Supporting Information

Unlocking the Reactivity of the C-In Bond: Alkyl Indium Reagents as a Source of Radicals Under Photocatalytic Conditions

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1. General Methods

Dimethylformamide was distilled from P_2O_5 and stored under argon atmosphere over 4Å MS. Dimethoxyethane and tetrahydrofuran were distilled from $LiAlH_4$ and stored under argon atmosphere over 3Å MS. Acetonitrile was distilled from CaH_2 and stored under argon atmosphere over 3Å MS. Column chromatography was carried out employing silica gel (230-400 mesh) or neutral alumina, Brockmann II. Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or acidic aq. $KMnO_4$ solution. NMR spectra were recorded on Bruker Avance II 300 spectrometer. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and time-of-flight (TOF) mass analyzer. The measurements were done in a positive ion mode (interface capillary voltage –4500 V) or in a negative ion mode (3200 V); mass range from m/z 50 to m/z 3000. Melting points were measured with Stuart SMP30 apparatus. Sonications were run with a UZV-5,7 system emitting a 35-KHz wave. Photo-induced reactions were performed in Duran culture tubes (Roth cat. no K248.1, outside diameter = 12 mm). For irradiation, the reaction vessel was placed in a glass jacket for cooling (Huber circulating chiller BR-03 was used, water temperature 20 °C). As a light source, 400 nm COB LED matrix Hontiey (29−32 V, 3000 mA, 100 W; operated at 60 W) was used. The distance between the reaction vessel and the LED chip was about 10 mm. The reaction set-up was used as previously described.[1]

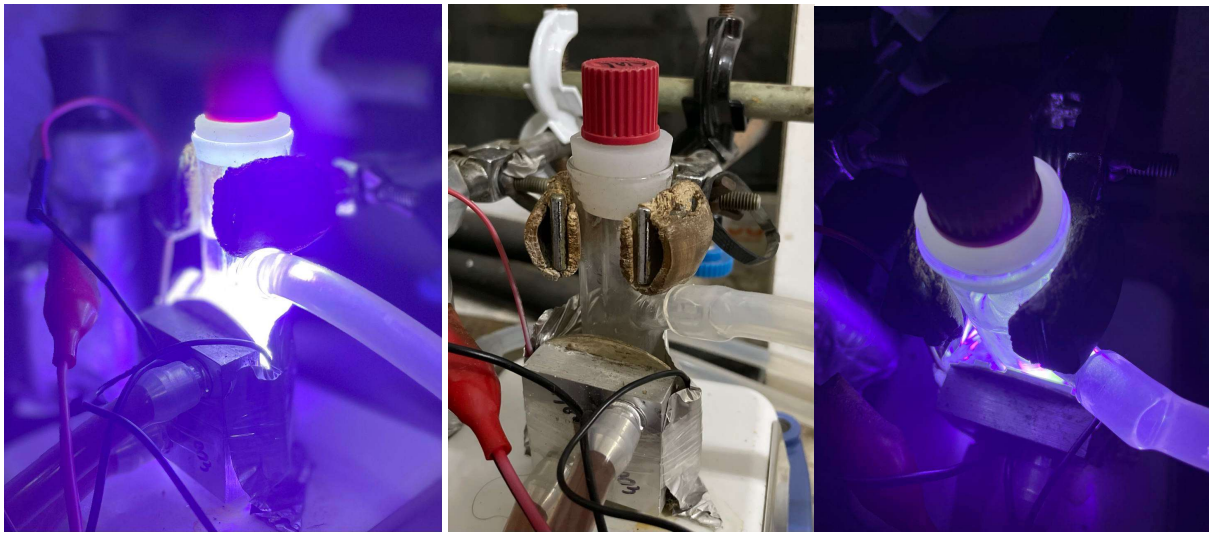


Figure S1. Photocatalytic reaction set-up.

2. Starting Materials

All commercially available reagents were purchased from Acros Organics or ABCR. Reagents shown below were synthesized according to literature procedures:

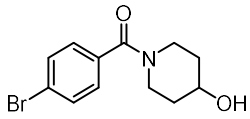
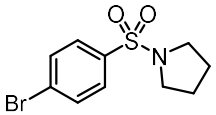
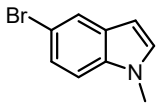
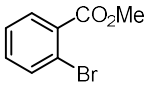
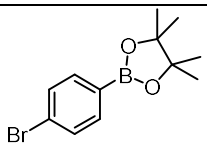
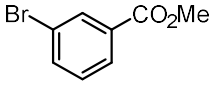
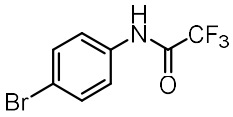
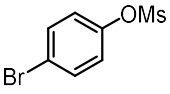
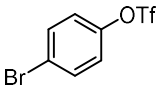
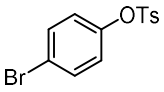
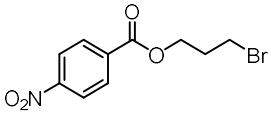
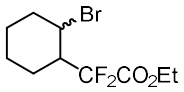
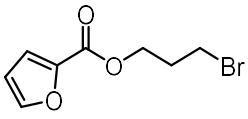
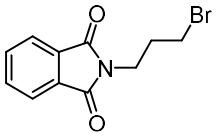
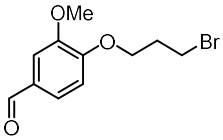
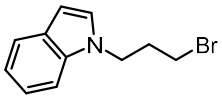
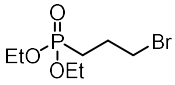
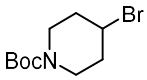
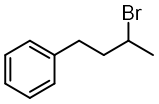
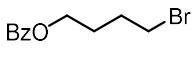
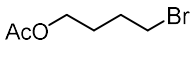
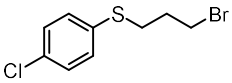
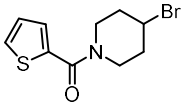
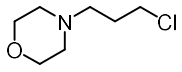
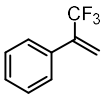
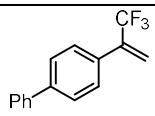
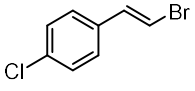
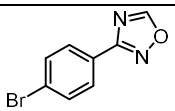
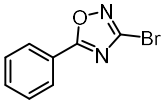
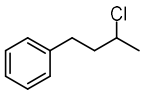
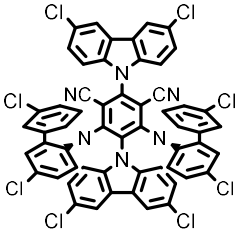
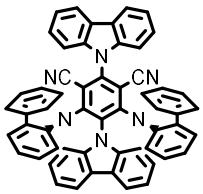
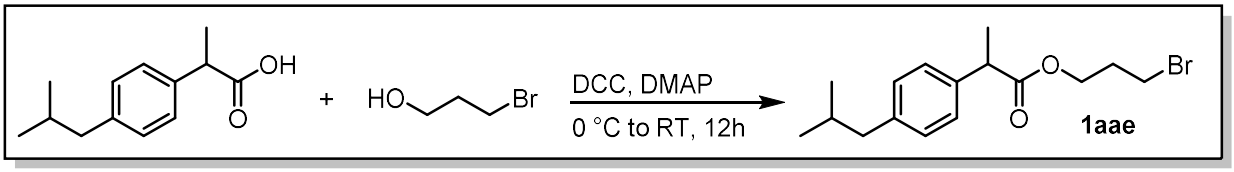
 **1aa**[2]	 **1ab**[3]	 **1ac**[4]	 **1ad**[5]
 **1ae**[6]	 **1af**[7]	 **1ag**[8]	 **1ah**[9]
 **1ai**[10]	 **1aj**[11]	 **1ak**[12]	 **1al**[13]
 **1am**[14]	 **1an**[15]	 **1ao**[16]	 **1ap**[17]
 **1aq**[18]	 **1ar**[19]	 **1as**[20]	 **1at**[21]
 **1au**[22]	 **1av**[23]	 **1aw**[24]	 **1ax**[25]
 **1ay**[26]	 **1az**[27]	 **1aaa**[28]	 **1aab**[29]
 **1aac**[30]	 **1aad**[31]	 8Cl4CzIPN[32]	 4CzIPN[33]

Table S1. List of starting materials synthesized according to literature procedures.

3-Bromopropyl 2-(4-isobutylphenyl)propanoate (1aae)



To a 50 mL round-bottom flask were added 2-(4-isobutylphenyl)propanoic acid (0.649 g, 3.15 mmol, 1.05 equiv), DMAP (73.2 mg, 0.60 mmol, 0.20 equiv), anhydrous dichloromethane (10 mL), and 3-bromopropan-1-ol (0.417 g, 3.00 mmol, 1.00 equiv). A solution of N,N'-Dicyclohexylcarbodiimide (0.619 g, 3.0 mmol, 1.00 equiv) in dichloromethane (6.0 mL) was added dropwise at 0 °C. After stirring for 12 h at room temperature, the reaction mixture was filtered through a pad of celite and washed with MTBE. The filtrate was concentrated and the residue was purified by silica gel chromatography (petroleum ether : ethyl acetate, 15 : 1).

Yield 0.706 g (72%). Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 7.7 Hz, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 4.29 – 4.10 (m, 2H), 3.70 (q, *J* = 7.2 Hz, 1H), 3.27 (t, *J* = 6.0 Hz, 2H), 2.45 (d, *J* = 7.1 Hz, 2H), 2.16 – 2.02 (m, 2H), 1.94 – 1.77 (m, 1H), 1.50 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 174.6, 140.7, 137.8, 129.5, 127.2, 62.3, 45.2, 45.1, 31.7, 30.30 29.3, 22.5, 18.4.

HRMS (ESI-TOF): calculated for $C_{16}H_{24}BrO_2$ (M+H) 327.0954, found 327.0949.

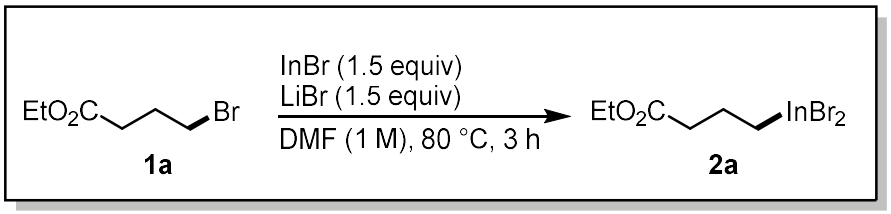
Synthesis of Indium(I) bromide (modified literature procedure).[34]

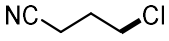
Indium metal cut in cubes (size ~5–7 mm, 30.0 g, 0.26 mol, 1.8 eq) was placed in a thick-walled glass vessel (rated up to 20 bar) with a thread. The reaction vessel was evacuated twice and filled with argon. Acetonitrile (120 mL) and an appropriate stirring bar were added. Bromine (7.4 mL, 0.14 mol, 1.0 eq) was added dropwise allowing bromine color to disappear between the drops to avoid excessive heating. After the addition was complete, the vessel was closed with a threaded PTFE stopper. The reaction mixture was heated at 110 °C (oil bath) with stirring for 88 hours. Bright orange precipitate formed copiously above few remaining indium nuggets (see **Figure S2**). The precipitate was filtered off and washed once with acetonitrile (40 mL) and twice with MTBE (total 50 mL). Indium nuggets were mechanically separated (through a 0.5 mm sieve) and preserved for the next reaction run. The precipitate was collected from the filter, and dried under vacuum (60 °C, 0.5 torr) to provide indium(I) bromide as orange powder (38.7 g, 76%).

Figure S2. Reaction mixture after completion of the reaction.

3. Optimization of the preparation of alkyl indium reagents

Primary alkyl indium reagents



Entry	Deviation from stnd. cond.	Yield **2a**, %[a]
1	**none**	**99%**
2	Air atmosphere	71%
3	InBr and LiBr (1.2 equiv)	97%
4	60 °C	80%
5[b]	rt	40%
6	50 °C + ultrasound	90%
7	LiCl (1.5 equiv) instead of LiBr	35%
8	No LiBr	48%
9	In (1.5 equiv) instead of InBr	41%
10[b]	THF as solvent	75%
11[b]	MeCN as solvent	77%
12[b]	DME as solvent	95%
13[c]	 as substrate	98%[d]

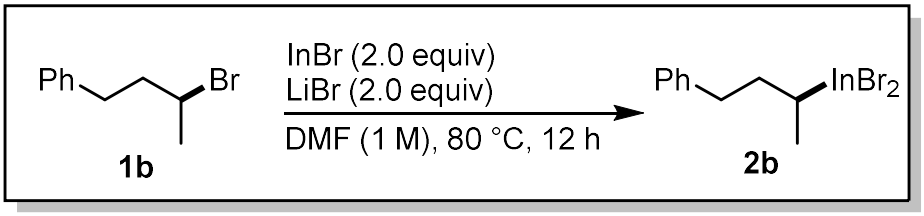
[a] Determined by ^{1}H NMR with 1,3,5-trioxane as an internal standard.

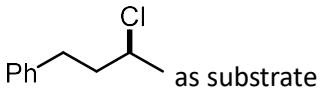
[b] 16 hours of stirring.

[c] 6 hours of stirring.

[d] Reagent **2e** as product.

Secondary alkyl indium reagents



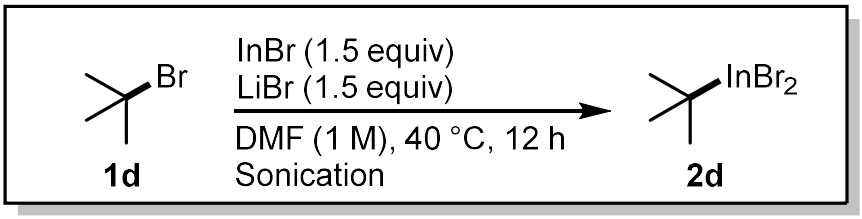
Entry	Deviation from stnd. cond.	Yield **2b**, %[a]
1	**none**	**97%**
2	3 h reaction time	88%
4	InBr and LiBr (1.5 equiv)	92%
5	LiCl (2.0 equiv) instead of LiBr	82%
6[b]	THF as solvent	87%
7[b]	MeCN as solvent	91%
8[c]	 as substrate	84%

[a] Determined by ^{1}H NMR with 1,3,5-trioxane as an internal standard.

[b] 16 hours of stirring.

[c] LiBr (3.0 equiv) was used.

Tertiary alkyl indium reagents



Entry	Deviation from stnd. cond.	Y. 2**d**, %[a]
1	**none**	**63%**
2	LiCl (1.5 equiv) instead of LiBr	56%
3	50 ^{0}C	48%
4	heat at 80 ^{0}C instead of sonication	22%

[a] Determined by ^{1}H NMR with 1,3,5-trioxane as an internal standard.

4. Compounds preparation and characterization

4.1. General procedures for the preparation of alkyl indium reagents

Preparation of alkyl indium reagents from primary and secondary alkyl bromides (General procedure I)

Lithium bromide (for *primary alkyl bromide* 65.3 mg, 0.75 mmol; for *secondary alkyl bromide* 87.0 mg/ 1.00 mmol) was dried under vacuum (250 °C, 12 torr) in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*) for 10 minutes. The tube was evacuated and filled with argon twice. A magnetic stirring bar, dimethylformamide (DMF) (0.5 mL) and alkyl bromide (0.5 mmol) were added. Indium(I) bromide (for *primary alkyl bromide* 146.3 mg, 0.75 mmol; for *secondary alkyl bromide* 195.0 mg, 1.00 mmol) was added last to the reaction mixture. The tube was closed with a screw cap. The reaction mixture was heated at 80 °C (PEG bath) with stirring for 0.5 – 12 hours (see **Table S2**). After the reaction was completed, the tube was centrifuged at 2600 rpm for 2 minutes. The conversion of alkyl bromide to the corresponding alkyl indium compound (**2a,b,c,e-Br,f-c'**) was monitored by treatment of the formed alkyl indium compound with iodine as follows: an excess of iodine was placed in a 1 mL chromatographic vial. Methyl *tert*-butyl ether (MTBE) (0.8 mL) and an aliquot of the analysed organoindium solution (2 - 5 µl) were added. After heating (70 °C) this mixture for 20 seconds, the ratio of alkyl iodide / alkyl bromide was determined by GC-MS.

Figure S3. organoindium reaction set-up.

Preparation of *tert*-butylindium(III) bromide from 2-bromo-2-methylpropane

Lithium bromide (65.3 mg, 0.75 mmol) was dried under vacuum (250 °C, 12 torr) in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*) for 10 minutes. The tube was evacuated and filled with argon twice. A magnetic stirring bar, dimethylformamide (DMF) (0.5 mL) and 2-bromo-2-methylpropane (68.5 mg, 0.5 mmol) were added. Indium(I) bromide (146.3 mg, 0.75 mmol) was added last to the reaction mixture. The tube was closed with a screw cap. The reaction mixture was heated at 40 °C (*sonication was performed with a system emitting a 35-KHz wave (150 W), volume of water in the bath 500 mL*) with stirring for 12 hours. After the reaction was completed, the tube was centrifuged at 2600 rpm for 2 minutes. The conversion of 2-bromo-2-methylpropane to the corresponding tert-butylindium(III) bromide (**2d**) was monitored by ^{1}H NMR with 1,3,5-trioxane as an internal standard. Yield: 63% (determined by ^{1}H NMR with 1,3,5-trioxane as an internal standard).

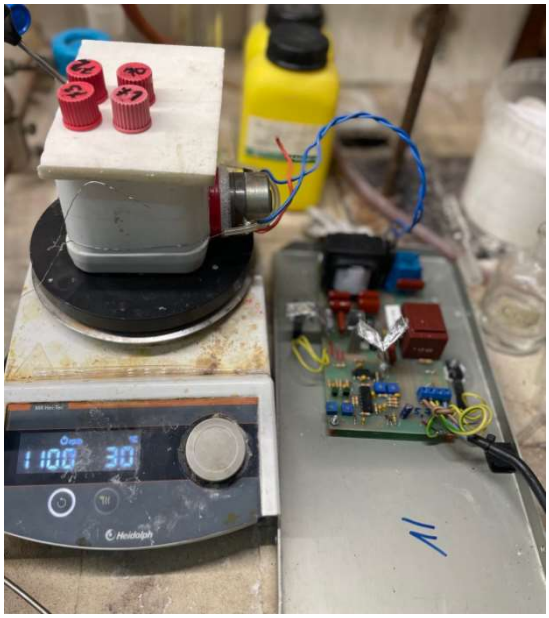


Figure S4. *tert*-Butylindium(III) bromide reaction set-up.

Preparation of alkyl indium reagents from primary and secondary alkyl chlorides

(General procedure II)

Lithium bromide (for *primary alkyl chloride* 65.3 mg, 0.75 mmol; for *secondary alkyl chloride* 130.5 mg, 1.50 mmol) was dried under vacuum (250 °C, 12 torr) in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*) for 10 minutes. The tube was evacuated and filled with argon twice. A magnetic stirring bar, dimethylformamide (DMF) (0.5 mL) and alkyl chloride (0.5 mmol) were added. Indium(I) bromide (for *primary alkyl chloride* 146.3 mg; for *secondary alkyl chloride* 0.75 mmol / 195.0 mg, 1.00 mmol) was added last to the reaction mixture. The tube was closed with a screw cap. The reaction mixture was heated at 80 °C for *primary alkyl chloride* (or at 100 °C for *secondary alkyl chloride*) (PEG bath) with stirring for 6 – 12 hours (see **Table S2**) (Reaction set-up as shown in **Figure S3**). After the reaction was completed, the tube was centrifuged at 2600 rpm for 2 minutes. The conversion of alkyl chloride to the corresponding alkyl indium compound (**2b-Cl,e,d',e'**) was monitored by treatment of the formed alkyl indium compound with iodine as follows: an excess of iodine was placed in a 1 mL chromatographic vial. Methyl *tert*-butyl ether (MTBE) (0.8 mL) and an aliquot of the analysed organoindium solution (2 - 5 µl) were added. After heating (70 °C) this mixture for 20 seconds, the ratio of alkyl iodide / alkyl chloride was determined by GC-MS.

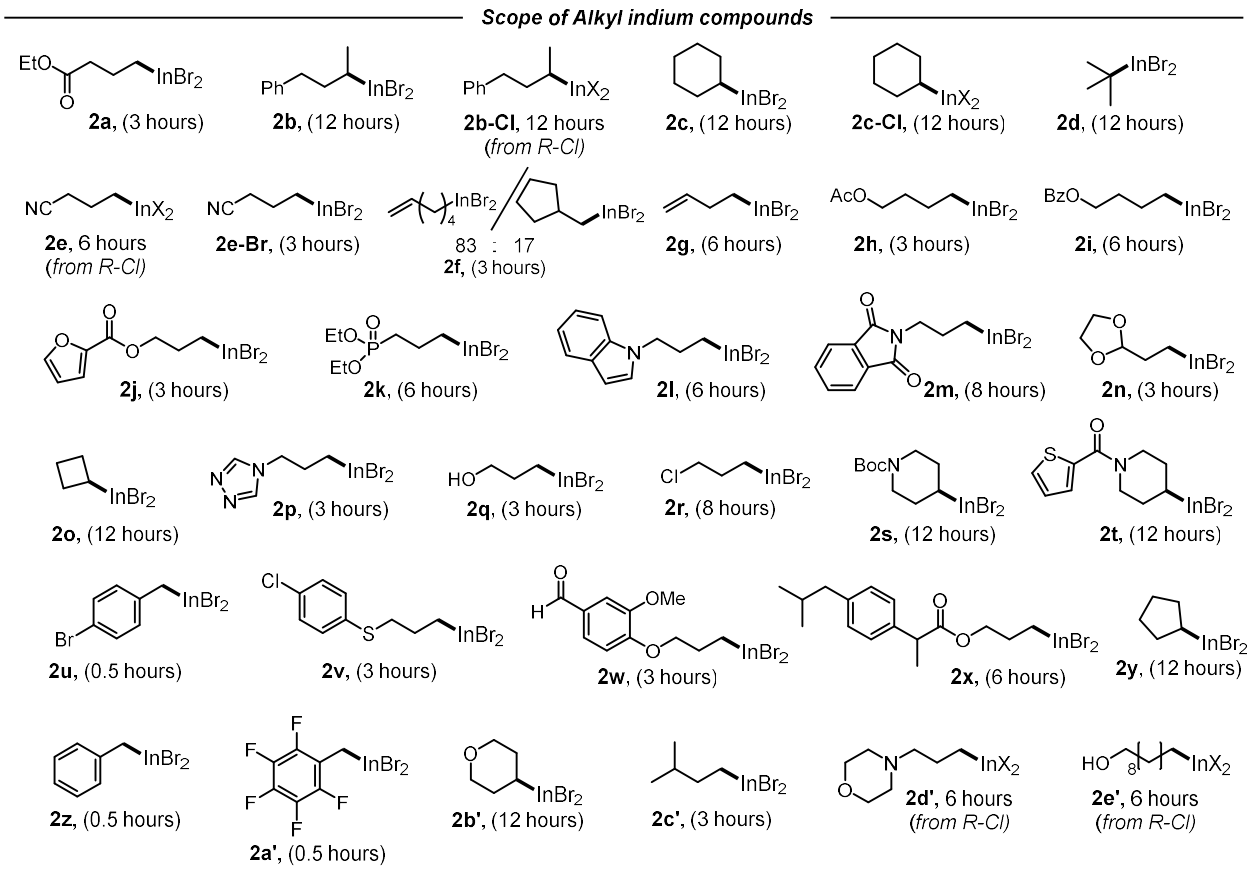


Table S2. Scope and reaction time of organoindium reagents prepared according to GP I and GP II.

4.2. Preparation of cyclohexylindium(III) halide(2c-Cl) stock solution

Lithium chloride (2.55 g, 60.00 mmol) was dried under vacuum (200 °C, 0.5 torr) in a 100 mL Schlenk vessel for 20 minutes. The vessel was evacuated and filled with argon twice. A magnetic stirring bar, dimethylformamide (DMF) (26.3 mL) and bromocyclohexane (4.89 g (3.69 mL), 30.00 mmol) were added. Indium(I) bromide (11.70 g, 60.00 mmol) was added last to the reaction mixture portionwise. The Schlenk vessel was closed, and the reaction mixture was heated at 80 °C (PEG bath) with stirring for 12 hours. After the reaction was completed, the indium powder was allowed to settle out (*indium formed during the disproportionation may precipitate either as powder or clump into nuggets* (**Figure S5**). *This circumstance had no influence on the rate and yield of the reaction*). The concentration of reagent (**2c-Cl**) in DMF was 0.651 M. The concentration of the resulting solution (**2c-Cl**) was determined by treatment of the formed cyclohexylindium(III) halide with iodine as follows: 1,2,3,4-tetrahydronaphthalene (1.0 mg, 0.008 mmol) and an excess of iodine was placed in a 1 mL chromatographic vial. Methyl *tert*-butyl ether (MTBE) (0.8 mL) and an aliquot of the analysed cyclohexylindium(III) halide solution (15 µL) were added. After heating (70 °C) this mixture for 20

seconds, the ratio between cyclohexyl Iodide and 1,2,3,4-tetrahydronaphthalene was determined by GC-FID (1,2,3,4-tetrahydronaphthalene as an internal standard).

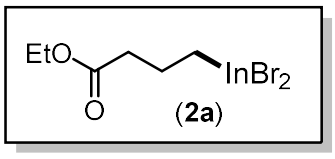
Figure S5. Preparation of reagent **2c-Cl** with indium precipitation in the form of powder (left) or nuggets (right).

4.3. Preparation and characterization of alkyl indium (2a) and (2b)

Synthesis and characterization of reagent (2a) in DMF-d7

Lithium bromide (65.3 mg, 0.75 mmol) was dried under vacuum (250 °C, 12 torr) in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*) for 10 minutes. The tube was evacuated and filled with argon twice. A magnetic stirring bar, DMF-d7 (0.5 mL) and ethyl 4-bromobutanoate (**1a**) (97.5 mg, 0.5 mmol) were added. Indium(I) bromide (146.3 mg, 0.75 mmol) was added last to the reaction mixture. The tube was closed with a screw cap. The reaction mixture was heated at 80 °C (PEG bath) with stirring for 3 hours. After the reaction was completed, the tube was centrifuged at 2600 rpm for 2 minutes.

(4-Ethoxy-4-oxobutyl)indium(III) bromide (2a)



(**2a**)

Yield determined by ^{1}H NMR with 1,3,5-trioxane as an internal standard: 99%.

^{1}H NMR (300 MHz, DMF-d7) δ 4.05 (q, *J* = 7.1 Hz, 2H), 2.37 (t, *J* = 7.6 Hz, 2H), 1.90 (p, *J* = 7.6 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.9 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, DMF-d7) δ 173.8, 60.9, 38.6, 23.9, 22.0, 15.1.

HRMS (ESI-TOF): calculated for $C_6H_{11}{}^{79}Br^{115}InO_2$ (M-^{79}Br) 308.8975, found 308.8970.

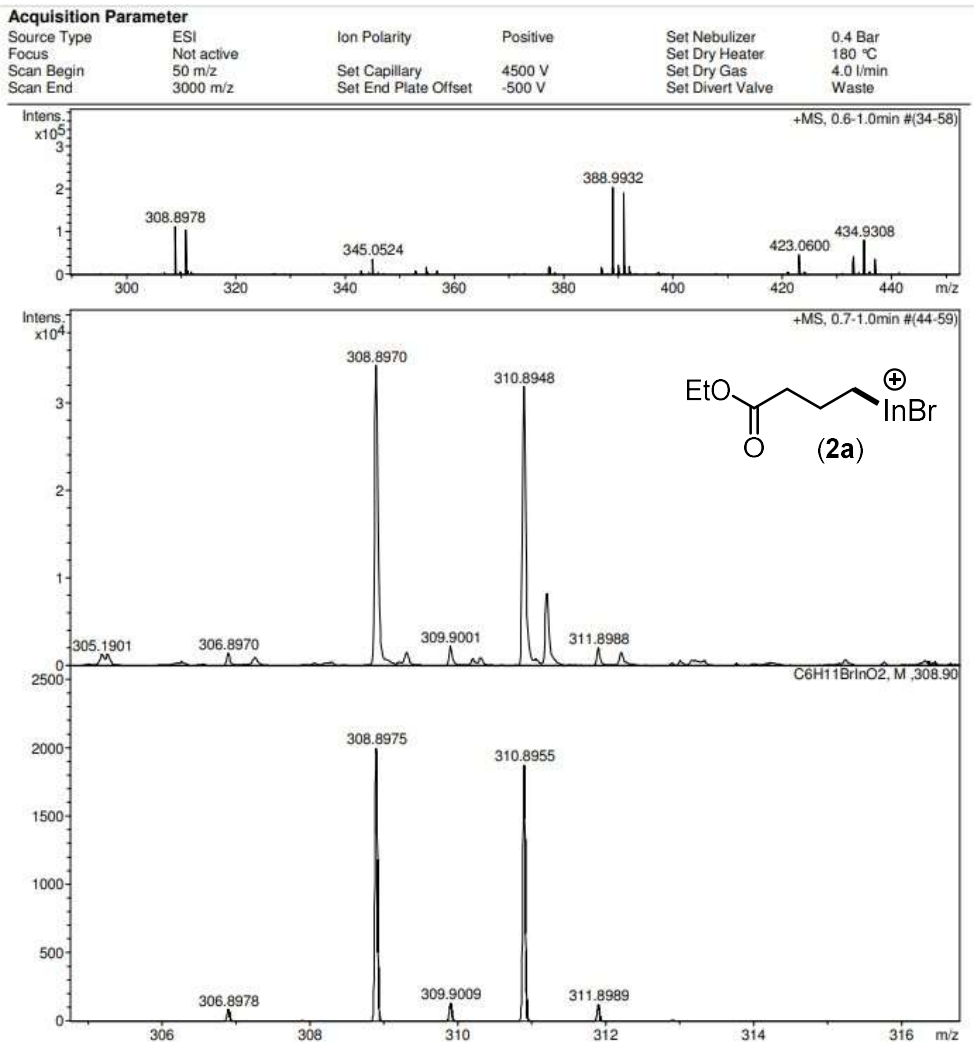
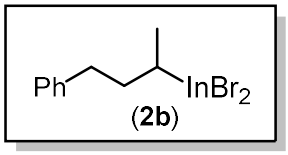


Figure S6. HRMS (ESI-TOF) of (**2a**).

Synthesis and characterization of reagent (2b) in DMF-d7

Lithium bromide (87.0 mg, 1.00 mmol) was dried under vacuum (250 °C, 12 torr) in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*) for 10 minutes. The tube was evacuated and filled with argon twice. A magnetic stirring bar, DMF-d7 (0.5 mL) and (3-bromobutyl)benzene (**1b**) (106.5 mg, 0.5 mmol) were added. Indium(I) bromide (195.0 mg, 1.00 mmol) was added last to the reaction mixture. The tube was closed with a screw cap. The reaction mixture was heated at 80 °C (PEG bath) with stirring for 12 hours. After the reaction was completed, the tube was centrifuged at 2600 rpm for 2 minutes.

(4-Phenylbutan-2-yl)indium(III) bromide (2b)



Yield determined by ^{1}H NMR with 1,3,5-trioxane as an internal standard: 97%.

^{1}H NMR (300 MHz, DMF-d7) δ 7.34 – 7.24 (m, 4H), 7.28 – 7.12 (m, 1H), 2.97 – 2.81 (m, 1H), 2.79 – 2.65 (m, 1H), 2.12 – 1.85 (m, 2H), 1.54 (h, *J* = 7.5 Hz, 1H), 1.30 (d, *J* = 7.5 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, DMF-d7) δ 143.9, 129.4, 129.3, 126.7, 40.5, 37.3, 34.1, 20.2.

HRMS (ESI-TOF): calculated for $C_{10}H_{13}{}^{79}Br^{115}In$ (M-^{79}Br) 326.9233, found 326.9219.

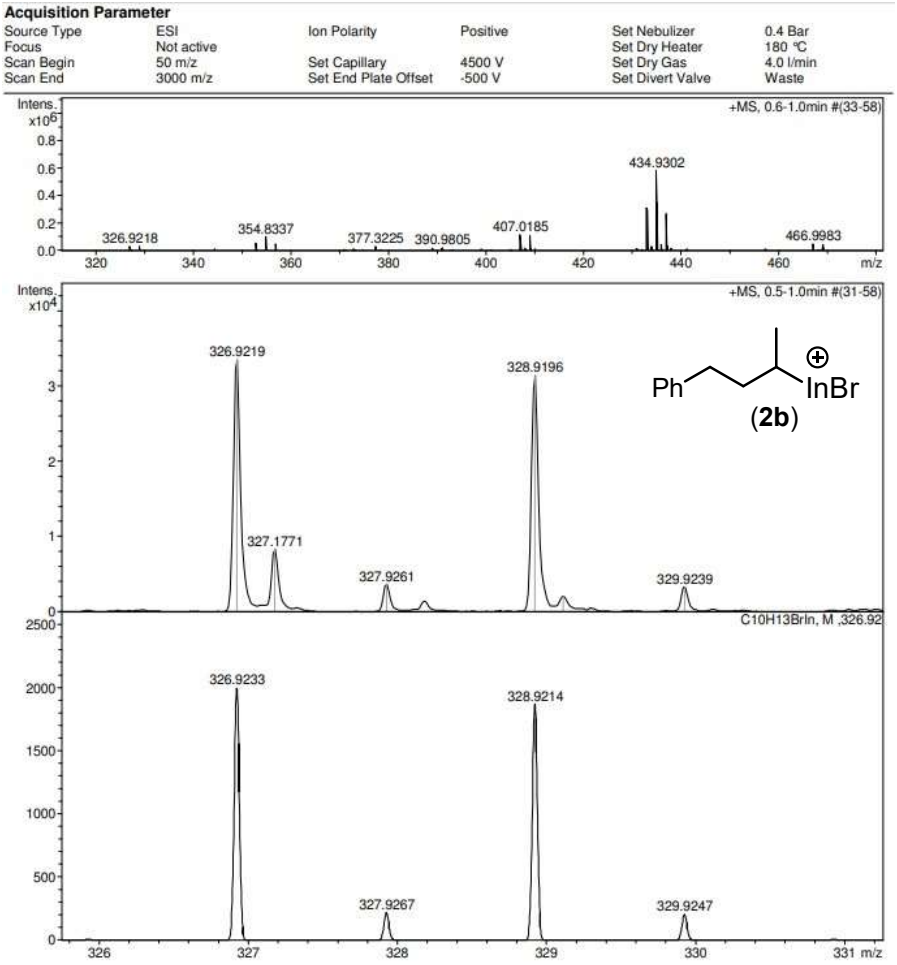
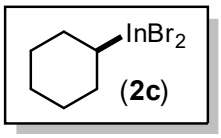


Figure S7. HRMS (ESI-TOF) of (**2b**).

Synthesis and characterization of reagent (2c) in DMF-d7

Lithium bromide (43.5 mg, 0.50 mmol) was dried under vacuum (250 °C, 12 torr) in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*) for 10 minutes. The tube was evacuated and filled with argon twice. A magnetic stirring bar, DMF-d7 (0.25 mL) and bromocyclohexane (40.8 mg, 0.25 mmol) were added. Indium(I) bromide (97.5 mg, 0.50 mmol) was added last to the reaction mixture. The tube was closed with a screw cap. The reaction mixture was heated at 80 °C (PEG bath) with stirring for 12 hours. After the reaction was completed, the tube was centrifuged at 2600 rpm for 2 minutes.

Cyclohexylindium(III) bromide (2c)



Yield (determined after iodination by GC-FID with tetraline as internal standard): 83%.

^{1}H NMR (300 MHz, DMF-d7) δ 1.91 – 1.74 (m, 4H), 1.74 – 1.58 (m, 3H), 1.52 – 1.27 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, DMF-d7) δ 39.4 (brs), 31.2, 27.6, 26.6.

HRMS (ESI-TOF): calculated for $C_6H_{11}{}^{79}Br_3{}^{115}In$ (M+^{79}Br) 434.7455, found 434.7454.

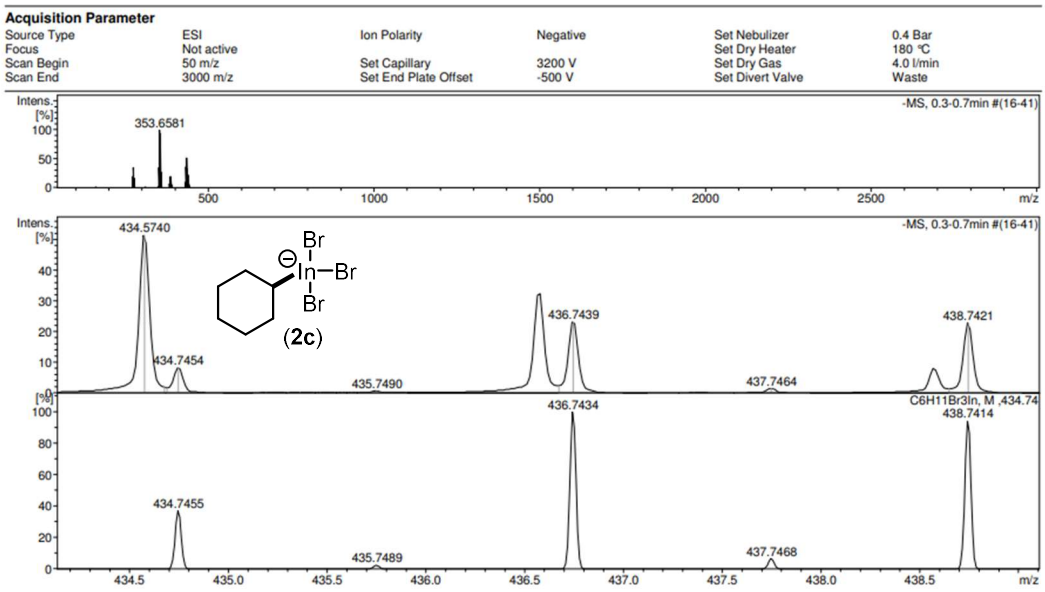


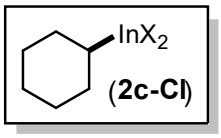
Figure S8. HRMS (ESI-TOF) of **2c**.

Synthesis and characterization of reagent (2c-Cl) in DMF-d7

Lithium chloride (21.3 mg, 0.50 mmol) was dried under vacuum (250 °C, 12 torr) in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*) for 10 minutes. The tube was evacuated and filled with argon twice. A magnetic stirring bar, DMF-d7 (0.25 mL) and bromocyclohexane

(40.8 mg, 0.25 mmol) were added. Indium(I) bromide (97.5 mg, 0.50 mmol) was added last to the reaction mixture. The tube was closed with a screw cap. The reaction mixture was heated at 80 °C (PEG bath) with stirring for 12 hours. After the reaction was completed, the tube was centrifuged at 2600 rpm for 2 minutes.

Cyclohexylindium(III) halide (2c-Cl)



Yield (determined after iodination by GC-FID with tetraline as internal standard): 73%.

^{1}H NMR (300 MHz, DMF-d7) δ 1.90 – 1.76 (m, 4H), 1.76 – 1.57 (m, 3H), 1.50 – 1.34 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, DMF-d7) δ 38.6 (brs), 31.3, 27.7, 26.6.

HRMS (ESI-TOF): calculated for $C_6H_{11}{}^{79}Br_2{}^{35}Cl^{115}In$ (M+^{79}Br) 390.7960, found 390.7956.

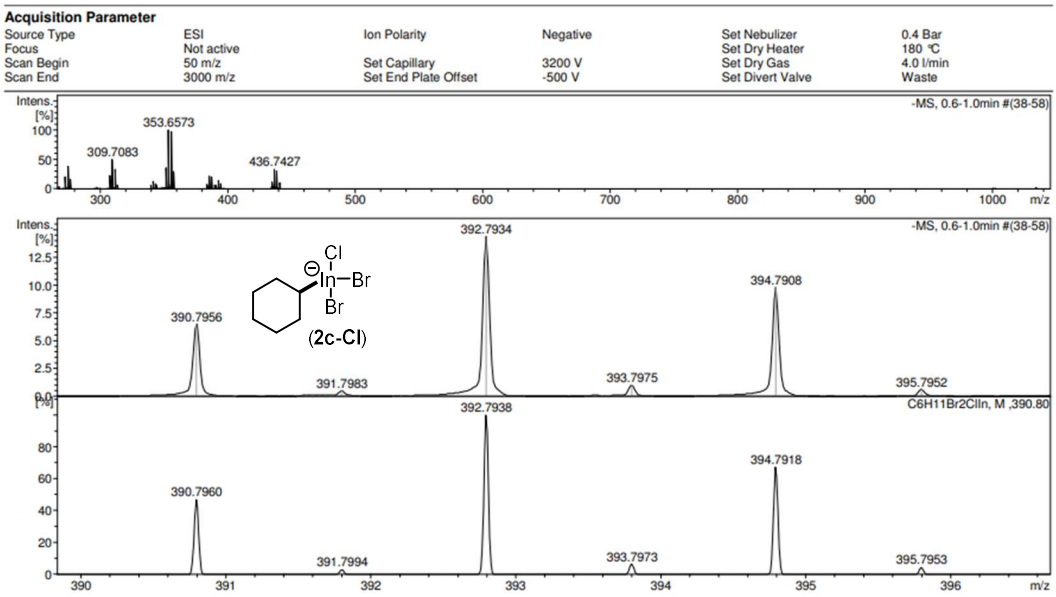
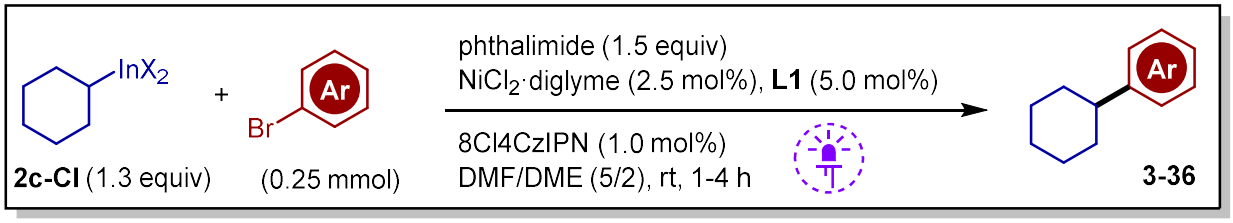


Figure S9. HRMS (ESI-TOF) of **2c-Cl**.

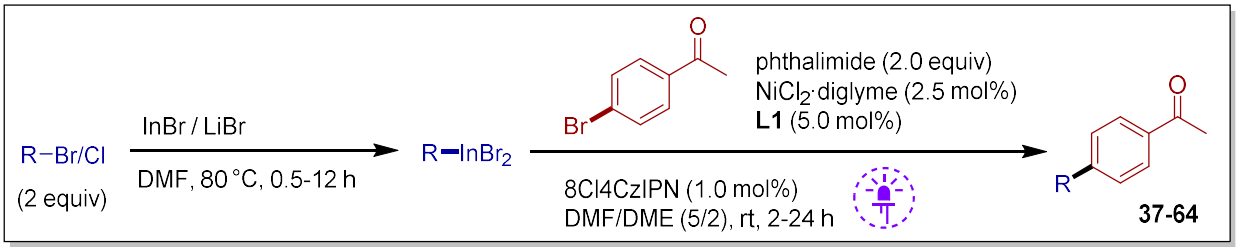
4.4. General procedures of Ni catalyzed photoredox cross-coupling reaction and characterization of the products (3-64)

Ni catalyzed photoredox cross-coupling reaction between cyclohexylindium(III) halide (2c-Cl) and aryl bromides (General procedure A)



4,4'-Dimethoxy-2,2'-bipyridine (2.70 mg, 0.0125 mmol), $NiCl_2$·diglyme (1.64 mg, 0.0063 mmol) and magnetic stirring bar were placed in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*). The tube was evacuated and filled with argon twice. DME (204 µL) was added and the mixture was stirred for 5 minutes. After that, cyclohexylindium(III) halide (**2c-Cl**) solution in DMF (510 µL, 0.3325 mmol), phthalimide (55.1 mg, 0.375 mmol), aryl bromide (0.25 mmol) and 8Cl4CzIPN (2.7 mg, 0.0025 mmol) were added. The tube was closed with a screw cap and placed in a glass jacket for cooling (Huber circulating chiller BR-03 was used, water temperature 20 °C) and irradiated by a LED matrix (400 nm, 60 W) for 1 - 4 hours (the irradiation time for each specific substrate is shown in **Table S3**). The conversion of aryl bromide was monitored by GC-MS. The distance between LED chip and the reaction tube was about 1 cm (*photocatalytic reaction set-up as* **Figure S1**). For the workup, 2M aq. HCl (2 mL, for **3-5,7,8,12,15,16,18,19,22,24,26,28,30,31**) or H_2O (2 mL, for **9-11,13,14,23,25,27**) or saturated aq. $NaHCO_3$ (2 mL, for **6,17,20,21,29**) was added, and the mixture was washed with hexanes (for **3,4,7,12,14-16,22,24,26,27,30,31**) or MTBE (for **5,8-11,18,19,21,25,28,29**) or EtOAc (for **6,13,17,20,23**) (5×3 mL). (*If precipitate was formed that made it difficult to separate the organic and aqueous layers, centrifugation was carried out at 2600 rpm for 2 minutes.*) The combined organic layers were filtered through Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography.

Ni catalyzed photoredox cross-coupling reaction between 1-(4-bromophenyl)ethan-1-one and alkyl indium reagents (2a-g') (General procedure B)



4,4'-Dimethoxy-2,2'-bipyridine (2.70 mg, 0.0125 mmol), $NiCl_2$·diglyme (1.64 mg, 0.0063 mmol) and magnetic stirring bar were placed in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*). The tube was evacuated and filled with argon twice. DME (230 µL) was added and the mixture was stirred for 5 minutes. After that, the clear solution of alkyl indium compound (prepared according to **GP I** or **GP II**) (550-600 µl, 0.50 mmol) was taken by a pipette as not to disturb the precipitate and added to the reaction mixture. Phthalimide (73.5 mg, 0.5 mmol), 1-(4-bromophenyl)ethan-1-one (49.8 mg, 0.25 mmol) and 8Cl4CzIPN (2.7 mg, 0.0025 mmol) were added. The tube was closed with a screw cap and placed in a glass jacket for cooling (Huber circulating chiller BR-03 was used, water temperature 20 °C) and irradiated by a LED matrix (400 nm, 60 W) for 2-24 hours (the irradiation time for each specific substrate is shown in **Table S3**). The conversion of aryl bromide was monitored by GC-MS. The distance between LED chip and the reaction tube was about 1 cm (*photocatalytic reaction set-up as* **Figure S1**). For the workup, 2M aq. HCl (2 mL, for **38,40-44,49,52,55,56,58-60,62-64**) or H_2O (2 mL, for **37,39,48,53,54,61**) or saturated aq. $NaHCO_3$ (2 mL, for **46,47,50,51,57**) was added, and the mixture was washed with hexanes (for **40-42,55,56,58-60,63,64**) or MTBE (for **37,38,44,45,47,49,50-54,57,61,62**) or EtOAc (for **39,43,46,48**) (5×3 mL). (*If precipitate was formed that made it difficult to separate the organic and aqueous layers, centrifugation was carried out at 2600 rpm for 2 minutes.*) The combined organic layers were filtered through Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography.

