Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A Base-controlled Chemoselective Transfer Hydrogenation of α,β-Unsaturated Ketones Catalyzed by $[IrCp^*Cl_2]_2$ With 2-Propanol

Shu-jie Chen[a], Guo-ping Lu[a], and Chun Cai*[a]

[a] Chemical Engineering College, Nanjing University of Science and Technology, Nanjing 210094, China.
Fax: +86(25)84315030
E-mail: c.cai@mail.njust.edu.cn

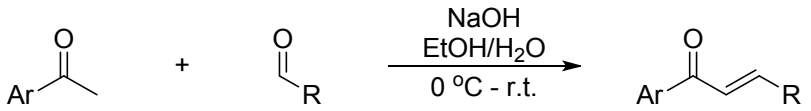
Table of Contents

1. General Details

All air-sensitive manipulations were carried out under the inert gas atmosphere using standard Schlenk techniques. Glassware was oven or flame dried immediately prior to use. DCM was freshly distilled from calcium hydride under nitrogen. All other solvents and commercial reagents were used as supplied without further purification unless stated otherwise.^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz, 125 MHz and 470 MHz in $CDCl_3$, respectively, and chemical shifts were reported in ppm from internal TMS(δ). GC-MS were performed on an ISQ Trace 1300 (electrospray ionization: EI). GC analysis were performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: N_2, FID detector. Elemental analyses were performed on a Yanagimoto MT3CHN recorder. $[IrCp^*Cl_2]_2$[1] and *α,β*-unsaturated ketones **1d-1r**, **1z** were prepared according to literature.[2]

2. General Procedure for Synthesis of *α,β*-Unsaturated Ketones

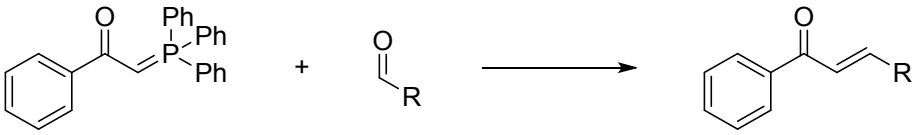
Synthesis of α,β-unsaturated ketones 1d-1r, and 1z[2]



1d-1r, 1z

Aromatic ketone(10 mmol, 1.0 equiv) in 6 mL ethanol was added a solution of NaOH(520 mg, 13 mmol, 1.3 equiv) in H_2O(10 mL), then the aldehyde(10 mmol, 1.0 equiv) was added gradually at 0 °C. The mixture was then allowed to warm to room temperature and stirred for 4 h after which a precipitate of the product formed. The product was collected by suction filtration on a Buchner funnel and washed repeatedly with cold water. Recrystallization from ethanol or purification by silica gel chromatography for liquid products.

Synthesis of α,β-unsaturated ketones 1s-1u, and 1aa



Preparation of phosphorane:[3]

To a solution of 2-bromoacetophenone (10 mmol) in CH_2Cl_2 (50 mL) at rt was added triphenylphosphine (10 mmol) and the solution was allowed to stir for 4 h before being concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2:H_2O (8 mL/12mL) and 2 M NaOH (10 mL, 20 mmol) was added. The reaction mixture was stirred overnight at rt before being extracted with CH_2Cl_2 (20 mL × 3). The combined organic fraction were washed with brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure to give the product as a white solid (3.23 g, 85%); mp 176-177 °C; {lit1[3] mp 174-176 °C}.

General procedure A

The dry phosphorane was dissolved in freshly distilled DCM under N_2, followed by addition of dry aldehyde. The reaction mixture was heated to reflux until all of the aldehyde was consumed as indicated by TLC. The reaction mixture was then concentrated under reduced pressure after filtration and the residue was purified by flash chromatography on silica gel (EtOAc/Petroleum ether) to afford the corresponding α,β-unsaturated ketone.

1-Phenylprop-2-en-1-one(1s)[4]

The title compound was prepared from 1-phenyl-2-(triphenylphosphoranylidene)ethanone(380 mg, 1 mmol) and dry $(CH_2O)_n$ (90 mg, 3.00 mmol) in freshly distilled DCM(10 mL) according to the general procedure **A**. The desired α,β-unsaturated ketone **1s**(119 mg, 90%) was obtained as a colourless oil after flash chromatography (2.5-5% EtOAc/ Petroleum ether). R_f 0.36 (5 % EtOAc/Petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.17 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.45 (d, *J* = 17.1 Hz, 1H), 5.93 (d, *J* = 10.6 Hz, 1H).

(*E*)-1,5-Diphenylpent-2-en-1-one(1t)[5]

The title compound was prepared from 1-phenyl-2-(triphenylphosphoranylidene)ethanone (380 mg, 1 mmol) and 3-phenylprpanal (134 mg, 1.00 mmol) in freshly distilled DCM (5 mL) according to the general procedure **A**. The desired α,β-unsaturated ketone **1t** (221 mg, 94%) was obtained as a colourless oil after flash chromatography (5-10% EtOAc/ Petroleum ether). R_f 0.28 (5 % EtOAc/Petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.59 – 7.54 (m, 1H), 7.50 – 7.45 (m, 2H), 7.36 – 7.30 (m, 2H), 7.24 (dd, *J* = 7.2, 5.5 Hz, 3H), 7.10 (dt, *J* = 15.4, 6.9 Hz, 1H), 6.89 (dt, *J* = 15.4, 1.4 Hz, 1H), 2.90 – 2.84 (m, 2H), 2.70 – 2.63 (m, 2H).

(*E*)-1-Phenylnon-2-en-1-one(1u)[6]

The title compound was prepared from 1-phenyl-2-(triphenylphosphoranylidene)ethanone (380 mg, 1 mmol) and heptanal (114 mg, 1.00 mmol) in freshly distilled DCM (5 mL) according to the general procedure **A**. The desired α,β-unsaturated ketone **1u** (196 mg, 91%) was obtained as a colourless oil after flash chromatography (2.5-5% EtOAc/ Petroleum ether). R_f 0.38 (5 % EtOAc/Petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dt, *J* = 8.5, 1.6 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.51 – 7.44 (m, 2H), 7.08 (dt, *J* = 15.4, 6.9 Hz, 1H), 6.88 (dt, *J* = 15.4, 1.5 Hz, 1H), 2.37 – 2.27 (m, 2H), 1.60 – 1.48 (m, 2H), 1.40 – 1.30 (m, 6H), 0.90 (t, *J* = 7.0 Hz, 3H).

(*E*)-5,9-Dimethyl-1-phenyldeca-2,8-dien-1-one(1aa)[7]

The title compound was prepared from 1-phenyl-2-(triphenylphosphoranylidene)ethanone (380 mg, 1 mmol) and citronellal (202 mg, 1.00 mmol) in freshly distilled DCM(5 mL) according to the general procedure **A**. The desired α,β-unsaturated ketone **1aa** (217mg, 85%) was obtained as a colourless oil after flash chromatography (2.5-5% EtOAc/ Petroleum ether). R_f 0.42 (5 % EtOAc/Petroleum ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 7.59 – 7.54 (m, 1H), 7.49 – 7.45 (m, 2H), 7.06 (dt, *J* = 15.0, 7.4 Hz, 1H), 6.88 (dt, *J* = 15.3, 1.2 Hz, 1H), 5.13 – 5.03 (m, 1H), 2.40 – 2.28 (m, 1H), 2.18 (ddt, *J* = 8.7, 7.5, 4.4 Hz, 1H), 2.07 – 1.96 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.36 – 1.26 (m, 3H), 0.95 (d, *J* = 6.7 Hz, 3H).

3. General Procedure for Transfer Hydrogenation

General procedure of condition A for the $[IrCp^*Cl_2]_2$ catalyzed conjugate reduction of α,β-unsaturated ketones.

An Ar purged flame-dried Schlenk tube (25 mL) containing α,β-unsaturated ketone **1** (0.40 mmol, 1 equiv), $[IrCp^*Cl_2]_2$ (1 mol%), and K_2CO_3 (5 mol%) were added 2-PrOH (4 mL). The reaction mixture was stirred at 85 °C for 5 h unless stated otherwise. After the reaction was complete, the solvent was removed under reduced pressure. The crude residue was purified by flash column silica gel chromatography (petroleum ether/ ethyl acetate: 95:5 to 90:10) to yield the product **2**.

General procedure of condition B for the $[IrCp^*Cl_2]_2$ catalyzed transfer hydrogenation of α,β-unsaturated ketones.

An Ar purged flame-dried Schlenk tube (25 mL) containing α,β-unsaturated ketone **1** (0.40 mmol, 1 equiv), $[IrCp^*Cl_2]_2$ (1 mol%), and KOH (50 mol%) were added 2-PrOH (4 mL, containing 40 μL *n*-hexadecane as internal standard). The reaction mixture was stirred at 85 °C for 5 h unless stated otherwise. The reaction mixture was cooled to ambient temperature. A sample of the mixture was filtered with 0.22μ organic filter head and then directly subjected to GC analysis.

General procedure for the conjugate reduction of 1aa

An Ar purged flame-dried Schlenk tube (25 mL) containing α,β-unsaturated ketone **1aa** (0.50 mmol, 1 equiv), $[IrCp^*Cl_2]_2$ (2 mol%), and K_2CO_3 (10 mol%) were added 2-PrOH (4 mL). The reaction mixture was stirred at 100 °C for 10 h. After the reaction was complete, the solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to yield the product **2aa**.

4. Data of NMR

1,3-Diphenylpropan-1-one (2a)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 7.1 Hz, 1H), 3.34 (t, *J* = 7.7 Hz, 2H), 3.12 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.26, 140.35, 135.90, 132.12, 127.66, 127.59, 127.49, 127.10, 125.20, 39.49, 29.18.

1,3-Diphenylpropan-1-ol (3a)[8]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 4.2 Hz, 4H), 7.32 (t, *J* = 6.9 Hz, 3H), 7.26 – 7.19 (m, 3H), 4.72 (s, 1H), 2.87 – 2.64 (m, 2H), 2.22 – 2.02 (m, 2H), 1.96 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.68, 141.89, 128.64, 128.55, 127.77, 126.04, 77.40, 77.15, 76.89, 74.01, 40.58, 32.18.

3-Phenyl-1-(p-tolyl)propan-1-one (2b)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.8 Hz, 2H), 7.29 (dt, *J* = 8.9, 6.5 Hz, 6H), 7.22 (t, *J* = 7.1 Hz, 1H), 3.28 (t, *J* = 7.7 Hz, 2H), 3.07 (t, *J* = 7.4 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.02, 143.94, 141.52, 134.52, 129.40, 128.63, 128.55, 128.29, 126.21, 40.45, 30.34, 21.74.

1-(4-Methoxyphenyl)-3-phenylpropan-1-one (2c)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.9 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.26 (d, *J* = 7.1 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 3.25 (dd, *J* = 10.0, 5.5 Hz, 2H), 3.06 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.84, 162.48, 140.49, 129.32, 129.02, 127.52, 127.44, 125.10, 112.76, 54.47, 39.12, 29.37.

1-(4-Fluorophenyl)-3-phenylpropan-1-one (2d)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.21 (dd, *J* = 5.1, 3.2 Hz, 2H), 7.17 (dd, *J* = 11.4, 4.3 Hz, 1H), 7.11 – 7.04 (m, 2H), 3.23 (t, *J* = 7.7 Hz, 2H), 3.05 – 3.00 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.69, 165.83 (d, *J* = 254.4 Hz), 141.25, 133.44, 130.76 (d, *J* = 8.5 Hz), 128.66, 128.52, 126.30, 115.78 (d, *J* = 21.7 Hz), 40.45, 30.23. ^{19}F NMR (470 MHz, $CDCl_3$) δ -105.32.

1-(4-Chlorophenyl)-3-phenylpropan-1-one (2e)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.21 (m, 3H), 3.29 (t, *J* = 7.6 Hz, 2H), 3.09 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.01, 140.08, 138.53, 134.18, 128.49, 127.95, 127.60, 127.44, 125.26, 39.45, 29.07.

1-(4-Bromophenyl)-3-phenylpropan-1-one (2f)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.18 (m, 3H), 3.26 (dd, *J* = 10.0, 5.3 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.29, 141.14, 135.67, 132.03, 129.68, 128.68, 128.52, 128.34, 126.34, 40.51, 30.14.

1-(3-Chlorophenyl)-3-phenylpropan-1-one (2g)[9]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.40 (t, *J* = 7.9 Hz,

1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 3.28 (t, *J* = 7.7 Hz, 2H), 3.07 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.95, 141.06, 138.53, 135.08, 133.05, 130.02, 128.66, 128.49, 128.29, 126.33, 126.18, 40.62, 30.08.

3-Phenyl-1-(o-tolyl)propan-1-one (2h)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.4 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.19 (m, 5H), 3.24 (t, *J* = 7.6 Hz, 2H), 3.06 (t, *J* = 7.6 Hz, 2H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.49, 141.31, 138.20, 138.03, 132.08, 131.36, 128.63, 128.54, 126.24, 125.79, 43.34, 30.46, 21.36.

1-(Naphthalen-2-yl)-3-phenylpropan-1-one (2i)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.05 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.89 (t, *J* = 8.9 Hz, 2H), 7.65 – 7.58 (m, 1H), 7.55 (dd, *J* = 11.0, 3.9 Hz, 1H), 7.37 – 7.27 (m, 4H), 7.25 – 7.20 (m, 1H), 3.50 – 3.40 (m, 2H), 3.19 – 3.08 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.27, 141.46, 135.70, 134.32, 132.65, 129.79, 129.65, 128.66, 128.57, 127.88, 126.87, 126.27, 123.96, 40.67, 30.40.

1-Phenyl-3-(p-tolyl)propan-1-one (2j)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.15 (dd, *J* = 19.7, 8.0 Hz, 4H), 3.30 (dd, *J* = 10.0, 5.5 Hz, 2H), 3.05 (t, *J* = 7.7 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.36, 137.23, 135.96, 134.64, 132.04, 128.24, 127.62, 127.33, 127.08, 39.63, 28.77, 20.03.

3-(4-Methoxyphenyl)-1-phenylpropan-1-one (2k)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.5 Hz, 31H), 7.57 (t, *J* = 7.4 Hz, 16H), 7.47 (t, *J* = 7.6 Hz, 31H), 7.28 (s, 2H), 7.19 (d, *J* = 8.5 Hz, 31H), 6.87 (d, *J* = 8.5 Hz, 31H), 3.81 (s, 46H), 3.29 (t, *J* = 7.7 Hz, 32H), 3.04 (t, *J* = 7.6 Hz, 32H), 0.03 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.42, 157.04, 135.96, 132.35, 132.04, 128.37, 127.61, 127.06, 112.99, 54.29, 39.71, 28.32.

3-(4-Chlorophenyl)-1-phenylpropan-1-one (2l)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 3.30 (t, *J* = 7.5 Hz, 2H), 3.06 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.87, 138.78, 135.77, 132.21, 130.88, 128.87, 127.67, 127.63, 127.04, 76.36, 76.10, 75.85, 39.15, 28.39.

1-Phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (2m)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.3 Hz, 2H), 7.56 (dd, *J* = 13.3, 7.6 Hz, 3H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.33 (t, *J* = 7.5 Hz, 2H), 3.14 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.57, 144.48, 135.71, 132.25, 127.83, 127.69, 127.42, 127.02, 124.44, 123.34(q, $J_{C\text{-}F}$ = 274.8 Hz), 38.81, 28.79. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.35.

1-Phenyl-3-(3-(trifluoromethyl)phenyl)propan-1-one (2n)[10]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.52 (s, 1H), 7.46 (t, *J* = 7.7 Hz, 4H), 7.43 – 7.38 (m, 1H), 3.33 (t, *J* = 7.6 Hz, 2H), 3.14 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.60, 141.23, 135.72, 132.23, 130.98, 129.84 (q, *J* = 32.4 Hz), 127.95, 127.67, 127.03, 124.15, 123.18(q, *J* = 271.4 Hz), 122.06, 38.97, 28.80. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.56.

1-Phenyl-3-(2-(trifluoromethyl)phenyl)propan-1-one (2o)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.49 (dt, *J* = 15.4, 7.8 Hz, 3H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 3.34 – 3.29 (m, 2H), 3.29 – 3.24 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.64, 139.16, 135.70, 132.18, 130.99, 130.37, 127.65, 127.05, 125.35, 125.11, 123.64 (q, *J* = 272 Hz), 39.55, 26.10. ^{19}F NMR (470 MHz, $CDCl_3$) δ -59.69. GCMS (EI) m/z: 278 (M^+); Anal. Calcd for $C_{16}H_{13}F_3O$: C, 69.06; H, 4.71%. Found: C, 68.97; H, 4.95%.

1-(4-Chlorophenyl)-3-(2-(trifluoromethyl)phenyl)propan-1-one (2p)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 3.26 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.40, 138.90, 138.66, 133.99, 131.03, 130.35, 128.46, 127.97, 127.97 (q, *J* = 30.1 Hz), 125.45, 125.18, 123.62(q, *J* = 271.7 Hz), 39.52, 26.05. ^{19}F NMR (470 MHz, $CDCl_3$) δ -59.67. GCMS (EI) m/z: 312 (M^+); Anal. Calcd for $C_{16}H_{12}ClF_3O$: C, 61.45; H, 3.87%. Found: C, 61.15; H, 4.04%.

1-(Furan-2-yl)-3-phenylpropan-1-one (2q)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 1.1 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.25 (d, *J* = 6.8 Hz, 2H), 7.21 (dd, *J* = 11.4, 4.2 Hz, 1H), 7.18 – 7.16 (m, 1H), 6.52 (dd, *J* = 3.5, 1.7 Hz, 1H), 3.18 – 3.13 (m, 2H), 3.05 (dd, *J* = 9.9, 5.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.59, 152.78, 146.41, 141.08, 128.62, 128.52, 126.28, 117.10, 112.30, 40.28, 30.06.

3-Phenyl-1-(thiophen-2-yl)propan-1-one (2r)[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.63 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.28 – 7.24 (m, 2H), 7.24 – 7.18 (m, 1H), 7.12 (dd, *J* = 4.9, 3.8 Hz, 1H), 3.27 – 3.21 (m, 2H), 3.08 (dd, *J* = 9.8, 5.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.28, 144.28, 141.12, 133.69, 131.95, 128.67, 128.55, 128.22, 126.34, 41.26, 30.50.

Propiophenone (2s)[11]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.90 (m, 2H), 7.53 (dd, *J* = 10.5, 4.2 Hz, 1H), 7.43 (dd, *J* = 10.7, 4.7 Hz, 2H), 2.98 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.90, 137.00, 132.97, 128.65, 128.06, 31.87, 8.33.

1,5-Diphenylpentan-1-one (2t)[12]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.61 – 7.55 (m, 1H), 7.48 (dd, *J* = 10.7, 4.8 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 1.87 – 1.79 (m, 2H), 1.79 – 1.70 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.40, 142.36, 137.15, 133.03, 128.67, 128.51, 128.42, 128.15, 125.86, 38.52, 35.91, 31.21, 24.10.

1-Phenylnonan-1-one (2u)[13]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.61 – 7.54 (m, 1H), 7.52 – 7.44 (m, 2H), 3.03 – 2.94 (m, 2H), 1.80 – 1.70 (m, 2H), 1.42 – 1.24 (m, 10H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.74, 137.21, 132.95, 128.64, 128.16, 38.75, 31.94, 29.50, 29.27, 24.50, 22.76, 14.20.

4-Phenylbutan-2-one (2v)[14]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.5 Hz, 2H), 7.15 (t, *J* = 7.7 Hz, 3H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.6

Hz, 2H), 2.09 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.96, 141.09, 128.59, 128.38, 126.21, 45.26, 30.13, 29.86.

4-(Furan-2-yl)butan-2-one (**2w**)[14]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 1.0 Hz, 1H), 6.29 (dd, *J* = 2.8, 2.0 Hz, 1H), 6.01 (d, *J* = 2.6 Hz, 1H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.81 (t, *J* = 7.4 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.44, 154.60, 141.19, 110.31, 105.29, 41.80, 30.02, 22.28.

Cyclohexanone (**2x**)[11]

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.30 (t, *J* = 6.5 Hz, 4H), 1.87 – 1.78 (m, 4H), 1.72 – 1.65 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.24, 42.06, 27.10, 25.07.

5,9-Dimethyl-1-phenyldec-8-en-1-one (**2aa**)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 5.17 – 4.48 (m, 1H), 2.92 (t, *J* = 7.5 Hz, 2H), 1.95 (qd, *J* = 14.5, 7.4 Hz, 2H), 1.80 – 1.67 (m, 2H), 1.65 (s, 3H), 1.58 (s, 3H), 1.48 – 1.40 (m, 1H), 1.34 (dddd, *J* = 19.6, 15.3, 7.5, 4.0 Hz, 2H), 1.23 – 1.13 (m, 2H), 0.88 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.68, 137.21, 132.97, 131.20, 128.65, 128.15, 125.00, 39.02, 37.08, 36.73, 32.44, 25.82, 25.62, 22.00, 19.58, 17.74. GCMS (EI) m/z: 287 (M^+); Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14%. Found: C, 83.49; H, 10.25%.

5. References

1 C. White, A. Yates, P. M. Maitlis, *Inorg. Synth*. **1992**, *29*, 228-234.

2 B. Ding, Z. Zhang, Y. Liu, M. Sugiya, T. Imamoto, W. Zhang, *Org. Lett.* **2013**, *15*, 3690-3693, and references therein.

3 D. G. Stark, L. C. Morrill, P.-P. Yeh, A. M. Z. Slawin, T. J. C. O'Riordan, A. D. Smith, *Angew. Chem. Int. Ed.* **2013**, 52, 11642-11646.

4 X. L. An, J. R. Chen, C. F. Li, F. G. Zhang, Y. Q. Zou, Y. C. Guo, W. J. Xiao, *Chem. Asian. J.* **2010**, *5*, 2258-2265.

5 H. Lebel, M. Davi, *Adv. Synth. Catal.* **2008**, 350, 2352-2358.

6 J. M. Chong, L. Shen, N. J. Taylor, *J. Am. Chem. Soc.* **2000**, 122, 1822-1823.

7 S. G. Zlotin, G. V. Kryshtal, G. M. Zhdankina, A. V. Bogolyubov, S. G. Postikova, V. A. Tartakovsky, *Russ.Chem.Bull.* **2007**, 56, 1487-1494.

8 C. E. Hartmann, V. Jurcik, O. Songis, C. S. Cazin, *Chem. Commun.* **2013**, *49*, 1005-1007.

9 Lukas J. Gooßen, K. Ghosh, *Eur. J. Org. Chem.* **2002**, 3254-3267.

10 T. Kuwahara, T. Fukuyama, I. Ryu, *Org. Lett.* **2012**, *14*, 4703-4705.

11 S. Manzini, A. Poater, D. J. Nelson, L. Cavallo and S. P. Nolan, *Chem. Sci.* **2014**, 5, 180-188.

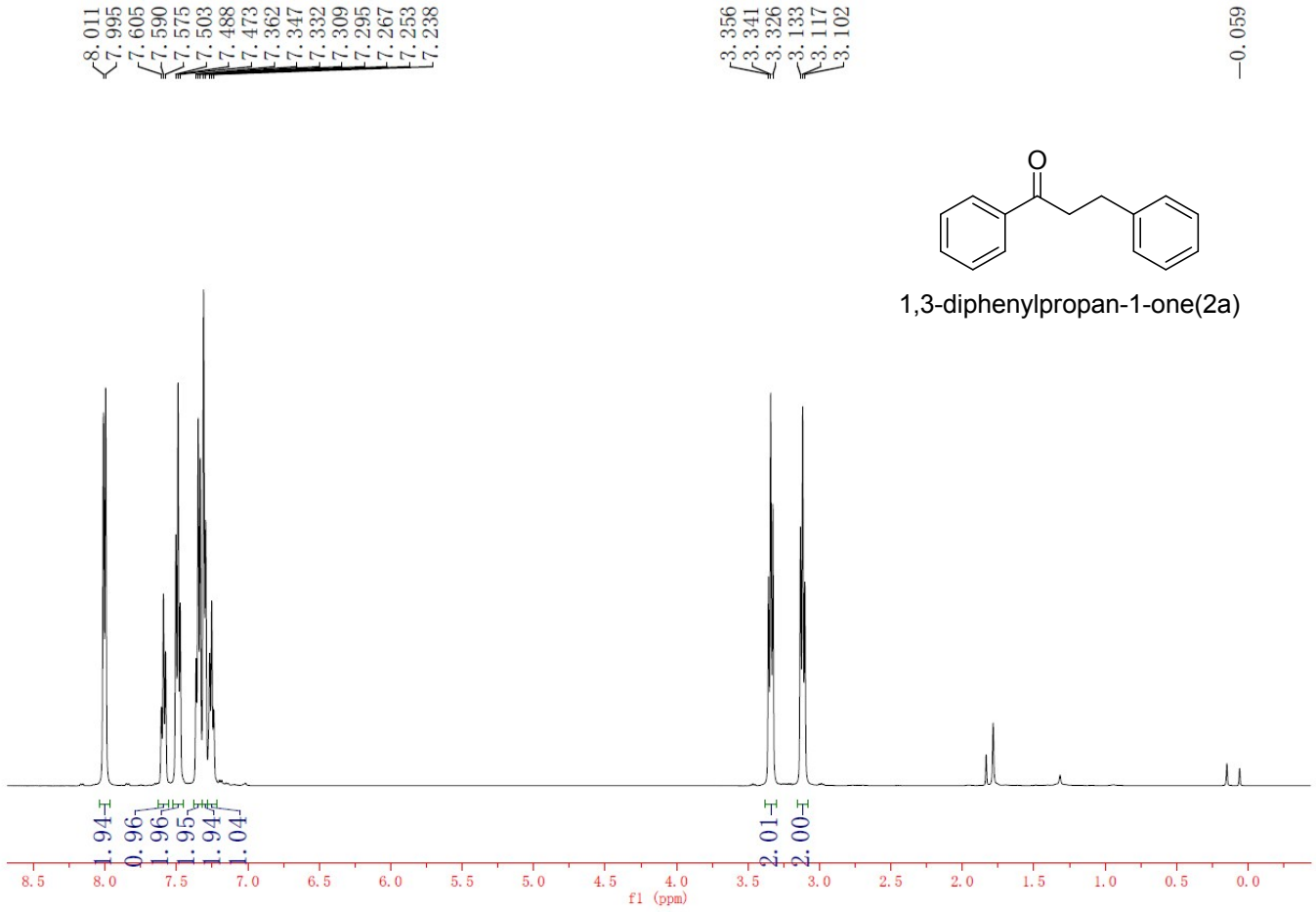
12 F. Chahdoura, C. Pradel, M. Gómez, *Adv. Synth. Catal.* **2013**, *355*, 3648-3660.

