Electrochemical 1,4-Reduction of α, β-Unsaturated Ketones with Methanol and Ammonium Chloride as Hydrogen Sources

Binbin Huang[†], Yanan Li[†], Chao Yang[†] and Wujiong Xia[†,*]

[†]State Key Lab of Urban Water Resource and Environment, School of Chemistry and Chemical Engineering, Harbin Institute of Technology (Shenzhen), Shenzhen, 518055, China

Electronic Supplementary Information

Table Contents:

1. General and Experimental Details

General Information:

All commercially available reagents were directly used as received without further purification. Reaction solvents applied (DMSO/MeOH, *v*:*v*) were premixed and filtered after dried over $MgSO_4$. The electrochemical reactions were performed on a DJS-292B potentiostat (made in China) in constant current mode. All yields of products refer to the isolated yields after chromatography.

^1H NMR (400 MHz) and ^{13}C NMR (100 or 150 MHz) spectra were recorded on a Bruker AV-400 spectrometer in $CDCl_3$. For ^1H NMR (400MHz), $CDCl_3$ (δ = 7.26 ppm) or tetramethylsilane (TMS, δ = 0 ppm) serves as the internal standard; for ^{13}C NMR (100MHz), $CDCl_3$ (δ = 77.16 ppm) serves as the internal standard. Data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (in Hz), and integration.

GC analysis was performed on 7890B/Agilent, while GC-MS analysis was performed on 7890A-5975C/Agilent. IR spectra were performed on a PerkinElmer FT-IR spectrometer (Spectrum 100). HR-MS spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization.

Preparation of substrates:

Substrates **1a** and **33a** were purchased from commercial sources; **2a** – **28a**, **32a** and **34a** were prepared from the corresponding aldehydes and ketones according to the same literature[1]; **29a** was acquired by treating **28a** with 4-toluene sulfonyl chloride[2]; while **30a**[3], **31a**[4] and **35a**[5] were prepared as reported in respective literature.

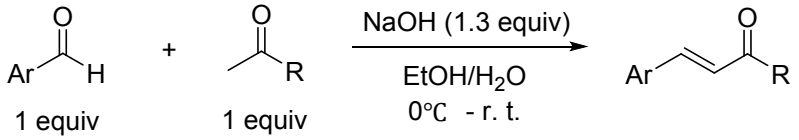
Intermediates **22aa**, **23aa** and **24aa** were prepared from 4-hydroxybenzaldehyde and the corresponding alkyl bromides according to the same literature[6].

Intermediate **25aa** was prepared from 4-aminoacetophenone and methacryloylchloride.

For the previously reported substrates, all characterization data are in good agreement with the literature (**2a**[7], **3a**[7], **4a**[8], **5a**[7], **7a**[7], **8a**[7], **9a**[9], **10a**[10], **11a**[11], **12a**[7], **13a**[7], **14a**[7], **15a**[11], **16a**[7], **19a**[12], **20a**[13], **26a**[8], **27a**[14], **28a**[15], **30a**[16], **31a**[4], **32a**[17], **34a**[18], **35a**[5]).

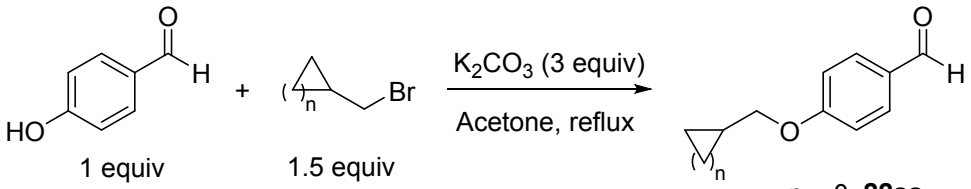
Substrate **36a** was prepared according to literature[33], and the characterization data are in good agreement with those therein.

Preparation of the α,β-unsaturated ketones[1]:



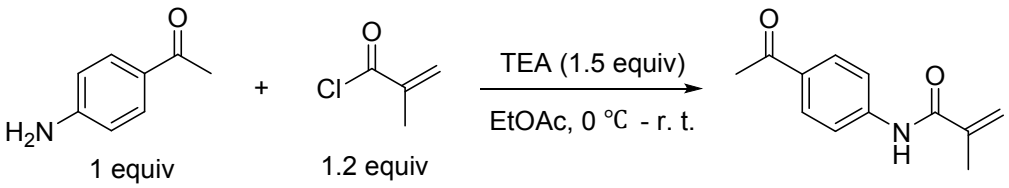
To a solution of ketone (10 mmol, 1.0 equiv) in 6 mL ethanol was added a solution of NaOH (520 mg, 13 mmol, 1.3 equiv) in water (10 mL), then the corresponding aldehyde (10 mmol, 1.0 equiv) was added gradually at 0 °C. The mixture was then allowed to warm to room temperature and stirred overnight. The solid 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.

O-alkylation of 4-hydroxybenzaldehyde[6]:



A 100-mL round-bottom flask was equipped with a condenser and a magnetic stir bar. To the flask was added 4-hydroxybenzaldehyde (1.22 g, 10 mmol, 1.0 equiv), K_2CO_3 (4.14 g, 30 mmol, 3 equiv), and 25 mL of anhydrous acetone. A solution of alkyl bromide (20 mmol, 1.5 equiv) in 5 mL of anhydrous acetone was added dropwise to the reaction mixture at room temperature. After being stirred for 30 min at room temperature, the reaction mixture was refluxed overnight. The reaction was cooled to room temperature and filtered. The filtrate was concentrated to afford the crude product, which was then purified by flash chromatography to yield the intermediate.

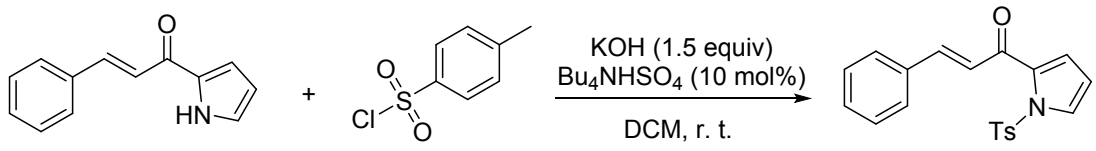
N-acylation of 4-aminoacetophenone:



25aa

To a solution of 4-aminoacetophenone (675 mg, 5 mmol, 1.0 equiv) and triethylamine (1.0 mL, 7.5 mmol, 1.5 equiv) in 10 mL EtOAc was dropwise added methacryloylchloride (0.6 mL, 6 mmol, 1.2 equiv) at 0 °C. The mixture was then allowed to warm to room temperature and stirred overnight. The system was extracted with EtOAc/water and the combined organic layer was dried over Na_2SO_4 and concentrated. The intermediate **25aa** was acquired by recrystallization from EtOAc with PE as a light yellow solid (860 mg, 85%).

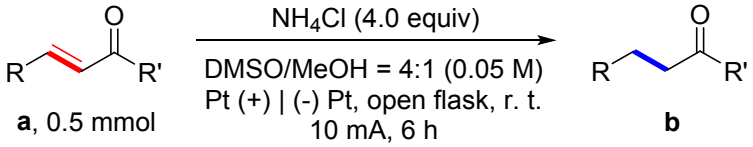
Preparation of 28a[2]:



28a, 1 equiv 1.2 equiv **29a**

Following a literature procedure, to a solution of **28a** (985 mg, 5 mmol, 1 equiv) in dichloromethane (25 mL) were added KOH (420 mg, 7.5 mmol, 1.5 equiv) and tetrabutylammonium hydrogensulfate (170 mg, 0.5 mmol, 0.1 equiv), and the mixture was allowed to stir for 15 min followed by addition of a solution of 4-toluene sulfonyl chloride (1.14 g, 6 mmol, 1.2 equiv) in dichloromethane (10 mL), and the mixture was stirred at room temperature overnight. The system was extracted with dichloromethane and the combined organic layer was dried over Na_2SO_4 and concentrated. The resulting residue was purified by flash chromatography to yield **29a** as a light brown solid (1.14g, 65%).

General Procedure for the hydrogenation of α,β-unsaturated ketones:



a, 0.5 mmol **b**

To a 25 mL three-necked flask was added the substrate ketone **a** (0.5 mmol) and NH_4Cl (107.0 mg, 2.0 mmol), followed by 10 mL premixed solvent (DMSO:MeOH = 4:1, *v*:*v*). Then the flask was equipped with two platinum plate electrodes (10×10×0.1 mm, the distance between them was approximately 2 cm). The constant current (10 mA) electrolysis was performed at room temperature for 6 hours with the system directly exposed to air. The reaction mixture was then poured into 30 mL brine and extracted with 20 mL EtOAc for three times (for the reactions of **9a**, **25a**, **28a** and **29a**, extraction was performed with dichloromethane/water). The combined organic layer was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with EtOAc/PE) to afford the desired product.

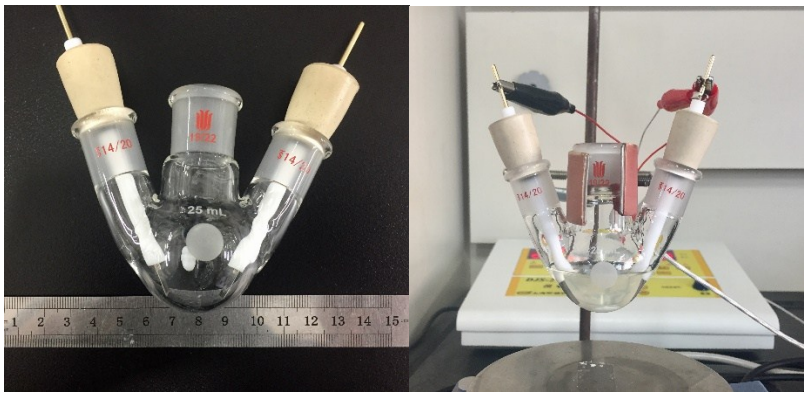
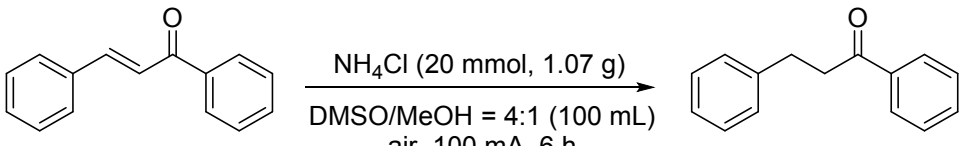


Fig. S1 Reaction setup for the electrochemical hydrogenation

Gram scale synthesis of 1b:



1a, 5 mmol, 1.04 g

1b, 0.828 g, 79%

To a 250 mL beaker was added substrate **1a** (1.04 g, 5.0 mmol) and NH_4Cl (1.07 g, 20 mmol), followed by 100 mL premixed solvent (DMSO:MeOH = 4:1, *v*:*v*). Then the beaker was equipped with two platinum plate electrodes (30×30×0.2 mm, the distance between them was approximately 5 cm). The constant current (100 mA) electrolysis was performed at room temperature for 6 hours. The reaction mixture was then poured into 200 mL brine and extracted with EtOAc (100 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4, and the

solvent was removed under reduced pressure. The resulting mixture was purified by column chromatography on silica gel (eluted with EtOAc/PE) to afford **1b** in 79% yield (828 mg).

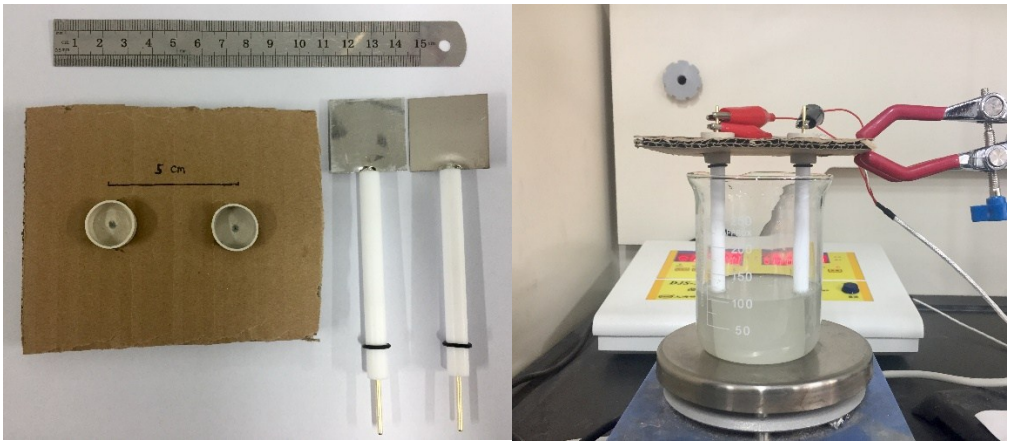
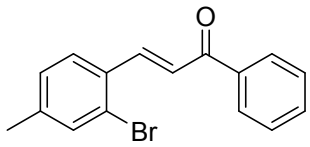


Fig. S2 Reaction setup for the gram scale reaction

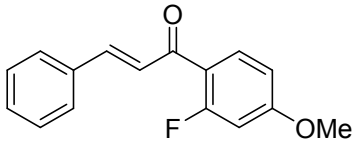
2. Characterization Data

Data of unreported α,β-unsaturated ketone substrates:



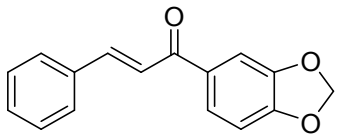
(E)-3-(2-bromo-4-methylphenyl)-1-phenylprop-2-en-1-one (**6a**)

Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 15.7 Hz, 1H), 8.06 – 7.97 (m, 2H), 7.66 – 7.55 (m, 2H), 7.55 – 7.44 (m, 3H), 7.40 (dd, *J* = 15.7, 1.7 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.65, 143.33, 142.38, 138.13, 134.12, 132.96, 132.15, 128.75, 128.73, 127.66, 126.04, 124.11, 21.19. GC-MS (EI): 302.1, 300.1, 222.1, 221.2, 178.1, 115.1, 77.1. HRMS (ESI) calcd for $C_{16}H_{14}BrO^+$ m/z $[M+H]^+$: 301.0223; found: 301.0227.



(E)-1-(2-fluoro-4-methoxyphenyl)-3-phenylprop-2-en-1-one (**17a**)

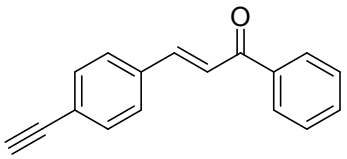
White soild. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (t, *J* = 8.7 Hz, 1H), 7.78 (dd, *J* = 15.7, 2.2 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.51 – 7.37 (m, 4H), 6.79 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.66 (dd, *J* = 13.0, 2.4 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 187.31, 187.28, 164.73, 164.65, 164.07, 162.38, 144.02, 135.10, 132.84, 132.81, 130.56, 129.04, 128.65, 125.71, 125.66, 119.82, 110.96, 110.94, 102.02, 101.83, 56.01. ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.66 (m). GC-MS (EI): 256.1, 255.2, 228.1, 153.1, 131.1, 103.1, 77.1. HRMS (ESI) calcd for $C_{16}H_{14}FO_2^+$ m/z $[M+H]^+$: 257.0972; found: 257.0978.



(E)-1-(benzo[d][1,3]dioxol-5-yl)-3-phenylprop-2-en-1-one (**18a**)

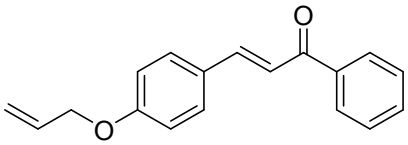
Off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 15.6 Hz, 1H), 7.68 – 7.61 (m, 3H), 7.54 (d, *J* = 1.7 Hz, 1H), 7.49 (d, *J* = 15.6 Hz, 1H), 7.42 (dd, *J* = 5.0, 1.9 Hz, 3H), 6.90 (d, *J* = 8.1 Hz,

1H), 6.07 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.41, 151.86, 148.45, 144.40, 135.12, 133.11, 130.56, 129.09, 128.53, 124.83, 121.83, 108.59, 108.07, 102.02. GC-MS (EI): 252.1, 222.1, 194.1, 165.1, 149.1, 103.1, 77.1. HRMS (ESI) calcd for $C_{16}H_{13}O_3^+$ m/z $[M+H]^+$: 253.0859; found: 253.0855.



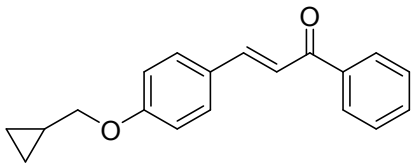
(E)-3-(4-ethynylphenyl)-1-phenylprop-2-en-1-one (**21a**)

Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.97 (m, 2H), 7.78 (d, *J* = 15.7 Hz, 1H), 7.66 – 7.47 (m, 8H), 3.21 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.37, 143.74, 138.15, 135.33, 133.08, 132.77, 128.81, 128.65, 128.40, 124.26, 122.99, 83.32, 79.57, 79.55. GC-MS (EI): 232.1, 202.1, 155.1, 127.1, 105.1, 77.1. HRMS (ESI) calcd for $C_{17}H_{13}O^+$ m/z $[M+H]^+$: 233.0961; found: 233.0969.



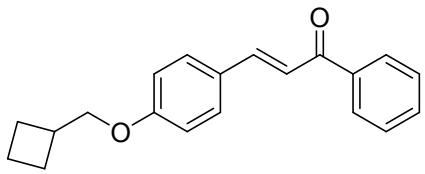
(E)-3-(4-(allyloxy)phenyl)-1-phenylprop-2-en-1-one (**22a**)

Light green solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.96 (m, 2H), 7.79 (d, *J* = 15.6 Hz, 1H), 7.64 – 7.54 (m, 3H), 7.54 – 7.47 (m, 2H), 7.42 (d, *J* = 15.7 Hz, 1H), 7.00 – 6.90 (m, 2H), 6.06 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1H), 5.43 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.32 (dq, *J* = 10.5, 1.4 Hz, 1H), 4.59 (dt, *J* = 5.3, 1.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.70, 160.79, 144.79, 138.61, 132.82, 132.70, 130.34, 128.69, 128.54, 127.84, 119.94, 118.23, 115.27, 68.99. GC-MS (EI): 264.1, 223.1, 195.1, 167.1, 105.1, 77.1, 55.2. HRMS (ESI) calcd for $C_{18}H_{17}O_2^+$ m/z $[M+H]^+$: 265.1223; found: 265.1225.



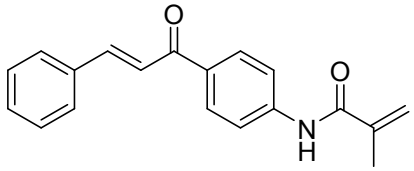
(E)-3-(4-(cyclopropylmethoxy)phenyl)-1-phenylprop-2-en-1-one (**23a**)

Light green solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.95 (m, 2H), 7.78 (d, *J* = 15.7 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.50 (dd, *J* = 8.1, 6.6 Hz, 2H), 7.41 (d, *J* = 15.7 Hz, 1H), 7.00 – 6.88 (m, 2H), 3.85 (d, *J* = 6.9 Hz, 2H), 1.35 – 1.21 (m, 1H), 0.73 – 0.61 (m, 2H), 0.37 (dt, *J* = 6.2, 4.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.73, 161.28, 144.90, 138.65, 132.69, 130.38, 128.70, 128.55, 127.61, 119.79, 115.10, 73.05, 10.28, 3.39. GC-MS (EI): 278.1, 223.1, 207.1, 147.1, 105.1, 77.1, 55.2. HRMS (ESI) calcd for $C_{19}H_{19}O_2^+$ m/z $[M+H]^+$: 279.1380; found: 279.1384.



(E)-3-(4-(cyclobutylmethoxy)phenyl)-1-phenylprop-2-en-1-one (**24a**)

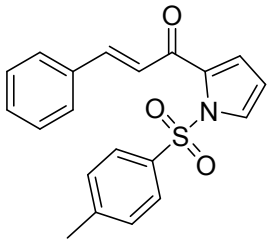
Light green solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.99 (m, 2H), 7.81 (d, *J* = 15.6 Hz, 1H), 7.66 – 7.57 (m, 3H), 7.52 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.44 (d, *J* = 15.6 Hz, 1H), 7.01 – 6.91 (m, 2H), 4.00 (d, *J* = 6.6 Hz, 2H), 2.81 (hept, *J* = 7.2 Hz, 1H), 2.18 (dddd, *J* = 10.4, 8.0, 4.9, 1.6 Hz, 2H), 2.06 – 1.85 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 190.76, 161.60, 144.98, 138.68, 132.67, 130.37, 128.70, 128.55, 127.51, 119.72, 115.10, 72.32, 34.62, 24.98, 18.72. GC-MS (EI): 292.1, 224.1, 207.1, 147.1, 94.1, 77.1, 41.1. HRMS (ESI) calcd for $C_{20}H_{21}O_2^+$ m/z $[M+H]^+$: 293.1536; found: 293.1537.



N-(4-cinnamoylphenyl)methacrylamide (**25a**)

Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.93 (s, 1H), 7.85 – 7.72 (m, 3H), 7.63 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.54 (d, *J* = 15.6 Hz, 1H), 7.46 – 7.37 (m, 3H), 5.84 (s, 1H), 5.51 (s, 1H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.11, 166.88, 144.71, 142.24, 140.80, 135.04, 133.99, 130.64, 130.06, 129.08, 128.57, 121.89, 120.65, 119.45, 18.82. GC-MS (EI): 291.1,

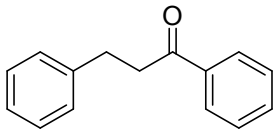
194.1, 131.1, 103.1, 77.0, 69.0, 41.1. HRMS (ESI) calcd for $C_{19}H_{18}NO_2^+$ m/z $[M+H]^+$: 292.1332; found: 292.1336.



(E)-3-phenyl-1-(1-tosyl-1H-pyrrol-2-yl)prop-2-en-1-one (**29a**)

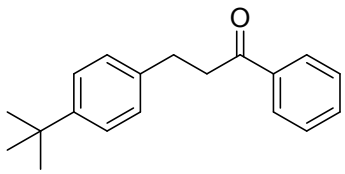
Light brown solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.91 (m, 2H), 7.83 (d, *J* = 3.8 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.55 (t, *J* = 4.5 Hz, 2H), 7.42 – 7.32 (m, 5H), 7.23 – 7.17 (m, 1H), 7.14 (d, *J* = 3.7 Hz, 1H), 6.39 (q, *J* = 3.8 Hz, 1H), 2.43 (d, *J* = 3.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 178.80, 144.91, 143.98, 136.31, 134.78, 134.48, 130.57, 130.46, 129.54, 129.05, 128.44, 128.37, 123.33, 123.00, 110.67, 21.86. GC-MS (EI): 351.1, 196.1, 167.1, 104.1, 91.1, 77.1, 65.1. HRMS (ESI) calcd for $C_{20}H_{18}NO_3S^+$ m/z $[M+H]^+$: 352.1002; found: 352.1008.

Data of hydrogenated ketone products:



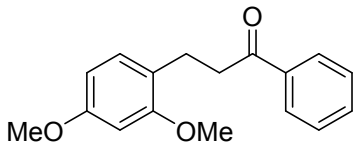
1,3-diphenylpropan-1-one (**1b**)[19]

White solid, 89.0 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.91 (m, 2H), 7.60 – 7.52 (m, 1H), 7.48 – 7.42 (m, 2H), 7.34 – 7.24 (m, 4H), 7.23 – 7.17 (m, 1H), 3.34 – 3.28 (m, 2H), 3.10 – 3.04 (m, 2H).



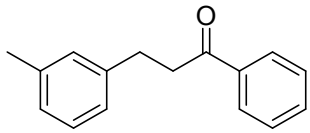
3-(4-(tert-butyl)phenyl)-1-phenylpropan-1-one (**2b**)[20]

White solid, 110.3 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 2H), 7.60 – 7.53 (m, 1H), 7.50 – 7.43 (m, 2H), 7.38 – 7.31 (m, 2H), 7.24 – 7.17 (m, 2H), 3.35 – 3.28 (m, 2H), 3.10 – 3.02 (m, 2H), 1.33 (s, 9H).



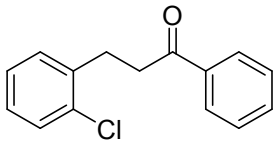
3-(2,4-dimethoxyphenyl)-1-phenylpropan-1-one (**3b**)[21]

White solid, 119.9 mg, 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.59 – 7.51 (m, 1H), 7.49 – 7.40 (m, 2H), 7.10 (d, J = 8.1 Hz, 1H), 6.46 (d, J = 2.4 Hz, 1H), 6.42 (dd, J = 8.2, 2.5 Hz, 1H), 3.80 (s, 3H), 3.80 (s, 3H), 3.26 – 3.19 (m, 2H), 3.01 – 2.94 (m, 2H).



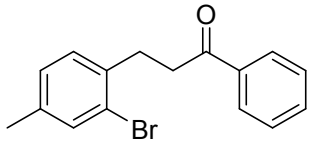
1-phenyl-3-(m-tolyl)propan-1-one (**4b**)[19]

Light yellow solid, 90.0 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 2H), 7.58 – 7.49 (m, 1H), 7.47 – 7.39 (m, 2H), 7.21 – 7.14 (m, 1H), 7.12 – 6.95 (m, 3H), 3.33 – 3.23 (m, 2H), 3.07 – 2.97 (m, 2H), 2.33 (s, 3H).



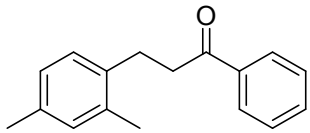
3-(2-chlorophenyl)-1-phenylpropan-1-one (**5b**)[22]

Light yellow oil, 106.4 mg, 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 2H), 7.60 – 7.52 (m, 1H), 7.49 – 7.42 (m, 2H), 7.39 – 7.30 (m, 2H), 7.23 – 7.13 (m, 2H), 3.36 – 3.29 (m, 2H), 3.23 – 3.15 (m, 2H).



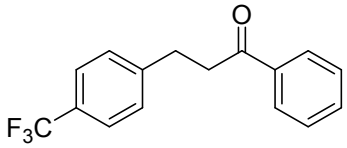
3-(2-bromo-4-methylphenyl)-1-phenylpropan-1-one (**6b**)

Light yellow oil, 119.8 mg, 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 2H), 7.60 – 7.52 (m, 1H), 7.50 – 7.43 (m, 2H), 7.39 (s, 1H), 7.20 (d, J = 7.7 Hz, 1H), 7.05 (dd, J = 8.0, 1.8 Hz, 1H), 3.35 – 3.25 (m, 2H), 3.21 – 3.10 (m, 2H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.11, 138.07, 137.42, 136.83, 133.36, 133.18, 130.56, 128.68, 128.51, 128.16, 124.15, 38.87, 30.42, 20.69. GC-MS (EI): 303.1, 223.1, 183.0, 115.1, 105.1, 77.1, 51.1. HRMS (ESI) calcd for $C_{16}H_{16}BrO^+$ m/z $[M+H]^+$: 303.0379; found: 303.0376.



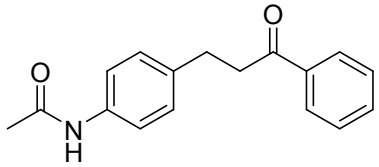
3-(2,4-dimethylphenyl)-1-phenylpropan-1-one (**7b**)

White solid, 97.7 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.96 (m, 2H), 7.62 – 7.55 (m, 1H), 7.53 – 7.44 (m, 2H), 7.12 (d, J = 7.6 Hz, 1H), 7.06 – 6.94 (m, 2H), 3.31 – 3.22 (m, 2H), 3.10 – 3.00 (m, 2H), 2.35 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.53, 136.92, 136.38, 135.89, 133.16, 131.26, 128.79, 128.71, 128.13, 126.90, 39.40, 27.21, 21.01, 19.39. GC-MS (EI): 238.2, 220.2, 205.1, 133.1, 118.1, 105.1, 77.1. HRMS (ESI) calcd for $C_{17}H_{19}O^+$ m/z $[M+H]^+$: 239.1430; found: 239.1433.



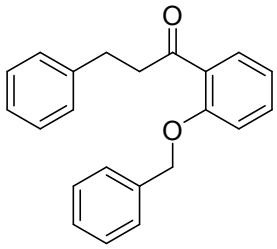
1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (**8b**)[19]

White solid, 126.5 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.7 Hz, 2H), 7.61 – 7.52 (m, 3H), 7.46 (t, J = 7.6 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 3.33 (t, J = 7.4 Hz, 2H), 3.14 (t, J = 7.5 Hz, 2H).



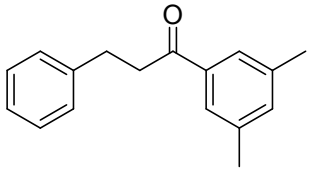
N-(4-(3-oxo-3-phenylpropyl)phenyl)acetamide (**9b**)

Light yellow solid, 112.3 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.79 (m, 3H), 7.59 – 7.51 (m, 1H), 7.44 (t, J = 7.9 Hz, 4H), 7.16 (d, J = 8.1 Hz, 2H), 3.26 (t, J = 7.6 Hz, 2H), 3.01 (t, J = 7.6 Hz, 2H), 2.13 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.52, 168.83, 137.17, 136.84, 136.30, 133.20, 128.87, 128.69, 128.08, 120.42, 40.41, 29.59, 24.43. GC-MS (EI): 267.1, 162.1, 148.1, 120.1, 106.1, 77.1, 43.1. HRMS (ESI) calcd for $C_{17}H_{18}NO_2^+$ m/z $[M+H]^+$: 268.1332; found: 268.1331.



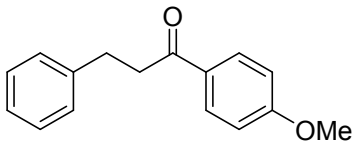
1-(2-(benzyloxy)phenyl)-3-phenylpropan-1-one (**10b**)[23]

White solid, 139.2 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.66 (m, 1H), 7.45 – 7.40 (m, 1H), 7.39 – 7.35 (m, 2H), 7.35 – 7.30 (m, 3H), 7.24 – 7.17 (m, 2H), 7.17 – 7.12 (m, 1H), 7.07 – 6.96 (m, 4H), 5.11 (s, 2H), 3.36 – 3.25 (m, 2H), 3.02 – 2.90 (m, 2H).



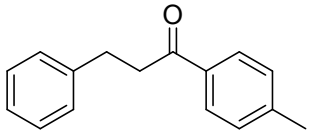
1-(3,5-dimethylphenyl)-3-phenylpropan-1-one (**11b**)

Light yellow oil, 95.4 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 2H), 7.35 – 7.11 (m, 6H), 3.31 – 3.19 (m, 2H), 3.12 – 2.97 (m, 2H), 2.34 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.66, 140.52, 137.28, 136.03, 133.76, 127.59, 127.52, 125.17, 124.93, 39.67, 29.26, 20.32. GC-MS (EI): 238.2, 223.1, 133.1, 105.1, 91.1, 77.1. HRMS (ESI) calcd for $C_{17}H_{19}O^+$ m/z $[M+H]^+$: 239.1430; found: 239.1435.



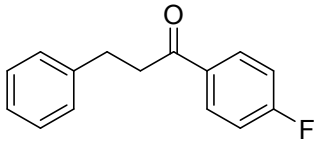
1-(4-methoxyphenyl)-3-phenylpropan-1-one (**12b**)[19]

White solid, 103.3 mg, 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 2H), 7.33 – 7.23 (m, 4H), 7.23 – 7.15 (m, 1H), 6.96 – 6.87 (m, 2H), 3.85 (s, 3H), 3.28 – 3.20 (m, 2H), 3.09 – 3.01 (m, 2H).



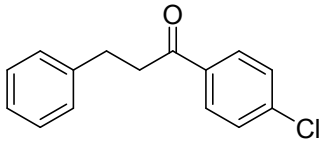
3-phenyl-1-(p-tolyl)propan-1-one (**13b**)[19]

White solid, 87.5 mg, 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.32 – 7.16 (m, 7H), 3.30 – 3.22 (m, 2H), 3.10 – 3.01 (m, 2H), 2.39 (s, 3H).



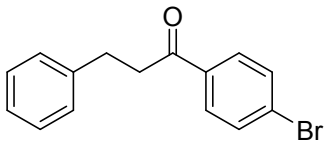
1-(4-fluorophenyl)-3-phenylpropan-1-one (**14b**)[19]

White solid, 92.4 mg, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.91 (m, 2H), 7.34 – 7.16 (m, 5H), 7.14 – 7.04 (m, 2H), 3.31 – 3.21 (m, 2H), 3.01 – 3.11 (m, 2H).



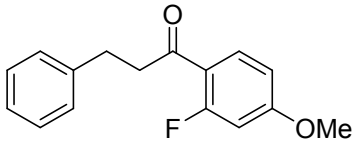
1-(4-chlorophenyl)-3-phenylpropan-1-one (**15b**)[19]

White solid, 104.0 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.86 (m, 2H), 7.50 – 7.42 (m, 2H), 7.39 – 7.20 (m, 5H), 3.35 – 3.25 (m, 2H), 3.16 – 3.05 (m, 2H).



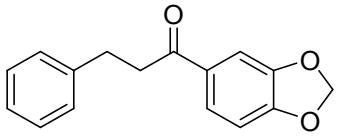
1-(4-bromophenyl)-3-phenylpropan-1-one (**16b**)[19]

White solid, 108.5 mg, 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.3 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H), 7.32 – 7.16 (m, 5H), 3.23 (t, J = 7.7 Hz, 2H), 3.04 (t, J = 7.6 Hz, 2H).



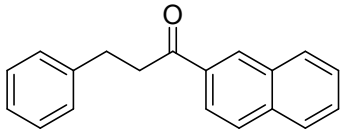
1-(2-fluoro-4-methoxyphenyl)-3-phenylpropan-1-one (**17b**)

White solid, 98.2 mg, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (t, J = 8.7 Hz, 1H), 7.33 – 7.22 (m, 4H), 7.22 – 7.14 (m, 1H), 6.74 (dd, J = 8.9, 2.4 Hz, 1H), 6.59 (dd, J = 13.2, 2.5 Hz, 1H), 3.83 (s, 3H), 3.30 – 3.20 (m, 2H), 3.03 (t, J = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 196.11, 196.08, 164.87, 164.79, 164.56, 162.87, 141.49, 132.27, 132.24, 128.57, 128.54, 126.09, 118.40, 118.31, 110.88, 110.86, 101.84, 101.66, 55.97, 55.94, 55.91, 55.89, 45.06, 45.00, 30.17. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.48 (m). GC-MS (EI): 258.1, 227.1, 153.1, 139.1, 110.1, 91.1, 77.1. HRMS (ESI) calcd for $C_{16}H_{16}FO_2^+$ m/z $[M+H]^+$: 259.1129; found: 259.1134.



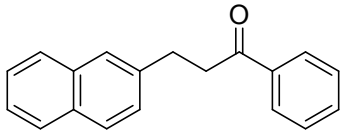
1-(benzo[d][1,3]dioxol-5-yl)-3-phenylpropan-1-one (**18b**)[24]

White solid, 114.3 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 8.2, 1.7 Hz, 1H), 7.42 (d, J = 1.7 Hz, 1H), 7.34 – 7.14 (m, 5H), 6.80 (d, J = 8.2 Hz, 1H), 5.99 (s, 2H), 3.24 – 3.15 (m, 2H), 2.98 – 3.08 (m, 2H).



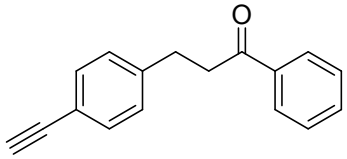
1-(naphthalen-2-yl)-3-phenylpropan-1-one (**19b**)[25]

White solid, 101.6 mg, 78%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 1.8 Hz, 1H), 8.07 – 8.00 (m, 1H), 7.96 – 7.83 (m, 3H), 7.63 – 7.50 (m, 2H), 7.36 – 7.26 (m, 4H), 7.25 – 7.18 (m, 1H), 3.50 – 3.38 (m, 2H), 3.20 – 3.05 (m, 2H).



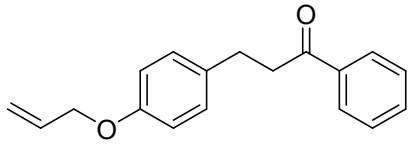
3-(naphthalen-2-yl)-1-phenylpropan-1-one (**20b**)[19]

White solid, 107.9 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.98 (m, 2H), 7.83 (t, J = 7.9 Hz, 3H), 7.72 (s, 1H), 7.58 (t, J = 7.4 Hz, 1H), 7.53 – 7.40 (m, 5H), 3.45 – 3.37 (m, 2H), 3.31 – 3.22 (m, 2H).



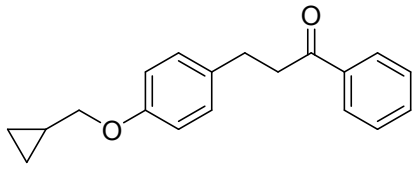
3-(4-ethynylphenyl)-1-phenylpropan-1-one (**21b**)

White solid, 96.1 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.59 – 7.53 (m, 1H), 7.50 – 7.40 (m, 4H), 7.24 – 7.17 (m, 2H), 3.33 – 3.25 (m, 2H), 3.11 – 3.02 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.91, 142.39, 136.86, 133.24, 132.38, 128.73, 128.58, 128.11, 119.97, 83.75, 76.94, 40.07, 30.04. GC-MS (EI): 234.1, 128.1, 116.1, 105.1, 77.1, 51.1. HRMS (ESI) calcd for $C_{17}H_{15}O^{+}$ m/z $[M+H]^{+}$: 235.1117; found: 235.1116.



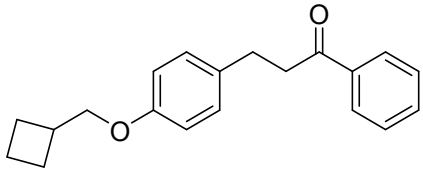
3-(4-(allyloxy)phenyl)-1-phenylpropan-1-one (**22b**)[26]

Light yellow oil, 107.8 mg, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.92 (m, 2H), 7.59 – 7.53 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.22 – 7.14 (m, 2H), 6.91 – 6.84 (m, 2H), 6.12 – 6.00 (m, 1H), 5.46 – 5.38 (m, 1H), 5.32 – 5.25 (m, 1H), 4.56 – 4.49 (m, 2H), 3.31 – 3.23 (m, 2H), 3.07 – 2.97 (m, 2H).



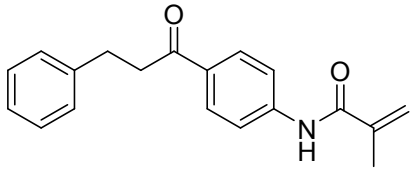
3-(4-(cyclopropylmethoxy)phenyl)-1-phenylpropan-1-one (**23b**)

Light yellow oil, 109.5 mg, 78%.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.90 (m, 2H), 7.59 – 7.52 (m, 1H), 7.50 – 7.41 (m, 2H), 7.23 – 7.13 (m, 2H), 6.92 – 6.82 (m, 2H), 3.78 (d, J = 6.9 Hz, 2H), 3.33 – 3.22 (m, 2H), 3.10 – 2.97 (m, 2H), 1.34 – 1.21 (m, 1H), 0.70 – 0.60 (m, 2H), 0.35 (dt, J = 6.2, 4.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.33, 157.43, 136.87, 133.24, 133.03, 129.34, 128.60, 128.04, 114.62, 72.79, 72.76, 72.73, 40.70, 29.27, 29.26, 10.35, 3.22. GC-MS (EI): 280.1, 252.1, 226.1, 161.1, 105.1, 77.1, 55.1, 29.1. HRMS (ESI) calcd for $C_{19}H_{21}O_2^+$ m/z $[M+H]^+$: 281.1536; found: 281.1540.



