Photocatalytic Heck-Matsuda Reaction: Selective Arylation of *N*-vinyl- and *N*-allyl- lactams using $Pd_2(dba)_3$

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General Procedures: NMR spectra were recorded on a Bruker Advance III TM 400Hz (400.13 MHz), chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of quartets (dq), triplet (t), triplet of doublets (td), quartet (q), quintet (quin), and multiplet (m). Gas chromatography was carried out on a GC-2014 Shimadzu with flame ionization detector using a 30 meter, 0.25 mmID, 0.25 μm df Rtx®-5 column.

GC-FID Method Parameters: The carrier gas used was N_2, with a constant pressure of 100 kPa. The method ramp used starts at 70.00º C for 4 minutes, and then the temperature rises at a rate of 21.00º C per minute until it reaches 300.00º C, then it holds for 19 minutes.

	Rate (ºC/min)	Temperature (ºC)	Hold Time (min)
1	-	40.00	4.00
2	21	300.00	10.00

Materials and methods: Substrates (allylphthalimide),[1] (allylester)**,**[2] (allylisatin)**,**[3] and (allylcaprolactam)[4] were synthesized using literature procedures. The other *N*-Vinylamides or N-Allylamides were commercially availabe. Aryl diazonium tetrafluoroborate salts were prepared according to a literature procedure.[5]

Experimental procedure: $Pd_2(dba)_3$ (0.01 equiv) Ag_2CO_3 (0.10 equiv), and Aryldiazonium salt (4.0 equiv.) were weighed into a 15 mL Schlenk tube. The Schlenk tube was purged with Ar, and a solution of the corresponding enamide (0.15 mmol, 1.0 equiv) in Ethanol (2.0 mL) was added. The Schlenk tube was placed on a stir plate with two 26 W compact fluorescent light bulbs (one on either side of the tube). The reaction mixture was allowed to stir at room temperature for 3 h and the prodcut was purified by flash chromatography. In some cases further recrystallization in methanol was possible.

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Compound Characterization

(E)-1-(4-(trifluoromethyl)styryl)pyrrolidin-2-one 3a: dark yellow oil (37,7 mg, 94%, yield). ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 14.8 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 5.88 (d, *J* = 14.8 Hz, 1H), 3.68 (t, *J* = 7.2 Hz, 2H), 2.57 (t, *J* = 8.1 Hz, 2H), 2.23 – 2.16 (m, 2H). ^{13}C-NMR (101 MHz, Chloroform-*d*) δ 173.8, 140.3, 128.6(q, *J*= 33.1 Hz), 125.8 (q, *J*= 3.37 Hz), 124.3 (q, *J*= 280 Hz), 110.3, 45.3, 31.3, 17.6. (QTOF-MS/UHPLC) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}F_3NO$ 256.0944, found 256.0945.

(E)-1-(3-(4-(trifluoromethyl)phenyl)allyl)pyrrolidin-2-one 3d: dark yellow oil (38.3 mg, 95%, yield). ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 6.56 (d, *J* = 15.3 Hz, 1H), 6.24 (t, *J* = 10.3 Hz, 1H), 4.17 – 4.00 (m, 2H), 3.44 (d, *J* = 7.7 Hz, 2H), 2.45 (t, *J* = 7.6 Hz, 2H), 2.06 (t, *J* = 7.8 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 175.4, 139.9, 131.7, 129.8, (q, J= 32.2 Hz), 126.9, 126.7, 125.6 (q, *J*=3.0 Hz), 124.2 (q, *J*=271 Hz) 122.8, 120.1, 47.1, 44.7, 31.1, 17.9. (QTOF-MS/UHPLC) m/z: $[M+H]^+$ Calcd for $C_{14}H_{14}F_3NO$ 270.1100, found 270.1104.

1-cinnamylazepan-2-one 3e: yellow oil (27.2 mg, 79%, yield). ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.15 (m, 1H), 4.16 (d, *J* = 6.5 Hz, 2H), 3.39 – 3.30 (m, 2H), 2.65 – 2.51 (m, 2H), 1.77 – 1.67 (m, 4H), 1.63 (d, *J* = 5.2 Hz, 2H). ^{13}C-NMR (101 MHz, Chloroform-*d*) δ 175.8, 136.7, 132.7, 128.6, 127.7, 126.4,

125.2, 49.9, 48.7, 37.2, 30.00, 29.7, 28.5, 23.5. (QTOF-MS/UHPLC) m/z: $[M-H]^+$ Calcd for $C_{15}H_{19}NO$ 230.1539 (M+H), found 230.1538.

(E)-1-(3-(4-(trifluoromethyl)phenyl)allyl)azepan-2-one 3f: dark brown oil (31.2 mg, 70%, yield). ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.27-6.20 (m, 1H), 4.17 (d, *J* = 6.3 Hz, 2H), 3.33 (s, 2H), 2.56 (s, 2H), 1.71 (s, 4H), 1.61 (s, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 175.9, 140.3, 131.6, 129.5 (q, J=32.2 Hz), 128.2, 126.7, 125.7 (q, *J*= 3.9 Hz), 124.1 (q, *J*=273 Hz), 50.0, 49.1, 37.3, 30.1, 28.6, 23.6. (QTOF-MS/UHPLC) m/z: $[M-H]^+$ Calcd for $C_{16}H_{18}F_3NO$ 298.1413 (M+H), found 298.1416.

(E)-1-(3-(p-tolyl)allyl)azepan-2-one 3g: dark yellow oil (20.8 mg, 57%, yield). ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.09 (m, 1H), 4.15 (d, *J* = 6.5 Hz, 2H), 3.36 – 3.30 (m, 2H), 2.60 – 2.51 (m, 2H), 2.33 (s, 3H), 1.74 – 1.67 (m, 4H), 1.65 – 1.59 (m, 2H). ^{13}C-NMR (101 MHz, Chloroform-*d*) δ 175.9, 136.8, 131.8, 128.7, 127.8, 126.9, 125.4, 50.1, 48.8, 37.3, 30.1, 28.0, 22.9, 22.6. (QTOF-MS/UHPLC) m/z: $[M-H]^+$ Calcd for $C_{16}H_{21}NO$ 244.1696 (M+H), found 244.1694.

(E)-2-(4-(trifluoromethyl)styryl)isoindoline-1,3-dione 3h : pale gray solid (46.3 mg, 97% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.91-7.87 (m, 2H), 7.78-7.74 (m, 2H), 7.67 (d, J = 15 Hz, 1H), 7.55 (q, J =8.1 Hz, 4H), 7.41 (d, J = 15 Hz, 1H), ^{13}C-NMR (400 MHz, CDC_{l3}): δ 166.7, 140.2, 135.2, 132.1 (q, *J*=32 Hz), 126.2 (q, *J*= 3.8 Hz), 124.8 (q, *J*=271 Hz), 119.4, 118.9. (QTOF-MS/UHPLC) m/z: $[M+H]^+$ Calcd for $C_{17}H_{10}F_3NO_2$ 318.0736, found 318.0736.

(E)-2-(4-methylstyryl)isoindoline-1,3-dione 3j: pale gray solid (19.8 mg, 50% yield). ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.90 (m, 2H), 7.76 (m, 2H), 7.62 (d, *J* = 15.1 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 15.1 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 2.36 (s, 3H).^{13}C-NMR (101 MHz, $CDCl_3$) δ 166.6, 137.7, 134.6, 133.2, 131.9, 129.6, 126.3, 123.8, 120.5, 116.9, 31.1, 21.4. (QTOF-MS/UHPLC) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}NO_2$ 264.1019, found 264.102.

Methyl (E)-2-(1,3-dioxoisoindolin-2-yl)-3-phenylacrylate 3k: crystalline colorless solid (32.8 mg, 71%, yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.93-7.91 (m, 2H), 7.80-7.78 (m, 2H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.33-7.26 (m, 3H), 3.83 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 166.9, 164.0, 143.3, 133.5, 132.0, 131.3, 129.1, 128.9, 122.4, 121.0, 120.1, 53.0. (QTOF-MS/UHPLC) m/z: $[M+H]^+$ Calcd for $C_{18}H_{13}NO_4$ 308.0917, found 308.0910.

Methyl (E)-2-(1,3-dioxoisoindolin-2-yl)-3-(p-tolyl)acrylate 3l: a white solid (43.7 mg, 91%, yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.08 (s,1H), 7.93-7.91 (m, 2H), 7.80-7.78 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.82 (s, 3H), 2.30 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.0, 164.2, 143.2, 139.9, 133.5, 129.9, 129.6, 129.7, 127.6, 124.5, 119.1, 52.9, 21.6. (QTOF-MS/UHPLC) m/z: $[M-H]^+$ Calcd for $C_{19}H_{15}NO_4$ 356.0684 (M+Cl), found 354.9786.

(E)-2-(3-(4-(trifluoromethyl)phenyl)allyl)isoindoline-1,3-dione 3m: gray solid (45.8 mg, 92% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.88-7.86 (m, 2H), 7.74-7.73 (m, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.38-6.31 (m, 1H), 4.47 (d, *J* = 6.5 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.0, 139.8, 134.2, 132.4, 132.3, 130.0 (q, J=32.8 Hz), 126.8, 125.7, 125.7, 125.6, 124.8 (q, J=282 Hz), 123.6, 39.6. (QTOF-MS/UHPLC) m/z: $[M+H]^+$ Calcd for $C_{17}H_{10}F_3NO_2$ 332.0893, found. 332.0893

2-cinnamylisoindoline-1,3-dione 3n: dark gray solid (34,0 mg, 86% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.86-7.85 (m, 2H), 7.77-7.71 (m, 2H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.23-7.20 (m, 1H), 6.68-6.4 (d, *J* = 15,80 Hz, 1H), 6.29-6.22 (m, 1H), 4.45 (d, *J* = 6.5 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 166.1, 136.4, 133.9, 132.5, 131.6, 128.6, 127.9, 122.9, 39.8. (QTOF-MS/UHPLC) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}NO_2$ 264.1019, found 264.1017.