13 S. Sumino, T. Ui, I. Ryu, *Org. Lett.* **2013**, *15*, 3142-3145.

14 X. Li, L. Li, Y. Tang, L. Zhong, L. Cun, J. Zhu, J. Liao, J. Deng, *J. Org. Chem.* **2010**, *75*, 2981-2988.

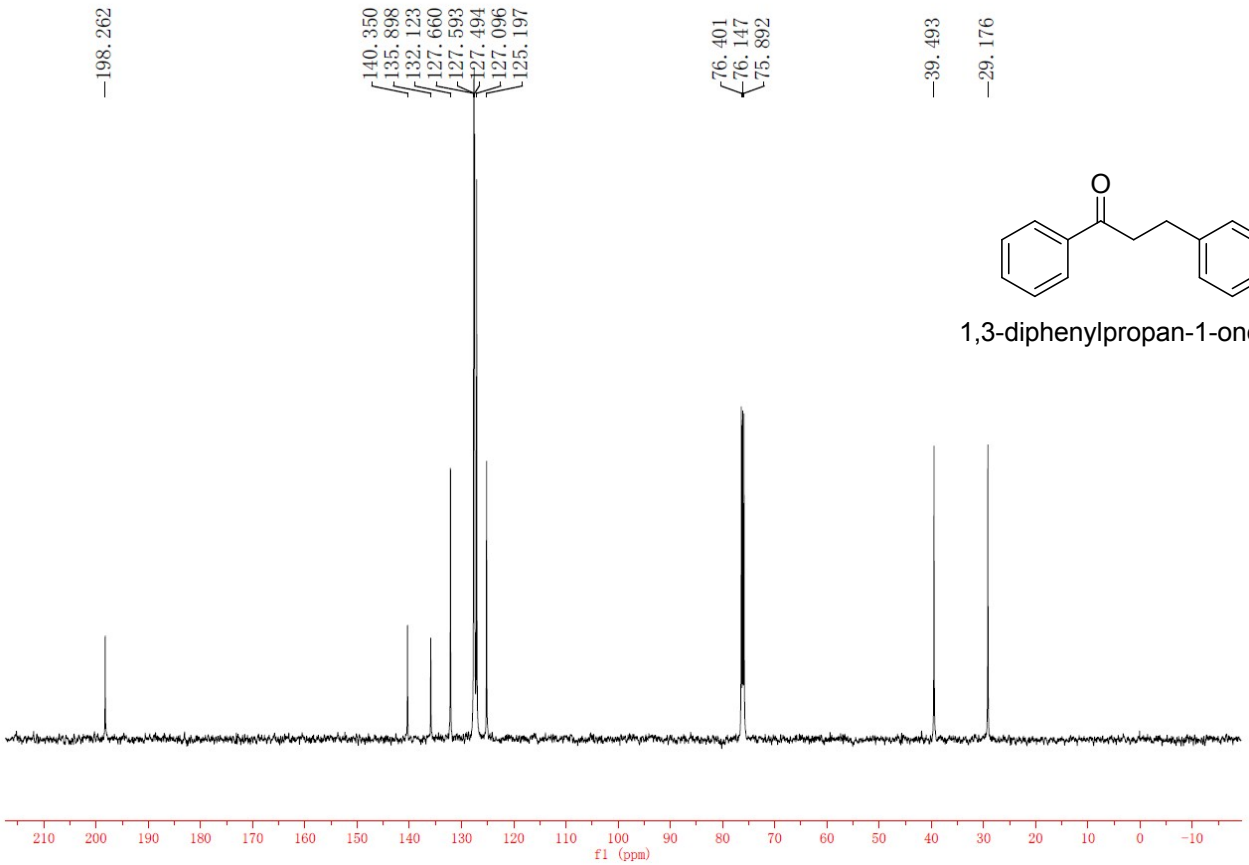
6. Spectra of Products

^{1}H NMR (500 MHz, $CDCl_3$)



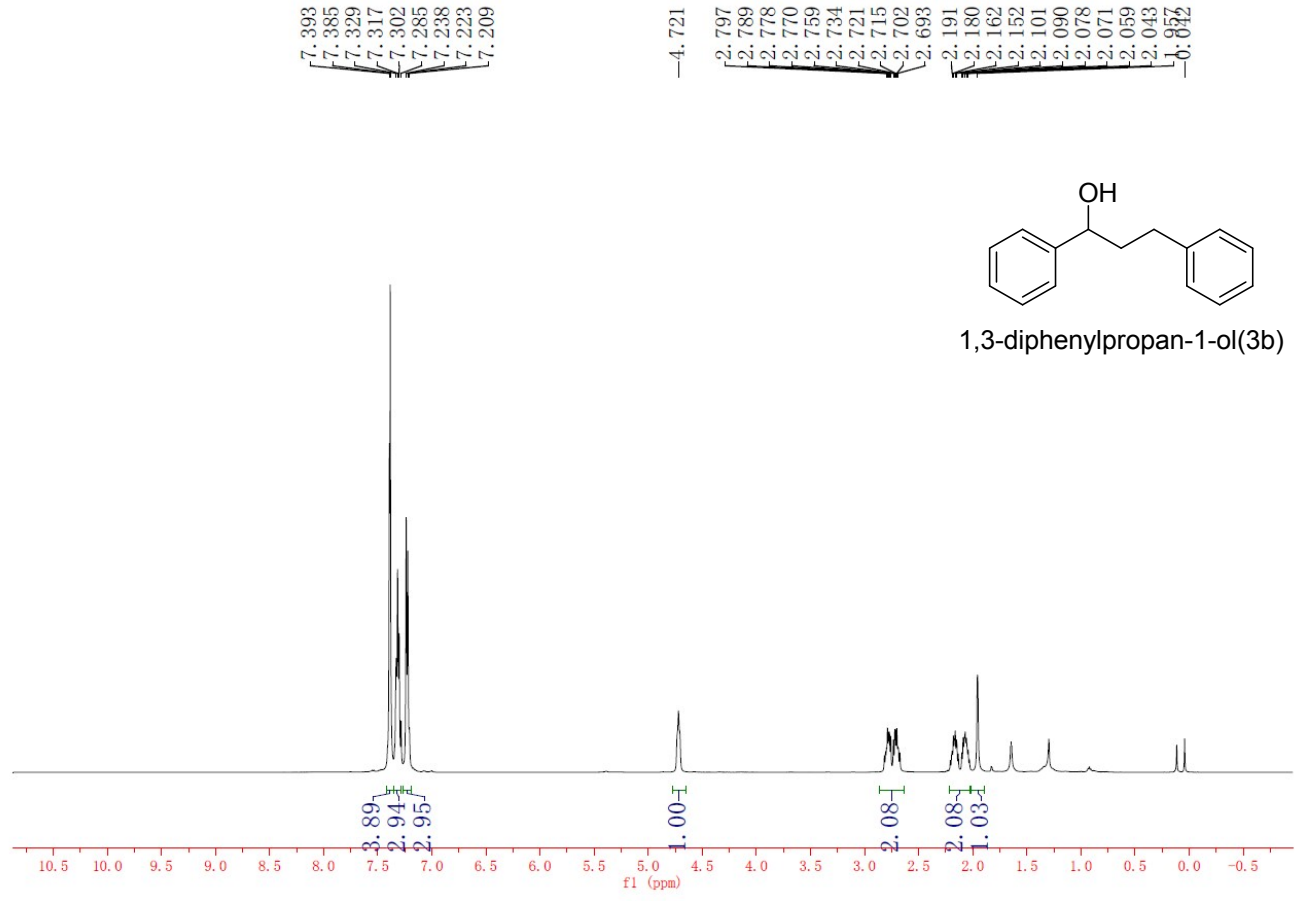
1,3-diphenylpropan-1-one(2a)

^{13}C NMR (125 MHz, $CDCl_3$)



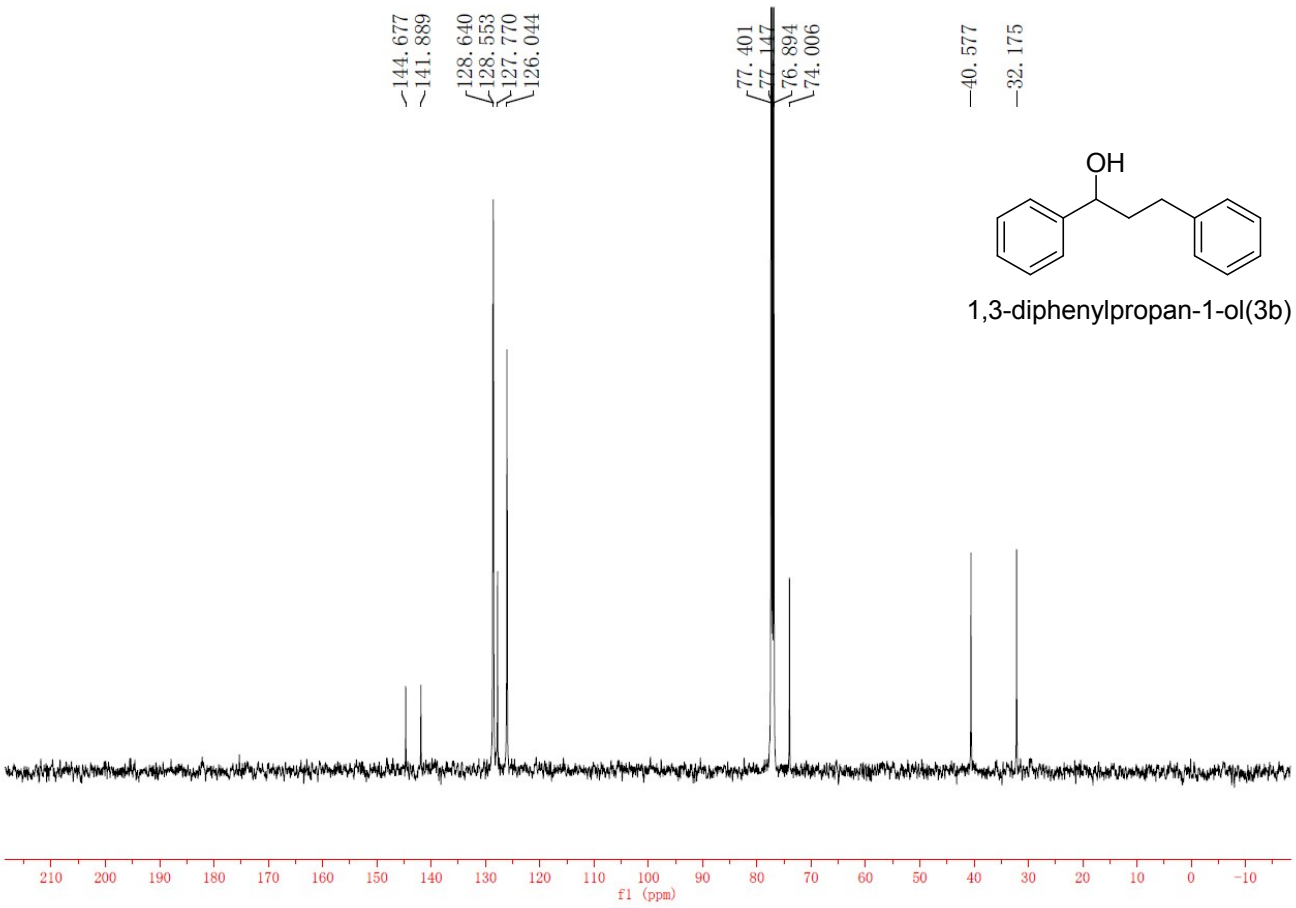
1,3-diphenylpropan-1-one(2a)

^{1}H NMR (500 MHz, $CDCl_3$)



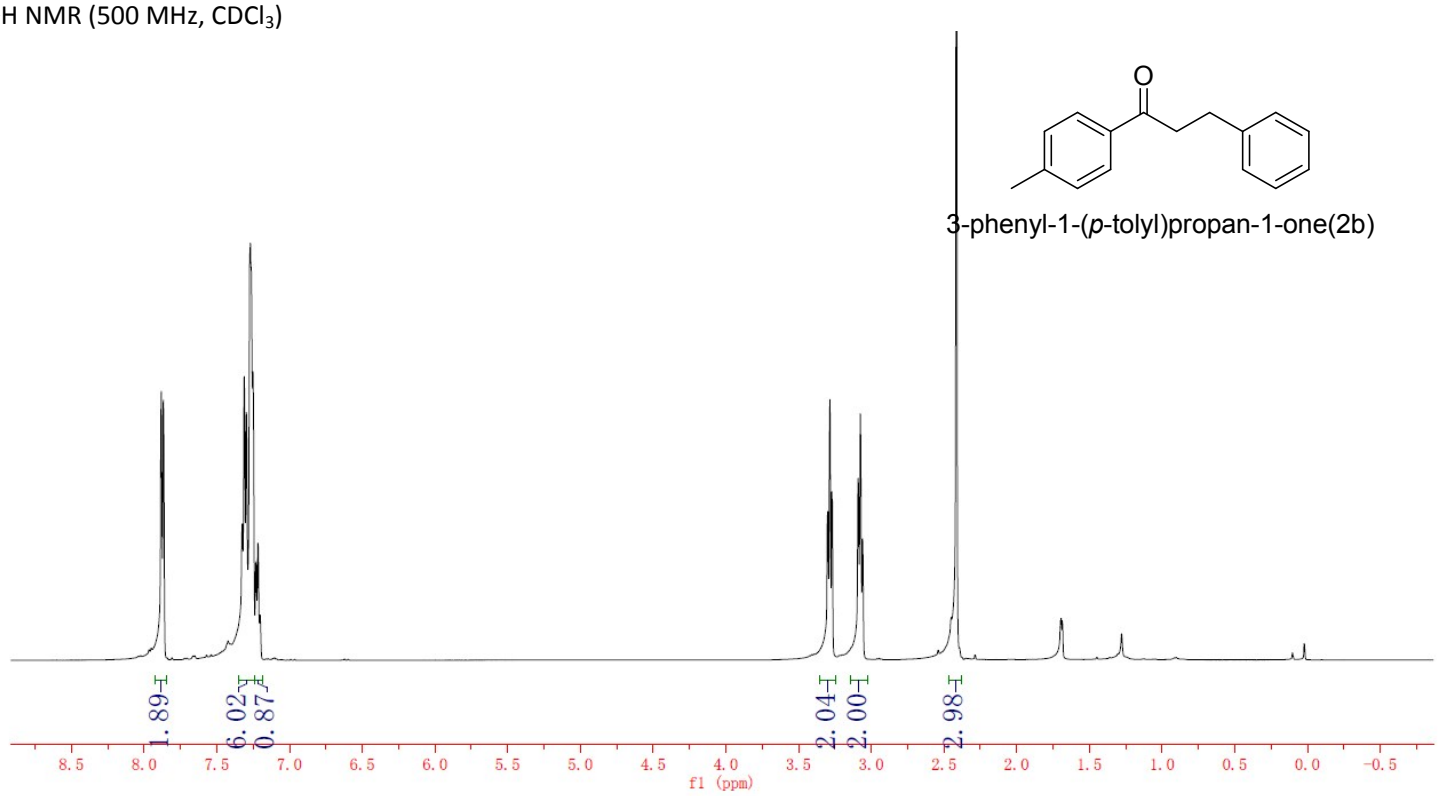
1,3-diphenylpropan-1-ol(3b)

^{13}C NMR (125 MHz, $CDCl_3$)



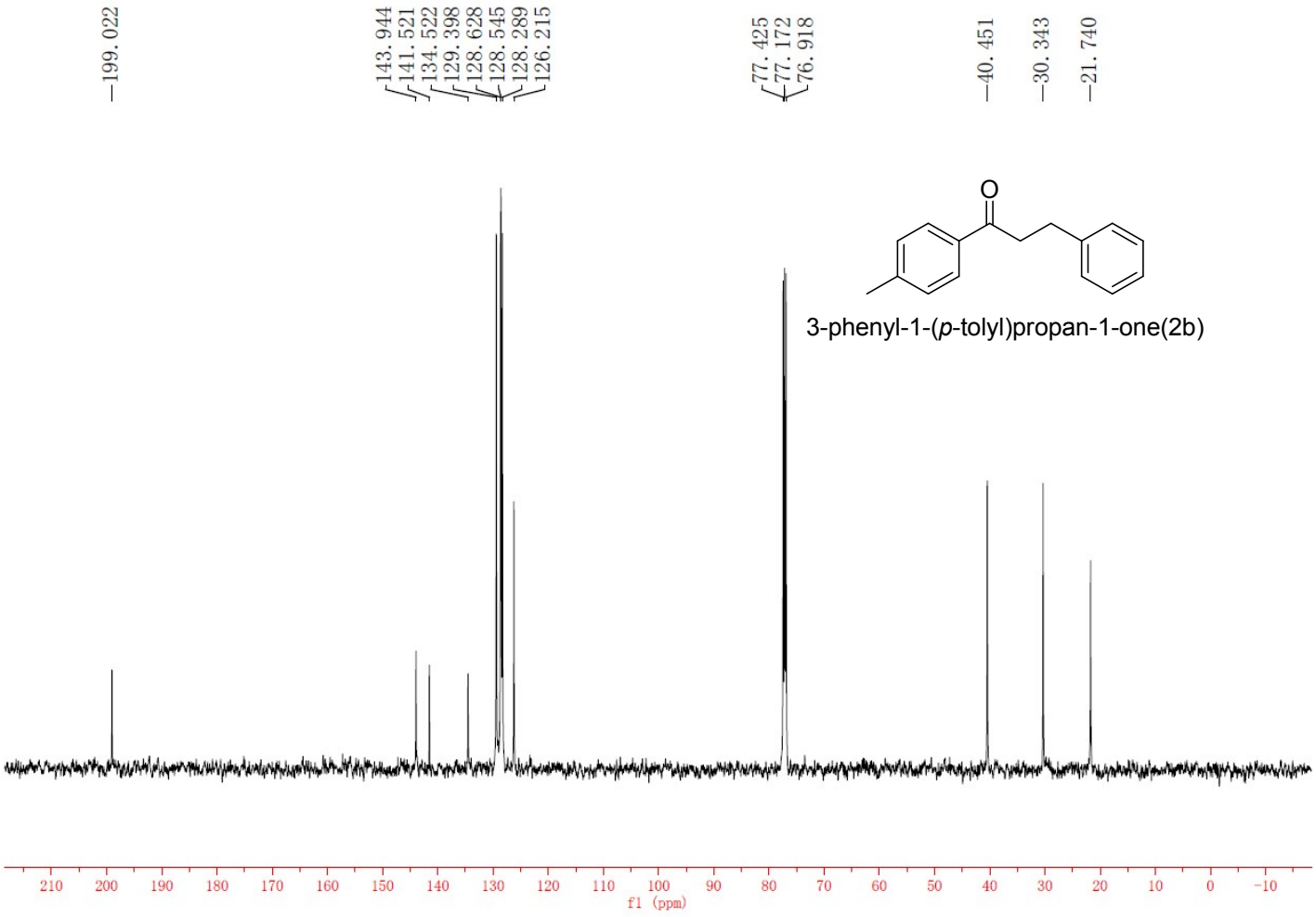
1,3-diphenylpropan-1-ol(3b)

^{1}H NMR (500 MHz, $CDCl_3$)

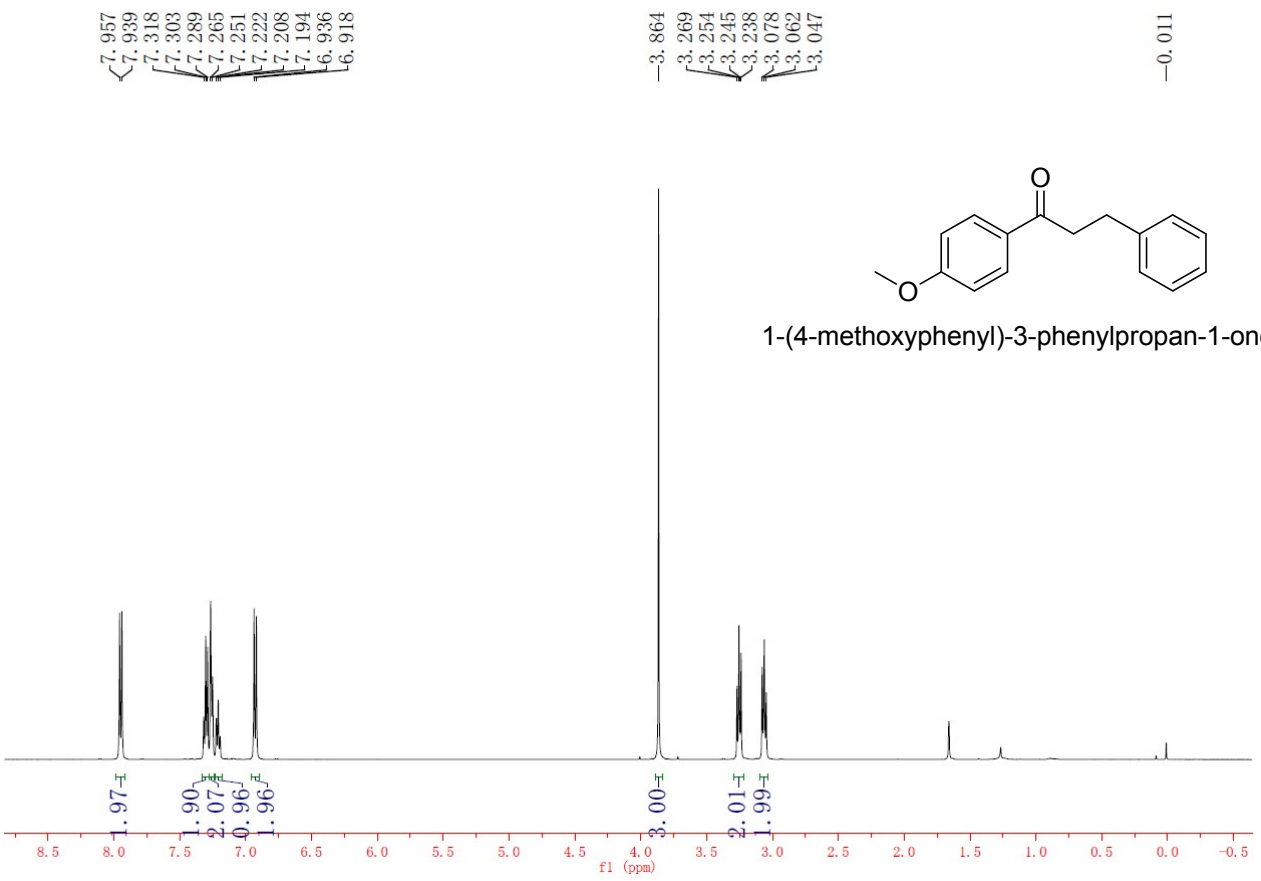


3-phenyl-1-(*p*-tolyl)propan-1-one(2b)

^{13}C NMR (125 MHz, $CDCl_3$)

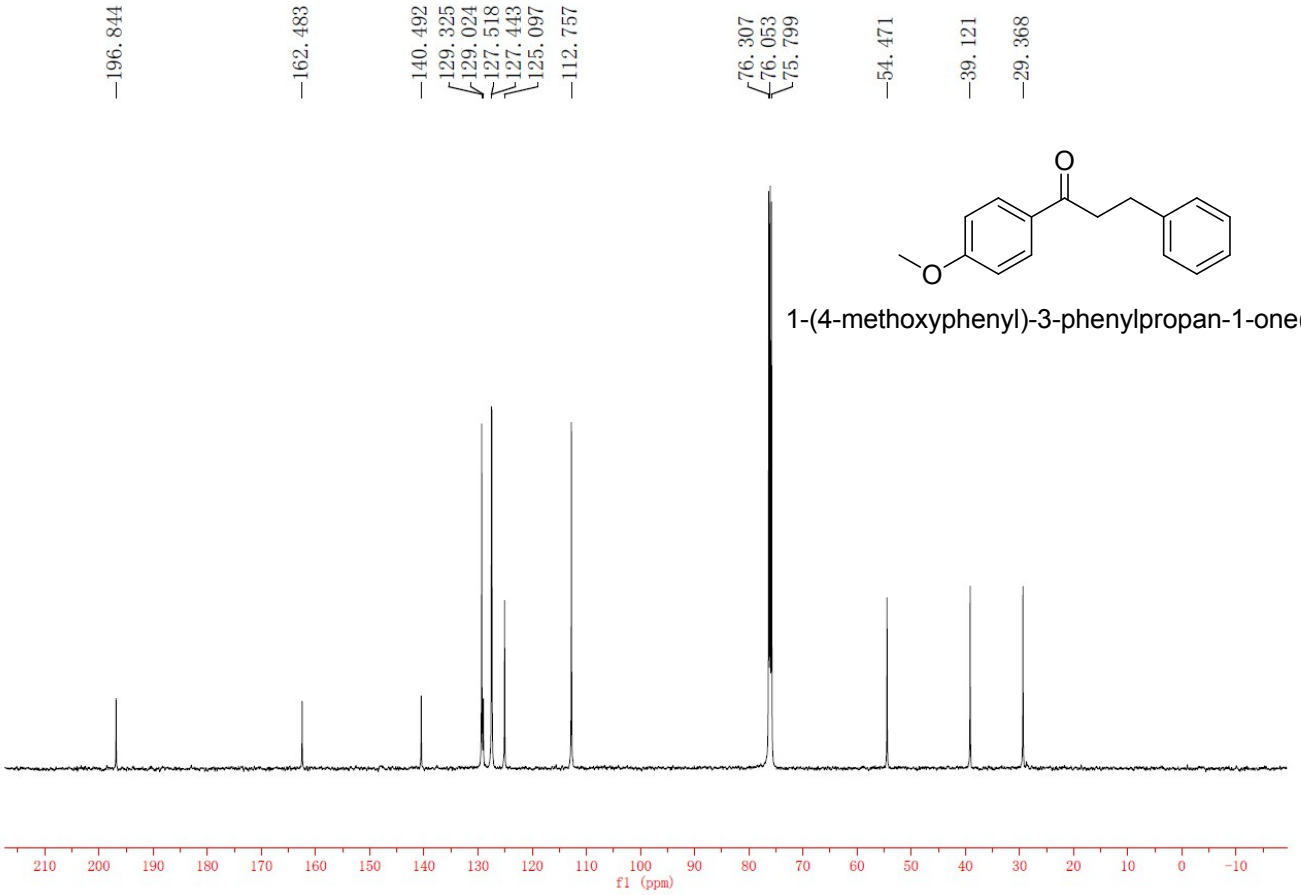


^{1}H NMR (500 MHz, $CDCl_3$)



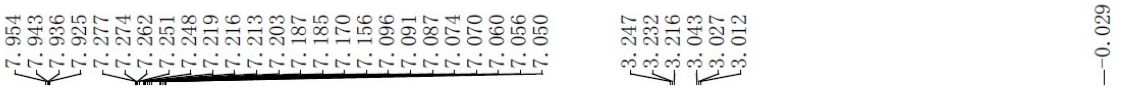
1-(4-methoxyphenyl)-3-phenylpropan-1-one(2c)

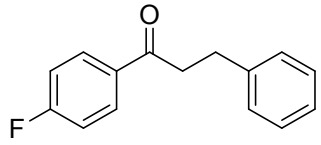
^{13}C NMR (125 MHz, $CDCl_3$)



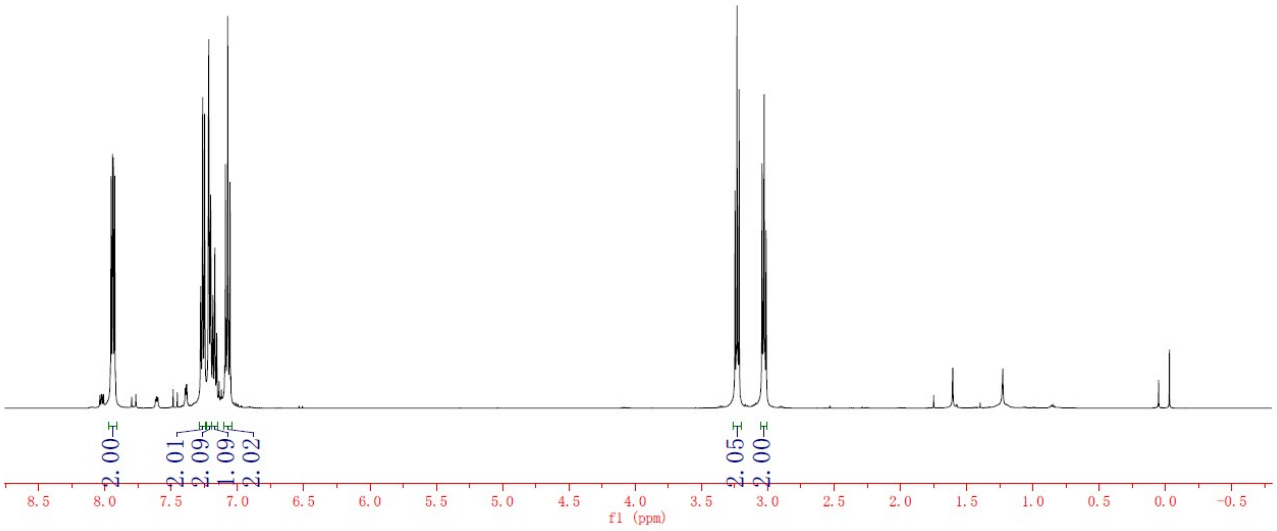
1-(4-methoxyphenyl)-3-phenylpropan-1-one(2c)

^{1}H NMR (500 MHz, $CDCl_3$)

