Electronic Supplementary Material (ESI) for RSC Advances.

Reusable magnetic Pd_x-Co_y nanoalloys confined in mesoporous carbons for green Suzuki-Miyaura reactions

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ELECTRONIC SUPPORTING INFORMATION

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General procedure for the determination of the Pd content of C1-C4

Concentrated H_2SO_4 (3 mL) was added to a sample of **C1-C4** (ca. 1 mg, precisely weighted). The mixture was brought to reflux in a fume hood. After cooling to 100 °C, fuming HNO_3 (2 mL) was then added and the heating resumed until disappearance of nitric fumes, complete evaporation of HNO_3 and beginning of the reflux of the remaining H_2SO_4. After cooling to 100 °C, fuming HNO_3 (2 mL) was then added, the mixture was heated until evaporation of HNO_3 and of most of the H_2SO_4. Concentrated HNO_3 (3 mL) and concentrated HCl (3 mL) were successively added and the mixture heated until evaporation of the acids. The residue was then dissolved in H_2O (25 mL) and the amount of Pd present in this mixture was determined by complexation following a procedure described in the literature. Two independent experiments were performed and the average value retained.

Determination of the Pd leached in the reaction medium during the Suzuki reaction

After Suzuki reaction, the catalyst **C3** was magnetically recovered and washed with AcOEt (3x15 mL). The combined organic phase was evaporated under high vacuum. Concentrated H_2SO_4 (5 mL) was added to the residue and brought to reflux in a fume hood. After cooling to 100 °C fuming HNO_3 (5 mL) was then slowly added and the heating resumed until disappearance of the nitric fumes, complete evaporation of HNO_3 and beginning of the reflux of the remaining H_2SO_4. After cooling to 100 °C, fuming HNO_3 (5 mL) was then slowly added, the mixture was heated until evaporation of HNO_3 and this process was repeated twice, the heating of the sample in acids during, as a whole, 15-20 min. Most of the H_2SO_4 was then boiled off, concentrated HNO_3 (3 mL) and concentrated HCl (3 mL) were successively added and the mixture heated until evaporation of the acids. The residue was then dissolved in H_2O (25 mL) and the amount of Pd present in this mixture was determined by complexation following a procedure described in the literature. Two independent experiments were performed and the average value retained.

^{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 (95 mg, 97 % yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 2.65 (s, 3H), 7.45 (m, 3H), 7.64 (d, ^3J(H,H) = 7.0 Hz, 2H), 7.70 (d, ^3J(H,H) = 6.7 Hz, 2H), 8.05 (d, ^3J(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.

1-(4-(4'-Methyl)biphenylyl)ethanone (1b): Elution with AcOEt / cyclohexane 5:95 afforded **1b** as a white solid (104 mg, 99 % yield). ^{1}H NMR (300 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 (75 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-(3'-Methyl)biphenylyl)ethanone (1c): Elution with AcOEt / cyclohexane 5:95 afforded **1c** as a white solid (103 mg, 98 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.43 (s, 3H), 2.61 (s, 3H), 7.21

(m, 1H), 7.42 (d, m, 3H), 7.65 (d, ^3J(H,H) = 9 Hz, 2H), 8.01 (d, ^3J(H,H) = 9 Hz, 2H).[3] ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 21.3, 26.4, 124.2, 127.0, 127.1, 128.7, 128.8, 135.6, 138.4, 139.8, 145.6, 197.4.

1-(4-(4'-Methoxy)biphenylyl)ethanone (1d): Elution with AcOEt / cyclohexane 5:95 afforded **1d** as a white solid (97 mg, 86 % 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).[4] ^{13}C NMR (75 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.

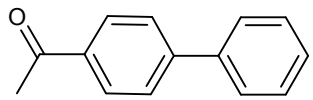
1-(4-(4'-chlorobiphenylyl)ethanone (1e): Elution with AcOEt / cyclohexane 5:95 afforded **1e** as a white solid (114 mg, 99% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.43 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.55 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.64 (d, ^3J(H,H) = 8.1 Hz, 2H), 8.03 (d, ^3J(H,H) = 8.1 Hz, 2H).[5] ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 26.6, 126.9, 127.0, 128.5, 129.0, 134.4, 136.1, 138.3, 144.4, 197.5.

1-(4-Biphenylyl)propanone (1f): Elution with AcOEt / cyclohexane 5:95 as eluant afforded **1f** as a white solid (103 mg, 98 % yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 1.26 (t, ^3J(H,H) = 9 Hz, 3H), 3.04 (q, ^3J(H,H) = 9 Hz, 2H), 7.45 (m, 3H), 7.67 (m, 4H), 8.04 (d, ^3J(H,H) = 9 Hz, 2H).[6] ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 8.3, 31.8, 127.2, 128.5, 128.9, 135.6, 139.9, 145.5, 200.4.

(4-Biphenylyl)phenylmethanone (1g): Elution with AcOEt / cyclohexane 5:95 as eluant afforded **1g** as a white solid (86 mg, 67 % yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.45 (m, 5H), 7.66 (m, 5H), 7.90 (m, 4H).[7] ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 126.9, 127.0, 128.3, 128.9, 130.0, 130.7, 132.3, 136.2, 137.8, 140.0, 145.2, 196.3.

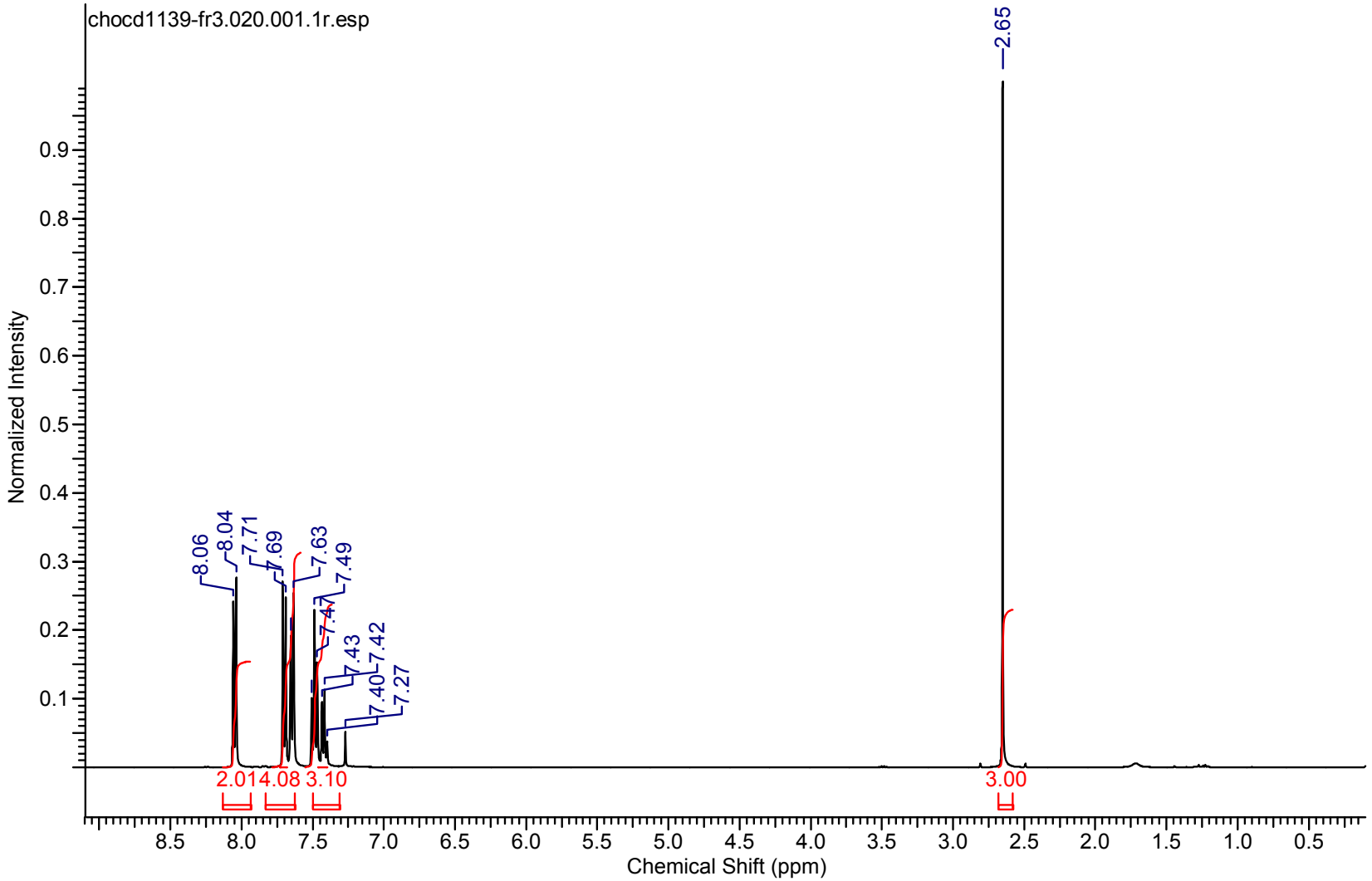
4-Biphenylcarbaldehyde (1h): Elution with AcOEt / cyclohexane 5:95 as eluant afforded **1h** as a white solid (56 mg, 62 % yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.45 (m, 4H), 7.63 (d, ^3J(H,H) = 8.1 Hz, 2H), 7.75 (d, ^3J(H,H) = 8.1 Hz, 2H), 7.95 (d, ^3J(H,H) = 8.1 Hz, 2H), 10.06 (s, 1H).[7] ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 127.1, 127.2, 127.3, 129.0, 130.7, 140.0, 146.5, 171.4, 191.9.

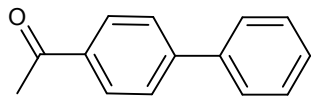
4-Biphenylcarbonitrile (1i): Elution with AcOEt / cyclohexane 5:95 as eluant afforded **1i** as a white solid (89 mg, 99 % yield). ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 7.46 (m, 3H), 7.59 (d, ^3J(H,H) = 6.8 Hz, 2H), 7.71 (m, 4H).[7] ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 110.9, 118.9, 127.2, 127.7, 128.6, 129.0, 132.5, 139.1, 145.6.



