Supporting Information

Intermolecular C−C/C−N σ-Bond Metathesis Enabled by Visible-Light

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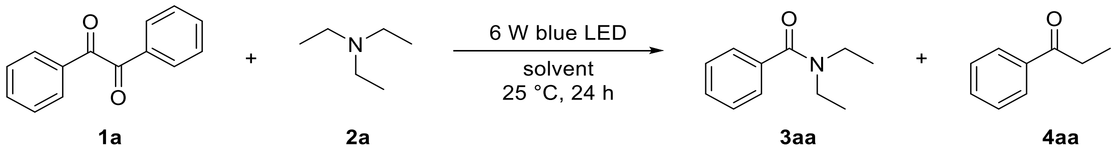
I. General Methods

All reagents and solvents were purchased from commercial sources (Adamas-beta, TCI, Acros, Alfa and Ark) and used without further purification unless otherwise stated. All reactions were monitored by thin-layer chromatography (TLC). All reactions were carried out in argon atmosphere unless otherwise stated. Column chromatography was performed on silica gel (200-300 mesh) and visualized with ultraviolet light. Ethyl acetate and petroleum ether were used as eluents. ^{1}H, ^{19}F and ^{13}C NMR spectra obtained using a Bruker AVANCE III 400 (^{1}H 400 MHz, ^{13}C 101 MHz), Bruker AVANCE III HD 400 (^{1}H 400 MHz, ^{13}C 101 MHz, ^{19}F 376 MHz), JEOL JNM-ECS 400M (^{1}H 400 MHz, ^{13}C 101 MHz, ^{19}F 376 MHz), Bruker AVANCE NEO 600 (^{1}H 600 MHz, ^{13}C 151 MHz), and Agilent INOVA 600 (^{1}H 600 MHz, ^{13}C 151 MHz). Chemical shifts of ^{1}H NMR spectra were reported using either a residual solvent signal or TMS (δ = 0.0 ppm) as an internal standard. Chemical shifts of ^{13}C NMR spectra were reported using the solvent signal of $CDCl_3$ (δ = 77.16 ppm) as an internal standard. Chemical shifts of ^{19}F NMR spectra were reported without an internal standard. GC-MS analyses were performed with a Thermo TRACE 1300 ISQ LT spectrometer. HRMS analyses were made by Lanzhou University by means of APCI. All solvents were purified and dried by standard techniques. UV-vis absorption spectra were recorded using a Lengguang Technology UV1901 Dual-Beam UV-Visible Spectrophotometer. The samples were measured in UV quartz cuvettes (chamber volume = 4 mL, H × W × D = 40 mm × 10 mm, 10 mm) fitted with a PTFE stopper.

II. Optimization of Reaction Conditions

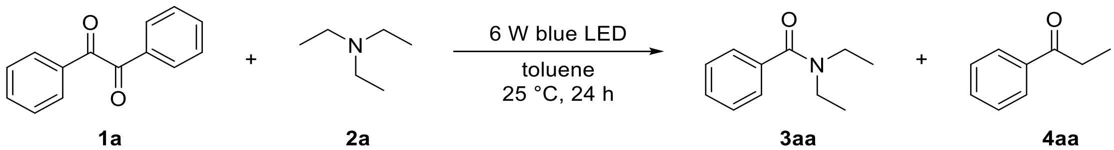
1) Optimizing solvents



Entry	Solvent	Yield (3aa) /%	Yield (4aa) /%
1	DMSO	22	trace
2	DMF	46	trace
3	CH_3CN	55	7
4	THF	46	20
5	CH_3OH	34	36
6	toluene	48	40
7	DCM	28	11

General conditions: **1a** (0.1 mmol), **2a** (0.1 mmol) and solvent (1.0 mL) were irradiated by 405 nm LED (3 W × 2) for 24 h under an argon atmosphere at 25 °C. Yields were determined by ^{1}H NMR with dibromomethane as internal standard.

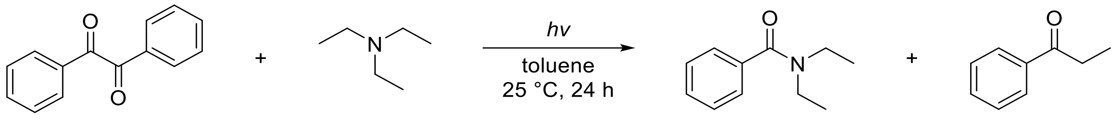
2) Optimizing the amount of benzil



Entry	benzil (equiv)	Yield (3aa) /%	Yield (4aa) /%
1	1.0	46	38
2	1.2	45	40
3	1.5	55	40
4	1.7	50	32
5	2.0	28	12

General conditions: **1a** (x equiv), **2a** (0.1 mmol) and toluene (1.0 mL) were irradiated by 405 nm LED (3 W × 2) for 24 h under an argon atmosphere at 25 °C. Yields were determined by ^{1}H NMR with dibromomethane as internal standard.

3) Optimizing the wavelength

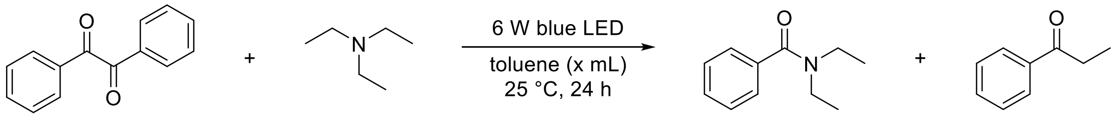


1a **2a** **3aa** **4aa**

Entry	Wavelength (nm)	Yield (3aa) /%	Yield (4aa) /%
1	365	29	9
2	380	13	6
3	405	52	41
4	425	trace	46
5	465	trace	38

General conditions: **1a** (1.5 equiv), **2a** (0.1 mmol) and toluene (1.0 mL) were irradiated by light (x nm) for 24 h under an argon atmosphere at 25 °C. Yields were determined by ^{1}H NMR with dibromomethane as internal standard.

4) Optimizing the concentration of reaction

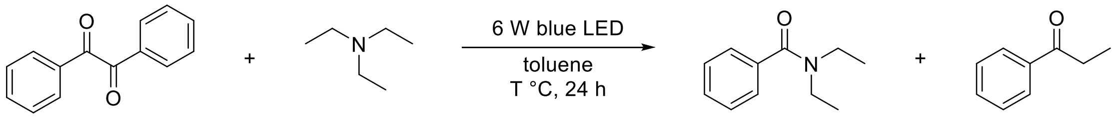


1a **2a** **3aa** **4aa**

Entry	toluene (x mL)	Yield (3aa) /%	Yield (4aa) /%
1	0.5	40	17
2	1	53	39
3	1.5	55	51
4	2	56	51

General conditions: **1a** (1.5 equiv), **2a** (0.1 mmol) and toluene (x mL) were irradiated by 405 nm LED (3 W × 2) for 24 h under an argon atmosphere at 25 °C. Yields were determined by ^{1}H NMR with dibromomethane as internal standard.

5) Optimizing reaction temperature

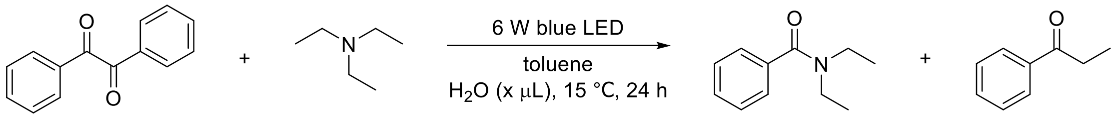


1a **2a** **3aa** **4aa**

Entry	T (°C)	Yield (3aa) /%	Yield (4aa) /%
1[a]	40	27	16
2[b]	25	53	44
3[c]	15	58	55

General conditions: **1a** (1.5 equiv), **2a** (0.1 mmol) and toluene (1.5 mL) were irradiated by 405 nm LED (3 W × 2) for 24 h under an argon atmosphere at T °C. Yields were determined by ^{1}H NMR with dibromomethane as internal standard. [a] Without electric fan. [b] With electric fan. [c] With electric fan (in refrigerator).

6) Optimizing the amount of water



1a **2a** **3aa** **4aa**

Entry	H_2O(μL)	Yield (3aa) /%	Yield (4aa) /%
1	10	38	30
2	50	51	40
3	75	64	58
4	100	45	37

General conditions: **1a** (1.5 equiv), **2a** (0.1 mmol), toluene (1.5 mL) and H_2O (x μL) were irradiated by 405 nm LED (3 W × 2) for 24 h under an argon atmosphere at 15 °C. Yields were determined by ^{1}H NMR with dibromomethane as internal standard.

7) Optimizing reaction temperature

1a **2a** **3aa** **4aa**

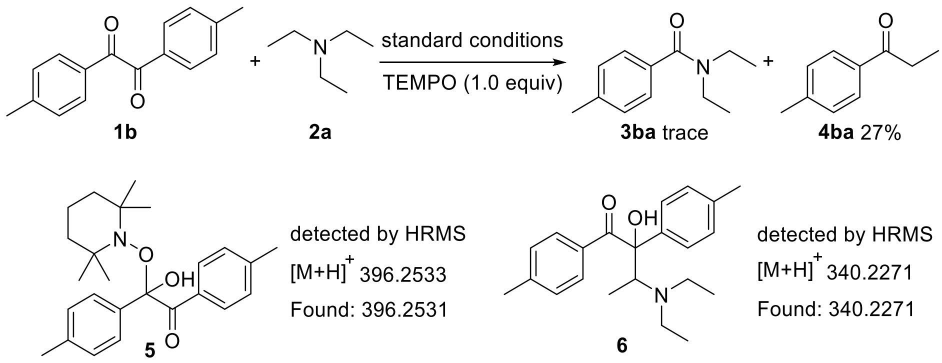
Entry	T (°C)	Yield (3aa) /%	Yield (4aa) /%
1	15	50	36
2	5	49	36
3	-5	36	38

General conditions: **1a** (1.5 equiv), **2a** (0.1 mmol), toluene (1.5 mL) and H_2O (75 μL) were irradiated by 405 nm LED (3 W × 2) for 24 h under an argon atmosphere at T °C (in low temperature reactor). Yields were determined by ^{1}H NMR with dibromomethane as internal standard.

III. Mechanistic Study

(1) Radical capture experiment (TEMPO)

When 1.0 equiv of TEMPO was added to the reaction of **1b** and **2a** under the standard conditions (Scheme S1), the reaction was inhibited and the TEMPO-adduct products **5** and reaction intermediate **6** were detected by HRMS (Figure S1).



Scheme S1. Radical capture experiment

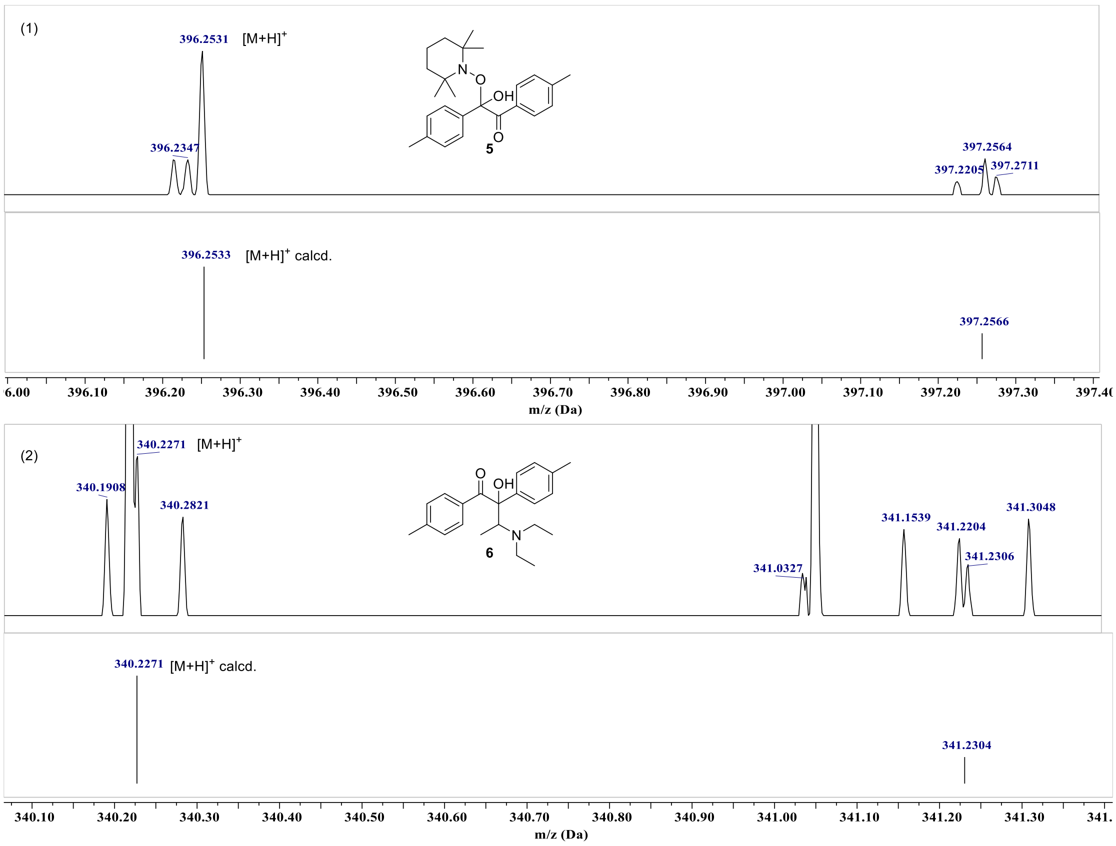
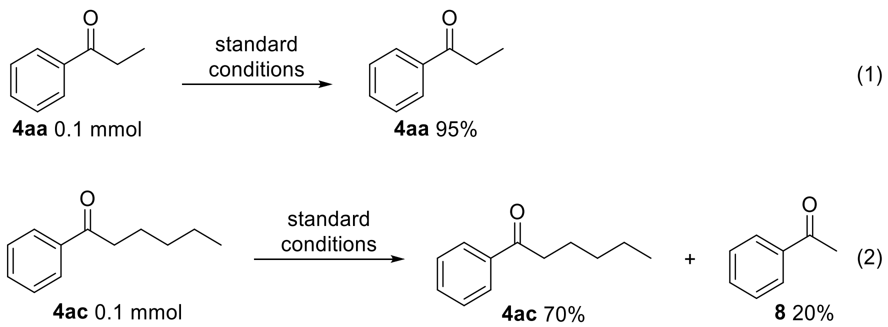


Figure S1. HRMS of reaction intermediates captured by TEMPO

(2) Side reactions of aryl alkyl ketone compounds under standard conditions

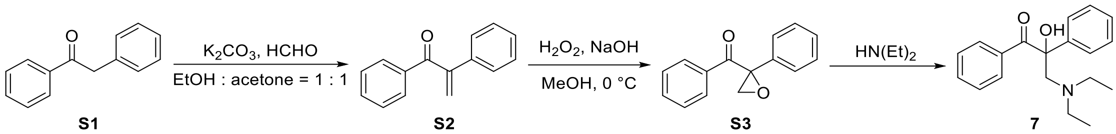


Scheme S2 degradation of long chain ketone and short chain ketone

Due to the yield of product ketones were lower than amides when long chain alkyl amines were used as substrates, we proposed that the corresponding long chain ketone may be degraded via Norrish II-type process under light irradiation. To prove this proposal, the long chain aryl alkyl ketone **4ac** was individually investigated under standard reaction conditions for 24 hours, resulting in the detection of a 20% yield of the Norrish II-type degradation product aryl methyl ketone **8**, with 70% of the starting material **4ac** remaining (Scheme S2-2). As comparison, the short chain ketone **4aa** were more stable than long chain ketone at the same reaction conditions, remaining 95% starting material under irradiation for 24 hours (Scheme S2-1). This information further confirm that Norrish II-type degradation has important influence for long chain ketone degradation.

(3) Intermediate experiment

Preparation of the intermediate 7



Scheme S3. Synthesis of compound **7**

To confirm that compound **6** is an intermediate in the reaction, we synthesized its analogue compound **7** by following three steps.

Step 1: A 100 mL round-bottomed flask with a magnetic stirring bar was charged with **S1** (2.0 g, 10.0 mmol) and K_2CO_3 (1.48 g, 10.7 mmol) and it was dissolved in 50 mL EtOH : acetone (1 : 1), and then HCHO (1.5 mL, 18.0 mmol) was added. The resulting mixture was stirred at room temperature for 4 h. More water was added and the mixture was extracted three times with EtOAc. The combined organic fractions were washed once with water, once with brine and dried over anhydrous Na_2SO_4, concentrated in vacuum, and the crude product was purified by flash column chromatography in SiO_2 using petroleum ether/EtOAc (100:1) as eluent, giving product **S2**.[1]

Step 2: To a solution of **S2** (1.2 g, 5.8mmol) in MeOH (60 mL) was added H_2O_2 (6.0 mL, 30% in water) slowly dropwised at 0 °C. then 6.0 mL aqueous NaOH solution (6 N) was slowly added into reaction mixture at 0 °C. The reaction suspension was monitored by TLC until no **S2** remained. The reaction mixture was poured into an $Na_2S_2O_3$ saturated solution and extracted with EtOAc. The combined organic fractions were washed once with water, once with brine and dried over anhydrous Na_2SO_4, concentrated in vacuum, the residue was purified by column chromatography (silica gel, petroleum ether/EtOAc = 50/1) to give product **S3**.[1]

Step 3: A 10 mL round-bottom flask with a magnetic stirring bar was charged with **S3** (1.0 g) and $HN(Et)_2$ (1.0 mL). The resulting mixture was stirred at room temperature for 8 h. The target product **7** can be obtained by concentrated in vacuum to remove diethyl amine without further purification (product **7** is unstable on silica gel plates).

UV-Vis absorption spectrum of the intermediate 7

The absorbance of compound **7** in toluene of varying concentrations was measured. Experimental results indicated that the primary absorbance peak for compound **7** occurred at 350 nm, with significant absorbance persisting above 400 nm at system concentrations. Additionally, the introduction of triethylamine **2a** had no effect on the absorption properties of compound **7**.

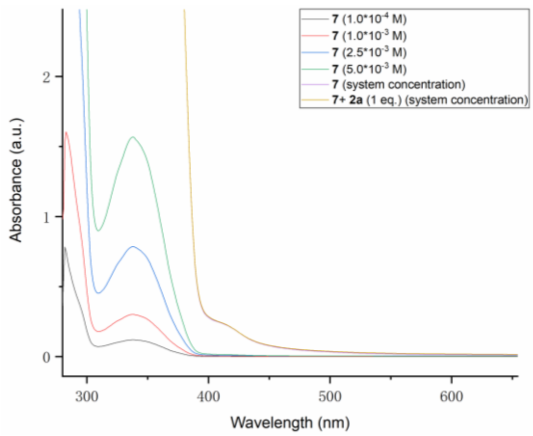
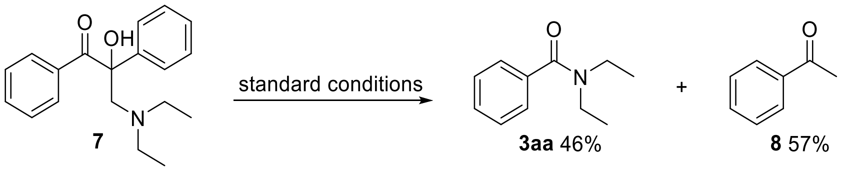


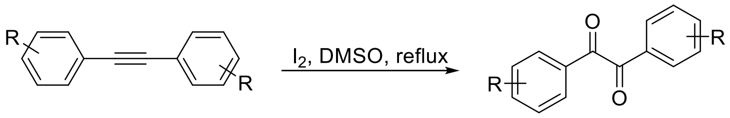
Figure S2. UV-vis absorption spectra

Intermediate experiment.



The compound (3-(diethylamino)-2-hydroxy-1,2-diphenylpropan-1-one) **7** was explored under standard conditions: The reaction was carried out with **7** (29.7 mg, 0.1 mmol) for 24 h. The corresponding product **3aa** (46% yield) and product **8** (57% yield) were obtained. This information further supports that the compound **6** is an important intermediate for this transformation.

IV. General procedure for the preparation of the starting materials



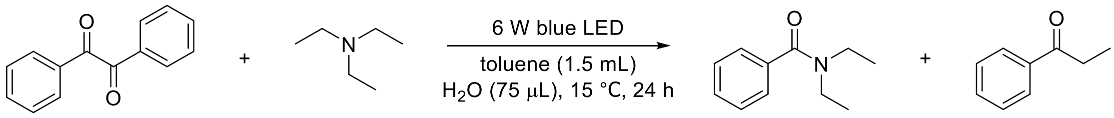
A typical procedure is shown[2]: A solution of diphenylacetylene compound (1.0 mmol) and I_2 (0.509 g, 2.0 mmol) were dissolved in DMSO (23 mL). The mixture was heated at reflux for three hours and allowed to cool down to room temperature. The reaction mixture was poured into an $Na_2S_2O_3$ saturated solution and extracted with DCM (20 mL). The combined organic fractions were washed once with water, once with brine and dried over anhydrous Na_2SO_4, concentrated in vacuum, the residue was purified by column chromatography (silica gel, petroleum ether/EtOAc = 50/1) to give diketone.

V. General procedure for the metathesis reaction of the benzil and triethylamine

The picture of reaction device in refrigerator

Parallel reaction device

The Blue LED (405 nm, 2 centimeters, 3 W × 2) were purchased from Taobao http://m.tb.cn/h.5AQKiK1LBYT3g5W?tk=dU8SWqULA64



1a **2a** **3aa** **4aa**

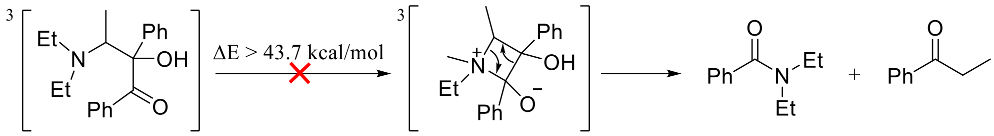
To a 20 mL glass tube with a stir bar were added benzil (0.15 mmol), triethylamine (0.1 mmol), toluene (1.5 mL) and H_2O (75 µL). Add the solid first and then the liquid. The tube was sealed with rubber plug and evacuated by three freeze-pump-thaw cycles and backfilled with ultra-purified argon. The reaction was stirred on an intensity of 6 W 405 nm LED lamp at 15 °C for 24 h. When the reaction was completed, the solvent was removed and the residue was purified by flash chromatography on silica gel to obtain the desired product.

VI. Computational Detail

All the calculations were carried out with Gaussian 16 software package.[3] Geometry optimizations were carried out at M06-2X[4]/6-31G(d)[5-7]/SMD[8](toluene) level of theory. Vibrational frequencies were also calculated for all stationary points to verify them as energy minima or transition states and to evaluate the zero-point vibrational energy (ZPVE) and thermal corrections. Intrinsic reaction coordinate (IRC)[9,10] calculations were carried out as well to confirm whether the transition states were connected with expected reactants and products. The single-point energies were computed at M06-2X/6-311G(d,p)/SMD(toluene) level of theory. Excited state geometry optimizations and single point calculations were performed using the time-dependent density functional theory (TDDFT) as the same level of ground state. The spin population analysis was conducted using Multiwfn 3.8 (dev)[11] and visualized with VMD 1.9.3[12].

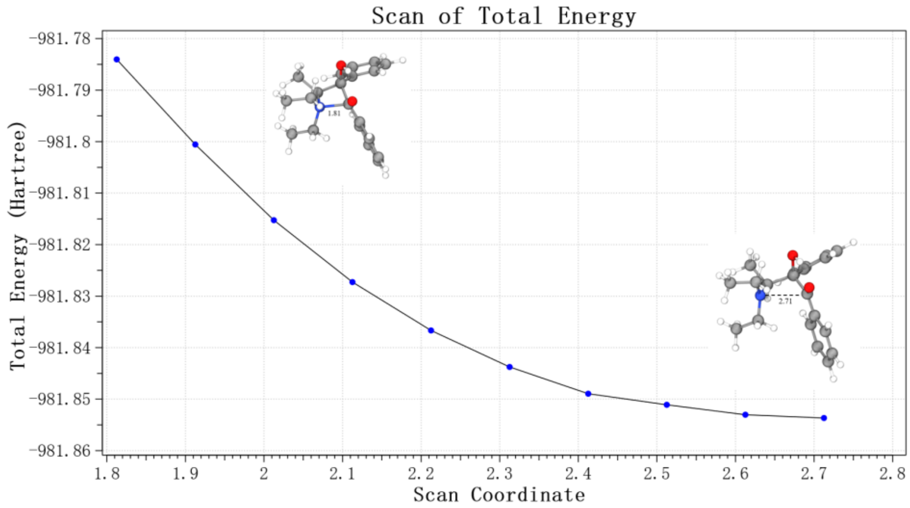
(1) Investigate the four-membered ring transition state mechanism

We also explored the feasibility of a four-membered ring transition state mechanism. Computational results indicate that such a four-membered ring intermediate is not stable and requires more than 43.7 kcal/mol to form, rendering this pathway less likely.



^{3}**IM2-T1**

Figure S3. four-membered ring transition state mechanism



(2) Summary of electronic energies and Gibbs free energies

Geometry	Electronic Energy	Thermal Correction to Free Energy	Gibbs Free Energy
^{1}R1	-689.85731	0.16271	-689.69460
^{1}R1-S1	-689.75988	0.16005	-689.59983
^{3}R1-T1	-689.76418	0.15808	-689.60610
^{3}TS1	-982.13079	0.35547	-981.77532
^{1}R2	-292.34505	0.17487	-292.17019
^{3}IM1	-982.14298	0.35524	-981.78774
^{1}IM2	-982.22474	0.36627	-981.85847
^{1}IM2-S1	-982.10743	0.36375	-981.74368
^{3}IM2-T1	-982.12095	0.36143	-981.75952
^{3}TS2	-982.09240	0.35992	-981.73247
^{3}IM3	-982.11420	0.36607	-981.74813
^{3}TS3	-982.10067	0.36205	-981.73863
^{3}IM4	-424.03053	0.12726	-423.90327
^{1}IM5	-424.12088	0.13412	-423.98675
H_2O	-76.41646	0.00375	-76.41270
^{1}TS4	-424.02586	0.12887	-423.89699
^{1}TS5	-500.50207	0.15215	-500.34992
^{1}TS6	-576.95024	0.17351	-576.77673
^{1}P2	-424.14086	0.13426	-424.00660
^{1}P1	-558.10108	0.20523	-557.89585

(3) Cartesian coordinate

^{1}R1

C	-4.46533200	0.34199200	-0.78638100
C	-3.45017700	1.27860100	-0.96575900
C	-2.17077900	1.02275500	-0.48229300
C	-1.90648800	-0.18053500	0.18038600
C	-2.92858100	-1.12170400	0.35191300
C	-4.20462400	-0.85947600	-0.12612400
H	-5.46324300	0.54732000	-1.16220100
H	-3.65508800	2.21205000	-1.48016300
H	-1.38653600	1.75945100	-0.61590900
H	-2.70089200	-2.05144100	0.86359700
H	-4.99703500	-1.58829600	0.01202000
C	-0.55221100	-0.53558400	0.68167200
O	-0.28957700	-1.62238400	1.15776500

C	0.55222100	0.53565500	0.68165600
O	0.28962100	1.62245100	1.15777700
C	1.90648800	0.18056900	0.18037800
C	2.17074300	-1.02275600	-0.48225100
C	2.92860700	1.12171500	0.35187200
C	3.45013200	-1.27865500	-0.96571300
H	1.38647700	-1.75943600	-0.61582800
C	4.20464100	0.85943300	-0.12615900
H	2.70094500	2.05147700	0.86352400
C	4.46531300	-0.34206600	-0.78637400
H	3.65501500	-2.21213000	-1.48007900
H	4.99707400	1.58823500	0.01195600
H	5.46321700	-0.54743700	-1.16218800

[1]R1-S1

C	-4.70810000	-0.25402600	-0.00123400
C	-3.83458300	-1.20235100	0.52447100
C	-2.46215400	-0.96933500	0.53799000
C	-1.96101900	0.22446900	0.01292300
C	-2.84137300	1.19007600	-0.49499800
C	-4.20754400	0.94381700	-0.50912400
H	-5.77674100	-0.44524800	-0.01037600
H	-4.21998800	-2.12877800	0.93837600
H	-1.79623800	-1.70810200	0.96684800
H	-2.44164100	2.11856300	-0.88856700
H	-4.88272100	1.68807500	-0.91989300
C	-0.50536200	0.55781300	-0.00100500
O	-0.13795300	1.73687100	-0.06298300
C	0.50532100	-0.55765100	-0.00055100
O	0.13788800	-1.73667000	-0.06302800
C	1.96100500	-0.22438000	0.01319600
C	2.46233500	0.96937300	0.53820000
C	2.84120500	-1.19008300	-0.49480900
C	3.83478700	1.20224400	0.52451200
H	1.79656600	1.70820400	0.96716600
C	4.20740000	-0.94396700	-0.50910900
H	2.44133100	-2.11853800	-0.88831200
C	4.70814300	0.25382900	-0.00129600
H	4.22034000	2.12862800	0.93837600
H	4.88244900	-1.68830300	-0.91994800
H	5.77680200	0.44493800	-0.01056600

[3]R1-T1

C	-4.70877300	-0.24979100	0.00036300
C	-3.83744000	-1.20330400	0.52014500
C	-2.46444900	-0.97470300	0.53313700
C	-1.95892700	0.21983800	0.01299300
C	-2.83847100	1.19162300	-0.48673900
C	-4.20495400	0.94955700	-0.50151100
H	-5.77802100	-0.43751300	-0.00836100
H	-4.22537300	-2.13059700	0.92968700
H	-1.79996600	-1.71722100	0.95707700
H	-2.43605200	2.12142100	-0.87456400
H	-4.87830800	1.69803100	-0.90753500
C	-0.50786400	0.55578000	-0.00262500
O	-0.13103800	1.73109100	-0.06905800
C	0.50783900	-0.55566300	-0.00254000
O	0.13096900	-1.73096100	-0.06888900
C	1.95892200	-0.21978100	0.01304800
C	2.46454300	0.97472300	0.53318700
C	2.83839600	-1.19162800	-0.48668700
C	3.83754900	1.20323200	0.52016300
H	1.80012900	1.71728100	0.95716400
C	4.20489400	-0.94965500	-0.50149300
H	2.43590600	-2.12140200	-0.87449500
C	4.70880600	0.24966100	0.00036100
H	4.22555500	2.13049600	0.92970400
H	4.87818900	-1.69817700	-0.90752700
H	5.77806700	0.43731000	-0.00838400

[3]TS1

Imaginary frequency = -196.77 cm^{-1}

C	-3.54295900	-2.53417100	-0.09649300
C	-2.63381200	-2.63639900	0.95676000
C	-1.35072900	-2.10820000	0.84673300
C	-0.94727400	-1.44938200	-0.33085300
C	-1.87730200	-1.35344600	-1.38432900
C	-3.15258700	-1.89467900	-1.27322700
H	-4.53922300	-2.95651600	-0.00535700
H	-2.92505300	-3.13691300	1.87604200
H	-0.64833200	-2.20518300	1.66343100
H	-1.56942200	-0.86765200	-2.30558900
H	-3.84255700	-1.82427200	-2.10981400
C	0.38089700	-0.82473800	-0.53336800
O	0.47603700	0.14004500	-1.39553700
C	1.54775300	-1.27212200	0.20679300
O	1.46558200	-2.16088700	1.07836500
C	2.88902700	-0.61974800	-0.01570500
C	3.28066500	0.05840800	-1.17820700

C	3.82136300	-0.75940600	1.02177000
C	4.56497300	0.58769500	-1.28533100
H	2.58243700	0.16497200	-1.99759300
C	5.09695000	-0.21846800	0.91856900
H	3.52067100	-1.30901900	1.90758600
C	5.47458700	0.46035300	-0.23890700
H	4.85590100	1.10189700	-2.19711400
H	5.80047800	-0.33112900	1.73864800
H	6.47241100	0.88057900	-0.32661600
N	-1.84666000	1.63600000	0.33339200
C	-1.38517100	1.96335000	-0.94332900
H	-2.21187000	2.06437300	-1.64527000
H	-0.70177300	1.01669300	-1.29265800
C	-3.18074900	1.10415600	0.60272900
H	-3.48583000	1.53116800	1.56638700
H	-3.08767400	0.01939300	0.75153300
C	-0.90917700	1.56502600	1.45098000
H	0.09388200	1.39886400	1.04866300
H	-1.17664400	0.68366800	2.04368000
C	-0.38537400	3.11149600	-1.03960800
H	0.51338500	2.92758100	-0.44591900
H	-0.07171300	3.20466100	-2.08207100
H	-0.83749600	4.05833500	-0.72627600
C	-0.95567000	2.82541300	2.31311700
H	-1.96165500	2.99454400	2.70888000
H	-0.27132700	2.71135400	3.15807000
H	-0.65394900	3.70673600	1.74157600
C	-4.22572000	1.40580600	-0.45427400
H	-4.00894400	0.90024000	-1.39827000
H	-5.18954400	1.03372300	-0.09654500
H	-4.32063600	2.48097400	-0.63469300

[1]R2

N	0.00010800	-0.00064700	0.00058100
C	0.41740900	1.32943900	0.44529400
H	1.50987700	1.37611500	0.39957700
H	0.14242900	1.49570700	1.50405500
C	0.94410800	-1.02664000	0.44508500
H	0.43945800	-1.99668500	0.40010200
H	1.22602800	-0.87093900	1.50361000
C	-1.36044700	-0.30415200	0.44575600
H	-1.94647800	0.61909100	0.40157500
H	-1.36659100	-0.62674000	1.50412100
C	-0.14990900	2.43747400	-0.43278500
H	-1.24407000	2.45750800	-0.41545500
H	0.20423300	3.41608800	-0.09318900
H	0.16785600	2.29027000	-1.46908200
C	-2.03833300	-1.34746700	-0.43325300
H	-1.51002100	-2.30582600	-0.41782200
H	-3.06287800	-1.52914400	-0.09306100
H	-2.07021100	-0.99715800	-1.46903600
C	2.18713500	-1.08848200	-0.43337300
H	2.75057500	-0.15030200	-0.41673500
H	2.85855900	-1.88358900	-0.09357900
H	1.90070300	-1.29090300	-1.46949000

[3]IM1

C	-3.46383200	-2.66743100	-0.12239100
C	-2.56071400	-2.78720600	0.93287300
C	-1.29297300	-2.22159900	0.85204100
C	-0.90525300	-1.50929100	-0.29881500
C	-1.82746900	-1.39659900	-1.35841200
C	-3.08745200	-1.97417400	-1.27233000
H	-4.45006500	-3.11602900	-0.05280800
H	-2.84541500	-3.32588700	1.83176300
H	-0.59643300	-2.32126100	1.67318000
H	-1.53976600	-0.87576500	-2.26710600
H	-3.77580200	-1.88838800	-2.10796500
C	0.40063300	-0.86323500	-0.43786200
O	0.51108600	0.18120000	-1.26476600
C	1.60014300	-1.30669400	0.24293200
O	1.55168900	-2.23371000	1.06492600
C	2.91641000	-0.61401600	0.01265100
C	3.31278300	-0.03537100	-1.19852400
C	3.81763300	-0.62917600	1.08379500
C	4.58074400	0.52646800	-1.32346500
H	2.63987200	-0.03332700	-2.04685100
C	5.07559000	-0.05160100	0.96260600
H	3.51288500	-1.10664000	2.00947300
C	5.46069800	0.52943600	-0.24425500
H	4.88183000	0.96289900	-2.27118800
H	5.75878500	-0.06025500	1.80668400
H	6.44522400	0.97665300	-0.34509800
N	-1.92518800	1.76985000	0.30986900
C	-1.58641900	2.03367300	-1.00382200
H	-2.43004900	1.98416700	-1.68605400
H	-0.36653200	0.67756300	-1.34397200
C	-3.15141000	1.06701300	0.67957400

H	-3.43008300	1.43132600	1.67622100
H	-2.94680300	-0.00837400	0.78205500
C	-0.90388700	1.77999000	1.35373600
H	0.08462200	1.70058200	0.89189900
H	-1.03589700	0.87657500	1.96348600
C	-0.59097900	3.12960800	-1.28754000
H	0.37147400	2.97540900	-0.78792800
H	-0.39242400	3.17272100	-2.36221800
H	-0.96862300	4.11693400	-0.97874000
C	-0.98426500	3.02669600	2.22870200
H	-1.97554000	3.12216400	2.68352600
H	-0.24338800	2.97875700	3.03272400
H	-0.79370300	3.92672200	1.63659600
C	-4.31857600	1.27897100	-0.26939700
H	-4.14654800	0.81111000	-1.24232600
H	-5.21095800	0.81672800	0.16249200
H	-4.52098100	2.34397800	-0.42078900

[1]IM2

C	4.65646900	-0.32143700	0.69999800
C	3.68600000	-0.58632300	1.66024000
C	2.35449700	-0.76580300	1.28525500
C	1.97749400	-0.68642000	-0.05700400
C	2.96454000	-0.42917300	-1.01450900
C	4.29039600	-0.24235500	-0.64280700
H	5.69193300	-0.17942800	0.99391700
H	3.96072900	-0.65695900	2.70845600
H	1.61703400	-0.96510100	2.05713700
H	2.68347800	-0.38225500	-2.06352300
H	5.03949600	-0.03734700	-1.40160200
C	0.54583700	-0.88338400	-0.56921800
O	0.57830400	-1.92249600	-1.52748600
C	0.06404600	0.39360200	-1.31380600
O	-0.09310200	0.31303600	-2.52057900
C	-0.23323000	1.67262400	-0.60331400
C	0.33843000	2.04174000	0.61741200
C	-1.16748700	2.52178800	-1.20902300
C	-0.02352100	3.24401500	1.22172600
H	1.08235300	1.41181300	1.09121400
C	-1.53729900	3.71187000	-0.59678200
H	-1.60485200	2.22296500	-2.15615100
C	-0.96388200	4.07611500	0.62158800
H	0.43450700	3.52910300	2.16372500
H	-2.27188500	4.35742700	-1.06814800
H	-1.24893800	5.00827800	1.10002600
N	-1.83650100	-0.79232900	0.02876300
C	-0.51993800	-1.20002000	0.51478900
H	-0.31548900	-0.54142400	1.36699700
H	0.35430000	-1.49566200	-2.37801800
C	-2.52068300	-1.62863100	-0.94931000
H	-1.75412300	-2.14478000	-1.53160700
C	-2.67459600	-0.06373100	0.96678900
H	-3.61124600	0.17038600	0.44623800
C	-0.41612100	-2.65713900	0.97153300
H	-1.10163200	-2.84873200	1.80242100
H	-0.66311600	-3.33063600	0.14740900
H	0.60087800	-2.90195600	1.29449000
H	-3.04720200	-0.96329700	-1.64907900
H	-2.19347100	0.90174100	1.18220100
C	-3.52657900	-2.64982500	-0.40833900
H	-4.36244100	-2.15782900	0.09967900
H	-3.94386500	-3.23148500	-1.23768500
H	-3.06150900	-3.34729800	0.29499000
C	-2.98272500	-0.75355300	2.30038700
H	-3.63080000	-0.11447600	2.91023900
H	-3.48409900	-1.71546600	2.16224400
H	-2.06604400	-0.92936100	2.87396800

[1]IM2-S1

C	4.48659900	-1.16706800	0.54791200
C	3.52462300	-1.22741600	1.54885700
C	2.16897700	-1.15021600	1.22782600
C	1.75566200	-1.01062900	-0.09807600
C	2.73406400	-0.95847800	-1.09785100
C	4.08418300	-1.02986100	-0.78017000
H	5.54154100	-1.22472900	0.79796100
H	3.82222700	-1.33399800	2.58774400
H	1.44766100	-1.19037100	2.03935100
H	2.41848500	-0.85734400	-2.13161500
H	4.82538900	-0.97840400	-1.57212000
C	0.31106800	-0.89953400	-0.58943600
O	0.12090800	-1.84440700	-1.59405200
C	-0.08568400	0.46126600	-1.21535900
O	-0.75945800	0.30950900	-2.30189900
C	0.10352900	1.73112400	-0.58939600
C	0.72051400	1.94810400	0.67674100
C	-0.44933400	2.87910500	-1.23388200
C	0.77184400	3.21535300	1.24069800

H	1.18134700	1.12493200	1.20875700
C	-0.38667800	4.13115200	-0.65581900
H	-0.92412300	2.73278200	-2.19777300
C	0.22128100	4.32347600	0.59403600
H	1.25775500	3.34059900	2.20528200
H	-0.81770100	4.98041700	-1.18056200
H	0.26881500	5.30955500	1.04365500
N	-2.03445700	-0.78709400	0.19267800
C	-0.73386000	-1.21386200	0.60477100
H	-0.45576400	-0.57943100	1.45001200
H	-0.32648700	-1.27142900	-2.28876200
C	-2.78542100	-1.49754200	-0.82245300
H	-2.11857900	-2.21271400	-1.29856400
C	-2.63335900	0.38258700	0.79646900
H	-3.49939200	0.66532900	0.19539300
C	-0.72081800	-2.69601100	0.98525900
H	-1.38370900	-2.88179500	1.83606000
H	-1.02468900	-3.32006000	0.14341100
H	0.29310700	-2.99133100	1.25905900
H	-3.07849600	-0.74755100	-1.56486500
H	-1.89531900	1.19175000	0.75189500
C	-4.01776600	-2.19227700	-0.23150000
H	-4.71098800	-1.47253200	0.21234500
H	-4.53862300	-2.71444600	-1.03716700
H	-3.72958700	-2.92401300	0.52783900
C	-3.03483800	0.12413900	2.25470900
H	-3.48671700	1.03450000	2.65428700
H	-3.75991700	-0.69048300	2.32882400
H	-2.16415600	-0.12087300	2.86840500

^{3}IM2-T1

C	4.42444500	-1.36398400	0.53156600
C	3.46520300	-1.40127700	1.53601700
C	2.11235700	-1.26335900	1.22274900
C	1.69964500	-1.08532000	-0.09860700
C	2.67522600	-1.05427500	-1.10163800
C	4.02238500	-1.18739000	-0.79218800
H	5.47720800	-1.46891000	0.77539900
H	3.76263700	-1.53691000	2.57158600
H	1.39267600	-1.28706500	2.03651600
H	2.35899300	-0.92156100	-2.13181400
H	4.76194400	-1.15255000	-1.58658700
C	0.25677800	-0.91513200	-0.57729200
O	0.01928400	-1.83755100	-1.59510600
C	-0.07386100	0.47789300	-1.19790300
O	-0.74302000	0.36541300	-2.29219900
C	0.18010800	1.72951200	-0.56964800
C	0.80220300	1.90897500	0.70346500
C	-0.28466800	2.91458300	-1.22191100
C	0.94391300	3.17065600	1.26039200
H	1.19461800	1.05514100	1.24377400
C	-0.13217300	4.16095400	-0.64900700
H	-0.76353500	2.80110700	-2.18851900
C	0.48286800	4.31506600	0.60293800
H	1.43035300	3.26486900	2.22862600
H	-0.49651000	5.03713100	-1.18081000
H	0.60147800	5.29762800	1.04789600
N	-2.08002900	-0.70662500	0.19144300
C	-0.78722600	-1.19464900	0.60607900
H	-0.49427400	-0.57739400	1.45974700
H	-0.39028200	-1.23007900	-2.28658600
C	-2.85702800	-1.36725300	-0.84555900
H	-2.21848600	-2.10700300	-1.32401600
C	-2.61863800	0.49169800	0.80857700
H	-3.44629700	0.84667700	0.19089400
C	-0.85358900	-2.67617900	0.97928900
H	-1.54169800	-2.83580400	1.81530600
H	-1.16679800	-3.28065100	0.12648500
H	0.14006300	-3.01966700	1.27305700
H	-3.10586300	-0.59255200	-1.57832800
H	-1.82234100	1.24672000	0.80295600
C	-4.12331900	-2.00684600	-0.26701500
H	-4.78706300	-1.25886800	0.17555100
H	-4.66112500	-2.49991700	-1.08057900
H	-3.87548000	-2.75677100	0.48920800
C	-3.07391100	0.21501100	2.24649100
H	-3.46751500	1.14387800	2.66649300
H	-3.85871300	-0.54491800	2.27973800
H	-2.23820500	-0.11115300	2.87157300

^{3}TS2

Imaginary frequency = -279.09 cm^{-1}

C	4.66522700	-0.20572800	0.71473800
C	3.65813900	-0.25964700	1.67652200
C	2.34307200	-0.51128800	1.30128400
C	2.01788100	-0.72808100	-0.04654000
C	3.04339200	-0.67754800	-1.00461000
C	4.35314800	-0.41382000	-0.62797100

