Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information For

Regio- and stereoselective multisubstituted olefin synthesis *via* hydro/carboalumination of alkynes and subsequent iron-catalysed cross-coupling reaction with alkyl halides

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General. All the reactions dealing with air- or moisture-sensitive compounds were carried out in dry reaction vessels under a positive pressure of argon gas. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a PFA tube. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck, #1.05715.0009). The TLC plates were visualized by exposure to ultraviolet light (254 nm) and/or by immersion in an acidic staining solution of *p*-anisaldehyde, followed by heating on a hot plate. The organic solutions were concentrated using rotary evaporation at *ca.* 30 mmHg. Flash column chromatography was performed on SilliCycle SiliaFlash Irregular Silica Gels F60 Silica (spherical, 40–63 μm) , Merck silica gel 60 (spherical, 140–325 mesh), and Wakogel® 60N (fractured, 38–100 μm) as described by Still *et al.*[1]

Instrumentation. The proton nuclear magnetic resonance (^{1}H NMR) and carbon NMR (^{13}C NMR), were recorded on a JEOL ECS-400NR (392 MHz) NMR spectrometer. The proton chemical shift values are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane, and are referenced to the residual proton signal of $CHCl_3$ (δ 7.26). The ^{13}C NMR spectra were recorded at 98.5 MHz. The chemical shifts of the carbon atoms are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane, and are referenced to the carbon resonance of $CDCl_3$ (δ 77.16). The data are presented as: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiplet resonances, and br = broad), coupling constant in hertz (Hz), signal area integration in natural numbers, and assignment (in *italics*). High-resolution mass spectra (HRMS) were obtained in fast atom bombardment (FAB) ionization or electron ionization (EI) mode on a JEOL JMS-700 mass spectrometer. IR spectra were

(1) W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.

recorded on a PerkinElmer Spectrum One FT-IR Spectrometer, and characteristic IR absorptions are reported in cm^{-1}.

Solvent. The anhydrous tetrahydrofuran (THF) and 1,2-dichloroethane used were purchased from the Wako Chemical Co. and distilled from benzophenone ketyl and P_2O_5 respectively under argon (at atmospheric pressure) immediately before use. Water contents of the solvents were determined using a Karl-Fischer moisture titrator (MCU-610 or MKC-610, Kyoto Electronics Company) and found to be < 15 ppm.

Materials. The chemical reagents used were purchased from Wako Pure Chemical Industries, Ltd (Wako), Tokyo Chemical Industry Co. Ltd, Aldrich Inc., and other commercial suppliers. Florisil® (100–200 mesh) was purchased from Nacalai Tesque Inc. $FeCl_2$-SciOPP complexes were synthesized according to the literature,[2] and dissolved in THF at 0 °C prior to use. Diisobutylaluminum hydride (neat) was supplied from Tosoh Finechem Corporation, and dissolved in hexane at 0 °C prior to use.

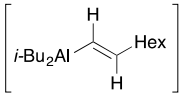
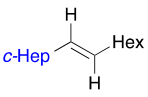
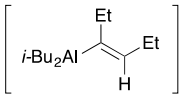
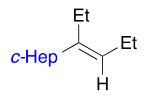
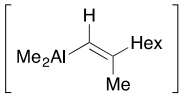
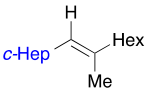
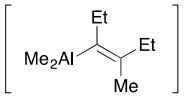
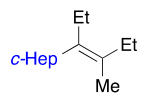
GC analysis. The yield (using undecane as an internal standard) was determined for the crude product using GLC analysis on a Shimadzu GC-2010 Plus analyser equipped with an FID detector and a capillary column, ZB-1MS (10 m × 0.1 mm i.d., film thickness = 0.1 μm).

(2) T. Hatakeyama, T. Hashimoto, Y. Kondo, Y. Fujiwara, H. Seike, H. Takaya, Y. Tamada, T. Ono and M. Nakamura, *J. Am. Chem. Soc.*, 2010**, 132**, 10674.

Additional Data of the effect of KF in the cross coupling reaction (supplement to Scheme 3)

· *Effect of KF on the product yield in the reactions with various alkenylaluminium reagents*

Table S1. The reaction of various alkenyl aluminum reagents

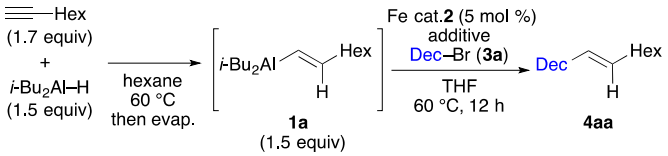
entry[a]	organoaluminum reagent	coupling product	product yield (%)	
			with KF[b,c]	without KF[c,d]
1	 **1a**	 **4ab**	91 (>99% *E*)	29 (>99% *E*)
2	 **1b**	 **4bb**	86 (*E*/*Z* = 97/3)	20 (*E*/*Z* = 97/3)
3	 **1c**	 **4cb**	86 (>99% *E*)	36 (>99% *E*)
4	 **1d**	 **4db**	19 (*E*/*Z* = 70/30)	4 (*E*/*Z* = 78/22)

[a]See the experimental section in this SI for details of the reaction conditions for each entries. [b]Isolated yield. [c]The ratio of stereoisomers was determined by GLC analysis. [d]The yields were determined by ^{1}H NMR analysis, using 1,1,2,2-tetrachloroethane as an internal standard.

· *Effect of the amount of KF on the product yield and selectivity*

The effect of the amount of KF on the reaction of 1-bromodecane **3a** with alkenyl aluminum reagent **1a** was examined (Table S2). While 3 equivalents of KF to the alkenyl aluminium gave the virtually same result with the reaction of 1.5 equivalents of KF (entry 1), a catalytic amount (20 mol%) of KF led to a decrease in the conversion (20% yield) as well as the lower product selectivity (entry 3). Addition of 18-crown-6 to increase the solubility of KF in THF but did not improve the yield and the product selectivity.

Table S2. Effect of the amount of KF in the reaction



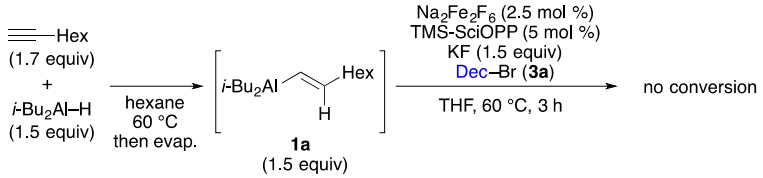
entry[a]	additive	GC yield (%)[b]			RSM[b,c] (%)
		4aa (*E*/*Z*)	decane (**5**)	1-decene (**6**)	
1	KF (3.0 equiv)	78 (>99% *E*)	10	12	0
2	KF (1.5 equiv)	76 (>99% *E*)[d]	9	10	0
3	KF (20 mol %)	20 (>99% *E*)	10	20	44
4	KF (1.5 equiv) + 18-crown-6 (1.5 equiv)	30 (>99% *E*)	26	16	22

[a]For reaction conditions, see Table 1. [b]Yields and stereoisomeric ratio were determined by GLC analysis, using undecane as an internal standard. [c]Recovery of starting material **3a**. [d]Isolated yield.

· *Reaction with iron fluoride*

The combination of an iron fluoride ($Na_2Fe_2F_6$) and TMS-SciOPP was used as a precatalyst instead of $FeCl_2$(TMS-SciOPP) to study the catalytic competency of ferrate species, which is supposed to form in the presence of excess fluoride anion source (Scheme S1). The ferrate precatalyst was found ineffective and no cross-coupling product was obtained under the similar conditions of the reaction with $FeCl_2$(TMS-SciOPP), suggesting that the presence of excess fluoride anion may impair the reactivity of iron catalyst through the formation of ferrate species.

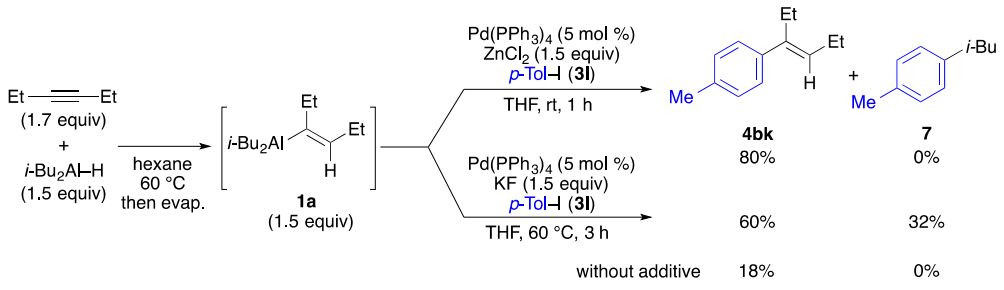
Scheme S1. Iron-catalyzed cross coupling of alkenyl aluminum reagents prepared by zirconium-mediated carbometalation in the presence of iron fluoride



· *Effect of KF in the Negishi coupling of alkenyl aluminium reagents*

The effect of KF in the conventional palladium-catalyzed Negishi coupling of alkenyl aluminum **1b** with 4-tolyl iodide **3k** was examined (Scheme S2). The typical Negishi coupling, where alkenyl aluminium is converted to the corresponding zinc reagent by transmetallation, proceeded readily at room temperature in the presence of a catalytic amount of $Pd(PPh_3)_4$ to afford the desired coupling product **4bk** in high yield. Addition of KF, instead of $ZnCl_2$, resulted in substantial decrease of the catalytic activity as the reaction proceeded at higher temperature (60 °C) along with the formation of side product **7**. The cross coupling reaction without any additive also proceeded at 60 °C to give the alkenylation product in 18% yield. These results suggest that KF enhances the transmetalation by forming higher reactive alkenylaluminium species but causes non-selective transfer of organic ligands on the organoaluminum reagent (e.g., alkyl vs. alkenyl) to decrease the cross-coupling selectivity.

Scheme S2. Effect of KF addition on the conventional Pd-catalyzed Negishi coupling



· *^{19}F NMR analysis of a mixture of alkenylaluminum and KF*

A mixture of alkenyl aluminum **1a** and KF in THF-d_8 at 60 °C was analyzed with ^{19}F NMR; however, no significant change in the signal was observed, and only a very weak broad signal (ca. 5%) was detected at –164.9 ppm, which suggested the formation of organoaluminate, albeit in a small amount (Figure S1).[3]

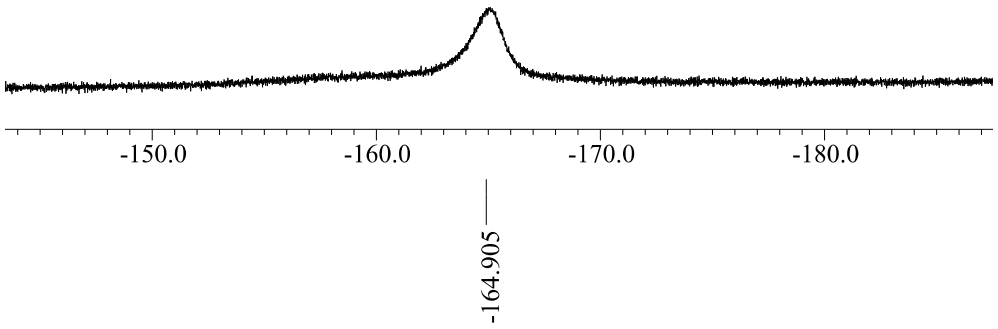


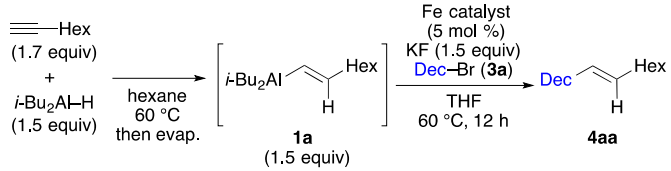
Figure S1. ^{19}F NMR spectrum of a mixture of **1a** and KF in THF-d_8 at 60 °C

Because the coupling reaction did not take place in the absence of KF, we tentatively consider that the organoaluminate species generated *in situ* is responsible for the transmetalation of alkenyl group form aluminium to iron to facilitate the coupling reaction. However, the details are not clear at the present stage and additional study is requisite for further discussion of the reaction mechanism.

(3) Harrison and Beach reported the chemical shift of the ^{19}F NMR signal derived from $K[(Et_3Al)_2F]$ to lie at $\delta_F = -160.6$ ppm: J. J. Harrison, D. L. Beach, D. C. Young, K. S. Seshadri and J. D. Nelligan, *Organometallics.*, 1987, **6**, 343.

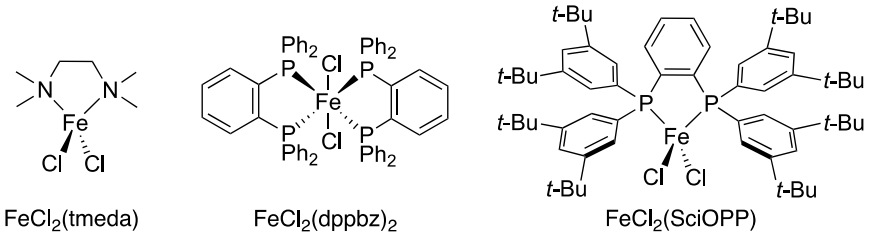
Screening of catalysts

Table S3. Screening of iron catalysts



entry[a]	Fe catalyst	GC yield (%)[b]			diene[b,c] (%)	RSM[b,d] (%)
		4aa (*E*/*Z*)	**5**	**6**		
1	$FeCl_2$	10 (>99% *E*)	15	31	4	18
2	$FeCl_2$(tmeda)	2 (>99% *E*)	0	6	0	90
3	$FeCl_2(dppbz)_2$	0	0	2	0	95
4	$FeCl_2$(SciOPP)	65 (>99% *E*)	22	10	2	0
5	$FeCl_2$(TMS-SciOPP)	76 (>99% *E*)[e]	9	10	1	0
6	none	0	2	0	0	97

[a]For reaction conditions, see Table 1, entry 3. [b]Yields and stereoisomeric ratio were determined by GLC analysis, using undecane as an internal standard. [c]Yield of hexadeca-7,9-diene was determined based on the starting 1-bromodecane **3a** [d]Recovery of starting material **3a**. [e]Isolated yield.



$FeCl_2$(tmeda) $FeCl_2(dppbz)_2$ $FeCl_2$(SciOPP)

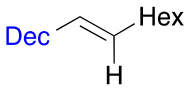
Figure S2. Structures of the iron complexes used as the cross-coupling catalysts

Procedure for the screening of the additives (Table 1)

1-Octyne (92.2 mg, 0.84 mmol) was added to a solution of diisobutylaluminum hydride (0.75 mL, 0.75 mmol) at 0 °C. The reaction mixture was stirred at 50–60 °C for overnight, and then, dried *in vacuo* to remove solvent.[4] To the residue, 0.50 mL of THF was added at 0 °C, followed by additives (0.75–1.50 mmol), 1-bromodecane (110.6 mg, 0.50 mmol) and a THF solution of $FeCl_2$(TMS-SciOPP) (0.25 mL, 0.03 mmol) in that order. The coupling reaction was carried out at 60 °C for 3 h. After cooling the mixture to ambient temperature, an aliquot of the reaction mixture was taken to determine the yield of the products by GLC analysis using undecane as an internal standard.

Typical procedures for the reactions shown in Scheme 3 and Table 2

· General procedure A (hydroalumination/cross-coupling reactions); synthesis of (*E*)-octadec-7-ene (*4aa*)



4aa

1-Octyne (184 mg, 1.70 mmol) was added to a 1.00 M solution of diisobutylaluminum hydride (1.50 mL, 1.50 mmol) at 0 °C. The reaction mixture was stirred at 50–60 °C for 12 h, and then, dried *in vacuo*. To the residue, 1.00 mL of THF was added at 0 °C, followed by potassium fluoride (87.2 mg, 1.50 mmol), 1-bromodecane (221 mg, 1.00 mmol) and a 0.10 M THF solution of $FeCl_2$(TMS-SciOPP) (0.50 mL, 0.05 mmol) in that order. The coupling reaction was conducted at 60 °C for 3 h. After cooling the mixture to ambient temperature, aqueous HCl (1 N, 4 mL) were added at 0 °C. The aqueous layer was extracted with ethyl acetate three times (2 mL × 3). The combined organic extracts were filtered using a pad of Florisil®. After removal of the solvent *in vacuo*, the crude product was purified using chromatography on a silica gel to obtain the desired compound (192 mg, 76% yield, 98% purity on GC analysis) as a colourless oil.

^{1}H NMR (391.8 MHz, $CDCl_3$)

0.87 (t, J = 6.7 Hz, 6H, -CH_2CH_3), 1.08–1.50 (m, 24H, overlap), 1.97, (dt, J = 4.0, 5.8 Hz, 4H, -C=CCH_2-), 5.38 (t, J = 4.0 Hz, 2H, -C*H*=C*H*-)

^{13}C NMR (98.5 MHz, $CDCl_3$)

14.3 (2C), 22.8 (2C), 22.9 (2C), 29.0, 29.3, 29.5, 29.7, 29.8 (2C), 31.9, 32.1, 32.8 (2C), 130.5 (2C)

IR (neat, cm^{-1})

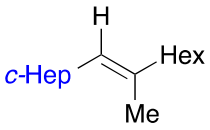
2956, 2921, 2852, 1466, 1378, 965, 721

Elemental analysis

Anal. calcd. for $C_{18}H_{36}$, C, 85.63; H, 14.37. Found C, 85.49; H, 14.44

(4) The reagent can be stocked in a refrigerator for several days and available for the reaction without loss of the yield and selectivity of the desired product.

