Electronic Supplementary Material (ESI) for Chemical Communications

$ZrCl_2(\eta\text{-}C_5Me_5)_2\text{-}AlHCl_2\bullet(THF)_2$: Efficient hydroalumination of terminal alkynes and cross-coupling of the derived alanes

Philip Andrews,[a] Christopher M. Latham,[a] Marc Magre,[a] Darren Willcox[a] and Simon Woodward*[a]

[a] *School of Chemistry, The University of Nottingham, University Park, Nottingham, United Kingdom. Fax: +44-(0)115-9513564; Tel: +44-(0)115-9513541; E-mail: simon.woodward@nottingham.ac.uk*

List of Contents

General S2
General Procedures
Preparation of $HAlCl_2\bullet 2THF$ S2
$Cp^*_2ZrCl_2$ catalysed hydroalumination-cross coupling of alkynes S2
Cp_2TiCl_2 catalysed hydroalumination-cross coupling of alkynes S3
$^2H\{^1H\}$ and ^1H NMR monitoring of the hydroalumination procedure S3
Compound data S4
Comparison of hydroaluminations conditions S23
Spectra S24
References S94

General

All reactions were carried out in flame-dried or oven-dried glassware, under an argon atmosphere. THF was freshly distilled from sodium benzophenone-ketyl. Solid 1,4-Diazabicyclo[2.2.2]octane (DABCO) was freshly sublimed before use. Crystalline $HAlCl_2$•2THF was stored in a glovebox or in standard Schlenk-ware and its purity determined by evolved H_2 volume on aqueous quench. Dichloroalane adducts were typically weighed out in the glovebox but could equally be promptly weighed in air on gram scales with less than 5% degradation (within 30 mins). Such 'in air' preparations demonstrated identical coupling efficiencies to those weighed under rigorously anaerobic conditions (observed maximum handling times in air: $HAlCl_2$•2THF 30 min; $HAlCl_2$•dioxane 45 min). Alkynes were distilled and aryl halides were dried with and stored over 4 Å molecular sieves. All other commercially available compounds used without further purification. Flash column chromatography was carried out using Davisil silica gel 60 (0.035-0.070 mm particle size), eluting with pentane. Thin layer chromatography was carried out using Merck F_{254} aluminium-backed silica plates.

Proton (400 MHz) and carbon-13 (100.6 MHz) NMR spectra were recorded on a Bruker DPX400, AV400 or AV(III)400 instrument. Chemical shifts are quoted as parts per million and referenced to $CHCl_3$ (7.27 ppm for ^1H and 77.0 ppm for ^{13}C). Carbon-13 NMR spectra were recorded with broadband proton decoupling. Infra-red spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Mass spectrometry was carried out using either a Bruker MicroTOF or a Micromass AutoSpec instrument.

Preparation of $HAlCl_2$•2THF[S1]

A solution of $AlCl_3$ (22.0 g, 165 mmol, 3.0 equiv.) in Et_2O (80 mL) was added to a suspension (solution) of $LiAlH_4$ (2.08 g, 54.8 mmol, 1.0 equiv.) in Et_2O (80 mL) at ambient temperature. The mixture was stirred for 15 minutes before the solids are removed by cannula filtration. THF (36.0 mL, 440 mmol, 8.0 equiv.) was added dropwise *via* a syringe to the colourless filtrate (mild exothermic reaction) to yield a two layer system. The flask is placed into a -20 ^oC freezer overnight which induces complete crystallization. The solid is separated *via* cannula filtration, washed with pentane (3 x 30 mL) and dried under vacuum. Yield: 49.8 g (93 %). The compound has literature properties.

The dioxane adduct was similarly prepared from $AlCl_3$ (5.50 g, 41.3 mmol), $LiAlH_4$ (0.52 g, 13.7 mmol), 1,4-dioxane (4.30 mL, 50.1 mmol) to yield the title compound as a colourless solid (8.20 g, 88%).

General Procedure 1: $Cp^*_2ZrCl_2$-catalysed hydroalumination-cross coupling

A flame-dried argon filled Radley's carousel reaction tube was charged with $HAlCl_2$•2THF (1.02 g, 4.20 mmol, 2.1 equiv.) and $Cp^*_2ZrCl_2$ (60 mg, 0.14 mmol, 5.0 mol% based on alkyne). Under an inert atmosphere, THF (4 mL) and alkyne (2.80 mmol, 1.4 equiv.) were added, the reaction mixture stirred at reflux for 2-16 h (typically 4 h) and then removed from the heat. In a flame-dried, stirrer-equipped Schlenk tube under an inert atmosphere, X-Phos (38 mg, 0.08 mmol, 4.0 mol% based on ArX), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol, 1.5 mol% based on ArX) and DABCO (0.160 g, 1.40 mmol, 0.7 equiv.) were dissolved in THF (4 mL) and transferred to the hydroalumination mixture *via* cannula leading to the formation of a fine suspension. Aryl halide (2.00 mmol, 1.0 equiv.) was added and the reaction mixture was heated at reflux for 2 h. Aqueous HCl (2 M, 6 mL) was added, the layers were separated

and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic extracts were evaporated under reduced pressure to give the crude product, which was purified by flash column chromatography (solid load). Alternatively, for acid sensitive substrates, the reaction was quenched with aqueous Rochelle's salt (saturated, 6 mL) and the extraction procedure same as above.

General Procedure 2: Cp_2TiCl_2-catalysed hydroalumination-cross coupling

A flame-dried argon filled Radley's carousel reaction tube was charged with $HAlCl_2$•2THF(1.02 g, 4.20 mmol, 2.1 equiv.) weighed as described above. Under an inert atmosphere, Cp_2TiCl_2 (36 mg, 0.14 mmol, 5.0 mol% based on alkyne), THF (4 mL) and alkyne (2.80 mmol, 1.4 equiv.) were added, the reaction mixture stirred at reflux for 2 h and then removed from the heat. In a flame-dried, stirrer-equipped Schlenk tube under an inert atmosphere, X-Phos (38 mg, 0.08 mmol, 4.0 mol% based on ArX), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol, 1.5 mol% based on ArX) and DABCO (0.160 g, 1.40 mmol, 0.7 equiv.) were dissolved in THF (4 mL) and transferred to the hydroalumination mixture *via* cannula laeding to a fine suspension. Aryl halide (2.00 mmol, 1.0 equiv.) was added and the reaction mixture was heated at reflux for 2 h. Aqueous HCl (2 M, 6 mL) was added, the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic extracts were evaporated under reduced pressure to give the crude product, which was purified by flash column chromatography (solid load).

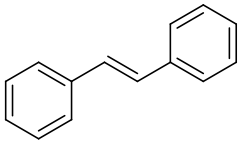
General Procedure 3: $^2H\{^1H\}$ and ^1H NMR monitoring of the hydroalumination procedure

Hydroaluminations were carried out as described above. The crude mixture of alanes (from alkyne (2.80 mmol) and $HAlCl_2$•2THF (4.20 mmol) in THF (4 mL) was quenched with D_2O (0.50 mL) at room temperature. The crude reaction mixture was apportioned into two equal parts. To the first part $CDCl_3$ (50 μL, internal standard) was added and the $^2H\{^1H\}$ spectrum acquired.

The $^2H\{^1H\}$ spectra were run unlocked using the spectrometer lock channel. Samples were shimmed by means of gradient shimming using the ^1H NMR signal of the THF solvent. The 'zgig2h' pulse sequence of a Bruker AVANCE I type instrument was used and the ^2H spectra acquired using power gated ^1H decoupling. Use of coupled ^2H spectra was ineffective due to signal overlaps in the alkene region. The relative populations of (*E*)-**1**:(*Z*)-**1**:**2**:**3**:**4**:**5** (R = C_8H_{17}, Y = Cl) were determined by the integrals of the singlets at δ_D 4.97 (=C(1)D), 5.03 (=C(1)D'), 5.85 (=C(2)D), 1.95 (≡CD), 0.93 (-CD_2H), 1.31 (-CHD-) respectively of the D-quenched products. No evidence for the formation of *n*-$C_8H_{17}CD_2CH_3$ (potentially from double C(2)-Al addition) was detected and its concentration was assumed minimal. The second part of the reaction mixture was evaporated to a crude oil. The alkyne conversion was determined by comparison of the ^1H NMR spectrum of the residual 1-decyne ≡CH integral at δ_H 1.95 to integral of the non-terminal alkene signal at δ_H 5.85 after correction for deuterium incorporation. Total deuterium incorporation in the 1-decene was determined by GC-MS, while the fraction at C(1)/C(2) was available from the $^2H\{1H\}$ studies above.

Compound Data

***(E)-stilbene* (*1*) *(Table 2, Run 2)*[S2]**

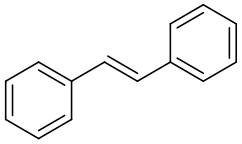


Prepared by General Procedure 2, $HAlCl_2$•2THF (1.04 g, 4.28 mmol), Cp_2TiCl_2 (35 mg, 0.14 mmol), phenylacetylene (310 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (32 mg, 0.03 mmol), DABCO (156 mg, 1.39 mmol) and bromobenzene (210 μL, 2.00 mmol) afforded **1** (339 mg, 94 %) as a white crystalline solid. $\boldsymbol{R_F}$ (pentane) 0.30.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.14 (s, 2H, CH=CH), 7.32-7.26 (m, 2H, Ar), 7.41-7.35 (m, 4H, Ar), 7.56-7.50 (m, 4H, Ar).

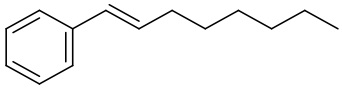
^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 126.5 (Ar), 127.6 (Ar), 128.7 (2C, CH=CH), 137.3 (Ar). Data were consistent with literature values.

***(E)-stilbene (1) (Table 2, Run 4)*[S3]**



Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (59 mg, 0.14 mmol), phenylacetylene (310 μL, 2.80 mmol), X-Phos (39 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (157 mg, 1.40 mmol) and bromobenzene (210 μL, 2.00 mmol) afforded **1** (338 mg, 94 %) as a white crystalline solid. Data as above.

***(E)-1-phenyl-1-octene (2) (Table 3, Run 1)*[S3]**

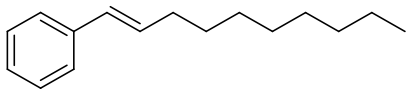


Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (64 mg, 0.15 mmol), 1-octyne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (164 mg, 1.46 mmol) and bromobenzene (210 μL, 2.00 mmol) afforded **2** (367 mg, 98 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.70.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.97-0.87 (m, 3H, CH_3), 1.43-1.22 (m, 6H, 3 x CH_2), 1.55-1.44 (m, 2H, CH_2), 2.24 (q, 2H, J = 7.0 Hz, CHCH_2), 6.26 (dt, 1H, J = 16.0, 7.0 Hz, CH_2C*H*), 6.41 (d, 1H, J = 16.0 Hz, PhC*H*), 7.22 (t, 1H, J = 8.0 Hz, Ar), 7.32 (t, 2H, J = 8.0 Hz, Ar), 7.38 (d, 2H, J = 8.0 Hz, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (CH_3), 22.6 (CH_2), 28.9 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 33.1 (CH_2), 125.9 (Ar), 126.7 (Ar), 128.4 (Ar), 129.7 (Ar*C*H), 131.2 (ArCH=*C*H), 138.0 (Ar). Data were consistent with literature values.

(E)-(Dec-1-en-1-yl)benzene (3) (Table 3, Run 2)[S4]



Prepared by General Procedure 1, $HAlCl_2$•2THF(1.02 g, 4.20 mmol), $ZrCp^*_2Cl_2$ (68 mg, 0.14 mmol), Dec-1-yne (504 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (166 mg, 1.48 mmol) and 1-bromobenzene (210 μL, 2.00 mmol) afforded **3** (416 mg, 96 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.95.

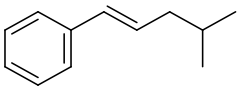
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.91 (t, 3H, *J* = 6.8 Hz, CH_2*Me*), 1.25-1.42 (m, 10H, CH_2), 1.44-1.53 (m, 2H, CH_2), 2.23 (qd, 2H, *J* = 6.8, 1.6 Hz, C=CH_2), 6.25 (dt, 1H, *J* = 15.8, 7.2 Hz, C=C*H*CH_2), 6.40 (d, 1H, *J* = 15.8 Hz, PhC*H*=CHCH_2), 7.18-7.24 (m, 1H, Ar), 7.27-7.34 (m, 2H, Ar), 7.36-7.39 (m, 2H, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (Me), 22.7 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 31.9 (CH_2), 33.1 (CH_2), 125.9 (2 x Ar), 126.7 (C=*C*H), 128.5 (2 x Ar), 129.7 (Ar), 131.3 (*C*H=CH), 138.0 (*ipso*-C_0, Ar).

IR ($CHCl_3$): $\tilde{\nu}$ 3082, 3062, 3005, 2958, 2928, 2856, 1947, 1876, 1804, 1651, 1598, 1577, 1494, 1466, 1378, 1308, 1072, 1028, 966, 912, 644, 606 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{16}H_{24}$ 216.1878, found 216.1879.

(E)-4-methyl-1-phenylpent-1-ene (4) (Table 3, Run 3)[S5]

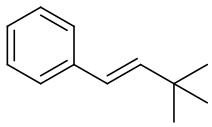


Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (61 mg, 0.14 mmol), 4-methyl-1-pentyne (330 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (158 mg, 1.41 mmol) and bromobenzene (210 μL, 2.00 mmol) afforded **4** (281 mg, 88 %) as a pale yellow oil; $\boldsymbol{R_F}$ (pentane) 0.70.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.95 (dd, 6H, *J* = 6.5, 1.5 Hz, 2 x CH_3), 1.74 (sept, 1H, *J* = 6.5 Hz, $(CH_3)_2$C*H*), 2.10 (t, 2H, *J* = 7.0 Hz, ^{i}PrCH_2), 6.27-6.15 (m, 1H, CH), 6.37 (d, 1H, *J* = 16.0 Hz, CH),7.42-7.13 (m, 5H, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 22.4 (2 x CH_3), 28.6 (C*H*$(CH_3)_2$), 42.4 (CH_2), 125.9 (Ar), 126.8 (Ar), 128.4 (Ar), 129.6 (Ar*C*H), 130.8 (ArCH=*C*H), 137.9 (Ar).
Data were consistent with literature values.

(E)-3,3-dimethyl-1-phenylbut-1-ene (5) (Table 3, Run 4)[S6]



Prepared by General Procedure 2, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), Cp_2TiCl_2 (35 mg, 0.14 mmol), 3,3-dimethyl-1-butyne (350 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (32 mg, 0.03 mmol), DABCO (158 mg, 1.40 mmol) and bromobenzene (210 μL, 2.00 mmol) afforded **5** (298 mg, 93 %) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.15 (s, 9H, 3 x CH_3), 6.28 (d, 1H, *J* = 16.0 Hz, CH), 6.34 (d, 1H, *J* = 16.0 Hz, CH), 7.21 (tt, 1H, *J* = 7.5, 1.5 Hz, Ar), 7.32 (t, 2H, *J* = 7.5 Hz, Ar), 7.39 (dd, 2H, *J* = 8.5, 1.5 Hz, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 29.6 (3 x CH_3), 33.3 ($C(CH_3)_3$), 124.6 (Ar), 126.0 (Ar), 126.7 (Ar*C*H), 128.5 (Ar), 138.1 (Ar), 141.8 (ArCH=*C*H). Data were consistent with literature values.

(E)-stilbene* (*1*) *(Table 3, Run 5)[S3]

Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (64 mg, 0.15 mmol), phenylacetylene (310 μL, 2.80 mmol), X-Phos (39 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (162 mg, 1.44 mmol) and iodobenzene (220 μL, 2.00 mmol) afforded **1** (355 mg, 98 %) as a white crystalline solid. Data were consistent with literature values.

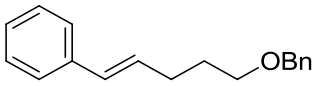
(E)-stilbene* (*1*) *(Table 3, Run 6) [S3]

Prepared by General Procedure 1, $HAlCl_2$•2THF (1.03 g, 4.24 mmol), $Cp^*_2ZrCl_2$ (61 mg, 0.14 mmol), phenylacetylene (310 μL, 2.80 mmol), X-Phos (39 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (164 mg, 1.47 mmol) and chlorobenzene (200 μL, 2.00 mmol) afforded **1** (146 mg, 40 %) as a white crystalline solid. Data were consistent with literature values.

(E)-stilbene* (*1*) *(Table 3, Run 7) [S3]

Prepared by General Procedure 1, $HAlCl_2$•2THF(1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (59 mg, 0.14 mmol), phenylacetylene (310 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (30 mg, 0.03 mmol), DABCO (162 mg, 1.44 mmol) and phenyl triflate (320 μL, 2.00 mmol) afforded **1** (310 mg, 86 %) as a white crystalline solid. Data were consistent with literature values.

(E)-(5-(benzyloxy)pent-1-en-1-yl)benzene (6) (Table 3, Run 8)[S7]



Prepared by General Procedure 1, $HAlCl_2$•2THF(1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (61 mg, 0.14 mmol), ((pent-4-yn-1-yloxy)methyl)benzene (487 mg, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (157 mg, 1.40 mmol) and bromobenzene (210 μL, 2 mmol) to afforded **6** (356.2 mg, 75%) as a colourless oil; $\boldsymbol{R_F}$ (pentane/Et_2O 1:1) 0.36.

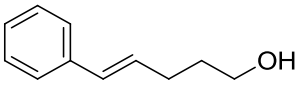
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.91 (m, 2H, $BnOCH_2CH_2$), 2.40 (ddt, 2H, *J* = 7.8, 7.1, 1.0 Hz, CH_2CH=CHAr), 3.60 (t, 2H, *J* = 6.4 Hz, $BnOCH_2$), 4.60 (s, 2H, $PhCH_2O$) 6.28 (dt, 1H, *J* = 15.8, 7.1 Hz, CH_2CH=CHAr), 6.45 (dt, 1H, *J* = 15.8, 1.0 Hz, CH=C*H*Ar), 7.40 (m, 10H, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 29.0 ($BnOCH_2CH_2$), 29.5 (ArCHCHCH_2), 69.7 (BnOCH_2), 73.0 (OCH_2Ph), 125.7 (C^2(Ph) and C^6(Ph)), 126.1 (C^4(Ph)), 127.9 (C^2(Bn) and C^4(Bn) and C^6(Bn)), 128.2 (C^3(Bn) and C^5(Bn)), 128.3 (C^3(Ph) and C^5(Ph)), 128.9 (ArCH*C*H), 130.3 (Ar*C*HCH), 137.8 (C1(Ph), 138.6 (C^1(Bn).

IR ($CHCl_3$): $\tilde{\nu}$ = 3065, 3009, 2940, 2862, 1495, 1453, 1100, 965, 909 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{18}H_{20}O$ 252.1514 found 252.1524

(E)-5-phenylpent-4-en-1-ol (7) (Table 3, Run 9)[S8]



Prepared by General Procedure 1, $HAlCl_2$•2THF(1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (31 mg, 0.07 mmol), 5-pentynol (130 μL, 1.4 mmol), X-Phos (19 mg, 0.04 mmol), $Pd_2(dba)_3.CHCl_3$ (15.5 mg, 0.015 mmol), DABCO (78.5 mg, 0.70 mmol), $InCl_3$ (31.0 mg, 0.14 mmol) and bromobenzene (110 μL, 1.00 mmol) afforded **7** (99.1 mg, 61 %) as a yellow oil; $\boldsymbol{R_F}$ (pentane/Et_2O 1:1) 0.44.

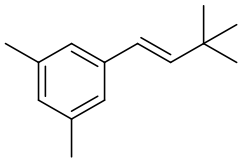
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.81 (m, 2H, $HOCH_2CH_2$), 2.35 (ddt, 2H, *J* = 7.8, 7.2, 1.5 Hz, CH_2CH=CHAr), 3.75 (t, 2H, *J* = 6.5 Hz, $HOCH_2$), 6.27 (dt, 1H, *J* = 15.8, 7.2 Hz, CH_2CH=CHAr), 6.45 (dt, 1H, *J* = 15.8, 1.5 Hz, CH=C*H*Ar), 7.23 (m, 1H, C^4*H*Ar), 7.35 (m, 4H, C^2*H*(Ar), C^3*H*(Ar), C^5*H*(Ar) and C^6*H*(Ar)).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 29.3 (ArCHCHCH_2), 32.3 ($HOCH_2CH_2$), 62.4 ($HOCH_2$), 125.9 (C^2(Ar) and C^6(Ar)), 126.9 (C^4(Ar)), 128.5 (C^3(Ph) and C^5(Ph)), 130.3 (Ar*C*HCH), 130.0 (ArCH*C*H), 137.6 (C^1(Ar)).

IR ($CHCl_3$): $\tilde{\nu}$ = 3624, 2938, 2255, 1599, 1056, 966 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{11}H_{14}O$ 162.1045, found 162.1045

(E)-1-(3,3-dimethylbut-1-en-1-yl)-3,5-dimethylbenzene (8) (Table 3, Run 10)



Prepared by General Procedure 2, $HAlCl_2$•2THF(1.02 g, 4.20 mmol), Cp_2TiCl_2 (34.9 mg, 0.14 mmol), *tert*-Butylacetylene (340 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (166 mg, 1.48 mmol) and 5-bromo-*m*-xylene (273 μL, 2.00 mmol) afforded, **8** (327 mg, 87 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.92.

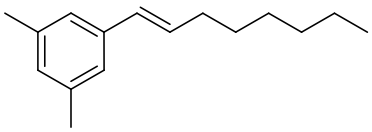
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.21 (s, 9H, 3 x C*Me*$_3$), 2.39 (s, 6H, 2 x Ar*Me*), 6.34 (s, 2H, ArC*H*=C*H*t*Bu*), 6.93 (s, 1H, *p*-Ar), 7.09 (s, 2H, 2 x *o*-Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 21.3 (2 x Ar-*C*H_3), 29.7 (3 x C(*C*H_3)$_3$), 33.4 (*C*Me$_3$), 124.0 (2 x Ar), 124.7 (ArC=*C*H), 128.5 (Ar-*C*H), 137.9 (*ipso-C*, Ar), 138.0 (*ipso-C*, Ar), 141.5 (Ar*C*=CH).

IR ($CHCl_3$): $\tilde{\nu}$ 3009, 2964, 2905, 2866, 2775, 1895, 1827, 1794, 1774, 1753, 1709, 1648, 1600, 1537, 1475, 1463, 1391, 1378, 1363, 1319, 1272, 1250, 1187, 1163, 1039, 971, 921, 897, 857, 827, 645 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{14}H_{20}$ 188.1565, found 188.1568.

(E)-1,3-dimethyl-5-(oct-1-en-1-yl)benzene (9) (Table 3, Run 11)



Prepared by General Procedure 1, $HAlCl_2$•2THF(1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (61 mg, 0.14 mmol), 1-octyne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (157 mg, 1.40 mmol) and 5-bromo-*m*-xylene (368 mg, 2.00 mmol) afforded **9** (412 mg, 95 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.44.

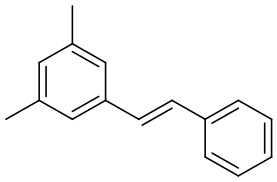
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.93 (t, 3H, *J* = 6.8 Hz, CH_2CH_3), 1.34 (m, 6H, $(CH_2)_3CH_3$), 1.50 (m, 2H, $CH_2(CH_2)_3CH_3$), 2.21 (ddt, 2H, *J* = 7.6, 6.8, 1.2 Hz, CH_2CH=CH), 2.33 (s, 6H, 2x ArCH_3), 6.25 (dt, 1H, *J* = 16.0, 6.8 Hz, C*H*=CH-Ar), 6.37 (dt, 1H, *J* = 16.0, 1.2 Hz, CH=C*H*-Ar), 6.57 (s, 1H, *p*-C$H_{(Ar)}$), 7.00 (s, 2H, 2x *o*-C$H_{(Ar)}$).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (CH_2CH_3), 21.3 (ArCH_3), 22.6 (CH_2Me), 28.9 (CH_2Bu), 29.4 (CH_2Pr), 31.8 (CH_2Et), 33.0 (CH=CHCH_2), 123.8 (C^2(Ar) and C^6(Ar)), 128.5 (ArCH=*C*H), 129.8 (C^4(Ar)), 130.9 (Ar*C*H=CH), 137.8 (C^1(Ar)), 137.9 (C^3CH_3 and C^5CH_3).

IR ($CHCl_3$): $\tilde{\nu}$ = 3010, 2958, 2928, 2856, 1600, 1466, 1378, 966 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{16}H_{24}$ 216.1878, found 216.1880.

(E)-1,3-dimethyl-5-styrylbenzene (10) (Table 3, Run 12)[S9]

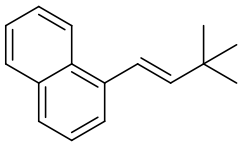


Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (62 mg, 0.14 mmol), phenylacetylene (310 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (30 mg, 0.03 mmol), DABCO (166 mg, 1.48 mmol) and 5-bromo-*m*-xylene (270 μL, 2.00 mmol) afforded **10** (411 mg, 96 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.20.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 2.41 (s, 6H, 2 x CH_3), 6.98 (s, 1H, PhCH=C*H*), 7.15 (s, 1H, Ar) overlapped by 7.14 (s, 1H, PhC*H*), 7.21 (s, 2H, Ar), 7.35-7.28 (m, 1H, Ar), 7.42 (t, 2H, *J* = 7.5 Hz, Ar),7.57 (d, 2H, *J* = 7.0 Hz, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 21.3 (2 x CH_3), 124.4 (Ar), 126.4 (Ar), 127.4 (Ph*C*H), 128.3 (Ar), 128.6 (Ar), 128.9 (Ar), 129.4 (PhCH=*C*H), 137.2 (Ar), 137.5 (Ar), 138.1 (CH_3*C*).

(E)-1-(3,3-dimethylbut-1-en-1-yl)naphthalene (11) (Table 3, Run 13)[S10]



Prepared by General Procedure 2, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), Cp_2TiCl_2 (34.9 mg, 0.14 mmol), *tert*-butylacetylene (340 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (166 mg, 1.48 mmol) and 1-bromo naphthalene (273 μL, 2.00 mmol) afforded **11** (299 mg, 71 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.93.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.49 (s, 9H, 3 x C*Me*$_3$), 6.54 (d, 1H, *J* = 16.0 Hz, ArC=C*H*CMe$_3$), 7.34 (d, 1H, *J* = 16.0 Hz, ArC*H*=CHCMe$_3$), 7.65-7.77 (m, 4H, Ar), 7.81 (d, 1H, *J* = 6.8 Hz, Ar), 7.97 (d, *J* = 8.4 Hz, 1H, Ar), 8.05-8.08 (m, 2H, Ar), 8.41 (dd, 1H, *J* = 8.4, 1.2 Hz, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 30.0 (3 x C(*C*H$_3$)$_3$), 34.1 (*C*Me$_3$), 122.1 (C=*C*Ar), 123.8 (Ar-*C*H), 124.2 (Ar-*C*H), 125.9 (Ar-*C*H), 125.9 (Ar-*C*H), 126.0 (Ar-*C*H), 126.1 (Ar-*C*H), 127.5 (Ar-*C*H), 128.1 (Ar-*C*H), 128.7 (Ar-*C*H), 131.7 (*ipso-C*, Ar), 133.9 (*ipso-C*, Ar), 136.2 (*ipso-C*, Ar), 145.5 (H*C*=CAr).

IR ($CHCl_3$): $\tilde{\nu}$ = 3363, 3306, 3175, 3062, 3010, 2963, 2903, 2867, 2030, 1990, 1948, 1930, 1869, 1837, 1810, 1779, 1739, 1698, 1642, 1591, 1578, 1509, 1475, 1462, 1394, 1363, 1345, 1299, 1269, 1255, 1239, 1188, 1169, 1142, 1128, 1083, 1035, 1025, 1013, 973, 945, 925, 906, 877, 863, 839, 824, 640, 618 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{16}H_{18}$ 210.1409, found 210.1406.

The 2-regioisomer was formed from the analogous 2-bromonaphthalene derivative to give a comparable yield.

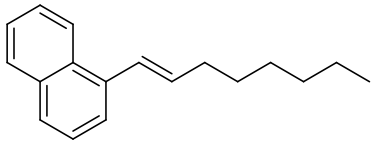
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.28 (s, 9H, 3 x C*Me*$_3$), 6.50 (d, 1H, *J* = 16.0 Hz, ArC=C*H*CMe$_3$), 6.57 (d, 1H, *J* = 16.0 Hz, ArC*H*=CHCMe$_3$), 7.49-7.56 (m, 2H, Ar), 7.68-7.71 (m, 1H, Ar), 7.80 (s, 1H, Ar), 7.83-7.89 (m, 3H, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 29.8 (3 x C(*C*H$_3$)$_3$), 33.6 (*C*Me$_3$), 123.8 (C=*C*Ar), 124.9 (Ar-*C*H), 125.5 (Ar-*C*H), 125.5 (Ar-*C*H), 126.2 (Ar-*C*H), 127.8 (Ar-*C*H), 127.9 (Ar-*C*H), 128.1 (Ar-*C*H), 132.8 (*ipso-C*, Ar), 133.9 (*ipso-C*, Ar), 135.6 (*ipso-C*, Ar), 142.4 (H*C*=CAr).

HRMS (EI+) *m/z*: Calcd. for $C_{16}H_{18}$ 210.1409, found 210.1406.

For $C_{16}H_{18}$ (210.31): Calcd. C 91.3, H 8.63%; found C 90.9, H 8.73%.

(E)-1-(oct-1-en-1-yl)naphthalene (12) (Table 3, Run 14)[S11]



Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $ZrCp^*_2Cl_2$ (68 mg, 0.14 mmol), Oct-1-yne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (166 mg, 1.48 mmol) and 1-bromonaphthalene (280 μL, 2.00 mmol) afforded **12** (325 mg, 57 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.84.

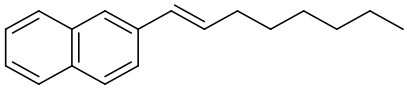
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.19 (t, 3H, *J* = 6.4 Hz, CH_2*Me*), 1.54-1.68 (m, 6H, CH_2), 1.74-1.81 (m, 2H, CH_2), 2.55 (qd, 2H, *J* = 7.6, 1.2 Hz, CH_2), 6.46 (dt, 1H, *J* = 15.6, 6.8 Hz, CH_2C*H*=CAr), 7.36 (d, 1H, *J* = 15.2 Hz, CH_2C=C*H*Ar), 7.62-7.73 (m, 3H, Ar), 7.79 (d, 1H, *J* = 7.2 Hz, Ar), 7.95 (d, 1H, *J* = 8.4 Hz, Ar), 8.04 (dd, 1H, *J* = 7.6, 2.4 Hz, Ar), 8.38 (dd, 1H, *J* = 8.0, 1.2 Hz, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.4 (CH_2*C*H$_3$), 23.0 (CH_2CH_2*C*H$_2$CH$_3$), 29.2 (CH_2*C*H$_2$CH$_2$CH$_3$), 29.7 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 32.1 (*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 33.7 (*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 123.8 (C=*C*Ar), 124.2 (Ar-*C*H), 125.8 (Ar-*C*H), 125.9 (Ar-*C*H), 125.9 (Ar-*C*H), 127.2 (Ar-*C*H), 127.4 (Ar-*C*H), 128.7 (Ar-*C*H), 131.5 (*ipso-C*, Ar), 133.9 (*ipso-C*, Ar), 134.7 (H*C*=CAr), 136 (*ipso-C*, Ar).

IR ($CHCl_3$ solution): $\tilde{\nu}$ = 3062, 3009, 2959, 2925, 2872, 2856, 2731, 2029, 1928, 1871, 1836, 1810, 1722, 1690, 1649, 1624, 1591, 1577, 1509, 1466, 1438, 1395, 1379, 1345, 1331, 1311, 1258, 1170, 1142, 1120, 1086, 1056, 1032, 1015, 967, 909, 887, 862, 838, 649, 617 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{18}H_{22}$ 238.1722, found 238.1723.

(E)-2-(oct-1-en-1-yl)naphthalene (13) (Table 3, Run 15)[S3]



Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $ZrCp^*_2Cl_2$ (68.0 mg, 0.14 mmol), Oct-1-yne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (166 mg, 1.48 mmol) and 2-bromonaphthalene (420 mg, 2.00 mmol) afforded **13** (435 mg, 91 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.91.

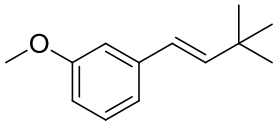
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.19 (t, 3H, *J* = 6.4 Hz, CH_2*Me*), 1.54-1.64 (m, 6H, CH_2), 1.72-1.76 (m, 2H, CH_2), 2.48 (qd, 2H, *J* = 6.8, 1.2 Hz, CH_2), 6.57 (dt, 1H, *J* = 15.8, 6.8 Hz, CH_2C*H*=CAr), 6.76 (d, 1H, *J* = 15.8 Hz, CH_2C=C*H*Ar), 7.60-7.68 (m, 2H, Ar), 7.80 (dd, 1H, *J* = 8.4, 1.6 Hz, Ar), 7.88 (br s, 1H, Ar), 7.95-8.01 (m, 3H, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.4 (CH_2*C*H_3), 23.0 (CH_2CH_2*C*H_2CH_3), 29.3 (CH_2*C*$H_2CH_2CH_3$), 29.7 (*C*$H_2CH_2CH_2CH_3$), 32.1 (*C*$H_2CH_2CH_2CH_2CH_3$), 33.5 (*C*$H_2CH_2CH_2CH_2CH_2CH_3$), 123.8 (C=*C*Ar), 125.6 (Ar-*C*H), 126.3 (Ar-*C*H), 127.9 (Ar-*C*H), 128.1 (Ar-*C*H), 128.3 (Ar-*C*H), 130.1 (Ar-*C*H), 131.8 (H*C*=CAr), 133.0 (*ipso-C*, Ar), 134.0 (*ipso-C*, Ar), 135.7 (*ipso-C*, Ar).

IR ($CHCl_3$): $\tilde{\nu}$ 3170, 3060, 3009, 2961, 2855, 1950, 1920, 1834, 1804, 1779, 1693, 1652, 1627, 1598, 1574, 1508, 1466, 1437, 1379, 1367, 1312, 1269, 1240, 1176, 1155, 1144, 1126, 1061, 1018, 964, 909, 894, 859, 821, 642, 624 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{18}H_{22}$ 238.1722, found 238.1723.

(E)-1-(3,3-dimethylbut-1-en-1-yl)-3-methoxybenzene (14) (Table 3, Run 16)



Prepared by General Procedure 2, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), Cp_2TiCl_2 (34.9 mg, 0.14 mmol), *tert*-Butylacetylene (340 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (166 mg, 1.48 mmol) and 3-bromoanisole (251 μL, 2.00 mmol) afforded **14** (272 mg, 71 %) as a lime-yellow oil; $\boldsymbol{R_F}$ (pentane:Et_2O, 40:1) 0.41.

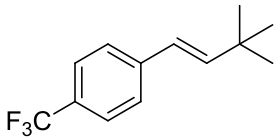
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.21 (s, 9H, 3 x C*Me*$_3$), 3.88 (s, 3H, O*Me*), 6.35 (d, 1H, *J* = 16.0 Hz, C=C*H*Ar); *overlapped by* 6.35 (d, 1H, *J* = 16.0 Hz, C*H*=CAr), 6.83 (ddd, 1H, *J* = 8.4, 2.8, 0.8 Hz, Ar), 6.99 (t, 1H, *J* = 1.6 Hz, Ar), 7.04 (d, 1H, *J* = 7.6 Hz, Ar), 7.28 (t, 1H, *J* = 8.0 Hz, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 29.7 (3 x C(*C*H_3)$_3$), 33.4 (*C*Me_3), 55.2 (O*C*H_3), 111.4 (Ar-*C*H), 112.5 (Ar-*C*H), 118.8 (Ar-*C*H), 124.6 (C=*C*Ar), 129.5 (Ar-*C*H), 139.6 (*ipso-C*, Ar), 142.2 (*C*=CAr), 159.9 (*ipso-C*, Ar).

IR ($CHCl_3$): $\tilde{\nu}$ 3184, 3102, 3009, 2962, 2906, 2867, 2837, 2743, 1800, 1751, 1648, 1598, 1579, 1528, 1489, 1476, 1465, 1431, 1391, 1364, 1324, 1289, 1272, 1247, 1157, 1115, 1082, 1051, 995, 972, 950, 909, 882, 867, 832, 651, 607 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{13}H_{18}O$ 190.1358, found 190.1352.

(E)-1-(3,3-dimethylbut-1-en-1-yl)-4-(trifluoromethyl)benzene (15) (Table 3, Run 17)[S12]



Prepared by General Procedure 2, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), Cp_2TiCl_2 (34.9 mg, 0.14 mmol), *tert*-Butylacetylene (340 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (166 mg, 1.48 mmol) and 4-bromo-1-(trifluoromethyl) benzene (280 μL, 2.00 mmol) afforded **15** (329 mg, 72 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.95.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.24 (s, 9H, 3 x C*Me*$_3$), 6.44 (d, 1H, *J* = 16.0 Hz, C=C*H*Ar); *overlapped by* 6.44 (d, 1H, *J* = 16.0 Hz, C*H*=CAr), 7.52 (d, 2H, *J* = 8.0 Hz, Ar), 7.63 (d, 2H, *J* = 8.0 Hz, Ar).

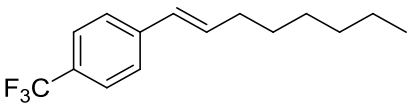
^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 29.4 (3 x C(*C*H$_3$)$_3$), 33.6 (*C*Me$_3$), 123.7 (C=*C*Ar), 124.5 (q, *J* = 271.5 Hz, 1 C, *C*F$_3$), 125.4 (q, *J* = 3.8 Hz, 2 C, H*C*CCF$_3$, Ar-*C*H), 126.2 (2 C, Ar-*C*H), 128.7 (q, *J* = 32.2 Hz, *ipso*-*C*CF$_3$, Ar), 141.7 (*ipso*-*C*, Ar), 144.6 (*C*=CAr).

^{19}F NMR (376.5 MHz, $CDCl_3$): δ_F -62.3.

IR ($CHCl_3$): $\tilde{\nu}$ 3190, 3138, 3100, 2967, 2907, 2868, 2777, 2744, 1917, 1837, 1818, 1796, 1745, 1698, 1679, 1648, 1616, 1578, 1515, 1476, 1464, 1413, 1393, 1364, 1316, 1284, 1264, 1132, 1068, 1016, 973, 953, 923, 909, 866, 821, 644 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{13}H_{15}F_3$ 228.1126, found 228.1133.

(E)-1-(oct-1-en-1-yl)-4-(trifluoromethyl)benzene (16) (Table 3, Run 18)[S13]



Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (61 mg, 0.14 mmol), 1-octyne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (157 mg, 1.40 mmol) and 4-(trifluoromethyl)bromobenzene (280 μL, 2.00 mmol) afforded **16** (484.1 mg, 94%) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.52.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.93 (t, 3H, *J* = 6.8 Hz, CH_2CH_3), 1.34 (m, 6H, $(CH_2)_3$Me), 1.51 (m, 2H, $CH_2(CH_2)_3$Me), 2.27 (ddt, 2H, *J* = 7.1, 6.8, 1.2 Hz, CH_2CH=CHAr), 6.35 (dt, 1H, *J* = 16.0, 7.1 Hz, CH_2CH=CHAr), 6.42, (m, 1H, CHC*H*Ar), 7.44 (d, 2H, *J* = 8.4 Hz, Ar), 7.55 (d, 2H, *J* = 8.4 Hz, Ar).

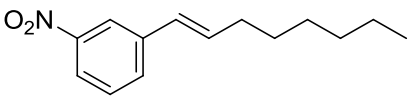
^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (CH_2CH_3), 22.6 (CH_2Me), 28.9 (CH_2Bu), 29.3 (CH_2Pr), 31.7 (CH_2Et), 33.0 (ArCH=CHCH_2), 118.6 (C^3(Ar) and C^5(Ar)), 123.5 (q, J = 272.0 Hz, CF_3), 129.4 (C^2(Ar) and C^6(Ar)), 129.5 (ArCHCH), 130.5 (C^4(Ar)), 131.6 (ArCHCH), 139.4 (C^1(Ar)).

^{19}F NMR (376.5 MHz, $CDCl_3$): δ_F -69.3.

IR ($CHCl_3$): $\tilde{\nu}$ = 2958, 2929, 2857, 1615, 1329, 1166, 1124, 968 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{15}H_{19}F_3$ 256.1439 found 256.1441.

(E)-1-nitro-3-(oct-1-en-1-yl)benzene (17) (Table 3, Run 19) [S14]



Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (61 mg, 0.14 mmol), 1-octyne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3$.$CHCl_3$ (31 mg, 0.03 mmol), DABCO (157 mg, 1.40 mmol) and 3-nitrobromobenzene (404 mg, 2.00 mmol) afforded **17** (215 mg, 55 %) as a light brown oil; $\boldsymbol{R_F}$ (pentane/Et_2O 49:1) 0.36.

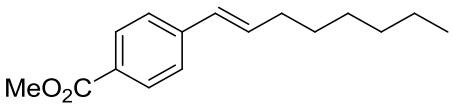
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.92 (t, 3H, J = 7.2 Hz, CH_2CH_3), 1.34 (m, 6H, $(CH_2)_3$Me), 1.51 (m, 2H, $CH_2(CH_2)_3$Me), 2.27 (ddt, 2H, J = 7.2, 6.0, 2.0 Hz, CH_2CH=CHAr), 6.38 (dt, 1H, J = 16.0, 6.0 Hz, CH_2CH=CHAr), 6.44, (d, 1H, J = 16.0 Hz, CH=CHAr), 7.46 (t, 1H, J = 8.0 Hz, C^5H(Ar)), 7.63 (dt, 1H, J = 7.2, 1.2 Hz, C^4H(Ar)), 8.04 (qd, 1H, J = 2.0, 1.2 Hz, C^6H(Ar)), 8.20 (t, 1H, J = 2.0 Hz, C^2H(Ar)).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (CH_3), 22.6 (CH_2Me), 28.9 (CH_2Et), 29.0 (CH_2Pr), 31.7 (CH_2Bu), 33.0 (ArCHCHCH_2), 120.5 (C^2(Ar)), 121.4 (C^6(Ar)), 127.6 (C^5(Ar)), 129.3 (ArCHCH), 131.8 (C^4(Ar)), 134.7 (ArCHCH), 139.7 (C^3(Ar), 147.2 (C^1(Ar)).

IR ($CHCl_3$): $\tilde{\nu}$ = 2958, 2929, 2857, 1529, 1352, 964 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{14}H_{19}NO_2$ 233.1416, found 233.1407.

(E)-methyl 4-(oct-1-en-1-yl)benzoate (18) (Table 3, Run 20) [S14]



Prepared by General Procedure 1, $HAlCl_2$•2THF(1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (61 mg, 0.14 mmol), 1-octyne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3$.$CHCl_3$ (31 mg, 0.03 mmol), DABCO (157 mg, 1.40 mmol) and methyl-4-bromobenzoate (430 mg, 2.00 mmol) afforded **18** (417.8 mg, 85 %) as a yellow oil; $\boldsymbol{R_F}$ (pentane/Et_2O 10:1) 0.44.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.92 (t, 3H, J = 7.0 Hz, CH_2CH_3), 1.33 (m, 6H, $(CH_2)_3$Me), 1.48 (m, 2H, $CH_2(CH_2)_3$Me), 2.26 (ddt, 2H, J = 7.6, 5.5, 2.0 Hz, CH_2CH=CHAr), 3.92 (s, 3H, $ArCO_2CH_3$) 6.37 (dt, 1H, J = 15.7, 5.5 Hz, CH_2CH=CHAr), 6.44, (d, 1H, J = 15.7 Hz,

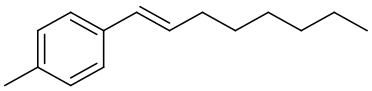
CH=C*H*Ar), 7.41 (d, 2H, *J* = 8.4 Hz, C^2*H*(Ar) and C^6*H*(Ar)), 7.98 (d, 2H, *J* = 8.4 Hz, C^3*H*(Ar) and C^5*H*(Ar)).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (*C*H$_3$), 22.6 (*C*H$_2$Me), 28.9 (*C*H$_2$Et), 29.1 (*C*H$_2$Pr), 31.7 (*C*H$_2$Bu), 33.2 (ArCHCHCH$_2$), 51.9 (CO_2*C*H$_3$), 125.7 (*C*^{2}(Ar) and *C*^{6}(Ar)), 128.2 (*C*^{4}(Ar)), 128.9 (ArCH*C*H), 129.9 (*C*^{3}(Ar) and *C*^{5}(Ar)), 134.3 (Ar*C*HCH), 142.5 (*C*^{1}(Ar)), 167.0 (C=O).

