Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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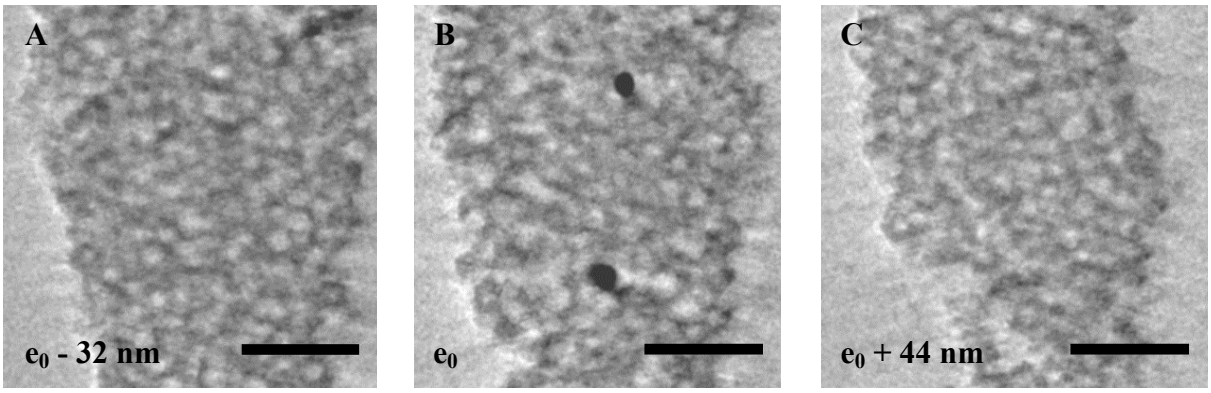
SUPPORTING INFORMATION

Complementary TEM experiments

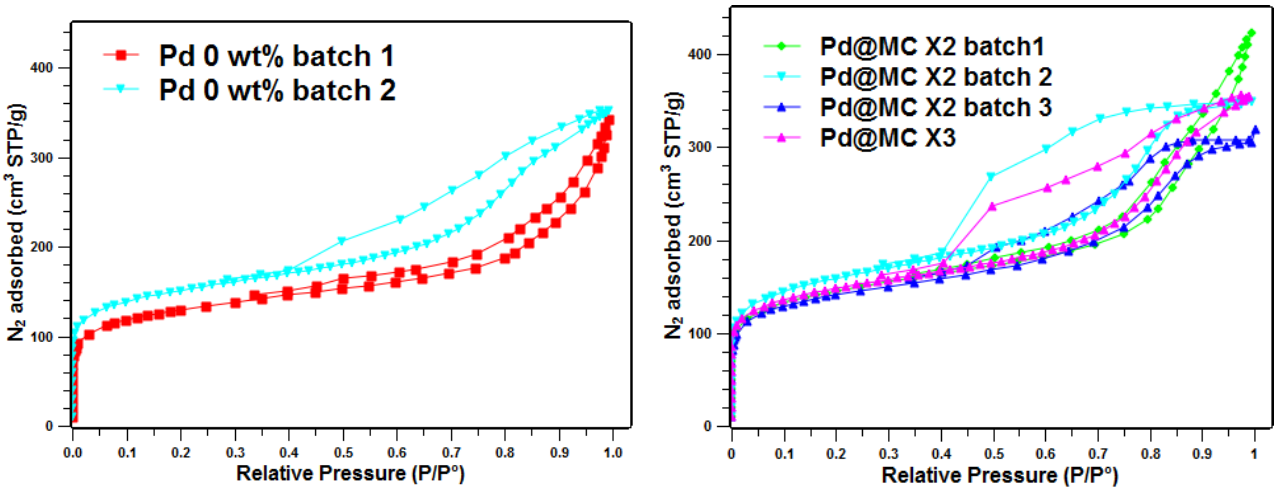
For a better understanding of the local influence of Pd NPs on their surrounding porosity, a detailed analysis of the general aspect of the carbon matrix above and below the Pd particles is shown in Figure SI1. The slices presented in Figures SI1a and SI1c show clearly that before and after several nm thickness from the NPs (Figure SI1b), the general aspect of the C support is the same as in areas containing no Pd particles. It confirms that the particles are surrounded by large voids within the C support with local distortion of the worm-like mesoporous framework around them.



(a) (b) (c)

Figure SI1. Representative slices details extracted from the reconstructed volume of Pd@MC X3 sample to evidence the influence of metallic Pd nanoparticles on the porosity: a) slice at thickness e_0 – 32 nm; b) slice of reference at thickness e_0 and b) slice at thickness e_0 + 44 nm. The scale in the three slices is 100 nm.

N_2 adsorption/desorption isotherms of Pd@MCXi materials



(a) (b)

Figure SI2: N_2 adsorption/desorption isotherms measured at 77K on (a) tanin-derived carbon samples and, (b) Pd@MC Xi samples. The figure evidences the variability of the synthesis and the negligible influence of Pd^{2+} traces on the pore size distribution.

^{1}H and ^{13}C-NMR Spectra of Biaryls 1a-i

1-(4-Biphenylyl)ethanone (1a): Elution with AcOEt / cyclohexane 5:95 as eluant afforded **1a** as a white solid (195 mg, 98% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 2.65 (s, 3H), 7.45 (m, 3H), 7.64 (d, ^{3}J(H,H) = 7.0 Hz, 2H), 7.70 (d, ^{3}J(H,H) = 6.7 Hz, 2H), 8.05 (d, ^{3}J(H,H) = 6.7 Hz, 2H).[1] ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 26.6, 127.2, 128.0, 128.8, 135.8, 139.8, 145.7, 197.7.

4-Methoxybiphenyl (1b): Elution with AcOEt / cyclohexane 5:95 afforded **1b** as a white solid (177 mg, 96% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.88 (s, 3H), 7.01 (d, ^{3}J(H,H) = 8.8 Hz, 2H), 7.33 (t, ^{3}J(H,H) = 7.3 Hz, 1H), 7.44 (m, 2H), 7.58 (m, 4H).**[3]** ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 55.3, 114.2, 126.7, 128.1, 128.7, 133.7, 140.8, 159.1.

4-Methylbiphenyl (1c): Elution with AcOEt / cyclohexane 1:99 afforded **1c** as a white solid (160 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.30 (s, 3H), 7.17 (m, 3H), 7.33 (t, ^{3}J(H,H) = 7.6 Hz, 2H), 7.40 (d, ^{3}J(H,H) = 8.4 Hz, 2H), 7.49 (d, ^{3}J(H,H) = 8.4 Hz, 2H).**[3]** ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 21.1, 127.0, 129.3, 129.5, 137.0, 138.4, 141.2.

3-Methylbiphenyl (1d): Elution with AcOEt / cyclohexane 1:99 afforded **1d** as a colorless oil (165 mg, 98% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.45 (s, 3H), 7.20 (m, 1H), 7.40 (m, 6H), 7.63 (d, ^{3}J(H,H) = 7.3 Hz, 2H).**[3]** ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 21.5, 124.2, 127.2, 127.6, 128.7, 138.3, 141.2, 178.3.

2-Methylbiphenyl (1e): Elution with AcOEt / cyclohexane 1:99 afforded **1e** as a yellowish oil (166 mg, 99% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.19 (s, 3H), 7.16 (m, 4H), 7.26 (m, 3H), 7.32 (m, 2H).**[3]** ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 20.5, 125.7, 126.7, 126.8, 128.0, 129.1, 129.2, 130.1, 130.3, 135.3, 141.9.

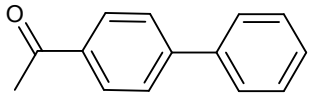
2-Isopropylbiphenyl (2d): Elution with Et_2O / Cyclohexane 1 : 99 afforded 137 mg (70% yield) of a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.07 (d, ^{3}J(H,H) = 6.9 Hz, 6H), 2.97 (hept, ^{3}J(H,H) = 6.9 Hz, 1H), 7.15 (m, 9H).[29] ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 24.3, 29.3, 125.3, 125.5, 126.7, 127.6, 127.9, 129.3, 141.0, 142.1, 146.3.

1-(4-(4'-Methyl)biphenylyl)ethanone (1g): Elution with AcOEt / cyclohexane 5:95 afforded **1g** as a white solid (203 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.30 (s, 3H), 2.52 (s, 3H), 7.17 (d,

^3J(H,H) = 8.1 Hz, 2H), 7.42 (d, ^3J(H,H) = 8.1 Hz, 2H), 7.56 (d, ^3J(H,H) = 8.3 Hz, 2H), 7.90 (d, ^3J(H,H) = 8.3 Hz, 2H).[2] ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 21.0, 26.5, 126.8, 126.9, 128.8, 129.6, 136.8, 137.6, 145.6, 197.6.

