Supporting Information

Ligand-Tuned Cobalt-Containing Coordination Polymers and Application in Water†

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Table of contents

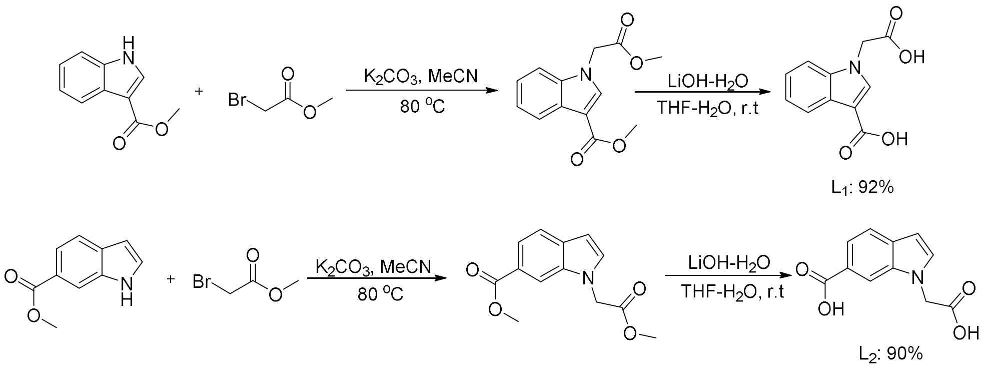
1. General methods and materials……S2
2. Preparation of coordination polymer **1a** and **1b**…… S2-S3
3. Other characterizations of catalyst **1a** and **1b** ……S3-S4
4. General procedure for **4**……S4
5. General procedure for **4** from alcohols and alcohols……S4-S5
6. General procedure for **8**……S5
7. Recycling experiments ……S5
8. Mechanism studies ……S6
9. Analytical data of the obtained compounds……S6-S14
10. NMR spectra of obtained compounds……S15-S50
11. References……S51

1. General methods and materials

All of the reactions dealing with air were carried out in a high purity argon or nitrogen atmosphere using standard Schlenk techniques or glovebox techniques. Unless the special instructions, all the reagents were used without further purification. All the obtained products were characterized by ^{1}H-NMR, ^{13}C-NMR and referenced to $CDCl_3$ (7.26 ppm for ^{1}H, and 77.1 ppm for ^{13}C) or DMSO-d_6 (2.50 ppm for ^{1}H, and 39.5 ppm for ^{13}C) with tetramethylsilane as internal standard (0 ppm). ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Varian 400 or 101 MHz respectively on Bruker Advance III HD 400 MHz spectrometer. Analytical thin layer chromatography (TLC) was performed using commercially prepared 100-400 mesh silica gel plates (SGF254), and visualization was realized by means of accurate UV light (254 nm). Flash column chromatography was performed on 230-430 mesh silica gel. Thermogravimetric analysis was carried out using a TGA /1100SF instrument in dry nitrogen atmosphere at a heating rate of 10 °C/min from 50 to 650 °C.

2. Preparation of coordination polymer (1a) and (1b)

2.1 The synthesis of ligand (L_1 and L_2)

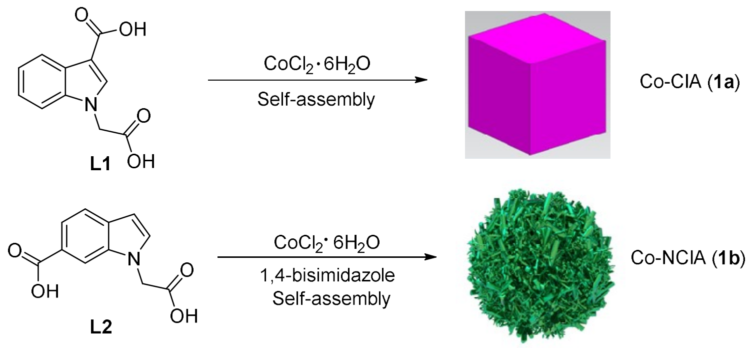


The 100 mL round bottom flask was added successively indole-3-carboxylate (0.998 g, 5.70 mmol), 2-bromoacetate (3.48 g, 22.80 mmol), anhydrous potassium carbonate (6.30 g, 45.60 mmol), MeCN (25 mL). The reaction mixture was refluxed for 12 hours and monitored by TLC until the reaction was complete, confirming the disappearance of methyl indole-3-carboxylic acid. Water was then added and extracted with ethyl acetate. The combined organic phases were washed and dried under anhydrous conditions. The solvent was extracted under reduced pressure, and column chromatography (petroleum ether / ethyl acetate = 10: 1) gave the compound as a pale yellow solid with a yield of 86% (1.210 g). The obtained compound was further hydrolyzed. THF was added to dissolve the compound and a mixed solution of LiOH and water (30 mL) was added. Of note is THF / H_2O (1: 1). After stirring at room temperature for 4 hours, the reaction solution was acidified to pH = 2 and finally washed with H_2O and evaporated to dryness to make the desired product (L_1) 92% yield (1.148 g). Using the same method and the obtained the acid product (L_2) in 90% yield (1.123 g).

The acid product L_1 was finally obtained as a white solid. Mp: 164 -165 ° C. ^{1}H NMR (400 MHz, DMSO) δ 12.83 (s, 2H), 8.04 (s, 1H), 7.65 (dd, J = 17.7, 8.3 Hz, 2H), 7.56 (d, J = 3.0 Hz, 1H), 6.56 (d, J = 2.8 Hz, 1H), 5.14 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ 170.90, 163.45, 139.58, 128.81, 125.91, 125.25, 122.68, 121.05, 111.20, 110.44, 46.78. Similarly, L_2 was obtained as a white solid. ^{1}H NMR (400 MHz, DMSO): δ 12.83 (s, 2H), 8.04 (s, 1H), 7.65 (dd, J = 17.7, 8.3 Hz, 2H), 7.56 (d, J = 3.0 Hz, 1H), 6.56 (d, J = 2.8 Hz, 1H), 5.14 (s, 2H).^{13}C NMR (101 MHz, DMSO): δ 170.79, 168.77, 136.19, 133.77, 132.09, 123.96, 120.56 (d, J = 15.8 Hz), 112.43, 101.84, 47.71. $L_{3:}$ ^{1}H NMR (400 MHz, DMSO): δ 7.61 (s, 2H), 7.14 (s, 2H), 6.88 (s, 2H), 3.96 (s, 4H), 1.62 (s, 4H). ^{13}C NMR (101 MHz, DMSO): δ 137.41, 128.76, 119.69, 45.73, 28.31.

2.2 The synthesis of (1a) and (1b)

The mixture of the dissolved diacid (1-(carboxymethyl)-1H-indole-3-carboxylic acid, L_1, (0.0219 g, 0.1 mmol) and $CoCl_2·6H_2O$ (0.0118 g, 0.05 mmol) in 8 mL DMF-ethanol-water (5: 2: 1, v / v / v) was stirred slowly for 30 minutes at room temperature. Then, the mixture was placed in a 15 mL autoclave lined with a Teflon stopper, heated for 72 hours at 110 °C. Subsequently, the resulting mixture was cooled to room temperature and the obtained solid was washed three times with anhydrous ethanol, centrifuged three times, and dried to gain the material Co-CIA (**1a**) in 85% yield (0.0186 g). Using the same hydrothermal synthesis method, under the condition of a high temperature 140 ^{o}C for 72 hours, material Co-NCIA (**1b**) was gained in 77% yield (0.0168 g).



3. Other characterizations of catalyst (1a) and (1b)

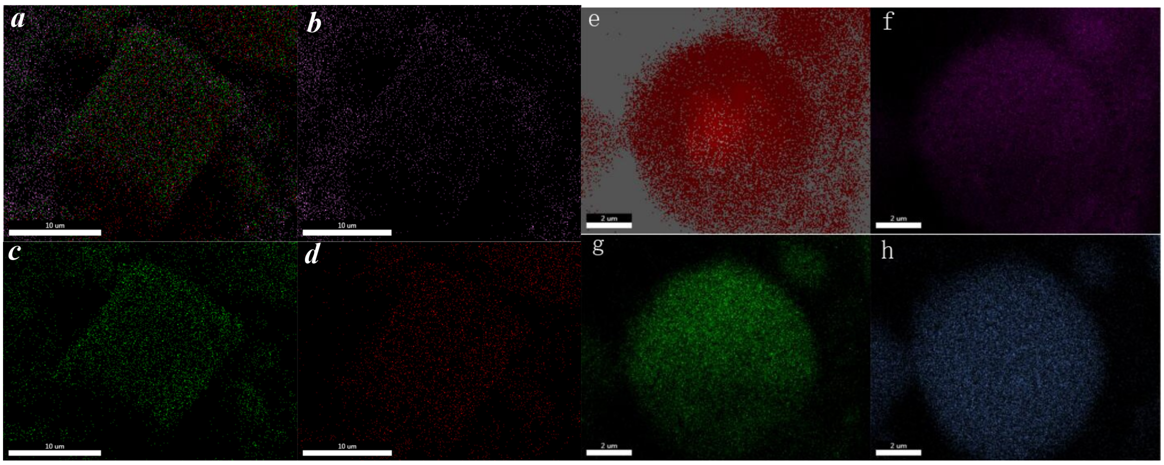


Figure .S1. The EDX image of Co-CIA(1a) and Co-NCIA(1b). The corresponding element mapping images of (a): Co-CIA(1a), (b): C, (c): O, (d): Co, (e): Co-NCIA(1b), (f): C, (g): O, (h): Co.

Table S1. Quantitative elemental composition of C, O, and Co from the Co-CIA(1a) XPS data.

Name	Start (BE)	Peak (BE)	End (BE)	Height (CPS)	FWHM (eV)	Area (P) CPS. (eV)	Area (N) TPP-2M	Atomic (%)
Co2p	810	780.99	775	7836.37	1.59	64000.59	73.44	4.47
C1s	296	284.95	281	28280.5	2.72	86452.75	1212.39	73.83

O1s	540	531.22	526	22057.6	2.69	61439.34	356.23	21.69

Table S2. Quantitative elemental composition of C, O, and Co from the Co-NCIA(1b) XPS data.

Name	Start (BE)	Peak (BE)	End (BE)	Height (CPS)	FWHM (eV)	Area (P) CPS. (eV)	Area (N) TPP-2M	Atomic (%)
Co2p	810	781.34	775	15390.0	2.51	134701.58	154.63	8.41
C1s	296	284.72	281	15530.9	3.05	71268.56	999.31	54.33
O1s	540	531.7	526	64305.1	1.6	118188.51	685.53	37.27

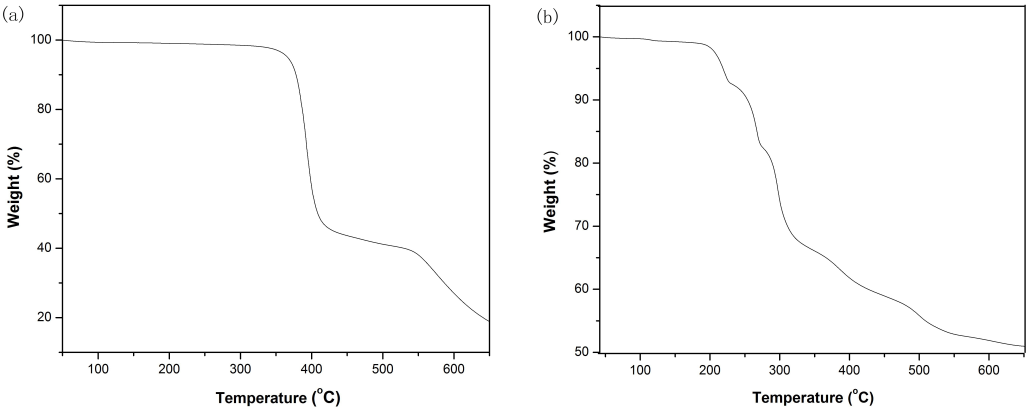
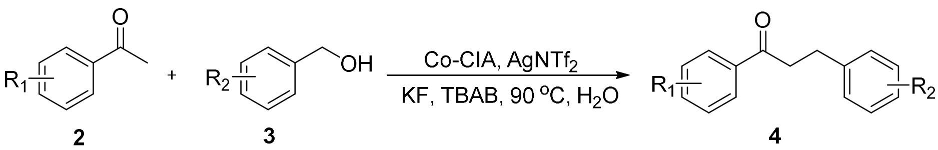


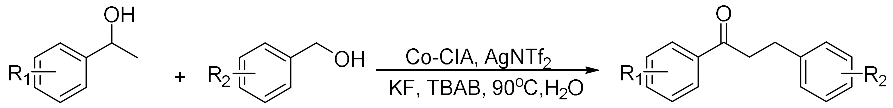
Figure S2. (a) TG pattern of Co-CIA (1a). Thermo gravimetric analysis results show that the synthesized Co-CIA is very stable below 350 °C, and the structure begins to decompose at a temperature of 350 °C to 400 °C. (b) TG pattern of Co-NCIA (1b). Thermo gravimetric analysis results show that the synthesized Co-NCIA is very stable below 200 °C, and the structure begins to decompose at a temperature of 200 °C to 500 °C.

4. General procedure for 4



To a 25 mL reaction tube was added the catalyst Co-CIA (10 mg), $AgNTf_2$ (1.0 mmol), KF (1.0 equiv.), TBAB (0.2 mmol), H_2O (3 mL), ketone (1.0 mmol), alcohol (1.2 mmol). The mixture was heated at 90 °C for 16 h and then cooled to room temperature. The resulting solution was extracted by a mixed solution of ethyl acetate / distilled water (v / v = 1: 1) ratio, and purified by column chromatography using an eluent of petroleum ether / ethyl acetate (v / v = 40: 1) to afford the desired compounds **4**.

5. General procedure for 4 from alcohols and alcohols.



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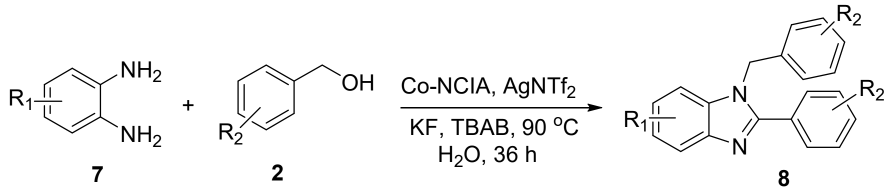
To a 25 mL reaction tube was added the catalyst Co-CIA (10 mg), $AgNTf_2$ (1.0 mmol), KF (1.0 equiv.), TBAB (0.2 mmol), H_2O (3 mL), secondary alcohol (1.0 mmol) and primary alcohol (1.2 mmol). The mixture was heated at 90 °C for 24 h and then cooled to room temperature. The resulting solution was extracted by a mixed solution of ethyl acetate / distilled water (v / v = 1: 1) ratio, and purified by column chromatography using an eluent of petroleum ether / ethyl acetate (v / v = 40: 1) to afford the desired compound **4**.

6. General procedure for 8



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8

To a 25 mL reaction tube was added the catalyst Co-NCIA (10 mg), $AgNTf_2$ (1.0 mmol), KF (1.0 equiv.), TBAB (0.2 mmol), H_2O (3 mL), diamine (1.0 mmol) and alcohol (3 mmol). The mixture was heated at 90 °C for 36 h and then cooled to room temperature. The resulting solution was extracted by a mixed solution of ethyl acetate / distilled water (v / v = 1: 1) ratio, and purified by column chromatography using an eluent of petroleum ether / ethyl acetate (v / v = 10: 1) to afford the desired compound **8**.

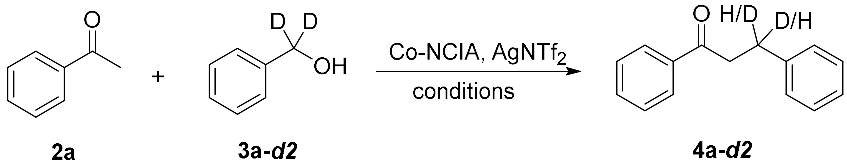
7. Recycling experiments

To a 25 mL reaction tube was added the catalyst Co-CIA (10 mg), $AgNTf_2$ (1.0 mmol), KF (1.0 equiv.), TBAB (0.2 mmol), H_2O (3 mL), acetophenone (1.0 mmol), benzyl alcohol (1.2 mmol). The mixture was heated at 90 °C for 16 h and then cooled to room temperature. When the first reaction was finished, the catalyst Co-CIA was centrifuged and washed several times with water (5 mL X3) and EtOH (5 mL X3), and dried for 48 h. Then the recovered catalyst was reused for the next time.

To a 25 mL reaction tube was added the catalyst Co-CIA (10 mg), $AgNTf_2$ (1.0 mmol), KF (1.0 equiv.), TBAB (0.2 mmol), H_2O (3 mL), 1-phenylethan-1-ol (1.0 mmol) and benzyl alcohol (1.2 mmol). The mixture was heated at 90 °C for 24 h and then cooled to room temperature. When the first reaction was finished, the catalyst Co-CIA was centrifuged and washed several times with water (5 mL X3) and EtOH (5 mL X3), and dried for 48 h. Then the recovered catalyst was reused for the next time.

To a 25 mL reaction tube was added the catalyst Co-NCIA (10 mg), $AgNTf_2$ (1.0 mmol), KF (1.0 equiv.), TBAB (0.2 mmol), H_2O (3 mL), *o*-phenylenediamine (1.0 mmol) and benzyl alcohol (3 mmol). The mixture was heated at 90 °C for 36 h and then cooled to room temperature. When the first reaction was finished, the catalyst Co-CIA was centrifuged and washed several times with water (5 mL X3) and EtOH (5 mL X3), and dried for 48 h. Then the recovered catalyst was reused for the next time.

8. Mechanism studies



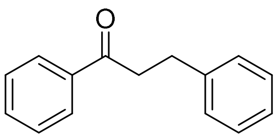
Kinetic plot of benzyl alcohol and benzyl alcohol-d_2.

Experimental procedure: To a 25 mL reaction tube was added the catalyst Co-CIA (2 mol%, 5% loading, w/w), $AgNTf_2$ (1.0 mmol), KF (1.0 equiv.), TBAB (0.2 mmol), H_2O (3 mL), secondary alcohol (1.0 mmol) and primary alcohol (1.2 mmol) and the mixture was stirred at 90 ° C. The yield of **3a**-*d2* or **3a** was determined by NMR.

Time	0 h	1 h	2 h	3 h	4 h	5 h
Concentration of **2a** (mol/L)	0.50	0.25	0.16	0.10	0.08	0.03
Concentration of **3a-d_2** (mol/L)	0.50	0.40	0.28	0.20	0.16	0.12

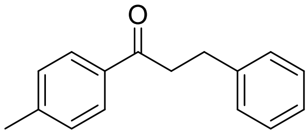
9. Analytical data of the obtained compounds

(1) 1,3-diphenylpropan-1-one (4a) [1].



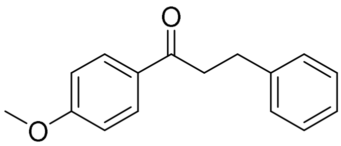
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.31 (m, 4H), 7.28 (t, *J* = 7.0 Hz, 1H), 3.36 (t, *J* = 7.7 Hz, 2H), 3.17 – 3.12 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$): δ 199.20, 141.39, 136.98, 133.11, 128.68, 128.61, 128.52, 128.12, 126.22, 40.47, 30.22.

(2) 3-phenyl-1-(*p*-tolyl)propan-1-one (4b)[2]



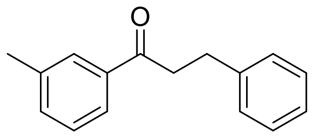
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.9 Hz, 2H), 7.39 (d, *J* = 10.1, 7.1 Hz, 2H), 7.31 (m, *J* = 14.4, 6.0 Hz, 4H), 7.17 (d, *J* = 7.7 Hz, 1H), 3.36 – 3.29 (m, 2H), 3.12 – 3.06 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.47, 141.39, 138.41, 133.83, 128.61, 128.54, 128.45, 126.13, 125.27, 40.54, 30.20, 21.37.

(3) 1-(4-methoxyphenyl)-3-phenylpropan-1-one (4c)[3].



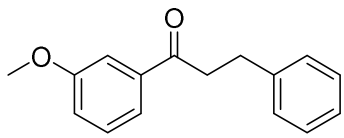
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.9 Hz, 2H), 7.31 (d, J = 14.7, 7.0 Hz, 4H), 7.18 (d, J = 7.2 Hz, 1H), 6.96 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H), 3.31 – 3.26 (m, 2H), 3.13 – 3.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.83, 163.49, 141.51, 130.34, 129.04, 128.54, 128.46, 126.12, 113.77, 55.48, 40.13, 30.37.

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



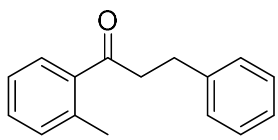
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.9 Hz, 2H), 7.39 (dd, J = 10.1, 7.1 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.23 (d, J = 3.7 Hz, 1H), 3.35 – 3.30 (m, 2H), 3.12 – 3.07 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.47, 141.39, 138.41, 136.94, 133.83, 128.61, 128.54, 128.49, 128.45, 126.13, 125.27, 40.54, 30.20, 21.37.

(5) 1-(3-methoxyphenyl)-3-phenylpropan-1-one (4e)[2]



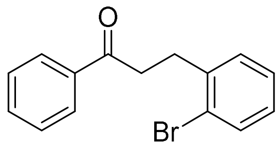
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 2H), 7.40 (d, J = 8.0 Hz, 1H), 7.31 (m, J = 16.0, 7.1 Hz, 4H), 7.25 (t, J = 7.1 Hz, 1H), 7.14 (d, J = 10.1 Hz, 1H), 3.88 (s, 3H), 3.33 (t, J = 7.7 Hz, 2H), 3.11 (t, J = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.04, 159.91, 141.32, 138.31, 129.61, 128.56, 128.46, 126.17, 120.70, 119.57, 112.36, 55.45, 40.56, 30.23.

(6) 3-phenyl-1-(*o*-tolyl)propan-1-one (4f)[3]



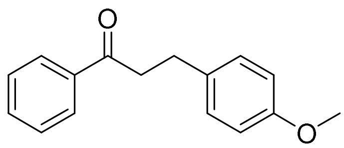
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.5 Hz, 1H), 7.35 (t, J = 7.4 Hz, 1H), 7.28 (t, J = 7.4 Hz, 2H), 7.23 (d, J = 6.3 Hz, 5H), 3.22 (t, J = 7.6 Hz, 2H), 3.04 (t, J = 7.6 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.40, 141.23, 138.13, 137.93, 132.00, 131.28, 128.54, 128.46, 128.41, 126.15, 125.70, 43.25, 30.37, 21.29.

(7) 3-(2-bromophenyl)-1-phenylpropan-1-one (4g)[4]



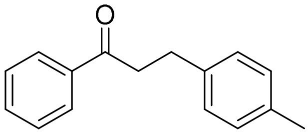
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.96 (m, 2H), 7.59 (t, J = 7.3 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.35 (d, J = 7.6, 1.5 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.11 (td, J = 7.7, 1.6 Hz, 1H), 3.38 – 3.31 (m, 2H), 3.25 – 3.18 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.01, 140.68, 136.76, 133.09, 132.95, 130.87, 128.59, 128.07, 127.96, 127.72, 124.39, 38.56, 30.78.

(8) 3-(4-methoxyphenyl)-1-phenylpropan-1-one (4h)[5]



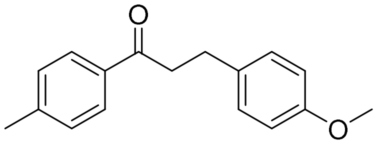
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.5 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 3.82 (s, 3H), 3.30 (t, J = 9.8, 5.5 Hz, 2H), 3.05 (t, J = 9.8, 5.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.42, 158.03, 136.94, 133.34, 133.05, 129.38, 128.62, 128.06, 113.97, 55.30, 40.73, 29.31.

(9) 1-phenyl-3-(*p*-tolyl)propan-1-one (4i)[2]



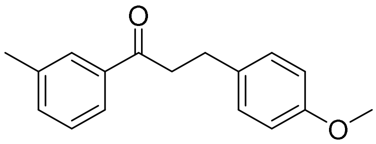
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.1 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.16 (q, J = 8.1 Hz, 4H), 3.34 – 3.28 (m, 2H), 3.08 – 3.02 (m, 2H), 2.35 (s, 3H). ^{13}C NMR: (101 MHz, $CDCl_3$) δ 199.37, 138.20, 136.91, 135.64, 133.04, 129.22, 128.61, 128.30, 128.06, 40.63, 29.74, 21.01.

(10) 3-(4-methoxyphenyl)-1-(*p*-tolyl)propan-1-one (4j)[3]



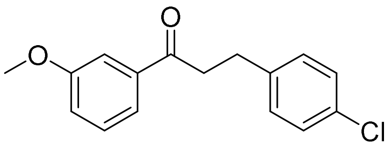
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 3.81 (s, 3H), 3.27 (t, J = 7.7 Hz, 2H), 3.04 (t, J = 7.7 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.03, 158.04, 143.80, 134.51, 133.46, 129.40, 129.32, 128.22, 113.98, 55.27, 40.60, 29.42, 21.65.

(11) 3-(4-methoxyphenyl)-1-(*m*-tolyl)propan-1-one (4k)[6]



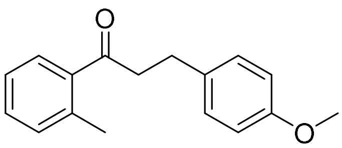
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 10.8 Hz, 2H), 7.42 – 7.33 (m, 2H), 7.21 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 3.82 (s, 3H), 3.29 (t, J = 7.7 Hz, 2H), 3.05 (t, J = 7.6 Hz, 2H), 2.44 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ 199.59, 158.04, 138.39, 137.00, 133.82, 133.43, 129.40, 128.63, 128.51, 125.30, 113.98, 55.28, 40.79, 29.36, 21.39.

(12) 3-(4-chlorophenyl)-1-(3-methoxyphenyl)propan-1-one (4l)[6]



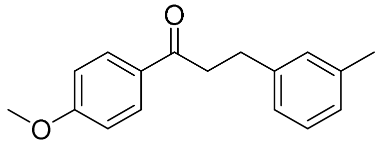
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 2H), 7.38 (t, J = 7.9 Hz, 1H), 7.29 – 7.27 (m, 2H), 7.21 (d, J = 8.3 Hz, 2H), 7.13 (dd, J = 8.2, 2.6 Hz, 1H), 3.87 (s, 3H), 3.29 (t, J = 7.5 Hz, 2H), 3.06 (t, J = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.65, 159.91, 139.73, 138.17, 131.90, 130.36, 129.83, 129.63, 128.61, 120.63, 119.62, 112.34, 55.45, 40.23, 29.46.

(13) 3-(4-methoxyphenyl)-1-(*o*-tolyl)propan-1-one (4m)[7]



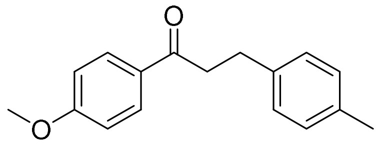
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.18 (s, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 3.22 (t, *J* = 7.6 Hz, 2H), 3.01 (t, *J* = 7.6 Hz, 2H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 203.60, 158.02, 138.06, 138.02, 133.24, 131.93, 131.18, 129.35, 128.33, 125.65, 113.94, 55.28, 43.53, 29.50, 21.20.

(14) 1-(4-methoxyphenyl)-3-(*m*-tolyl)propan-1-one (4n)[8]



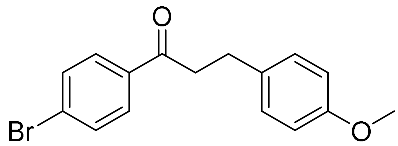
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 2H), 7.26 (dd, *J* = 14.5, 7.0 Hz, 1H), 7.10 (dd, *J* = 16.0, 9.5 Hz, 3H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 3.30 – 3.25 (m, 2H), 3.10 – 3.05 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.83, 163.50, 141.48, 138.07, 130.35, 130.08, 129.29, 128.47, 126.88, 125.46, 113.78, 55.45, 40.19, 30.33, 21.44.

(15) 1-(4-methoxyphenyl)-3-(*p*-tolyl)propan-1-one (4o)[11]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.17 (q, *J* = 8.0 Hz, 4H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 3.33 – 3.18 (m, 2H), 3.13 – 2.96 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz,$CDCl_3$) :δ 197.94, 163.46, 138.40, 135.57, 130.33, 130.06, 129.21, 128.32, 113.75, 55.47, 40.29, 29.96, 21.02.

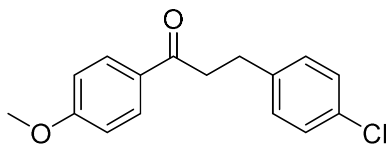
(16) 1-(4-bromophenyl)-3-(4-methoxyphenyl)propan-1-one (4p)[12]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 2H), 7.65 – 7.58 (m, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.89 – 6.84 (m, 2H), 3.81 (s, 3H), 3.25 (t, *J* = 7.6 Hz, 2H), 3.03 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.30, 158.10, 135.67, 133.08, 129.59, 129.36, 128.61, 128.06, 114.02, 55.29, 40.65, 29.23.

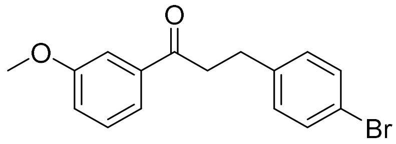
(17) 3-(4-chlorophenyl)-1-(4-methoxyphenyl)propan-1-one (4q)[6]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 3.93 (s, 3H), 3.33 (t, *J* = 7.6 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.55, 163.61, 140.00, 131.93, 130.42, 130.27, 129.93, 128.42, 113.81, 55.53, 39.84, 29.62.

(17) 3-(4-chlorophenyl)-1-(4-methoxyphenyl)propan-1-one (4q)[6]**.**



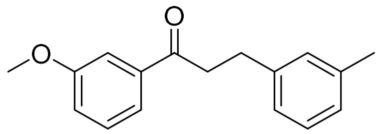
^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.9 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 3.24 (t, J = 7.6 Hz, 2H), 3.04 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.41, 163.55, 139.96, 137.93, 130.31, 129.86, 128.58, 113.79, 55.49, 39.78, 29.58.

(18) 3-(4-bromophenyl)-1-(3-methoxyphenyl)propan-1-one (4r)[4].



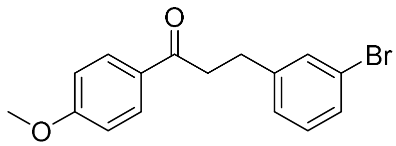
^1H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.38 (t, J = 7.9 Hz, 1H), 7.13 (dd, J = 13.6, 5.5 Hz, 3H), 3.86 (s, 3H), 3.28 (t, J = 7.5 Hz, 2H), 3.04 (t, J = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.59, 159.91, 140.28, 138.16, 131.56, 130.26, 129.64, 120.63, 119.91, 119.62, 112.35, 55.45, 40.15, 29.51.

(19) 1-(3-methoxyphenyl)-3-(*m*-tolyl)propan-1-one (4s)[5]



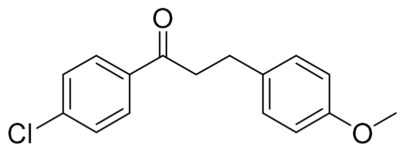
^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 2H), 7.39 (t, J = 7.9 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 7.15 – 7.04 (m, 4H), 3.88 (s, 3H), 3.34 – 3.27 (m, 2H), 3.10 – 3.02 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 199.14, 159.87, 141.23, 138.28, 138.14, 129.59, 129.26, 128.46, 126.90, 125.42, 120.70, 119.58, 112.28, 55.46, 40.67, 30.14, 21.42.

(20) 3-(3-bromophenyl)-1-(4-methoxyphenyl)propan-1-one (4t)[3]



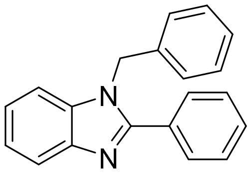
^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.9 Hz, 2H), 7.42 (s, 1H), 7.35 (d, J = 7.3 Hz, 1H), 7.22 – 7.14 (m, 2H), 6.94 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 3.25 (t, J = 7.7 Hz, 2H), 3.04 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.19, 163.56, 143.91, 131.51, 130.30, 130.07, 129.22, 127.22, 122.52, 122.48, 113.80, 55.48, 39.64, 29.84.

(21) 1-(4-chlorophenyl)-3-(4-methoxyphenyl)propan-1-one (4u)[2]



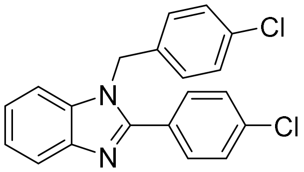
^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.7 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 7.19 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H), 3.26 (t, J = 7.6 Hz, 2H), 3.03 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 198.15, 158.08, 139.47, 135.24, 133.09, 129.48, 129.36, 128.92, 114.00, 55.29, 40.69, 29.23.

(22) 1-benzyl-2-phenyl-1H-benzo[d]imidazole (8a)[9]



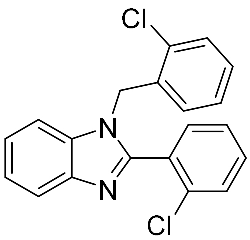
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.72 (m, *J* = 7.6, 1.9 Hz, 2H), 7.52 – 7.43 (m, 3H), 7.38 – 7.30 (m, 4H), 7.24 (td, *J* = 7.8, 1.3 Hz, 2H), 7.15 – 7.10 (m, 2H), 5.48 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.18, 143.22, 136.43, 136.10, 130.14, 129.93, 129.30, 129.07, 128.77, 127.80, 126.01, 123.07, 122.71, 120.02, 110.56, 48.40.

(23) 1-(4-chlorobenzyl)-2-(4-chlorophenyl)-1H-benzo[d]imidazole (8b)



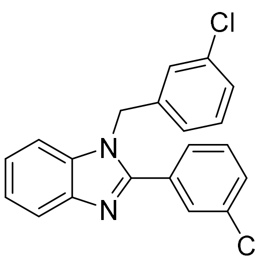
^{1}H NMR (400 MHz, DMSO) δ 7.75 (m, *J* = 9.5, 5.4 Hz, 3H), 7.60 – 7.54 (m, 2H), 7.48 (m, *J* = 6.0, 2.7 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.25 (m, *J* = 9.4, 5.7 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 5.59 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ 152.56, 143.12, 136.37, 136.28, 135.28, 132.62, 131.60, 131.25, 129.39, 129.34, 129.26, 129.17, 128.47, 123.47, 122.92, 119.90, 111.55, 47.37.

(24) 1-(2-chlorobenzyl)-2-(2-chlorophenyl)-1H-benzo[d]imidazole (8c)[10]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.38 – 7.26 (m, 4H), 7.26 – 7.16 (m, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 5.39 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.52, 143.08, 134.84, 134.39, 133.31, 132.41, 132.16, 131.43, 129.93, 129.71, 129.60, 129.00, 127.79, 127.13, 126.97, 123.39, 122.74, 120.39, 110.54, 45.73.

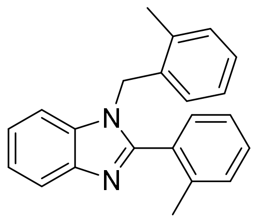
(25) 1-(3-chlorobenzyl)-2-(3-chlorophenyl)-1H-benzo[d]imidazole (8d)[11]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* =8.1 Hz, 1H), 7.73 (t, *J* = 1.7 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.44 – 7.33 (m, 2H), 7.34 –7.29 (m, 3H), 7.25 (t, *J* = 8.0 Hz, 1H), 7.13 (s, 1H), 6.95 (d, *J* = 7.0 Hz, 1H), 5.44 (s, 2H). ^{13}C NMR (101

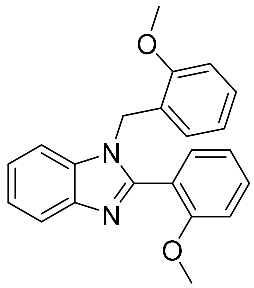
MHz, $CDCl_3$): δ= 152.54, 143.10, 138.24, 135.99, 135.25, 135.00, 131.70, 130.54, 130.15, 130.09, 129.52, 128.31, 127.09, 126.26, 124.11, 123.67, 123.11, 120.35, 110.37, 47.96.

(26) 1-(2-methylbenzyl)-2-(o-tolyl)-1H-benzo[d]imidazole (8e)[12]



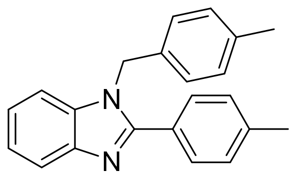
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.39 – 7.31 (m, 4H), 7.27 – 7.19 (m, 3H), 7.18 – 7.11 (m, 2H), 7.07 – 7.01 (m, 1H), 6.69 (d, *J* = 7.7 Hz, 1H), 5.22 (s, 2H), 2.30 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.95, 143.23, 138.40, 135.15, 134.90, 134.11, 130.65, 130.44, 129.92, 129.87, 127.59, 126.40, 126.11, 125.68, 122.89, 122.41, 120.08, 110.61, 45.82, 19.87, 19.09.

(27) 1-(2-methoxybenzyl)-2-(2-methoxyphenyl)-1H-benzo[d]imidazole (8f)[13]



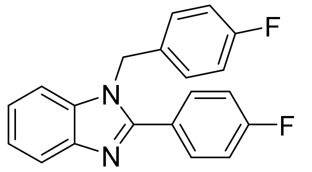
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.31 (m, *J* = 6.6, 4.9, 2.2 Hz, 1H), 7.22 (m, *J* = 6.1, 3.1 Hz, 2H), 7.01 (m, *J* = 21.9, 8.7 Hz, 4H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.38 (s, 2H), 3.85 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.02, 159.16, 154.10, 143.18, 136.11, 130.72, 128.50, 127.24, 122.74, 122.52, 122.48, 119.70, 114.45, 114.21, 110.43, 55.36, 55.28, 47.88.

(28) 1-(4-methylbenzyl)-2-(p-tolyl)-1H-benzo[d]imidazole (8g)[14]



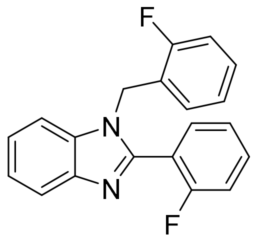
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 2H), 7.33 (m, *J* = 8.2, 6.2, 2.1 Hz, 1H), 7.27 (m, *J* = 8.7, 4.4 Hz, 2H), 7.25 – 7.19 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 5.42 (s, 2H), 2.43 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.34, 143.21, 140.04, 137.44, 136.14, 133.50, 129.72, 129.46, 129.20, 127.24, 125.94, 122.87, 122.57, 119.83, 110.55, 48.20, 21.43, 21.09.

(29) 1-(4-fluorobenzyl)-2-(4-fluorophenyl)-1H-benzo[d]imidazole (8h)[11]



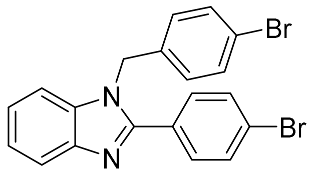
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.71 – 7.60 (m, 2H), 7.40 – 7.32 (m, 1H), 7.32 – 7.21 (m, 2H), 7.21 – 7.14 (m, 2H), 7.10 – 6.98 (m, 4H), 5.42 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.05, 163.54, 162.56, 161.09, 153.05, 142.95, 135.85, 131.93, 131.90 (d, *J* = 8.6 Hz), 131.29, 127.69 (d, *J* = 8.2 Hz), 127.60, 123.34(d, *J* = 37.4 Hz), 120.04, 117.34, 116.13 (d, *J* = 21.8, 10.1 Hz), 110.34, 47.72.

(30) 1-(2-fluorobenzyl)-2-(2-fluorophenyl)-1H-benzo[d]imidazole(8i)[11]



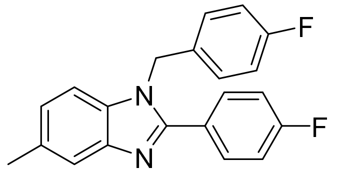
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.45 (dd, *J* = 13.4, 7.2 Hz, 1H), 7.27 – 7.06 (m, 6H), 6.96 (dt, *J* = 15.1, 8.3 Hz, 2H), 6.77 (t, *J* = 7.5 Hz, 1H), 5.39 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.40, 158.94, 149.35, 143.32, 135.29, 132.29 (dd, *J* = 10.7, 5.3 Hz), 131.38 (d, *J* = 8.9 Hz), 130.29, 129.61 (d, *J* = 8.1 Hz), 128.45 (d, *J* = 3.4 Hz), 124.74 (d, *J* = 3.5 Hz), 124.40 (d, *J* = 3.6 Hz), 123.36, 123.12 – 122.58 (m), 120.15, 118.45 (d, *J* = 14.9 Hz), 116.09 (d, *J* = 21.4 Hz), 115.43 (d, *J* = 21.0 Hz), 110.59, 42.23 (d, *J* = 0.7 Hz).

(31) 1-(4-bromobenzyl)-2-(4-bromophenyl)-1H-benzo[d]imidazole (8j)[12]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 5.3 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 5.37 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.84, 142.84, 135.83, 135.11, 132.34, 132.14, 130.69, 128.60, 127.61, 124.81, 123.62, 123.21, 121.96, 120.12, 110.38, 47.85.

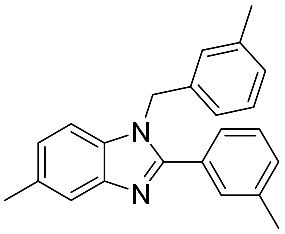
(32) 1-(4-fluorobenzyl)-2-(4-fluorophenyl)-5-methyl-1H-benzo[d]imidazole (8k)[10]



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (m, *J* = 24.4, 12.4, 6.7 Hz, 3H), 7.20 – 7.11 (m, 3H), 7.08 (s, 1H), 7.03 (m, *J* = 7.9, 2.6 Hz, 4H), 5.35 (s, 2H), 2.49 (d, *J* = 20.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.94 (d, *J* = 2.9 Hz), 162.44 (d, *J* = 2.8

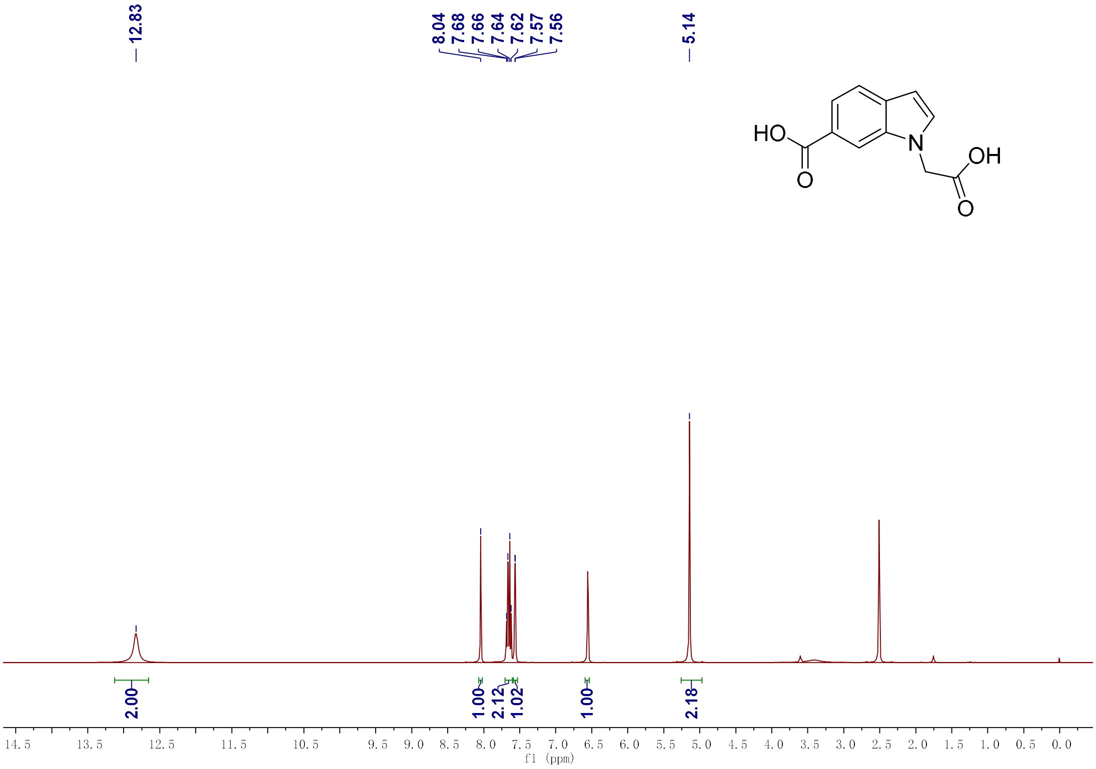
Hz), 152.79 (d, J = 38.6 Hz), 143.45, 141.24, 136.23, 133.72 (d, J = 67.8 Hz), 132.24 (dd, J = 26.4, 23.4 Hz), 131.15 (dd, J = 8.5, 5.2 Hz), 127.63 (dd, J = 8.1, 5.9 Hz), 126.37, 124.64 (d, J = 23.1 Hz), 119.72 (d, J = 25.7 Hz), 115.99 (ddd, J = 21.8, 14.4, 2.9 Hz), 110.00 (d, J = 26.4 Hz), 47.67 (d, J = 12.4 Hz), 21.54 (d, J = 28.4 Hz).

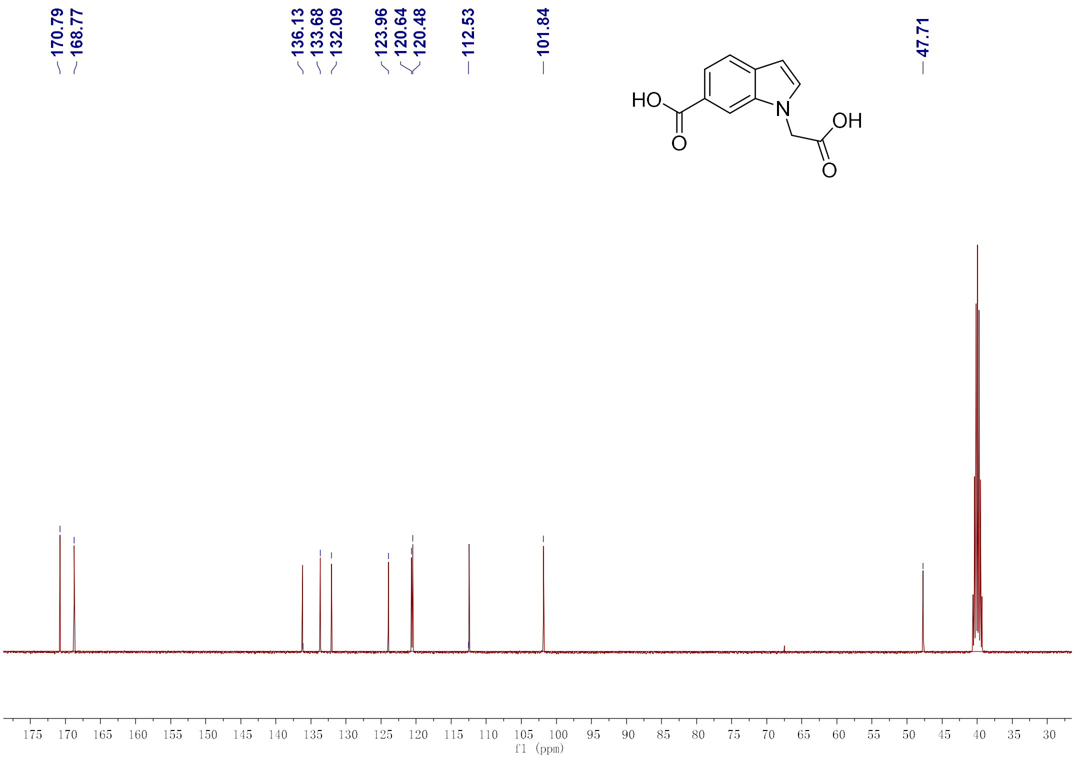
(33) 5-methyl-1-(2-methylbenzyl)-2-(*o*-tolyl)-1H-benzo[d]imidazole (8l)[12]

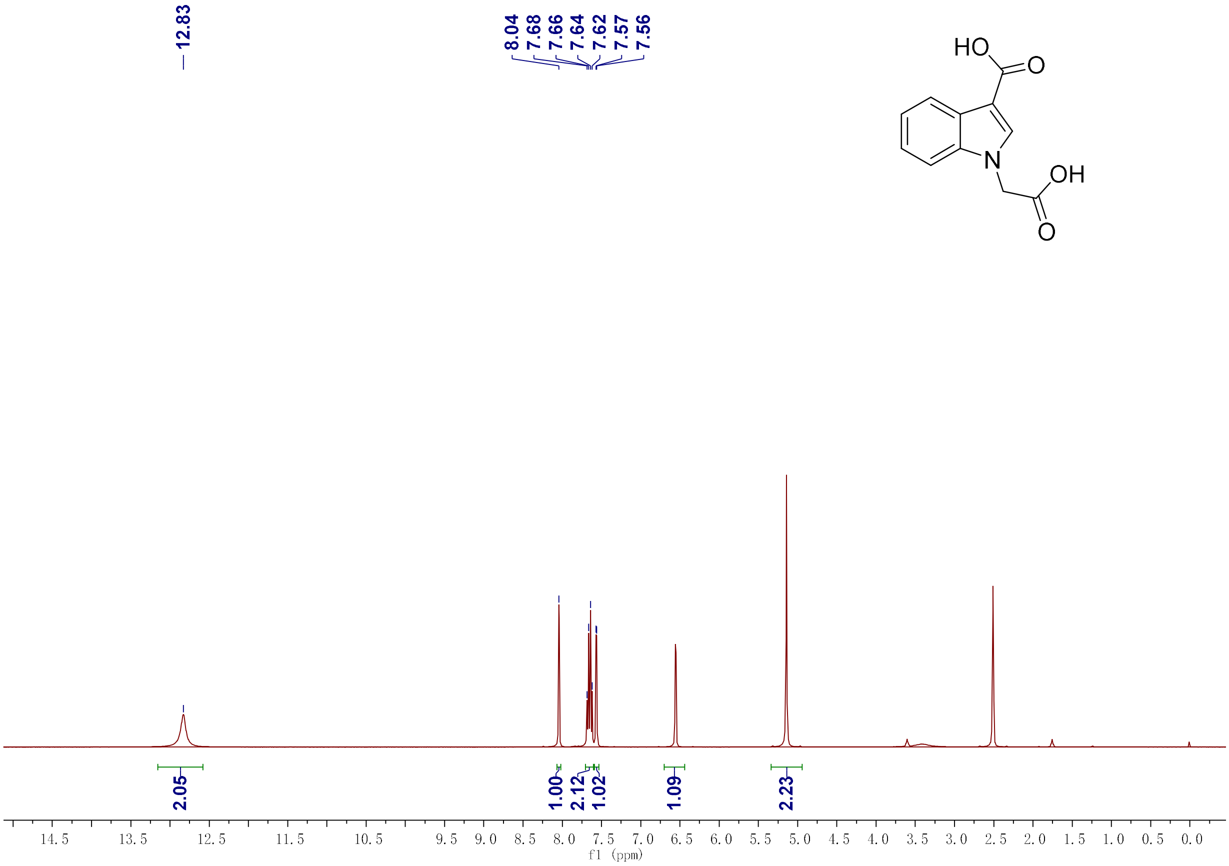


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.72 (m, 1H), 7.63 (s, 1H), 7.45 (m, J = 6.6, 5.1 Hz, 1H), 7.35 – 7.25 (m, 2H), 7.25 – 7.09 (m, 3H), 7.05 (d, J = 12.7 Hz, 1H), 6.93 (m, J = 16.6, 10.0 Hz, 2H), 5.37 (s, 2H), 2.48, 2.38, 2.31. ^{13}C NMR (101 MHz, $CDCl_3$): δ =154.3, 153.9, 130.5, 130.3, 130.2, 130.1, 130.0, 128.9, 128.9, 128.5, 126.5, 125.9, 124.3, 124.2, 123.1, 123.0, 119.4, 110.3, 110.1. 48.3, 21.9, 21.5, 21.4.

10. NMR spectra of obtained compounds







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HO
O
N
OH
O
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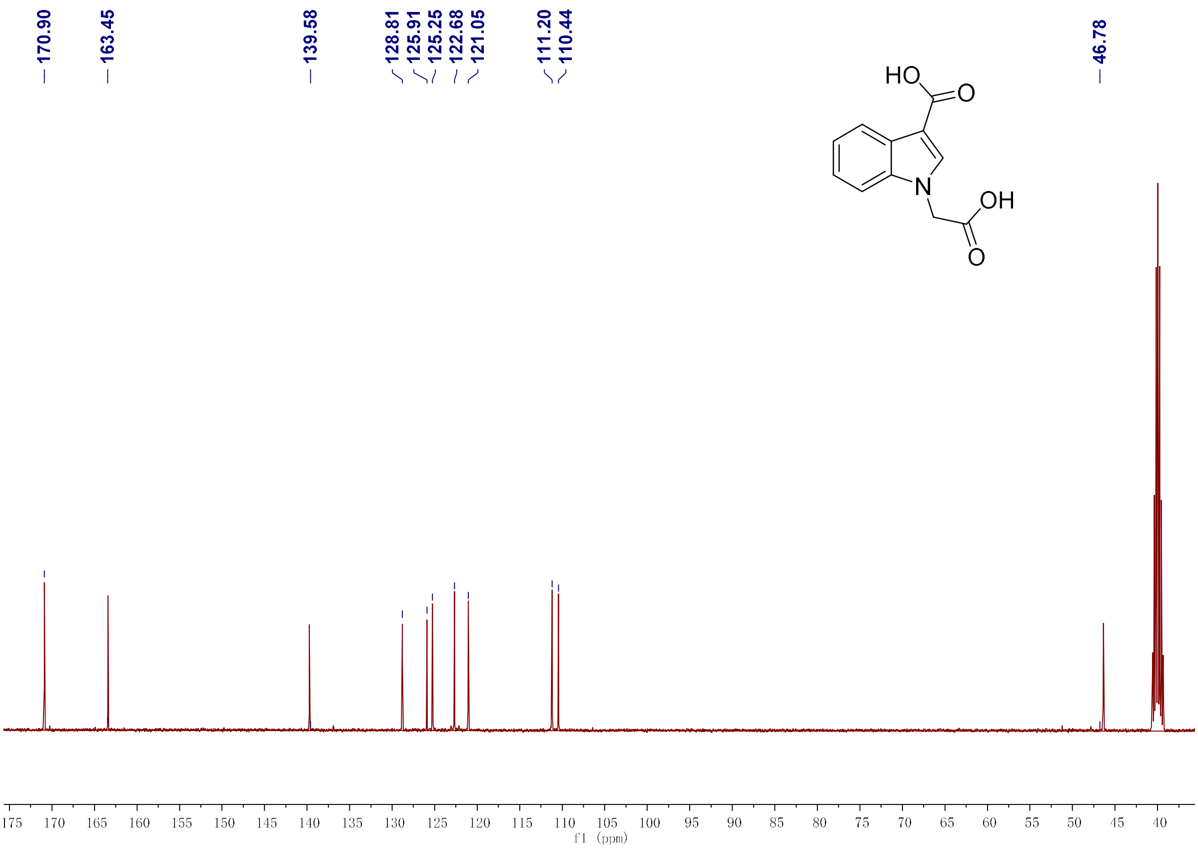
1.00
2.12
1.02
1.09
2.23
14.5 13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



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139.58
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125.25
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121.05
111.20
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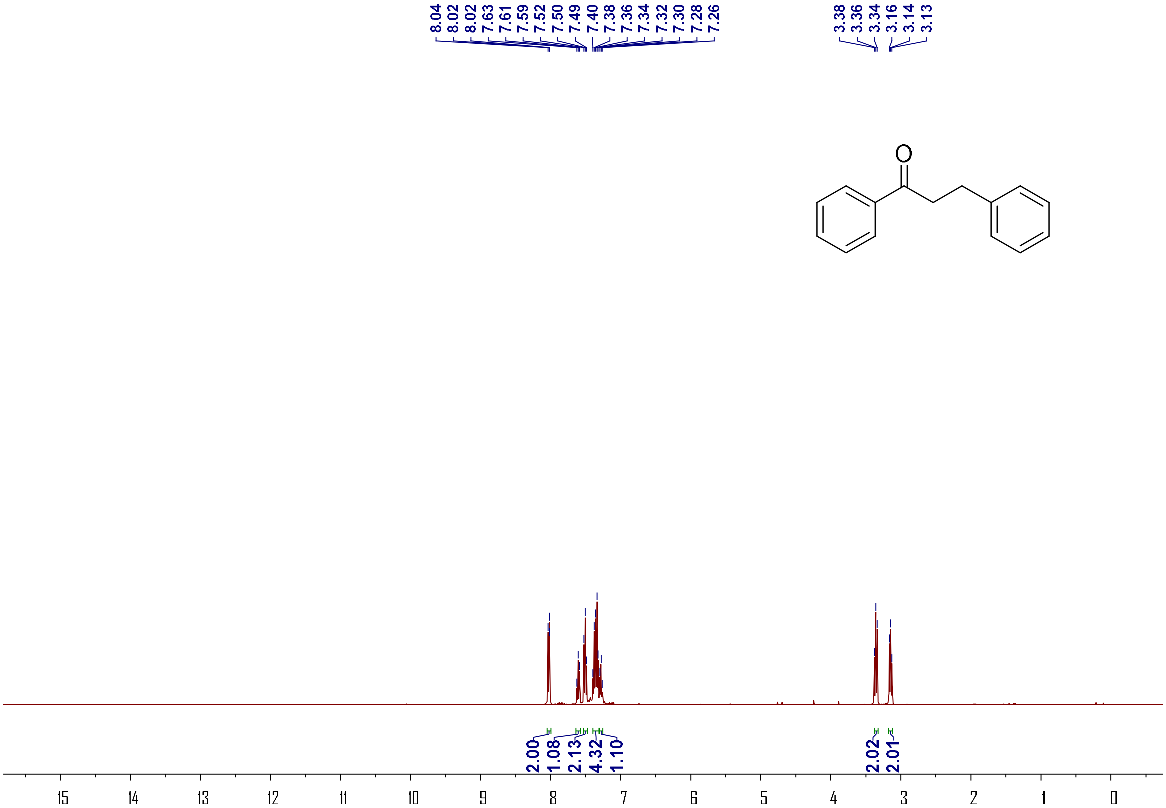
O
N
OH
O
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40
f1 (ppm)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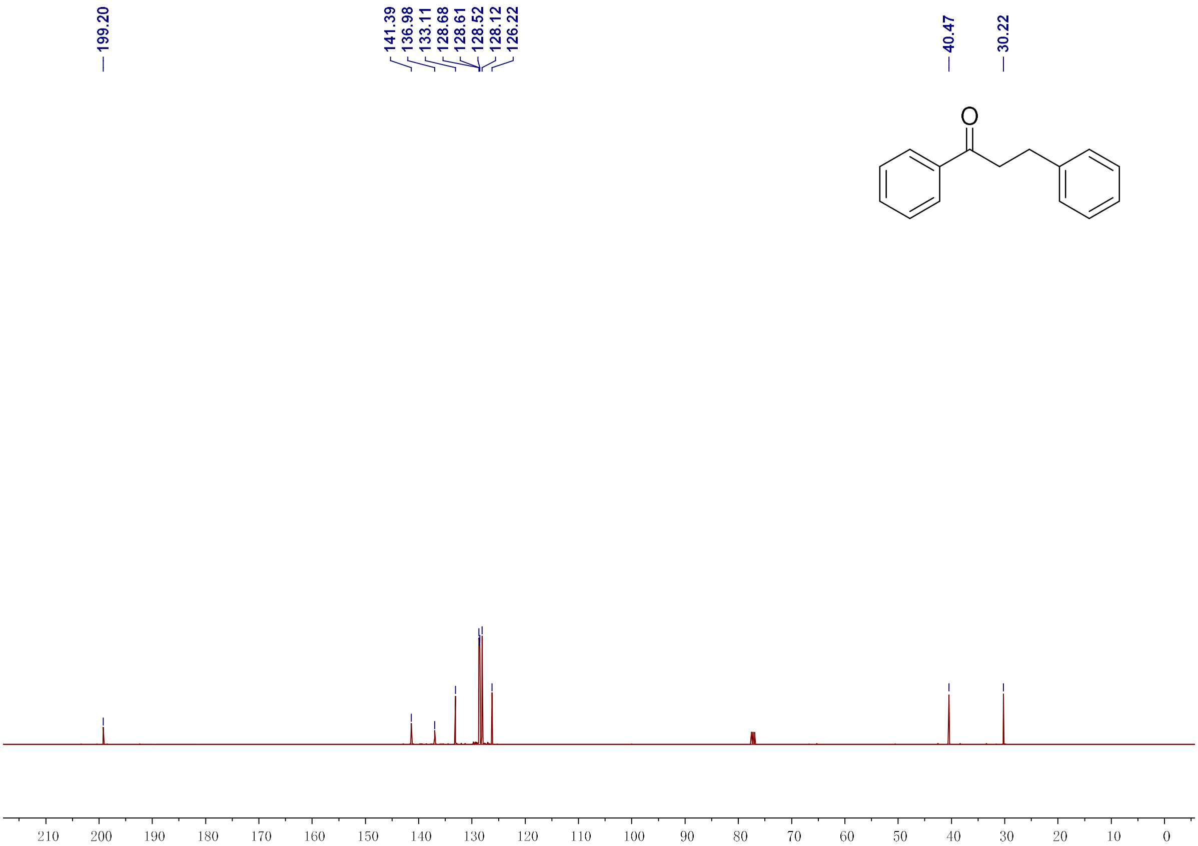
2.02
2.01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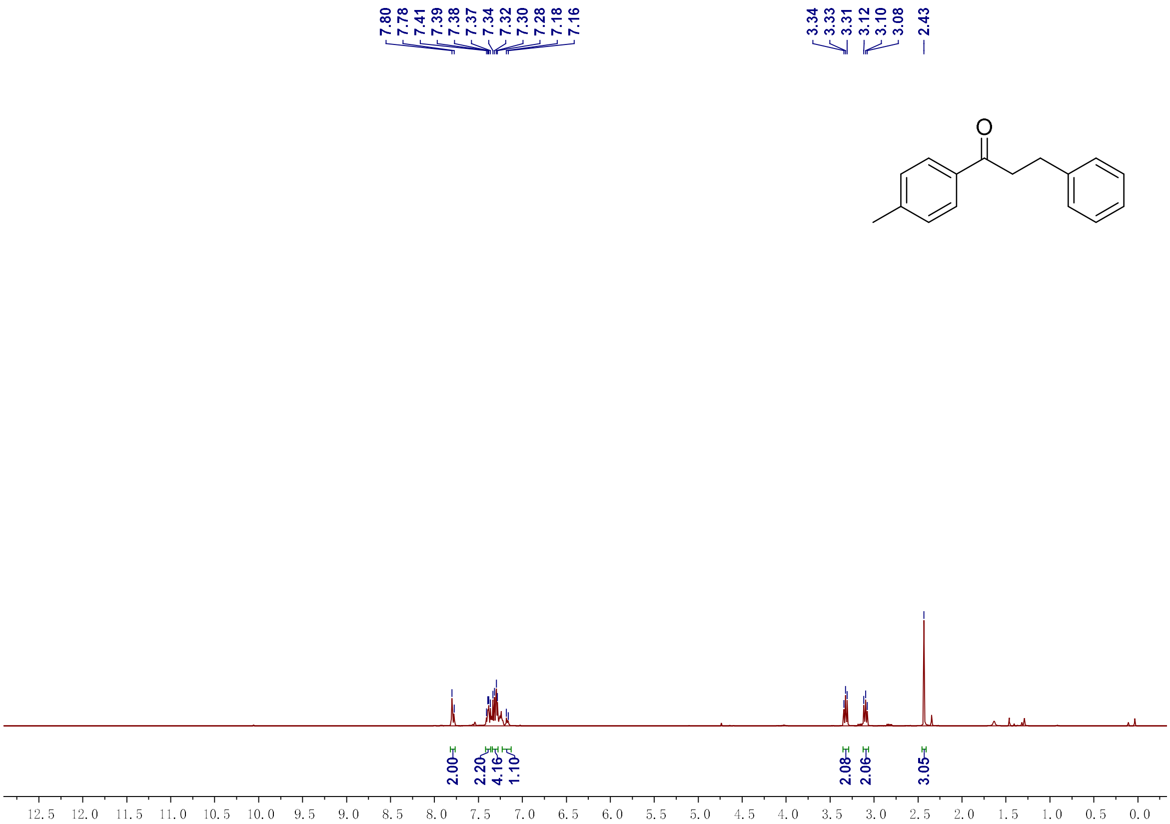
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3.31
3.12
3.10
3.08
2.43
O
2.00
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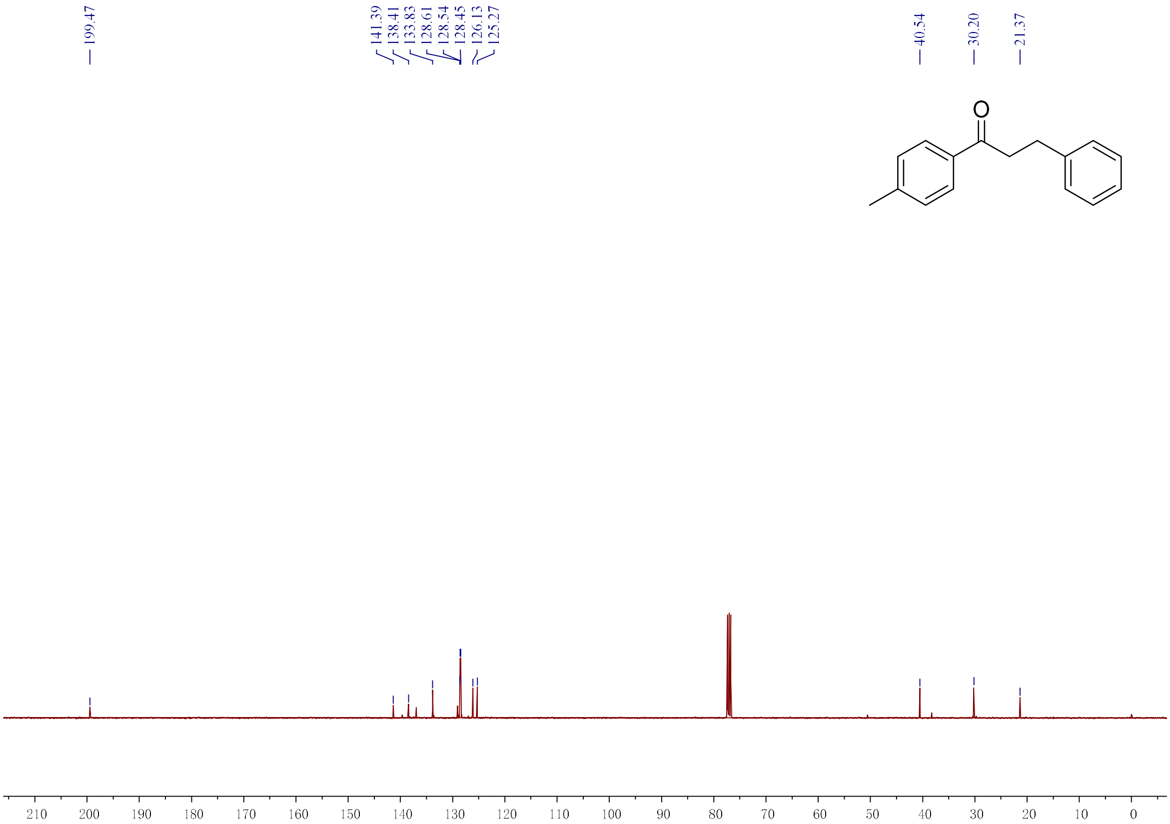
1.10
2.08
2.06
3.05
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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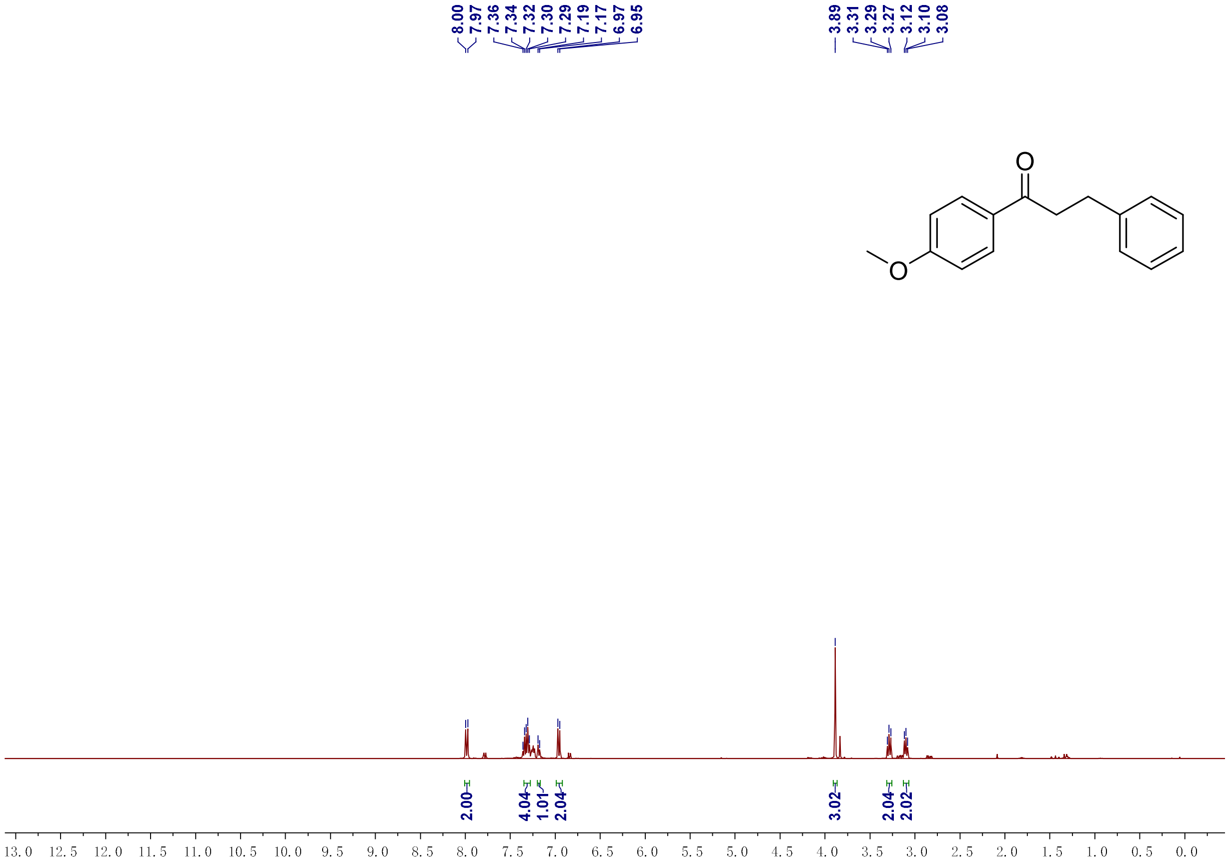
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3.10
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1.01
2.04
3.02
2.04
2.02
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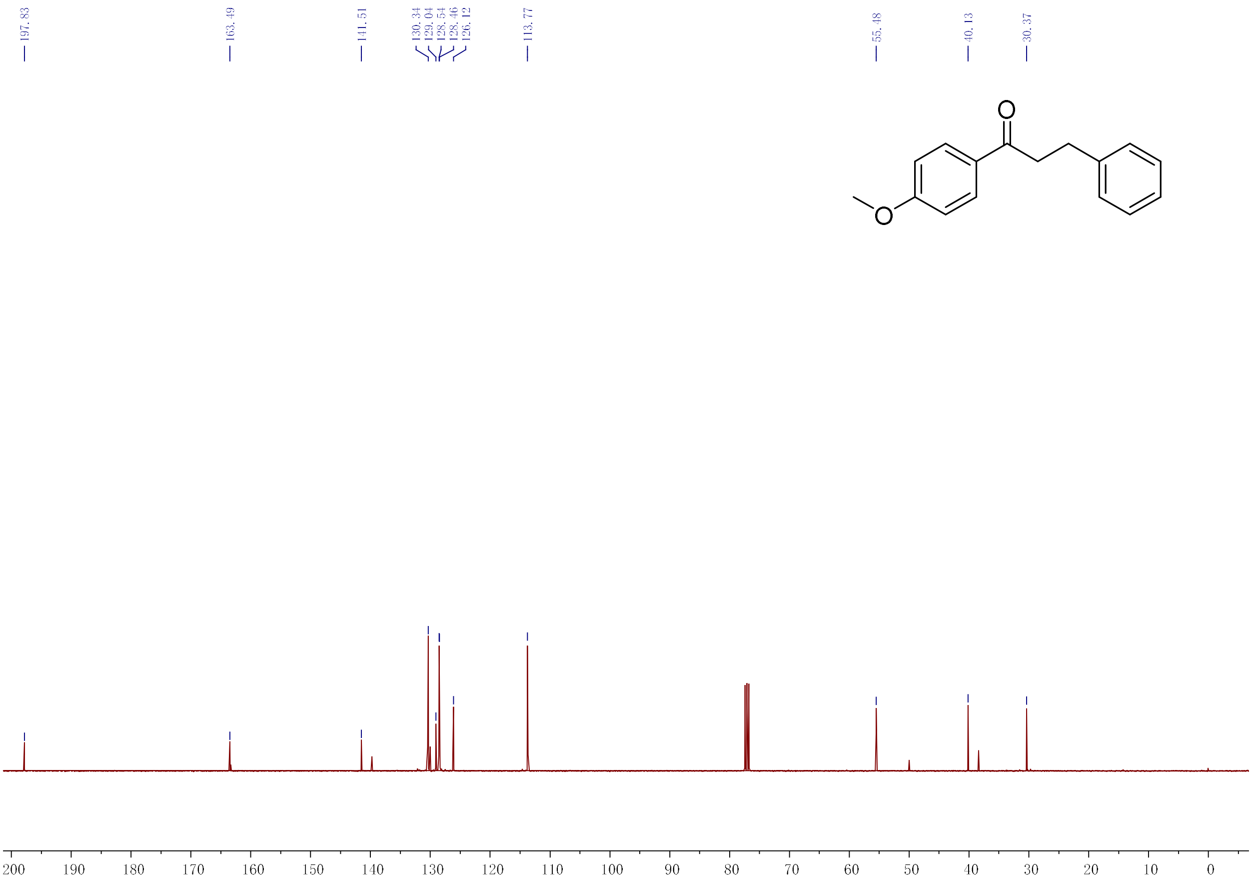
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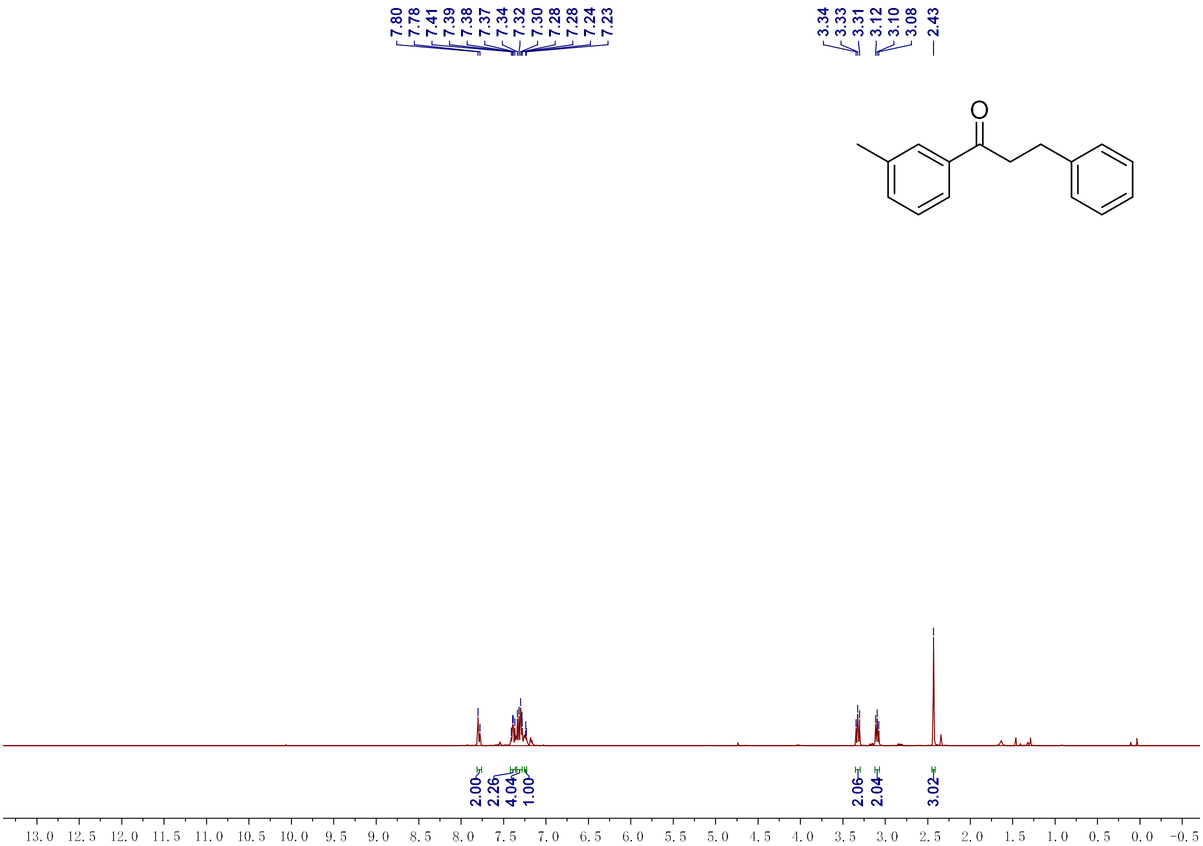
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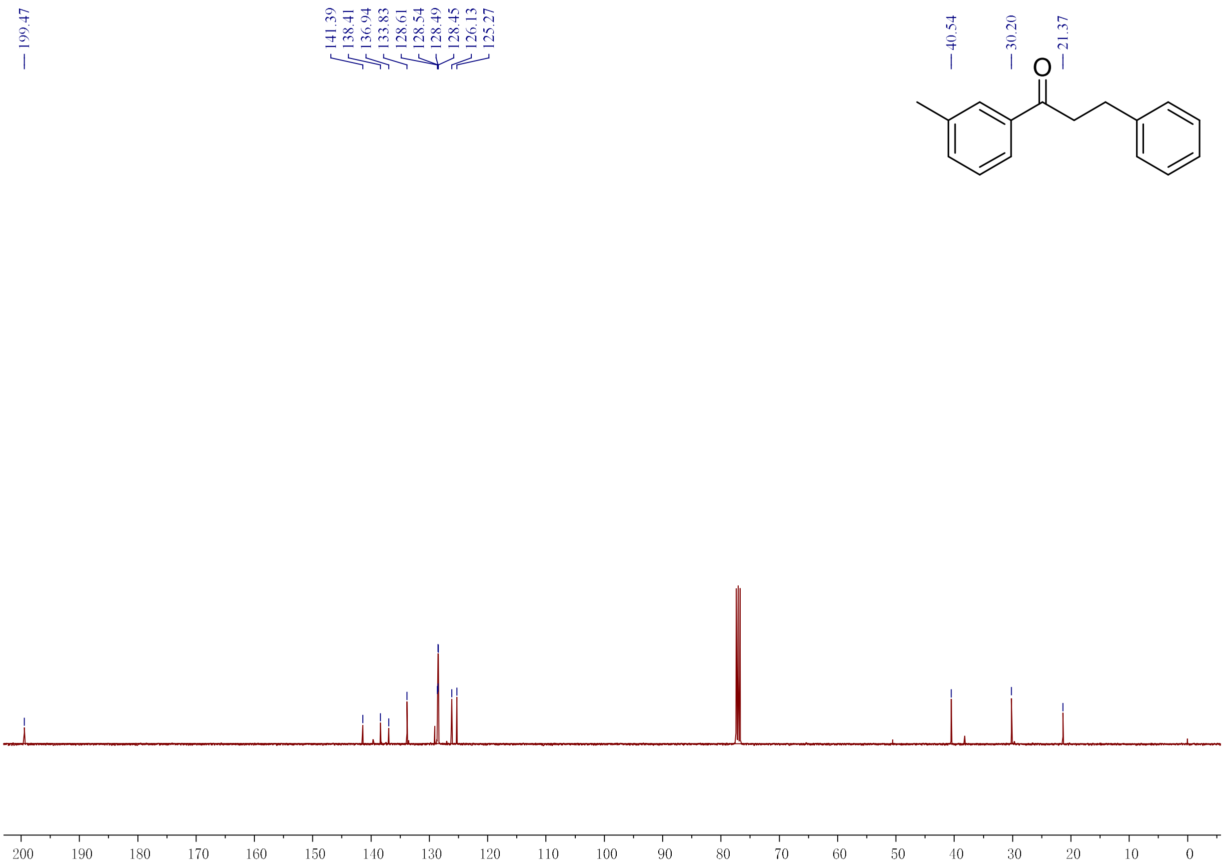
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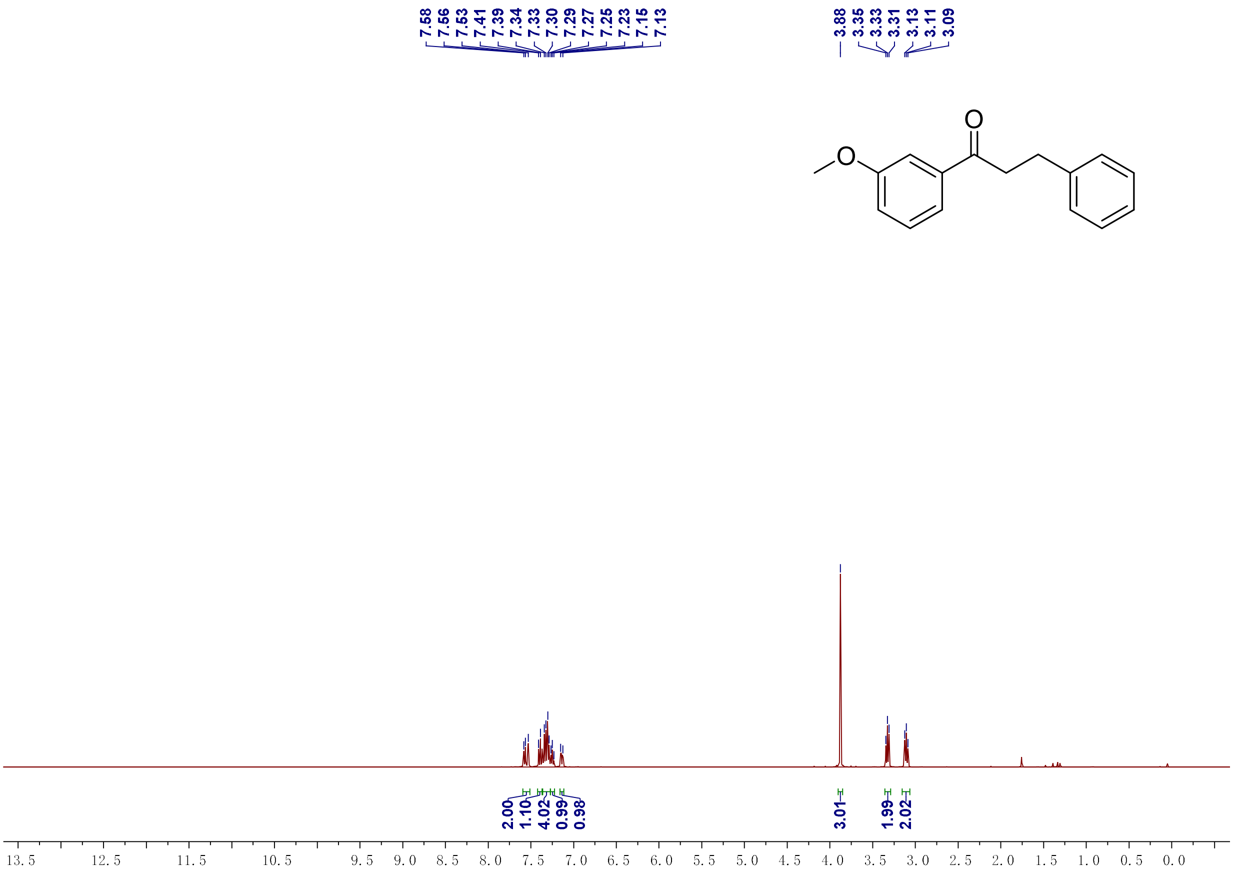
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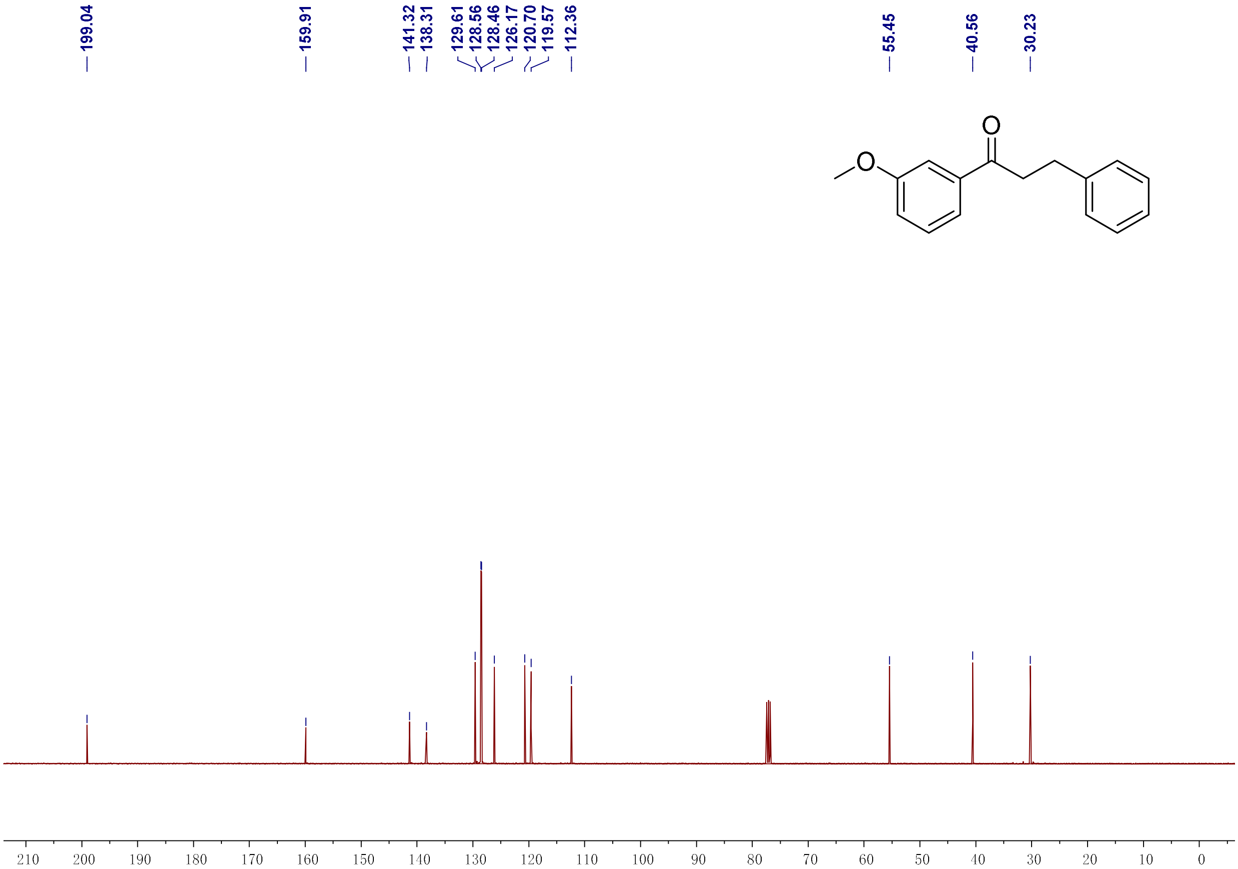
2.02



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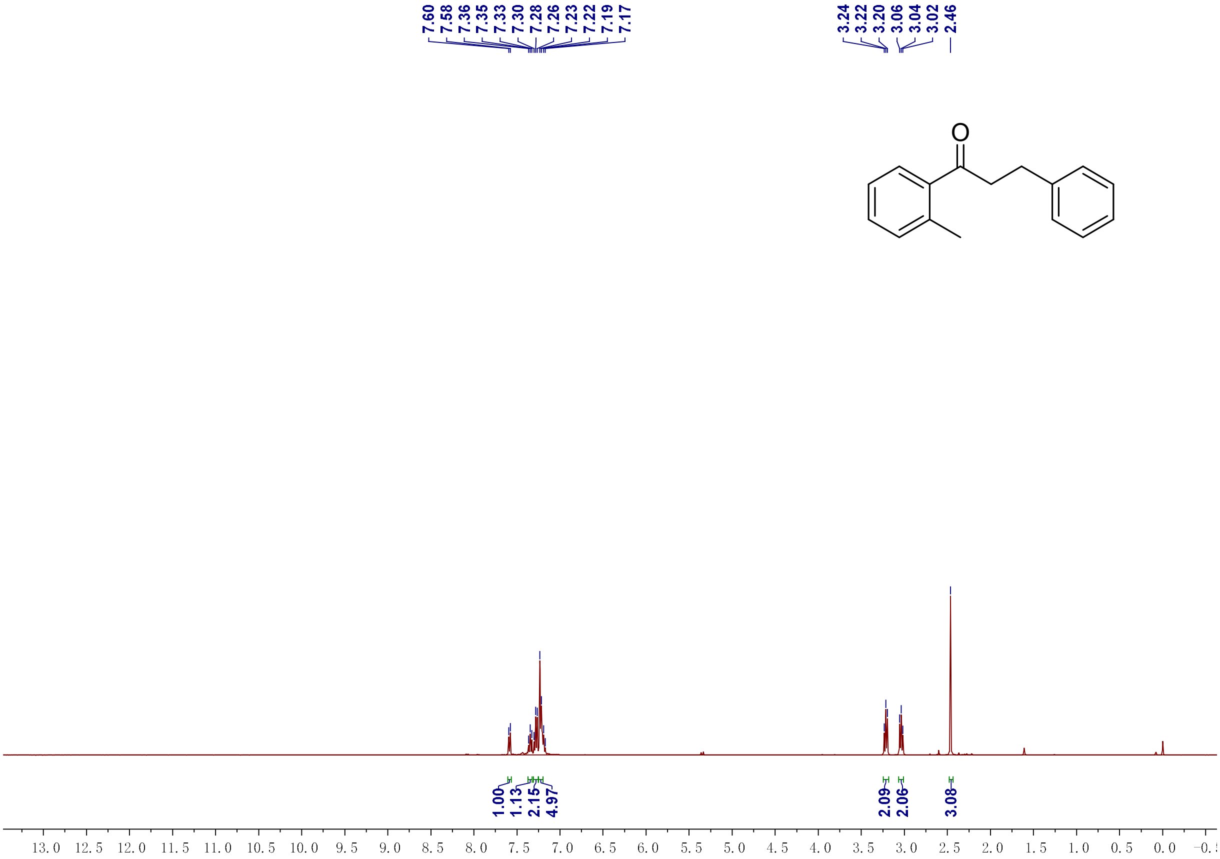
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3.06
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3.02
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1.00
1.13
2.15
4.97
2.09
2.06
3.08
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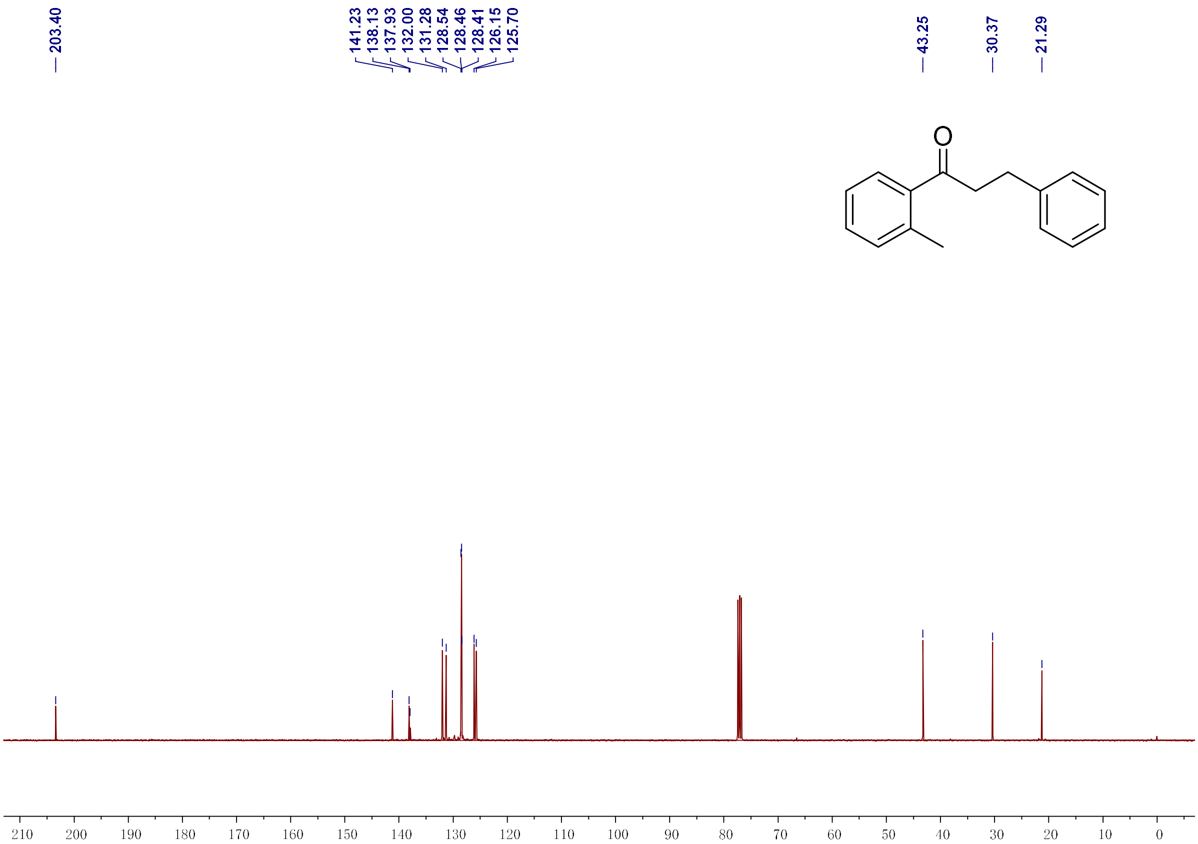
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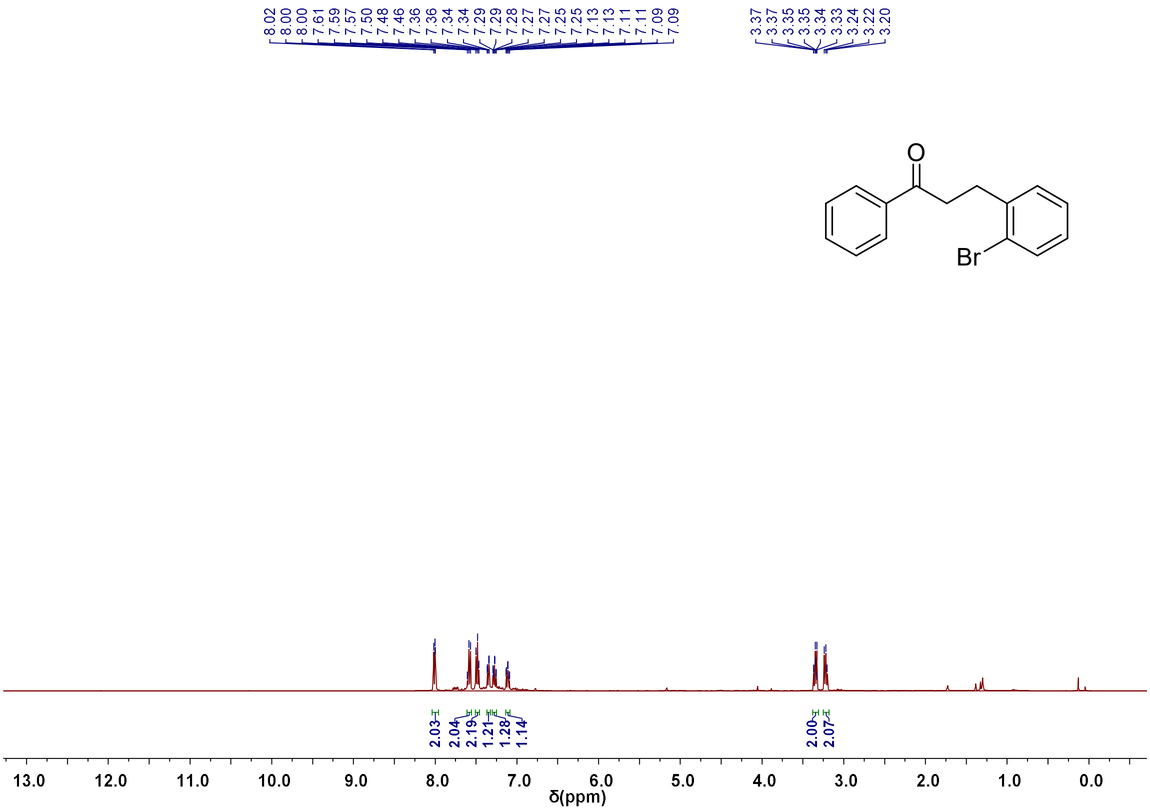
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3.37 3.37 3.35 3.35 3.34 3.33 3.24 3.22 3.20
O
Br
2.03 2.04 2.19 1.21 1.28 1.14
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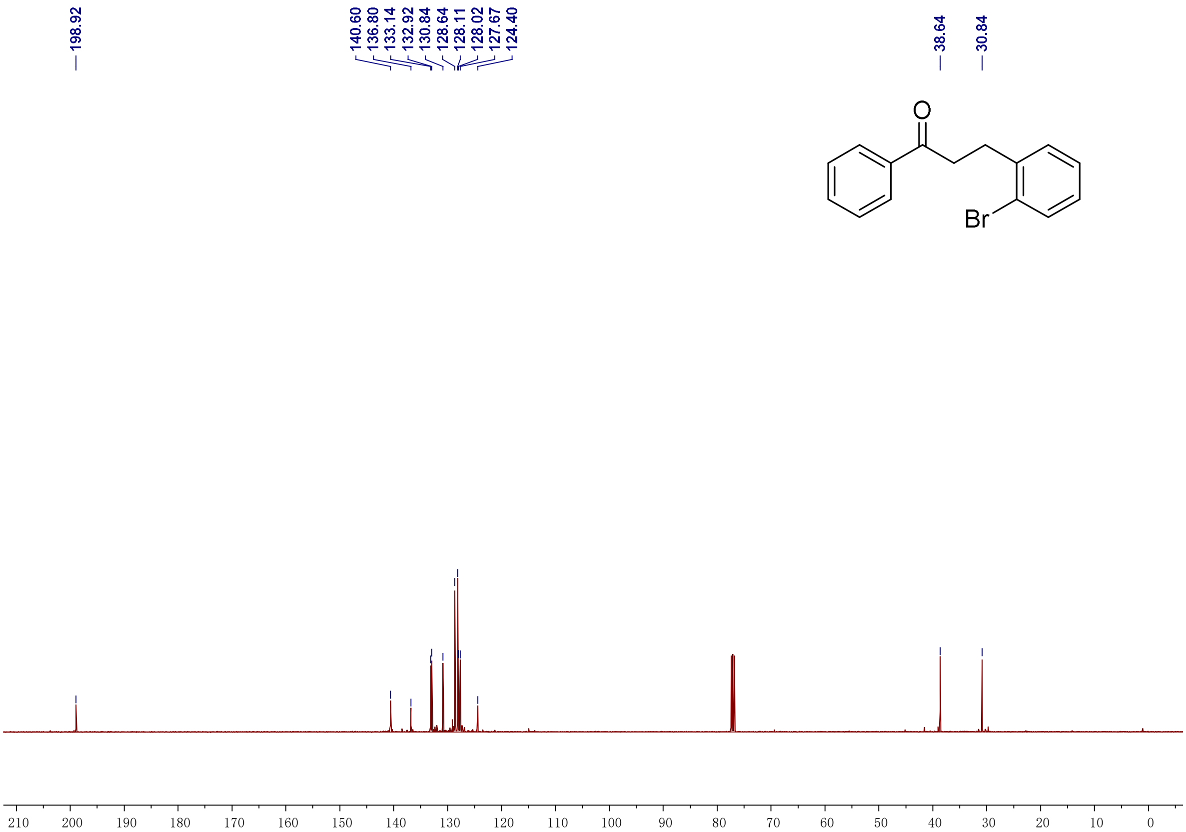
δ(ppm)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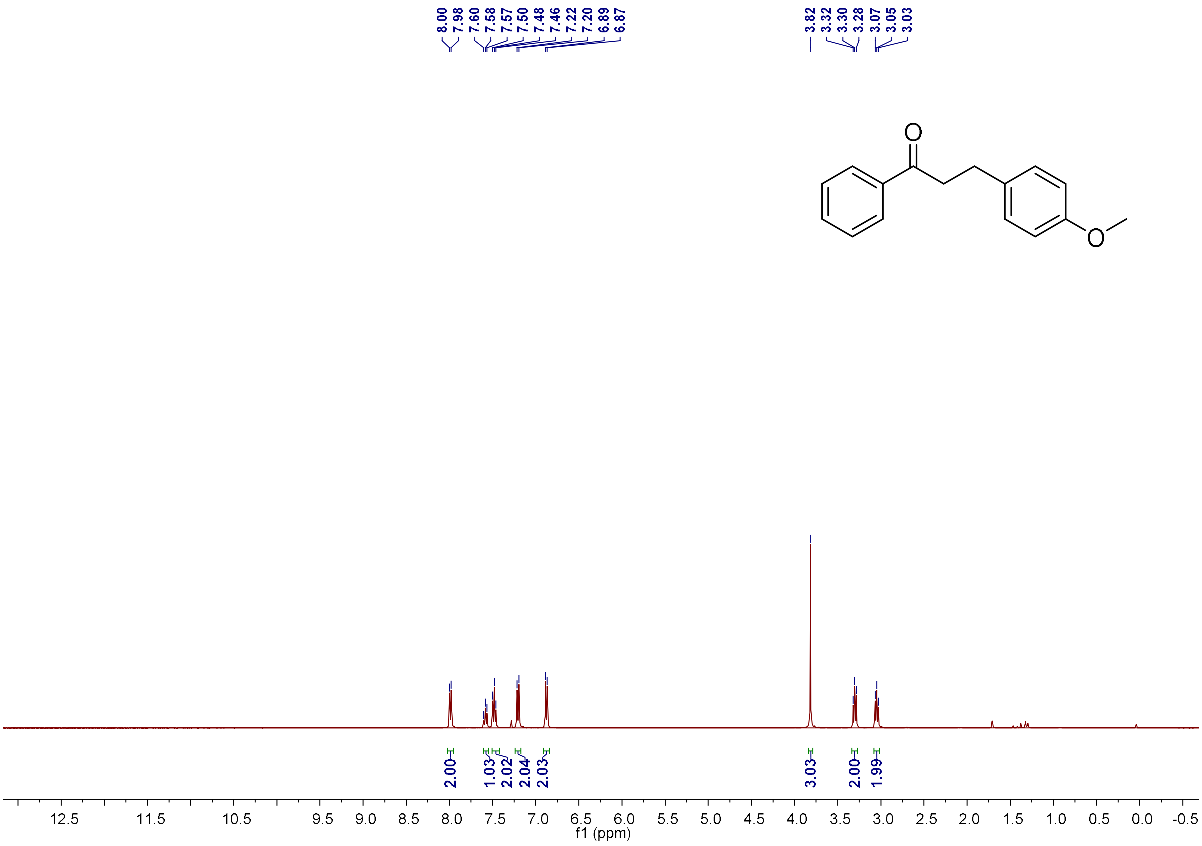
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3.32
3.30
3.28
3.07
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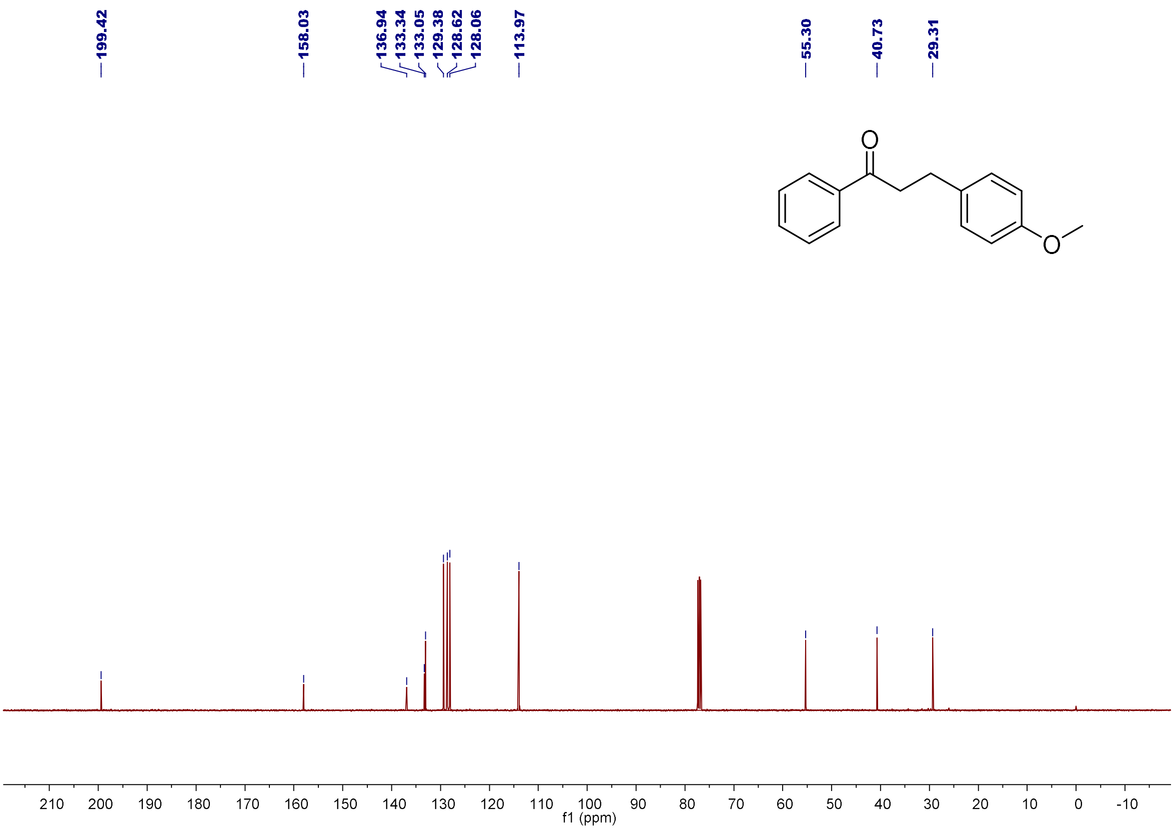
f1 (ppm)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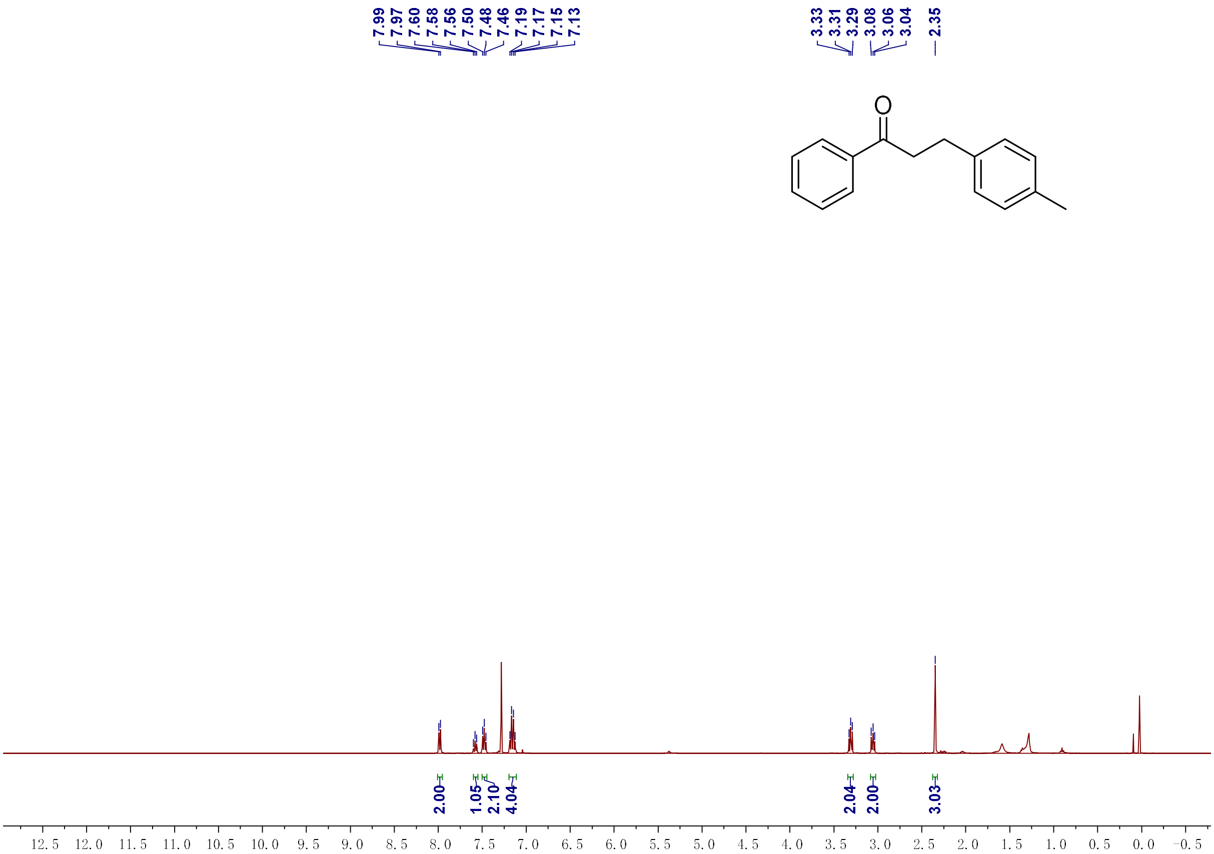
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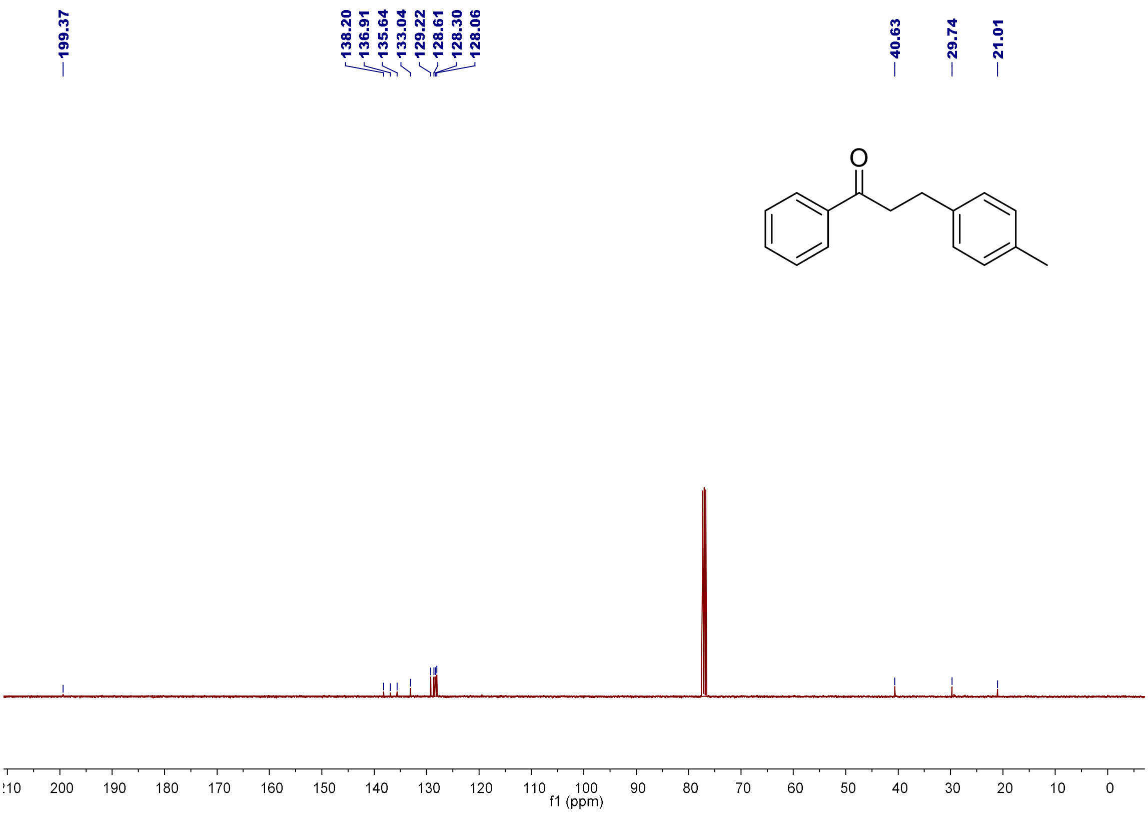
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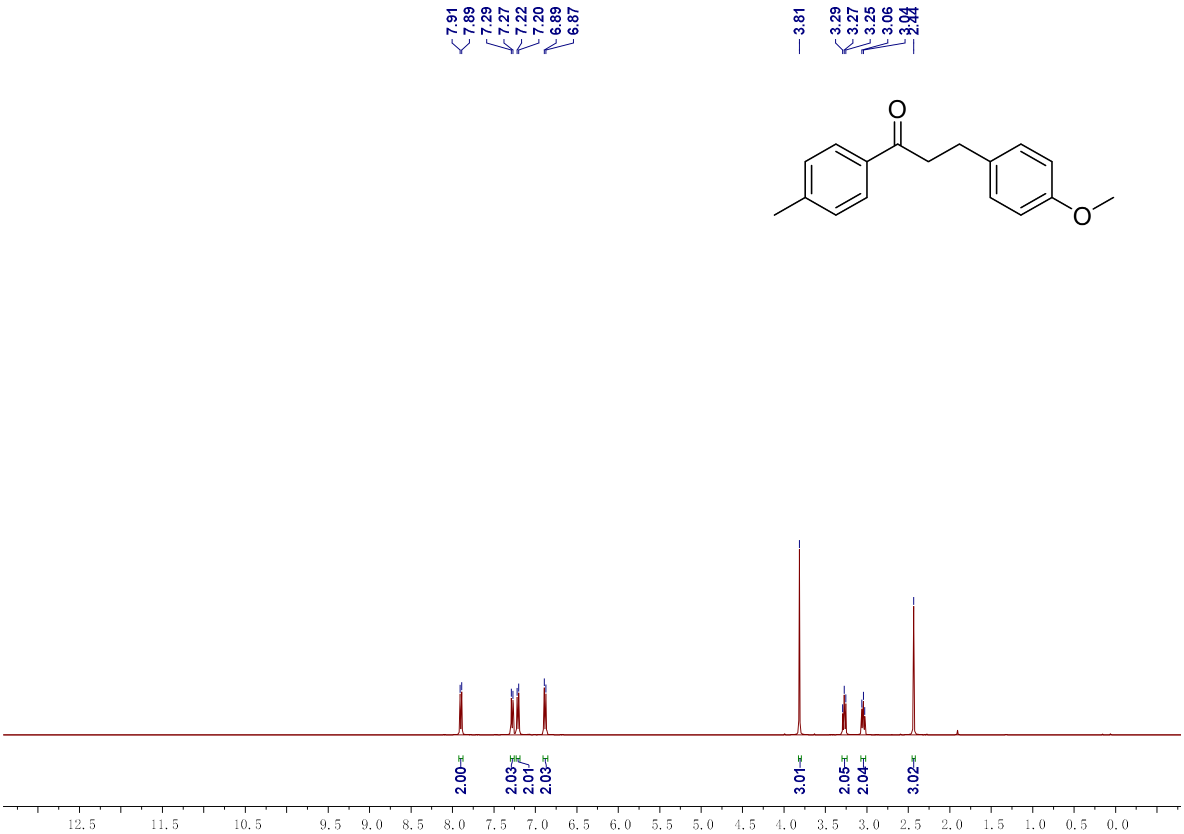
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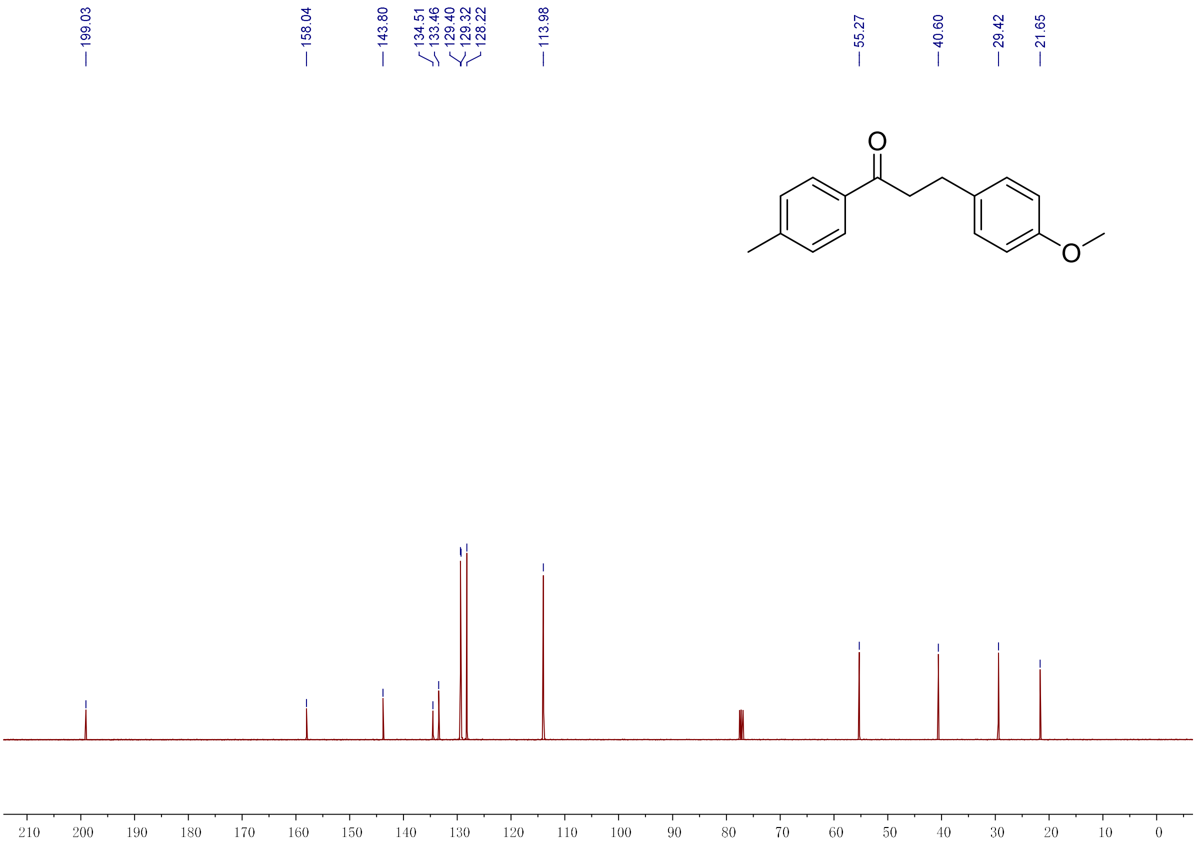
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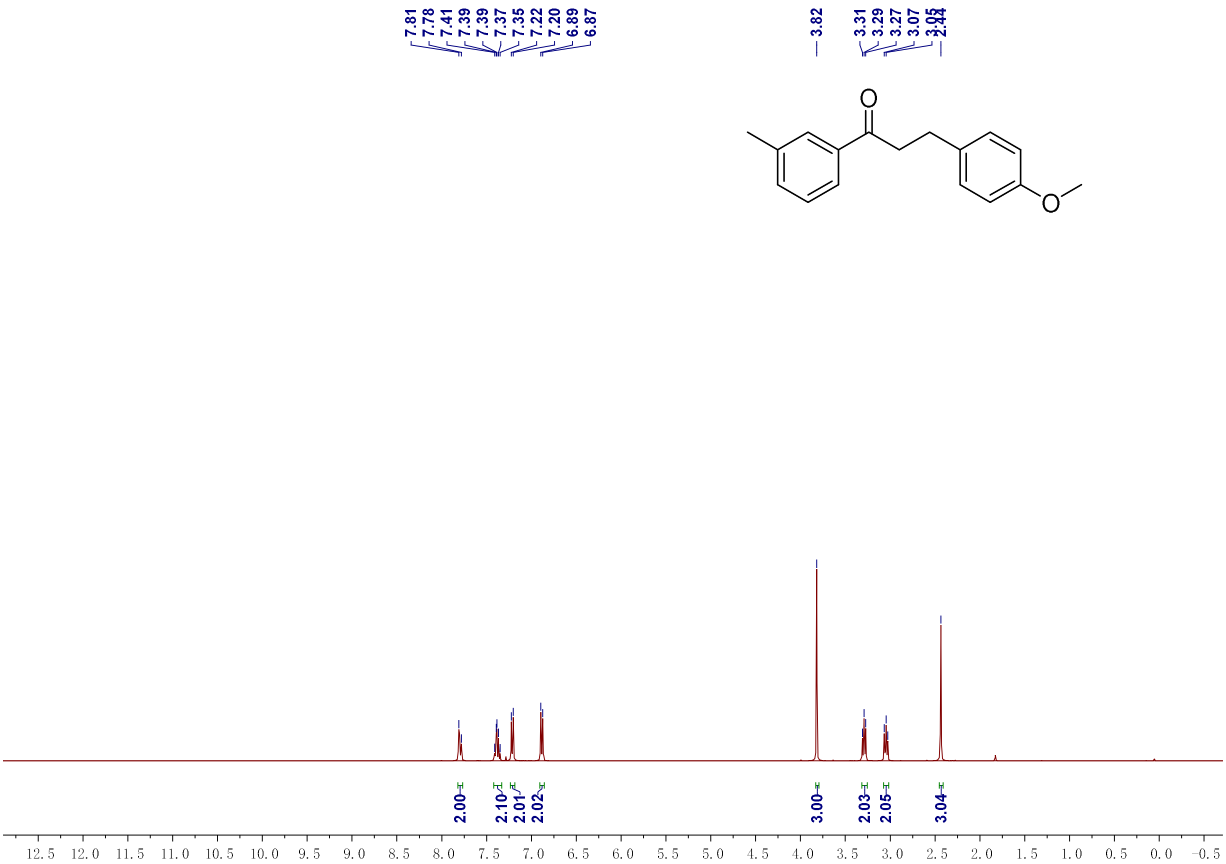
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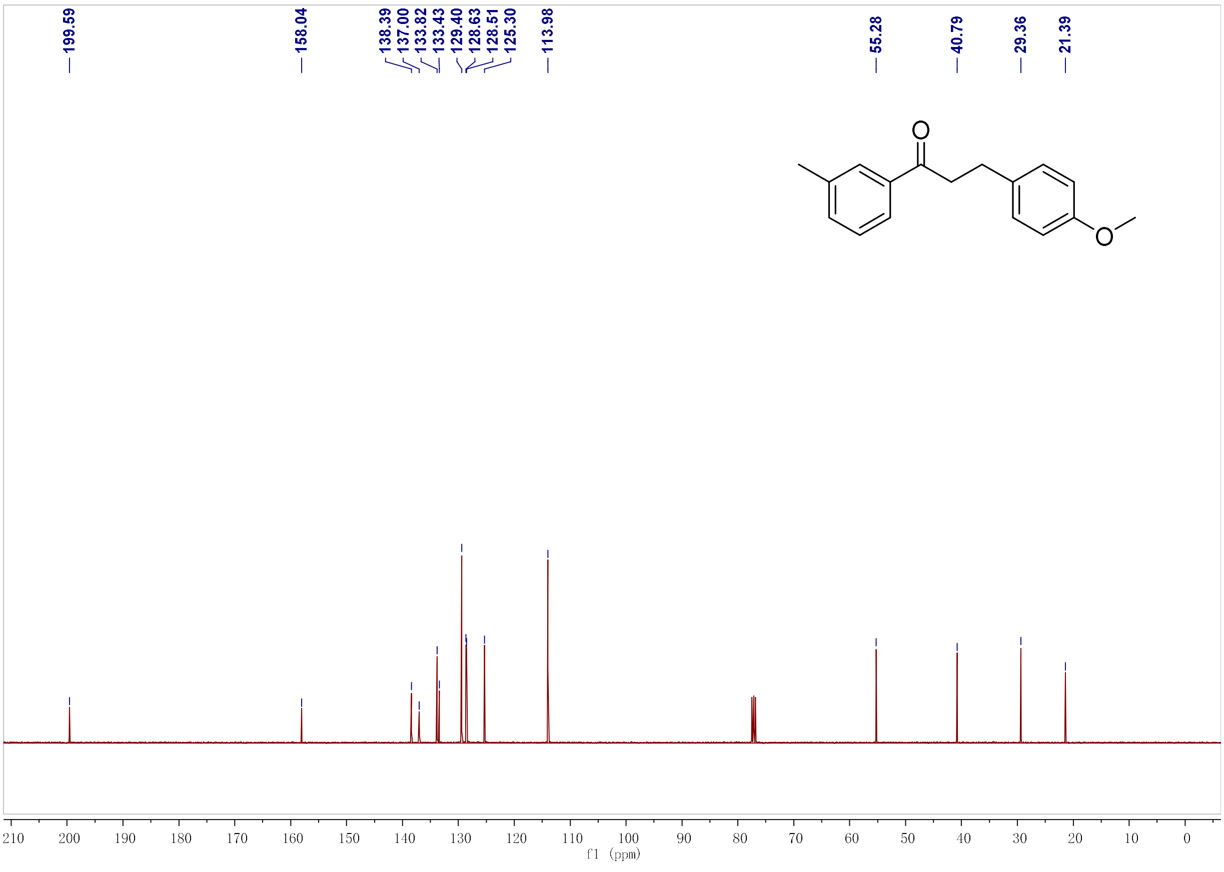
3.05
2.44
2.00
2.10
2.01
2.02
3.00
2.03
2.05
3.04
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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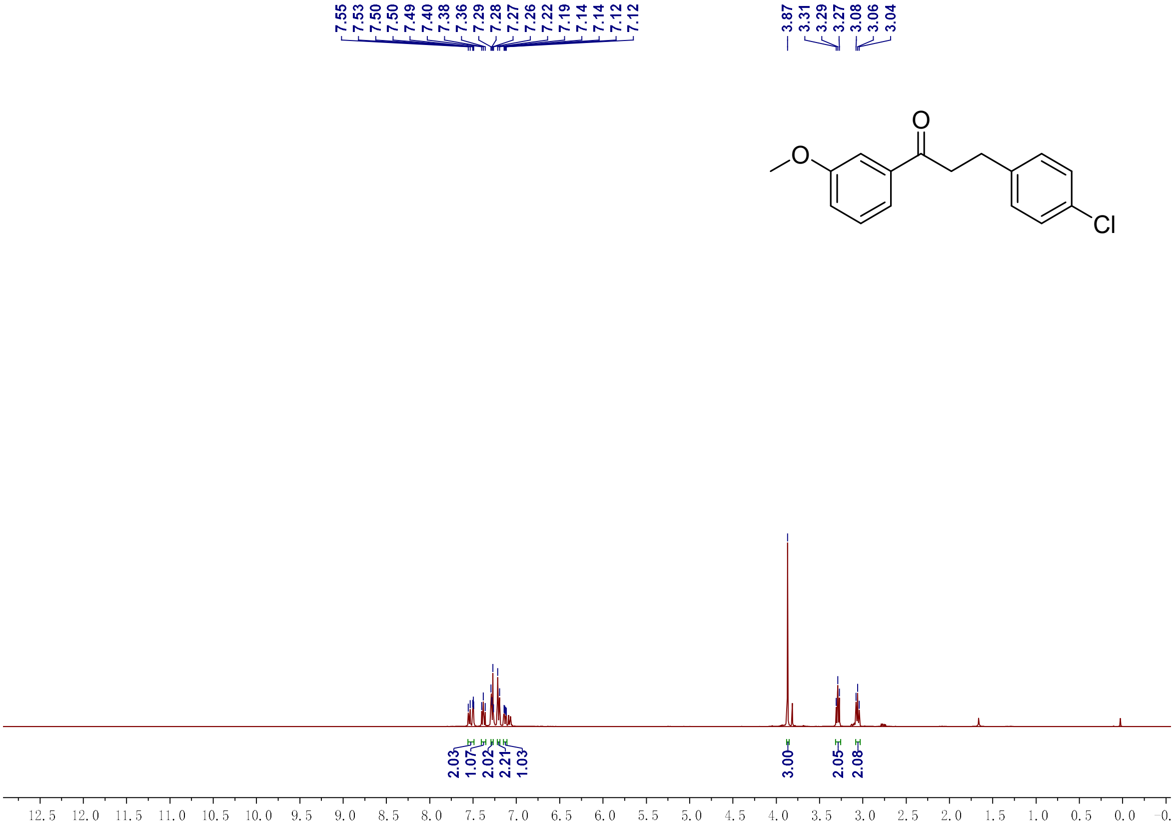
f1 (ppm)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O
Cl
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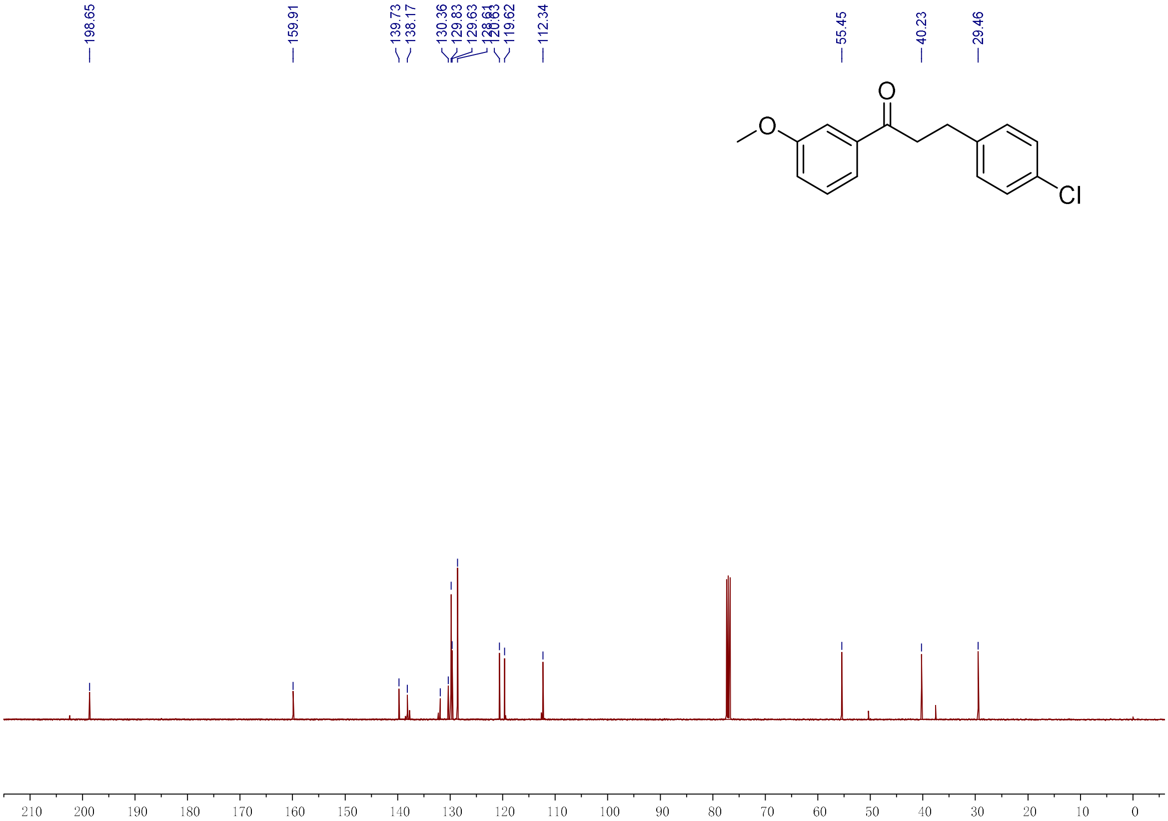
3.00
2.05 2.08
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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Cl
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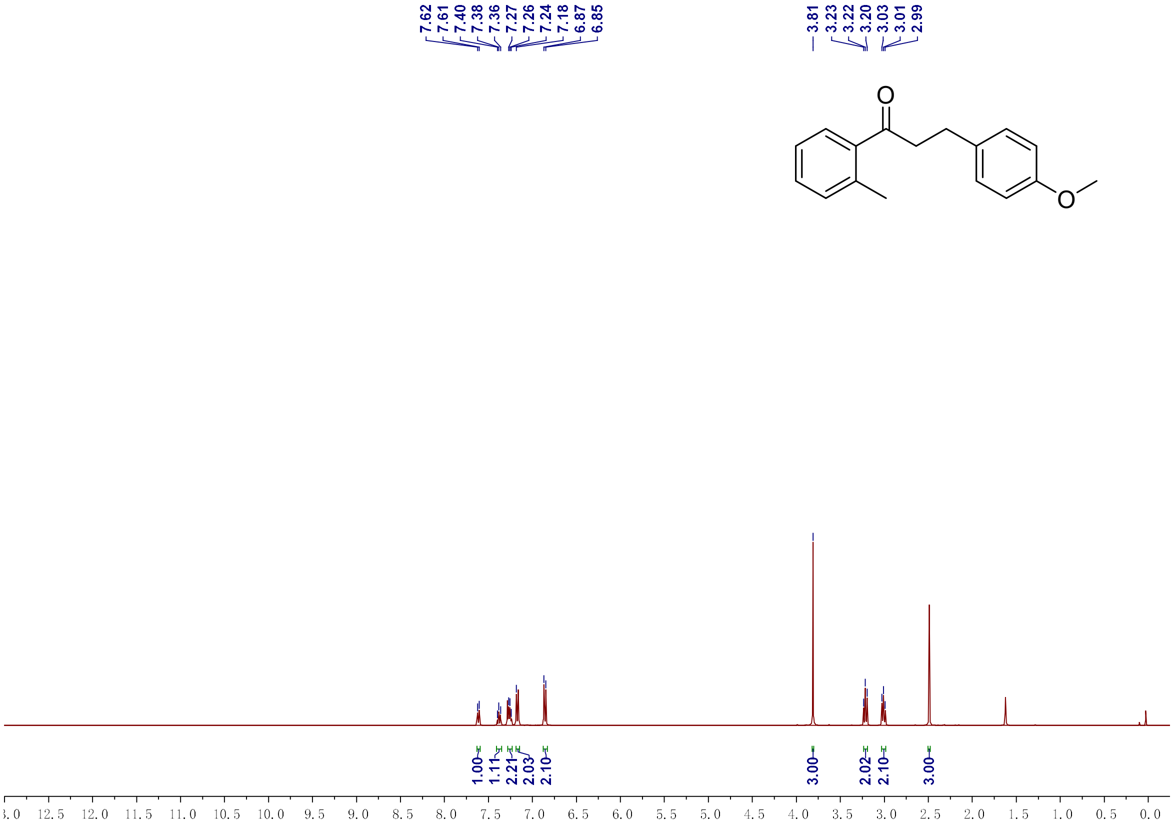
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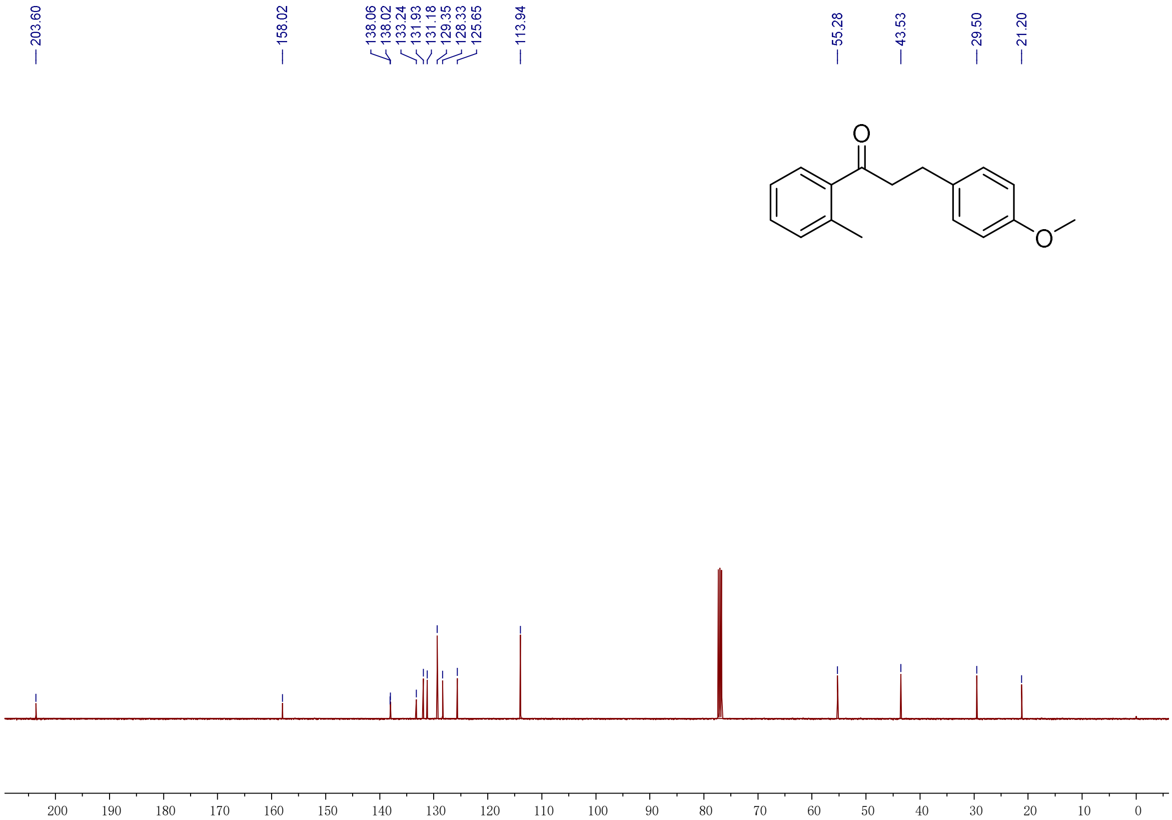
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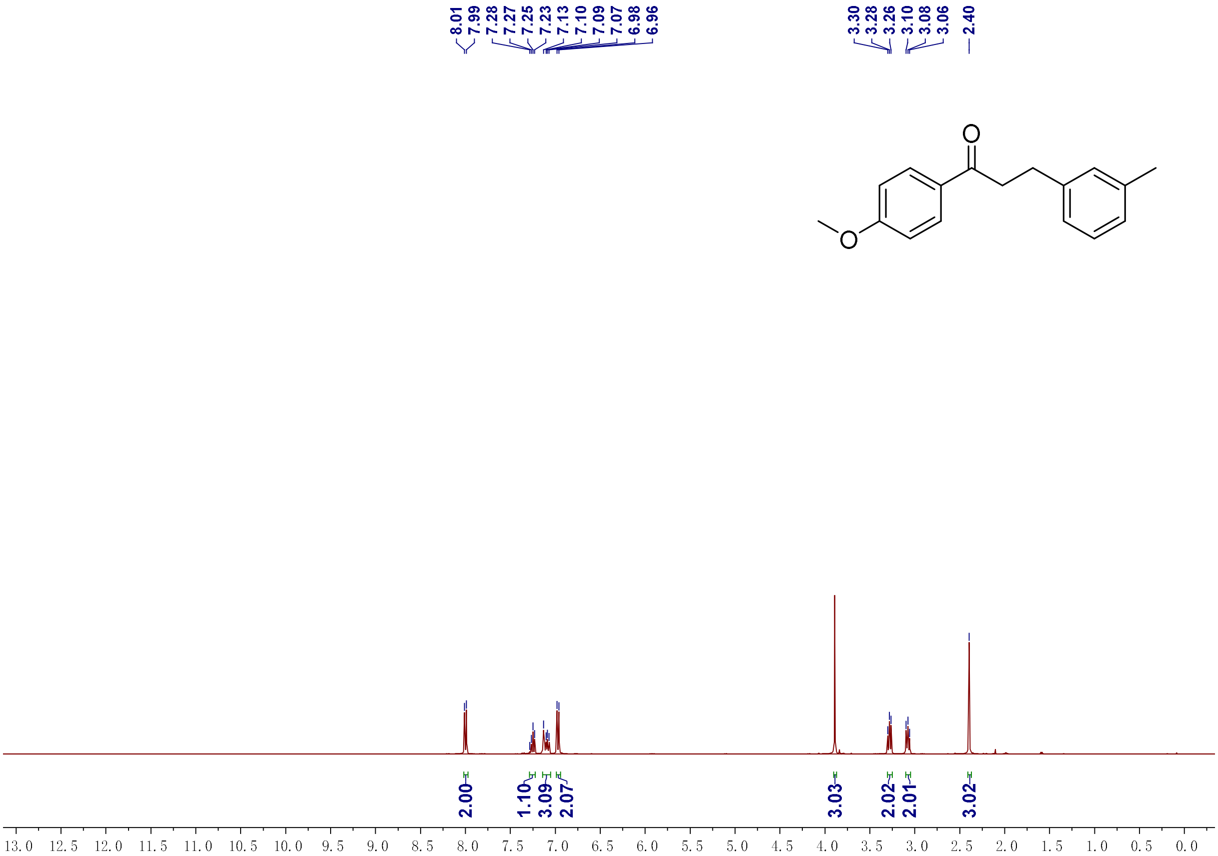
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3.03
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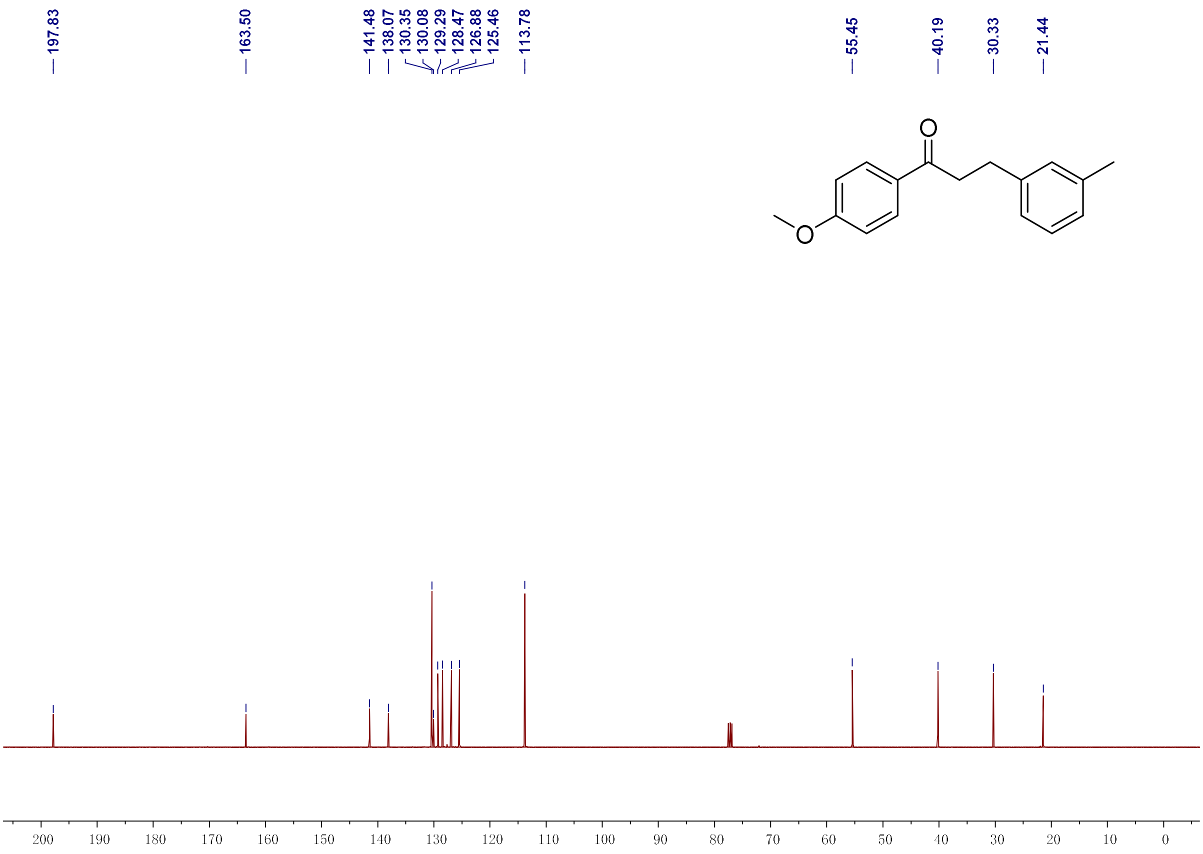
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30.33
21.44
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O
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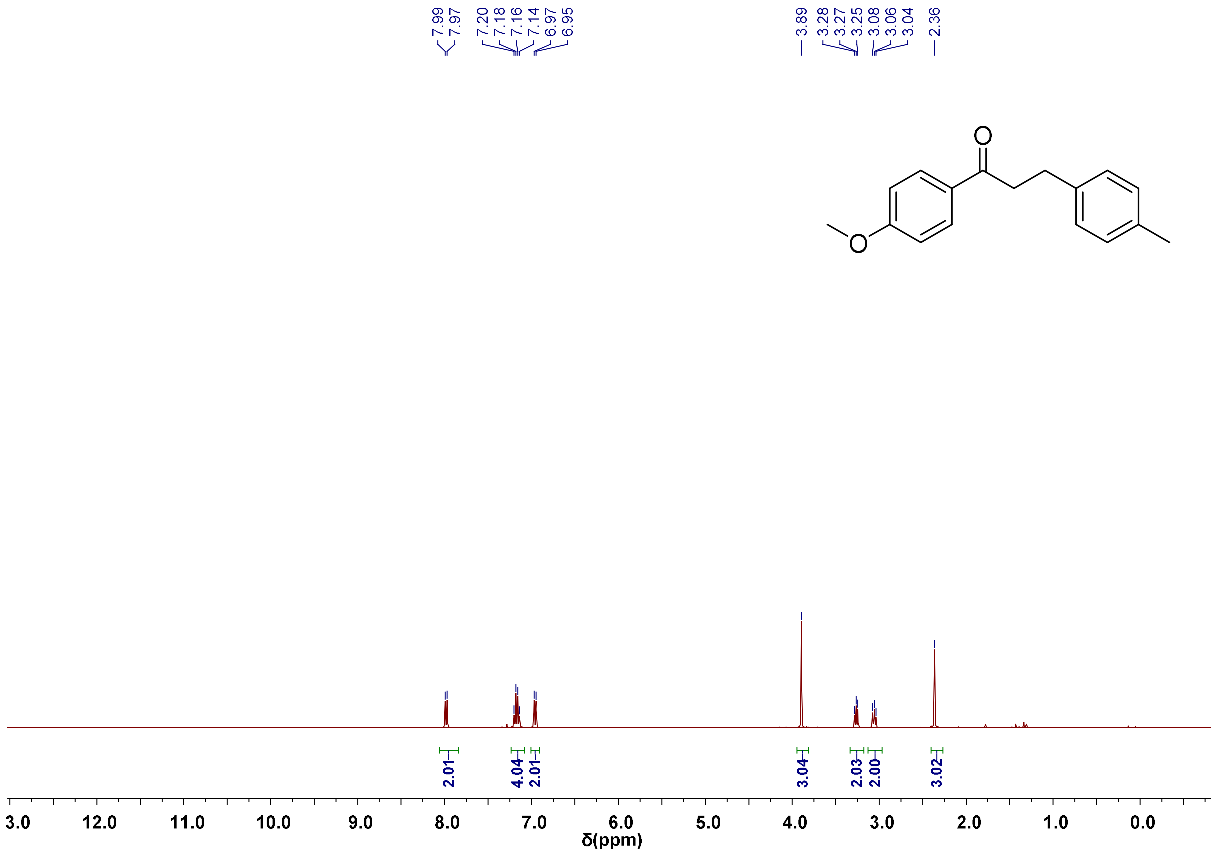

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3.08
3.06
3.04
2.36
O
O
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4.04
2.01
3.04
2.03
2.00
3.02
3.0
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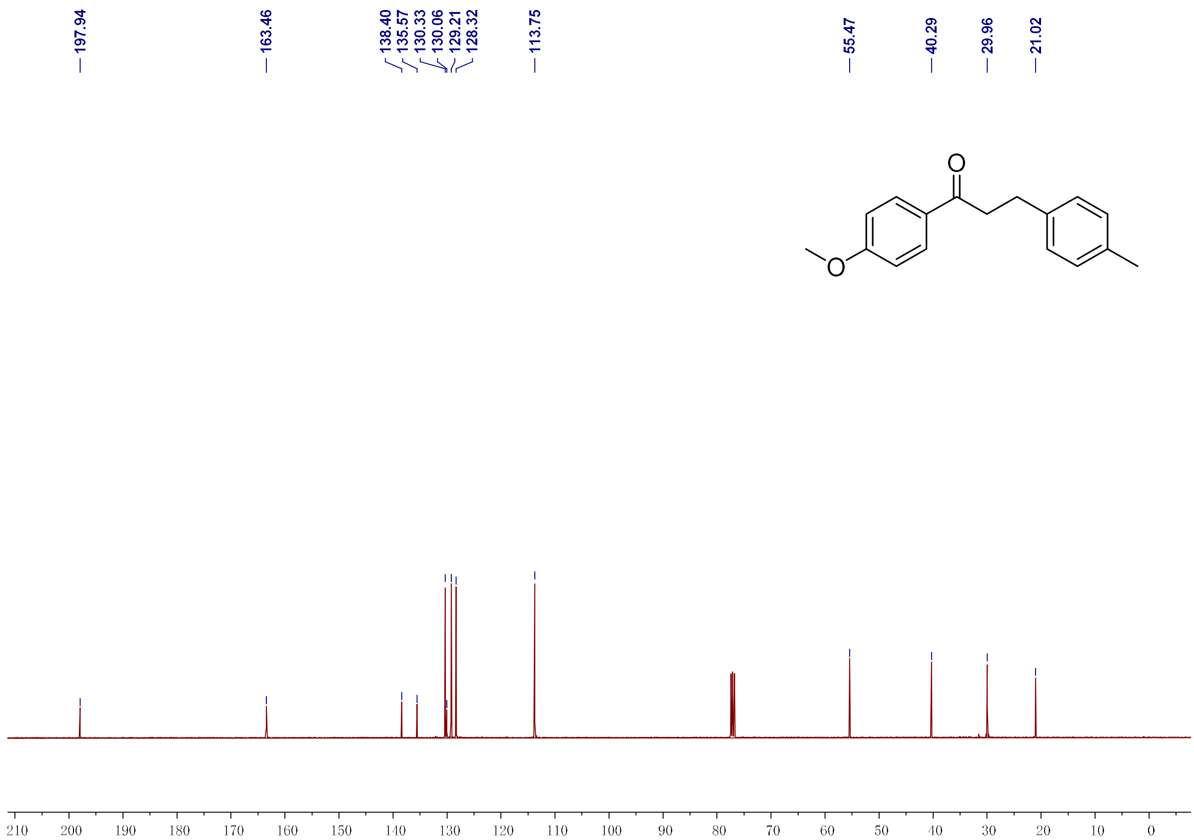
δ(ppm)



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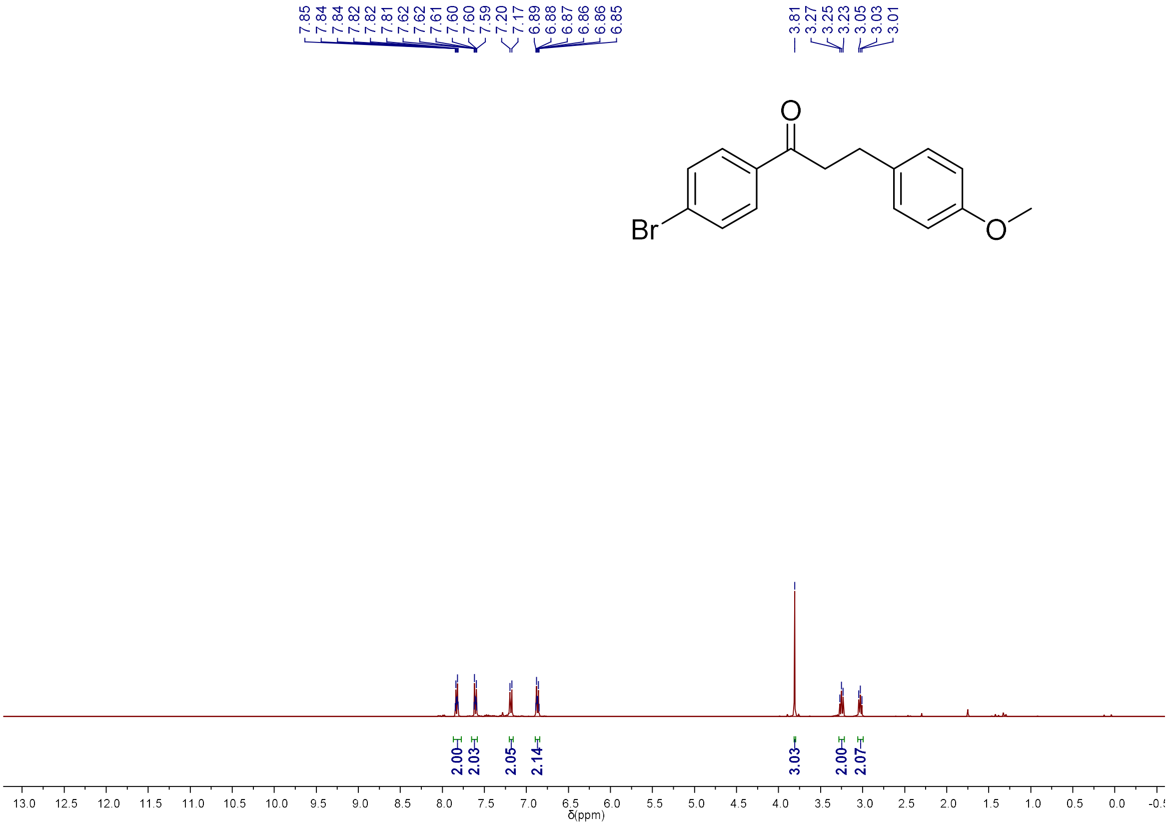
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3.03
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2.05
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3.03
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2.07
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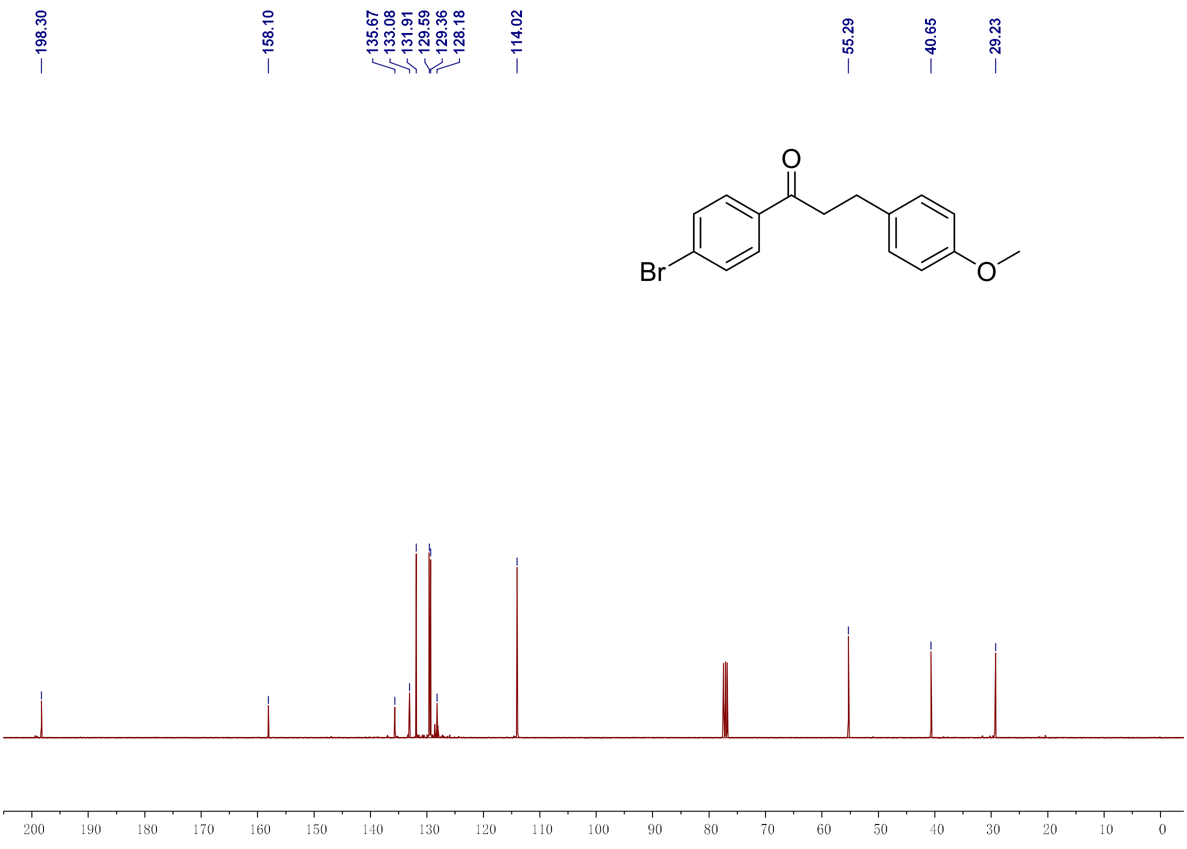
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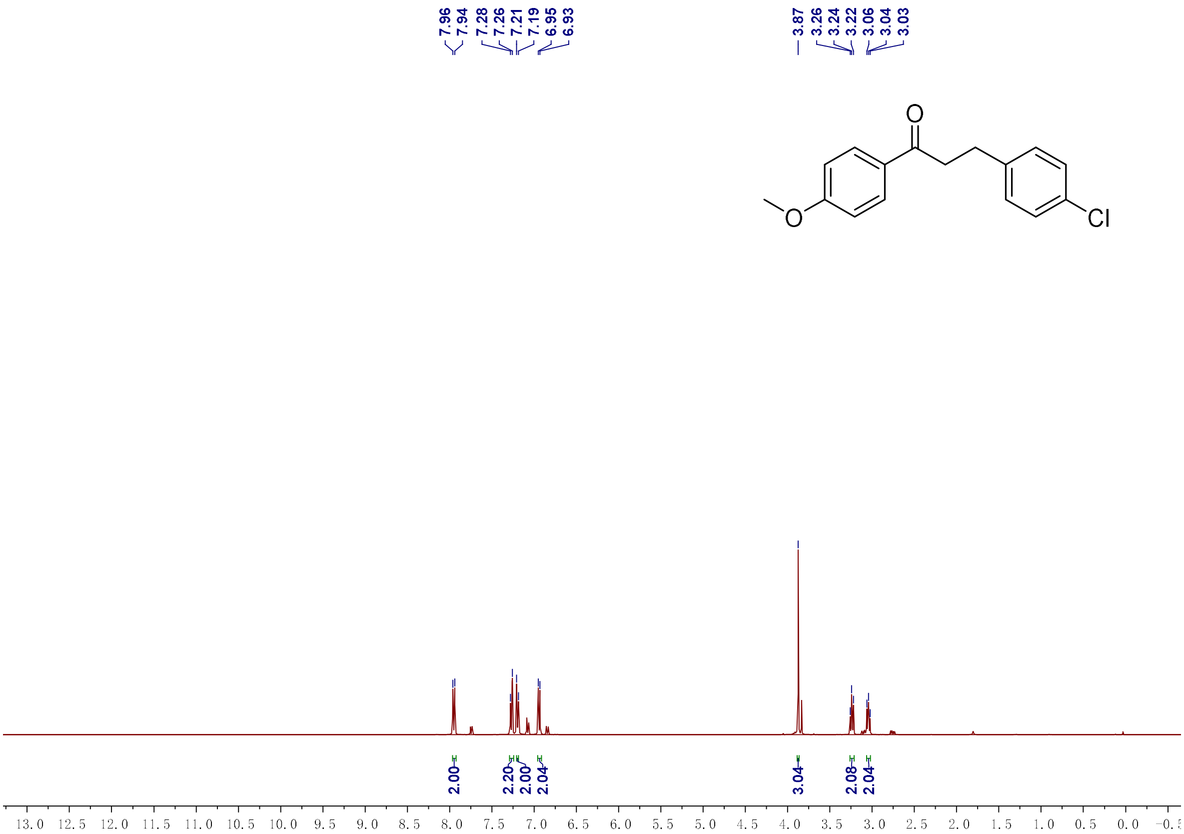
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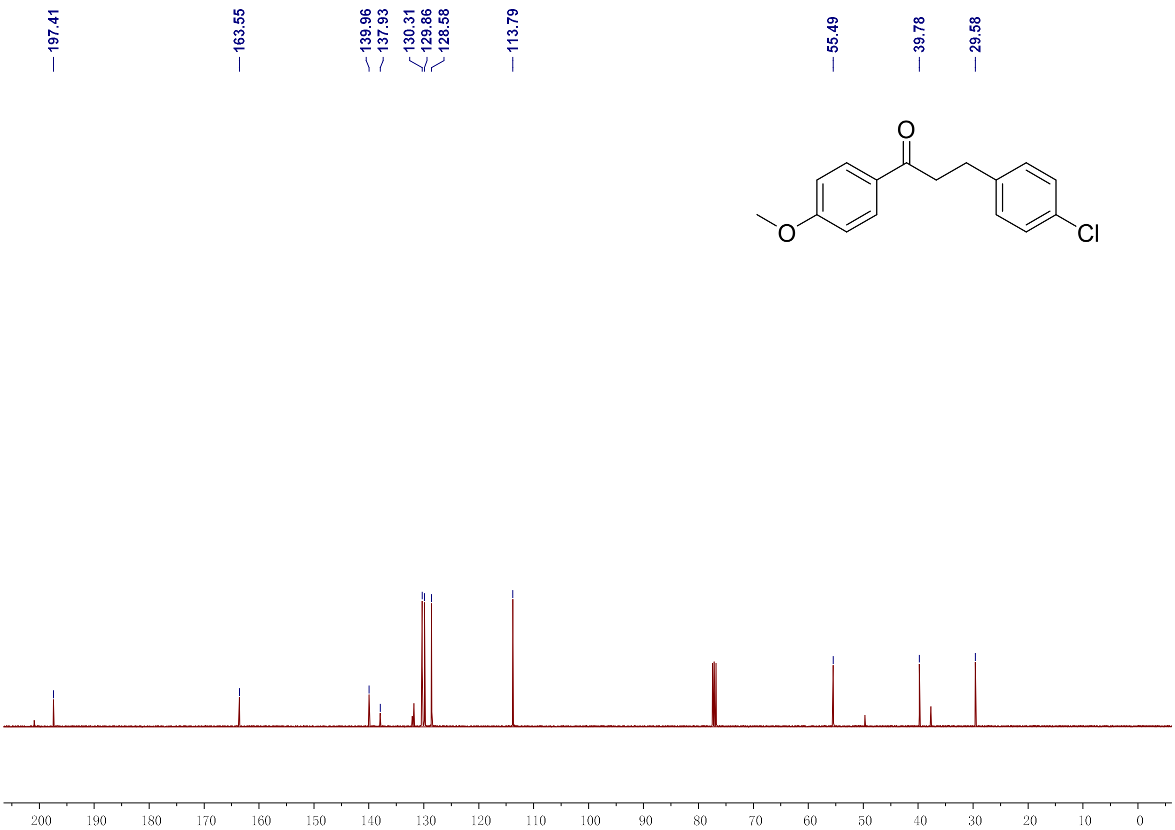
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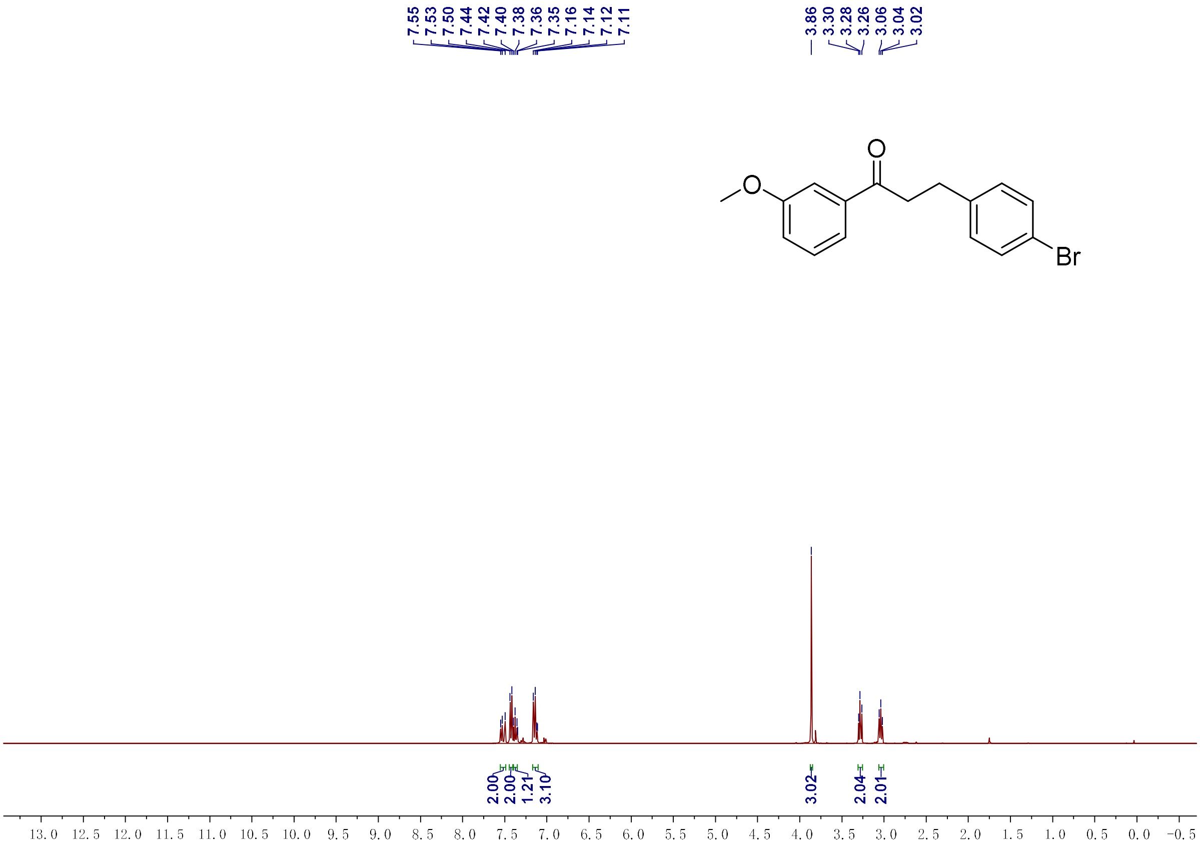
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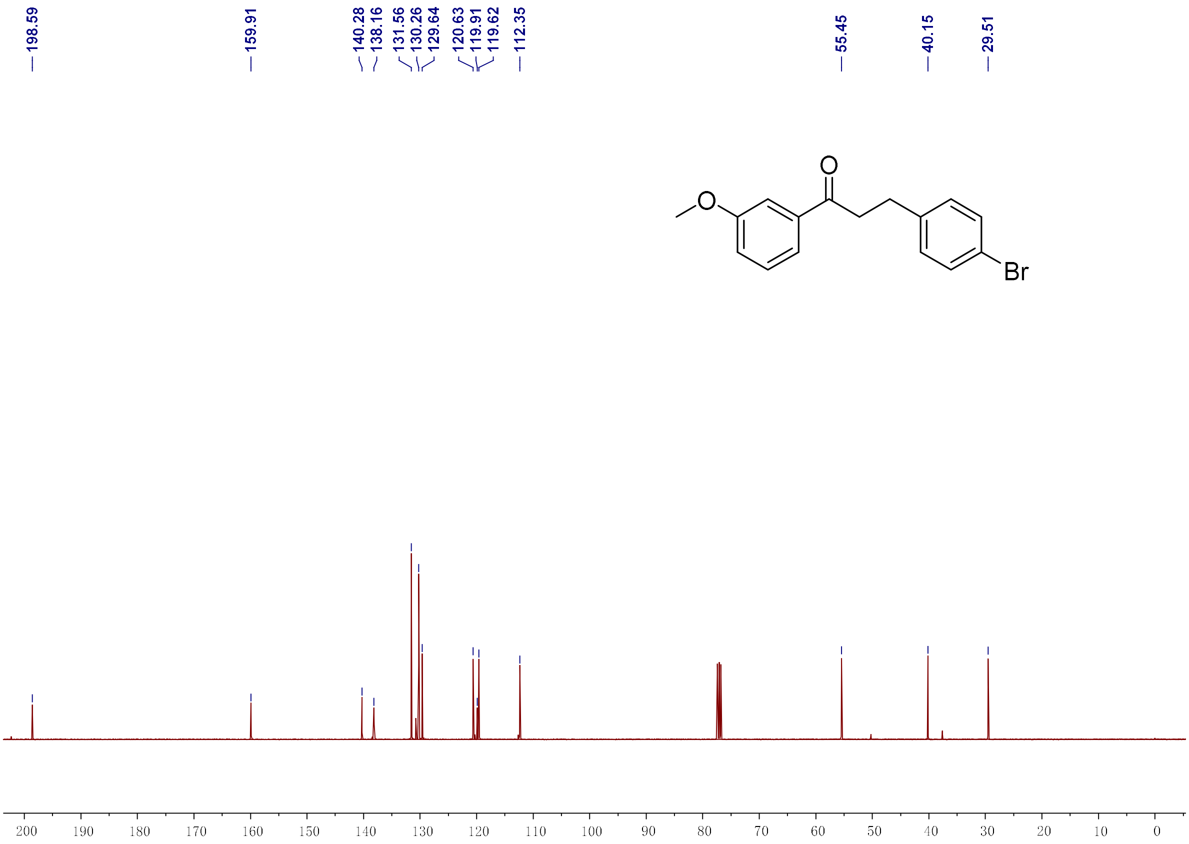
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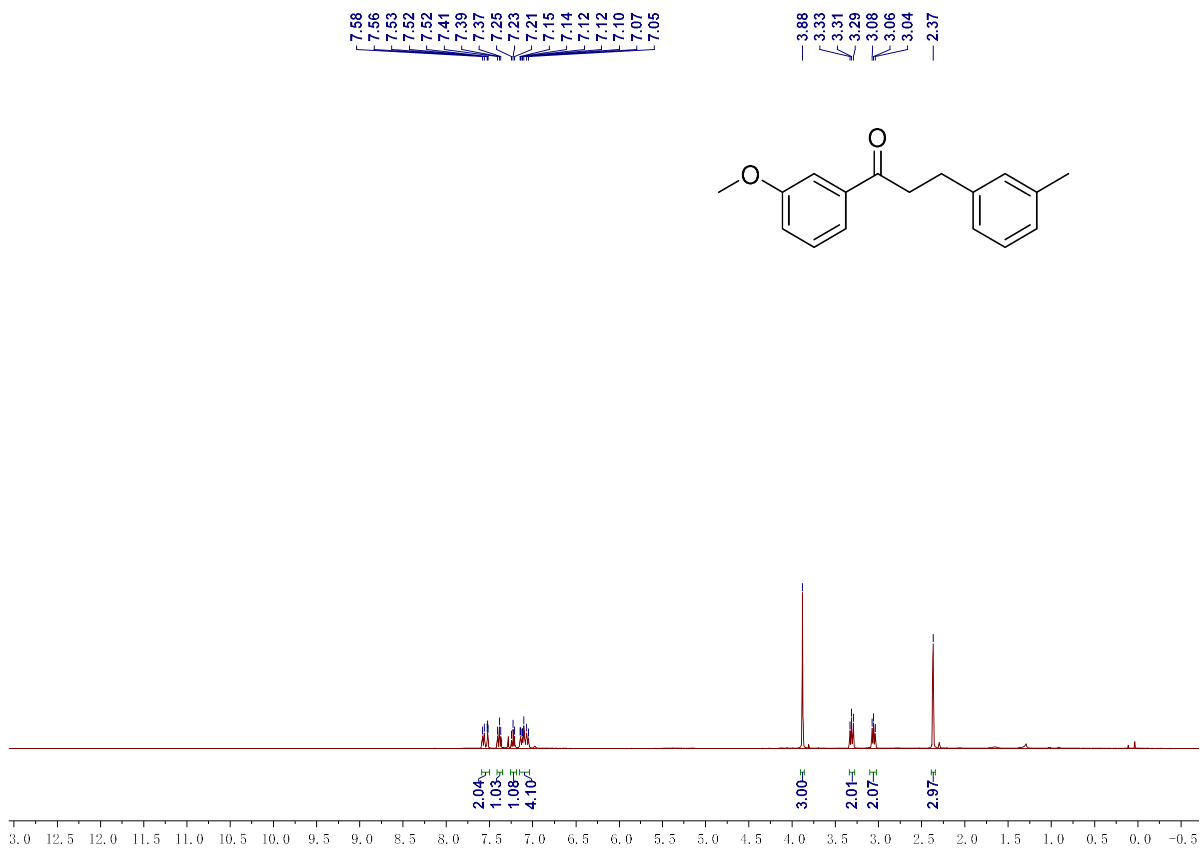
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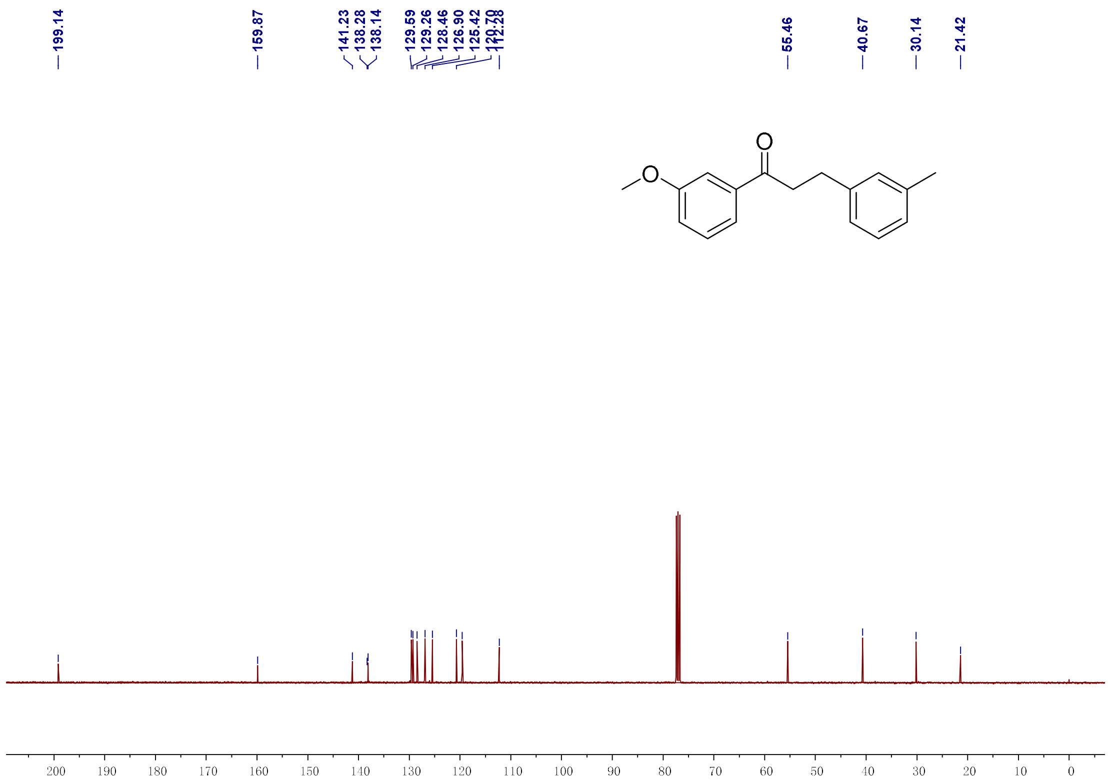
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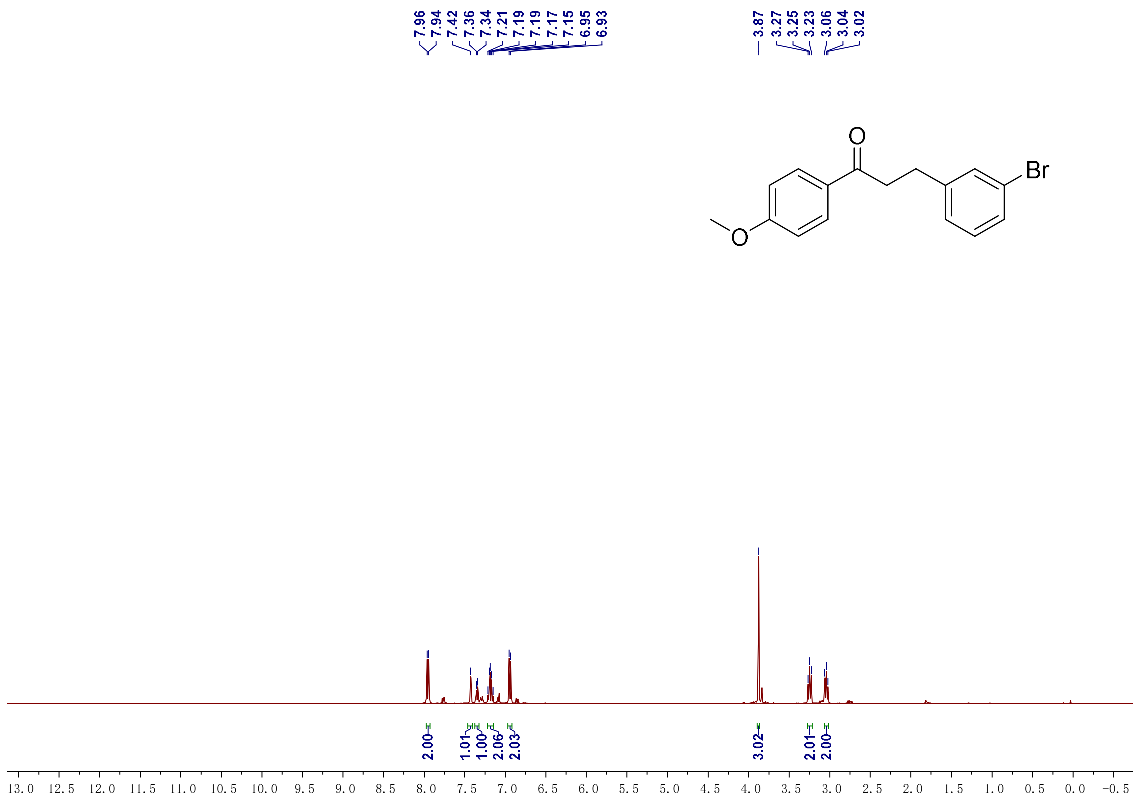
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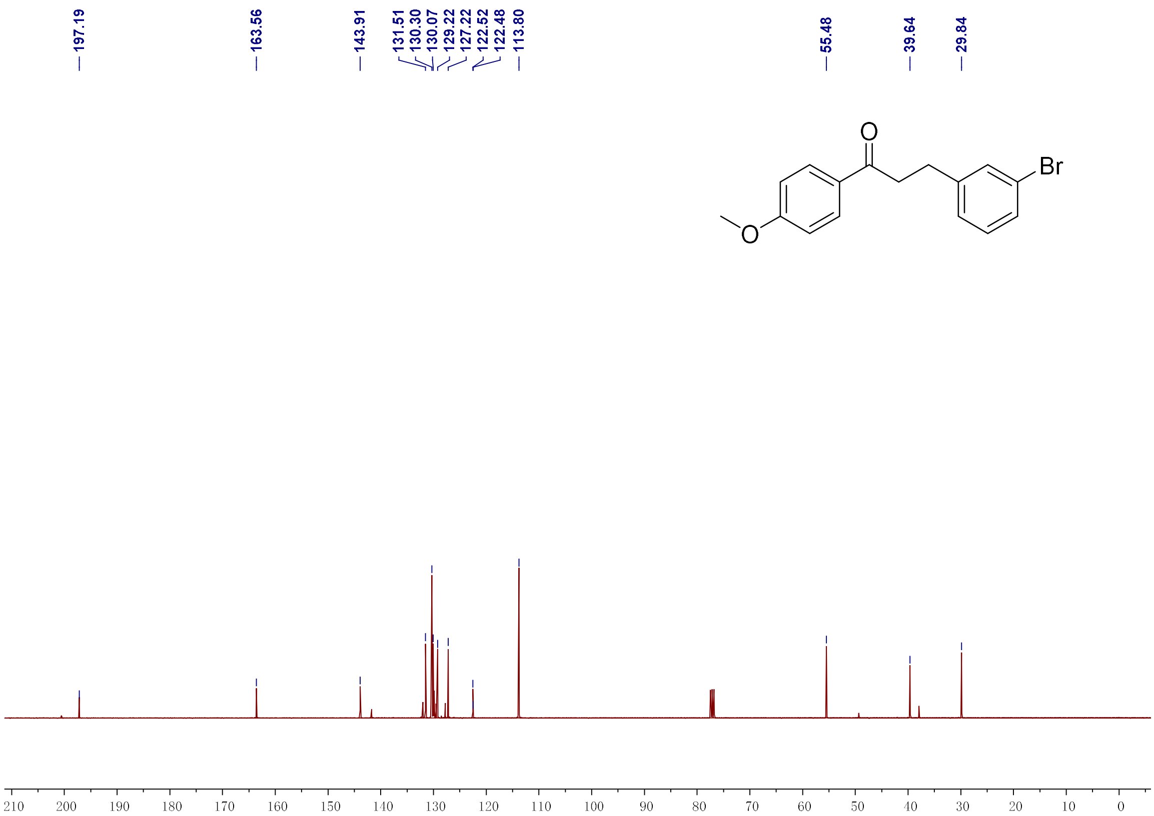
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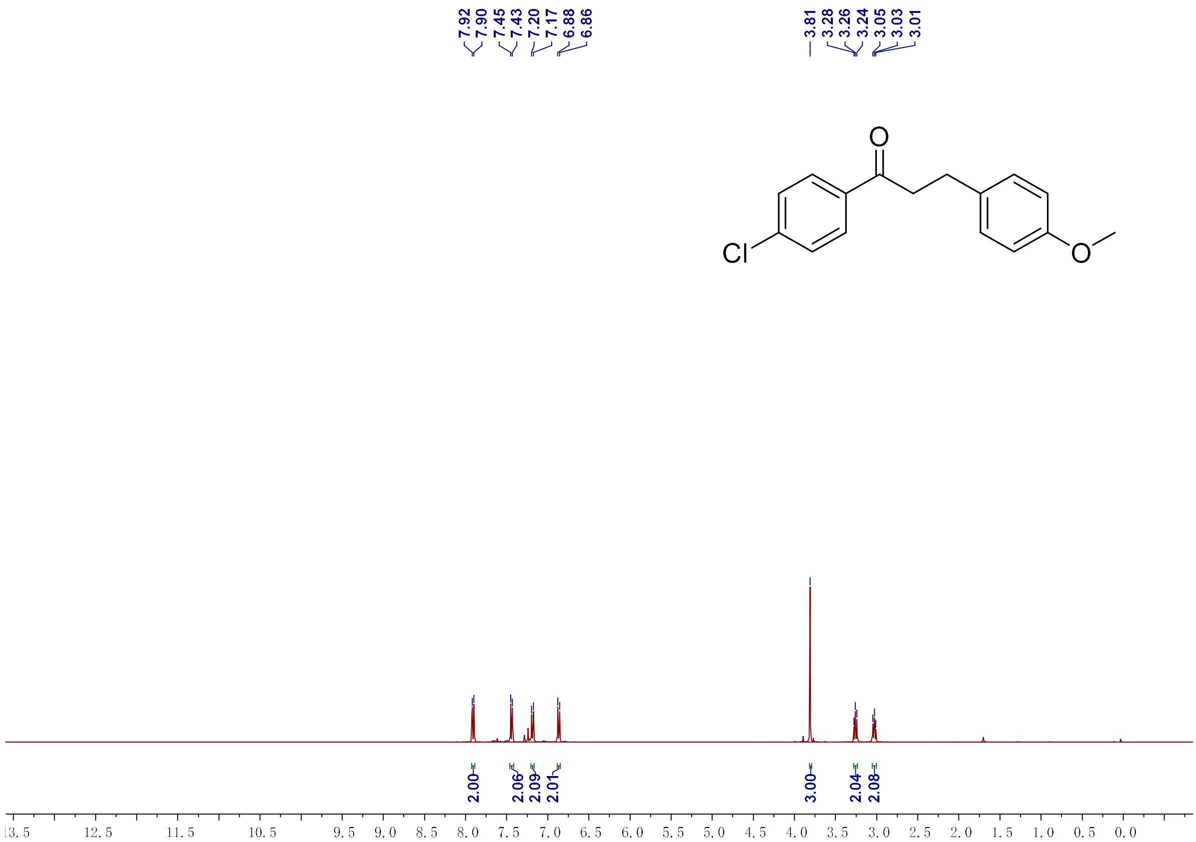
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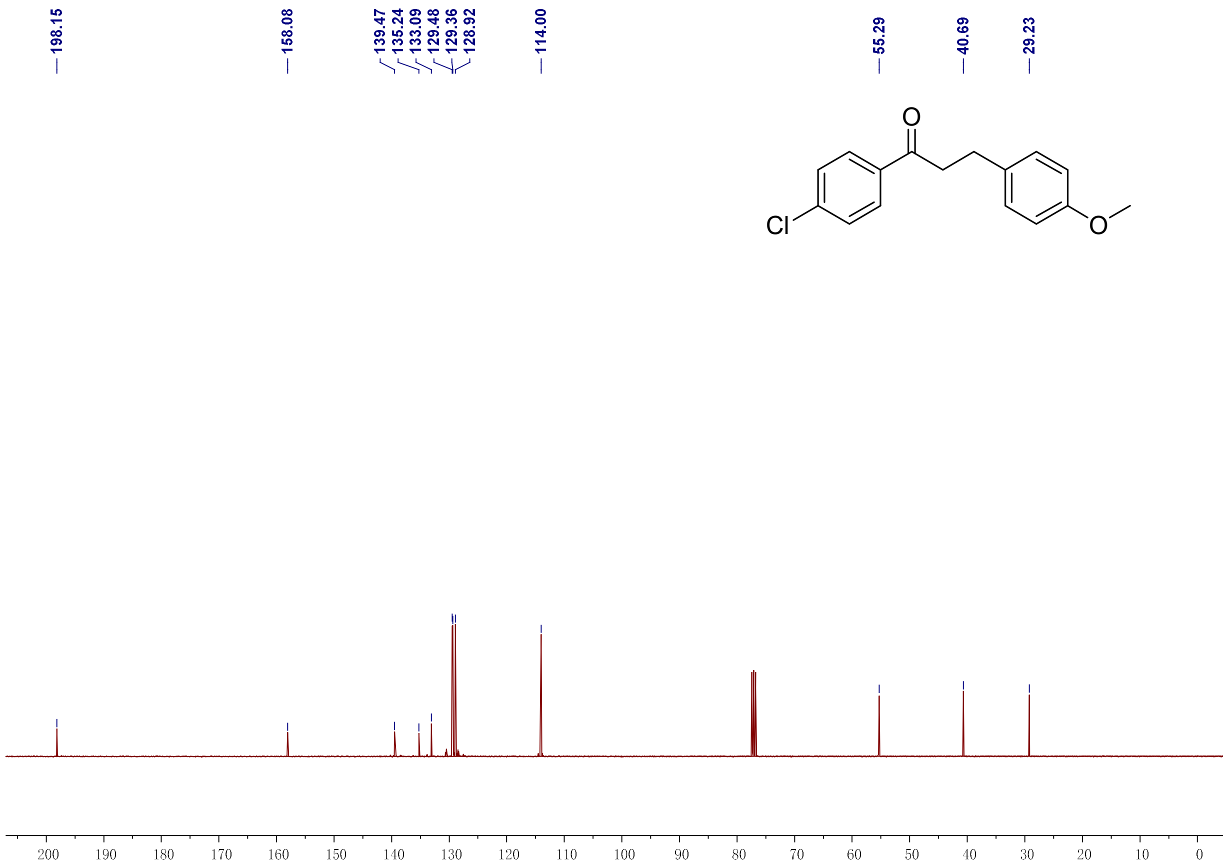
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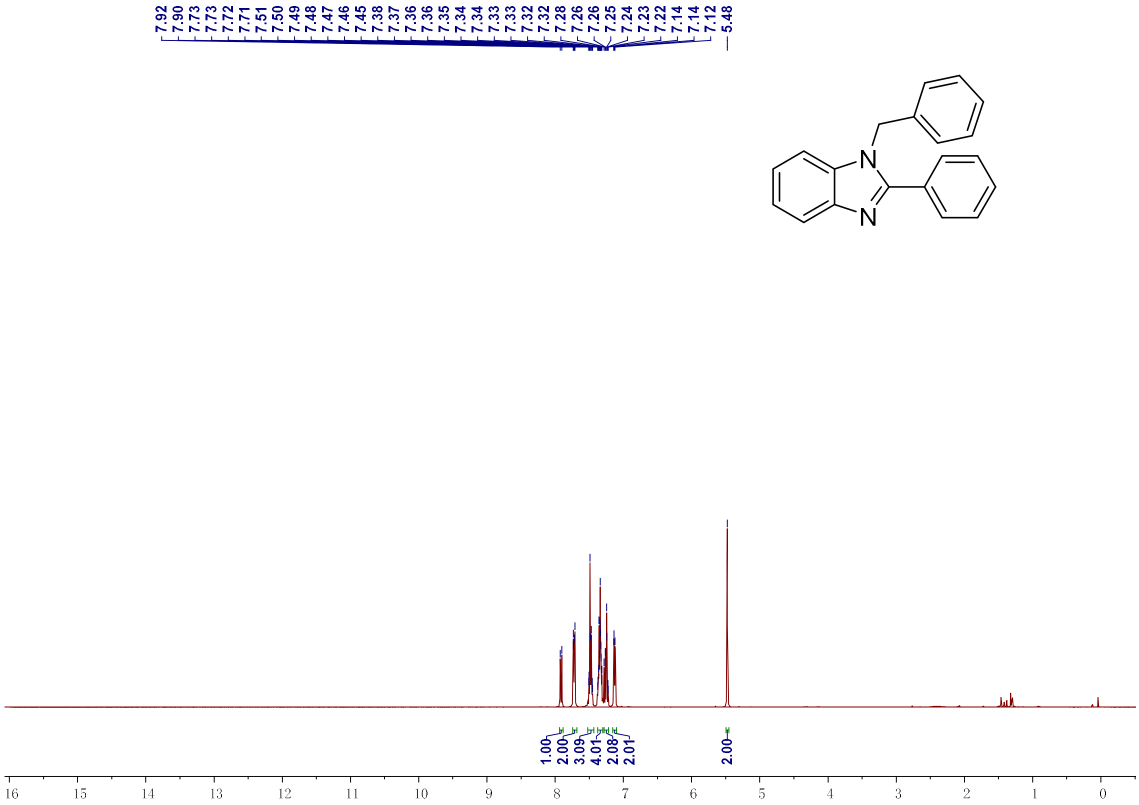
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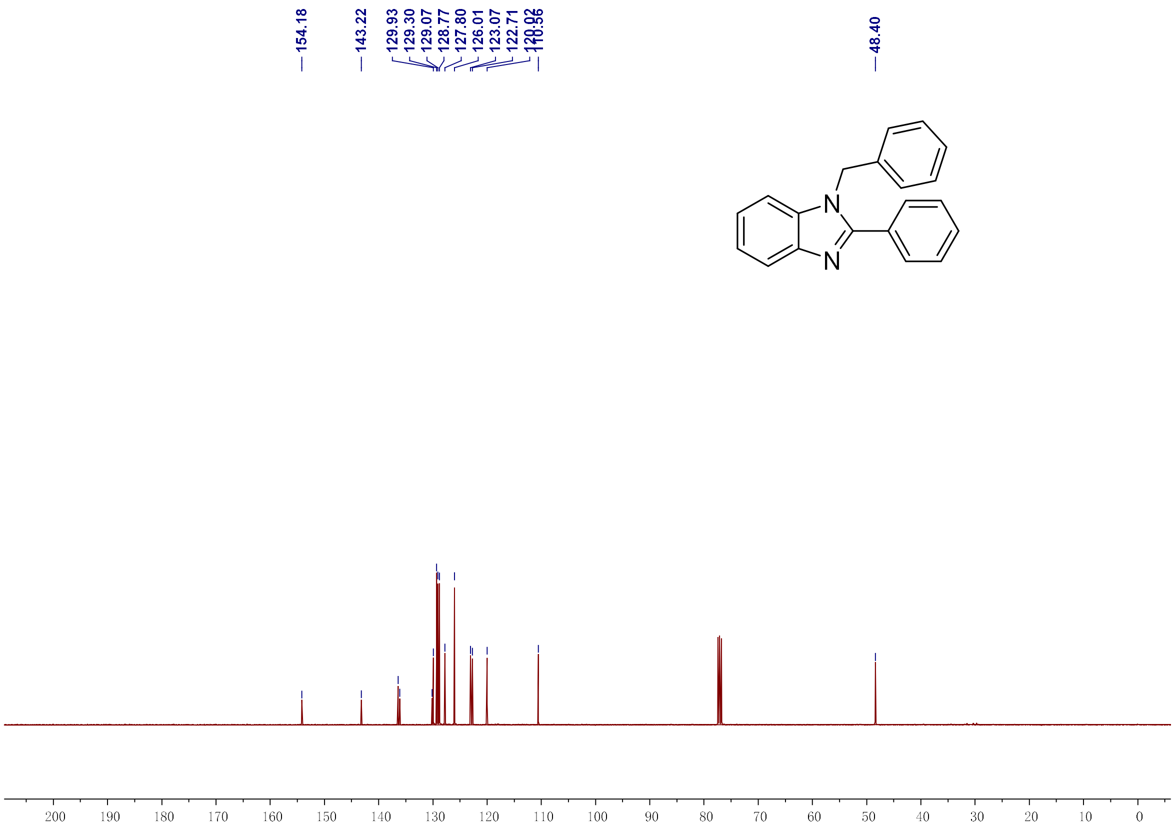
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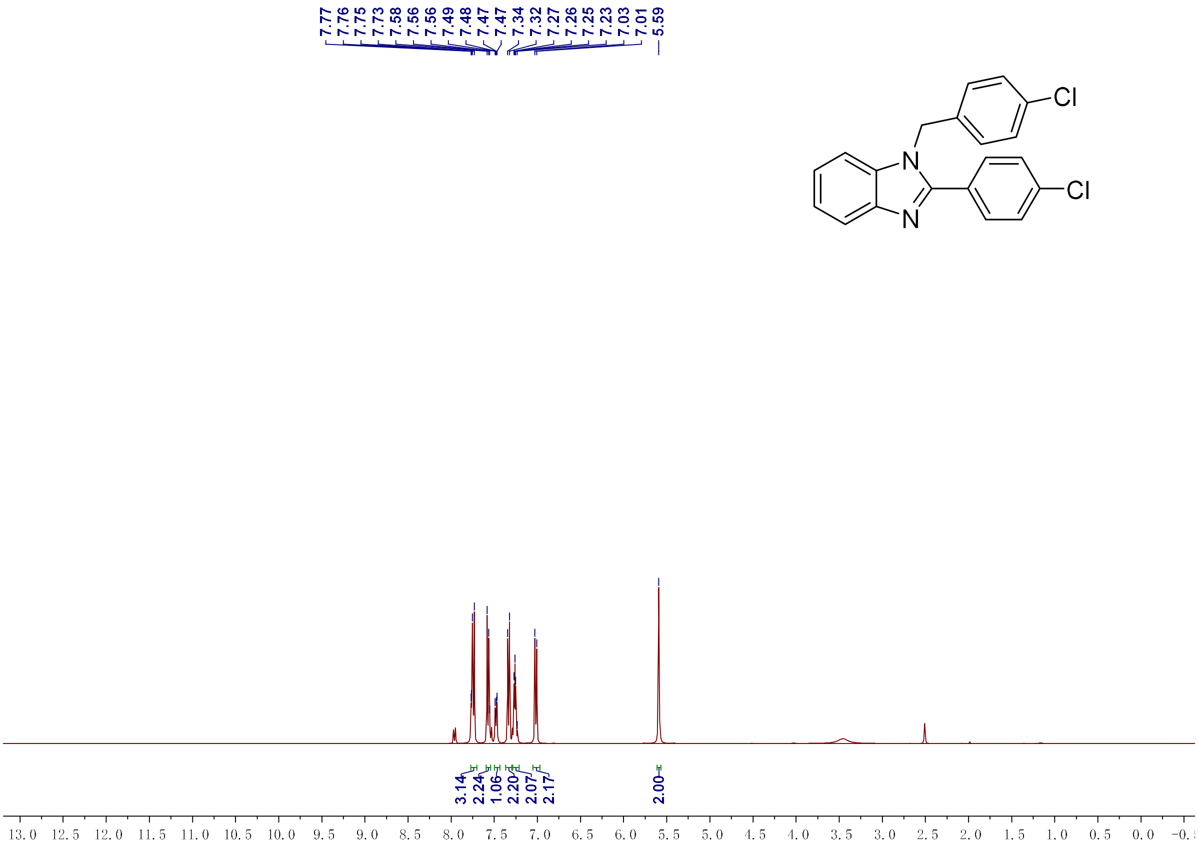
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2.17
2.00
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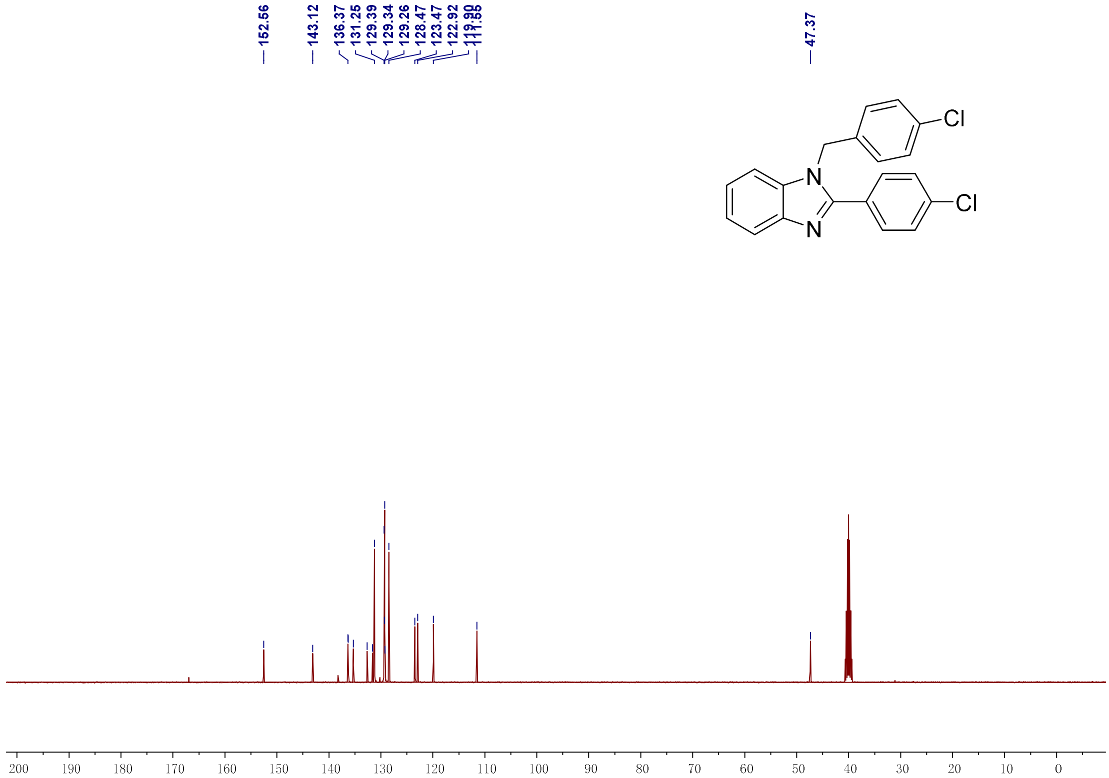
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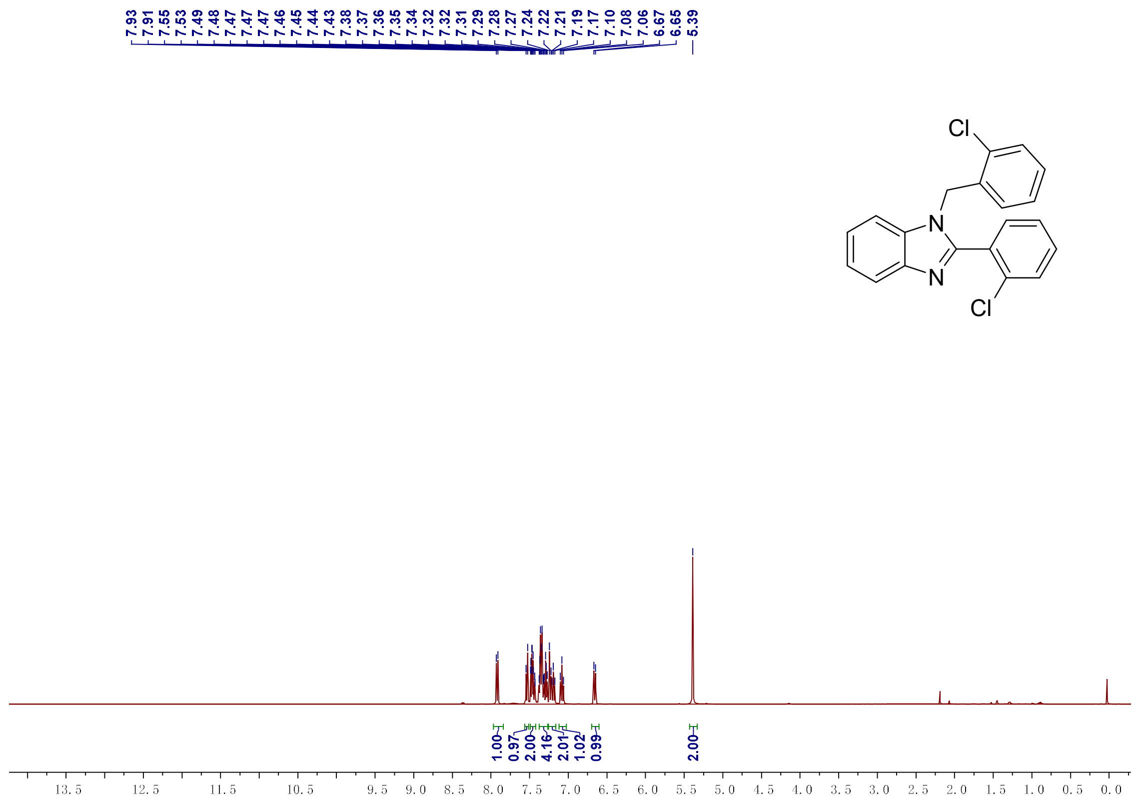
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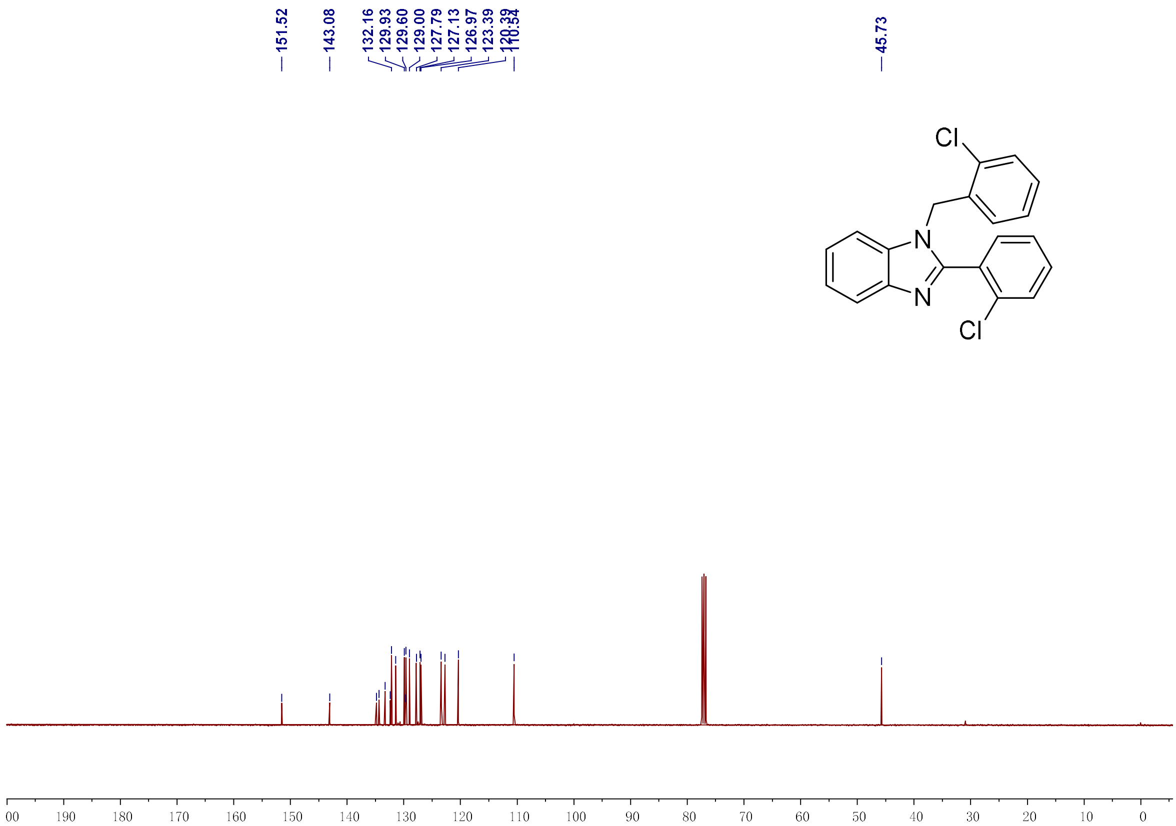
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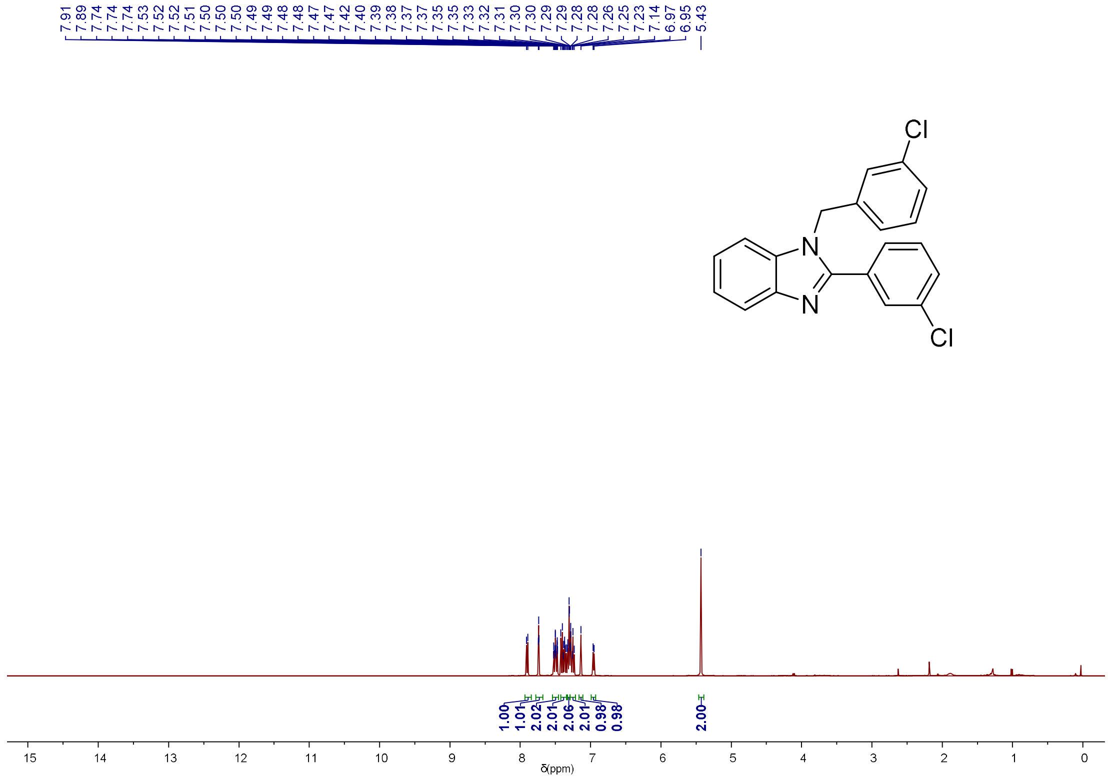
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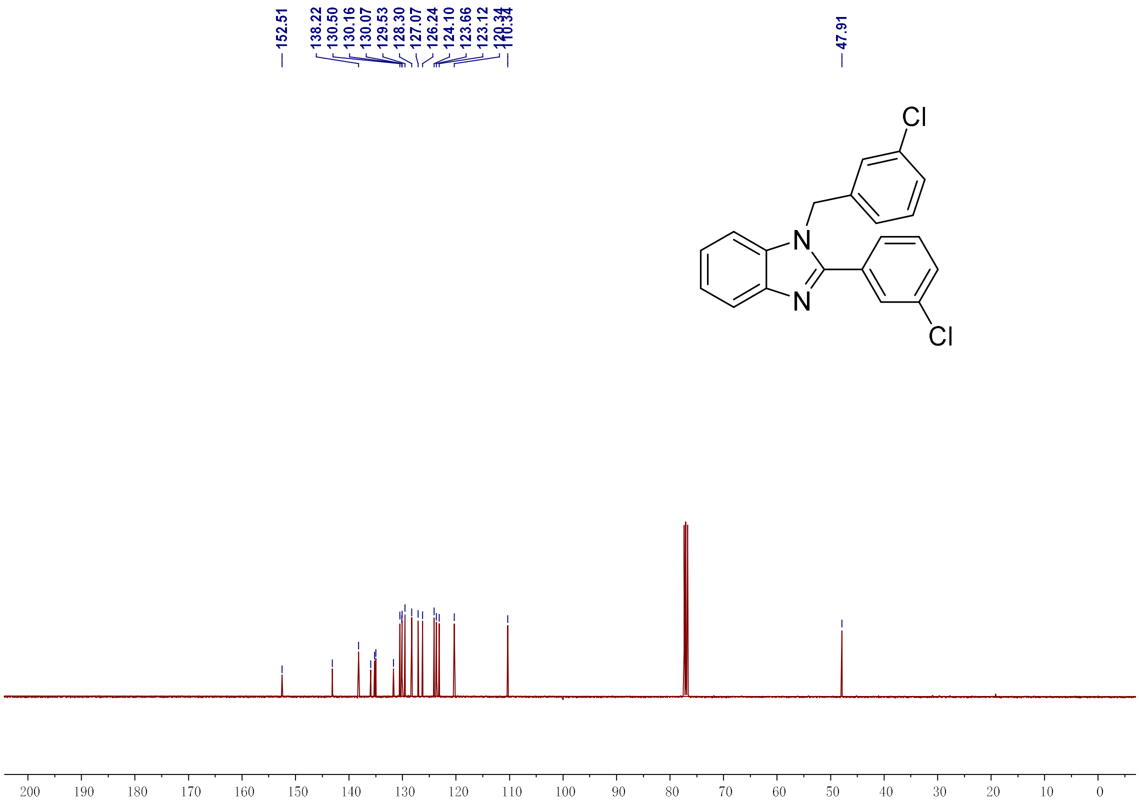
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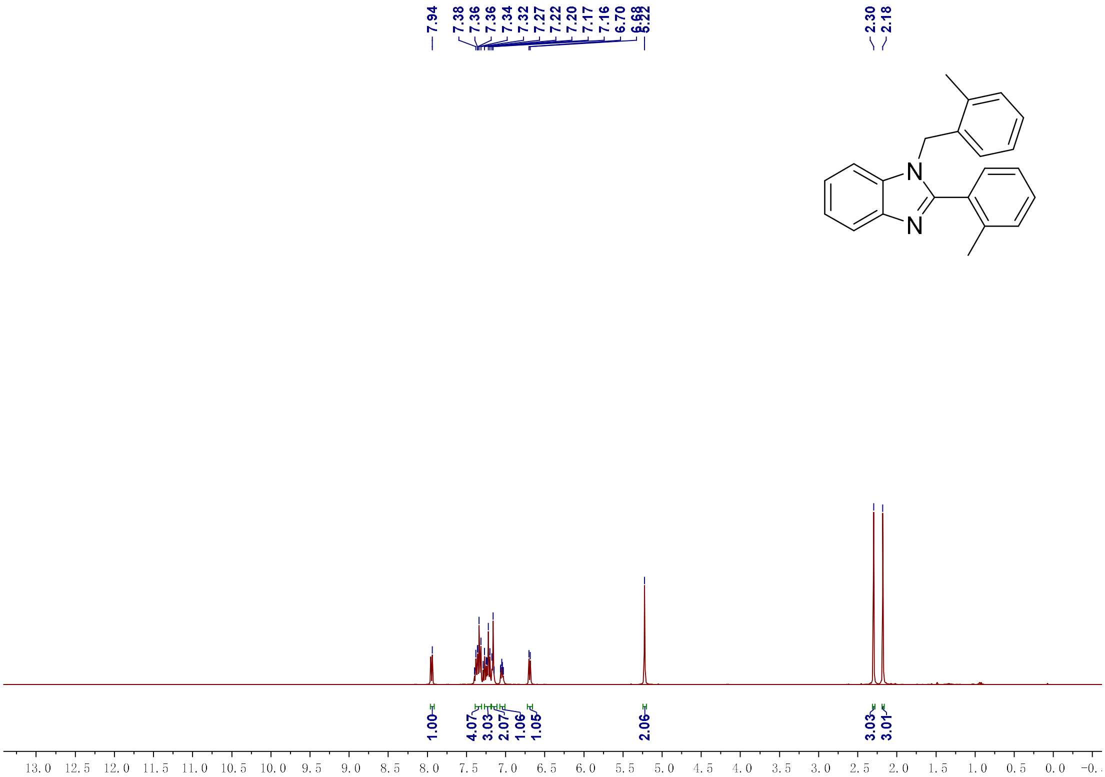
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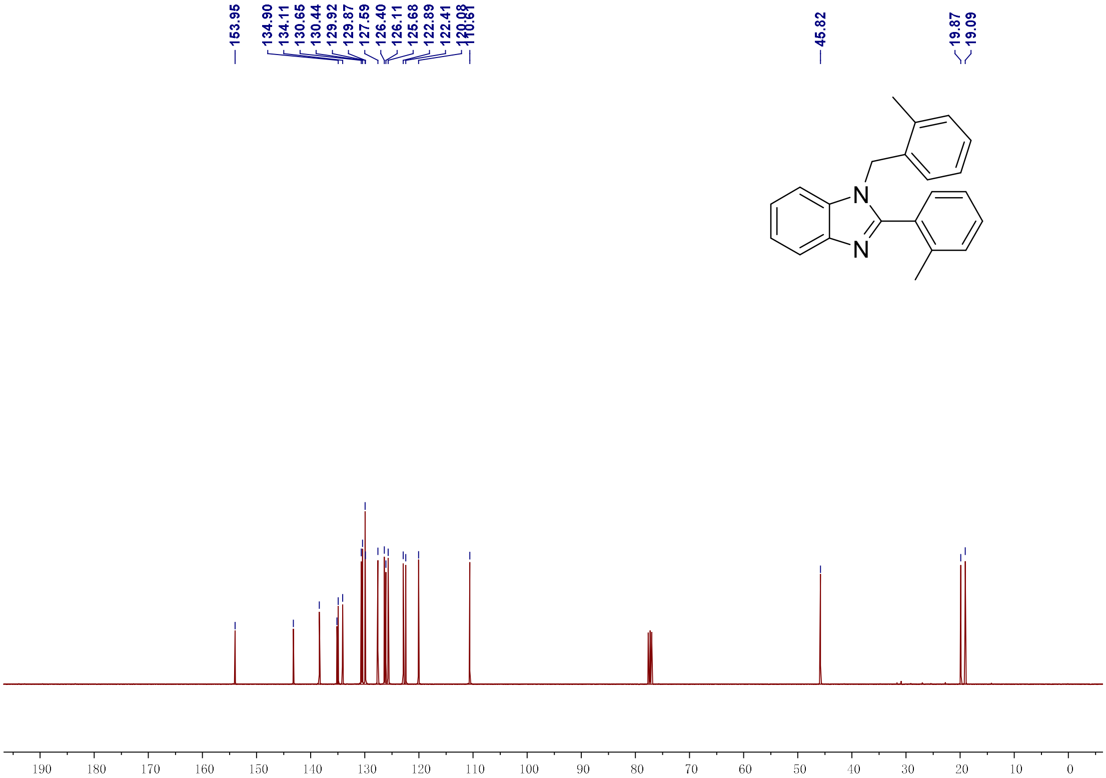
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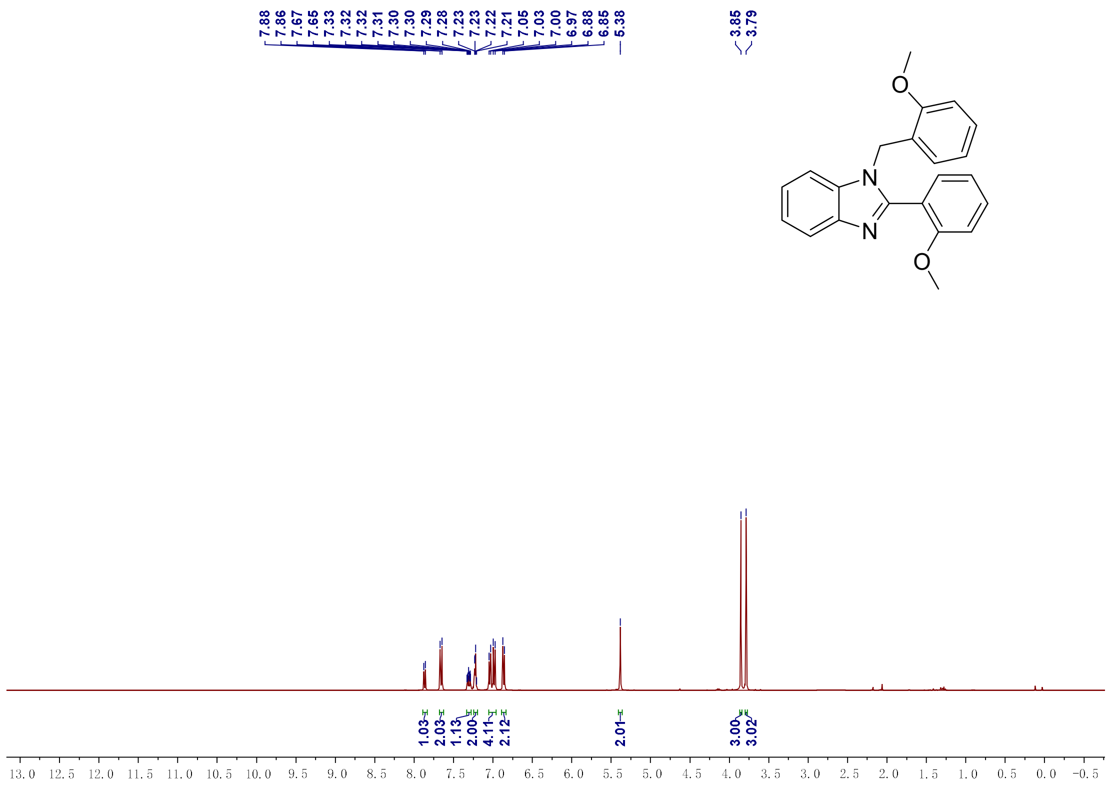

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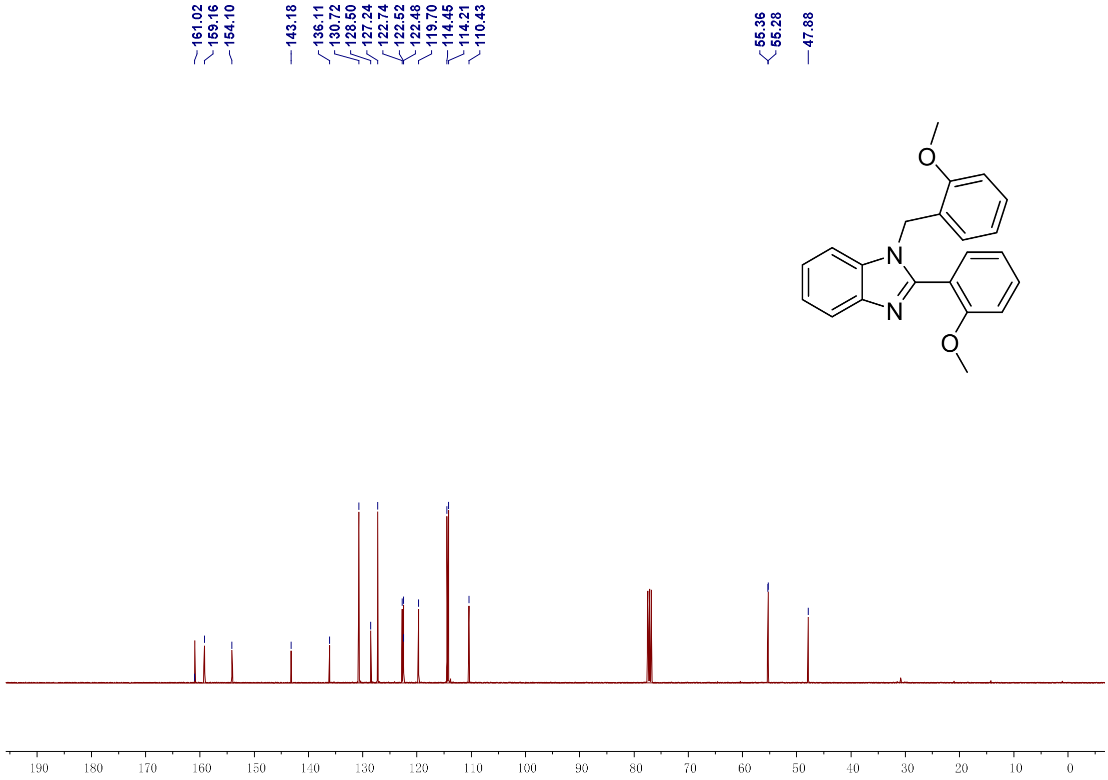

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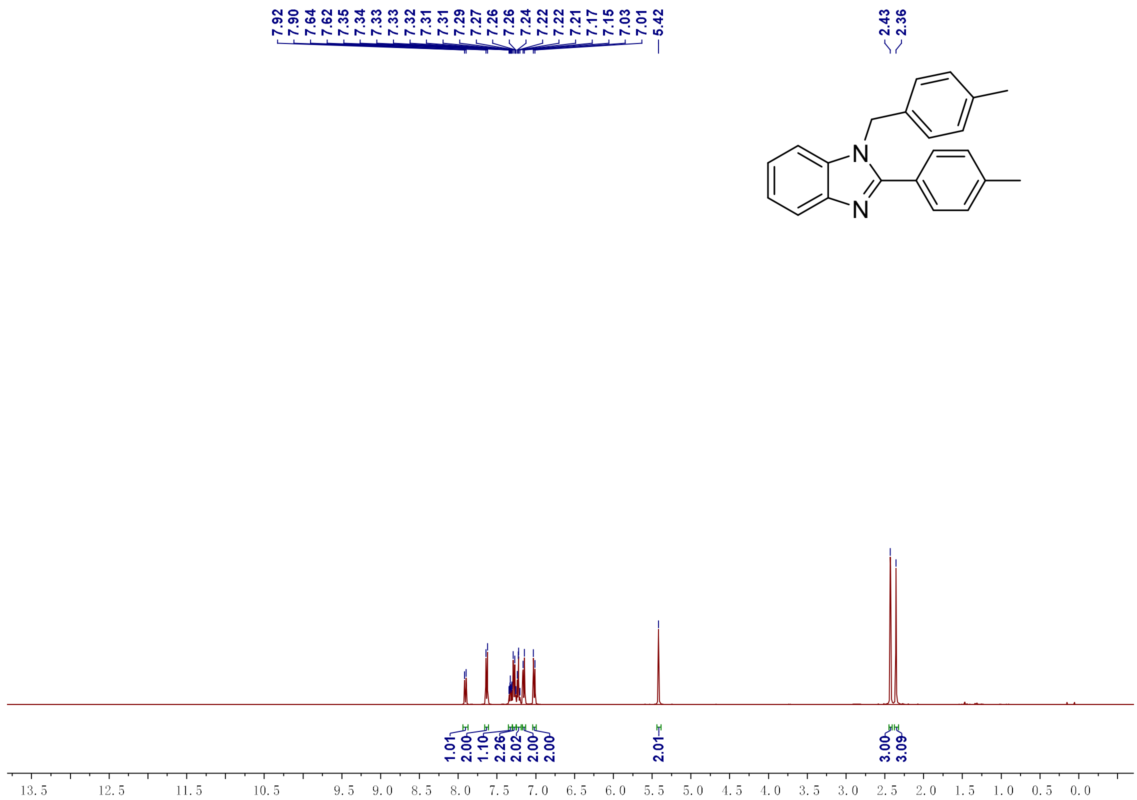
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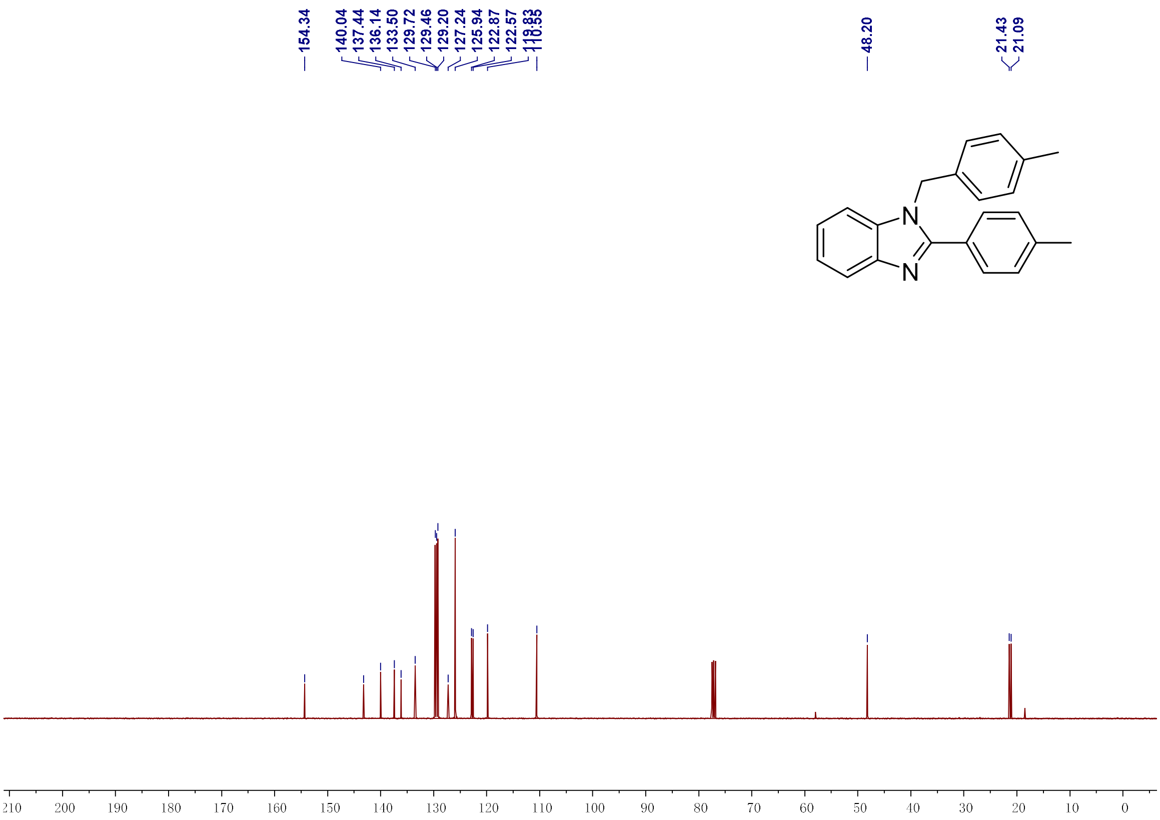
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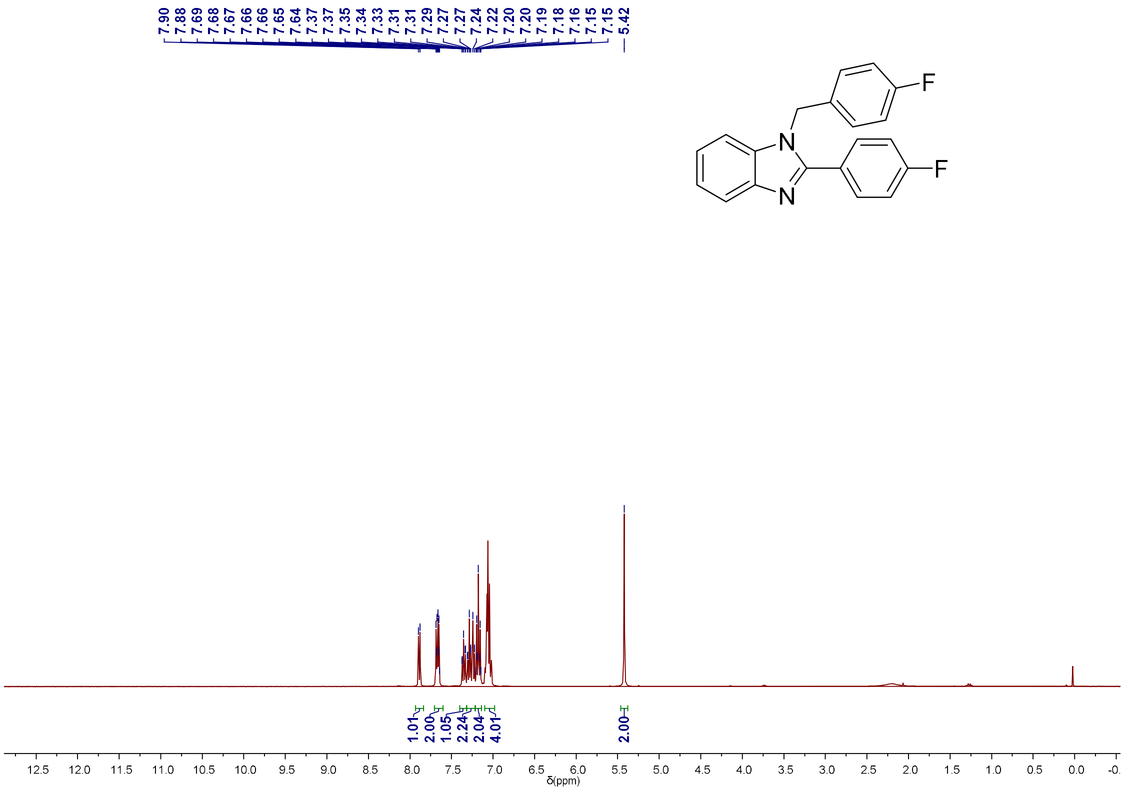
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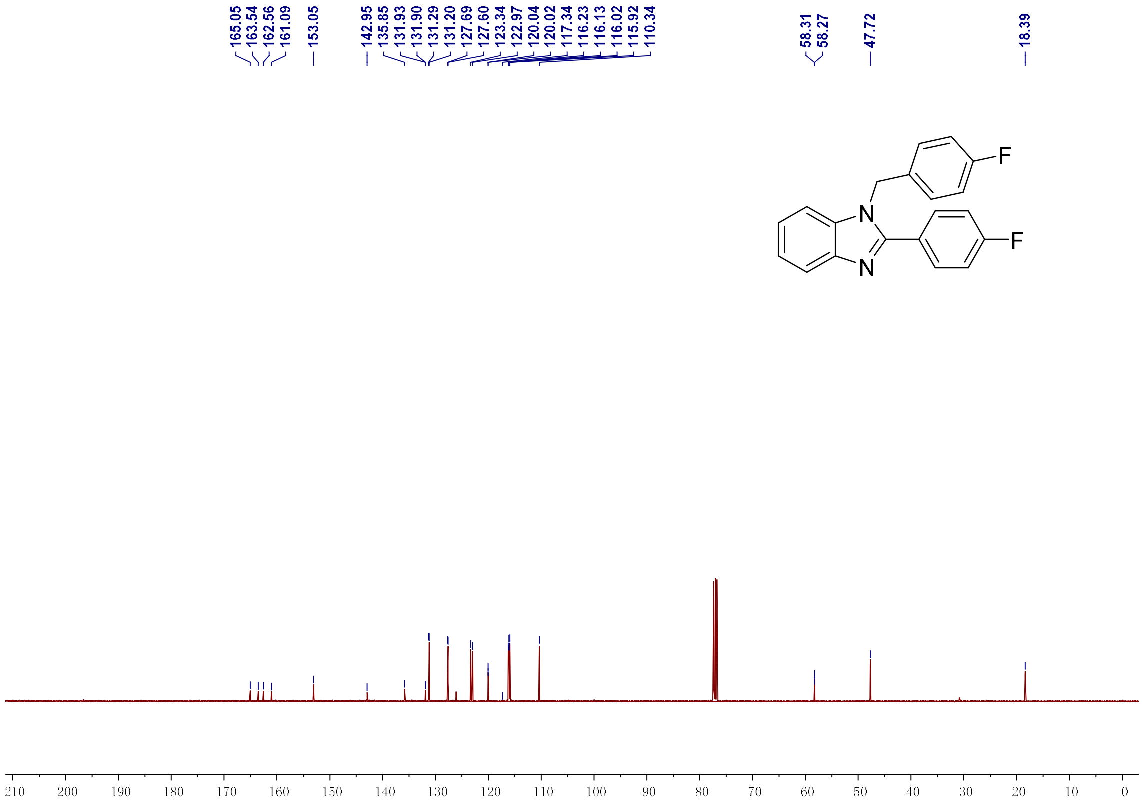
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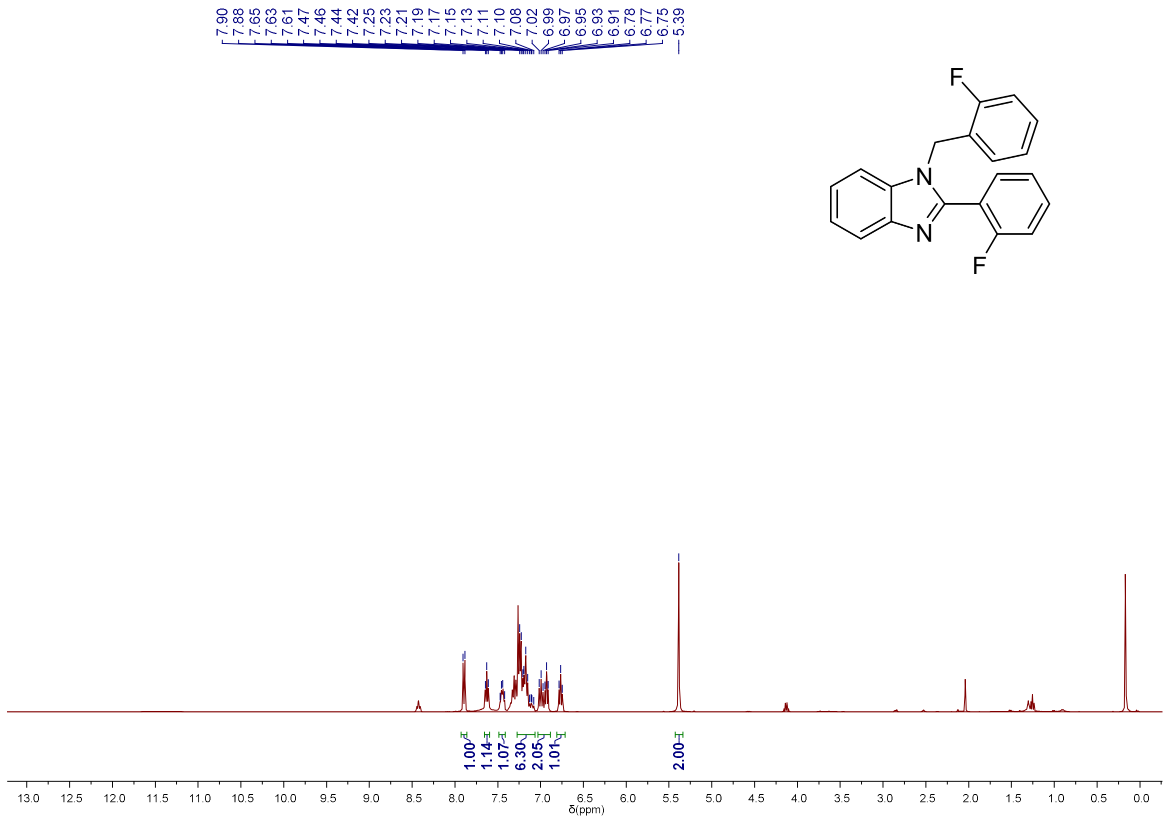
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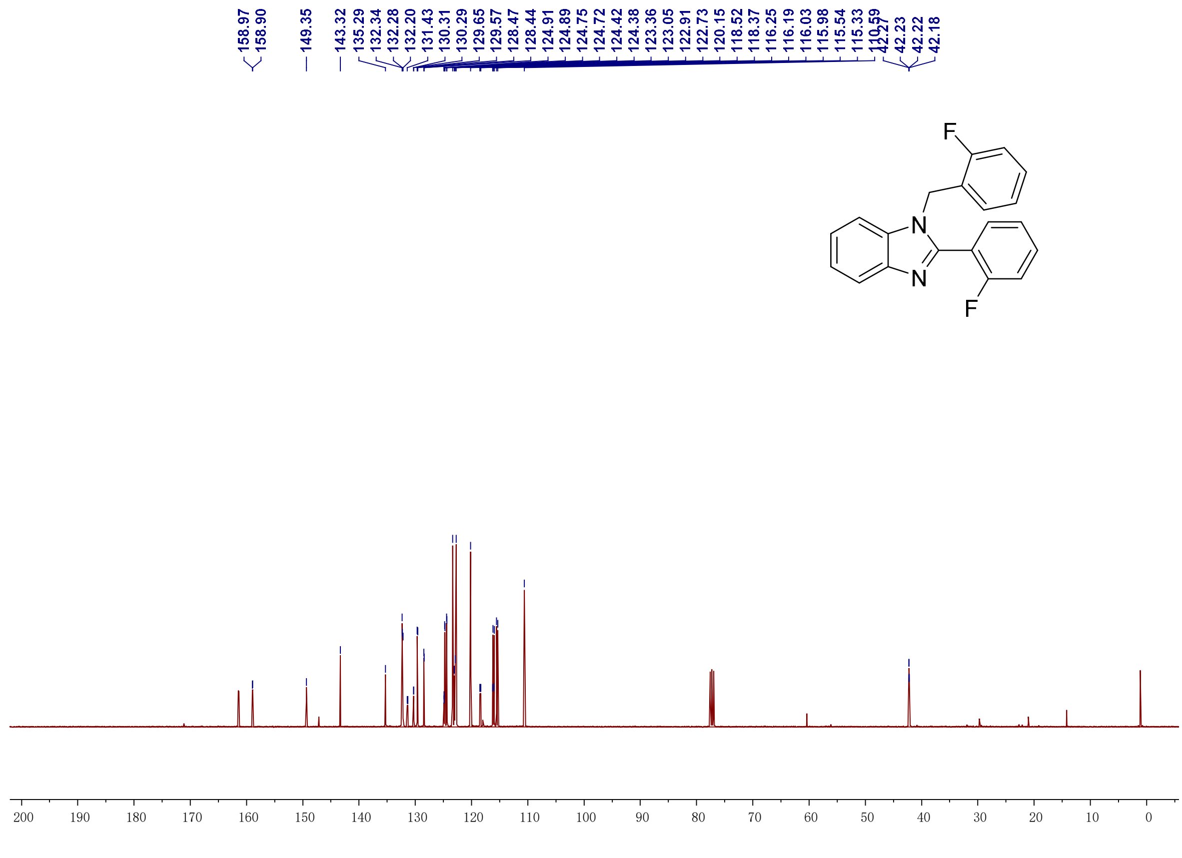
δ(ppm)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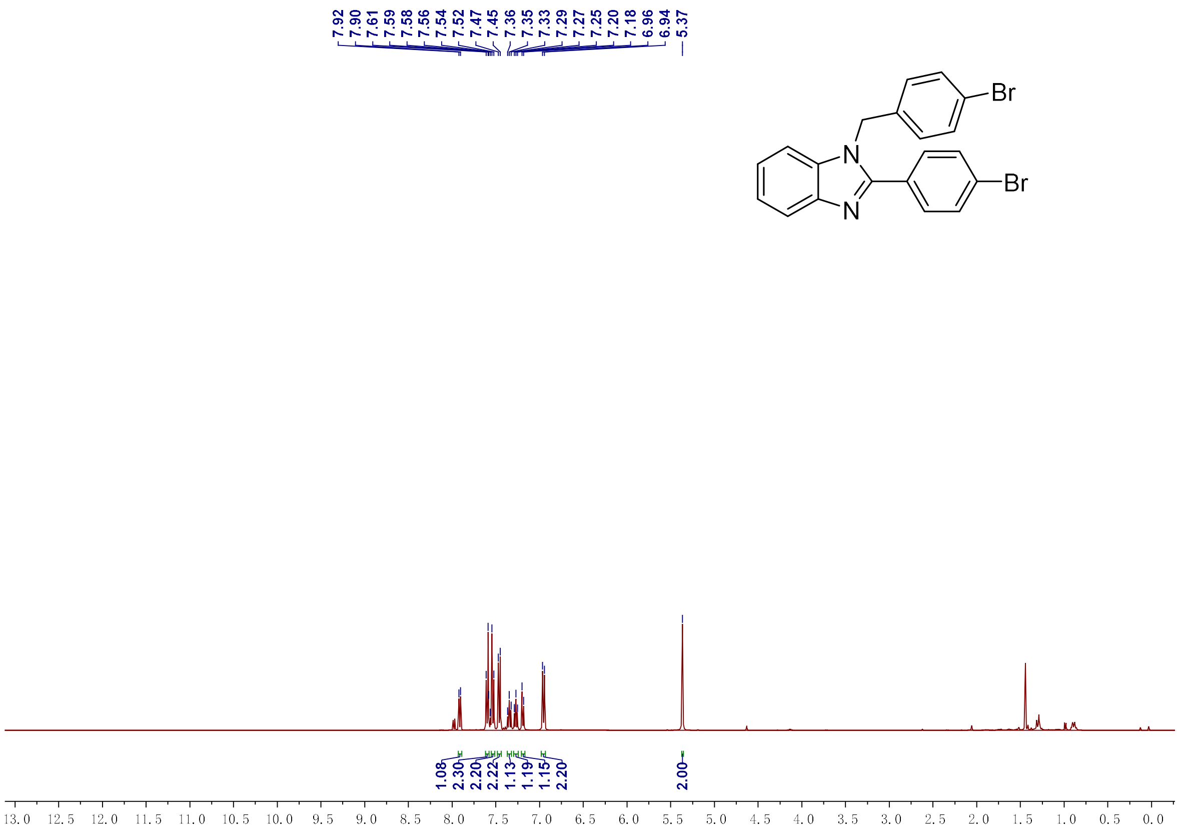
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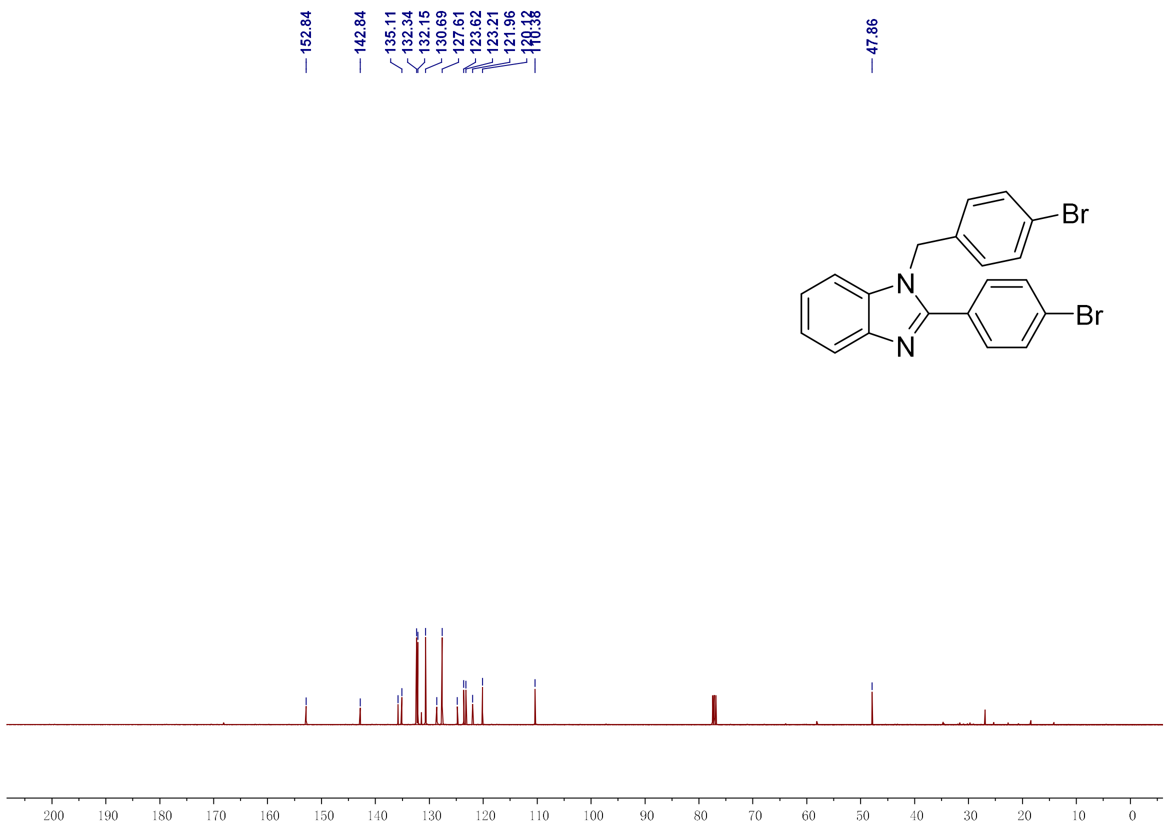
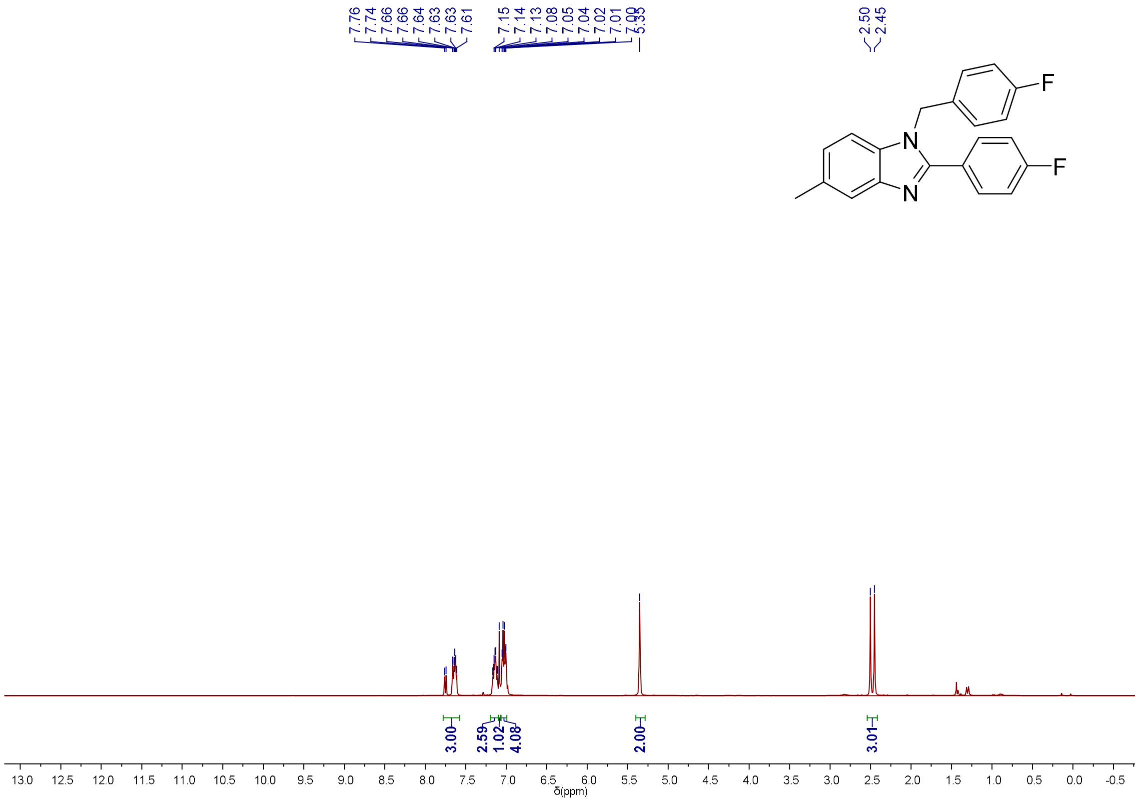
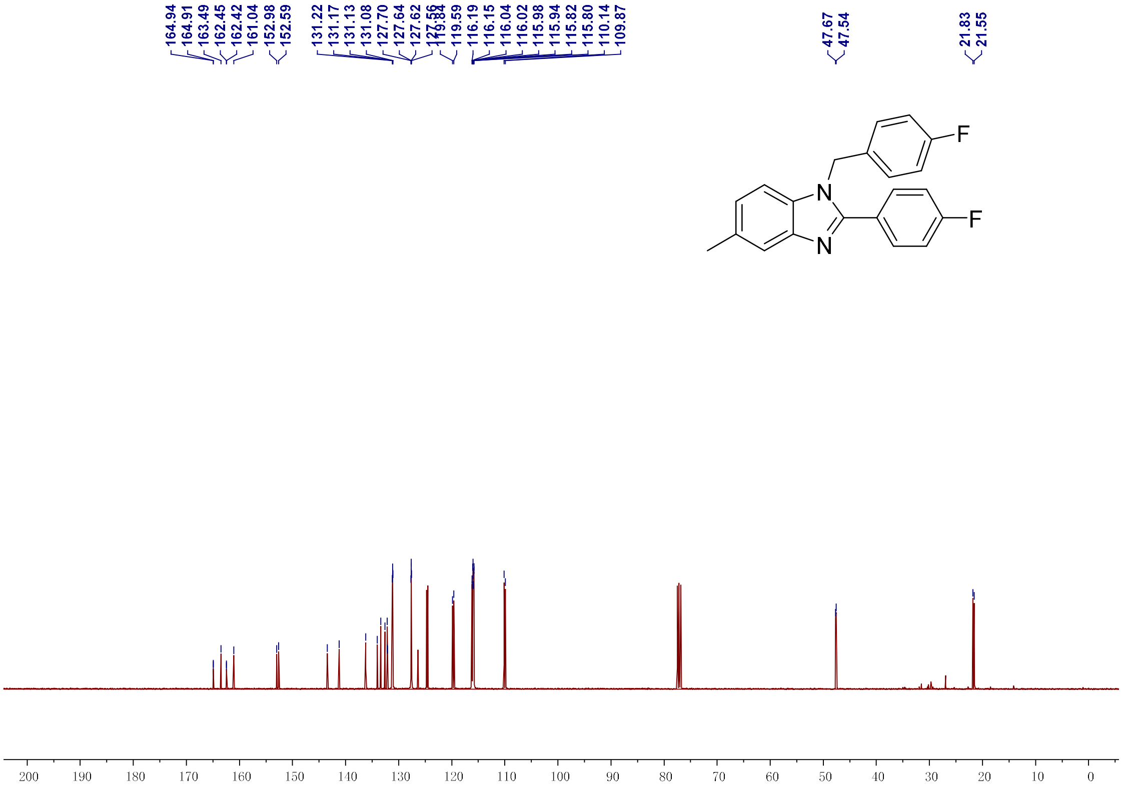
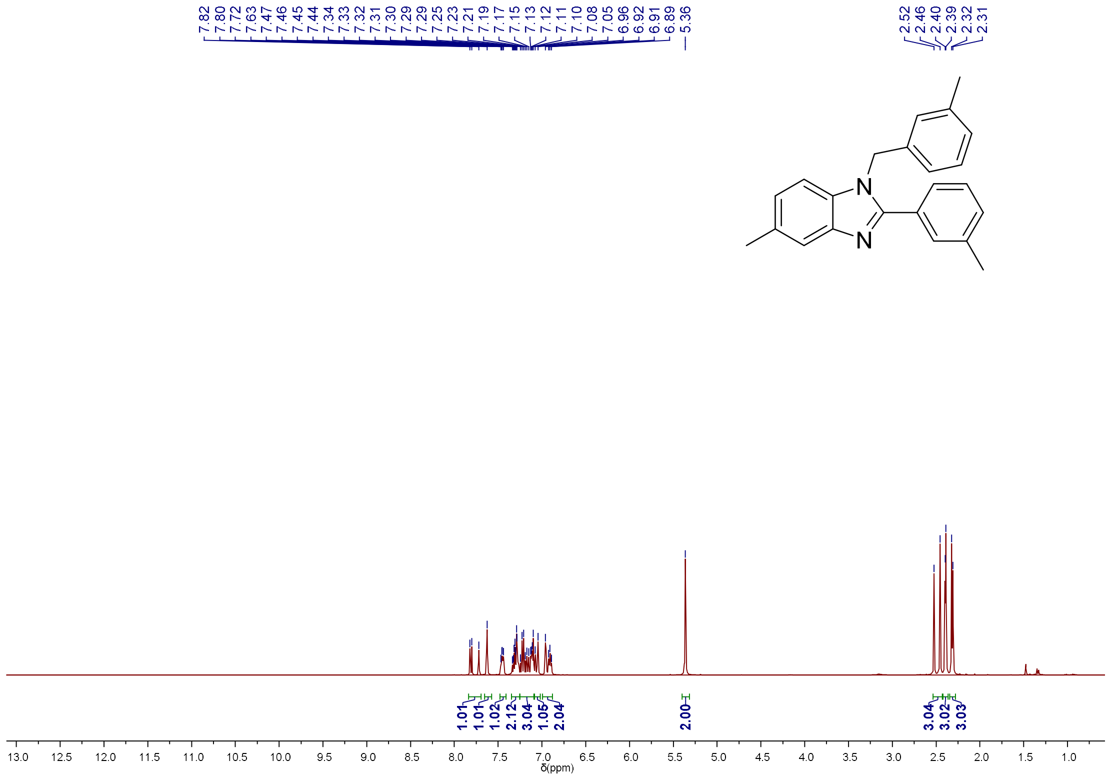
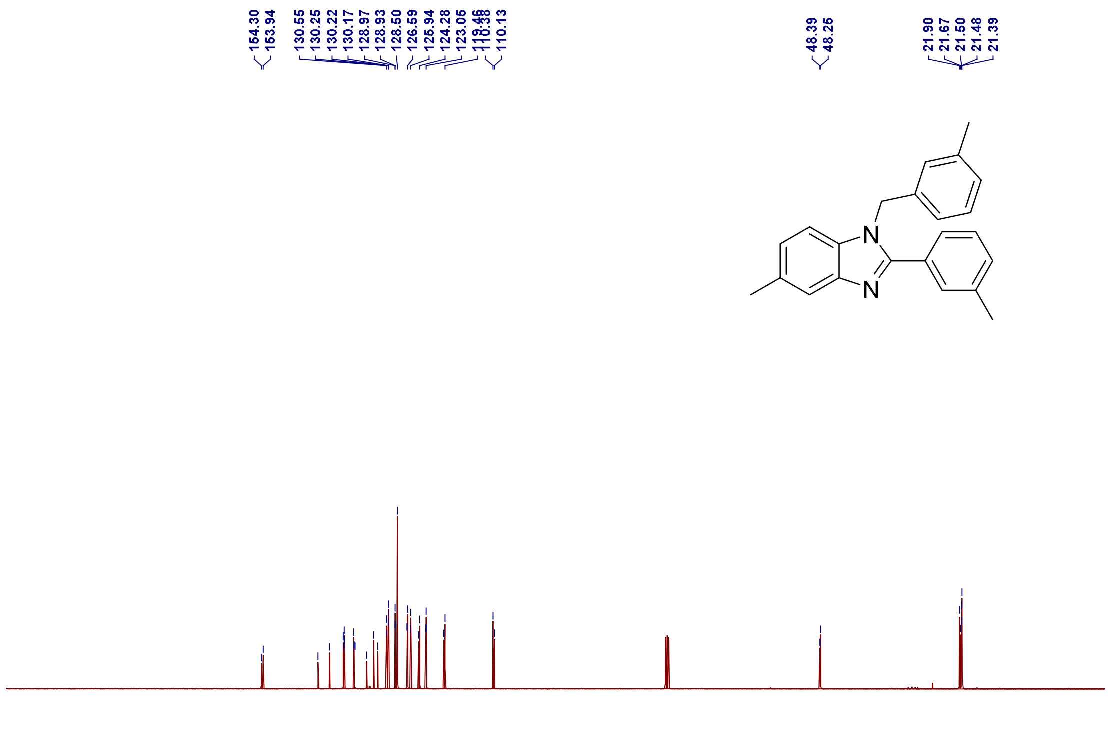
2.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


152.84
142.84
135.11
132.34
132.15
130.69
127.61
123.62
123.21
121.96
47.86
Br
N
N
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.76
7.74
7.66
7.66
7.64
7.63
7.63
7.61
7.15
7.14
7.13
7.08
7.05
7.04
7.02
7.01
2.50
2.45
N
N
F
F
3.00
2.59
1.02
4.08
2.00
3.01
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ(ppm)


164.94
164.91
163.49
162.45
162.42
161.04
152.98
152.59
131.22
131.17
131.13
131.08
127.70
127.64
127.62
119.59
116.19
116.15
116.04
116.02
115.98
115.94
115.82
115.80
110.14
109.87
47.67
47.54
21.83
21.55
N
N
F
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.82 7.80 7.72 7.63 7.47 7.46 7.45 7.44 7.34 7.33 7.32 7.31 7.30 7.29 7.29 7.25 7.23 7.21 7.19 7.17 7.15 7.13 7.12 7.11 7.10 7.08 7.05 6.96 6.92 6.91 6.89
5.36
2.52 2.46 2.40 2.39 2.32 2.31
N
N
1.01 1.01 1.02 2.12 3.04 1.05 2.04
2.00
3.04 3.02 3.03
δ(ppm)


154.30 153.94
130.55 130.25 130.22 130.17 128.97 128.93 128.50 126.59 125.94 124.28 123.05 110.13
48.39 48.25
21.90 21.67 21.50 21.48 21.39
N
N

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