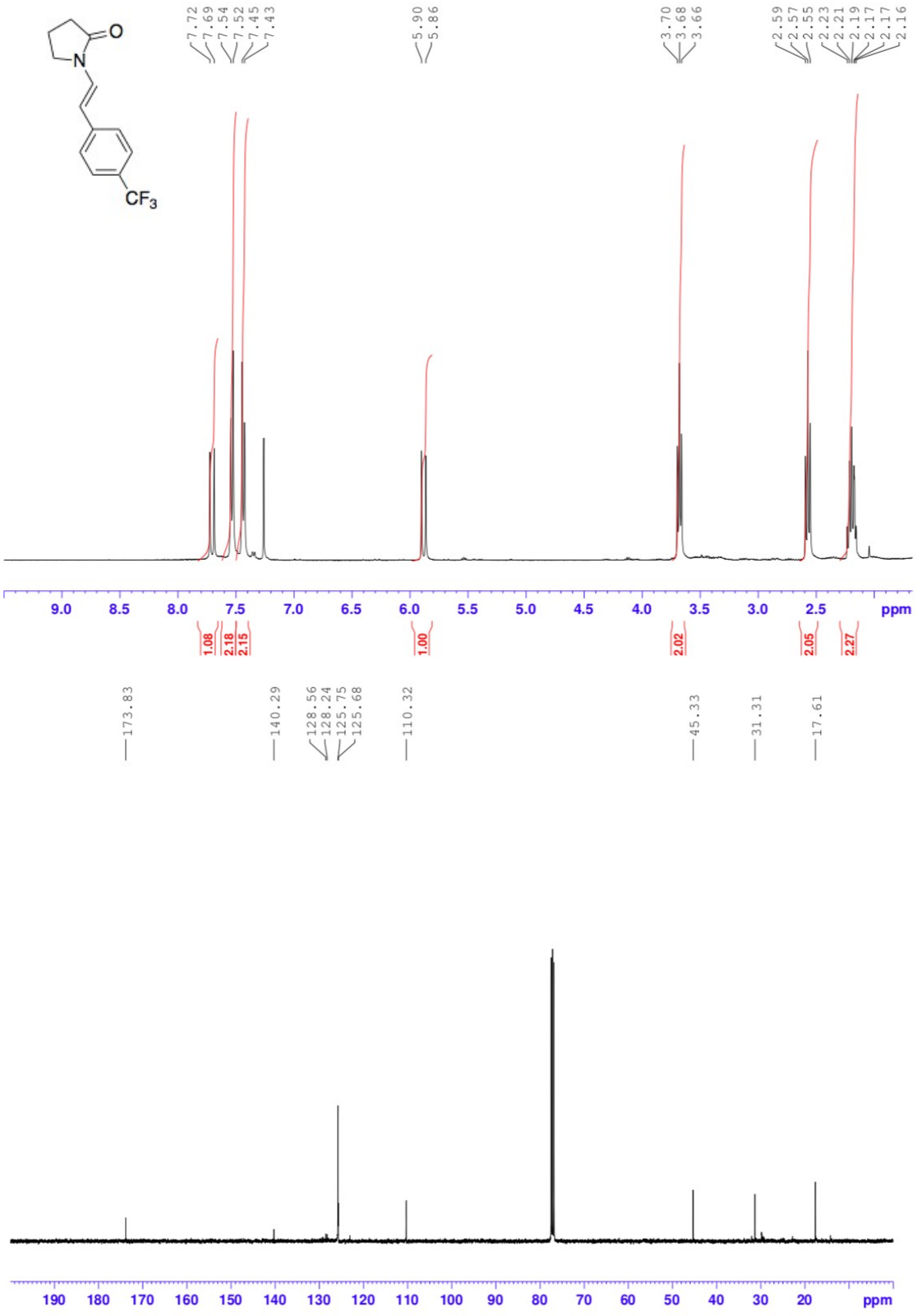
(E)-2-(3-(p-tolyl)allyl)isoindoline-1,3-dione 3o: white solid (28.9 mg, 73% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.87-7.85 (m, 2H), 7.72-7.70 (m, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.63 (d, *J* = 15,8 Hz, 1H), 6.23-6.16 (m, 1H), 4.43 (d, *J* = 6.5 Hz, 2H), 2.31 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.1, 137.9, 133.0, 131.1, 129.5, 129.4, 126.6, 126.5, 122.8, 121.8, 39.9, 21.3. (QTOF-MS/UHPLC) m/z: $[M+H]^+$ Calcd for $C_{18}H_{15}NO_2$ 278.1176, found 278.1185.

(E)-1-(3-(4-(trifluoromethyl)phenyl)allyl)indoline-2,3-dione 3p: dark brown solid (47,3 mg, 94%, yield). ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.15 (t, *J* = 7.5, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 16.0 Hz, 2H), 6.32 – 6.28 (m, 1H), 4.56 (d, *J* = 5.8 Hz, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 183.2, 158.1, 150.8, 139.3, 138.6, 132.6, 126.8, 125.8 (q, *J*= 4.4 Hz), 124.3 (q, *J*=273 Hz), 124.3 (q, *J*=32.5 Hz), 117.9, 110.8, 42.1. (QTOF-MS/UHPLC) m/z: $[M-H]^+$ Calcd for $C_{18}H_{12}F_3NO_2$ 332.0893 (M+H), found 332.0897.

(E)-1-(3-(p-tolyl)allyl)indoline-2,3-dione 3q: bright orange solid (26.2 mg, 83%, yield). ^{1}H-NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.13-7.09 (m, 3H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 15.5 Hz, 2H), 6.14 – 6.10 (m, 1H), 4.52 (d, *J* = 6.1 Hz, 2H), 2.33 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 183.3, 157.9, 150.9, 138.3, 132.6, 131.0, 129.3, 128.3, 125.7, 124.9, 122.7, 121.1, 117.9, 110.9, 42.3, 29.7. (QTOF-MS/UHPLC) m/z: $[M-H]^+$ Calcd for $C_{18}H_{15}NO_2$ 278.1176 (M+H), found 278.1174.

1-cinnamylindoline-2,3-dione 3r: bright orange solid (37,1 mg, 94%, yield).^{1}H-NMR (400 MHz, Chloroform-*d*) 7.63 (d, *J*=7.39 Hz, 1H), 7.56 (t, 1H), 7.33 (m, 4H), 7.27 (m, 1H), 7.12 (t, 1H), 6.96 (d, *J*=7.93 Hz, 2H), 6.68 (d, *J*=15.88 Hz, 2H), 6.20 (m, 1H), 4.53 (d, *J*=5.89 Hz, 1H). ^{13}C-NMR (101 MHz, Chloroform-*d*) δ 183.4, 158.1, 151.0, 138.5, 135.9, 134.2, 128.6, 126.0, 123.6, 121.8, 117.8, 111.0, 42.3. (QTOF-MS/UHPLC) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}NO_2$ 264.1019, found 264.1017.

Compound 3a (^{1}H-NMR 400 MHz, $CDCl_3$; $^{13}C\{^{1}H\}$-NMR 101 MHz)