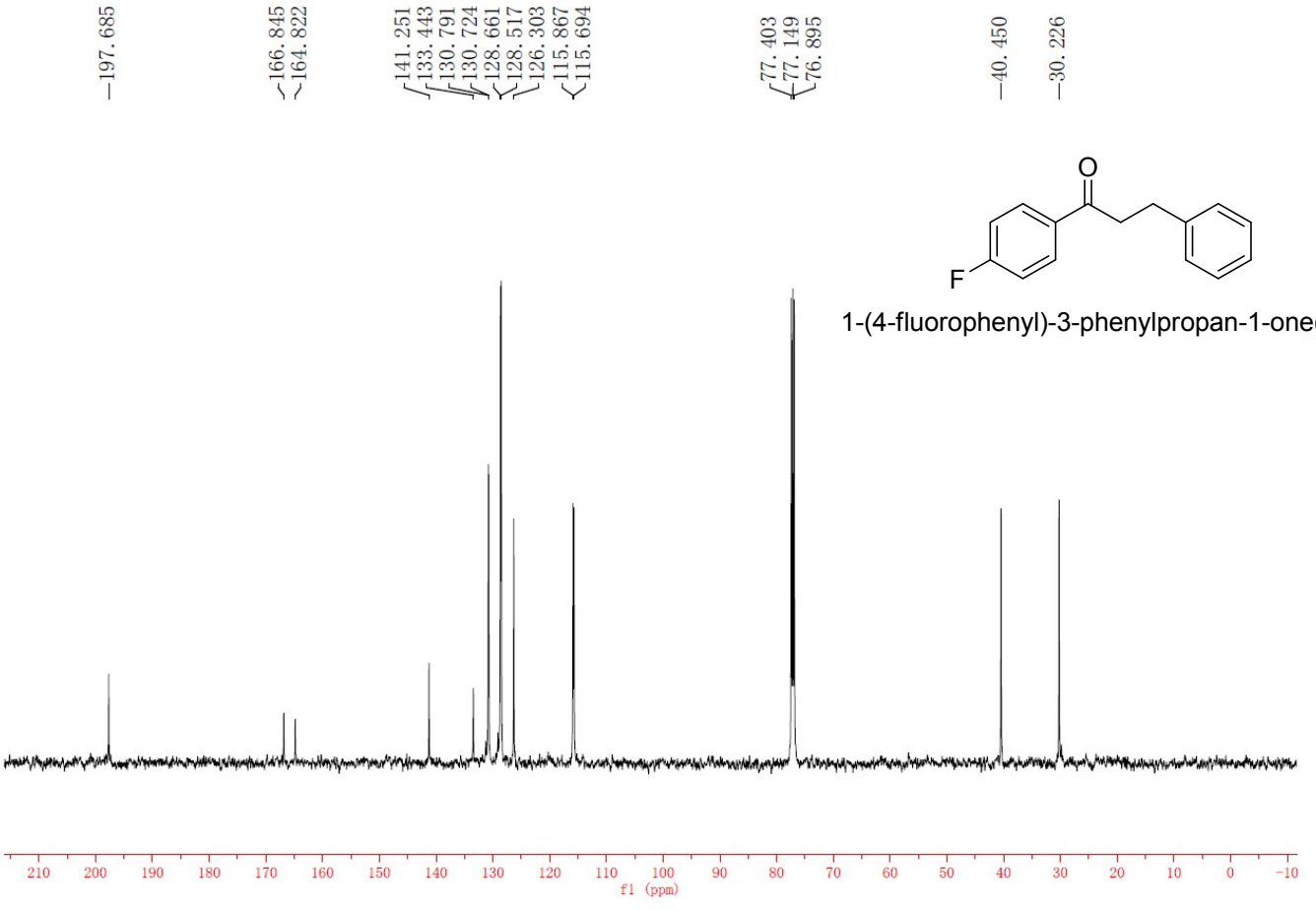




1-(4-fluorophenyl)-3-phenylpropan-1-one(2d)

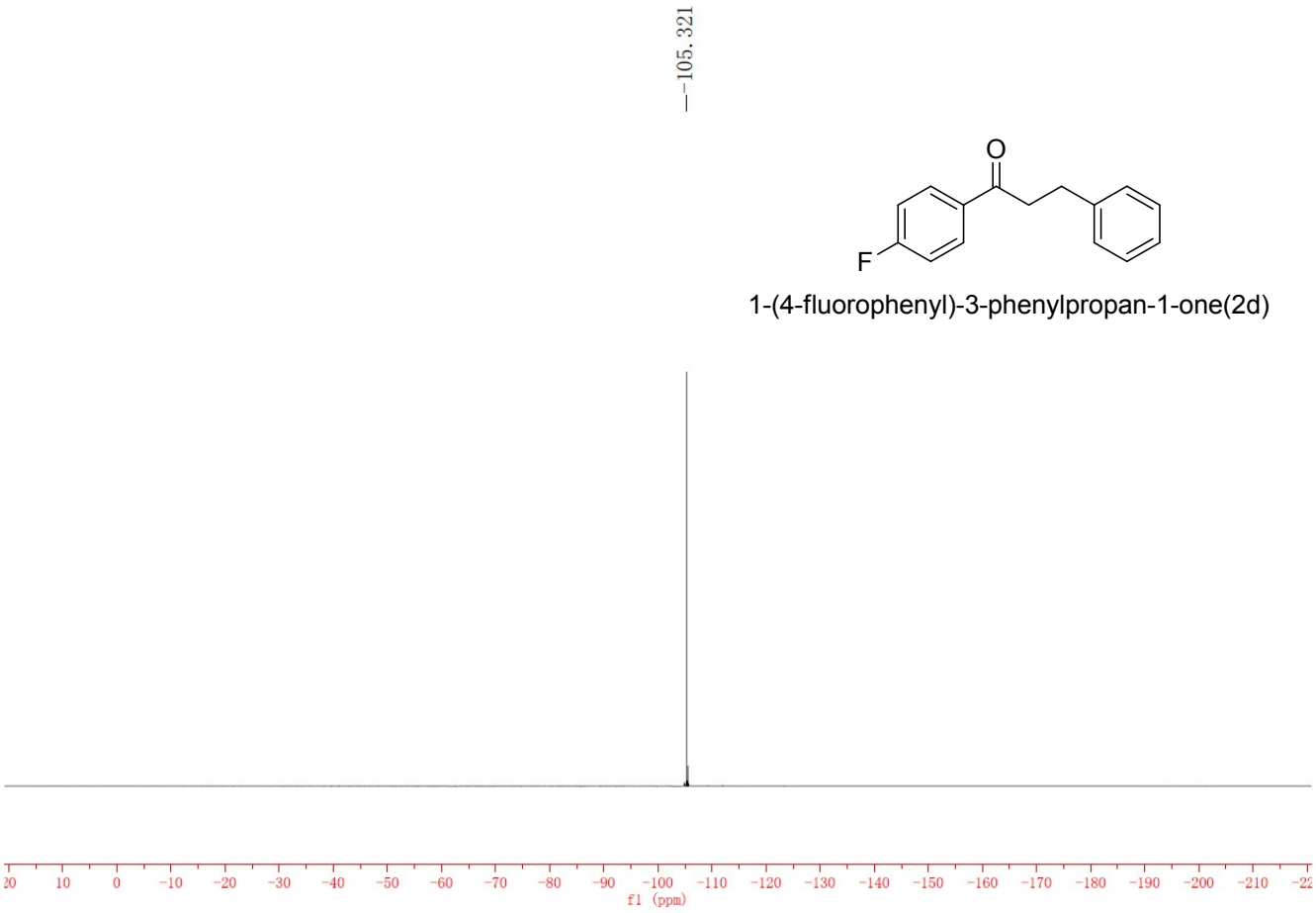


^{13}C NMR (125 MHz, $CDCl_3$)

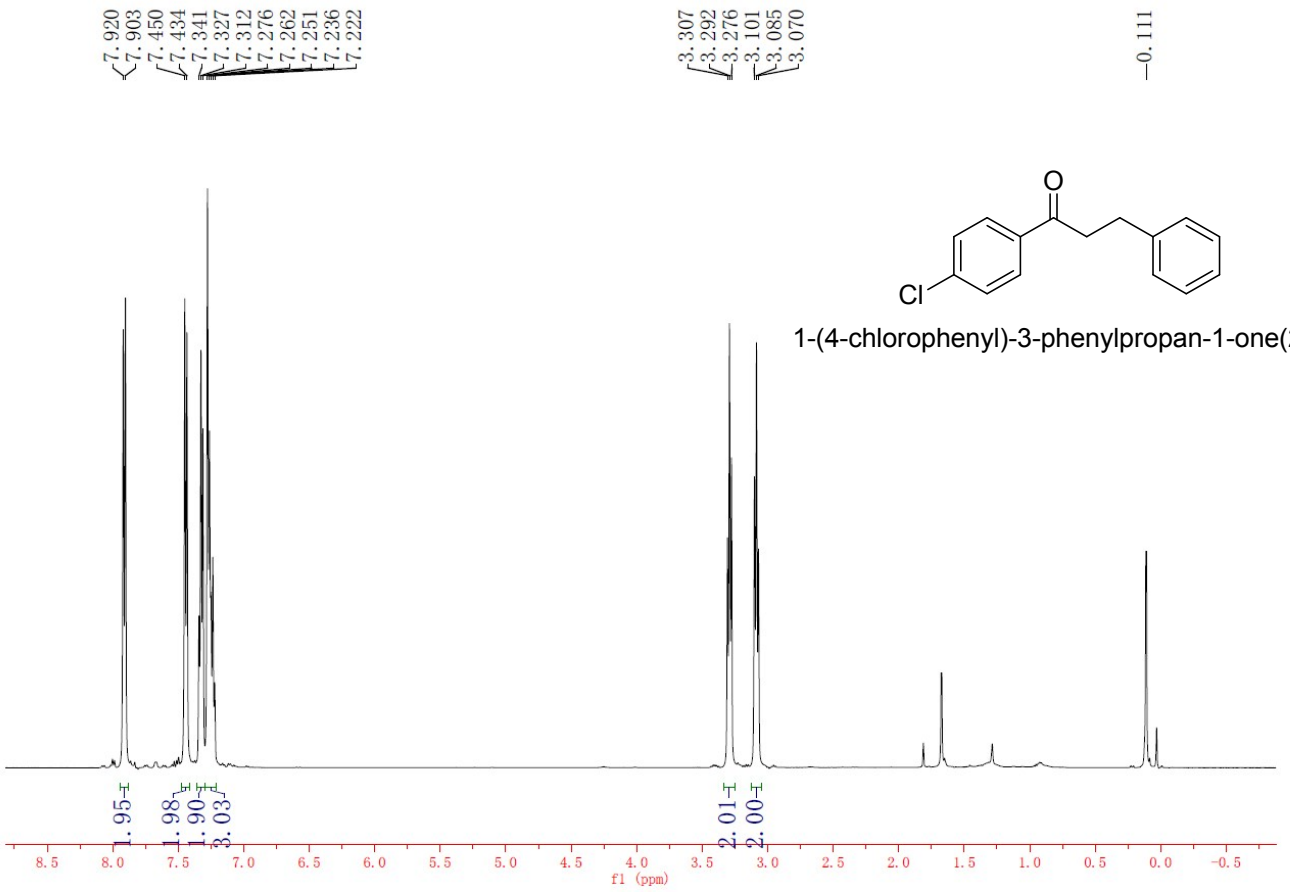


1-(4-fluorophenyl)-3-phenylpropan-1-one(2d)

^{19}F NMR (470 MHz, $CDCl_3$)

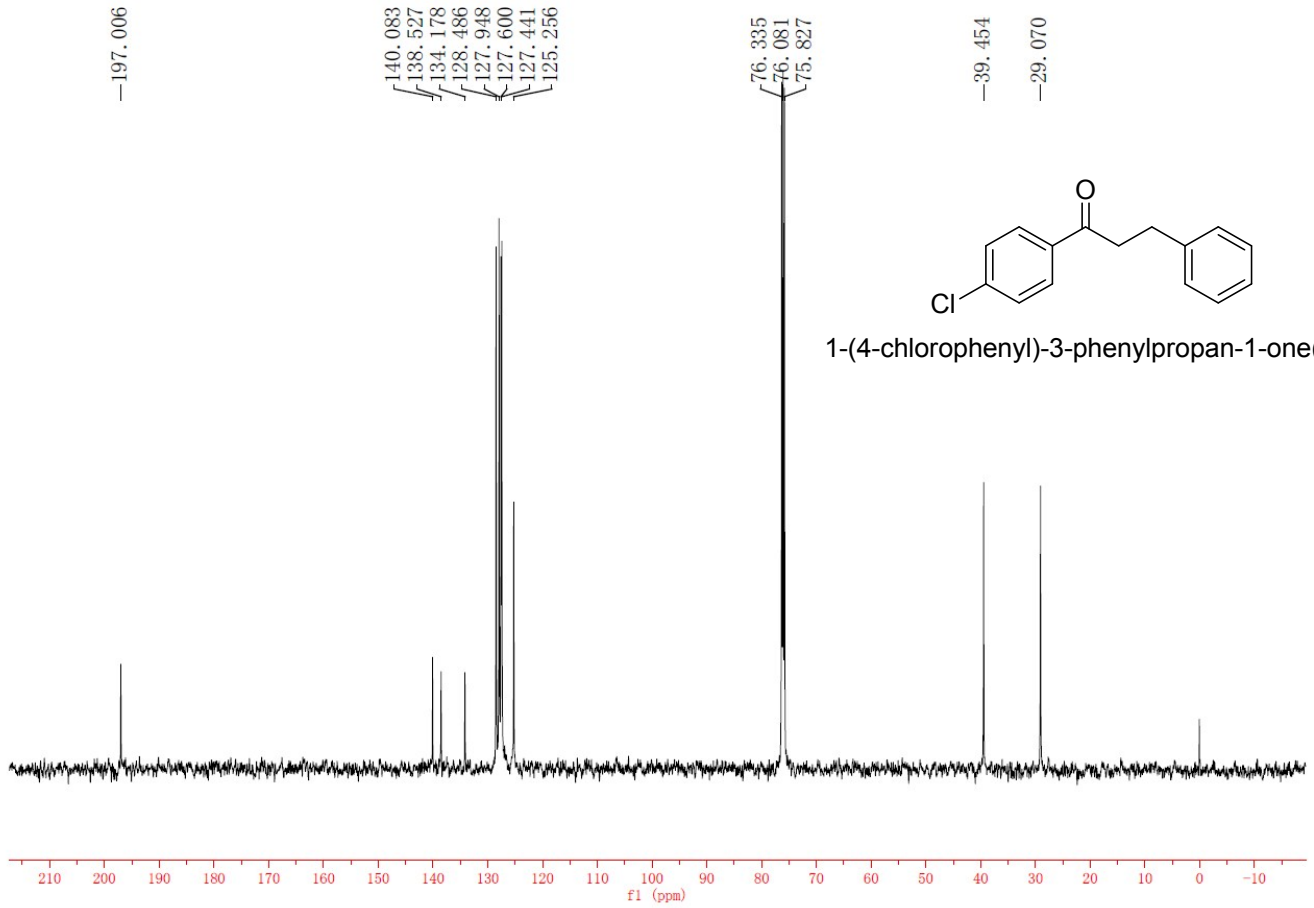


^{1}H NMR (500 MHz, $CDCl_3$)



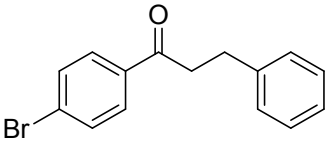
1-(4-chlorophenyl)-3-phenylpropan-1-one(2e)

^{13}C NMR (125 MHz, $CDCl_3$)

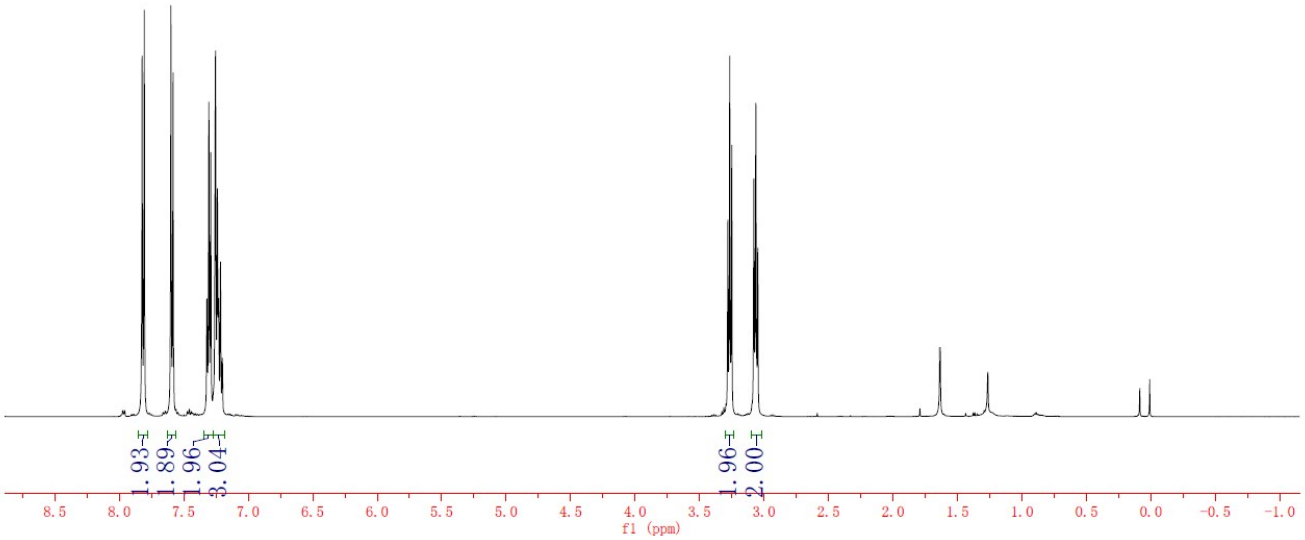


1-(4-chlorophenyl)-3-phenylpropan-1-one(2e)

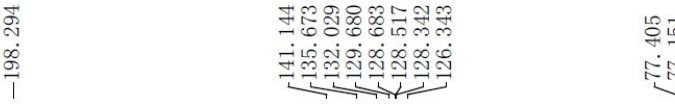
^{1}H NMR (500 MHz, $CDCl_3$)

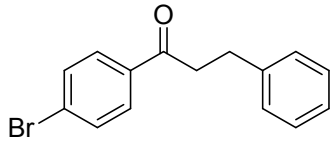


1-(4-bromophenyl)-3-phenylpropan-1-one(2f)



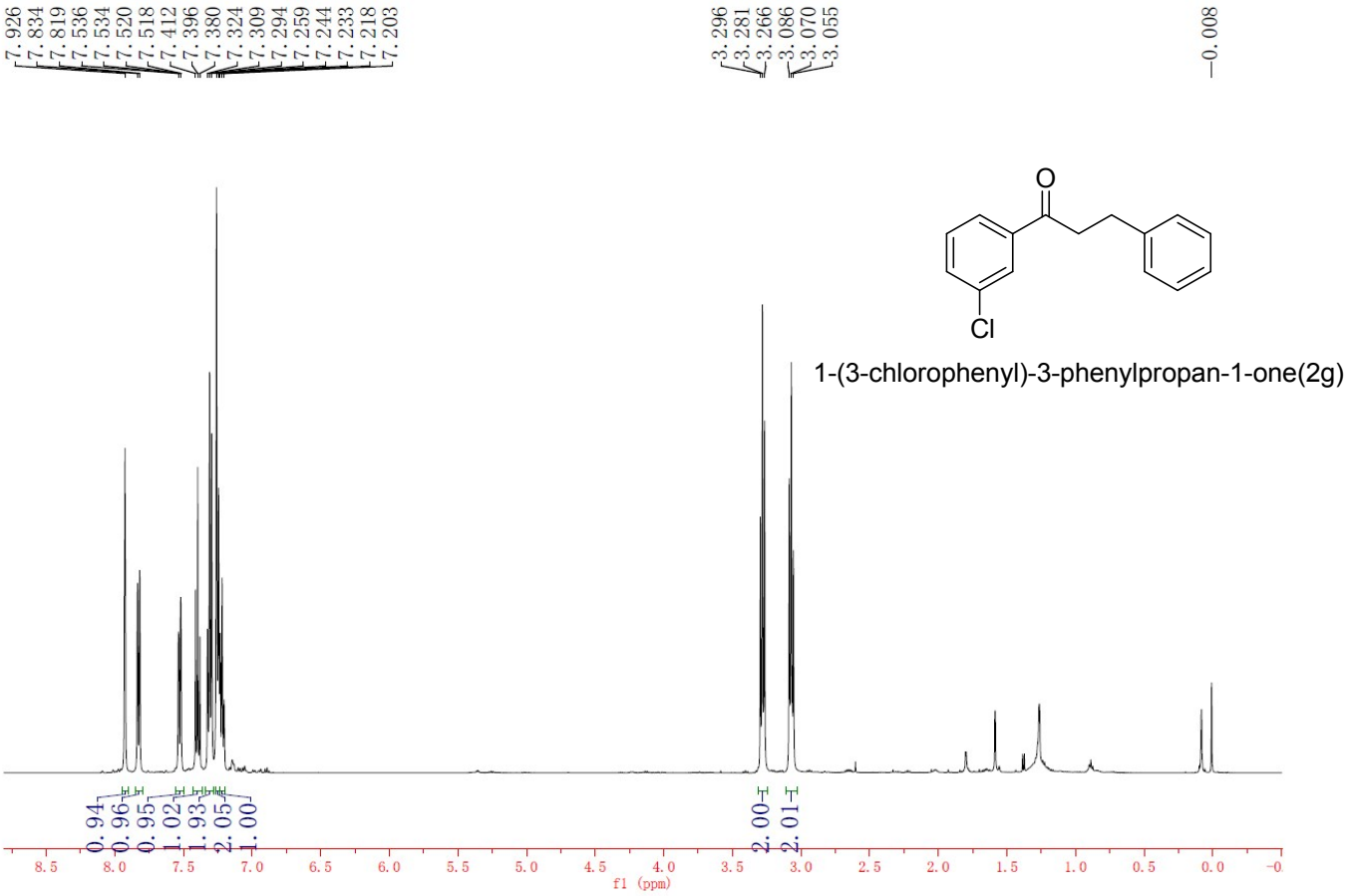
^{13}C NMR (125 MHz, $CDCl_3$)





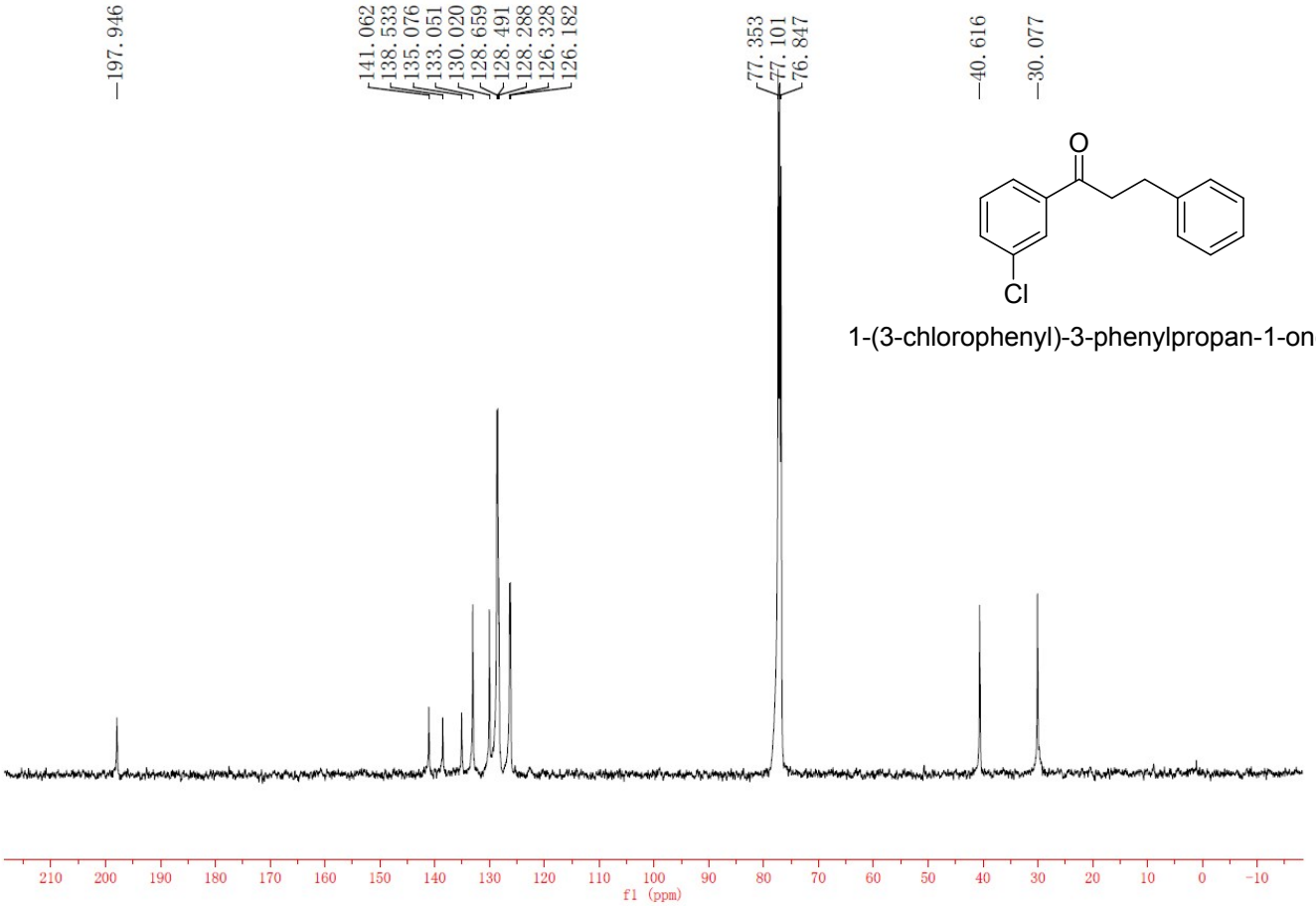
1-(4-bromophenyl)-3-phenylpropan-1-one(2f)

^{1}H NMR (500 MHz, $CDCl_3$)



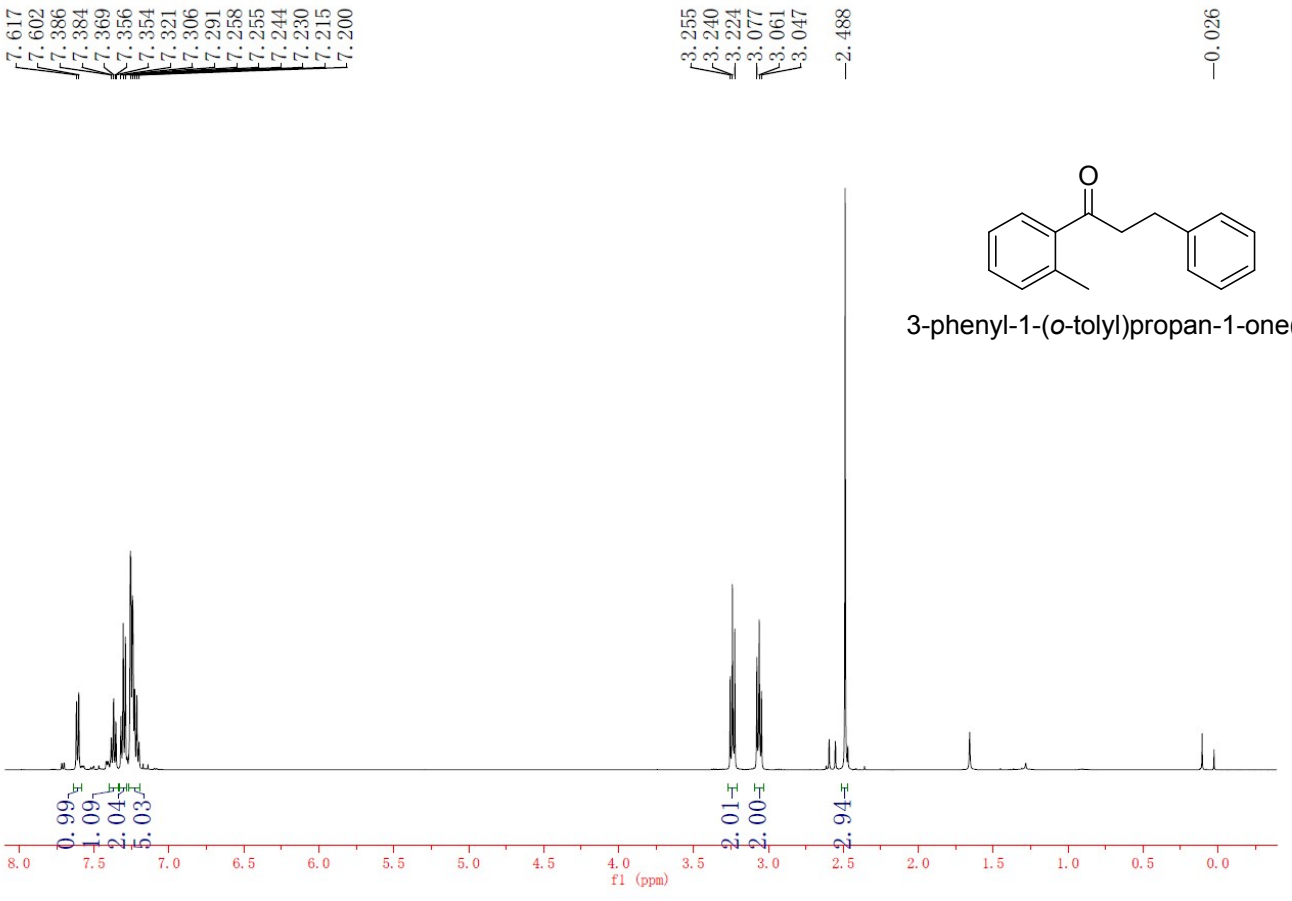
1-(3-chlorophenyl)-3-phenylpropan-1-one(2g)