Compound **1a**

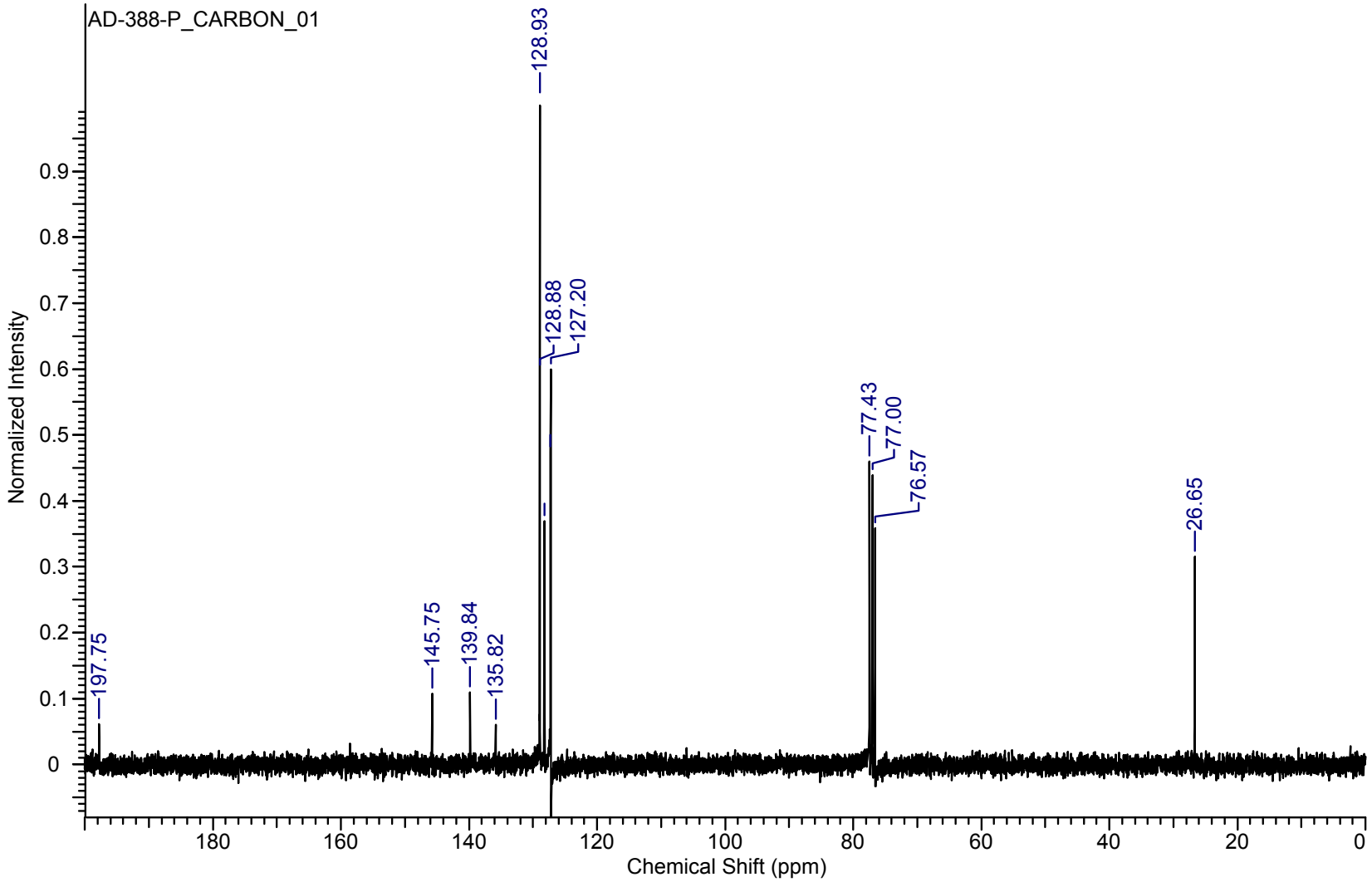
^{1}H-NMR, 300 MHz, $CDCl_3$





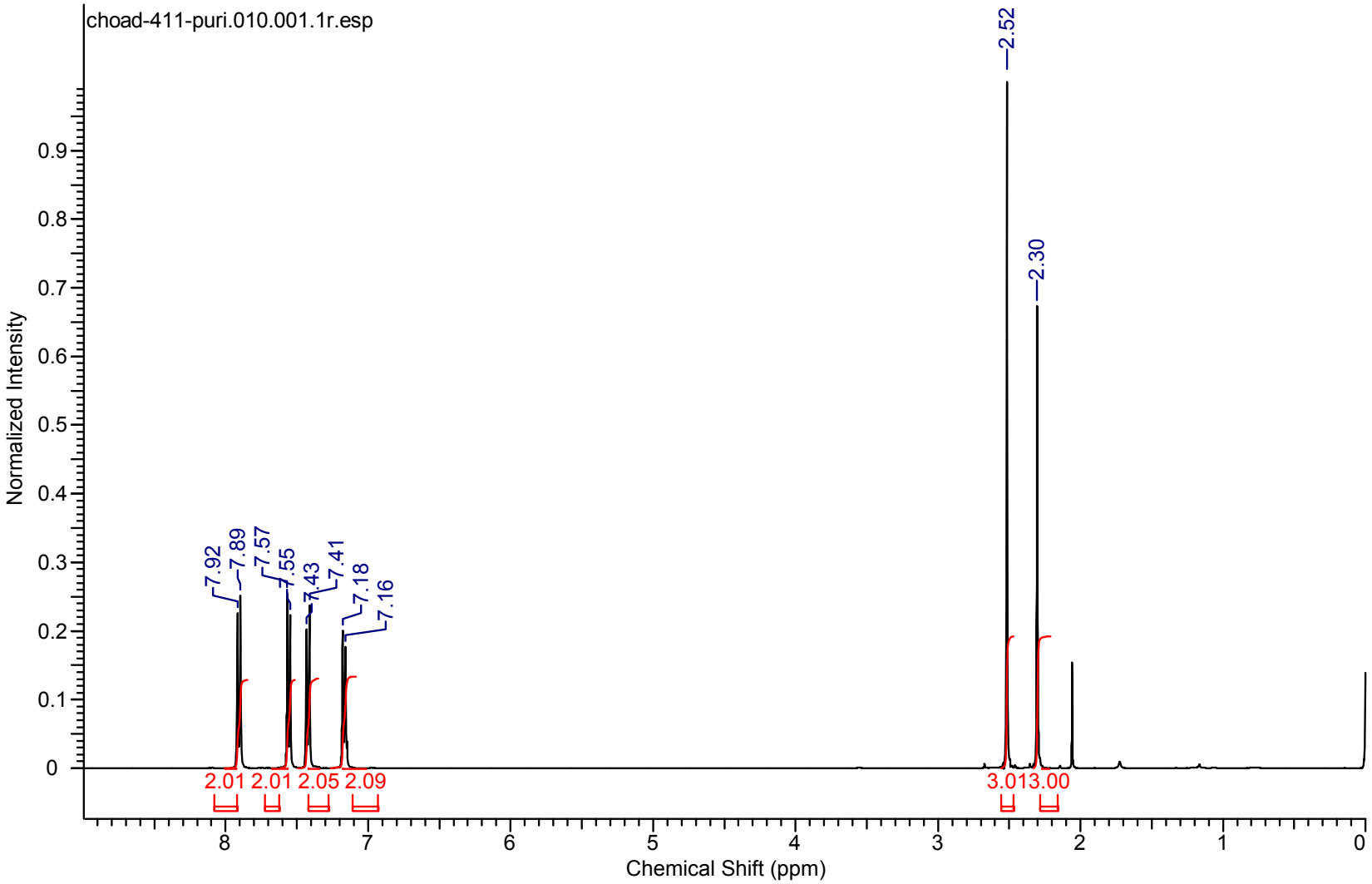
Compound **1a**

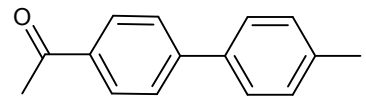
^{13}C-NMR, 75 MHz, $CDCl_3$



Compound **1b**

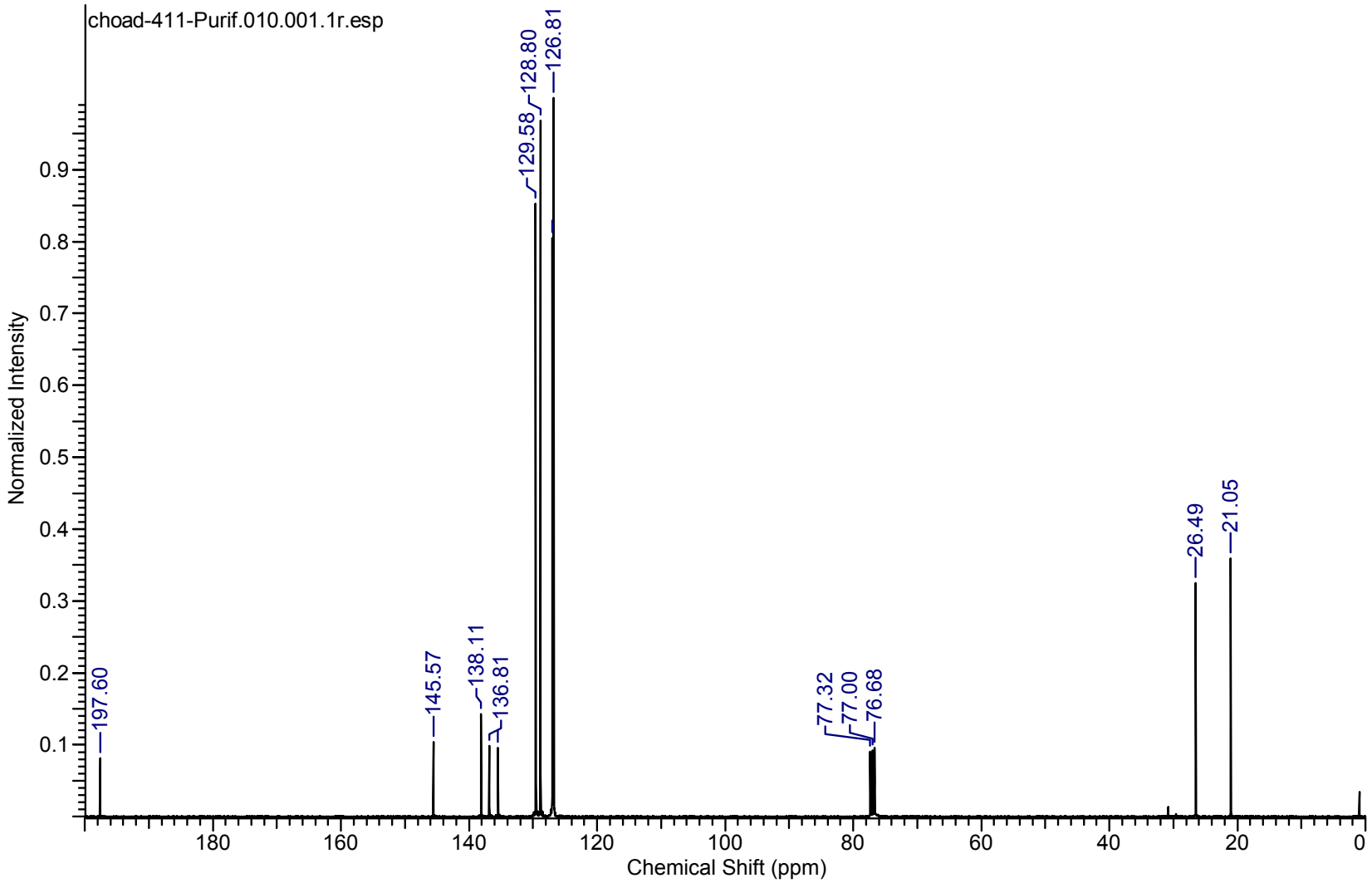
^{1}H-NMR, 300 MHz, $CDCl_3$

