Supplementary Information

Benzylic Aroylation of Toluenes with Unactivated Tertiary Benzamides Promoted by Directed *ortho*-Lithiation

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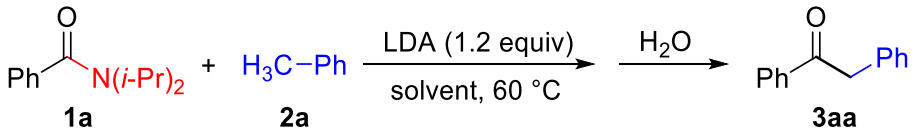
1. General Information

All manipulations of air- and moisture-sensitive compounds were performed under an argon or nitrogen atmosphere by use of standard Schlenk techniques or in a glovebox. Benzene, toluene, THF, Et_2O, dioxane and hexane, were dried by distillation over sodium/benzophenone. THF-d_8, benzene-d_6, $CDCl_3$ purchased from J&K were dried over CaH_2, degassed prior to use. Lithium diisopropylamide (LDA) was purchased from MERYER Co., Ltd. TLC were performed on silica gel Huanghai HSGF254 plates and visualized by quenching of UV fluorescence (λmax= 254 nm). Silica gel (200–300 mesh) was purchased from Qingdao Haiyang Chemical Co., Ltd. China. ^{1}H NMR, ^{13}C NMR were recorded on a Bruker AVANCE AV 400 (400 MHz and 101 MHz). Signal positions were recorded in ppm with the abbreviations s, d, t and m denoting singlet, doublet, triplet, and multiplet, respectively. All NMR chemical shifts are reported with the residual solvent resonance as internal standard (^{1}H NMR: $CDCl_3$ = δ 7.26 ppm; ^{13}C NMR: $CDCl_3$ = δ 77.16 ppm). Gas chromatography (GC) data were recorded on Shimadzu GC-2014 AOC-20i. High resolution mass spectra (HRMS) were recorded on an Agilent 6520 Q-TOF LC/MS with Electron Spray Ionization (ESI) resource and Agilent GCQTOF 7200 with EI scan.

2. Supplementary Condition Optimization

Table S1. Benzylic benzoylation of toluenes in different solvents[a]

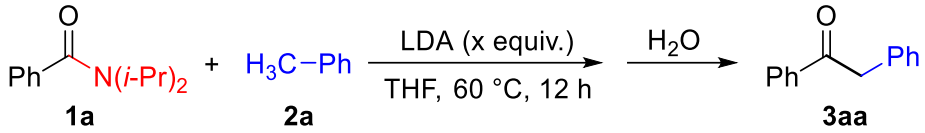


entry	solvent	time (h)	conv. (%)[b]	yield (%)[b]
1	Et_2O	24	76	23
2	*t*-BuOMe	24	91	29
3	Hexane	24	98	17
4	Benzene	24	88	36
5	THF	12	99	81
6	**THF**	**12**	**97**	**92 (91)[c]**

[a]Condition: tertiary bezamide **1a** (0.4 mmol), toluene **2a** (0.8 mmol), LDA (0.48 mmol), 60 °C. [b]GC yields with *n*-tridecane as an internal standard; isolated yield in parentheses. [c]3.0 equiv. of toluene.

The aroylation of toluene in Et_2O, *t*-BuOMe, hexane and benzene as solvent gave low yields (23%-36%), however, the amide **1a** was mostly consumed. THF was found to be the suitable solvent, giving 81% yield of aroylation product in shorter time (12 h). With 3.0 equiv. of toluene, the desired aroylation product was isolated in an even higher yield of 91%.

