

Supporting Information

Revisiting Nucleophilic Substitution Reactions: Microwave-assisted Synthesis of Azides, Thiocyanates and Sulfones in Aqueous Medium

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Experimental procedures:

General

All starting alkylhalides, sodium azide, potassium thiocyanate, sodium sulfinates were used as obtained. 1,3-Propane-diol-ditosylate, and 1,4-butane-diol-ditosylate were prepared according to literature.¹ The crude products were identified by GC/MS qualitative analysis using a GC system with a Mass selective detector or FT-IR data of the characteristic azido functionality. The identities were further confirmed by ¹H and ¹³C NMR spectra that were recorded in chloroform-*d* (CDCl₃) with TMS as internal reference using a 300 MHz NMR spectrometer. All melting points of synthesized sulfones were uncorrected.

Typical representative procedures

Synthesis of azides: 1,4-dibromobutane (1 mmol, 0.215 g), sodium azide (2.5 mmol, 0.163 g) in water (2 mL) were placed in a 10 mL crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. The reaction tube was placed inside the cavity of a CEM Discover focused microwave synthesis system, operated at 120 ± 5 °C (temperature monitored by a built-in infrared sensor), power 70 - 100 Watt and pressure 60 – 100 psi for 30 minutes. After completion of the reaction, diethyl ether was added to extract the alkyl azide. GC/MS analysis indicated the disappearance of alkyl halides, FT-IR spectrum of crude product was obtained using a FT-IR spectrometer and the formation of alkyl azide was confirmed by the characteristic IR adsorption around 2100 cm⁻¹. Removal of the solvent under reduced pressure (rotary evaporator) afforded the product, 1,4-diazido-butane (0.125 g) in 89% yield. ¹H and ¹³C NMR were recorded in chloroform-*d* (CDCl₃) with TMS as internal reference using a 300 MHz NMR spectrometer, and were consistent with literature.

Synthesis of thiocyanates: benzylchloride (1 mmol, 0.127 g), potassium thiocyanate (1.3 mmol, 0.126 g) in water (2 mL) were placed in a 10 mL crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. The reaction tube was placed inside the cavity of a CEM Discover focused microwave synthesis system, operated at 110 ± 5 °C (temperature monitored by a built-in infrared sensor), power 70 - 100 Watt and pressure 60 – 80 psi for 20 minutes. After completion of the reaction, diethyl ether was added to extract the alkyl thiocyanate. GC/MS analysis indicated the disappearance of alkyl halides, FT-IR spectrum of crude product was obtained using a FT-IR spectrometer and the formation of alkylthiocyanate was confirmed by the characteristic IR adsorption around 2150-2160 cm^{-1} . Removal of the solvent under reduced pressure (rotary evaporator) afforded the crude product, thiocyanatomethyl-benzene (0.142 g) in 95% yield; no flash column chromatograph was needed to purify the product. ^1H and ^{13}C NMR were recorded in chloroform-*d* (CDCl_3) with TMS as internal reference using a 300 MHz NMR spectrometer, and were consistent with literature.

Synthesis of sulfones: benzylbromide (1 mmol, 0.171 g), sodium *p*-toluenesulfinate hydrate (1.3 mmol, 0.252 g) in water (2 mL) were placed in a 10 mL crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. The reaction tube was placed inside the cavity of a CEM Discover focused microwave synthesis system, operated at 120 ± 5 °C (temperature monitored by a built-in infrared sensor), power 70 - 100 Watt and pressure 40 – 60 psi for 30 minutes. After completion of the reaction, diethyl ether was added to extract the alkyl thiocyanate. GC/MS analysis indicated the disappearance of alkyl halides. Removal of the solvent under reduced pressure (rotary evaporator) and flash column chromatography using hexane/ethyl acetate (75/25) as eluent afforded benzyl *p*-toluene sulfone (0.216 g) in 88% yield.

^1H and ^{13}C NMR were recorded in chloroform-*d* (CDCl_3) with TMS as internal reference using a 300 MHz NMR spectrometer, and were consistent with literature.

The typical microwave-assisted reaction conditions, in terms of temperature ($^\circ\text{C}$), pressure (psi), microwave power (W) and reaction time are shown in **Figure 1**.

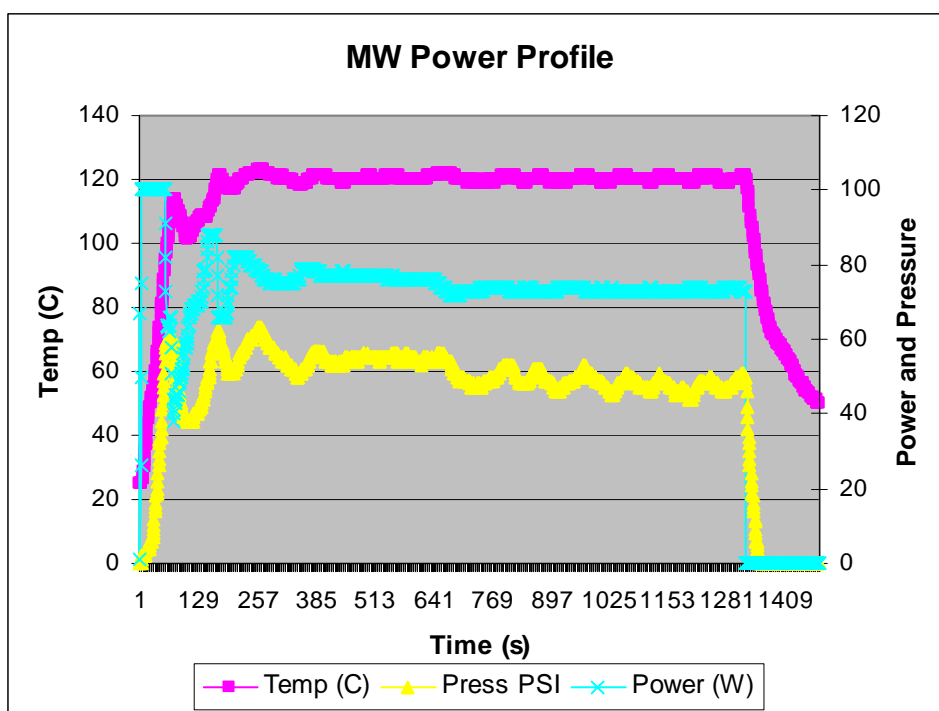
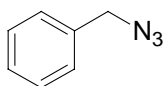
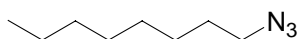


Figure 1. Typical MW reaction condition profile

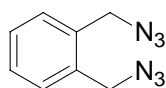
The NMR spectroscopic data of synthesized compounds is as follows:



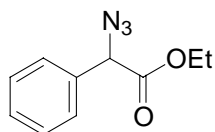
Azidomethyl-benzene (1a).² The reaction of benzylbromide (1.0 mmol, 0.171 g) and sodium azide (1.3 mmol, 0.085 g) was carried out as described earlier and produced 0.126 g (95%) of azidomethyl-benzene. ^1H NMR (300 MHz, CDCl_3/TMS) δ ppm 7.37- 7.30 (m, 5H), 4.30 (s, 2H); ^{13}C NMR (75.5 MHz, CDCl_3/TMS) δ ppm 135.4, 128.9, 128.3, 128.2, 54.8.



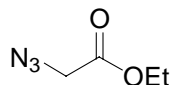
1-Azido-octane (1b).³ The reaction of 1-bromo-octane (1.0 mmol, 0.193 g) and sodium azide (1.3 mmol, 0.085 g) was carried out as described earlier and produced 0.135 g (89%) of 1-azido-octane (GC yield; crude product NMR showed 85 % of azidooctane with 15% 1-bromobutane mixture). ¹H NMR (300 MHz, CDCl₃/TMS) δ ppm 3.34 (t, 2H, *J* = 6.9 Hz), 1.79 (m, 2H), 1.23 (m, 10H), 0.82 (t, 3H, *J* = 6.9 Hz); ¹³C NMR (75.5 MHz, CDCl₃/TMS) δ ppm 51.2 (-CH₂N₃).



1,2-Bis-azidomethyl-benzene (1c).⁴ The reaction of 1,2-bis(chloromethyl)-benzene (1.0 mmol, 0.175 g) and sodium azide (2.5 mmol, 0.164 g) was carried out as described earlier and produced 0.180 g (95%) of 1,2-bis-azidomethyl-benzene as a colorless liquid. ¹H NMR (300 MHz, CDCl₃/TMS) δ ppm 7.36 (s, 4H), 4.41 (s, 4H); ¹³C NMR (75.5 MHz, CDCl₃/TMS) δ ppm 133.8, 130.1, 130.0, 128.9, 52.1.

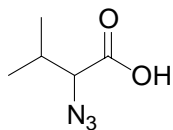


Azido-phenylacetic acid ethyl ester (1d).⁵ The reaction of α-bromo-phenylacetic acid ethyl ester (1.0 mmol, 0.243 g) and sodium azide (1.3 mmol, 0.085 g) was carried out as described earlier and produced 0.161 g (85%) of azido-phenylacetic acid ethyl ester. ¹H NMR (300 MHz, CDCl₃/TMS) δ ppm 7.40 (m, 5H), 4.94 (s, 1H), 4.26 (q, 2H, *J* = 7.2 Hz), 1.26 (t, 3H, *J* = 7.5 Hz); ¹³C NMR (75.5 MHz, CDCl₃/TMS) δ ppm 169.1, 134.0, 129.2, 129.1, 127.6, 65.4, 62.1, 14.0.

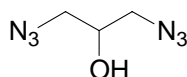


Azido-acetic acid ethyl ester (1e).⁶ The reaction of chloroacetic acid ethyl ester (1.0 mmol, 0.126 g) and sodium azide (1.3 mmol, 0.085 g) was carried out as described earlier and produced

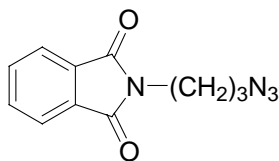
0.068 g (53%) of azido-acetic acid ethyl ester. ^1H NMR (300 MHz CDCl_3/TMS with pentane and hexane) δ ppm 4.26 (q, 2H, $J = 7.2$ Hz), 3.86 (s, 2H), 1.30 (m, mixed with protons from hexane and pentane); ^{13}C NMR (75.5 MHz CDCl_3/TMS) δ ppm 168.2, 61.7, 50.3, 13.9.



2-Azido-3-methyl-butyric acid (1f).⁷ The reaction of 2-bromo-3-methyl-butyric acid (1.0 mmol, 0.180 g) and sodium azide (1.3 mmol, 0.085 g) was carried out as described earlier and produced 0.067 g (47%) of 2-azido-3-methyl-butyric acid. ^1H NMR (300 MHz CDCl_3/TMS) δ ppm 9.19 (b, 1H), 3.72 (d, 1H, $J = 6.9$ Hz), 2.20 (m, 1H), 1.00 (tt, 6H, $J = 7.2$ Hz); ^{13}C NMR (75.5 MHz CDCl_3/TMS) δ ppm 176.0, 67.9, 30.9, 19.3, 17.7.

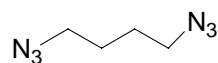


1,3-Diazido-2-propanol (1g).⁸ The reaction of 1,3-dibromo-2-propanol (1.0 mmol, 0.218 g) and sodium azide (2.5 mmol, 0.164 g) was carried out as described earlier and produced 0.141 g (99%) of 1,3-diazido-2-propanol. ^1H NMR (300 MHz CDCl_3/TMS) δ ppm 3.92 (m, 1H), 3.39 (dd, 4H, $J = 7.8$ Hz), 2.98 (b, 1H); ^{13}C NMR (75.5 MHz CDCl_3/TMS) δ ppm 69.5, 53.8.

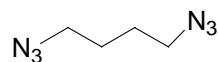


2-(3-Azidopropyl)-isoindole-1,3-dione (1h).⁹ The reaction of 2-(3-bromopropyl)-isoindole-1,3-dione (1.0 mmol, 0.268 g) and sodium azide (1.3 mmol, 0.085 g) was carried out as described earlier and produced 0.202 g (88%) of 2-(3-azidopropyl)-isoindole-1,3-dione. ^1H NMR (300 MHz CDCl_3/TMS) δ ppm 7.78 (m, 2H), 7.68 (m, 2H), 3.72 (t, 2H, $J = 6.9$ Hz), 3.33

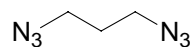
(t, 2H, $J = 6.9$ Hz), 1.90 (tt, 2H, $J = 6.9$ Hz); ^{13}C NMR (75.5 MHz CDCl_3/TMS) δ ppm 168.0, 133.9, 131.8, 123.1, 48.9, 35.2, 27.8.



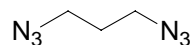
1,4-Bisazido-butane (1i).¹⁰ The reaction of 1,4-ditosyl-butane (1.0 mmol, 0.398 g) and sodium azide (2.5 mmol, 0.163 g) was carried out as described earlier and produced 0.108 g (77%) of 1,4-bisazido-butane. ^1H NMR (300 MHz CDCl_3/TMS) δ ppm 3.28 (t, 4H, $J = 8.4$ Hz), 1.63 (p, 4H, $J = 6.0$ Hz); ^{13}C NMR (75.5 MHz CDCl_3/TMS) δ ppm 50.8, 26.0.



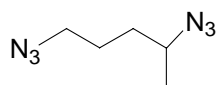
1,4-Bisazido-butane (1i).¹⁰ The reaction of 1,4-dibromo-butane (1.0 mmol, 0.216 g) and sodium azide (2.5 mmol, 0.164 g) was carried out as described earlier and produced 0.125 g (89%) of 1,4-bisazido-butane. ^1H NMR (300 MHz CDCl_3/TMS) δ ppm 3.28 (t, 4H, $J = 8.4$ Hz), 1.63 (p, 4H, $J = 6.0$ Hz); ^{13}C NMR (75.5 MHz CDCl_3/TMS) δ ppm 50.8, 26.0.



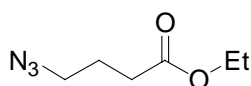
1,3-Bisazido-propane (1j).¹¹ The reaction of 1,3-ditosyl-propane (1.0 mmol, 0.384 g) and sodium azide (2.5 mmol, 0.164 g) was carried out as described earlier and produced 0.076 g (60%) of 1,3-bisazido-propane. ^1H NMR (300 MHz CDCl_3/TMS) δ ppm 3.42 (t, 4H, $J = 6.2$ Hz), 1.83 (p, 2H, $J = 6.6$ Hz); ^{13}C NMR (75.5 MHz CDCl_3/TMS) δ ppm 48.5, 28.3.



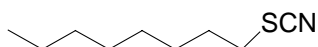
1,3-Bisazido-propane (1j).¹¹ The reaction of 1,3-dibromo-propane (1.0 mmol, 0.202 g) and sodium azide (2.5 mmol, 0.164 g) was carried out as described earlier and produced 0.098 g (78%) of 1,3-bisazido-propane. ^1H NMR (300 MHz CDCl_3/TMS) δ ppm 3.42 (t, 4H, $J = 6.2$ Hz), 1.83 (p, 2H, $J = 6.6$ Hz); ^{13}C NMR (75.5 MHz CDCl_3/TMS) δ ppm 48.5, 28.3.



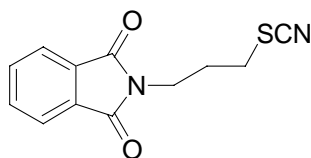
1-4-Bisazido-pentane (1k).¹² The reaction of 1,4-dibromo-pentane (1.0 mmol, 0.229 g) and sodium azide (2.5 mmol, 0.163 g) was carried out as described earlier and produced 0.126 g (82%) of 1-azido-4-chloro-butane. ¹H NMR (300 MHz CDCl₃/TMS) δ ppm 3.49 (m, 1H), 3.29 (t, 2H, J = 6.9 Hz), 1.62 (m, 4H), 1.19 (d, 3H, J = 6.4 Hz); ¹³C NMR (75.5 MHz CDCl₃/TMS) δ ppm 57.4, 52.1, 33.3, 25.5, 19.4.



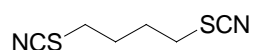
4-Azido-butyric acid ethyl ester (1l).¹³ The reaction of 4-bromo-butyric acid ethyl ester (1.0 mmol, 0.195 g) and sodium azide (1.3 mmol, 0.085 g) was carried out as described earlier and produced 0.137 g (87%) of 1-azido-butyric acid ethyl ester. ¹H NMR (300 MHz CDCl₃/TMS) δ ppm 4.09 (q, 2H, J = 6.6 Hz), 3.33 (t, 2H, J = 7.8 Hz), 2.06 (m, 2H), 1.69 (m, 4H); ¹³C NMR (75.5 MHz CDCl₃/TMS) δ ppm 171.0, 63.7, 51.0, 25.9, 25.5, 20.9.



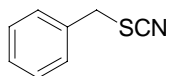
1-Thiocyanato-octane (2a).¹⁴ The reaction of 1-bromo-octane (1.0 mmol, 0.193 g) and potassium thiocyanate (1.3 mmol, 0.126 g) was carried out as described earlier and produced 0.147 g (86%) of 1-thiocyanato-octane. ¹H NMR (300 MHz CDCl₃/TMS) δ ppm 2.95 (t, 2H, J = 7.2 Hz), 1.81 (dd, 2H, J = 7.5, 7.2 Hz), 1.42 (m, 2H), 1.29 (m, 8H), 0.89 (t, 3H, J = 6.9 Hz); ¹³C NMR (75.5 MHz, CDCl₃/TMS) δ ppm 112.2, 33.9, 31.5, 29.7, 28.9, 28.7, 27.3, 22.4, 13.9.



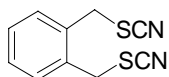
2-(3-Thiocyanatopropyl)-isoindole-1,3-dione (2b).¹⁵ The reaction of 2-(3-bromopropyl)-isoindole-1,3-dione (1.0 mmol, 0.268 g) and potassium thiocyanate (1.3 mmol, 0.126 g) was carried out as described earlier and produced 0.222 g (90%) of 2-(3-thiocyanatopropyl)-isoindole-1,3-dione, m.p. 97-98 °C (lit. 140-141 °C). ¹H NMR (300 MHz CDCl₃/TMS) δ ppm 7.85 (dd, 2H, *J* = 6.4, 3.0 Hz), 7.74 (m, 2H), 3.87 (t, 2H, *J* = 6.3 Hz), 3.008 (t, 2H, *J* = 7.2 Hz), 2.23 (m, 2H); ¹³C NMR (75.5 MHz CDCl₃/TMS) δ ppm 168.2, 134.2, 131.8, 123.4, 111.8, 35.2, 31.5, 29.2.



1,4-Bisthiocyanato-butane (2c).¹⁶ The reaction of 1,4-ditosyl-butane (1.0 mmol, 0.398 g) and potassium thiocyanate (2.5 mmol, 0.243 g) was carried out as described earlier and produced 0.134 g (78%) of 1,4-bisthiocyanato-butane. ¹H NMR (300 MHz CDCl₃/TMS) δ ppm 3.02 (t, 4H, *J* = 8.2 Hz), 2.02 (m, 4H); ¹³C NMR (75.5 MHz CDCl₃/TMS) δ ppm 111.5, 32.8, 27.6.

