Supporting Information For:

Iron-Catalyzed Negishi Coupling Toward an Effective Olefin Synthesis

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General. All the reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of argon or nitrogen. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. 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). 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. Organic solutions were concentrated by rotary evaporation at *ca.* 30–400 mmHg. Flash column chromatography was performed on Kanto silica gel 60 (spherical, neutral, 140–325 mesh) as described by Still et al.[1]

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) and carbon NMR (^{13}C NMR) spectra were recorded on JEOL EX-270 (270 MHz) NMR spectrometers. 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 $CDCl_3$ (δ 7.26). ^{13}C NMR spectra were recorded at 67.8 MHz: chemical shifts for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of $CDCl_3$ (δ 77.0). 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, br = broad), coupling constant in hertz (Hz), signal area integration in natural numbers, and assignment (*italic*). IR spectra were recorded on a JASCO FT/IR-460 Plus. Characteristic IR absorptions are reported in cm^{-1}. High-

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(1) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

resolution mass spectra (HRMS) were obtained using the electron impact (EI) method with JEOL JMS-700. NMR yield was determined for a crude product by ^{1}H NMR analyses by using pyradine as an internal standard and GC yield was determined upon calibration by using undecane as an internal standard. Purity of isolated compounds was determined by GC analysis on Shimadzu GC-17A instrument equipped with an FID detector and a capillary column, HR-1 (Shinwa, 25 m × 0.25 mm i.d., 0.25 μm film thickness) and/or ^{1}H NMR analyses.

Solvent. Anhydrous tetrahydrofuran (THF) was purchased from Wako Chemical Co. and distilled from benzophenone ketyl at ambient pressure under argon immediately before use. Water content of the solvent was determined with a Karl-Fischer Moisture Titrator (MKC-210, Kyoto Electronics Company) to be less than 15 ppm.

Materials. Materials were purchased from Wako Pure Chemical Industries, Ltd. (Wako), Tokyo Chemical Industry Co., Ltd. (TCI), Acros Organics Co. (ACROS), and other commercial suppliers, and were used after appropriate purification unless otherwise noted. Florisil® (100–200 mesh) was purchased from Nacalai Tesque, Inc. Anhydrous $FeCl_3$ (powder, 99.99%) was purchased from Aldrich Inc. and dissolved in THF at 0 °C prior to use. (Iodomethyl)trimethylsilane (ACROS, 99%) was used without purification. Zinc powder (–325 mesh, Strem Chemicals, 99.9%) was purified according to the reported procedure[2] and stored under argon. Lithium chloride (99.9%) was purchased from Wako and stored under argon. (Chloromethyl)trimethylsilane (ACROS, > 98%), β-bromostyrene (Wako, > 97%), chlorotrimethylsilane (TCI, > 98%), and *N,N,N',N'*-tetrametylethylenediamine (TMEDA, Wako) were distilled from CaH_2 prior to use. (Trimethylsilyl)methylmagnesium chloride, β-styrylmagnesium bromide, and 1-(trimethylsilyl)vinylmagnesium bromide were prepared from the corresponding halides and magnesium (turnings) and titrated prior to use. (Prop-1-en-2-yl)magnesium bromide and (2-methylprop-1-enyl)magnesium bromide were purchased from Sigma-Aldrich Co. and titrated prior to use.

GC analyses. Yield (using undecane as an internal standard) was determined for a crude product by GC analysis on a Shimadzu GC-17A instrument equipped with an FID detector and a capillary column, HR-1 (Shinwa, 25 m × 0.25 mm i.d., 0.25 μm film thickness). Purity of an isolated compound was determined by GC analysis.

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(2) *Purification of Laboratory Chemicals*, 5th ed.; Armarego, W. L. F., Chai, C. L. L., Eds.; Butterworth Heinemann: Amsterdam, 2003; pp 497.

Preparation of β-styrylzinc bromide

Preparation of β-styrylzinc bromide was carried out according to the previous report[3] with a modification. In a 200 mL Schlenk tube, equipped with a Teflon screw cock, were placed anhydrous lithium chloride (3.56 g, 84.0 mmol) and zinc powder (22.9 g, 350 mmol) under argon and the mixture was stirred at 170 °C for 2 h *in vacuo* (0.2 mm Hg). THF (84 mL) and chlorotrimethylsilane (0.380 g, 0.45 mL, 3.50 mmol) were added and the mixture was heated with a heat gun to gentle reflux. β-Bromostyrene (12.9 g, 9.2 mL, 70.0 mmol) was added at room temperature then stirred at 80 °C for 5 days until the conversion was determined to be > 98% by a GLC analysis. The reaction mixture was transferred to a centrifuge tube via cannula under argon and then centrifuged (20 rpm, 30 min). The supernatant was carefully transferred to a Schlenk tube via syringe under argon. The concentration and *E*:*Z* ratio were determined by I_2 titration and a following GC analysis.

Preparation of (trimethylsilylmethyl)zinc iodide

Preparation of (trimethylsilyl)methylzinc iodide was carried out according to the previous report[4] with a modification. In a 200 mL Schlenk tube, chlorotrimethylsilane (0.219 g, 0.26 mL, 2.02 mmol) was slowly added to a stirred mixture of zinc powder (13.2 g, 202 mmol) in THF (65 mL) and the mixture was heated with a heat gun to gentle reflux. (Iodomethyl)trimethylsilane (14.4 g, 10 mL, 67.3 mmol) was slowly added at 25 °C for 30 min then stirred at that temperature for 24 h. The reaction mixture was transferred to centrifuge tube via cannula under argon and then centrifuged (20 rpm, 30 min). The supernatant was carefully transferred to a Schlenk tube via syringe under argon. The concentration was determined by I_2 titration and a following GC analysis.

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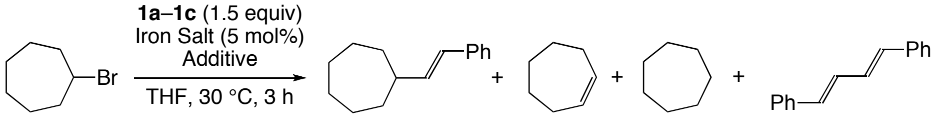
(3) Krasovskiy, A.; Malakhov, V.; Gavryushin, A.; Knochel, P. *Angew. Chem.* **2006**, *118*, 6186–6190; *Angew. Chem. Int. Ed.* **2006**, *45*, 6040–6044.

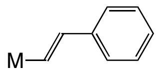
(4) Jones, P.; Reddy, C. K.; Knochel, P. *Tetrahedron* **1998**, *54*, 1471–1490.

Screening of additives and metal salts (Table 1 with additional data)

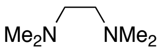
To a THF solution of β-styrylzinc bromide (1.04 mL, 0.72 M, 0.75 mmol) was added a THF solution of (trimethylsilyl)methylmagnesium chloride (0.75 mL, 1.00 M, 0.75 mmol), TMEDA, bromocycloheptane (88.5 mg, 0.50 mmol), undecane (62.5 mg, 42.4 μL, 0.40 mmol), and a THF solution of $FeCl_3$ (0.25 mL, 0.10 M, 0.025 mmol, 5 mol%) successively at 0 °C and then stirred for 30 min. The reaction was carried out at 30 °C for 3 h. After cooling to 0 °C, aqueous ammonium chloride (saturated, 1.0 mL) was added. The aqueous layer was extracted three times with hexane, then two times with Et_2O. The combined organic extracts were filtered with a pad of Florisil®. The yield of the products was determined for the crude products by GC analysis using undecane as an internal standard. The reactions in entries 6[5a], 9[5b], and 10[5c] were carried out according to previous reports.



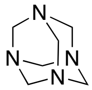
2 **3** **4** **5** **6**



1a (M = ZnBr)
1b (M = ZnR)
1c (M = MgBr)



TMEDA



HMTA

Entry[a]	M	Additive (equiv)	Iron Salt	Yield (%)[b]				
				3	**4**	**5**	**2**	**6** (mmol)
1	**1a**	none	$FeCl_3$	8	<1	1	70	0.05
2	**1b**	none	$FeCl_3$	25	4	17	0	0.12
3	**1b**	TMEDA (1.5)	$FeCl_3$	56	4	13	0	0.11
4	**1b**	TMEDA (3.0)	$FeCl_3$	91	<1	3	0	0.10
5	**1b**	TMEDA (3.5)	$FeCl_3$	95	<1	3	0	0.08
6[c]	**1c**	TMEDA (3.5)	$FeCl_3$	35	12	4	35	0.03
7	**1b**	TMEDA (3.5)	$FeCl_2$	97	<1	3	0	0.05
8	**1b**	TMEDA (3.5)	$Fe(acac)_3$	85	0	3	10	0.06
9[d]	**1c**	TMEDA (1.9)	$FeCl_3$	56	26	7	0	0.09
10[d]	**1c**	HMTA/TMEDA (0.05/0.10)	$Fe(acac)_3$	35	28	12	0	0.08

[a] Reactions were carried out on a 0.50 mmol scale. [b] The yield was determined by GC analysis using undecane as an internal standard. [c] **1c** was slowly added for 30 min then stirred for 30 min at 0 ºC. [d] **1c** was slowly added for 1 h then stirred for 30 min at 0 ºC.

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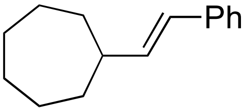
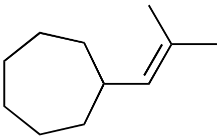
(5) (a) Nakamura, M.; Matsuo, K.; Ito, S.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *126*, 3686–3687. (b) Guérinot, A.; Reymond, S.; Cossy, J. *Angew. Chem.* **2007**, *119*, 6641–6644; *Angew. Chem. Int. Ed.* **2007**, *46*, 6521–6524. (c) Cahiez, G.; Habiak, V.; Duplais, C.; Moyeux, A. *Org. Lett.* **2007**, *9*, 3253–3254.

Procedure A; Synthesis of (*E*) and (*Z*)-(2-cycloheptylethenyl)benzene (3)



To a THF solution of β-styrylzinc bromide (10.4 mL, 0.72 M, 7.50 mmol) was added a THF solution of (trimethylsilyl)methylmagnesium chloride (7.5 mL, 1.00 M, 7.50 mmol), TMEDA (2.03 g, 2.61 mL, 17.5 mmol), bromocycloheptane (0.897 g, 5.06 mmol), and a THF solution of $FeCl_3$ (2.50 mL, 0.10 M, 0.250 mmol, 5 mol%) successively at 0 °C and then stirred for 30 min. The reaction was carried out at 30 °C for 3 h. After cooling to 0 °C, aqueous ammonium chloride (saturated, 5.0 mL) was added. The aqueous layer was extracted three times with hexane, then two times with Et_2O. The combined organic extracts were washed with brine then dried over Na_2SO_4. The yield of the products was determined for the crude products by GC analysis using undecane as an internal standard (95%). After the solvent was removed *in vacuo*, the crude product was purified by chromatography on silica gel (hexane) to obtain the title compound **3** (0.952 g, 94% yield, *E*:*Z* = 80:20, 99% pure on GC analysis) as a colorless liquid. ^{1}H and ^{13}C NMR spectra have been attached. Analytical data for the title compound have been reported.[6]

Procedure B; Synthesis of 3-cycloheptyl-2-methylprop-2-ene (S1)



To a THF solution of (trimethylsilyl)methylzinc iodide (2.41 mL, 0.83 M, 2.00 mmol) was added a THF solution of (2-methylprop-1-enyl)magnesium bromide (2.94 mL, 0.68 M, 2.00 mmol), TMEDA (0.523 g, 0.67 mL, 4.50 mmol), chlorocycloheptane (0.134 g, 1.00 mmol), and a THF solution of $FeCl_3$ (0.50 mL, 0.10 M, 0.050 mmol, 5 mol%) at 0 °C and then stirred for 30 min. The reaction mixture was stirred at that temperature for 30 min and at 30 °C for 18 h. After cooling to 0 °C, aqueous ammonium chloride (saturated, 1.0 mL) was added. The aqueous layer was extracted three times with hexane, then two times with Et_2O. The combined organic extracts were filtered with a pad of Florisil®. The solvent was carefully removed *in vacuo* (400 Torr). The NMR yield of the title compound **S1** was determined for the crude product by ^{1}H NMR analysis (96% yield, pyradine was used as an internal standard). The crude product was purified by chromatography on silica gel (pentane) to give **S1** (0.134 g, 88% yield, > 99% pure on the GC analysis). R_f = 0.84 (pentane); IR (neat) 2965, 2921, 2851, 1457, 1374, 1217; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.19–1.66 (m, $(CH_2)_6$, 12H), 1.60 (d, J = 1.3 Hz, $C(CH_3)CH_3$, 3H), 1.66 (d, J = 1.3 Hz, $C(CH_3)CH_3$, 3H), 2.32 (qt, J = 9.2 Hz, 3.5 Hz, $CHCH{=}C$, 1H), 5.05 (dsept, J = 9.2 Hz, 1.3 Hz, $CH{=}C$, 1H). ^{13}C NMR (67.5 MHz,

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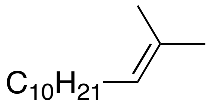
[6] Jang, Y.-J.; Shih, Y.-K.; Liu, J.-Y.; Kuo, W.-Y.; Yao, C.-F. *Chem. Eur. J.* **2003**, *9*, 2123–2128.

$CDCl_3$) δ 17.7, 25.7, 26.5 (2C), 28.5 (2C), 35.3 (2C), 38.7, 128.0, 132.2. Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.61; H, 13.42. ^1H and ^{13}C NMR spectra have been attached.

Synthesis of 2-methyltridec-2-ene (S2)



The reaction was carried out according to Procedure B on a 1.00 mmol scale by using a THF solution of (trimethylsilyl)methylzinc iodide (2.41 mL, 0.83 M, 2.00 mmol), a THF solution of (2-methylprop-1-enyl)magnesium bromide (2.94 mL, 0.68 M, 2.00 mmol), TMEDA (0.523 g, 0.67 mL, 4.50 mmol), 1-iodododecane (0.269 g, 1.00 mmol) and a THF solution of $FeCl_3$ (0.50 mL, 0.10 M, 0.050 mmol, 5 mol%). Conditions: 30 °C, 15 h. The title compound **S2** (0.193 g, 98% yield, > 99% pure on the GC analysis) was obtained as a colorless liquid after silica gel column chromatography (pentane). ^1H and ^{13}C NMR spectra have been attached. Analytical data for the title compound have been reported.[7]

The reaction was carried out according to Procedure B on a 1.00 mmol scale by using a THF solution of (trimethylsilyl)methylzinc iodide (1.81 mL, 0.83 M, 1.50 mmol), a THF solution of (2-methylprop-1-enyl)magnesium bromide (2.21 mL, 0.68 M, 1.50 mmol), TMEDA (0.407 g, 0.52 mL, 3.50 mmol), 1-bromodecane (0.220 g, 0.99 mmol) and a THF solution of $FeCl_3$ (0.50 mL, 0.10 M, 0.050 mmol, 5 mol%). Conditions: 40 °C, 18 h. The title compound **S2** (0.174 g, 89% yield, > 99% pure on the GC analysis) was obtained as a colorless liquid after silica gel column chromatography (pentane).

The reaction was carried out according to Procedure B on a 1.00 mmol scale by using a THF solution of (trimethylsilyl)methylzinc iodide (3.61 mL, 0.83 M, 3.00 mmol), a THF solution of (2-methylprop-1-enyl)magnesium bromide (4.41 mL, 0.68 M, 3.00 mmol), TMEDA (0.756 g, 0.97 mL, 6.50 mmol), 1-chlorodecane (0.176 g, 1.00 mmol) and a THF solution of $FeCl_3$ (1.0 mL, 0.10 M, 0.10 mmol, 10 mol%). Conditions: 50 °C, 24 h. The NMR yield of the title compound **S2** was determined for the crude product by ^1H NMR analysis (91% yield, pyradine was used as an internal standard). The title compound **S2** (0.158 g, 80% yield, > 99% pure on the GC analysis) was obtained as a colorless liquid after silica gel column chromatography (pentane).

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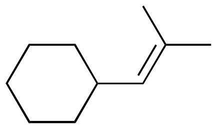
(7) Wang, Z.-X.; Tu, Y.-T.; Frohn, M.; Zhang, J.-R.; Shi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11224–11235.

Synthesis of 3-cyclohexyl-2-methylprop-2-ene (S3)

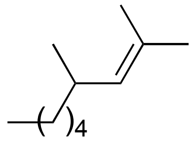


The reaction was carried out according to Procedure B on a 1.00 mmol scale by using a THF solution of (trimethylsilyl)methylzinc iodide (2.41 mL, 0.83 M, 2.00 mmol), a THF solution of (2-methylprop-1-enyl)magnesium bromide (2.94 mL, 0.68 M, 2.00 mmol), TMEDA (0.523 g, 0.67 mL, 4.50 mmol), iodocyclohexane (0.211 g, 1.00 mmol) and a THF solution of $FeCl_3$ (0.50 mL, 0.10 M, 0.050 mmol, 5 mol%). Conditions: 30 °C, 18 h. The NMR yield of the title compound **S3** was determined for the crude product by ^1H NMR analysis (95% yield, pyradine was used as an internal standard). The title compound **S3** (0.125 g, 83% yield, > 99% pure on GC analysis, 8% of pentane) (0.100 g, 73% yield, > 99% pure on the GC analysis) was obtained as a colorless liquid after silica gel column chromatography (pentane). ^1H and ^{13}C NMR spectra have been attached. Analytical data for the title compound have been reported.[5c]

The reaction was carried out according to Procedure B on a 1.00 mmol scale by using a THF solution of (trimethylsilyl)methylzinc iodide (1.81 mL, 0.83 M, 1.50 mmol), a THF solution of (2-methylprop-1-enyl)magnesium bromide (2.21 mL, 0.68 M, 1.50 mmol), TMEDA (0.407 g, 0.52 mL, 3.50 mmol), bromocyclohexane (0.164 g, 1.00 mmol) and a THF solution of $FeCl_3$ (0.50 mL, 0.10 M, 0.050 mmol, 5 mol%). Conditions: 30 °C, 24 h. The NMR yield of the title compound **S3** was determined for the crude product by ^1H NMR analysis (99% yield, pyradine was used as an internal standard). The title compound **S3** (0.119 g, 80% yield, > 99% pure on GC analysis, 7% of pentane) (97.6 mg, 71% yield, > 99% pure on the GC analysis) was obtained as a colorless liquid after silica gel column chromatography (pentane).

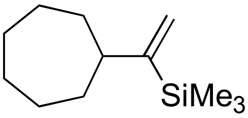
The reaction was carried out according to Procedure B on a 1.00 mmol scale by using a THF solution of (trimethylsilyl)methylzinc iodide (2.41 mL, 0.83 M, 2.00 mmol), a THF solution of (2-methylprop-1-enyl)magnesium bromide (2.94 mL, 0.68 M, 2.00 mmol), TMEDA (0.523 g, 0.67 mL, 4.50 mmol), chlorocyclohexane (0.119 g, 1.00 mmol) and a THF solution of $FeCl_3$ (0.50 mL, 0.10 M, 0.050 mmol, 5 mol%). Conditions: 40 °C, 24 h. The NMR yield of the title compound **S3** was determined for the crude product by ^1H NMR analysis (91% yield, pyradine was used as an internal standard).