3-(4-(cyclobutylmethoxy)phenyl)-1-phenylpropan-1-one (**24b**)

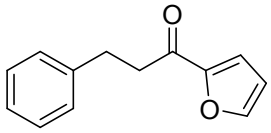
Light yellow oil, 113.4 mg, 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.91 (m, 2H), 7.60 – 7.52 (m, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.23 – 7.11 (m, 2H), 6.91 – 6.80 (m, 2H), 3.91 (d, J = 6.7 Hz, 2H), 3.28 (t, J = 7.7 Hz, 2H), 3.02 (t, J = 7.7 Hz, 2H), 2.83 – 2.70 (m, 1H), 2.21 – 2.09 (m, 2H), 2.03 – 1.81 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.49, 157.83, 137.04, 133.24, 133.10, 129.39, 128.69, 128.14, 114.76, 72.30, 40.84, 34.79, 29.42, 25.00, 18.71. GC-MS (EI): 294.1, 226.1, 121.1, 105.1, 91.1, 77.1, 41.1. HRMS (ESI) calcd for $C_{20}H_{23}O_2^+$ m/z $[M+H]^+$: 295.1693; found:295.1696.



N-(4-(3-phenylpropanoyl)phenyl)methacrylamide (**25b**)

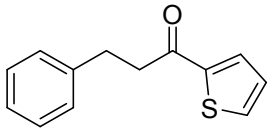
White solid, 127.6 mg, 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.87 (m, 3H), 7.67 (d, J = 8.3 Hz, 2H), 7.36 – 7.13 (m, 5H), 5.81 (s, 1H), 5.49 (s, 1H), 3.26 (t, J = 7.7 Hz, 2H), 3.04 (t, J = 7.7 Hz,

2H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.21, 166.91, 142.35, 141.32, 140.71, 132.67, 129.49, 128.60, 128.48, 126.22, 120.63, 119.37, 40.29, 30.31, 18.77. GC-MS (EI): 293.1, 278.1, 188.1, 121.1, 91.1, 69.1, 41.1. HRMS (ESI) calcd for $C_{19}H_{20}NO_2^+$ m/z $[M+H]^+$: 294.1489; found: 294.1484.



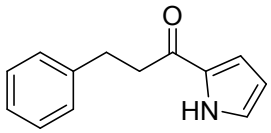
1-(furan-2-yl)-3-phenylpropan-1-one (**26b**)[19]

Light yellow oil, 85.8 mg, 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 1.8 Hz, 1H), 7.33 – 7.12 (m, 6H), 6.50 (dd, J = 3.6, 1.7 Hz, 1H), 3.18 – 3.10 (m, 2H), 3.08 – 3.00 (m, 2H).



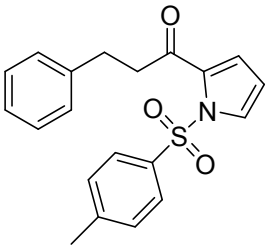
3-phenyl-1-(thiophen-2-yl)propan-1-one (**27b**)[19]

Colorless oil, 88.5 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 3.8, 1.2 Hz, 1H), 7.60 (dd, J = 4.9, 1.1 Hz, 1H), 7.32 – 7.17 (m, 5H), 7.09 (dd, J = 4.9, 3.8 Hz, 1H), 3.25 – 3.18 (m, 2H), 3.10 – 3.01 (m, 2H).



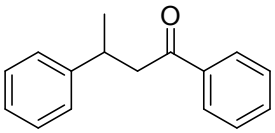
3-phenyl-1-(1H-pyrrol-2-yl)propan-1-one (**28b**)[27]

White solid, 89.8 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1H), 7.33 – 7.23 (m, 4H), 7.22 – 7.16 (m, 1H), 7.02 (td, J = 2.7, 1.3 Hz, 1H), 6.90 (ddd, J = 3.9, 2.5, 1.3 Hz, 1H), 6.26 (dt, J = 3.8, 2.5 Hz, 1H), 3.15 – 3.08 (m, 2H), 3.07 – 3.01 (m, 2H).



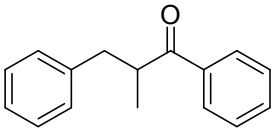
3-phenyl-1-(1-tosyl-1H-pyrrol-2-yl)propan-1-one (**29b**)

White solid, 160.7 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 2H), 7.80 (dd, J = 3.2, 1.7 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.20 – 7.09 (m, 3H), 6.99 (dd, J = 3.8, 1.7 Hz, 1H), 6.30 (t, J = 3.5 Hz, 1H), 3.02 – 2.96 (m, 2H), 2.94 – 2.87 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.74, 144.86, 141.08, 136.09, 133.23, 130.38, 129.48, 128.60, 128.44, 128.43, 126.24, 123.57, 110.39, 41.25, 30.63, 21.83. GC-MS (EI): 353.1, 248.0, 221.0, 198.0, 155.0, 91.0, 65.0. HRMS (ESI) calcd for $C_{20}H_{20}NO_3S^+$ m/z $[M+H]^+$: 354.1158; found: 354.1158.



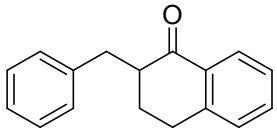
1,3-diphenylbutan-1-one (**30b**)[28]

White solid, 103.2 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.84 (m, 2H), 7.55 – 7.48 (m, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.34 – 7.22 (m, 4H), 7.21 – 7.13 (m, 1H), 3.57 – 3.43 (m, 1H), 3.28 (dd, J = 16.5, 5.7 Hz, 1H), 3.16 (dd, J = 16.5, 8.2 Hz, 1H), 1.33 (dd, J = 6.9, 1.2 Hz, 3H).



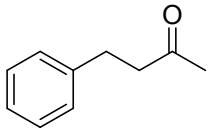
2-methyl-1,3-diphenylpropan-1-one (**31b**)[29]

Colorless oil, 87.5 mg, 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.86 (m, 2H), 7.55 – 7.49 (m, 1H), 7.45 – 7.39 (m, 2H), 7.29 – 7.22 (m, 2H), 7.22 – 7.13 (m, 3H), 3.82 – 3.66 (m, 1H), 3.17 (dd, J = 13.7, 6.3 Hz, 1H), 2.69 (dd, J = 13.7, 7.8 Hz, 1H), 1.19 (d, J = 6.9 Hz, 3H).



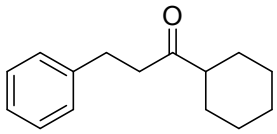
2-benzyl-3,4-dihydronaphthalen-1(2H)-one (**32b**)[30]

Colorless oil, 93.4 mg, 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, J = 7.8, 1.5 Hz, 1H), 7.44 (td, J = 7.5, 1.5 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.26 – 7.17 (m, 4H), 3.49 (dd, J = 13.6, 3.9 Hz, 1H), 2.99 – 2.83 (m, 2H), 2.73 (ddt, J = 11.4, 9.6, 4.2 Hz, 1H), 2.64 (dd, J = 13.6, 9.6 Hz, 1H), 2.09 (dq, J = 13.4, 4.5 Hz, 1H), 1.77 (dddd, J = 13.4, 11.6, 10.0, 5.6 Hz, 1H).



4-phenylbutan-2-one (**33b**)[31]

Colorless oil, 42.9 mg, 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.23 – 7.14 (m, 3H), 2.90 (t, J = 7.6 Hz, 2H), 2.76 (t, J = 7.6 Hz, 2H), 2.14 (s, 3H).

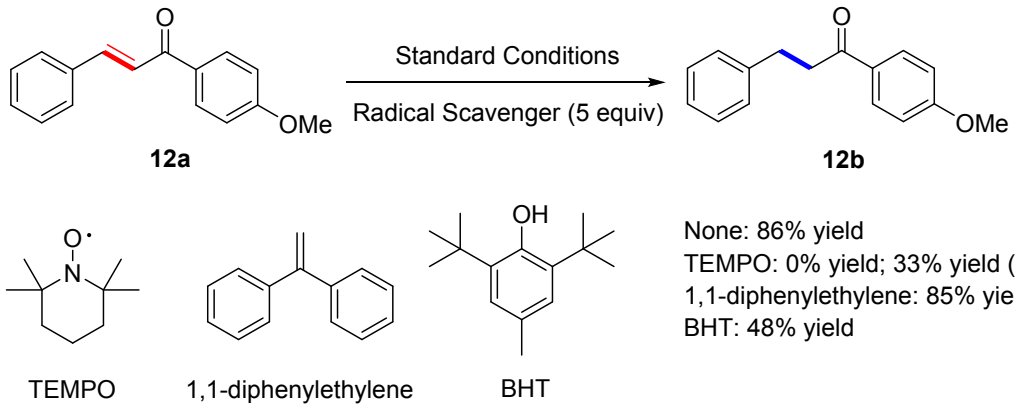


1-cyclohexyl-3-phenylpropan-1-one (**34b**)[18]

White solid, 56.2 mg, 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 7.5 Hz, 2H), 7.17 (dd, J = 7.4, 5.0 Hz, 3H), 2.87 (t, J = 7.6 Hz, 2H), 2.74 (t, J = 7.6 Hz, 2H), 2.30 (tt, J = 11.2, 3.6 Hz, 1H), 1.88 – 1.71 (m, 4H), 1.69 – 1.60 (m, 1H), 1.38 – 1.14 (m, 5H).

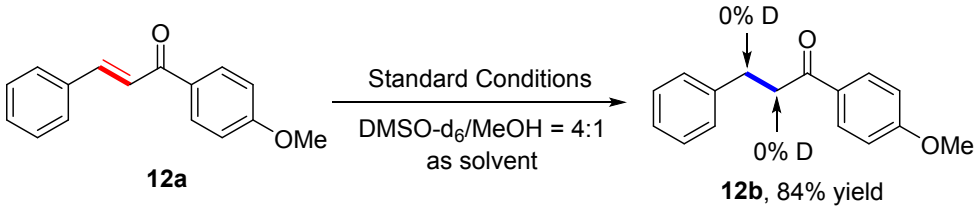
3. Mechanistic Studies

Radical trapping experiments



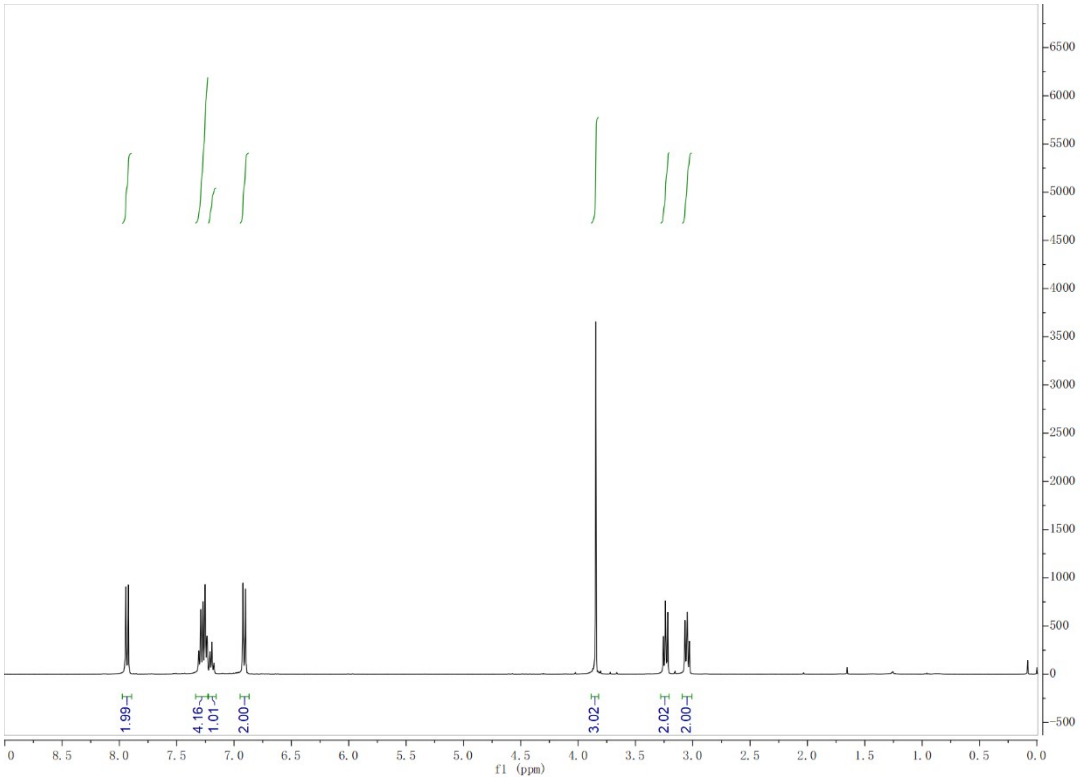
A series of radical scavenger addition experiments were performed. Among the tested reagents, TEMPO appeared to be the most effective one. These results indicate that a radical process is likely to be involved in this reaction.

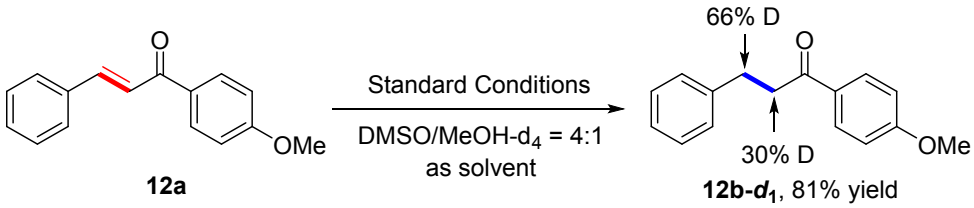
Deuterium labeling experiments



Eq. 1

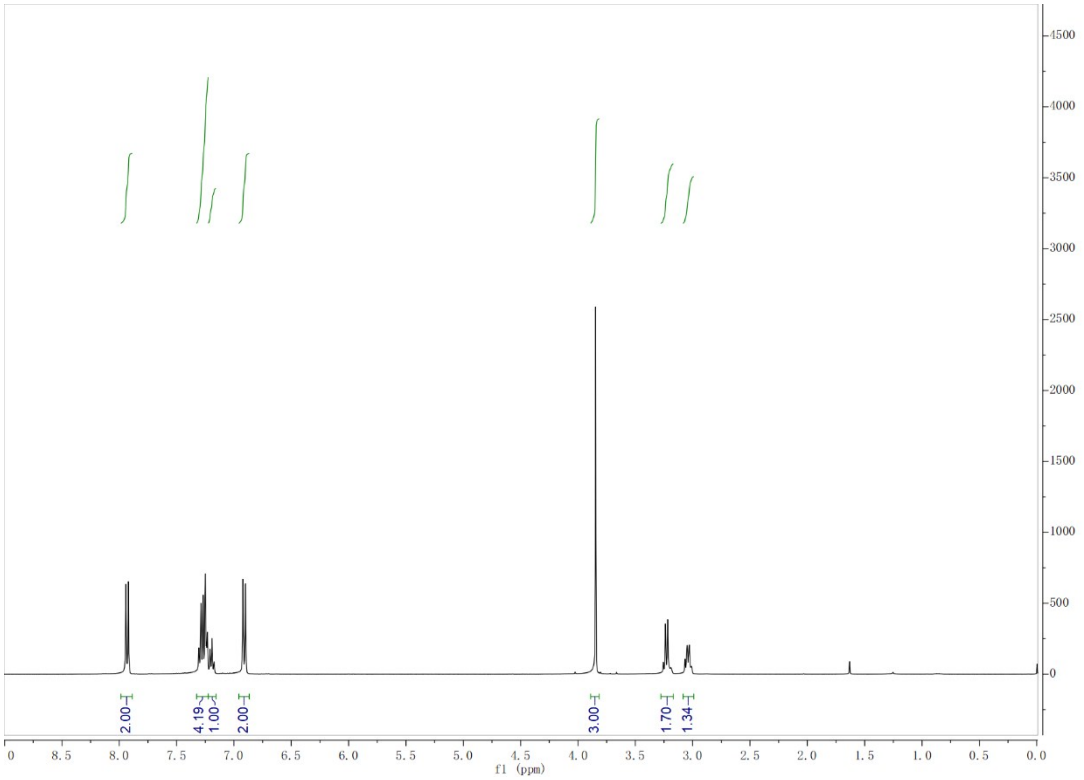
Follow the **General Procedure**, the reaction of **12a** was carried out with a mixed solvent of DMSO-d_6 and methanol (4:1 *v:v*, 10 mL). **12b** was isolated in 84% yield, and the ^{1}H NMR spectrum showed 0% *d*-incorporation at either α or β position:

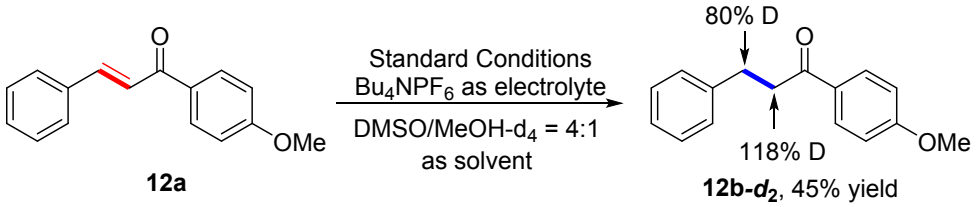




Eq. 2

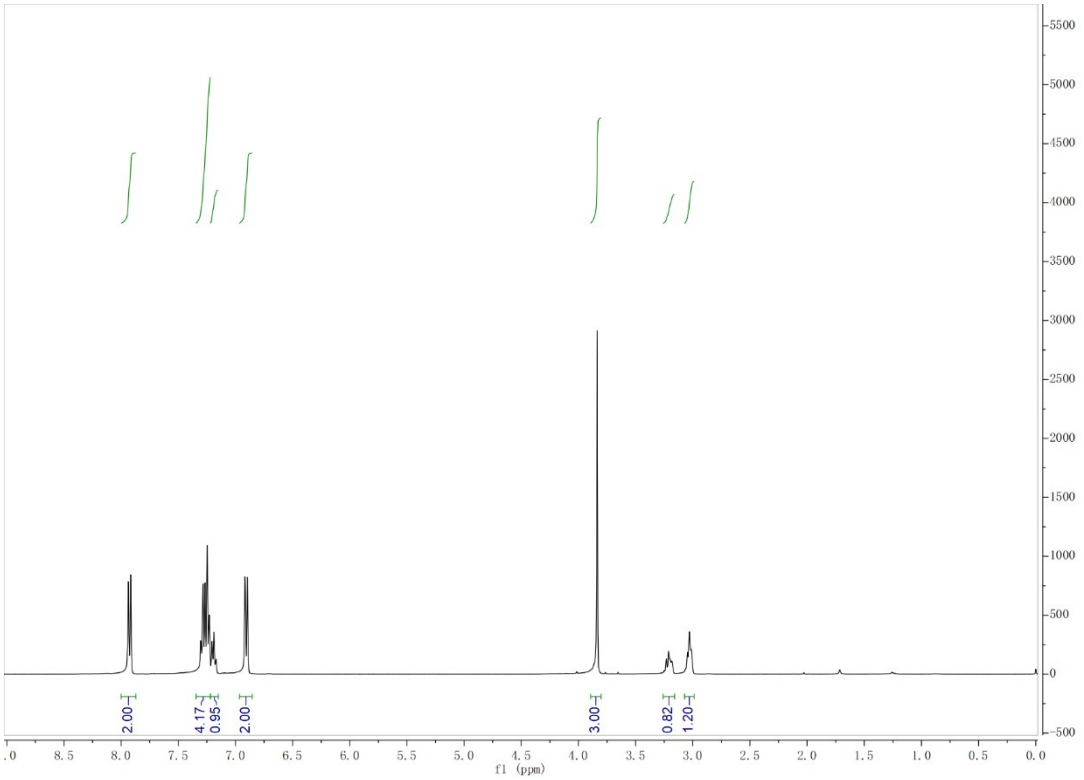
Follow the **General Procedure**, the reaction of **12a** was carried out with a mixed solvent of DMSO and methanol-d_4 (4:1 *v:v*, 10 mL). **12b-*d*$_1$** was isolated in 81% yield, and the ^{1}H NMR spectrum showed 66% *d*-incorporation at the β position and 30% *d*-incorporation at α position:



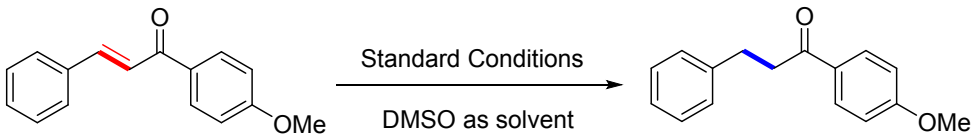


Eq. 3

Follow the **General Procedure**, the reaction of **12a** was carried out with a mixed solvent of DMSO and methanol-d_4 (4:1 *v:v*, 10 mL), and the electrolyte NH_4Cl was replaced with Bu_4NPF_6 at the same time. **12b-*d*$_2$** was isolated in 45% yield, and the ^{1}H NMR spectrum showed 80% *d*-incorporation at the β position and 118% *d*-incorporation at α position:



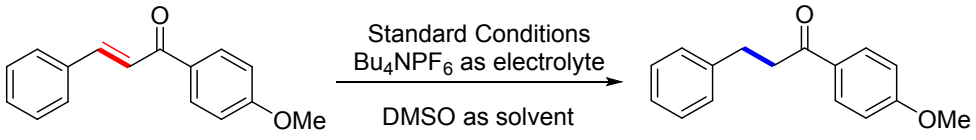
Further control experiments



12a **12b**, 58% yield

Eq. 4

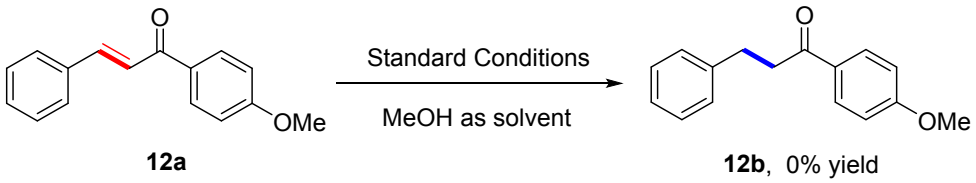
Follow the **General Procedure**, the reaction of **12a** was carried out with DMSO (10 mL) as solvent. **12b** was isolated in 58% yield.



12a **12b**, 0% yield

Eq. 5

Follow the **General Procedure**, the reaction of **12a** was carried out with DMSO (10 mL) as solvent, and the electrolyte NH_4Cl was replaced with Bu_4NPF_6 at the same time. No **12b** was detected after the process.

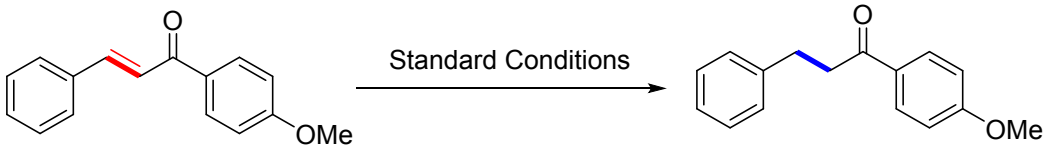


12a **12b**, 0% yield

Eq. 6

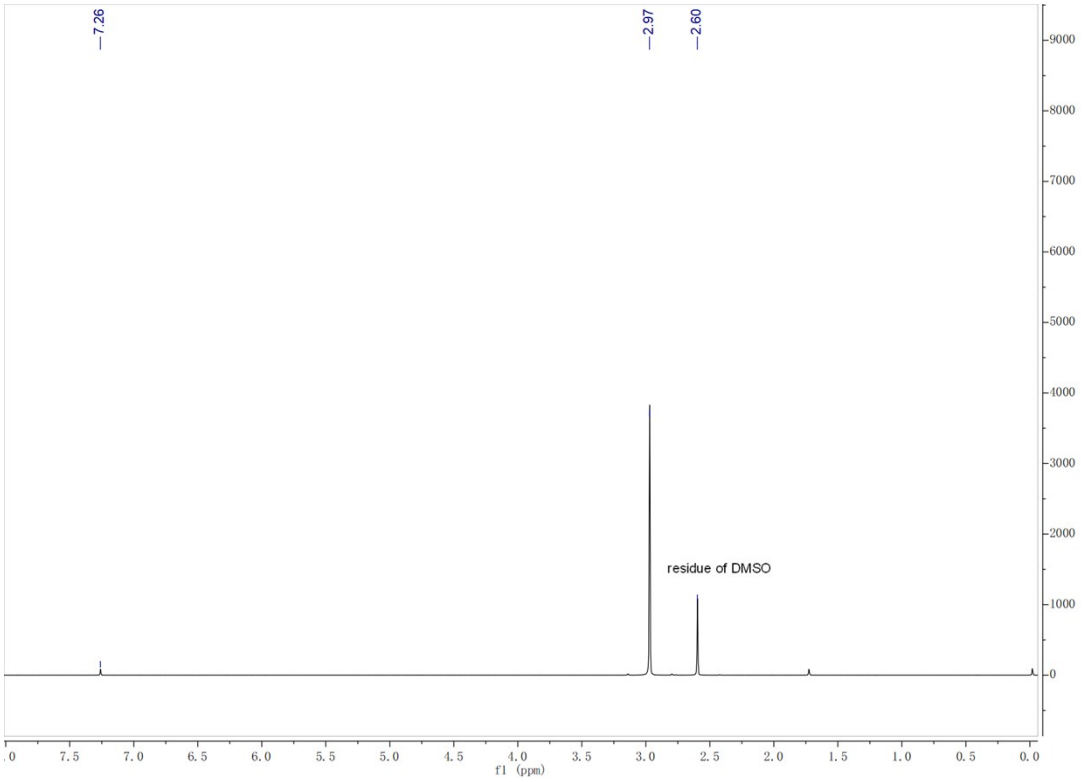
Follow the **General Procedure**, the reaction of **12a** was carried out with methanol (10 mL) as solvent. No **12b** was detected after the process.

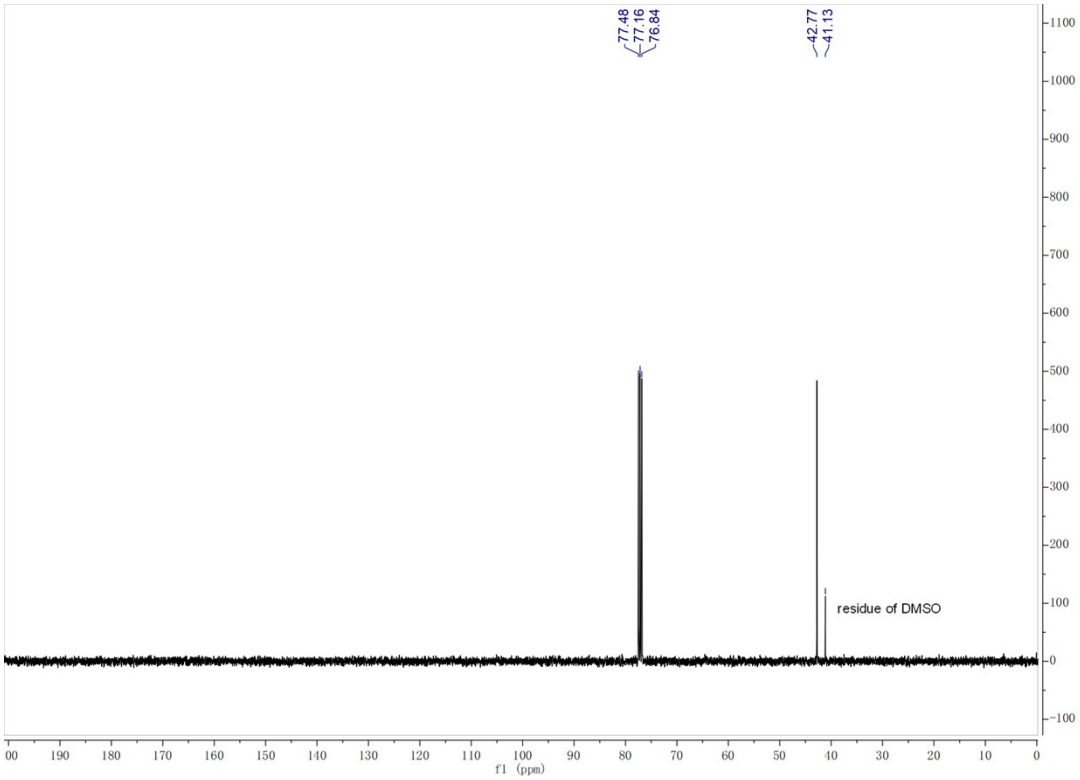
Isolation of methyl sulfone



12a **12b**

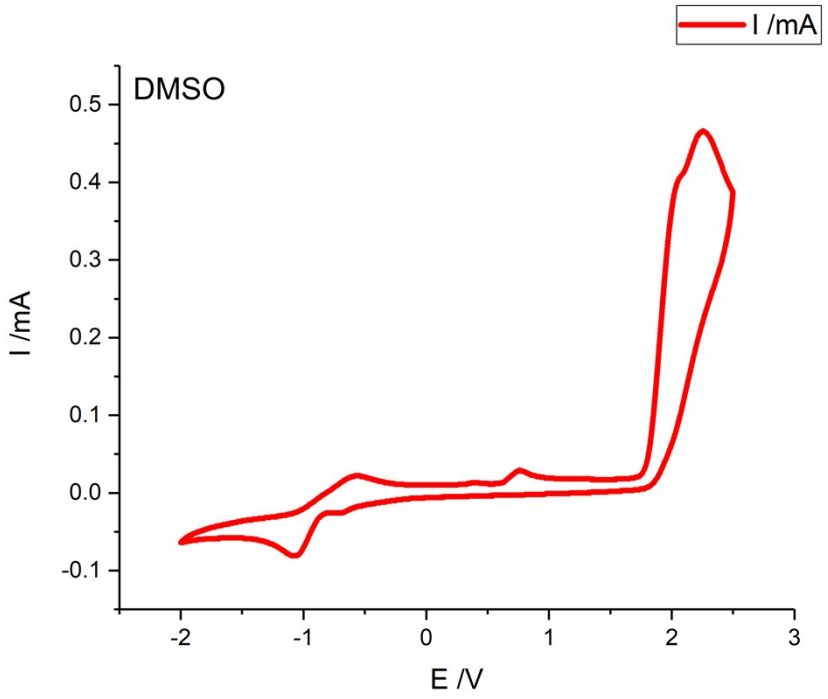
A typical reaction of **12a** was carried out and approximately 2 mL of the resulting reaction mixture was taken and directly subjected to column chromatography purification. The product was identified as methyl sulfone. NMR spectra are listed as follow[32]:



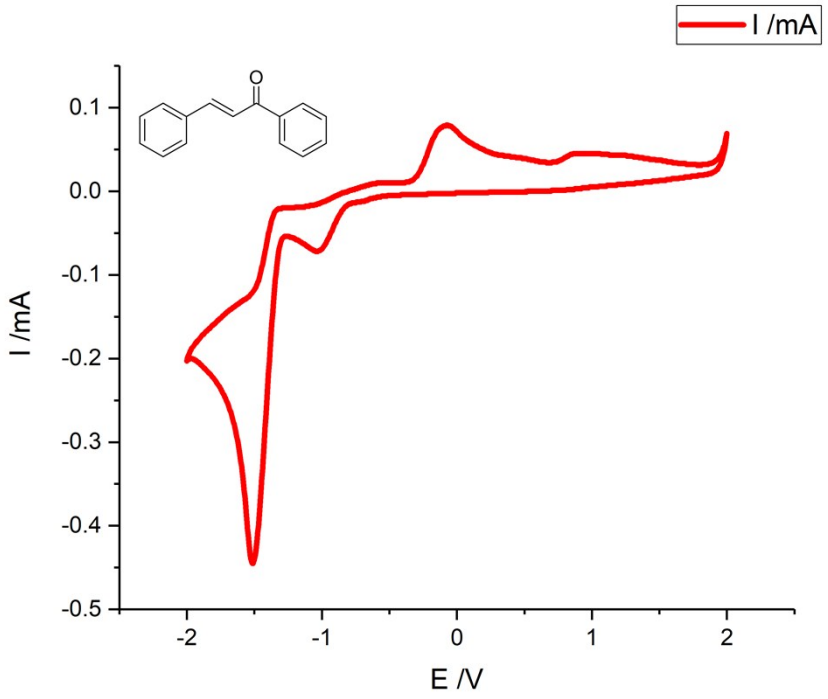


Electrochemical Potential Measurements

Cyclic voltammograms were collected with a Potentiostat. Samples were prepared with 0.2 mmol of substrate in 10 mL of 0.1 M Bu_4NPF_6 in dry, degassed acetonitrile. Measurements employed a glassy carbon working electrode, platinum plate counter electrode and a 3.5 M NaCl silver-silver chloride reference electrode. The applied scan rate was 0.1 V/s. Maximum current (C_p) of each substrate was obtained using Origin and the potential ($E_{p/2}$) was then determined at half of this value ($C_{p/2}$). Note the obtained $E_{p/2}$ was referenced to Ag| AgCl, it was converted to SCE by subtracting 0.03 V.

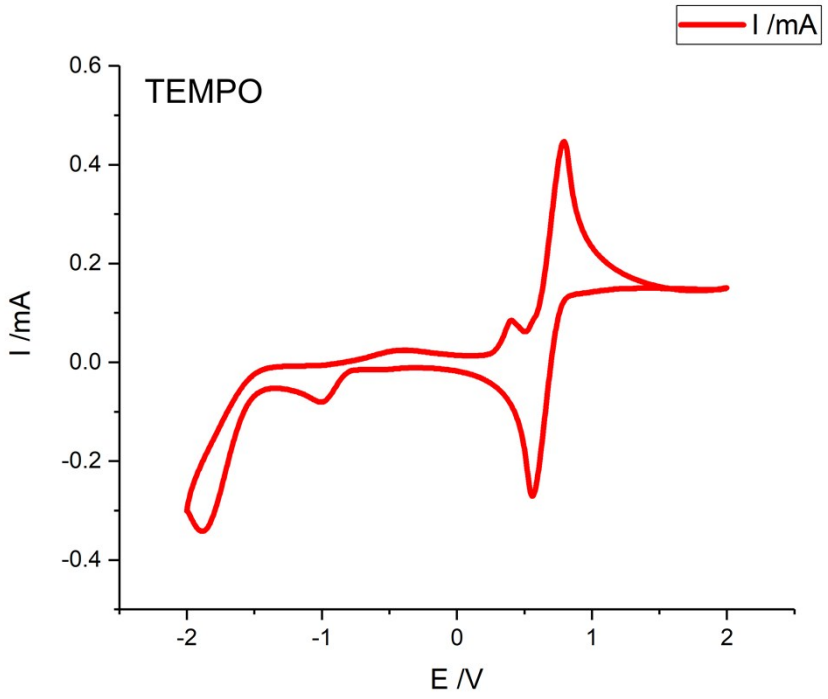


C_p (DMSO) = 0.466 mA; $C_{p/2}$ (DMSO) = 0.233 mA; $E_{p/2}$ (DMSO) = 1.92V (1.89V vs. SCE)



C_p (chalcone) = - 0.445 mA; $C_{p/2}$ (chalcone) = - 0.223 mA;

$E_{p/2}$ (chalcone) = -1.40 V (-1.43 V vs. SCE)



C_p (TEMPO) = 0.447 mA; $C_{p/2}$ (TEMPO) = 0.224 mA; $E_{p/2}$ (TEMPO) = 0.66 V (0.63 V vs. SCE)

*NH_4Cl and methanol exhibit no obvious redox peak in the tested region (-3 V to 3 V).