· General procedure B (carbometalation/cross-coupling reaction); synthesis of (*E*)-(2-methyloct-1-en-1-yl)cycloheptane (*4cb*)



4cb

1-Octyne (110 mg, 1.00 mmol) was added to a mixuture of trimethylaluminum (1.87 mL, 1.07 M, 2.00 mmol) in hexane and zirconocene dichloride (146 mg, 0.50 mmol) in 3 mL of 1,2-dichloroethane at 0 °C. The reaction mixture was stirred at room temperature for 24 h, and then, dried *in vacuo*. To the residue, 1.00 mL of THF was added at 0 °C, followed by potassium fluoride (58.1 mg, 1.00 mmol), bromocycloheptane (119 mg, 0.67 mmol) and a 0.10 M THF solution of $FeCl_2$(TMS-SciOPP) (0.33 mL, 0.03 mmol) in that order. The coupling reaction was carried out at 60 °C for 3 h. After cooling the mixture to ambient temperature, aqueous HCl (1 N, 4 mL) were added. The aqueous layer was extracted with ethyl acetate three times (2 mL × 3). The combined organic extracts were filtered using a pad of Florisil®. After removal of the solvent *in vacuo*, the crude product was purified using chromatography on a silica gel to obtain the desired compound (191 mg, 86% yield, 98% purity on GC analysis) as a colourless oil.

^{1}H NMR (391.8 MHz, $CDCl_3$)

0.90 (t, J = 7.2 Hz, 3H, -CH_2CH_3), 1.04–1.78 (m, 24H, overlap), 1.93 (m, 1H, -C=CCH_2-), 2.32 (m, 1H, -$(CH_2)_2CH$C=C-), 5.05 (d, J = 9.0 Hz, 1H, -CH=CCH_3)

^{13}C NMR (98.5 MHz, $CDCl_3$)

14.3, 16.1, 22.8, 26.7 (2C), 28.1, 28.6 (2C), 29.0, 31.9, 35.5 (2C), 38.7, 39.8, 132.0, 132.1

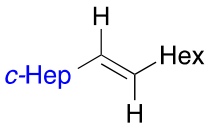
IR (neat, cm^{-1})

2955, 2922, 2852, 1458, 1378, 883, 724

Elemental analysis

Anal. calcd. for $C_{16}H_{30}$, C, 86.40; H, 13.60. Found C, 86.73; H, 13.93

Synthesis of (*E*)-oct-1-en-1-ylcycloheptane (*4ab*)



4ab

The reaction was carried out according to the general procedure A using **3b-Br** (177 mg, 1.00 mmol). The titled compound (190 mg, 91% yield) was obtained as a colorless oil after silica gel column chromatography.

^{1}H NMR (391.8 MHz, $CDCl_3$)

0.88 (t, J = 6.7 Hz, 3H, -CH_2CH_3), 1.10–1.78 (m, 20H, overlap), 1.95 (dt, J = 6.7, 7.0 Hz, 2H, -C=CCH_2-), 2.87 (m, 1H, -$(CH_2)_2CH$C=C-), 5.35 (m, 2H, -CH=CH-)

^{13}C NMR (98.5 MHz, $CDCl_3$)

14.3, 22.8, 26.4 (2C), 28.6 (2C), 29.0, 29.8, 31.9, 32.8, 35.2 (2C), 43.0, 127.2, 137.4

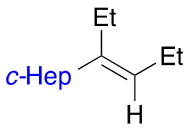
IR (neat, cm^{-1})

2961, 2921, 2853, 1458, 1373, 1066, 907, 844, 751

Elemental analysis

Anal. calcd. for $C_{15}H_{28}$, C, 86.46; H, 13.54. Found C, 86.16; H, 13.59

Synthesis of (*E*)-hex-3-en-3-ylcycloheptane (*4bb*)



4bb

The reaction was carried out according to the general procedure A using 3-hexyne (1.70 mmol, 140 mg) and **3b-Br** (177 mg, 1.00 mmol). The titled compound (155 mg, 86% yield) was obtained as a colorless oil after silica gel column chromatography.

^{1}H NMR (391.8 MHz, $CDCl_3$)

0.95 (t, J = 7.2 Hz, 3H, -CH_2CH_3) 0.96 (t, J = 7.2 Hz, 3H, $CH_3CH(C_8H_{17})CH$=C-), 1.10–1.80 (m, 12H, overlap), 1.99 (m, 5H, -$(CH_2)_2CH$C=C-, -CH_2C=CCH_2-), 5.05 (t, 7.2 Hz, 1H, -C=C*H*-)

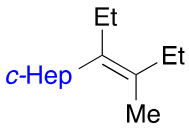
^{13}C NMR (98.5 MHz, $CDCl_3$)

14.5, 14.9, 21.0, 23.1, 27.4 (2C), 28.1 (2C), 35.0 (2C), 47.6, 124.0, 147.6

Elemental analysis

Anal. calcd. for $C_{13}H_{24}$, C, 86.58; H, 13.42. Found C, 86.40; H, 13.59

Synthesis of (4-methylhex-3-en-3yl)cycloheptane (*4db*)



4db

The reaction was carried out according to the general procedure B. The carboalumination using 3-hexyne (2.01 mmol, 169 mg) and the coupling reaction of **3b-Br** (118 mg, 0.67 mmol) were conducted for 50 ºC for 24 h and at 80 °C for 36 h respectively. The titled compound (25.2 mg, 19% yield, *E*/*Z* = 70/30) was obtained as a colorless oil after silica gel column chromatography. The stereochemistry of the isomers was analogized from that of the starting alkenylaluminum reagent.[5]

^{1}H NMR (391.8 MHz, $CDCl_3$)

E/*Z* mixture: 0.92–0.99 (m, 6H, -C*H*$_3$) 1.38–1.74 (m, 15H, overlap), 1.95–2.05 (m, 4H, CH_3CH_2C=CCH_2CH_3), 2.48–2.59 (m, 1H, -C=CC*H*-)

^{13}C NMR (98.5 MHz, $CDCl_3$)

E/*Z* mixture: 13.3, 13.8, 15.1, 16.0, 17.3, 18.1, 21.7, 21.9, 27.2, 27.4, 28.0 (4C), 28.1 (4C), 33.7 (2C), 34.0 (2C), 43.4, 43.9, 128.1, 128.2, 140.1, 140.2

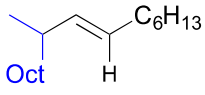
IR (neat, cm^{-1})

2961, 2923, 2854, 1455, 1374, 1059, 786

Elemental analysis

Anal. calcd. for $C_{14}H_{26}$, C, 86.52; H, 13.48. Found C, 86.41; H, 13.52

Synthesis of (*E*)-9-methylheptadec-7-ene (*4ac*)



4ac

The reaction was carried out according to the general procedure A using **3c** (177 mg, 1.00 mmol). The titled compound (217 mg, 86% yield) was obtained as a colorless oil after silica gel column chromatography.

^{1}H NMR (391.8 MHz, $CDCl_3$)

(5) J. P. Maye and E. Negishi, Tetrahedron Lett., 1993, **34,** 3359.

0.87 (t, J = 6.7 Hz, 6H, -CH_2CH_3), 0.93 (d, J = 6.7 Hz, 3H, -$CHCH_3$), 1.10–1.14 (m, 22H, overlap), 1.95 (q, J = 6.7 Hz, 2H, -C=CHCH_2-), 2.02 (m, 1H, CH_3CHC=C-), 5.22 (dd, J = 6.7, 15.3 Hz, 1H, -C=C$H$$CH_2$-), 5.32 (dt, J = 6.7, 15.3 Hz, 1H, CH_3CHCH=C-)

^{13}C NMR (98.5 MHz, $CDCl_3$)

14.3 (2C), 21.1, 22.8, 22.9, 27.5, 29.0, 29.5, 29.8 (2C), 30.0, 31.9, 32.1, 32.8, 36.9, 37.4, 128.6, 136.6

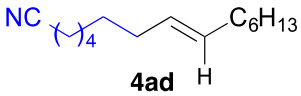
IR (neat, cm^{-1})

2956, 2922, 2853, 1457, 1377, 966, 722

Elemental analysis

Anal. calcd. for $C_{18}H_{36}$, C, 85.63; H, 14.37. Found C, 85.70; H, 14.58

Synthesis of (*E*)-undec-4-enenitrile (*4ad*)



4ad

The reaction was carried out according to the general procedure A using **3d** (190 mg, 1.00 mmol). The titled compound (199 mg, 90% yield) was obtained as a colorless oil after silica gel column chromatography.

^{1}H NMR (391.8 MHz, $CDCl_3$)

0.87 (t, 5.7 Hz, 3H, -CH_2CH_3), 1.10–1.50 (m, 9H, overlap), 1.43 (quint, J = 7.2 Hz, 2H, NC$(CH_2)_2CH_2CH_2$-), 1.64 (quint, J = 7.2 Hz, 2H, $NCCH_2CH_2CH_2$-), 1.97 (m, 4H, -CH_2CH=CHCH_2-), 2.32 (t, J = 7.2 Hz, 2H, $NCCH_2CH_2$-), 5.36 (m, 2H, -CH=CH-)

^{13}C NMR (98.5 MHz, $CDCl_3$)

14.2, 17.3, 22.8, 25.5, 28.3, 28.6, 29.0, 29.3, 29.7, 31.9, 32.5, 32.7, 120.0, 129.9, 131.0

IR (neat, cm^{-1})

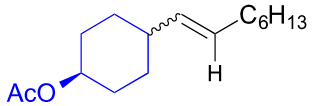
2923, 2854, 2247, 1464, 1378, 967, 724

Elemental analysis

Anal. calcd. for $C_{15}H_{27}N$, C, 81.38; H, 12.29; N, 6.33.

Found C, 81.10; H, 12.19; N, 6.54

Synthesis of 4-((*E*)-oct-1-en-1-yl)cyclohexyl acetate (*4ae*)



4ae

The reaction was carried out according to the general procedure A for 6 h using **3e** (222 mg, 1.01 mmol). The titled compound (*trans*-isomer 72.4 mg; *cis*-isomer 51.5 mg, 49% yield) was obtained as a colorless oil after GPC using toluene as the eluent.

^{1}H NMR (391.8 MHz, $CDCl_3$)

trans-isomer: 0.88 (t, J = 7.1 Hz, 3H, -CH_2CH_3), 1.13–1.42 (m, 12H, overlap), 1.74–1.80 (m, 2H, -OCH$(CH_2CH_2)_2$-), 1.85–2.00 (m, 5H, overlap), 2.03 (s, 3H, -$COCH_3$), 4.65 (tt, J = 4.7, 10.6 Hz, 1H, -OC$H$$(CH_2CH_2)_2$-), 5.30 (dd, J = 5.9, 15.5 Hz, 1H, -CHCH=C$H$$CH_2$-), 5.39 (dt, 5.8, 15.5 Hz, 1H, -CHCH=CHCH_2-);

cis-isomer: 0.88 (t, J = 7.1 Hz, 3H, -CH_2CH_3), 1.28–1.38 (m, 14H, overlap), 1.80–1.86 (m, 2H, -OCH(CH_2CH_2)$_2$-), 1.96–2.03 (m, 3H, -CHCH=CHCH_2-), 2.05 (s, 3H, -COCH_3), 4.94–5.00 (m, 1H, -OCH(CH_2CH_2)$_2$-), 5.39–5.41 (m, 2H, -CHCH=$CH$$CH_2$-)

^{13}C NMR (98.5 MHz, $CDCl_3$)

trans-isomer: 14.2, 21.6, 22.8, 28.9, 29.7, 31.1 (2C), 31.5 (2C), 31.9, 32.7, 39.8, 73.3, 129.0, 134.7, 170.8

cis-isomer: 14.2, 21.6, 22.8, 27.8 (2C), 28.9, 29.4 (2C), 29.7, 31.9, 32.8, 39.1, 70.1, 128.9, 135.0, 170.8

IR (neat, cm^{-1})

trans-isomer: 2925, 2856, 1734, 1452, 1369, 1237, 1031, 968, 733

cis-isomer: 2926, 2856, 1736, 1445, 1368, 1239, 1034, 966, 733

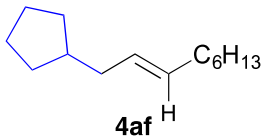
HRMS (FAB)

trans-isomer: m/z [M–H]$^+$ calcd for $C_{16}H_{27}O_2$: 251.2011; found: 251.2016.

HRMS (EI)

cis-isomer: m/z [M]$^+$ calcd for $C_{16}H_{28}O_2$: 252.2089; found: 252.2089.

Synthesis of (*E*)-non-2-en-1-ylcyclopentane (*4af*)



4af

The reaction was carried out according to the general procedure A for 6 h using **3f** (163 mg, 1.00 mmol). The titled compound (89.3 mg, 46% yield) was obtained as a colorless oil after GPC using toluene as the eluent.

^{1}H NMR (391.8 MHz, $CDCl_3$)

0.88 (t, J = 7.5 Hz, 3H, -CH_2CH_3), 1.07–1.16 (m, 2H, -CH_2CH_2CH-(^{c}Pent)), 1.26–1.35 (m, 8H, overlap), 1.45–1.52 (m, 2H, -CH_2CH_2CH-(^{c}Pent)), 1.56–1.63 (m, 2H, -CH_2CH_2CH-(^{c}Pent)), 1.67–1.75 (m, 2H, -CH_2CH_2CH-(^{c}Pent)), 1.75–1.87 (m, 1H, -CH_2CH_2CH-(^{c}Pent)), 1.95–1.99 (m, 4 H, -CH_2CH=CHCH_2-), 5.38–5.40 (m, 2H, -CH=CH-)

^{13}C NMR (98.5 MHz, $CDCl_3$)

14.3, 22.8, 25.3 (2C), 29.0, 29.8, 31.9, 32.4 (2C), 32.8, 39.2, 40.3, 129.8, 131.0

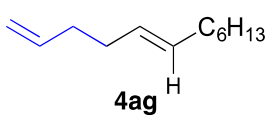
IR (neat, cm^{-1})

2952, 2924, 2855, 1453, 1243, 966

HRMS (EI)

m/z [M]$^+$ calcd for $C_{14}H_{26}$: 194.2035; found: 194.2027.

Synthesis of (*E*)-dodeca-1,5-diene (*4ag*)



4ag

The reaction was carried out according to the general procedure A at 80 ºC for 6 h using **3g** (137 mg, 1.01 mmol). The titled compound (27.9 mg, 17% yield) was obtained as a colorless oil after silica gel column chromatography using pentane as the eluent and GPC using chloroform as the eluent.

^{1}H NMR (391.8 MHz, $CDCl_3$)

0.88 (t, J = 7.1 Hz, 3H, -CH_2CH_3), 1.25–1.36 (m, 8H, overlap), 1.94–1.99 (m, 2H, CH_2=HCCH_2CH_2-), 2.03–2.12 (m, 4H, -CH_2CH_2CH=CHCH_2CH_2-), 4.94 (m, 1H, CH_2=CH-), 5.00 (m, 1H, CH_2=CH-), 5.35–5.46 (m, 2H, -CH_2CH=CHCH_2-), 5.81 (ddt, J = 16.9, 9.8, 5.8 Hz, 1H, CH_2=CHCH_2-)

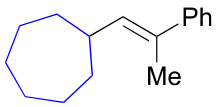
^{13}C NMR (98.5 MHz, $CDCl_3$)

14.3, 22.8, 29.0, 29.7, 31.9, 32.2, 32.7, 34.0, 114.6, 129.5, 131.1, 138.7

IR (neat, cm^{-1})

2958, 2924, 2854, 1641, 1452, 1378, 966, 910

Synthesis of (*E*)-(2-phenylprop-1-en-1-yl)cycloheptane (*4eb*)



4eb

The reaction was carried out according to the general procedure B using ethynylbenzene (105 mg, 1.02 mmol) and **3b–Br** (87.9 mg, 0.50 mmol). The titled compound (52.6 mg, 49% yield) was obtained as a colorless oil after silica gel column chromatography.

^{1}H NMR (391.8 MHz, $CDCl_3$)

1.34–1.79 (m, 12H, -CH_2- (^{c}Hep)), 2.03 (s, 3H, -CH=CPhCH_3), 2.48–2.57 (m, 1H, -CH_2CHCH_2-), 5.71 (d, J = 9.0 Hz, 1H, -CHCH=CPh(CH_3)), 7.20 (t, J = 7.8 Hz, 1H, Ph (4-position)), 7.29 (t, J = 7.8 Hz, 2H, Ph (3-position)), 7.38 (d, J = 1.2 Hz, 2H, Ph (2-position))

^{13}C NMR (98.5 MHz, $CDCl_3$)

15.9, 26.7 (2C), 28.6 (2C), 35.1 (2C), 39.4, 125.8 (2C), 126.5, 128.2 (2C), 131.6, 135.7, 144.3

IR (neat, cm^{-1})

2917, 2851, 1598, 1494, 1458, 1444, 1379, 1027, 880

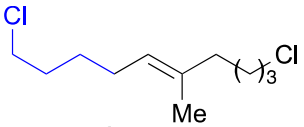
Elemental analysis

Anal. calcd. for $C_{16}H_{22}$, C, 89.65; H, 10.35. Found C, 89.38; H, 10.45

HRMS (FAB)

$[M]^+$ calcd for $C_{16}H_{22}$: 214.1722; found: 214.1720

Synthesis of (*E*)-1,10-dichloro-5-methyldec-5-ene (*4fh*)



4fh

The reaction was carried out according to the general procedure B using 6-chloro-1-hexyne (117 mg, 1.00 mmol) and **3h** (171 mg, 0.67 mmol). The titled compound (119 mg, 78% yield) was obtained as a colorless oil after silica gel column chromatography.