Synthesis of 2,4-dimethylnon-2-ene (S4)



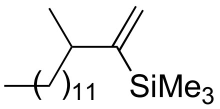
The reaction was carried out according to Procedure B on a 1.00 mmol scale by using a THF solution of (trimethylsilyl)methylzinc iodide (2.41 mL, 0.83 M, 2.00 mmol), a THF solution of (2-methylprop-1-enyl)magnesium bromide (2.94 mL, 0.68 M, 2.00 mmol), TMEDA (0.523 g, 0.67 mL, 4.50 mmol), 2-chloroheptane (0.134 g, 0.99 mmol) and a THF solution of $FeCl_3$ (0.50 mL, 0.10 M, 0.050 mmol, 5 mol%). Conditions: 30 °C, 18 h. The NMR yield of the title compound **S4** was determined for the crude product by ^{1}H NMR analysis (91% yield, pyradine was used as an internal standard). The title compound **S4** (0.126 g, 82% yield, > 99% pure on the GC analysis) was obtained as a colorless liquid after silica gel column chromatography (pentane). R_f = 0.86 (pentane); IR (neat) 2956, 2923, 2854, 1456, 1377, 834; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.85–0.90 (m, $CH_3CH(CH_2)_4CH_3$, 6H), 1.10–1.36 (m, $(CH_2)_4$, 8H), 1.60 (d, J = 1.3 Hz, $C(CH_3)CH_3$, 3H), 1.68 (d, J = 1.3 Hz, $C(CH_3)CH_3$, 3H), 2.26–2.34 (m, $CHCH{=}C$, 1H), 4.87 (dsept, J = 9.5 Hz, 1.3 Hz, $CH{=}C$, 1H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 14.1, 17.9, 21.3, 22.7, 25.8, 27.2, 32.1, 32.4, 37.8, 129.5, 131.7. HRMS *m*/*z* calcd for $C_{11}H_{22}$ (M^+) 154.1722, found 154.1720. ^{1}H and ^{13}C NMR spectra have been attached.

Synthesis of (1-cycloheptylvinyl)trimethylsilane (S5)



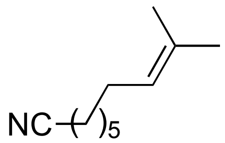
The reaction was carried out according to Procedure B on a 1.00 mmol scale by using a THF solution of (trimethylsilyl)methylzinc iodide (2.41 mL, 0.83 M, 2.00 mmol), a THF solution of 1-(trimethylsilyl)vinylmagnesium bromide (1.80 mL, 1.11 M, 2.00 mmol), TMEDA (0.523 g, 0.67 mL, 4.50 mmol), chlorocycloheptane (0.135 g, 1.02 mmol) and a THF solution of $FeCl_3$ (0.50 mL, 0.10 M, 0.050 mmol, 5 mol%). Conditions: 30 °C, 48 h. The NMR yield of the title compound **S5** was determined for a crude product by ^{1}H NMR analysis (78% yield, pyradine was used as an internal standard). The title compound **S5** (0.161 g, 79% yield, 98% pure on the GC analysis) was obtained as a colorless liquid after silica gel column chromatography (pentane). R_f = 0.84 (pentane); IR (neat) 2953, 2922, 2853, 1247, 923, 833, 756, 689; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.09 (s, $Si(CH_3)_3$, 9H), 1.26–1.73 (m, $(CH_2)_6$, 12H), 2.13–2.29 (m, $CHC{=}CH_2$, 1H), 5.26 (d, J = 2.7 Hz, $C{=}CHH$, 1H), 5.57 (dd, J = 2.7 Hz, 0.8 Hz, $C{=}CHH$, 1H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ –1.0 (3C), 27.2 (2C), 27.8 (2C), 35.5 (2C), 45.7, 121.5, 159.7. HRMS *m*/*z* calcd for $C_{12}H_{24}Si$ (M^+) 196.1647, found 196.1655. ^{1}H and ^{13}C NMR spectra have been attached.

Synthesis of [1-(2-tetradecyl)vinyl]trimethylsilane (S6)



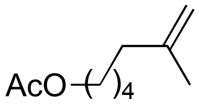
The reaction was carried out according to Procedure B on a 1.00 mmol scale by using a THF solution of (trimethylsilyl)methylzinc iodide (2.41 mL, 0.83 M, 2.00 mmol), a THF solution of 1-(trimethylsilyl)vinylmagnesium bromide (1.80 mL, 1.11 M, 2.00 mmol), TMEDA (0.523 g, 0.67 mL, 4.50 mmol), 2-bromotetradecane (0.279 g, 1.00 mmol) and a THF solution of $FeCl_3$ (0.50 mL, 0.10 M, 0.050 mmol, 5 mol%). Conditions: 30 °C, 48 h. The NMR yield of the title compound **S6** was determined for a crude product by ^{1}H NMR analysis (84% yield, pyradine was used as an internal standard). The title compound **S6** (0.252 g, 83% yield, 98% pure on the GC analysis) was obtained as a colorless liquid after silica gel column chromatography (hexane). R_f = 0.84 (hexane); IR (neat) 2955, 2923, 2853, 1247, 924, 836; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.09 (s, 9H, Si(CH_3)$_3$), 0.88 (t, J = 7.0 Hz, CH_2CH_3, 3H), 0.99 (d, J = 7.0 Hz, CH_3CH, 3H), 1.14–1.54 (m, (CH_2)$_{11}$, 22H), 2.26 (brsext, J = 7.0 Hz, C*H*C=CH_2, 1H), 5.34 (d, J = 2.7 Hz, C=C*H*H, 1H), 5.57 (dd, J = 2.7 Hz, 0.8 Hz, C=CH*H*, 1H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ –0.9 (3C), 14.1, 21.3, 22.7, 27.8, 29.4, 29.7 (5C), 29.9, 31.9, 36.9, 38.8, 122.3, 158.1. HRMS *m*/*z* calcd for $C_{19}H_{40}Si$ (M^+) 296.2899, found 296.2896. ^{1}H and ^{13}C NMR spectra have been attached.

Synthesis of 9-methyldec-8-enenitrile (S7)



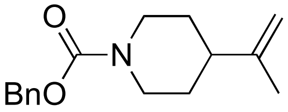
The reaction was carried out according to Procedure B on a 1.00 mmol scale by using a THF solution of (trimethylsilyl)methylzinc iodide (1.81 mL, 0.83 M, 1.50 mmol), a THF solution of (2-methylprop-1-enyl)magnesium bromide (2.21 mL, 0.68 M, 1.50 mmol), TMEDA (0.407 g, 0.52 mL, 3.50 mmol), 7-bromoheptanenitrile (0.193 g, 1.01 mmol) and a THF solution of $FeCl_3$ (0.50 mL, 0.10 M, 0.050 mmol, 5 mol%). Conditions: 30 °C, 3 h then 40 °C, 6 h. The title compound **S7** (0.159 g, 95% yield, > 99% pure on the GC analysis) was obtained as a colorless liquid after silica gel column chromatography (2, 3, and 5% Et_2O in hexane). ^{1}H and ^{13}C NMR spectra have been attached. Analytical data for the title compound have been reported.[5c]

Synthesis of 6-methylhept-6-enyl acetate (S8)



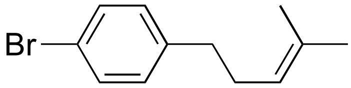
The reaction was carried out according to Procedure B on a 1.00 mmol scale by using a THF solution of (trimethylsilyl)methylzinc iodide (2.41 mL, 0.83 M, 2.00 mmol), a THF solution of (prop-1-en-2-yl)magnesium bromide (3.64 mL, 0.55 M, 2.00 mmol), TMEDA (0.523 g, 0.67 mL, 4.50 mmol), 5-bromopentyl acetate (0.210 g, 1.00 mmol) and a THF solution of $FeCl_3$ (0.50 mL, 0.10 M, 0.050 mmol, 5 mol%). Conditions: 30 °C, 3 h. The title compound **S8** (0.164 g, 97% yield, > 99% pure on the GC analysis) was obtained as a colorless liquid after silica gel column chromatography (2, 3, and 5% Et_2O in hexane). $R_f = 0.14$ (3% Et_2O in hexane); IR (neat) 2935, 2860, 1739, 1232, 1046, 886; ^1H NMR (270 MHz, $CDCl_3$) δ 1.31–1.52 (m, $O(CH_2)_2(CH_2)_2$, 4H), 1.64 (quint, $J = 7.0$ Hz, OCH_2CH_2, 2H), 1.71 (s, $CH_2{=}CCH_3$, 3H), 2.02 (t, $J = 7.6$ Hz, $O(CH_2)_4CH_2$, 2H), 2.05 (s, $CH_3C({=}O)$, 3H), 4.06 (t, $J = 7.0$ Hz, OCH_2, 2H), 4.66 (d, $J = 1.3$ Hz, $C{=}CHH$, 1H), 4.69 (d, $J = 1.3$ Hz, $C{=}CHH$, 1H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 21.0, 22.3, 25.5, 27.2, 28.5, 37.6, 64.5, 109.8, 145.8, 171.2. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.44; H, 10.72. ^1H and ^{13}C NMR spectra have been attached.

Synthesis of 1-benzyloxycarbonyl-4-(prop-1-en-2-yl)piperidine (S9)



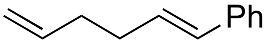
The reaction was carried out according to Procedure B on a 1.00 mmol scale by using a THF solution of (trimethylsilyl)methylzinc iodide (2.41 mL, 0.83 M, 2.00 mmol), a THF solution of (prop-1-en-2-yl)magnesium bromide (3.64 mL, 0.55 M, 2.00 mmol), TMEDA (0.523 g, 0.67 mL, 4.50 mmol), 1-benzyloxycarbonyl-4-bromopiperidine (0.301 g, 1.01 mmol) and a THF solution of $FeCl_3$ (0.50 mL, 0.10 M, 0.050 mmol, 5 mol%). Conditions: 30 °C, 3 h. The title compound **S9** (0.249 g, 95% yield, 98% pure on the GC analysis) was obtained as a colorless liquid after silica gel column chromatography (3 and 9% EtOAc in hexane). $R_f = 0.20$ (9% EtOAc in hexane); IR (neat) 2938, 2852, 1695, 1426, 1214, 695; ^1H NMR (270 MHz, $CDCl_3$) δ 1.20–1.74 (m, $N(CH_2CH_2)_2CH$, 4H), 1.74 (s, CH_3, 3H), 2.03 (tt, J = 11.9, 3.3 Hz, $N(CH_2CH_2)_2CH$, 1H), 2.64–2.92 (m, $N(CHHCH_2)_2CH$, 2H), 4.11–4.39 (m, $N(CHHCH_2)_2CH$, 2H), 4.69 (brd, $J = 1.2$ Hz, $C{=}CHH$, 1H), 4.73 (brd, $J = 1.2$ Hz, $C{=}CHH$, 1H), 5.15 (s, CH_2Ph, 2H), 7.26–7.37 (m, $(CH)_5$, 5H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 20.8, 30.7 (2C), 43.4, 44.4 (2C), 67.0, 109.2, 127.8 (2C), 127.9, 128.4 (2C), 136.9, 148.7, 155.2. Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 73.84; H, 8.29; N, 5.40. ^1H and ^{13}C NMR spectra have been attached.

Synthesis of 5-(4-bromophenyl)-2-methylpent-2-ene (S10)



The reaction was carried out according to Procedure B on a 1.00 mmol scale by using a THF solution of (trimethylsilyl)methylzinc iodide (1.81 mL, 0.83 M, 1.50 mmol), a THF solution of (2-methylprop-1-enyl)magnesium bromide (2.21 mL, 0.68 M, 1.50 mmol), TMEDA (0.407 g, 0.52 mL, 3.50 mmol), 1-bromo-4-(2-bromoethyl)benzene (0.265 g, 1.01 mmol) and a THF solution of $FeCl_3$ (0.50 mL, 0.10 M, 0.050 mmol, 5 mol%). Conditions: 30 °C, 48 h. The title compound **S10** (0.173 g, 73% yield, > 96% pure on the GC analysis) was obtained as a colorless liquid after silica gel column chromatography (hexane). R_f = 0.37 (hexane); IR (neat) 2969, 2925, 2856, 1734, 1488, 1071, 1011, 815, 793; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.55 (d, J = 1.4 Hz, C(CH_3)CH_3, 3H), 1.68 (d, J = 1.4 Hz, C(CH_3)CH_3, 3H), 2.26 (dt, J = 7.2, 7.7 Hz, CH_2CH, 2H), 2.58 (t, J = 7.7 Hz, ArCH_2, 2H), 5.12 (tsept, J = 7.2 Hz, 1.4 Hz, C*H*=C, 1H), 7.05 (d, J = 8.6 Hz, C*H*CHCBrCHC*H*, 2H), 7.38 (d, J = 8.6 Hz, C*H*CBrC*H*, 2H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 17.7, 25.7, 29.8, 35.5, 119.4, 123.2, 130.2 (2C), 131.2 (2C), 132.5, 141.3. Anal. Calcd for $C_{12}H_{15}Br$: C, 60.27; H, 6.32. Found: C, 60.51; H, 6.51. ^{1}H and ^{13}C NMR spectra have been attached.

Synthesis of (*E*)- or (*Z*)-1-phenyl-1, 5-hexadiene (S11)



The reaction was carried out according to Procedure A on a 1.00 mmol scale by using a THF solution of β-styrylzinc bromide (2.38 mL, 0.63 M, 1.50 mmol), a THF solution of (trimethylsilyl)methylmagnesium chloride (1.50 mL, 1.00 M, 1.50 mmol), TMEDA (0.407 g, 0.52 mL, 3.50 mmol), (bromomethyl)cyclopropane (0.133 g, 0.98 mmol) and a THF solution of $FeCl_3$ (0.50 mL, 0.10 M, 0.050 mmol, 5 mol%). Conditions: 30 °C, 6 h. The NMR yield of the title compound **S11** was determined for a crude product by ^{1}H NMR analysis (90% yield, pyradine was used as an internal standard). The title compound **S11** (0.134 g, 86% yield, *E*:*Z* = 90:10, 98% pure on the GC analysis) was obtained as a colorless liquid after silica gel column chromatography (hexane). ^{1}H and ^{13}C NMR spectra have been attached. Analytical data for the title compound have been reported.[8a,b]

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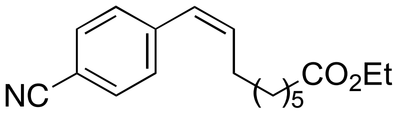
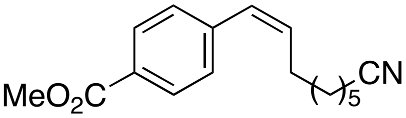
(8) *E*-isomer: (a) Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, *103*, 1969–1975. *Z*-isomer: (b) Antonsson, T.; Moberg, C.; Tottie, L.; Heumann, A. *J. Org. Chem.* **1989**, *54*, 4914–4929.

Synthesis of (*Z*)-ethyl 9-(4-cyanophenyl)non-8-enoate (9)



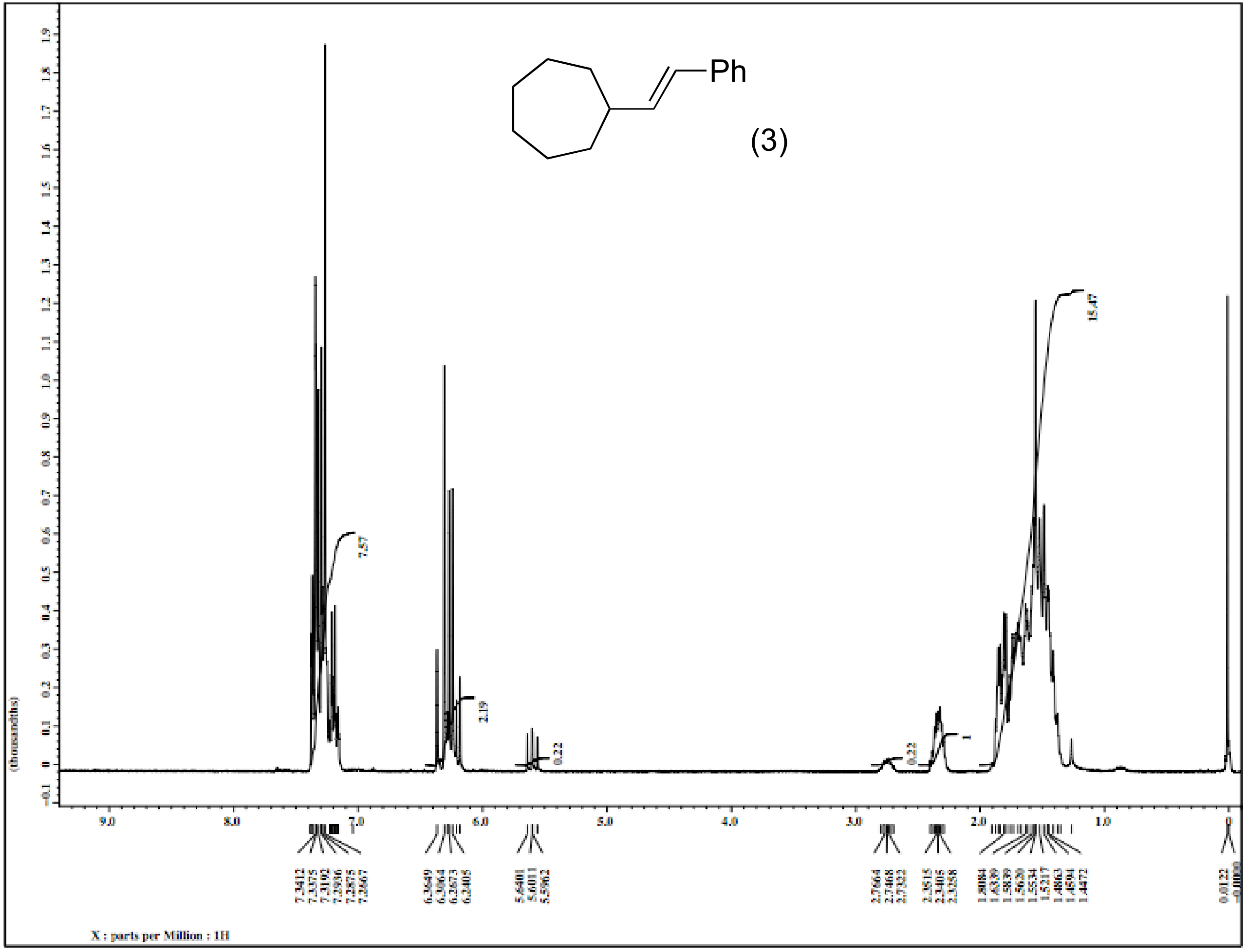
The reaction was carried out according to Procedure A on a 1.00 mmol scale by using a THF solution of (*Z*)-(4-cyanostyryl)zinc bromide (4.41 mL, 0.34 M, 1.50 mmol), a THF solution of (trimethylsilyl)methylmagnesium chloride (1.50 mL, 1.00 M, 1.50 mmol), TMEDA (0.581 g, 0.74 mL, 5.00 mmol), ethyl 4-bromoheptanoate (0.238 g, 1.00 mmol) and a THF solution of $FeCl_3$ (0.50 mL, 0.10 M, 0.050 mmol, 5 mol%). Conditions: 30 °C, 6 h. The title compound **9** (0.250 g, 87% yield, *E*:*Z* = 4:96, > 99% pure on the GC analysis) was obtained as a colorless liquid after silica gel column chromatography (5 and 9% EtOAc in hexane). R_f = 0.18 (9% EtOAc in hexane); IR (neat) 2928, 2856, 2227, 1733, 1174, 1033, 854, 671; ^{1}H NMR (270 MHz, $CDCl_3$) For **9-*Z***: δ 1.25 (t, *J* = 7.2 Hz, CH_3, 3H), 1.17–1.69 (m, $CH_2(CH_2)_4CH_2$, 8H), 2.28 (t, *J* = 7.6 Hz, $CH_2CH_2C(=O)$, 2H), 2.20–2.34 (m, $CHCHCH_2$, 2H), 4.12 (q, *J* = 7.3 Hz, OCH_2, 2H), 5.81 (dt, *J* = 11.9 Hz, 7.3 Hz, ArCHC*H*, 1H), 6.40 (d, *J* = 11.9 Hz, ArC*H*, 1H), 7.35 (d, *J* = 8.1 Hz, C*H*CHC(CN)CHC*H*, 2H), 7.61 (d, *J* = 8.1 Hz, CHC*H*C(CN)C*H*CH, 2H). ^{13}C NMR (67.5 MHz, $CDCl_3$) For **9-*Z***: δ 14.2, 24.8, 28.6, 28.9 (2C), 29.5, 34.2, 60.2, 109.9, 119.0, 127.4, 129.2 (2C), 131.9 (2C), 136.3, 142.4, 173.7. HRMS *m*/*z* calcd for $C_{18}H_{23}NO_2$ (M^+) 285.1729, found 285.1730. ^{1}H and ^{13}C NMR spectra have been attached.