Table S2. Benzylic benzoylation of toluenes with different amount of LDA[a]

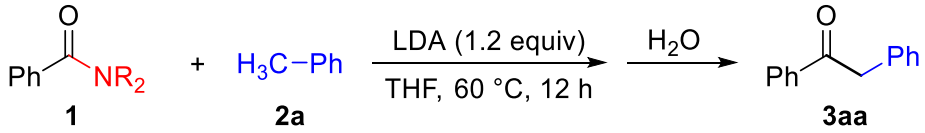


entry	LDA (equiv.)	conv. (%)[b]	yield (%)[b]
1	**1.2**	**97**	**92 (91)[c]**
2	1.0	86	79
3	0.8	72	67
4	0.6	55	53
5	0.4	34	34
6	0.2	17	17

[a]Condition: bezamide **1a** (0.4 mmol), toluene **2a** (0.8 mmol), 60 °C, 12 h. [b]GC yields with *n*-tridecane as an internal standard; isolated yield in parentheses. [c]3.0 equiv. of toluene.

The aroylation of toluene was carried with different equivalent of LDA, and the yields increased with the amount of LDA. The results in table S2 indicates that the aroylation of toluene is a stoichiometric transformation and 1.2 equiv. of LDA gives the best yield.

Table S3. Benzylic benzoylation of toluenes with different *N*-substituted benzamides[a]



entry	NR_2	yield **3aa** (%)[b]
1	NMe_2	12
2	NEt_2	26
3	$N(i\text{-}Pr)_2$	91
4	$N(Cy)_2$	94
5	NPh_2	<5[c]
6		22

[a]Conditions: **1** (0.6 mmol), **2a** (1.8 mmol), LDA (0.72 mmol), THF (1 mL), 60 ℃, 12 h. [b]Isolated yields. [c]Yield determined by ^{1}H NMR analysis using 2-methoxynaphthalene as an internal standard.

Various amides with different N-substituents were adopted to reaction with toluene and the *N*,*N*-diisopropyl benzamide gave much better efficiency than the N,N-dimethyl, N,N-diethyl and pyrrolidine analogs, suggesting that the steric hindrance could be crucial for the reaction.

3. Benzylic Benzoylation of Toluenes and Analysis Data

A typical procedure for the benzylic benzoylation of toluenes

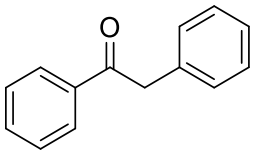
To a 25 mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added tertiary benzamide **1** (0.6 mmol), LDA (0.72 mmol), THF (1.0 mL) and toluene **2** (1.8 mmol). The tube was sealed, and stirred at 60 ℃ for 12 hours. The mixture was then cooled to room temperature, quenched by adding H_2O and diluted by ethyl acetate (EtOAc, 10 mL). The aqueous solution was extracted with EtOAc (10 mL × 3) and the combined organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration by rotary evaporation, the mixture was purified by silica gel column chromatography (PE/EtOAc = 40/1) to afford the desired product **3**.

Benzylic metalation of toluene

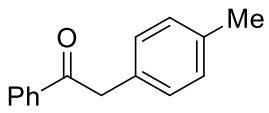
To a 25 mL Schlenk tube equipped with a Teflon septum and magnetic stir bar was charged with the mixture of *n*-BuLi (1.6 M in hexane, 1.33 mmol) and TMEDA (1.33 mmol) in hexane (1 mL). The mixture was stirred at room temperature for 5 minutes and then toluene (13.3 mmol, 10 equiv.) was added into this mixture. This mixture was stirred at room temperature for 1 hours, affording BnLi with approximate 90% purity [1]. This *in situ* formed BnLi was used directly for the direct benzylation reaction of unactivated tertiary benzamides.

Gram-scale benzylic benzoylation of toluene

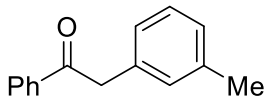
To a 25 mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added LDA (0.77 g, 7.2 mmol), tertiary benzamide **1a** (1.23 g, 6.0 mmol), THF (10 mL) and toluene **2a** (1.92 mL, 18.0 mmol). The tube was sealed and stirred at 60 ℃ for 12 hours. The mixture was then cooled to room temperature and quenched by adding H_2O and diluted by ethyl acetate (EtOAc, 50 mL). The aqueous solution was extracted with EtOAc (30 mL ×3) and the combined organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration by rotary evaporation, the mixture was purified by silica gel column chromatography (PE/EtOAc = 40/1) to afford the desired product **3aa** (1.04 g, 88% yield).



