Supporting Information For:

Iron-catalysed fluoroaromatic coupling reactions under catalytic modulation with 1,2-bis(diphenylphosphino)benzene

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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 mmHg. Flash column chromatography was performed on Kanto silica gel 60 (spherical, neutral, 140–325 mesh) as described by Still et al.[1] Reversed-phase chromatography was performed on YFLC-CARTRIDGE column (ODS-SM-50C-M, Yamazen Co.) with YFLC-Wprep preparative liquid chromatograph instrument (Yamazen Co.).

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) and carbon NMR (^{13}C NMR) spectra were recorded on JEOL EX-270 (270 MHz) or VARIAN MercuryVX (300 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 or 75.5 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

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

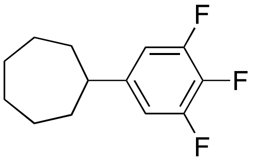
multiplet resonances, br = broad), coupling constant in hertz (Hz), signal area integration in natural numbers, and assignment (*italic*). IR spectra were recorded on an FT/IR-Spectrum One (PerkinElmer). Characteristic IR absorptions are reported in cm^{-1}.

Solvent. Anhydrous tetrahydrofuran (THF) was purchased from Wako Chemical Co. and distilled, immediately before use, from benzophenone ketyl under argon (atmospheric pressure). 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., Aldrich Inc., and other commercial suppliers. 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. Zinc chloride (beads, 99.999%) and magnesium bromide (98%) were purchased from Aldrich Inc. Arylmagnesium bromides (ArMgBr) were prepared from the corresponding aryl bromides and magnesium (turnings) using a standard method and titrated before use.

GC analyses. Yield (using undecane as an internal standard) was determined for a crude product by GC analyses 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). Diastereoselectity was determined for a crude product and an isolated product by GC analyses.

Screening of additives and arylmetal reagents (Table 1 with additional data)



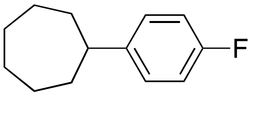
A THF solution of $FeCl_3$ (0.060 mL, 0.10 M, 0.006 mmol) was added to a mixture of an additive, $ZnCl_2$ (0.240 mL, 1.00 M THF solution, 0.24 mmol), 3,4,5-trifluorophenylmagnesium bromide (0.540 mL, 0.89 M THF solution, 0.48 mmol), undecane (15.6 mg, 0.10 mmol), and bromocycloheptane (27.5 mg, 0.20 mmol) at room temperature. The coupling reaction was carried out at 60 °C for 3 h. After cooling to ambient temperature, aliquot of the reaction mixture was taken to determine the yields of products **3–8** by GC analysis using undecane as an internal standard.

Table 1 Cross-Coupling between Bromocycloheptane **2** and 3,4,5-Trifluorophenyl Metal Reagents (ArM) in the Presence of Various Additives and Ligands[a]

Entry	ArM	Additive or Ligand (mol%)	Products (%)[b]					Recov. **2** (%)[b]	Biaryls (%)[c]	
			3	**4**	**5**	**6**	**7**		**8-F$_6$**	**8-F$_5$**
1	**1f**	TMEDA (120)	**1**	0	< 1	42	1	56	3	3
2	**1h**	TMEDA (120)	**0**	3	4	2	0	90	7	27
3	**1h**	DPPBz (6)	**91**	3	0	4	2	0	2	0
4	**1h**	DPPEn[d] (6)	**60**	8	1	7	3	19	5	< 1
5	**1h**	DPPE[d] (6)	**29**	3	< 1	4	0	63	4	1
6	**1h**	DPPP[d] (6)	**25**	4	0	3	0	66	4	1
7	**1h**	DPPF[d] (6)	**1**	1	0	2	0	96	2	14
8	**1h**	PPh_3 (12)	**1**	3	0	4	0	90	5	12
9	**1h**	DPPBz (3)	**72**	5	< 1	4	1	18	6	< 1
10	**1g**	DPPBz (6)	**18**	0	0	1	1	74	3	4
11[e]	**1g**	DPPBz (9)	**86**	0	0	1	4	7	5	5
12	**1f**	DPPBz (6)	**7**	0	0	89	2	0	4	0
13[f]	**1h**	none	**3**	2	0	6	0	85	4	0
14[g]	**1h**	$FeCl_2(dppbz)_2$ (3)	**93**	2	0	2	1	0	2	0

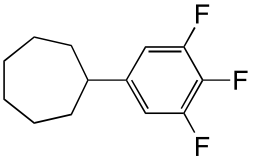
[a] Reactions were carried out on a 0.2–0.4 mmol scale. [b] The yield was determined by GC analysis using undecane as an internal standard. [c] The yield was based on the amount of ArM. [d] DPPEn = 1,2-bis(diphenylphosphino)ethylene, DPPE = 1,2-bis(diphenylphosphino)ethane, DPPP = 1,3-bis(diphenylphosphino)propane, DPPF = 1,2-bis(diphenylphosphino)ferrocene. [e] The reaction was carried out for 24 h. [f] The reaction was carried out for 6 h. [g] $FeCl_2(dppbz)_2$ (3 mol%) was used instead of $FeCl_3$ and an additive.

Typical procedure (A) for the reaction shown in Table 2; Synthesis of (4-fluorophenyl)cycloheptane (*9*)



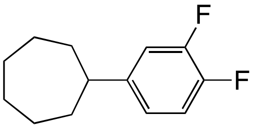
To 1,2-bis(diphenylphosphino)benzene (DPPBz, 26.8 mg, 0.06 mmol) were added $ZnCl_2$ (1.20 mL, 1.00 M THF solution, 1.20 mmol), 4-fluorophenylmagnesium bromide (2.33 mL, 1.03 M THF solution, 2.40 mmol), and bromocycloheptane (0.177 g, 1.00 mmol) at 0 °C. After 10 min, $FeCl_3$ (0.30 mL, 0.10 M THF solution, 0.03 mmol) was added at the same temperature. The coupling reaction was carried out at 60 °C for 3 h. After cooling to ambient temperature, aqueous ammonium chloride (saturated, 5.0 mL) was added. The aqueous layer was extracted with Et_2O three times. The combined organic extracts were filtered with a pad of Florisil (100–200 mesh, Nacalai Tesque Inc.). After removal of solvents *in vacuo*, the crude product was purified by chromatography on silica gel (hexane) to obtain the title compound (0.177 g, 92% yield, > 98% pure on GC analysis) as a colorless liquid. $R_f = 0.53$ (hexane); IR (neat) 2922, 2853, 1604, 1508, 1459, 1222, 1157, 818, 534; ^1H NMR δ 1.45–1.94 (m, 12H, $(CH_2)_6$), 2.66 (tt, $J = 3.3, 9.9$ Hz, 1H, ArC*H*), 6.92–7.00 (m, 2H, C*H*CFC*H*), 7.11–7.18 (m, 2H, C*H*CC*H*); ^{13}C NMR δ 27.3 (2C), 28.1 (2C), 37.2 (2C), 46.5, 115.1 (d, $J = 21.2$ Hz, 2C), 128.1 (d, $J = 7.4$ Hz, 2C), 145.8 (d, $J = 3.2$ Hz), 161.2 (d, $J = 243.0$ Hz); Anal. calcd for $C_{13}H_{17}F$ C, 81.21; H, 8.91. found C, 81.20; H, 8.91.

Typical procedure (B) for the reaction shown in Table 2 and equations 1 and 2; Synthesis of (3,4,5-trifluorophenyl)cycloheptane (*3*)



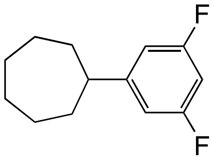
To $ZnCl_2$ (12.0 mL, 1.00 M THF solution, 12.0 mmol) were added 3,4,5-trifluorophenylmagnesium bromide (27.0 mL, 0.89 M THF solution, 24.0 mmol) and bromocycloheptane (1.77 g, 10.0 mmol) at 0 °C. After 10 min, $FeCl_2(dppbz)_2$ (0.306 g, 0.30 mmol) was added at the same temperature. The coupling reaction was carried out at 60 °C for 3 h. After cooling to ambient temperature, aqueous ammonium chloride (saturated, 30 mL) was added. The aqueous layer was extracted with hexane three times. The combined organic extracts were filtered with a pad of Florisil (100–200 mesh, Nacalai Tesque Inc.), and concentrated *in vacuo*. The title compound (2.05 g, 90% yield, 97% pure on GC analysis, including 3% of defluorinated compound) was obtained as a colorless liquid after silica gel column chromatography (hexane). $R_f = 0.57$ (hexane); IR (neat) 2925, 2857, 1612, 1529, 1443, 1344, 1234, 1040; ^1H NMR δ 1.46–1.90 (m, 12H, $(CH_2)_6$), 2.55–2.63 (m, 1H, ArC*H*), 6.73–6.83 (m, 2H, CFC*H*CC*H*CF); ^{13}C NMR δ 27.1 (2C), 27.9 (2C), 36.7 (2C), 46.6, 110.6 (dd, $J = 6.0, 14.0$ Hz, 2C), 137.9 (dt, $J = 15.4, 248.2$ Hz), 146.23 (td, $J = 4.3, 6.6$ Hz), 151.2 (ddd, $J = 4.1, 9.8, 248.6$ Hz, 2C). Anal. calcd for $C_{13}H_{15}F_3$ C, 68.41; H, 6.62. found C, 68.31; H, 6.70.

Synthesis of (3,4-difluorophenyl)cycloheptane (*4*)



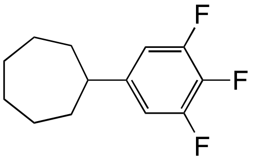
The reaction was carried out according to the typical procedure A on a 1.0 mmol scale by using 3,4-difluorophenylmagnesium bromide (2.76 mL, 0.87 M THF solution, 2.40 mmol) and bromocycloheptane (0.177 g, 1.00 mmol). Conditions: 60 °C, 3 h. The title compound (0.192 g, 91% yield, > 99% pure on GC analysis, including 0.4% of defluorinated compound) was obtained as a colorless liquid after silica gel column chromatography (hexane). $R_f = 0.54$ (hexane); IR (neat) 2923, 2855, 1607, 1518, 1460, 1430, 1280, 1205, 810, 772; ^{1}H NMR δ 1.45–1.92 (m, 12H, $(CH_2)_6$), 2.59–2.67 (m, 1H, Ar*CH*), 6.85–6.91 (m, 1H, CFCHC*H*), 6.98 (ddd, $J = 2.0, 7.8, 11.7$ Hz, 1H, CFC*H*C), 7.04 (td, $J = 8.4, 10.5$ Hz, 1H, CFC*H*CH); ^{13}C NMR δ 27.2 (2C), 28.0 (2C), 37.0 (2C), 46.5 (d, $J = 0.9$ Hz), 115.5 (d, $J = 16.9$ Hz), 116.9 (d, $J = 17.2$ Hz), 122.5 (dd, $J = 3.4, 5.7$ Hz), 147.1 (dd, $J = 4.0, 4.6$ Hz), 148.6 (dd, $J = 12.8, 245.0$ Hz), 150.3 (dd, $J = 12.6, 246.8$ Hz). Anal. calcd for $C_{13}H_{16}F_2$ C, 74.26; H, 7.67. found C, 74.18; H, 7.74.

Synthesis of (3,5-difluorophenyl)cycloheptane (*5*)



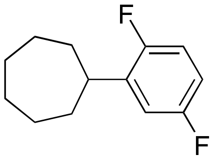
The reaction was carried out according to the typical procedure A on a 1.0 mmol scale by using 3,5-difluorophenylmagnesium bromide (3.16 mL, 0.76 M THF solution, 2.40 mmol) and bromocycloheptane (0.177 g, 1.00 mmol). Conditions: 60 °C, 3 h. The yield of the title compound was determined by ^{1}H NMR analysis (84% yield) upon comparison with the integration of an internal standard (1,1,2,2-tetrachloroethane, 0.089 g, 0.51 mmol). A part of the crude product (0.150 / 0.197 g, Ratio A) was purified by GPC to obtain the title compound (0.115 g, 55% yield, > 98% pure on GC analysis, including 2% of defluorinated compound, 72% yield calculated from Ratio A). $R_f = 0.63$ (hexane); IR (neat) 2923, 2856, 1623, 1594, 1455, 1316, 1114, 994, 977, 843, 689, 510; ^{1}H NMR δ 1.44–1.93 (m, 12H, $(CH_2)_6$), 2.58–2.68 (m, 1H, Ar*CH*), 6.49–6.79 (m, 3H, C*H*CFC*H*CFC*H*); ^{13}C NMR δ 27.1 (2C), 28.0 (2C), 36.5 (2C), 47.0 (t, $J = 1.7$ Hz), 100.9 (t, $J = 25.5$ Hz), 109.5 (dd, $J = 7.3$ 16.8 Hz, 2C), 154.0 (t, $J = 8.3$ Hz), 163.1 (dd, $J = 12.8, 247.1$ Hz, 2C). Anal. calcd for $C_{13}H_{16}F_2$ C, 74.26; H, 7.67. found C, 74.38; H, 7.82.

Synthesis of (3,4,5-trifluorophenyl)cycloheptane (*3*)



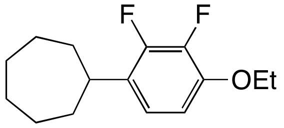
The reaction was carried out according to the typical procedure A on a 2.0 mmol scale by using 3,4,5-trifluorophenylmagnesium bromide (5.40 mL, 0.89 M THF solution, 4.80 mmol) and bromocycloheptane (0.354 g, 2.00 mmol). Conditions: 60 °C, 3 h. The title compound (0.413 g, 90% yield, 97% pure on GC analysis, including 3% of defluorinated compound) was obtained as a colorless liquid after silica gel column chromatography (hexane).

Synthesis of (2,5-difluorophenyl)cycloheptane (*10*)



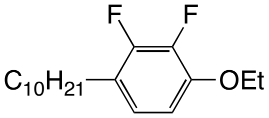
The reaction was carried out according to the typical procedure A on a 1.0 mmol scale by using 2,5-difluorophenylmagnesium bromide (3.33 mL, 0.90 M THF solution, 3.0 mmol) and 1,2-bis(diphenylphosphino)benzene (DPPBz, 40.1 mg, 0.09 mmol) and bromocycloheptane (0.177 g, 1.00 mmol). Conditions: 60 ℃, 12 h. The title compound (0.167 g, 79% yield, > 99% pure on GC analysis) was obtained as a colorless liquid after silica gel column chromatography (pentane). R_f = 0.49 (hexane); IR (neat) 2925, 2856, 1594, 1492, 1461, 1240, 1181, 860, 809, 742; ^{1}H NMR δ 1.52–1.92 (m, 12H, (C*H*$_2$)$_6$), 2.93–3.03 (m, 1H, ArC*H*), 6.74–6.97 (m, 3H, C*H*CFC*H*C*H*); ^{13}C NMR δ 27.1 (2C), 27.8 (2C), 35.2 (2C), 39.2 (t, *J* = 1.1 Hz), 112.9 (dd, *J* = 8.3, 23.8 Hz), 114.3 (dd, *J* = 5.7, 23.9 Hz), 116.0 (dd, *J* = 8.4, 26.1 Hz), 138.1 (dd, *J* = 7.2, 17.8 Hz), 155.8 (dd, *J* = 2.2, 237.6 Hz), 159.1 (dd, *J* = 2.2, 239.2 Hz). Anal. calcd for $C_{13}H_{16}F_2$ C, 74.26; H, 7.67. found C, 74.16; H, 7.74.

Synthesis of (4-ethoxy-2,3-difluorophenyl)cycloheptane (*SI-1*)



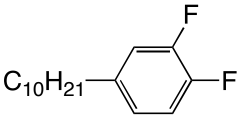
The reaction was carried out according to the typical procedure A on a 1.0 mmol scale by using 4-ethoxy-2,3-difluorophenylmagnesium bromide (2.42 mL, 0.99 M THF solution, 2.40 mmol), $FeCl_3$ (0.50 mL, 0.10 M THF solution, 0.05 mmol), 1,2-bis(diphenylphosphino)benzene (DPPBz, 67.0 mg, 0.15 mmol) and bromocycloheptane (0.177 g, 1.00 mmol). Conditions: 80 °C, 24 h. The title compound (0.155 g, 60% yield, 99% pure on GC analysis) was obtained as a colorless liquid after silica gel column chromatography (hexane). R_f = 0.13 (hexane); IR (neat) 2924, 2856, 1636, 1509, 1474, 1296, 1169, 1114, 1078, 794; ^{1}H NMR δ 1.43 (t, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.51–1.91 (m, 12H, (C*H*$_2$)$_6$), 2.92 (tt, *J* = 3.6, 10.2 Hz, 1H, ArC*H*), 4.08 (q, *J* = 6.9 Hz, 2H, OC*H*$_2$), 6.65 (ddd, *J* = 2.1, 7.5, 8.7, 1H, COC*H*), 6.80–6.87 (m, 1H, COCHC*H*); ^{13}C NMR δ 14.9, 27.3 (2C), 28.0 (2C), 35.6 (2C), 39.3, 65.5, 109.6 (d, *J* = 3.2 Hz), 120.8 (dd, *J* = 4.6, 6.0 Hz), 130.5 (d, *J* = 12.9 Hz), 141.6 (dd, *J* = 15.2, 246.5 Hz), 146.0 (dd, *J* = 3.0, 8.2 Hz), 149.0 (dd, *J* = 10.3, 244.8 Hz). Anal. calcd for $\mathrm{C_{15}H_{20}F_2O}$ C, 70.84; H, 7.93. found C, 70.78; H, 7.98.

Synthesis of 1-decyl-4-ethoxy-2,3-difluorobenzene (*11*)



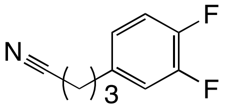
The reaction was carried out according to the typical procedure A on a 1.0 mmol scale by using 4-ethoxy-5,6-difluorophenylmagnesium bromide (4.05 mL, 0.74 M THF solution, 3.00 mmol) and iododecane (0.268 g, 1.00 mmol). Conditions: 60 °C, 24 h. The title compound (0.274 g, 92% yield, 99% pure on GC analysis) was obtained as a colorless liquid after silica gel column chromatography (hexane). R_f = 0.13 (hexane); IR (neat) 2925, 2855, 1637, 1509, 1478, 1293, 1175, 1116, 1080, 794; ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H, $\mathrm{(CH_2)_9C}H_3$), 1.22–1.35 (m, 14H, $\mathrm{(C}H_2\mathrm{)_7CH_3}$), 1.43 (t, *J* = 6.9 Hz, 3H, $\mathrm{OCH_2C}H_3$), 1.52–1.58 (m, 2H, $\mathrm{ArCH_2C}H_2$), 2.57 (td, *J* = 1.1, 7.7 Hz, 2H, $\mathrm{ArC}H_2$), 4.09 (q, *J* = 6.9 Hz, 2H, $\mathrm{OC}H_2$), 6.64 (ddd, *J* = 1.9, 7.3, 8.9 Hz, 1H, $\mathrm{COC}H$), 6.80 (dt, *J* = 2.3, 8.3, 1H, $\mathrm{COCHC}H$); ^{13}C NMR δ 14.3, 15.0, 22.8, 28.6, 29.4, 29.5, 29.6, 29.7, 29.8, 30.4, 32.0, 65.5, 109.4 (d, *J* = 3.2 Hz), 123.4 (dd, *J* = 4.6, 5.7 Hz), 123.6 (dd, *J* = 1.5, 13.7 Hz), 141.7 (dd, *J* = 14.9, 246.5 Hz), 146.4 (dd, *J* = 2.9, 8.3 Hz), 149.9 (dd, *J* = 10.5, 240.1 Hz). Anal. calcd for $\mathrm{C_{18}H_{28}F_2O}$ C, 72.45; H, 9.46. found C, 72.19; H, 9.57.

Synthesis of 1-decyl-3,4-difluorobenzene (*12*)



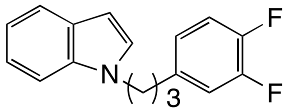
The reaction was carried out according to the typical procedure A on a 1.0 mmol scale by using 3,4-difluorophenylmagnesium bromide (2.76 mL, 0.87 M THF solution, 2.40 mmol) and bromodecane (0.221 g, 1.00 mmol). Conditions: 80 °C, 12 h. The title compound (0.213 g, 84% yield, 96% pure on GC analysis, including 4% of defluorinated compound) was obtained as a colorless liquid after silica gel column chromatography (hexane). R_f = 0.61 (hexane); IR (neat) 2925, 2855, 1609, 1519, 1466, 1432, 1282, 1211, 1119, 815, 778; ^{1}H NMR δ 0.89 (t, *J* = 6.8 Hz, 3H, $\mathrm{C}H_3$), 1.26–1.30 (m, 14H, $\mathrm{(C}H_2\mathrm{)_7CH_3}$), 1.58 (quint, *J* = 7.5 Hz, 2H, $\mathrm{ArCH_2C}H_2$), 2.55 (t, *J* = 7.5 Hz, 2H, $\mathrm{ArC}H_2$), 6.84–6.88 (m, 1H, $\mathrm{CFCHC}H$), 6.96 (ddd, *J* = 2.1, 7.7, 11.4, 1H, $\mathrm{CFC}H\mathrm{C}$), 7.04 (td, *J* = 8.5, 10.3, 1H, $\mathrm{CFC}H\mathrm{CH}$); ^{13}C NMR δ 14.2, 22.8, 29.3, 29.5, 29.6, 29.7, 29.8, 31.4, 32.1, 35.3 (d, *J* = 1.2 Hz), 116.9 (d, *J* = 16.6 Hz), 117.2 (d, *J* = 16.3 Hz), 124.2 (dd, *J* = 3.4, 5.7 Hz), 140.2 (dd, *J* = 4.0, 5.5 Hz), 148.8 (dd, *J* = 12.7, 245.0 Hz), 150.4 (dd, *J* = 12.5, 247.2 Hz). Anal. calcd for $\mathrm{C_{16}H_{24}F_2}$ C, 75.55; H, 9.51. found C, 75.71; H, 9.55.

Synthesis of 4-(3,4-difluorophenyl)butyronitrile (*14*)



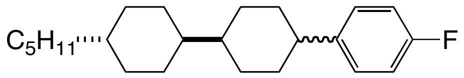
The reaction was carried out according to the typical procedure A on a 1.0 mmol scale by using 3,4-difluorophenylmagnesium bromide (2.76 mL, 0.87 M, 2.40 mmol) and 1-bromo-3-cyanopropane (0.148 g, 1.00 mmol). Conditions: 80 °C, 12 h. The title compound (0.144 g, 79% yield, 99% pure on GC analysis, including 1% of defluorinated compound) was obtained as a colorless liquid after silica gel column chromatography (1 and 3% AcOEt in hexane). R_f = 0.29 (20% EtOAc in hexane); IR (neat) 2940, 2874, 2248, 1610, 1518, 1434, 1282, 1210, 1117, 818, 779; ^{1}H NMR δ 1.96 (quint, *J* = 7.2 Hz, 2H, $ArCH_2CH_2$), 2.34 (t, *J* = 7.2 Hz, 2H, CH_2CN), 2.75 (t, *J* = 7.2 Hz, 2H, $ArCH_2$), 6.88–6.93 (m, 1H, CFCHC*H*), 6.99 (ddd, *J* = 2.2, 7.8, 11.2, 1H, CFC*H*C), 7.10 (td, *J* = 8.3, 10.2, 1H, CFC*H*CH); ^{13}C NMR δ 16.5, 26.9, 33.7 (d, *J* = 1.1 Hz), 117.3 (d, *J* = 16.9 Hz), 117.5 (d, *J* = 16.6 Hz), 119.3, 124.5 (dd, *J* = 3.6, 6.2 Hz), 136.8 (dd, *J* = 4.0, 5.5 Hz), 149.3 (dd, *J* = 12.6, 246.8 Hz), 150.5 (dd, *J* = 12.8, 248.4 Hz). Anal. calcd for $C_{10}H_9F_2N$ C, 66.29; H, 5.01; N, 7.73. found C, 66.34; H, 5.09; N, 7.57.

Synthesis of *N*-[3-(3,4-difluorophenyl)propyl]indole (*16*)



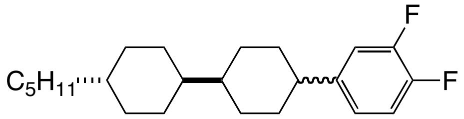
The reaction was carried out according to the typical procedure A on a 1.0 mmol scale by using 3,4-difluorophenylmagnesium bromide (2.76 mL, 0.87 M THF solution, 2.40 mmol) and *N*-(3-iodopropyl)indole (0.285 g, 1.00 mmol). Conditions: 60 °C, 3 h. The title compound (0.225 g, 83% yield, > 99% pure on GC analysis) was obtained as an orange liquid after silica gel column chromatography (1 and 3% AcOEt in hexane). R_f = 0.21 (3% EtOAc in hexane); IR (neat) 3051, 2936, 2864, 1609, 1513, 1280, 1208, 1115, 738; ^{1}H NMR δ 2.16 (quint, *J* = 7.4 Hz, 2H, $CH_2CH_2CH_2$), 2.58 (t, *J* = 7.4 Hz, 2H, $ArCH_2$), 4.14 (t, *J* = 7.4 Hz, 2H, NCH_2), 6.51 (dd, *J* = 0.8, 3.0 Hz, 1H, NCHC*H*), 6.81–6.87 (m, 1H, CFCHC*H*), 6.95 (ddd, *J* = 2.2, 7.6, 11.3 Hz, 1H, CFC*H*C), 7.06 (td, *J* = 8.4, 10.1, 1H, CFC*H*CH), 7.08 (d, *J* = 3.0 Hz, 1H, NC*H*), 7.11 (ddd, *J* = 1.2, 6.8, 8.2 Hz, 1H, NCCHCHC*H*), 7.21 (ddd, *J* = 1.2, 6.8, 8.2 Hz, 1H, NCCHC*H*), 7.29 (dd, *J* = 1.2, 8.2 Hz, 1H, NCC*H*), 7.64 (ddd, *J* = 0.8, 1.2, 8.2 Hz, 1H, NCCHCHCHC*H*); ^{13}C NMR δ 31.5, 32.3, 45.6, 101.4, 109.4, 117.2 (d, *J* = 16.6 Hz), 117.2 (d, *J* = 16.9 Hz), 119.5, 121.2, 121.6, 124.3 (dd, *J* = 3.4, 6.0 Hz), 127.7, 128.8, 136.0, 138.0 (dd, *J* = 4.0, 5.4 Hz), 150.0 (dd, *J* = 12.6, 254.9 Hz), 150.3 (dd, *J* = 12.6, 248.0). Anal. calcd for $C_{17}H_{15}F_2N$ C, 75.26; H, 5.57; N, 5.16. found C, 75.24; H, 5.82; N, 5.13.