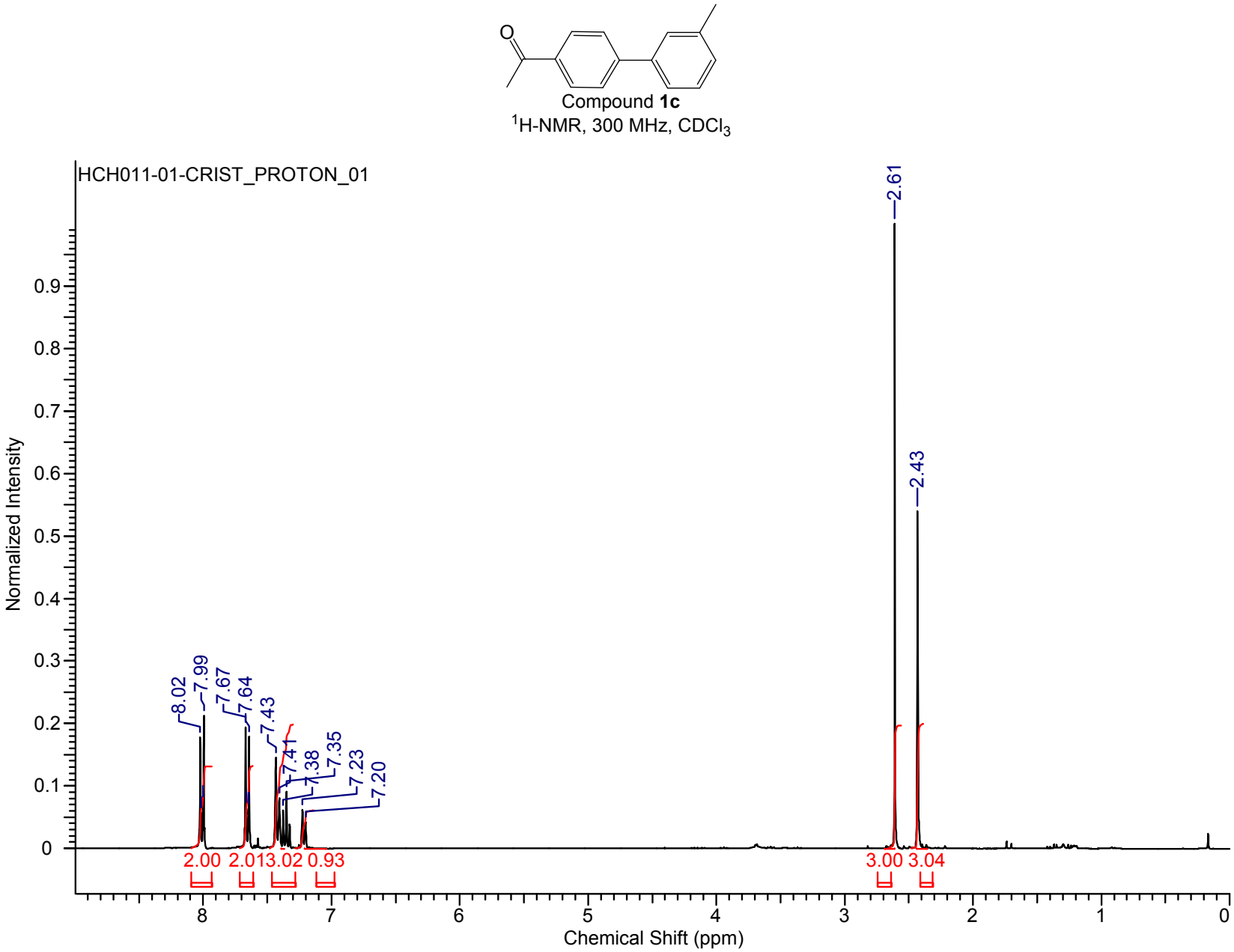


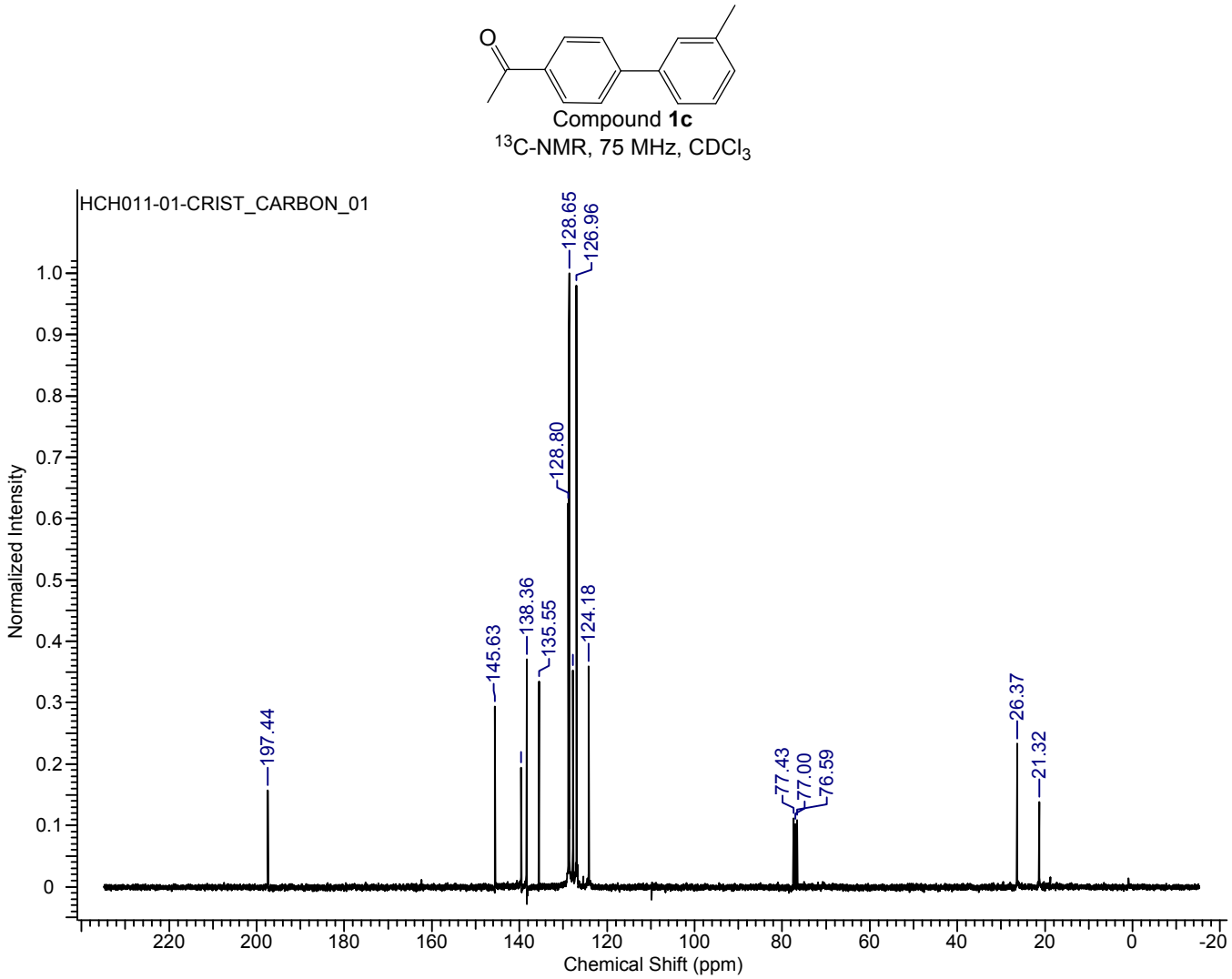


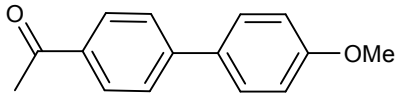
Compound **1b**

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



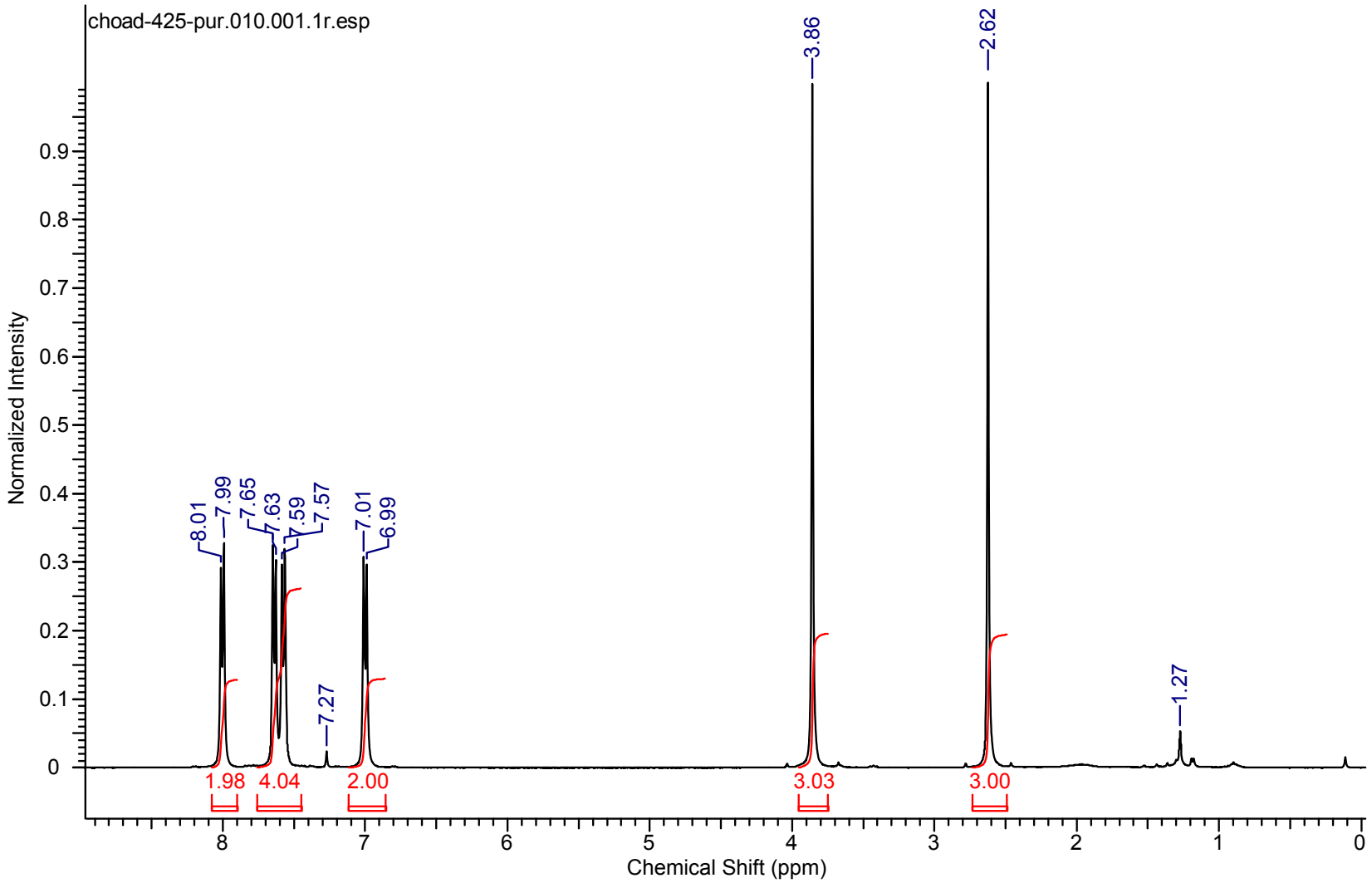

O
Compound 1c
1H-NMR, 300 MHz, CDCl3
HCH011-01-CRIST_PROTON_01
Normalized Intensity
Chemical Shift (ppm)