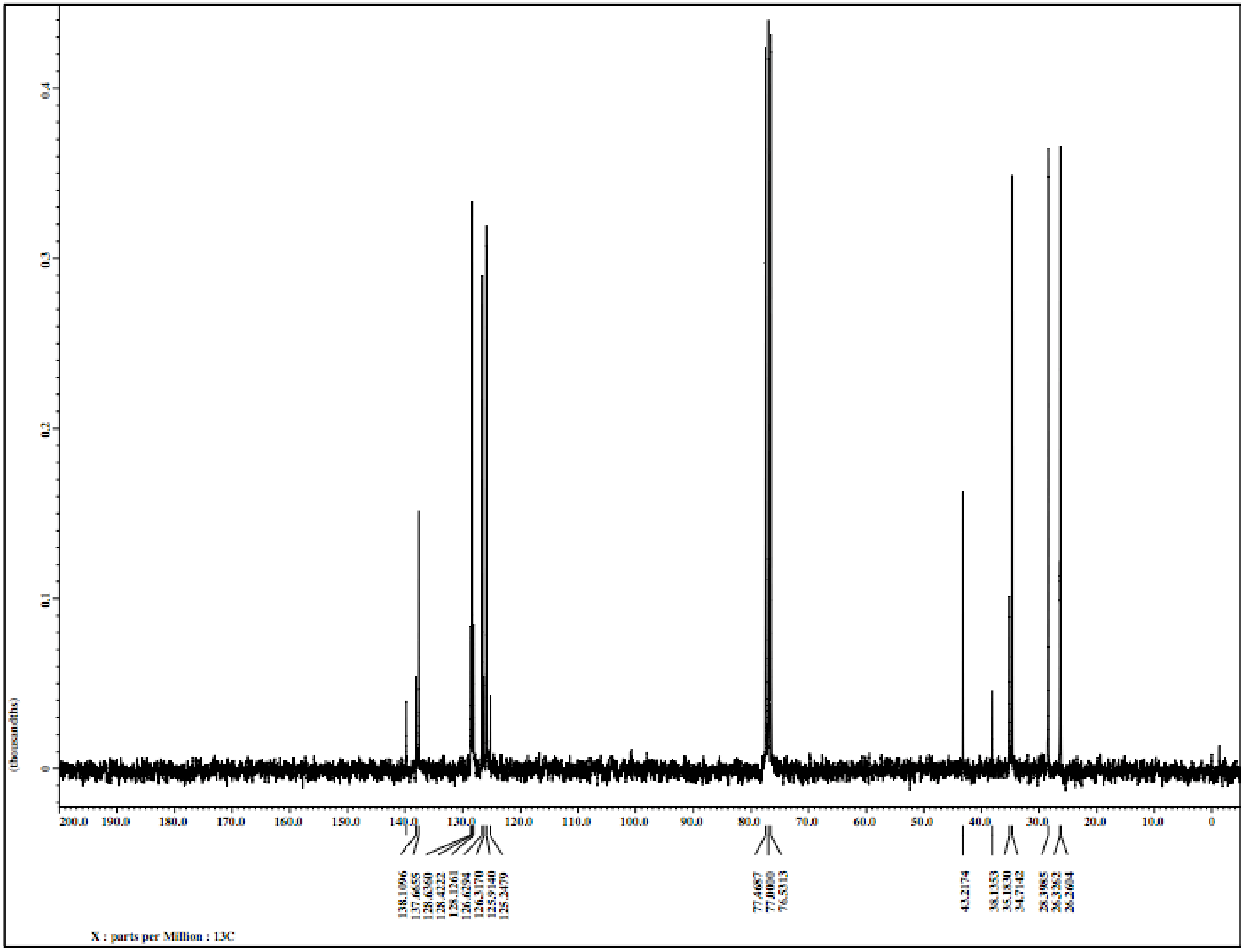
Synthesis of (*Z*)-methyl 4-(8-cyanooct-1-enyl)benzoate (11)

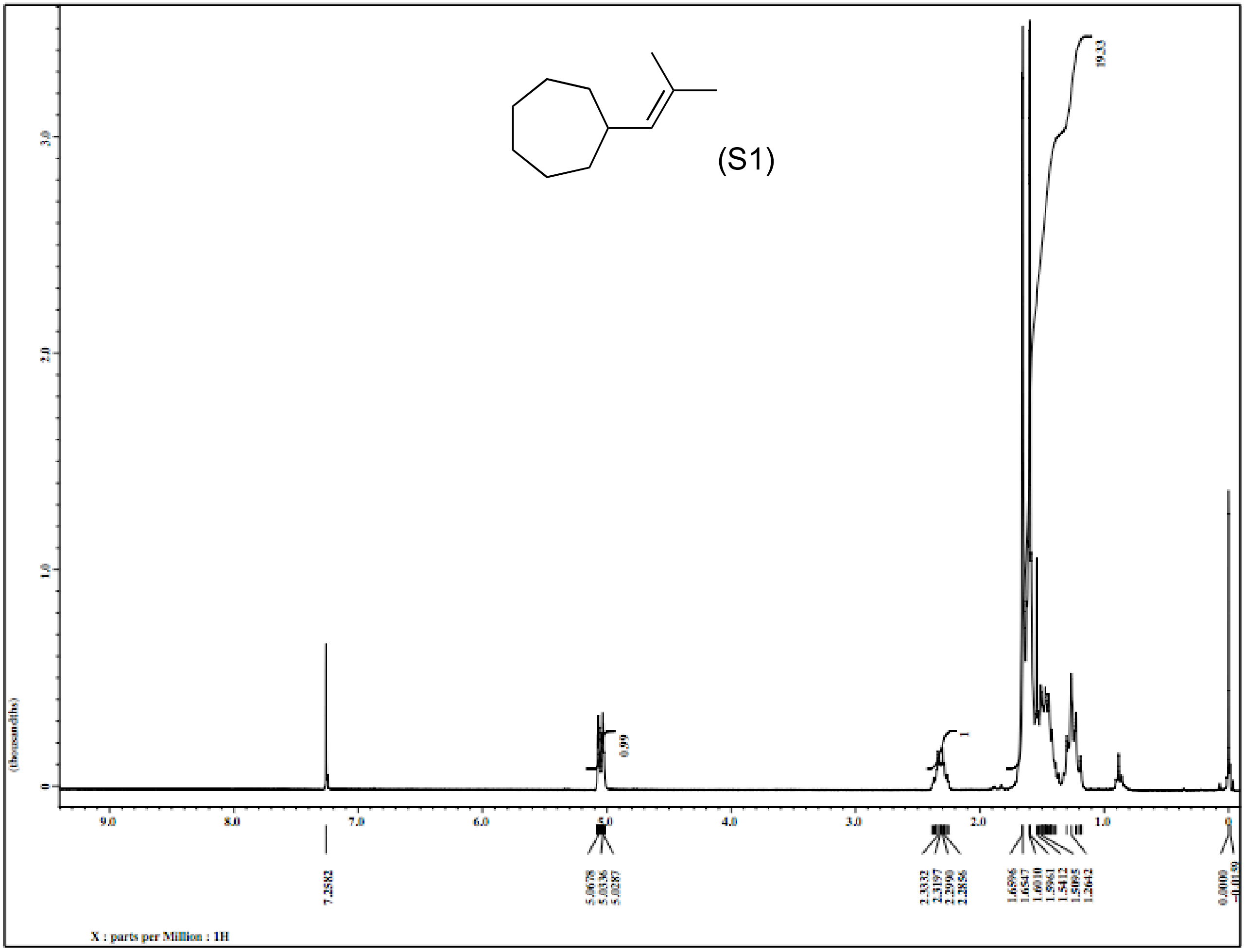


The reaction was carried out according to Procedure A on a 0.50 mmol scale by using a THF solution of (*Z*)-(4-methoxycarbonylstyryl)zinc bromide (2.27 mL, 0.33 M, 0.75 mmol), a THF solution of (trimethylsilyl)methylmagnesium chloride (0.75 mL, 1.00 M, 0.75 mmol), TMEDA (0.203 g, 0.26 mL, 1.75 mmol), 7-bromoheptanenitrile (95.2 mg, 0.50 mmol) and a THF solution of $FeCl_3$ (0.25 mL, 0.10 M, 0.025 mmol, 5 mol%). Conditions: 30°C, 6 h. The title compound **11** (0.125g, 92% yield, *E*:*Z* = 89:11, > 99% pure on the GC analysis) was obtained as a pale yellow liquid after silica gel column chromatography (5 and 9% EtOAc in hexane). R_f = 0.26 (17% EtOAc in hexane); IR (neat) 3008, 2932, 2857, 2246, 1720, 1607, 1435, 1281; ^{1}H NMR (270 MHz, $CDCl_3$) For **11-*Z***: δ 1.26–1.53 (m, $CHCH_2(CH_2)_3CH_2$, 6H), 1.65 (quint, *J* = 7.3 Hz, CH_2CH_2CN, 2H), 2.32 (t, *J* = 7.3 Hz, CH_2CH_2CN, 2H), 2.28–2.38 (m, $CHCHCH_2$, 2H), 3.92 (s, OCH_3, 3H), 5.75 (dt, *J* = 11.9 Hz, 7.3 Hz, ArCHC*H*, 1H), 6.45 (d, *J* = 11.9 Hz, ArC*H*, 1H), 7.32 (d, *J* = 8.2 Hz, C*H*CHC(CO_2CH_3)CHC*H*, 2H), 8.00 (d, *J* = 8.2 Hz, CHC*H*C(CO_2CH_3)C*H*CH, 2H). ^{13}C NMR (67.5 MHz, $CDCl_3$) For **11-*Z***: δ 17.1, 25.3, 28.4, 28.5, 28.5, 29.4, 52.0, 119.7, 128.1, 128.3, 128.6 (2C), 129.5 (2C), 134.8, 142.3, 166.9. HRMS *m*/*z* calcd for $C_{17}H_{21}NO_2$ (M^+) 271.1572, found 271.1573. ^1H and ^{13}C NMR spectra have been attached.

1H and 13C NMR spectra for isolated compounds (3), (9), (11), (S1)–(S11)







(S1)

19.33
0.99
1
(thousandths)
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2582
5.0678
5.0336
5.0287
2.3332
2.3197
2.2990
2.2856
1.6596
1.6547
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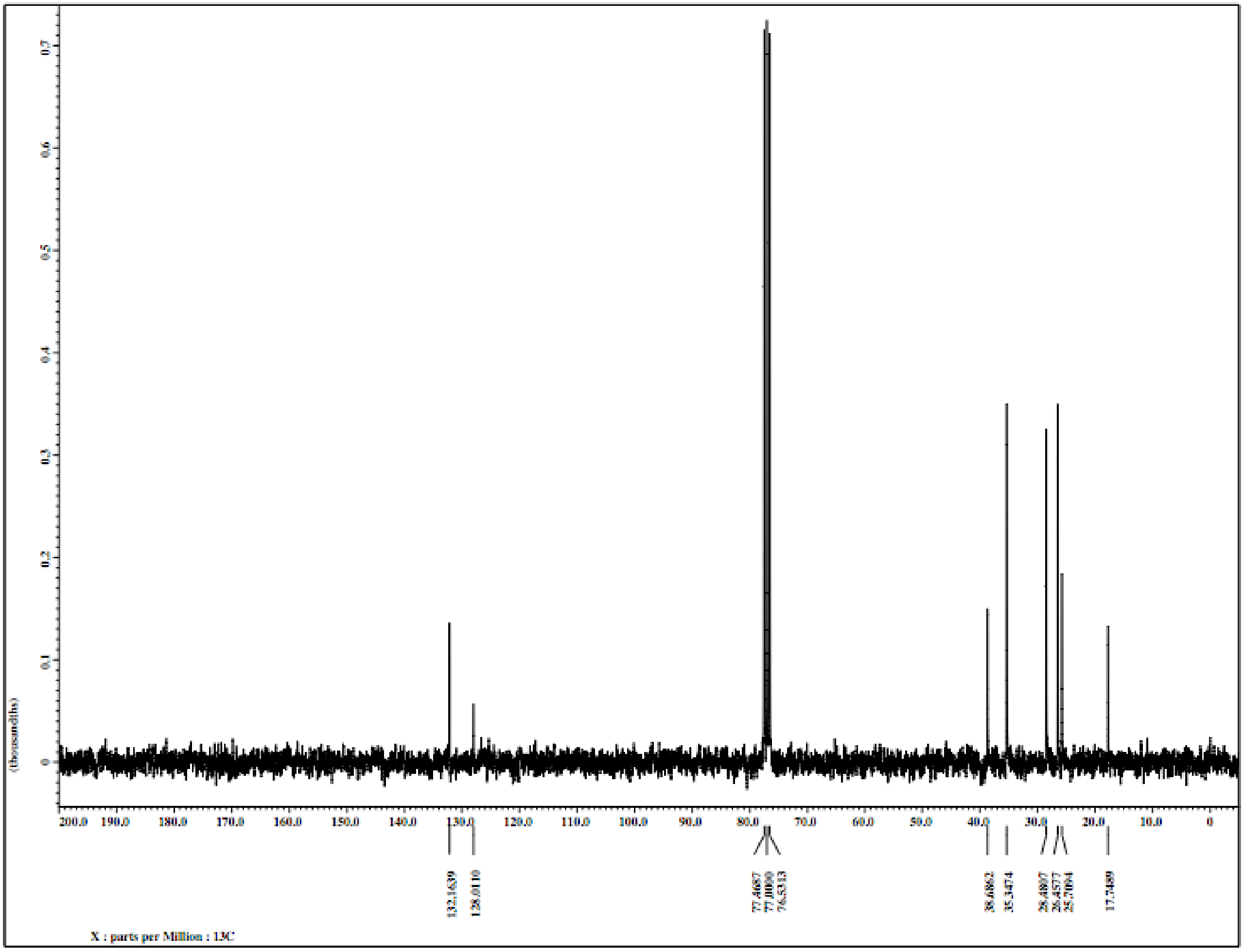
0.0000
-0.0159
X : parts per Million : 1H



(thousandths)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
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
0
132.1639
128.0110
77.4687
77.0000
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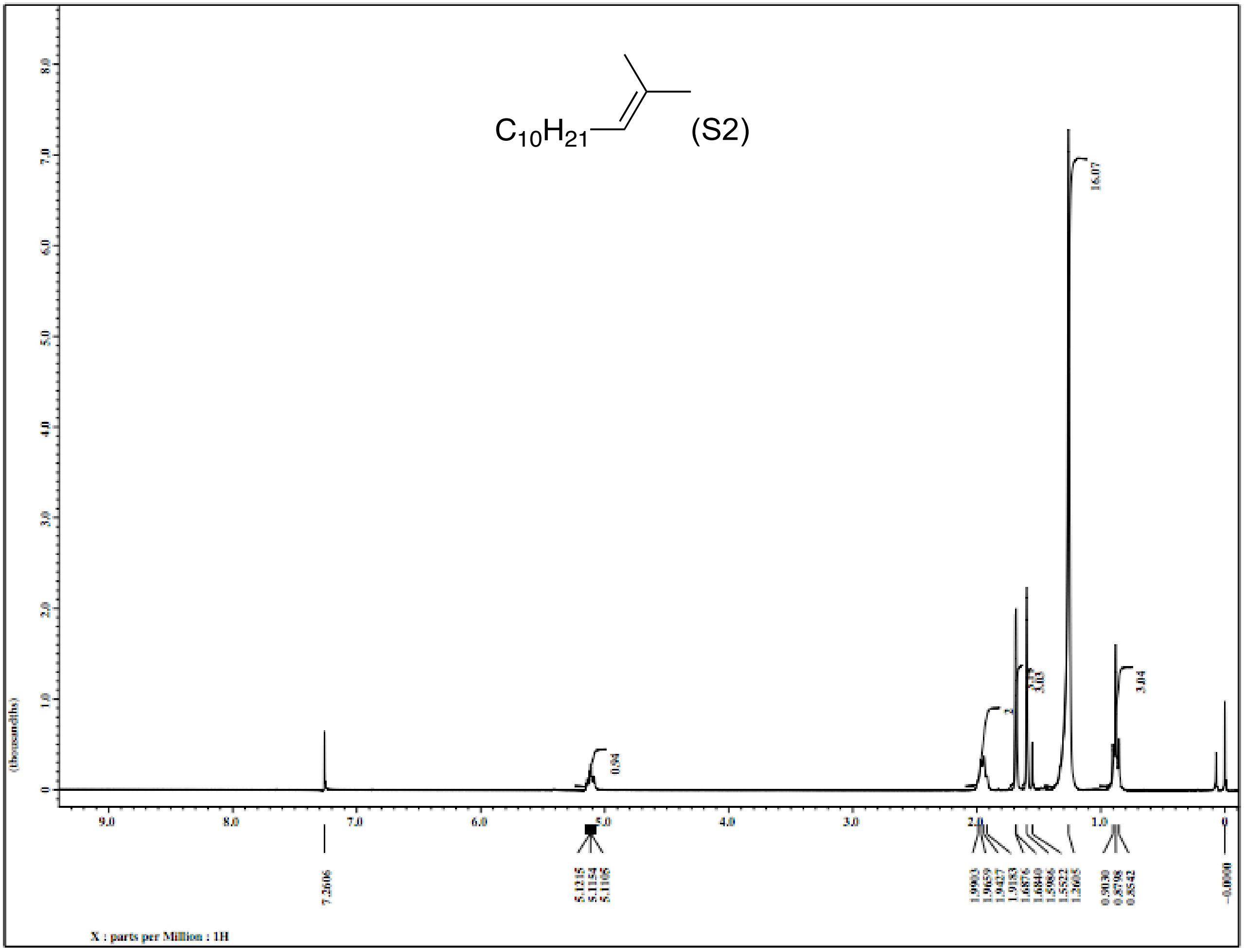
17.7489
X : parts per Million : 13C