4. References

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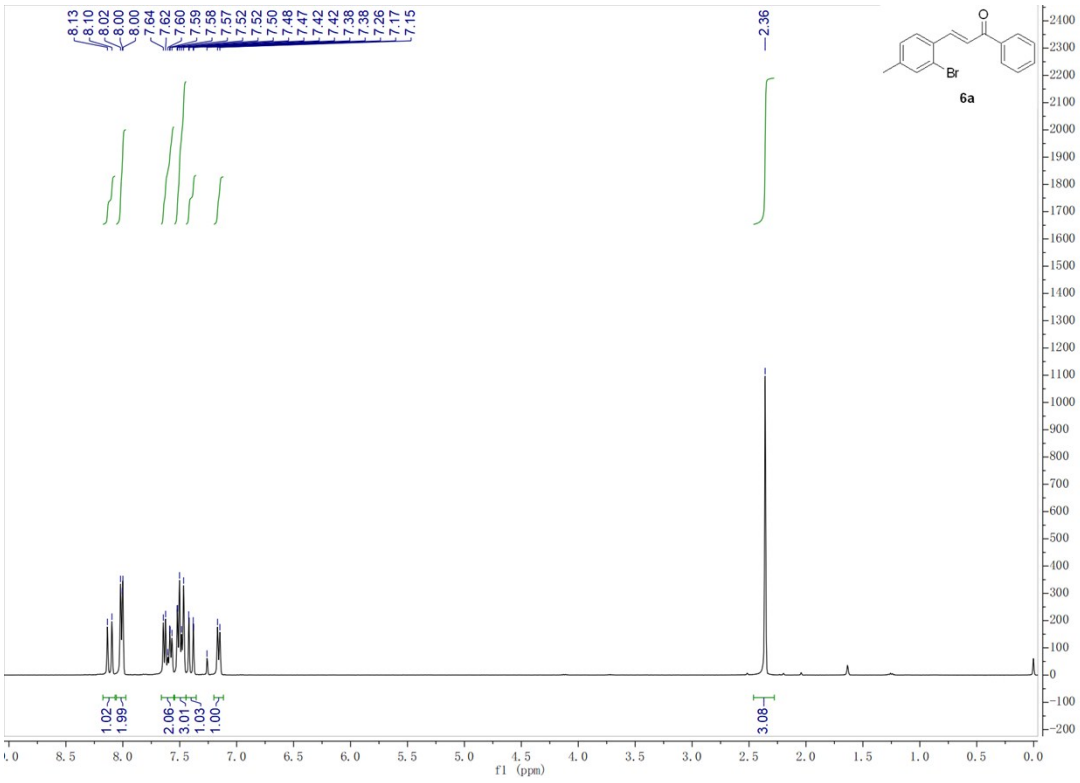
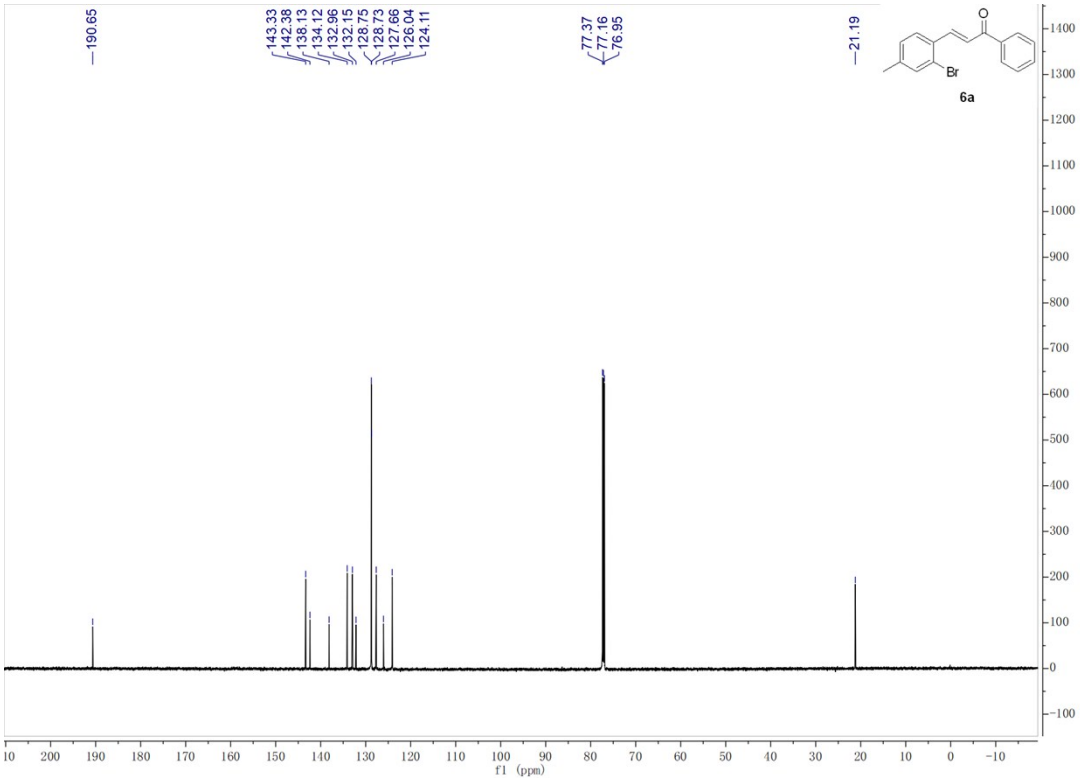
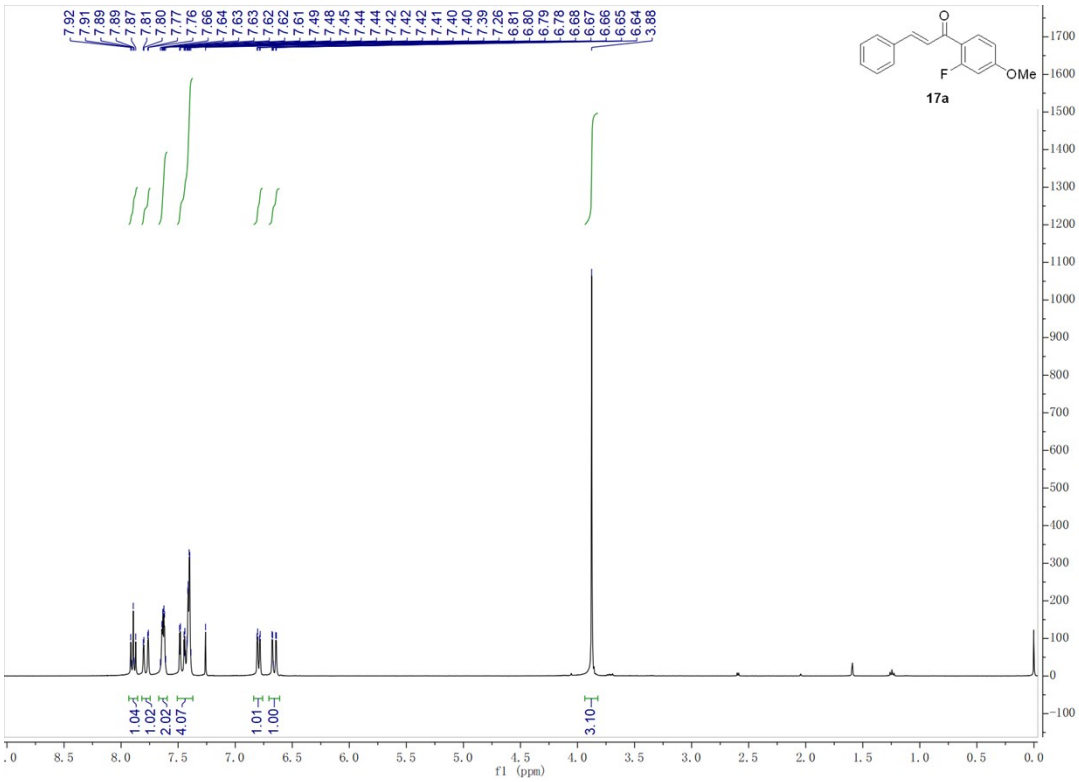
5. NMR Spectra