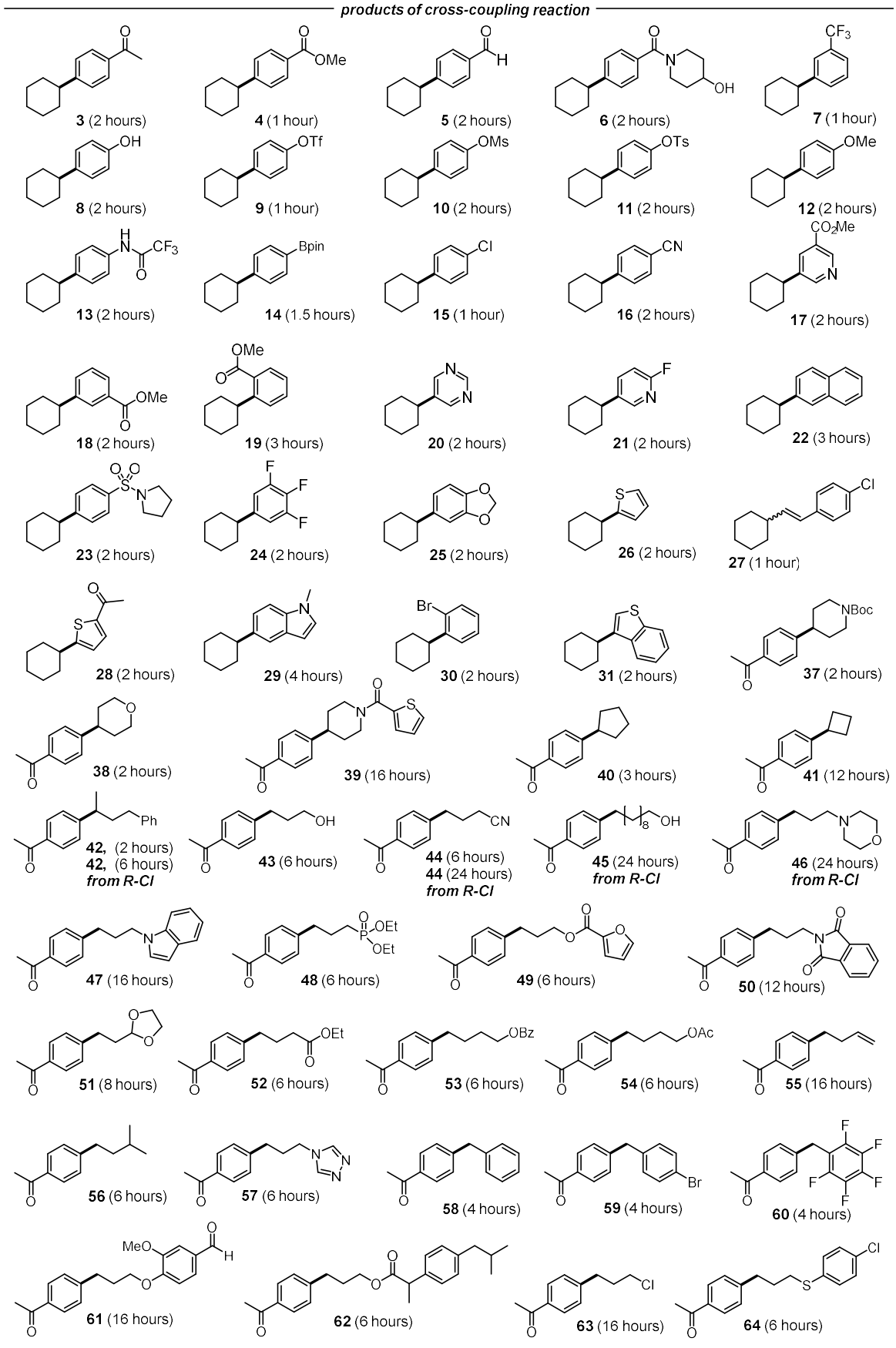
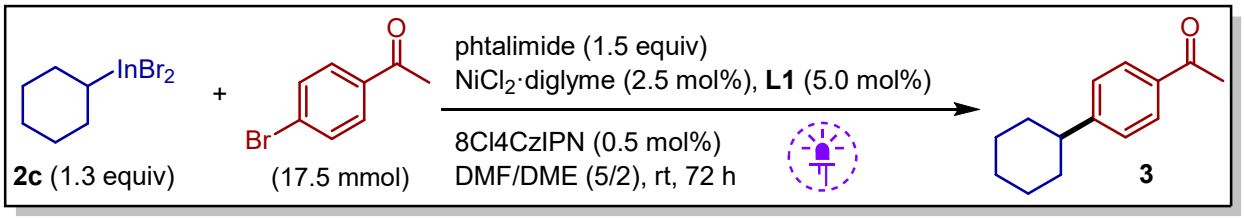


Table S3. Products and reaction time of cross-coupling reaction according to **GP A** and **GP B**.

Gram scale synthesis of 1-(4-Cyclohexylphenyl)ethan-1-one (3)



Step 1. Preparation of the stock solution of reagent **2c**.

Lithium bromide (3.92 g, 45.00 mmol) was dried under vacuum (200 °C, 0.5 torr) in a 50 mL Schlenk vessel for 20 minutes. The vessel was evacuated and filled with argon twice. A magnetic stirring bar, N,N-dimethylformamide (24.0 mL) and bromocyclohexane (4.89 g, 3.69 mL, 30.00 mmol) were added. Indium(I) bromide (8.78 g, 45.00 mmol) was added last to the reaction mixture portionwise. The Schlenk vessel was closed, and the reaction mixture was heated at 80 °C (PEG bath) with stirring for 16 hours. (*As the loading of indium(I) bromide and lithium bromide was reduced compared to small scale experiments, the heating time was extended from 12 h to 16 h.*) After the reaction was completed, the solution of **2c** was transferred to a centrifuge tube (50 mL). The tube was centrifuged at 3000 rpm for 5 minutes, which resulted in the formation of a clear solution **2c** (**Figure S10**). The concentration of reagent **2c** in DMF was 0.872 M. The concentration of the resulting solution of **2c** was determined by treatment of the formed cyclohexylindium(III) bromide with iodine as follows: 1,2,3,4-tetrahydronaphthalene (1.0 mg, 0.008 mmol) and an excess of iodine was placed in a 1 mL chromatographic vial. Methyl *tert*-butyl ether (MTBE) (0.8 mL) and an aliquot of the analysed cyclohexylindium(III) halide solution (15 µL) were added. After heating (70 °C) this mixture for 20 seconds, the ratio between cyclohexyl Iodide and 1,2,3,4-tetrahydronaphthalene was determined by GC-FID (1,2,3,4-tetrahydronaphthalene as an internal standard).

Figure S10. Solution of **2c** in DMF

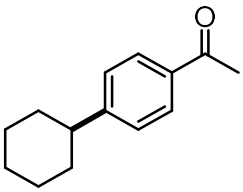
Step 2. Synthesis of 1-(4-cyclohexylphenyl)ethan-1-one (**3**)

4,4'-Dimethoxy-2,2'-bipyridine (**L1**) (198.5 mg, 0.875 mmol), $NiCl_2$·diglyme (115.0 mg, 0.438 mmol), phthalimide (3.86 g, 26.25 mmol), 1-(4-bromophenyl)ethan-1-one (3.48 g, 17.50 mmol) and 8Cl4CzIPN (93.6 mg, 0.0088 mmol) were added to a 50 mL flat-bottom flask. The flask was flushed with argon using a crooked needle for 5 minutes. After that, 1,2-dimethoxyethane (10.4 mL) and cyclohexylindium(III) bromide (**2c**) solution in DMF (26 mL, 22.75 mmol) were added. The flask was closed with a stopper, placed into a beaker, cooled with water flow at room

Figure S11. Gram scale reaction photocatalytic set-up

temperature, and irradiated for 72 h with a 400 nm 60 W LED matrix placed under the bottom of the beaker. The reaction was quenched 2M aq. HCl (100 mL), and the mixture was washed with MTBE (4×50 mL). The combined organic layers were filtered through Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography (hexanes/EtOAc, 20/1). Yield 3.18 g (90%).

1-(4-Cyclohexylphenyl)ethan-1-one (3)[35]



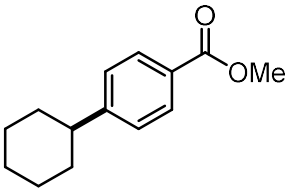
Procedure A. Yield 46.0 mg (91%).

White solid. Mp 66.2-66.9 °C. Chromatography: hexanes/EtOAc 15:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.65 – 2.50 (m, 4H), 1.93 – 1.71 (m, 5H), 1.53 – 1.17 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.9, 153.8, 135.2, 128.6, 127.1, 44.8, 34.2, 26.8, 26.6, 26.1.

Methyl 4-cyclohexylbenzoate (4)[36]



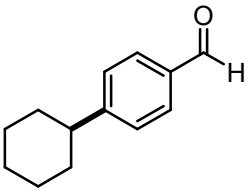
Procedure A. Yield 49.6 mg (91%).

White solid. Chromatography: hexanes/EtOAc 20:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 3.72 (s, 3H), 2.45 – 2.32 (m, 1H), 1.80 – 1.48 (m, 5H), 1.31 – 0.98 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 167.3, 153.6, 129.8, 127.8, 127.0, 52.1, 44.8, 34.3, 26.9, 26.2.

4-Cyclohexylbenzaldehyde (5)



Procedure A. Yield 32.9 mg (70%).

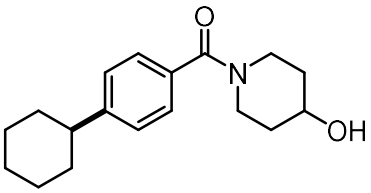
Colorless oil. Chromatography: hexanes/EtOAc 12:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 2.67 – 2.48 (m, 1H), 1.94 – 1.70 (m, 5H), 1.54 – 1.15 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 192.1, 155.5, 134.6, 130.1, 127.6, 45.0, 34.2, 26.8, 26.1.

HRMS (ESI-TOF): calculated for $C_{13}H_{16}ONa$ (M+Na) 211.1093, found 211.1098.

(4-Cyclohexylphenyl)(4-hydroxypiperidin-1-yl)methanone (6)



Procedure A. Yield 53.1 mg (74%).

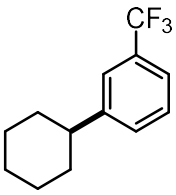
Colorless oil. Chromatography on neutral alumina: hexanes/EtOAc 1:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 4.25 – 3.99 (m, 1H), 3.94 – 3.79 (m, 1H), 3.77 – 3.52 (m, 1H), 3.40 – 3.06 (m, 2H), 3.00 (s, 1H), 2.59 – 2.40 (m, 1H), 1.99 – 1.63 (m, 7H), 1.64 – 1.09 (m, 7H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 170.8, 149.9, 133.4, 126.93, 126.92, 66.9, 44.5, 39.7, 34.3, 34.1, 26.8, 26.1.

HRMS (ESI-TOF): calculated for $C_{18}H_{26}NO_2$ (M+H) 288.1958, found 288.1966.

1-Cyclohexyl-3-(trifluoromethyl)benzene (7)[37]



Procedure A. Yield 45.0 mg (79%).

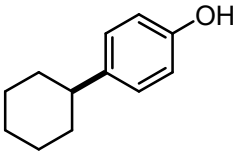
Colorless oil. Chromatography: hexane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.36 (m, 4H), 2.66 – 2.50 (m, 1H), 2.00 – 1.70 (m, 5H), 1.57 – 1.16 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 149.0, 130.7 (q, *J* = 31.5 Hz), 130.4, 128.8, 124.5 (q, *J* = 273.1 Hz), 123.7 (q, *J* = 3.8 Hz), 122.8 (q, *J* = 3.8 Hz), 44.6, 34.5, 26.9, 26.2.

^{19}F NMR (282 MHz, $CDCl_3$) δ -64.16 (s, 3F).

4-Cyclohexylphenol (8)



Procedure A. Yield 37.4 mg (85%).

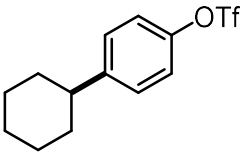
White solid. Mp 106.0-107.1 °C. Chromatography: hexanes/EtOAc 6:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.1 Hz, 2H), 6.76 (d, *J* = 8.1 Hz, 2H), 4.75 (s, 1H), 2.56 – 2.30 (m, 1H), 1.93 – 1.67 (m, 5H), 1.48 – 1.16 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.6, 140.7, 128.0, 115.2, 43.8, 34.9, 27.1, 26.3.

HRMS (ESI-TOF): calculated for $C_{12}H_{16}O$ (M) 176.1196, found 176.1202.

4-Cyclohexylphenyl trifluoromethanesulfonate (9)



Procedure A. Yield 57.0 mg (74%).

Colorless oil. Chromatography: hexanes/EtOAc 100:1

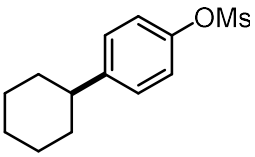
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 2.54 (tt, *J* = 11.6, 3.0 Hz, 1H), 2.01 – 1.73 (m, 5H), 1.53 – 1.17 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 148.7, 147.8, 128.6, 121.1, 119.36 (q, *J* = 321.5 Hz), 44.1, 34.5, 26.9, 26.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -72.97 (s, 3F).

HRMS (ESI-TOF): calculated for $C_{13}H_{15}F_3O_3SNa$ (M+Na) 331.0586, found 331.0578.

4-Cyclohexylphenyl methanesulfonate (10)[38]



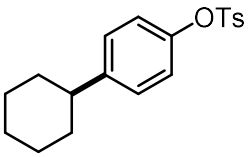
Procedure A. Yield 46.4 mg (73%).

White solid. Mp 92.8-94.4 °C. Chromatography: hexanes/EtOAc 8:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 4H), 3.21 (s, 3H), 2.61 (tt, *J* = 11.4, 3.0 Hz, 1H), 2.10 – 1.77 (m, 5H), 1.60 – 1.22 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 147.5, 147.3, 128.4, 121.8, 44.1, 37.3, 34.5, 26.9, 26.1.

4-Cyclohexylphenyl 4-methylbenzenesulfonate (11)



Procedure A. Yield 38.8 mg (47%).

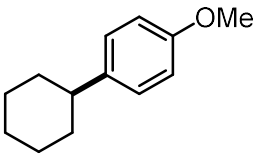
White solid. Mp 81.2-81.9 °C. Chromatography: hexanes/EtOAc 15:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 2.53 – 2.38 (m, 4H), 1.92 – 1.66 (m, 5H), 1.47 – 1.12 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 147.7, 147.1, 145.3, 132.8, 129.8, 128.6, 128.0, 122.1, 44.1, 34.5, 26.9, 26.2, 21.8.

HRMS (ESI-TOF): calculated for $C_{19}H_{23}O_3S$ (M+H) 331.1362, found 331.1364.

1-Cyclohexyl-4-methoxybenzene (12)[35]



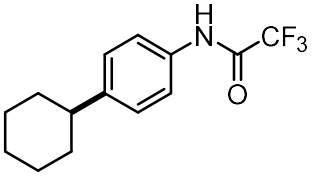
Procedure A. Yield 36.6 mg (77%).

White solid. Mp 56.8-58.4 °C. Chromatography: hexanes/EtOAc from 100:1 to 50:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 3.81 (s, 3H), 2.57 – 2.38 (m, 1H), 1.96 – 1.71 (m, 5H), 1.51 – 1.21 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 157.8, 140.5, 127.7, 113.8, 55.3, 43.8, 34.9, 27.1, 26.3.

N-(4-Cyclohexylphenyl)-2,2,2-trifluoroacetamide (13)



Procedure A. Yield 58.9 mg (87%).

White solid. Mp 142.0-143.0 °C. Chromatography: hexanes/EtOAc 20:1

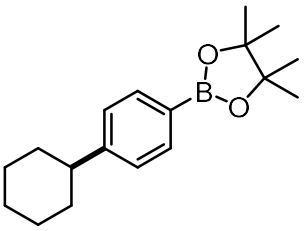
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 2.62 – 2.41 (m, 1H), 1.99 – 1.71 (m, 5H), 1.51 – 1.18 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, DMSO-d6) 154.3 (q, *J* = 36.8 Hz), 145.1, 134.0, 127.1, 121.1, 116.91 (q, *J* = 288.2 Hz), 43.3, 33.9, 26.3, 25.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ -76.52 (s, 3F).

HRMS (ESI-TOF): calculated for $C_{14}H_{16}F_3NONa$ (M+Na) 294.1076, found 294.1074.

2-(4-Cyclohexylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14)[39]



Procedure A. Yield 42.2 mg (59%).

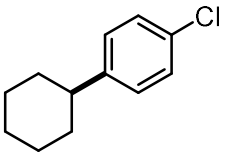
White solid. Mp 93.2-94.7 °C. Chromatography: hexanes/EtOAc 50:1

Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 μm), flow rate 6 mL·min−1; mobile phase: isocratic, acetonitrile/water, 5% water; tR = 40.1 min).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 2.59 – 2.44 (m, 1H), 1.95 – 1.69 (m, 5H), 1.49 – 1.36 (m, 3H), 1.34 (s, 12H), 1.31 – 1.18 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.6, 135.0, 126.5, 83.7, 45.0, 34.4, 29.9, 27.0, 26.3, 25.0.

1-Chloro-4-cyclohexylbenzene (15)[36]



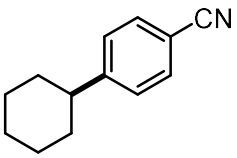
Procedure A. Yield 40.8 mg (84%).

Colorless oil. Chromatography: hexane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.25 (d, *J* = 7.3 Hz, 2H), 2.66 – 2.53 (m, 1H), 2.06 – 1.82 (m, 5H), 1.60 – 1.25 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 146.6, 131.4, 128.5, 128.3, 44.1, 34.6, 27.0, 26.2.

4-Cyclohexylbenzonitrile (16)[36]



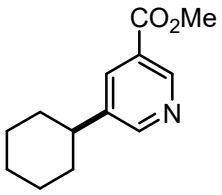
Procedure A. Yield 39.8 mg (86%).

Colorless oil. Chromatography: hexanes/EtOAc 25:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 2.68 – 2.42 (m, 1H), 1.93 – 1.70 (m, 5H), 1.50 – 1.19 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.6, 132.3, 127.8, 119.3, 109.6, 44.8, 34.1, 26.7, 26.0.

Methyl 5-cyclohexylnicotinate (17)



Procedure A. Yield 32.3 mg (59%).

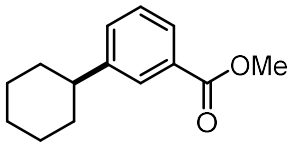
Colorless oil. Chromatography: hexanes/EtOAc 4:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.61 (s, 1H), 8.11 (s, 1H), 3.93 (s, 3H), 2.65 – 2.52 (m, 1H), 1.94 – 1.70 (m, 5H), 1.53 – 1.17 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 166.2, 152.9, 148.6, 142.9, 135.2, 125.8, 52.4, 41.9, 34.1, 26.7, 25.9.

HRMS (ESI-TOF): calculated for $C_{13}H_{18}NO_2$ (M+H) 220.1332, found 220.1340.

Methyl 3-cyclohexylbenzoate (18)



Procedure A. Yield 48.0 mg (88%).

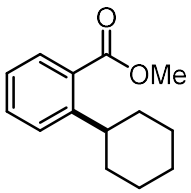
Colorless oil. Chromatography: hexanes/EtOAc 25:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.85 (d, *J* = 7.3 Hz, 1H), 7.47 – 7.28 (m, 2H), 3.91 (s, 3H), 2.63 – 2.48 (m, 1H), 1.96 – 1.68 (m, 5H), 1.54 – 1.15 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 167.5, 148.4, 131.7, 130.2, 128.4, 128.1, 127.2, 52.1, 44.5, 34.4, 26.9, 26.2.

HRMS (ESI-TOF): calculated for $C_{14}H_{18}O_2Na$ (M+Na) 241.1199, found 241.1202.

Methyl 2-cyclohexylbenzoate (19)



Procedure A. Yield 27.8 mg (51%).

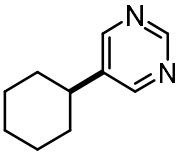
Colorless oil. Chromatography: hexanes/EtOAc 25:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.33 (m, 2H), 7.27 – 7.16 (m, 1H), 3.88 (s, 3H), 3.36 – 3.23 (m, 1H), 1.91 – 1.70 (m, 5H), 1.49 – 1.20 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 169.0, 148.8, 131.8, 130.1, 130.0, 127.0, 125.5, 52.1, 40.4, 34.5, 27.1, 26.4.

HRMS (ESI-TOF): calculated for $C_{14}H_{18}O_2Na$ (M+Na) 241.1199, found 241.1204.

5-Cyclohexylpyrimidine (20)



Procedure A. Yield 24.7 mg (61%).

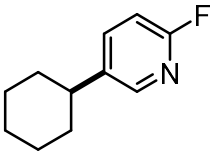
White solid. Mp 49.1-51.5 °C. Chromatography: hexanes/EtOAc 1:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.56 (s, 2H), 2.59 – 2.43 (m, 1H), 1.94 – 1.70 (m, 5H), 1.52 – 1.15 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 156.9, 155.7, 140.2, 40.0, 33.8, 26.6, 25.8.

HRMS (ESI-TOF): calculated for $C_{10}H_{15}N_2$ (M+H) 163.1230, found 163.1235.

5-Cyclohexyl-2-fluoropyridine (21)[40]



Procedure A. Yield 27.3 mg (61%).

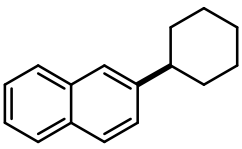
Colorless oil. Chromatography: hexanes/EtOAc 8:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.59 (td, *J* = 5.8, 2.3 Hz, 1H), 6.83 (dd, *J* = 8.5, 2.9 Hz, 1H), 2.61 – 2.39 (m, 1H), 1.94 – 1.68 (m, 5H), 1.49 – 1.16 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.31 (d, *J* = 236.5 Hz), 146.0 (d, *J* = 14.0 Hz), 140.7 (d, *J* = 4.4 Hz), 139.4 (d, *J* = 7.2 Hz), 109.1 (d, *J* = 36.9 Hz), 41.3, 34.4, 26.7, 26.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.28 (s, 1F).

2-Cyclohexylnaphthalene (22)[35]



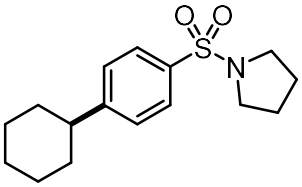
Procedure A. Yield 43.1 mg (82%).

Colorless oil. Chromatography: hexane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 – 7.78 (m, 3H), 7.68 (s, 1H), 7.57 – 7.39 (m, 3H), 2.72 (tt, *J* = 11.5, 3.4 Hz, 1H), 2.13 – 1.78 (m, 5H), 1.69 – 1.27 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.7, 133.8, 132.3, 127.9, 127.73, 127.68, 126.3, 125.9, 125.1, 124.7, 44.8, 34.6, 27.1, 26.4.

1-((4-Cyclohexylphenyl)sulfonyl)pyrrolidine (23)



Procedure A. Yield 46.9 mg (64%).

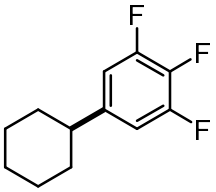
White solid. Mp 102.4-103.9 °C. Chromatography: hexanes/EtOAc 6:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 3.27 – 3.17 (m, 4H), 2.62 – 2.49 (m, 1H), 1.92 – 1.66 (m, 9H), 1.50 – 1.18 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.2, 134.3, 127.7, 127.5, 48.0, 44.6, 34.2, 26.7, 26.0, 25.3.

HRMS (ESI-TOF): calculated for $C_{16}H_{27}N_2O_2S$ ($M+NH_4$) 311.1788, found 311.1787.

5-Cyclohexyl-1,2,3-trifluorobenzene (24)[41]



Procedure A. Yield 27.8 mg (52%).

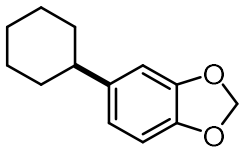
Colorless oil. Chromatography: hexane

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 – 6.70 (m, 2H), 2.58 – 2.32 (m, 1H), 1.97 – 1.59 (m, 5H), 1.49 – 1.07 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 151.18 (ddd, *J* = 248.5, 9.7, 4.1 Hz), 144.39 (td, *J* = 6.5, 4.6 Hz), 137.96 (dt, *J* = 248.5, 15.4 Hz), 110.68 (dd, *J* = 8.6, 5.8 Hz), 44.0, 34.3, 26.7, 26.0

^{19}F NMR (282 MHz, $CDCl_3$) δ -136.27 (dd, *J* = 21.1, 8.9 Hz, 2F), -165.73 (tt, *J* = 21.1, 6.4 Hz, 1F).

5-Cyclohexylbenzo[d][1,3]dioxole (25)[42]



Procedure A. Yield 26.5 mg (52%).

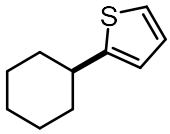
Colorless oil. Chromatography: hexanes/EtOAc 50:1

Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 µm), flow rate 6 mL·min−1; mobile phase: isocratic, acetonitrile/water, 5% water; tR = 20.6 min).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.77 – 6.61 (m, 3H), 5.91 (s, 2H), 2.50 – 2.35 (m, 1H), 1.93 – 1.67 (m, 5H), 1.48 – 1.11 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 147.6, 145.5, 142.46, 119.6, 108.2, 107.5, 100.8, 44.5, 34.9, 27.0, 26.3.

2-Cyclohexylthiophene (26)



Procedure A. Yield 21.2 mg (51%).

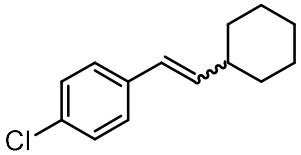
Colorless oil. Chromatography: hexane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, *J* = 4.7 Hz, 1H), 6.94 (dd, *J* = 4.1, 3.4 Hz, 1H), 6.81 (d, *J* = 3.0 Hz, 1H), 2.92 – 2.69 (m, 1H), 2.12 – 1.97 (m, 2H), 1.88 – 1.62 (m, 3H), 1.55 – 1.15 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 152.5, 126.6, 122.3, 121.9, 39.5, 35.7, 26.6, 26.1.

HRMS (ESI-TOF): calculated for $C_{10}H_{15}S$ (M+H) 167.0889, found 167.0883.

1-Chloro-4-(2-cyclohexylvinyl)benzene (27)[43]



Procedure A. Yield 44.0 mg (80%).

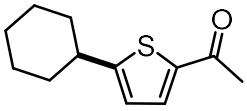
Colorless oil. Chromatography: hexane

Z : *E* = 1.94 : 1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.02 (m, 4H), 6.38 – 6.11 (m, 1H), 5.61 – 5.01 (m, 1H), 2.60 – 2.44 (m, 0.66H), 2.20 – 2.05 (m, 0.34H),1.90 – 1.59 (m, 5H), 1.43 – 1.06 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) for E isomer: δ 137.7, 136.7, 132.27, 128.7, 127.3, 126.3, 41.3, 33.0, 26.3, 26.1; for Z isomer: δ 139.8, 136.5, 132.27, 130.0, 128.5, 125.9, 37.1, 33.3, 26.2, 25.8.

1-(5-Cyclohexylthiophen-2-yl)ethan-1-one (28)[44]



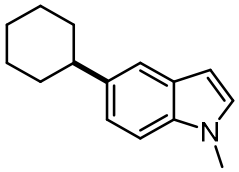
Procedure A. Yield 26.0 mg (50%).

Colorless oil. Chromatography: hexanes/EtOAc 25:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 3.8 Hz, 1H), 6.82 (d, *J* = 3.8 Hz, 1H), 2.89 – 2.73 (m, 1H), 2.50 (s, 3H), 2.12 – 1.96 (m, 2H), 1.90 – 1.61 (m, 3H), 1.53 – 1.10 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 190.7, 162.4, 141.4, 132.8, 123.6, 40.2, 35.2, 26.6, 26.4, 25.9.

5-Cyclohexyl-1-methyl-1H-indole (29)



Procedure A. Yield 25.0 mg (47%).

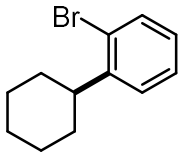
Colorless oil. Chromatography: hexanes/EtOAc 20:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.06 (d, *J* = 2.8 Hz, 1H), 6.48 (d, *J* = 2.8 Hz, 1H), 3.81 (s, 3H), 2.72 – 2.58 (m, 1H), 2.04 – 1.76 (m, 5H), 1.66 – 1.25 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.4, 135.6, 128.9, 128.7, 121.4, 118.3, 109.0, 100.8, 44.9, 35.4, 32.9, 27.3, 26.5.

HRMS (ESI-TOF): calculated for $C_{15}H_{20}N$ (M+H) 214.1590, found 214.1600.

1-Bromo-2-cyclohexylbenzene (30)



Procedure A. Yield 26.9 mg (45%).

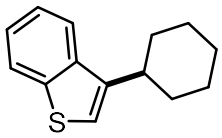
Colorless oil. Chromatography: hexane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.08 – 6.99 (m, 1H), 2.98 (tt, *J* = 11.3, 3.1 Hz, 1H), 1.97 – 1.72 (m, 5H), 1.57 – 1.22 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 146.5, 132.9, 127.7, 127.4, 127.3, 124.6, 43.4, 33.4, 27.0, 26.4.

Anal. Calcd for $C_{12}H_{15}Br$: C, 60.27; H, 6.32. Found: C 60.47, H 6.39.

3-Cyclohexylbenzo[b]thiophene (31)[45]



Procedure A. Yield 31.3 mg (58%).

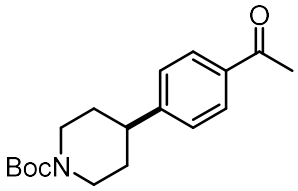
Colorless oil. Chromatography: hexane

Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 µm), flow rate 8 mL·min−1; mobile phase: isocratic, acetonitrile/water, 5% water; tR = 24.1 min).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.3 Hz, 1H), 7.80 (d, *J* = 7.3 Hz, 1H), 7.44 – 7.28 (m, 2H), 7.08 (s, 1H), 3.01 – 2.88 (m, 1H), 2.12 (d, *J* = 8.5 Hz, 2H), 1.97 – 1.76 (m, 3H), 1.61 – 1.24 (m, 5H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.0, 140.7, 138.7, 124.2, 123.8, 123.1, 121.9, 119.3, 38.1, 33.7, 27.0, 26.6.

***tert*-Butyl 4-(4-acetylphenyl)piperidine-1-carboxylate (37)**[46]



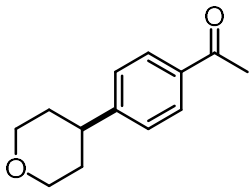
Procedure B. Yield 62.9 mg (83%).

Colorless oil. Chromatography on neutral alumina: hexanes/EtOAc 5:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 4.39 – 4.05 (m, 2H), 2.88 – 2.65 (m, 3H), 2.57 (s, 3H), 1.88 – 1.75 (m, 2H), 1.66 (dd, *J* = 12.6, 4.2 Hz, 1H), 1.58 (dd, *J* = 12.6, 4.2 Hz, 1H), 1.47 (s, 9H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.8, 154.9, 151.4, 135.6, 128.8, 127.1, 79.7, 42.9, 41.2, 33.0, 28.6, 26.7.

1-(4-(Tetrahydro-2H-pyran-4-yl)phenyl)ethan-1-one (38)[47]



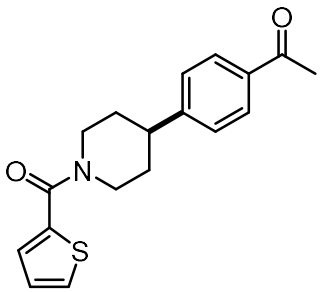
Procedure B. Yield 41.8 mg (82%)

White solid. Mp 72.2-74.4 °C. Chromatography on neutral alumina: hexanes/EtOAc 8:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 4.12 – 4.03 (m, 2H), 3.52 (td, *J* = 11.4, 3.0 Hz, 2H), 2.88 – 2.75 (m, 1H), 2.57 (s, 3H), 1.93 – 1.69 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 197.8, 151.4, 135.6, 128.8, 127.1, 68.2, 41.7, 33.6, 26.6.

1-(4-(1-(Thiophene-2-carbonyl)piperidin-4-yl)phenyl)ethan-1-one (39)



Procedure B. Yield 46.2 mg (59%)

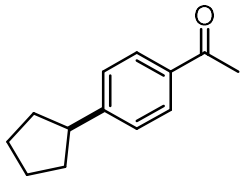
White solid. Mp 167.1-169.0 °C. Chromatography: hexanes/EtOAc 2:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.43 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.03 (dd, *J* = 5.0, 3.6 Hz, 1H), 4.74 – 4.43 (m, 2H), 3.05 (t, *J* = 11.5 Hz, 2H), 2.87 (tt, *J* = 12.1, 3.8 Hz, 1H), 2.56 (s, 3H), 1.99 – 1.86 (m, 2H), 1.77 (dd, *J* = 12.5, 4.1 Hz, 1H), 1.69 (dd, *J* = 12.7, 4.1 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 197.8, 163.7, 150.6, 137.3, 135.7, 128.8, 128.7, 128.5, 127.1, 126.7, 46.0, 42.9, 33.2, 26.6.

HRMS (ESI-TOF): calculated for $C_{18}H_{19}NO_2SNa$ (M+Na) 336.1029, found 336.1034.

1-(4-Cyclopentylphenyl)ethan-1-one (40)[9]



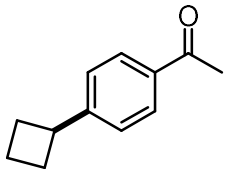
Procedure B. Yield 32.9 mg (70%).

Colorless oil. Chromatography: hexanes/EtOAc 20:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 3.05 (p, *J* = 8.4 Hz, 1H), 2.57 (s, 3H), 2.17 – 2.02 (m, 2H), 1.91 – 1.52 (m, 6H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 197.9, 152.6, 135.1, 128.6, 127.4, 46.1, 34.6, 26.6, 25.7.

1-(4-Cyclobutylphenyl)ethan-1-one (41)[48]



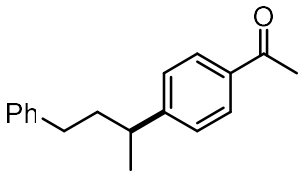
Procedure B. Yield 31.8 mg (73%).

Colorless oil. Chromatography: hexanes/EtOAc 20:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 3.59 (p, *J* = 8.7 Hz, 1H), 2.57 (s, 3H), 2.45 – 2.30 (m, 2H), 2.24 – 1.96 (m, 3H), 1.94 – 1.80 (m, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 198.0, 152.1, 135.0, 128.5, 126.6, 40.3, 29.6, 26.7, 18.4.

1-(4-(4-Phenylbutan-2-yl)phenyl)ethan-1-one (42)



Procedure B. Yield 41.0 mg from *Alk-Br* and 34.7 mg from *Alk-Cl* (65% from *Alk-Br*, 55% from *Alk-Cl*).

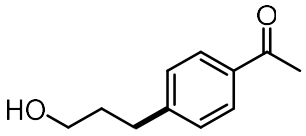
Colorless oil. Chromatography: hexanes/EtOAc 20:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.06 (m, 5H), 2.77 (h, *J* = 7.0 Hz, 1H), 2.56 (s, 3H), 2.53 – 2.44 (m, 2H), 1.91 (q, *J* = 7.5 Hz, 2H), 1.27 (d, *J* = 7.0 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.9, 153.2, 142.2, 135.4, 128.8, 128.43, 128.42, 127.4, 125.9, 39.7, 39.6, 33.9, 26.6, 22.3.

HRMS (ESI-TOF): calculated for $C_{18}H_{20}ONa$ (M+Na) 275.1406, found 275.1406.

1-(4-(3-Hydroxypropyl)phenyl)ethan-1-one (43)



Procedure B. Yield 32.5 mg (73%).

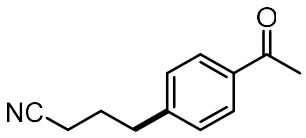
Colorless oil. Chromatography: hexanes/EtOAc 1:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 3.68 (t, *J* = 6.4 Hz, 2H), 2.76 (t, *J* = 7.8 Hz, 2H), 2.57 (s, 3H), 2.42 (s, 1H), 1.91 (p, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 198.4, 147.9, 135.2, 128.78, 128.75, 62.2, 33.7, 32.2, 26.7.

HRMS (ESI-TOF): calculated for $C_{11}H_{15}O_2$ (M+H) 179.1067, found 179.1059.

4-(4-Acetylphenyl)butanenitrile (44)[49]



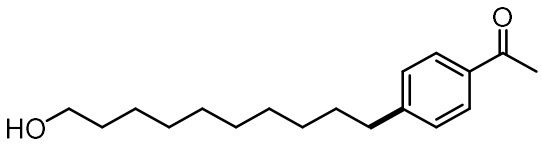
Procedure B. Yield 30.4 mg from *Alk-Br* and 29.0 mg from *Alk-Cl* (65% from *Alk-Br*, 62% from *Alk-Cl*)

Colorless oil. Chromatography on neutral alumina: hexanes/EtOAc 6:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 2.83 (t, *J* = 7.5 Hz, 2H), 2.57 (s, 3H), 2.33 (t, *J* = 7.0 Hz, 2H), 2.00 (p, *J* = 7.2 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.8, 145.5, 135.7, 128.9, 128.8, 119.3, 34.4, 26.7, 26.6, 16.5.

1-(4-(10-Hydroxydecyl)phenyl)ethan-1-one (45)



Procedure B. Yield 31.1 mg (45%)

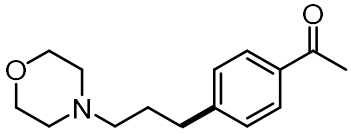
White solid. Mp 49.0-51.0 °C. Chromatography on neutral alumina: hexanes/EtOAc 4:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.62 (t, *J* = 6.6 Hz, 2H), 2.64 (t, *J* = 7.7 Hz, 2H), 2.57 (s, 3H), 1.68 – 1.50 (m, 4H), 1.39 – 1.22 (m, 13H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 198.1, 149.0, 135.0, 128.7, 128.6, 63.1, 36.1, 32.9, 31.2, 29.7, 29.6, 29.53, 29.51, 29.3, 26.7, 25.9.

HRMS (ESI-TOF): calculated for $C_{18}H_{32}O_2N$ (M+NH_4) 294.2428, found 294.2429.

1-(4-(3-Morpholinopropyl)phenyl)ethan-1-one (46)



Procedure B. Yield 26.6 mg (43%)

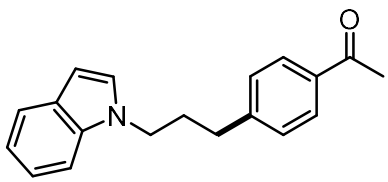
Colorless oil. Chromatography on neutral alumina: hexanes/EtOAc 3:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 3.71 (t, *J* = 4.7 Hz, 4H), 2.70 (t, *J* = 7.7 Hz, 2H), 2.58 (s, 3H), 2.42 (t, *J* = 4.5 Hz, 4H), 2.38 – 2.31 (m, 2H), 1.83 (p, *J* = 7.5 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 198.0, 148.1, 135.2, 128.8, 128.7, 67.1, 58.2, 53.8, 33.7, 28.0, 26.7.

HRMS (ESI-TOF): calculated for $C_{15}H_{22}NO_2$ (M+H) 248.1645, found 248.1647.

1-(4-(3-(1H-Indol-1-yl)propyl)phenyl)ethan-1-one (47)



Procedure B. Yield 44.3 mg (64%).

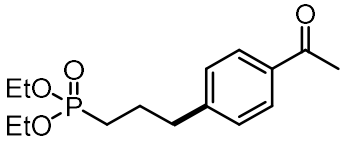
Green oil. Chromatography: hexanes/EtOAc 8:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.21 (m, 5H), 7.18 (d, *J* = 3.1 Hz, 1H), 6.62 (d, *J* = 3.1 Hz, 1H), 4.23 (t, *J* = 7.0 Hz, 2H), 2.77 (t, *J* = 7.7 Hz, 2H), 2.68 (s, 3H), 2.31 (p, *J* = 7.3 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.8, 146.8, 136.0, 135.4, 128.72, 128.65, 127.7, 121.6, 121.1, 119.4, 109.4, 101.4, 45.6, 33.1, 31.2, 26.6.

HRMS (ESI-TOF): calculated for $C_{19}H_{20}NO$ (M+H) 278.1539, found 278.1543.

Diethyl (3-(4-acetylphenyl)propyl)phosphonate (48)



Procedure B. Yield 46.2 mg (62%).

Colorless oil. Chromatography: EtOAc

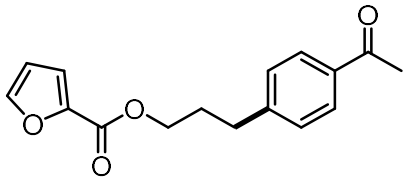
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 4.15 – 3.97 (m, 4H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.55 (s, 3H), 2.01 – 1.84 (m, 2H), 1.77 – 1.63 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.8, 146.9, 135.4, 128.8, 128.7, 61.6 (d, *J* = 6.6 Hz), 36.4 (d, *J* = 16.6 Hz), 26.6, 25.1 (d, *J* = 141.5 Hz), 23.9 (d, *J* = 4.7 Hz), 16.5 (d, *J* = 6.0 Hz).

^{31}P NMR (122 MHz, $CDCl_3$) δ 32.48.

HRMS (ESI-TOF): calculated for $C_{15}H_{24}O_4P$ (M+H) 299.1407, found 299.1411.

3-(4-Acetylphenyl)propyl furan-2-carboxylate (49)



Procedure B. Yield 38.1 mg (56%).

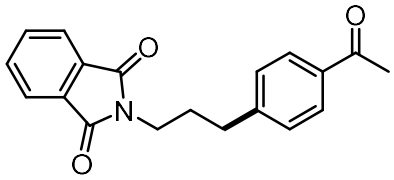
Colorless oil. Chromatography: hexanes/EtOAc 5:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.60 – 7.53 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 3.4 Hz, 1H), 6.50 (dd, *J* = 3.3, 1.6 Hz, 1H), 4.32 (t, *J* = 6.5 Hz, 2H), 2.81 (t, *J* = 7.7 Hz, 2H), 2.57 (s, 3H), 2.10 (p, *J* = 7.0 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.9, 158.8, 147.0, 146.5, 135.4, 134.4, 128.8, 118.0, 112.0, 64.1, 32.3, 30.0, 26.7.

HRMS (ESI-TOF): calculated for $C_{16}H_{20}O_4N$ ($M+NH_4$) 290.1387, found 290.1387.

2-(3-(4-Acetylphenyl)propyl)isoindoline-1,3-dione (50)[50]



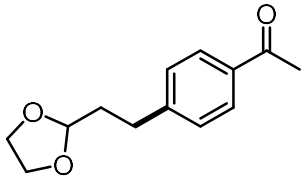
Procedure B. Yield 45.3 mg (59%).

Yellow oil. Chromatography on neutral alumina: hexanes/EtOAc 5:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 4H), 7.72 – 7.66 (m, 2H), 7.27 (d, *J* = 8.5 Hz, 1H), 3.74 (t, *J* = 7.1 Hz, 2H), 2.74 (t, *J* = 7.7 Hz, 2H), 2.53 (s, 3H), 2.06 (p, *J* = 7.3 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.8, 168.5, 146.9, 135.3, 134.1, 132.2, 128.7, 128.6, 123.3, 37.8, 33.3, 29.4, 26.6.

1-(4-(2-(1,3-Dioxolan-2-yl)ethyl)phenyl)ethan-1-one (51)[51]



Procedure B. Yield 46.2 mg (84%)

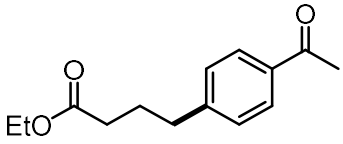
Colorless oil. Chromatography on neutral alumina: hexanes/EtOAc 8:1

Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 µm), flow rate 5 mL·min−1; mobile phase: isocratic, acetonitrile/water, 20% water; tR = 14.8 min).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.89 (t, *J* = 4.6 Hz, 1H), 4.03 – 3.93 (m, 2H), 3.93 – 3.83 (m, 2H), 2.81 (t, *J* = 8.2 Hz, 2H), 2.58 (s, 3H), 2.05 – 1.91 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.7, 147.6, 135.3, 128.7, 103.7, 65.1, 35.2, 30.2, 26.7.

Ethyl 4-(4-acetylphenyl)butanoate (52)[50]



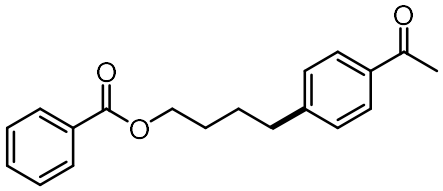
Procedure B. Yield 35.7 mg (61%).

Colorless oil. Chromatography: hexanes/EtOAc 8:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.56 (s, 3H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.95 (p, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.9, 173.3, 147.3, 135.3, 128.8, 128.7, 60.4, 35.2, 33.6, 26.6, 26.2, 14.3.

4-(4-Acetylphenyl)butyl benzoate (53)



Procedure B. Yield 36.3 mg (49%).

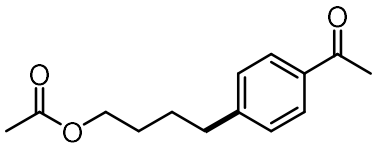
Yellow oil. Chromatography: hexanes/EtOAc 8:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.34 (t, *J* = 5.6 Hz, 2H), 2.75 (t, *J* = 6.2 Hz, 2H), 2.58 (s, 3H), 1.81 (p, *J* = 3.2 Hz, 4H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.9, 166.7, 147.9, 135.3, 133.0, 130.4, 129.6, 128.72, 128.68, 128.5, 64.7, 35.6, 28.4, 27.6, 26.7.

HRMS (ESI-TOF): calculated for $C_{19}H_{21}O_3$ (M+H) 297.1485, found 297.1483.

3-(4-Acetylphenyl)propyl acetate (54)



Procedure B. Yield 32.2 mg (55%).

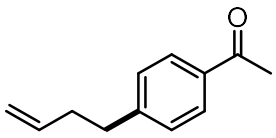
Colorless oil. Chromatography: hexanes/EtOAc 10:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 4.07 (t, *J* = 6.1 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H), 2.56 (s, 3H), 2.03 (s, 3H), 1.77 – 1.58 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.9, 171.2, 147.9, 135.2, 128.69, 128.65, 64.2, 35.5, 28.2, 27.5, 26.6, 21.1.

HRMS (ESI-TOF): calculated for $C_{14}H_{19}O_3$ (M+H) 235.1329, found 235.1326.

1-(4-(But-3-en-1-yl)phenyl)ethan-1-one (55)[52]



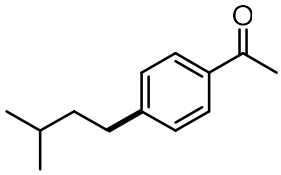
Procedure B. Yield 15.7 mg (36%).

Colorless oil. Chromatography: hexanes/EtOAc 20:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.07 – 4.93 (m, 2H), 2.75 (t, *J* = 7.7 Hz, 2H), 2.56 (s, 3H), 2.38 (q, *J* = 7.2 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 198.0, 147.8, 137.6, 135.3, 128.8, 128.6, 115.5, 35.5, 35.1, 26.7.

1-(4-Isopentylphenyl)ethan-1-one (56)[53]



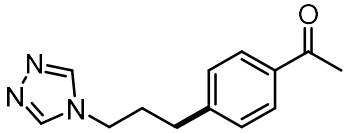
Procedure B. Yield 36.6 mg (77%).

Colorless oil. Chromatography: hexanes/EtOAc 20:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.67 (t, *J* = 7.9 Hz, 1H), 2.58 (s, 3H), 1.69 – 1.46 (m, 3H), 0.94 (d, *J* = 6.2 Hz, 6H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 198.0, 149.2, 135.0, 128.67, 128.62, 40.5, 34.0, 27.8, 26.7, 22.6.

1-(4-(3-(4H-1,2,4-Triazol-4-yl)propyl)phenyl)ethan-1-one (57)



Procedure B. Yield 30.9 mg (54%)

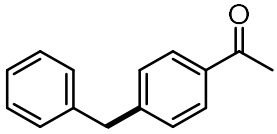
Colorless oil. Chromatography: EtOAc

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.94 (s, 1H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 4.16 (t, *J* = 6.9 Hz, 2H), 2.67 (t, *J* = 7.6 Hz, 2H), 2.56 (s, 3H), 2.24 (p, *J* = 7.2 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 197.8, 152.2, 146.0, 143.1, 135.6, 128.8, 128.7, 48.7, 32.5, 30.8, 26.7.