Synthesis of *a mixture of trans*-4-pentyl-*trans*-4'-(4-fluorophenyl)-1,1'-bi(cyclohexyl) and *trans*-4-pentyl-*cis*-4'-(4-fluorophenyl)-1,1'-bi(cyclohexyl) (*SI-2*)



The reaction was carried out according to the typical procedure A on a 1.0 mmol scale by using 4-fluorophenylmagnesium bromide (2.33 mL, 1.03 M THF solution, 2.40 mmol) and *cis*-4-bromo-*trans*-4'-pentyl-1,1'-bi(cyclohexyl) (0.315 g, 1.00 mmol). Conditions: 60 °C, 24 h. The title compound (0.285 g, 86% yield, > 99 % pure on GC analysis, *cis*:*trans* = 44:56) was obtained as a colorless liquid after silica gel column chromatography (hexane). R_f = 0.54 (hexane); IR (neat) 2918, 2847, 1603, 1509, 1447, 1220, 1159, 828, 532; ^{1}H NMR For *trans* isomer: δ 0.82–1.92 (m, 30H, ArCHC$_{16}H_{30}$), 2.43 (tt, J = 3.3, 12.2 Hz, 1H, ArCH), 6.92–7.00 (m, 2H, CHCFCH), 7.12–7.19 (m, 2H, CHCCH), for *cis* isomer: δ 0.82–1.92 (m, 30H, ArCHC$_{16}H_{30}$), 2.64 (quint, J = 7.0 Hz, 1H, ArCH), 6.93–7.01 (m, 2H, CHCFCH), 7.17–7.24 (m, 2H, CHCCH); ^{13}C NMR For *trans* isomer: δ 14.2, 22.9, 26.8, 30.4 (2C), 30.6 (2C), 32.4, 33.9 (2C), 35.0 (2C), 37.7, 38.2, 43.2, 43.7, 44.2, 115.0 (d, J = 20.9 Hz, 2C), 128.2 (d, J = 7.7 Hz, 2C), 143.7 (d, J = 3.2 Hz), 161.4 (d, J = 243.0 Hz), for *cis* isomer: δ 14.2, 22.9, 26.8, 27.7 (2C), 29.8 (2C), 31.2 (2C), 32.4, 33.8 (2C), 37.3, 37.6, 37.9, 39.6, 42.3, 115.0 (d, J = 20.9 Hz, 2C), 128.5 (d, J = 7.5 Hz, 2C), 143.1 (d, J = 3.1 Hz), 161.3 (d, J = 243.1 Hz). Anal. calcd for $C_{23}H_{35}F$ C, 83.58; H, 10.67. found C, 83.42; H, 10.87.

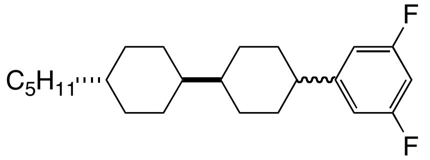
Synthesis of *a mixture of trans*-4-pentyl-*trans*-4'-(3,4-difluorophenyl)-1,1'-bi(cyclohexyl) and *trans*-4-pentyl-*cis*-4'-(3,4-difluorophenyl)-1,1'-bi(cyclohexyl) (*18*)



The reaction was carried out according to the typical procedure A on a 1.0 mmol scale by using 3,4-difluorophenylmagnesium bromide (4.07 mL, 0.59 M THF solution, 2.40 mmol) and *cis*-4-bromo-*trans*-4'-pentyl-1,1'-bi(cyclohexyl) (0.315 g, 1.00 mmol). Conditions: 60 °C, 24 h. The title compound (0.296 g, 85% yield, 97% pure on GC analysis, including 3% of defluorinated compound, *cis*:*trans* = 44:56) was obtained as a colorless liquid after silica gel column chromatography (hexane). R_f = 0.56 (hexane); IR (neat) 2919, 2851, 1607, 1517, 1448, 1277, 1212, 814, 771; ^{1}H NMR For *trans* isomer: δ 0.81–1.92 (m, 30H, ArCHC$_{16}H_{30}$), 2.41 (tt, J = 3.3, 12.1 Hz, 1H, ArCH), 6.86–7.10 (m, 3H, CHCFCFCHCH), for *cis* isomer: δ 0.81–1.92 (m, 30H, ArCHC$_{16}H_{30}$), 2.62 (quint, J = 6.9 Hz, 1H, ArCH), 6.86–7.10 (m, 3H, CHCFCFCHCH); ^{13}C NMR For *trans* isomer: δ 14.3, 22.9, 26.8, 30.3 (2C), 30.3 (2C), 32.4, 33.8 (2C), 34.7 (2C), 37.6, 38.1, 43.0, 43.5, 44.0 (d, J = 1.1 Hz), 115.5 (d, J = 16.9 Hz), 116.9 (d, J = 17.1 Hz), 122.6 (dd, J = 3.4, 5.7 Hz), 145.0 (dd, J = 3.7, 4.9 Hz), 148.7 (dd, J = 12.9, 245.1 Hz), 150.3 (dd, J = 12.6, 246.8 Hz), for *cis* isomer: δ 14.3, 22.9, 26.8, 27.5 (2C), 29.5 (2C), 31.1 (2C), 32.4, 33.7 (2C), 37.1, 37.6, 37.8, 39.5, 42.2, 115.8 (d, J = 16.9

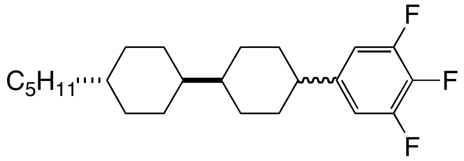
Hz), 116.8 (d, *J* = 16.0 Hz), 122.9 (dd, *J* = 3.5, 6.0 Hz), 144.5 (dd, *J* = 3.8, 4.8 Hz), 148.6 (dd, *J* = 12.6, 245.0 Hz), 150.3 (dd, *J* = 12.6, 246.8 Hz). Anal. calcd for $C_{23}H_{34}F_2$ C, 79.26; H, 9.83. found C, 79.16; H, 9.93.

Synthesis of *a mixture of trans*-4-pentyl-*trans*-4'-(3,5-difluorophenyl)-1,1'-bi(cyclohexyl) and *trans*-4-pentyl-*cis*-4'-(3,5-difluorophenyl)-1,1'-bi(cyclohexyl) (*SI-3*)



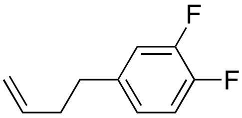
The reaction was carried out according to the typical procedure A on a 1.0 mmol scale by using 3,5-difluorophenylmagnesium bromide (3.87 mL, 0.62 M THF solution, 2.40 mmol) and *cis*-4-bromo-*trans*-4'-pentyl-1,1'-bi(cyclohexyl) (0.315 g, 1.00 mmol). Conditions: 60 °C, 24 h. The title compound (0.268 g, 77% yield, 96% pure on GC analysis, including 3% of defluorinated compound, *cis*:*trans* = 44:56) was obtained as a colorless liquid after silica gel column chromatography (hexane). R_f = 0.62 (hexane); IR (neat) 2919, 2847, 1624, 1596, 1450, 1321, 1114, 983, 850; ^{1}H NMR For *trans* isomer: δ 0.82–1.94 (m, 30H, ArCHC$_{16}$*H*$_{30}$), 2.44 (tt, *J* = 3.2 12.2 Hz, 1H, ArC*H*), 6.51–6.82 (m, 3H, C*H*CFC*H*CFC*H*), for *cis* isomer: δ 0.82–1.94 (m, 30H, ArCHC$_{16}$*H*$_{30}$), 2.65 (quint, *J* = 6.8 Hz, 1H, ArC*H*), 6.51–6.82 (m, 3H, C*H*CFC*H*CFC*H*); ^{13}C NMR For *trans* isomer: δ 14.3, 22.9, 26.9, 30.3 (4C), 32.4, 33.8 (2C), 34.4 (2C), 37.6, 38.1, 43.0, 43.5, 44.6, 101.2 (t, *J* = 25.5 Hz), 109.7 (dd, *J* = 7.2 16.6 Hz, 2C), 152.1 (t, *J* = 8.5 Hz), 163.2 (dd, *J* = 12.9, 247.4 Hz, 2C), for *cis* isomer: δ 14.3, 22.9, 26.8, 27.4 (2C), 29.2 (2C), 31.1 (2C), 32.4, 33.6 (2C), 37.2, 37.6, 37.9, 39.5, 42.7, 101.1 (t, *J* = 25.5 Hz), 109.9 (dd, *J* = 7.2, 16.8 Hz, 2C), 151.5 (t, *J* = 8.3 Hz), 163.2 (dd, *J* = 12.9, 247.1 Hz, 2C). Anal. calcd for $C_{23}H_{34}F_2$ C, 79.26; H, 9.83. found C, 79.34; H, 10.01.

Synthesis of *a mixture of trans*-4-pentyl-*trans*-4'-(3,4,5-trifluorophenyl)-1,1'-bi(cyclohexyl) and *trans*-4-pentyl-*cis*-4'-(3,4,5-trifluorophenyl)-1,1'-bi(cyclohexyl) (*19*)



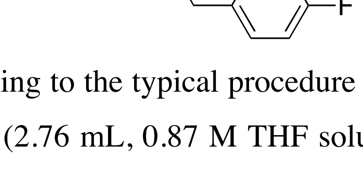
The reaction was carried out according to the typical procedure A on a 1.0 mmol scale by using 3,4,5-trifluorophenylmagnesium bromide (2.40 mL, 1.00 M THF solution, 2.40 mmol) and *cis*-4-bromo-*trans*-4'-pentyl-1,1'-bi(cyclohexyl) (0.315 g, 1.00 mmol). Conditions: 60 °C, 24 h. The title compound (0.253 g, 69% yield, 94% pure on GC analysis, including 6% of defluorinated compound, *cis*:*trans* = 44:56) was obtained as a colorless liquid after silica gel column chromatography (hexane); ^{1}H NMR For *trans* isomer: δ 0.80–1.90 (m, 30H, ArCHC$_{16}$*H*$_{30}$), 2.38 (tt, *J* = 2.3, 8.9 Hz, 1H, ArC*H*), 6.74–6.84 (m, 2H, CFC*H*CC*H*CF), for *cis* isomer: δ 0.80–1.90 (m, 30H, ArCHC$_{16}$*H*$_{30}$), 2.59 (quint, *J* = 6.8 Hz, 1H, ArC*H*), 6.79–6.89 (m, 2H, CFC*H*CC*H*CF). R_f = 0.62 (hexane); IR (neat) 2921, 2849, 1615, 1529, 1445, 1347, 1233, 1039, 847; ^{13}C NMR For *trans* isomer: δ 14.3, 22.9, 26.8, 30.2 (2C), 30.2 (2C), 32.4, 33.7 (2C), 34.5 (2C), 37.6, 38.0, 42.9, 43.4, 44.1, 110.7 (dd, *J* = 6.0, 14.0 Hz, 2C), 138.80 (dt, *J* = 15.5, 248.6 Hz), 144.2 (td, *J* = 4.5 6.6 Hz), 151.2 (ddd, *J* = 4.0, 9.7, 248.4 Hz, 2C), for *cis* isomer: δ 14.3, 22.9, 26.8, 27.3 (2C), 29.3 (2C), 31.0 (2C), 32.4, 33.6 (2C), 37.2, 37.6, 37.8, 39.5, 42.2, 111.0 (dd, *J* = 6.0, 14.0 Hz, 2C), 136.8 (dt, *J* = 15.5, 248.8 Hz), 143.6 (td, *J* = 4.6 6.5 Hz), 151.2 (ddd, *J* = 4.0, 9.7, 248.4 Hz, 2C). Anal. calcd for $C_{23}H_{33}F_3$ C, 75.37; H, 9.08. found C, 75.55; H, 9.11.

Synthesis of 4-(but-3-enyl)-1,2-difluorobenzene (*21*)



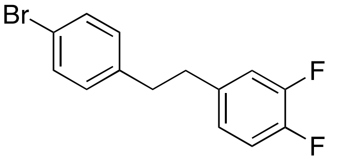
The reaction was carried out according to the typical procedure B on a 1.0 mmol scale by using 3,4-difluorophenylmagnesium bromide (2.76 mL, 0.87 M THF solution, 2.40 mmol) and cyclopropane methylbromide (0.135 g, 1.00 mmol). Conditions: 60 °C, 6 h. The yield of the title compound was determined by ^{1}H NMR analysis (77% yield) upon comparison with the integration of an internal standard (pyrazine, 0.012 g, 0.16 mmol). The crude product was purified by silica gel column chromatography (pentane) to obtain the title compound (0.129 g, 77% yield, 98% pure on ^{1}H NMR analysis, 2 % ether) as a colorless liquid. R_f = 0.62 (hexane); IR (neat) 2928, 2858, 1609, 1516, 1433, 1282, 1210, 1117, 914, 867, 815, 774, 578; ^{1}H NMR δ 2.34 (dt, *J* = 6.5, 7.8 Hz, 2H, ArCH$_2$C*H*$_2$), 2.67 (t, *J* = 7.8 Hz, 2H, ArC*H*$_2$), 4.99 (ddt, *J* = 1.1, 1.6, 10.3, 1H, C*H*HCH), 5.03 (ddt, *J* = 1.1, 1.6, 16.8, 1H, CH*H*CH), 5.81 (ddt, *J* = 6.5, 10.3, 16.8, 1H, CH$_2$C*H*CH$_2$), 6.85–6.90 (m, 1H, CFCHC*H*), 6.98 (ddd, *J* = 2.4, 8.1, 10.7, 1H, CFC*H*C), 7.05 (dt, *J* = 8.1, 10.7, 1H, CFC*H*CH); ^{13}C NMR δ 34.5 (d, *J* = 1.1 Hz), 35.2, 115.5, 116.9 (dd, *J* = 1.1, 16.1 Hz), 117.1 (d, *J* = 16.1 Hz), 124.2 (dd, *J* = 3.4, 6.1 Hz), 137.3, 138.7 (dd, *J* = 3.8, 5.5 Hz), 148.7 (dd, *J* = 12.8, 243.7 Hz), 150.1 (dd, *J* = 12.8, 243.9 Hz). Anal. calcd for $C_{10}H_{10}F_2$ C, 71.41; H, 5.99. found C, 71.44; H, 6.07.

Synthesis of 5-butoxy-2,2-dimethyl-3-(3,4-difluorophenylmethyl)tetrahydrofuran (*23*)



The reaction was carried out according to the typical procedure B on a 1.0 mmol scale by using 3,4-difluorophenylmagnesium bromide (2.76 mL, 0.87 M THF solution, 2.40 mmol) and 2-iodoethanal butyl 1,1-dimethyl-2-propenyl acetal (0.312 g, 1.00 mmol). Conditions: 60 °C, 15 h. The yield of the title compound was determined by ^{1}H NMR analysis (84% yield) upon comparison with the integration of an internal standard (pyrazine, 0.016 g, 0.20 mmol). The crude product was purified by silica gel column chromatography (hexane:CH_2Cl_2 = 100:0 to 50:50) to obtain the title compound (0.253 g, 85% yield, *cis*:*trans* = 39:61 and > 99% pure on GC analysis) as a pale yellow liquid. IR (neat) 2933, 2873, 1609, 1519, 1282, 1212, 1116, 1095, 1035, 980, 771, 543; For *cis* isomer R_f = 0.50 (20% EtOAc in hexane); ^1H NMR δ 0.92 (t, *J* = 7.0 Hz, 3H, $C\textit{H}_3CH_2$), 1.23 (s, 3H, $CH_3CC\textit{H}_3$), 1.25 (s, 3H, $CH_3CC\textit{H}_3$), 1.30–1.43 (m, 2H, $CH_3C\textit{H}_2CH_2$), 1.46–1.61 (m, 2H, $CH_3CH_2C\textit{H}_2$), 1.68–1.79 (m, 1H, $OCHC\textit{H}H$), 1.97–2.09 (m, 1H, $OCHCH\textit{H}$), 2.15–2.26 (m, 1H, $ArCH_2C\textit{H}$), 2.45–2.54 (m, 1H, $ArC\textit{H}HCH$), 2.65–2.72 (m, 1H, $ArCH\textit{H}CH$), 3.35 (dt, *J* = 6.2, 9.4, 1H, $OC\textit{H}HCH_2$), 3.71 (dt, *J* = 6.5, 9.4, 1H, $OCH\textit{H}CH_2$), 5.02 (dd, *J* = 4.3, 5.9, 1H, $OC\textit{H}O$), 6.84–6.90 (m, 1H, $CFCHC\textit{H}$), 6.97 (ddd, *J* = 2.2, 8.2, 10.7, 1H, $CFC\textit{H}C$), 7.06 (dt, *J* = 8.2, 10.7, 1H, $CFC\textit{H}CH$); ^{13}C NMR δ 13.9, 19.4, 23.3, 28.1, 31.9, 35.8 (d, *J* = 1.1 Hz), 38.8, 50.0, 67.7, 82.6, 102.9, 117.0 (d, *J* = 16.1 Hz), 117.3 (d, *J* = 16.6 Hz), 124.4 (dd, *J* = 2.8, 6.1 Hz), 137.9 (dd, *J* = 3.9, 5.5 Hz), 148.9 (dd, *J* = 12.2, 244.8 Hz), 150.2 (dd, *J* = 12.2, 246.5 Hz). For *trans* isomer R_f = 0.45 (20% EtOAc in hexane); ^1H NMR δ 0.90 (t, *J* = 7.0 Hz, 3H, $C\textit{H}_3CH_2$), 1.11 (s, 3H, $CH_3CC\textit{H}_3$), 1.31 (s, 3H, $CH_3CC\textit{H}_3$), 1.23–1.40 (m, 2H, $CH_3C\textit{H}_2CH_2$), 1.43–1.56 (m, 2H, $CH_3CH_2C\textit{H}_2$), 1.68–1.81 (m, 1H, $OCHC\textit{H}H$), 1.85–1.92 (m, 1H, $OCHCH\textit{H}$), 2.33–2.46 (m, 2H, $ArC\textit{H}HC\textit{H}$), 2.61–2.73 (m, 1H, $ArC\textit{H}HCH$), 3.31 (dt, *J* = 6.5, 9.6, 1H, $OC\textit{H}HCH_2$), 3.65 (dt, *J* = 6.8, 9.6, 1H, $OCH\textit{H}CH_2$), 4.97 (d, *J* = 4.9, 1H, $OC\textit{H}O$), 6.85–6.91 (m, 1H, $CFCHC\textit{H}$), 6.98 (ddd, *J* = 2.2, 8.1, 10.5, 1H, $CFC\textit{H}C$), 7.06 (dt, *J* = 8.1, 10.5, 1H, $CFC\textit{H}CH$); ^{13}C NMR δ 13.9, 19.4, 23.8, 29.7, 31.8, 35.7 (d, *J* = 1.1 Hz), 38.9, 47.6, 66.7, 83.2, 101.7, 117.1 (dd, *J* = 1.1, 17.3 Hz), 117.4 (d, *J* = 17.2 Hz), 124.5 (dd, *J* = 3.4, 5.6 Hz), 137.8 (dd, *J* = 3.9, 5.6 Hz), 148.9 (dd, *J* = 12.2, 244.2 Hz), 150.2 (dd, *J* = 12.8, 245.9 Hz). Anal. calcd for $C_{17}H_{24}F_2O_2$ C, 68.43; H, 8.11. found C, 68.34; H, 8.14.

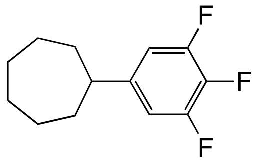
Synthesis of 4-(4-bromophenethyl)-1,2-difluorobenzene (*25*)



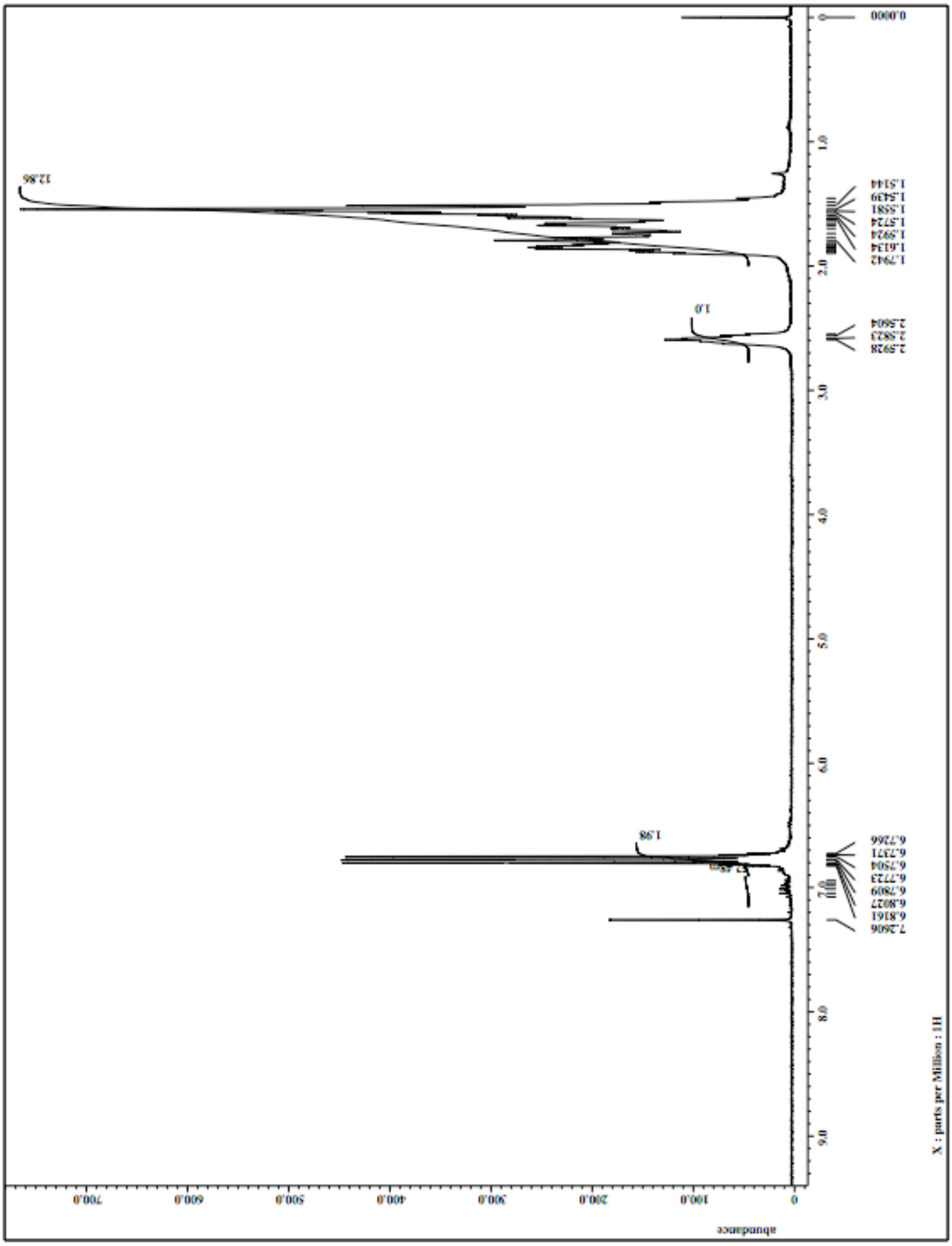
The reaction was carried out according to the typical procedure B on a 1.0 mmol scale by using 3,4-difluorophenylmagnesium bromide (2.76 mL, 0.87 M THF solution, 2.40 mmol) and 4-bromophenethyl bromide (0.264 g, 1.00 mmol). Conditions: 60 °C, 15 h. The yield of the title compound was determined by ^1H NMR analysis (77% yield) upon comparison with the integration of an internal standard (pyrazine, 0.026 g, 0.33 mmol). The crude product was purified by chromatography on silica gel (pentane) to give the title compound (0.205 g, 69% yield, 90% pure on GC analysis, including 3% of defluorinated compound, 2% of 3,4-difluoro-4'-ethylbiphenyl, 5% of 3,4-difluoro-4'-vinylbiphenyl). The compound was achieved by reversed-phase chromatography (MeOH:H_2O = 65:35 to 100:0) to give the title compound (0.180 g, 61% yield, 97% pure on GC analysis, including 3% of defluorinated compound) as a colorless liquid. R_f = 0.44 (hexane); IR (neat) 2930, 2861, 1609, 1515, 1487, 1433, 1282, 1209, 1115, 1072, 1011, 814, 777, 578, 495; ^1H

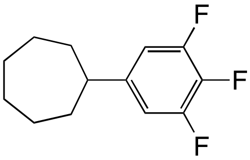
NMR δ 2.85 (brs, 4H, ArCH_2CH_2), 6.77–6.83 (m, 1H, CFCHC*H*), 6.93 (ddd, J = 2.2, 8.1, 10.8, 1H, CFC*H*C), 6.99 (m, 2H, C*H*CHCBrCHC*H*), 7.04 (td, J = 8.1, 10.8, 1H, CFC*H*CH), 7.39 (m, 2H, C*H*CBrC*H*); ^{13}C NMR δ 36.7 (d, J = 1.1 Hz), 37.0 (d, J = 1.1 Hz), 117.0 (dd, J = 1.1, 16.7 Hz), 117.2 (d, J = 16.7 Hz), 119.9, 124.3 (dd, J = 3.3, 6.1 Hz), 130.2 (2C), 131.5 (2C), 138.0 (dd, J = 3.9, 5.6 Hz), 139.8, 148.9 (dd, J = 12.2, 244.3 Hz), 150.1 (dd, J = 12.8, 245.9 Hz). Anal. calcd for $C_{14}H_{11}BrF_2$ C, 56.59; H, 3.73. found C, 56.71; H, 3.84.