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O
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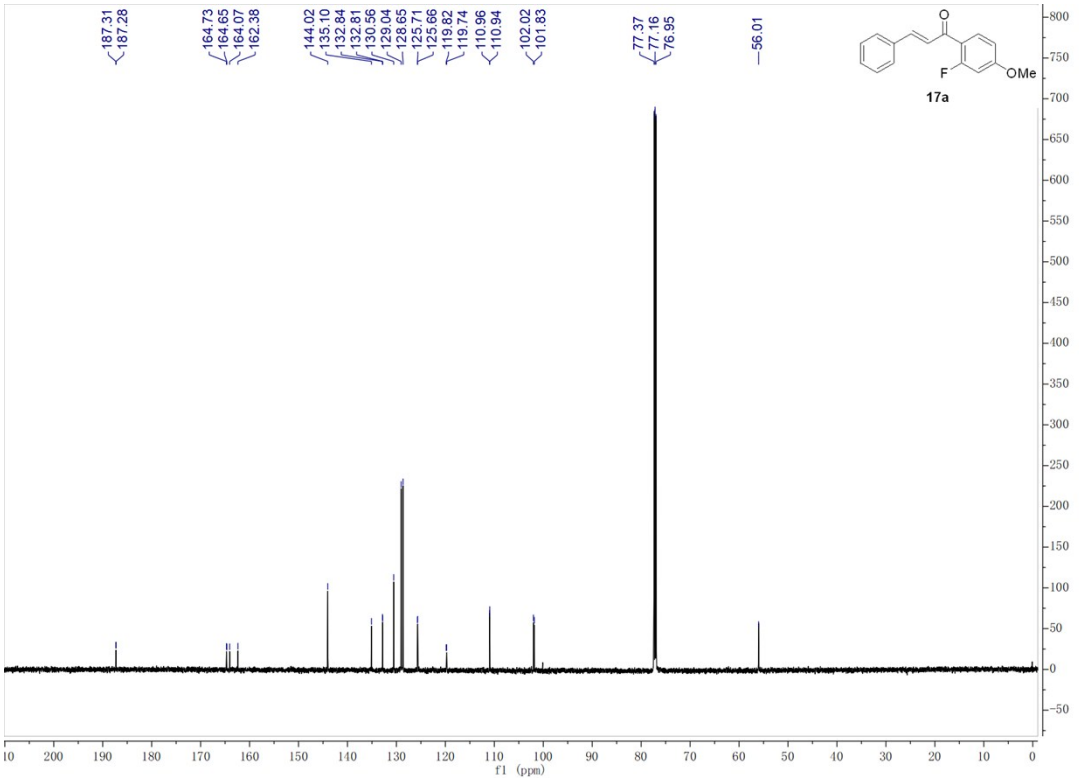
OMe
17a
1.04
1.02
2.02
4.07
1.01
1.00
3.10
f1 (ppm)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162.38
144.02
135.10
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132.81
130.56
129.04
128.65
125.71
125.66
119.82
119.74
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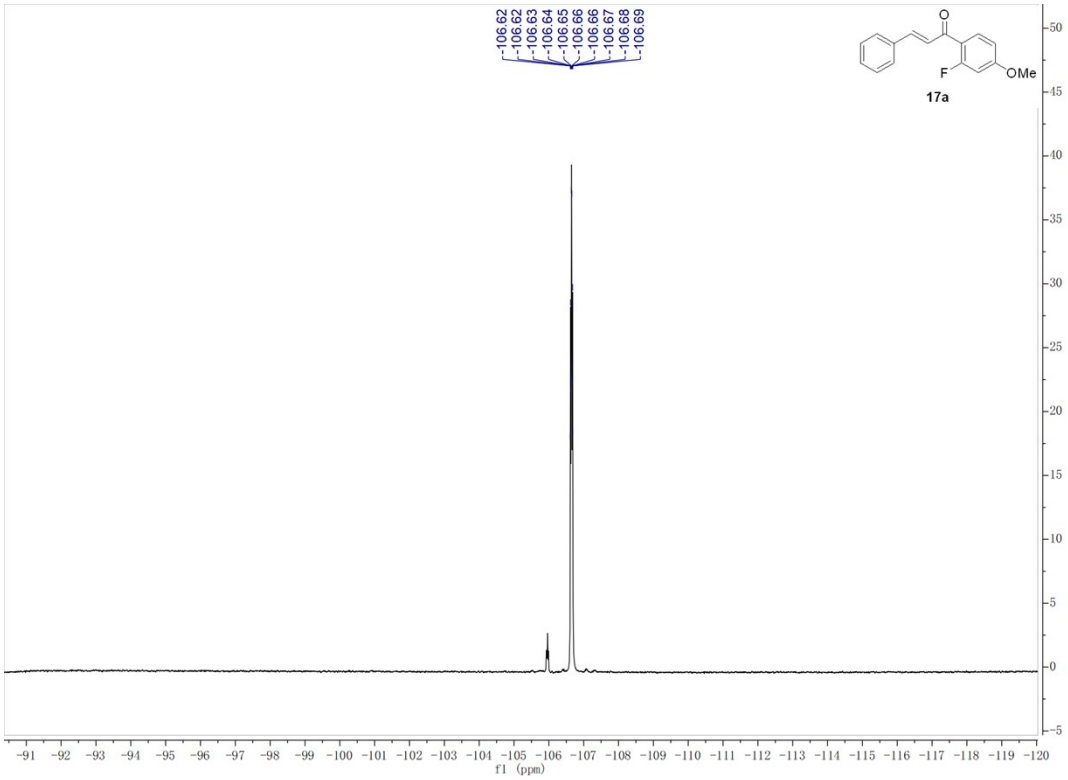
110.94
102.02
101.83
77.37
77.16
76.95
56.01
O
F
OMe
17a
f1 (ppm)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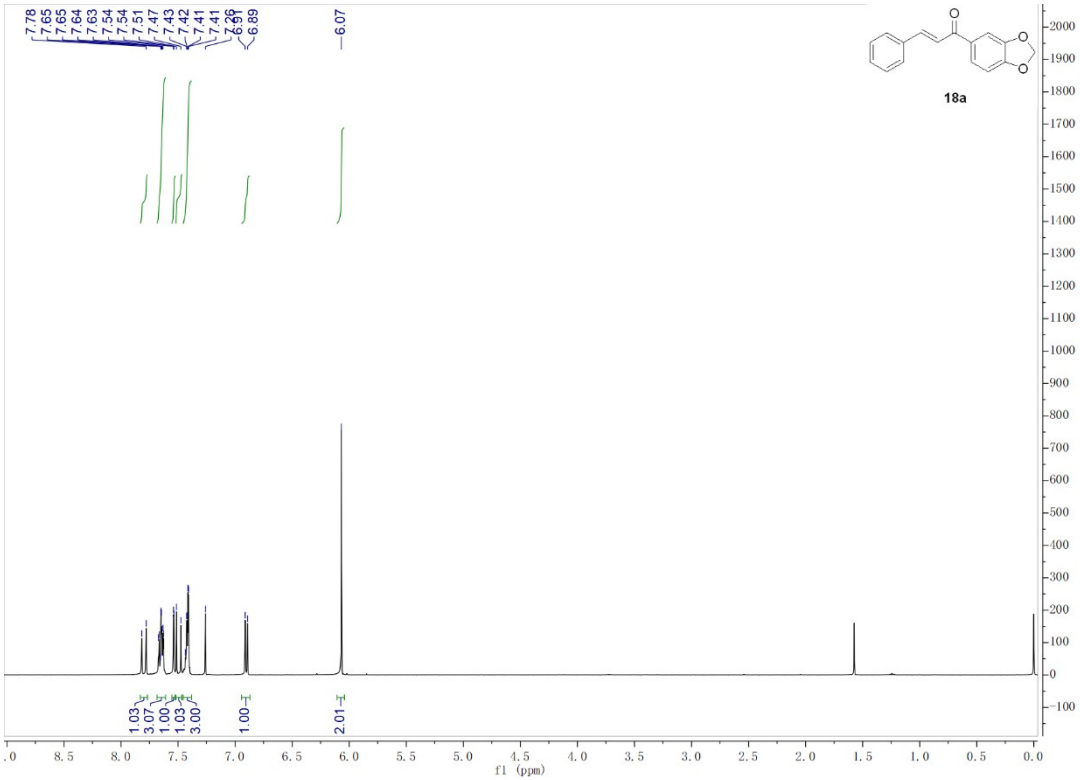
-106.69
F
OMe
17a
f1 (ppm)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7.41
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18a
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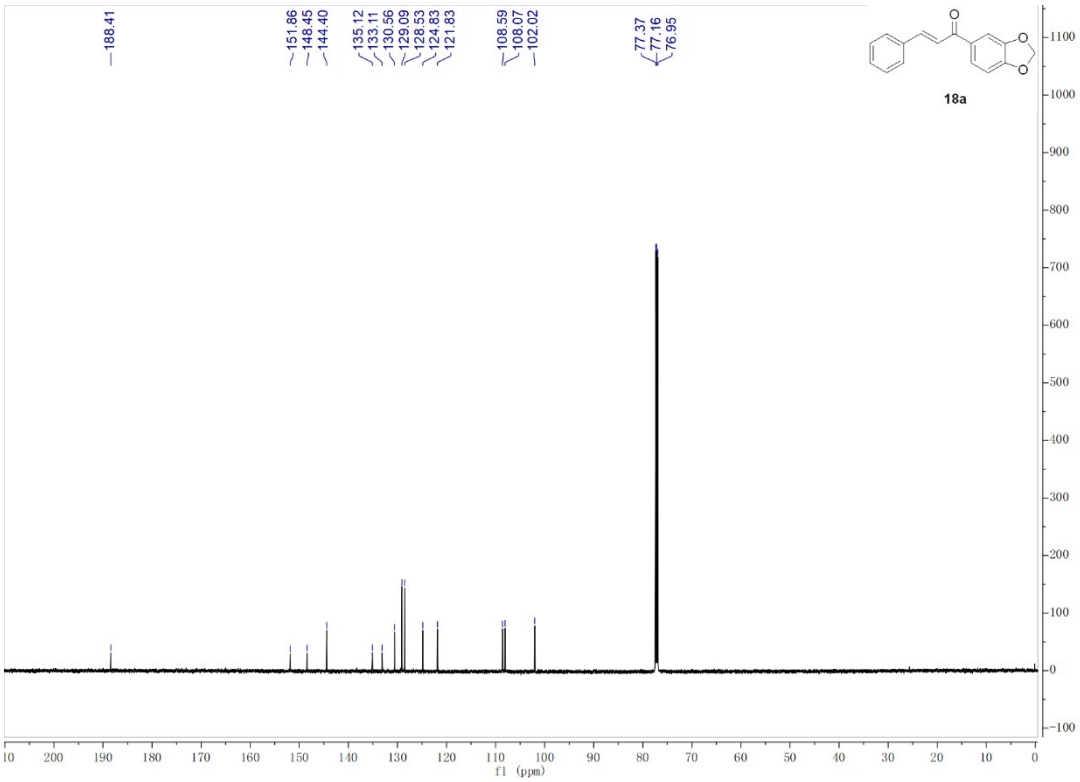
3.07
1.00
1.03
3.00
1.00
2.01
f1 (ppm)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121.83
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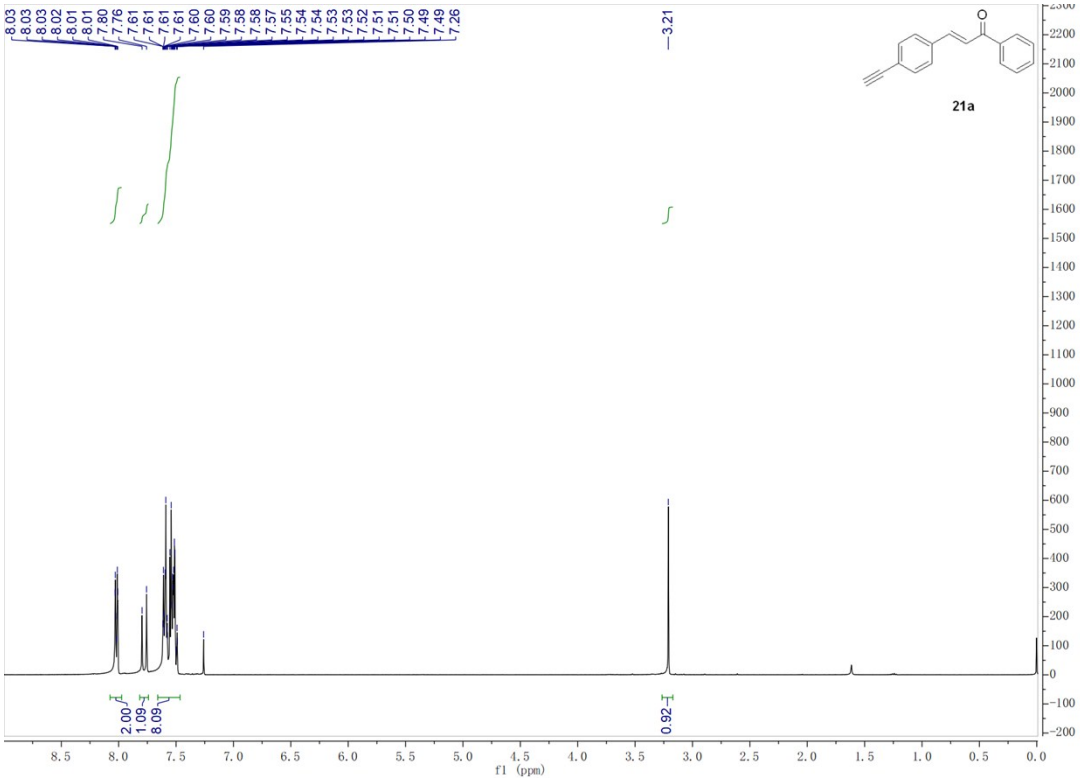
108.07
102.02
77.37
77.16
76.95
18a
f1 (ppm)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7.51
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7.49
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21a
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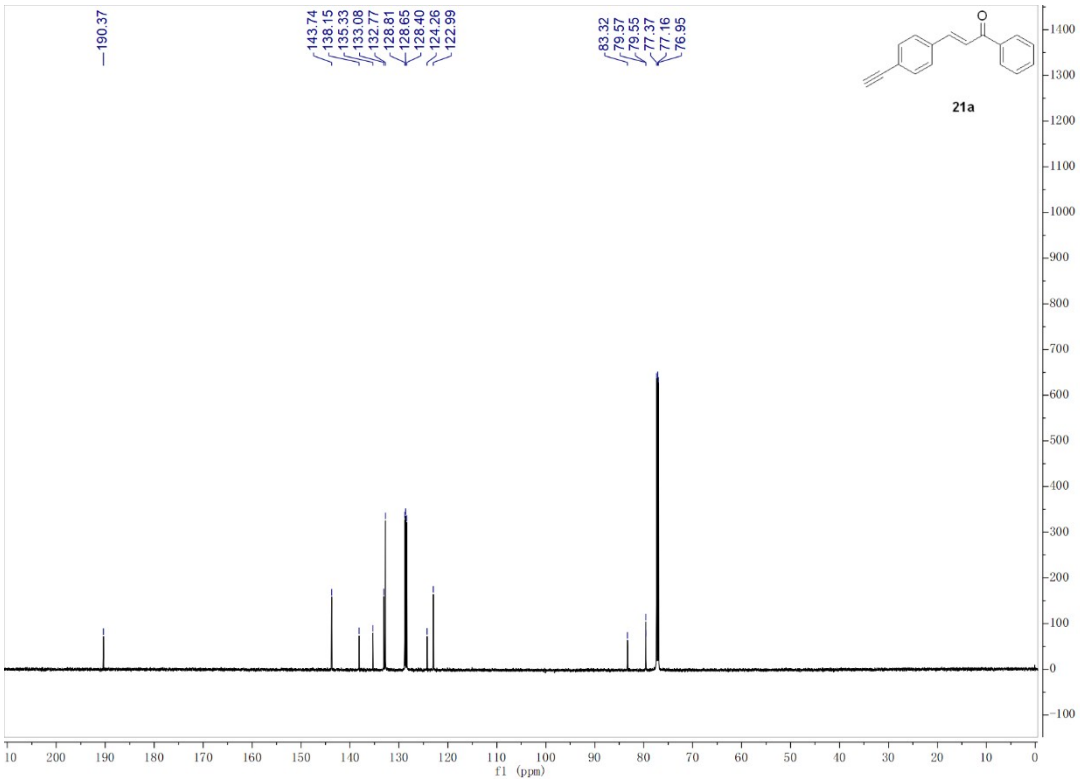
8.09
0.92
f1 (ppm)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128.81
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122.99
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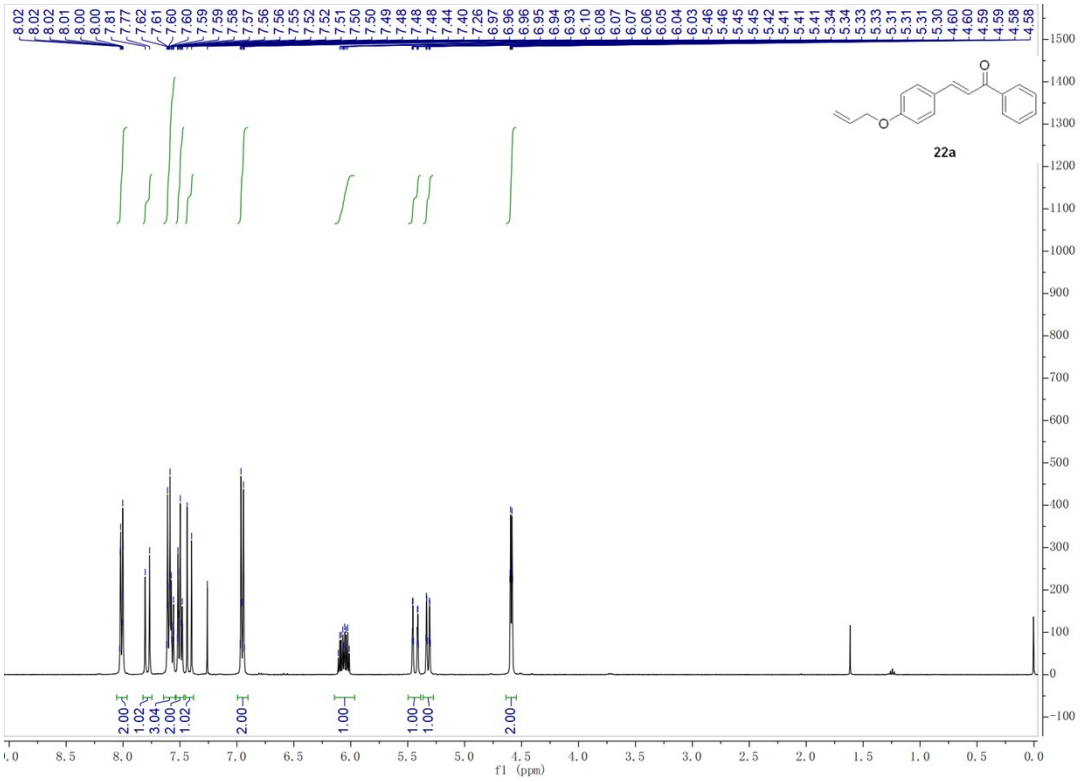
79.55
77.37
77.16
76.95
21a
f1 (ppm)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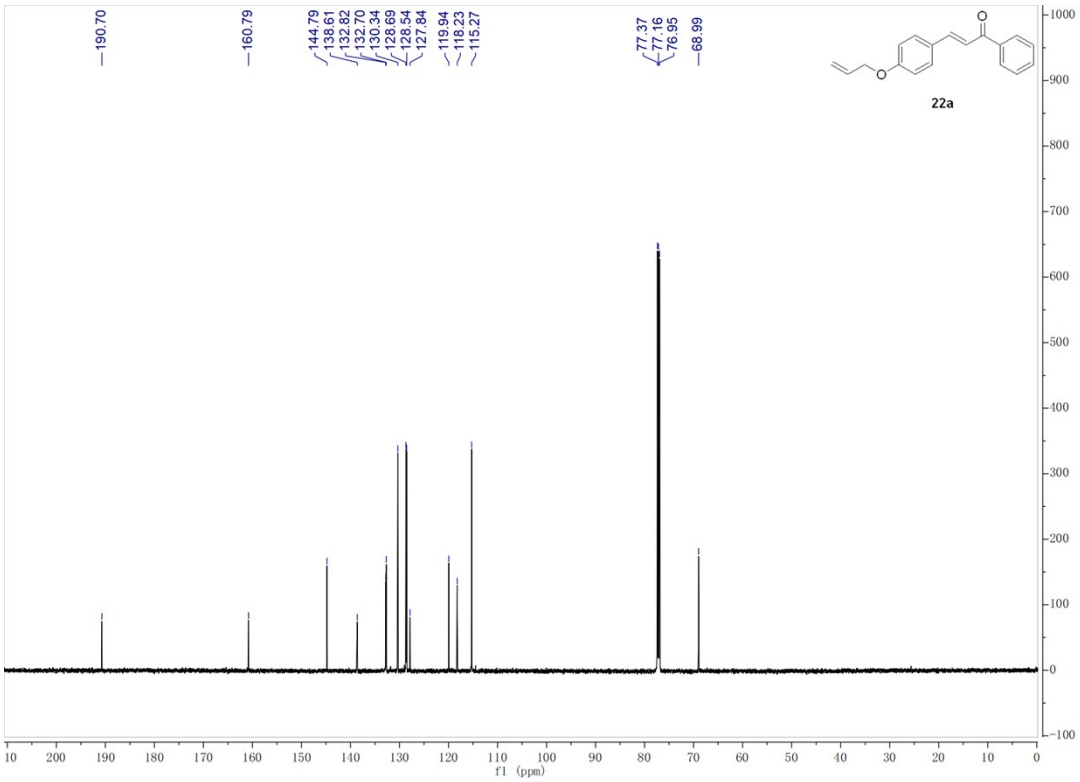
f1 (ppm)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115.27
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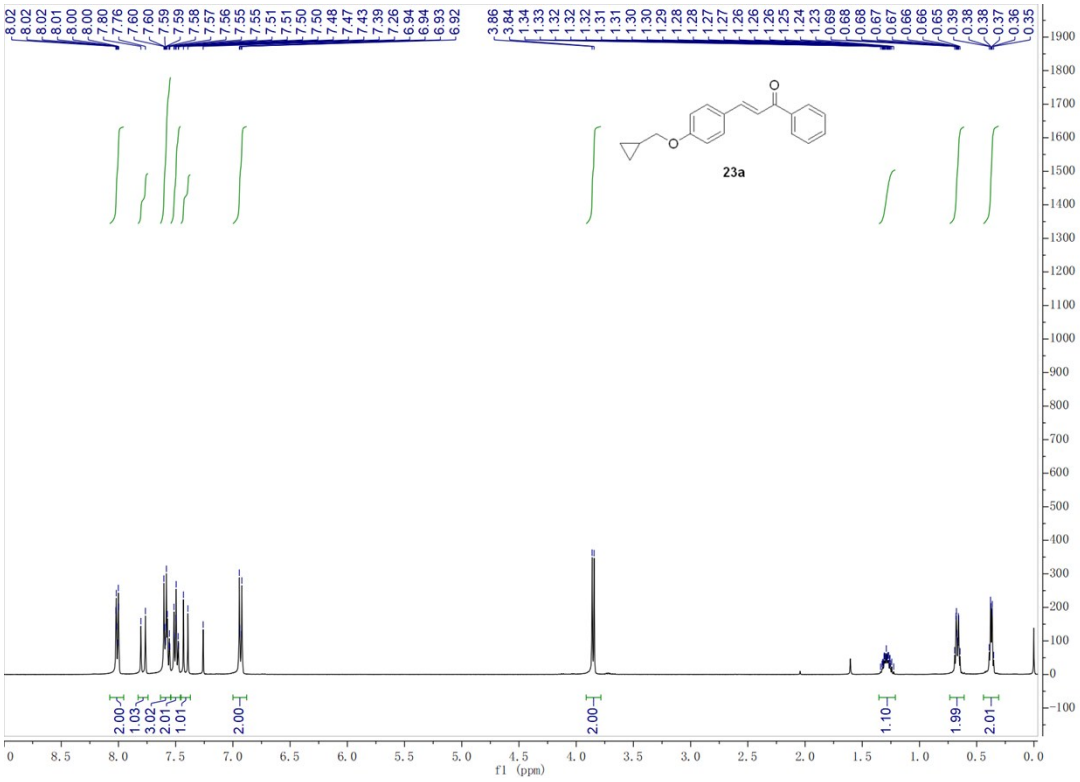
77.16
76.95
68.99
22a
f1 (ppm)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7.48
7.47
7.43
7.39
7.26
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6.93
6.92
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1.33
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1.32
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1.28
1.28
1.27
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1.26
1.26
1.25
1.24
1.23
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0.68
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0.39
0.38
0.38
0.37
0.36
0.35
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1.01
2.00
2.00
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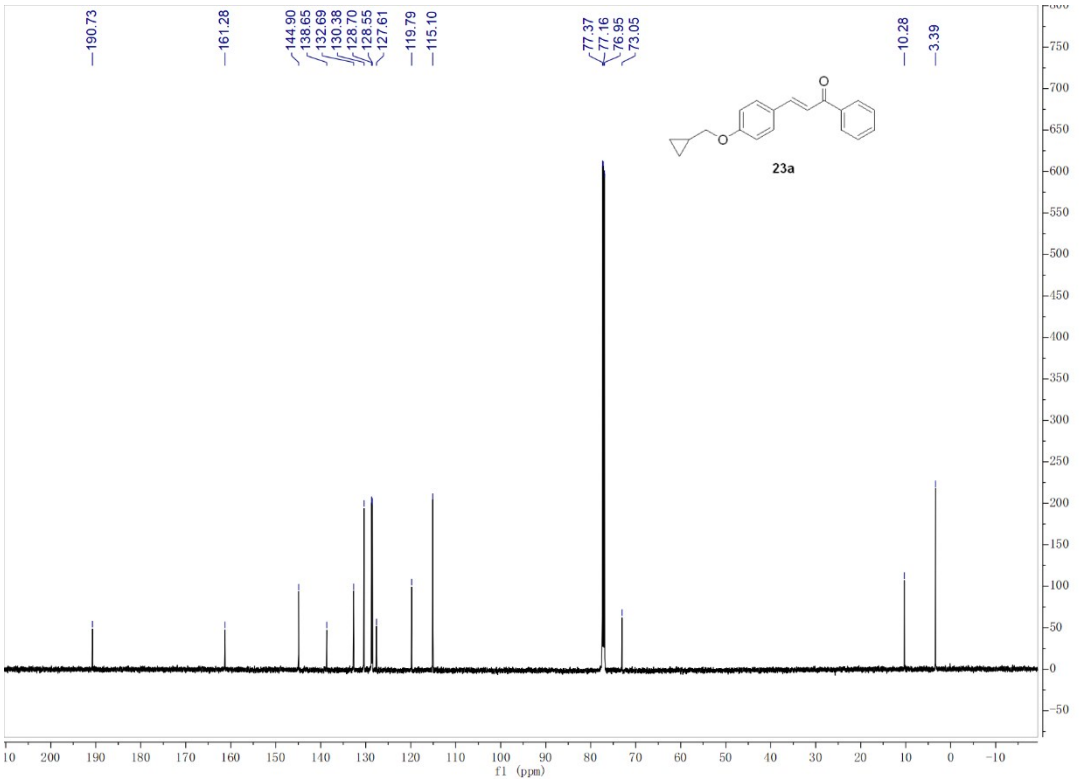
1.99
2.01
f1 (ppm)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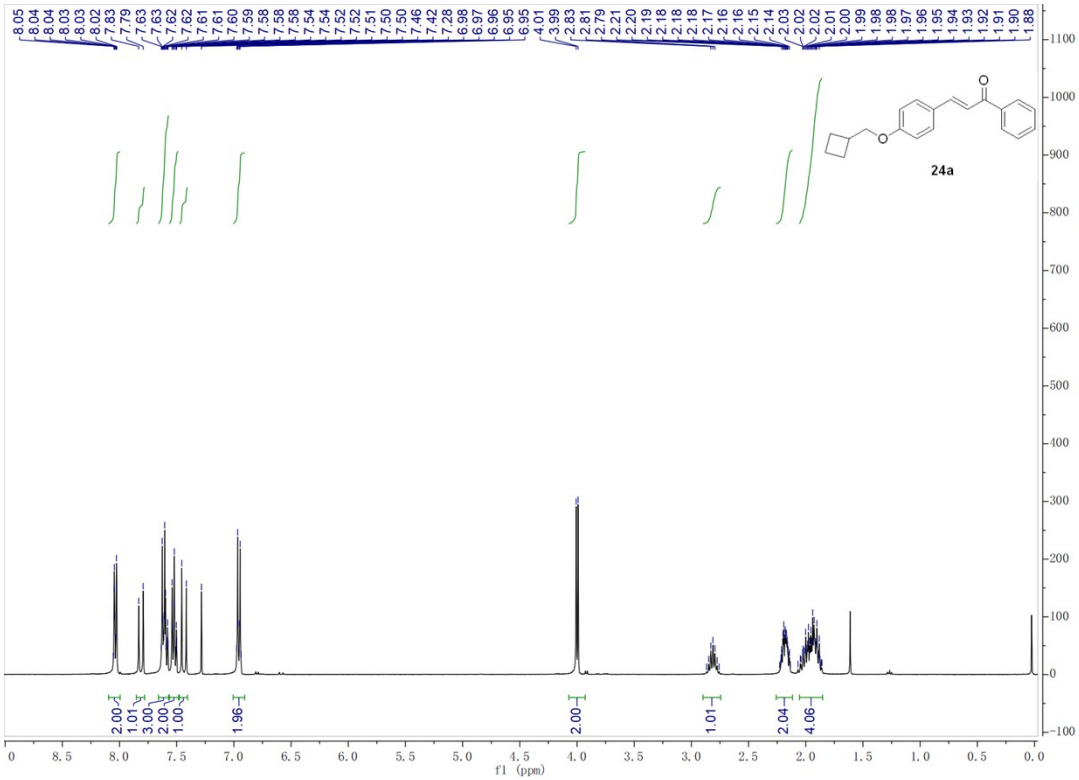
77.16
76.95
73.05
10.28
3.39
23a
f1 (ppm)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2.00
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4.06
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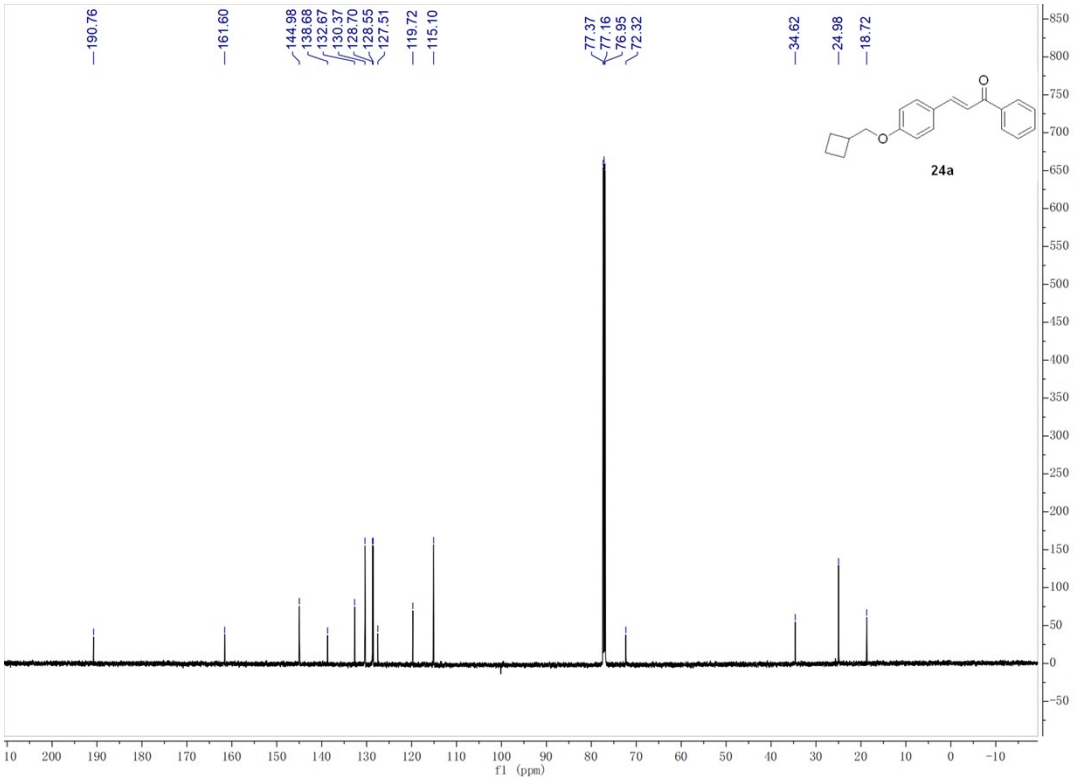
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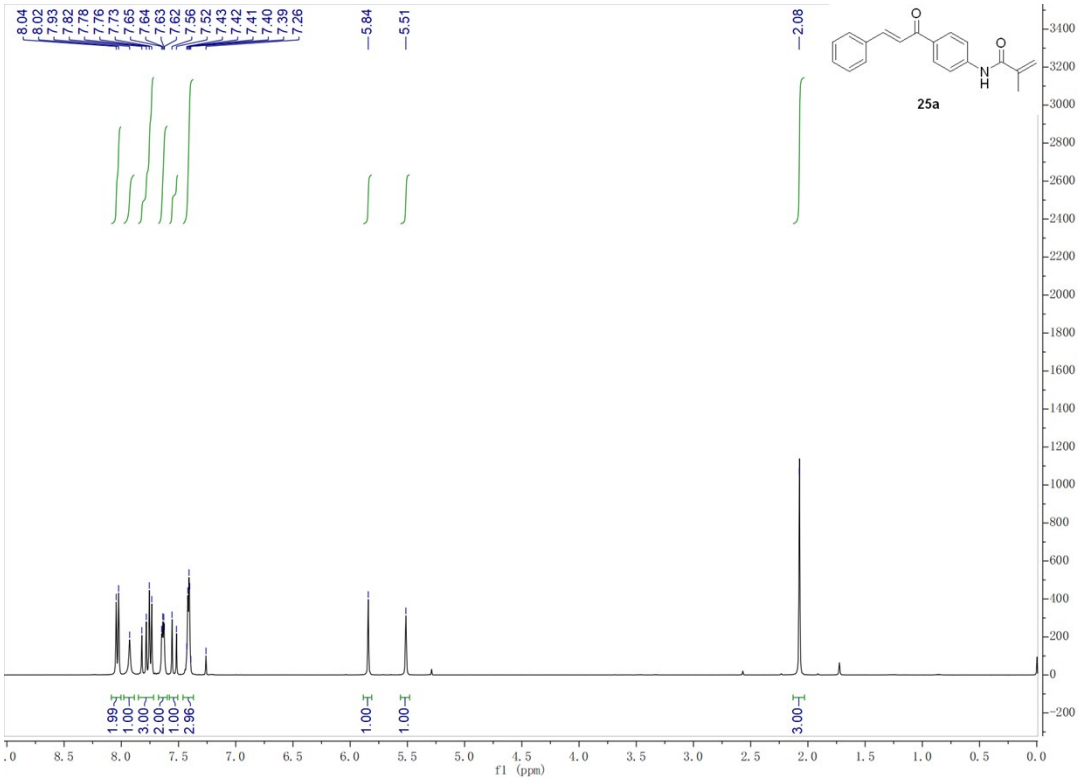
24a
f1 (ppm)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7.43
7.42
7.41
7.40
7.39
7.26
5.84
5.51