HRMS (ESI-TOF): calculated for $C_{13}H_{16}N_3O$ (M+H) 230.1288, found 230.1291.

1-(4-Benzylphenyl)ethan-1-one (58)[54]



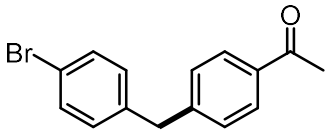
Procedure B. Yield 39.9 mg (76%).

Colorless oil. Chromatography: hexanes/EtOAc 20:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.08 (m, 7H), 3.96 (s, 2H), 2.49 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 197.8, 146.9, 140.1, 135.3, 129.2, 129.0, 128.7, 126.5, 42.0, 26.6.

1-(4-(4-Bromobenzyl)phenyl)ethan-1-one (59)[55]



Procedure B. Yield 49.1 mg (68%).

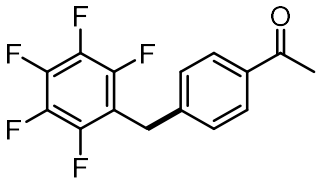
Colorless oil. Chromatography: hexanes/EtOAc from 20:1 to 15:1

Final purification was performed by preparative HPLC (reversed-phase column C18, 21×250 mm, 5 µm), flow rate 6 mL·min−1; mobile phase: isocratic, acetonitrile/water, 5% water; tR = 19.5 min).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 3.98 (s, 2H), 2.58 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.8, 146.2, 139.1, 135.6, 131.8, 130.8, 129.2, 128.9, 120.5, 41.4, 26.7.

1-(4-((Perfluorophenyl)methyl)phenyl)ethan-1-one (60)[56]



Procedure B. Yield 42.8 mg (57%).

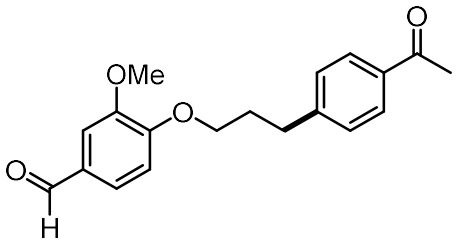
White solid. Mp 77.0-78.0 °C. Chromatography: hexanes/EtOAc 30:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 4.11 – 4.05 (m, 2H), 2.57 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.6, 145.2 (dm, *J* = 246.0 Hz), 142.8, 140.0 (dm, *J* = 253.1 Hz), 138.61 (dm, *J* = 253.1 Hz), 136.1, 129.1, 128.7, 113.6 (td, *J* = 19.2, 4.1 Hz), 28.2, 26.7.

^{19}F NMR (282 MHz, $CDCl_3$) δ -143.06 (dd, *J* = 22.3, 8.4 Hz, 2F), -156.16 (t, *J* = 20.8 Hz, 1F), -161.76 – -162.01 (m, 2F).

4-(3-(4-Acetylphenyl)propoxy)-3-methoxybenzaldehyde (61)



Procedure B. Yield 31.2 mg (40%).

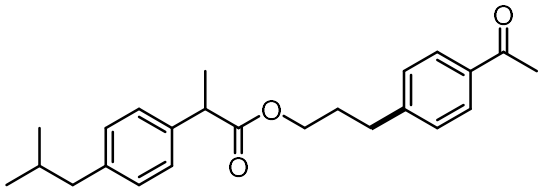
Colorless oil. Chromatography on neutral alumina: hexanes/EtOAc 3:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.94 – 6.88 (m, 1H), 4.09 (t, *J* = 6.4 Hz, 2H), 3.93 (s, 3H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.58 (s, 3H), 2.22 (p, *J* = 6.8 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.9, 191.0, 154.0, 150.0, 147.0, 135.4, 130.2, 128.82, 128.76, 126.8, 111.6, 109.4, 67.9, 56.2, 32.2, 30.2, 26.7.

HRMS (ESI-TOF): calculated for $C_{19}H_{21}O_4$ (M+H) 313.1434, found 313.1436.

3-(4-Acetylphenyl)propyl 2-(4-isobutylphenyl)propanoate (62)



Procedure B. Yield 38.4 mg (42%)

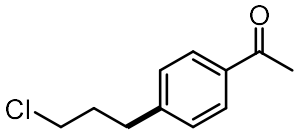
Colorless oil. Chromatography: hexanes/EtOAc 10:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.15 – 7.09 (m, 4H), 4.13 – 3.98 (m, 2H), 3.70 (q, *J* = 7.2 Hz, 1H), 2.63 – 2.54 (m, 5H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.96 – 1.78 (m, 3H), 1.50 (d, *J* = 7.2 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.8, 174.8, 147.0, 140.7, 137.9, 135.3, 129.4, 128.71, 128.65, 127.3, 63.5, 45.3, 45.1, 32.0, 30.3, 29.9, 26.6, 22.5, 18.4.

HRMS (ESI-TOF): calculated for $C_{24}H_{31}O_3$ (M+H) 367.2268, found 367.2259.

1-(4-(3-Chloropropyl)phenyl)ethan-1-one (63)[57]



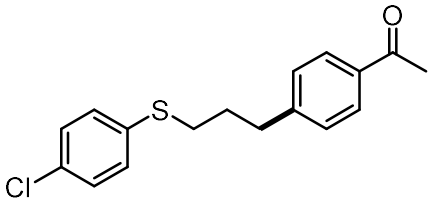
Procedure B. Yield 14.2 mg (29%).

Colorless oil. Chromatography: hexanes/EtOAc 12:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.52 (t, *J* = 6.4 Hz, 2H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.58 (s, 3H), 2.10 (p, *J* = 6.9 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.9, 146.6, 135.5, 128.9, 128.8, 44.1, 33.7, 32.9, 26.7.

1-(4-(3-((4-Chlorophenyl)thio)propyl)phenyl)ethan-1-one (64)



Procedure B. Yield 19.8 mg (26%).

White solid. Mp 48.4-50.8 °C. Chromatography: hexanes/EtOAc 15:1

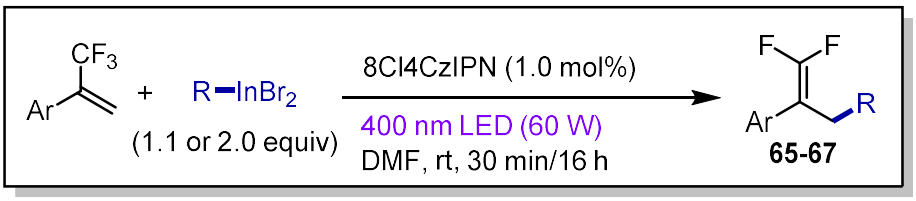
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.21 (m, 6H), 2.89 (t, *J* = 7.2 Hz, 2H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.58 (s, 3H), 1.96 (p, *J* = 7.3 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 197.9, 147.0, 135.4, 134.9, 132.1, 130.8, 129.2, 128.81, 128.75, 34.6, 33.3, 30.2, 26.7.

HRMS (ESI-TOF): calculated for $C_{17}H_{18}{}^{35}ClOS$ (M+H) 305.0761, found 305.0767.

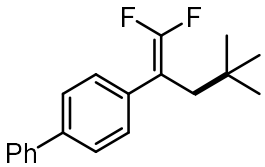
4.5. Reaction alkyl indium reagents with α-(trifluoromethyl)styrenes and characterization of the products (65-67)

General procedure C



8Cl4CzIPN (2.7 mg, 0.0025 mmol) and magnetic stirring bar were placed in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*). The tube was evacuated and filled with argon twice. For product **66**: alkyl indium reagent (**2c-Cl**) solution in DMF (0.651 M) (422 µL, 0.275 mmol), α-(trifluoromethyl)styrene (**1ay**) (43.00 mg, 0.25 mmol) and DMF (578 µL); for product **65**: alkyl indium reagent (**2d**) solution in DMF (0.548 M) (502 µL, 0.275 mmol), α-(trifluoromethyl)styrene (**1az**) (62.00 mg, 0.25 mmol) and DMF (498 µL); for product **67**: alkyl indium reagent (**2a**) solution in DMF (0.83 M) (602 µL, 0.50 mmol), α-(trifluoromethyl)styrene (**1ay**) (43.00 mg, 0.25 mmol) and DMF (398 µL) were added. The tube was closed with a screw cap and placed in a glass jacket for cooling (Huber circulating chiller BR-03 was used, water temperature 20 °C) and irradiated by a LED matrix (400 nm, 60 W) for 30 minutes (for **65**,**66**) and 16 hours (for **67**). The conversion of α-(trifluoromethyl)styrene was monitored by GC-MS. The distance between LED chip and the reaction tube was about 1 cm (*photocatalytic reaction set-up as* **Figure S1**). For the workup, 2M aq. HCl (2 mL) was added, and the mixture was washed with hexanes (5×3 mL). The combined organic layers were filtered through Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography.

4-(1,1-Difluoro-4,4-dimethylpent-1-en-2-yl)-1,1'-biphenyl (65)[58]



Procedure C. Yield 65.1 mg (91%)

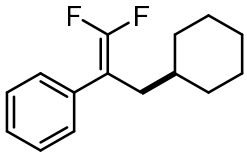
Colorless oil. Chromatography: hexane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 – 7.57 (m, 4H), 7.52 – 7.33 (m, 5H), 2.45 – 2.38 (m, 2H), 0.88 (s, 9H).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 154.6 (dd, *J* = 290.5, 287.7 Hz), 140.7, 139.8, 134.7 (dd, *J* = 4.5, 2.8 Hz), 129.0, 128.9, 127.5, 127.11, 127.05, 91.0 (dd, *J* = 21.5, 12.8 Hz), 41.2, 32.9 (t, *J* = 2.5 Hz), 29.9.

^{19}F NMR (282 MHz, $CDCl_3$) δ -90.02 (d, *J* = 40.3 Hz, 1F), -92.68 (d, *J* = 40.3 Hz, 1F).

(3-cyclohexyl-1,1-difluoroprop-1-en-2-yl)benzene (66)[59]



Procedure C. Yield 42.5 mg (72%)

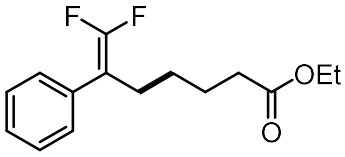
Colorless oil. Chromatography: hexane

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.16 (m, 5H), 2.26 – 2.17 (m, 2H), 1.68 – 1.50 (m, 5H), 1.33 – 0.95 (m, 4H), 0.95 – 0.76 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 154.1 (dd, *J* = 290.0, 286.0 Hz), 134.3 (dd, *J* = 4.4, 3.1 Hz), 128.5, 128.4 (t, *J* = 3.2 Hz), 127.2, 91.2 (dd, *J* = 21.8, 12.8 Hz), 35.8 (t, *J* = 2.3 Hz), 35.4, 33.0, 26.6, 26.2.

^{19}F NMR (282 MHz, $CDCl_3$) δ -92.19 (d, *J* = 44.4 Hz, 1F), -92.65 (d, *J* = 44.4 Hz, 1F).

Ethyl 7,7-difluoro-6-phenylhept-6-enoate (67)



Procedure C. Yield 38.2 mg (57%)

Colorless oil. Chromatography: hexanes/EtOAc 15:1

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.44 (t, *J* = 7.5 Hz, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 1.66 (p, *J* = 7.5 Hz, 2H), 1.42 (p, *J* = 7.7 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).

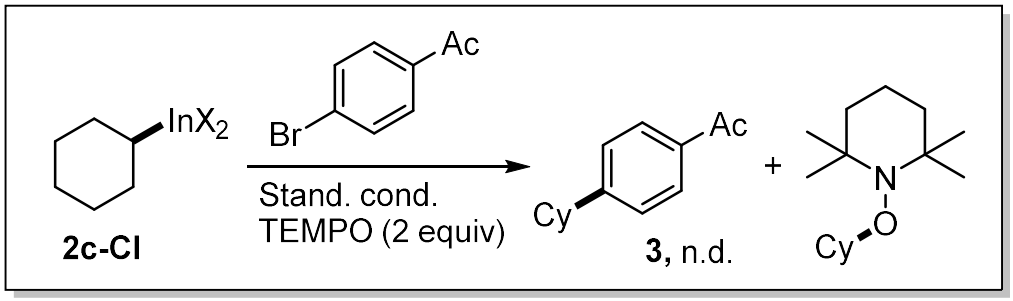
^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 173.6, 153.7 (t, *J* = 288.4 Hz), 133.7, 128.6, 128.3 (t, *J* = 3.2 Hz), 127.4, 92.2 (t, *J* = 17.4 Hz), 60.4, 34.1, 27.4, 27.3 (t, *J* = 2.4 Hz), 24.4, 14.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ -92.45 (s, 2F).

HRMS (ESI-TOF): calculated for $C_{15}H_{19}F_2O_2$ (M+H) 269.1348, found 269.1346.

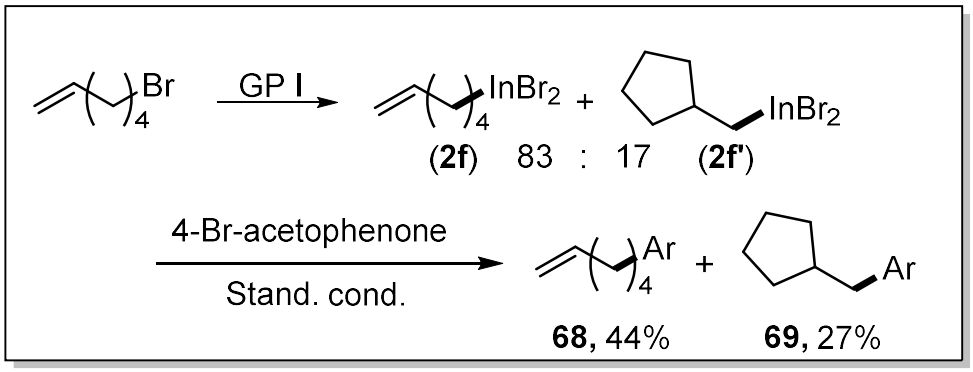
5. Mechanistic studies

5.1. Radical trapping experiment



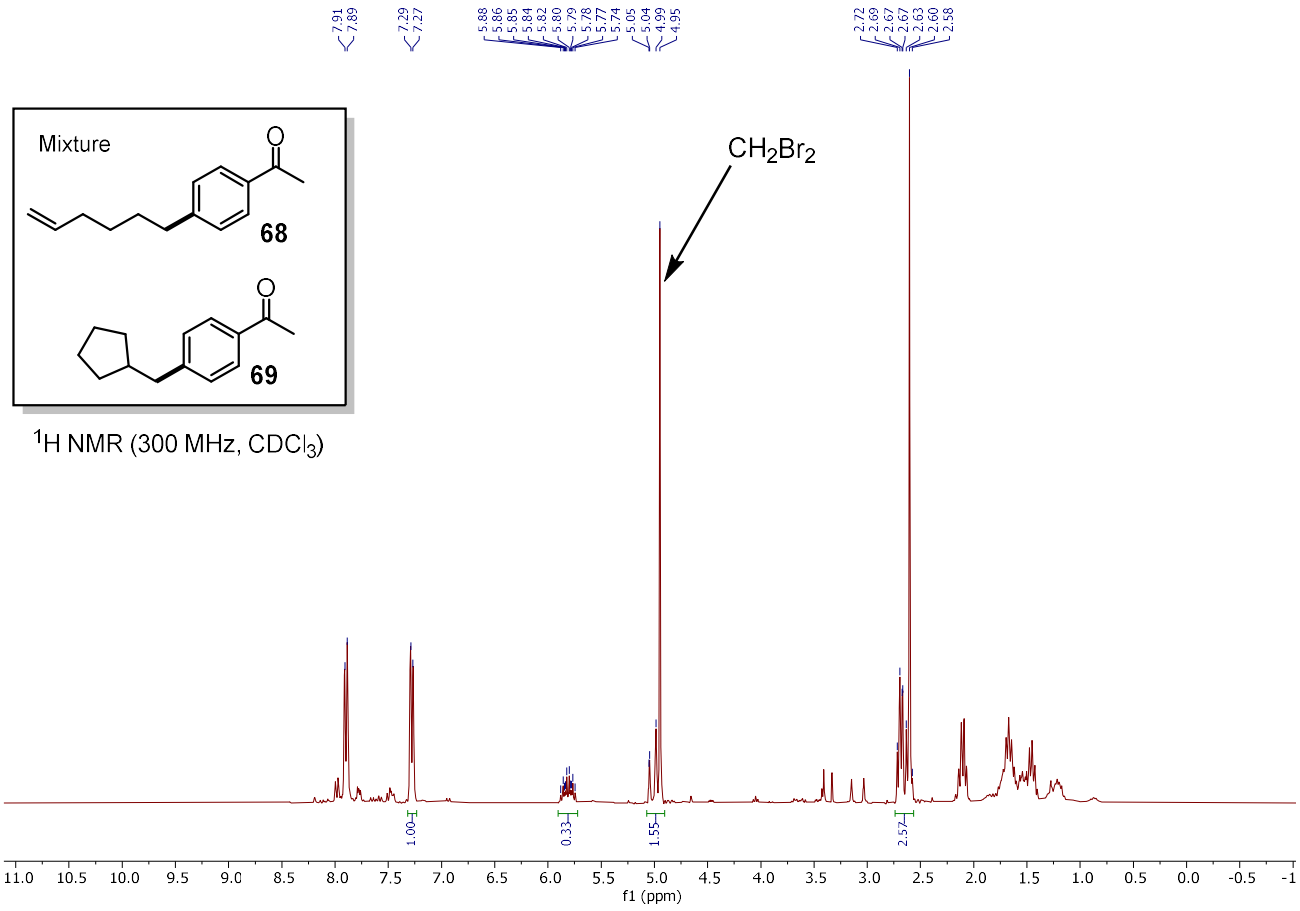
4,4'-Dimethoxy-2,2'-bipyridine (2.70 mg, 0.0125 mmol), $NiCl_2$·diglyme (1.64 mg, 0.0063 mmol) and magnetic stirring bar were placed in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*). The tube was evacuated and filled with argon twice. DME (204 µL) was added and the mixture was stirred for 5 minutes. After that, cyclohexylindium(III) halide (**2c-Cl**) solution in DMF (510 µL, 0.3325 mmol), phthalimide (55.1 mg, 0.375 mmol), 1-(4-bromophenyl)ethan-1-one (49.8 mg, 0.25 mmol), 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) (78.0 mg, 0.50 mmol) and 8Cl4CzIPN (2.7 mg, 0.0025 mmol) were added. The tube was closed with a screw cap and placed in a glass jacket for cooling (Huber circulating chiller BR-03 was used, water temperature 20 °C) and irradiated by a LED matrix (400 nm, 60 W) for 2 hours. The distance between LED chip and the reaction tube was about 1 cm (*photocatalytic reaction set-up as* **Figure S1**). The reaction mixture was analyzed by GC-MS.

5.2. Radical clock experiment

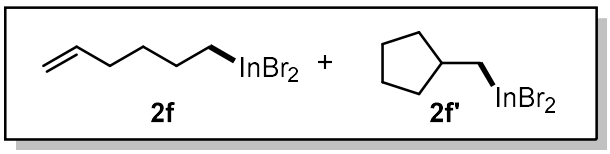


4,4'-Dimethoxy-2,2'-bipyridine (2.70 mg, 0.0125 mmol), $NiCl_2$·diglyme (1.64 mg, 0.0063 mmol) and magnetic stirring bar were placed in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*). The tube was evacuated and filled with argon twice. DME (230 µL) was added and the mixture was stirred for 5 minutes. After that, the clear solution of alkyl indium compound (**2f** prepared according **GP I**) (575 µl, 0.50 mmol) was taken by a pipette as not to disturb the precipitate and added to the reaction

mixture. Phthalimide (73.5 mg, 0.5 mmol), 1-(4-bromophenyl)ethan-1-one (49.8 mg, 0.25 mmol) and 8Cl4CzIPN (2.7 mg, 0.0025 mmol) were added. The tube was closed with a screw cap and placed in a glass jacket for cooling (Huber circulating chiller BR-03 was used, water temperature 20 °C) and irradiated by a LED matrix (400 nm, 60 W) for 6 hours. The distance between LED chip and the reaction tube was about 1 cm (*photocatalytic reaction set-up as* **Figure S1**). For the workup, 2M aq. HCl (2 mL) was added, and the mixture was washed with hexanes (5×3 mL). The combined organic layers were filtered through Na_2SO_4, concentrated under vacuum, and the residue was analyzed by ^1H NMR with dibromomethane (25.7 mg, 0.1477 mmol) as an internal standard.



Mixture of **2f** and **2f'**

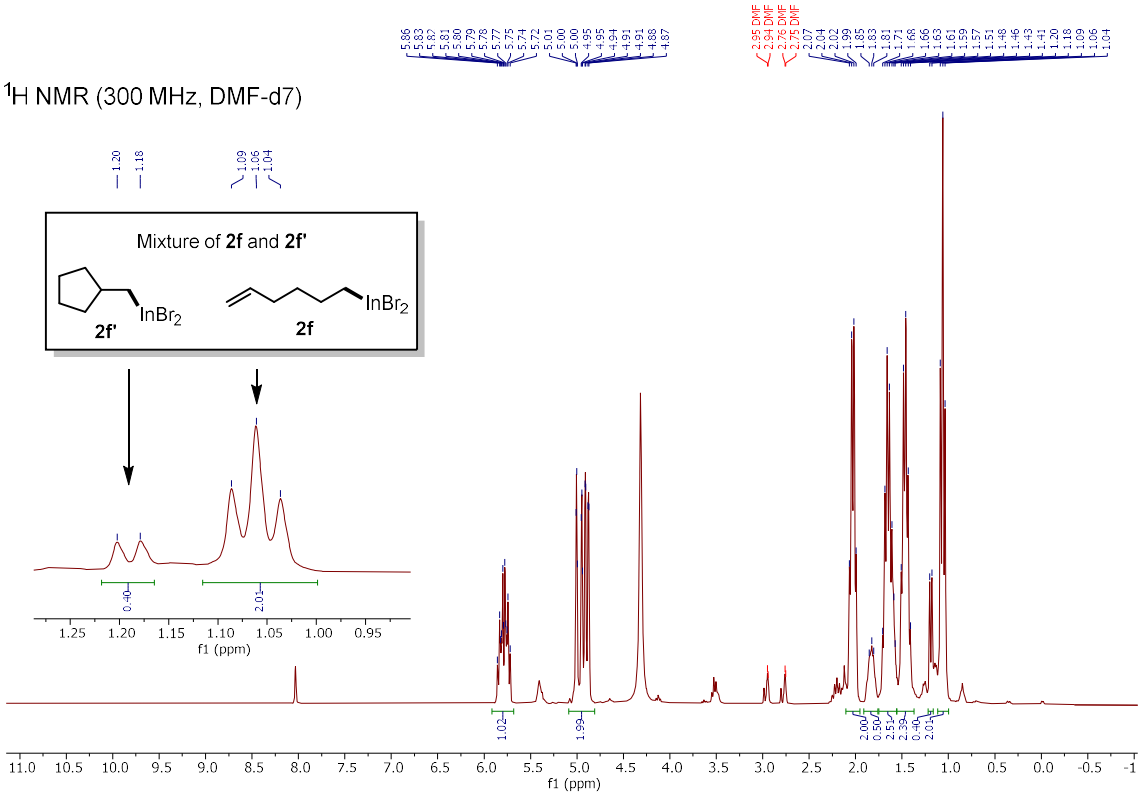


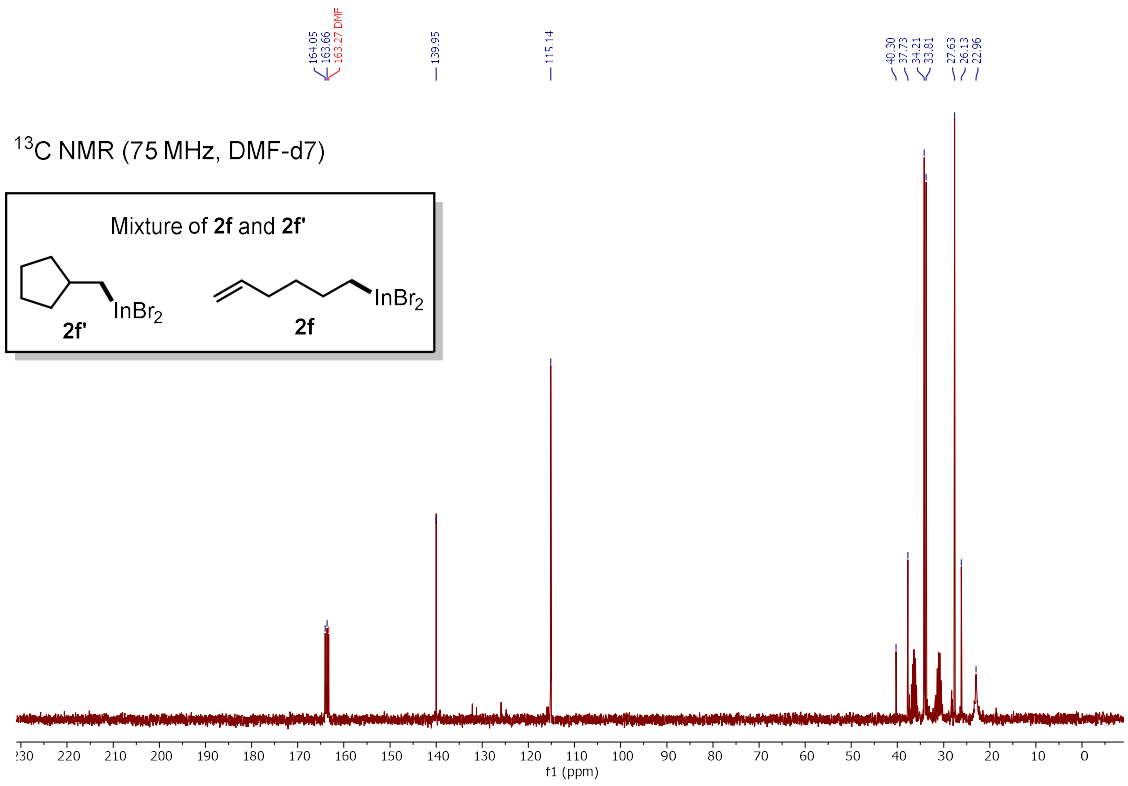
^{1}H NMR (300 MHz, DMF-d7) δ 5.79 (ddt, *J* = 16.9, 10.4, 6.7 Hz, 1H), 5.08 – 4.83 (m, 2H), 2.03 (q, *J* = 7.2 Hz, 2H), 1.74 – 1.56 (m, 2H), 1.46 (p, *J* = 7.5 Hz, 2H), 1.06 (t, *J* = 7.5 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, DMF-d7):

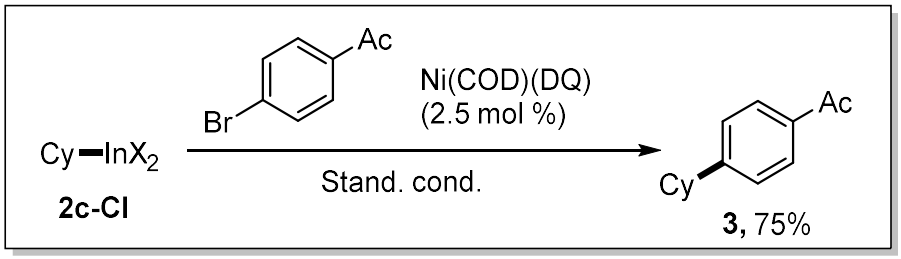
for **2f**: δ 134.0, 115.1, 34.2, 33.8, 27.6, 23.0.

for **2f'**: δ 40.3, 37.7, 26.1, 23.0.



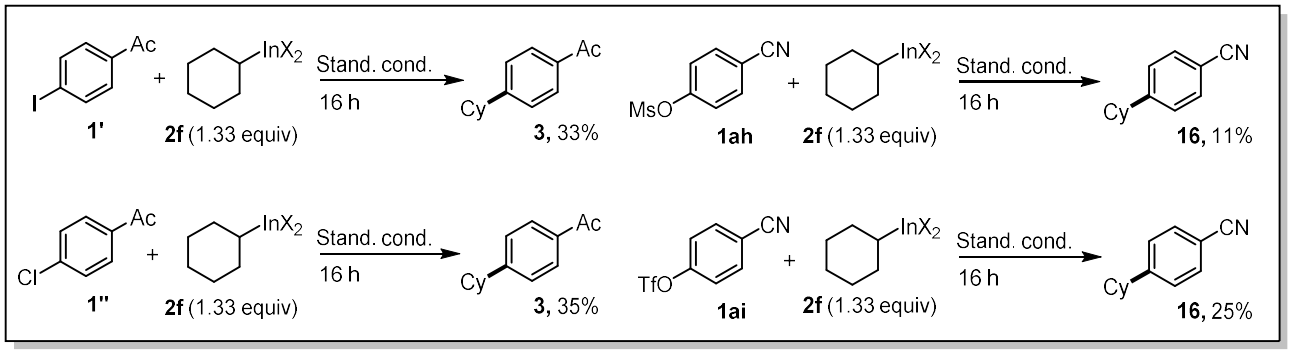


5.3. Test of Ni(0) catalyst



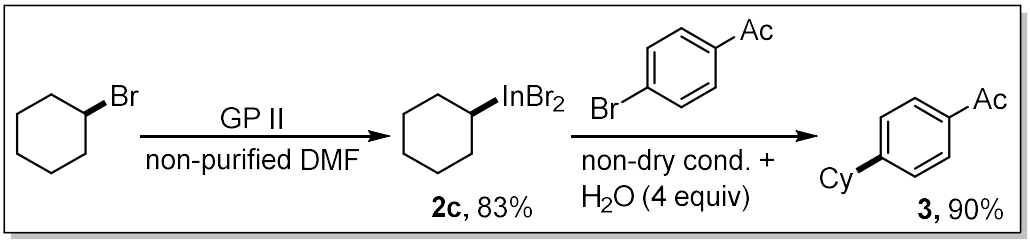
4,4'-Dimethoxy-2,2'-bipyridine (2.70 mg, 0.0125 mmol), Ni(COD)(DQ) (2.07 mg, 0.0063 mmol) and magnetic stirring bar were placed in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*). The tube was evacuated and filled with argon twice. DME (204 µL) was added and the mixture was stirred for 5 minutes. After that, cyclohexylindium(III) halide (**2c-Cl**) solution in DMF (510 µL, 0.3325 mmol), phthalimide (55.1 mg, 0.375 mmol), 1-(4-bromophenyl)ethan-1-one (49.8 mg, 0.25 mmol) and 8Cl4CzIPN (2.7 mg, 0.0025 mmol) were added. The tube was closed with a screw cap and placed in a glass jacket for cooling (Huber circulating chiller BR-03 was used, water temperature 20 °C) and irradiated by a LED matrix (400 nm, 60 W) for 2 hours. The distance between LED chip and the reaction tube was about 1 cm (*photocatalytic reaction set-up as* **Figure S1**). For the workup, 2M aq. HCl (2 mL) was added, and the mixture was washed with hexanes (5×3 mL). The combined organic layers were filtered through Na_2SO_4, concentrated under vacuum, and the residue was analyzed by ^{1}H NMR with dibromomethane as an internal standard.

5.4. Comparison of leaving groups



4,4'-Dimethoxy-2,2'-bipyridine (2.70 mg, 0.0125 mmol), $NiCl_2$·diglyme (1.64 mg, 0.0063 mmol) and magnetic stirring bar were placed in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*). The tube was evacuated and filled with argon twice. DME (204 µL) was added and the mixture was stirred for 5 minutes. After that, cyclohexylindium(III) halide (**2c-Cl**) solution in DMF (510 µL, 0.3325 mmol), phthalimide (55.1 mg, 0.375 mmol), 1-(4-iodophenyl)ethan-1-one (**1'**) (61.5 mg, 0.25 mmol) and 8Cl4CzIPN (2.7 mg, 0.0025 mmol) were added. The tube was closed with a screw cap and placed in a glass jacket for cooling (Huber circulating chiller BR-03 was used, water temperature 20 °C) and irradiated by a LED matrix (400 nm, 60 W) for 16 hours. The distance between LED chip and the reaction tube was about 1 cm (*photocatalytic reaction set-up as* **Figure S1**). For the workup, 2M aq. HCl (2 mL) was added, and the mixture was washed with hexanes (5×3 mL). The combined organic layers were filtered through Na_2SO_4, concentrated under vacuum, and the residue was analyzed by ^1H NMR with dibromomethane as an internal standard. Reactions were carried out in a similar condition for 1-(4-chlorophenyl)ethan-1-one (**1''**) (38.5 mg, 0.25 mmol), 4-cyanophenyl methanesulfonate (**1ah**) (49.3 mg, 0.25 mmol) and 4-cyanophenyl trifluoromethanesulfonate (**1ai**) (62.5 mg, 0.25 mmol).

5.5. Non-dry experiment



Step 1. Lithium bromide (87.0 mg, 1.00 mmol) and magnetic stirring bar were placed in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*). The tube was evacuated and filled with argon twice. DMF (was used as is) (0.5 mL) and bromocyclohexane (81.5 mg, 0.50 mmol) were added. Indium(I) bromide (195.0 mg, 1.00 mmol) was added last to the reaction mixture. The tube was closed with a

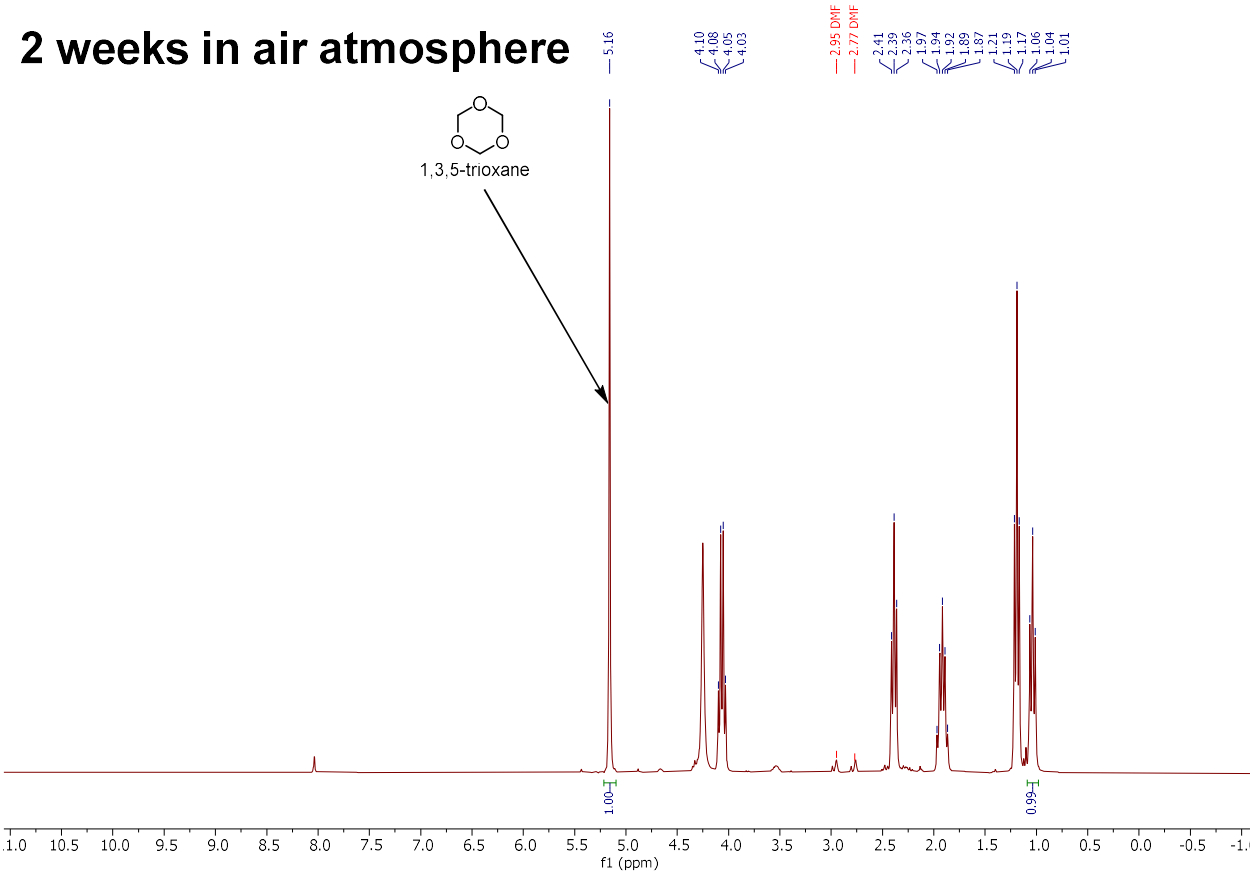
screw cap. The reaction mixture was heated at 80 °C (PEG bath) with stirring for 12 hours. After the reaction was completed, the tube was centrifuged at 2600 rpm for 2 minutes. The yield of (**2c**) was determined by titrating the formed (**2c**) with iodine as follows: 1,2,3,4-tetrahydronaphthalene (61.0 mg, 0.46 mmol) was added to the resulting solution of reagent (**2c**). An excess of iodine was placed in a 1 mL chromatographic vial. Methyl tert-butyl ether (MTBE) (0.8 mL) and an aliquot of the analysed (**2c**) solution with internal standard (15 µL) were added. After heating (70 °C) this mixture for 20 seconds, the ratio between cyclohexyl Iodide and 1,2,3,4-tetrahydronaphthalene was determined by GC-FID. Yield of (**2c**) = 83% (1,2,3,4-tetrahydronaphthalene as an internal standard).

Step 2. 4,4'-Dimethoxy-2,2'-bipyridine (2.70 mg, 0.0125 mmol), $NiCl_2$·diglyme (1.64 mg, 0.0063 mmol) and magnetic stirring bar were placed in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*). The tube was evacuated and filled with argon twice. DME (was used as is) (230 µL) was added and the mixture was stirred for 5 minutes. After that, cyclohexylindium(III) bromide (**2c-Cl**) solution in DMF (480 µL, 0.3325 mmol), phthalimide (55.1 mg, 0.375 mmol), 1-(4-bromophenyl)ethan-1-one (49.8 mg, 0.25 mmol), H_2O (18.0 mg, 1.00 mmol) and 8Cl4CzIPN (2.7 mg, 0.0025 mmol) were added. The tube was closed with a screw cap and placed in a glass jacket for cooling (Huber circulating chiller BR-03 was used, water temperature 20 °C) and irradiated by a LED matrix (400 nm, 60 W) for 2 hours. The distance between LED chip and the reaction tube was about 1 cm (*photocatalytic reaction set-up as* **Figure S1**). For the workup, 2M aq. HCl (2 mL) was added, and the mixture was washed with hexanes (5×3 mL). The combined organic layers were filtered through Na_2SO_4, concentrated under vacuum, and the residue was analyzed by ^{1}H NMR with dibromomethane as an internal standard. Yield of (**3**): 90% (dibromomethane as an internal standard).

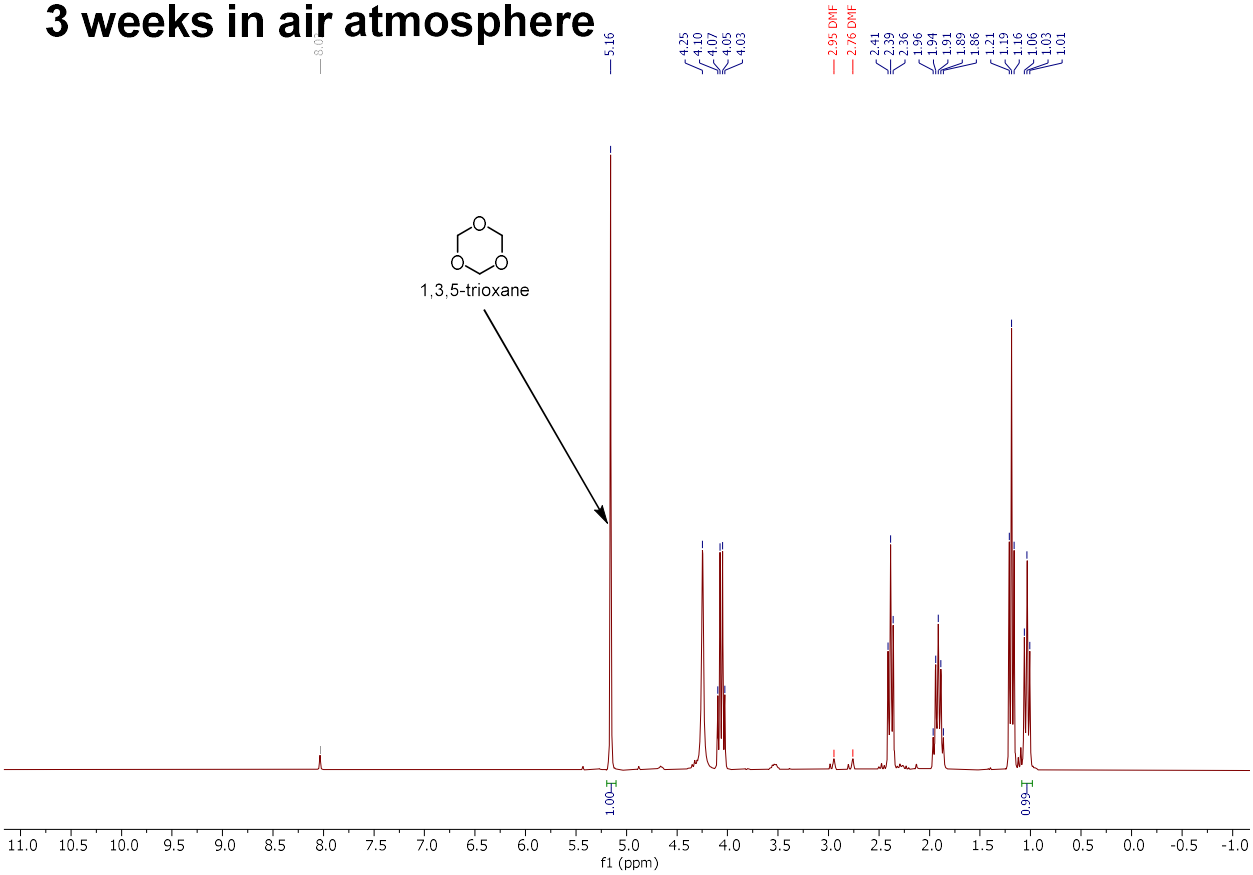
5.6. Stability of alkyl indium reagent (2a) to air atmosphere

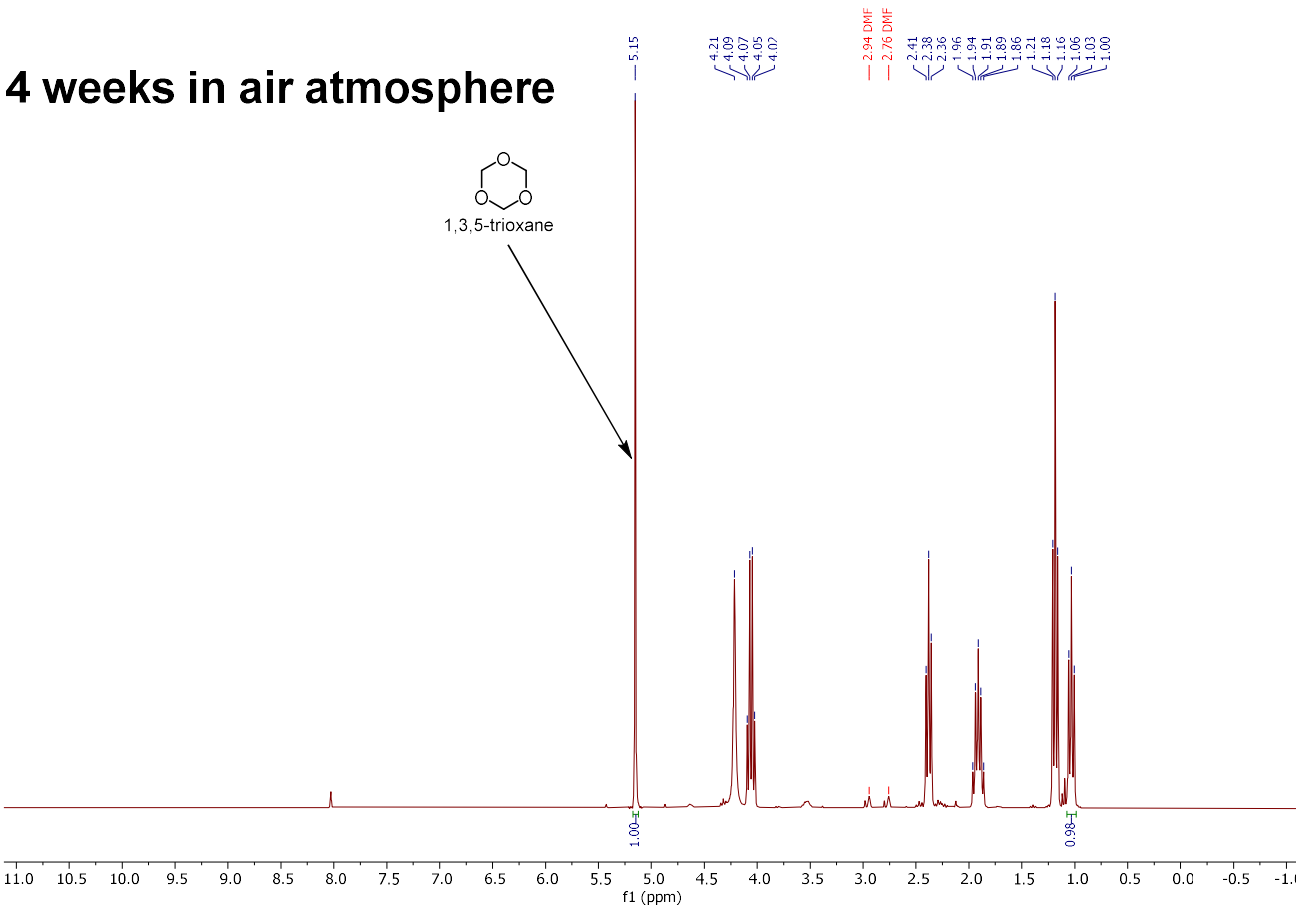
(4-Ethoxy-4-oxobutyl)indium(III) bromide (**2a**) was prepared according to **GP I** in DMF-d7. 1,3,5-Trioxane (14.9 mg, 0.1656 mmol) was added to the resulting solution of **2a**, and the solution was transferred to a chromatographic vial under air, the vial was capped. The solution was periodically transferred into NMR tube, analyzed by ^{1}H NMR, and then poured back into the vial. After one month, there was no decrease in concentration of **2a**.

2 weeks in air atmosphere

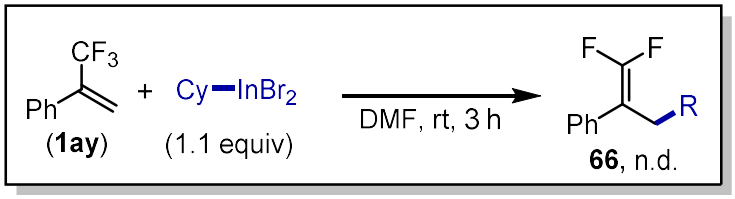


3 weeks in air atmosphere





5.7. Blank experiment with α-(trifluoromethyl)styrene



Magnetic stirring bar were placed in a test tube (*Duran cat. no. 261351155, Roth cat. no. K248.1, outside diameter = 12 mm, 6 mL*). The tube was evacuated and filled with argon twice. Alkyl indium reagent (**2c-Cl**) solution in DMF (0.651 M) (422 µL, 0.275 mmol), α-(trifluoromethyl)styrene (**1ay**) (43.00 mg, 0.25 mmol) and DMF (578 µL) were added. The tube was closed with a screw cap and stirred for 3 hours without irradiation. The reaction mixture was analyzed by GC-MS. Product **66** was not detected in GC-MS.