^{1}H and ^{13}C NMR Spectra of the compounds *3–5*, *9–12*, *14*, *16*, *18*, *19*, *21*, *23*, *25*, *SI-1*, *SI-2*, *SI-3*.



(**3**)

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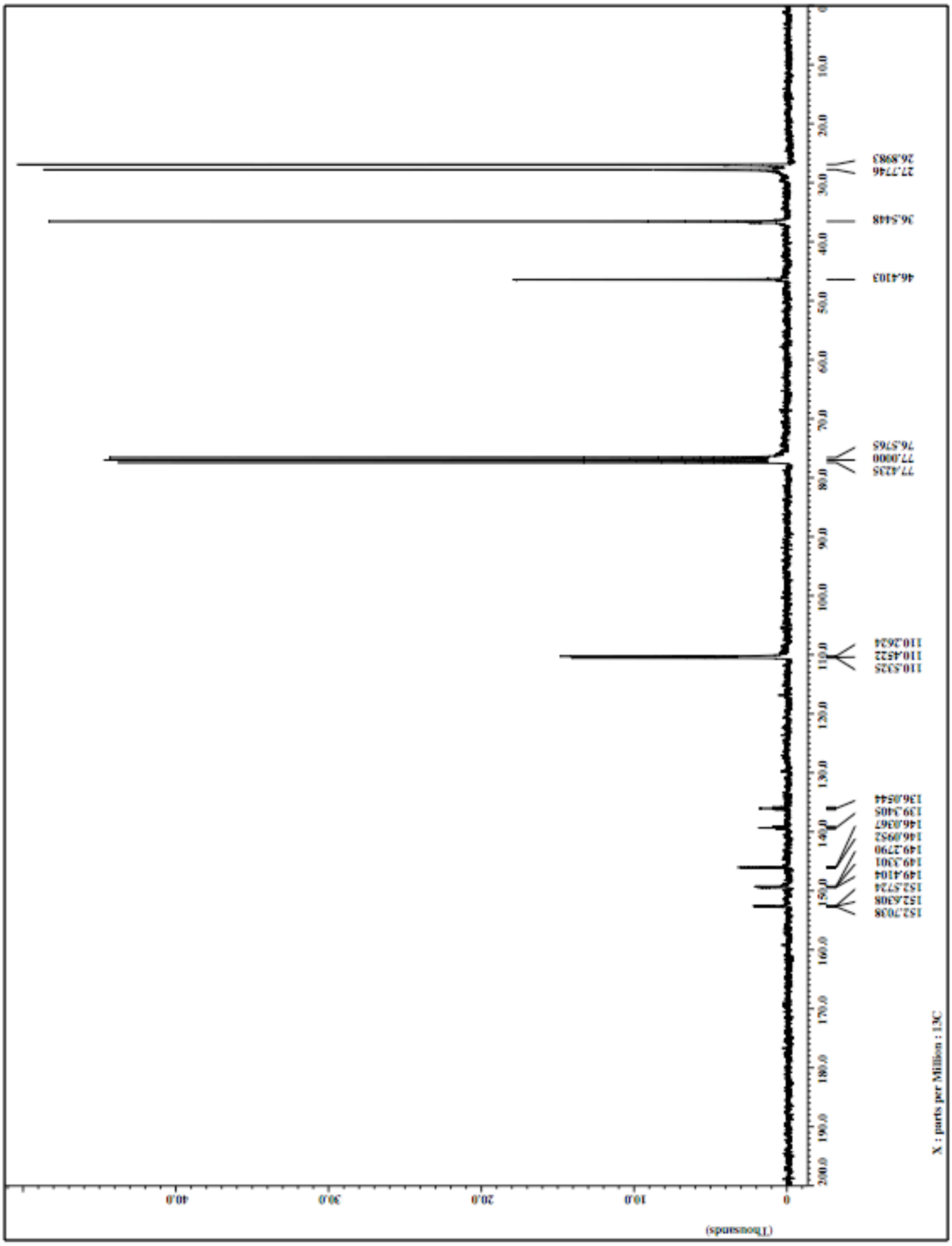
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77.4235
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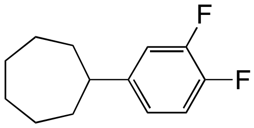
136.0544
139.3405
146.0367
146.0952
149.2790
149.3301
149.4104
152.5724
152.6308
152.7038
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
X : parts per Million : 13C
0
10.0
20.0
30.0
40.0
(Thousands)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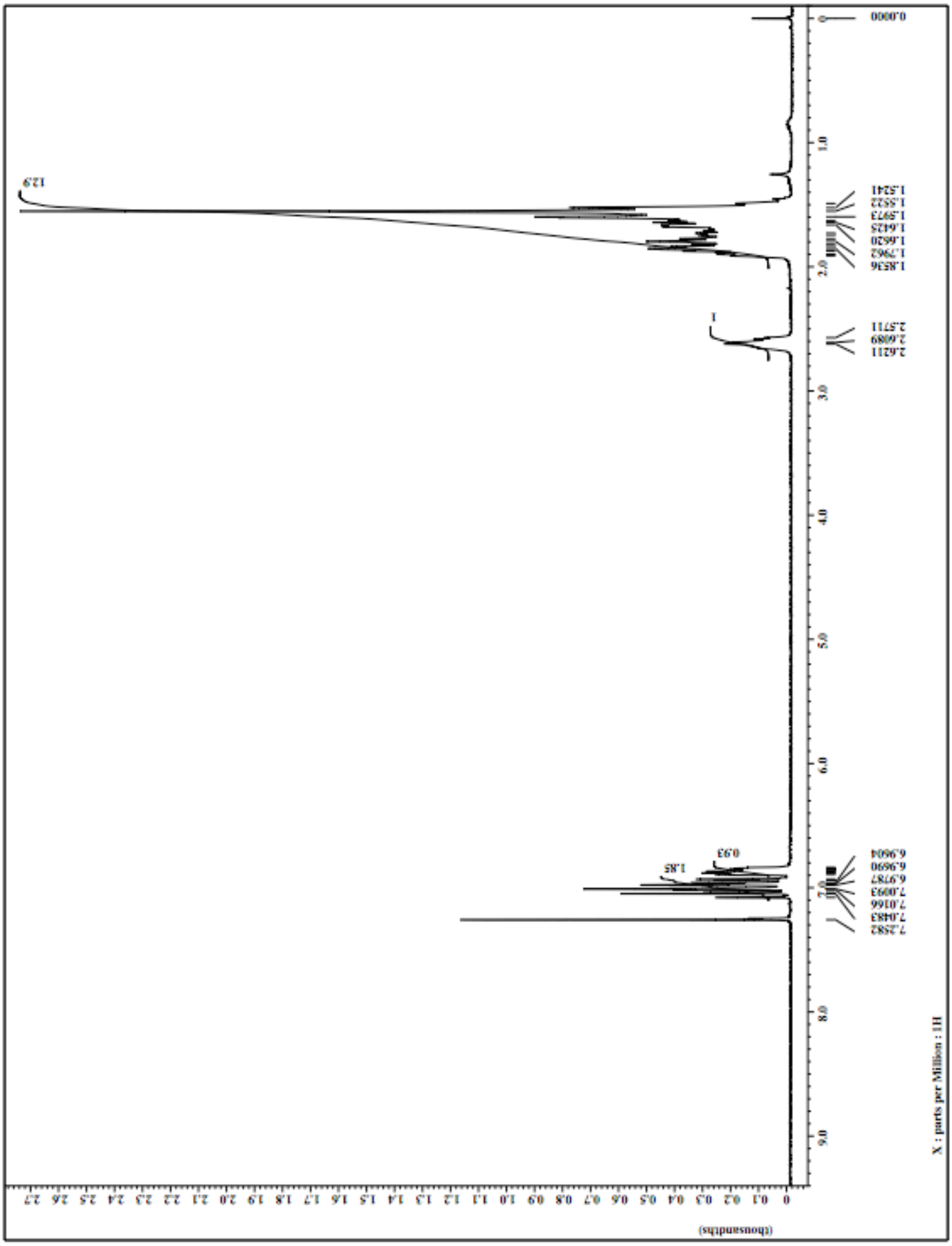
(4)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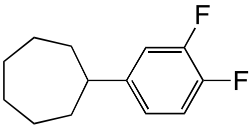
1.5973
1.6425
1.6520
1.7962
1.8536
2.5711
2.6089
2.6211
6.9604
6.9690
6.9787
7.0093
7.0166
7.0483
7.2582
12.9
1
0.93
1.85
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : 1H
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7
(thousandths)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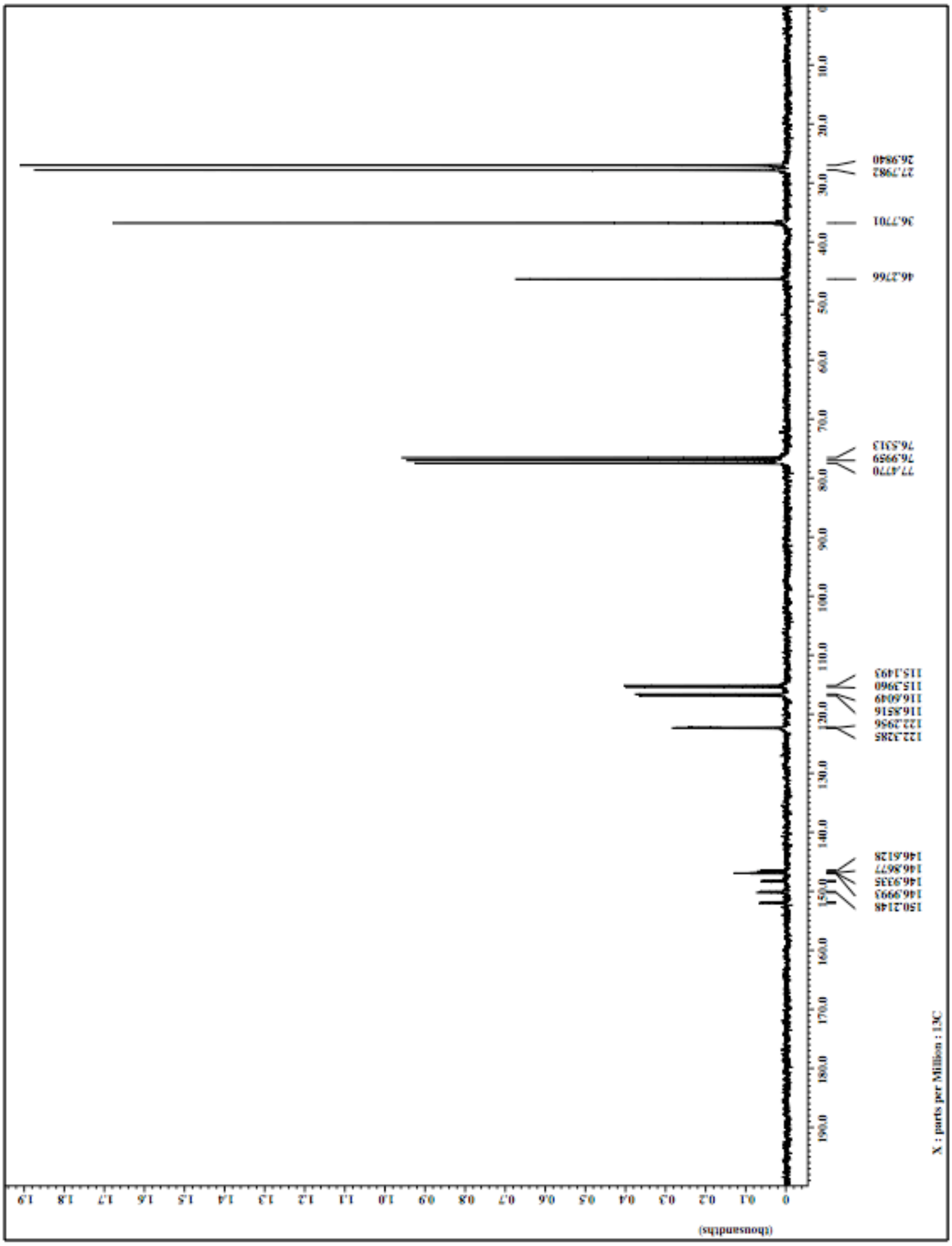
(4)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36.7701
46.2766
76.5313
76.9959
77.4770
115.1495
115.3960
116.6049
116.8516
122.2956
122.3285
146.6128
146.8677
146.9335
146.9993
150.2148
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
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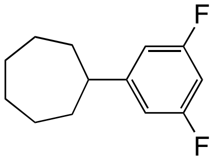
150.0
160.0
170.0
180.0
190.0
X : parts per Million : 13C
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
(thousandths)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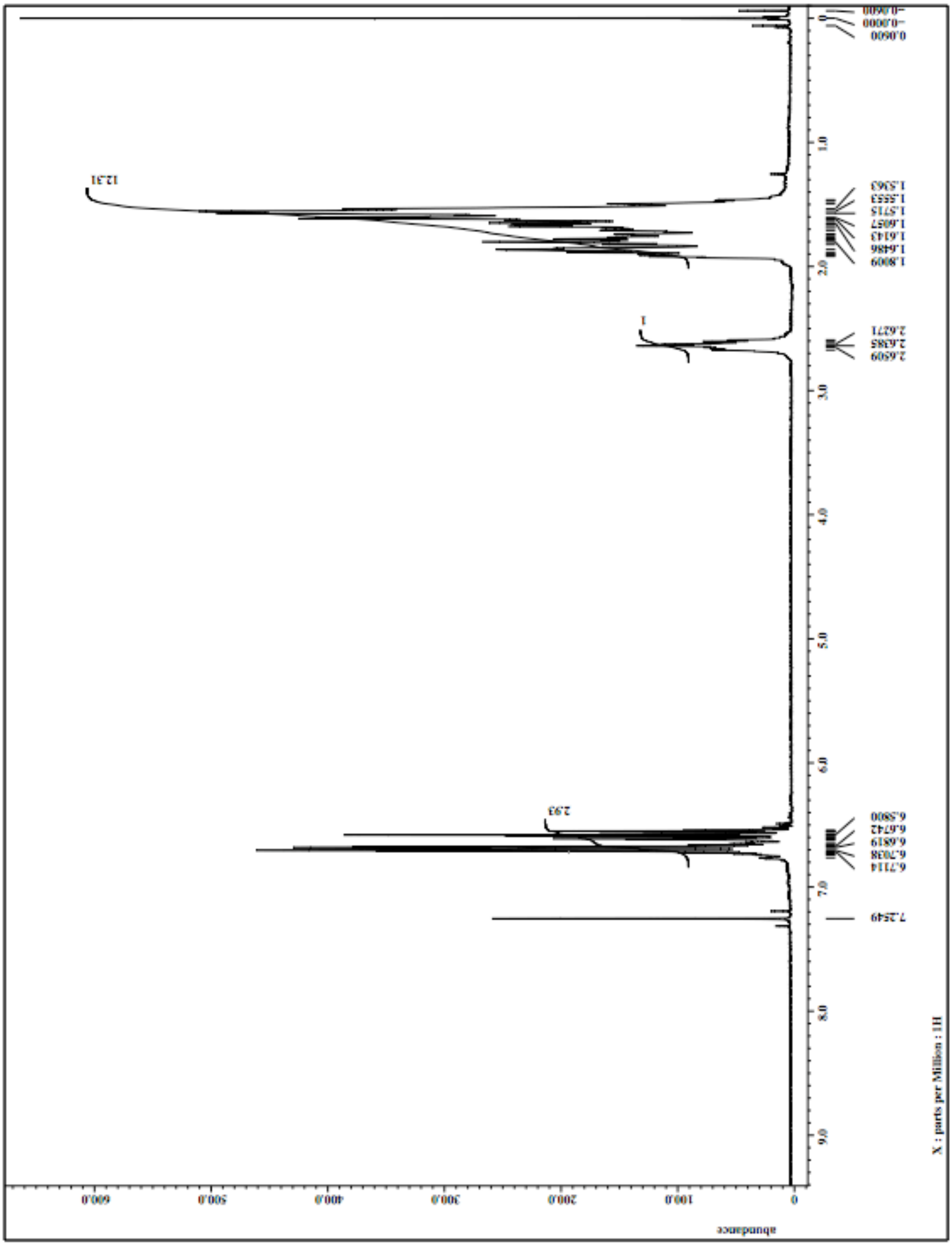
(5)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1.6486
1.8009
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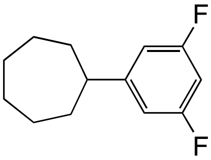
2.6385
2.6509
6.5800
6.6742
6.6819
6.7038
6.7114
7.2549
12.31
1
2.93
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : 1H
0
100.0
200.0
300.0
400.0
500.0
600.0
abundance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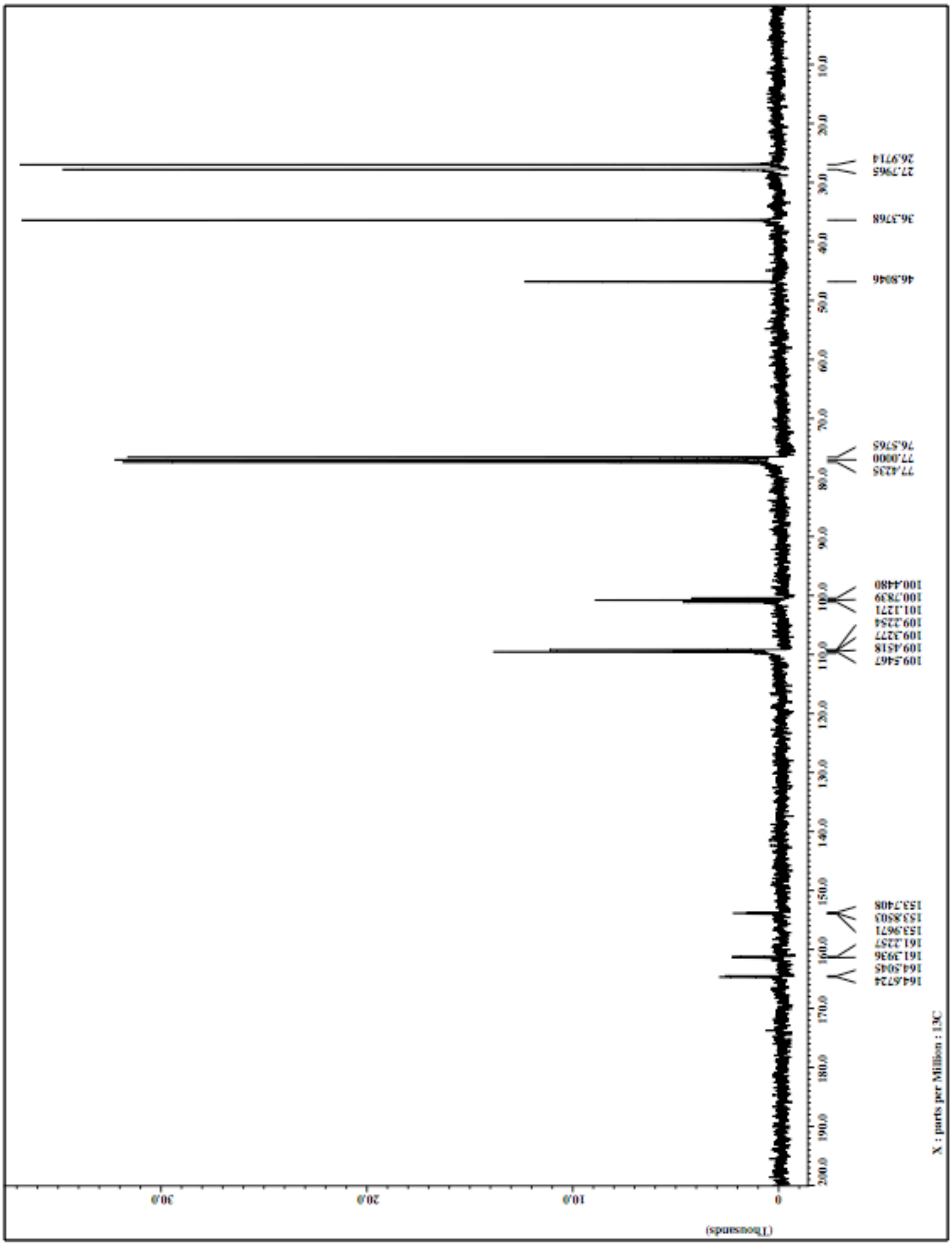
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46.8046
76.5765
77.0000
77.4235
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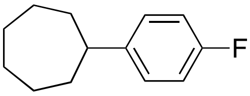
100.7839
101.1271
109.2254
109.3277
109.4518
109.5467
153.7408
153.8503
153.9671
161.2257
161.3936
164.5045
164.6724
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
X : parts per Million : 13C
0
10.0
20.0
30.0
(Thousands)



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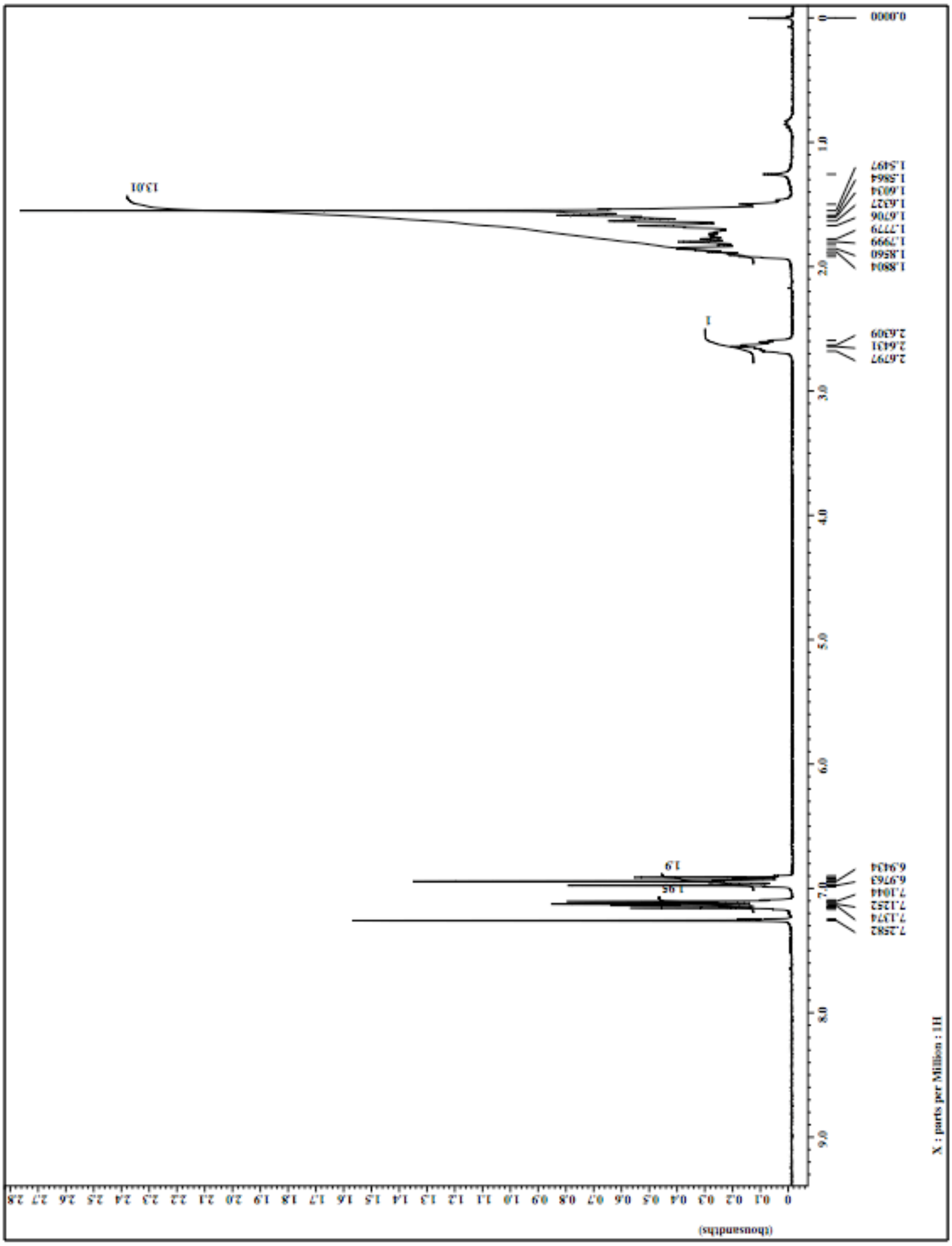
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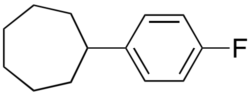
1.8804
2.6309
2.6431
2.6797
6.9434
6.9763
7.1044
7.1252
7.1374
7.2582
13.01
1
1.9
1.95
X : parts per Million : 1H
(thousandths)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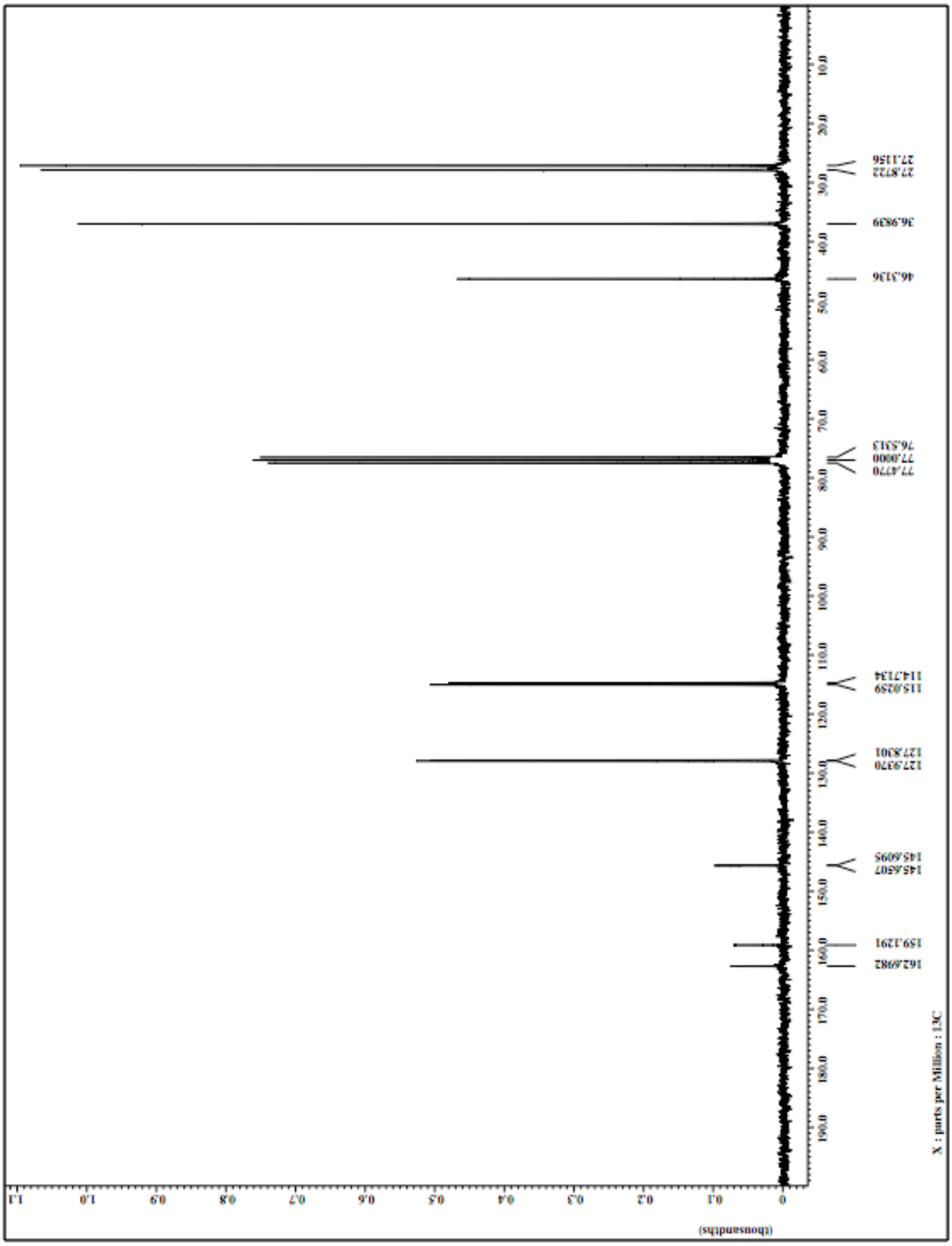
(**9**)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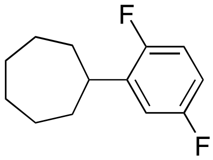
46.3136
76.5313
77.0000
77.4770
114.7134
115.0259
127.8301
127.9370
145.6095
145.6507
159.1291
162.6982
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
X : parts per Million : 13C
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
(thousandths)