8.02
7.99
7.67
7.64
7.43
7.41
7.38
7.35
7.23
7.20
2.61
2.43
2.00
2.01
3.02
0.93
3.00
3.04

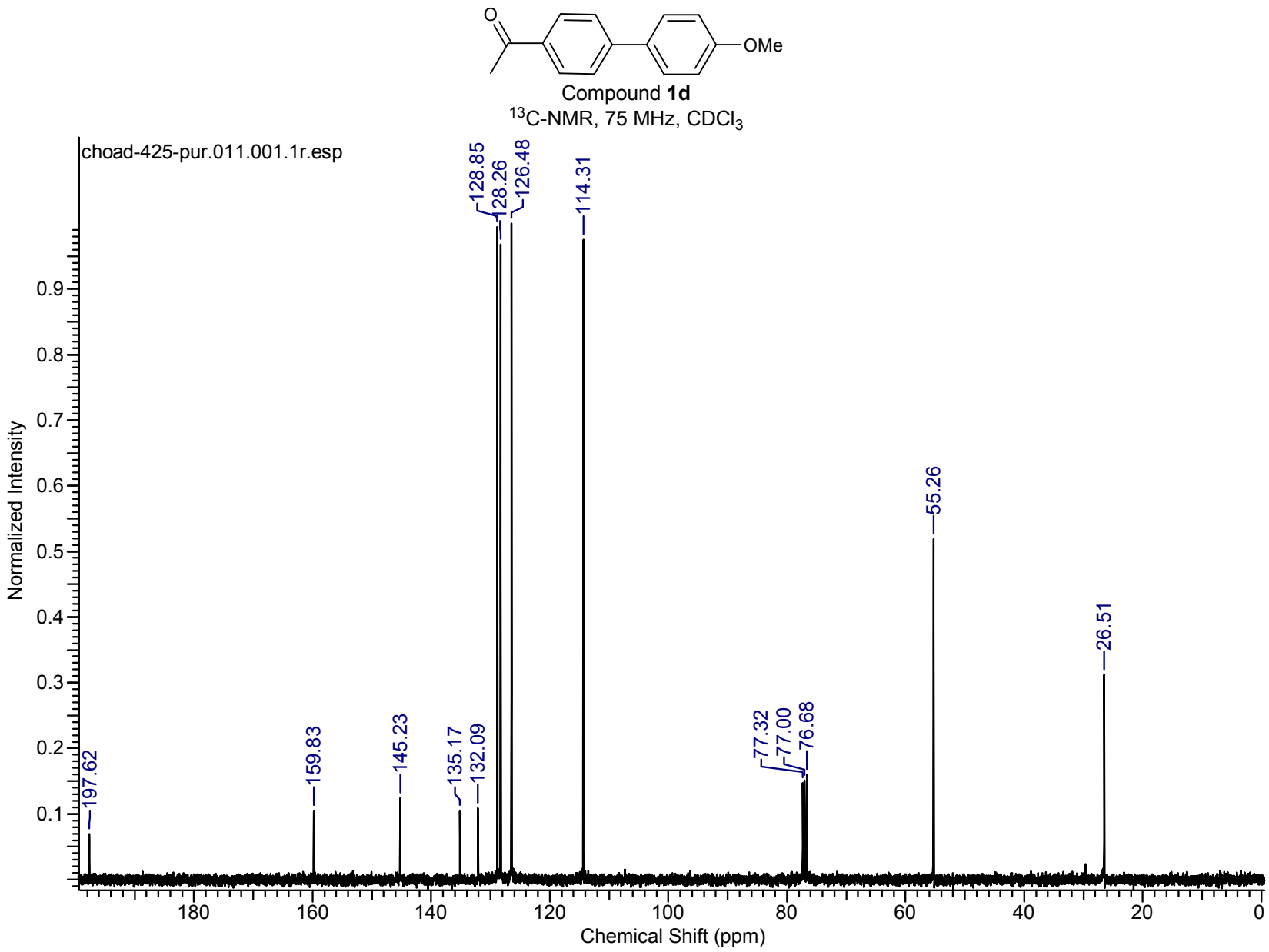

O
Compound 1c
13C-NMR, 75 MHz, CDCl3
HCH011-01-CRIST_CARBON_01
Normalized Intensity
Chemical Shift (ppm)
197.44
145.63
138.36
135.55
128.80
128.65
126.96
124.18
77.43
77.00
76.59
26.37
21.32