5.8. Stern-Volmer fluorescence quenching studies

Experiments were performed in a screw-capped quartz vial (10 mm × 10 mm). The solvent was degassed, and the vial was filled with argon. The concentration of 8Cl4CzIPN was 0.01 mmol/L. Excitation wavelength was 344 nm, and fluorescence wavelength was 536 nm. Measurements were performed at room temperature.

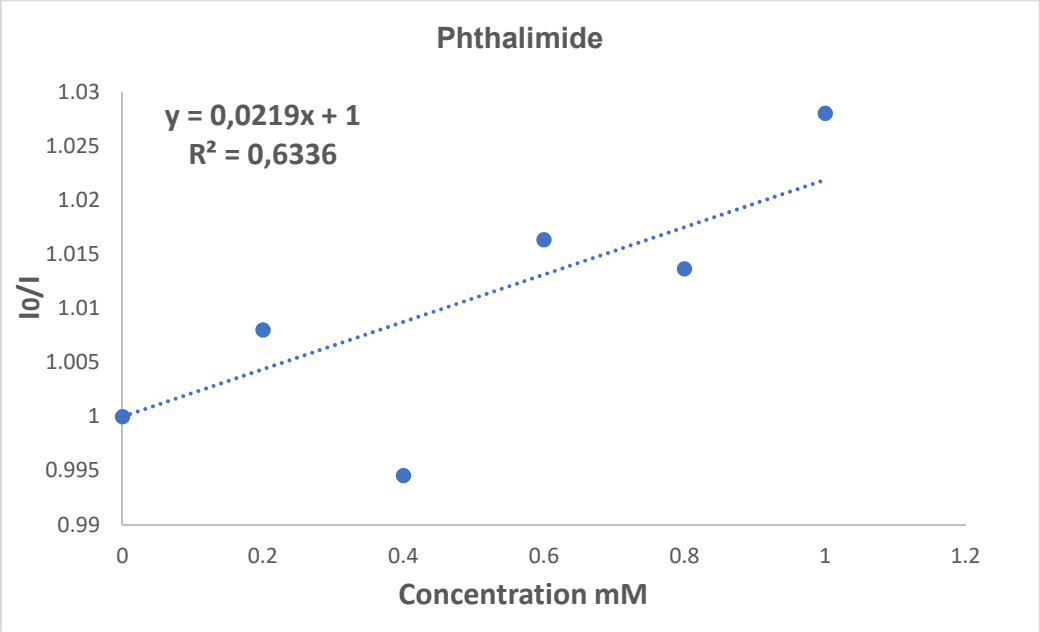


Figure S12. Fluorescence quenching of the emission of 8Cl4CzIPN (0.01 mmol/L in DMF) with phthalimide.

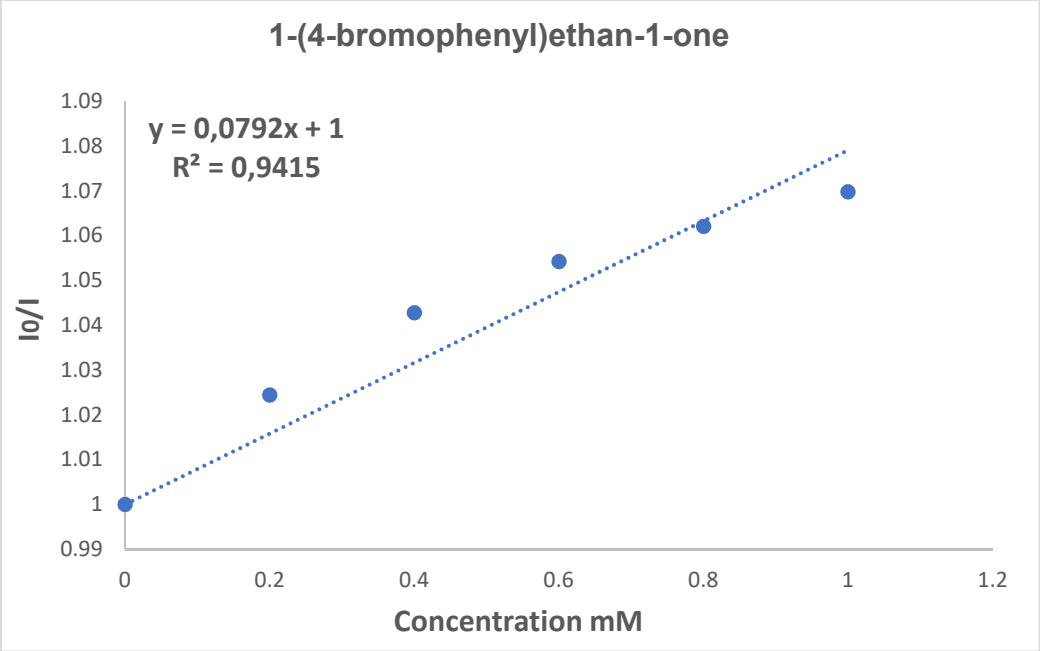


Figure S13. Fluorescence quenching of the emission of 8Cl4CzIPN (0.01 mmol/L in DMF) with 1-(4-bromophenyl)ethan-1-one.

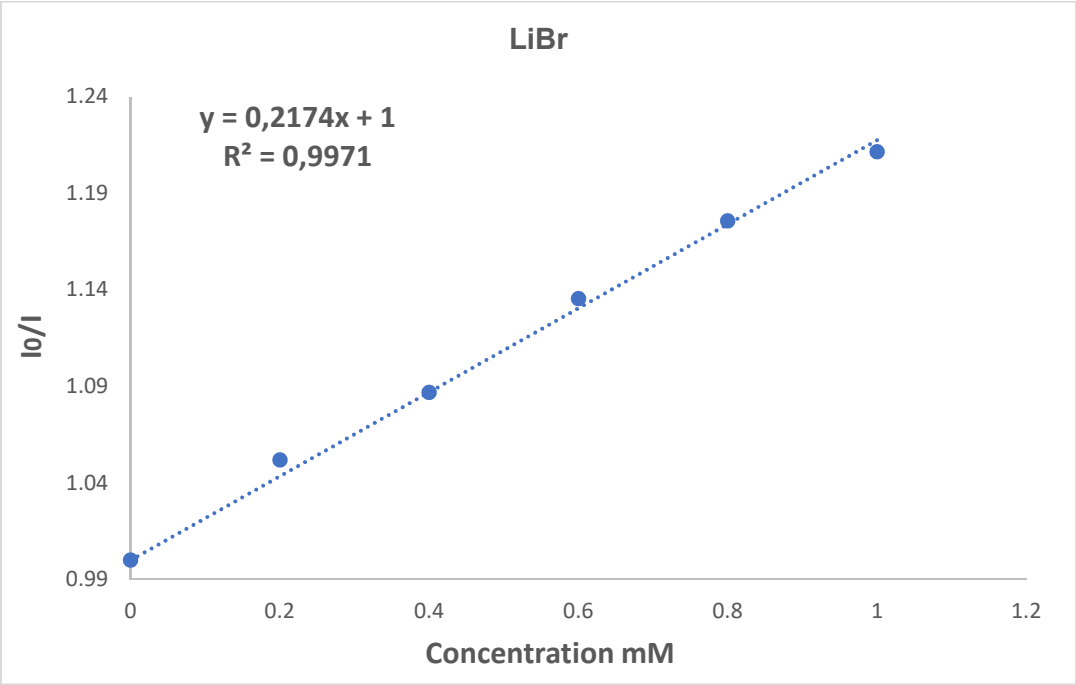


Figure S14. Fluorescence quenching of the emission of 8Cl4CzIPN (0.01 mmol/L in DMF) with LiBr.

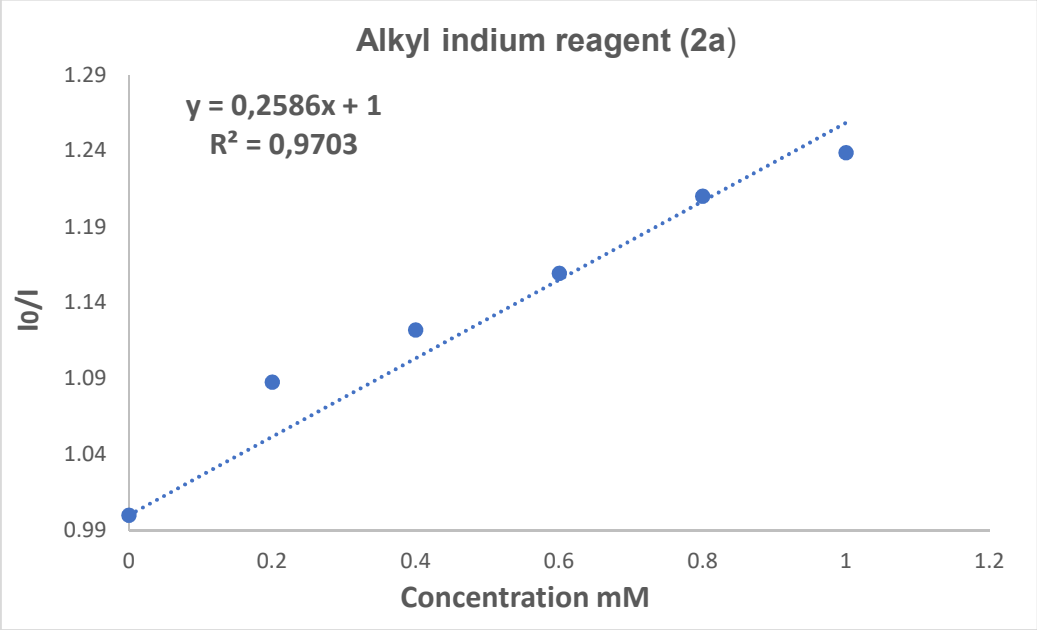


Figure S15. Fluorescence quenching of the emission of 8Cl4CzIPN (0.01 mmol/L in DMF) with alkyl indium reagent **2a**.

5.9. Cyclic voltammetry

Voltammetric studies were carried out using potentiostat P30JM with a scan rates of 0.1 $V \cdot s^{-1}$ in a temperature-controlled (25 °C) glass cell (V = 10 mL) under an argon atmosphere using 0.1 M solution of Et_4NClO_4 in DMF as supporting electrolyte. Software *iR* compensation using ferrocene (*R* = 950 Ω) was used in all experiments. A glassy carbon disk (*d* = 2.9 mm) was used as the working electrode (carefully polished by chromium paste before each measurement). A saturated calomel electrode (SCE) separated from the solution being studied by a salt bridge filled with the supporting electrolyte was used as the reference electrode. A platinum plate (*S* = 3 cm^2) was used as the counter electrode. All experiments were performed with the concentration of reagent **2a** of 1 mM in DMF.

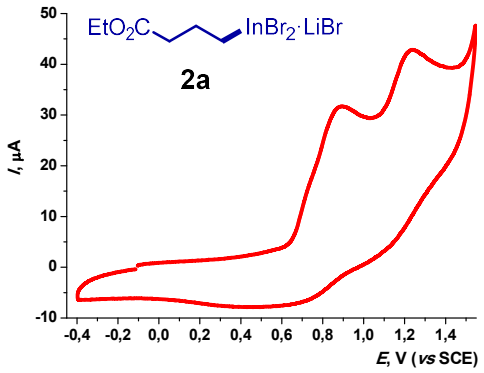


Figure S16. Reagent **2a** (initial anodic scan).

E_{onset} = +0.60 V; E_{p1}^{ox} = +0.89 V, i_{p1} = 27.86 µA; E_{p2}^{ox} = +1.24 V;

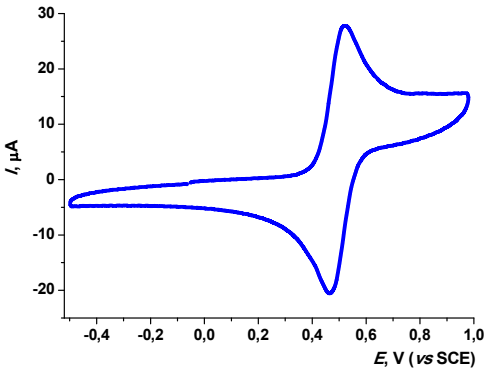


Figure S17. Ferrocene (initial anodic scan).

E_p^{ox} = +0.52 V, i_p = 27.49 µA; E_p^{rered} = +0.46 V.

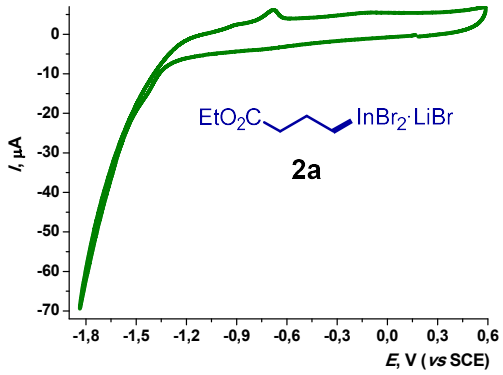
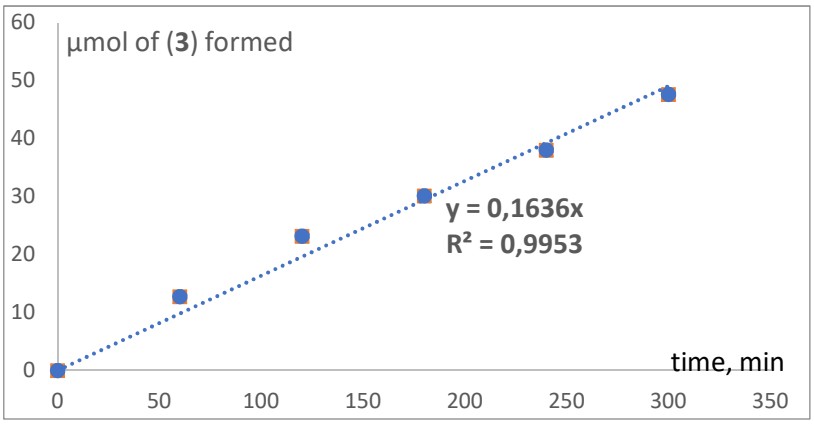


Figure S18. Reagent **2a** (initial cathodic scan).

Reagent **2a** exhibits two quasi-reversible anodic peaks at +0.89 V and +1.24 V (see Figure S16), very similar to the previously describedcurve for the bromide ion. Thus, the first peak corresponds to the one-electron (cf. the ferrocene curve, Figure S17) oxidation of the bromide ion to bromine, whereas the second peak corresponds to the oxidation of the tribromide ion. [60] In the cathodic region, reagent **2a** does not exhibit any reduction peaks (see Figure S18), only the discharge of the supporting electrolyte is observed.

5.10. Quantum yield measurement

Quantum yield for the reaction of 1-(4-bromophenyl)ethan-1-one with cyclohexylindium(III) bromide (**2c**) was estimated using irradiation with a 1.4 W laser (405 nm). Photon flux of the laser was measured by standard ferrioxalate actinometry – 10,75 µEs/min. A mixture of 4,4'-dimethoxy-2,2'-bipyridine (2.70 mg, 0.0125 mmol), $NiCl_2$·diglyme (1.64 mg, 0.0063 mmol), phthalimide (55.1 mg, 0.375 mmol), 1-(4-bromophenyl)ethan-1-one (49.8 mg, 0.25 mmol), 8Cl4CzIPN (2.7 mg, 0.0025 mmol) and 43.5 mg of 4-phenylcyclohexan-1-one (internal standard) were placed in a square quartz cuvette (10×10 mm). The cuvette was evacuated and filled with argon twice. DME (550 µL), cyclohexylindium(III) bromide (**2c**) solution in DMF (380 µL, 0.3325 mmol) and DMF (995 µL) were added. At 405 nm, the reaction mixture completely absorbs the laser light. The cuvette was irradiated for 5 hours, and every 60 minutes the mixture was analyzed by GC-FID. The quantum yield Φ was calculated by the following equation:



$$\phi = \frac{\text{moles of product formed}}{\text{photon flux} \cdot \text{reaction time}} / Q = \frac{0{,}1636}{0{,}676 \cdot 10{,}75} = 0{,}023$$

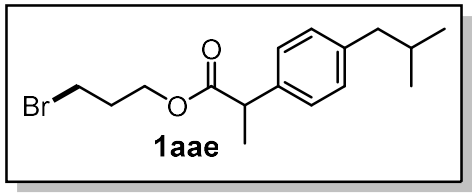
$$Q = \text{quenching fraction} = \frac{I_0 - I}{I_0} = 0{,}676$$

Measurement and calculation of Q-factor was essential because strong fluorescence of the reaction mixture was observed. The fluorescence of 8Cl4CzIPN (2.7 mg, 0.0025 mmol) in DMF/DME (5/2) (2 mL) was taken as I_0 and the fluorescence of a mixture of 4,4'-dimethoxy-2,2'-bipyridine (2.70 mg, 0.0125 mmol), $NiCl_2$·diglyme (1.64 mg, 0.0063 mmol), phthalimide (55.1 mg, 0.375 mmol), 1-(4-bromophenyl)ethan-1-one (49.8 mg, 0.25 mmol), 8Cl4CzIPN (2.7 mg, 0.0025 mmol), 4-phenylcyclohexan-1-one (43.5 mg, 0.25 mmol) and cyclohexylindium(III) bromide (**2c**) solution in DMF (380 µL, 0.3325 mmol) was taken as I. The excitation wavelength was 405 nm, the registration wavelength was 534 nm.

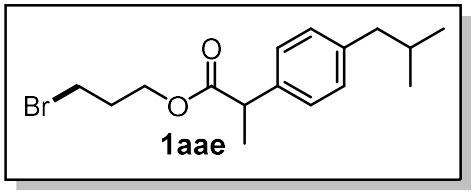
6. References

[1] M. O. Zubkov, M. D. Kosobokov, V. V. Levin, V. A. Kokorekin, A. A. Korlyukov, J. Hu, A. D. Dilman, *Chem. Sci.* **2020**, *11*, 737–741.
[2] L. Geniller, M. Taillefer, F. Jaroschik, A. Prieto, *ACS Catal.* **2023**, *13*, 8624–8630.
[3] X. Tang, L. Huang, C. Qi, X. Wu, W. Wu, H. Jiang, *Chem. Commun.* **2013**, *49*, 6102–6104.
[4] S. Li, S. Nakahara, T. Adachi, T. Murata, K. Takaishi, T. Ema, *J. Am. Chem. Soc.* **2024**, *146*, 14935–14941.
[5] Q. Yan, X. Shen, G. Zi, G. Hou, *Chem. Eur. J.* **2020**, *26*, 5961–5964.
[6] A. Ganguly, R. Chandrasekaran, B. S. S. Balamurugan, R. Rasappan, *Adv. Synth. Catal.* **2024**, *366*, 1442–1447.
[7] G. Lu, W. Nie, M. Xin, Y. Meng, J. Gu, H. Miao, X. Cheng, A. S. C. Chan, Y. Zou, *Eur. J. Med. Chem.* **2022**, *243*, 114790.
[8] C. Liu, K. Li, R. Shang, *ACS Catal.* **2022**, *12*, 4103–4109.
[9] S. K. Jana, R. Bhattacharya, P. Dey, S. Chakraborty, B. Maji, *ACS Catal.* **2024**, *14*, 14172–14182.
[10] T. Zhang, J. Rabeah, S. Das, *Nat. Commun.* **2024**, *15*, 5208.
[11] W. Xie, P. Ma, Y. Zhang, L. Xi, S. Qiu, X. Huang, B. Yang, Y. Gao, J. Zhang, *Org. Lett.* **2022**, *24*, 6099–6104.
[12] I. Biljan, M. Kralj, T. M. Radić, V. Svetličić, H. Vančik, *J. Phys. Chem. C* **2011**, *115*, 20267–20273.
[13] G. Wu, A. Jacobi von Wangelin, *Chem. Sci.* **2018**, *9*, 1795–1802.
[14] Q. Fan, Y. Zhao, J. Liang, Y. Zhang, Y. Xu, Q. Zhang, H. Zhu, M. Jiang, X. Shao, *Org. Chem. Front.* **2024**, *11*, 2518–2527.
[15] P. Li, Z. Zhu, C. Guo, G. Kou, S. Wang, P. Xie, D. Ma, T. Feng, Y. Wang, Y. Qiu, *Nat. Catal.* **2024**, *7*, 412–421.
[16] X. Zhu, M. Jiang, X. Li, E. Zhu, Q. Deng, X. Song, J. Lv, D. Yang, *Org. Chem. Front.* **2022**, *9*, 347–355.
[17] Y. Gao, J. Li, S. Bai, D. Tu, C. Yang, Z. Ye, B. Hu, X. Qi, C. Jiang, *Org. Chem. Front.* **2020**, *7*, 1149–1157.
[18] A. Baber, J. G. de Vries, A. G. Orpen, P. G. Pringle, K. von der Luehe, *Dalton Trans.* **2006**, 4821–4828.
[19] K.-R. Li, X.-C. He, J. Gao, Y.-L. Liu, H.-B. Chen, H.-Y. Xiang, K. Chen, H. Yang, *J. Org. Chem.* **2024**, *89*, 12658–12667.
[20] Y.-L. Liu, X.-C. He, J. Gao, K.-R. Li, K. Chen, H.-Y. Xiang, H. Yang, *J. Org. Chem.* **2024**, *89*, 10987–10997.
[21] P. Gopinath, S. Chandrasekaran, *Eur. J. Org. Chem.* **2018**, *2018*, 6541–6547.
[22] A. Kumari, I. Pani, M. U. Lone, A. Aggarwal, S. K. Pal, R. K. Roy, *ACS Appl. Mater. Interfaces* **2023**, *15*, 31233–31242.
[23] C. Fei, Y. Chen, Z. Jiang, D. Jiang, *Bioorg. Med. Chem. Lett.* **2018**, *28*, 1792–1796.
[24] G.-W. Wang, M. Wheatley, M. Simonetti, D. M. Cannas, I. Larrosa, *Chem* **2020**, *6*, 1459–1468.
[25] D. R. Cullen, A. Gallagher, C. L. Duncan, J. Pengon, R. Rattanajak, J. Chaplin, H. Gunosewoyo, S. Kamchonwongpaisan, A. Payne, M. Mocerino, *Eur. J. Med. Chem.* **2021**, *226*, 113861.
[26] T. Kanbara, Y. Ito, A. Yamaguchi, T. Yajima, *Molecules* **2024**, *29*, 1214.
[27] V. V. Levin, A. D. Dilman, *Mendeleev Commun.* **2021**, *31*, 684–685.
[28] K. Li, B. Zu, C. Mazet, *Org. Lett.* **2024**, *26*, 6047–6052.
[29] D. Suresh, K. Kanagaraj, K. Pitchumani, *Tetrahedron Lett.* **2014**, *55*, 3678–3682.
[30] G. R. Humphrey, S. H. B. Wright, *J. Heterocycl. Chem.* **1989**, *26*, 23–24.
[31] P. H. Huy, S. Motsch, S. M. Kappler, *Angew. Chem. Int. Ed.* **2016**, *55*, 10145–10149.
[32] F. Le Vaillant, M. Garreau, S. Nicolai, G. Gryn'ova, C. Corminboeuf, J. Waser, *Chem. Sci.* **2018**, *9*, 5883–5889.
[33] E. Speckmeier, T. G. Fischer, K. Zeitler, *J. Am. Chem. Soc.* **2018**, *140*, 15353–15365.
[34] V. I. Supranovich, V. V. Levin, A. D. Dilman, *Org. Lett.* **2024**, *26*, 4537–4541.
[35] J. Luo, M. T. Davenport, D. H. Ess, T. L. Liu, *Angew. Chem. Int. Ed.* **2024**, *63*, e202407118.
[36] L. Zou, S. Xiang, R. Sun, Q. Lu, *Nat. Commun.* **2023**, *14*, 7992.
[37] F. Toriyama, J. Cornella, L. Wimmer, T.-G. Chen, D. D. Dixon, G. Creech, P. S. Baran, *J. Am. Chem. Soc.* **2016**, *138*, 11132–11135.
[38] A. Mori, T. Mizusaki, T. Ikawa, T. Maegawa, Y. Monguchi, H. Sajiki, *Tetrahedron* **2007**, *63*, 1270–1280.
[39] S. Kubosaki, H. Takeuchi, Y. Iwata, Y. Tanaka, K. Osaka, M. Yamawaki, T. Morita, Y. Yoshimi, *J. Org. Chem.* **2020**, *85*, 5362–5369.
[40] I. B. Perry, T. F. Brewer, P. J. Sarver, D. M. Schultz, D. A. DiRocco, D. W. C. MacMillan, *Nature* **2018**, *560*, 70–75.
[41] A. Dahadha, W. Imhof, *ARKIVOC* **2013**, *2013*, 200–216.
[42] J. Zhou, G. C. Fu, *J. Am. Chem. Soc.* **2004**, *126*, 1340–1341.
[43] F. Yue, J. Dong, Y. Liu, Q. Wang, *Org. Lett.* **2021**, *23*, 2477–2481.
[44] Á. Gutiérrez-Bonet, J. C. Tellis, J. K. Matsui, B. A. Vara, G. A. Molander, *ACS Catal.* **2016**, *6*, 8004–8008.
[45] X. Tian, J. Kaur, S. Yakubov, J. P. Barham, *ChemSusChem* **2022**, *15*, e202200906.

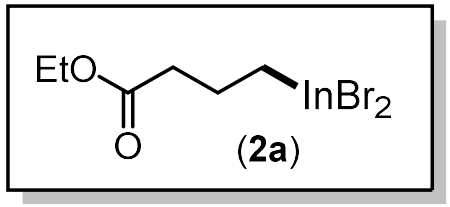
[46] S. Biswas, B. Qu, J.-N. Desrosiers, Y. Choi, N. Haddad, N. K. Yee, J. J. Song, C. H. Senanayake, *J. Org. Chem.* 2020, *85*, 8214–8220.
[47] T. Knauber, R. Chandrasekaran, J. W. Tucker, J. M. Chen, M. Reese, D. A. Rankic, N. Sach, C. Helal, *Org. Lett.* 2017, *19*, 6566–6569.
[48] I. Abdiaj, A. Fontana, M. V. Gomez, A. de la Hoz, J. Alcázar, *Angew. Chem. Int. Ed.* 2018, *57*, 8473–8477.
[49] P. Wang, B.-Z. Chen, Y.-C. Guo, W. Rao, Z.-L. Shen, *Tetrahedron Lett.* 2019, *60*, 151288.
[50] M.-L. Zhi, B.-Z. Chen, W. Deng, X.-Q. Chu, T.-P. Loh, Z.-L. Shen, *J. Org. Chem.* 2019, *84*, 3017–3023.
[51] V. B. Phapale, M. Guisán-Ceinos, E. Buñuel, D. J. Cárdenas, *Chem. Eur. J.* 2009, *15*, 12681–12688.
[52] Y. Sato, K. Nakamura, Y. Sumida, D. Hashizume, T. Hosoya, H. Ohmiya, *J. Am. Chem. Soc.* 2020, *142*, 9938–9943.
[53] Z.-L. Shen, K. K. K. Goh, Y.-S. Yang, Y.-C. Lai, C. H. A. Wong, H.-L. Cheong, T.-P. Loh, *Angew. Chem. Int. Ed.* 2011, *50*, 511–514.
[54] Y. Shi, J. S. Derasp, T. Maschmeyer, J. E. Hein, *Nat. Commun.* 2024, *15*, 5436.
[55] K. Itami, M. Mineno, T. Kamei, J.-i. Yoshida, *Org. Lett.* 2002, *4*, 3635–3638.
[56] S. Fan, C.-Y. He, X. Zhang, *Chem. Commun.* 2010, *46*, 4926–4928.
[57] Y. Yu, Y. Feng, W. Ma, H. Li, M. Yang, G. Zhang, Y. Yang, *ChemistrySelect* 2022, *7*, e202202061.
[58] W. Chen, S. Ni, Y. Wang, Y. Pan, *Org. Lett.* 2022, *24*, 3647–3651.
[59] A. A. Gladkov, G. N. Chernov, V. V. Levin, V. A. Kokorekin, A. D. Dilman, *Org. Lett.* 2021, *23*, 9645–9648.
[60] M. Tariq, *Z. Phys. Chem.* 2020, *234*, 295–312.



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

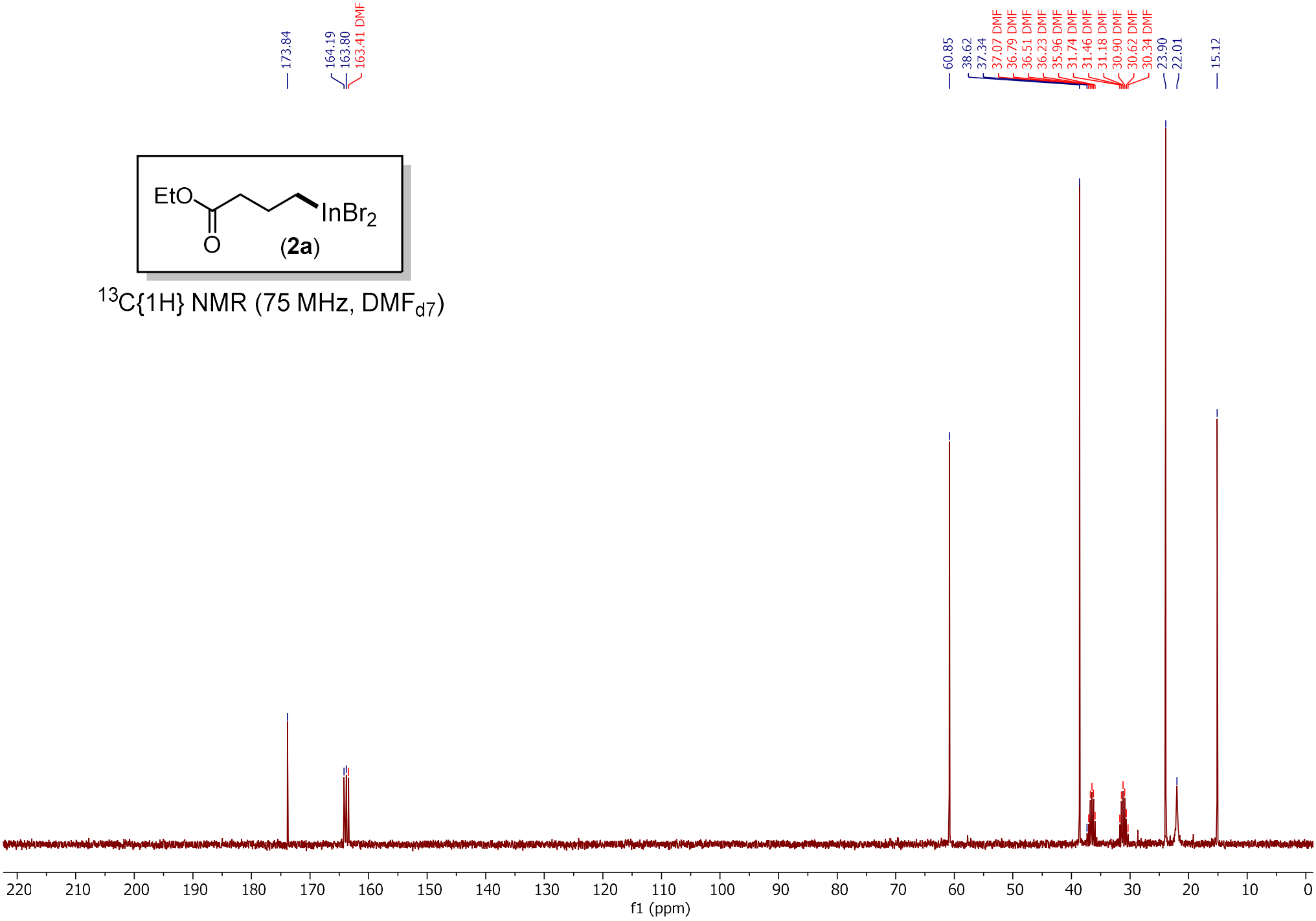


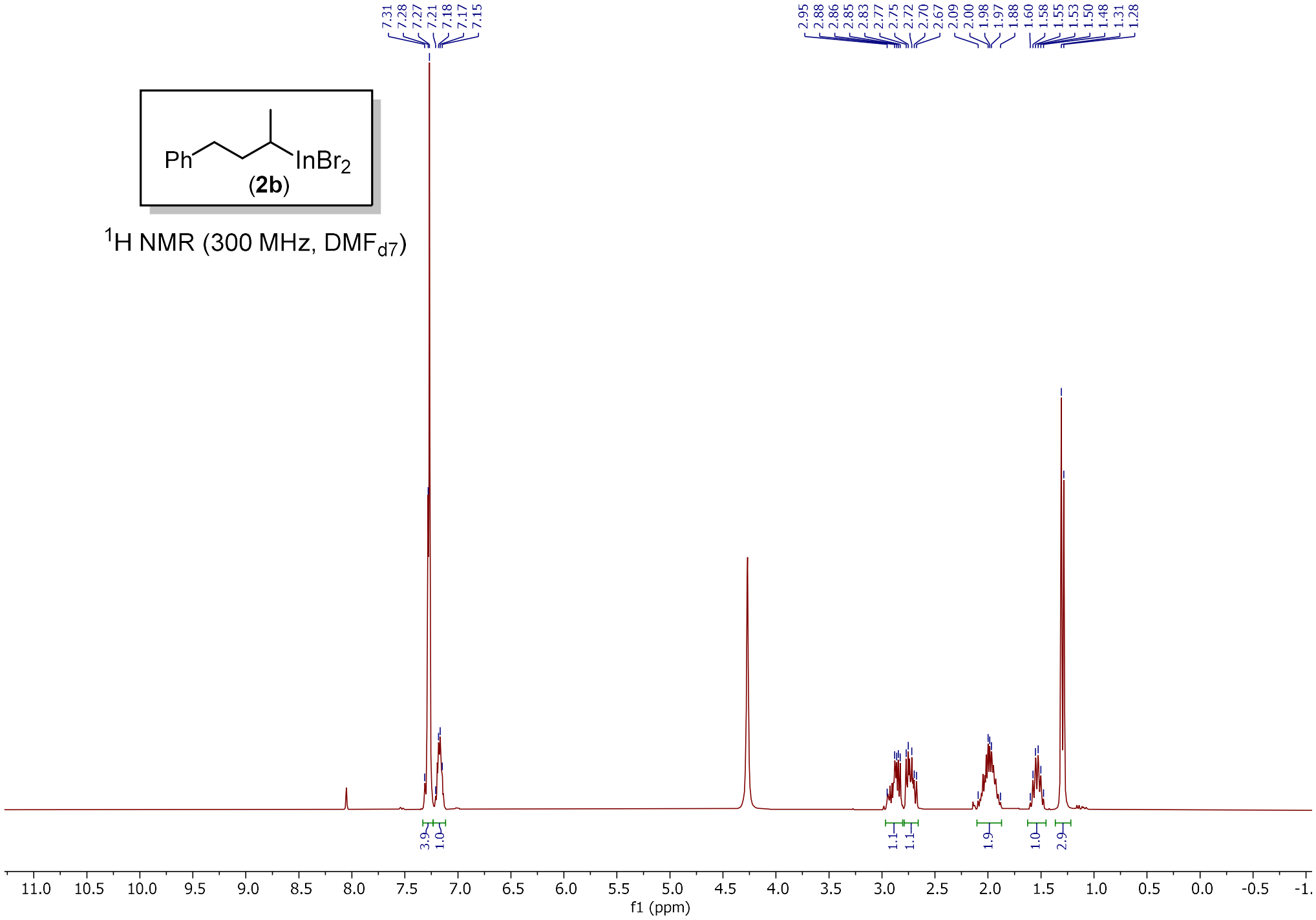
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)

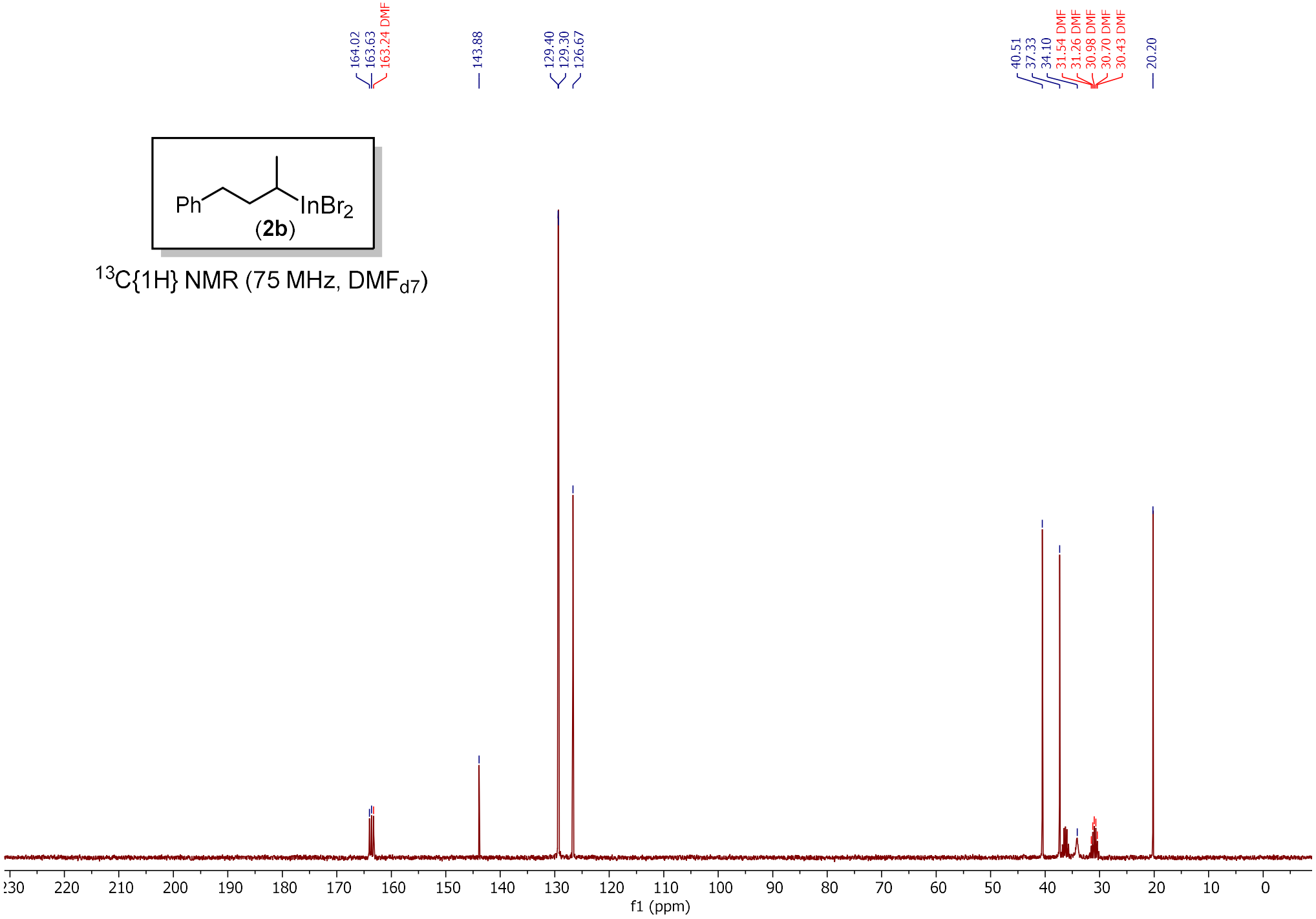


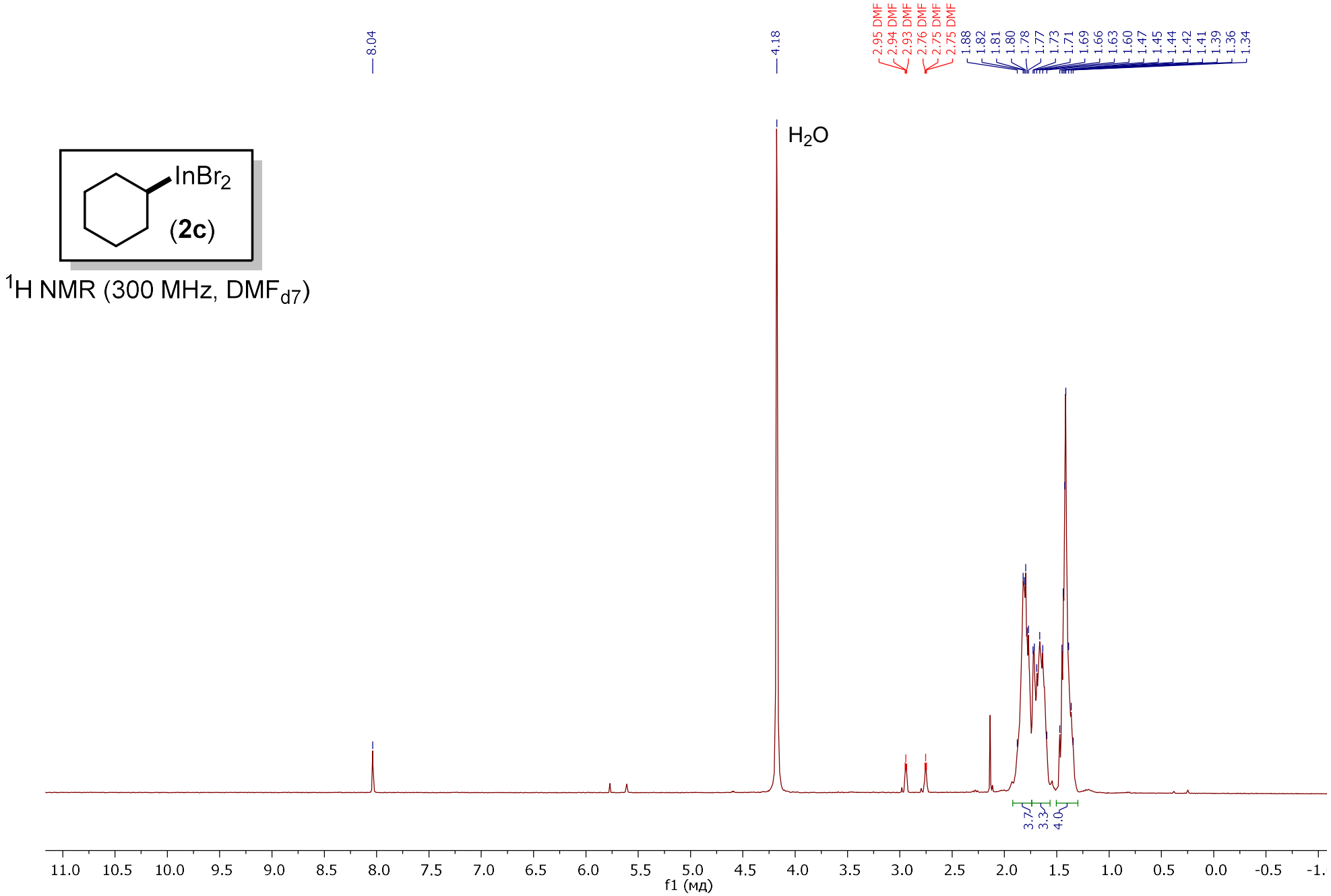
(**2a**)

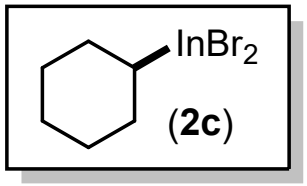
^{1}H NMR (300 MHz, DMF_{d7})


173.84
164.19
163.80
163.41 DMF
60.85
38.62
37.34
37.07 DMF
36.79 DMF
36.51 DMF
36.23 DMF
35.96 DMF
31.74 DMF
31.46 DMF
31.18 DMF
30.90 DMF
30.62 DMF
30.34 DMF
23.90
22.01
15.12
EtO
O
InBr2
(2a)
13C{1H} NMR (75 MHz, DMFd7)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

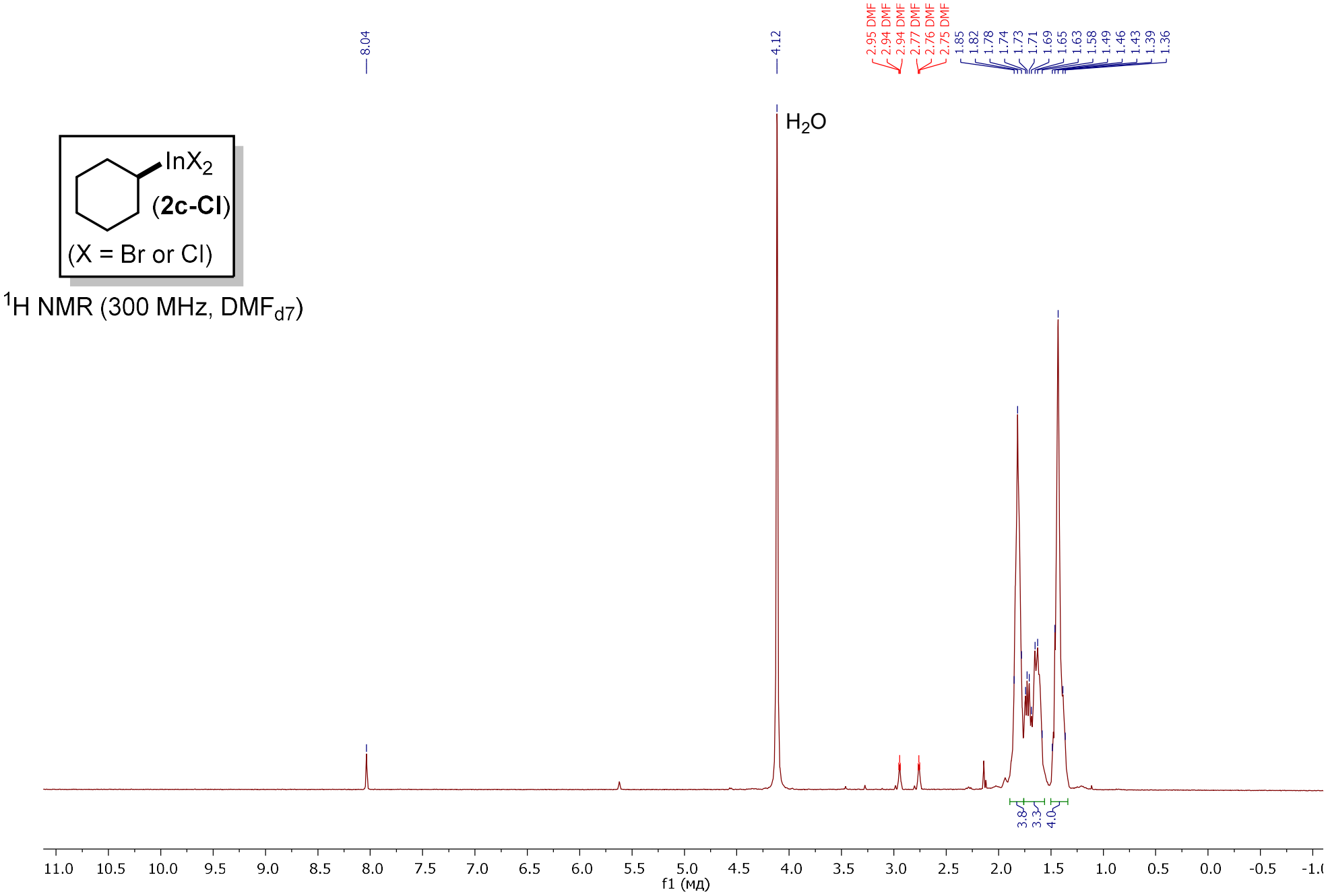

7.31
7.28
7.27
7.21
7.18
7.17
7.15
2.95
2.88
2.86
2.85
2.83
2.77
2.75
2.72
2.70
2.67
2.09
2.00
1.98
1.97
1.88
1.60
1.58
1.55
1.53
1.50
1.48
1.31
1.28
Ph
InBr2
(2b)
1H NMR (300 MHz, DMFd7)
3.9
1.0
1.1
1.1
1.9
1.0
2.9
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