^{13}C NMR (125 MHz, $CDCl_3$)



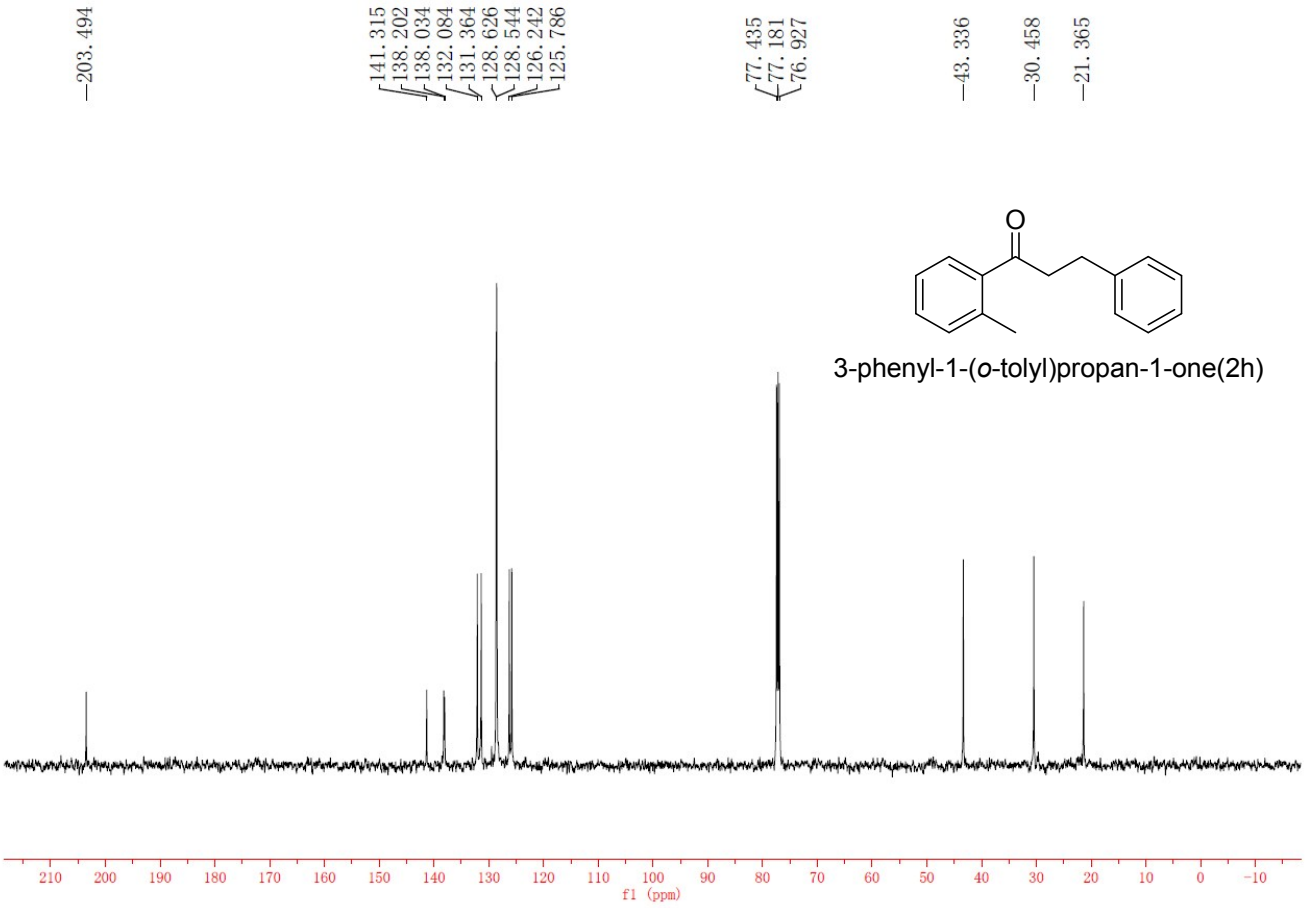
1-(3-chlorophenyl)-3-phenylpropan-1-one(2g)

^{1}H NMR (500 MHz, $CDCl_3$)



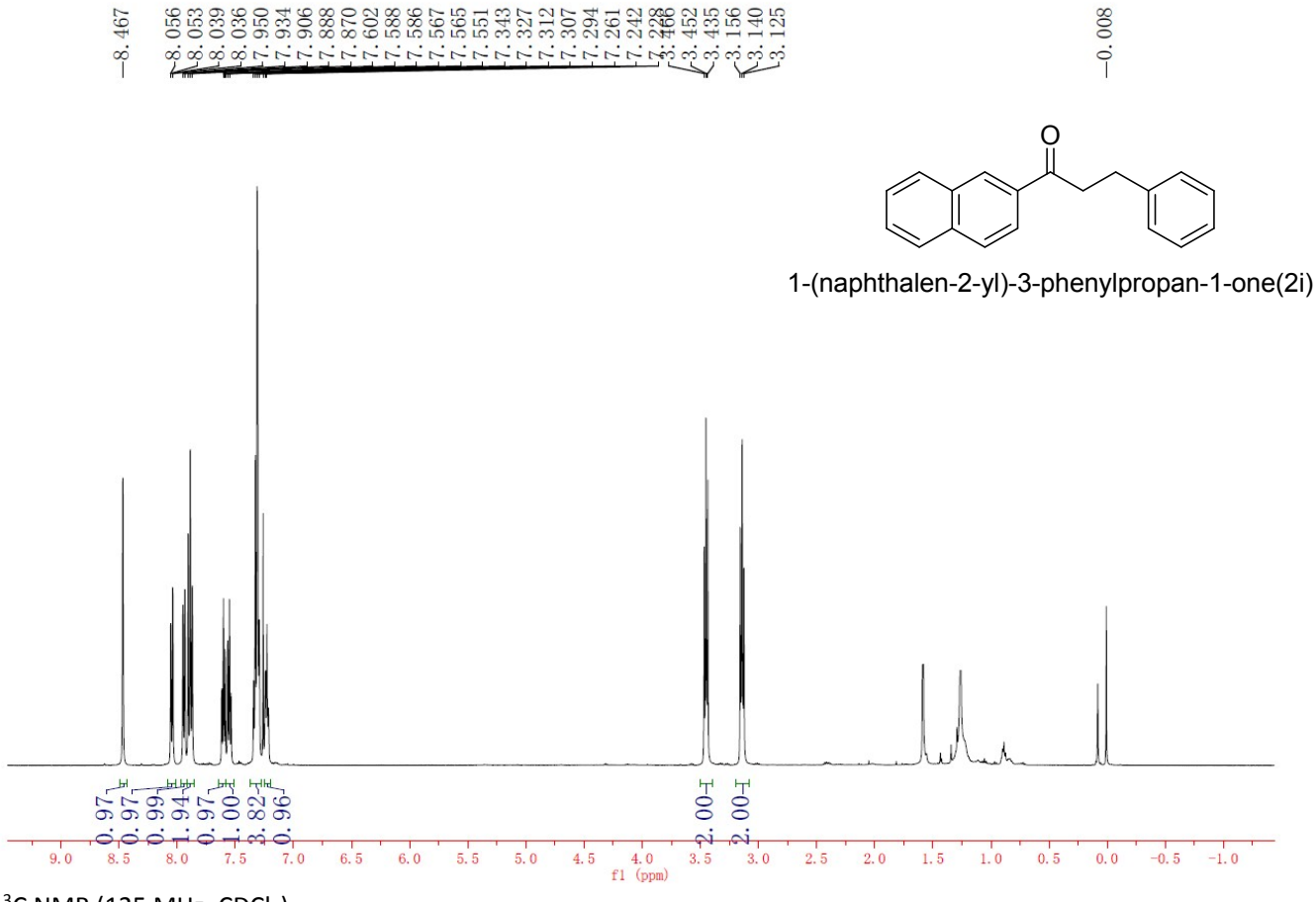
3-phenyl-1-(*o*-tolyl)propan-1-one(2h)

^{13}C NMR (125 MHz, $CDCl_3$)



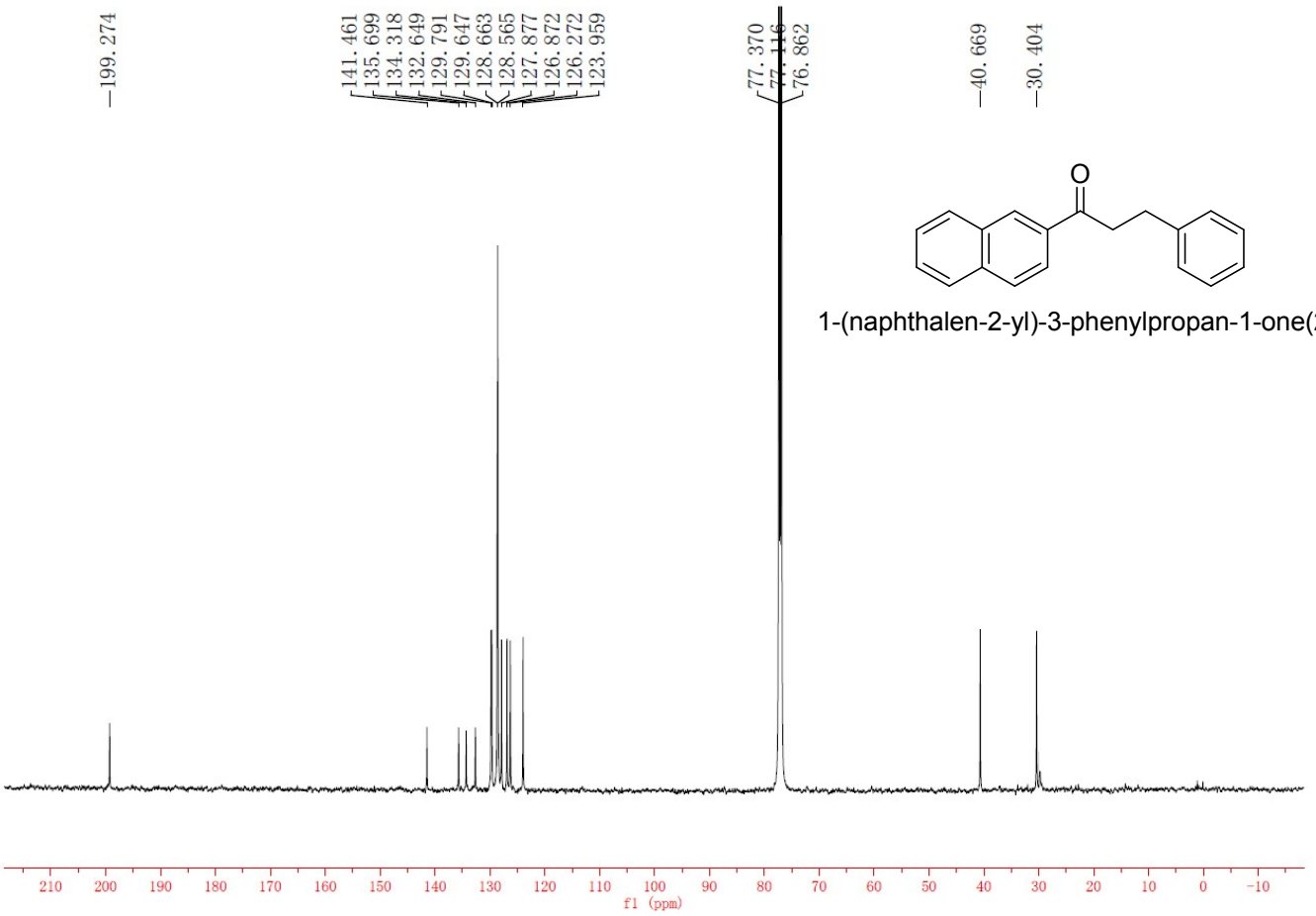
3-phenyl-1-(*o*-tolyl)propan-1-one(2h)

^{1}H NMR (500 MHz, $CDCl_3$)



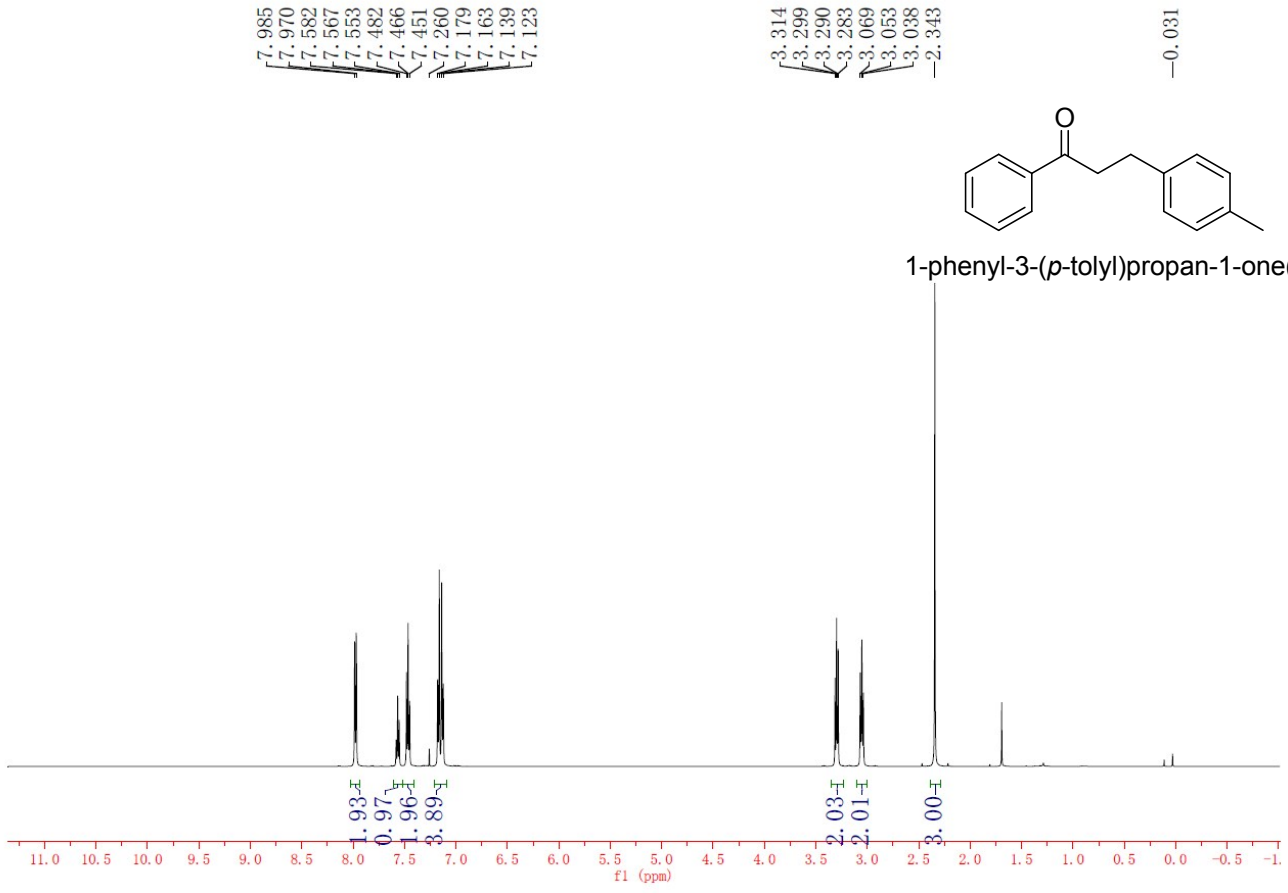
1-(naphthalen-2-yl)-3-phenylpropan-1-one(2i)

^{13}C NMR (125 MHz, $CDCl_3$)



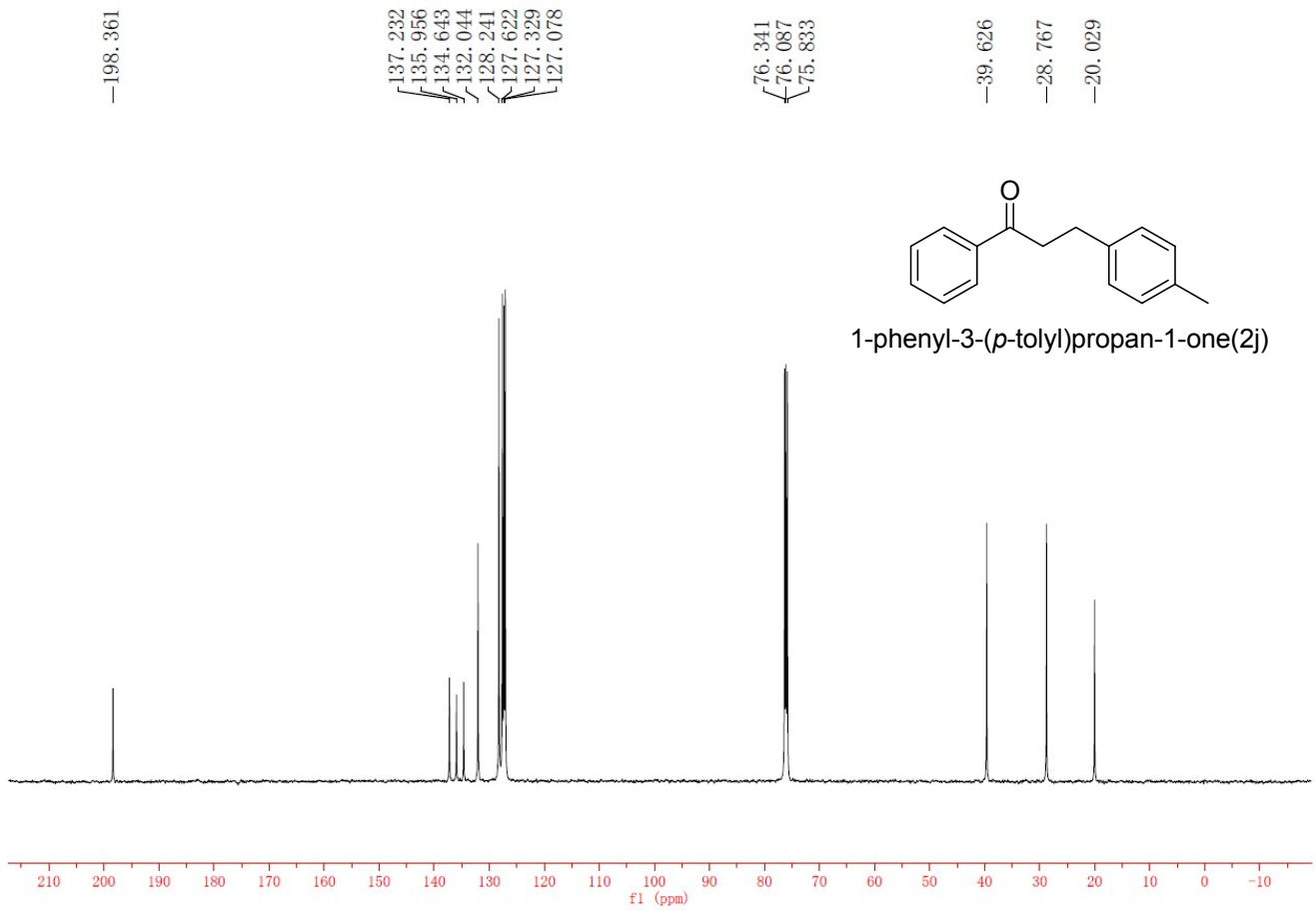
1-(naphthalen-2-yl)-3-phenylpropan-1-one(2i)

^{1}H NMR (500 MHz, $CDCl_3$)



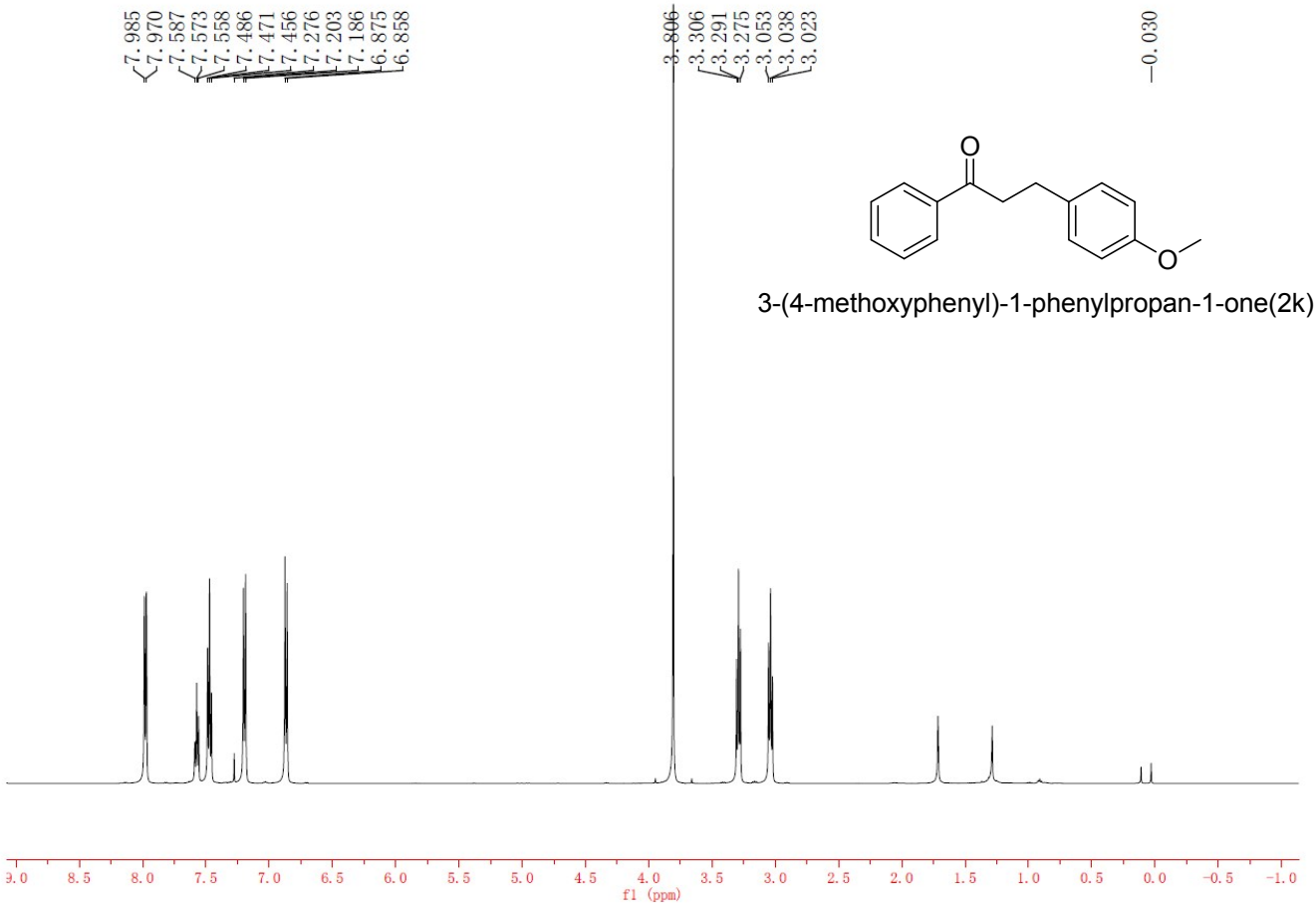
1-phenyl-3-(*p*-tolyl)propan-1-one(2j)

^{13}C NMR (125 MHz, $CDCl_3$)



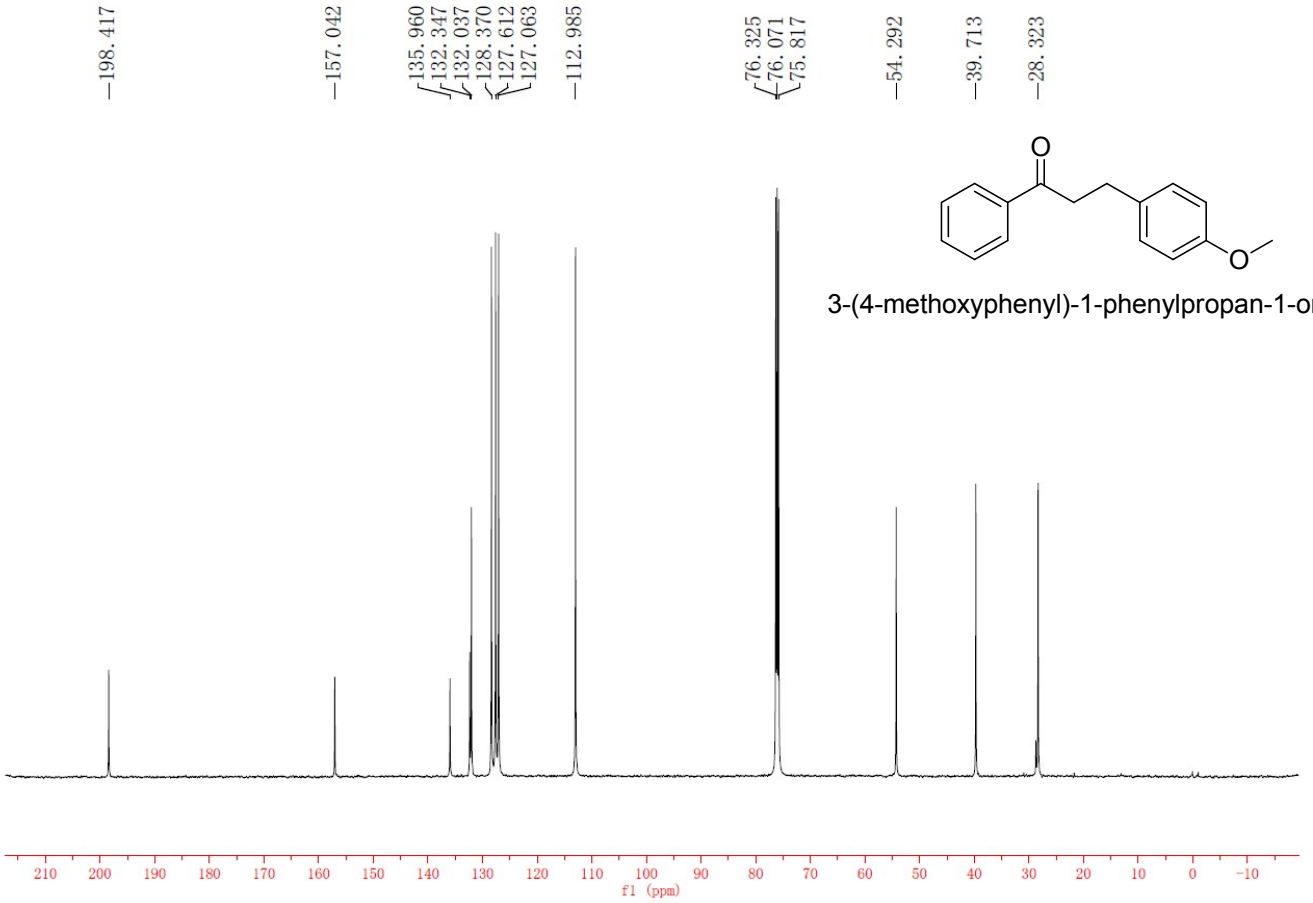
1-phenyl-3-(*p*-tolyl)propan-1-one(2j)

^{1}H NMR (500 MHz, $CDCl_3$)