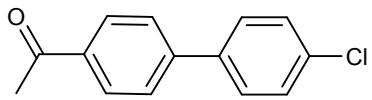


Compound **1d**

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

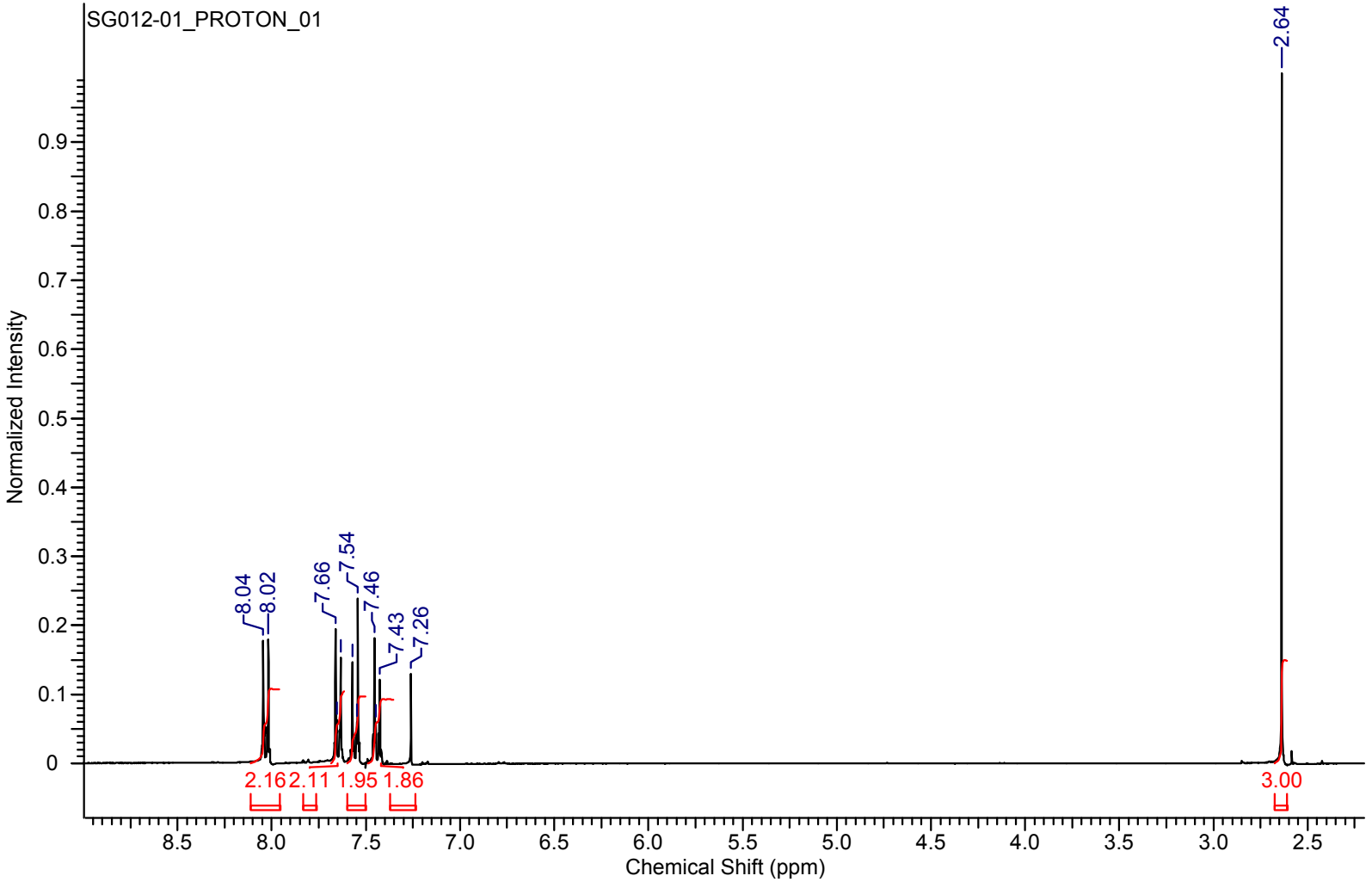


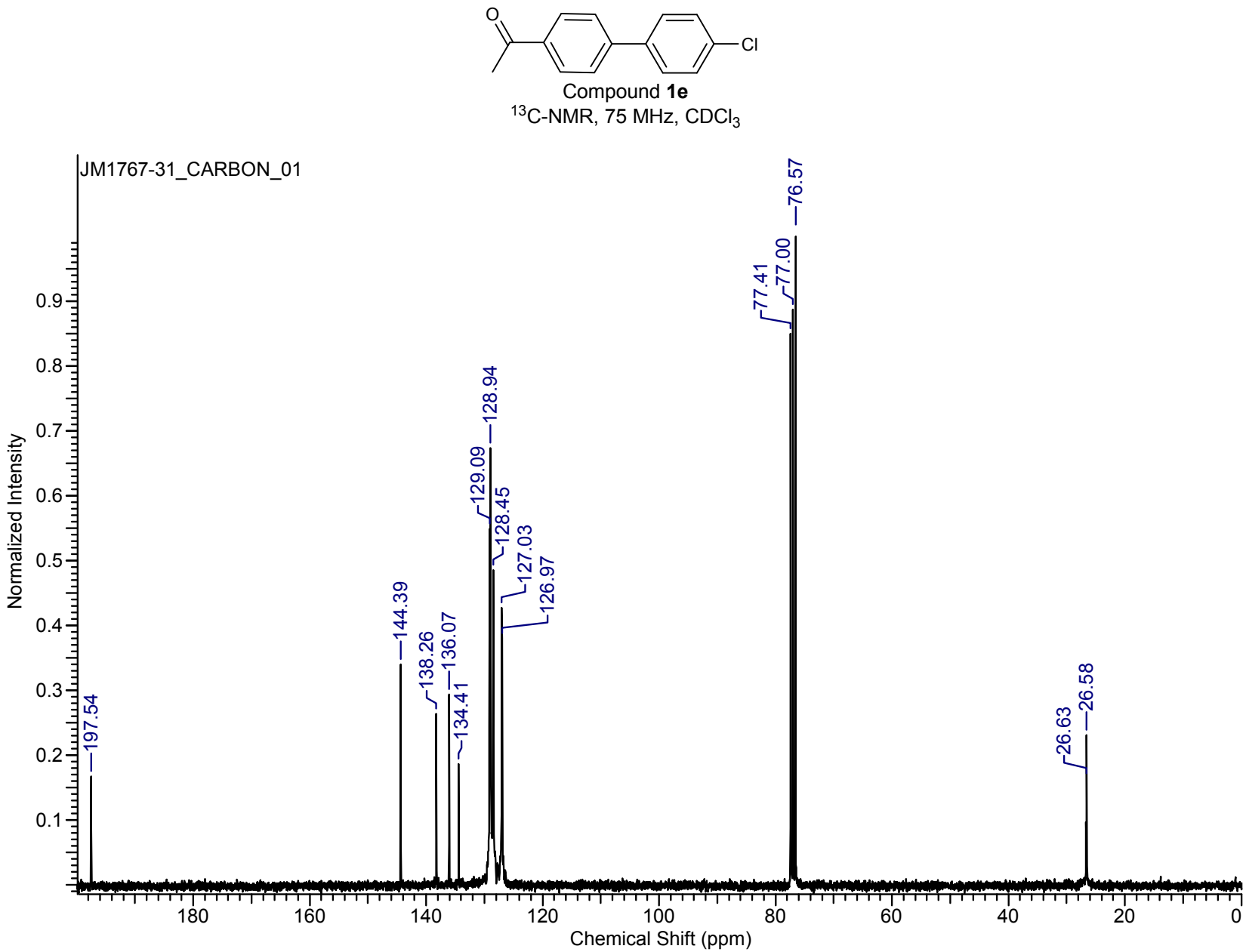

O
OMe
Compound 1d
13C-NMR, 75 MHz, CDCl3
choad-425-pur.011.001.1r.esp
128.85
128.26
126.48
114.31
55.26
26.51
197.62
159.83
145.23
135.17
132.09
77.32
77.00
76.68
Normalized Intensity
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