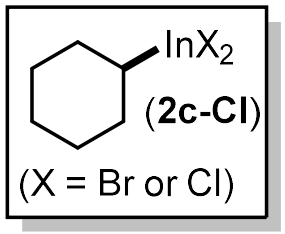

164.02
163.63
163.24 DMF
143.88
129.40
129.30
126.67
40.51
37.33
34.10
31.54 DMF
31.26 DMF
30.98 DMF
30.70 DMF
30.43 DMF
20.20
Ph
InBr2
(2b)
13C{1H} NMR (75 MHz, DMFd7)
f1 (ppm)


InBr2
(2c)
1H NMR (300 MHz, DMFd7)
8.04
4.18
H2O
2.95 DMF
2.94 DMF
2.93 DMF
2.76 DMF
2.75 DMF
2.75 DMF
1.88
1.82
1.81
1.80
1.78
1.77
1.73
1.71
1.69
1.66
1.63
1.60
1.47
1.45
1.44
1.42
1.41
1.39
1.36
1.34
3.7
3.3
4.0
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.
f1 (мд)

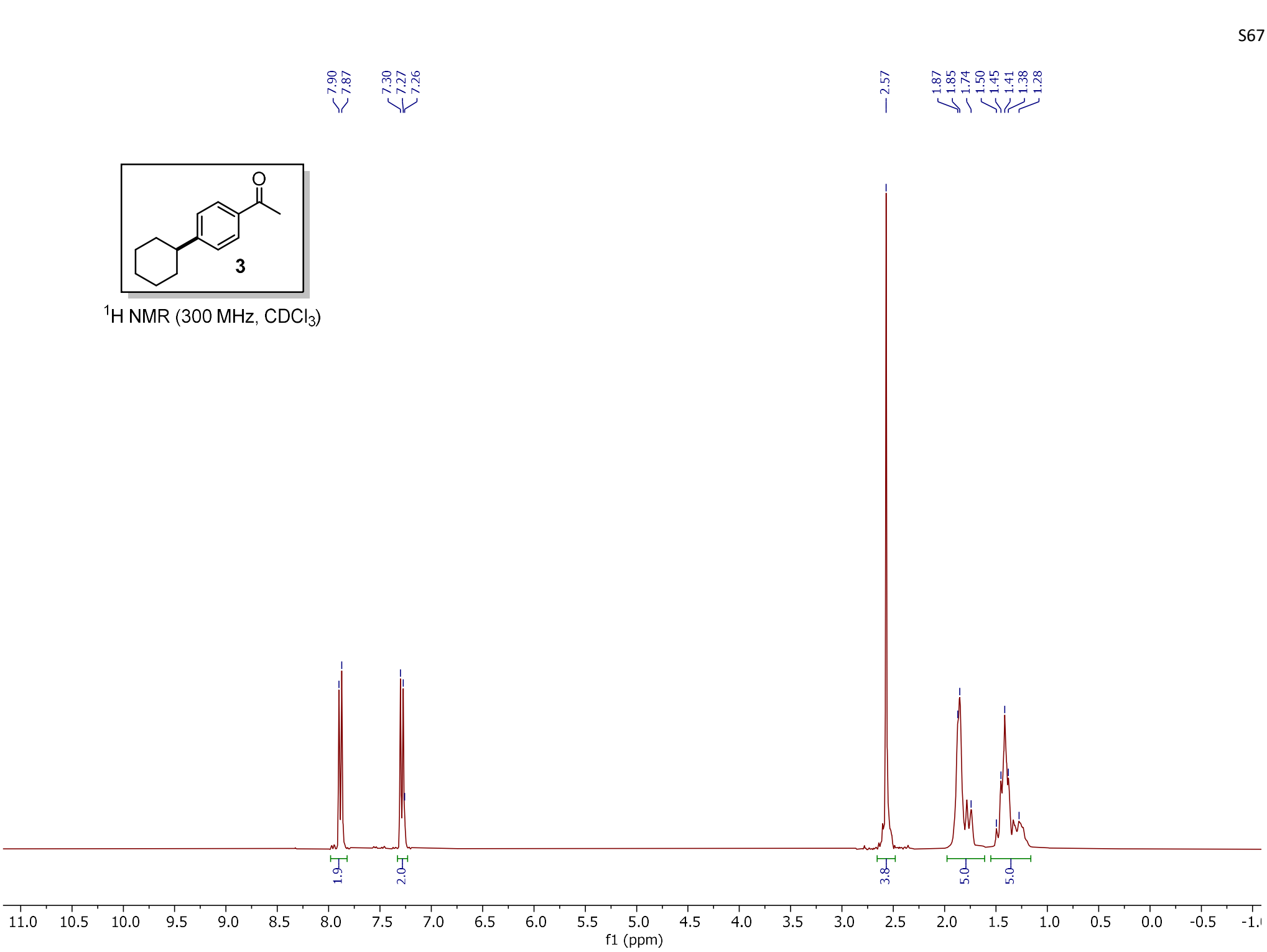


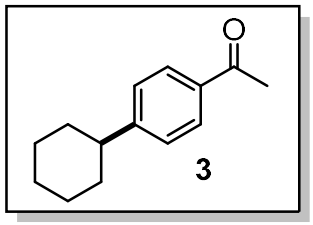
$^{13}C\{^{1}H\}$ NMR (75 MHz, DMF_{d7})


8.04
4.12
2.95 DMF
2.94 DMF
2.94 DMF
2.77 DMF
2.76 DMF
2.75 DMF
1.85
1.82
1.78
1.74
1.73
1.71
1.69
1.65
1.63
1.58
1.49
1.46
1.43
1.39
1.36
H2O
InX2
(2c-Cl)
(X = Br or Cl)
1H NMR (300 MHz, DMFd7)
3.8
3.3
4.0
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
f1 (мд)

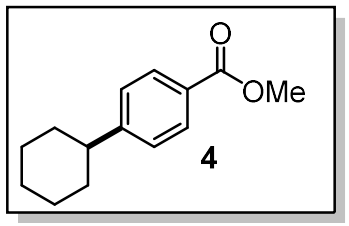


$^{13}C\{^{1}H\}$ NMR (75 MHz, DMF_{d7})

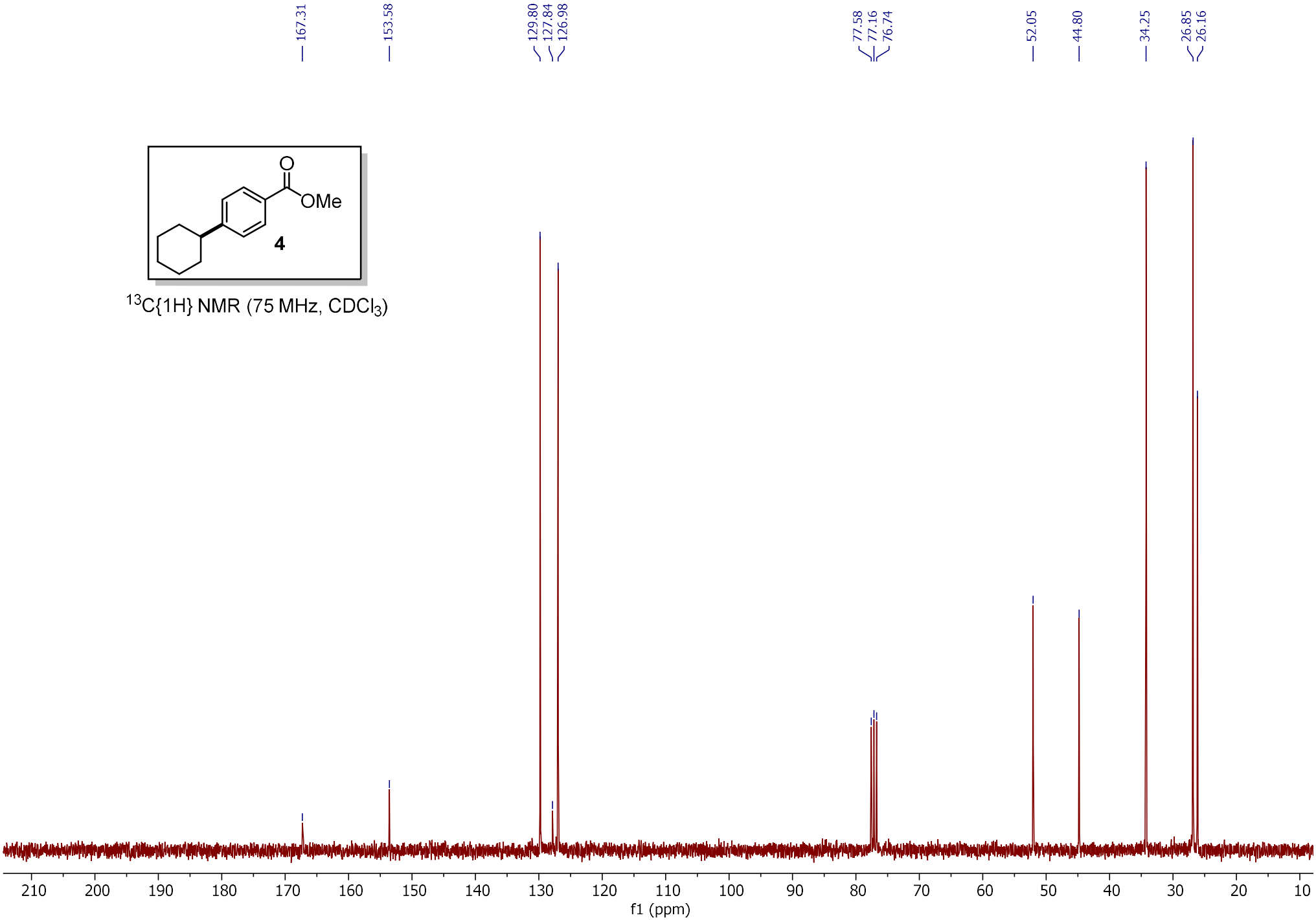

7.90
7.87
7.30
7.27
7.26
2.57
1.87
1.85
1.74
1.50
1.45
1.41
1.38
1.28
O
3
1H NMR (300 MHz, CDCl3)
1.9
2.0
3.8
5.0
5.0
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

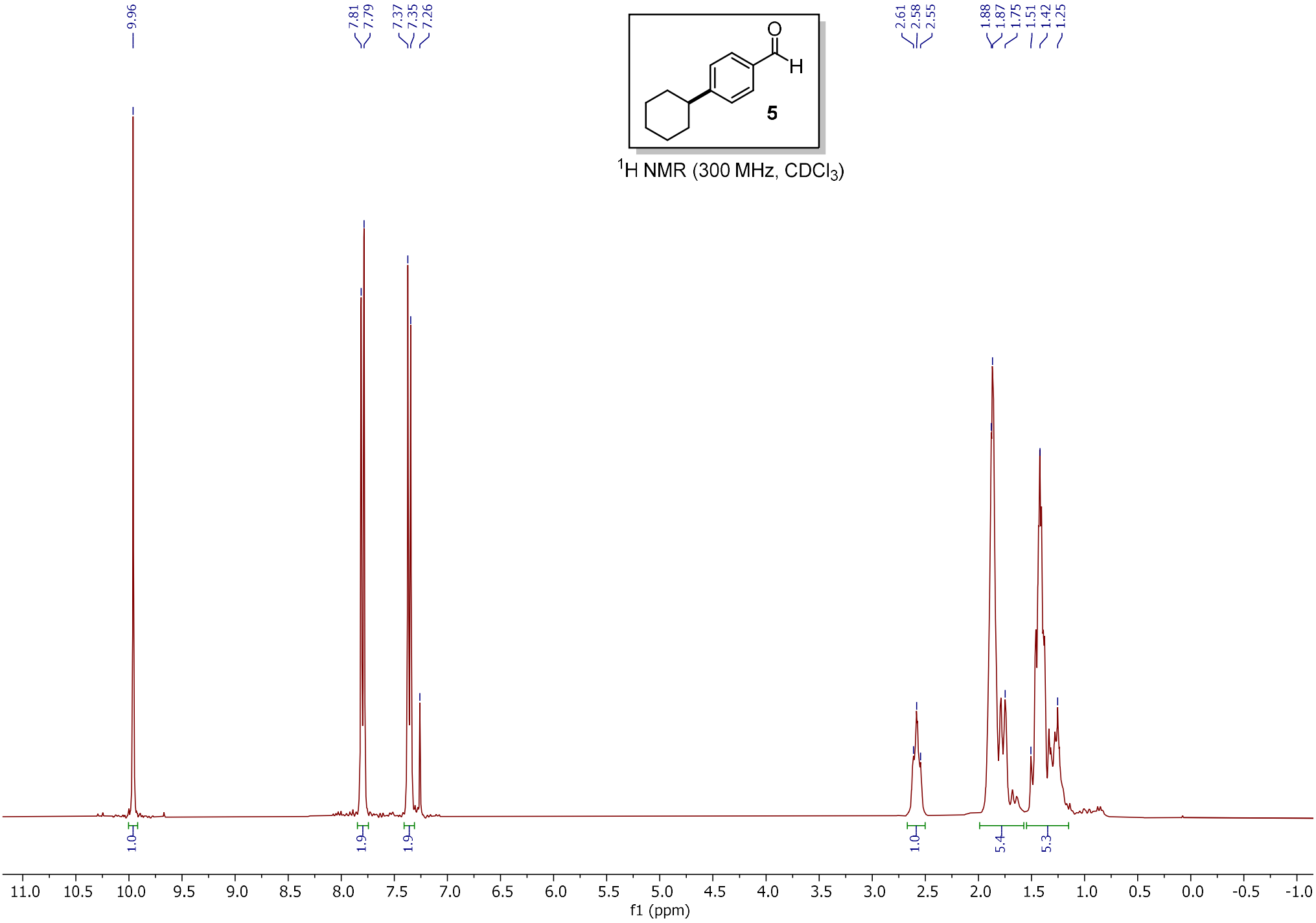


$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)

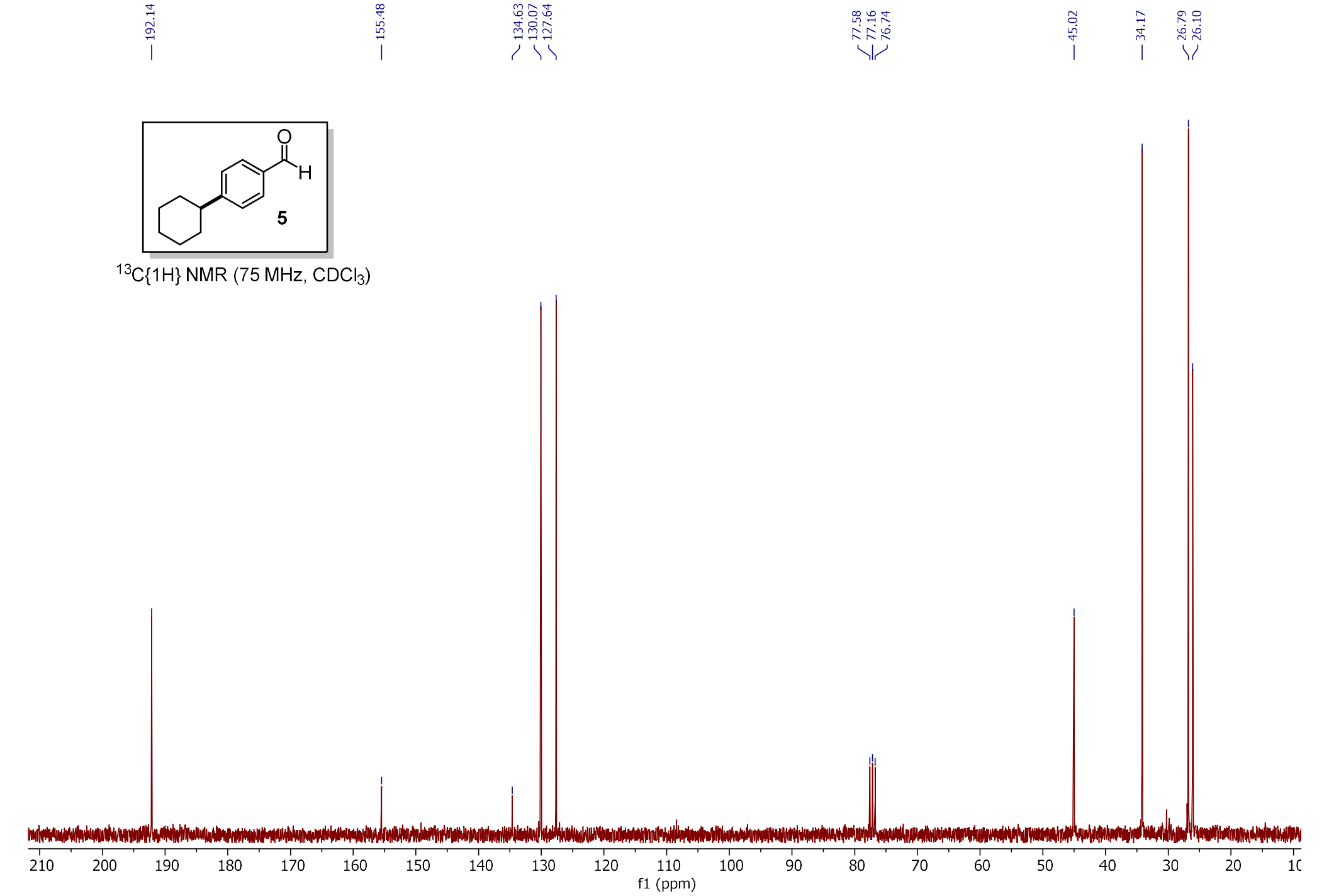


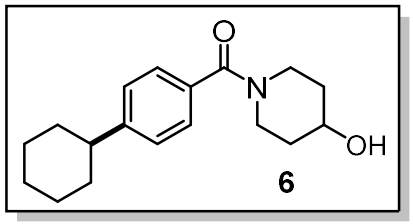
^{1}H NMR (300 MHz, $CDCl_3$)


167.31
153.58
129.80
127.84
126.98
77.58
77.16
76.74
52.05
44.80
34.25
26.85
26.16
O
OMe
4
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

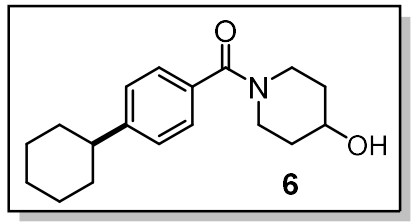


^{1}H NMR (300 MHz, $CDCl_3$)

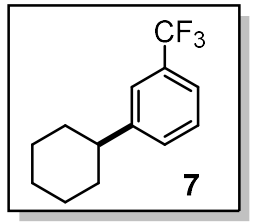

192.14
155.48
134.63
130.07
127.64
77.58
77.16
76.74
45.02
34.17
26.79
26.10
O
H
5
^{13}C{1H} NMR (75 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



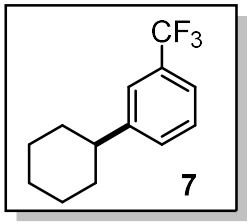
^{1}H NMR (300 MHz, $CDCl_3$)



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



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



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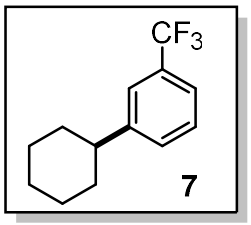

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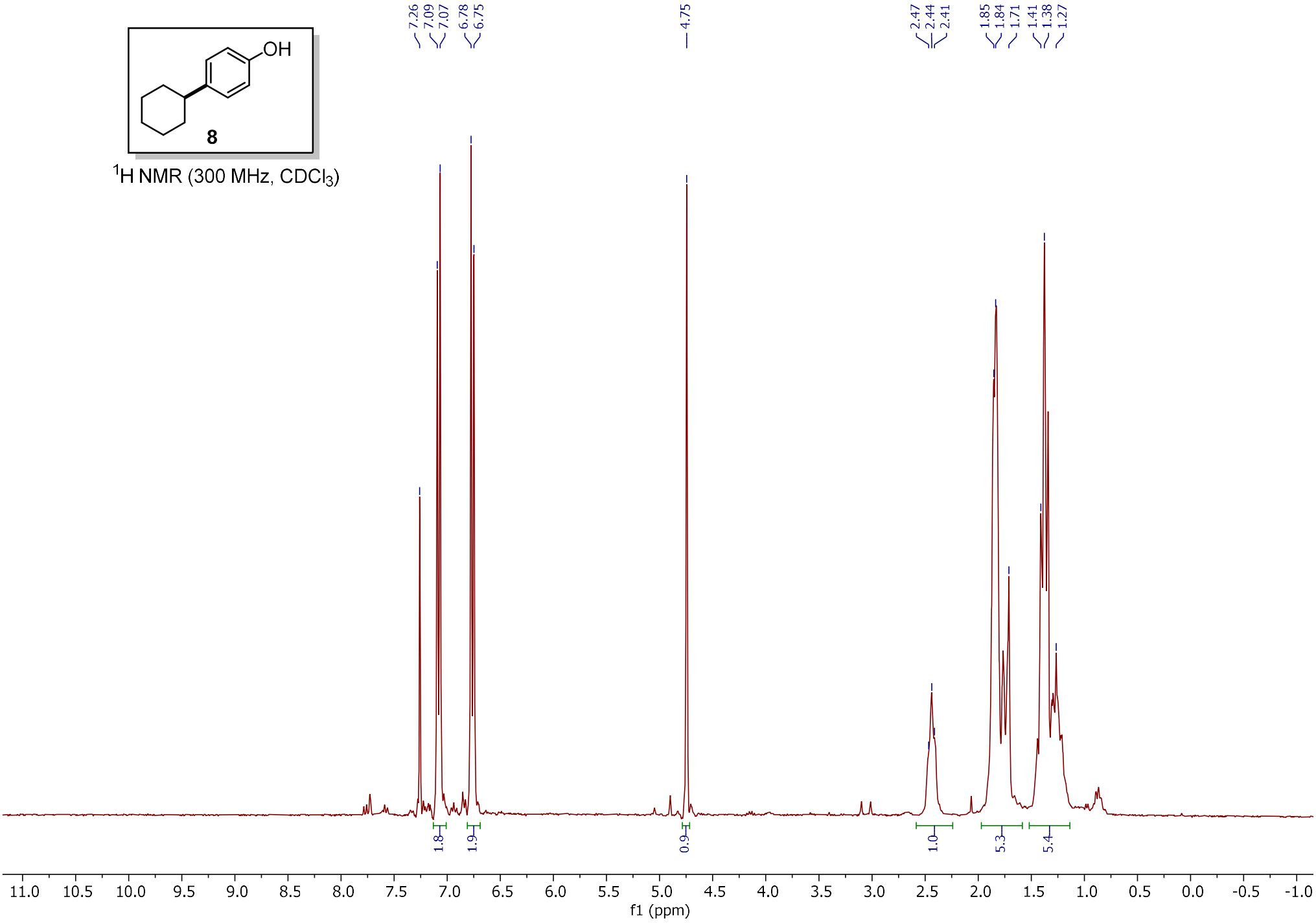
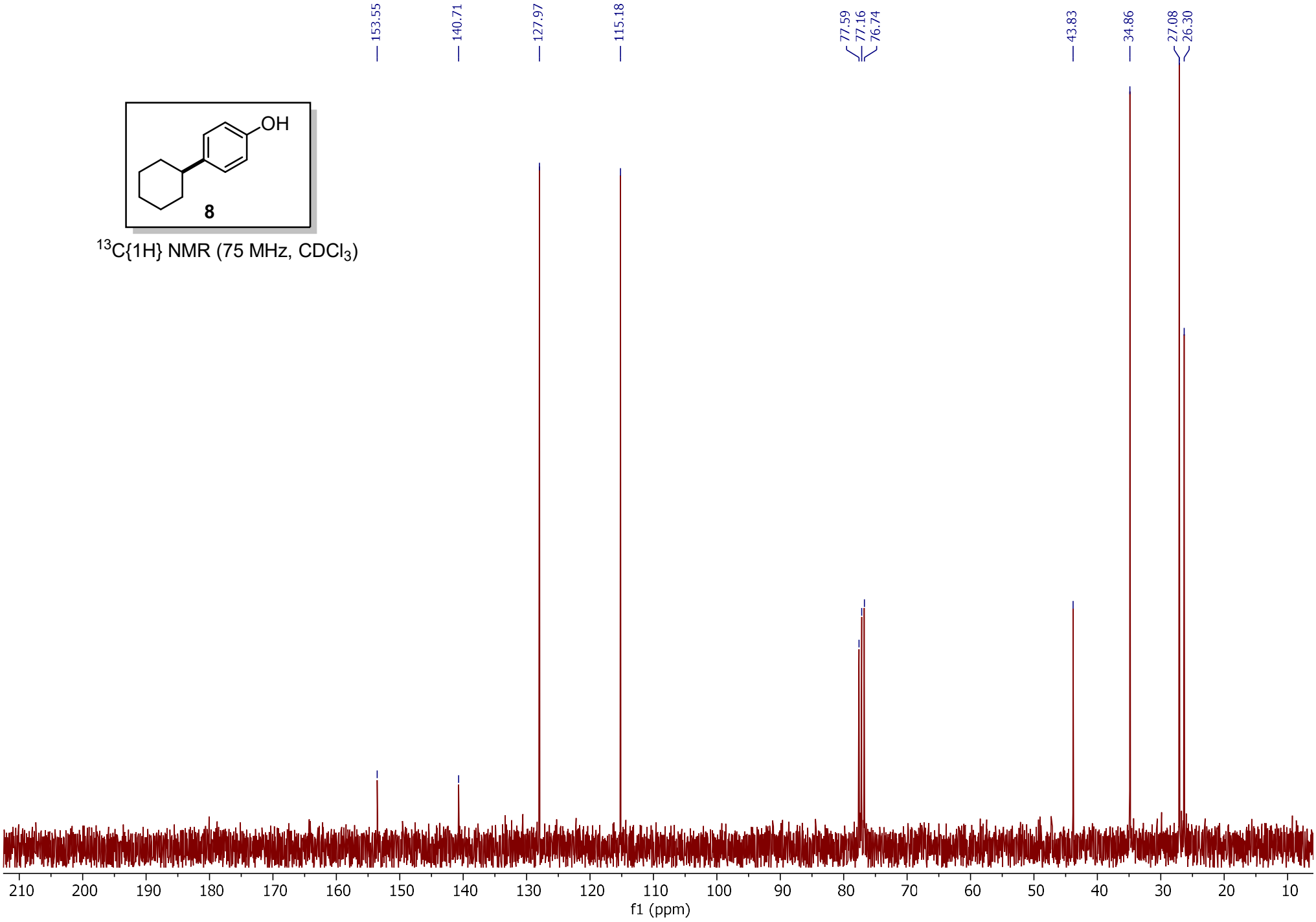
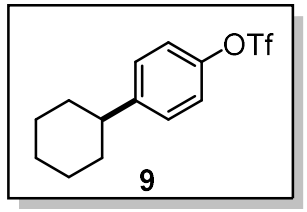
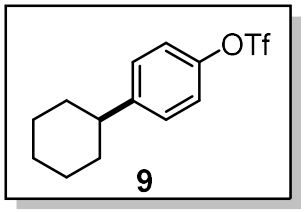

OH
8
^{1}H NMR (300 MHz, $CDCl_3$)
7.26
7.09
7.07
6.78
6.75
4.75
2.47
2.44
2.41
1.85
1.84
1.71
1.41
1.38
1.27
1.8
1.9
0.9
1.0
5.3
5.4
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


153.55
140.71
127.97
115.18
77.59
77.16
76.74
43.83
34.86
27.08
26.30
OH
8
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

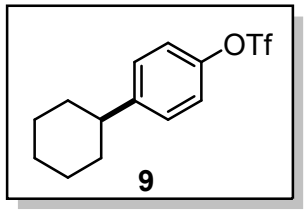


^{1}H NMR (300 MHz, $CDCl_3$)

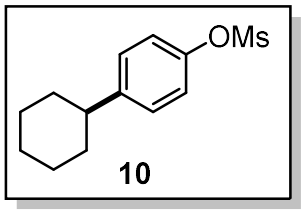


9

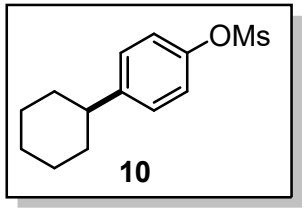
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



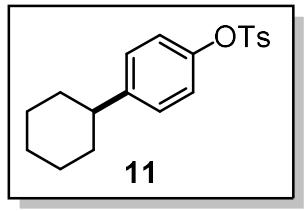
^{19}F NMR (282 MHz, $CDCl_3$)



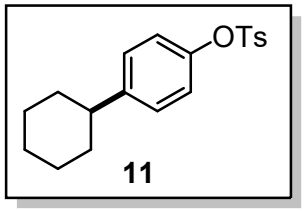
^{1}H NMR (300 MHz, $CDCl_3$)



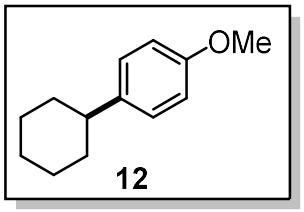
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



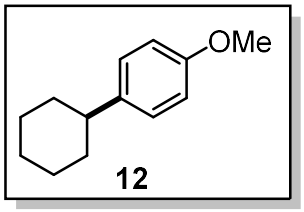
^{1}H NMR (300 MHz, $CDCl_3$)



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

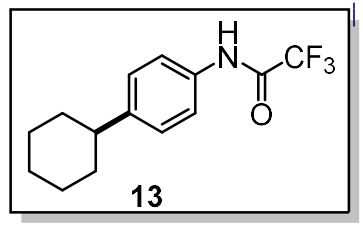


^{1}H NMR (300 MHz, $CDCl_3$)

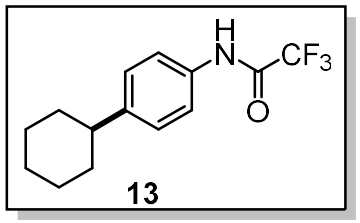


12

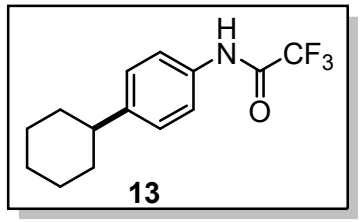
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



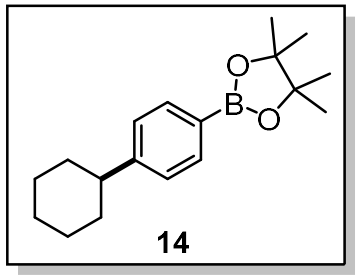
^{1}H NMR (300 MHz, $CDCl_3$)



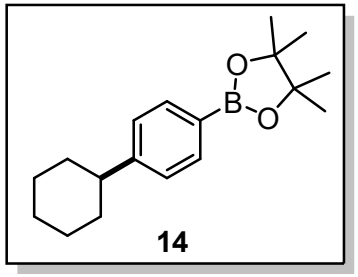
$^{13}C\{1H\}$ NMR (75 MHz, DMSO-d6)



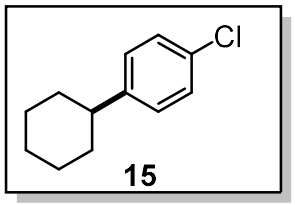
^{19}F NMR (282 MHz, $CDCl_3$)



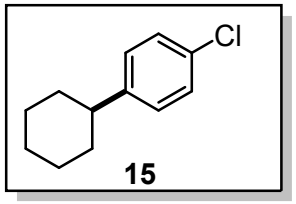
^{1}H NMR (300 MHz, $CDCl_3$)



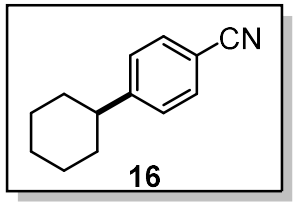
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



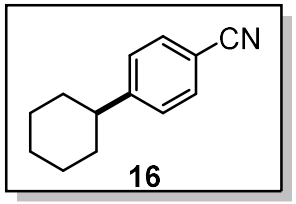
^{1}H NMR (300 MHz, $CDCl_3$)



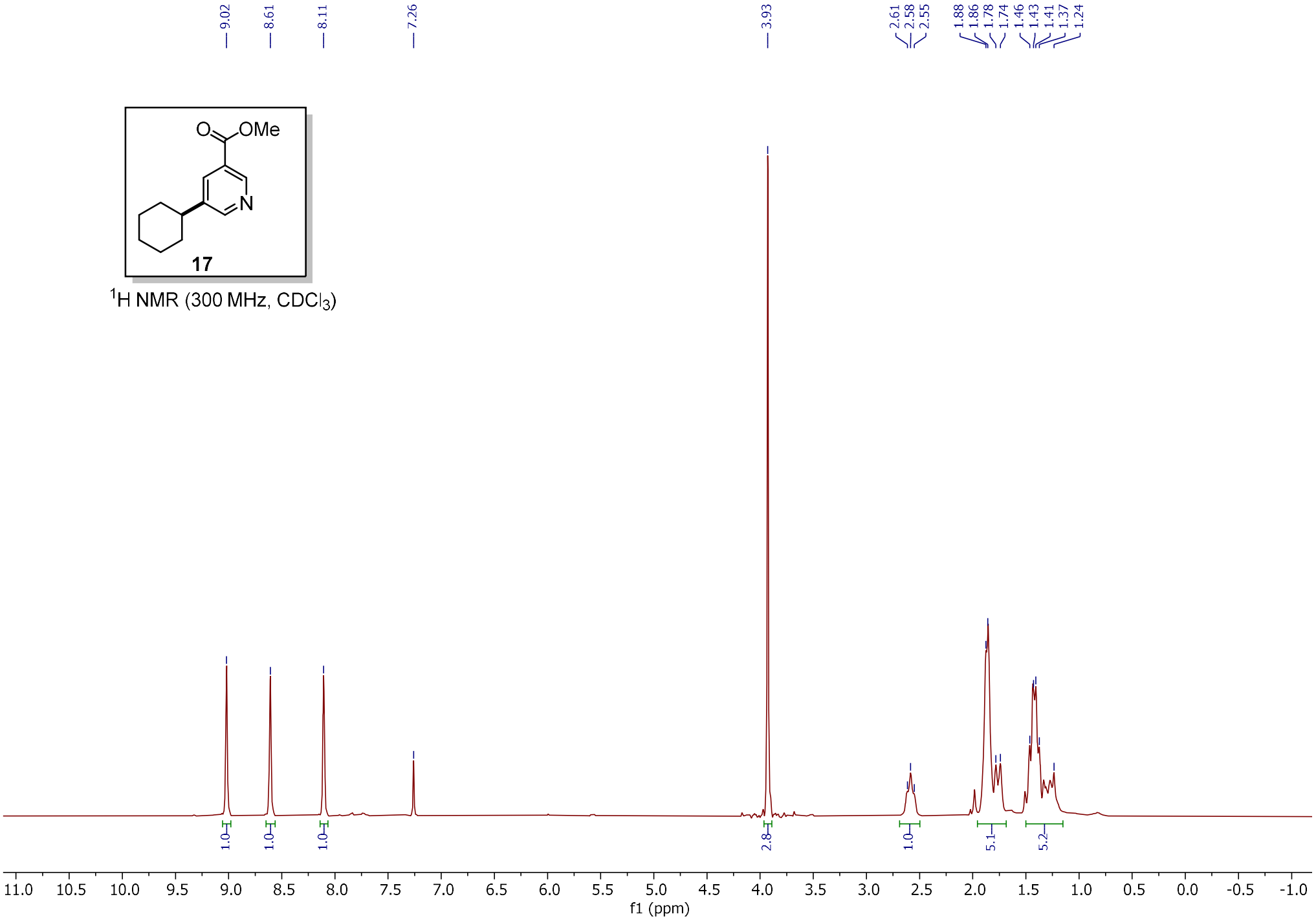
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



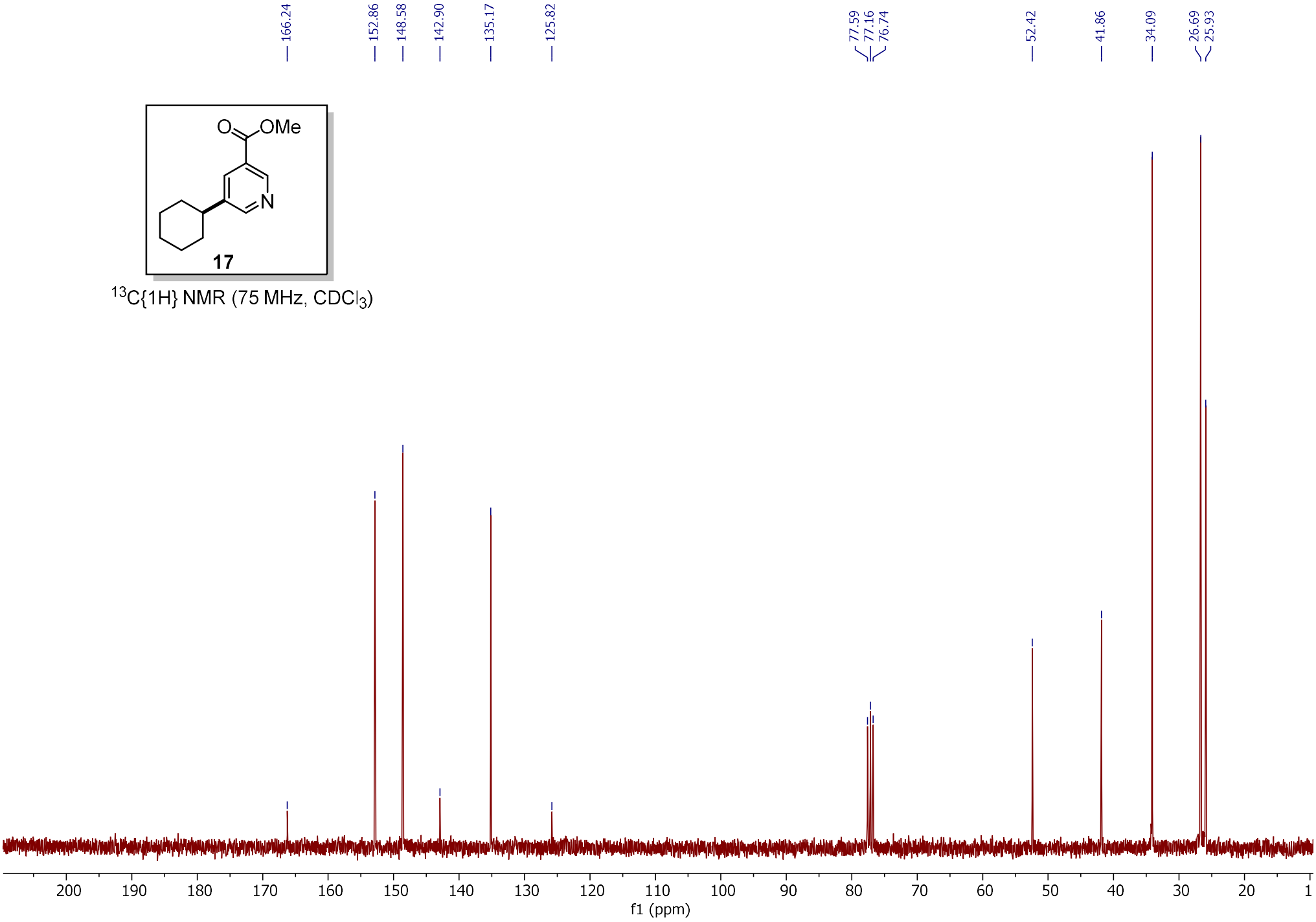
^{1}H NMR (300 MHz, $CDCl_3$)



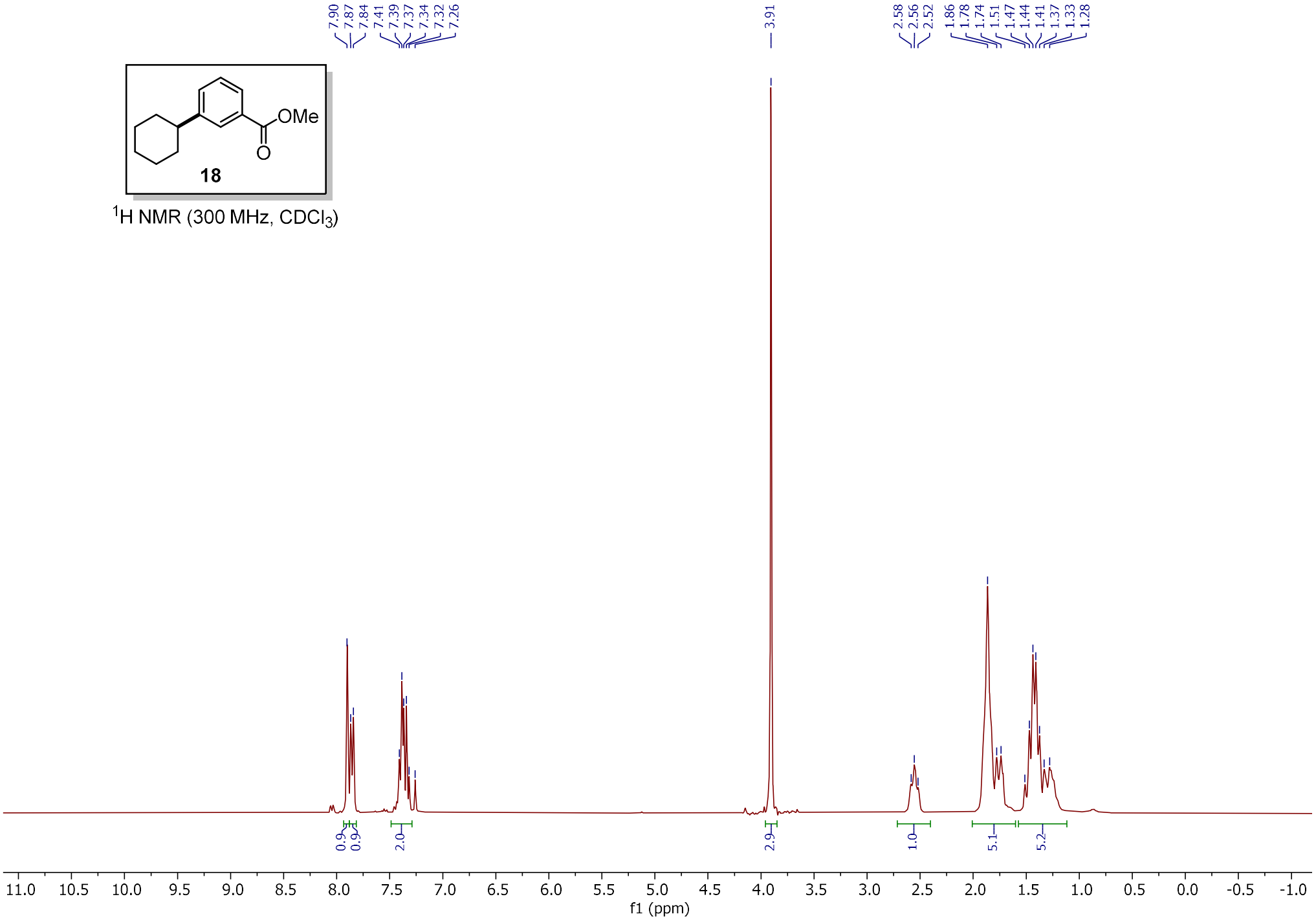
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



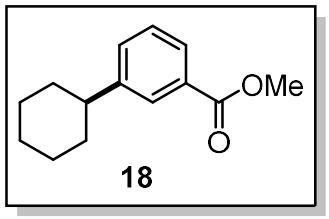
^{1}H NMR (300 MHz, $CDCl_3$)



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

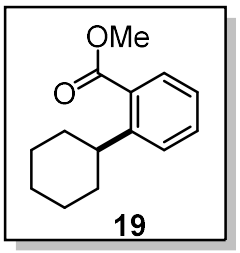


^{1}H NMR (300 MHz, $CDCl_3$)

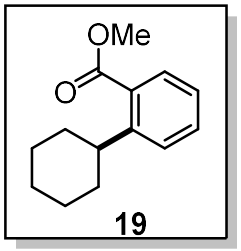


18

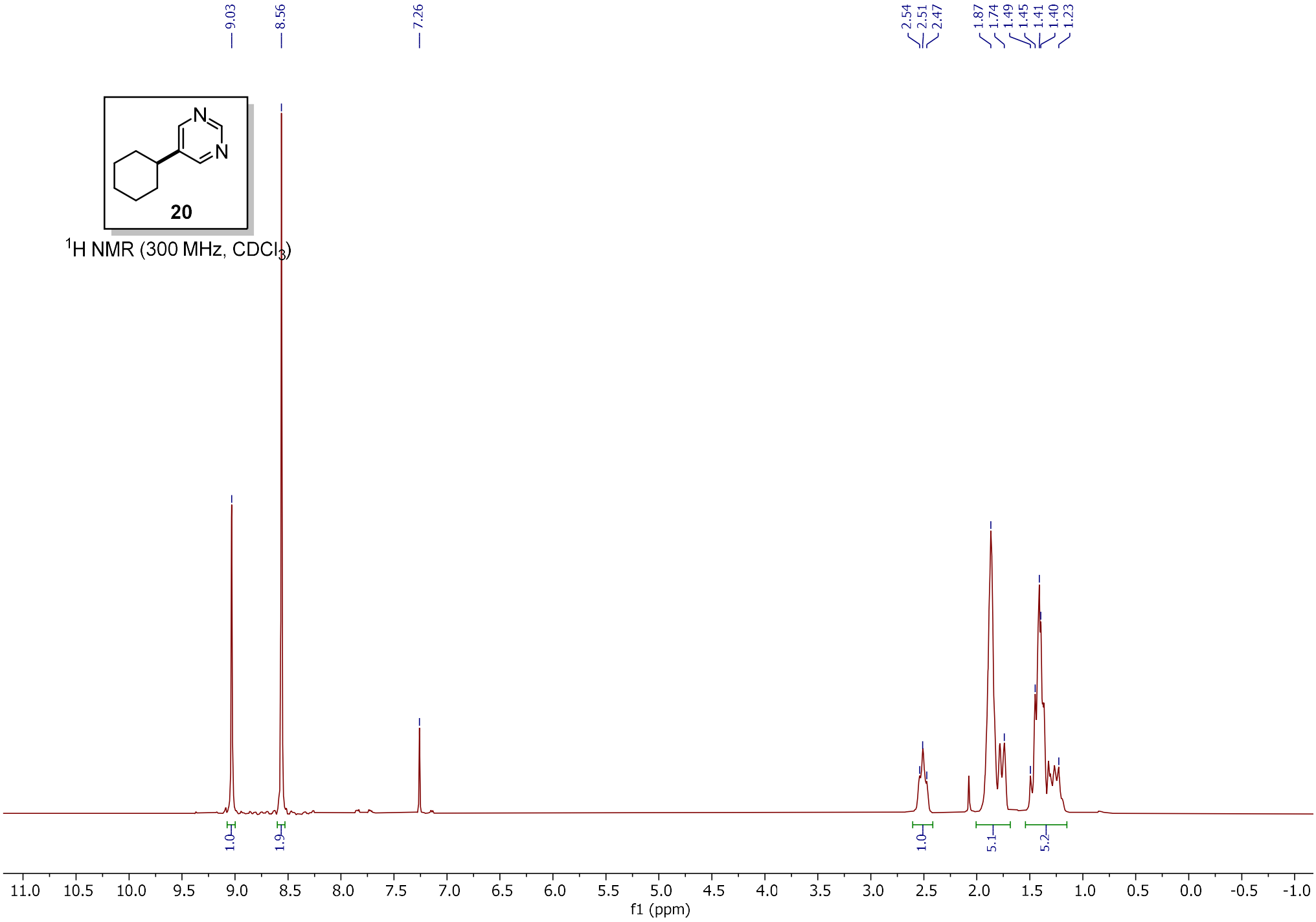
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)

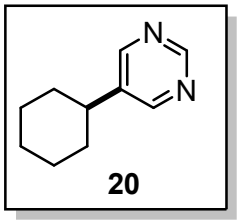


^{1}H NMR (300 MHz, $CDCl_3$)