F
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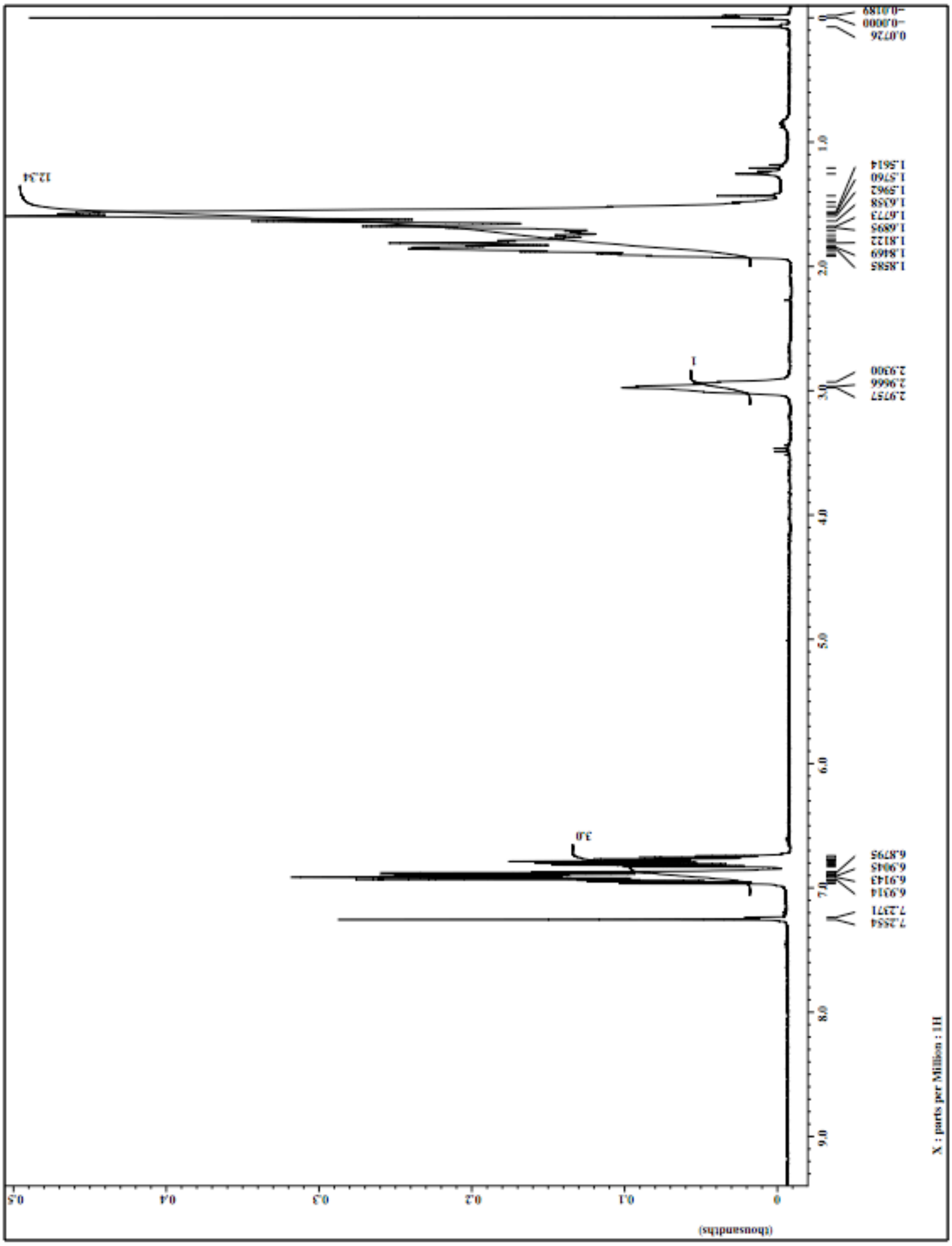
(**10**)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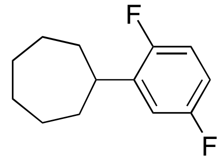
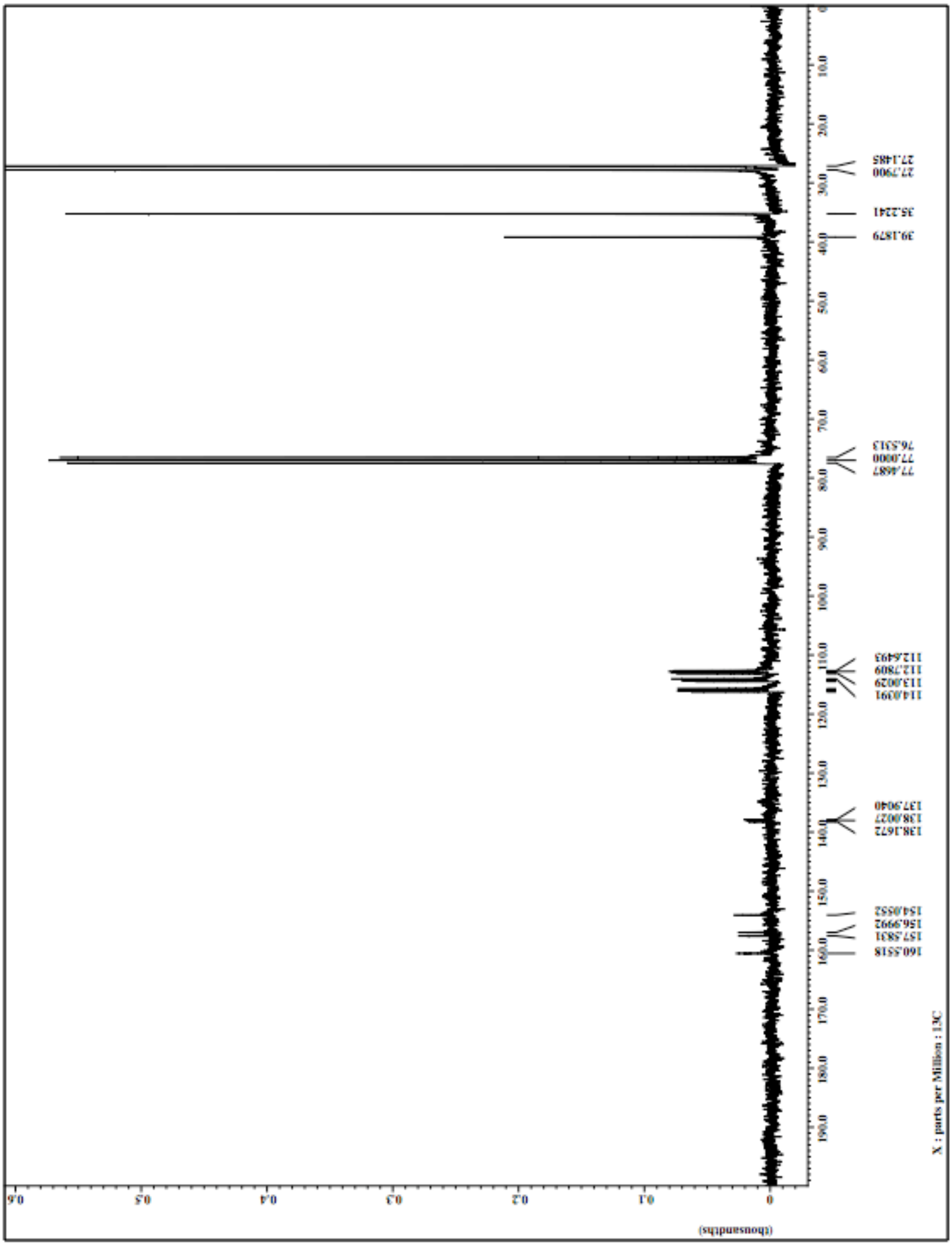
1.8469
1.8585
2.9300
2.9666
2.9757
6.8795
6.9045
6.9143
6.9314
7.2371
7.2554
12.34
1
3.0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : 1H
0
0.1
0.2
0.3
0.4
0.5
(thousandths)


F
F

(10)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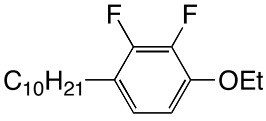
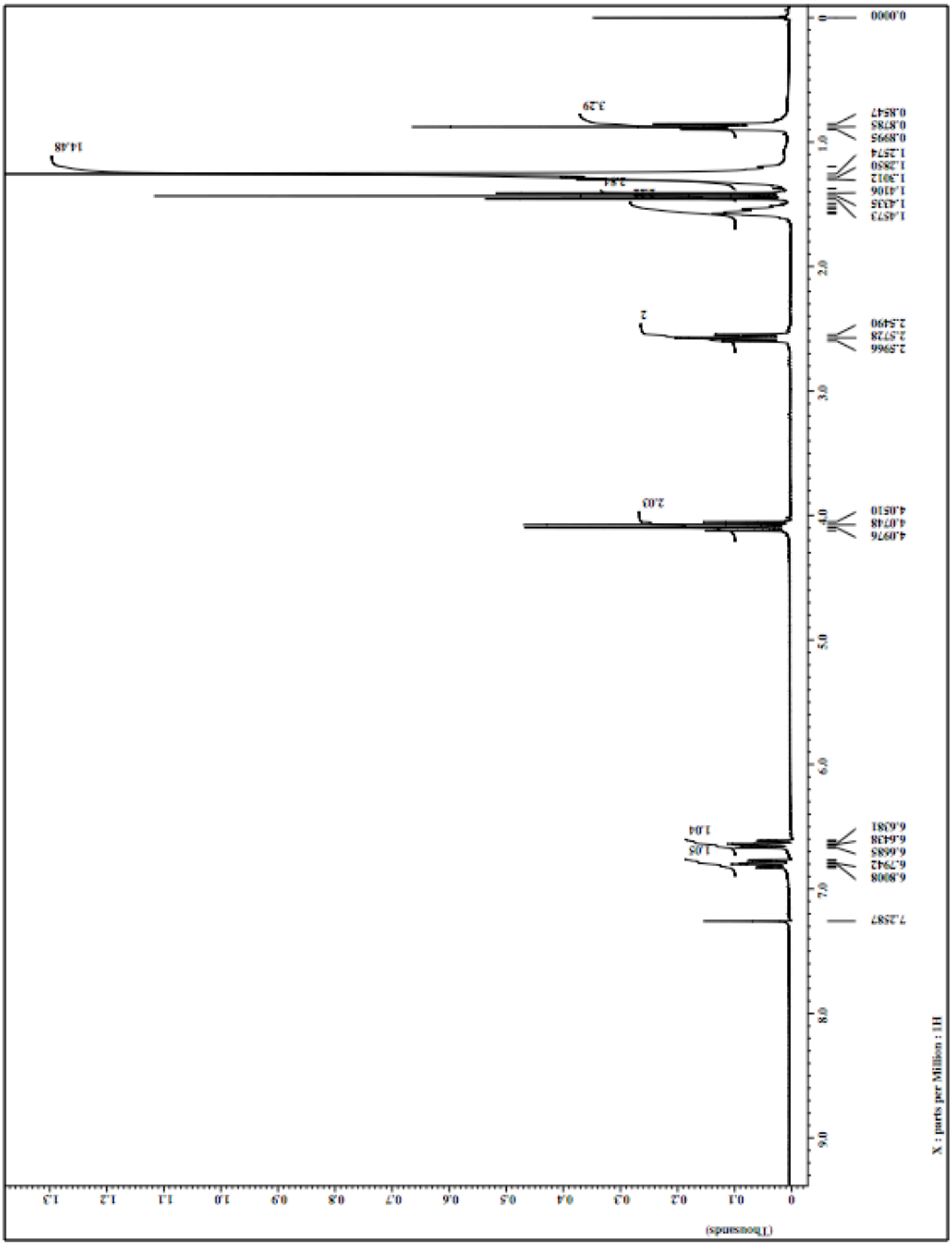
77.0000
77.4687
112.6493
112.7809
113.0029
114.0391
137.9040
138.0027
138.1672
154.0552
156.9992
157.5831
160.5518
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
X : parts per Million : 13C
0
0.1
0.2
0.3
0.4
0.5
0.6
(thousandths)


F
F
$C_{10}H_{21}$
OEt

(11)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1.3012
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1.4335
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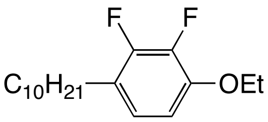
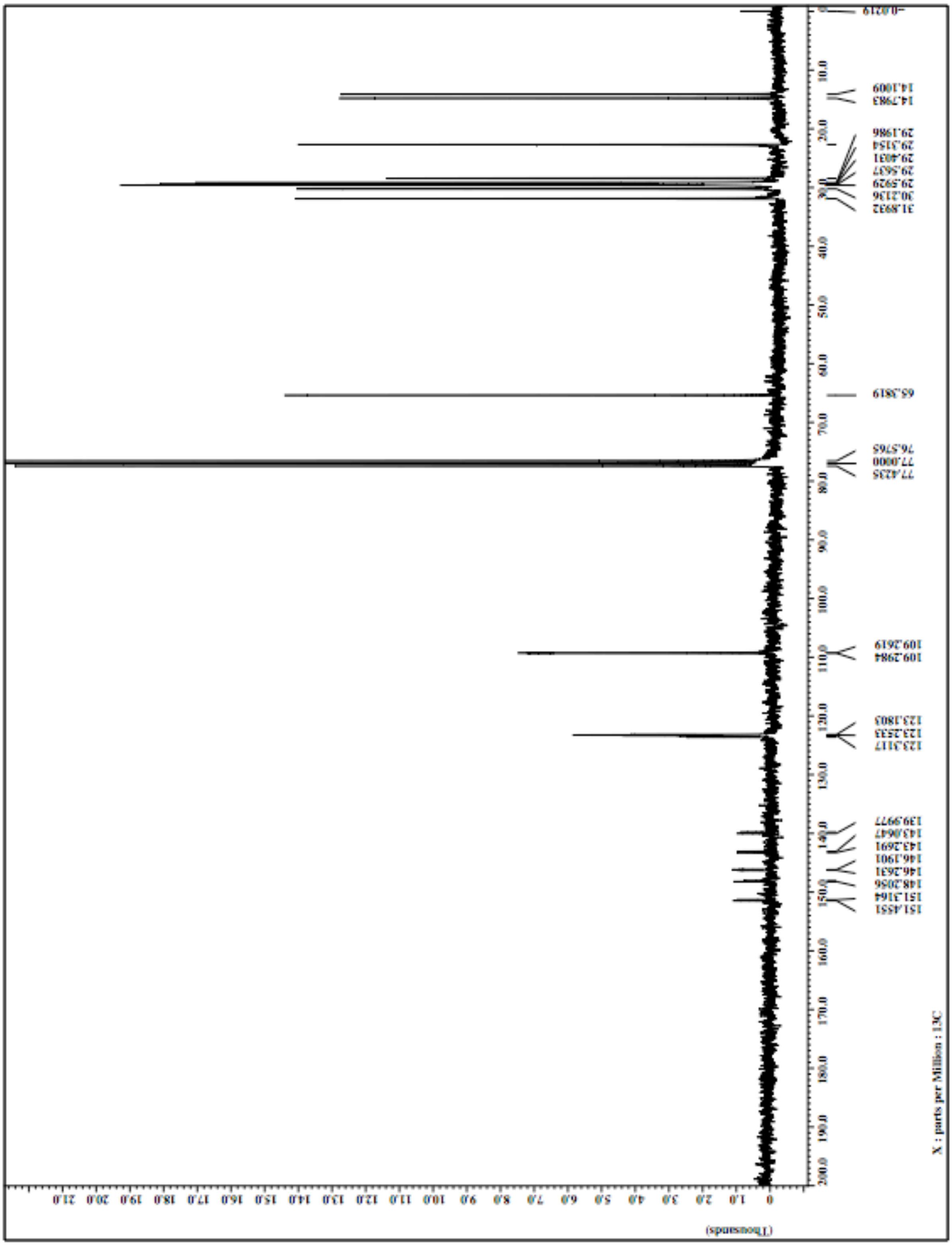
2.5490
2.5728
2.5966
4.0510
4.0748
4.0976
6.6381
6.6438
6.6685
6.7942
6.8008
7.2587
3.29
14.48
2.84
2
2.03
1.04
1.05
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : 1H
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
(Thousands)


F
F
C10H21
OEt

(**11**)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123.3117
139.9977
143.0647
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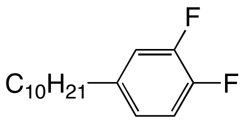
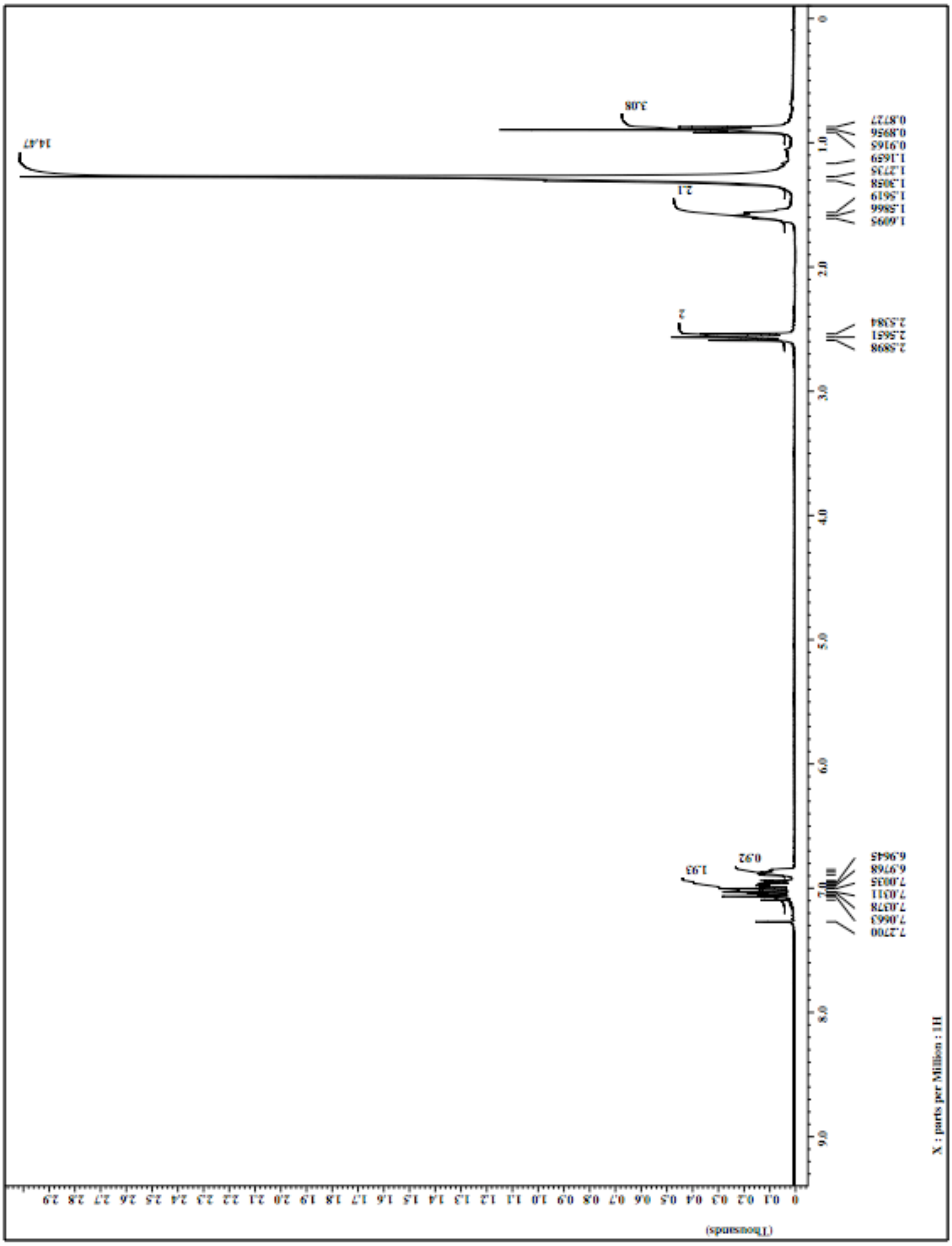
151.4551
X : parts per Million : 13C
(Thousands)


F
C10H21
F

(12)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14.47
2.1
2
0.92
1.93
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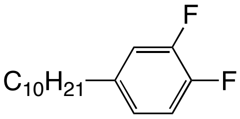
0.8956
0.9165
1.1659
1.2735
1.3058
1.5619
1.5866
1.6095
2.5384
2.5651
2.5898
6.9645
6.9768
7.0035
7.0311
7.0378
7.0663
7.2700
0
1.0
2.0
3.0
4.0
5.0
6.0
8.0
9.0
X : parts per Million : 1H
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.9
(Thousands)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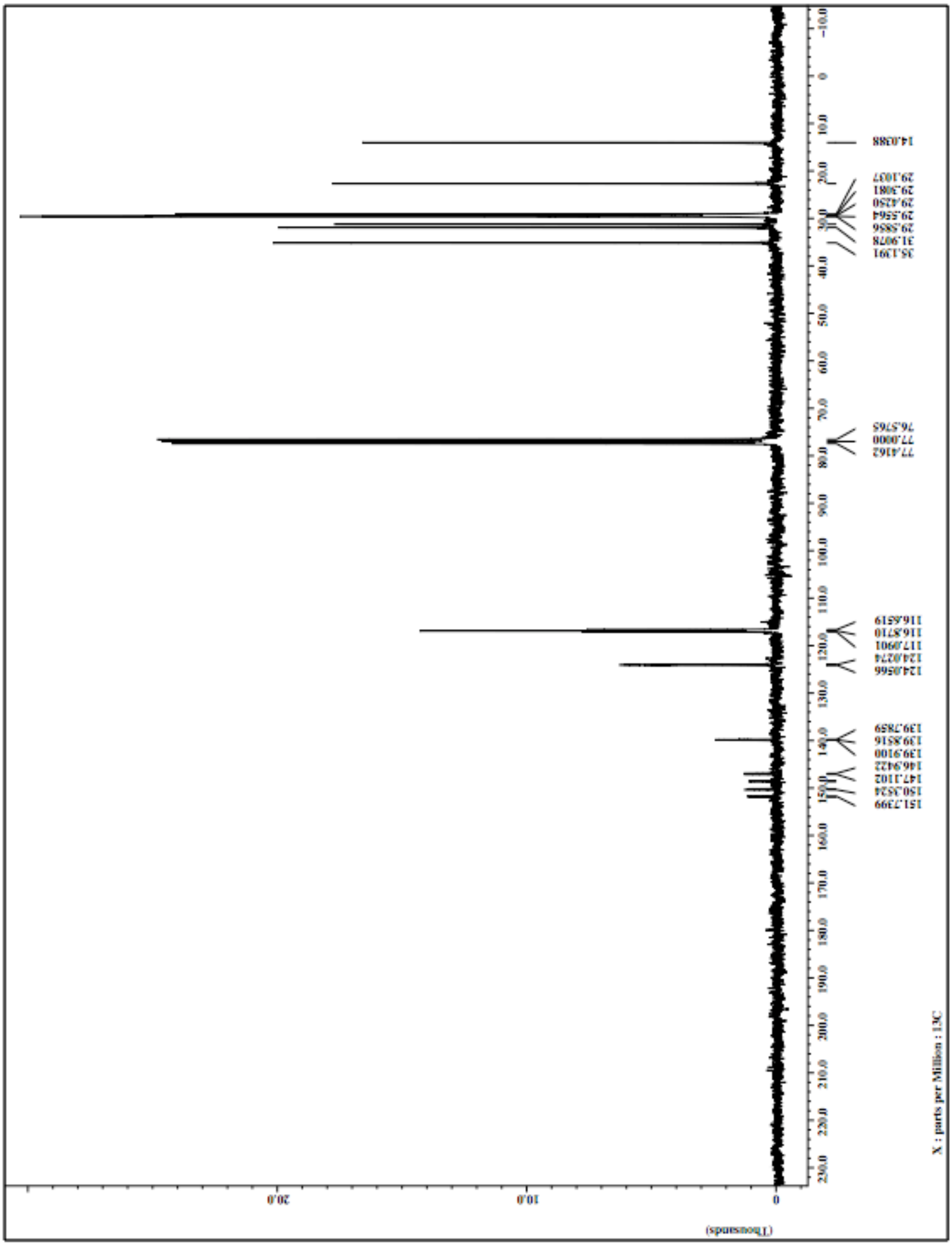
$C_{10}H_{21}$
F