H	5.68952300	-0.00156200	1.01114100
H	3.89611000	-0.10527000	2.72429500
H	1.57697600	-0.54586300	2.06914200
H	2.78904100	-0.83445900	-2.04736000
H	5.13234500	-0.36752200	-1.38224600
C	0.63705100	-0.98829400	-0.53931700
O	0.68631900	-1.98808100	-1.47463200
C	0.14881200	0.50743000	-1.57895500
O	-0.52173600	0.01881200	-2.50156200
C	-0.22223900	1.67672000	-0.78768300
C	0.54245000	2.19591900	0.27179600
C	-1.38044200	2.37771900	-1.19105300
C	0.13953200	3.35444900	0.92439900
H	1.46050400	1.70407500	0.57158800
C	-1.76325600	3.54070000	-0.53926400
H	-1.96901700	1.97777600	-2.01043700
C	-1.01346600	4.03440500	0.52971300
H	0.74086200	3.73748100	1.74399800
H	-2.66007300	4.06285500	-0.86135800
H	-1.31711200	4.94221200	1.04136600
N	-1.82745500	-0.84861800	0.05541400
C	-0.49445400	-1.12311000	0.52123400
H	-0.28464700	-0.35173700	1.26914600
H	-0.04608800	-1.83231300	-2.10039600
C	-2.52066900	-1.80452700	-0.79267300
H	-1.76984400	-2.42226000	-1.29273600
C	-2.64647100	0.00090600	0.90542300
H	-3.58817900	0.17854700	0.37164600
C	-0.32758000	-2.51598200	1.16864500
H	-1.00674000	-2.60635100	2.02118600
H	-0.56435900	-3.30132300	0.44591100
H	0.69628700	-2.68622100	1.51474600
H	-3.03478500	-1.24618400	-1.58731100
H	-2.15547200	0.97859700	0.99339800
C	-3.52825100	-2.73230900	-0.10734400
H	-4.35468100	-2.16748500	0.33532200
H	-3.95793900	-3.41956700	-0.84415600
H	-3.05812300	-3.32785100	0.68165000
C	-2.93722200	-0.51967900	2.31767900
H	-3.57404900	0.19304000	2.85309600
H	-3.44190800	-1.48966000	2.30982700
H	-2.01104500	-0.62389000	2.89406300

^{3}IM3

C	4.56285000	-1.42011500	0.47836300
C	3.58967400	-1.30465100	1.47202200
C	2.24688800	-1.20589300	1.14241800
C	1.82695600	-1.21212000	-0.21229800
C	2.83071000	-1.33348400	-1.20695400
C	4.16722100	-1.43359600	-0.86170700
H	5.61230100	-1.49763700	0.74370000
H	3.88179300	-1.29309100	2.51816300
H	1.52186200	-1.12299100	1.94670000
H	2.52834900	-1.34033000	-2.24755400
H	4.91415100	-1.52166600	-1.64557300
C	0.45999600	-1.10802100	-0.60871600
O	0.16971900	-1.29817400	-1.91842500
C	-1.36198600	0.91603500	-0.89576500
O	-1.49351300	0.76519500	-2.14345600
C	-0.52722200	1.90631000	-0.27541700
C	-0.08043500	1.99872800	1.07277900
C	-0.07053900	2.92793100	-1.16001900
C	0.73417200	3.04348200	1.49081800
H	-0.34657300	1.25557500	1.81587900
C	0.73603100	3.95996100	-0.72523400
H	-0.37756500	2.86892300	-2.19767800
C	1.14963000	4.03879100	0.61033900
H	1.05632900	3.06901400	2.52836600
H	1.05671400	4.71563900	-1.43736200
H	1.78704600	4.84874300	0.94908600
N	-1.88683400	-0.31153800	-0.04551300
C	-0.66004700	-1.13816400	0.40780000
H	-0.30939100	-0.63157600	1.30391000
H	-0.44551300	-0.58193100	-2.23446600
C	-2.80188300	-1.11426500	-0.96410100
H	-2.15263400	-1.69841400	-1.61433400
C	-2.71328500	0.27123800	1.09092800
H	-3.69057900	0.47787300	0.65002100
C	-0.95965300	-2.60009500	0.75835700
H	-1.72871800	-2.71894300	1.52249800
H	-1.23138700	-3.17618000	-0.12970000
H	-0.03153400	-3.02668300	1.15119400
H	-3.28856500	-0.36709000	-1.58776400
H	-2.28050800	1.23628800	1.33505300
C	-3.86084500	-2.00085300	-0.32293300
H	-4.59170600	-1.43477600	0.25912900
H	-4.40660600	-2.46193100	-1.15233200
H	-3.46583400	-2.80778400	0.29299400

C	-2.85306500	-0.54981400	2.36289700
H	-3.44032600	0.05011900	3.06488700
H	-3.37533000	-1.49639100	2.21811100
H	-1.88860200	-0.74859600	2.83925800

[3]TS3

Imaginary frequency = -387.60 cm^{-1}

C	4.06222600	-1.49743300	0.53150500
C	3.16311700	-1.33975800	1.58628900
C	1.79619500	-1.36465100	1.35385300
C	1.29071200	-1.54924200	0.04878600
C	2.21391700	-1.72065800	-1.00516300
C	3.57805600	-1.69070100	-0.76329800
H	5.13142100	-1.47369300	0.71787900
H	3.53197200	-1.19713600	2.59767200
H	1.11619200	-1.25792600	2.19373300
H	1.83361500	-1.86440500	-2.01001900
H	4.27203900	-1.81452400	-1.58926900
C	-0.12085300	-1.55915900	-0.24736100
O	-0.50522500	-1.96605800	-1.47969800
C	-0.93649400	0.87296600	-1.02753700
O	-0.98251800	0.48831600	-2.23759200
C	0.22669100	1.54763700	-0.47704900
C	0.55926500	1.69435100	0.89154200
C	1.16368500	2.03636400	-1.42121600
C	1.74057500	2.31479400	1.27958300
H	-0.07970800	1.28918700	1.67008400
C	2.33444800	2.65515000	-1.02225000
H	0.93736600	1.90360900	-2.47312600
C	2.63652400	2.80851200	0.33477600
H	1.96849900	2.39726000	2.33904300
H	3.02727500	3.01953400	-1.77585500
H	3.55718500	3.29149100	0.64608800
N	-1.99408000	0.37568400	-0.14358200
C	-1.16875500	-1.20717800	0.70239700
H	-0.79403500	-0.73834700	1.60629200
H	-0.73743500	-1.14007500	-2.01099300
C	-3.13445900	-0.12710700	-0.99272700
H	-2.79221300	-1.03808700	-1.48076300
C	-2.48912500	1.42623700	0.80882200
H	-3.34067000	1.90850100	0.31967200
C	-2.20753700	-2.26739700	0.96237400
H	-2.96654300	-1.93754100	1.67369900
H	-2.68267100	-2.61789100	0.04316100
H	-1.69845100	-3.13244700	1.40850300
H	-3.26947500	0.61670400	-1.78136100
H	-1.72484900	2.19270100	0.89748300
C	-4.47215200	-0.36949100	-0.30531200
H	-4.90436900	0.53726200	0.12477200
H	-5.16220100	-0.71100800	-1.08344000
H	-4.44582200	-1.14037300	0.46383300
C	-2.89012500	0.93620400	2.19161300
H	-3.30549300	1.78334100	2.74617900
H	-3.65226700	0.15523100	2.15999900
H	-2.03433200	0.56413900	2.76236100

[3]IM4

C	-2.91568300	-0.46925100	0.12555500
C	-1.95581800	-1.46409000	-0.09034100
C	-0.61738100	-1.14158300	-0.21394200
C	-0.17356900	0.20621600	-0.12244200
C	-1.16553900	1.20196500	0.08658200
C	-2.50323900	0.86172500	0.20831700
H	-3.96521100	-0.72689900	0.22138800
H	-2.26100400	-2.50415500	-0.16237600
H	0.11805600	-1.92341000	-0.38164100
H	-0.90408300	2.25685600	0.13184900
H	-3.23741400	1.64712000	0.36383600
C	1.21011200	0.50418900	-0.23894000
O	1.69777500	1.76431500	-0.07622200
C	2.24852800	-0.49172600	-0.51583400
H	2.60421700	-0.60370000	-1.53784700
H	0.99699000	2.35679200	0.23885000
C	3.07135200	-1.04992500	0.59985000
H	3.64183400	-1.92684600	0.28071300
H	3.79128900	-0.30437100	0.97112700
H	2.44054300	-1.33102700	1.45103600

[1]IM5

C	-3.03009900	-0.23748400	-0.07363400
C	-2.22026400	-1.33692600	0.20922300
C	-0.83913500	-1.19375600	0.26790600
C	-0.24216800	0.05035800	0.02929800
C	-1.06384200	1.15020300	-0.24782900
C	-2.44741800	1.00620300	-0.30009400
H	-4.10911600	-0.35051100	-0.11233700
H	-2.66853600	-2.30741800	0.39981100
H	-0.21364900	-2.04438900	0.52184200

H	-0.61412000	2.11796400	-0.45341900
H	-3.06946900	1.86715700	-0.52573800
C	1.22926200	0.22131800	0.07810900
O	1.67687400	1.46030100	0.46348600
C	2.11047600	-0.71719900	-0.28631000
H	1.71579300	-1.64566300	-0.68831800
H	1.01772400	1.85664000	1.05391200
C	3.59661500	-0.54973100	-0.22238300
H	4.06573800	-1.40762200	0.27259800
H	4.03432000	-0.48306900	-1.22595200
H	3.86575600	0.35659600	0.32401000

H_2O

O	0.00000000	0.00000000	0.11913300
H	0.00000000	0.76144700	-0.47653000
H	0.00000000	-0.76144700	-0.47653000

^{1}TS4

Imaginary frequency = -2256.66 cm^{-1}

C	2.97652800	-0.36277400	0.12028400
C	2.51372100	0.95330600	0.13793900
C	1.15393200	1.20991900	0.02062400
C	0.25078700	0.14575900	-0.09843700
C	0.71988000	-1.17329000	-0.11004800
C	2.08236400	-1.42539700	-0.00636300
H	4.04085800	-0.56131100	0.20437000
H	3.21595600	1.77532300	0.23329100
H	0.77338300	2.22625300	0.01442100
H	0.00946500	-1.99105500	-0.18841300
H	2.44839000	-2.44698100	-0.01613000
C	-1.18542600	0.41589600	-0.18835200
O	-1.63764300	1.61037100	0.02583400
C	-2.26770300	-0.42930200	-0.57137600
H	-2.58865200	1.04063600	-0.54651400
H	-2.04077600	-1.24593500	-1.25776300
C	-3.26983900	-0.81988400	0.52032900
H	-4.25126400	-1.02921900	0.08495500
H	-2.95260100	-1.71926100	1.06492100
H	-3.39907600	-0.01681100	1.25258500

^{1}TS5

Imaginary frequency = -1878.73 cm^{-1}

C	3.43116800	0.04193700	0.16275600
C	2.71426900	1.23493500	0.22789800
C	1.32993000	1.22340200	0.09161100
C	0.65163700	0.01669700	-0.10865300
C	1.37992400	-1.17556600	-0.18712000
C	2.76235500	-1.16339400	-0.04730800
H	4.51181600	0.05206000	0.26960300
H	3.23486400	2.17581500	0.37716800
H	0.77642200	2.15688000	0.11785000
H	0.84236000	-2.10257900	-0.35542300
H	3.32065500	-2.09295600	-0.10161100
C	-0.82724600	-0.03165000	-0.26961800
O	-1.31578500	-1.09585400	-0.80643300
C	-1.68242000	0.94359100	0.28629800
H	-1.20503300	1.73021800	0.86312400
H	-2.31574500	-1.34227400	-0.04507900
C	-2.94528000	1.35705500	-0.46115000
H	-3.79355100	1.53565000	0.20986700
H	-2.77870600	2.28445200	-1.02025500
H	-3.23672100	0.58881700	-1.18407800
O	-2.93665200	-1.21699300	0.93071200
H	-2.36575000	-0.15421400	1.00503200
H	-3.85713900	-1.01113300	0.70129200

^{1}TS6

Imaginary frequency = -1313.89 cm^{-1}

C	3.73807900	-0.19465000	0.27578500
C	3.15604000	1.07111000	0.27489700
C	1.79523700	1.21475700	0.02055000
C	0.99994700	0.09307300	-0.23469100
C	1.59706600	-1.17163300	-0.25023000
C	2.95531500	-1.31668200	0.00936300
H	4.80001600	-0.30512700	0.47447400
H	3.76475900	1.95020800	0.46404000
H	1.35762700	2.20770000	-0.00536600
H	0.97573700	-2.03249500	-0.47370800
H	3.40575500	-2.30481400	0.00065400
C	-0.47260500	0.18846800	-0.51448800
O	-0.98149200	-0.80062200	-1.14487400
C	-1.22446900	1.25427700	0.00137800
H	-0.67622800	2.06886700	0.46560500
H	-2.24834000	-1.15934300	-0.70956500
C	-2.56388300	1.60691200	-0.61965600
H	-2.57018800	2.64699800	-0.96178800
H	-2.75761400	0.97621000	-1.49406100
H	-3.41377700	1.50022600	0.06928400

O	-2.41937200	-0.23525500	1.82968600
H	-1.84262300	-0.78240700	2.39028800
H	-1.75164600	0.43081800	1.19378400
O	-3.12252000	-1.43712700	-0.13731000
H	-3.89192800	-1.00597600	-0.54127600
H	-2.84883900	-0.88061700	0.97017800

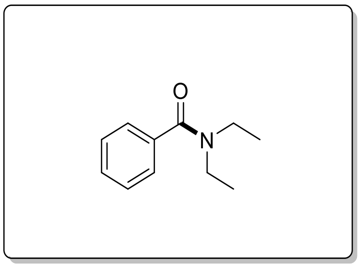
[1]P2

C	-3.04150500	-0.27100300	0.00006900
C	-2.18640500	-1.37030800	0.00007900
C	-0.80729100	-1.18024300	0.00003400
C	-0.27597200	0.11290000	-0.00000800
C	-1.14156200	1.21153000	-0.00001500
C	-2.51739300	1.02169200	0.00002900
H	-4.11699600	-0.42106100	0.00008800
H	-2.59299000	-2.37686900	0.00008900
H	-0.15097000	-2.04513200	0.00002500
H	-0.71197000	2.20814200	-0.00007200
H	-3.18367100	1.87891300	0.00007100
C	1.20238000	0.37652600	-0.00015400
O	1.62287200	1.51695400	-0.00003100
C	2.15212500	-0.80716800	-0.00038900
H	1.92389900	-1.42829800	-0.87627200
H	1.92324200	-1.42925000	0.87458200
C	3.61191100	-0.37992100	0.00036700
H	4.26697200	-1.25521800	-0.00025600
H	3.84107600	0.22534200	-0.88025800
H	3.84069800	0.22376700	0.88217900

[1]P1

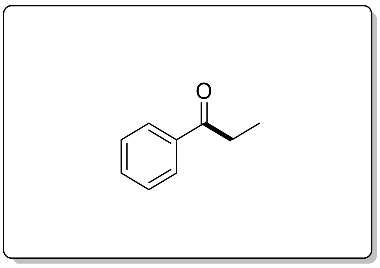
C	0.34741600	-1.03931100	-0.17320200
O	0.46658900	-2.22116200	-0.46638900
C	-1.02497700	-0.42672000	-0.10909500
C	-1.34613400	0.73799900	-0.80814100
C	-2.02091800	-1.11022200	0.59148500
C	-2.64955400	1.22804600	-0.78721600
H	-0.58205300	1.23770400	-1.39532500
C	-3.31759100	-0.60867800	0.62860700
H	-1.76773400	-2.03489800	1.10124900
C	-3.63289400	0.56220700	-0.05942000
H	-2.89797700	2.12629200	-1.34428000
H	-4.08577200	-1.13591300	1.18603800
H	-4.64744000	0.94849500	-0.03753000
N	1.42637300	-0.22166200	0.06930500
C	2.73804300	-0.87101400	-0.01730800
H	2.65221000	-1.65515500	-0.76902800
C	1.32676400	0.92664100	0.98029200
H	2.07047300	0.77260200	1.77315400
H	2.96001900	-1.36693700	0.93934900
H	0.34853400	0.90386800	1.46597200
C	3.86749200	0.08133800	-0.38140700
H	4.04597000	0.83357800	0.39285900
H	4.79193700	-0.49174000	-0.50063600
H	3.65975100	0.59343800	-1.32584300
C	1.53991900	2.29334600	0.33704100
H	1.54591600	3.06340600	1.11549700
H	2.48723400	2.35045100	-0.20293700
H	0.73620700	2.53395000	-0.36237300

VII. Analytical data



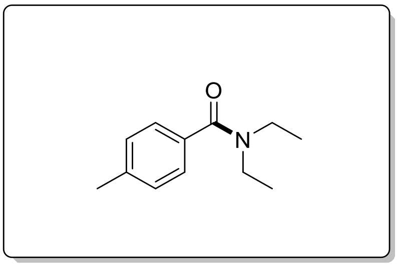
3aa: *N*,*N*-diethylbenzamide

Yellow oil; 11.9 mg, 67% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 – 7.34 (m, 5H), 3.55 (brs, 2H), 3.25 (brs, 2H), 1.25 (brs, 3H), 1.11 (brs, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.4, 137.4, 129.2, 128.5, 126.4, 43.4, 39.3, 14.3, 13.0. [13]



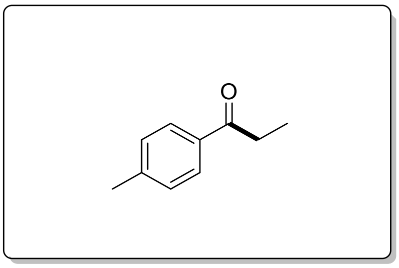
4aa: propiophenone

Colorless oil; 7.6 mg, 58% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.98 – 7.93 (m, 2H), 7.57 – 7.51 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 3.00 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 200.8, 137.0, 132.9, 128.6, 128.0, 31.8, 8.3. [14]



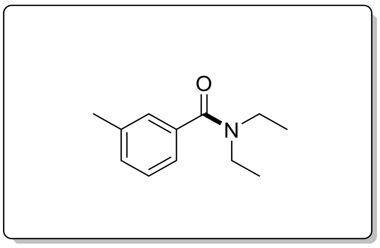
3ba: *N*,*N*-diethyl-4-methylbenzamide

Colorless oil; 12.8 mg, 67% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 3.54 (brs, 2H), 3.27 (brs, 2H), 2.37 (s, 3H), 1.24 (brs, 3H), 1.12 (brs, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.6, 139.2, 134.4, 129.1, 126.5, 44.1, 39.4, 21.5, 14.3, 13.0. [13]



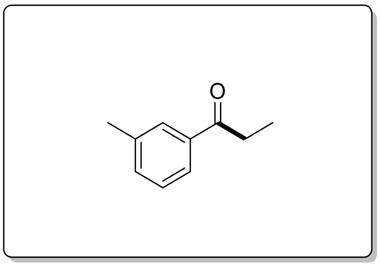
4ba: 1-(*p*-tolyl)propan-1-one

Colorless oil; 8.9 mg, 60% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.87 (d, *J* = 8.2, 2.1 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 2H), 2.99 (q, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.22 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.7, 143.7, 134.6, 129.4, 128.2, 31.8, 21.8, 8.5. [14]



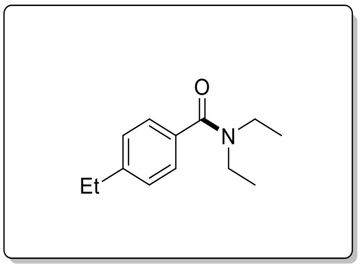
3ca: *N*,*N*-diethyl-3-methylbenzamide

Colorless oil; 12.8 mg, 67% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.27 (d, *J* = 7.3 Hz, 1H), 7.23 – 7.09 (m, 3H), 3.54 (brs, 2H), 3.25 (brs, 2H), 2.37 (s, 3H), 1.25 (brs, 3H), 1.10 (brs, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.6, 138.4, 137.4, 129.9, 128.3, 127.0, 123.3, 43.3, 39.2, 21.5, 14.3, 13.0. [15]



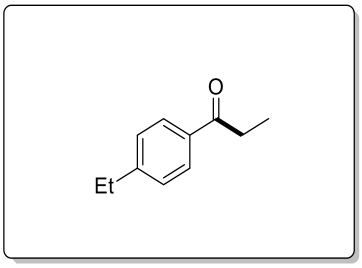
4ca: 1-(*m*-tolyl)propan-1-one

Yellow oil; 6.2 mg, 42% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.79 – 7.74 (m, 2H), 7.39 – 7.32 (m, 2H), 3.00 (q, *J* = 7.3 Hz, 2H), 2.42 (s, 3H), 1.22 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 182.9, 147.2, 141.0, 133.6, 128.5, 128.4, 125.2, 31.8, 21.4, 8.3. [16]



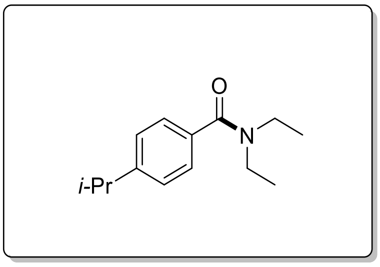
3da: *N*,*N*,4-triethylbenzamide

Colorless oil; 8.6 mg, 42% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.29 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.7 Hz, 2H), 3.54 (brs, 2H), 3.27 (brs, 2H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.29 – 1.18 (m, 6H), 1.12 (brs, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.6, 145.5, 134.7, 127.9, 126.5, 43.4, 39.3, 28.8, 15.6, 14.3, 13.1. [16]



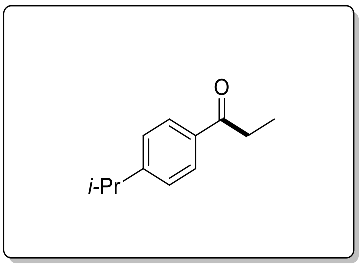
4da: 1-(4-ethylphenyl)propan-1-one

Colorless oil; 6.5 mg, 40% yield. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 2.98 (q, *J* = 7.3 Hz, 2H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H), 1.22 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 200.7, 149.9, 134.8, 128.3, 128.2, 31.8, 29.1, 15.4, 8.5. [17]



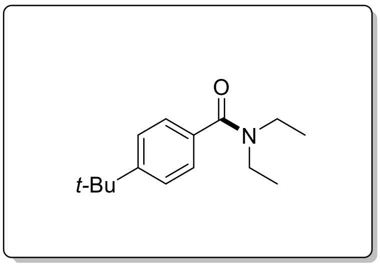
3ea: *N*,*N*-diethyl-4-isopropylbenzamide

Yellow oil; 14.6 mg, 67% yield. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.30 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.54 (brs, 2H), 3.28 (brs, 2H), 2.92 (hept, *J* = 6.9 Hz, 1H), 1.25 (d, *J* = 7.0 Hz, 6H), 1.29 – 1.19 (m, 3H), 1.12 (brs, 3H). **^{13}C NMR (151 MHz, CDCl$_3$)** δ 171.6, 150.1, 134.8, 126.5, 126.5, 43.4, 39.3, 34.1, 24.0, 14.4, 13.0. **HRMS** (APCI, m/z) Calcd. for $C_{14}H_{22}NO^+$ $[M+H]^+$: 220.1696; Found: 220.1694.



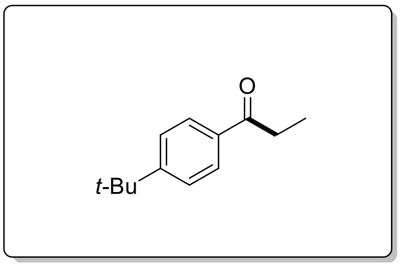
4ea: 1-(4-isopropylphenyl)propan-1-one

Colorless oil; 10.0 mg, 57% yield. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.90 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.02 – 2.93 (m, 3H), 1.27 (d, *J* = 6.9 Hz, 6H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 200.7, 154.5, 134.9, 128.4, 126.8, 34.4, 31.8, 23.8, 8.5. [17]



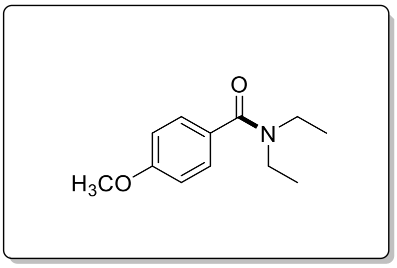
3fa: 4-(*tert*-butyl)-*N*,*N*-diethylbenzamide

Colorless oil; 15.9 mg, 68% yield. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 3.55 (brs, 2H), 3.29 (brs, 2H), 1.32 (s, 9H), 1.25 (brs, 3H), 1.13 (brs, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 171.6, 152.4, 134.5, 126.3, 125.4, 43.4, 39.3, 34.9, 31.4, 14.4, 13.1. **HRMS** (APCI, m/z) Calcd. for $C_{15}H_{24}NO^+$ $[M+H]^+$: 234.1852; Found: 234.1852.



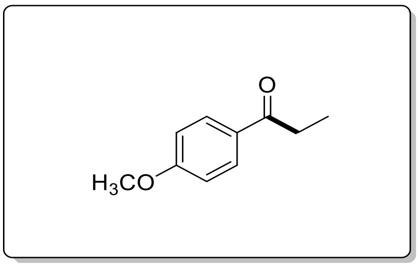
4fa: 1-(4-(*tert*-butyl)phenyl)propan-1-one

Yellow oil; 11.4 mg, 60% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 2.99 (q, *J* = 7.3 Hz, 2H), 1.34 (s, 9H), 1.22 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.7, 156.7, 134.5, 128.1, 125.6, 35.2, 31.8, 31.2, 8.5. [14]



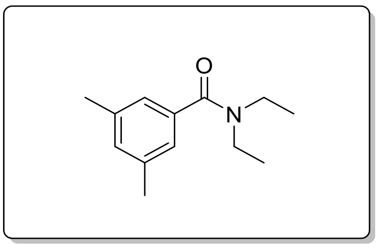
3ga: *N*,*N*-diethyl-4-methoxybenzamide

White solid; 8.7 mg, 42% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39 – 7.31 (m, 2H), 6.95 – 6.86 (m, 2H), 3.83 (s, 3H), 3.50 (brs, 2H), 3.33 (brs, 2H), 1.16 (brs, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.4, 160.4, 129.6, 128.3, 113.7, 55.4, 43.4, 38.6, 14.3, 13.1. [13]



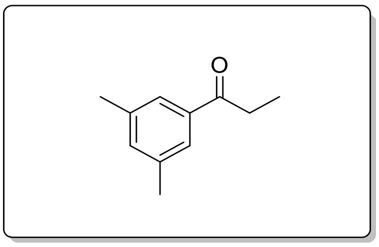
4ga: 1-(4-methoxyphenyl)propan-1-one

Yellow oil; 6.9 mg, 42% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H), 2.96 (q, *J* = 7.3 Hz, 2H), 1.22 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 199.6, 163.4, 130.4, 130.2, 113.8, 55.6, 31.6, 8.6. [14]



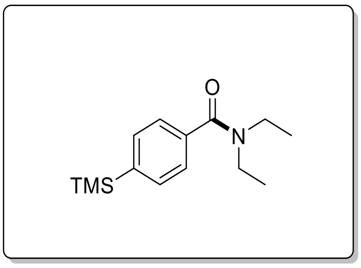
3ha: *N,N*-diethyl-3,5-dimethylbenzamide

Yellow oil; 11.3 mg, 55% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.01 (s, 1H), 6.96 (s, 2H), 3.53 (brs, 2H), 3.24 (brs, 2H), 2.32 (s, 6H), 1.24 (brs, 3H), 1.10 (brs, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.8, 138.1, 137.4, 130.7, 123.9, 43.3, 39.2, 21.4, 14.3, 13.1. [15]



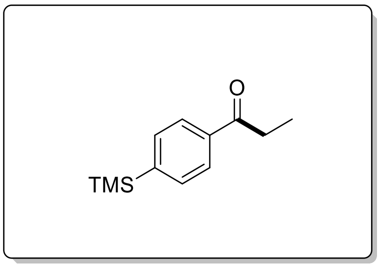
4ha: 1-(3,5-dimethylphenyl)propan-1-one

Yellow oil; 8.9 mg, 55% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.57 (s, 2H), 7.26 (s, 1H), 2.98 (q, *J* = 7.3 Hz, 2H), 2.37 (s, 6H), 1.21 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 201.5, 138.3, 137.2, 134.6, 125.9, 32.0, 21.4, 8.5. [18]



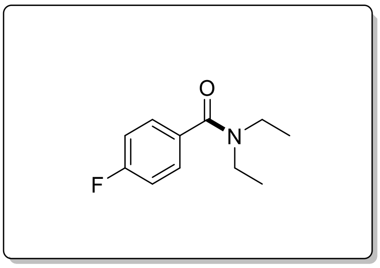
3ia: *N*,*N*-diethyl-4-(trimethylsilyl)benzamide

White solid; 15.2 mg, 61% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 3.55 (brs, 2H), 3.26 (brs, 2H), 1.25 (brs, 3H), 1.11 (brs, 3H), 0.27 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.5, 141.9, 137.6, 133.4, 125.5, 43.3, 39.3, 14.4, 13.0, -1.1. [19]



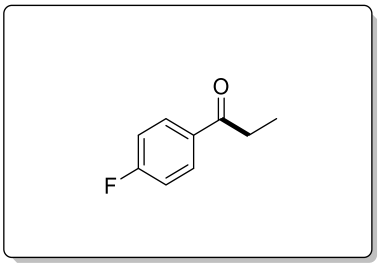
4ia: 1-(4-(trimethylsilyl)phenyl)propan-1-one

Yellow oil; 12.0 mg, 58% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 3.00 (q, *J* = 7.3 Hz, 2H), 1.23 (t, *J* = 7.3 Hz, 3H), 0.28 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 201.3, 147.1, 137.1, 133.7, 127.1, 32.0, 8.4, -1.2. [20]



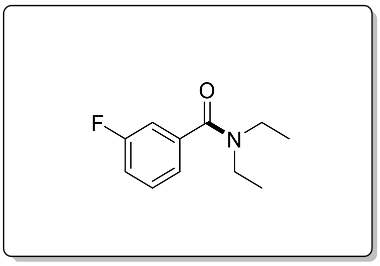
3ja: *N*,*N*-diethyl-4-fluorobenzamide

Colorless oil; 11.3 mg, 50% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.38 (dd, *J* = 8.1, 5.8 Hz, 2H), 7.08 (t, *J* = 8.6 Hz, 2H), 3.54 (brs, 2H), 3.26 (brs, 2H), 1.24 (brs, 3H), 1.13 (brs, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.5, 163.2 (d, *J* = 248.7 Hz), 133.4 (d, *J* = 3.7 Hz), 128.6 (d, *J* = 8.4 Hz), 115.6 (d, *J* = 21.7 Hz), 43.5, 39.5, 14.3, 12.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -111.25 – -111.49 (m). [13]



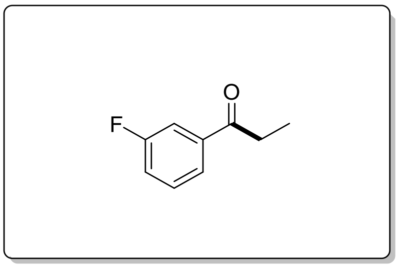
4ja: 1-(4-fluorophenyl)propan-1-one

Yellow oil; 7.6 mg, 50% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.01 – 7.97 (m, 2H), 7.15 – 7.10 (m, 2H), 2.98 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 199.4, 165.8 (d, *J* = 254.1 Hz), 133.5 (d, *J* = 3.1 Hz), 130.7 (d, *J* = 9.2 Hz), 115.8 (d, *J* = 21.8 Hz), 31.9, 8.3. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -111.25 – -111.49 (m). [14]



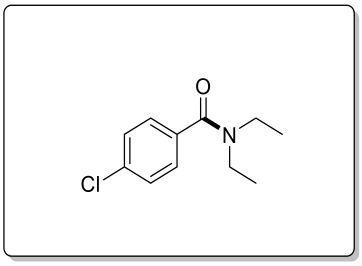
3ka: *N*,*N*-diethyl-3-fluorobenzamide

Colorless oil; 11.7 mg, 60% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.40 – 7.34 (m, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 8.2 Hz, 2H), 3.54 (brs, 2H), 3.25 (brs, 2H), 1.25 (brs, 3H), 1.12 (brs, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.9 (d, *J* = 2.0 Hz), 162.6 (d, *J* = 247.8 Hz), 139.3 (d, *J* = 6.9 Hz), 130.4 (d, *J* = 8.1 Hz), 122.1 (d, *J* = 3.3 Hz), 116.3 (d, *J* = 21.1 Hz), 113.7 (d, *J* = 22.7 Hz), 43.4, 39.4, 14.3, 13.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -106.95 – -120.27 (m). [21]



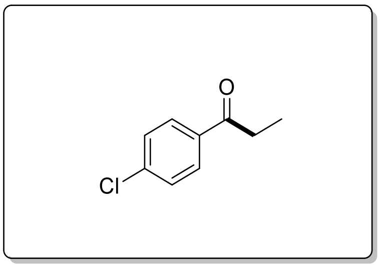
4ka: 1-(3-fluorophenyl)propan-1-one

Yellow oil; 5.3 mg, 35% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 9.5 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.29 – 7.23 (m, 1H), 2.99 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 199.6 (d, *J* = 8.8 Hz), 162.8 (d, *J* = 248,7 Hz), 139.4 (d, *J* = 39.4 Hz), 130.4 (d, *J* = 7.6 Hz), 123.9 (d, *J* = 3.0 Hz), 120.0 (d, *J* = 21.6 Hz), 114.9 (d, *J* = 22.3 Hz), 32.1, 8.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -107.85 – -121.45 (m). [22]



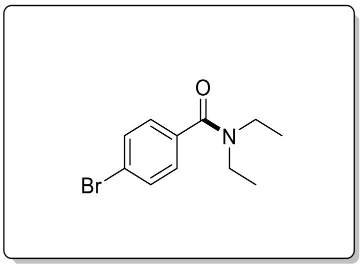
3la: 4-chloro-*N*,*N*-diethylbenzamide

Colorless oil; 13.2 mg, 62% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 3.54 (brs, 2H), 3.24 (brs, 2H), 1.24 (brs, 3H), 1.11 (brs, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.3, 135.8, 135.3, 128.8, 128.0, 43.5, 39.5, 14.3, 13.0. [15]



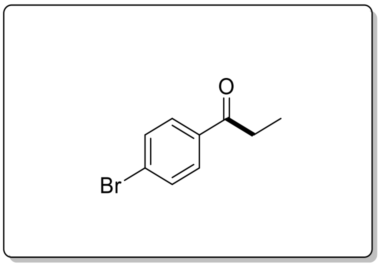
4la: 1-(4-chlorophenyl)propan-1-one

Yellow oil; 8.4 mg, 50% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 2.98 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 199.7, 139.4, 135.3, 129.5, 129.0, 31.9, 8.3. [17]



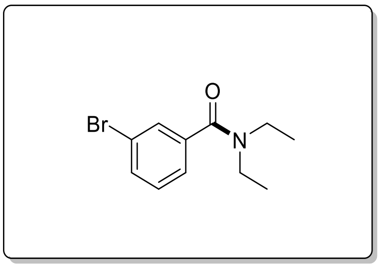
3ma: 4-bromo-*N*,*N*-diethylbenzamide

White solid; 17.4 mg, 68% yield. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 3.54 (brs, 2H), 3.24 (brs, 2H), 1.25 (brs, 3H), 1.11 (brs, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.4, 136.2, 131.8, 128.2, 123.5, 43.4, 39.5, 14.4, 13.0. [13]



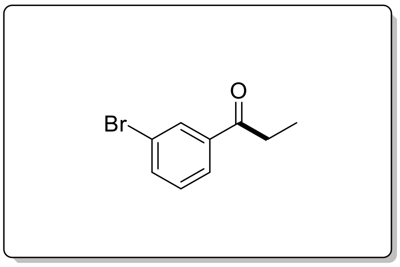
4ma: 1-(4-bromophenyl)propan-1-one

White solid; 10.2 mg, 48% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 2.98 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 199.9, 135.7, 132.0, 129.7, 128.1, 31.9, 8.3. [23]



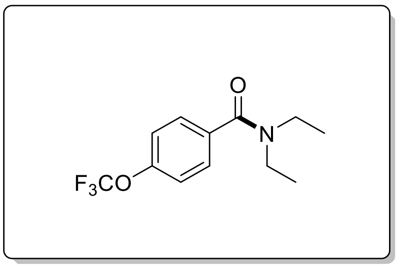
3na: 3-bromo-*N*,*N*-diethylbenzamide

Yellow oil; 16.0 mg, 62% yield. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.57 – 7.48 (m, 2H), 7.31 – 7.26 (m, 2H), 3.53 (brs, 2H), 3.24 (brs, 2H), 1.24 (brs, 3H), 1.12 (brs, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.6, 139.2, 132.3, 130.2, 129.5, 124.9, 122.7, 43.4, 39.5, 14.3, 13.0. [24]



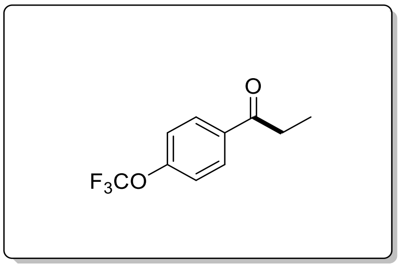
4na: 1-(3-bromophenyl)propan-1-one

Yellow oil; 8.9 mg, 42% yield. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 8.09 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 2.99 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 199.5, 138.7, 135.9, 131.2, 130.3, 126.6, 123.1, 32.1, 8.2. [25]



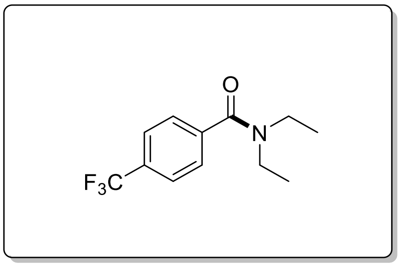
3oa: *N,N*-diethyl-4-(trifluoromethoxy)benzamide

Yellow oil; 18.3 mg, 70% yield. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.42 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 3.55 (brs, 2H), 3.25 (brs, 2H), 1.25 (brs, 3H), 1.13 (brs, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 170.1, 149.7 (q, *J* = 1.8 Hz), 135.9, 128.2, 121.0, 120.5 (q, *J* = 257.9 Hz), 43.5, 39.5, 14.4, 13.0. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -57.81 (s). [26]



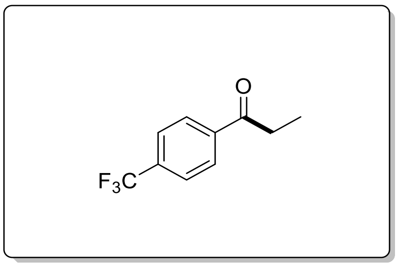
4oa: 1-(4-(trifluoromethoxy)phenyl)propan-1-one

Yellow oil; 9.8mg, 45% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.02 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 3.00 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H).**^{13}C NMR (101 MHz, CDCl$_3$)** δ 199.4, 152.6 (q, *J* = 1.8 Hz), 135.3, 130.1, 120.5, 120.4 (q, *J* = 258.9 Hz), 32.0, 8.3. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -57.63 (s). [27]



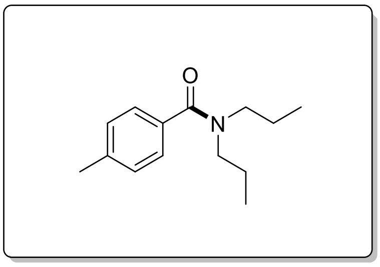
3pa: *N*,*N*-diethyl-4-(trifluoromethyl)benzamide

White solid; 17.2 mg, 70% yield. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 3.57 (q, *J* = 7.4 Hz, 2H), 3.22 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 6.9 Hz, 3H), 1.12 (t, *J* = 6.5 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.8, 140.7 (q, *J* = 1.2 Hz), 131.1 (q, *J* = 32.8 Hz), 126.6, 125.5 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 273.3 Hz), 43.2, 39.4, 14.2, 12.9. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -63.10 (s). [13]



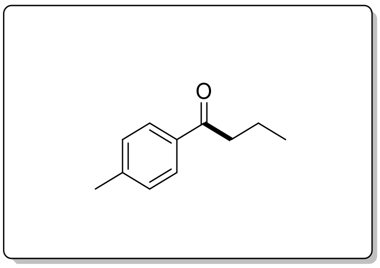
4pa: 1-(4-(trifluoromethyl)phenyl)propan-1-one

Yellow oil; 5.1 mg, 25% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 3.04 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 199.7, 139.5, 134.2 (q, *J* = 32.8 Hz), 128.3, 125.7 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 273.5 Hz), 32.1, 8.0. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -62.84 (s). [28]



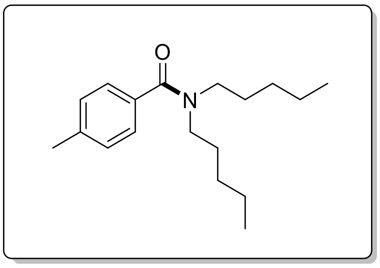
3ab: 4-methyl-*N*,*N*-dipropylbenzamide

Colorless oil; 15.5 mg, 71% yield. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.25 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 3.44 (brs, 2H), 3.17 (brs, 2H), 2.37 (s, 3H), 1.68 (brs, 2H), 1.53 (brs, 2H), 0.97 (brs, 3H), 0.75 (brs, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 172.1, 139.1, 134.6, 129.1, 126.6, 50.9, 46.4, 22.0, 21.5, 20.8, 11.6, 11.2. [13]



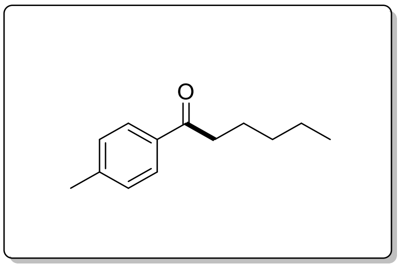
4ab: 1-(*p*-tolyl)butan-1-one

Colorless oil; 5.9 mg, 37% yield. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.41 (s, 3H), 1.76 (h, *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 200.3, 143.7, 134.8, 129.4, 128.3, 40.6, 21.8, 18.0, 14.1. [29]



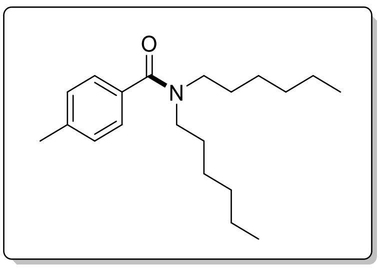
3ac: 4-methyl-*N*,*N*-dipentylbenzamide

Colorless oil; 18.1 mg, 66% yield. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.24 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 3.46 (brs, 2H), 3.19 (brs, 2H), 2.37 (s, 3H), 1.65 (brs, 2H), 1.49 (brs, 2H), 1.36 (brs, 4H), 1.19 (brs, 2H), 1.09 (brs, 2H), 0.93 (brs, 3H), 0.83 (brs, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 172.0, 139.1, 134.6, 129.0, 126.7, 49.2, 44.8, 29.4, 28.9, 28.5, 27.4, 22.7, 22.4, 21.5, 14.2, 14.1. **HRMS** (APCI, m/z) Calcd. for $C_{18}H_{30}NO^+$ [M+H]$^+$: 276.2322; Found: 276.2322.