^{1}H NMR (391.8 MHz, $CDCl_3$)

1,43–1.60 (m, 7H, overlap), 1.74 (m, 4H, ClCH_2CH_2-, -C$H_2$$CH_2$Cl), 1.94 (m, 4H, -$CH_2CH_2$CH=C($CH_3$)C$H_2$$CH_2$-), 3.52 (t, J = 6.8 Hz, 4H, ClC$H_2$$CH_2$-, -$CH_2CH_2$Cl), 5.11 (t, J = 7.0 Hz, 1H, -CH=C(CH_3)-)

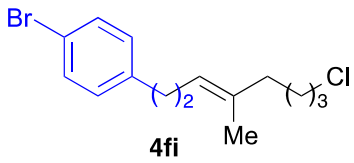
^{13}C NMR (98.5 MHz, $CDCl_3$)

15.9, 25.2, 27.2 (2C), 32.2, 32.3, 38.9, 45.2 (2C), 124.5, 135.2

Elemental analysis

Anal. calcd. for $C_{11}H_{20}Cl_2$, C, 59.20; H, 9.03. Found C, 59.10; H, 8.79

Synthesis of (*E*)-1-bromo-4-(8-chloro-4-methyloct-3-en-1-yl)benzene (*4fi*)



4fi

The reaction was carried out according to the general procedure B using 6-chloro-1-hexyne (117 mg, 1.00 mmol) and **3i** (157 mg, 0.67 mmol). The titled compound (160 mg, 76% yield) was obtained as a colorless oil after silica gel column chromatography.

^{1}H NMR (391.8 MHz, $CDCl_3$)

1.45–1.58 (m, 5H, -CH=C(C*H*$_3$)CH$_2$C*H*$_2$-), 1.68 (quint, *J* = 6.7 Hz, 2H, -CH$_2$C*H*$_2$CH$_2$Cl), 1.98 (t, *J* = 7.2 Hz, 2H, -CH=C(CH$_3$)C*H*$_2$-), 2.28 (dt, *J* = 7.2, 7.6 Hz, 2H, -C*H*$_2$CH=C(CH$_3$)-), 2.59 (t, *J* = 7.6 Hz, 2H, ArC*H*$_2$-), 3.52 (t, *J* = 6.7 Hz, 2H, -C*H*$_2$Cl), 5.12 (t, *J* = 7.2 Hz, 1H, -C*H*=C(CH$_3$)-), 7.03 (d, *J* = 8.5 Hz, 2H, Ar (3-position)), 7.37 (d, *J* = 8.5 Hz, 2H, Ar (2-position))

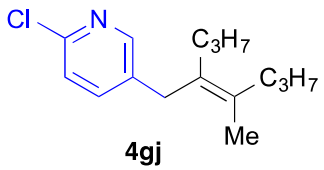
^{13}C NMR (98.5 MHz, $CDCl_3$)

15.9, 25.1, 29.8, 32.1, 35.6, 38.9, 45.2, 119.5, 123.8, 130.4 (2C), 131.4 (2C), 135.7, 141.3

Elemental analysis

Anal. calcd. for $C_{15}H_{20}ClBr$, C, 57.07; H, 6.39. Found C, 57.29; H, 6.56

Synthesis of 2-chloro-5-(3-methyl-2-propylhex-2-en-1-yl)pyridine (*4gj*)



4gj

The reaction was carried out according to the general procedure B. The carboalumination using 4-octyne (0.75 mmol, 82.1 mg) and the coupling reaction of **3j** (80.1 mg, 0.49 mmol) were conducted for 60 ºC for 24 h and at 80 °C for 15 h respectively. The titled compound (89.6 mg, 72% yield, *E*/*Z* = 64/36) was obtained as a brown oil after silica gel column chromatography hexane/EtOAc (10/1). Stereochemistry of isomers was determined by a NOE correlation.

^{1}H NMR (391.8 MHz, $CDCl_3$)

E/*Z* mixture:

0.84–0.94 (m, 6H, -CH$_2$C*H*$_3$), 1.25–1.37 (m, 2H, -C=C(CH$_3$)CH$_2$C*H*$_2$CH$_3$), 1.39–1.49 (m, 2H, CH$_3$C*H*$_2$CH$_2$C=C(CH$_3$)-), 1.70 (s, 3H, -C=C(C*H*$_3$)-[(*E*)-product]), 1.72 (s, 3H, -C=C(C*H*$_3$)-[(*Z*)-product]), 1.88–1.95 (m, 2H, CH$_3$CH$_2$C*H*$_2$C=C(CH$_3$)-), 2.04–2.10 (m, 2H, -C=C(CH$_3$)C*H*$_2$CH$_2$-), 3.36 (s, 2H, ArC*H*$_2$C=C-), 7.21 (d, *J* = 8.2 Hz, 1H, Ar (3-position)), 7.40 (d, *J* = 8.2 Hz, 1H, Ar (4-position)), 8.17 (s, 1H, Ar ([(*E*)-product], 6-position)), 8.18 (s, 1H, Ar ([(*Z*)-product], 6-position))

^{13}C NMR (98.5 MHz, $CDCl_3$)

E/*Z* mixture: 14.2 (2C), 14.3, 14.4, 18.2, 18.7, 21.7, 21.8 (2C), 22.2, 33.9, 34.2 (2C), 34.3, 36.4, 36.9, 123.9 (2C), 129.7, 130.0, 132.6 (2C), 135.6, 135.7, 138.8, 138.9, 148.9 (2C) 149.8, 149.9

IR (neat, cm^{-1})

E/*Z* mixture: 2957, 2930, 2870, 1583, 1563, 1456, 1379, 1102, 812

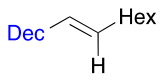
Elemental analysis

Anal. calcd. for $C_{15}H_{22}ClN$, C, 71.55; H, 8.81. Found C, 71.35; H, 9.01

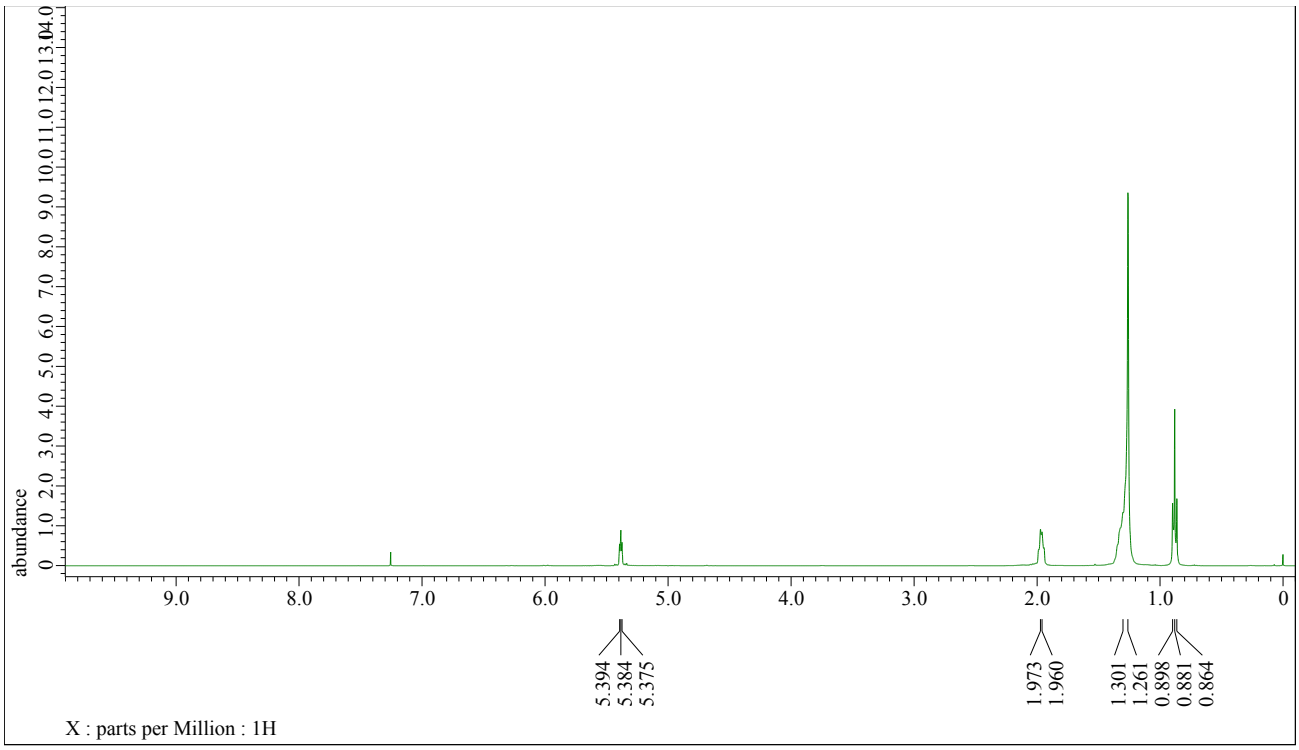
HRMS (FAB)

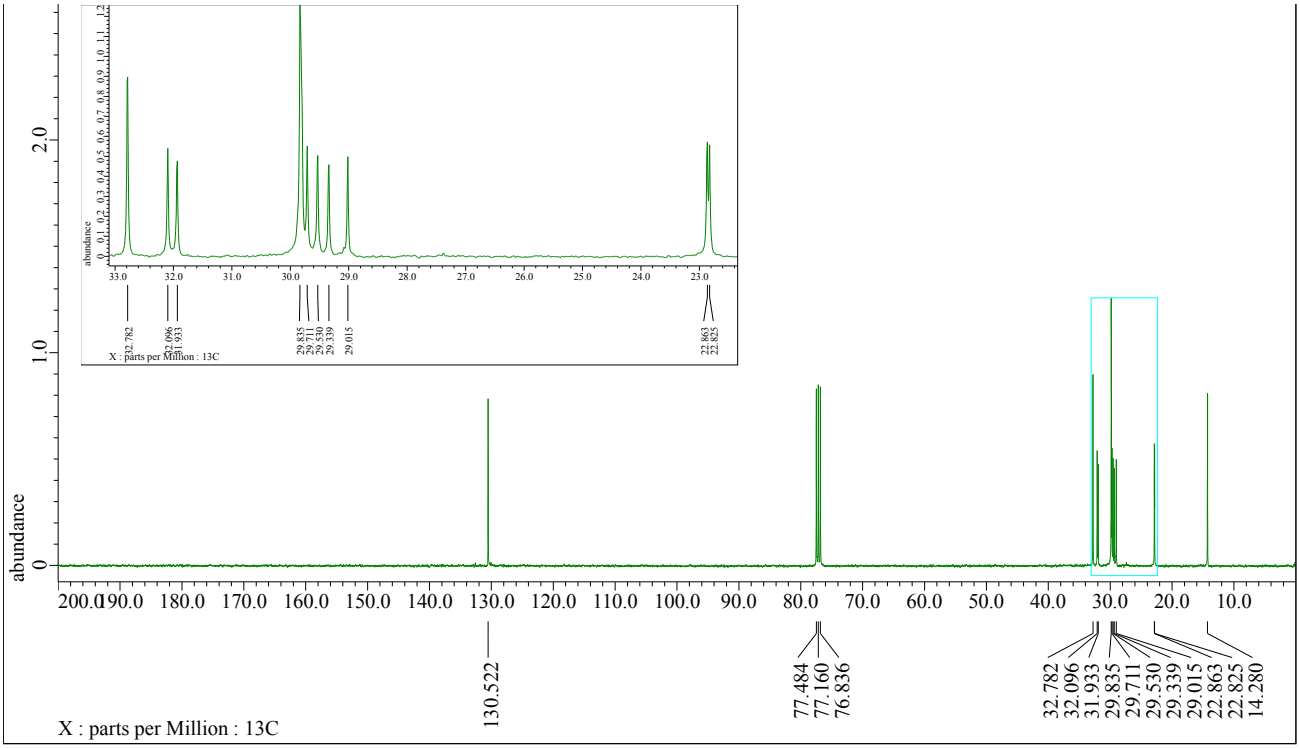
m/z $[M+H]^+$ calcd for $C_{15}H_{23}ClN$: 252.1519; found: 252.1517

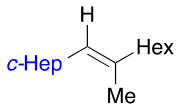
^{1}H and ^{13}C NMR spectra of the compounds



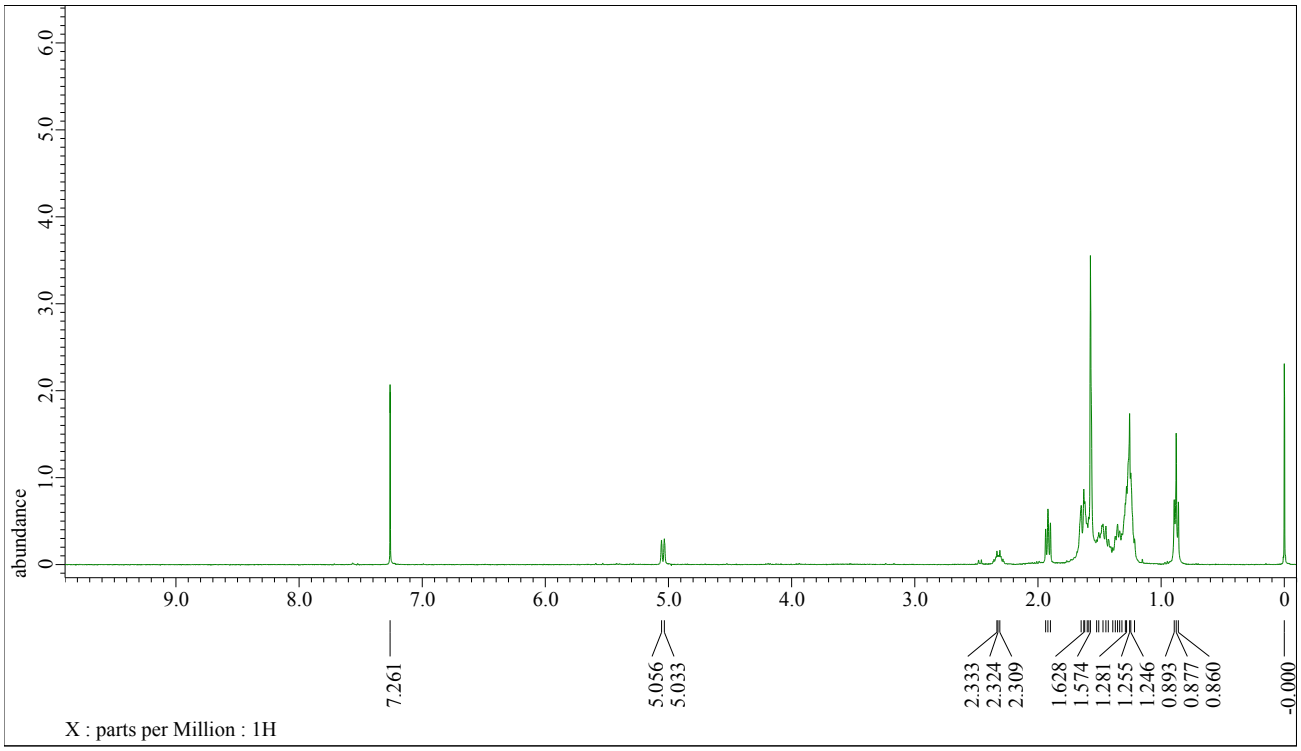
4aa






H
c-Hep
Hex
Me

4cb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4.0
3.0
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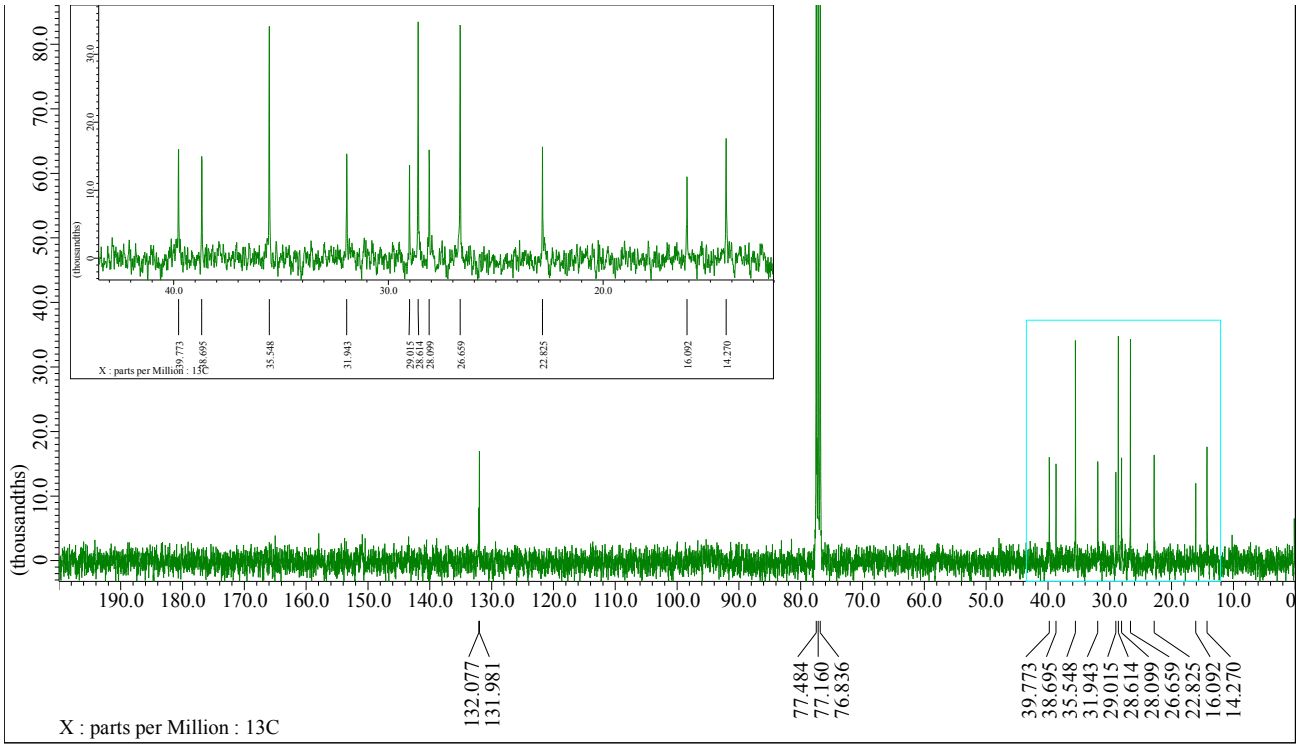
1.0
0
7.261
5.056
5.033
2.333
2.324
2.309
1.628
1.574
1.281
1.255
1.246
0.893
0.877
0.860
-0.000
X : parts per Million : 1H