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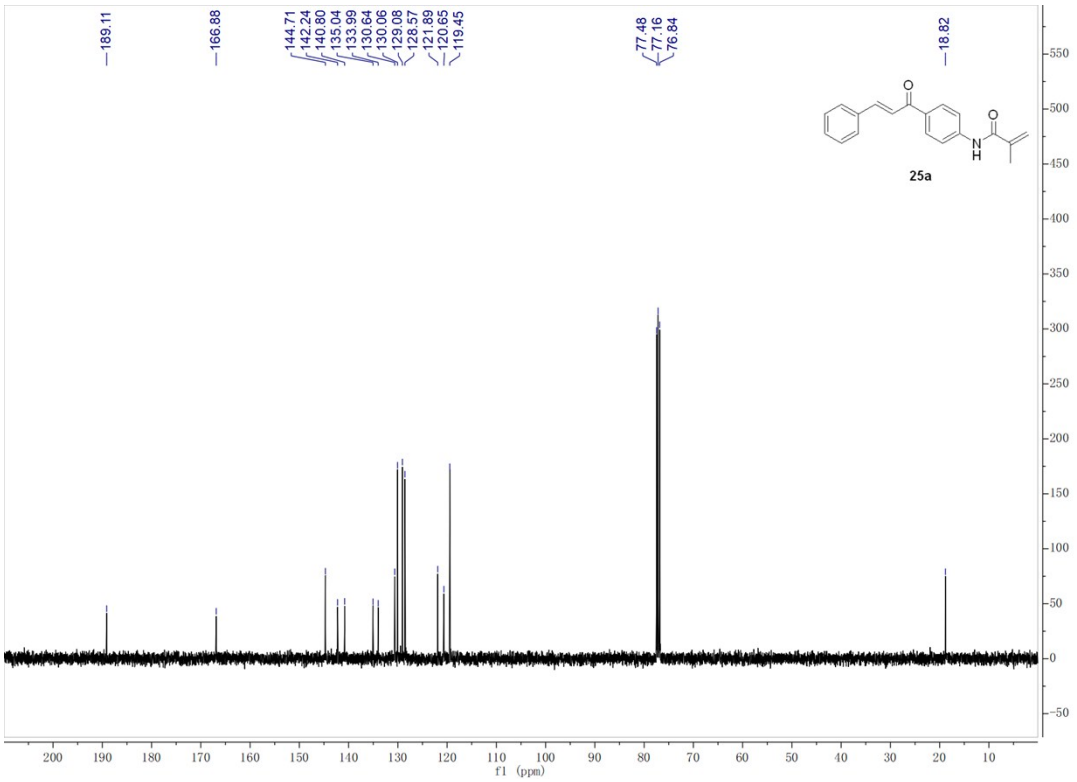
1.00
1.00
3.00
25a
f1 (ppm)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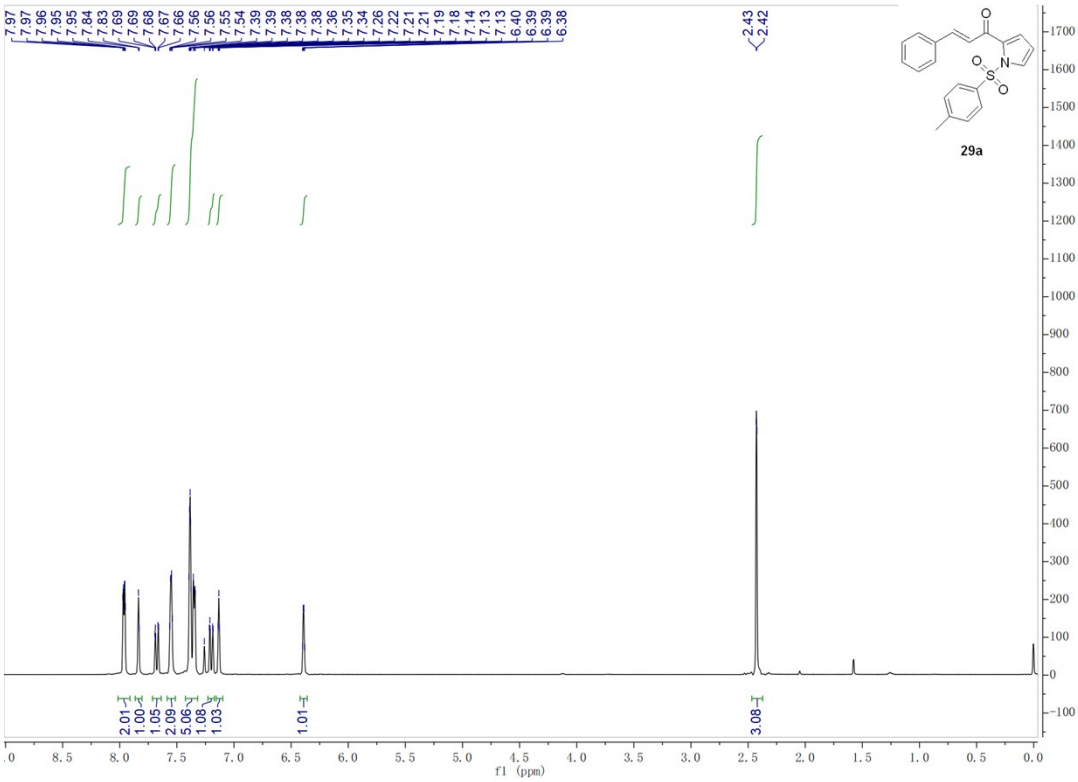
76.84
18.82
25a
f1 (ppm)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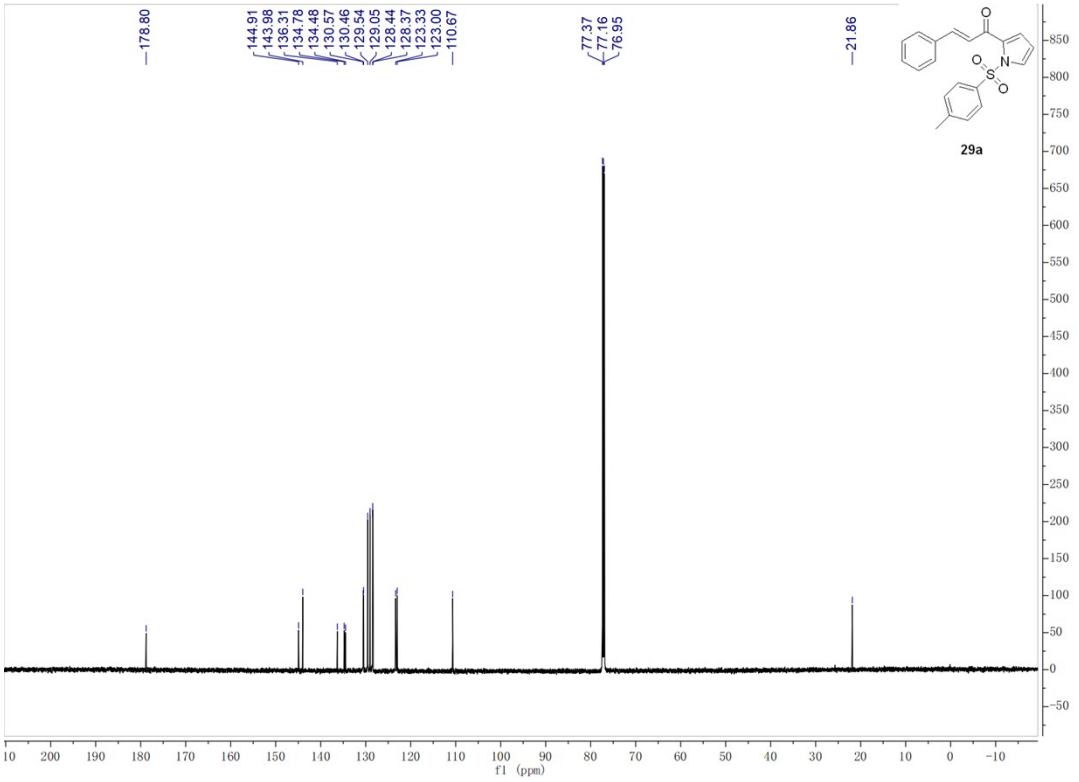
1.08
1.03
1.01
3.08
f1 (ppm)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77.16
76.95
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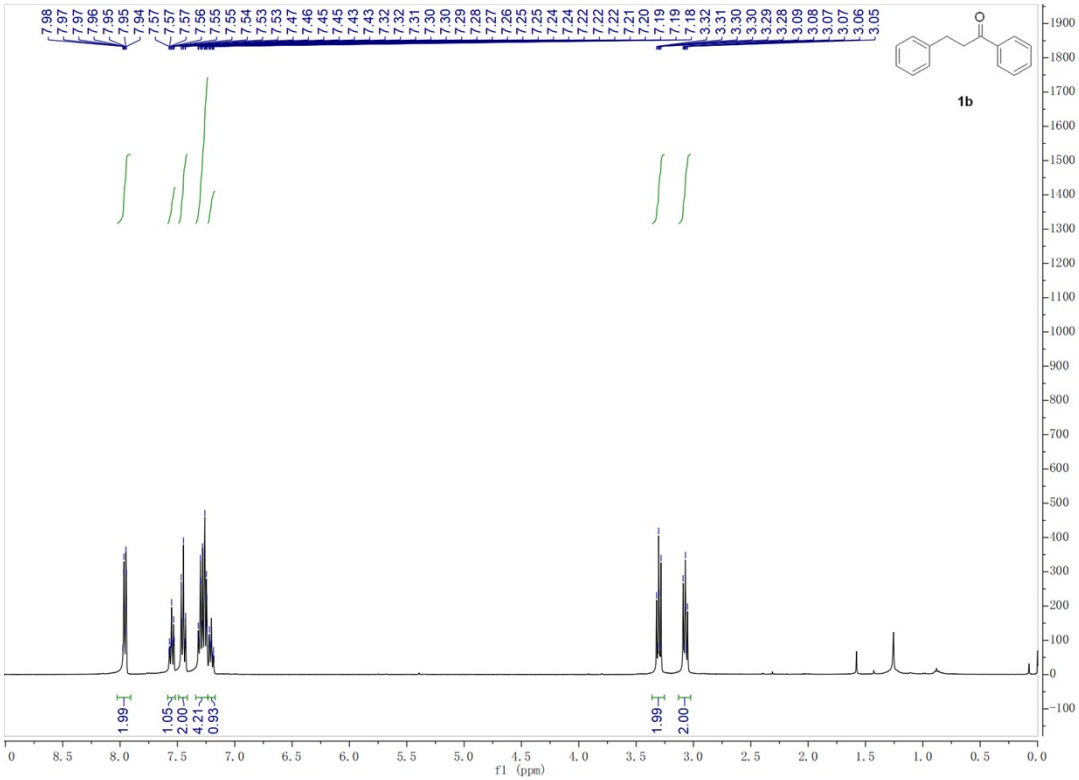
29a
f1 (ppm)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3.08
3.07
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2.00
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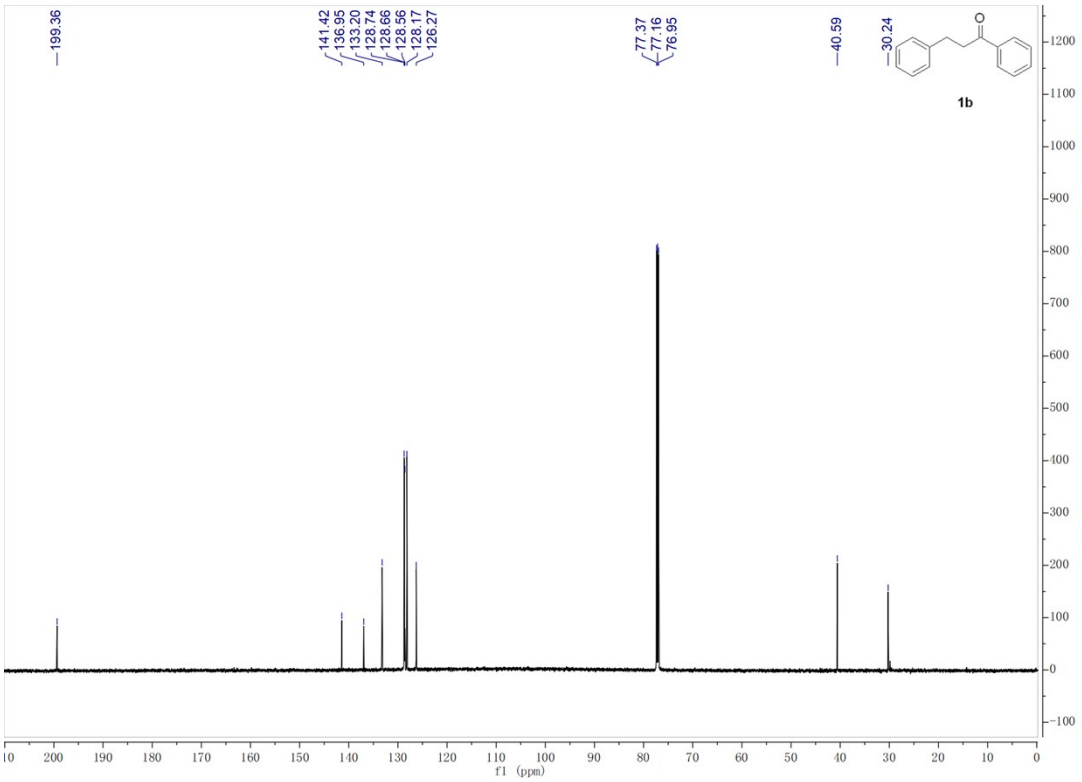
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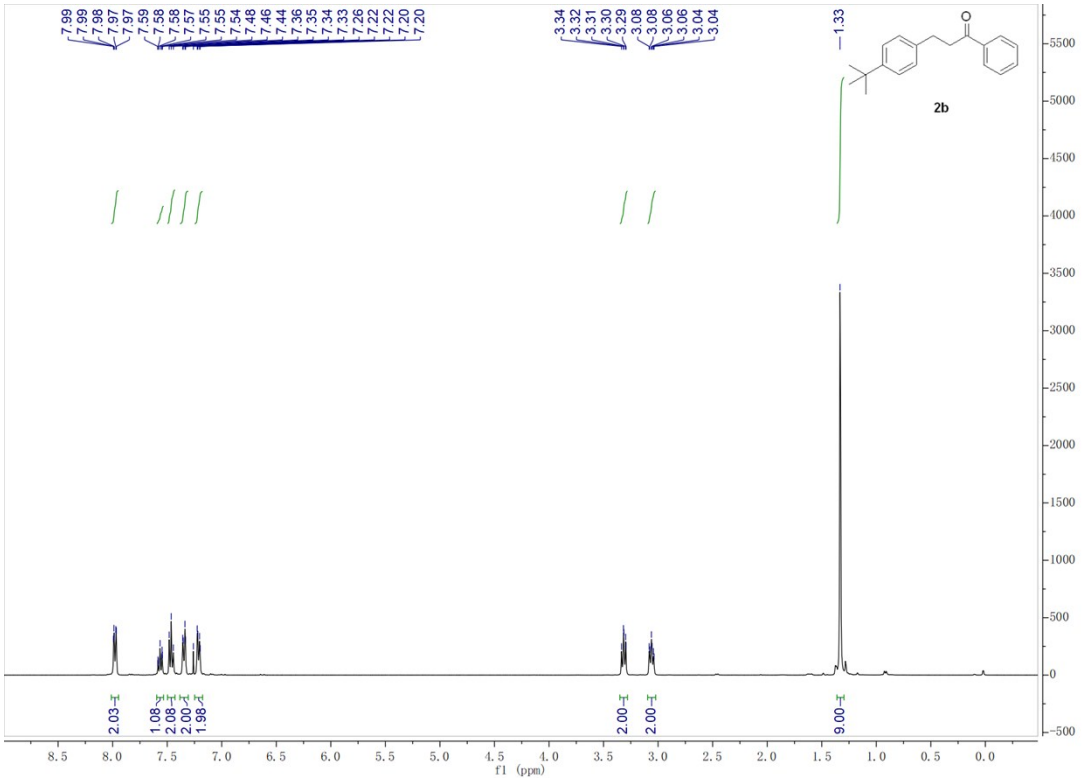
76.95
40.59
30.24
1b
f1 (ppm)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7.20
7.20
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3.32
3.31
3.30
3.29
3.08
3.08
3.06
3.06
3.04
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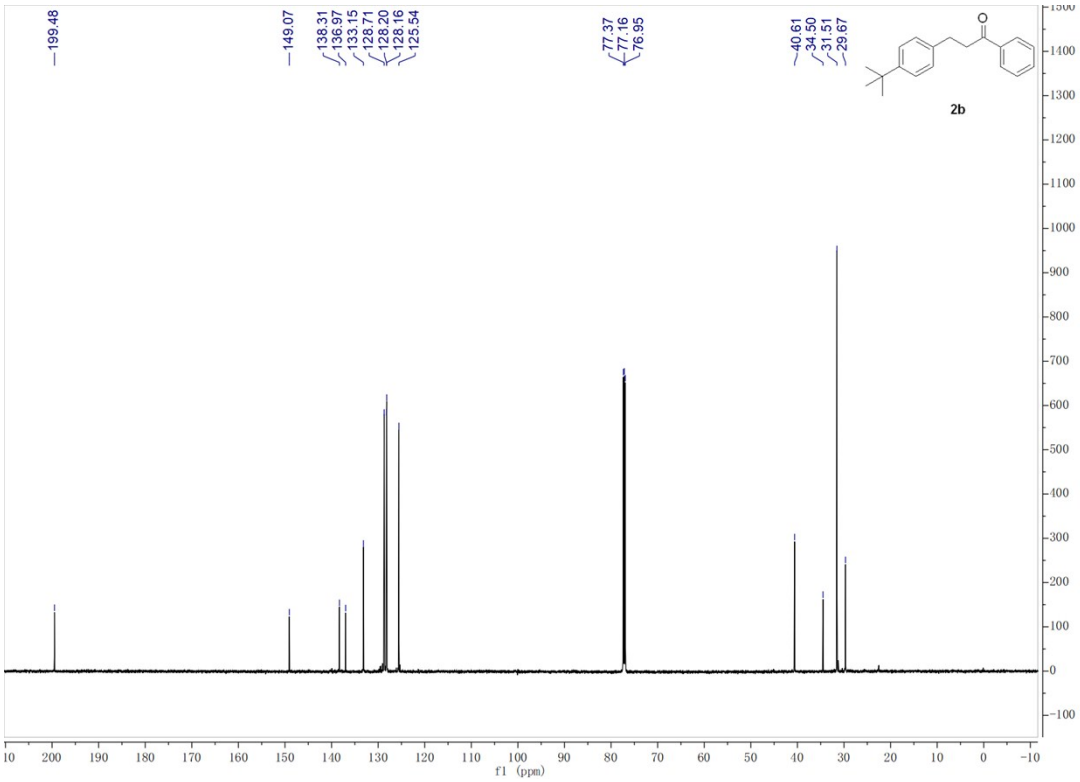
9.00
f1 (ppm)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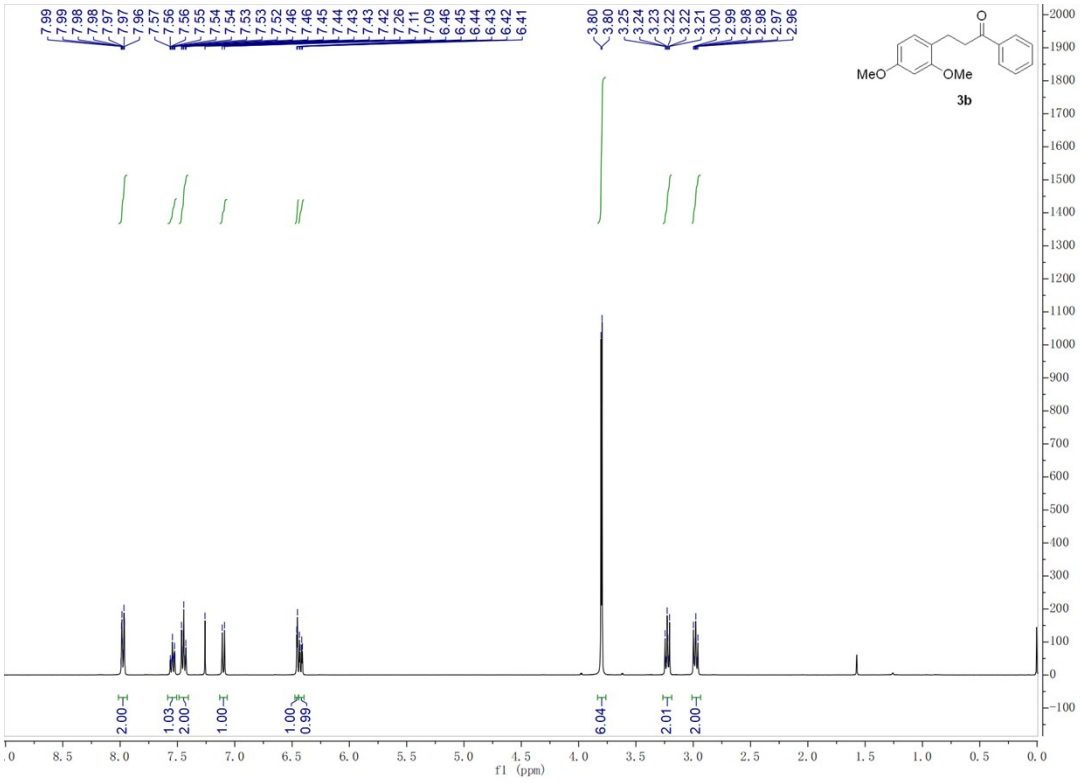
31.51
29.67
2b
f1 (ppm)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7.54
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7.26
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3.22
3.21
3.00
2.99
2.98
2.98
2.97
2.96
MeO
OMe
3b
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2.00
1.00
1.00
0.99
6.04
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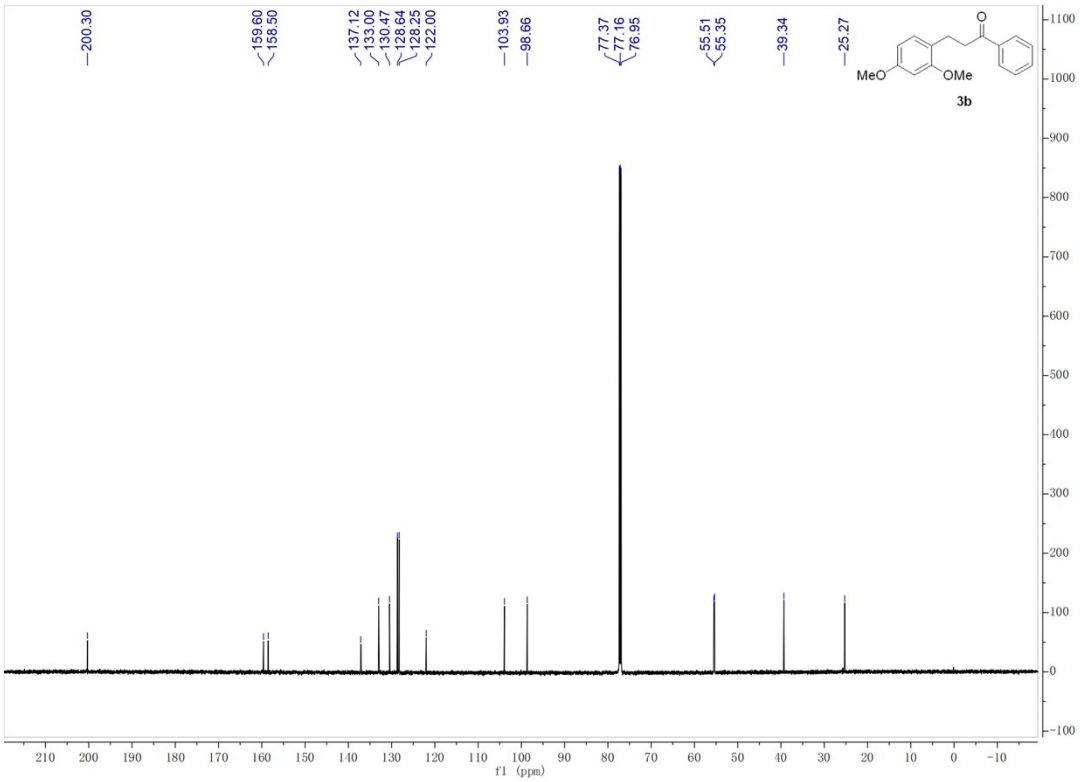
2.00
f1 (ppm)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76.95
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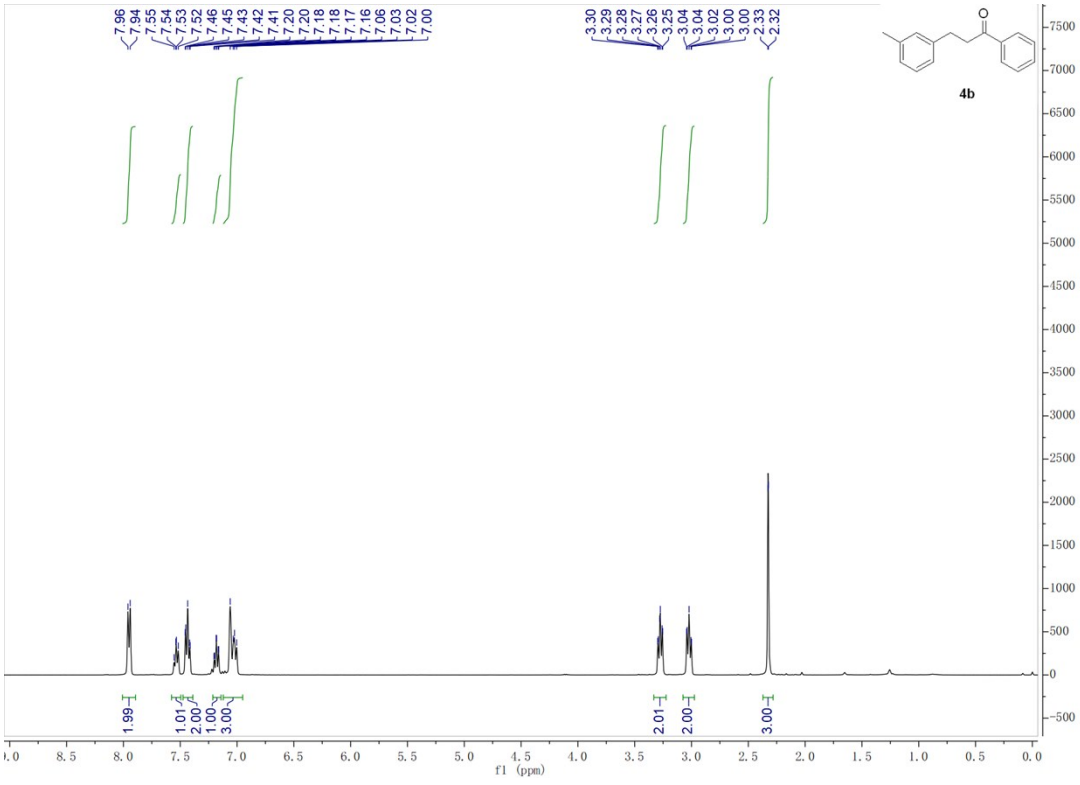
25.27
MeO
OMe
3b
f1 (ppm)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7.17
7.16
7.06
7.03
7.02
7.00
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3.29
3.28
3.27
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3.25
3.04
3.02
3.00
3.00
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3.00
2.01
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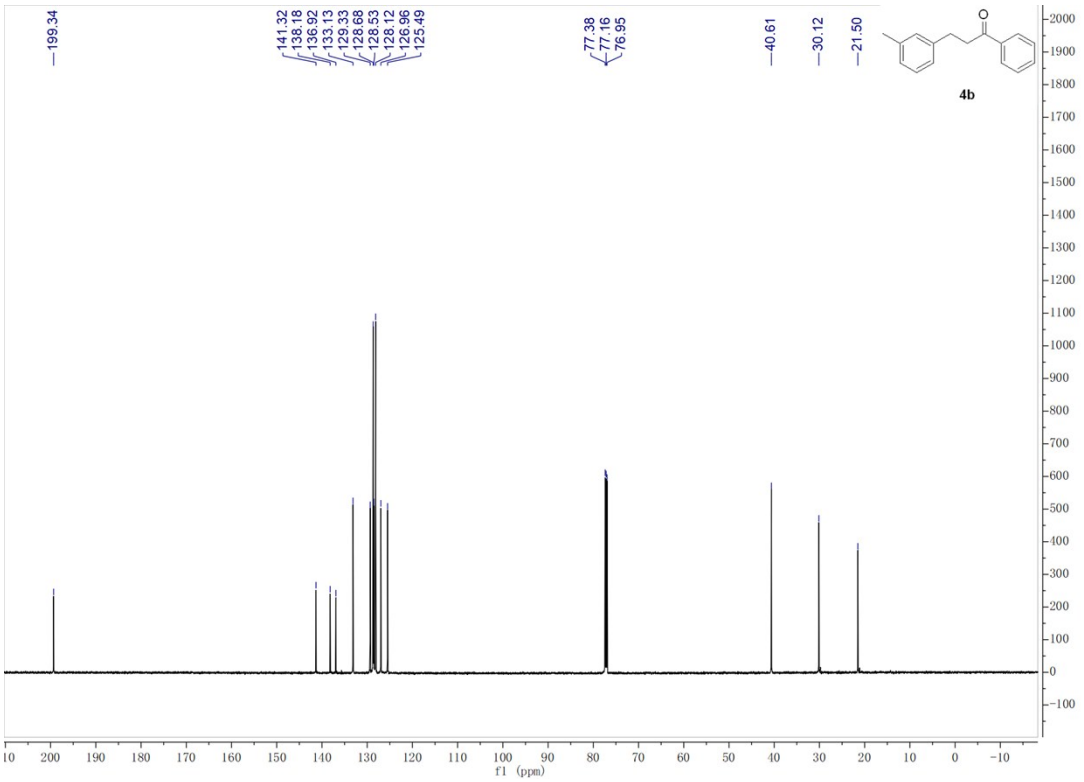
3.00
f1 (ppm)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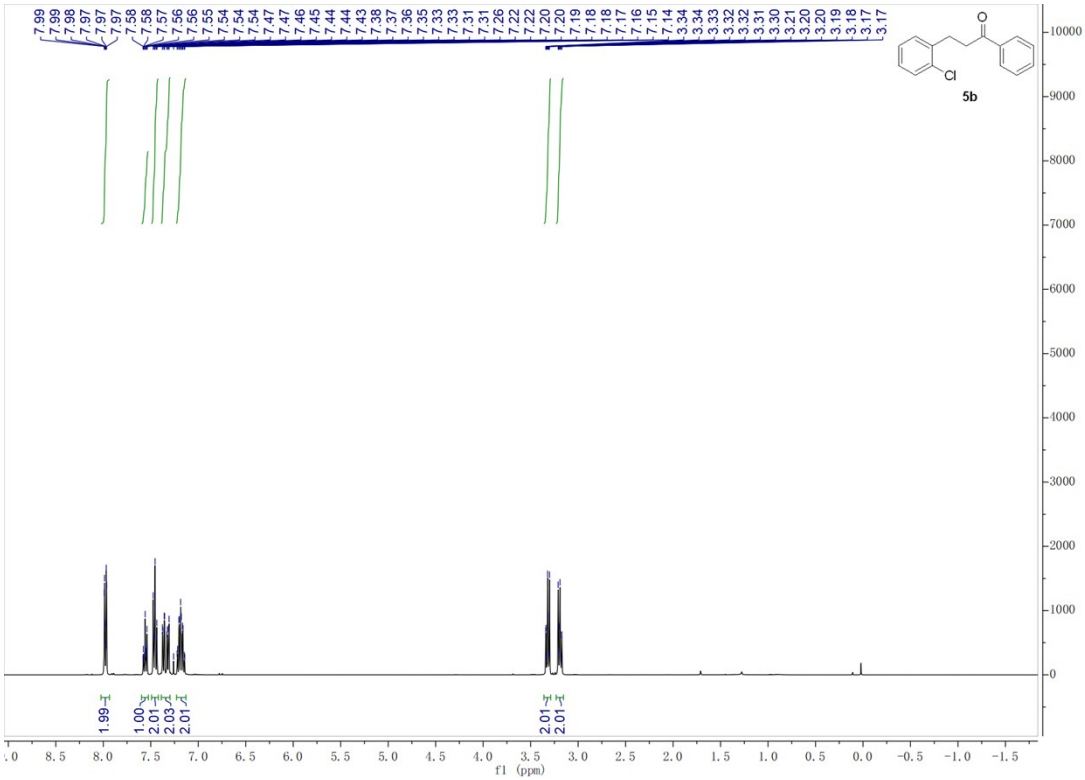
4b
f1 (ppm)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7.31
7.26
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7.19
7.18
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7.16
7.15
7.14
3.34
3.33
3.32
3.31
3.30
3.21
3.20
3.19
3.18
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Cl
5b
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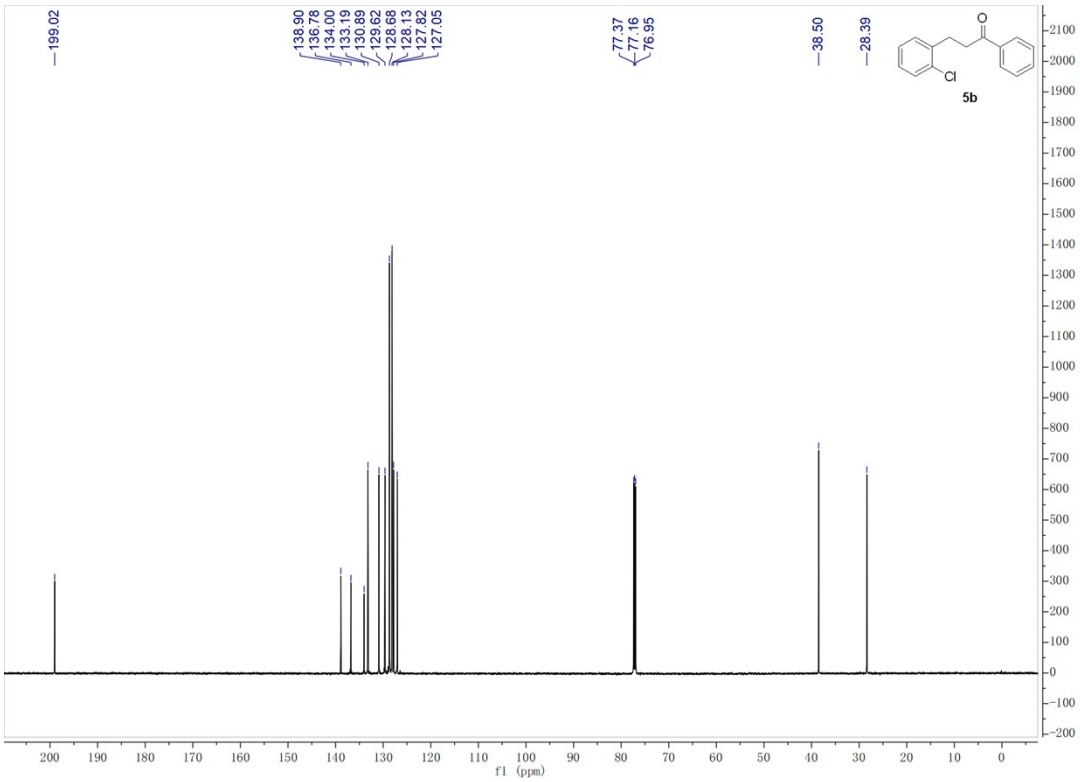
1.00
2.01
2.03
2.01
2.01
2.01
f1 (ppm)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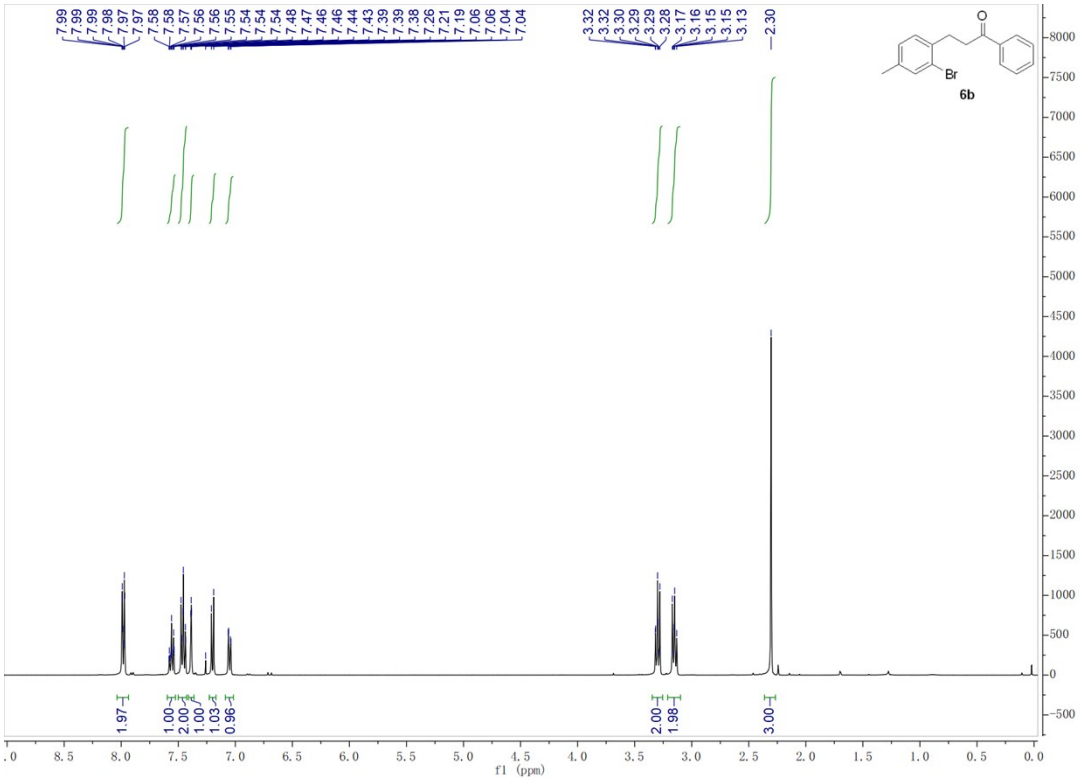
28.39
O
Cl
5b
f1 (ppm)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3.32
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3.29
3.28
3.17
3.16
3.15
3.15
3.13
2.30
O
Br
6b
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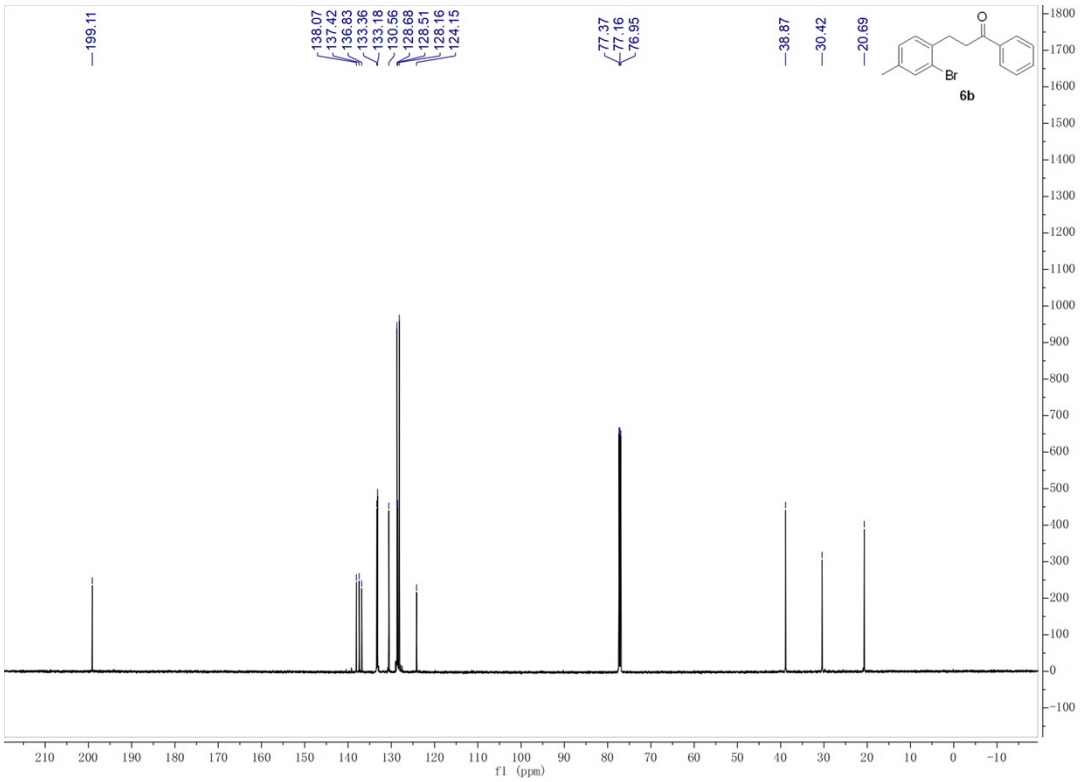
2.00
1.00
1.03
0.96
2.00
1.98
3.00