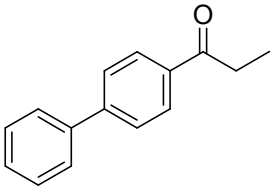


Compound **1e**

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

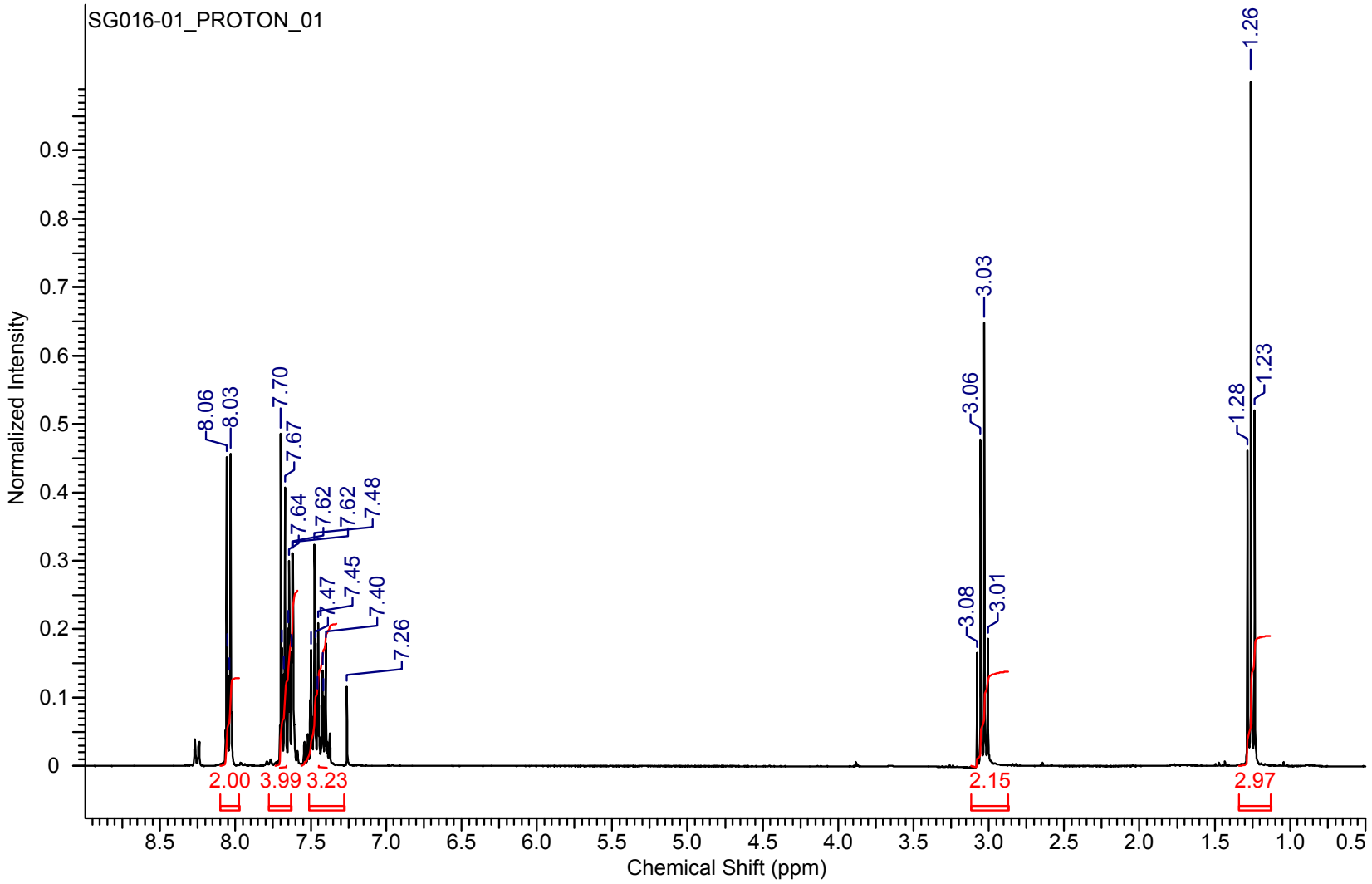


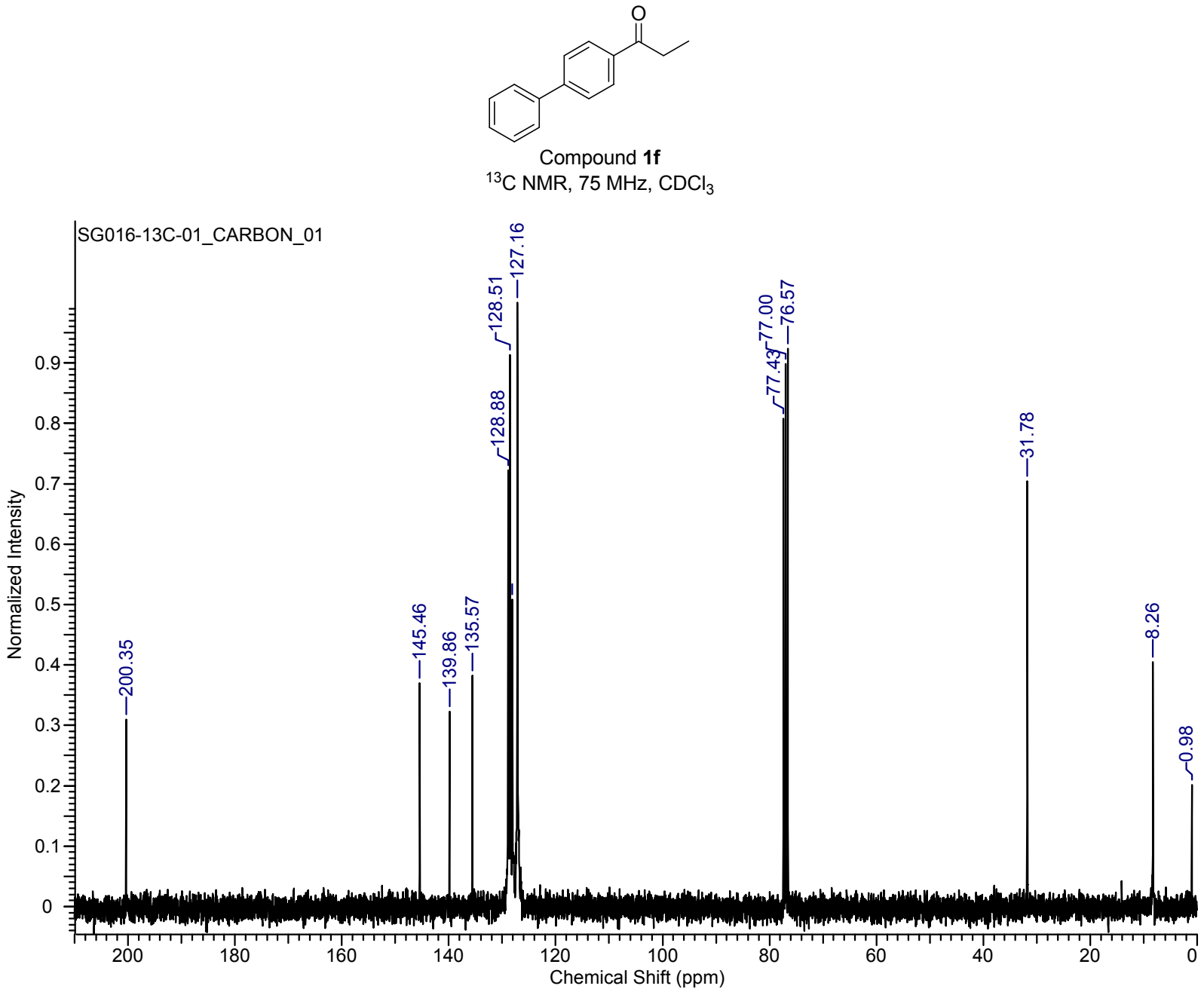

O
Cl
Compound **1e**
^{13}C-NMR, 75 MHz, $CDCl_3$
JM1767-31_CARBON_01
Normalized Intensity
Chemical Shift (ppm)
197.54
144.39
138.26
136.07
134.41
129.09
128.94
128.45
127.03
126.97
77.41
77.00
76.57
26.63
26.58

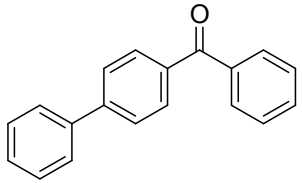


Compound **1f**

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

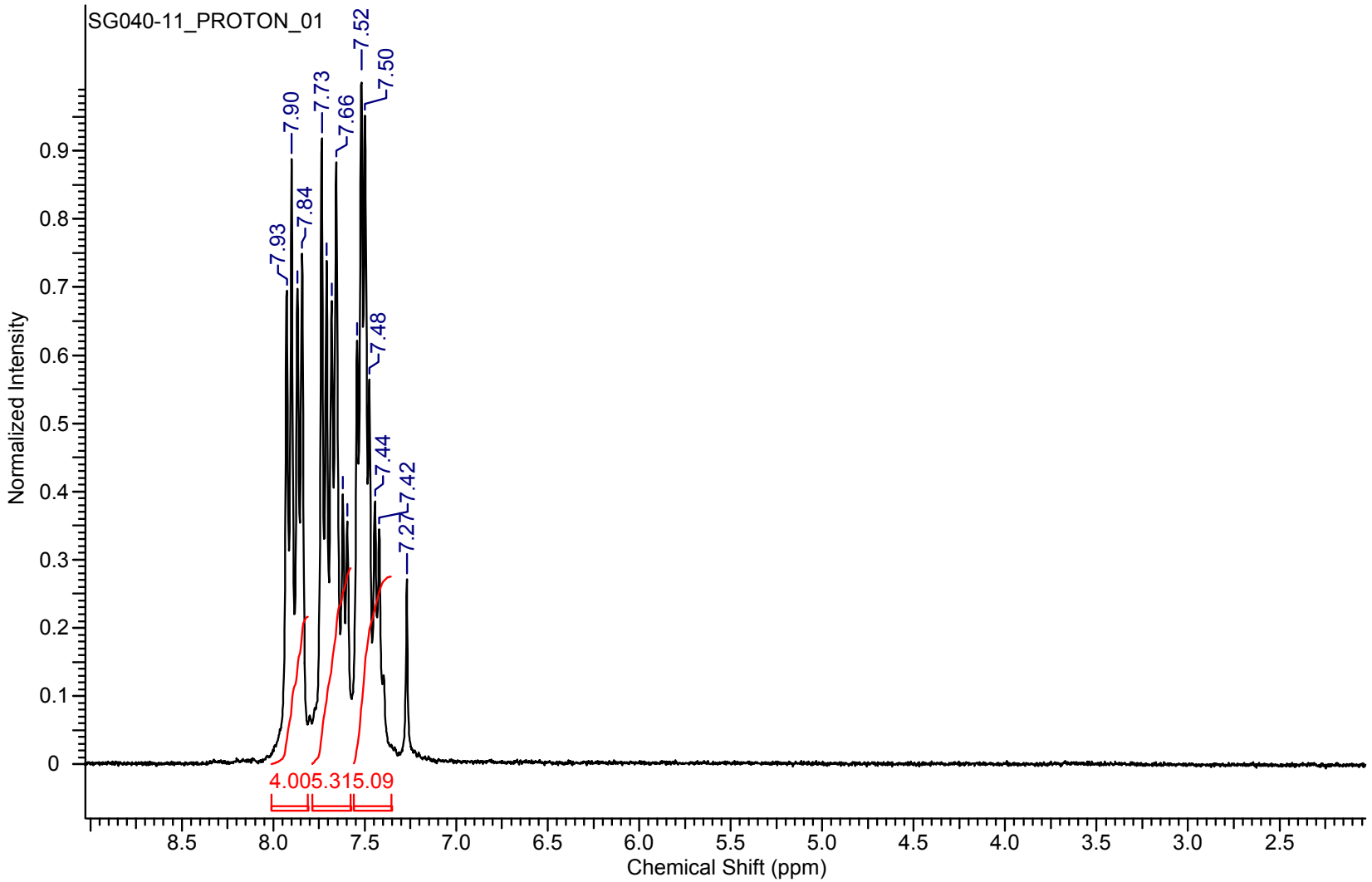


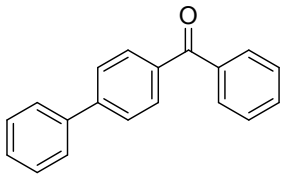

O
Compound 1f
13C NMR, 75 MHz, CDCl3
SG016-13C-01_CARBON_01
Normalized Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
200.35
145.46
139.86
135.57
128.88
128.51
127.16
77.43
77.00
76.57
31.78
8.26
0.98
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