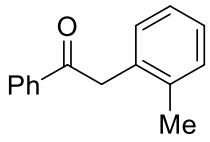
1,2-diphenylethan-1-one (3aa) [2]. White solid, 106.5 mg, 91% yield, m.p. 51-53 ℃ (Lit. 52.5-54.1 ℃ [3]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-7.95 (m, 2H), 7.61-7.52 (m, 1H), 7.51-7.41 (m, 2H), 7.39-7.29 (m, 1H), 7.29-7.21 (m, 3H), 4.29 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 136.7, 134.7, 133.3, 129.6, 128.81, 128.78, 128.7, 127.0, 45.6; IR (KBr, cm^{-1}) 3028, 2919, 2849, 1685, 1597, 1579, 1451, 1324, 1292, 1217, 1127, 727, 700, 686.



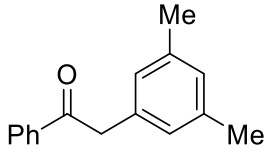
1-phenyl-2-(p-tolyl)ethan-1-one (3ab) [2]. White solid, 105.4 mg, 84% yield, m.p. 104-107 ℃ (Lit. 97.5-99 ℃ [4]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.61-7.52 (m, 1H), 7.51-7.41 (m, 2H), 7.22-7.11 (m, 4H), 4.26 (s, 2H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 136.7, 136.6, 133.2, 131.5, 129.5, 129.4, 128.7, 45.2, 21.2; IR (KBr, cm^{-1}) 2917, 2896, 1686, 1592, 1578, 1515, 1448, 1334, 1221, 1209, 1197, 995, 758, 692, 654.



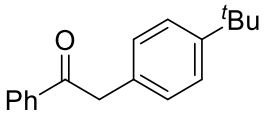
1-phenyl-2-(m-tolyl)ethan-1-one (3ac) [2]. Colorless oil, 102.0 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.50-7.41 (m, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.14-7.02 (m, 3H), 4.25 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 138.4, 136.7, 134.5, 133.3, 130.3, 128.8, 128.7, 127.8, 126.6, 45.6, 21.5; IR (liquid film, cm^{-1}) 3060, 3027, 2920, 1691, 1605, 1596, 1449, 1319, 1274, 1209, 1041, 775, 714, 692.



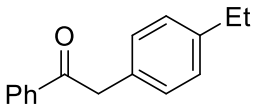
1-phenyl-2-(o-tolyl)ethan-1-one (3ad) [2, 5]. White solid, 100.3 mg, 81% yield, m.p. 66-69 ℃ (Lit. 66-69 ℃ [6]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.62-7.56 (m, 1H), 7.54-7.44 (m, 2H), 7.25-7.09 (m, 4H), 4.32 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 137.0, 133.6, 133.3, 130.5, 130.4, 128.8, 128.4, 127.3, 126.2, 43.6, 19.9; IR (KBr, cm^{-1}) 3067, 3026, 2927, 2899, 1685, 1593, 1579, 1447, 1338, 1213, 1185, 998, 753, 743, 689, 569.



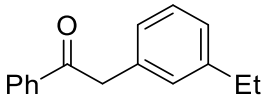
2-(3,5-dimethylphenyl)-1-phenylethan-1-one (3ae) [2]. Colorless oil, 112.9 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-7.99 (m, 2H), 7.60-7.52 (m, 1H), 7.50-7.43 (m, 2H), 6.90 (s, 3H), 4.22 (s, 2H), 2.30 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 138.3, 136.8, 134.5, 133.2, 128.8, 128.74, 128.72, 127.3, 45.5, 21.4; IR (liquid film, cm^{-1}) 3018, 2919, 1682, 1598, 1449, 1317, 1290, 1270, 1209, 754, 743, 691, 604, 572, 537.