IR ($CHCl_3$): $\tilde{\nu}$ = 3008, 2955, 2929, 2857, 1715, 1606, 1436, 1328, 1112, 969 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{16}H_{22}O_2$ 246.1020, found 246.1621.

(E)-1-methyl-4-(oct-1-en-1-yl)benzene (19) (Table 3, Run 21) [S15]



Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (61 mg, 0.14 mmol), 1-octyne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3$.$CHCl_3$ (31 mg, 0.03 mmol), DABCO (157 mg, 1.40 mmol) and from 4-bromotoluene (342 mg, 2.00 mmol) afforded **19** (375.3 mg, 87 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.50.

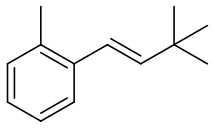
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.93 (t, 3H, *J* = 7.0 Hz, CH$_2$C*H*$_3$), 1.33 (m, 6H, (C*H*$_2$)$_3$Me), 1.42 (m, 2H, C*H*$_2$(CH$_2$)$_3$Me), 2.20 (ddt, 2H, *J* = 7.6, 7.1, 1.1 Hz, C*H*$_2$CH=CHAr), 2.35 (s, 3H, ArCH$_3$) 6.20 (dt, 1H, *J* = 15.0, 7.0 Hz, CH$_2$C*H*=CHAr), 6.35, (d, 1H, *J* = 15.0 Hz, CH=C*H*Ar), 7.13 (d, 2H, *J* = 8.0 Hz, C^2*H*(Ar) and C^6*H*(Ar)), 7.25 (d, 2H, *J* = 8.0, C^3*H*(Ar) and C^5*H*(Ar)).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (*C*H$_3$), 21.1 (Ar*C*H$_3$), 22.6 (*C*H$_2$Me), 28.9 (*C*H$_2$Bu), 29.4 (*C*H$_2$Pr), 31.7 (*C*H$_2$Et), 33.0 (ArCHCHCH$_2$), 125.8 (*C*^{3}(Ar) and *C*^{5}(Ar)), 129.1 (*C*^{2}(Ar) and *C*^{6}(Ar)), 129.5 (ArCH*C*H), 130.2 (Ar*C*HCH), 136.4 (*C*^{4}(Ar), 135.1 (*C*^{1}Ar).

IR ($CHCl_3$): $\tilde{\nu}$ = 3009, 2958, 2928, 2857, 2735, 1702, 1512, 1019 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{15}H_{22}$ 202.1722, found 202.1726.

(E)-1-(3,3-dimethylbut-1-en-1-yl)-2-methylbenzene (20) (Table 3, Run 22) [S16]



Prepared by General Procedure 2, $HAlCl_2$•2THF(1.02 g, 4.20 mmol), Cp_2TiCl_2 (34.9 mg, 0.14 mmol), *tert*-butylacetylene (340 μL, 2.80 mmol), X-Phos (38.0 mg, 0.08 mmol), $Pd_2(dba)_3$.$CHCl_3$ (31 mg, 0.03 mmol), DABCO (166 mg, 1.48 mmol) and 2-bromo-1-methyl-benzene (240 μL, 2.00 mmol) afforded **20** (282 mg, 81 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.94.

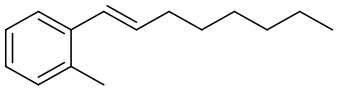
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.37 (s, 3H, ArC*H*$_3$), 2.55 (s, 9H, 3 x C*Me*$_3$), 6.35 (d, 1H, *J* = 16.0 Hz, C=C*H*Ar), 6.74 (d, 1H, *J* = 16.0 Hz, C*H*=CAr), 7.29-7.38 (m, 3H, Ar), 7.63 (d, 1H, *J* = 7.2 Hz, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 20.0 (Ar*C*H$_3$), 29.9 (3 x C(*C*H$_3$)$_3$), 33.8 (*C*Me$_3$), 122.7 (C=*C*Ar), 125.7 (Ar-*C*H), 126.2 (Ar-*C*H), 126.9 (Ar-*C*H), 130.3 (Ar-*C*H), 135.2 (*ipso*-*C*, Ar), 137.4 (*ipso*-*C*, Ar), 143.5 (H*C*=CAr).

IR ($CHCl_3$): $\tilde{\nu}$ 3188, 3139, 3094, 3064, 3046, 3009, 2961, 2905, 2866, 2775, 2741, 2708, 2668, 1948, 1914, 1841, 1808, 1693, 1644, 1619, 1601, 1572, 1483, 1475, 1462, 1391, 1381, 1363, 1314, 1290, 1277, 1264, 1186, 1159, 1103, 1049, 1034, 972, 945, 923, 870, 852, 841, 641, 615 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{13}H_{18}$ 174.1409, found 174.1404.

(E)-1-methyl-2-(oct-1-en-1-yl)benzene (21) (Table 3, Run 23)[S14]



Prepared by General Procedure 1, $HAlCl_2$•2THF(1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (61 mg, 0.14 mmol), 1-octyne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3$.$CHCl_3$ (31 mg, 0.03 mmol), DABCO (157 mg, 1.40 mmol) and 2-bromotoluene (240 μL, 2.00 mmol) afforded **21** (370.9 mg, 92 %) a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.54.

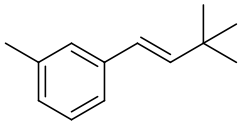
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.91 (t, 3H, *J* = 6.7 Hz, CH_2CH_3), 1.35 (m, 6H, (C*H*$_2$)$_3$Me), 1.55 (m, 2H, C*H*$_2$(CH$_2$)$_3$Me), 2.25 (ddt, 2H, *J* = 7.5, 7.0, 1.3 Hz, C*H*$_2$CH=CHAr), 2.35 (s, 3H, ArC*H*$_3$) 6.12 (dt, 1H, *J* = 15.6, 7.0 Hz, CH_2CH=CHAr), 6.60 (dt, 1H, *J* = 15.6, 1.3 Hz, CH=C*H*Ar), 7.14 (m, 3H, C^4*H*(Ar) and C^5*H*(Ar) and C^6*H*(Ar)), 7.43 (m, 1H, C^3*H*(Ar)).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (*C*H$_3$), 19.8 (Ar*C*H$_3$), 22.6 (*C*H$_2$Me), 28.7 (*C*H$_2$Bu), 29.4 (*C*H$_2$Pr), 31.7 (*C*H$_2$Et), 33.3 (ArCHCHCH$_2$), 125.4 (*C*^{4}(Ar)), 125.9 (*C*^{5}(Ar), 126.7 (ArCH*C*H), 127.5 (*C*^{3}(Ar)), 130.1 (*C*^{6}(Ar)), 132.6 (Ar*C*HCH), 134.8 (*C*^{2}Ar), 137.1 (*C*^{1}(Ar)).

IR ($CHCl_3$): $\tilde{\nu}$ = 3009, 2958, 2928, 2857, 2735, 1702, 1512, 1019 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{15}H_{22}$ 202.1722, found 202.1726.

(E)-1-(3,3-dimethylbut-1-en-1-yl)-3-methylbenzene (22) (Table 3, Run 24)[S17]



Prepared by General Procedure 2, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), Cp_2TiCl_2 (34.9 mg, 0.14 mmol), *tert*-Butylacetylene (340 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3$.$CHCl_3$ (31 mg, 0.03 mmol), DABCO (166 mg, 1.48 mmol) and 3-bromo-1-methyl-benzene (242 μL, 2.00 mmol) afforded **22** (228 mg, 65 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.85.

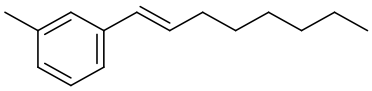
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.29 (s, 9H, 3 x C*Me*$_3$), 2.49 (s, 3H, Ar*C*H$_3$), 6.42 (d, 1H, *J* = 16.0 Hz, C=C*H*Ar); *overlapped by* 6.42 (d, 1H, *J* = 16.0 Hz, C*H*=CAr), 7.14-7.17 (m, 1H, Ar), 7.32-7.35 (m, 3H, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 21.5 (s, 3 H, Ar*C*H$_3$), 29.8 (s, 9 H, 3 x C*Me*$_3$), 33.4 (*C*Me$_3$), 123.4 (C=*C*Ar), 124.8 (Ar-*C*H), 126.9 (Ar-*C*H), 127.7 (Ar-*C*H), 128.5 (Ar-*C*H), 138.0 (*ipso*-*C*, Ar), 138.1 (*ipso*-*C*, Ar), 141.7 (H*C*=CAr).

IR ($CHCl_3$): $\tilde{\nu}$ = 3235, 3186, 3098, 3009, 2962, 2905, 2866, 2774, 2737, 2710, 1938, 1870, 1808, 1783, 1747, 1648, 1602, 1583, 1522, 1488, 1475, 1463, 1390, 1380, 1363, 1311, 1270, 1240, 1189, 1167, 1091, 1041, 1025, 972, 944, 905, 882, 842, 642, 621, 612 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{13}H_{18}$ 174.1409, found 174.1410.

(E)-1-methyl-3-(oct-1-en-1-yl)benzene (23) (Table 3, Run 25)



Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), Cp*$_2$ZrCl_2 (61 mg, 0.14 mmol), 1-octyne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3$.$CHCl_3$ (31 mg, 0.03 mmol), DABCO (157 mg, 1.40 mmol) and 3-bromotoluene (240 μL, 2.00 mmol) afforded ***23*** (384 mg, 95 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.47.

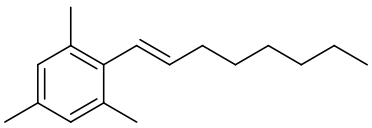
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.93 (t, 3H, *J* = 6.7 Hz, CH_2CH_3), 1.33 (m, 6H, $(CH_2)_3$Me), 1.55 (m, 2H, $CH_2(CH_2)_3$Me), 2.22 (ddt, 2H, *J* = 7.6, 7.0, 1.0 Hz, CH_2CH=CHAr), 2.36 (s, 3H, ArCH_3) 6.24 (dt, 1H, *J* = 15.8, 6.7 Hz, CH_2CH=CHAr), 6.37, (dt, 1H, *J* = 15.8, 1.0 Hz, CH=C*H*Ar), 7.03 (d, 1H, *J* = 8.1 Hz, C^4*H*(Ar), 7.17 (m, 1H, C^5*H*(Ar)), 7.19 (s, 1H, (C^2*H*(Ar)), 7.22 (d, 1H, *J* = 7.6 Hz(C^6*H*(Ar)).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (CH_3), 21.4 (ArCH_3), 22.6 (CH_2Me), 28.9 (CH_2Bu), 29.3 (CH_2Pr), 31.7 (CH_2Et) 33.1 (ArCHCHCH_2), 123.1 (*C*^{4}(Ar)), 126.6 (*C*^{6}(Ar)), 127.7 (*C*^{5}(Ar), 128.4 (ArCH*C*H), 129.7 (Ar*C*HCH), 131.0 (*C*^{2}(Ar)), 137.9 (*C*^{1}Ar), 137.9 (*C*^{3}(Ar) ppm;

IR ($CHCl_3$): $\tilde{\nu}$ = 3009, 2958, 2928, 2857, 2735, 1702, 1512, 1019 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{15}H_{22}$ 202.1722, found 202.1718.

(E)-1,3,5-trimethyl-2-(oct-1-en-1-yl)benzene (24) (Table 3, Run 26)



Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $ZrCp^*_2Cl_2$ (68 mg, 0.14 mmol), Oct-1-yne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (166 mg, 1.48 mmol) and 1-bromomesitylene (310 μL, 2.00 mmol) afforded **24** (467 mg, 99 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.75.

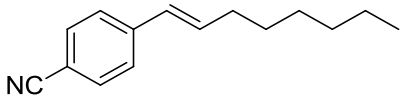
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.20 (t, 3H, *J* = 6.8 Hz, CH_2Me), 1.55-1.69 (m, 6H, CH_2), 1.74-1.79 (m, 2H, CH_2), 2.47-2.51 (m, 2H, CH_2), 2.52 (s, 3H, Ar*Me*); *overlapped by* 2.54 (s, 6H, 2 x Ar*Me*), 5.91 (dt, 1H, *J* = 16.0, 6.8 Hz, CH_2CH=CAr), 6.55 (d, 1H, *J* = 16.0 Hz, CH_2C=C*H*Ar), 7.11 (s, 2H, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.4 (CH_2CH_3), 21.1 (3 x ArCH_3), 23.0 ($CH_2CH_2CH_2CH_3$), 29.2 ($CH_2CH_2CH_2CH_3$), 29.8 ($CH_2CH_2CH_2CH_3$), 32.1 ($CH_2CH_2CH_2CH_2CH_3$), 33.7 ($CH_2CH_2CH_2CH_2CH_2CH_3$), 127.5 (C=*C*Ar), 128.6 (2 x Ar-*C*H), 135.0 (*ipso-C*, Ar), 135.6 (*ipso-C*, Ar), 135.8 (H*C*=CAr), 136.0 (2 x *ipso-C*, Ar).

IR ($CHCl_3$): $\tilde{\nu}$ 3008, 2924, 2857, 2735, 1733, 1657, 1610, 1568, 1479, 1466, 1378, 1305, 1176, 1110, 1031, 1017, 973, 952, 908, 888, 855, 643 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{17}H_{26}$ 230.2035, found 230.2027.

(E)-4-(oct-1-en-1-yl)benzonitrile (25) (Table 3, Run 27)[S18]



Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $ZrCp^*_2Cl_2$ (68 mg, 0.14 mmol), 1-octyne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (166 mg, 1.48 mmol) and 1-bromo-4-cyanobenzene (364 mg , 2.00 mmol) afforded **25** (405 mg, 95 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.07.

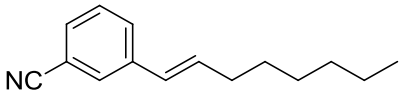
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.90 (t, 3H, *J* = 6.8 Hz, CH_2Me), 1.20-1.38 (m, 6H, CH_2), 1.44-1.50 (m, 2H, CH_2), 2.20-2.25 (m, 2H, CH_2), 6.37 (app t, 1H, *J* = 4 Hz, CH_2CH=CAr); *overlapped by* 6.32-6.42 (m, 1H, CH_2C=C*H*Ar), 7.38-7.40 (m, 2H, Ar), 7.52-7.55 (m, 2H, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (CH_2CH_3), 22.6 ($CH_2CH_2CH_2CH_3$), 28.9 ($CH_2CH_2CH_2CH_3$), 29.0 ($CH_2CH_2CH_2CH_3$), 31.7 ($CH_2CH_2CH_2CH_2CH_3$), 33.1 ($CH_2CH_2CH_2CH_2CH_2CH_3$), 109.9 (*C*≡N), 119.1 (*ipso-C*, Ar-CN), 126.4 (C=*C*Ar), 128.4 (Ar-*C*H), 132.2 (Ar-*C*H), 135.5 (H*C*=CAr), 142.3 (*ipso-C*, Ar).

IR ($CHCl_3$): $\tilde{\nu}$ 3118, 3086, 3009, 2959, 2932, 2857, 2228, 2175, 1916, 1795, 1710, 1688, 1650, 1605, 1503, 1466, 1412, 1379, 1367, 1344, 1308, 1240, 1176, 1106, 1053, 1017, 968, 953, 909, 855, 648 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{15}H_{19}N$ 213.1517, found 213.1515.

(E)-3-(oct-1-en-1-yl)benzonitrile (26) (Table 3, Run 28)



Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (61 mg, 0.14 mmol), 1-octyne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (157 mg, 1.40 mmol) and 3-bromobenzonitrile (364 mg, 2.00 mmol) afforeded **26** (398.1 mg, 94 %) as a yellow oil; $\boldsymbol{R_F}$ (pentane/Et_2O 19:1) 0.14.

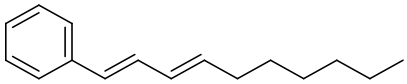
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.92 (t, 3H, *J* = 7.2 Hz, CH_2CH_3), 1.33 (m, 6H, $(CH_2)_3Me$), 1.50 (m, 2H, $CH_2(CH_2)_3Me$), 2.24 (ddt, 2H, *J* = 6.8, 6.0, 1.2 Hz, CH_2CH=CHAr), 6.32 (dt, 1H, *J* = 16.0, 6.0 Hz, CH_2CH=CHAr), 6.36, (dt, 1H, *J* = 16.0, 1.2 Hz, CH=CHAr), 7.40 (t, 1H, *J* = 8.0 Hz, C^5H(Ar)), 7.47 (dt, 1H, *J* = 8.0, 1.6 Hz, C^4H(Ar)), 7.55 (dt, 1H, *J* = 8.0, 1.6 Hz, C^6H(Ar)), 7.62 (s, 1H, C^2H(Ar)).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (CH_3), 22.6 (CH_2Me), 28.9 (CH_2Et), 29.0 (CH_2Pr), 31.7 (CH_2Bu), 33.0 (ArCHCHCH_2), 112.6 (C^1(Ar)), 118.9 (ArCN), 127.7 (C^5(Ar)), 129.2 (C^4(Ar)), 129.4 (ArCHCH), 130.0 (C^2(Ar)), 130.1 (C^6(Ar)), 134.3 (ArCHCH), 139.2 (C^3(Ar)).

IR ($CHCl_3$): $\tilde{\nu}$ 3009, 2958, 2929, 2857, 2232, 1651, 1598, 1466, 964 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. For $C_{15}H_{19}N$ 213.1517, found 213.1517.

(1E,3E)-deca-1,3-dien-1-ylbenzene (27) (Table 3, Run 29)[S19]



Prepared by General Procedure 1, $HAlCl_2$•2THF(1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (61 mg, 0.14 mmol), 1-octyne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (157 mg, 1.40 mmol), $InCl_3$ (69.0 mg, 0.28 mmol) and β-bromostyrene (260 μL, 2.00 mmol) afforded **27** (271 mg, 63 %) as a yellow oil; $\boldsymbol{R_F}$ (pentane) 0.46.

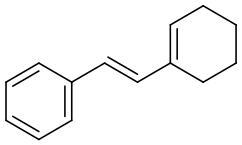
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.91 (t, 3H, *J* = 6.7 Hz, CH_2CH_3), 1.31 (m, 6H, $(CH_2)_3Me$), 1.45 (m, 2H, $CH_2(CH_2)_3Me$), 2.17 (ddt, 2H, *J* = 7.8, 6.8, 1.0 Hz, CH_2CH=CHAr), 5.86 (dt, 1H, *J* = 15.6, 6.8 Hz, CH=C*H*CH_2), 6.25 (dd, 1H, *J* = 15.6, 11.1 Hz, CH_2CH=C*H*), 6.46 (d, 1H, *J* = 15.6 Hz, CH=C*H*Ar), 6.78 (dd, 1H, *J* = 15.5, 11.1 Hz, ArCH=C*H*) 7.28 (m, 5H, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (CH_3), 22.6 (CH_2Me), 29.4 (CH_2Pr), 29.7 (CH_2Bu), 31.7 (CH_2Et), 33.1 (CH=CHCH_2), 125.4 (C^2(Ar) and C^6(Ar)), 126.1 (C^4(Ar)), 128.2 (C^3(Ar) and C^5(Ar)), 129.9 (ArCH=CH), 130.4 (ArCH=CH), 131.9 (ArCH=CHCH=CH), 131.3 (ArCH=CHCH=CH), 137.7 (C^1(Ar)).

IR ($CHCl_3$): $\tilde{\nu}$ = 2957, 2930, 2958, 1676, 1451, 1167, 970 cm^{-1};

HRMS (EI+) *m/z*: Calcd. for $C_{16}H_{22}$ 214.1722, found 214.1720

(E)-(2-(cyclohex-1-en-1-yl)vinyl)benzene (28) (Table 3, Run 30)[S20]



Prepared by General Procedure 1, $HAlCl_2$•2THF (510 mg, 2.10 mmol), $Cp^*_2ZrCl_2$ (30 mg, 0.07 mmol), 1-ethynylcyclohexene (164 μL, 1.4 mmol), X-Phos (19 mg, 0.04 mmol), $Pd_2(dba)_3.CHCl_3$ (15 mg, 0.015 mmol), DABCO (79 mg, 0.70 mmol), and bromobenzene (100 μL, 1.0 mmol) and quenched with Rochelle's salt (3 mL of saturated aqueous solution) afforded **28** (125 mg, 68%) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.25.

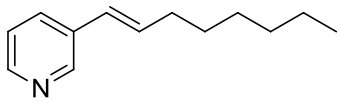
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.65 – 1.71 (m, 2H, Cy), 1.74 – 1.80 (m, 2H, Cy), 2.22 – 2.24 (m, 2H, Cy), 2.33-2.39 (m, 2H, Cy), 5.94 (t, 1H, *J* = 4.4 Hz, C*H*,Cyclohexenyl), 6.49 (d, 1H, *J* = 16.4 Hz, C*H*=CHPh), 6.82 (d, 1H, *J* = 16.4 Hz, CH=C*H*Ph), 7.22 (tt, 1H, *J* = 7.2, 1.6 Hz, C^4*H*(Ar)), 7.33 (tt, 2H, *J* = 7.6, 1.6 Hz, C^2*H*(Ar), C^6*H*(Ar)), 7.44 (dt, 2H, J = 7.2, 1.6 Hz, C^3*H*(Ar) and C^5*H*(Ar)).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 22.5 (CH_2(*C*y)), 22.6 (CH_2(*C*y)), 24.6 (CH_2(*C*y)), 26.2 (*C*H_2(Cy)), 124.6 (*C*HC_q), 126.1 (C^{2}H(Ar) and C^{6}H(Ar)), 126.8 (C^{4}H(Ar)), 128.5 (C^{3}H(Ar) and C^{5}H(Ar)), 130.8 (CyCH=C*H*Ar), 132.6 (CyC*H*=CHAr), 135.8 (C_q(Cy)), 138.0 (C_{ipso}(Ar)).

IR ($CHCl_3$): $\tilde{\nu}$ 3010, 2930, 2861, 1632, 1616, 1494, 1447, 962 cm^{-1}

HRMS (EI+) *m/z*: Calcd. for $C_{14}H_{16}$ 184.1252, found 184.1254.

(E)-3-(oct-1-en-1-yl)pyridine (29) (Table 3, Run 31)[S21]



Prepared by General Procedure 1, $HAlCl_2$•2THF (1.43 g, 5.88 mmol), $ZrCp^*_2Cl_2$ (68 mg, 0.14 mmol), oct-1-yne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (166 mg, 1.48 mmol) and 3-bromopyridine (192 μL , 2.00 mmol) afforded ***29*** (167 mg, 63 %) as a colourless oil; $\boldsymbol{R_F}$ (1:1 pentane/Et_2O) 0.18.

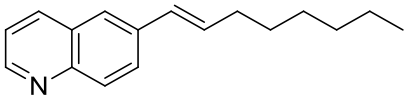
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.88 (t, 3H, *J* = 6.8 Hz, CH_2*Me*), 1.25-1.35 (m, 6H, CH_2), 1.44-1.49 (m, 2H, CH_2), 2.21 (q, 2H, *J* = 6.8 Hz, CH_2), 6.27 (dt, 1H, *J* = 15.8, 6.4 Hz, CH_2C*H*=CAr); *overlapped by* 6.33 (d, 1H, *J* = 15.8 Hz, CH_2C=C*H*Ar), 7.17 (dd, 1H, *J* = 7.6, 4.8 Hz, Ar), 7.61 (dt, 1H, *J* = 8.0, 1.6 Hz, Ar), 8.41 (br s, 1H, Ar), 8.55 (br s, 1H, Ar).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (CH_2*C*H_3), 22.6 (CH_2CH_2*C*H_2CH_3), 28.9 (CH_2*C*$H_2CH_2CH_3$), 29.1 (*C*$H_2CH_2CH_2CH_3$), 31.7 (*C*$H_2CH_2CH_2CH_2CH_3$), 33.1 (*C*$H_2CH_2CH_2CH_2CH_2CH_3$), 123.3 (C=*C*Ar), 126.2 (Ar-*C*H), 132.3 (Ar-*C*H), 133.4 (*ipso*-*C*, Ar), 133.7 (Ar-*C*H), 147.8 (Ar-*C*H), 147.9 (H*C*=CAr).

IR ($CHCl_3$): $\tilde{\nu}$ 3139, 3086, 3054, 3008, 2959, 2929, 2872, 2857, 2732, 1959, 1923, 1901, 1864, 1796, 1713, 1652, 1587, 1571, 1481, 1467, 1416, 1379, 1344, 1330, 1312, 1247, 1185, 1124, 1099, 1044, 1025, 966, 909, 890, 835, 660, 645, 615 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{13}H_{19}N$ 189.1517, found 189.1515.

(E)-6-(oct-1-en-1-yl)quinolone (30) (Table 3, Run 32)



Prepared by General Procedure 1, $HAlCl_2$•2THF (766 mg, 3.15 mmol), $Cp^*_2ZrCl_2$ (45 mg, 0.11 mmol), 1-octyne (310 μL, 2.10 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (157 mg, 1.40 mmol), $InCl_3$ (46.4 mg, 0.21 mmol) and 6-bromoquinoline (130 μL, 1.0 mmol) and quenched with Rochelle's salt (3 mL of saturated aqueous solution) afforded **30** (226.4 mg, 94 %) as a yellow oil; $\boldsymbol{R_F}$ (pentane/Et_2O 1:1) 0.25.

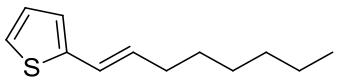
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.94 (t, 3H, *J* = 6.5 Hz, CH_2CH_3), 1.38 (m, 6H, $(CH_2)_3Me$), 1.55 (2 H, m, $CH_2(CH_2)_3Me$), 2.31 (ddt, 2H, *J* = 7.8, 7.0, 1.2 Hz, CH_2CH=CHAr), 6.45 (dt, 1H, *J* = 15.8, 7.0 Hz, ArCH=C*H*), 6.58 (d, 1H, *J* = 15.8 Hz, ArC*H*=CH), 7.42 (dd, 1H, *J* = 8.3, 4.0 Hz, C^3H) 7.58 (d, 1H, *J* = 1.7 Hz C^5H), 7.87 (d, 1H, *J* = 8.8 Hz, C^7H) 8.10 (d, 1H, *J* = 8.8 Hz, C^8H), 8.18 (d, 1H, *J* = 8.3 Hz, C^4H), 8.85 (dd, 1H, *J* = 4.0, 1.7 Hz, C^2H).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (CH_3), 22.6 (CH_2Me), 31.3 (CH_2Bu), 31.7 (CH_2Pr), 33.1 (CH_2Et), 35.3 (ArCHCHCH_2), 124.3 (C^3(Ar), 124.6 (C^6(Ar)), 128.0 (C^8(Ar), 128.5 (C^5(Ar)), 129.0 (C^9(Ar)), 129.3 (ArCH=CH), 132.5 (ArCH=CH), 135.5 (C^4(Ar)), 136.2 (C^7(Ar), 147.7 (C^{10}(Ar), 149.6 (C^2(Ar)).

IR ($CHCl_3$): $\tilde{\nu}$ 3011, 2959, 2929, 2857, 1500, 962 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{17}H_{21}N$ 239.1674, found 239.1675.

(E)-2-(oct-1-en-1-yl)thiophene (31) (Table 3, Run 33)[S22]



Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (61 mg, 0.14 mmol), 1-octyne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (157 mg, 1.40 mmol) and 2-bromothiophene (190 μL, 2.00 mmol) afforded **31** (280.5 mg, 72 %) as a colourless oil; $\boldsymbol{R_F}$ = 0.56 (Pentane).

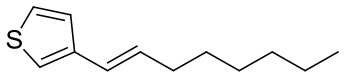
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.92 (t, 3H, *J* = 7.2 Hz, CH_2CH_3), 1.33 (m, 6H, $(CH_2)_3Me$), 1.48 (m, 2H, $CH_2(CH_2)_3Me$), 2.19 (ddt, 2H, *J* = 7.5, 7.0, 1.5 Hz, CH_2CH=CHAr), 6.10 (dt, 1H, *J* = 15.8, 7.0 Hz, CH_2CH=CHAr), 6.53 (ddt, 1H, *J* = 15.8, 1.5, 1.0 Hz, CH=C*H*Ar), 6.89 (d, 1H, *J* = 3.0 Hz C^3H(Ar), 6.96 (dd, 1H, *J* = 3.0, 5.0 Hz C^4H(Ar)) 7.11 (dt, 1H, *J* = 5.0, 1.0 Hz, C^5H(Ar)).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (CH_3), 22.6 (CH_2Me), 28.7 (CH_2Bu), 29.4 (CH_2Pr), 31.7 (CH_2Et), 33.3 (ArCHCHCH$_2$), 122.8 (ArCH*C*H), 123.0 (C^5(Ar)), 124.1 (C^3(Ar)), 127.2 (C^4(Ar)), 131.3 (Ar*C*HCH), 143.3 (C^2(Ar)).

IR ($CHCl_3$): $\tilde{\nu}$ = 3074, 3009, 2958, 2929, 2857, 1466, 955 cm^{-1};

HRMS (EI+) *m/z*: Calcd. for $C_{12}H_{18}S$ 194.1129, found 194.1123.

(E)-3-(oct-1-en-1-yl)thiophene (32) (Table 3, Run 34)



Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (61 mg, 0.14 mmol), 1-octyne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (157 mg, 1.40 mmol) and 3-bromothiophene (190 μL, 2 mmol) afforded **32** (350.8 mg, 90 %) as a colourless oil; $\boldsymbol{R_F}$ (pentane) 0.48.

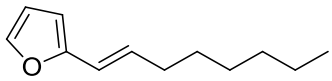
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.92 (t, 3H, *J* = 7.0 Hz, CH_2CH_3), 1.32 (m, 6H, $(CH_2)_3Me$), 1.47 (m, 2H, $CH_2(CH_2)_3Me$), 2.19 (ddt, 2H, *J* = 7.0, 6.0, 1.5 Hz, CH_2CH=CHAr), 6.10 (dt, 1H, *J* = 15.0, 7.0 Hz, CH_2CH=CHAr), 6.41 (dq, 1H, *J* = 15.8, 2.0, 1.5 Hz, CH=CHAr), 7.07 (dd, 1H, *J* = 3.0, 1.5 Hz C^2H(Ar), 7.21 (dd, 1H, *J* = 1.5, 0.6 Hz C^4H(Ar)) 7.27 (m, 1H, C^5H(Ar)).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (CH_3), 22.6 (CH_2Me), 28.9 (CH_2Bu), 29.3 (CH_2Pr), 31.7 (CH_2Et), 32.9 (ArCHCHCH$_2$), 120.2 (C^4(Ar)), 123.9 (C^5(Ar)), 124.9 (C^2(Ar)), 125.7 (ArCHCH), 131.2 (ArCHCH), 143.3 (C^3(Ar).

IR ($CHCl_3$): $\tilde{\nu}$ = 3009, 2958, 2928, 2856, 1495, 963 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{12}H_{18}S$ 194.1129 found 194.1131.

(E)-2-(oct-1-en-1-yl)furan (33) (Table 3, Run 35)



Prepared by General Procedure 1, $HAlCl_2$•2THF (1.02 g, 4.20 mmol), $Cp^*_2ZrCl_2$ (61 mg, 0.14 mmol), 1-octyne (410 μL, 2.80 mmol), X-Phos (38 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (31 mg, 0.03 mmol), DABCO (157 mg, 1.40 mmol) and 2-bromofuran (180 μL, 2 mmol) to afforded **33** (291.6 mg, 78 %) as a yellow oil; $\boldsymbol{R_F}$ (pentane) 0.48.

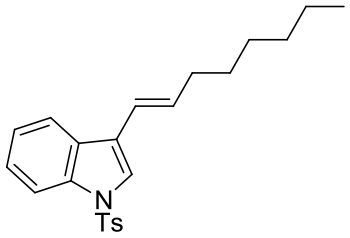
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.95 (t, 3H, *J* = 6.8 Hz, CH_2CH_3), 1.35 (m, 6H, $(CH_2)_3Me$), 1.48 (quin, 2H, *J* = 8.6, 7.0 Hz, $CH_2(CH_2)_3Me$), 2.21 (q, 2H, *J* = 8.6, 7.0, CH_2CH=CHAr), 6.10 (d, 1H, *J* = 3.2 Hz, C^3(Ar) 6.22 (m, 2H, CH_2CH=CHAr), 6.39 (dd, 1H, *J* = 3.2, 2.0 Hz, C^4H(Ar), 7.29 (d, 1H, *J* = 2.0 Hz C^5H(Ar)).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (CH_3), 22.6 (CH_2Me), 28.9 (CH_2Bu), 29.3 (CH_2Pr), 31.8 (CH_2Et), 33.8 (ArCHCHCH$_2$), 105.8 (C^3(Ar)), 111.1 (C^4(Ar)), 118.4 (ArCHCH), 130.3 (ArCHCH), 141.3 (C^5(Ar)), 153.3 (C^2(Ar)).

IR ($CHCl_3$): $\tilde{\nu}$ = 2957, 2930, 2858, 1722, 1677, 1466, 1016 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{12}H_{18}O$ 178.1358, found 178.1358.

(E)-3-(oct-1-en-1-yl)-1-tosyl-1H-indole (34) (Table 4, Run 36)



Prepared by General Procedure 1, $HAlCl_2$•2THF (766 mg, 3.15 mmol), $Cp^*_2ZrCl_2$ (45 mg, 0.11 mmol), 1-octyne (310 μL, 2.10 mmol), X-Phos (19 mg, 0.08 mmol), $Pd_2(dba)_3.CHCl_3$ (15.5 mg, 0.015 mmol), DABCO (117 mg, 1.05 mmol), $InCl_3$ (46.4 mg, 0.21 mmol) and *N*-tosyl-3-bromoindole (350.2 mg, 1.00 mmol) and quenching with Rochelle's salt (3 mL of saturated aqueous solution) afforded ***34*** (219.9 mg, 77 %) as a yellow oil; $\boldsymbol{R_F}$ (pentane/Et_2O 6:1) 0.51.

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 0.94 (t, 3H, *J* = 6.7 Hz, CH_2CH_3), 1.43 (m, 6H, $(CH_2)_3Me$), 1.50 (m, 2H, $CH_2(CH_2)_3Me$), 2.25 (ddt, 2H, *J* = 7.6, 7.3, 1.5 Hz, $CH_2CH{=}CHAr$), 2.35 (s, 3H, $ArCH_3$), 6.30 (dt, 1H, *J* = 16.0, 7.3 Hz, ArCH=CH), 6.45 (d, 1H, *J* = 16.0 Hz, ArCH=CH), 7.2 (d, 2H, *J* = 8.5 Hz, C^2H(tol) and C^6H(tol)) 7.30 (2H, m, C^5H(indole) and C^6H(indole)), 7.53 (s, 1H, C^2H(indole) 7.70 (d, 1H, *J* = 7.3 Hz, C^4H(indole)), 7.80 (d, 2H, *J* = 8.5 Hz, C^3H(tol) and C^5H(tol)), 8.02 (d, 1H, *J* = 7.3 Hz, C^7H(indole)).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 14.1 (CH_3), 21.5 (CH_3(tosyl)), 22.6 (CH_2Me), 28.9 (CH_2Bu), 29.4 (CH_2Pr), 31.7 (CH_2Et), 33.5 ($ArCHCHCH_2$), 113.7 (C7(indole), 120.0 (C^4(indole)), 120.3 (C^5(indole)), 122.6 (C^3(indole), 123.3 (ArCH=CH), 124.7 (C^2(indole), 126.8 (C^6(indole), 126.9 (C^3(tosyl) and C^5(tosyl)), 129.3 (C^9(indole)), 129.8 (C^2(tosyl) and C^6(tosyl)), 132.9 (ArCH=CH), 125.2 (C^4(tosyl), 135.5 (C^8(indole), 144.0 (C^1(tosyl)).

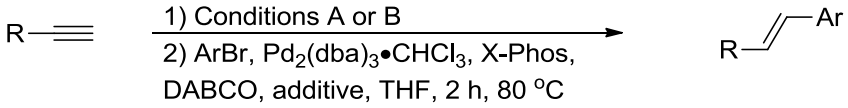
IR ($CHCl_3$): $\tilde{\nu}$ 3133, 3011, 2958, 2928, 2856, 1644, 1446, 1373, 1188, 976 cm^{-1}.

HRMS (EI+) *m/z*: Calcd. for $C_{23}H_{27}NO_2S$ 381.1762, found 381.1721.

Comparison of hydroaluminations conditions

Hydroalumination using $HAlCl_2•(THF)_2$ under the present conditions was compared to DIBAL-H, under literature conditions. The subsequent cross-coupling was conducted with an identical catalyst (Pd-X-phos) to allow valid comparison of the cross-coupled yields, which are shown in Table S1.

Table S1. Comparison of the Hydroalumination/Cross-coupling procedures.

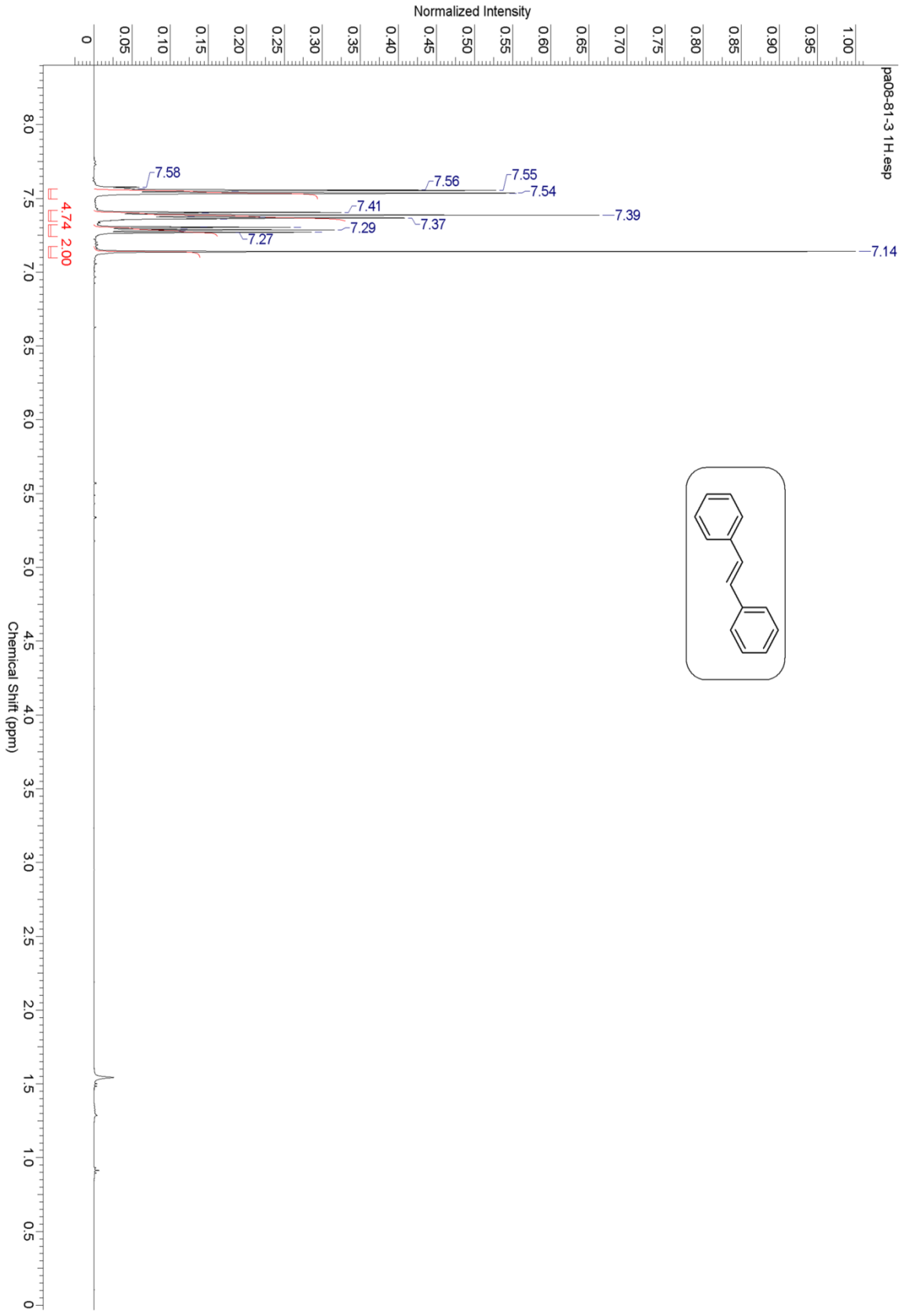


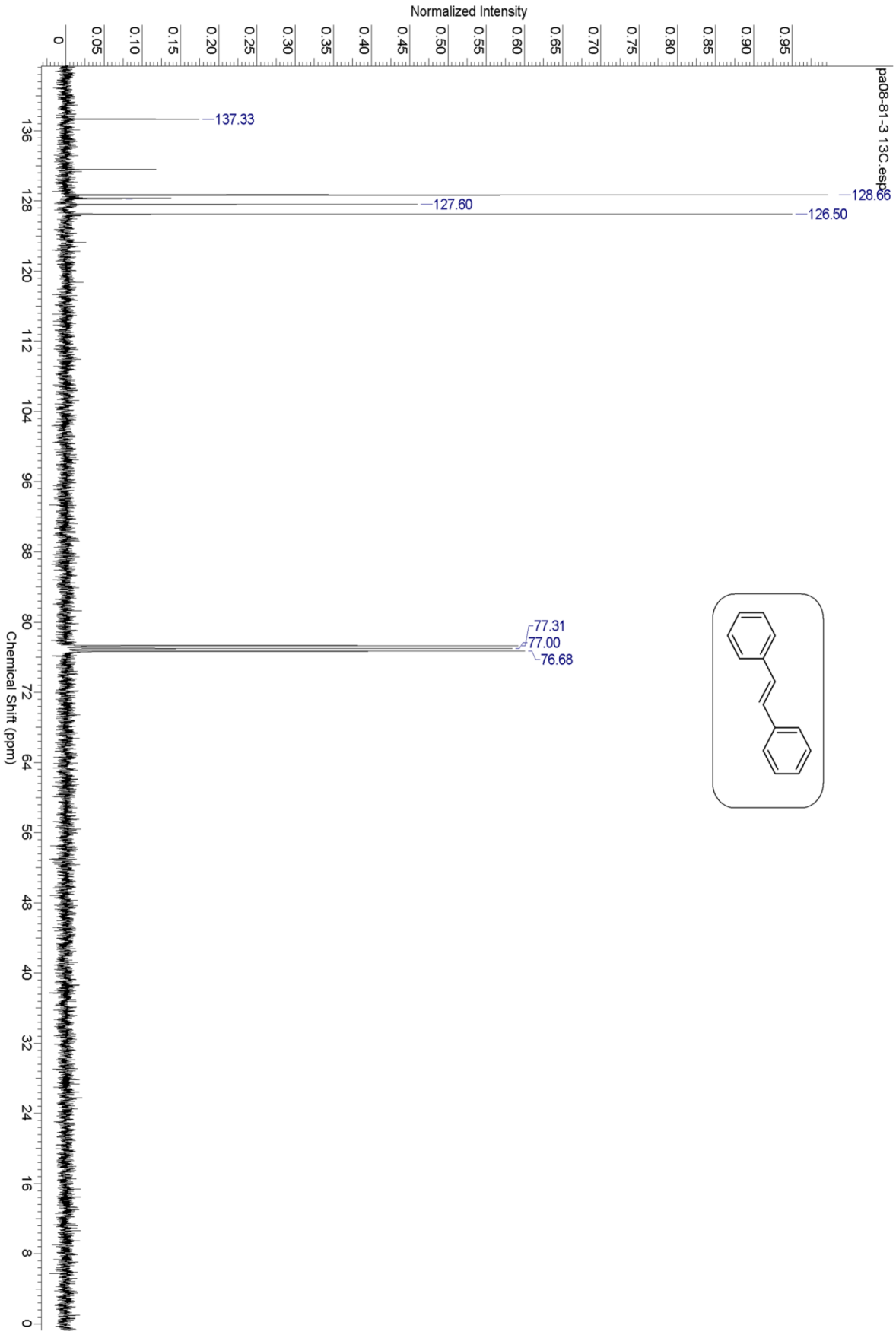
Hydroalumination conditions A: alkyne (1.0 equiv.) $HAlCl_2.2THF$ (1.5 equiv.), $Cp^*_2ZrCl_2$ (5 mol%), THF, 16 h, 80 °C; hydroalumination conditions B: alkyne (1 equiv.), $HAlBu^i_2$ (1.0 equiv.), hexanes, 6 h, 50 °C.