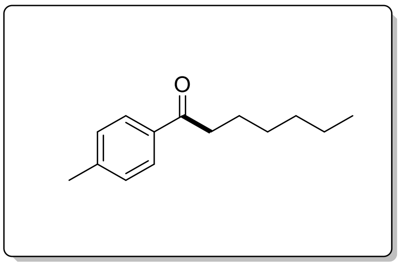
4ac: 1-(*p*-tolyl)hexan-1-one

Colorless oil; 6.6 mg, 35% yield. **^{1}H NMR (600 MHz, CDCl$_3$)** δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 2.93 (t, *J* = 7.5 Hz, 2H), 2.41 (s, 3H), 1.73 (p, *J* = 7.3 Hz, 2H), 1.42 – 1.30 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 200.5, 143.7, 134.7, 129.4, 128.3, 38.6, 31.7, 24.3, 22.7, 21.8, 14.1. [29]



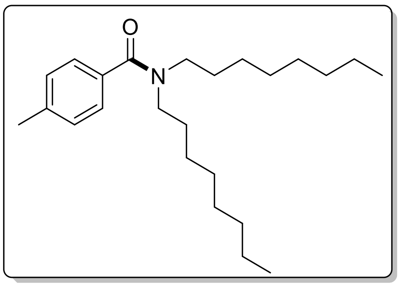
3ad: *N*,*N*-dihexyl-4-methylbenzamide

Colorless oil; 18.8 mg, 62% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 3.46 (brs, 2H), 3.19 (brs, 2H), 2.36 (s, 3H), 1.63 (brs, 2H), 1.48 (brs, 2H), 1.34 (brs, 6H), 1.22 (brs, 2H), 1.12 (brs, 4H), 0.95 – 0.77 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.9, 139.1, 134.6, 129.0, 126.6, 49.2, 44.8, 31.7, 31.4, 29.8, 28.8, 27.6, 26.9, 26.3, 22.7, 22.6, 21.5, 14.1. [13]



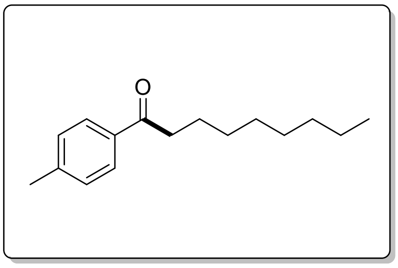
4ad: 1-(*p*-tolyl)heptan-1-one

Colorless oil; 6.1 mg, 30% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 2.96 – 2.90 (m, 2H), 2.41 (s, 3H), 1.72 (p, *J* = 7.4 Hz, 2H), 1.40 – 1.29 (m, 6H), 0.90 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.5, 143.7, 134.8, 129.4, 128.3, 38.7, 31.8, 29.2, 24.6, 22.7, 21.8, 14.2. [30]



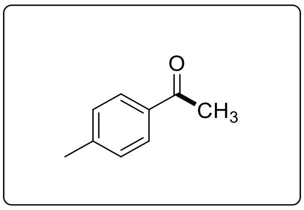
3ae: 4-methyl-*N,N*-dioctylbenzamide

Colorless oil; 21.9 mg, 61% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 3.46 (brs, 2H), 3.18 (brs, 2H), 2.36 (s, 3H), 1.64 (brs, 2H), 1.48 (brs, 2H), 1.34 – 1.12 (m, 20H), 0.91 – 0.86 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.9, 139.0, 134.6, 129.0, 126.6, 49.1, 44.8, 31.9, 31.8, 29.5, 29.4, 29.4, 29.2, 28.7, 27.6, 27.2, 26.8, 26.6, 23.0, 22.8, 21.5, 14.2. **HRMS** (APCI, m/z) Calcd. for $C_{24}H_{42}NO^+$ $[M+H]^+$: 360.3261; Found: 360.3264.



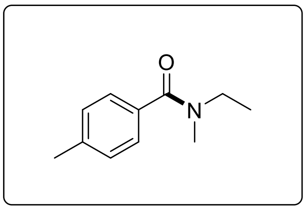
4ae: 1-(*p*-tolyl)nonan-1-one

Colorless oil; 7.7 mg, 33% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 2.93 (t, *J* = 7.5 Hz, 2H), 2.41 (s, 3H), 1.77 – 1.67 (m, 2H), 1.34 – 1.26 (m, 10H), 0.89 – 0.86 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.5, 143.7, 134.8, 129.4, 128.3, 38.7, 32.0, 29.6, 29.6, 29.3, 24.7, 22.8, 21.8, 14.2. [32]



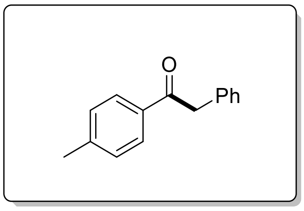
4af: 1-(*p*-tolyl)ethan-1-one

Colourless oil; 2.9 mg, 22% yield. **^{1}H NMR (400 MHz, CDCl3)** δ 7.86 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 7.9 Hz, 2H), 2.57 (s, 3H), 2.41 (s, 3H). **^{13}C NMR (101 MHz, CDCl3)** δ 197.9, 144.0, 134.8, 129.3, 128.5, 26.6, 21.7. [29]



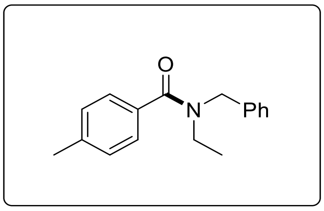
3af: *N*-ethyl-*N*,4-dimethylbenzamide

Colourless oil; 3.2 mg, 18% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29 (d, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 3.57 (s) & 3.29 (s, 2H combined), 3.05 (s) & 2.94 (s, 3H combined), 2.37 (s, 3H), 1.37 (s) & 0.95 (s, 3H combined). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.4, 133.9, 129.0, 127.1, 126.6, 46.1, 42.3, 36.9, 32.3, 21.5, 13.8, 12.2. [33]



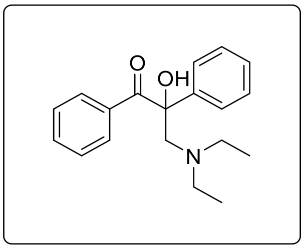
4ag: 2-phenyl-1-(*p*-tolyl)ethan-1-one

White solid; 5.0 mg, 24% yield. **^{1}H NMR (400 MHz, CDCl3)** δ 7.92 (d, J = 8.3 Hz, 2H), 7.55 – 7.05 (m, 7H), 4.26 (s, 2H), 2.40 (s, 3H). **^{13}C NMR (101 MHz, CDCl3)** δ 197.4, 144.1, 134.9, 134.3, 129.6, 129.5, 128.9, 128.8, 127.0, 45.6, 21.8. [34]



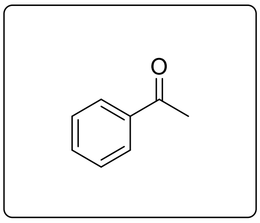
3ag: *N*-benzyl-*N*-ethyl-4-methylbenzamide

Colourless oil; 8.1 mg, 32% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.54 – 7.09 (m, 9H), 4.76 (s) & 4.52 (s, 2H combined), 3.49 (s) & 3.22 (s, 2H combined), 2.35 (s, 3H), 1.38 (s) & 0.87 (s, 3H combined). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.2, 139.5, 137.6, 133.9, 129.1, 128.8, 128.1, 127.5, 126.7, 52.2, 47.1, 42.9, 39.7, 21.5, 13.7, 12.3. [35]



7: 3-(diethylamino)-2-hydroxy-1,2-diphenylpropan-1-one

Colourless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99 (d, *J* = 7.1 Hz, 2H), 7.61 (d, *J* = 7.1 Hz, 2H), 7.46 – 7.18 (m, 6H), 3.83 (d, *J* = 13.4 Hz, 1H), 2.61 (d, *J* = 13.4 Hz, 1H), 2.61 – 2.41 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 202.0, 143.5, 135.8, 132.4, 130.6, 128.8, 127.9, 127.4, 124.5, 79.2, 61.7, 47.5, 11.8. [36]



8: acetophenone

Colourless oil; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.95 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 2.58 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 198.1, 137.1, 133.1, 128.6, 128.3, 26.6. [29]

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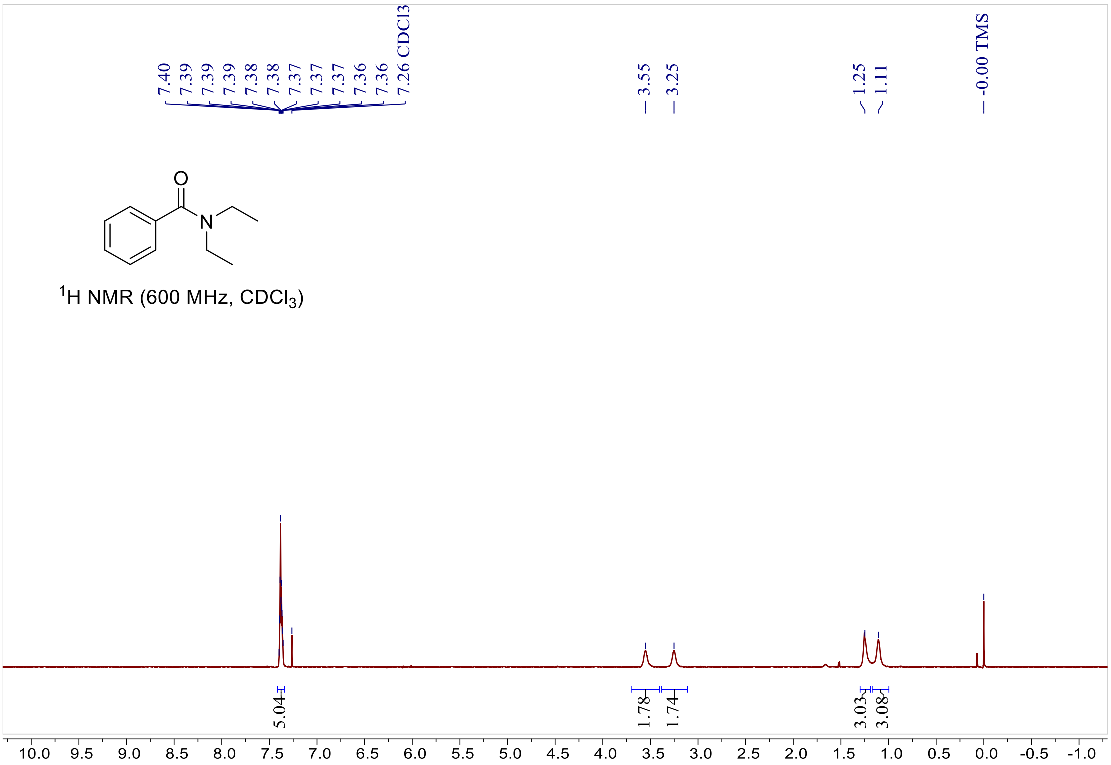
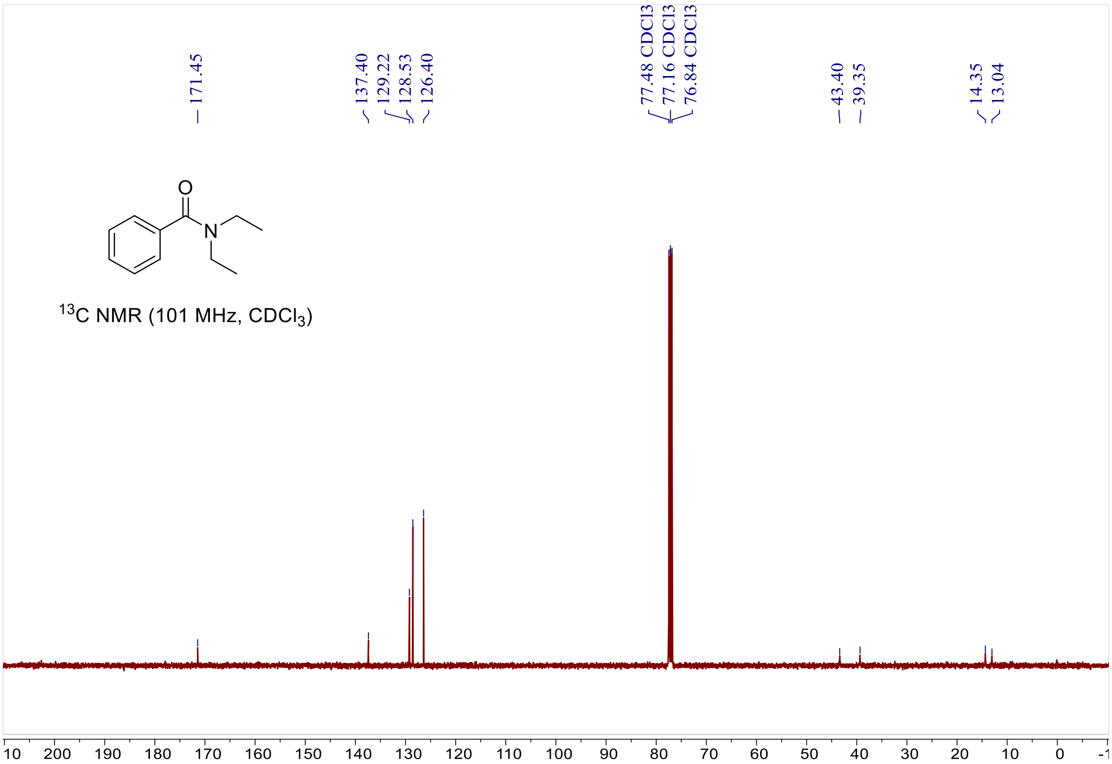
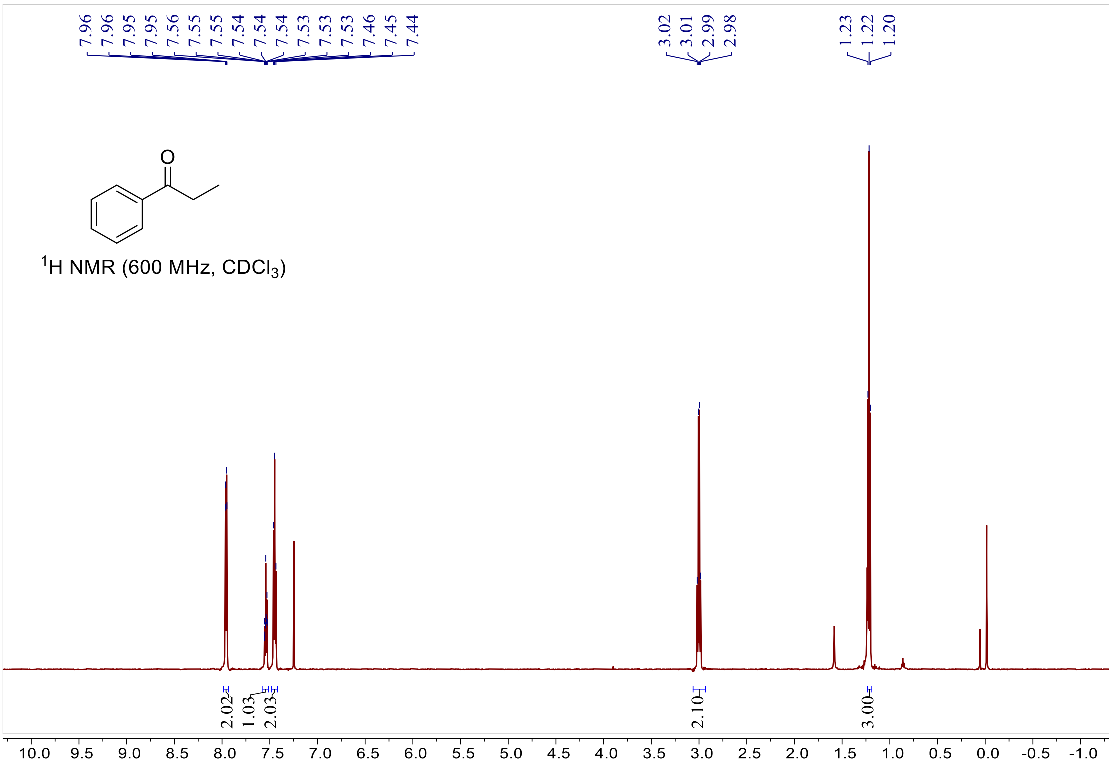
VIII. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

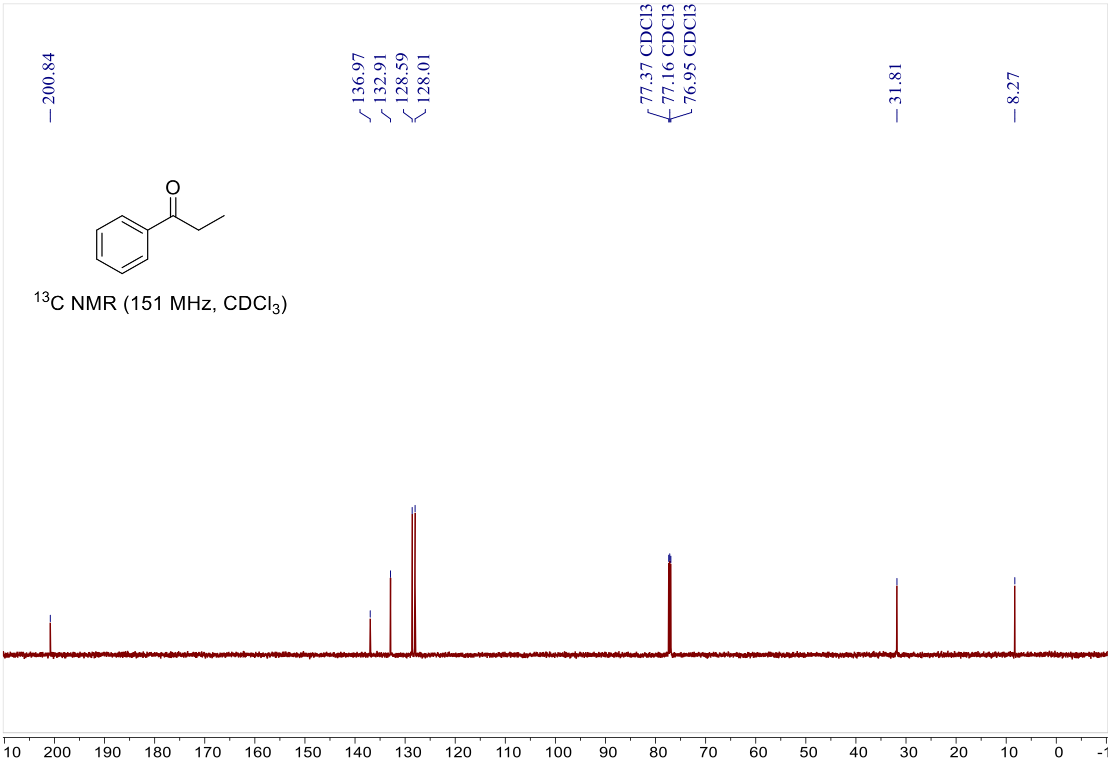
^{1}H and ^{13}C NMR spectra of compound **3aa**



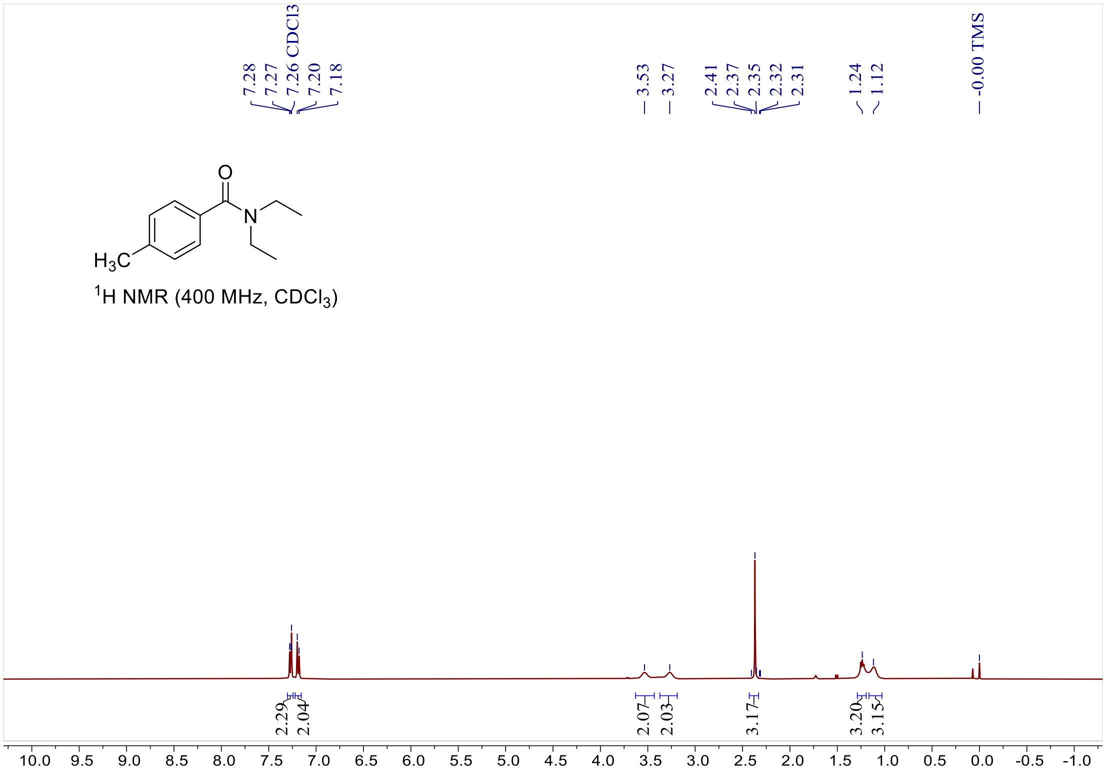


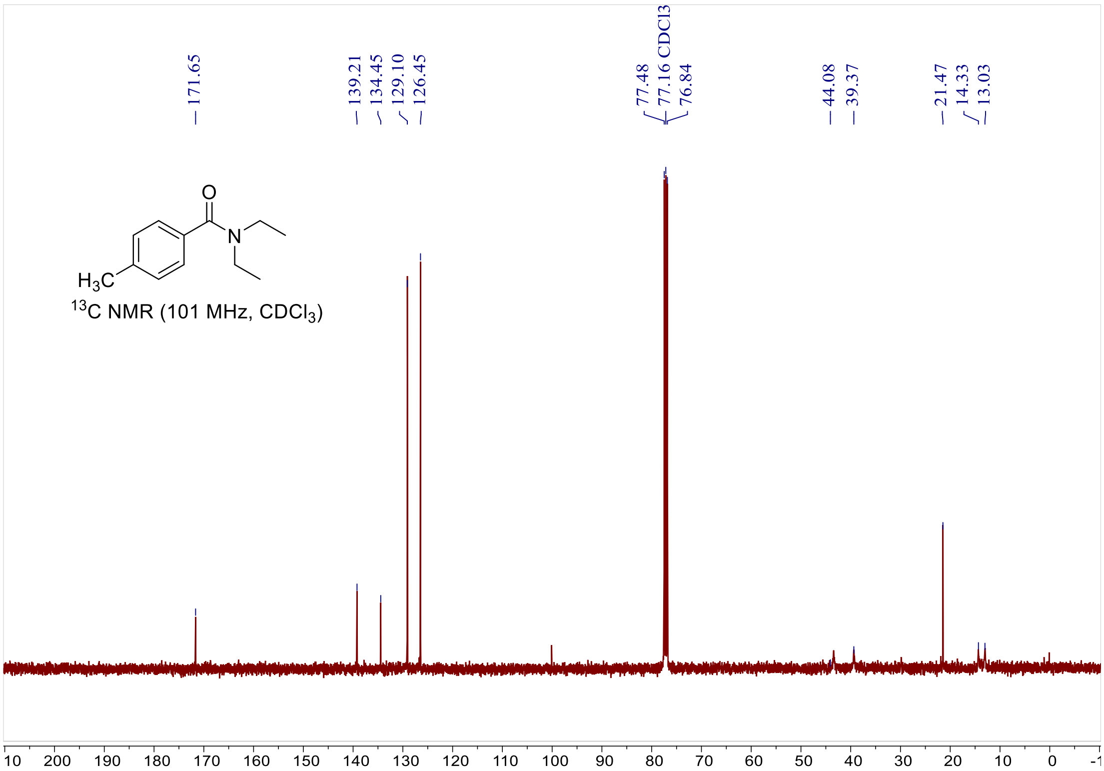
[1]H and [13]C NMR spectra of compound **4aa**





^{1}H and ^{13}C NMR spectra of compound **3ba**





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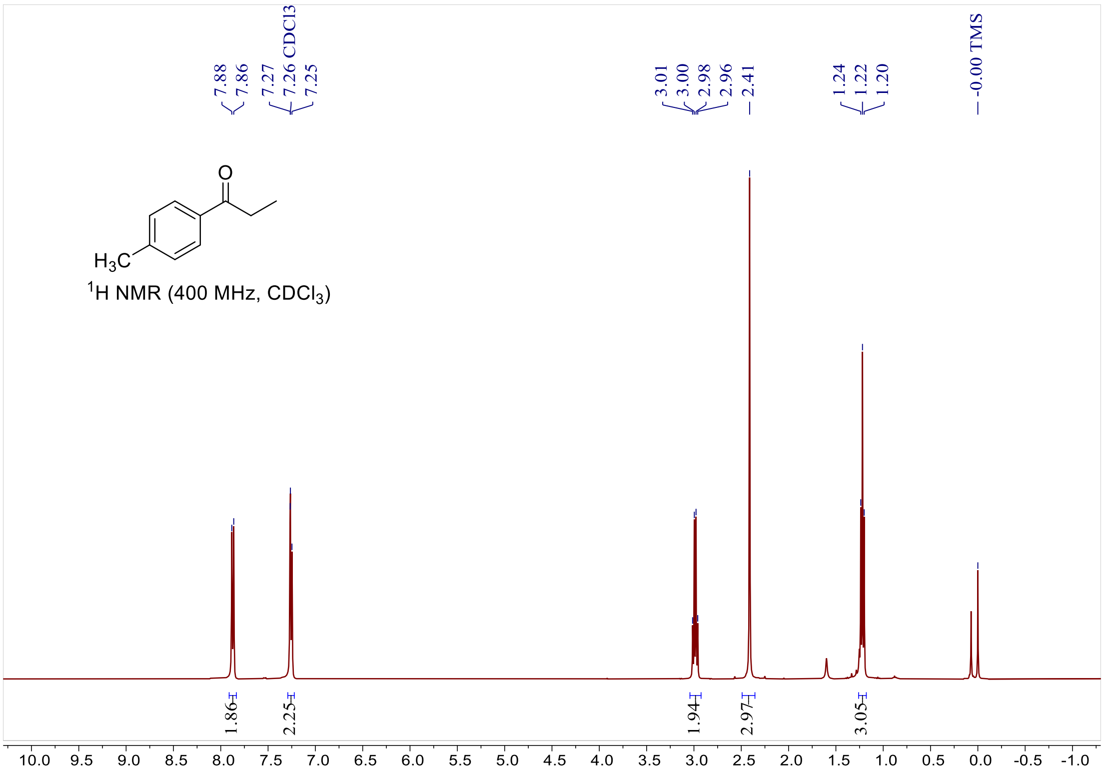
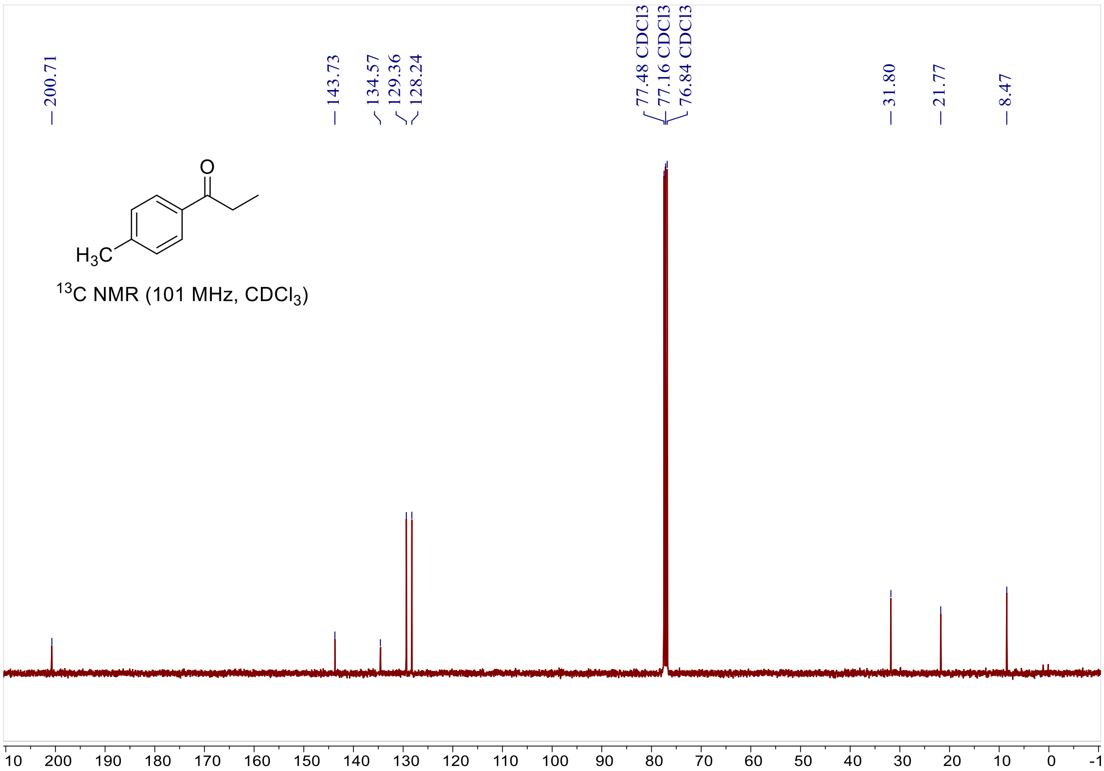
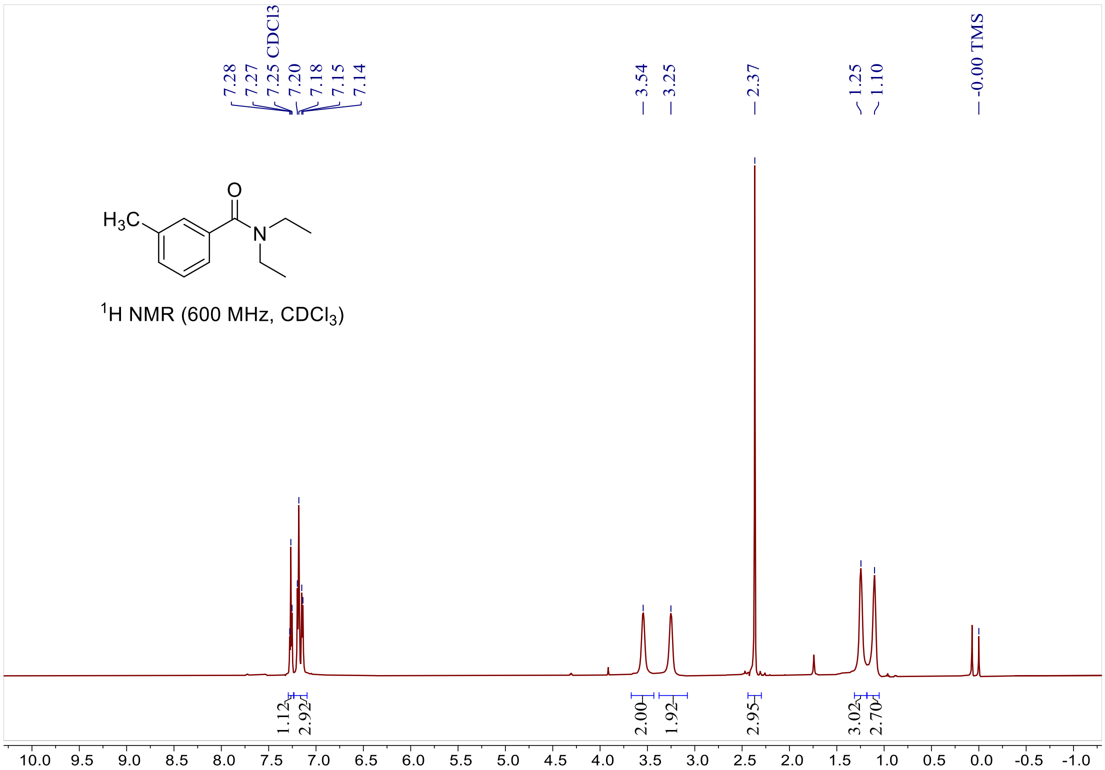
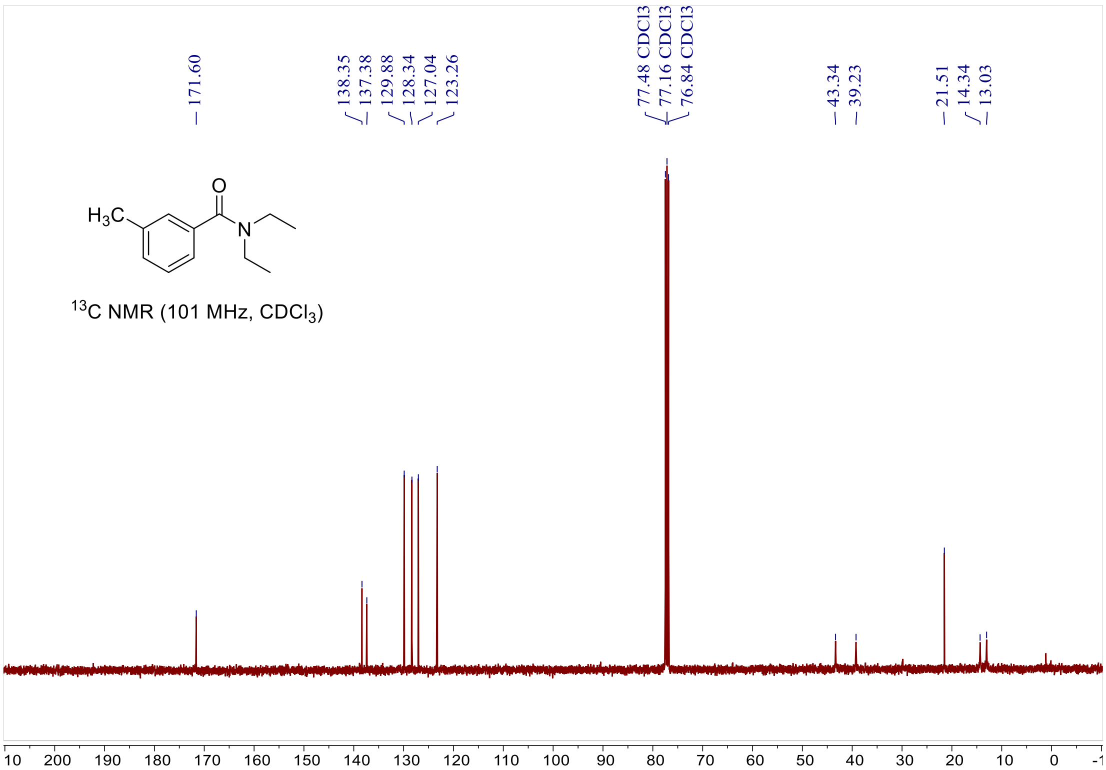


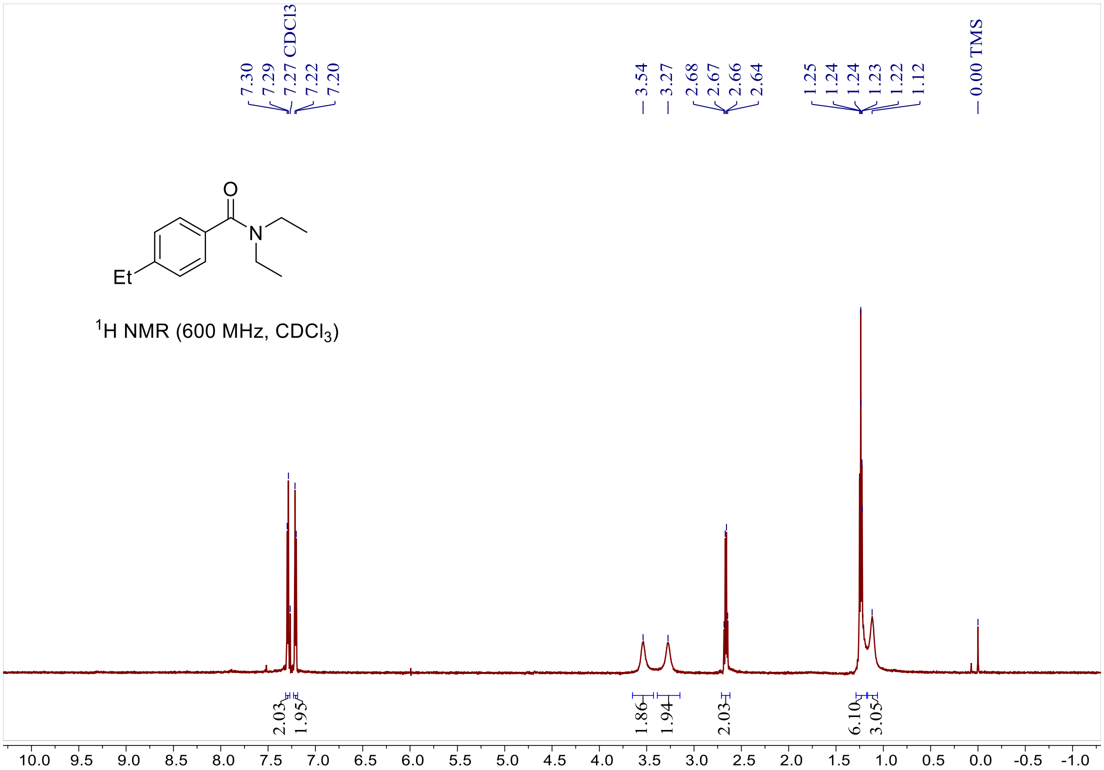


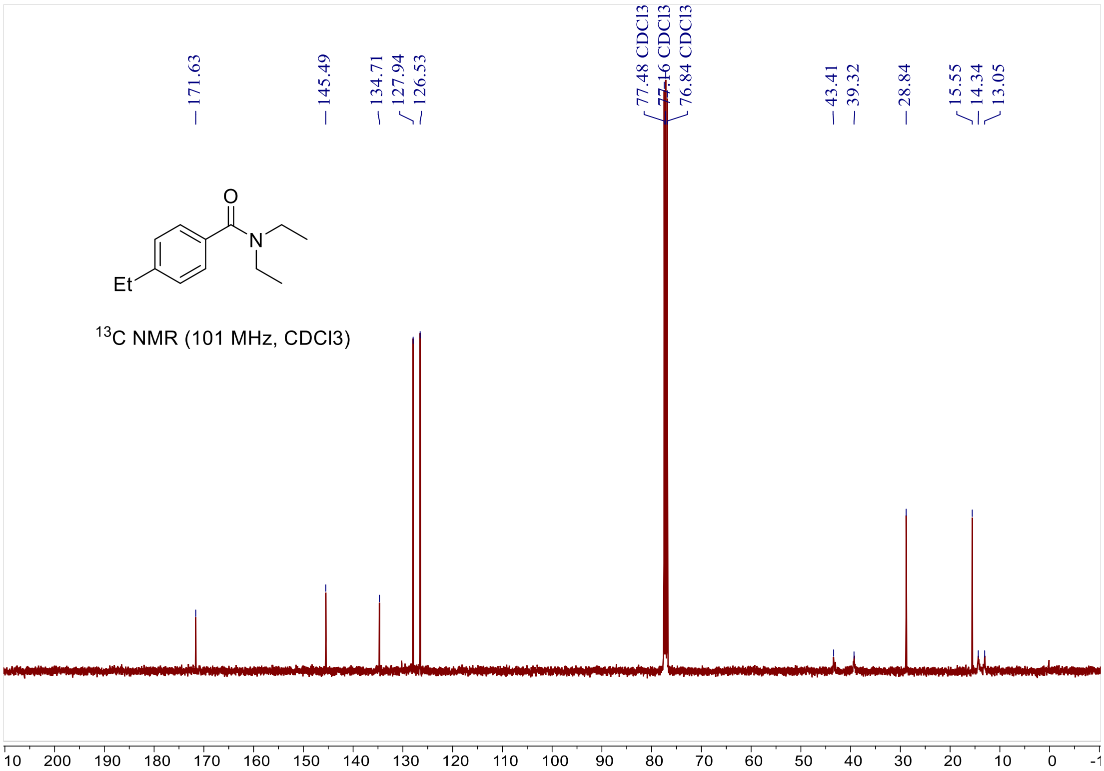
^{1}H and ^{13}C NMR spectra of compound **3ca**



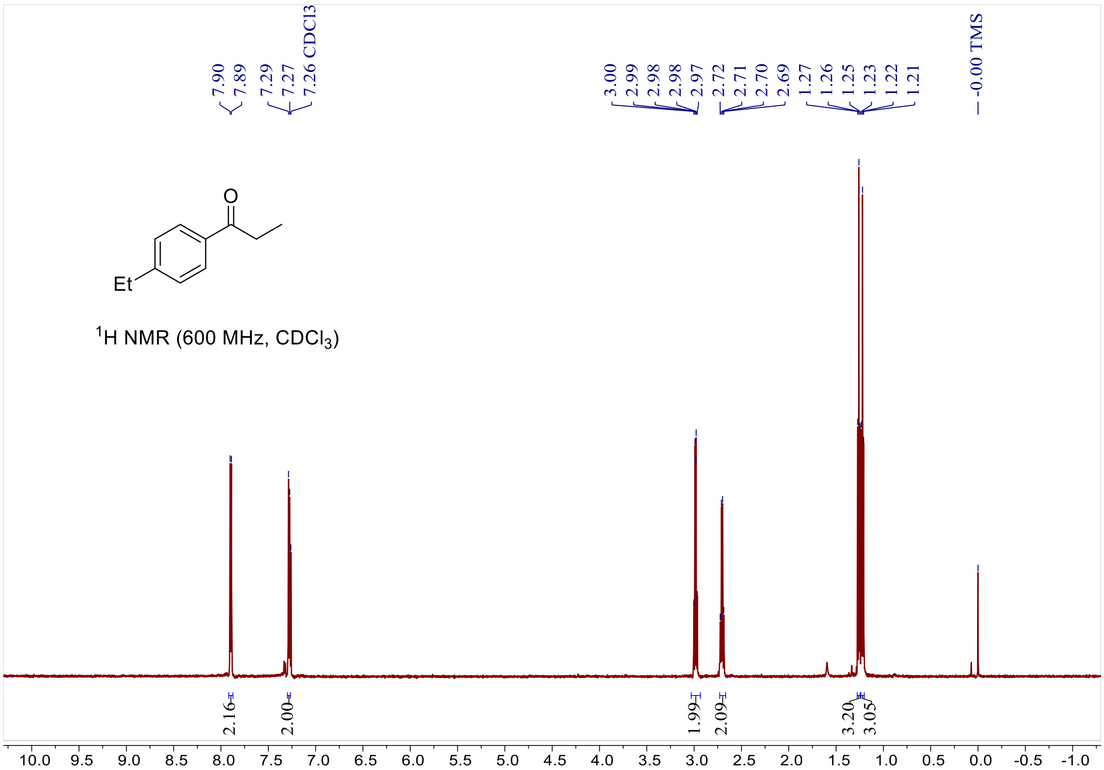


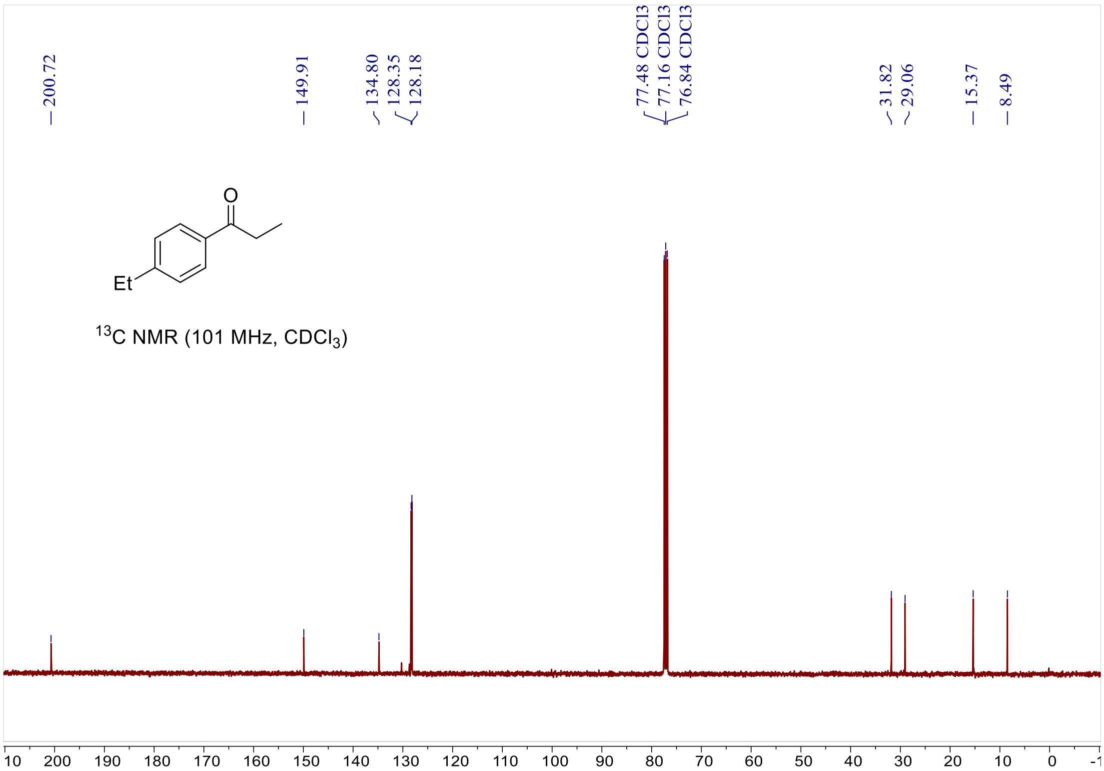
^1H and ^{13}C NMR spectra of compound **3da**