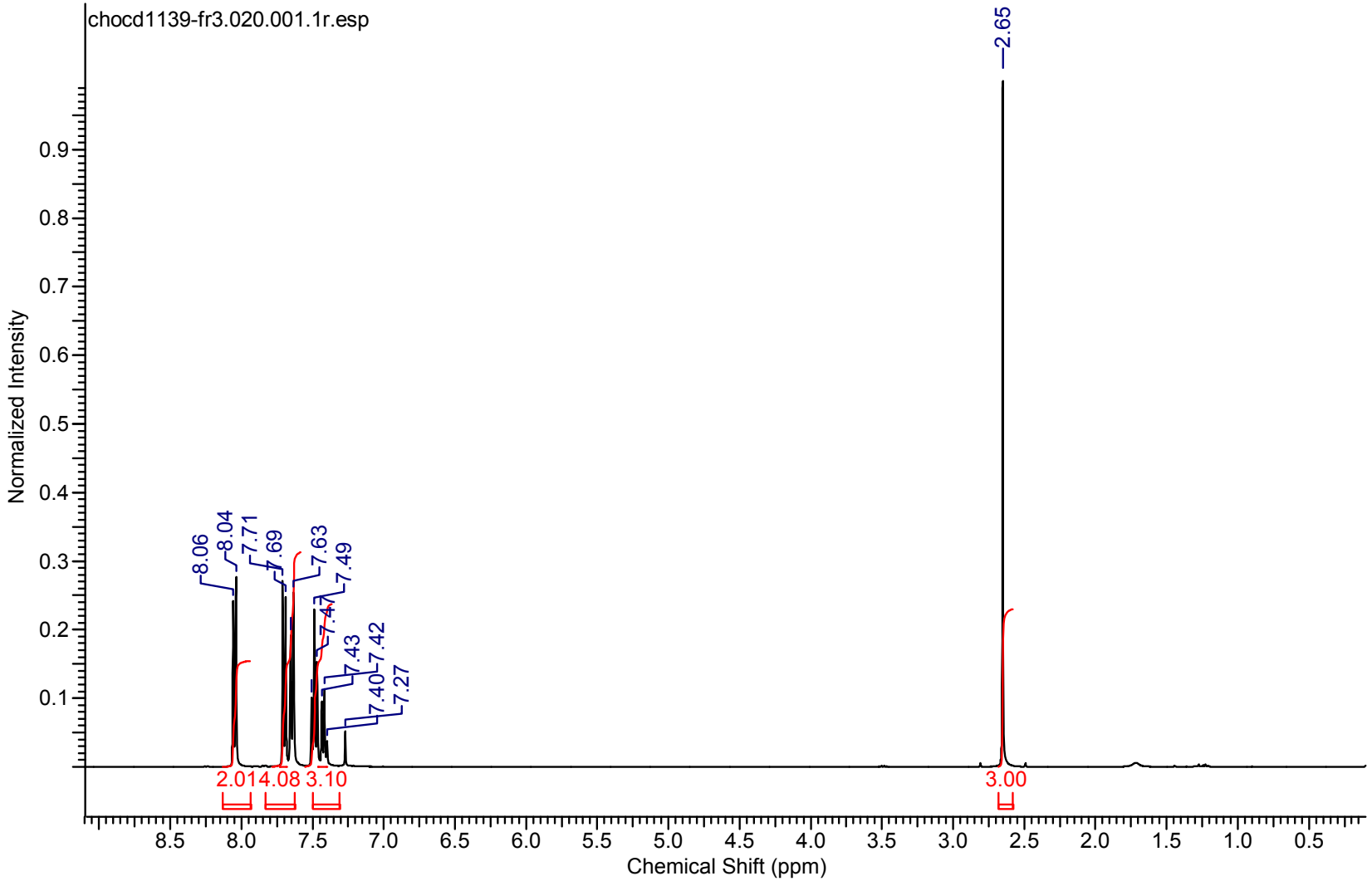
1-(4-(2'-Methyl)biphenylyl)ethanone (1h): Elution with AcOEt / cyclohexane 5:95 afforded **1h** as a colorless oil (196 mg, 93% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.29 (s, 3H), 2.65 (s, 3H), 7.26 (m, 4H), 7.44 (d, ^3J(H,H) = 8.5 Hz, 2H), 8.03 (d, ^3J(H,H) = 8.5 Hz, 2H).[5] ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 20.2, 26.5, 125.8, 127.8, 128.1, 129.2, 129.3, 130.4, 134.9, 140.6, 146.8, 197.6.

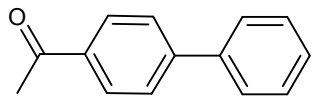
1-(4-(4'-Methoxy)biphenylyl)ethanone (1i): Elution with AcOEt / cyclohexane 5:95 afforded **1i** as a white solid (210 mg, 93% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.62 (s, 3H), 3.86 (s, 3H), 7.00 (d, ^3J(H,H) = 8.8 Hz, 2H), 7.58 (d, ^3J(H,H) = 8.8 Hz, 2H), 7.64 (d, ^3J(H,H) = 8.3 Hz, 2H), 8.00 (d, ^3J(H,H) = 8.3 Hz, 2H).[5] ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 26.5, 55.3, 114.3, 126.5, 128.3, 128.9, 132.1, 135.2, 145.2, 159.8, 197.6.