Compound **1g**

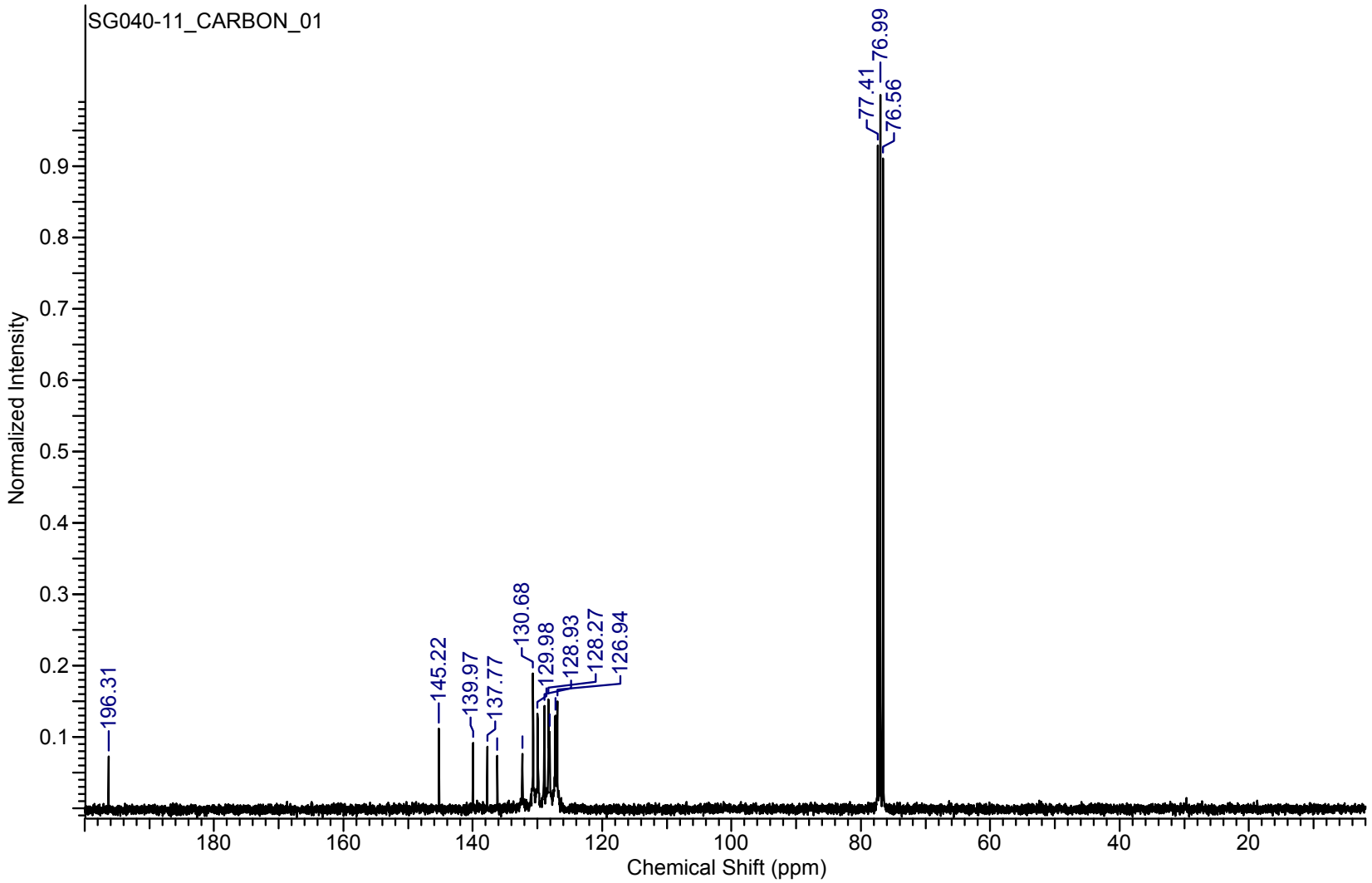
^{1}H NMR, 300 MHz, $CDCl_3$

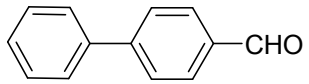




Compound **1g**

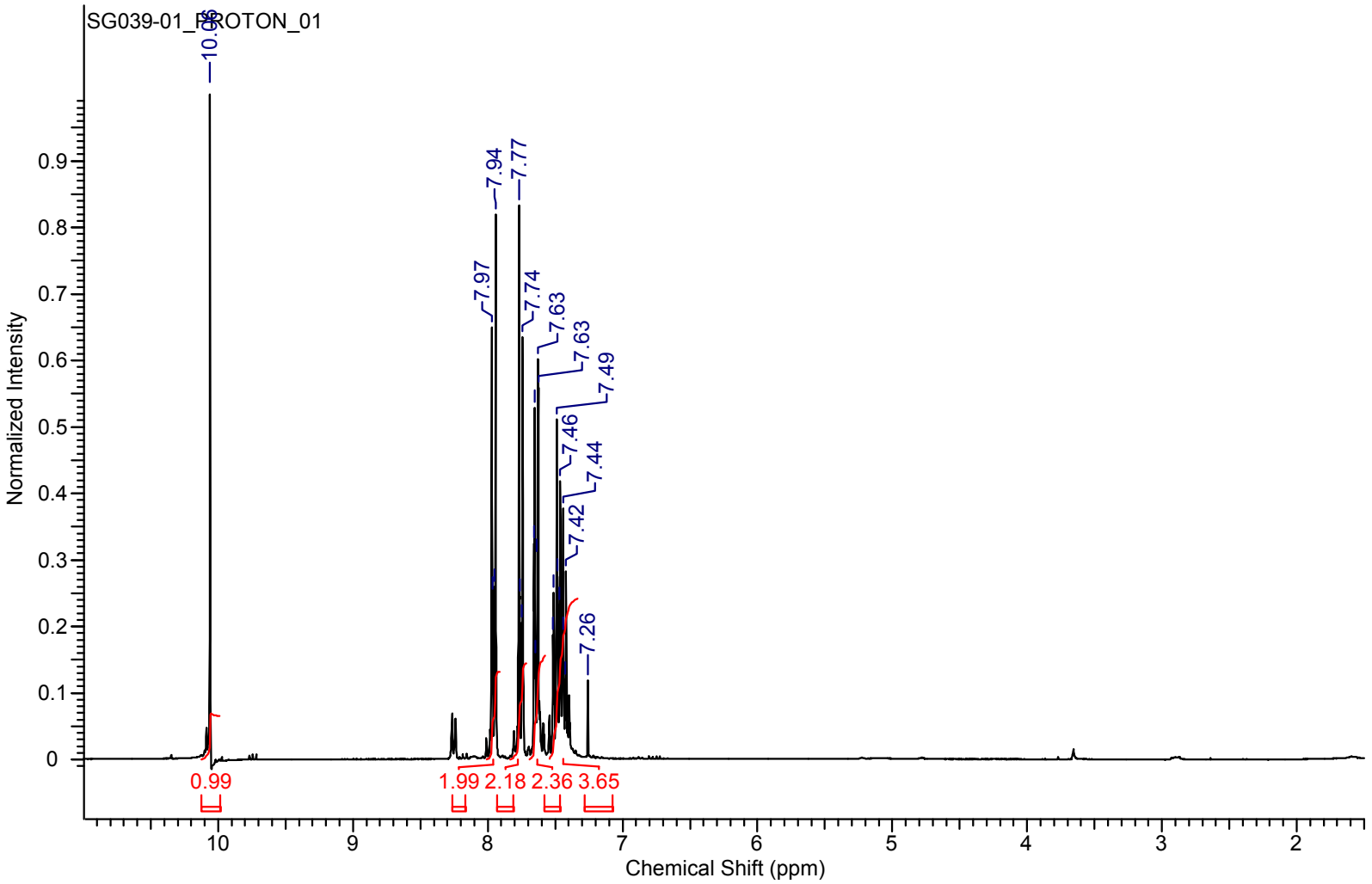
^{13}C NMR, 75 MHz, $CDCl_3$

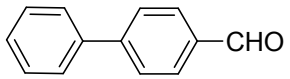




Compound **1h**

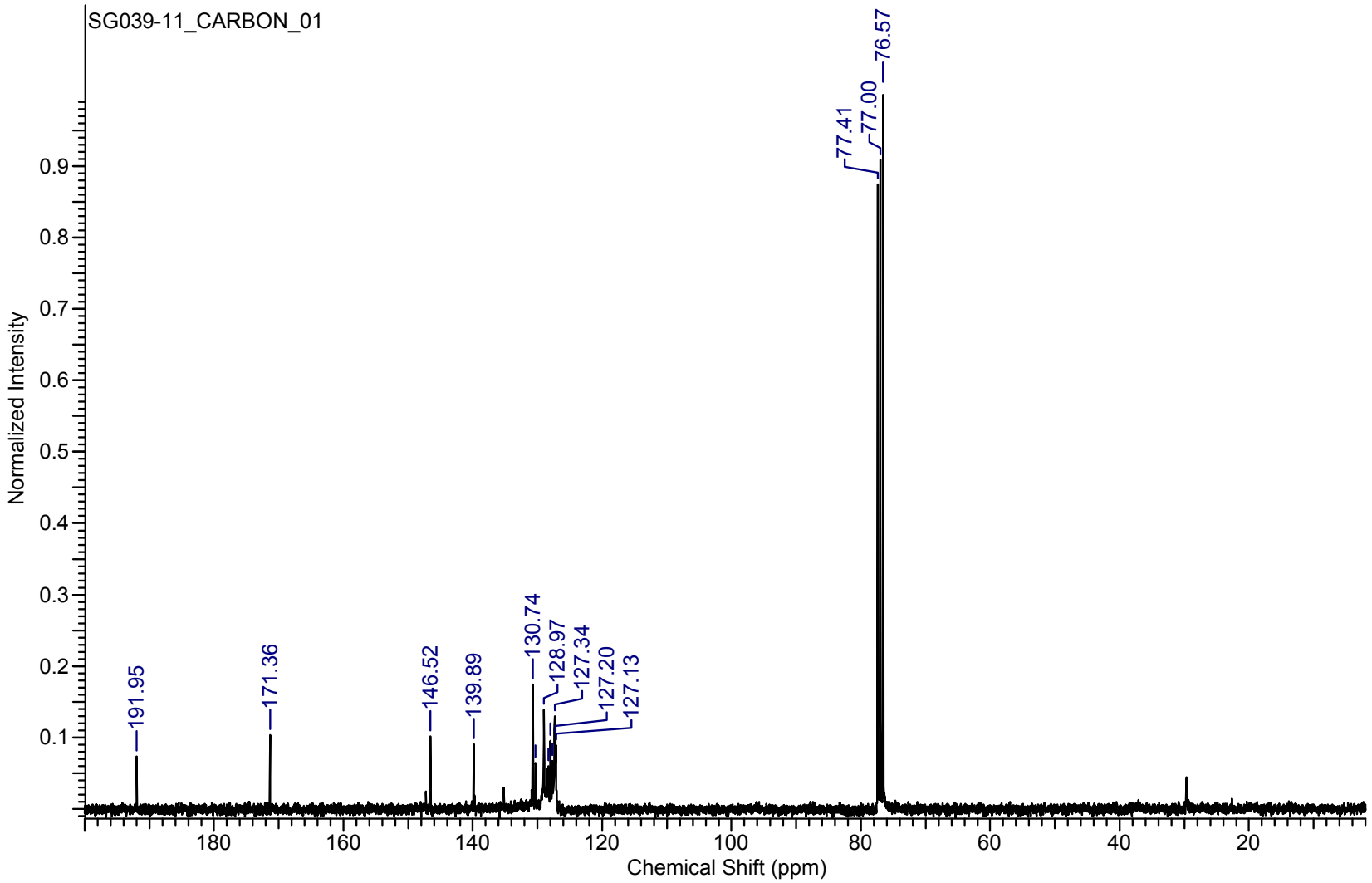
^{1}H-NMR, 300 MHz, $CDCl_3$





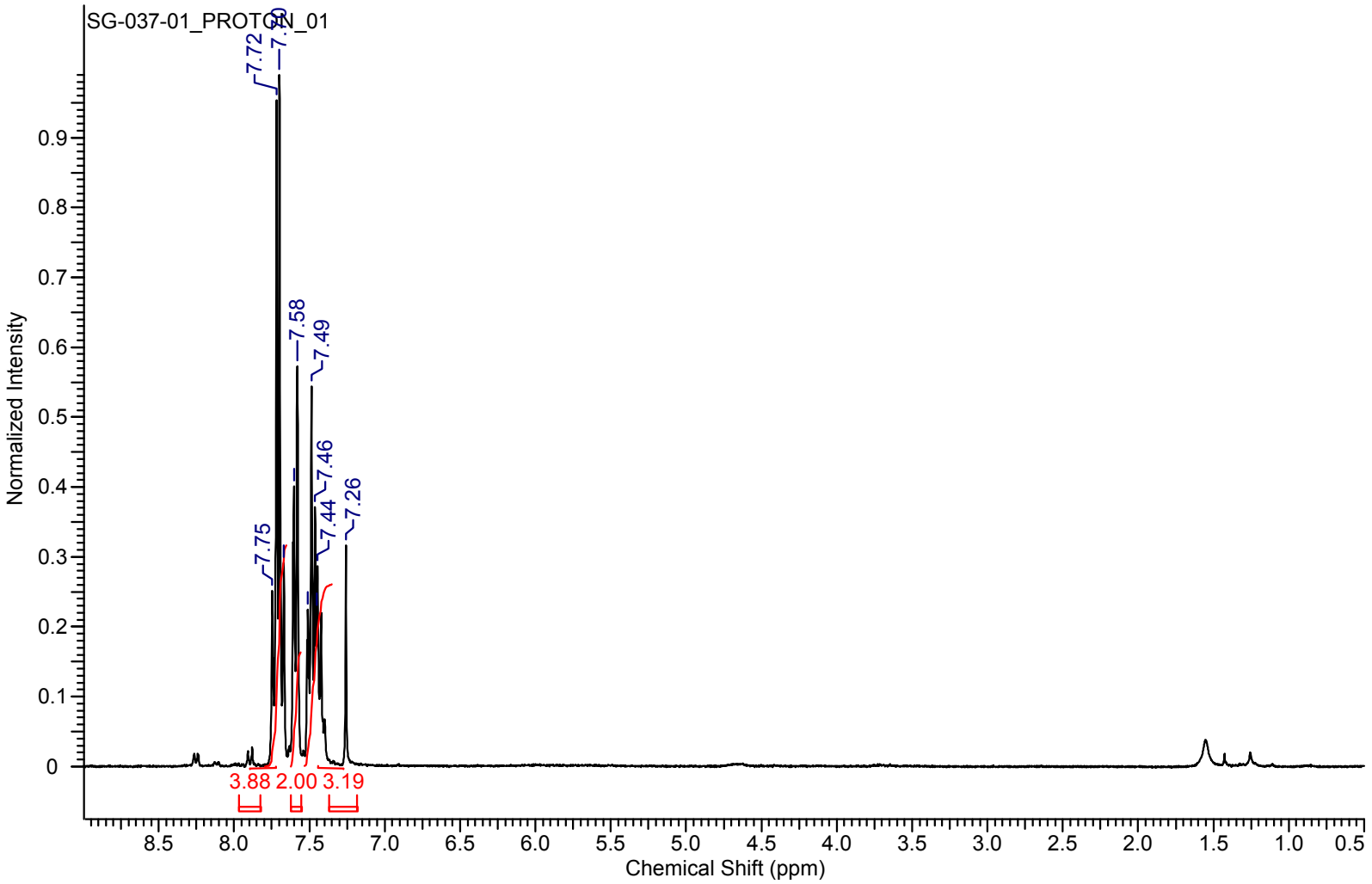
Compound **1h**

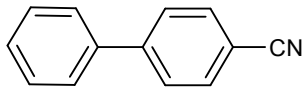
^{13}C NMR, 75 MHz, $CDCl_3$



Compound **1i**

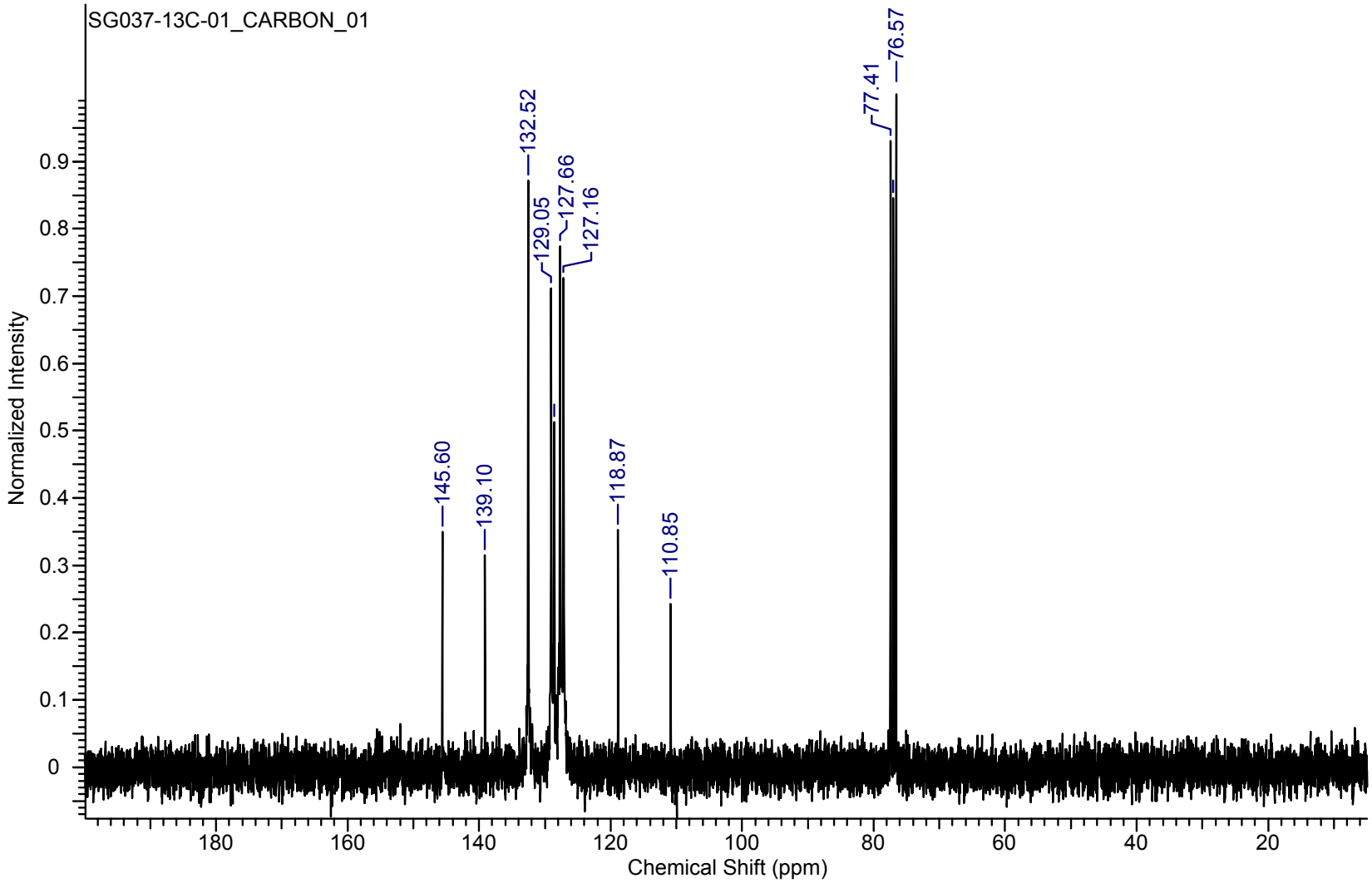
^{1}H-NMR, 300 MHz, $CDCl_3$