Entry	Hydroalumination conditions	R	Ar in ArBr	Additive	Yield/ %[a]
1	A	Ph	Ph	-	94[a]
2	B	Ph	Ph	-	34[a]
3	B	Ph	Ph	$ZnCl_2$ (1.0 equi.v)	13[a]
4	A	C_6H_{13}	3,5-Me_2Ph	-	95
5	B	C_6H_{13}	3,5-Me_2Ph	-	82
6	B	C_6H_{13}	3,5-Me_2Ph	$ZnCl_2$ (1.0 equiv.)	40
7	A	C_6H_{13}	3-(CN)Ph	-	94
8	B	C_6H_{13}	3-(CN)Ph	-	88
9	B	C_6H_{13}	3-(CN)Ph	$ZnCl_2$ (1.0 equiv.)	35
10	A	C_6H_{13}	6-quinoyl	$InCl_3$ (10 mol%)	94
11	B	C_6H_{13}	6-quinoyl	$InCl_3$ (10 mol%)	78

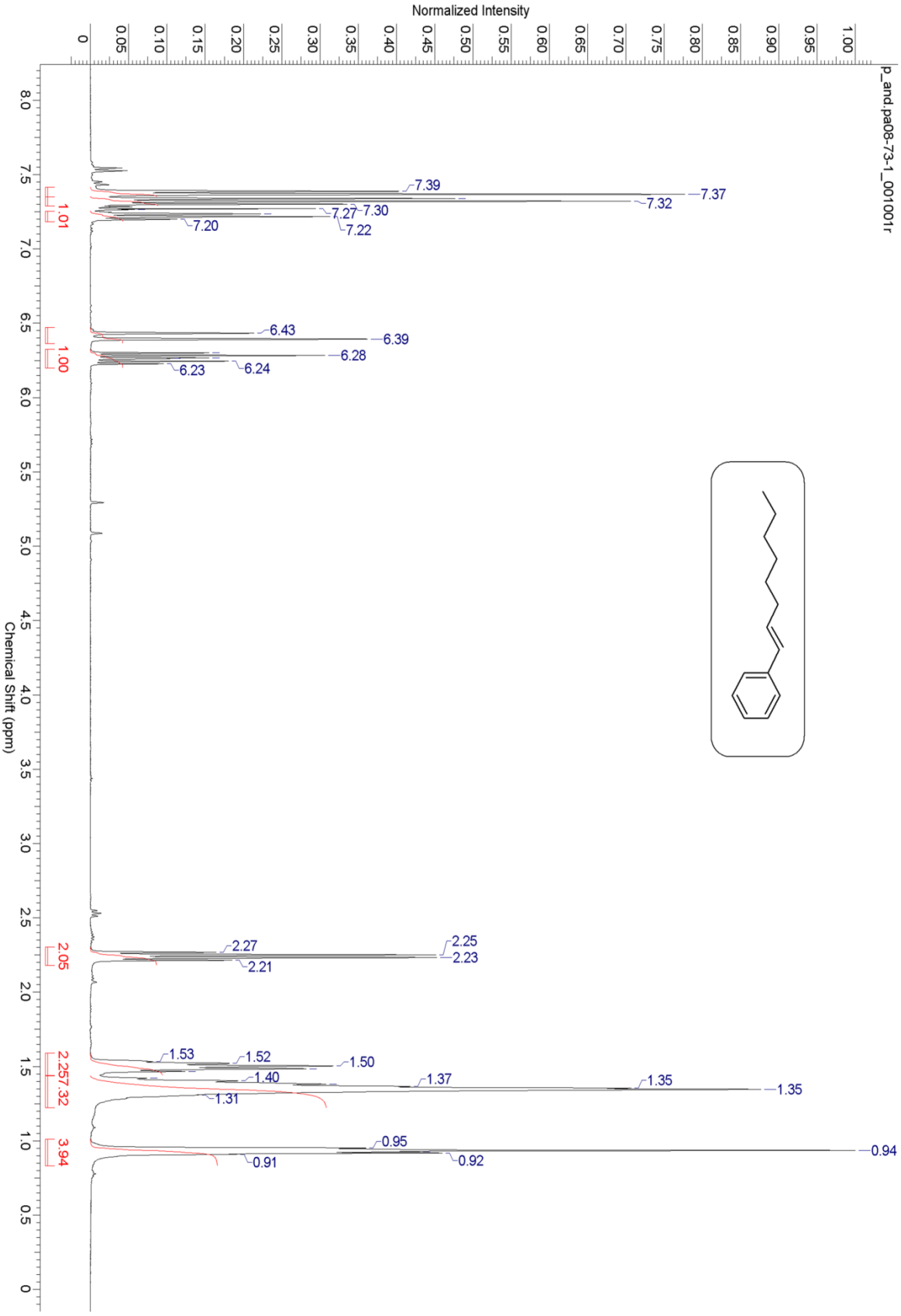
a) All yields isolated except for Runs 1-3 which were determined by GC using a factorFour column with tridecane as internal standard.

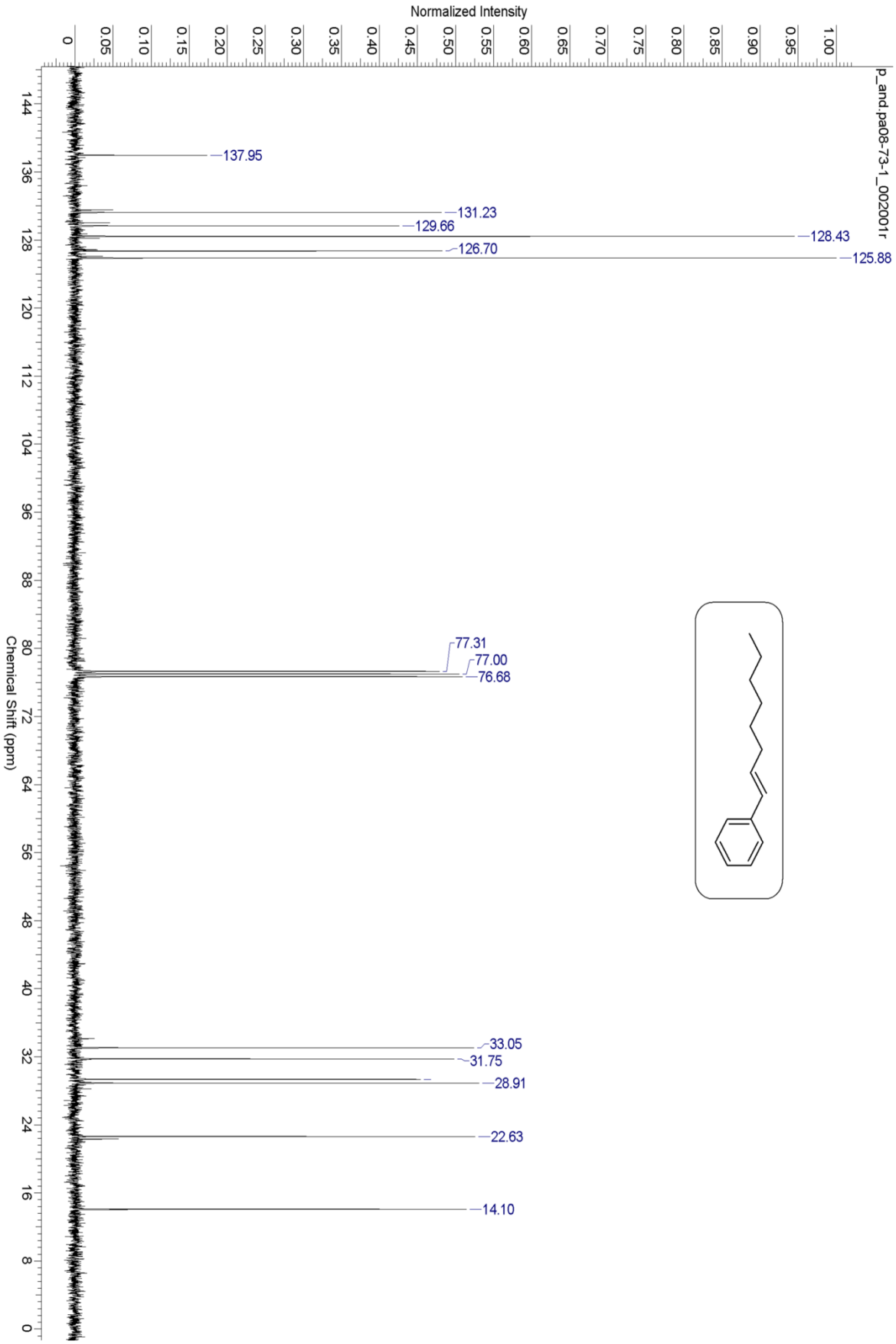
(E)-stilbene, 1


Normalized Intensity
pa08-81-3 1H.esp
7.58
7.56
7.55
7.54
7.41
7.39
7.37
7.29
7.27
7.14
4.74
2.00
Chemical Shift (ppm)

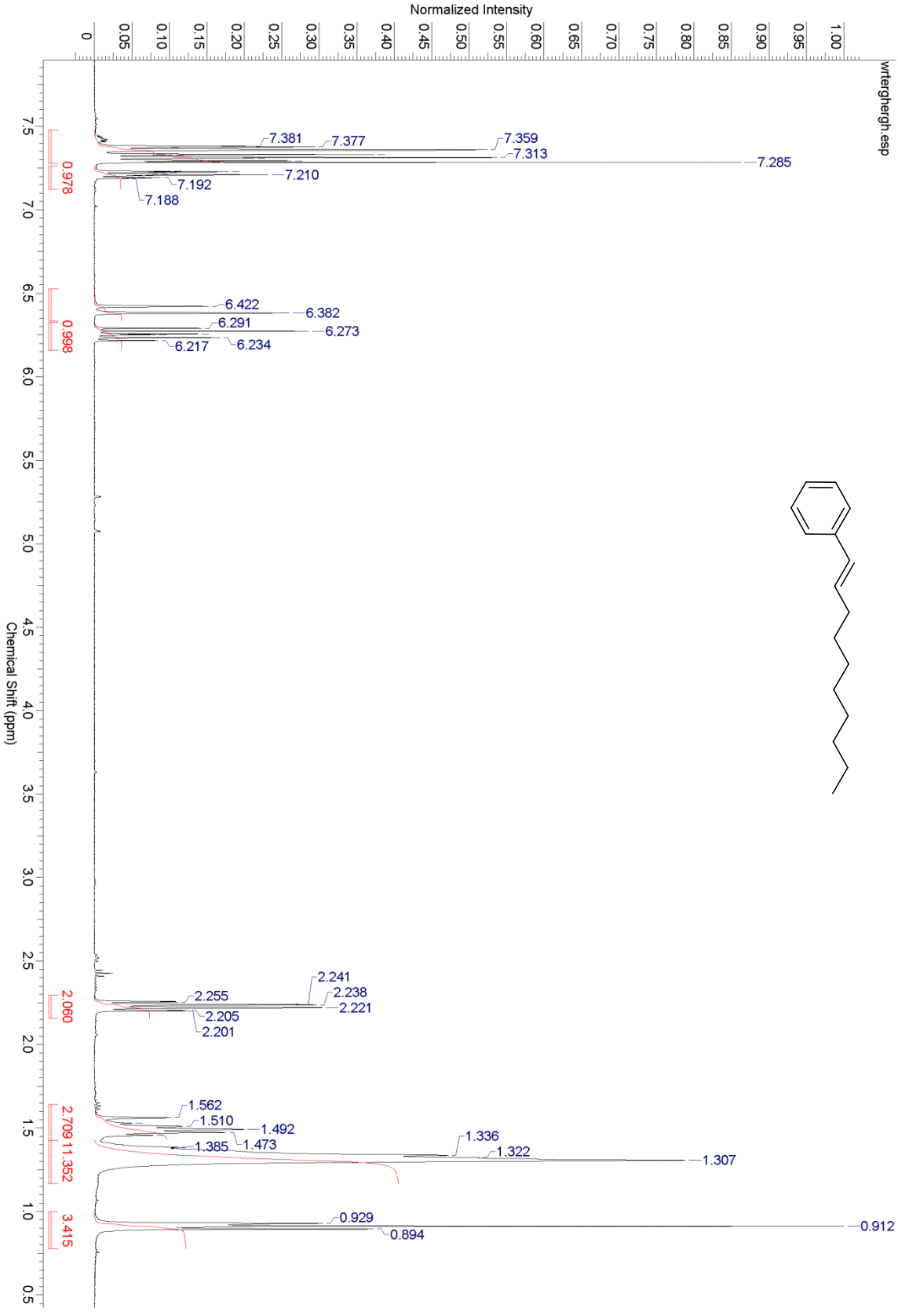

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
pa08-81-3 13C.esp
137.33
128.66
127.60
126.50
77.31
77.00
76.68
Chemical Shift (ppm)
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0

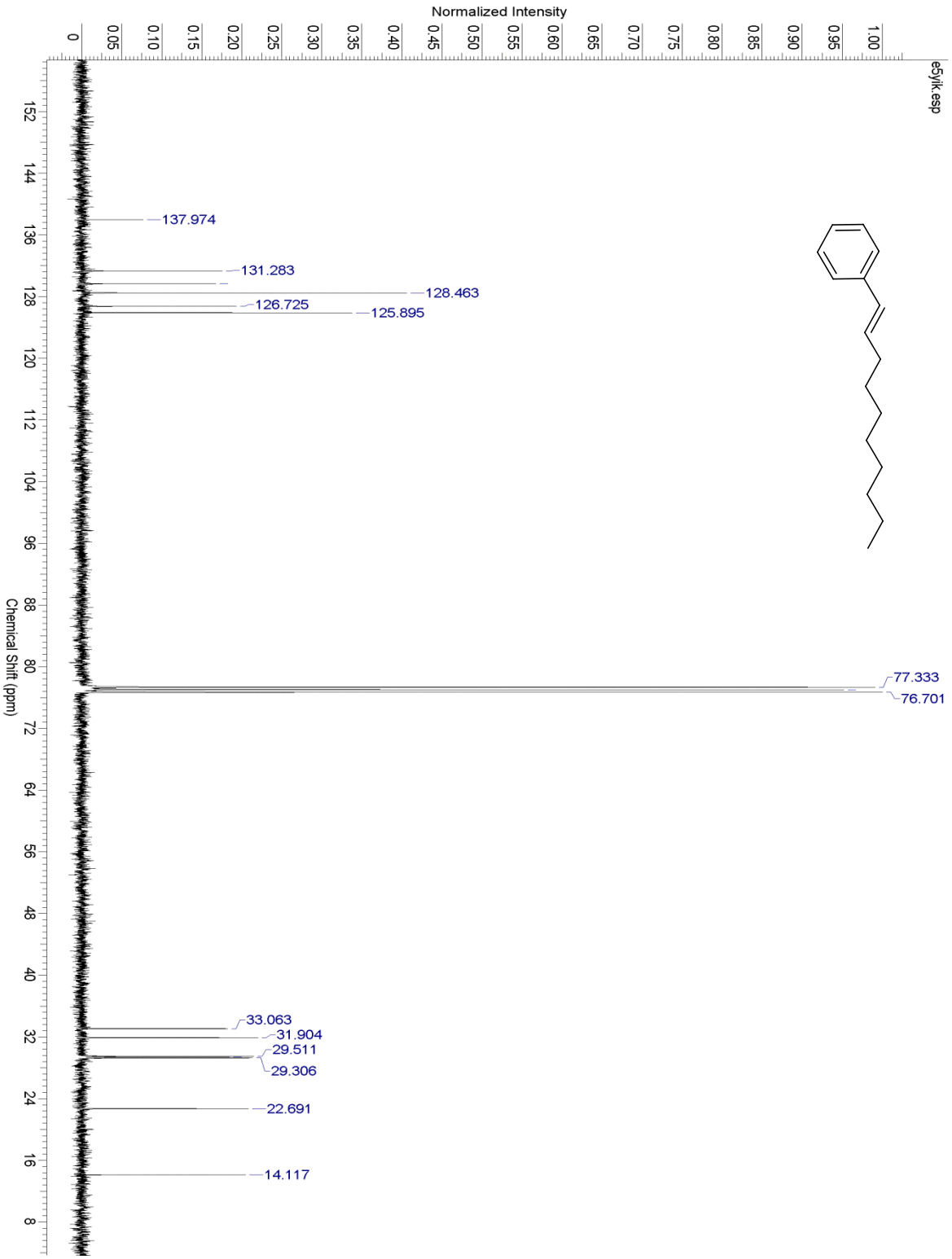
(E)-1-phenyl-1-octene, 2,



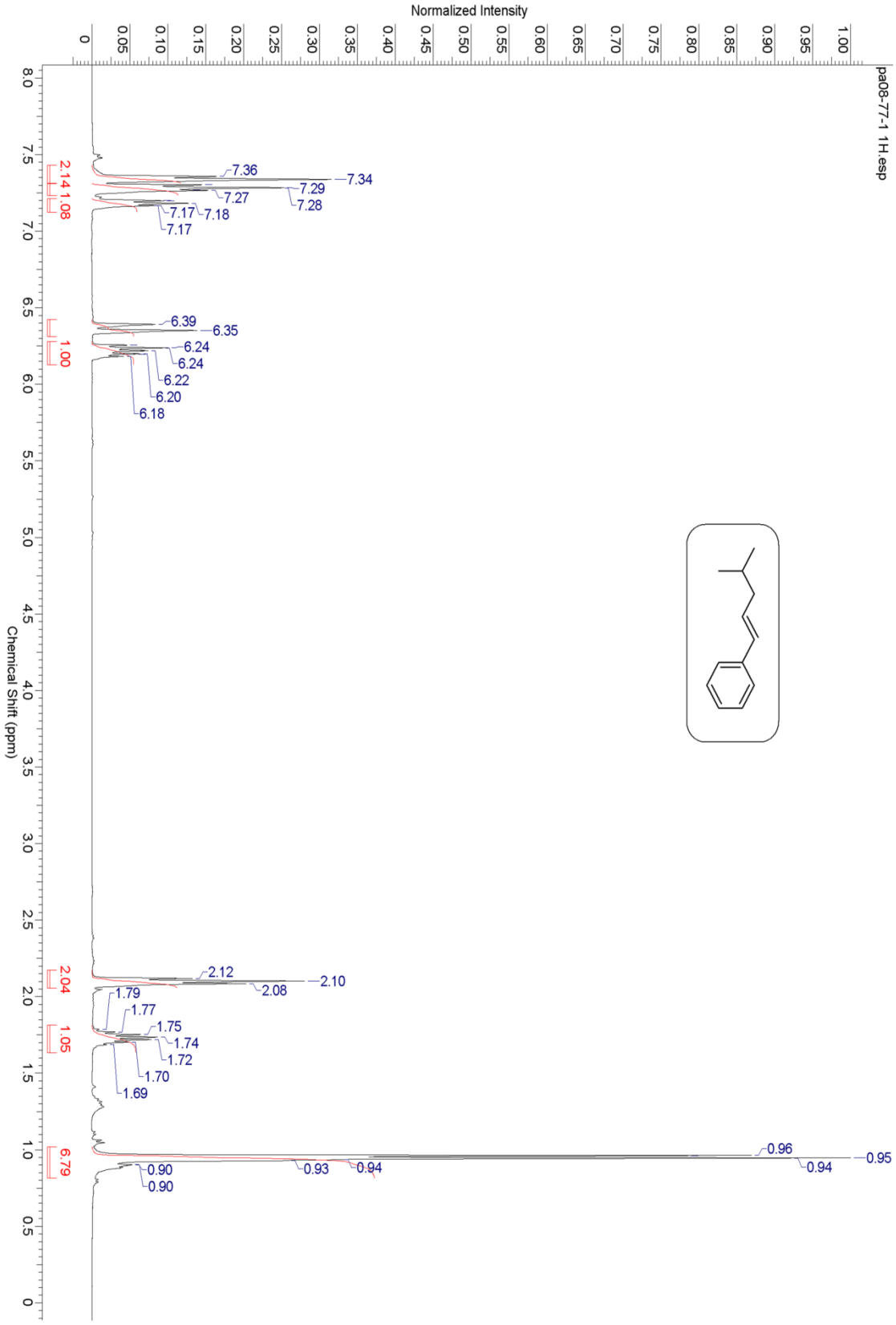

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
p_and.pa08-73-1_002001r
Chemical Shift (ppm)
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
137.95
131.23
129.66
128.43
126.70
125.88
77.31
77.00
76.68
33.05
31.75
28.91
22.63
14.10

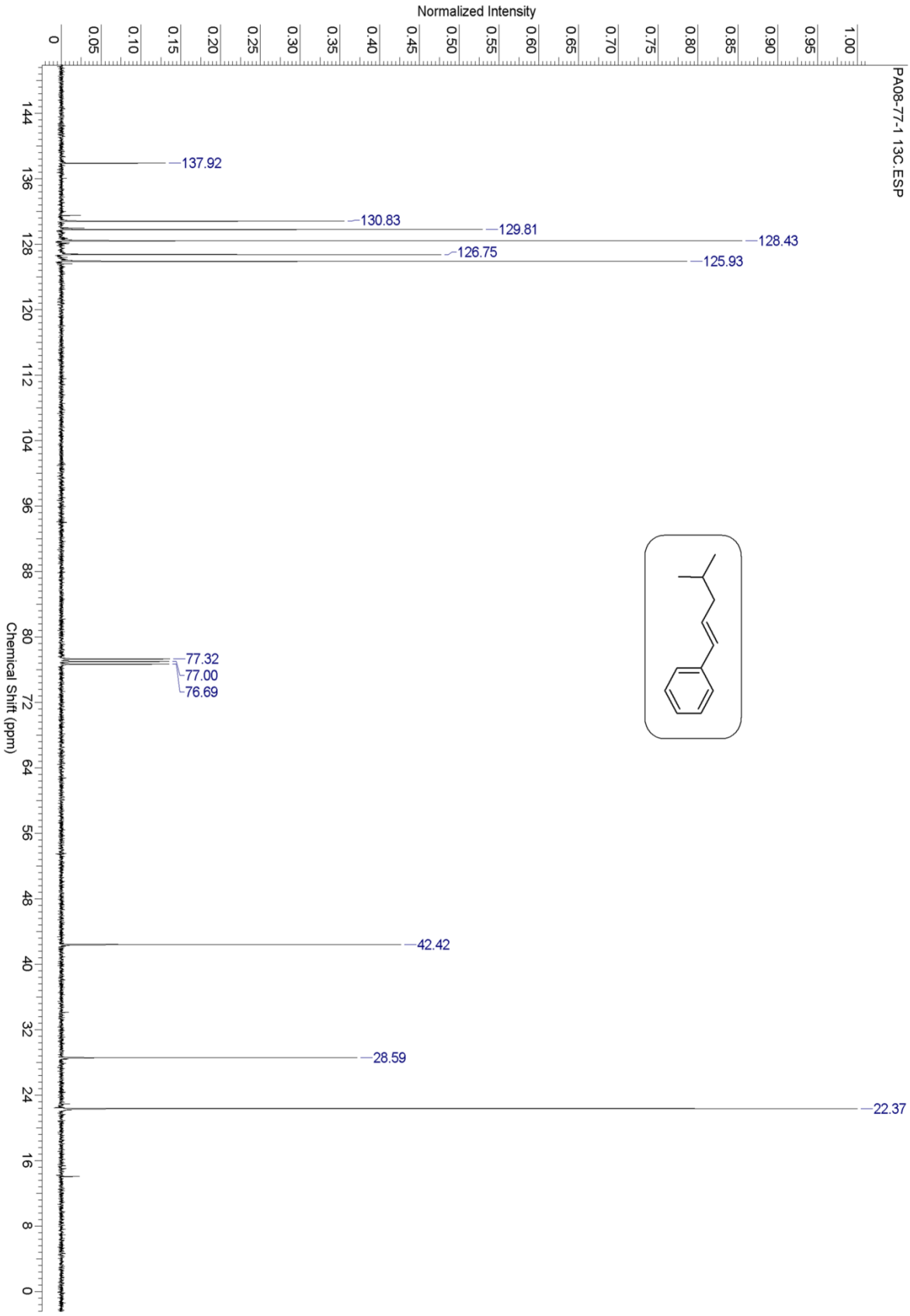
(E)-(Dec-1-en-1-yl)benzene, 3



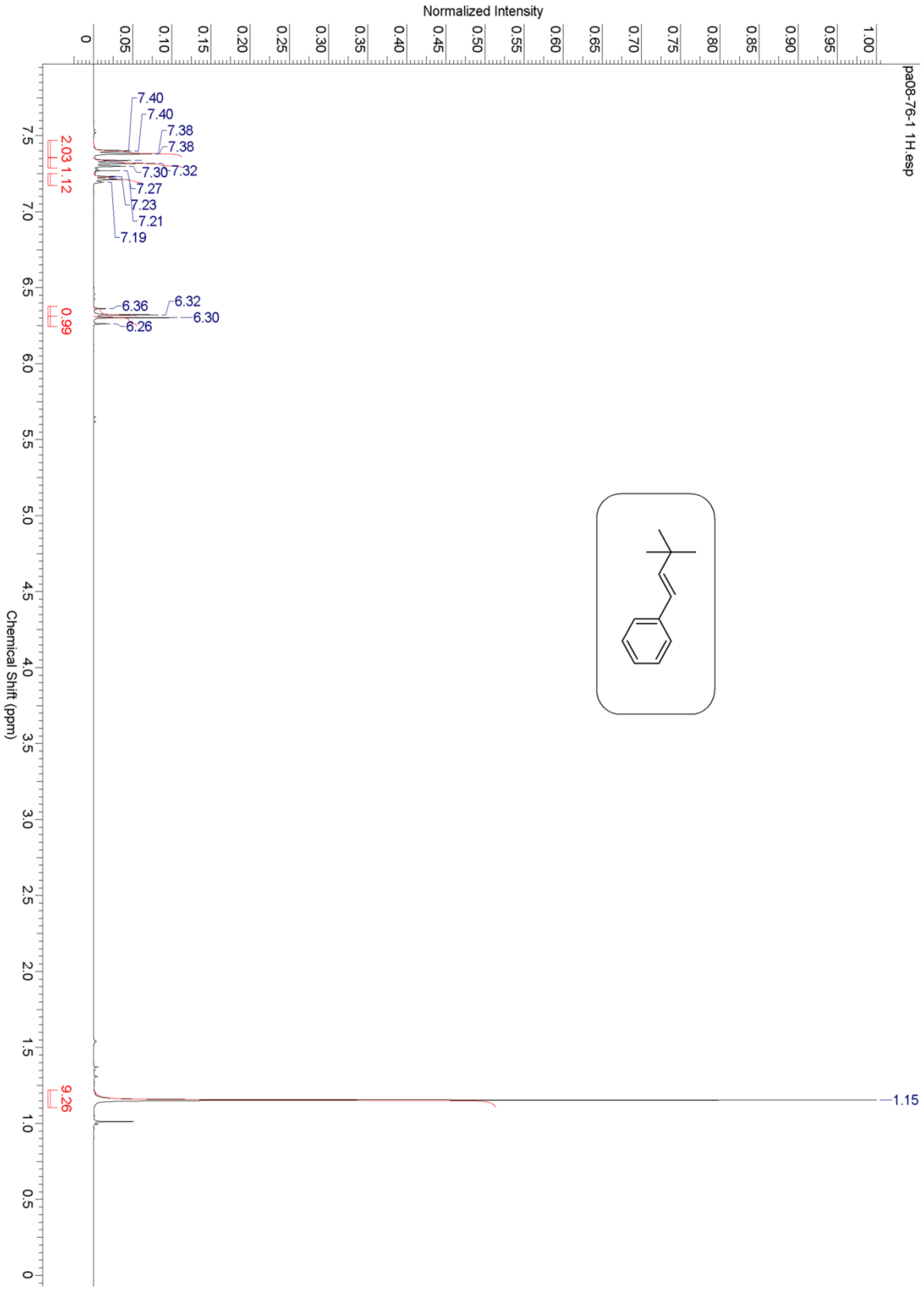

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
e5yik.esp
Chemical Shift (ppm)
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
137.974
131.283
128.463
126.725
125.895
77.333
76.701
33.063
31.904
29.511
29.306
22.691
14.117

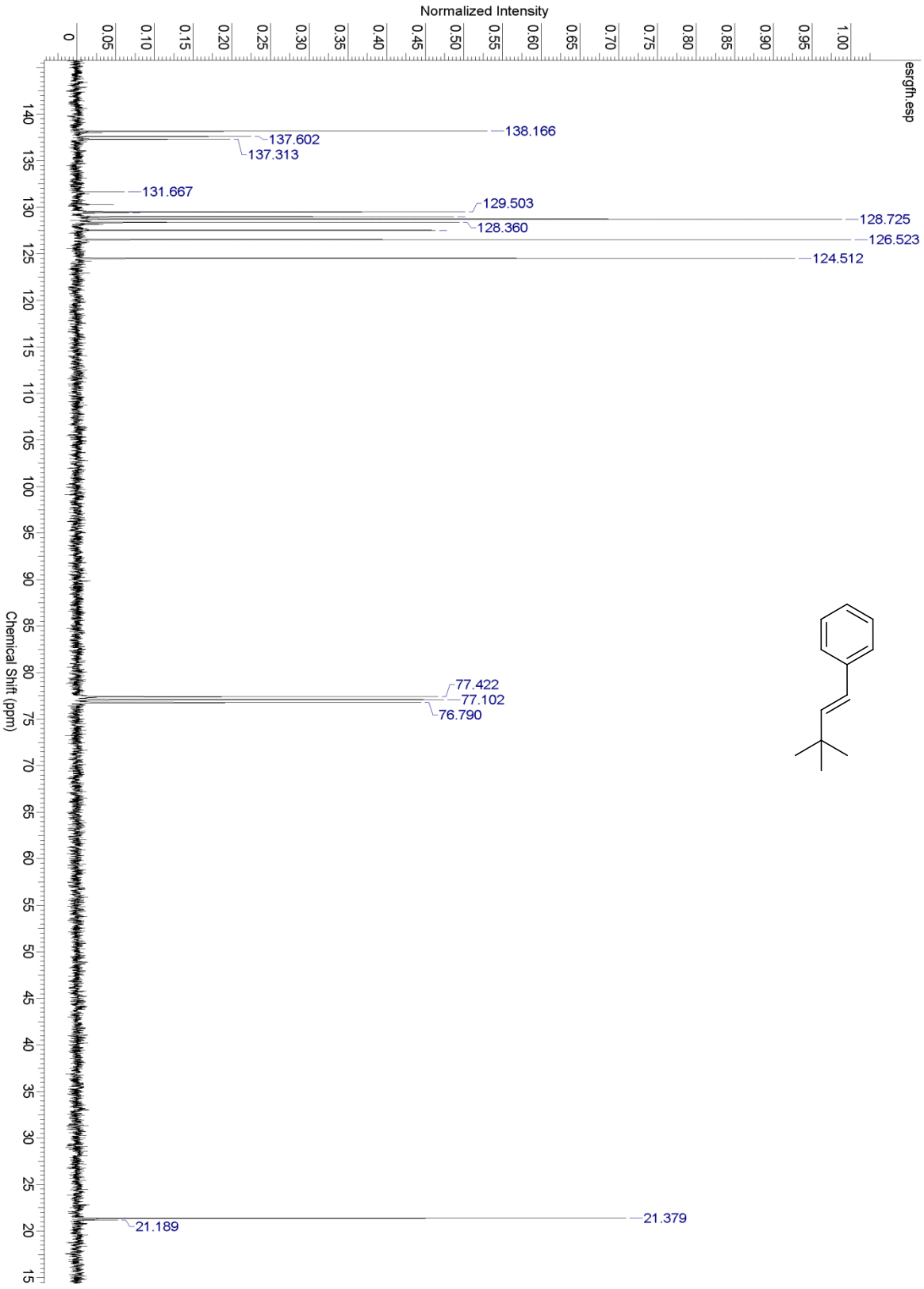
(E)-4-methyl-1-phenylpent-1-ene, 4



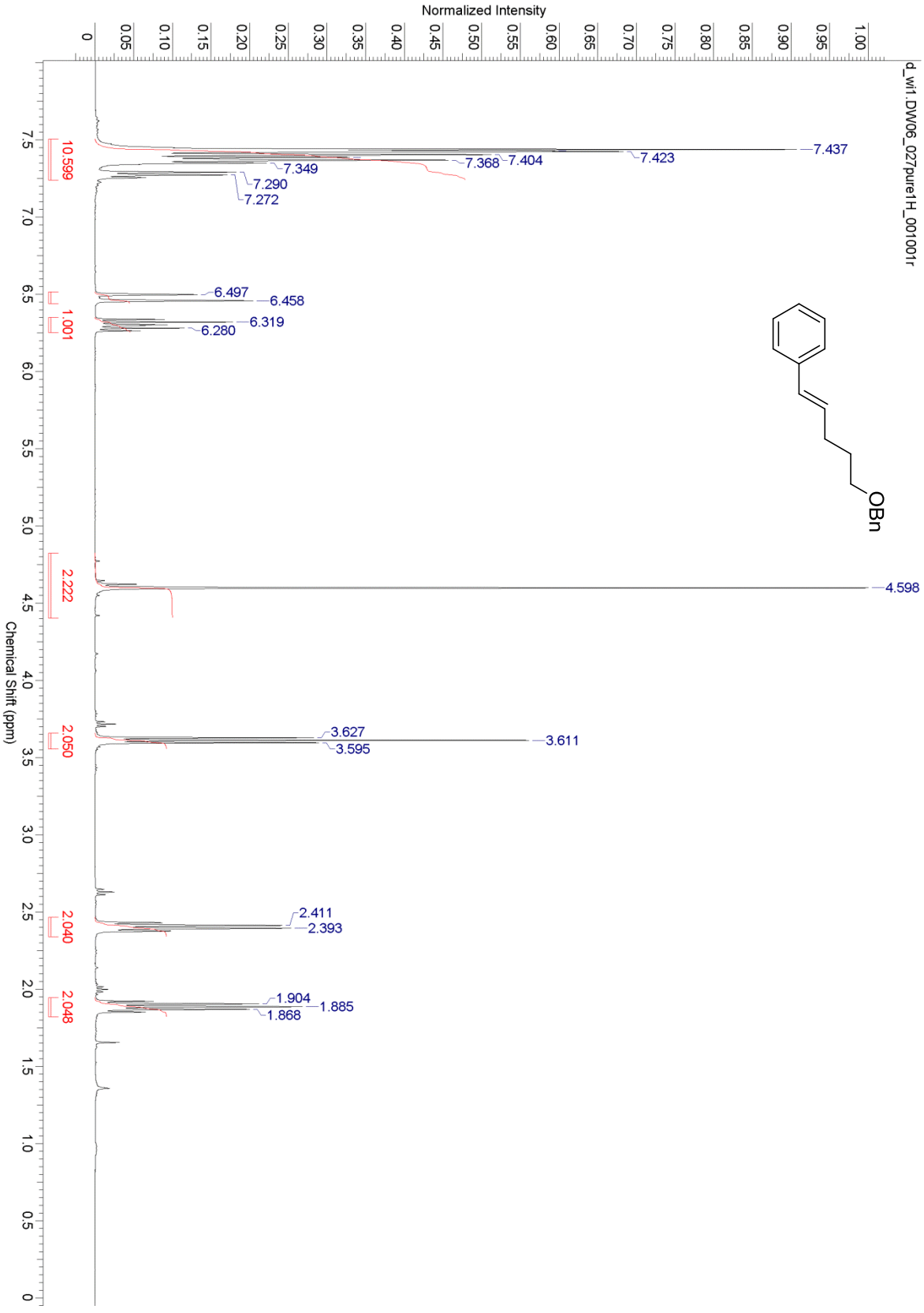

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
PA08-77-1 13C.ESP
Chemical Shift (ppm)
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
137.92
130.83
129.81
128.43
126.75
125.93
77.32
77.00
76.69
42.42
28.59
22.37

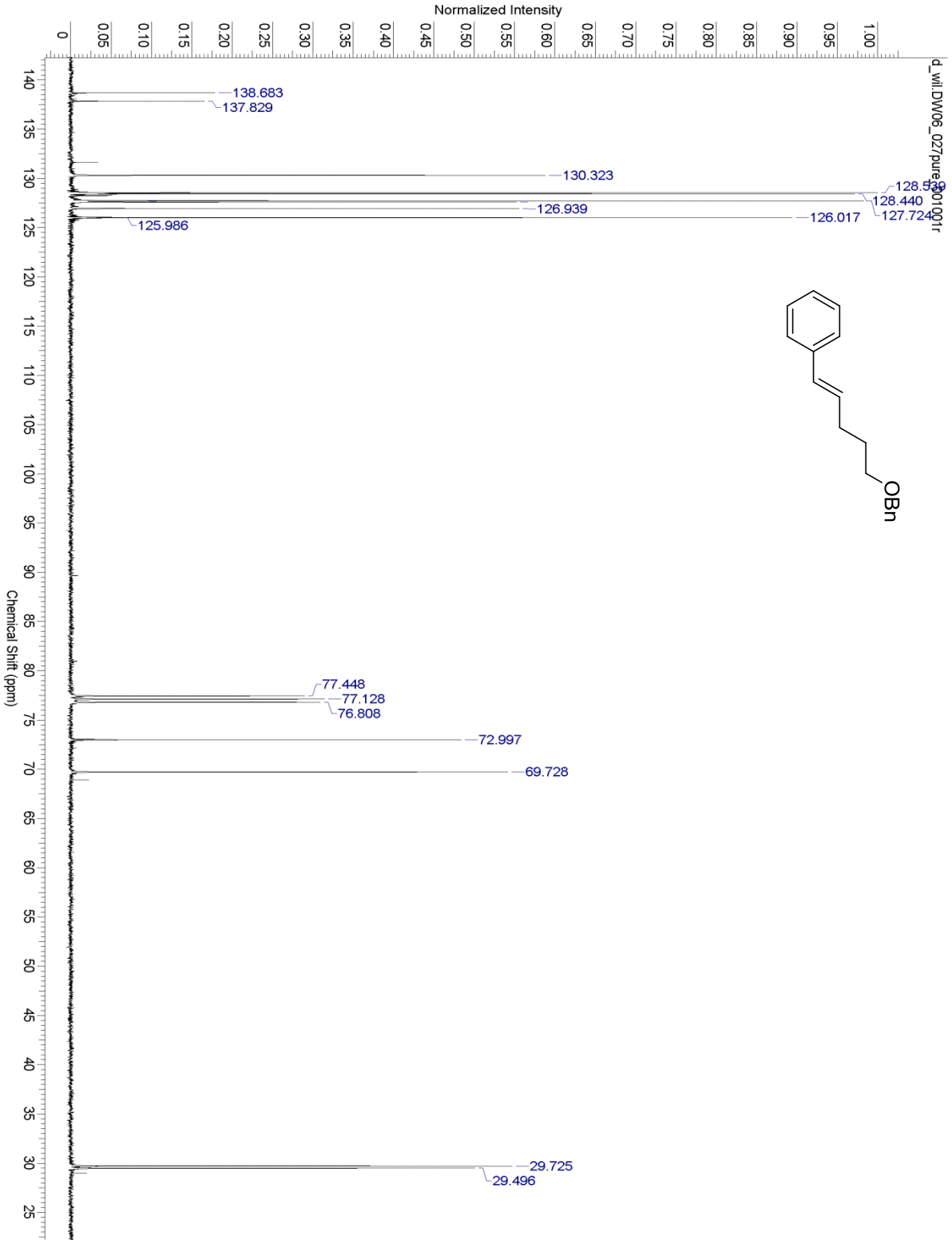
(E)-3,3-dimethyl-1-phenylbut-1-ene, 5



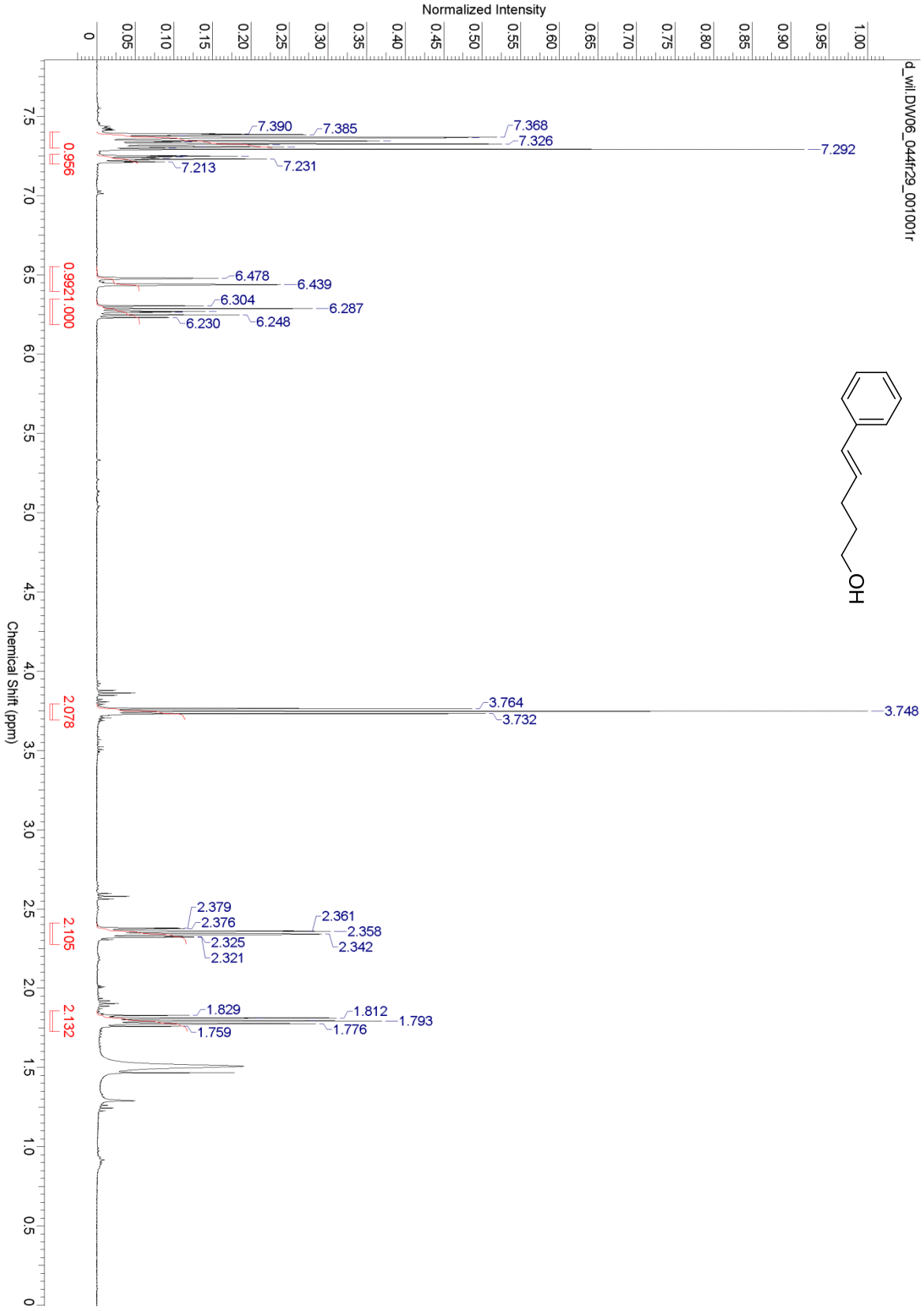

Normalized Intensity
esrgfh.esp
Chemical Shift (ppm)
138.166
137.602
137.313
131.667
129.503
128.725
128.360
126.523
124.512
77.422
77.102
76.790
21.379
21.189