Compound **1a**

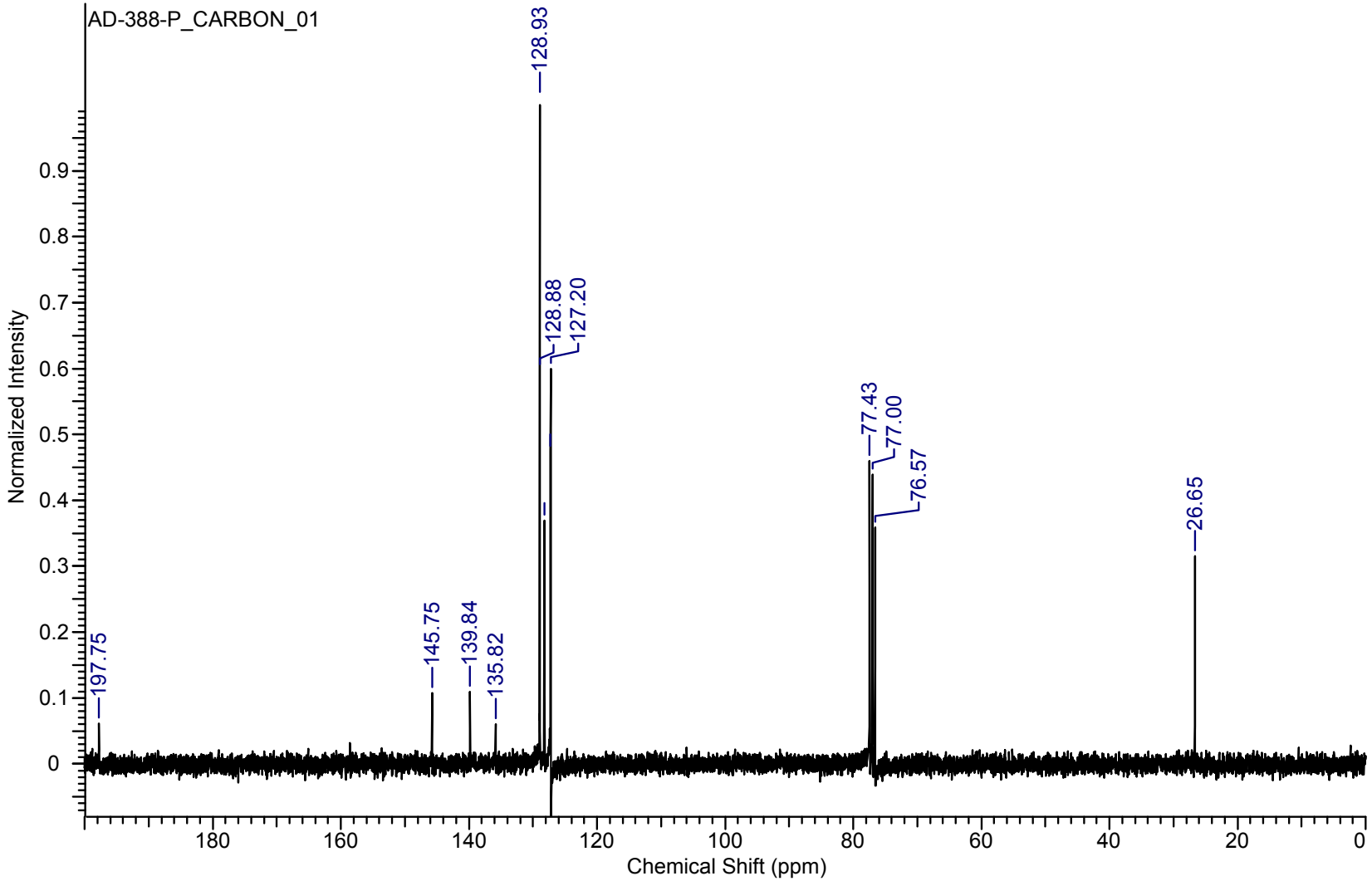
^{1}H-NMR, 400 MHz, $CDCl_3$

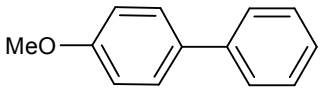




Compound **1a**

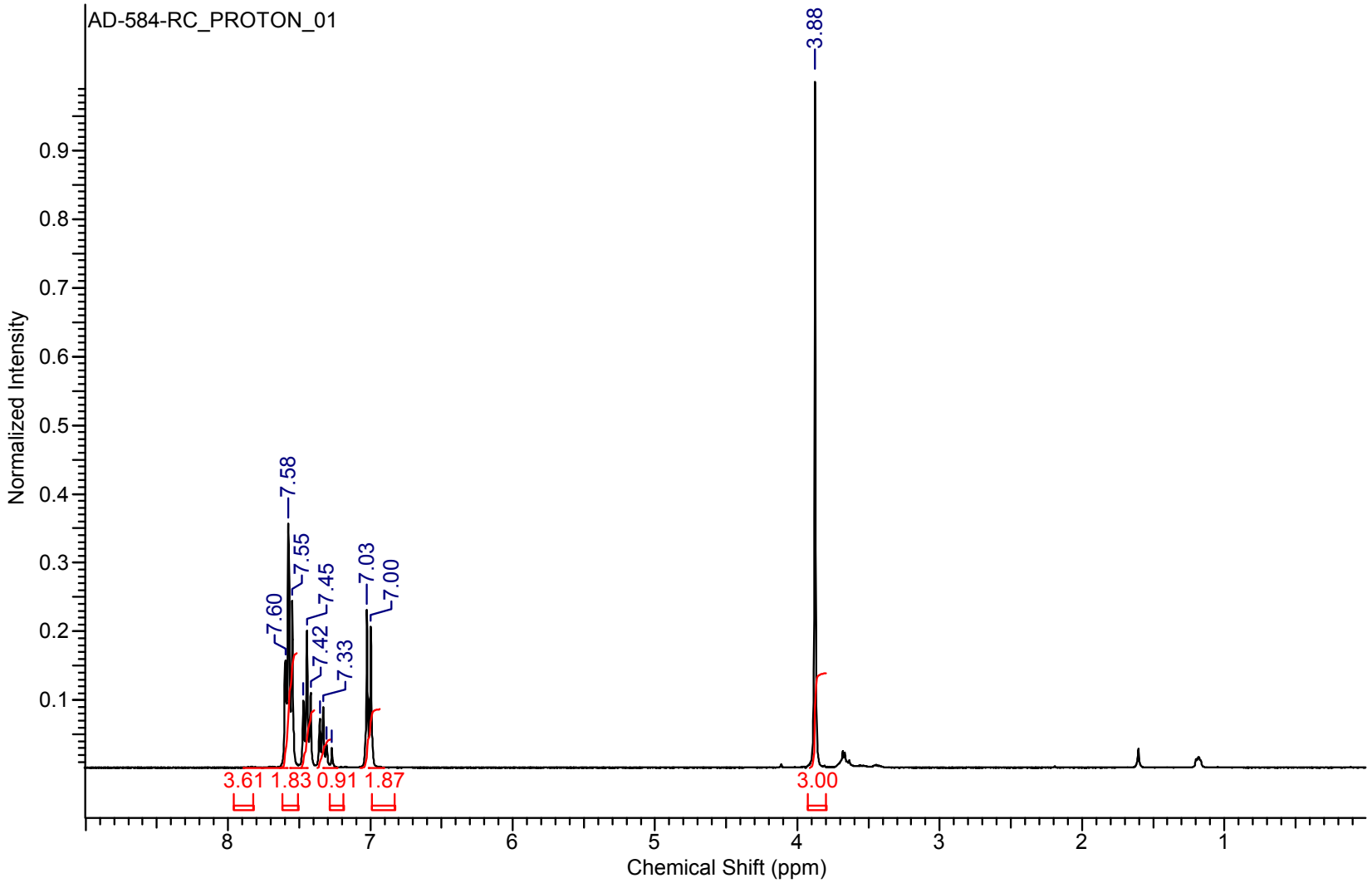
^{13}C-NMR, 75 MHz, $CDCl_3$

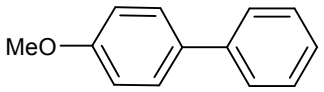




Compound **1b**

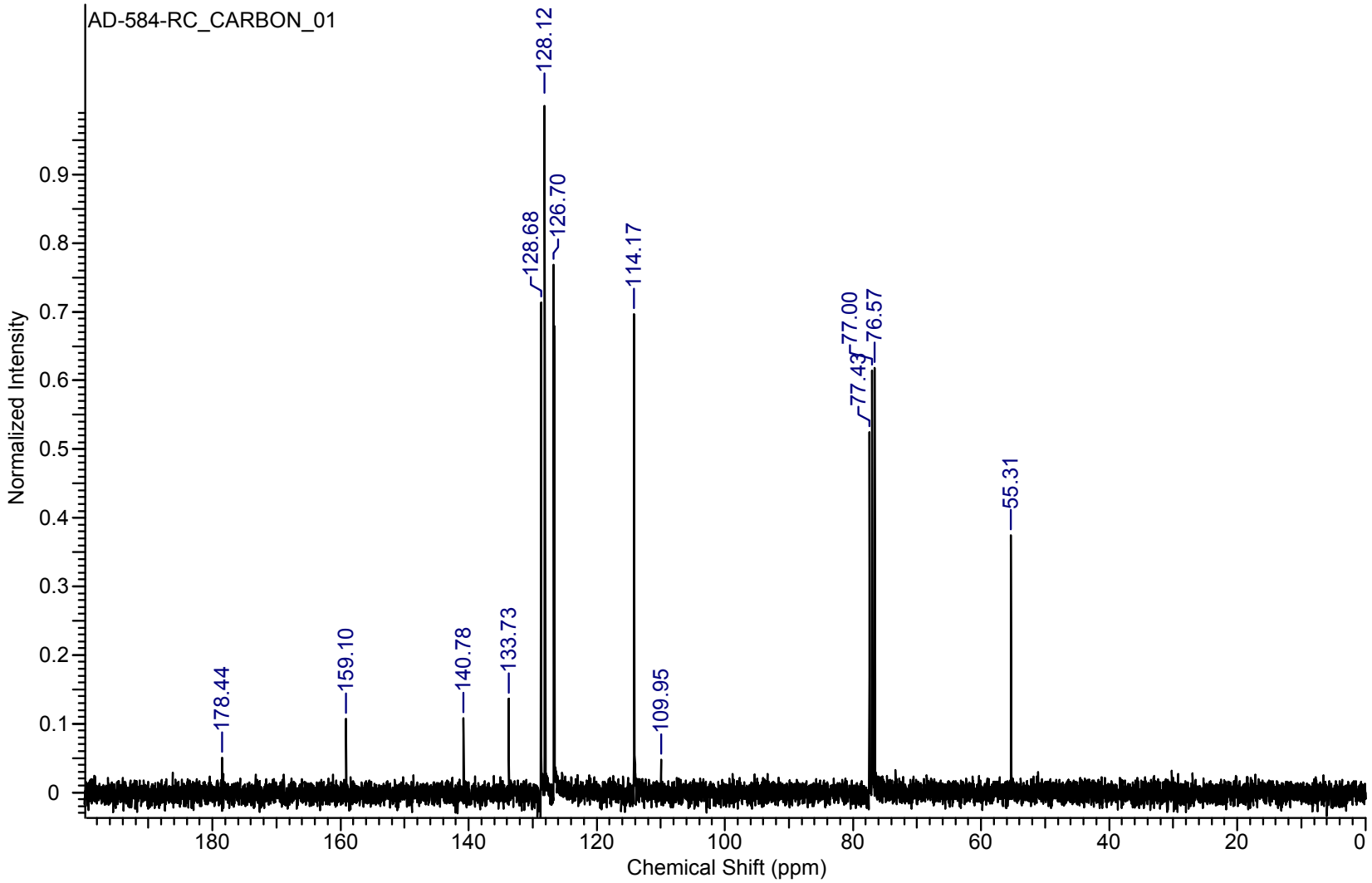
^{1}H-NMR, 300 MHz, $CDCl_3$

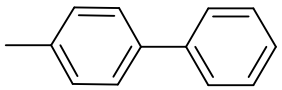