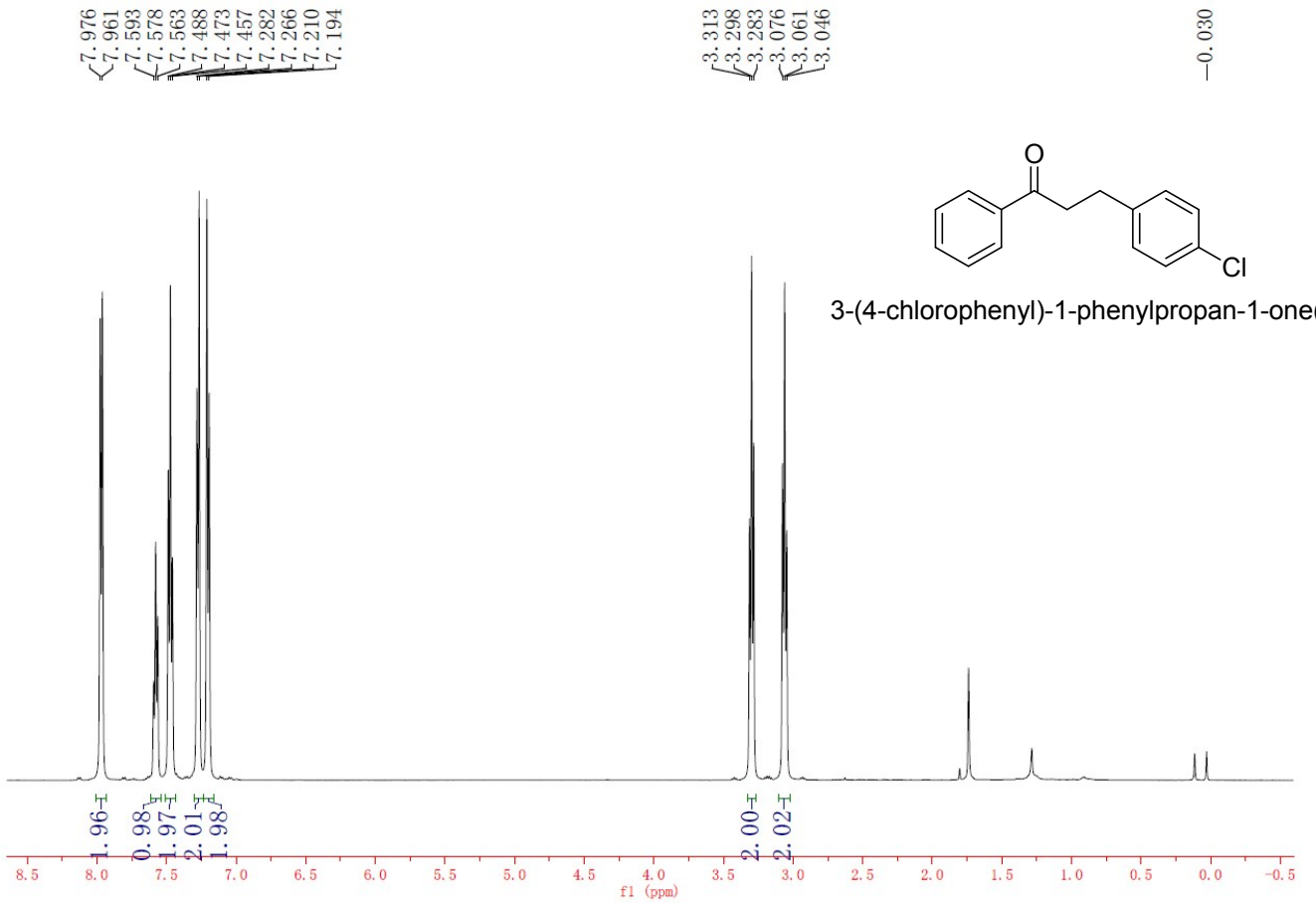


3-(4-methoxyphenyl)-1-phenylpropan-1-one(2k)

^{13}C NMR (125 MHz, $CDCl_3$)

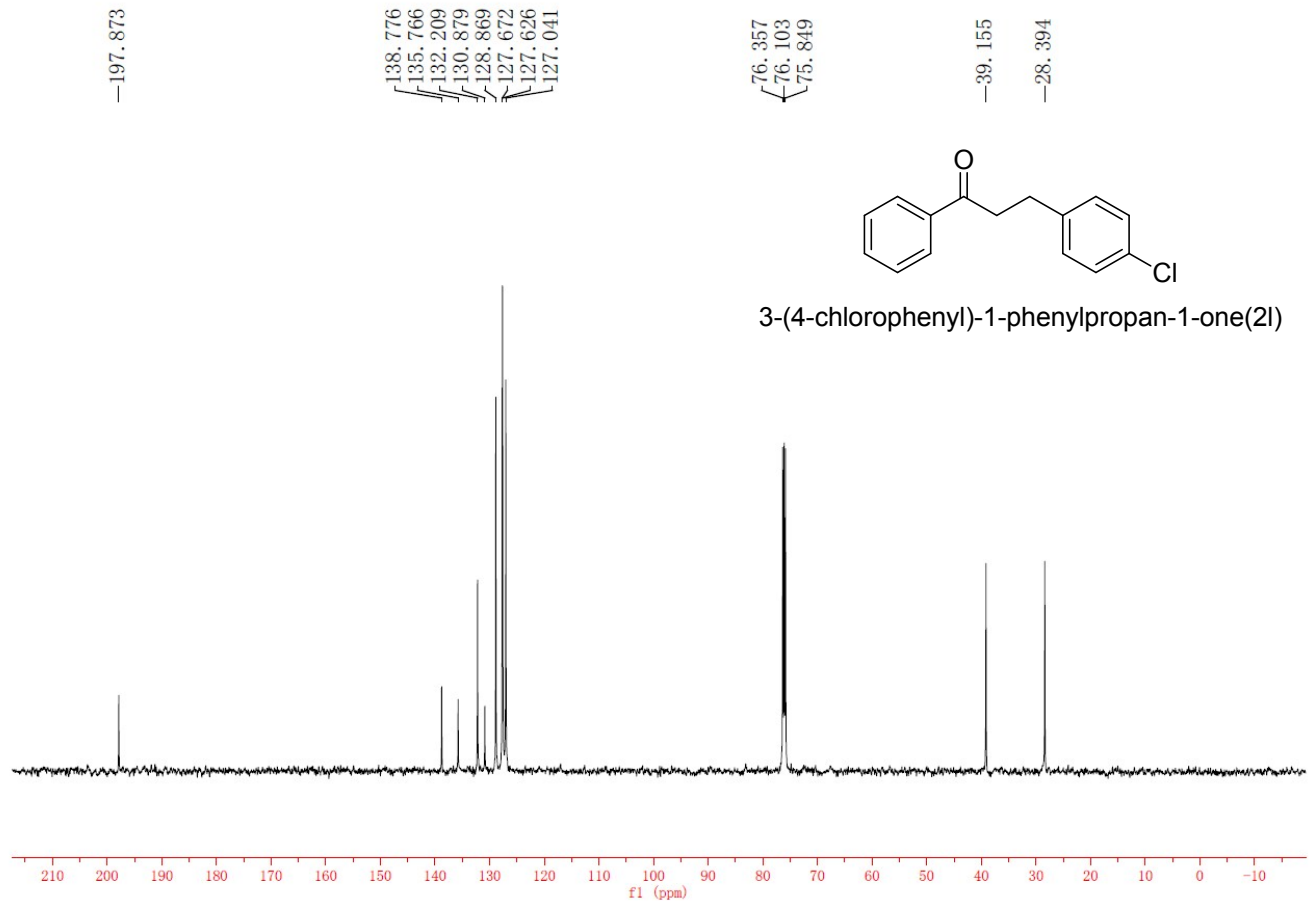


^{1}H NMR (500 MHz, $CDCl_3$)



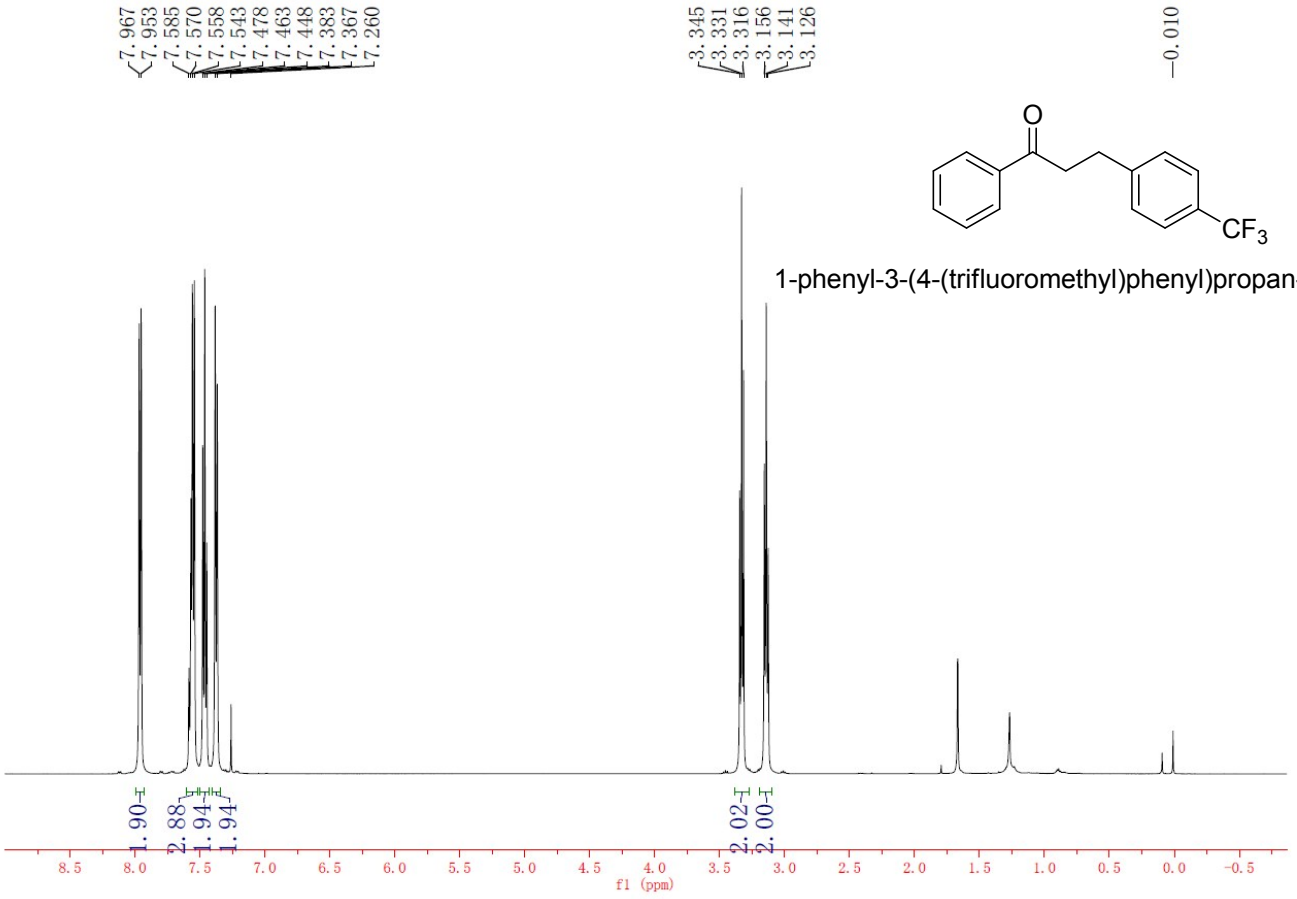
3-(4-chlorophenyl)-1-phenylpropan-1-one(2l)

^{13}C NMR (125 MHz, $CDCl_3$)



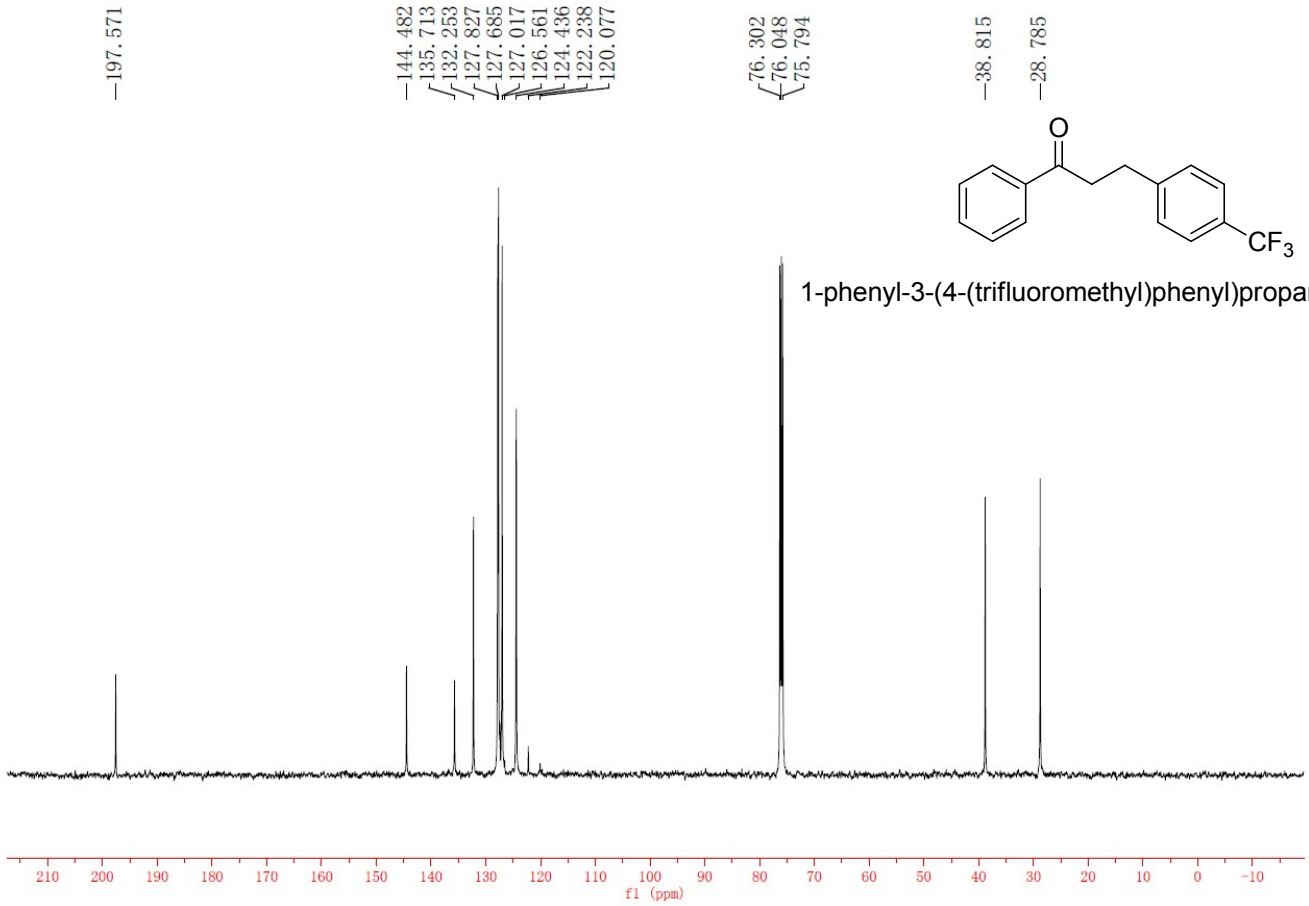
3-(4-chlorophenyl)-1-phenylpropan-1-one(2l)

^{1}H NMR (500 MHz, $CDCl_3$)



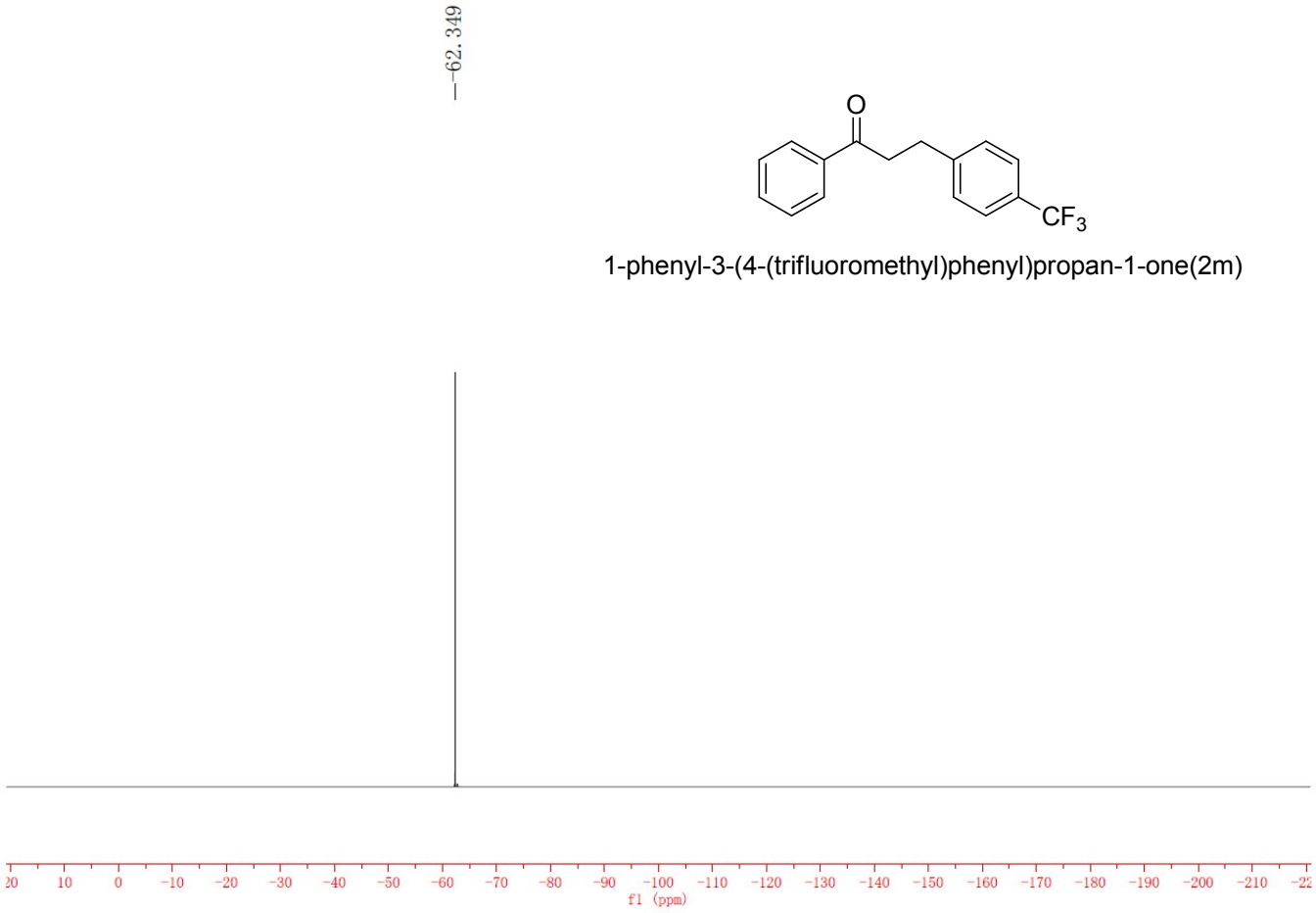
1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one(2m)

^{13}C NMR (125 MHz, $CDCl_3$)



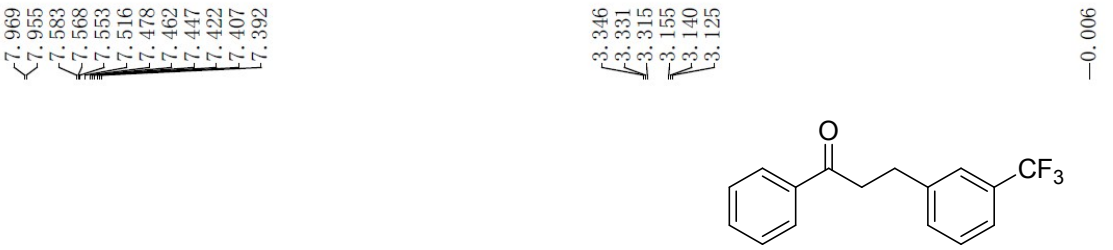
1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one(2m)

^{19}F NMR (470 MHz, $CDCl_3$)

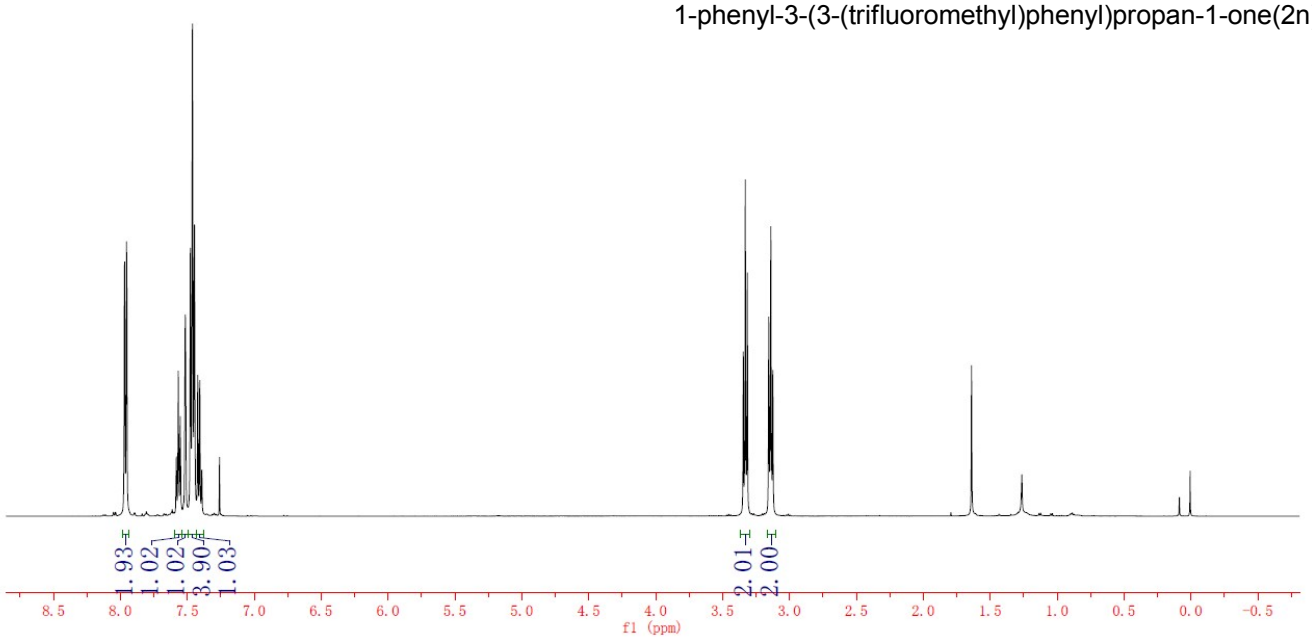


1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one(2m)

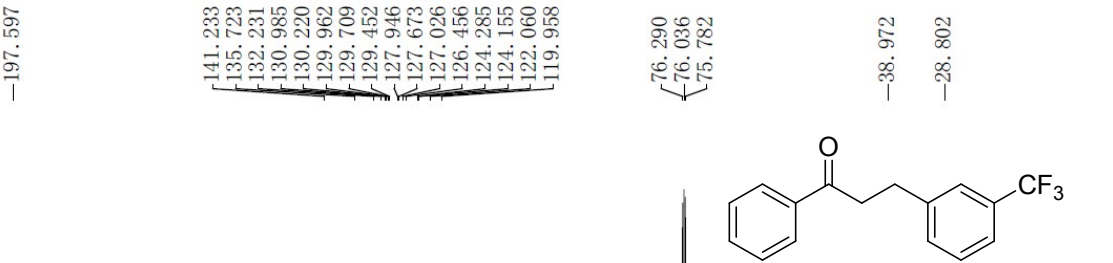
^{1}H NMR (500 MHz, $CDCl_3$)



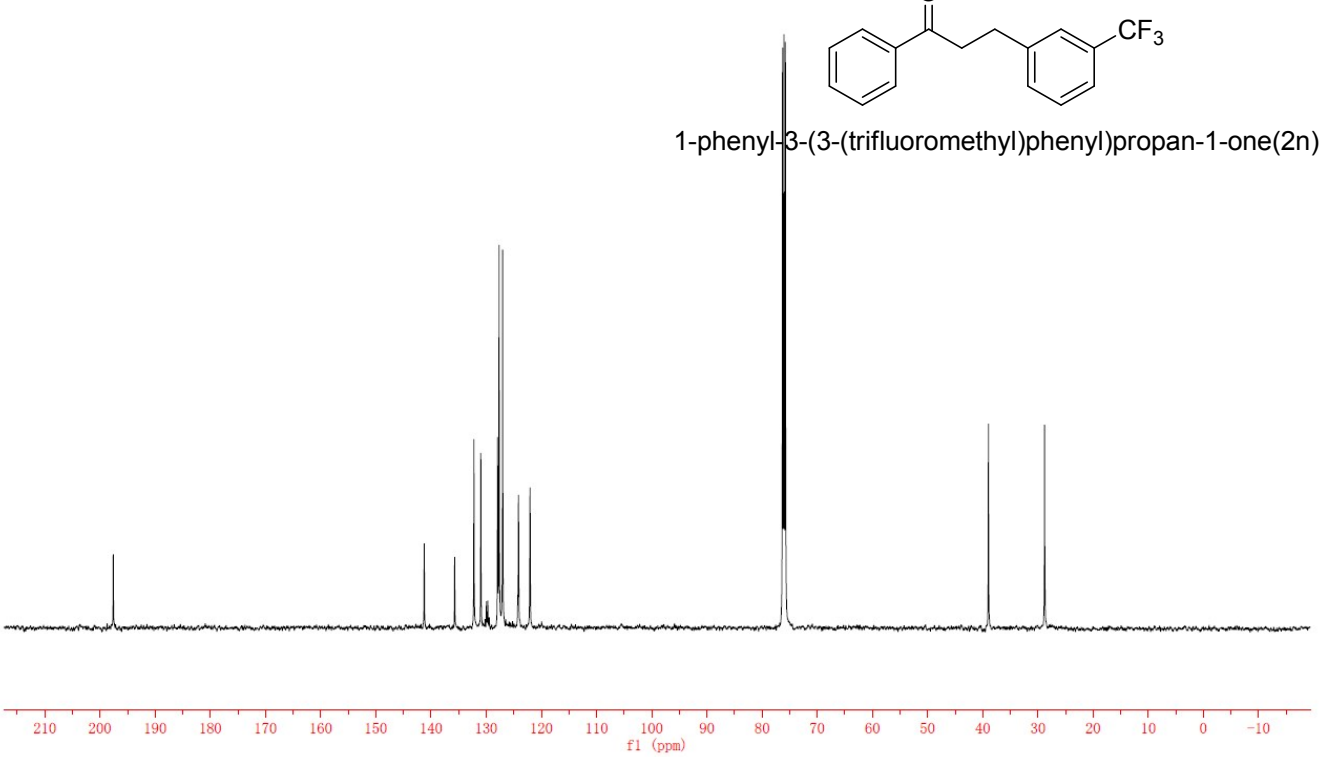
1-phenyl-3-(3-(trifluoromethyl)phenyl)propan-1-one(2n)



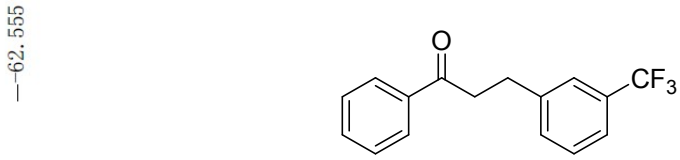
^{13}C NMR (125 MHz, $CDCl_3$)



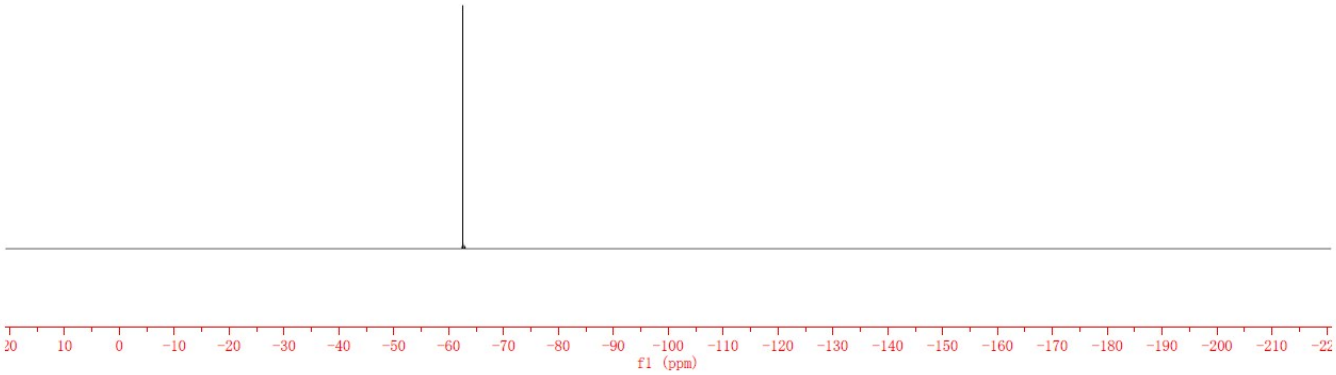
1-phenyl-3-(3-(trifluoromethyl)phenyl)propan-1-one(2n)