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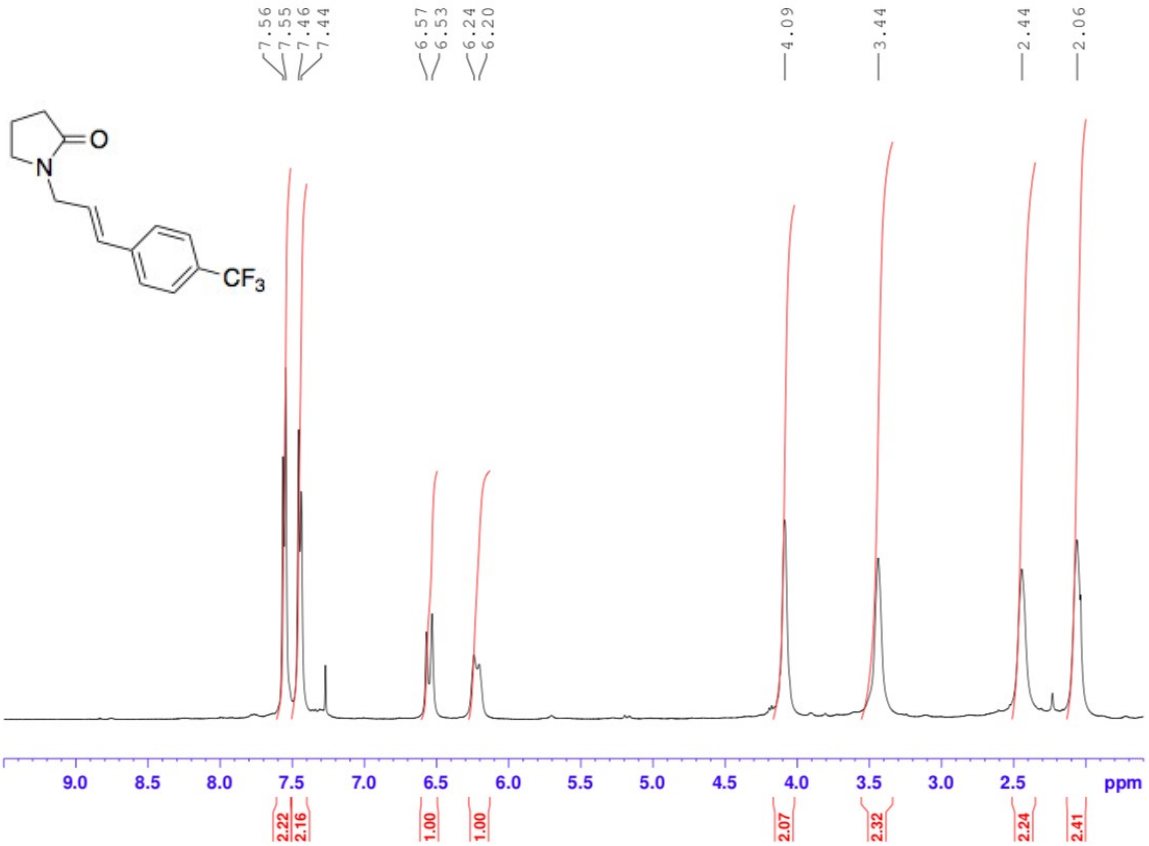
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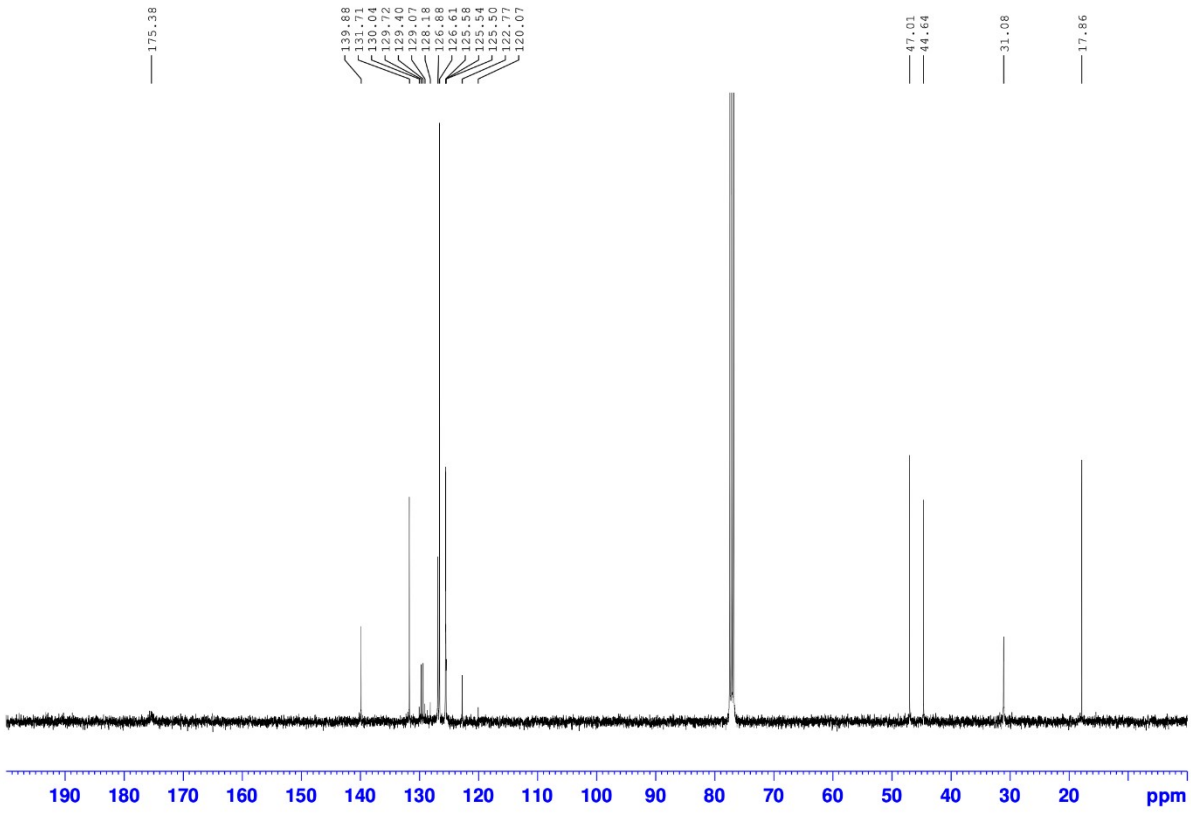
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31.08
17.86
190
180
170
160
150
140
130
120
110
100
90
80
70
60
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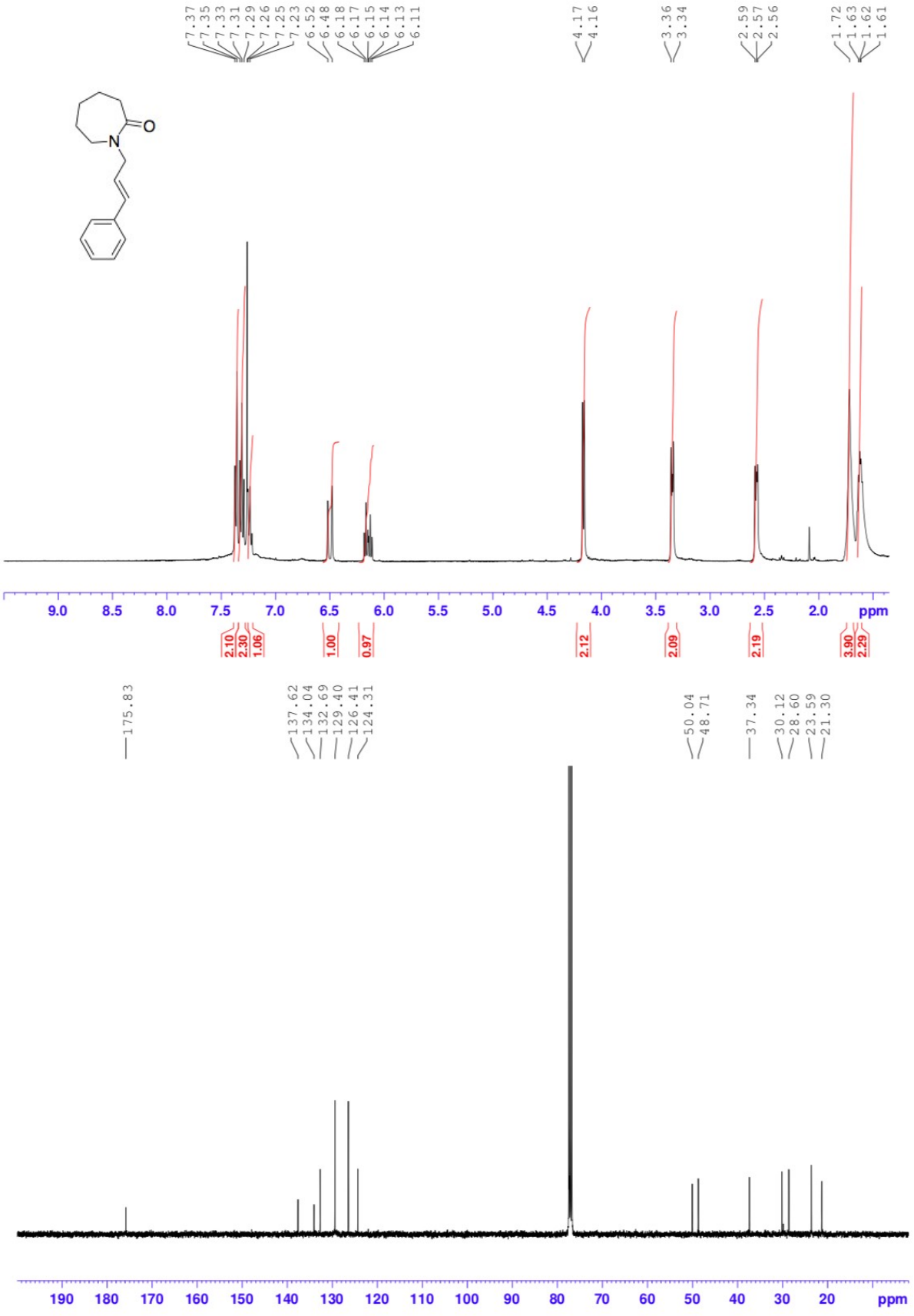
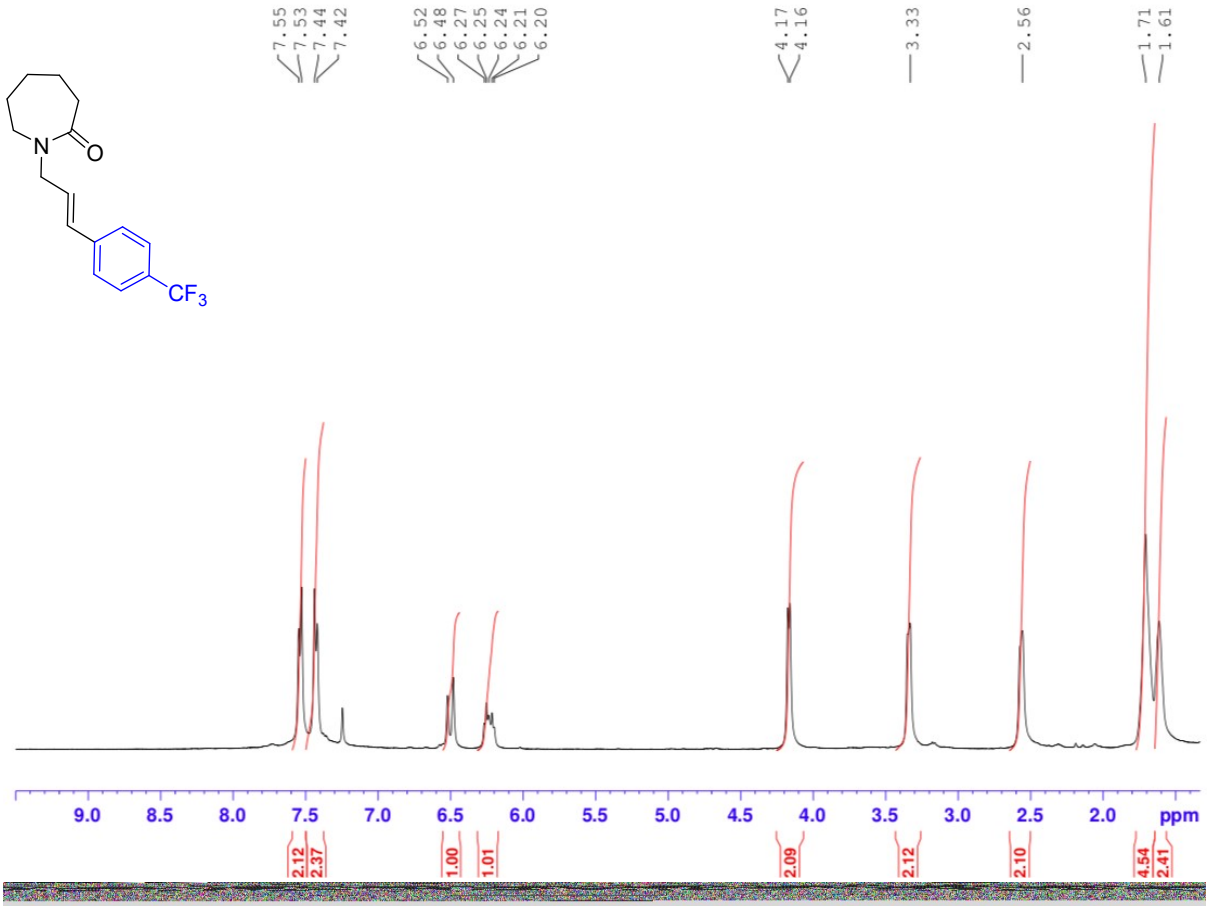
40
30
20
ppm