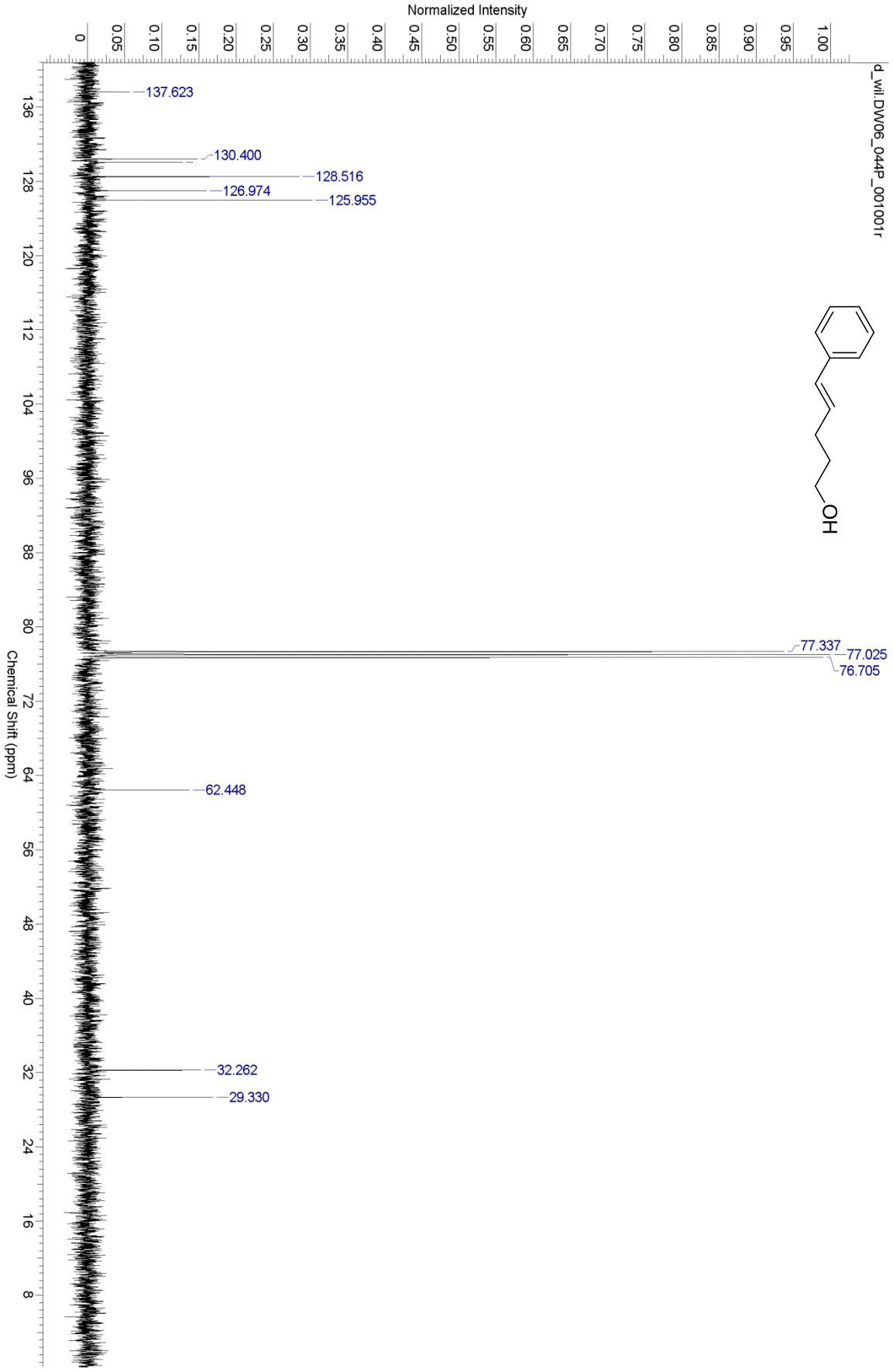
(E)-(5-(benzyloxy)pent-1-en-1-yl)benzene, 6



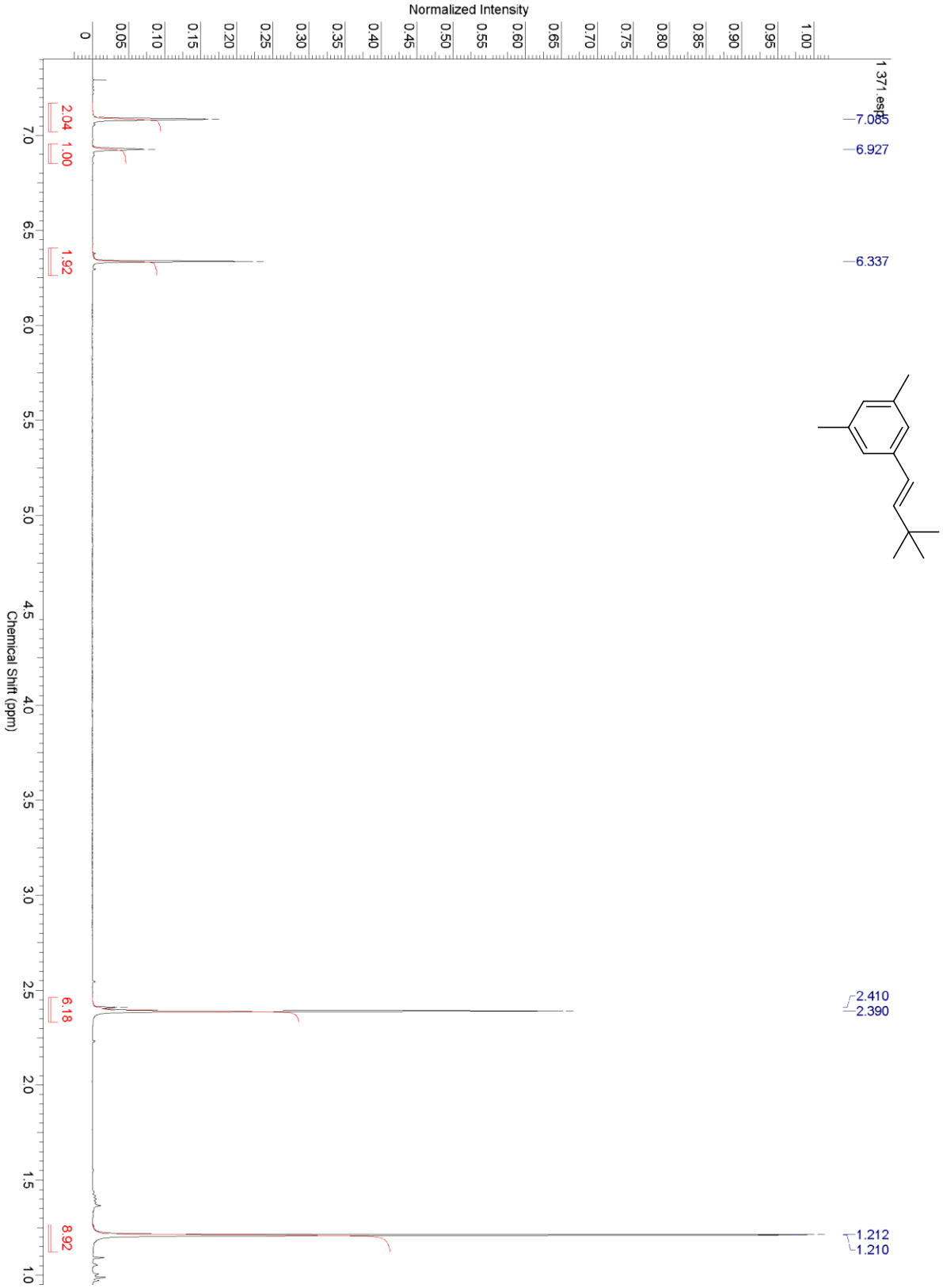

Normalized Intensity
Chemical Shift (ppm)
d_wil.DW06_027pure_20101001r
138.683
137.829
130.323
128.440
126.939
127.724
126.017
125.986
77.448
77.128
76.808
72.997
69.728
29.725
29.496
OBn

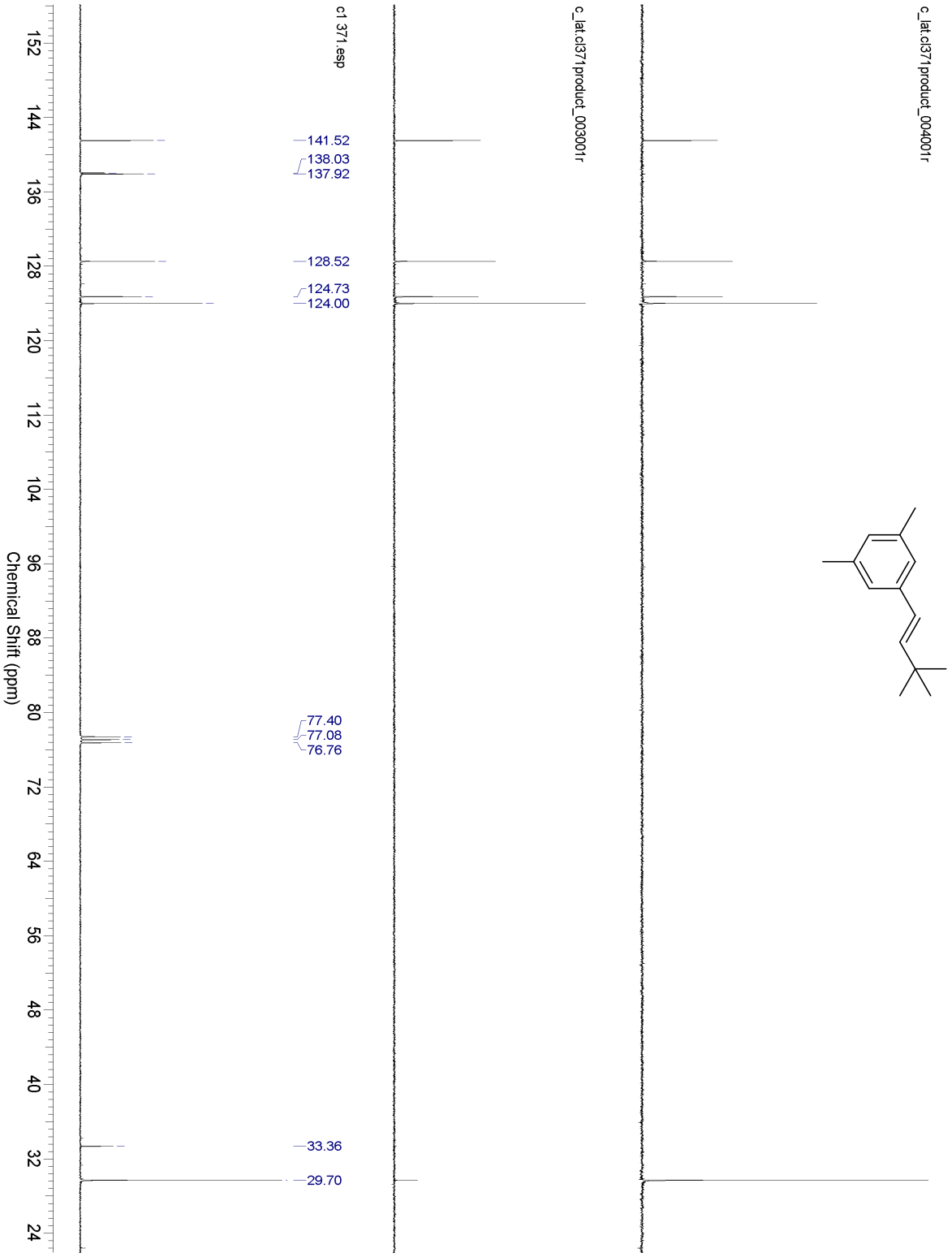
(E)-5-phenylpent-4-en-1-ol, 7



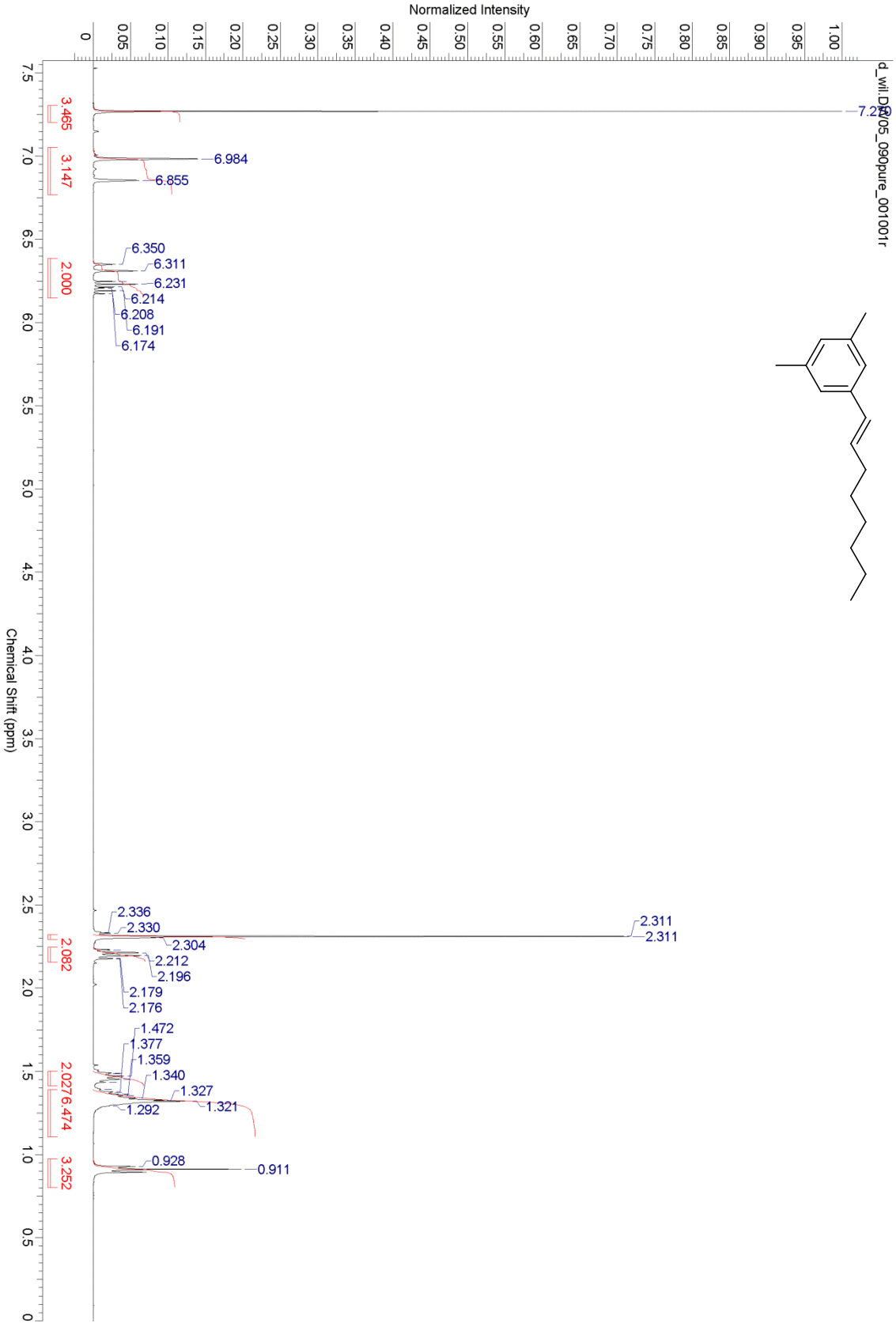

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wil.DW06_044P_001001r
137.623
130.400
128.516
126.974
125.955
77.337
77.025
76.705
62.448
32.262
29.330
OH
Chemical Shift (ppm)
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8

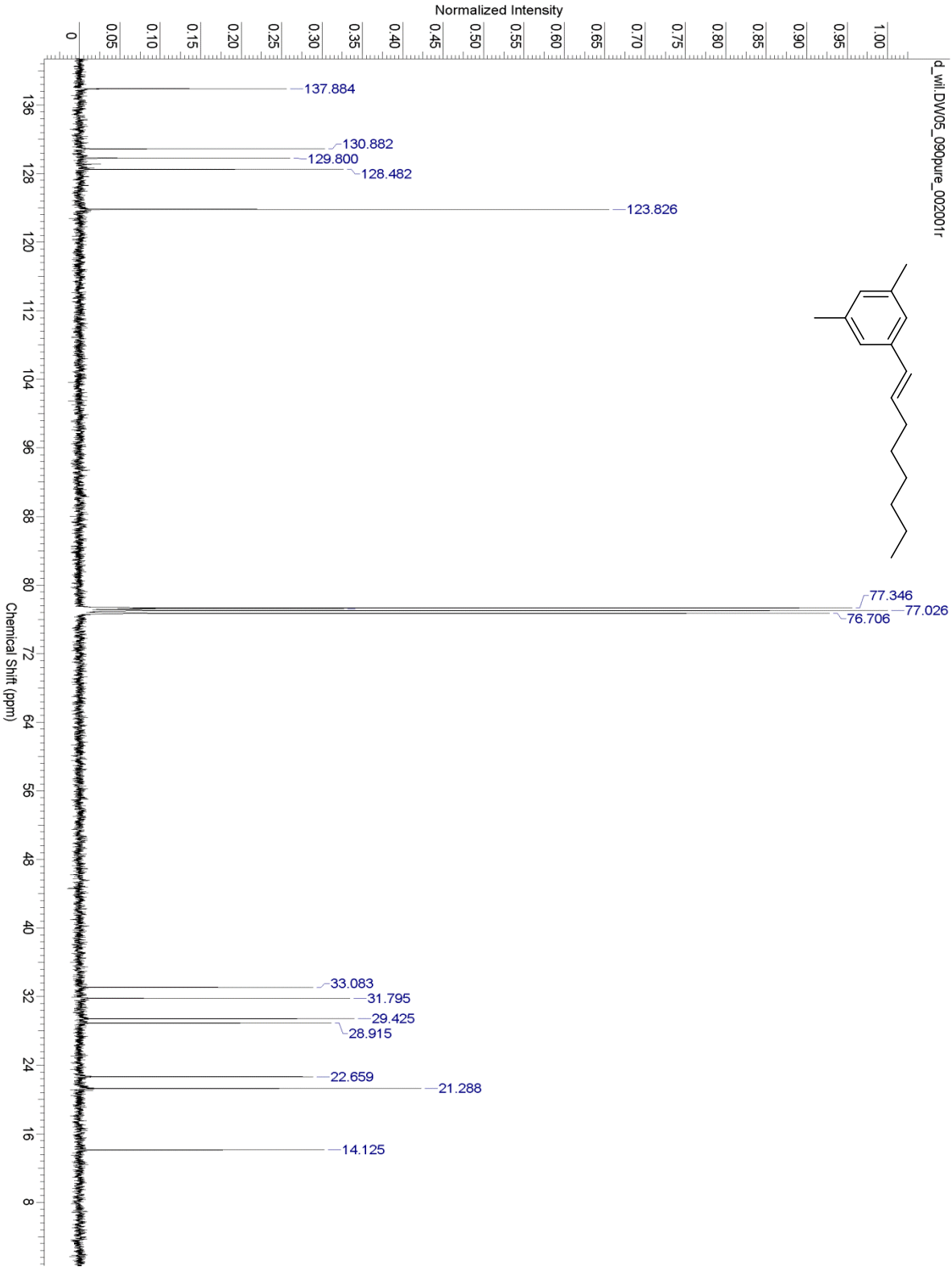
(E)-1-(3,3-dimethylbut-1-en-1-yl)-3,5-dimethylbenzene, 8



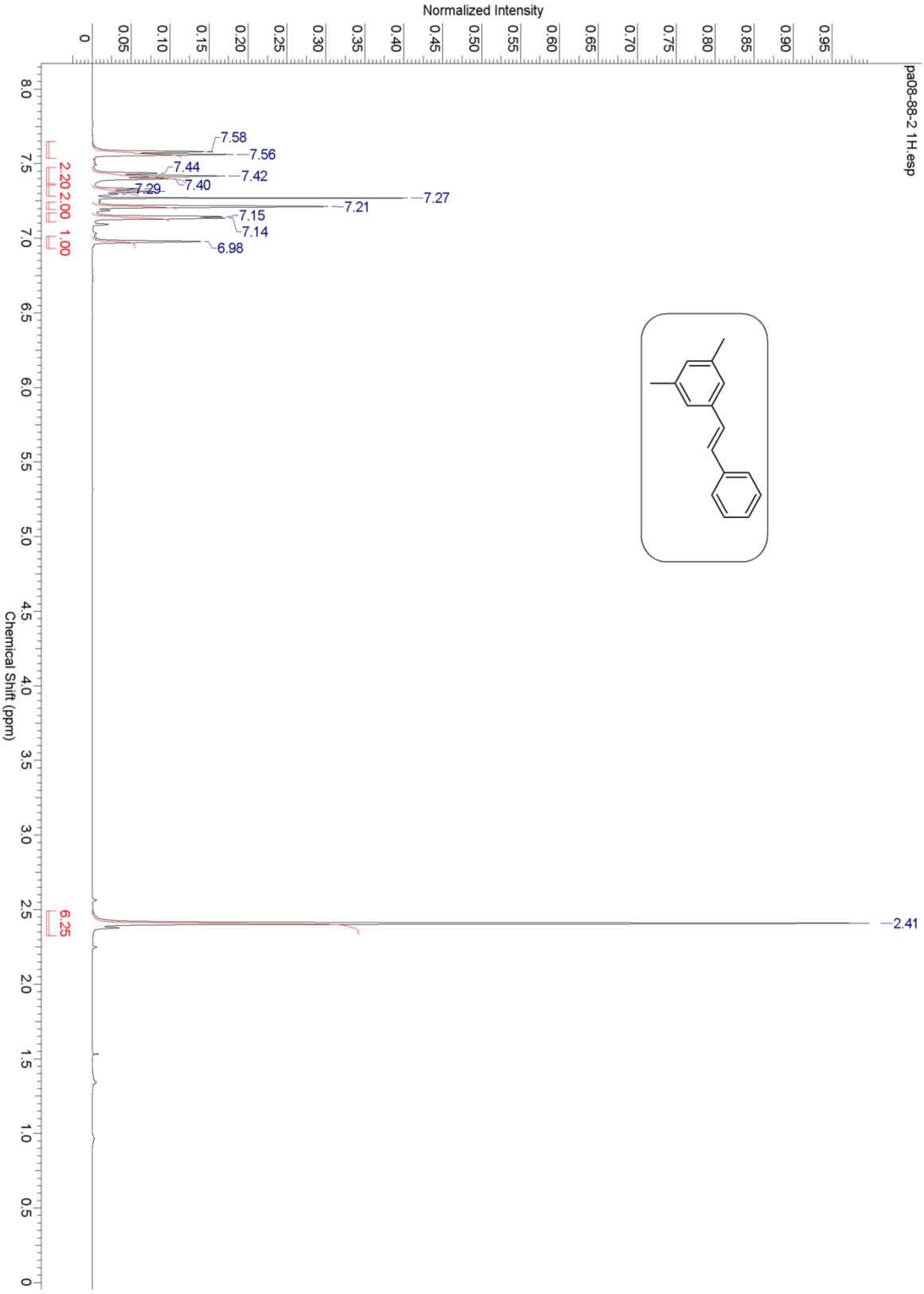

c1 371.esp
c_lat.c1371product_003001r
c_lat.c1371product_004001r
141.52
138.03
137.92
128.52
124.73
124.00
77.40
77.08
76.76
33.36
29.70
Chemical Shift (ppm)
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24

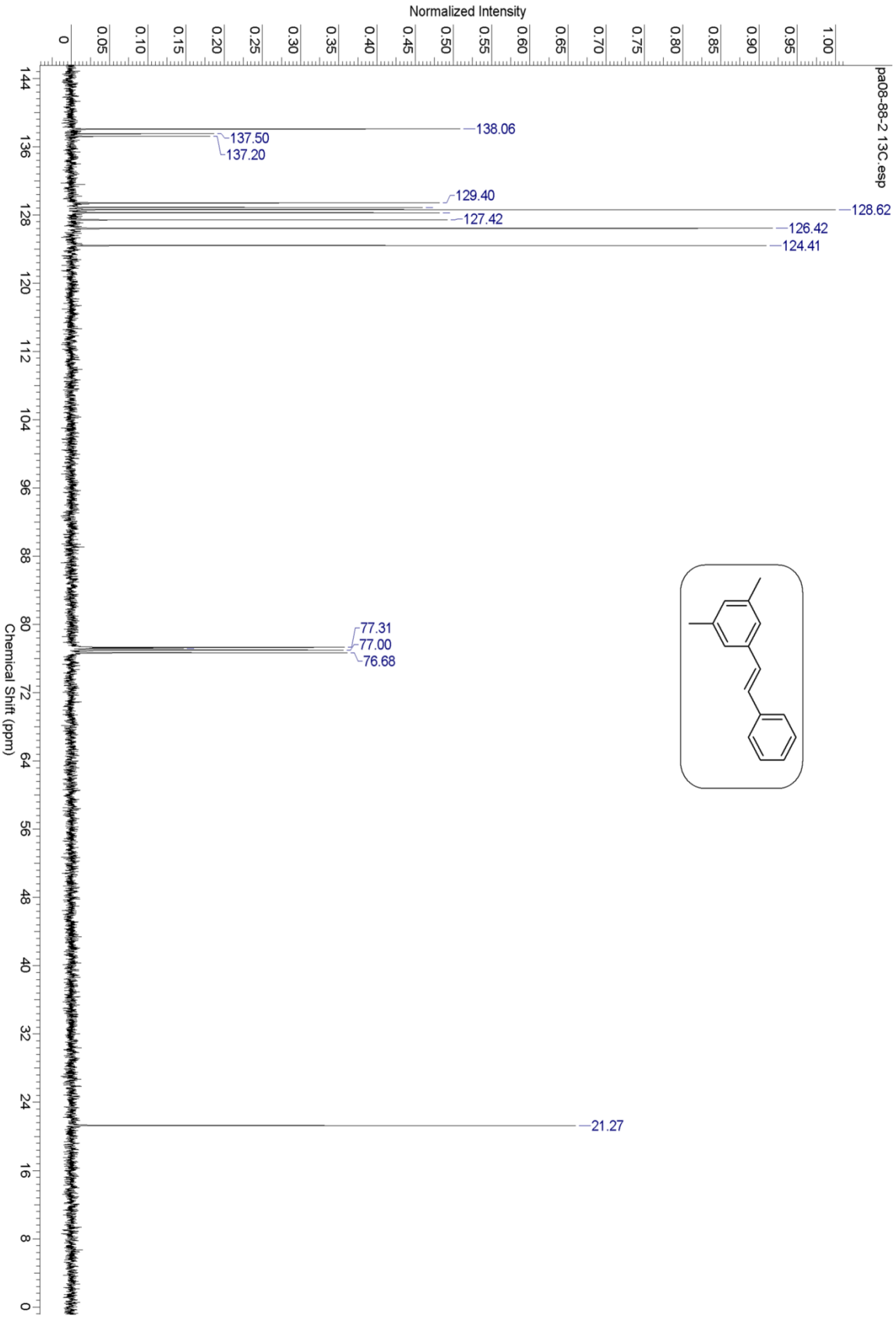
(E)-1,3-dimethyl-5-(oct-1-en-1-yl)benzene, 9



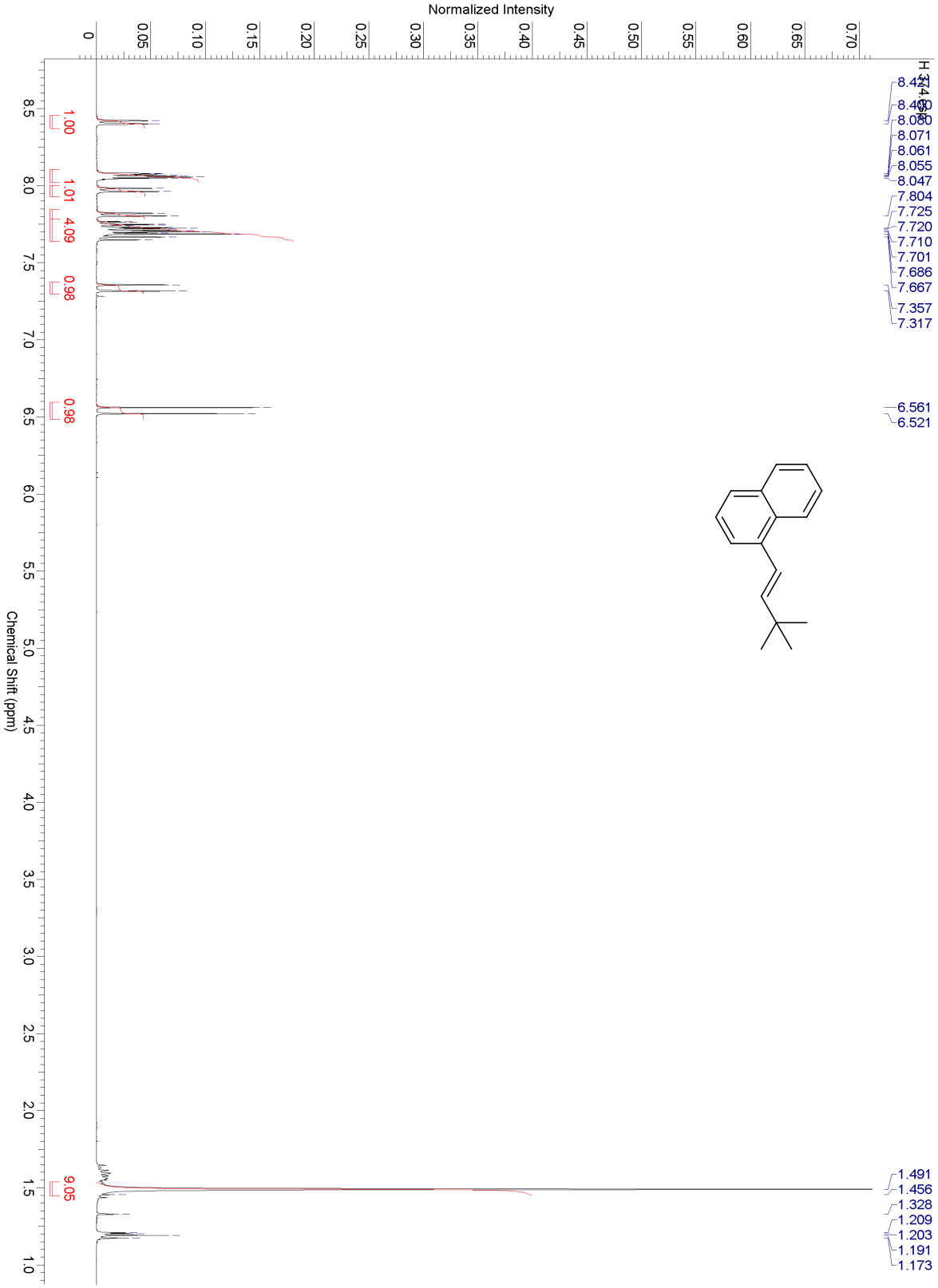

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wil.DW05_090pure_002001r
Chemical Shift (ppm)
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
137.884
130.882
129.800
128.482
123.826
77.346
77.026
76.706
33.083
31.795
29.425
28.915
22.659
21.288
14.125

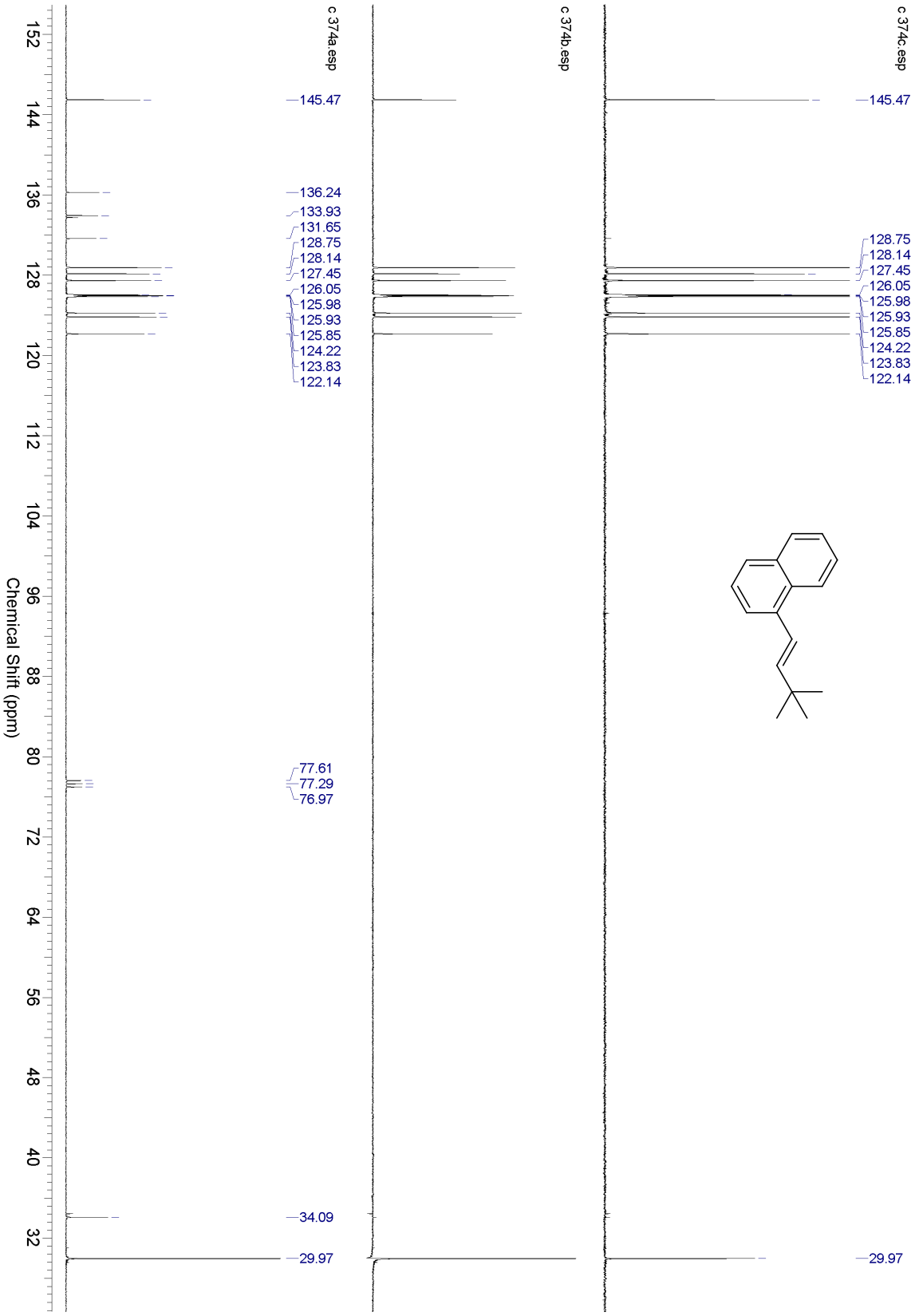
(E)-1,3-dimethyl-5-styrylbenzene, 10



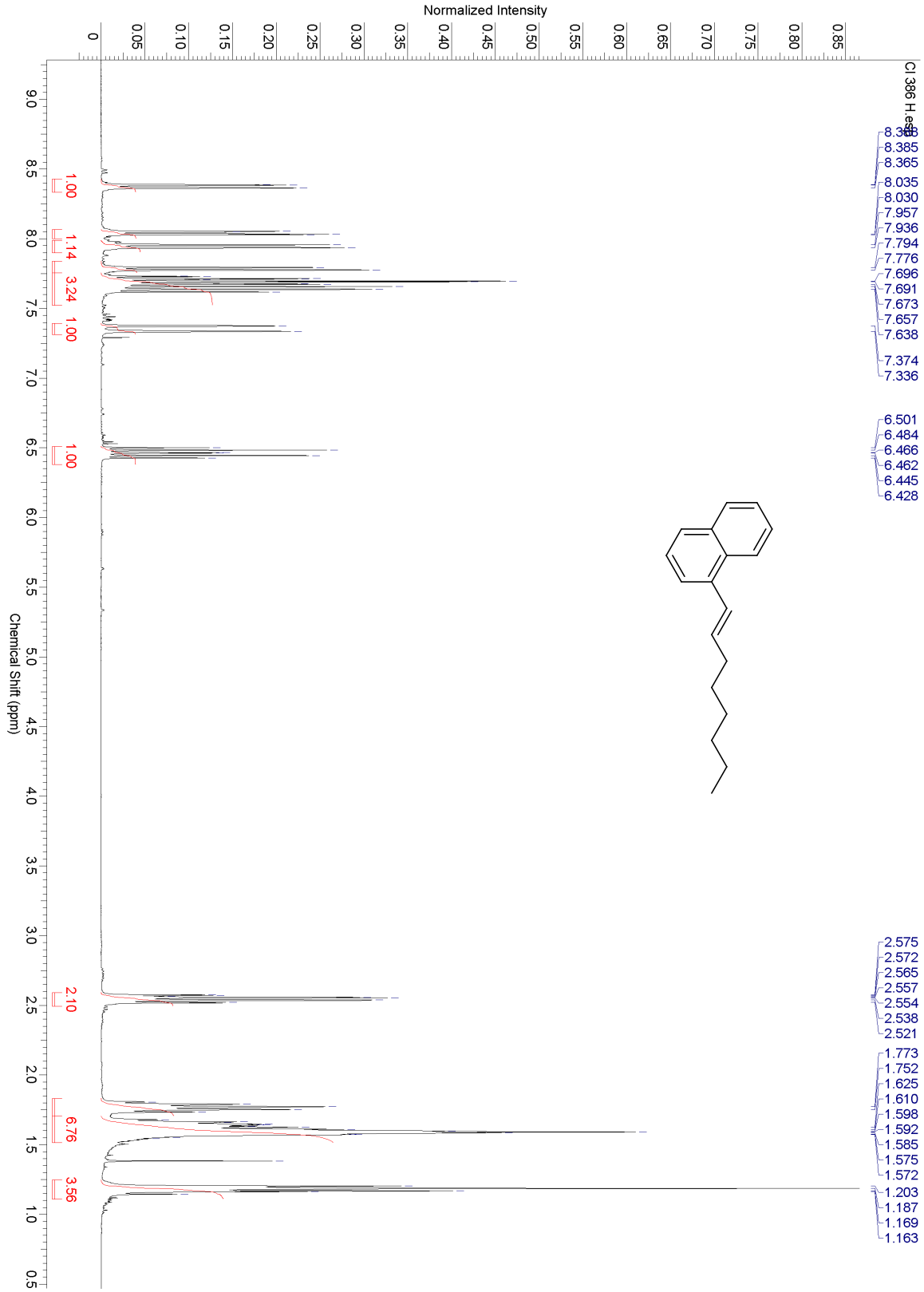

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
pa08-88-2 13C.esp
138.06
137.50
137.20
129.40
128.62
127.42
126.42
124.41
77.31
77.00
76.68
21.27
Chemical Shift (ppm)
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0

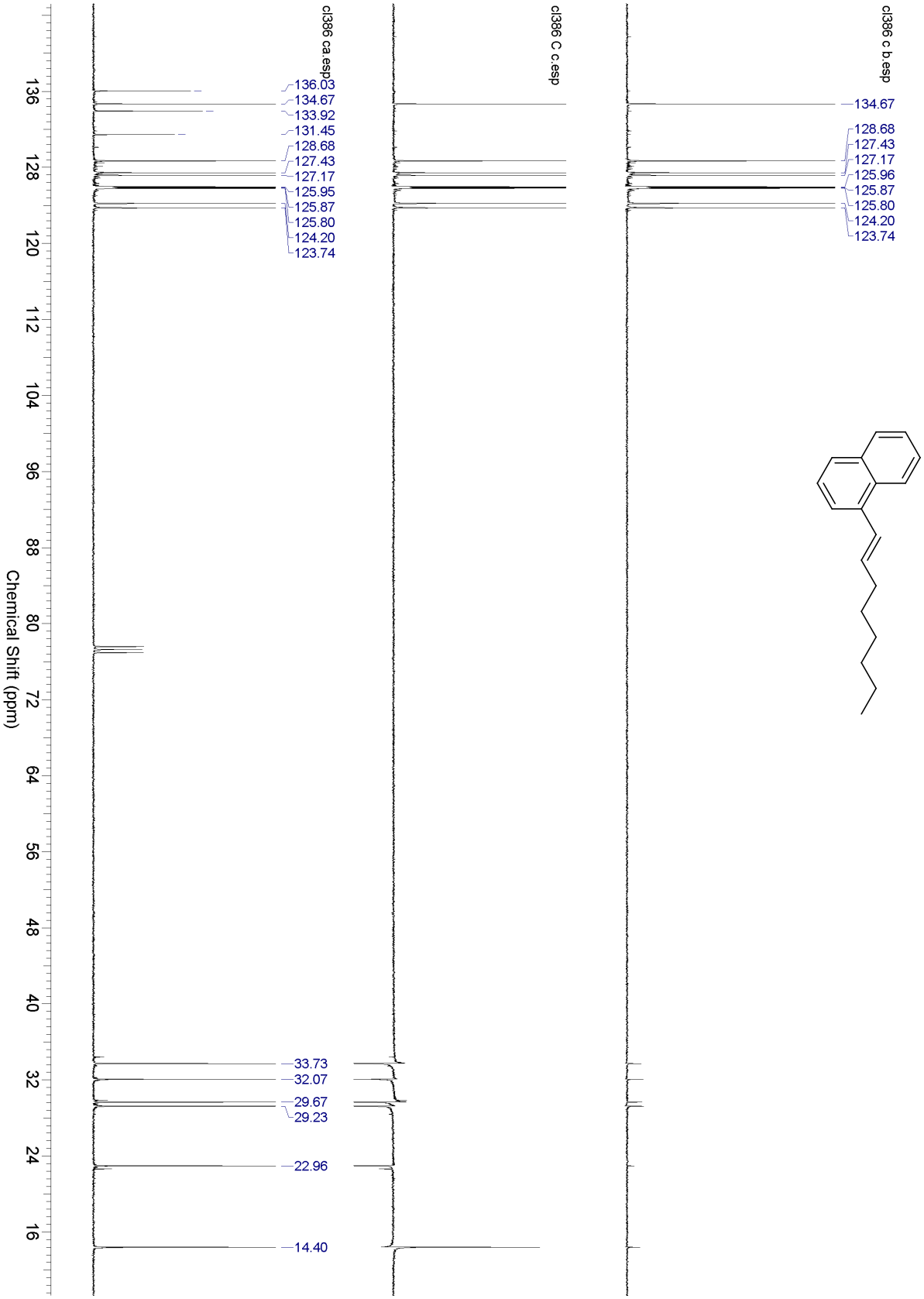
(E)-1-(3,3-dimethylbut-1-en-1-yl)naphthalene, 11



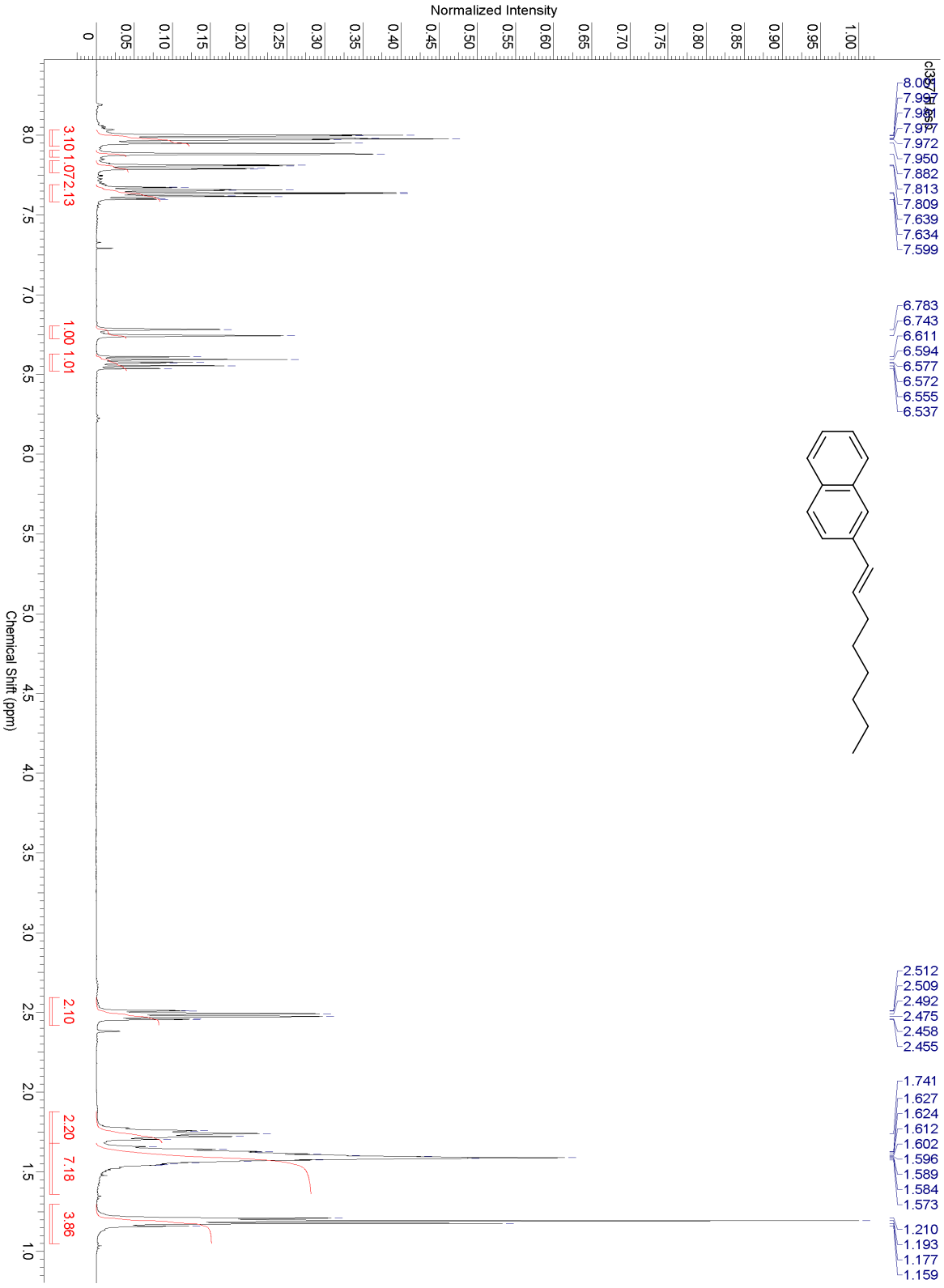

c 374a.esp
c 374b.esp
c 374c.esp
Chemical Shift (ppm)
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
145.47
136.24
133.93
131.65
128.75
128.14
127.45
126.05
125.98
125.93
125.85
124.22
123.83
122.14
77.61
77.29
76.97
34.09
29.97