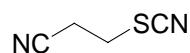


Thiothiocyanatomethyl-benzene (2d).¹⁷ The reaction of benzylchloride (1.0 mmol, 0.127 g) and potassium thiocyanate (1.3 mmol, 0.126 g) was carried out as described earlier and produced 0.142 g (95%) of thiocyanatomethyl-benzene, m.p. 43-44 °C. ¹H NMR (300 MHz, CDCl₃/TMS) δ ppm 7.27 (m, 5H), 4.03 (s, 2H); ¹³C NMR (75.5 MHz, CDCl₃/TMS) δ ppm 134.3, 129.0, 128.8, 128.7, 111.8, 38.2.

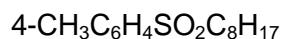


1,2-Bis-thiocyanatomethyl-benzene (2e).¹⁸ The reaction of 1,2-bis(chloromethyl)-benzene (1.0 mmol, 0.175 g) and potassium thiocyanate (2.5 mmol, 0.243 g) was carried out as described earlier and produced 0.201 g (91%) of 1,2-bis-thiocyanatomethyl-benzene. ¹H NMR (300 MHz,

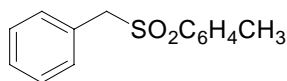
CDCl_3/TMS) δ ppm 7.40 (s, 4H), 4.27 (s, 4H); ^{13}C NMR (75.5 MHz, CDCl_3/TMS) δ ppm 132.7, 131.4, 129.8, 111.2, 34.9.



3-Thiothiocyanato-propionitrile (2f).¹⁹ The reaction of 3-bromopropionitrile (1.0 mmol, 0.134 g) and potassium thiocyanate (1.3 mmol, 0.126 g) was carried out as described earlier and produced 0.095 g (85%) of thiocyanato-propionitrile. ^1H NMR (300 MHz, CDCl_3/TMS) δ ppm 3.15 (t, 2H, $J = 6.9$ Hz), 2.88 (t, 2H, $J = 6.9$ Hz); ^{13}C NMR (75.5 MHz, CDCl_3/TMS) δ ppm 116.1, 110.1, 29.1, 19.0.

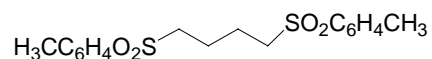


1-Methyl-4-(octane-1-sulfonyl) benzene (3a).²⁰ The reaction of 1-bromooctane (1 mmol, 0.193 g) and sodium *p*-toluenesulfinate hydrate (1.3 mmol, 0.254 g) in water (2 mL) was carried out as described earlier and produced 0.217 g (81%) of 1-methyl-4-(octane-1-sulfonyl) benzene, m.p. 33-34 °C (lit. 34.4-34.5 °C). ^1H NMR (300 MHz, CDCl_3/TMS) δ ppm 7.78 (dd, 2H, $J = 6.6, 1.5$ Hz), 7.34 (d, 2H, $J = 7.8$ Hz), 3.07 (m, 2H), 2.44 (s, 3H), 1.68 (m, 2H), 1.26 (m, 10H), 0.86 (t, 3H, $J = 6.9$ Hz); ^{13}C NMR (75.5 MHz, CDCl_3/TMS) δ ppm 144.3, 136.1, 129.6, 127.8, 56.1, 31.4, 28.7, 28.6, 28.0, 22.5, 22.3, 21.3, 13.8.

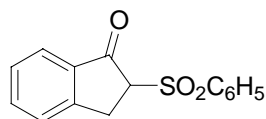


1-Methyl-4-(benzylsulfonyl) benzene (3b).²¹ The reaction of benzylbromide (1 mmol, 0.171 g) and sodium *p*-toluenesulfinate hydrate (1.3 mmol, 0.254 g) in water (2 mL) was carried out as described earlier and produced 0.217 g (88%) of 1-methyl-4-(benzylsulfonyl) benzene, m.p. 140-141 °C (lit. 140-141 °C). ^1H NMR (300 MHz, CDCl_3/TMS) δ ppm 7.41 (s, 2H), 7.18 (m, 5H),

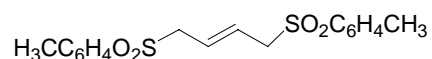
7.01 (s, 2H), 4.21 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3/TMS) δ ppm 144.6, 135.0, 130.8, 129.4, 128.61, 128.57, 128.48, 128.3, 62.9, 21.6.



1,4-Bistoluenesulfonyl-butane (3c).²² The reaction of 1,4-dibromobutane (1 mmol, 0.215 g) and sodium *p*-toluenesulfinate hydrate (2.5 mmol, 0.495 g) in water (2 mL) was carried out as described earlier and produced 0.257 g (70%) of 1,4-bistoluenesulfonyl-butane, m.p. 148-149 °C (lit. 149-150 °C). ^1H NMR (300 MHz, CDCl_3/TMS) δ ppm 7.73 (d, 4H, $J = 8.1$ Hz), 7.34 (d, 4H, $J = 7.8$ Hz), 3.05 (m, 4H), 2.43 (s, 6H), 1.78 (m, 4H); ^{13}C NMR (75.5 MHz, CDCl_3/TMS) δ ppm 144.7, 135.7, 129.8, 127.8, 55.3, 21.4.

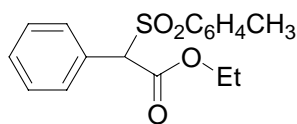


2-Bezenesulfonyl-1-indanone (3d).²³ The reaction of 2-bromoindanone (1 mmol, 0.211 g) and sodium benzenesulfinate (1.3 mmol, 0.213 g) in water (2 mL) was carried out as described earlier and produced 0.248 g (91%) of 2-benzenesulfonyl-1-indanone, m.p. 145-146 °C (lit. 147-148 °C). ^1H NMR (300 MHz, CDCl_3/TMS) δ ppm 7.92 (m, 2H), 7.66 (t, 3H, $J = 7.5$ Hz), 7.58-7.38 (m, 4H), 4.29 (t, 1H, $J = 2.4$ Hz), 3.82 (d, 1H, $J = 18.0$ Hz), 3.55 (dd, 1H, $J = 17.7$ Hz); ^{13}C NMR (75.5 MHz, CDCl_3/TMS) δ ppm 194.4, 151.8, 137.5, 135.9, 135.7, 134.2, 129.2, 129.0, 128.2, 126.4, 124.8, 68.6, 28.0.

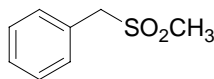


1,4-Bis-(*p*-toluenesulfonyl)-2-butene (3e).²⁴ The reaction of 1,4-dibromo-2-butene (1 mmol, 0.213 g) and sodium *p*-toluenesulfinate hydrate (2.5 mmol, 0.495 g) in water (2 mL) was carried out as described earlier and produced 0.310 g (85%) of 1,4-bis(*p*-toluenesulfonyl)-2-butene, m.p. 103-104 °C (lit. 198-200 °C). ^1H NMR (300 MHz, CDCl_3/TMS) δ ppm 7.70 (d, 4H, $J = 7.8$ Hz),

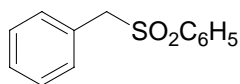
7.34 (d, 4H, $J = 7.8$ Hz), 5.59 (d, 2H, $J = 4.2, 1.8$ Hz), 3.76 (dd, 4H, $J = 4.5, 1.8$ Hz), 2.45 (s, 6H); ^{13}C NMR (75.5 MHz, CDCl_3/TMS) δ ppm 145.0, 135.4, 129.8, 128.3, 126.3, 59.6, 21.6.



2-Phenyl-(toluene-4-sulfonyl)-acetic acid ethyl ester (3f).²⁵ The reaction of 2-bromophenylacetic acid ethyl ester (1 mmol, 0.243 g) and sodium *p*-toluenesulfinate hydrate (1.3 mmol, 0.252 g) in water (2 mL) was carried out as described earlier and produced 0.271 g (85%) of 2-phenyl-(toluene-4-sulfonyl)-acetic acid ethyl ester, m.p. 112-113 °C (lit. 112-113 °C). ^1H NMR (300 MHz, CDCl_3/TMS) δ ppm 7.40 (d, 2H, $J = 8.1$ Hz), 7.28-7.18 (m, 5H), 7.13 (d, 2H, $J = 8.1$ Hz), 5.00 (s, 1H), 4.13 (q, 2H, $J = 10.2$ Hz) 2.33 (s, 3H), 1.15 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (75.5 MHz, CDCl_3/TMS) δ ppm 164.7, 145.1, 133.4, 130.1, 129.8, 129.7, 129.4, 129.0, 128.3, 127.8, 75.1, 62.3, 21.5, 13.7.

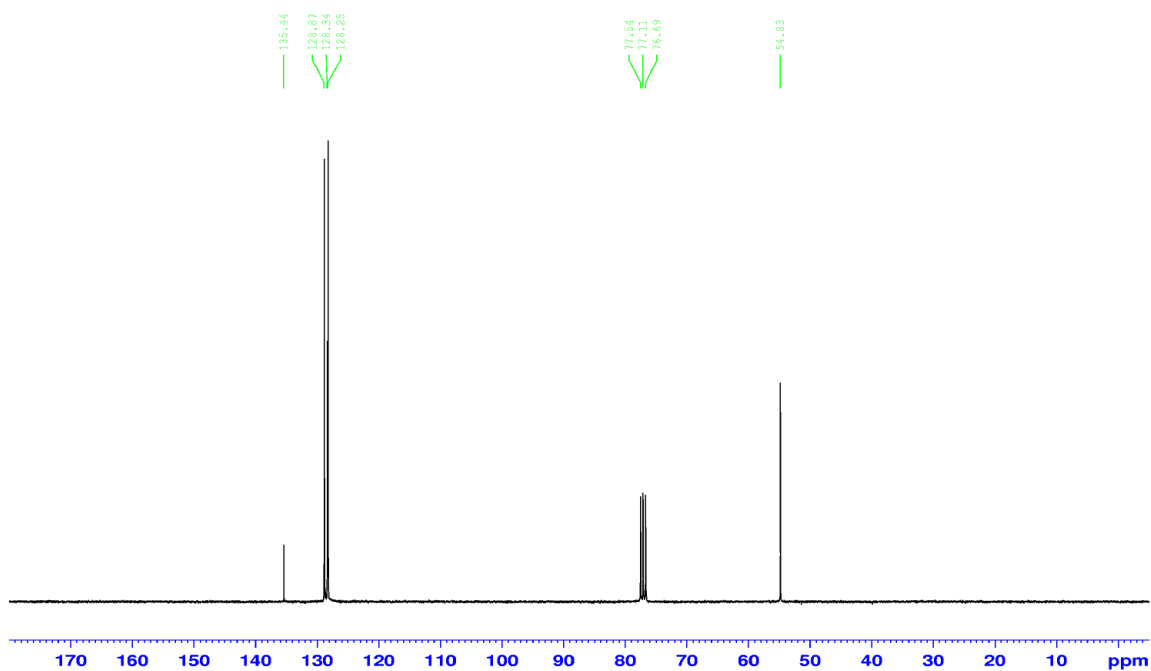
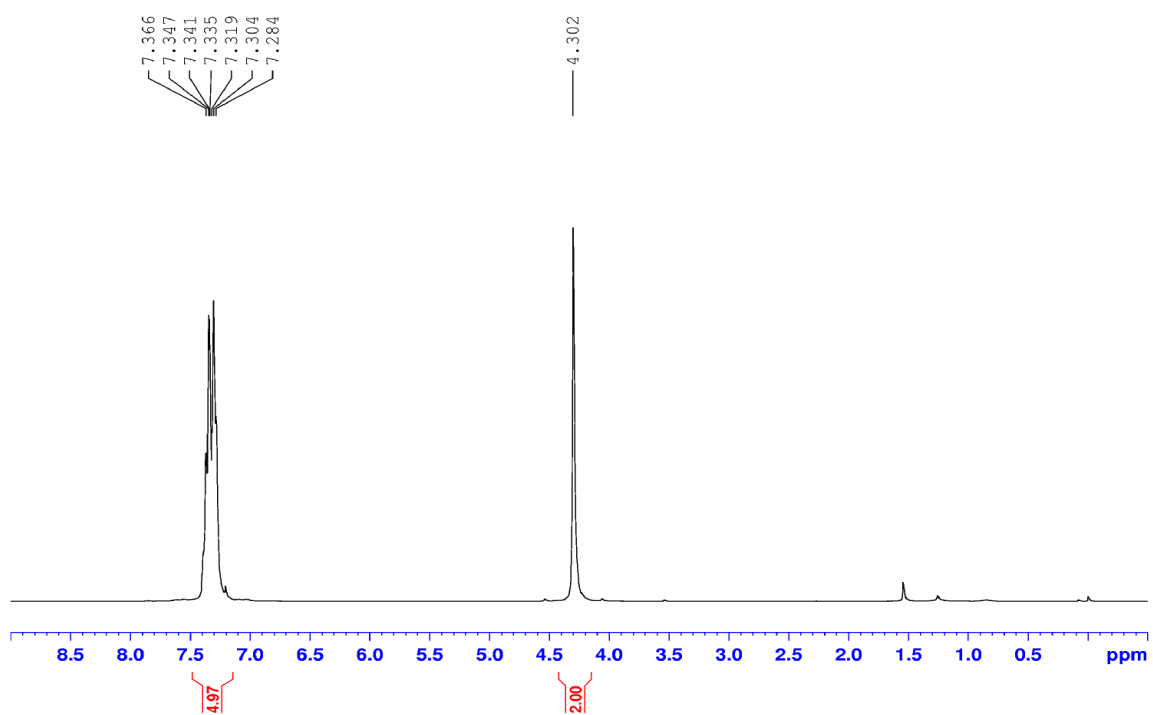
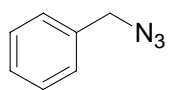


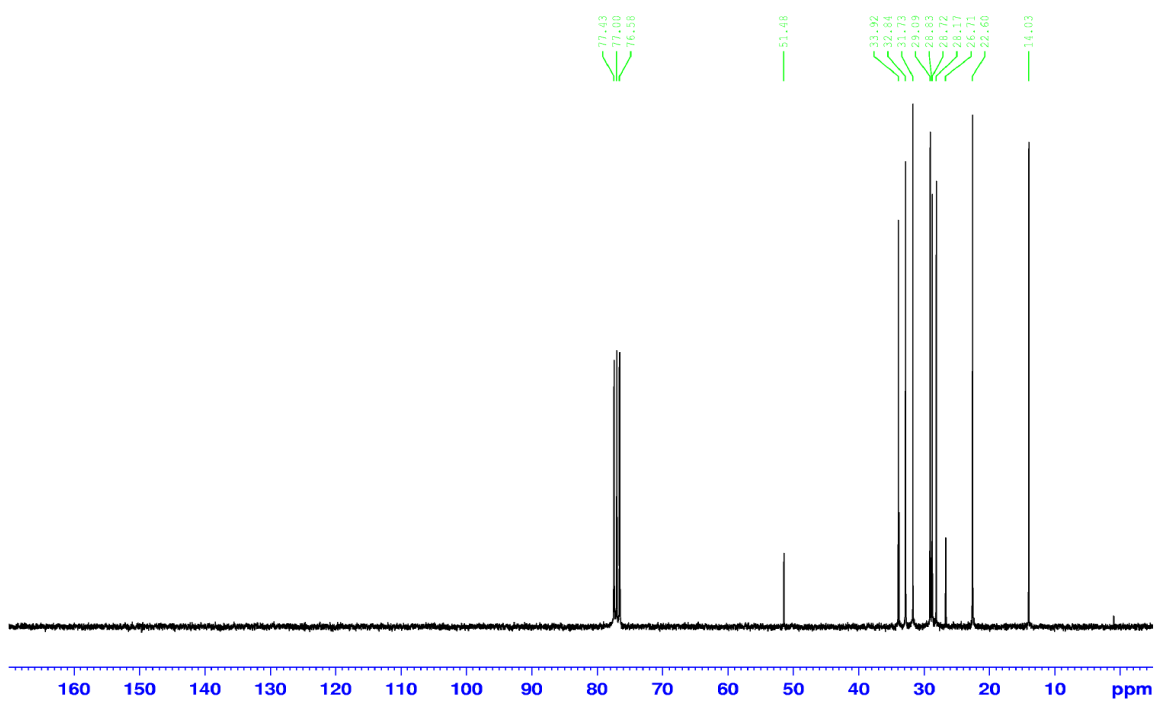
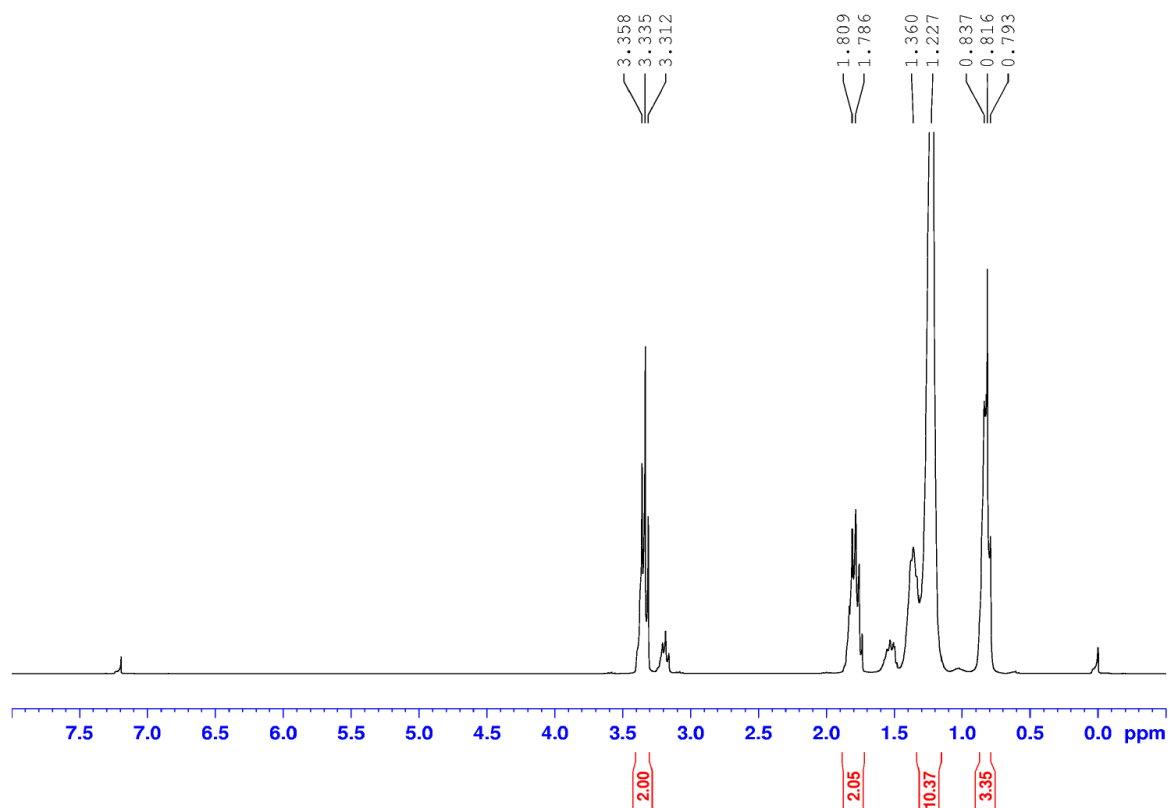
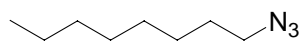
Methanesulfonylmethyl-benzene (3g).²⁶ The reaction of benzylchloride(1 mmol, 0.127 g) and methanesulfinic acid, sodium salt (1.3 mmol, 0.133 g) in water (2 mL) was carried out as described earlier and produced 0.139 g (82%) of methanesulfonylmethyl-benzene, m.p. 125-126.5°C (lit. 126-127 °C). ^1H NMR (300 MHz, CDCl_3/TMS) δ ppm 7.42(s, 5H), 4.26 (s, 2H), 2.76 (s, 3H); ^{13}C NMR (75.5 MHz, CDCl_3/TMS) δ ppm 130.5, 129.1, 128.3, 61.4, 39.0.