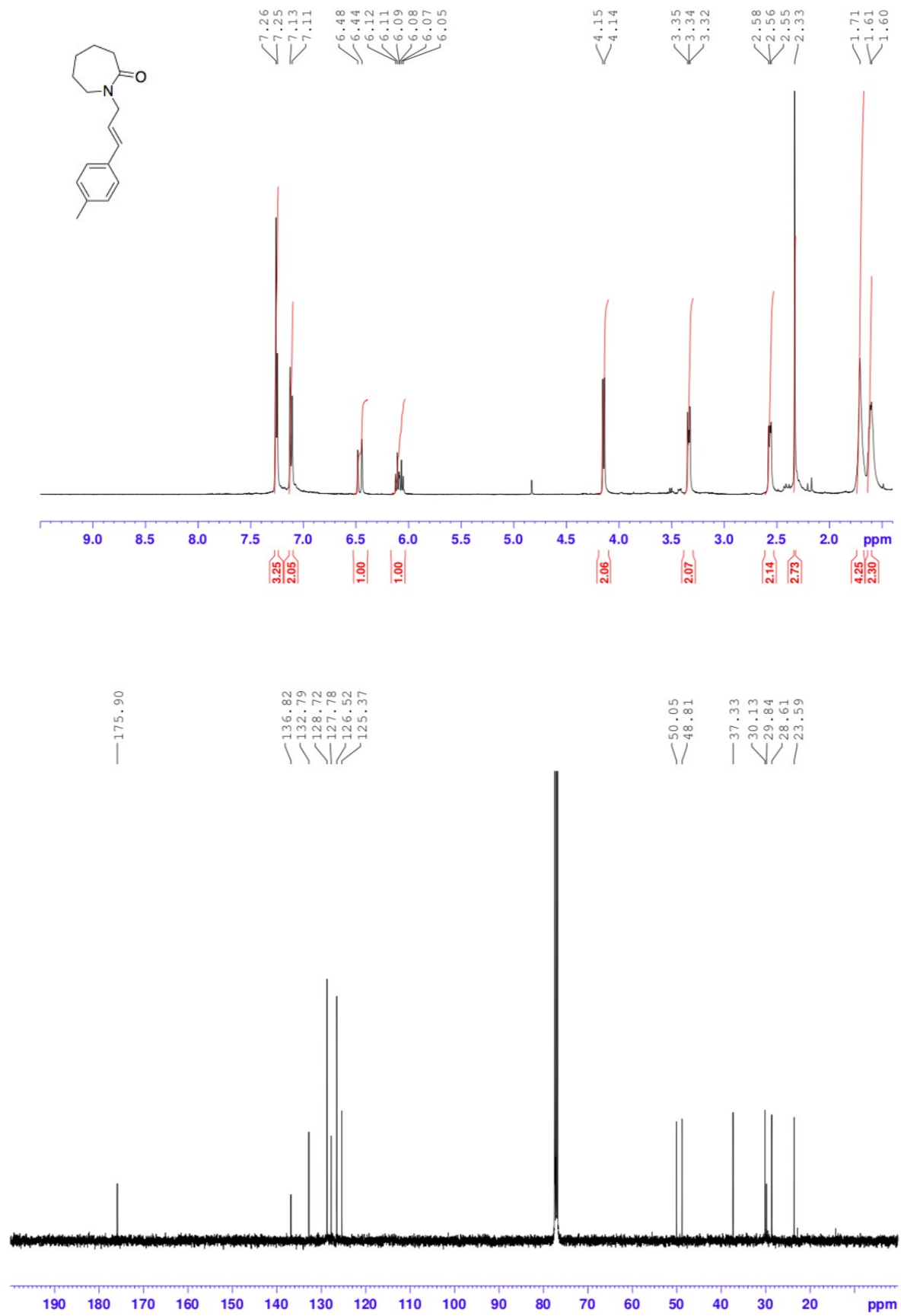
Compound 3e (^{1}H-NMR 400 MHz, $CDCl_3$; $^{13}C\{^{1}H\}$-NMR 101 MHz)



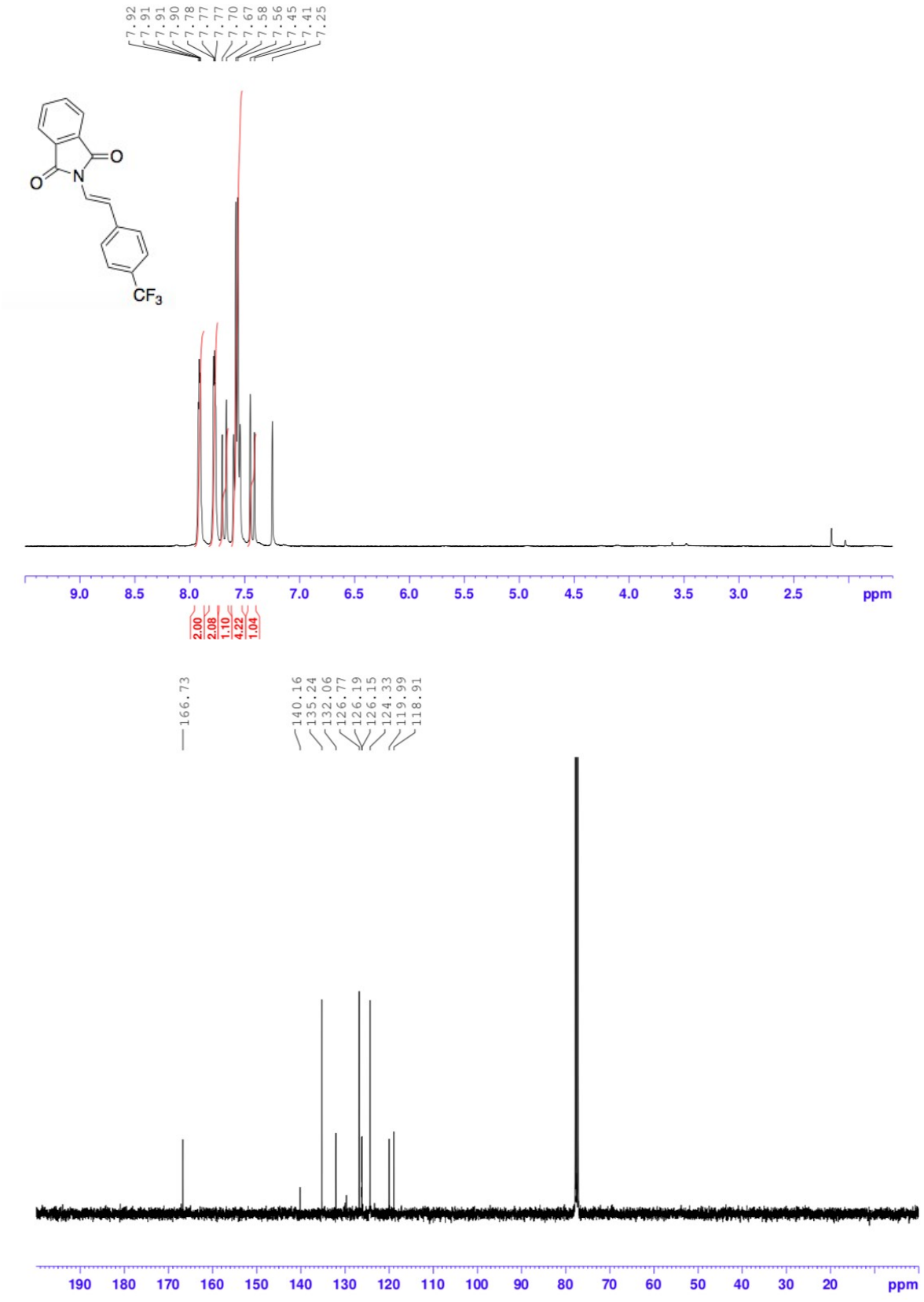
Compound 3f (^{1}H-NMR 400 MHz, $CDCl_3$; $^{13}C\{^{1}H\}$-NMR 101 MHz)



