i*PrOH (5.0 mL/mmol) under N_2 atmosphere. Then, the reaction mixture is placed in a pre-heated heating block at 140 °C for 24 h. Then, the reaction is stopped and the reaction mixture is allow to cool down to room temperature. The reaction mixture is diluted with *tert*-butyl methyl ether and filtered over a pad of silica (2.5 x 2.5 cm) eluted with *tert*-butyl methyl ether (30 mL/mmol). Reaction is subsequently analyzed by GC, and GC-MS.

9 Cu(I)-Catalyzed Transfer Semihydrogenation of Aldehydes



S4 **S5**

not observed the expected alcohol By GC-MS

To a flame dried 5 ml pressure tube was equipped with a magnetic stir bar was added 4-chlorobenzaldehyde (28.0 mg, 0.2 mmol, 1.0 equiv) with [SIMesCuCl] (8.1 mg, 0.02 mmol, 10 mol%), NaO*t*Bu (21.1 mg, 0.22 mmol, 1.0 equiv) followed by the addition of *i*PrOH (5.0 mL/mmol) under N_2 atmosphere. Then, the reaction mixture is placed in a pre-heated heating block at 140 °C for 24 h. Then, the reaction is stopped and the reaction mixture is allow to cool down to room temperature. The reaction mixture is diluted with *tert*-butyl methyl ether and filtered over a pad of silica (2.5 x 2.5 cm) eluted with *tert*-butyl methyl ether (30 mL/mmol). Reaction is subsequently analyzed by GC, and GC-MS.

10 References

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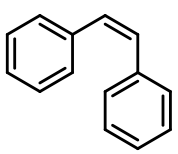
11 Spectra

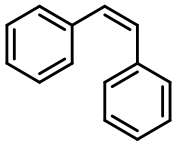
^{1}H NMR



8a

7.30
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.22
7.21
6.64
10.17
2.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

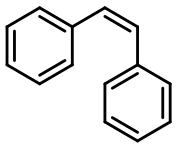
^{13}C NMR



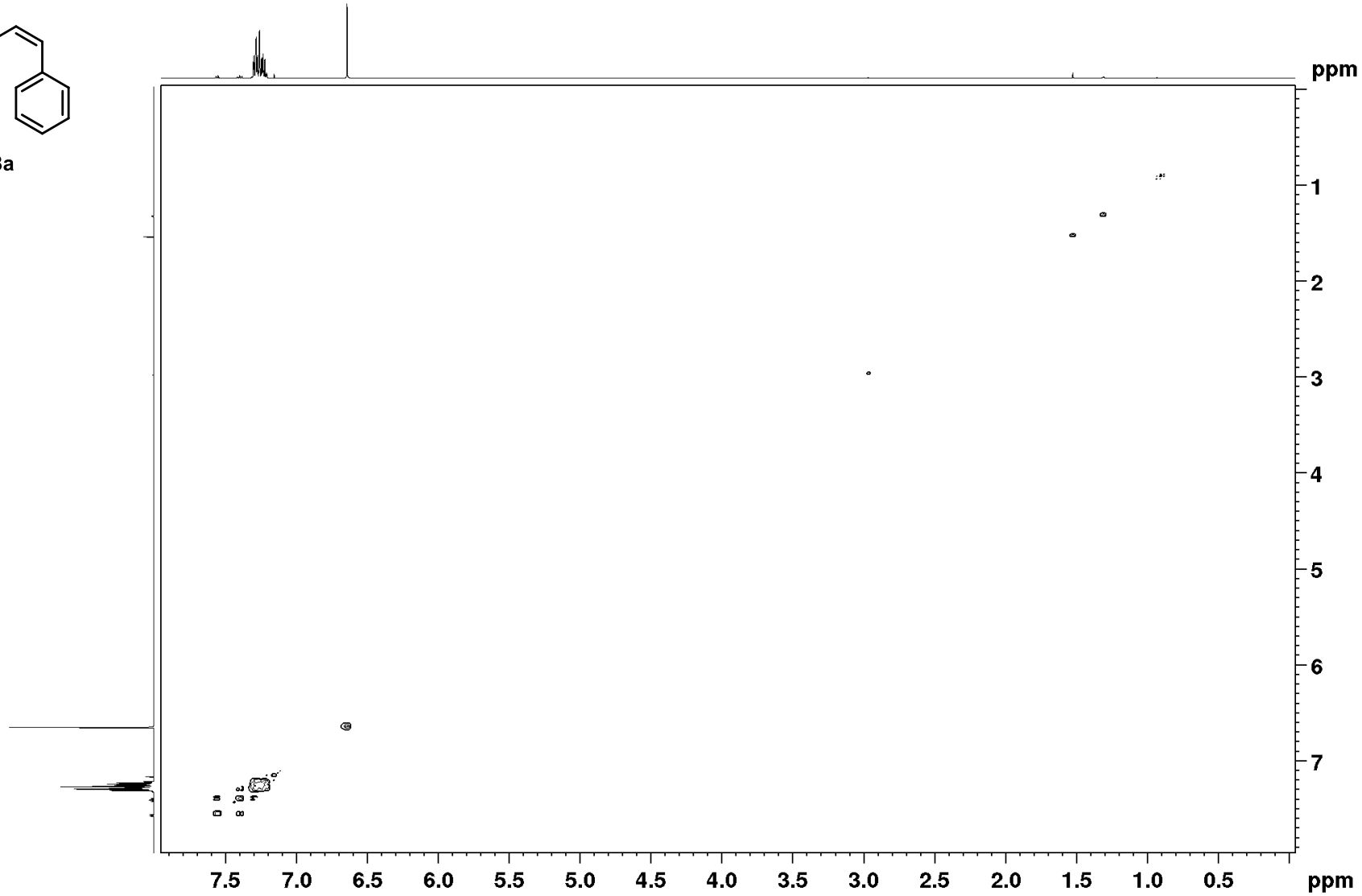
8a

137.4
130.4
129.0
128.3
127.2
77.4
77.2
76.9
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

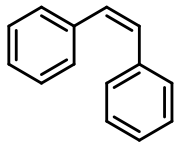
$^{1}H,^{1}H$ COSY NMR



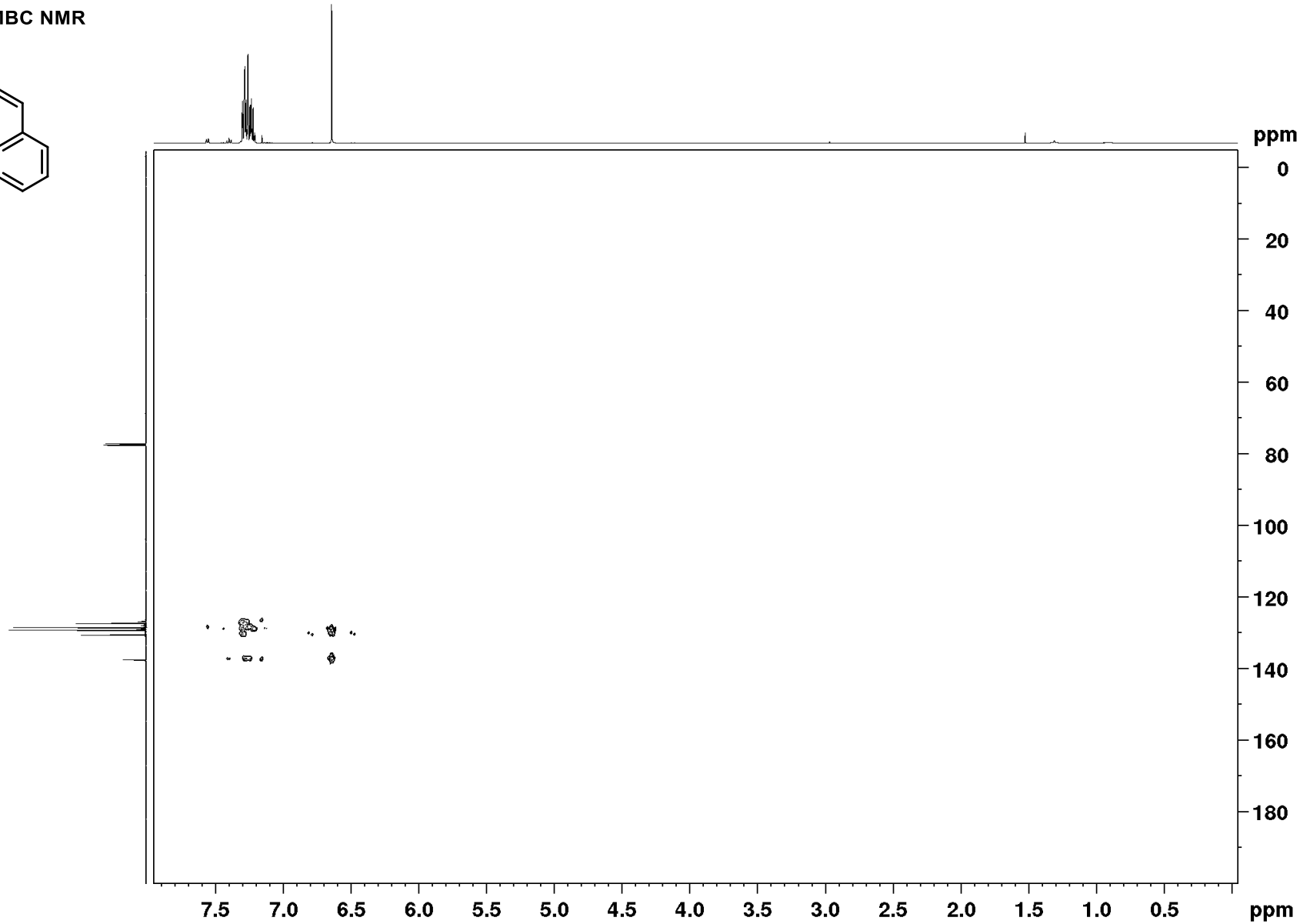
8a



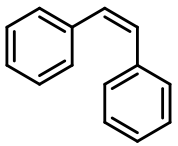
$^{1}H,^{13}C$ HMBC NMR



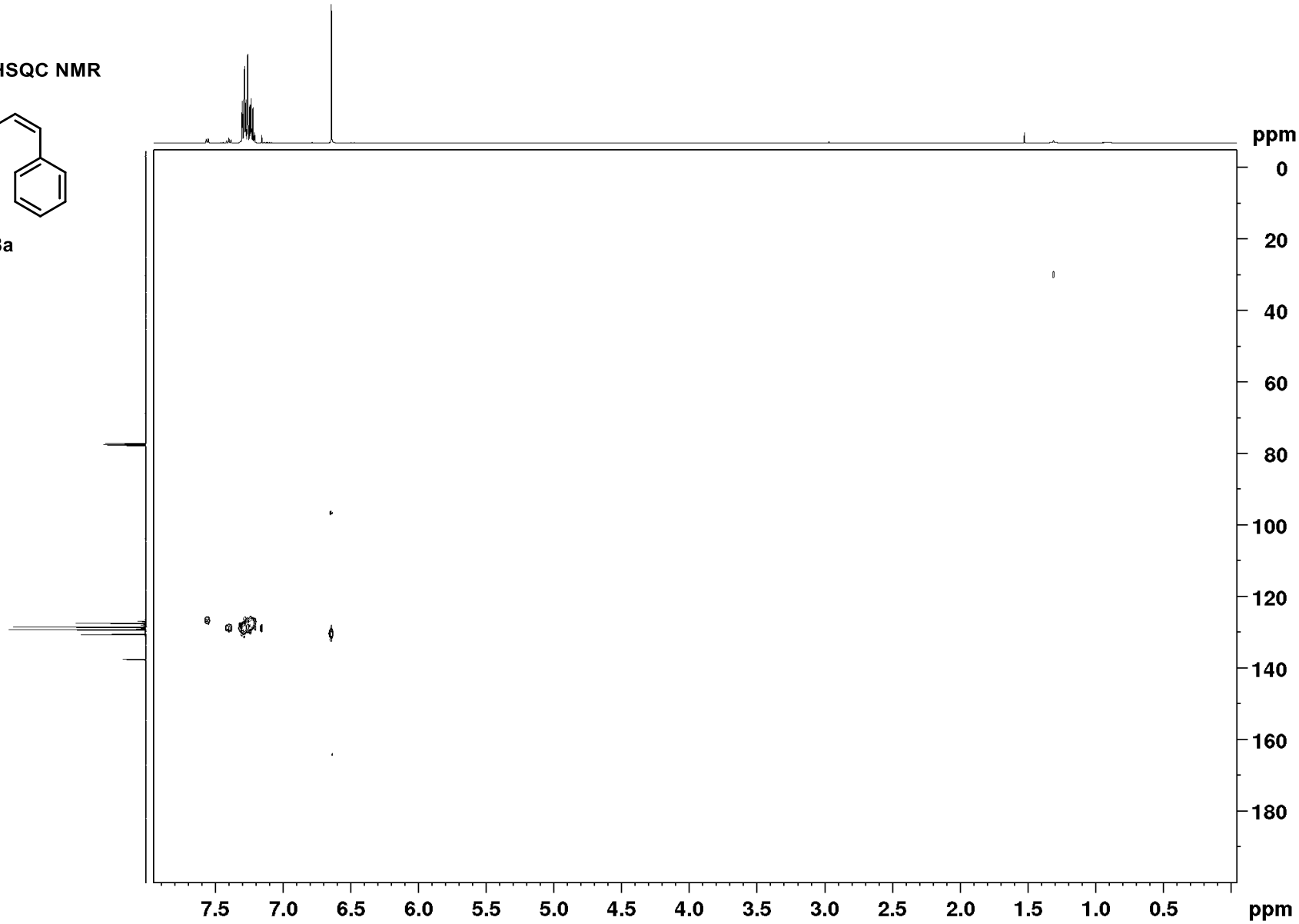
8a



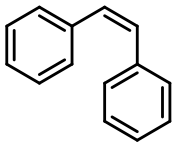
$^{1}H,^{13}C$ HSQC NMR



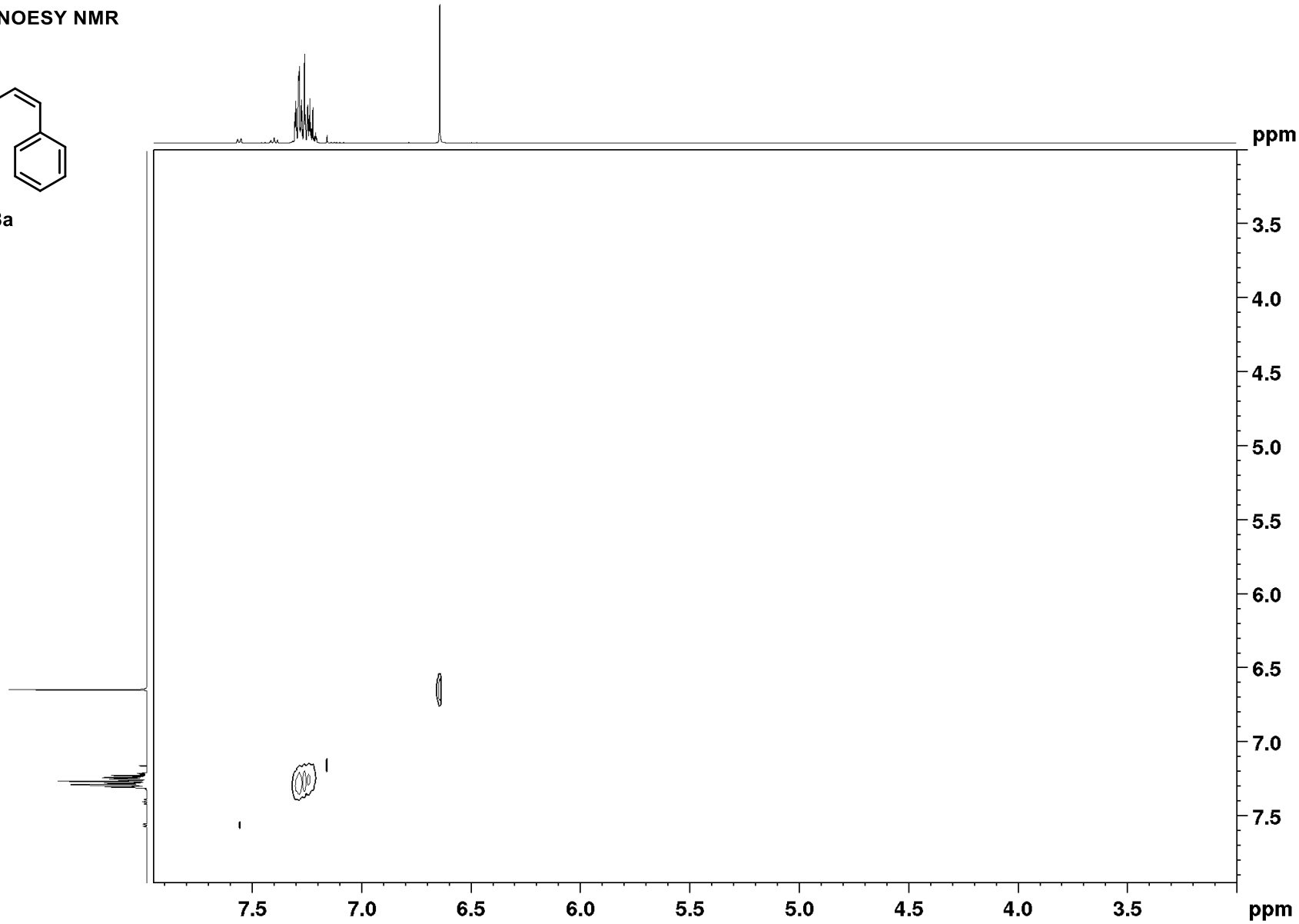
8a

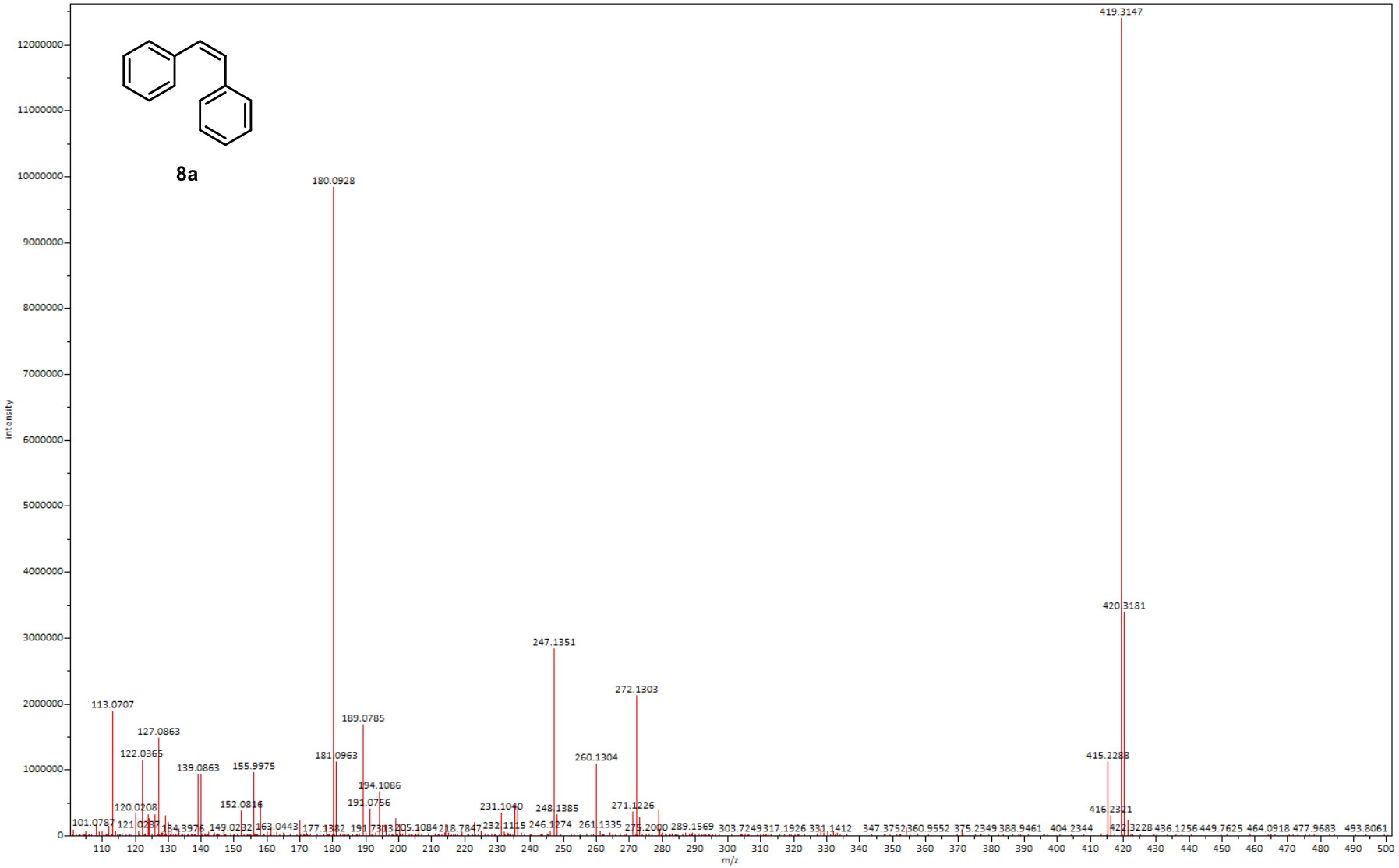


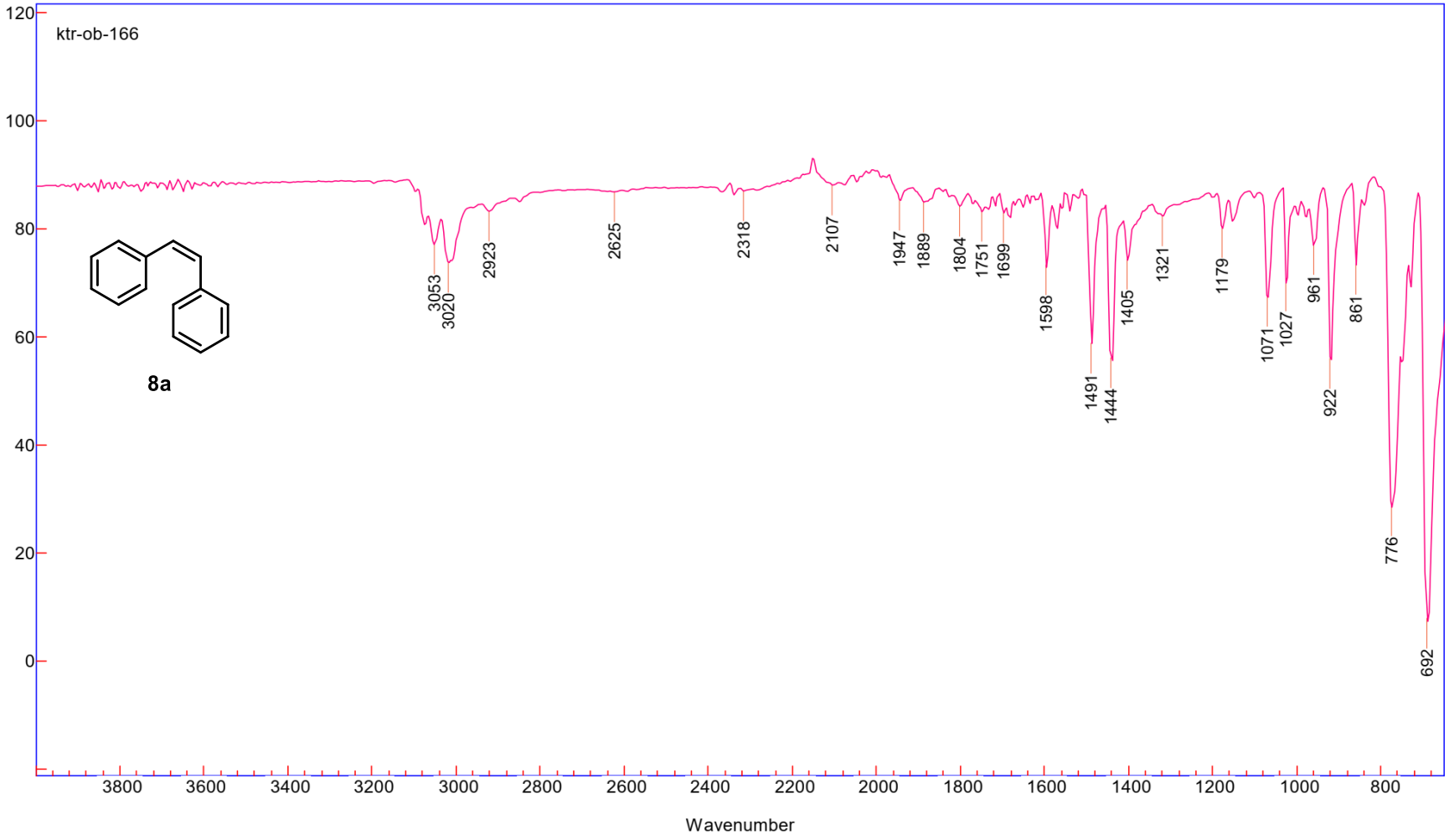
$^{1}H,^{1}H$ NOESY NMR



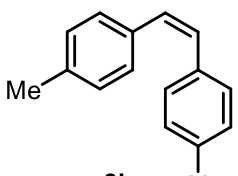
8a




8a
intensity
m/z
419.3147
180.0928
420.3181
247.1351
272.1303
189.0785
113.0707
127.0863
122.0365
260.1304
415.2288
139.0863
155.9975
194.1086
191.0756
181.0963
120.0208
152.0816
231.1040
248.1385
271.1226
416.2321
101.0787
121.0287
184.3976
149.0232
163.0443
177.1382
191.7313
205.1084
218.7847
232.1115
246.1274
261.1335
275.2000
289.1569
303.7249
317.1926
331.1412
347.3752
360.9552
375.2349
388.9461
404.2344
422.3228
436.1256
449.7625
464.0918
477.9683
493.8061


ktr-ob-166
8a
3053
3020
2923
2625
2318
2107
1947
1889
1804
1751
1699
1598
1491
1444
1405
1321
1179
1071
1027
961
922
861
776
692
120
100
80
60
40
20
0
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber

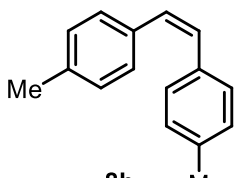
^{1}H NMR


Me
Me

8b

7.21
7.19
7.07
7.06
6.55
2.35
4.05
4.00
2.00
6.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

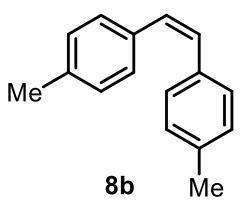
^{13}C NMR


Me
Me

8b

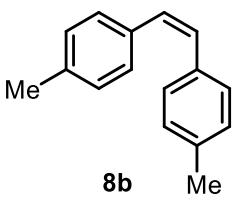
136.8
134.7
129.7
129.0
128.9
77.4
77.2
76.9
21.4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

$^{1}H,^{1}H$ COSY NMR



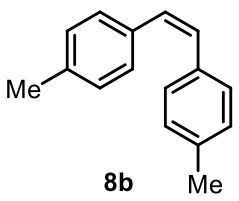
8b

$^{1}H,^{13}C$ HMBC NMR



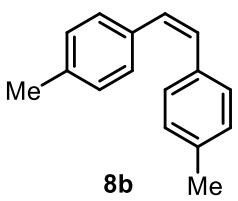
8b

$^{1}H,^{13}C$ HSQC NMR

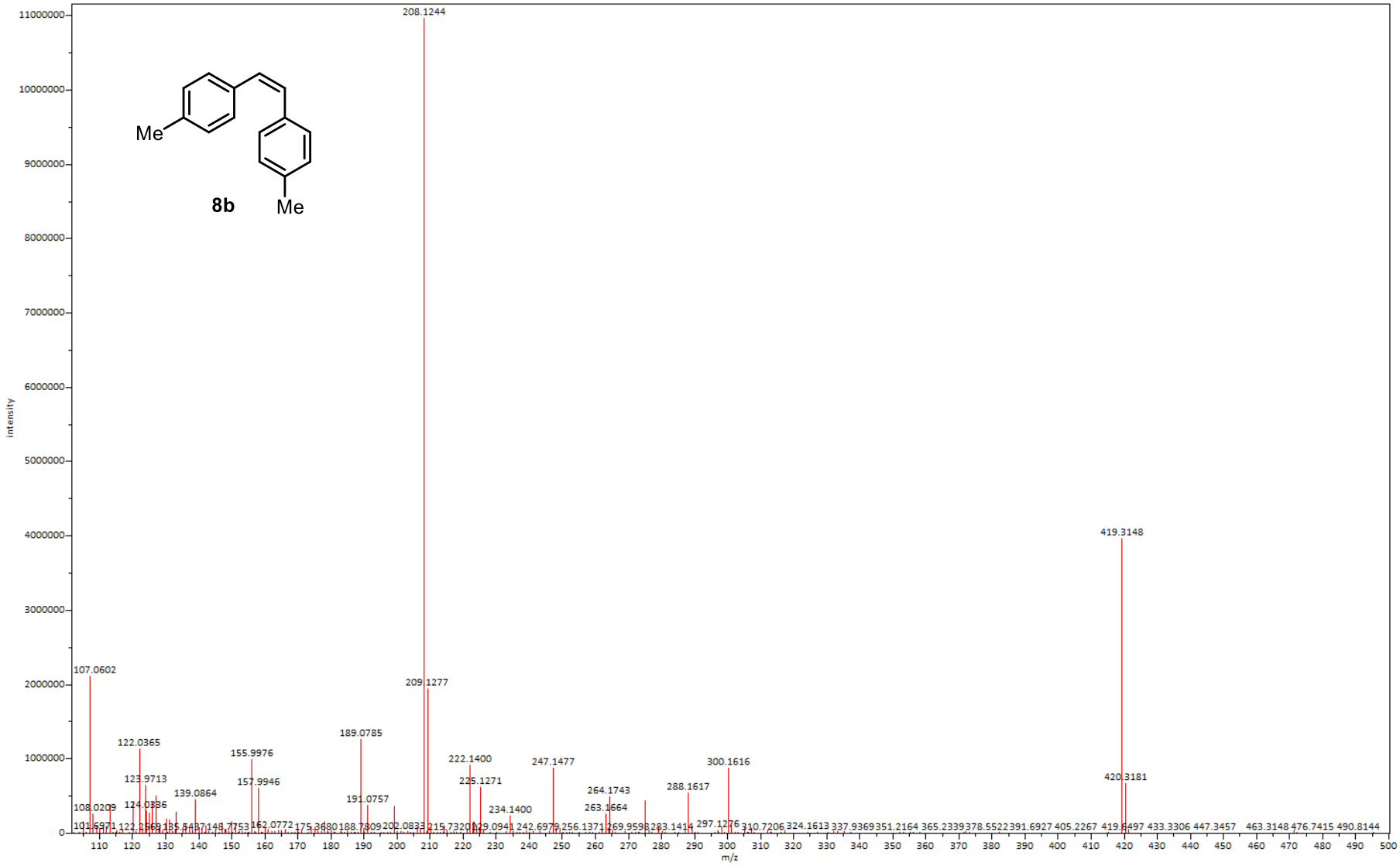


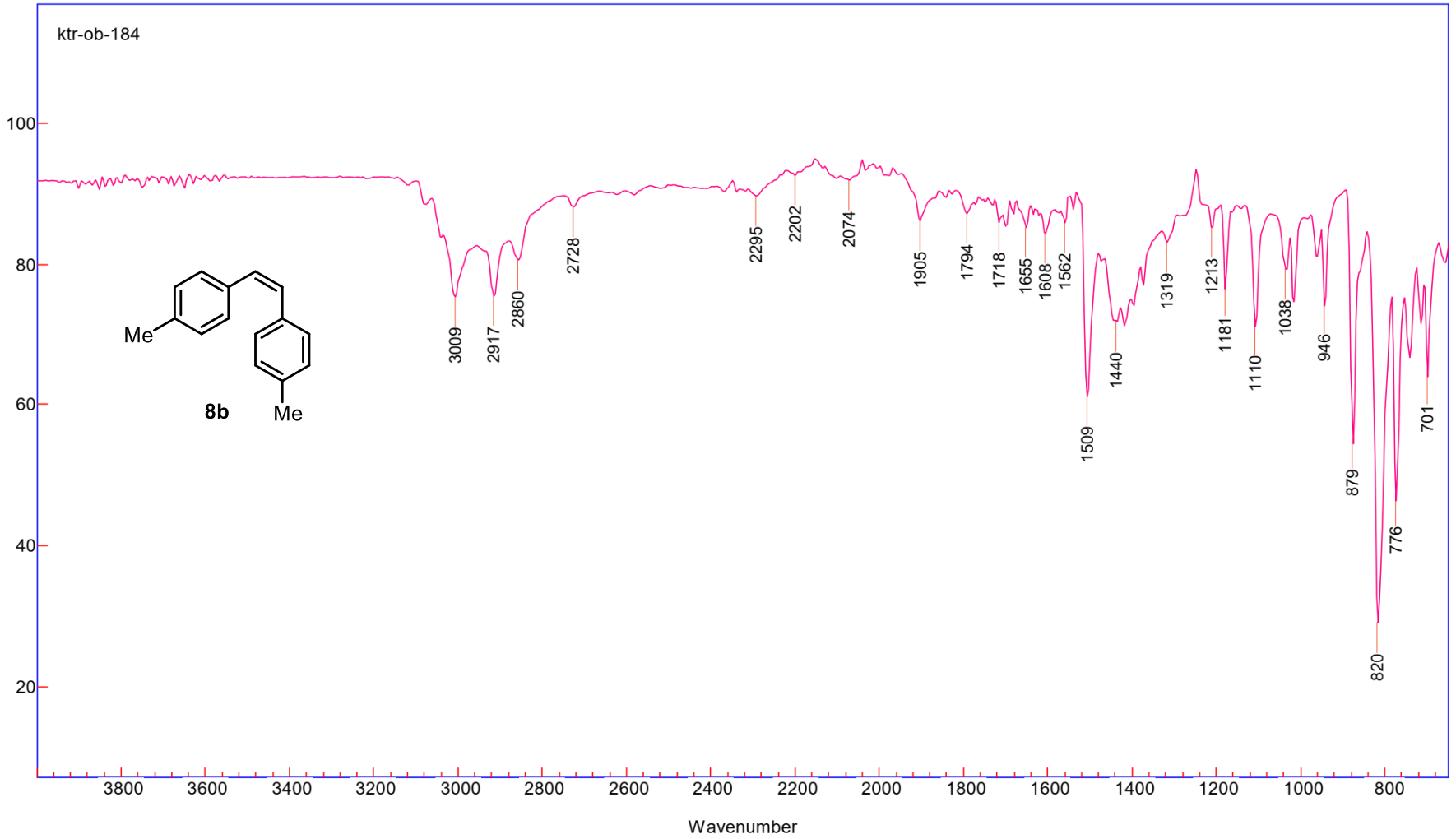
8b

$^{1}H,^{1}H$ NOESY NMR

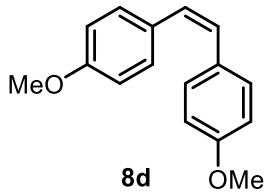


8b


Me
8b
Me
208.1244
419.3148
107.0602
209.1277
189.0785
122.0365
155.9976
222.1400
247.1477
300.1616
157.9946
123.9713
225.1271
264.1743
288.1617
420.3181
139.0864
191.0757
263.1664
124.0336
234.1400
108.0209
intensity
m/z


ktr-ob-184
100
80
60
40
20
Me
8b
Me
3009
2917
2860
2728
2295
2202
2074
1905
1794
1718
1655
1608
1562
1509
1440
1319
1213
1181
1110
1038
946
879
820
776
701
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber

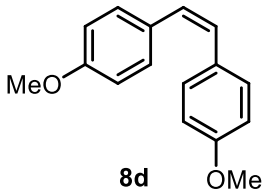
^{1}H NMR


MeO
OMe

8d

7.23
7.22
7.21
7.21
6.79
6.79
6.78
6.77
6.46
3.80
4.01
4.00
2.02
6.16
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

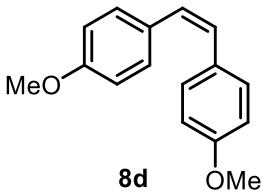
^{13}C NMR


MeO
OMe

8d

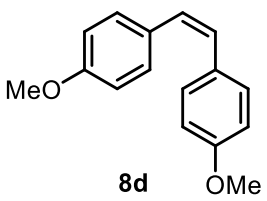
158.7
130.2
130.1
128.5
113.7
77.4
77.2
76.9
55.3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

^{1}H,^{1}H COSY NMR



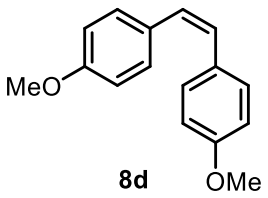
8d

$^{1}H,^{13}C$ HMBC NMR



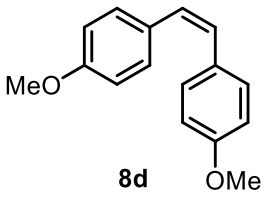
8d

$^{1}H,^{13}C$ HSQC NMR

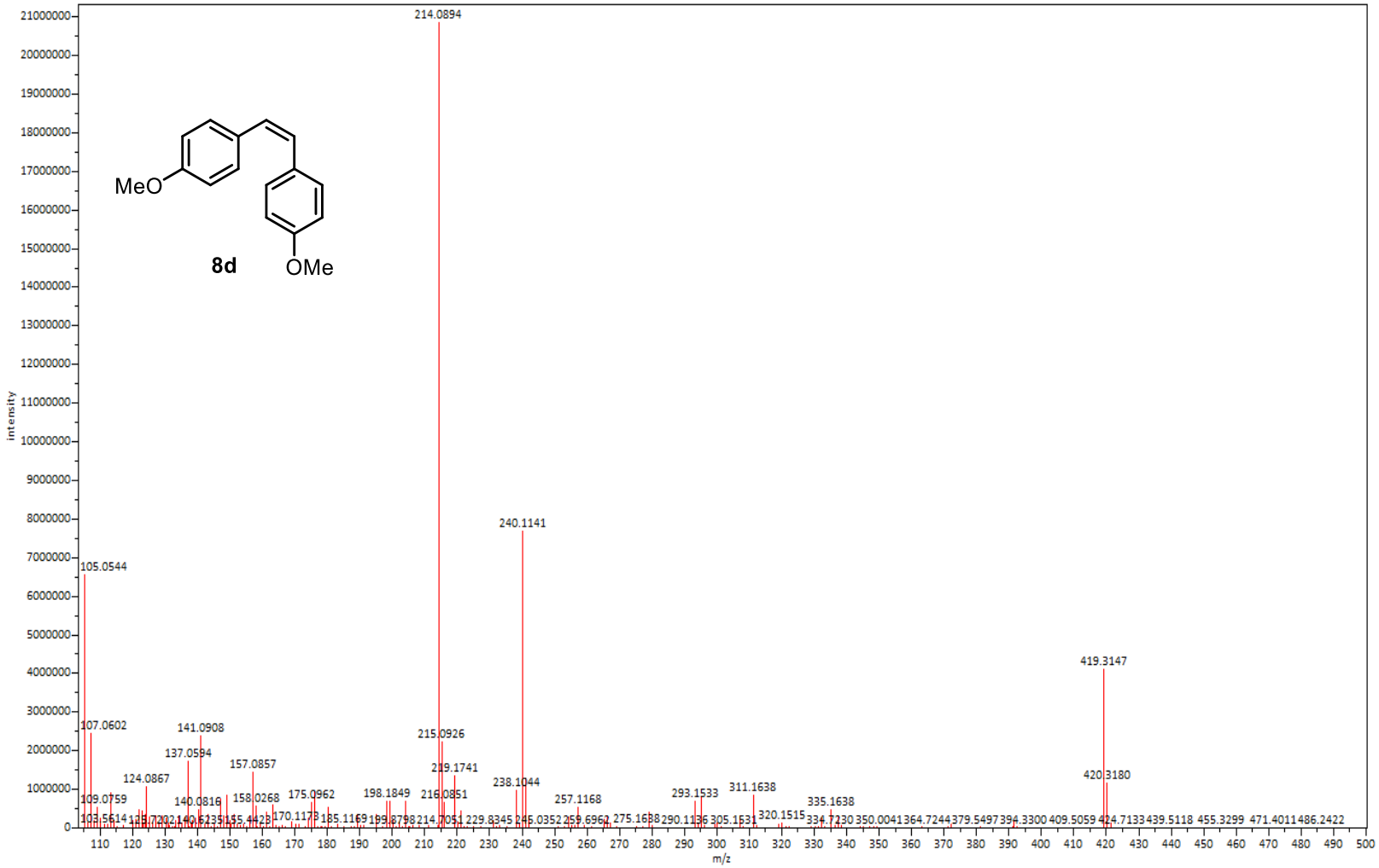


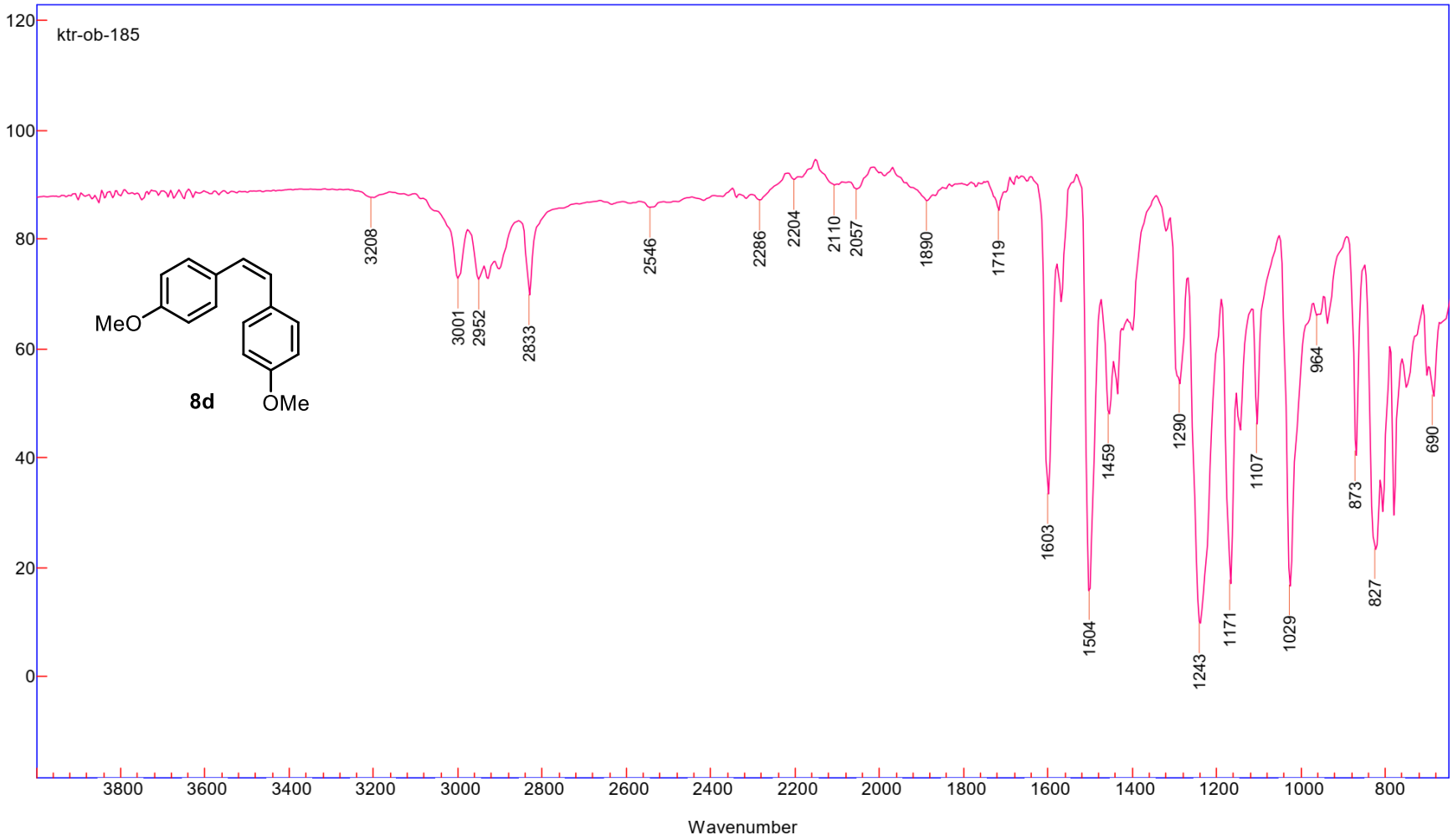
8d

$^{1}H,^{1}H$ NOESY NMR

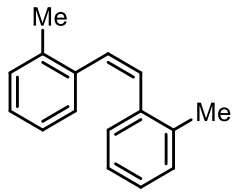


8d


MeO
OMe
8d
intensity
m/z
214.0894
240.1141
105.0544
107.0602
141.0908
137.0594
157.0857
124.0867
215.0926
219.1741
238.1044
419.3147
420.3180
311.1638
293.1533
335.1638
198.1849
216.0851
175.0962
158.0268
257.1168
320.1515


ktr-ob-185
MeO
OMe
8d
3208
3001
2952
2833
2546
2286
2204
2110
2057
1890
1719
1603
1504
1459
1290
1243
1171
1107
1029
964
873
827
690
120
100
80
60
40
20
0
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber

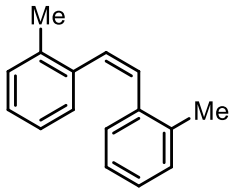
^{1}H NMR


Me
Me

8c

7.18
7.17
7.17
7.12
7.12
7.11
7.11
7.10
7.09
6.99
6.98
6.97
6.97
6.96
6.95
6.93
6.93
6.75
2.32
2.05
2.00
3.95
2.01
6.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

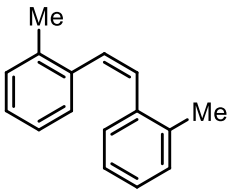
^{13}C NMR


Me
Me

8c

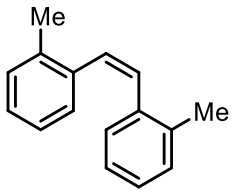
136.7
136.3
130.1
129.6
129.2
127.1
125.5
77.4
77.2
76.9
20.0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