Compound **1i**

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


SG037-13C-01_CARBON_01
Normalized Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
145.60
139.10
132.52
129.05
127.66
127.16
118.87
110.85
77.41
76.57
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

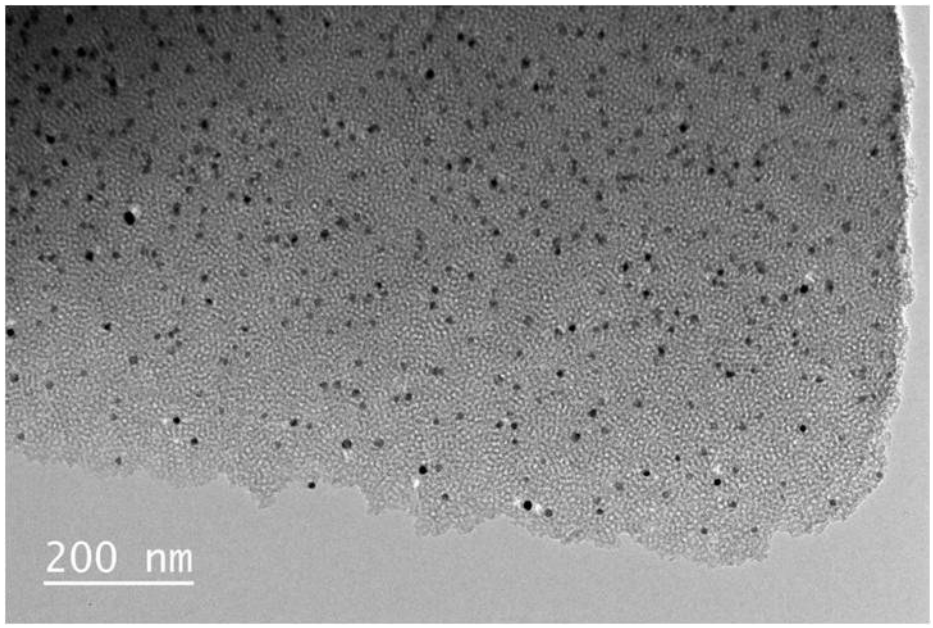


Figure S1.

[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.

[3] G. A. Edwards, M. A. Trafford, A. E. Hamilton, A. M. Buxton, M. C. Bardeaux, J. M. Chalker, *J. Org. Chem.* **2014,** 2094-2104

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