(thousandths)
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130.0
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110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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131.981
77.484
77.160
76.836
39.773
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28.099
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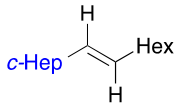
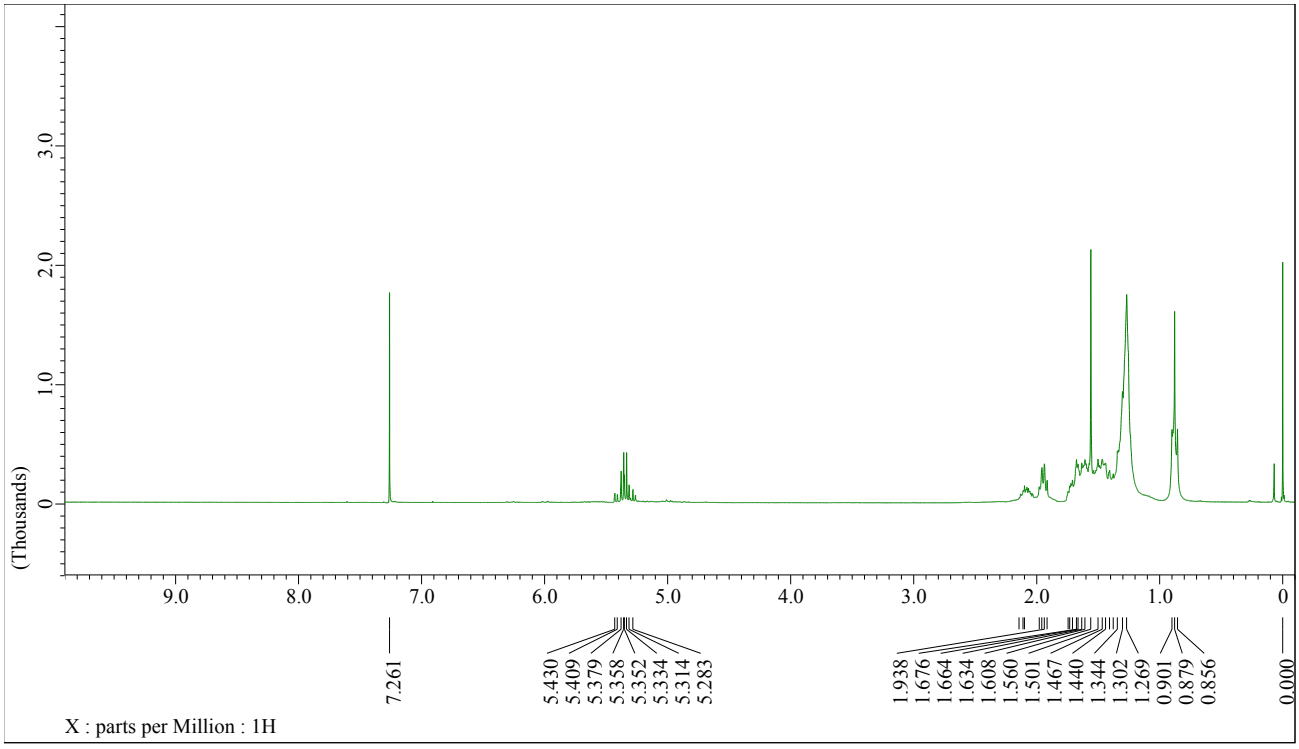
16.092
14.270
X : parts per Million : 13C


H
c-Hep
Hex
H

4ab


(Thousands)
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3.0
2.0
1.0
0
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5.379
5.358
5.352
5.334
5.314
5.283
1.938
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1.664
1.634
1.608
1.560
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1.269
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0.879
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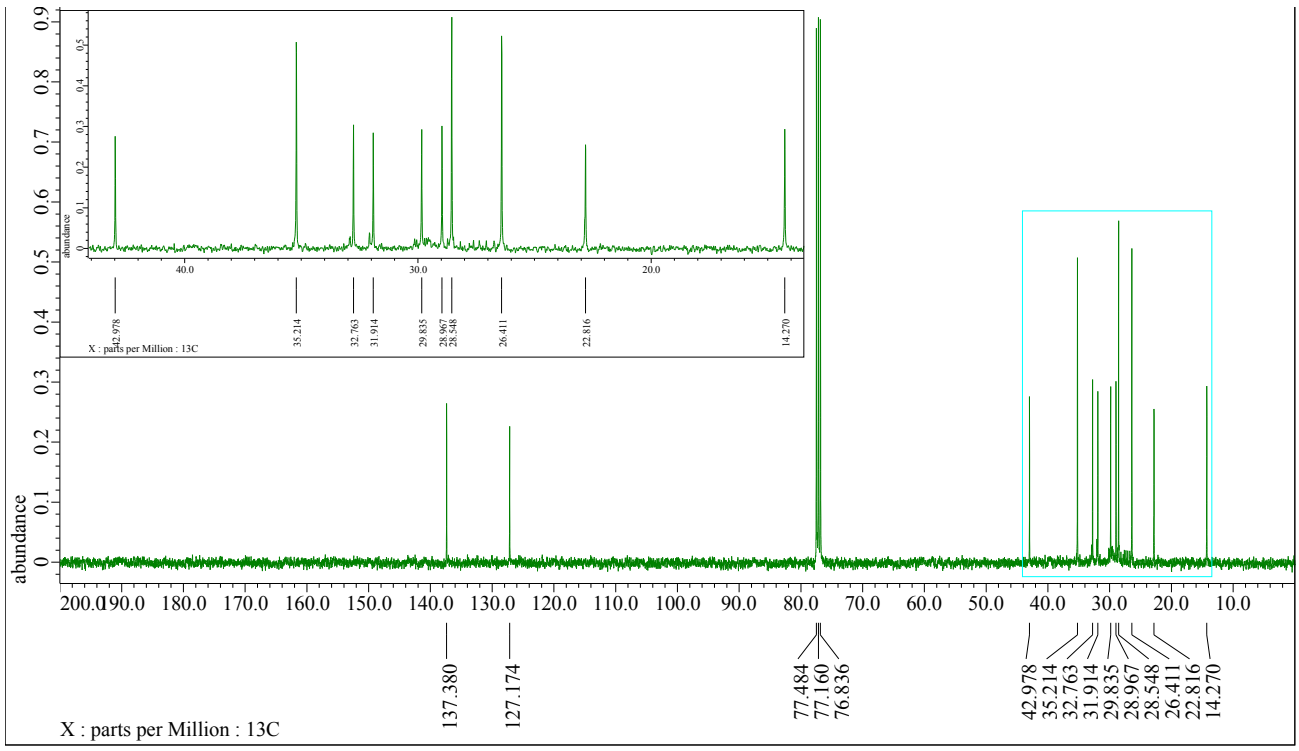
0.000
X : parts per Million : 1H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0.4
0.3
0.2
0.1
0
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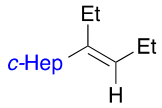
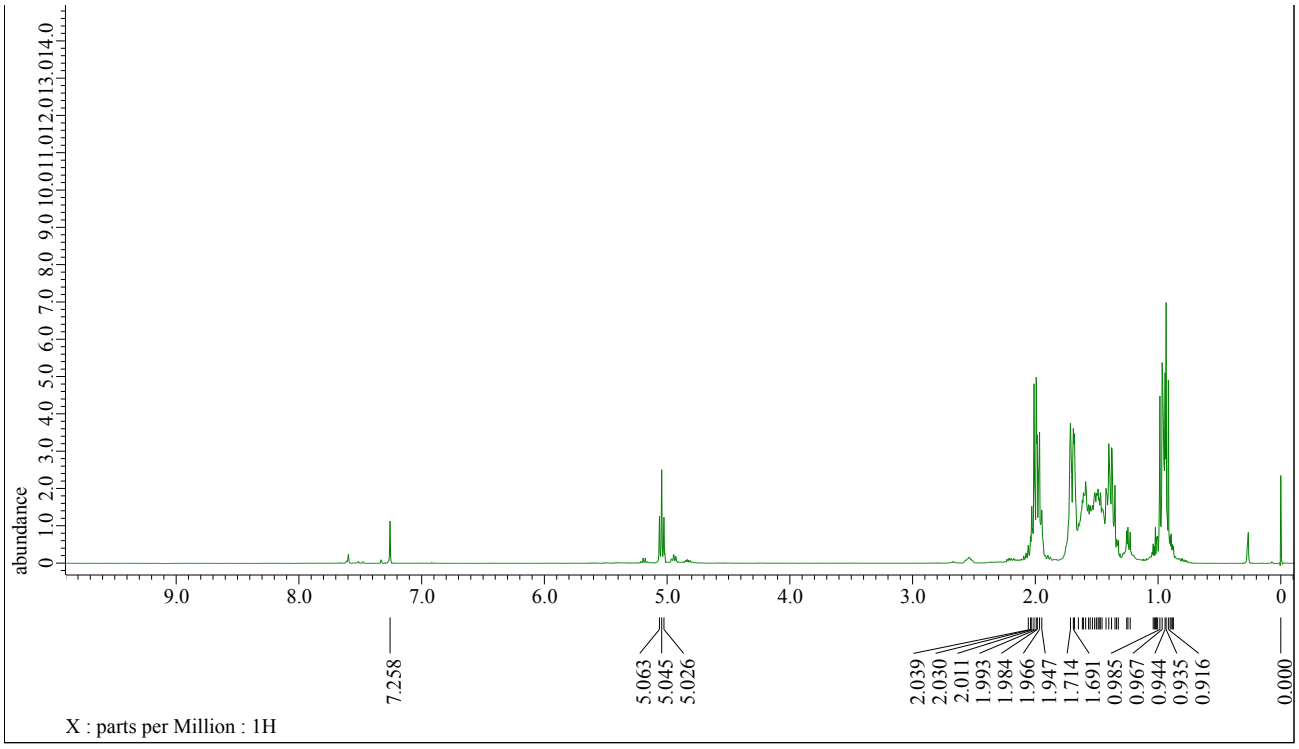
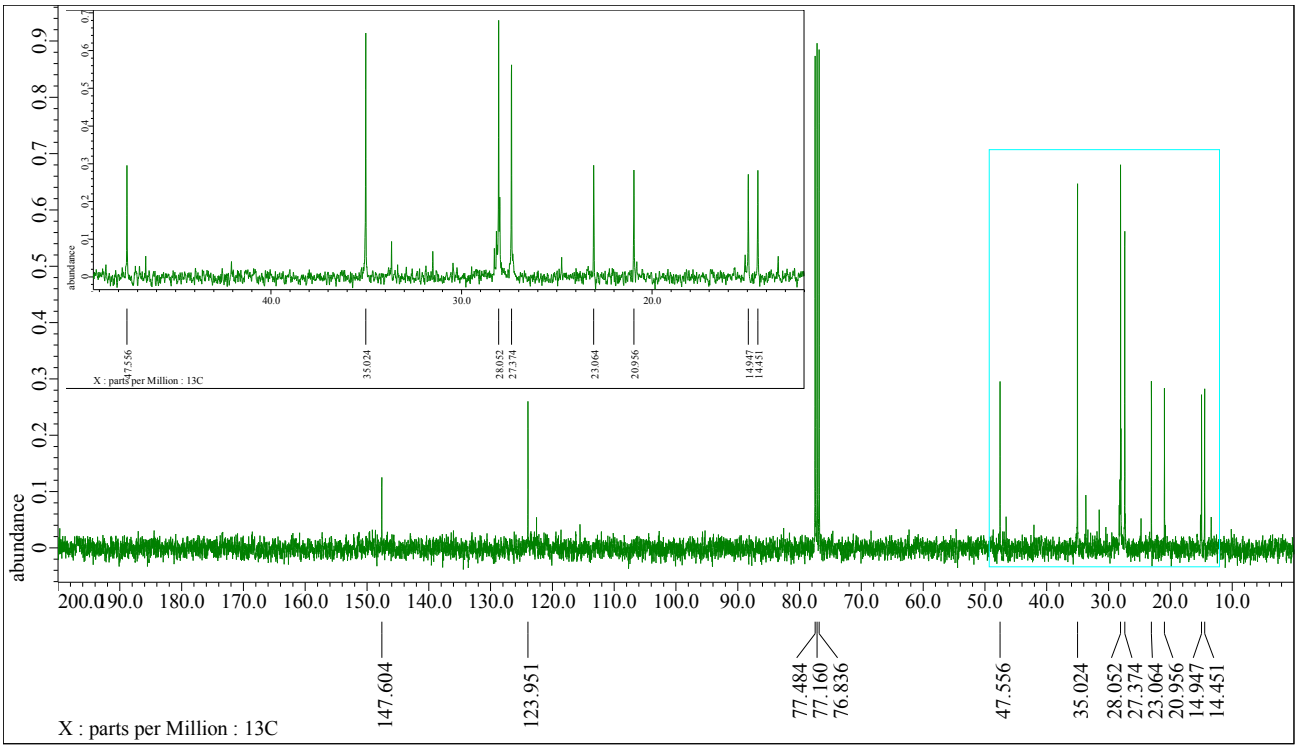
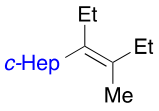
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
137.380
127.174
77.484
77.160
76.836
42.978
35.214
32.763
31.914
29.835
28.967
28.548
26.411
22.816
14.270
X : parts per Million : 13C


Et
c-Hep
Et
H

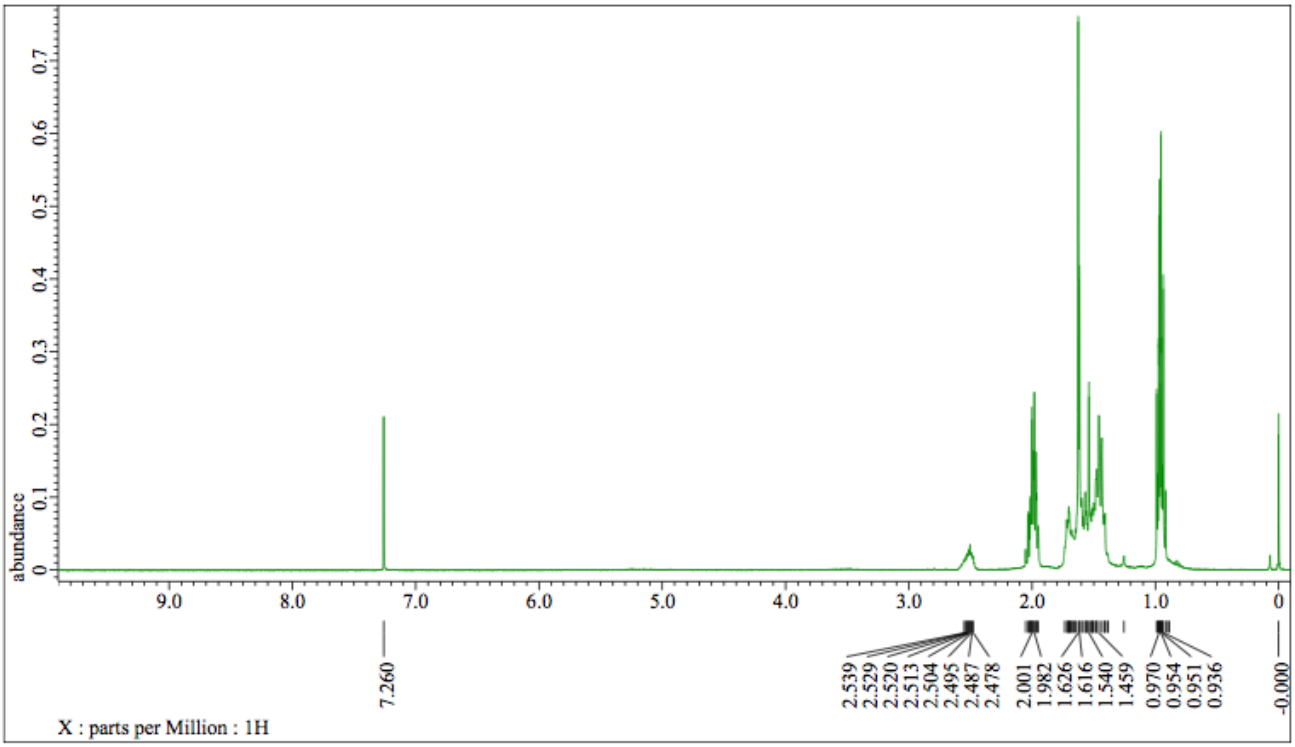
4bb

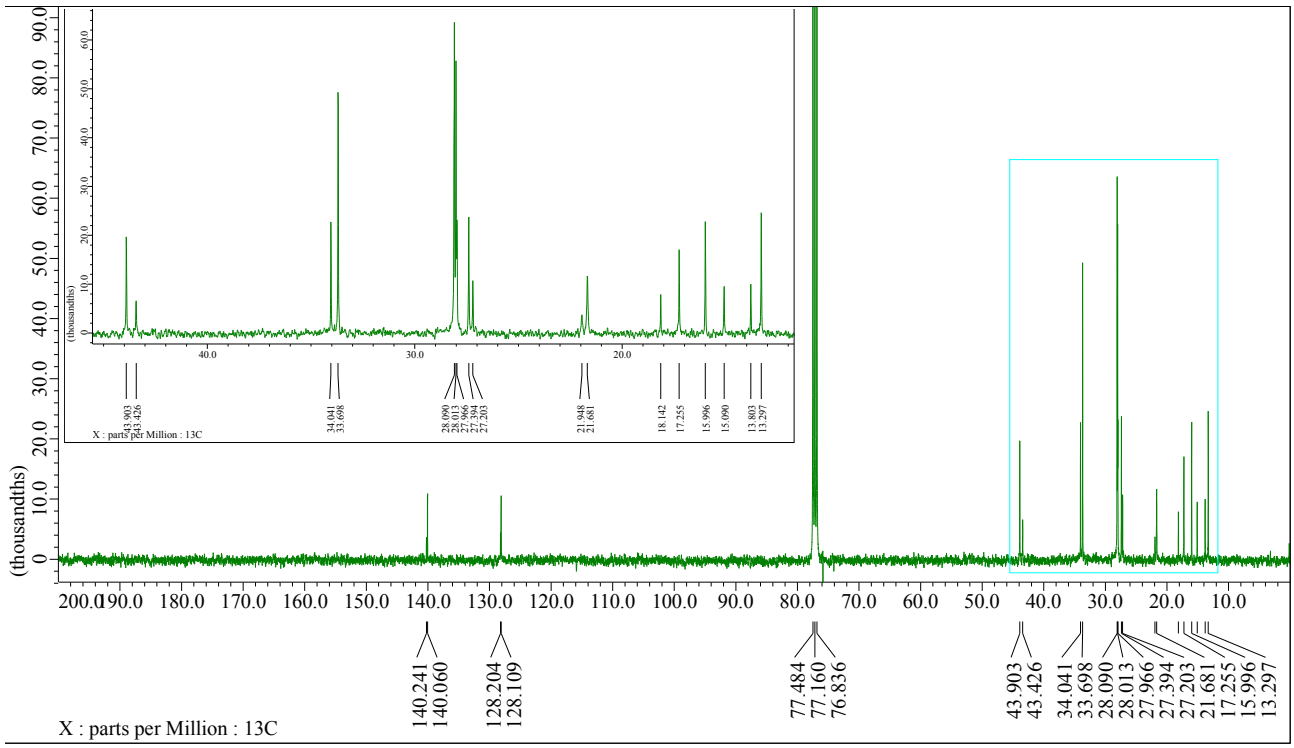

abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.258
5.063
5.045
5.026
2.039
2.030
2.011
1.993
1.984
1.966
1.947
1.714
1.691
0.985
0.967
0.944
0.935
0.916
0.000
X : parts per Million : 1H