$^{1}H,^{1}H$ COSY NMR



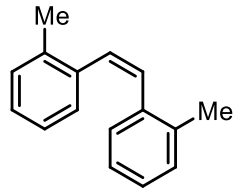
8c

$^{1}H,^{13}C$ HMBC NMR



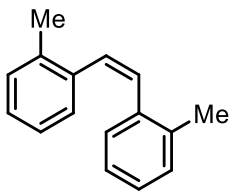
8c

$^{1}H,^{13}C$ HSQC NMR

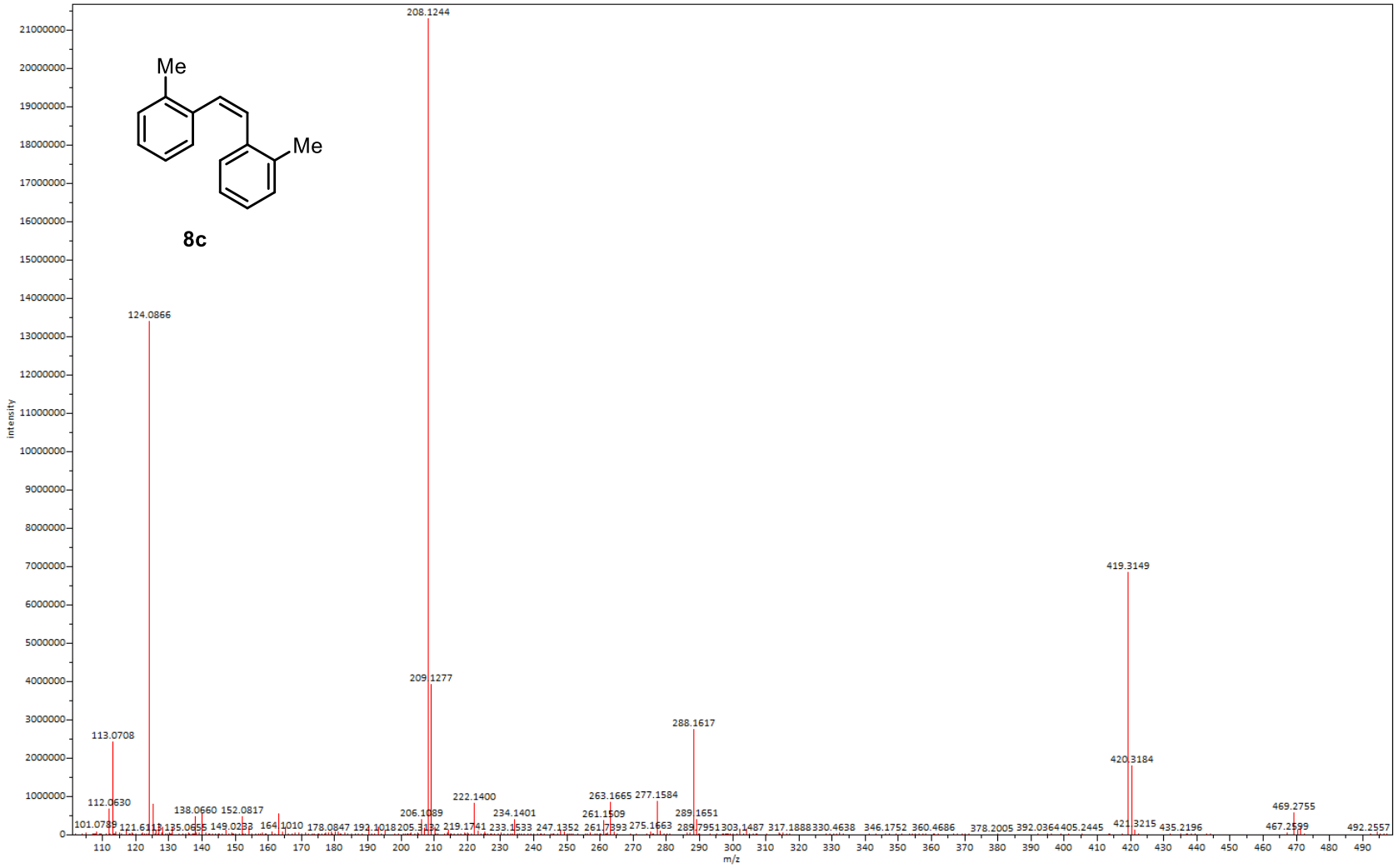


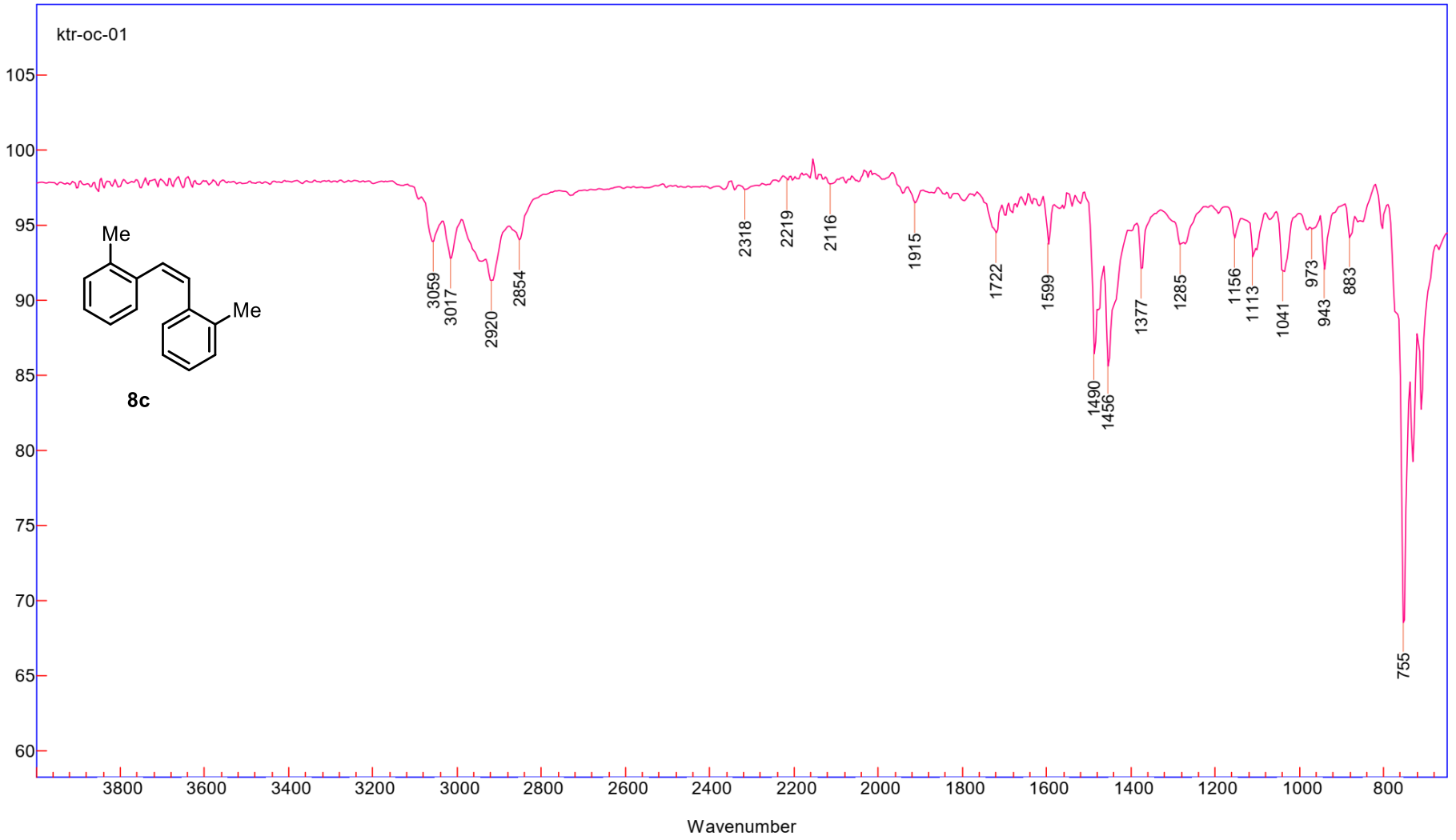
8c

$^{1}H,^{1}H$ NOESY NMR

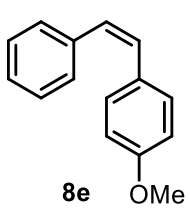


8c

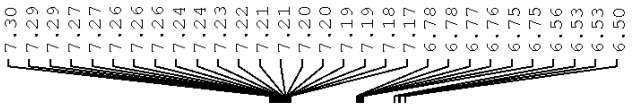

Me
Me
8c
208.1244
124.0866
209.1277
419.3149
420.3184
288.1617
113.0708
112.0630
222.1400
263.1665
277.1584
289.1651
469.2755
138.0660
152.0817
234.1401
261.1509
intensity
m/z


ktr-oc-01
Me
Me
8c
3059
3017
2920
2854
2318
2219
2116
1915
1722
1599
1490
1456
1377
1285
1156
1113
1041
973
943
883
755
105
100
95
90
85
80
75
70
65
60
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber

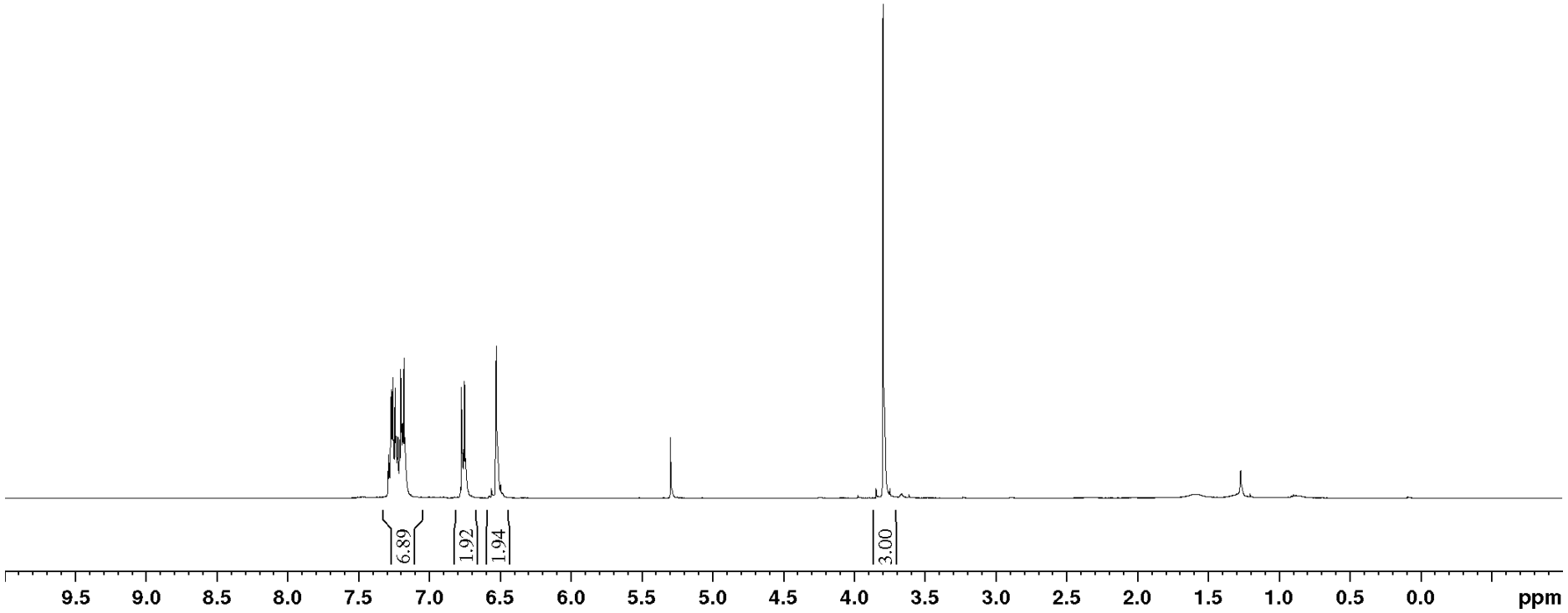
^{1}H NMR



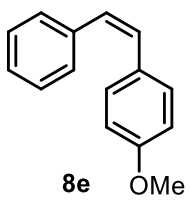
8e OMe


7.30
7.29
7.29
7.27
7.27
7.26
7.26
7.24
7.24
7.23
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.17
6.78
6.78
6.77
6.76
6.75
6.75
6.56
6.53
6.50

3.79

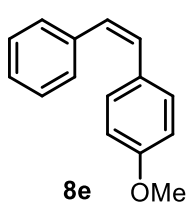

6.89
1.92
1.94
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

^{13}C NMR

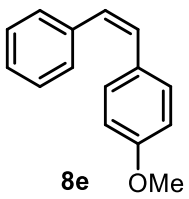

8e
OMe

158.8
137.8
130.3
129.9
129.8
128.9
128.9
128.4
127.0
113.7
55.3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

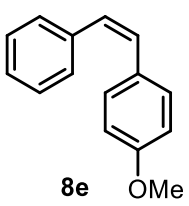
$^{1}H,^{1}H$ COSY NMR



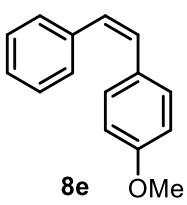
$^{1}H,^{13}C$ HMBC NMR

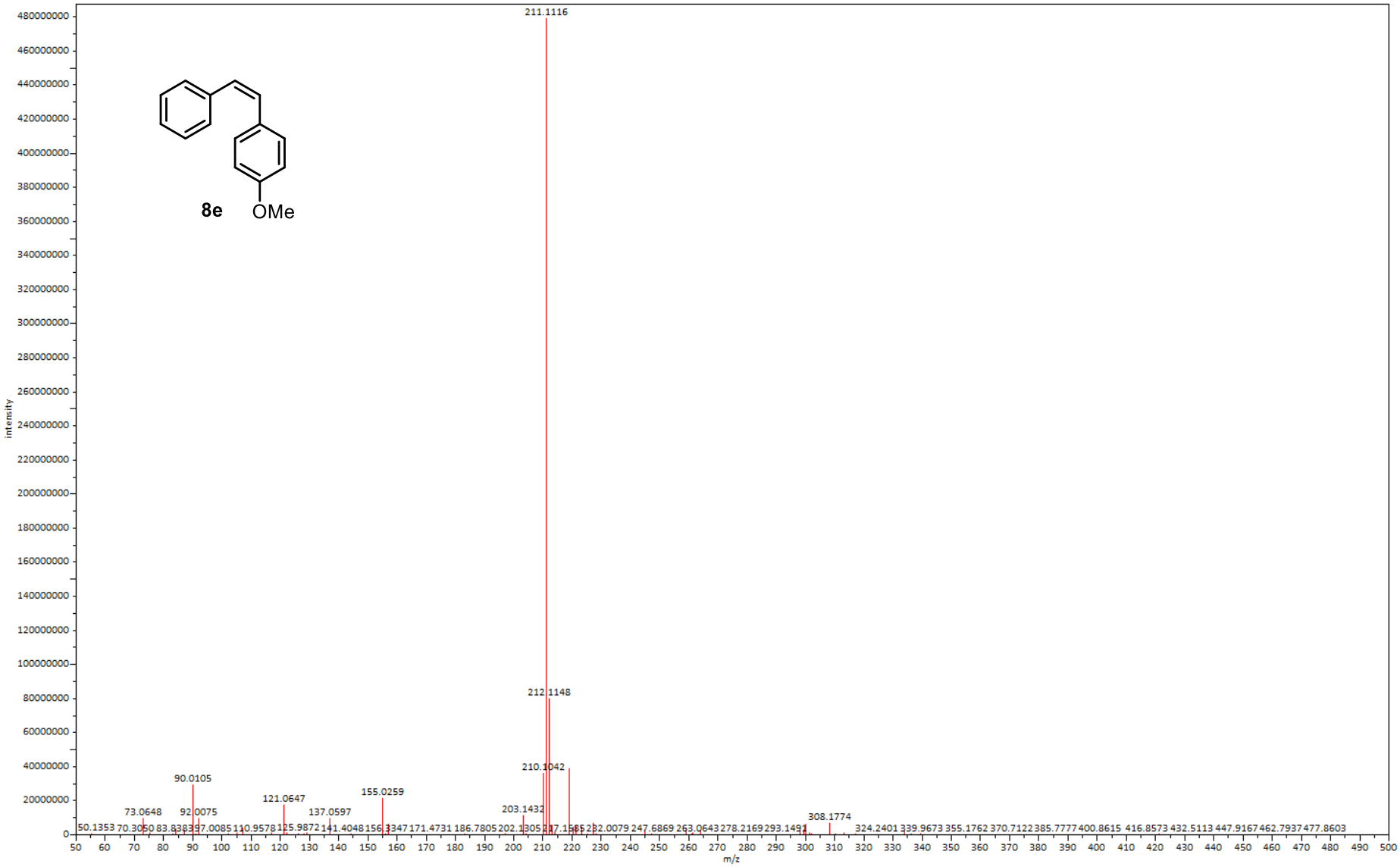


$^{1}H,^{13}C$ HSQC NMR



$^{1}H,^{1}H$ NOESY NMR




8e
OMe
intensity
m/z
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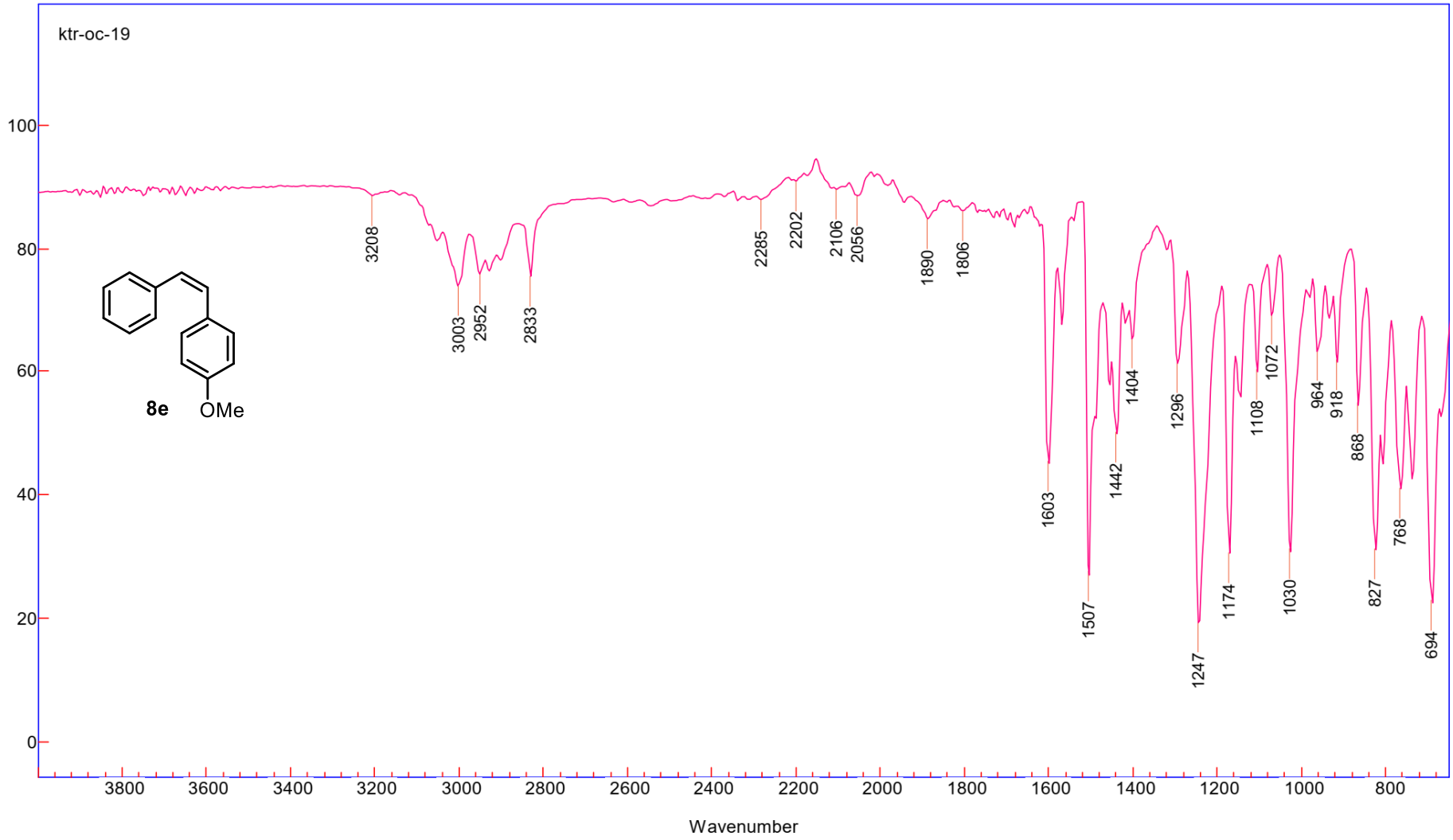
212.1148
210.1042
90.0105
121.0647
155.0259
73.0648
92.0075
137.0597
203.1432
308.1774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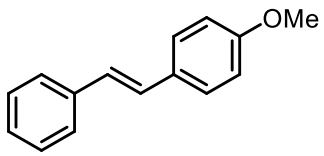
40
20
0
3208
3003
2952
2833
2285
2202
2106
2056
1890
1806
1603
1507
1442
1404
1296
1247
1174
1108
1072
1030
964
918
868
827
768
694
8e
OMe
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber

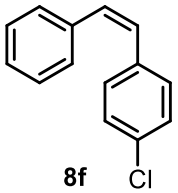
^{1}H NMR

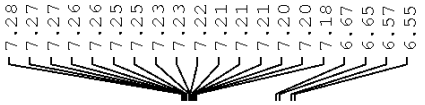

OMe

***E*-8e**

7.50
7.48
7.47
7.47
7.45
7.45
7.37
7.35
7.33
7.25
7.24
7.22
7.09
7.05
7.00
6.96
6.92
6.91
6.90
6.90
3.84
4.04
1.98
1.19
2.21
2.00
3.00
11
10
9
8
7
6
5
4
3
2
1
0
ppm

^{1}H NMR


8f
Cl


7.28
7.27
7.27
7.26
7.26
7.25
7.25
7.23
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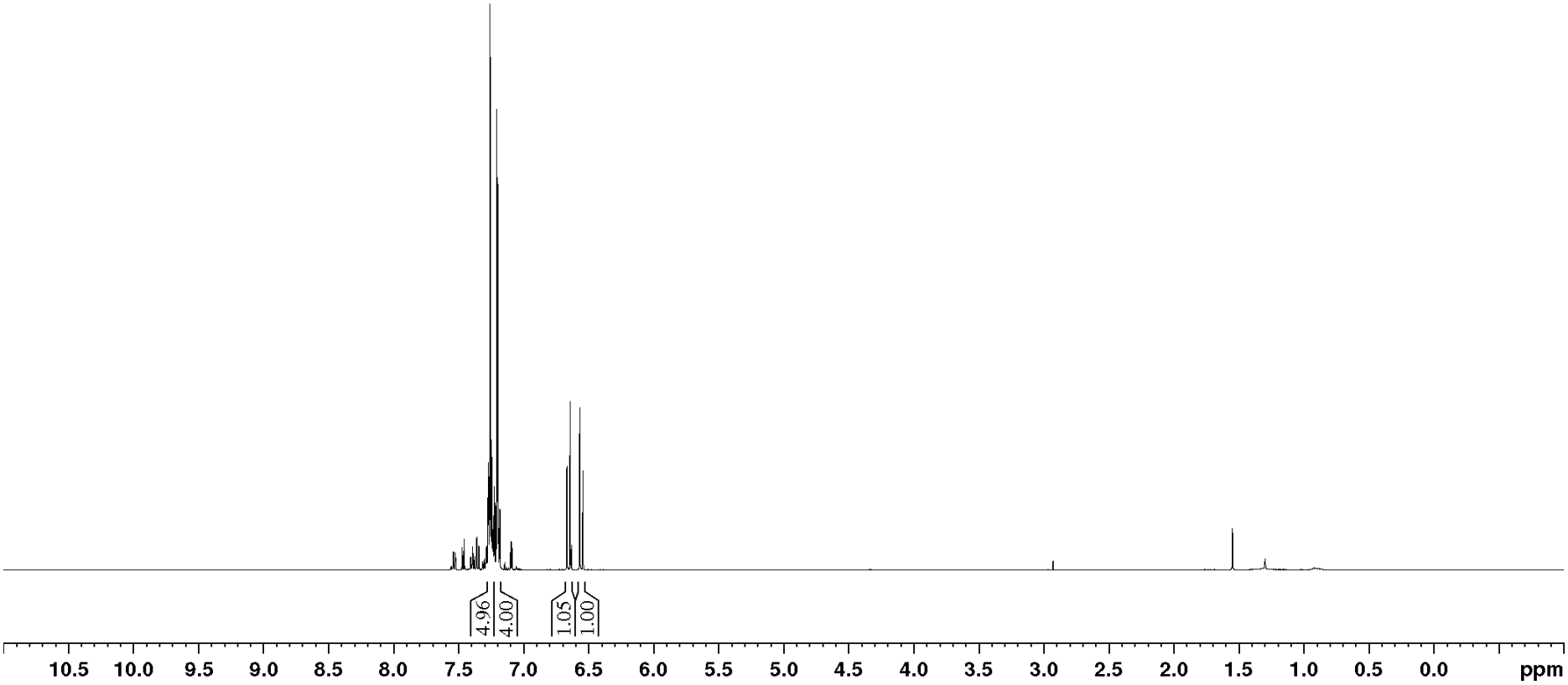
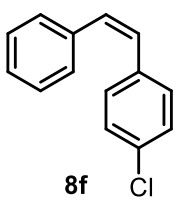
7.21
7.21
7.21
7.20
7.20
7.18
6.67
6.65
6.57
6.55


4.96
4.00
1.05
1.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

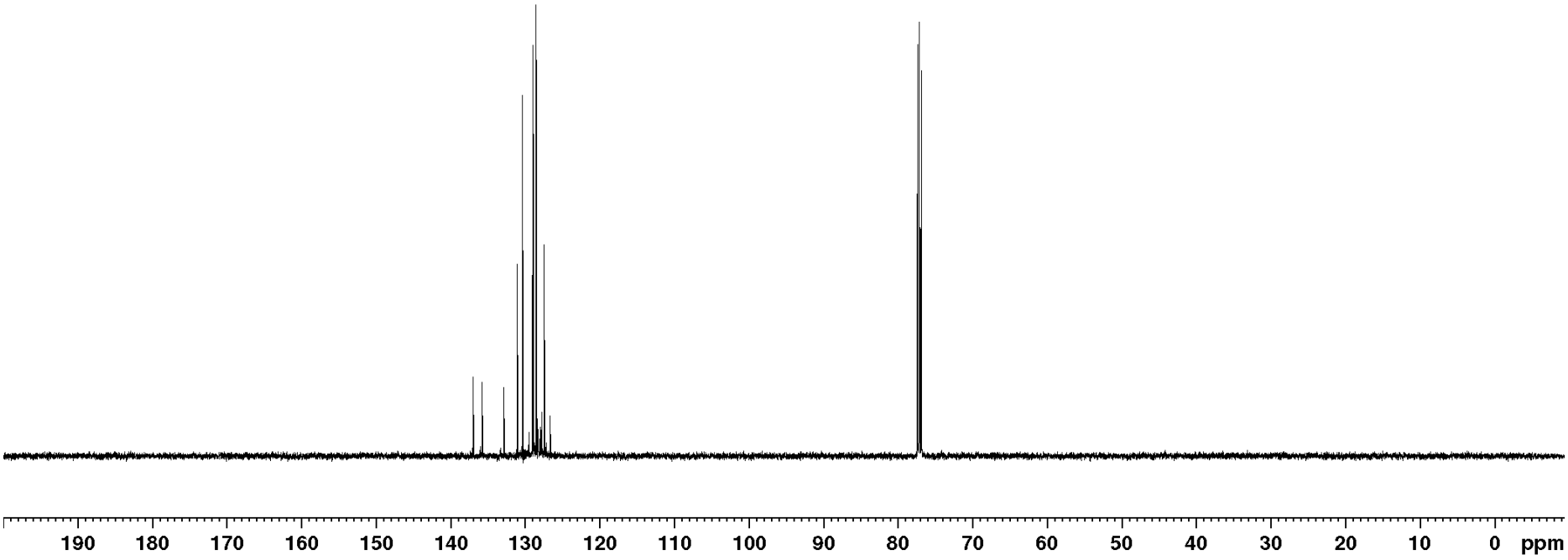
^{13}C NMR



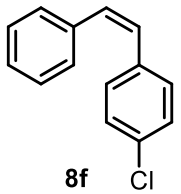
8f

137.0
135.8
132.9
131.1
130.3
129.1
128.9
128.5
128.5
127.5

77.4
77.2
76.9



$^{1}H,^{1}H$ COSY NMR



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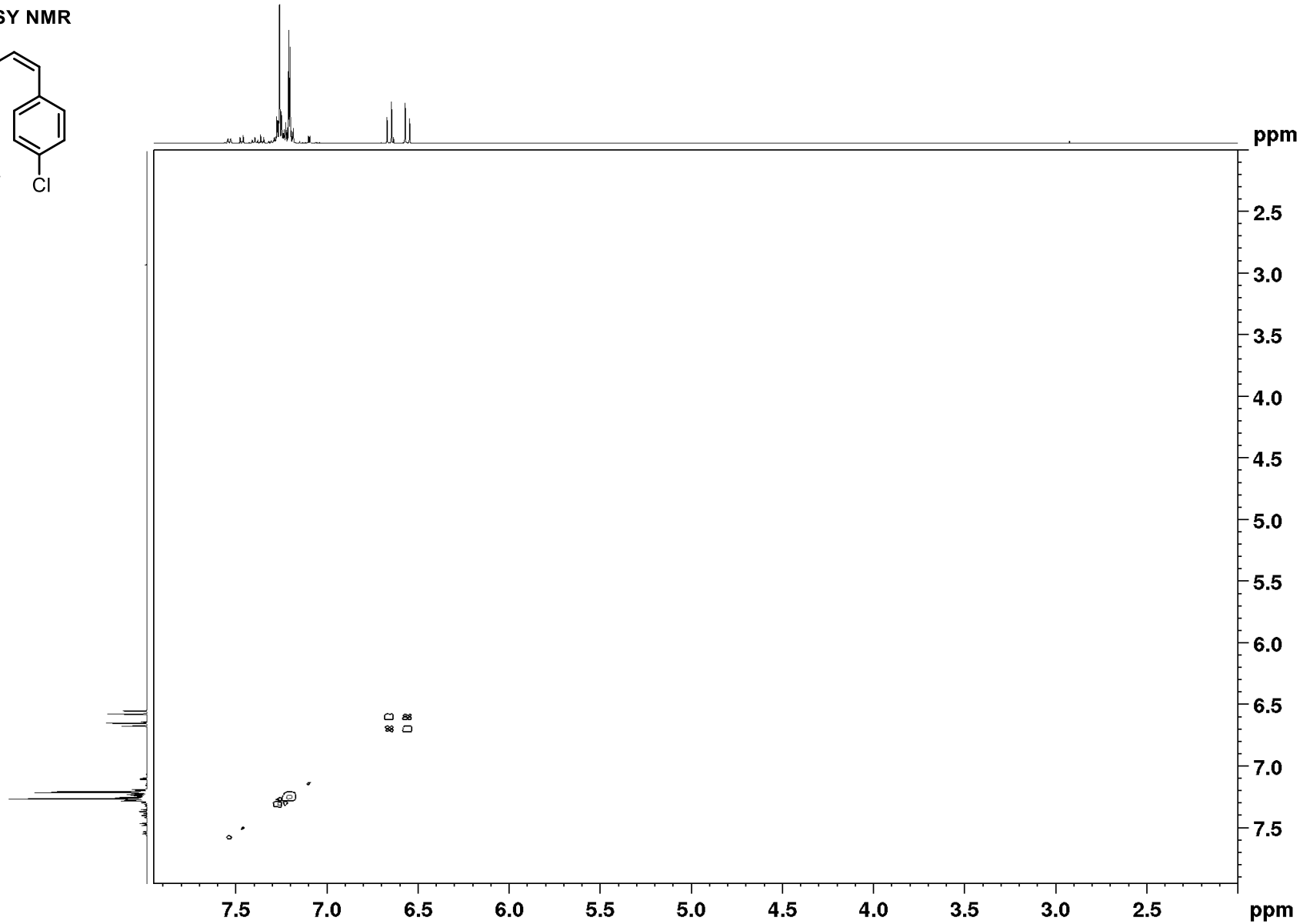
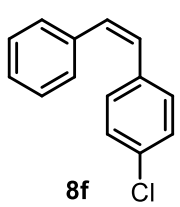
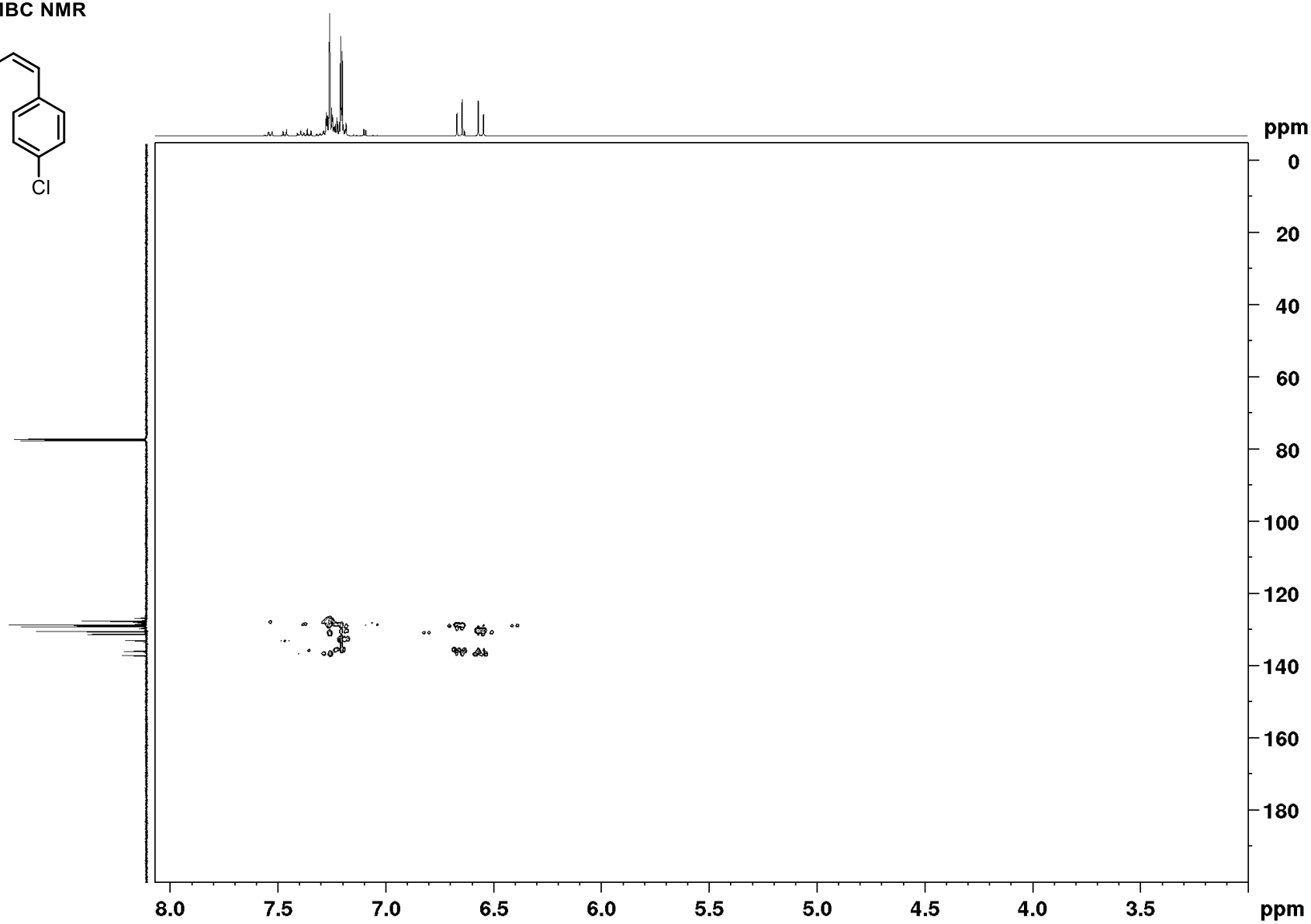


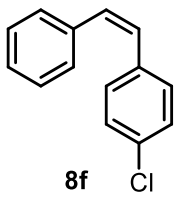
$^{1}H,^{13}C$ HMBC NMR

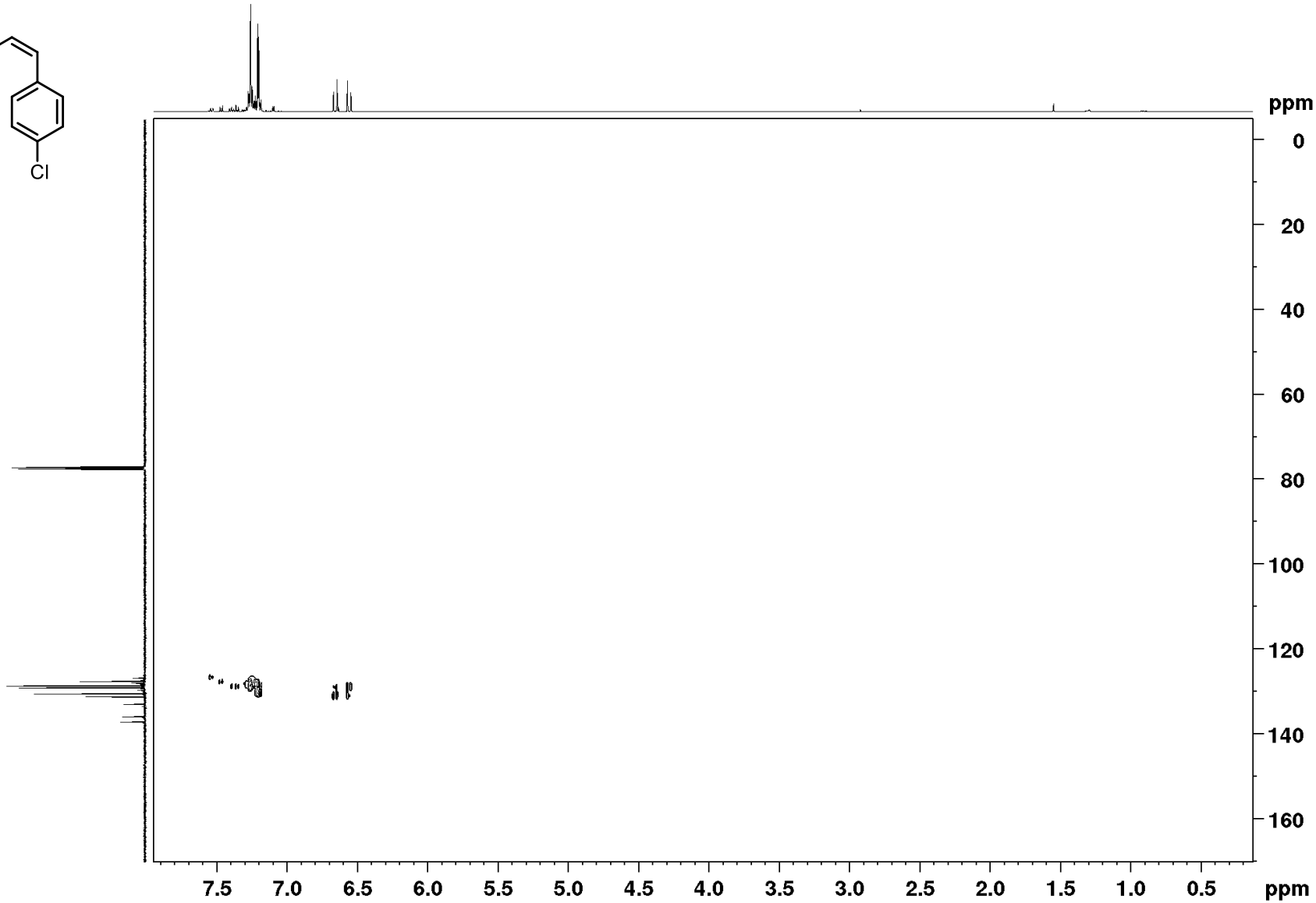


8f

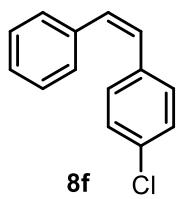


$^{1}H,^{13}C$ HSQC NMR





$^{1}H,^{1}H$ NOESY NMR



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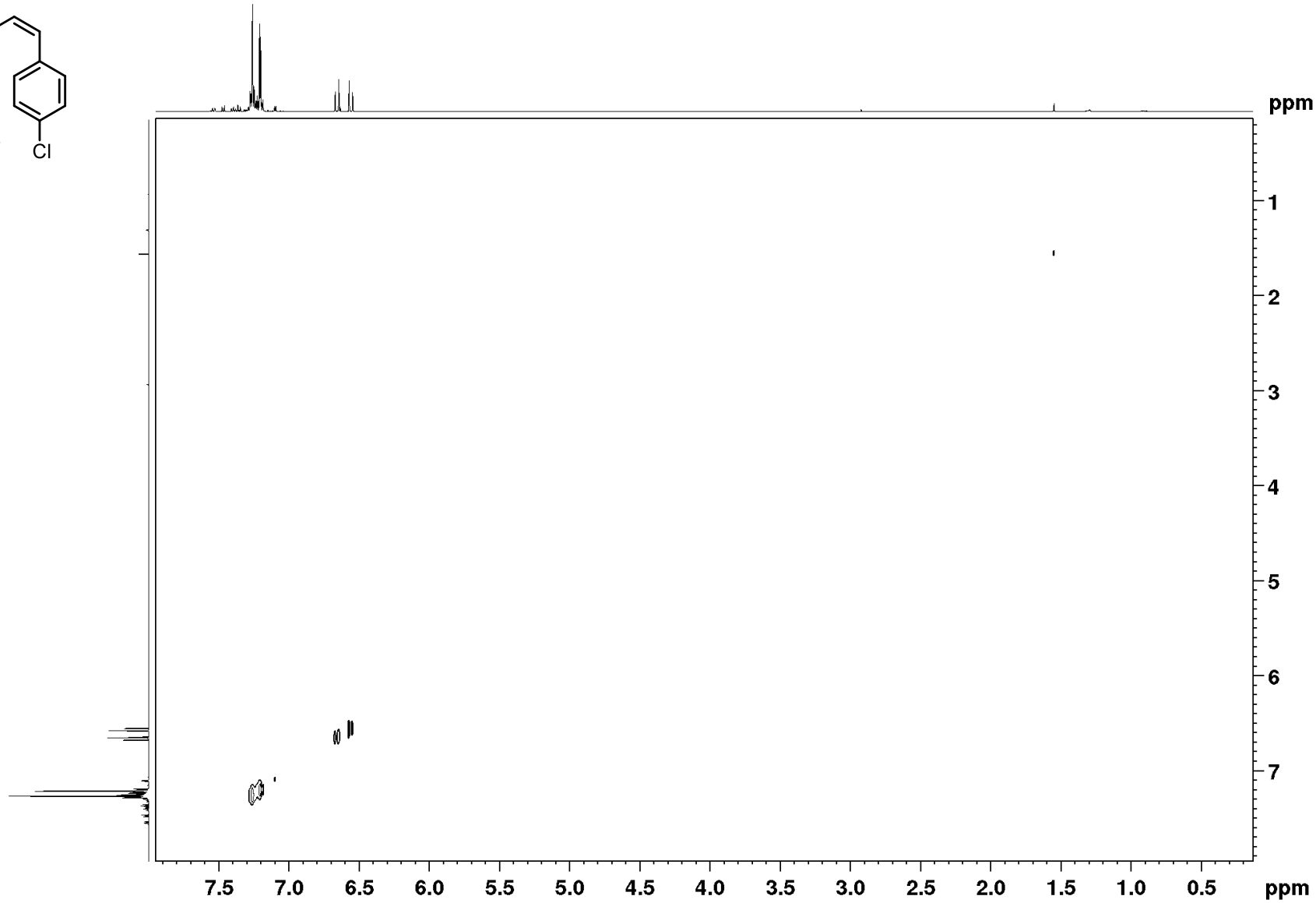

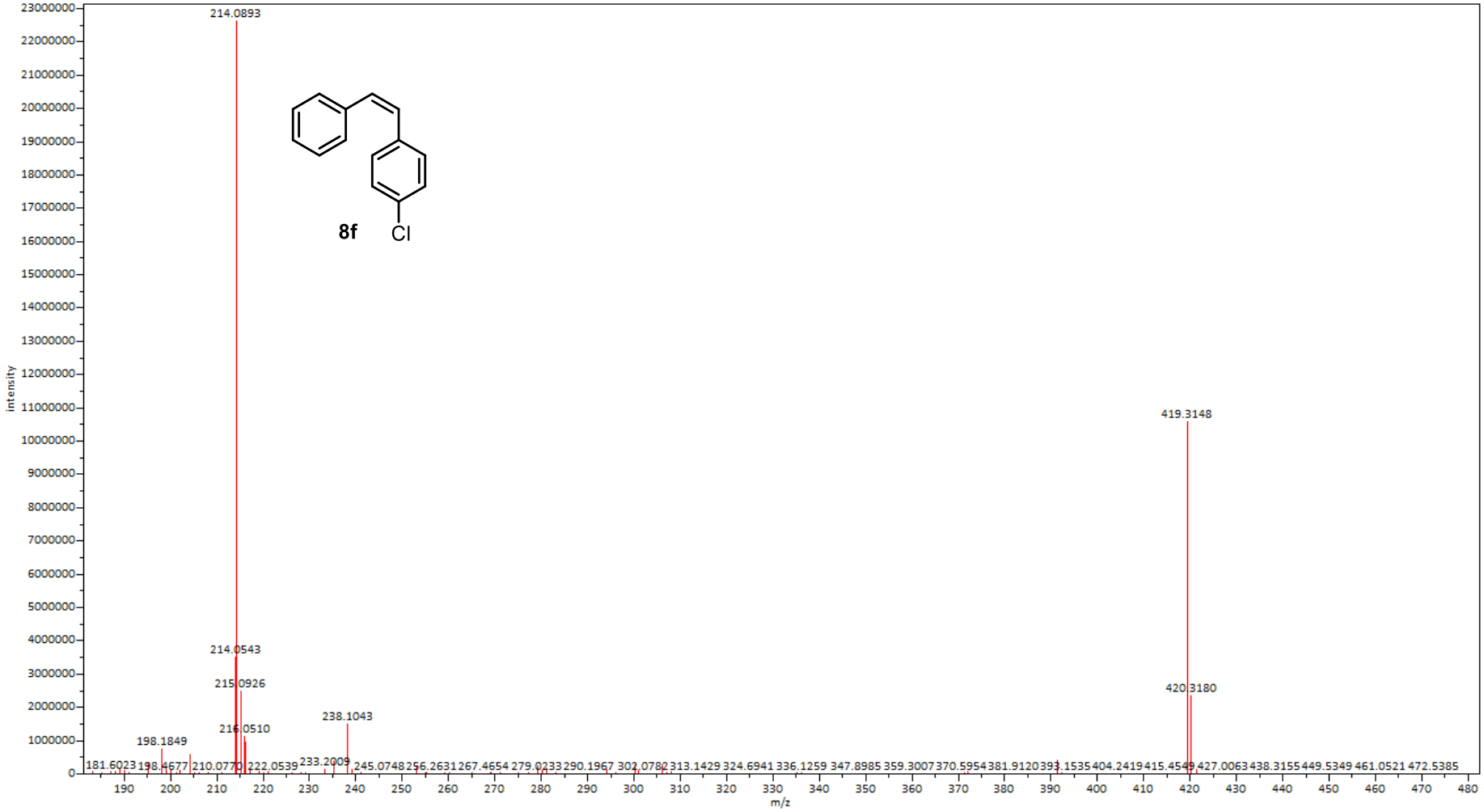
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8f
Cl
intensity
m/z
419.3148
420.3180
214.0543
215.0926
238.1043
216.0510
198.1849
181.6023
198.4677
210.0770
222.0539
233.2009
245.0748
256.2631
267.4654
279.0233
290.1967
302.0782
313.1429
324.6941
336.1259
347.8985
359.3007
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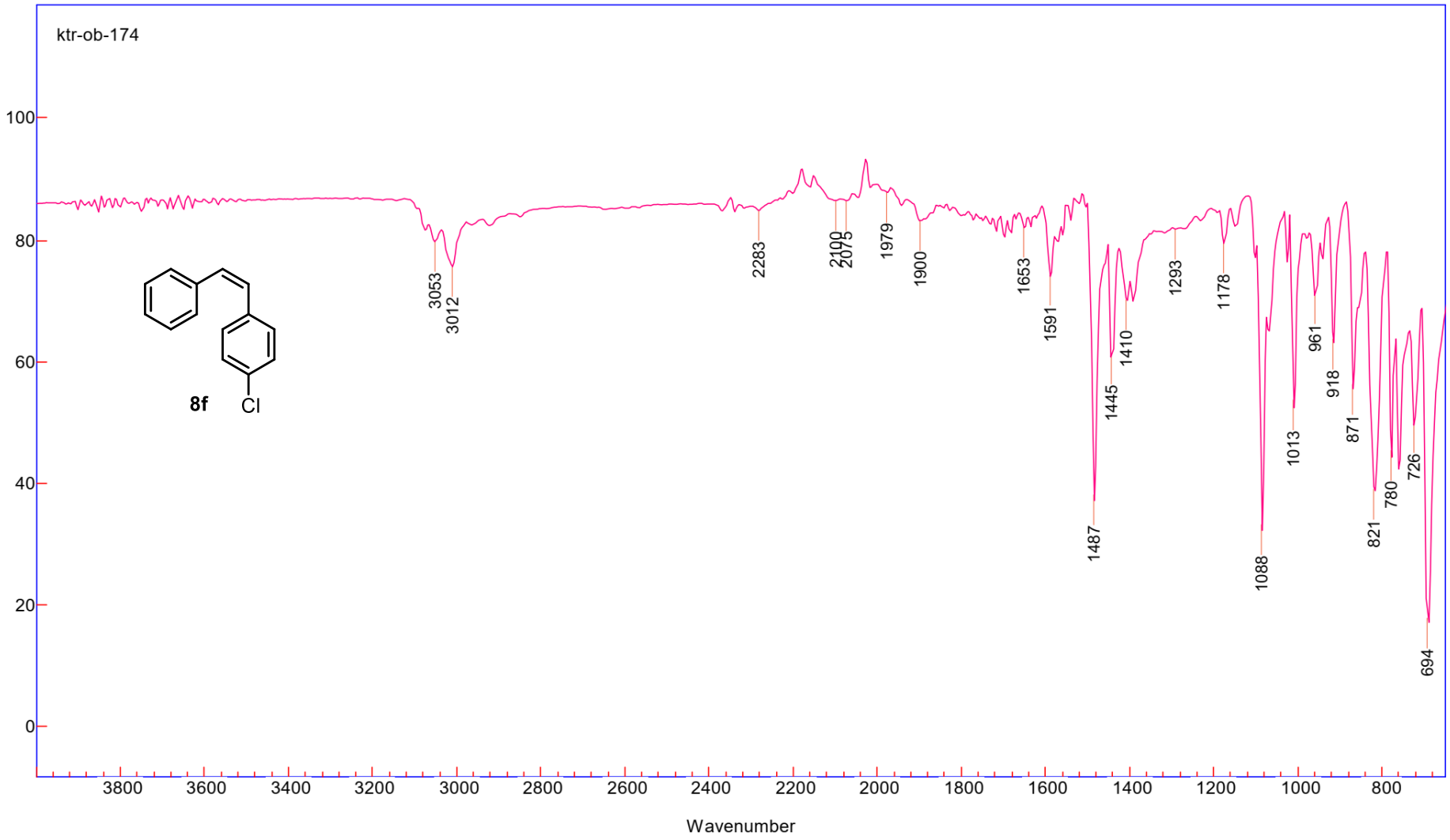
472.5385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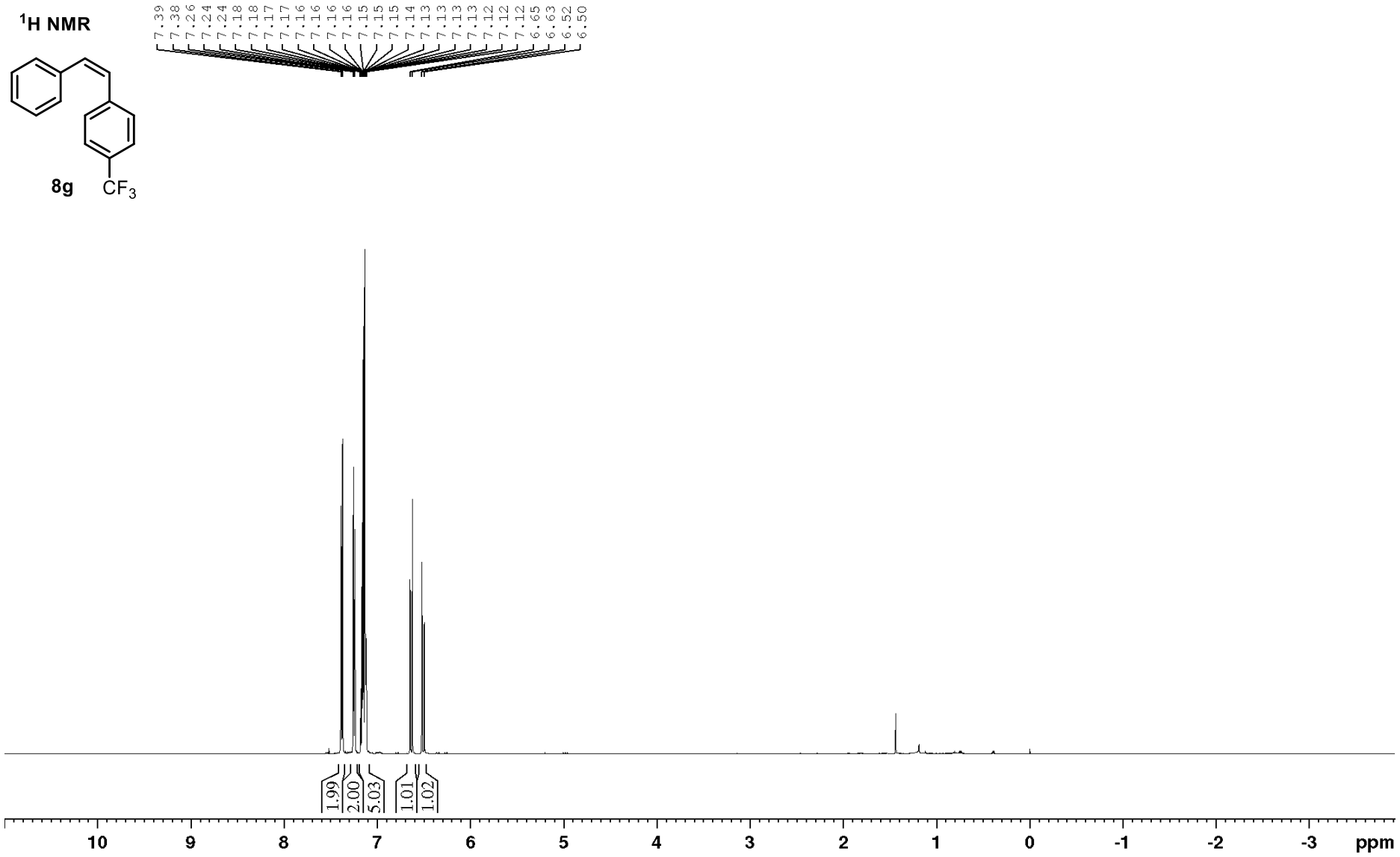
2100
2075
1979
1900
1653
1591
1487
1445
1410
1293
1178
1088
1013
961
918
871
821
780
726
694
8f
Cl
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber


1H NMR
8g
CF3
7.39
7.38
7.26
7.24
7.24
7.18
7.18
7.17
7.17
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7.16
7.16
7.16
7.15
7.15
7.15
7.14
7.13
7.13
7.13
7.12
7.12
7.12
6.65
6.63
6.52
6.50
1.99
2.00
5.03
1.01
1.02
10
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8
7
6
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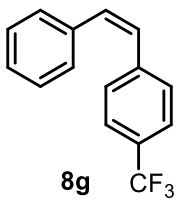
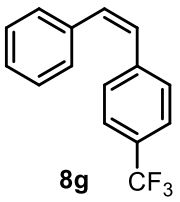
4
3
2
1
0
-1
-2
-3
ppm

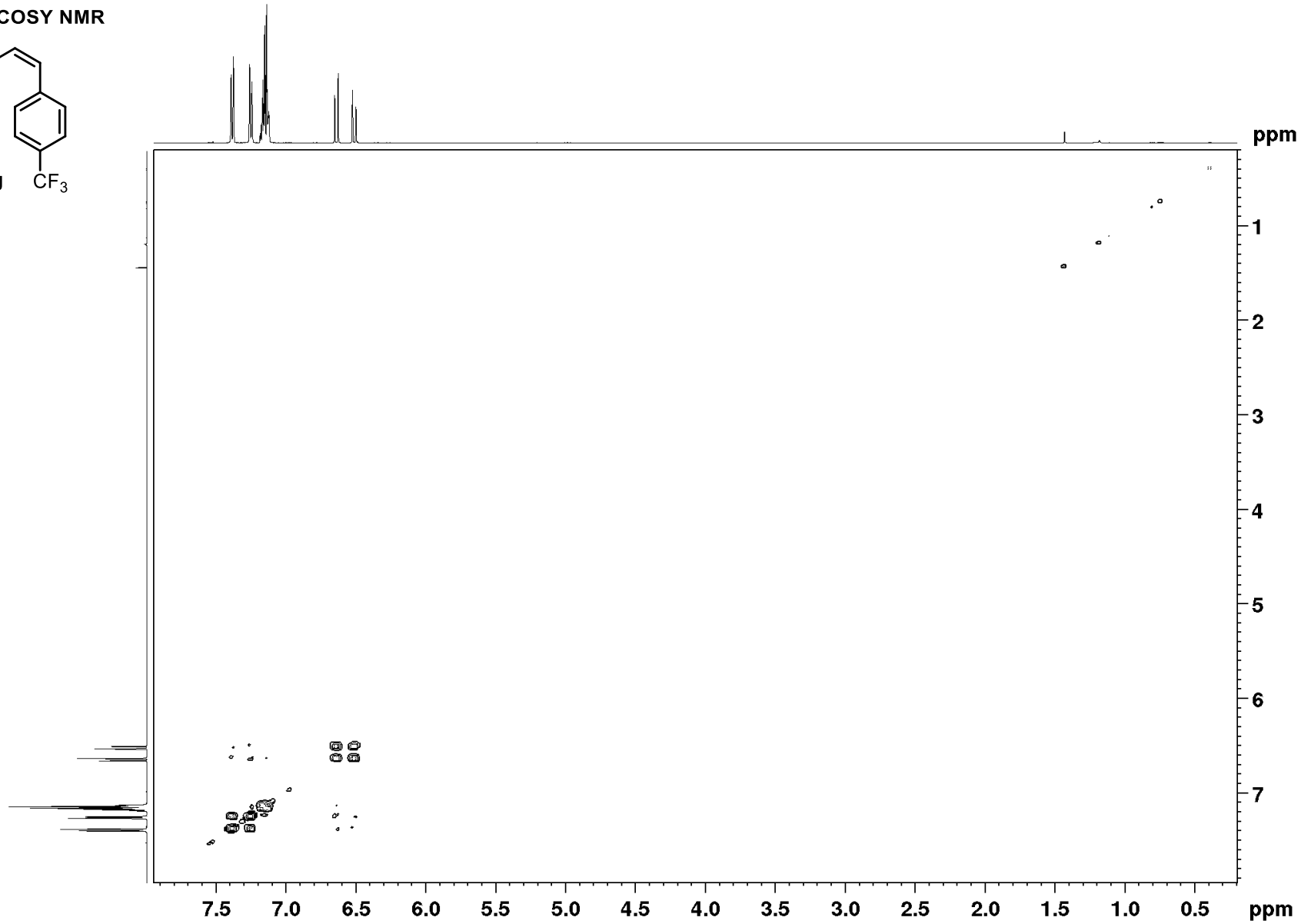
^{13}C NMR



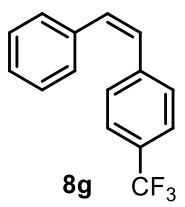
8g CF_3

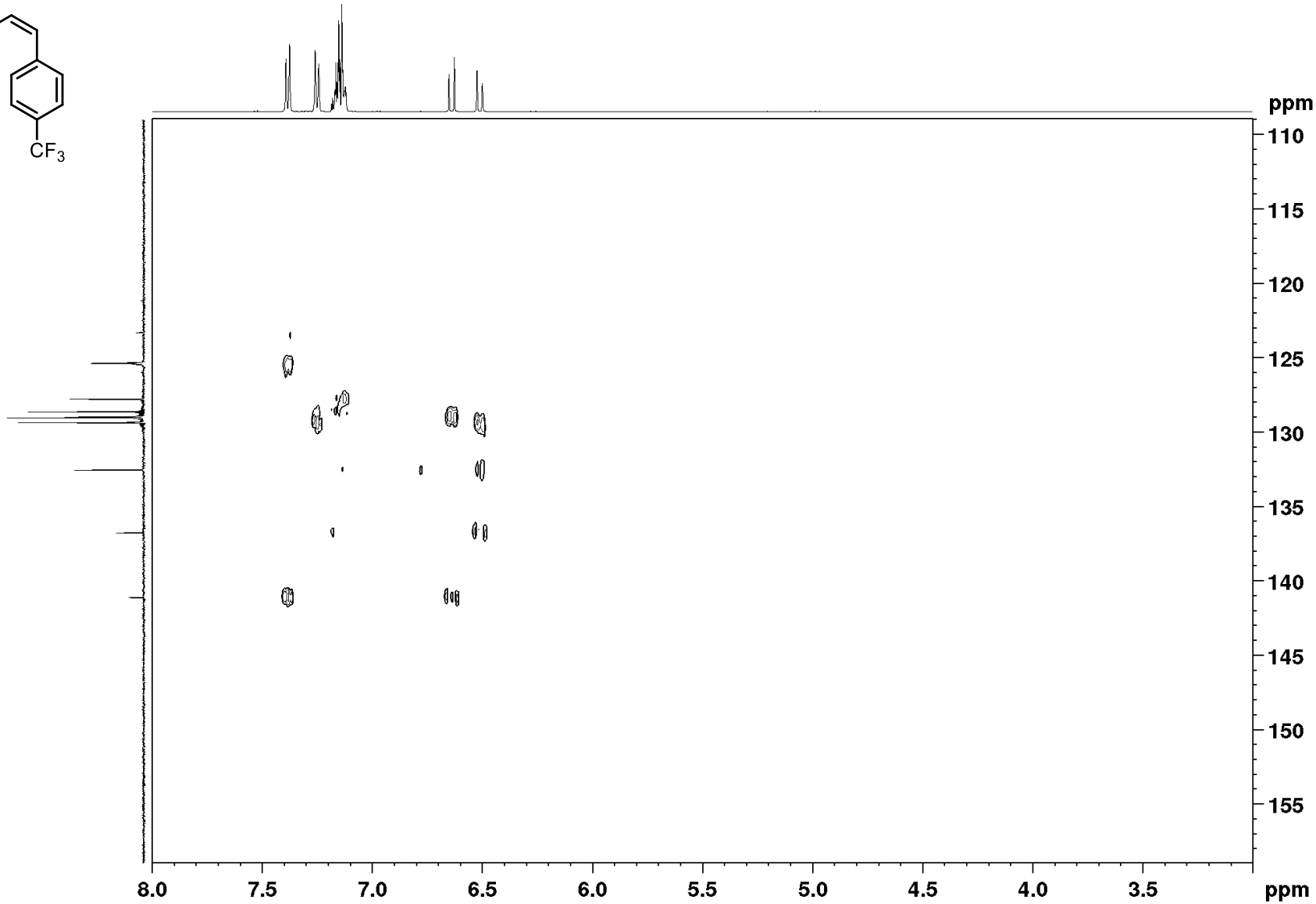
$^{1}H,^{1}H$ COSY NMR



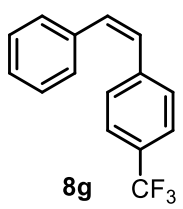


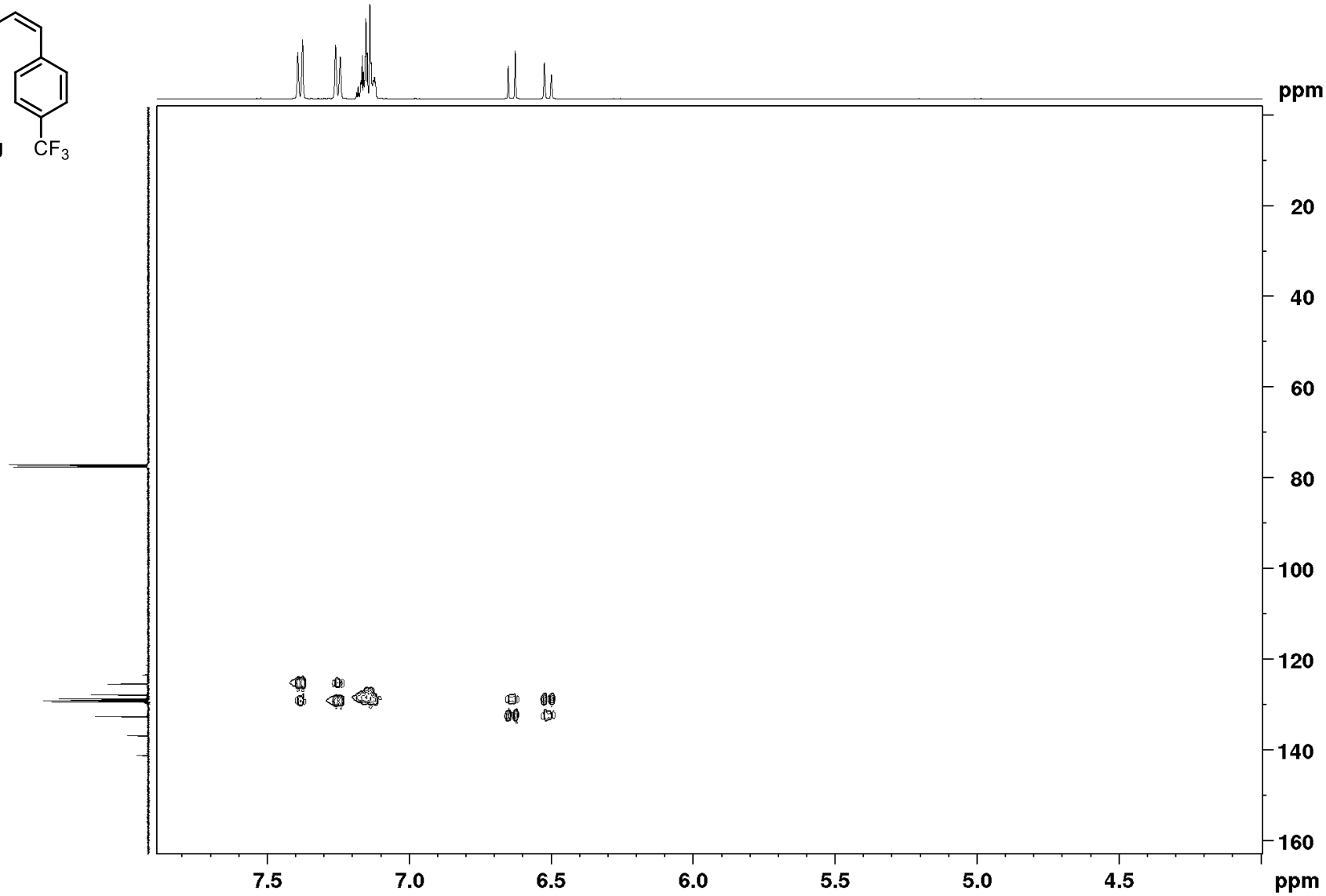
$^{1}H,^{13}C$ HMBC NMR



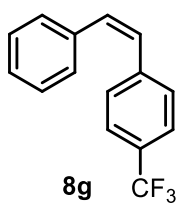


$^{1}H,^{13}C$ HSQC NMR

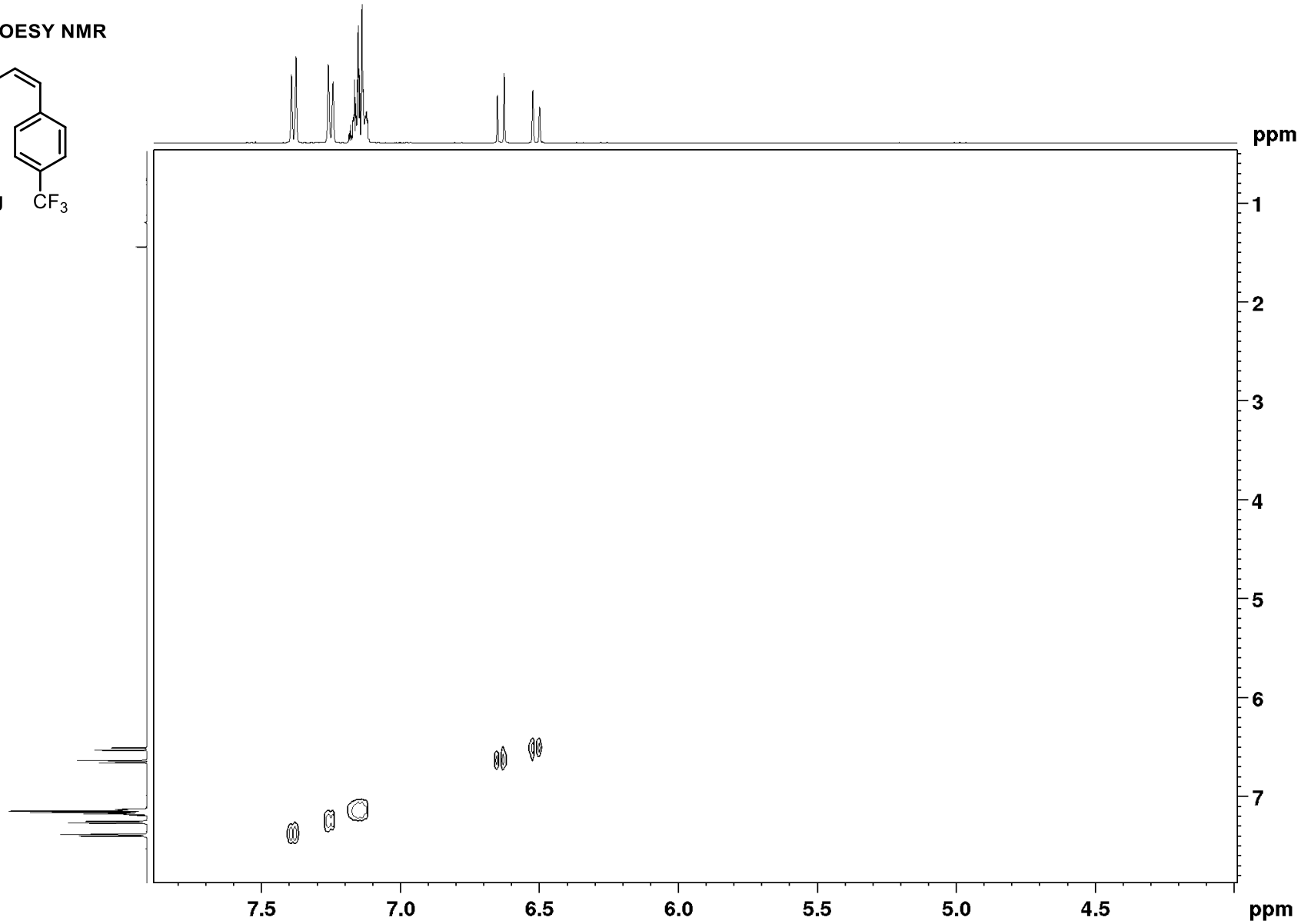




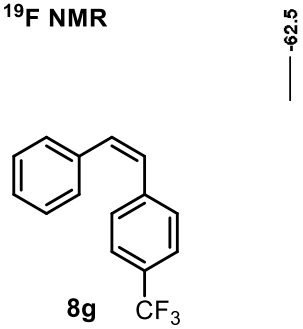
$^{1}H,^{1}H$ NOESY NMR

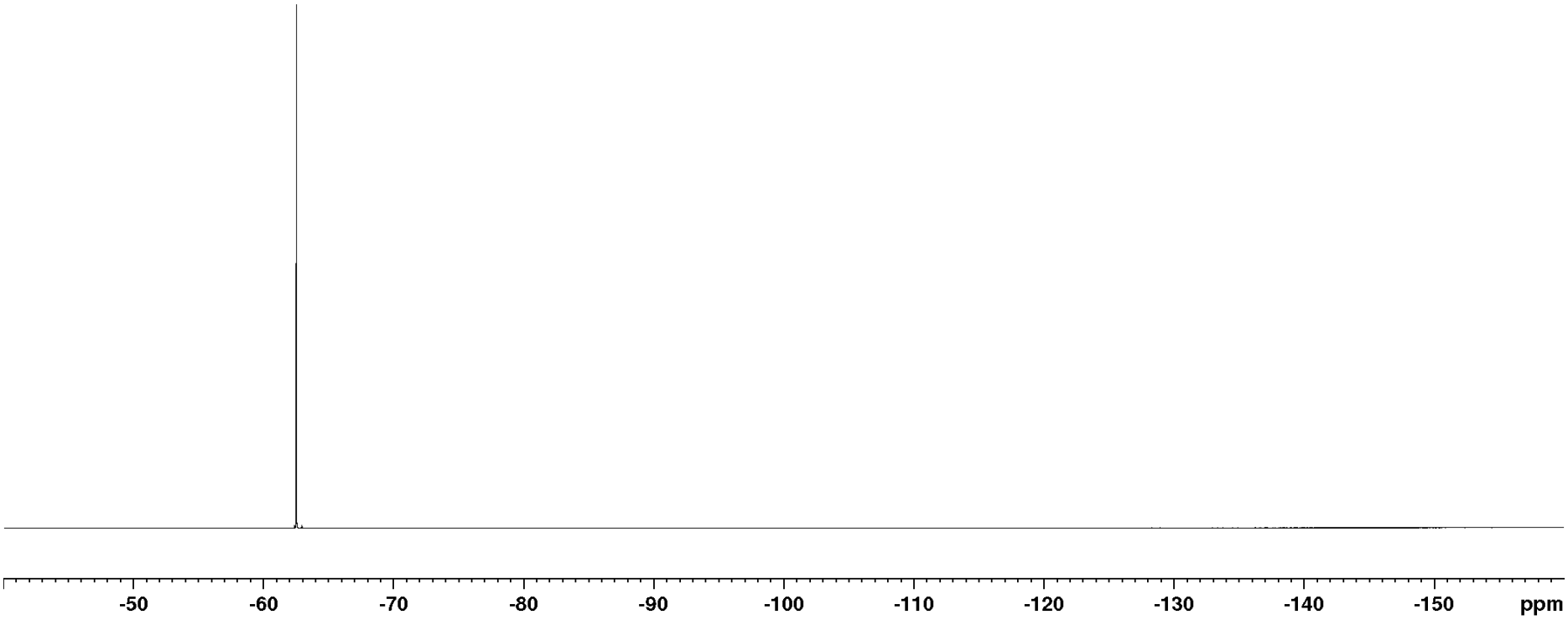


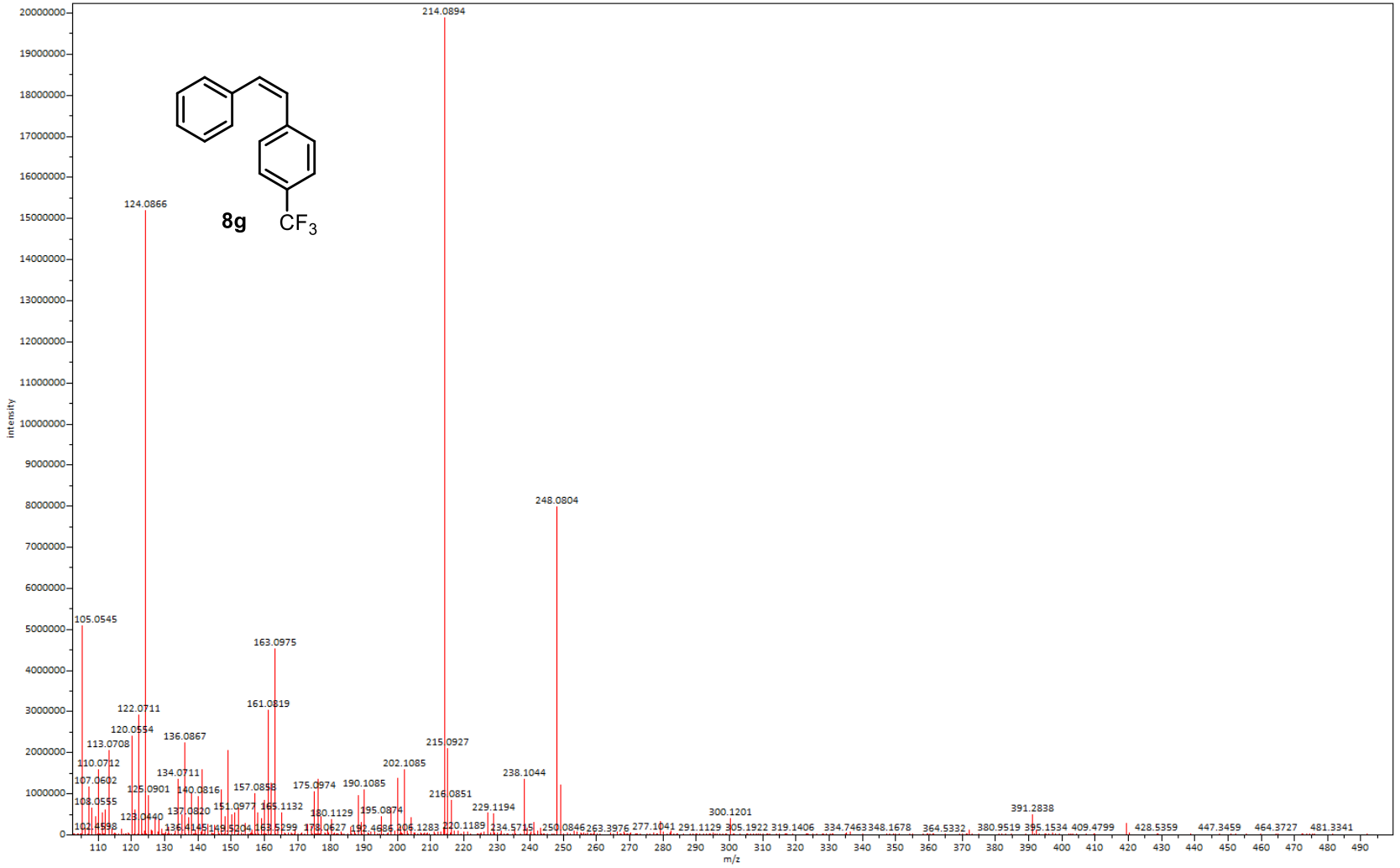
8g CF_3



^{19}F NMR






8g
CF3
intensity
m/z
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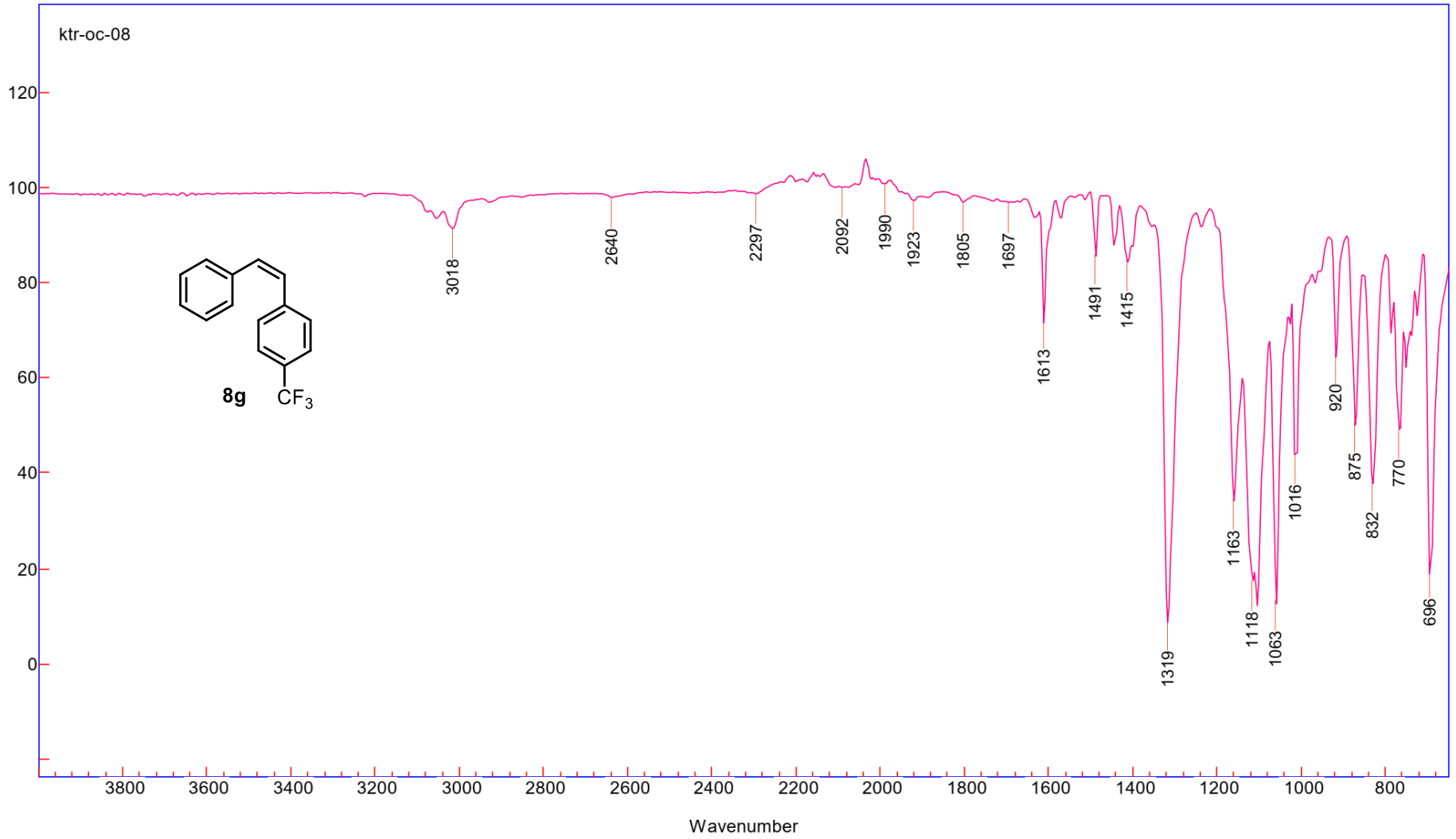
248.0804
105.0545
163.0975
161.0819
122.0711
120.0554
136.0867
113.0708
110.0712
215.0927
202.1085
238.1044
134.0711
107.0602
125.0901
140.0816
157.0858
175.0974
190.1085
216.0851
108.0555
151.0977
165.1132
180.1129
195.0874
229.1194
300.1201
391.2838


ktr-oc-08
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60
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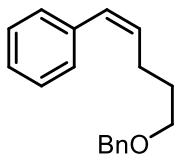
1990
1923
1805
1697
1613
1491
1415
1319
1163
1118
1063
1016
920
875
832
770
696
8g
CF3
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber

^{1}H NMR


BnO

8h


7.26
7.25
7.24
7.23
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.19
7.18
6.36
6.33
5.60
5.58
5.58
5.57
5.56
5.55
4.38
3.44
3.43
3.41
3.40
2.37
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2.35
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1.72
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1.71
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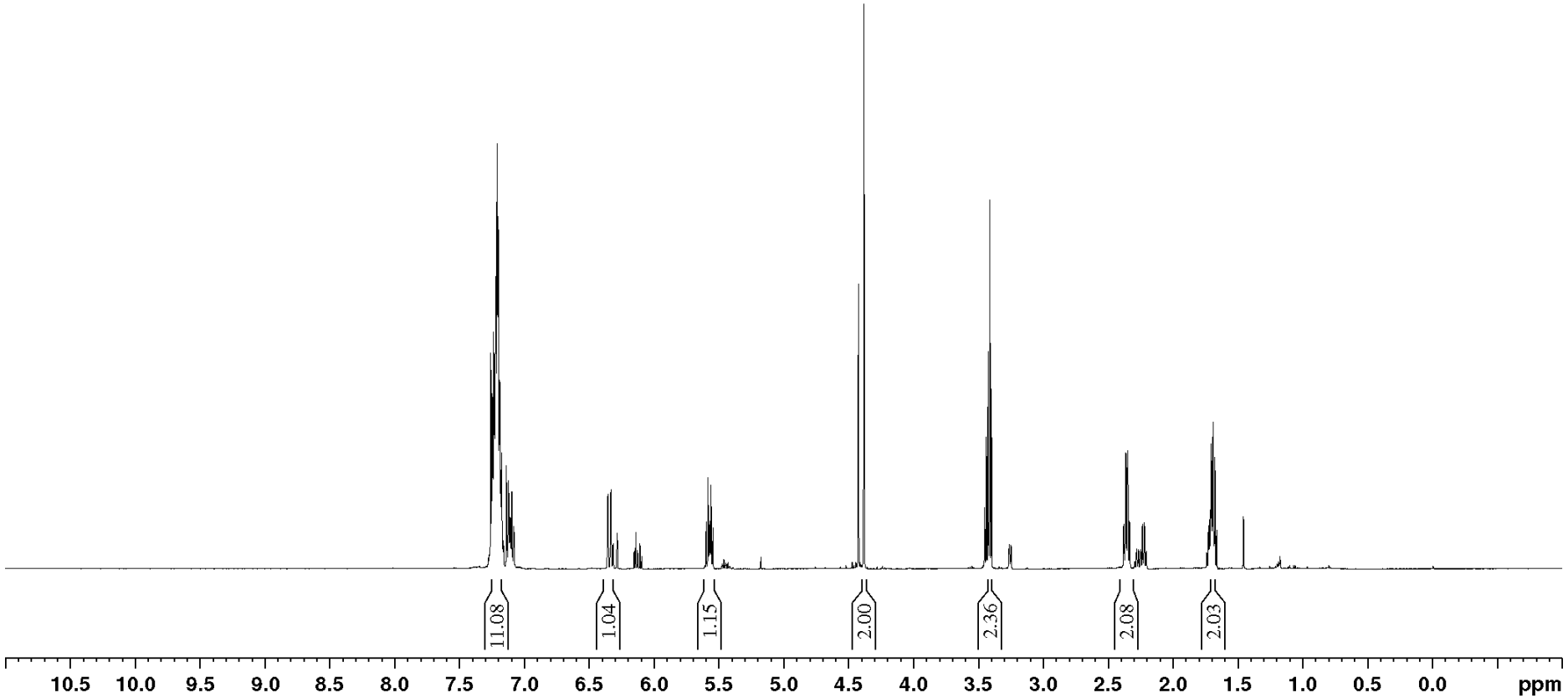
1.69
1.68
1.66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10.5
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9.0
8.5
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

^{13}C NMR


BnO

8h

138.8
137.8
132.5
129.6
129.0
128.6
128.4
127.7
126.7
126.2
77.5
77.3
77.0
73.1
70.0
30.2
25.5
190
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170
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150
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90
80
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10
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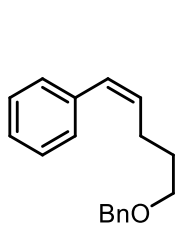
ppm

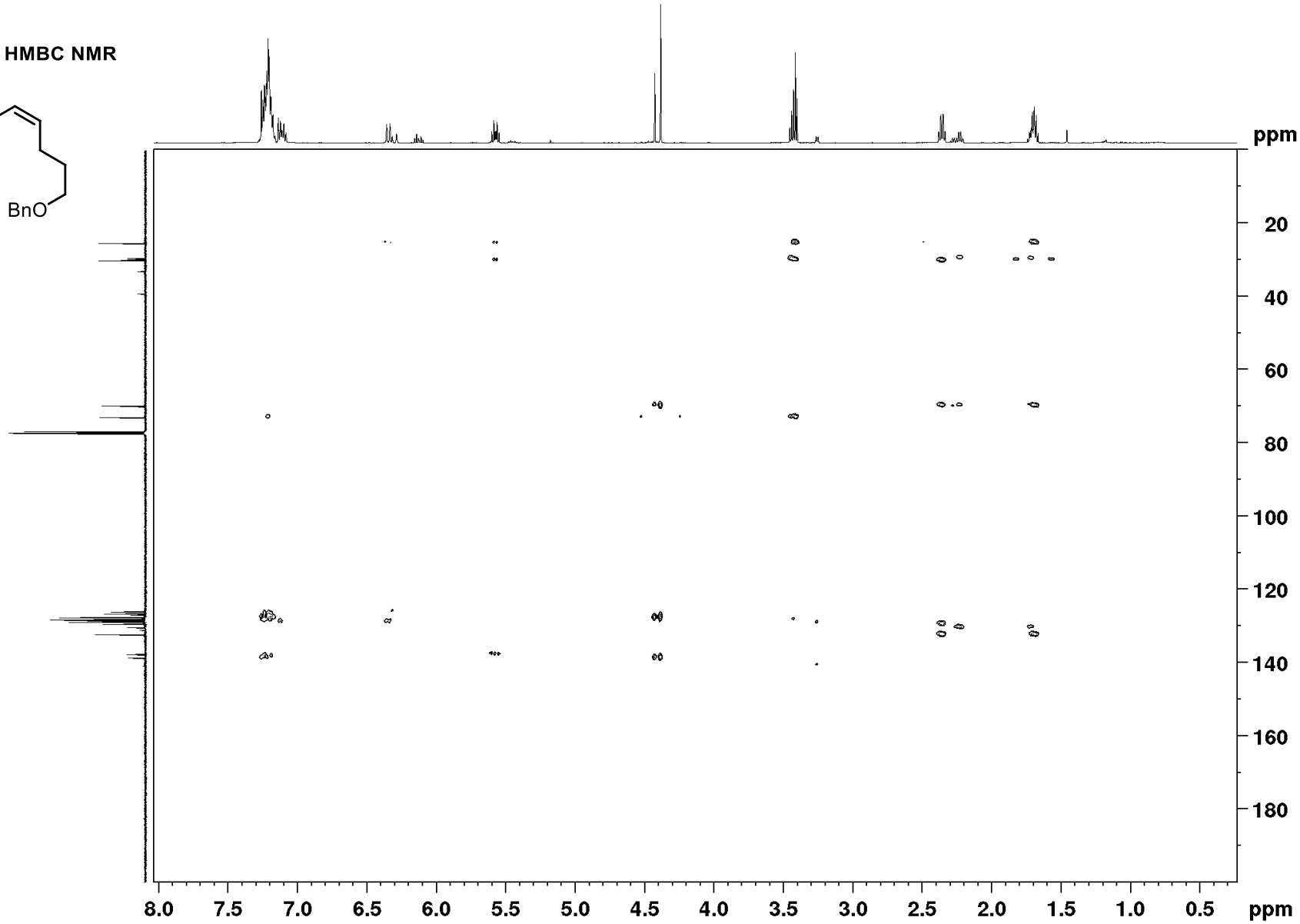
$^{1}H,^{1}H$ COSY NMR



8h

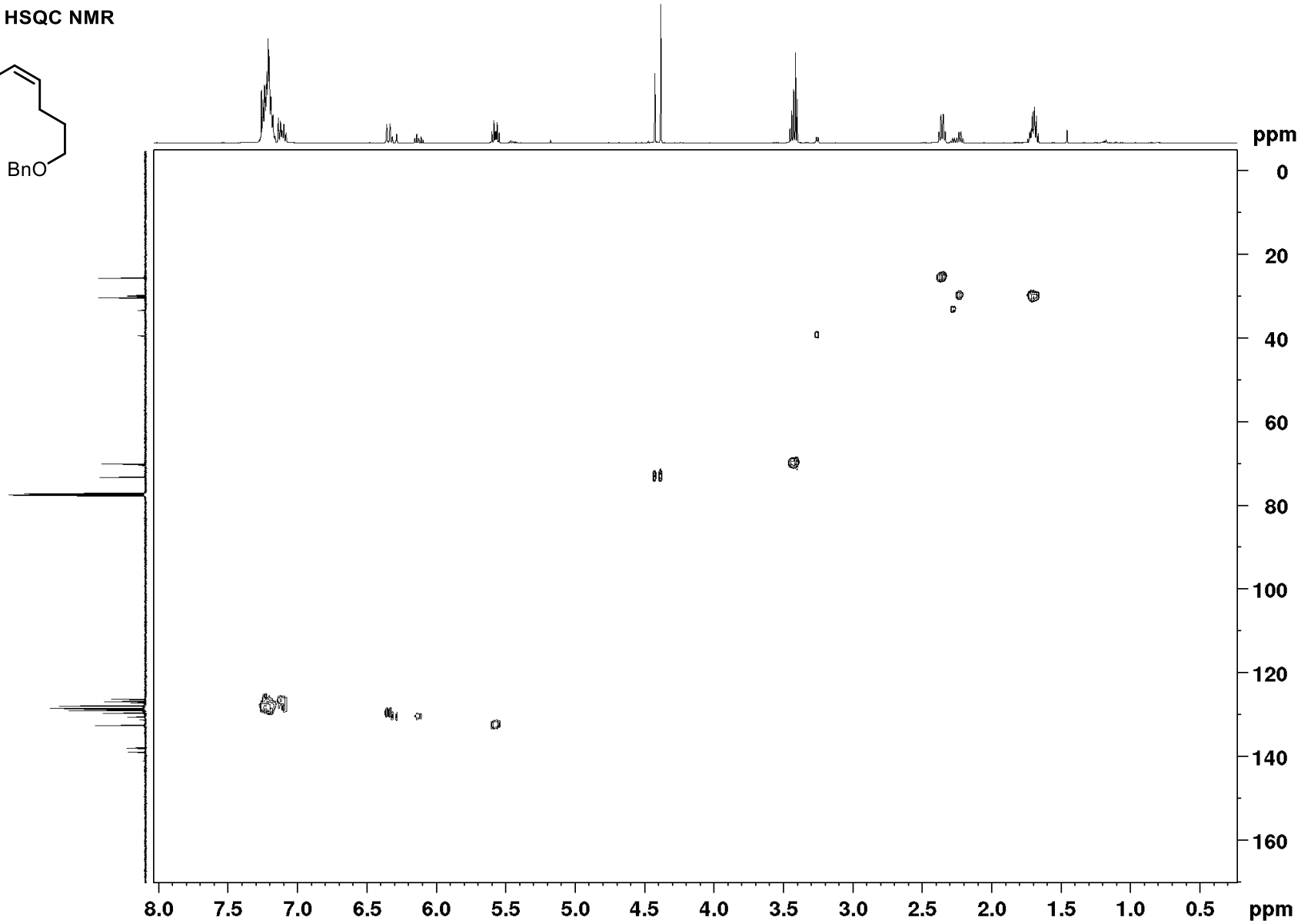
$^{1}H,^{13}C$ HMBC NMR

8h



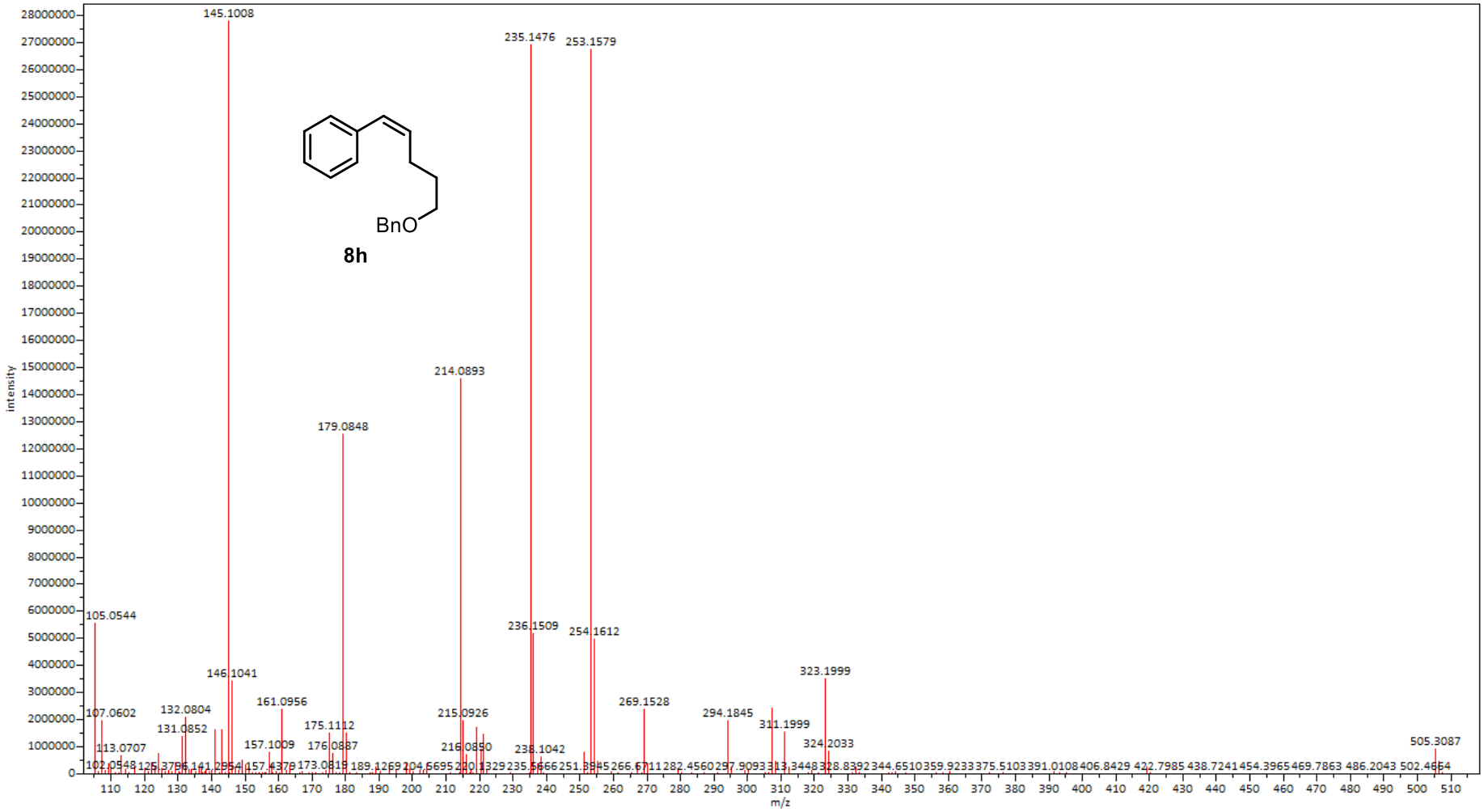
$^{1}H,^{13}C$ HSQC NMR

8h



$^{1}H,^{1}H$ NOESY NMR

8h


BnO
8h
intensity
m/z
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214.0893
179.0848
105.0544
236.1509
254.1612
146.1041
323.1999
161.0956
269.1528
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132.0804
215.0926
294.1845
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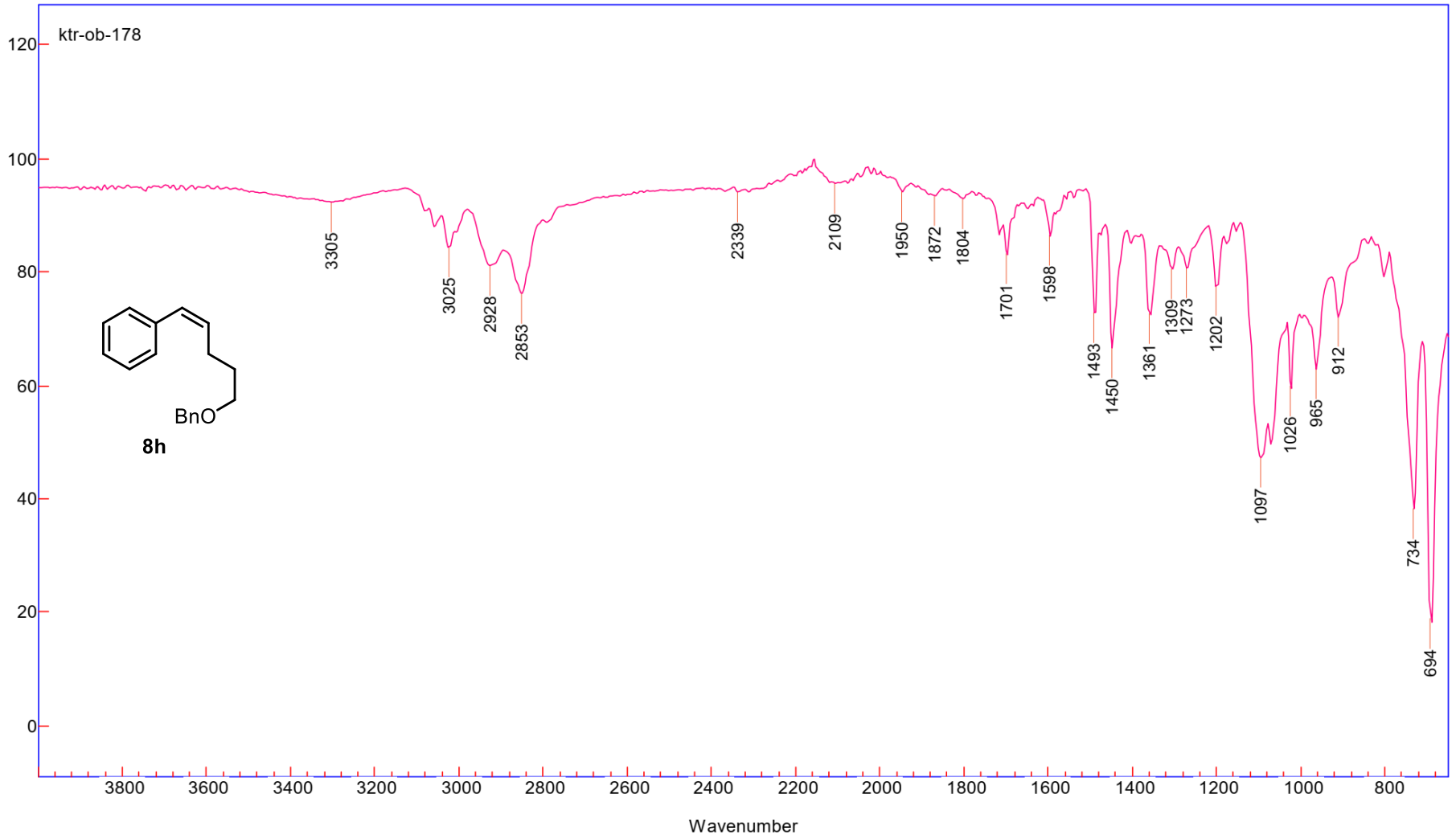
238.1042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1598
1493
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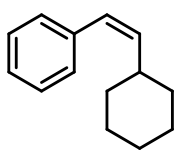
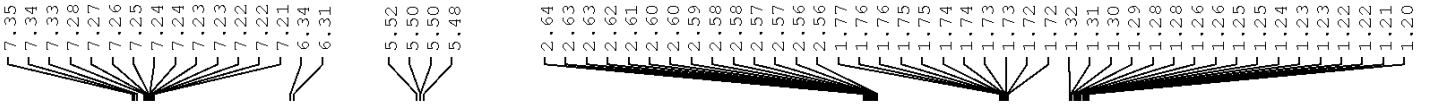
1361
1309
1273
1202
1097
1026
965
912
734
694
BnO
8h
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber

^{1}H NMR



8i


7.35
7.34
7.33
7.28
7.27
7.26
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
6.34
6.31
5.52
5.50
5.50
5.48
2.64
2.63
2.63
2.62
2.61
2.60
2.60
2.59
2.58
2.58
2.57
2.56
2.56
1.77
1.76
1.76
1.75
1.75
1.74
1.74
1.73
1.73
1.72
1.72
1.32
1.31
1.30
1.29
1.28
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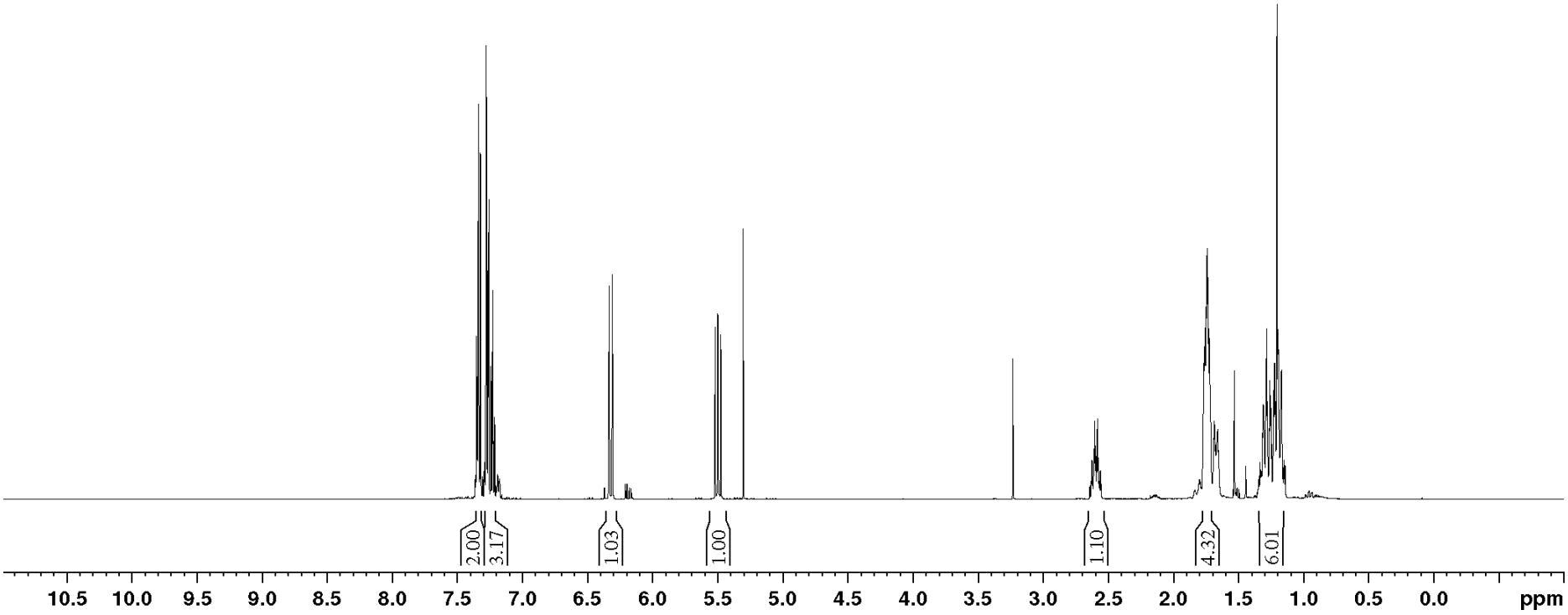
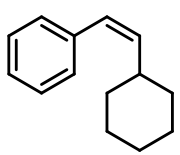
1.23
1.23
1.22
1.22
1.21
1.20


2.00
3.17
1.03
1.00
1.10
4.32
6.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

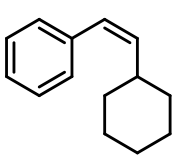
^{13}C NMR



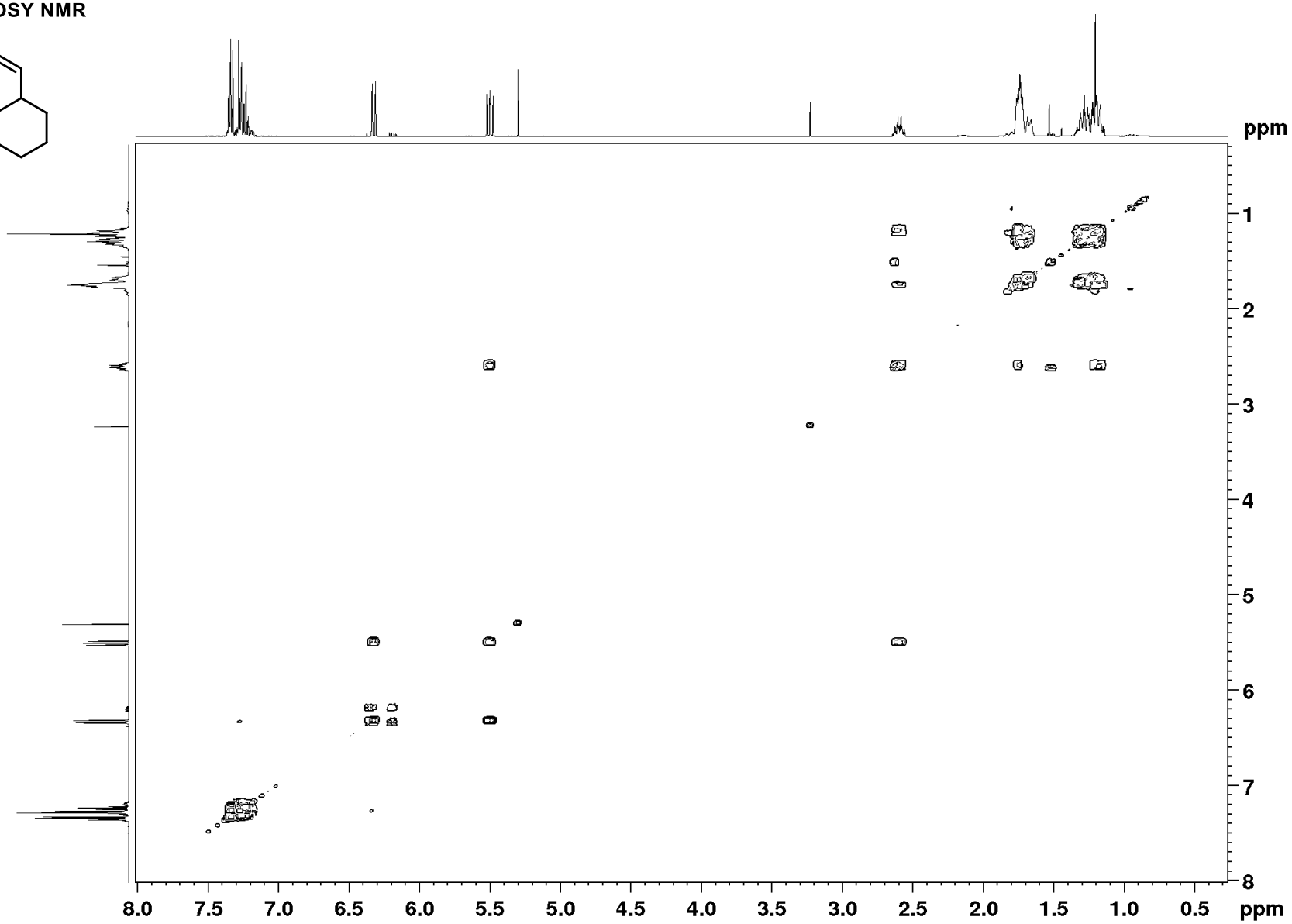
8i

139.1
138.1
128.7
128.3
127.0
126.5
77.4
77.2
76.9
37.0
33.4
26.2
25.8
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

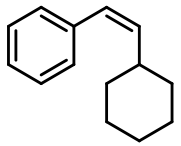
$^{1}H,^{1}H$ COSY NMR



8i

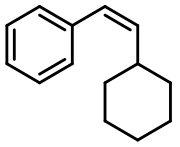


$^{1}H,^{13}C$ HMBC NMR



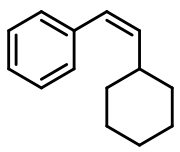
8i

$^{1}H,^{13}C$ HSQC NMR

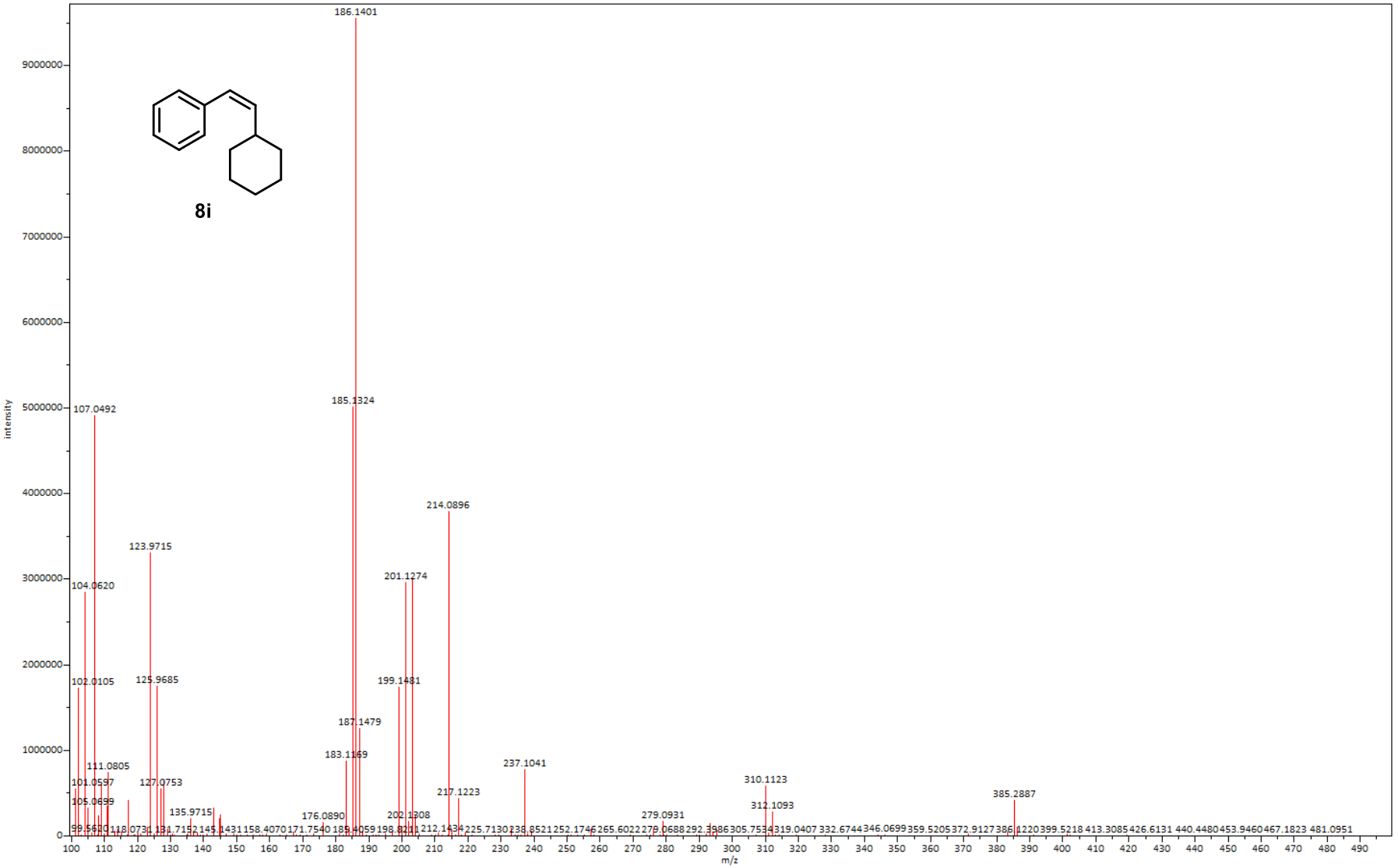


8i

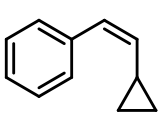
$^{1}H,^{1}H$ NOESY NMR



8i


8i
intensity
m/z
186.1401
185.1324
107.0492
214.0896
123.9715
201.1274
104.0620
125.9685
199.1481
102.0105
187.1479
183.1169
111.0805
237.1041
101.0597
127.0753
310.1123
217.1223
105.0699
385.2887
135.9715
312.1093
176.0890
279.0931
202.1308

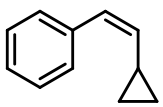
^{1}H NMR



8j

7.46
7.44
7.44
7.44
7.37
7.35
7.34
7.34
7.26
7.24
7.23
7.21
6.38
6.35
5.11
5.09
5.08
5.06
1.94
1.93
1.93
1.93
1.92
1.92
1.92
1.91
1.91
1.91
1.90
1.90
1.90
1.89
1.89
1.89
1.88
1.88
0.86
0.85
0.85
0.85
0.84
0.84
0.83
0.82
0.50
0.49
0.49
0.48
1.96
2.01
1.00
1.00
1.00
0.99
2.15
2.01
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

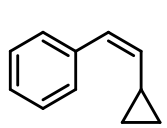
^{13}C NMR



8j

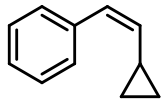
138.1
136.9
128.8
128.3
127.5
126.5
77.4
77.2
76.9
11.2
8.2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

$^{1}H,^{1}H$ COSY NMR

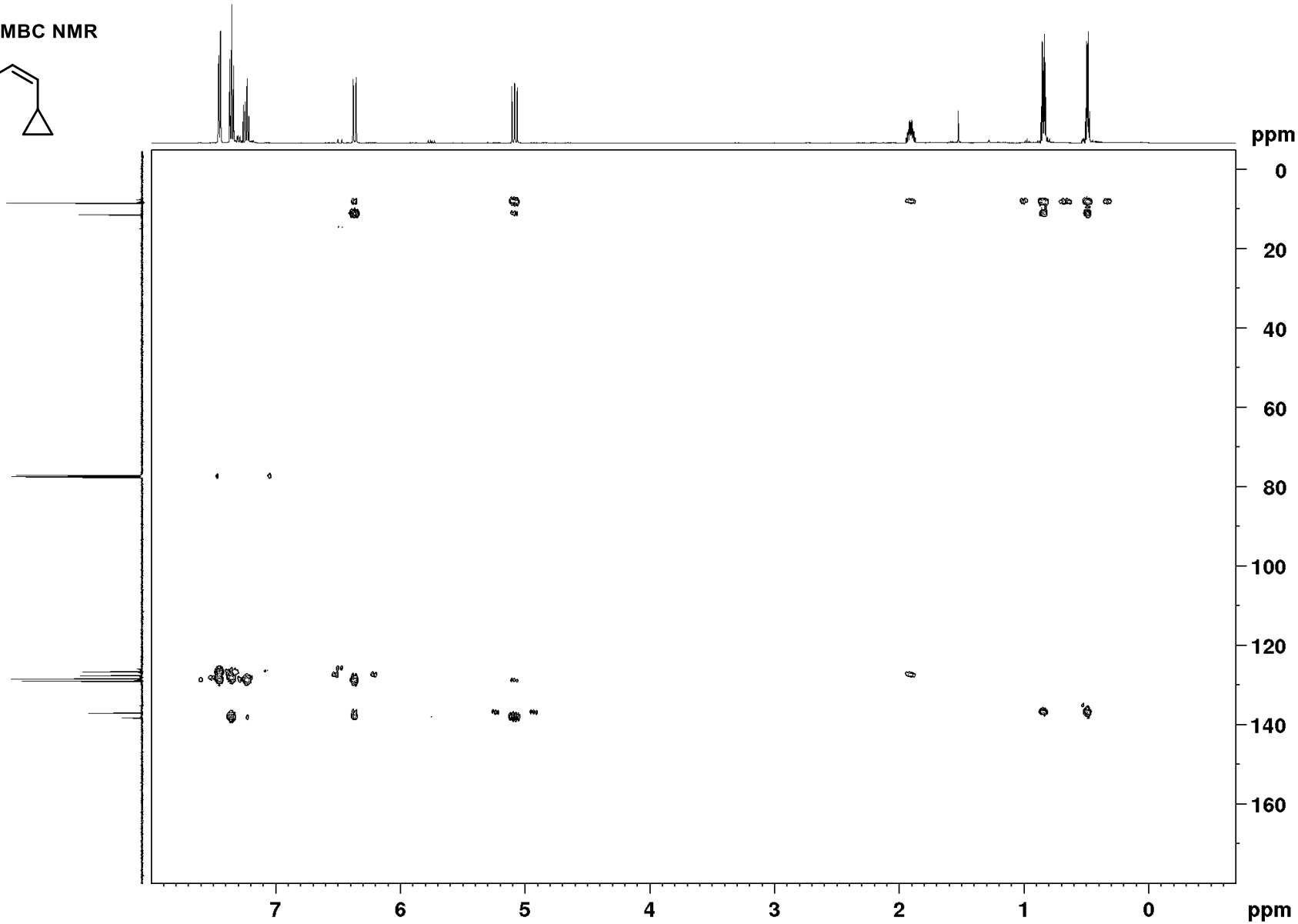


8j

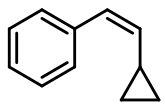
$^{1}H,^{13}C$ HMBC NMR



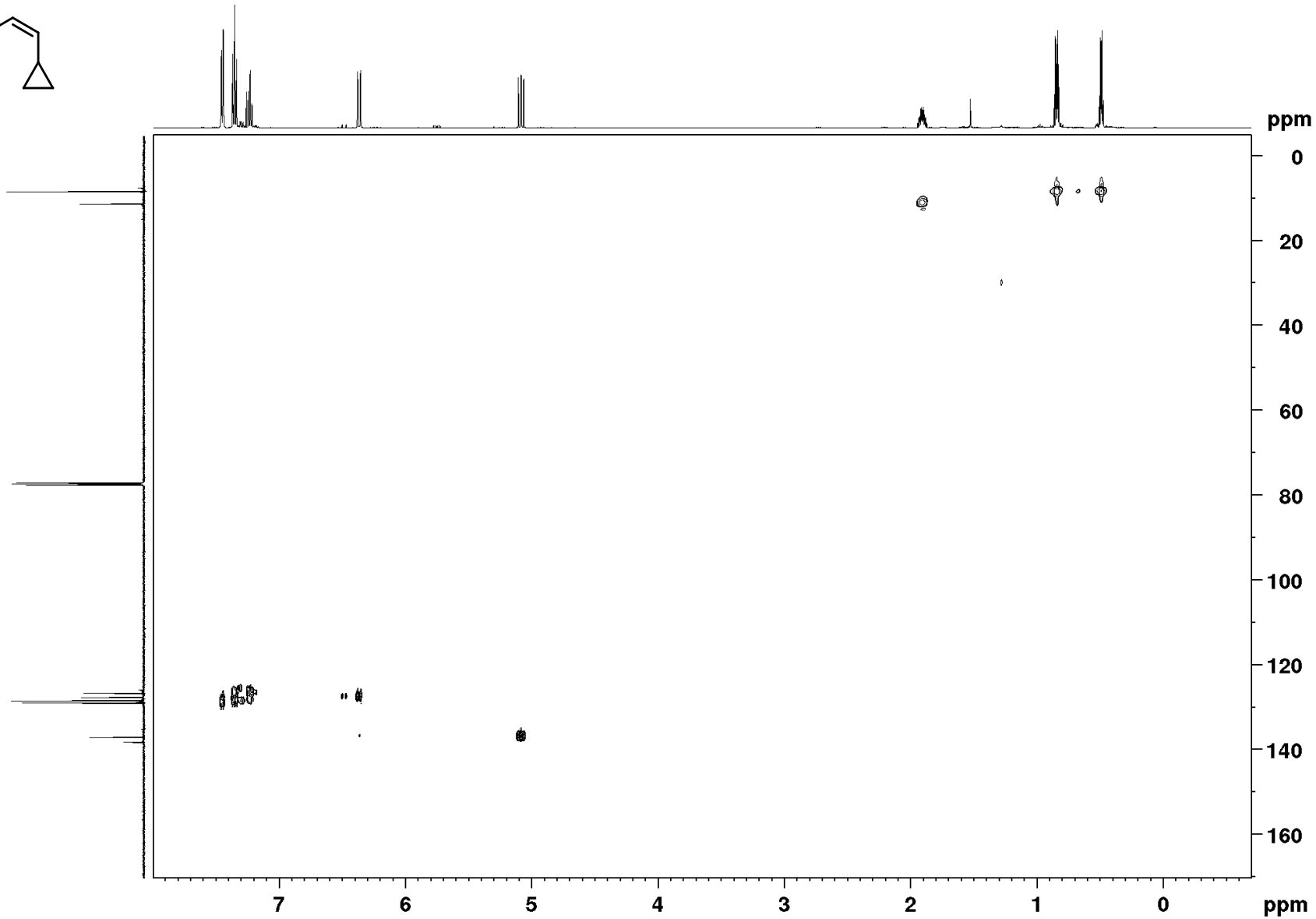
8j



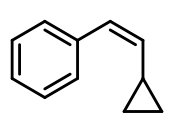
$^{1}H,^{13}C$ HSQC NMR



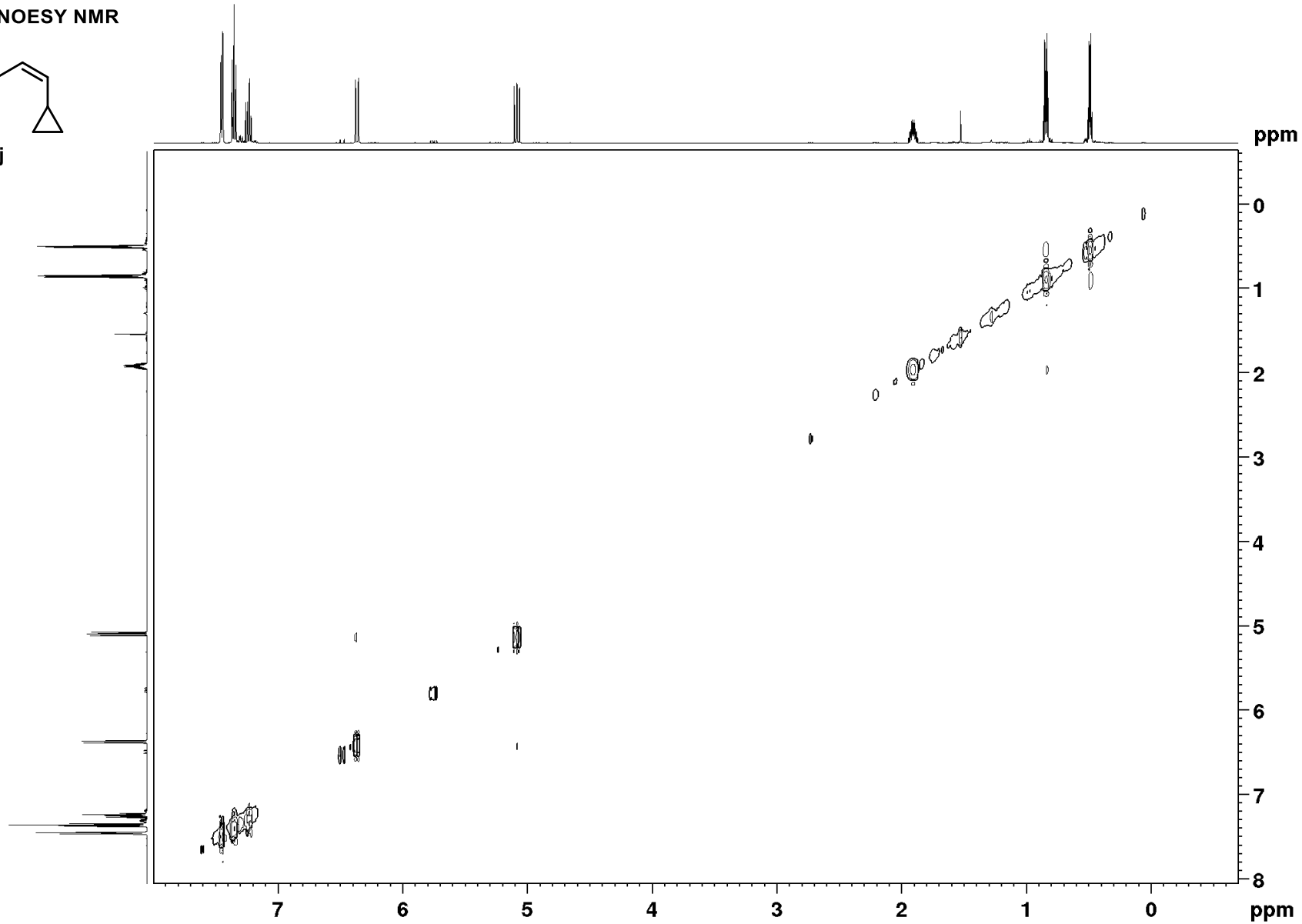
8j

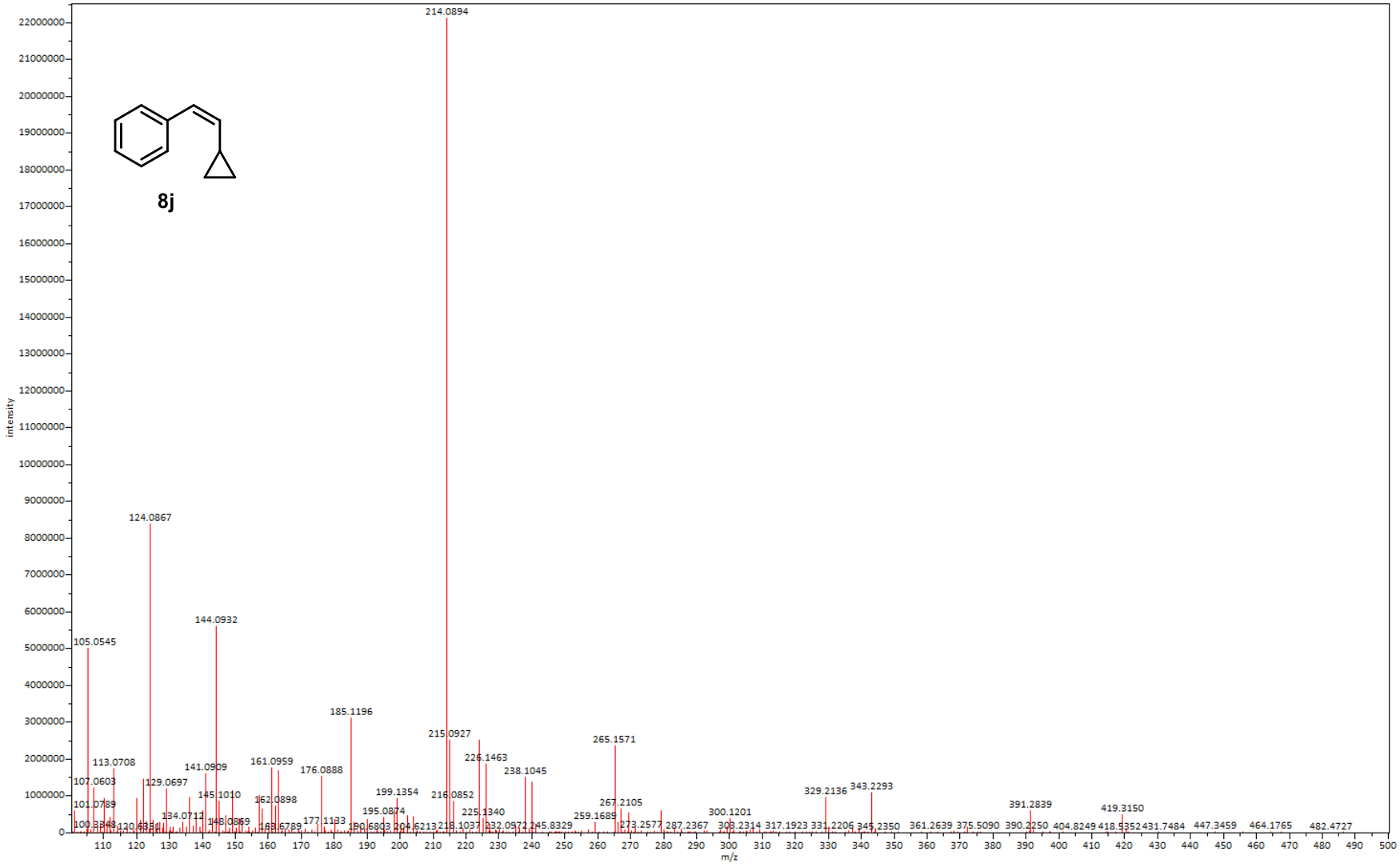


$^{1}H,^{1}H$ NOESY NMR



8j

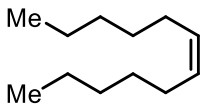



8j
intensity
m/z
214.0894
124.0867
144.0932
105.0545
185.1196
215.0927
265.1571
226.1463
238.1045
113.0708
107.0603
129.0697
141.0909
161.0959
176.0888
199.1354
216.0852
267.2105
329.2136
343.2293
391.2839
419.3150
101.0789
134.0711
145.1010
162.0898
195.0874
225.1340
259.1689
300.1201
447.3459
464.1765
482.4727

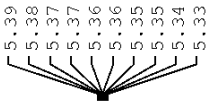

ktr-oc-05
100
90
80
70
60
50
40
30
20
3079
3004
2340
2087
1945
1685
1637
1598
1491
1447
1316
1253
1176
1018
935
771
94
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber

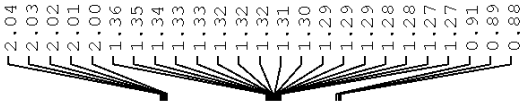
8j

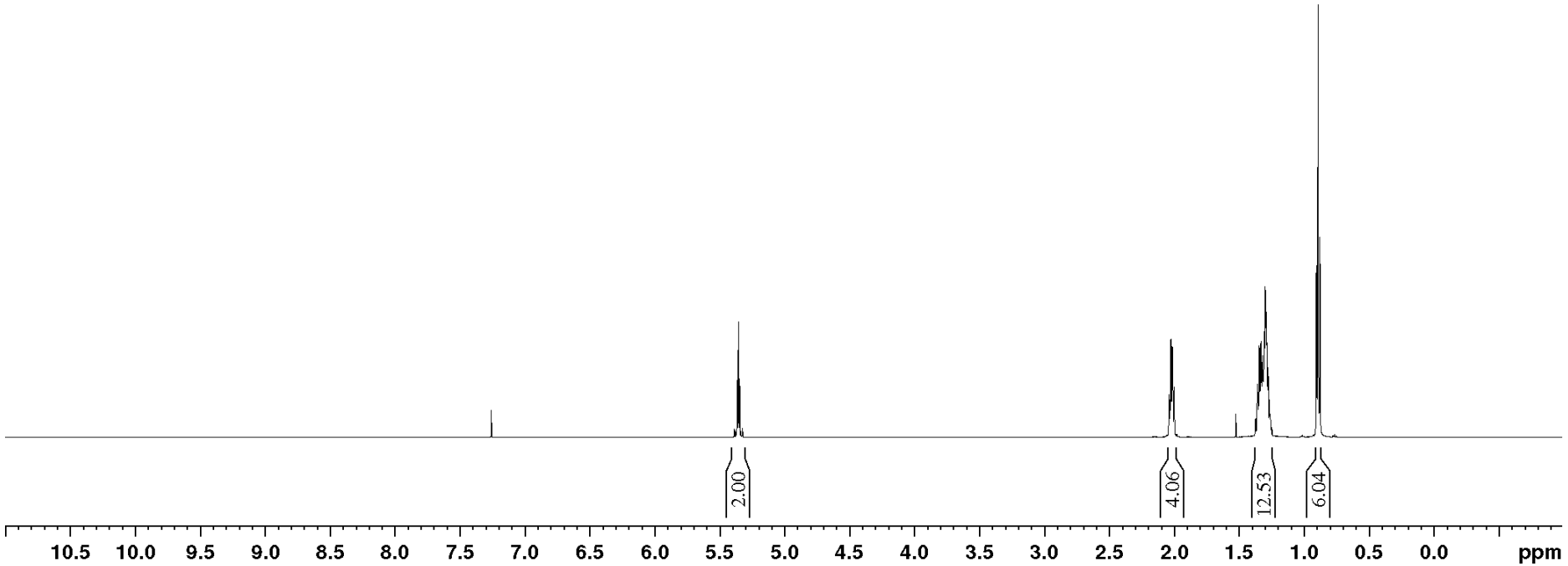
^{1}H NMR


Me
Me

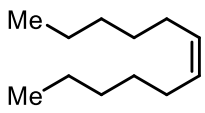
8k


5.39
5.38
5.37
5.37
5.36
5.36
5.35
5.35
5.34
5.33


2.04
2.03
2.02
2.01
2.00
1.36
1.35
1.34
1.33
1.33
1.32
1.32
1.32
1.31
1.30
1.29
1.29
1.29
1.28
1.28
1.27
1.27
0.91
0.89
0.88


2.00
4.06
12.53
6.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

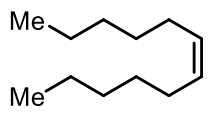
^{13}C NMR


Me
Me

8k

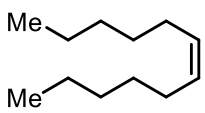
129.1
76.4
76.2
75.9
30.7
28.6
26.3
21.7
13.2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

$^{1}H,^{1}H$ COSY NMR



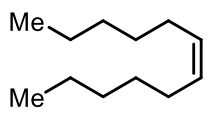
8k

$^{1}H,^{13}C$ HMBC NMR



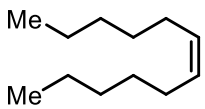
8k

$^{1}H,^{13}C$ HSQC NMR

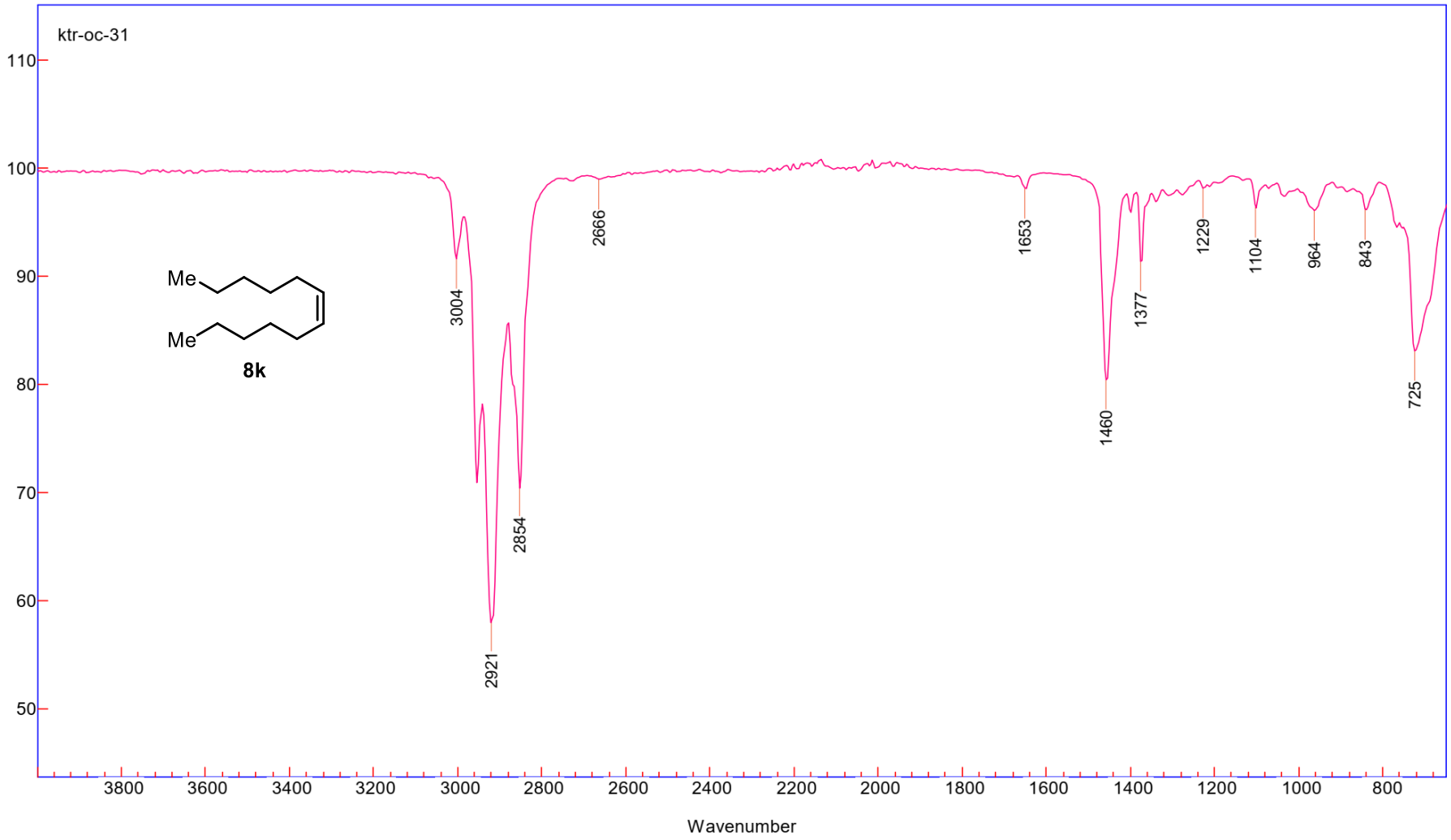


8k

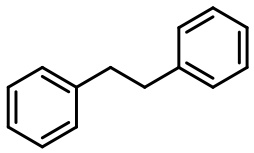
^{1}H,^{1}H NOESY NMR



8k


ktr-oc-31
110
100
90
80
70
60
50
Me
Me
8k
3004
2921
2854
2666
1653
1460
1377
1229
1104
964
843
725
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber

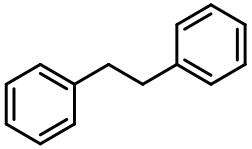
^{1}H NMR



9

7.32
7.31
7.31
7.30
7.29
7.26
7.23
7.23
7.22
7.20
2.95
4.00
5.99
4.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

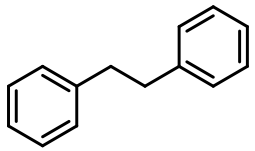
^{13}C NMR



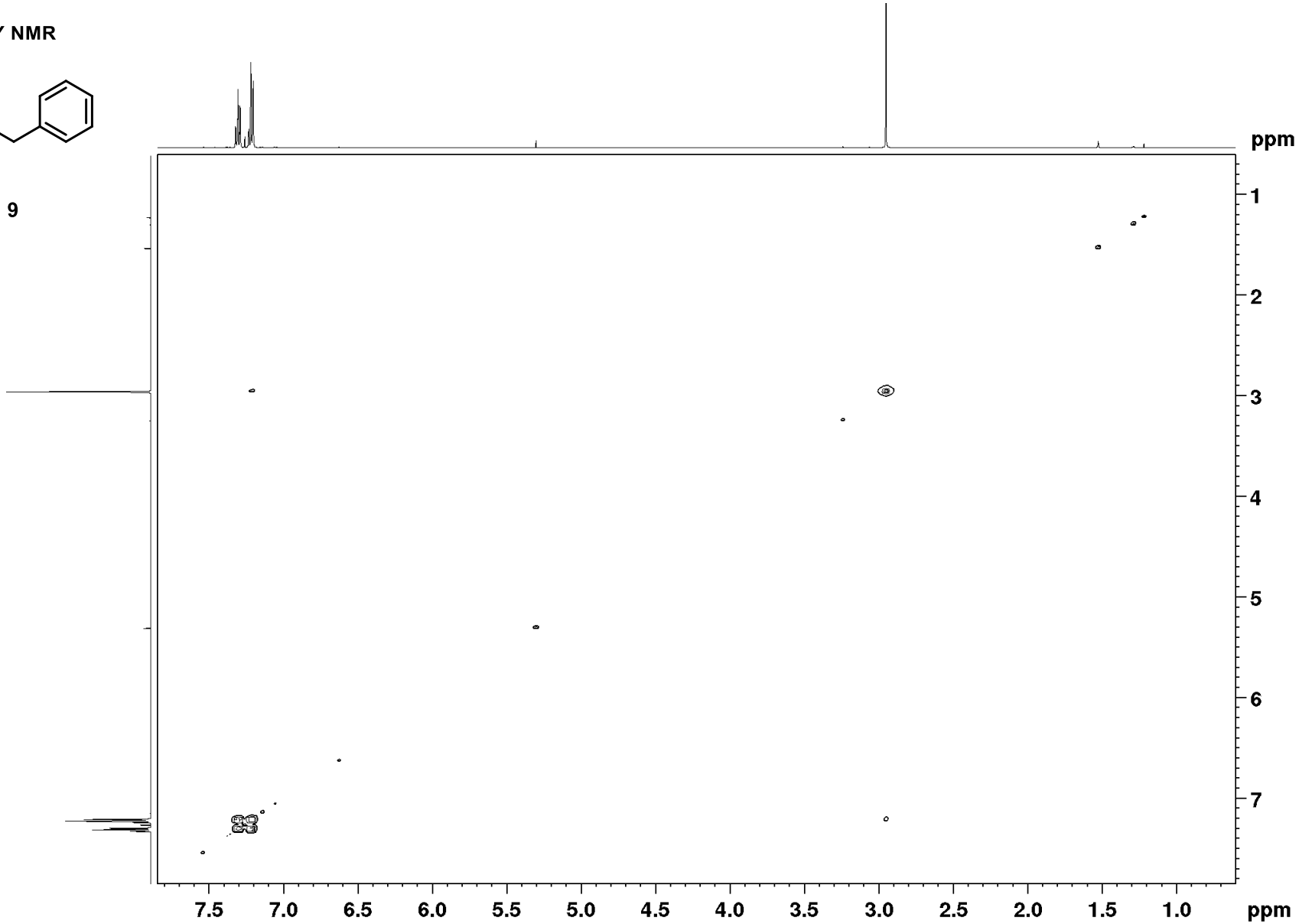
9

141.9
128.6
128.5
126.0
77.4
77.2
76.9
38.1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