Compound **1b**

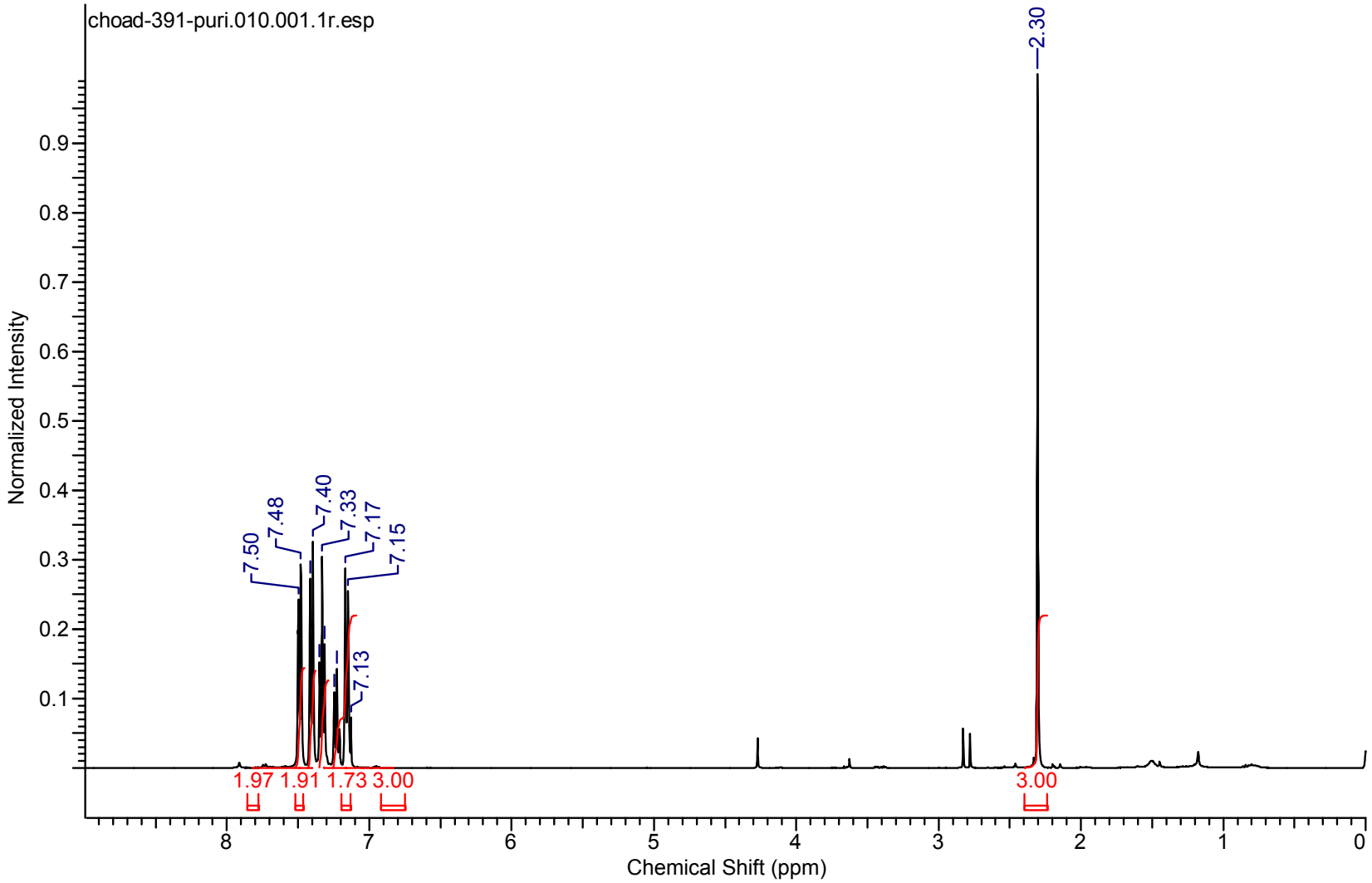
^{13}C-NMR, 75 MHz, $CDCl_3$

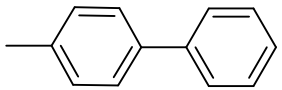




Compound **1c**

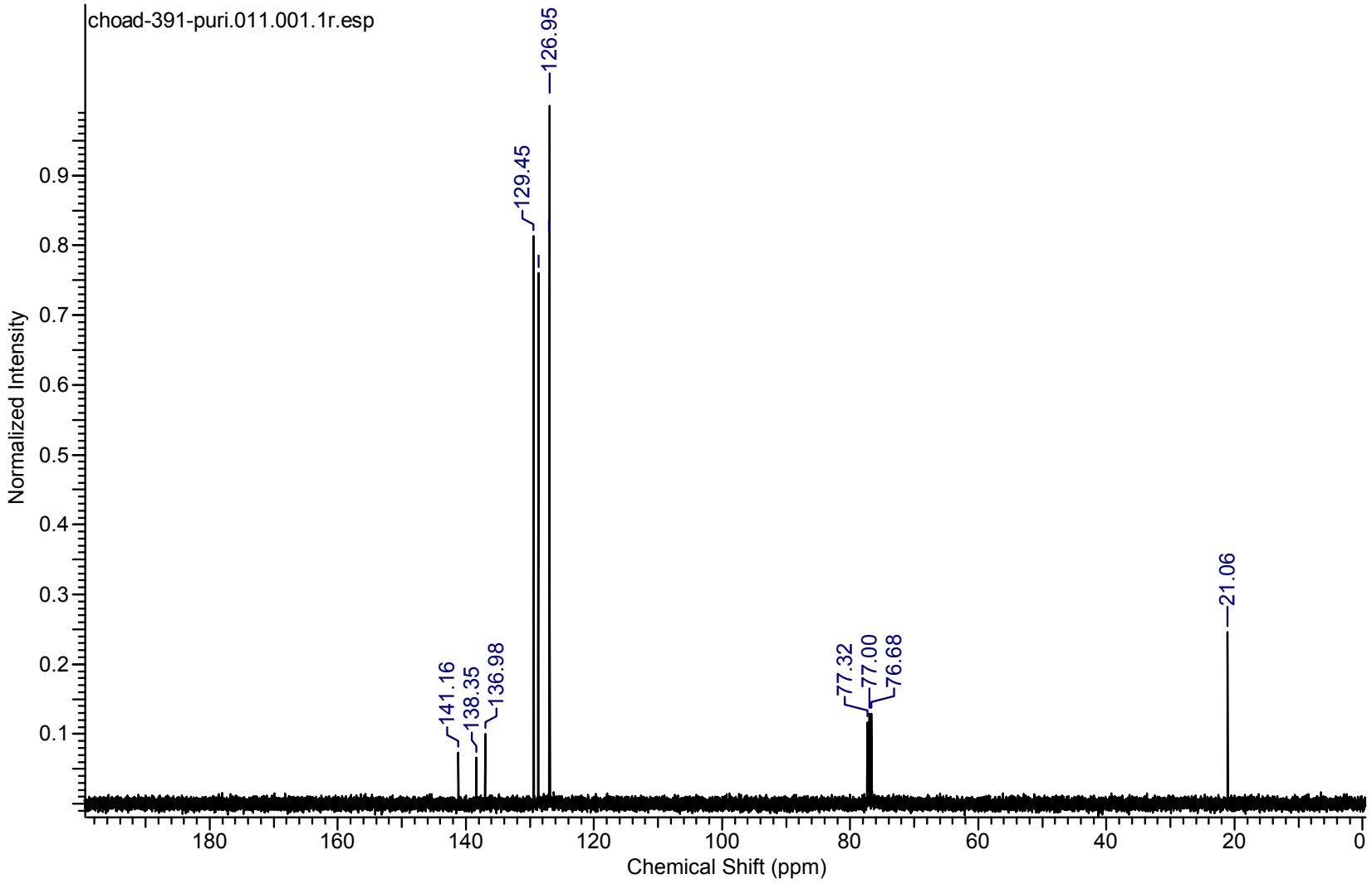
^{1}H-NMR, 400 MHz, $CDCl_3$

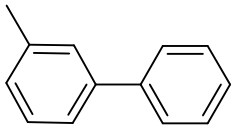




Compound **1c**

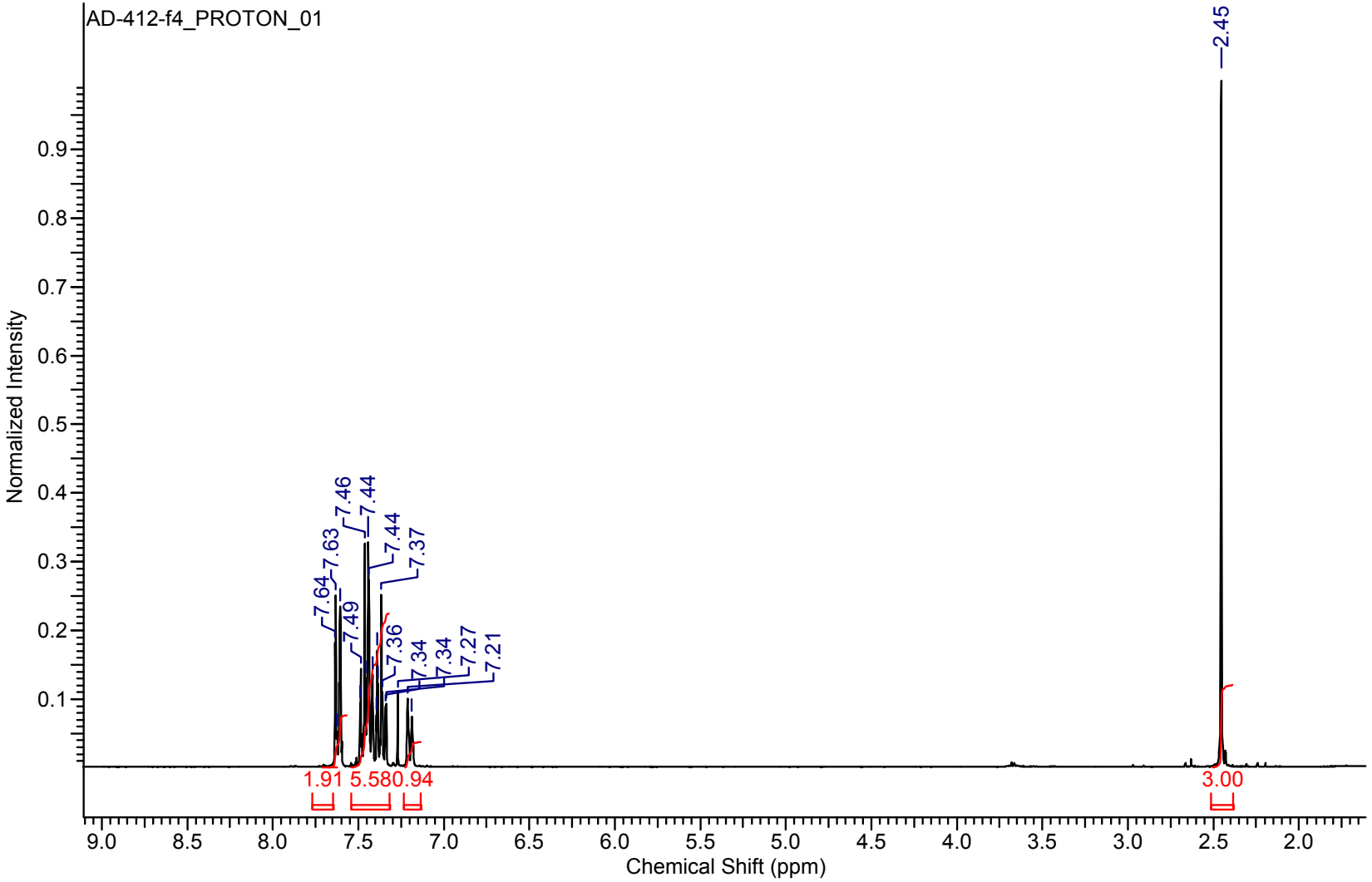
^{13}C-NMR, 100 MHz, $CDCl_3$