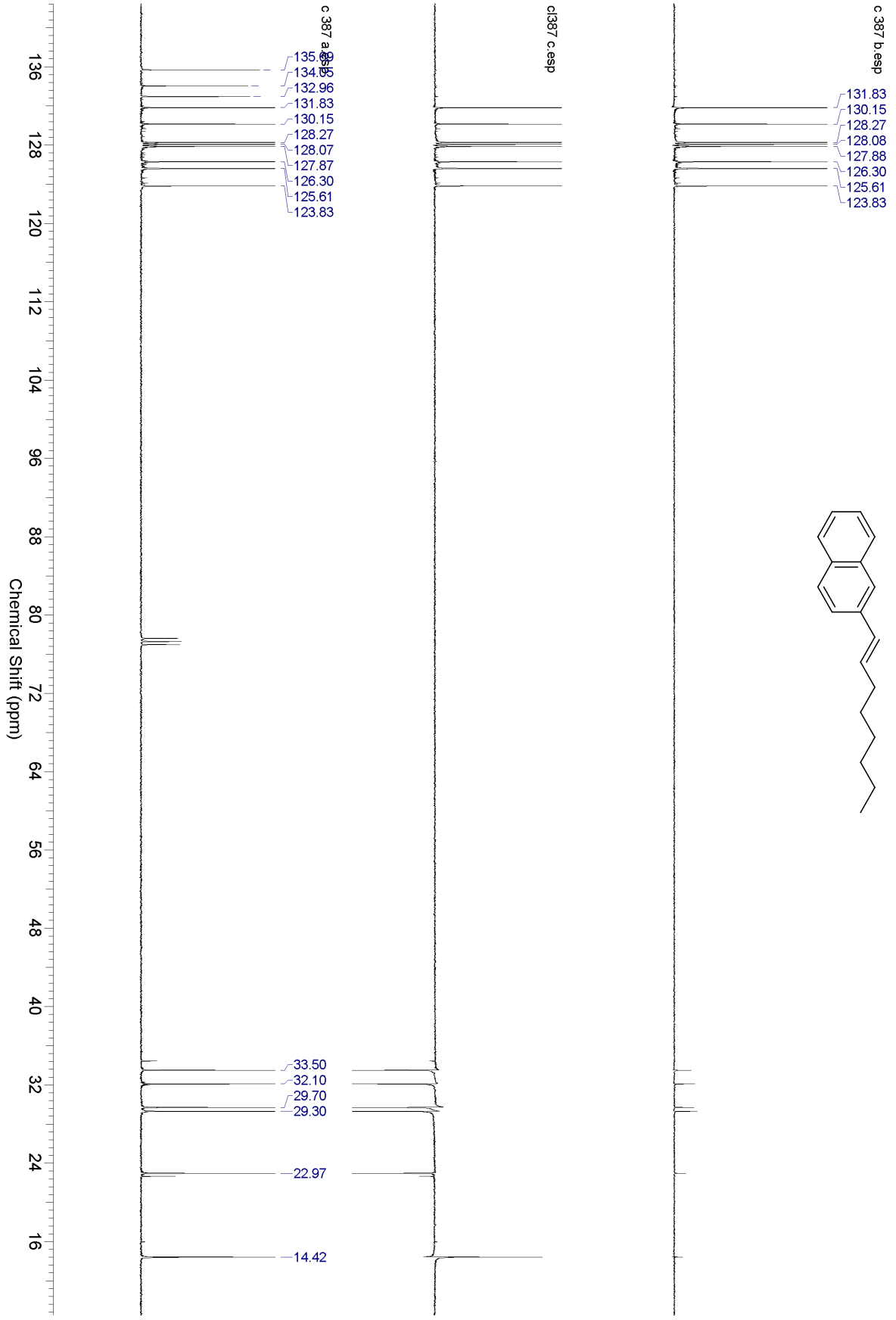
(E)-1-(oct-1-en-1-yl)naphthalene, 12



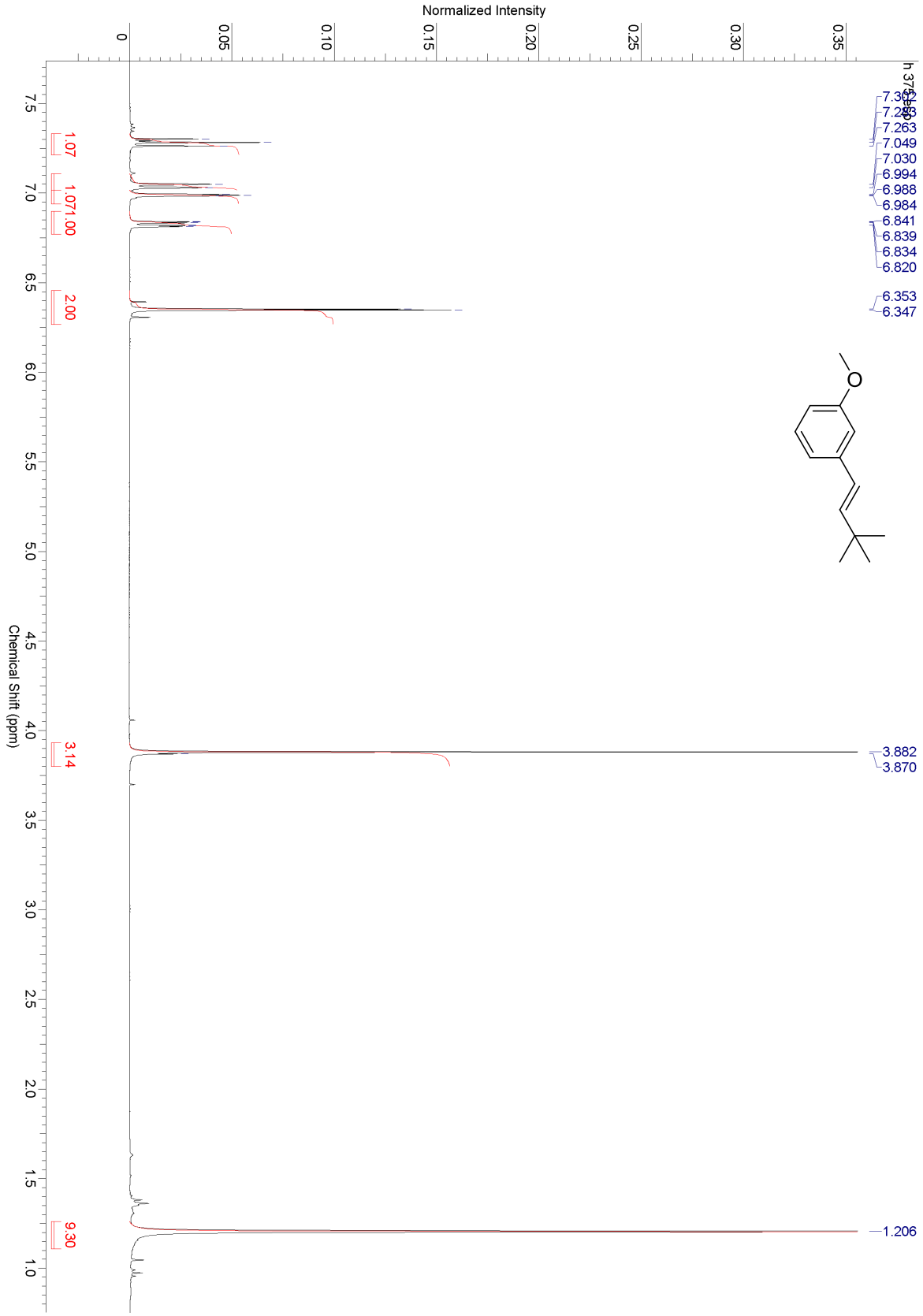

cl386 ca.esp
136.03
134.67
133.92
131.45
128.68
127.43
127.17
125.95
125.87
125.80
124.20
123.74
33.73
32.07
29.67
29.23
22.96
14.40
cl386 C c.esp
cl386 c b.esp
134.67
128.68
127.43
127.17
125.96
125.87
125.80
124.20
123.74
Chemical Shift (ppm)
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16

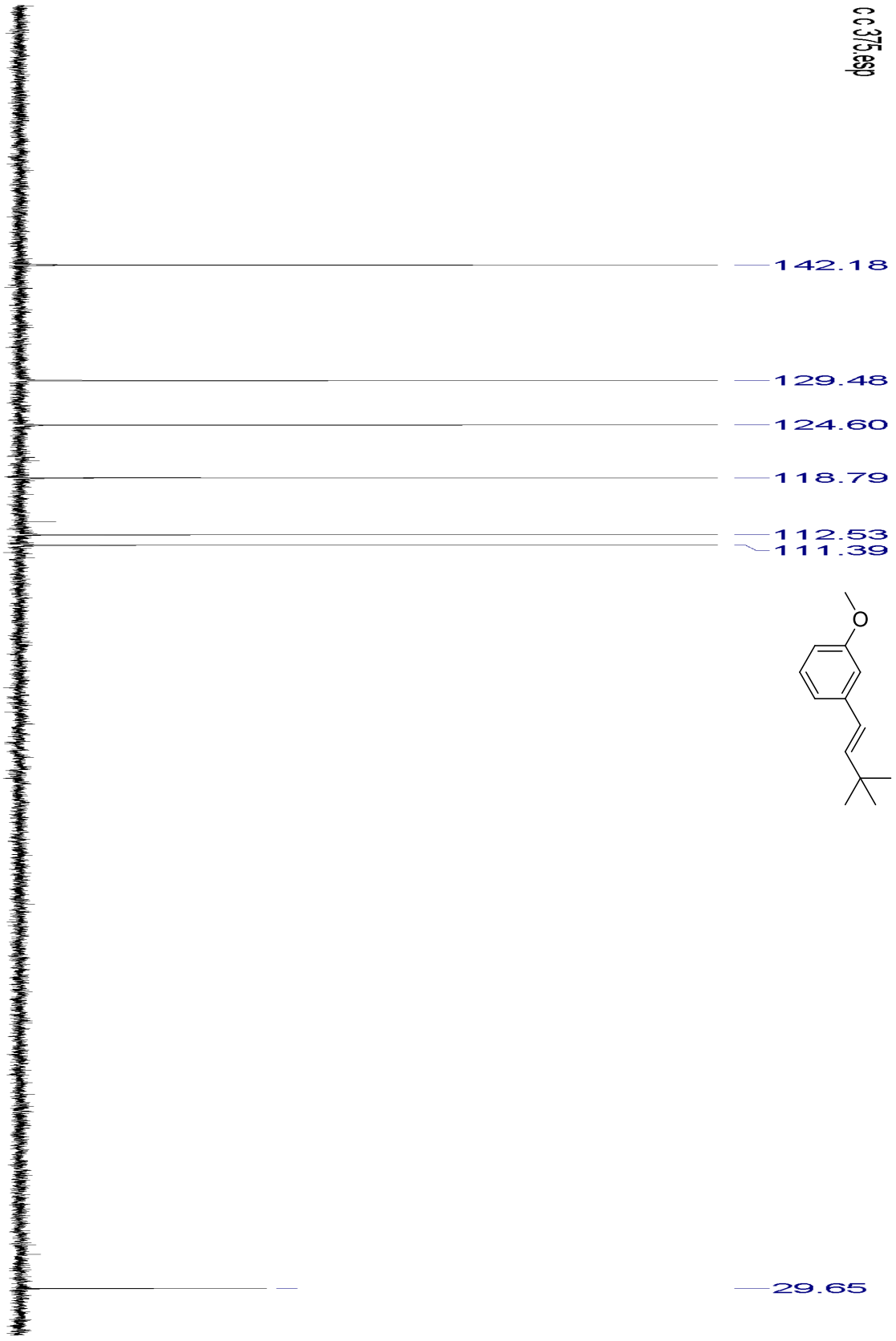
(E)-2-(oct-1-en-1-yl)naphthalene, 13



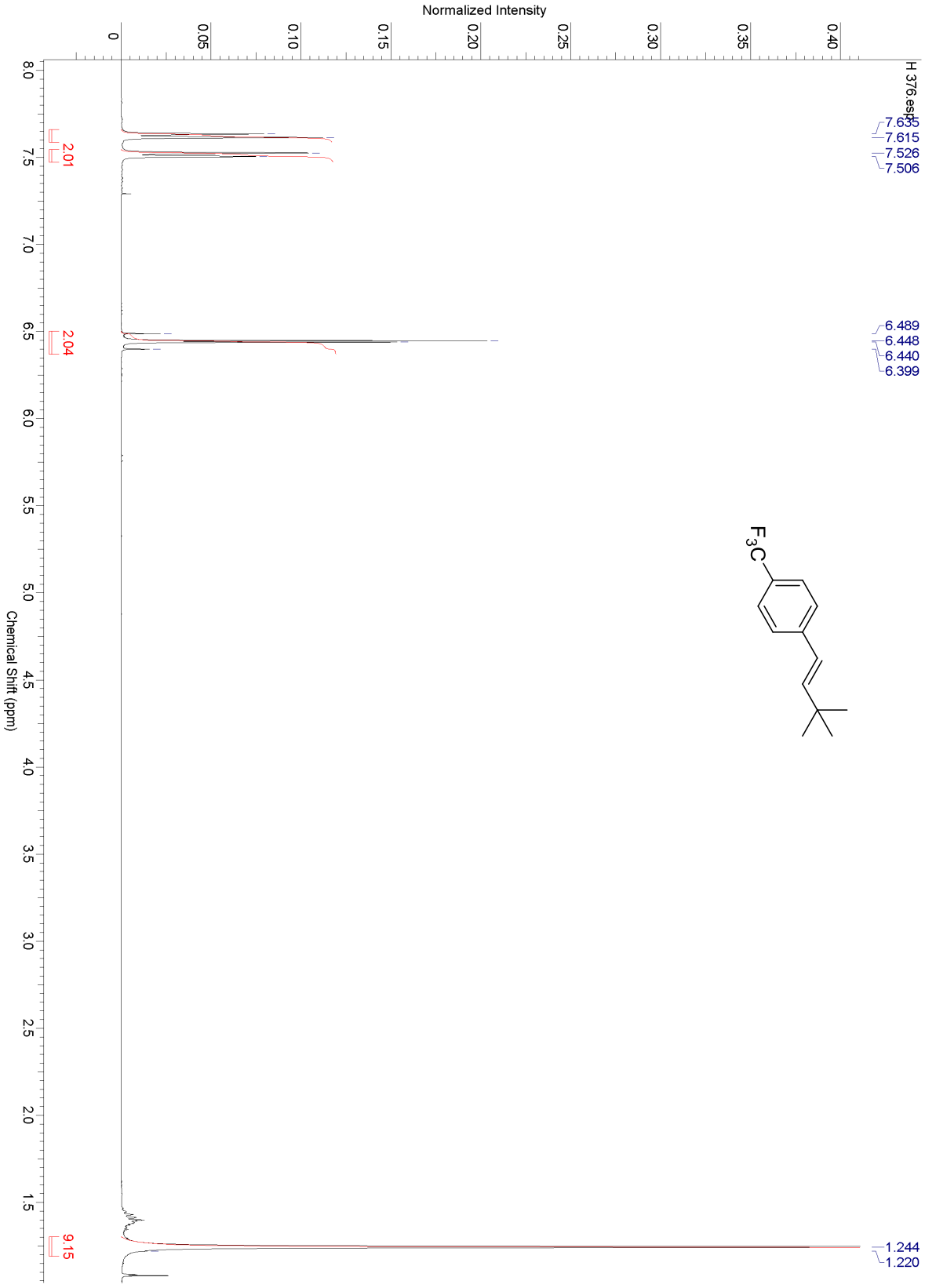

c 387 a.esp
135.89
134.95
132.96
131.83
130.15
128.27
128.07
127.87
126.30
125.61
123.83
33.50
32.10
29.70
29.30
22.97
14.42
cl387 c.esp
c 387 b.esp
131.83
130.15
128.27
128.08
127.88
126.30
125.61
123.83
Chemical Shift (ppm)
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16

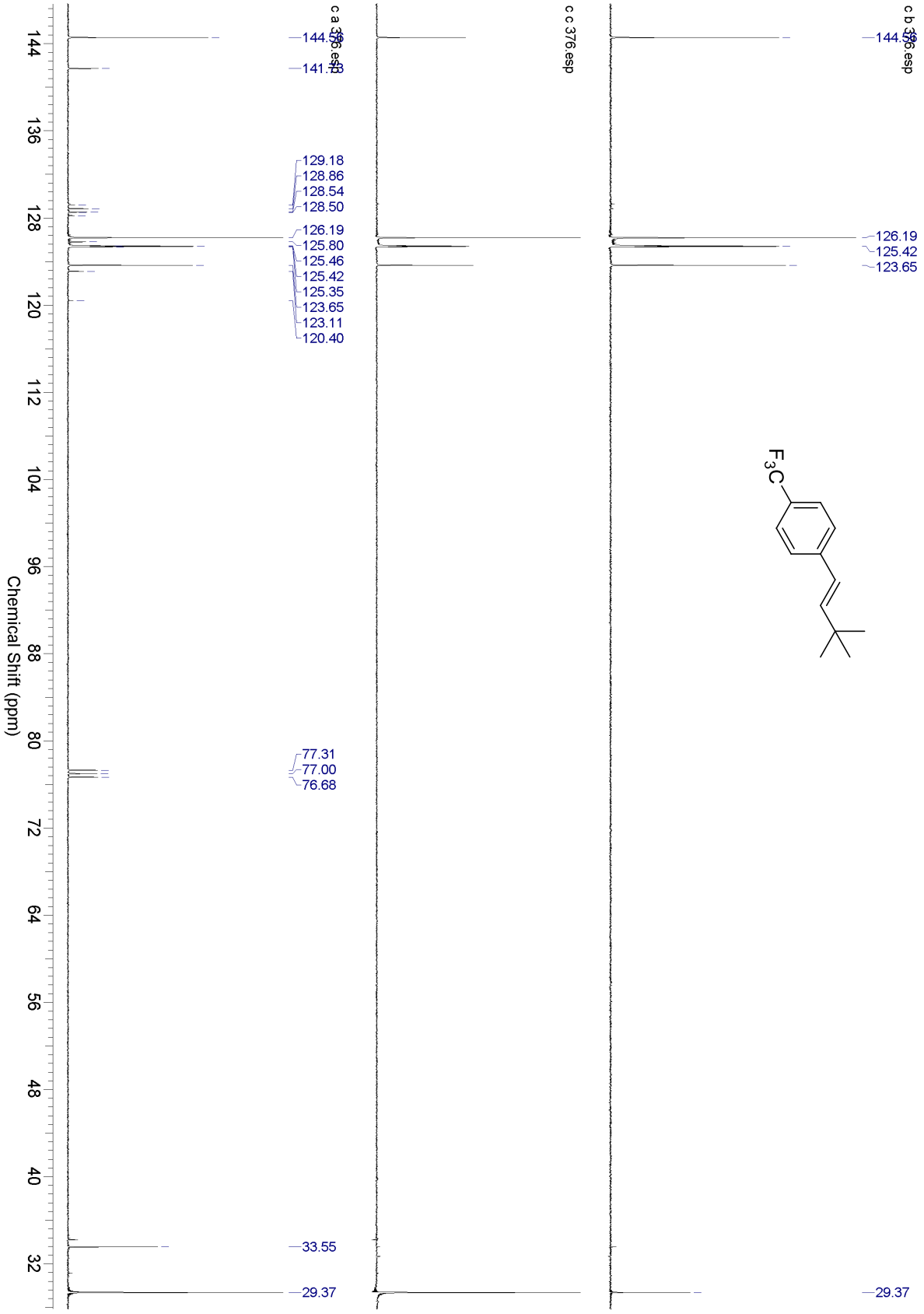
(E)-1-(3,3-dimethylbut-1-en-1-yl)-3-methoxybenzene, 14

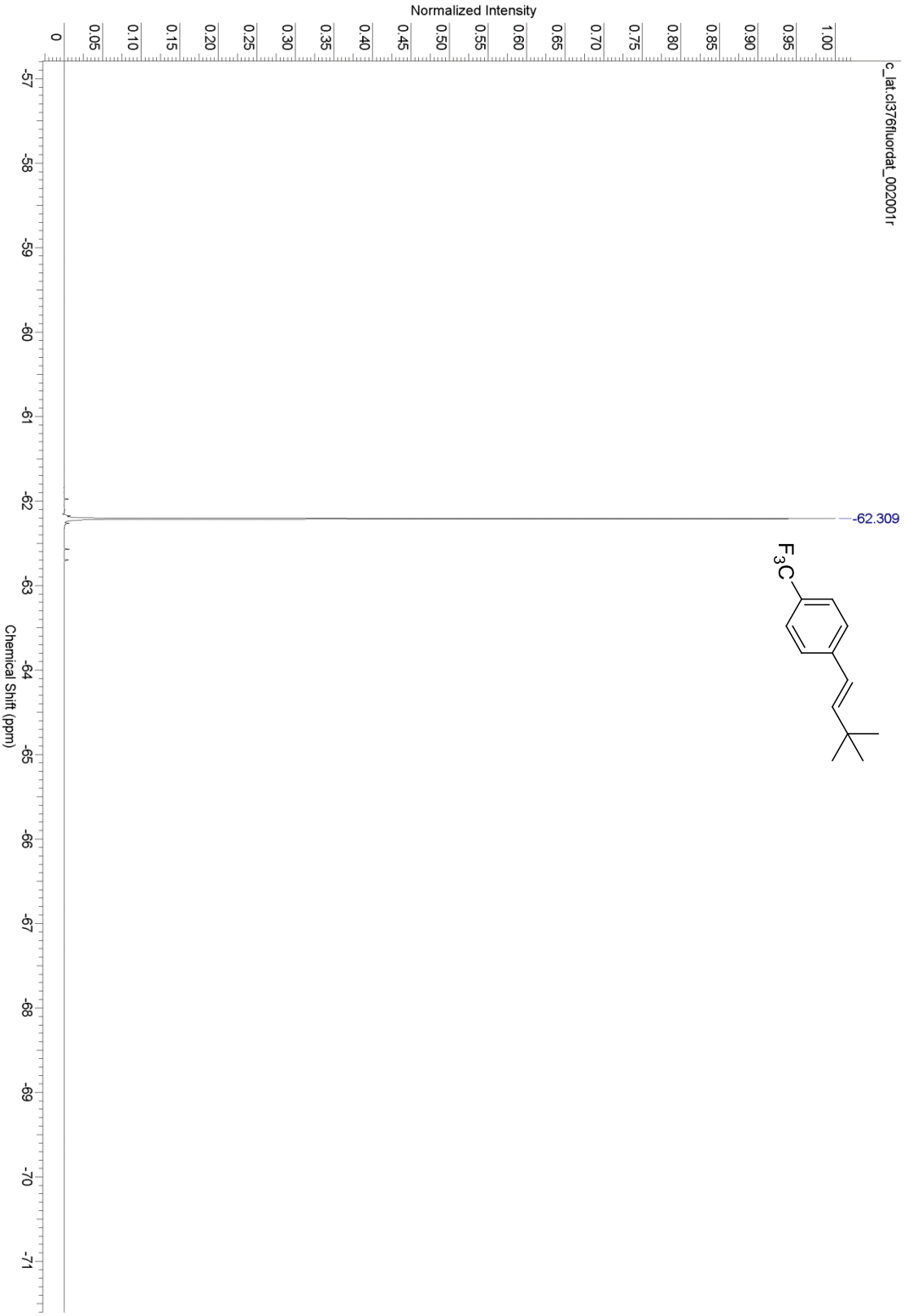



cc375.esp
142.18
129.48
124.60
118.79
112.53
111.39
O
29.65

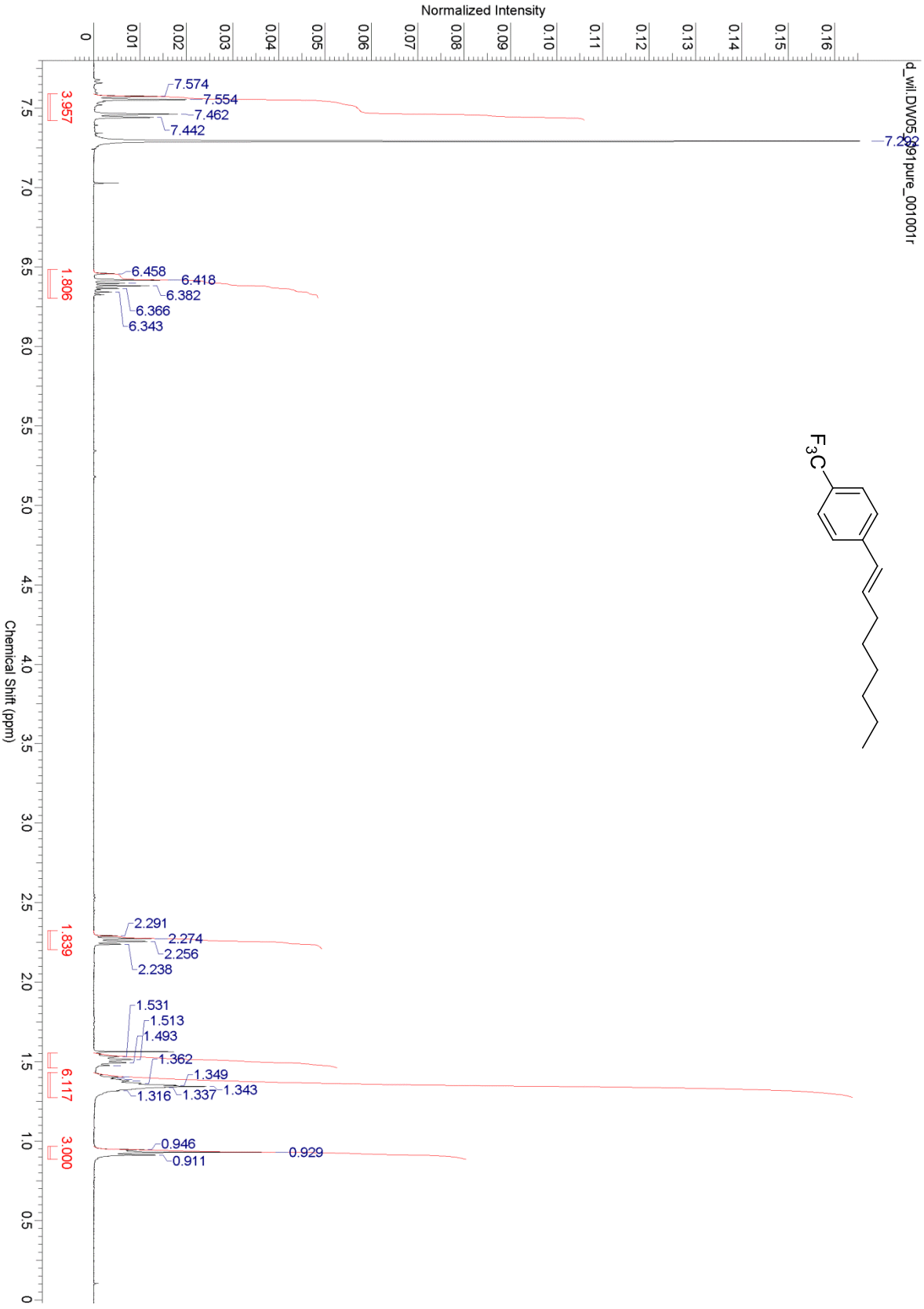
(E)-1-(3,3-dimethylbut-1-en-1-yl)-4-(trifluoromethyl)benzene, 15

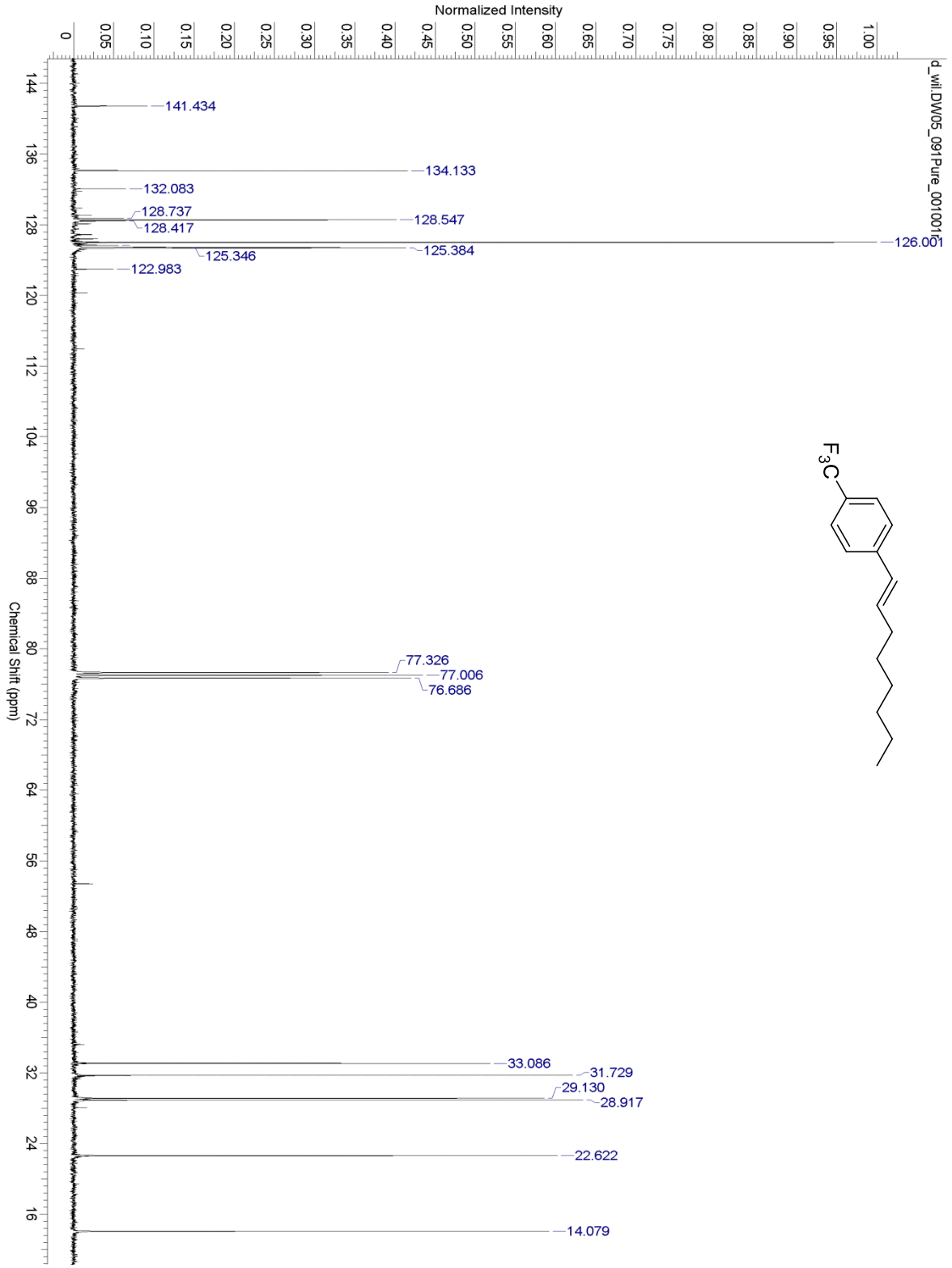


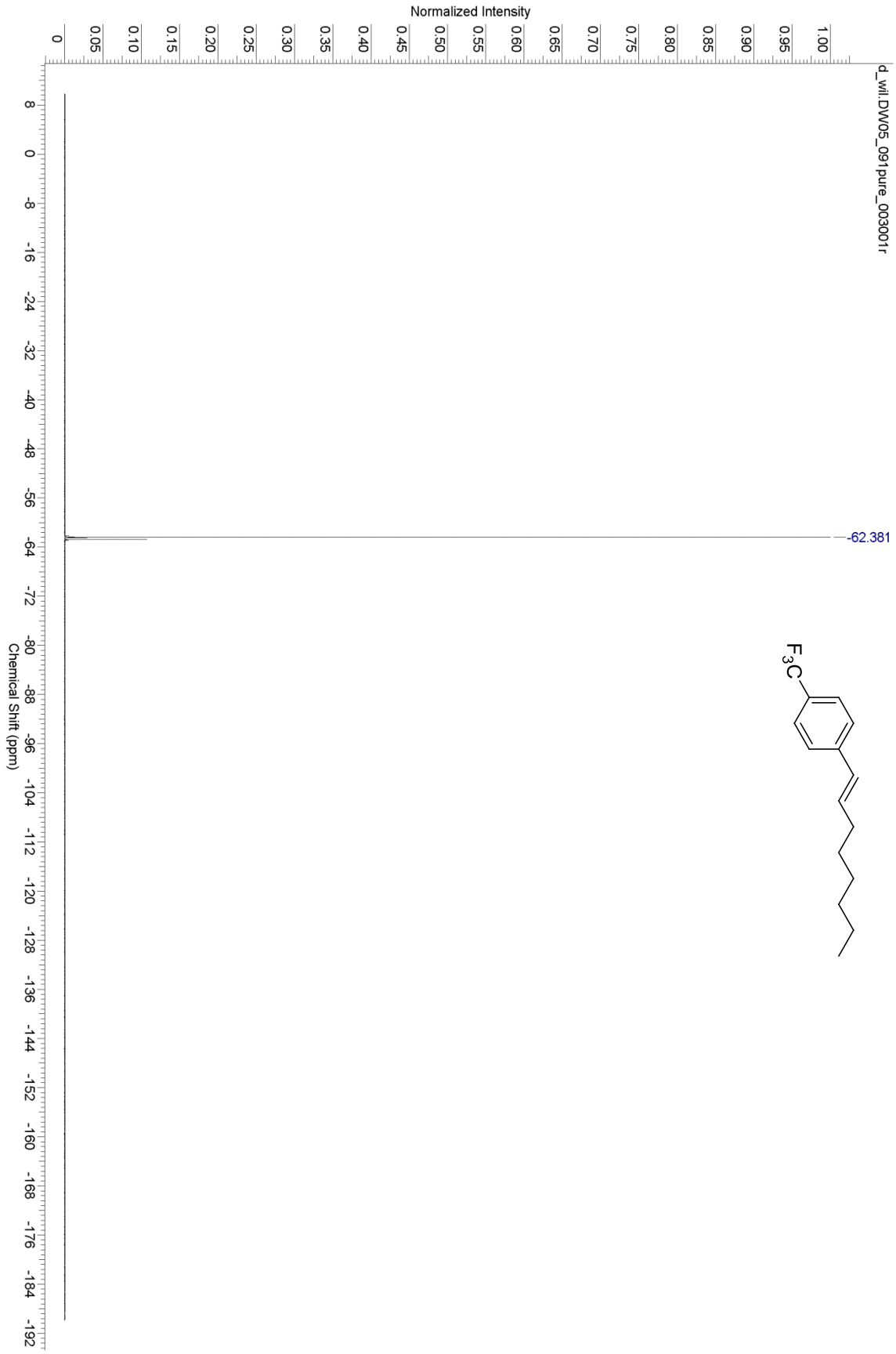

c a 376.esp
c c 376.esp
c b 376.esp
144.56
141.73
129.18
128.86
128.54
128.50
126.19
125.80
125.46
125.42
125.35
123.65
123.11
120.40
77.31
77.00
76.68
33.55
29.37
126.19
125.42
123.65
29.37
Chemical Shift (ppm)
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
F3C


Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
c_lat.cl376fluordat_002001r
-62.309
F3C
Chemical Shift (ppm)
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71

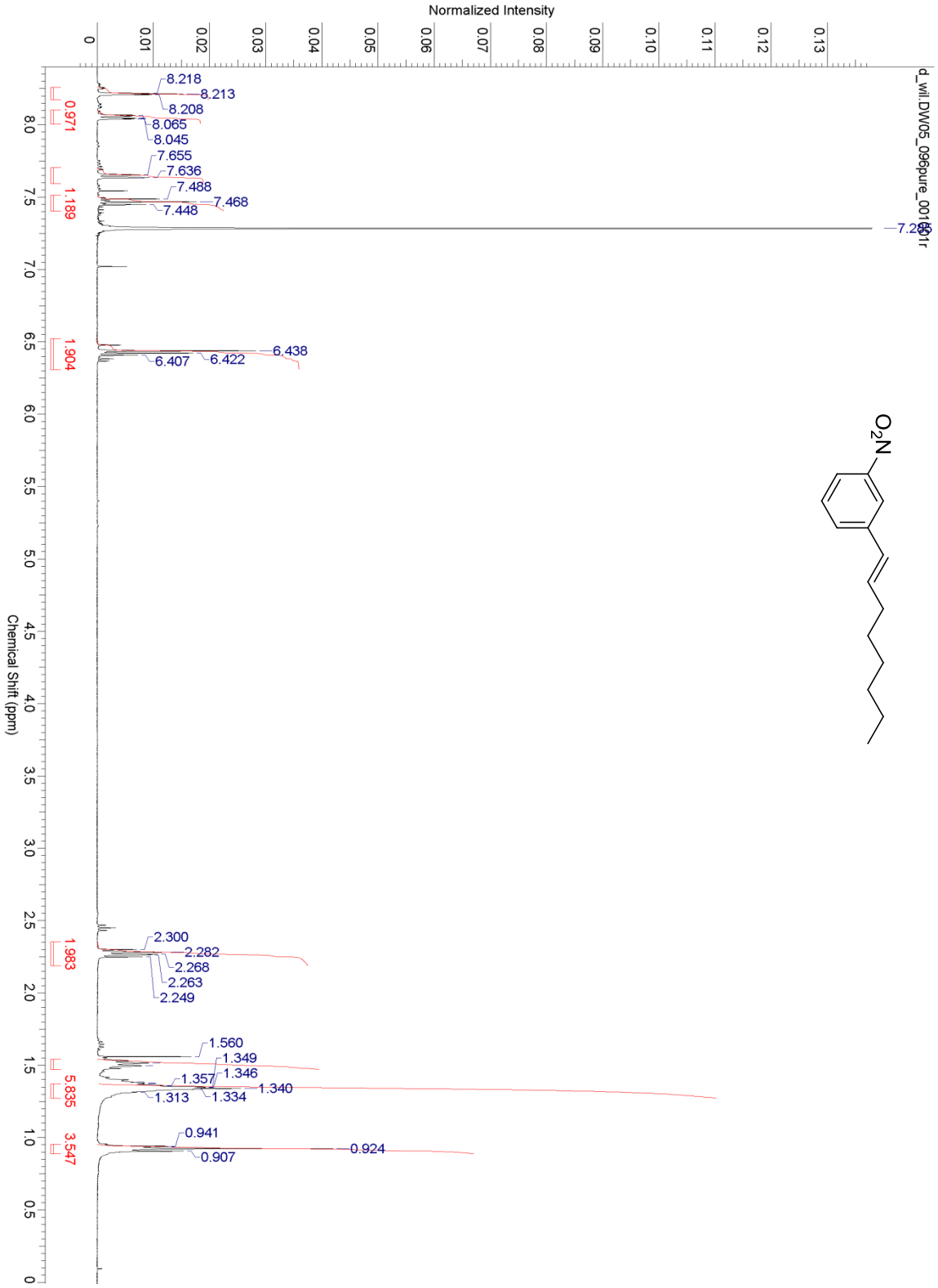
(E)-1-(oct-1-en-1-yl)-4-(trifluoromethyl)benzene, 16

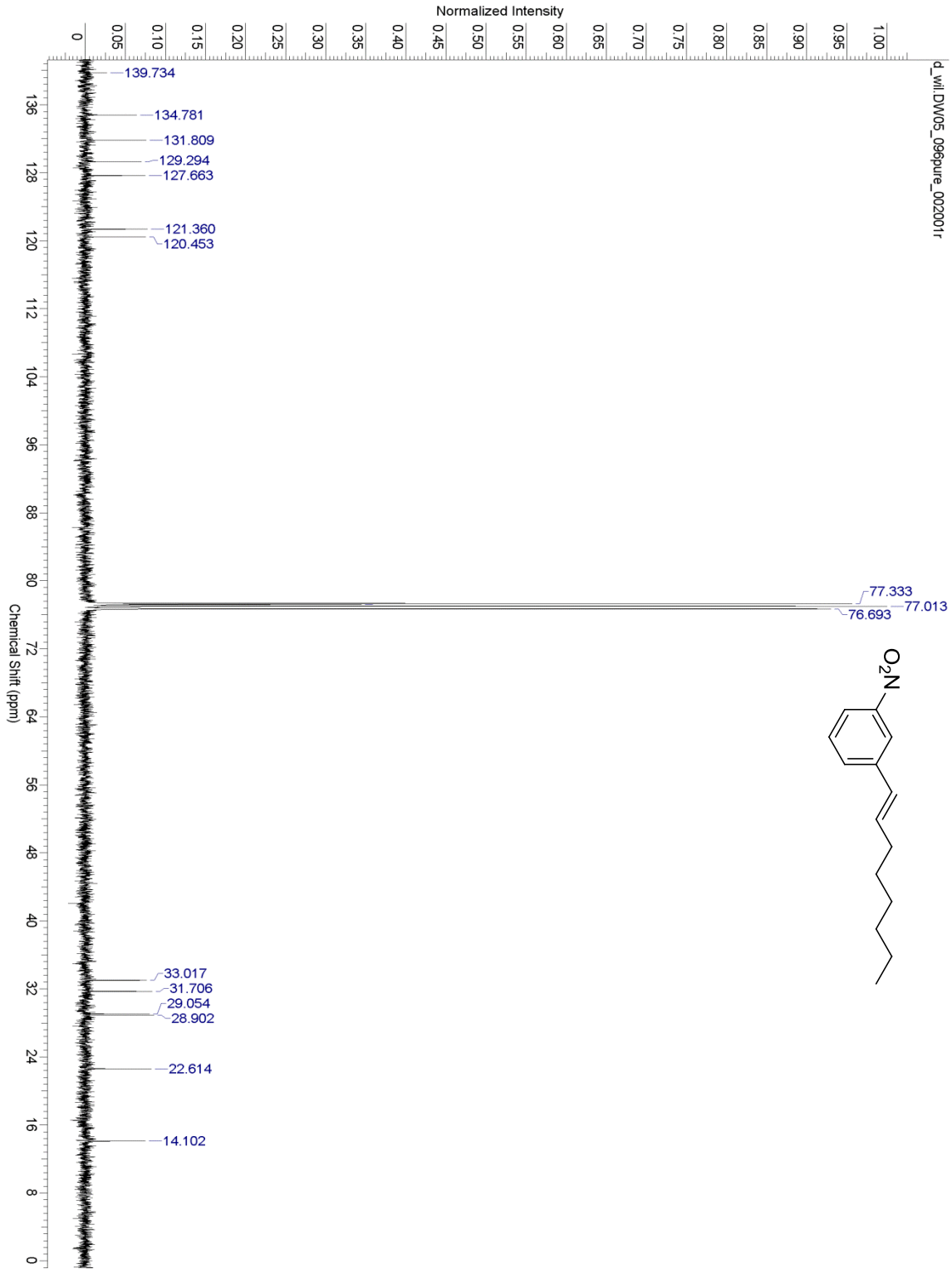



Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wil.DW05_091Pure_0010011
Chemical Shift (ppm)
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
141.434
134.133
132.083
128.737
128.417
128.547
126.001
125.346
125.384
122.983
77.326
77.006
76.686
33.086
31.729
29.130
28.917
22.622
14.079
F3C

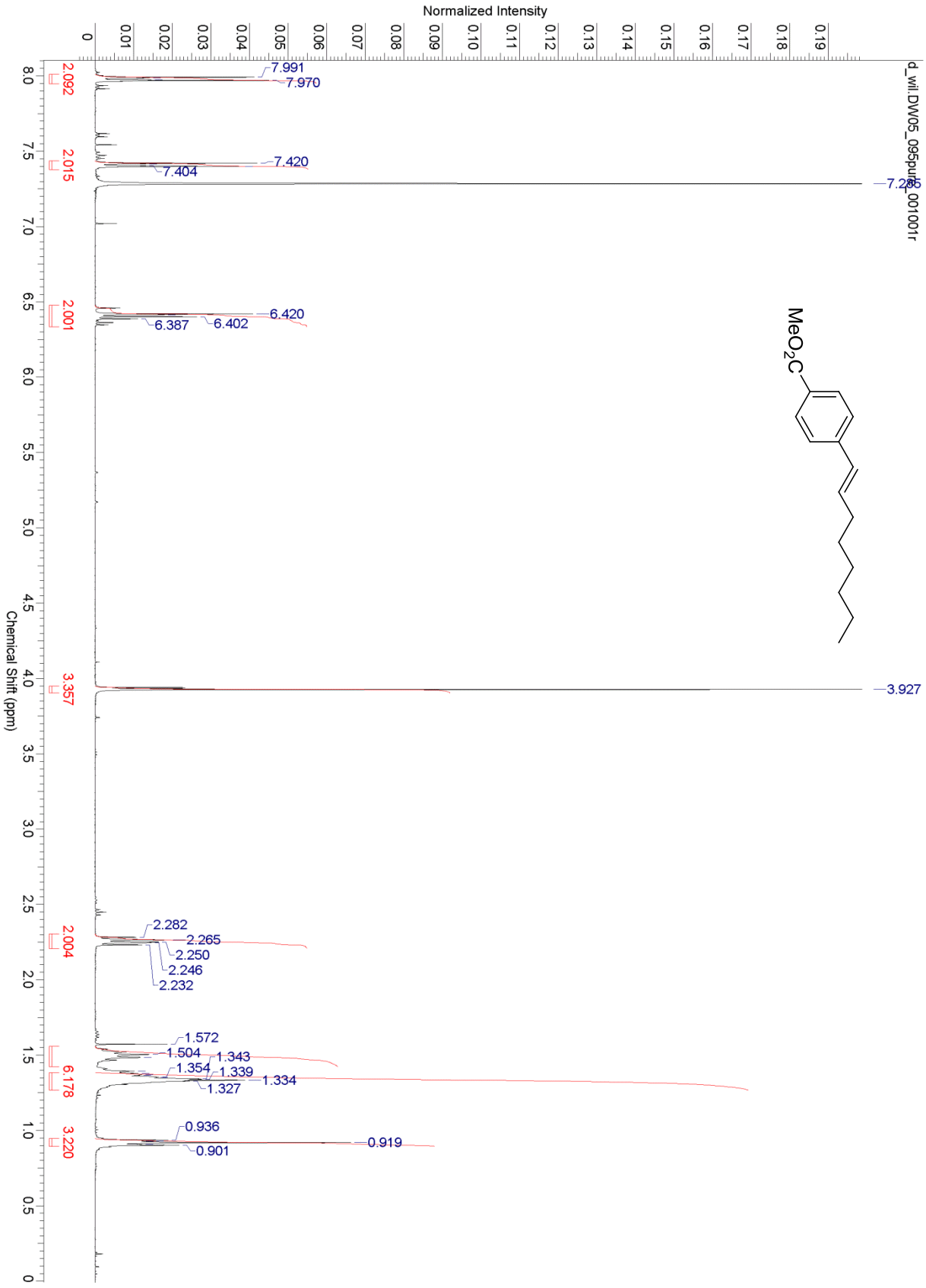

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wil.DW05_091pure_003001r
-62.381
F3C
Chemical Shift (ppm)
8
0
-8
-16
-24
-32
-40
-48
-56
-64
-72
-80
-88
-96
-104
-112
-120
-128
-136
-144
-152
-160
-168
-176
-184
-192

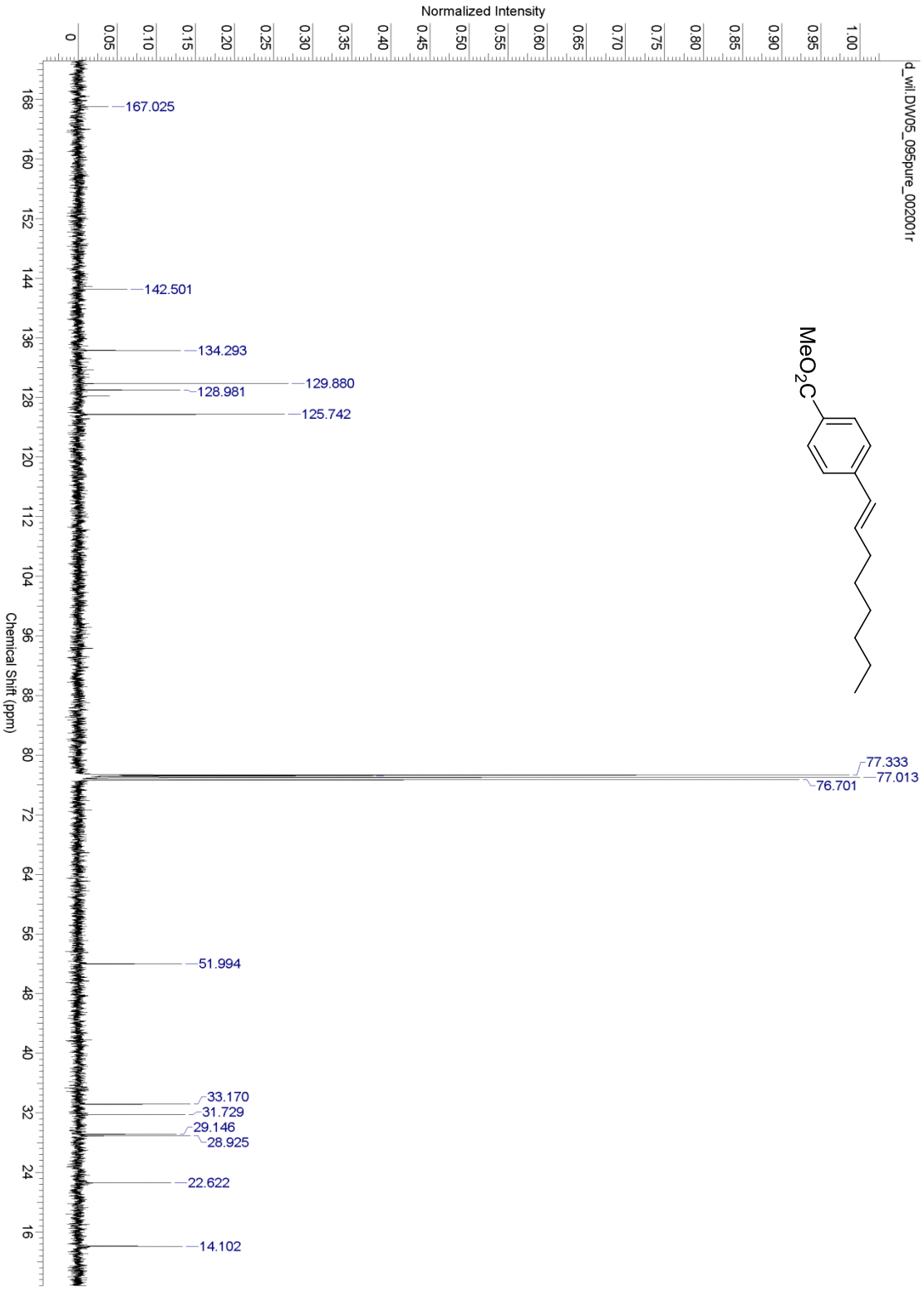
(E)-1-nitro-3-(oct-1-en-1-yl)benzene, 17



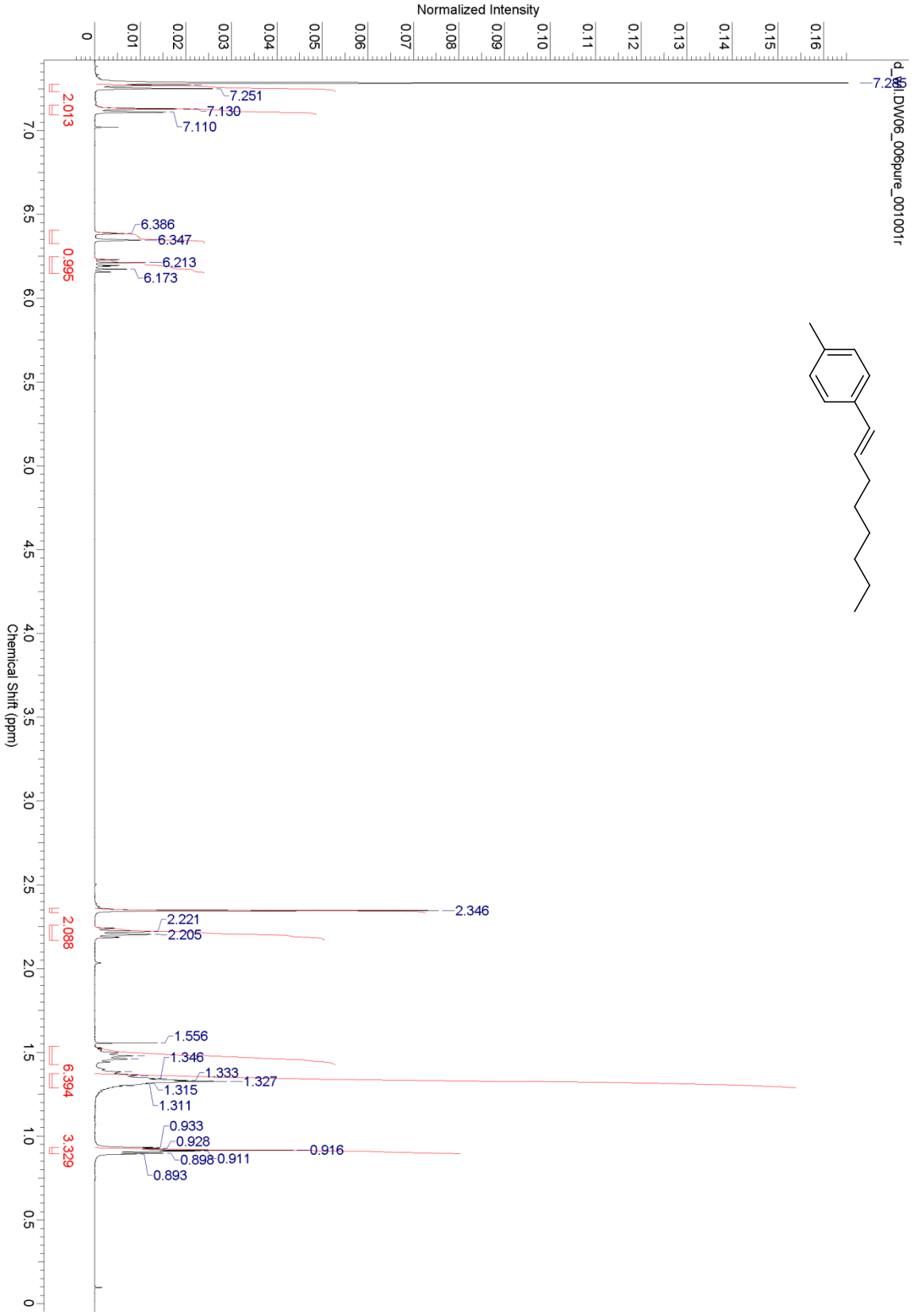

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wil.DW05_096pure_002001r
139.734
134.781
131.809
129.294
127.663
121.360
120.453
77.333
77.013
76.693
33.017
31.706
29.054
28.902
22.614
14.102
Chemical Shift (ppm)
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
O2N

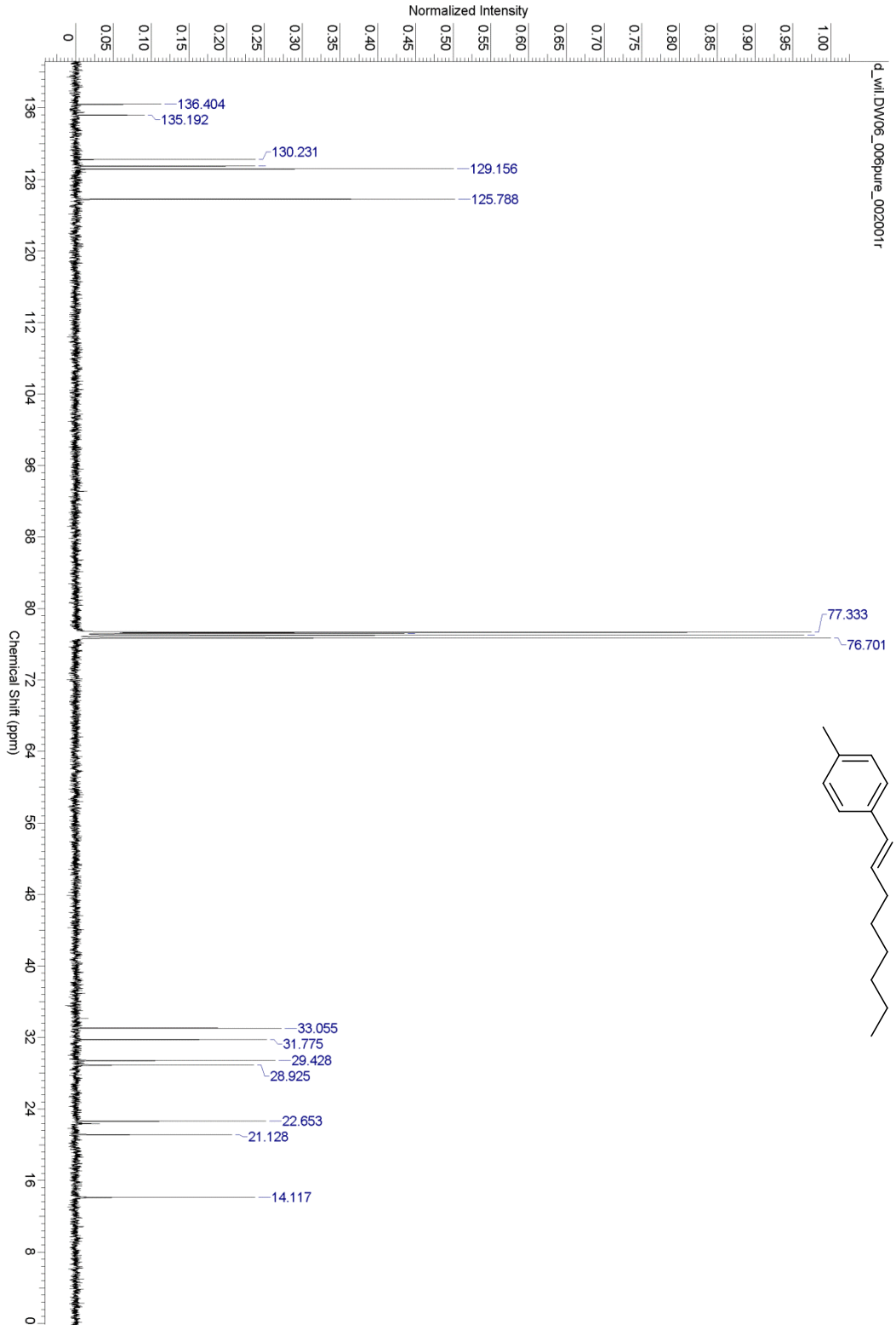
(E)-methyl 4-(oct-1-en-1-yl)benzoate, 18



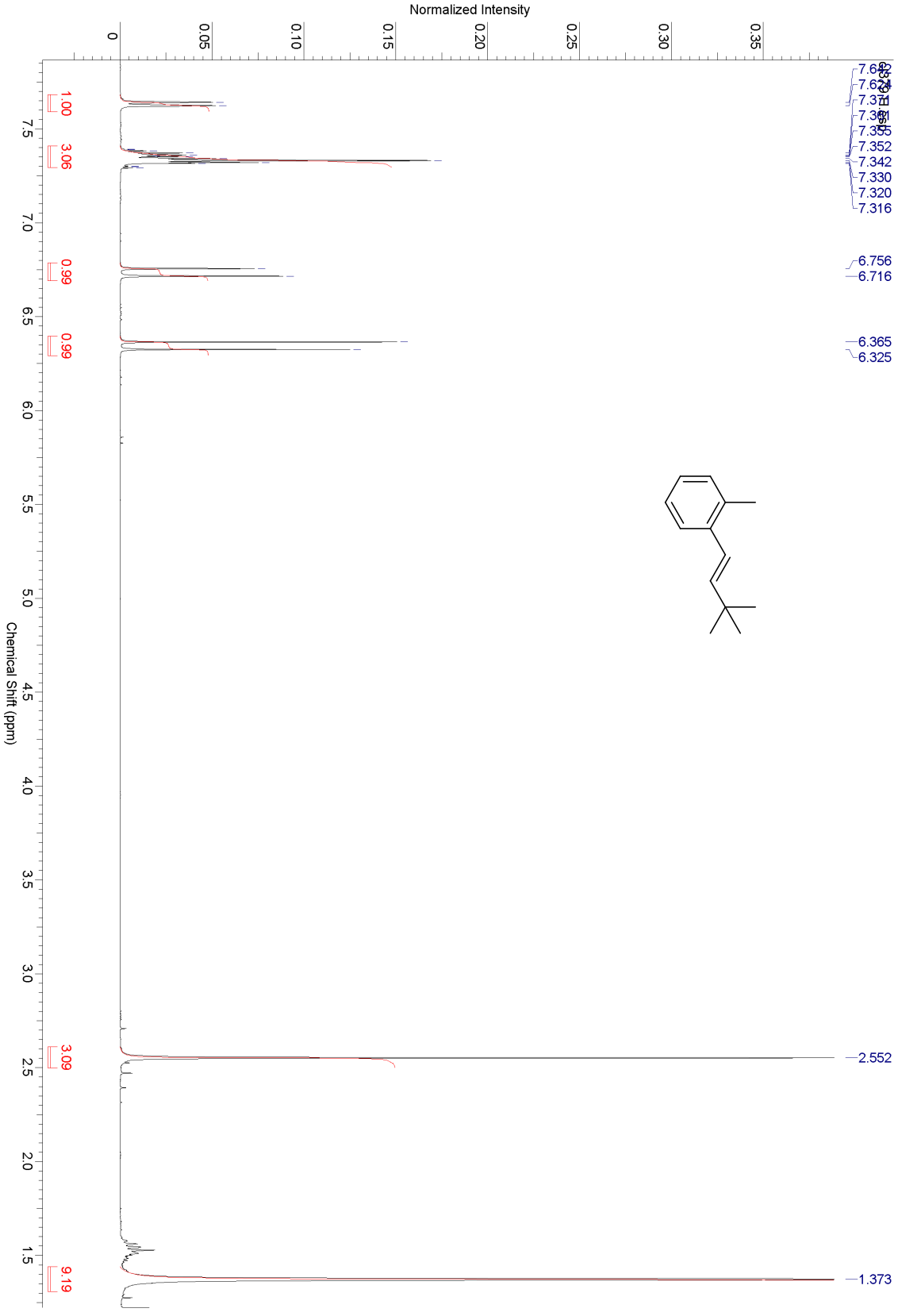

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wil.DW05_095pure_002001r
Chemical Shift (ppm)
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
167.025
142.501
134.293
129.880
128.981
125.742
77.333
77.013
76.701
51.994
33.170
31.729
29.146
28.925
22.622
14.102
MeO2C

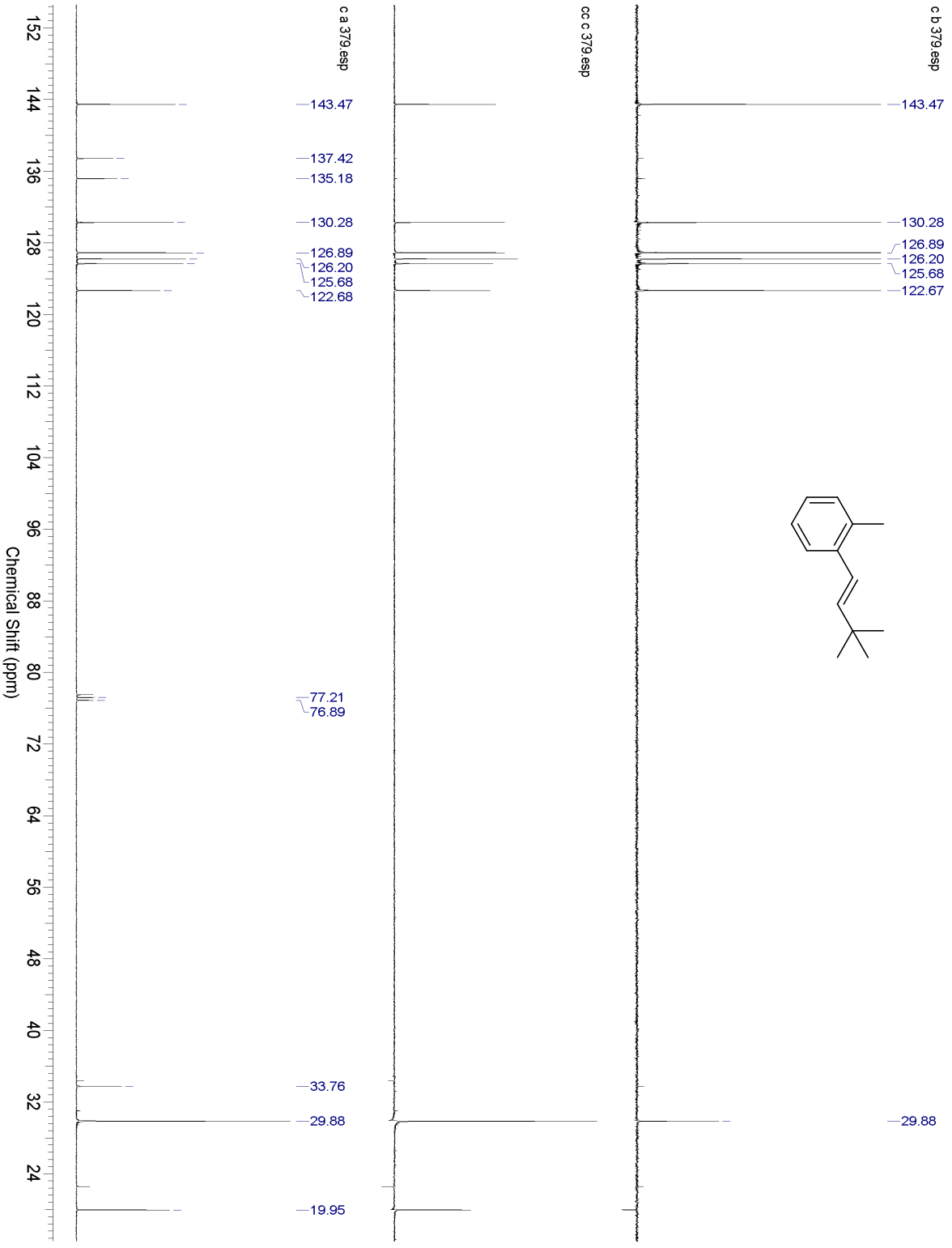
(E)-1-methyl-4-(oct-1-en-1-yl)benzene, 19



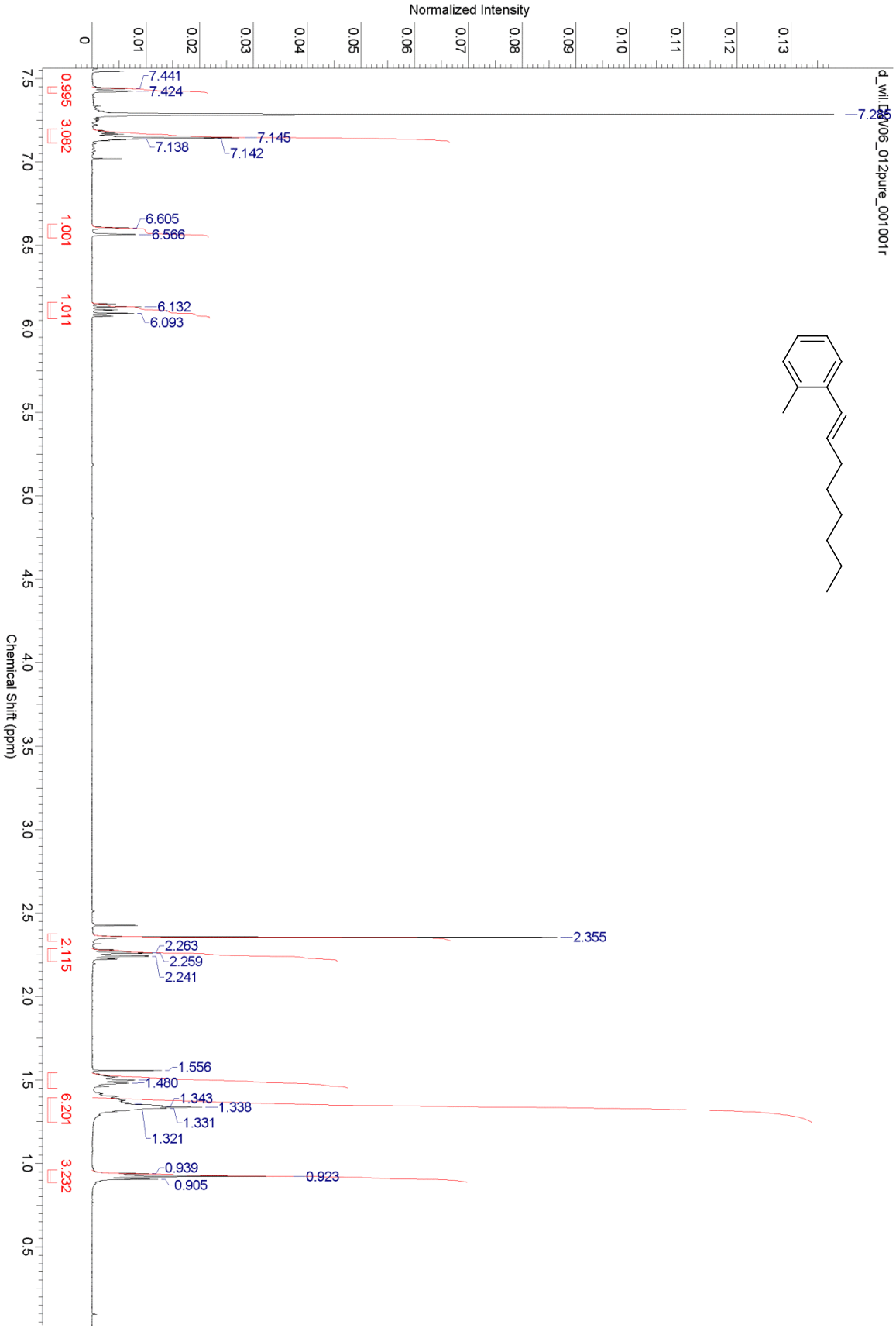

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wil.DW06_006pure_002001r
136.404
135.192
130.231
129.156
125.788
77.333
76.701
33.055
31.775
29.428
28.925
22.653
21.128
14.117
Chemical Shift (ppm)
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0

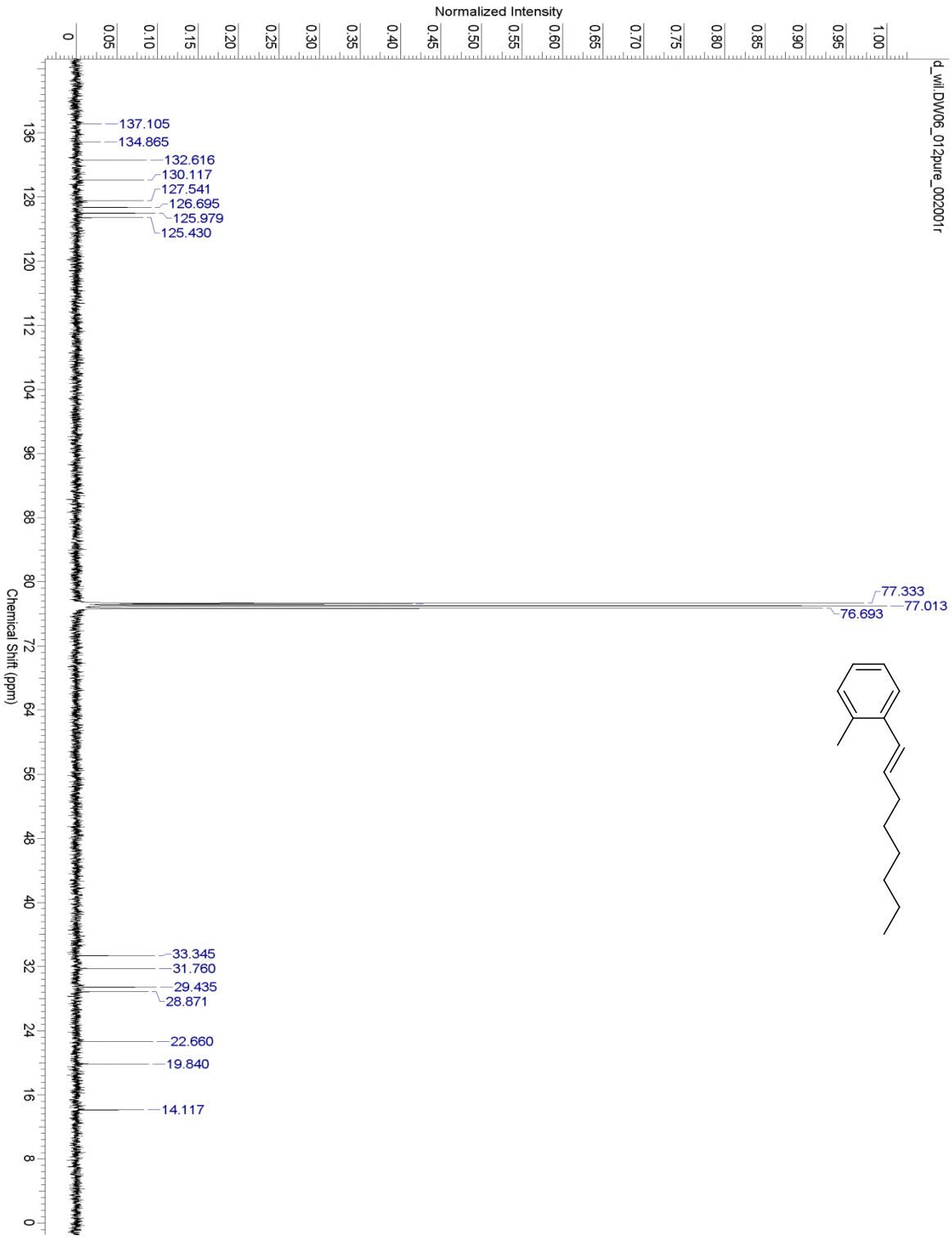
(E)-1-(3,3-dimethylbut-1-en-1-yl)-2-methylbenzene, 20



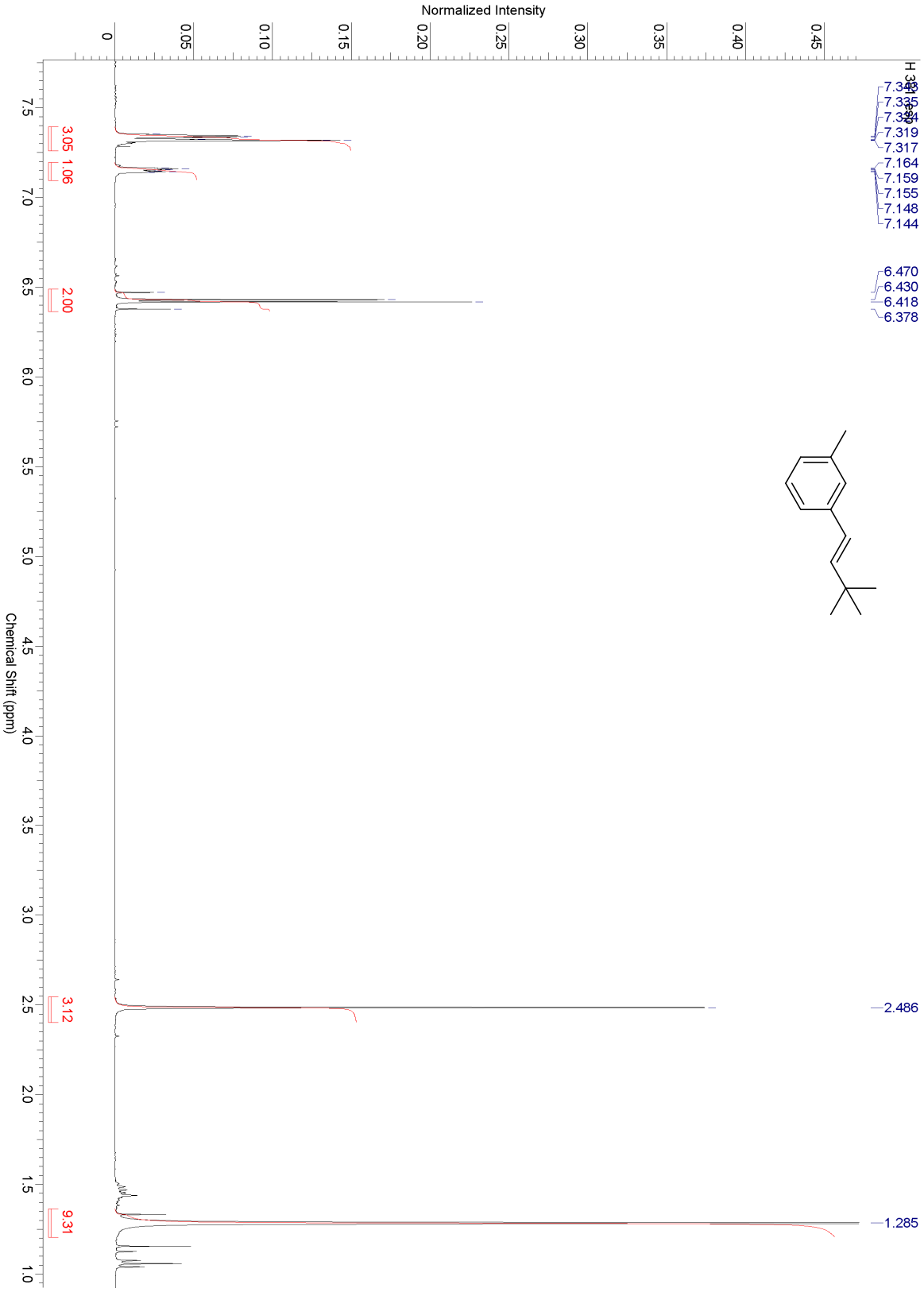

c a 379.esp
cc c 379.esp
c b 379.esp
Chemical Shift (ppm)
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
143.47
137.42
135.18
130.28
126.89
126.20
125.68
122.68
77.21
76.89
33.76
29.88
19.95
143.47
130.28
126.89
126.20
125.68
122.67
29.88

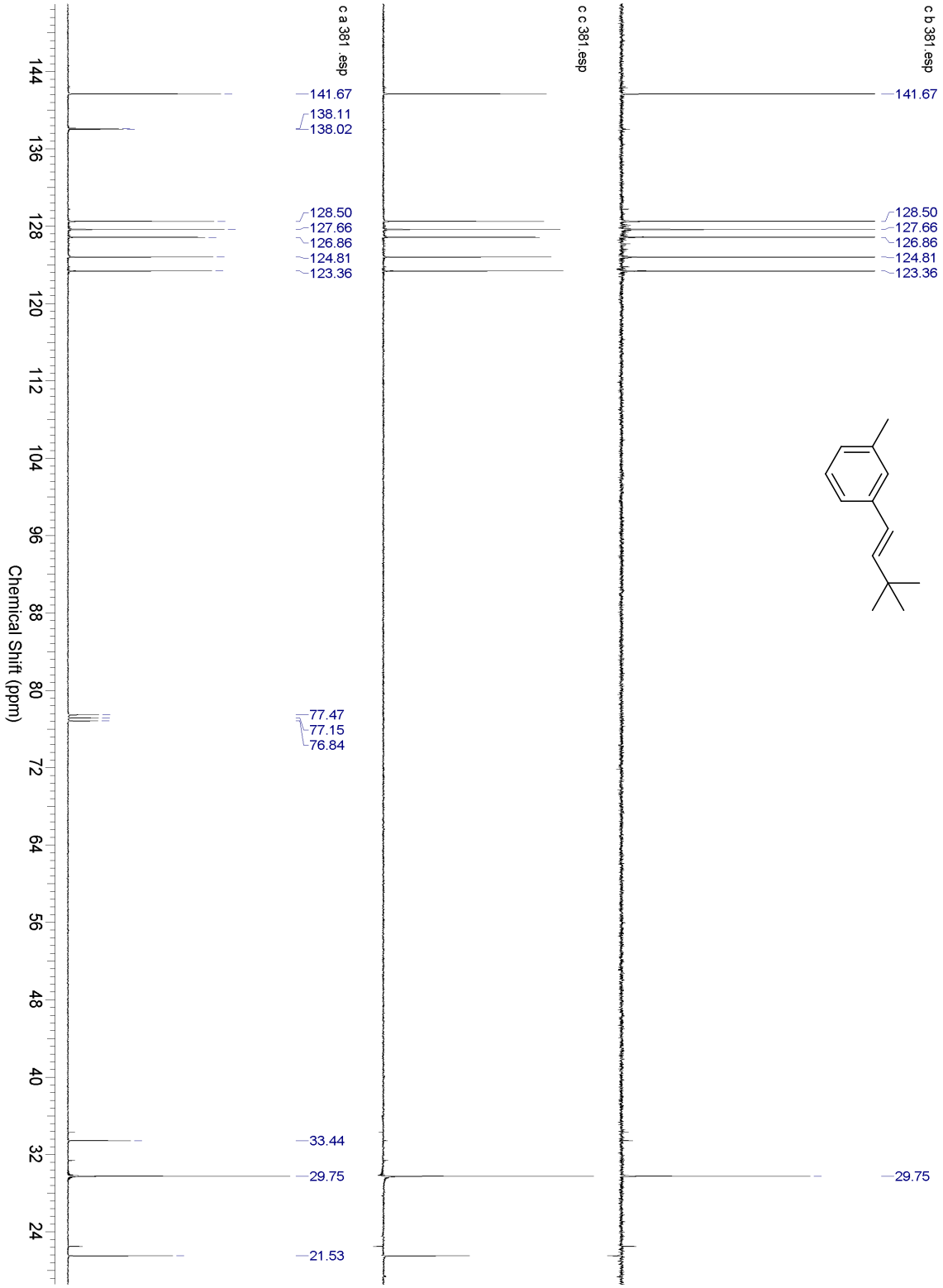
(E)-1-methyl-2-(oct-1-en-1-yl)benzene, 21



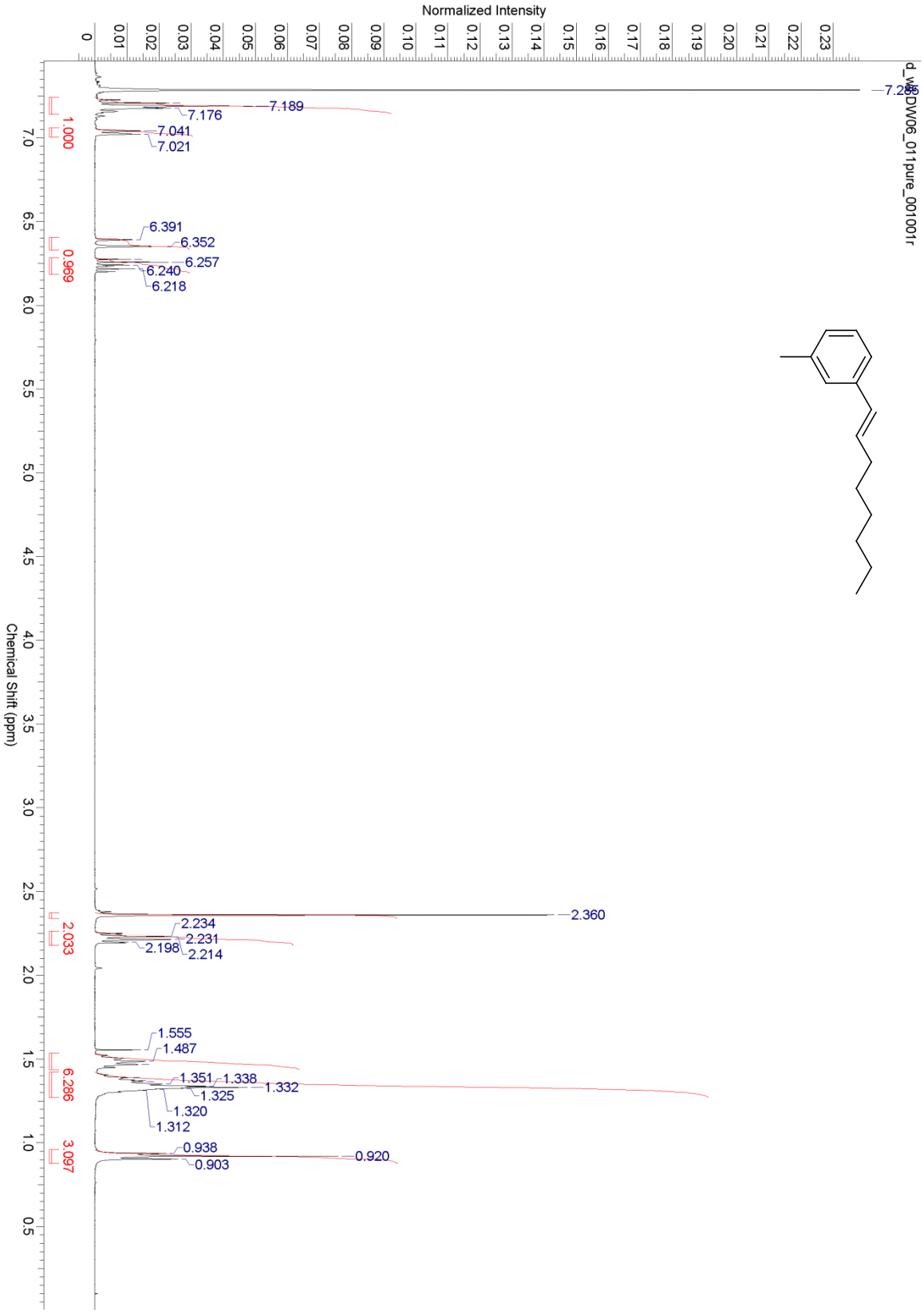

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wil.DW06_012pure_002001r
Chemical Shift (ppm)
137.105
134.865
132.616
130.117
127.541
126.695
125.979
125.430
77.333
77.013
76.693
33.345
31.760
29.435
28.871
22.660
19.840
14.117

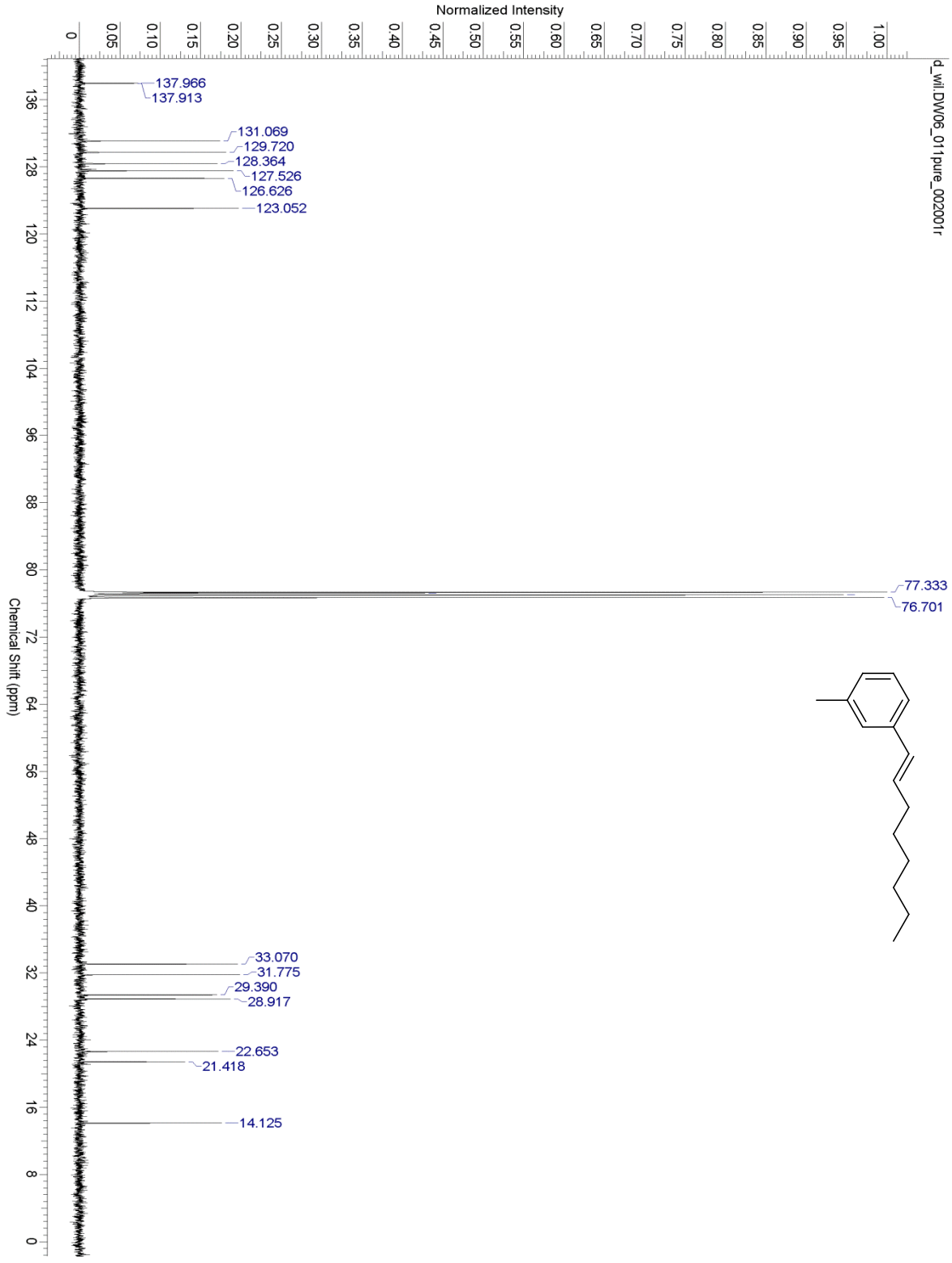
(E)-1-(3,3-dimethylbut-1-en-1-yl)-3-methylbenzene, 22