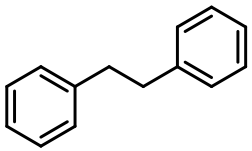
$^{1}H,^{1}H$ COSY NMR



9

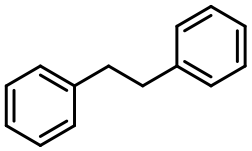


$^{1}H,^{13}C$ HMBC NMR



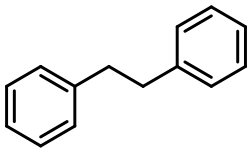
9

$^{1}H,^{13}C$ HSQC NMR

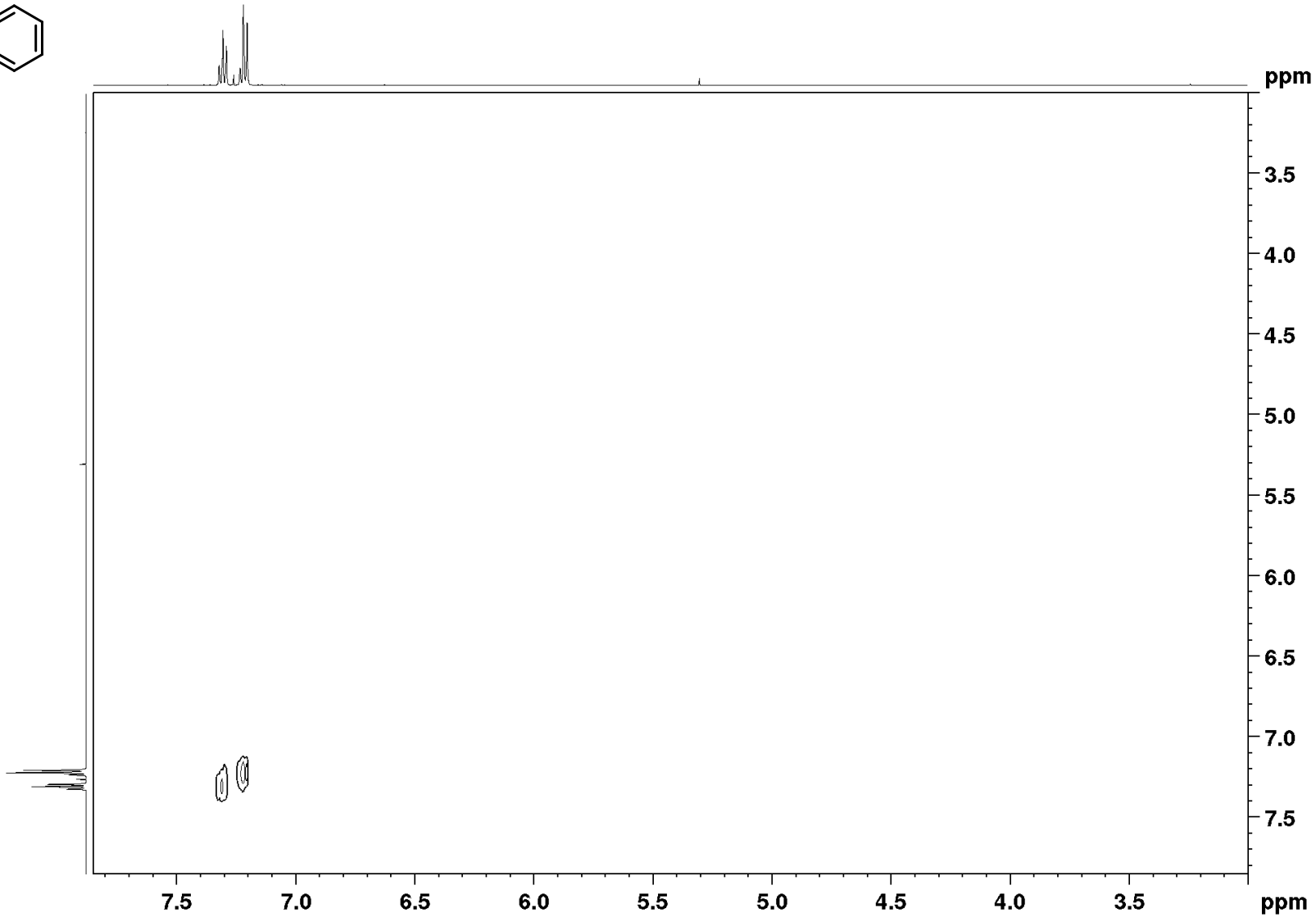


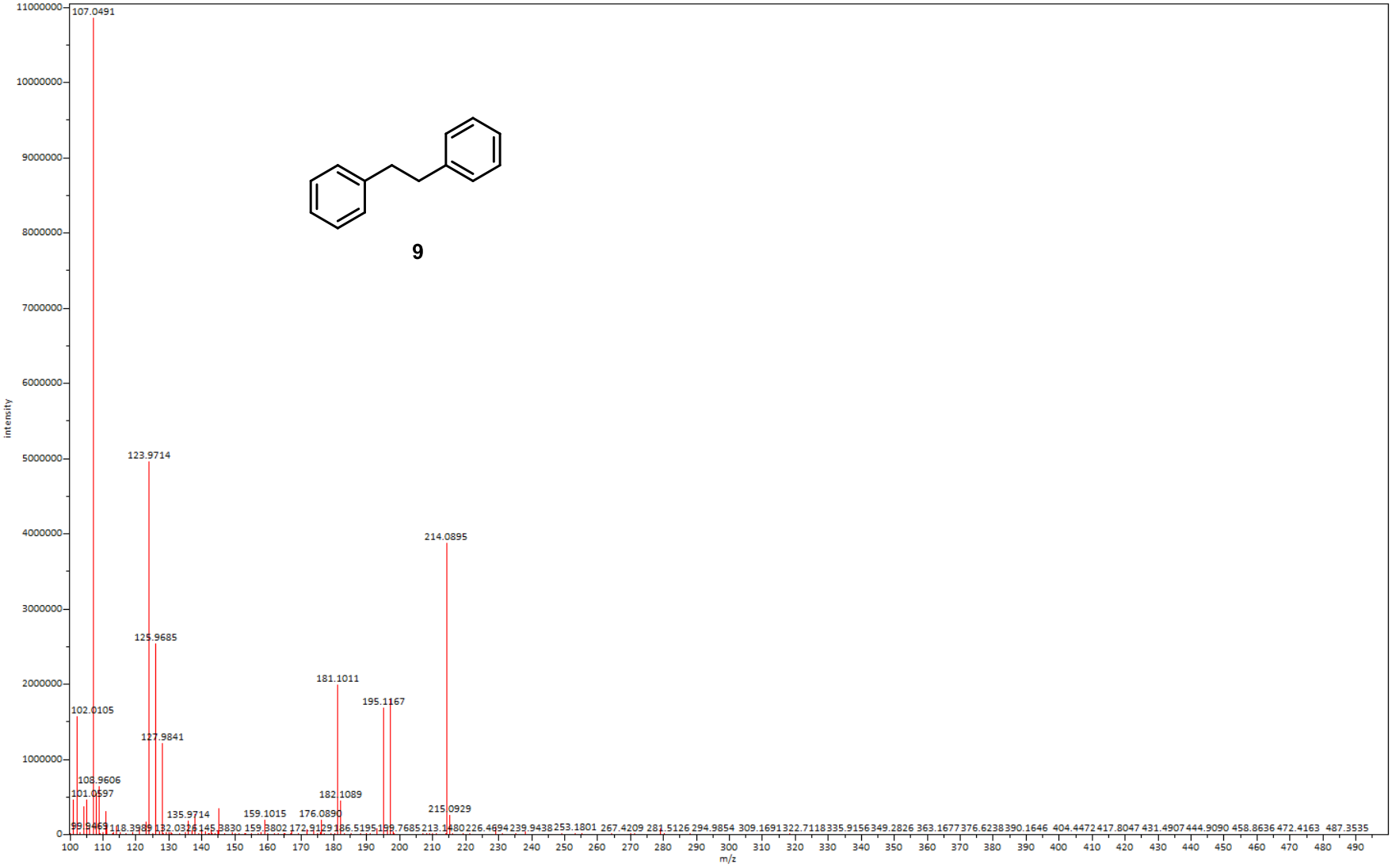
9

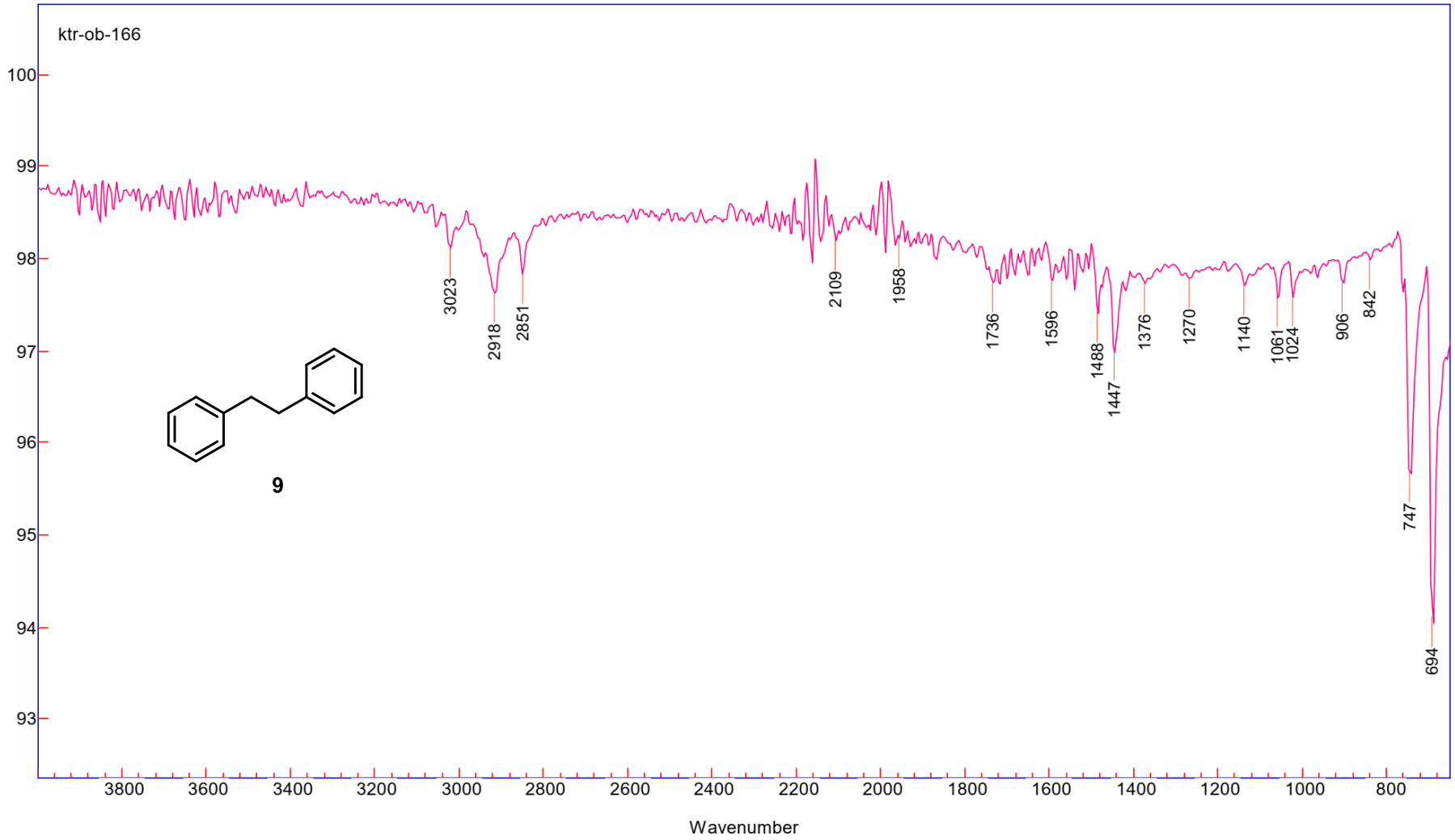
$^{1}H,^{1}H$ NOESY NMR



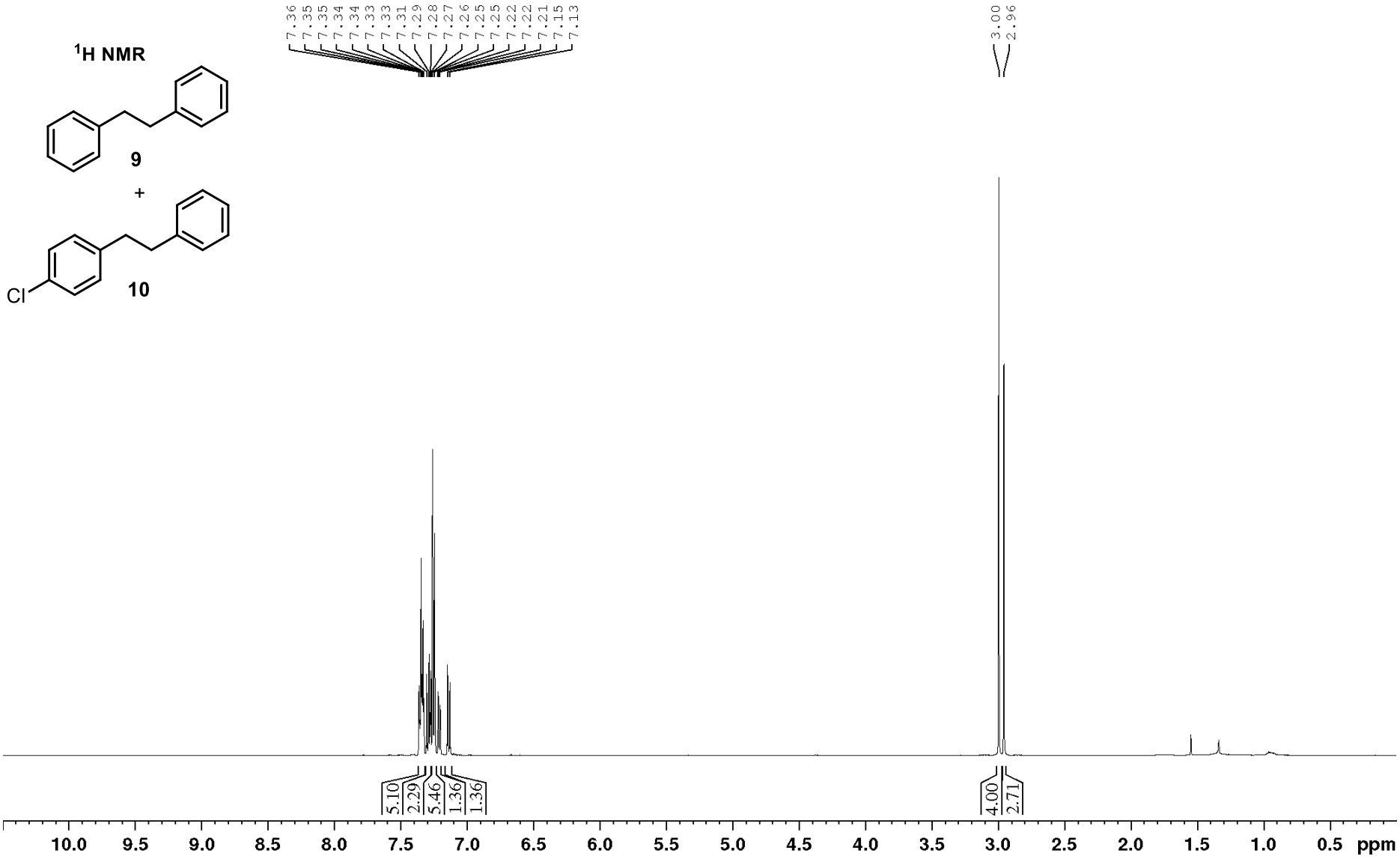
9

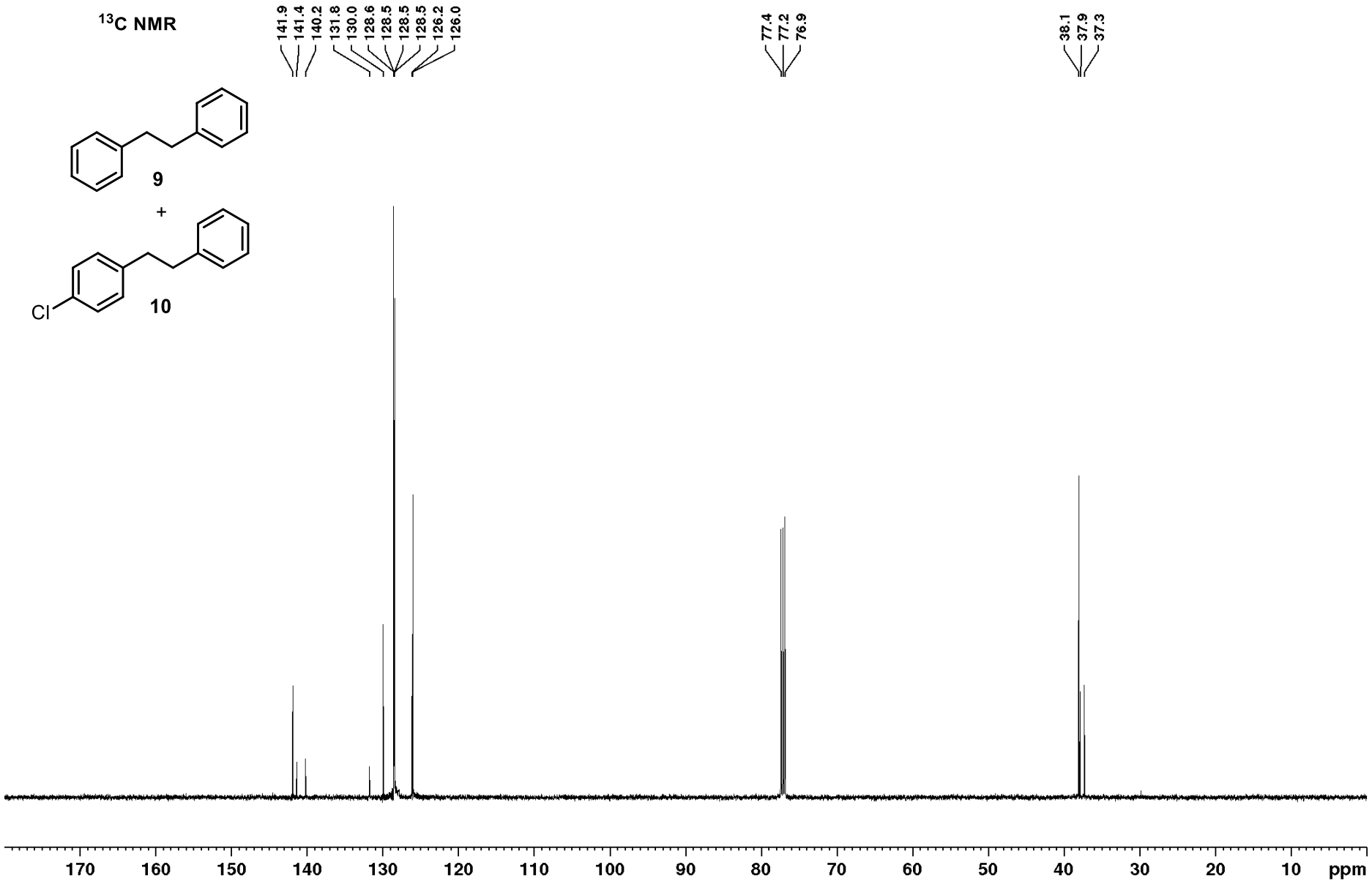



9
intensity
m/z
107.0491
123.9714
214.0895
125.9685
181.1011
195.1167
102.0105
127.9841
108.9606
101.0597
182.1089
135.9714
159.1015
176.0890
215.0929

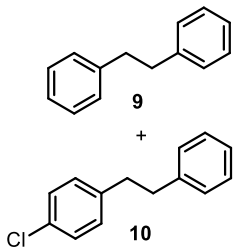

ktr-ob-166
100
99
98
97
96
95
94
93
3023
2918
2851
2109
1958
1736
1596
1488
1447
1376
1270
1140
1061
1024
906
842
747
694
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
Wavenumber

9

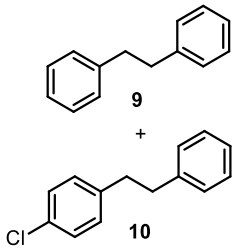

^{1}H NMR
9
+
Cl
10
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.31
7.29
7.28
7.27
7.26
7.25
7.25
7.22
7.22
7.21
7.15
7.13
3.00
2.96
5.10
2.29
5.46
1.36
1.36
4.00
2.71
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

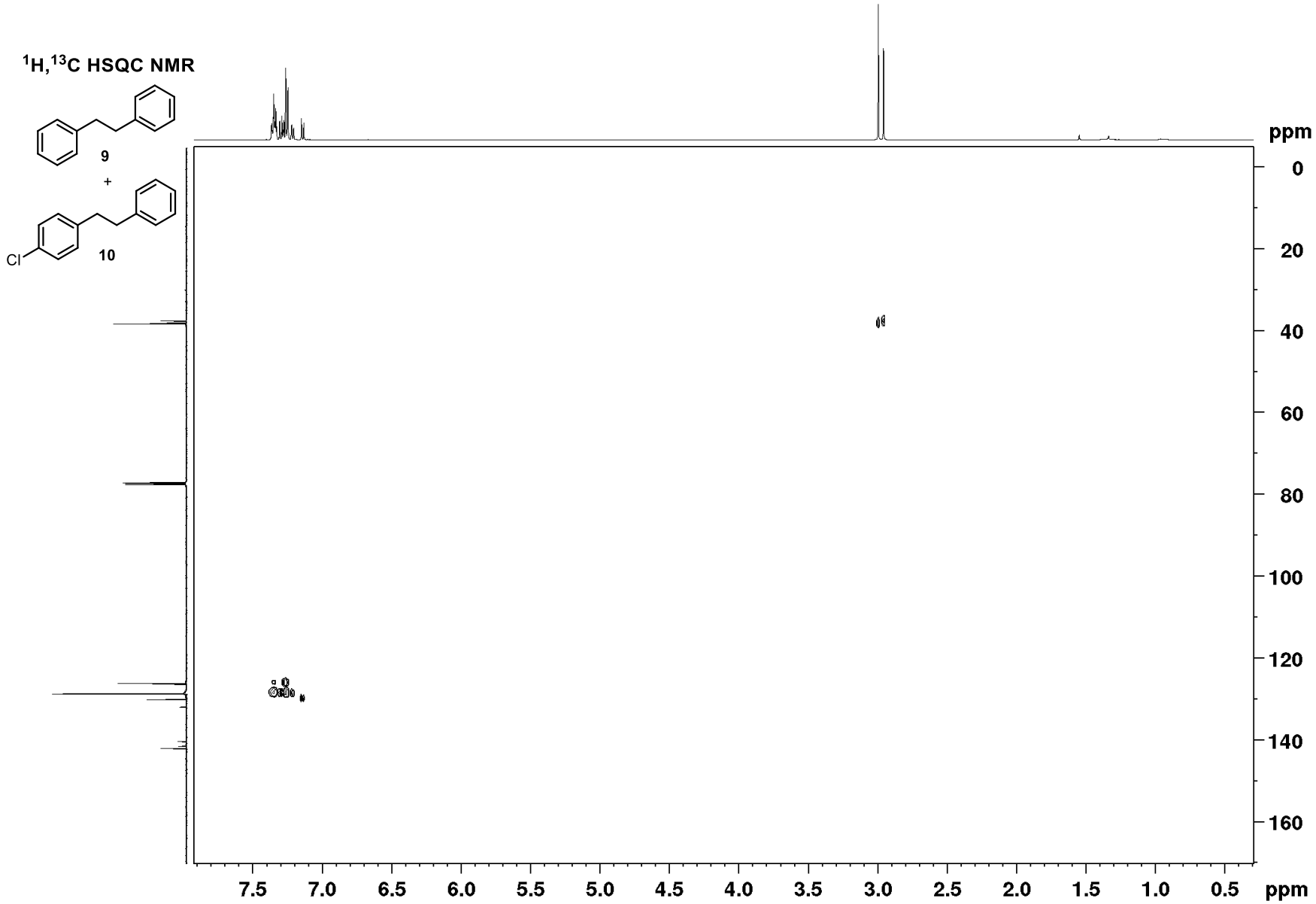

^{13}C NMR
141.9
141.4
140.2
131.8
130.0
128.6
128.5
128.5
128.5
126.2
126.0
77.4
77.2
76.9
38.1
37.9
37.3
9
+
Cl
10
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

$^{1}H,^{1}H$ COSY NMR

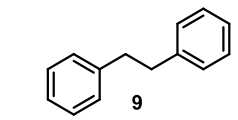


$^{1}H,^{13}C$ HMBC NMR



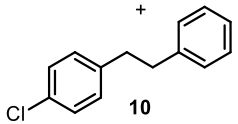

$^{1}H,^{13}C$ HSQC NMR
9
+
Cl
10
ppm
0
20
40
60
80
100
120
140
160
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

$^{1}H,^{1}H$ NOESY NMR

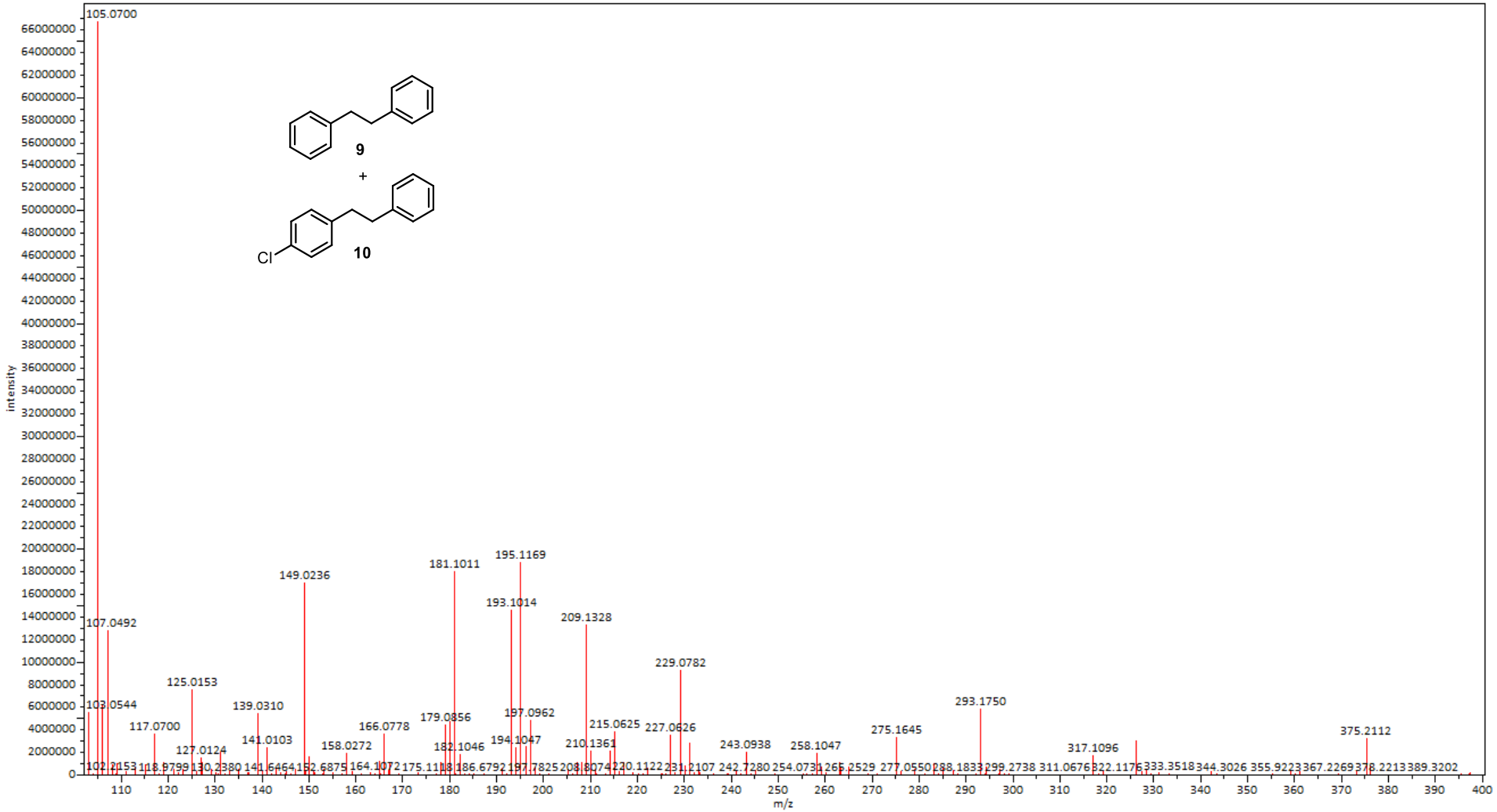


9

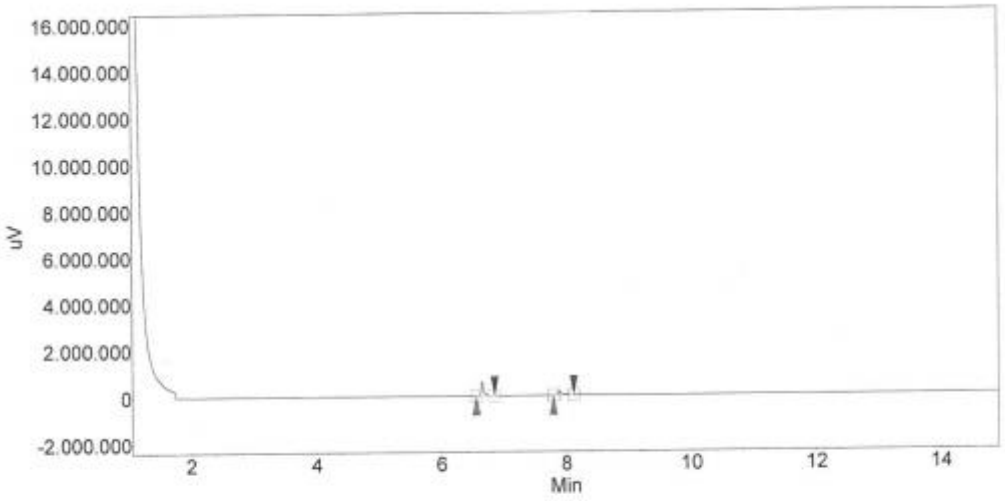
+



10

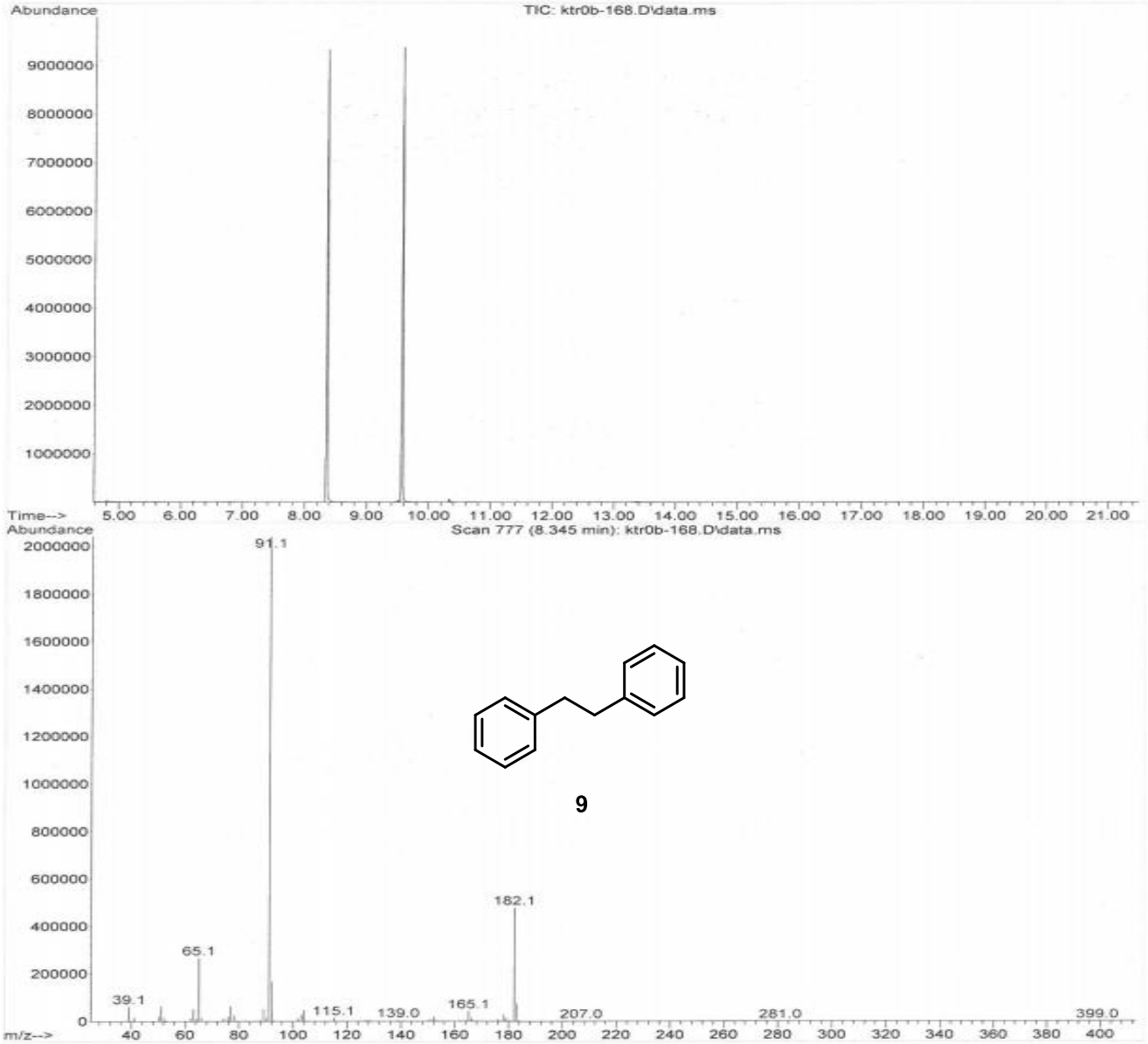

105.0700
9
+
Cl
10
intensity
m/z
149.0236
181.1011
195.1169
193.1014
209.1328
107.0492
229.0782
125.0153
293.1750
139.0310
103.0544
197.0962
215.0625
227.0626
117.0700
166.0778
179.0856
141.0103
275.1645
375.2112
243.0938
258.1047
317.1096
127.0124
158.0272
182.1046
194.1047
210.1361

GC-data **9** and **10**, LiO*t*Bu used as base

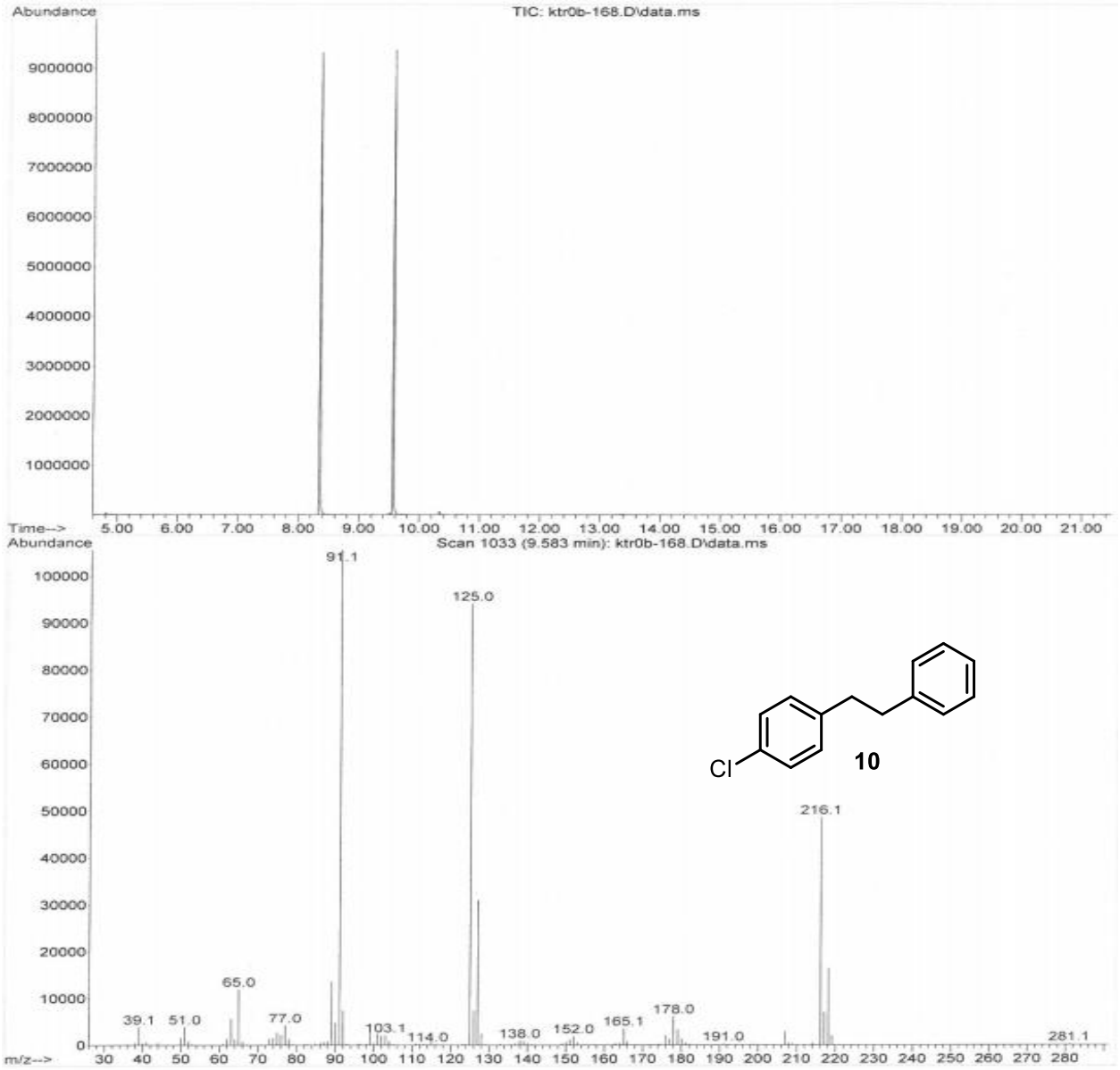


Peak results :

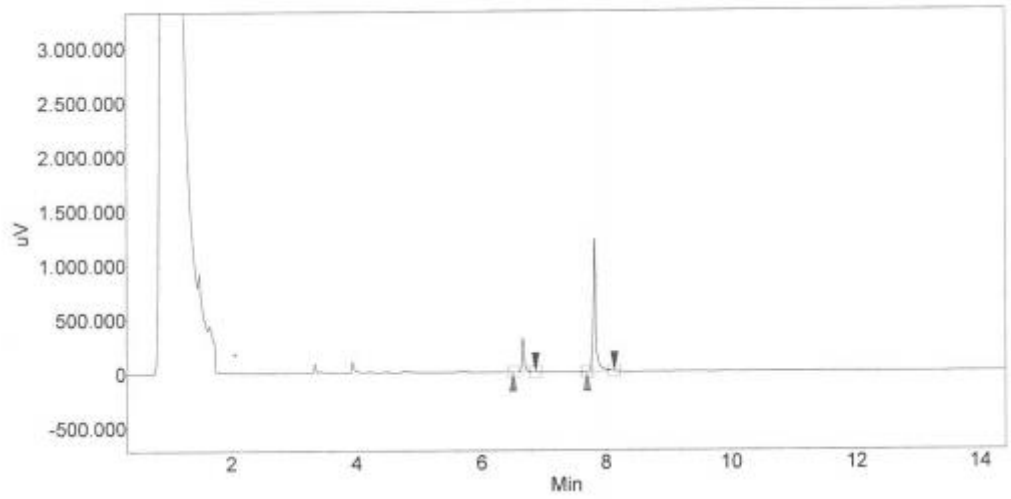
Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	6.64	65.85	598482.5	25558.0	65.847
2	UNKNOWN	7.88	34.15	197220.8	13256.3	34.153
Total			100.00	795703.3	38814.3	100.000


Abundance
TIC: ktr0b-168.D\data.ms
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 777 (8.345 min): ktr0b-168.D\data.ms
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
91.1
182.1
65.1
39.1
115.1
139.0
165.1
207.0
281.0
399.0
m/z-->
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400

9


Abundance
TIC: ktr0b-168.D\data.ms
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 1033 (9.583 min): ktr0b-168.D\data.ms
91.1
125.0
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
65.0
39.1
51.0
77.0
103.1
114.0
138.0
152.0
165.1
178.0
191.0
216.1
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
Cl
10

GC-data **9** and **10** NaO*t*Bu used as base

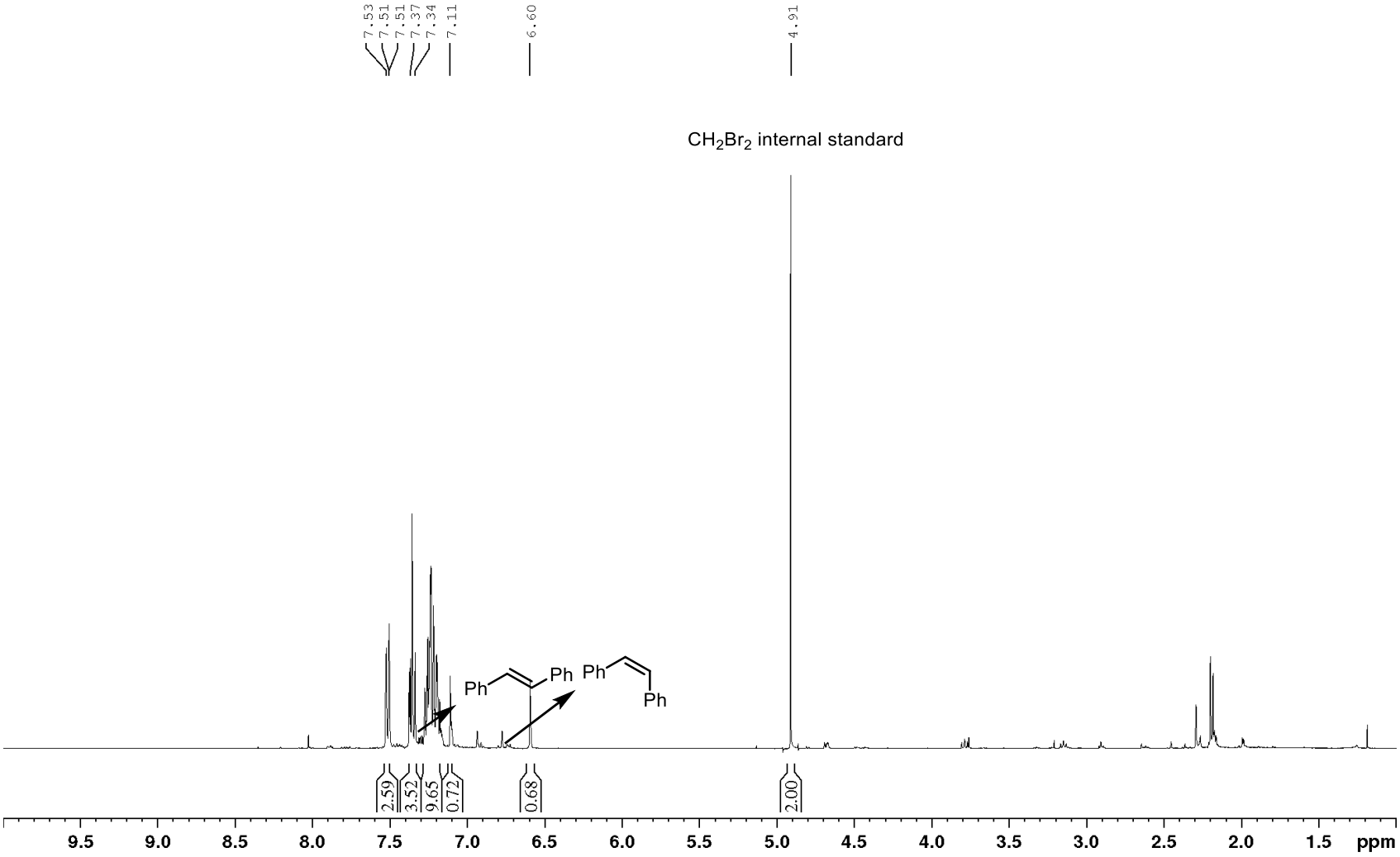


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	6.67	19.62	312268.7	13961.4	19.620
2	UNKNOWN	7.83	80.38	1230373.1	57197.8	80.380
Total			100.00	1542641.8	71159.2	100.000

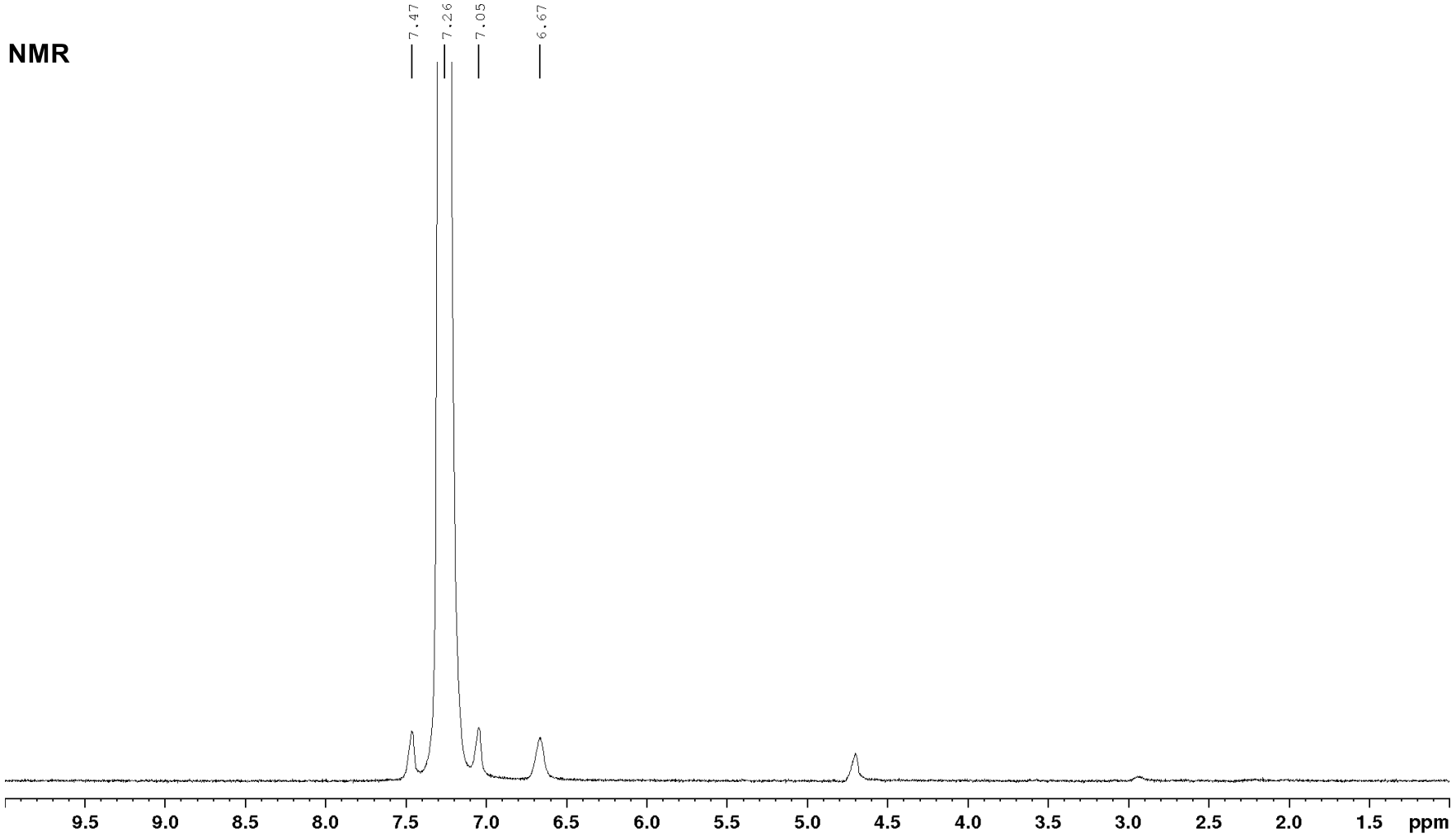
^{1}H NMR

Deuteration experiment with $BnOH\text{-}D_2$ (**2**-*d_2*)


7.53
7.51
7.51
7.37
7.34
7.11
6.60
4.91
CH2Br2 internal standard
Ph
Ph
Ph
Ph
2.59
3.52
9.65
0.72
0.68
2.00
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

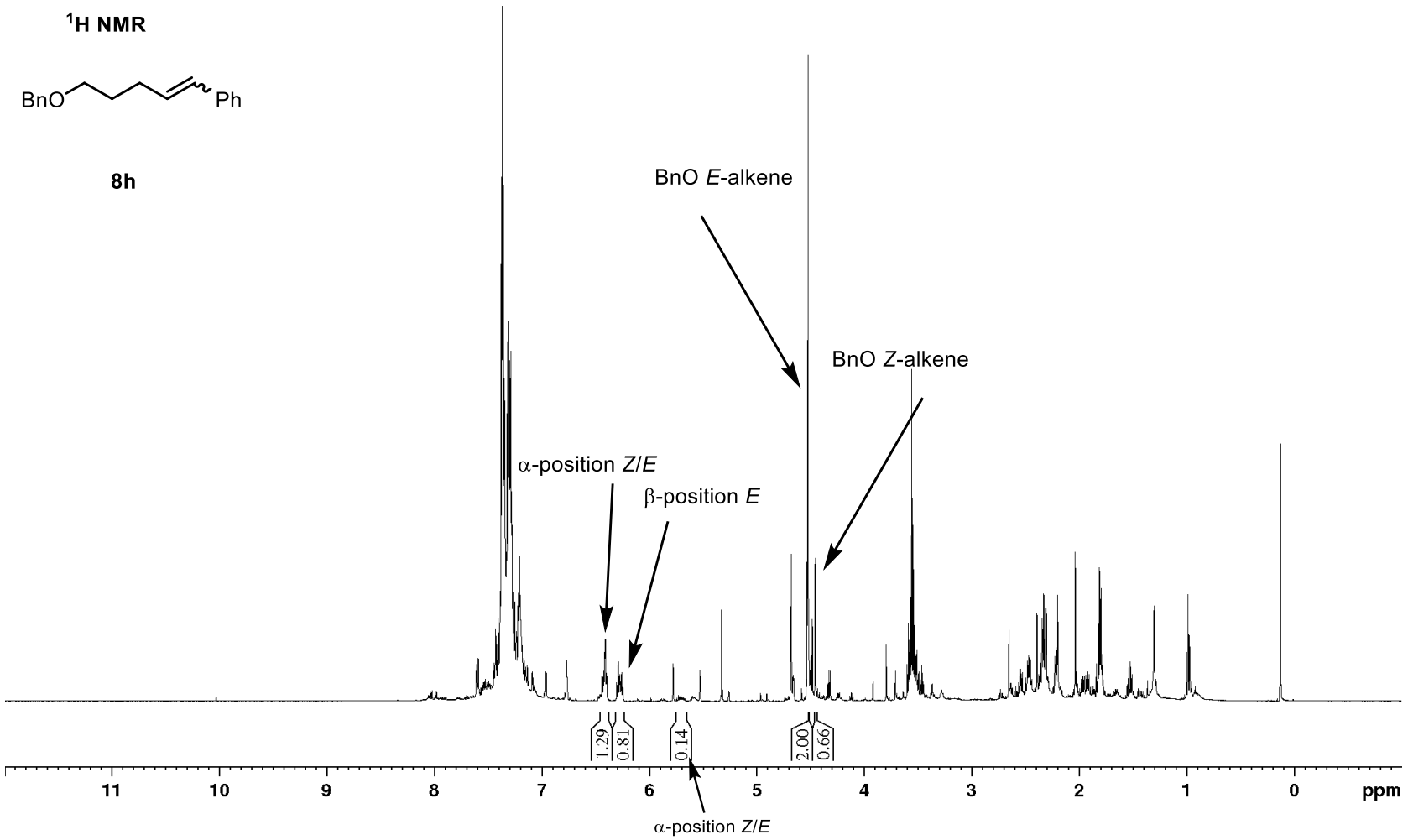
Deuteration experiment with $BnOH\text{-}D_2$ (**2**-*d_2*)

^{2}H NMR

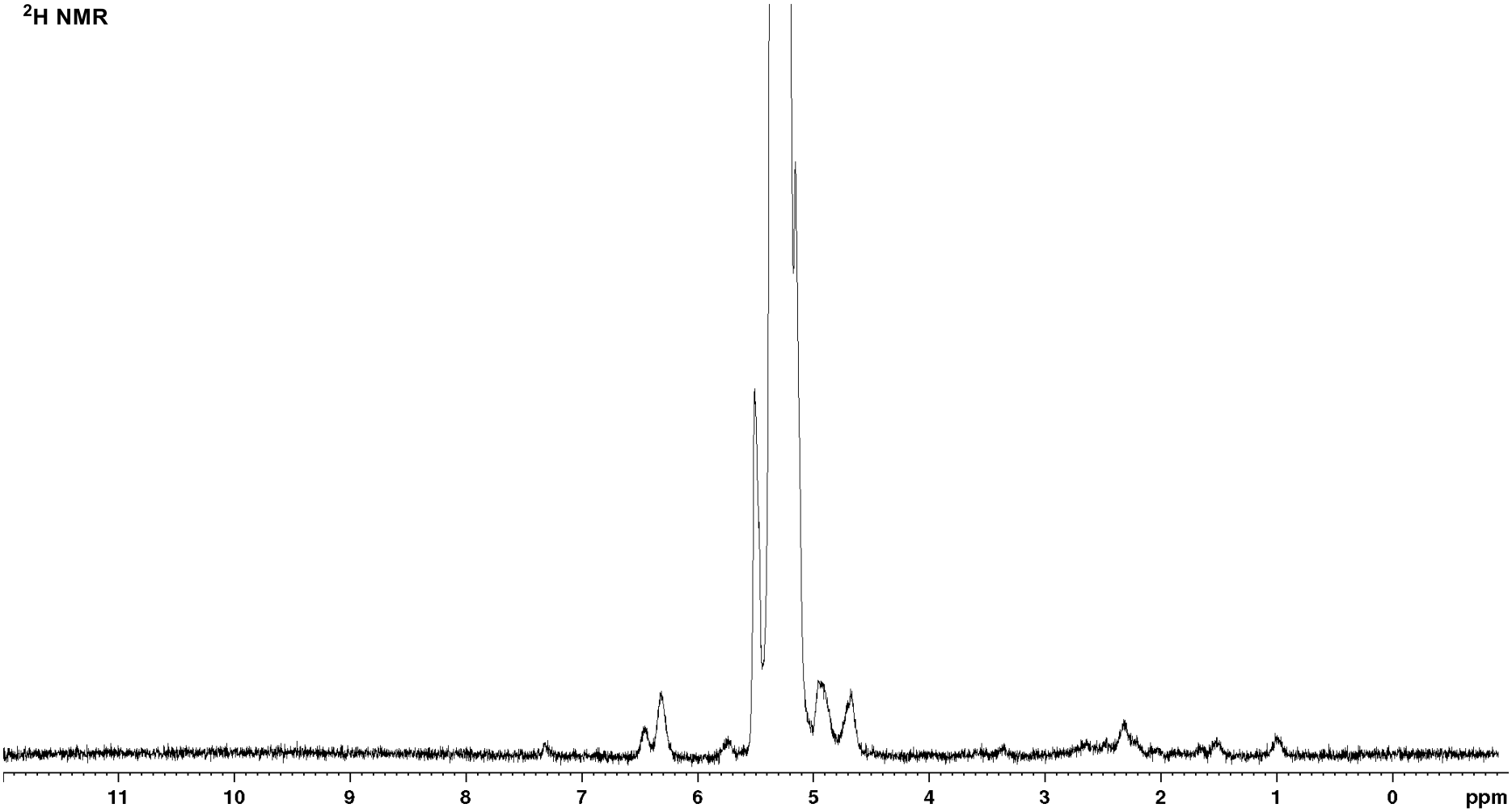


Extended deuteration experiments with BnOH-D_2 (**2**-d_2) and isomerization studies

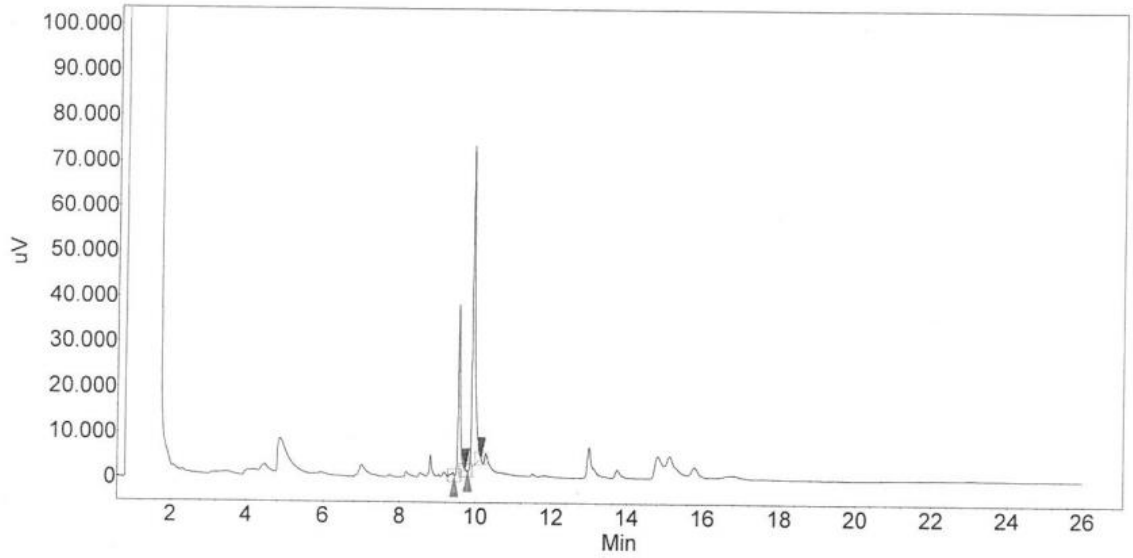
A: microwave heating


1H NMR
BnO
Ph
8h
BnO E-alkene
BnO Z-alkene
α-position Z/E
β-position E
1.29
0.81
0.14
2.00
0.66
11
10
9
8
7
6
5
4
3
2
1
0
ppm
α-position Z/E

^{2}H NMR



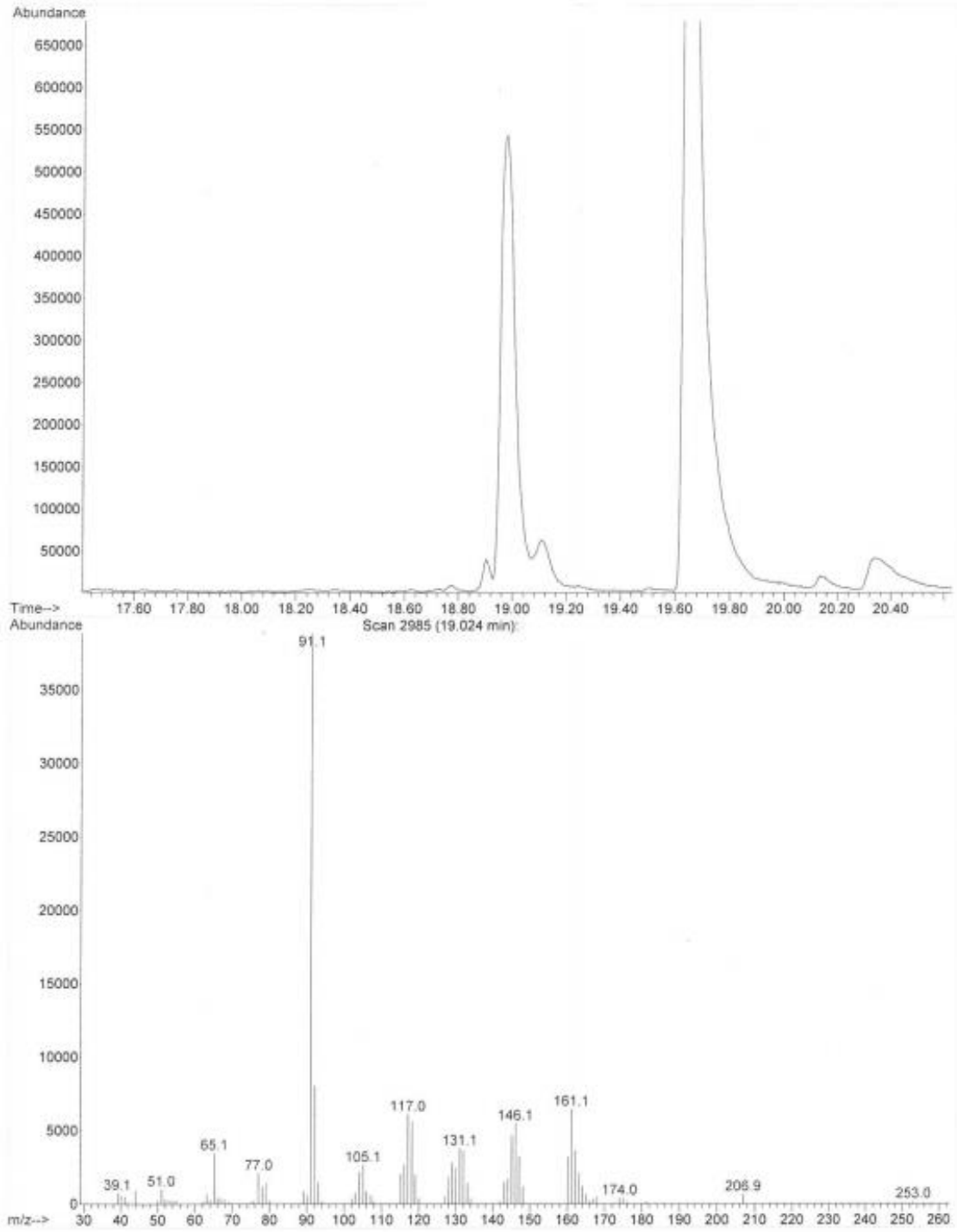
GC data

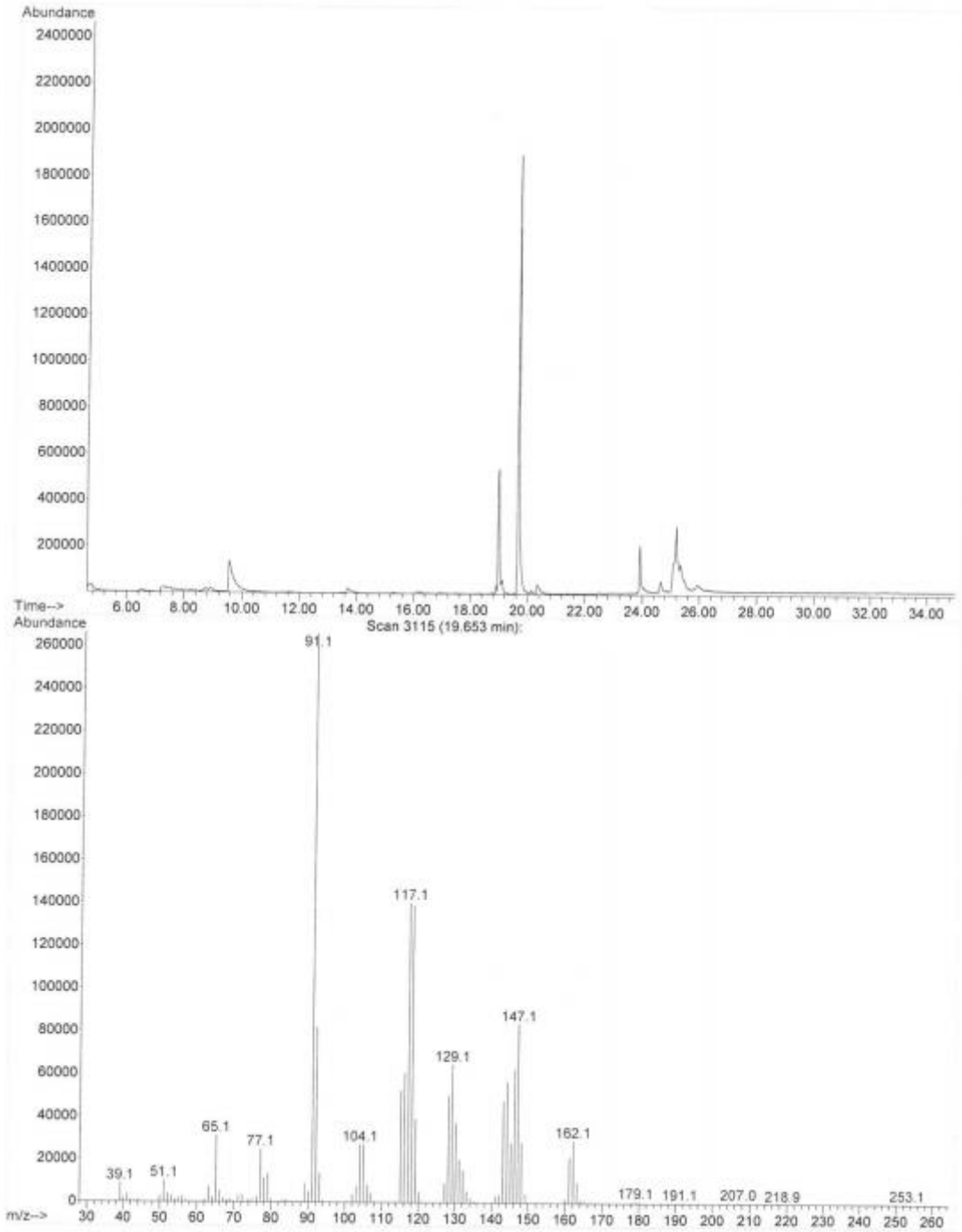


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	9.55	29.78	37404.1	2344.5	29.783
2	UNKNOWN	9.90	70.22	71032.7	5527.4	70.217
Total			100.00	108436.8	7871.9	100.000

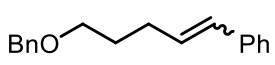
GC-MS data


Abundance
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
Time-->
17.60 17.80 18.00 18.20 18.40 18.60 18.80 19.00 19.20 19.40 19.60 19.80 20.00 20.20 20.40
Abundance
Scan 2985 (19.024 min)
91.1
35000
30000
25000
20000
15000
10000
5000
0
117.0
146.1
161.1
131.1
65.1
77.0
105.1
39.1
51.0
174.0
206.9
253.0
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

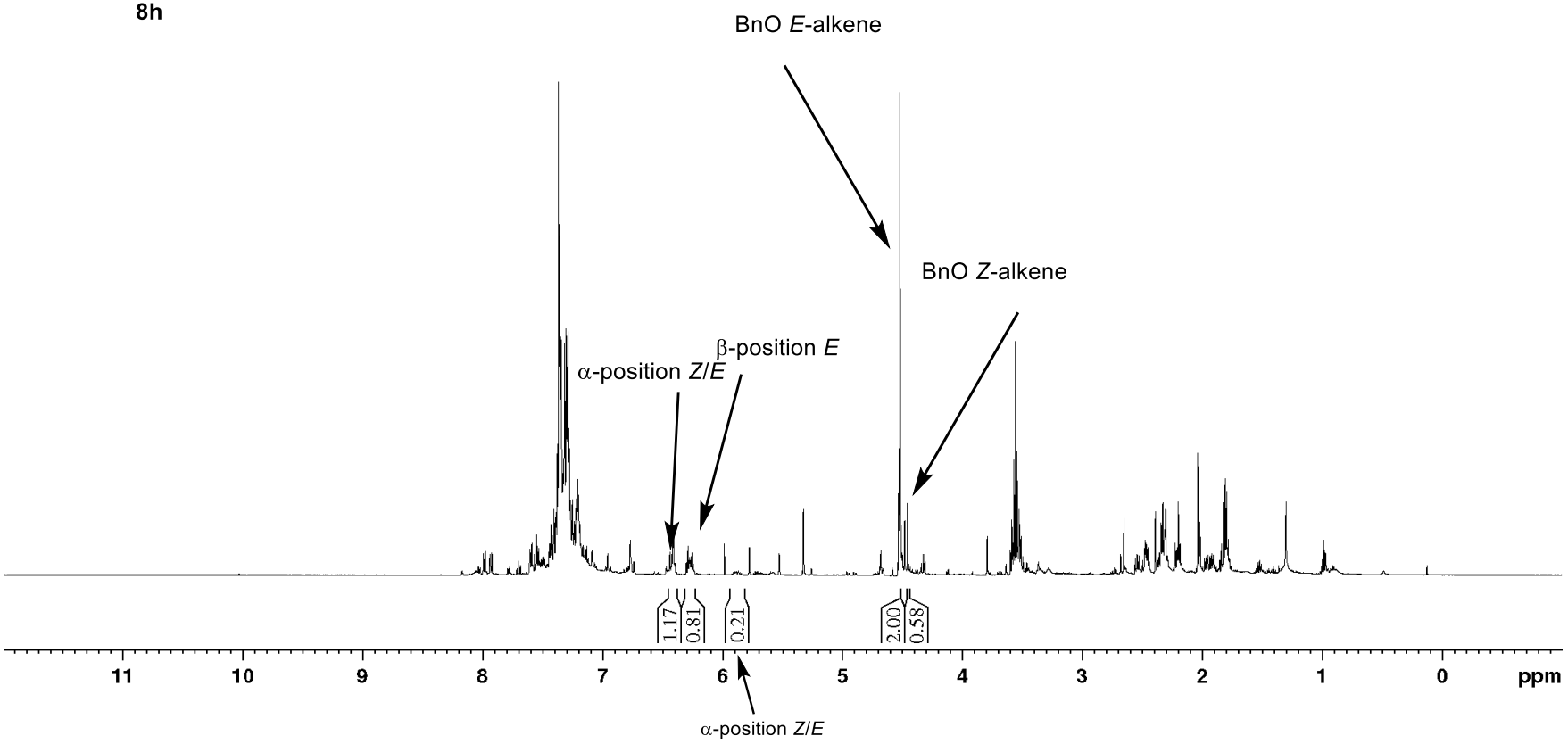

Abundance
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
Abundance
Scan 3115 (19.653 min):
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
91.1
117.1
147.1
129.1
65.1
77.1
104.1
162.1
39.1
51.1
179.1
191.1
207.0
218.9
253.1
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

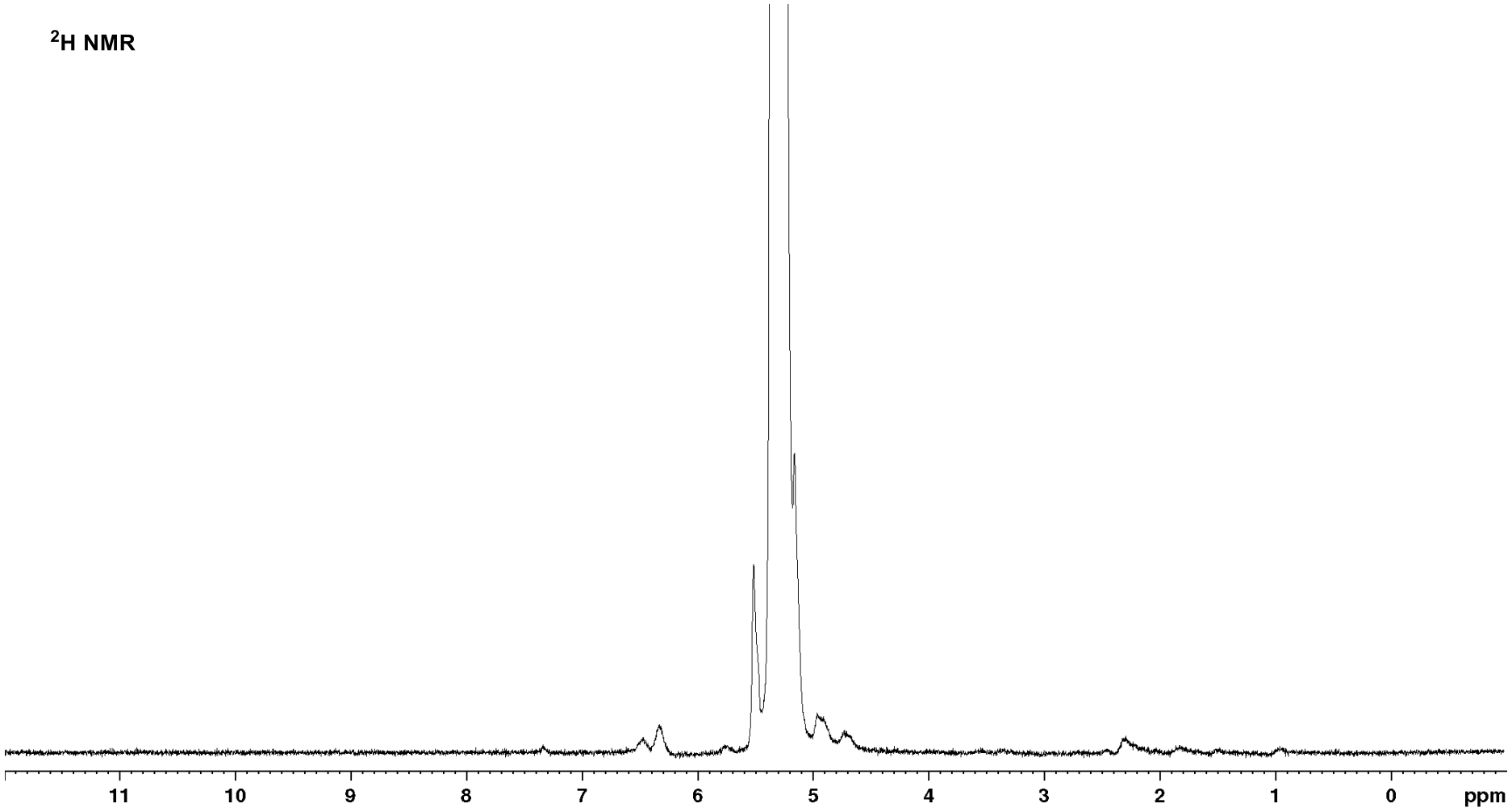
B: coventional heating

^{1}H NMR

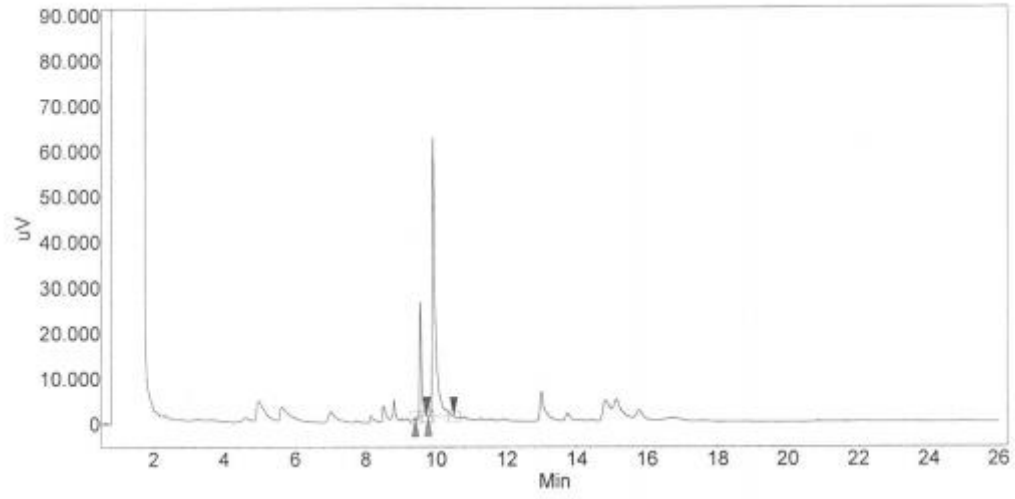


8h




^{2}H NMR
11
10
9
8
7
6
5
4
3
2
1
0
ppm

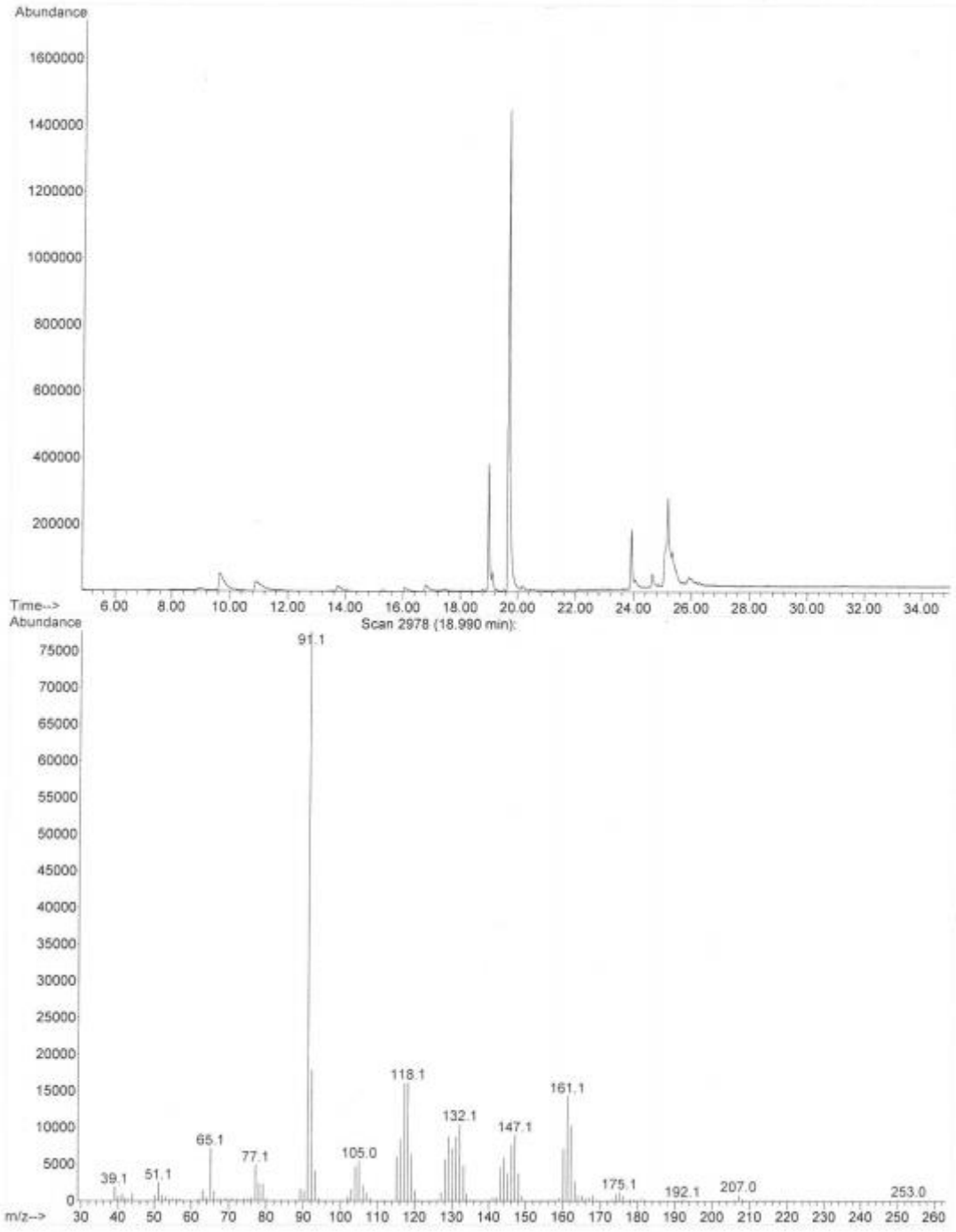
GC data

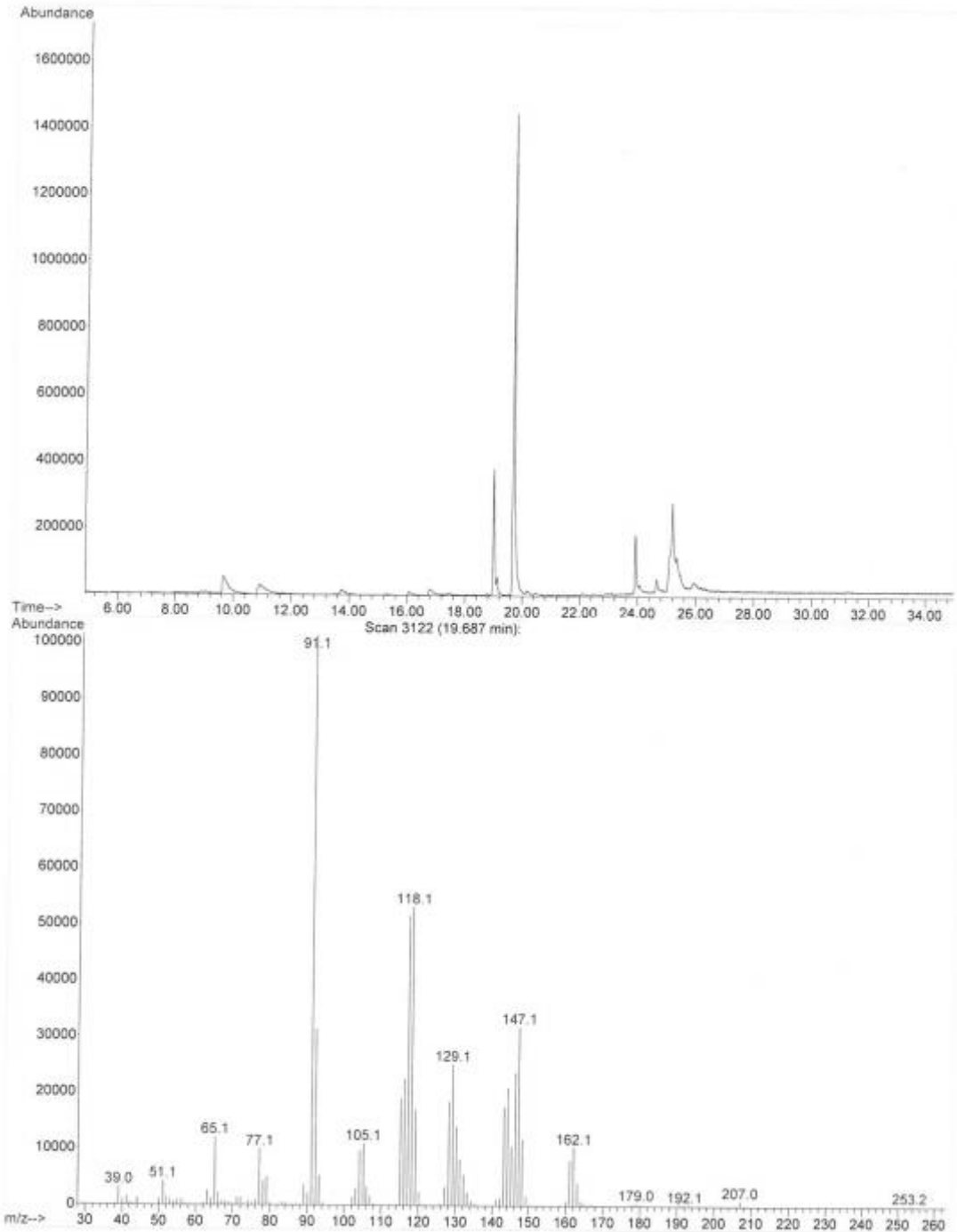


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	9.55	20.71	25232.4	1559.6	20.706
2	UNKNOWN	9.91	79.29	61376.8	5972.5	79.294
Total			100.00	86609.3	7532.1	100.000

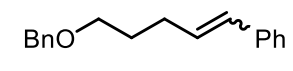
GCMS data


Abundance
1600000
1400000
1200000
1000000
800000
600000
400000
200000
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 2978 (18.990 min):
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
91.1
118.1
161.1
132.1
147.1
65.1
77.1
105.0
39.1
51.1
175.1
192.1
207.0
253.0
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


Abundance
1600000
1400000
1200000
1000000
800000
600000
400000
200000
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 3122 (19.687 min):
Abundance
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
91.1
118.1
147.1
129.1
65.1
77.1
105.1
162.1
39.0
51.1
179.0
192.1
207.0
253.2
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

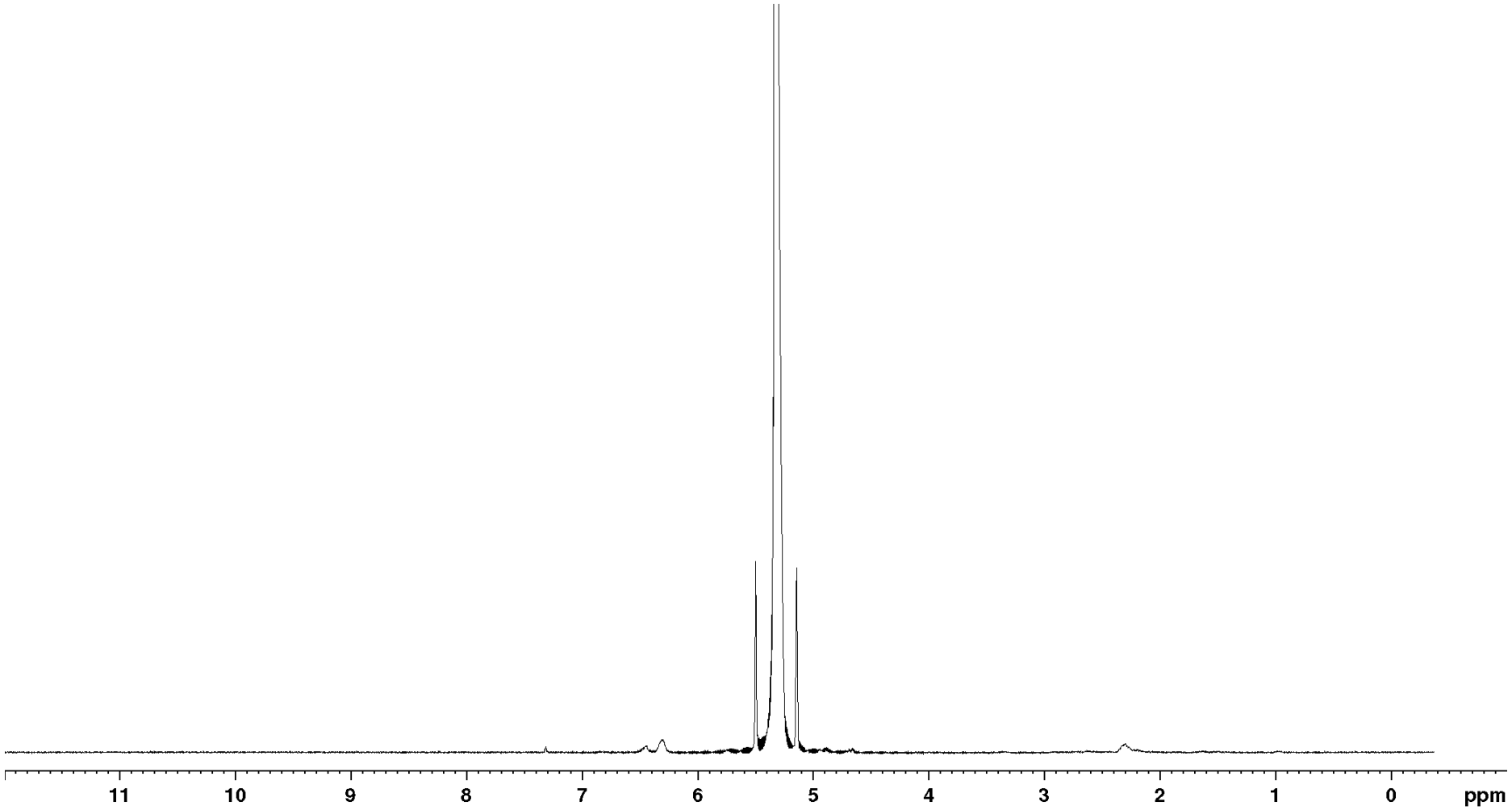
A: microwave heating after treating glaswear with D_2O

^{1}H NMR

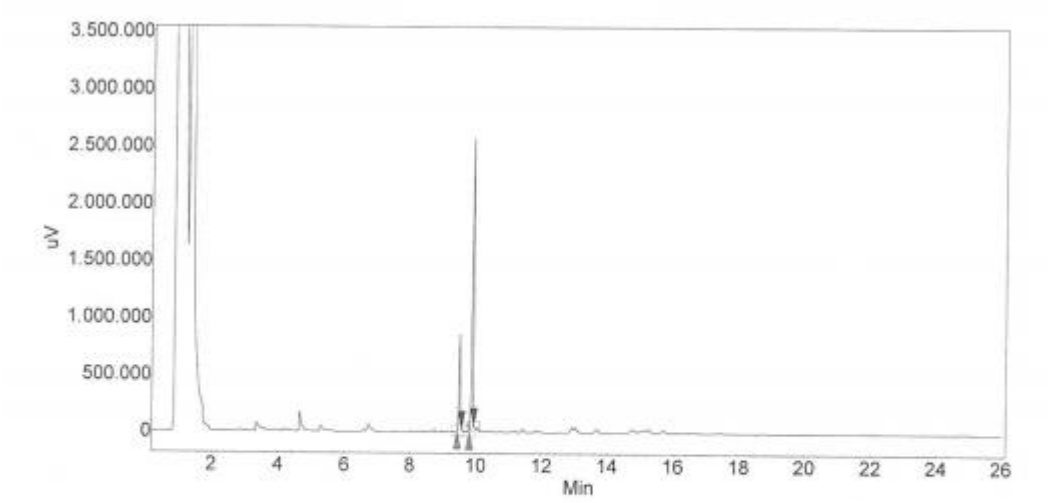


8h

^{2}H NMR



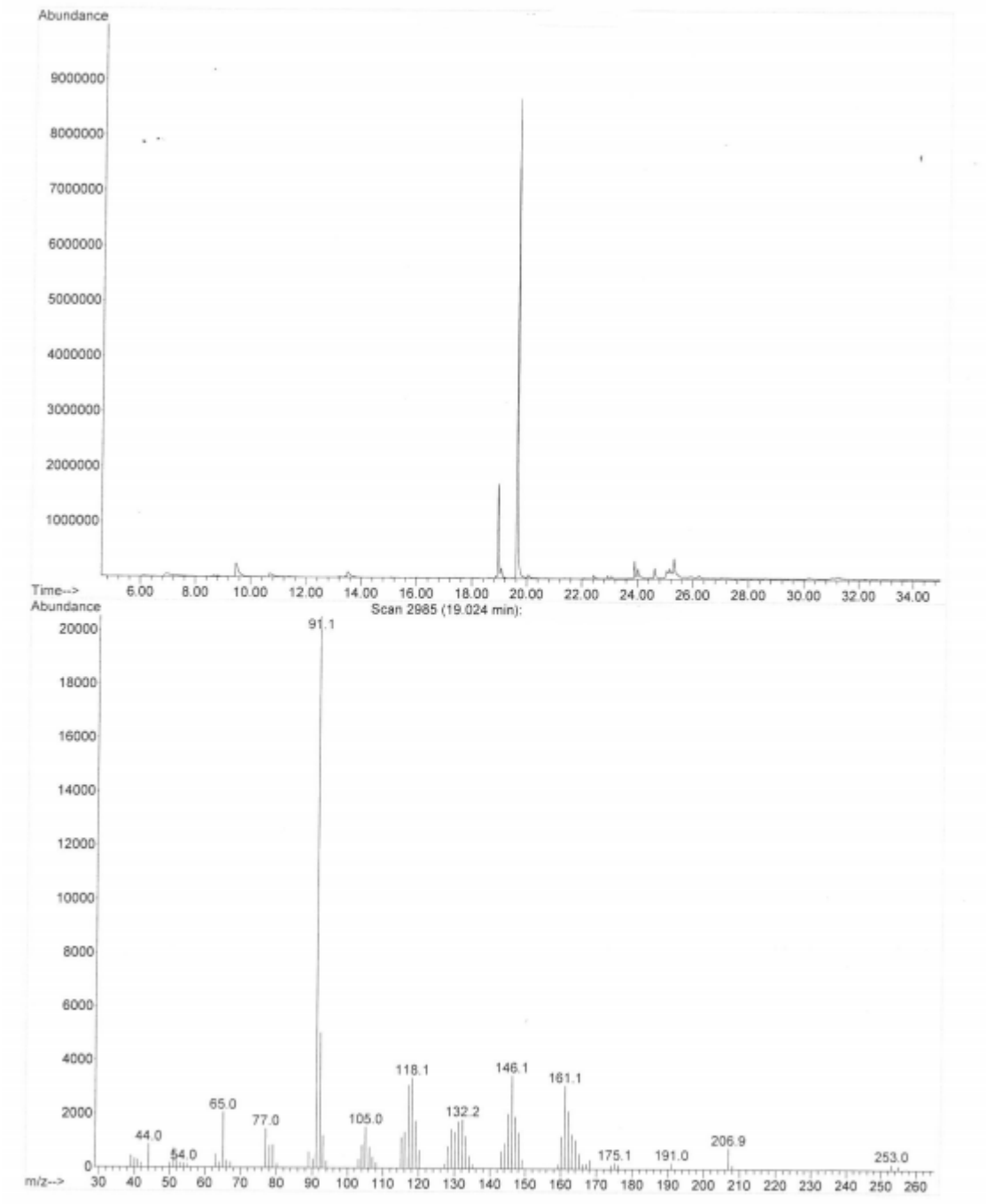
GC data

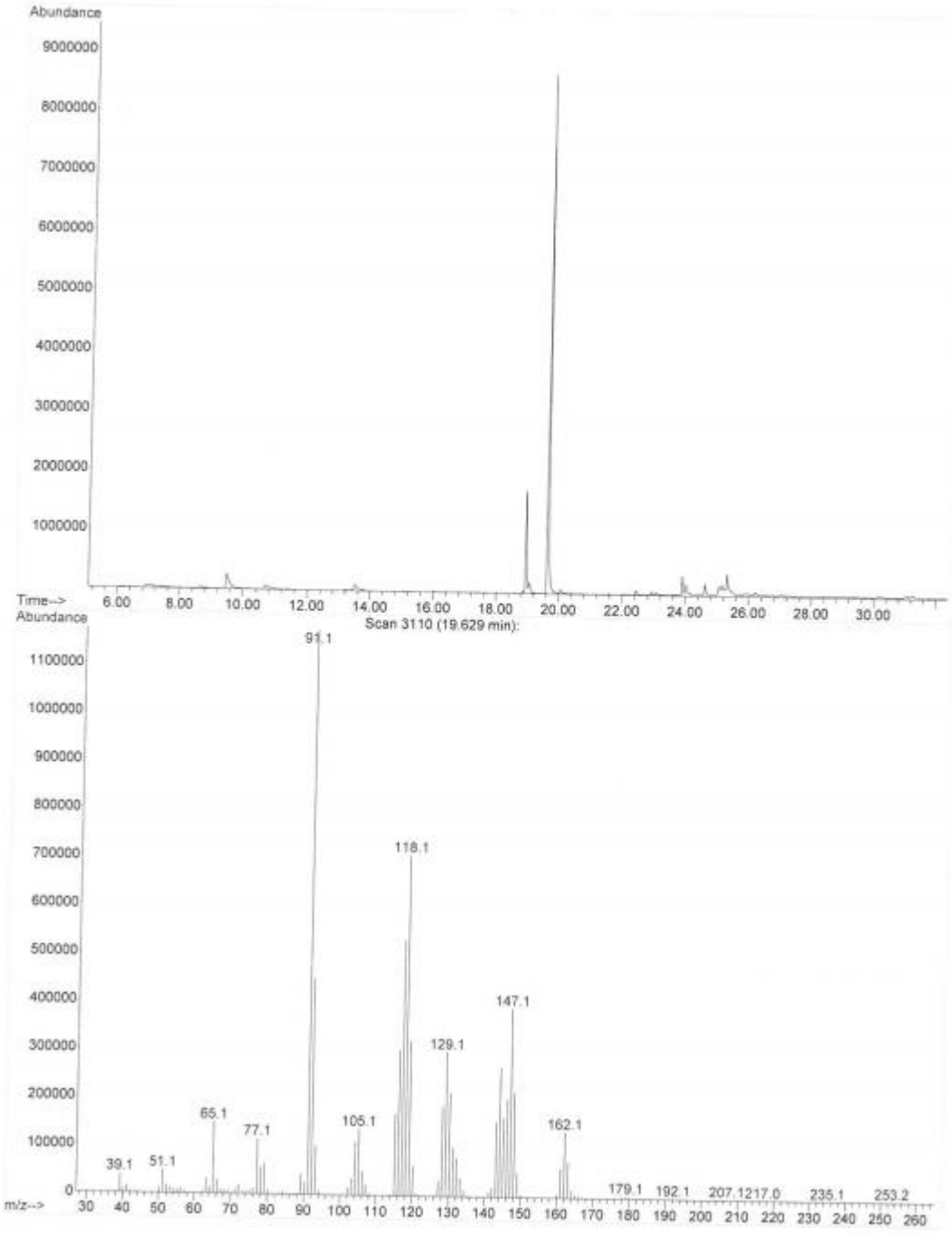


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	9.50	23.36	840292.5	35285.7	23.358
2	UNKNOWN	9.90	76.64	2535710.7	115780.7	76.642
Total			100.00	3376003.2	151066.3	100.000

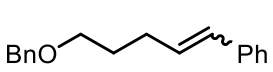
GC-MS data


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
Abundance
Scan 2985 (19.024 min):
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
m/z-->
91.1
118.1
146.1
161.1
65.0
77.0
105.0
132.2
44.0
54.0
175.1
191.0
206.9
253.0
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260

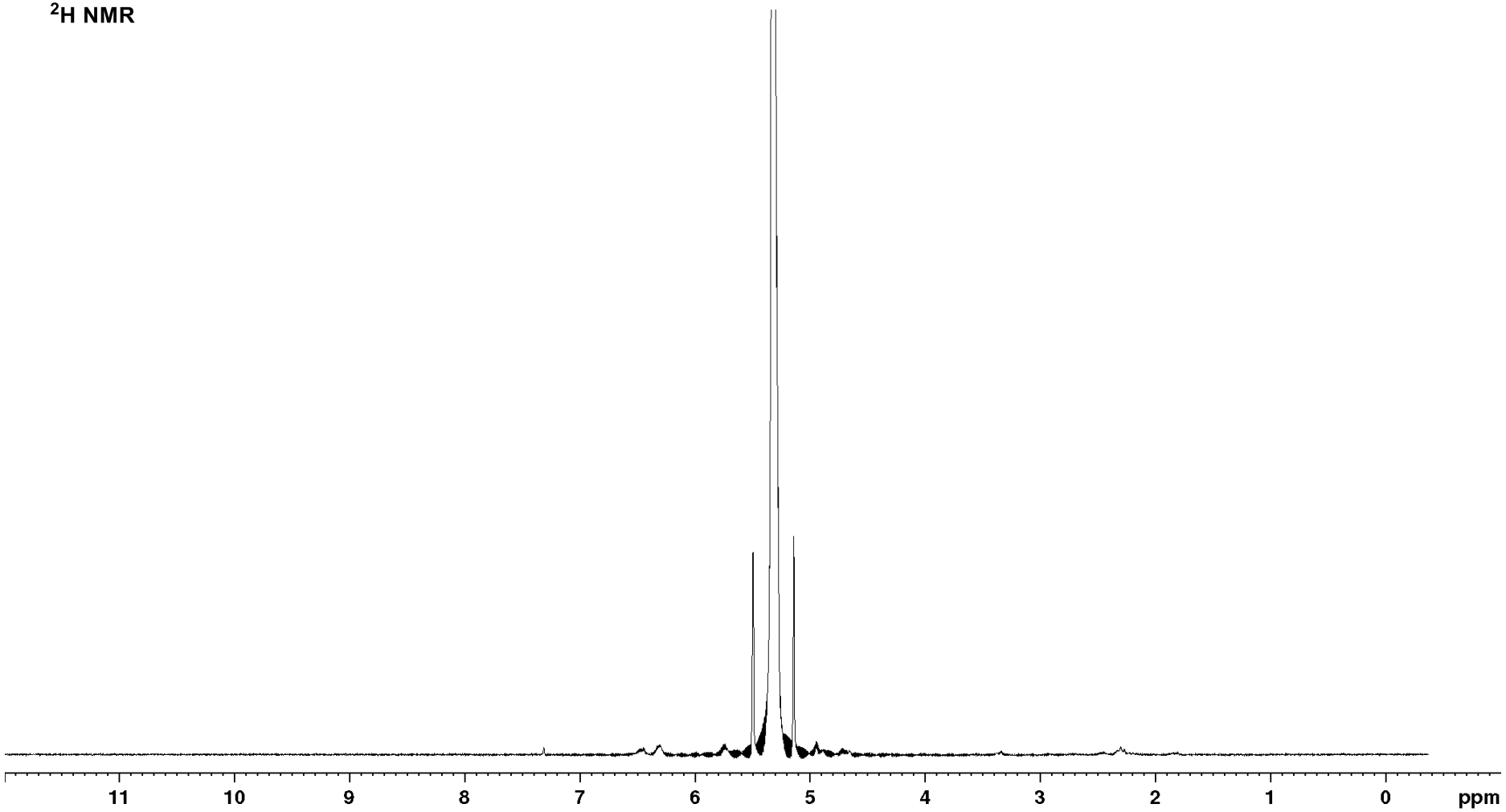

Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
22.00
24.00
26.00
28.00
30.00
Abundance
Scan 3110 (19.629 min):
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
m/z-->
91.1
118.1
147.1
129.1
65.1
77.1
105.1
162.1
39.1
51.1
179.1
192.1
207.1
217.0
235.1
253.2
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
260

B: coventional heating after treating glaswear with D_2O

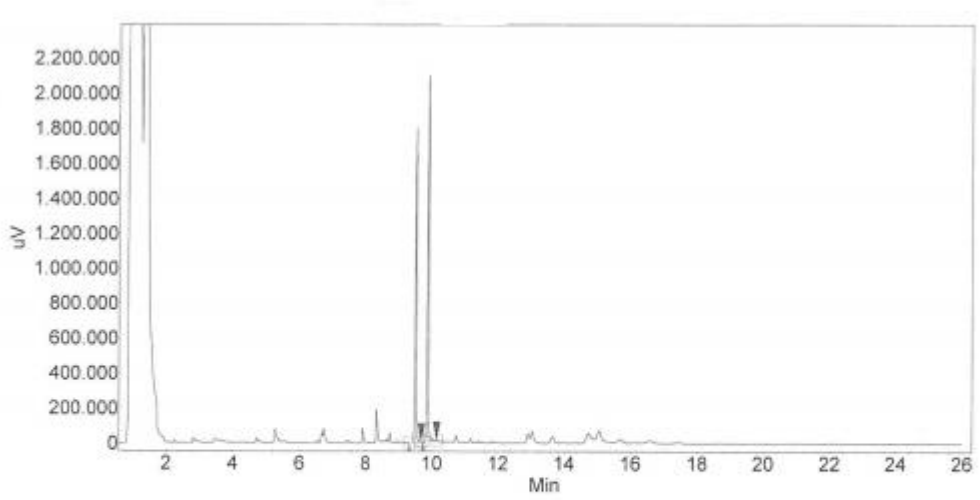
^{1}H NMR



8h


^{2}H NMR
11
10
9
8
7
6
5
4
3
2
1
0
ppm

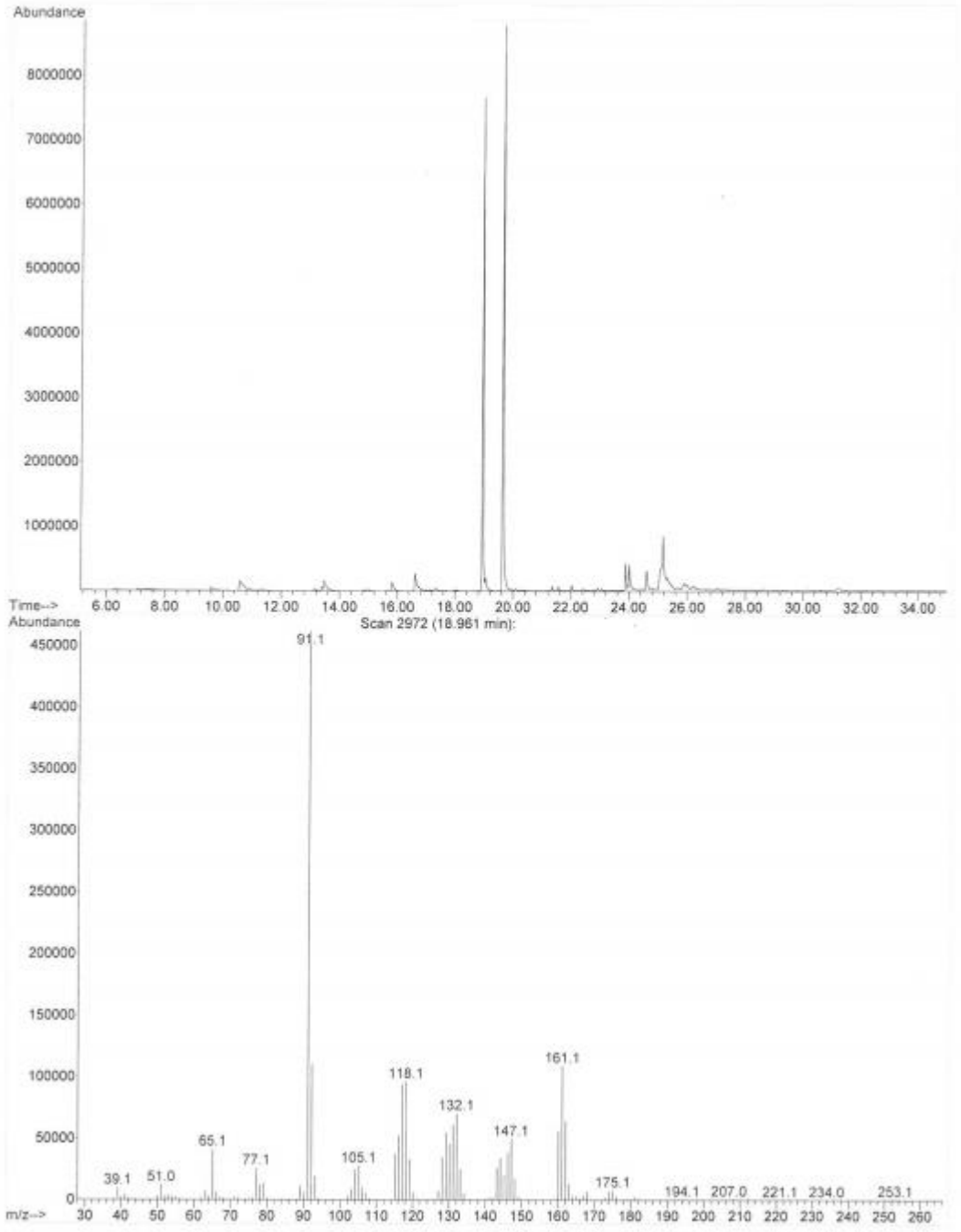
GC data

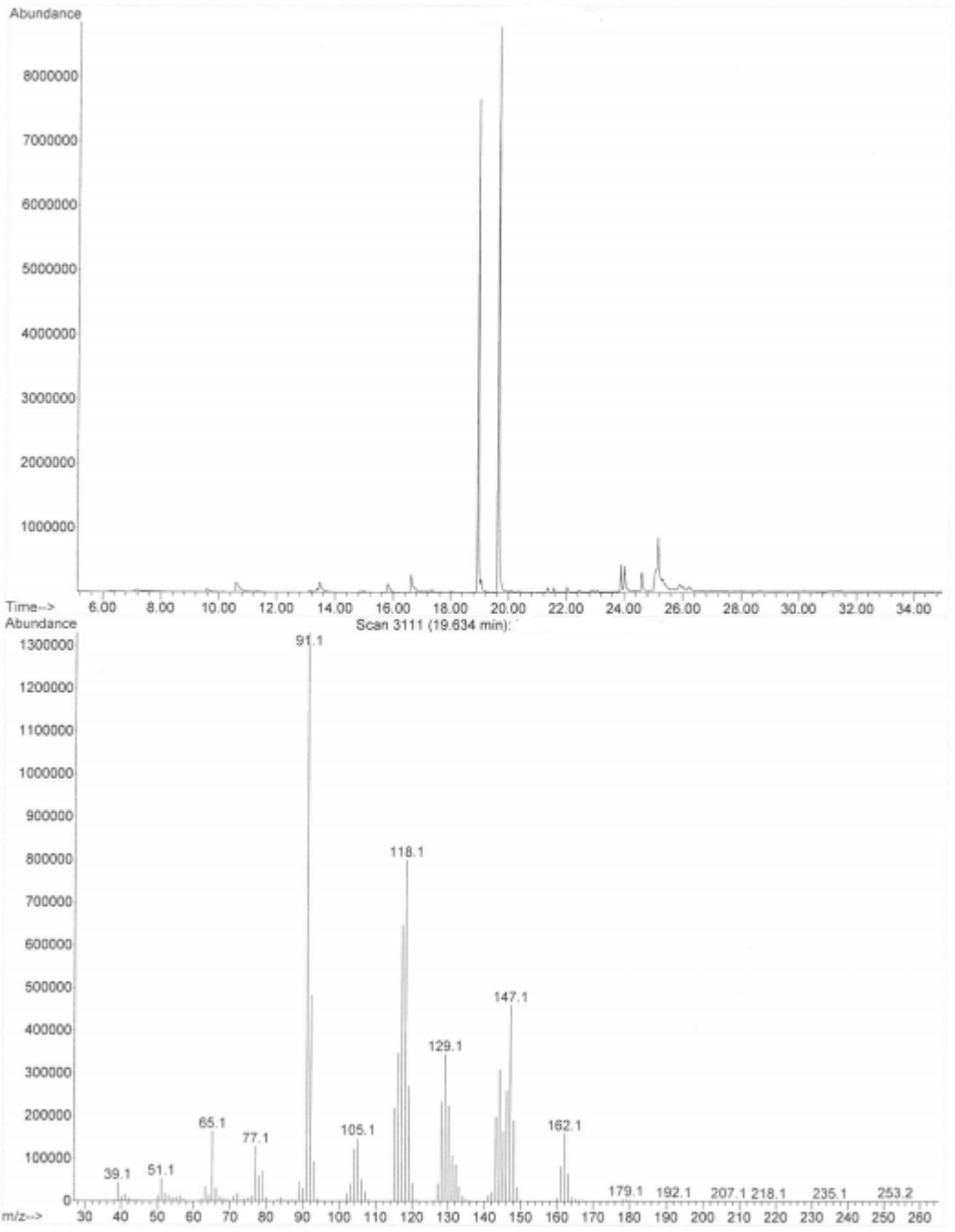


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	9.52	45.19	1796353.6	75185.4	45.190
2	UNKNOWN	9.89	54.81	2092034.3	91190.5	54.810
Total			100.00	3888387.8	166376.0	100.000

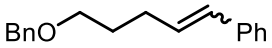
GCMS data


Abundance
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 2972 (18.981 min):
Abundance
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
91.1
118.1
132.1
161.1
147.1
65.1
77.1
105.1
39.1
51.0
175.1
194.1
207.0
221.1
234.0
253.1
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


Abundance
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
Abundance
Scan 3111 (19.634 min):
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
91.1
118.1
147.1
129.1
65.1
77.1
105.1
162.1
39.1
51.1
179.1
192.1
207.1
218.1
235.1
253.2
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

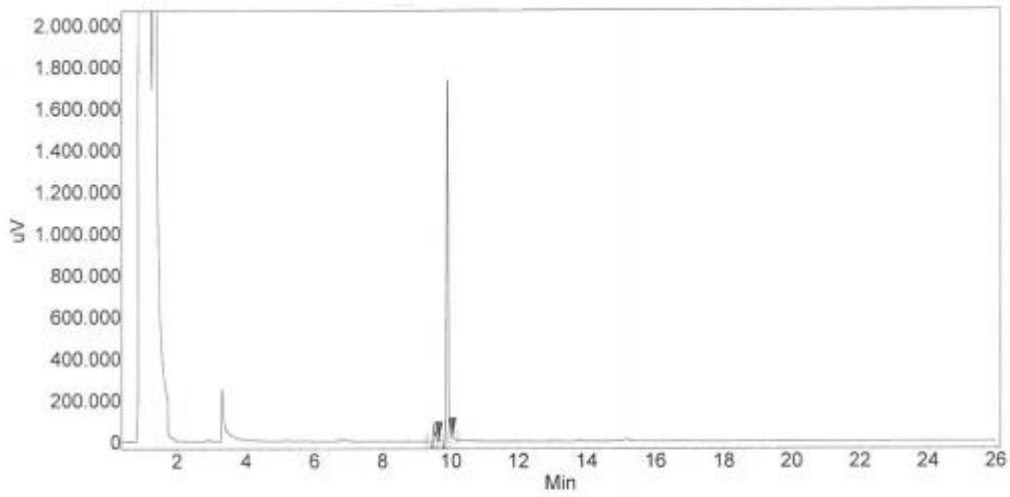
Microwave heating – isomerization experiments

30 min



8h

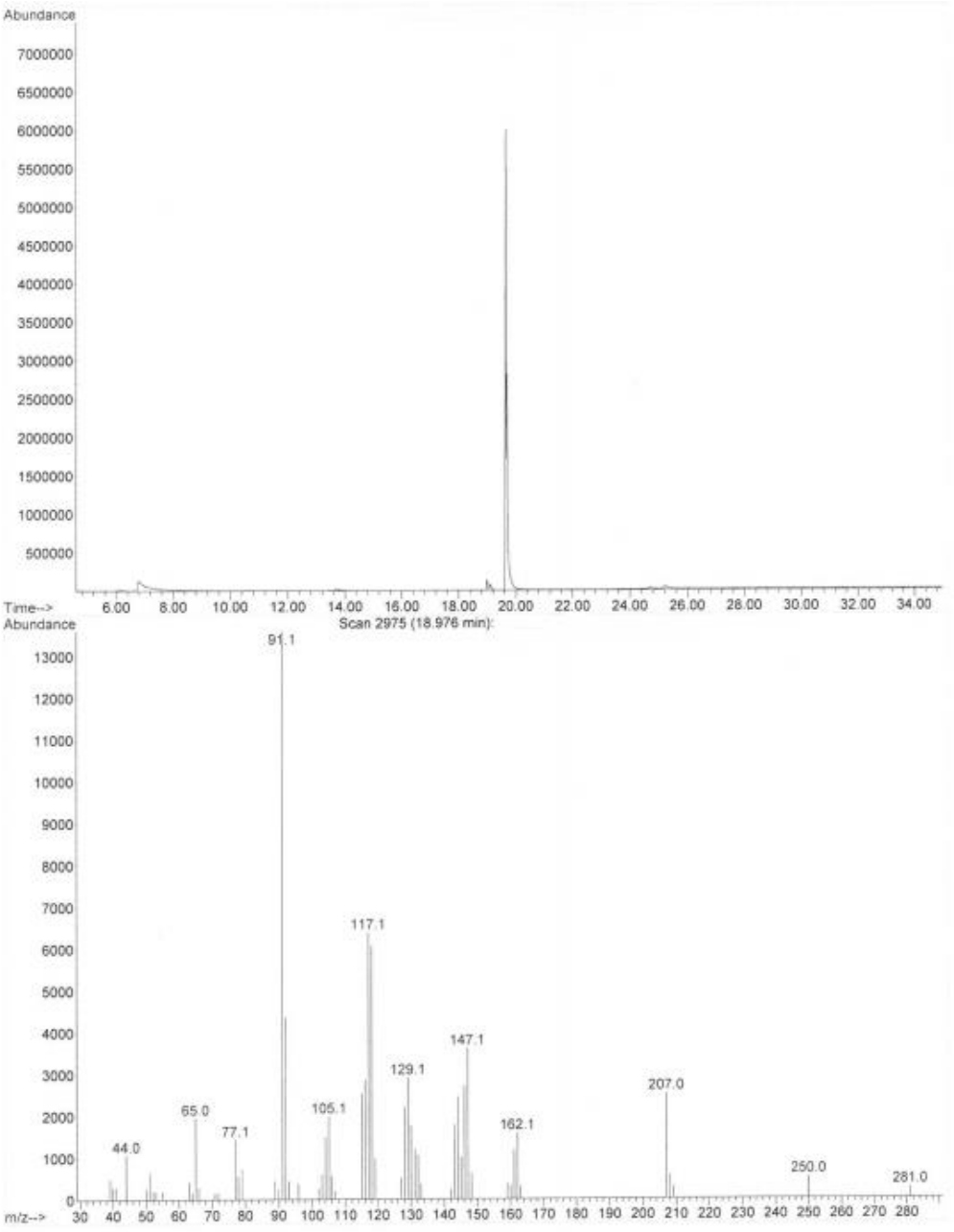
GC data

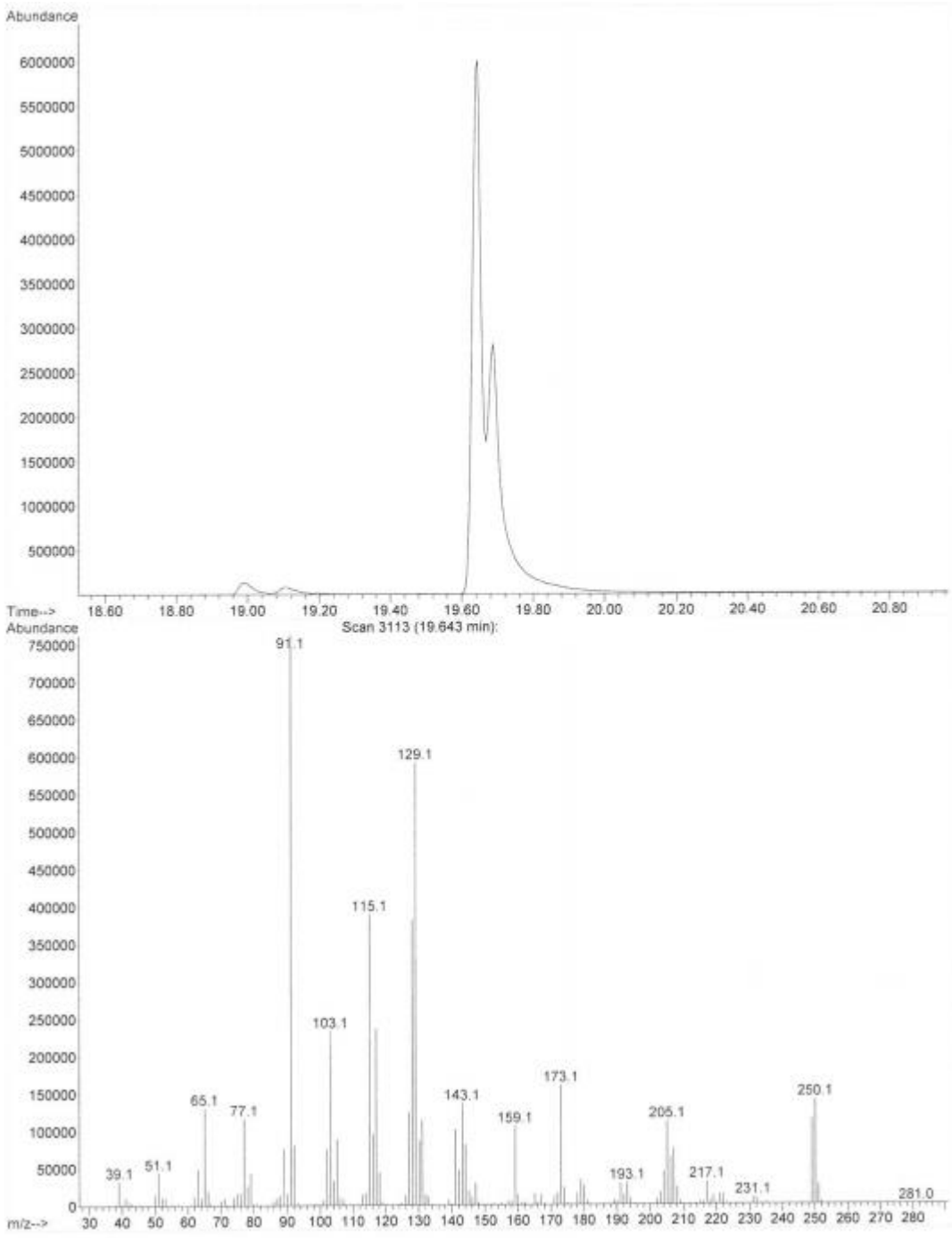


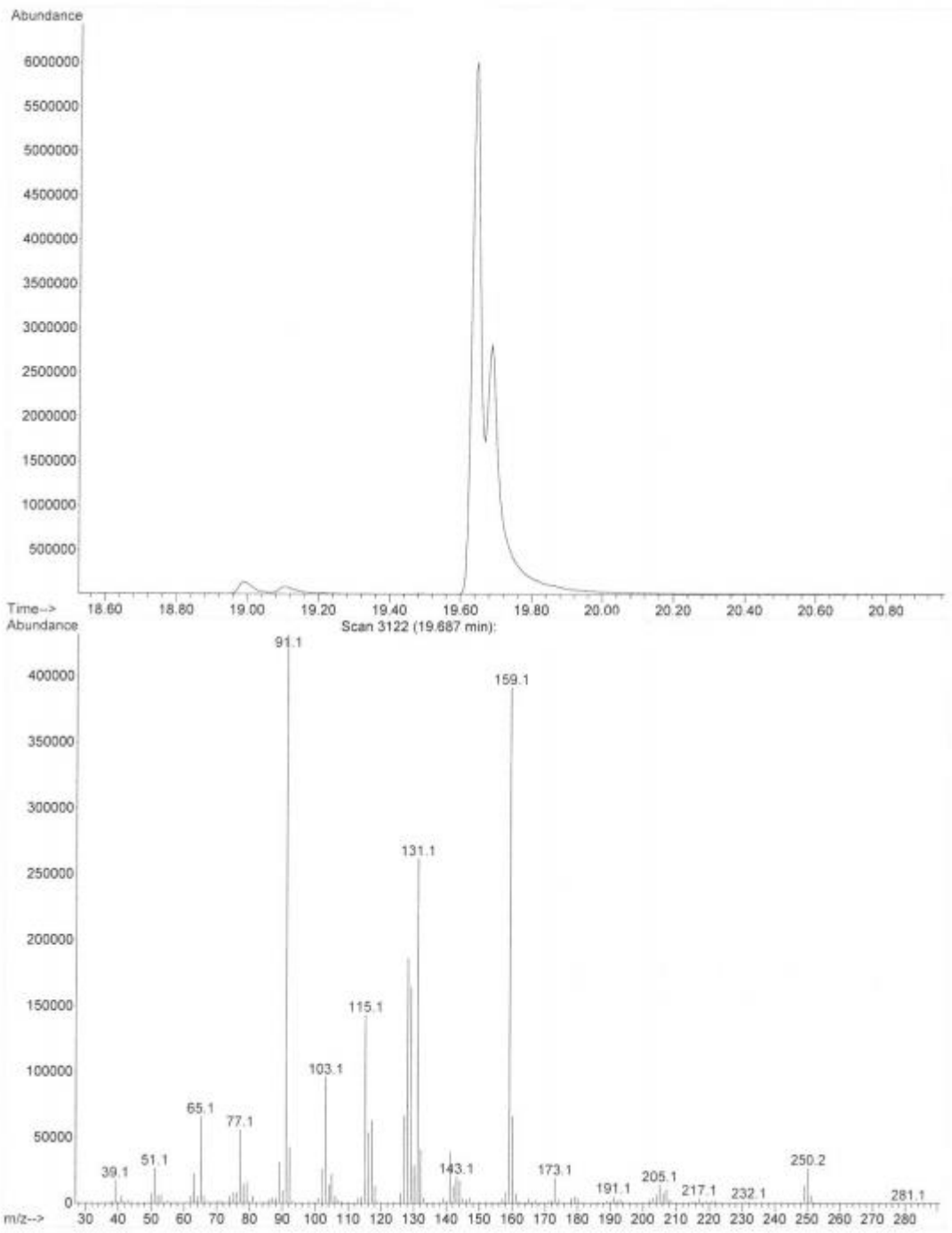
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	9,51	4,64	86051,5	4686,3	4,639
2	UNKNOWN	9,90	95,36	1723946,2	96327,2	95,361
Total			100,00	1809997,6	101013,4	100,000

GCMS data

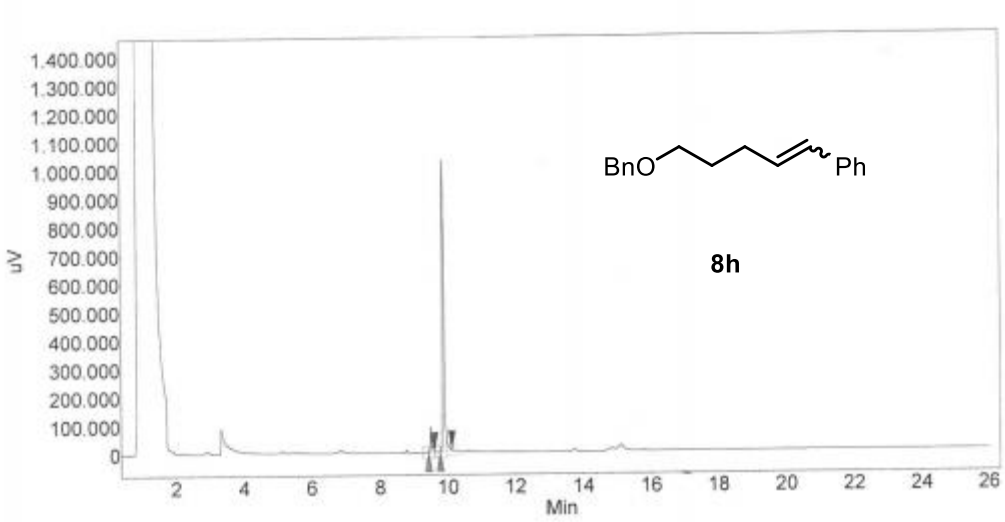

Abundance
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
Scan 2975 (18.976 min):
Abundance
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
91.1
117.1
147.1
129.1
207.0
65.0
105.1
77.1
162.1
44.0
250.0
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


Abundance
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
Time-->
18.60
18.80
19.00
19.20
19.40
19.60
19.80
20.00
20.20
20.40
20.60
20.80
Scan 3113 (19.643 min):
Abundance
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
m/z-->
91.1
129.1
115.1
103.1
65.1
77.1
143.1
159.1
173.1
205.1
250.1
39.1
51.1
193.1
217.1
231.1
281.0
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


Abundance
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
Time-->
18.60
18.80
19.00
19.20
19.40
19.60
19.80
20.00
20.20
20.40
20.60
20.80
Abundance
Scan 3122 (19.687 min):
91.1
159.1
131.1
115.1
103.1
65.1
77.1
51.1
39.1
143.1
173.1
191.1
205.1
217.1
232.1
250.2
281.1
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

90 min

GC data

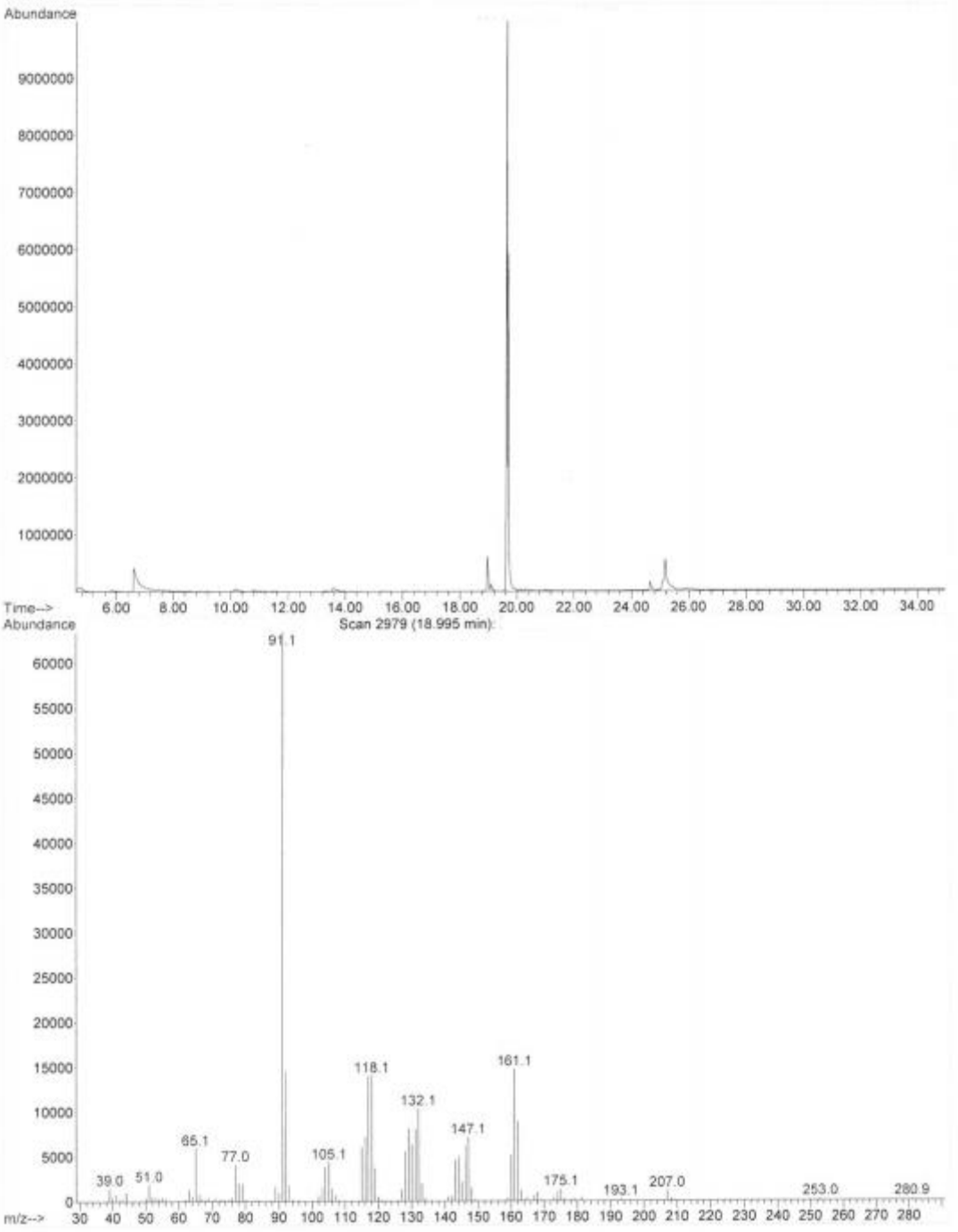


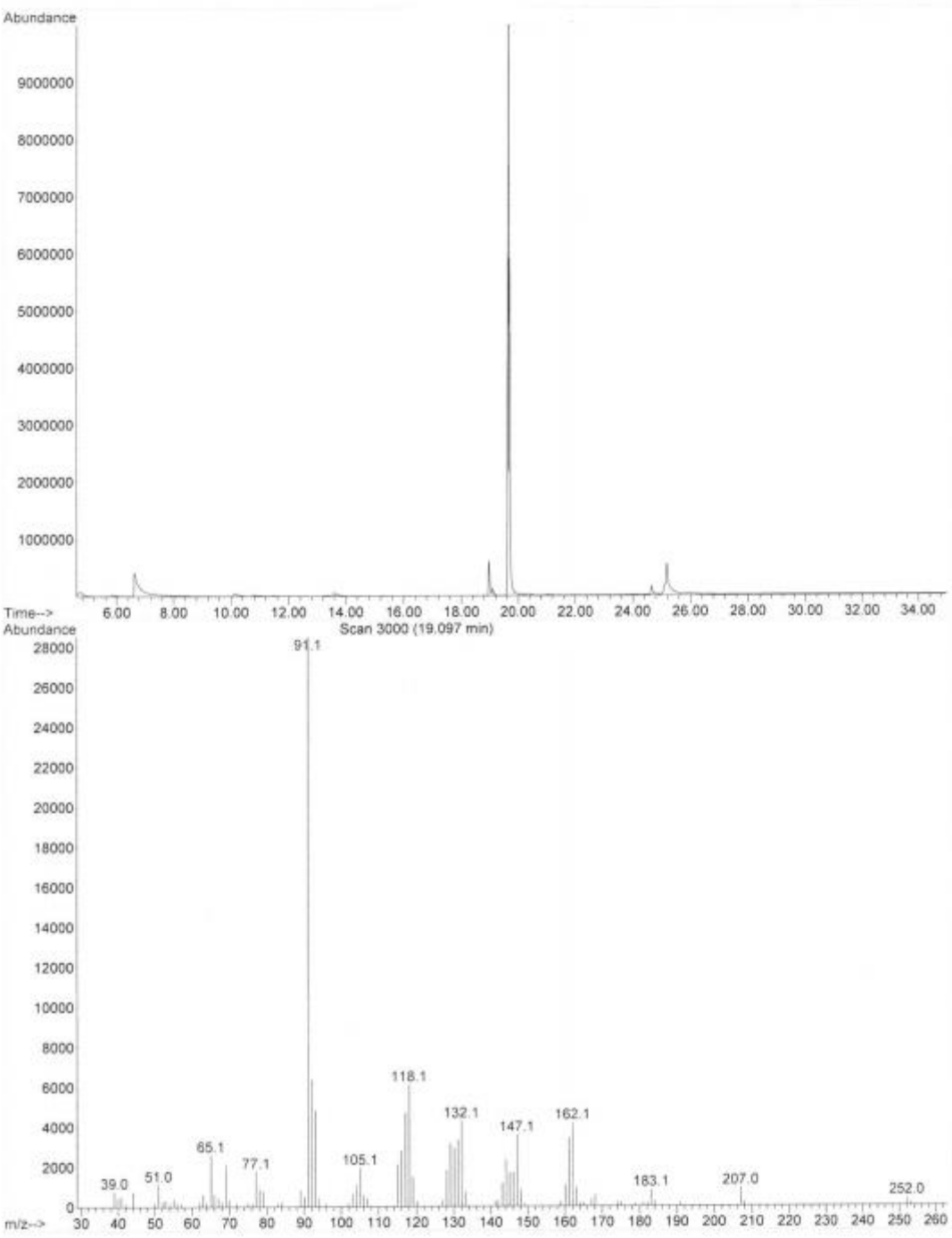
8h

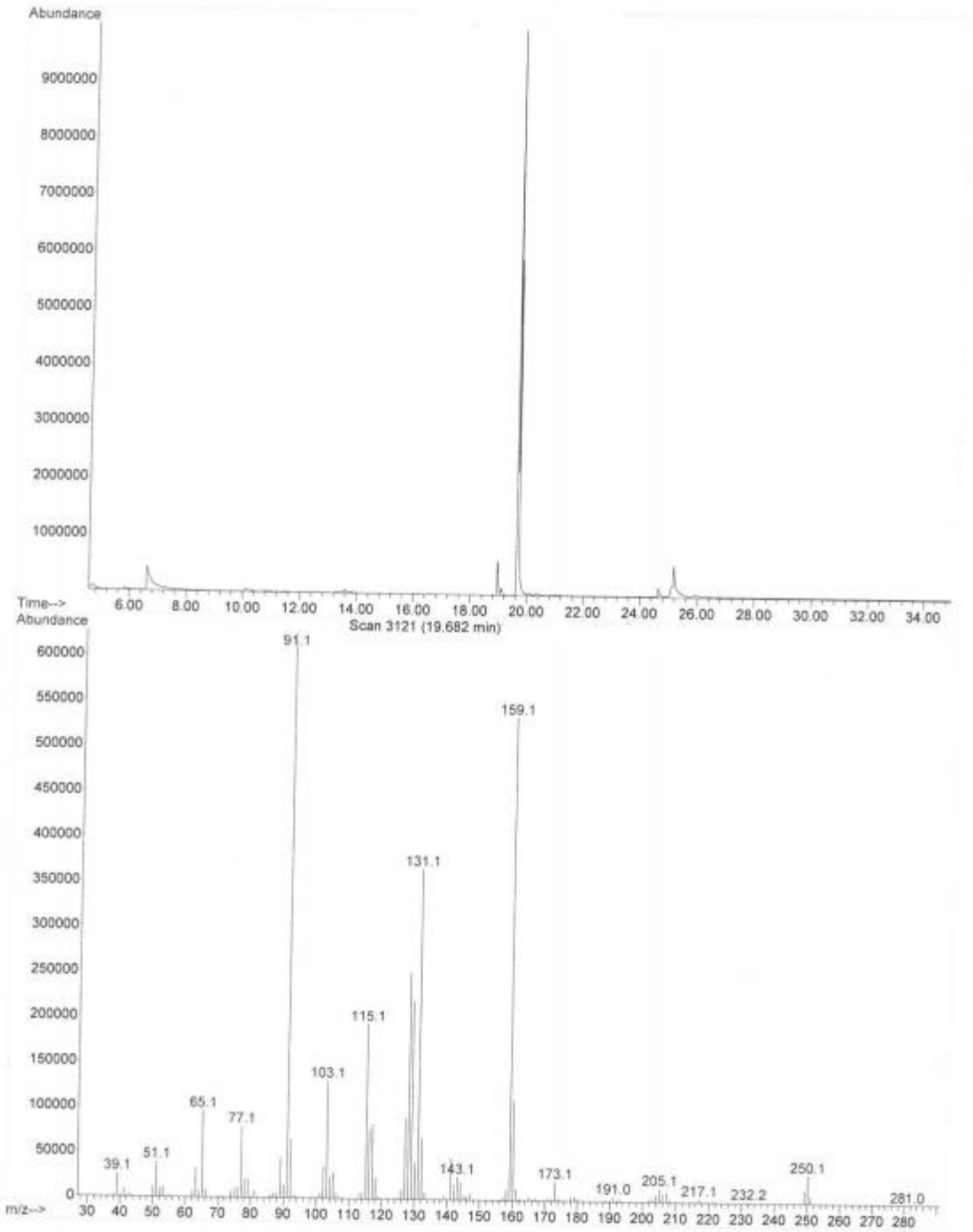
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	9.50	6.50	90660.7	3968.1	6.501
2	UNKNOWN	9.88	93.50	1027116.8	57067.3	93.499
Total			100.00	1117777.5	61035.4	100.000

GCMS data

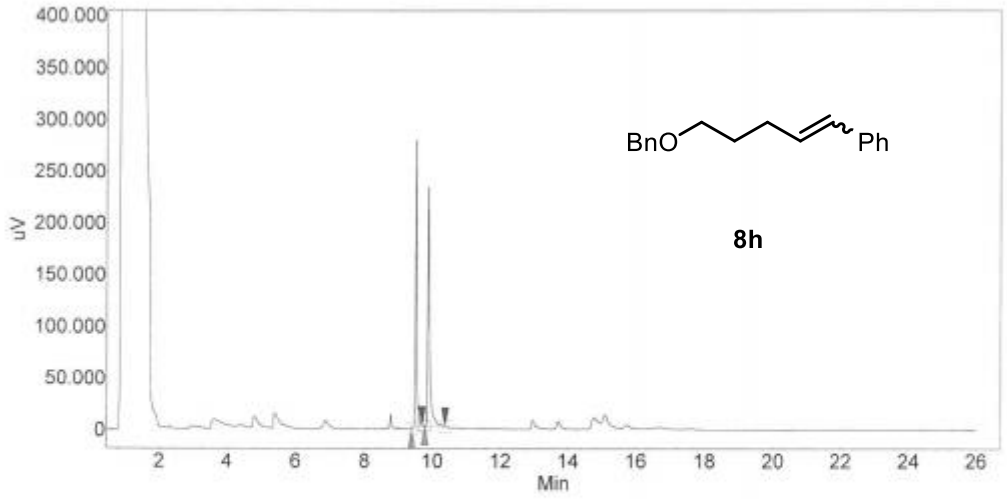

Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
Scan 2979 (18.995 min):
Abundance
91.1
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
118.1
161.1
132.1
147.1
65.1
77.0
105.1
39.0
51.0
175.1
193.1
207.0
253.0
280.9
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


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
Abundance
Scan 3000 (19.097 min)
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
m/z-->
91.1
118.1
132.1
147.1
162.1
65.1
77.1
105.1
39.0
51.0
183.1
207.0
252.0
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260


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 3121 (19.682 min)
Abundance
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
m/z-->
91.1
159.1
131.1
115.1
103.1
65.1
77.1
39.1
51.1
143.1
173.1
191.0
205.1
217.1
232.2
250.1
281.0
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 h:

GC data

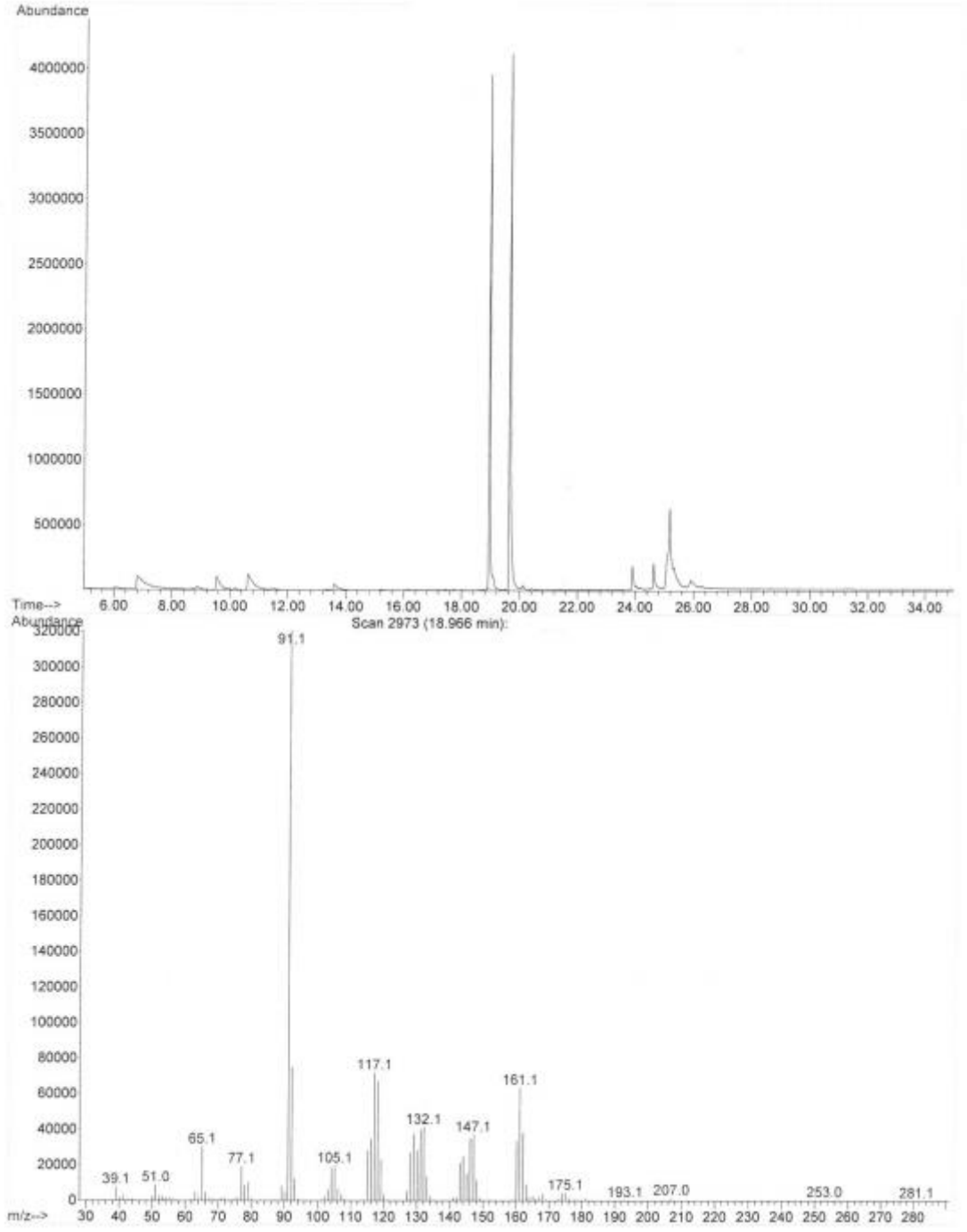


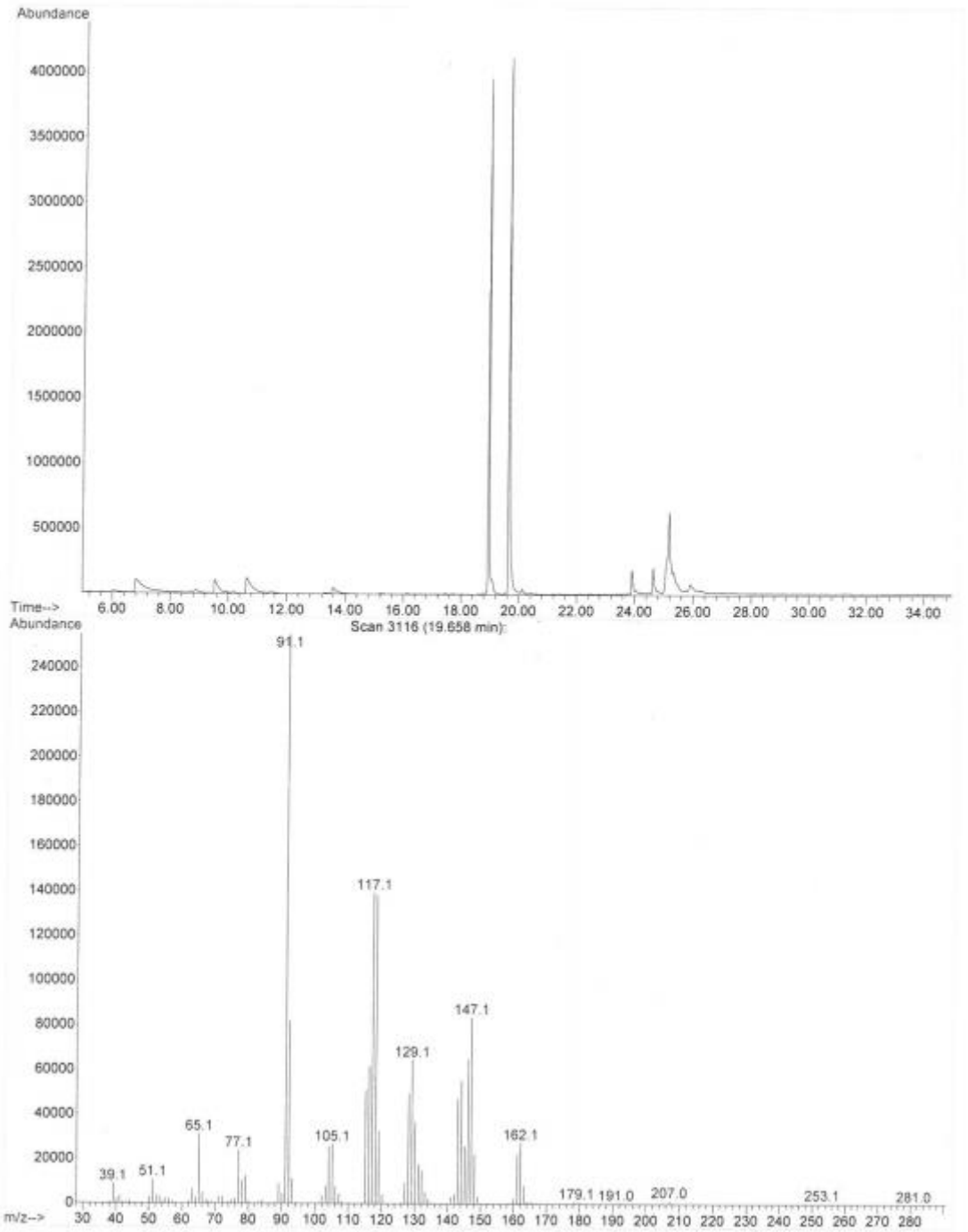
8h

Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV Min]	Area % [%]
1	UNKNOWN	9.51	45.95	278044.0	12647.8	45.952
2	UNKNOWN	9.87	54.05	231566.0	14876.3	54.048
Total			100.00	509610.1	27524.1	100.000

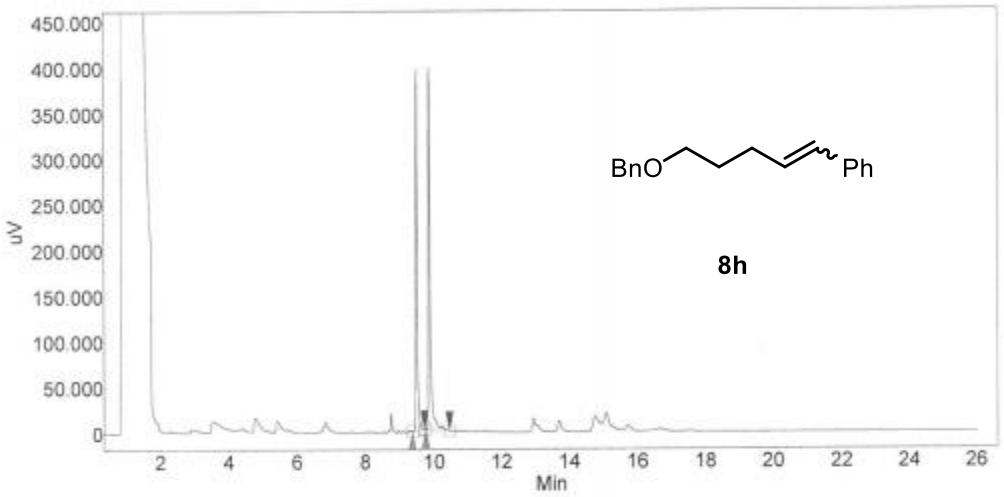
GCMS data


Abundance
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
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
Time-->
Abundance
Scan 2973 (18.966 min):
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
91.1
117.1
161.1
132.1
147.1
65.1
77.1
105.1
39.1
51.0
175.1
193.1
207.0
253.0
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


Abundance
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
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 3116 (19.658 min):
Abundance
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
m/z-->
91.1
117.1
147.1
129.1
65.1
77.1
105.1
162.1
39.1
51.1
179.1
191.0
207.0
253.1
281.0
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

6 h:

GC data

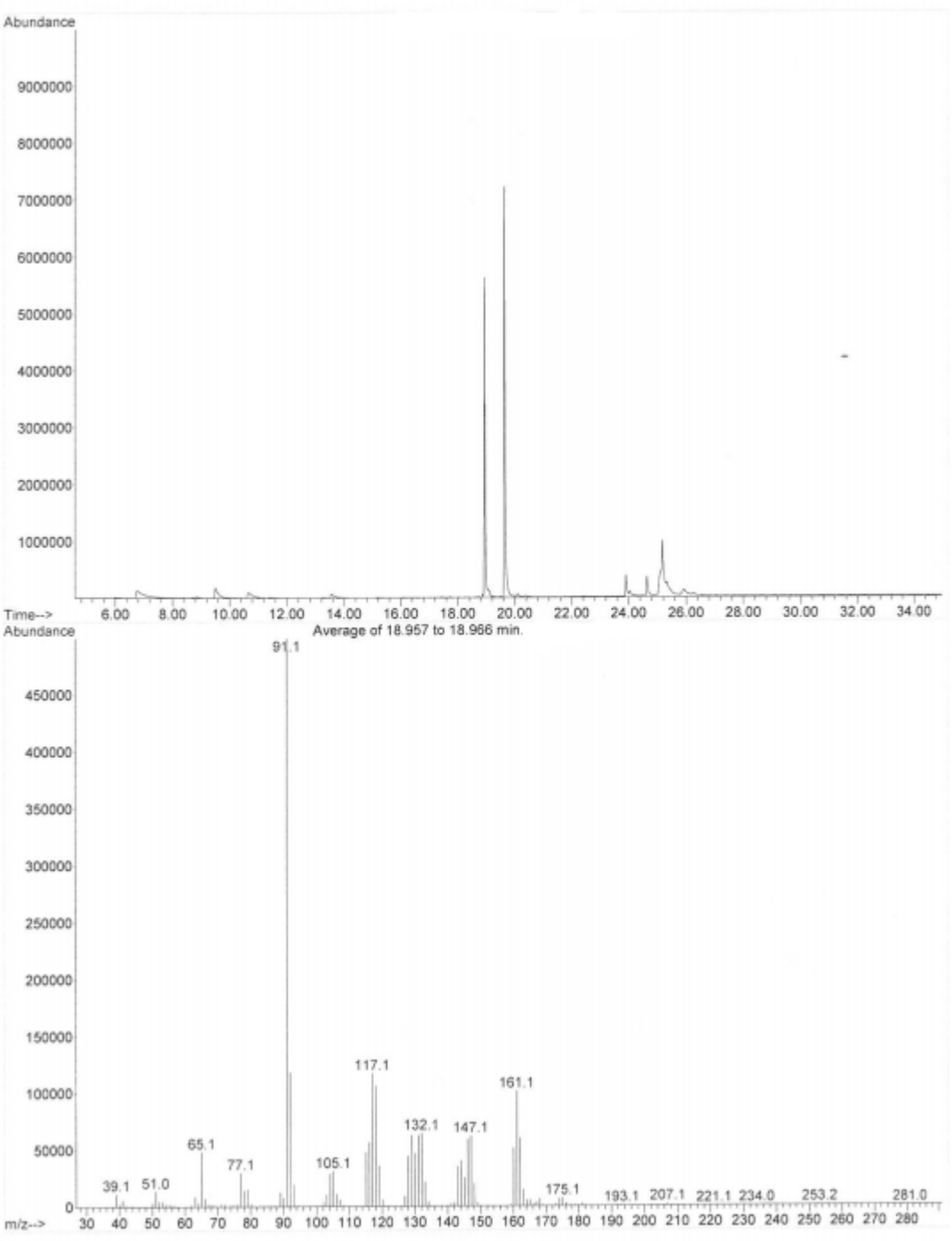


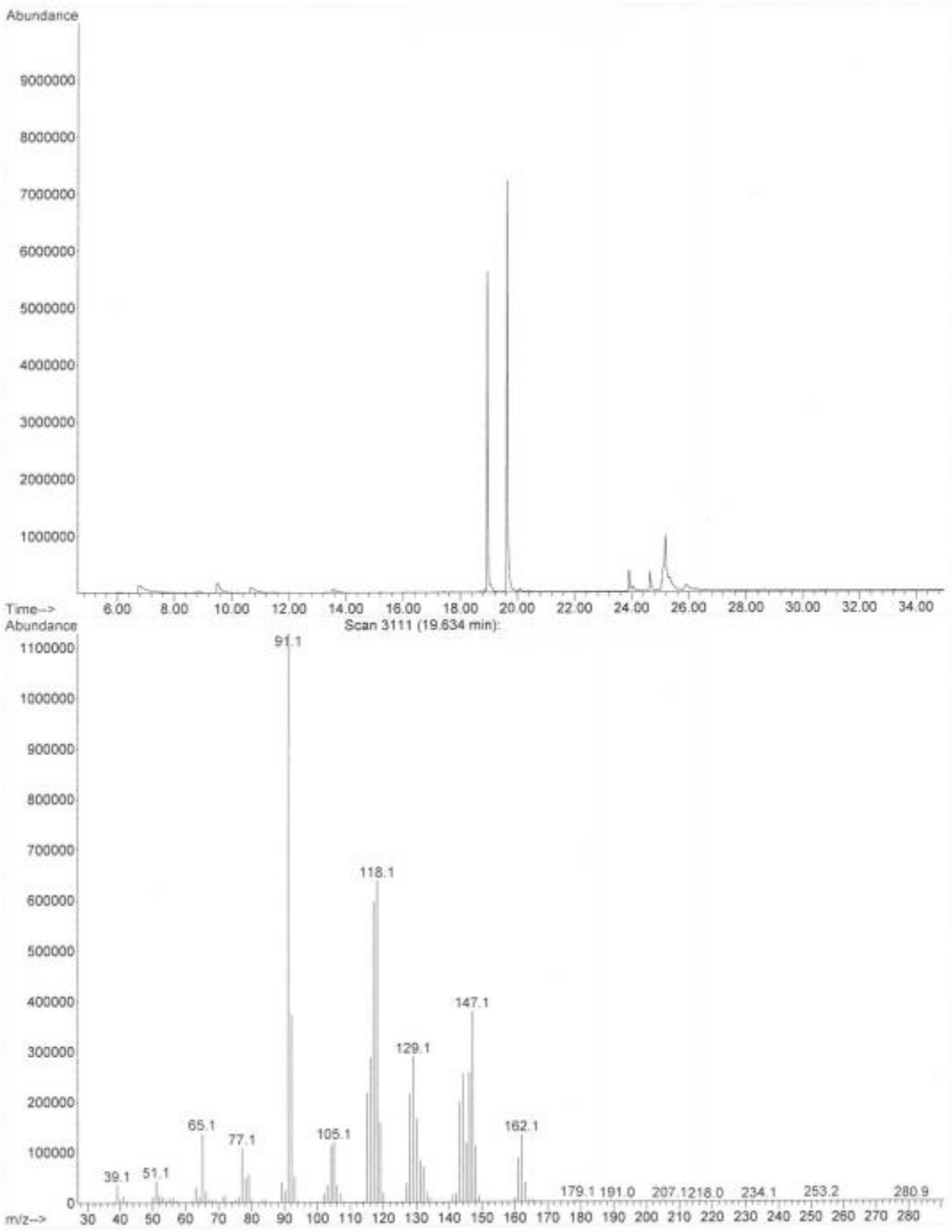
8h

Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV Min]	Area % [%]
1	UNKNOWN	9.50	43.24	396030.3	17075.7	43.240
2	UNKNOWN	9.87	56.76	395856.9	22414.5	56.760
Total			100.00	791887.3	39490.2	100.000

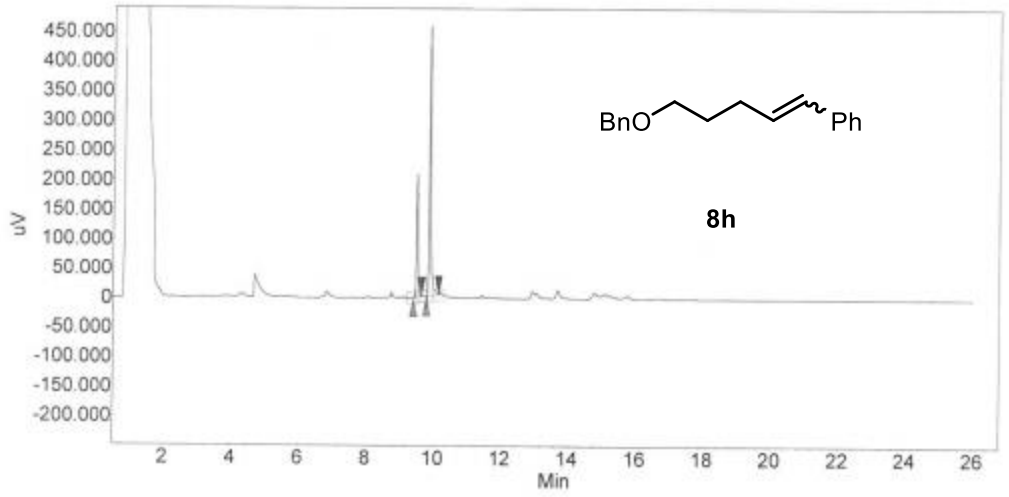
GCMS data


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
Average of 18.957 to 18.966 min.
Abundance
91.1
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
117.1
161.1
132.1
147.1
65.1
77.1
105.1
39.1
51.0
175.1
193.1
207.1
221.1
234.0
253.2
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


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 3111 (19.634 min):
Abundance
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
91.1
118.1
147.1
129.1
65.1
77.1
105.1
162.1
39.1
51.1
179.1 191.0 207.1218.0 234.1 253.2 280.9
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

22 h:

GC data



8h

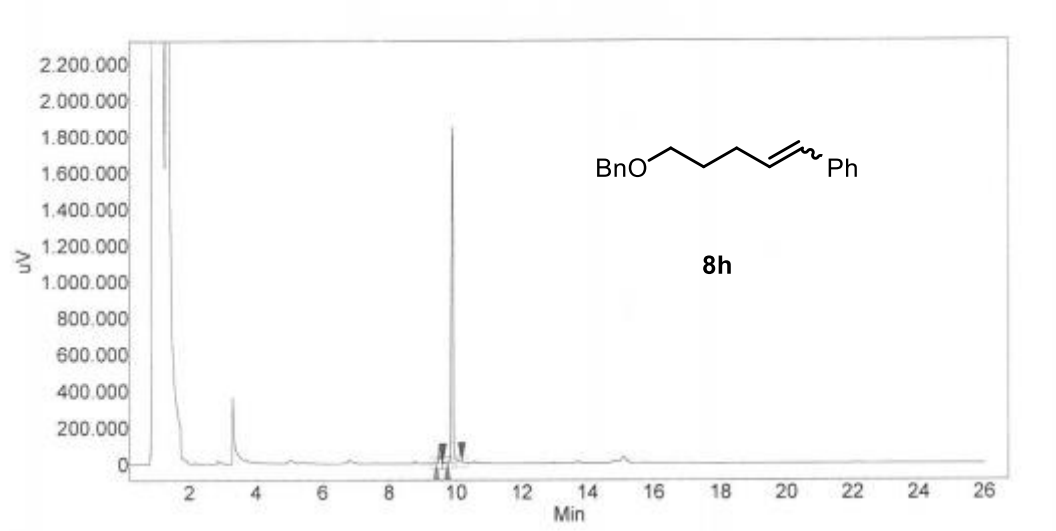
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	9.50	28.53	209177.7	9914.7	28.533
2	UNKNOWN	9.86	71.47	457443.3	24833.9	71.467
Total			100.00	666621.0	34748.6	100.000

conventional heating – isomerization experiments

30 min

GC data

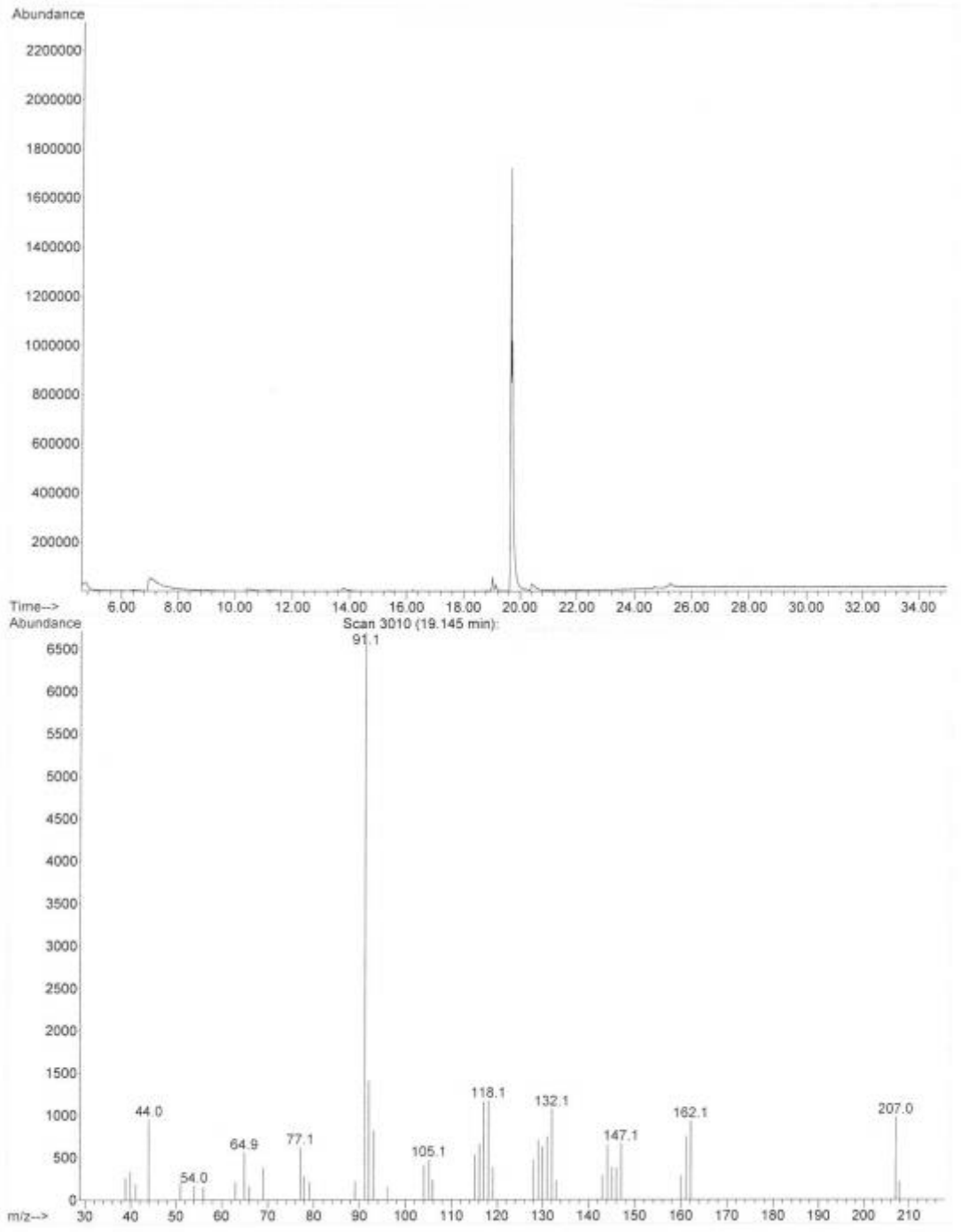


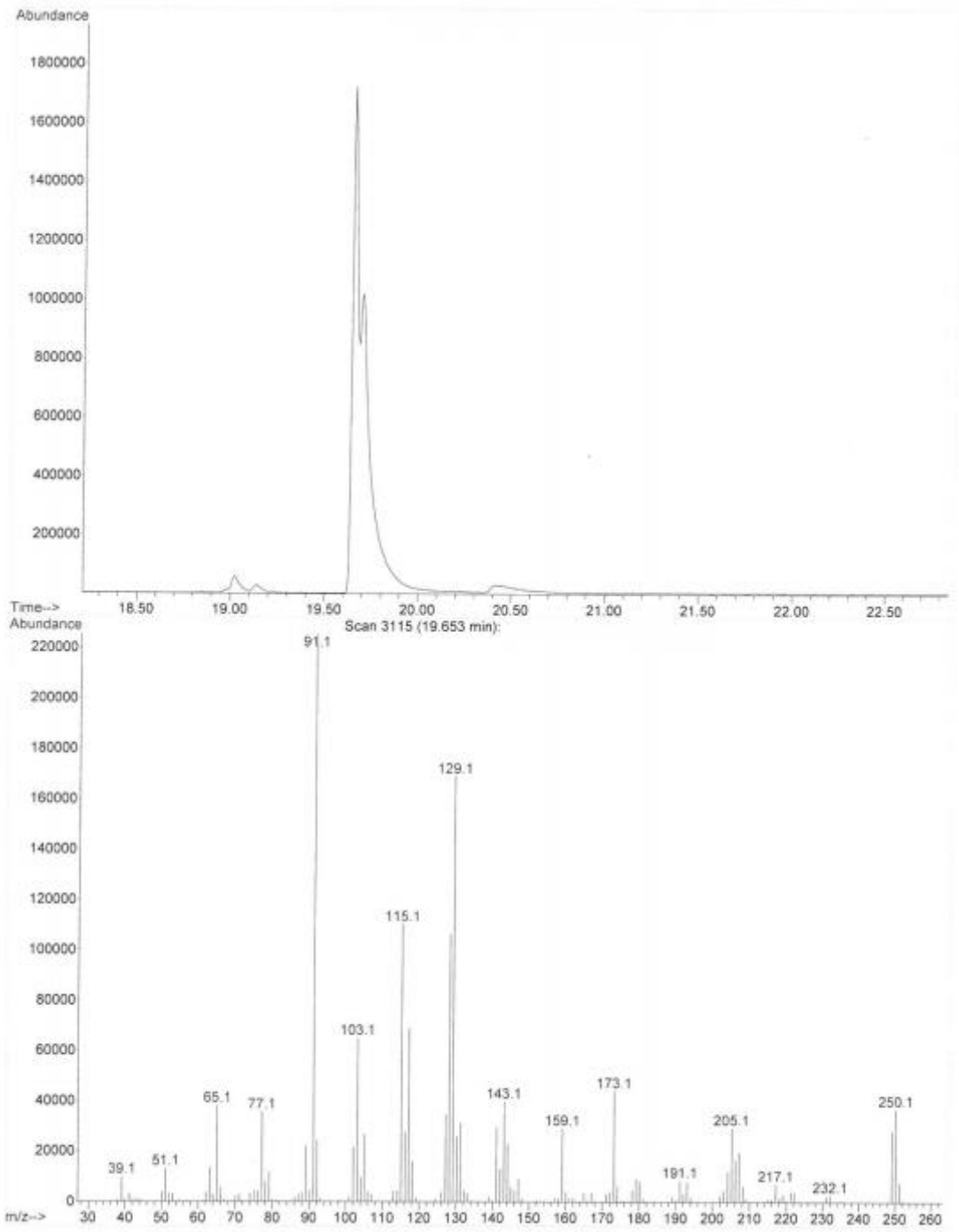
8h

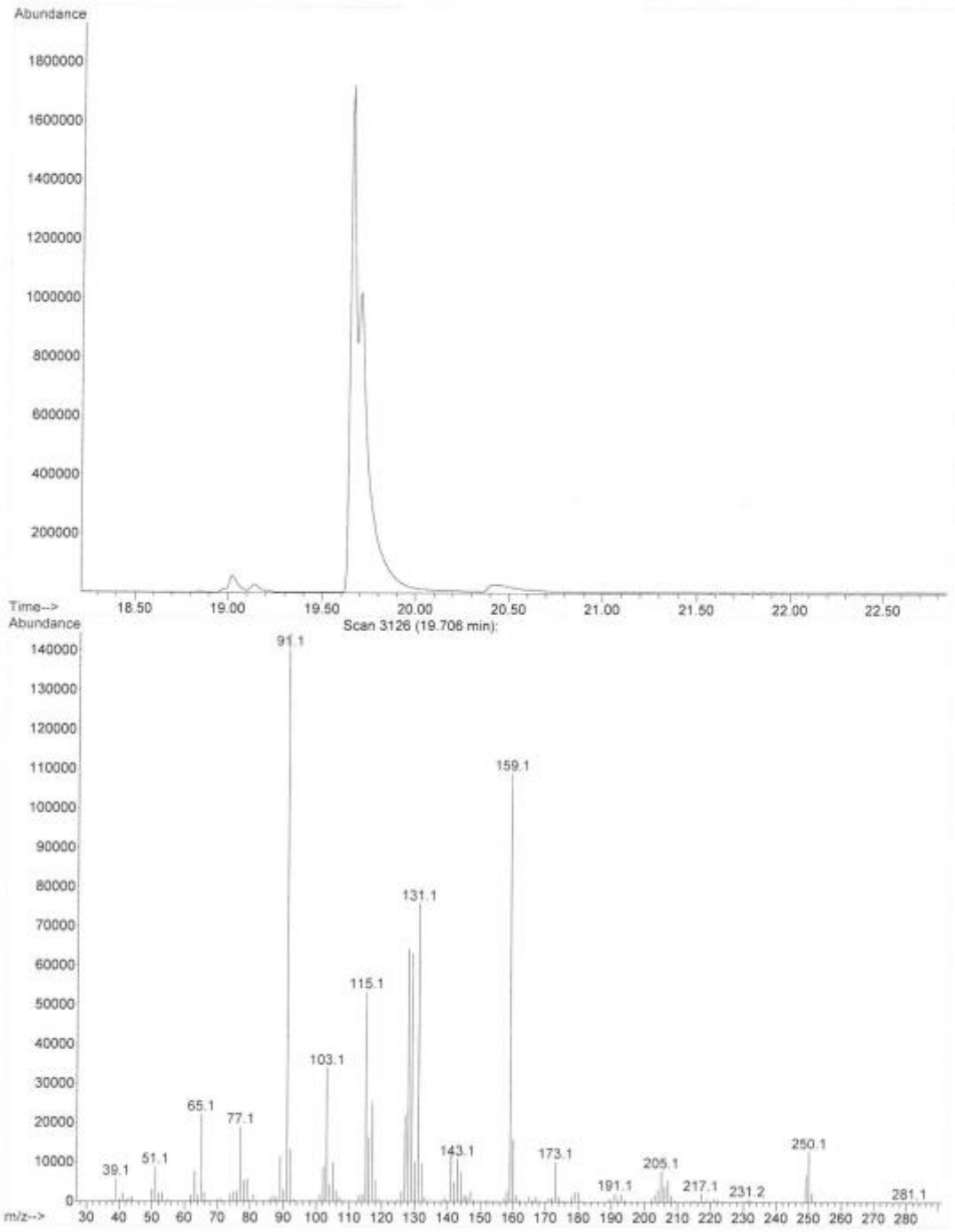
Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	9.50	4.24	94157.6	4646.3	4.240
2	UNKNOWN	9.90	95.76	1845606.7	104940.0	95.760
Total			100.00	1939764.3	109586.2	100.000

GCMS data

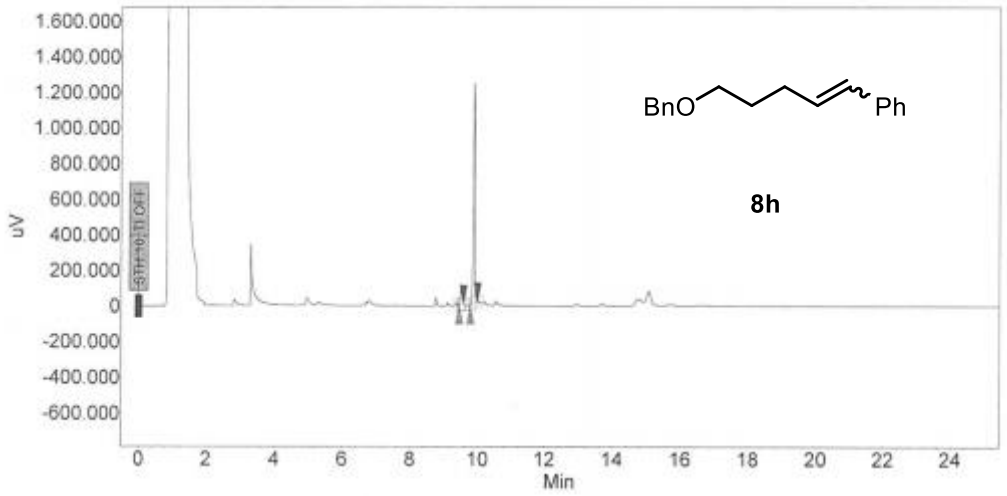

Abundance
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00
Abundance
Scan 3010 (19.145 min):
91.1
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
44.0
54.0
64.9
77.1
105.1
118.1
132.1
147.1
162.1
207.0
m/z-->
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210


Abundance
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
Time-->
18.50
19.00
19.50
20.00
20.50
21.00
21.50
22.00
22.50
Abundance
Scan 3115 (19.653 min):
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
m/z-->
91.1
129.1
115.1
103.1
65.1
77.1
143.1
173.1
159.1
205.1
250.1
39.1
51.1
191.1
217.1
232.1
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
260


Abundance
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
Time-->
18.50
19.00
19.50
20.00
20.50
21.00
21.50
22.00
22.50
Abundance
Scan 3126 (19.706 min):
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
91.1
159.1
131.1
115.1
103.1
65.1
77.1
39.1
51.1
143.1
173.1
205.1
191.1
217.1
231.2
250.1
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

90 min

GC data

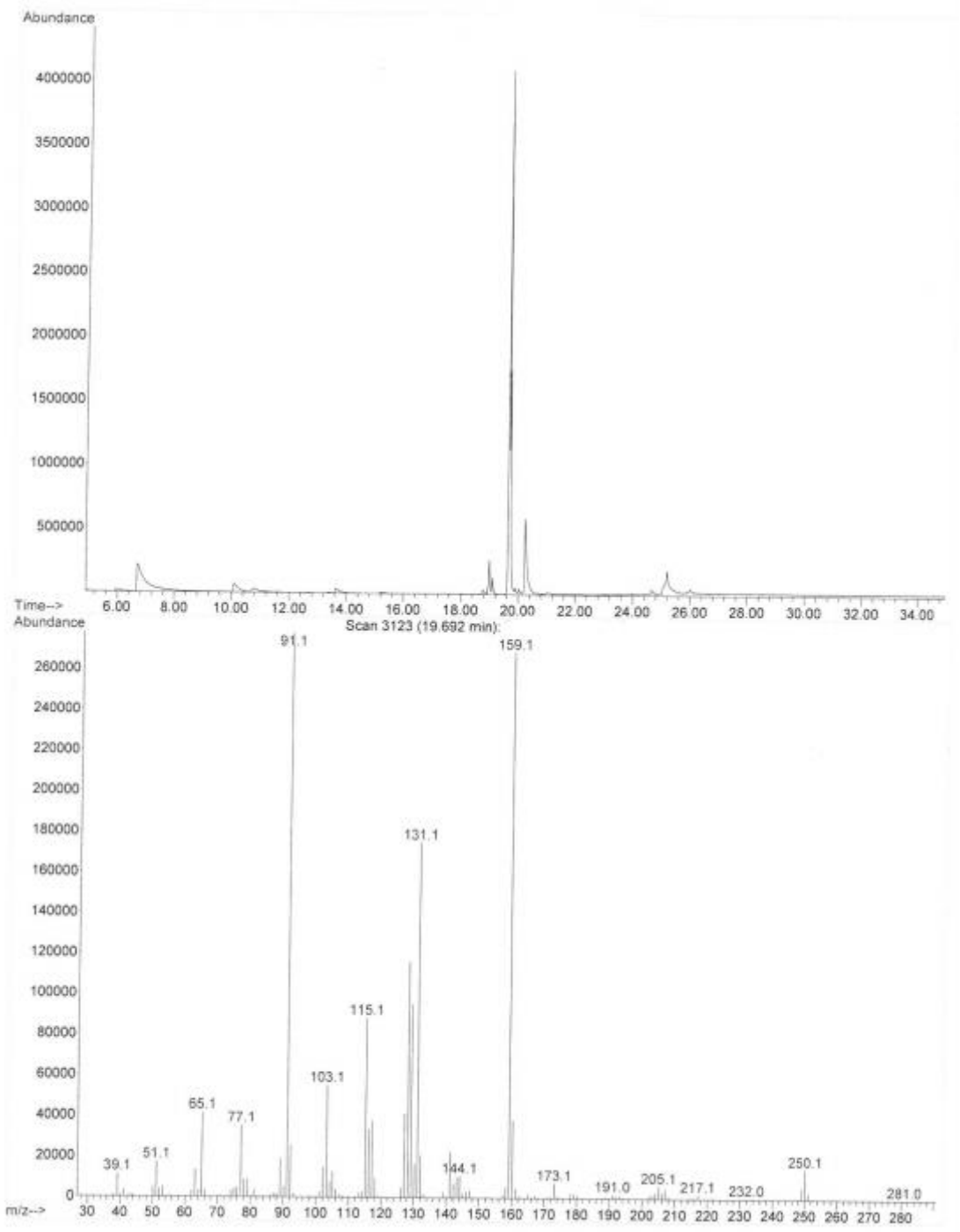


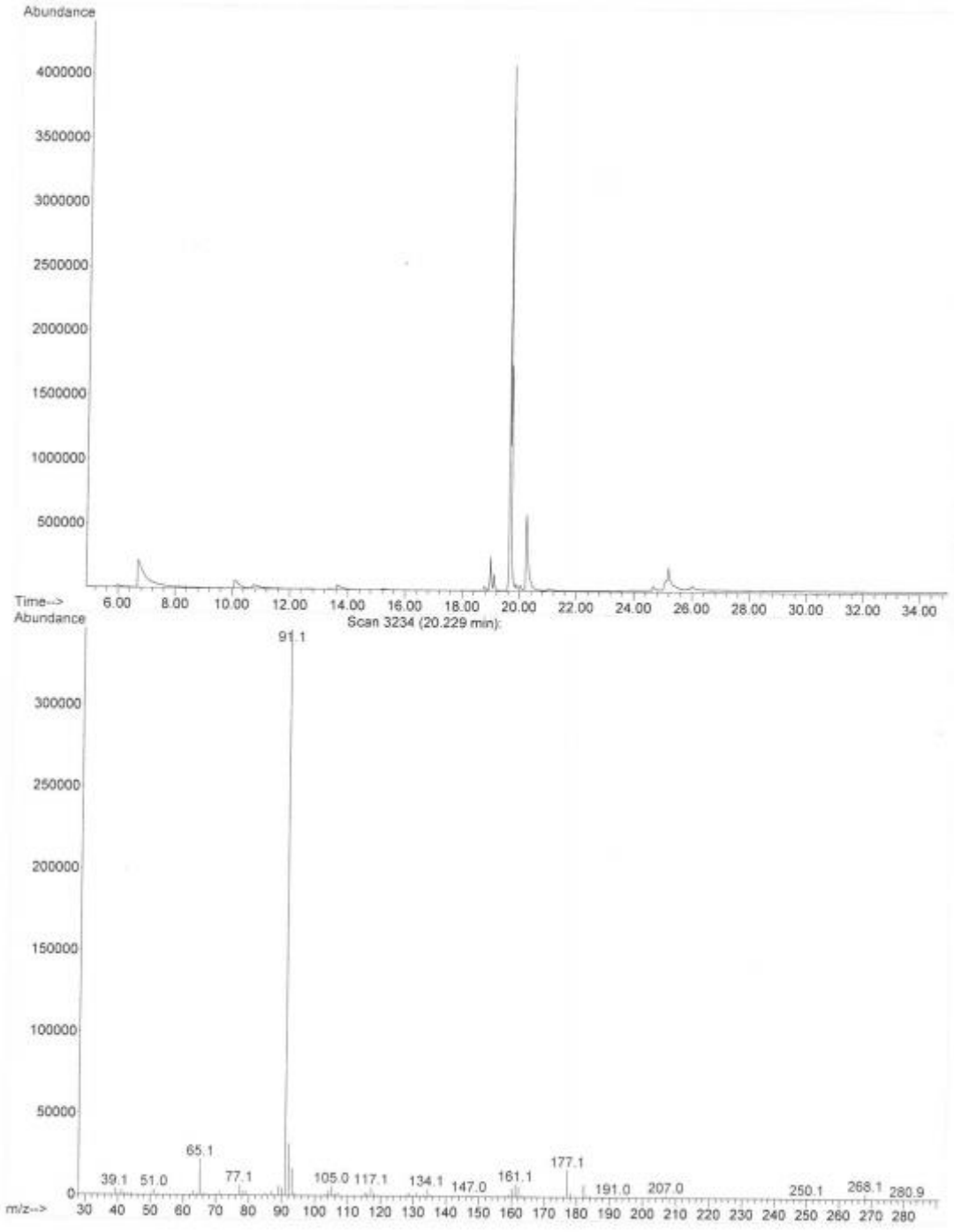
8h

Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	9.50	8.74	120320.2	6269.8	8.742
2	UNKNOWN	9.89	91.26	1241170.1	65450.4	91.258
Total			100.00	1361490.3	71720.3	100.000

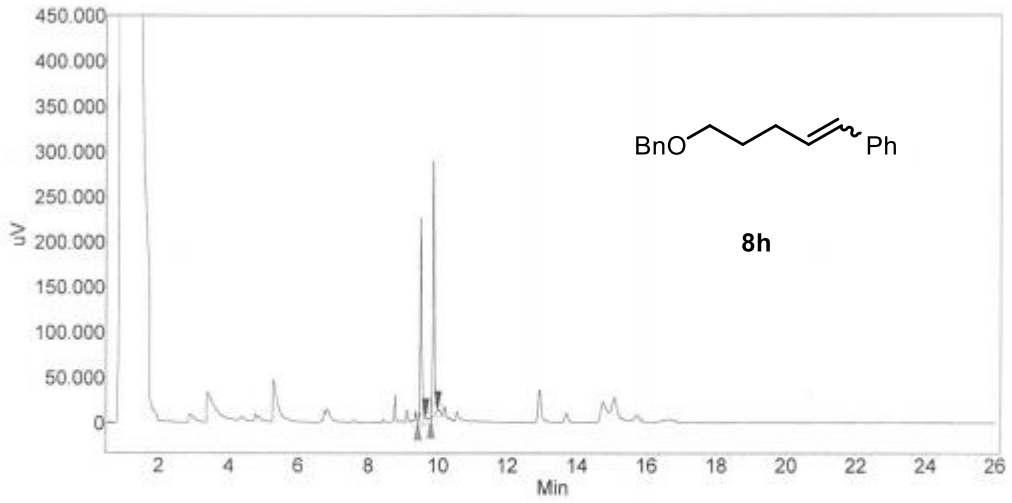
GCMS data


Abundance
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
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 3123 (19.692 min):
Abundance
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
91.1
159.1
131.1
115.1
103.1
65.1
77.1
39.1
51.1
144.1
173.1
191.0
205.1
217.1
232.0
250.1
281.0


Abundance
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
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 3234 (20.229 min):
91.1
300000
250000
200000
150000
100000
50000
0
65.1
39.1 51.0
77.1
105.0 117.1
134.1
147.0
161.1
177.1
191.0 207.0
250.1
268.1 280.9
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 h

GC data

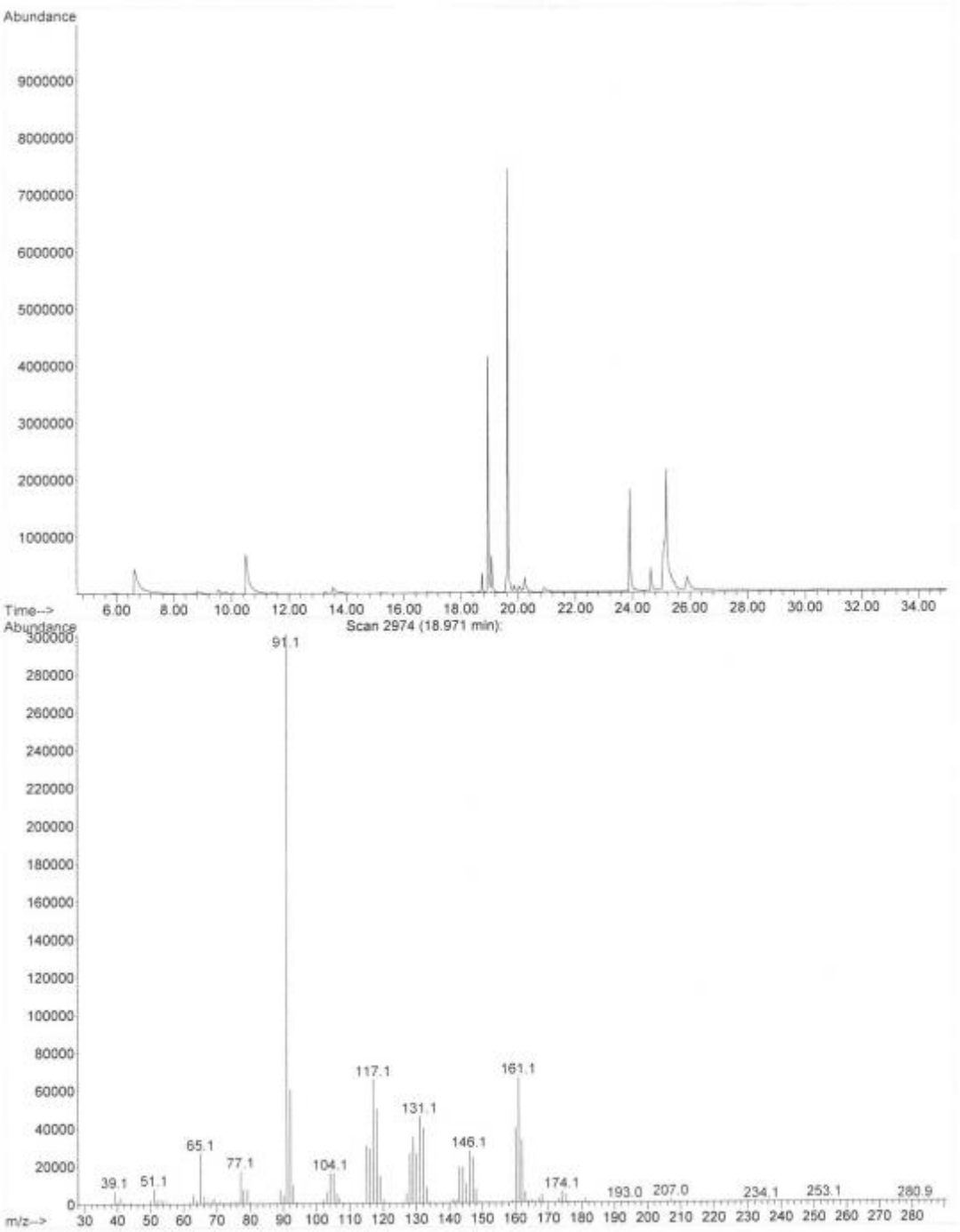


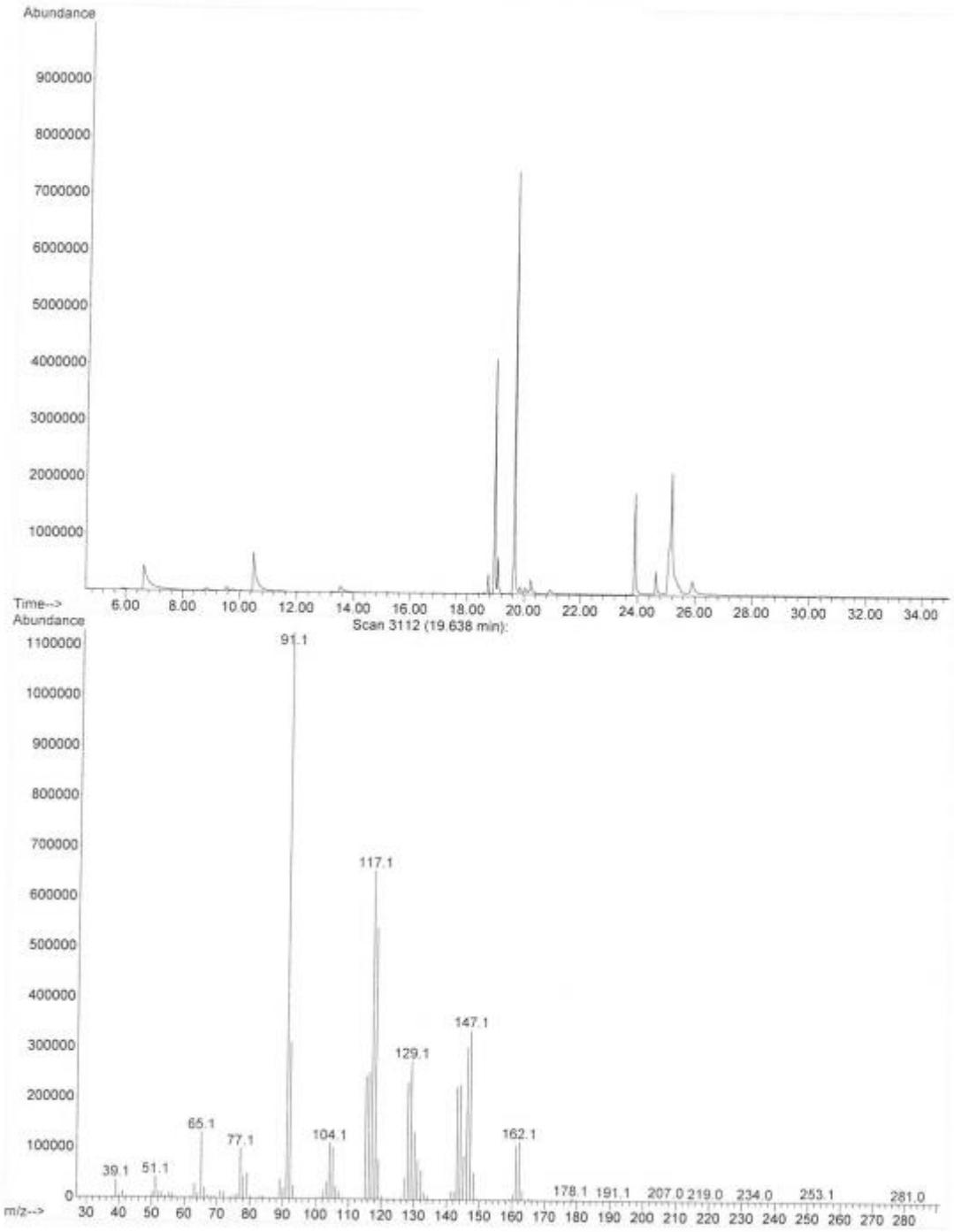
8h

Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	9.50	44.05	223795.7	10830.3	44.049
2	UNKNOWN	9.86	55.95	282923.1	13756.5	55.951
Total			100.00	506718.8	24586.8	100.000

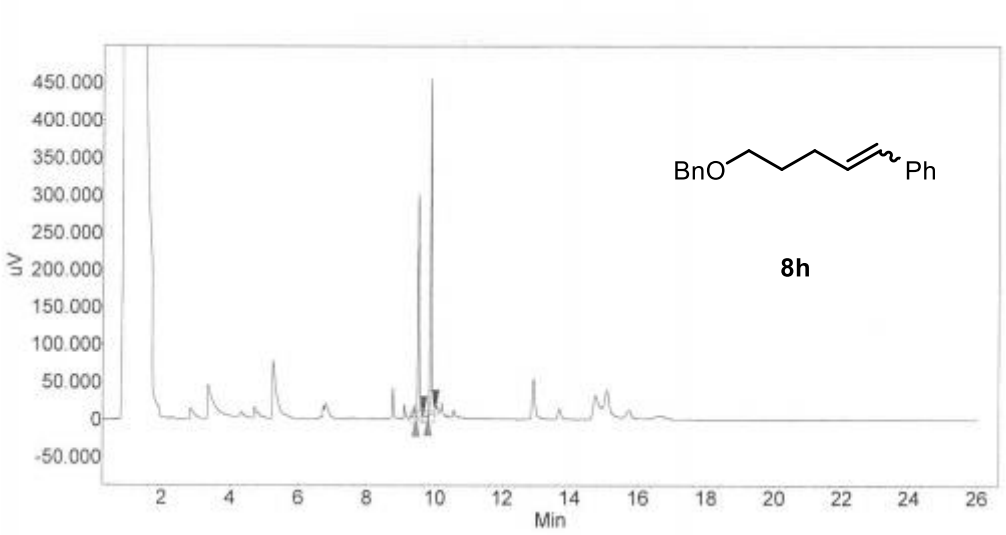
GCMS data


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
Abundance
Scan 2974 (18.971 min):
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
91.1
117.1
161.1
131.1
146.1
65.1
77.1
104.1
39.1
51.1
174.1
193.0
207.0
234.1
253.1
280.9
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


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 3112 (19.638 min):
Abundance
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
m/z-->
91.1
117.1
147.1
129.1
65.1
77.1
104.1
162.1
39.1
51.1
178.1
191.1
207.0
219.0
234.0
253.1
281.0
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

6 h

GC data

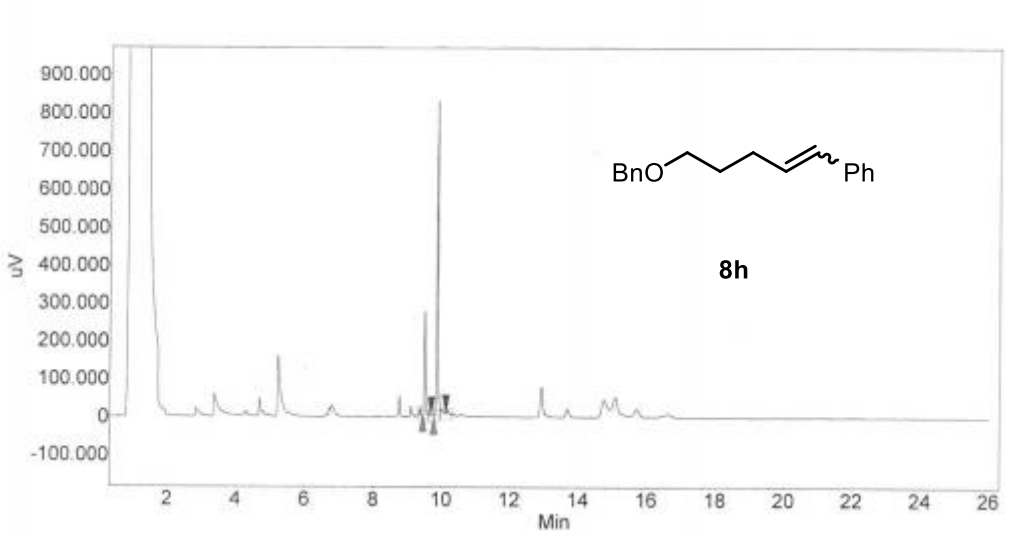


Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV.Min]	Area % [%]
1	UNKNOWN	9.50	40.18	297573.9	13870.0	40.176
2	UNKNOWN	9.87	59.82	448040.8	20653.2	59.824
Total			100.00	745614.7	34523.2	100.000

22 h

GC data



8h

Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [uV]	Area [uV Min]	Area % [%]
1	UNKNOWN	9.50	26.25	269726.8	13129.1	26.245
2	UNKNOWN	9.87	73.75	826524.8	36895.4	73.755
Total			100.00	1096251.6	50024.5	100.000