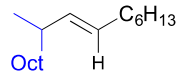

abundance
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
147.604
123.951
77.484
77.160
76.836
47.556
35.024
28.052
27.374
23.064
20.956
14.947
14.451
X : parts per Million : 13C


Et
c-Hep
Et
Me

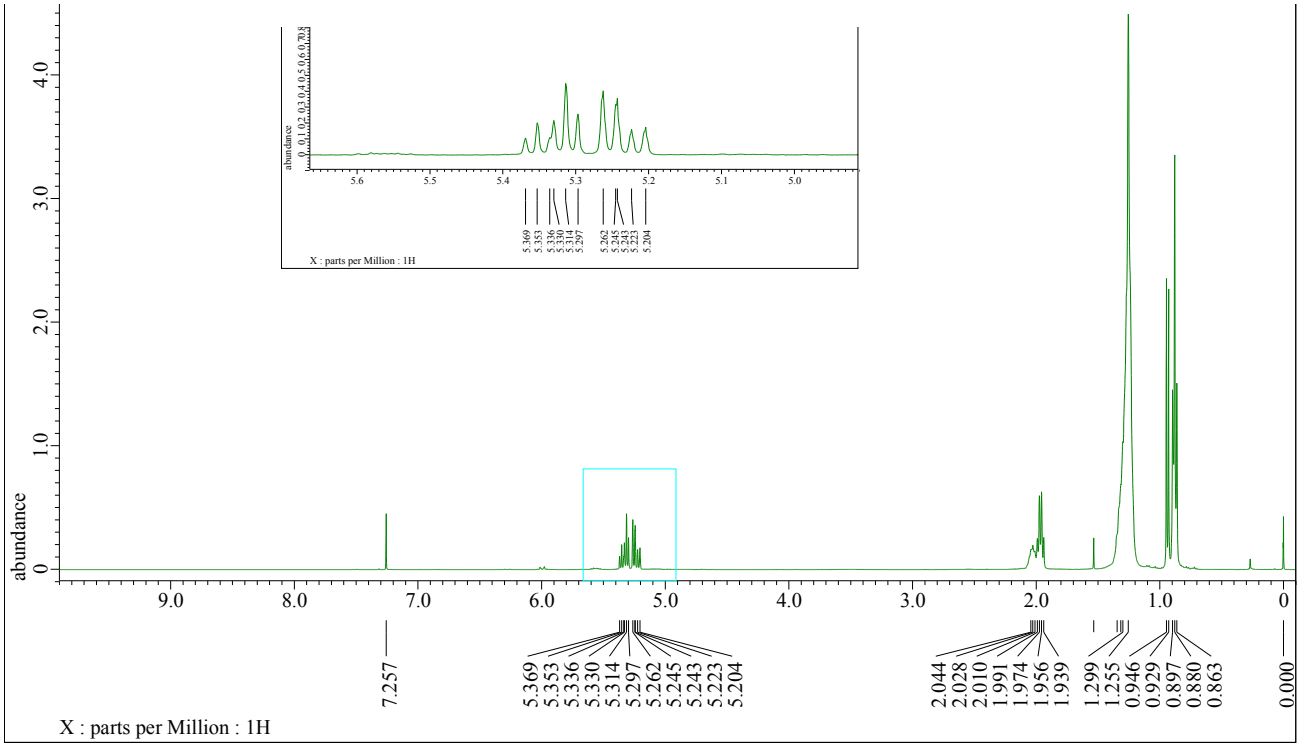
4db

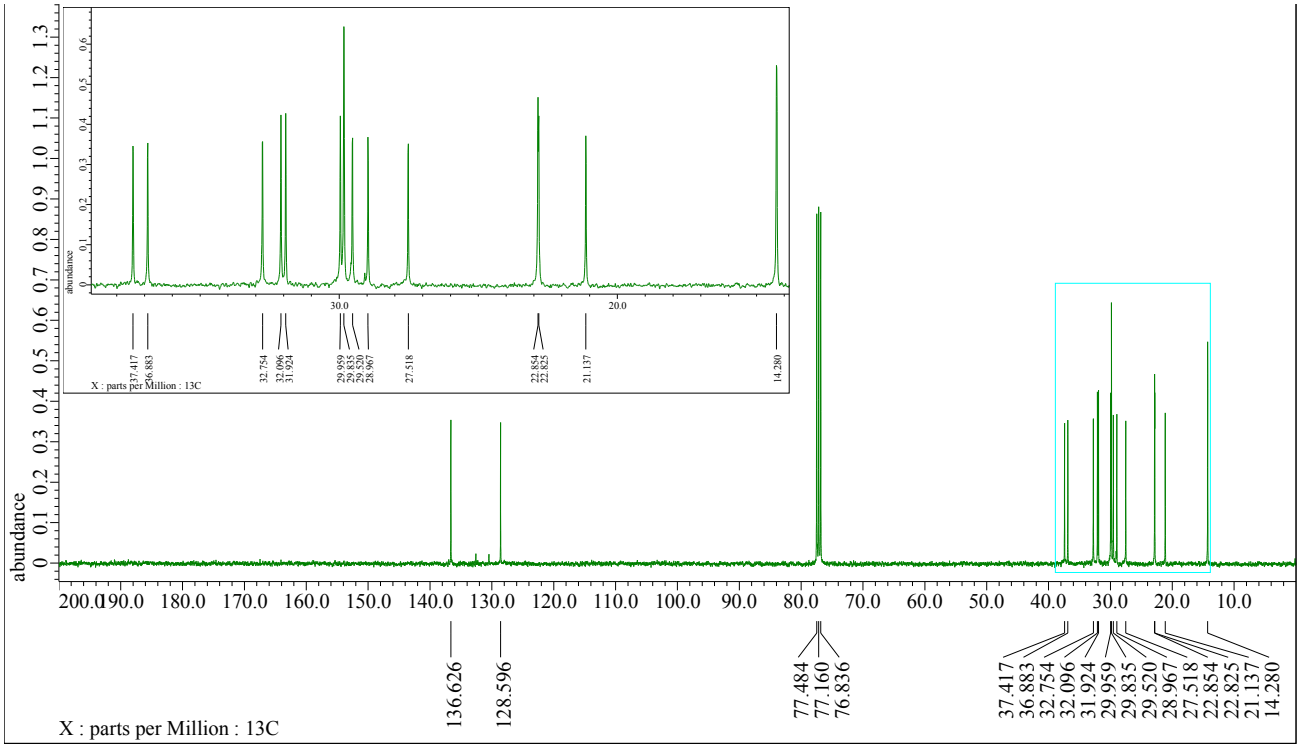

abundance
X : parts per Million : 1H
7.260
2.539
2.529
2.520
2.513
2.504
2.495
2.487
2.478
2.001
1.982
1.626
1.616
1.540
1.459
0.970
0.954
0.951
0.936
-0.000

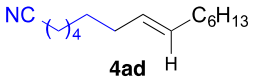

(thousandths)
X : parts per Million : 13C
140.241
140.060
128.204
128.109
77.484
77.160
76.836
43.903
43.426
34.041
33.698
28.090
28.013
27.966
27.394
27.203
21.681
17.255
15.996
13.297


C6H13
Oct
H

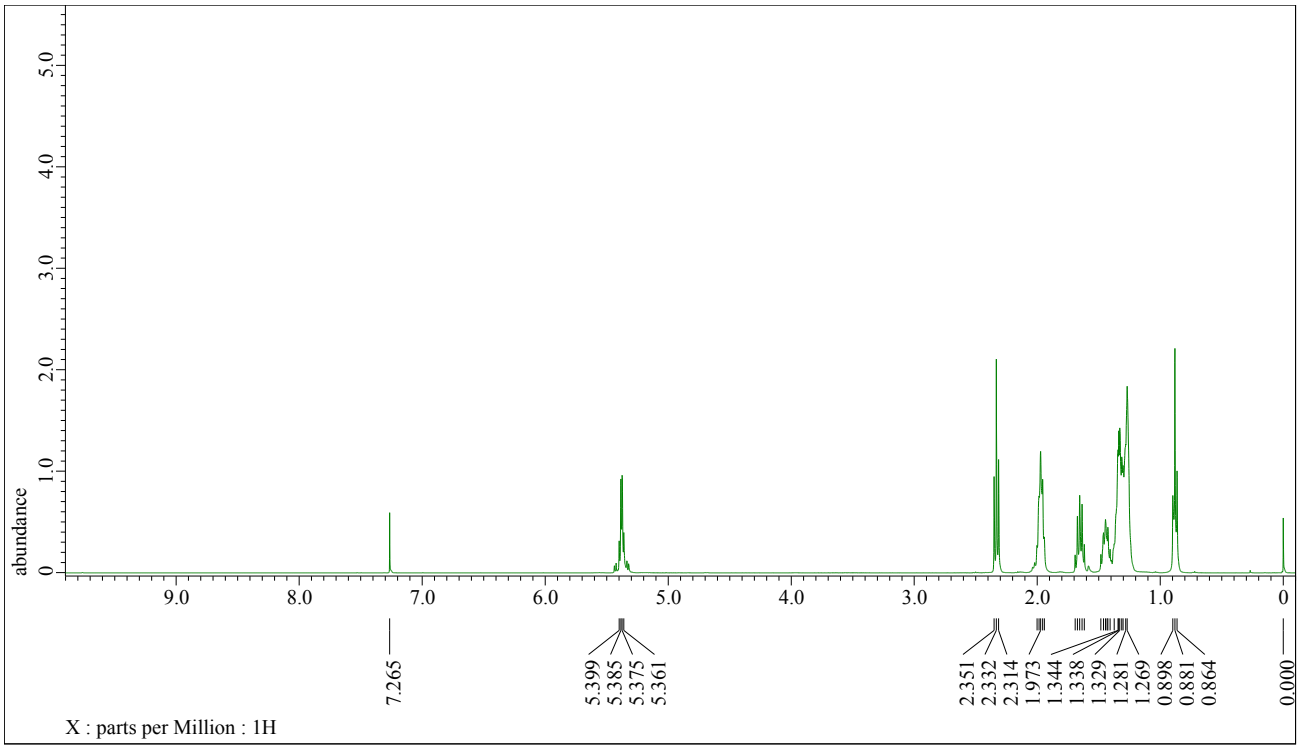
4ac

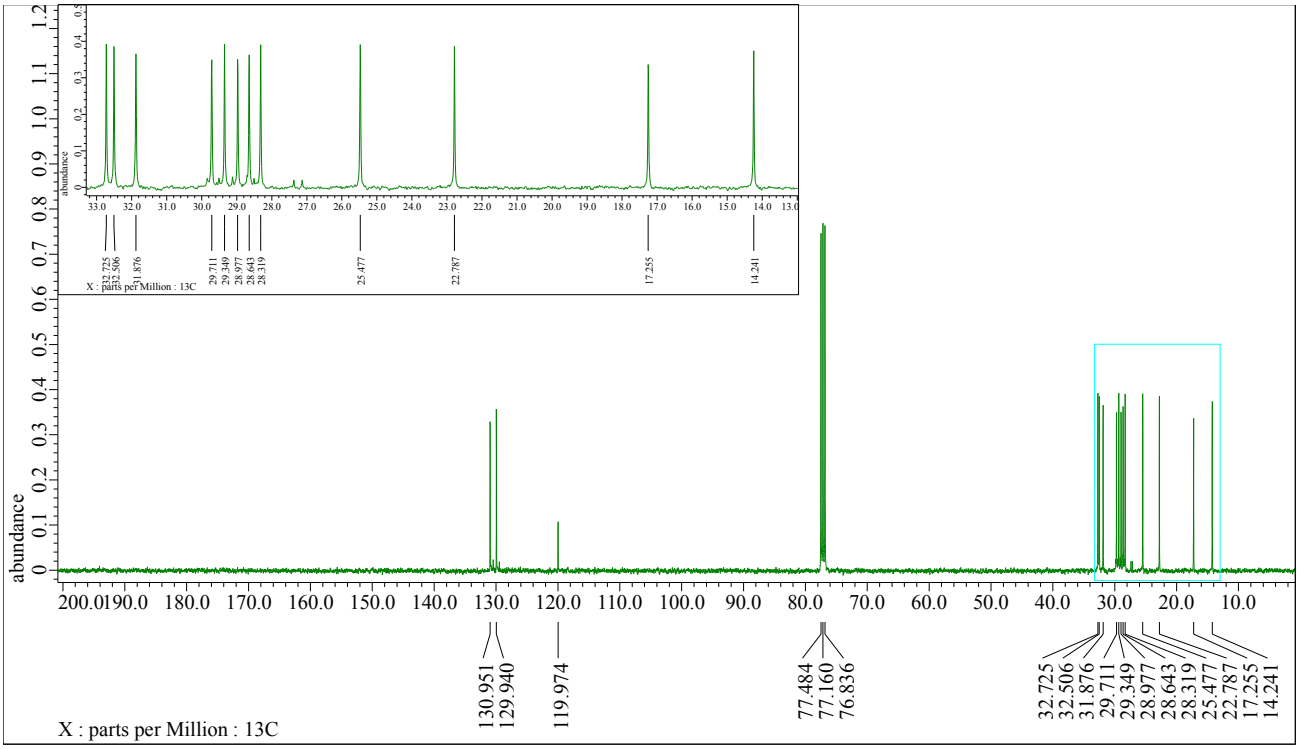

abundance
X : parts per Million : 1H
7.257
5.369
5.353
5.336
5.330
5.314
5.297
5.262
5.245
5.243
5.223
5.204
2.044
2.028
2.010
1.991
1.974
1.956
1.939
1.299
1.255
0.946
0.929
0.897
0.880
0.863
0.000

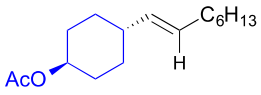

abundance
X : parts per Million : 13C
136.626
128.596
77.484
77.160
76.836
37.417
36.883
32.754
32.096
31.924
29.959
29.835
29.520
28.967
27.518
22.854
22.825
21.137
14.280