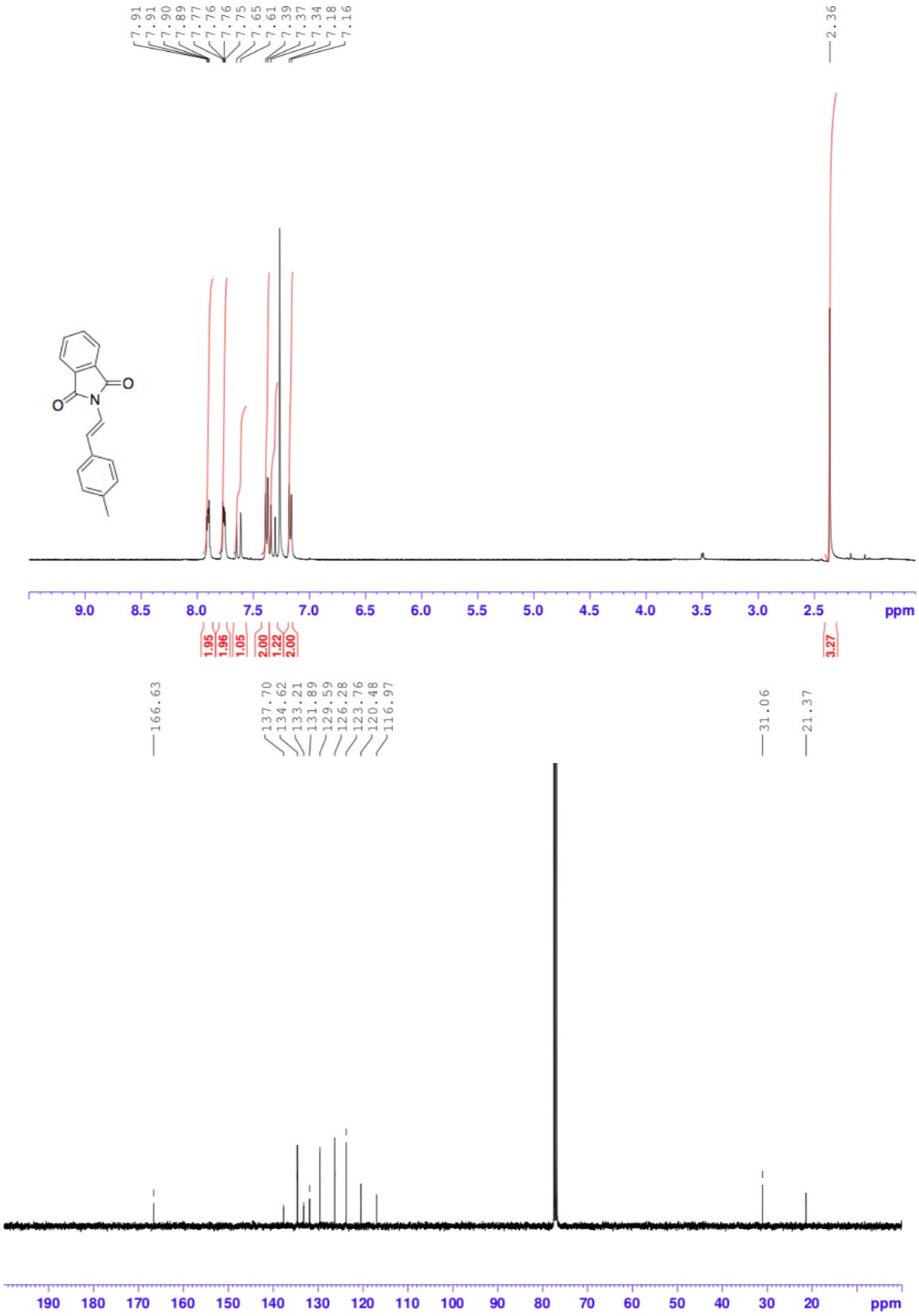
Compound 3g (^{1}H-NMR 400 MHz, $CDCl_3$; $^{13}C\{^{1}H\}$-NMR 101 MHz)



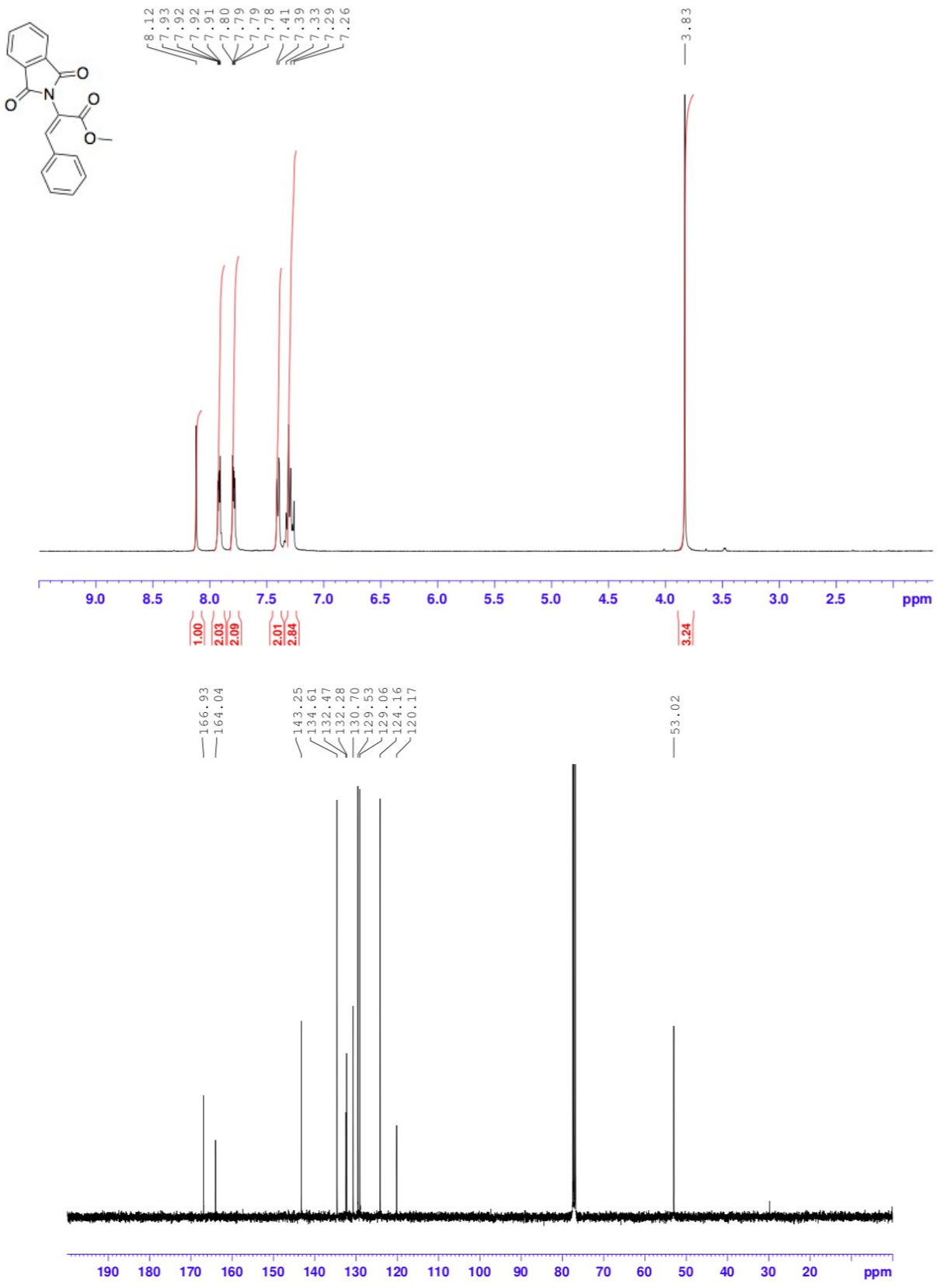
Compound 3h (^{1}H-NMR 400 MHz, $CDCl_3$; $^{13}C\{^{1}H\}$-NMR 101 MHz)



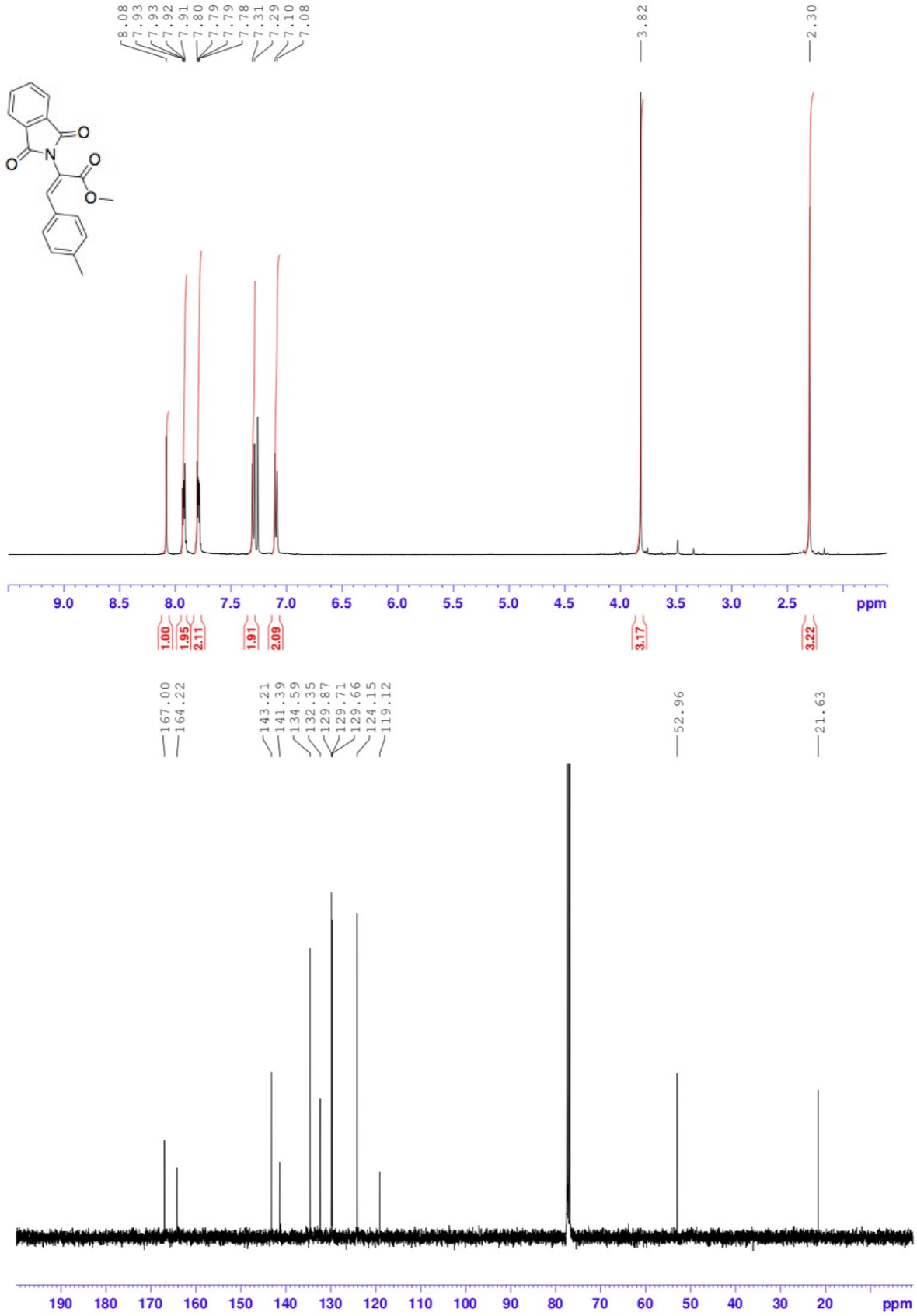
Compound 3j (^{1}H-NMR 400 MHz, $CDCl_3$; $^{13}C\{^{1}H\}$-NMR 101 MHz)