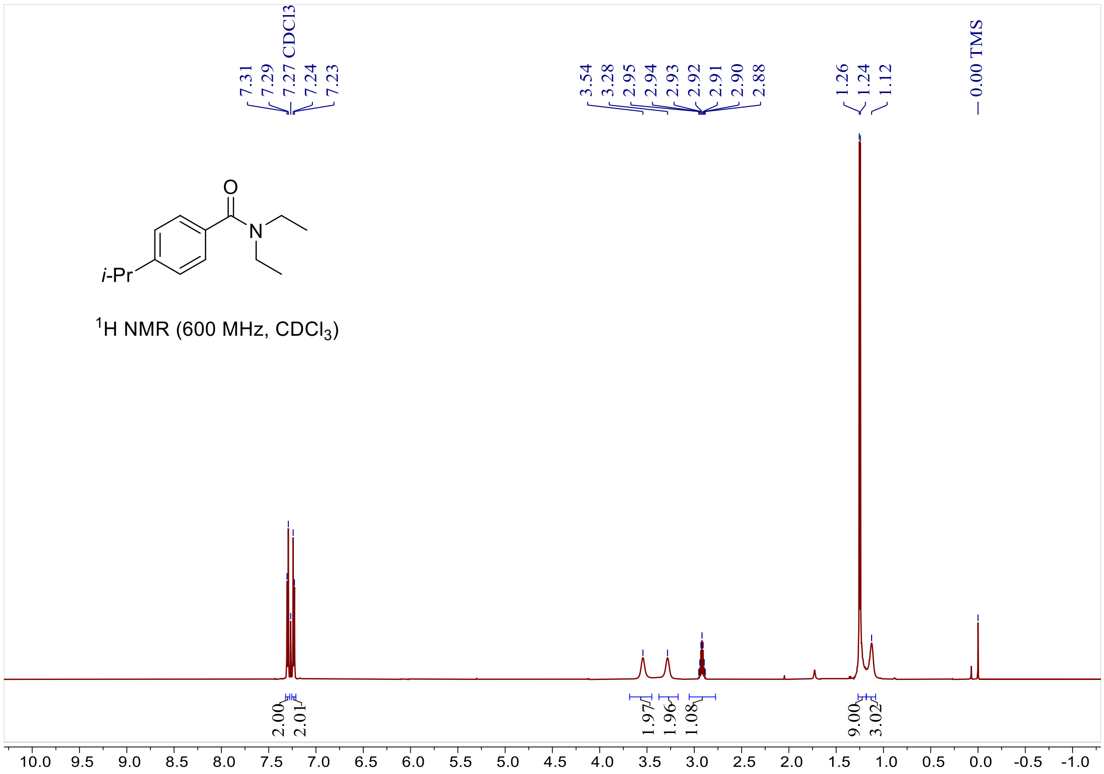


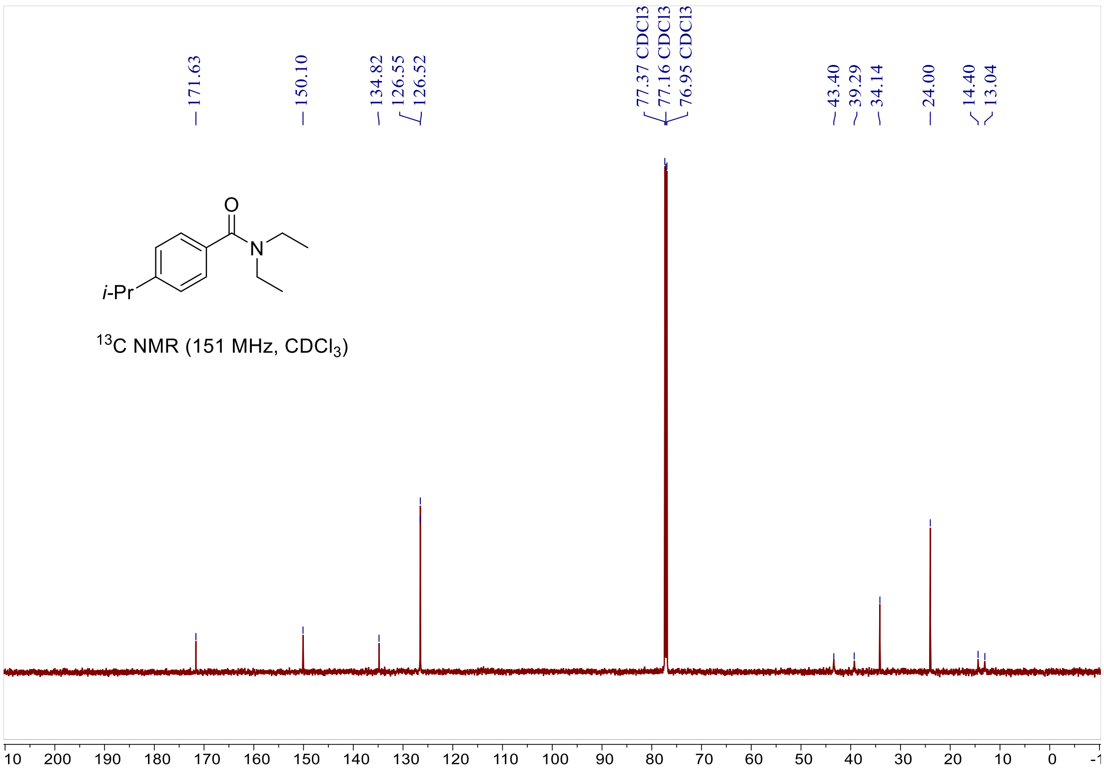
[1]H and [13]C NMR spectra of compound **4da**



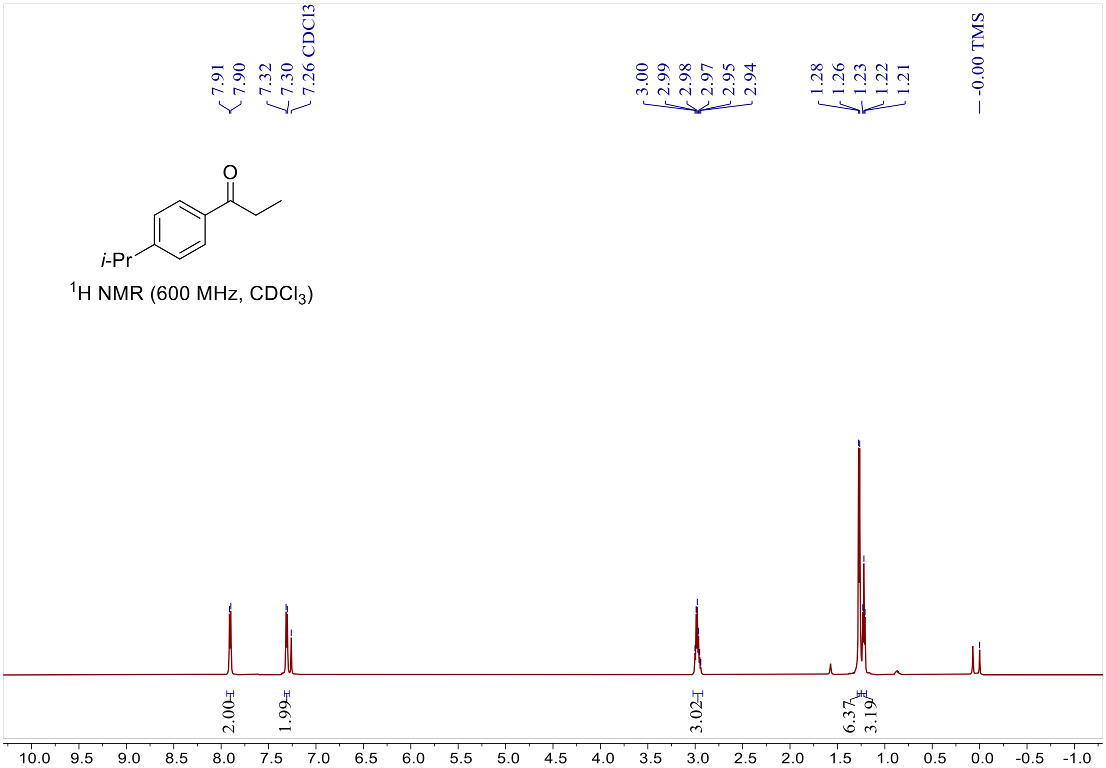


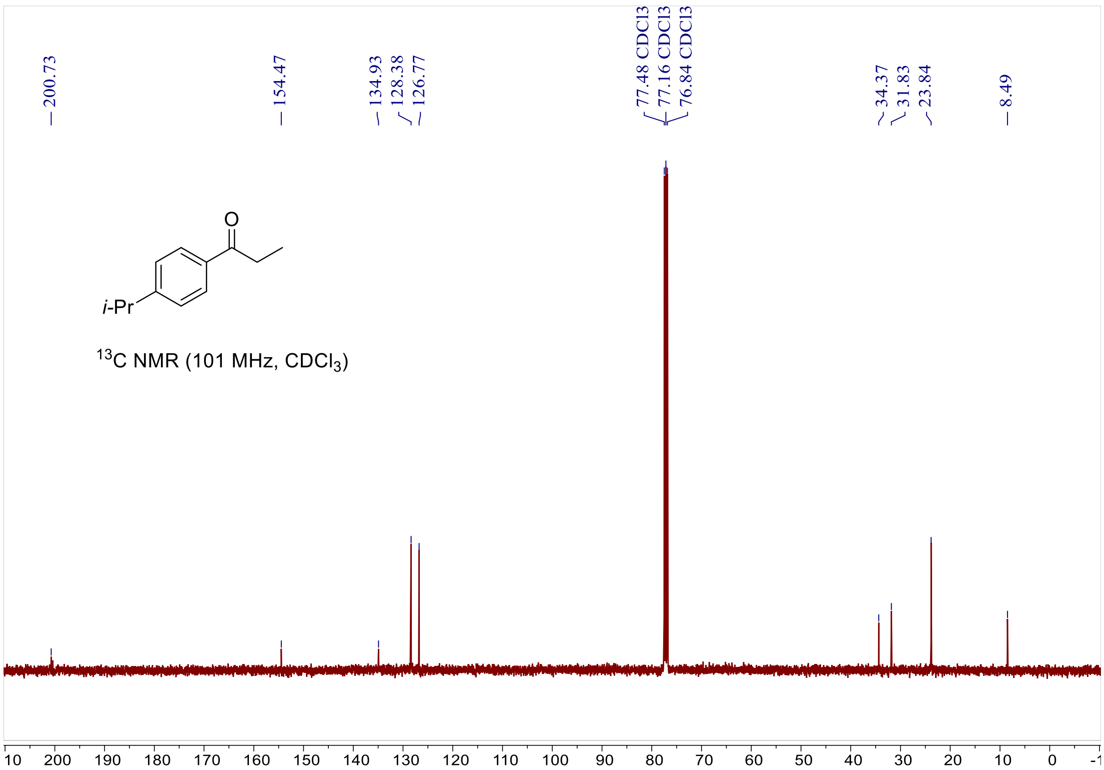
[1]H and [13]C NMR spectra of compound **3ea**



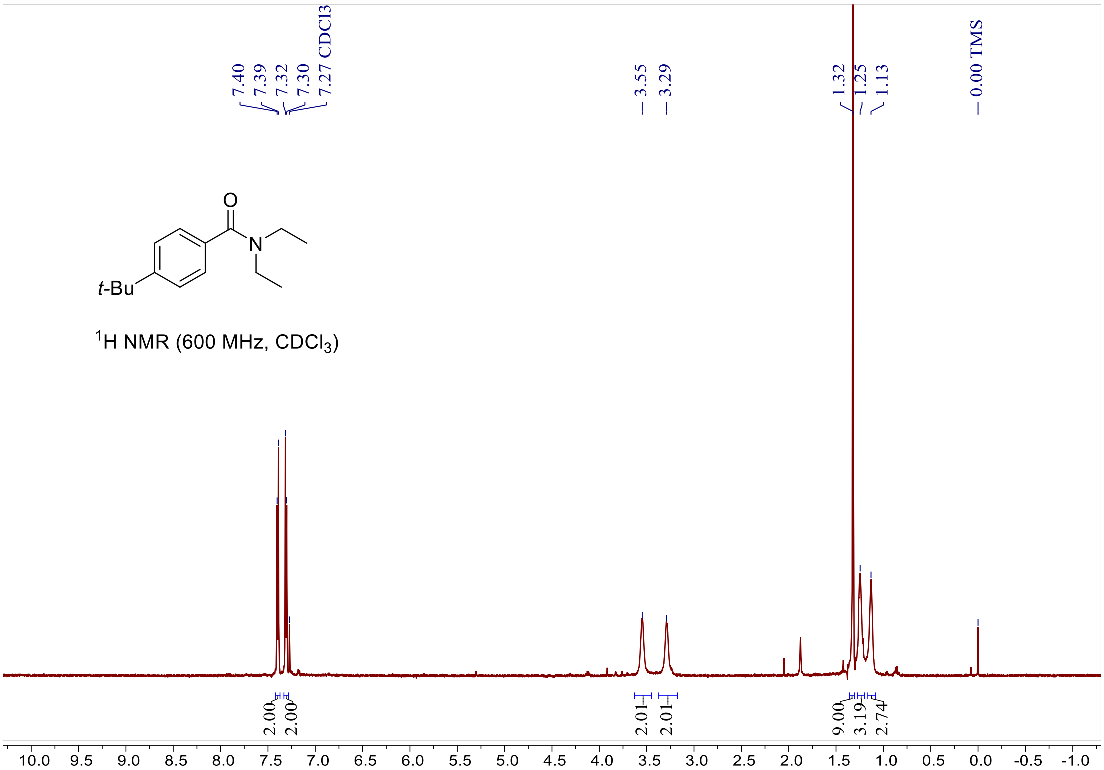


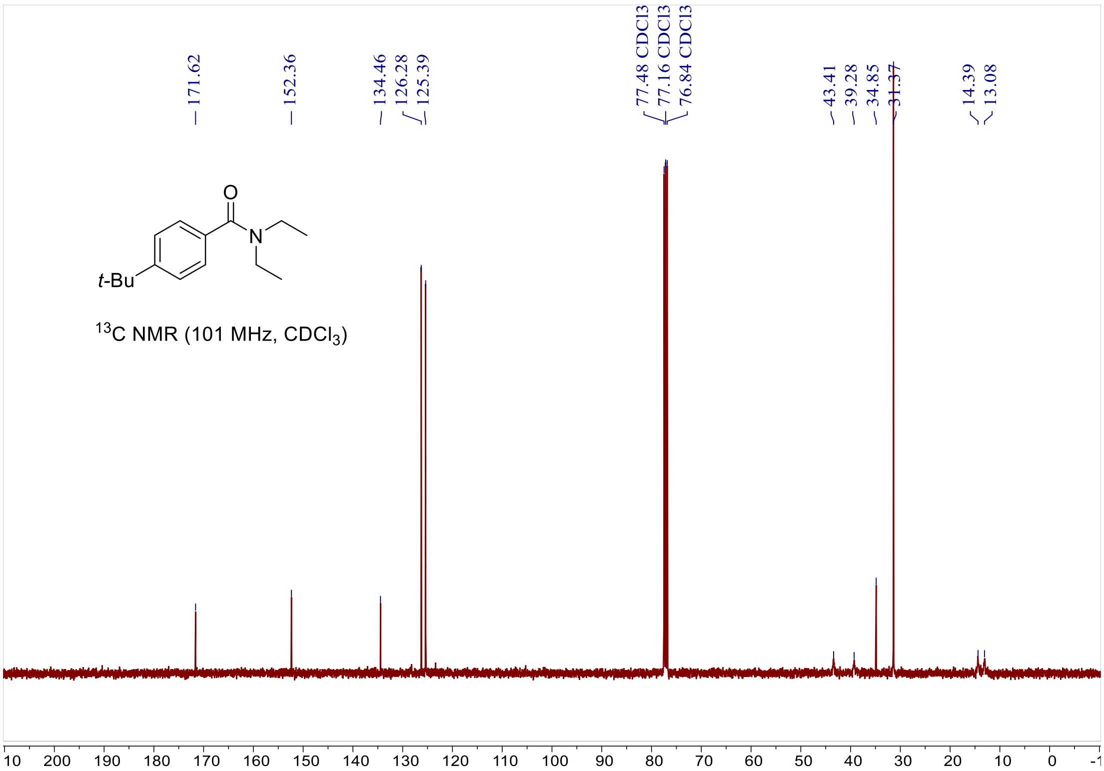
^1H and ^{13}C NMR spectra of compound **4ea**



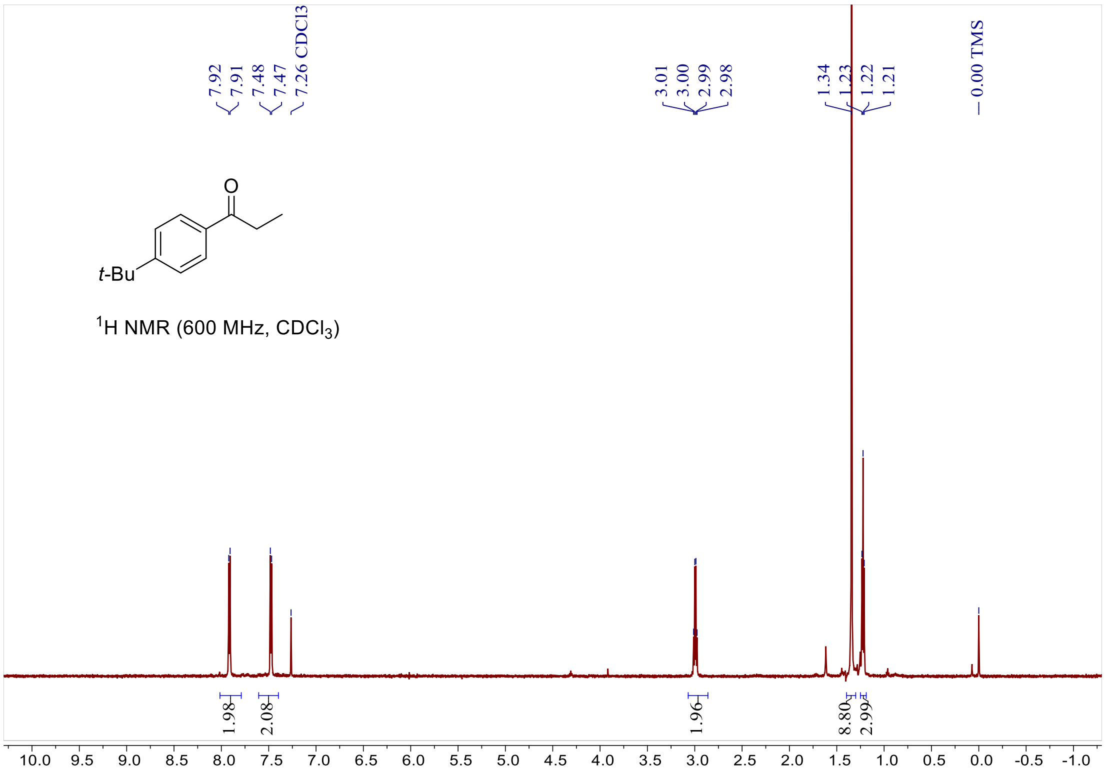


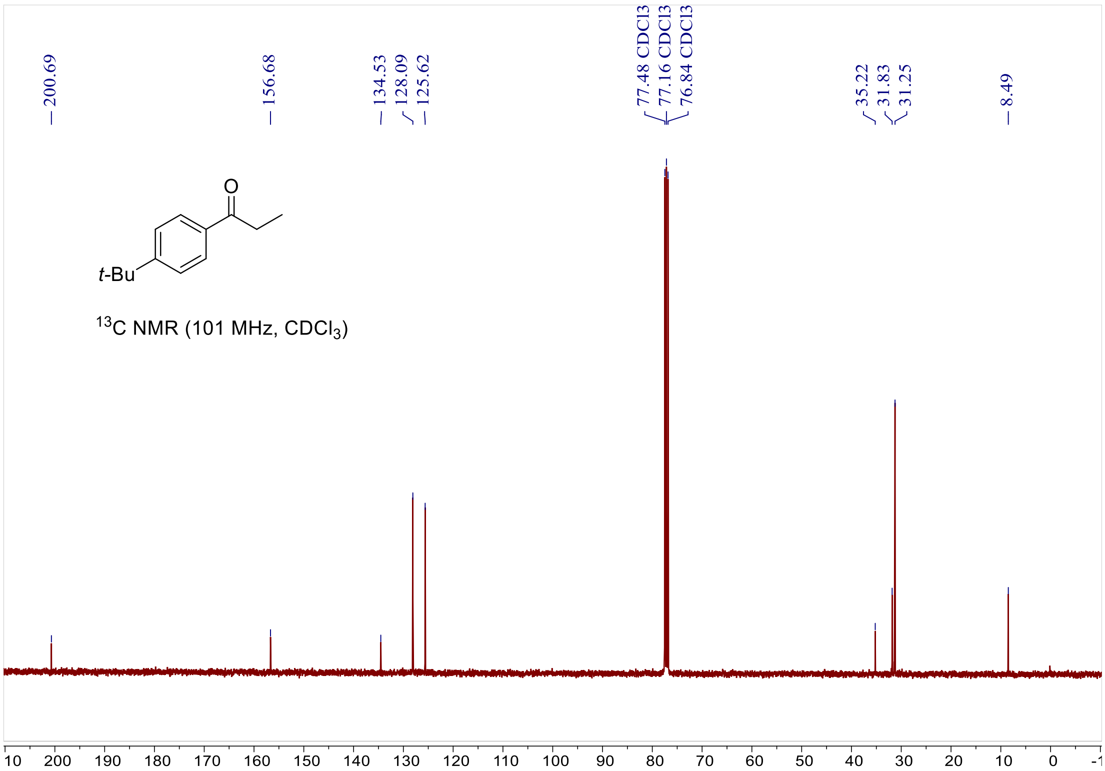
^{1}H and ^{13}C NMR spectra of compound **3fa**



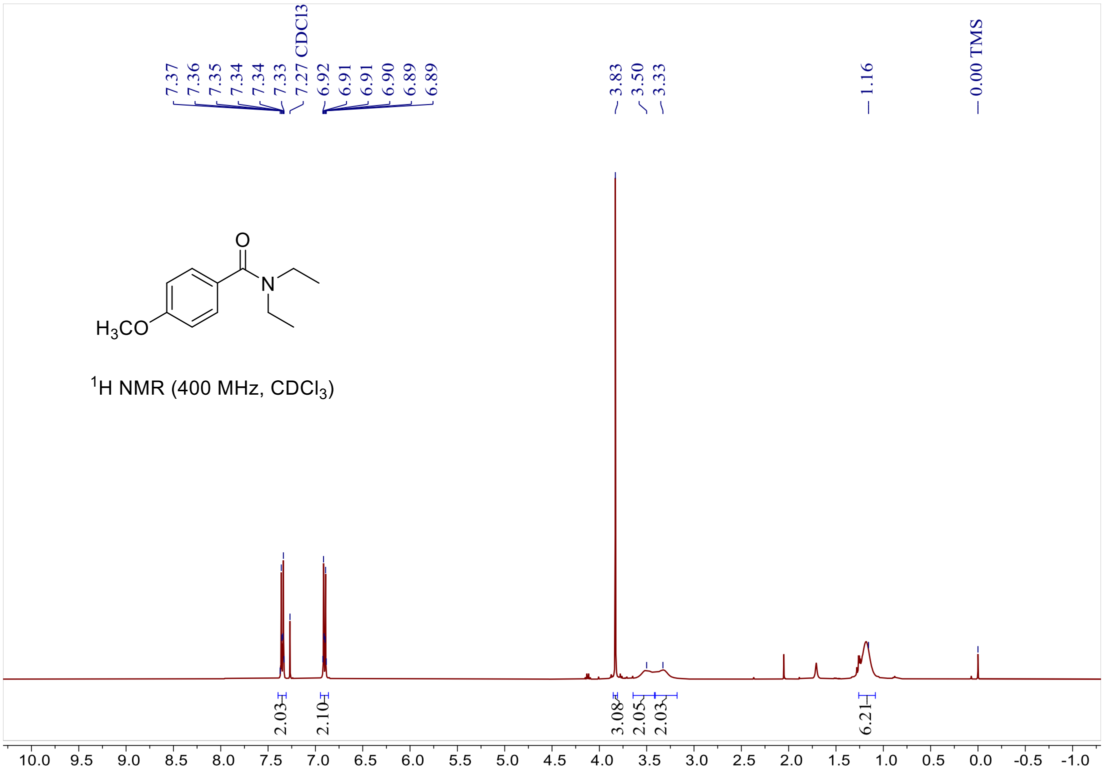


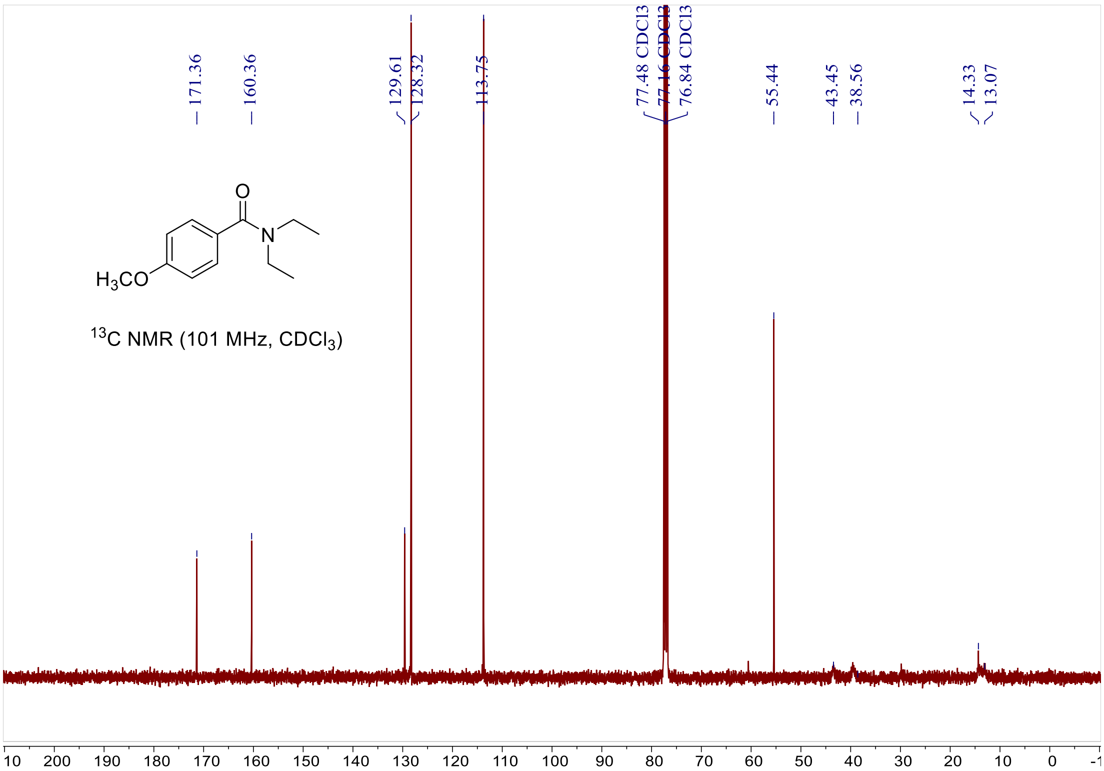
[1]H and [13]C NMR spectra of compound **4fa**



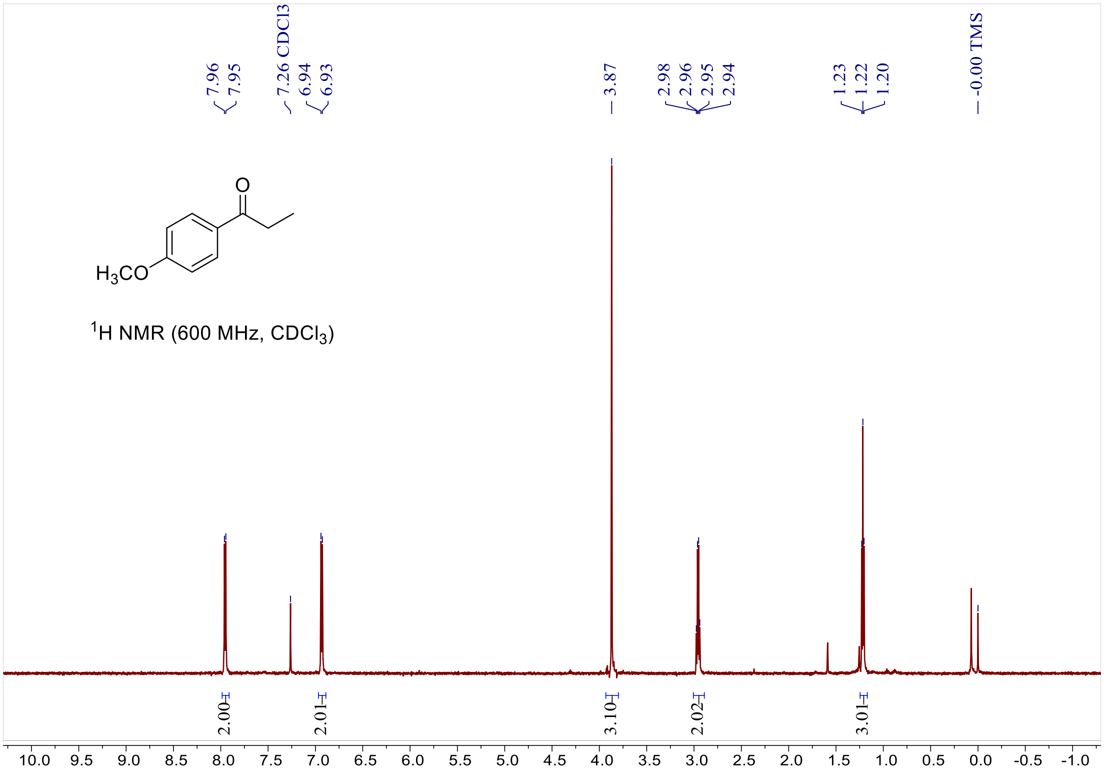


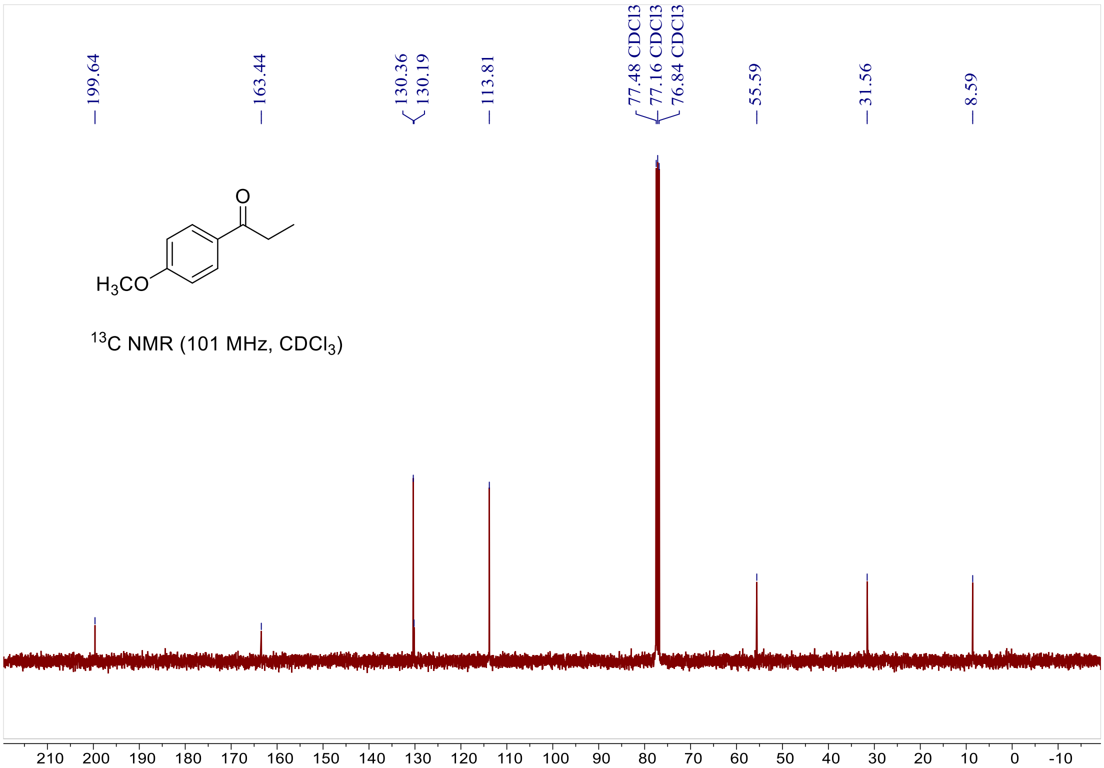
[1]H and [13]C NMR spectra of compound **3ga**



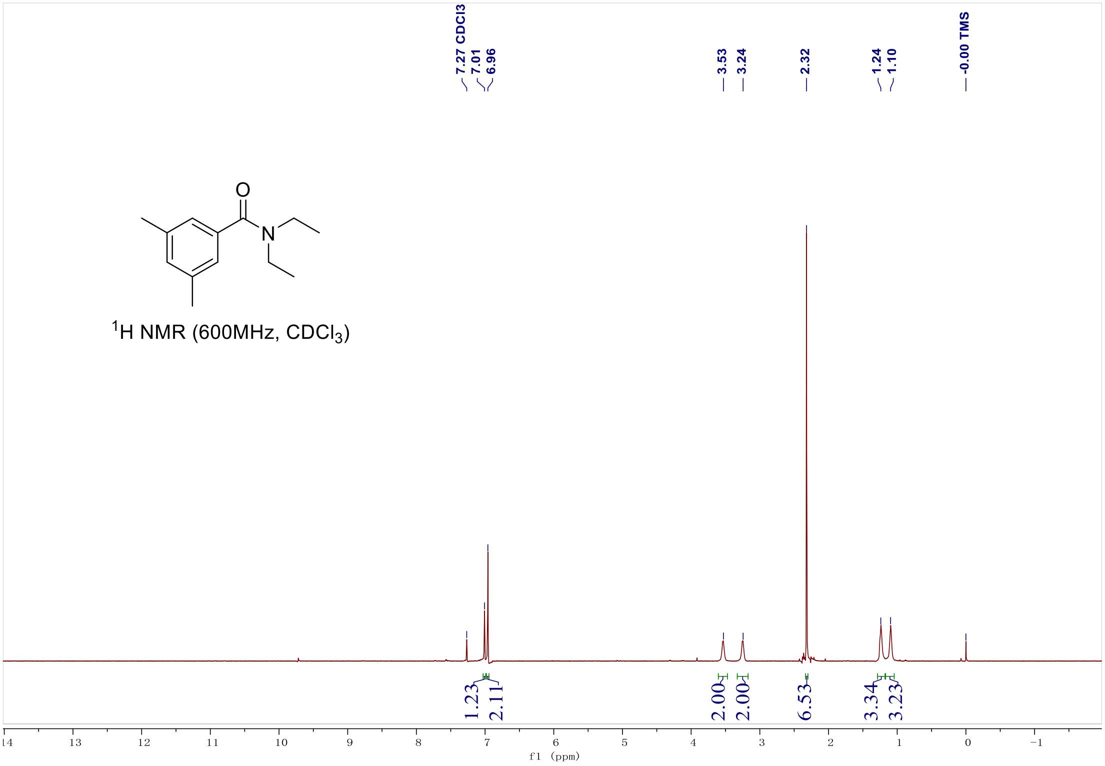


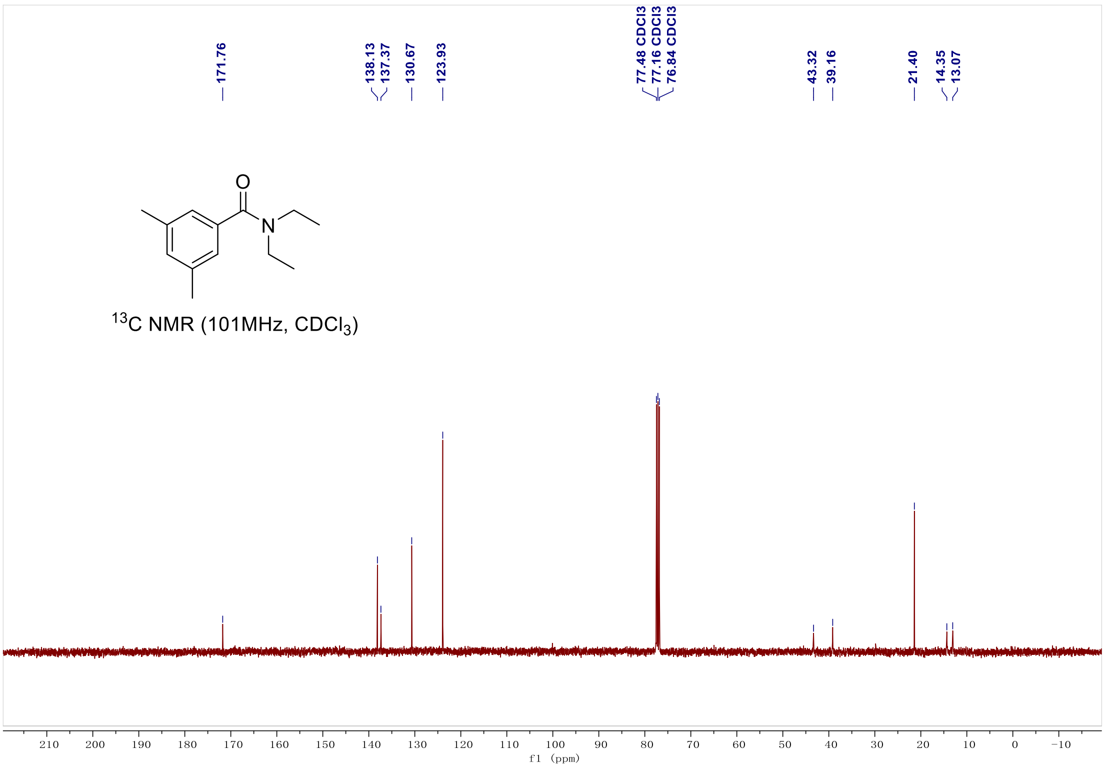
^{1}H and ^{13}C NMR spectra of compound **4ga**



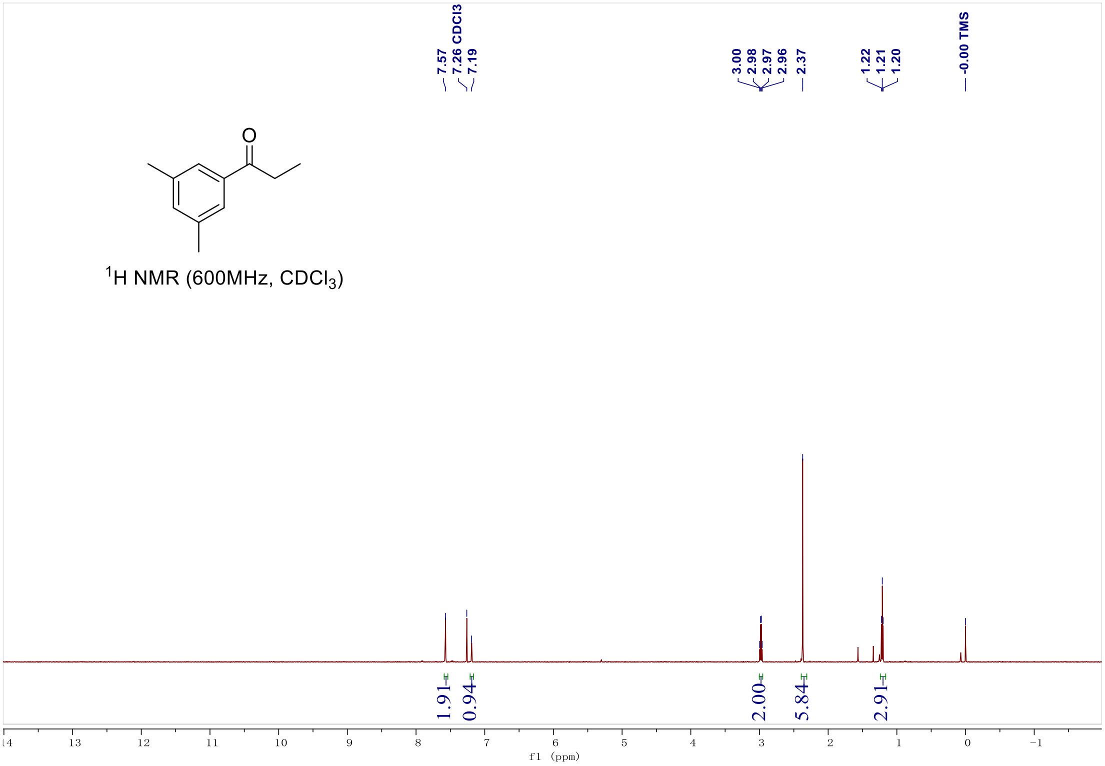


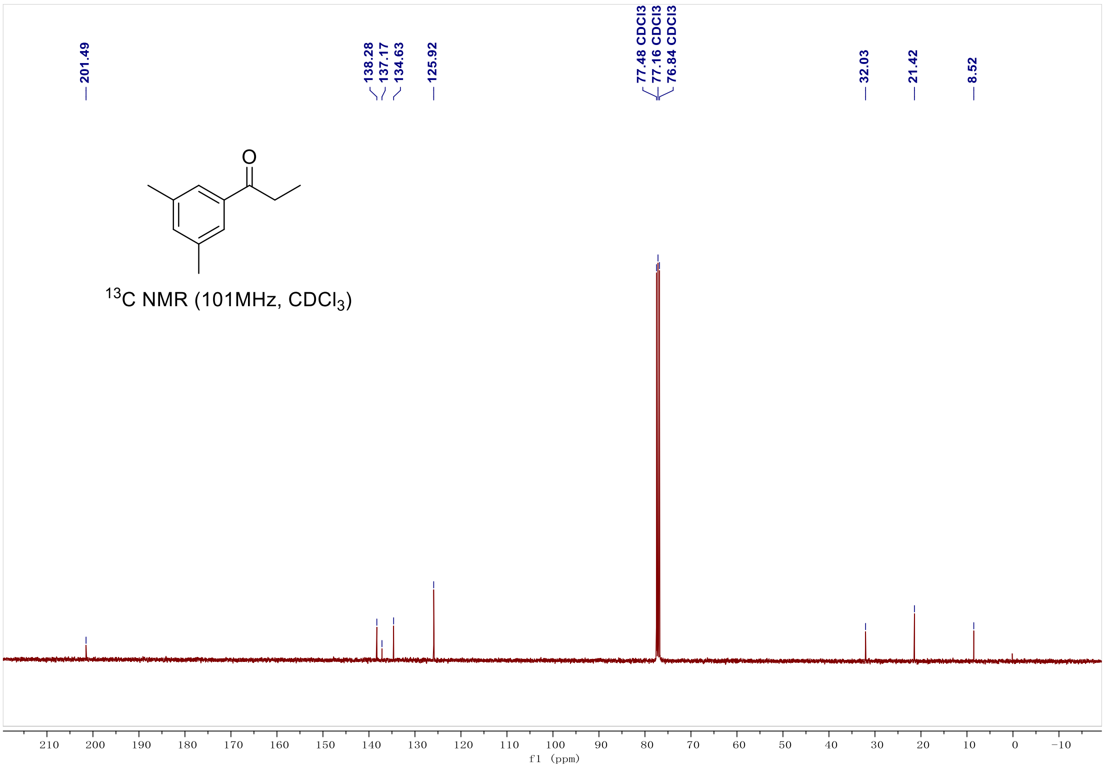
[1]H and [13]C NMR spectra of compound **3ha**



