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Supplementary Information

Ruthenium polypyridyl complex-catalysed aryl alkoxylation of styrenes: Improving reactivity using a continuous-flow photo-microreactor

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General Information

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received.

Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Merck silica gel 60 F254). Flash column chromatography was performed with Kanto silica gel 60N (Spherical, Neutral, 40–50 mm). Visualization of the developed chromatogram was performed by UV lamp (254 nm) and ceric ammonium molybdate solution stain.

NMR spectra were recorded on a JEOL ECA 500 spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR), and are internally referenced to residual protio solvent signals or TMS (note: CDCl3 referenced at δ 7.26 and 77.0 ppm respectively, TMS referenced at δ 0 and 0 ppm respectively). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets), coupling constant (Hz), integration, and assignment. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm).

IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in terms of frequency of absorption (cm^{-1}).

High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-T100TD and are reported as *m/z* (M+H+, relative intensity).

Melting points were measured on a Yanagimoto micro melting point apparatus without correlation.

Glass (borosilicate glass) Chip for microreactor was from Dexerials Corporation.

General Procedure for aryl alkoxylation of olefins with Flow Microreactor

A solution of aryldiazonium tetrafluoroborate (0.35 mol/L) in MeCN and a solution of styrene (0.7 mol/L, 2.0 equiv) and $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (1.75×10^{-3} mol/L, 0.5 mol%) in MeOH were degassed *via* Freeze-Pump-Thaw (FPT) cycling for three times and backfilled with Ar. The two solutions were introduced into different channels respectively by using a syringe pump. Both streams were mixed in the channel of the reactor chip. Light (450 nm) from an LED array (sum: 1.20 W x 2) was used to irradiate the flow from a distance of 1.5 cm from the chip surface. The residue was filtrated through silica gel, washed with $CHCl_3$, concentrated in vacuo. The resulting mixture was purified by flash column chromatography on silica gel (*n*-hexane : EtOAc = 40 : 1) to give product.

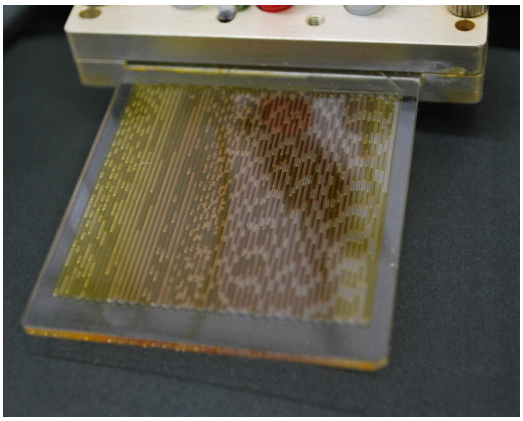
General Procedure for aryl alkoxylation of olefins with Flow Microreactor 4d

A solution of aryldiazonium tetrafluoroborate (0.35 mol/L) in MeCN and a solution of styrene (0.7 mol/L, 2.0 equiv) and $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (1.75×10^{-3} mol/L, 0.5 mol%) in DMF were degassed *via* Freeze-Pump-Thaw (FPT) cycling for three times and backfilled with Ar. The two solutions were introduced into different channels respectively by using a syringe pump. Both streams were mixed in the channel of the reactor chip. Light (450 nm) from an LED array (sum: 1.20 W x 2) was used to irradiate the flow from a distance of 1.5 cm from the chip surface. The residue was diluted with EtOAc, washed with water, dried with $MgSO_4$, and concentrated *in vacuo.* The resulting mixture was purified by flash column chromatography on silica gel (*n*-hexane : EtOAc = 40 : 1) to give product.

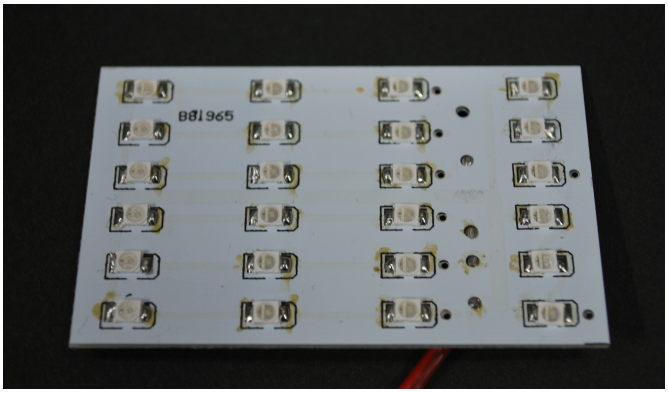
Preparation of aryldiazonium tetrafluoroborate

To a round-bottom flask, a solution of water (2.0 mL) and conc. HCl (2.0 mL) (1:1) was added to a mixture of aniline derivatives (10.0 mmol, 1.0 equiv) and conc. HCl (3.0 mL) at 0 °C. To this solution, a solution of $NaNO_2$ (1.1 equiv) in 1.5 mL of water was added dropwise and stirred for 30 min at 0 °C. After that, an ice cold solution of 45% aq. HBF_4 (10 mL) was added slowly to the reaction mixture and stirred for 15 min at 0 °C. The resulting solid precipitate was filtered and washed with ice cold water, dried under a vacuum desiccator, and stored at freezer.

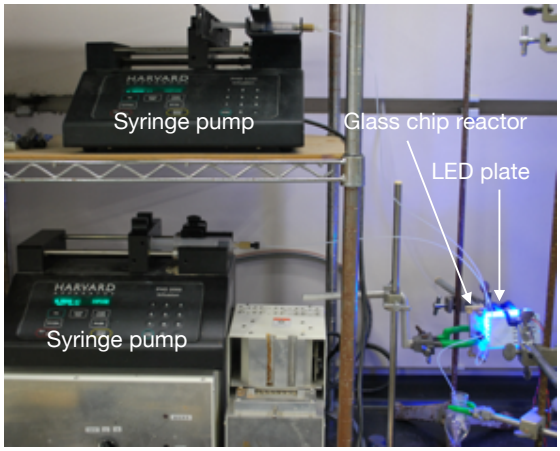
Picture S1. The glass chip during the reaction



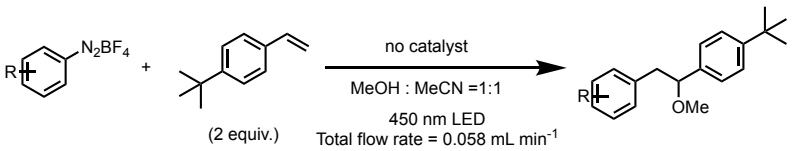
Picture S2. Picture for LEDs array (40 mm x 65 mm; 0.05 W x 4 x 6; 450 nm)



Picture S3. General reaction setup

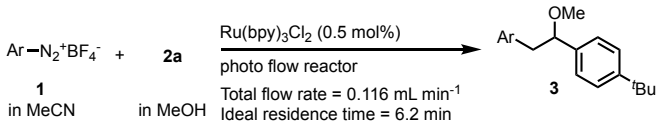


Scheme S1. Reaction without Ru complex



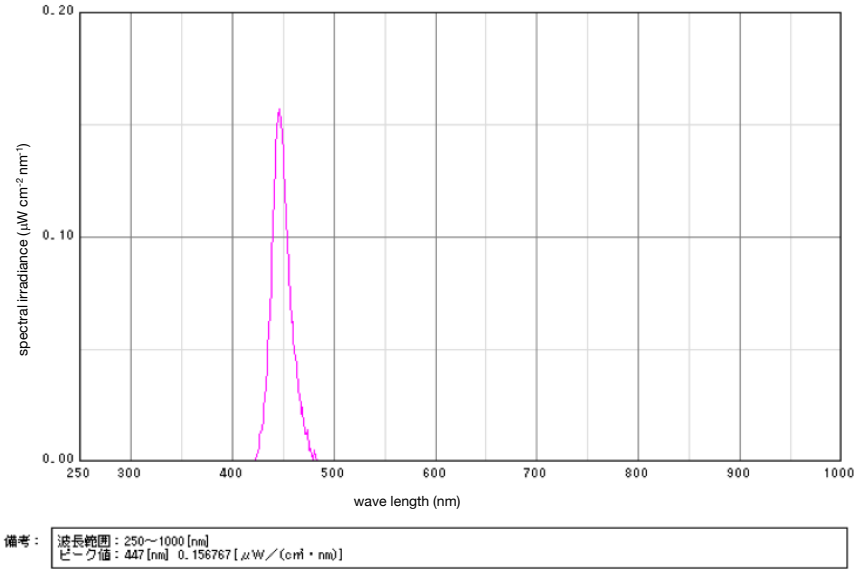
Entry	R	yield (%)	The reaction with Ru cat.; yield (%)
1	***p*-cyano**	**71**	**78**
2	***p*-nitro**	**<10**	**66**
3	***p*-methoxy**	**n.d.**	**35**
4	***p*-methyl**	**n.d.**	**41**

Scheme S2. Reaction efficiency of the flow reaction compared with batch reaction

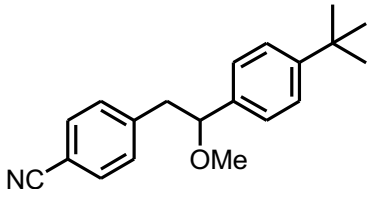


entry	**1**	Ar	conc. (mol/L)	**2** conc. (mol/L)	**3**	yield$_{flow}$ (%)	STY (g h $^{-1}$L^{-1})	yield$_{batch}$ (%)	STY (g h $^{-1}$L^{-1})
1	**1a**	4-CNC_6H_4	0.35	0.70	**3aa**	78	259.4	46	20.2
2	**1b**	4-MeC_6H_4	0.35	0.70	**3ba**	41	131.1	42	17.8
3	**1c**	4-^{t}BuC_6H_4	0.35	0.70	**3ca**	40	147	0	-
4	**1d**	4-$MeOC_6H_4$	0.35	0.70	**3da**	35	118.3	0	-
5	**1e**	C_6H_5	0.35	0.70	**3ea**	62	188.5	49	21.6
6[c]	**1f**	4-$NO_2C_6H_4$	0.175	0.35	**3fa**	66	234.3	58	27.2
7[d]	**1g**	2-CNC_6H_4	0.0875	0.175	**3ga**	58	192.8	60	26.4

Figure S1. The wave length and spectral irradiance of LED

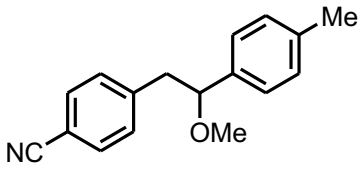


4-[2-Methoxy-2-(4-*tert*-butylphenyl)ethyl]benzonitrile (3aa) [1]



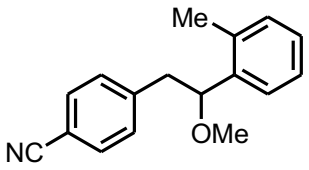
78% yield, 80 mg, 0.27 mmol (based on 0.35 mmol scale)
Yellow oil
TLC (SiO_2): R_f = 0.36 (*n*-hexane:ethyl acetate =10:1).
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H), 4.29 (dd, *J* = 8.2 Hz, 5.0 Hz, 1H), 3.16 (s, 3H), 3.11 (dd, *J* = 13.7 Hz, 8.2 Hz, 1H), 2.93 (dd, *J* = 13.7 Hz, 5.0 Hz, 1H), 1.32 (s, 9H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 150.9, 144.5, 137.8, 131.8, 130.2, 126.3, 125.3, 119.1, 110.0, 83.9, 56.7, 44.8, 34.5, 31.3.

4-[2-Methoxy-2-(4-methylphenyl)ethyl]benzonitrile (3ab)



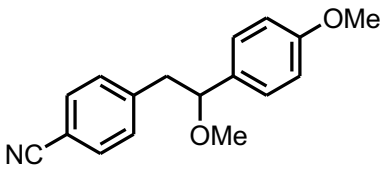
69% yield, 61 mg, 0.24 mmol (based on 0.35 mmol scale)
White solid
TLC (SiO_2): R_f = 0.22 (*n*-hexane:ethyl acetate =10:1).
m.p.: 70.2-71.9 ºC
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 4.28 (dd, *J* = 7.8 Hz, 5.5 Hz, 1H), 3.16 (s, 3H), 3.12 (dd, *J* = 13.7 Hz, 7.8 Hz, 1H), 2.93 (dd, *J* = 13.7 Hz, 5.5 Hz, 1H), 2.35 (s, 3H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 144.2, 137.7, 137.6, 131.8, 130.3, 129.1, 126.6, 119.1, 110.0, 84.0, 56.6, 44.8, 21.1.
HRMS: *m/z* (DART) calcd for $C_{17}H_{18}NO^+$ $(M+H)^+$ 252.1383, found 252.1387.
FTIR: (neat): 2927, 2823, 2228, 1609, 1512, 1449, 1414, 1350, 1178, 1097, 1021, 817 cm^{-1}

4-[2-Methoxy-2-(2-methylphenyl)ethyl]benzonitrile (3ac)



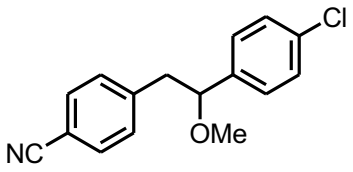
62% yield, 55 mg, 0.22 mmol (based on 0.35 mmol scale)
White solid
TLC (SiO_2): R_f = 0.22 (*n*-hexane:ethyl acetate =10:1).
m.p.: 51.5-53.0 ºC
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.24-7.17 (m, 4H), 7.12 (d, *J* = 7.8 Hz, 1H), 4.59 (dd, *J* = 7.8 Hz, 4.8 Hz , 1H), 3.16 (s, 3H), 3.06 (dd, *J* = 13.7 Hz, 7.8 Hz , 1H), 2.92 (dd, *J* = 13.7 Hz, 4.8 Hz , 1H), 2.20 (s, 3H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 144.3, 138.9, 135.2, 131.8, 130.4, 130.2, 127.5, 126.4, 125.8, 119.1, 110.1, 80.4, 56.7, 43.8, 18.9.
HRMS: *m/z* (DART) calcd for $C_{17}H_{18}NO^+$ $(M+H)^+$ 252.1383, found 252.1373.
FTIR: (neat): 2930, 2823, 2228, 1608, 1507, 1462, 1178, 1093, 825, 762, 734 cm^{-1}

4-[2-Methoxy-2-(4-methoxyphenyl)ethyl]benzonitrile (3ad)



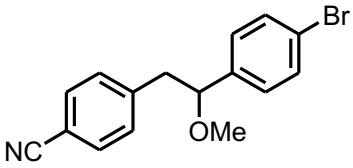
56% yield, 53 mg, 0.20 mmol (based on 0.35 mmol scale)
White solid
TLC (SiO_2): R_f = 0.13 (*n*-hexane:ethyl acetate =10:1).
m.p.: 73.7-75.7 ºC
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.26 (dd, *J* = 7.8 Hz, 6.0 Hz , 1H), 3.81 (s, 3H), 3.15 (s, 3H), 3.13 (dd, *J* = 13.7 Hz, 7.8 Hz, 1H), 2.93 (dd, *J* = 13.7 Hz, 6.0 Hz, 1H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 159.3, 144.2, 132.7, 131.8, 130.3, 127.9, 119.1, 113.8, 110.0, 83.7, 56.5, 55.2, 44.8.
HRMS: *m/z* (DART) calcd for $C_{16}H_{14}NO^+$ $(M-MeOH+H)^+$ 236.1070, found 236.1061.
FTIR: (neat): 2934, 2837, 2227, 1610, 1512, 1464, 1415, 1304, 1247, 1174, 1095, 1034, 835, 775 cm^{-1}

4-[2-Methoxy-2-(4-chlorophenyl)ethyl] benzonitrile (3ae)



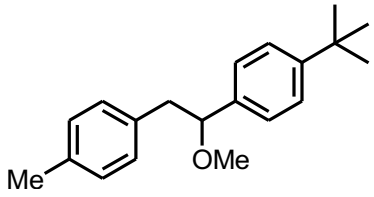
60% yield, 57 mg, 0.21 mmol (based on 0.35 mmol scale)
Yellow solid
TLC (SiO_2): R_f = 0.16 (*n*-hexane:ethyl acetate =10:1).
m.p.: 79.5-81.3 ºC
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 4.30 (dd, *J* = 7.8 Hz, 5.5 Hz, 1H), 3.17 (s, 3H), 3.11 (dd, *J* = 13.7 Hz, 7.8 Hz, 1H), 2.92 (dd, *J* = 13.7 Hz, 5.5 Hz, 1H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 143.6, 139.3, 133.6, 131.9, 130.3, 128.7, 128.0, 119.0, 110.2, 83.5, 56.8, 44.6.
HRMS: *m/z* (DART) calcd for $C_{16}H_{15}ClNO^+$ $(M+H)^+$ 272.0837, found 272.0847.
FTIR: (neat): 2932, 2824, 2731, 2228, 1608, 1507, 1490, 1465, 1410, 1346, 1290, 1250, 1178, 1091, 1015, 833, 743 cm^{-1}

4-[2-Methoxy-2-(4-bromophenyl)ethyl]benzonitrile (3af)



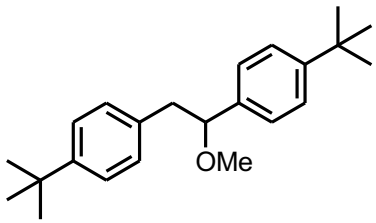
45% yield, 51 mg, 0.16 mmol (based on 0.35 mmol scale)
Colorless and crystalline solid
TLC (SiO_2): R_f = 0.13 (*n*-hexane:ethyl acetate =10:1).
m.p.: 103.9-105.4 ºC
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 4.29 (dd, *J* = 7.8 Hz, 5.5 Hz, 1H), 3.17 (s, 3H), 3.10 (dd, *J* = 13.7 Hz, 7.8 Hz, 1H), 2.92 (dd, *J* = 13.7 Hz, 5.5 Hz, 1H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 143.5, 139.8, 131.9, 131.6, 130.3, 128.3, 121.7, 119.0, 110.2, 83.5, 56.8, 44.6.
HRMS: *m/z* (EI+) calcd for $C_{15}H_{11}BrN^+$ $(M\text{-}MeOH+H)^+$ 284.0075, found 284.0067.
FTIR: (neat): 2986, 2931, 2824, 2227, 1608, 1592, 1507, 1485, 1404, 1344, 1297, 1228, 1178, 1095, 1071, 1011, 880, 830, 776, 746, 720 cm^{-1}