NC
4
C6H13
H

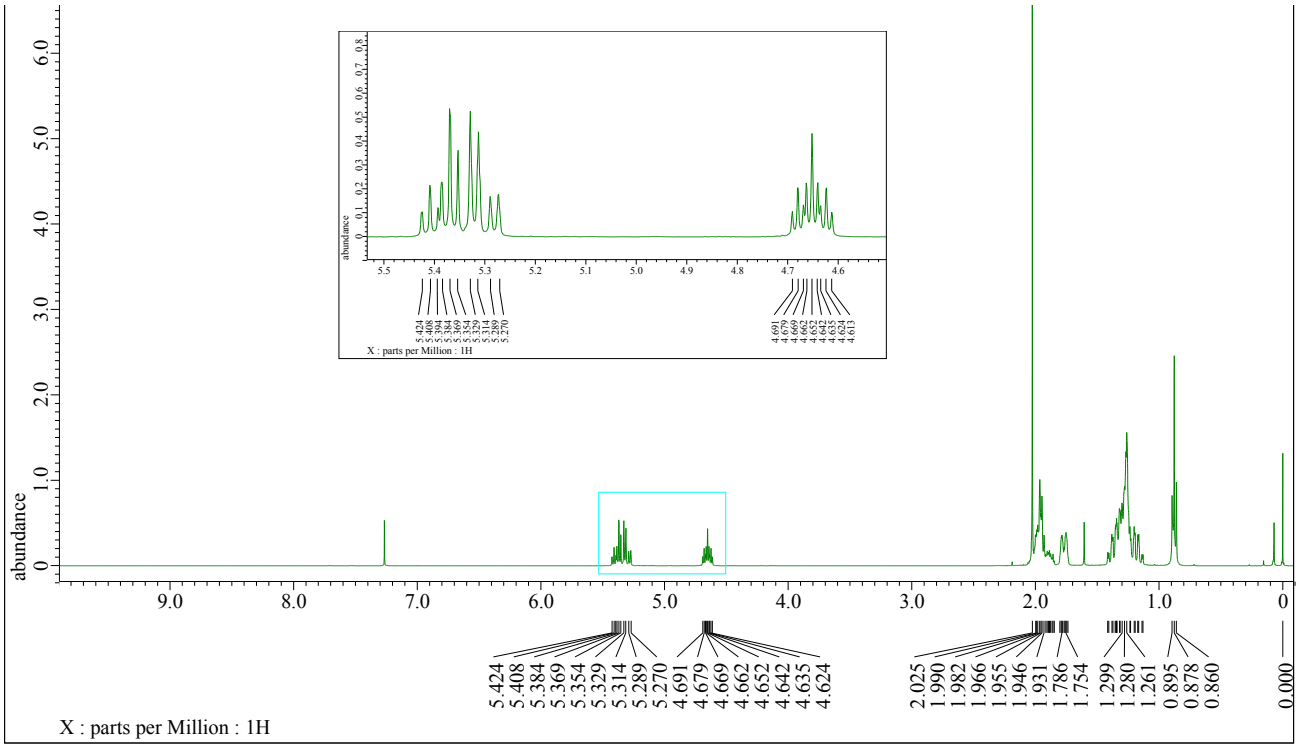
4ad

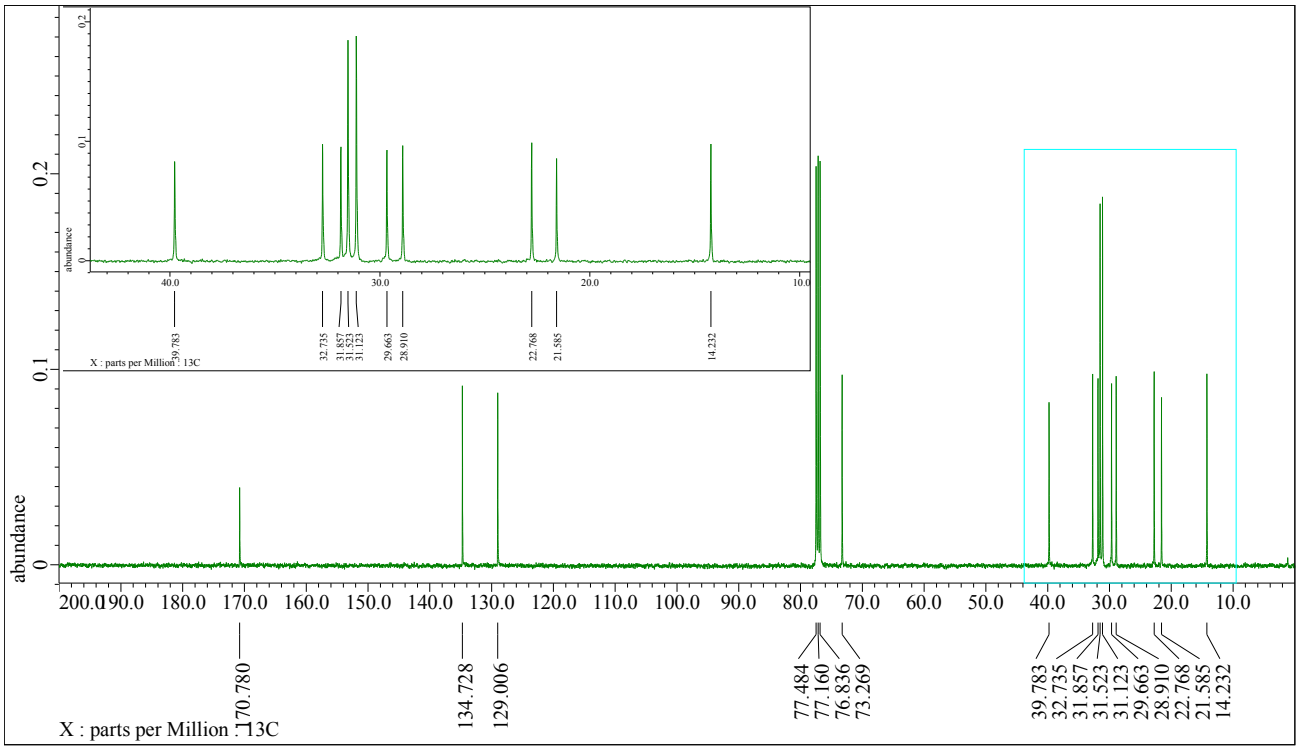

abundance
X : parts per Million : 1H
7.265
5.399
5.385
5.375
5.361
2.351
2.332
2.314
1.973
1.344
1.338
1.329
1.281
1.269
0.898
0.881
0.864
0.000

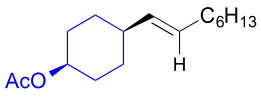

abundance
X : parts per Million : 13C
130.951
129.940
119.974
77.484
77.160
76.836
32.725
32.506
31.876
29.711
29.349
28.977
28.643
28.319
25.477
22.787
17.255
14.241


AcO
C_6H_{13}
H

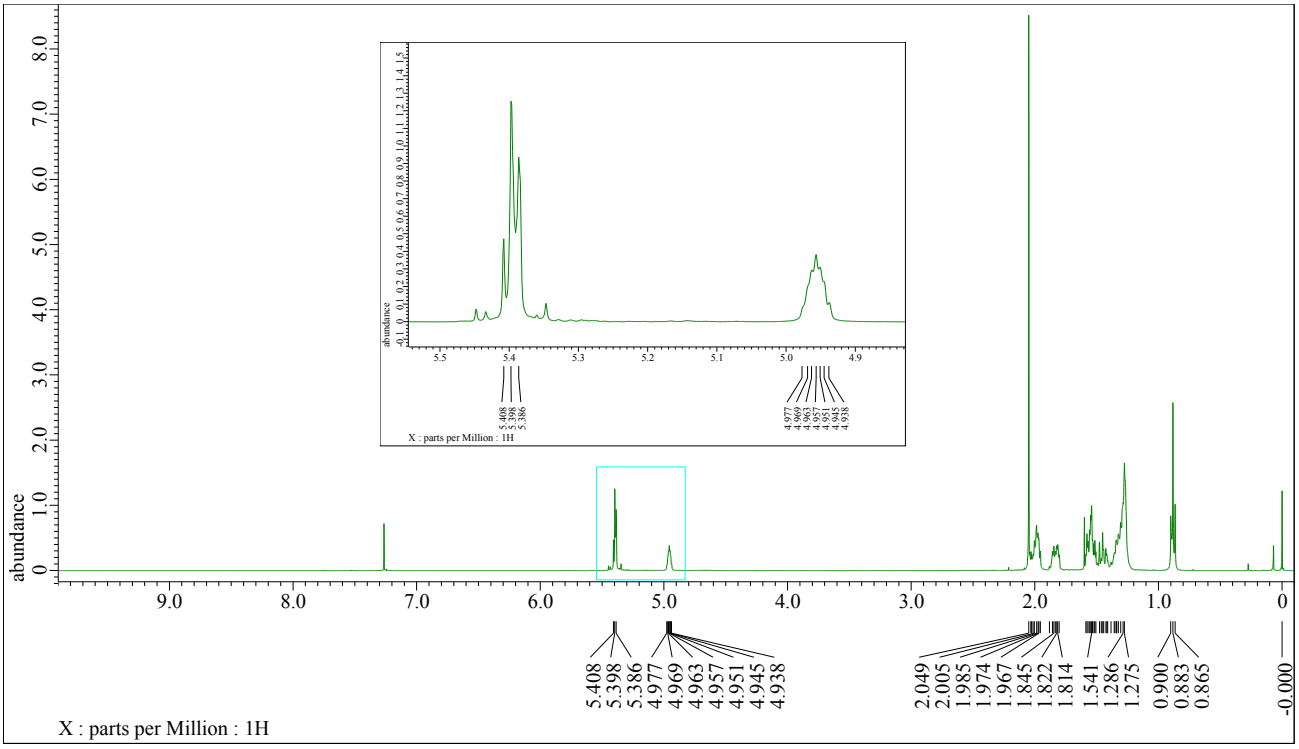
***trans*-4ae**

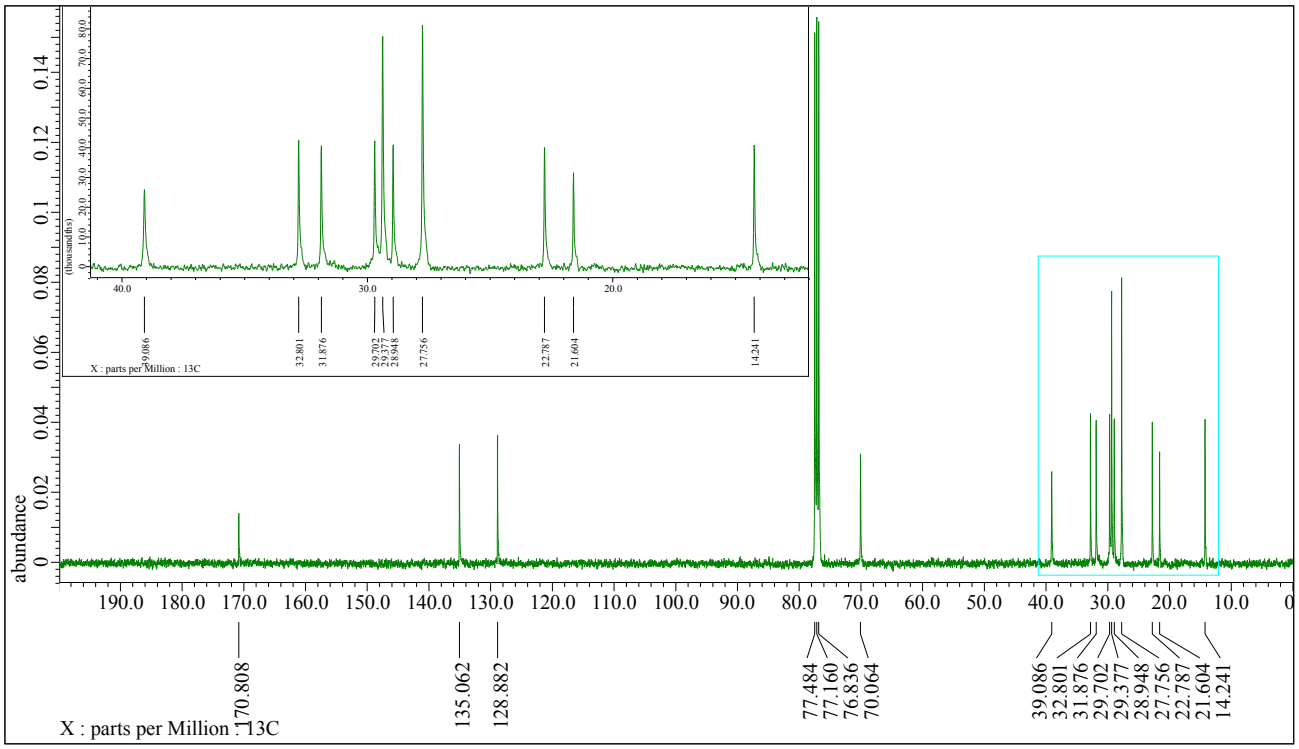

abundance
X : parts per Million : 1H
5.424
5.408
5.384
5.369
5.354
5.329
5.314
5.289
5.270
4.691
4.679
4.669
4.662
4.652
4.642
4.635
4.624
2.025
1.990
1.982
1.966
1.955
1.946
1.931
1.786
1.754
1.299
1.280
1.261
0.895
0.878
0.860
0.000

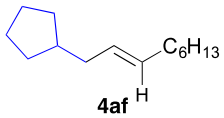

abundance
X : parts per Million : 13C
170.780
134.728
129.006
77.484
77.160
76.836
73.269
39.783
32.735
31.857
31.523
31.123
29.663
28.910
22.768
21.585
14.232


AcO
C6H13
H

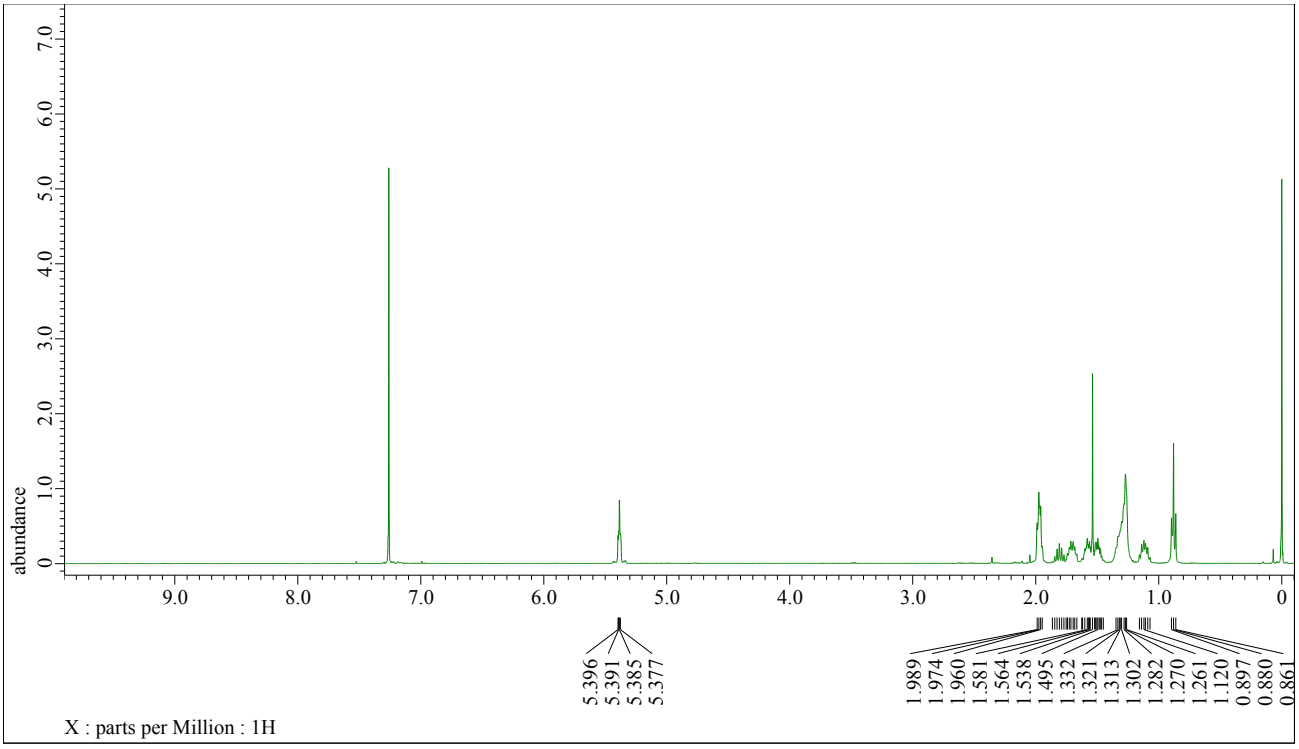
***cis*-4ae**

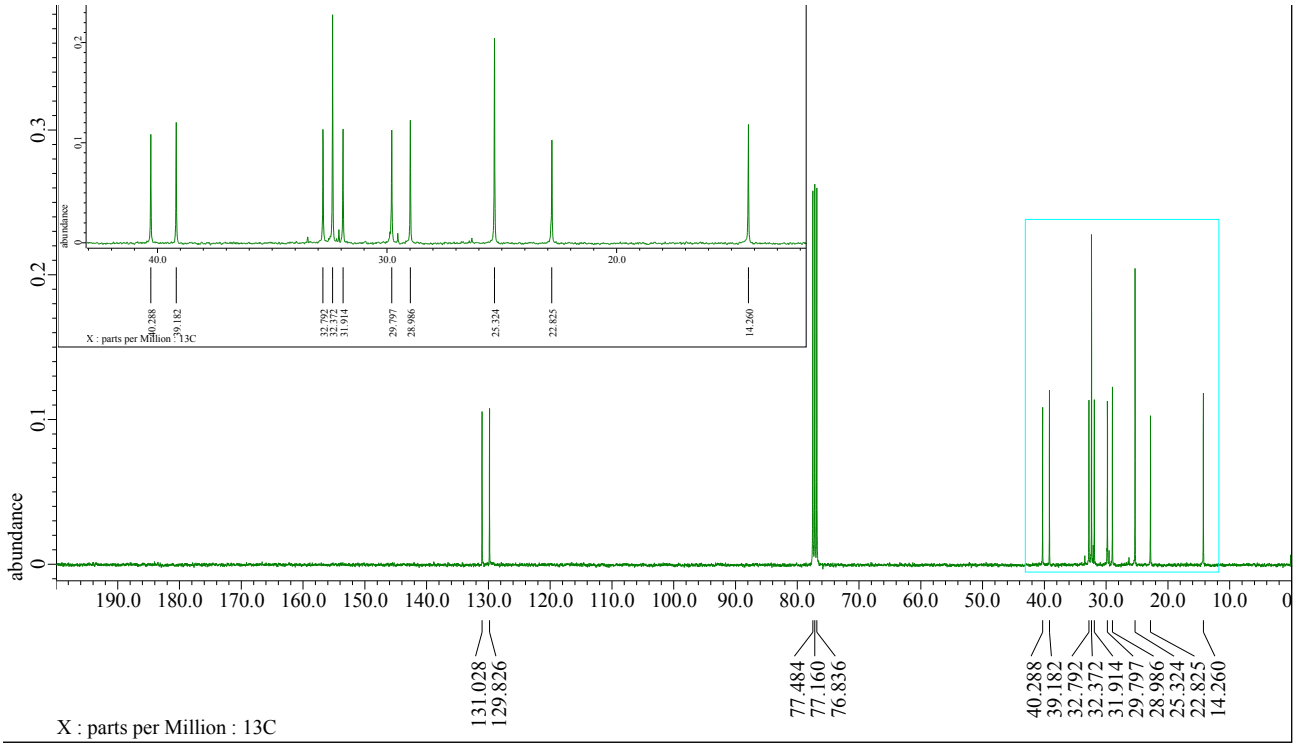

abundance
X : parts per Million : 1H
5.408
5.398
5.386
4.977
4.969
4.963
4.957
4.951
4.945
4.938
2.049
2.005
1.985
1.974
1.967
1.845
1.822
1.814
1.541
1.286
1.275
0.900
0.883
0.865
-0.000