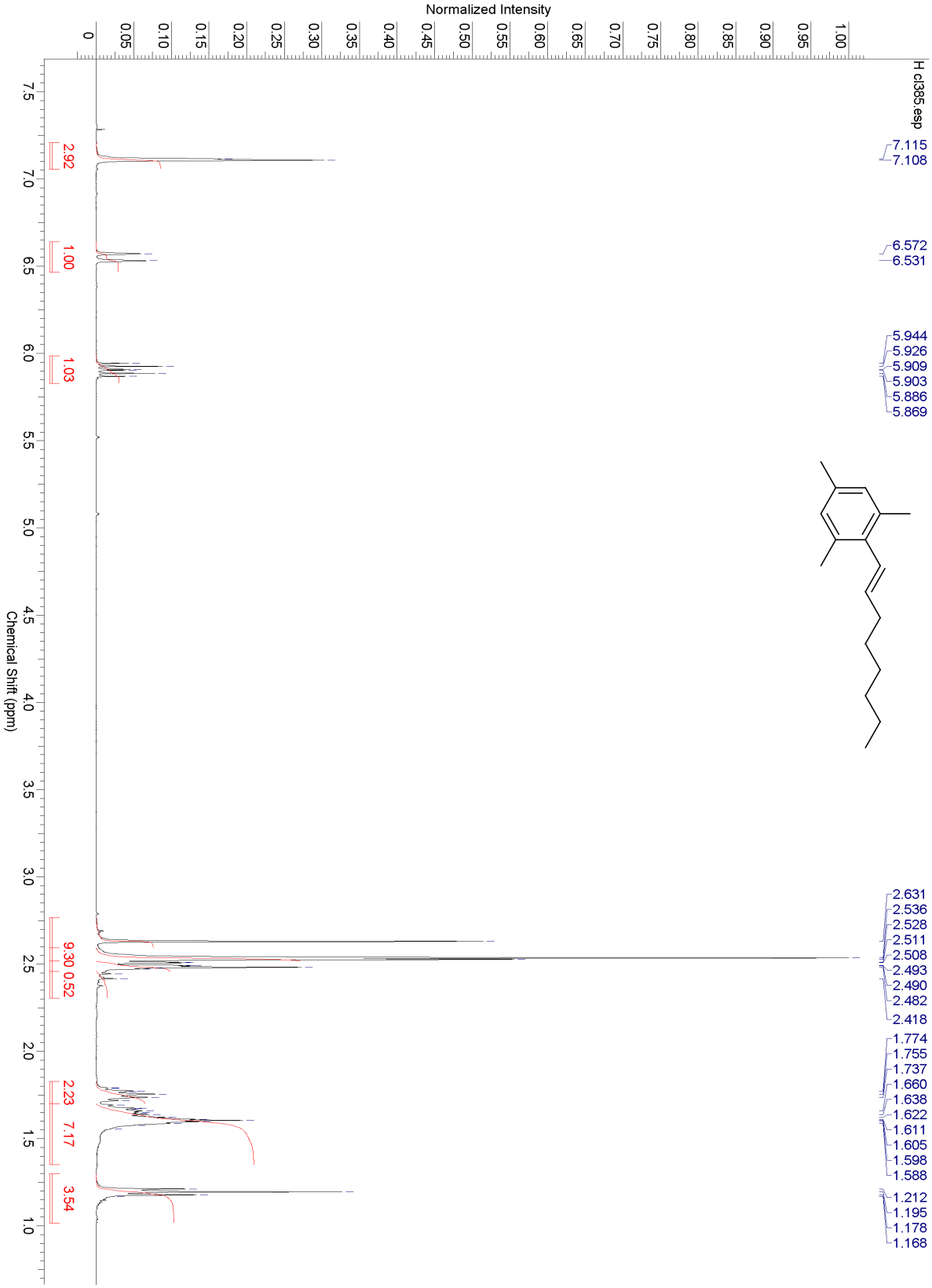

c a 381.esp
c c 381.esp
c b 381.esp
141.67
138.11
138.02
128.50
127.66
126.86
124.81
123.36
77.47
77.15
76.84
33.44
29.75
21.53
Chemical Shift (ppm)
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24

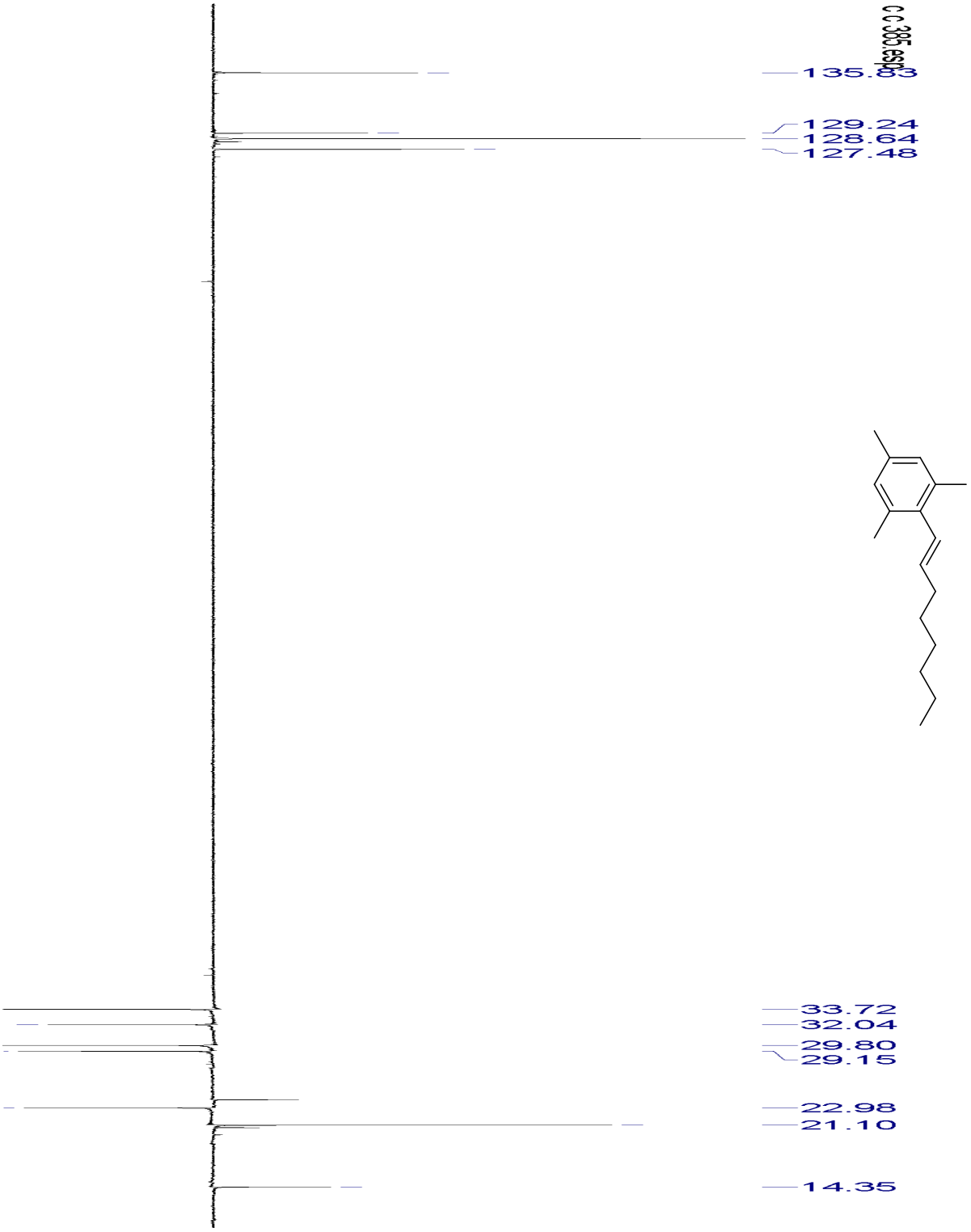
(E)-1-methyl-3-(oct-1-en-1-yl)benzene, 23



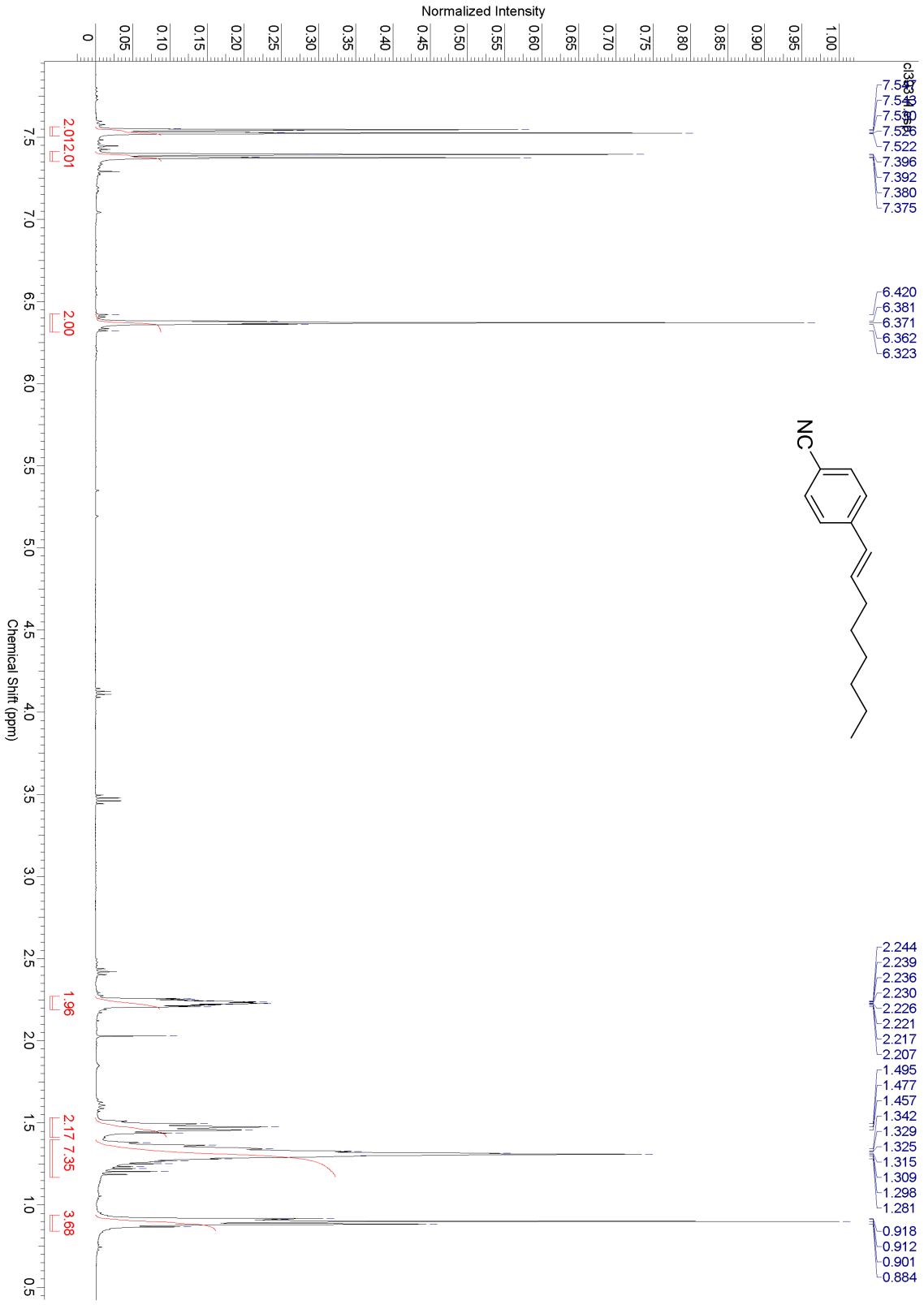

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wil:DW06_011pure_002001r
137.966
137.913
131.069
129.720
128.364
127.526
126.626
123.052
77.333
76.701
33.070
31.775
29.390
28.917
22.653
21.418
14.125
Chemical Shift (ppm)
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0

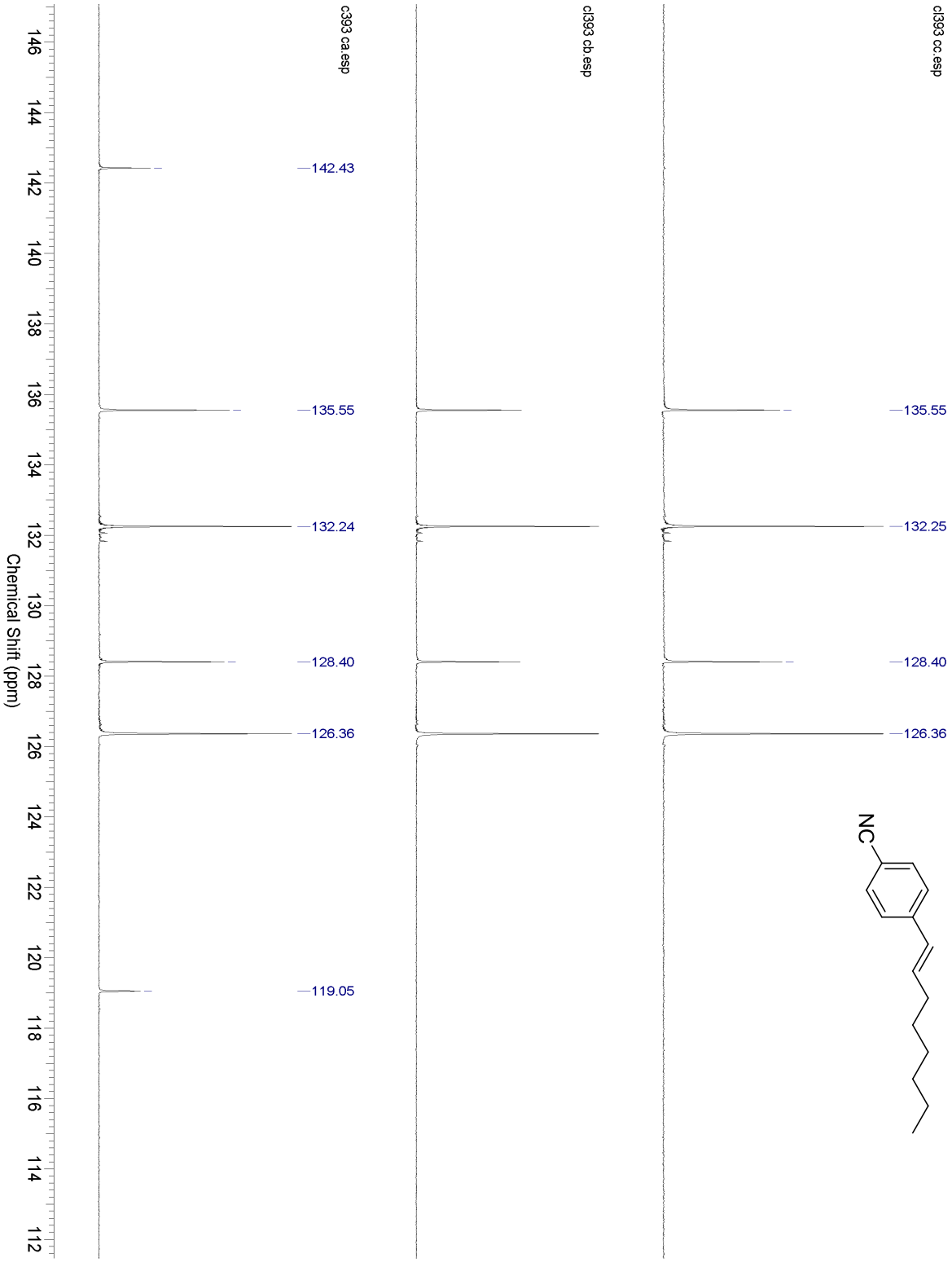
(E)-1,3,5-trimethyl-2-(oct-1-en-1-yl)benzene, 24



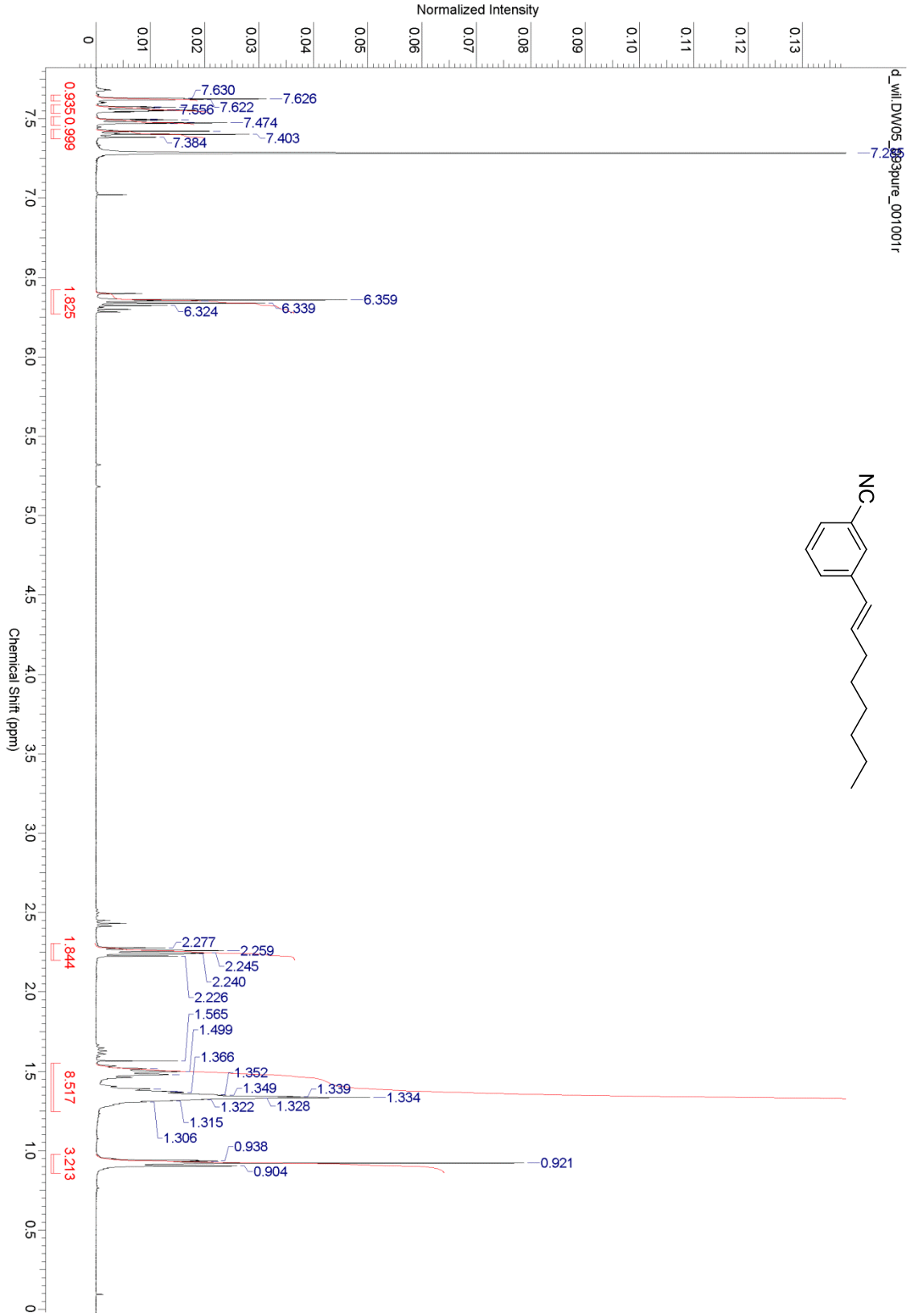

135.83
129.24
128.64
127.48
33.72
32.04
29.80
29.15
22.98
21.10
14.35

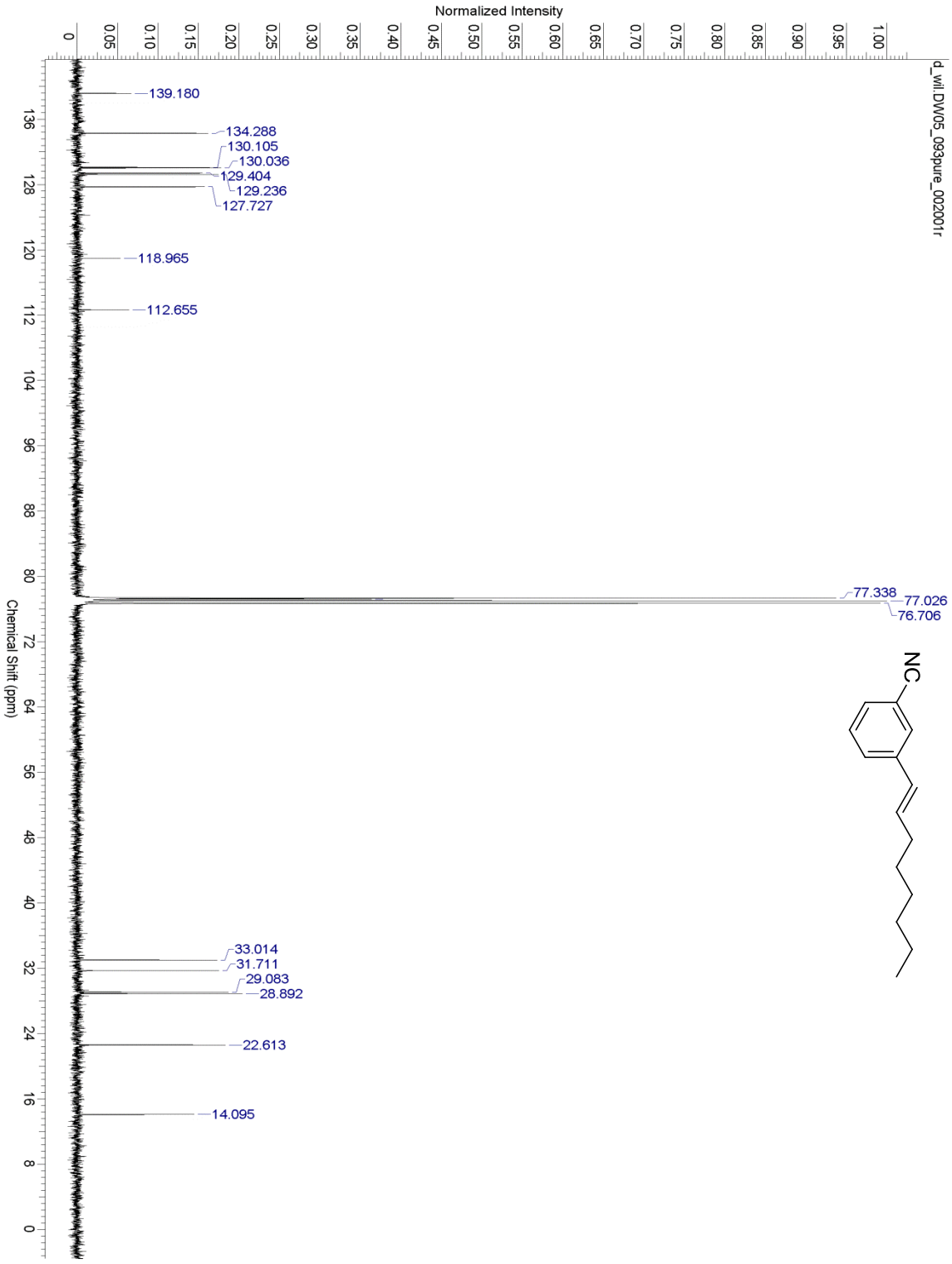
(E)-4-(oct-1-en-1-yl)benzonitrile, 25



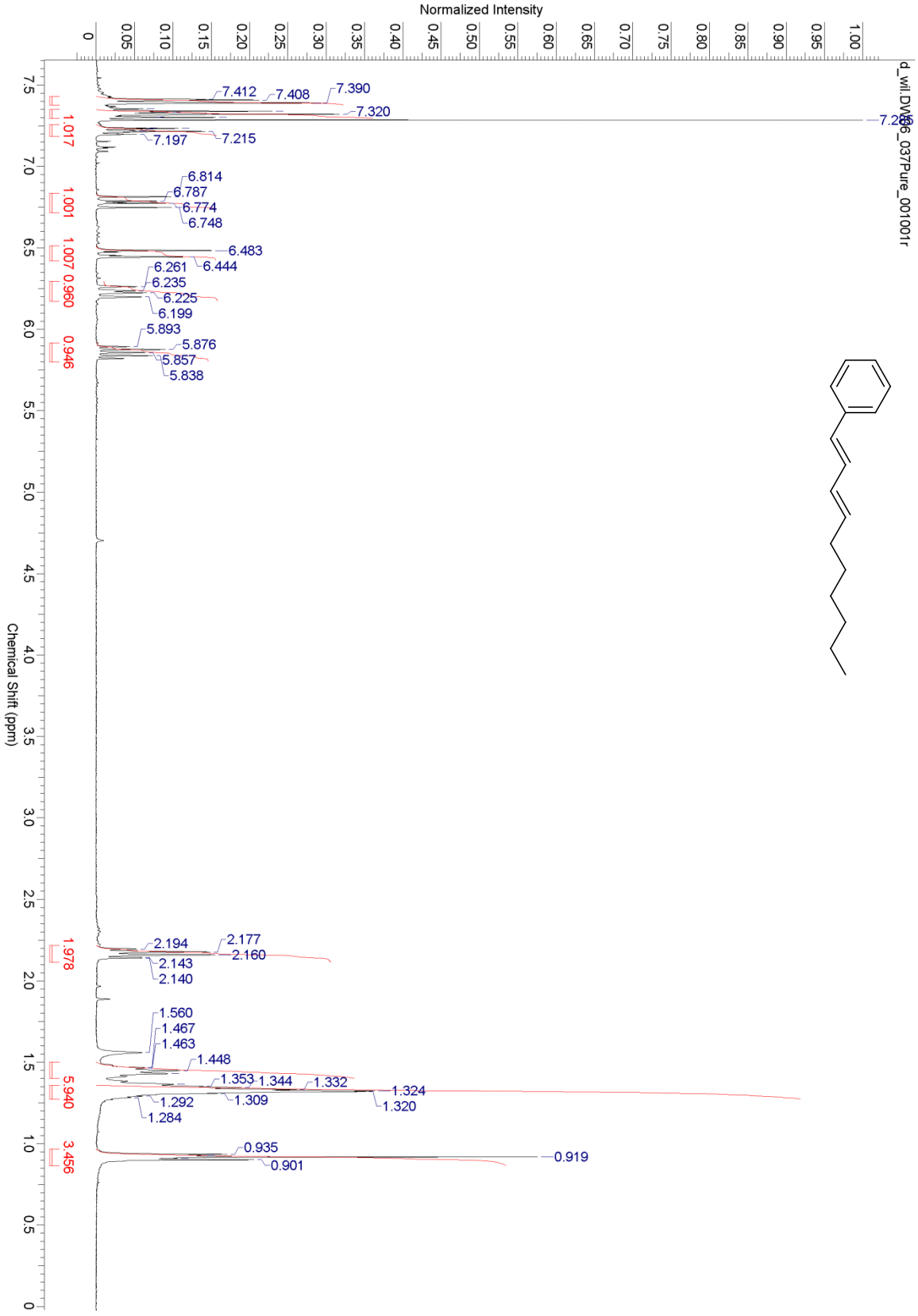

c393 ca.esp
c393 cb.esp
c393 cc.esp
142.43
135.55
132.24
128.40
126.36
119.05
135.55
132.25
128.40
126.36
NC
Chemical Shift (ppm)
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112

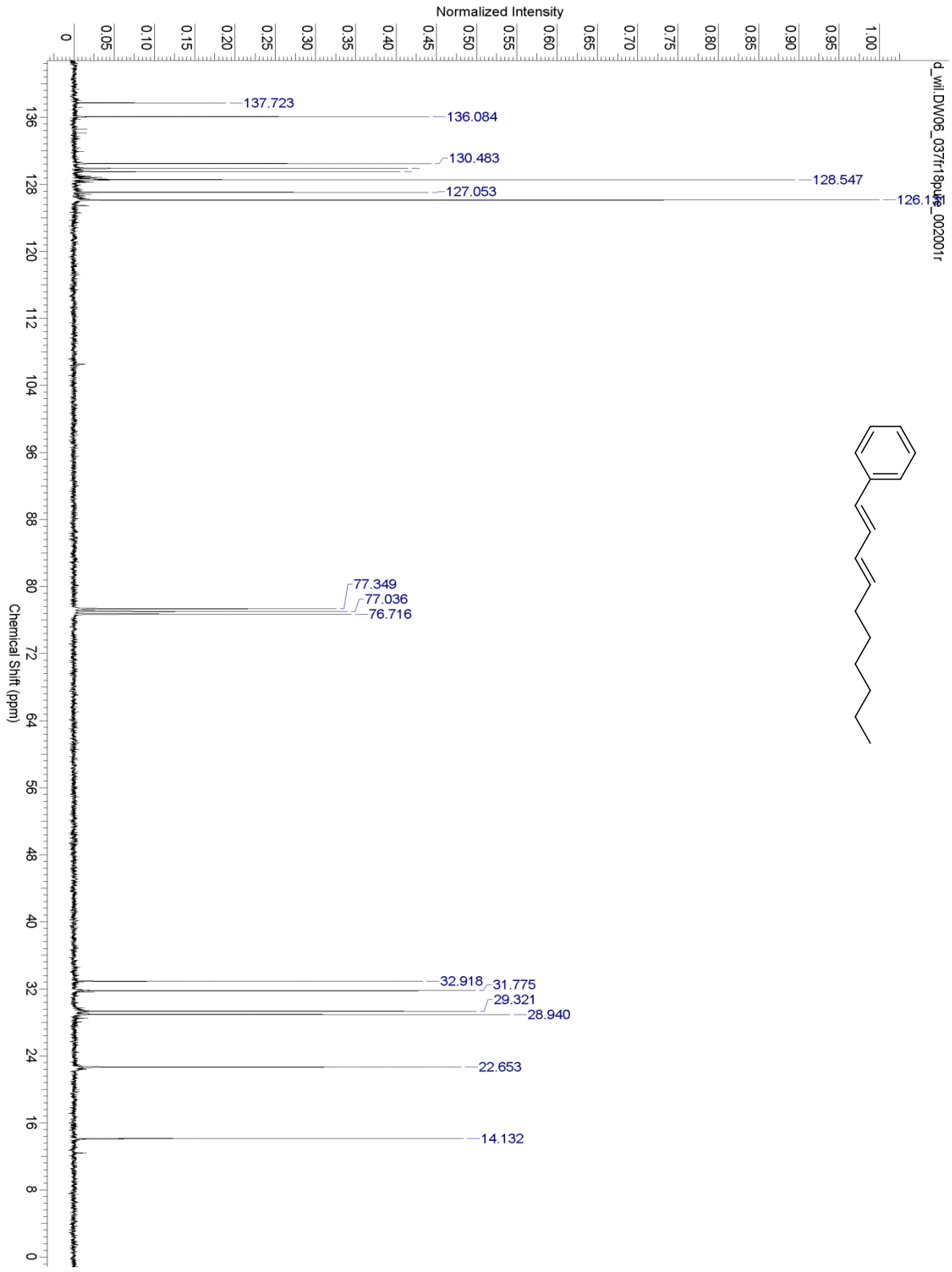
(E)-3-(oct-1-en-1-yl)benzonitrile, 26



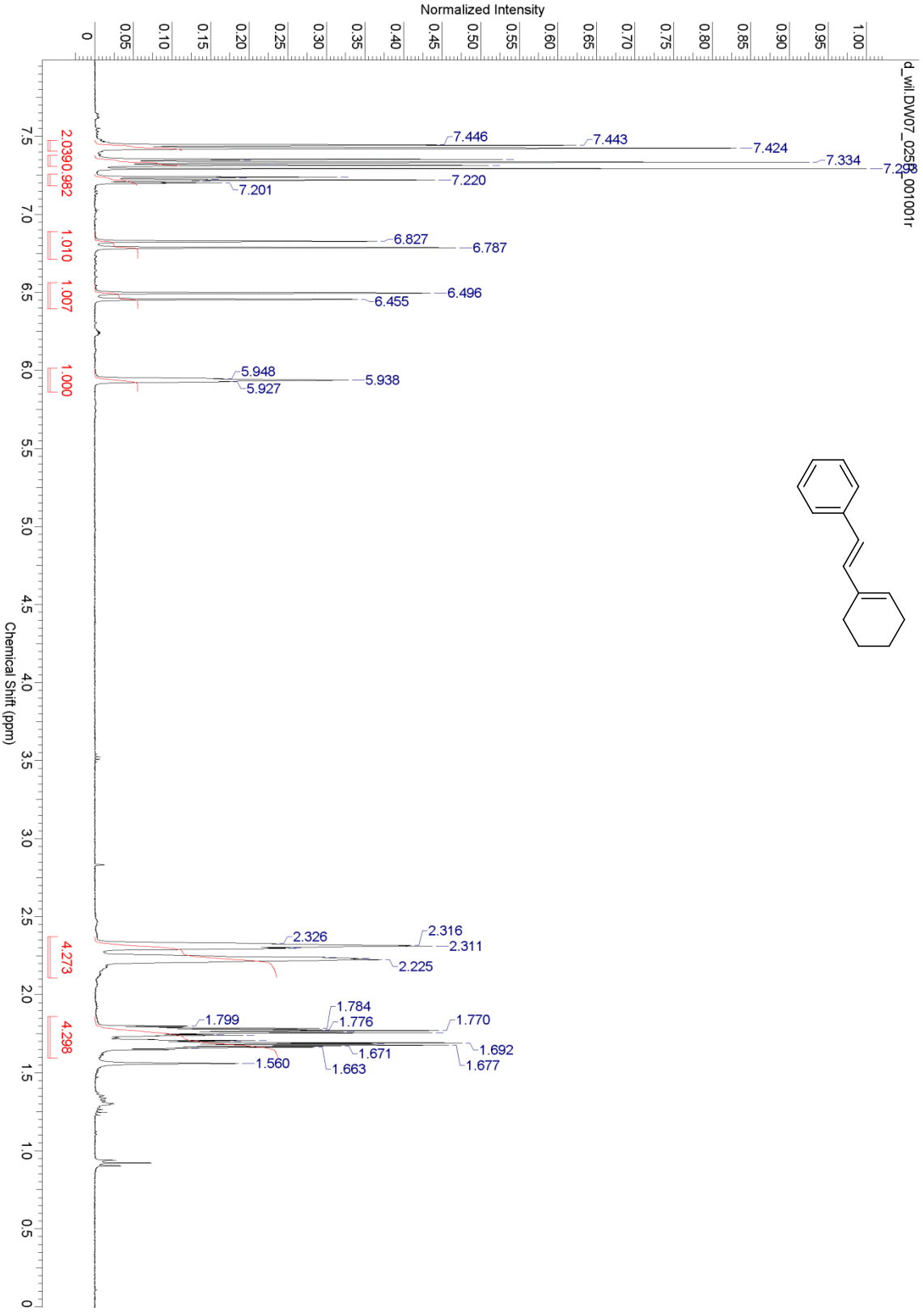

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wl.DW05_093pure_002001r
139.180
134.288
130.105
130.036
129.404
129.236
127.727
118.965
112.655
77.338
77.026
76.706
33.014
31.711
29.083
28.892
22.613
14.095
Chemical Shift (ppm)
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
NC

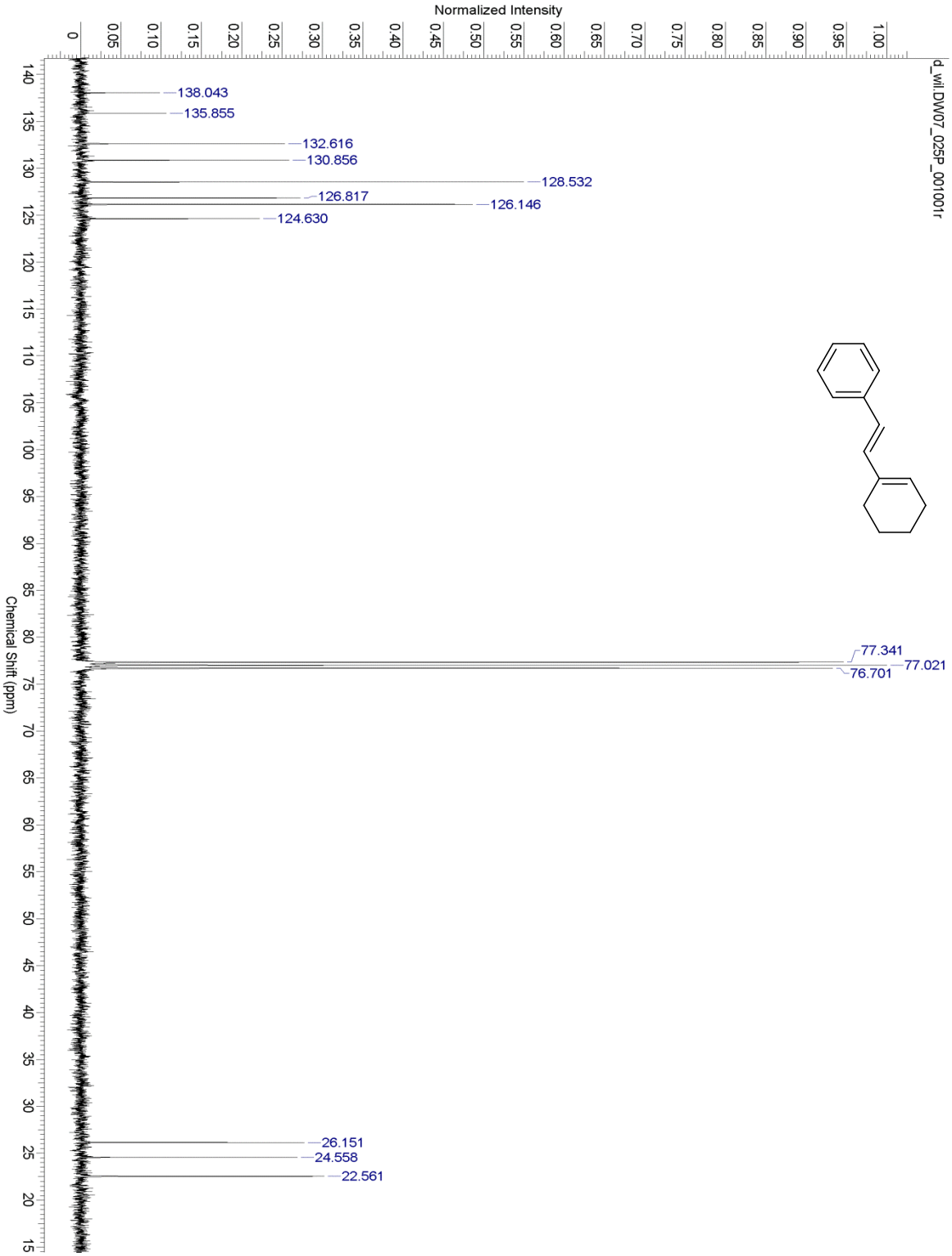
(1E,3E)-deca-1,3-dien-1-ylbenzene, 27



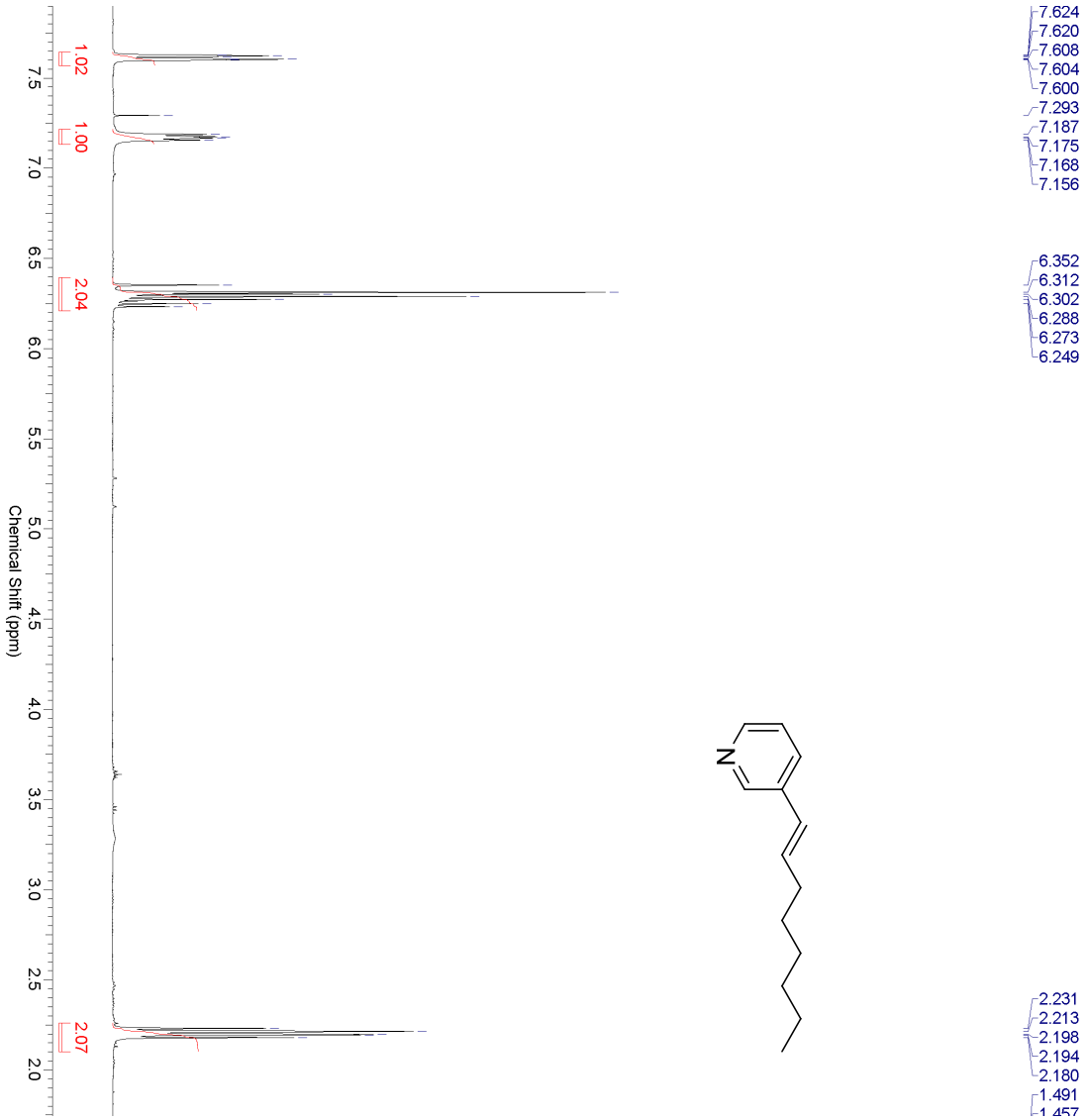

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wil.DW06_037fr18pure_002001r
137.723
136.084
130.483
128.547
127.053
126.1
77.349
77.036
76.716
32.918
31.775
29.321
28.940
22.653
14.132
Chemical Shift (ppm)
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0