1-[2-Methoxy-2-(4-*tert*-butylphenyl)ethyl]-4-methylbenzene (3ba)



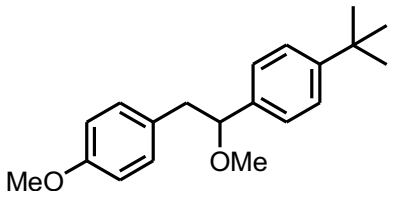
41% yield, 41 mg, 0.14 mmol (based on 0.35 mmol scale)
Orange oil
TLC (SiO_2): R_f = 0.47 (*n*-hexane:ethyl acetate =10:1).
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.05 (m, 4H), 4.28 (dd, *J* = 8.2 Hz, 5.0 Hz, 1H), 3.17 (s, 3H), 3.04 (dd, *J* = 14.2 Hz, 8.2 Hz, 1H), 2.84 (dd, *J* = 14.2 Hz, 5.0 Hz, 1H), 1.33 (s, 9H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 150.5, 138.9, 136.0, 135.6, 129.3, 128.9, 126.5, 125.3, 85.0, 56.9, 44.5, 34.6, 31.5, 21.2.
HRMS: *m/z* (DART) calcd for $C_{19}H_{23}^+$ $(M\text{-}MeOH+H)^+$ 251.1794, found 251.1788.
FTIR: (neat): 2963, 2867, 2820, 1899, 1612, 1515, 1463, 1409, 1363, 1308, 1269, 1231, 1202, 1156, 1098, 1040, 1022, 1005, 977, 942, 880, 831, 810, 797, 756, 712, 692, 672 cm^{-1}

1-[2-Methoxy-2-(4-*tert*-butylphenyl)ethyl]-4-tert-butylbenzene (3ca)



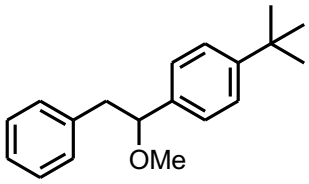
40% yield, 46 mg, 0.14 mmol (based on 0.35 mmol scale)
Brown crystalline solid
TLC (SiO_2): R_f = 0.47 (*n*-hexane:ethyl acetate =10:1).
m.p.: 68.1-69.9 ºC
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.21(d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 4.31 (dd, *J* = 8.5 Hz, 4.6 Hz, 1H), 3.17 (s, 3H), 3.04 (dd, *J* = 14.2 Hz, 8.5 Hz, 1H), 2.84 (dd, *J* = 14.2 Hz, 4.6 Hz, 1H), 1.32 (s, 9H), 1.30 (s, 9H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 150.4, 148.8, 139.0, 136.0, 128.9, 126.3, 125.2, 125.0, 84.7, 56.8, 44.3, 34.5, 34.4, 31.4.
HRMS: *m/z* (DART) calcd for $C_{22}H_{29}^+$ $(M\text{-}MeOH+H)^+$ 293.2264, found 293.2260.
FTIR: (neat): 2963, 2868, 1510, 1464, 1410, 1364, 1269, 1203, 1102, 1020, 834 cm^{-1}

1-Methoxy-4-[2-methoxy-2-(4-*tert*-butylphenyl)ethyl]benzene (3da)



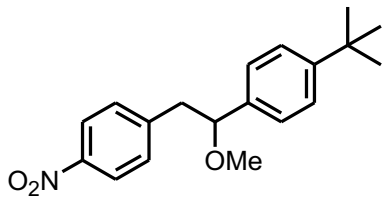
35% yield, 37 mg, 0.12 mmol (based on 0.35 mmol scale)
Yellow oil
TLC (SiO_2): R_f = 0.41 (*n*-hexane:ethyl acetate =10:1).
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 4.25 (dd, *J* = 8.0 Hz, 5.3 Hz, 1H), 3.78 (s, 3H), 3.17 (s, 3H), 3.03 (dd, *J* = 14.0 Hz, 8.0 Hz, 1H), 2.82 (dd, *J* = 14.0 Hz, 5.3 Hz, 1H), 1.32 (s, 9H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 157.9, 150.4, 138.7, 131.0, 130.3, 126.4, 125.1, 113.4, 85.0, 56.8, 55.2, 43.9, 34.5, 31.4.
HRMS: *m/z* (DART) calcd for $C_{19}H_{23}O^+$ $(M\text{-}MeOH+H)^+$ 267.1743, found 267.1745.
FTIR: (neat): 2961, 2905, 2868, 2835, 1613, 1585, 1512, 1464, 1442, 1408, 1363, 1301, 1246, 1203, 1177, 1098, 1038, 998, 978, 879, 833, 802, 756, 715, 692, 672 cm^{-1}

1-[1-Methoxy-2-phenylethyl]-4-*tert*-butylbenzene (3ea)



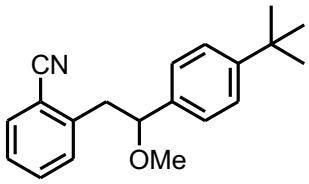
62% yield, 58 mg, 0.22 mmol (based on 0.35 mmol scale)
Yellow crystalline solid
TLC (SiO_2): R_f = 0.45 (*n*-hexane:ethyl acetate =10:1).
m.p.: 39.7-40.7 ºC
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.25 (t, *J* = 7.0 Hz, 2H), 7.21-7.17 (m, 3H), 7.15 (d, *J* = 7.0 Hz, 2H), 4.31 (dd, *J* = 8.2 Hz, 5.0 Hz, 1H), 3.17 (s, 3H), 3.08 (dd, *J* = 13.7 Hz, 8.2 Hz, 1H), 2.88 (dd, *J* = 13.7 Hz, 5.0 Hz, 1H), 1.32 (s, 9H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 150.5, 138.9, 138.7, 129.4, 128.1, 126.4, 126.1, 125.2, 84.8, 56.8, 44.8, 34.5, 31.4.
HRMS: *m/z* (DART) calcd for $C_{18}H_{21}^+$ $(M\text{-}MeOH+H)^+$ 237.1638, found 237.1645.
FTIR: (neat): 3029, 2964, 2868, 2821, 1605, 1510, 1496, 1454, 1409, 1363, 1269, 1202, 1100, 1078, 1031, 874, 833, 750, 701 cm^{-1}

1-[2-Methoxy-2-(4-*tert*-butylphenyl)ethyl]-4-nitrobenzene (3fa) [1]



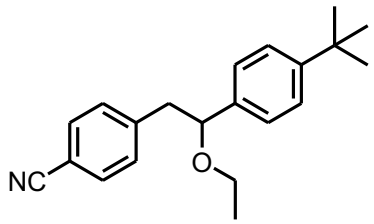
66% yield, 72 mg, 0.23 mmol (based on 0.35 mmol scale)
Yellow solid
TLC (SiO_2): R_f = 0.40 (*n*-hexane:ethyl acetate =10:1).
^{1}H NMR: (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 4.32 (dd, *J* = 8.2 Hz, 5.0 Hz, 1H), 3.16 (dd, 13.7 Hz, 8.2 Hz, 1H), 3.17 (s, 3H), 2.99 (dd, *J* = 13.7 Hz, 5.0 Hz, 1H), 1.33 (s, 9H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 151.0, 146.7, 146.5, 137.7, 130.3, 126.3, 125.4, 123.3, 83.9, 56.8, 44.5, 34.6, 31.4.

2-[2-Methoxy-2-(4-tert-butylphenyl)ethyl]benzonitrile (3ga) [1]



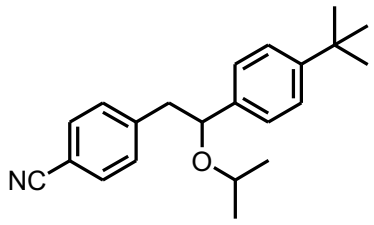
58% yield, 59 mg, 0.20 mmol (based on 0.35 mmol scale)
Yellow oil
TLC (SiO_2): R_f = 0.40 (*n*-hexane:ethyl acetate =10:1).
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.2 Hz, 1H), 7.47 (dd, *J* = 8.2 Hz, 6.8 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.30 (dd, *J* = 7.8 Hz, 6.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 4.42 (dd, *J* = 8.7 Hz, 4.6 Hz, 1H), 3.22 (dd, 14.2 Hz, 8.7 Hz, 1H), 3.17 (s, 3H), 3.13 (dd, *J* = 14.2 Hz, 4.6 Hz, 1H), 1.33 (s, 9H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 150.8, 142.8, 137.9, 132.6, 132.3, 131.1, 126.7, 126.2, 125.4, 118.2, 112.8, 83.4, 56.9, 43.4, 34.5, 31.4.

4-[2-Ethoxy-2-(4-*tert*-butylphenyl)ethyl]benzonitrile (4a)



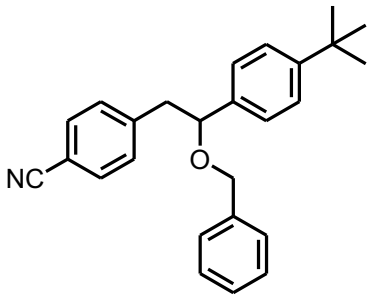
54% yield, 58 mg, 0.19 mmol (based on 0.35 mmol scale)
Yellow oil
TLC (SiO_2): R_f = 0.26 (*n*-hexane:ethyl acetate =10:1).
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 4.37 (dd, *J* = 8.2 Hz, 5.0 Hz, 1H), 3.38 (dq, *J* = 9.2 Hz, 6.9 Hz, 1H), 3.21 (dq, *J* = 9.2 Hz, 7.3 Hz, 1H), 3.11 (dd, *J* = 13.7 Hz, 8.2 Hz, 1H), 2.91 (dd, *J* = 13.7 Hz, 5.0 Hz, 1H), 1.32 (s, 9H), 1.10 (dd, *J* = 7.3 Hz, 6.9 Hz, 3H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 150.7, 144.7, 138.6, 131.7, 130.3, 126.1, 125.3, 119.2, 109.9, 82.1, 64.2, 44.9, 34.5, 31.4, 15.2.
HRMS: *m/z* (DART) calcd for $C_{19}H_{20}N^+$ $(M\text{-}EtOH+H)^+$ 262.1590, found 262.1590.
FTIR: (neat): 2965, 2903, 2868, 2228, 1917, 1608, 1506, 1463, 1444, 1413, 1396, 1364, 1341, 1308, 1269, 1222, 1202, 1178, 1158, 1091, 1015, 950, 925, 884, 838, 738, 683 cm^{-1}

4-[2-Isopropoxy-2-(4-*tert*-butylphenyl)ethyl]benzonitrile (4b)



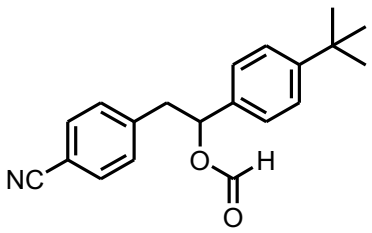
47% yield, 51 mg, 0.16 mmol (based on 0.35 mmol scale)
Yellow sticky oil
TLC (SiO_2): R_f = 0.26 (*n*-hexane:ethyl acetate =10:1).
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 4.47 (dd, *J* = 8.5 Hz, 4.7 Hz, 1H), 3.41 (sep, *J* = 6.1 Hz, 1H), 3.04 (dd, *J* = 13.7 Hz, 8.5 Hz, 1H), 2.88 (dd, *J* = 13.7 Hz, 4.7 Hz, 1H), 1.32 (s, 9H), 1.05 (d, *J* = 6.1 Hz, 3H), 0.91 (d, *J* = 6.1 Hz, 3H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 150.5, 144.9, 139.4, 131.6, 130.4, 126.1, 125.2, 119.2, 109.8, 79.4, 69.0, 45.5, 34.5, 31.4, 23.3, 20.9.
HRMS: *m/z* (DART) calcd for $C_{19}H_{20}N^+$ $(M\text{-}^i PrOH+H)^+$ 262.1590, found 262.1581.
FTIR: (neat): 2967, 2870, 2228, 1608, 1506, 1465, 1413, 1376, 1331, 1269, 1176, 1139, 1123, 1072, 1017, 964, 836 cm^{-1}

4-[2-Benzyloxy-2-(4-*tert*-butylphenyl)ethyl]benzonitrile (4c)



42% yield, 54 mg, 0.15 mmol (based on 0.35 mmol scale)
White solid
TLC (SiO_2): R_f = 0.22 (*n*-hexane:ethyl acetate =10:1).
m.p.: 91.2-93.0 ºC
^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.29-7.21 (m, 7H), 7.10-7.08 (m, 2H), 4.47 (dd, *J* = 8.7 Hz, 4.6 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.16 (d, *J* = 12.0 Hz, 1H), 3.15 (dd, *J* = 13.8 Hz, 8.7 Hz, 1H), 2.96 (dd, *J* = 13.8 Hz, 4.6 Hz, 1H), 1.34 (s, 9H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 151.0, 144.5, 138.1, 138.0, 131.8, 130.4, 128.2, 127.6, 127.5, 126.4, 125.4, 119.2, 109.9, 81.3, 70.3, 45.0, 34.6, 31.4.
HRMS: *m/z* (DART) calcd for $C_{19}H_{20}N^+$ $(M\text{-}BnOH+H)^+$ 262.1590, found 262.1579.
FTIR: (neat): 2963, 2867, 2228, 1608, 1507, 1455, 1413, 1363, 1269, 1204, 1073, 1018, 838, 736 cm^{-1}

[2-(4-cyanobenzene)-1-(4-tert-butylphenyl)ethyl]formate (4d)