$C_{10}H_{21}$
(S2)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
(thousandths)
16.07
3.13
3.03
3.04
2
0.94
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2606
5.1215
5.1154
5.1105
1.9903
1.9659
1.9427
1.9183
1.6876
1.6840
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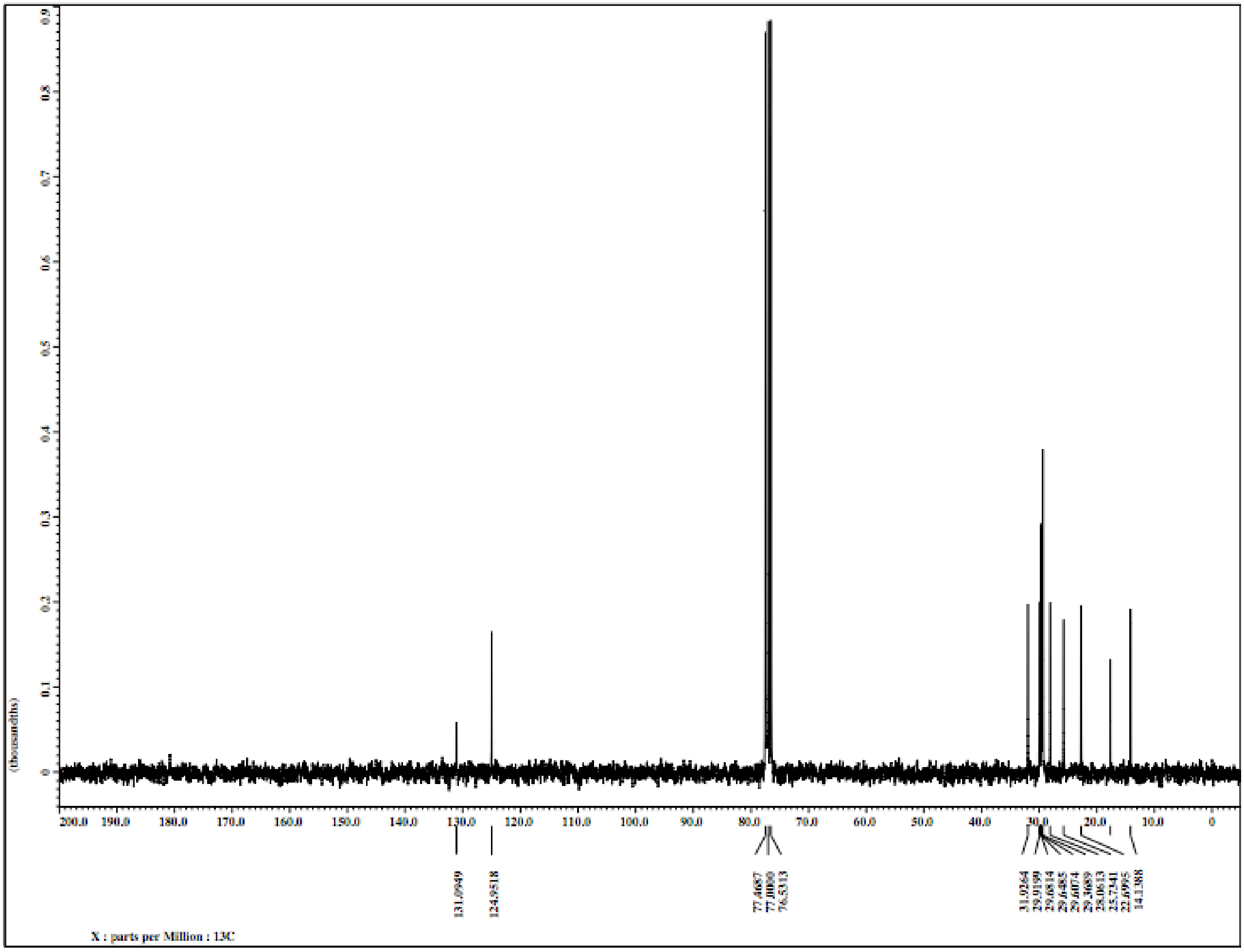
X : parts per Million : 1H



0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
(thousandths)
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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
0
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77.4687
77.0000
76.5313
31.9264
29.9199
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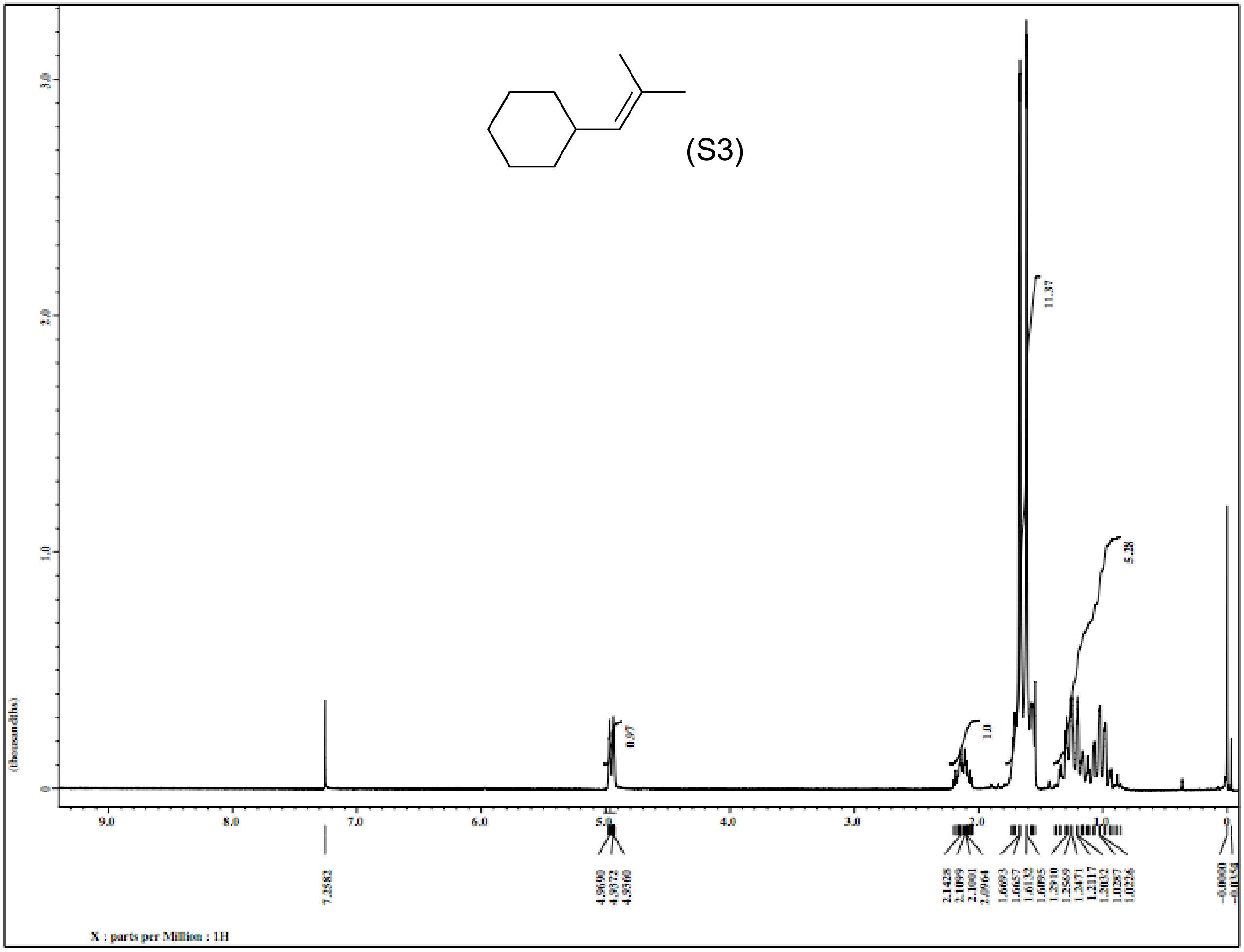
22.6995
14.1388
X : parts per Million : 13C


(S3)
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2.0
1.0
0
(thousandths)
9.0
8.0
7.0
6.0
5.0
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3.0
2.0
1.0
0
0.97
1.0
11.37
5.28
7.2582
4.9600
4.9372
4.9300
2.1428
2.1099
2.1001
2.0964
1.6693
1.6657
1.6132
1.6095
1.2910
1.2569
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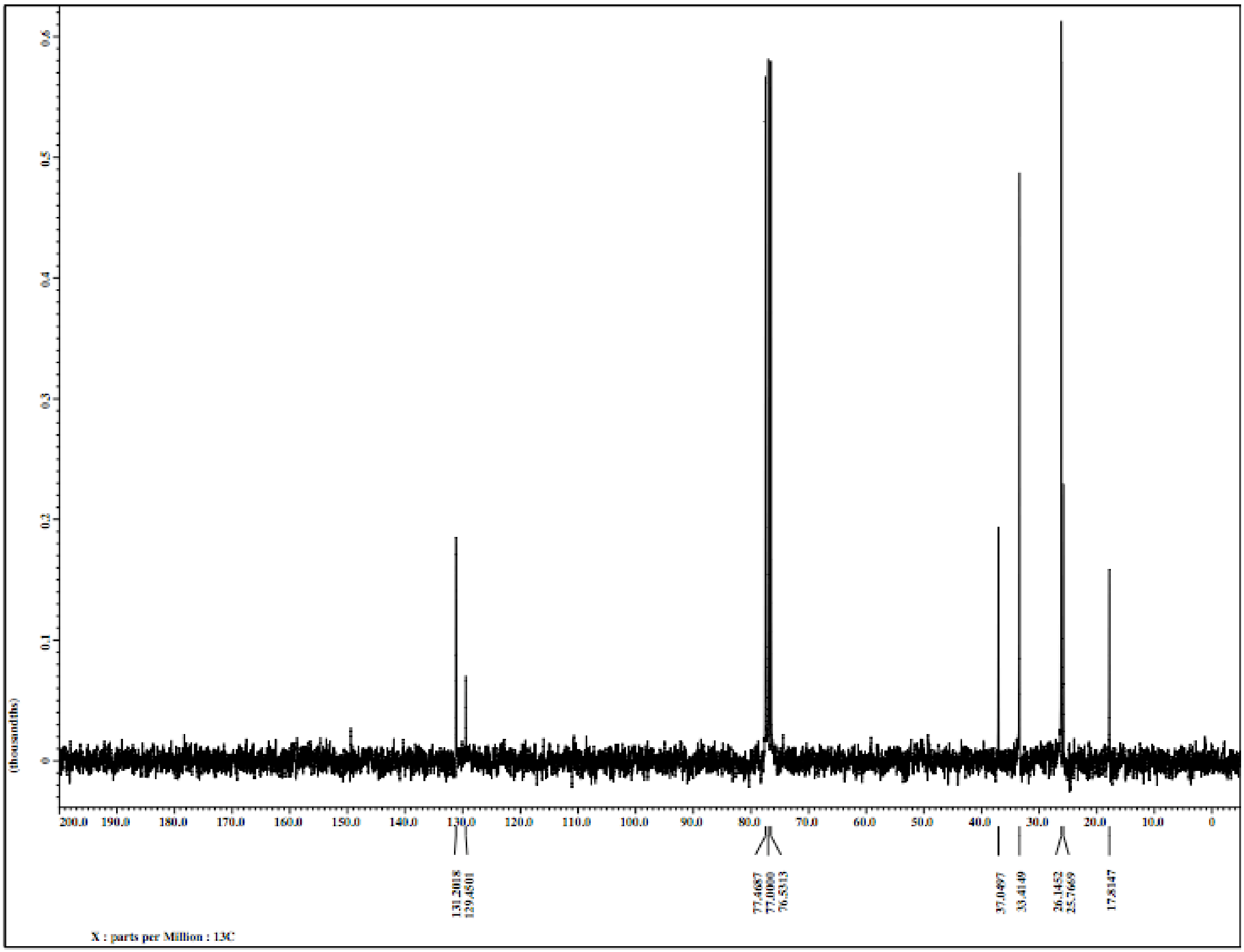
X : parts per Million : 1H


0.6
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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
0
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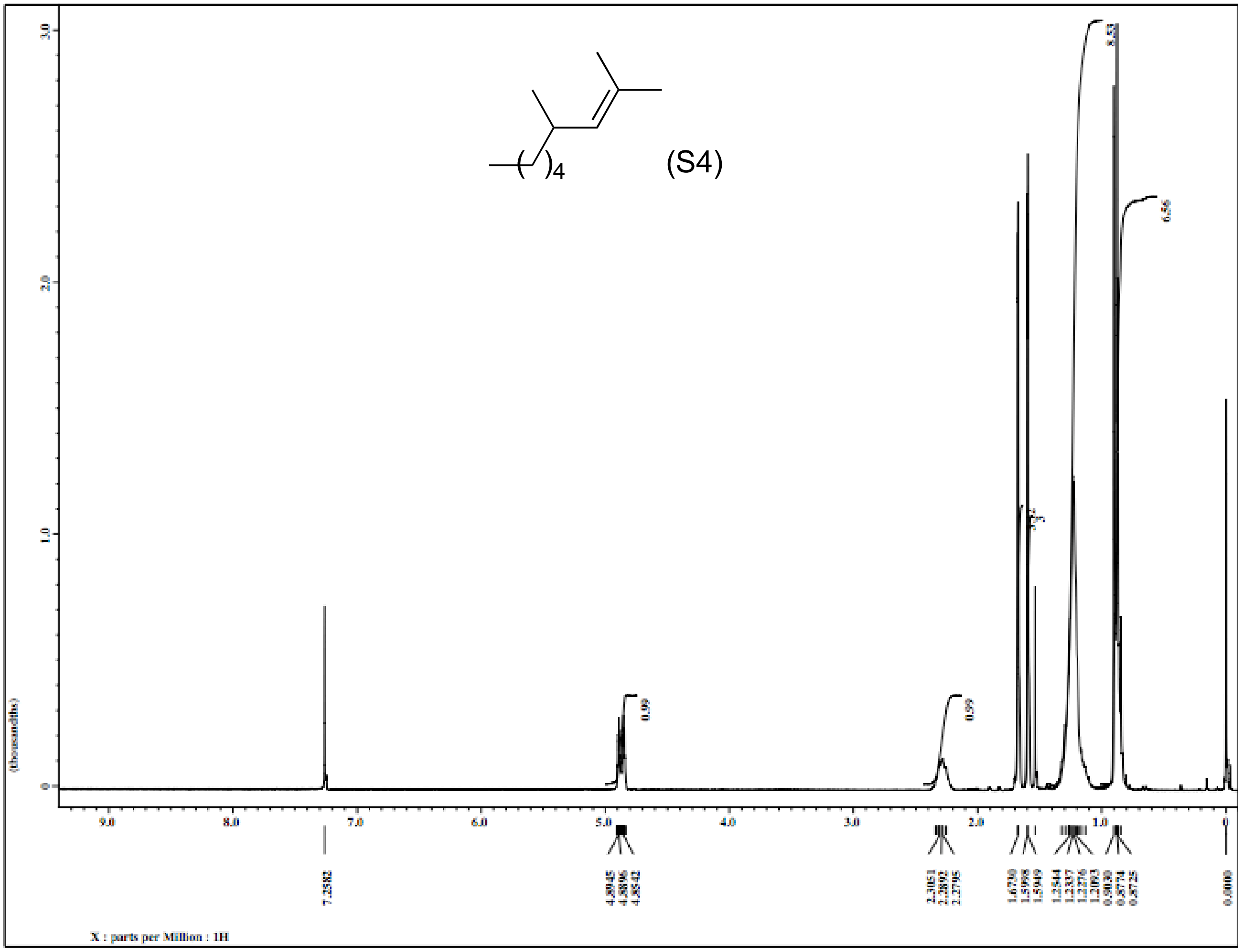
76.5313
37.0497
33.4149
26.1452
25.7669
17.8147
X : parts per Million : 13C


(S4)
4
(thousandths)
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.99
0.99
8.53
6.56
7.2582
4.8945
4.8896
4.8542
2.3051
2.2892
2.2795
1.6730
1.5988
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1.2544
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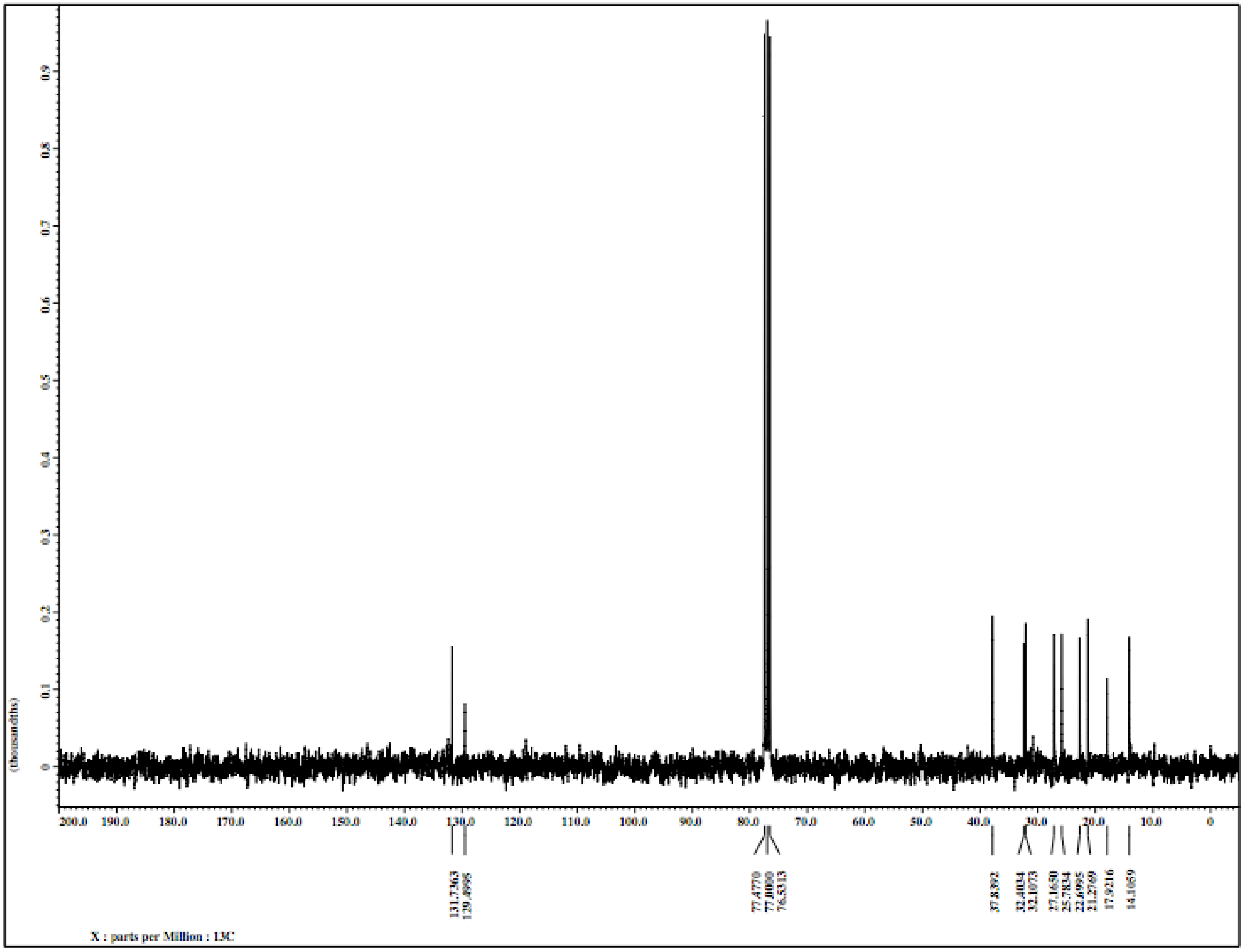
X : parts per Million : 1H


(thousandths)
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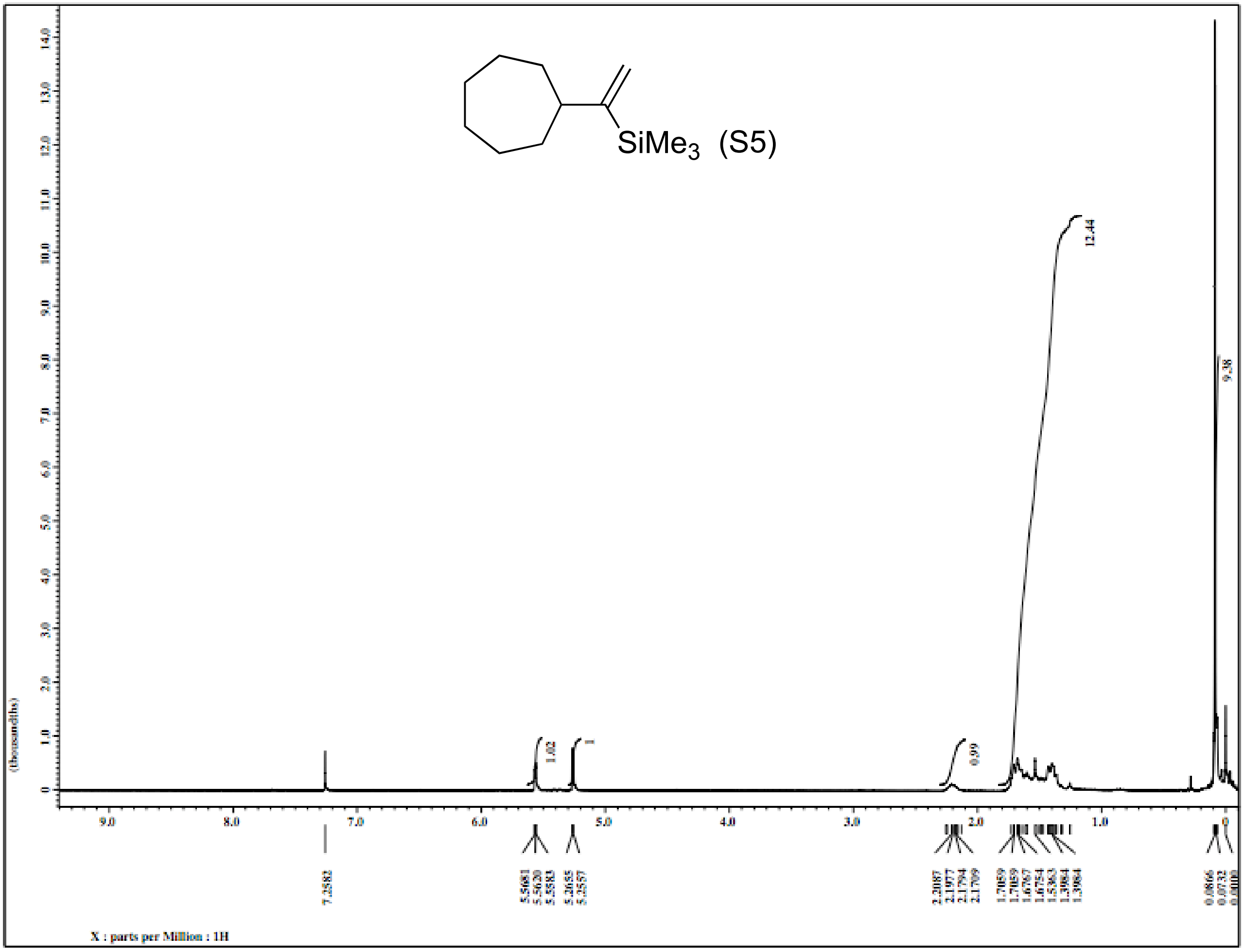
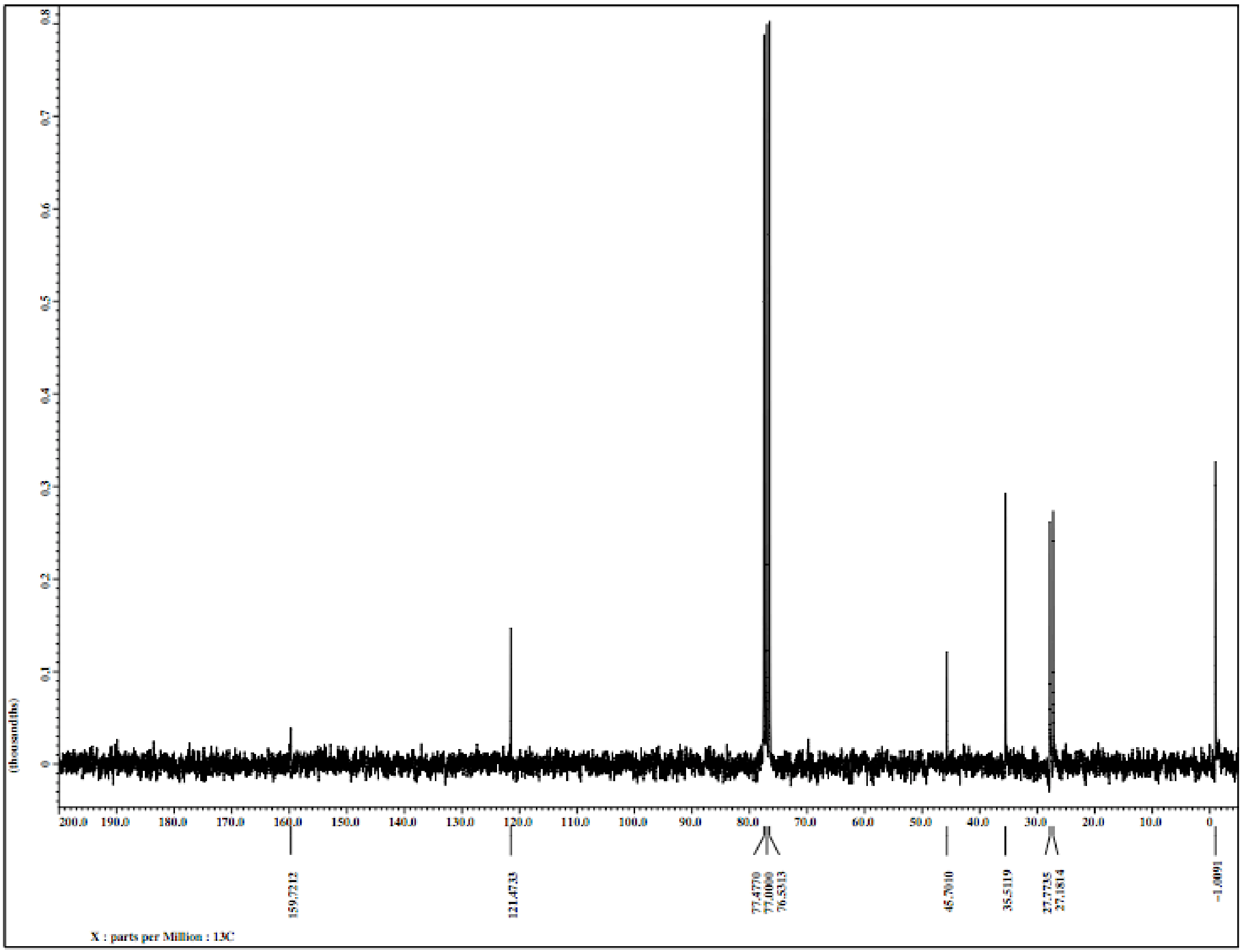
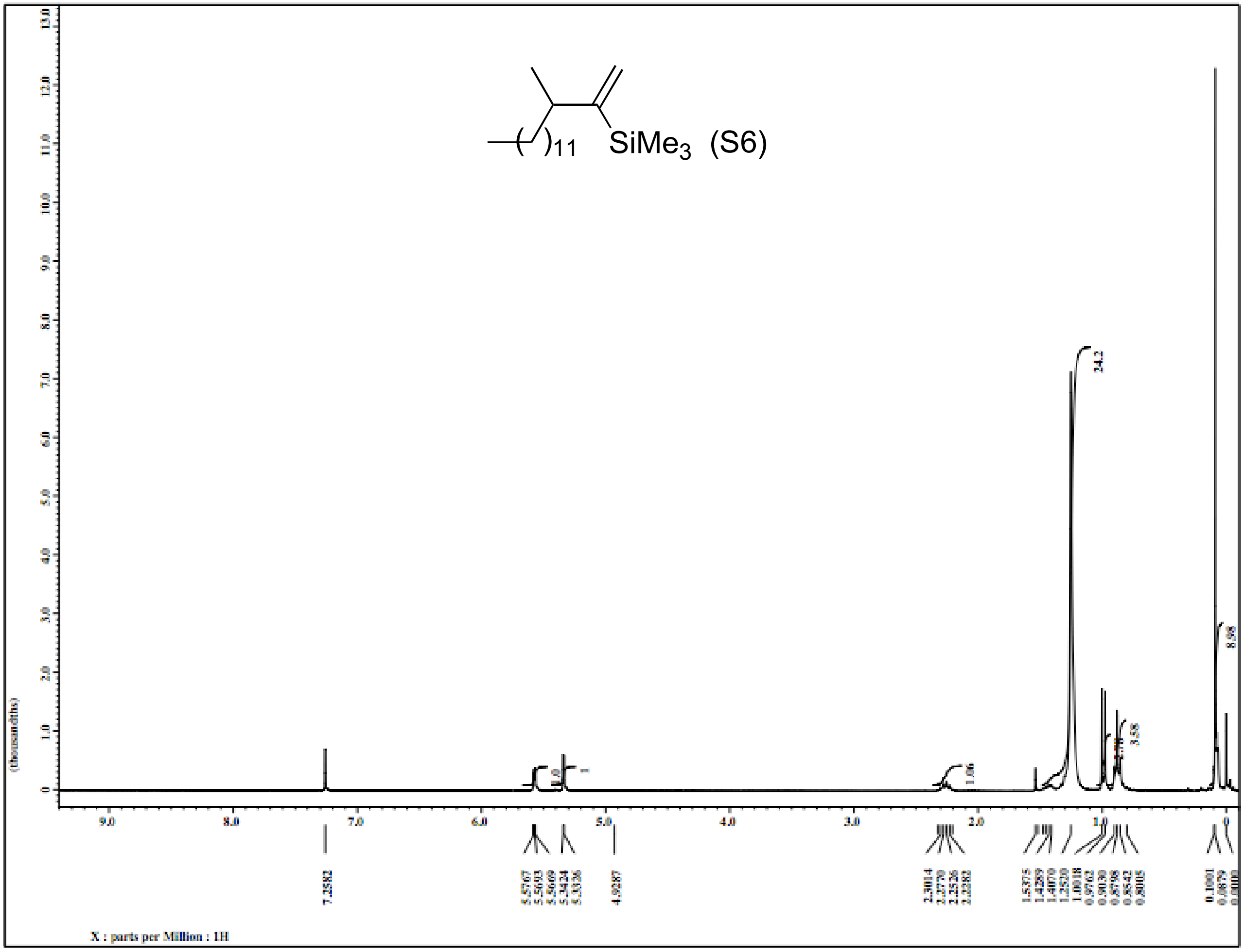
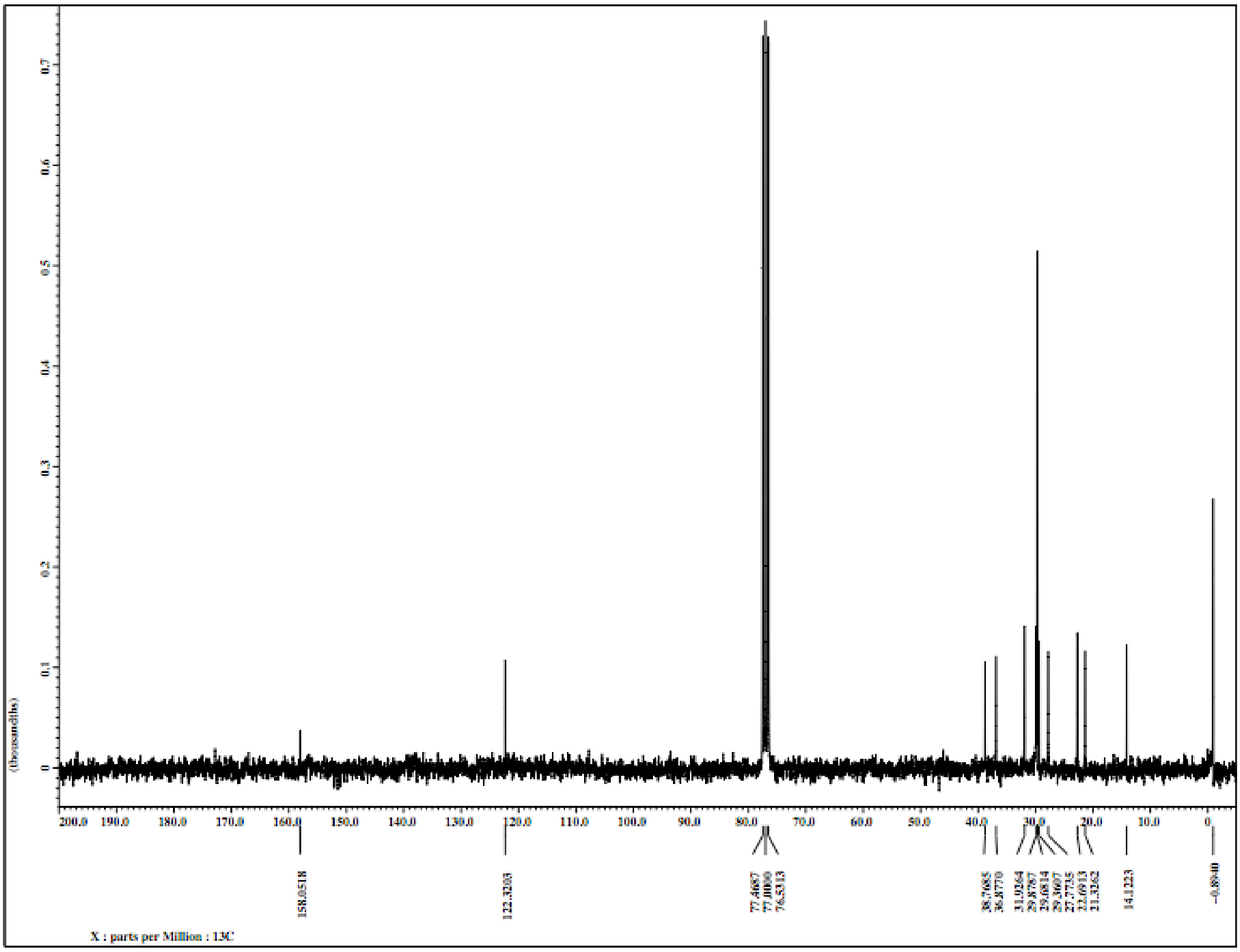
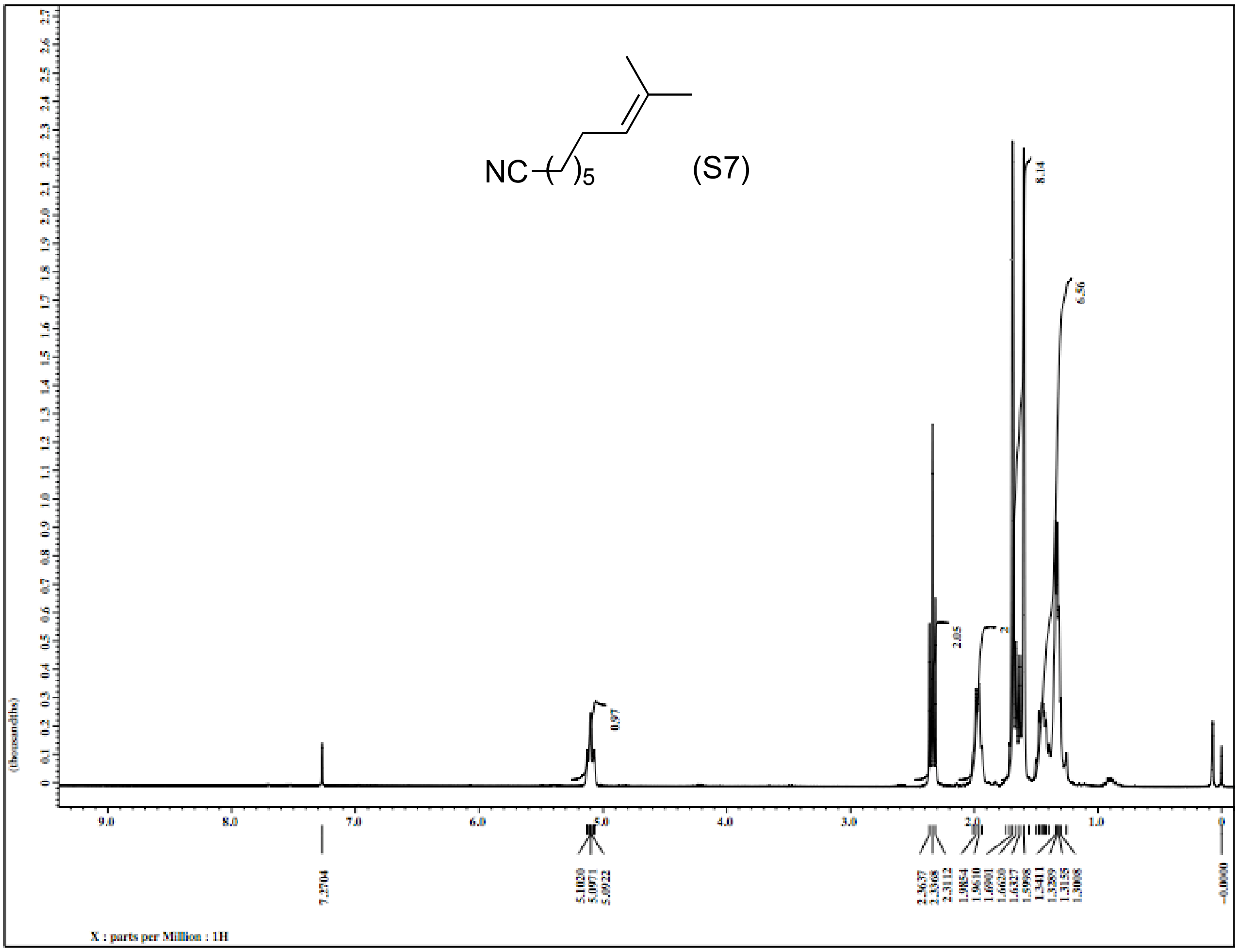
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
131.7363
129.4995
77.4770
77.0000
76.5313
37.8392
32.4034
32.1073
27.1650
25.7834
22.6995
21.2769
17.9216
14.1059
X : parts per Million : 13C