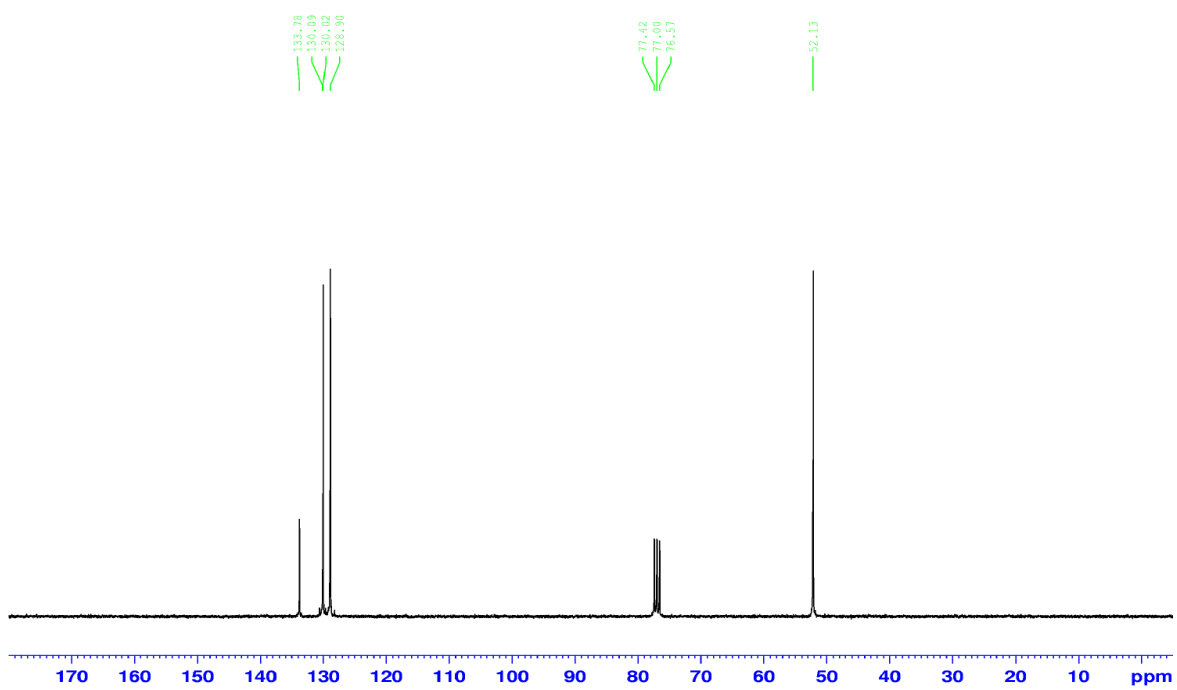
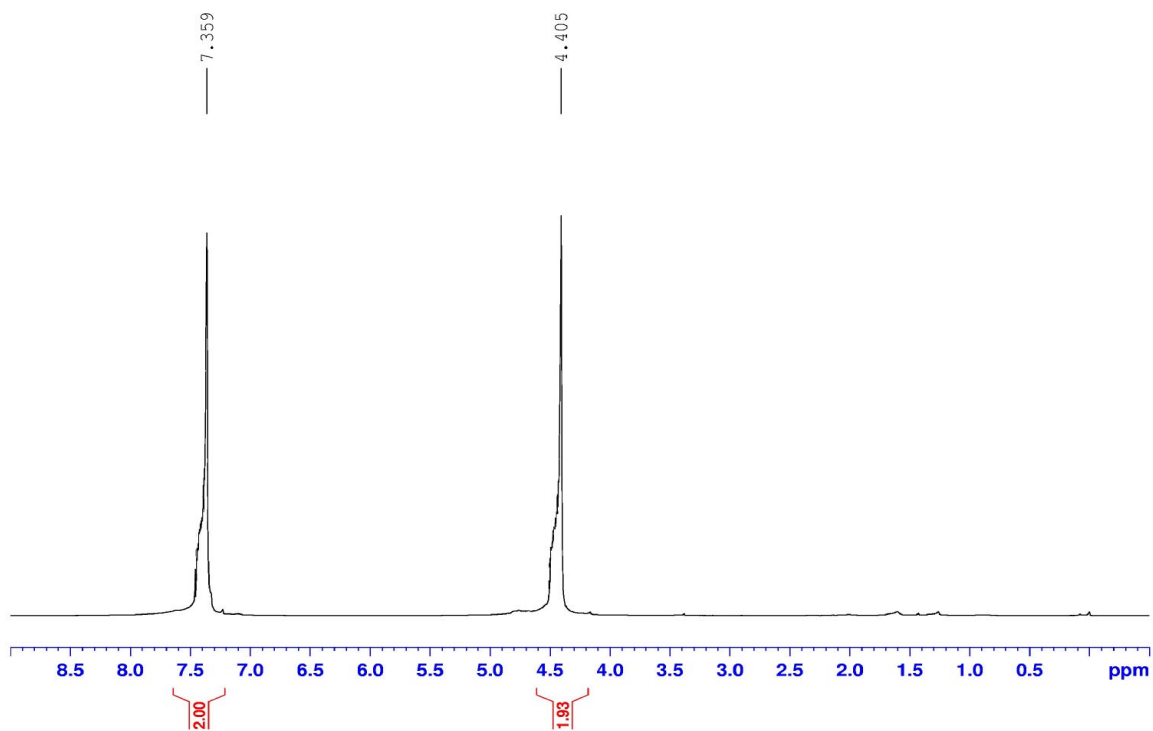
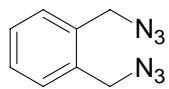


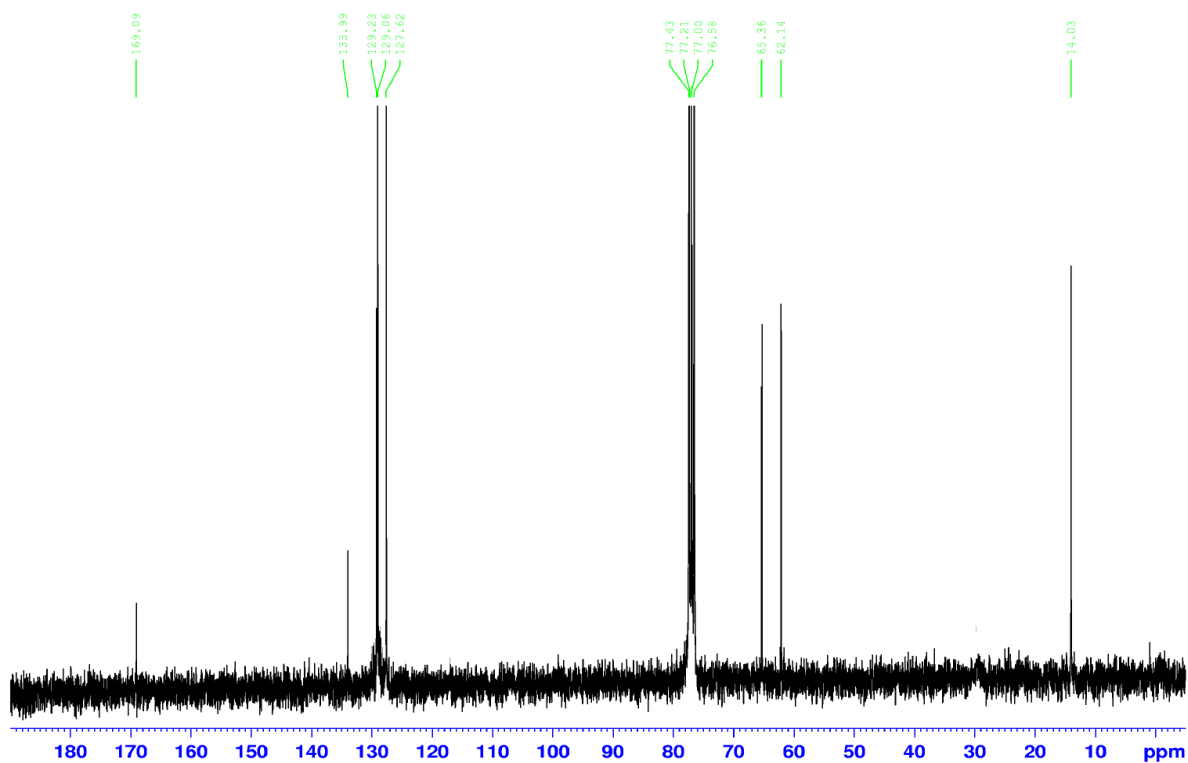
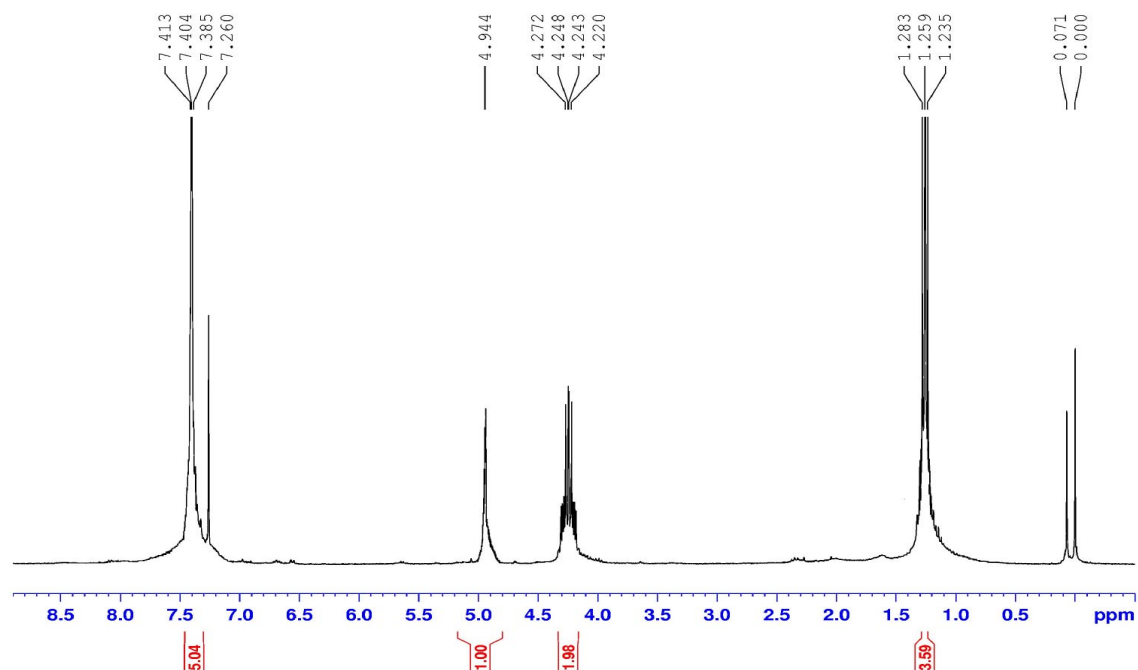
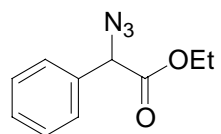
Benzylsulfonyl-benzene (3h).²⁷ The reaction of benzylchloride(1 mmol, 0.127 g) and sodium benzenesulfinate (1.3 mmol, 0.213 g) in water (2 mL) was carried out as described earlier and produced 0.197 g (85%) of benzylsulfonyl-benzene, m.p. 146.5-147.5 °C (lit. 151-155 °C). ^1H

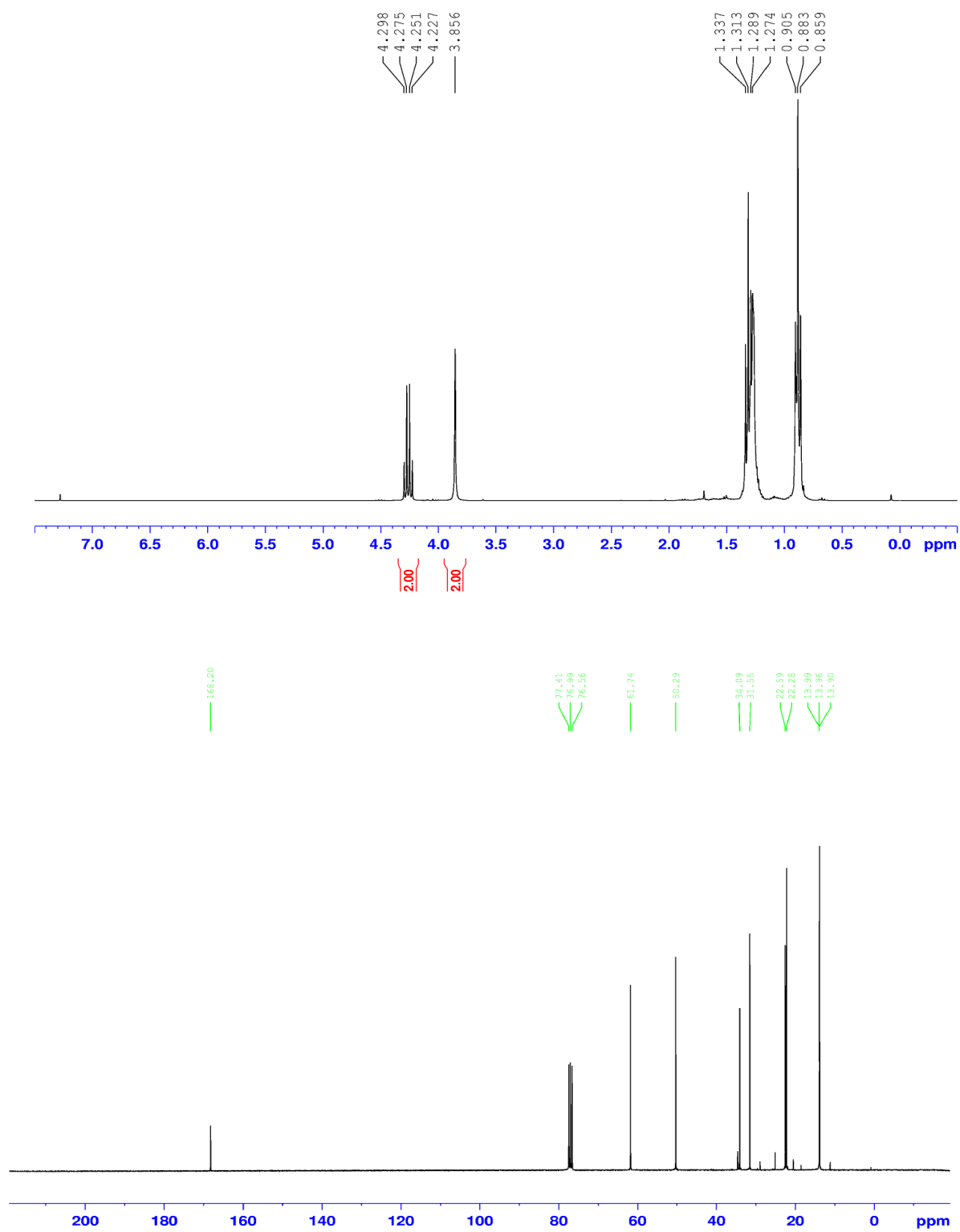
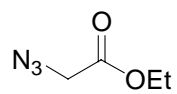
NMR (300 MHz, CDCl₃/TMS) δ ppm 7.63 (d, 3H, J = 6.6 Hz), 7.45 (d, 2H, J = 6.9 Hz), 7.31 (m, 1H), 7.27 (d, 2H, J = 5.8 Hz), 7.08 (d, 2H, J = 4.8 Hz), 4.31 (s, 2H); ¹³C NMR (75.5 MHz, CDCl₃/TMS) δ ppm 137.8, 133.6, 130.8, 128.8, 128.7, 128.6, 128.5, 128.1, 62.8.