f1 (ppm)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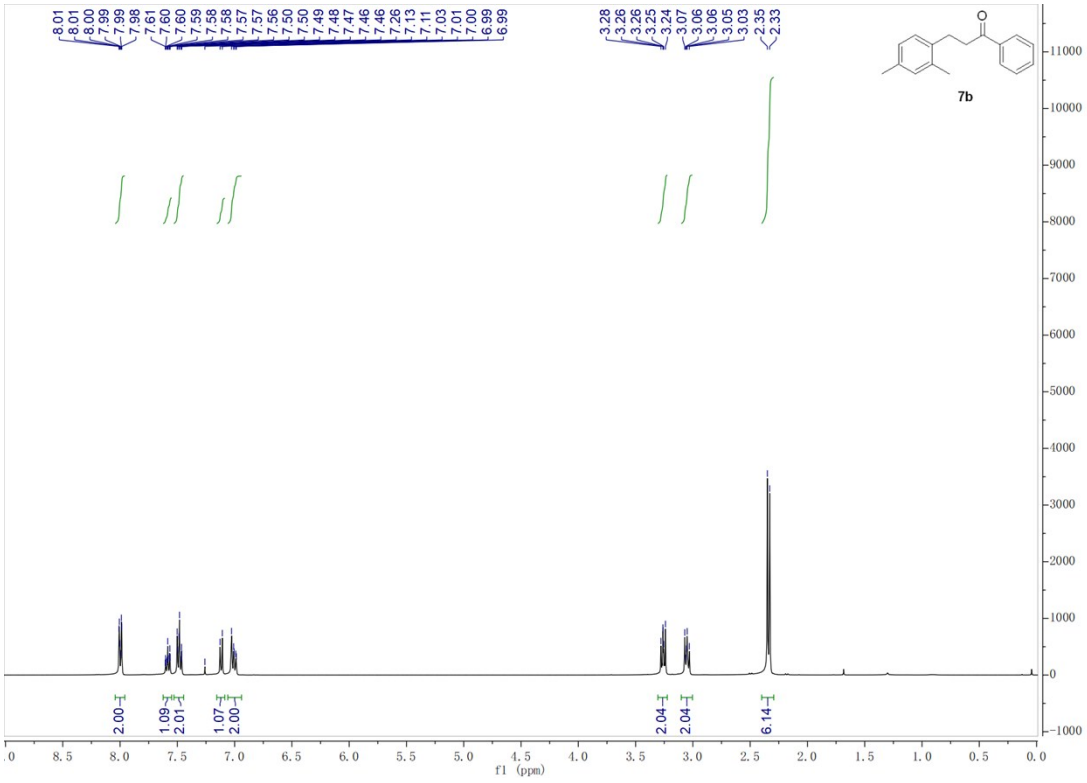
76.95
38.87
30.42
20.69
Br
6b
f1 (ppm)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7.00
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3.26
3.25
3.24
3.07
3.06
3.06
3.05
3.03
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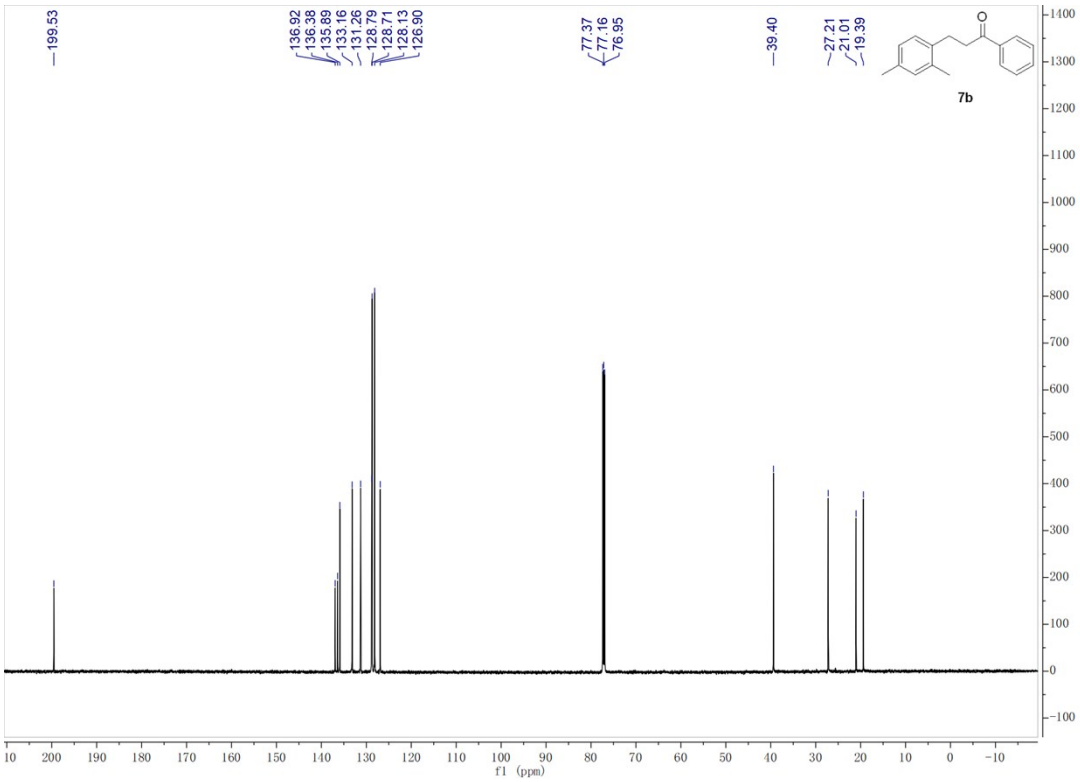
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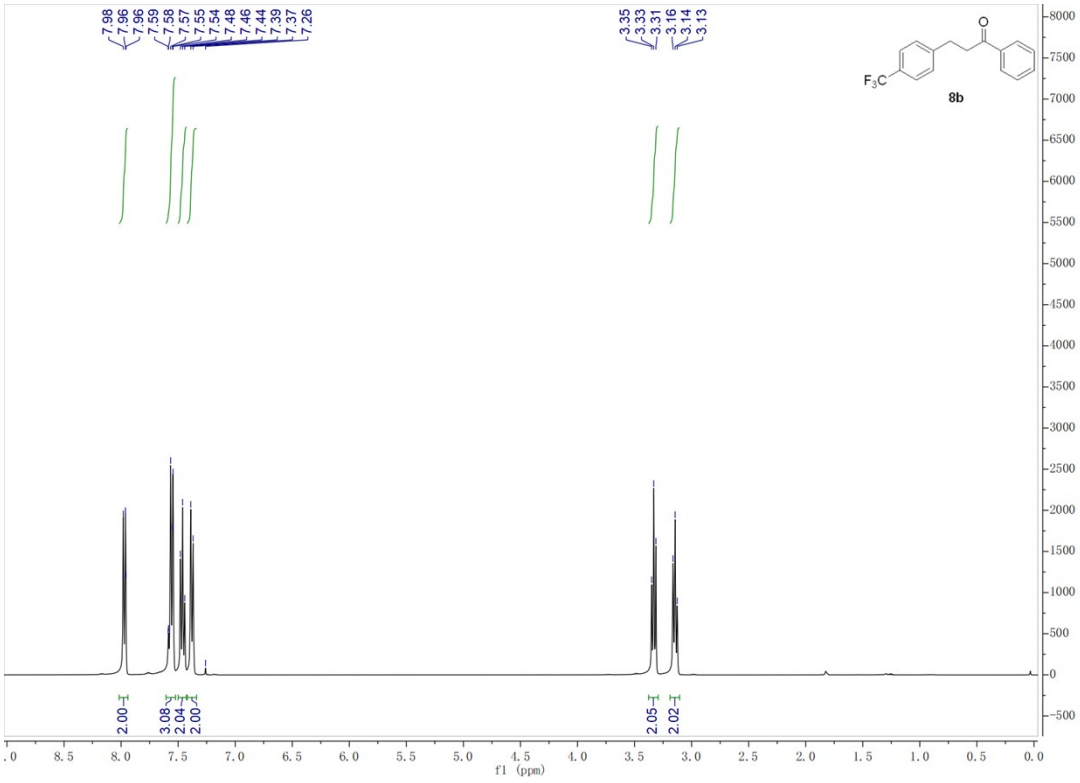
7b
f1 (ppm)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3.33
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2.00
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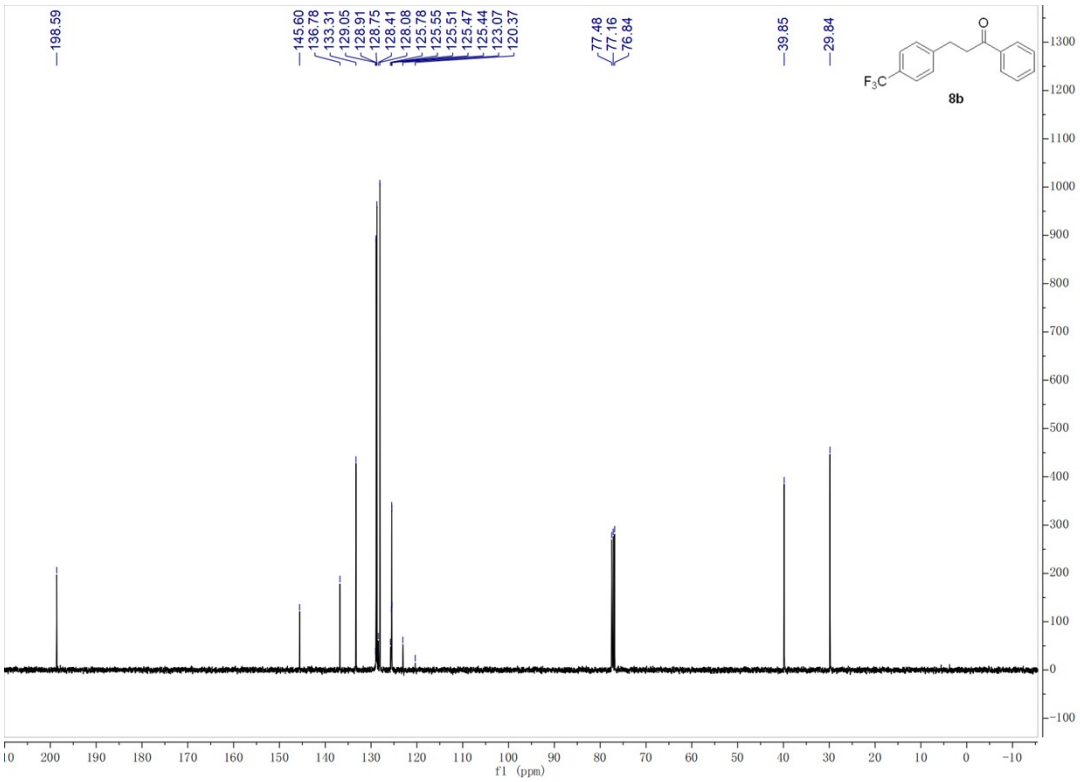
2.02
f1 (ppm)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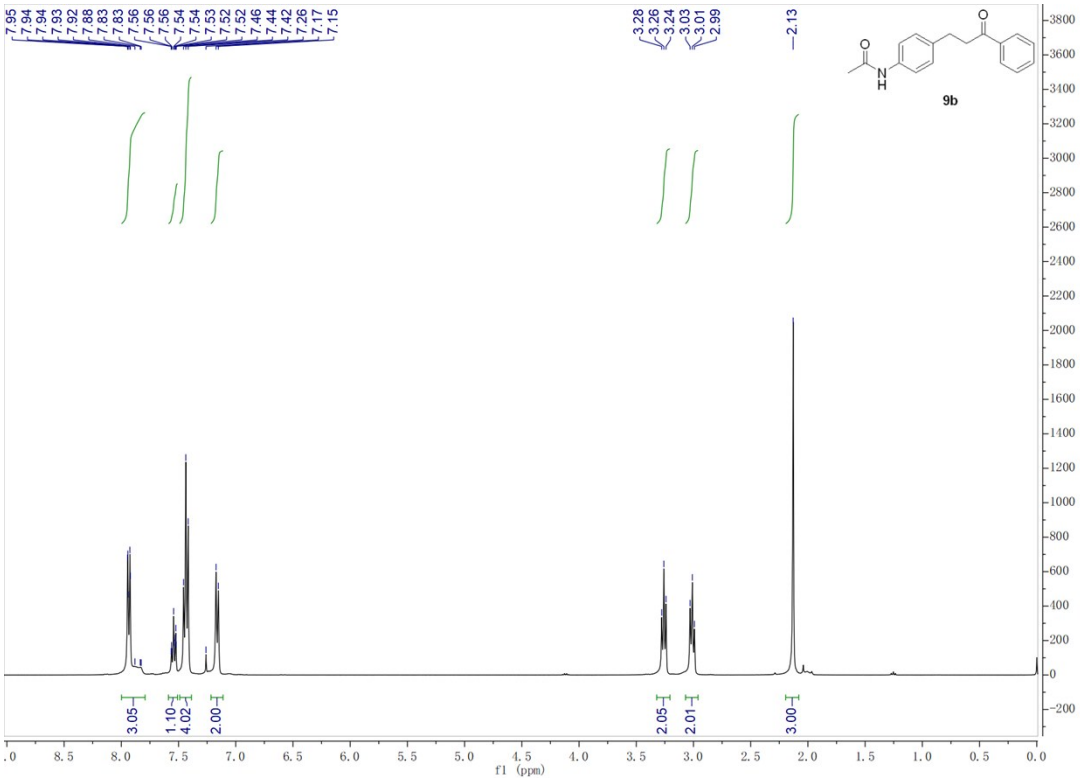
29.84
F3C
O
8b
f1 (ppm)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3.26
3.24
3.03
3.01
2.99
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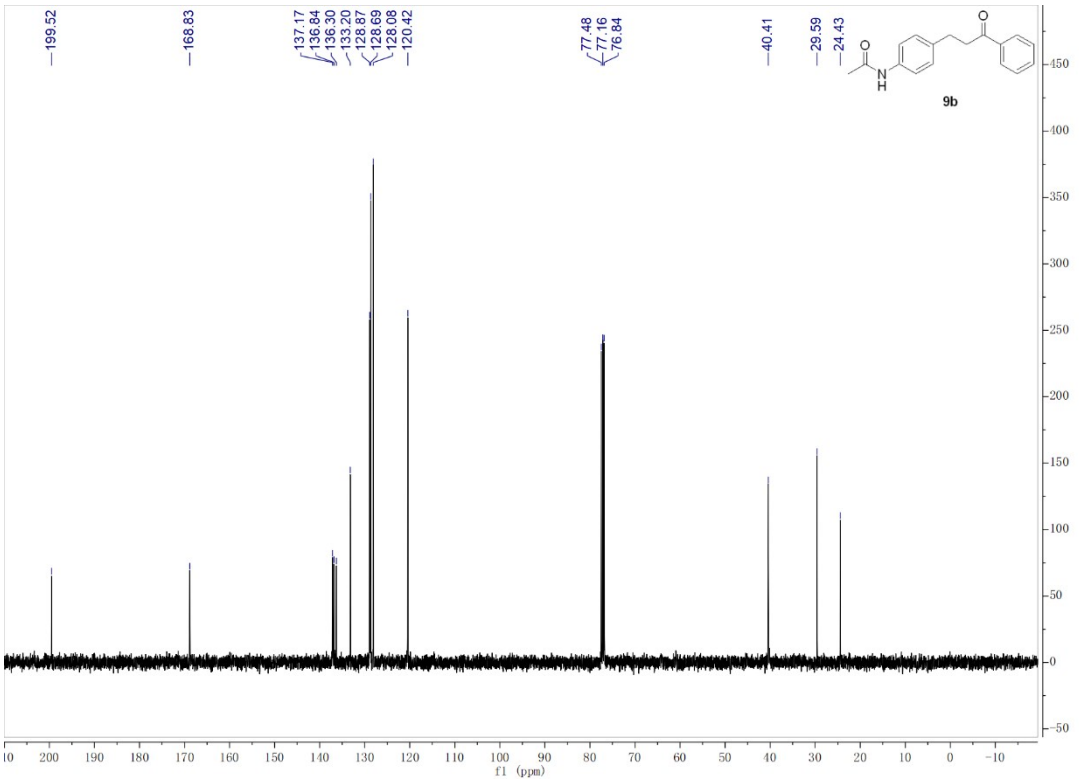
O
N
H
O
9b
f1 (ppm)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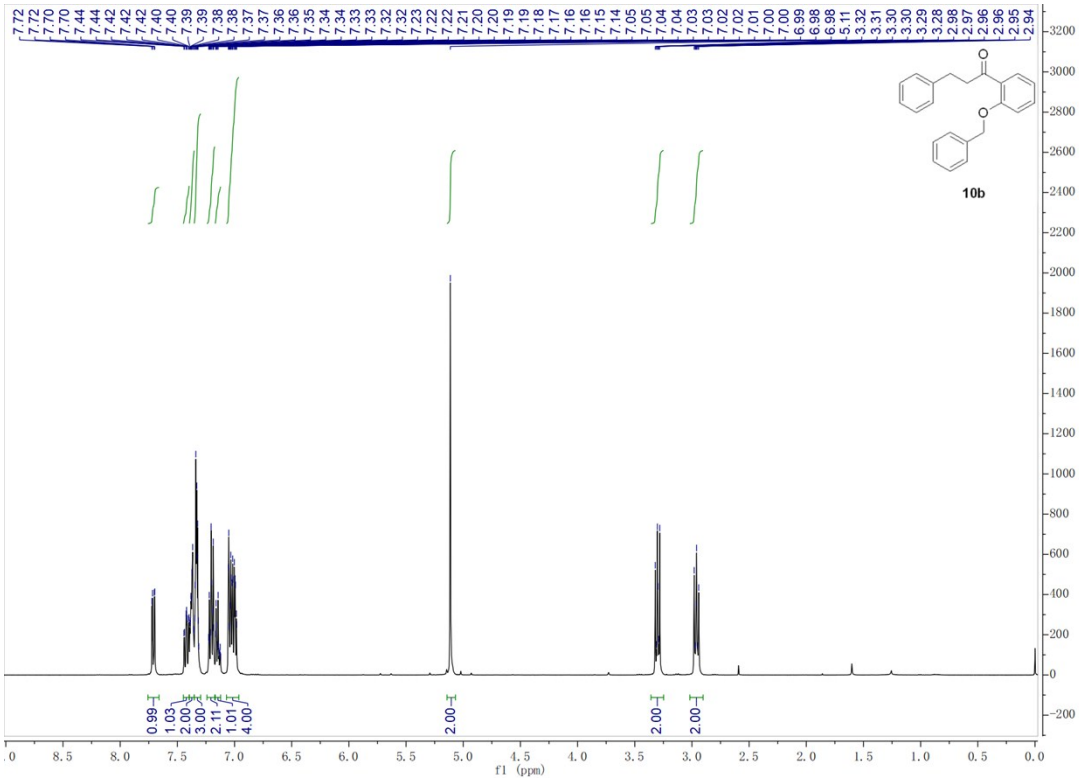
f1 (ppm)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4.00
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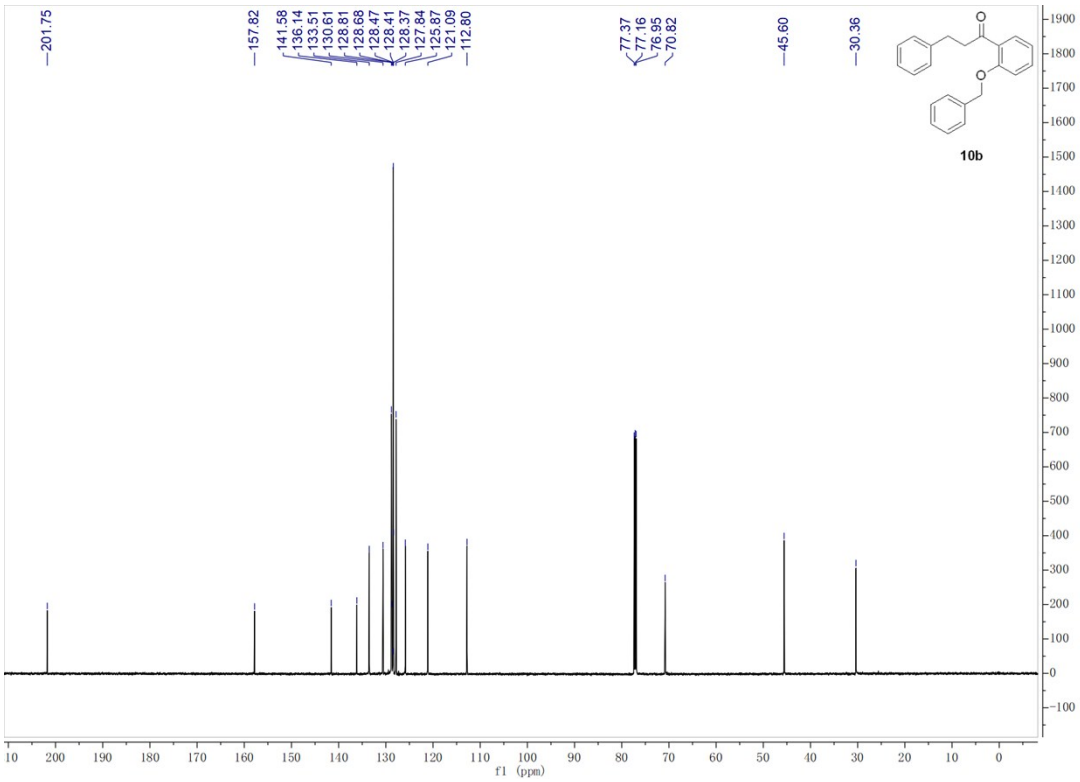
2.00
f1 (ppm)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70.82
45.60
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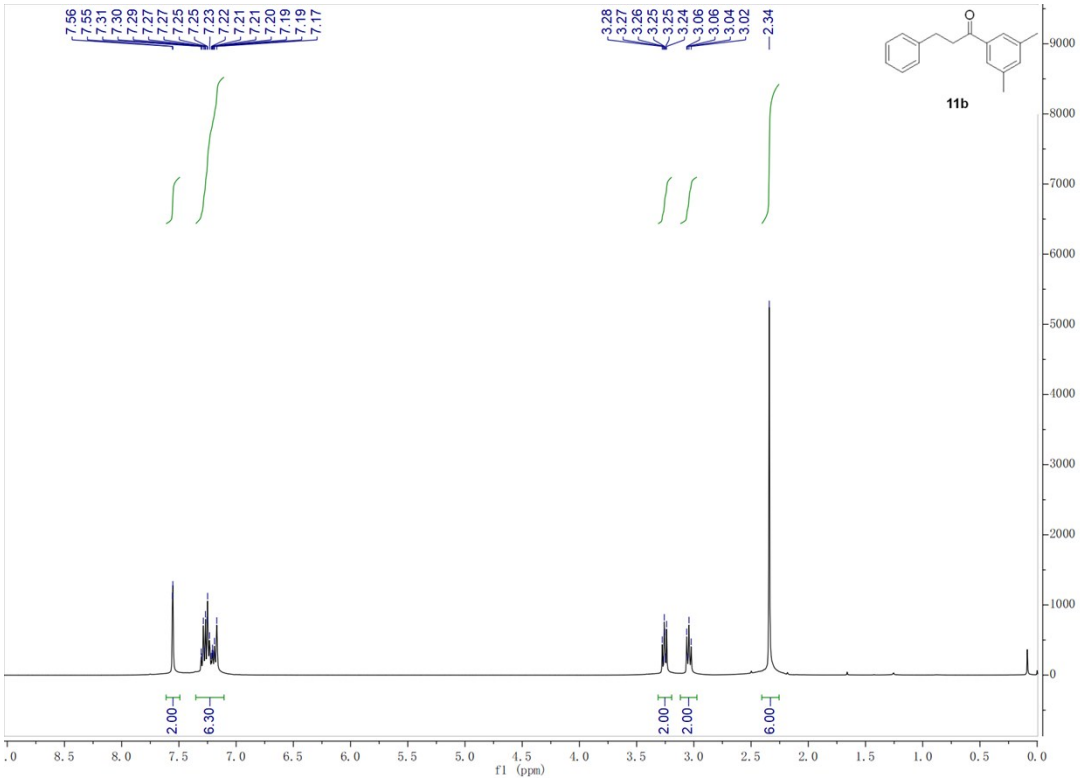
10b
f1 (ppm)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3.24
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6.00
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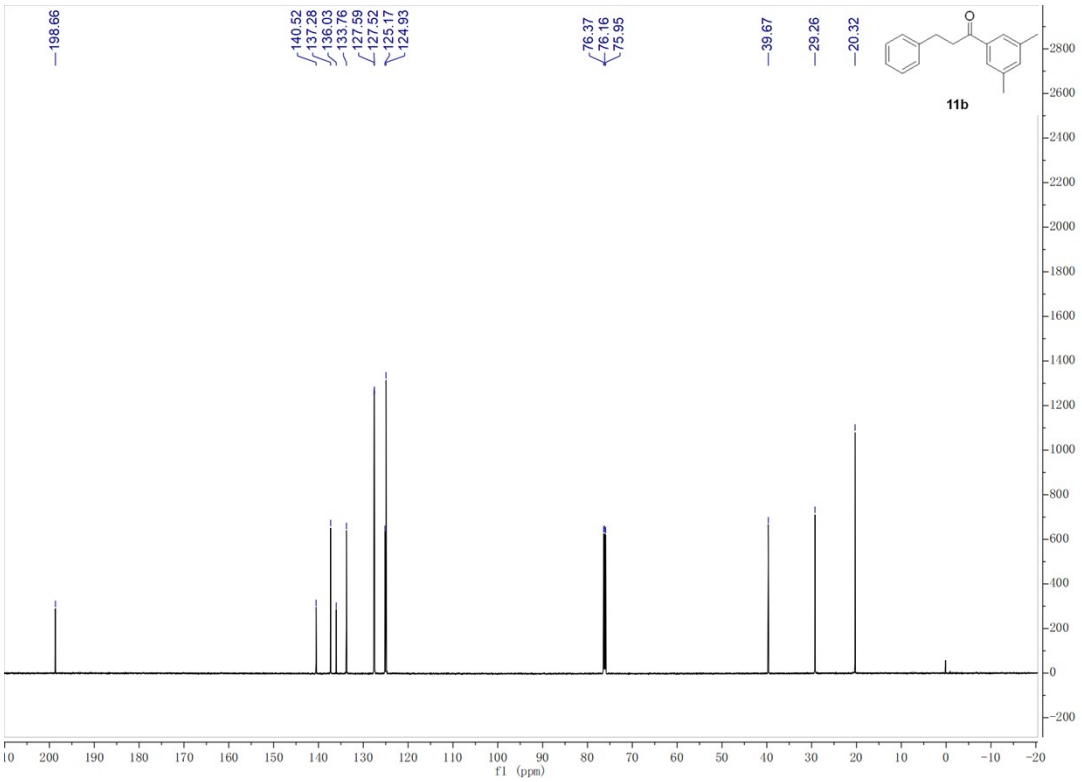
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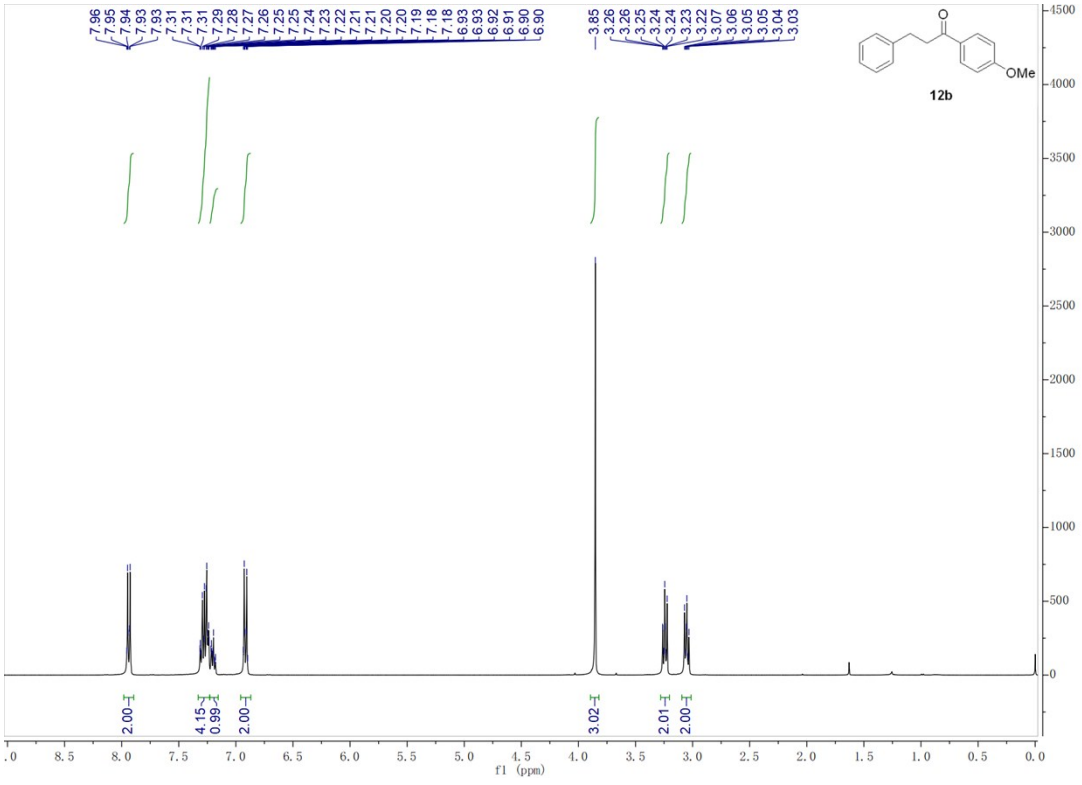
29.26
20.32
11b
f1 (ppm)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3.06
3.05
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3.03
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12b
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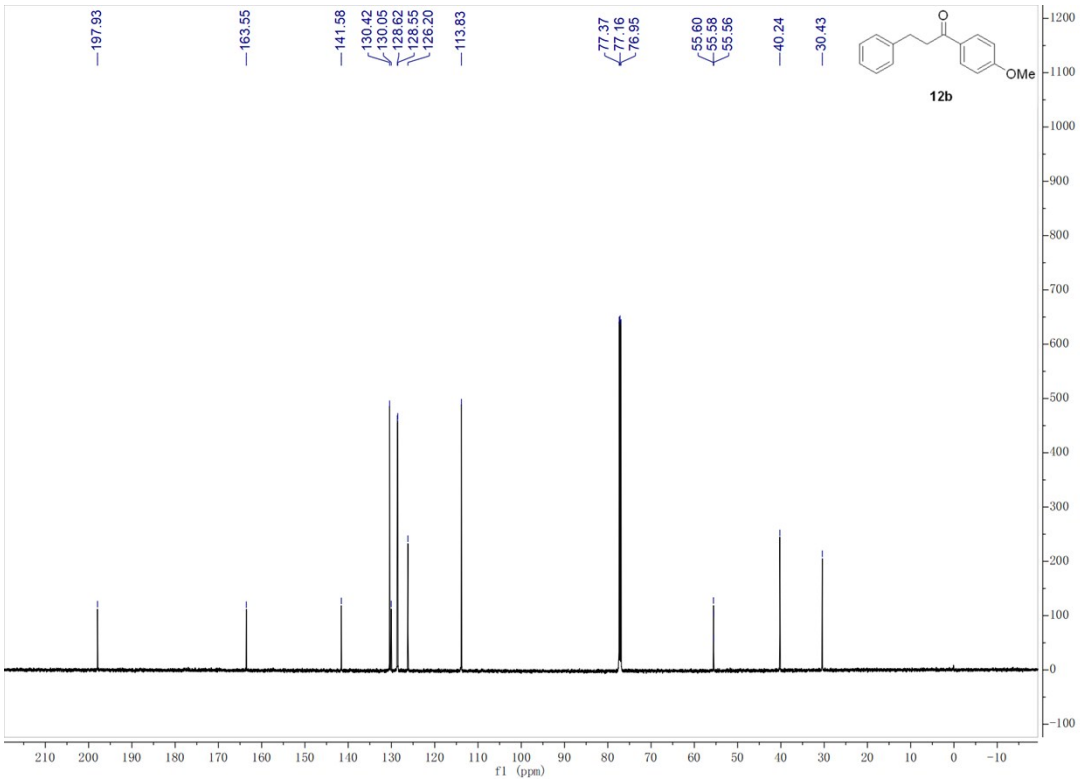
2.00
f1 (ppm)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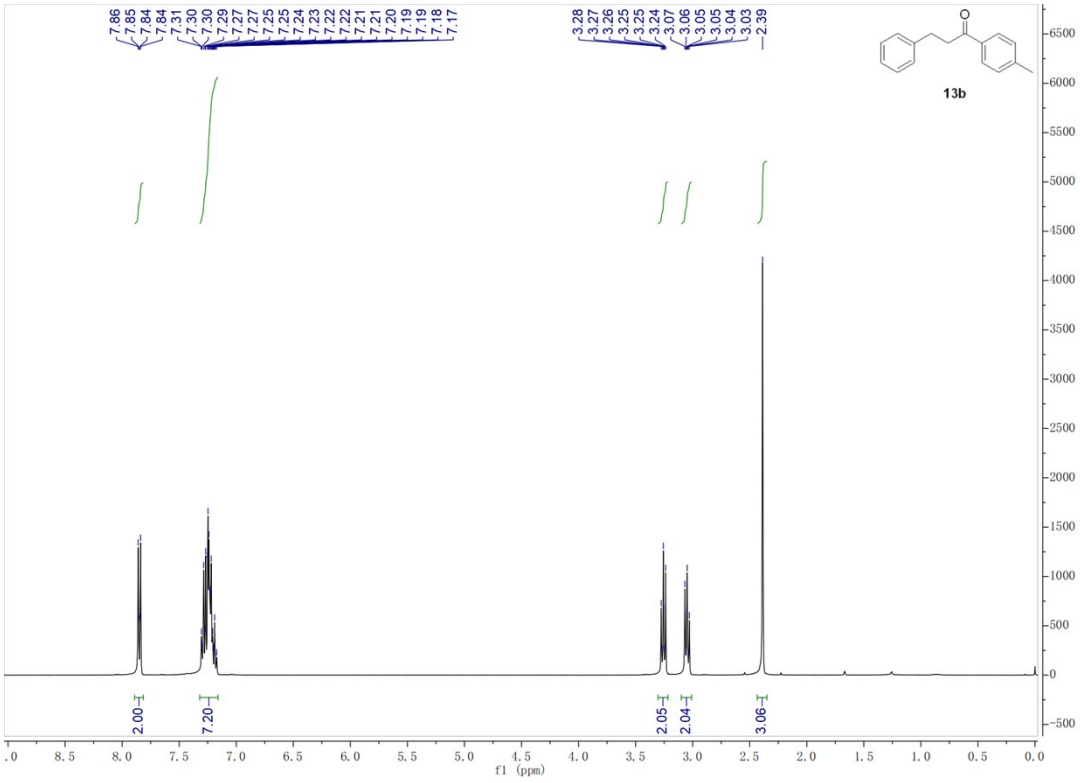
OMe
12b
f1 (ppm)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3.06
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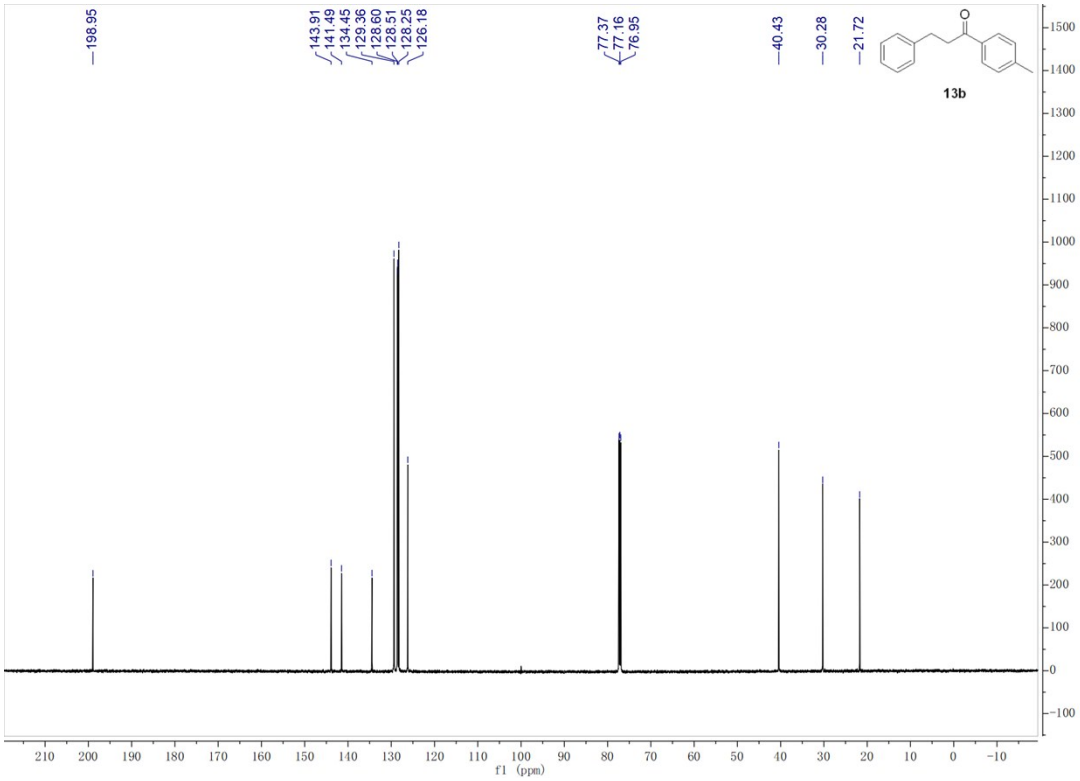
3.06
f1 (ppm)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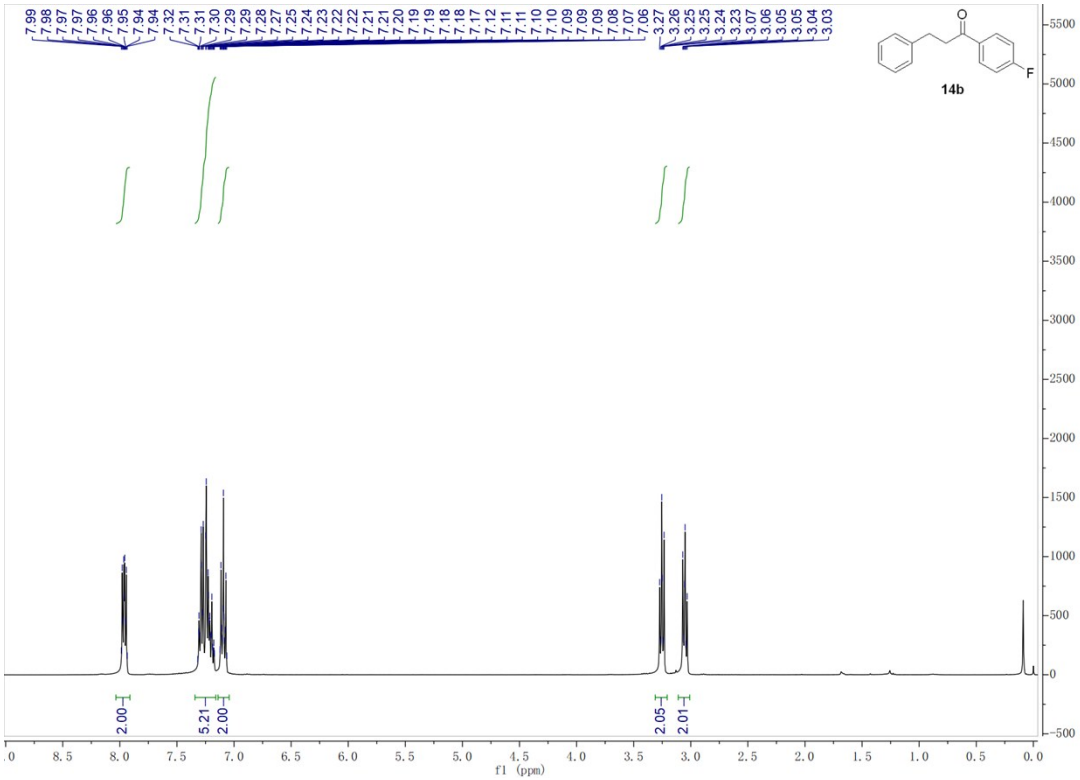
13b
f1 (ppm)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3.24
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3.06
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3.03
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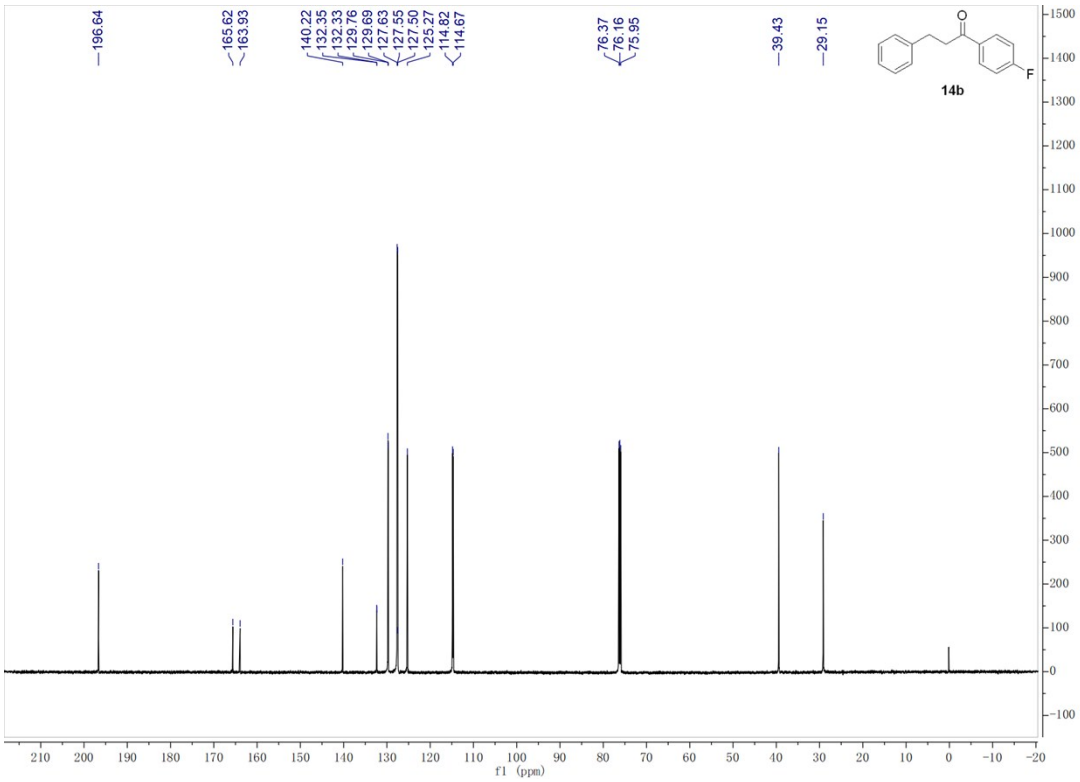
2.00
2.05
2.01
f1 (ppm)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76.16
75.95
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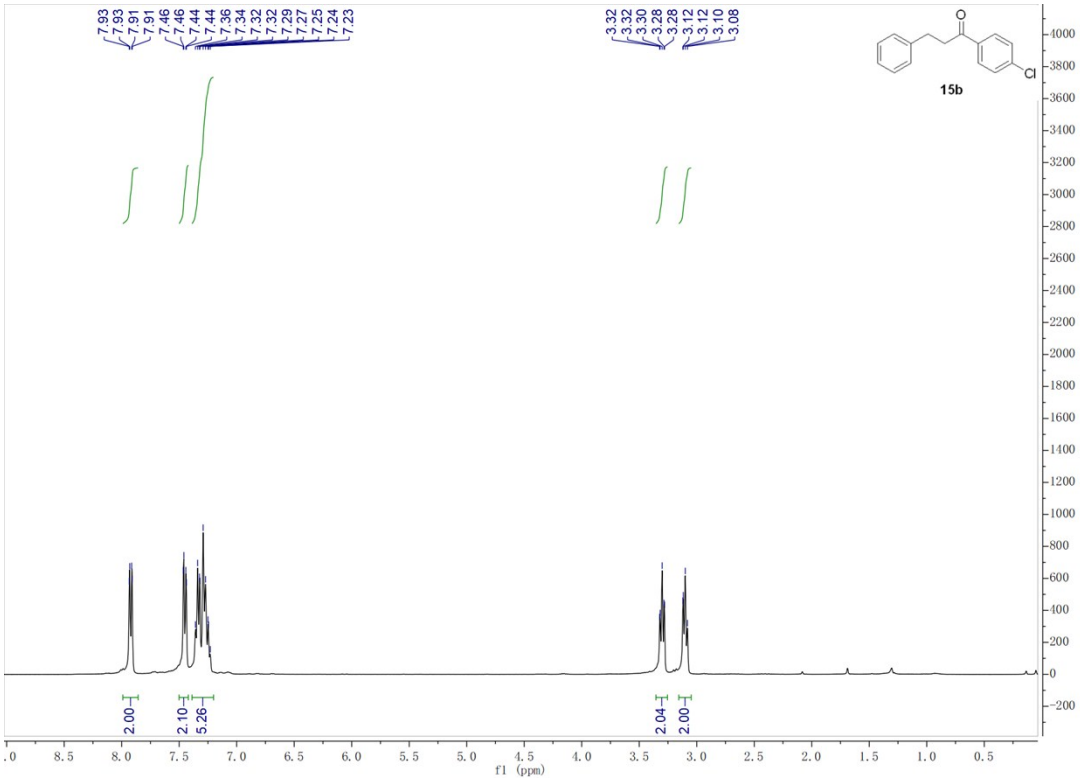
29.15
O
F
14b
f1 (ppm)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3.32
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3.30
3.28
3.28
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3.08
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15b