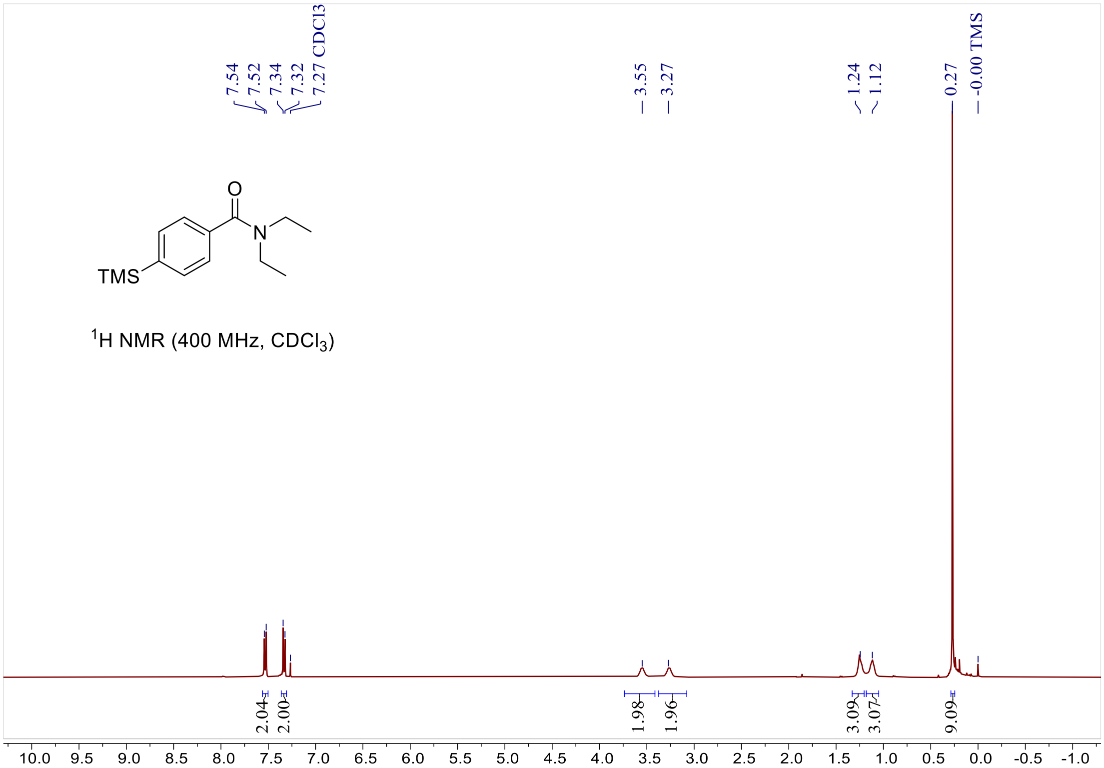


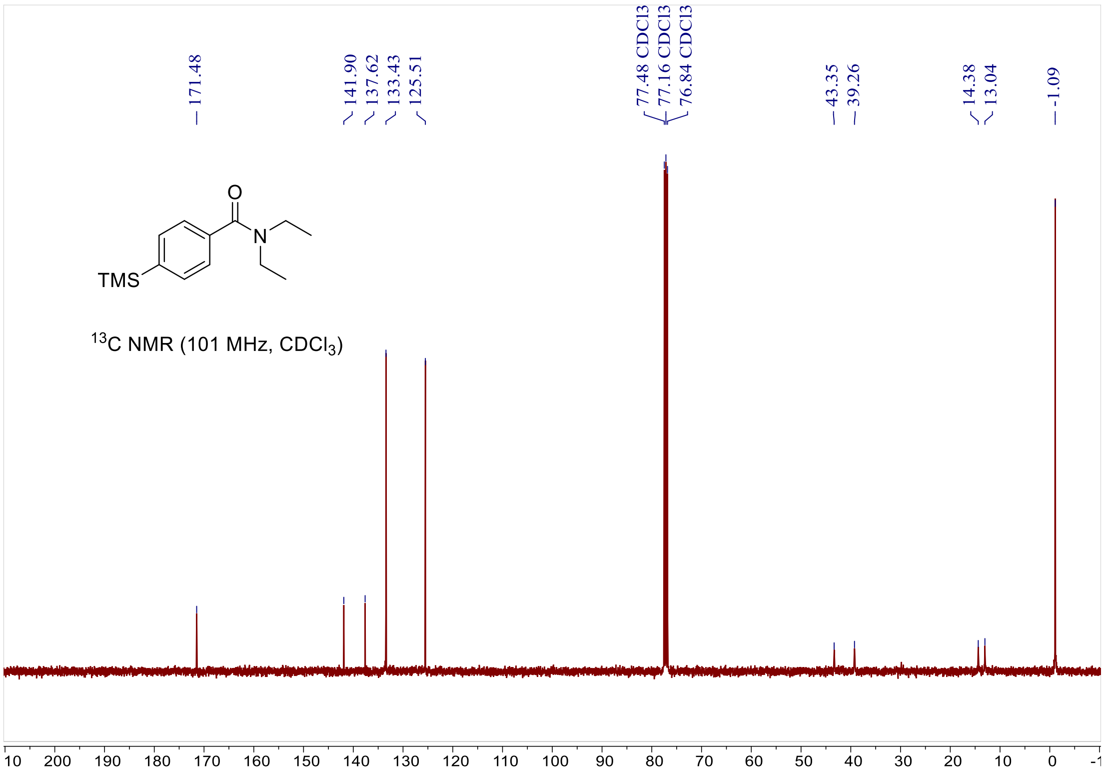
^{1}H and ^{13}C NMR spectra of compound **4ha**



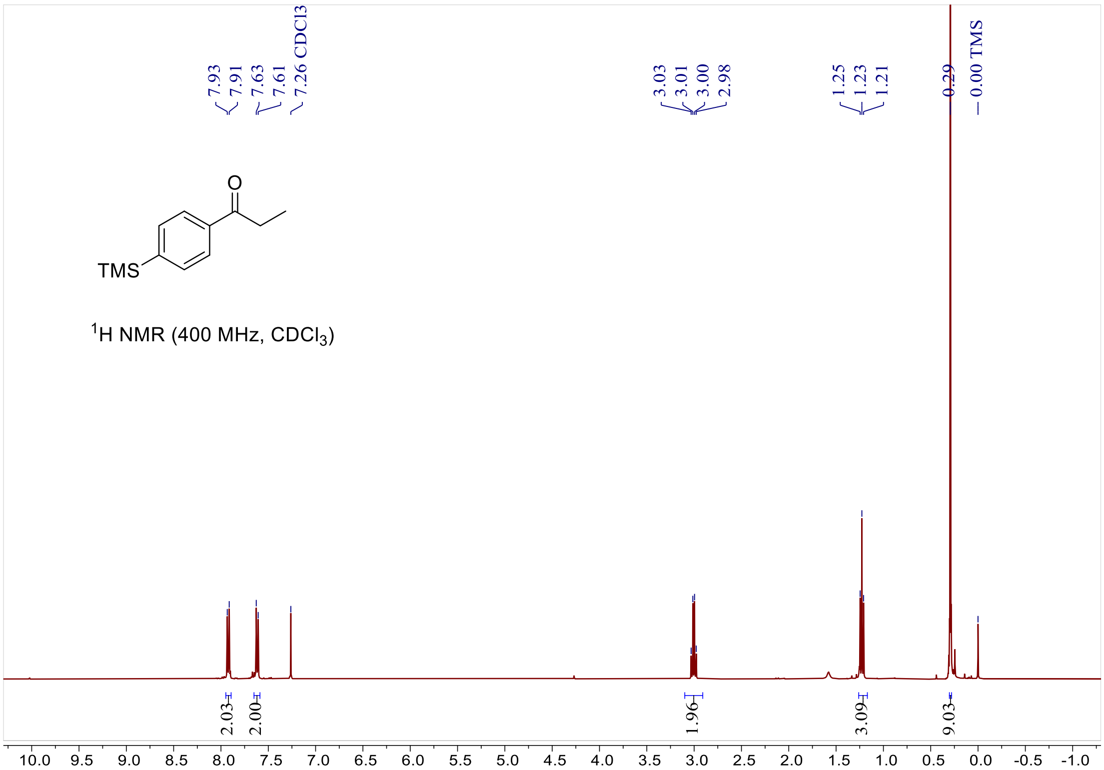


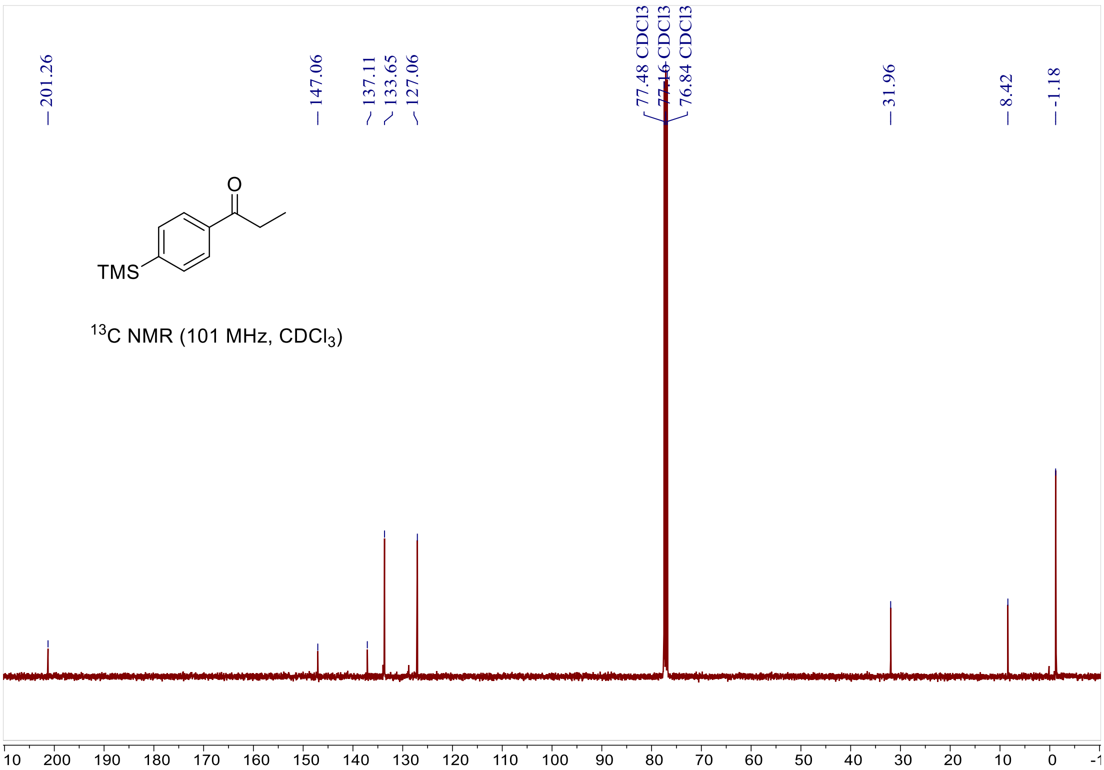
^1H and ^{13}C NMR spectra of compound **3ia**



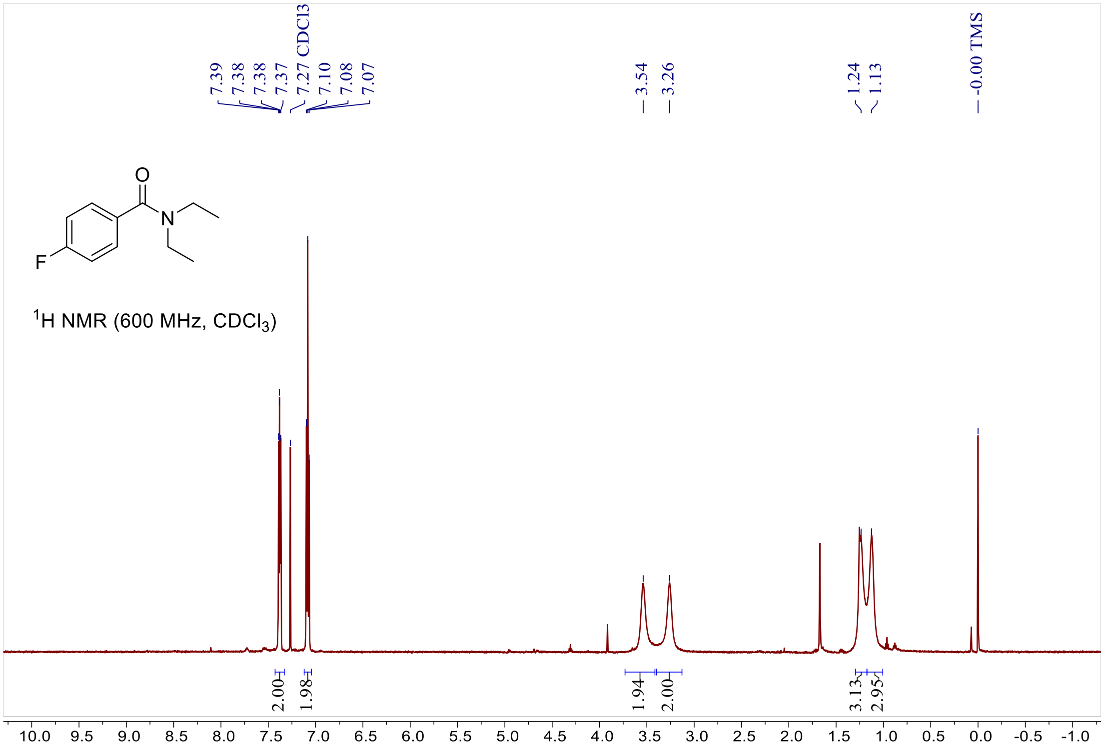


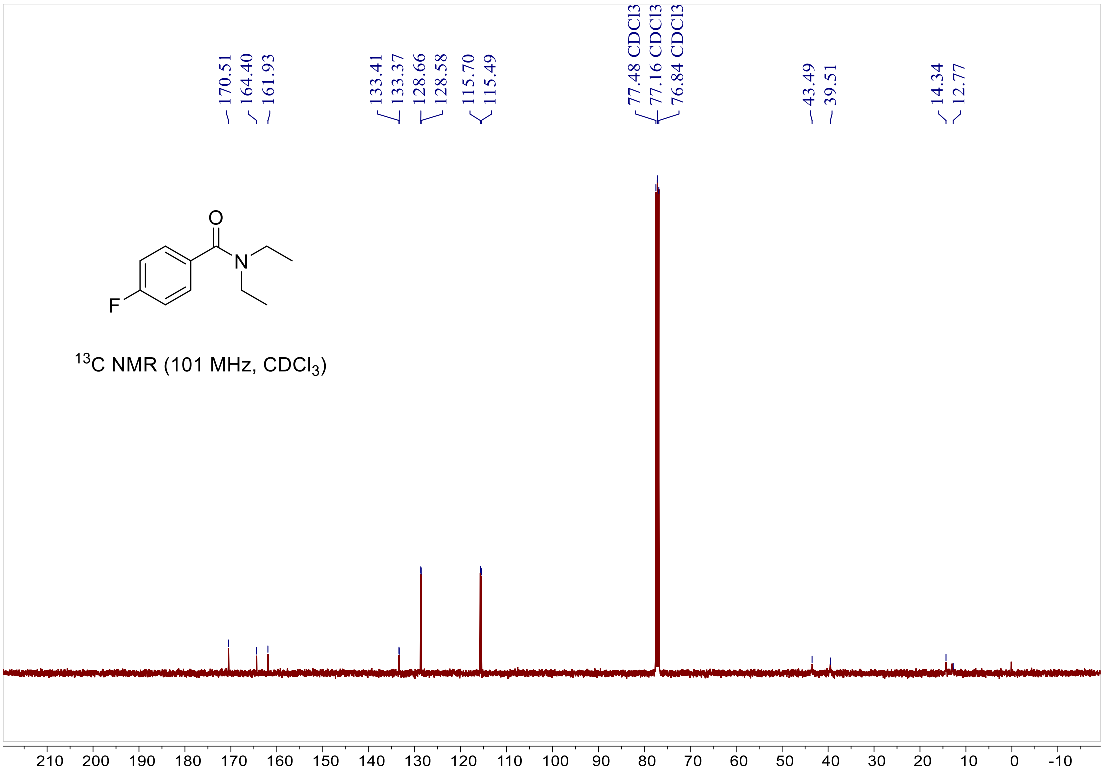
^{1}H and ^{13}C NMR spectra of compound **4ia**

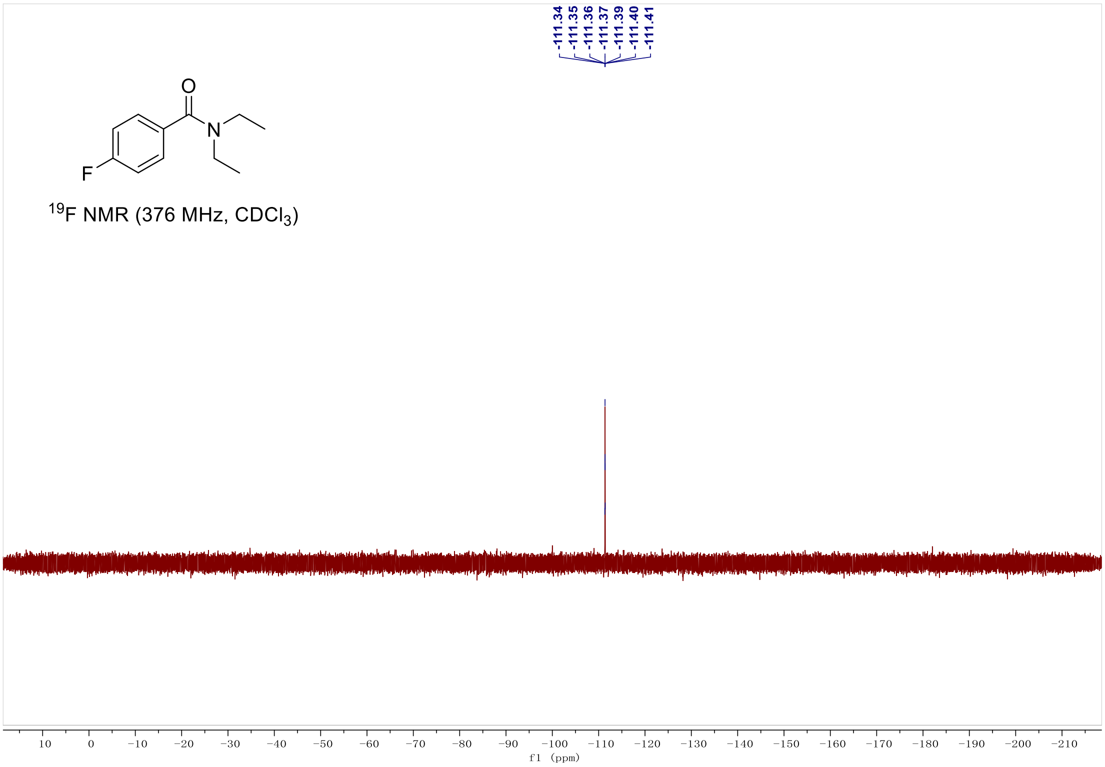




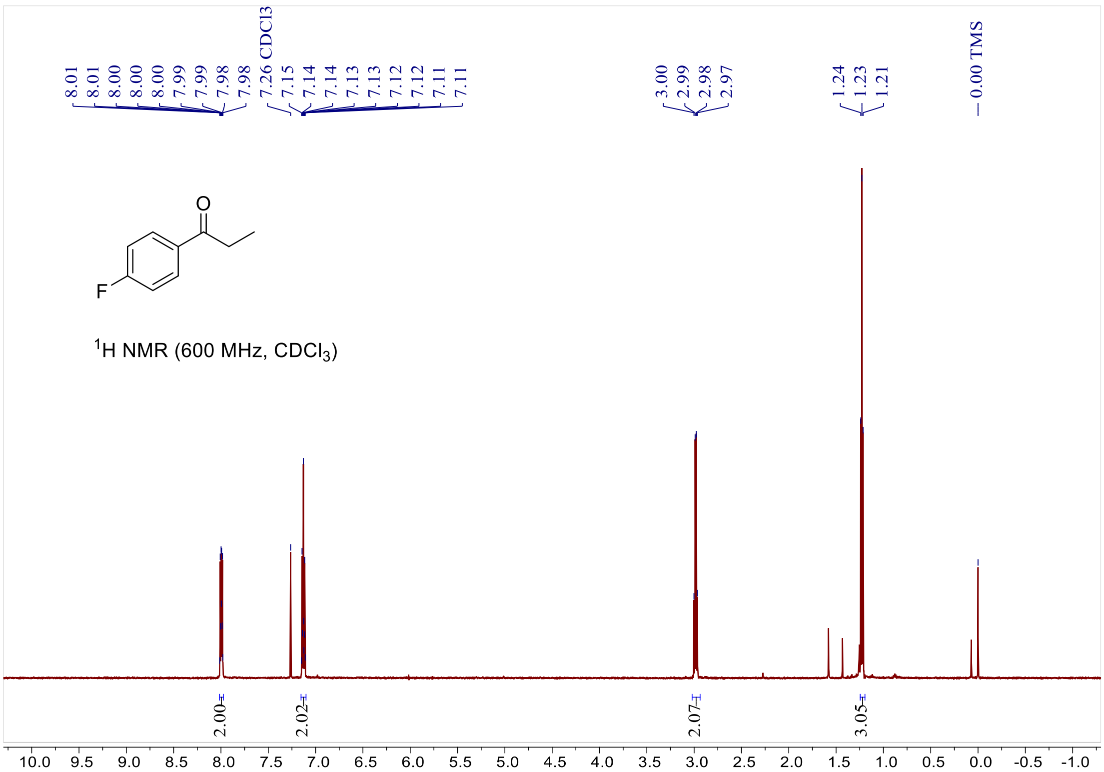
^{1}H, ^{13}C and ^{19}F NMR spectra of compound 3**ja**

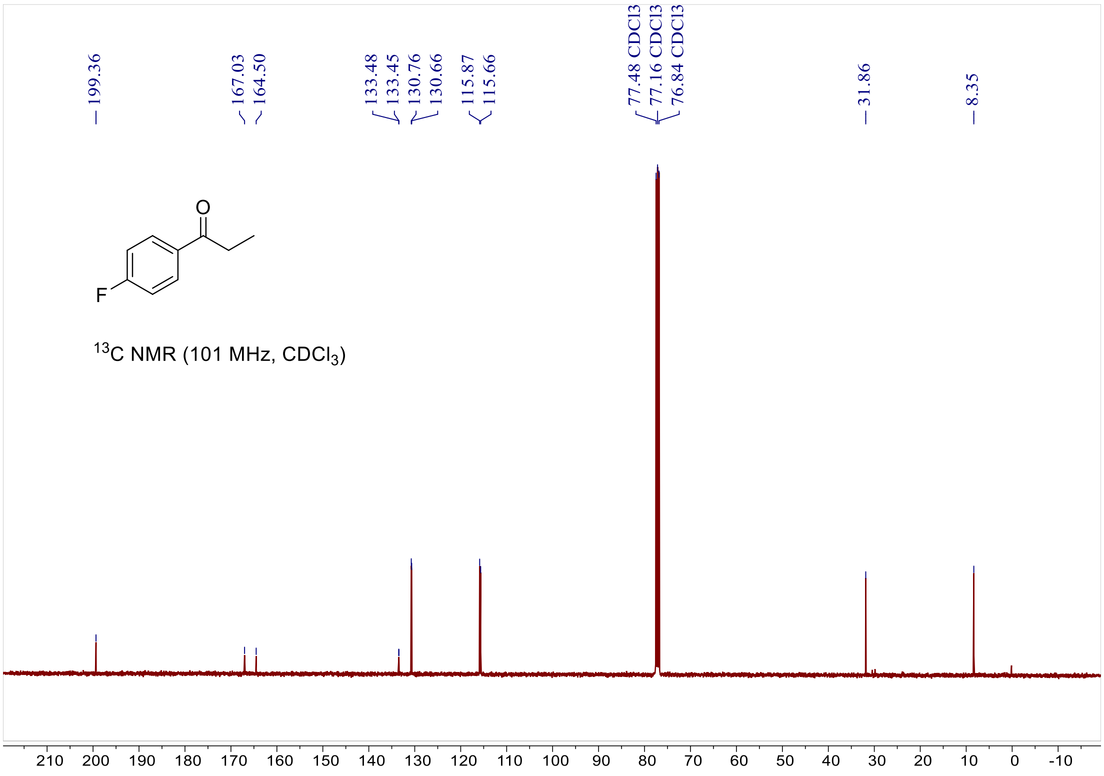


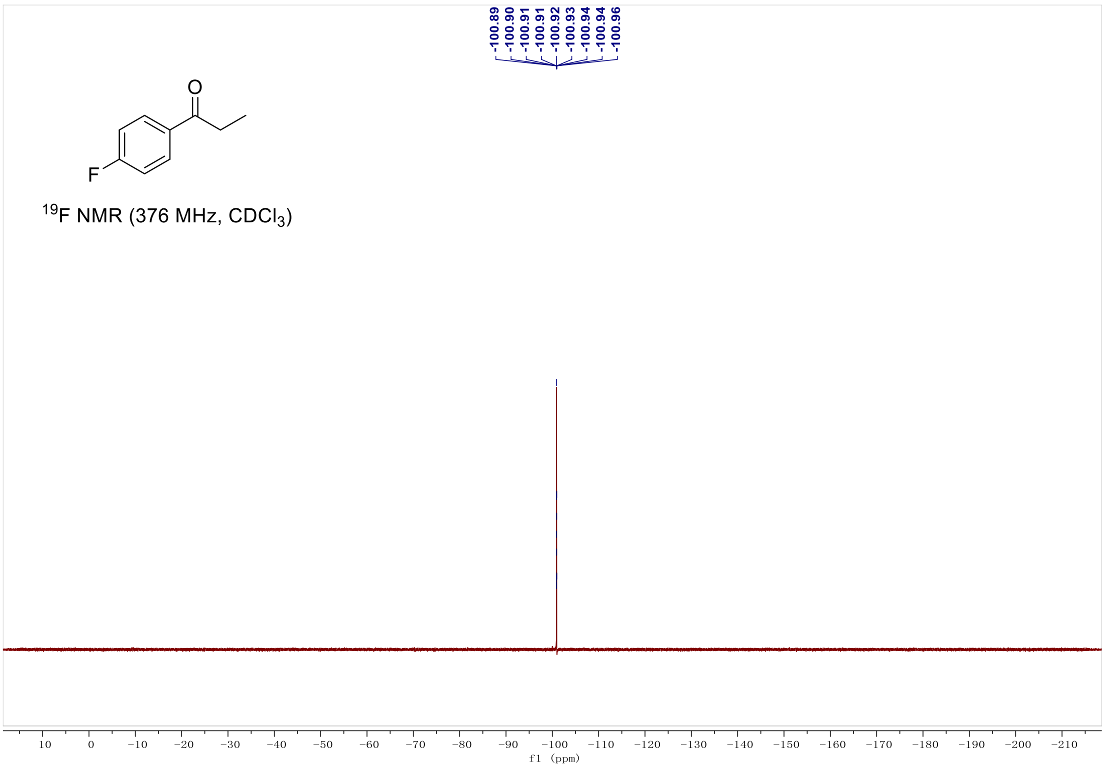




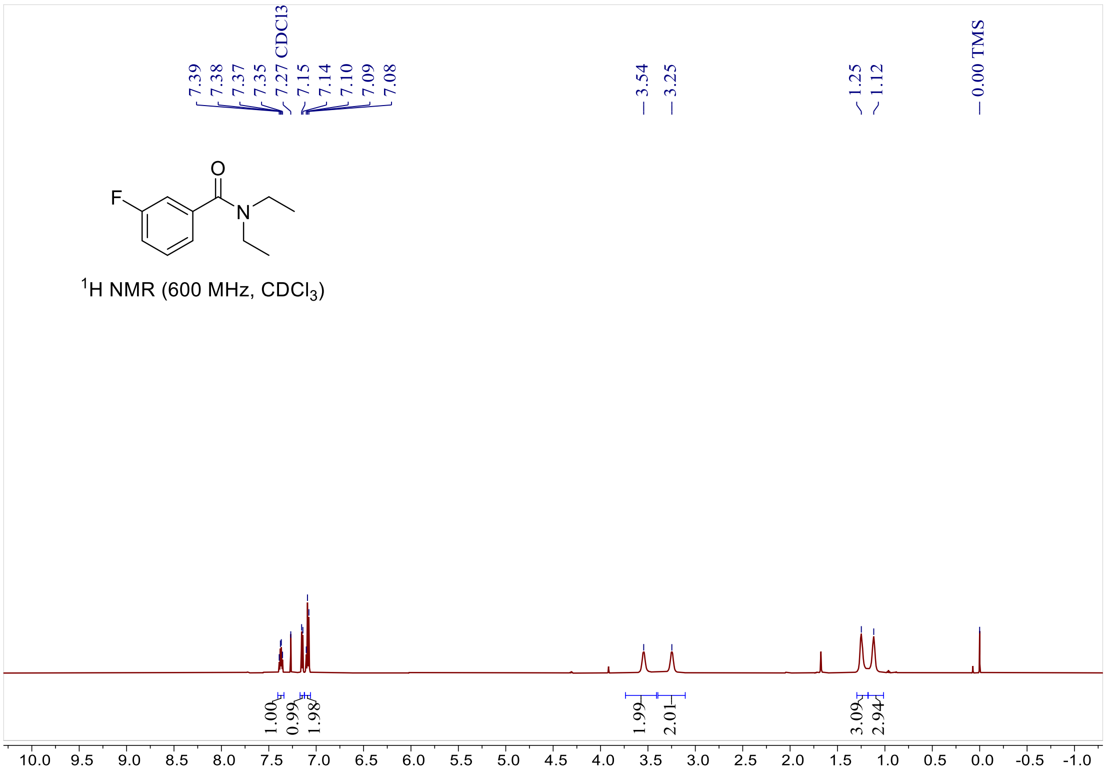
^{1}H, ^{13}C and ^{19}F NMR spectra of compound **4ja**

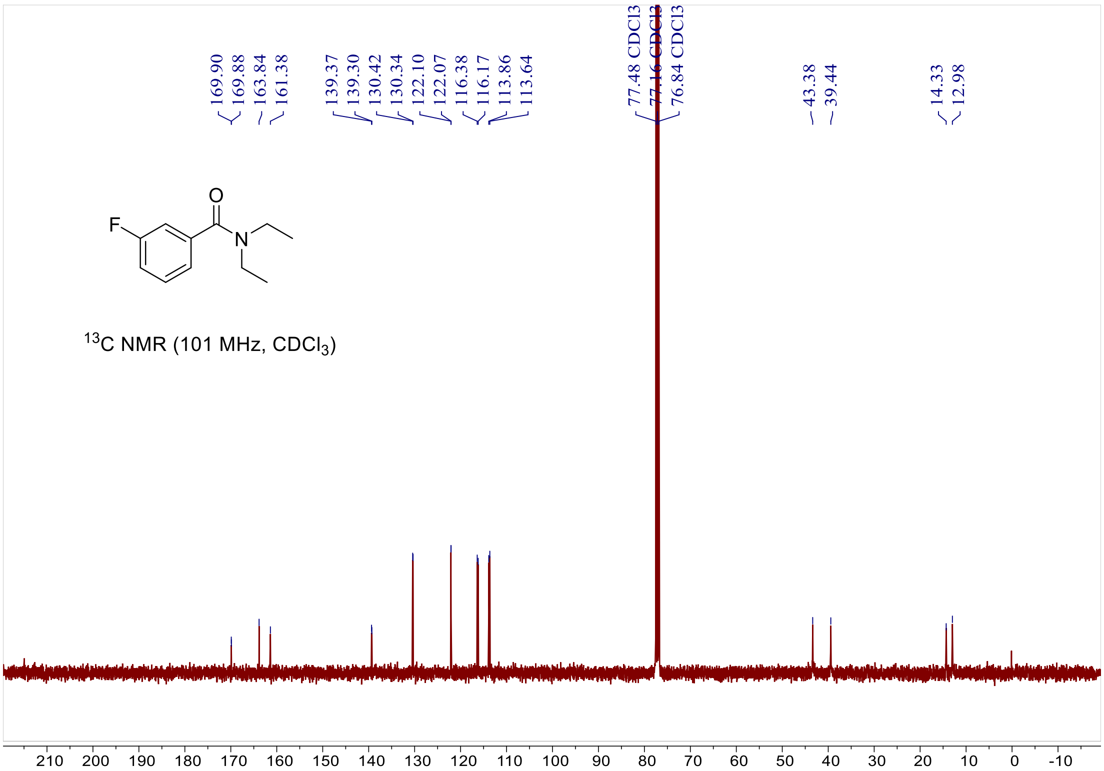


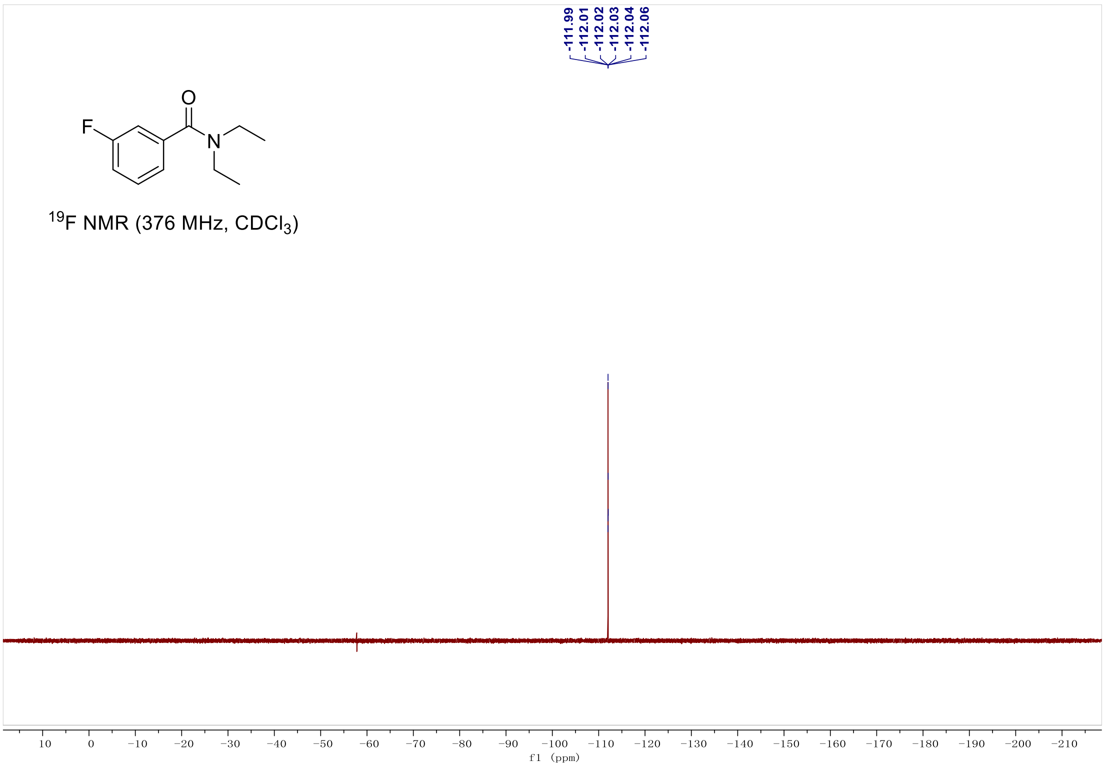

199.36
167.03
164.50
133.48
133.45
130.76
130.66
115.87
115.66
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
31.86
8.35
O
F
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


-100.89
-100.90
-100.91
-100.91
-100.92
-100.93
-100.94
-100.94
-100.96
O
F
19F NMR (376 MHz, CDCl3)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

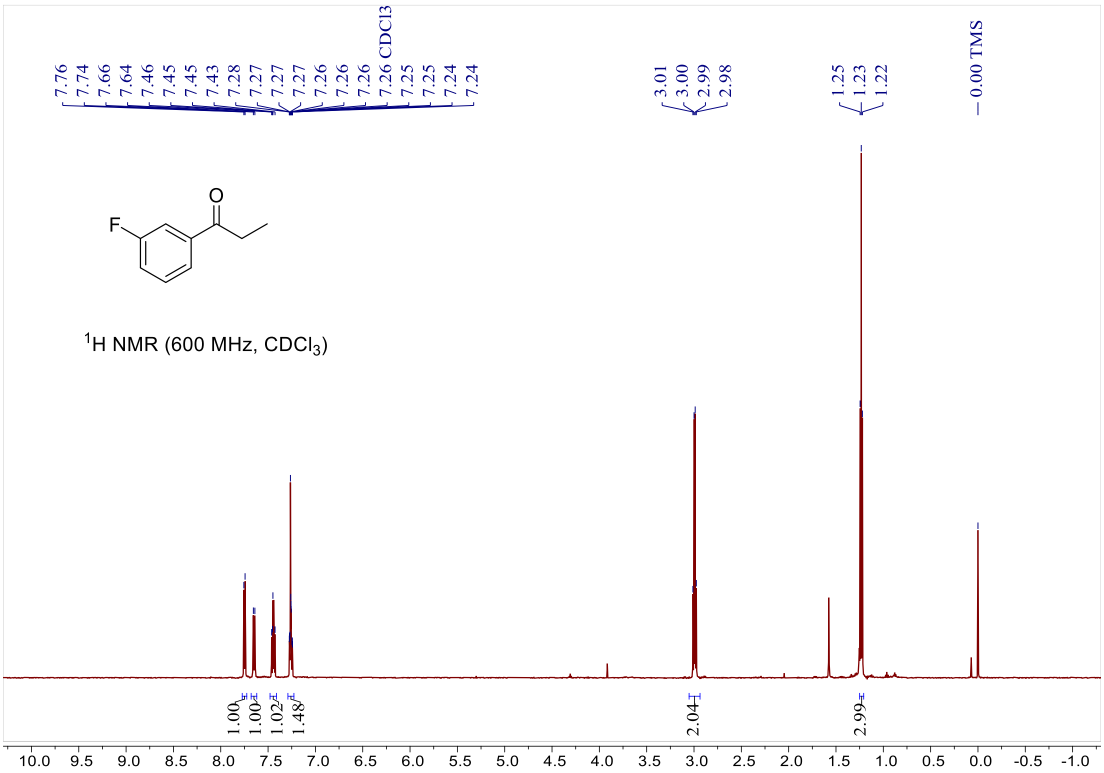
^{1}H, ^{13}C and ^{19}F NMR spectra of compound **3ka**

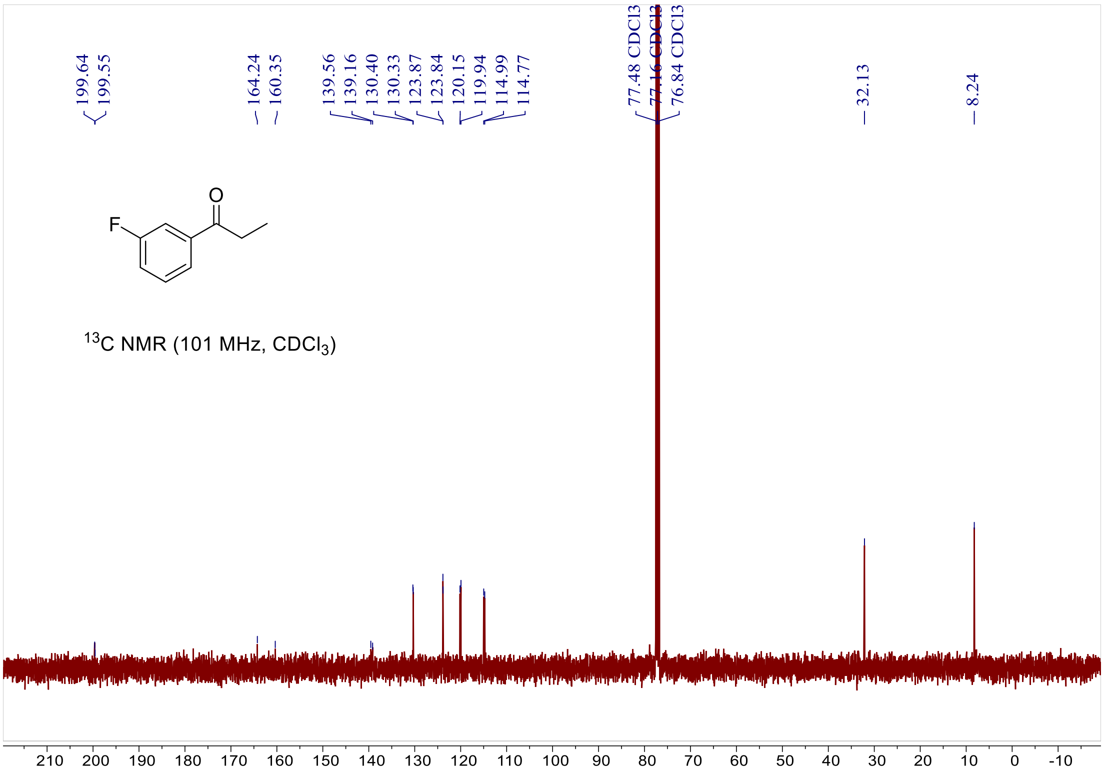


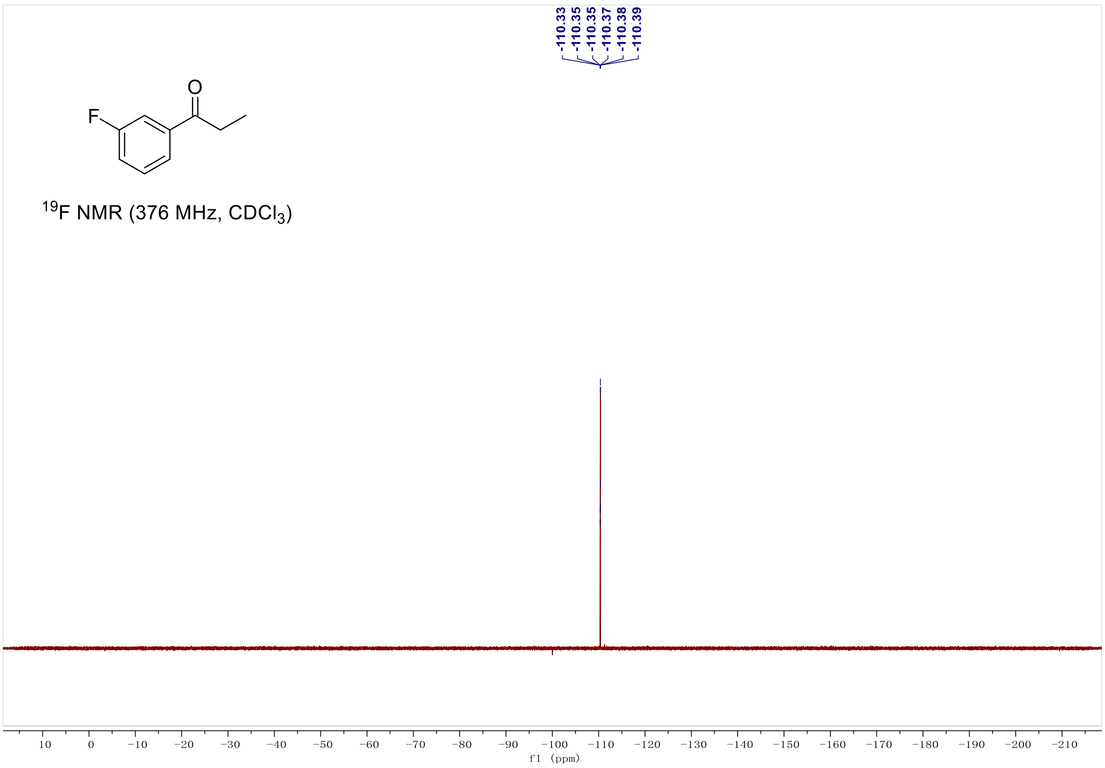




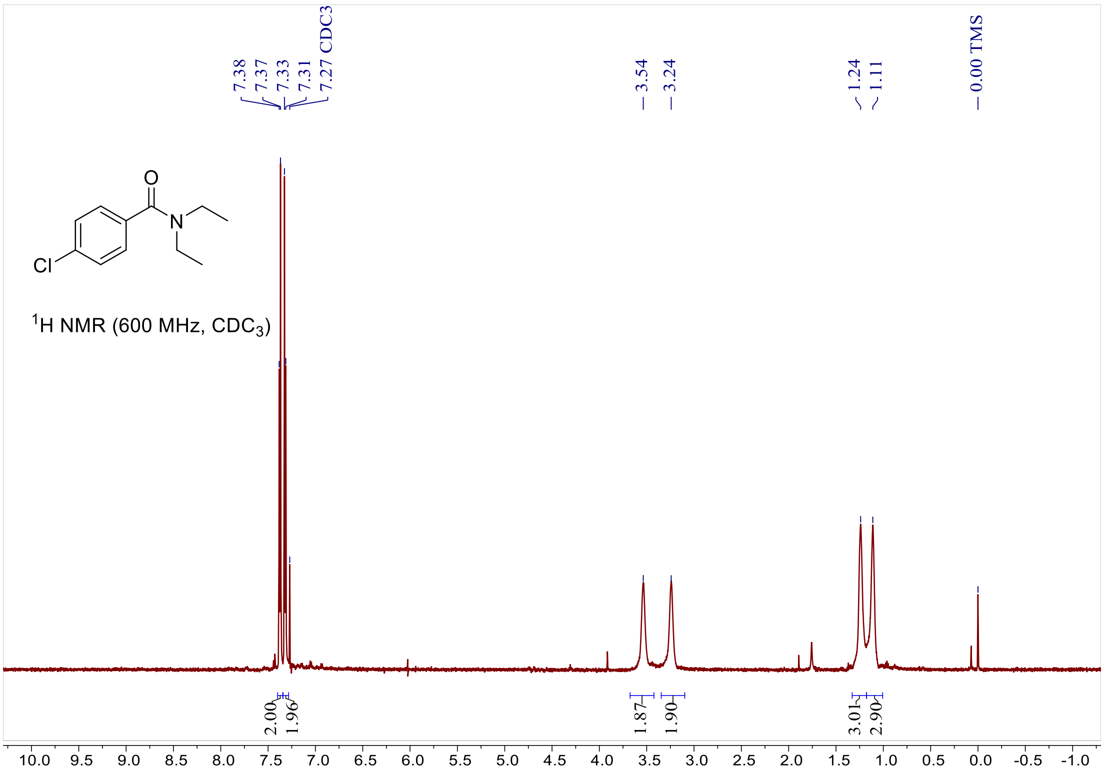
^{1}H, ^{13}C and ^{19}F NMR spectra of compound **4ka**