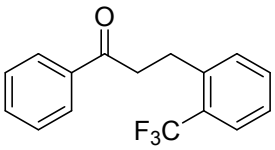
^{19}F NMR (470 MHz, $CDCl_3$)



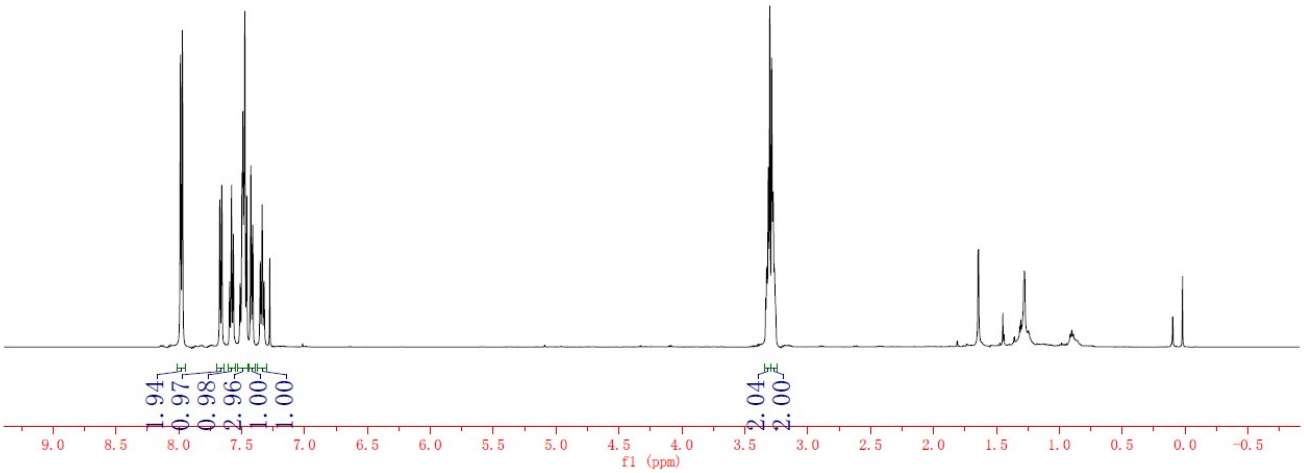
1-phenyl-3-(3-(trifluoromethyl)phenyl)propan-1-one(2n)



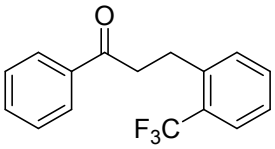
^{1}H NMR (500 MHz, $CDCl_3$)



1-phenyl-3-(2-(trifluoromethyl)phenyl)propan-1-one(2o)

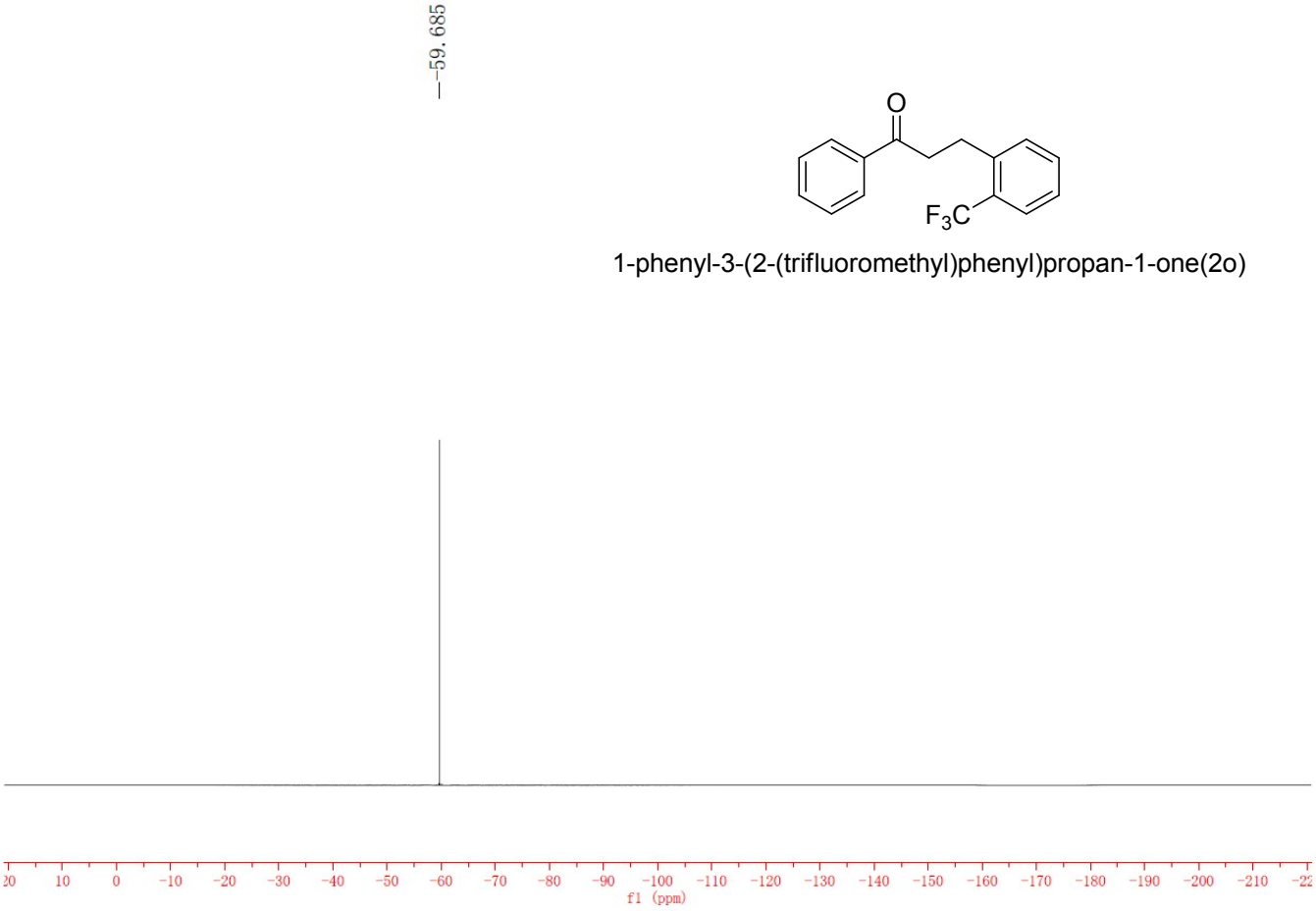


^{13}C NMR (125 MHz, $CDCl_3$)



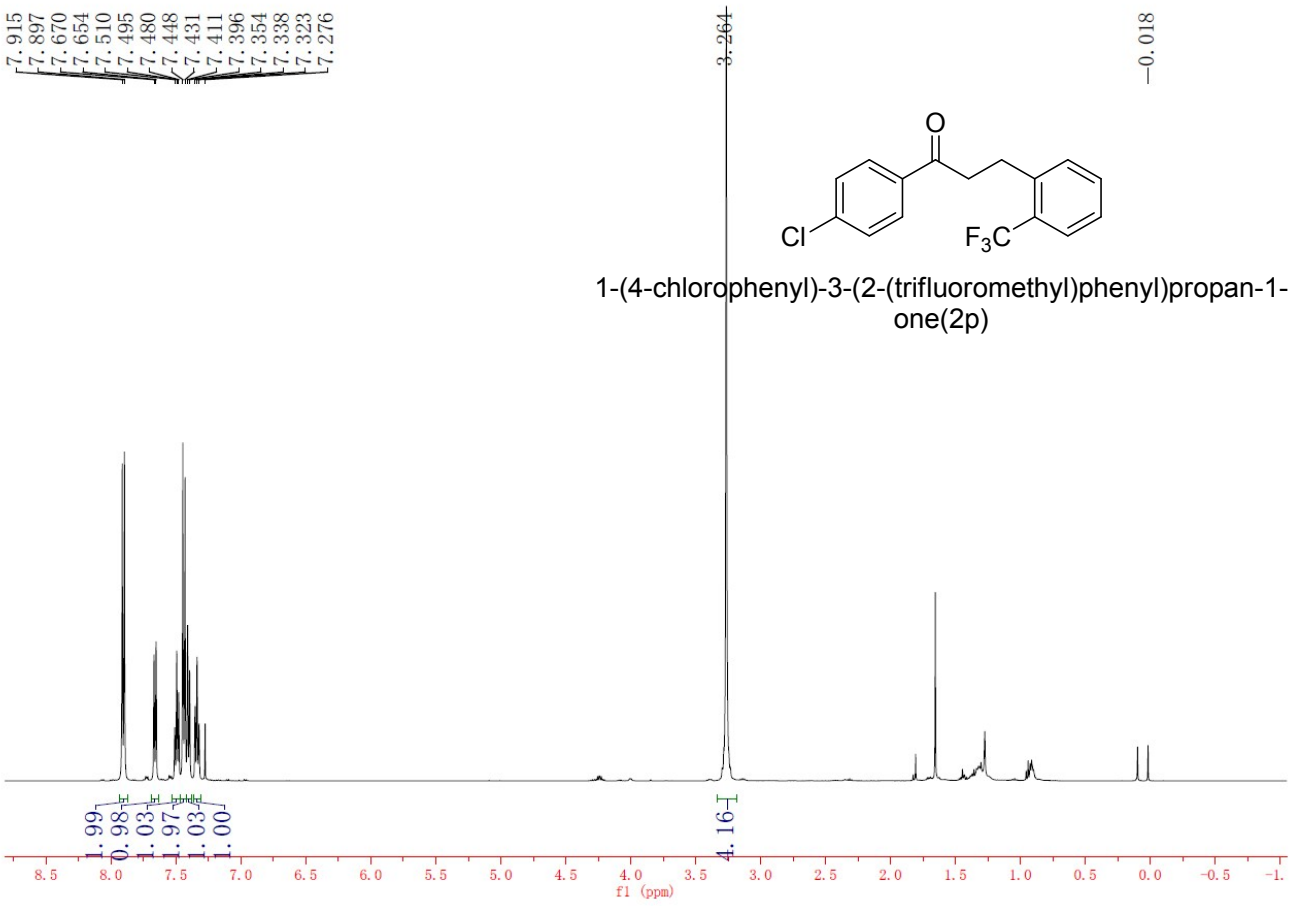
1-phenyl-3-(2-(trifluoromethyl)phenyl)propan-1-one(2o)

^{19}F NMR (470 MHz, $CDCl_3$)



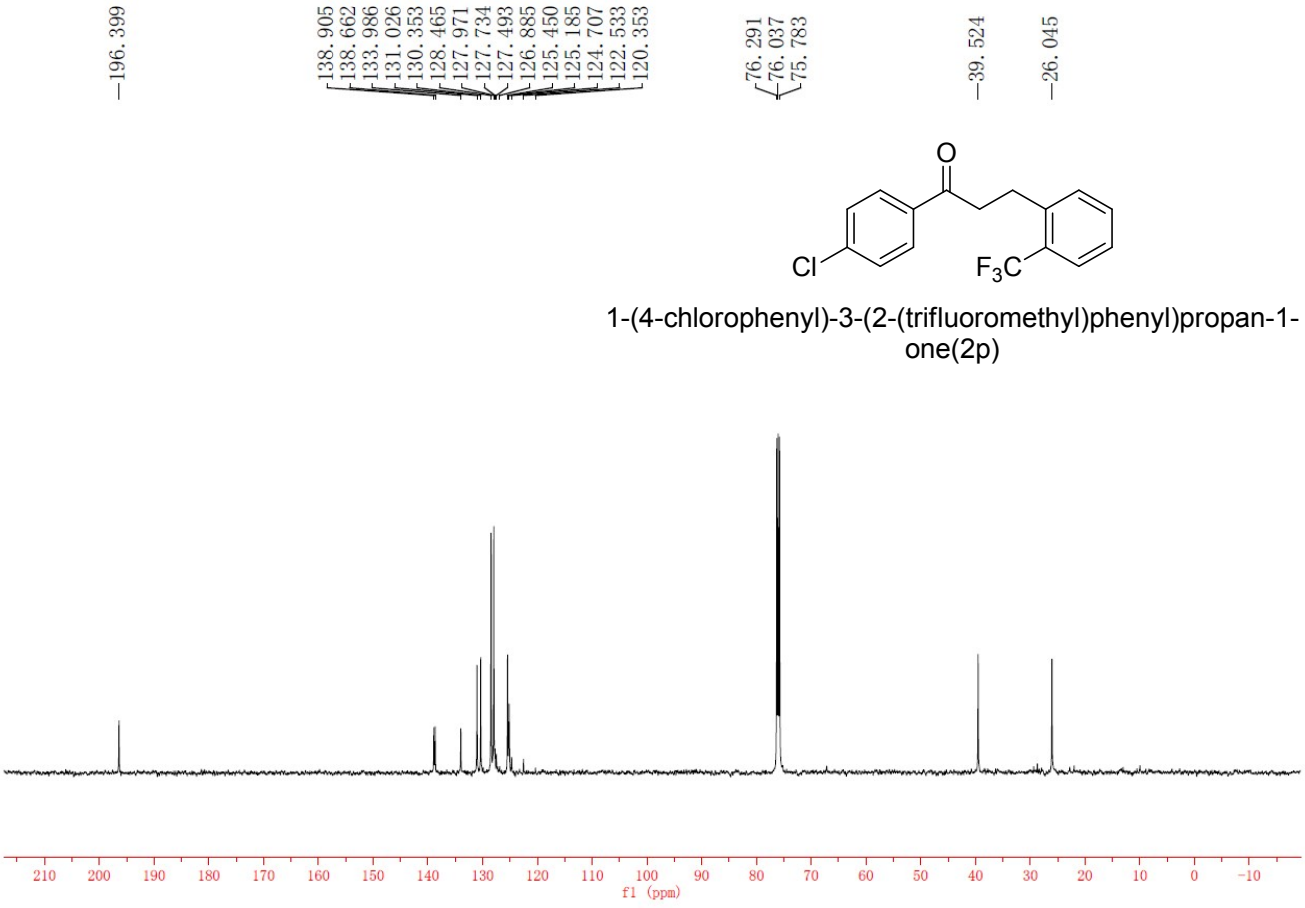
1-phenyl-3-(2-(trifluoromethyl)phenyl)propan-1-one(2o)

^{1}H NMR (500 MHz, $CDCl_3$)



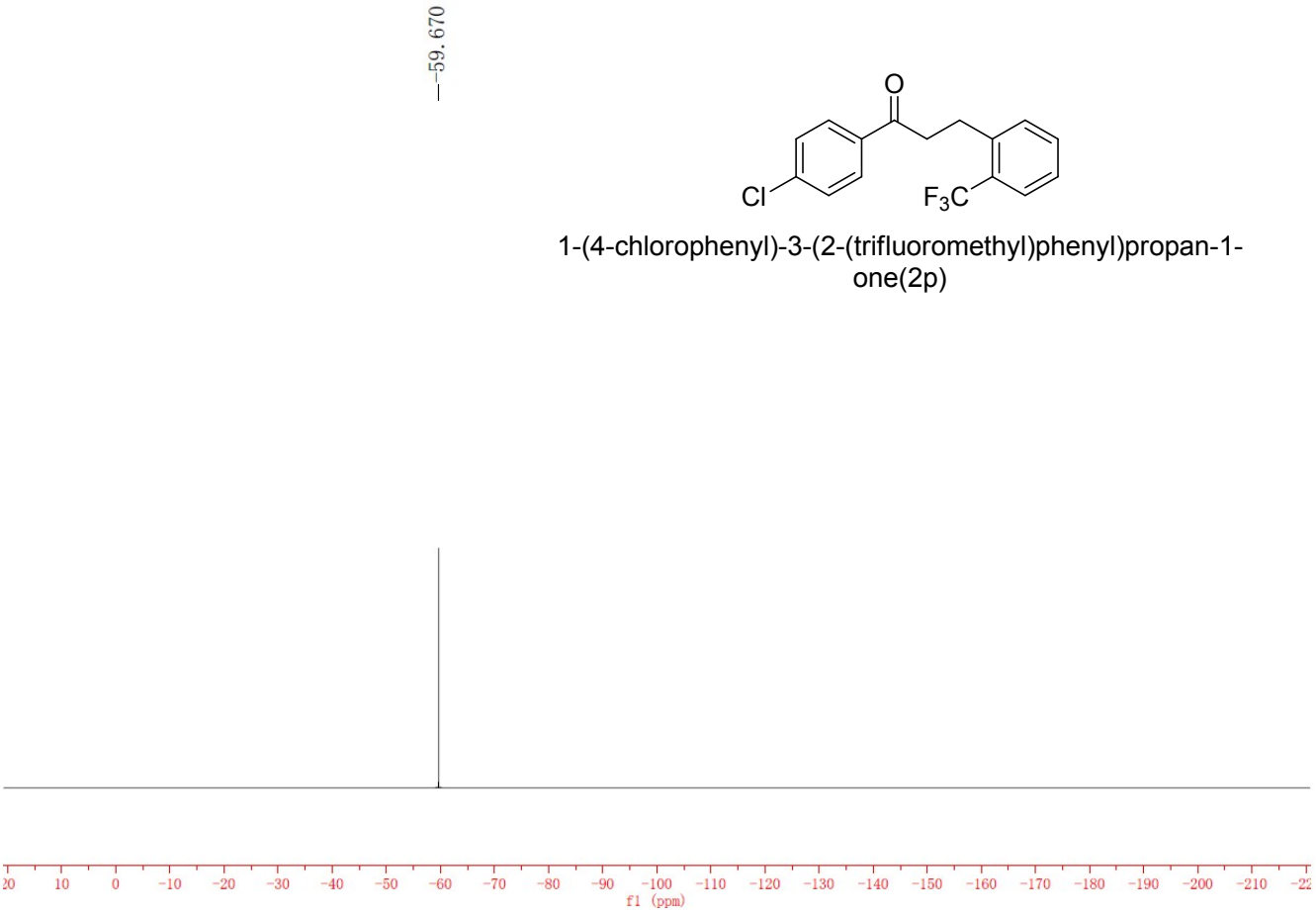
1-(4-chlorophenyl)-3-(2-(trifluoromethyl)phenyl)propan-1-one(2p)

^{13}C NMR (125 MHz, $CDCl_3$)



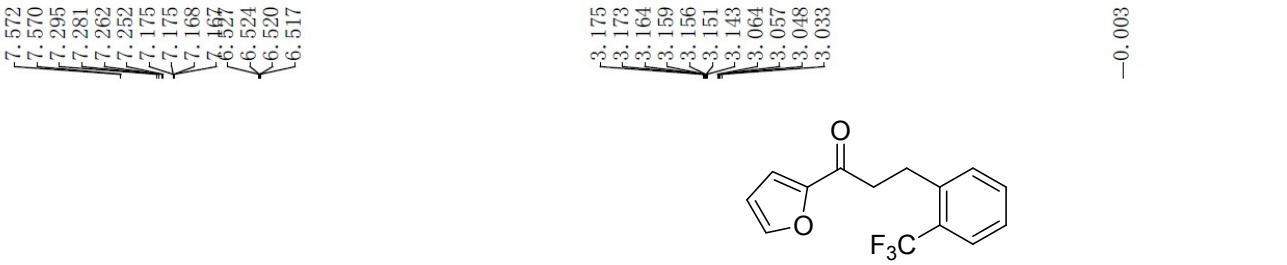
1-(4-chlorophenyl)-3-(2-(trifluoromethyl)phenyl)propan-1-one(2p)

^{19}F NMR (470 MHz, $CDCl_3$)

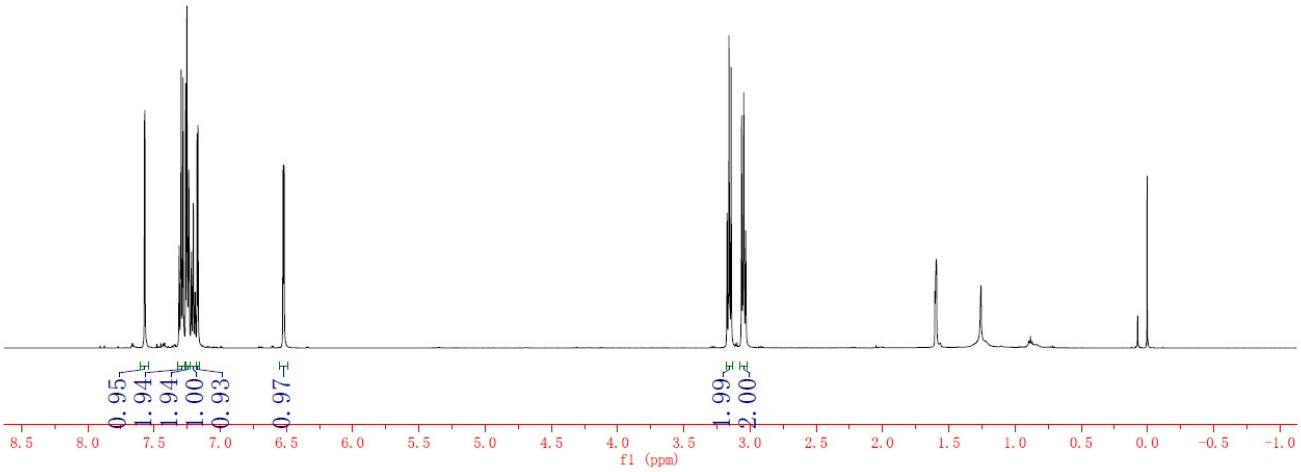


1-(4-chlorophenyl)-3-(2-(trifluoromethyl)phenyl)propan-1-one(2p)

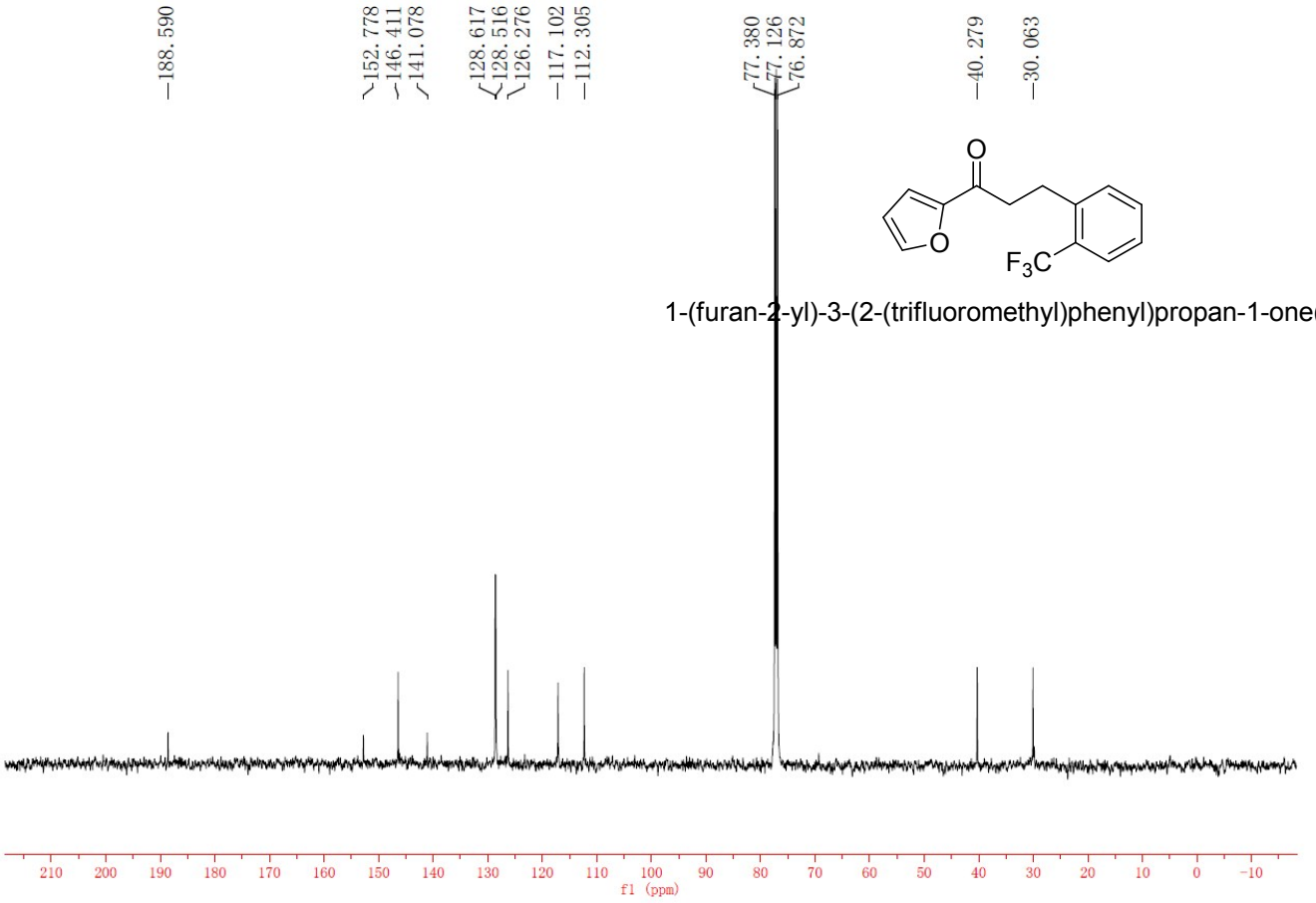
^{1}H NMR (500 MHz, $CDCl_3$)



1-(furan-2-yl)-3-(2-(trifluoromethyl)phenyl)propan-1-one(2q)

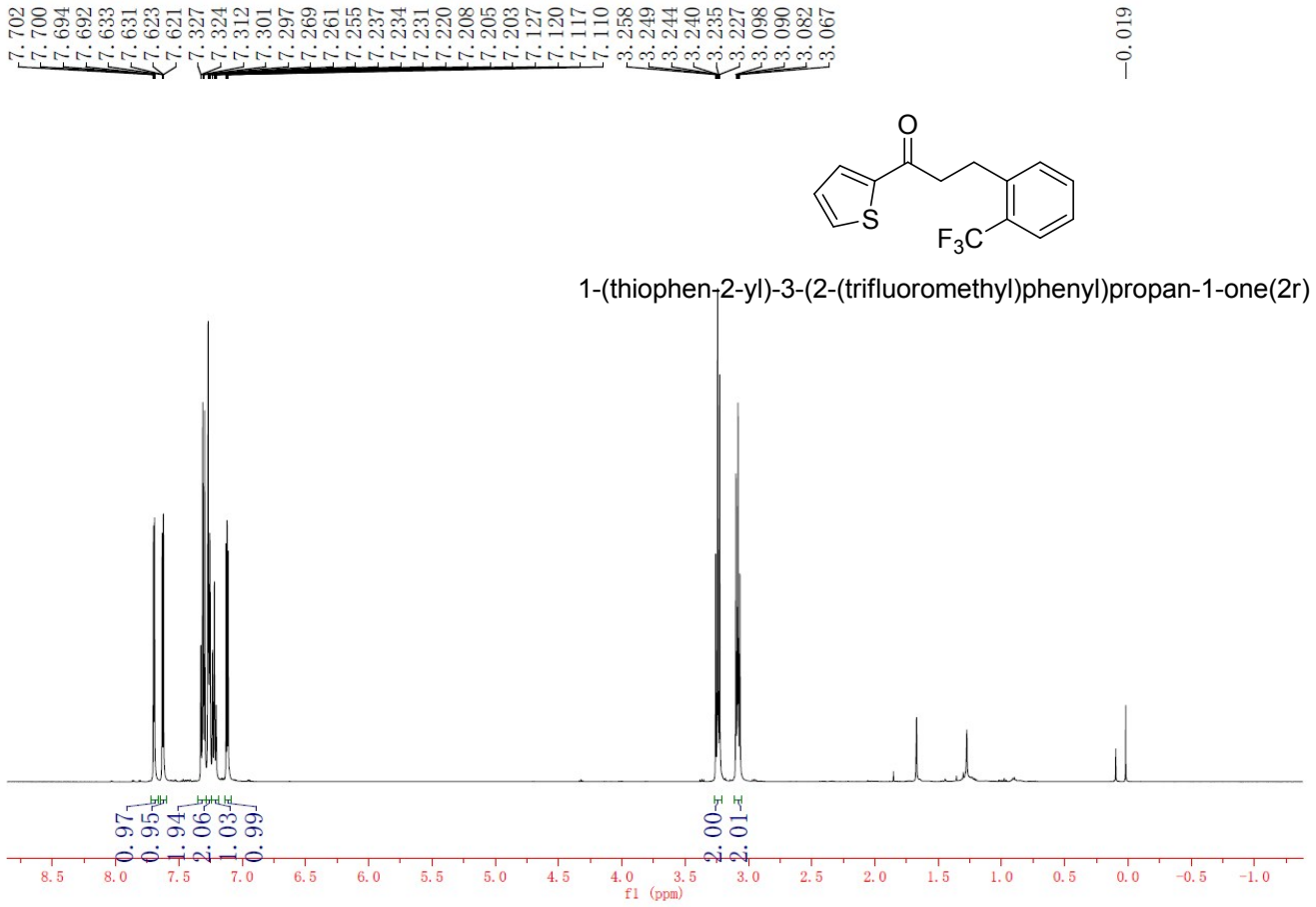


^{13}C NMR (125 MHz, $CDCl_3$)