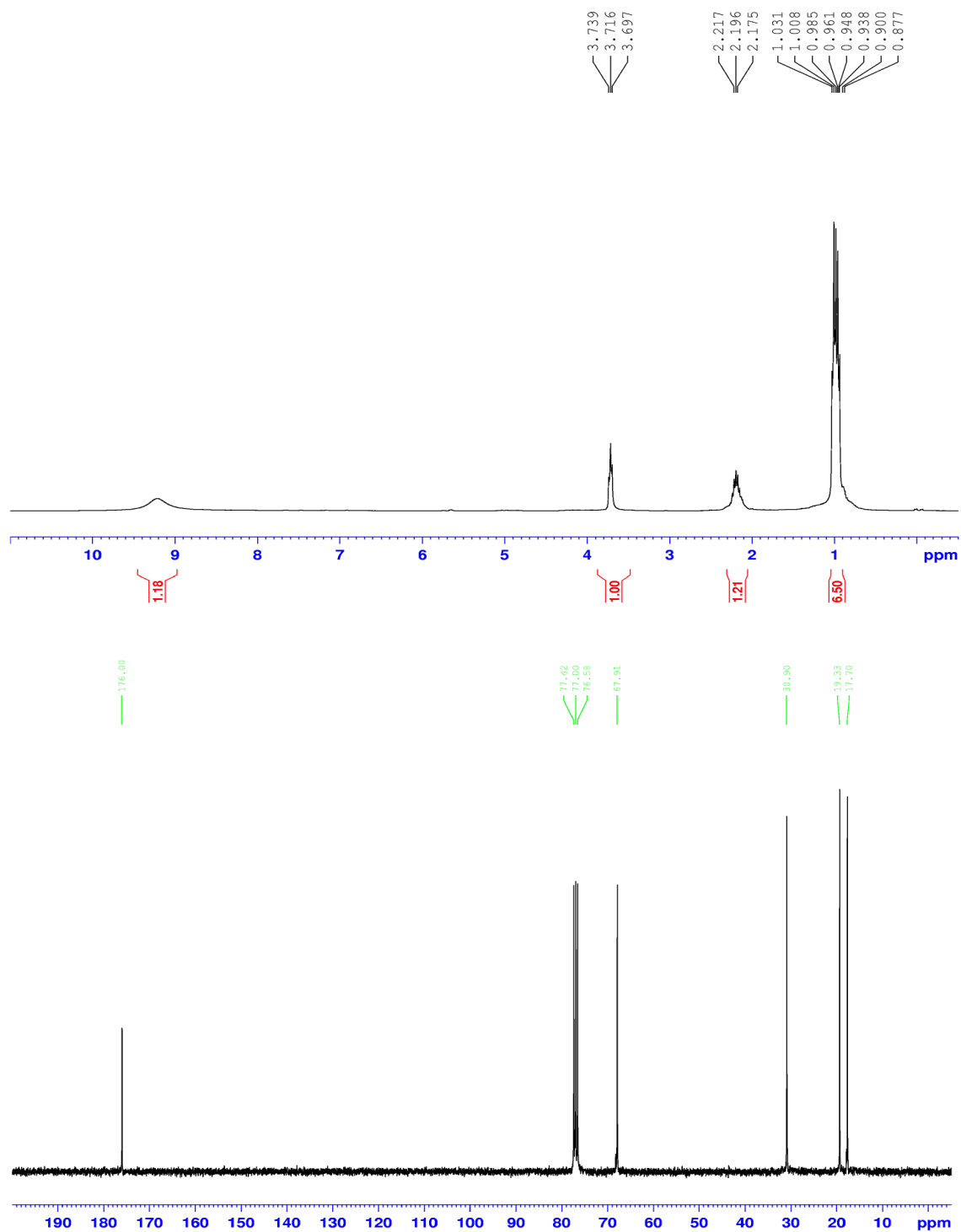
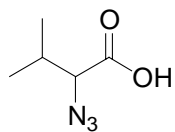


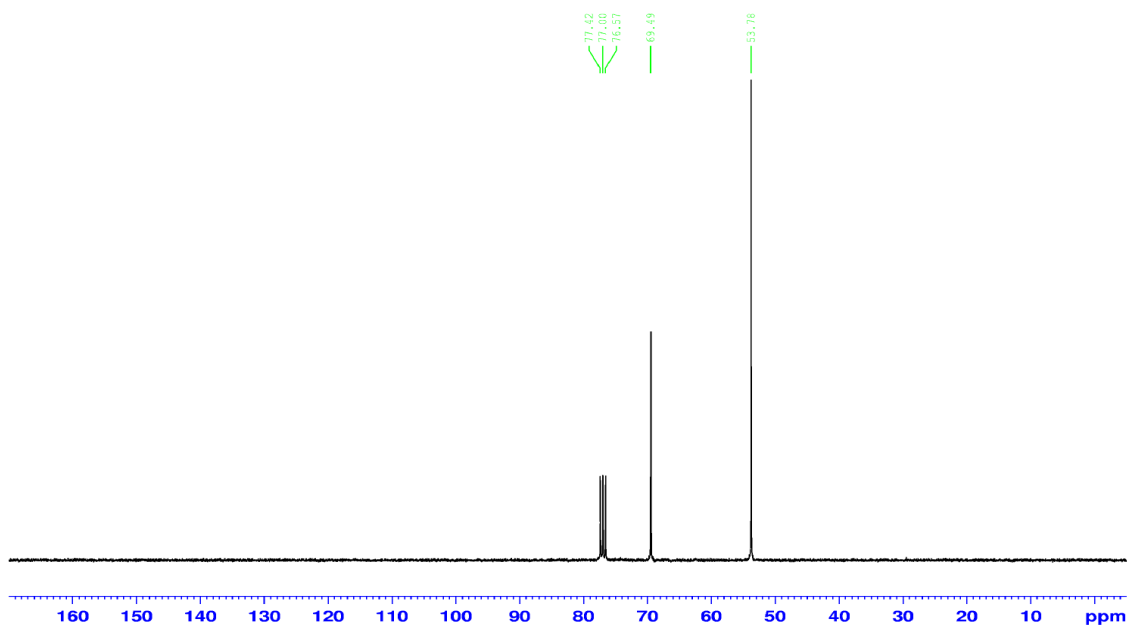
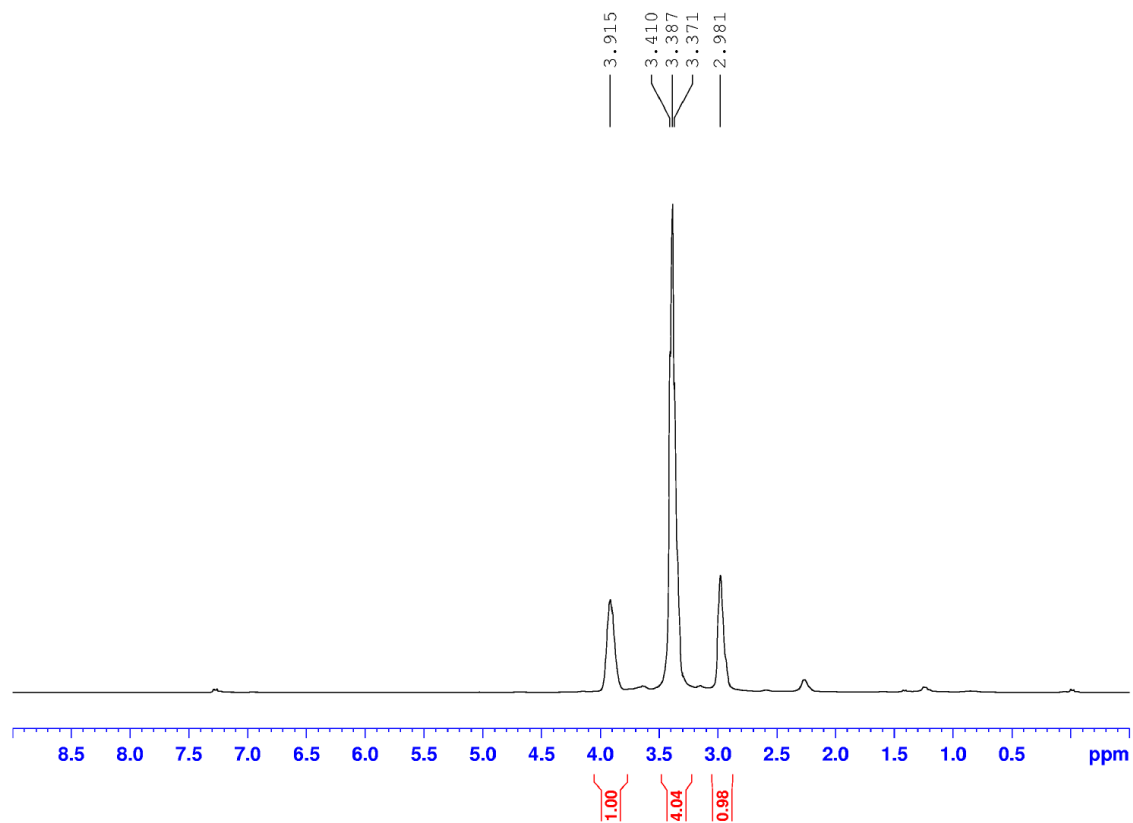
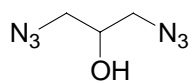


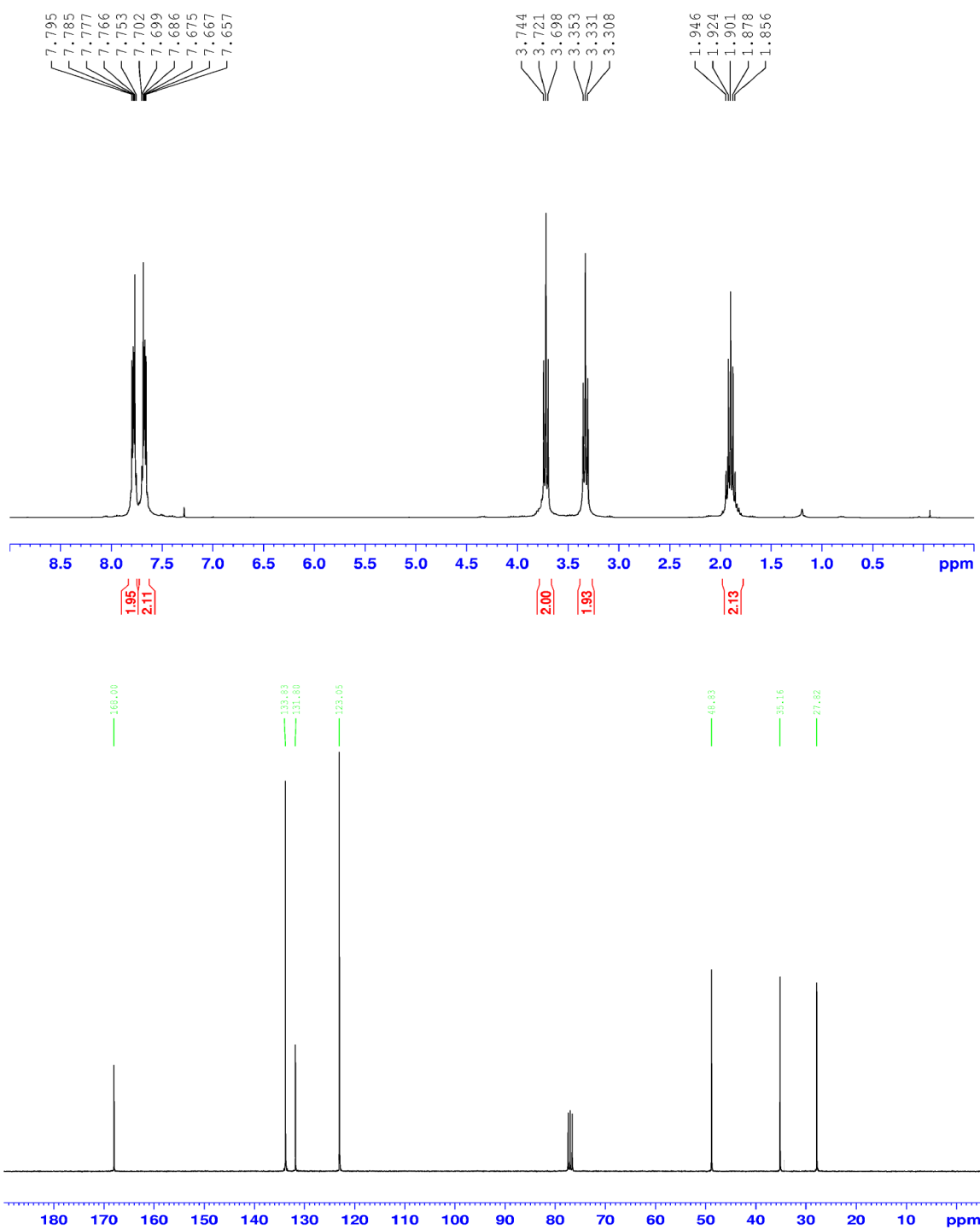
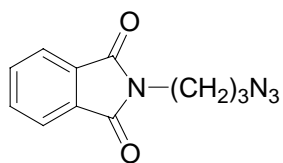


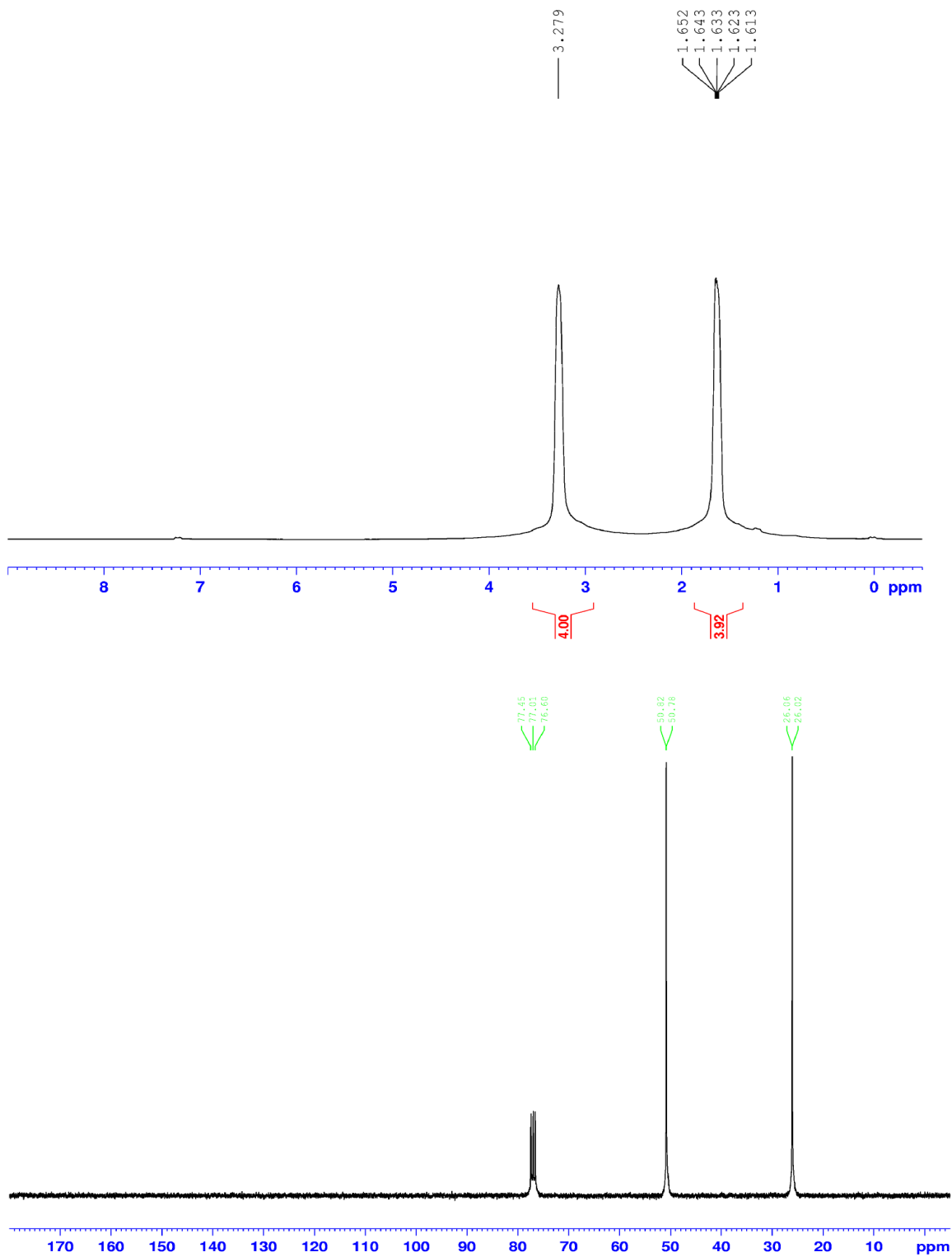
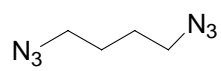


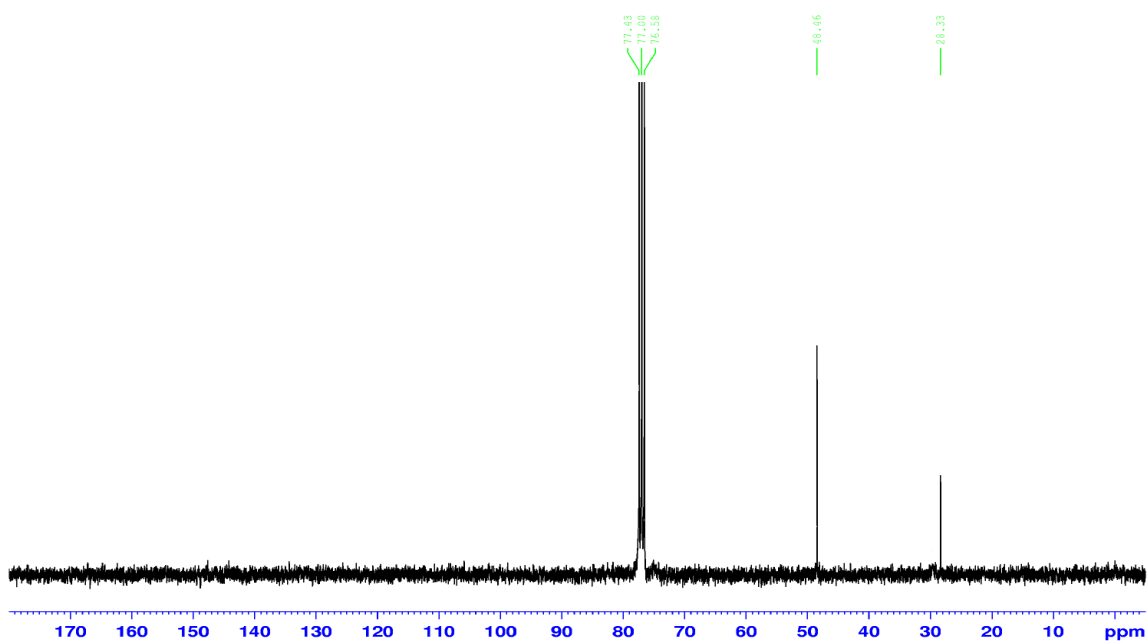
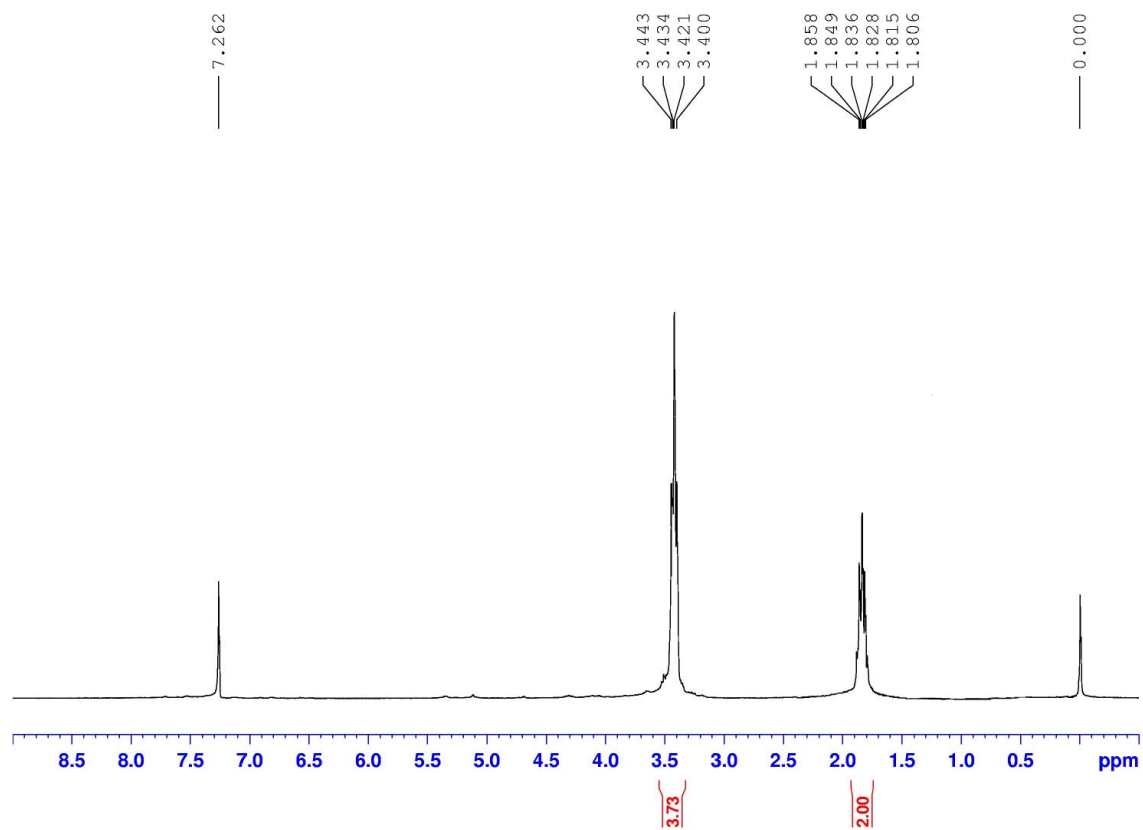
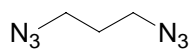