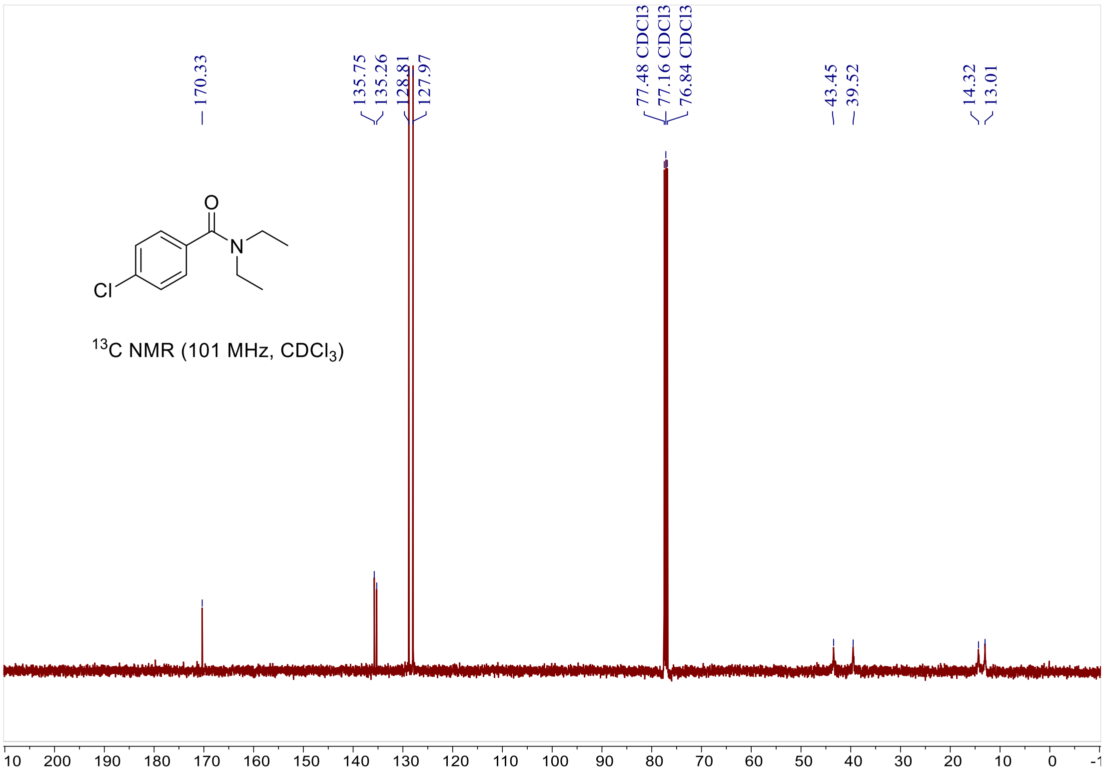



199.64
199.55
164.24
160.35
139.56
139.16
130.40
130.33
123.87
123.84
120.15
119.94
114.99
114.77
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
32.13
8.24
F
O
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

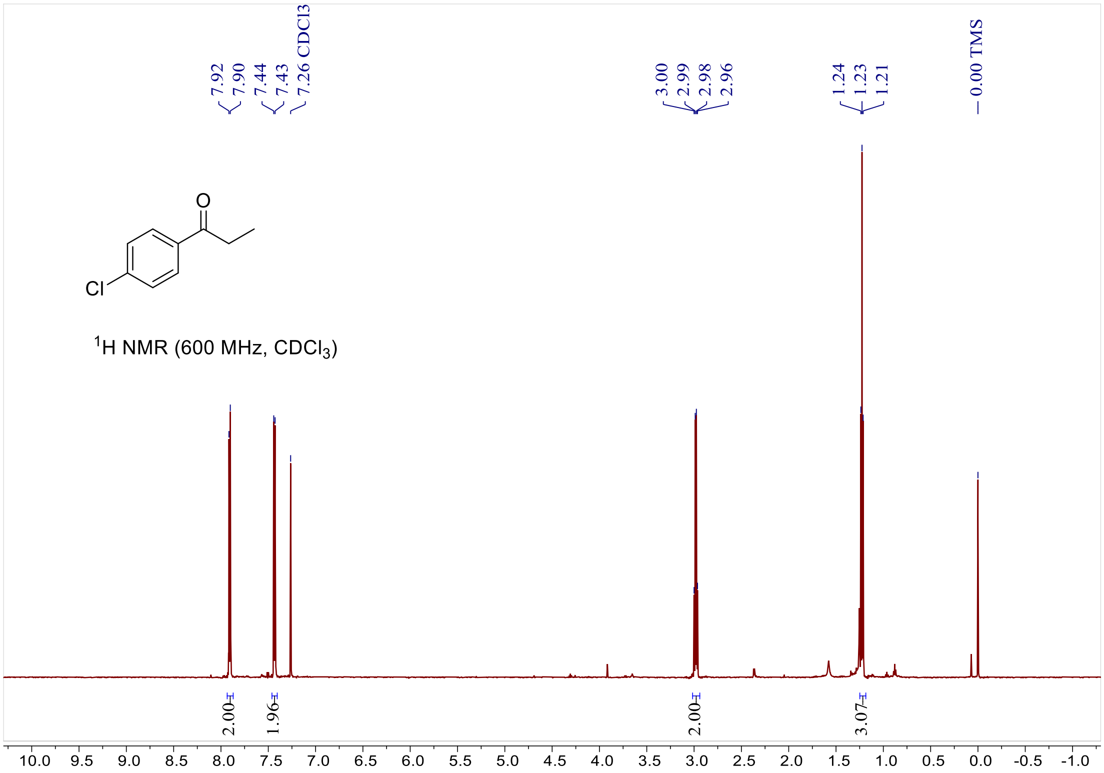

-110.33
-110.35
-110.35
-110.37
-110.38
-110.39
F
O
19F NMR (376 MHz, CDCl3)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

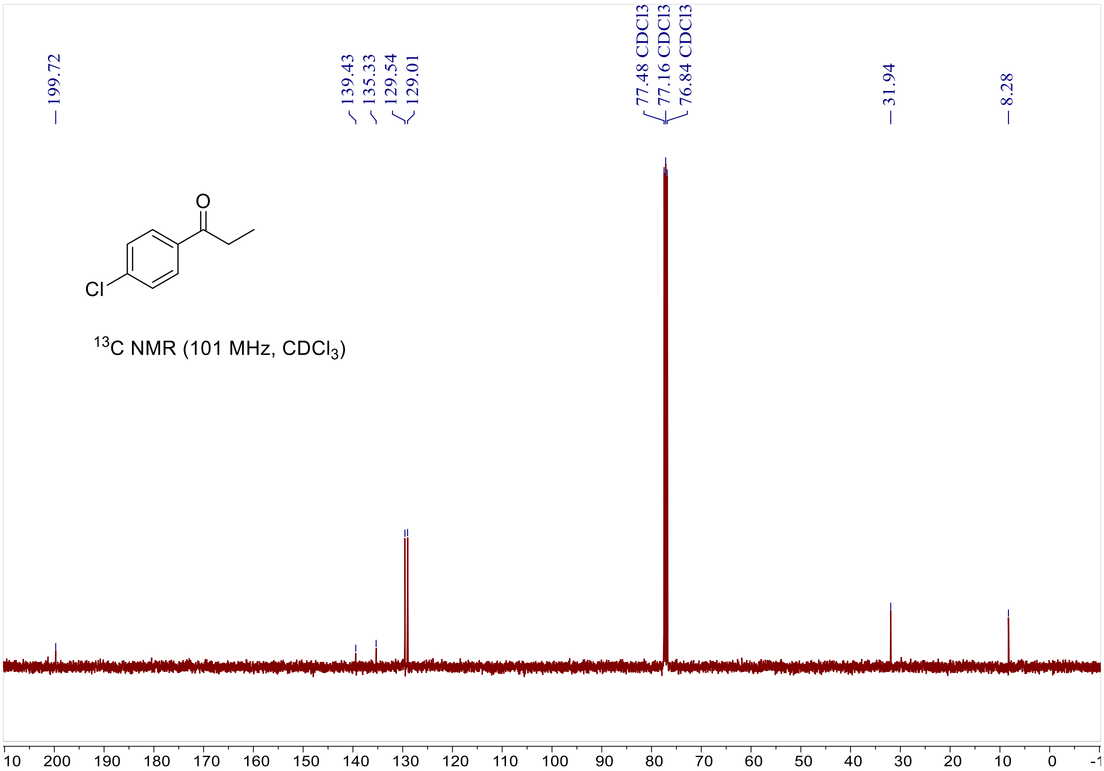
[1]H and [13]C NMR spectra of compound **3la**



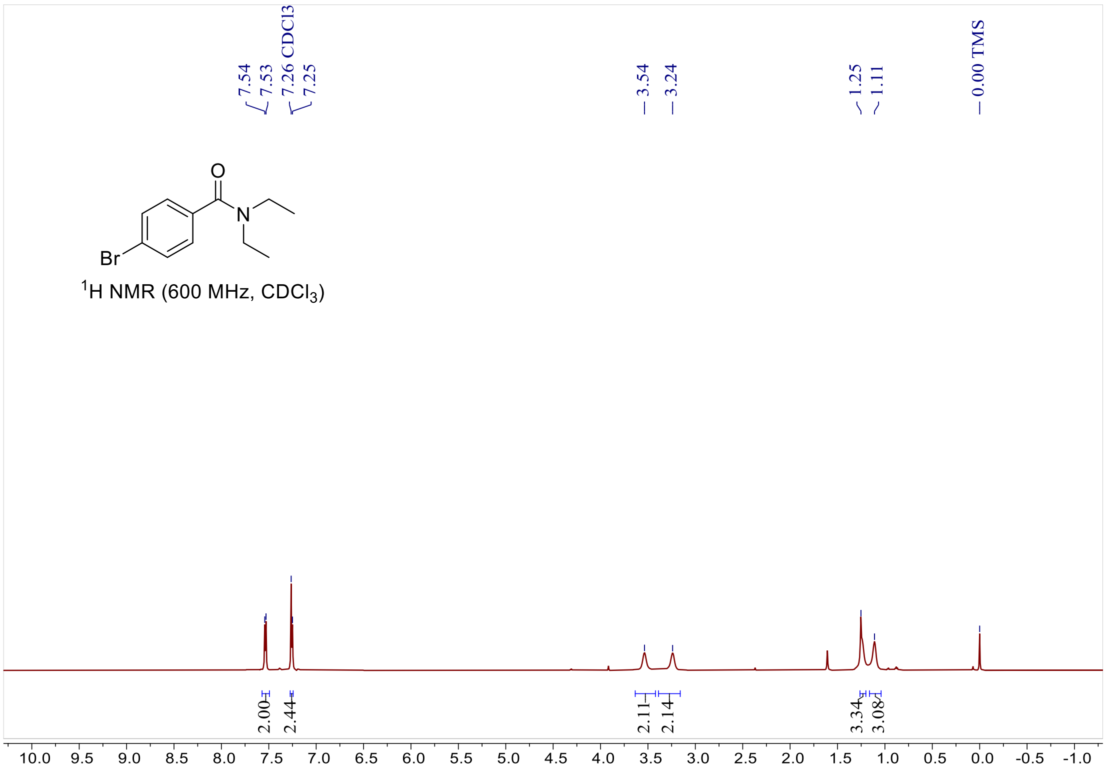


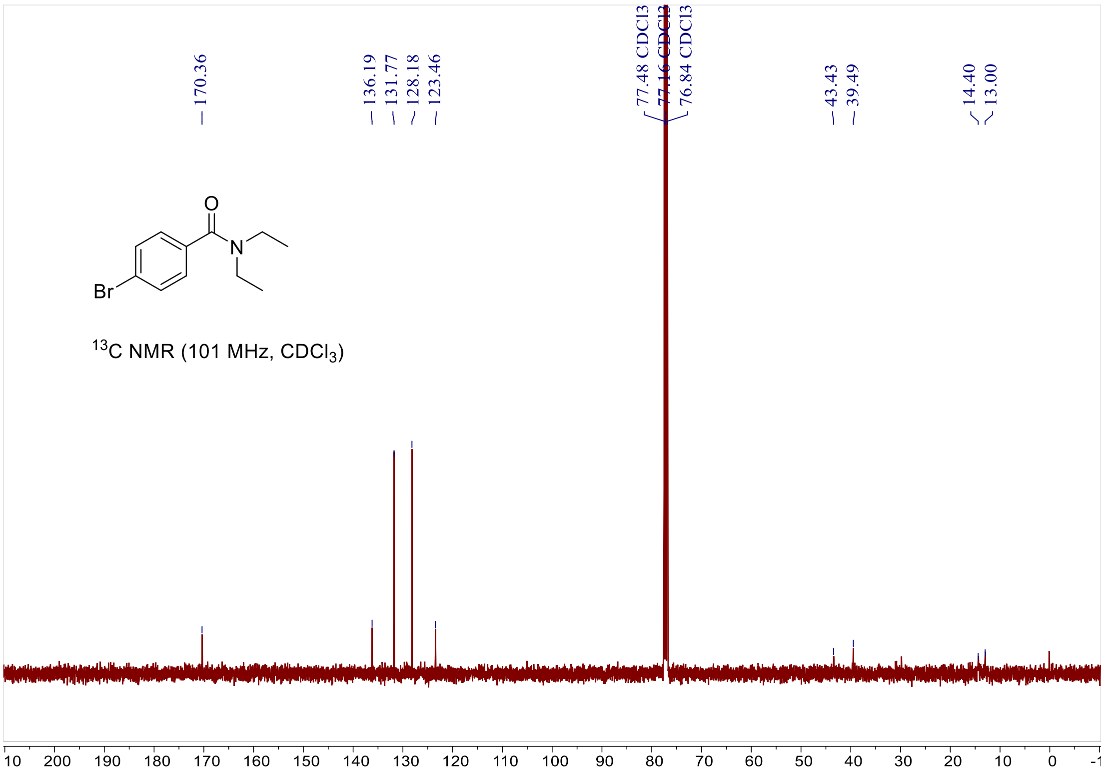
[1]H and [13]C NMR spectra of compound **4la**



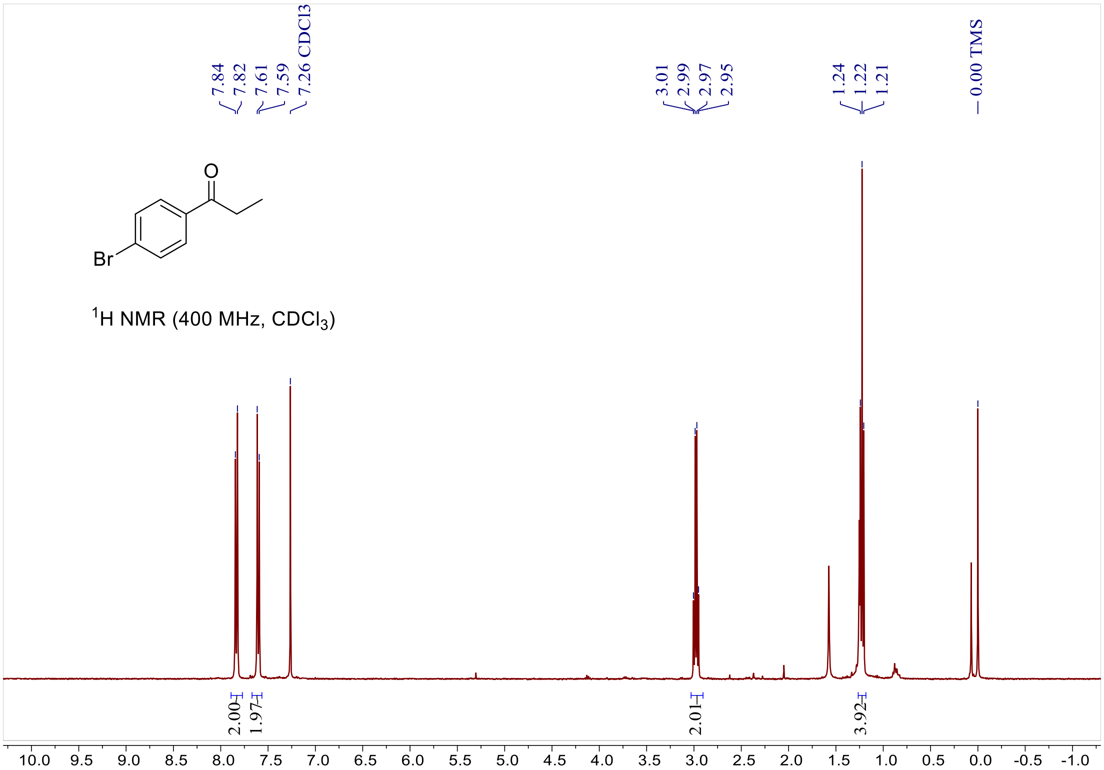


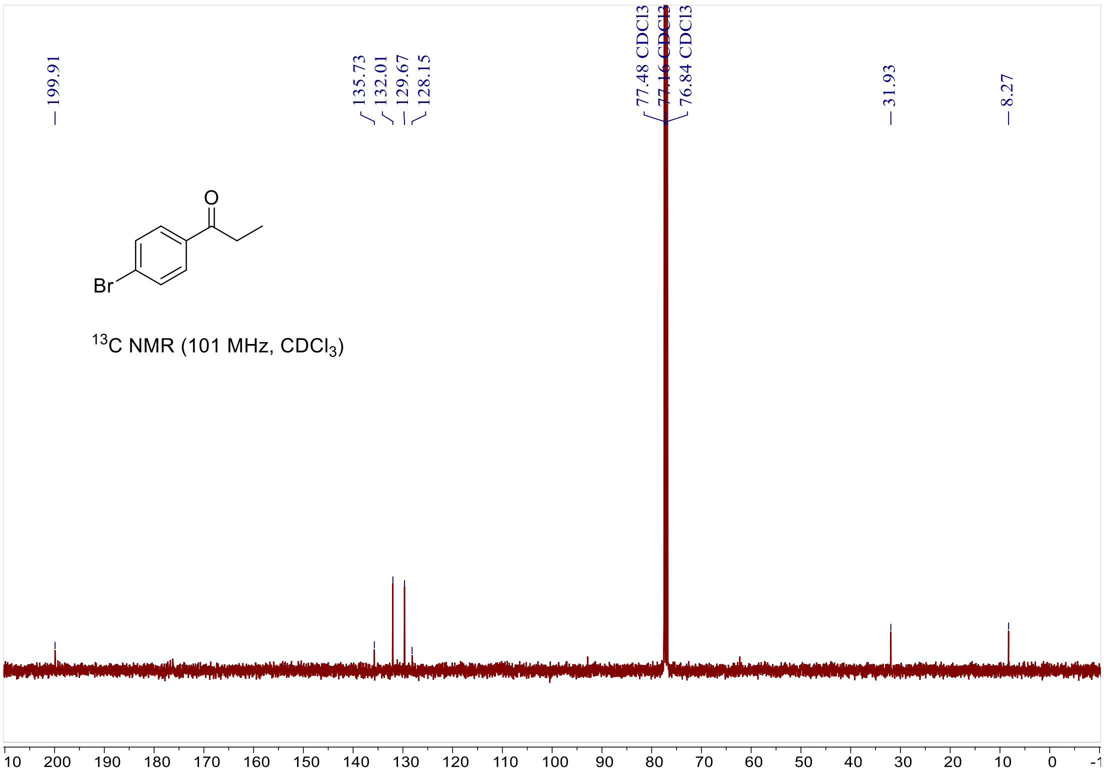
^{1}H and ^{13}C NMR spectra of compound **3ma**



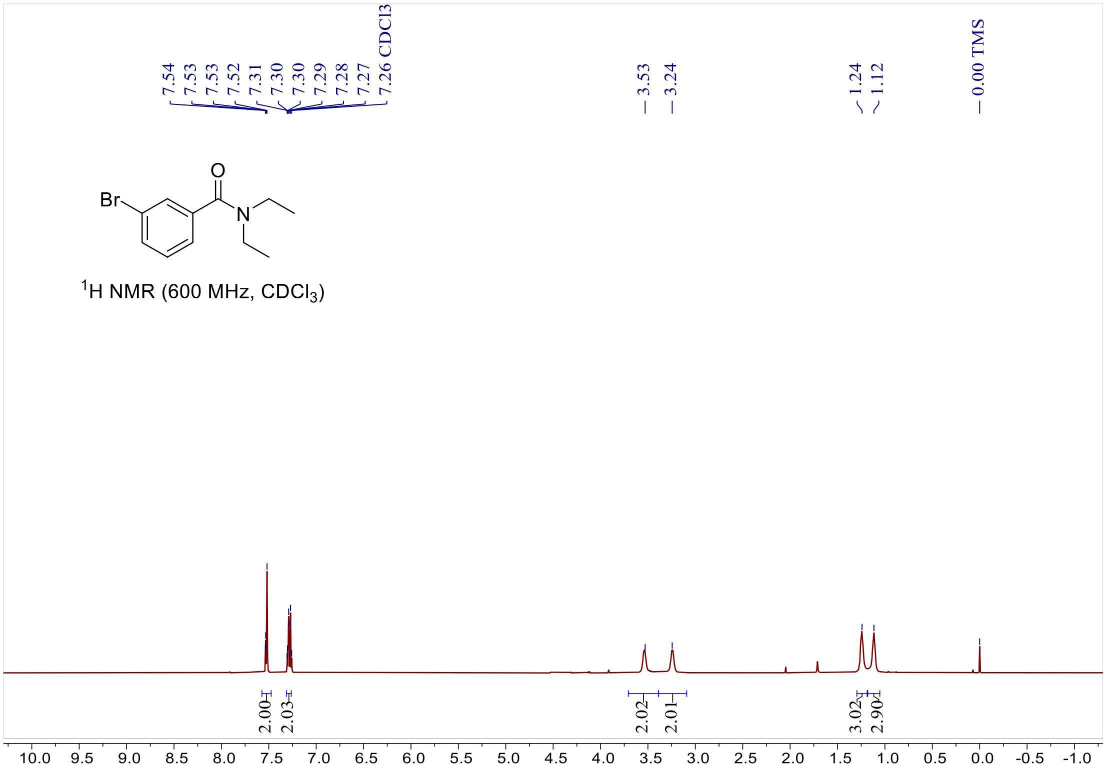


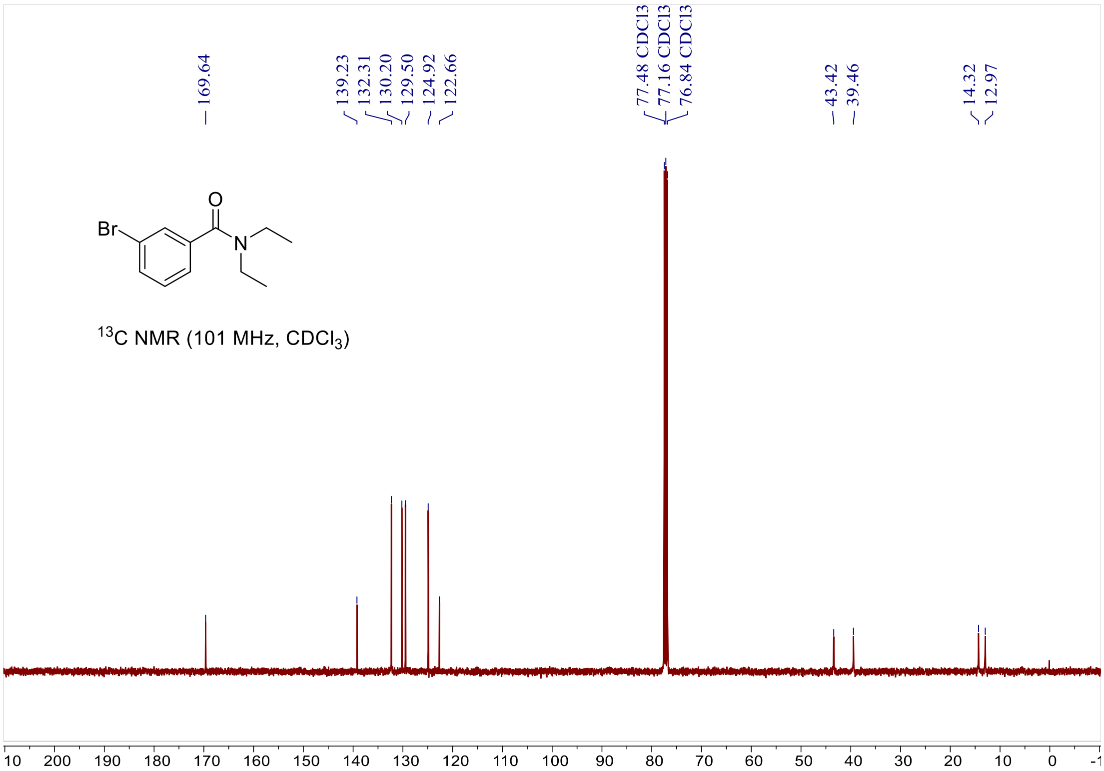
^{1}H and ^{13}C NMR spectra of compound **4ma**



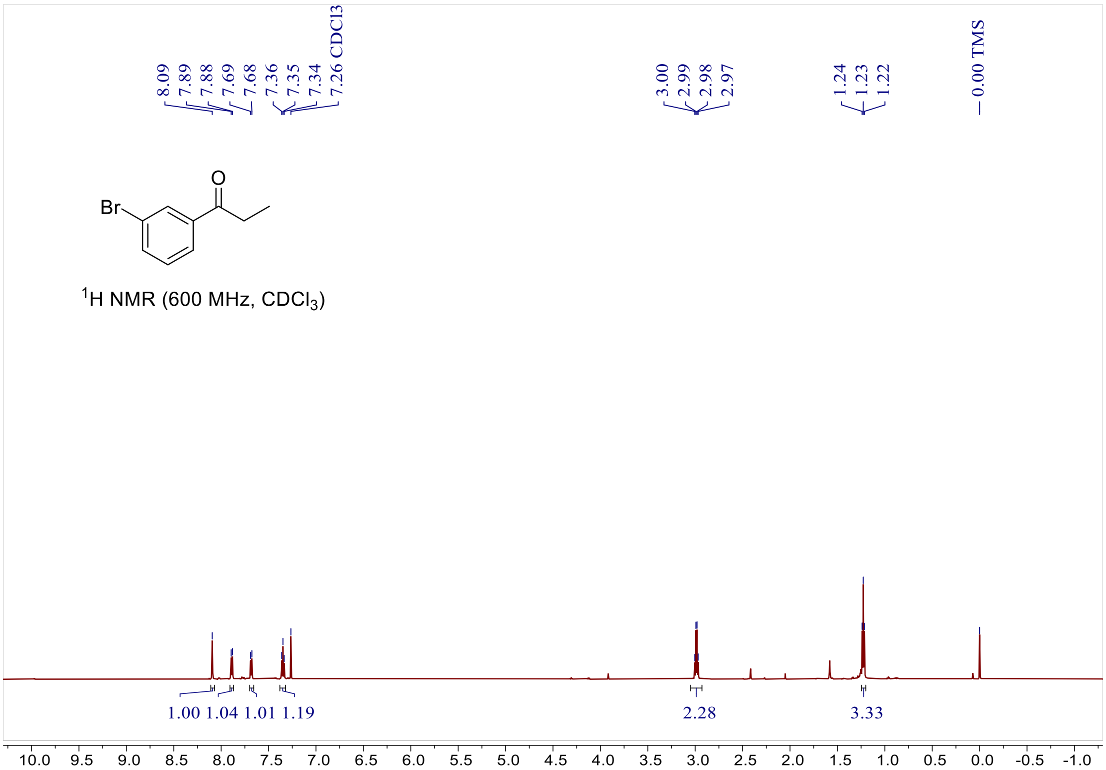


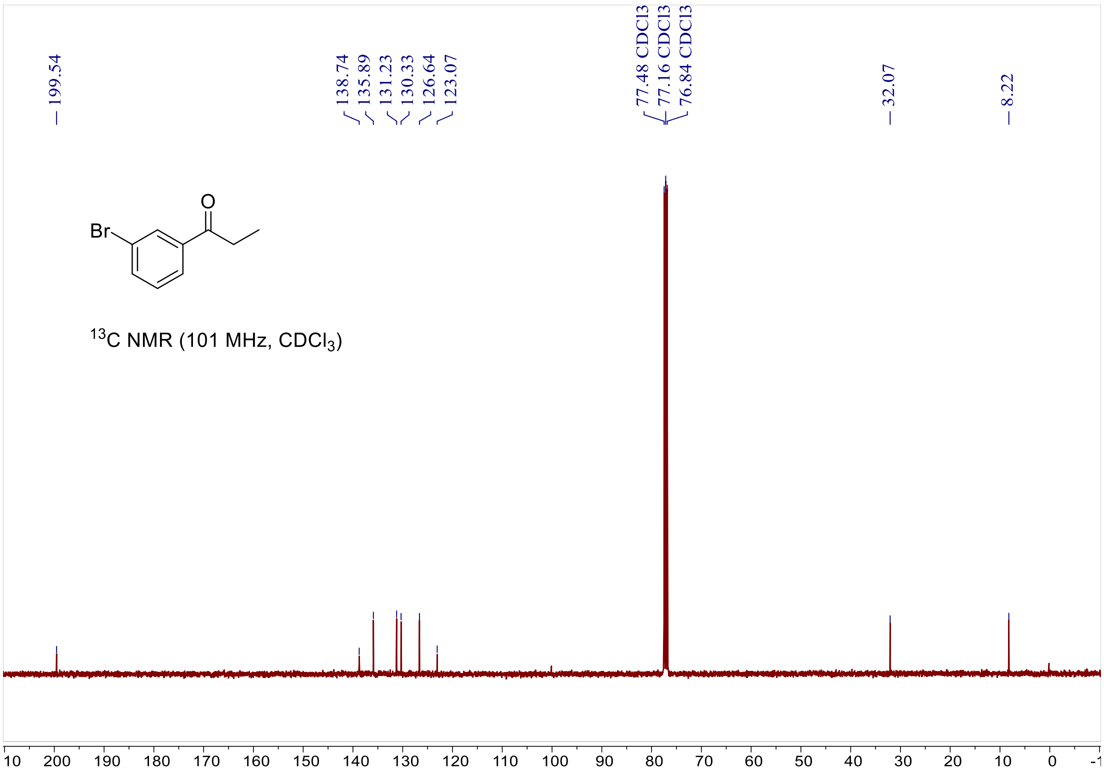
[1]H and [13]C NMR spectra of compound **3na**



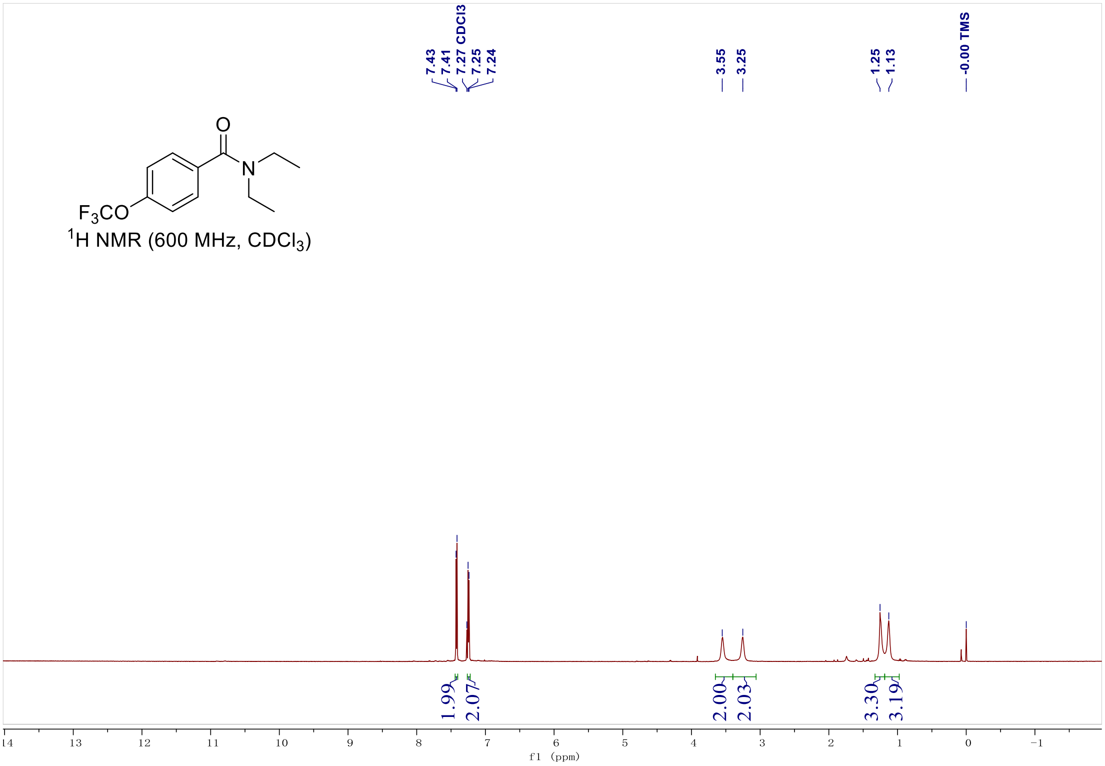


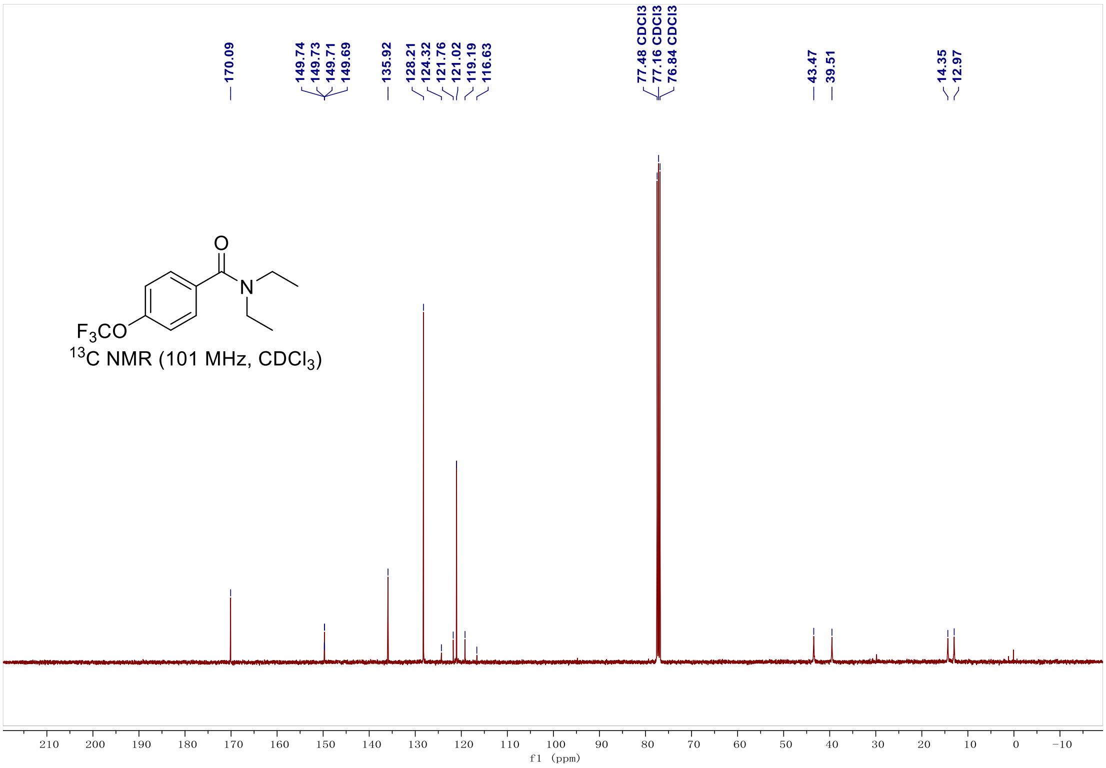
^1H and ^{13}C NMR spectra of compound **4na**

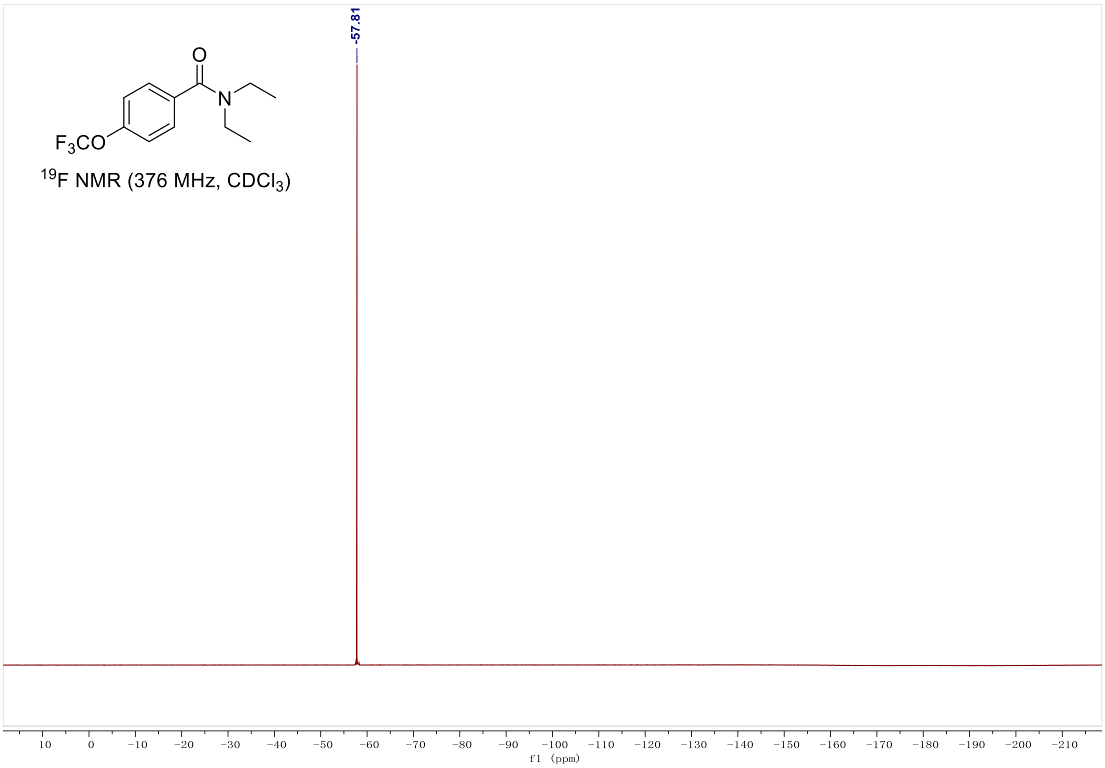




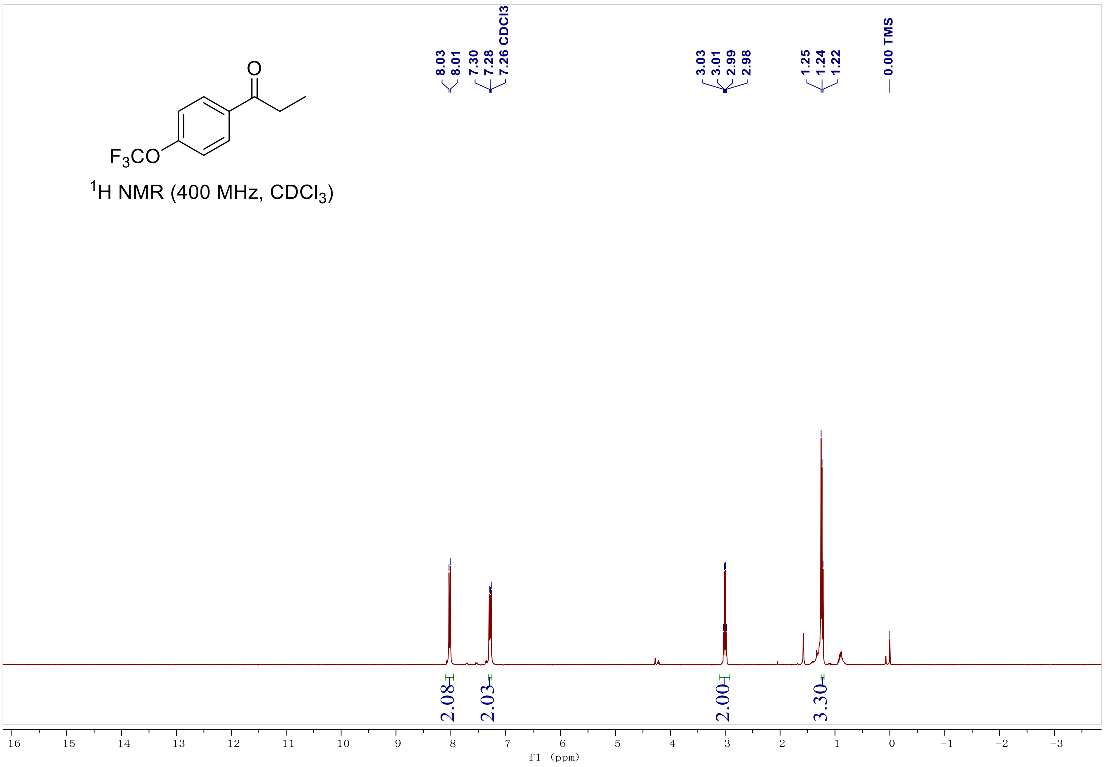
[1]H, [13]C and [19]F NMR spectra of compound **3oa**