Compound 3k (^{1}H-NMR 400 MHz, $CDCl_3$; $^{13}C\{^{1}H\}$-NMR 101 MHz)



Compound 3l (^{1}H-NMR 400 MHz, $CDCl_3$; $^{13}C\{^{1}H\}$-NMR 101 MHz)



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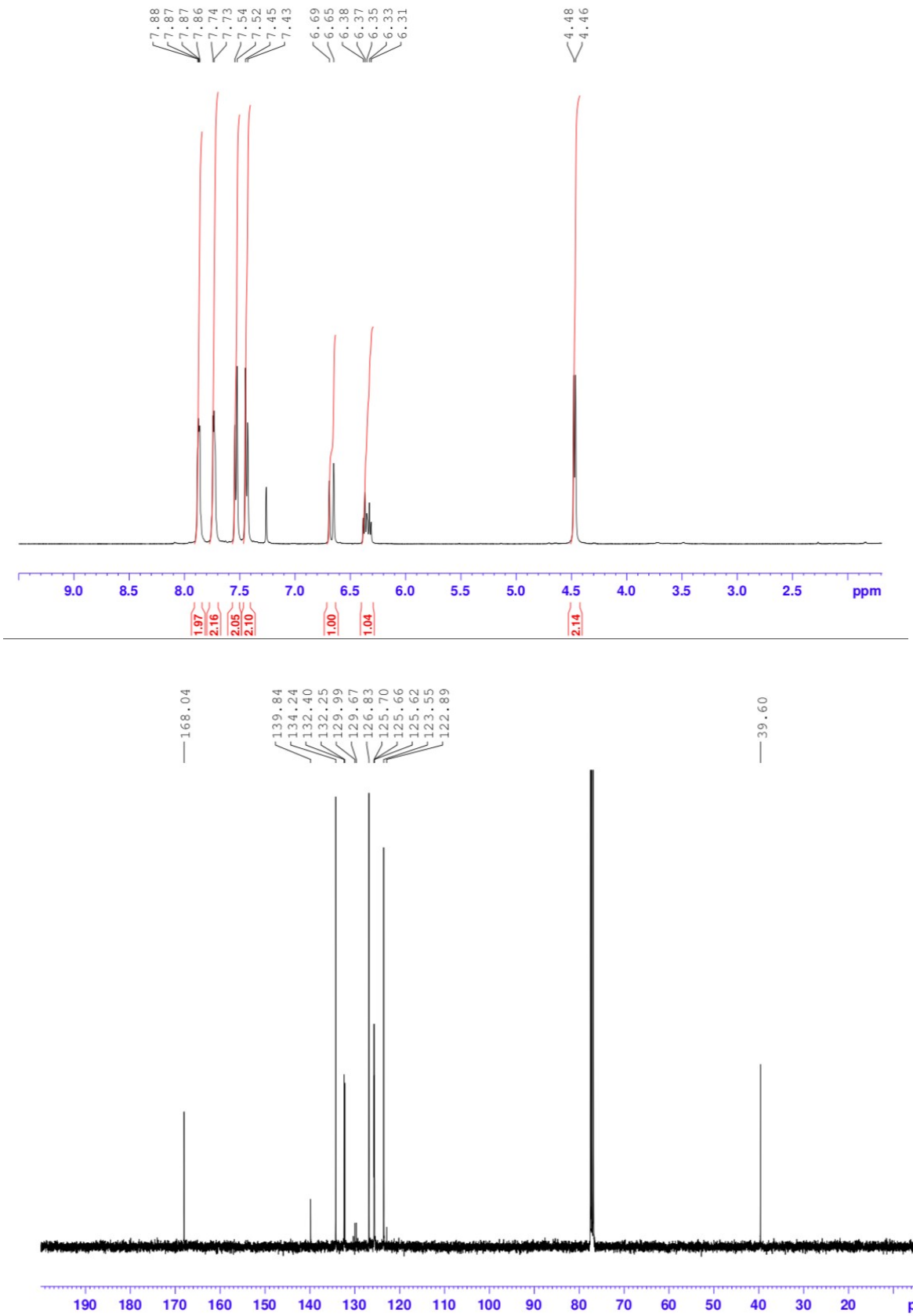