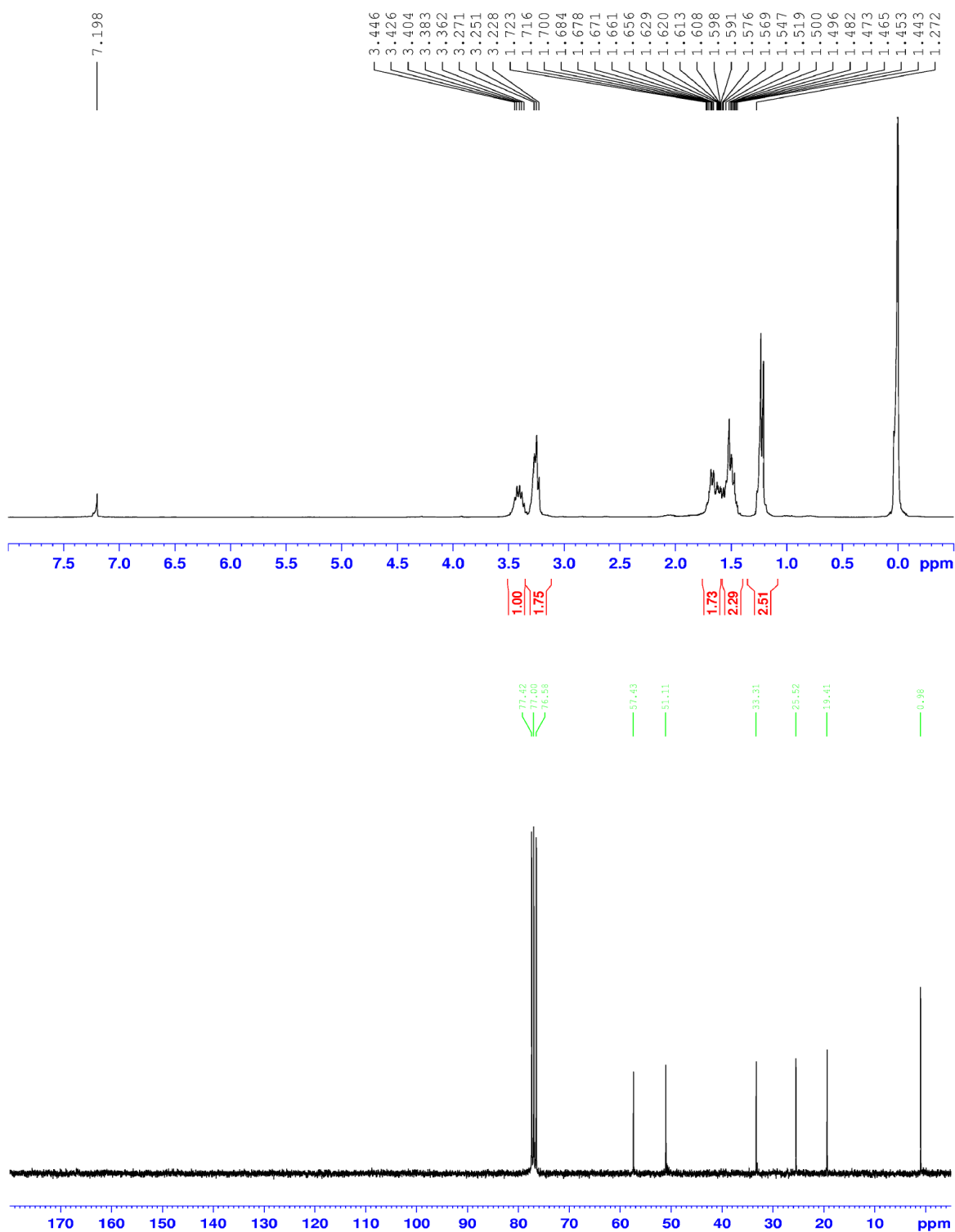
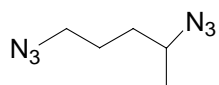


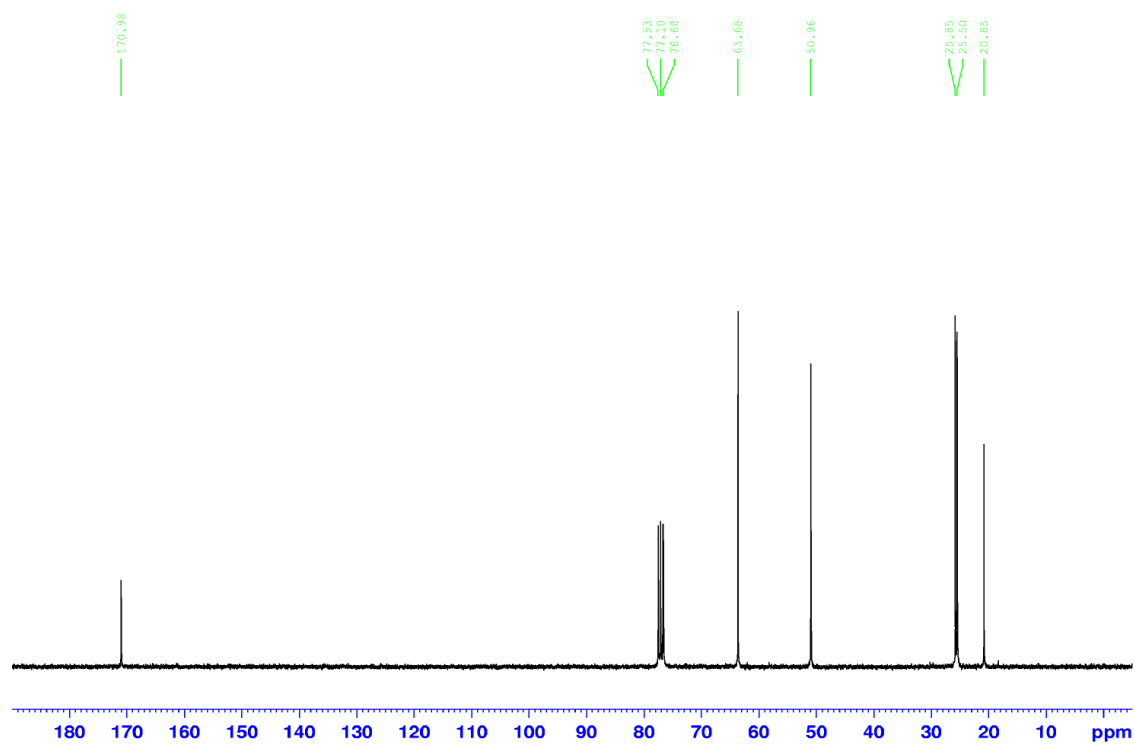
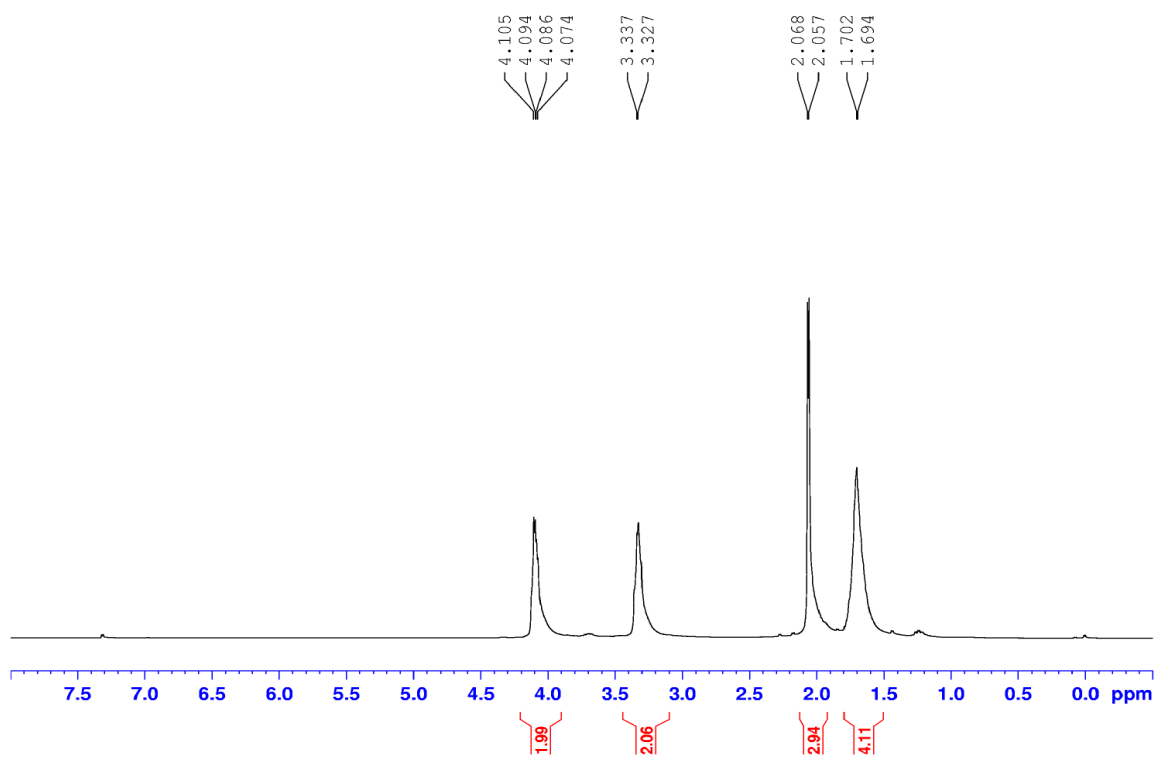
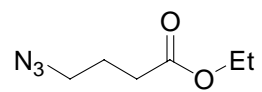


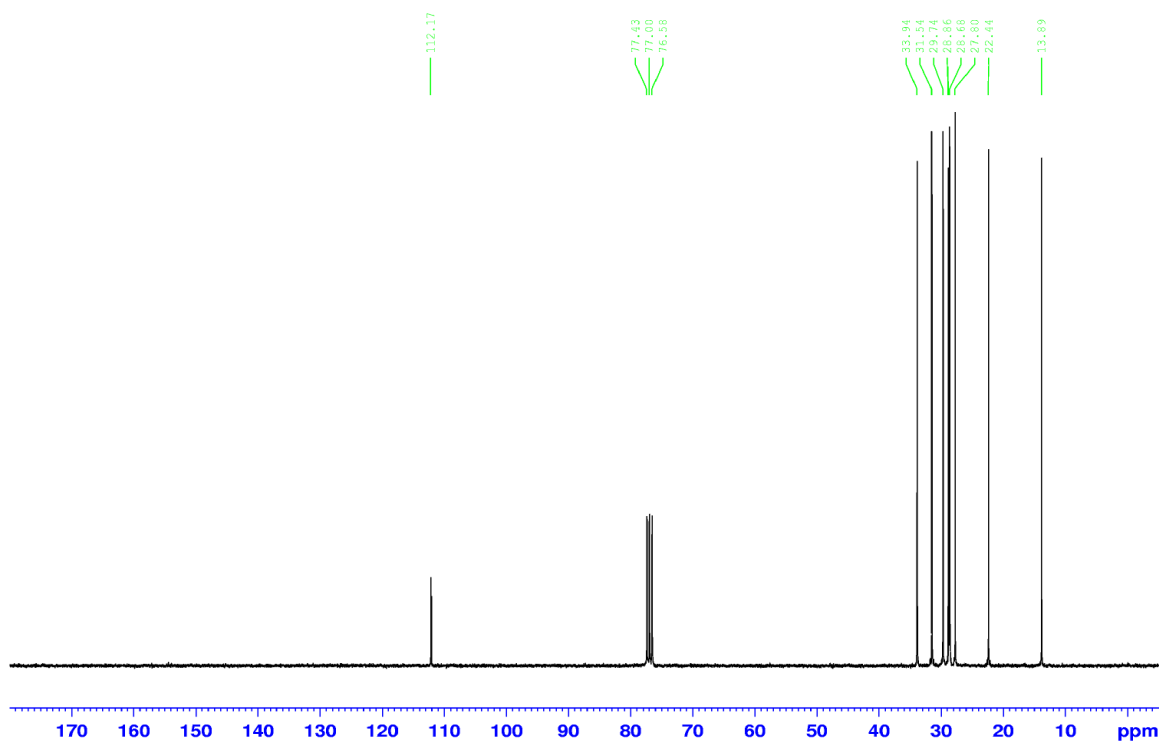
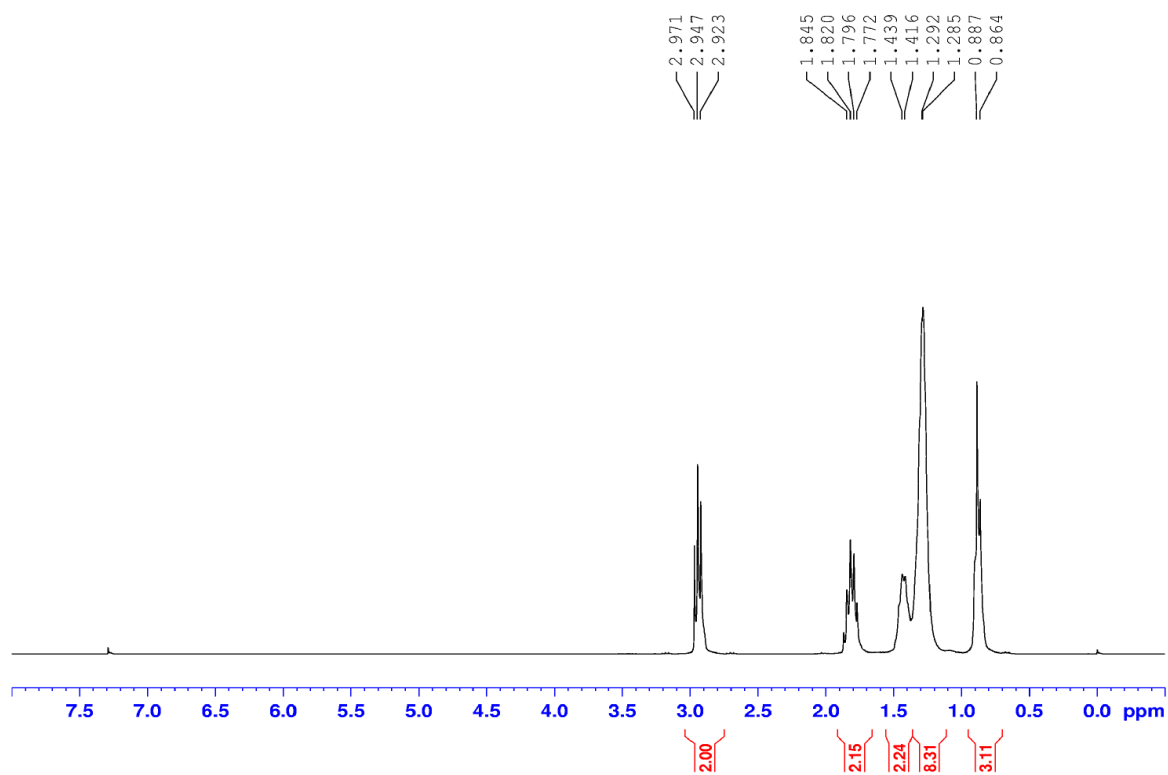
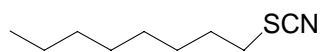


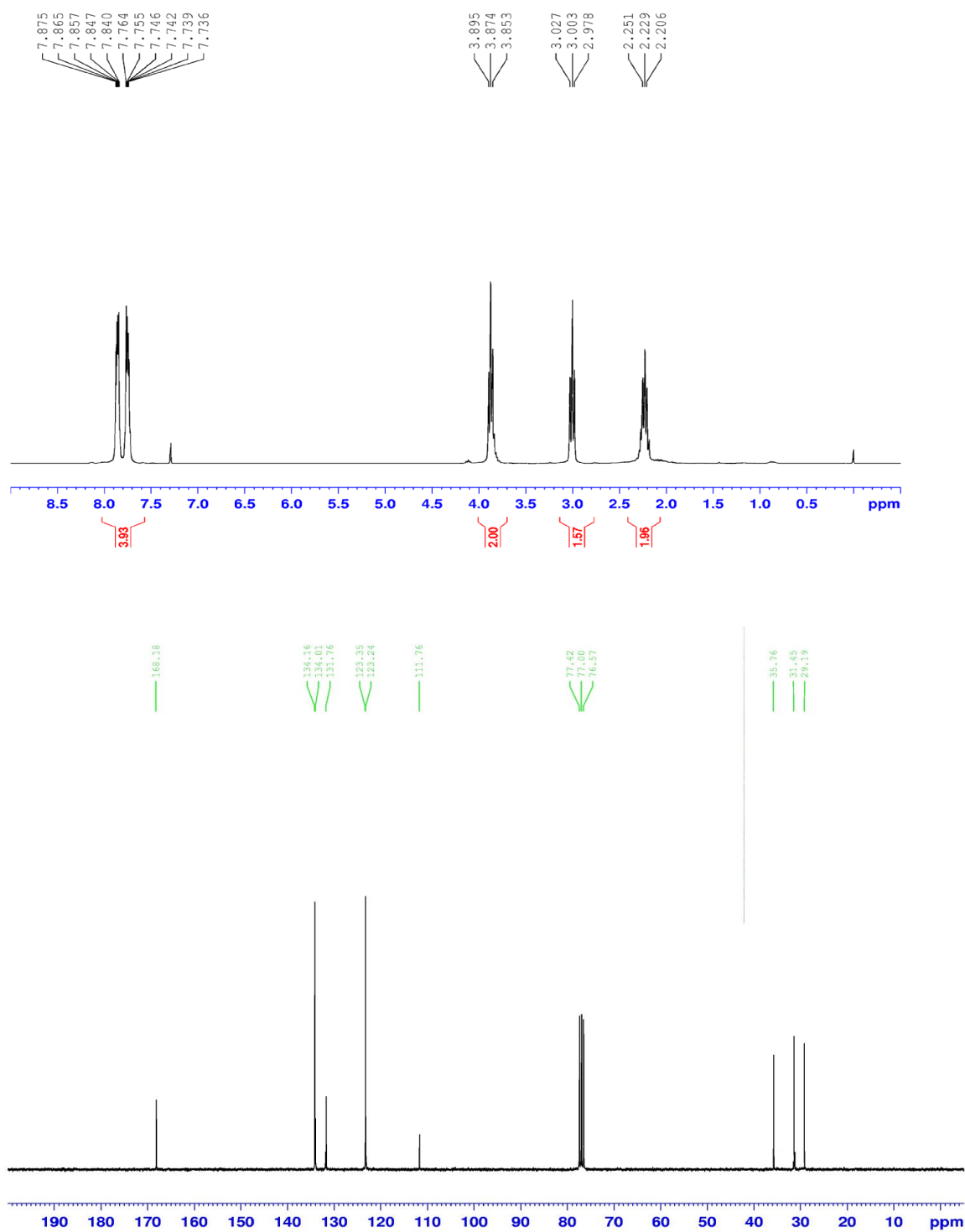
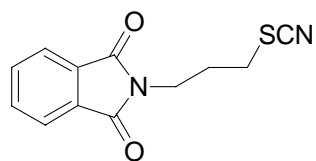