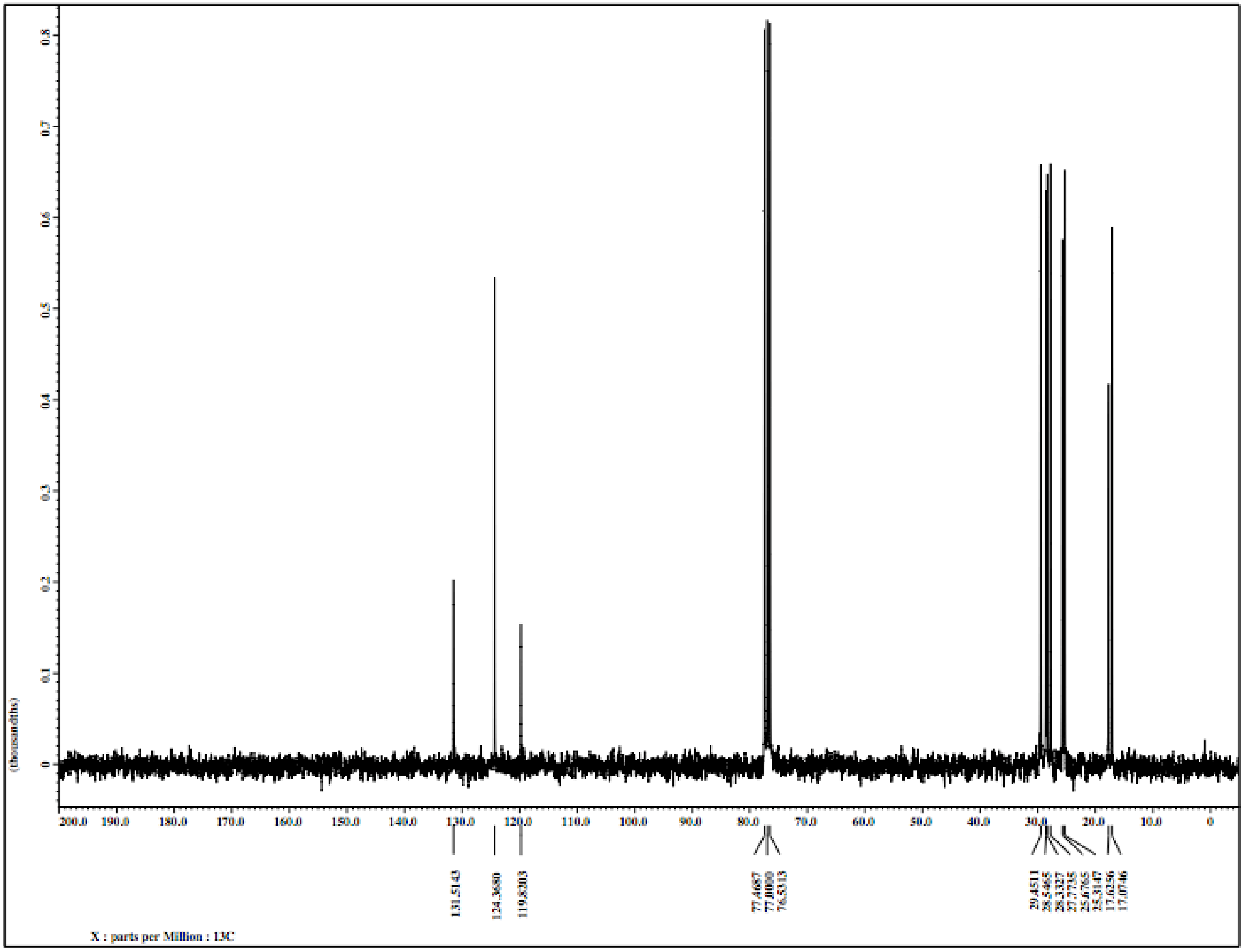

SiMe3 (S5)
(thousandths)
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
12.44
9.38
1.02
1
0.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2582
5.5681
5.5620
5.5583
5.2655
5.2557
2.2087
2.1977
2.1794
2.1709
1.7059
1.7059
1.6767
1.6754
1.5363
1.3984
1.3984
0.0866
0.0732
0.0000
X : parts per Million : 1H

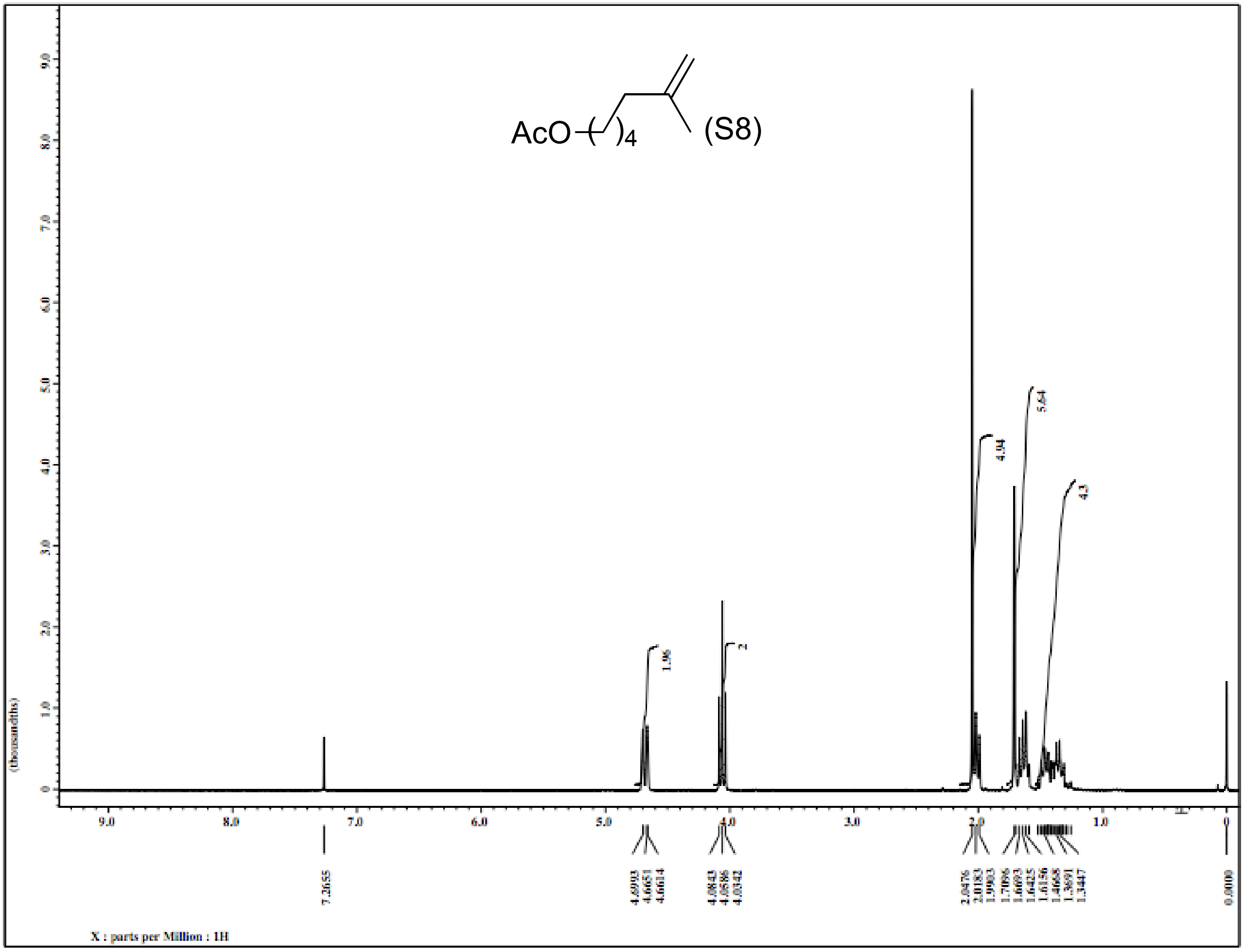

(thousandths)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
159.7212
121.4733
77.4770
77.0000
76.5313
45.7010
35.5119
27.7735
27.1814
−1.0091
X : parts per Million : 13C

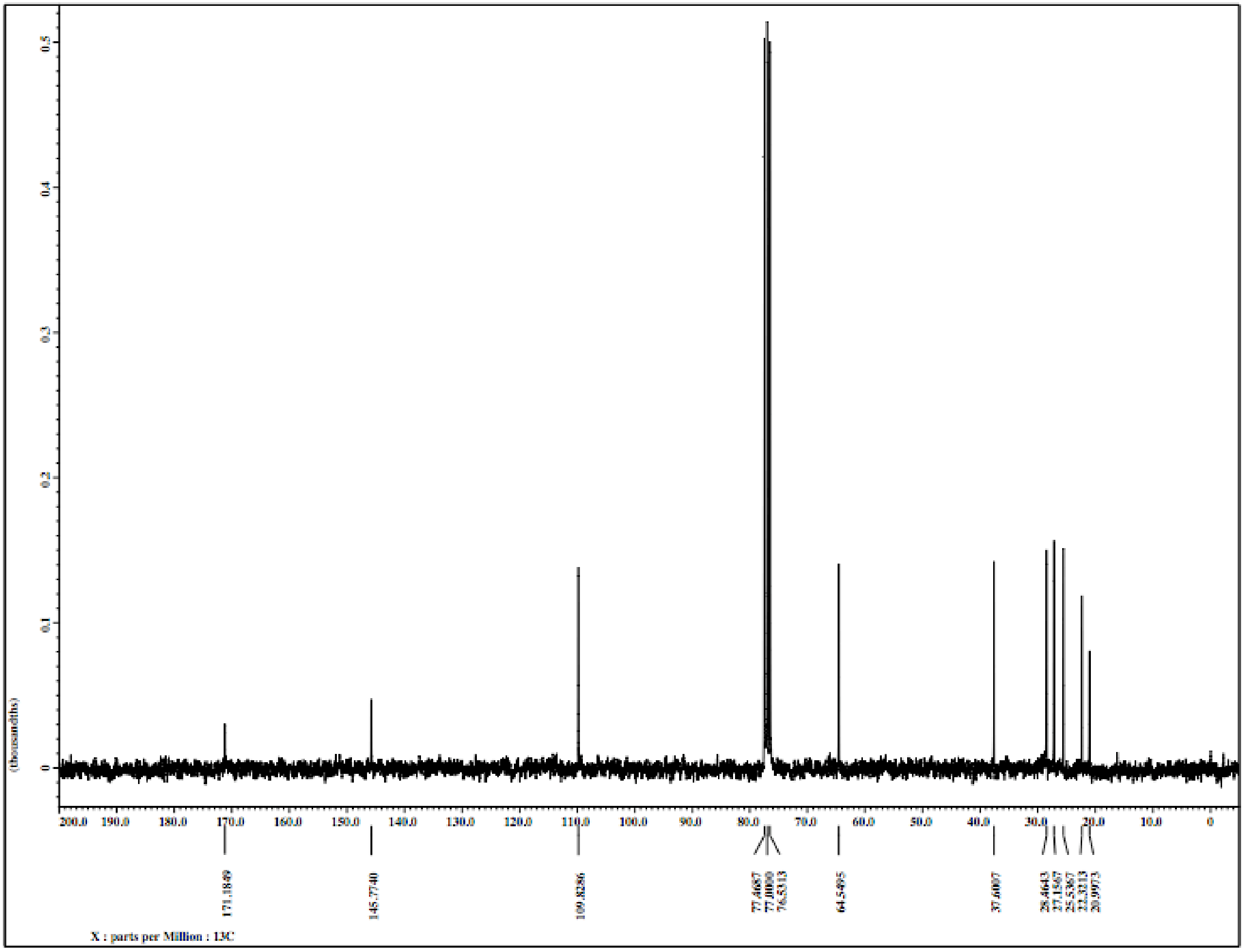

SiMe$_3$ (S6)
$)_{11}$
(thousandths)
24.2
8.98
3.58
1.06
1.0
1
7.2582
5.5767
5.5603
5.5669
5.3424
5.3326
4.9287
2.3014
2.2770
2.2526
2.2282
1.5375
1.4289
1.4070
1.2520
1.0018
0.9762
0.9030
0.8798
0.8542
0.8005
0.1001
0.0879
0.0000
X : parts per Million : 1H

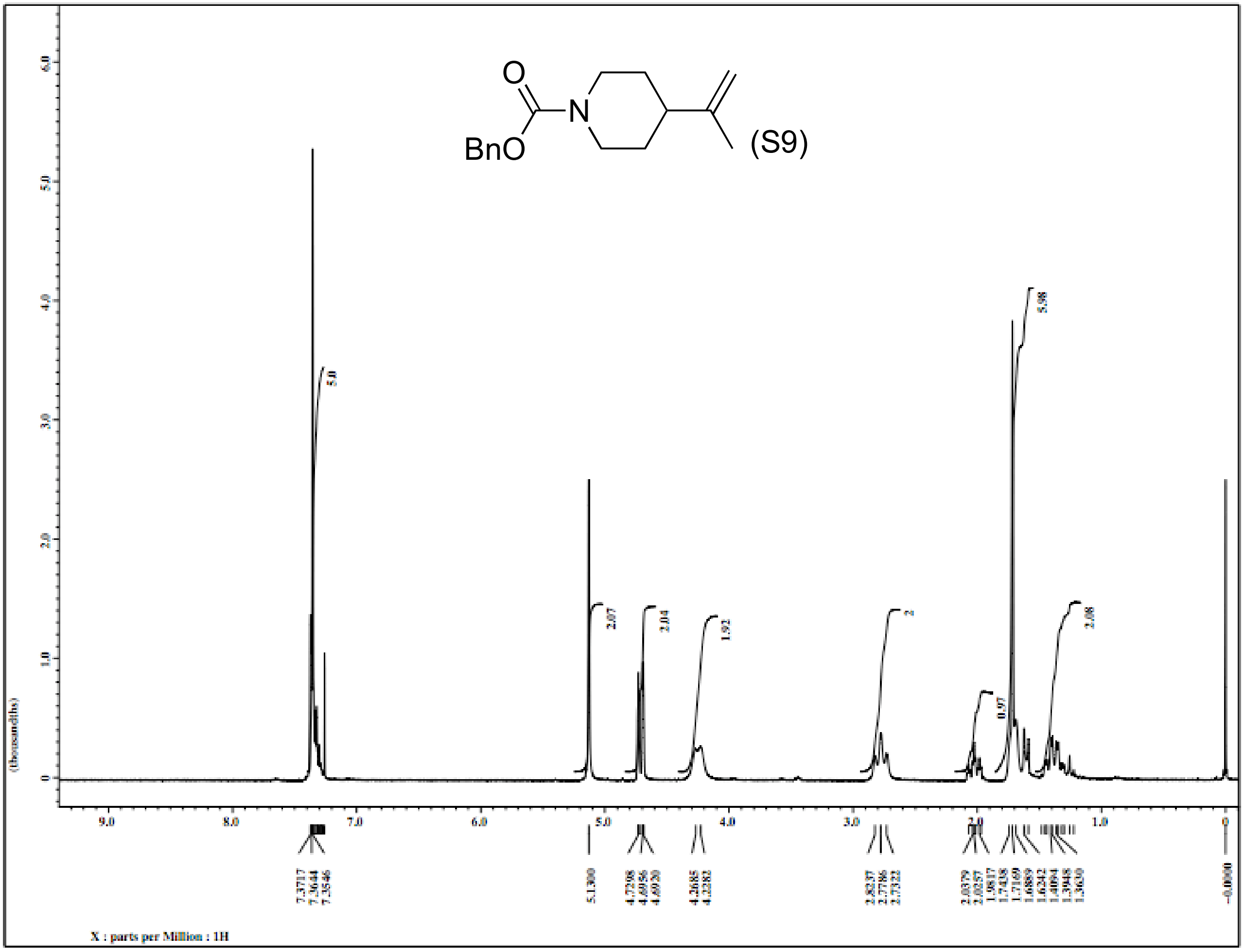

(thousandths)
158.0518
122.3203
77.4687
77.0000
76.5313
38.7685
36.8770
31.9264
29.8787
29.6814
29.3607
27.7735
22.6913
21.3262
14.1223
−0.8940
X : parts per Million : 13C

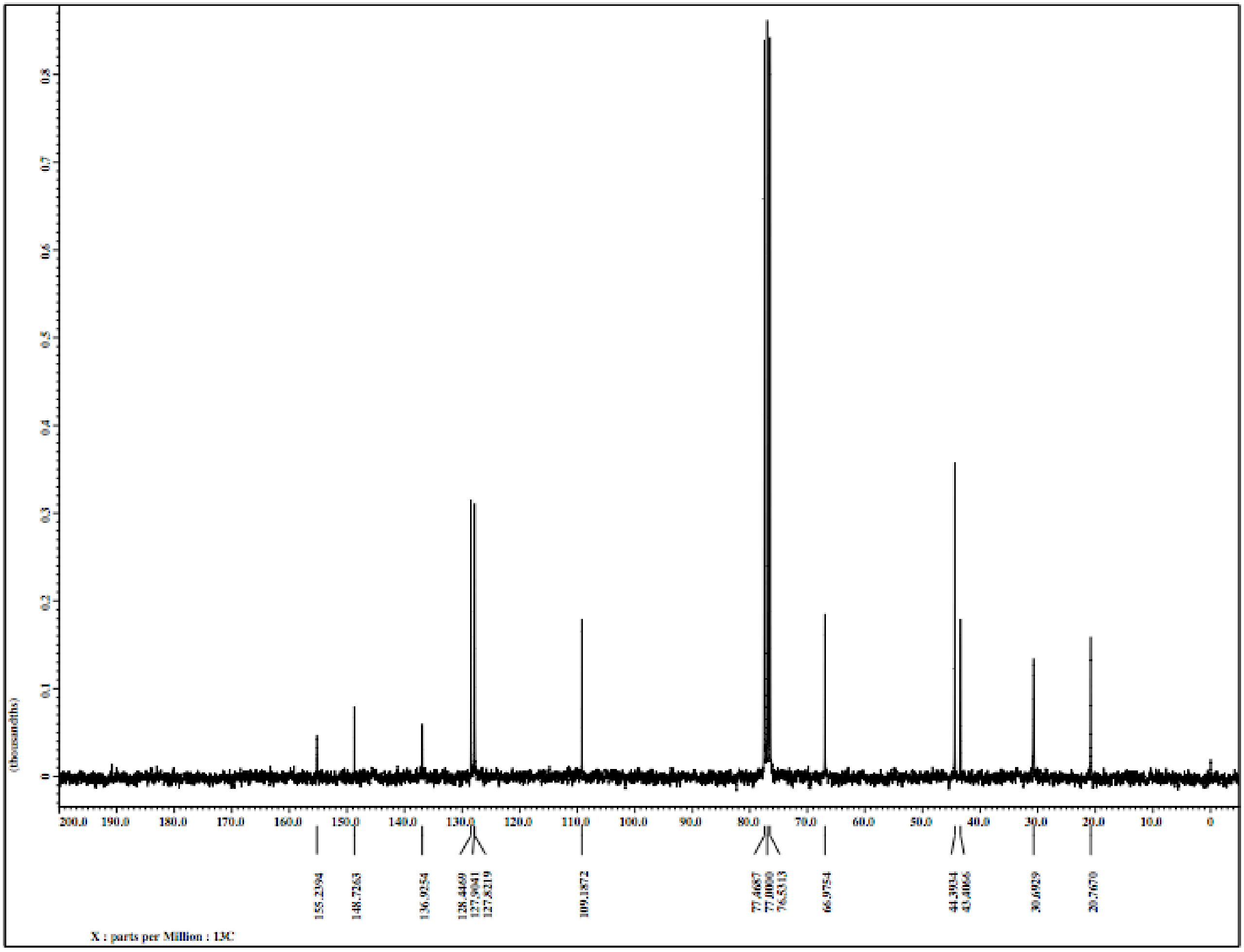

NC
5
(S7)
(thousandths)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
0.97
2.05
2
8.14
6.56
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2704
5.1020
5.0971
5.0922
2.3637
2.3368
2.3112
1.9854
1.9610
1.6901
1.6620
1.6327
1.5998
1.3411
1.3289
1.3155
1.3008
-0.0000
X : parts per Million : 1H

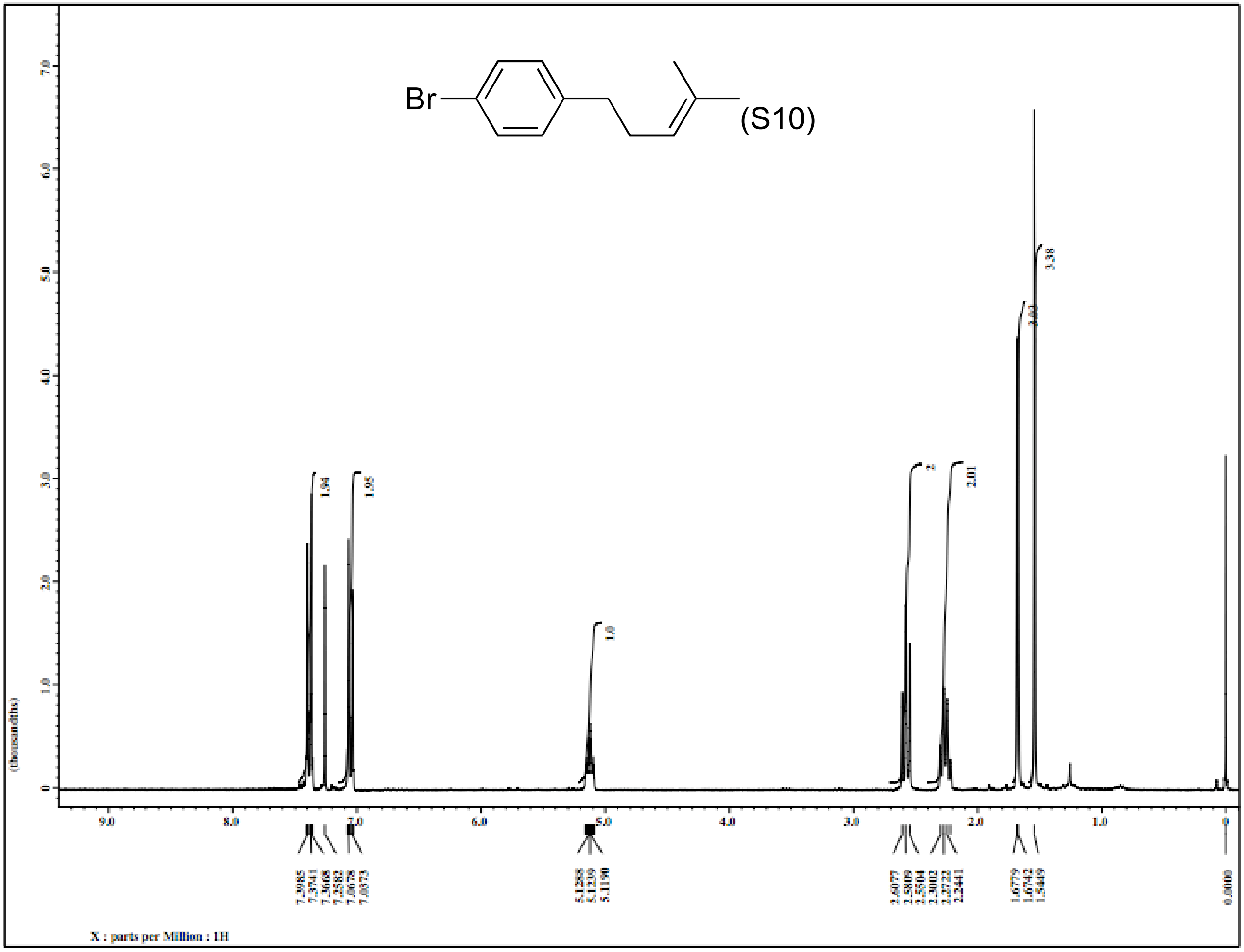

(thousandths)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
131.5143
124.3680
119.8203
77.4687
77.0000
76.5313
29.4511
28.5465
28.3327
27.7735
25.6765
25.3147
17.6256
17.0746
X : parts per Million : 13C


AcO
4
(S8)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
(thousandths)
1.96
2
4.94
5.64
4.3
7.2655
4.6903
4.6651
4.6614
4.0843
4.0586
4.0342
2.0476
2.0183
1.9903
1.7086
1.6693
1.6425
1.6156
1.4668
1.3691
1.3447
0.0000
X : parts per Million : 1H


0.5
0.4
0.3
0.2
0.1
0
(thousandths)
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
0
171.1849
145.7740
109.8286
77.4687
77.0000
76.5313
64.5495
37.6007
28.4643
27.1567
25.5367
22.3213
20.9973
X : parts per Million : 13C

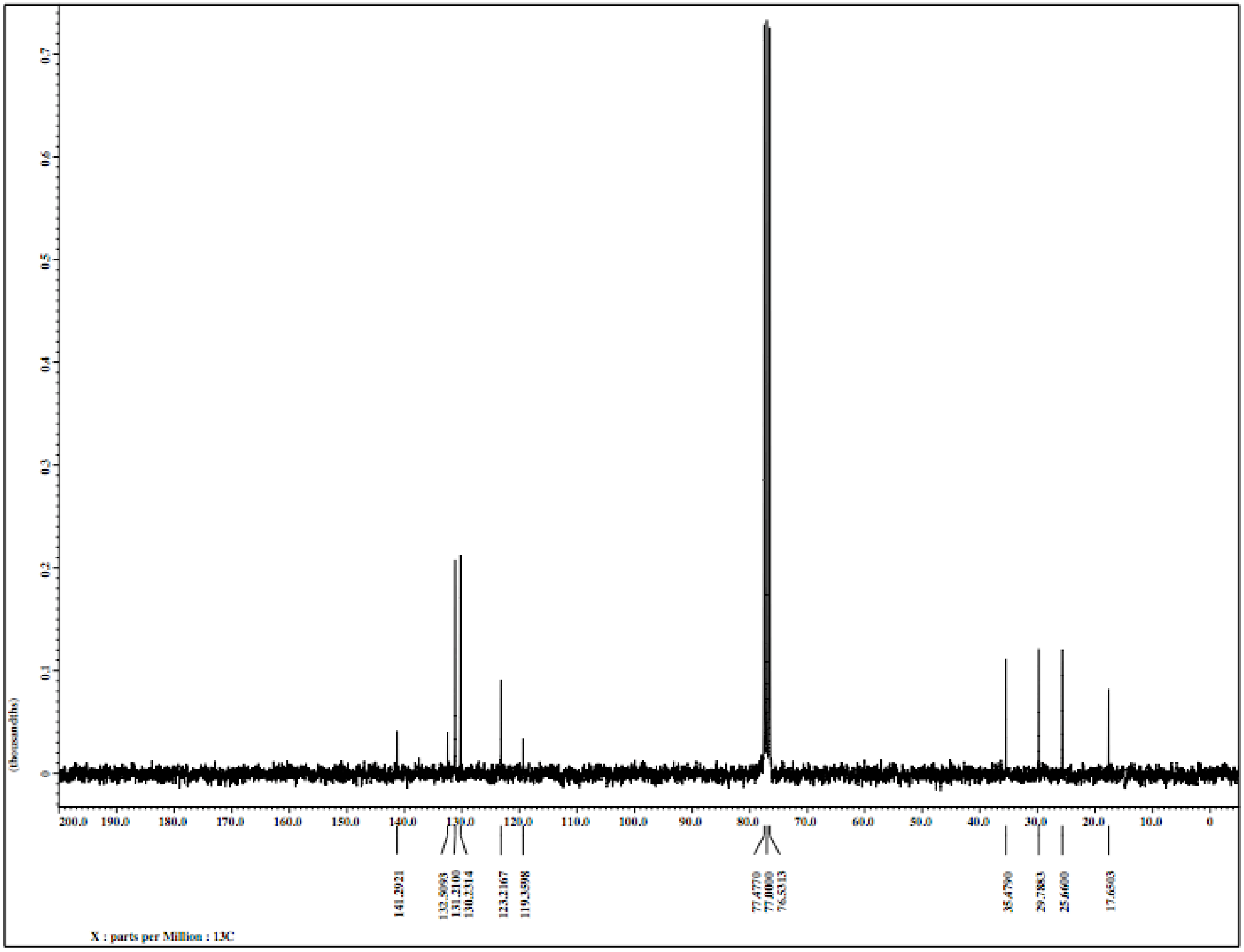

O
N
BnO
(S9)
6.0
5.0
4.0
3.0
2.0
1.0
0
(thousandths)
5.0
2.07
2.04
1.92
2
0.97
5.98
2.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3717
7.3644
7.3546
5.1300
4.7298
4.6956
4.6920
4.2685
4.2282
2.8237
2.7786
2.7322
2.0379
2.0257
1.9817
1.7438
1.7169
1.6889
1.6242
1.4094
1.3948
1.3630
-0.0000
X : parts per Million : 1H


0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
(thousandths)
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
0
155.2394
148.7263
136.9254
128.4460
127.9041
127.8219
109.1872
77.4687
77.0000
76.5313
66.9754
44.3934
43.4066
30.6929
20.7670
X : parts per Million : 13C

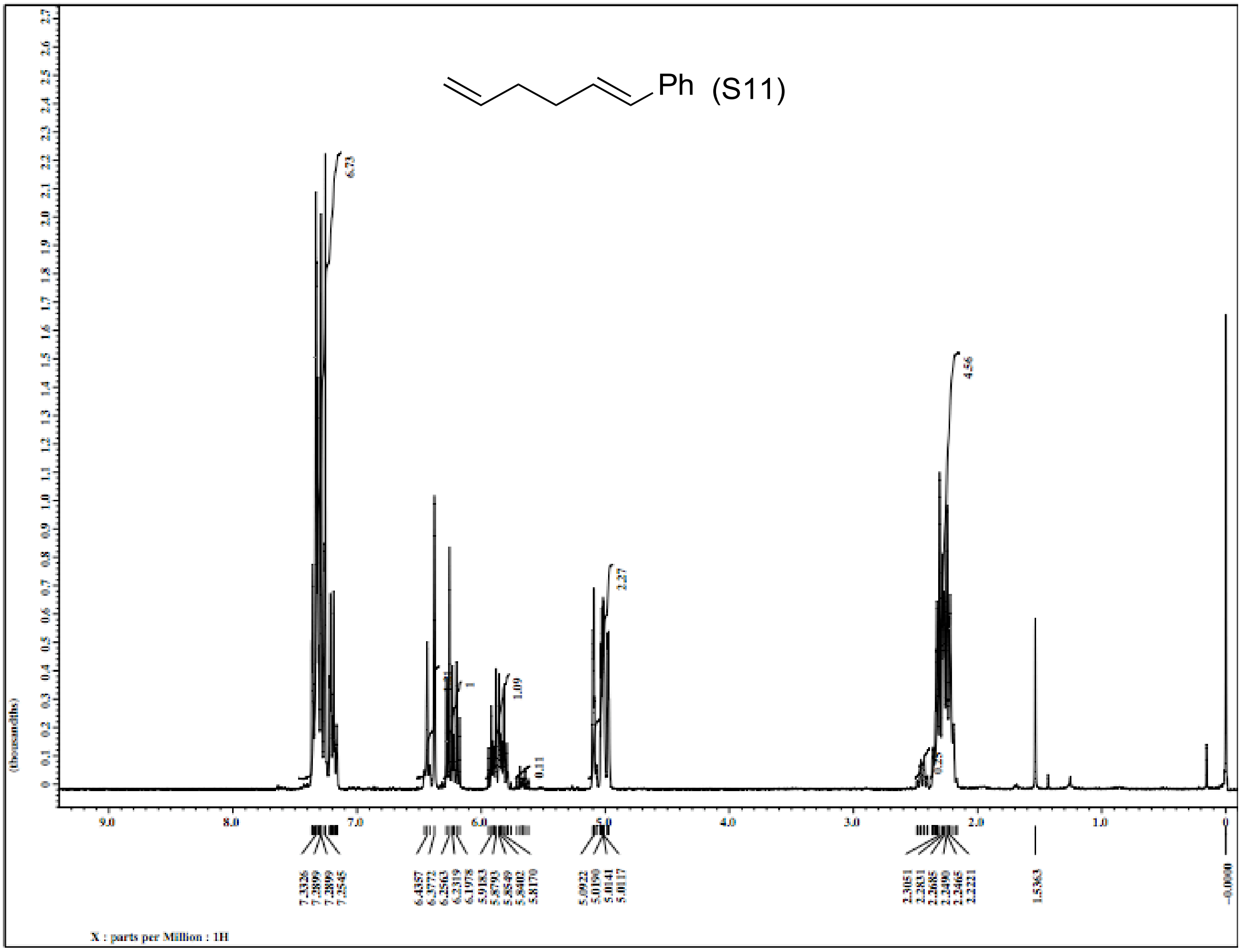


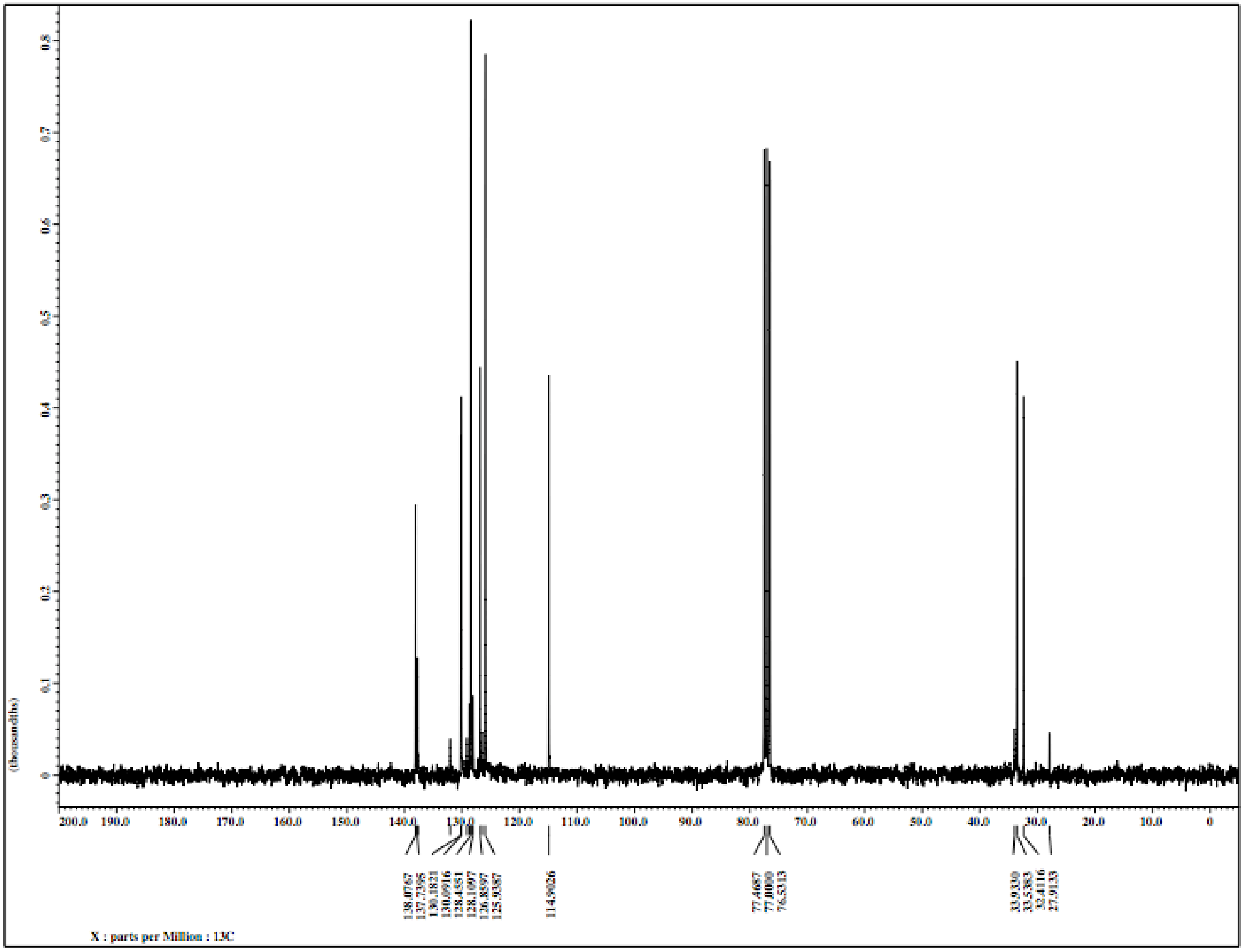
(S10)