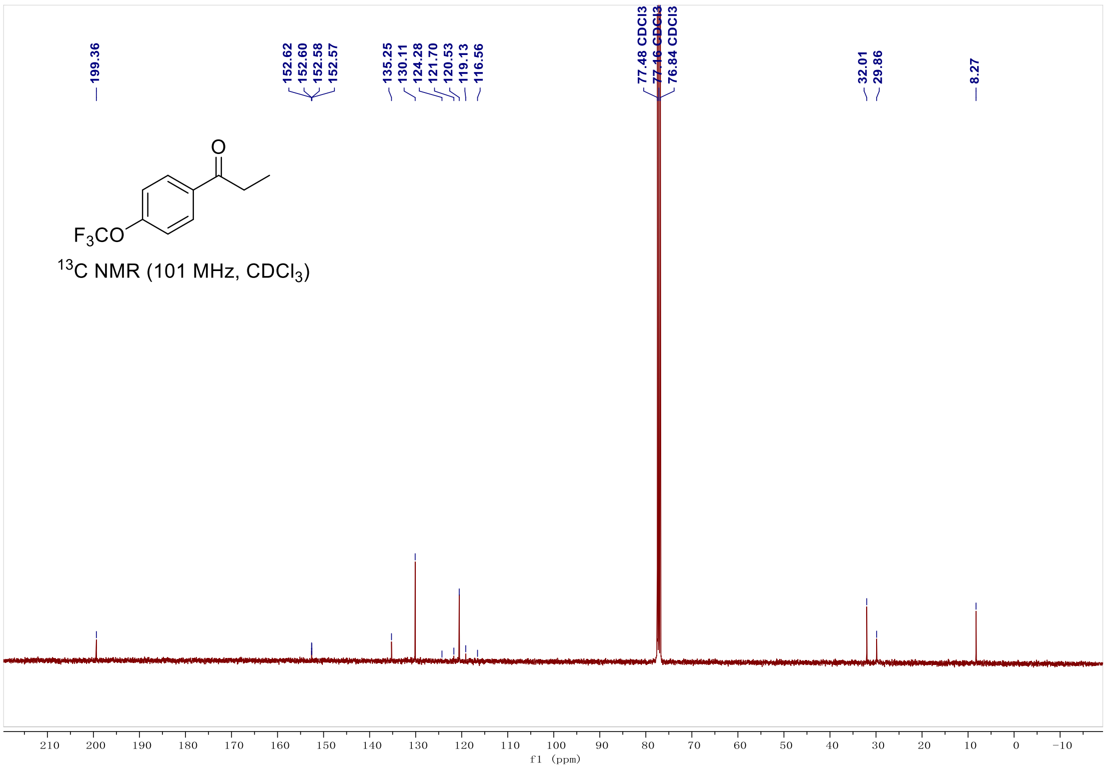


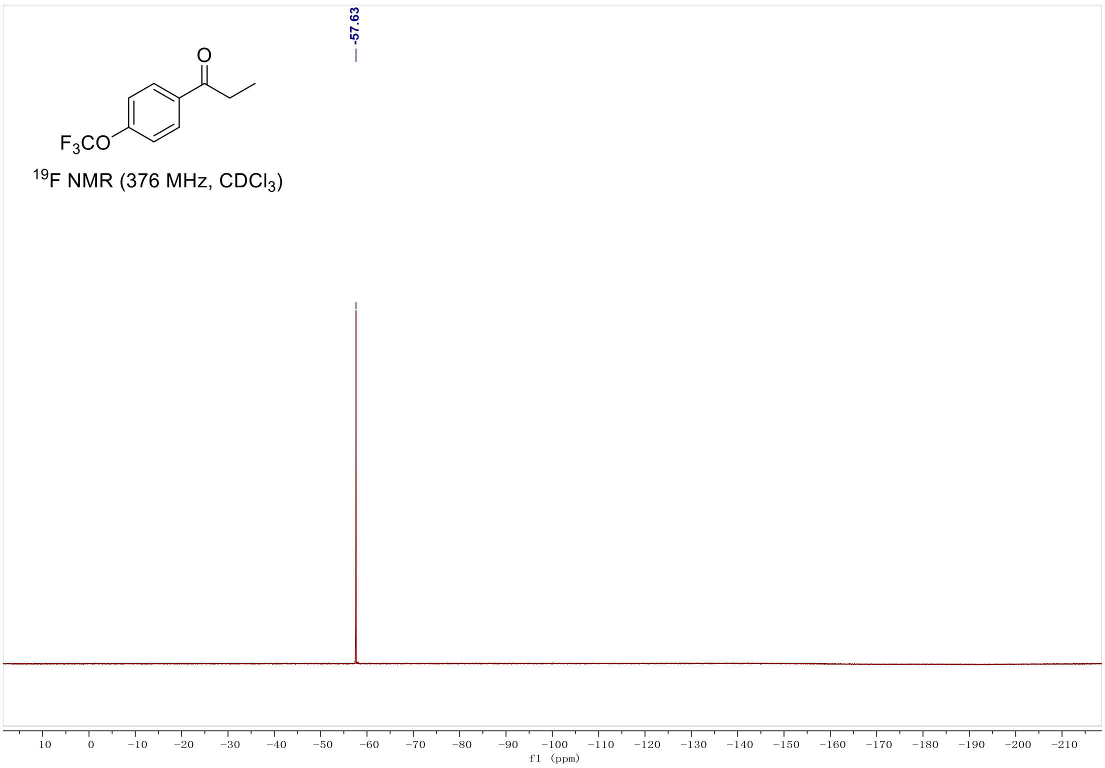




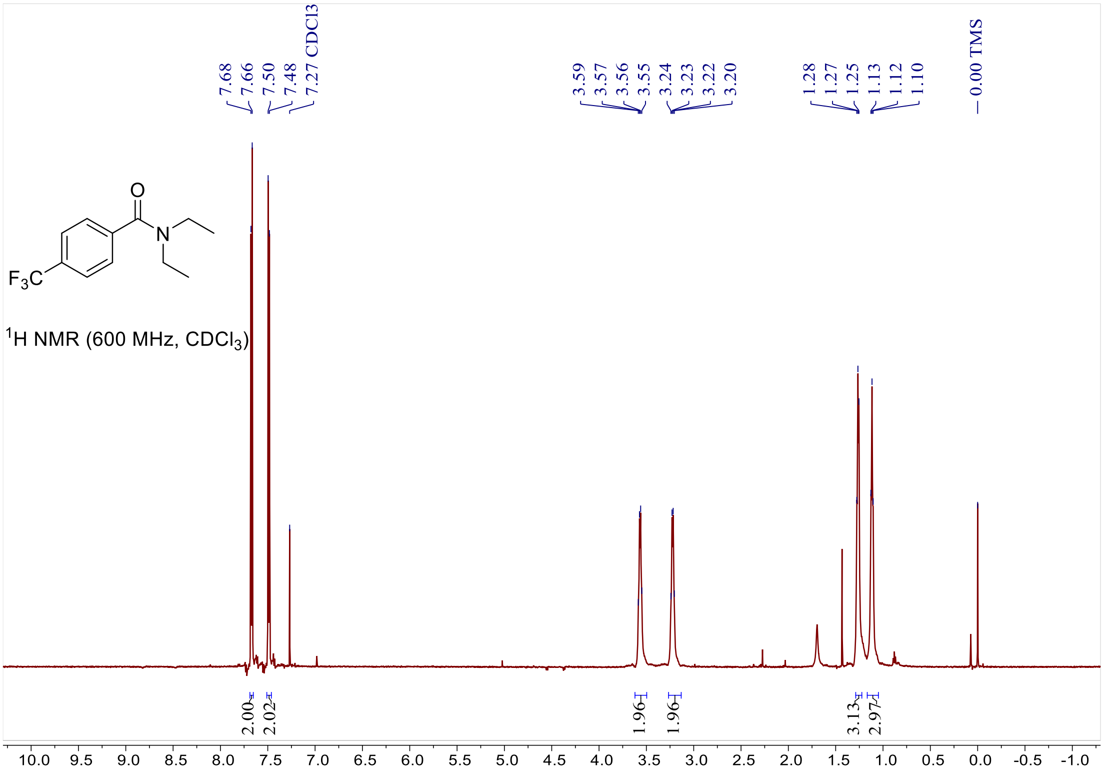
^{1}H, ^{13}C and ^{19}F NMR spectra of compound **4oa**

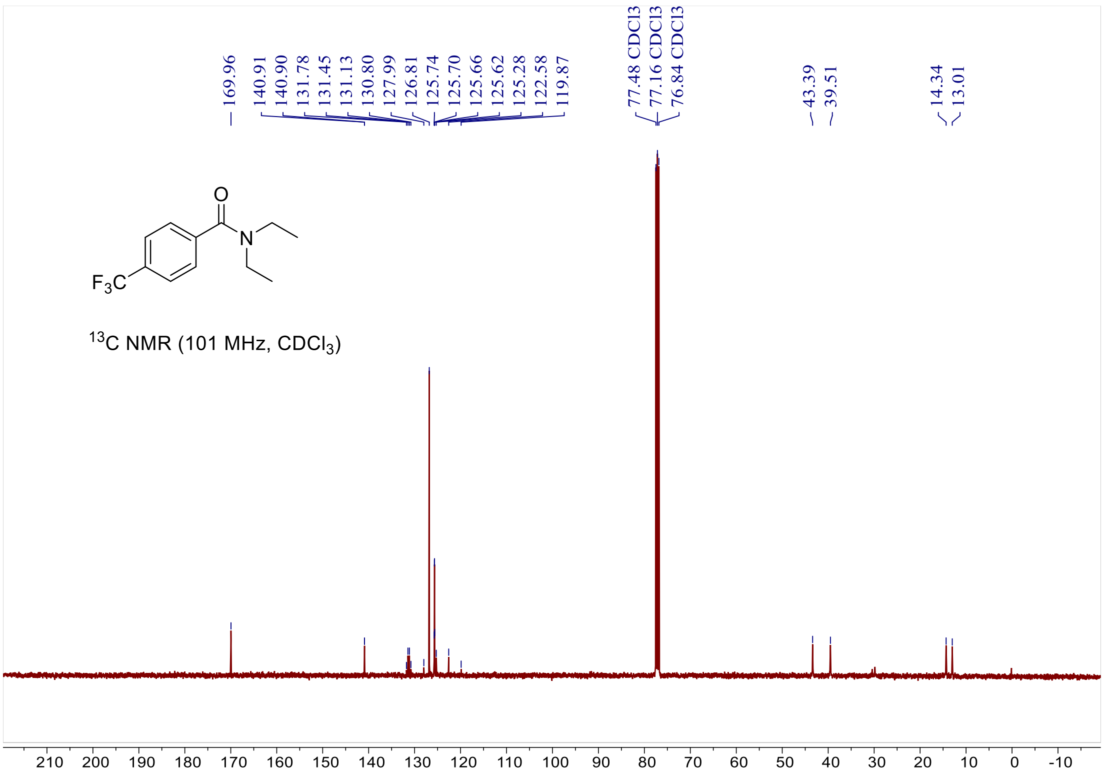


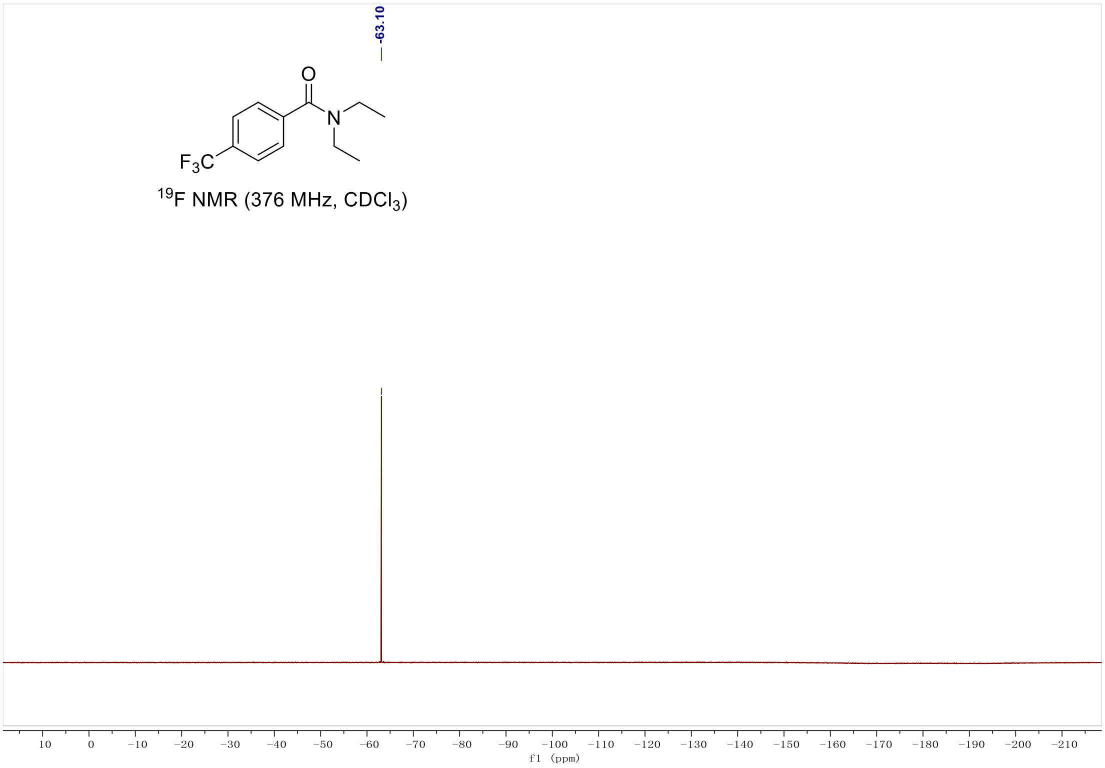

199.36
152.62
152.60
152.58
152.57
135.25
130.11
124.28
121.70
120.53
119.13
116.56
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
32.01
29.86
8.27
F3CO
O
13C NMR (101 MHz, CDCl3)
f1 (ppm)


-57.63
F3CO
O
19F NMR (376 MHz, CDCl3)
f1 (ppm)

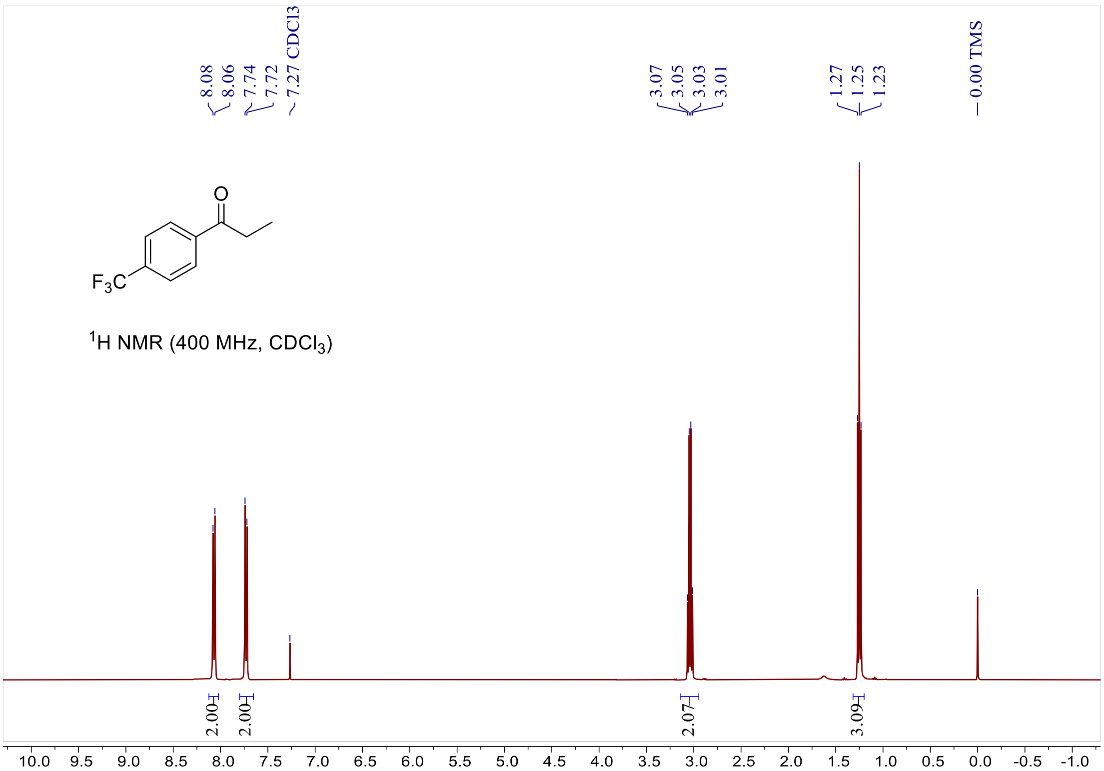
^{1}H, ^{13}C and ^{19}F NMR spectra of compound **3pa**

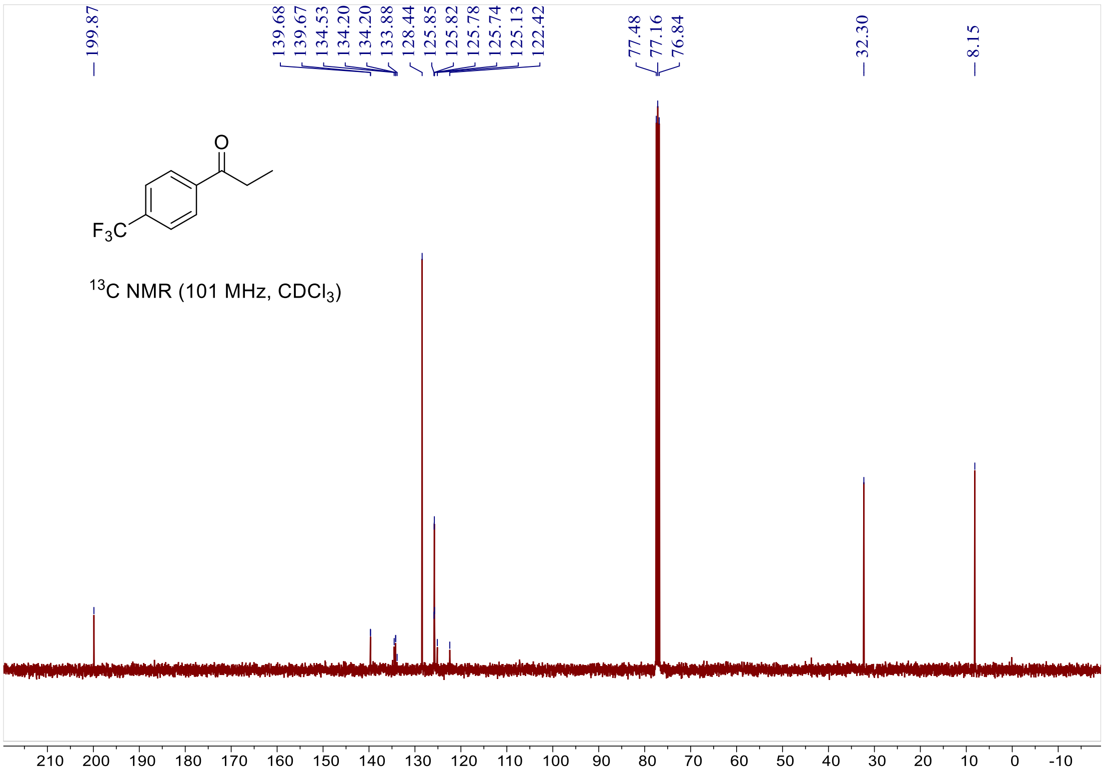






^{1}H, ^{13}C and ^{19}F NMR spectra of compound **4pa**

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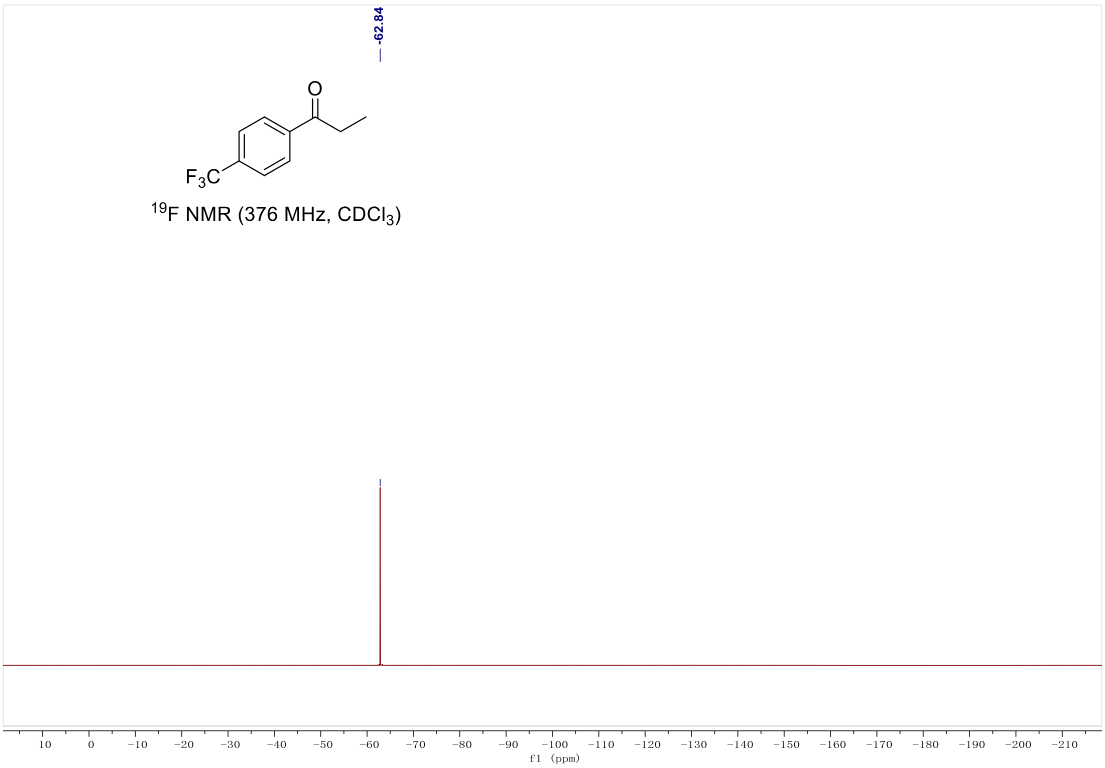
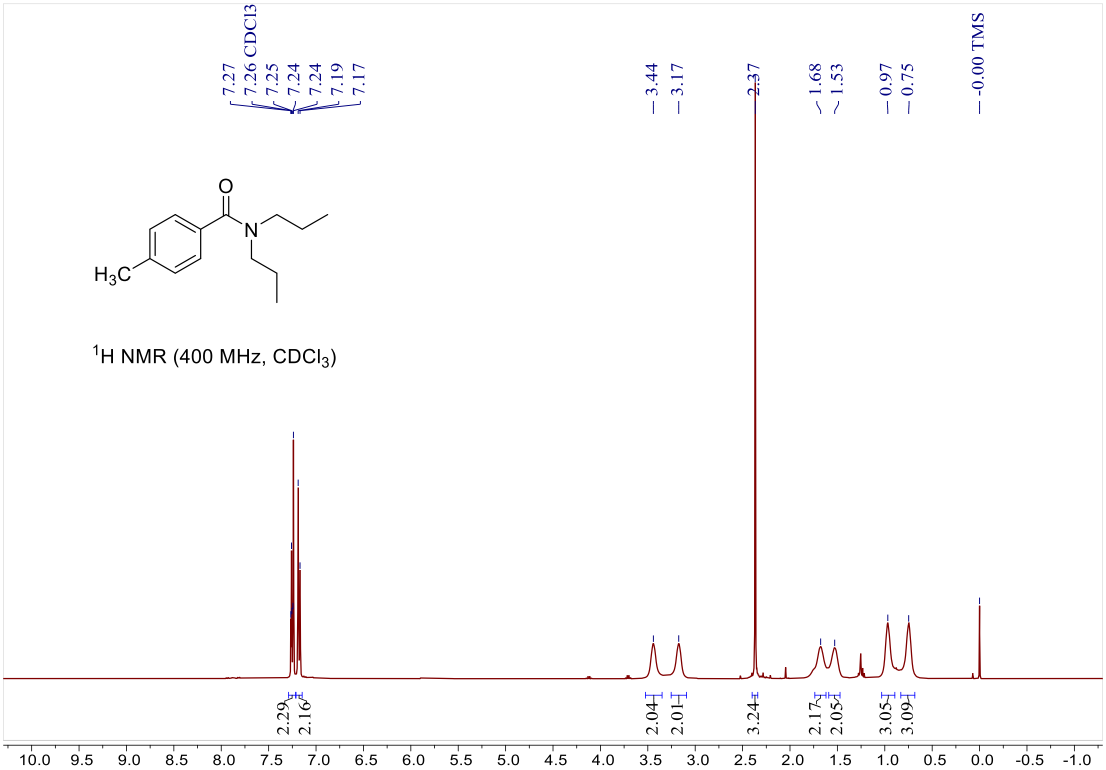
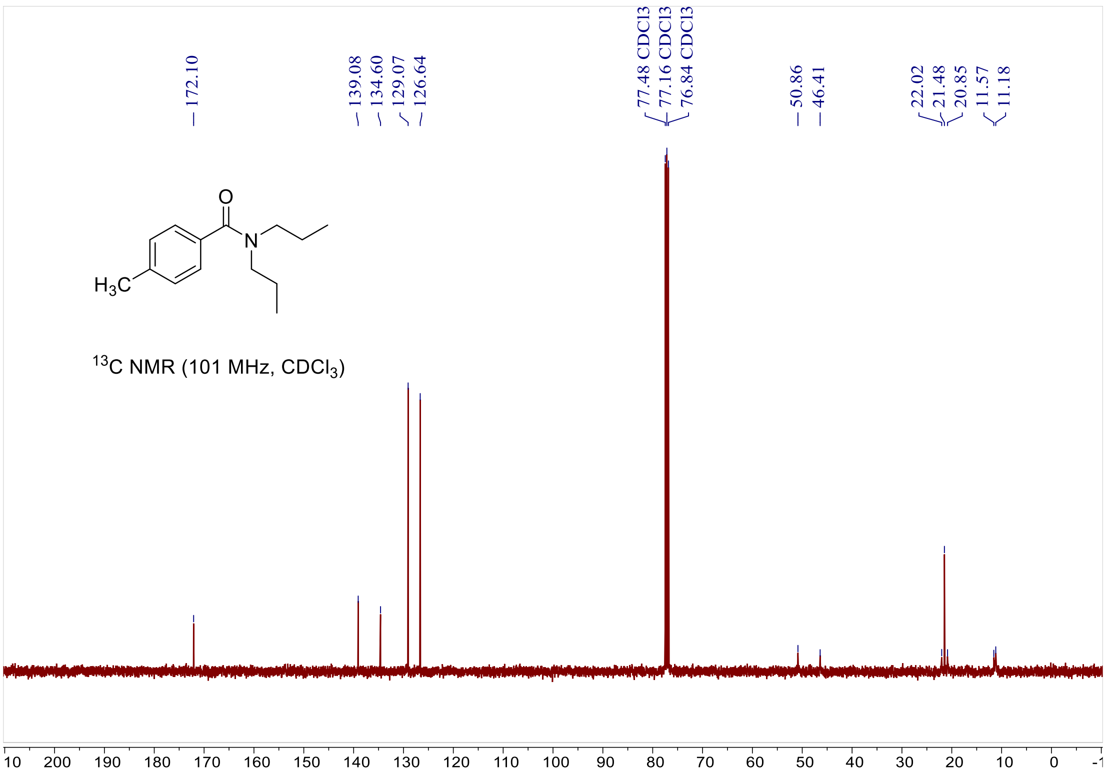
134.20
133.88
128.44
125.85
125.82
125.78
125.74
125.13
122.42
77.48
77.16
76.84
32.30
8.15
O
F3C
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

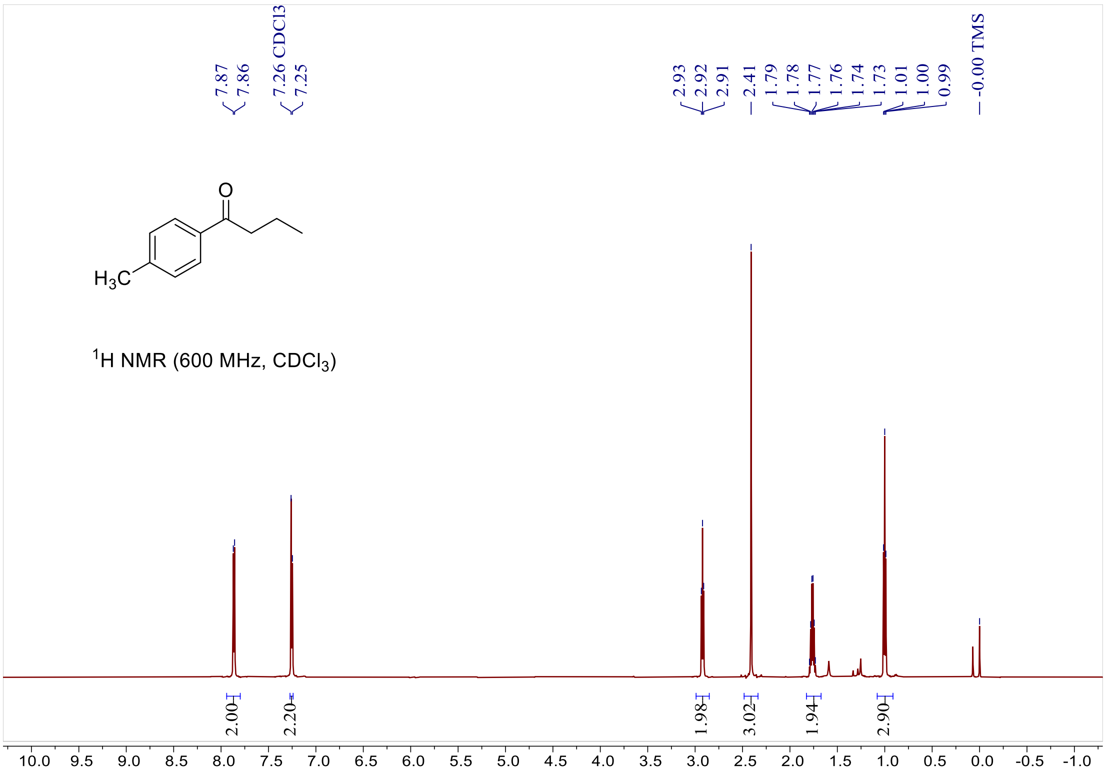

-62.84
O
F3C
19F NMR (376 MHz, CDCl3)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

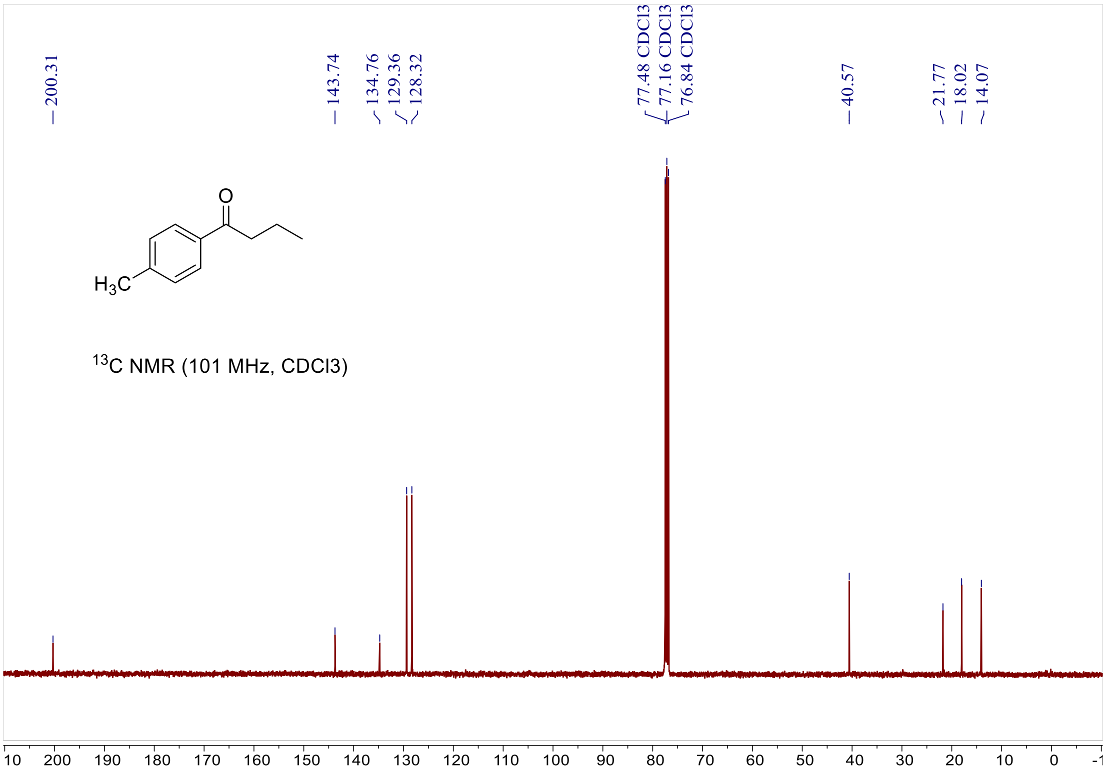
^{1}H and ^{13}C NMR spectra of compound **3ab**



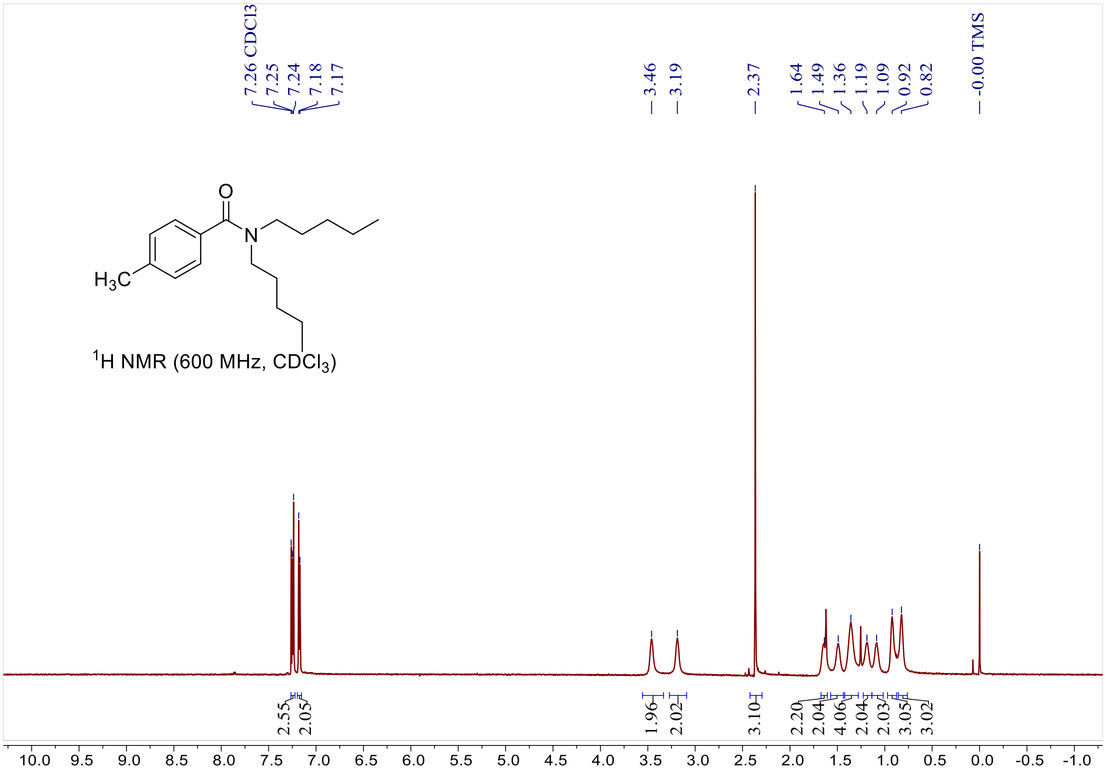


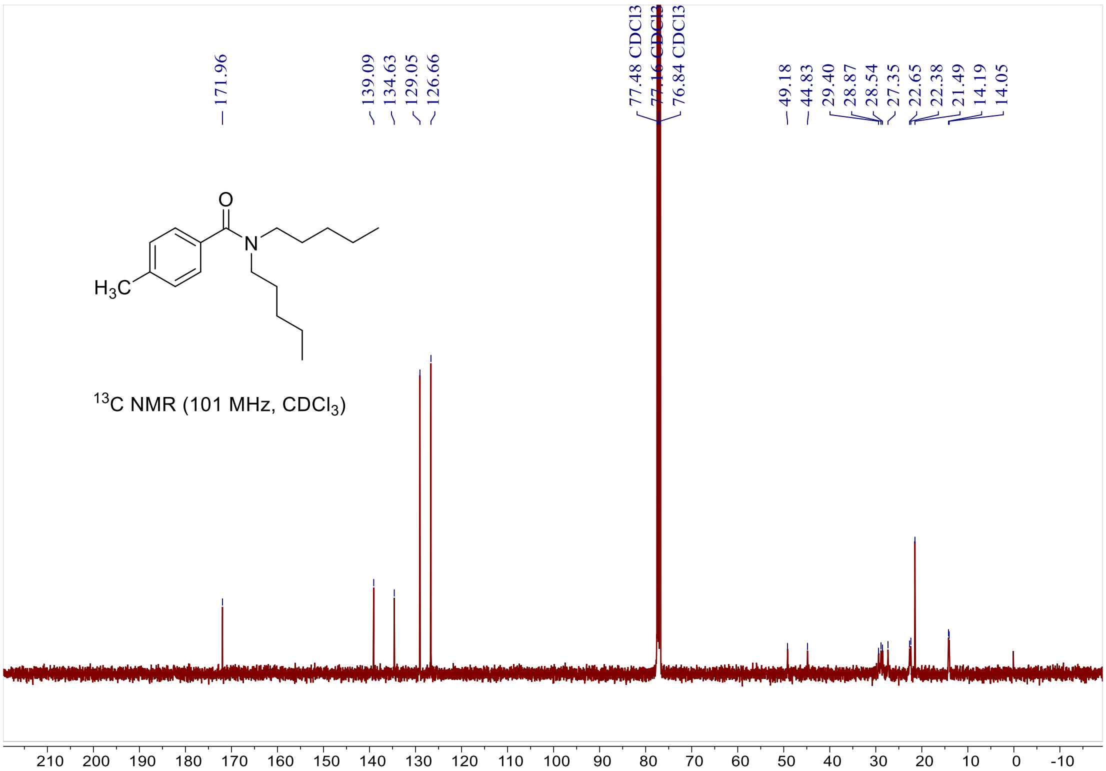
^{1}H and ^{13}C NMR spectra of compound **4ab**



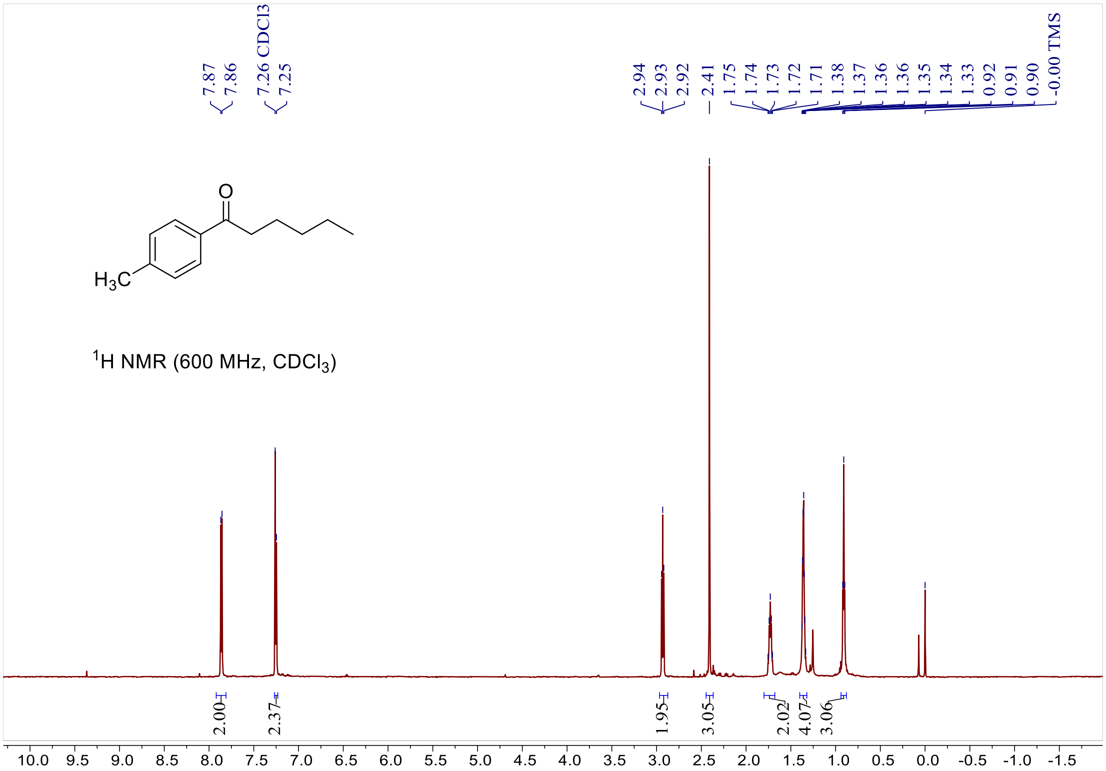


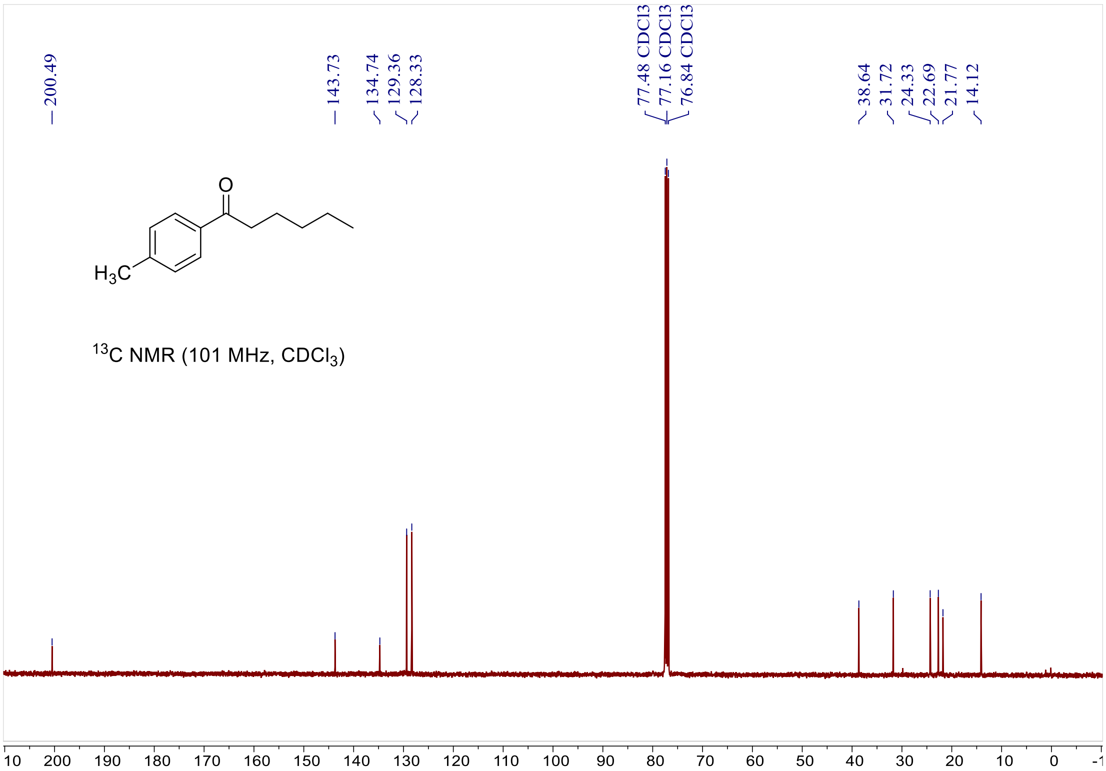
[1]H and [13]C NMR spectra of compound **3ac**



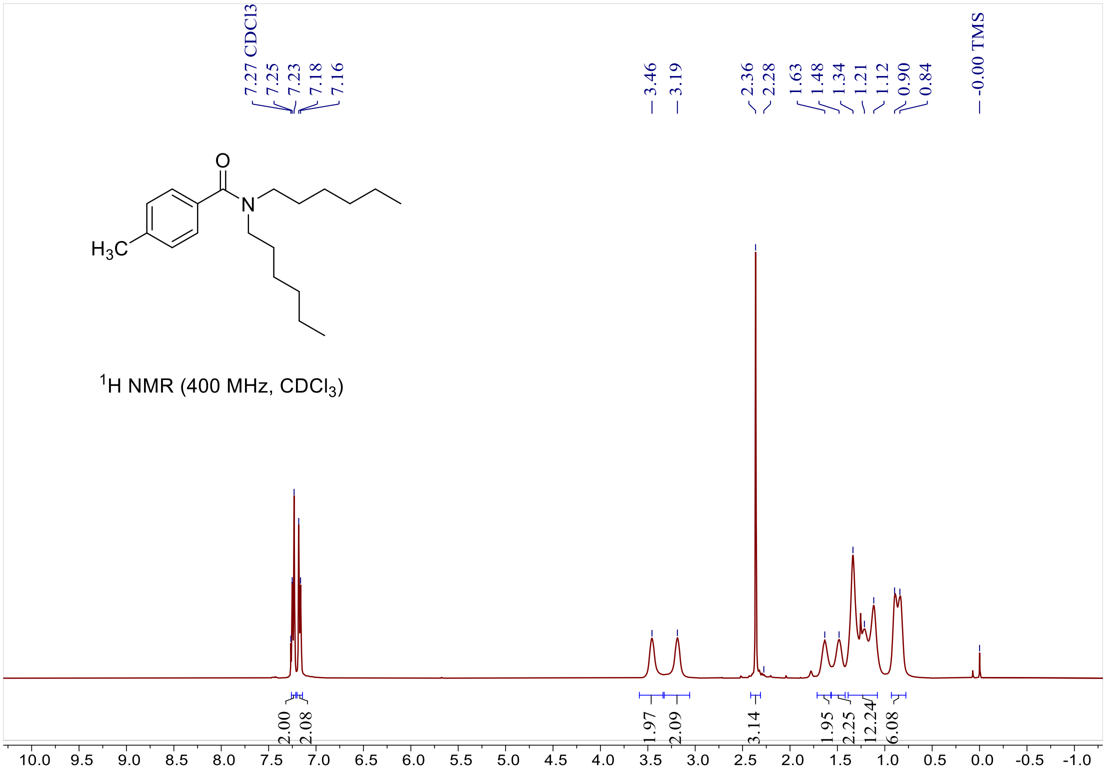


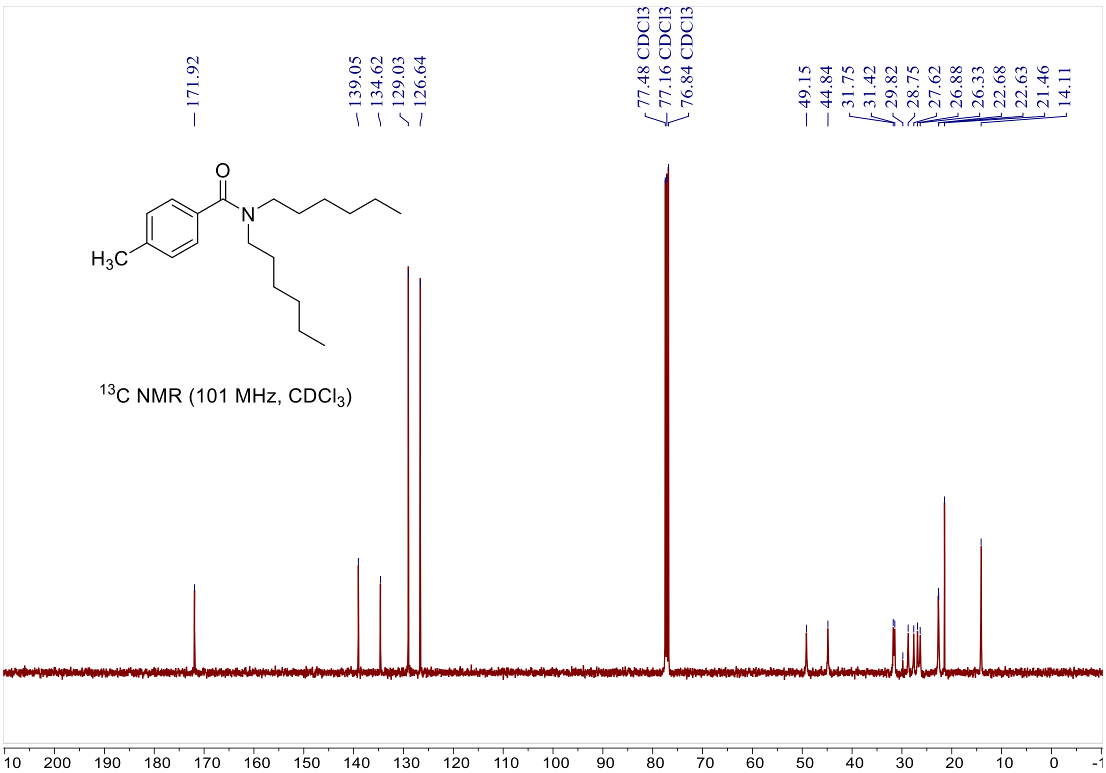
^{1}H and ^{13}C NMR spectra of compound **4ac**