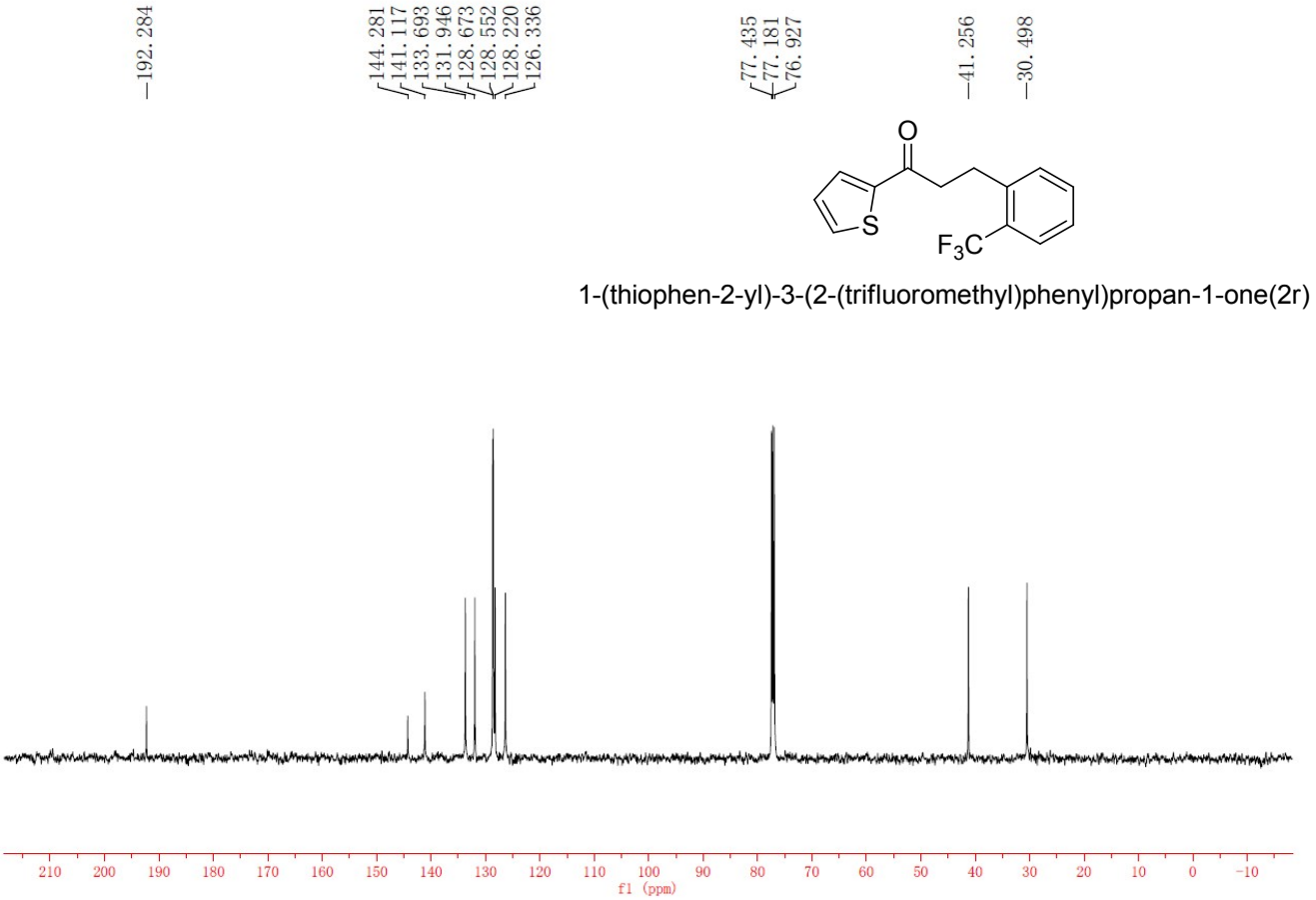
1-(furan-2-yl)-3-(2-(trifluoromethyl)phenyl)propan-1-one(2q)

^{1}H NMR (500 MHz, $CDCl_3$)



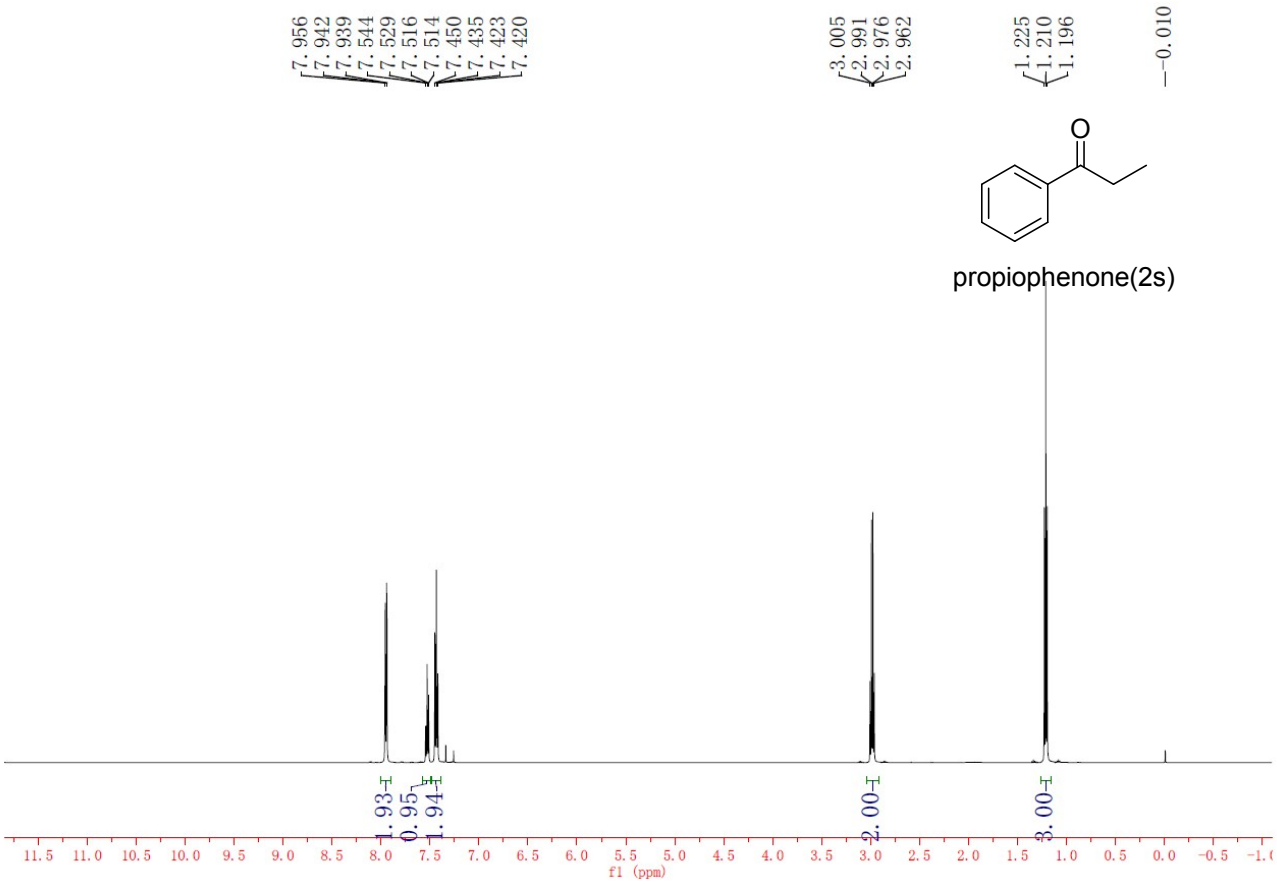
1-(thiophen-2-yl)-3-(2-(trifluoromethyl)phenyl)propan-1-one(2r)

^{13}C NMR (125 MHz, $CDCl_3$)

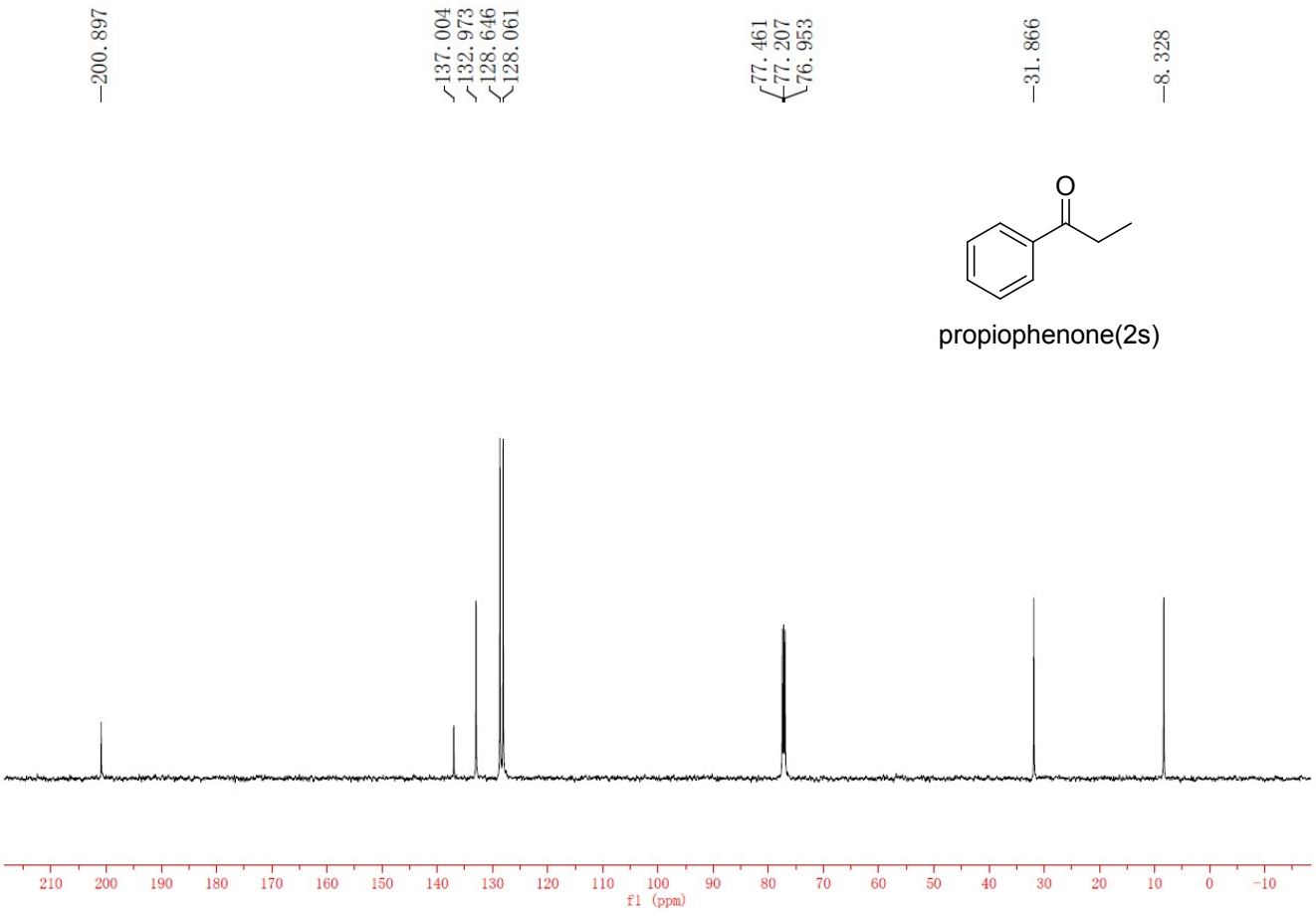


1-(thiophen-2-yl)-3-(2-(trifluoromethyl)phenyl)propan-1-one(2r)

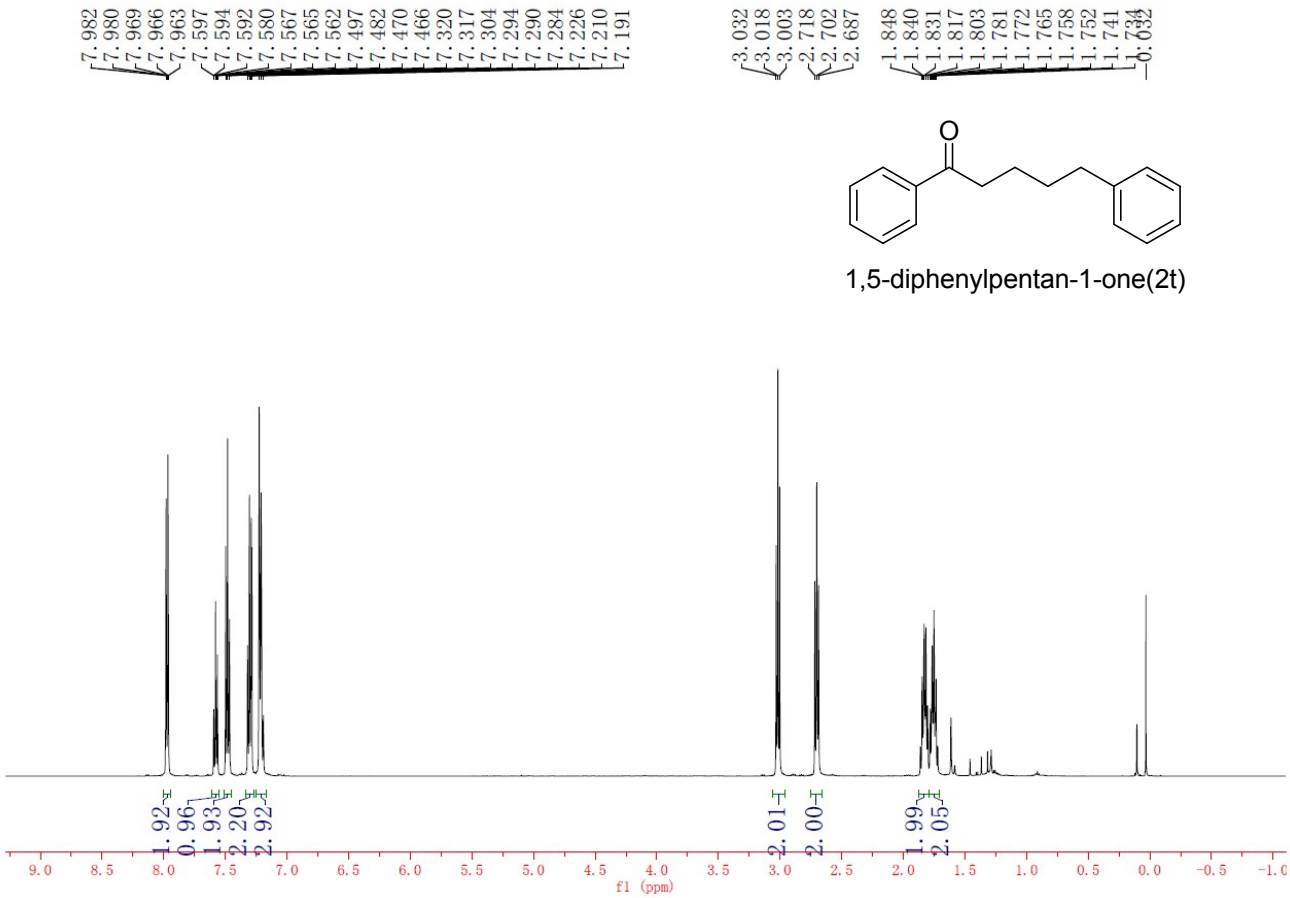
^{1}H NMR (500 MHz, $CDCl_3$)



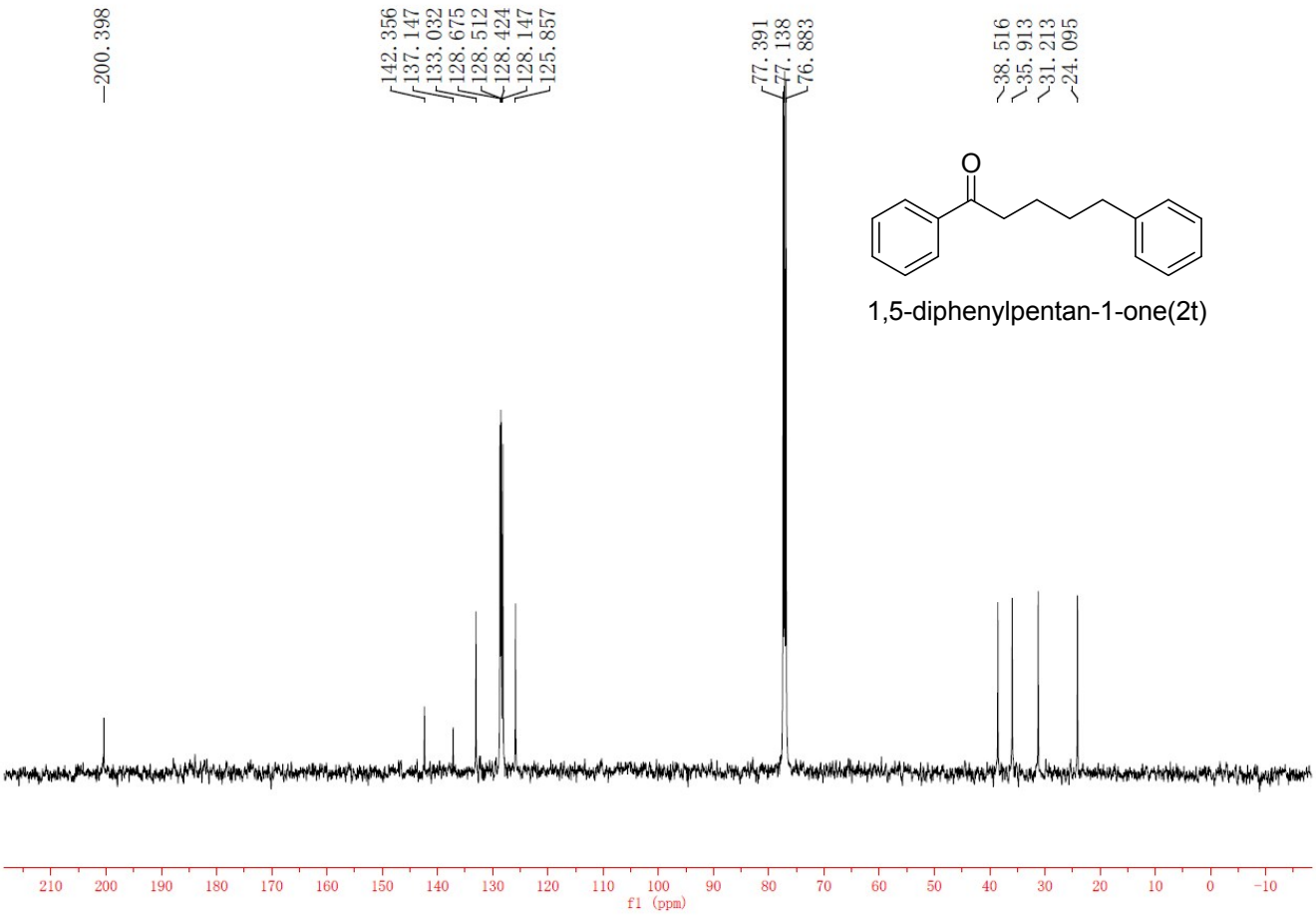
^{13}C NMR (125 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

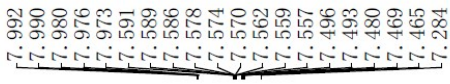


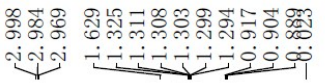
^{13}C NMR (125 MHz, $CDCl_3$)

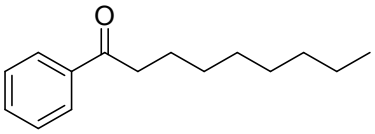


1,5-diphenylpentan-1-one(2t)

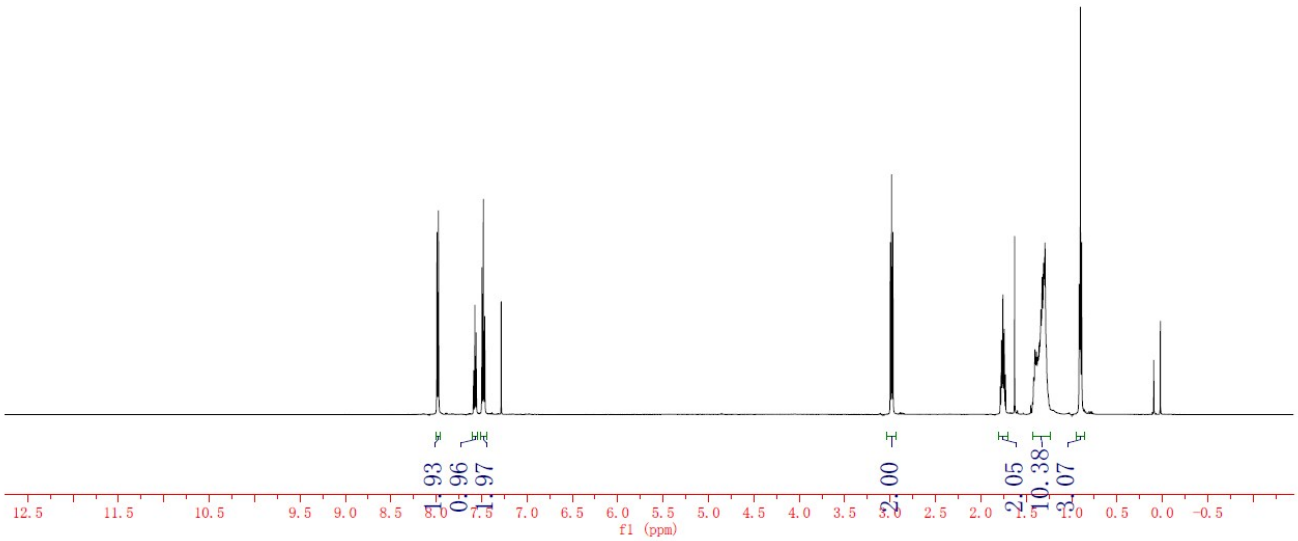
^{1}H NMR (500 MHz, $CDCl_3$)



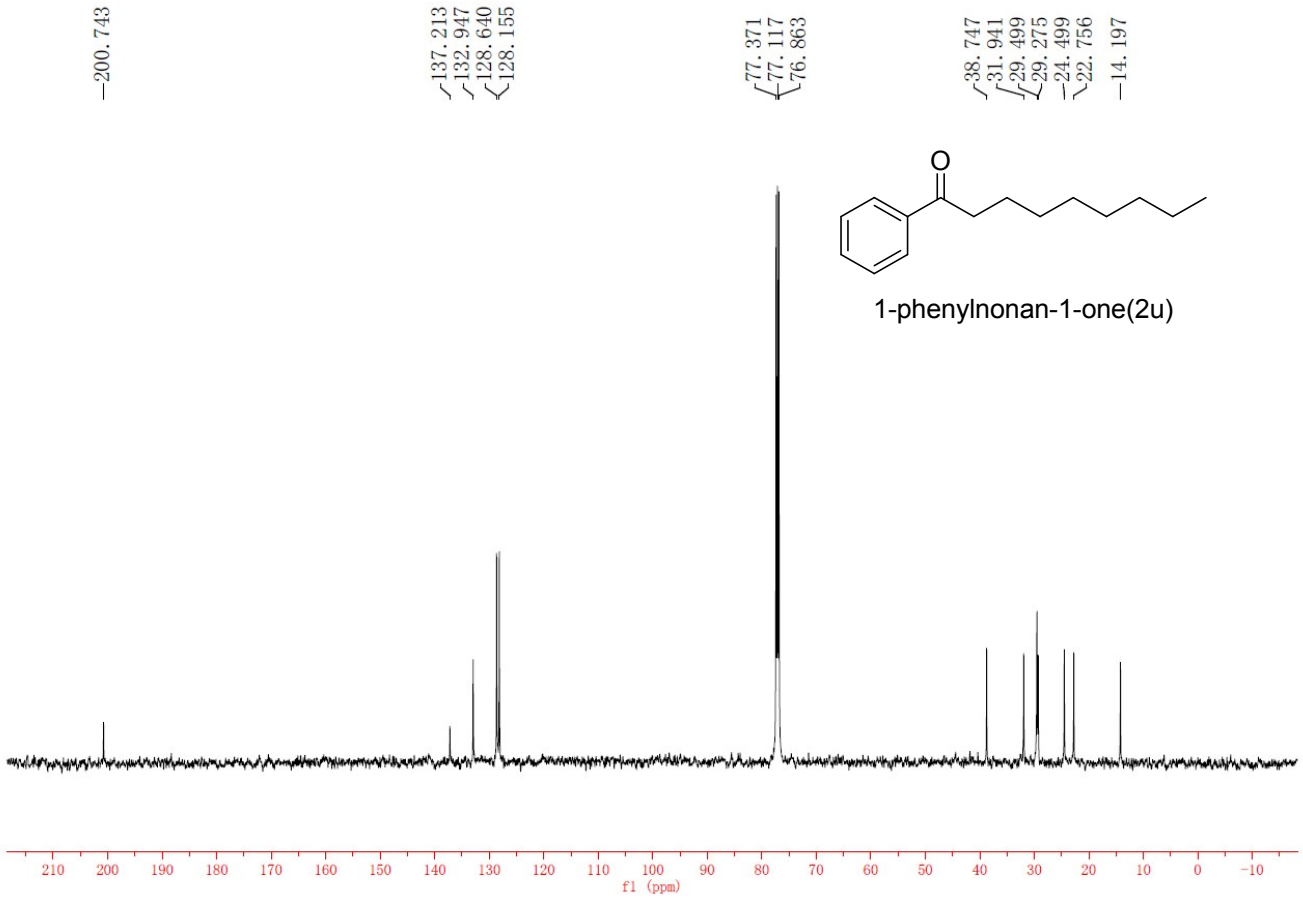




1-phenylnonan-1-one(2u)

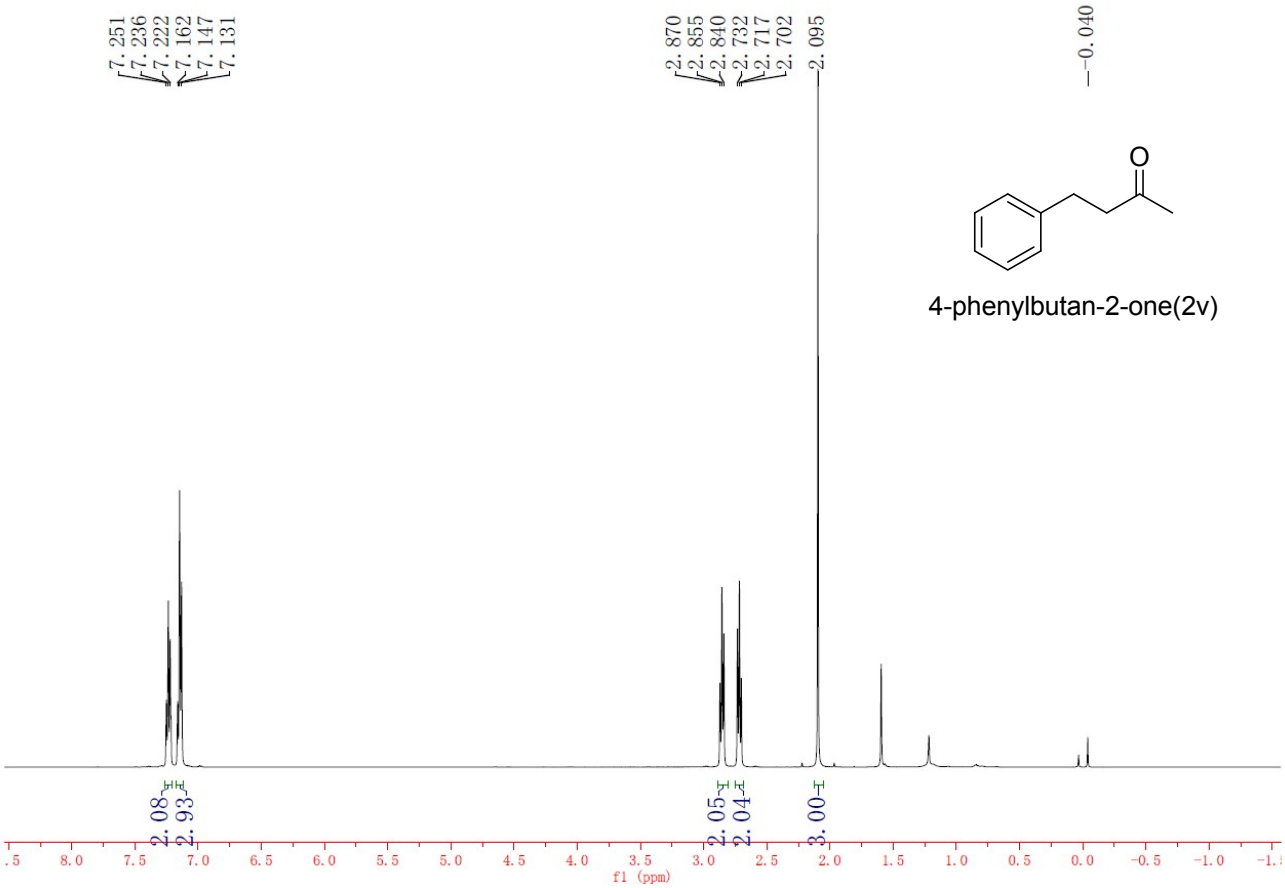


^{13}C NMR (125 MHz, $CDCl_3$)