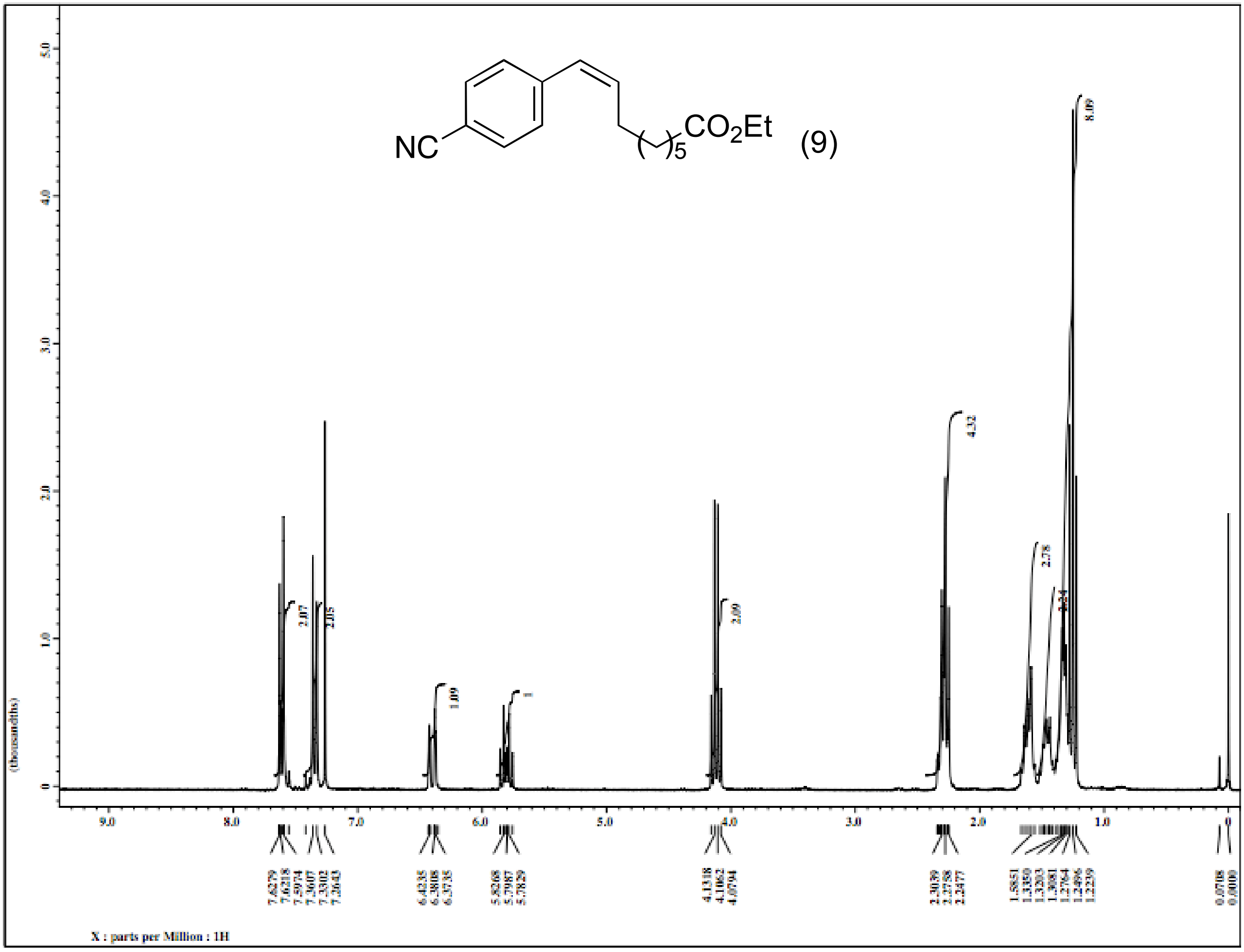
Br
(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
1.94
1.95
1.0
2
2.01
3.03
3.38
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3985
7.3741
7.3608
7.2582
7.0678
7.0373
5.1288
5.1239
5.1190
2.6077
2.5809
2.5504
2.3002
2.2722
2.2441
1.6779
1.6742
1.5449
0.0000
X : parts per Million : 1H

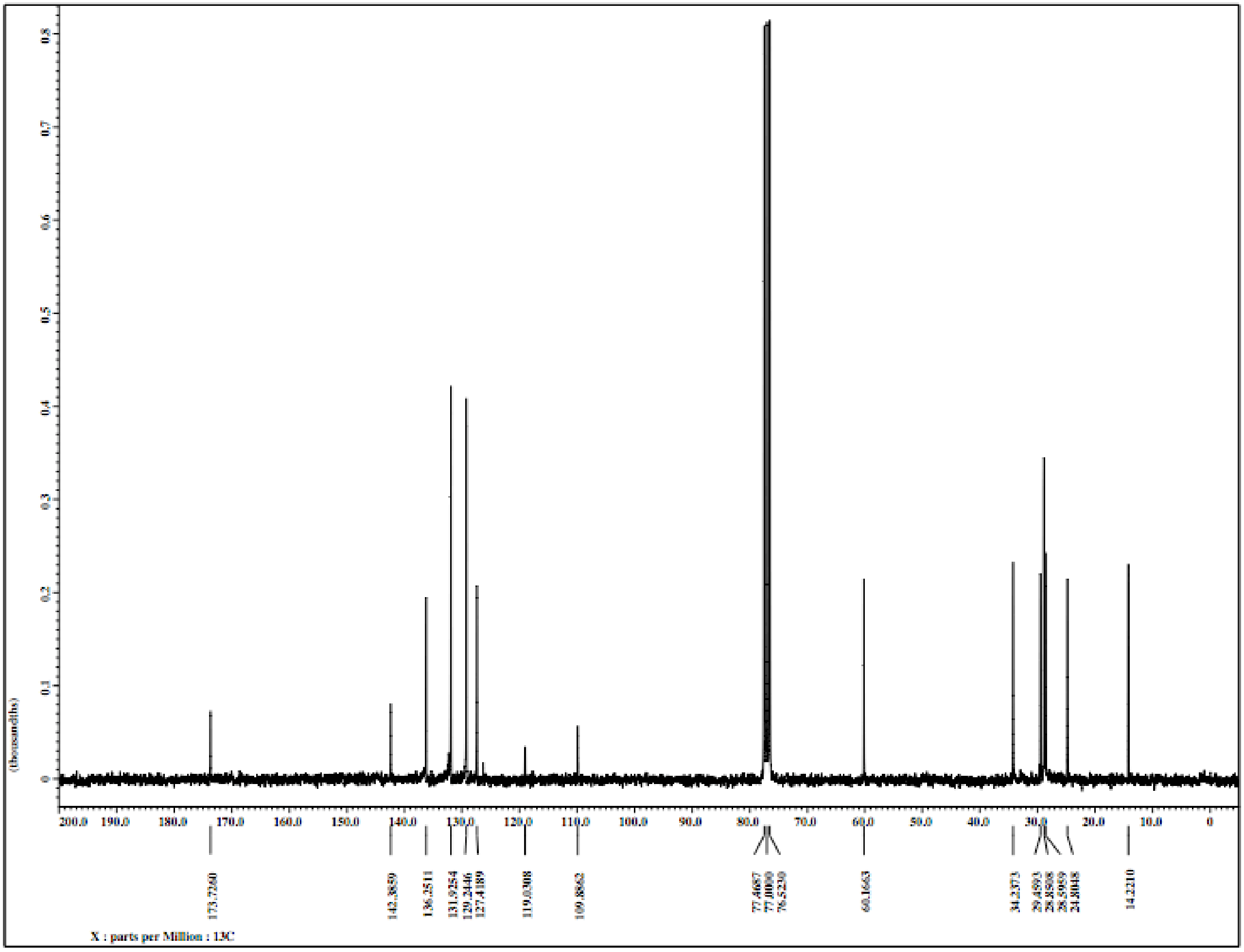


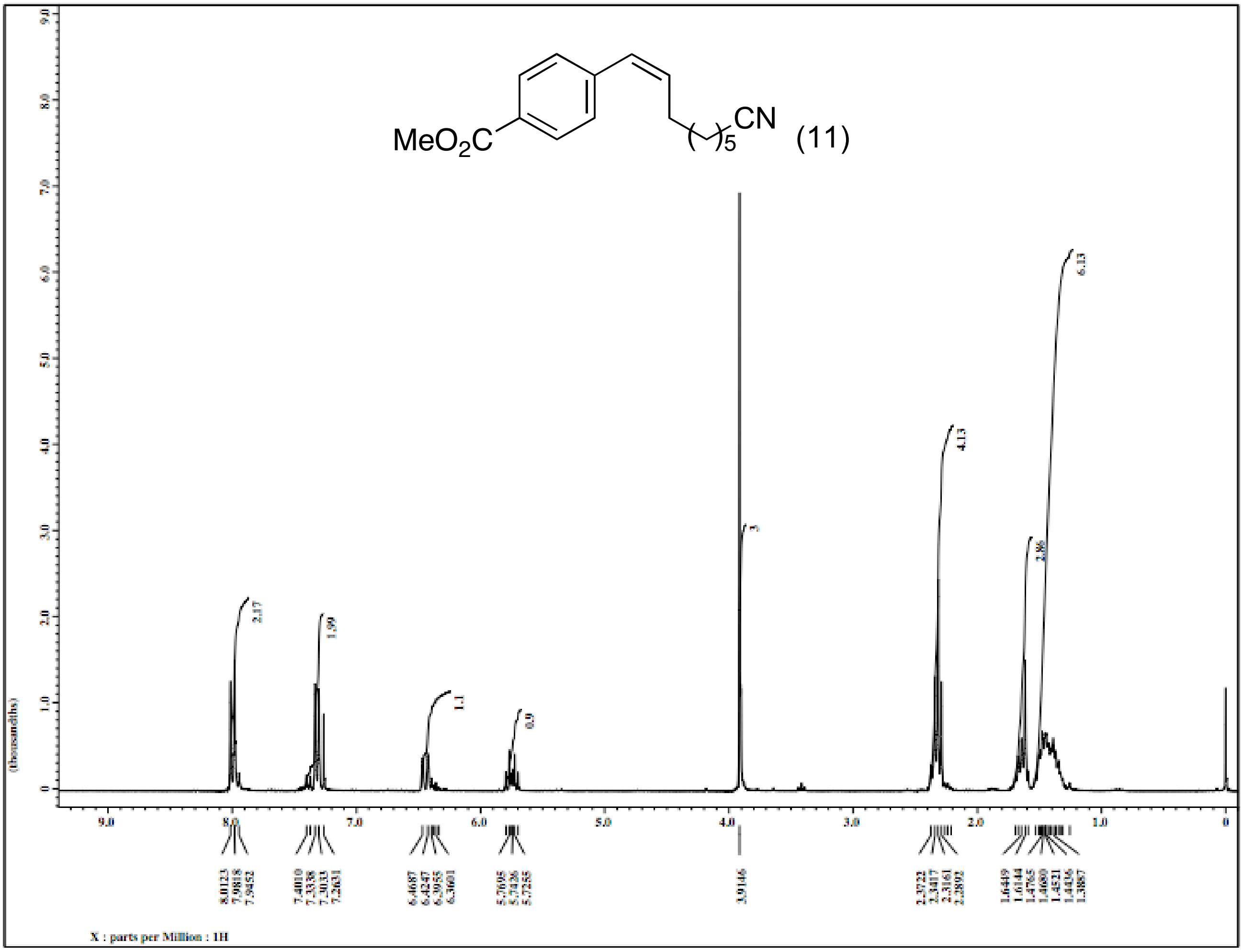
(thousandths)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
141.2921
132.5093
131.2100
130.2314
123.2167
119.3598
77.4770
77.0000
76.5313
35.4790
29.7863
25.6600
17.6503
X : parts per Million : 13C

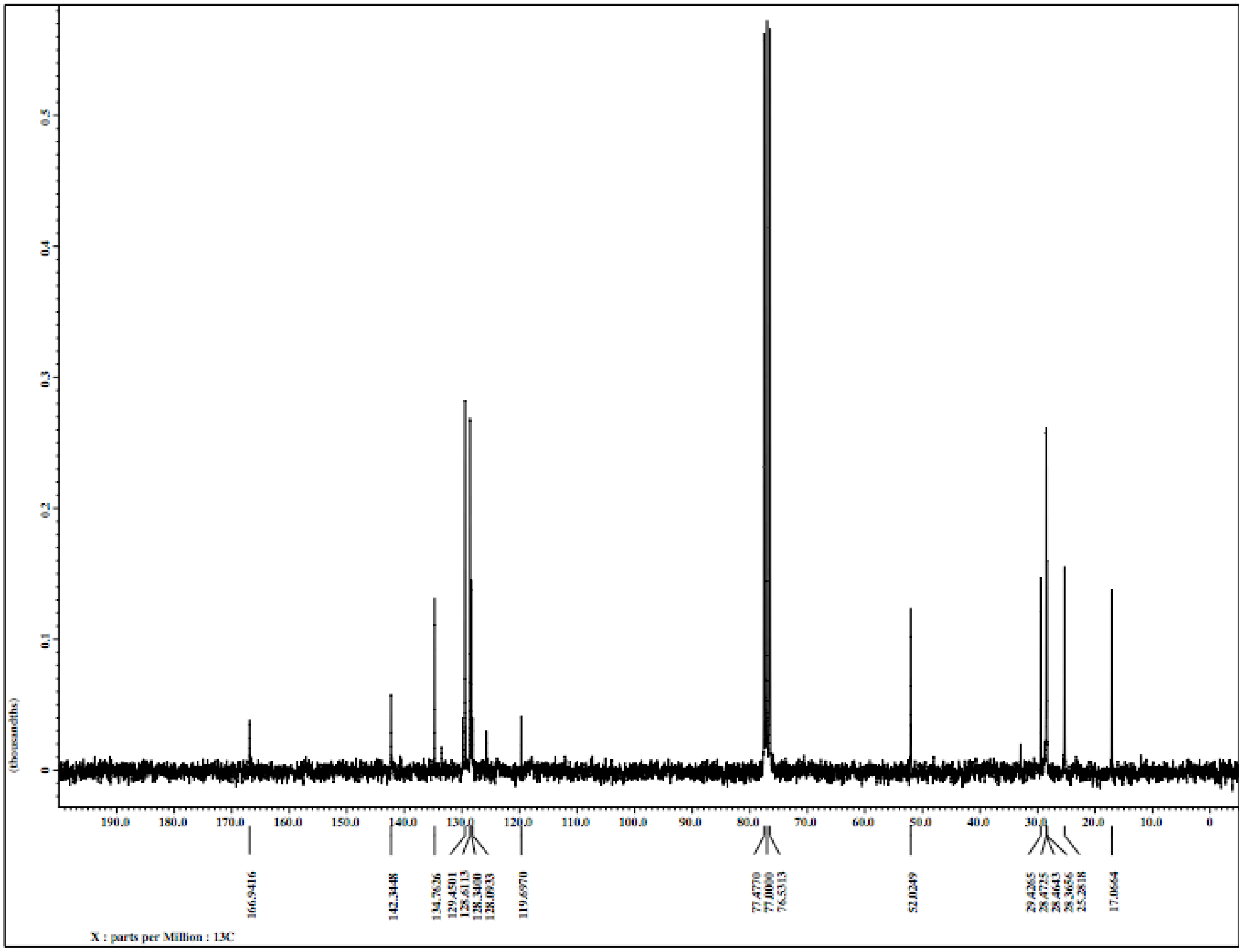

Ph (S11)
6.73
1
1.09
0.11
2.27
0.25
4.56
(thousandths)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3326
7.2899
7.2899
7.2545
6.4357
6.3772
6.2563
6.2319
6.1978
5.9183
5.8793
5.8549
5.8402
5.8170
5.0922
5.0190
5.0141
5.0117
2.3051
2.2831
2.2685
2.2490
2.2465
2.2221
1.5363
-0.0000
X : parts per Million : 1H


(thousandths)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
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
0
138.0767
137.7395
130.1821
130.0916
128.4551
128.1097
126.8597
125.9387
114.9026
77.4687
77.0000
76.5313
33.9330
33.5383
32.4116
27.9133
X : parts per Million : 13C


NC
CO2Et
5
(9)
(thousandths)
5.0
4.0
3.0
2.0
1.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.07
2.05
1.09
1
2.09
4.32
2.78
2.24
8.09
7.6279
7.6218
7.5974
7.3607
7.3302
7.2643
6.4235
6.3808
6.3735
5.8208
5.7987
5.7829
4.1318
4.1062
4.0794
2.3039
2.2758
2.2477
1.5851
1.3350
1.3203
1.3081
1.2764
1.2496
1.2239
0.0708
0.0000
X : parts per Million : 1H


(thousandths)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
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
0
173.7260
142.3859
136.2511
131.9254
129.2446
127.4189
119.0308
109.8862
77.4667
77.0000
76.5230
60.1663
34.2373
29.4593
28.8908
28.5959
24.8048
14.2210
X : parts per Million : 13C


MeO2C
CN
( )5
(11)
(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
2.17
1.99
1.1
0.9
3
4.13
2.86
6.13
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.0123
7.9818
7.9452
7.4010
7.3338
7.3033
7.2631
6.4687
6.4247
6.3955
6.3601
5.7695
5.7426
5.7255
3.9146
2.3722
2.3417
2.3161
2.2892
1.6449
1.6144
1.4765
1.4680
1.4521
1.4436
1.3887
X : parts per Million : 1H


(thousandths)
0
0.1
0.2
0.3
0.4
0.5
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
0
166.9416
142.3448
134.7636
129.4501
128.6113
128.3400
128.0933
119.6970
77.4770
77.0000
76.5313
52.0249
29.4265
28.4725
28.4643
28.3656
25.2818
17.0664
X : parts per Million : 13C