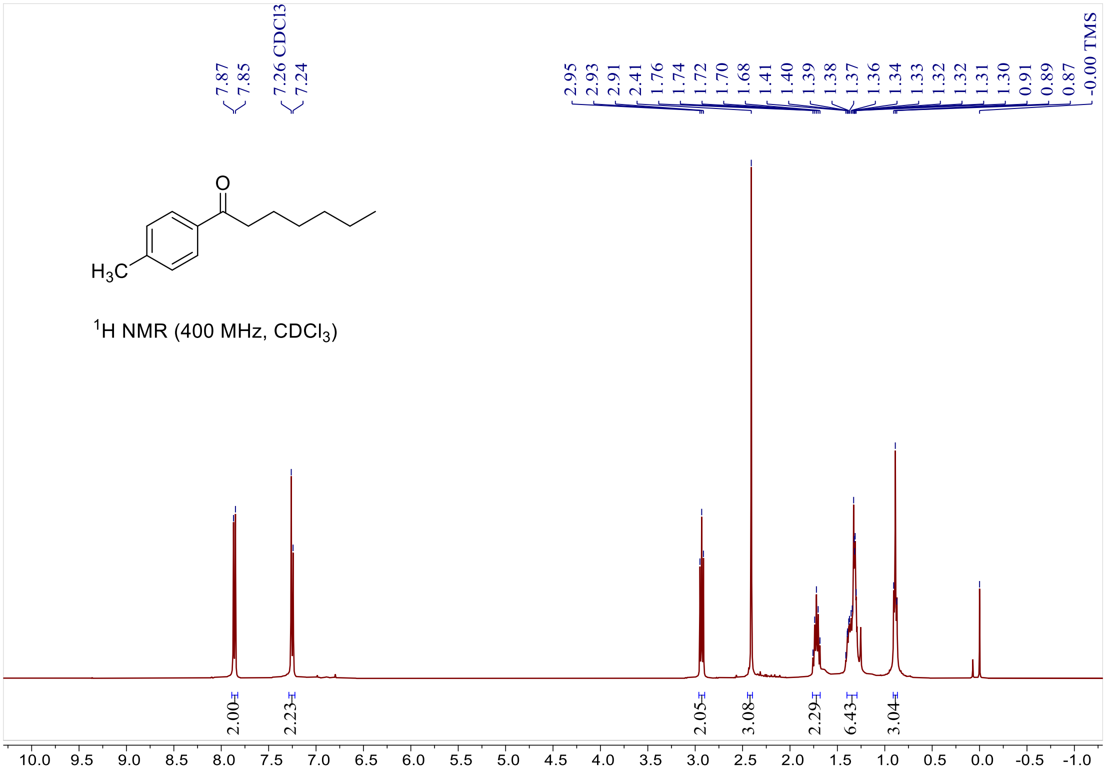


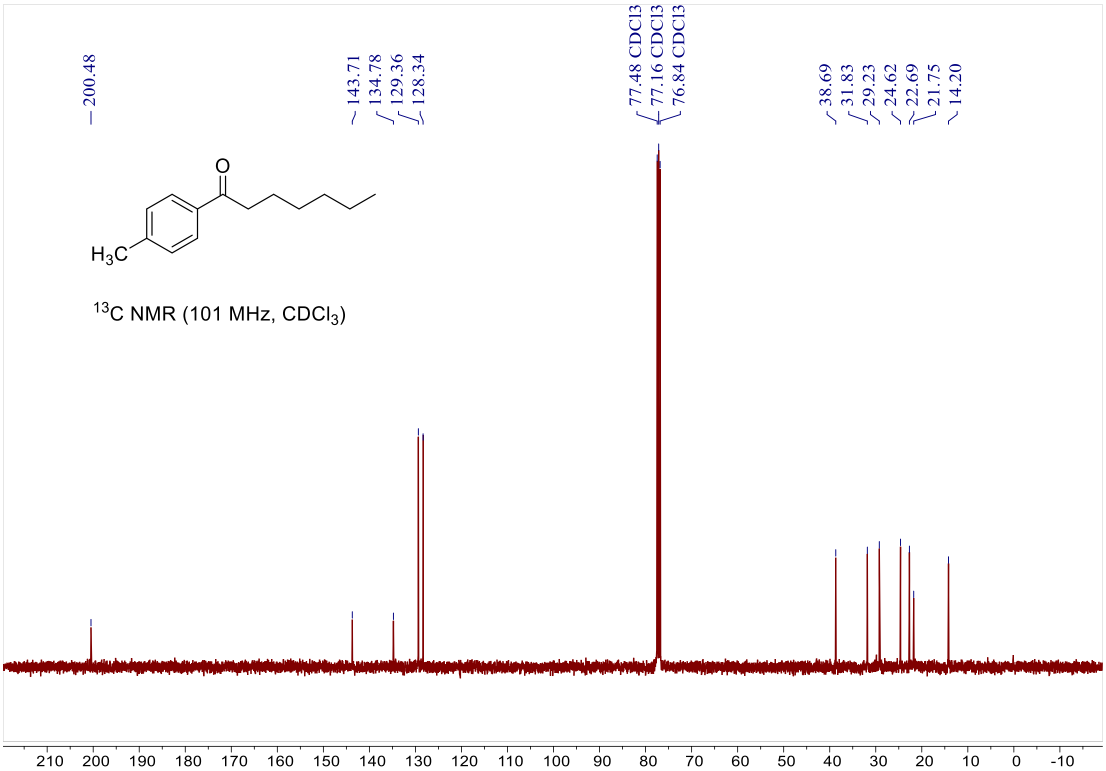
^{1}H and ^{13}C NMR spectra of compound **3ad**



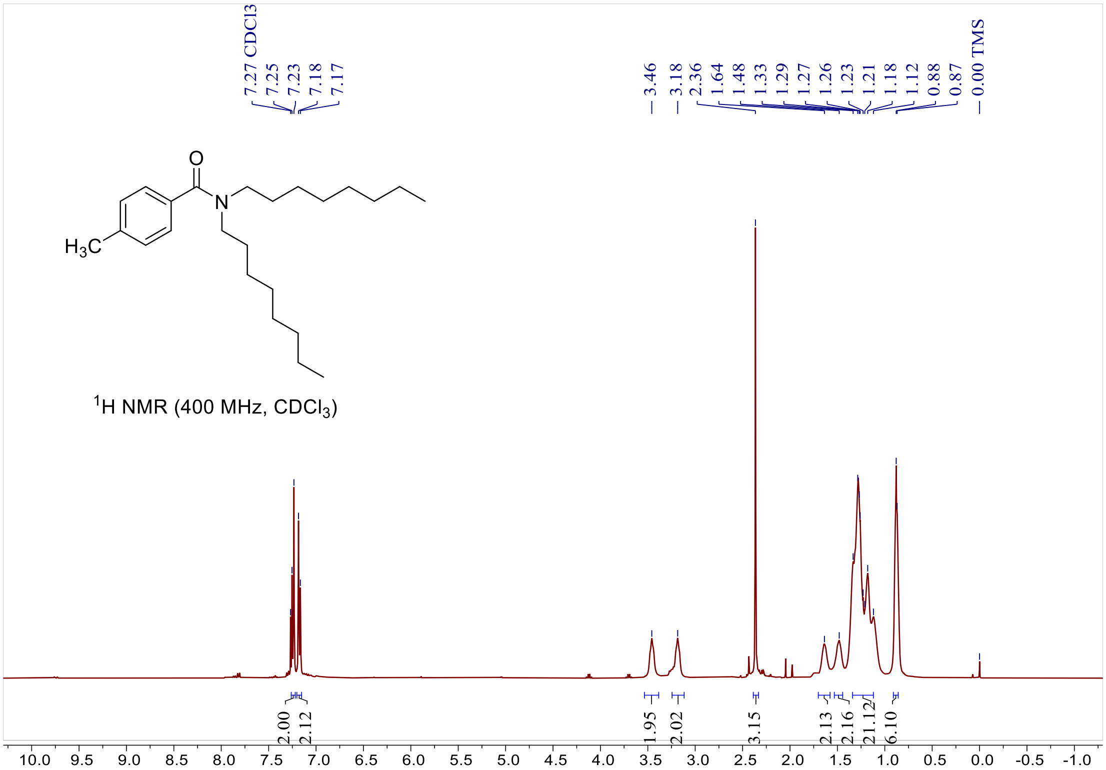


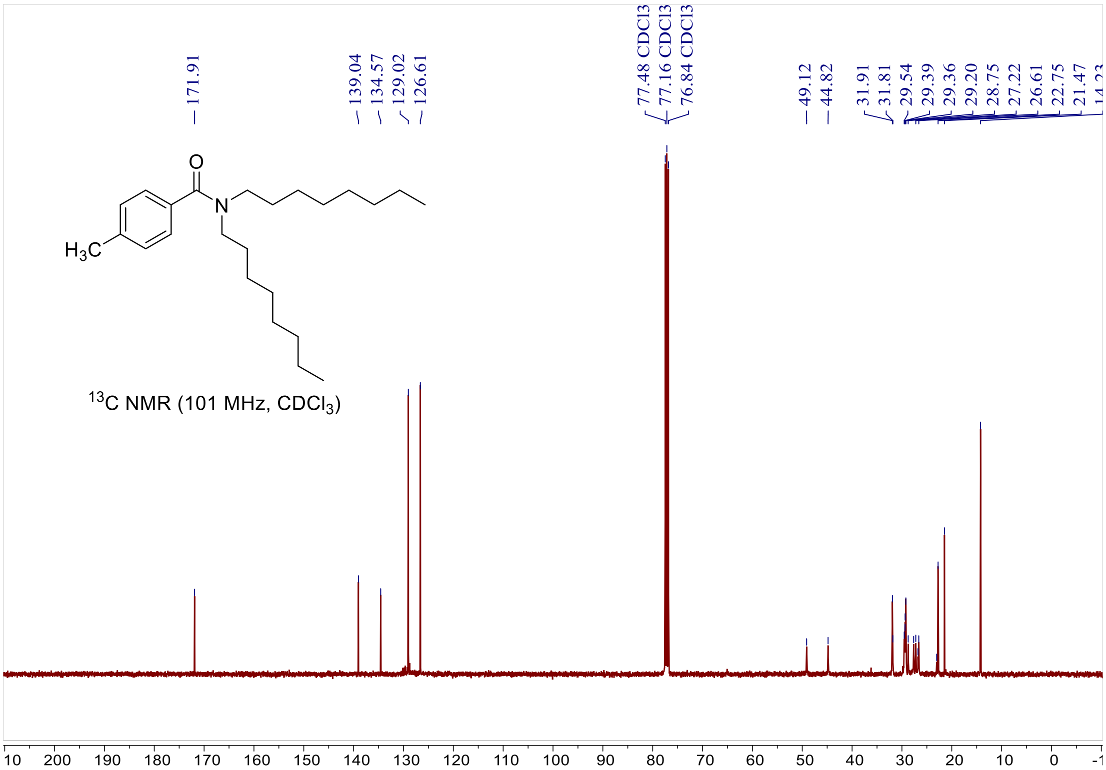
^1H and ^{13}C NMR spectra of compound **4ad**



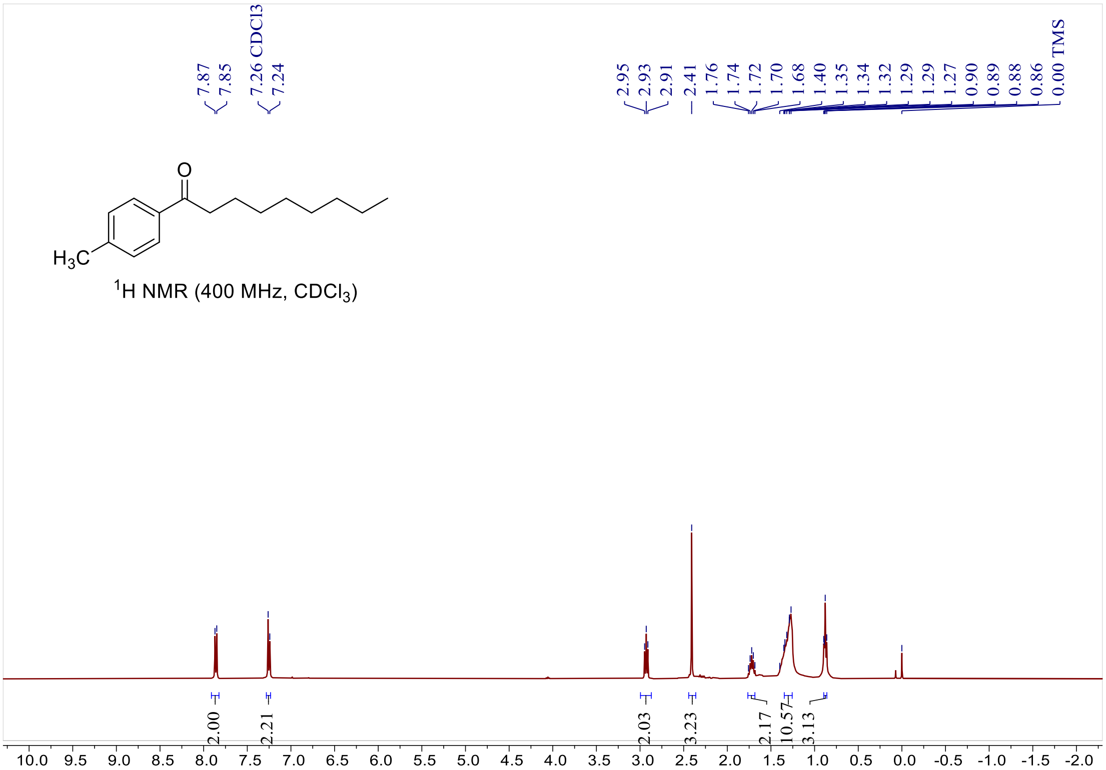


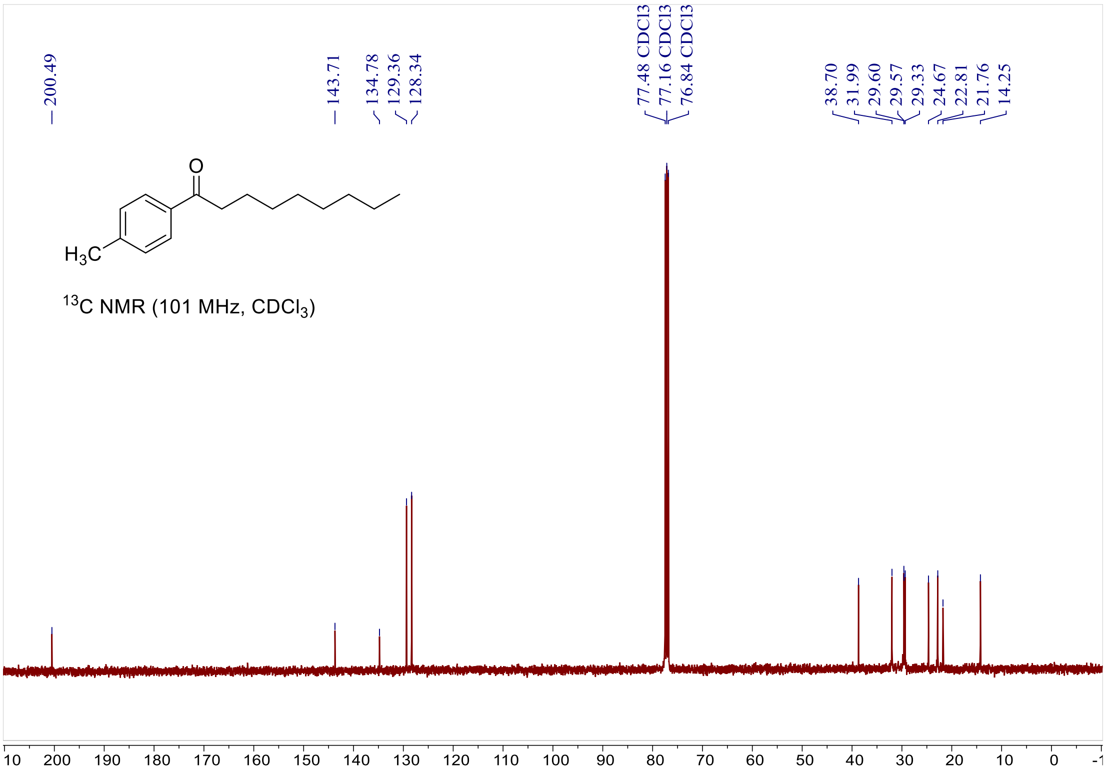
[1]H and [13]C NMR spectra of compound **3ae**



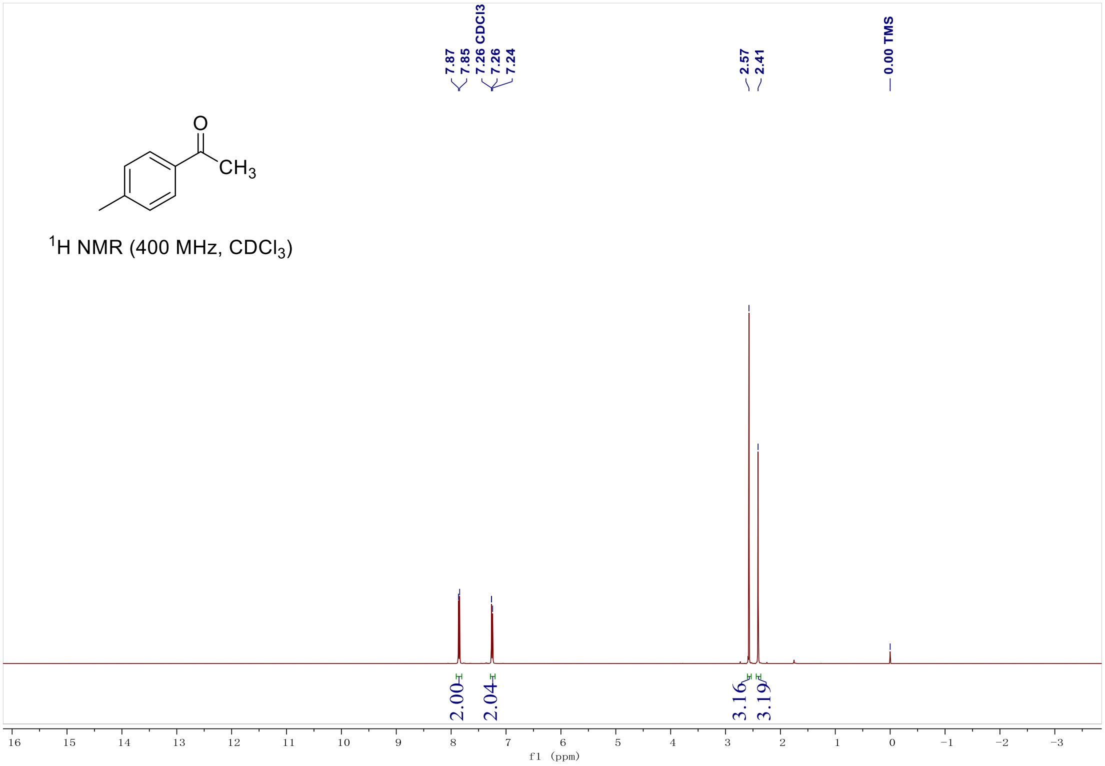


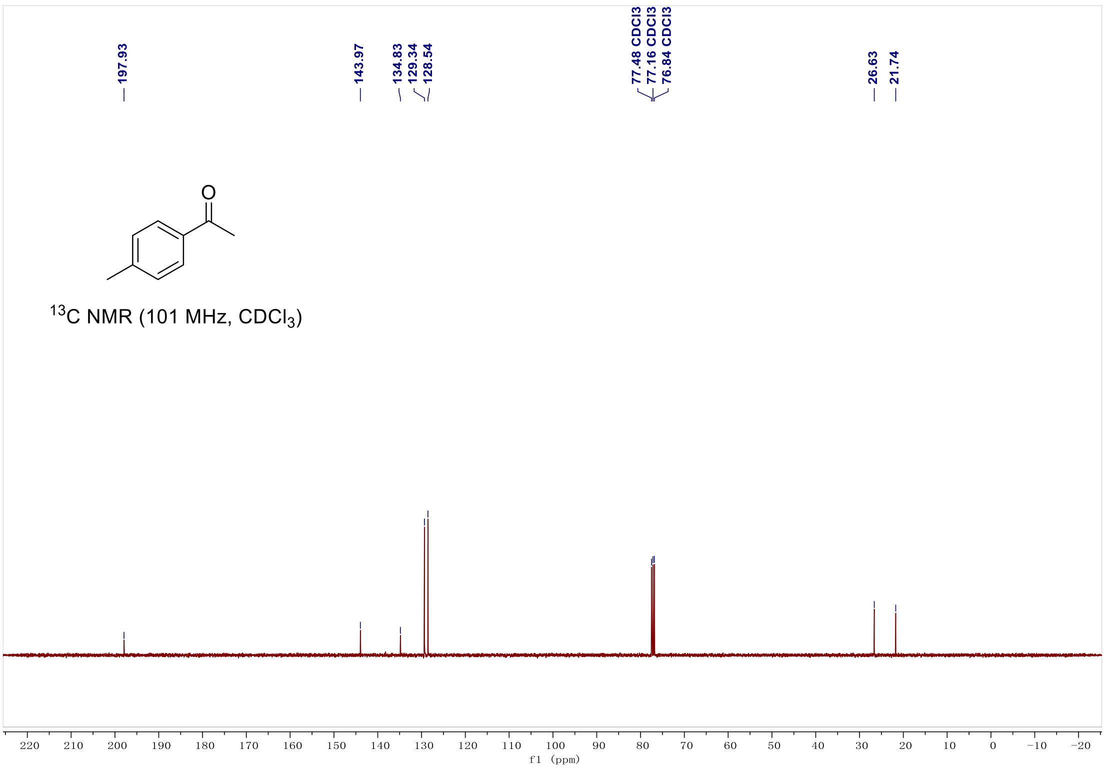
^1H and ^{13}C NMR spectra of compound **4ae**



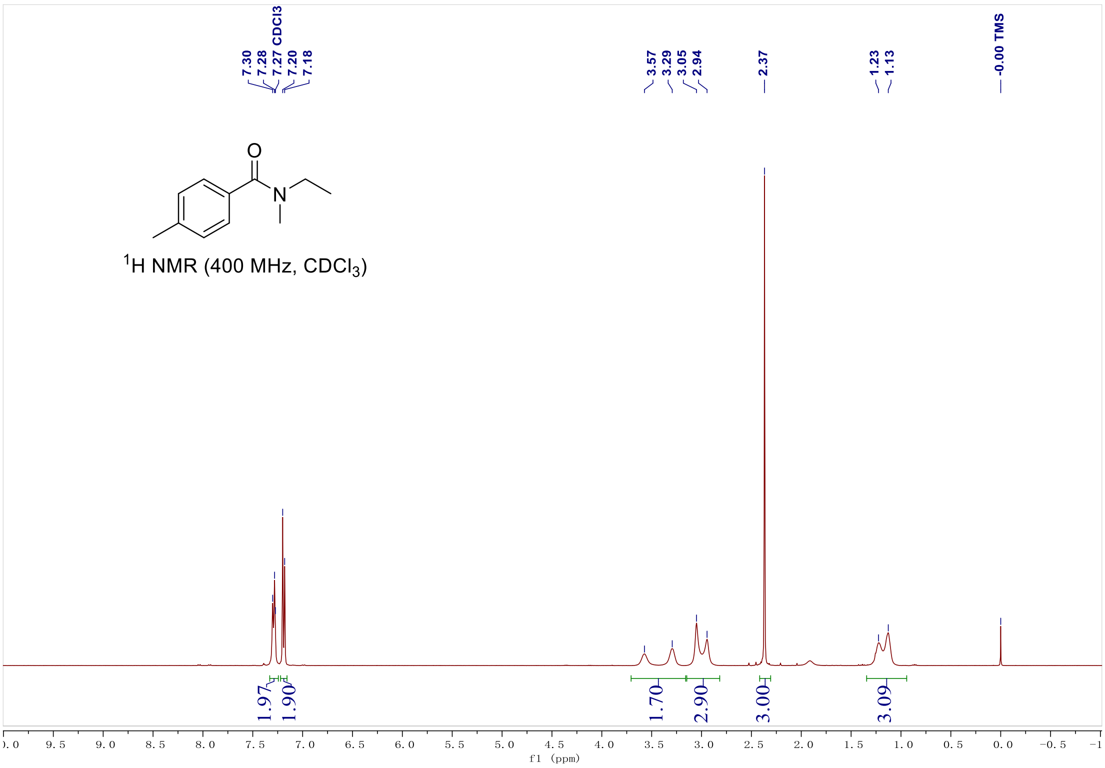


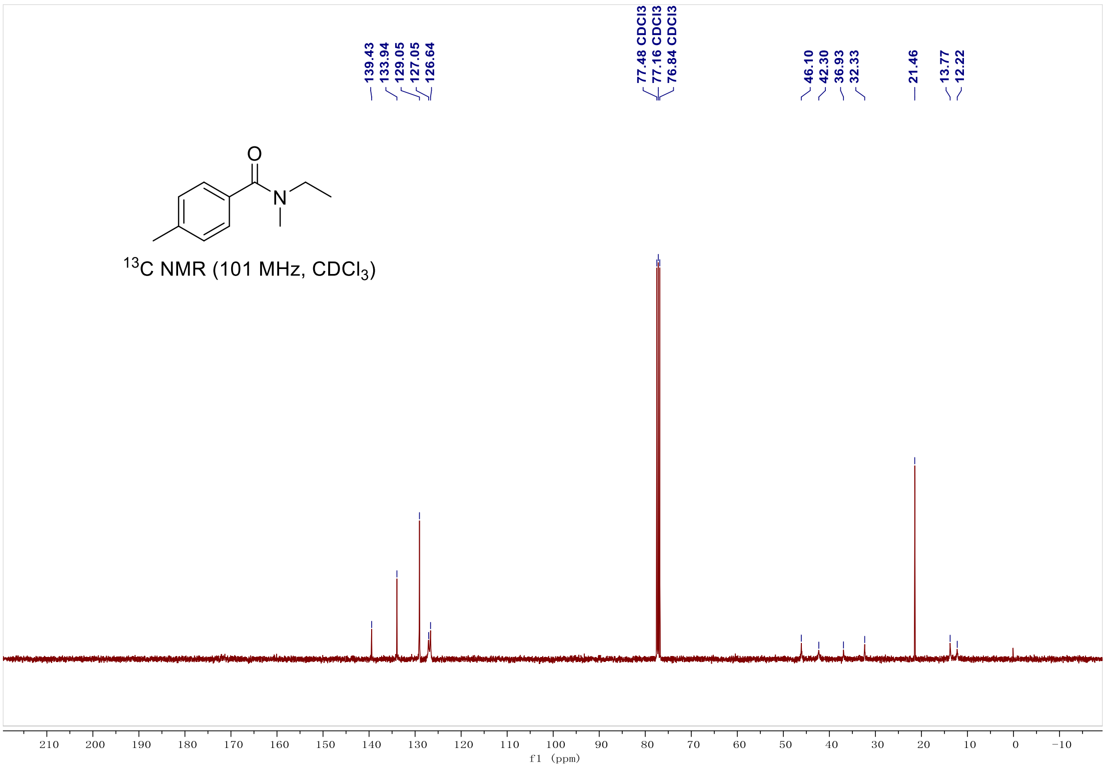
^{1}H and ^{13}C NMR spectra of compound **4af**



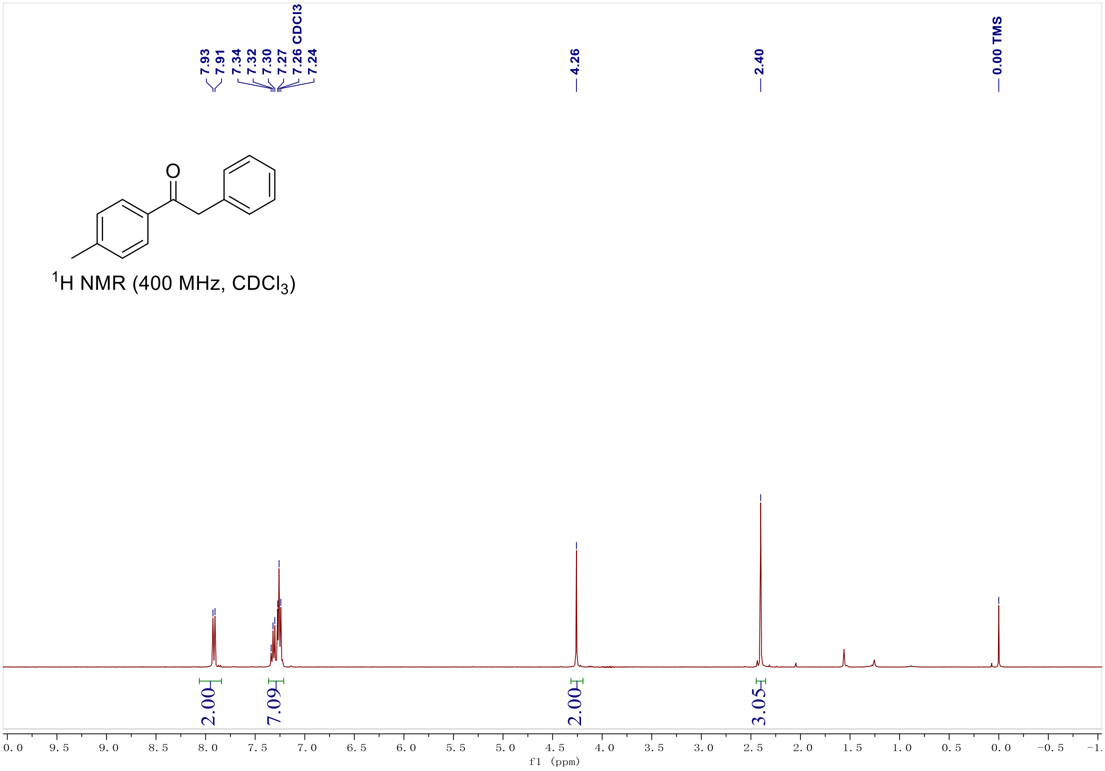


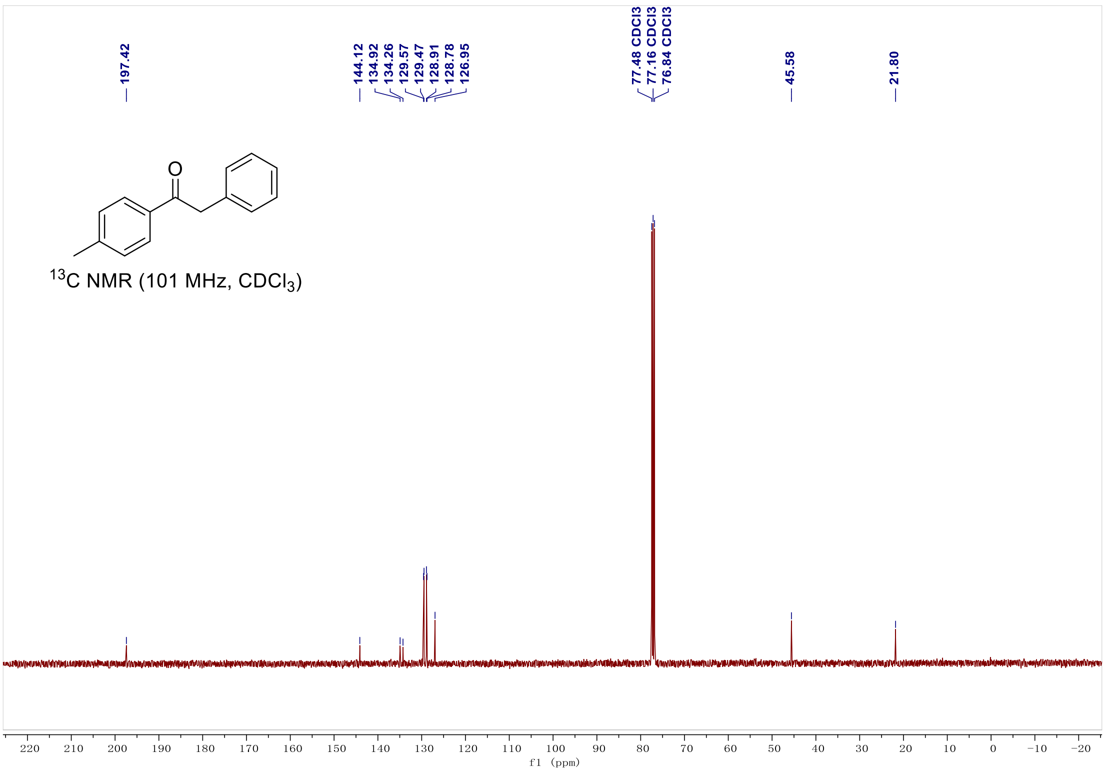
^1H and ^{13}C NMR spectra of compound **3af**



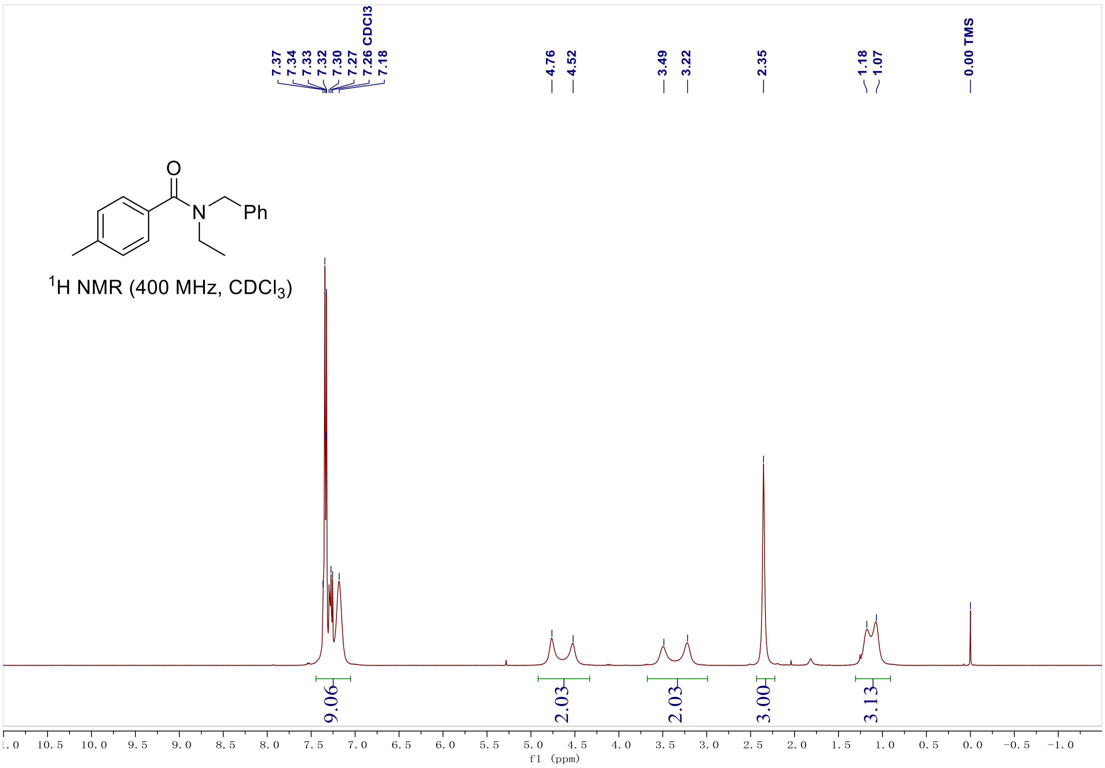


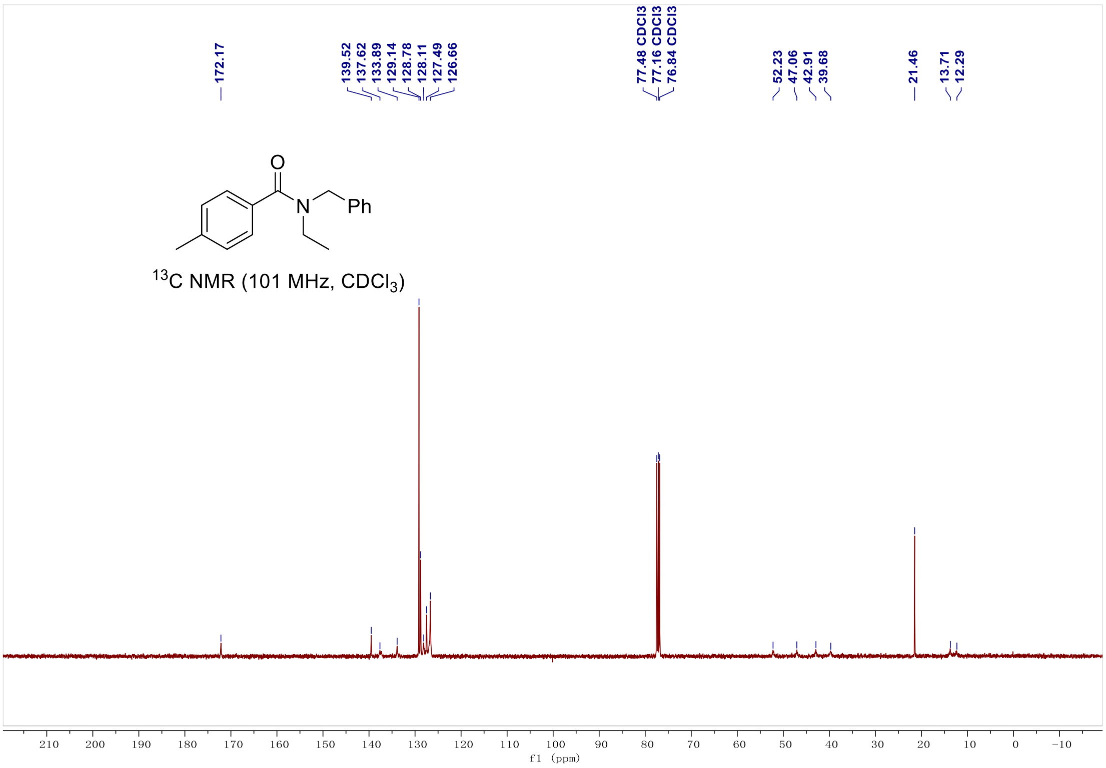
^{1}H and ^{13}C NMR spectra of compound **4ag**



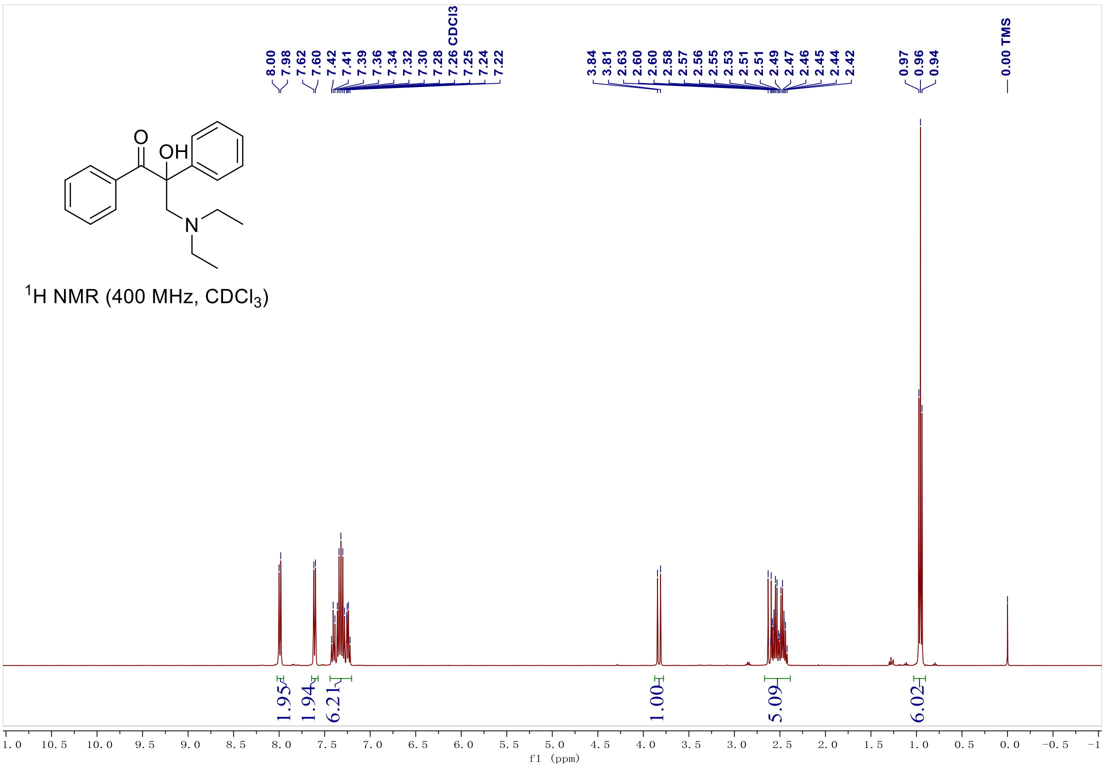


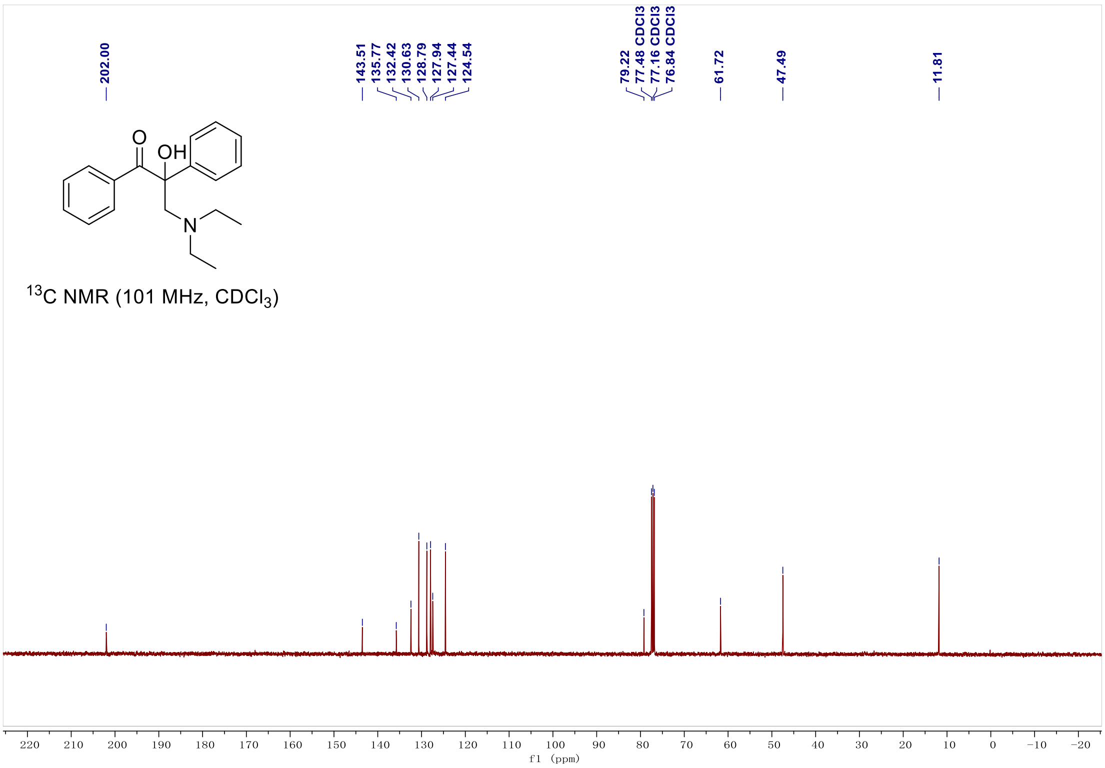
[1]H and [13]C NMR spectra of compound **3ag**





^1H and ^{13}C NMR spectra of compound **7**





^{1}H and ^{13}C NMR spectra of compound **8**