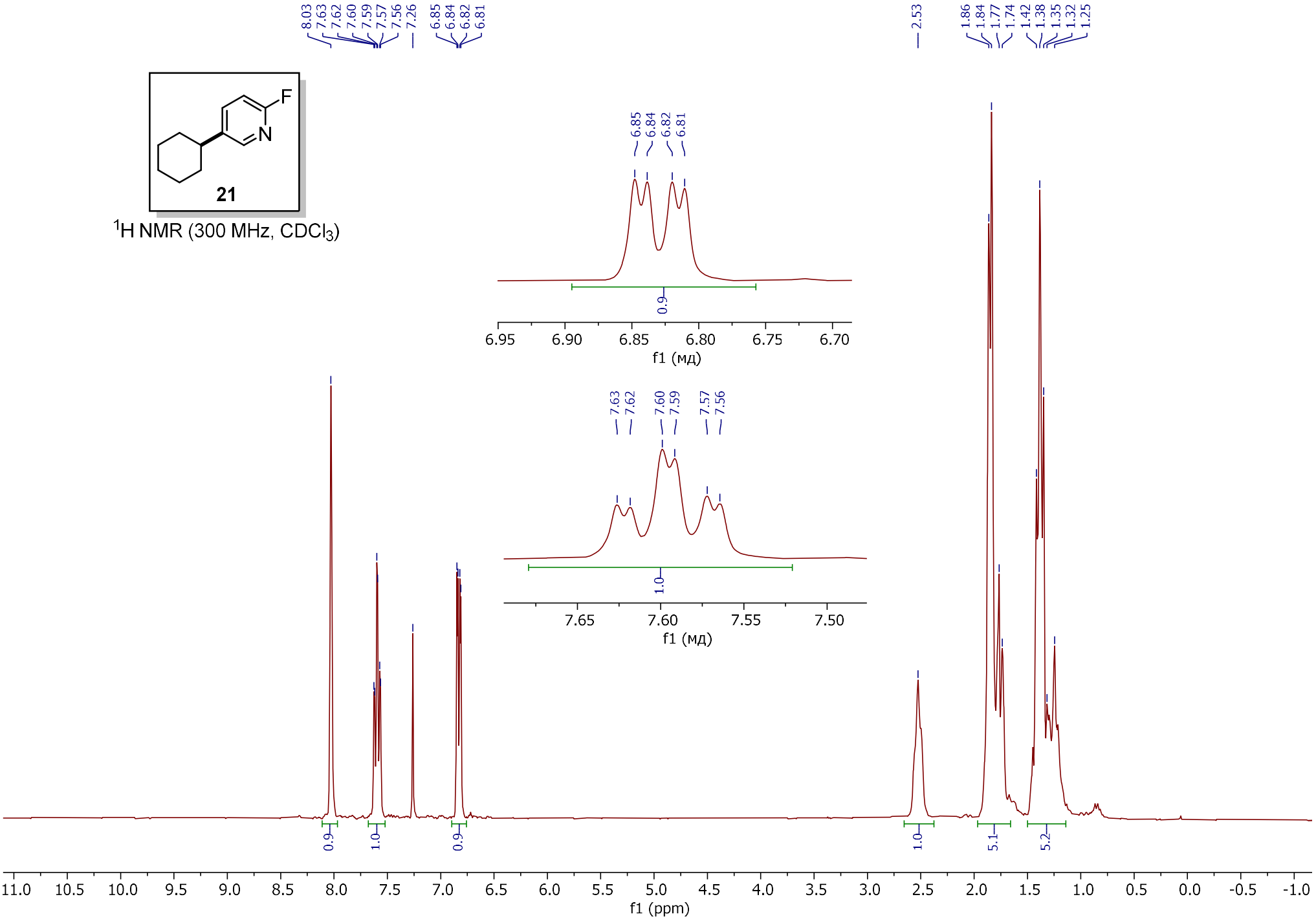
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)

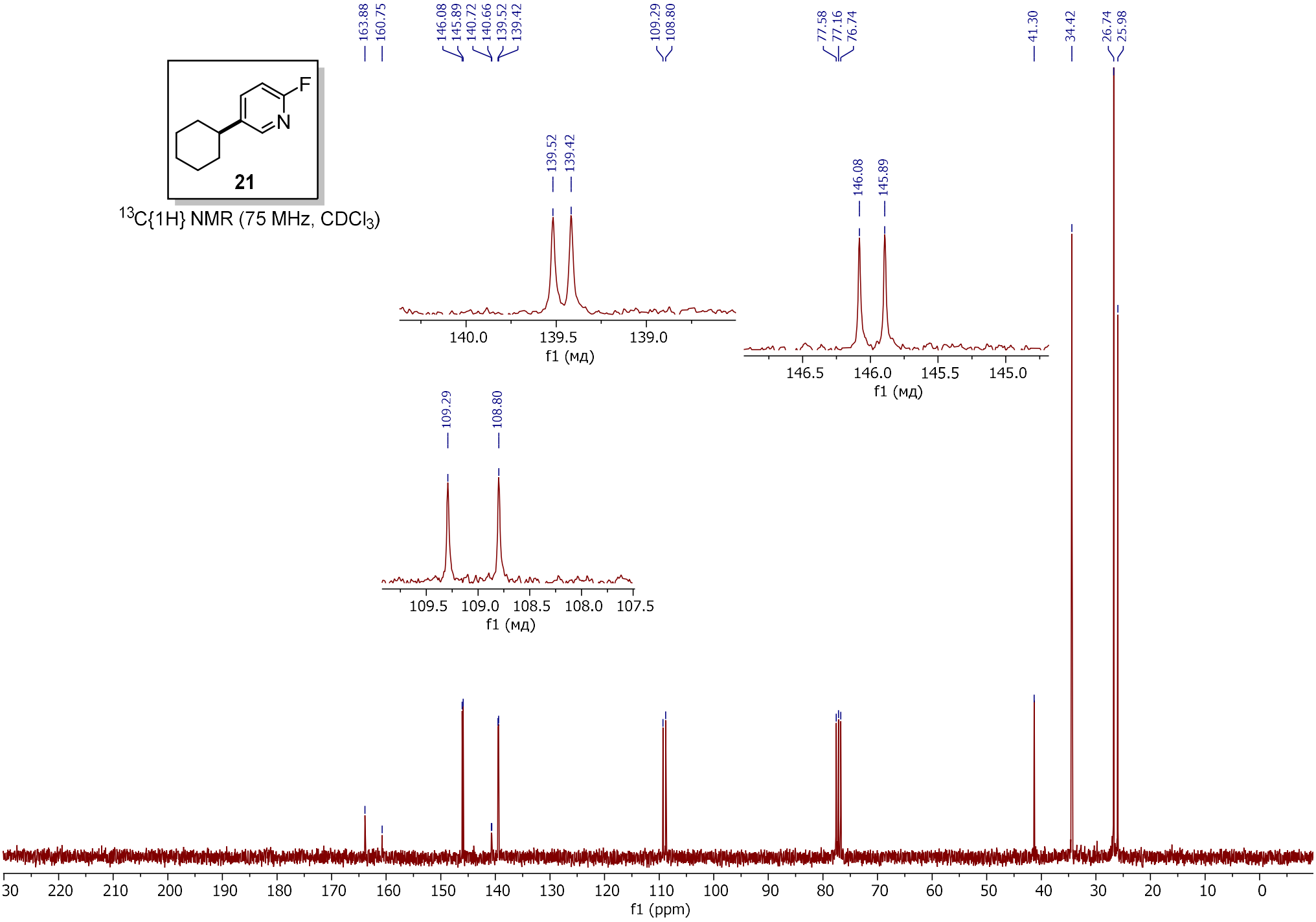

9.03
8.56
7.26
2.54
2.51
2.47
1.87
1.74
1.49
1.45
1.41
1.40
1.23
N
N
20
1H NMR (300 MHz, CDCl3)
1.0
1.9
1.0
5.1
5.2
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

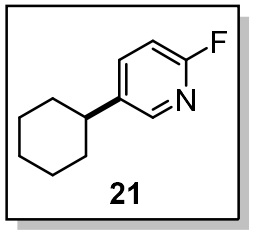


20

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

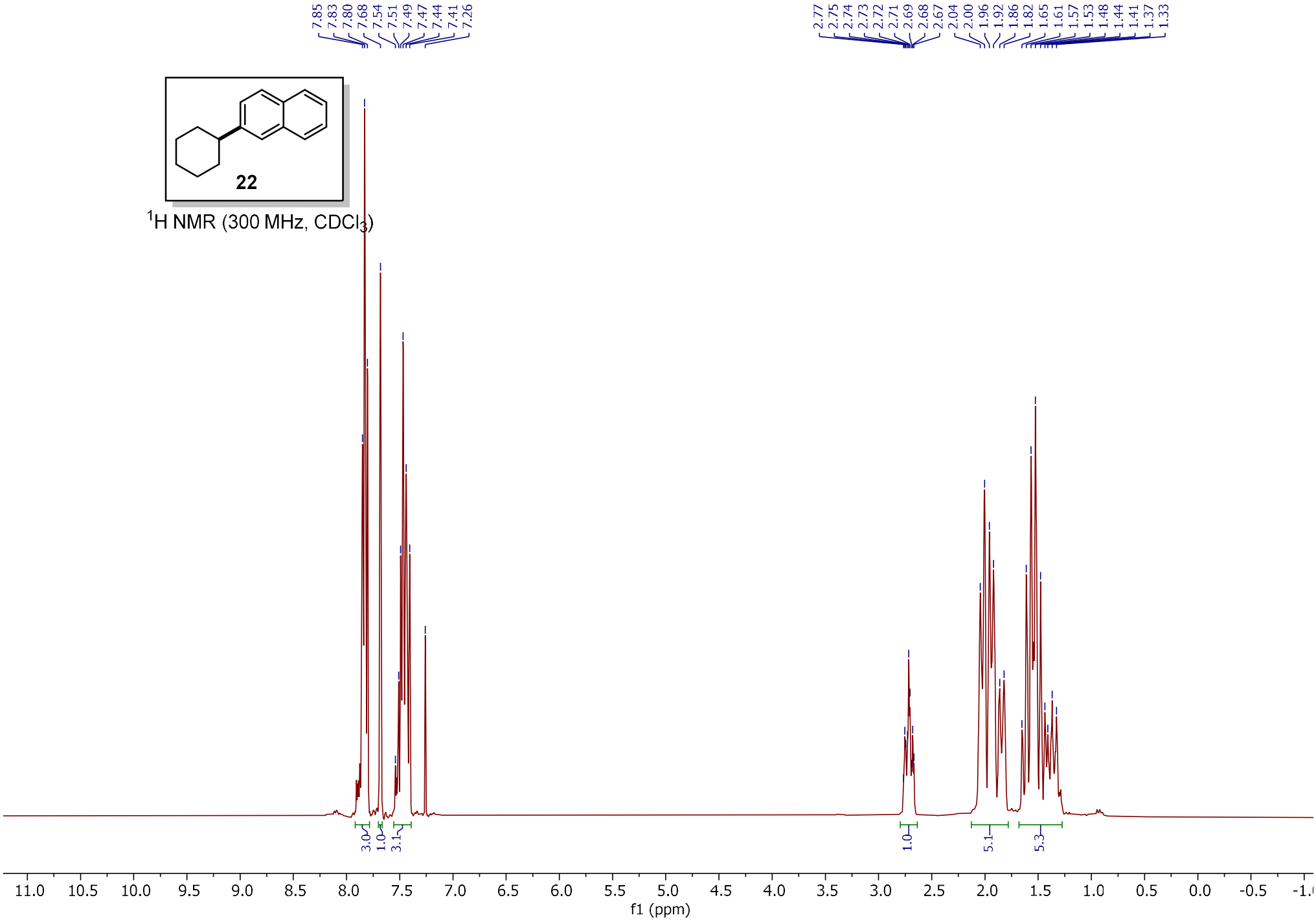

8.03
7.63
7.62
7.60
7.59
7.57
7.56
7.26
6.85
6.84
6.82
6.81
2.53
1.86
1.84
1.77
1.74
1.42
1.38
1.35
1.32
1.25
F
N
21
^{1}H NMR (300 MHz, $CDCl_3$)
6.85
6.84
6.82
6.81
0.9
6.95
6.90
6.85
6.80
6.75
6.70
f1 (мд)
7.63
7.62
7.60
7.59
7.57
7.56
1.0
7.65
7.60
7.55
7.50
f1 (мд)
0.9
1.0
0.9
1.0
5.1
5.2
11.0
10.5
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
f1 (ppm)

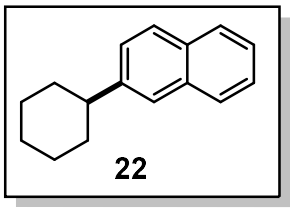

F
N
21
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)
163.88
160.75
146.08
145.89
140.72
140.66
139.52
139.42
109.29
108.80
77.58
77.16
76.74
41.30
34.42
26.74
25.98
f1 (ppm)
f1 (мд)



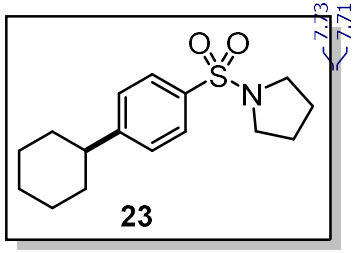
21

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

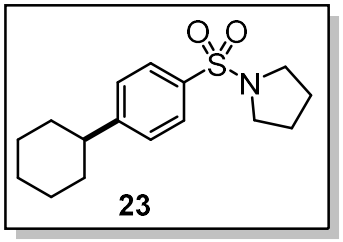

7.85
7.83
7.80
7.68
7.54
7.51
7.49
7.47
7.44
7.41
7.26
2.77
2.75
2.74
2.73
2.72
2.71
2.69
2.68
2.67
2.04
2.00
1.96
1.92
1.86
1.82
1.65
1.61
1.57
1.53
1.48
1.44
1.41
1.37
1.33
22
1H NMR (300 MHz, CDCl3)
3.0
1.0
3.1
1.0
5.1
5.3
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



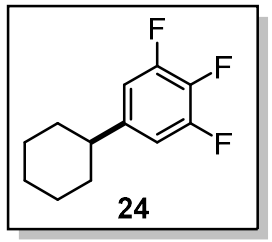
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



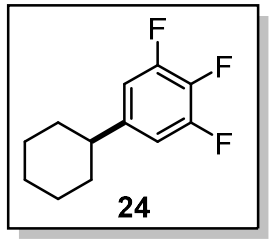
^{1}H NMR (300 MHz, $CDCl_3$)



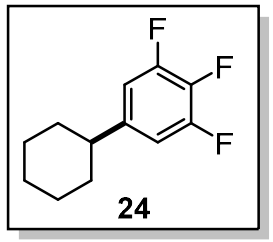
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



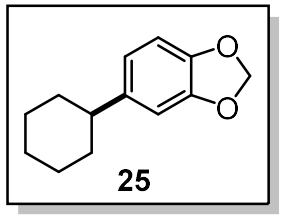
^{1}H NMR (300 MHz, $CDCl_3$)



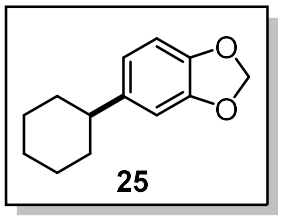
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



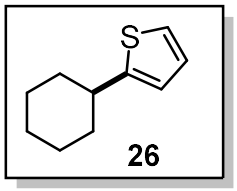
^{19}F NMR (282 MHz, $CDCl_3$)



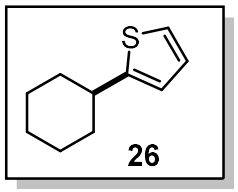
^{1}H NMR (300 MHz, $CDCl_3$)



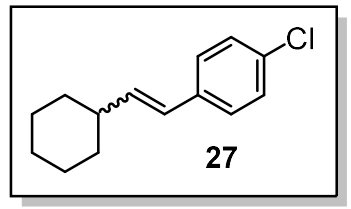
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



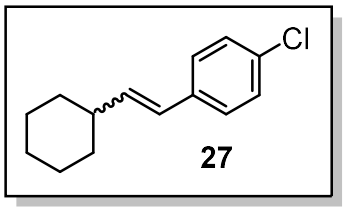
^{1}H NMR (300 MHz, $CDCl_3$)



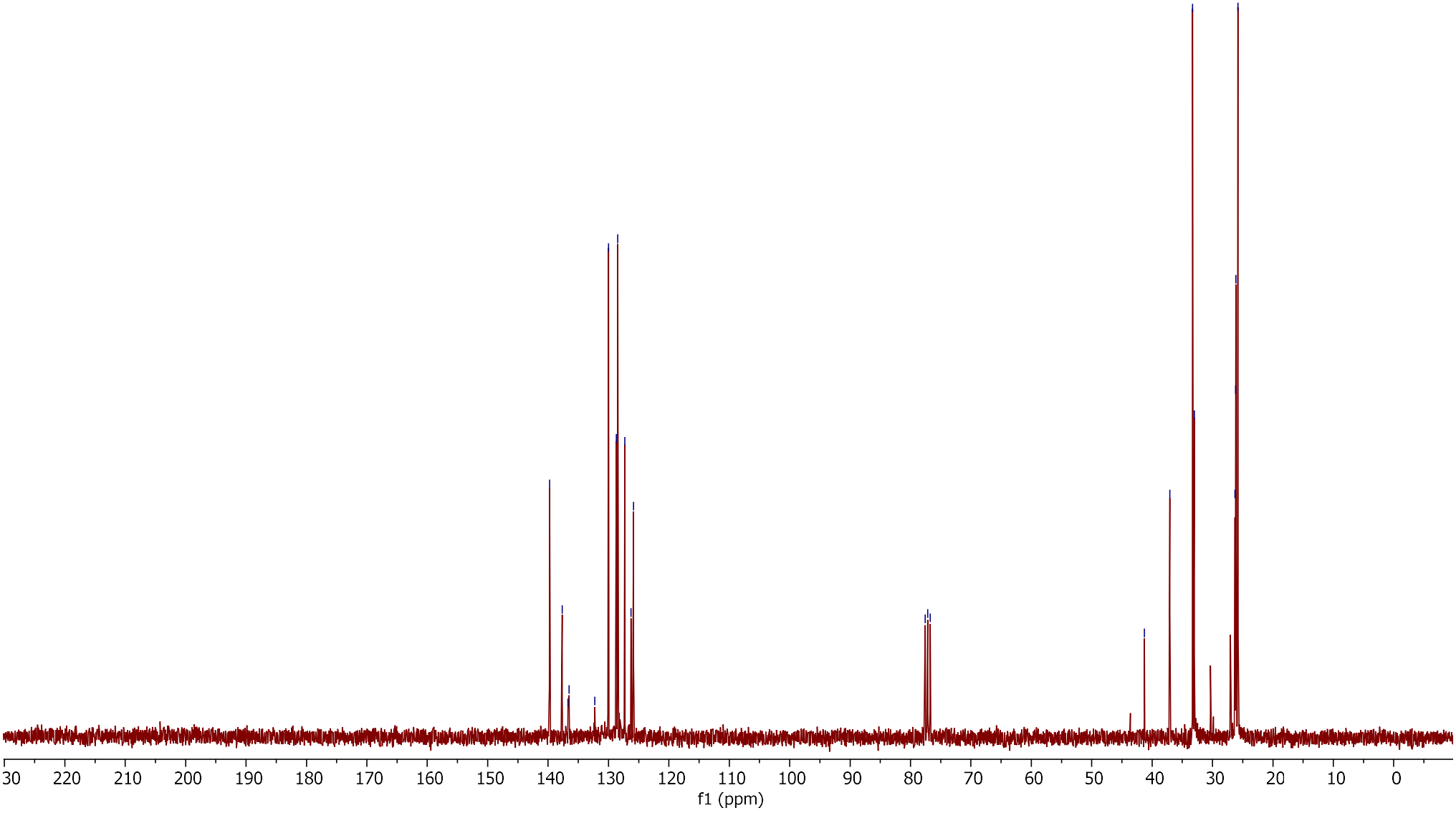
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)

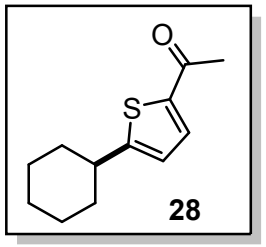


^{1}H NMR (300 MHz, $CDCl_3$)

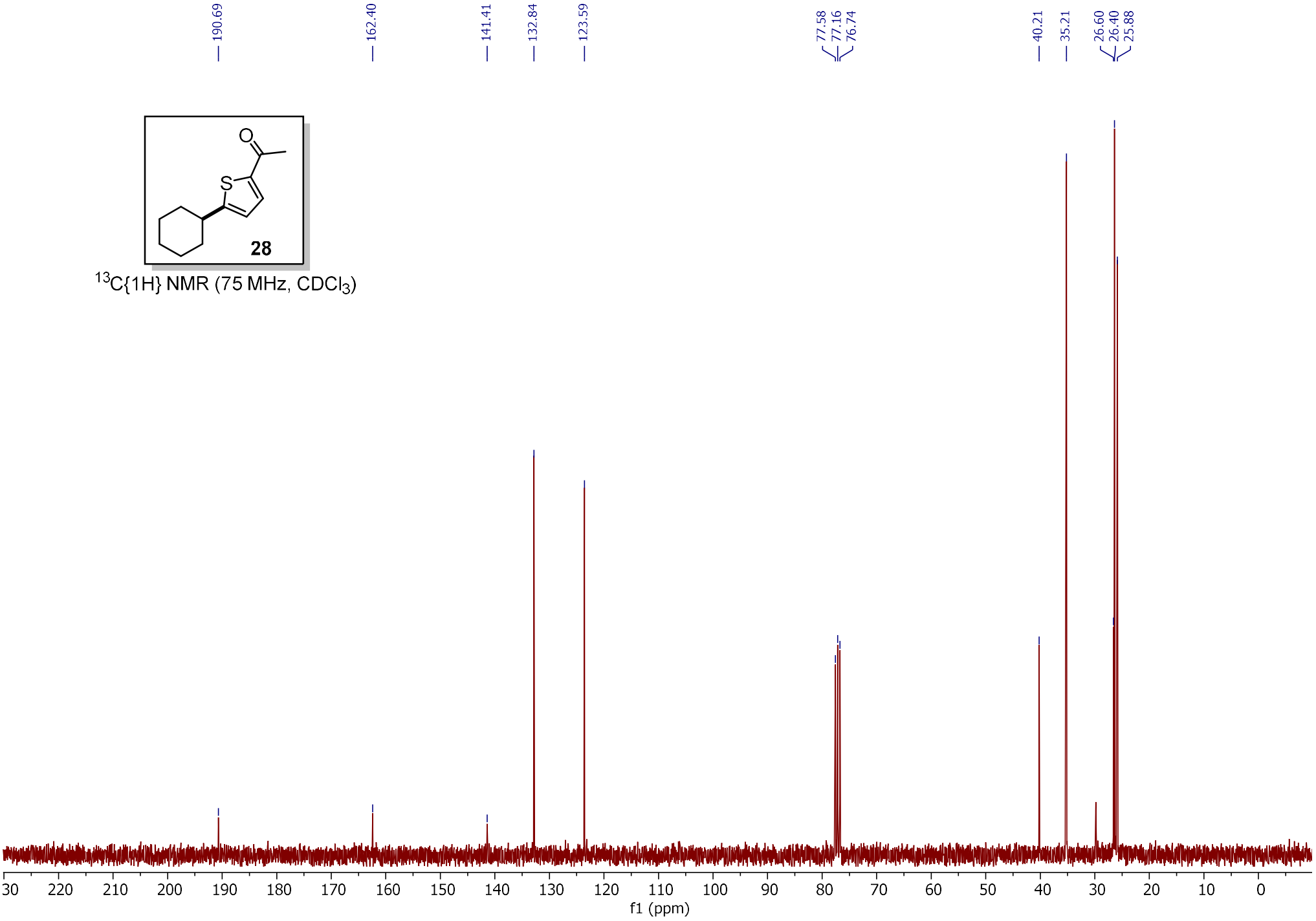


$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)

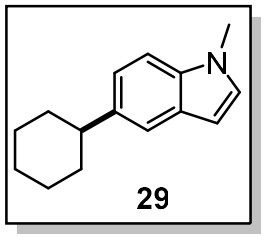




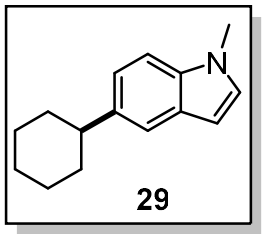
^{1}H NMR (300 MHz, $CDCl_3$)



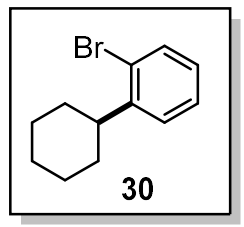
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



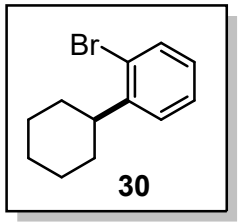
^{1}H NMR (300 MHz, $CDCl_3$)



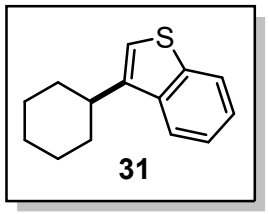
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



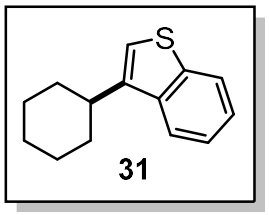
^{1}H NMR (300 MHz, $CDCl_3$)



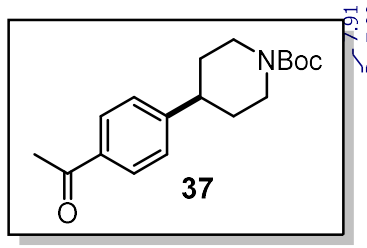
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



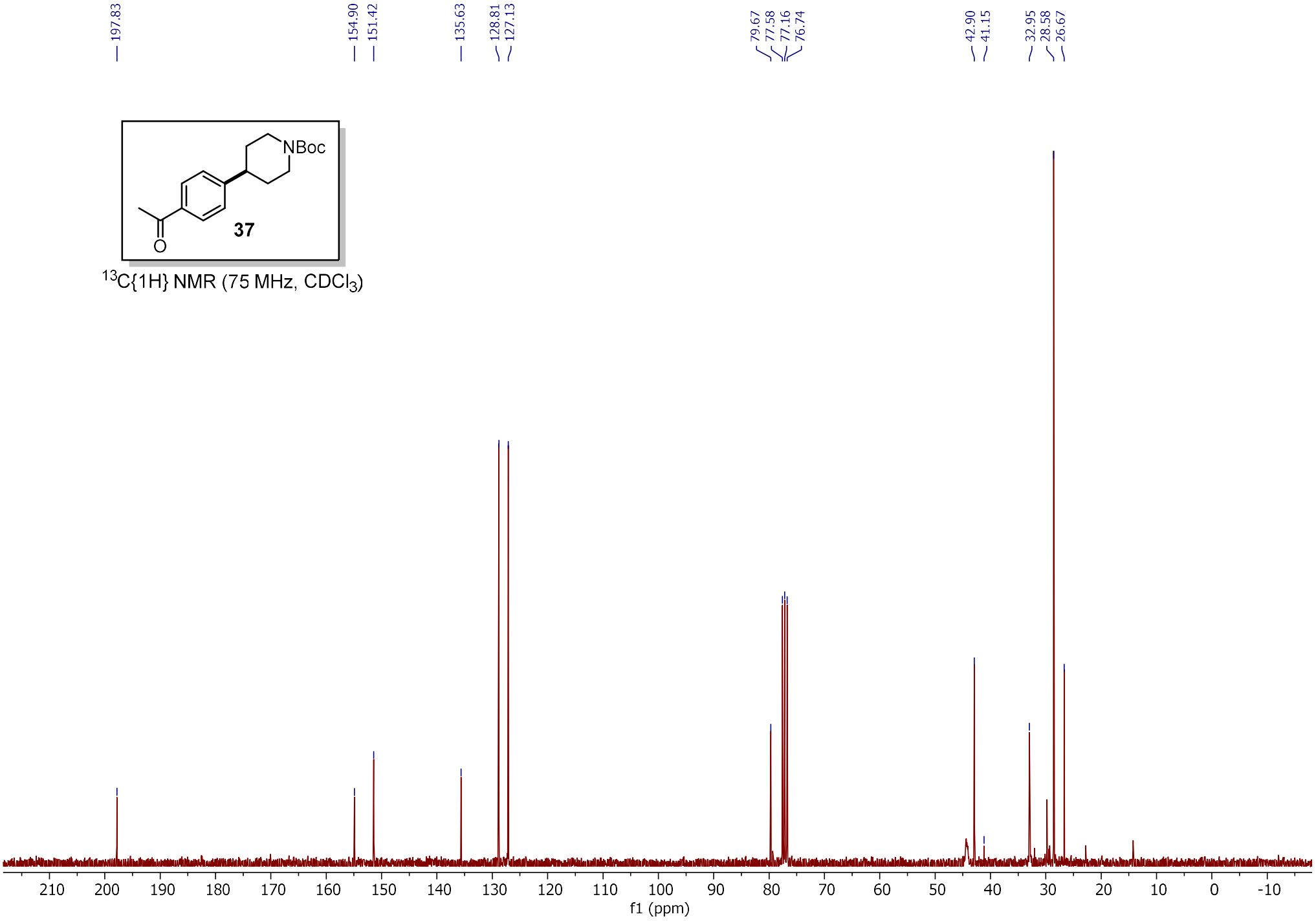
^{1}H NMR (300 MHz, $CDCl_3$)



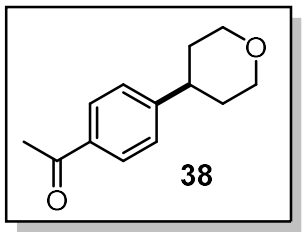
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



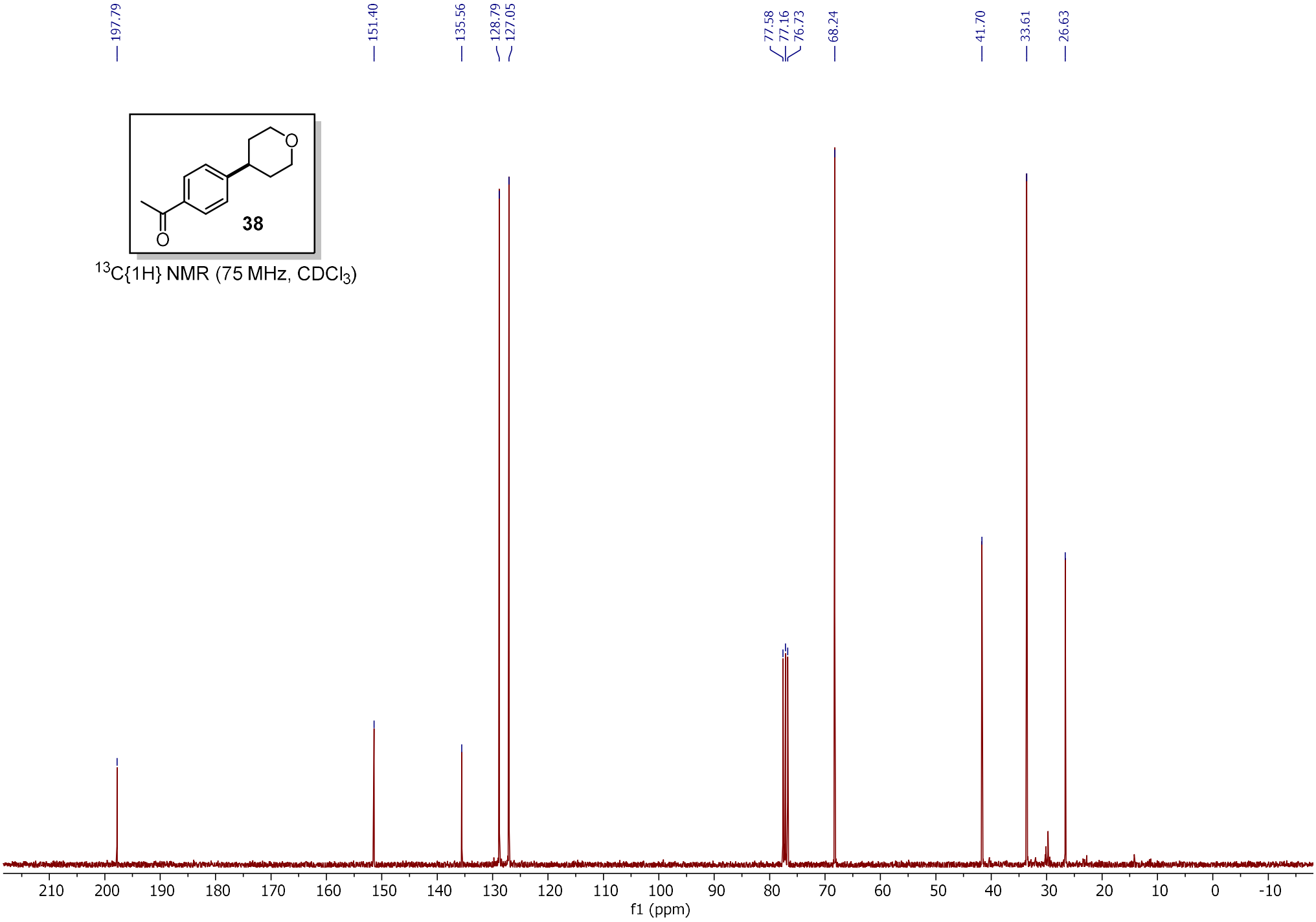
^{1}H NMR (300 MHz, $CDCl_3$)

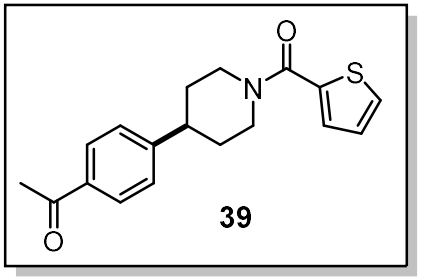


$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)

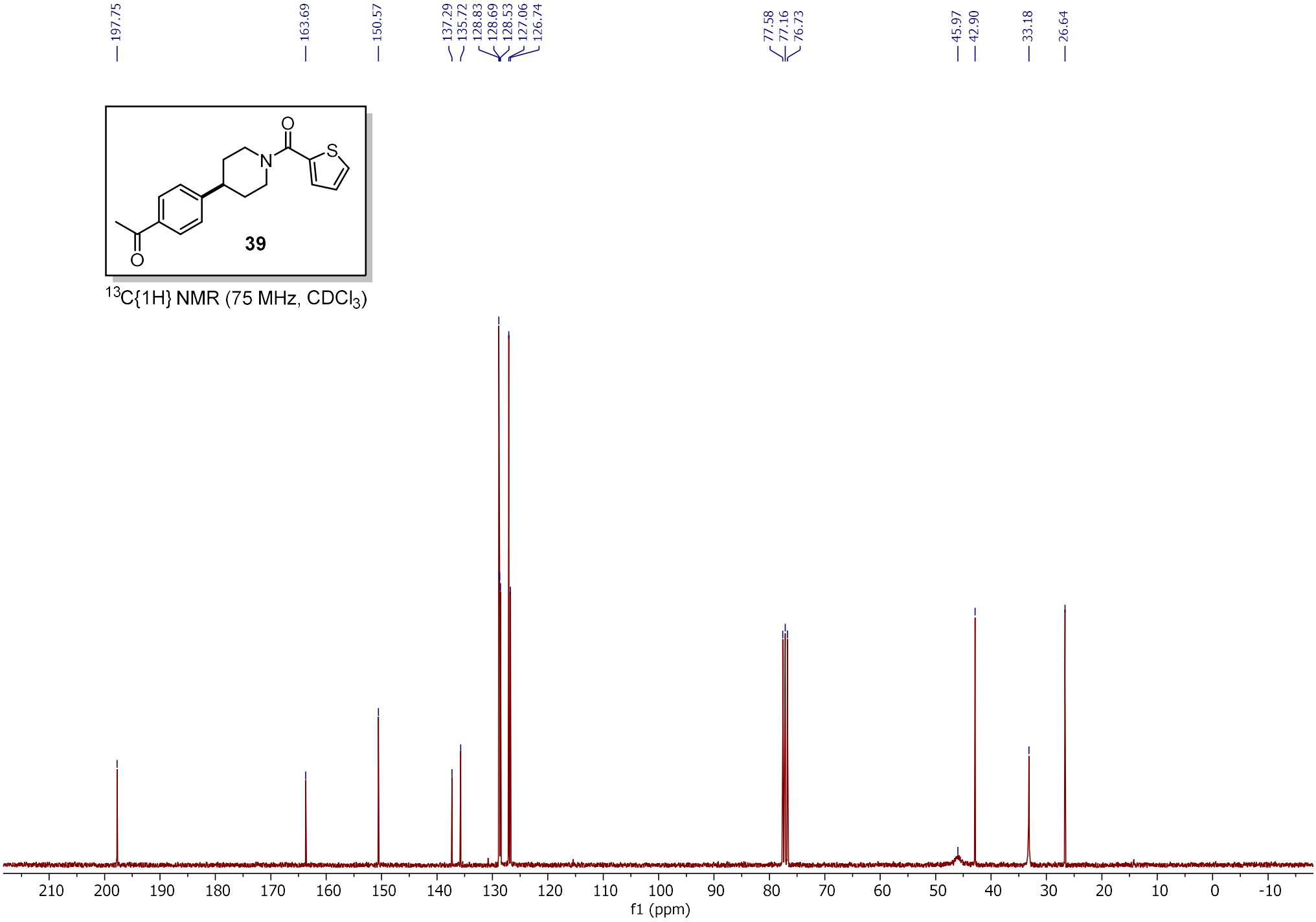


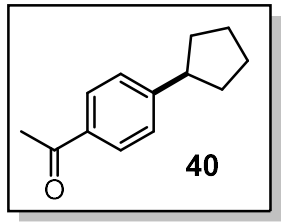
^{1}H NMR (300 MHz, $CDCl_3$)


197.79
151.40
135.56
128.79
127.05
77.58
77.16
76.73
68.24
41.70
33.61
26.63
38
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

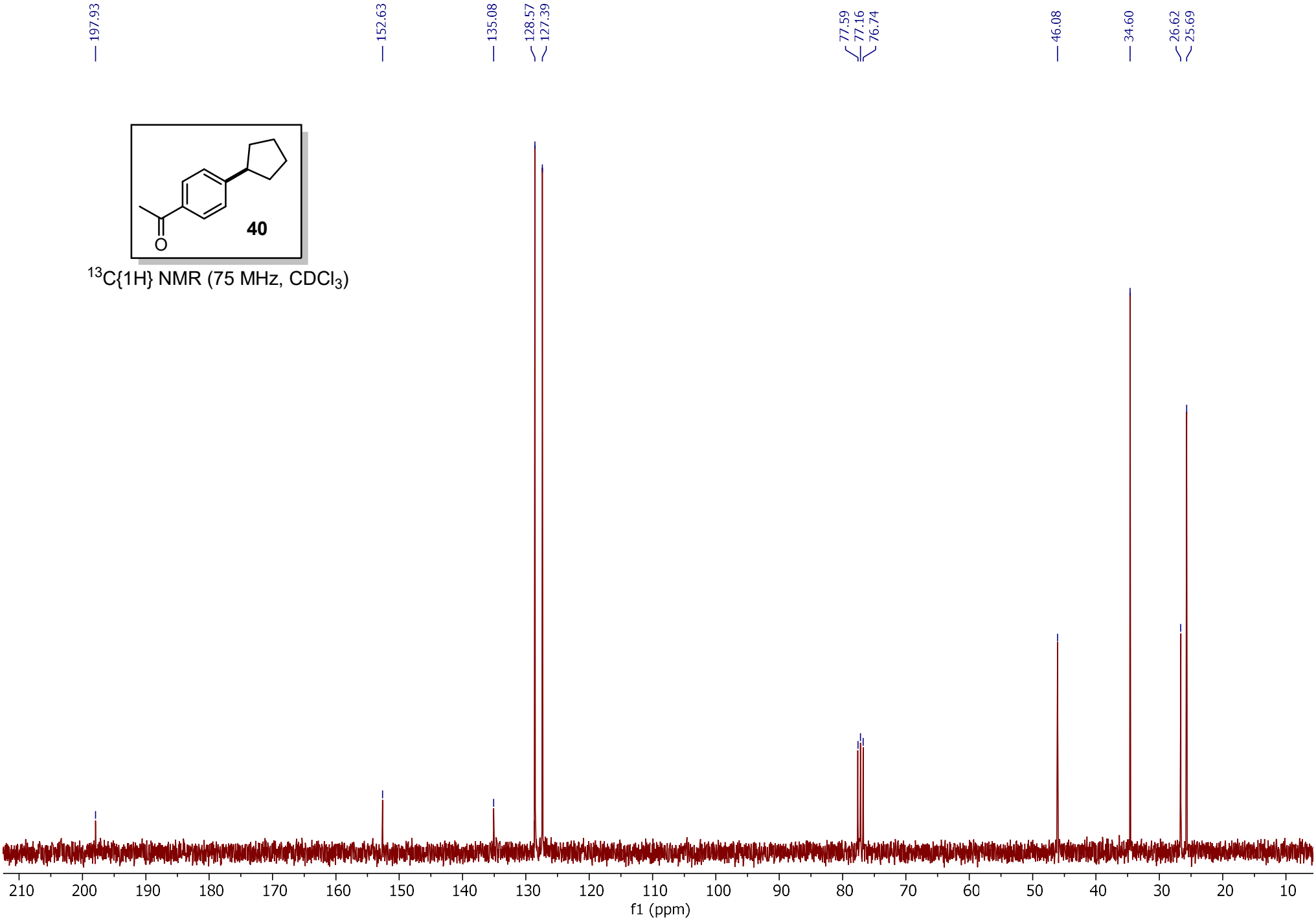


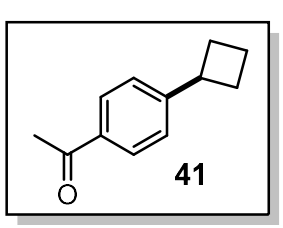
^{1}H NMR (300 MHz, $CDCl_3$)


197.75
163.69
150.57
137.29
135.72
128.83
128.69
128.53
127.06
126.74
77.58
77.16
76.73
45.97
42.90
33.18
26.64
O
N
S
O
39
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
f1 (ppm)

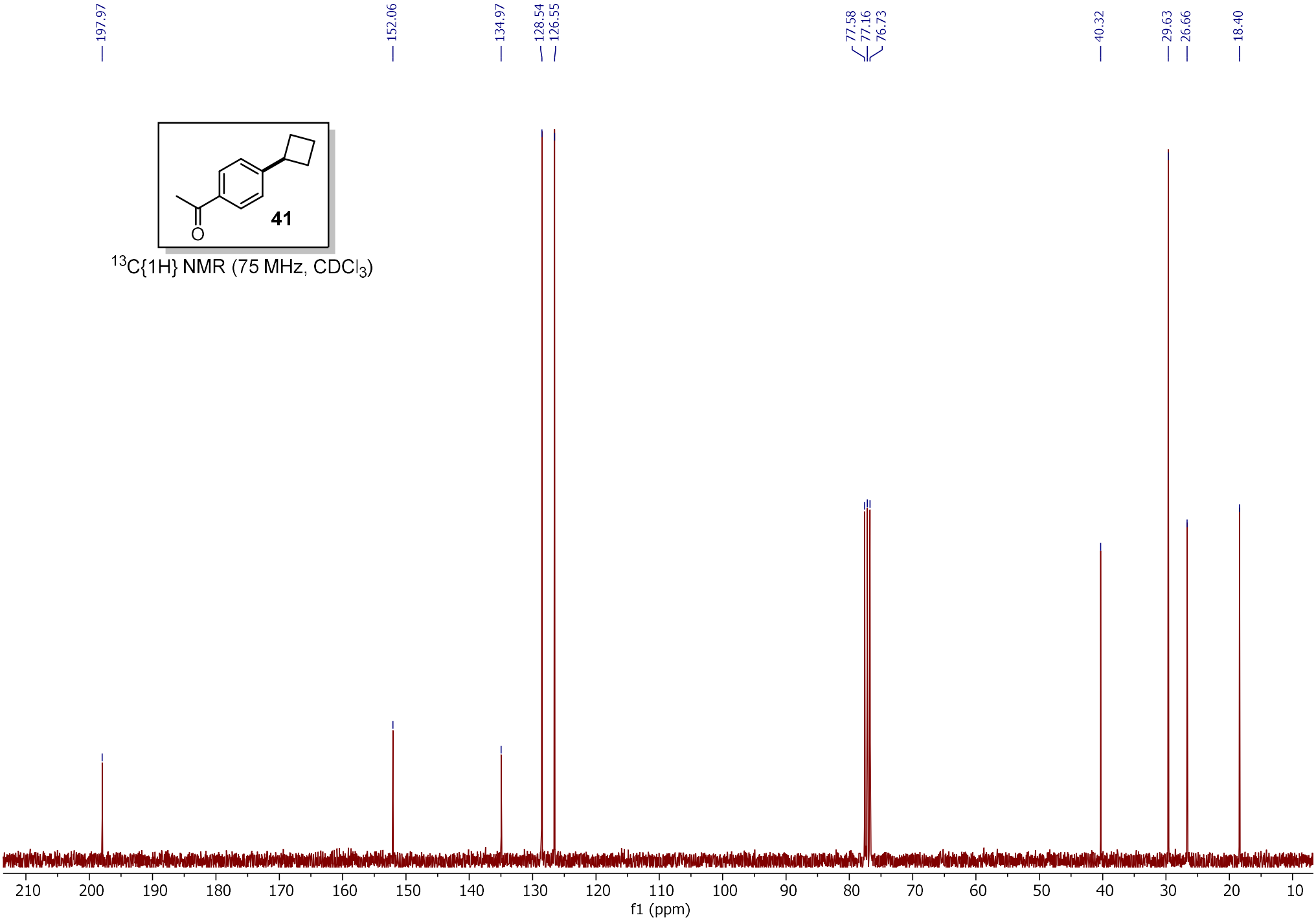


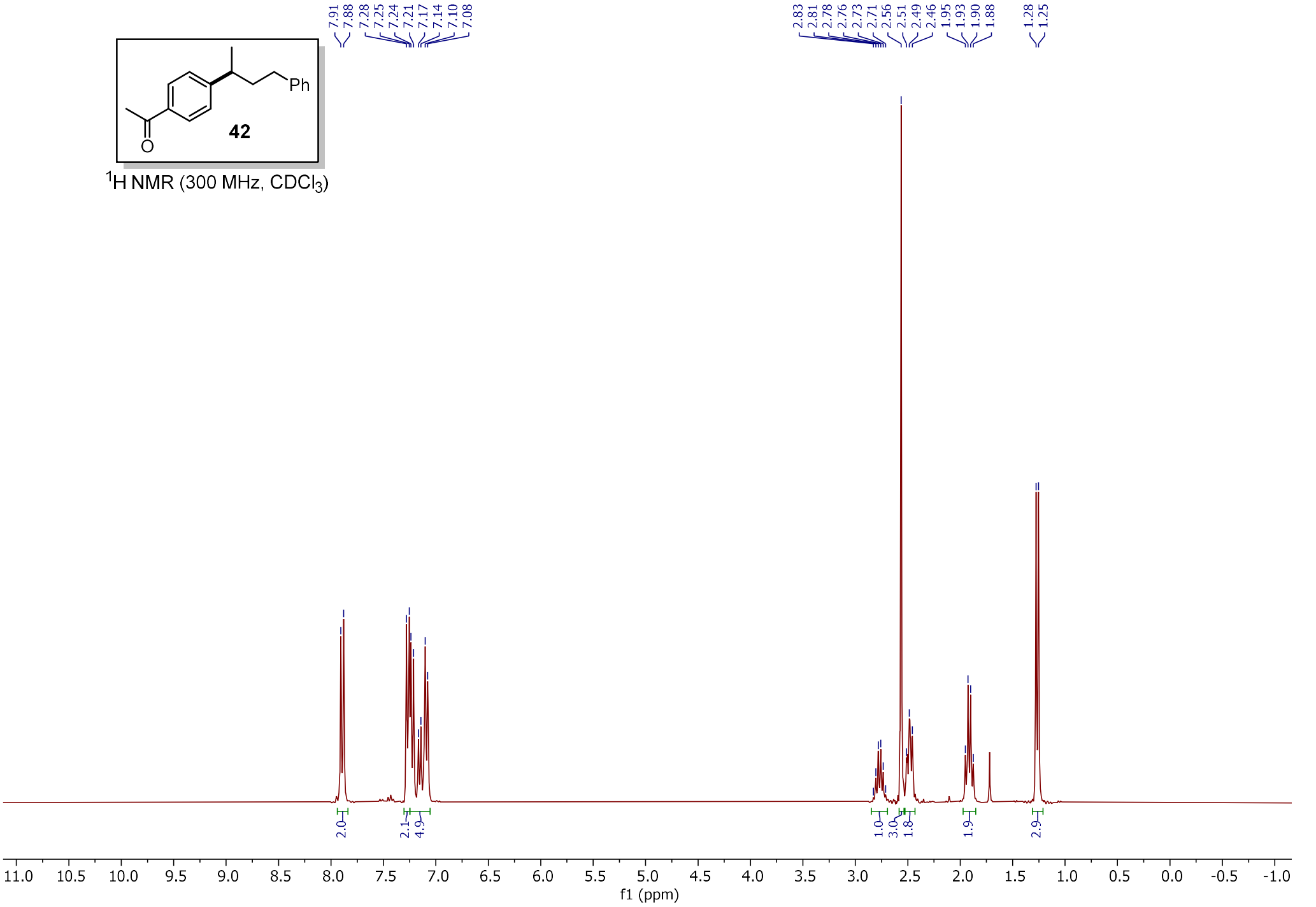
^{1}H NMR (300 MHz, $CDCl_3$)