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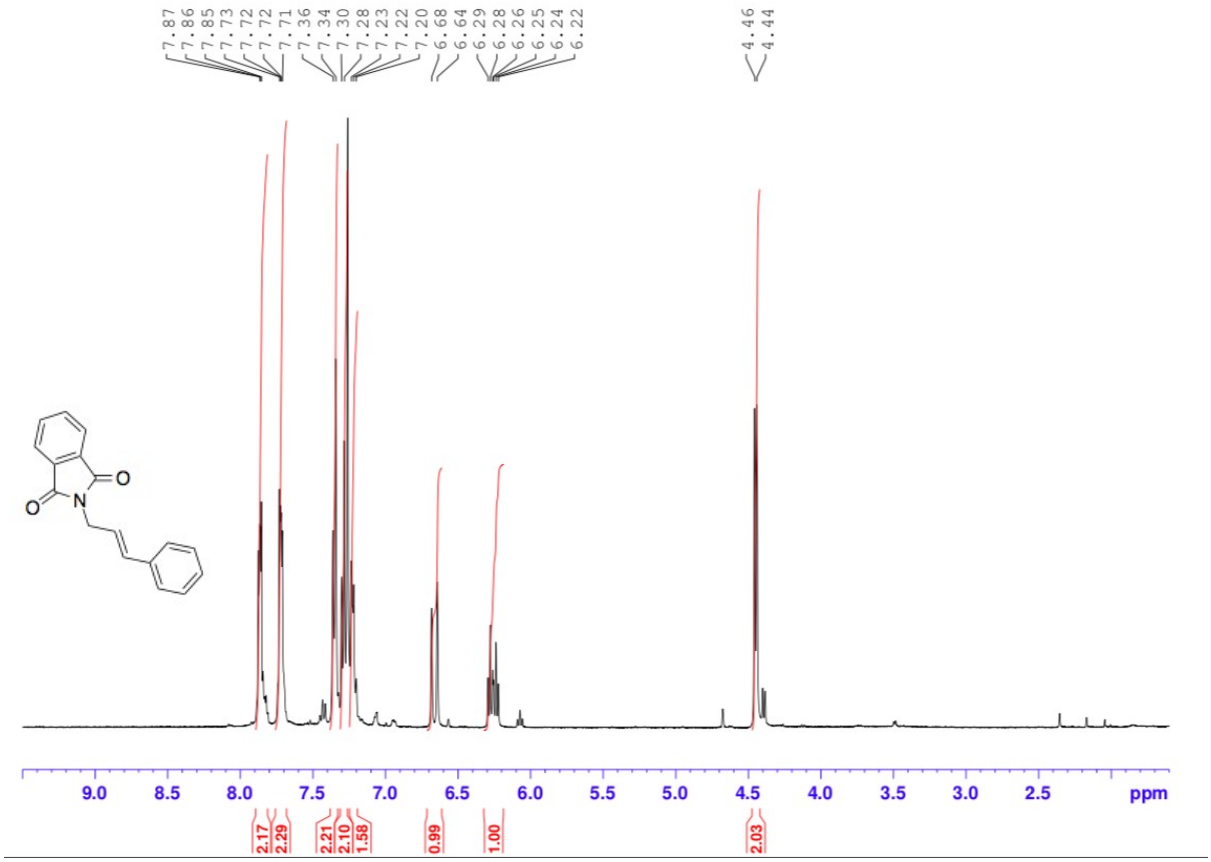
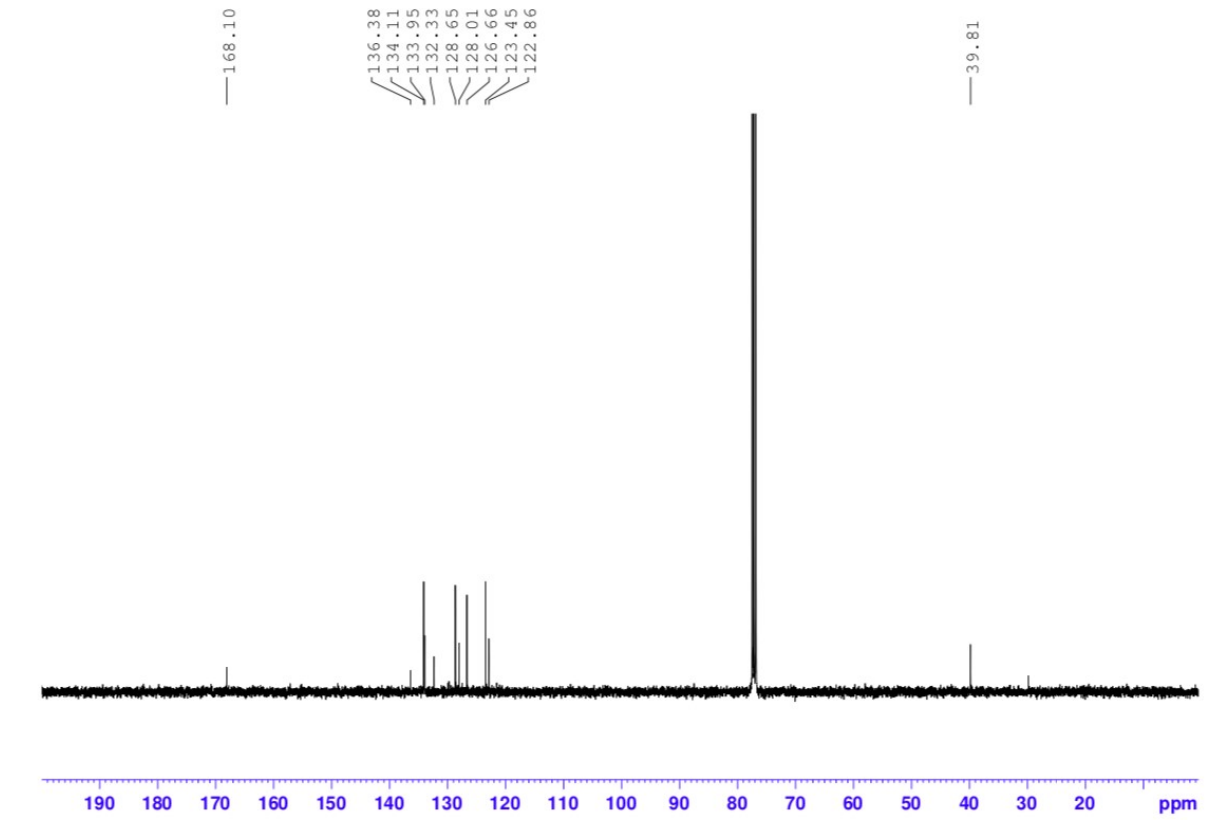
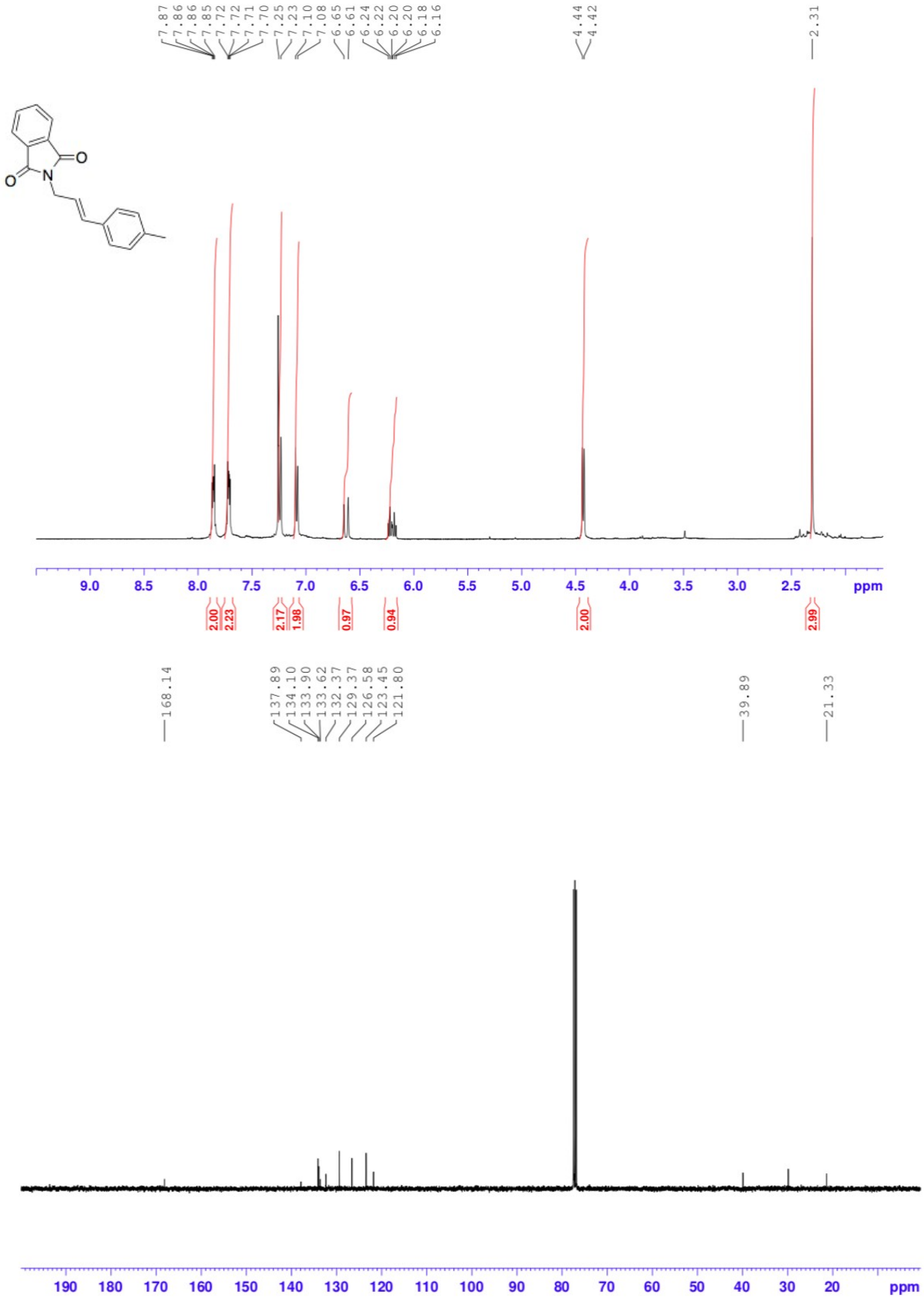
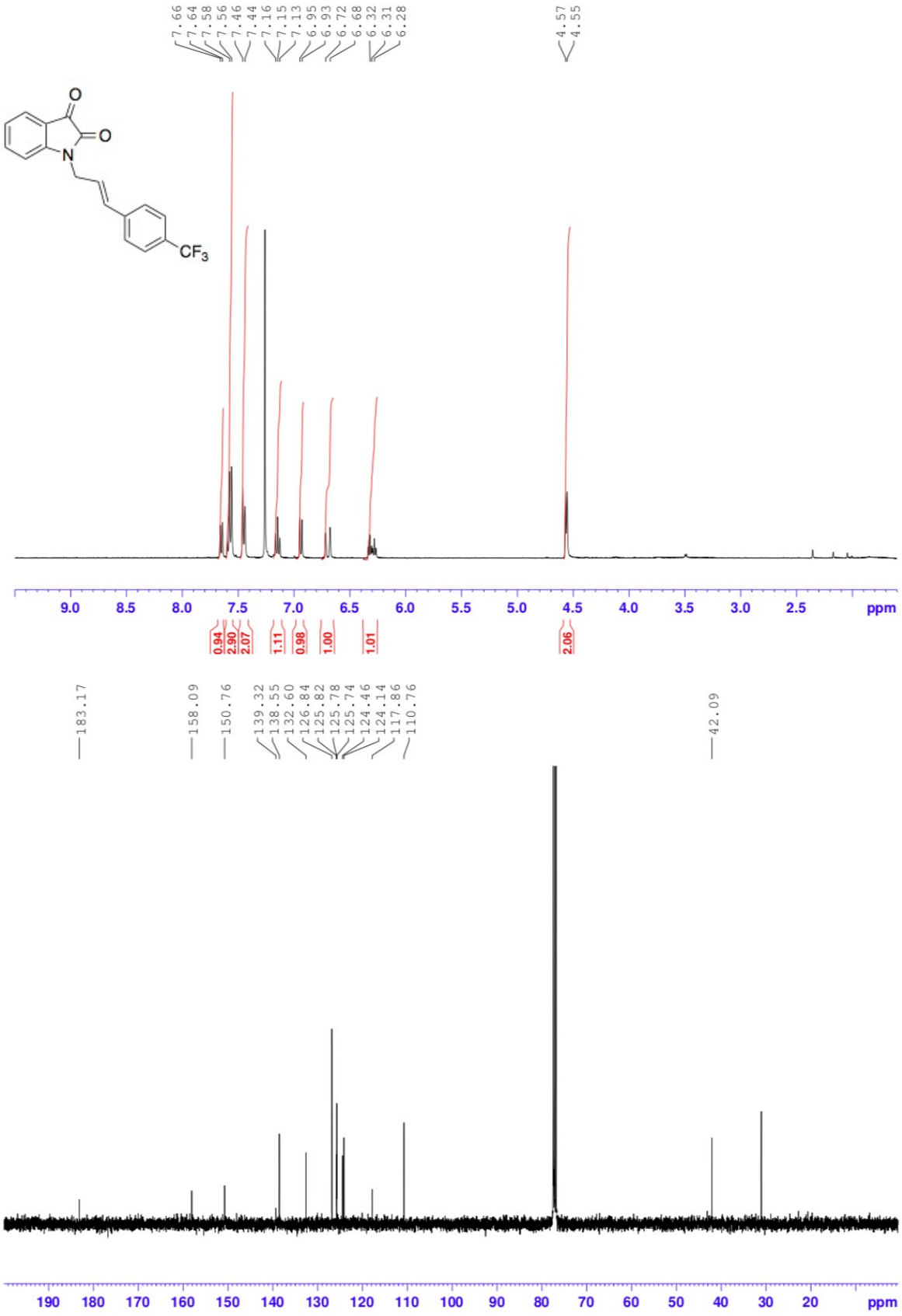