(12)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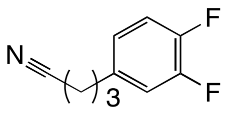
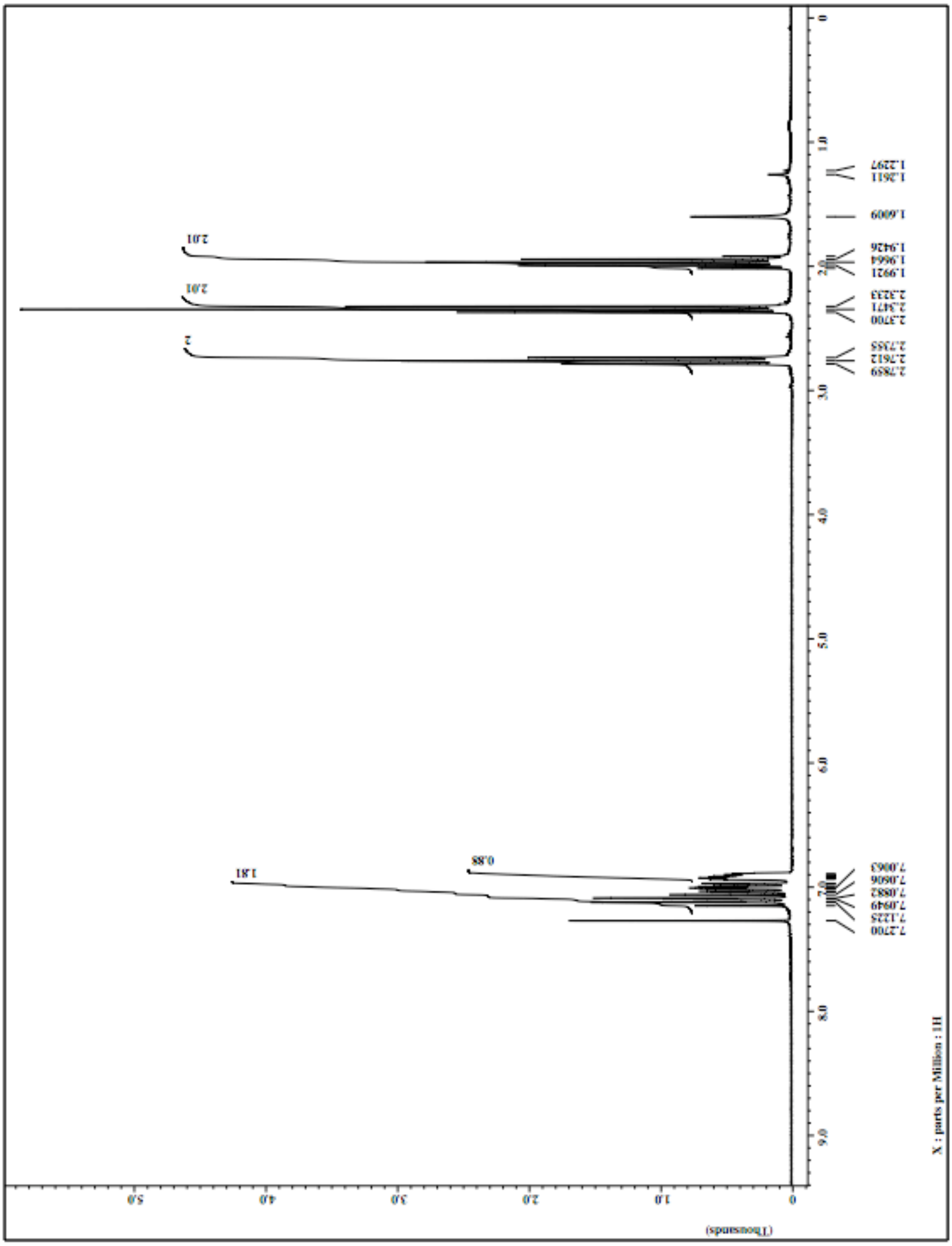
77.0000
77.4162
116.6519
116.8710
117.0901
124.0274
124.0566
139.7859
139.8516
139.9100
146.9422
147.1102
150.3524
151.7399
X : parts per Million : 13C
(Thousands)
0
10.0
20.0


N
F
F
3

(14)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1.9664
1.9921
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2.3471
2.3700
2.7355
2.7612
2.7859
7.0063
7.0606
7.0882
7.0949
7.1225
7.2700
2.01
2.01
2
0.88
1.81
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
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9.0
X : parts per Million : 1H
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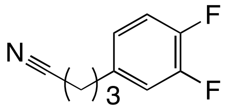
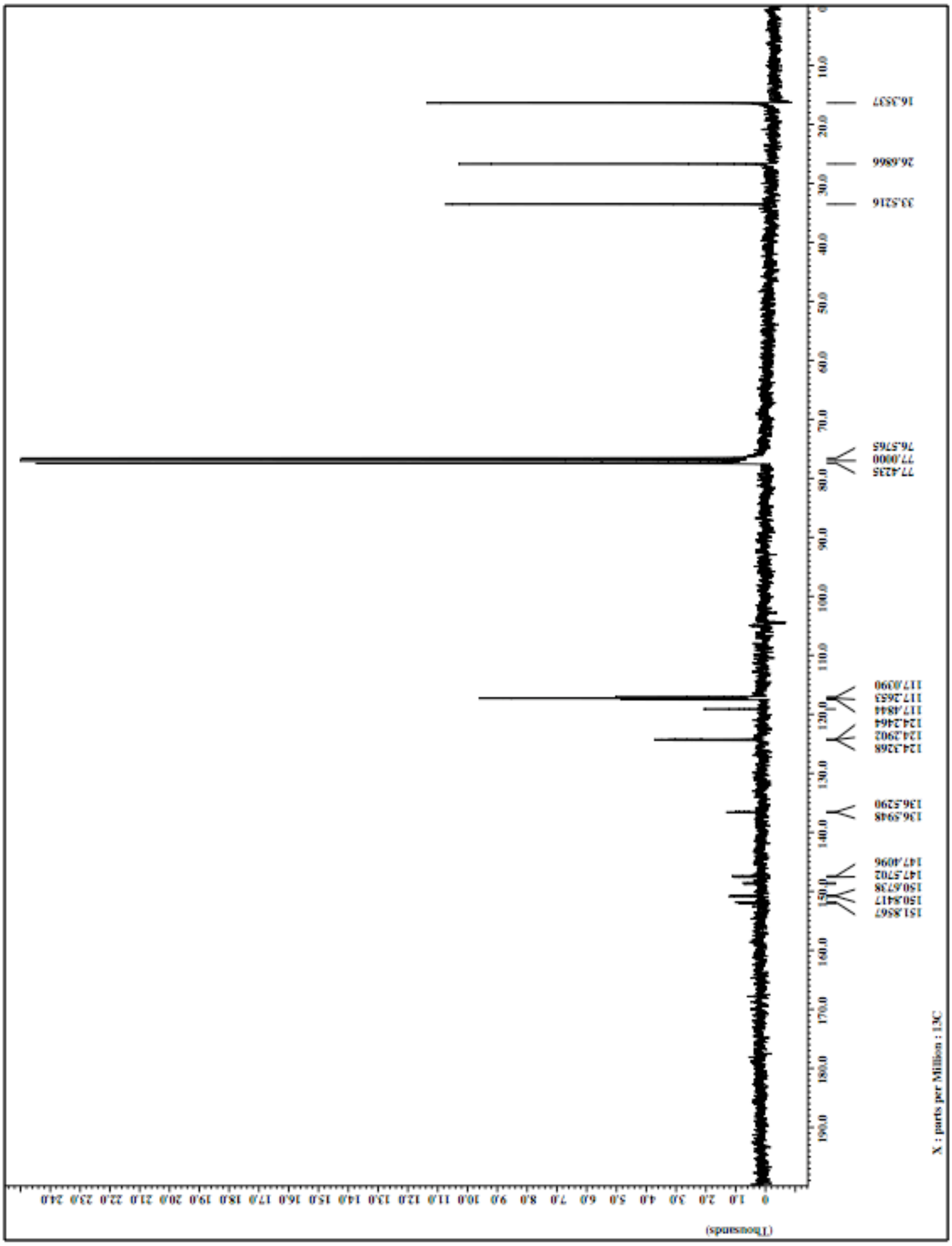
4.0
5.0
(Thousands)


N
3
F
F

(**14**)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77.0000
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124.2464
124.2902
124.3268
136.5290
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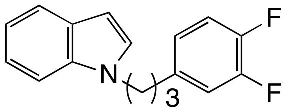
151.8567
X : parts per Million : 13C
(Thousands)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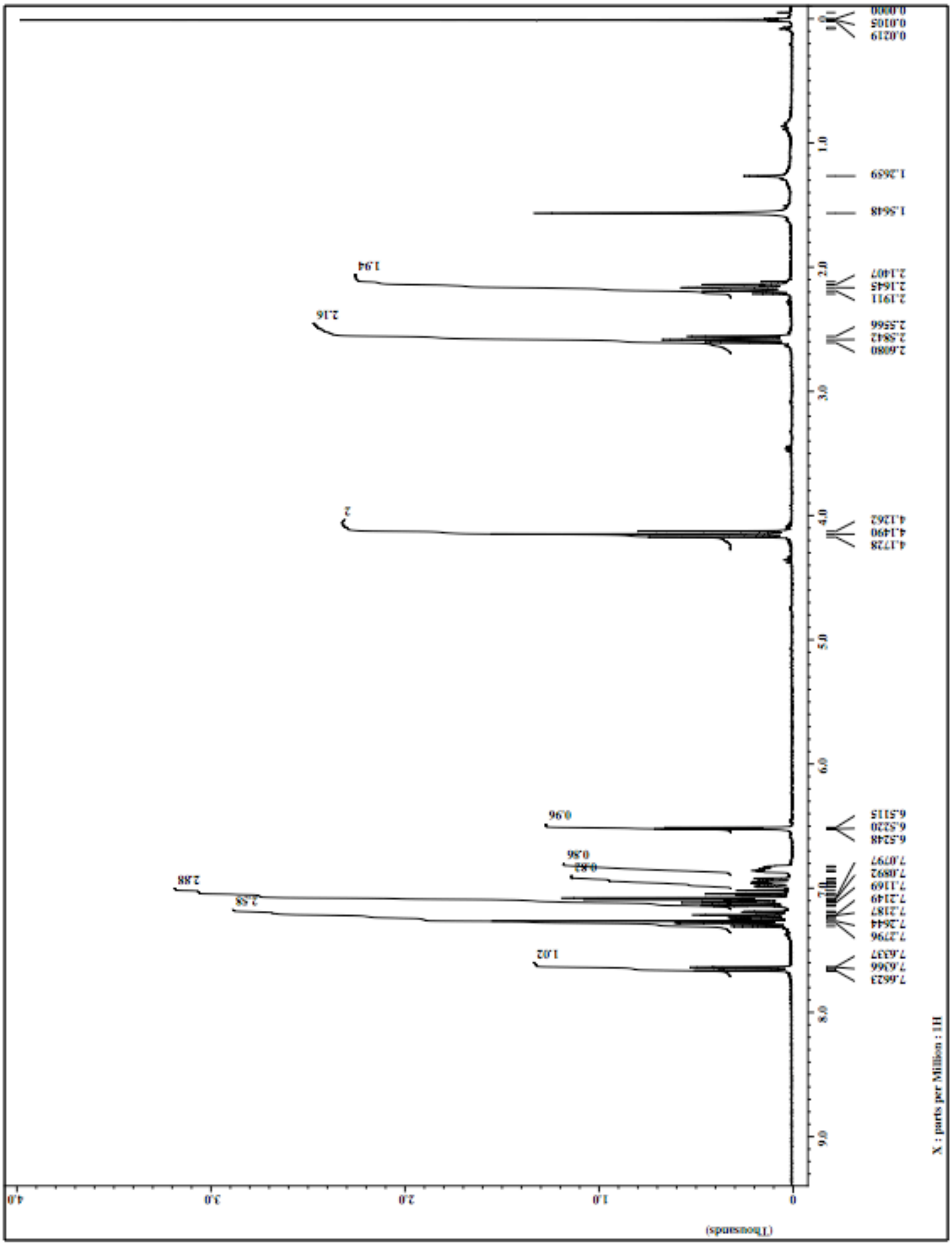
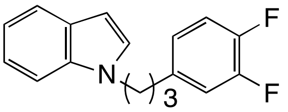
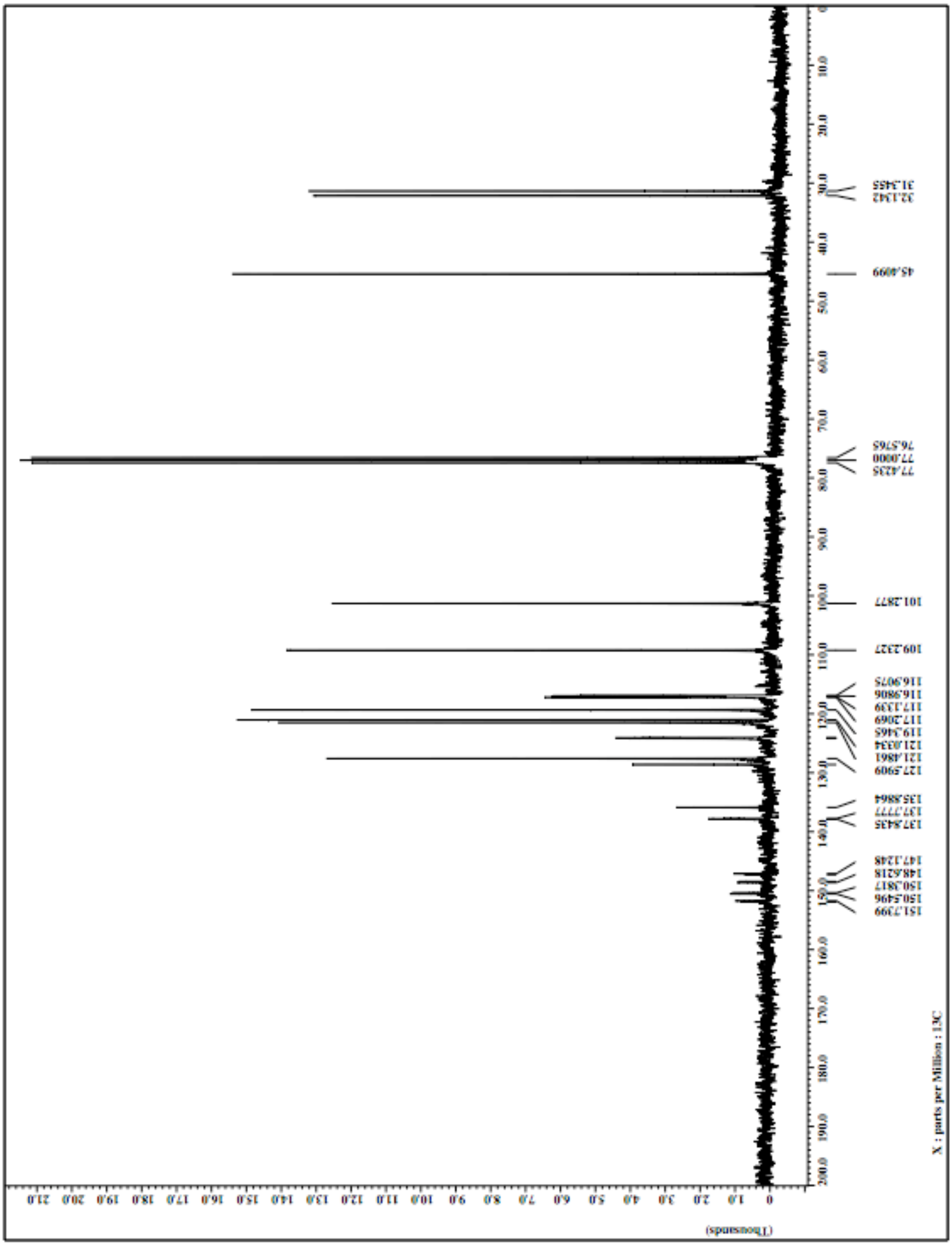
N
3
F

(**16**)


0.0000
0.0105
0.0219
1.2659
1.5648
2.1407
2.1645
2.1911
2.5566
2.5842
2.6080
4.1262
4.1490
4.1728
6.5115
6.5220
6.5248
7.0797
7.0892
7.1169
7.2149
7.2187
7.2644
7.2796
7.6337
7.6366
7.6623
1.94
2.16
2
0.96
0.86
0.82
2.88
2.58
1.02
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
0
1.0
2.0
3.0
4.0
(Thousands)
X : parts per Million : 1H


N
3
F
F

(16)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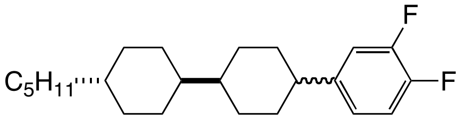
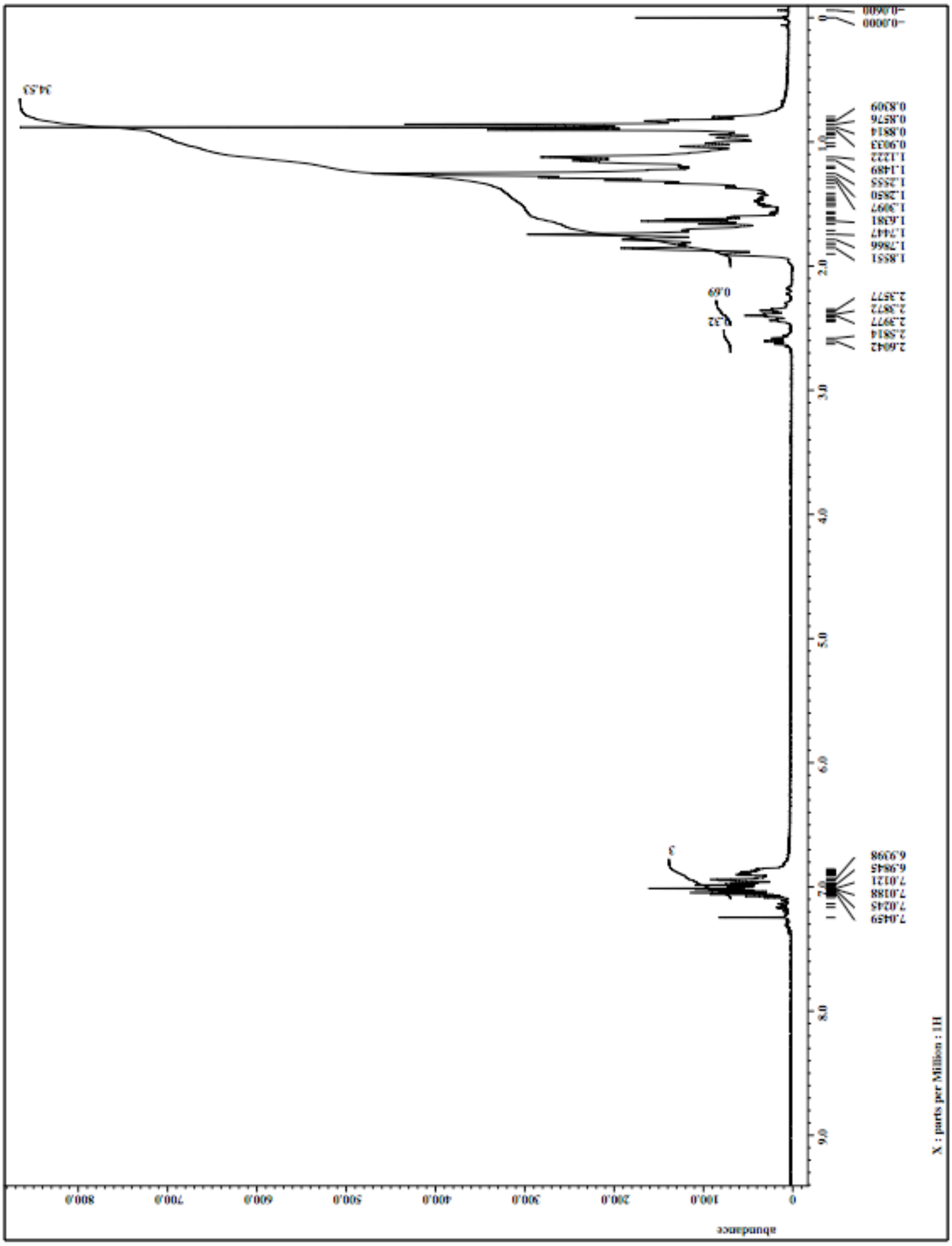
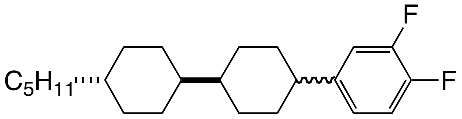
32.1342
45.4099
76.5765
77.0000
77.4235
101.2877
109.2327
116.9075
116.9806
117.1339
117.2069
119.3465
121.0334
121.4861
127.5909
135.8864
137.7777
137.8435
147.1248
148.6218
150.3817
150.5496
151.7399
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
X : parts per Million : 13C
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
(Thousands)



(18)

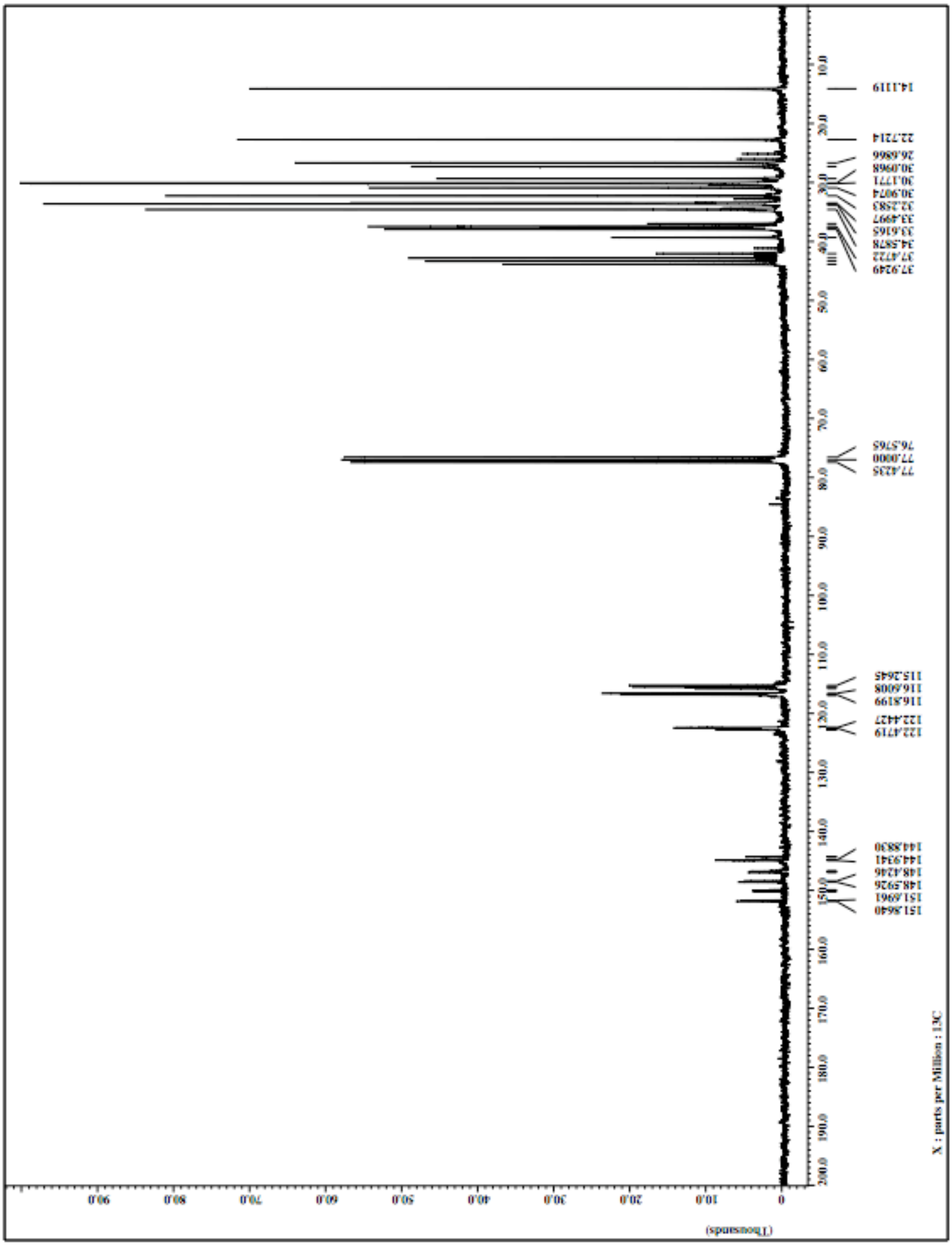
trans major (69%)