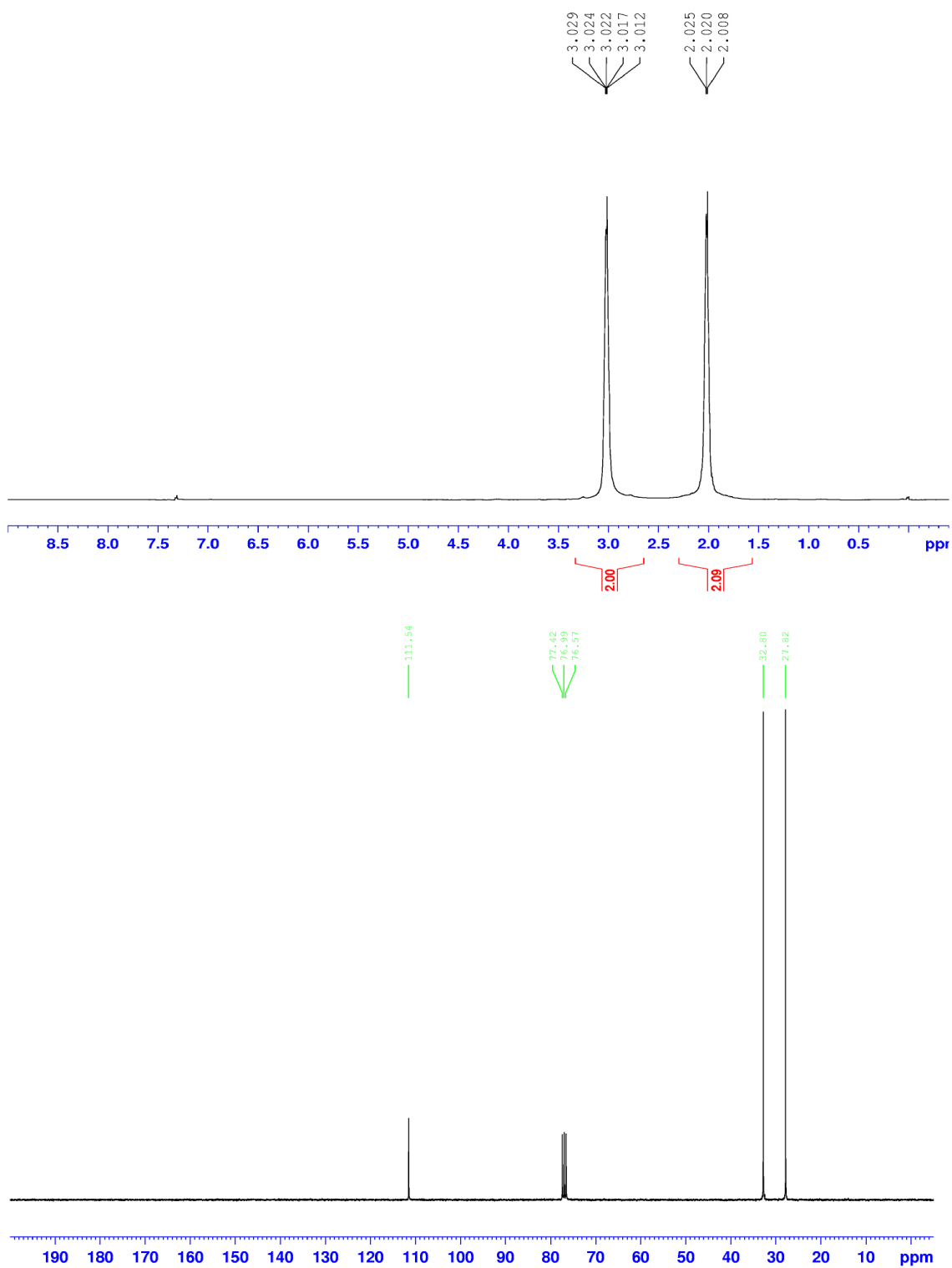
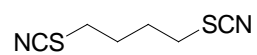


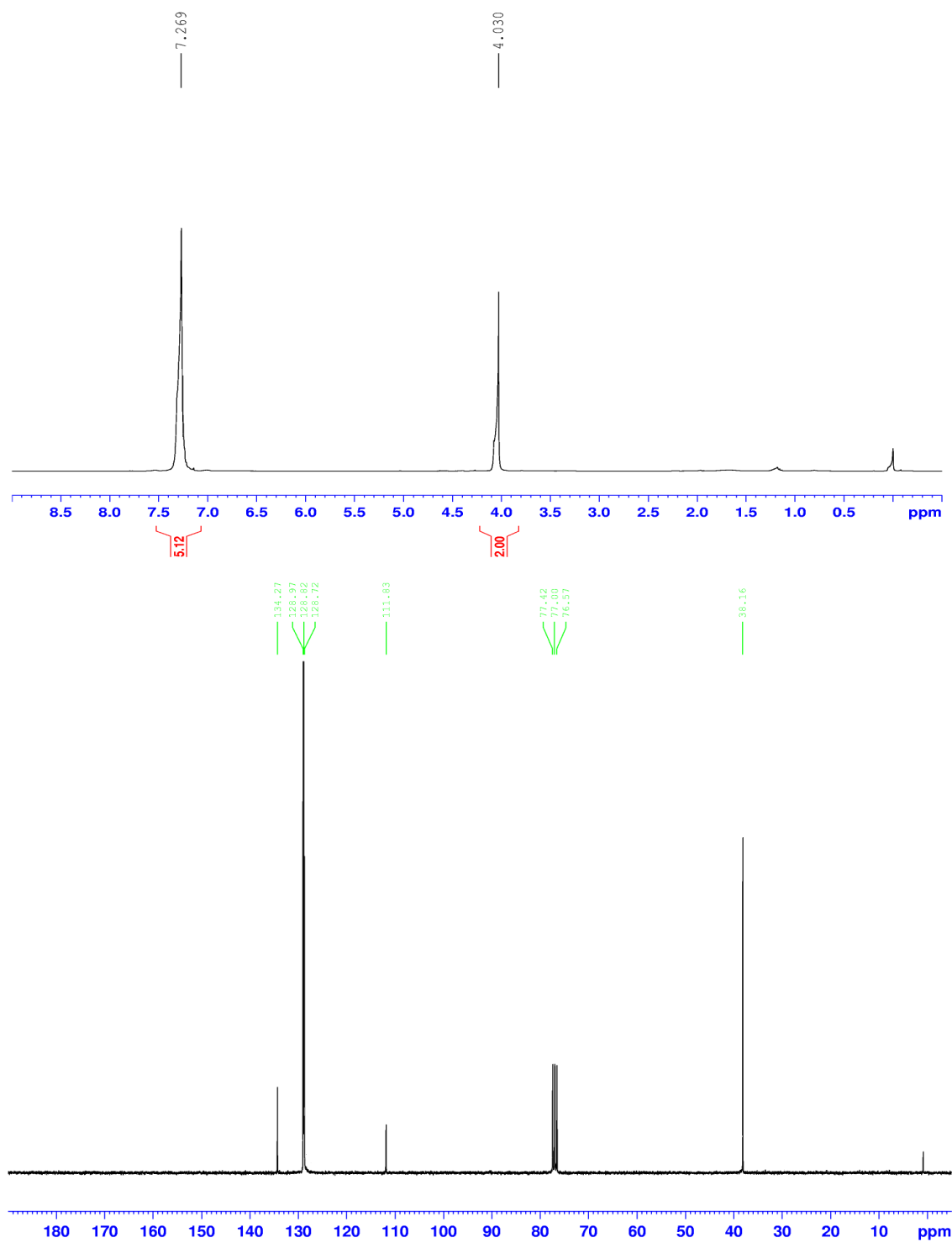
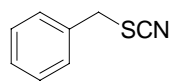


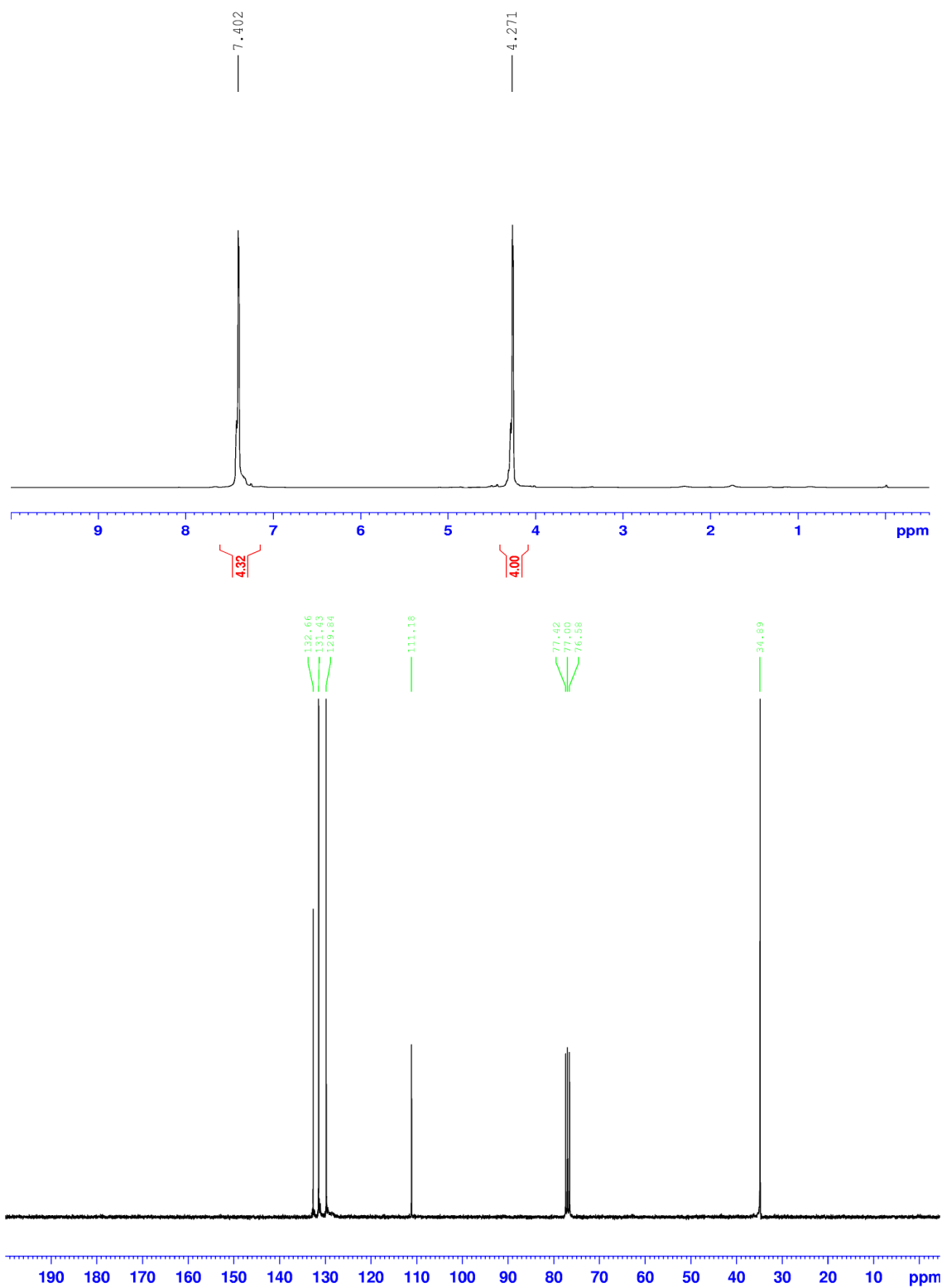
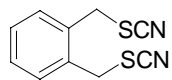


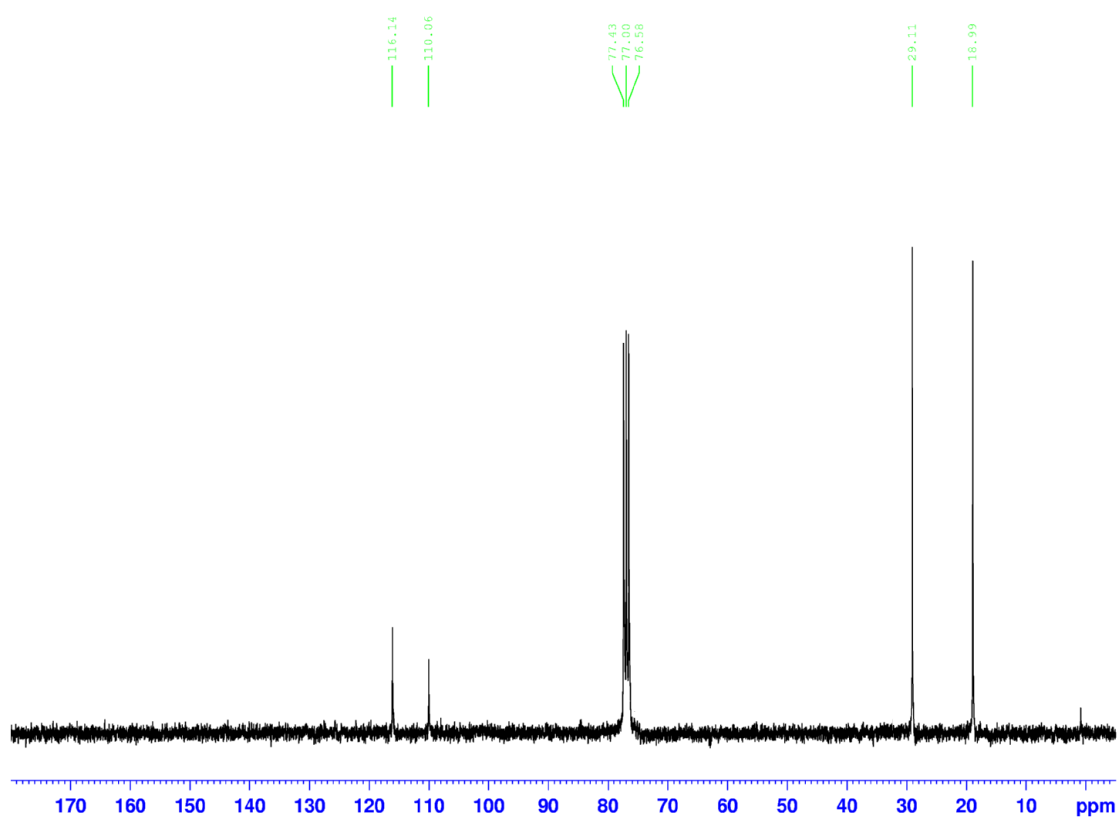
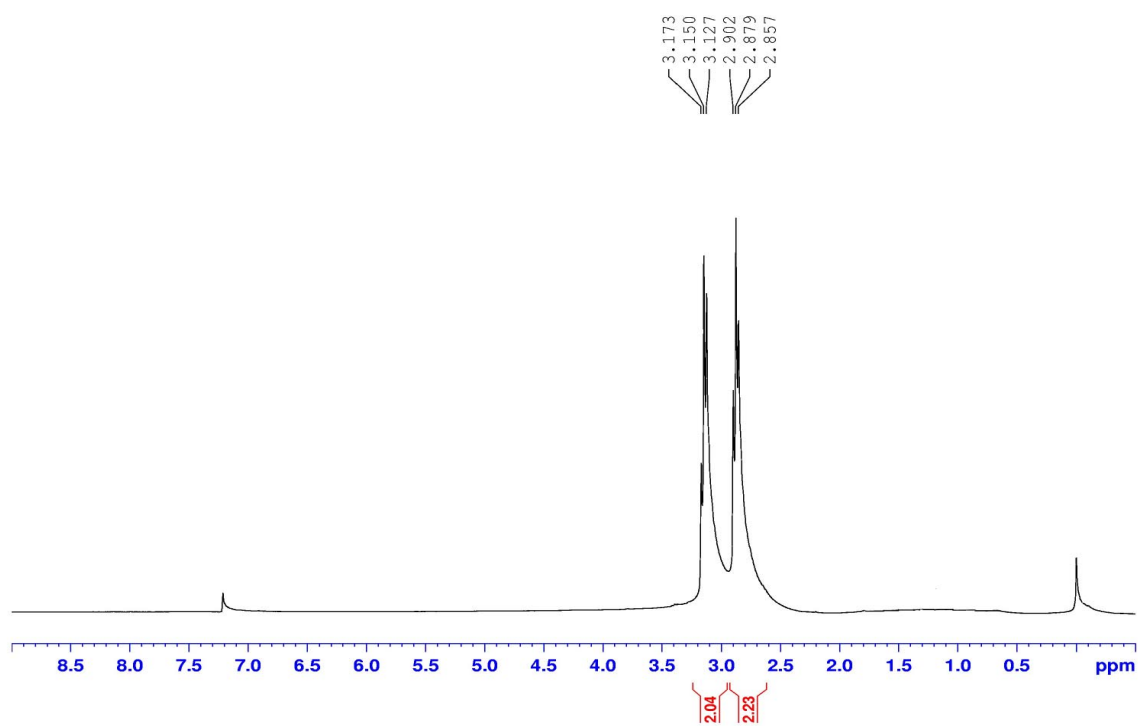
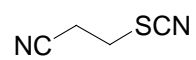