197.93
152.63
135.08
128.57
127.39
77.59
77.16
76.74
46.08
34.60
26.62
25.69
O
40
^{13}C{1H} NMR (75 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

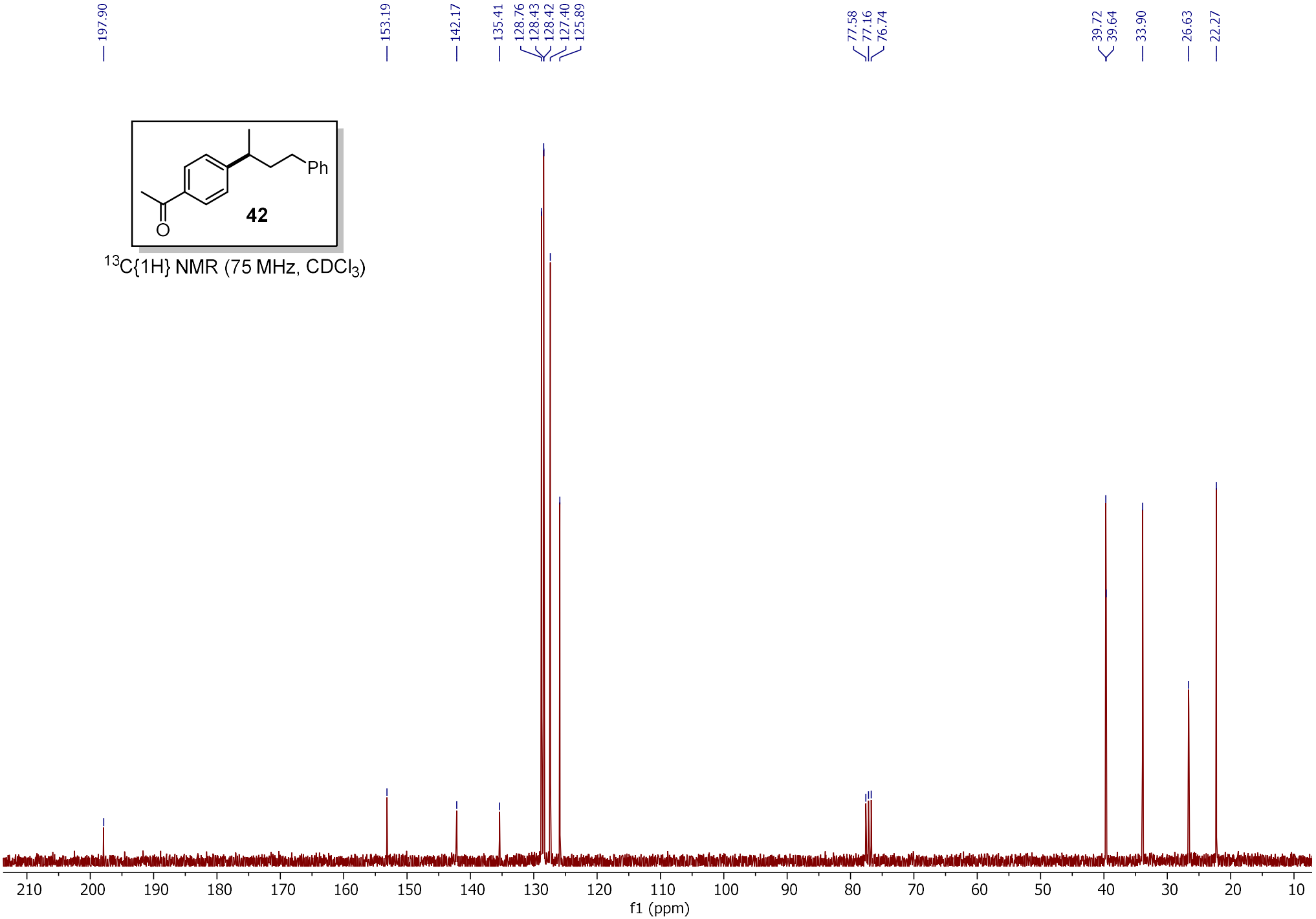


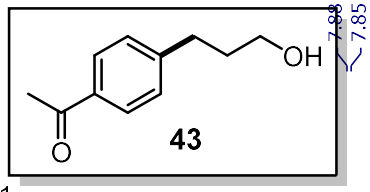
^{1}H NMR (300 MHz, $CDCl_3$)


197.97
152.06
134.97
128.54
126.55
77.58
77.16
76.73
40.32
29.63
26.66
18.40
41
O
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

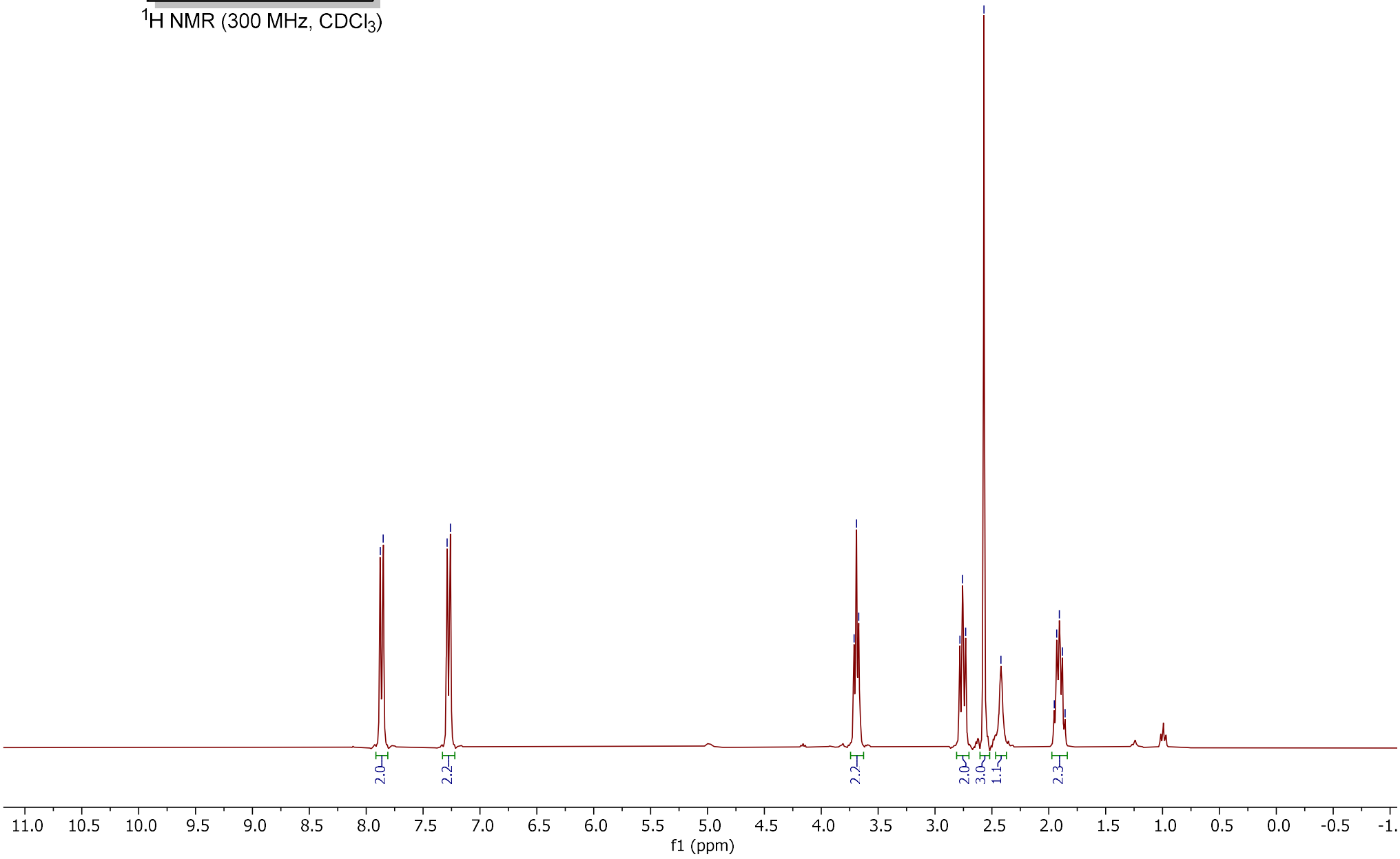


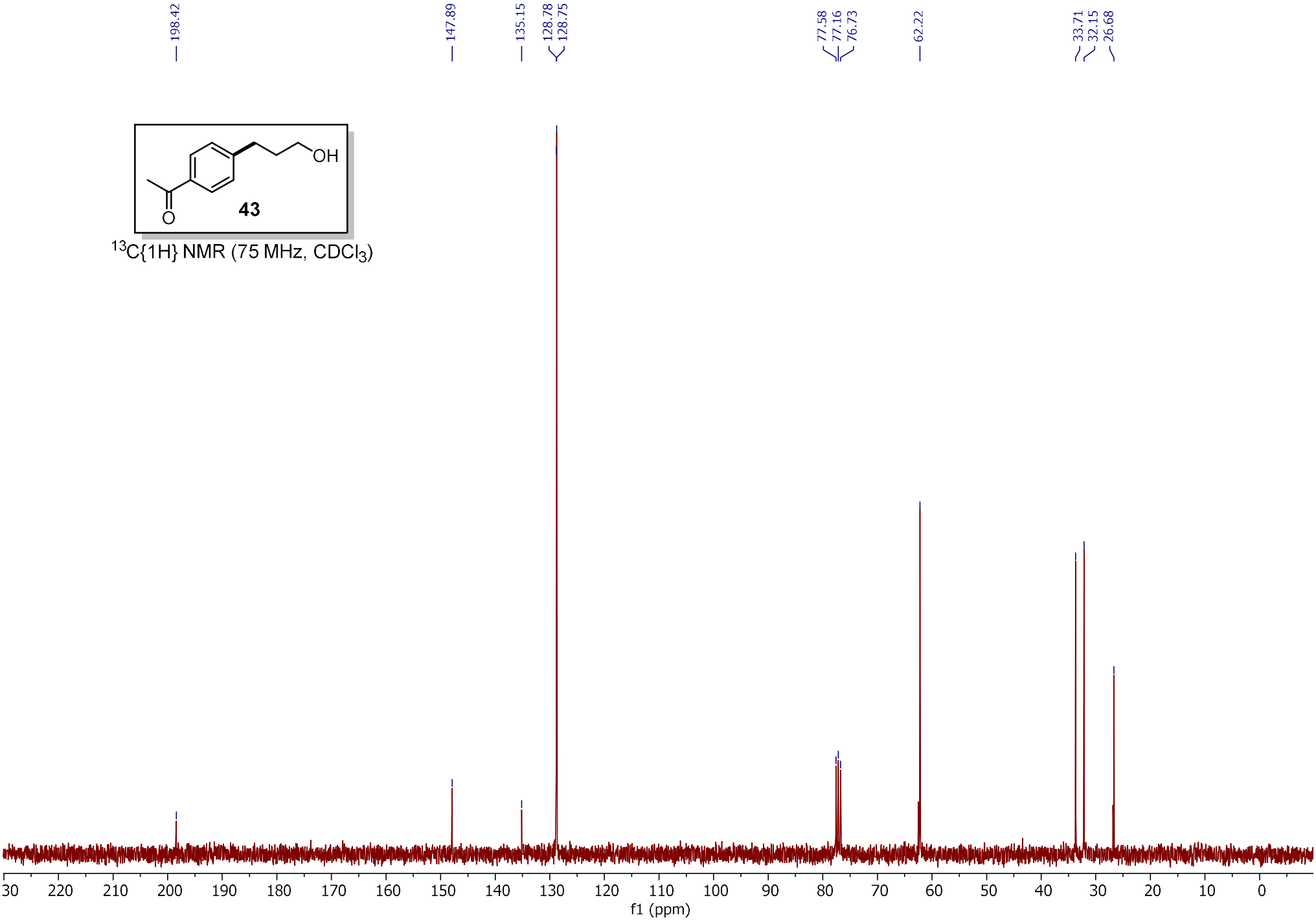
^{1}H NMR (300 MHz, $CDCl_3$)

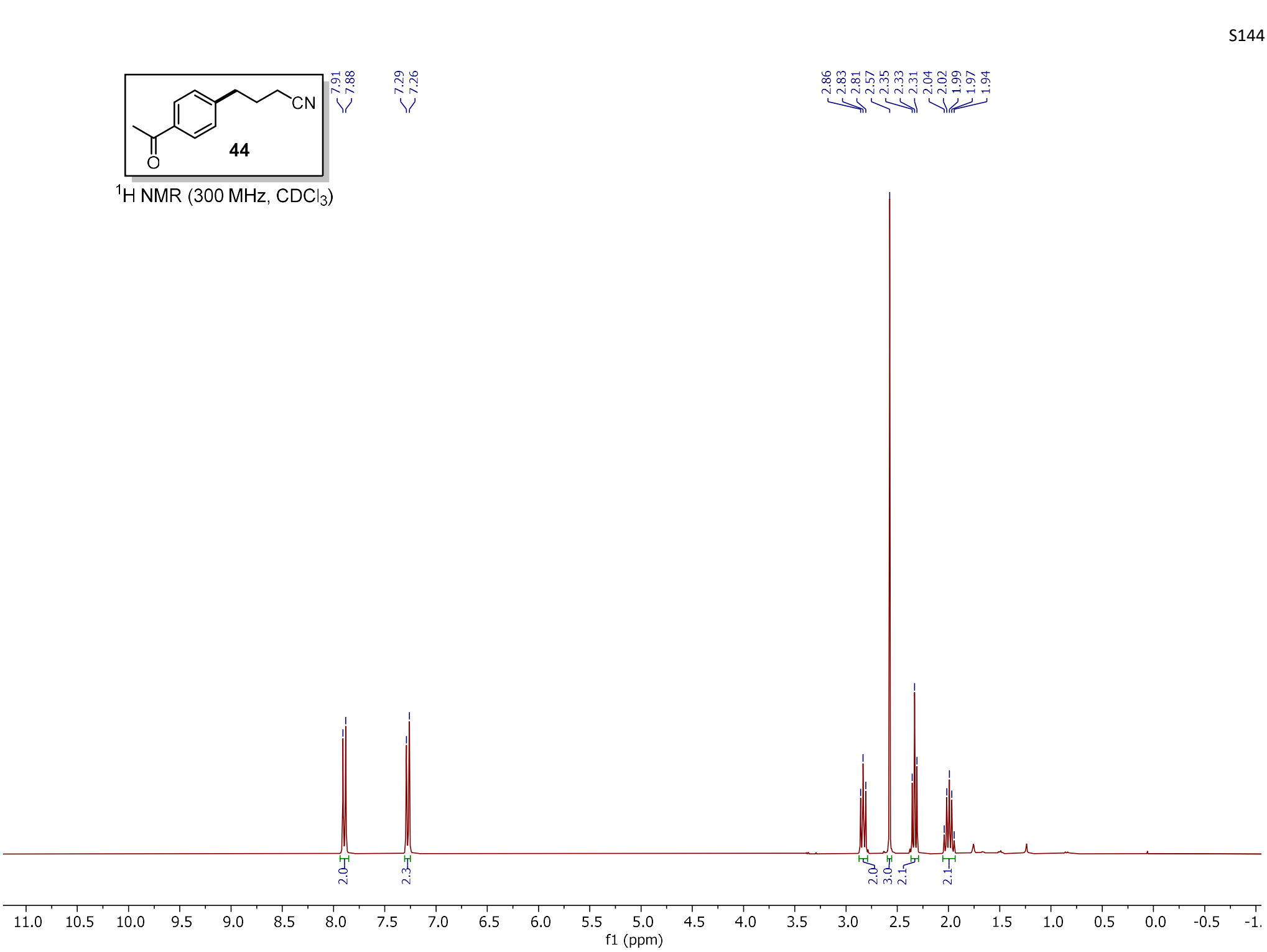

197.90
153.19
142.17
135.41
128.76
128.43
128.42
127.40
125.89
77.58
77.16
76.74
39.72
39.64
33.90
26.63
22.27
Ph
O
42
13C{1H} NMR (75 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



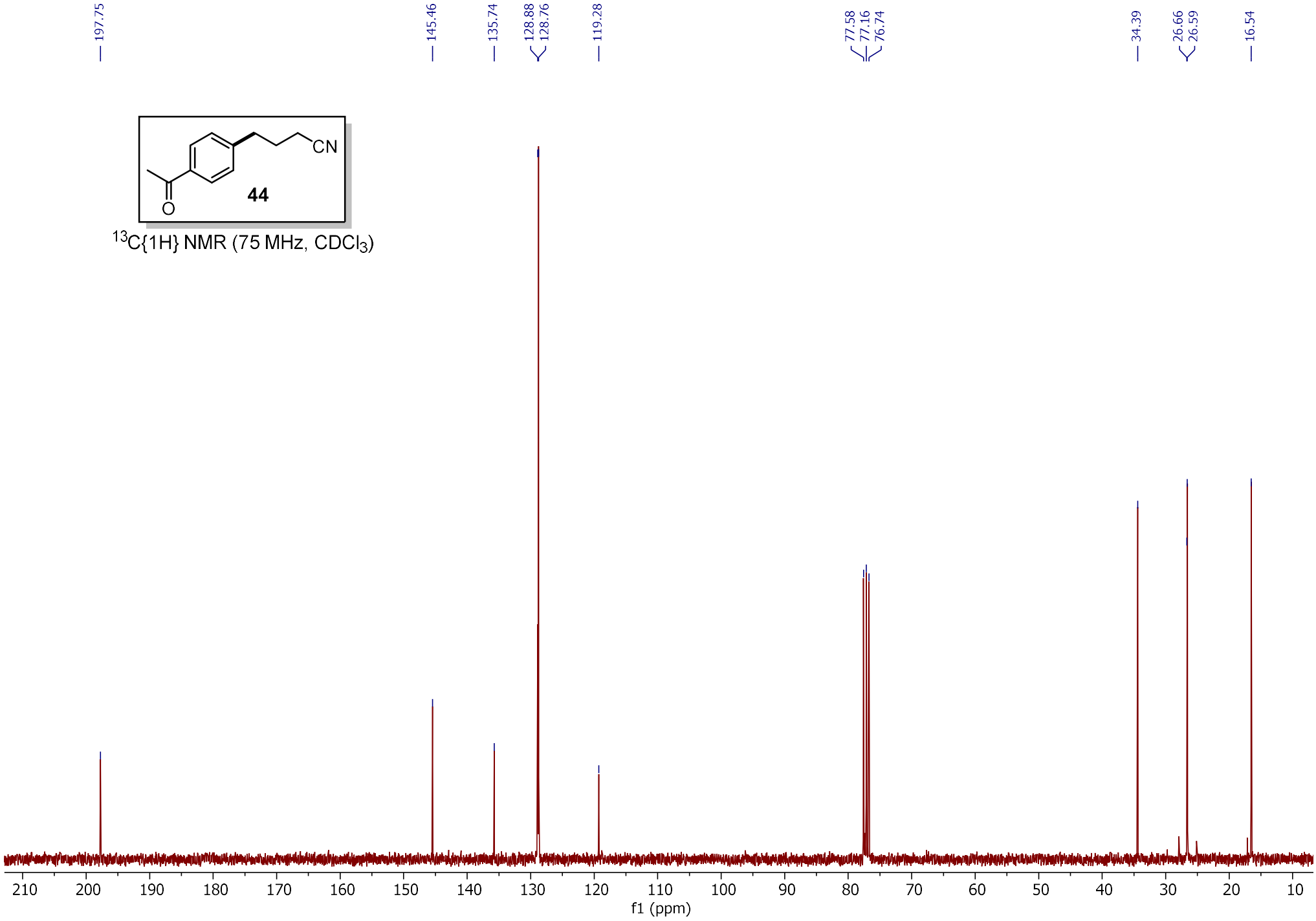
^{1}H NMR (300 MHz, $CDCl_3$)

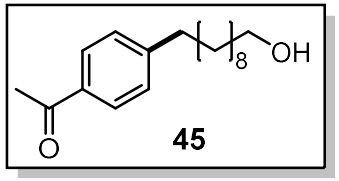



198.42
147.89
135.15
128.78
128.75
77.58
77.16
76.73
62.22
33.71
32.15
26.68
OH
O
43
13C{1H} NMR (75 MHz, CDCl3)
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

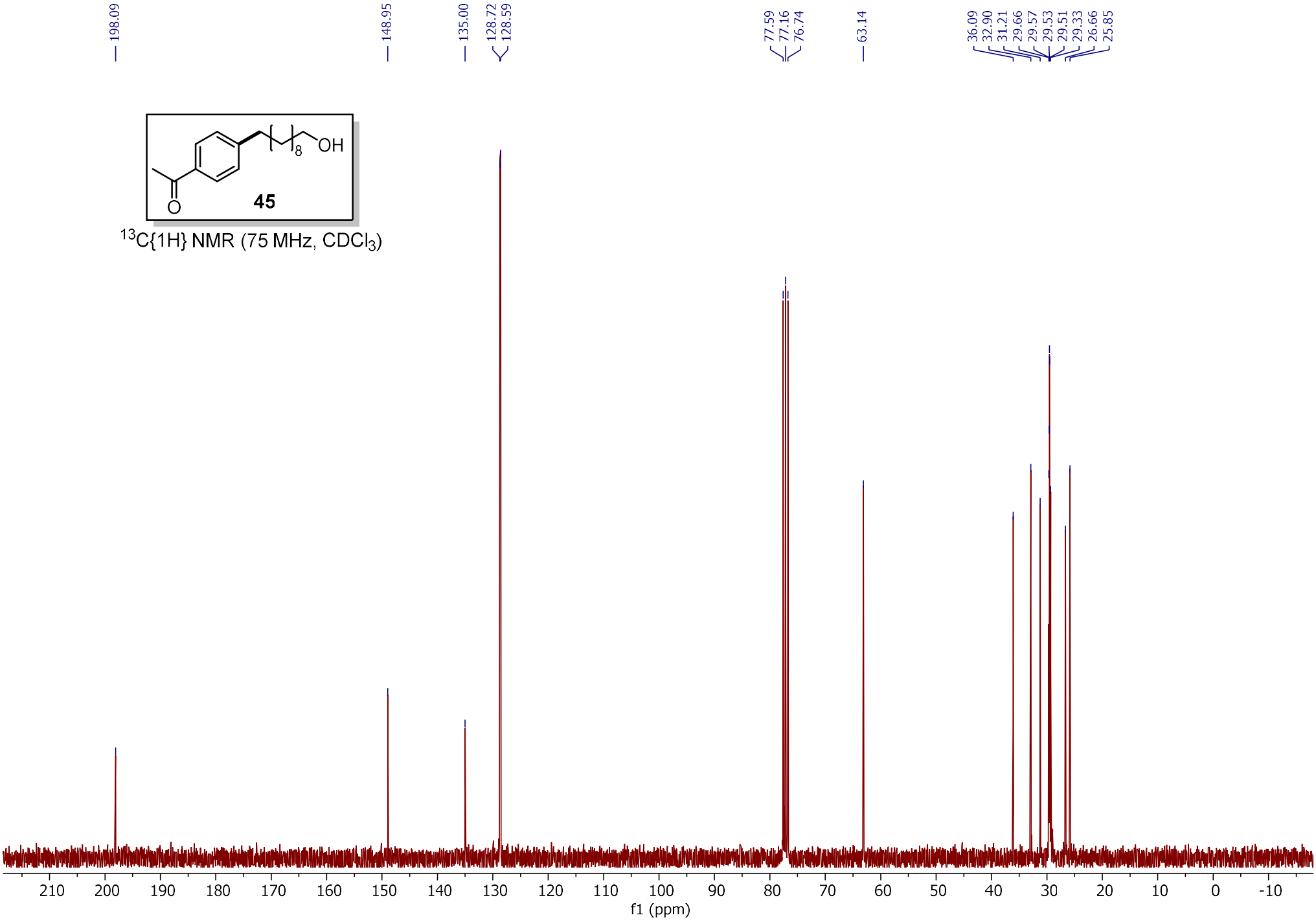


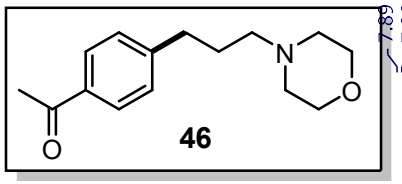
^{1}H NMR (300 MHz, $CDCl_3$)


197.75
145.46
135.74
128.88
128.76
119.28
77.58
77.16
76.74
34.39
26.66
26.59
16.54
CN
O
44
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
f1 (ppm)

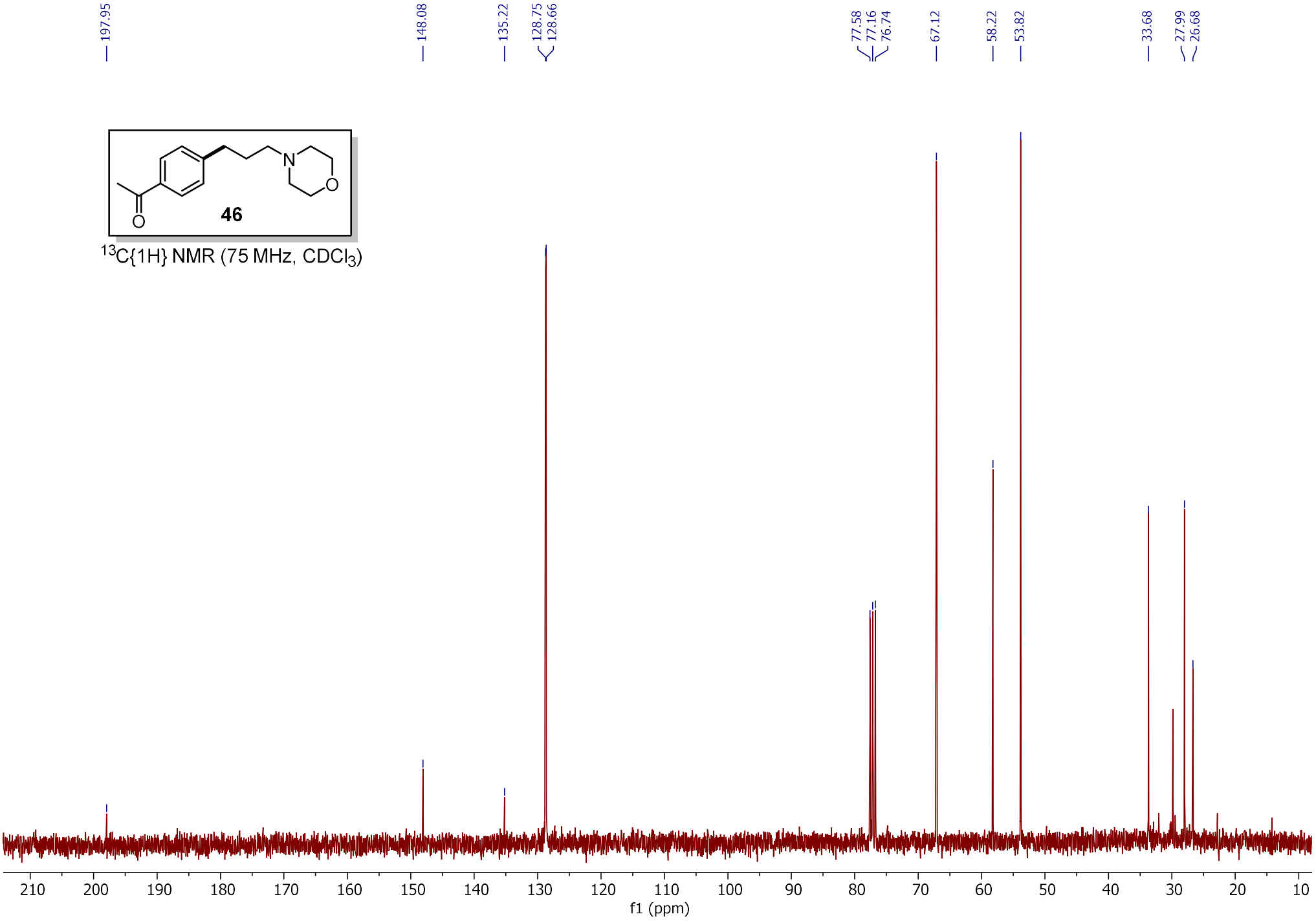


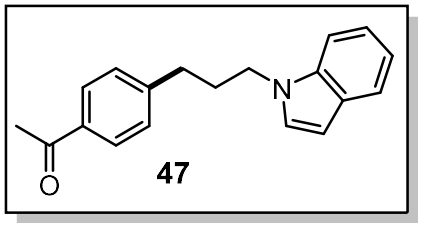
^{1}H NMR (300 MHz, $CDCl_3$)


198.09
148.95
135.00
128.72
128.59
77.59
77.16
76.74
63.14
36.09
32.90
31.21
29.66
29.57
29.53
29.51
29.33
26.66
25.85
OH
8
O
45
13C{1H} NMR (75 MHz, CDCl3)
f1 (ppm)



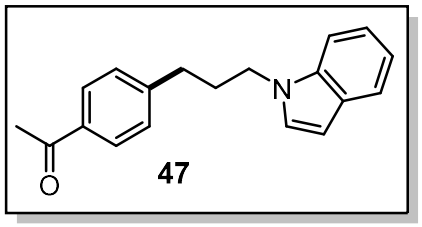
^{1}H NMR (300 MHz, $CDCl_3$)


197.95
148.08
135.22
128.75
128.66
77.58
77.16
76.74
67.12
58.22
53.82
33.68
27.99
26.68
N
O
O
46
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
f1 (ppm)

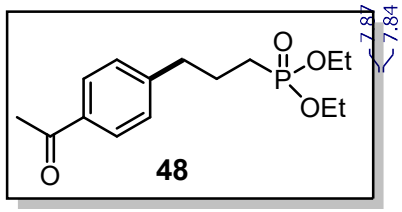


47

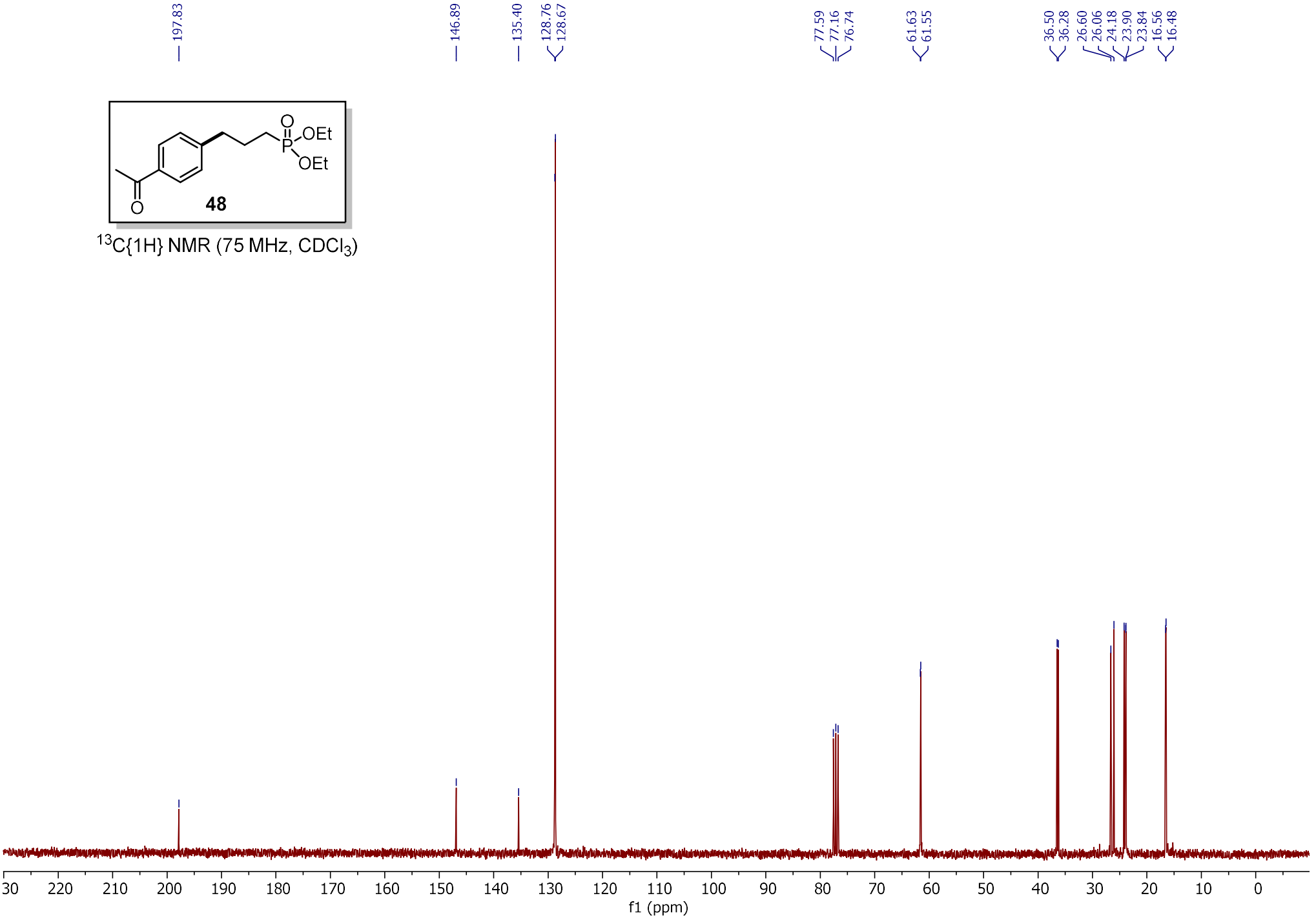
^{1}H NMR (300 MHz, $CDCl_3$)



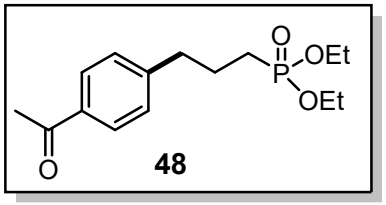
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



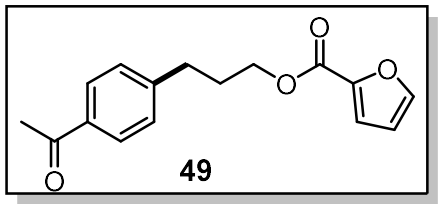
^{1}H NMR (300 MHz, $CDCl_3$)



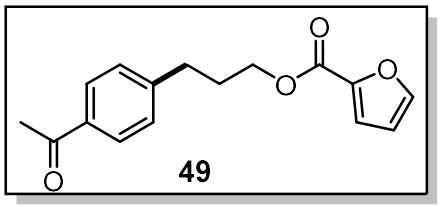
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



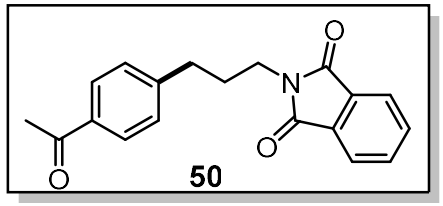
^{31}P NMR (122 MHz, $CDCl_3$)



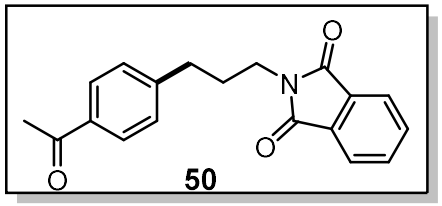
^{1}H NMR (300 MHz, $CDCl_3$)



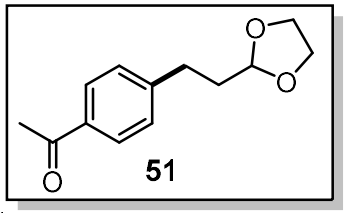
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



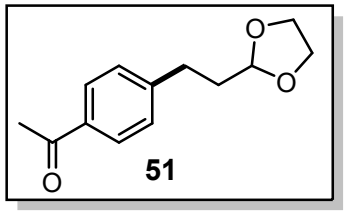
^{1}H NMR (300 MHz, $CDCl_3$)



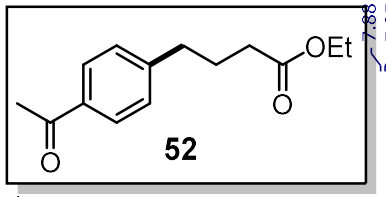
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



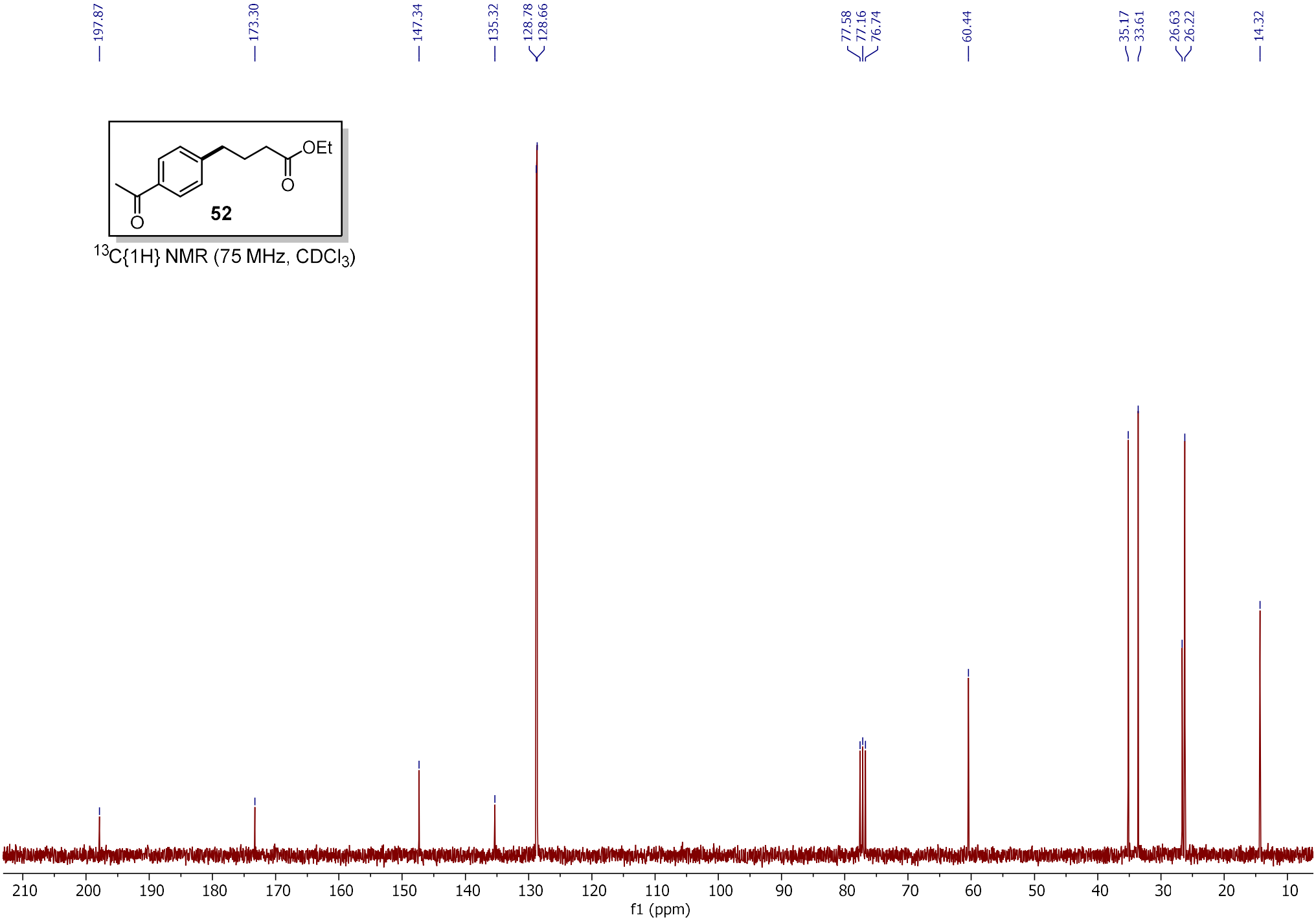
^{1}H NMR (300 MHz, $CDCl_3$)

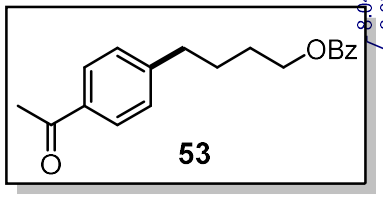


$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)

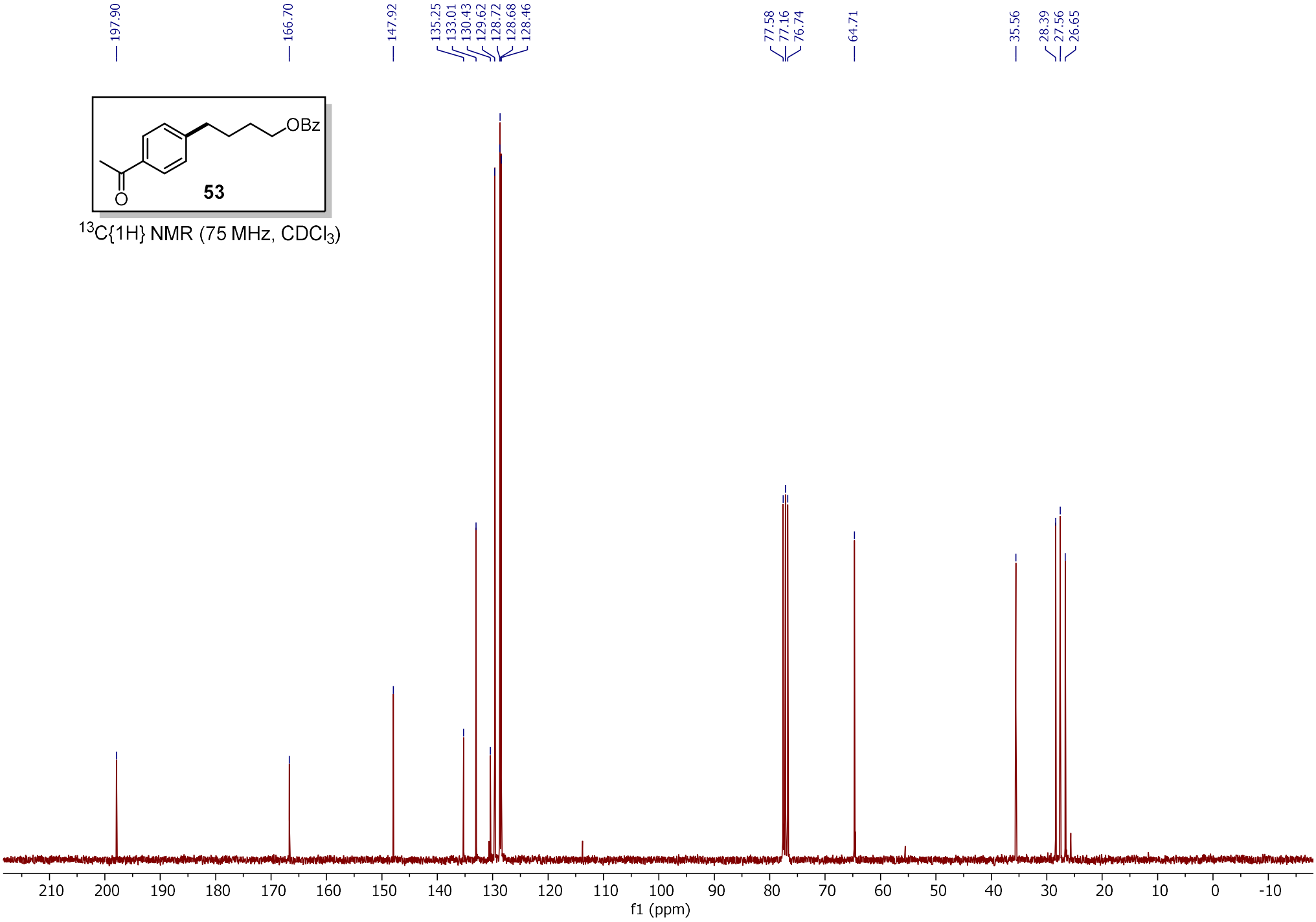


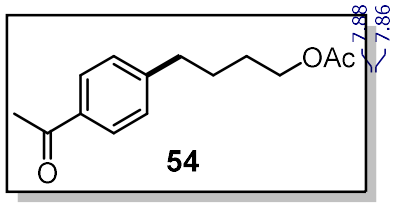
^{1}H NMR (300 MHz, $CDCl_3$)


197.87
173.30
147.34
135.32
128.78
128.66
77.58
77.16
76.74
60.44
35.17
33.61
26.63
26.22
14.32
OEt
O
O
52
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
f1 (ppm)