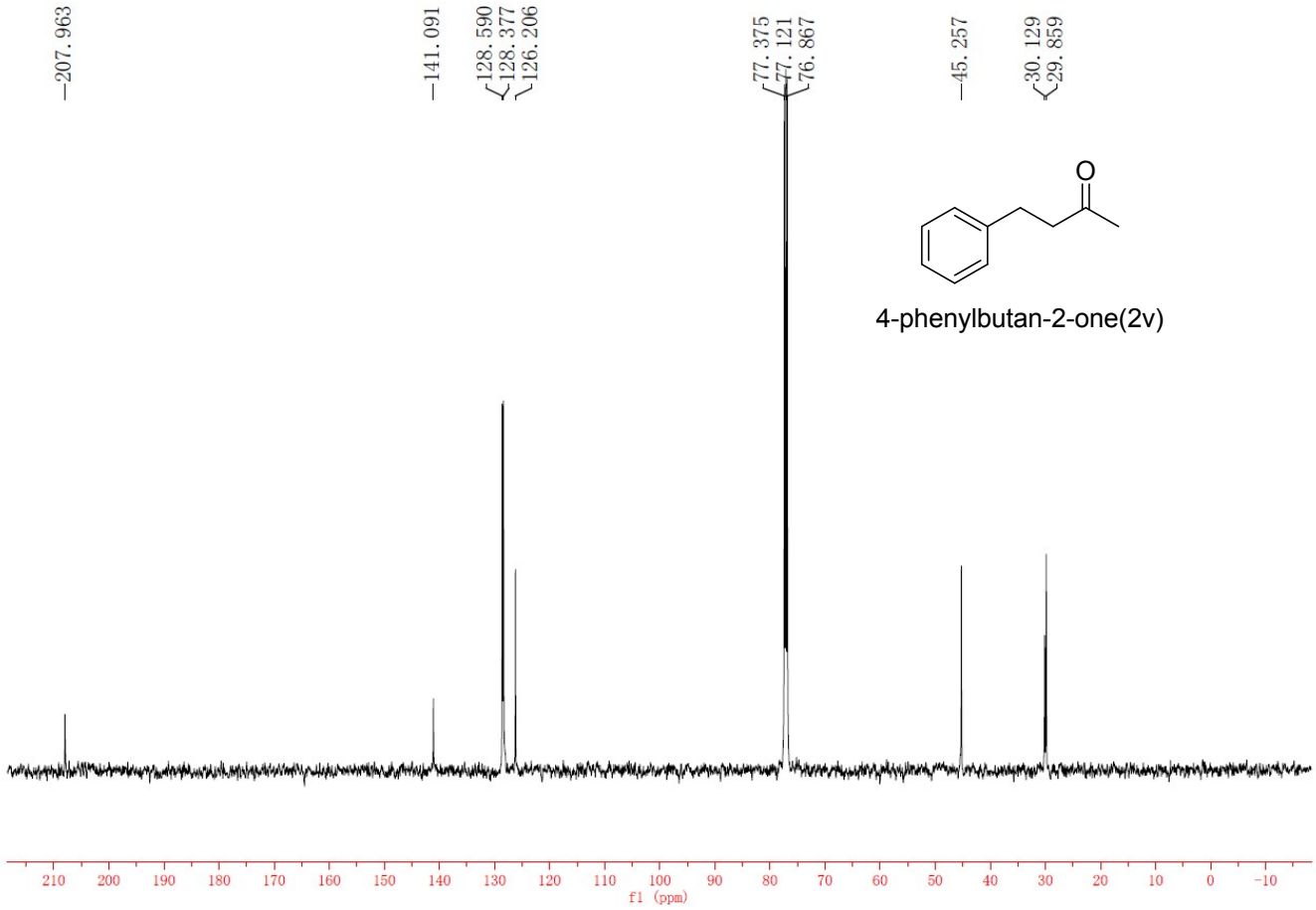
1-phenylnonan-1-one(2u)

^{1}H NMR (500 MHz, $CDCl_3$)

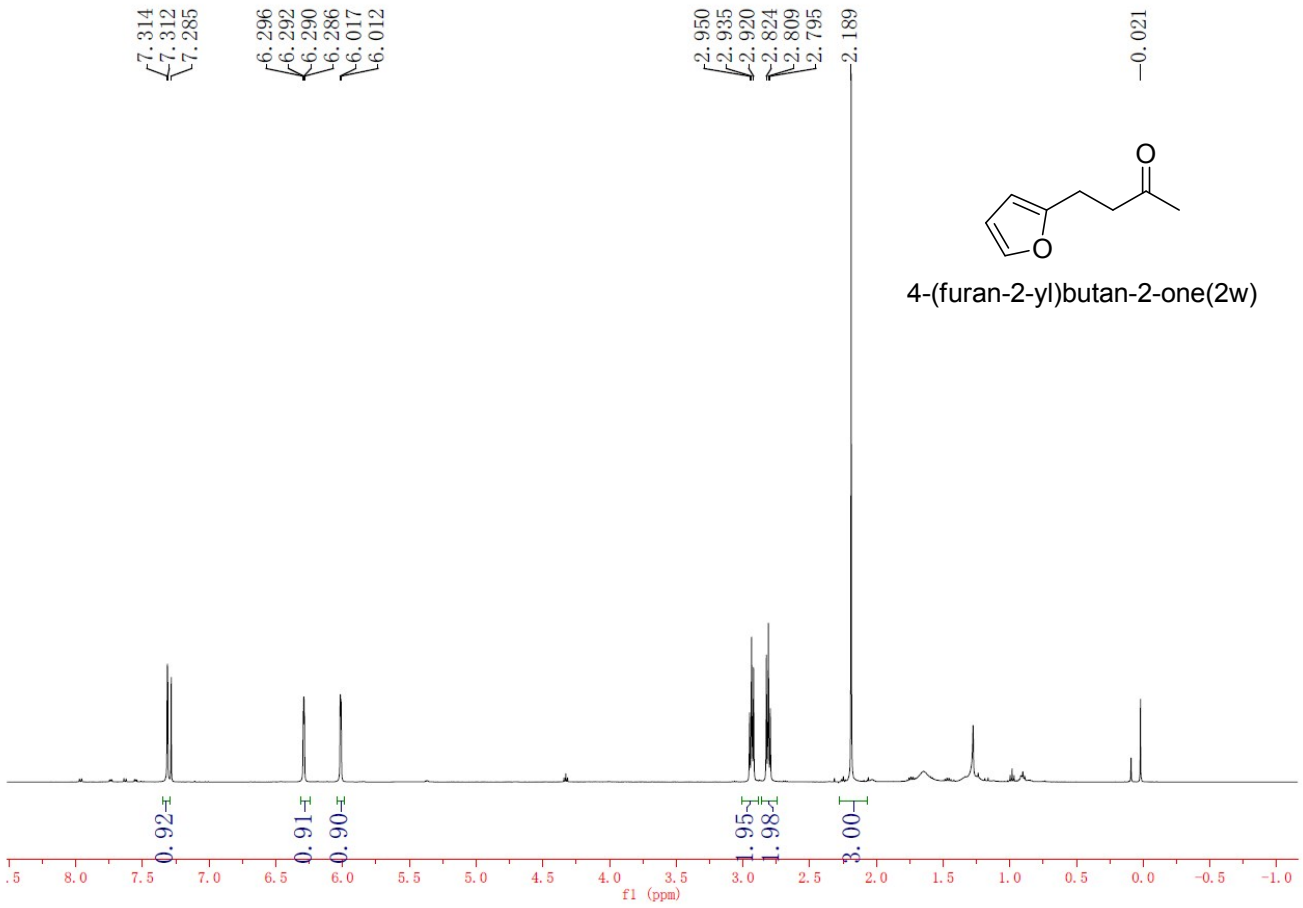


4-phenylbutan-2-one(2v)

^{13}C NMR (125 MHz, $CDCl_3$)

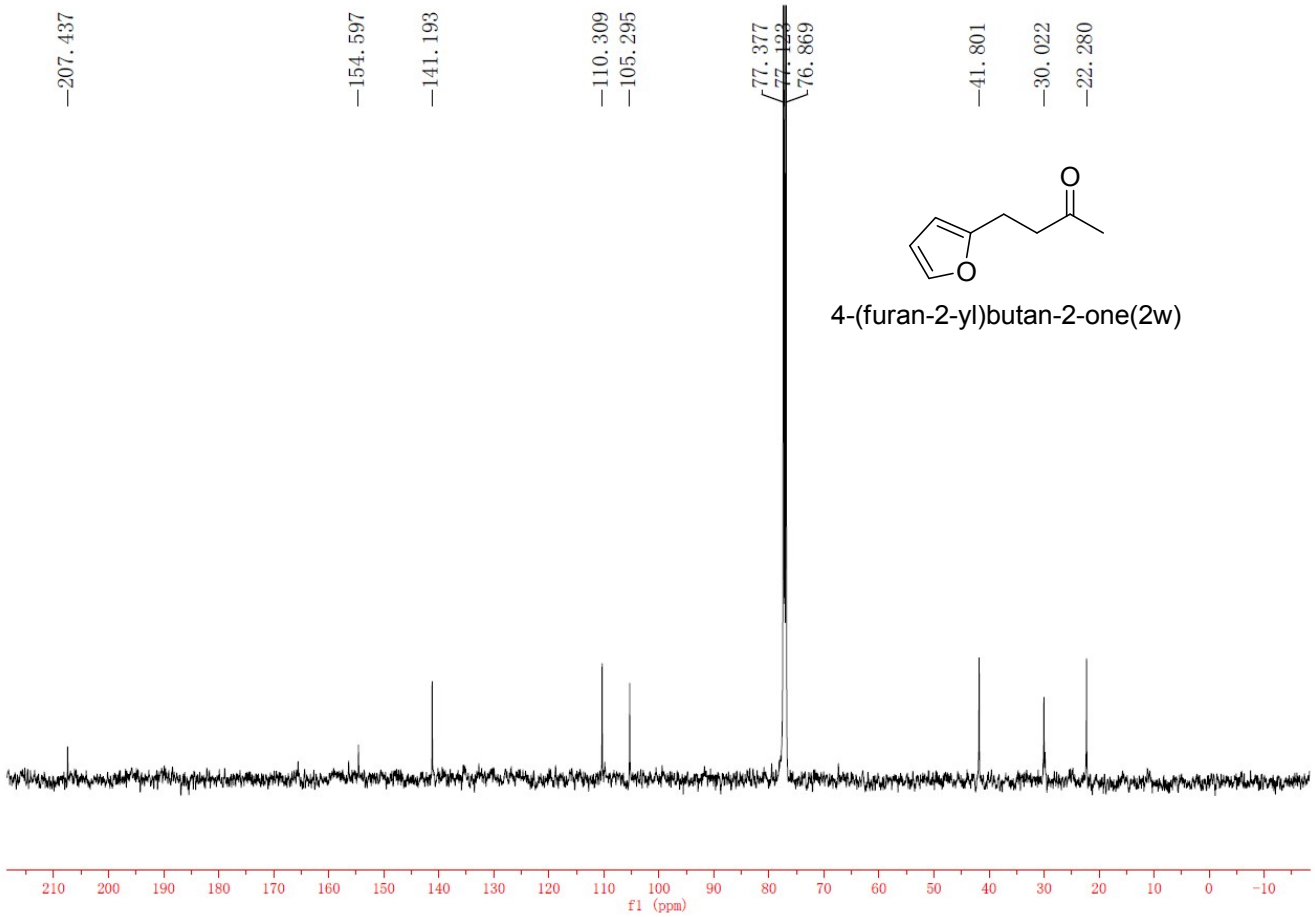


^{1}H NMR (500 MHz, $CDCl_3$)



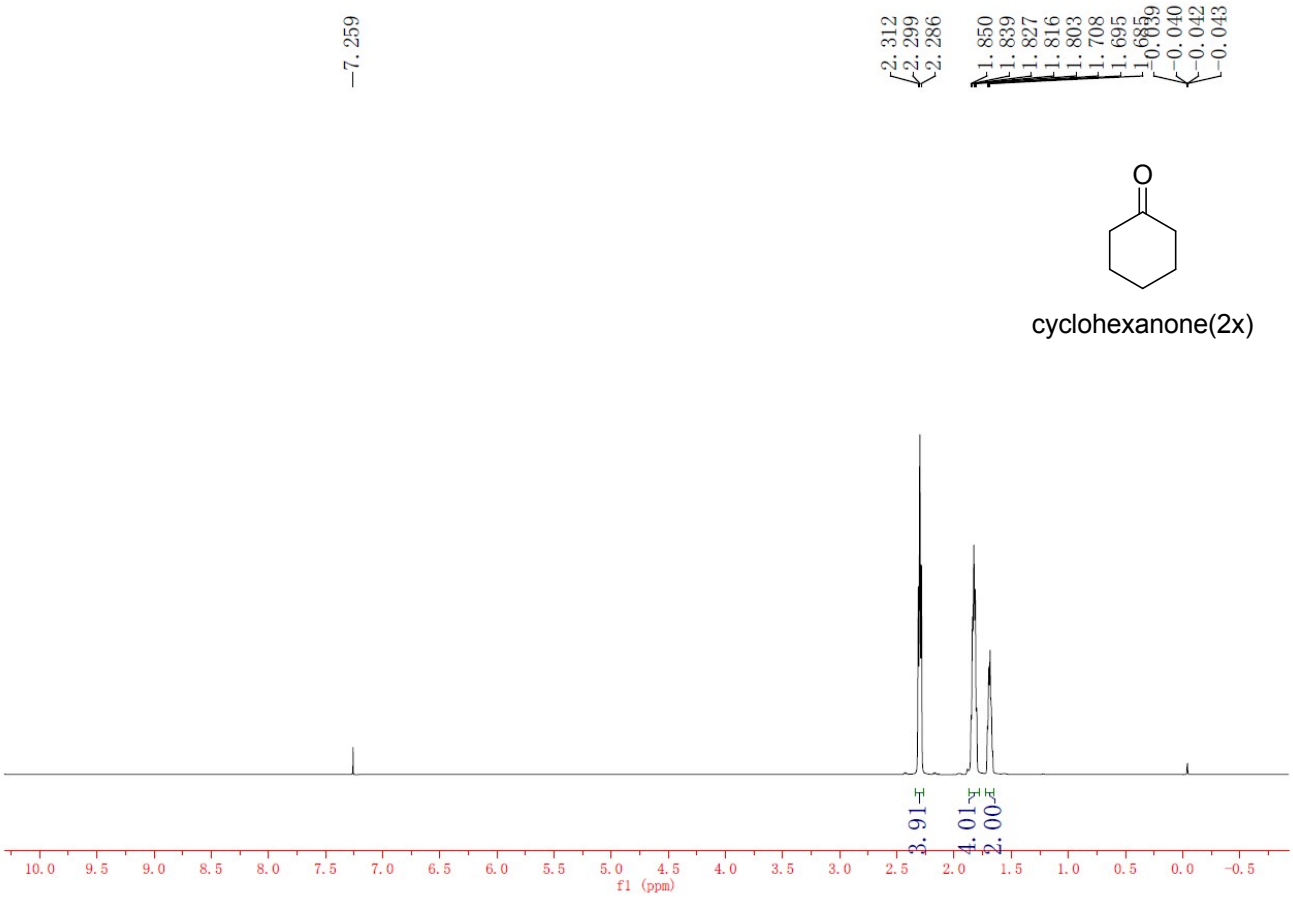
4-(furan-2-yl)butan-2-one(2w)

^{13}C NMR (125 MHz, $CDCl_3$)



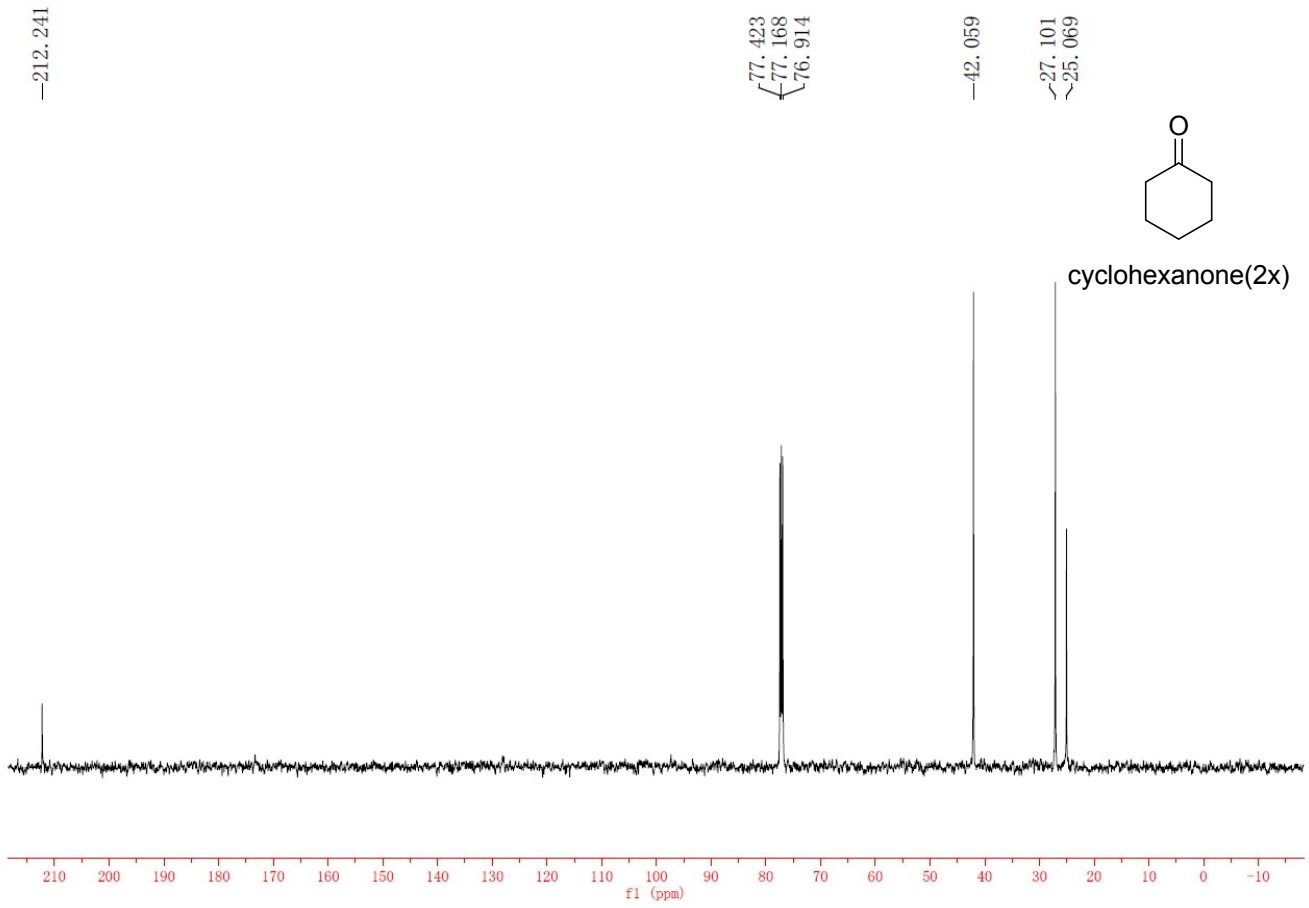
4-(furan-2-yl)butan-2-one(2w)

^{1}H NMR (500 MHz, $CDCl_3$)



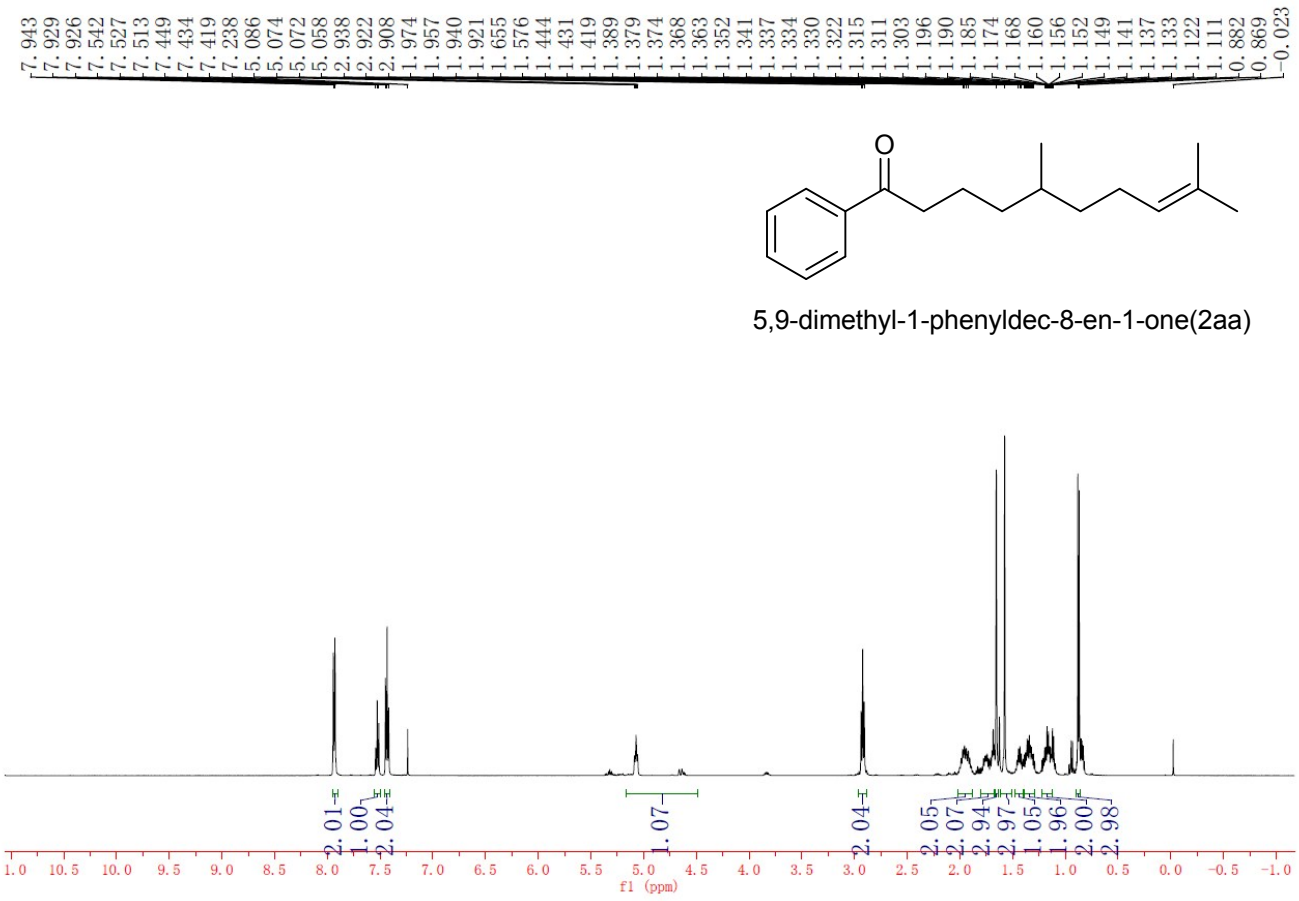
cyclohexanone(2x)

^{13}C NMR (125 MHz, $CDCl_3$)



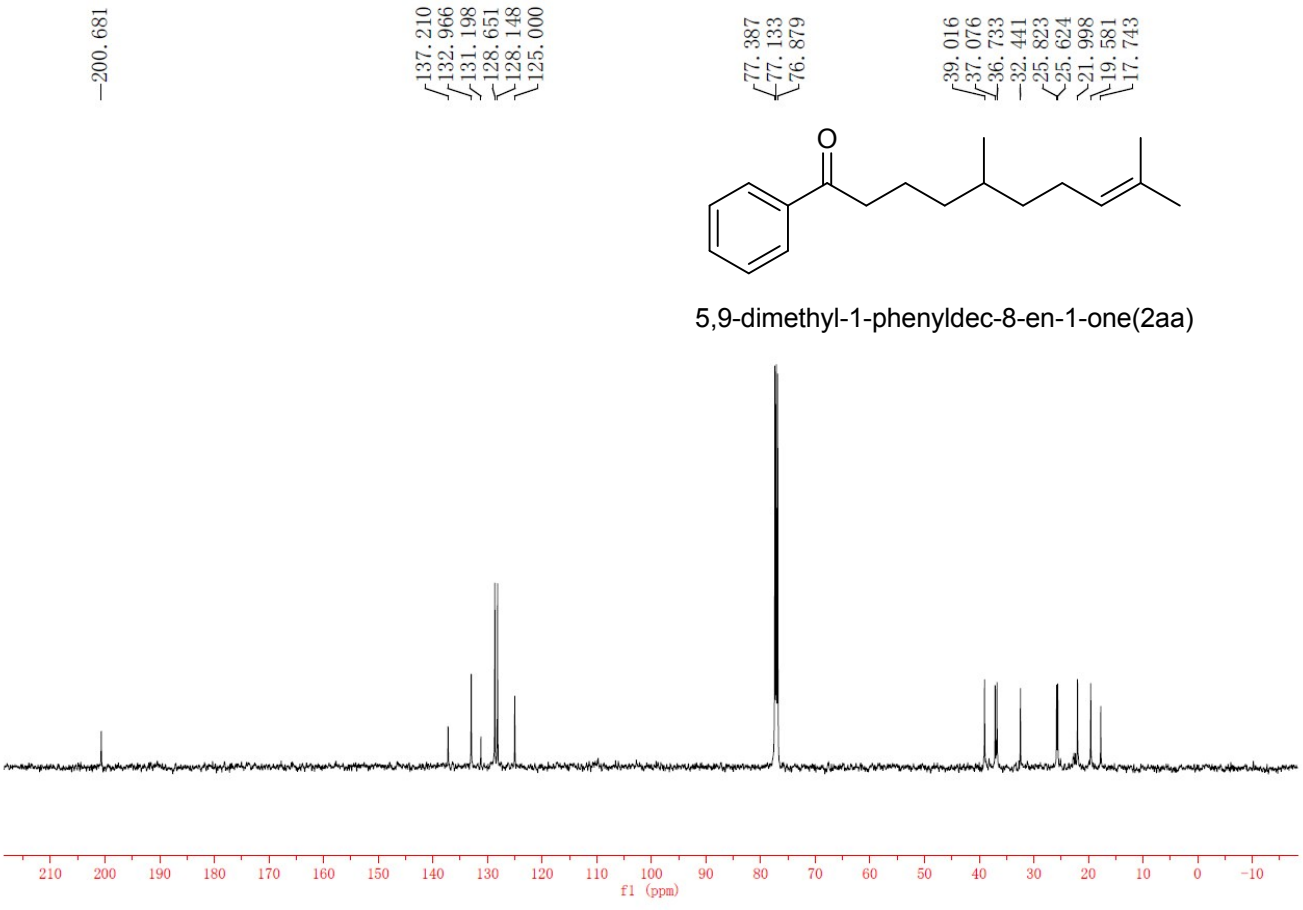
cyclohexanone(2x)

^{1}H NMR (500 MHz, $CDCl_3$)



5,9-dimethyl-1-phenyldec-8-en-1-one(2aa)

^{13}C NMR (125 MHz, $CDCl_3$)



5,9-dimethyl-1-phenyldec-8-en-1-one(2aa)