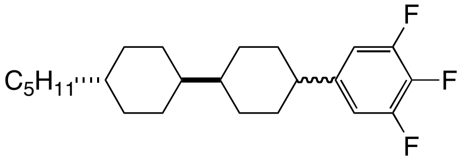




(18)

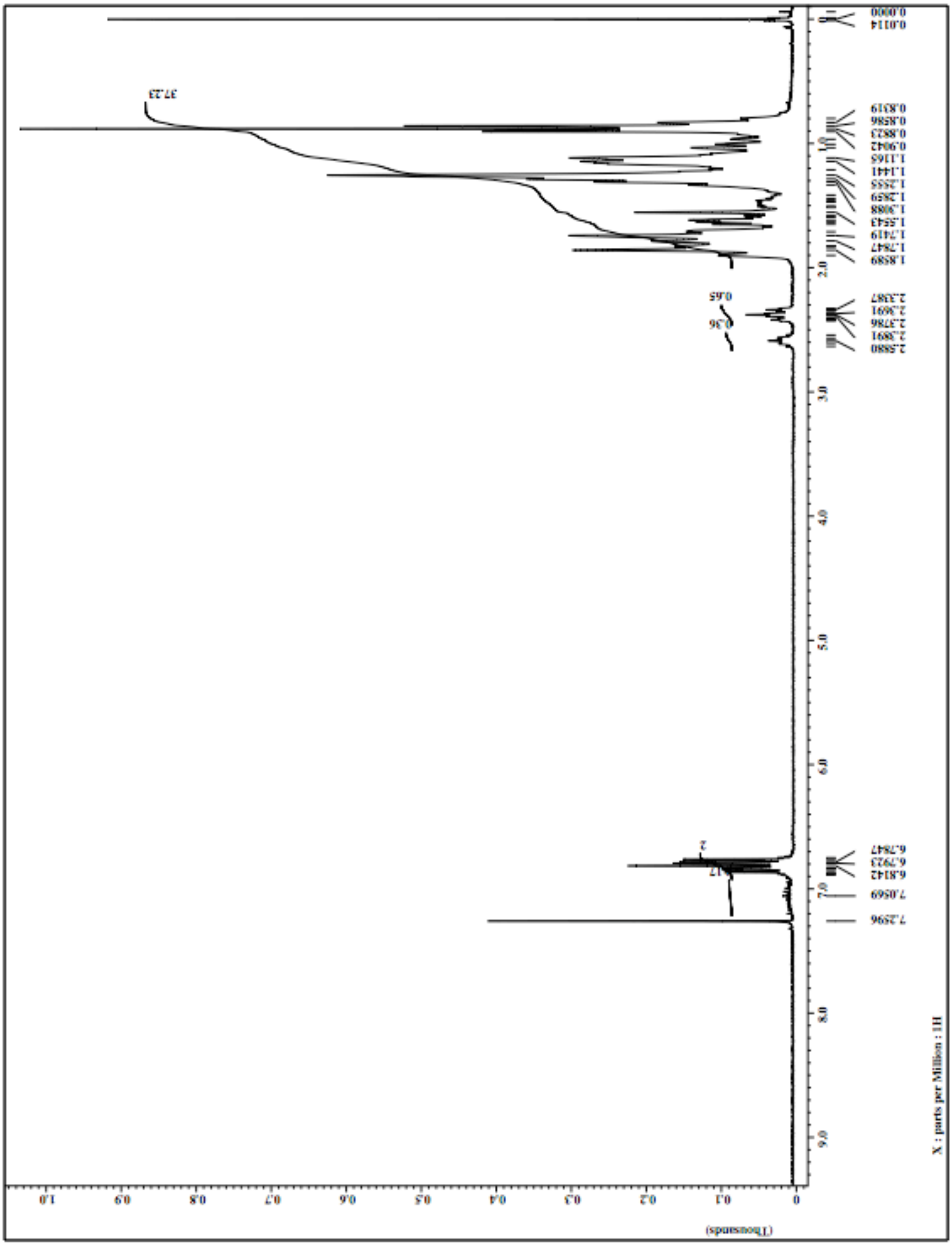
trans major (69%)

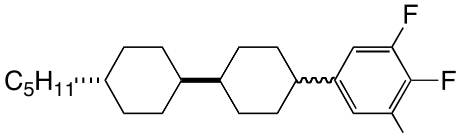




(**19**)

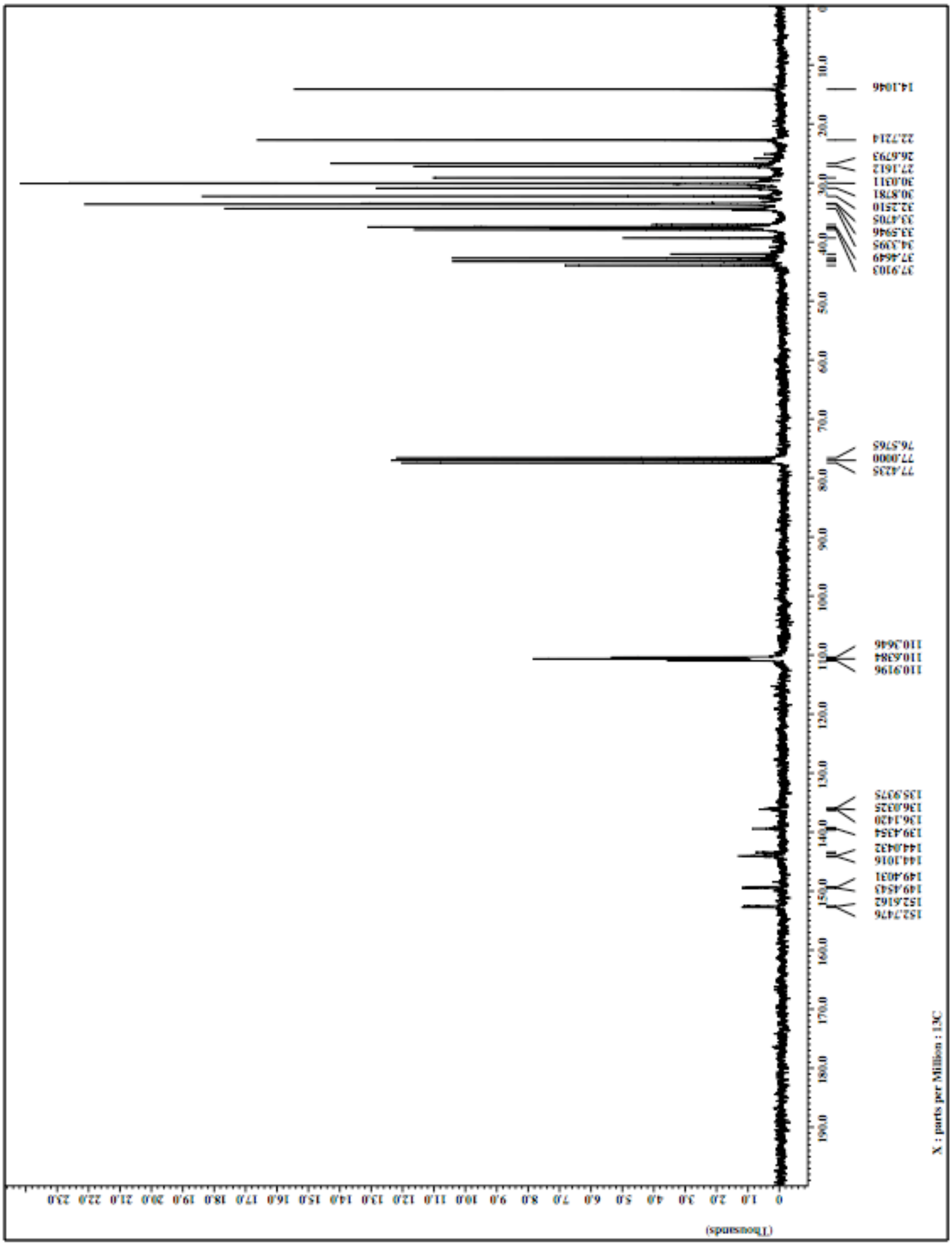
trans major (65%)

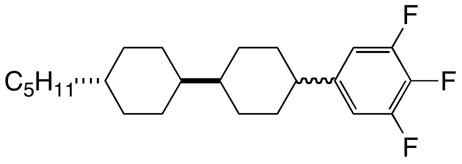




(**19**)

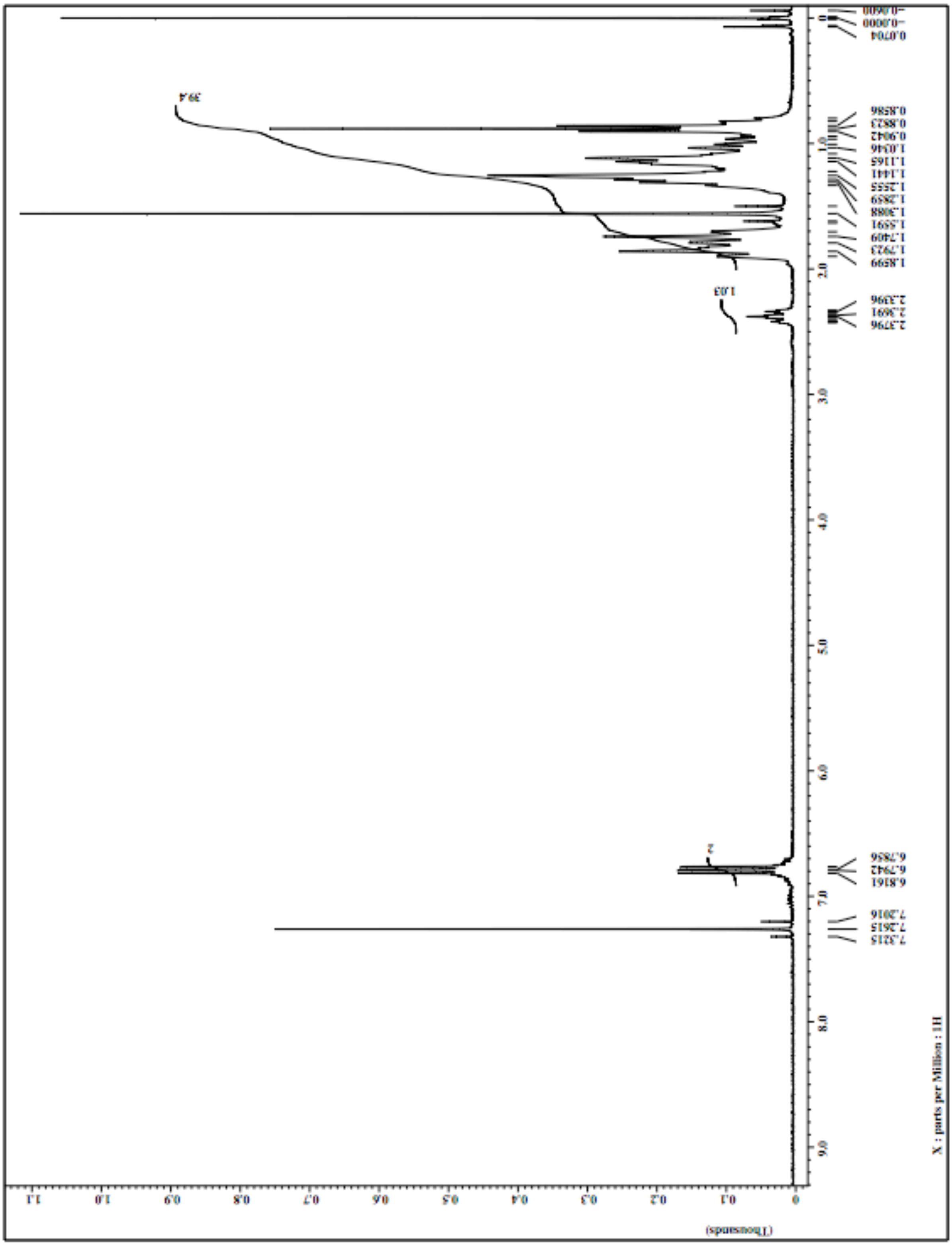
trans major (65%)

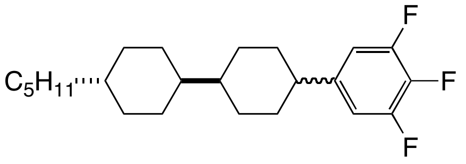




(**19**)

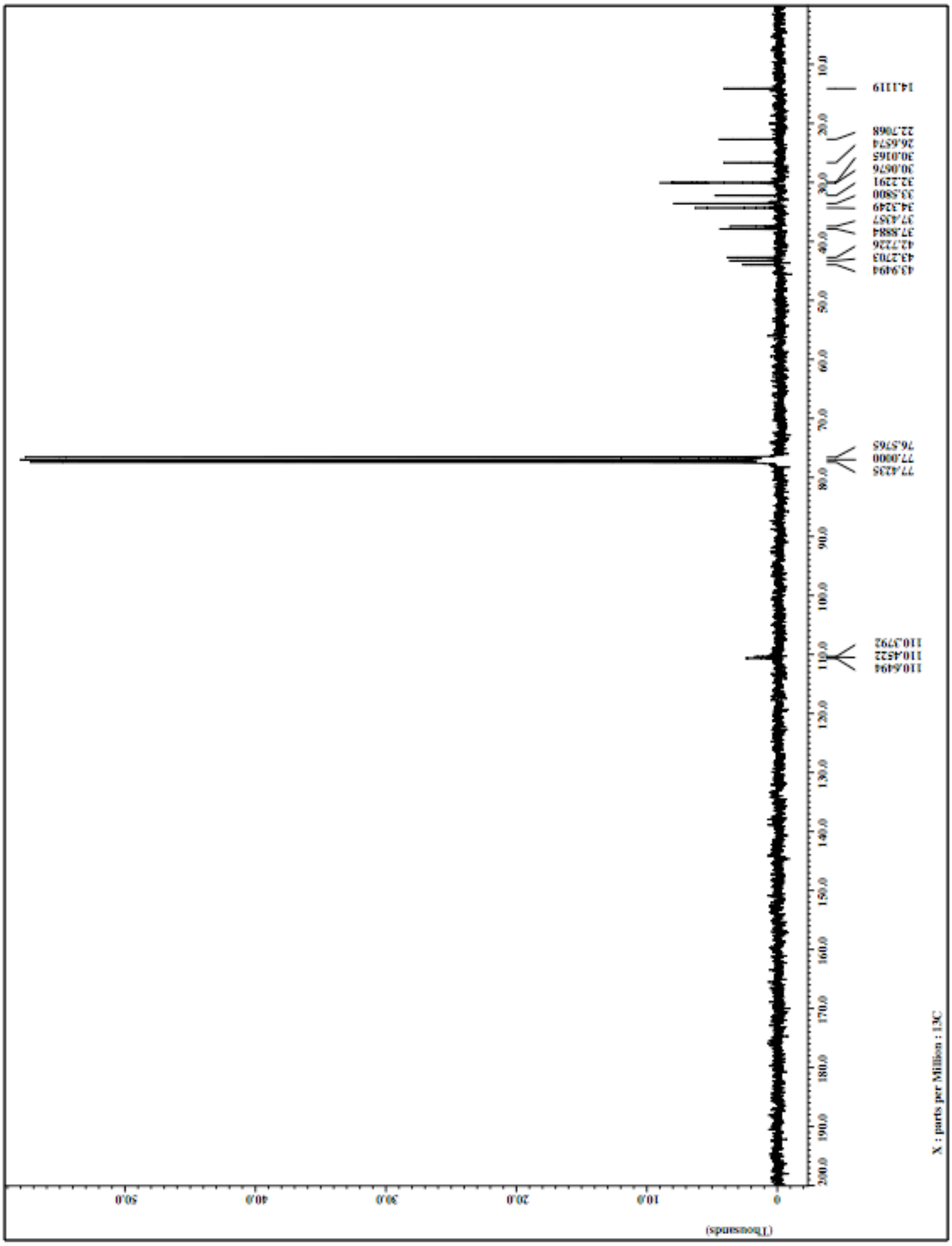
trans major (> 95%)

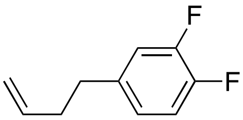




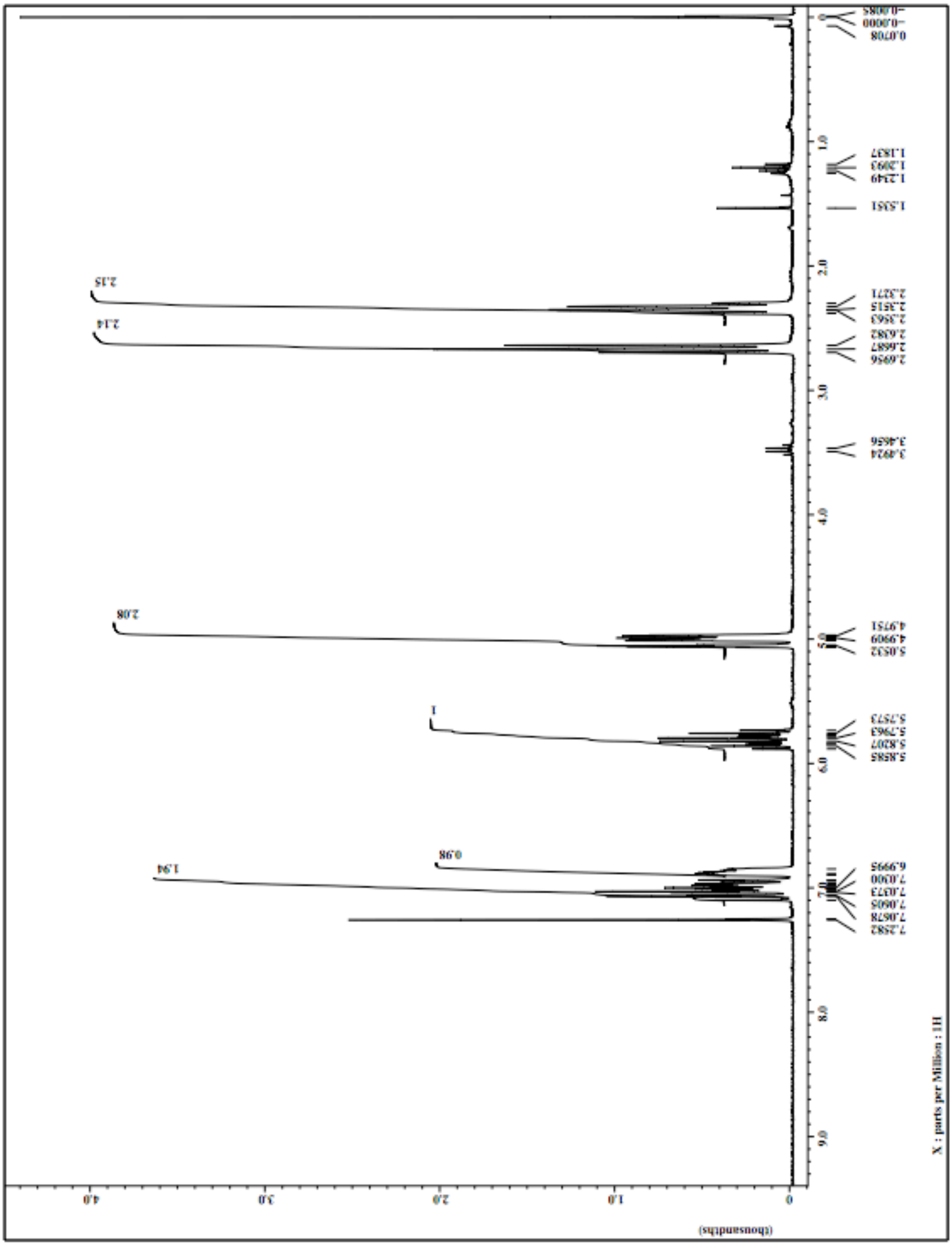
(19)

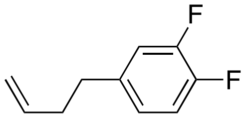
trans major (> 95%)



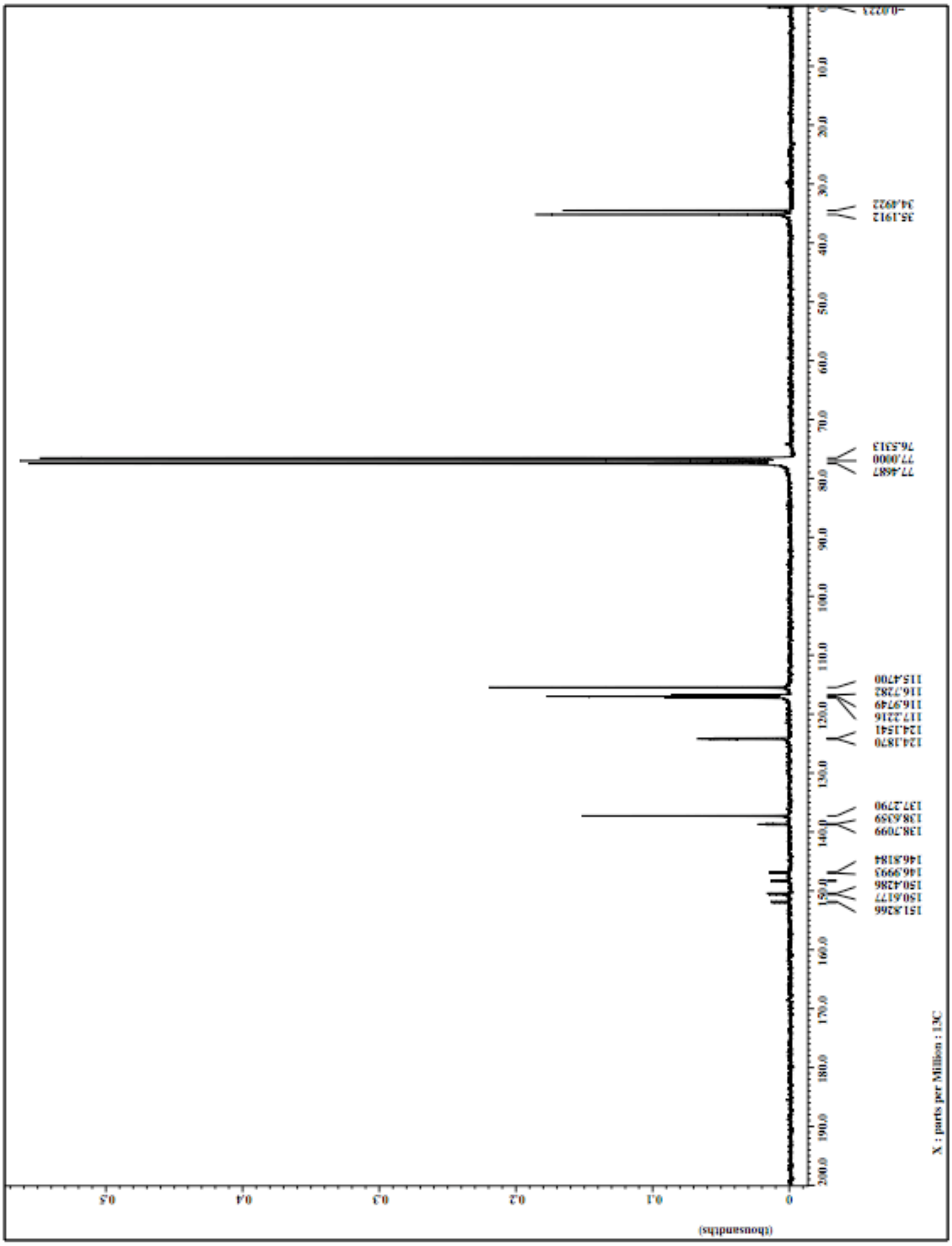

F
F

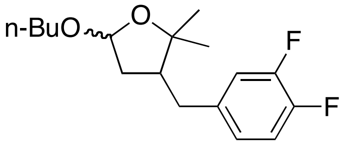
(**21**)


-0.0085
-0.0000
0.0708
1.1837
1.2093
1.2349
1.5351
2.3271
2.3515
2.3563
2.6382
2.6687
2.6956
3.4656
3.4924
4.9751
4.9909
5.0532
5.7573
5.7963
5.8207
5.8585
6.9995
7.0300
7.0373
7.0605
7.0678
7.2582
2.15
2.14
2.08
1
0.98
1.94
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : 1H
(thousandths)