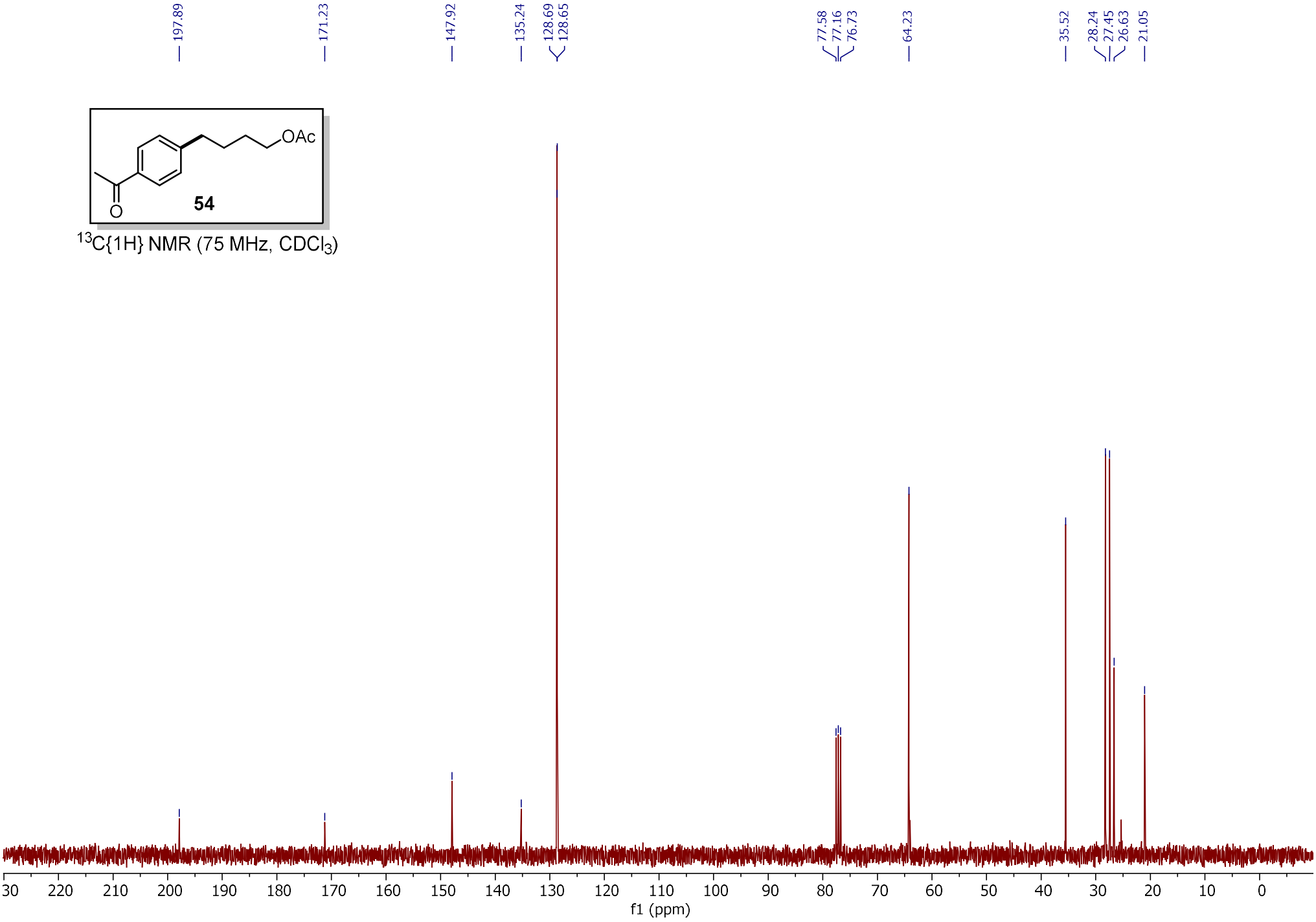


^{1}H NMR (300 MHz, $CDCl_3$)

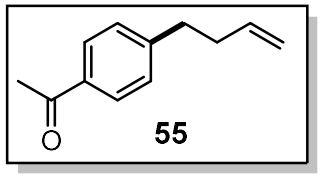

197.90
166.70
147.92
135.25
133.01
130.43
129.62
128.72
128.68
128.46
77.58
77.16
76.74
64.71
35.56
28.39
27.56
26.65
OBz
O
53
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



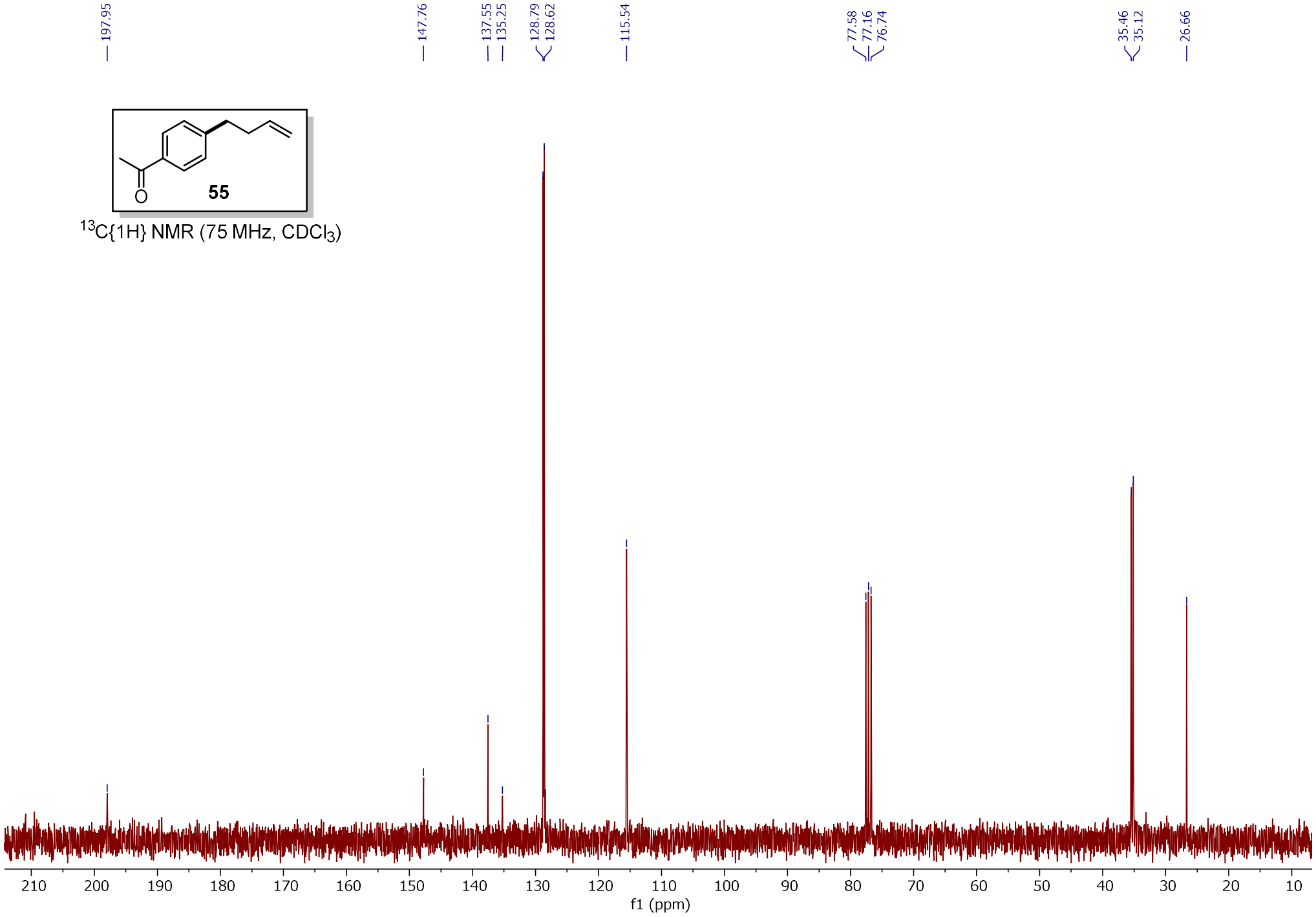
^{1}H NMR (300 MHz, $CDCl_3$)

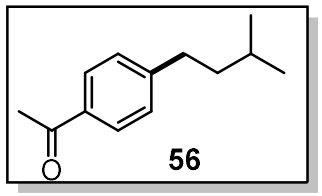


$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)

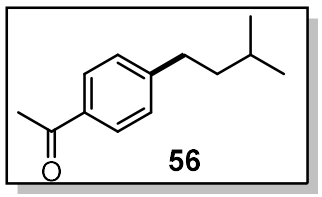


^{1}H NMR (300 MHz, $CDCl_3$)

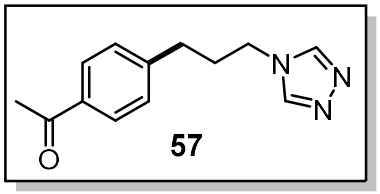

197.95
147.76
137.55
135.25
128.79
128.62
115.54
77.58
77.16
76.74
35.46
35.12
26.66
O
55
13C{1H} NMR (75 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



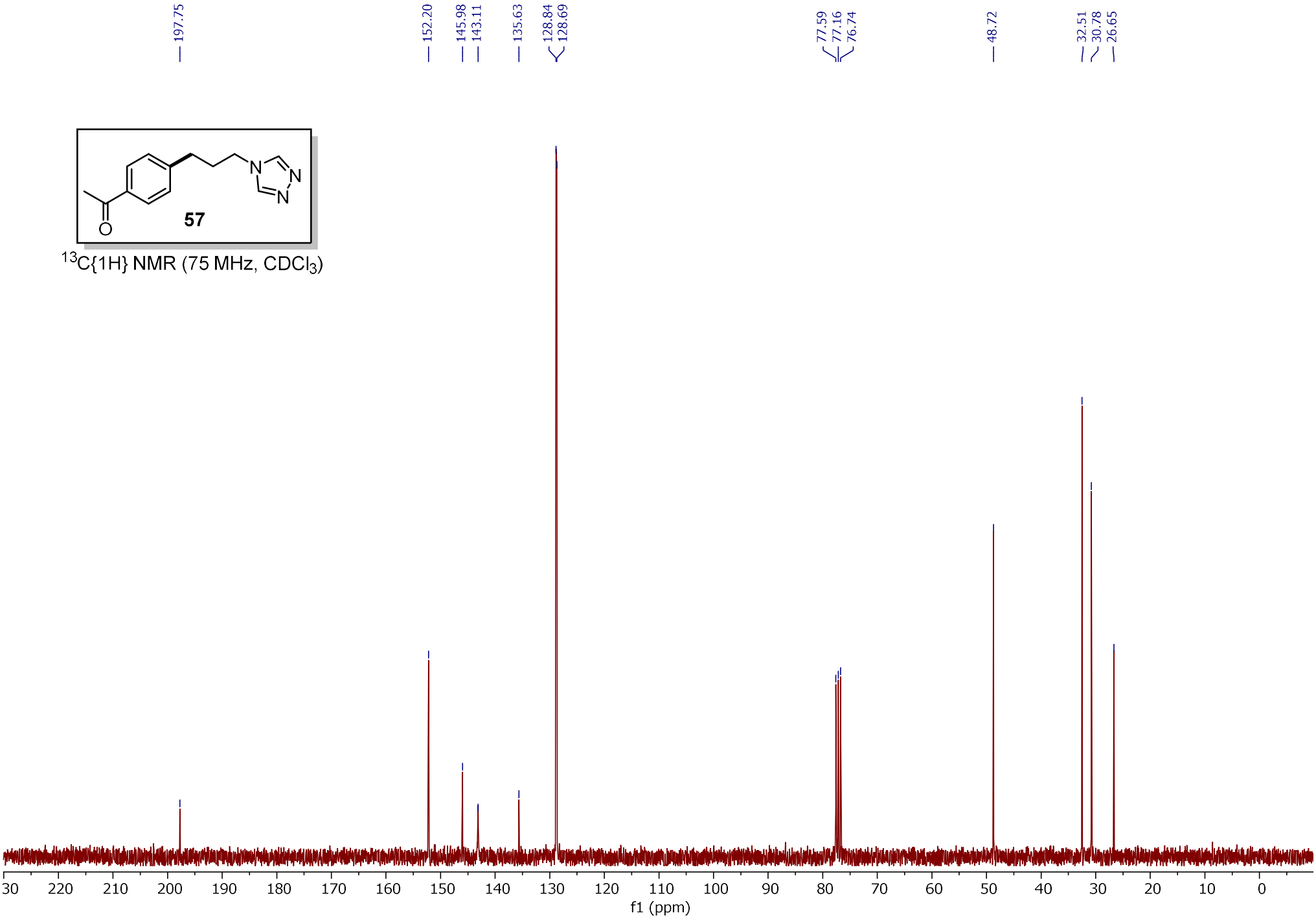
^{1}H NMR (300 MHz, $CDCl_3$)

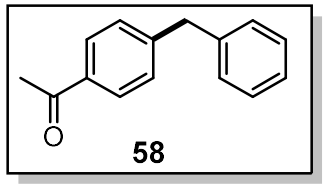


$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



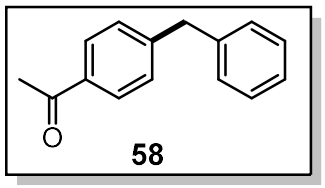
^{1}H NMR (300 MHz, $CDCl_3$)


197.75
152.20
145.98
143.11
135.63
128.84
128.69
77.59
77.16
76.74
48.72
32.51
30.78
26.65
57
^{13}C{1H} NMR (75 MHz, CDCl$_3$)
f1 (ppm)

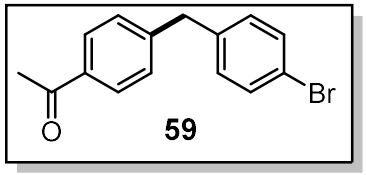


58

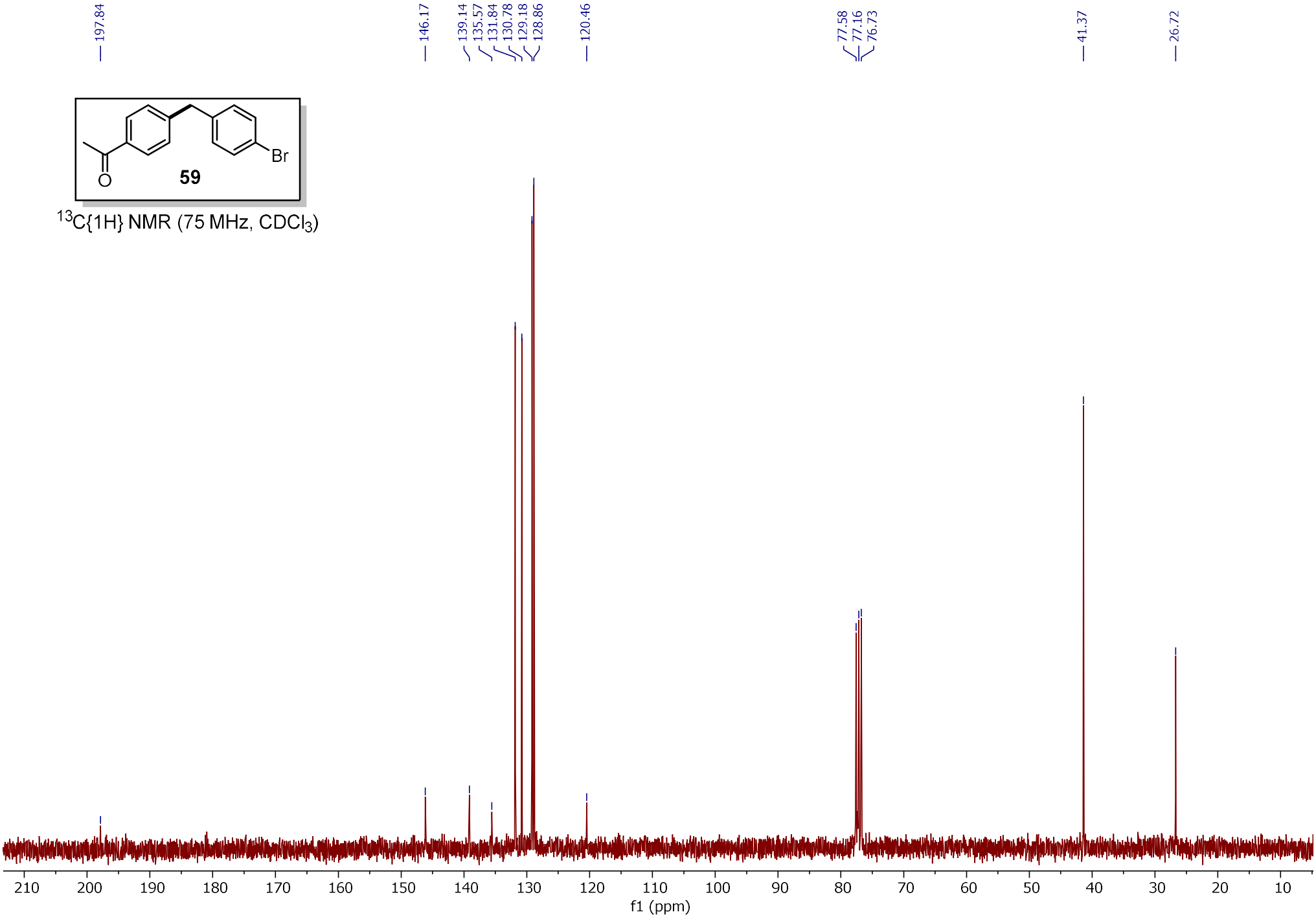
^{1}H NMR (300 MHz, $CDCl_3$)

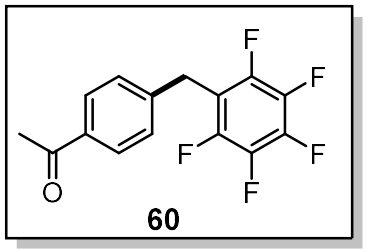


$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



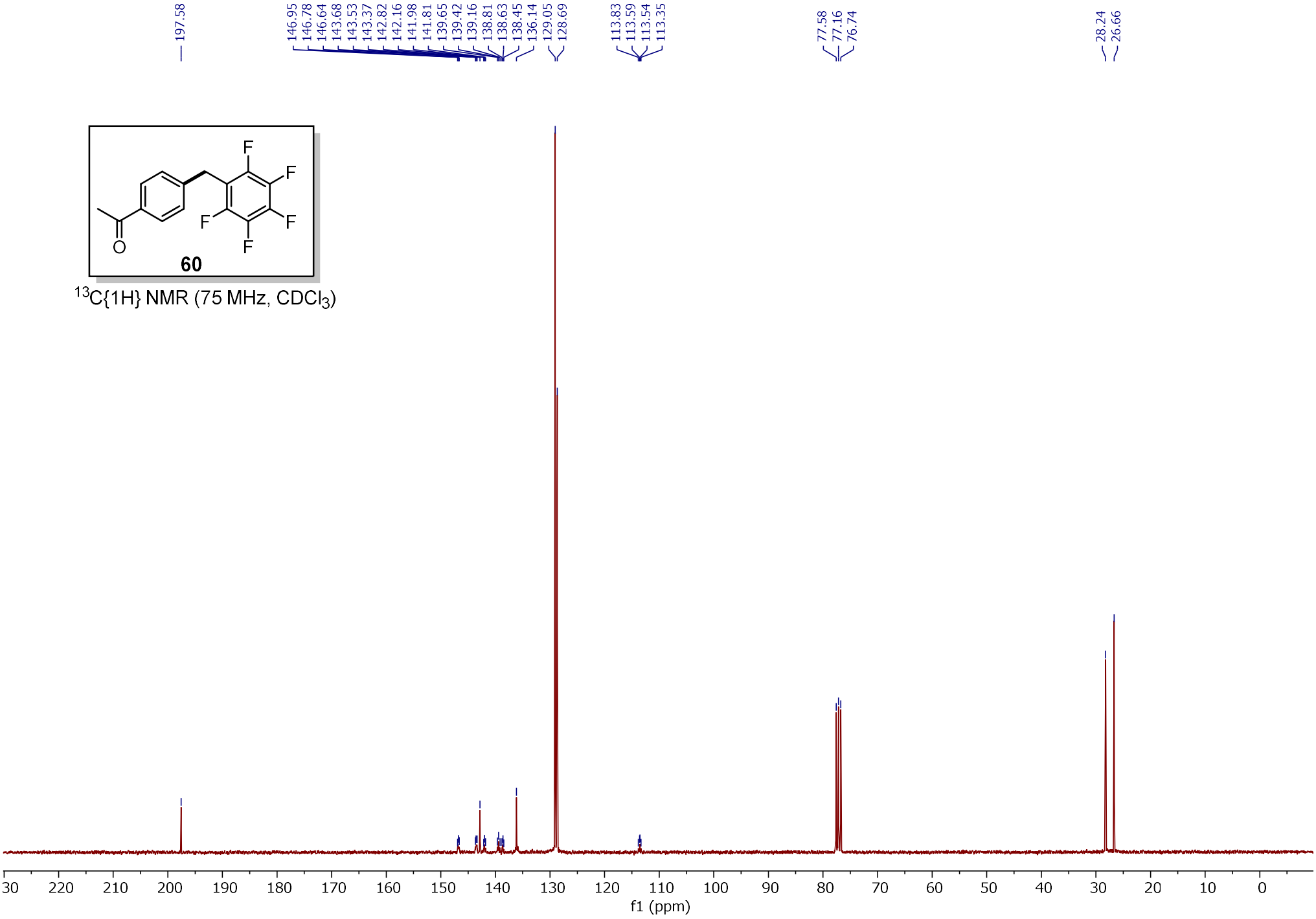
^{1}H NMR (300 MHz, $CDCl_3$)


197.84
146.17
139.14
135.57
131.84
130.78
129.18
128.86
120.46
77.58
77.16
76.73
41.37
26.72
Br
O
59
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
f1 (ppm)

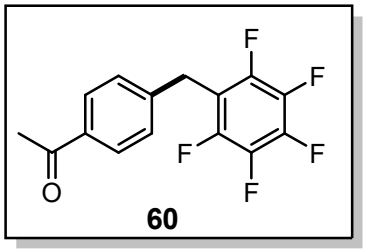


60

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

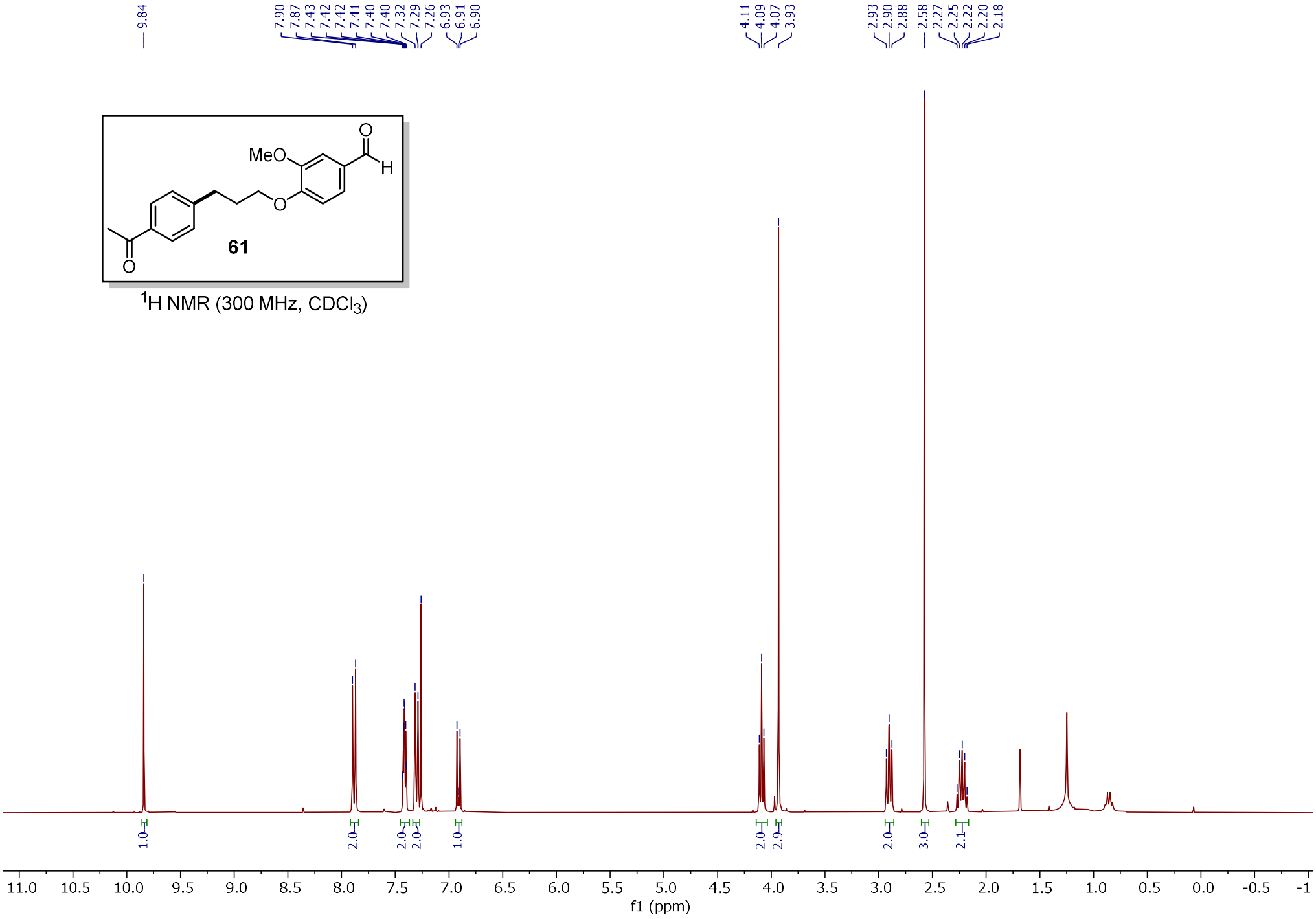


$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)

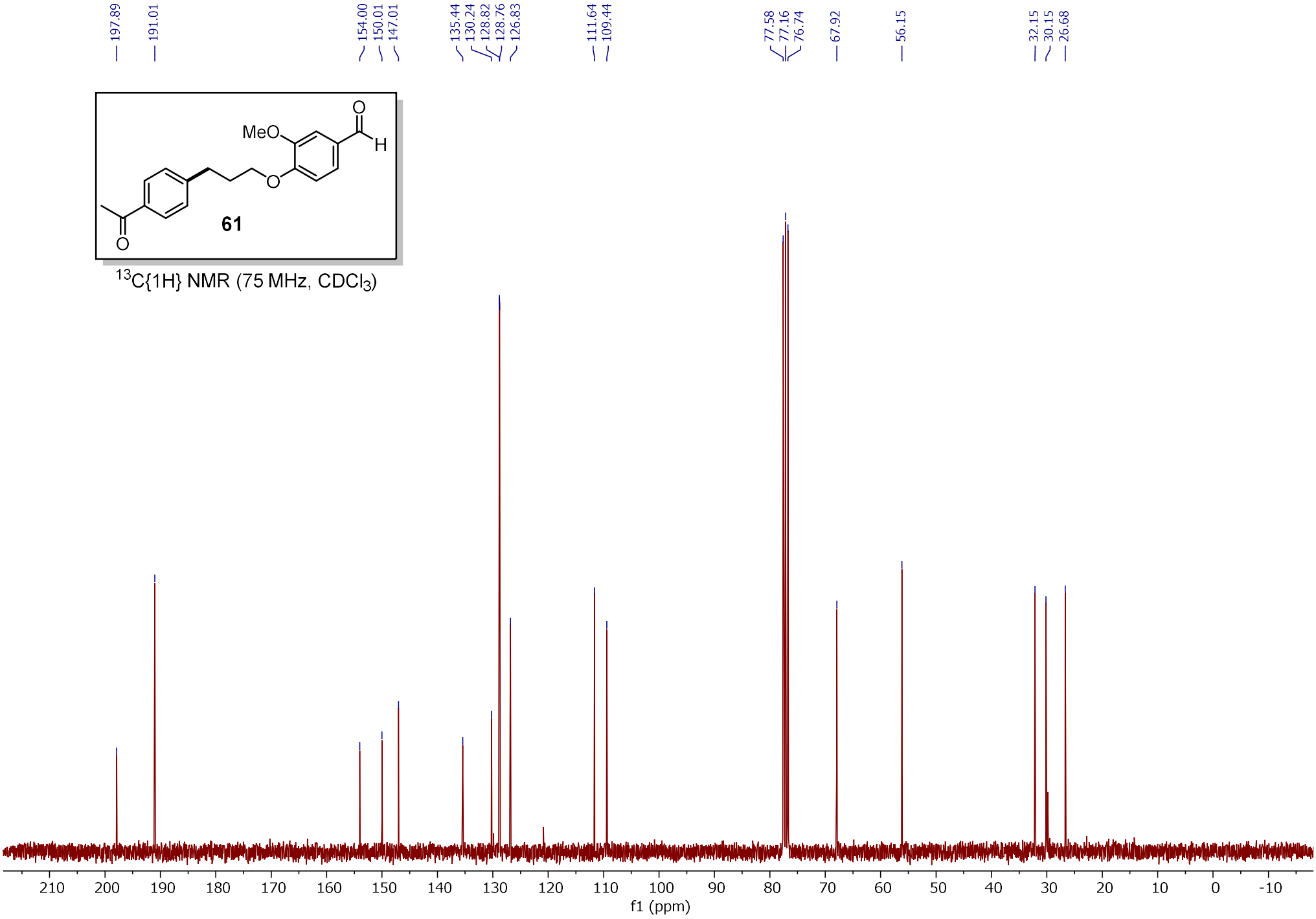


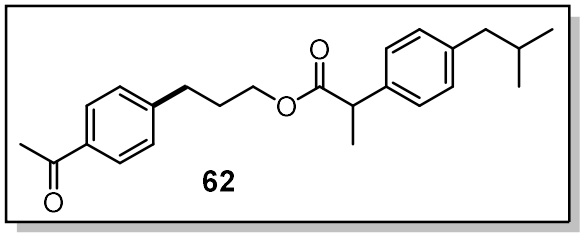
60

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

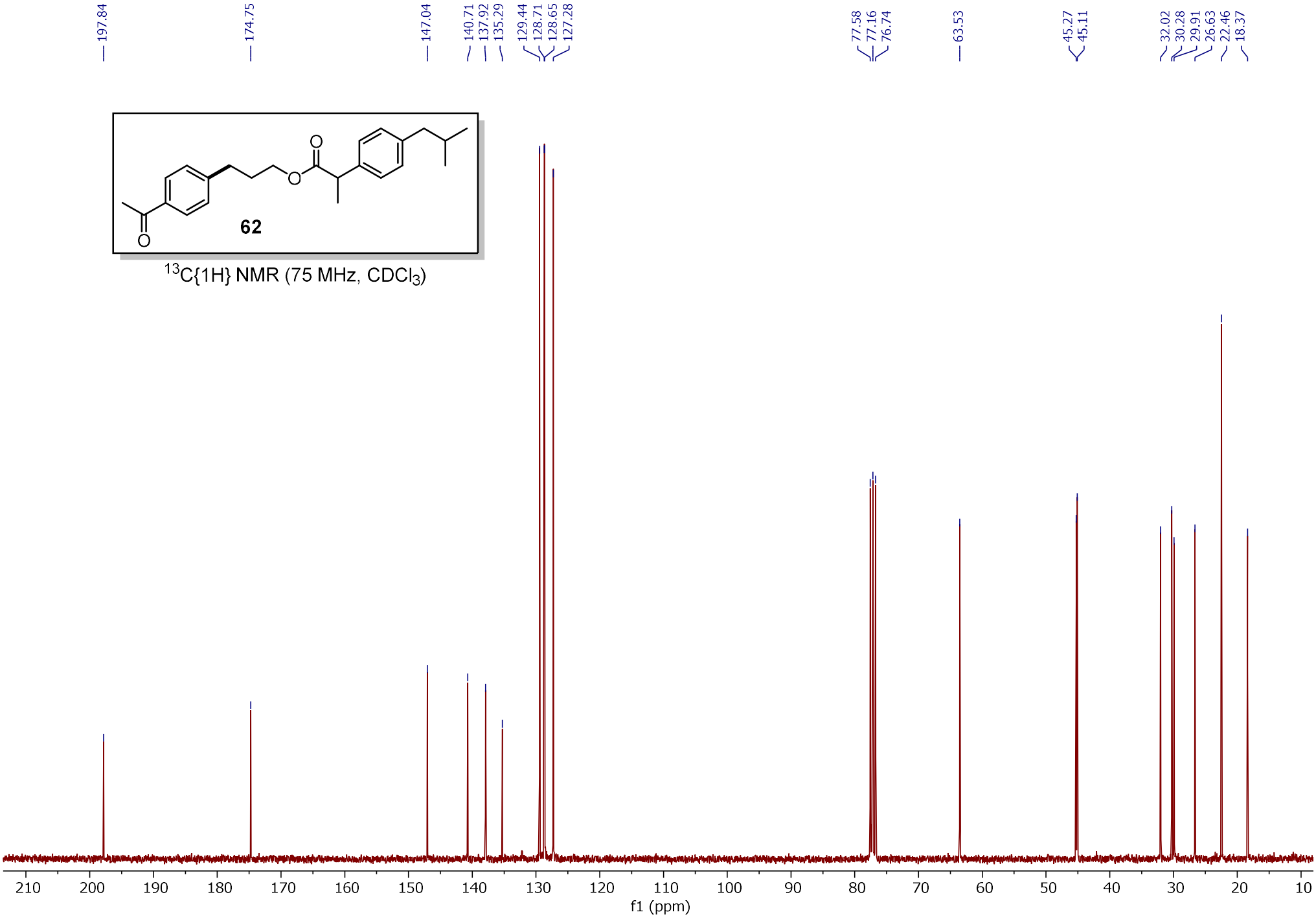


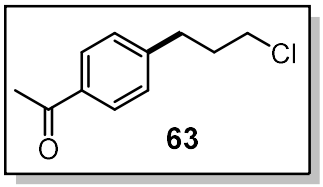
^{1}H NMR (300 MHz, $CDCl_3$)


197.89
191.01
154.00
150.01
147.01
135.44
130.24
128.82
128.76
126.83
111.64
109.44
77.58
77.16
76.74
67.92
56.15
32.15
30.15
26.68
MeO
O
H
O
O
61
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
f1 (ppm)

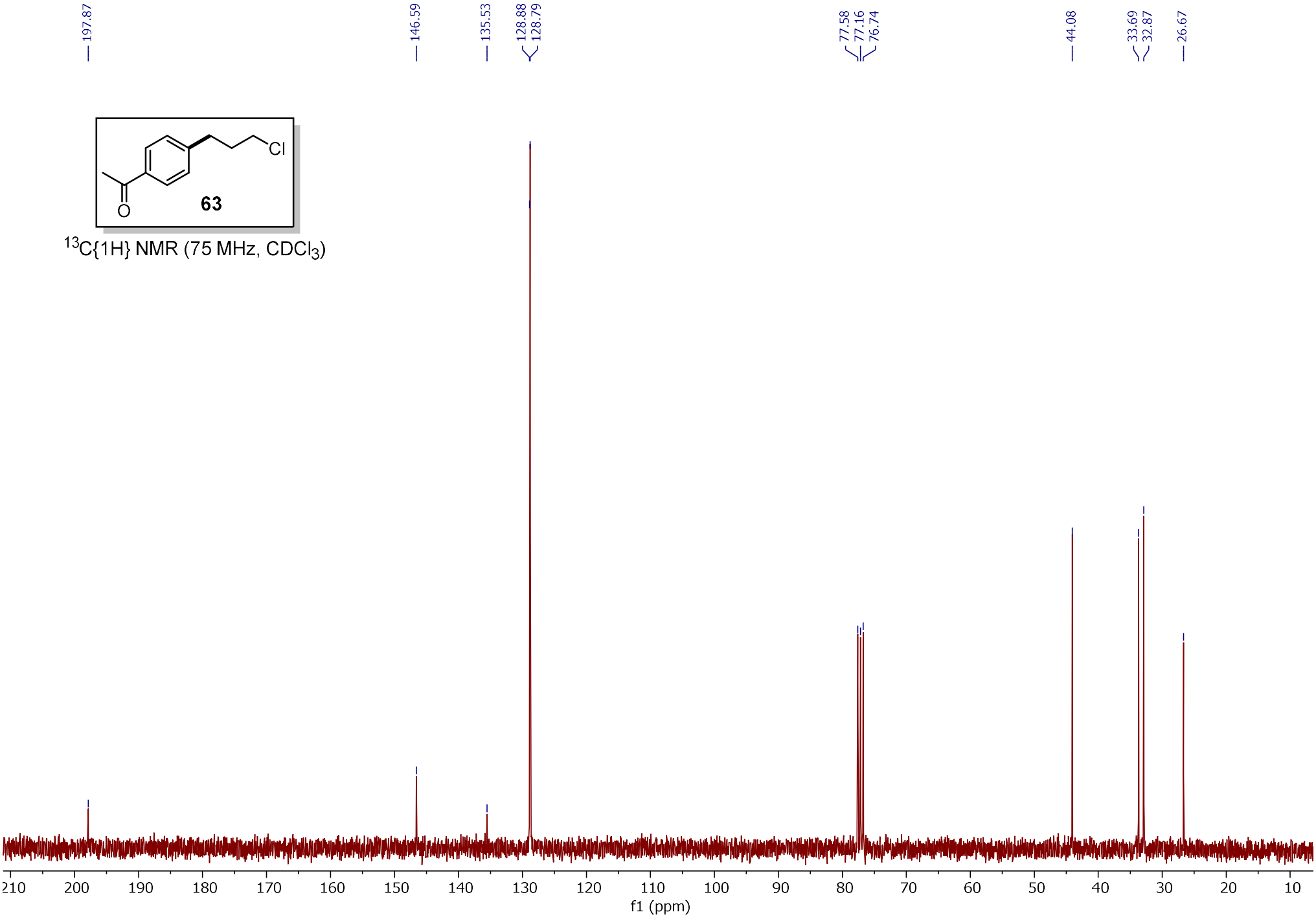


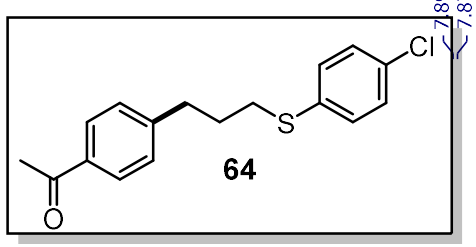
^{1}H NMR (300 MHz, $CDCl_3$)


197.84
174.75
147.04
140.71
137.92
135.29
129.44
128.71
128.65
127.28
77.58
77.16
76.74
63.53
45.27
45.11
32.02
30.28
29.91
26.63
22.46
18.37
62
13C{1H} NMR (75 MHz, CDCl3)
f1 (ppm)

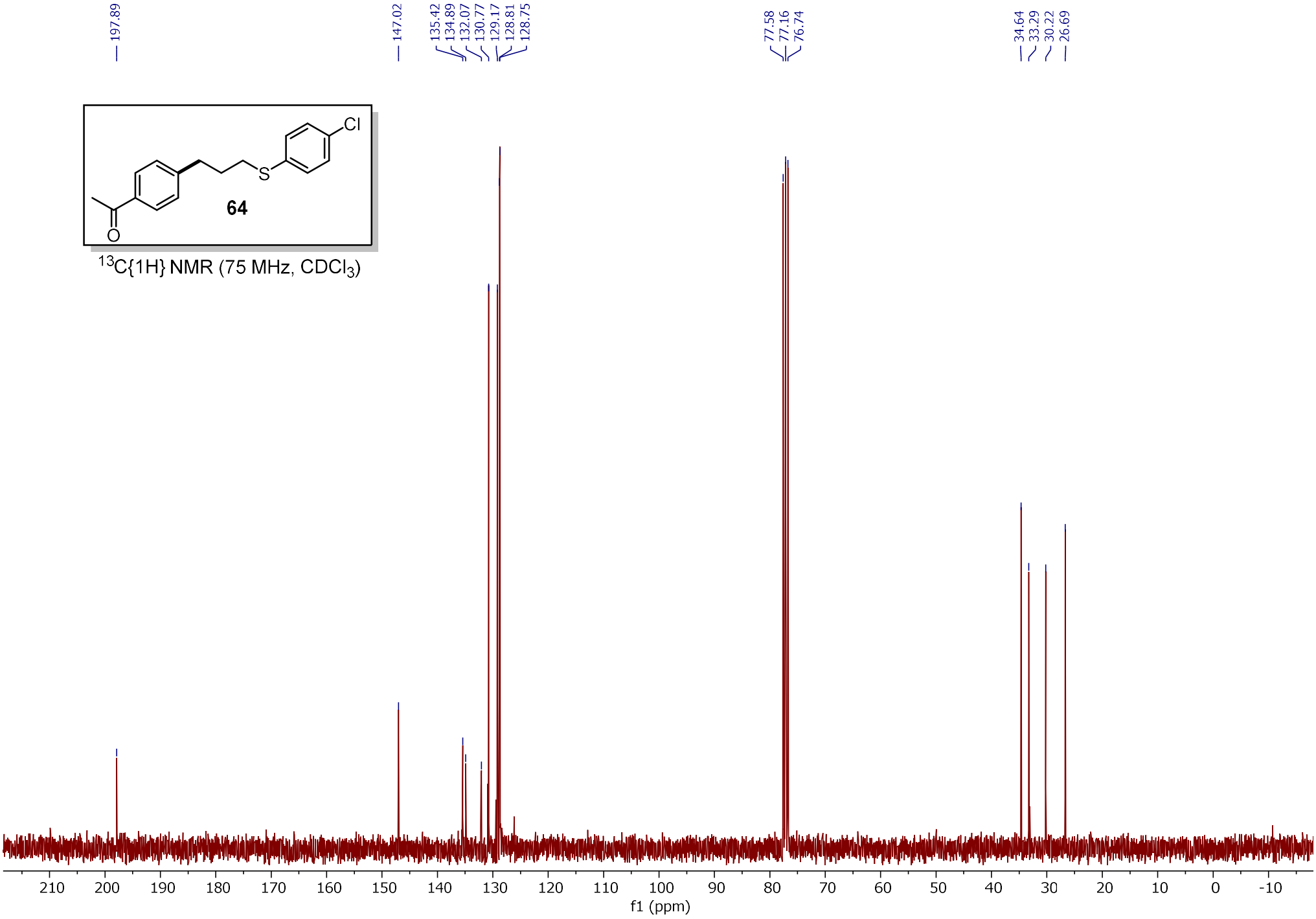


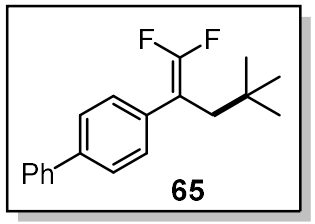
^{1}H NMR (300 MHz, $CDCl_3$)


197.87
146.59
135.53
128.88
128.79
77.58
77.16
76.74
44.08
33.69
32.87
26.67
Cl
O
63
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
f1 (ppm)

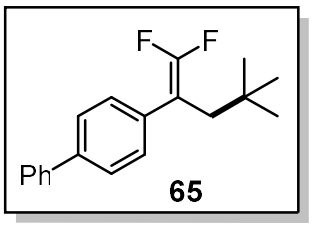


^{1}H NMR (300 MHz, $CDCl_3$)

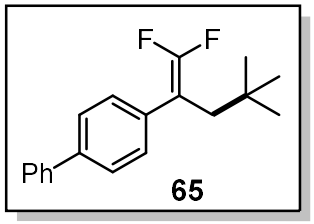

197.89
147.02
135.42
134.89
132.07
130.77
129.17
128.81
128.75
77.58
77.16
76.74
34.64
33.29
30.22
26.69
Cl
S
O
64
13C{1H} NMR (75 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



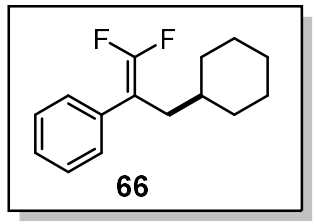
^{1}H NMR (300 MHz, $CDCl_3$)



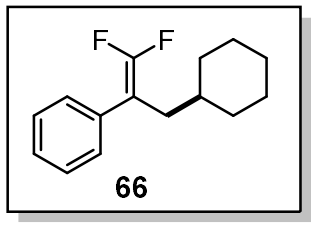
$^{13}C\{1H\}$ NMR (75 MHz, $CDCl_3$)



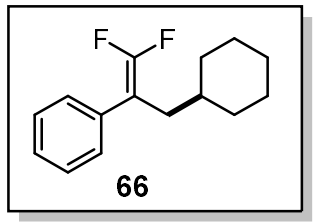
^{19}F NMR (282 MHz, $CDCl_3$)



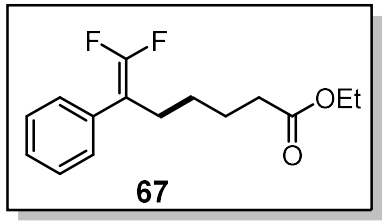
^{1}H NMR (300 MHz, $CDCl_3$)



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



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



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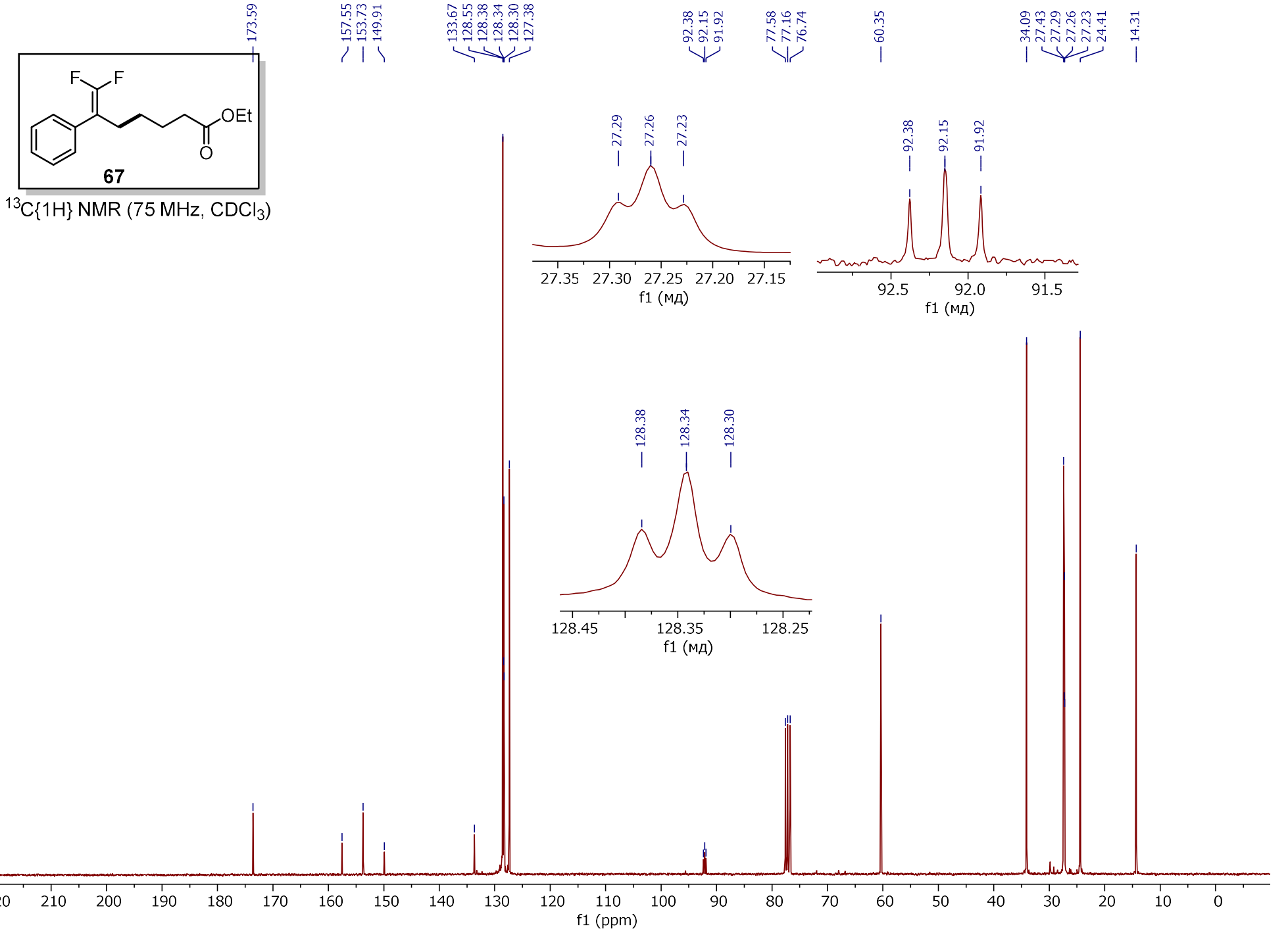
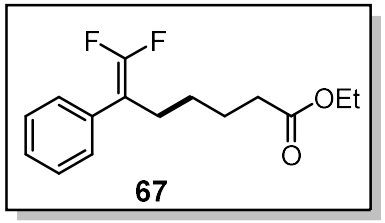
^{1}H NMR (300 MHz, $CDCl_3$)


F
F
OEt
O
67
^{13}C{1H} NMR (75 MHz, CDCl$_3$)
173.59
157.55
153.73
149.91
133.67
128.55
128.38
128.34
128.30
127.38
92.38
92.15
91.92
77.58
77.16
76.74
60.35
34.09
27.43
27.29
27.26
27.23
24.41
14.31
27.29
27.26
27.23
27.35 27.30 27.25 27.20 27.15
f1 (мд)
92.38
92.15
91.92
92.5 92.0 91.5
f1 (мд)
128.38
128.34
128.30
128.45 128.35 128.25
f1 (мд)
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



67

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