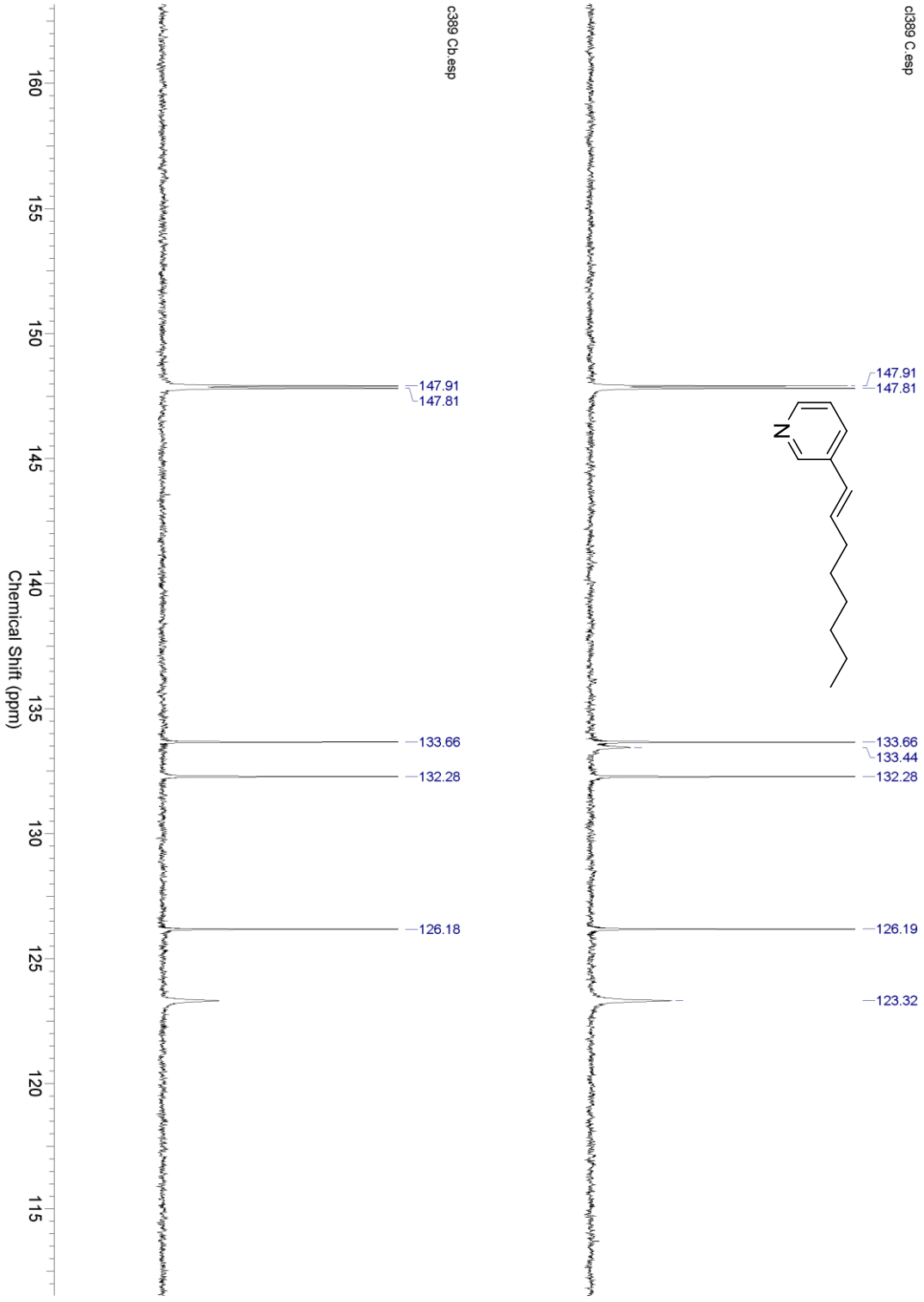
(E)-(2-(cyclohex-1-en-1-yl)vinyl)benzene, 28



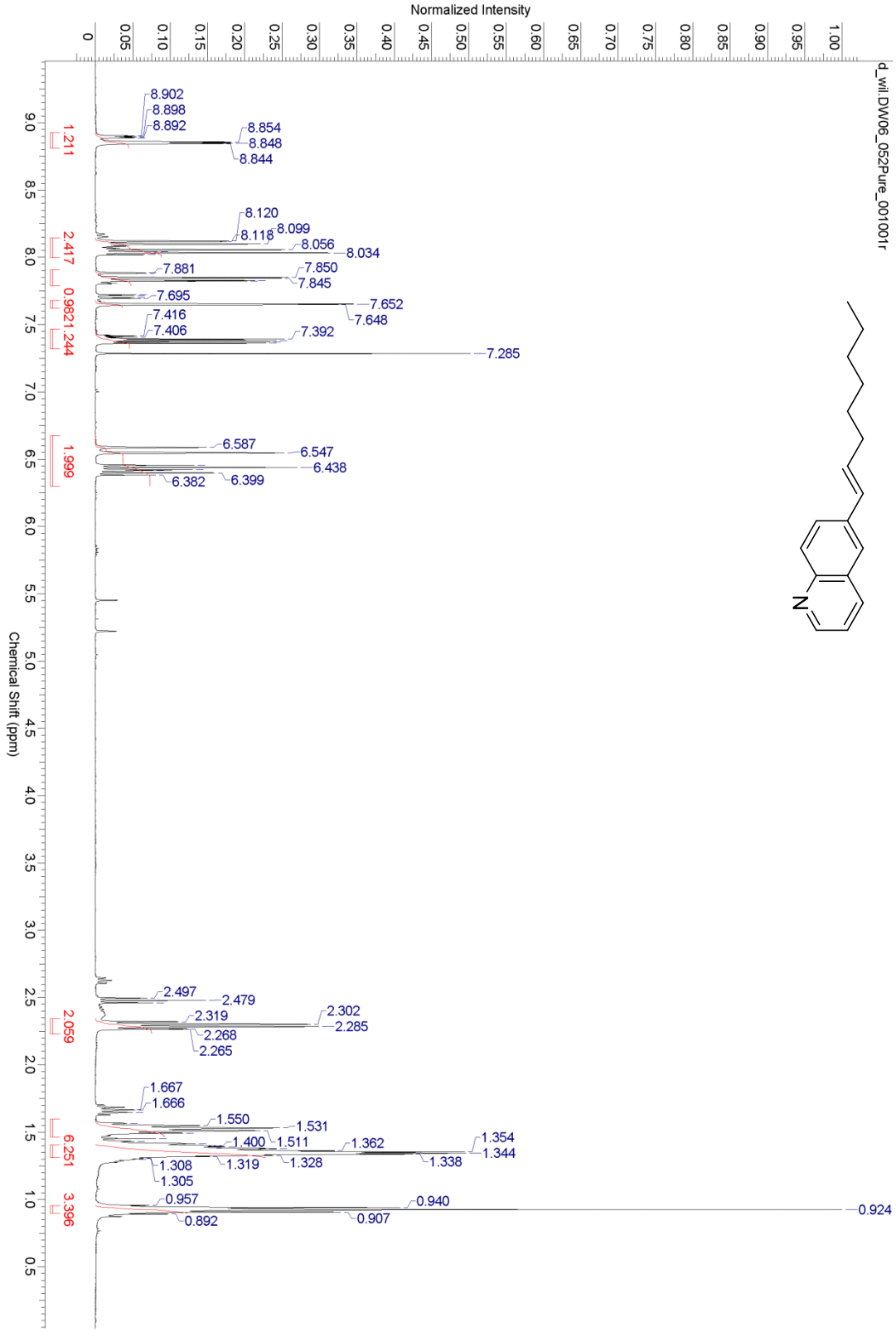

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wil DW07_025P_001001r
138.043
135.855
132.616
130.856
128.532
126.817
126.146
124.630
77.341
77.021
76.701
26.151
24.558
22.561
Chemical Shift (ppm)
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15

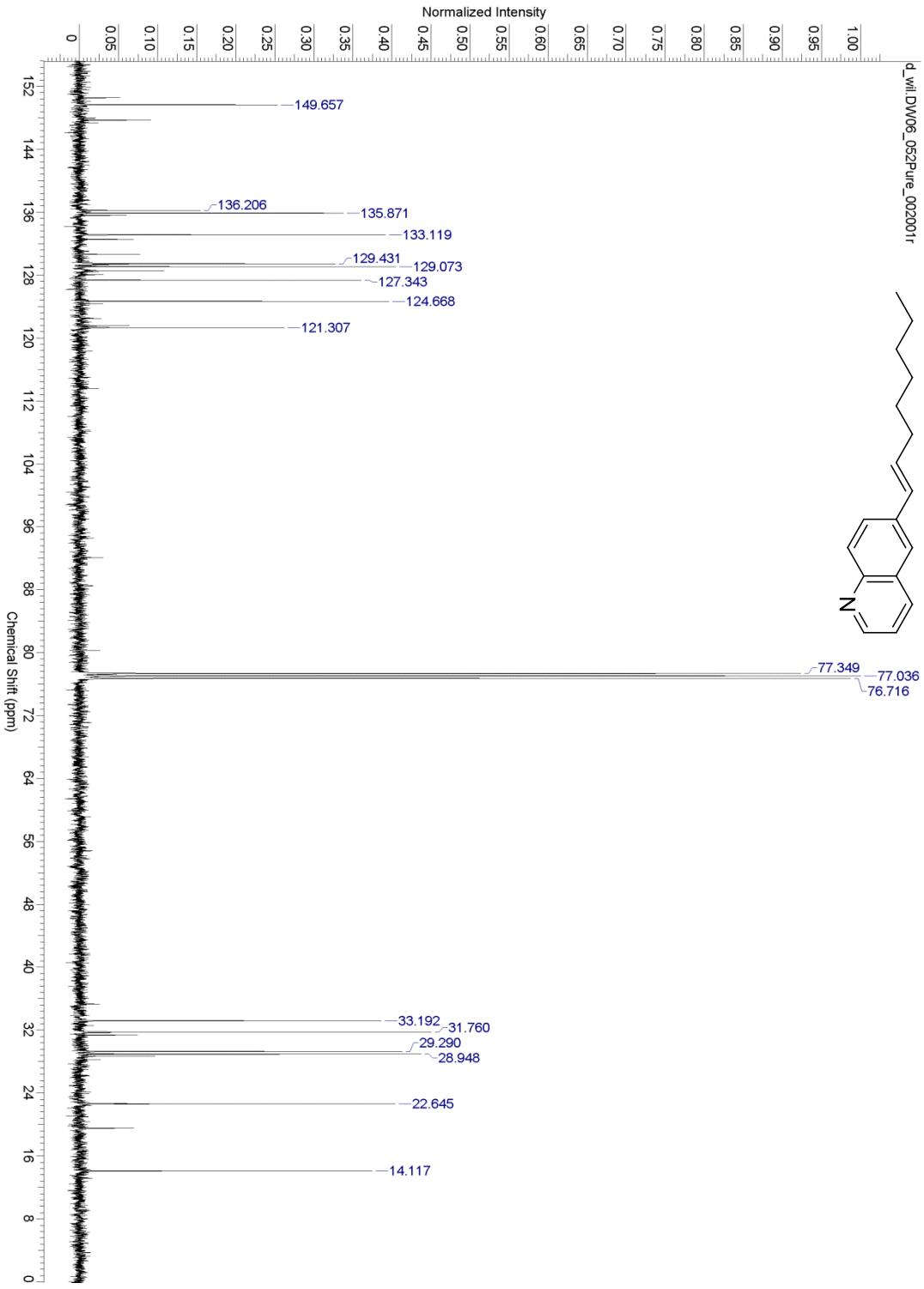
(E)-3-(oct-1-en-1-yl)pyridine, 29



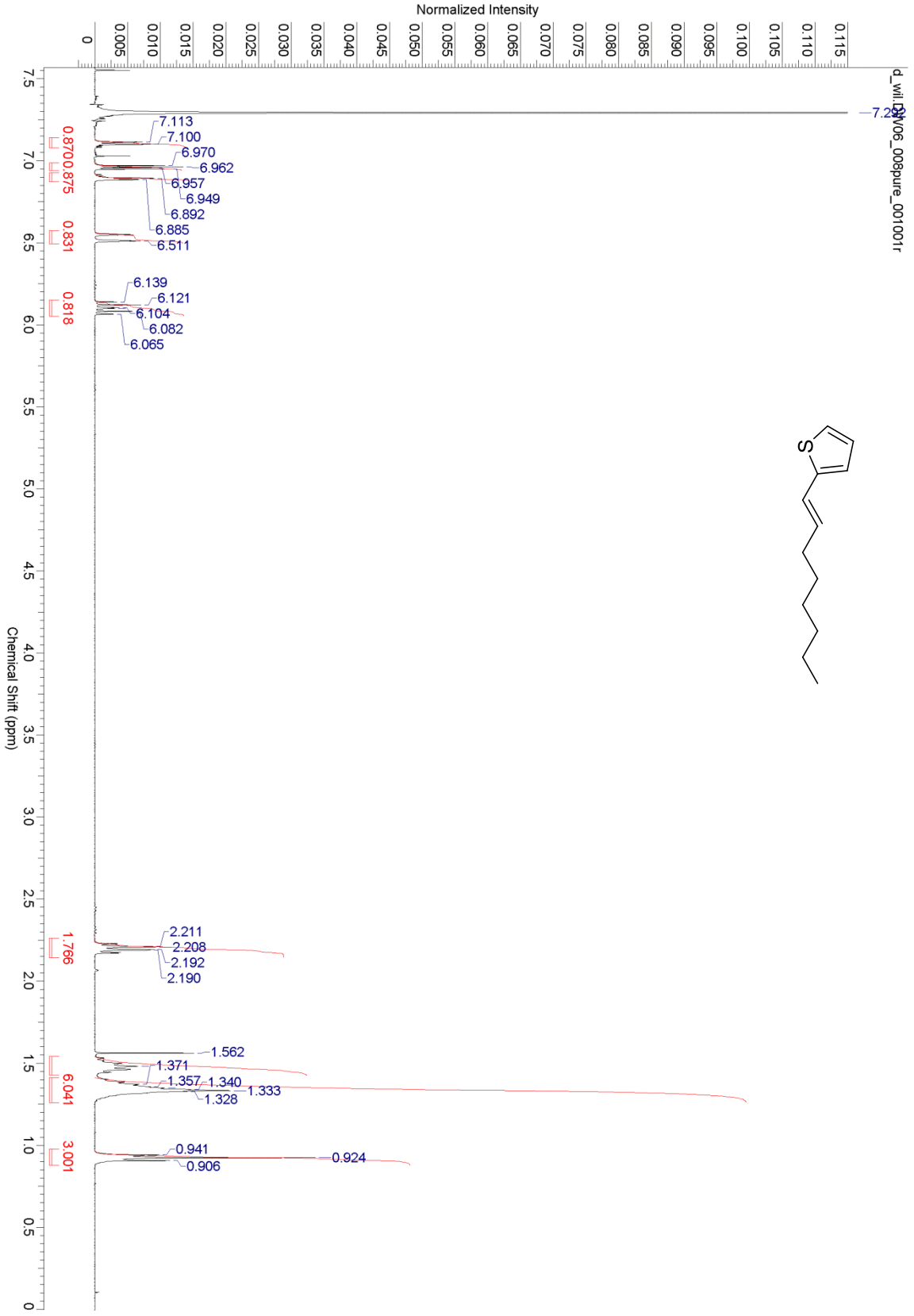

c389 Cb.esp
147.91
147.81
133.66
132.28
126.18
cl389 C.esp
147.91
147.81
133.66
133.44
132.28
126.19
123.32
N
160
155
150
145
140
135
130
125
120
115
Chemical Shift (ppm)

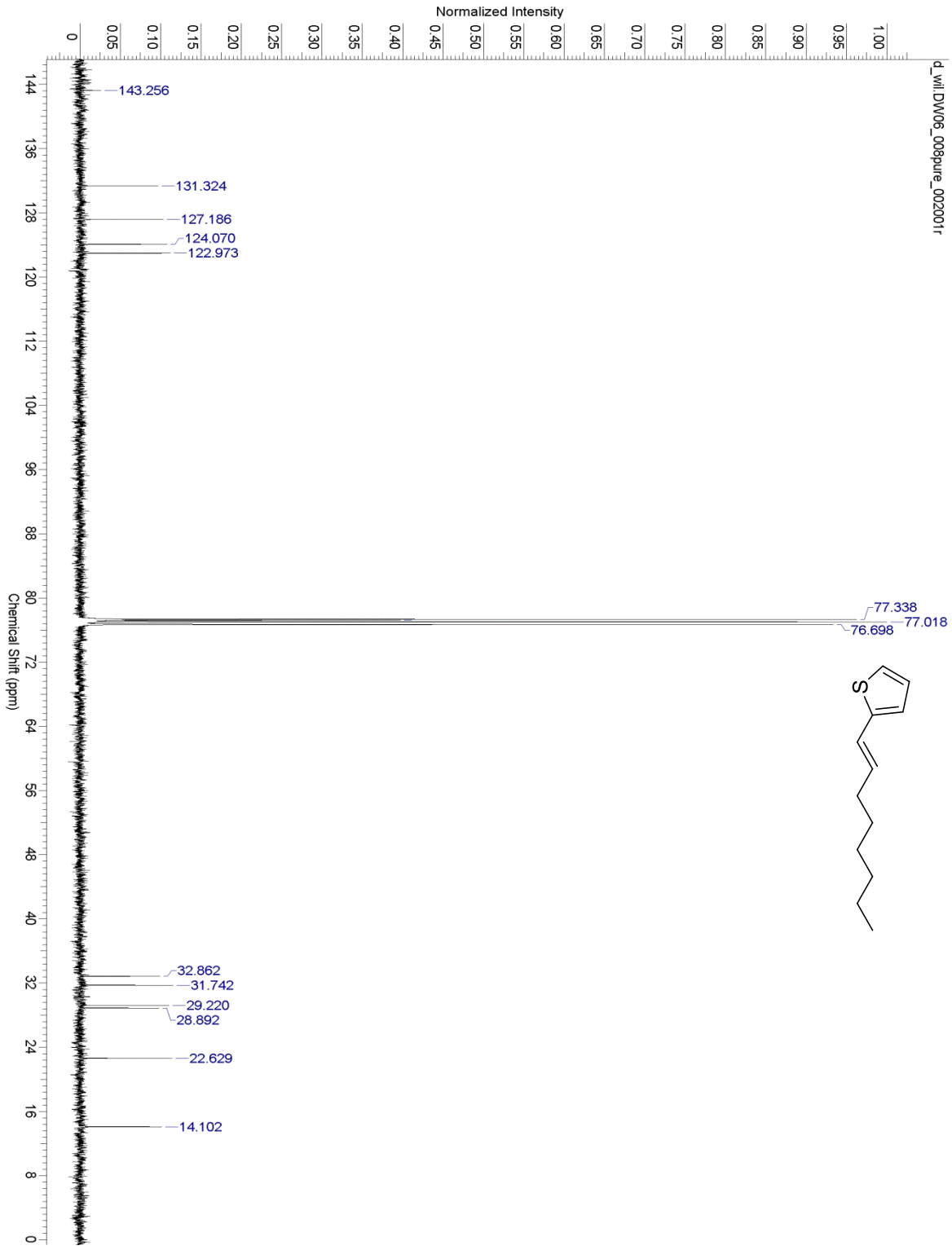
(E)-6-(oct-1-en-1-yl)quinolone, 30



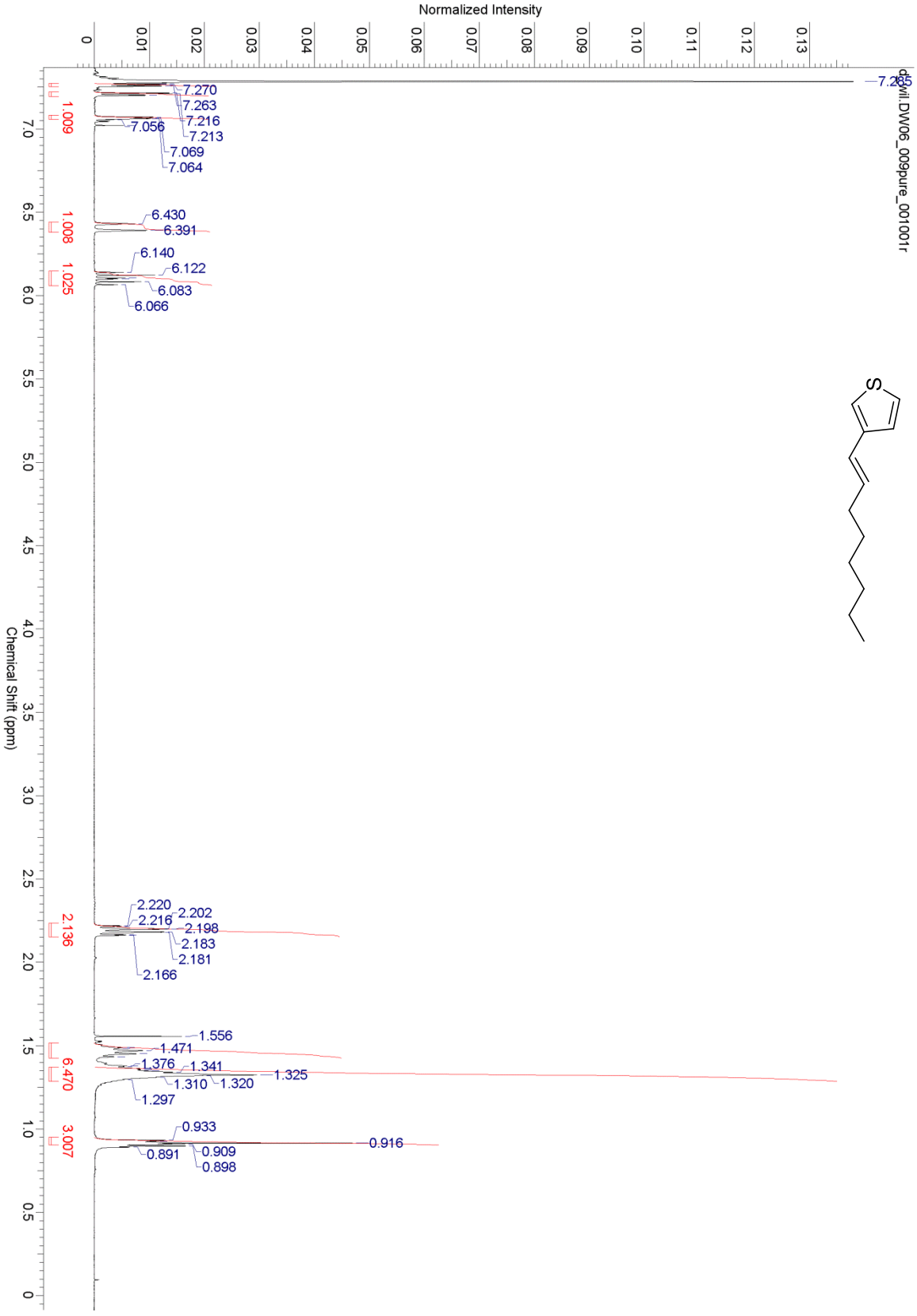

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wil:DW06_052Pure_002001r
Chemical Shift (ppm)
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
149.657
136.206
135.871
133.119
129.431
129.073
127.343
124.668
121.307
77.349
77.036
76.716
33.192
31.760
29.290
28.948
22.645
14.117
N

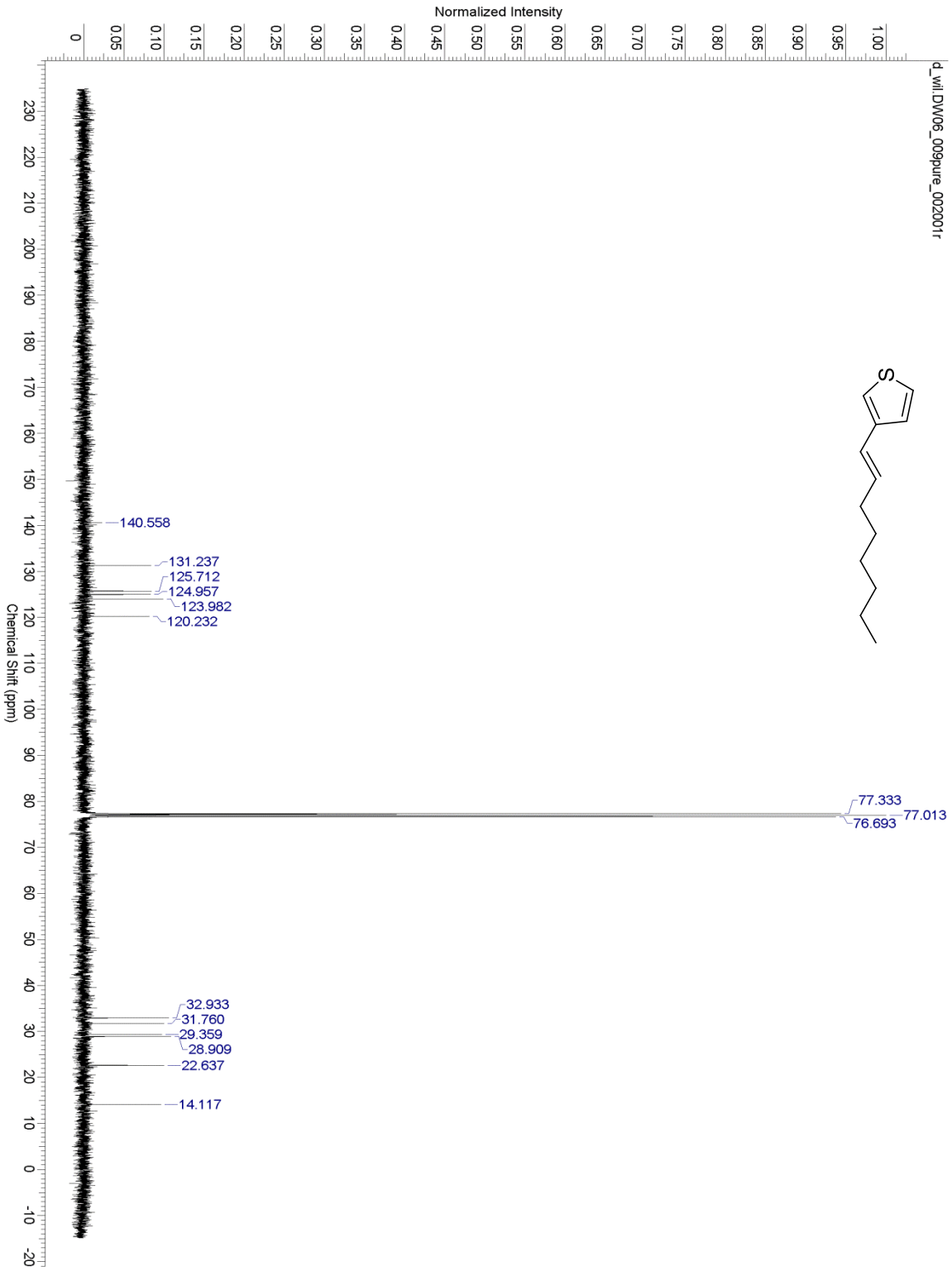
(E)-2-(oct-1-en-1-yl)thiophene, 31



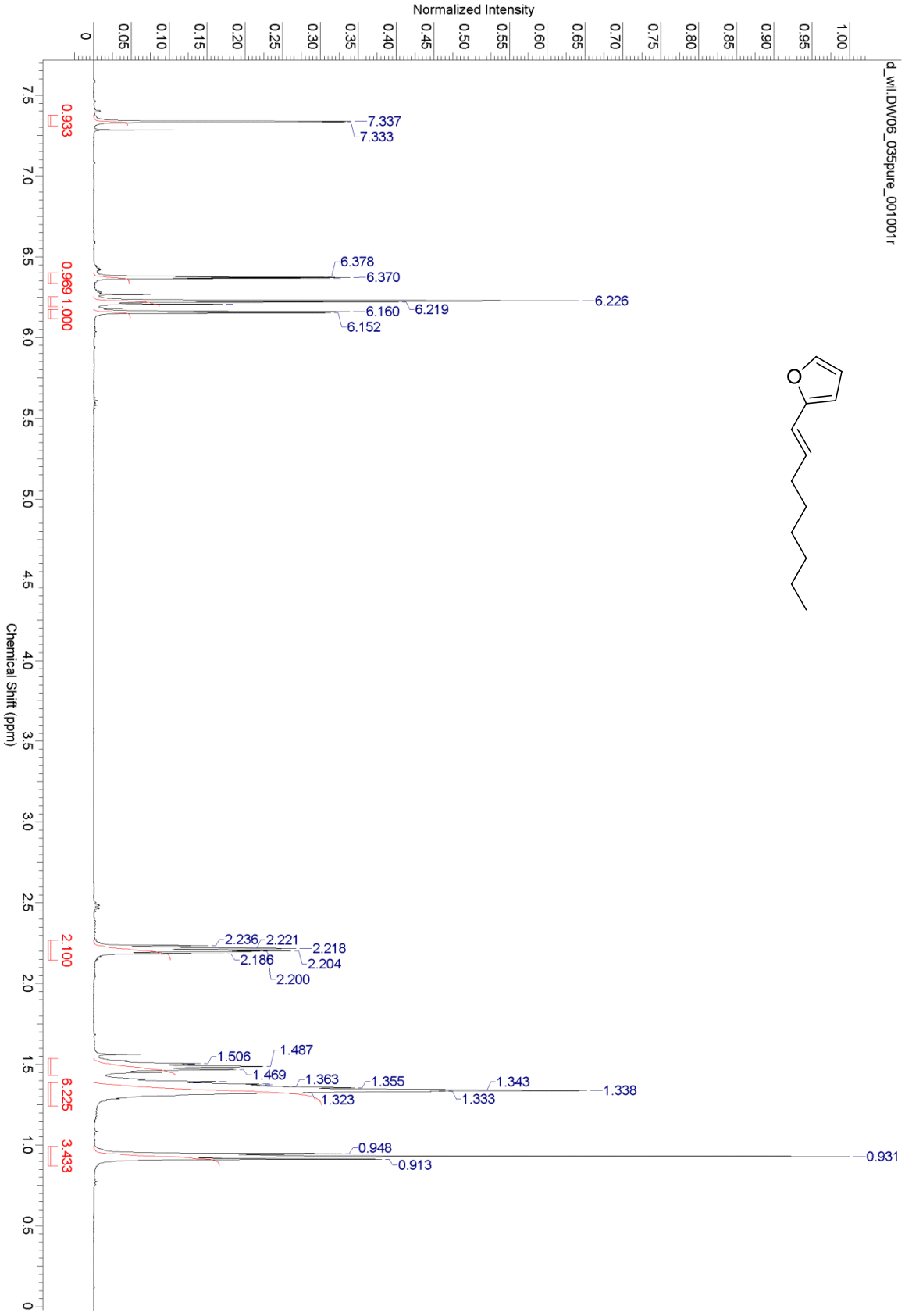

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wil.DW06_008pure_002001r
Chemical Shift (ppm)
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
143.256
131.324
127.186
124.070
122.973
77.338
77.018
76.698
32.862
31.742
29.220
28.892
22.629
14.102
S

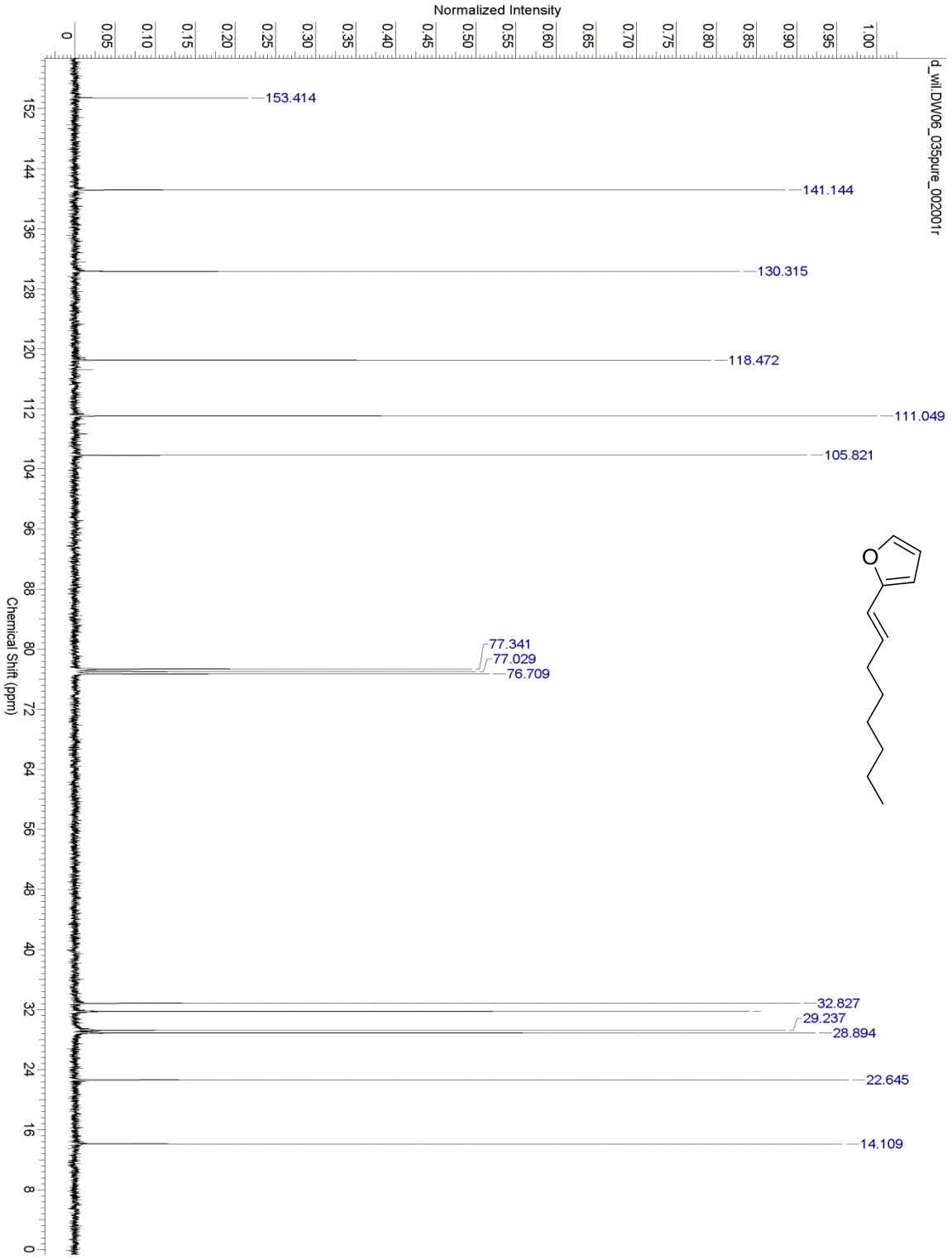
(E)-3-(oct-1-en-1-yl)thiophene, 32



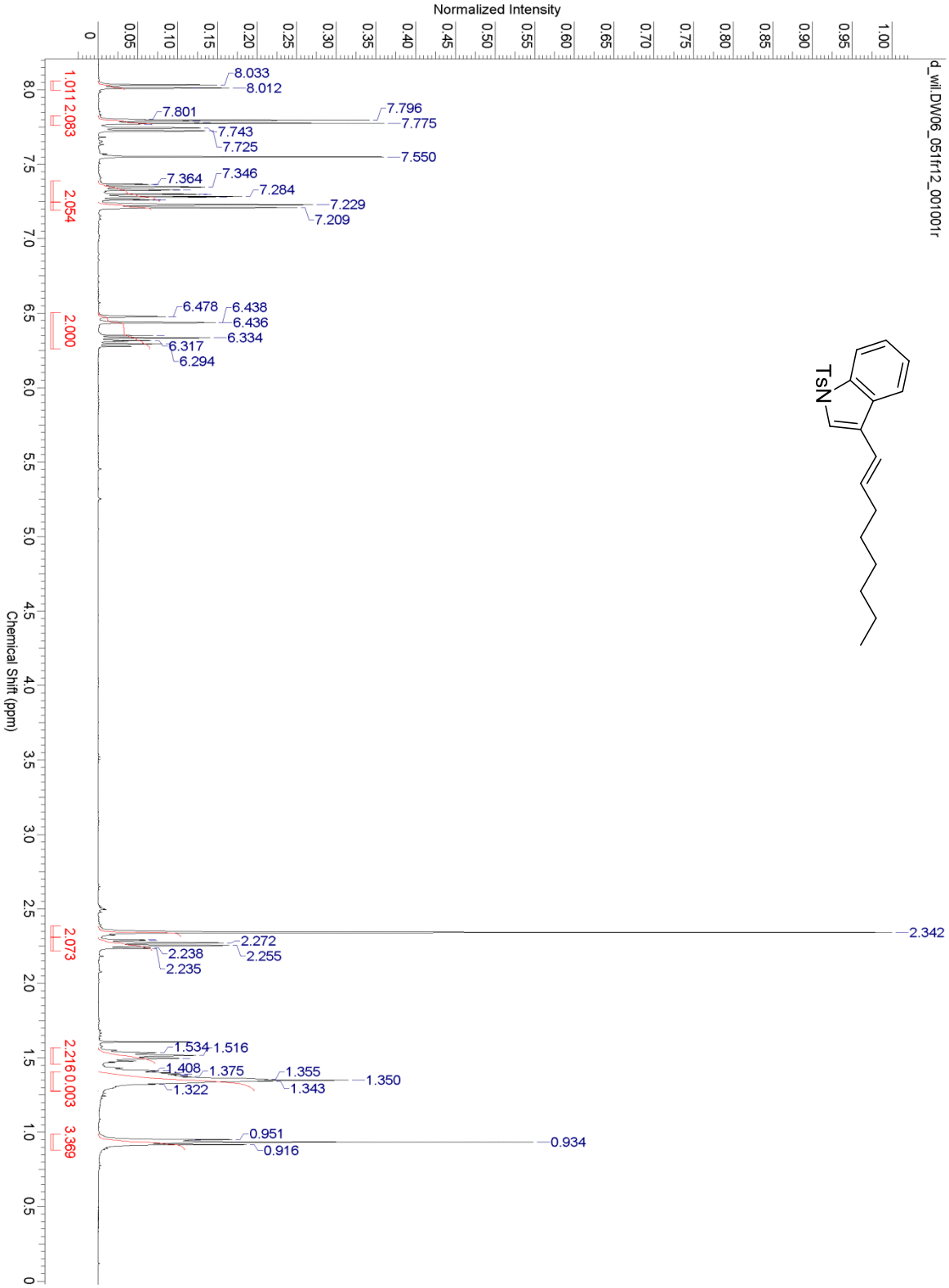

Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wiLDW06_009pure_002001r
Chemical Shift (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
140.558
131.237
125.712
124.957
123.982
120.232
77.333
77.013
76.693
32.933
31.760
29.359
28.909
22.637
14.117
S

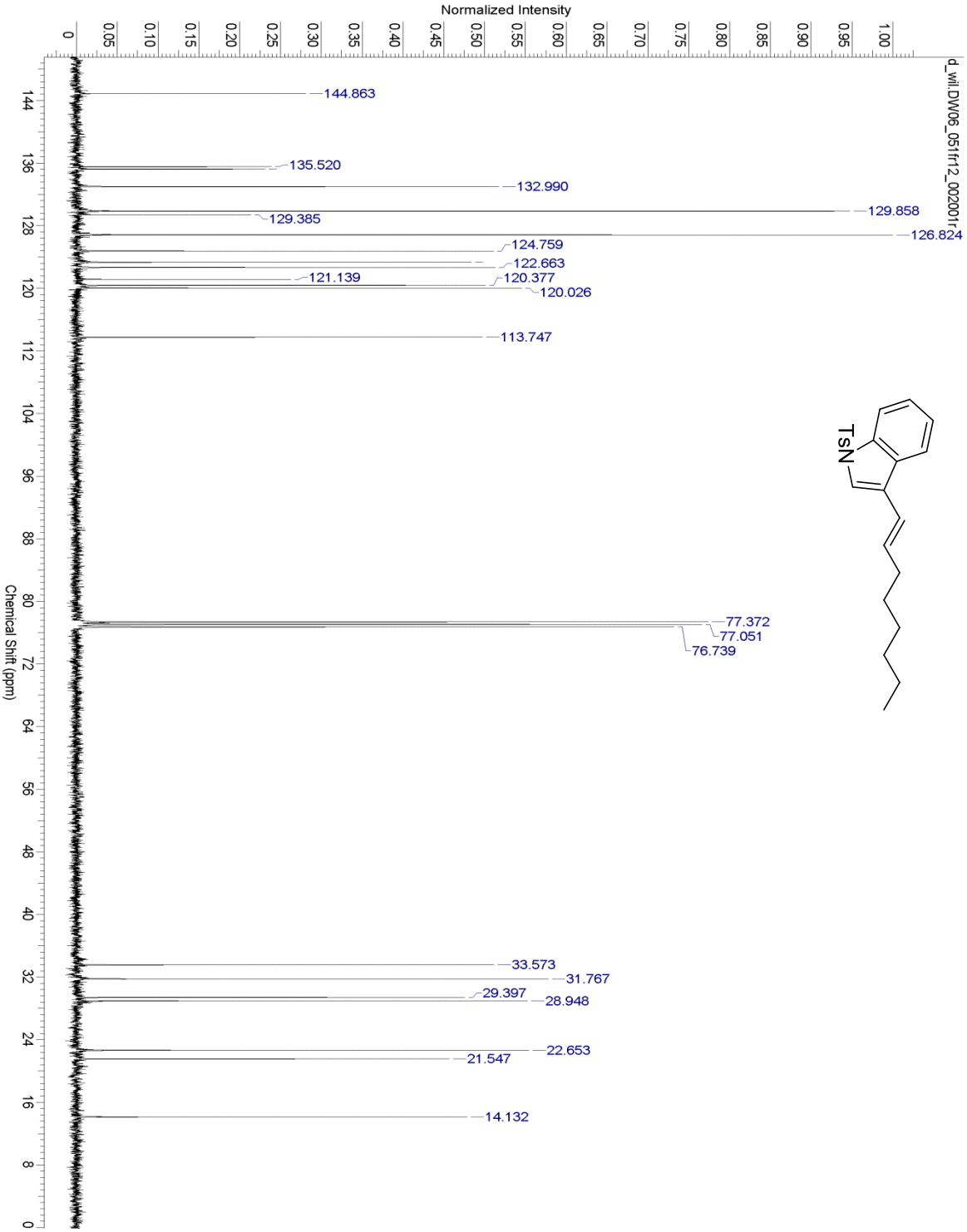
(E)-2-(oct-1-en-1-yl)furan, 33




Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wil.DW06_035pure_002001r
153.414
141.144
130.315
118.472
111.049
105.821
77.341
77.029
76.709
32.827
29.237
28.894
22.645
14.109
Chemical Shift (ppm)
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
O

(E)-3-(oct-1-en-1-yl)-1-tosyl-1H-indole, 34




Normalized Intensity
0
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0.55
0.60
0.65
0.70
0.75
0.80
0.85
0.90
0.95
1.00
d_wil.DW06_051f12_002001r
144.863
135.520
132.990
129.858
129.385
126.824
124.759
122.663
121.139
120.377
120.026
113.747
77.372
77.051
76.739
33.573
31.767
29.397
28.948
22.653
21.547
14.132
Chemical Shift (ppm)
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
TsN

References

S1. D. L. Schmidt, E. E., Flagg, *Inorg. Chem.* **1967**, *6*, 1262.
S2. Tobisu, M.; Yamakawa, K.; Shimasaki, T.; Chatani, N. *Chem. Commun.* **2011**, *47*, 2946.
S3. Cahiez, G.; Gager, O.; Lecomte, F. *Org. Lett.* **2008**, *10*, 5255.
S4. N. Miyaura, T. Ishiyama, M. Ishikawa, A. Suzuki, *Tetrahedron Lett*. **1986**, *27*, 52, 6369.
S5. Lauer, A. M.; Mahmud, F.; Wu, J. *J. Am. Chem. Soc.* **2011**, *133*, 9119.
S6. Delcamp, J. H.; White, M. C. *J. Am. Chem. Soc.* **2006**, *128*, 15076.
S7. I. Uchida, Y. Itoh, T. Namiki, M. Nishikawa, M. Hashimoto, *Tetrahedron Lett*. **1986**, *27*, 18, 2015.
S8. G. Lui, S. S. Stahl, *J. Am. Chem. Soc*, **2007**, *129*, 19, 6328.
S9. V. Polshetiwar, P. Heseman, J. J. E. Moreau, *Tetrahedron*, **2007**, *63*, 29, 6784.
S10. A. R. Katritzky, D. Cheng and J. Li, *J. Org. Chem*. **1998,** *63*, 10, 343.
S11. K. Tamao, K. Kobayashi, I. Yoshihiko, *Tetrahedron Lett.* **1989**, *30*, 44, 6051.
S12. F. Berthiol, H. Doucet, M. Santelli, *Tetrahedron Lett*. **2003**, *44*, 6, 1221.
S13. B. H. Lipshutz, B. Frieman, *Tetrahedron*, **2004**, 60, 6, 1309.
S14. Y. Fall, F. Berthiol, H. Doucet, M. Santelli, *Synthesis*, **2007**, 11, 1683.
S15. B. Huang, W. Hao, M-Z. Cai, P. Wang, *J. Organomet. Chem*. **2011**, *696*, 13, 2685.
S16. A. T. Lindhardt, T. M. Gogsig, T. Skrydstrup *J. Org. Chem*. **2009**, *74*, 1, 135.
S17. J. Mulzer, M. Zippel, *Tetrahedron Lett.* **1980**, *21*, 751.
S18. A. Mori, M. Suguro, *Synlett*, **2001**, *6*, 845.
S19. M. G. Organ, J. T. Cooper, L. R. Rogers, F. Soleymanzadeh, T. Payl, *J. Org. Chem*. **2000**, *65*, 23, 7959.
S20. SX - C-M. Ting, Y-L. Hsu, R-S. Liu, *Chem. Commun*. **2012,** *48*, 52, 6577.
S21. G. R. Peh, E. A. B. Kantchev, J-C. Er, J. Y. Ying**,** *Chem. Eur. J*. **2010**, 16, 13, 4010.
S22. E. Schulz, P. Kinderli, A. Perrard, M. Lemaire, *Applied Catalysis, A: General*, **1996**, *144*, 1-2, 293.