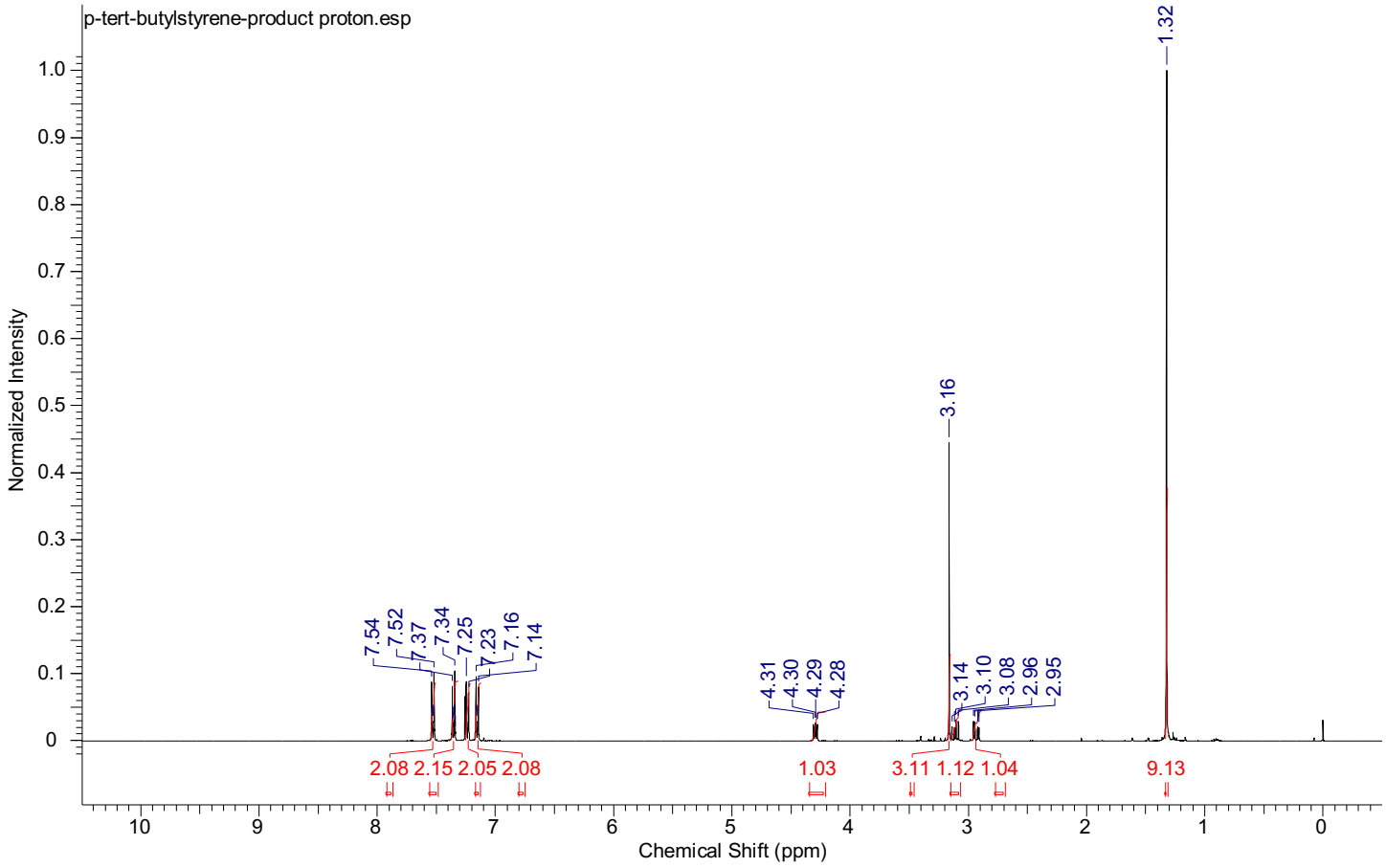


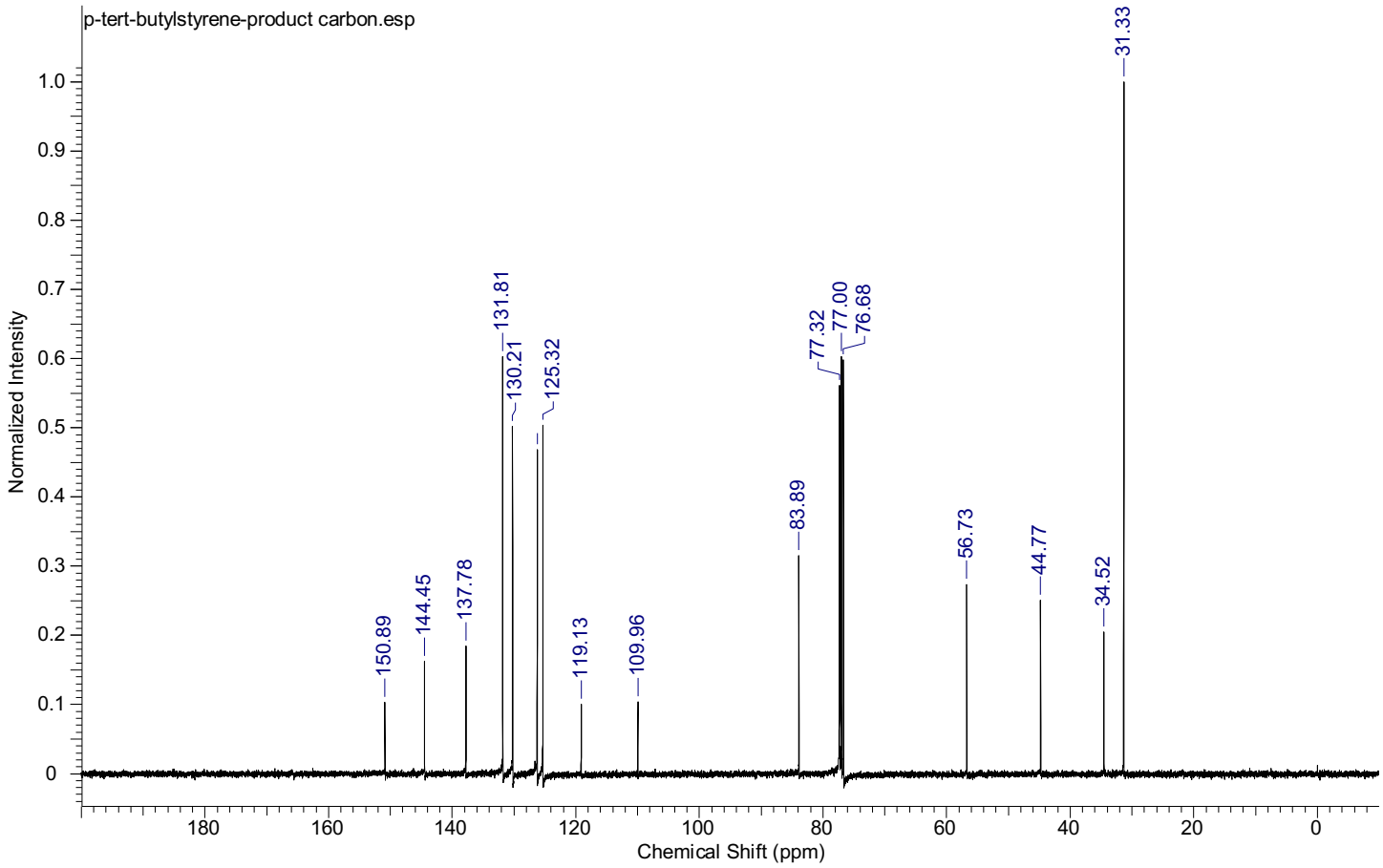
45% yield, 49 mg, 0.16 mmol (based on 0.35 mmol scale)
orange sticky oil
TLC (SiO_2): R_f = 0.17 (*n*-hexane:ethyl acetate =10:1).
^{1}H NMR: (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.25-7.21 (m, 4H), 6.05 (dd, *J* = 8.2 Hz, 6.0 Hz, 1H), 3.29 (dd, *J* = 13.7 Hz, 8.2 Hz, 1H), 3.15 (dd, *J* = 13.7 Hz, 6.0 Hz, 1H), 1.31 (s, 9H).
^{13}C NMR: (100 MHz, $CDCl_3$): δ 160.0, 151.7, 142.3, 135.5, 132.1, 130.3, 126.3, 125.6, 118.8, 110.7, 75.5, 42.7, 34.6, 31.3.
HRMS: *m/z* (DART) calcd for $C_{19}H_{20}N^+$ $(M\text{-}OCOH+H)^+$ 262.1590, found 262.1595.
FTIR: (neat): 2963. 2870, 2228, 1928, 1720, 1609, 1508, 1476, 1463, 1414, 1364, 1313, 1270, 1158, 1110, 1051, 1021, 984, 953, 889, 832, 776, 683 cm^{-1}

Reference

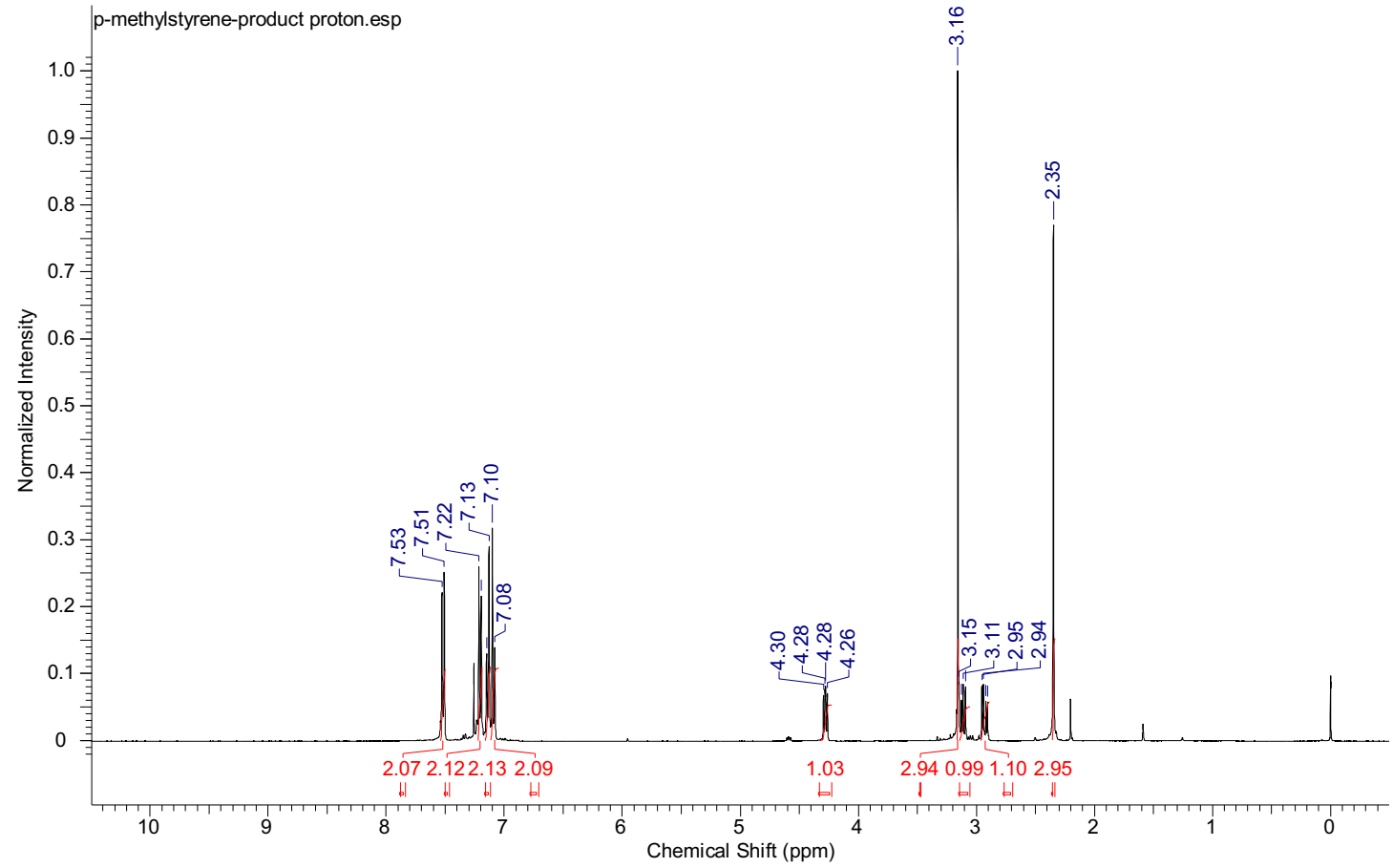
(1) E. Yamaguchi, W. Tanaka, A. Itoh, *Chem. Asian J.* **2019**, *14*, 121-124.