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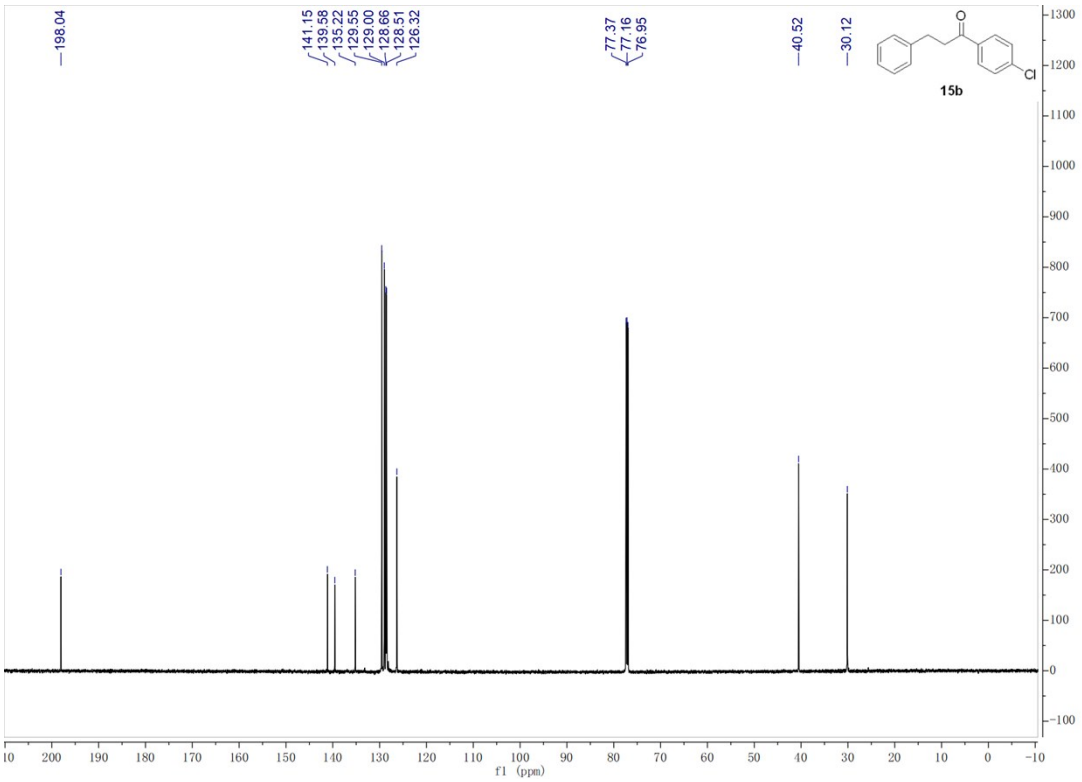
5.26
2.04
2.00
f1 (ppm)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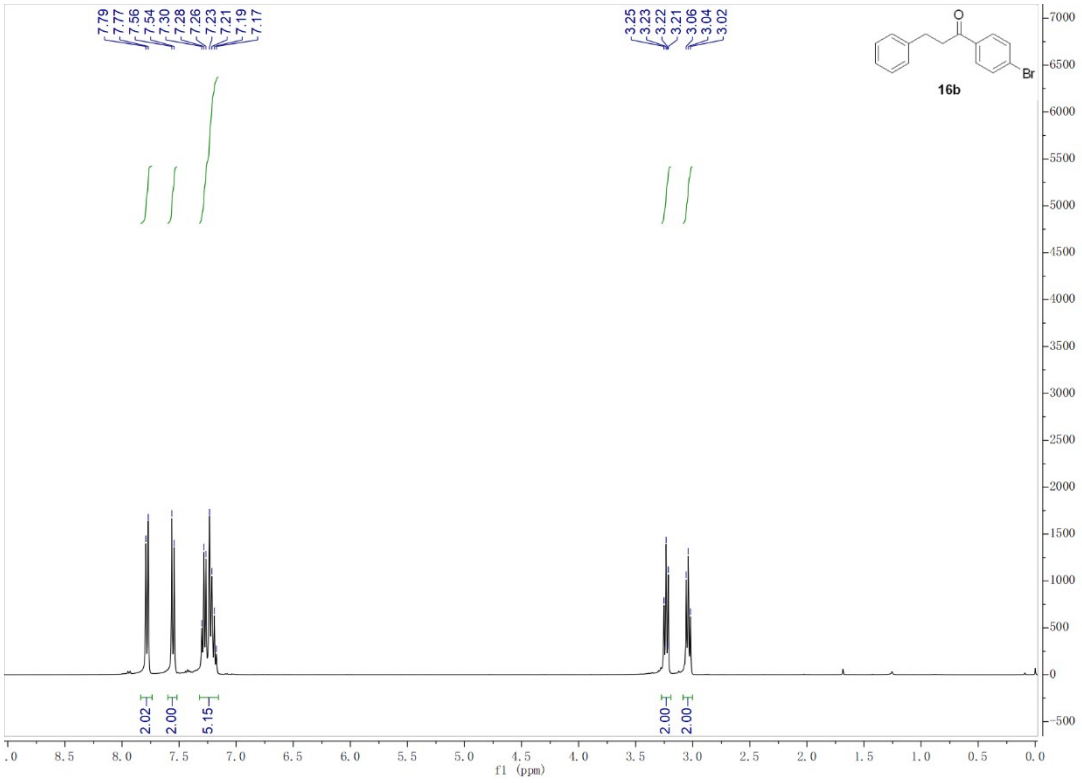
f1 (ppm)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3.22
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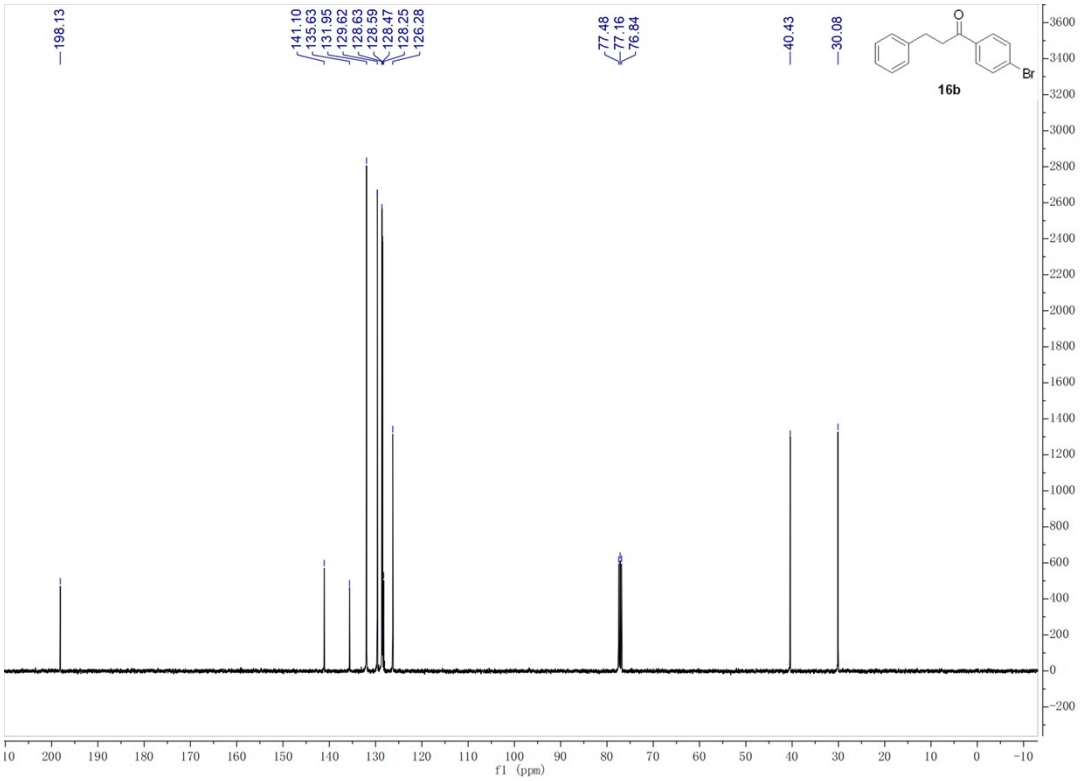
2.00
f1 (ppm)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76.84
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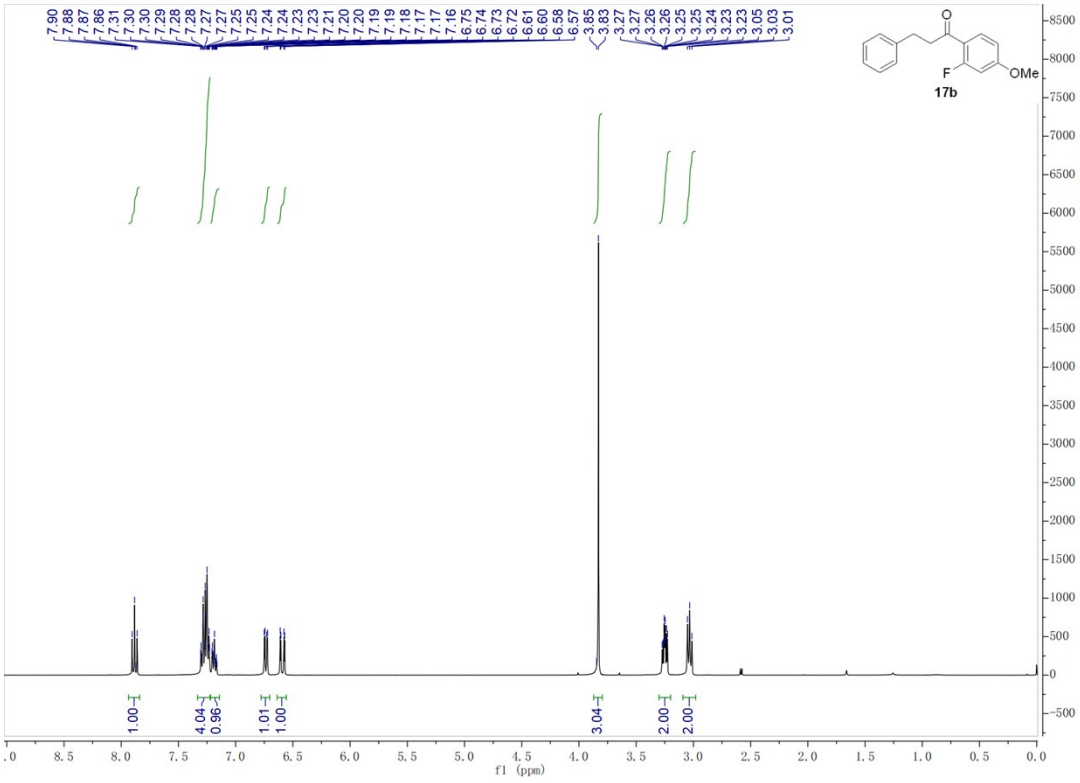
30.08
O
Br
16b
f1 (ppm)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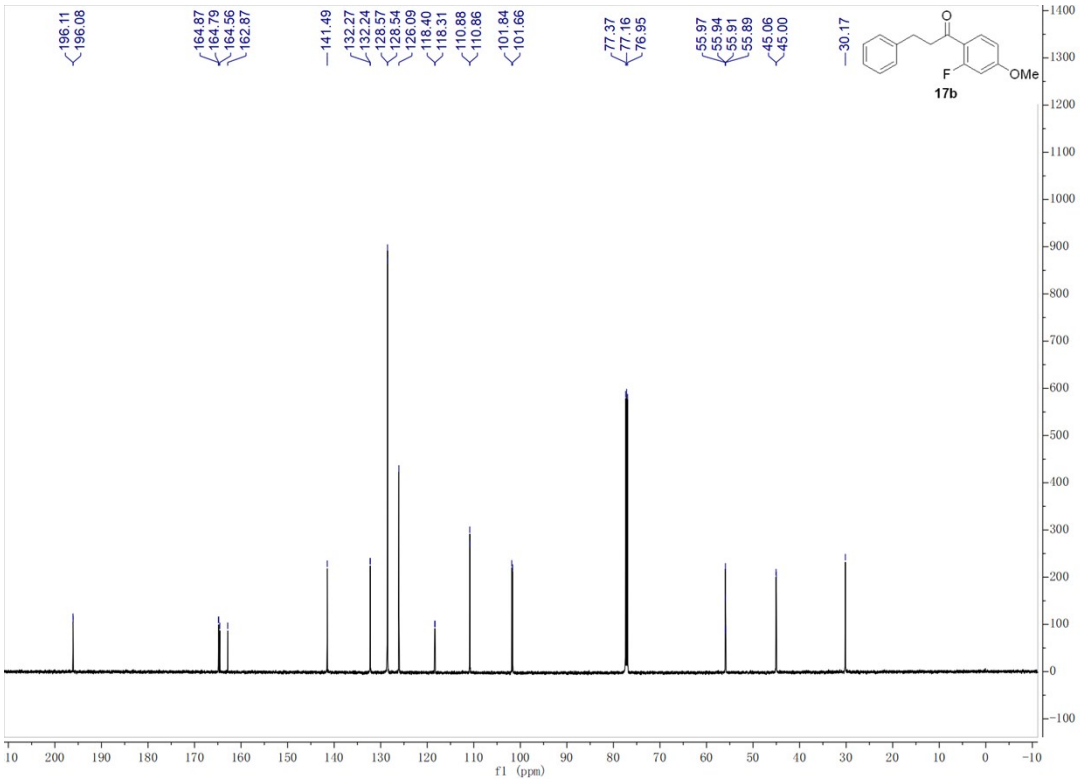
2.00
f1 (ppm)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77.16
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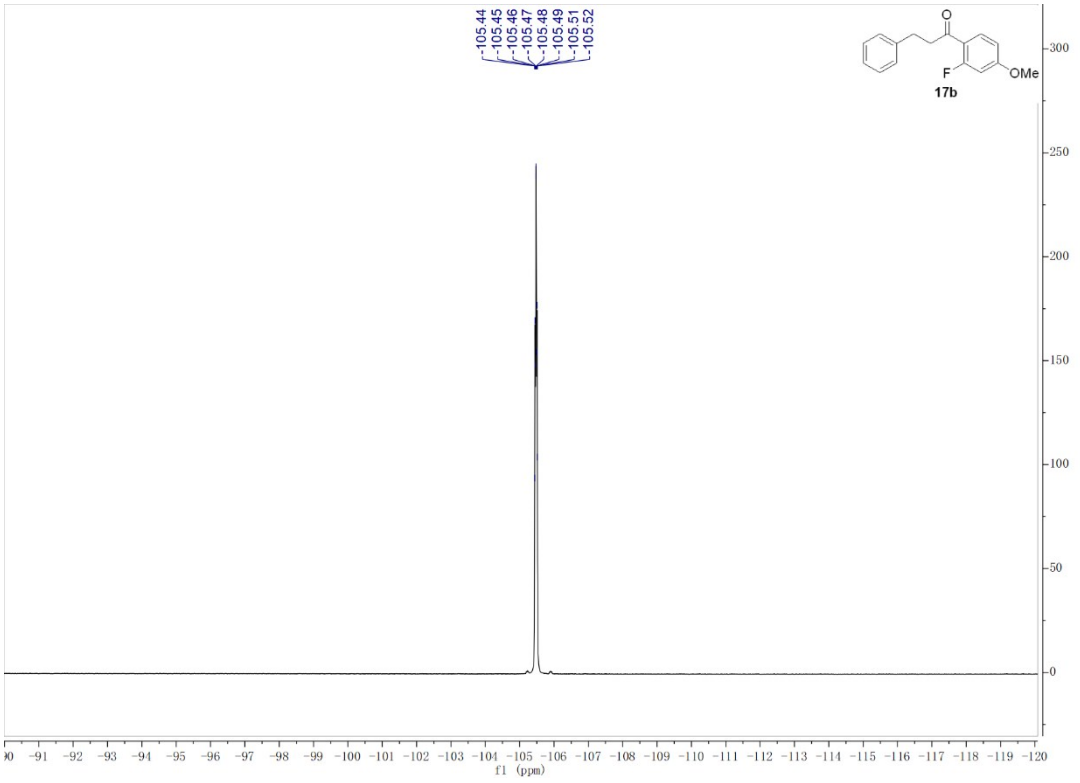
45.06
45.00
30.17
O
F
OMe
17b
f1 (ppm)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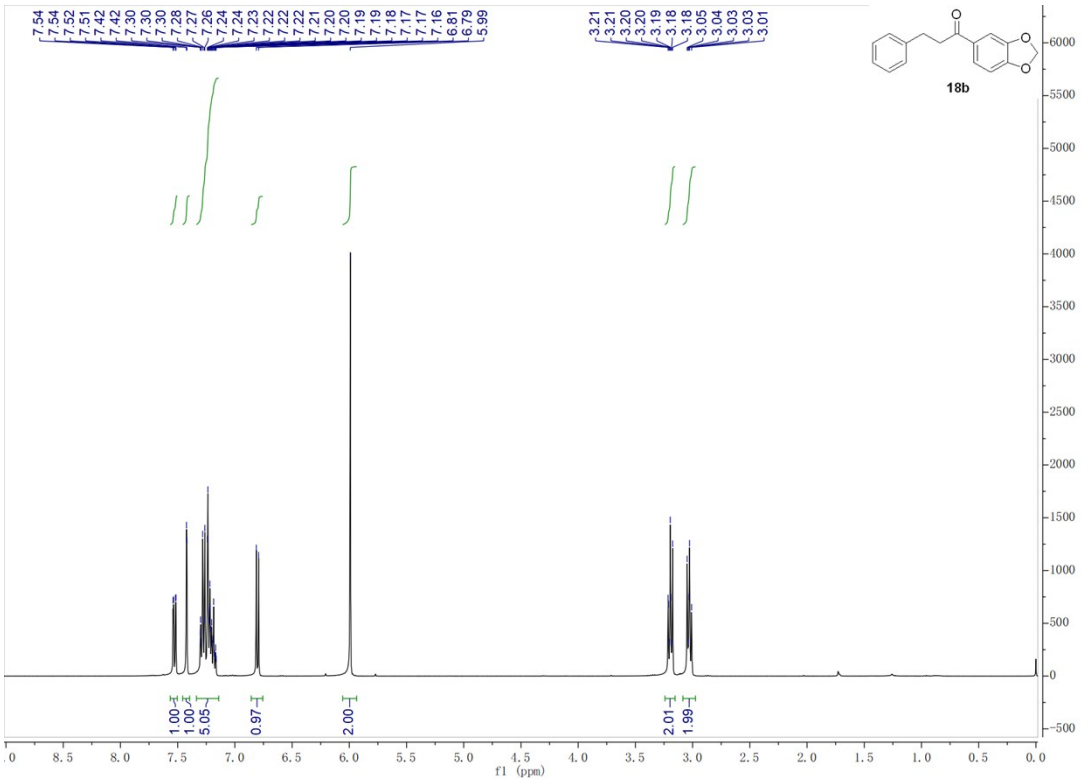
F
OMe
17b
f1 (ppm)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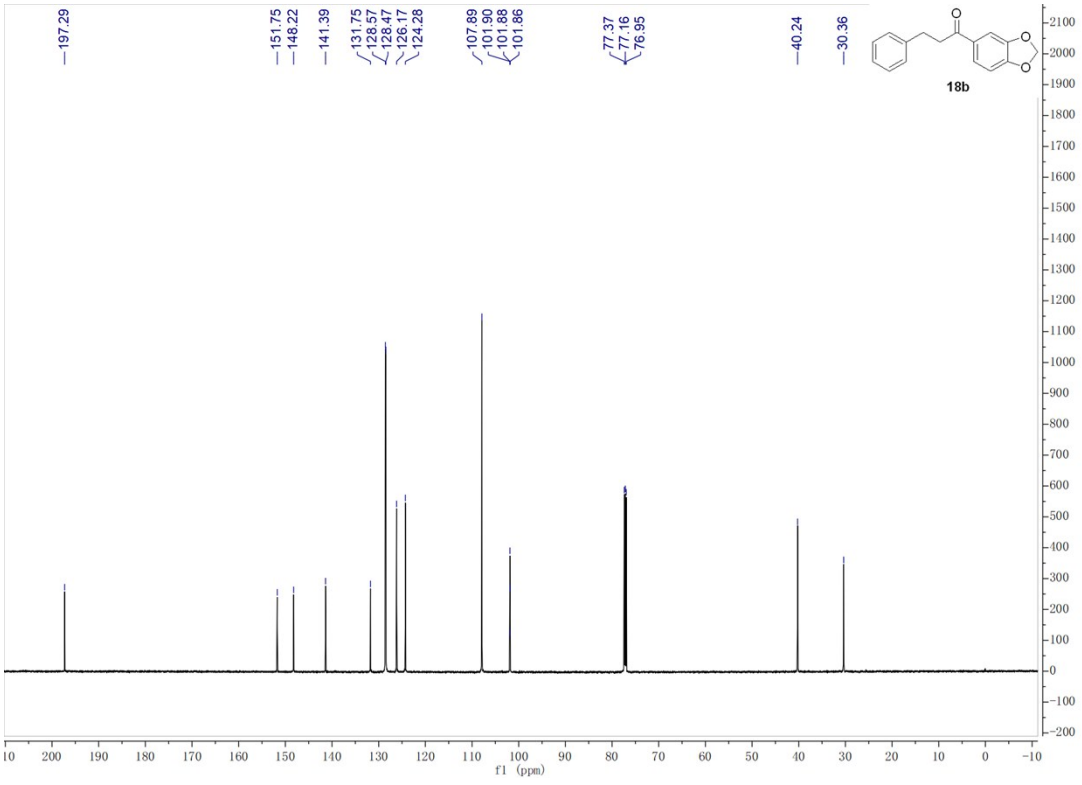
f1 (ppm)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40.24
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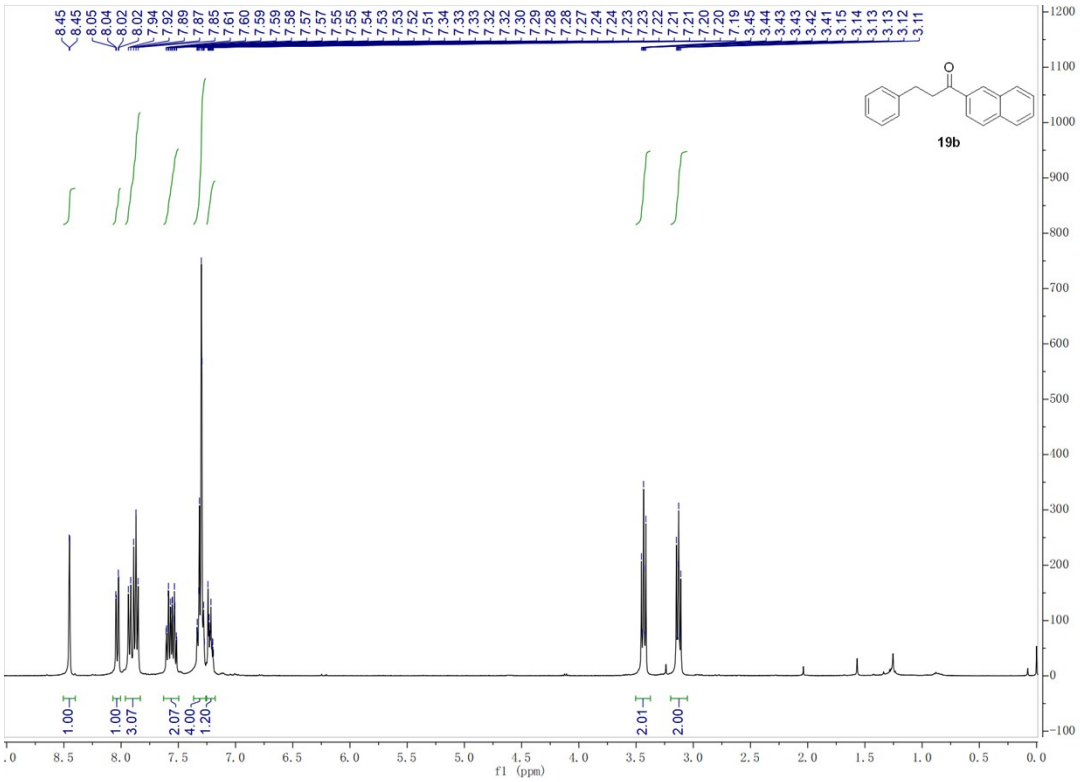
18b
f1 (ppm)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3.15
3.14
3.13
3.13
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3.11
19b
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1.00
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1.20
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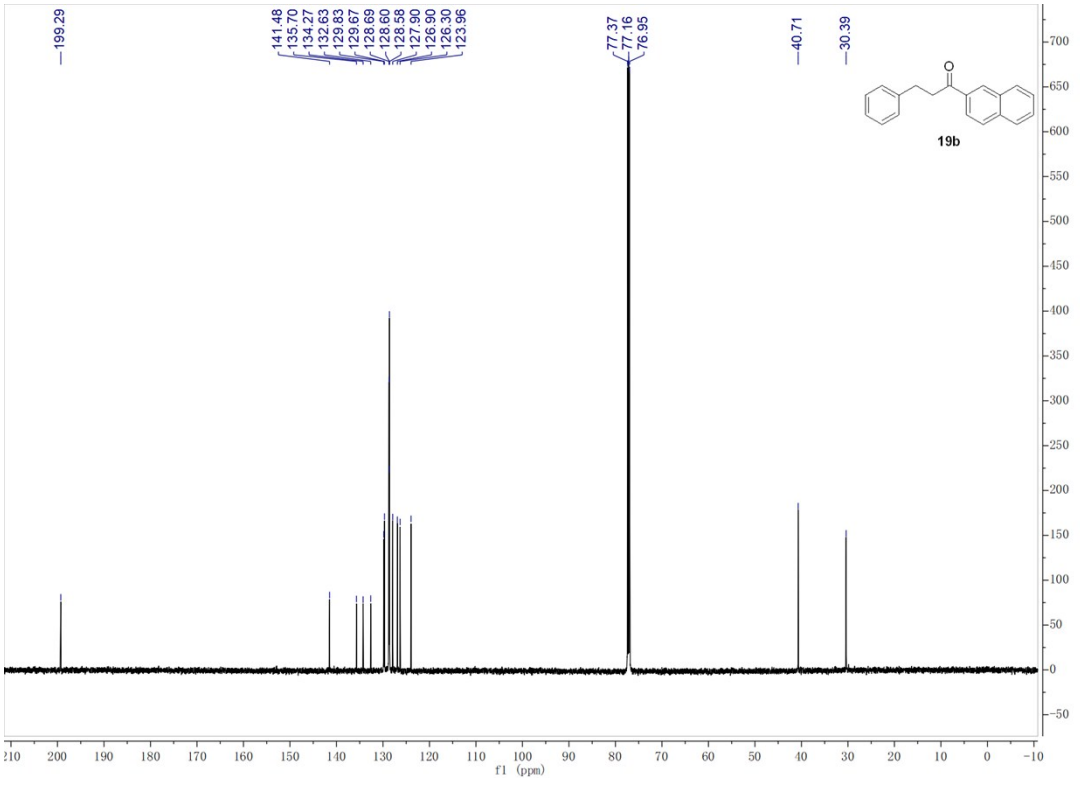
2.00
f1 (ppm)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76.95
40.71
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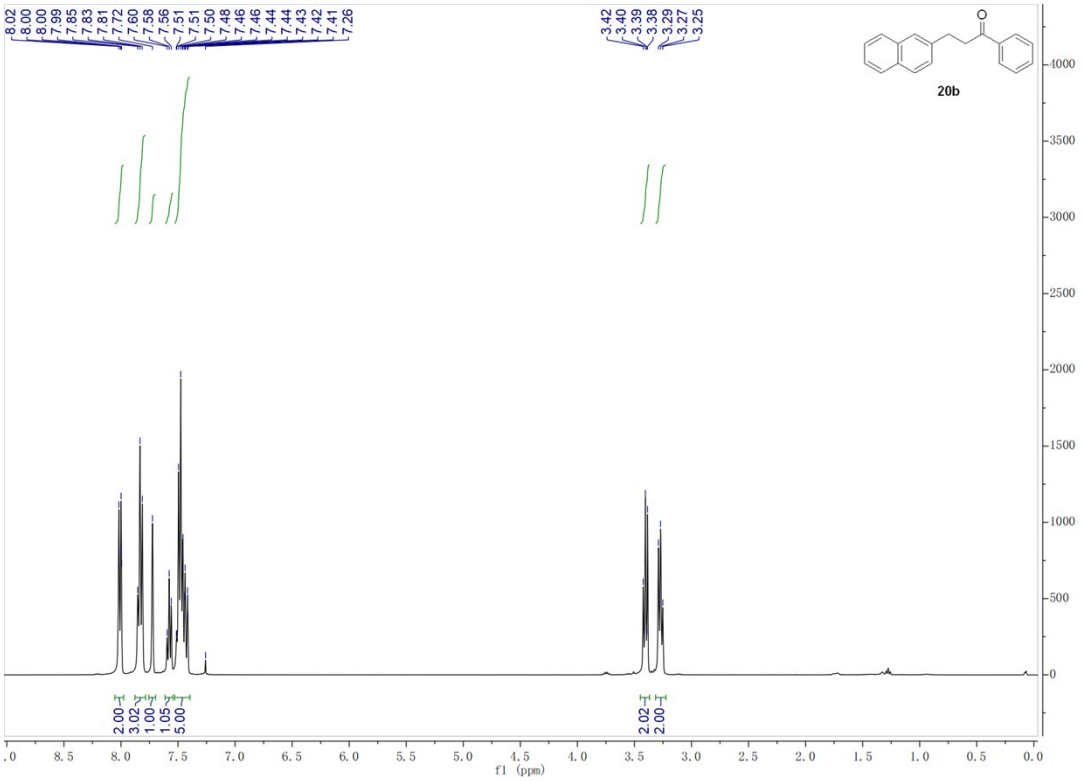
19b
f1 (ppm)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20b
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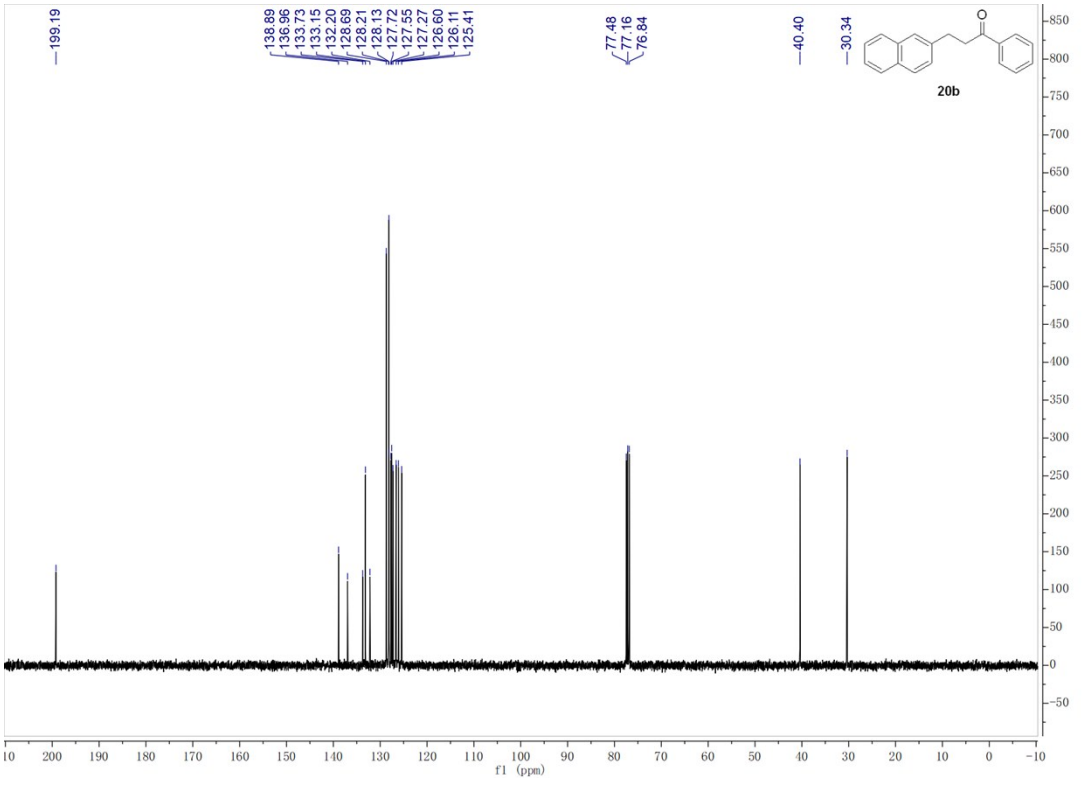
3.02
1.00
1.05
5.00
2.02
2.00
f1 (ppm)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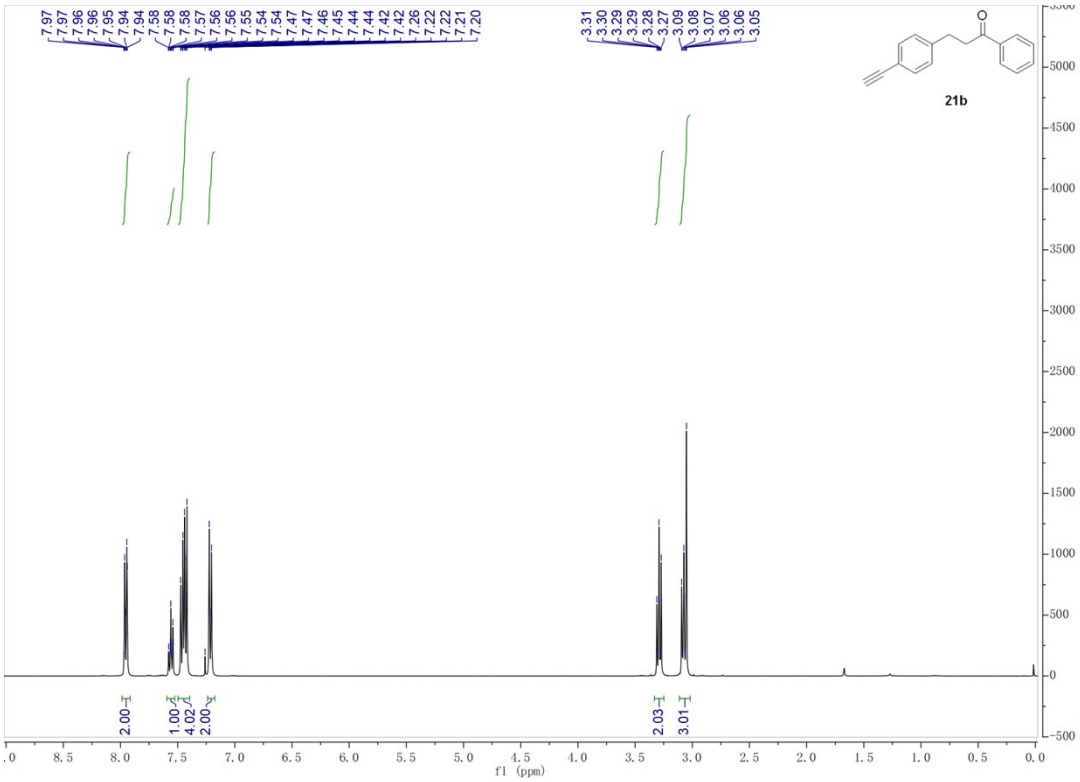
20b
f1 (ppm)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3.29
3.29
3.28
3.27
3.09
3.08
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3.05
21b
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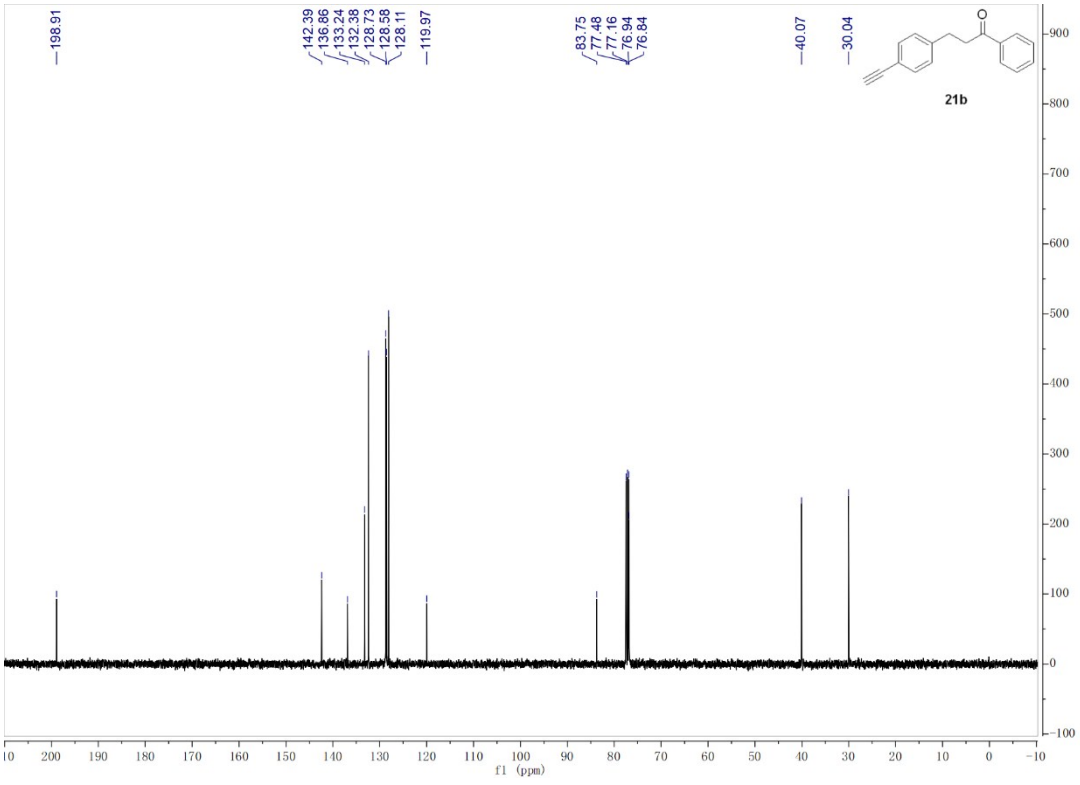
2.03
3.01
f1 (ppm)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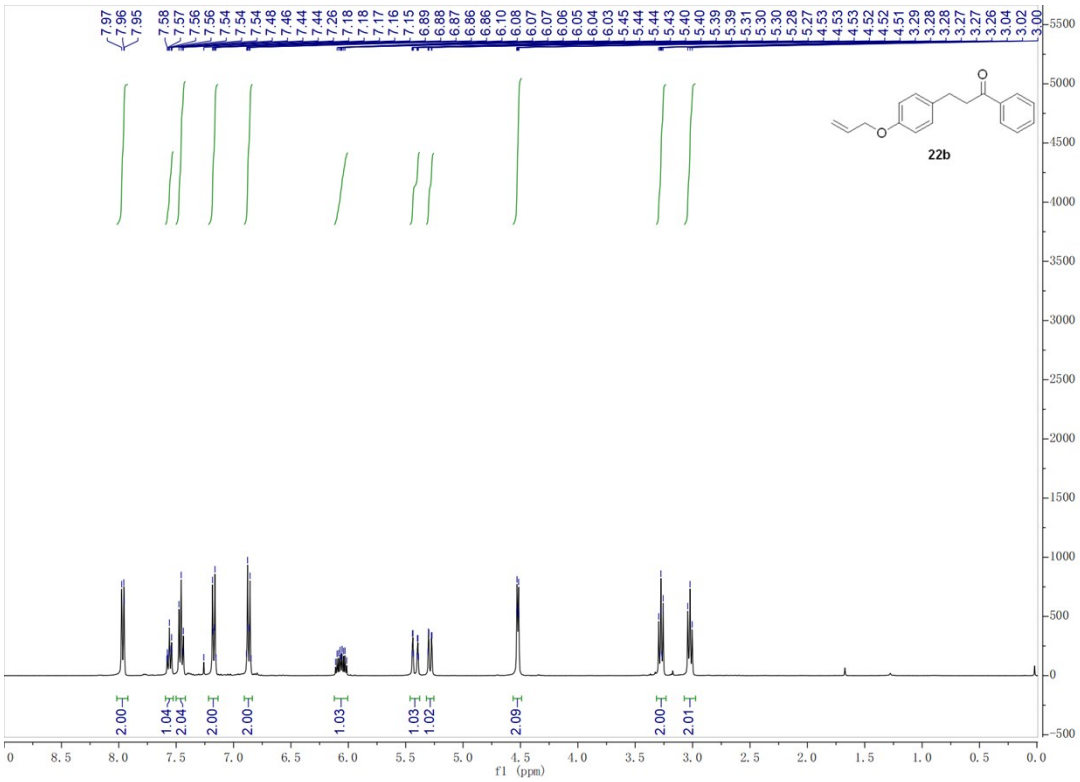
21b
f1 (ppm)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22b
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1.02
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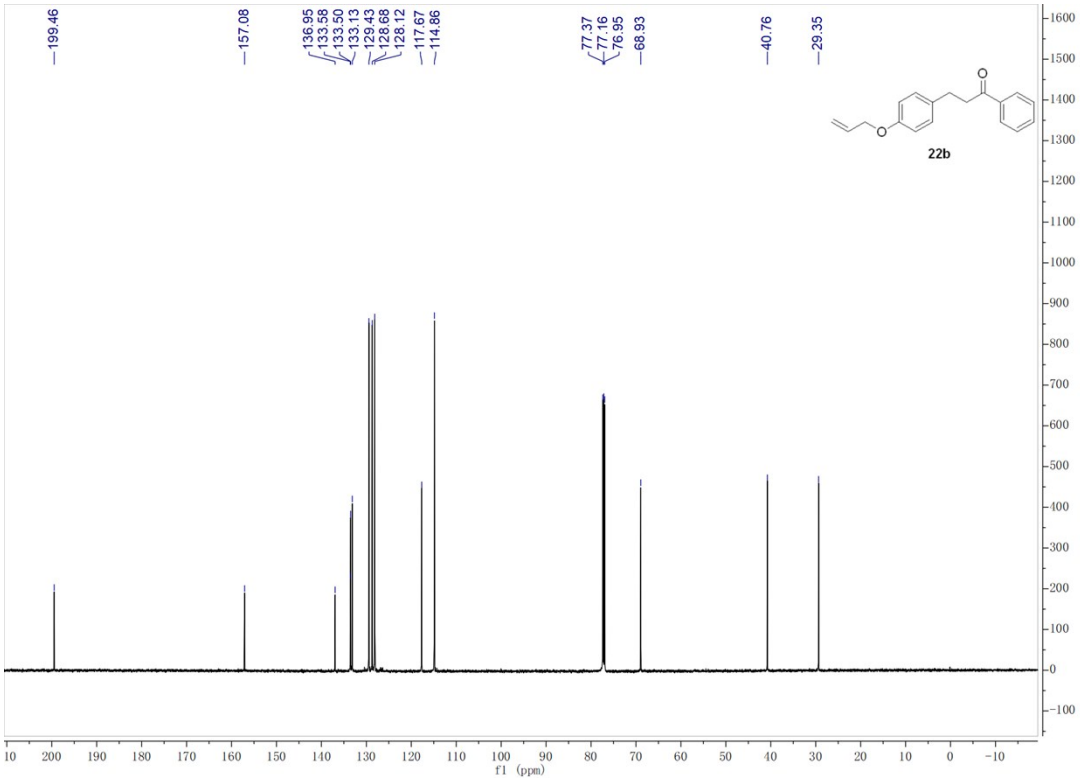
2.00
2.01
f1 (ppm)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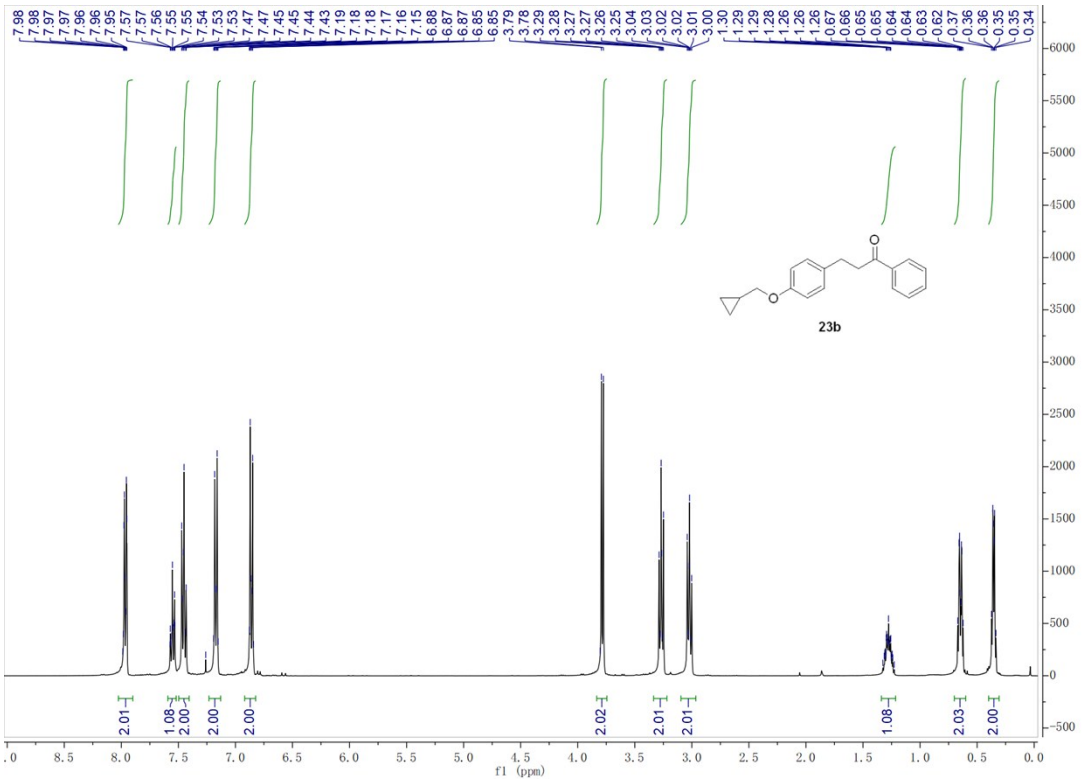
22b
f1 (ppm)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23b
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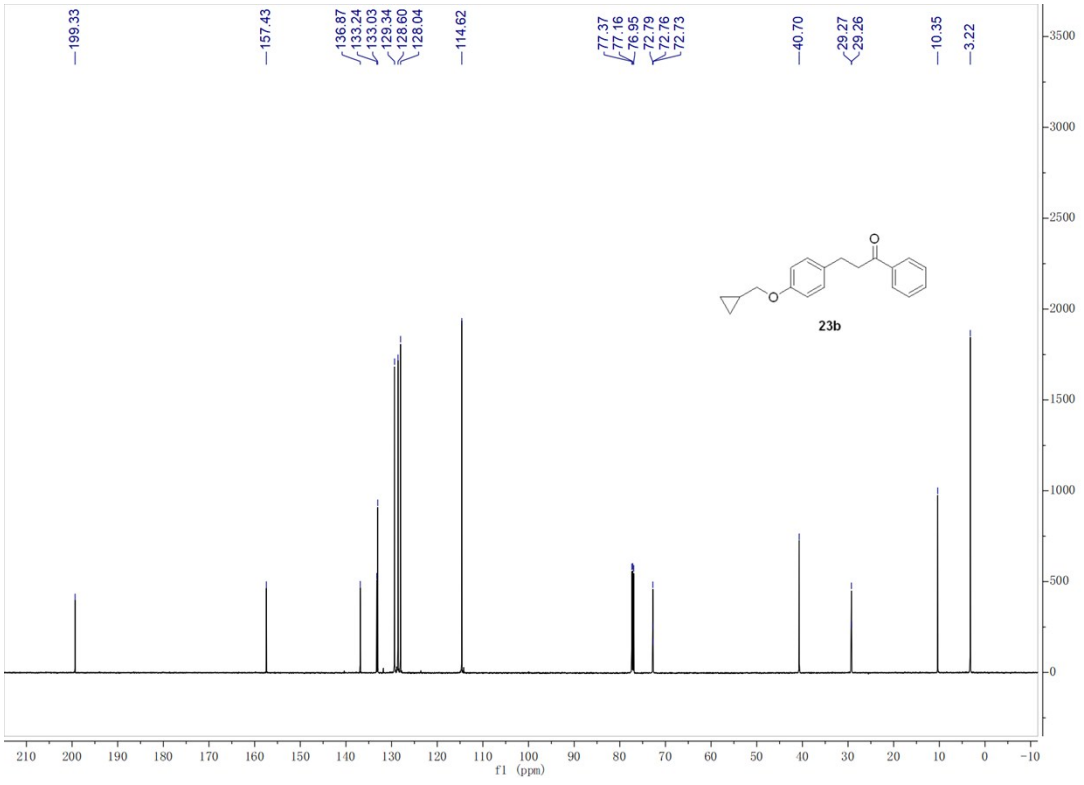
f1 (ppm)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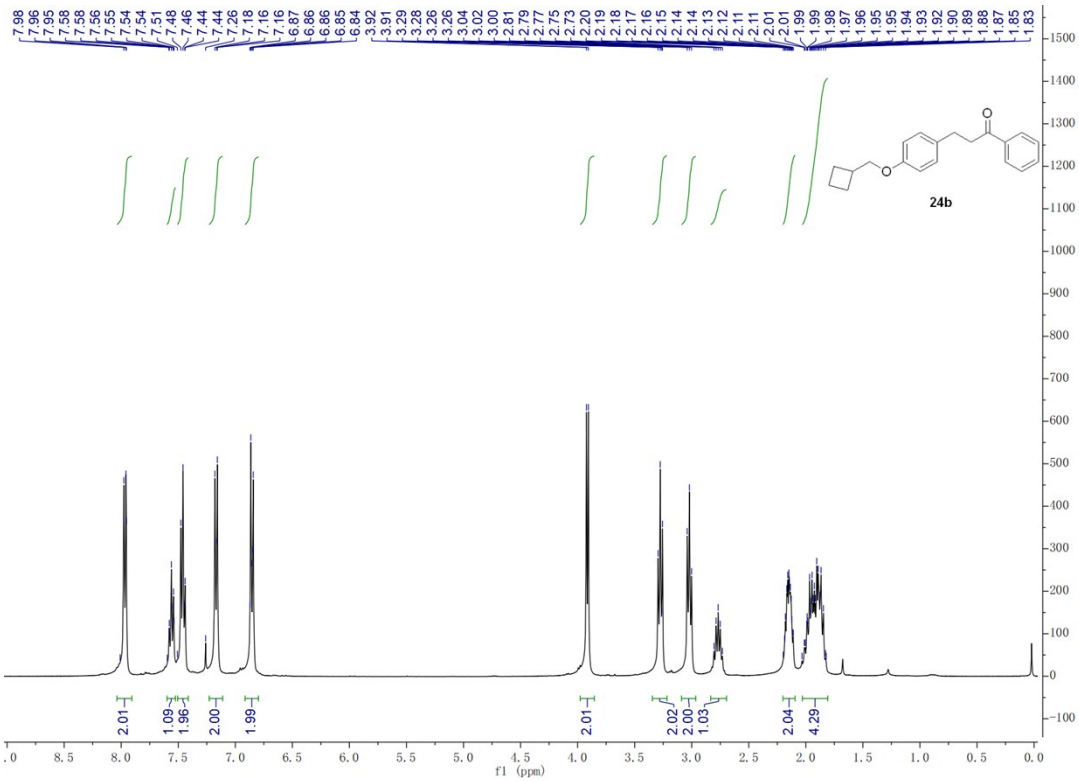
23b
f1 (ppm)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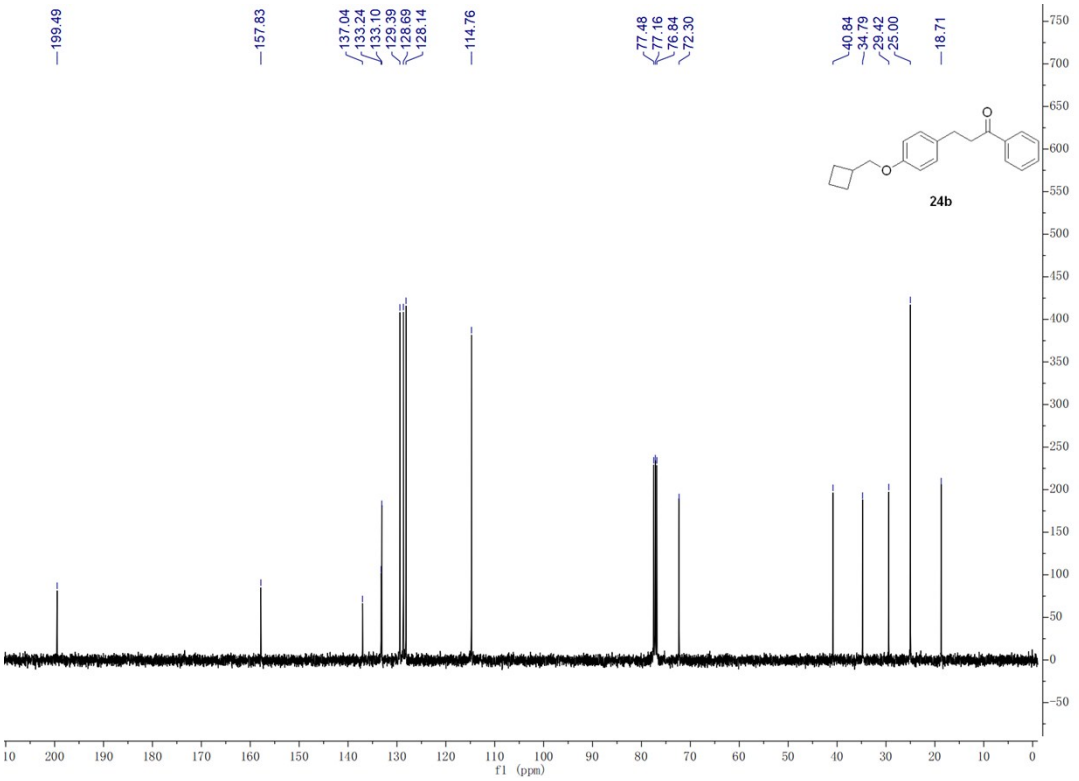
f1 (ppm)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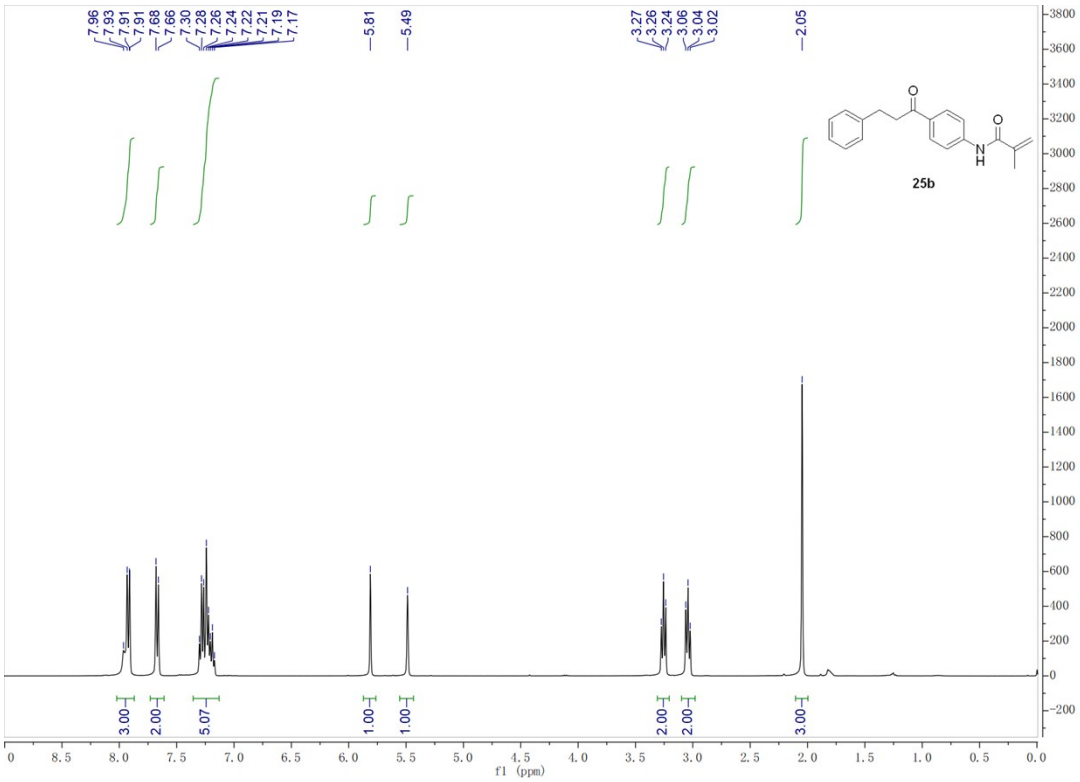
18.71
24b