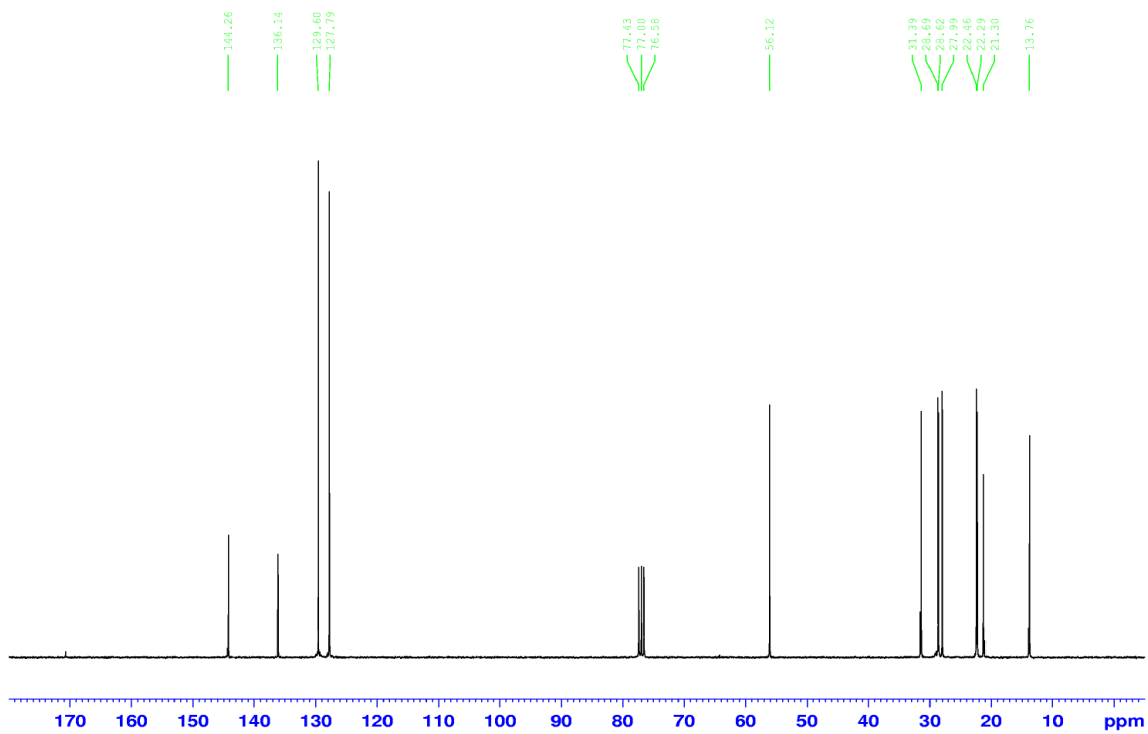
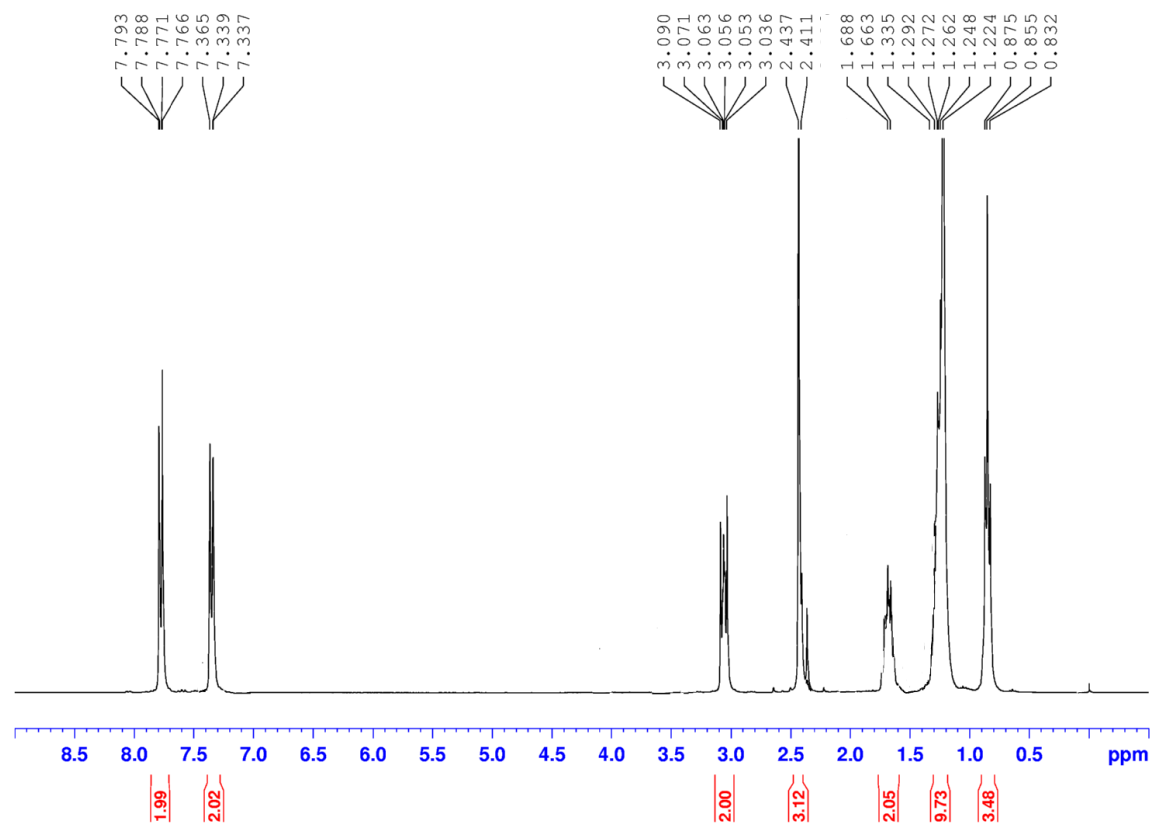
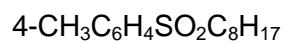


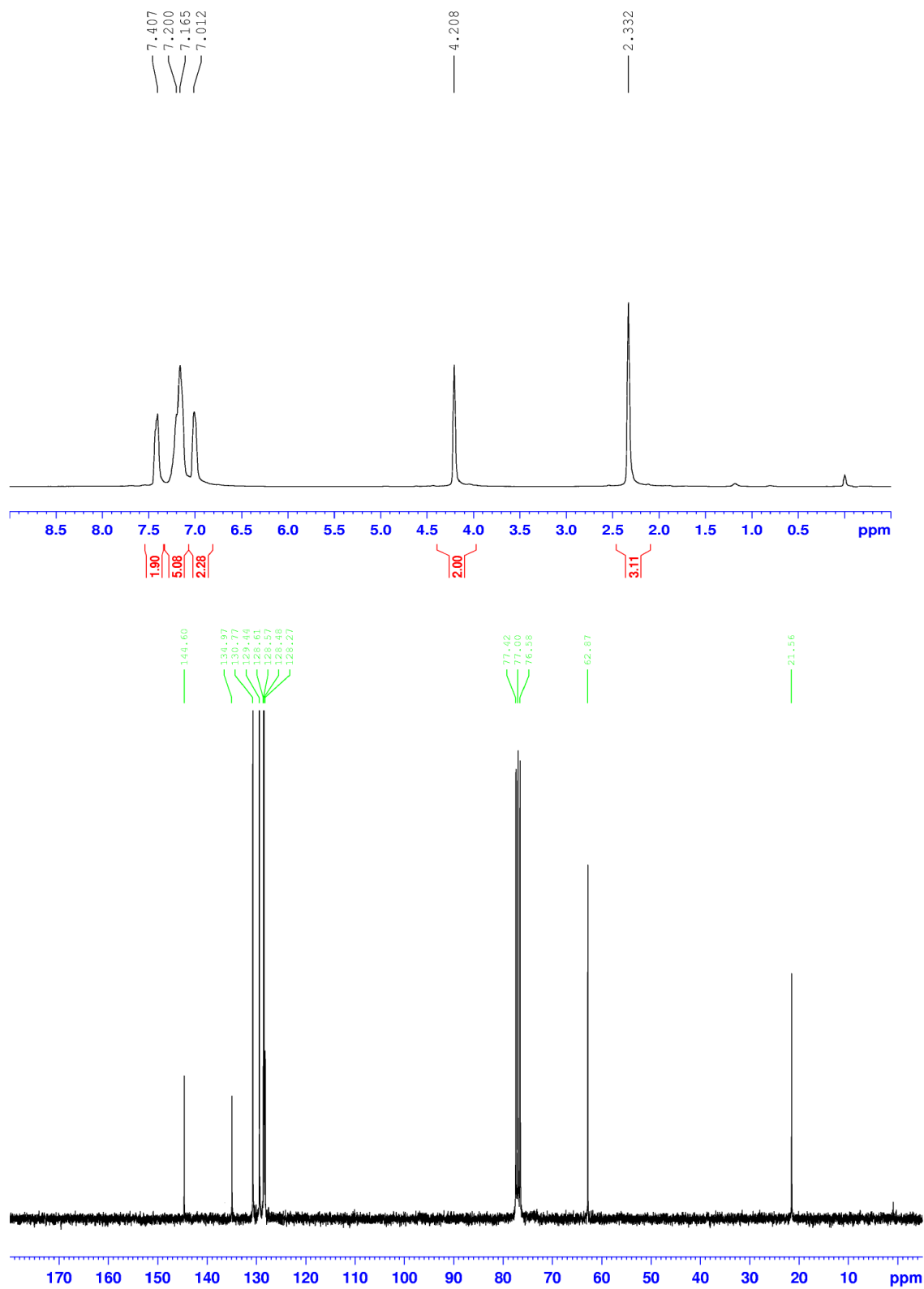
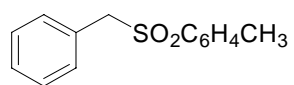


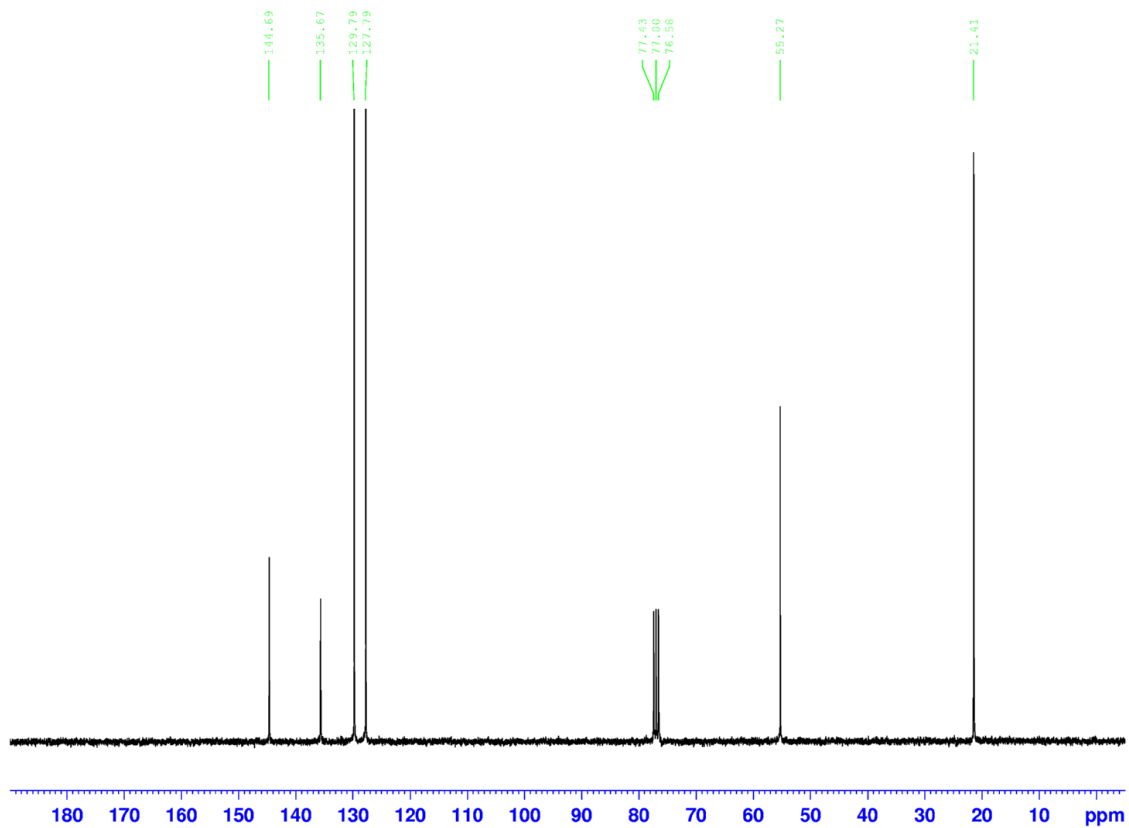
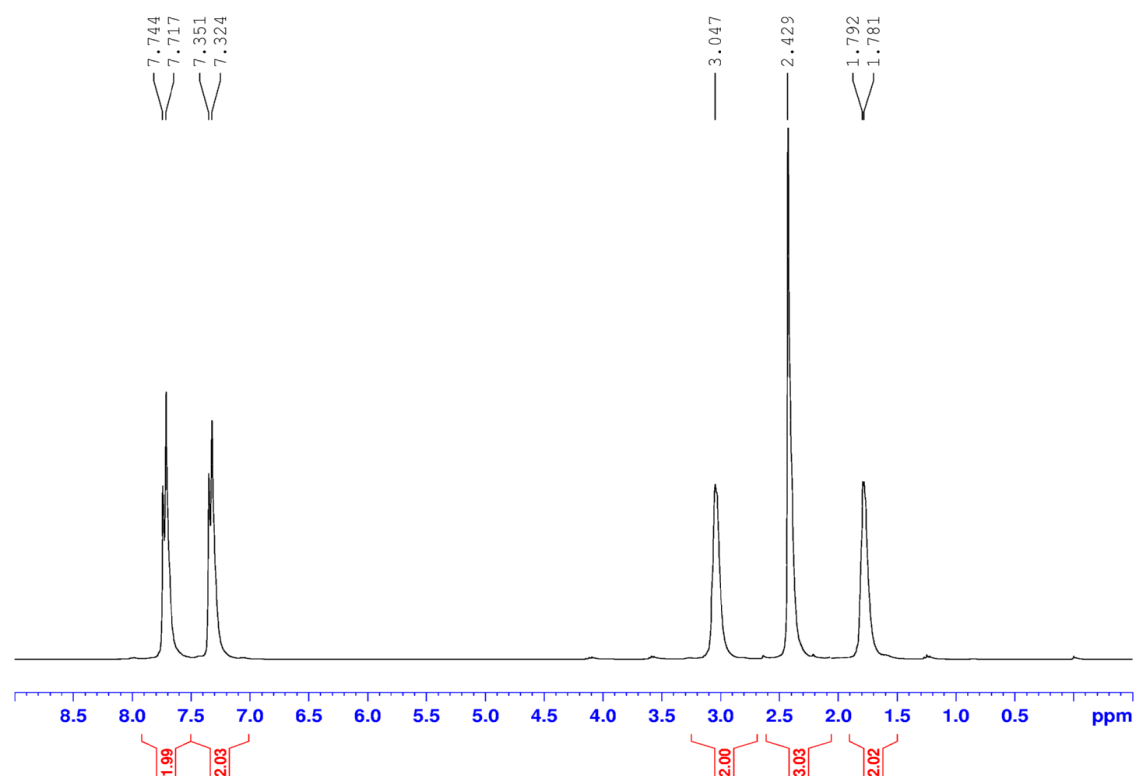
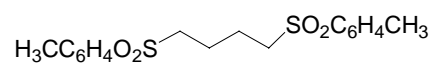


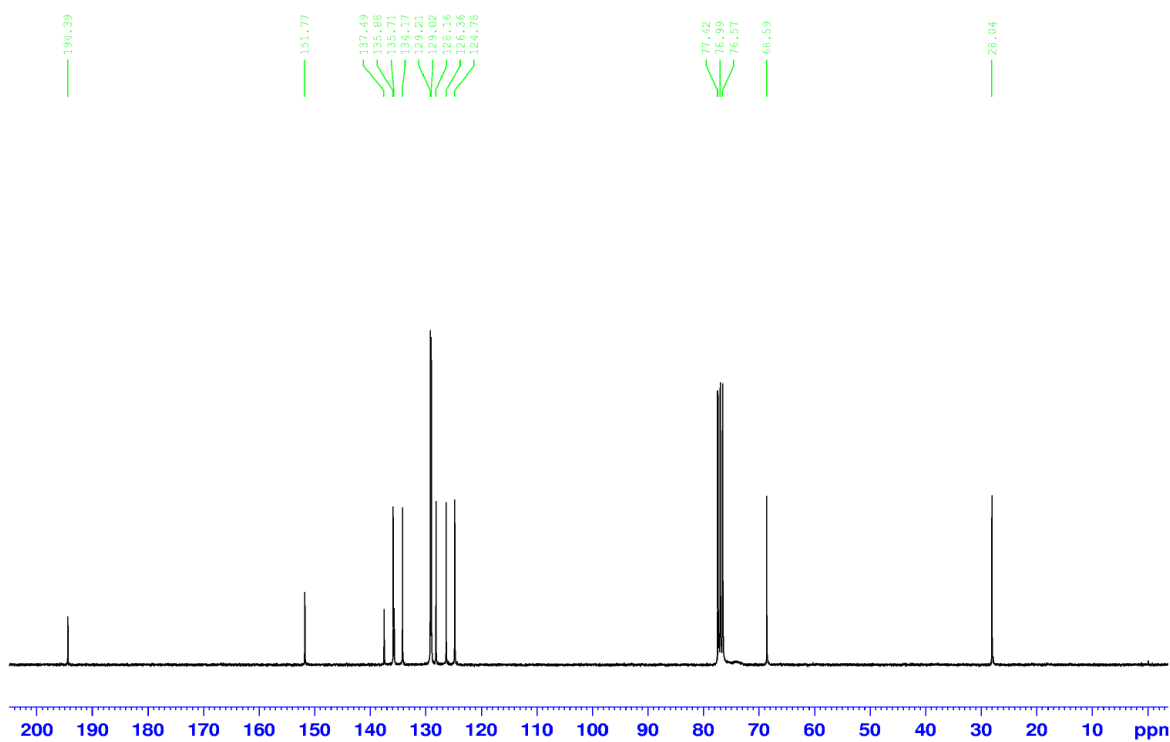
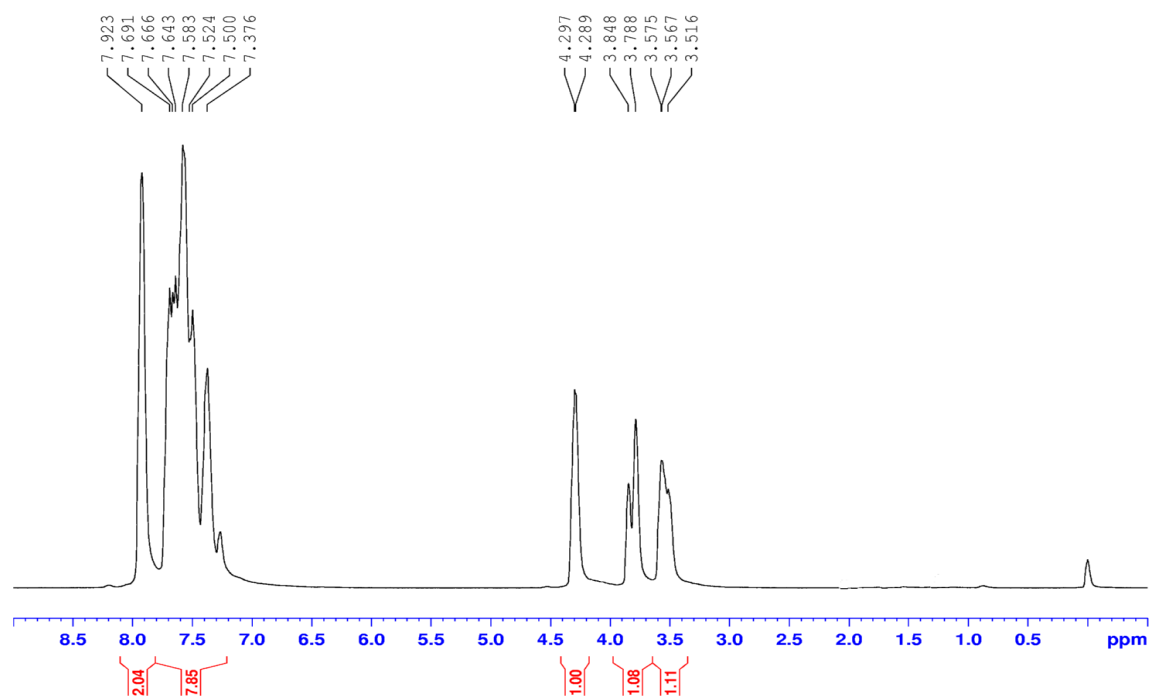
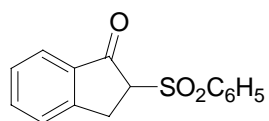