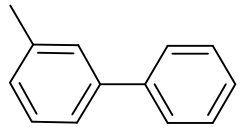




Compound **1d**

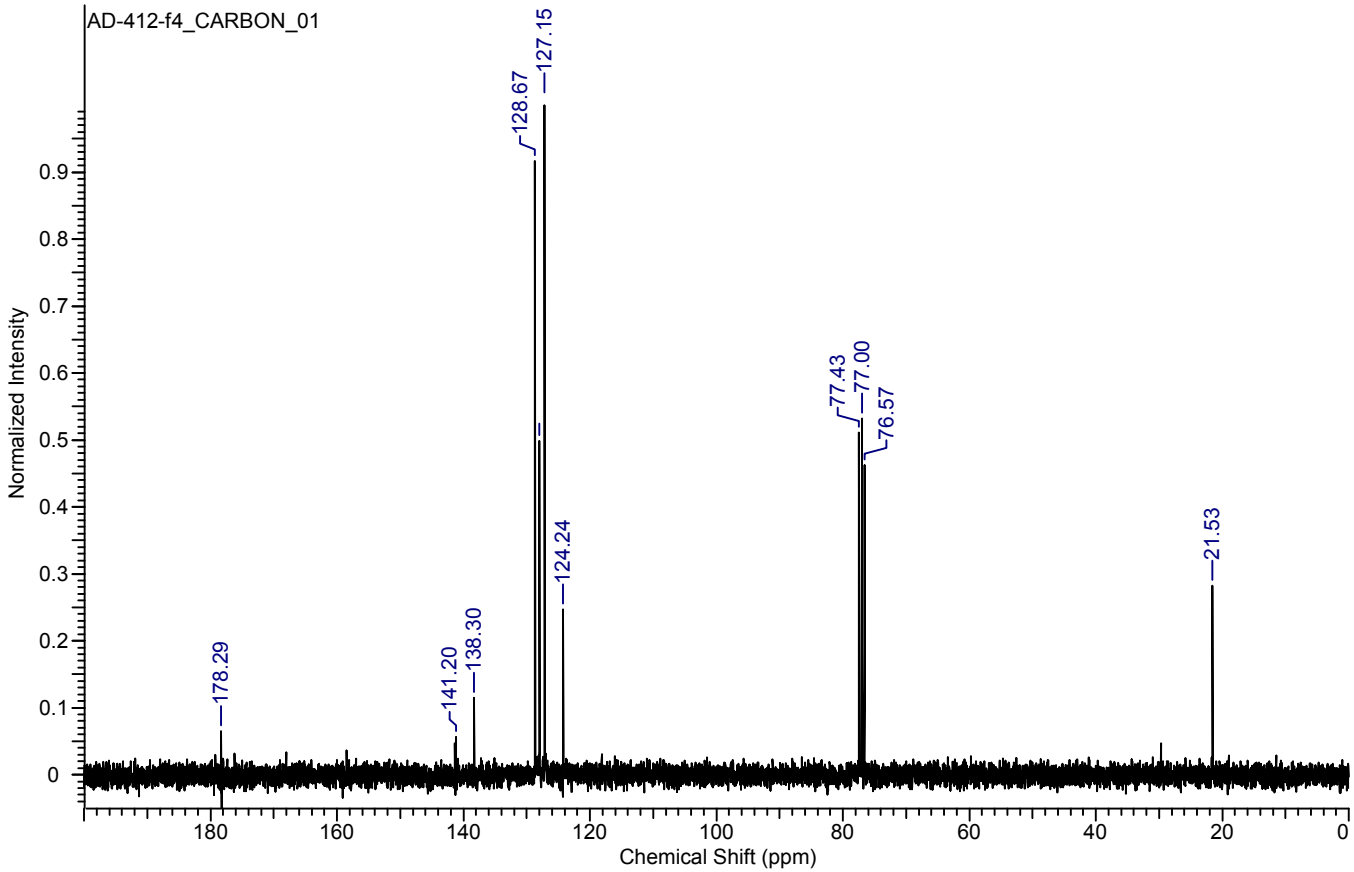
^{1}H-NMR, 300 MHz, $CDCl_3$

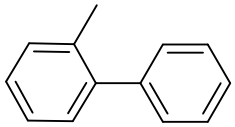




Compound **1d**

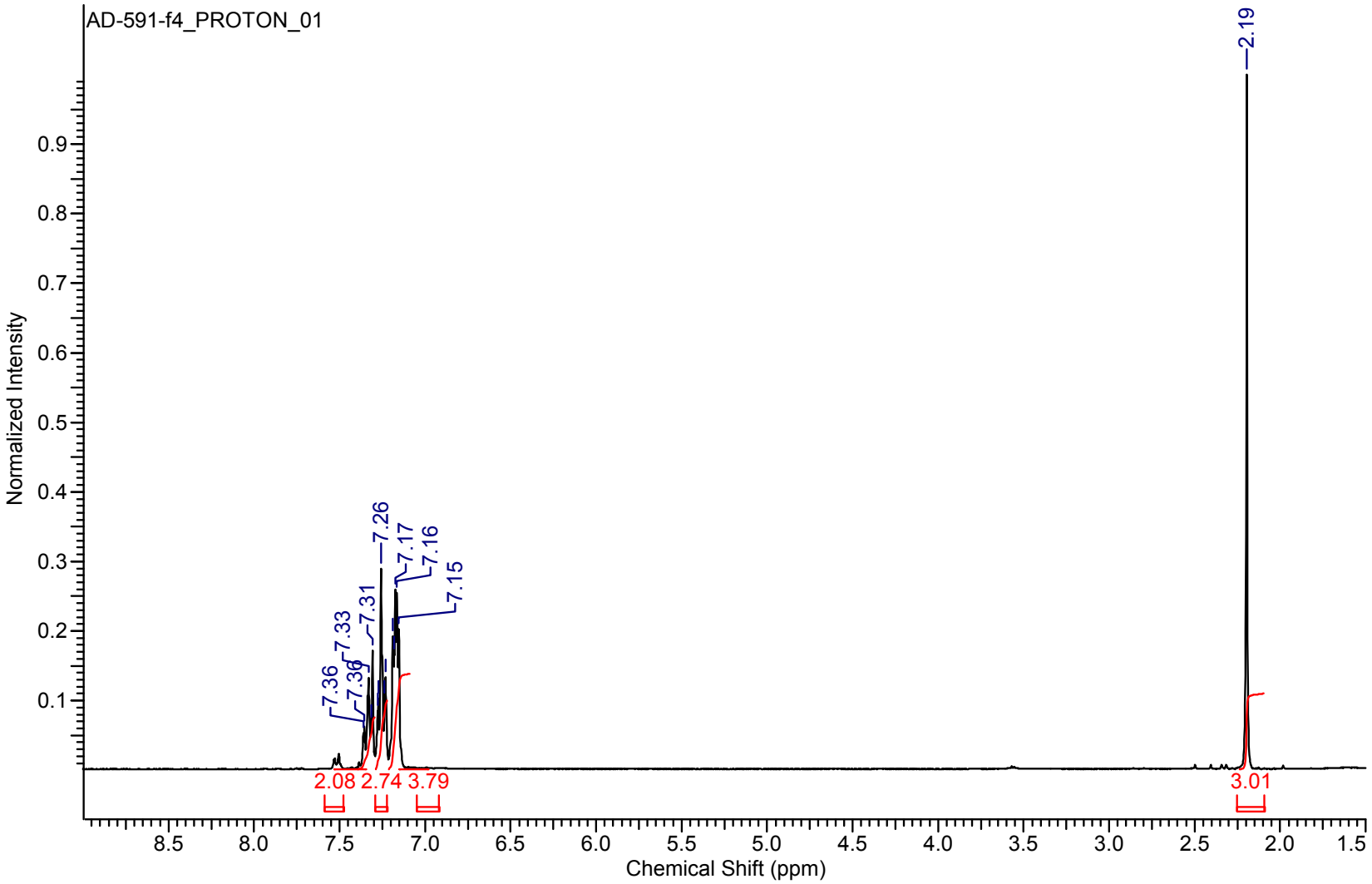
^{13}C-NMR, 75 MHz, $CDCl_3$

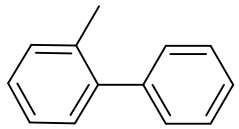




Compound **1e**

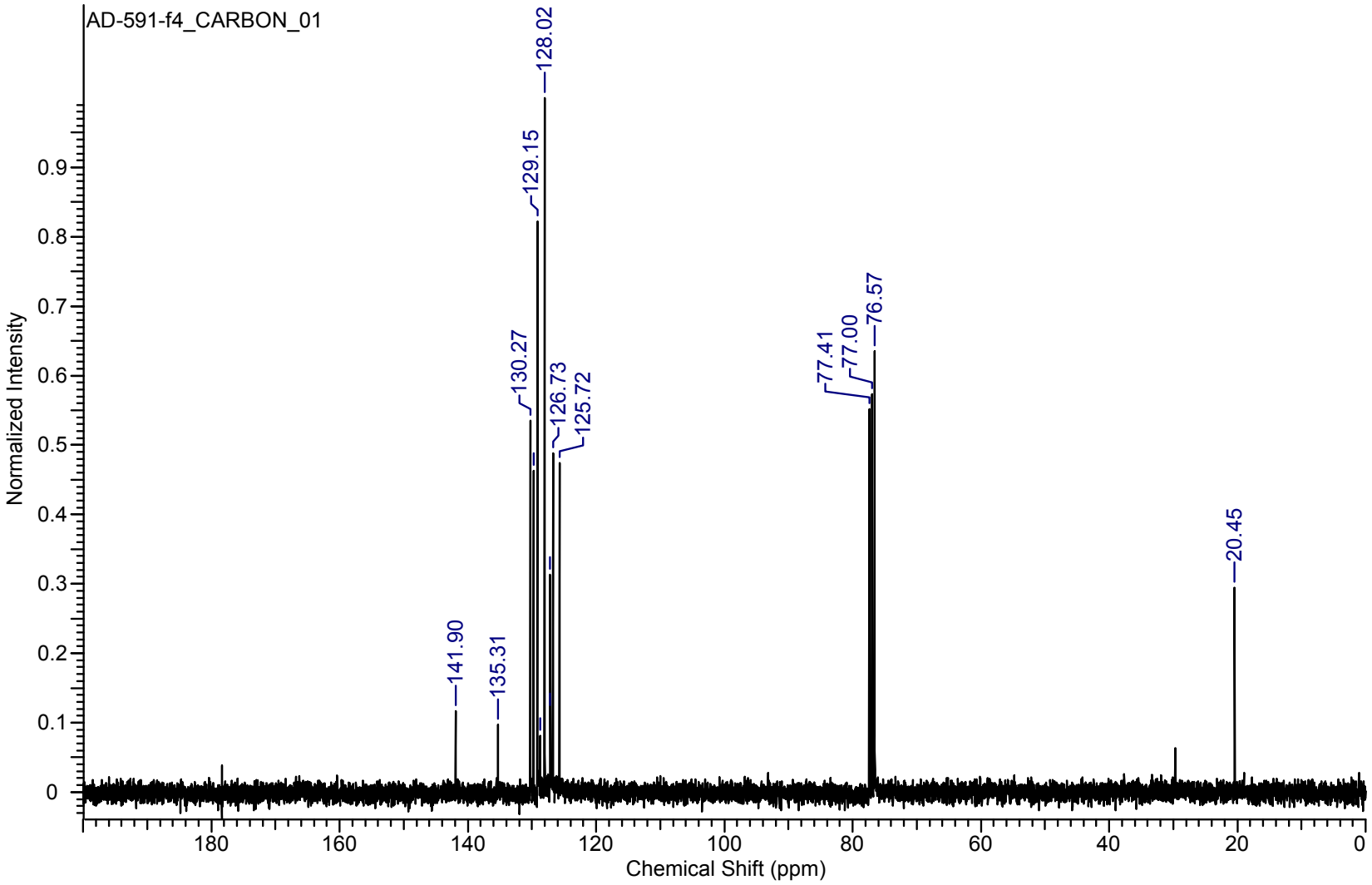
^{1}H-NMR, 300 MHz, $CDCl_3$