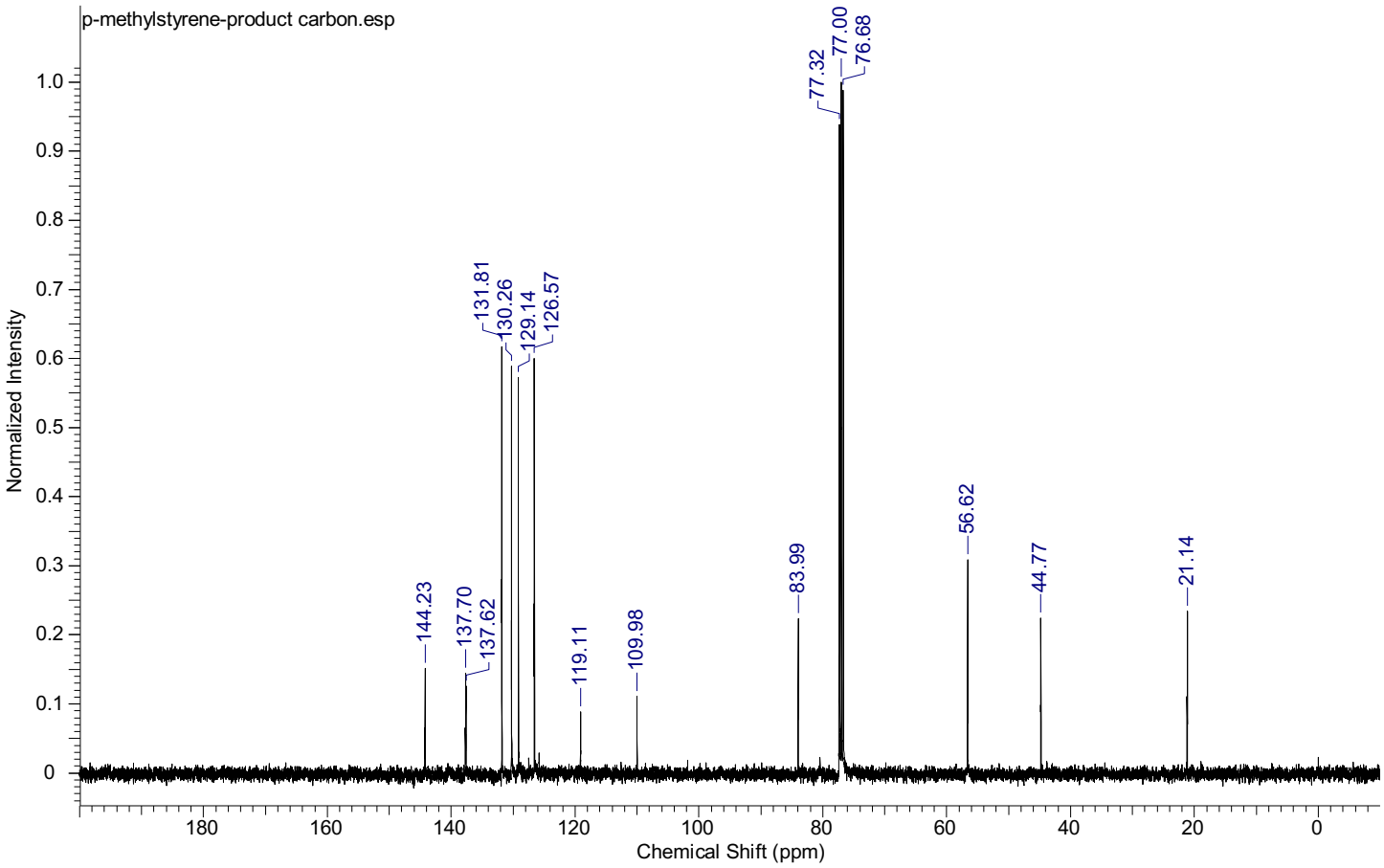
NMR spectra of 3aa



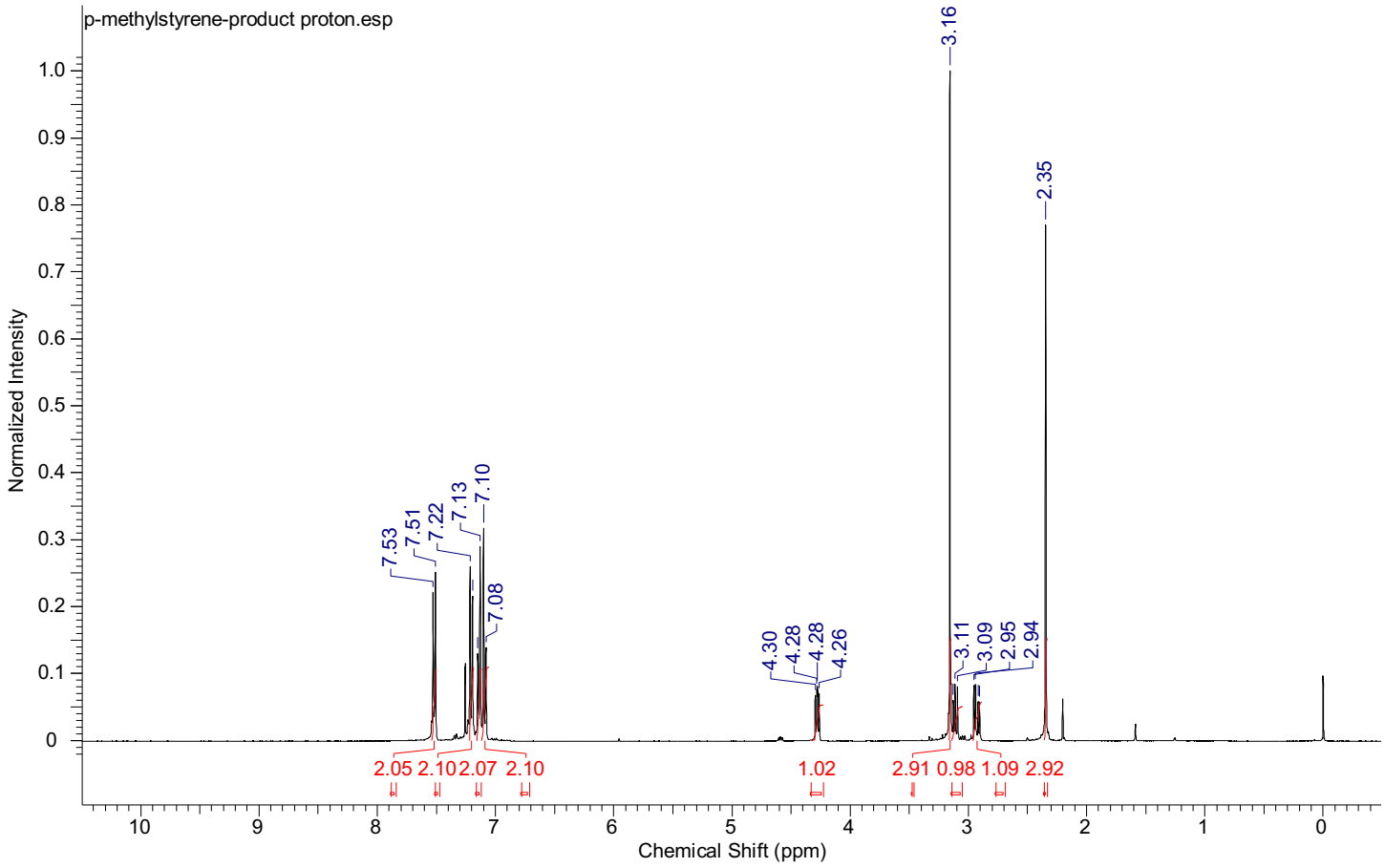


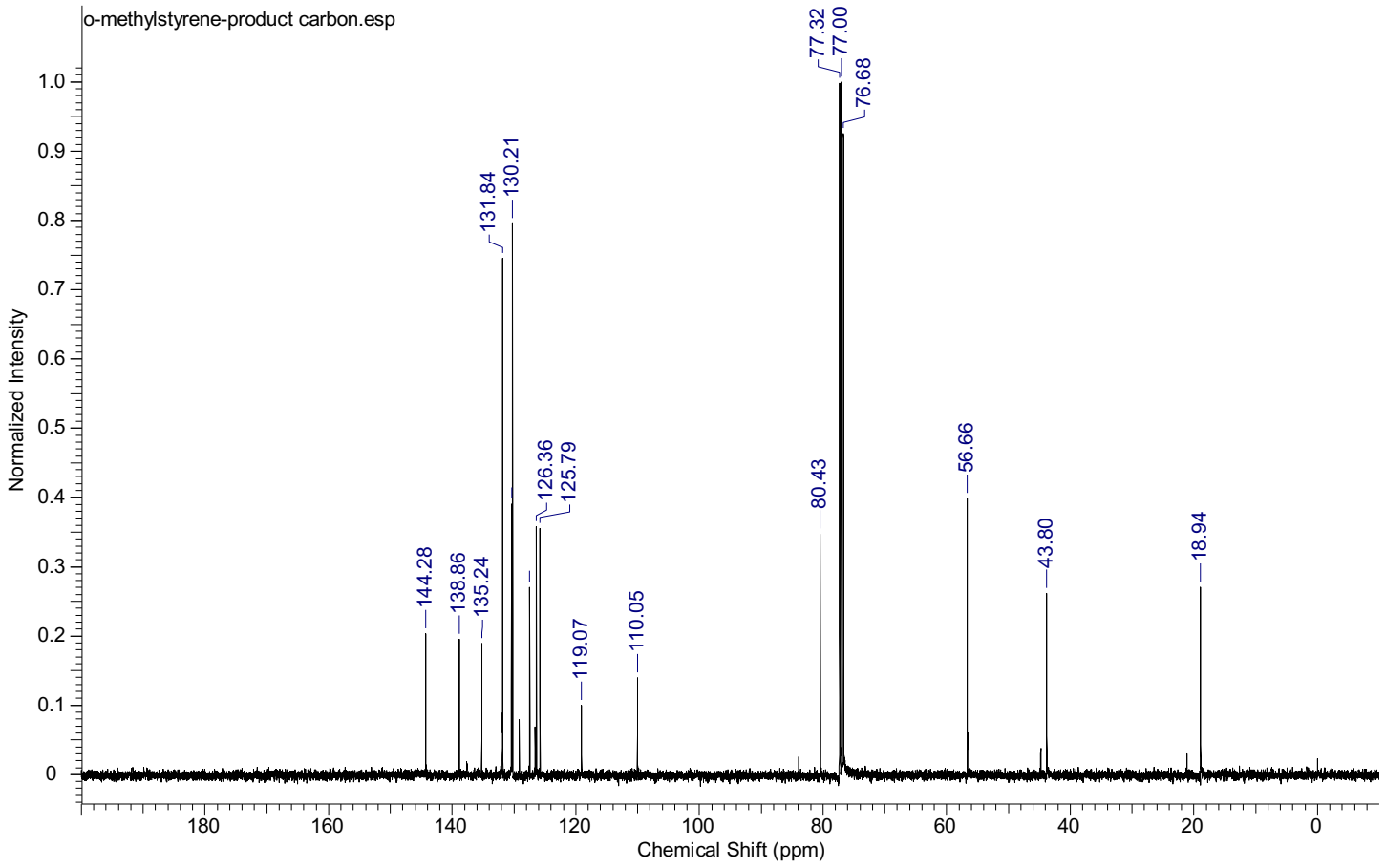
NMR spectra of 3ab



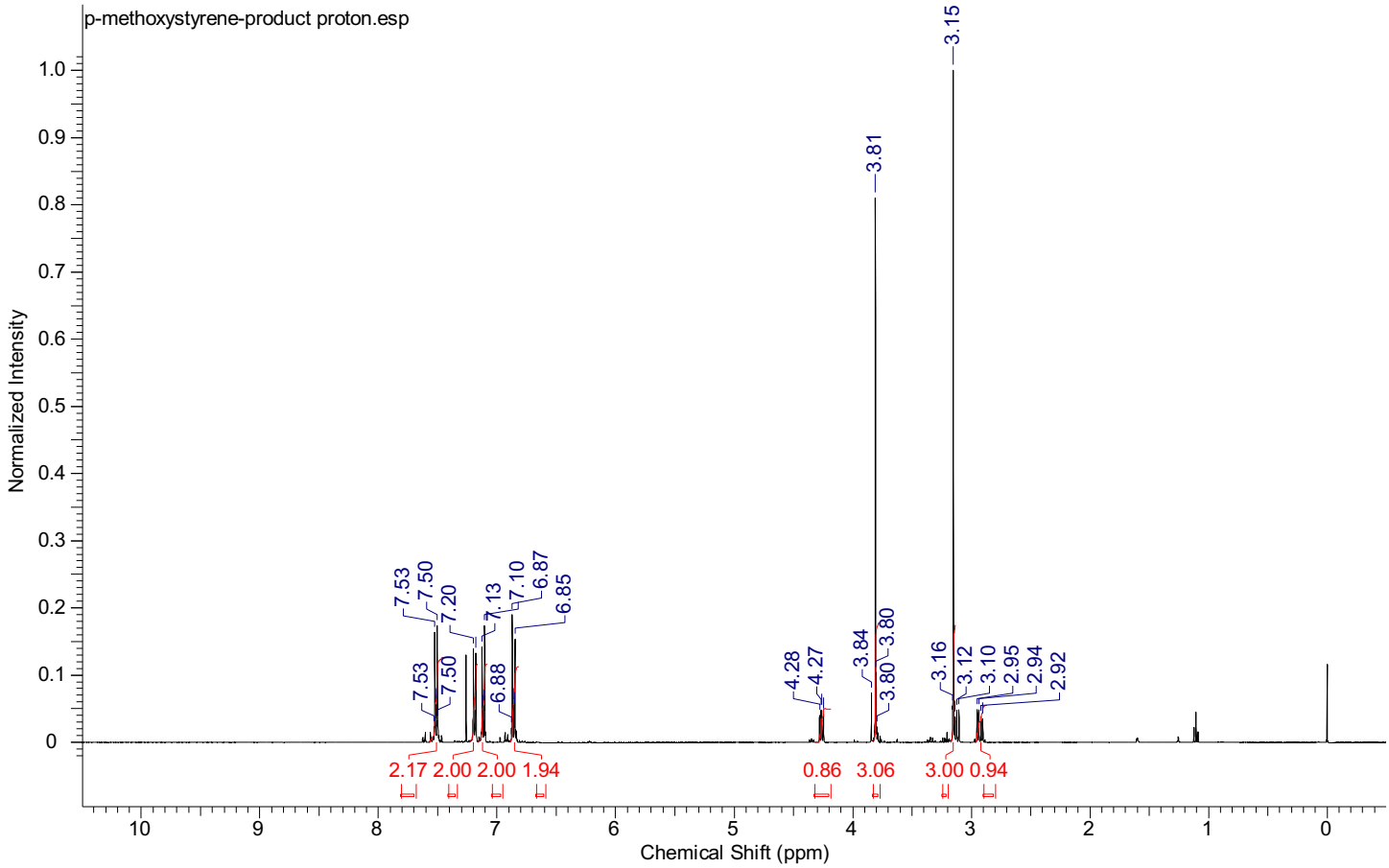


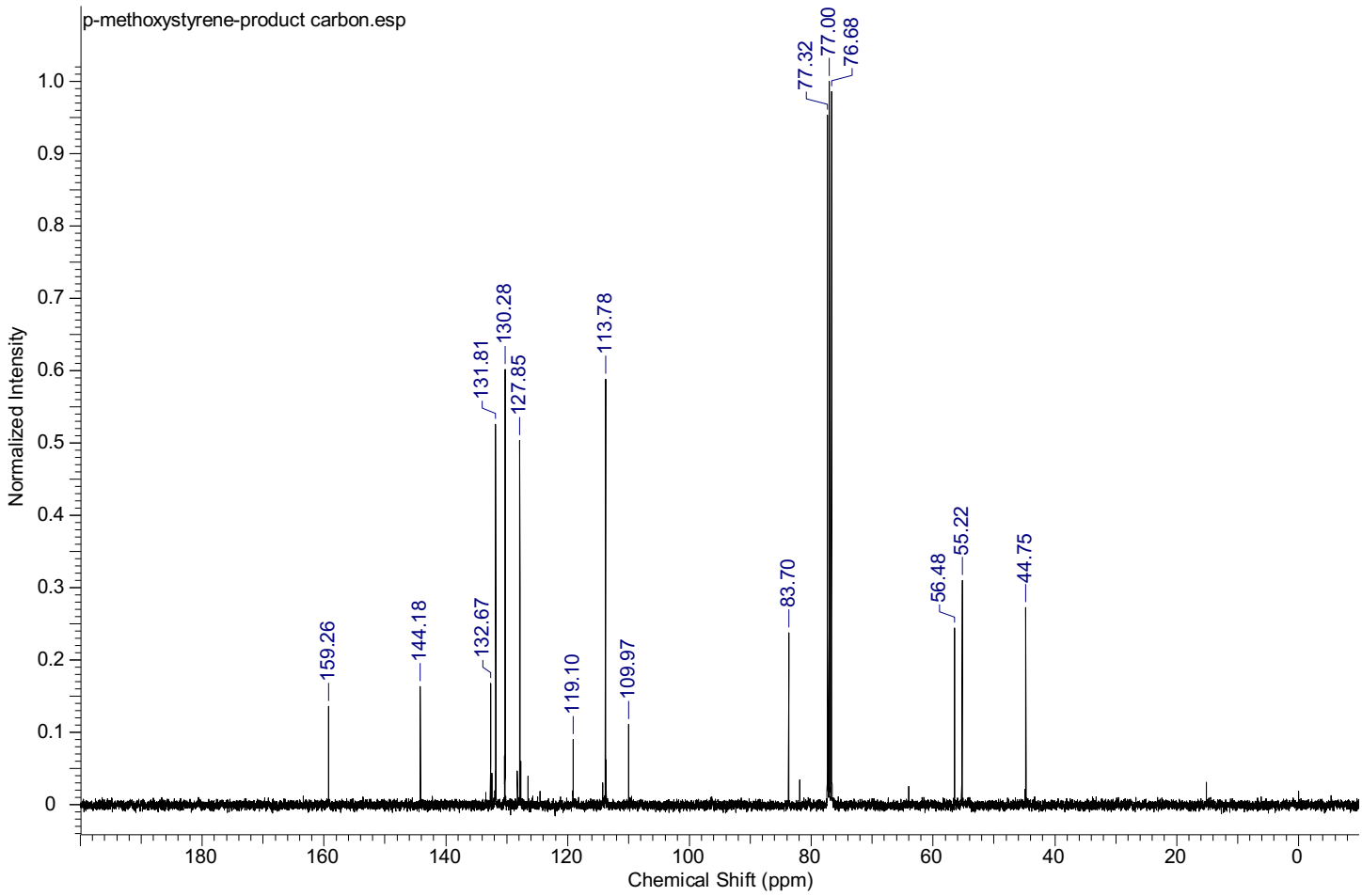
NMR spectra of 3ac