F
F

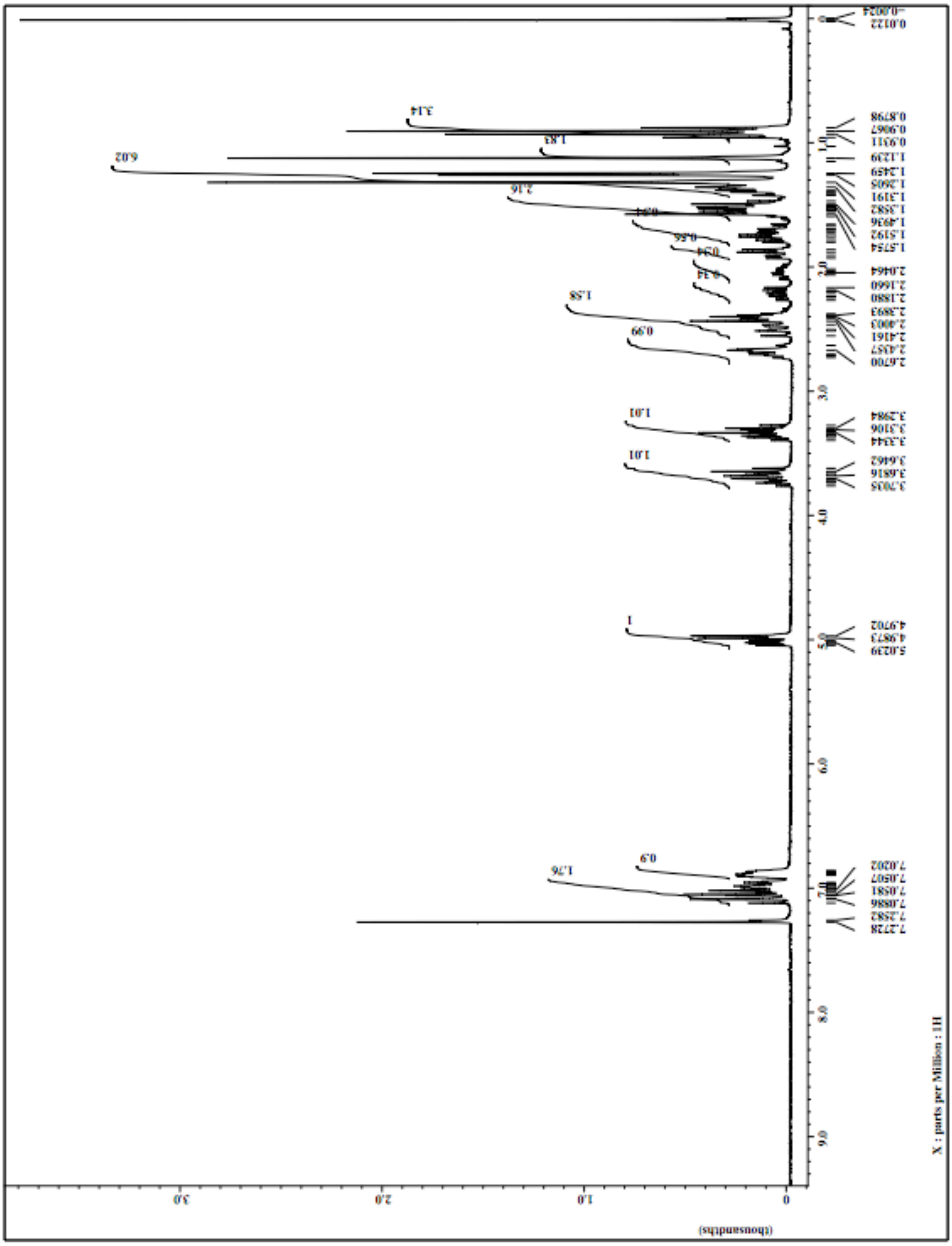
(**21**)

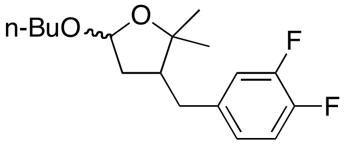

-0.0223
34.4922
35.1912
76.5313
77.0000
77.4687
115.4700
116.7282
116.9749
117.2216
124.1541
124.1870
137.2790
138.6359
138.7099
146.8184
146.9993
150.4286
150.6177
151.8266
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
X : parts per Million : 13C
0
0.1
0.2
0.3
0.4
0.5
(thousandths)



(**23**)

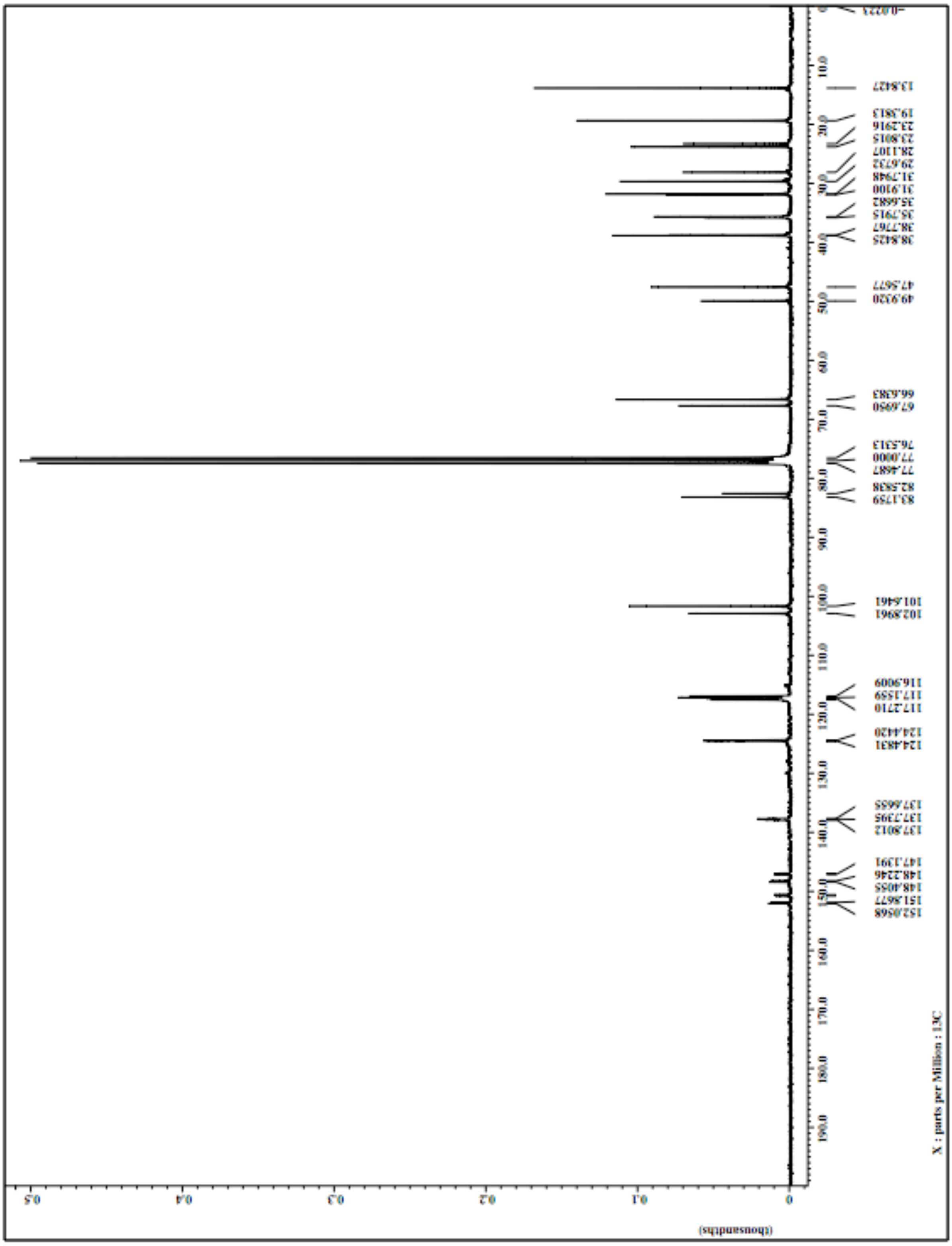
trans major (61%)

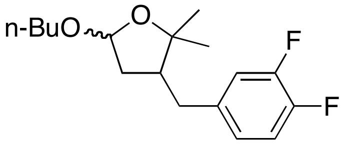




(**23**)

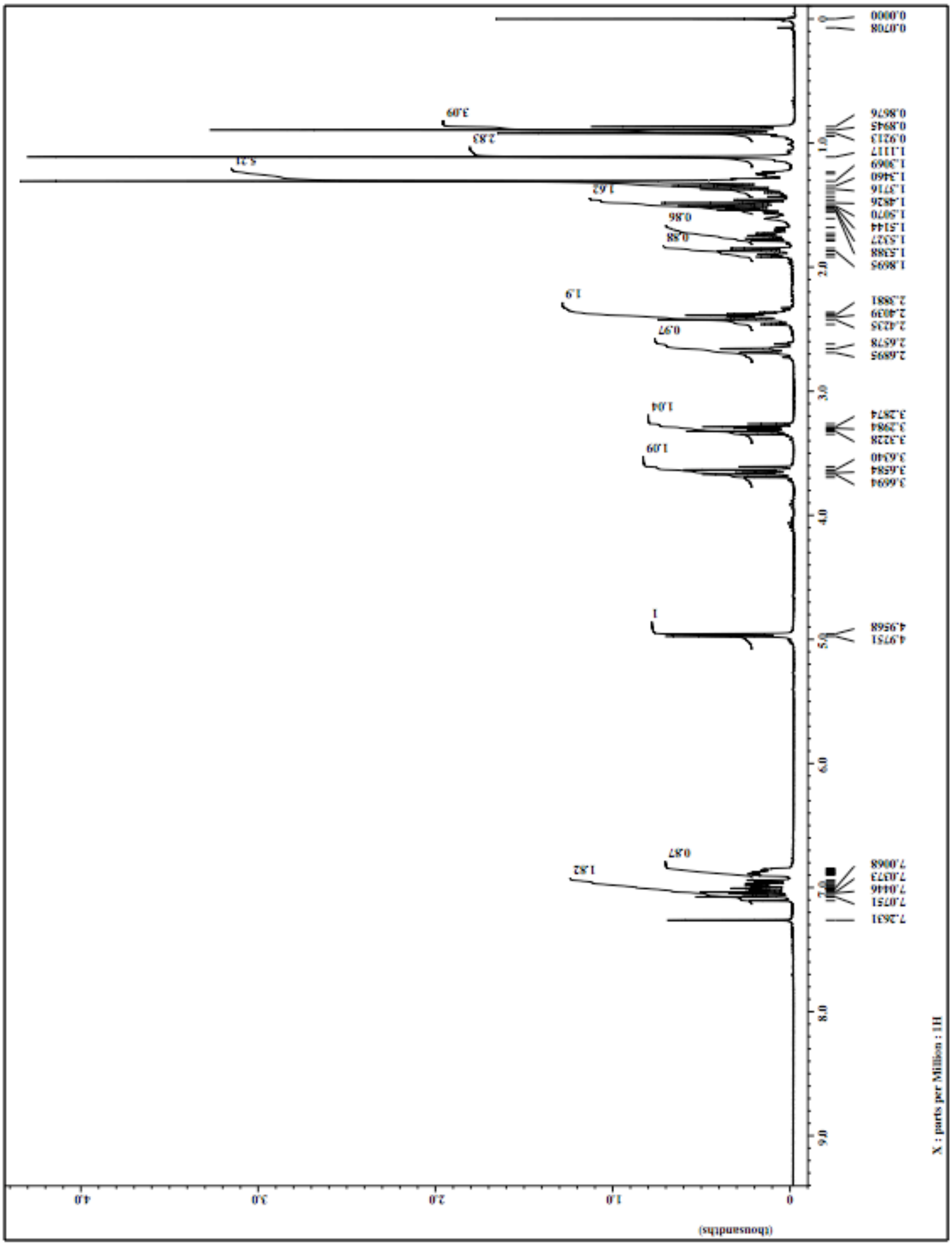
trans major (61%)

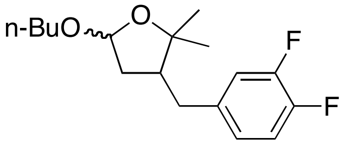




(23)

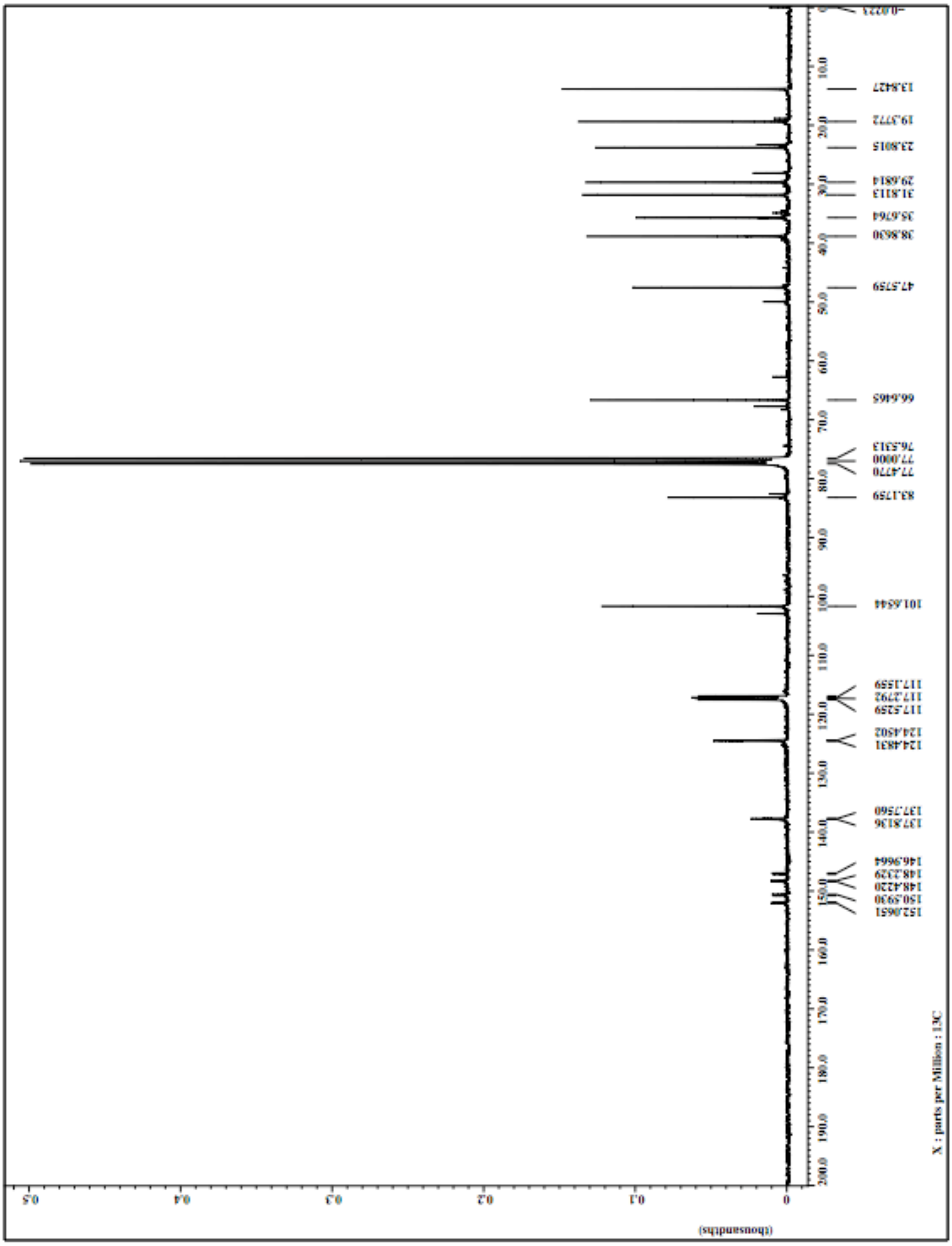
trans major (85%)

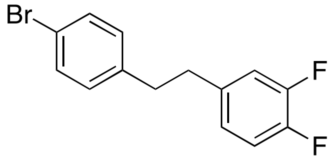




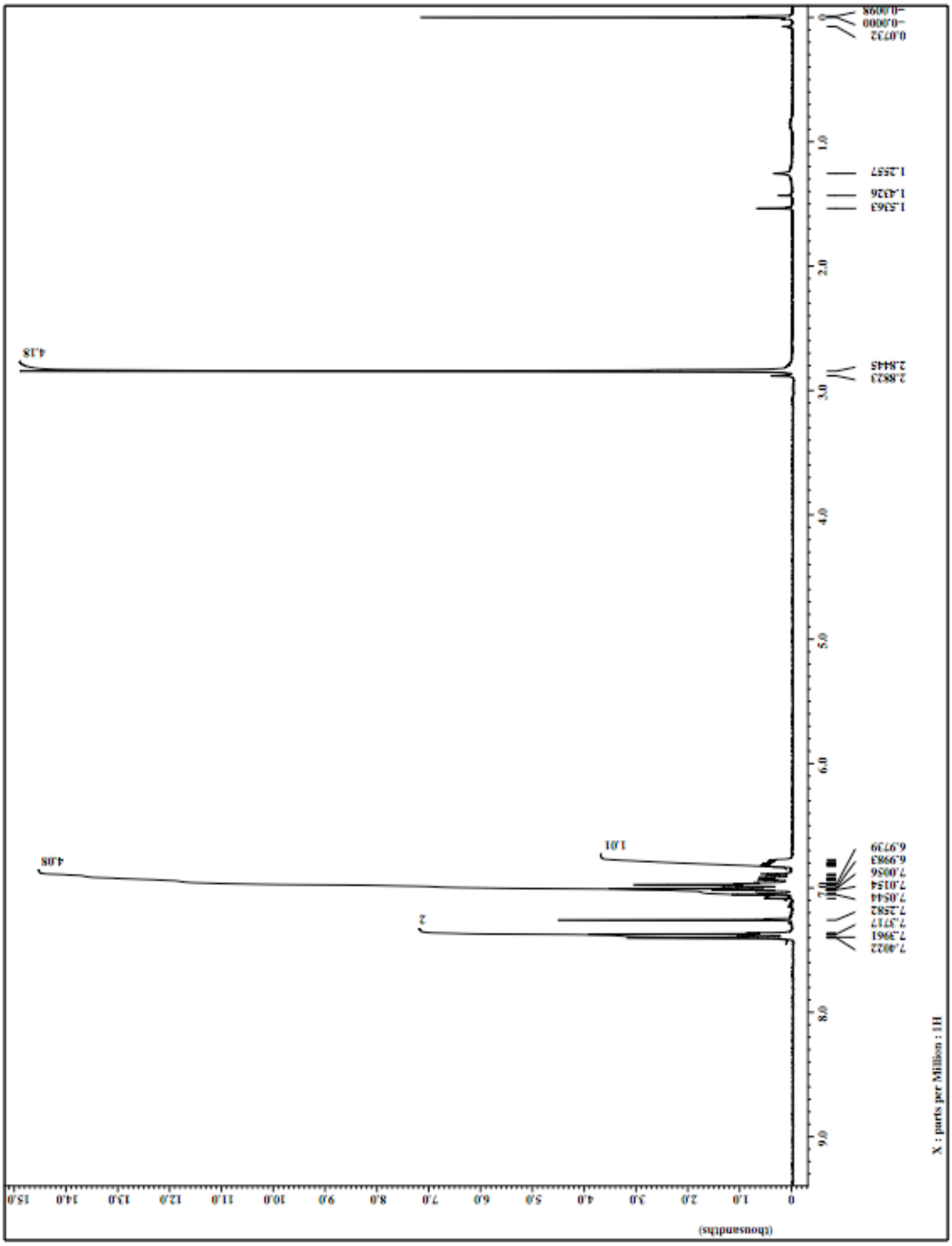
(23)

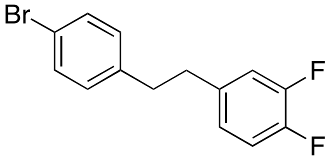
trans major (85%)



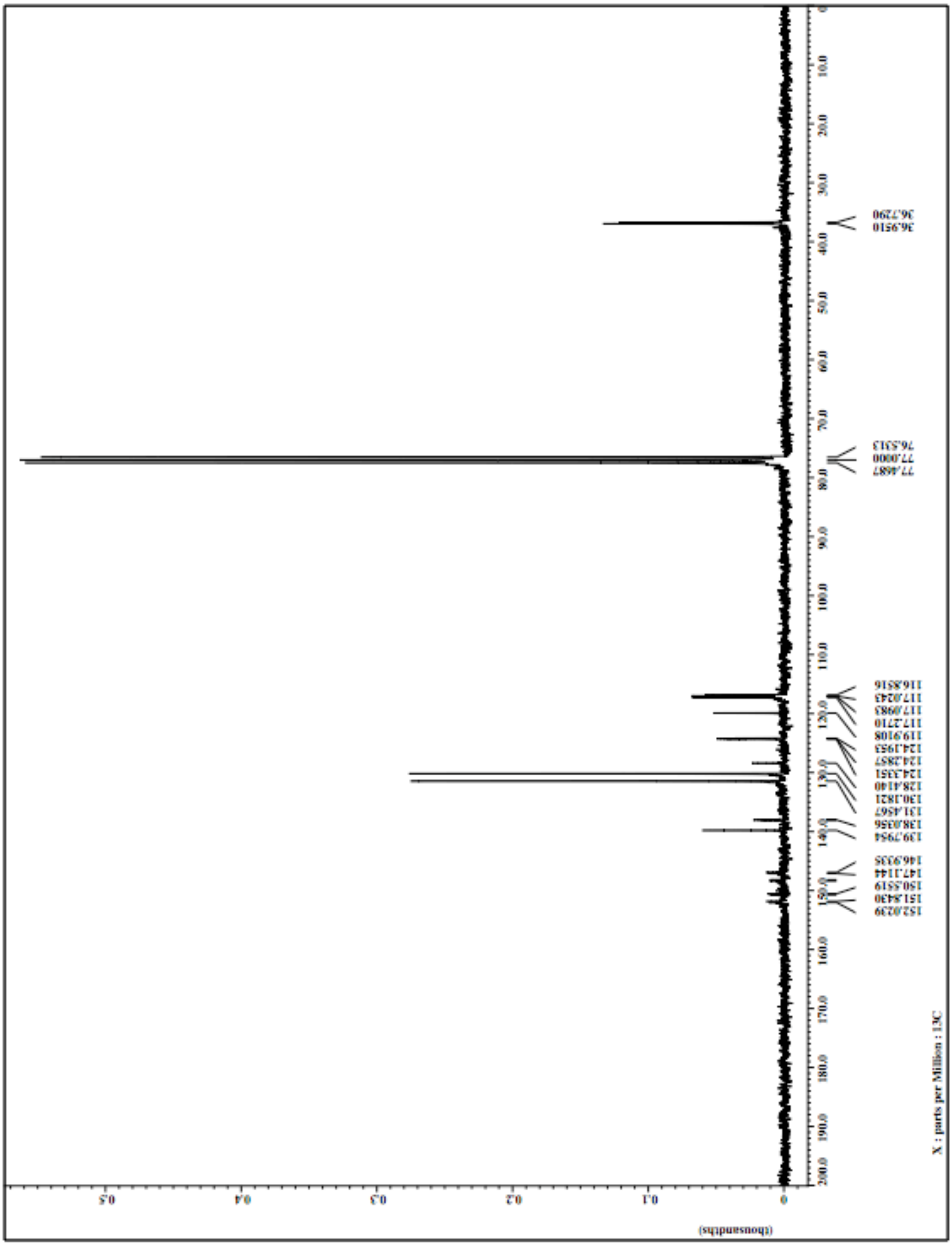

Br
F
F

(**25**)


-0.0098
-0.0000
0.0732
1.2557
1.4326
1.5363
2.8445
2.8823
6.9739
6.9983
7.0056
7.0154
7.0544
7.2582
7.3717
7.3961
7.4022
4.18
1.01
4.08
2
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : 1H
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
(thousandths)


Br
F
F

(**25**)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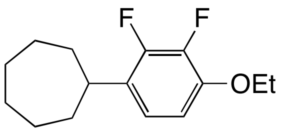
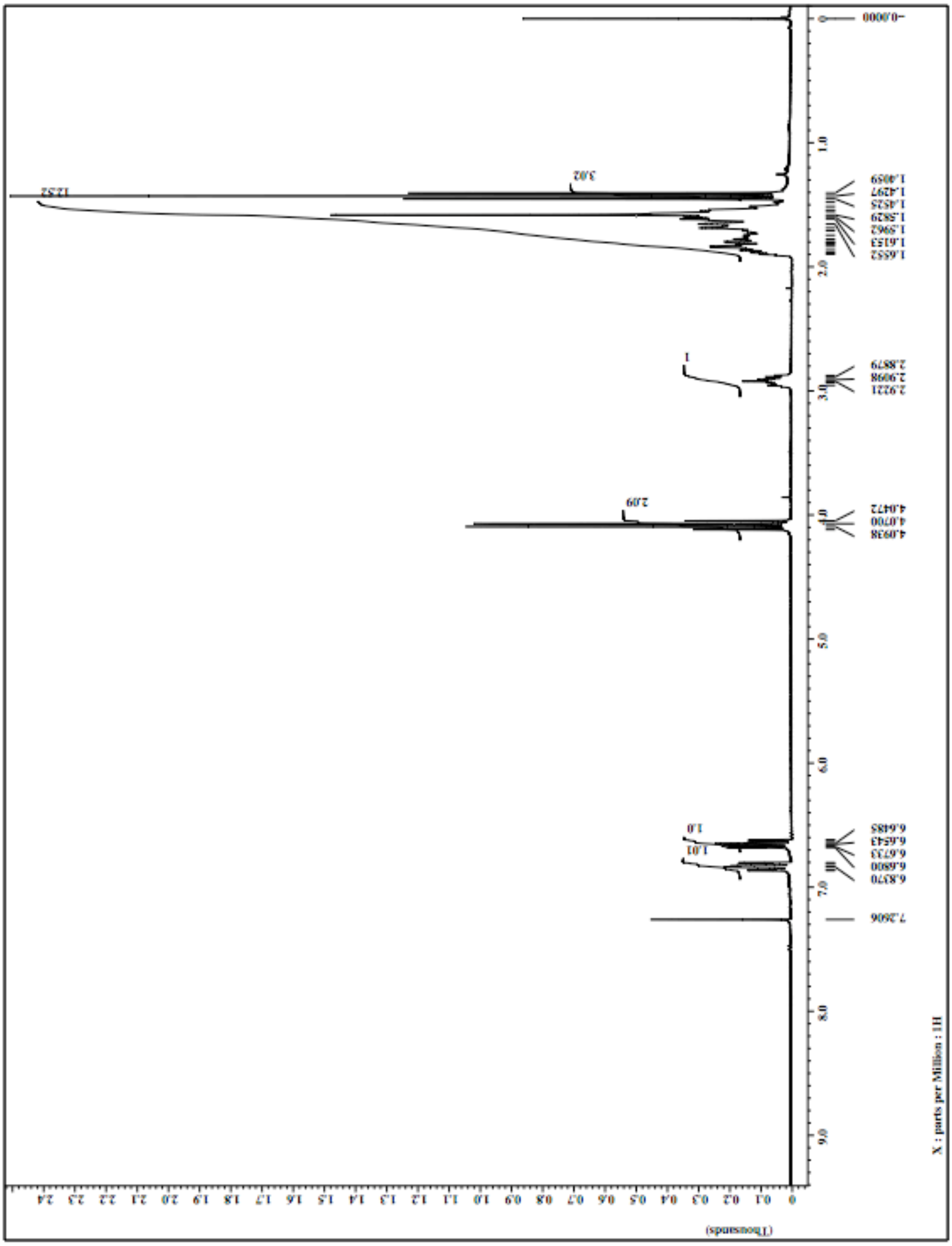
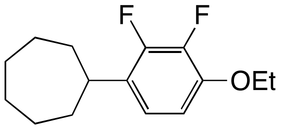
36.9510
76.5313
77.0000
77.4687
116.8516
117.0243
117.0983
117.2710
119.9108
124.1953
124.2857
124.3351
128.4140
130.1821
131.4567
138.0356
139.7954
146.9335
147.1144
150.5519
151.8430
152.0239
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
X : parts per Million : 13C
0
0.1
0.2
0.3
0.4
0.5
(thousandths)