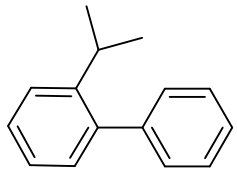




Compound **1e**

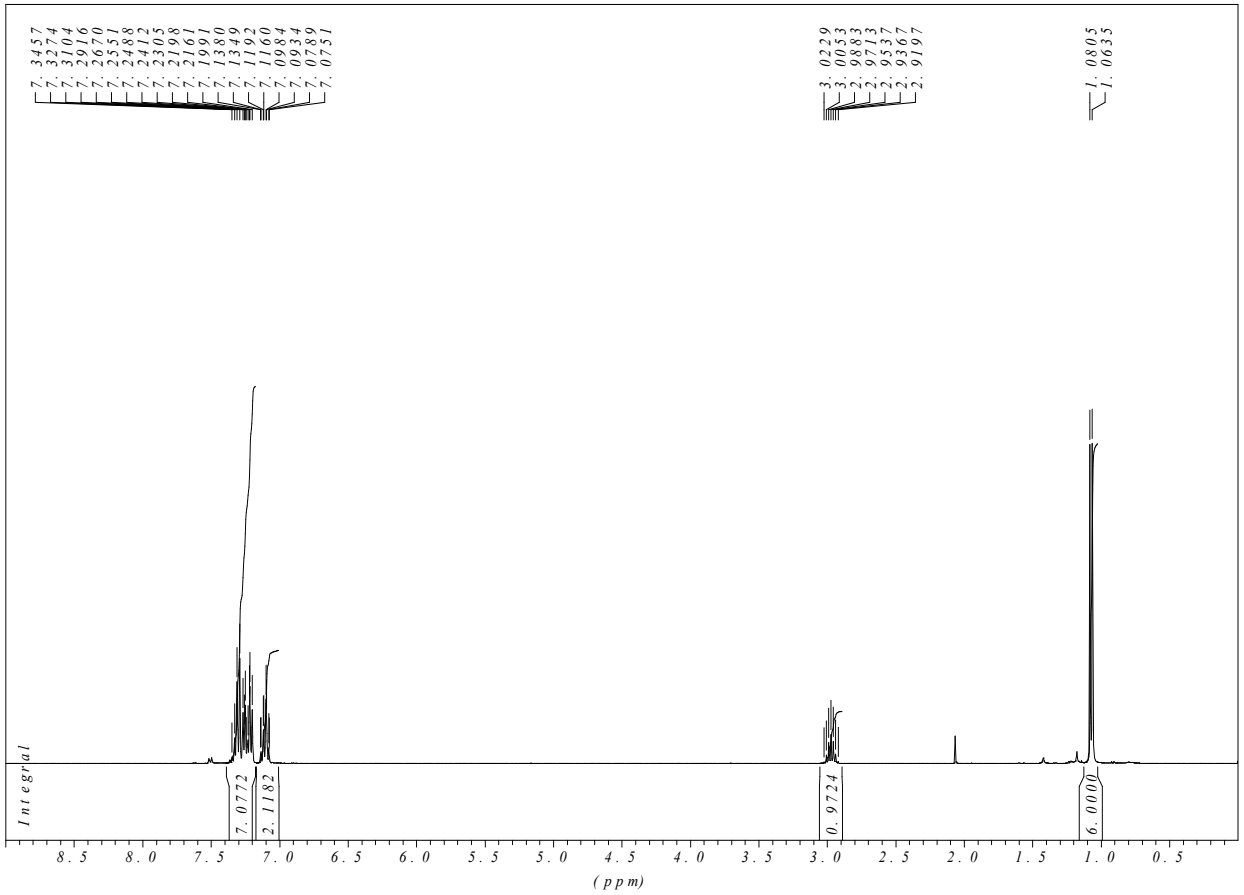
^{13}C-NMR, 75 MHz, $CDCl_3$

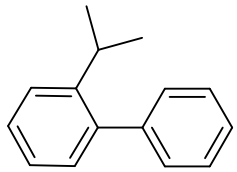




Compound **1f**

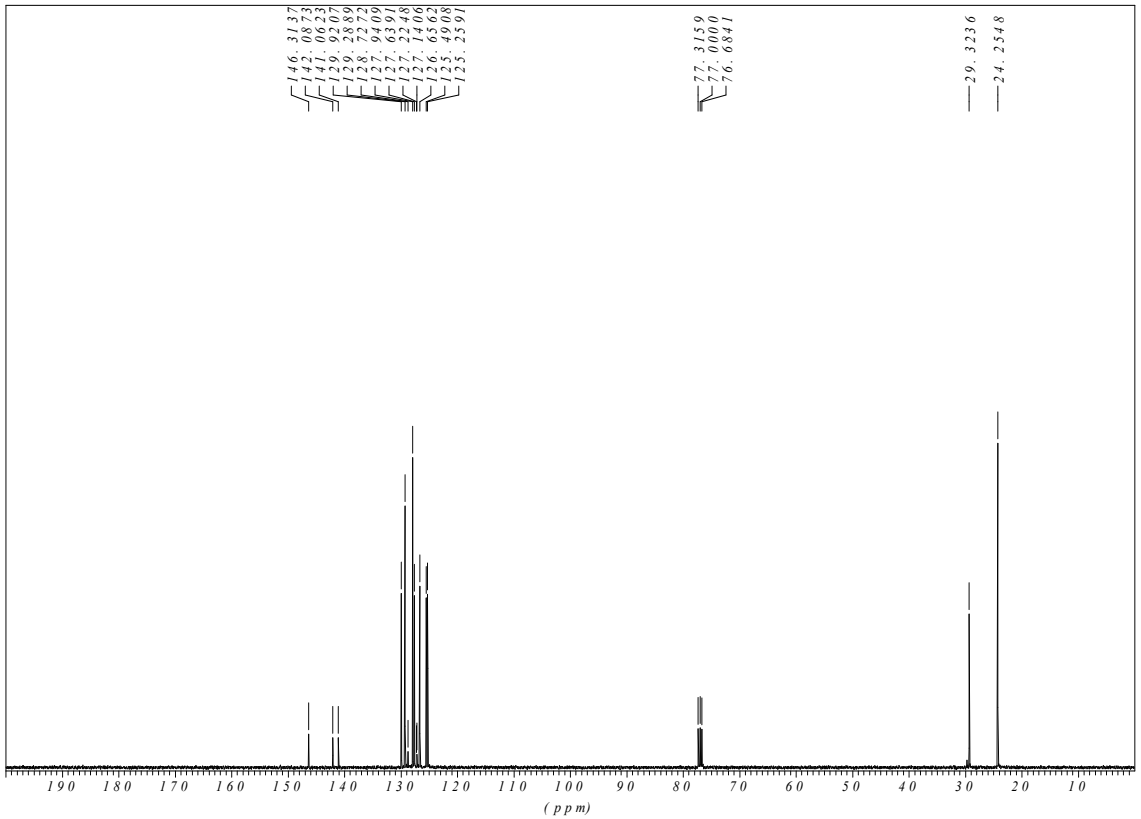
^{1}H-NMR, 300 MHz, $CDCl_3$





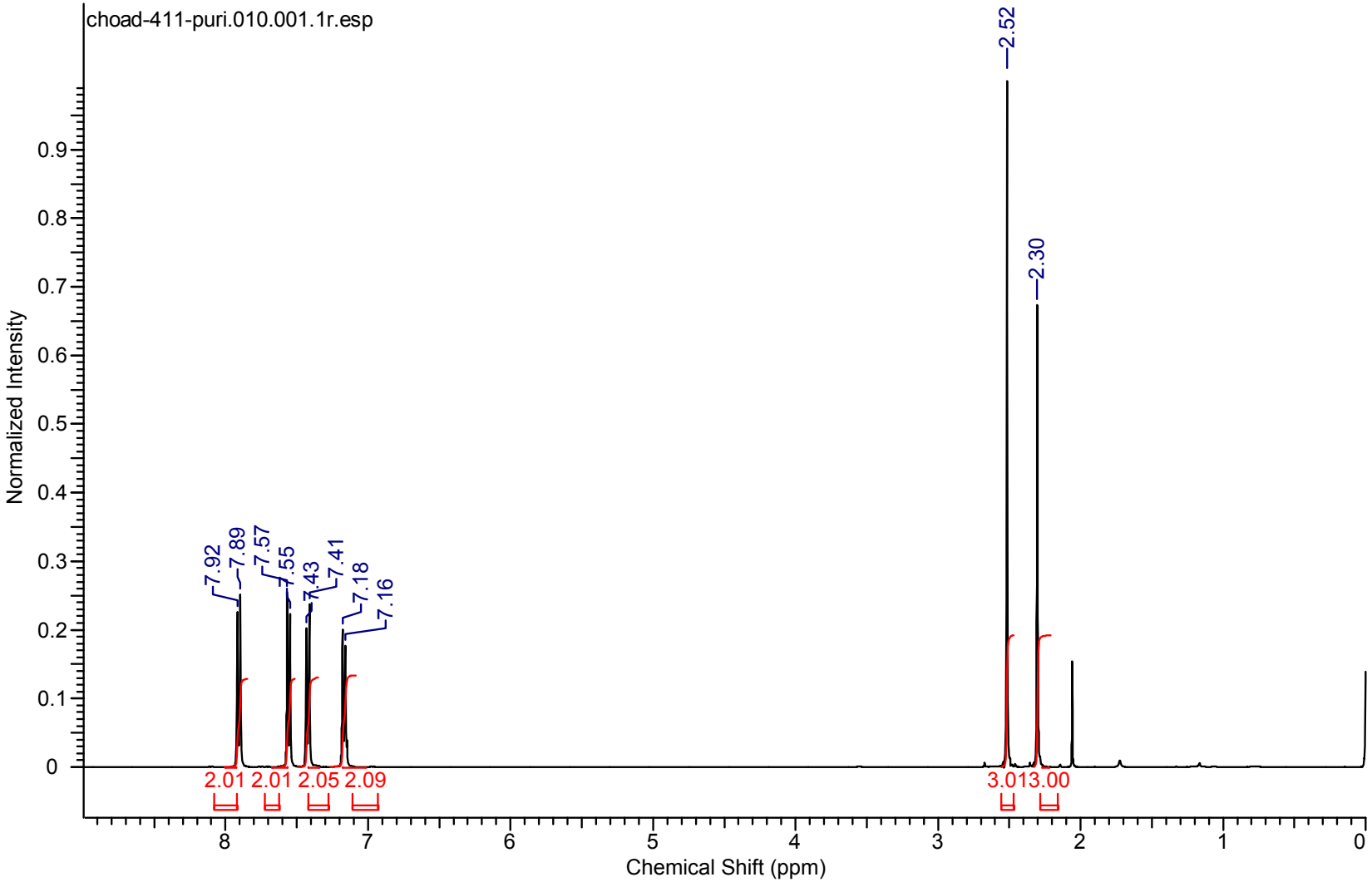
Compound **1f**

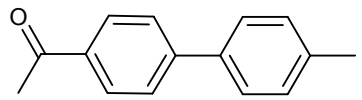
^{1}H-NMR, 300 MHz, $CDCl_3$