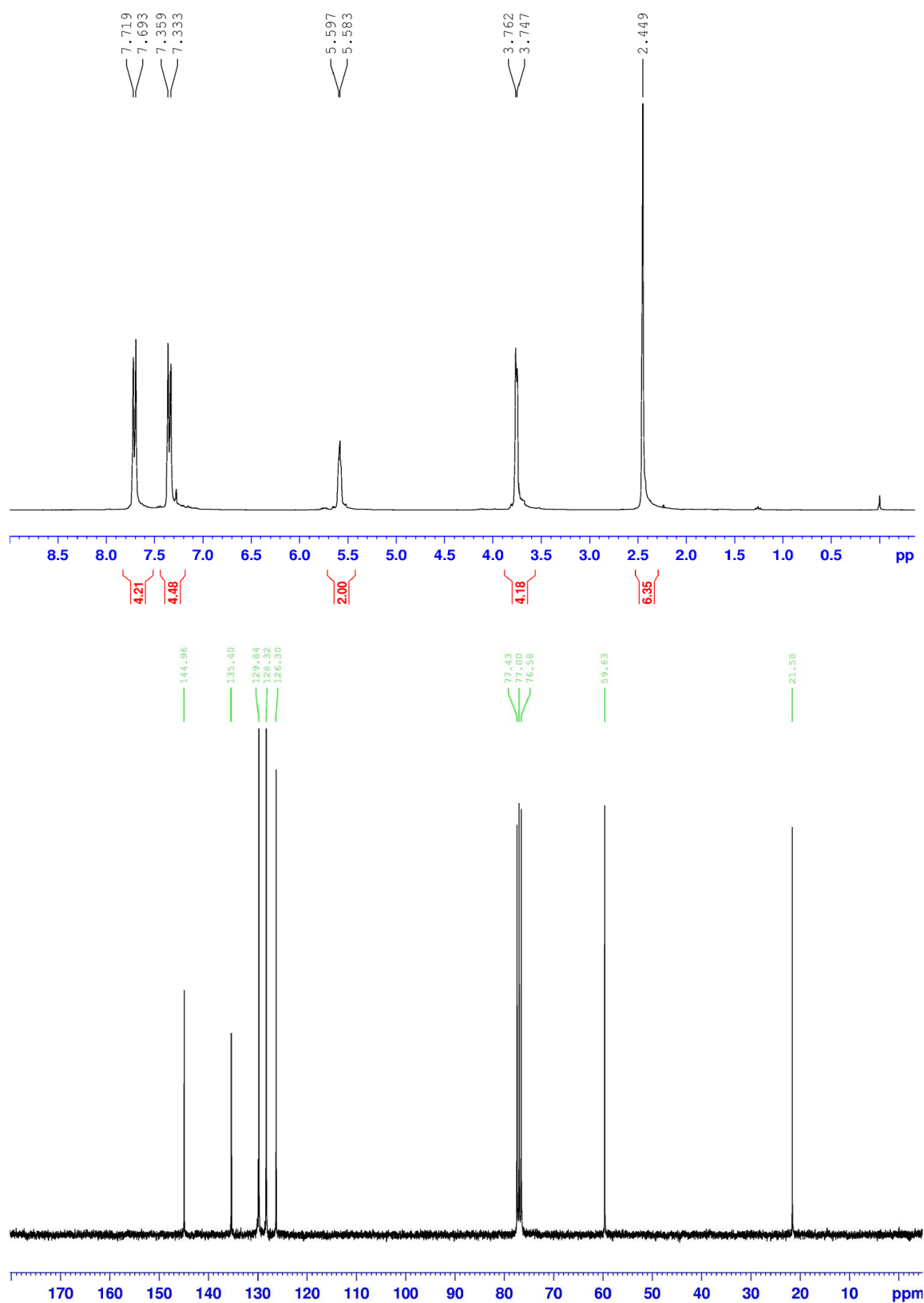
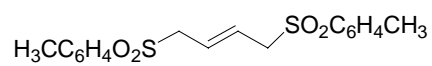


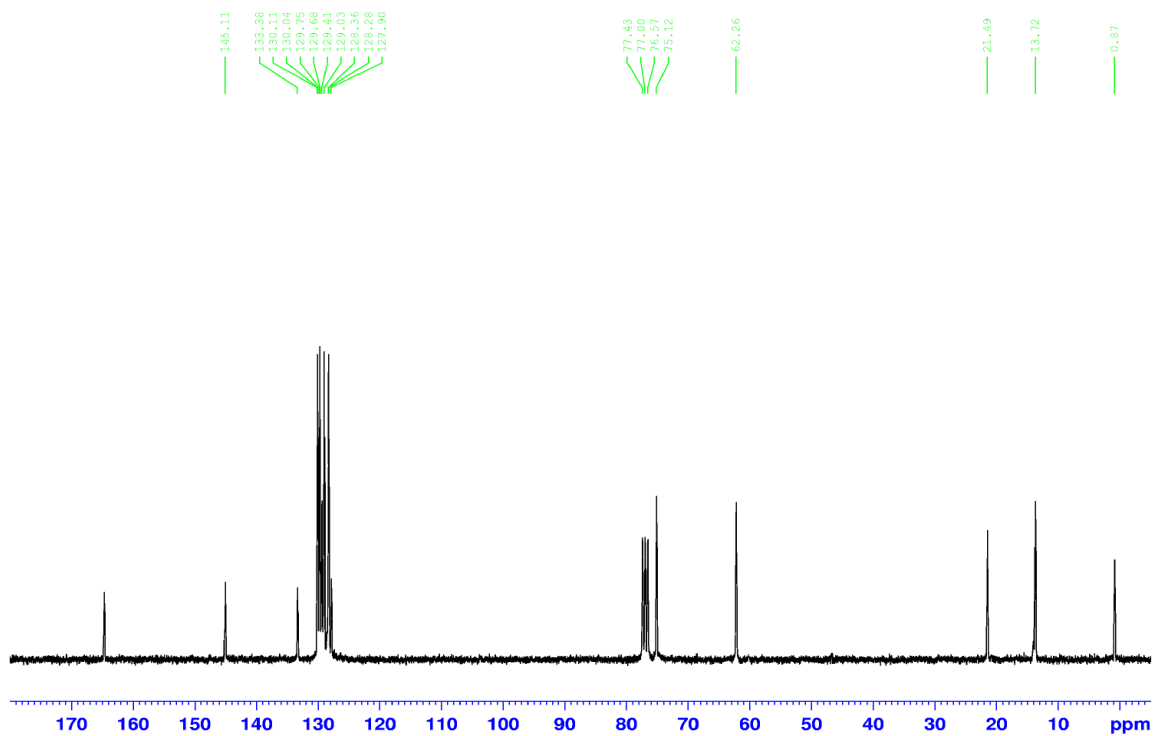
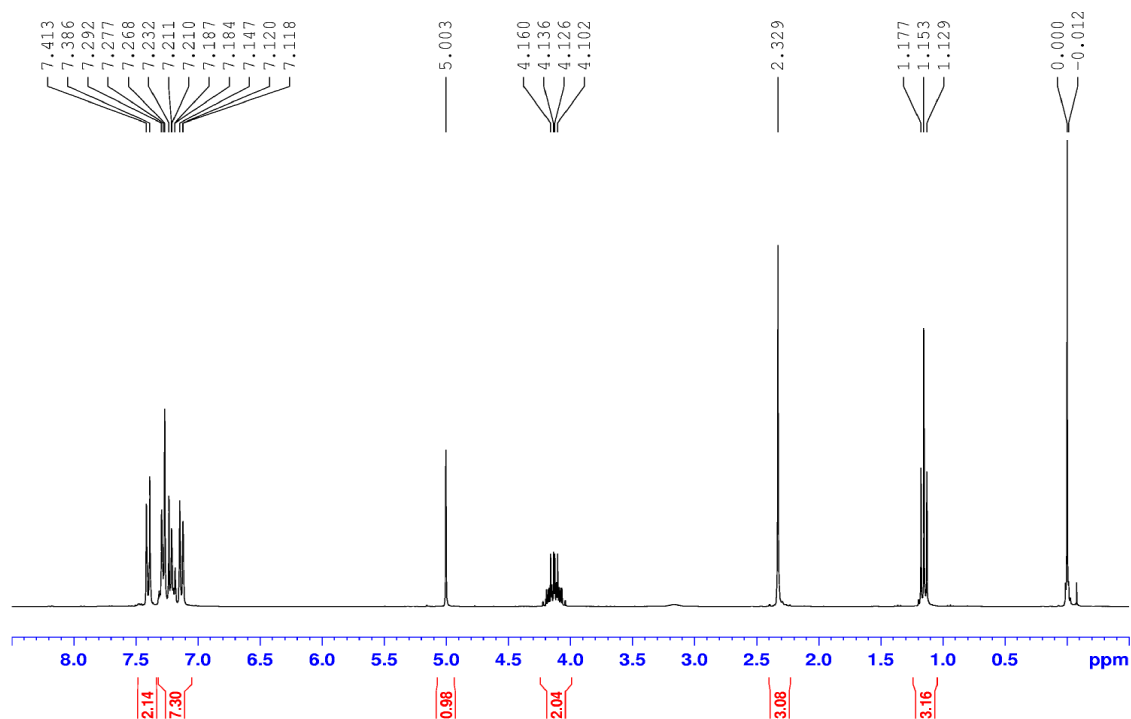
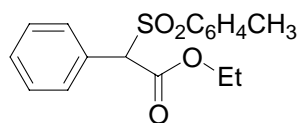


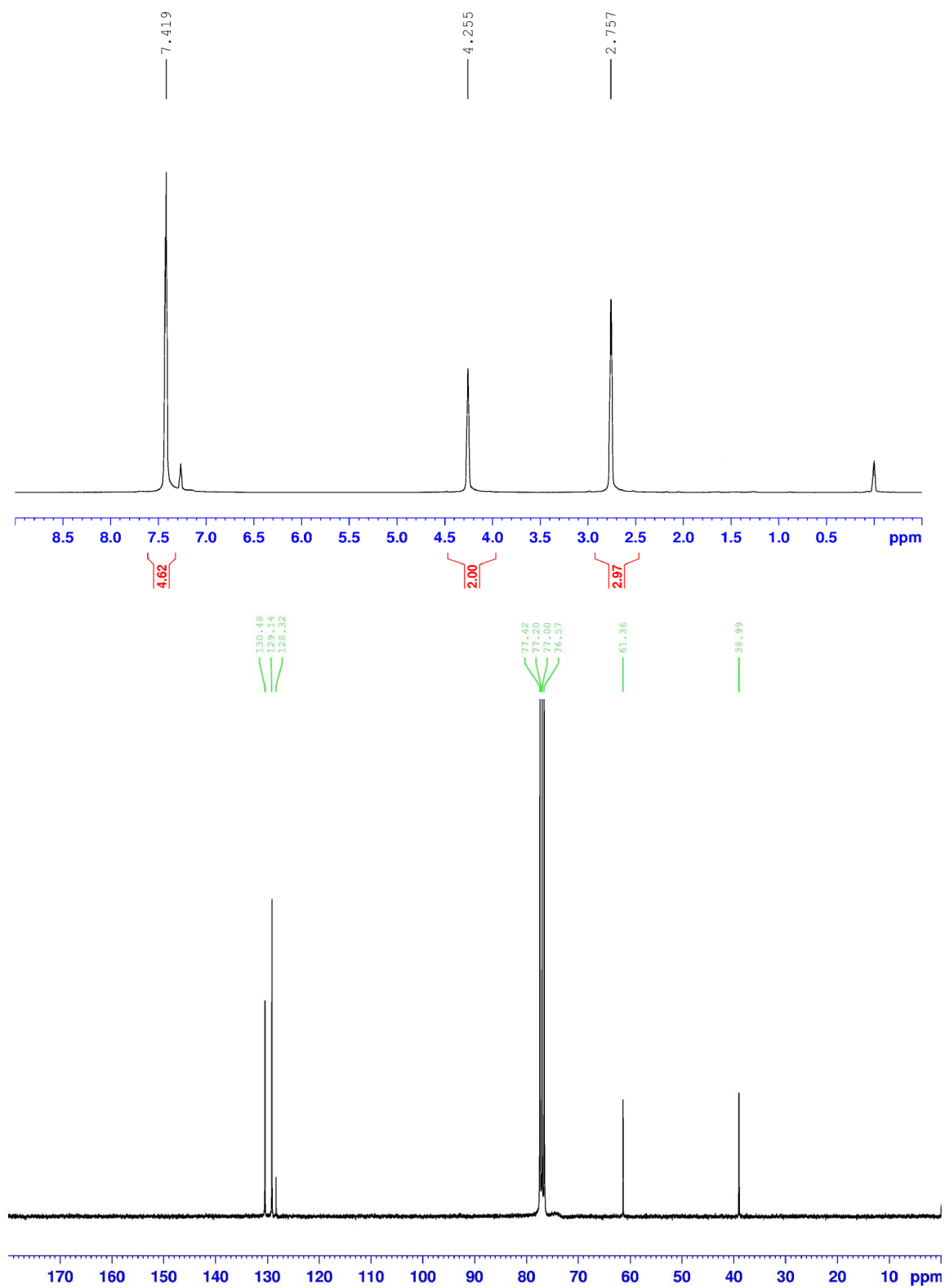
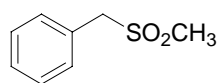


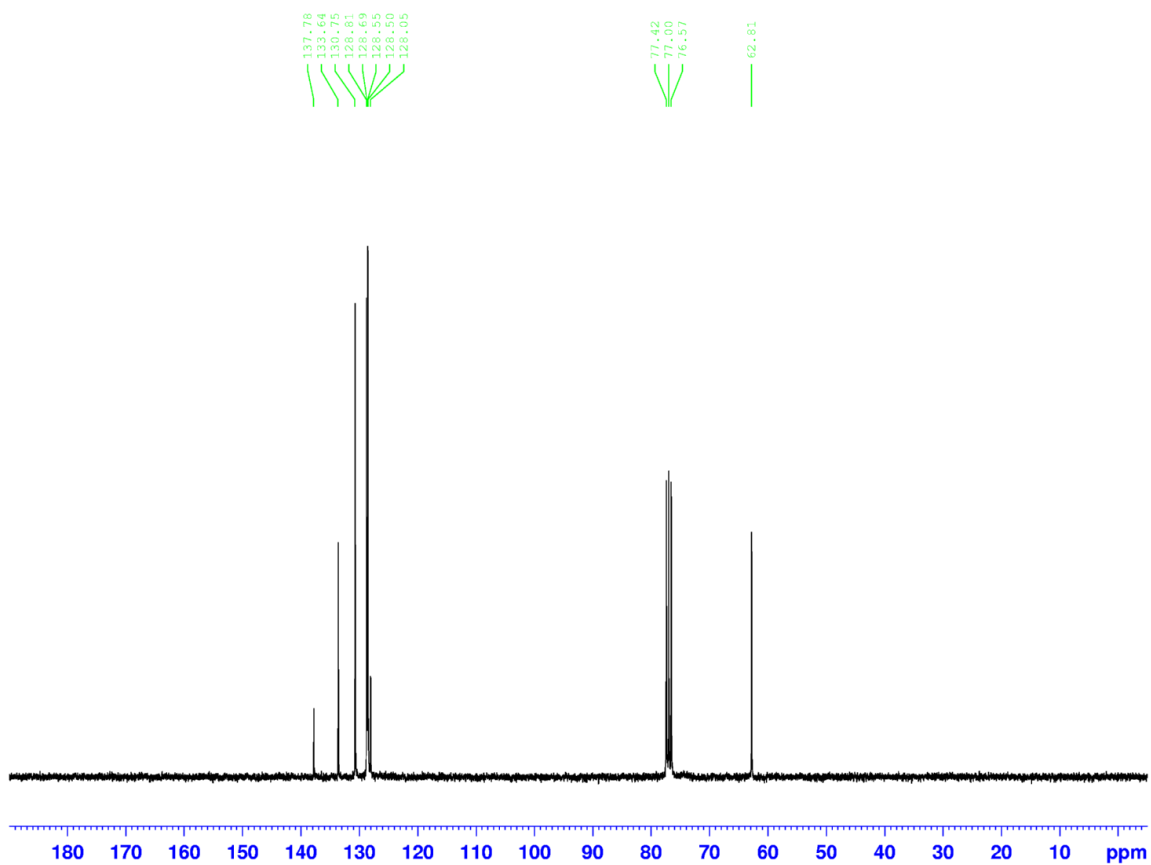
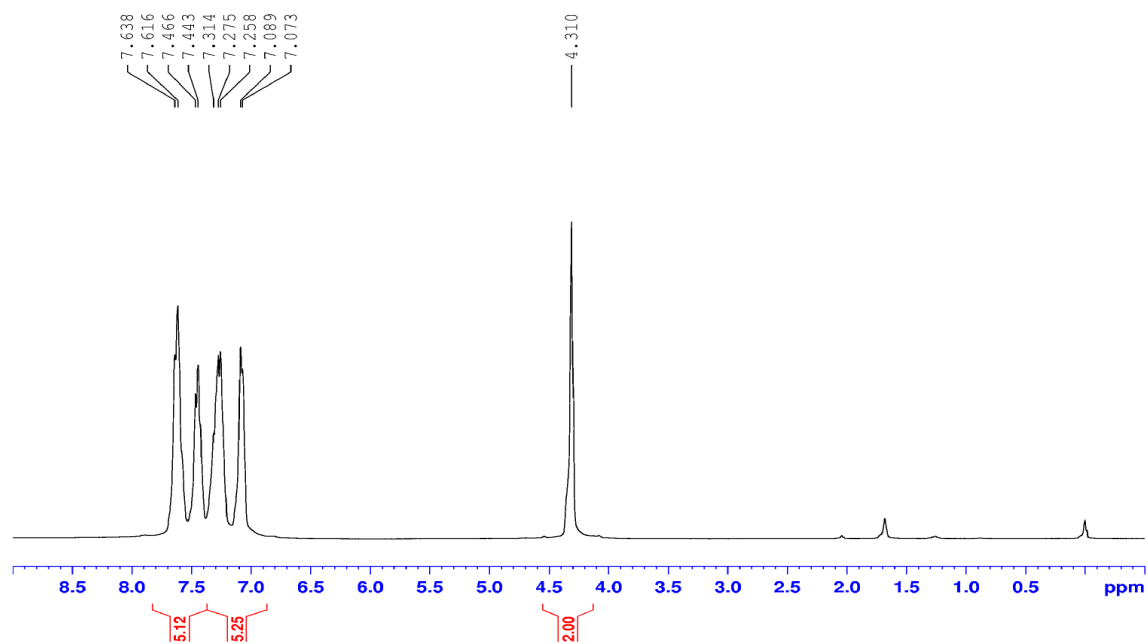
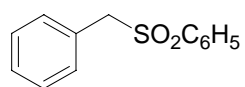












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