f1 (ppm)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3.24
3.06
3.04
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2.05
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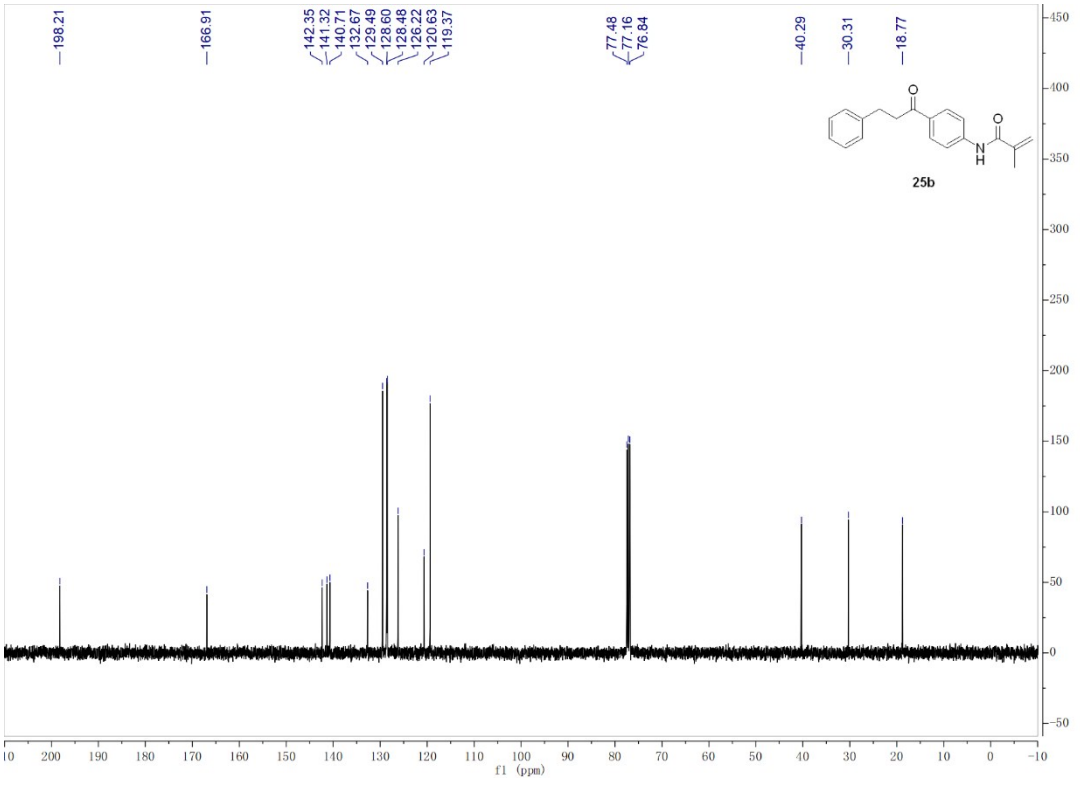
2.00
5.07
1.00
1.00
2.00
2.00
3.00
f1 (ppm)
25b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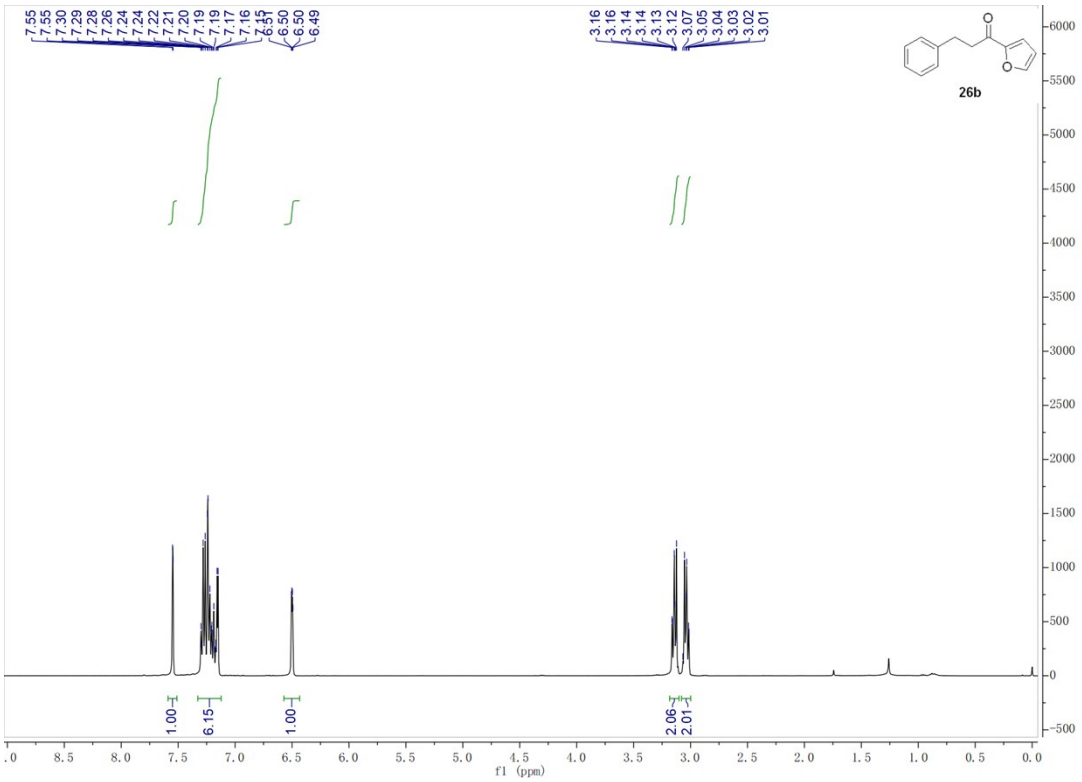
30.31
18.77
f1 (ppm)
25b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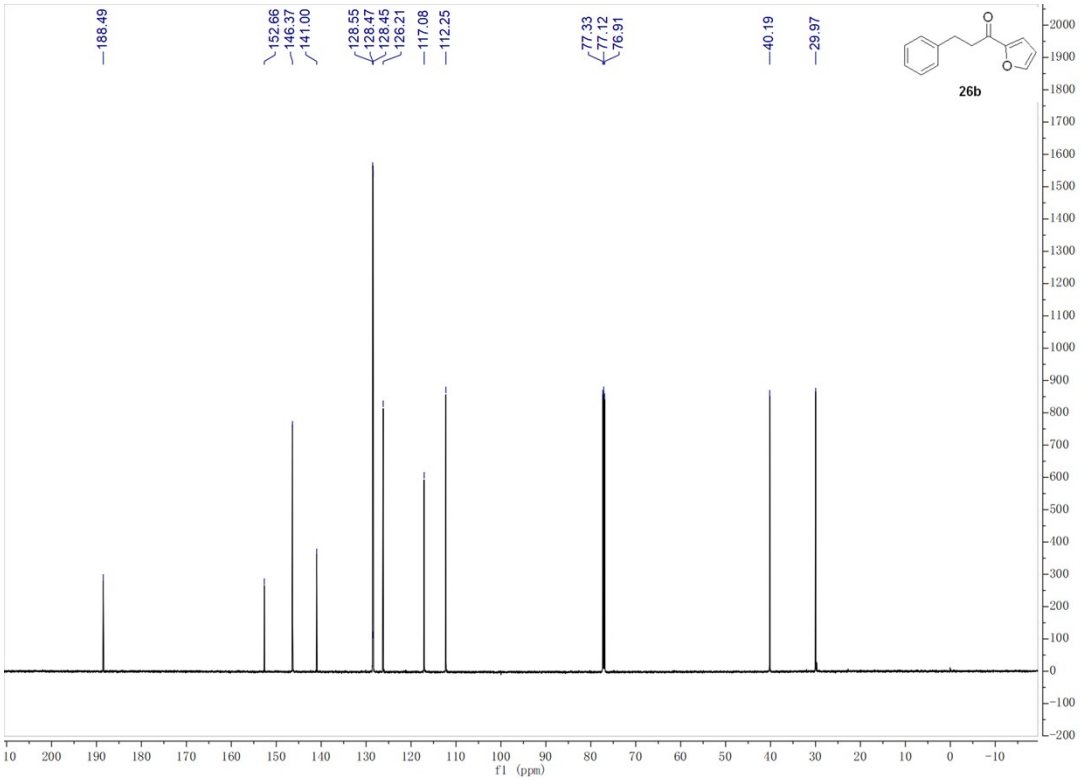
2.06
2.01
f1 (ppm)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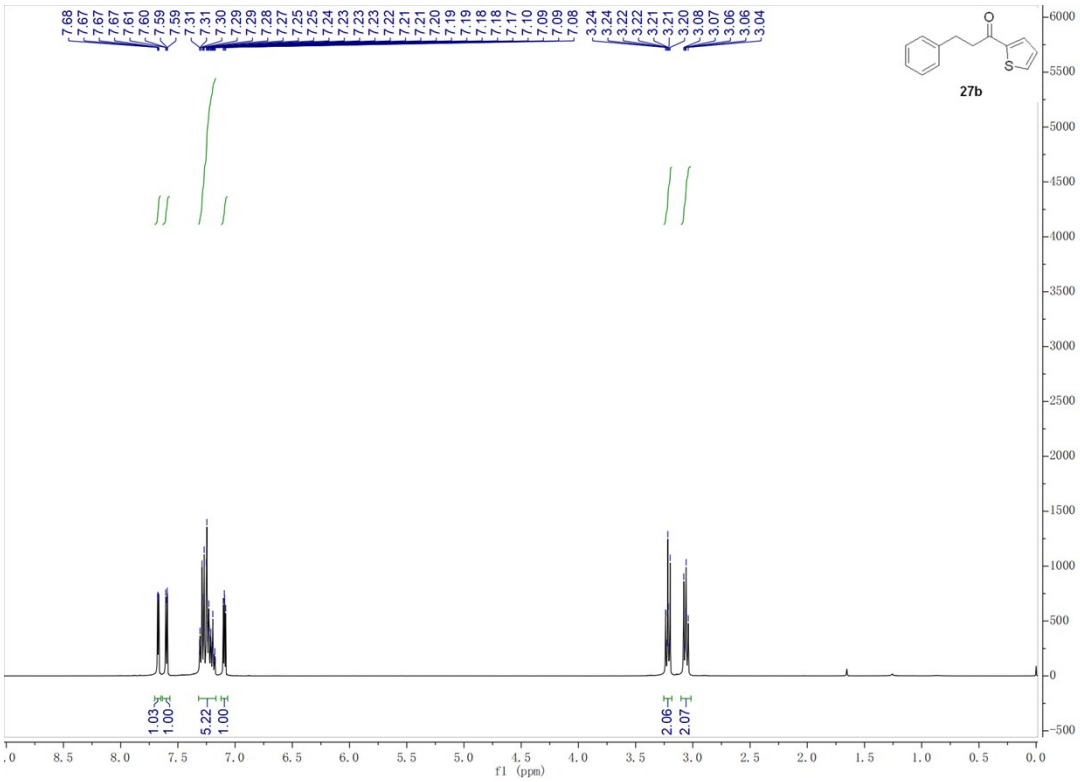
26b
f1 (ppm)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7.17
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7.09
7.09
7.08
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3.20
3.08
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3.06
3.04
27b
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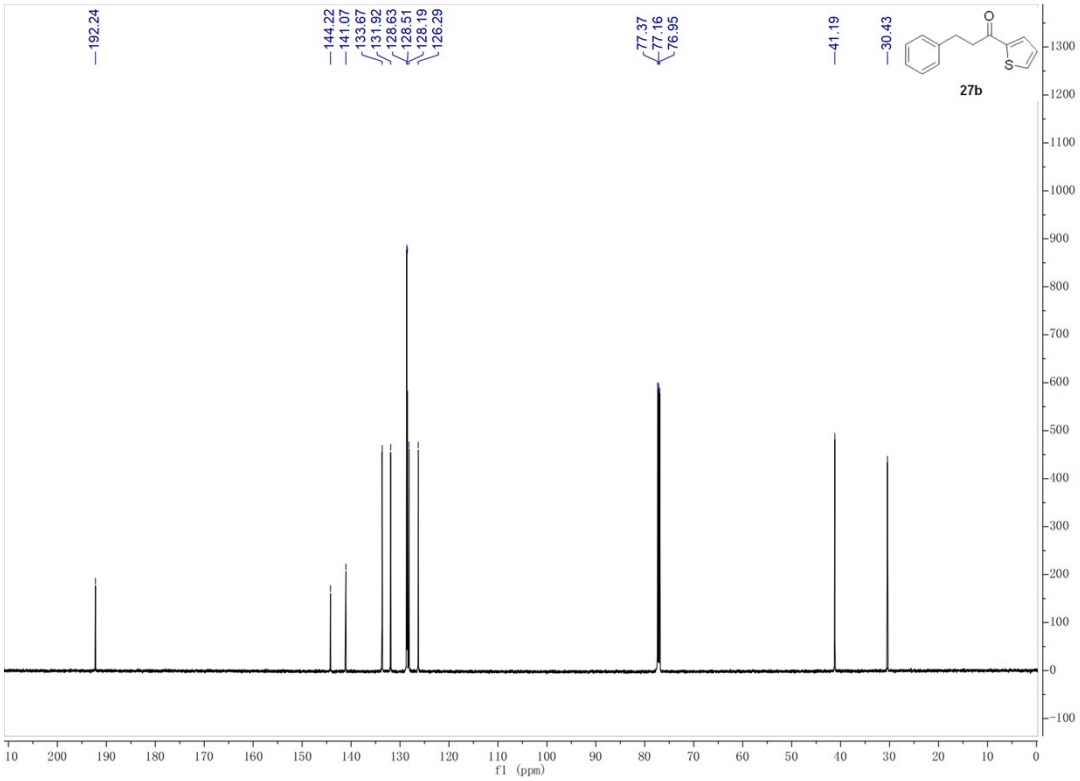
2.06
2.07
f1 (ppm)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76.95
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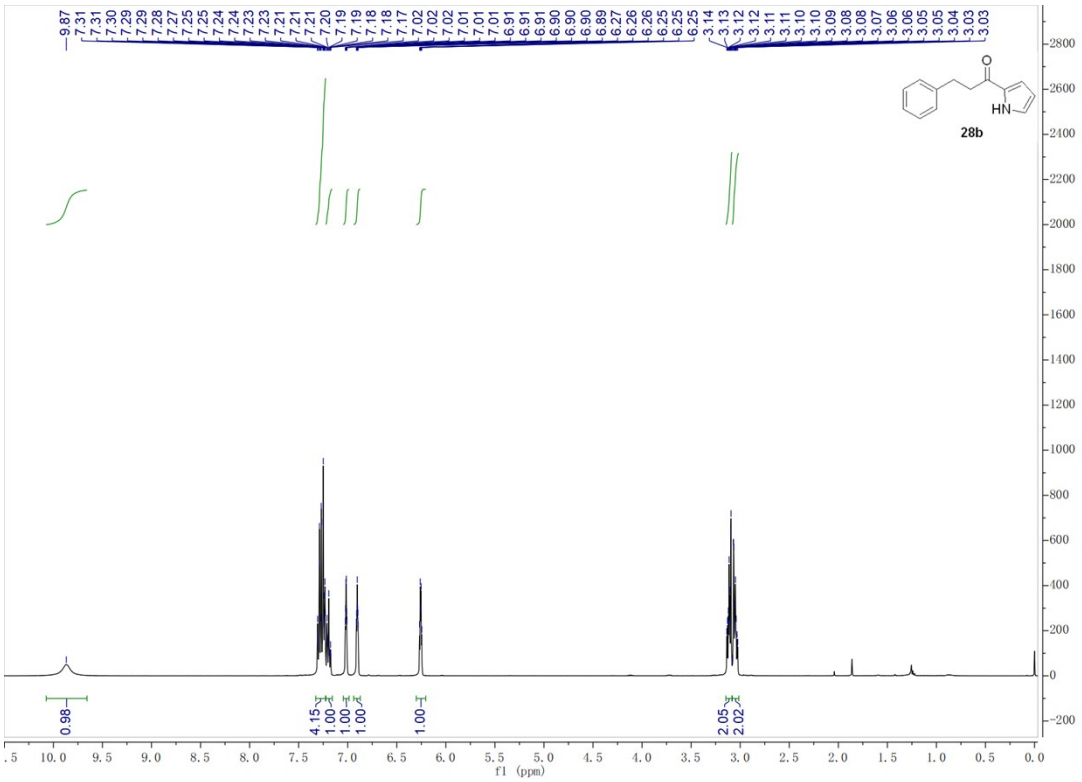
27b
f1 (ppm)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O
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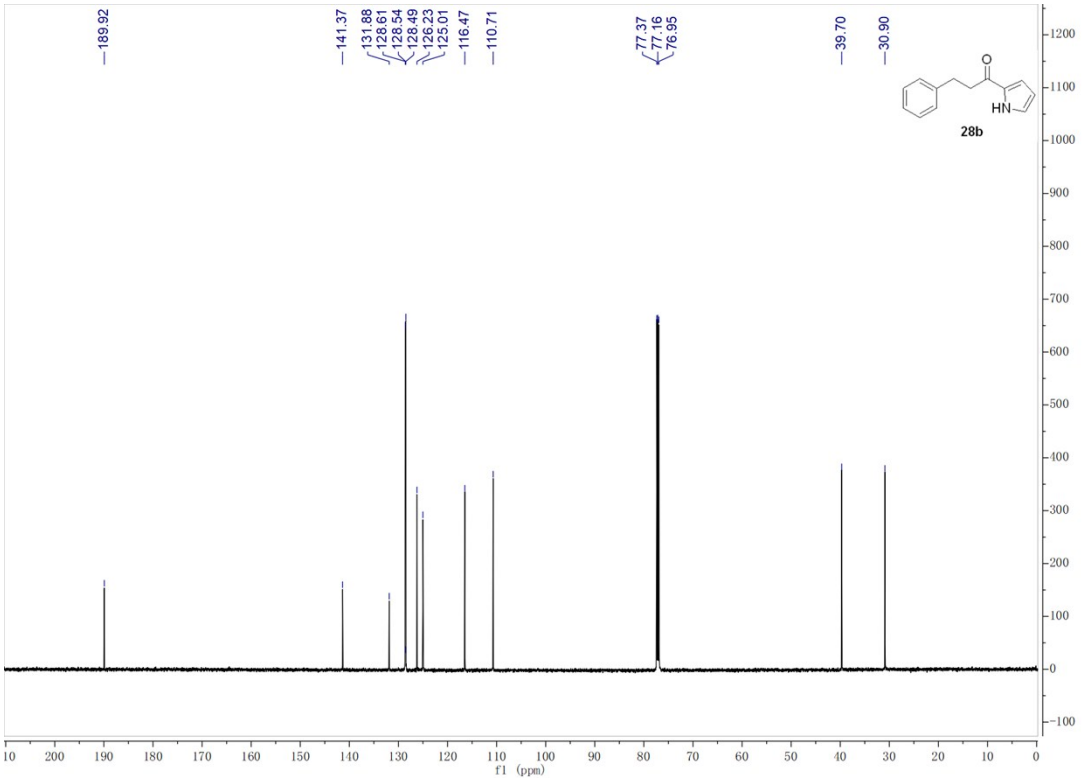
2.02
f1 (ppm)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HN
O
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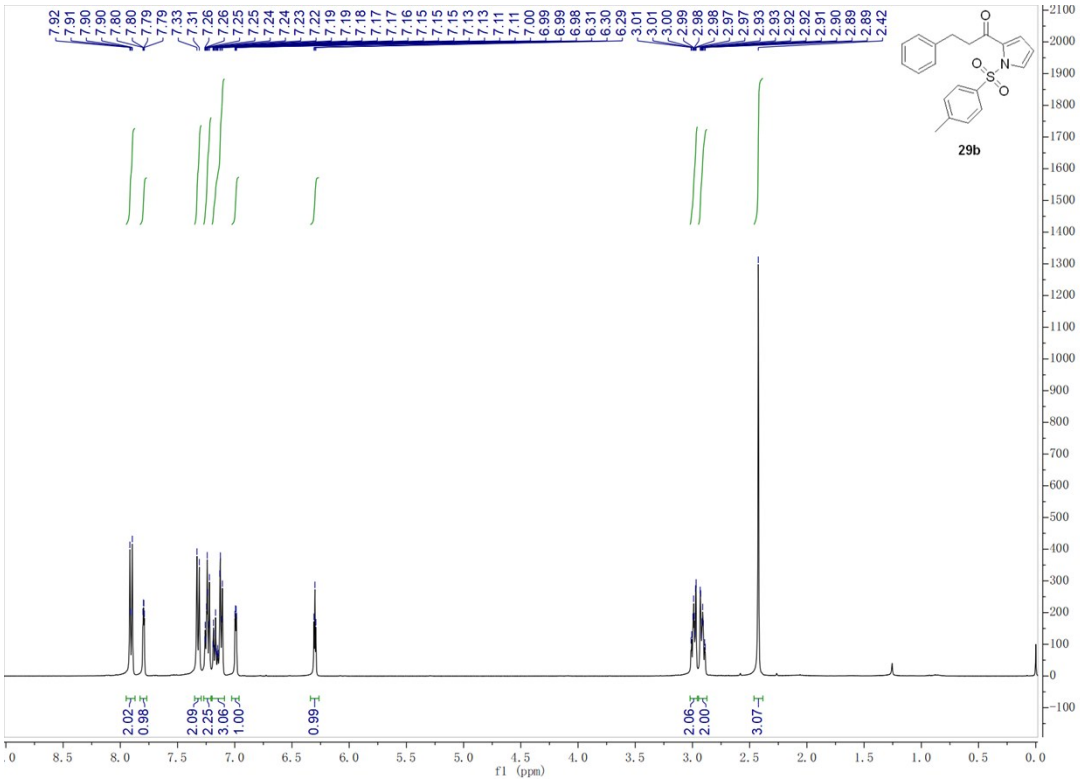
f1 (ppm)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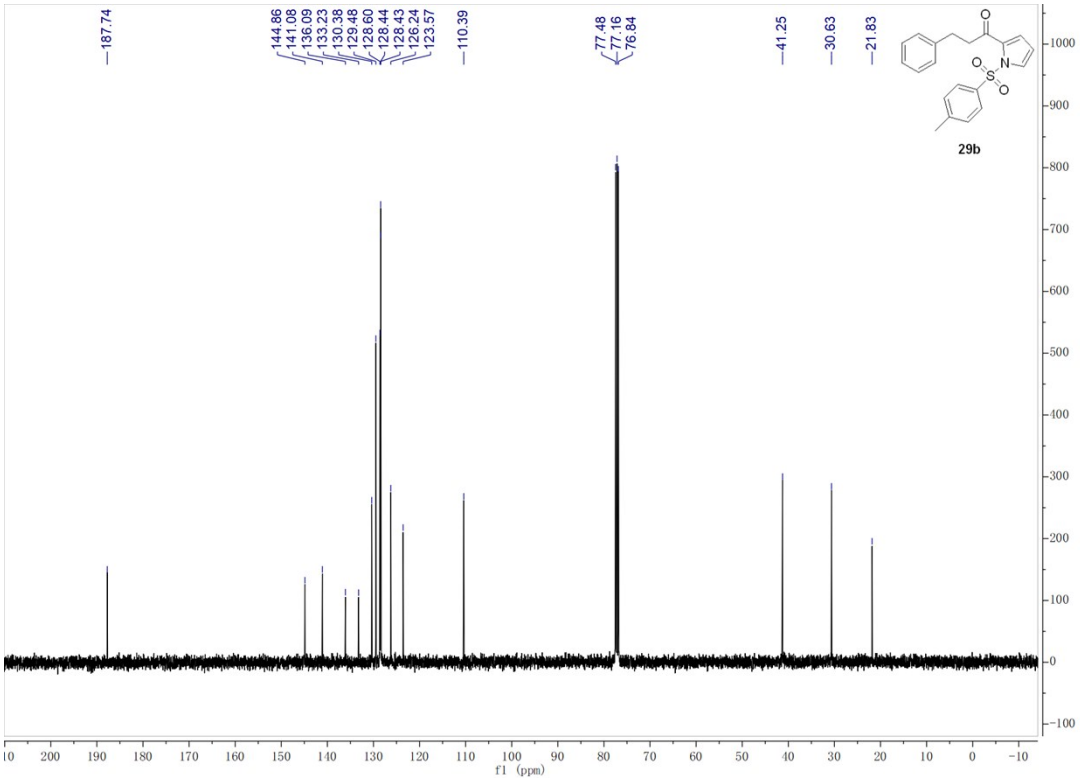
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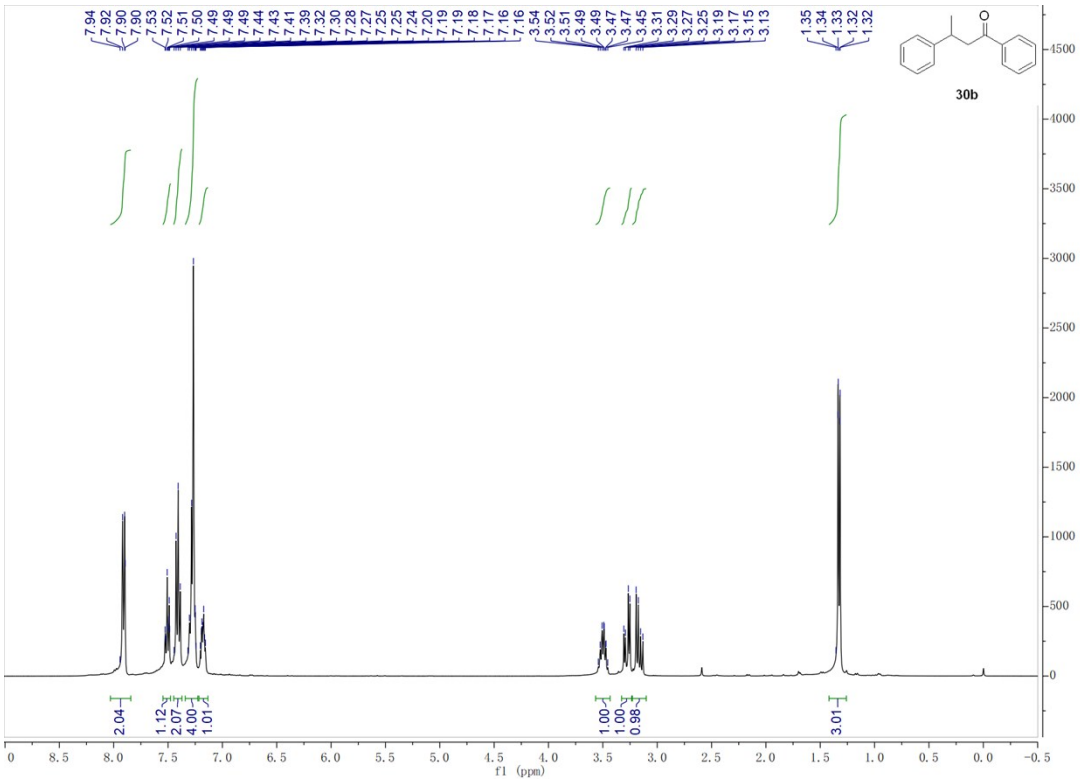
f1 (ppm)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1.34
1.33
1.32
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30b
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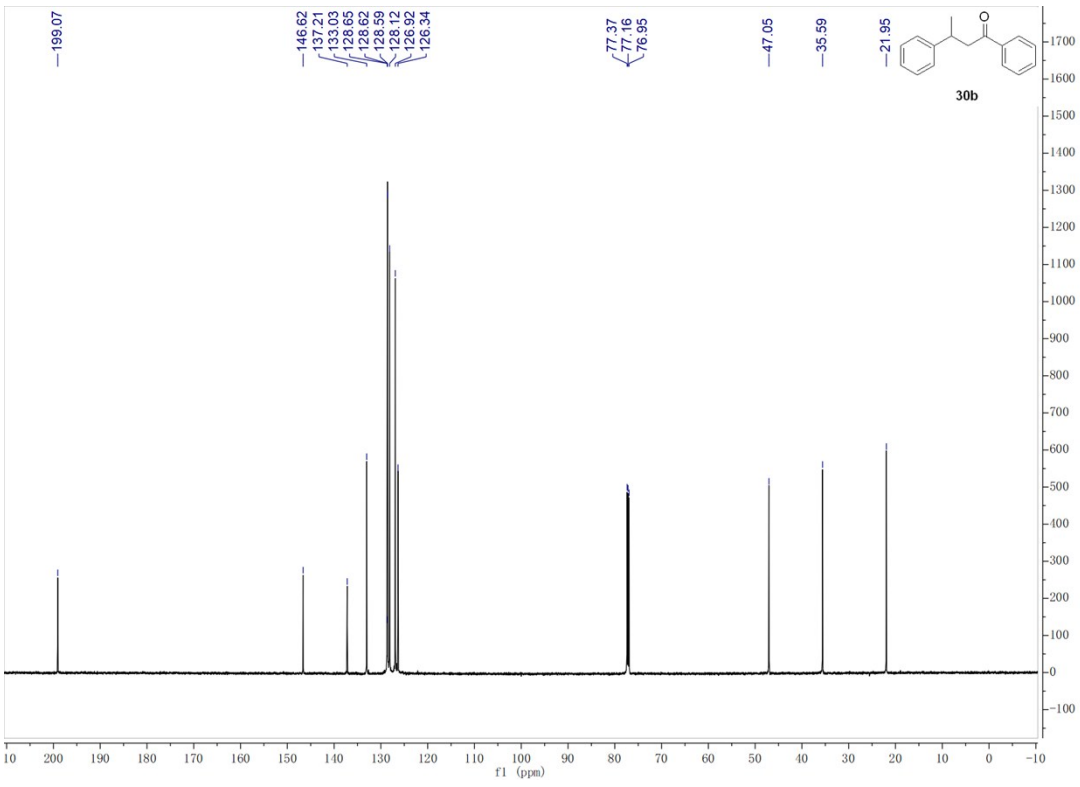
1.12
2.07
4.00
1.01
1.00
1.00
0.98
3.01
f1 (ppm)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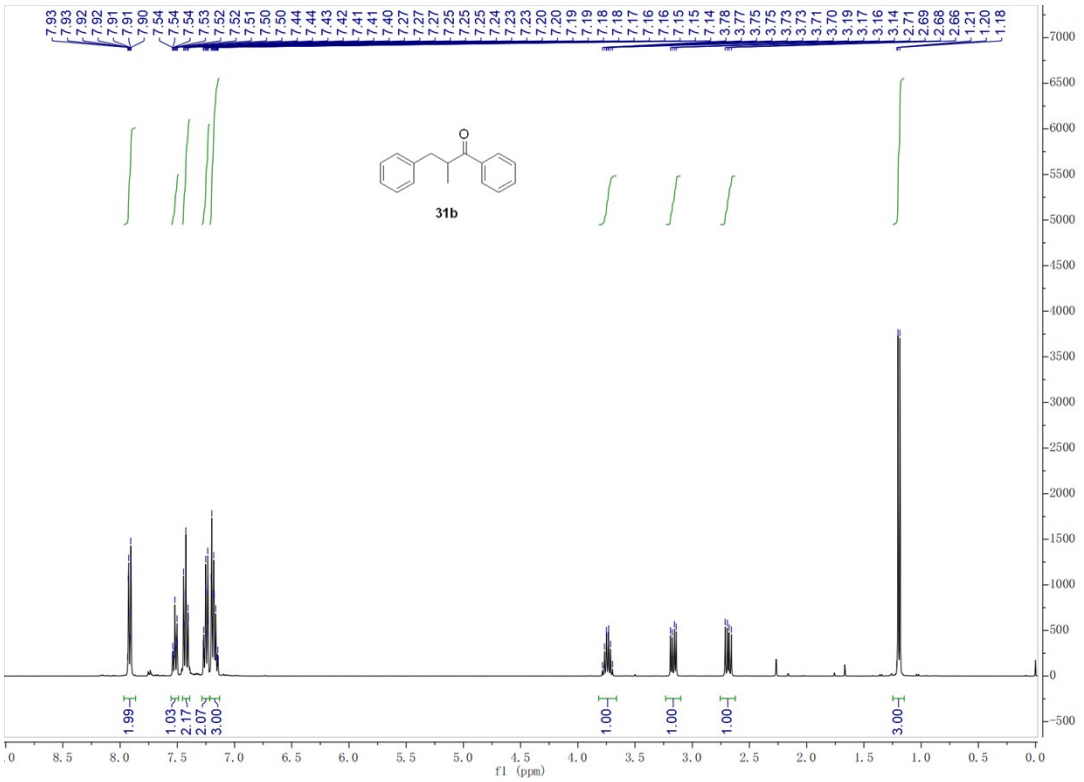
47.05
35.59
21.95
30b
f1 (ppm)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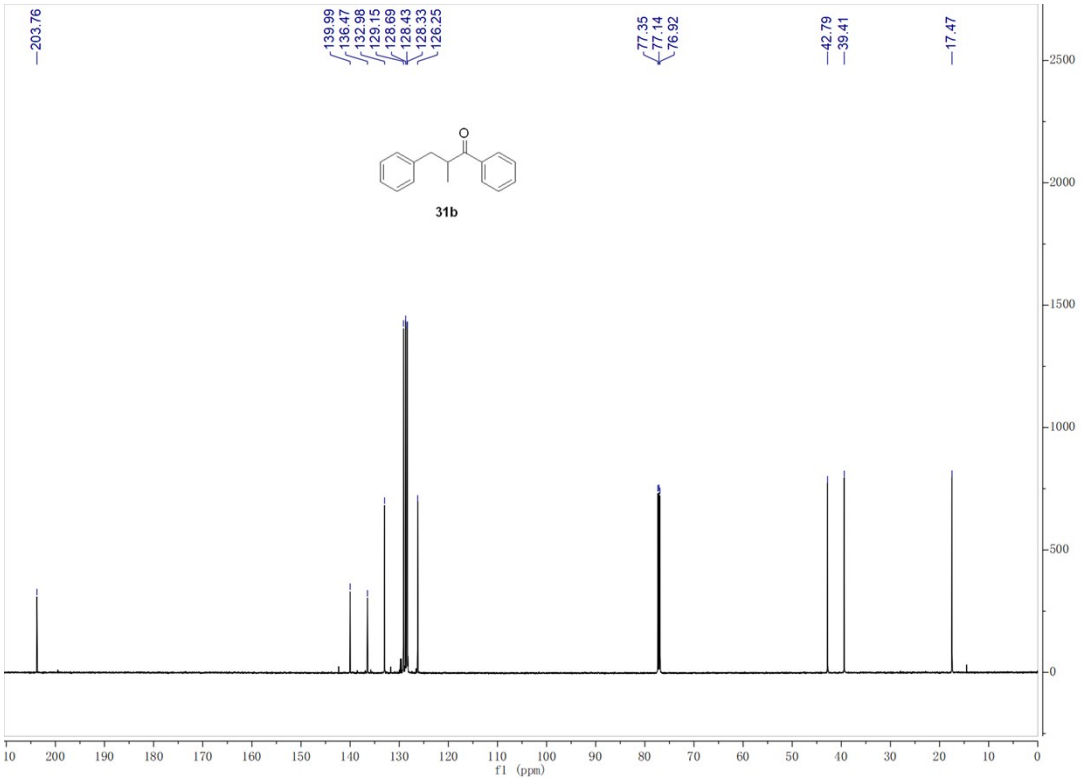
3.00
f1 (ppm)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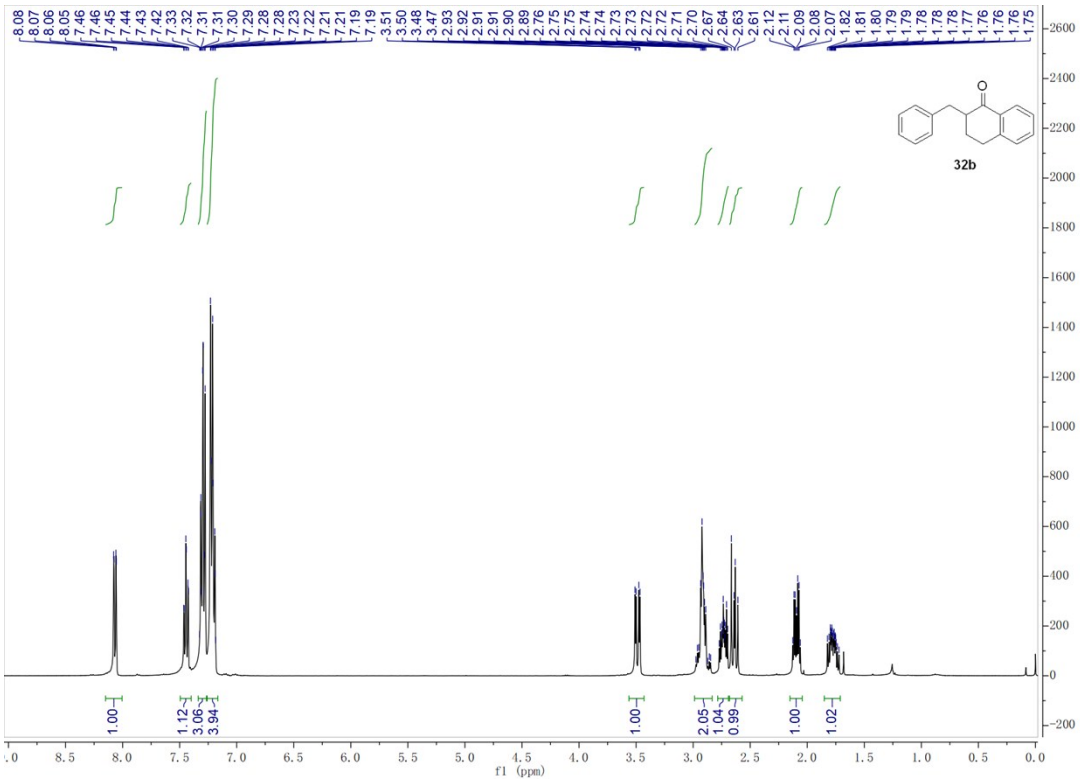
31b
f1 (ppm)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32b
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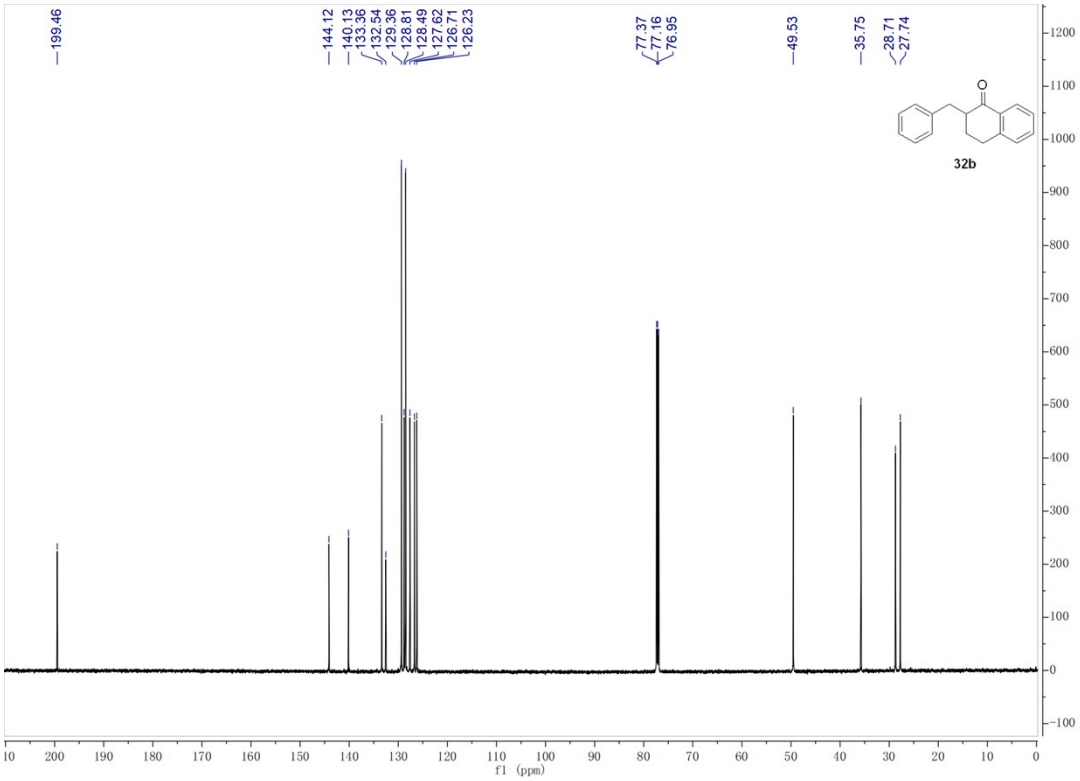
f1 (ppm)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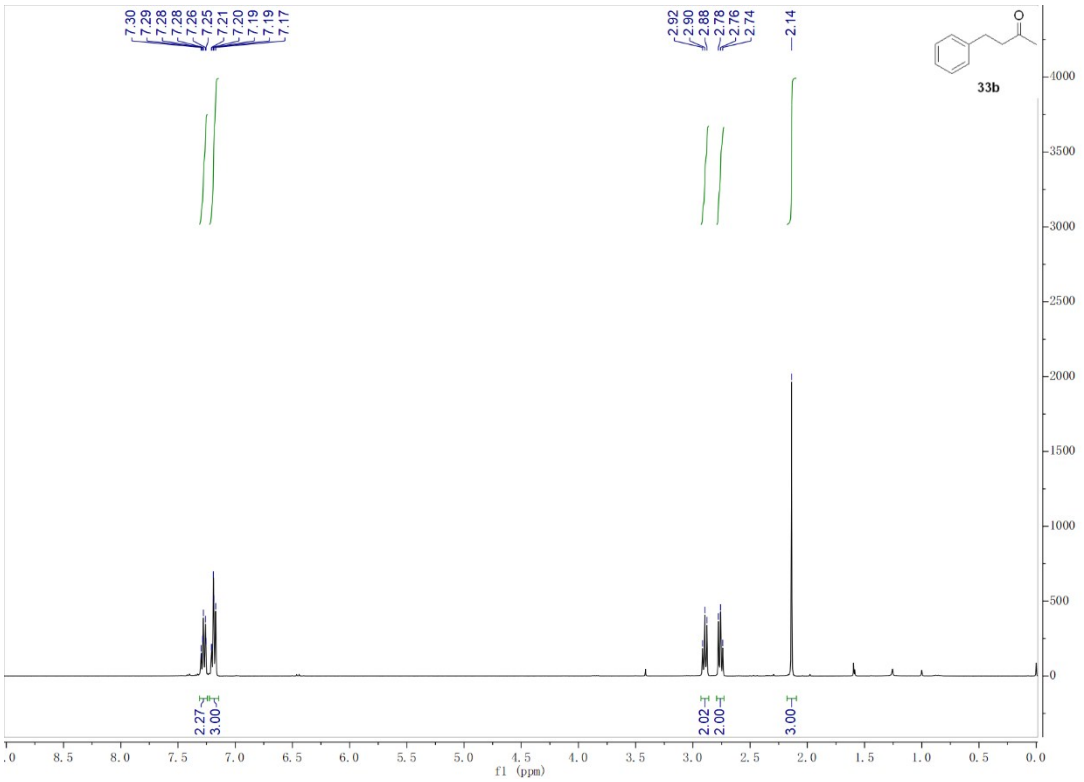
77.37 77.16 76.95
49.53
35.75
28.71 27.74
32b
f1 (ppm)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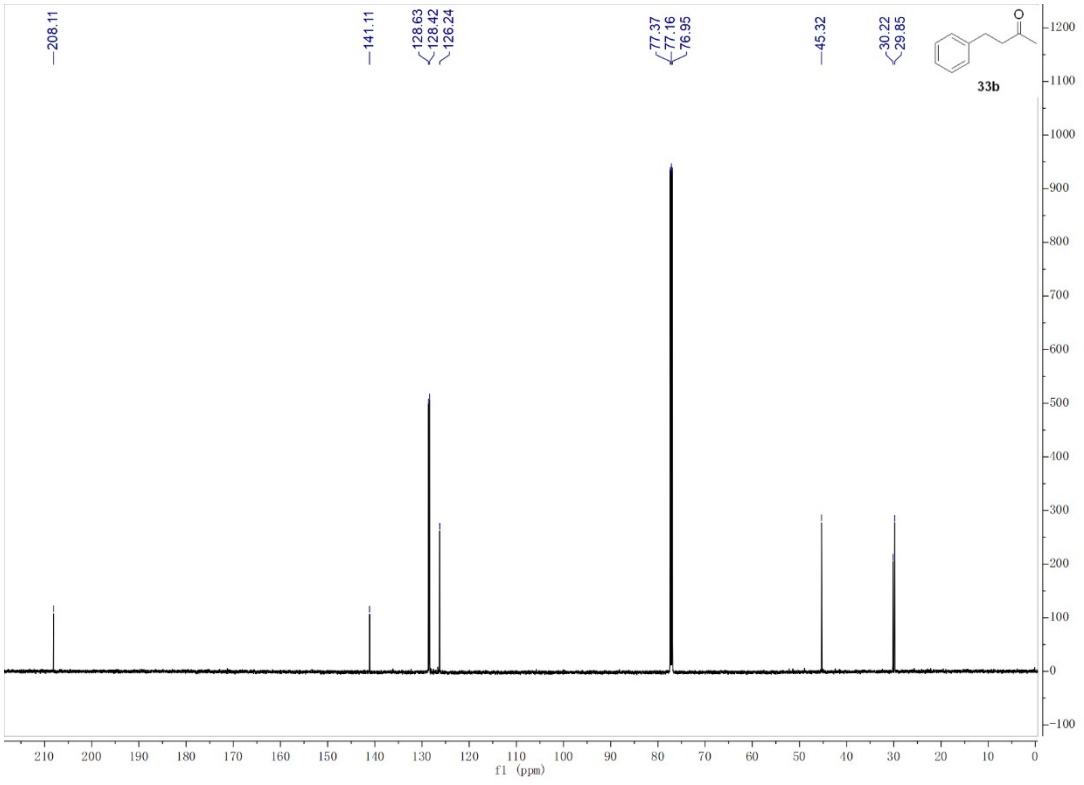
2.02
2.00
3.00
f1 (ppm)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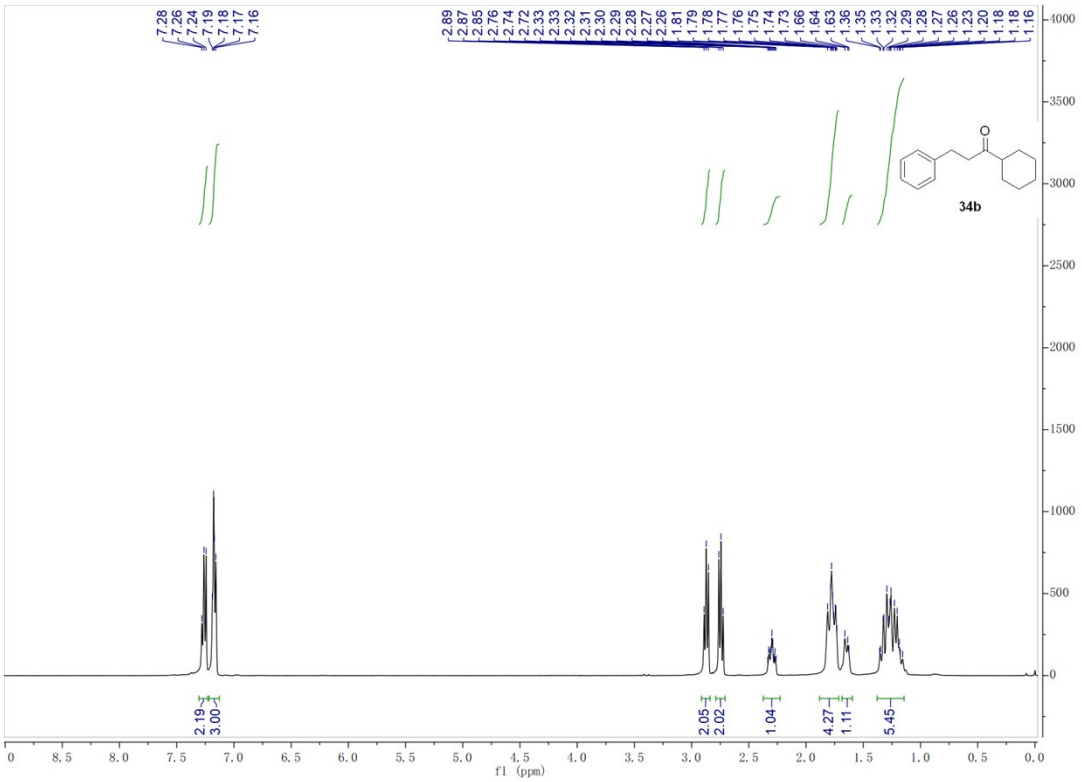
33b
f1 (ppm)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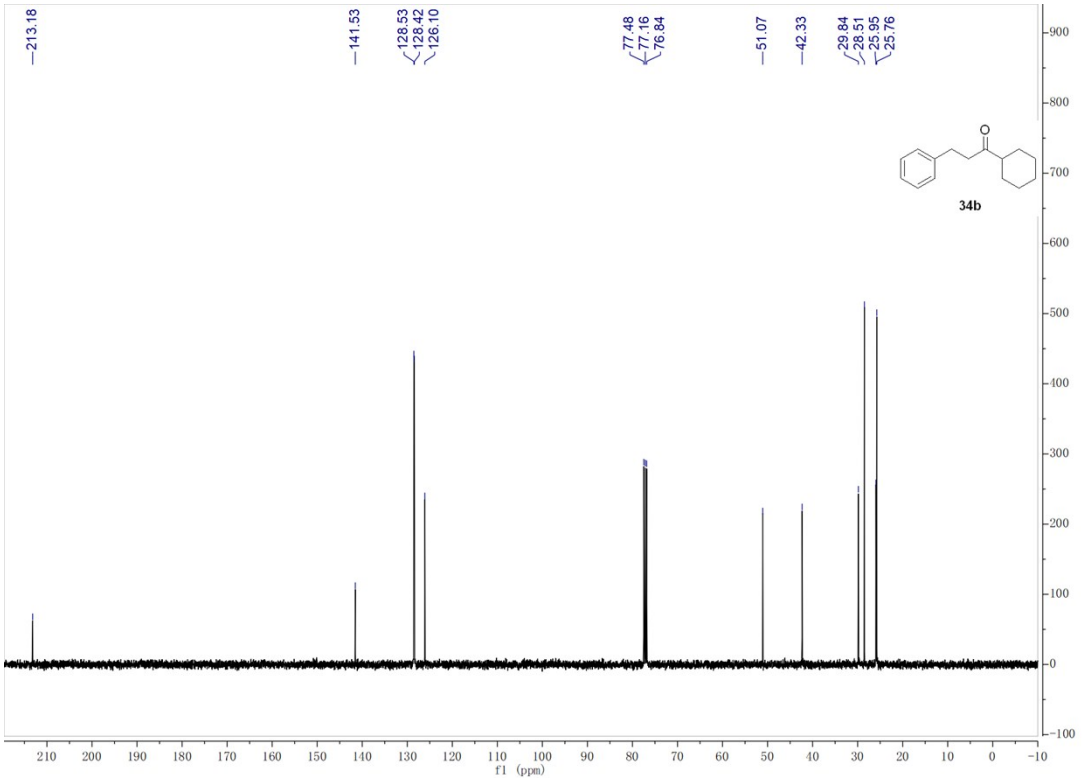
2.33
2.32
2.31
2.30
2.29
2.28
2.27
2.26
1.81
1.79
1.78
1.77
1.76
1.75
1.74
1.73
1.66
1.64
1.63
1.36
1.35
1.33
1.32
1.29
1.28
1.27
1.26
1.23
1.20
1.18
1.18
1.16
34b
2.19
3.00
2.05
2.02
1.04
4.27
1.11
5.45
f1 (ppm)


213.18
141.53
128.53
128.42
126.10
77.48
77.16
76.84
51.07
42.33
29.84
28.51
25.95
25.76
34b
f1 (ppm)