Compound **1g**

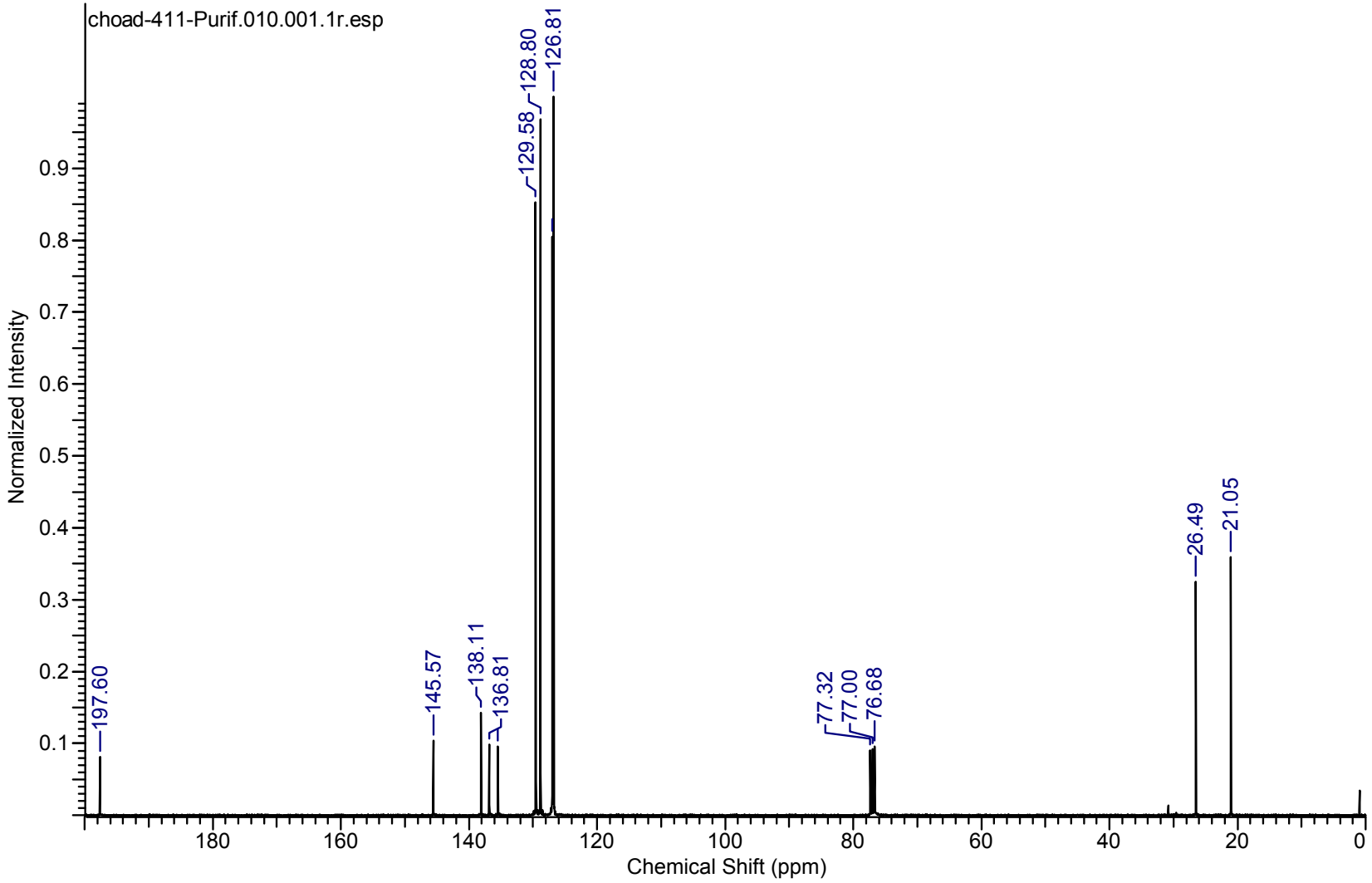
^{1}H-NMR, 400 MHz, $CDCl_3$

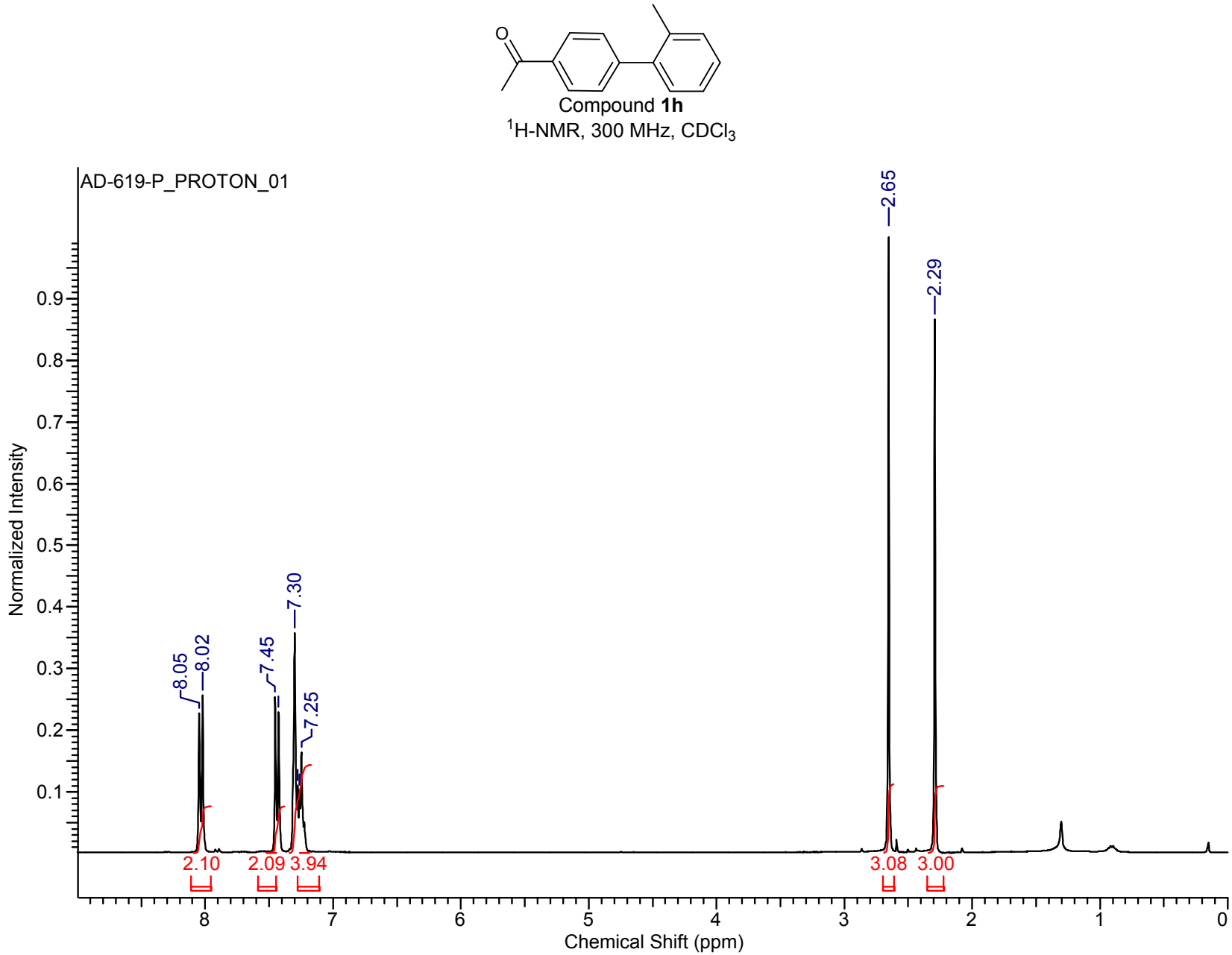


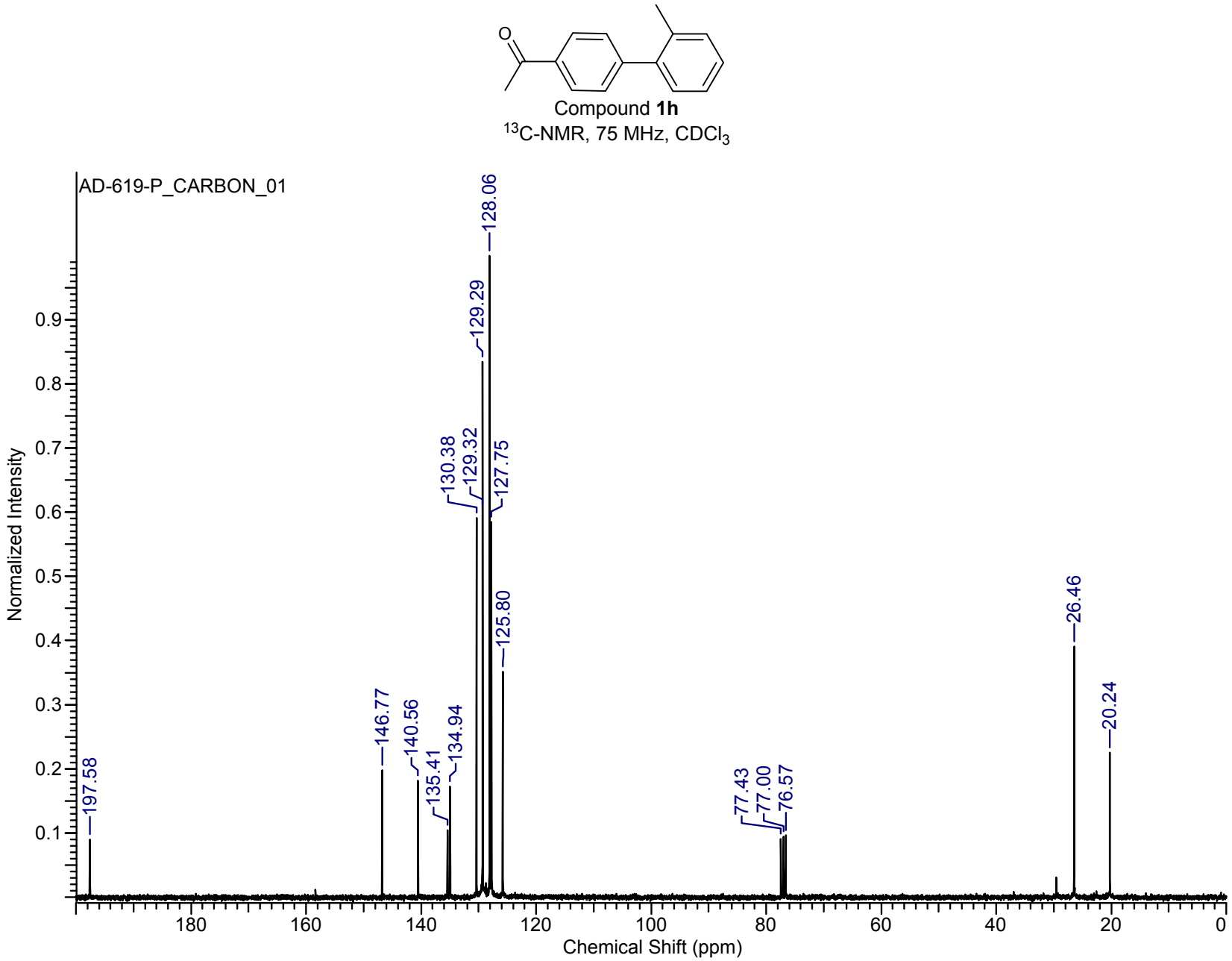


Compound **1g**

^{13}C-NMR, 100 MHz, $CDCl_3$




O
Compound 1h
1H-NMR, 300 MHz, CDCl3
AD-619-P_PROTON_01
Normalized Intensity
Chemical Shift (ppm)
8.05
8.02
7.45
7.30
7.25
2.65
2.29
2.10
2.09
3.94
3.08
3.00