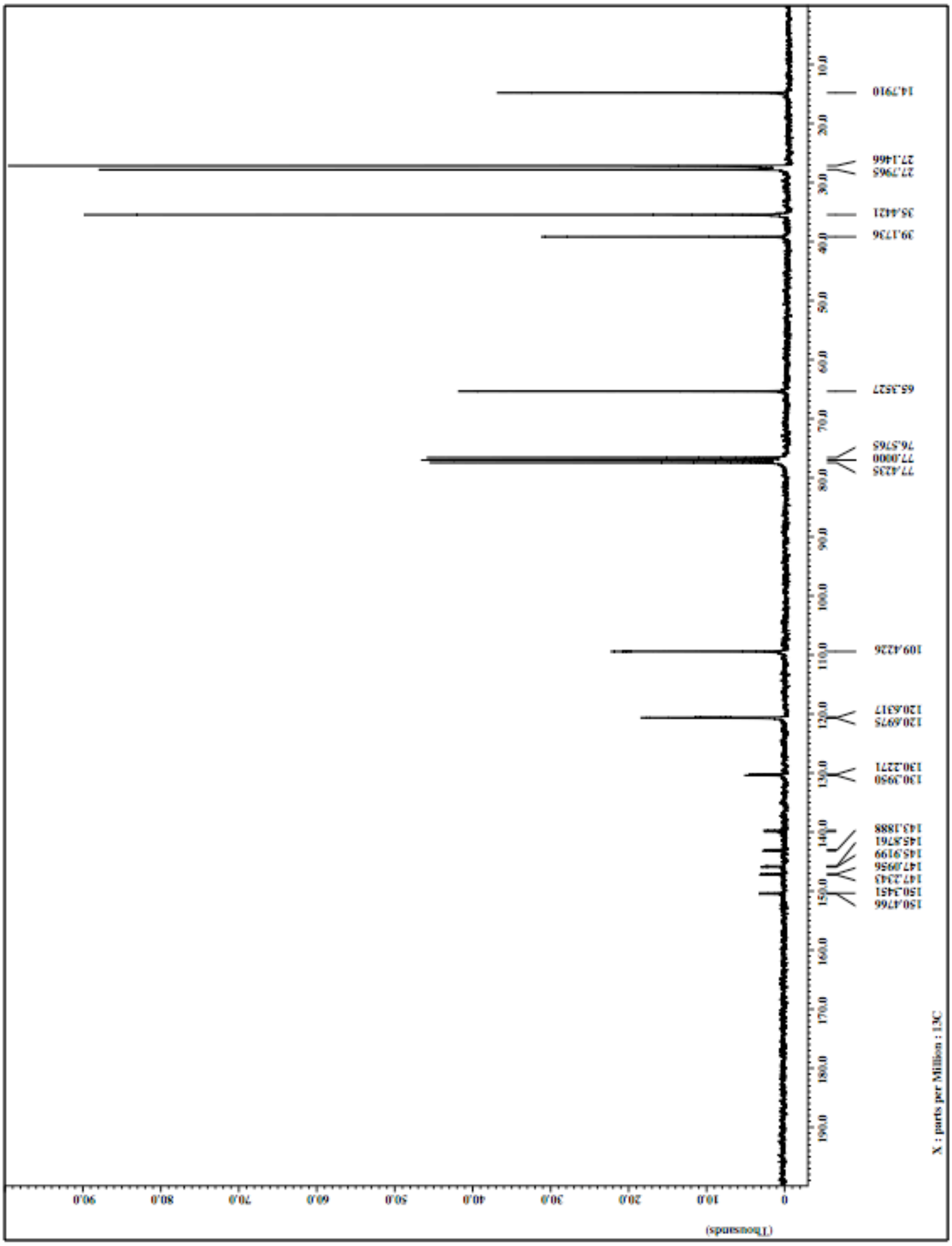

F
F
OEt

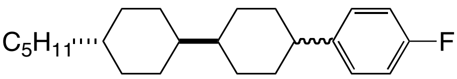
(**SI-1**)


-0.0000
1.4059
1.4297
1.4525
1.5829
1.5962
1.6153
1.6552
2.8879
2.9098
2.9221
4.0472
4.0700
4.0938
6.6485
6.6543
6.6733
6.6800
6.8370
7.2606
3.02
12.52
1
2.09
1.0
1.01
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
X : parts per Million : 1H
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
(Thousands)


F
F
OEt

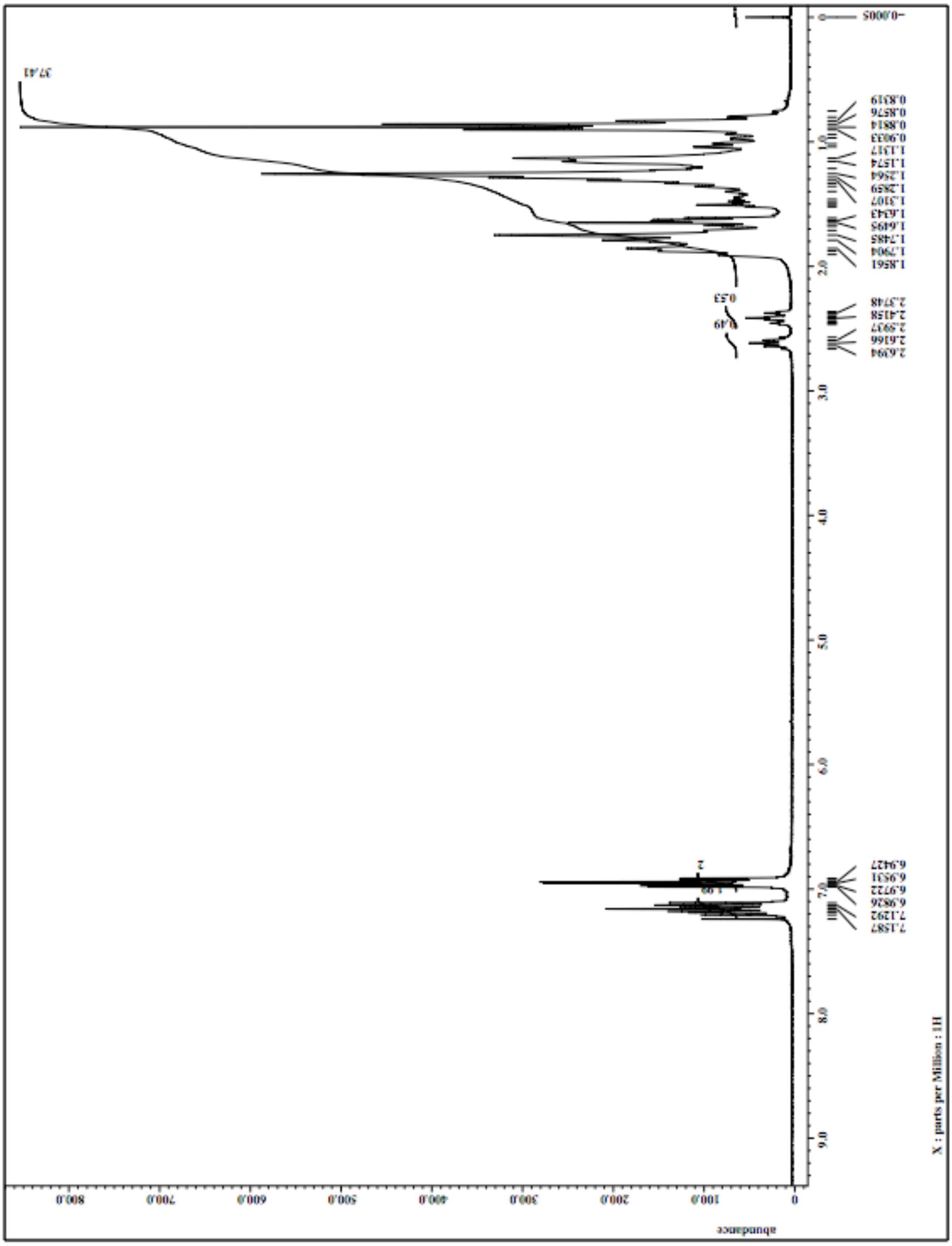
(SI-1)

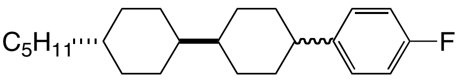

14.7910
27.1466
27.7965
35.4421
39.1736
65.3527
76.5765
77.0000
77.4235
109.4226
120.6317
120.6975
130.2271
130.2950
143.1888
145.8761
145.9199
147.0956
147.2343
150.3451
150.4766
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
X : parts per Million : 13C
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
(Thousands)



(**SI-2**)

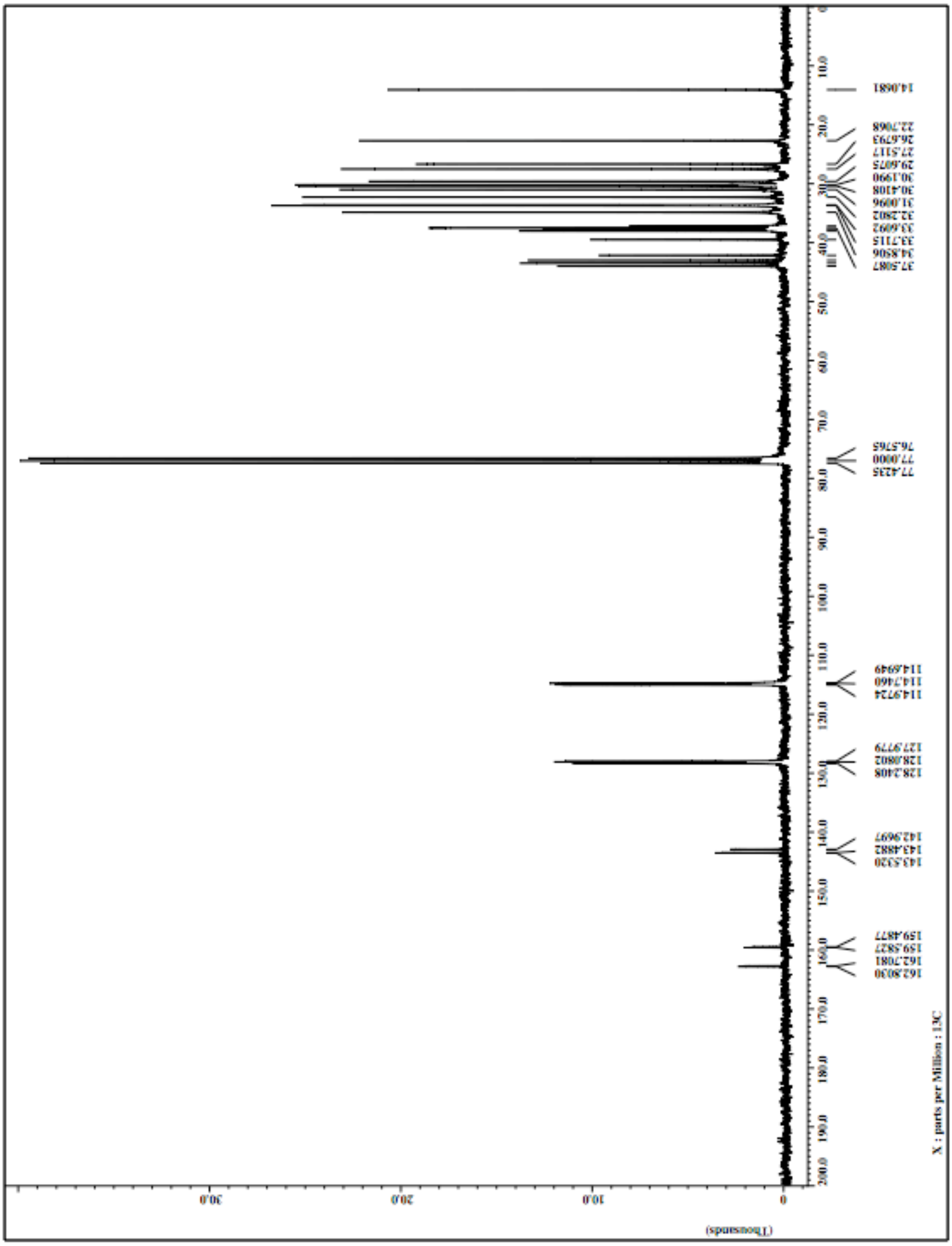
trans major (56%)

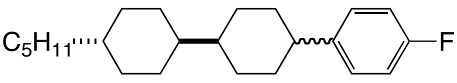




(**SI-2**)

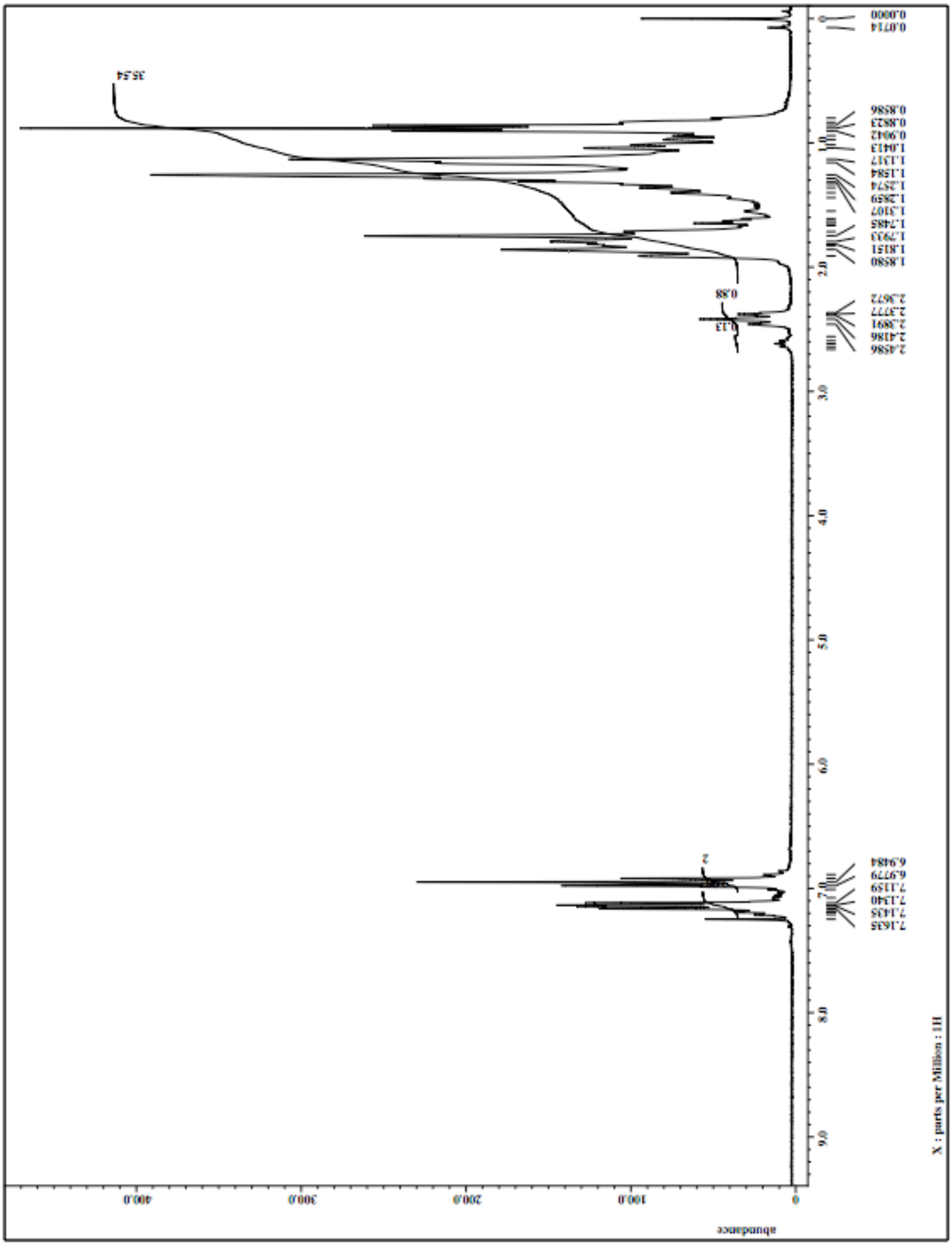
trans major (56%)

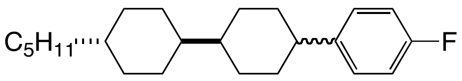




(**SI-2**)

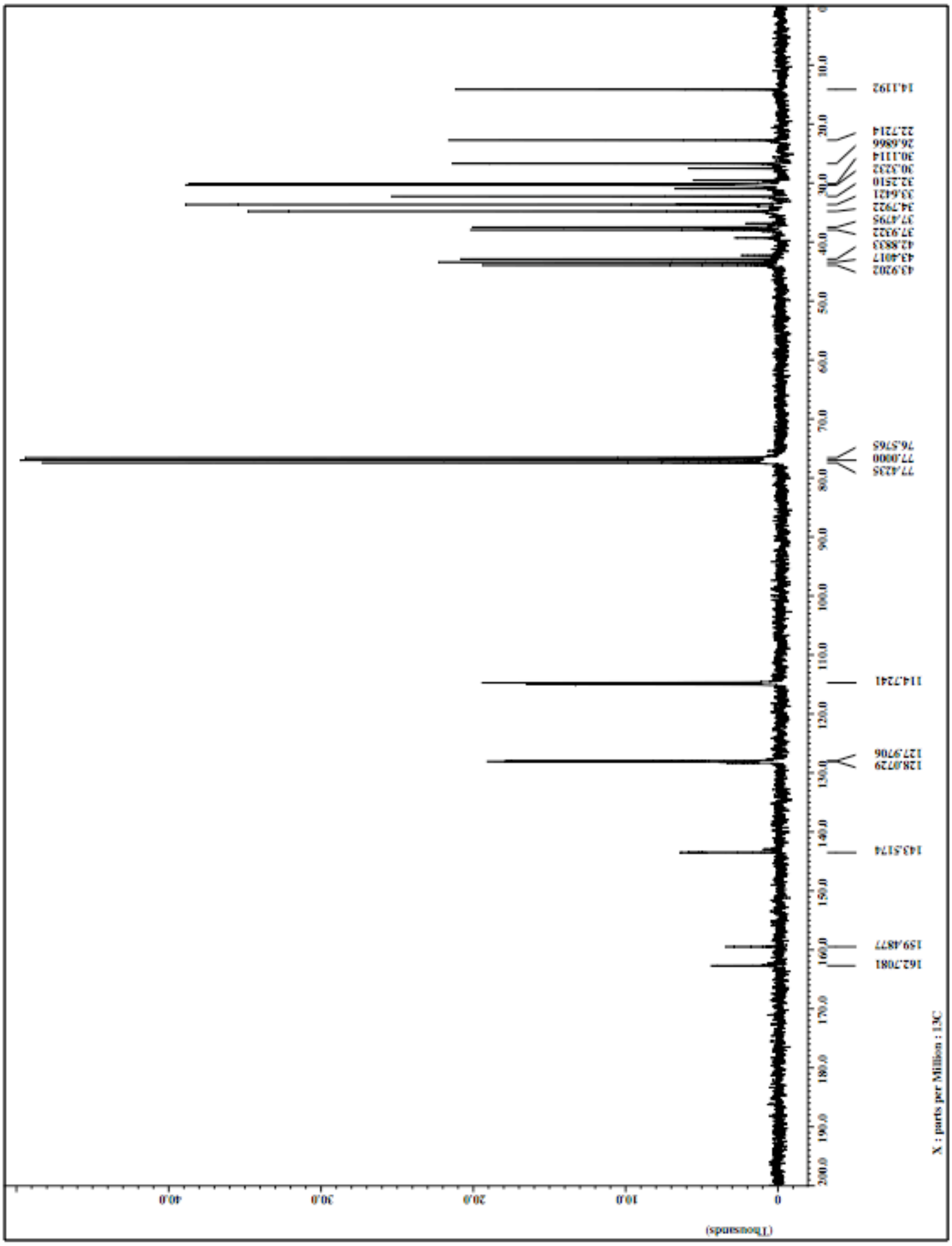
trans major (88%)

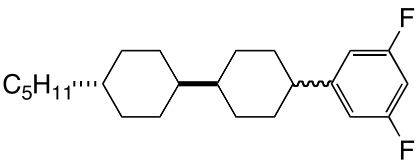




(**SI-2**)

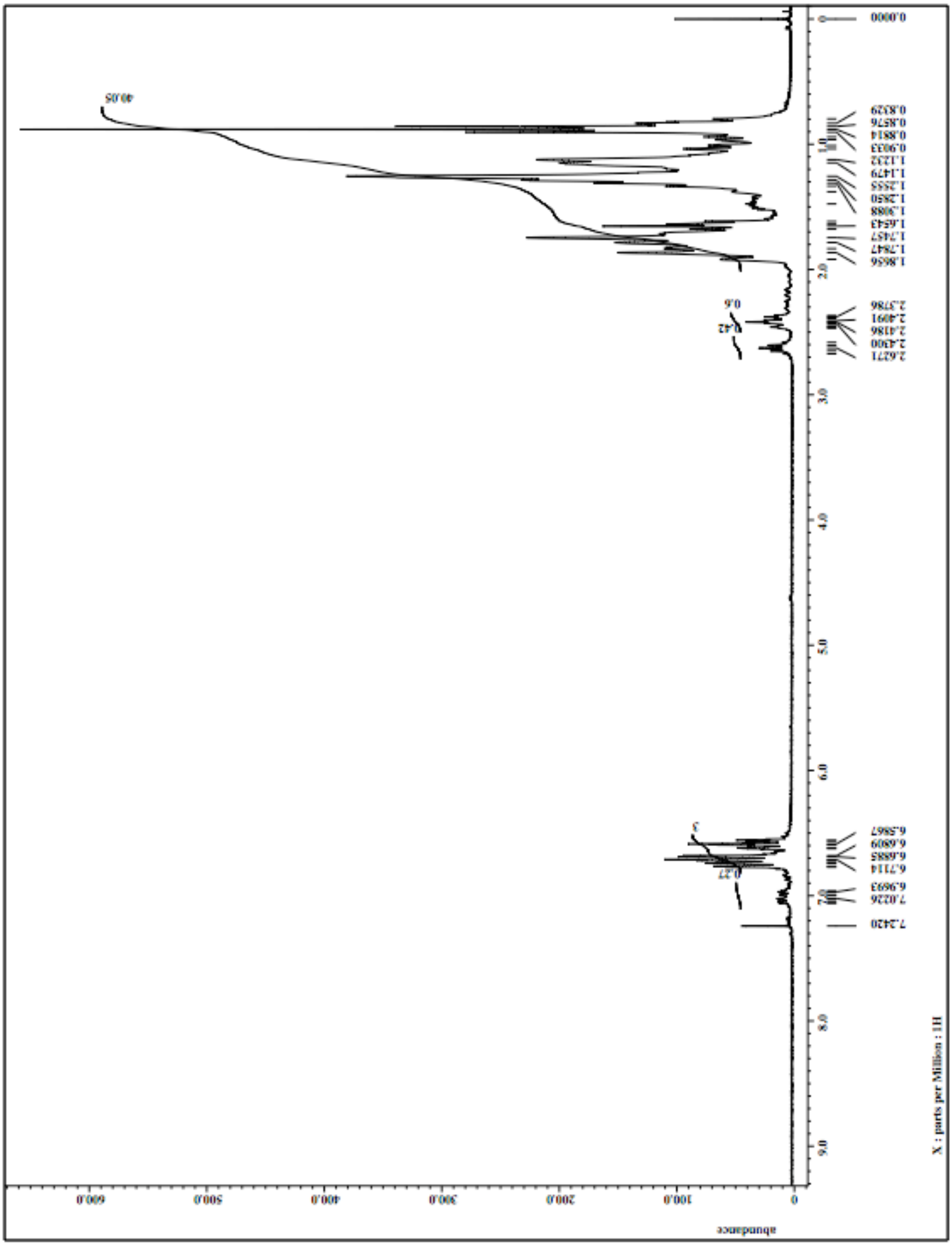
trans major (88%)

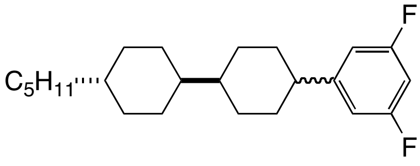




(**SI-3**)

cis:*trans* = 44:56





(SI-3)

cis:*trans* = 44:56