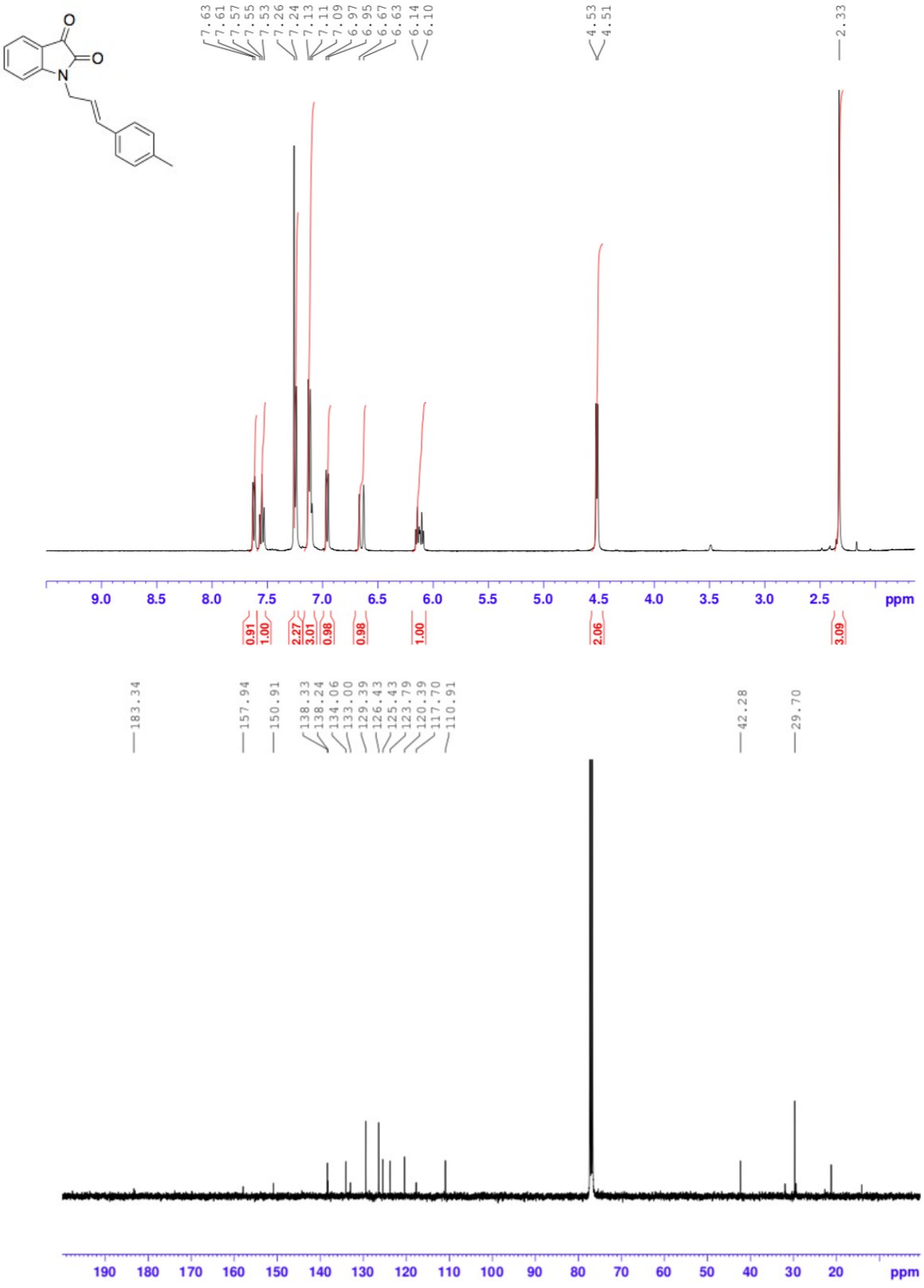
Compound 3o (^{1}H-NMR 400 MHz, $CDCl_3$; $^{13}C\{^{1}H\}$-NMR 101 MHz)



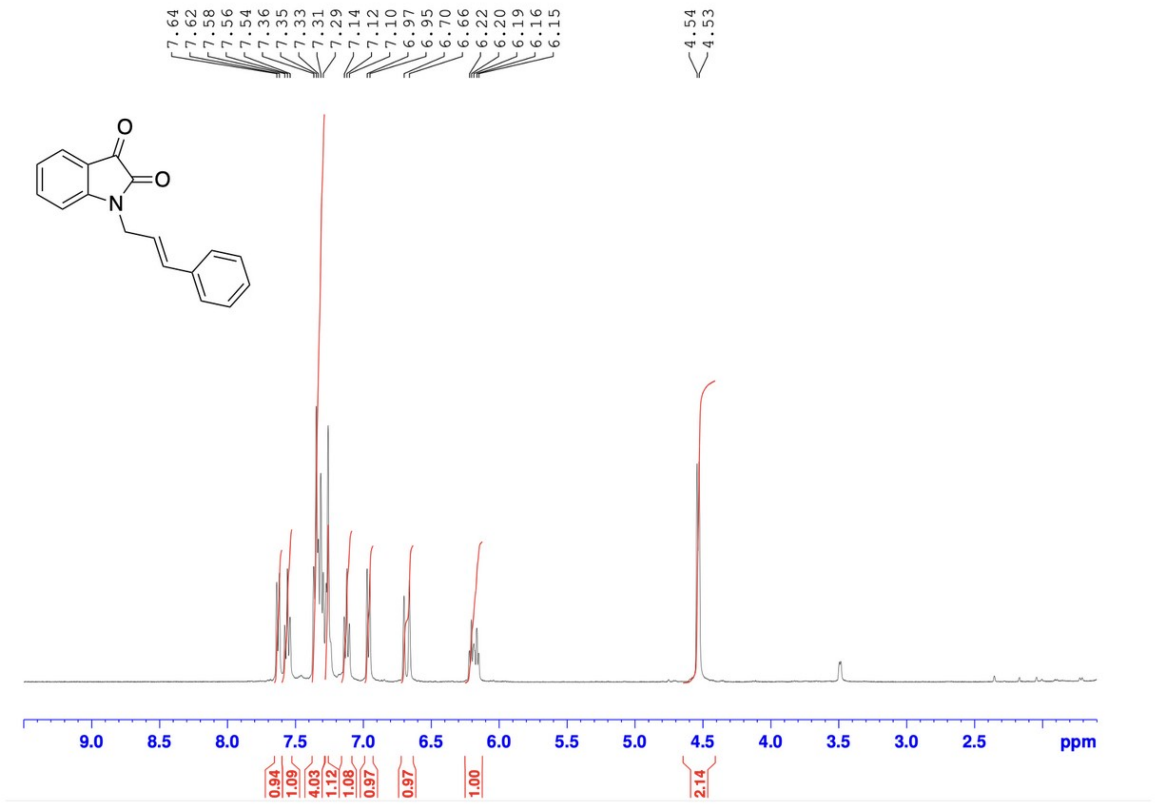
Compound 3p (^{1}H-NMR 400 MHz, $CDCl_3$; $^{13}C\{^{1}H\}$-NMR 101 MHz)



Compound 3q (^{1}H-NMR 400 MHz, $CDCl_3$; $^{13}C\{^{1}H\}$-NMR 101 MHz)



Compound 3r (^{1}H-NMR 400 MHz, $CDCl_3$; $^{13}C\{^{1}H\}$-NMR 101 MHz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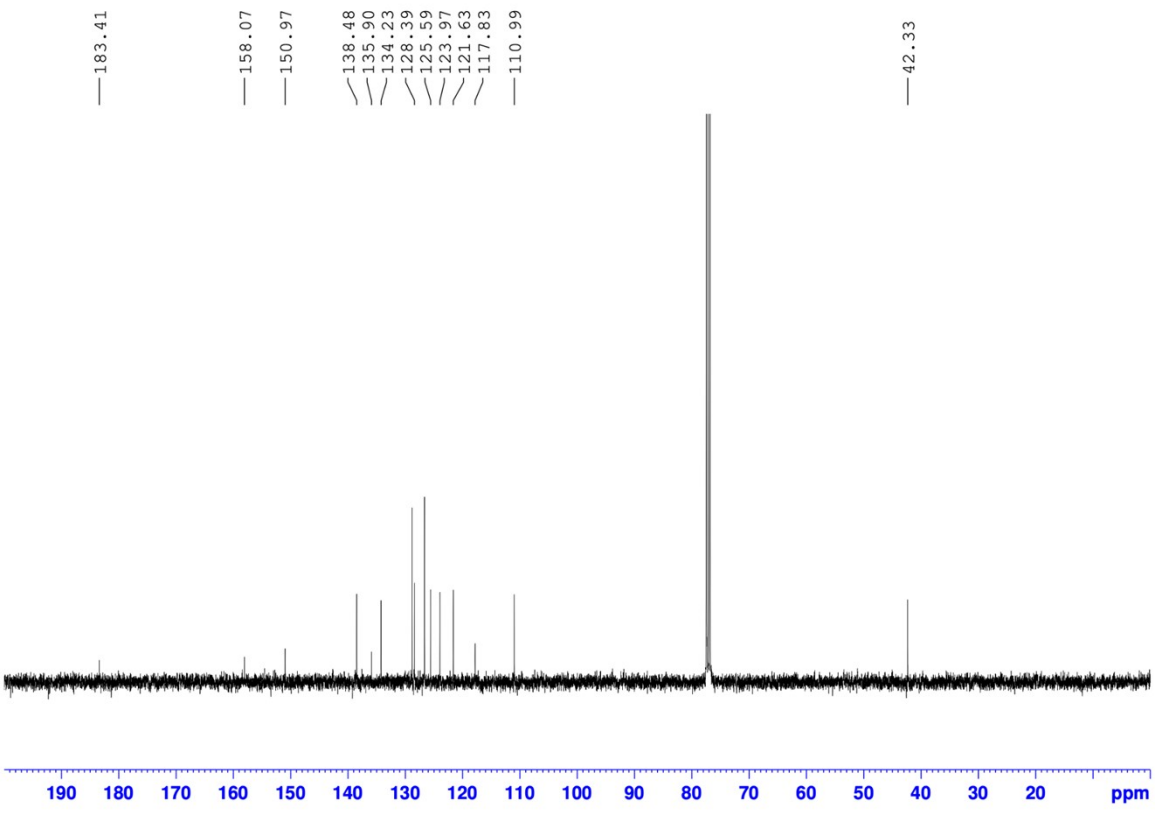
7.58
7.56
7.54
7.36
7.35
7.33
7.31
7.29
7.14
7.12
7.10
6.97
6.95
6.70
6.66
6.22
6.20
6.19
6.16
6.15
4.54
4.53
O
O
N
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
0.94
1.09
4.03
1.12
1.08
0.97
0.97
1.00
2.14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190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm