Supporting Information

Practical photocatalytic hydroalkylation of alkenes with chloroacetates mediated by formate ion

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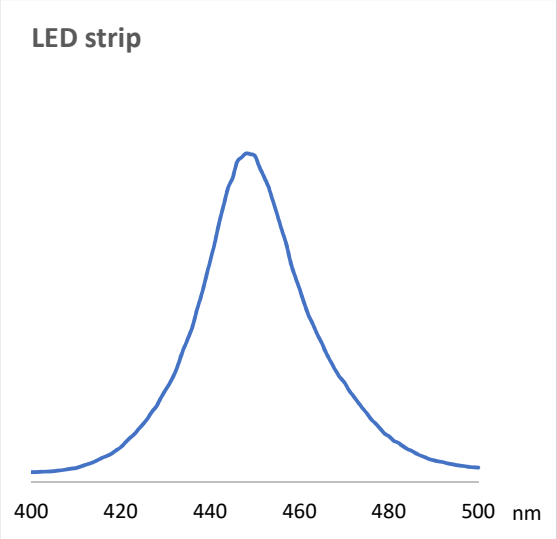
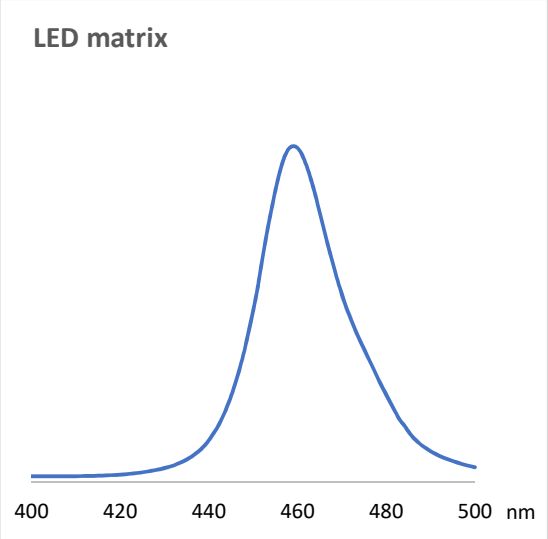
General methods

All reactions were performed under an argon atmosphere. DMSO was distilled from CaH_2 and stored over MS 4Å. Column chromatography was carried out employing silica gel (230−400 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or acidic aq. KMnO4 solution. High resolution mass-spectra (HRMS) were measured using electrospray ionization (ESI) and a time-of-flight (TOF) mass analyzer (Bruker MicrOTOF II). The measurements were done in a positive-ion mode (interface capillary voltage −4500 V) or in a negative-ion mode (3200 V); the mass ranged from m/z 50 to m/z 3000. Photo-induced reactions were performed in Duran culture tubes (Roth cat. no K248.1, outside diameter 12 mm). For irradiation, a strip of 450 nm light emitting diodes (SMD 2835−120 LED 1 M Blue, 12 V, 24 W/m; 50 cm strip length; operated at 10W) or 450 nm COB LED matrix Hontiey (29-32V, 3000mA, 100W; operated at 30W or 60W). The distance between the reaction vessel and diodes was about 5 mm. The reaction tube was placed in a glass jacket and cooled with water at room temperature. The reaction setup was used as previously described.[1]

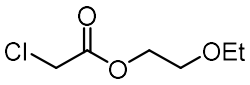
Emission spectra of used LED strip and LED matrix:





Starting materials

All commercially available reagents were purchased from Acros Organics, ABCR or P&M Invest. Alkenes were distilled prior to use. Reagents shown below were synthesized according to literature procedures:



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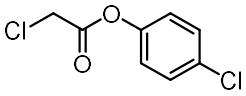

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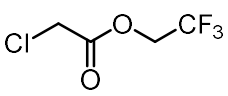

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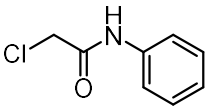

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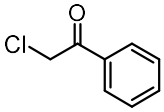

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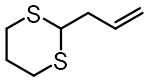

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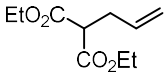

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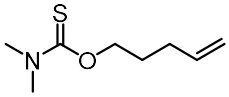

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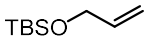

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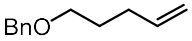

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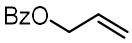

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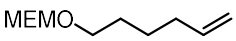

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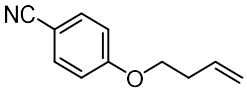

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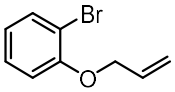

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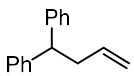

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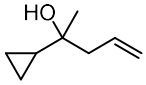

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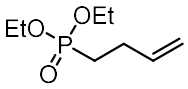

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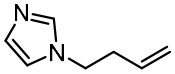

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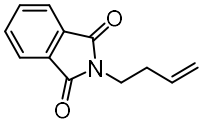

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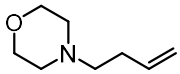

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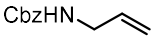

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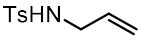

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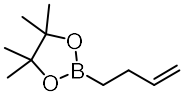

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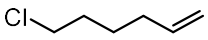

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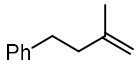

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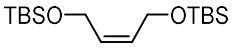

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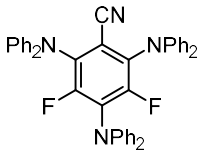
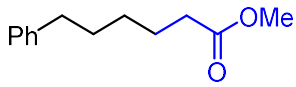


3DPA2FBN[26]

General procedure

A test tube was evacuated and filled with argon. Then, DMSO (1 mL), sodium formate (68 mg, 1mmol, 2 equiv), alkene (0.5 mmol, 1 equiv), organic chloride (1 mmol, 2 equiv), 2-methylpropane-2-thiol (6 µL, 0.05 mmol, 0.1 equiv), 3DPA2FBN (1.6 mg, 0.0025 mmol, 0.5 mol %) were added. The tube was screw-capped and irradiated with 455 nm (10W) LED strip for 16 hours. The reaction was quenched with water (5 mL) and extracted with hexane (3×1.5 mL). The combined organic layers were filtered through a short pad of Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified by column chromatography.

Methyl 6-phenylhexanoate (3a)[27]

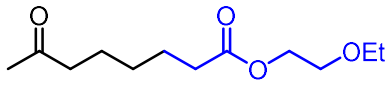


Yield: 85 mg (83%). Colorless oil. Chromatography: hexanes/EtOAc, 15/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 2H), 7.29 – 7.20 (m, 3H), 3.73 (d, *J* = 3.4 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 2.38 (t, *J* = 7.5 Hz, 2H), 1.73 (h, *J* = 7.3 Hz, 4H), 1.51 – 1.39 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 174.2, 142.5, 128.4 (d, *J* = 8.5 Hz), 125.7, 51.5, 35.8, 34.0, 31.1, 28.8, 24.8.

2-Ethoxyethyl 7-oxooctanoate (3b)



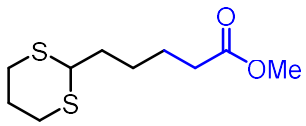
Yield: 97 mg (84%). Colorless oil. Chromatography: hexanes/EtOAc, 2/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.21 – 4.10 (m, 2H), 3.56 (t, *J* = 5.0 Hz, 2H), 3.47 (q, *J* = 7.0 Hz, 2H), 2.37 (t, *J* = 7.3 Hz, 2H), 2.28 (t, *J* = 7.4 Hz, 2H), 2.07 (s, 3H), 1.65 – 1.45 (m, 4H), 1.33 – 1.19 (m, 2H), 1.15 (t, *J* = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 208.8, 173.6, 68.4, 66.6, 63.5, 43.4, 34.0, 29.9, 28.6, 24.6, 23.4, 15.1.

HRMS (ESI): calcd for $C_{12}H_{22}O_4Na$ [M+Na] 253.1410, found 253.1414.

Methyl 5-(1,3-dithian-2-yl)pentanoate (3c)[28]



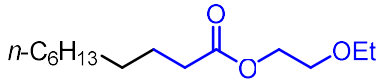
Modified General procedure: **2a** (176 µL, 1.5 mmol, 3 equiv), HCO_2Na (136 mg, 1.5 mmol, 3 equiv)

Yield: 81 mg (80%). Colorless oil. Chromatography: hexanes/EtOAc, 6/1

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.00 (t, *J* = 6.9 Hz, 1H), 3.62 (s, 3H), 2.90 – 2.70 (m, 4H), 2.28 (t, *J* = 7.3 Hz, 2H), 2.13 – 1.64 (m, 4H), 1.67 – 1.41 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 173.9, 51.5, 47.3, 35.1, 33.8, 30.5, 26.1, 24.5.

2-Ethoxyethyl decanoate (3d)



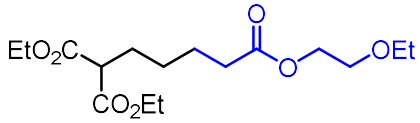
Yield: 101 mg (83%). Colorless oil. Chromatography: hexanes/EtOAc, 10/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.19 (t, *J* = 4.8 Hz, 2H), 3.59 (t, *J* = 4.8 Hz, 2H), 3.50 (q, *J* = 7.1 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.64 – 1.53 (m, 2H),1.36 – 1.17 (m, 15H), 0.90 – 0.77 (m, 3H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 174.0, 68.5, 66.7, 63.6, 34.3, 32.0, 29.5, 29.4, 29.3, 29.2, 25.0, 22.8, 15.2, 14.2.

HRMS (ESI): calcd for $C_{14}H_{28}O_3Na$ [M+Na] 267.1931, found 267.1928.

5-(2-Ethoxyethyl) 1,1-diethyl pentane-1,1,5-tricarboxylate (3e)



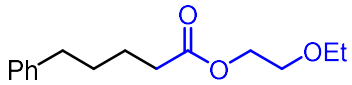
Yield: 110 mg (66%). Colorless oil. Chromatography: hexanes/EtOAc, 5/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.21 – 4.06 (m, 6H), 3.58 (t, *J* = 4.8 Hz, 2H), 3.49 (q, *J* = 7.0 Hz, 2H), 3.27 (t, *J* = 7.5 Hz, 1H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.86 (q, *J* = 7.7 Hz, 2H), 1.62 (p, *J* = 7.5 Hz, 2H), 1.39 – 1.27 (m, 2H), 1.26 – 1.10 (m, 9H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 173.4, 169.4, 68.4, 66.6, 63.6, 61.3, 51.9, 33.9, 28.0, 26.8, 24.5, 15.1, 14.1.

HRMS (ESI): calcd for $C_{16}H_{28}O_7Na$ [M+Na] 355.1727, found 355.1729.

2-Ethoxyethyl 6-phenylhexanoate (3f)



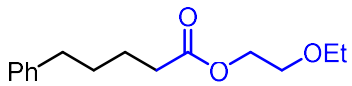
Yield: 113 mg (81%). Colorless oil. Chromatography: hexanes/EtOAc, 10/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.25 – 7.18 (m, 2H), 7.17 – 7.08 (m, 3H), 4.18 (t, *J* = 4.8 Hz, 2H), 3.58 (t, *J* = 4.9 Hz, 2H), 3.49 (q, *J* = 7.0 Hz, 2H), 2.57 (t, *J* = 7.7 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.70 – 1.53 (m, 4H), 1.42 – 1.24 (m, 2H), 1.18 (t, *J* = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 173.8, 142.5, 128.4, 128.3, 125.7, 68.4, 66.6, 63.5, 35.8, 34.2, 31.1, 28.8, 24.8, 15.2.

HRMS (ESI): calcd for $C_{15}H_{22}O_3Na$ [M+Na] 287.1618, found 287.1625.

2-Ethoxyethyl 6-phenylhexanoate (3f)



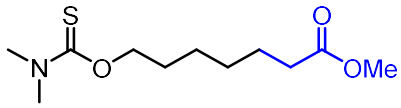
Yield: 113 mg (81%). Colorless oil. Chromatography: hexanes/EtOAc, 10/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.25 – 7.18 (m, 2H), 7.17 – 7.08 (m, 3H), 4.18 (t, *J* = 4.8 Hz, 2H), 3.58 (t, *J* = 4.9 Hz, 2H), 3.49 (q, *J* = 7.0 Hz, 2H), 2.57 (t, *J* = 7.7 Hz, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.70 – 1.53 (m, 4H), 1.42 – 1.24 (m, 2H), 1.18 (t, *J* = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 173.8, 142.5, 128.4, 128.3, 125.7, 68.4, 66.6, 63.5, 35.8, 34.2, 31.1, 28.8, 24.8, 15.2.

HRMS (ESI): calcd for $C_{15}H_{22}O_3Na$ [M+Na] 287.1618, found 287.1625.

Methyl 7-((dimethylcarbamothioyl)oxy)heptanoate (3g)



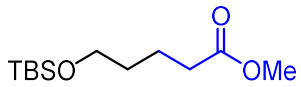
Yield: 98 mg (79%). Colorless oil. Chromatography: hexanes/EtOAc, 6/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.41 (t, *J* = 6.5 Hz, 2H), 3.65 (s, 3H), 3.34 (s, 3H), 3.09 (s, 3H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.78 – 1.56 (m, 4H), 1.48 – 1.27 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 188.5, 174.2, 71.6, 51.6, 42.7, 37.7, 34.1, 28.9, 28.7 25.7, 24.9.

HRMS (ESI): calcd for $C_{11}H_{21}NO_3SNa$ [M+Na] 270.1134, found 270.1126.

Methyl 5-((*tert*-butyldimethylsilyl)oxy)pentanoate (3h)



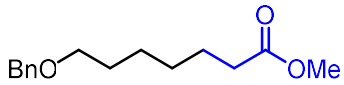
Yield: 87 mg (71%). Colorless oil. Chromatography: hexanes/EtOAc, 30/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 3.66 (s, 3H), 3.61 (t, *J* = 6.2 Hz, 2H), 2.33 (t, *J* = 7.4 Hz, 2H), 0.88 (s, 9H), 0.04 (s, 6H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 174.3, 62.8, 51.6, 34.0, 32.3, 26.1, 21.6, 18.5, -5.2.

HRMS (ESI): calcd for $C_{12}H_{26}O_3SiNa$ [M+Na] 269.1543, found 269.1542.

Methyl 7-(benzyloxy)heptanoate (3i)[29]



Modified General procedure: **2a** (176 µL, 1.5 mmol, 3 equiv), HCO_2Na (136 mg, 1.5 mmol, 3 equiv)

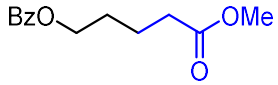
Yield: 70 mg (56%). Colorless oil. Chromatography: hexanes/EtOAc, 15/1

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 5H), 4.50 (s, 2H), 3.66 (s, 3H), 3.46 (t, *J* = 6.5 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.71 – 1.55 (m, 4H), 1.46 – 1.28 (m, 4H).

^{13}C{^{1}H} NMR (76 MHz, Chloroform-*d*) δ 174.4, 138.8, 128.5, 127.7, 127.6, 73.0, 70.4, 51.6, 34.1, 29.70, 29.1, 26.0, 25.0.

HRMS (ESI): calcd for $C_{15}H_{22}O_3K$ [M+K] 289.1201, found 289.1180.

5-Methoxy-5-oxopentyl benzoate(3j)



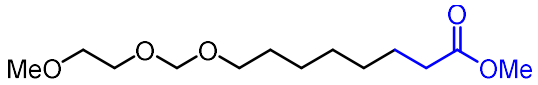
Yield: 86 mg (73%). Pale yellow oil. Chromatography: hexanes/EtOAc, 4/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.07 – 7.98 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 4.30 (t, *J* = 5.5 Hz, 2H), 3.65 (s, 3H), 2.38 (t, *J* = 6.3 Hz, 2H), 1.87 – 1.71 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 173.8, 166.6, 132.9, 130.4, 129.6, 128.4, 64.5, 51.6, 33.6, 28.2, 21.6.

HRMS (ESI): calcd for $C_{13}H_{20}NO_4$ [M+NH_4] 253.1387, found 254.1396.

Methyl 8-((2-methoxyethoxy)methoxy)octanoate (3k)[30]



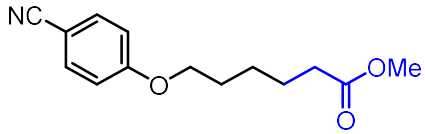
Yield: 86 mg (79 %). Colorless oil. Chromatography: hexanes/EtOAc, 5/2

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.65 (s, 2H), 3.68 – 3.59 (m, 2H), 3.61 (s, 3H), 3.55 – 3.43 (m, 4H), 3.34 (s, 3H), 2.25 (t, *J* = 7.5 Hz, 2H), 1.64 – 1.45 (m, 4H), 1.33 – 1.21 (m, 6H).

^{13}C{^{1}H} NMR (76 MHz, Chloroform-*d*) δ 174.2, 95.5, 71.8, 67.9, 66.7, 59.1, 51.4, 34.1, 29.6 29.08, 29.06, 26.0, 24.9.

HRMS (ESI): calcd for $C_{13}H_{26}O_5Na$ [M+Na] 285.1672, found 285.1674.

Methyl 6-(4-cyanophenoxy)hexanoate (3l)



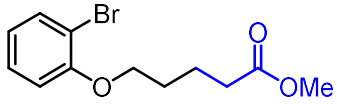
Yield: 72 mg (58 %). Colorless oil. Chromatography: hexanes/EtOAc, 7/2

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 9.0 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 3H), 3.97 (t, *J* = 6.4 Hz, 2H), 3.64 (s, 3H), 2.33 (t, *J* = 7.4 Hz, 2H),1.85 – 1.74 (m, 2H), 1.74 – 1.62 (m, 2H), 1.54 – 1.38 (m, 2H).

^{13}C{^{1}H} NMR (76 MHz, Chloroform-*d*) δ 173.8, 162.4, 133.9, 119.3, 115.2, 103.7, 68.1, 51.6, 33.9, 28.7, 25.6, 24.6.

HRMS (ESI): calcd for $C_{14}H_{21}N_2O_3$ [M+NH_4] 265.1547, found 265.1539.

Methyl 5-(2-bromophenoxy)pentanoate (3m)



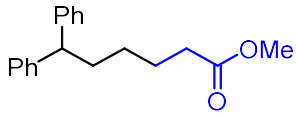
Yield: 63 mg (44 %). Colorless oil. Chromatography: hexanes/EtOAc, 10/1

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.50 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.26 – 7.20 (m, 1H), 6.88 – 6.74 (m, 2H), 4.08 – 3.92 (m, 2H), 3.65 (s, 3H), 2.49 – 2.35 (m, 2H), 1.95 – 1.77 (m, 4H).

^{13}C{^{1}H} NMR (76 MHz, Chloroform-*d*) δ 174.0, 155.4, 133.4, 128.5, 121.9, 113.2, 112.3, 68.6, 51.6, 33.7, 28.6, 21.7.

HRMS (ESI): calcd for $C_{12}H_{19}N^{79}BrO_3$ [M+NH_4] 304.0543, found 304.0555.

Methyl 6,6-diphenylhexanoate (3n)



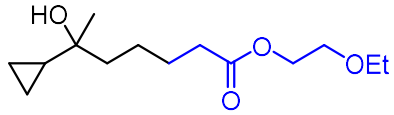
Yield: 110 mg (78%). Colorless oil. Chromatography: hexanes/EtOAc, 15/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.40 – 7.19 (m, 10H), 3.97 (t, *J* = 7.8 Hz, 1H), 3.70 (s, 3H), 2.35 (t, *J* = 7.6 Hz, 2H), 2.14 (q, *J* = 7.8 Hz, 2H), 1.75 (p, *J* = 7.6 Hz, 2H), 1.41 – 1.31 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 174.1, 145.1, 128.5, 127.9, 126.2, 51.5, 51.2, 35.4, 34.0, 27.6, 25.0.

HRMS (ESI): calcd for $C_{19}H_{22}O_2Na$ [M+Na] 305.1512, found 305.1513.

2-Ethoxyethyl 6-cyclopropyl-6-hydroxyheptanoate (3o)



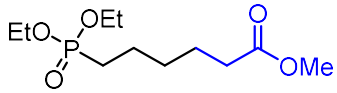
Yield: 103 mg (80%). Colorless oil. Chromatography: hexanes/EtOAc, 5/2

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.22 (t, *J* = 4.8 Hz, 2H), 3.62 (t, *J* = 4.8 Hz, 2H), 3.53 (q, *J* = 6.9 Hz, 2H), 2.37 (t, *J* = 7.4 Hz, 2H), 1.71 – 1.56 (m, 2H), 1.56 – 1.36 (m, 4H), 1.19 (t, *J* = 6.9 Hz, 3H), 1.07 (s, 3H), 0.95 – 0.78 (m, 1H), 0.41 – 0.21 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 173.9, 71., 68.5, 66.7, 63.6, 42.9, 34.3, 25.9, 25.6, 23.6, 21.2, 15.3, 0.8, 0.5.

HRMS (ESI): calcd for $C_{14}H_{26}O_4Na$ [M+Na] 281.1723, found 281.1733.

Methyl 6-(diethoxyphosphoryl)hexanoate (3p)[31]



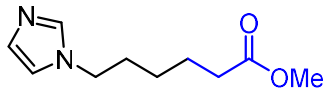
Yield: 94 mg (71 %). Colorless oil. Chromatography: EtOAc/EtOH, 20/1

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.13 – 3.97 (m, 4H), 3.62 (s, 3H), 2.27 (t, *J* = 7.4 Hz, 2H), 1.76 – 1.49 (m, 6H), 1.43 – 1.32 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 6H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 174.0, 61.5, 61.5, 51.6, 33.8, 30.2, 30.0, 26.6, 24.7, 24.5, 24.5, 16.6, 16.5.

HRMS (ESI): calcd for $C_{14}H_{26}O_4Na$ [M+Na] 281.1723, found 281.1733.

Methyl 6-(1H-imidazol-1-yl)hexanoate (3q)[30]

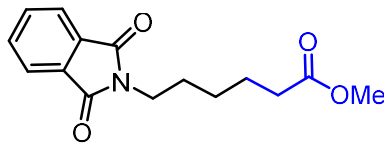


Yield: 64 mg (65 %). Colorless oil. Chromatography: DCM/iPrOH, 10/1

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.43 (s, 1H), 7.02 (s, 1H), 6.88 (s, 1H), 3.90 (t, *J* = 7.2 Hz, 2H), 3.62 (s, 3H), 2.27 (t, *J* = 7.4 Hz, 2H), 1.76 (p, *J* = 7.2 Hz, 2H), 1.61 (p, *J* = 7.4 Hz, 2H), 1.36 – 1.24 (m, 2H).

^{13}C{^{1}H} NMR (76 MHz, Chloroform-*d*) δ 173.7, 137.1, 129.4, 118.8, 51.5, 46.7, 33.7, 30.8, 26.0, 24.2.

Methyl 6-(1,3-dioxoisoindolin-2-yl)hexanoate (3r)[31]



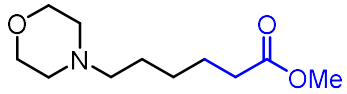
Modified General procedure: **2a** (176 µL, 2 mmol, 4 equiv), HCO_2Na (136 mg, 2 mmol, 4 equiv)

Yield: 88 mg (64 %). Colorless oil. Chromatography: hexanes/EtOAc, 3/1

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.65 (dd, *J* = 5.5, 3.1 Hz, 2H), 3.63 (t, *J* = 7.2 Hz, 2H), 3.59 (s, 3H), 2.25 (t, *J* = 7.5 Hz, 2H), 1.71 – 1.55 (m, 4H), 1.37 – 1.25 (m, 2H).

^{13}C{^{1}H} NMR (76 MHz, Chloroform-*d*) δ 173.6, 168.3, 133.9, 132.1, 123.1, 51.4, 37.7, 33.8, 28.2, 26.3, 24.4.

Methyl 6-morpholinohexanoate (3s)



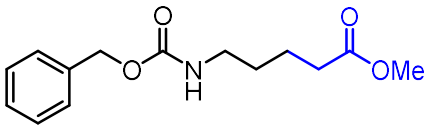
Yield: 66 mg (61 %). Colorless oil. Chromatography: EtOH

^{1}H NMR (300 MHz, Chloroform-*d*) δ 3.68 (t, *J* = 4.7 Hz, 4H), 3.63 (s, 3H), 2.41 (t, *J* = 4.8 Hz, 4H), 2.34 – 2.24 (m, 4H), 1.61 (p, *J* = 7.5 Hz, 2H), 1.54 – 1.40 (m, 2H), 1.38 – 1.23 (m, 2H).

^{13}C{^{1}H} NMR (76 MHz, Chloroform-*d*) δ 174.2, 67.1, 58.9, 53.8, 51.6, 34.1, 27.1, 26.3, 24.9.

HRMS (ESI): calcd for $C_{11}H_{21}NO_3Na$ [M+Na] 238.1414, found 238.1417.

Methyl 5-(((benzyloxy)carbonyl)amino)pentanoate (3t)



Modified General procedure: **2a** (176 µL, 1.5 mmol, 3 equiv), HCO_2Na (136 mg, 1.5 mmol, 3 equiv)

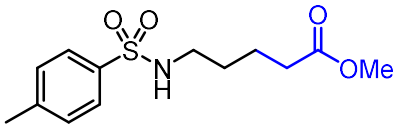
Yield: 106 mg (76 %). Colorless oil. Chromatography: hexanes/EtOAc, 5/2

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.43 – 7.16 (m, 5H), 5.23 – 4.79 (m, 3H), 3.63 (s, 3H), 3.16 (q, *J* = 6.9 Hz, 2H), 2.30 (t, *J* = 7.2 Hz, 2H), 1.63 (tt, *J* =7.2, 6.9 Hz, 2H), 1.50 (tt, *J* = 7.2 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 173.9, 156.5, 136.7, 128.5, 128.1, 66.6, 51.5, 40.6, 33.5, 29.4, 22.0

HRMS (ESI): calcd for $C_{14}H_{19}NO_4Na$ [M+Na] 288.1206, found 288.1211.

Methyl 5-((4-methylphenyl)sulfonamido)pentanoate (3u)



Modified General procedure: **2a** (176 µL, 2 mmol, 4 equiv), HCO_2Na (136 mg, 2 mmol, 4 equiv)

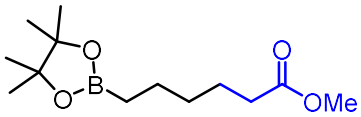
Yield: 106 mg (58 %). Colorless oil. Chromatography: hexanes/EtOAc, 3/2

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.82 (t, *J* = 6.4 Hz, 1H), 3.63 (s, 3H), 2.92 (td, *J* = 6.8, 6.4 Hz, 2H), 2.41 (s, 3H), 2.25 (t, *J* = 7.1 Hz, 2H), 1.60 (tt, *J* = 7.0, 6.8 Hz, 2H), 1.54 – 1.42 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 173.8, 143.5, 137.1, 129.8, 127.2, 51.7, 42.8, 33.4, 29.1, 21.8, 21.0.

HRMS (ESI): calcd for $C_{13}H_{19}NO4SNa$ [M+Na] 208.0927, found 308.0928.

Methyl 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate (3v)



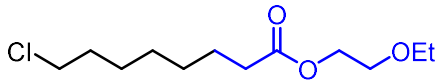
Yield:91 mg (71%). Colorless oil. Chromatography: hexanes/EtOAc, 8/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 3.60 (s, 3H), 2.24 (t, *J* = 7.6 Hz, 2H), 1.65 – 1.49 (m, 2H), 1.45 – 1.23 (m, 4H), 1.19 (s, 12H), 0.71 (t, *J* = 7.6 Hz, 2H)

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 174.3, 82.9, 51.4, 34.1, 31.9, 30.7, 24.9, 24.8, 23.7, 11.1.

HRMS (ESI): calcd for $C_{13}H_{25}BO_4$ [M+H] 257.1921, found 257.1925.

2-Ethoxyethyl 8-chlorooctanoate (3w)



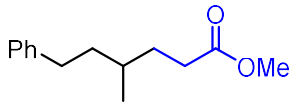
Yield: 84 mg (67%). Colorless oil. Chromatography: hexanes/EtOAc, 15/1

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.19 (t, *J* = 4.7 Hz, 2H), 3.60 (t, *J* = 4.7 Hz, 2H), 3.56 – 3.42 (m, 4H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.80 – 1.67 (m, 2H), 1.66 – 1.51 (m, 2H), 1.44 (m, 6H), 1.18 (t, *J* = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 173.8, 68.4, 66.6, 63.5, 45.1, 34.2, 32.6, 29.0, 28.6, 26.7, 24.8, 15.2.

HRMS (ESI): calcd for $C_{12}H_{23}ClO_3Na$ [M+Na] 273.1228, found 273.1233.

Methyl-6-phenylhexanoate (3x)



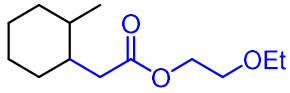
Yield: 77 mg (70%). Colorless oil. Chromatography: hexanes/EtOAc, 15/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.30 – 7.22 (m, 2H), 7.20 – 7.12 (m, 3H),3.65 (s, 3H), 2.71 – 2.50 (m, 2H), 2.41 – 2.20 (m, 2H), 1.79 – 1.39 (m, 5H), 0.94 (d, *J* = 5.1 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 174.5, 142.8, 128.4, 125.8, 51.6, 38.7, 33.4, 32.2, 31.9, 19.3.

HRMS (ESI): calcd for $C_{14}H_{20}O_2Na$ [M+Na] 243.1356, found 243.1367.

2-Ethoxyethyl 2-(2-methylcyclohexyl)acetate (3y)



Modified General procedure: **2a** (176 µL, 2 mmol , 4 equiv), HCO_2Na (136 mg, 2 mmol, 4 equiv)

Yield: 70 mg (61 %). Colorless oil. Chromatography: hexanes/EtOAc, 15/1

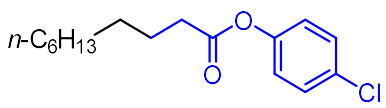
Mixture of isomers: 1/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 4.22 (t, *J* = 4.9 Hz, 4H), 3.62 (t, *J* = 4.9 Hz, 4H), 3.52 (q, *J* = 7.0 Hz, 4H), 2.57 (dd, *J* = 14.8, 4.5 Hz, 1H), 2.35 – 2.15 (m, 2H), 2.12 – 1.96 (m, 2H), 1.91 – 0.94 (m, 16H), 0.89 (d, *J* = 6.3 Hz, 3H), 0.85 (d, *J* = 7.0 Hz, 4H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 173.84, 68.55, 66.71, 63.50, 41.47, 39.61, 37.34, 37.14, 36.95, 35.70, 32.69, 32.66, 32.14, 28.10, 26.51, 26.42, 24.46, 22.34, 20.32, 15.24, 14.86.

HRMS (ESI): calcd for $C_{13}H_{24}O_3Na$ [M+Na] 251.1618, found 251.1617.

Nonyl 4-chlorobenzoate (3z)



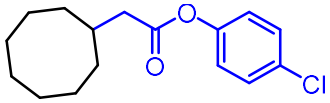
Yield: 93 mg (66%). Colorless oil. Chromatography: hexanes/EtOAc, 50/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 2.54 (t, *J* = 7.5 Hz, 2H), 1.74 (p, *J* = 7.3 Hz, 2H), 1.44 – 1.20 (m, 12H), 0.89 (t, *J* = 6.4 Hz, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, Chloroform-*d*) δ 172.2, 149.3, 131.1, 129.5, 123.1, 34.4, 31.9, 29.5, 29.3, 29.2, 25.0, 22.8, 14.2.

HRMS (ESI): calcd for $C_{16}H_{23}ClO_2Na$ (M+Na) 305.1279, found 305.1276.

Cyclooctylmethyl 4-chlorobenzoate (3ab)



Yield: 116 mg (83%). Colorless oil. Chromatography: hexanes/EtOAc, 100/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 2.40 (d, *J* = 7.3 Hz, 2H), 2.21 – 2.09 (m, 1H), 1.72 – 1.65 (m, 2H), 1.60 – 1.29 (m, 10H), 1.41 – 1.35 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, Chloroform-*d*) δ 171.6, 149.3, 131.1, 129.5, 123.0, 42.8, 34.7, 32.3, 27.1, 26.3, 25.3

HRMS (ESI): calcd for $C_{16}H_{25}{}^{35}ClNO_2$ ($M+NH_4$) 298.1570, found 298.1569.

Methyl 5-((tert-butyldimethylsilyl)oxy)-3-(((tert-butyldimethylsilyl)oxy)methyl)pentanoate (3ac)

Modified General procedure: **2a** (440 µL, 5 mmol, 10 equiv), HCO_2Na (340 mg, 5 mmol, 10 equiv), irradiation 60W blue LED (455 nm) was used.

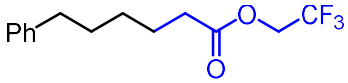
Yield 64 mg (33%). Colorless oil. Chromatography: hexanes/EtOAc, 50/1.

^{1}H NMR (300 MHz, Chloroform-d) δ 3.74 – 3.65 (m, 4H),3.6 (dd, J = 10.0, 4.8 Hz, 1H), 3.5 (dd, *J* = 10.0, 6.5 Hz, 1H), 2.5 (dd, *J* = 15.5, 6,7 Hz, 1H), 2.3 (dd, *J* = 15.5, 6.7 Hz, 1H), 2.2 (hept, *J* = 6.6, 6.4, 5.8 Hz, 1H), 1.7 – 1.6 (m, 1H), 1.6 – 1.4 (m, 1H).0.91 (s, 9H), 0.90 (s, 9H), 0.09 – 0.01 (m, 12H).

^{13}C NMR (76 MHz, Chloroform-*d*) δ 173.8, 65.3, 61.3, 51.5, 36.3, 35.2, 34.2, 26.1, 26.0, 18.4, -5.2, -5.2, -5.4

HRMS (ESI): calcd for $C_{19}H_{42}O_4Si_2Na$ [M+Na] 413.2514, found 413.2519.

2,2,2-Trifluoroethyl 6-phenylhexanoate (3ad)



Yield: 101 mg(74%). Colorless oil. Chromatography: hexanes/EtOAc, 20/1.

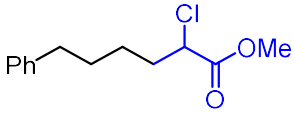
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 2H), 7.26 – 7.19 (m, 3H), 4.49 (q, *J* = 8.5 Hz, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.47 (t, *J* = 7.5 Hz, 2H), 1.83 – 1.63 (m, 4H), 1.50 – 1.34 (m, 2H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, Chloroform-*d*) δ 172.1, 142.5, 128.4 (d, *J* = 5.8 Hz), 125.8 123.16 (q, *J* = 277.0 Hz), 60.2 (q, *J* = 36.5 Hz), 35.8, 33.6, 31.1, 28.7, 24.7.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -74.66 (t, *J* = 8.5 Hz).

HRMS (ESI): calcd for $C_{14}H_{17}F_3O_2Na$ [M+Na] 297.1073, found 297.1073.

Methyl 2-chloro-6-phenylhexanoate (3ae)



Modified General procedure: HCO_2Na (136 mg, 1.5 mmol, 3 equiv)

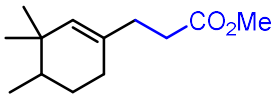
Yield: 96 mg (80%). Colorless oil. Chromatography: hexanes/EtOAc, 15/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.32 – 7.21 (m, 2H), 7.21 – 7.11 (m, 3H), 4.25 (t, *J* = 6.4 Hz, 1H), 3.75 (s, 3H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.10 – 1.85 (m, 2H), 1.71 – 1.21 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 170.2, 142.1, 128.4, 128.4, 125.9, 57.1, 52.9, 35.6, 34.8, 30.7, 25.6.

HRMS (ESI): calcd for $C_{13}H_{17}{}^{35}ClO_2Na$ (M+Na) 263.0809, found 263.0805.

Methyl 3-(3,3,4-trimethylcyclohex-1-en-1-yl)propanoate (4).



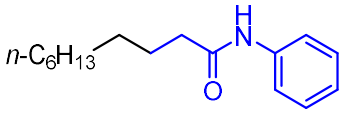
Yield 66 mg (68%). Colorless oil. Chromatography: hexanes/EtOAc, 25/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.45 – 5.35 (m, 1H), 3.66 (s, 3H), 2.48 – 2.32 (m, 2H), 2.29 – 2.21 (m, 2H), 2.07 – 1.86 (m, 3H), 1.80 – 1.61 (m, 2H), 1.53 – 1.36 (m, 1H), 1.32 – 1.11 (m, 2H), 0.87 (dd, *J* = 6.7, 4.0 Hz, 6H).

^{13}C NMR (76 MHz, Chloroform-*d*) δ 174.2, 136.1, 121.6, 51.6, 40.2, 32.9, 32.7, 32.4, 29.1, 29.0, 26.5, 20.0, 19.8.

HRMS (ESI): calcd for $C_{13}H_{22}O_2Na$ [M+Na] 233.1512, found 233.1512.

***N*-phenyldecanamide (3af)**



Modified General procedure: **2a** (176 µL, 1.5 mmol, 3 equiv), HCO_2Na (136 mg, 1.5 mmol, 3 equiv), 2-methylpropane-2-thiol (12 µL, 0.2 mmol).

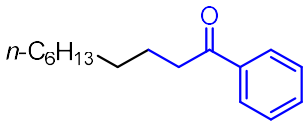
Yield: 78 mg (63%). Pale yellow solid. Mp 64-66 °C. Chromatography: hexanes/EtOAc, 6/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.73 (p, *J* = 7.5 Hz, 2H), 1.46 – 1.19 (m, 12H), 0.91 (t, *J* = 6.5 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 172.1, 138.3, 128.9, 124.2, 120.1, 37.8, 31.9, 29.5, 29.5, 29.4, 29.4, 25.8, 22.7, 14.2.

HRMS (ESI): calcd for $C_{16}H_{25}NONa$ [M+Na] 270.1828, found 270.1830.

1-Phenyldecan-1-one (3ag)



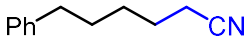
Yield: 85 mg (73%). Colorless oil. Chromatography: hexanes/EtOAc, 50/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.00 – 7.91 (m, 2H), 7.59 – 7.49 (m, 1H), 7.49 – 7.40 (m, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 1.73 (p, *J* = 7.3 Hz, 2H), 1.44 – 1.18 (m, 12H), 0.94 – 0.81 (m, 3H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 200.6, 137.2, 132.9, 128.6, 128.1, 38.7, 32.00, 29.6, 29.6, 29.5, 29.4, 24.5, 22.8, 14.2.

HRMS (ESI): calcd for $C_{16}H_{24}ONa$ [M+Na] 255.1719, found 255.1721.

6-Phenylhexanenitrile (3ah)



Modified General procedure: **2a** (176 µL, 1.5 mmol, 3 equiv), HCO_2Na (136 mg, 1.5 mmol, 3 equiv), 2-methylpropane-2-thiol (12 µL, 0.2 mmol).

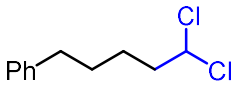
Yield: 60 mg (69%). Colorless oil. Chromatography: hexanes/EtOAc, 8/1.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.39 – 7.29 (m, 2H), 7.29 – 7.18 (m, 3H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.36 (t, *J* = 7.1 Hz, 2H), 1.80 – 1.63 (m, 4H), 1.61 – 1.47 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 142.00, 128.36, 125.86, 119.73, 35.57, 30.58, 28.26, 25.28, 17.06.

HRMS (ESI): calcd for $C_{12}H_{15}NNa$ [M+Na] 196.1097, found 196.1094.

(5,5-Dichloropentyl)benzene (3ai)[32]

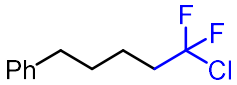


Yield: 69 mg (64%). Colorless oil. Chromatography: hexanes.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.37 – 7.28 (m, 2H), 7.27 – 7.15 (m, 3H), 5.75 (t, *J* = 6.4 Hz, 1H), 2.67 (t, *J* = 7.2 Hz, 2H), 2.25 (q, *J* = 6.4 Hz, 2H), 1.78 – 1.55 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 142.1, 128.5, 126.0, 73.6, 43.6, 35.8, 30.5, 25.8.

(5-Chloro-5,5-difluoropentyl)benzene (3aj)[33]



Modified General procedure: 4-chlorobenzenethiol (7.2 mg, 0.1 mmol) instead of, 2-methylpropane-2-thiol, 4CzIPN (2 mg, 0.005 mmol) as photocatalyst, irradiation 60W purple LED (455 nm) was used.

Yield: 33 mg (30%). Colorless oil. Chromatography: hexanes

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.38 – 7.15 (m, 5H), 2.69 (t, *J* = 7.0 Hz, 2H), 2.42 – 2.24 (m, 2H), 1.83 – 1.60 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*) δ 141.84, 130.09 (t, *J* = 291.7 Hz), 128.56, 128.50, 42.16, 41.85, 41.53, 35.67, 30.50, 23.05 (t, *J* = 3.0 Hz).

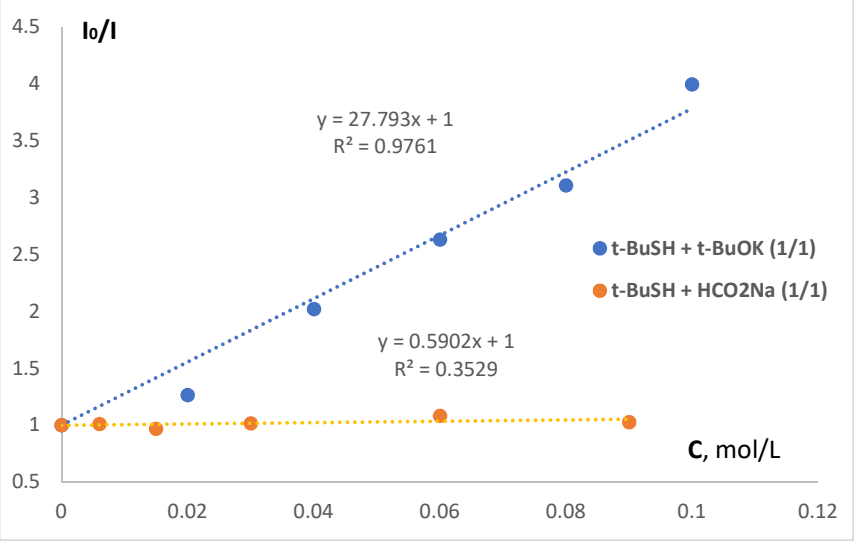
^{19}F NMR (282 MHz, Chloroform-*d*) δ -51.29 (t, *J* = 13.2 Hz).

Gram-scale synthesis of methyl 6-phenylhexanoate (3a)

A 100 mL thick wall screw-cap glass flask was evacuated and filled with argon. Then, DMSO (20 mL), sodium formate (3.4 g, 1 mmol, 2.5 equiv), 4-phenylbutene **1a** (2.64 g, 20 mmol, 1 equiv), methyl chloroacetate **2a** (4.4 mL, 50 mmol, 2.5 equiv), 2-methylpropane-2-thiol (0.36 mL, 3mmol, 15 mol%), 3DPA2FBN (32 mg, 0.05 mmol, 0.25 mol %) were added. The flask was screw-capped, placed into a beaker, cooled with water flow at room temperature, and irradiated for 16 h with a 455 nm 30 W S16 LED matrix placed under the bottom of the beaker. The reaction was quenched with water (50 mL) and extracted with hexane (3×20 mL). The combined organic layers were filtered through a short pad of Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified by column chromatography (hexanes/EtOAc 15:1). Yield 2.72 g (66%).

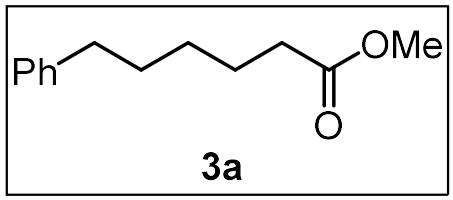
Stern-Volmer study

Experiments were performed in a screw-capped quartz vial (10×10 mm). The solvent was degassed, and the vial was filled with argon. The concentration of 3DPA2FBN was 0.1 mmol/L in DMSO. Excitation wavelength 380 nm, fluorescence wavelength 494 nm. Measurements were performed at room temperature.



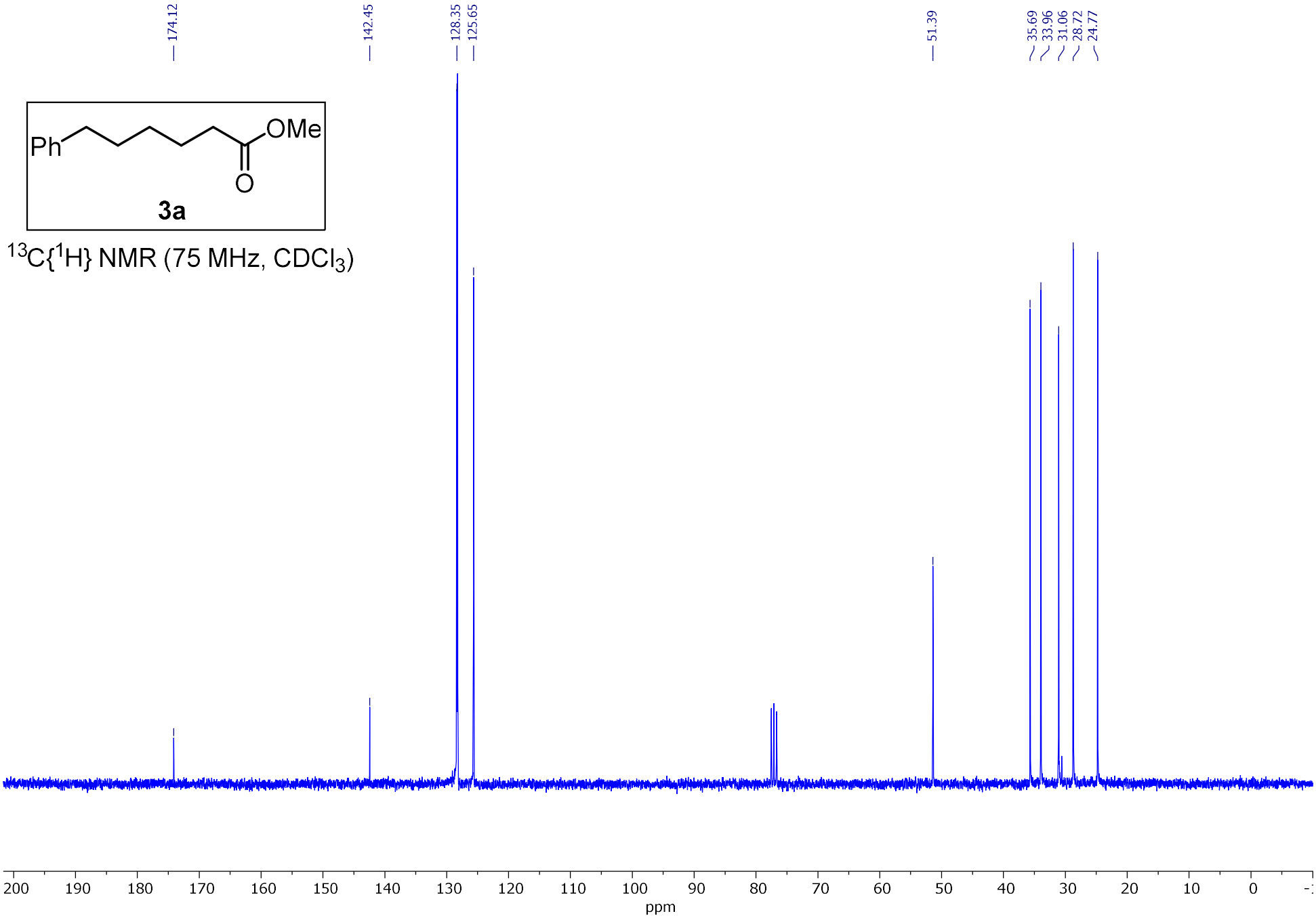
References

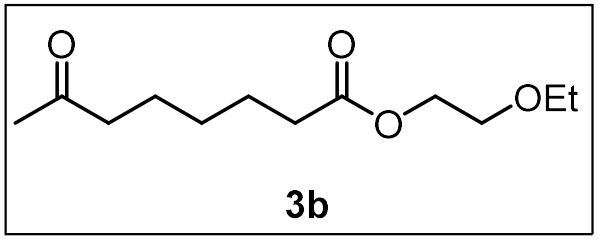
1. L. I. Panferova, V. V. Levin, M. I. Struchkova and A. D. Dilman, *Chem. Commun.*, 2019, **55**, 1314–1317.
2. J. Svoboda, J. Paleček and V. Dědek, *Collect. Czech. Chem. Commun.*, 1986, **51**, 1304–1310.
3. Z. Hu, S. Zhang, W. Zhou, X. Ma and G. Xiang, *Biorg. Med. Chem. Lett.*, 2017, **27**, 1854–1858.
4. J. Song, H. Yamataka and Z. Rappoport, *J. Org. Chem.*, 2007, **72**, 7605–7624.
5. L. Ma, S. Li, H. Zheng, J. Chen, L. Lin, X. Ye, Z. Chen, Q. Xu, T. Chen, J. Yang, N. Qiu, G. Wang, A. Peng, Y. Ding, Y. Wei and L. Chen, *Eur. J. Med. Chem.*, 2011, **46**, 2003–2010.
6. S. Arava, J. N. Kumar, S. Maksymenko, M. A. Iron, K. N. Parida, P. Fristrup and A. M. Szpilman, *Angew. Chem. Int. Ed.*, 2017, **56**, 2599–2603.
7. S. J. M. Mdachi, *Bull. Chem. Soc. Ethiop.*, 2012, **26**, 103–113.
8. G. A. Edwards, P. A. Culp and J. M. Chalker, *Chem. Commun.*, 2015, **51**, 515–518.
9. V. V. Levin and A. D. Dilman, *Chem. Commun.*, 2021, **57**, 749–752.
10. M. E. Scheller and B. Frei, *Helv. Chim. Acta*, 1986, **69**, 44–52.
11. S. K. Ginotra, J. A. Friest and D. B. Berkowitz, *Org. Lett.*, 2012, **14**, 968–971.
12. M. Yoshida, M. Higuchi and K. Shishido, *Org. Lett.*, 2009, **11**, 4752–4755.
13. B. H. Lipshutz, S. Ghorai and W. W. Y. Leong, *J. Org. Chem.*, 2009, **74**, 2854–2857.
14. C. E. Anson, A. V. Malkov, C. Roe, E. J. Sandoe and G. R. Stephenson, *Eur. J. Org. Chem.*, 2008, **2008**, 196–213.
15. H. Sharma, S. Santra, J. Debnath, T. Antonio, M. Reith and A. Dutta, *Bioorg. Med. Chem.*, 2014, **22**, 311–324.
16. V. S. Kostromitin, V. V. Levin and A. D. Dilman, *Catalysts*, 2023, **13**, 1126.
17. C. Courtens, M. Risseeuw, G. Caljon, L. Maes, A. Martin and S. Van Calenbergh, *Bioorg. Med. Chem.*, 2019, **27**, 729–747.
18. Y. Okayama, S. Tsuji, Y. Toyomori, A. Mori, S. Arae, W.-Y. Wu, T. Takahashi and M. Ogasawara, *Angew. Chem. Int. Ed.*, 2015, **54**, 4927–4931.
19. B.-Z. Fan, H. Hiasa, W. Lv, S. Brody, Z.-Y. Yang, C. Aldrich, M. Cushman and J.-H. Liang, *Eur. J. Med. Chem.*, 2020, **193**, 112222.
20. M. Warsitz and S. Doye, *Chem. Eur. J.*, 2020, **26**, 15121–15125.
21. E. Richmond, I. U. Khan and J. Moran, *Chem. Eur. J.*, 2016, **22**, 12274–12277.
22. A. Suzuki, Y. Kamei, M. Yamashita, Y. Seino, Y. Yamaguchi, T. Yoshino, M. Kojima and S. Matsunaga, *Angew. Chem. Int. Ed.*, 2023, **62**, e202214433.
23. P. Sušnik and G. Hilt, *Organometallics*, 2014, **33**, 5907–5910.
24. D. R. Jewell, L. Mathew and J. Warkentin, *Can. J. Chem.*, 1987, **65**, 311–315.
25. (a) D. P. Provencal, C. Gardelli, J. A. Lafontaine and J. W. Leahy, *Tetrahedron Lett.*, 1995, **36**, 6033–6036. (b) J. A. Lafontaine, D. P. Provencal, C. Gardelli and J. W. Leahy, *J. Org. Chem.*, 2003, **68**, 4215–4234.
26. M. Lux and M. Klussmann, *Org. Lett.*, 2020, **22**, 3697–3701.
27. L. Fu, Q. Chen, Z. Wang and Y. Nishihara, *Org. Lett.*, 2020, **22**, 2350–2353.
28. S. Kim, S. S. Kim, S. T. Lim and S. C. Shim, *J. Org. Chem.*, 1987, **52**, 2114–2116.
29. H. Chen, Y. Feng, Z. Xu and T. Ye, *Tetrahedron*, 2005, **61**, 11132–11140..
30. T. Ichikawa, T. Wako and N. Nemoto, *React. Funct. Polym.*, 2016, **99**, 1–8.
31. P. Shukla, A. Sharma, B. Pallavi and C. H. Cheng, *Tetrahedron*, 2015, **71**, 2260–2266.
32. C. Chen, Y. Li, Y. Pan, L. Duan and W. Liu, *Org. Chem. Front.*, 2019, **6**, 2032–2036.
33. V. S. Kostromitin, A. O. Sorokin, V. V. Levin and A. D. Dilman, *Chem. Sci.*, 2023, **14**, 3229–3234.



3a

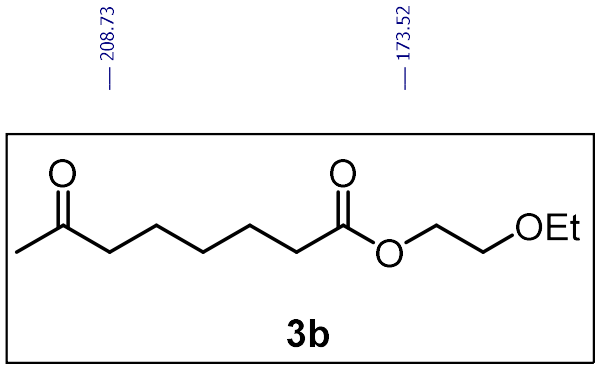
^{1}H NMR (300 MHz, $CDCl_3$)


174.12
142.45
128.35
125.65
51.39
35.69
33.96
31.06
28.72
24.77
Ph
OMe
O
3a
13C{1H} NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



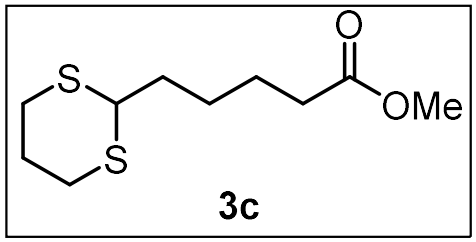
3b

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



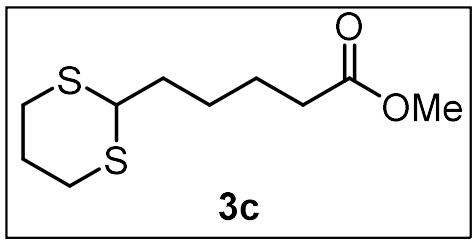
3b

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



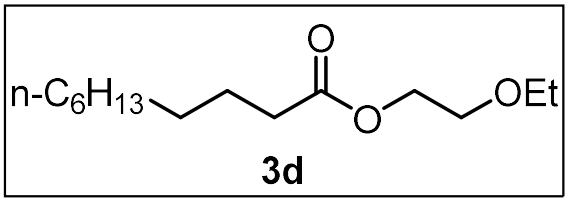
3c

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



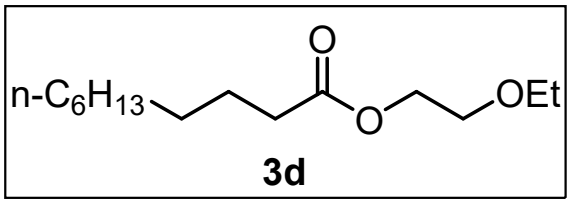
3c

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



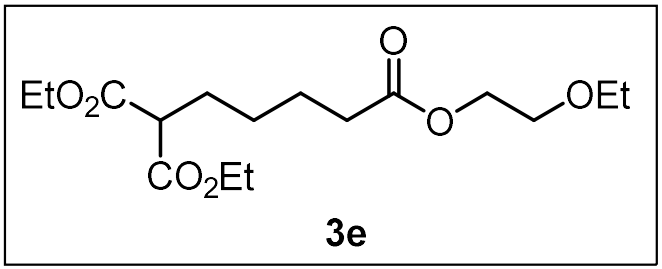
3d

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



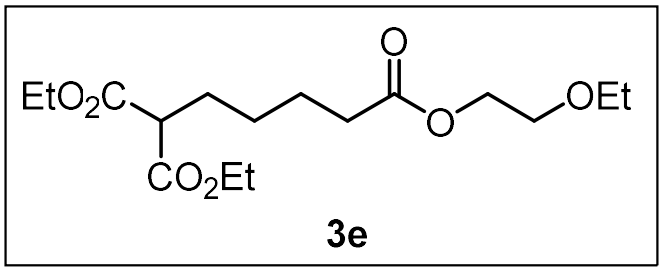
3d

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



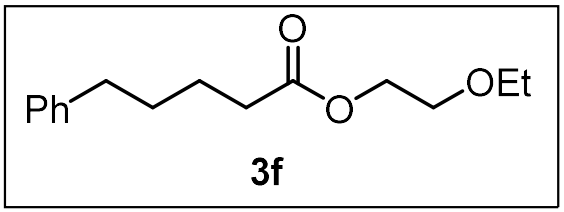
3e

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



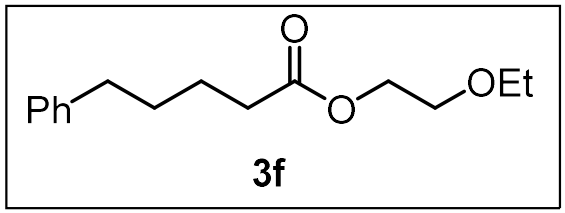
3e

$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



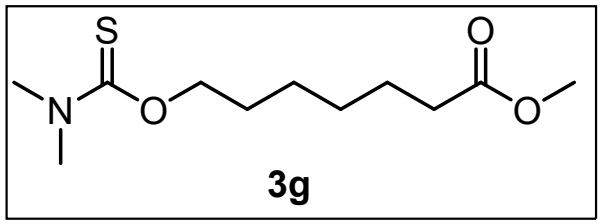
3f

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



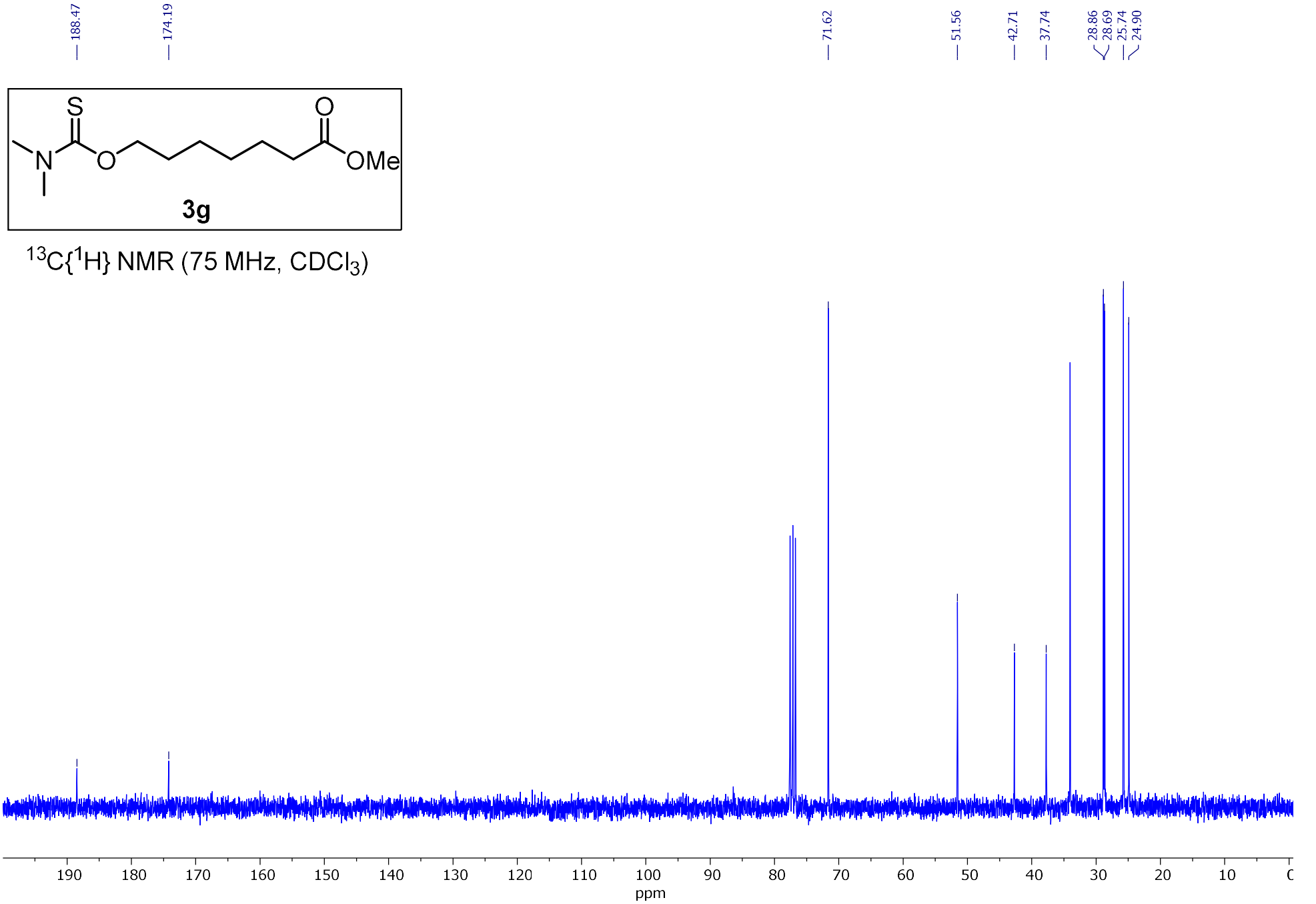
3f

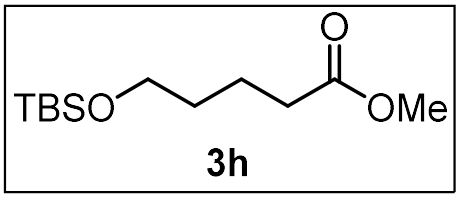
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



3g

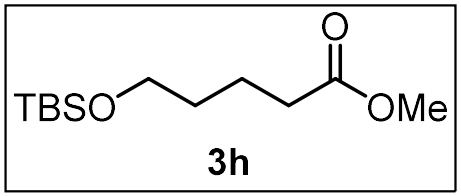
^{1}H NMR (300 MHz, $CDCl_3$)


188.47
174.19
71.62
51.56
42.71
37.74
28.86
28.69
25.74
24.90
S
O
N
O
OMe
3g
13C{1H} NMR (75 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



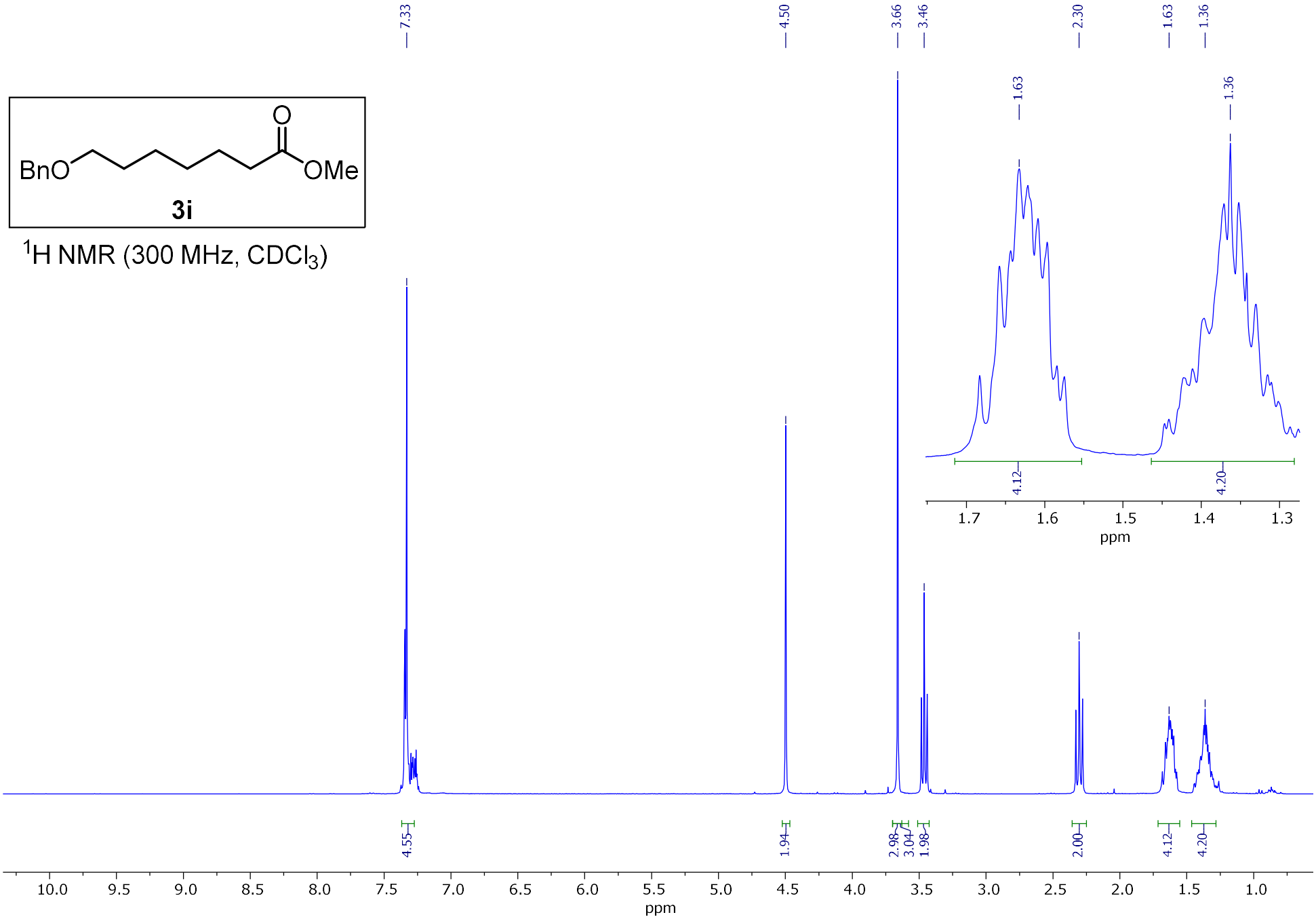
3h

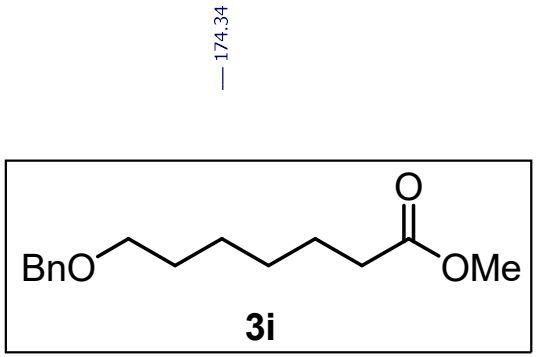
^{1}H NMR (300 MHz, $CDCl_3$)



3h

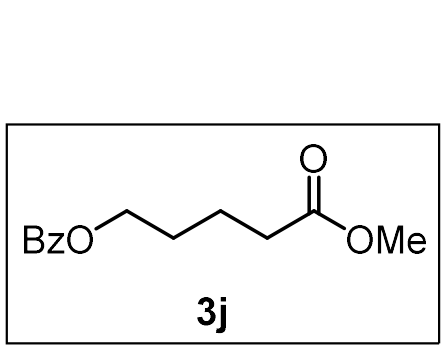
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)


7.33
4.50
3.66
3.46
2.30
1.63
1.36
BnO
OMe
O
3i
1H NMR (300 MHz, CDCl3)
4.55
1.94
2.98
3.04
1.98
2.00
4.12
4.20
ppm



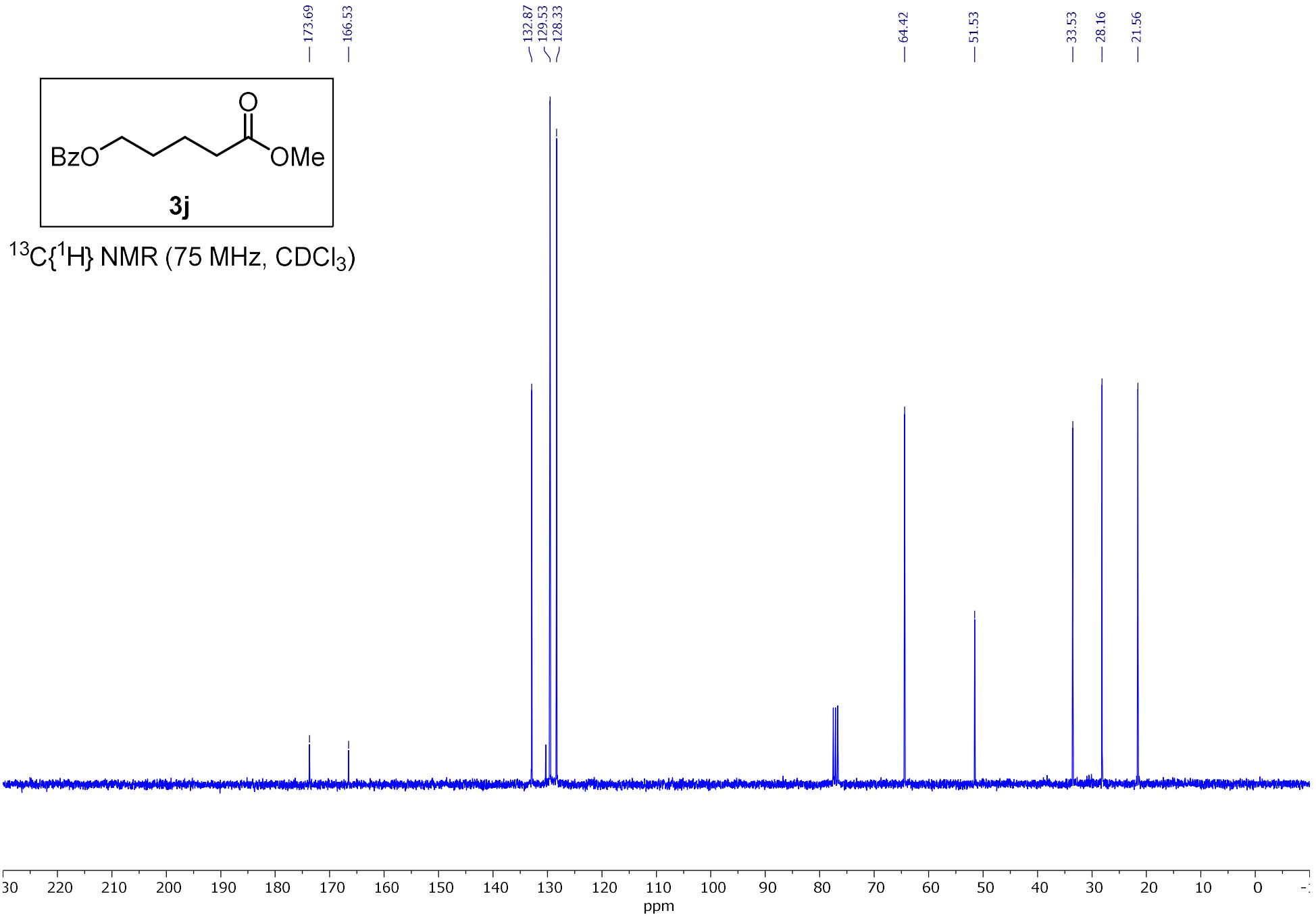
3i

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

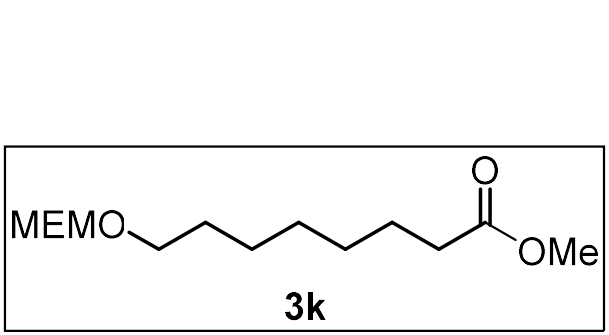


3j

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

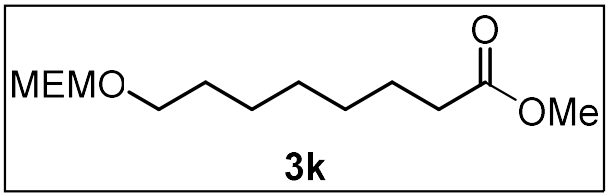


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



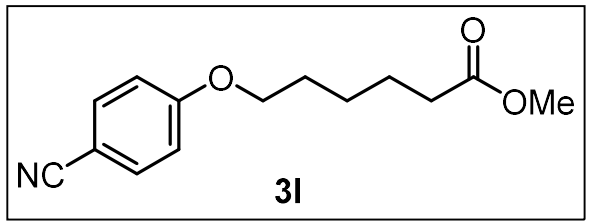
3k

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



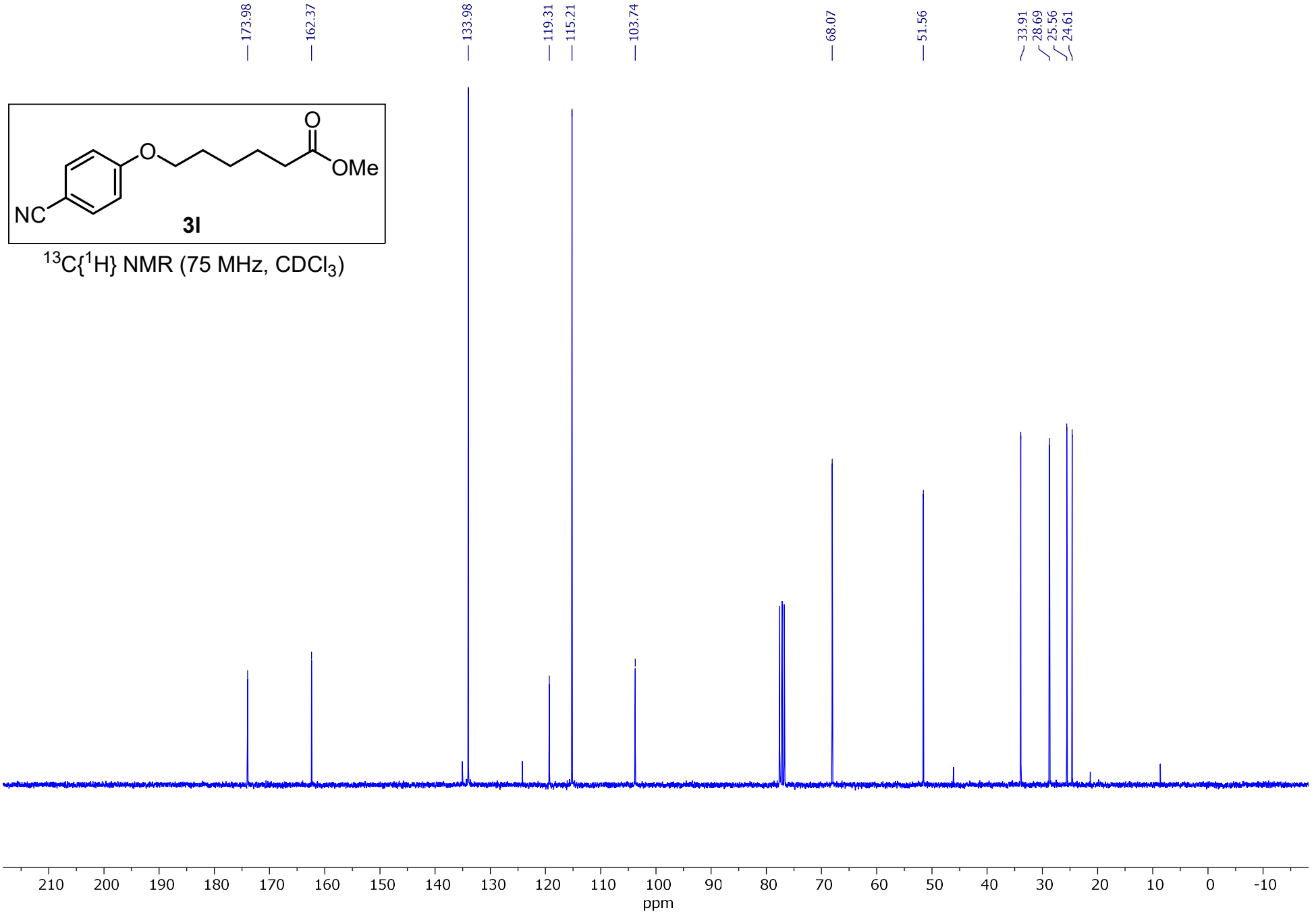
3k

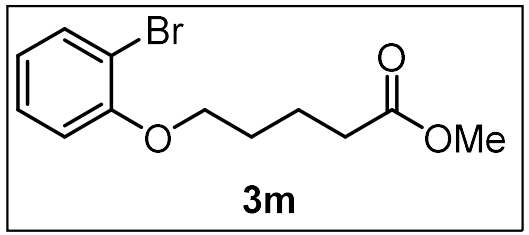
$^{13}C\{^{1}H\}$NMR (75 MHz, $CDCl_3$)



3l

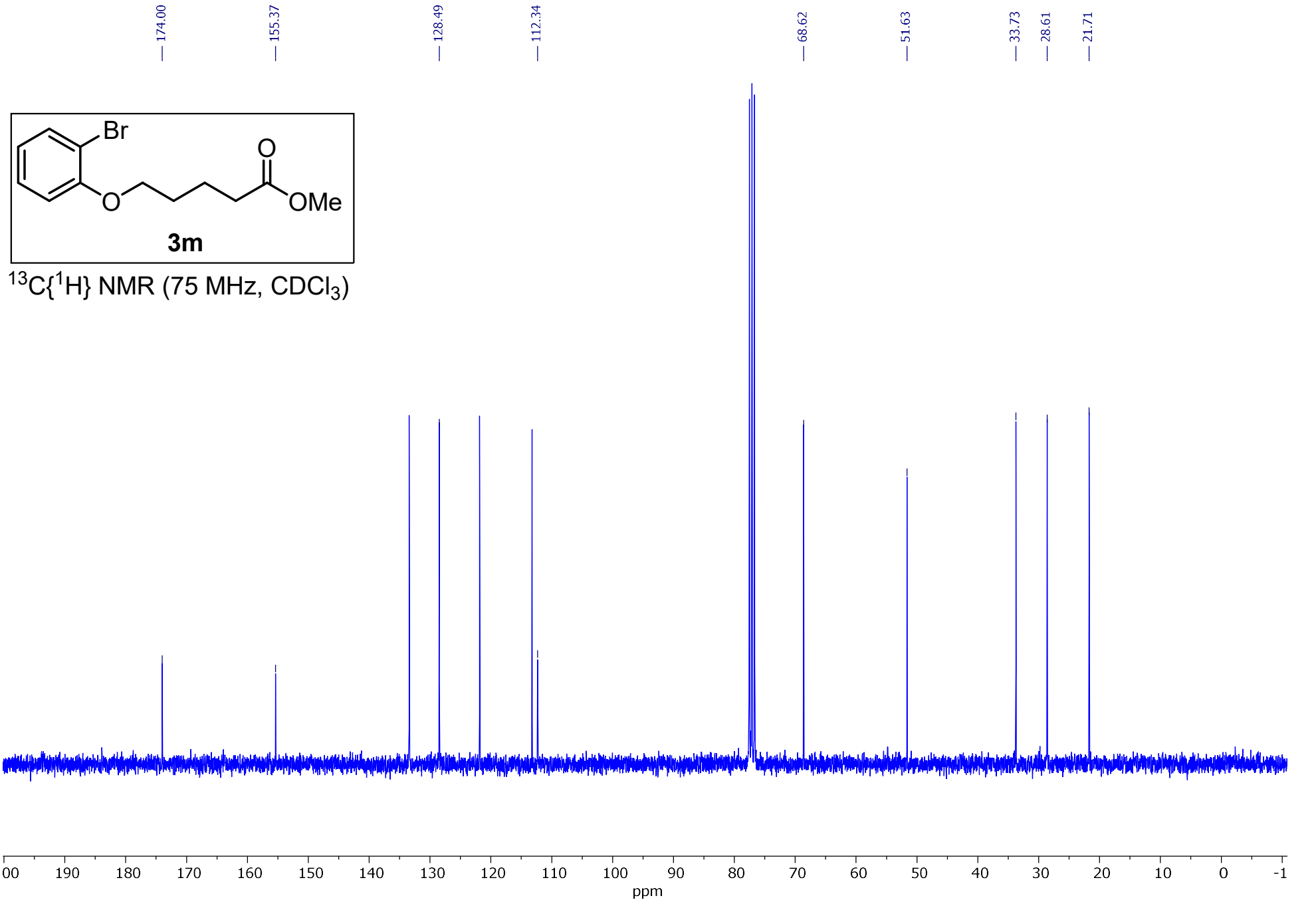
^{1}H NMR (300 MHz, $CDCl_3$)

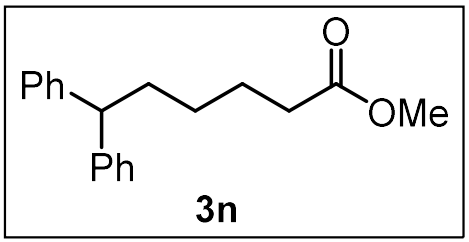

173.98
162.37
133.98
119.31
115.21
103.74
68.07
51.56
33.91
28.69
25.56
24.61
O
O
OMe
NC
3l
13C{1H} NMR (75 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm



3m

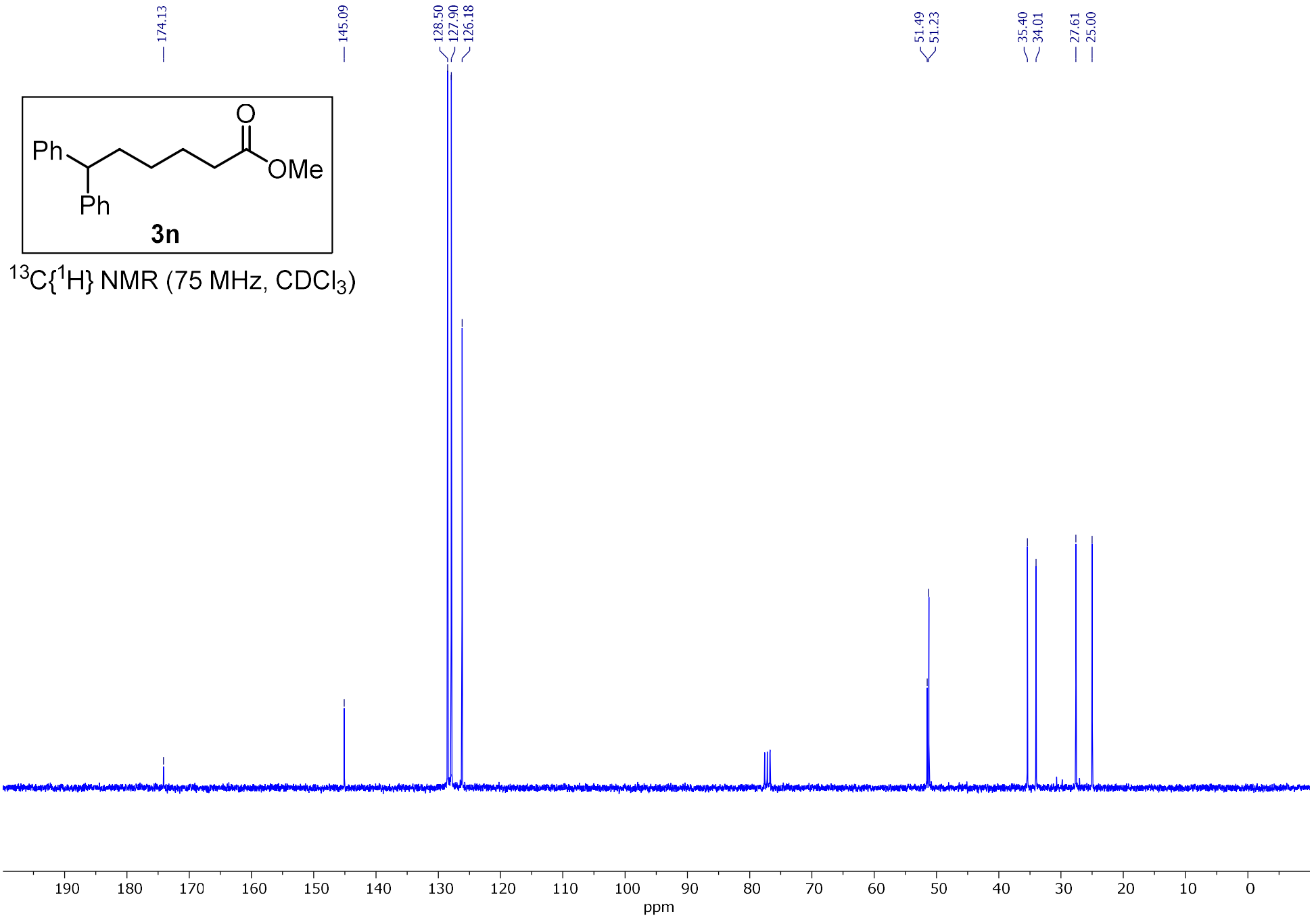
^{1}H NMR (300 MHz, $CDCl_3$)


174.00
155.37
128.49
112.34
68.62
51.63
33.73
28.61
21.71
Br
O
O
OMe
3m
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
ppm

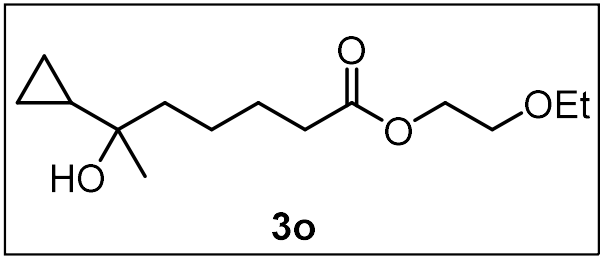


3n

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

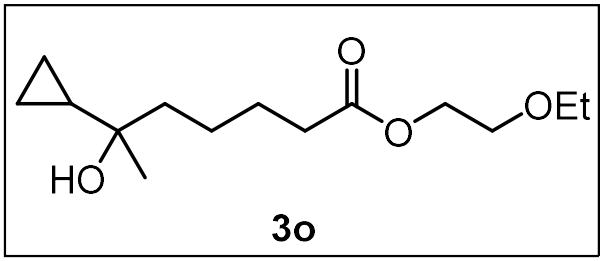


$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



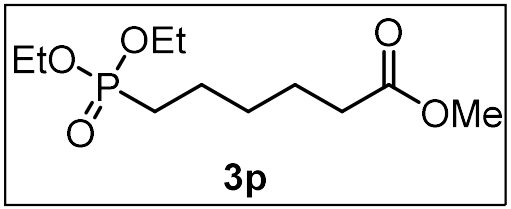
3o

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



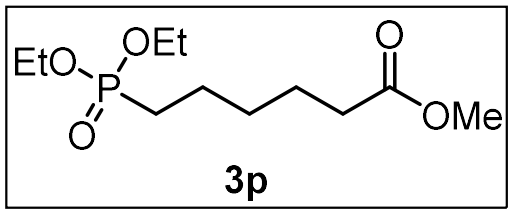
3o

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



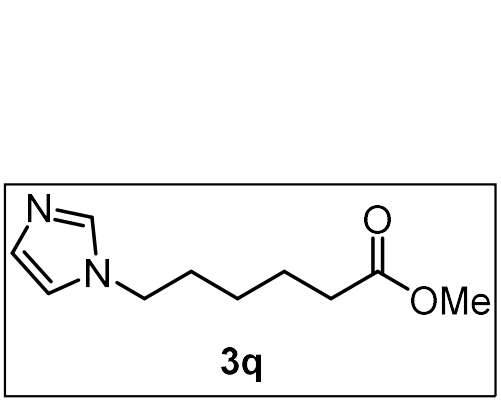
3p

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



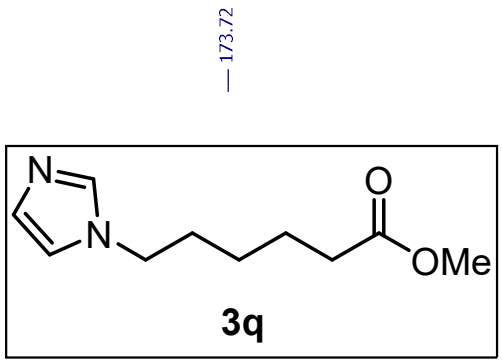
3p

$^{13}C\{^{1}H\}$NMR (75 MHz, $CDCl_3$)



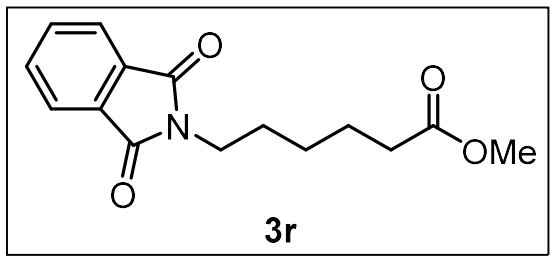
3q

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



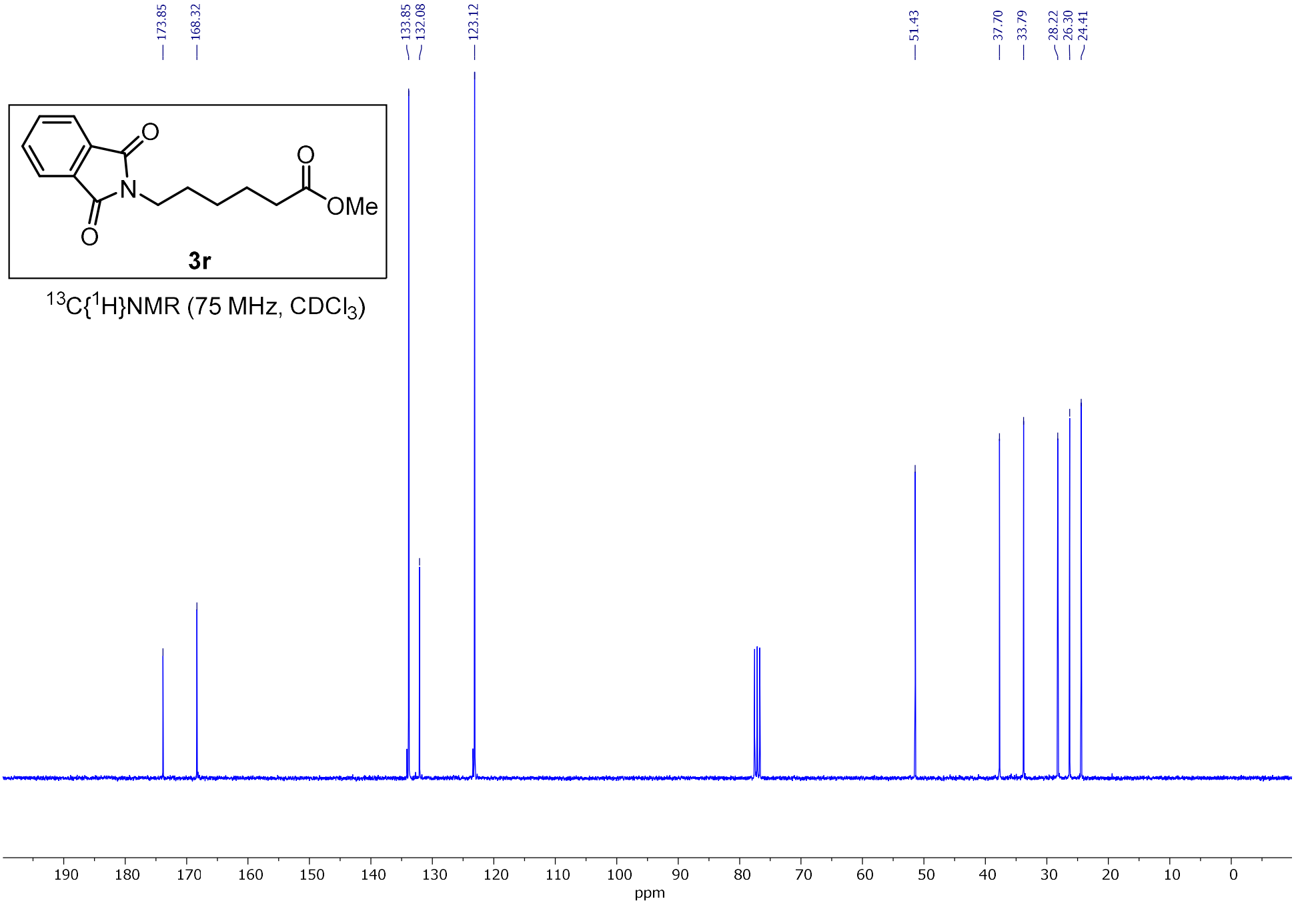
3q

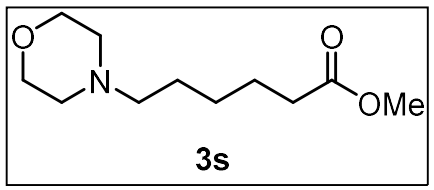
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



3r

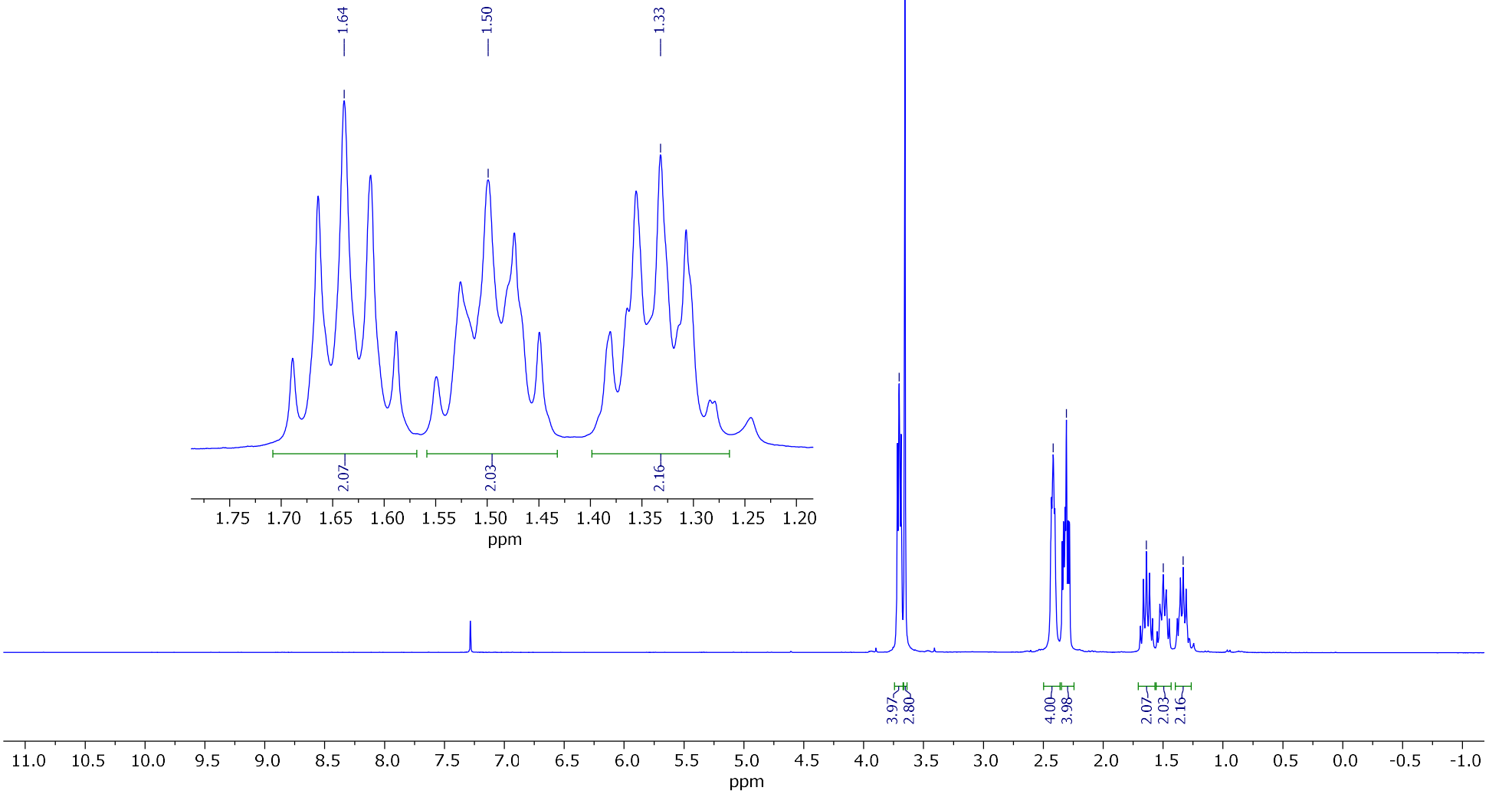
^{1}H NMR (300 MHz, $CDCl_3$)

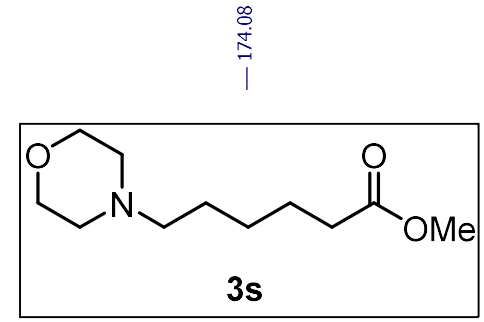

173.85
168.32
133.85
132.08
123.12
51.43
37.70
33.79
28.22
26.30
24.41
O
N
O
O
OMe
3r
$^{13}C\{^{1}H\}$NMR (75 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



3s

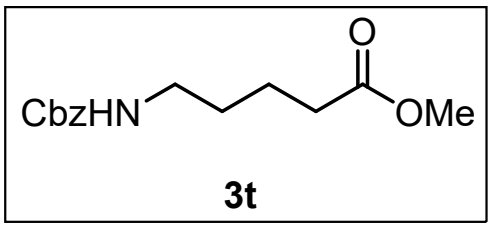
^{1}H NMR (300 MHz, $CDCl_3$)





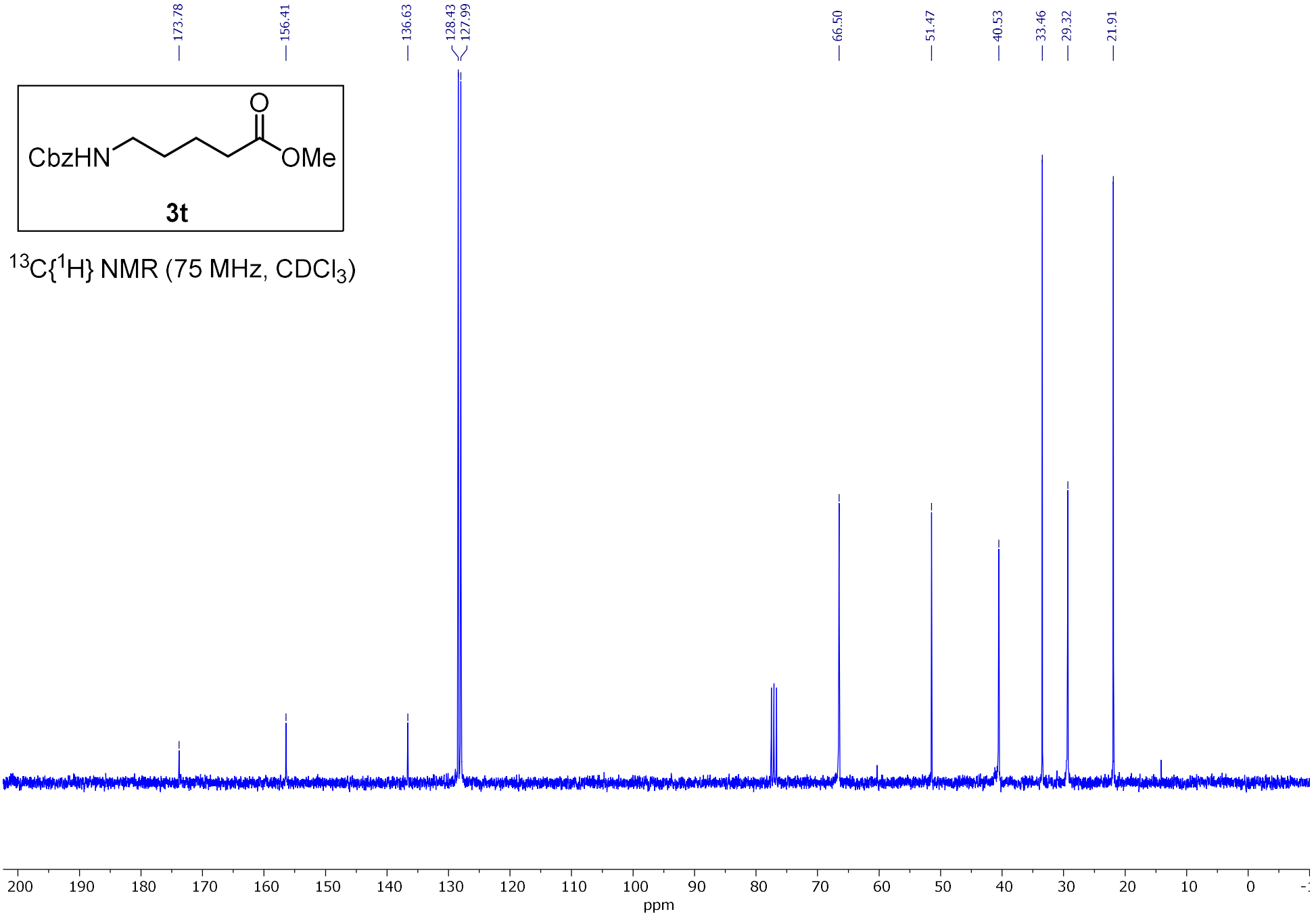
3s

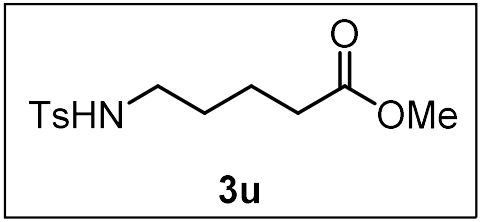
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



3t

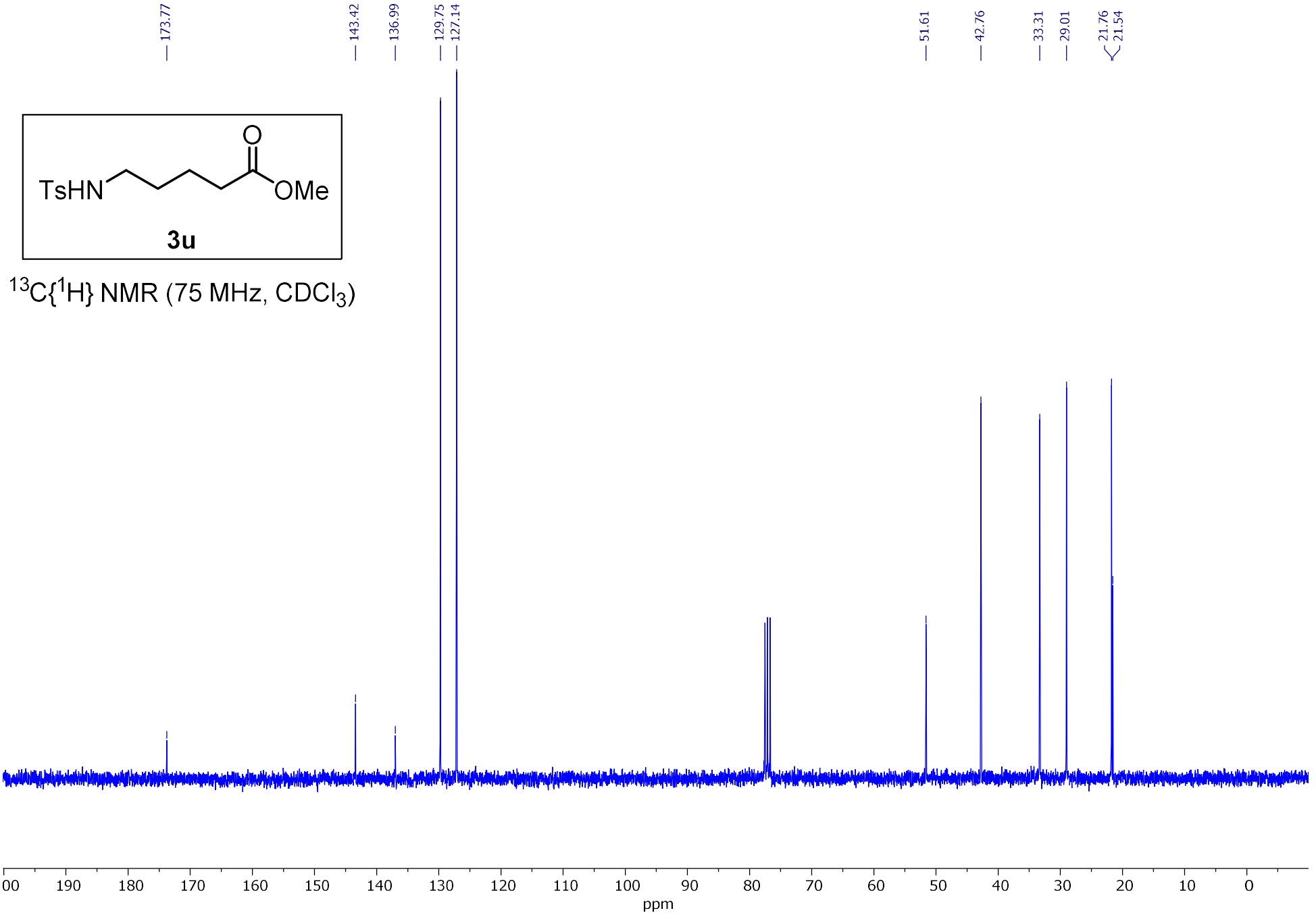
^{1}H NMR (300 MHz, $CDCl_3$)

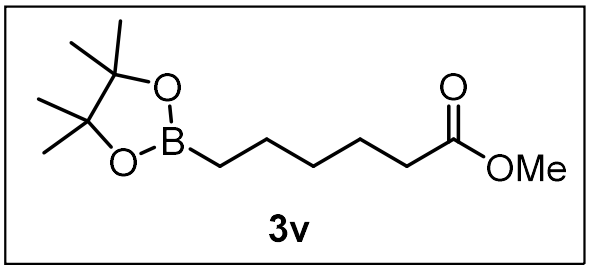

173.78
156.41
136.63
128.43
127.99
66.50
51.47
40.53
33.46
29.32
21.91
CbzHN
O
OMe
3t
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



3u

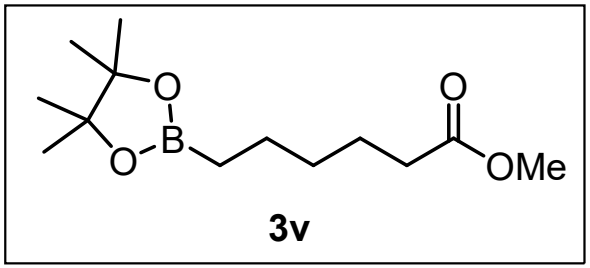
^{1}H NMR (300 MHz, $CDCl_3$)


173.77
143.42
136.99
129.75
127.14
51.61
42.76
33.31
29.01
21.76
21.54
TsHN
O
OMe
3u
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
ppm



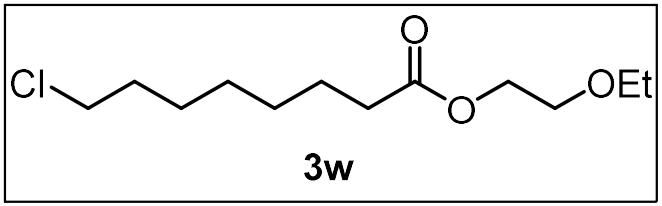
3v

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



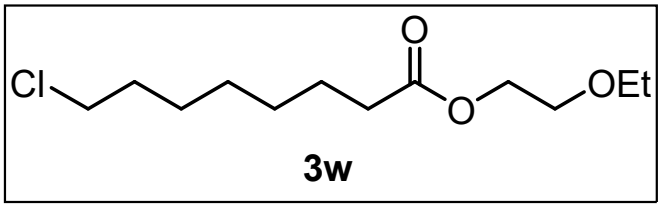
3v

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



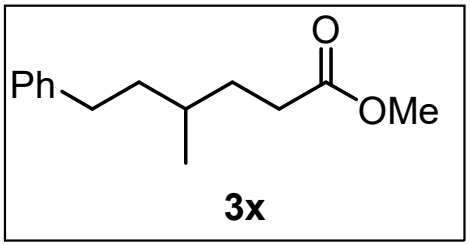
3w

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



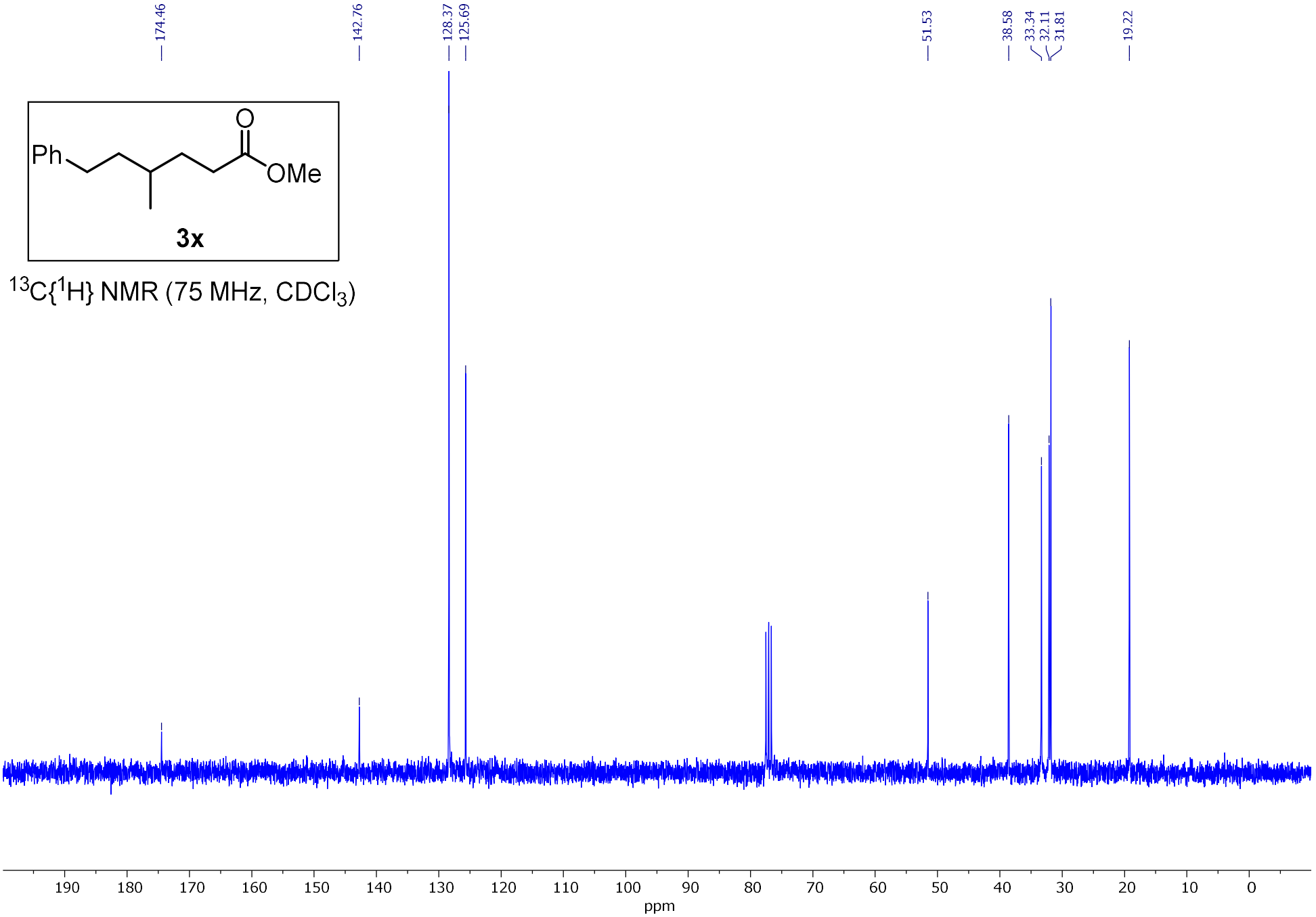
3w

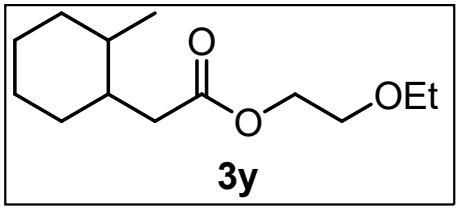
$^{13}C\{^{1}H\}$NMR (75 MHz, $CDCl_3$)



3x

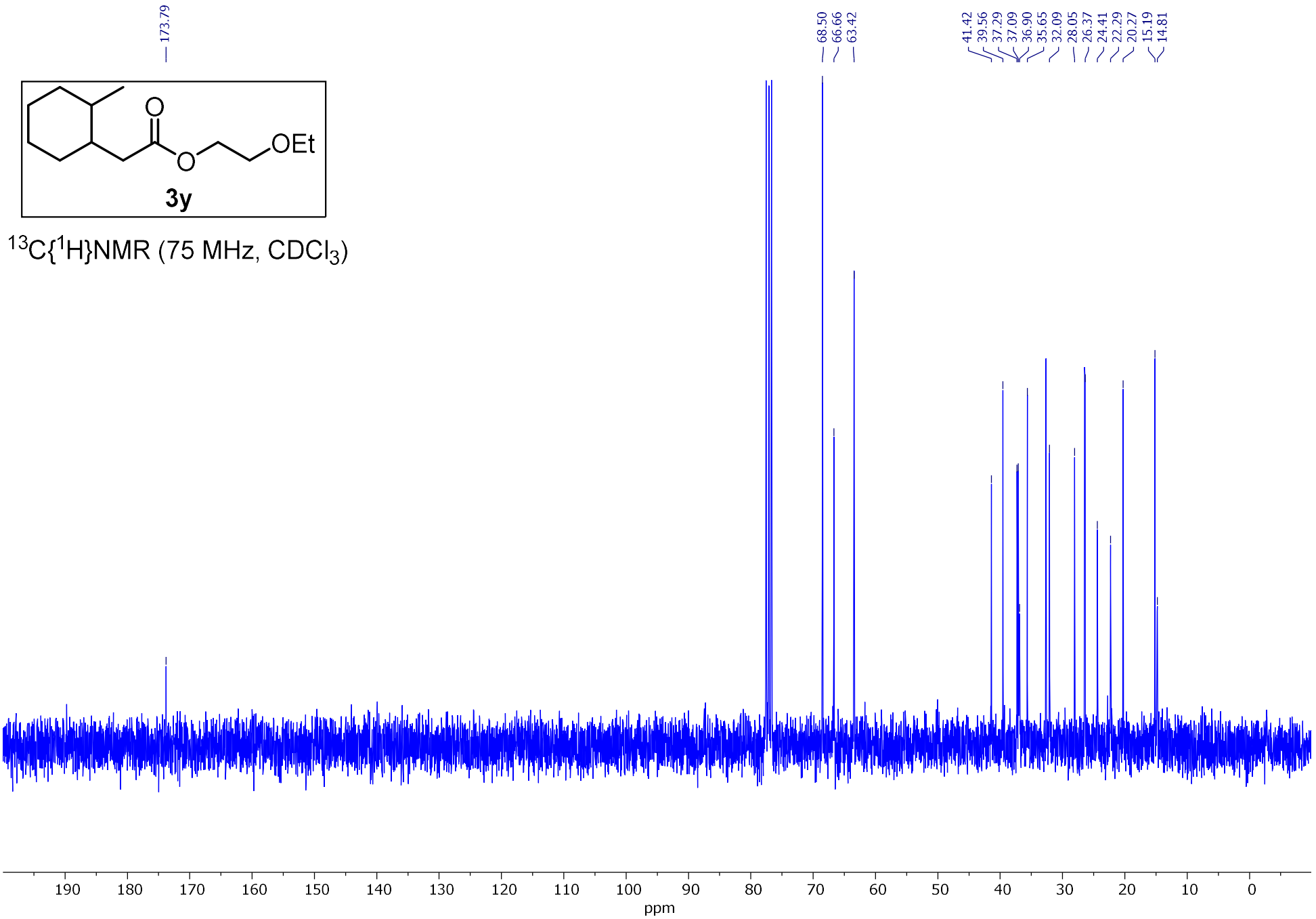
^{1}H NMR (300 MHz, $CDCl_3$)

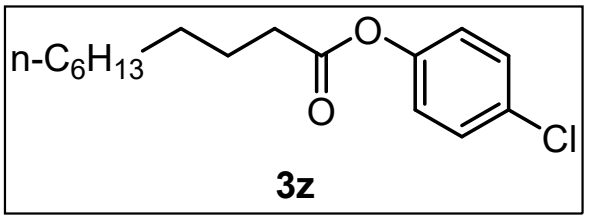

174.46
142.76
128.37
125.69
51.53
38.58
33.34
32.11
31.81
19.22
Ph
O
OMe
3x
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



3y

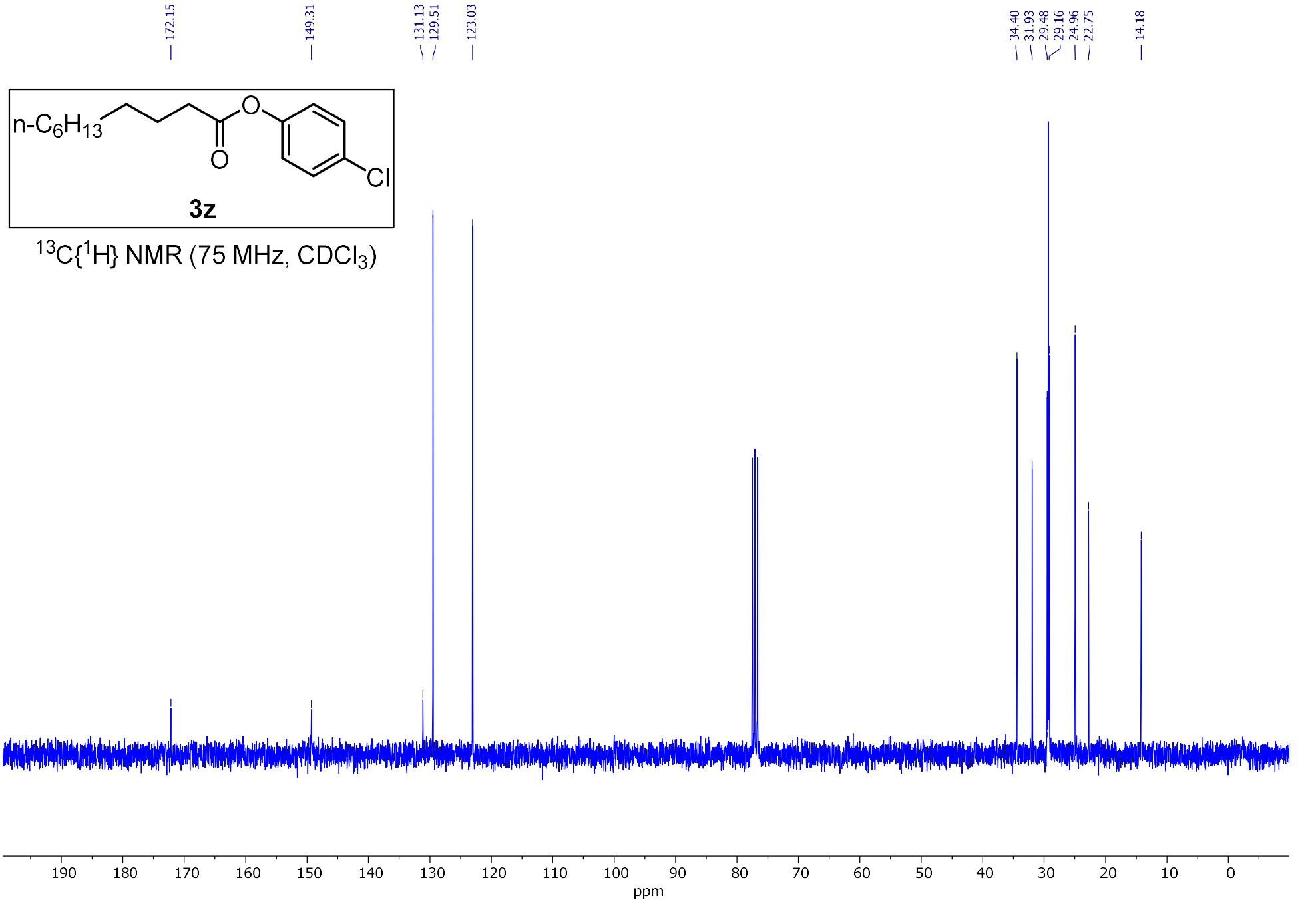
^{1}H NMR (300 MHz, $CDCl_3$)

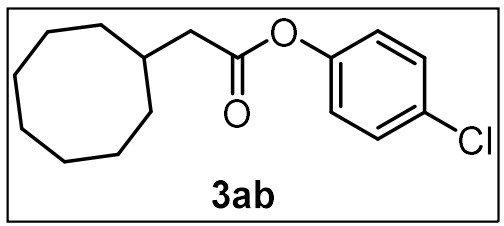

173.79
68.50
66.66
63.42
41.42
39.56
37.29
37.09
36.90
35.65
32.09
28.05
26.37
24.41
22.29
20.27
15.19
14.81
O
O
OEt
3y
$^{13}C\{^{1}H\}$NMR (75 MHz, $CDCl_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



3z

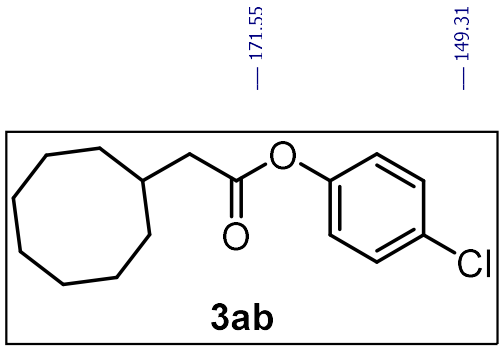
^{1}H NMR (300 MHz, $CDCl_3$)


172.15
149.31
131.13
129.51
123.03
34.40
31.93
29.48
29.16
24.96
22.75
14.18
n-C6H13
O
O
Cl
3z
13C{1H} NMR (75 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



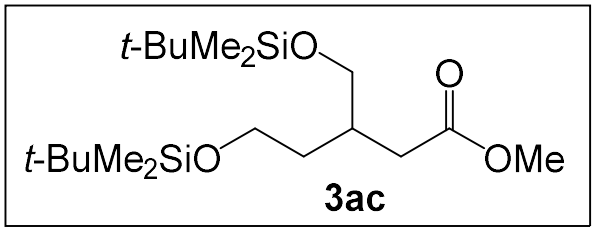
3ab

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



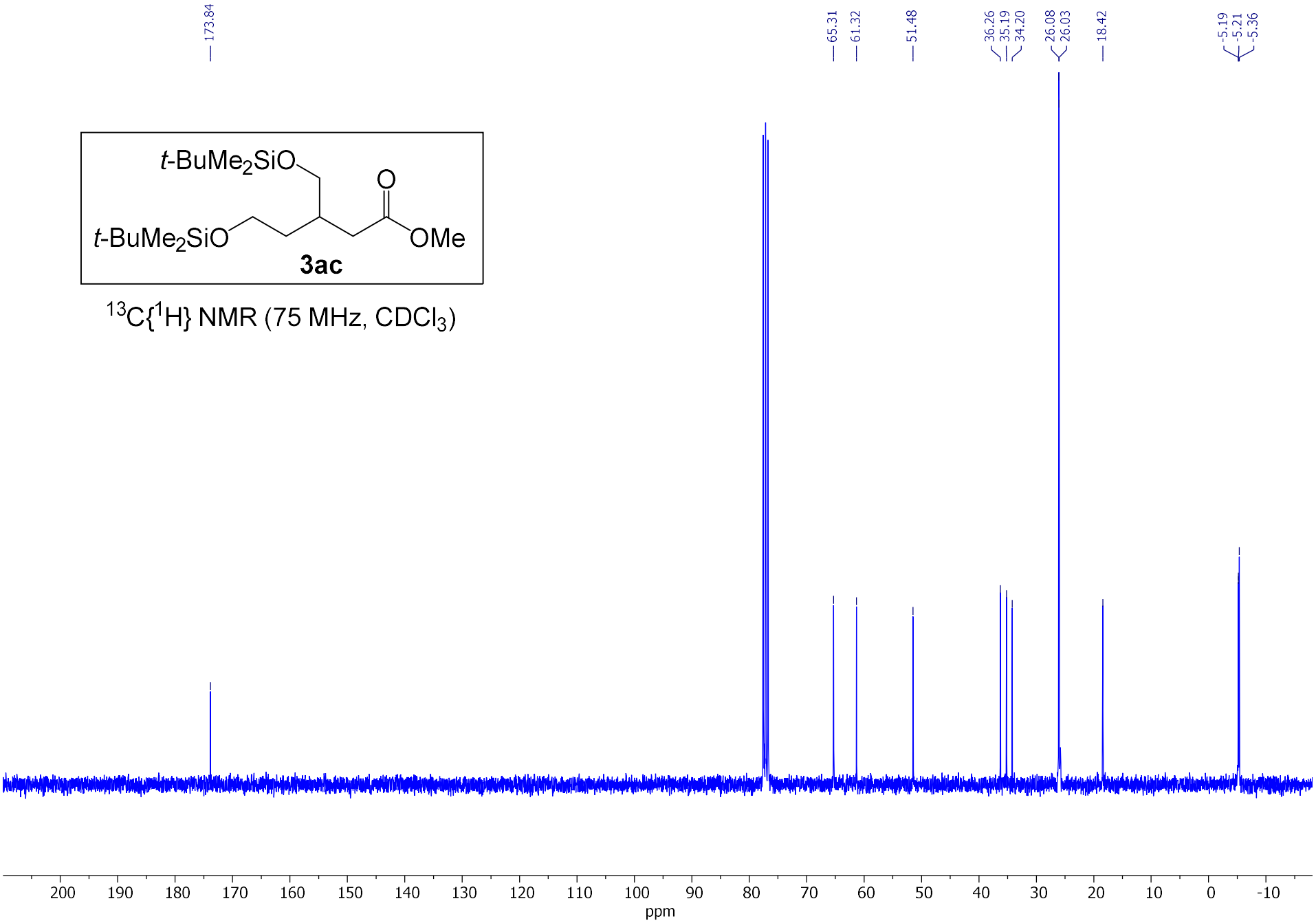
3ab

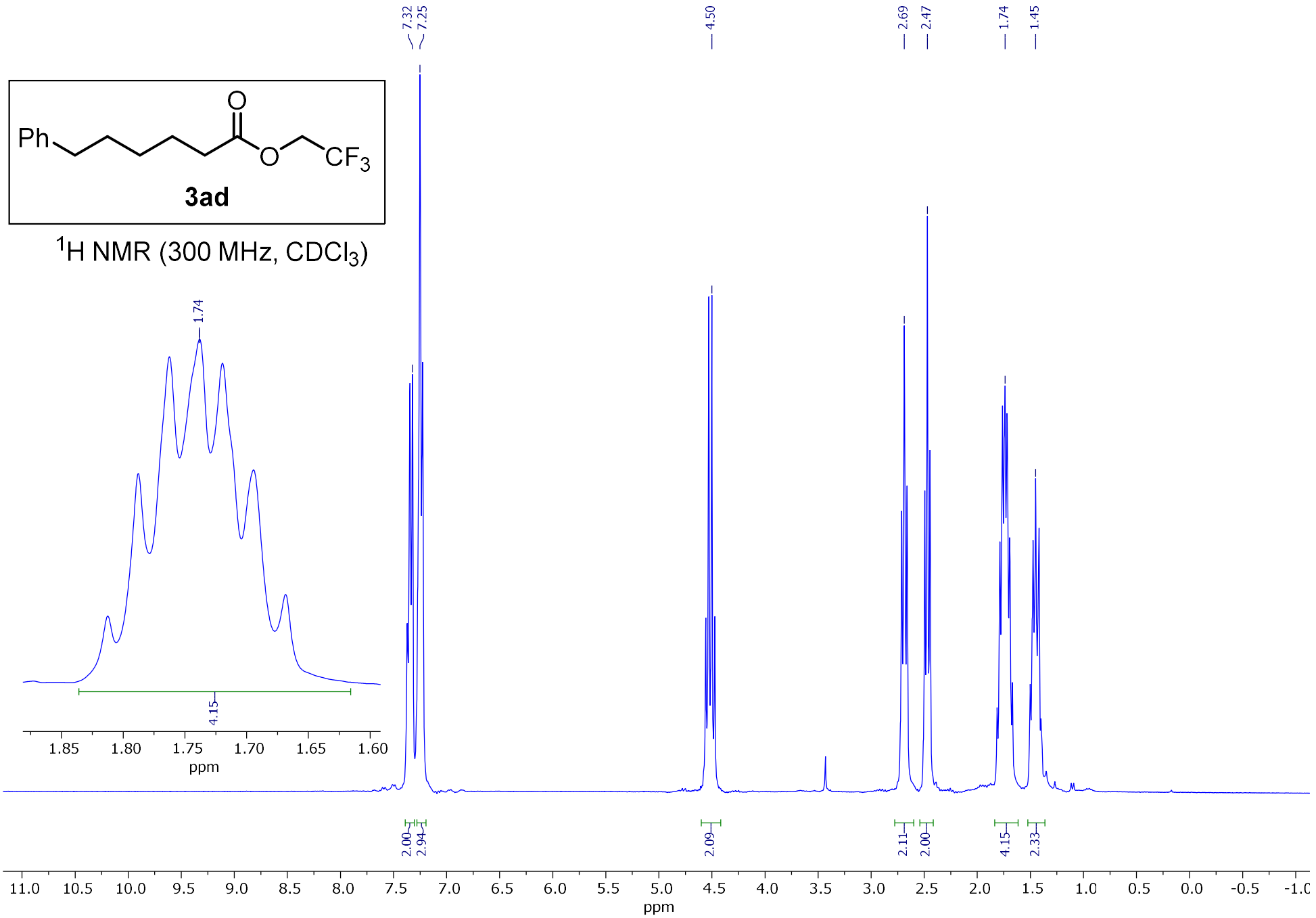
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

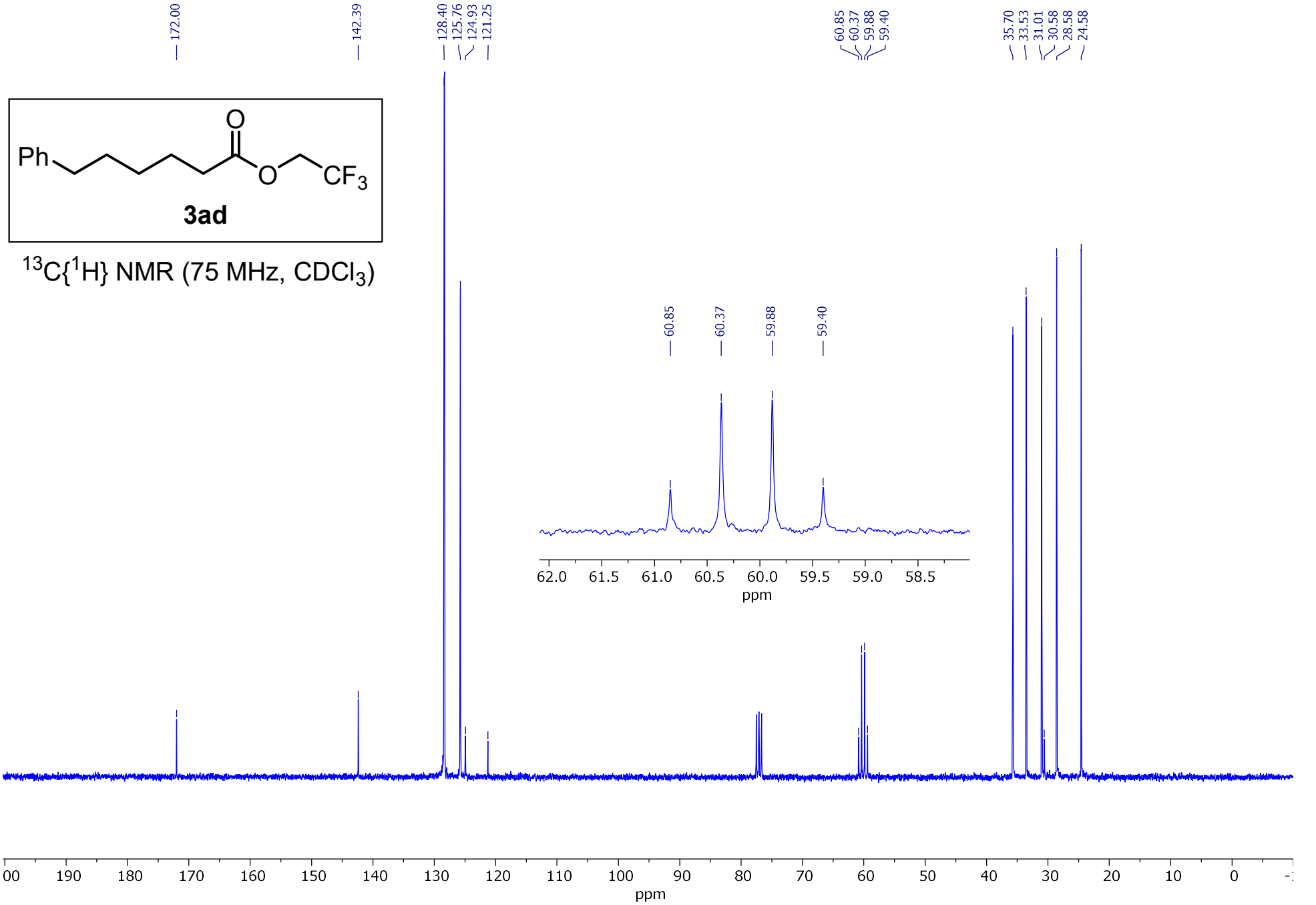


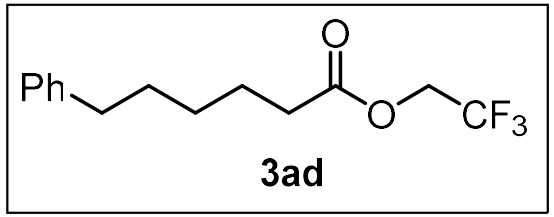
3ac

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


173.84
65.31
61.32
51.48
36.26
35.19
34.20
26.08
26.03
18.42
-5.19
-5.21
-5.36
t-BuMe2SiO
O
t-BuMe2SiO
OMe
3ac
13C{1H} NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

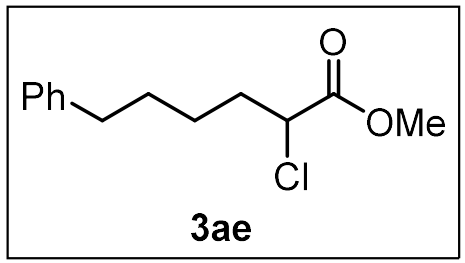

7.32
7.25
4.50
2.69
2.47
1.74
1.45
Ph
O
O
CF3
3ad
1H NMR (300 MHz, CDCl3)
1.74
4.15
1.85 1.80 1.75 1.70 1.65 1.60
ppm
2.00
2.94
2.09
2.11
2.00
4.15
2.33
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
ppm


172.00
142.39
128.40
125.76
124.93
121.25
60.85
60.37
59.88
59.40
35.70
33.53
31.01
30.58
28.58
24.58
Ph
O
O
CF3
3ad
13C{1H} NMR (75 MHz, CDCl3)
62.0
61.5
61.0
60.5
60.0
59.5
59.0
58.5
ppm
ppm



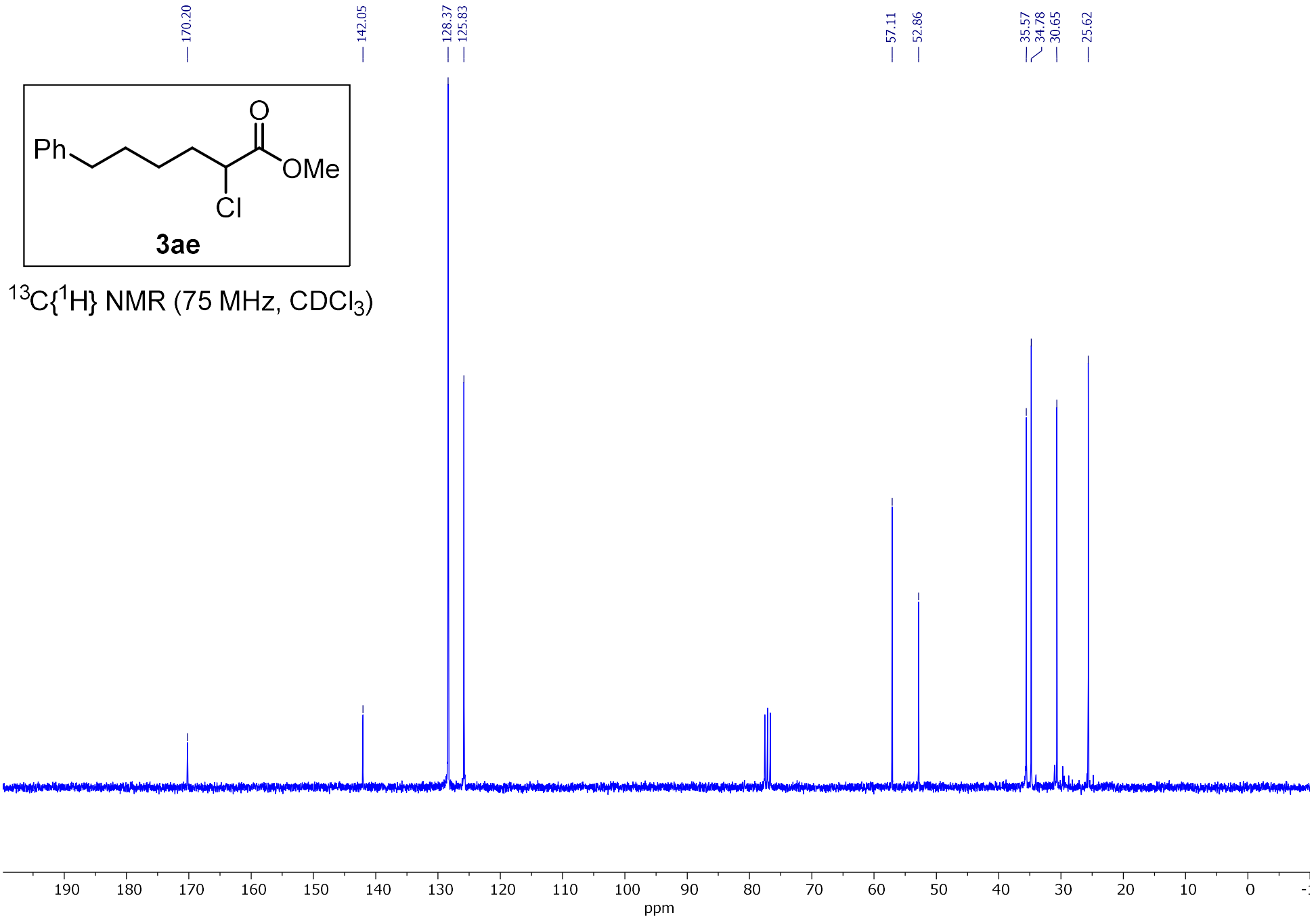
3ad

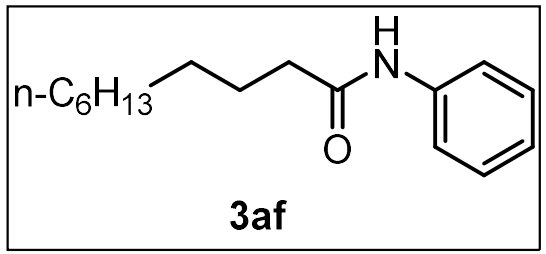
^{19}F NMR (282 MHz, $CDCl_3$)



3ae

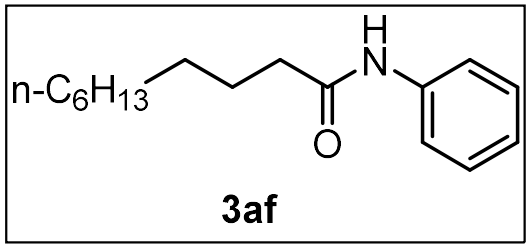
^{1}H NMR (300 MHz, $CDCl_3$)


170.20
142.05
128.37
125.83
57.11
52.86
35.57
34.78
30.65
25.62
Ph
O
OMe
Cl
3ae
13C{1H} NMR (75 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



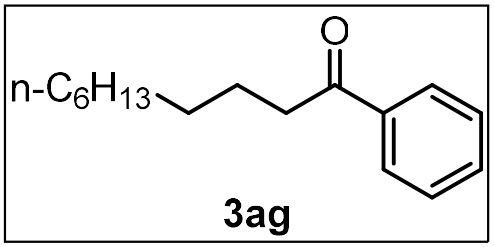
3af

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



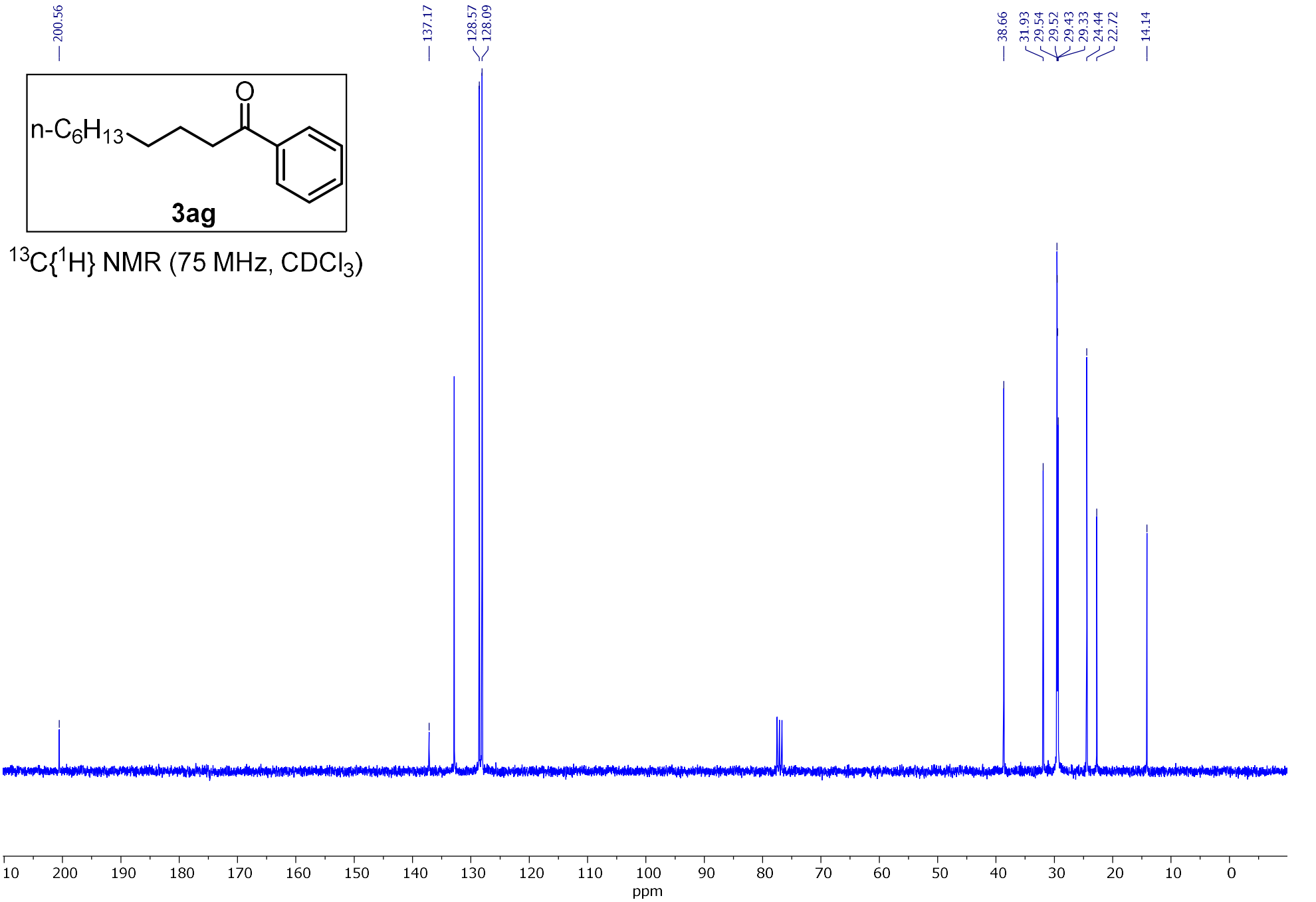
3af

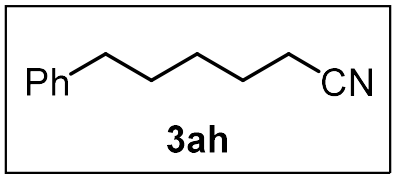
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



3ag

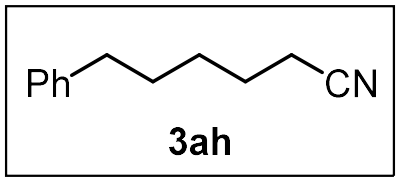
^{1}H NMR (300 MHz, $CDCl_3$)


200.56
137.17
128.57
128.09
38.66
31.93
29.54
29.52
29.43
29.33
24.44
22.72
14.14
n-C6H13
O
3ag
13C{1H} NMR (75 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm



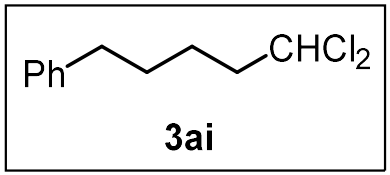
3ah

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



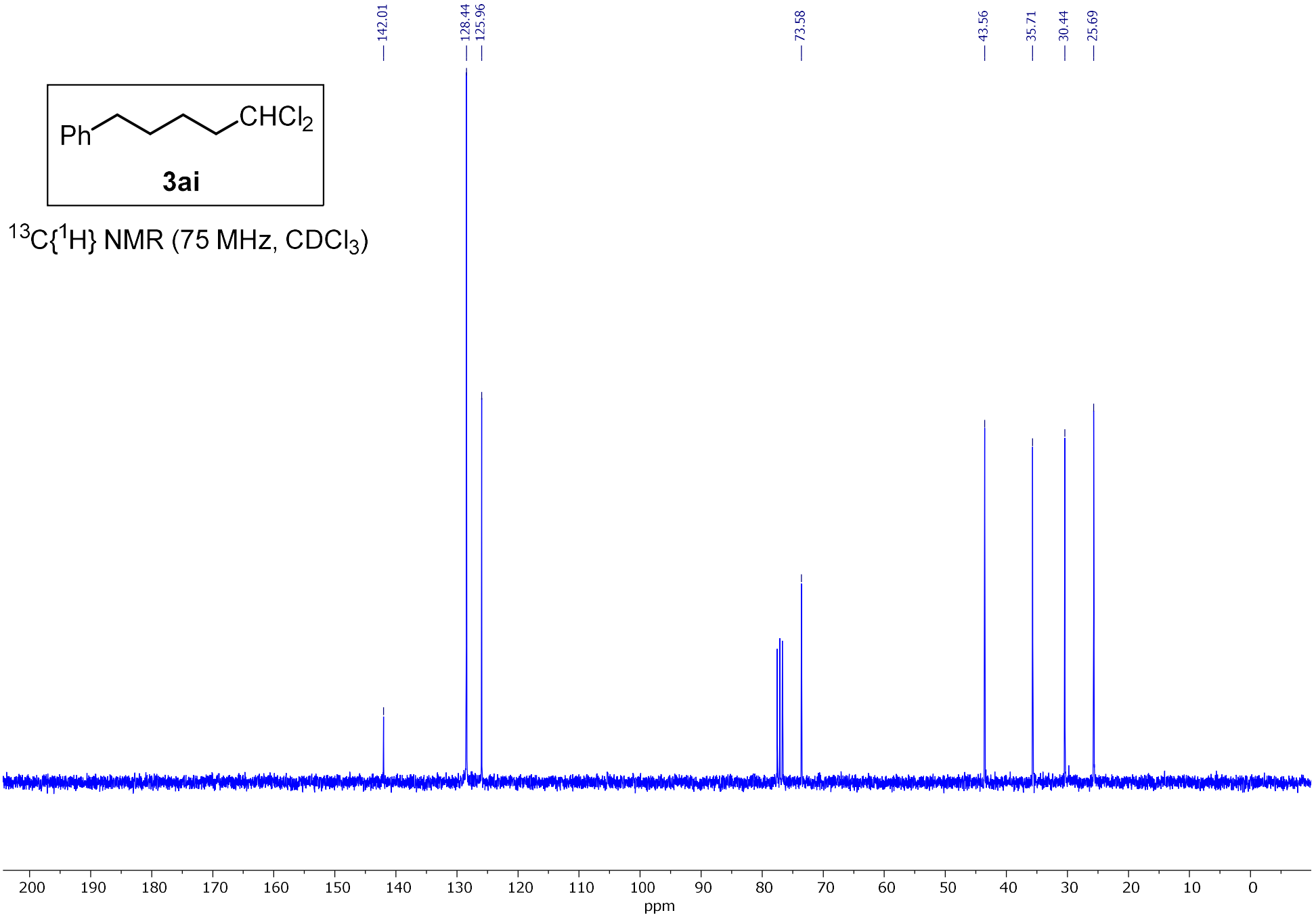
3ah

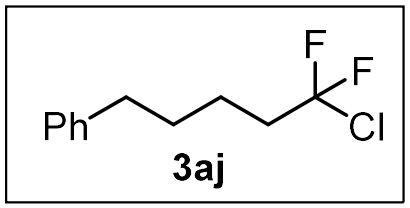
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



3ai

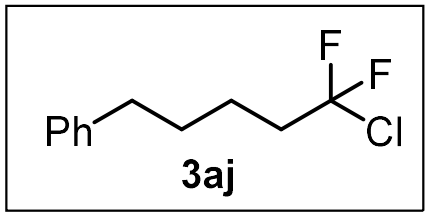
^{1}H NMR (300 MHz, $CDCl_3$)


142.01
128.44
125.96
73.58
43.56
35.71
30.44
25.69
Ph
CHCl2
3ai
13C{1H} NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



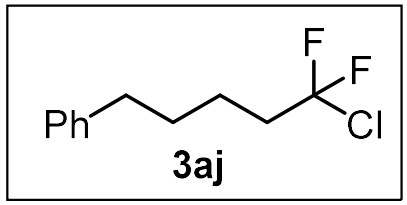
3aj

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



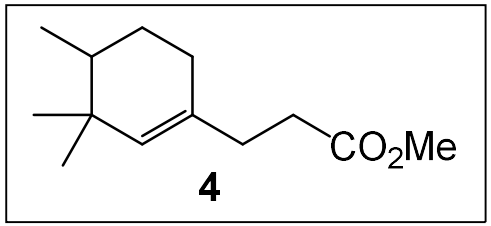
3aj

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)



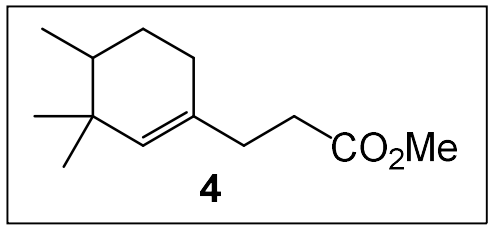
3aj

^{19}F NMR (282 MHz, $CDCl_3$)



4

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



4

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)