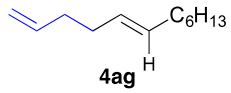

abundance
X : parts per Million : 13C
170.808
135.062
128.882
77.484
77.160
76.836
70.064
39.086
32.801
31.876
29.702
29.377
28.948
27.756
22.787
21.604
14.241


C_6H_{13}
H

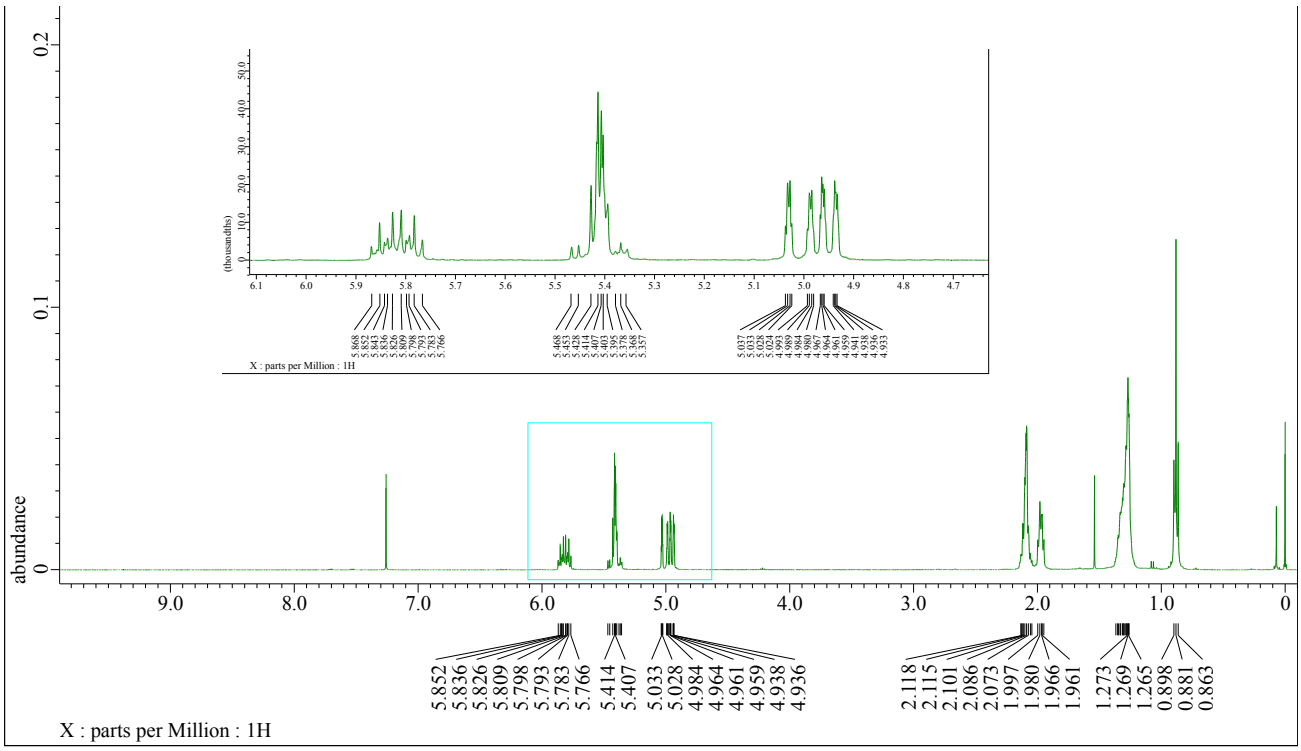
4af

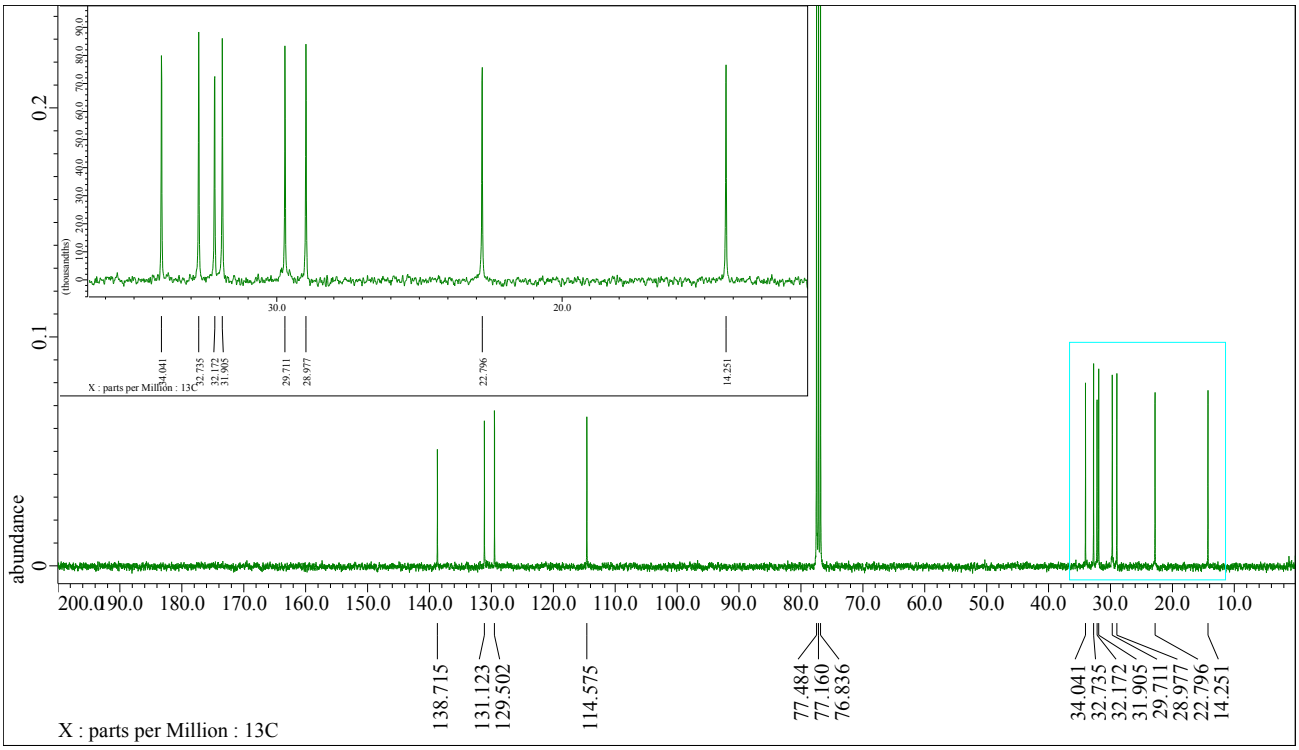

abundance
X : parts per Million : 1H
5.396
5.391
5.385
5.377
1.989
1.974
1.960
1.581
1.564
1.538
1.495
1.332
1.321
1.313
1.302
1.282
1.270
1.261
1.120
0.897
0.880
0.861

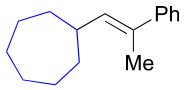

abundance
X : parts per Million : 13C
131.028
129.826
77.484
77.160
76.836
40.288
39.182
32.792
32.372
31.914
29.797
28.986
25.324
22.825
14.260


C_6H_{13}
H

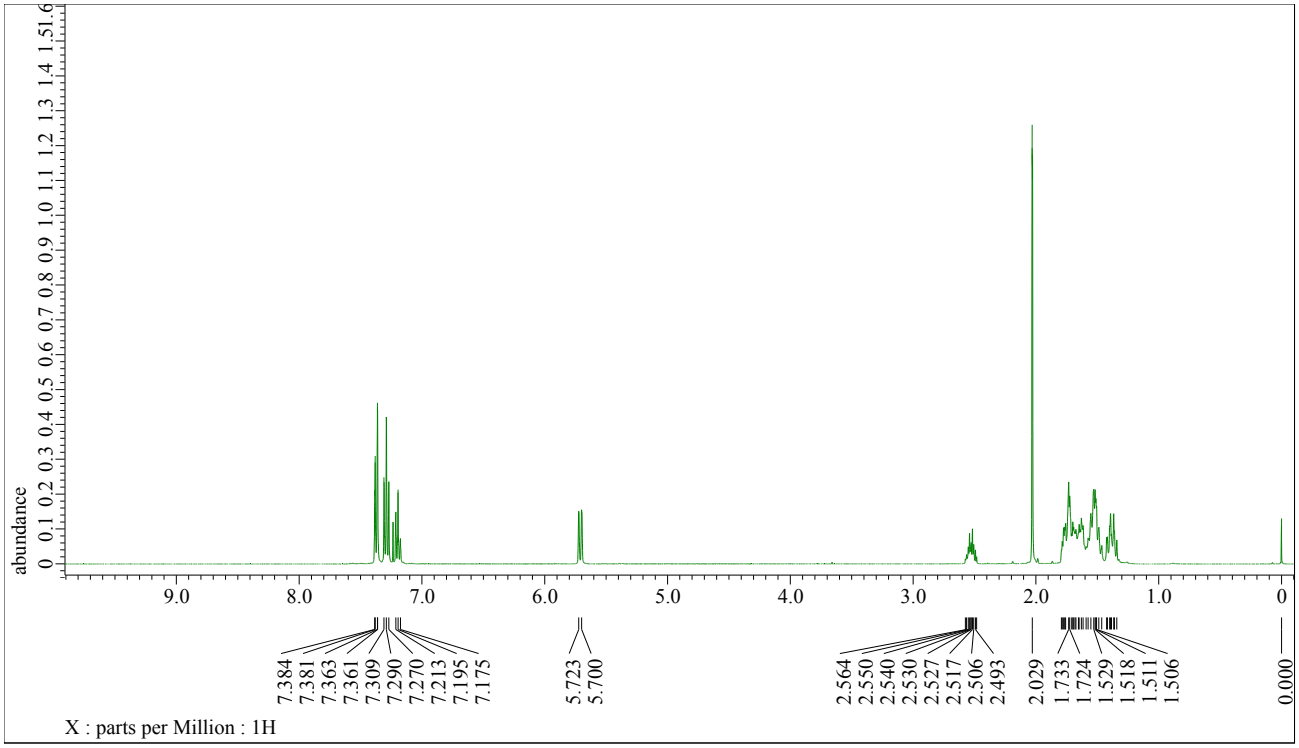
4ag

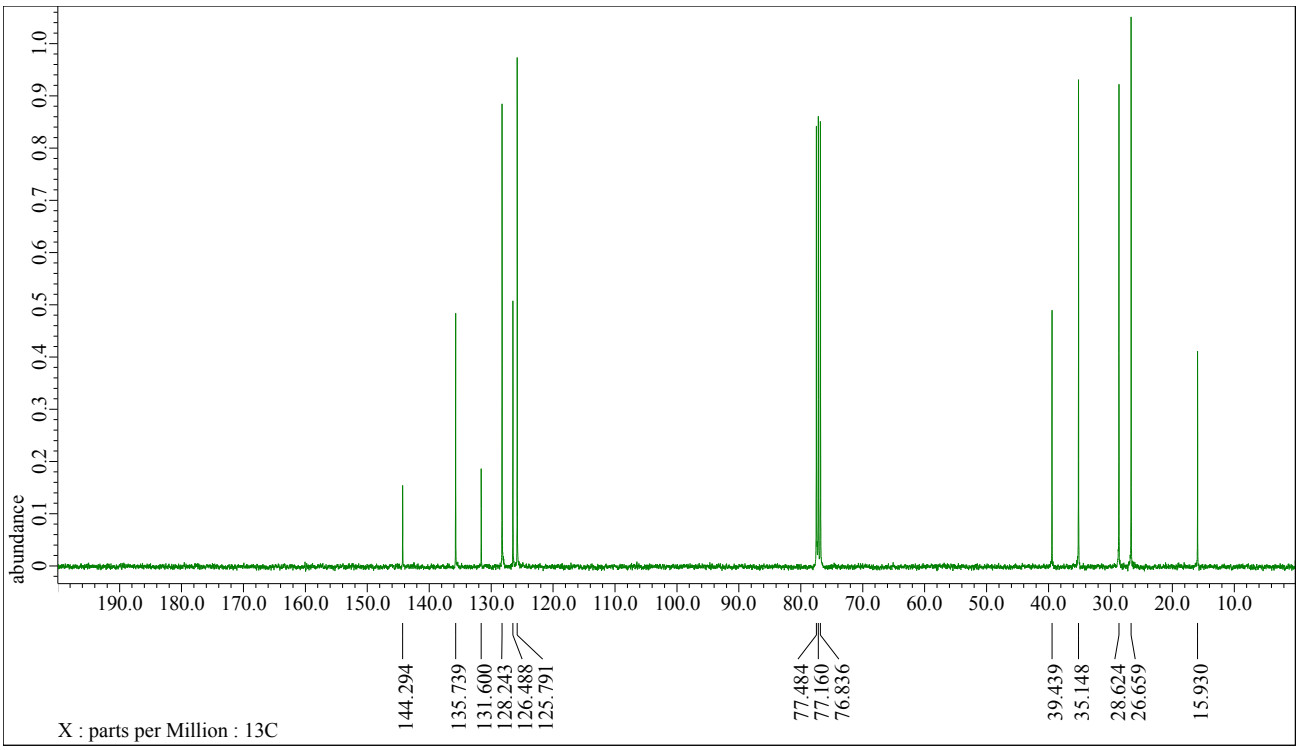

abundance
X : parts per Million : 1H
5.852
5.836
5.826
5.809
5.798
5.793
5.783
5.766
5.414
5.407
5.033
5.028
4.984
4.964
4.961
4.959
4.938
4.936
2.118
2.115
2.101
2.086
2.073
1.997
1.980
1.966
1.961
1.273
1.269
1.265
0.898
0.881
0.863

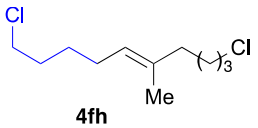

abundance
X : parts per Million : 13C
138.715
131.123
129.502
114.575
77.484
77.160
76.836
34.041
32.735
32.172
31.905
29.711
28.977
22.796
14.251


Ph
Me

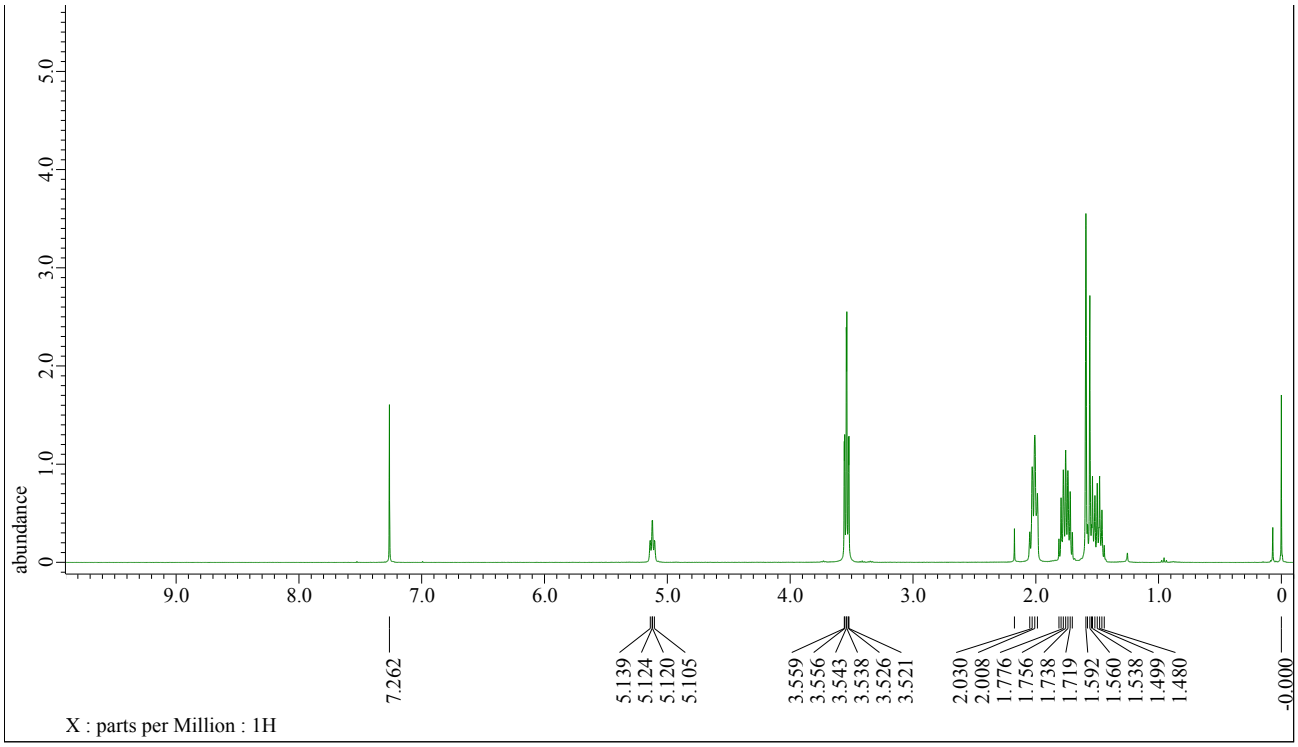
4eb

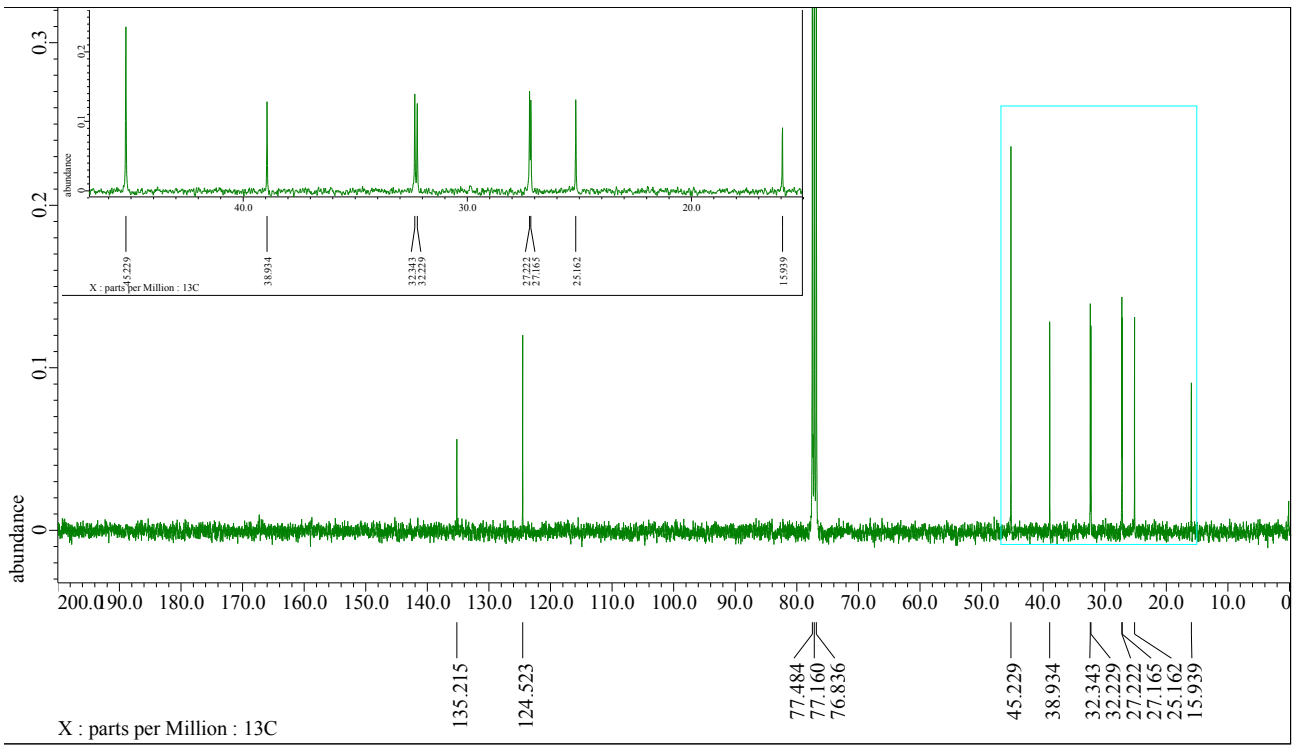

abundance
X : parts per Million : 1H
7.384
7.381
7.363
7.361
7.309
7.290
7.270
7.213
7.195
7.175
5.723
5.700
2.564
2.550
2.540
2.530
2.527
2.517
2.506
2.493
2.029
1.733
1.724
1.529
1.518
1.511
1.506
0.000

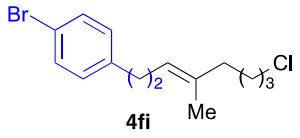

abundance
X : parts per Million : 13C
144.294
135.739
131.600
128.243
126.488
125.791
77.484
77.160
76.836
39.439
35.148
28.624
26.659
15.930


Cl
Cl
3
Me

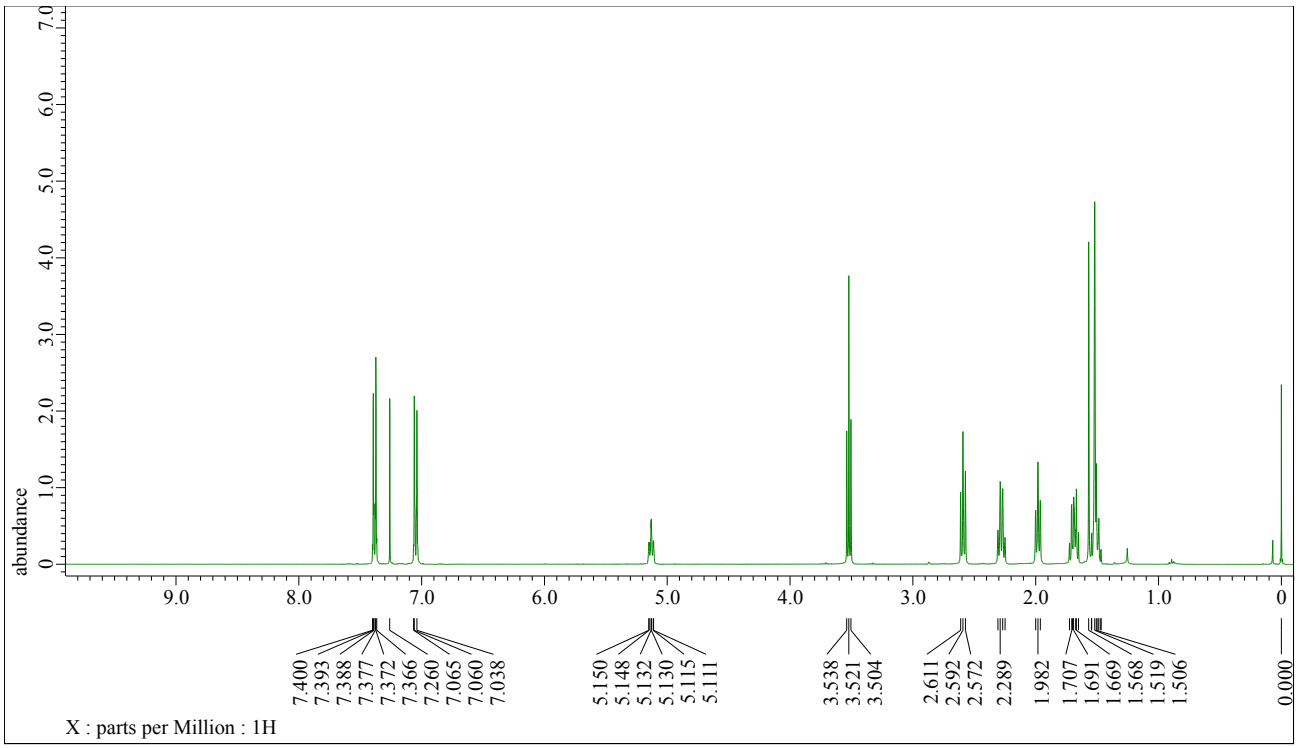
4fh

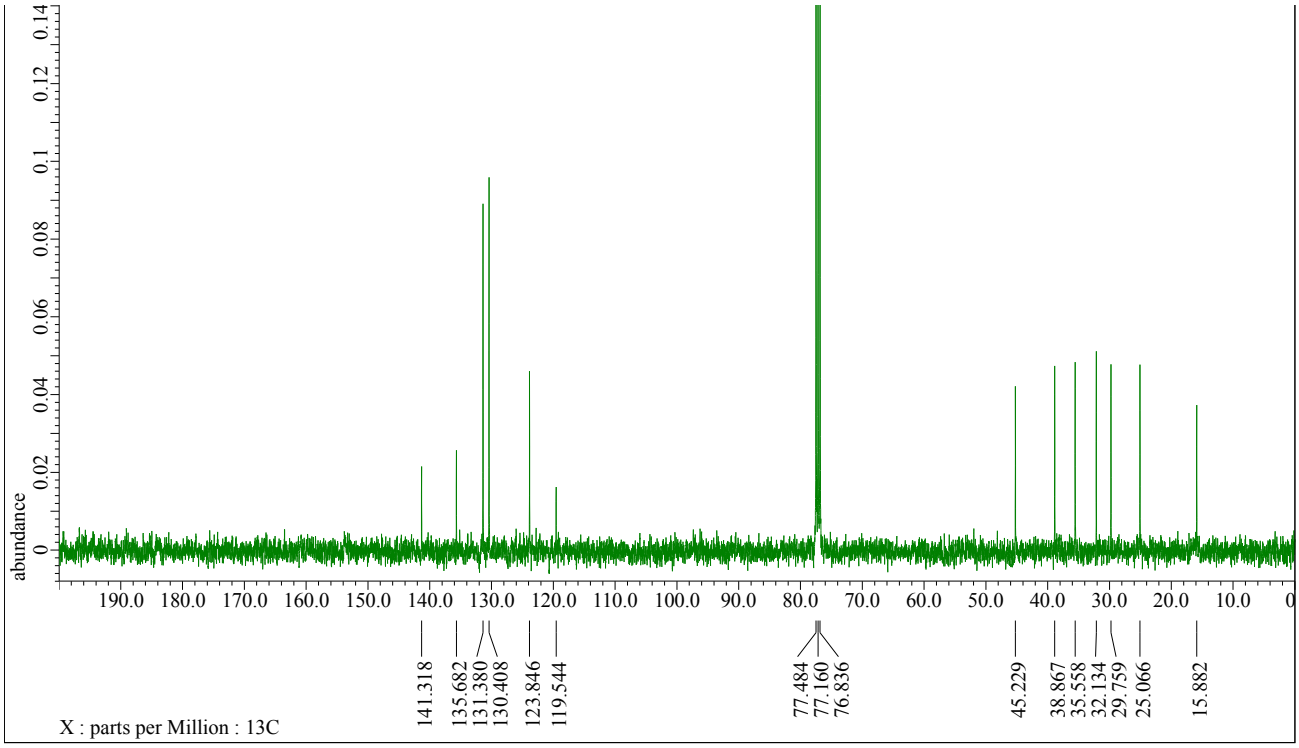

abundance
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.262
5.139
5.124
5.120
5.105
3.559
3.556
3.543
3.538
3.526
3.521
2.030
2.008
1.776
1.756
1.738
1.719
1.592
1.560
1.538
1.499
1.480
-0.000
X : parts per Million : 1H

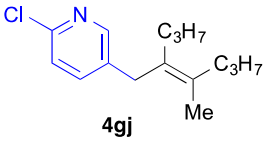

abundance
X : parts per Million : 13C
135.215
124.523
77.484
77.160
76.836
45.229
38.934
32.343
32.229
27.222
27.165
25.162
15.939


Br
Cl
Me

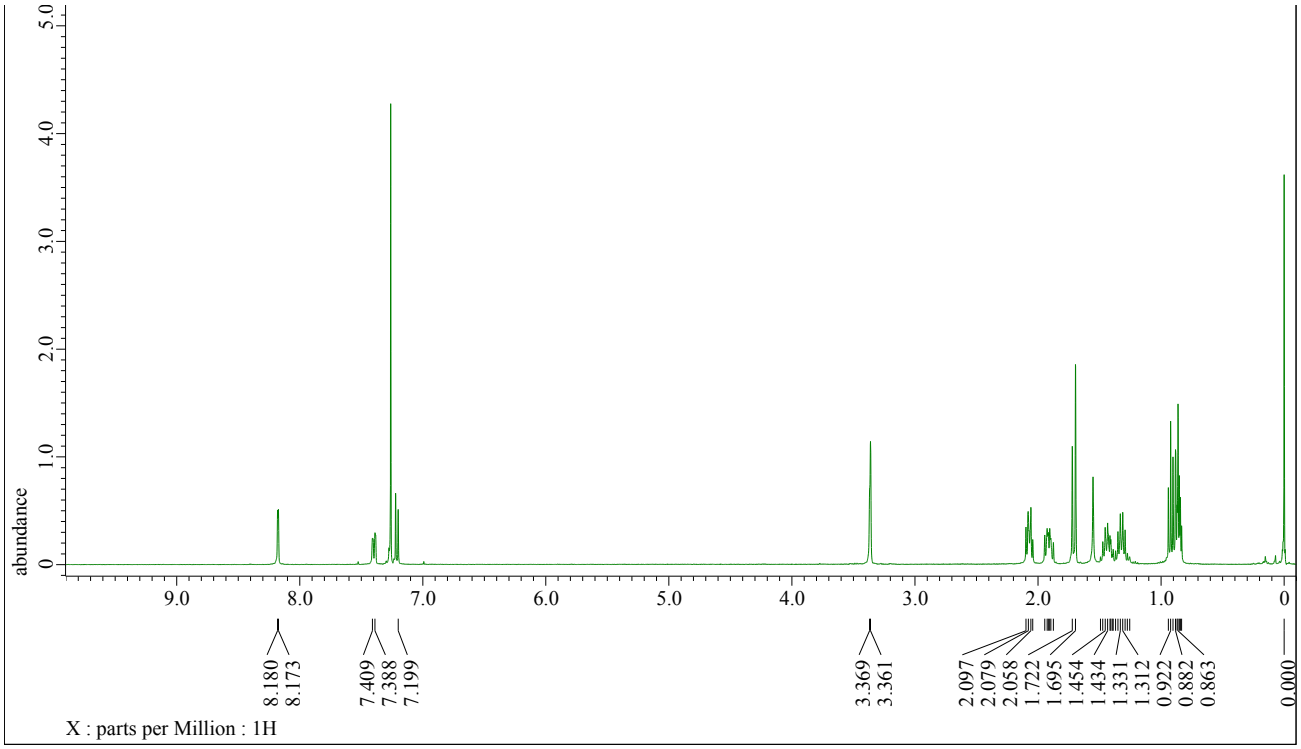
4fi

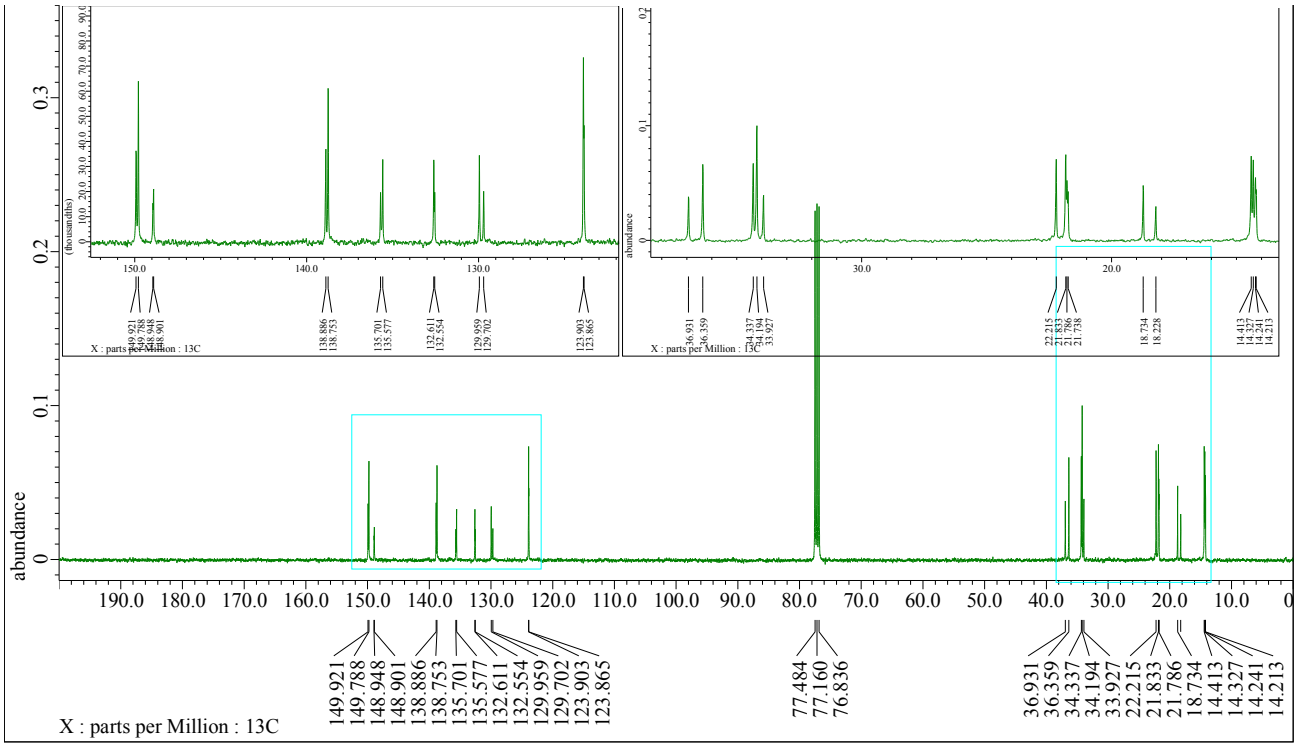

abundance
X : parts per Million : 1H
7.400
7.393
7.388
7.377
7.372
7.366
7.260
7.065
7.060
7.038
5.150
5.148
5.132
5.130
5.115
5.111
3.538
3.521
3.504
2.611
2.592
2.572
2.289
1.982
1.707
1.691
1.669
1.568
1.519
1.506
0.000


abundance
X : parts per Million : 13C
141.318
135.682
131.380
130.408
123.846
119.544
77.484
77.160
76.836
45.229
38.867
35.558
32.134
29.759
25.066
15.882


Cl
N
C_3H_7
C_3H_7
Me

4gj


abundance
X : parts per Million : 1H
8.180
8.173
7.409
7.388
7.199
3.369
3.361
2.097
2.079
2.058
1.722
1.695
1.454
1.434
1.331
1.312
0.922
0.882
0.863
0.000


abundance
X : parts per Million : 13C
149.921
149.788
148.948
148.901
138.886
138.753
135.701
135.577
132.611
132.554
129.959
129.702
123.903
123.865
77.484
77.160
76.836
36.931
36.359
34.337
34.194
33.927
22.215
21.833
21.786
18.734
14.413
14.327
14.241
14.213