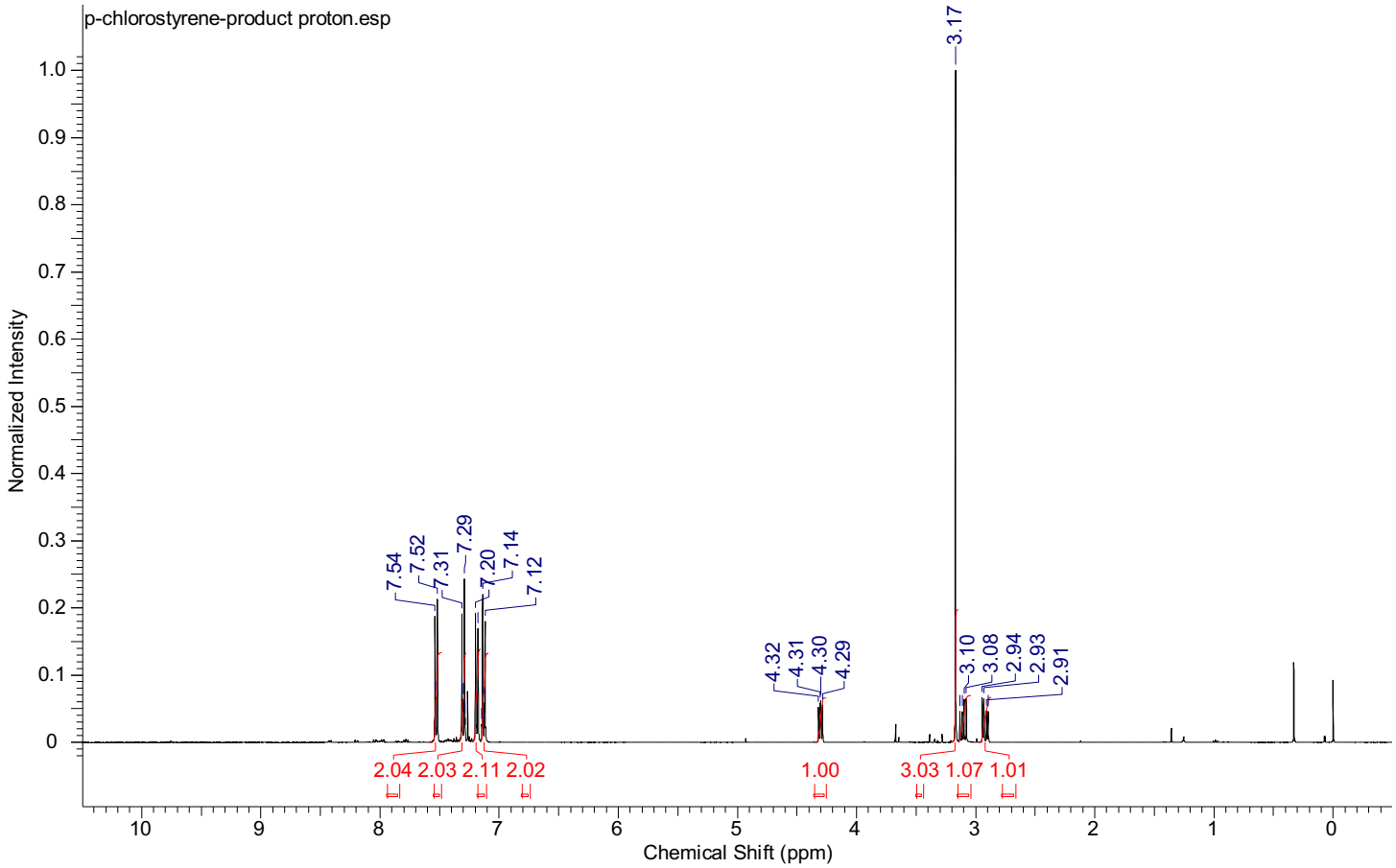


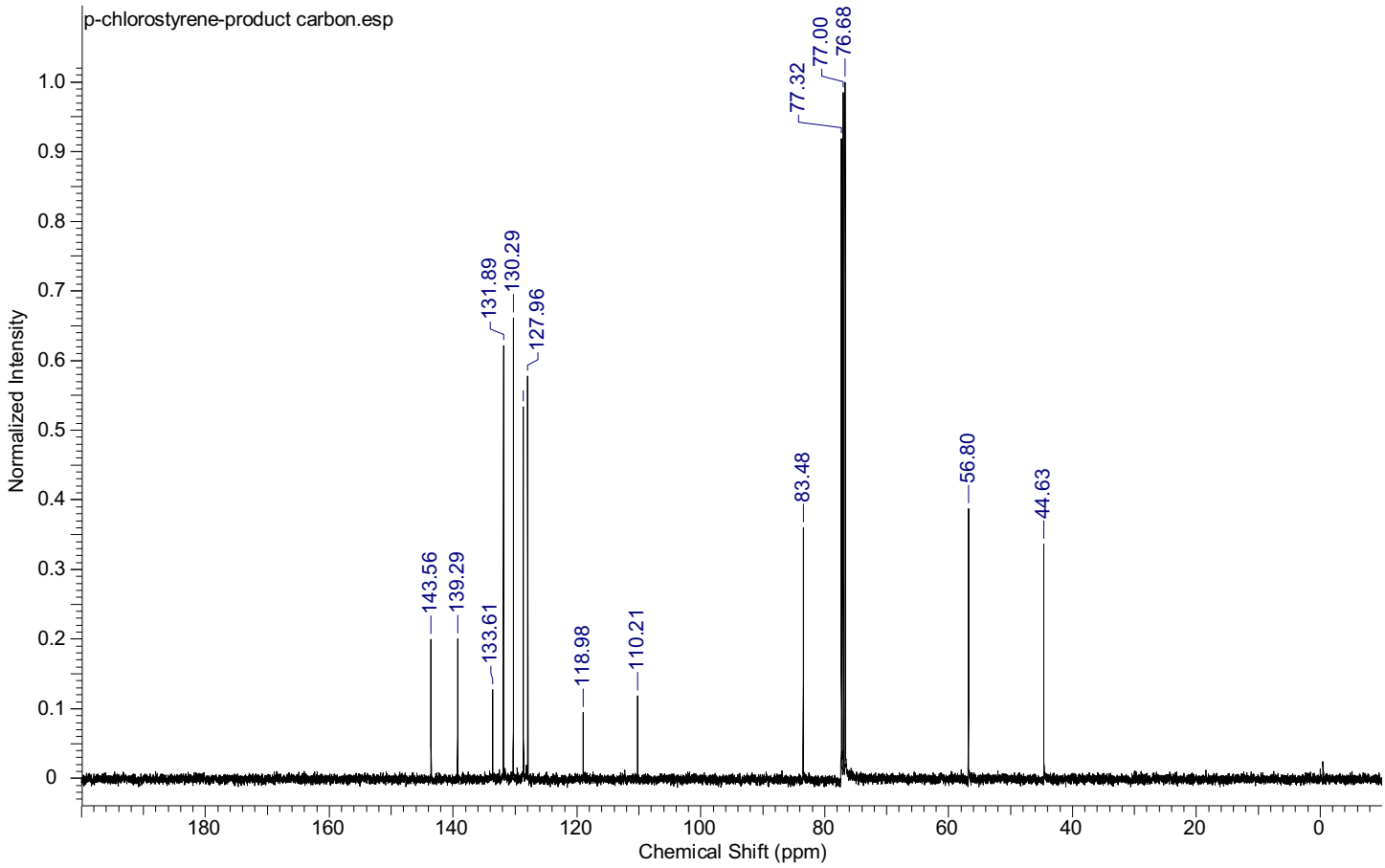
NMR spectra of 3ad



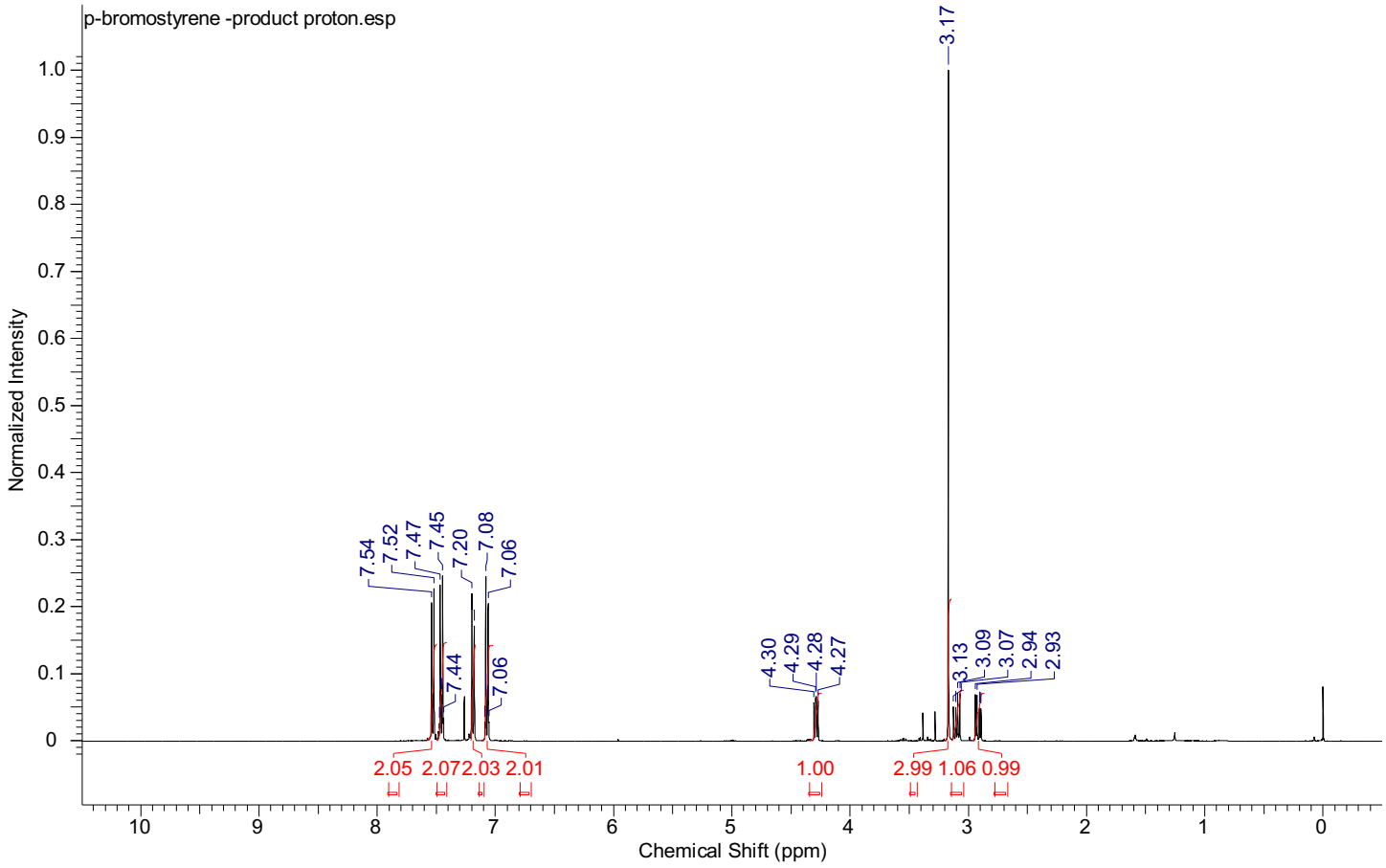


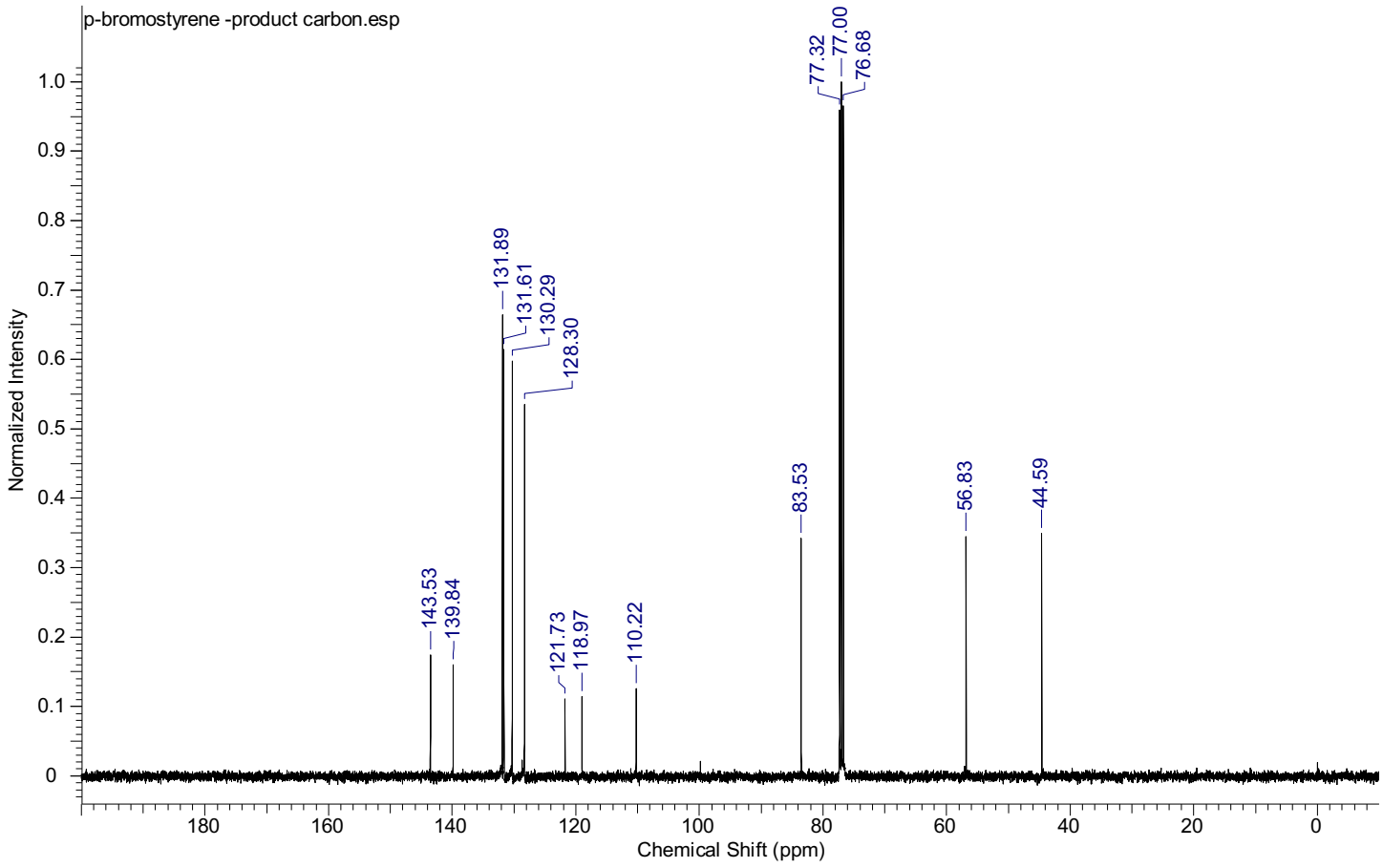
NMR spectra of 3ae



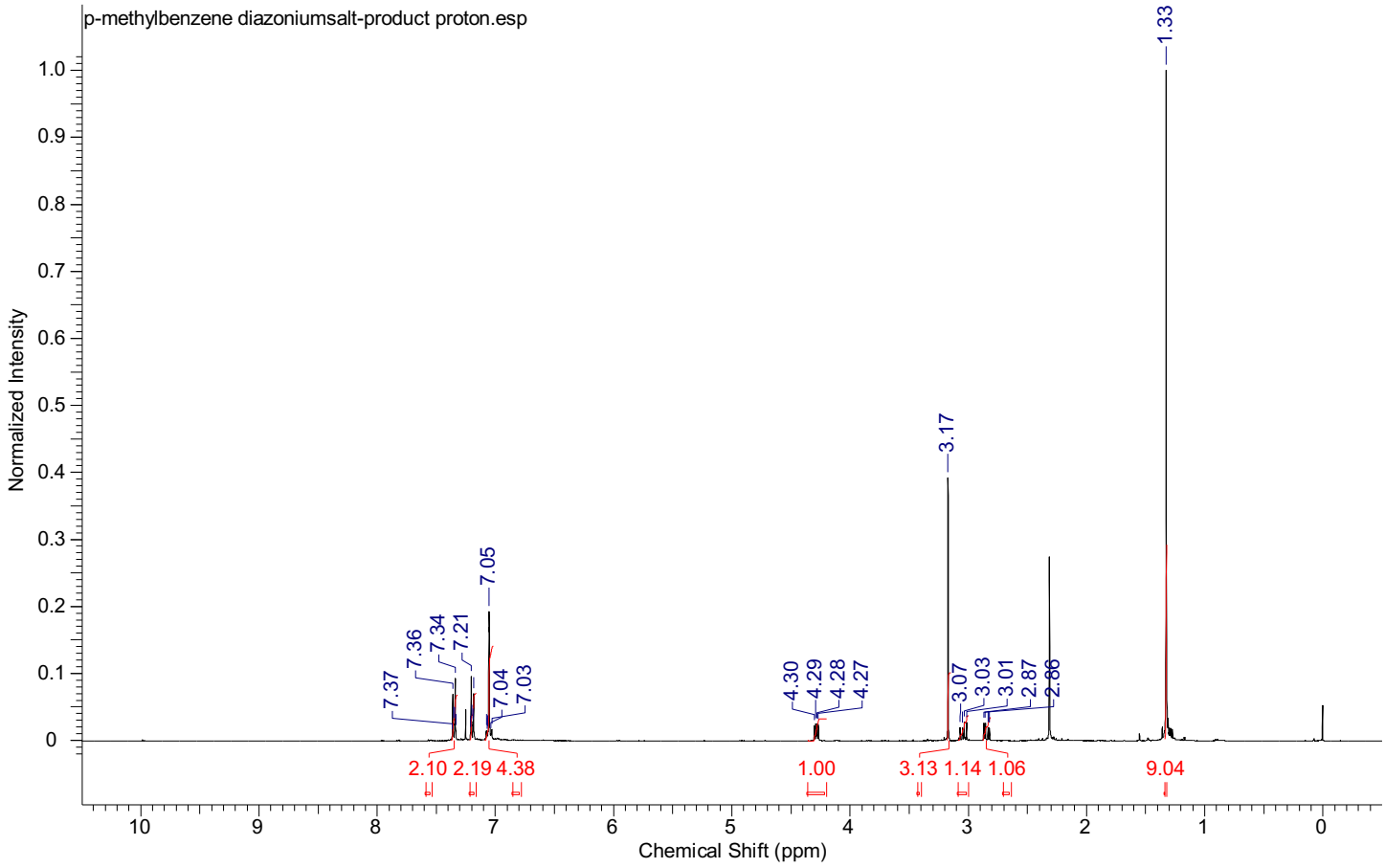


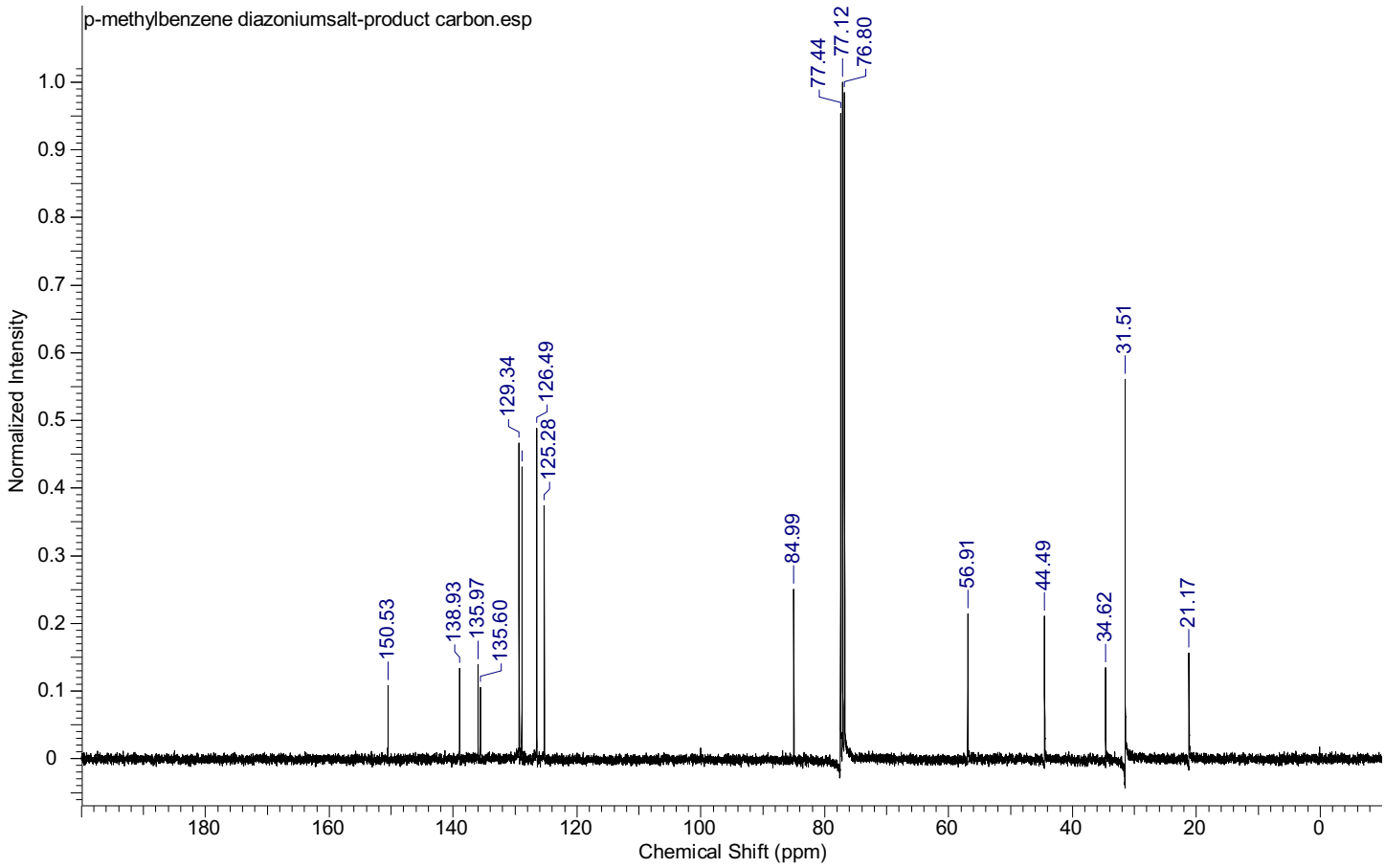
NMR spectra of 3af



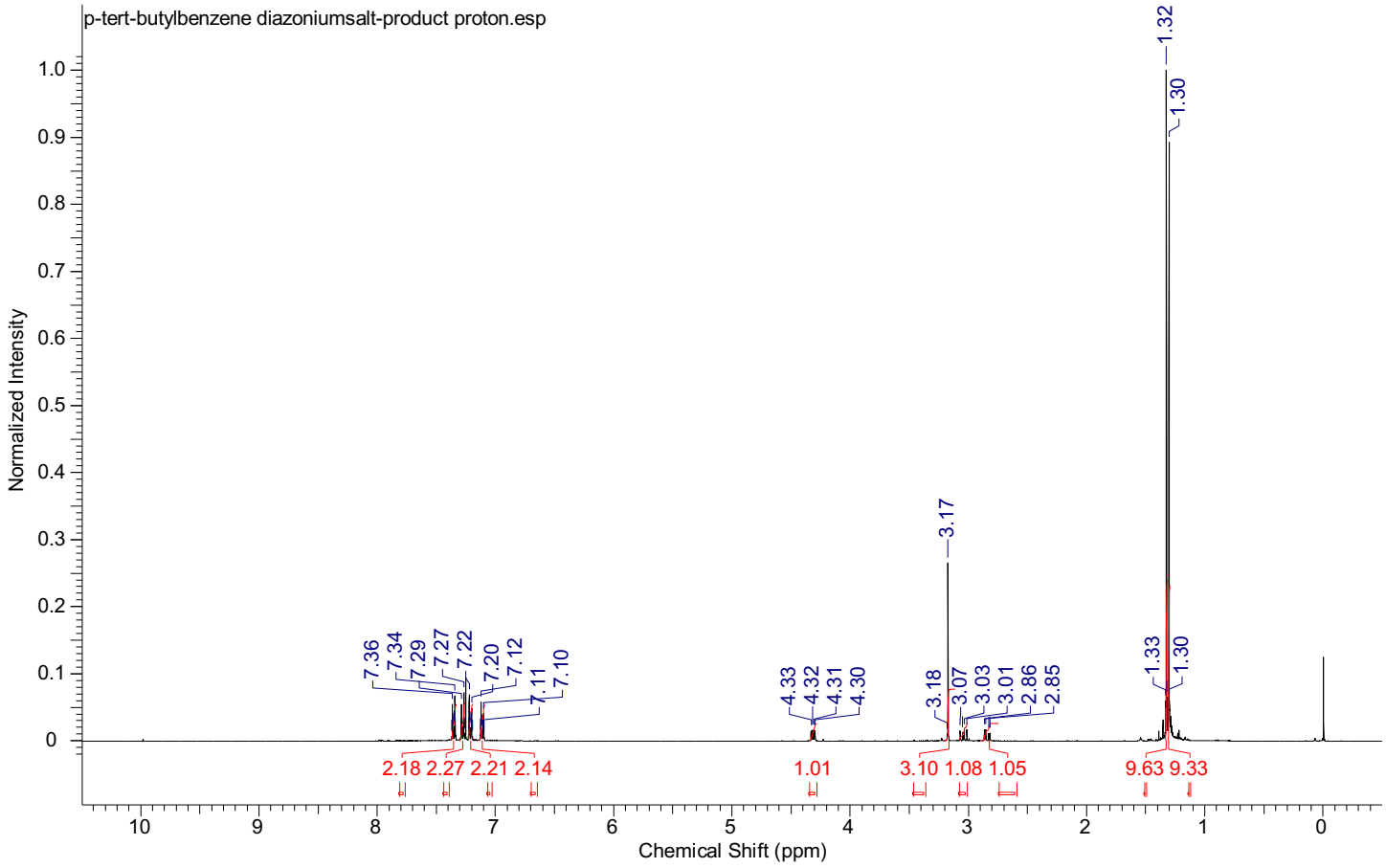


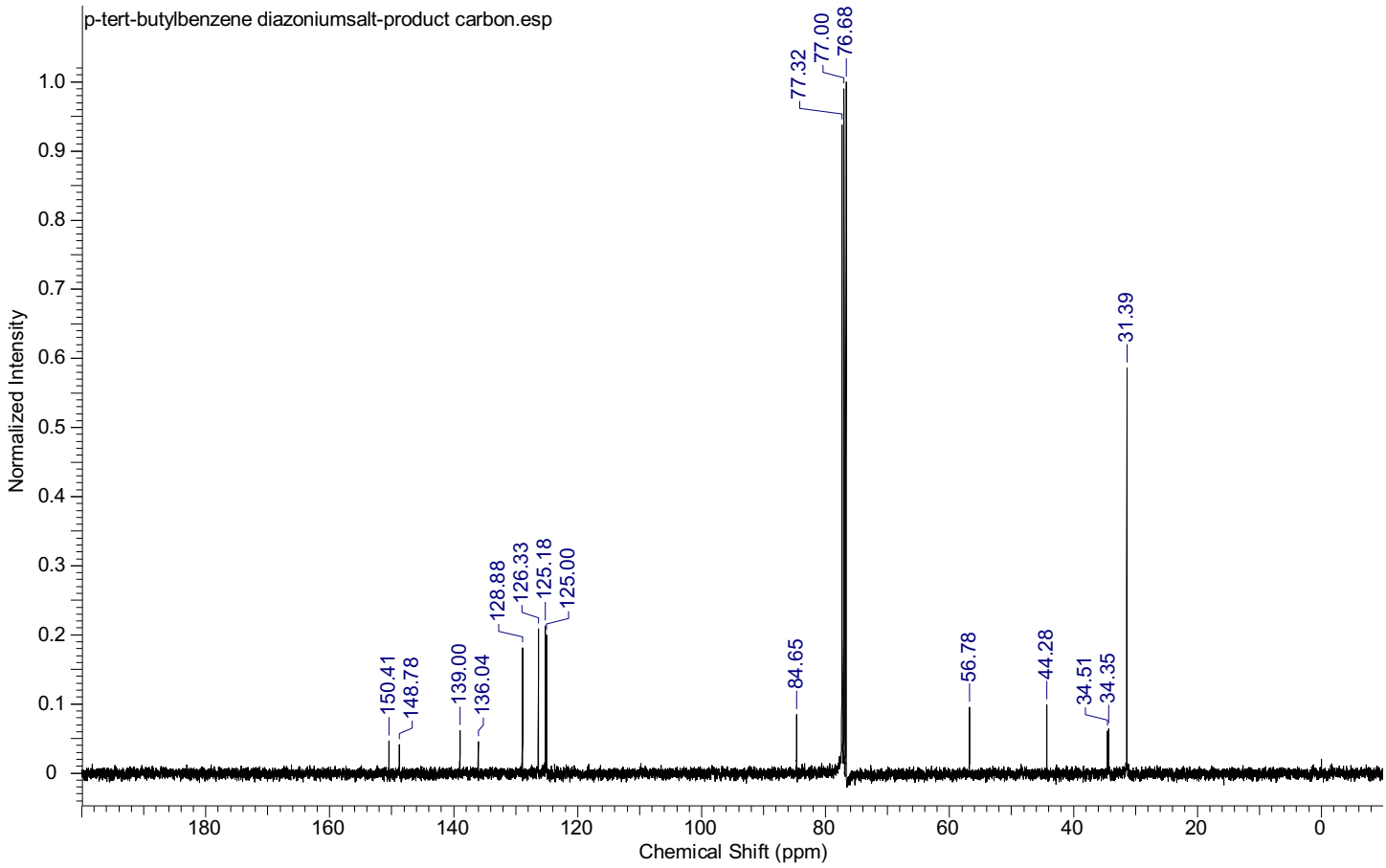
NMR spectra of 3ba



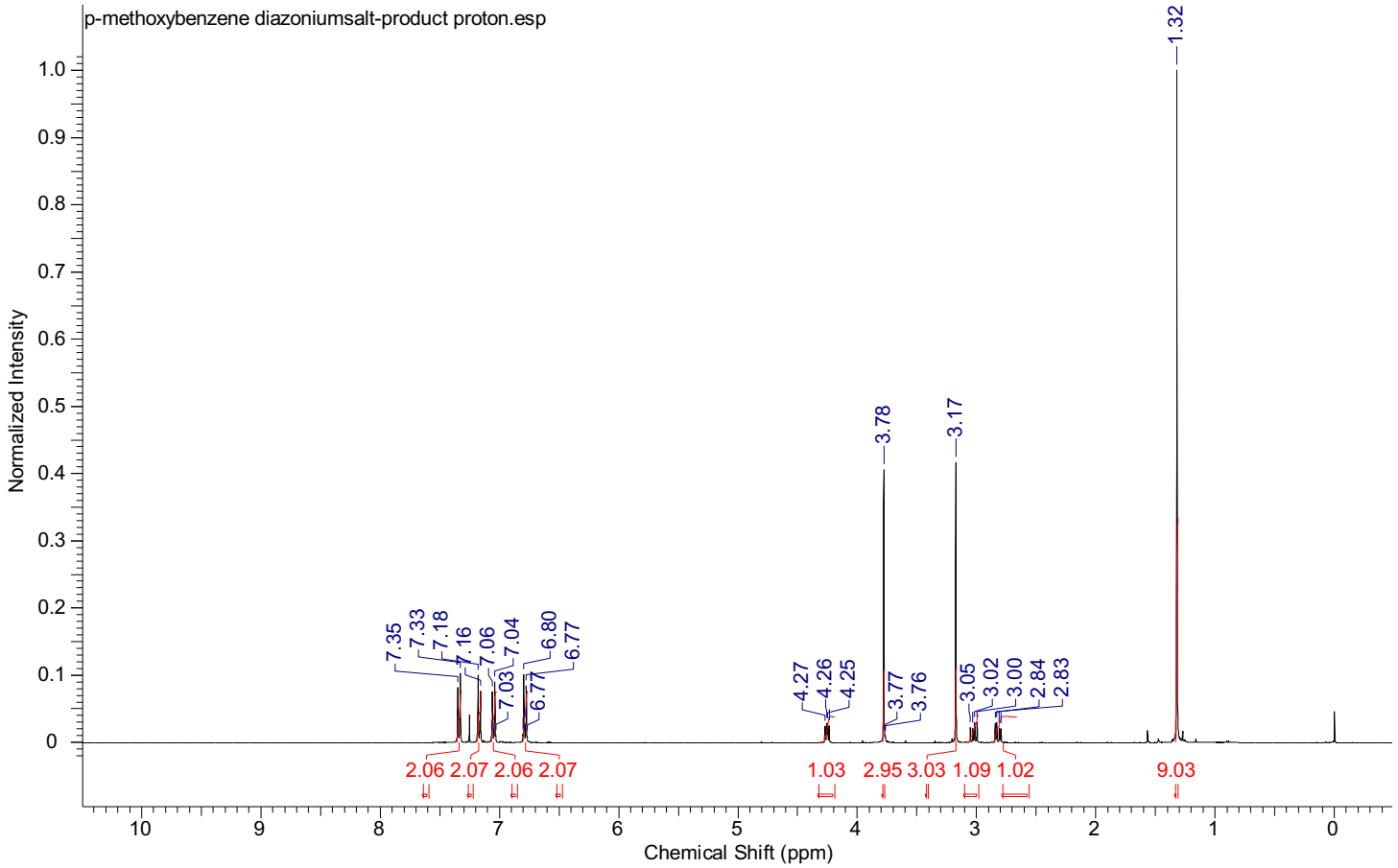


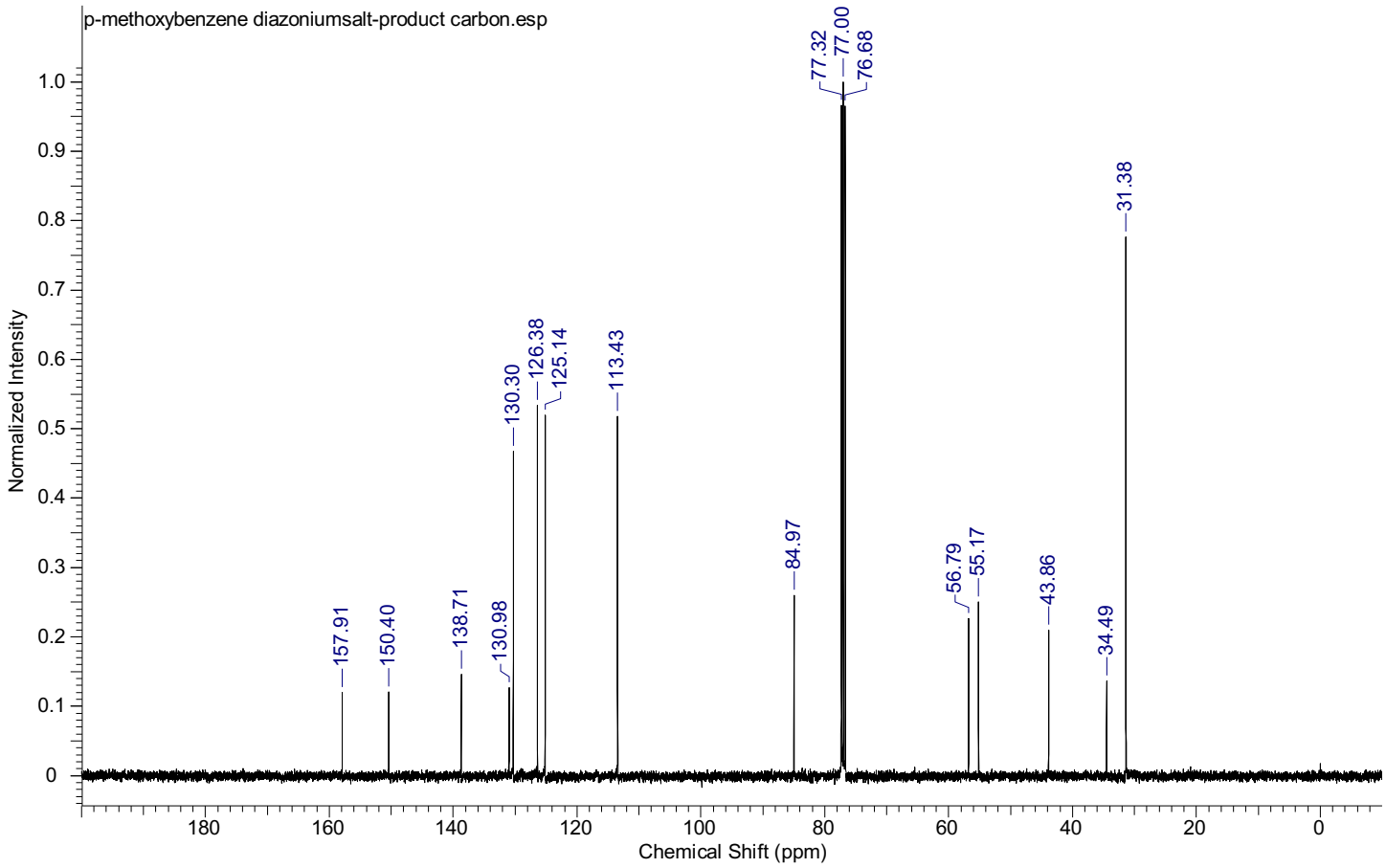
NMR spectra of 3ca



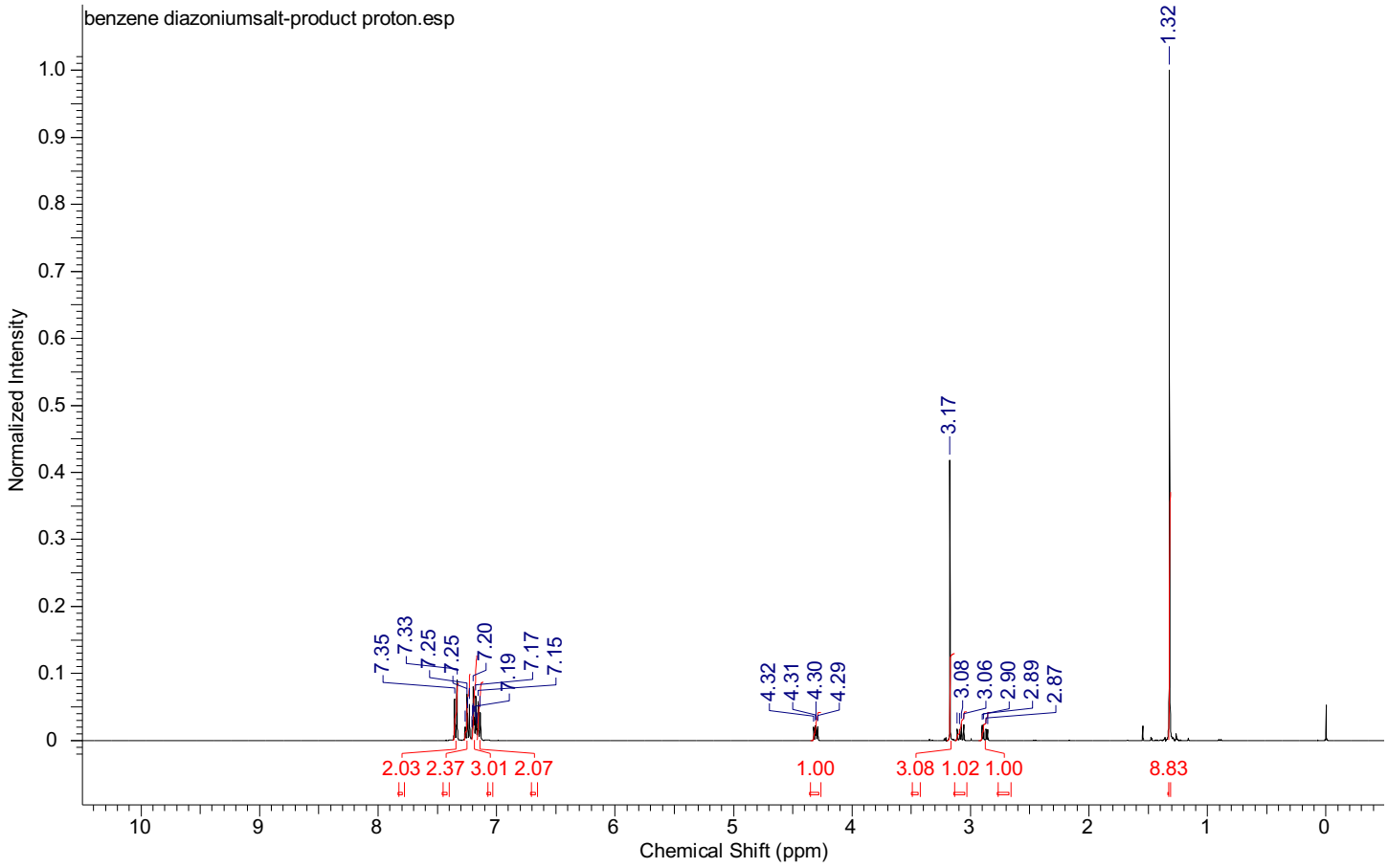


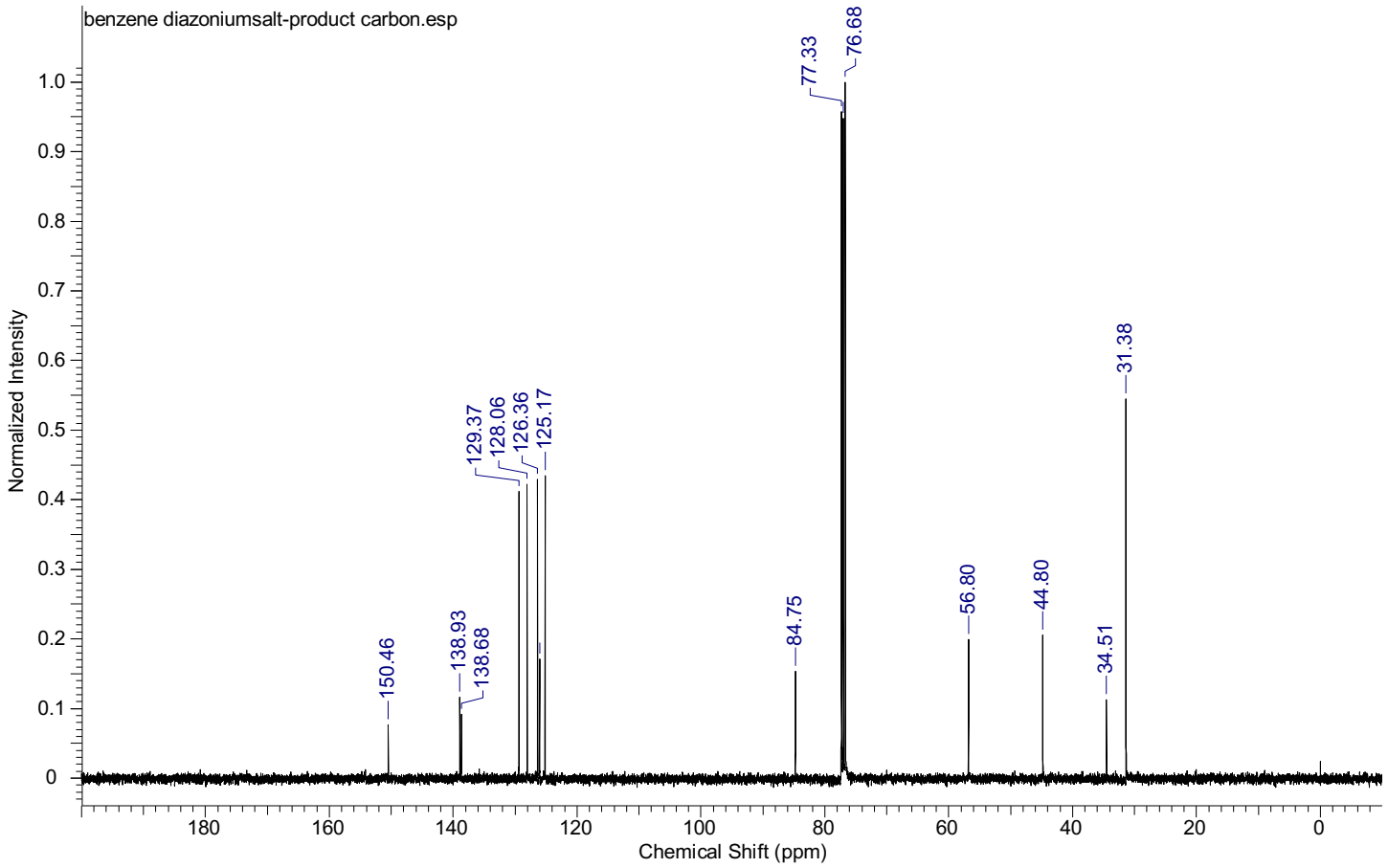
NMR spectra of 3da



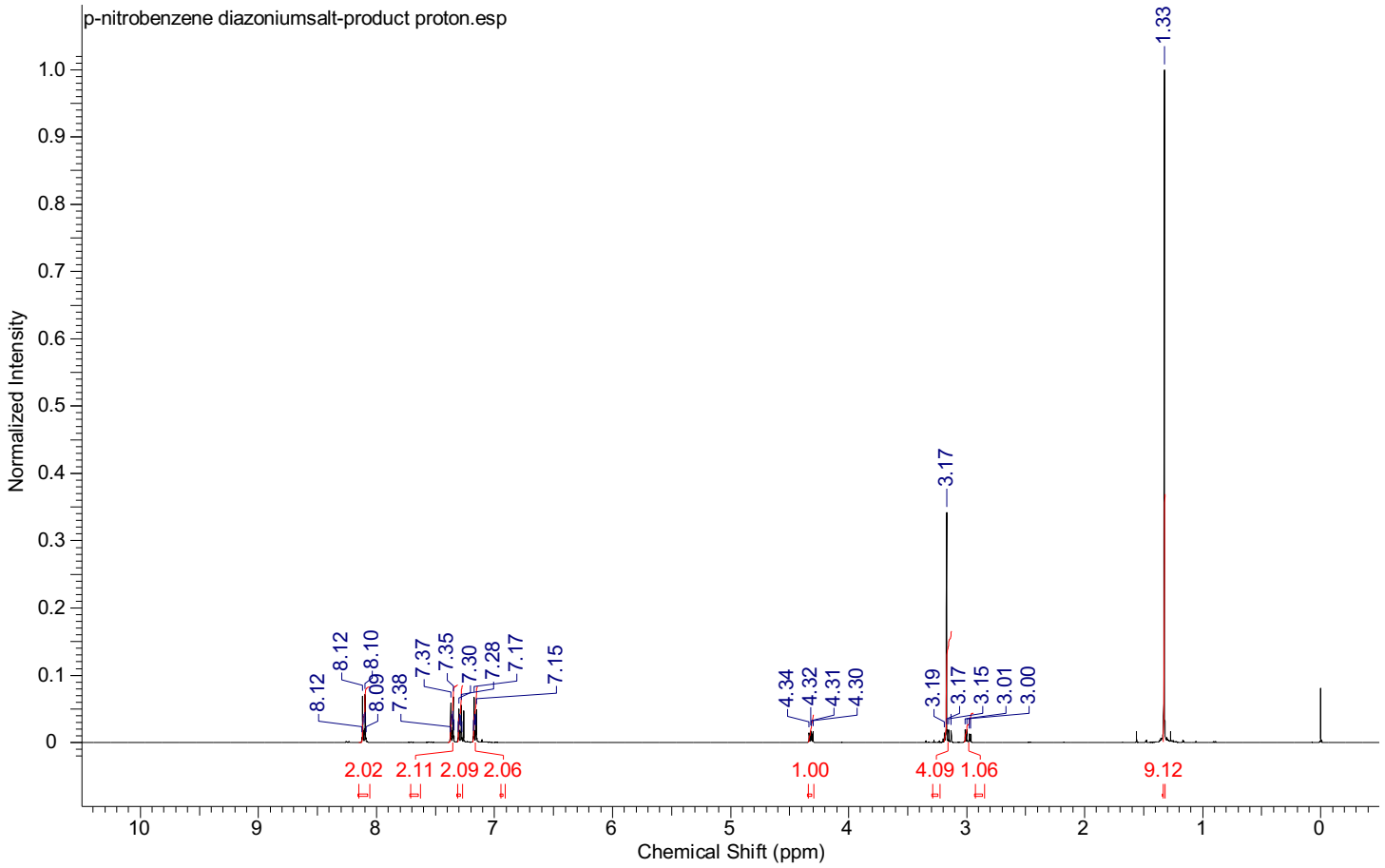


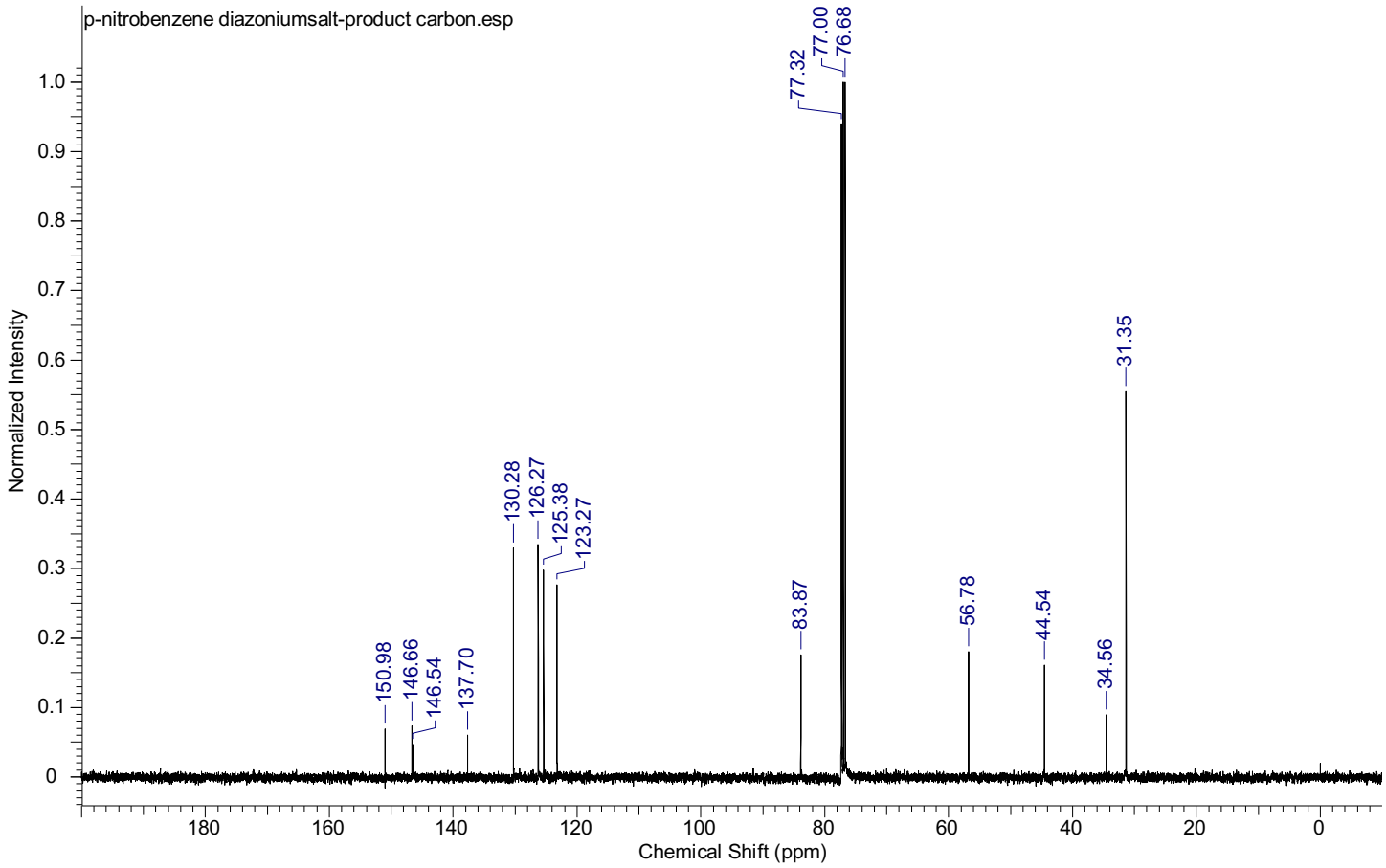
NMR spectra of 3ea



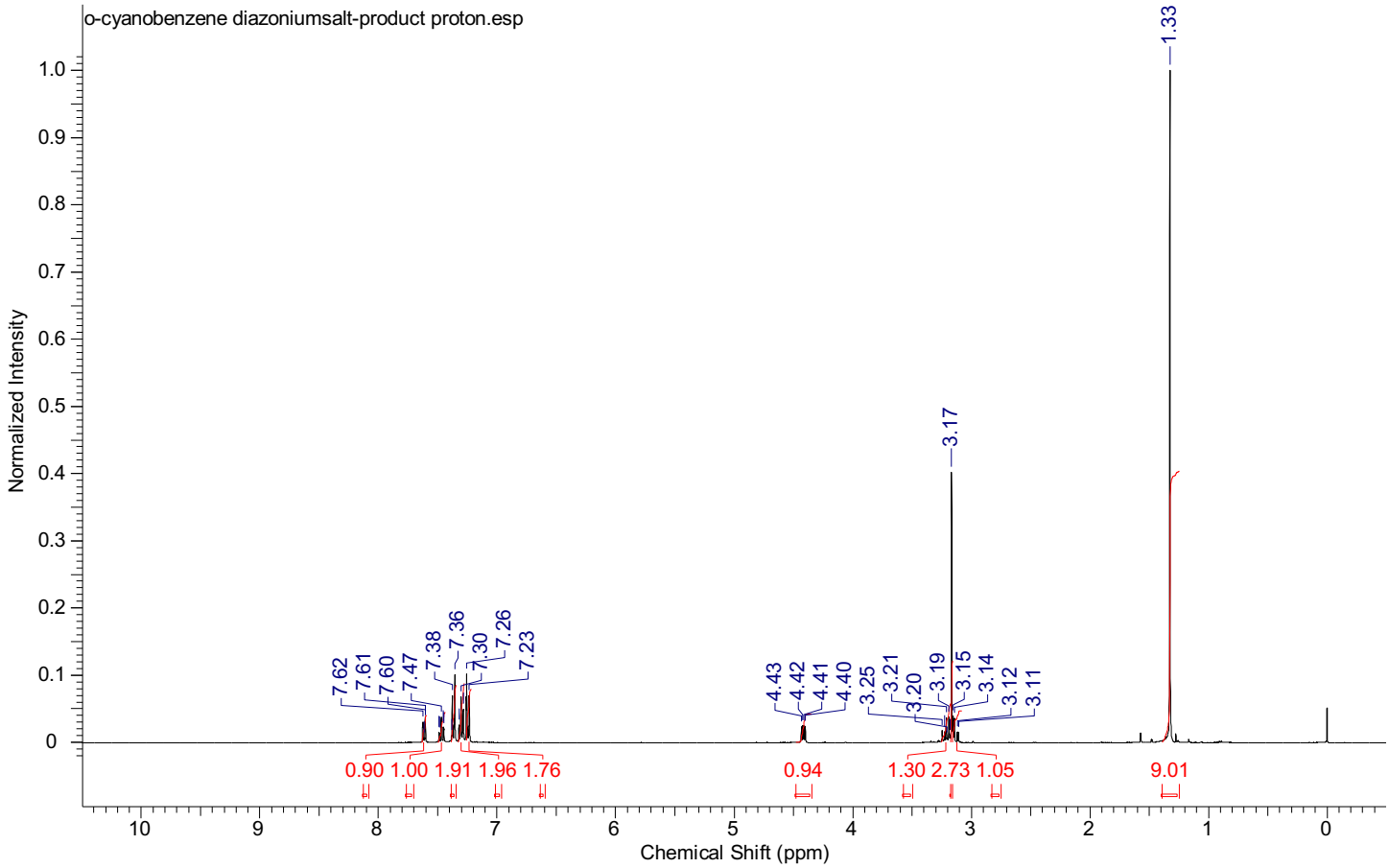


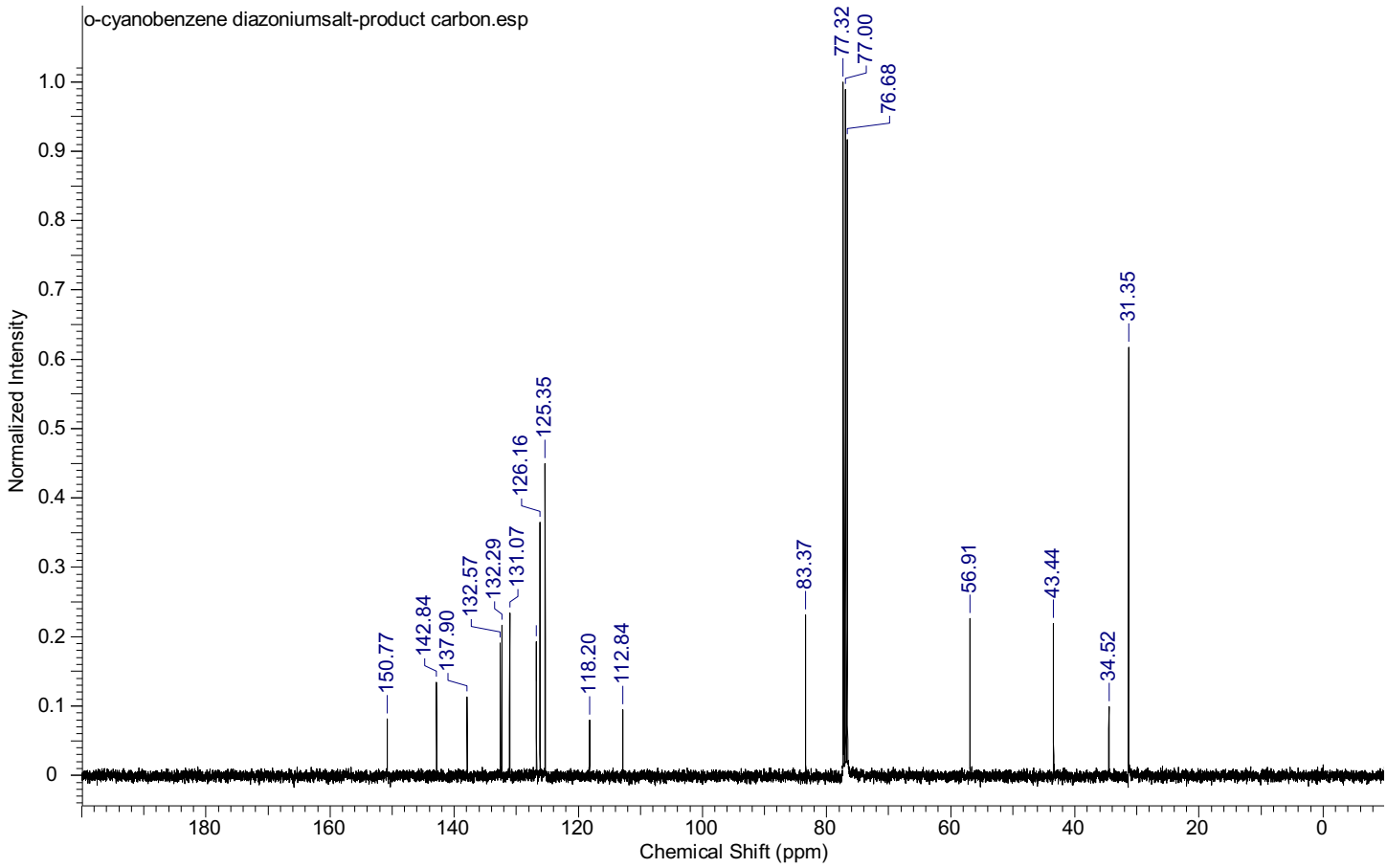
NMR spectra of 3fa



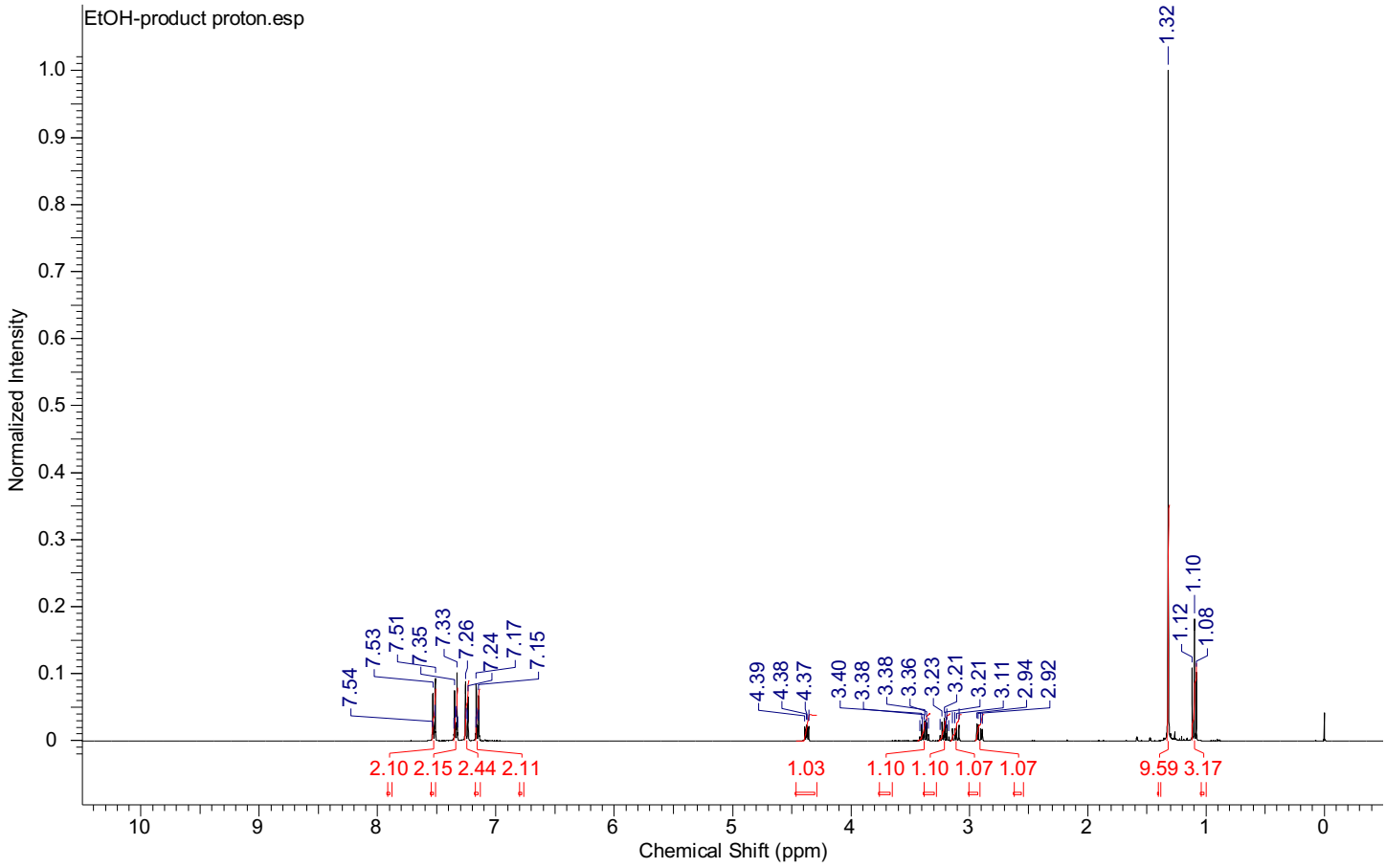


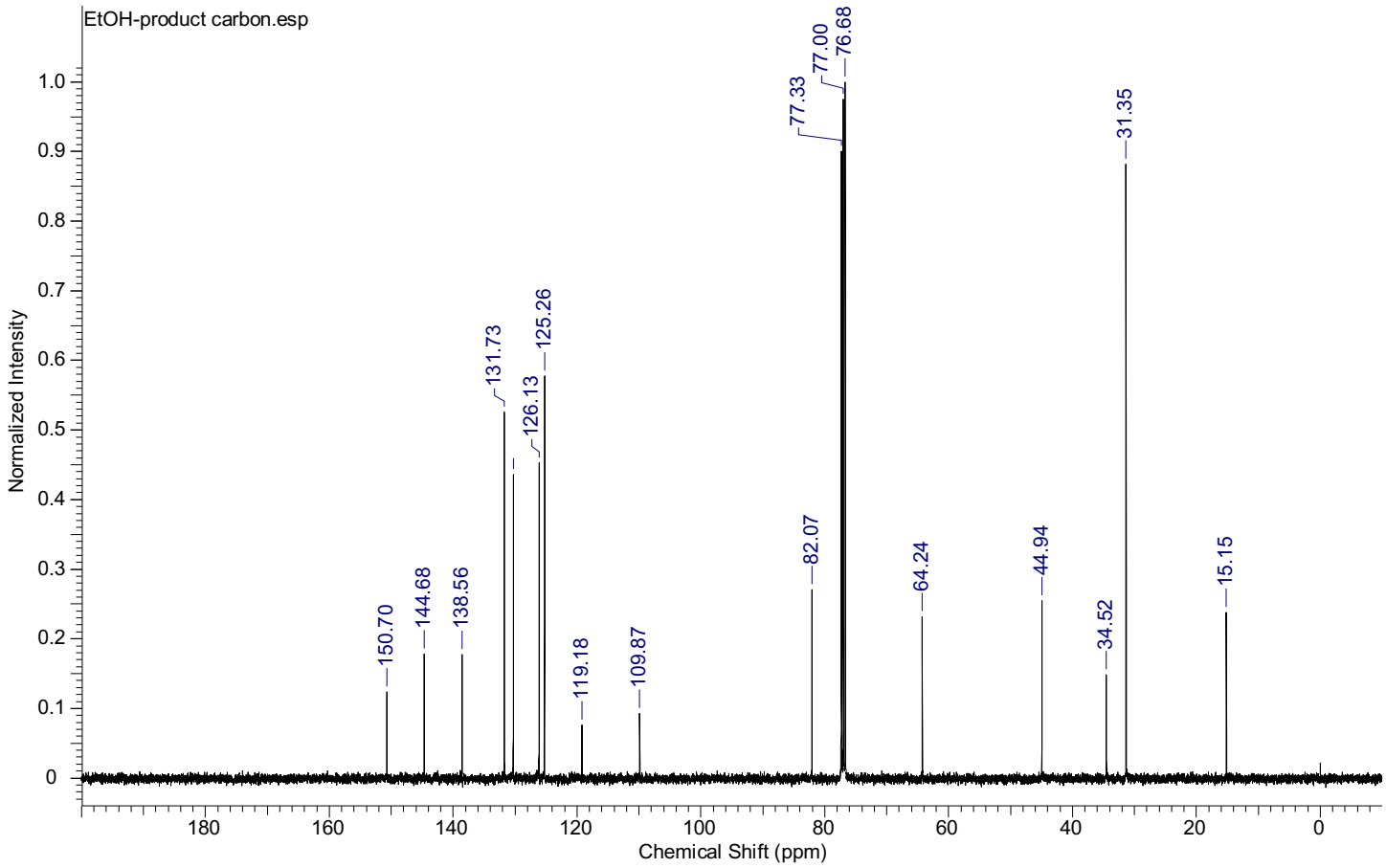
NMR spectra of 3ga



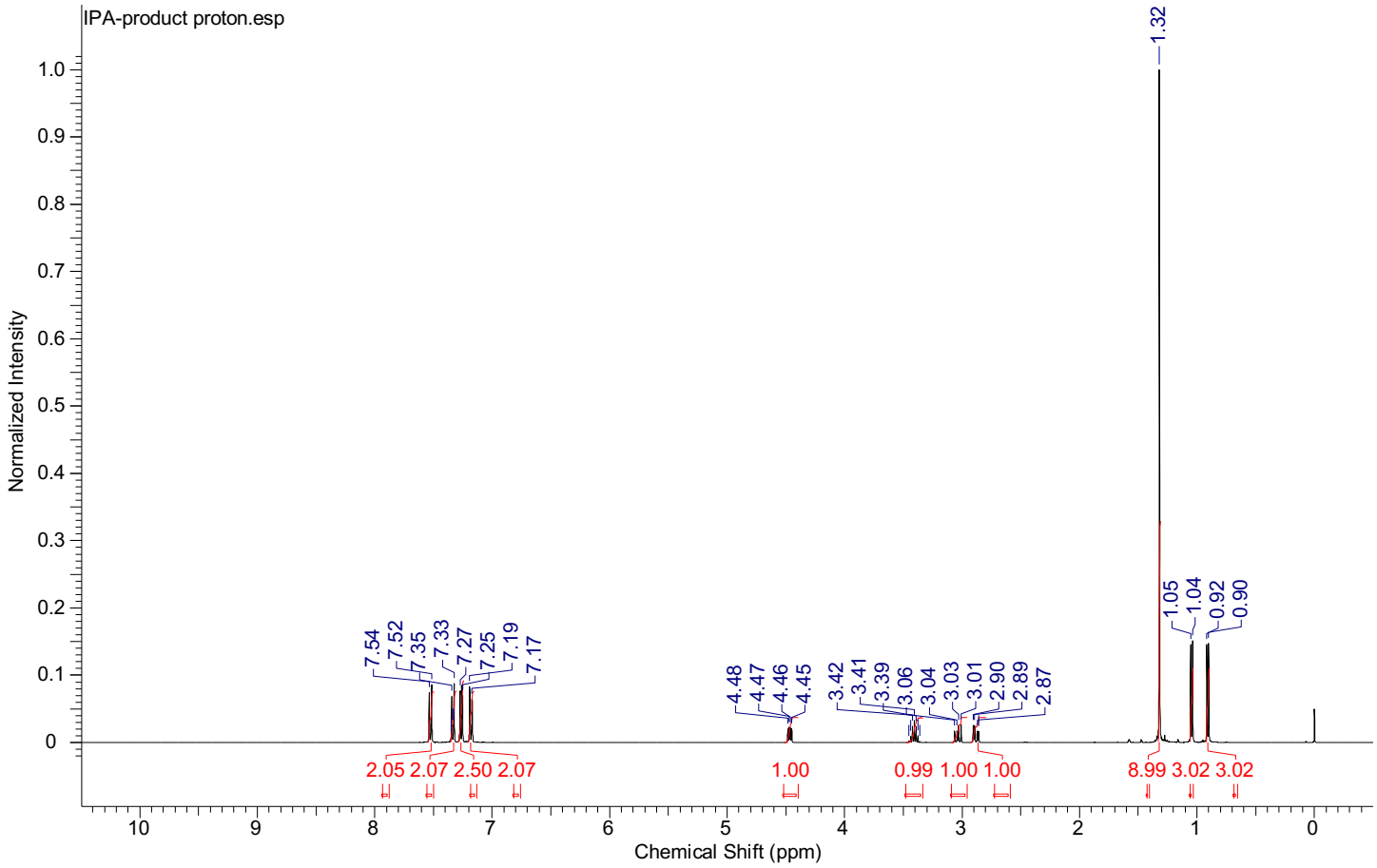


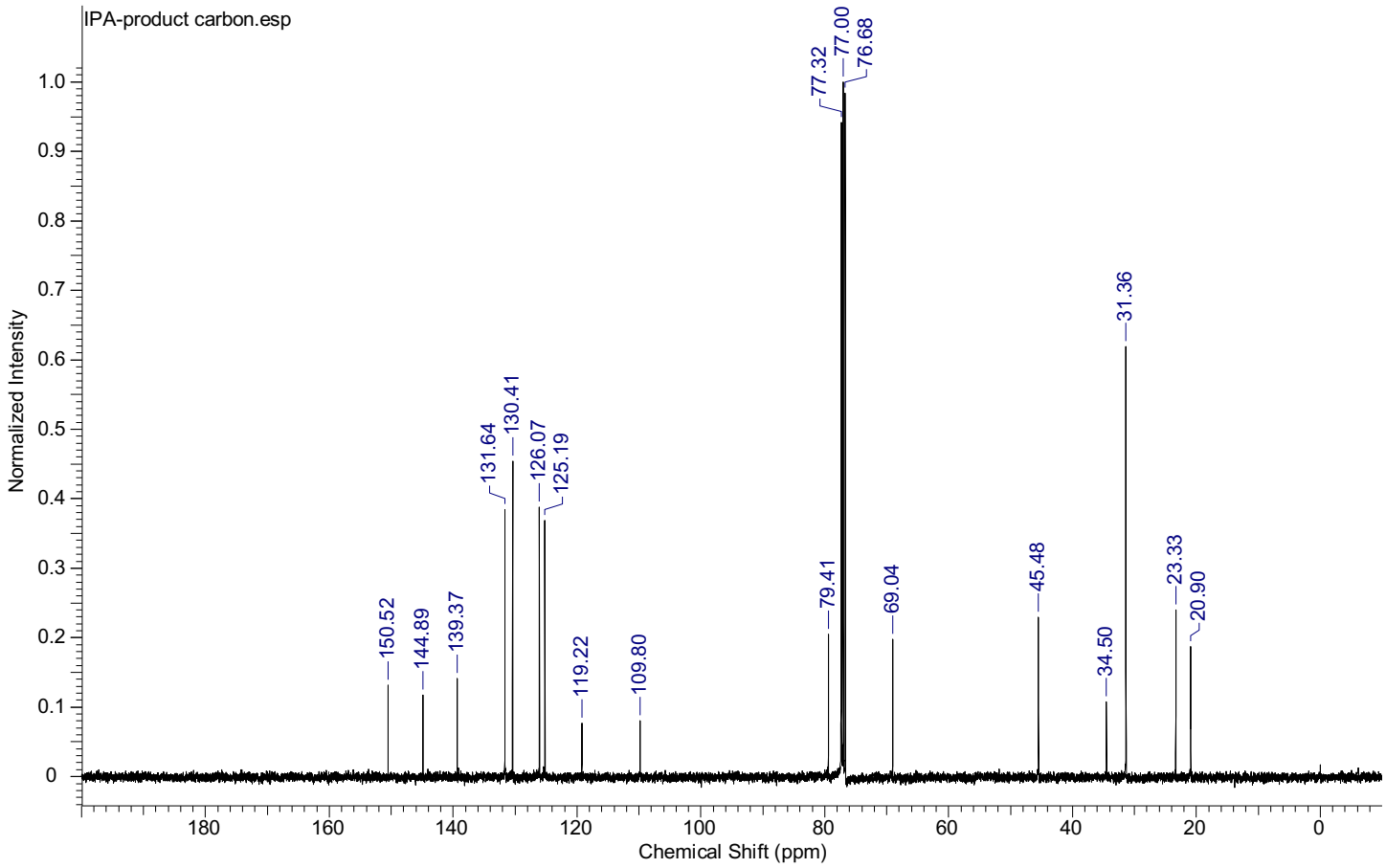
NMR spectra of 4a



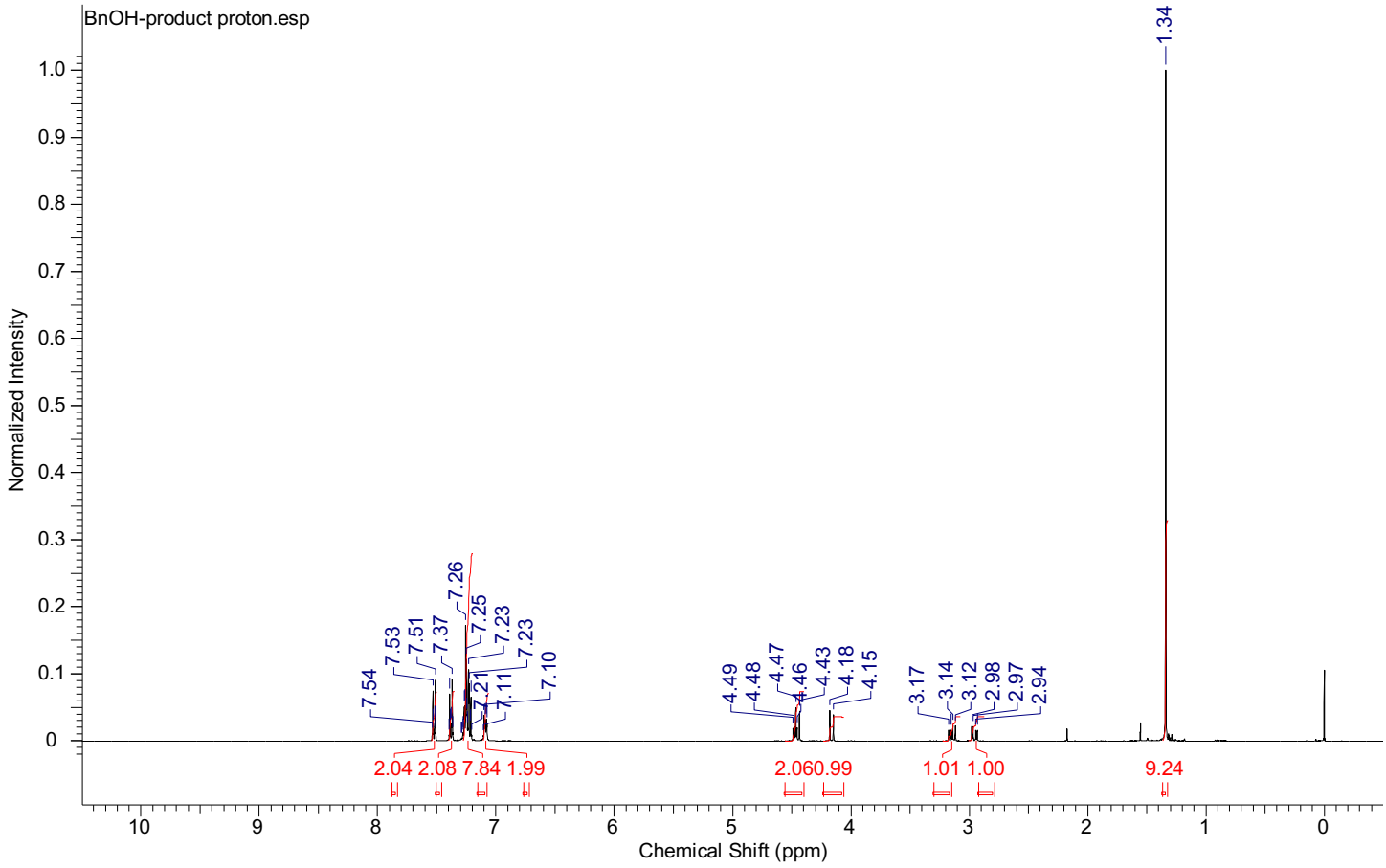


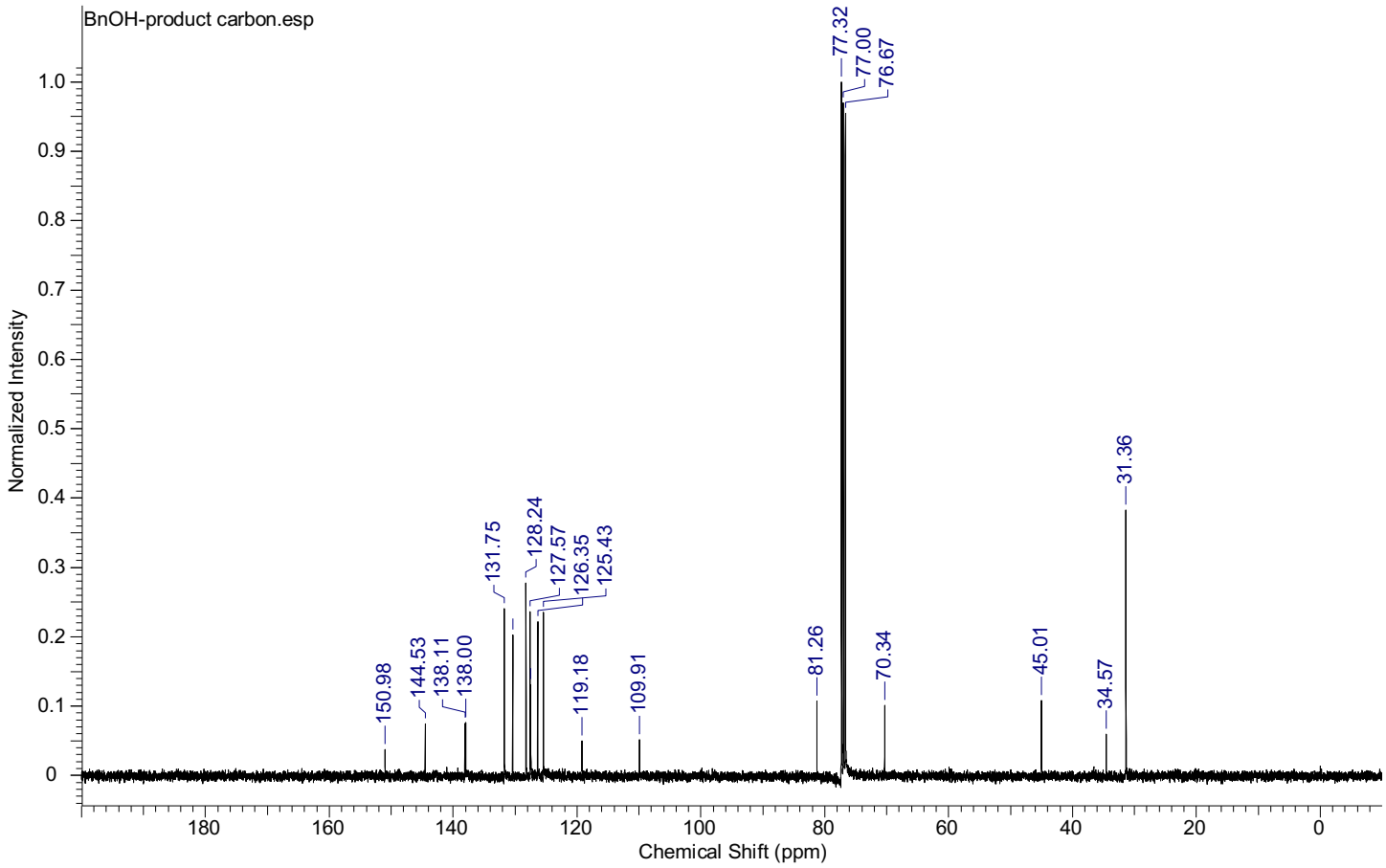
NMR spectra of 4b





NMR spectra of 4c





NMR spectra of 4d