O
Compound 1h
13C-NMR, 75 MHz, CDCl3
AD-619-P_CARBON_01
Normalized Intensity
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0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
197.58
146.77
140.56
135.41
134.94
130.38
129.32
129.29
128.06
127.75
125.80
77.43
77.00
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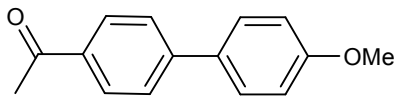
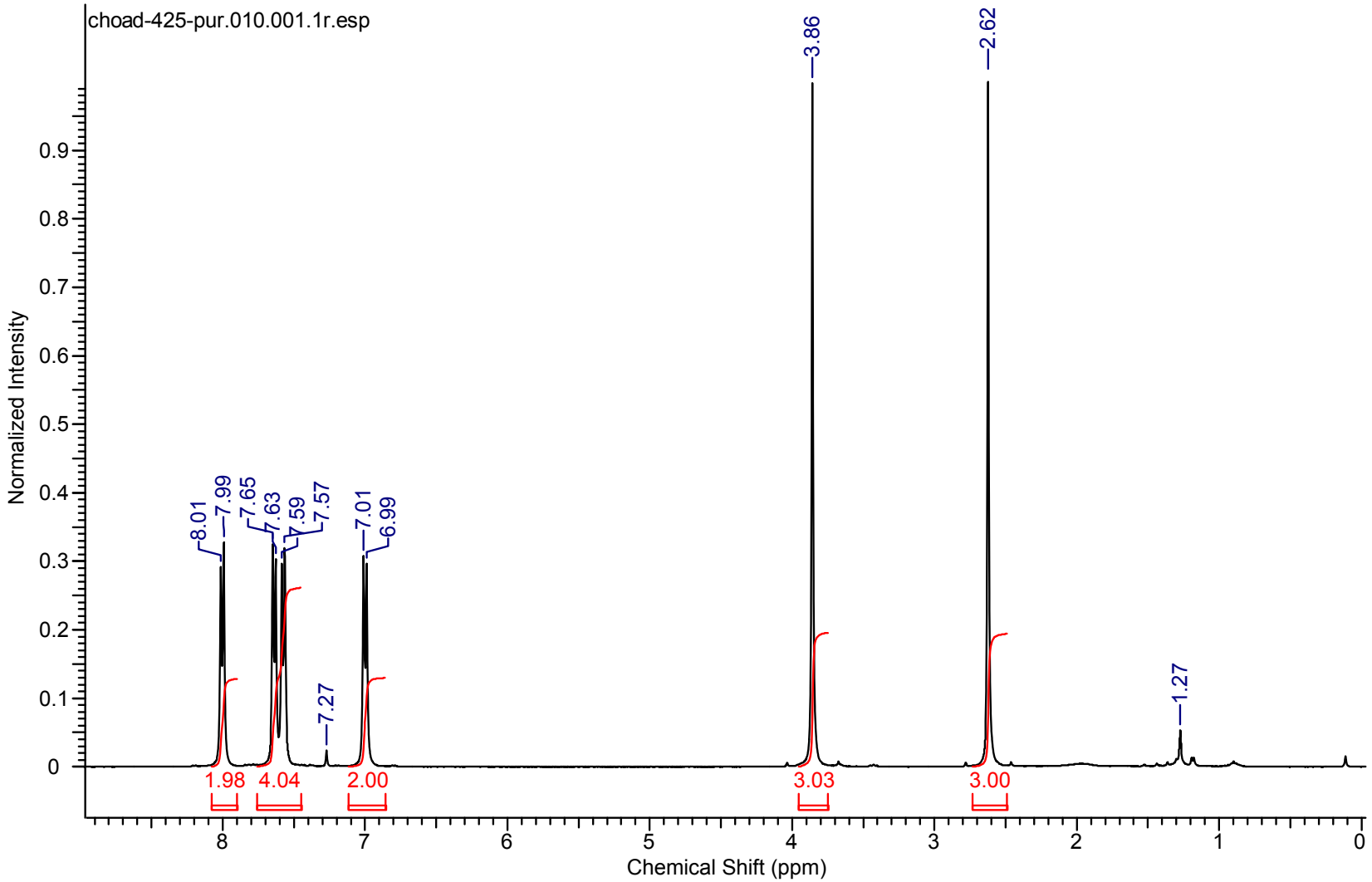
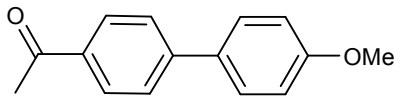
26.46
20.24
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



Compound **1i**

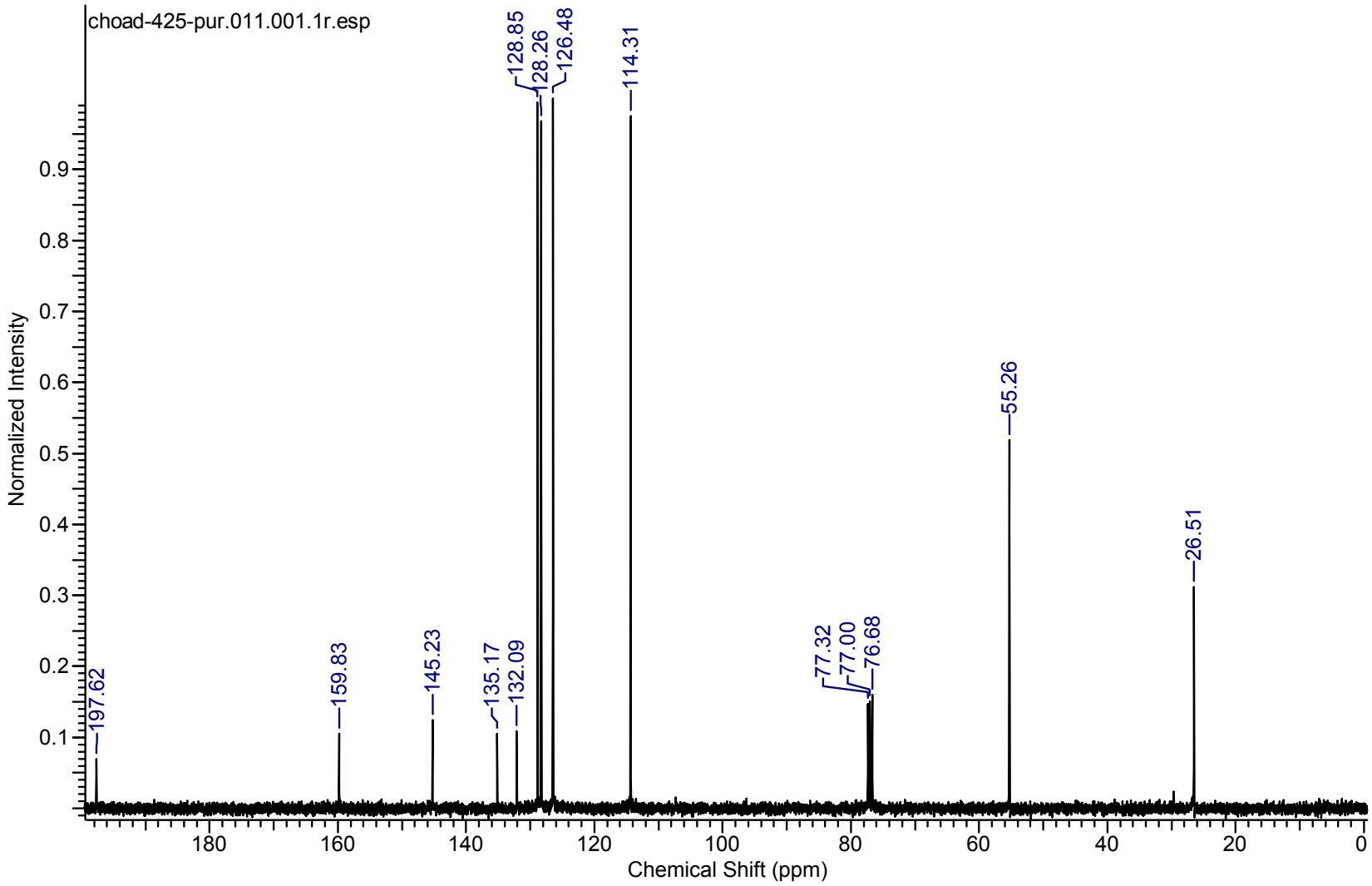
^{1}H-NMR, 300 MHz, $CDCl_3$





Compound **1i**

^{13}C-NMR, 75 MHz, $CDCl_3$



[1] C. Diebold, J.-M. Becht, J. Lu, P. H. Toy, C. Le Drian, *Eur. J. Org. Chem.* **2012**, 893.

[2] S. Schweizer, J.-M. Becht, C. Le Drian, *Org. Lett*. **2007**, *9*, 3777.