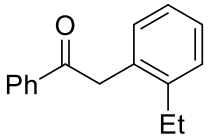
2-(4-(tert-butyl)phenyl)-1-phenylethan-1-one (3af) [2]. White solid, 114.3 mg, 76% yield, m.p. 42-44 ℃ (Lit. 42 ℃ [7]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-7.99 (m, 2H), 7.60-7.54 (m, 1H), 7.51-7.44 (m, 2H), 7.41-7.33 (m, 2H), 7.26-7.17 (m, 2H), 4.28 (s, 2H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 149.8, 136.8, 133.2, 131.5, 129.2, 128.8, 128.7, 125.7, 45.0, 34.5, 31.5; IR (KBr, cm^{-1}) 2962, 2905, 2868, 1690, 1598, 1515, 1449, 1412, 1318, 1270, 1221, 1201, 1109, 753, 712, 688, 550.



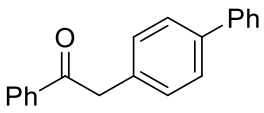
2-(4-ethylphenyl)-1-phenylethan-1-one (3ag). White solid, 103.5 mg, 78% yield, m.p. 83-85 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-8.00 (m, 2H), 7.60-7.53 (m, 1H), 7.50-7.43 (m, 2H), 7.25-7.14 (m, 4H), 4.28 (s, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 142.9, 136.7, 133.2, 131.7, 129.5, 128.7, 128.3, 45.2, 28.6, 15.6; IR (KBr, cm^{-1}) 2970, 2928, 2894, 1686, 1593, 1578, 1448, 1406, 1331, 1221, 1201, 994, 764, 693, 653, 570; HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{17}O$ $[M + H]^+$ 225.1274, found: 225.1277.



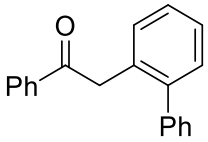
2-(3-ethylphenyl)-1-phenylethan-1-one (3ah). Colorless oil, 123.4 mg, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-7.95 (m, 2H), 7.58-7.50 (m, 1H), 7.49-7.39 (m, 2H), 7.27-7.21 (m, 1H), 7.16-7.04 (m, 3H), 4.25 (s, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 144.8, 136.8, 134.6, 133.2, 129.1, 128.7, 126.9, 126.6, 45.6, 28.9, 15.6; IR (liquid film, cm^{-1}) 2967, 2933, 1693, 1604, 1584, 1450, 1318, 1276, 1209, 755, 714, 692, 573; HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{16}NaO$ $[M + Na]^+$ 247.1093, found: 247.1098.



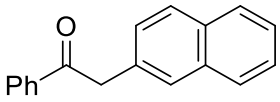
2-(2-ethylphenyl)-1-phenylethan-1-one (3ai) [8]. White solid, 88.4 mg, 66% yield, m.p. 36-38 ℃ (Lit. 35 ℃ [9]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-7.98 (m, 2H), 7.62-7.53 (m, 1H), 7.52-7.43 (m, 2H), 7.27-7.22 (m, 2H), 7.19-7.08 (m, 2H), 4.33 (s, 2H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 142.7, 137.0, 133.3, 132.8, 130.7, 128.8, 128.6, 128.5, 127.5, 126.1, 43.0, 26.1, 14.9; IR (KBr, cm^{-1}) 2969, 2931, 2903, 2874, 1685, 1591, 1577, 1447, 1333, 1206, 1186, 995, 761, 691, 662, 616, 597, 571, 558.



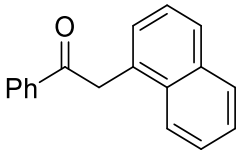
2-([1,1'-biphenyl]-4-yl)-1-phenylethan-1-one (3aj) [10]. White solid, 154.2 mg, 94% yield, m.p. 149-152 ℃ (Lit. 146-148 ℃ [11]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.67-7.53 (m, 5H), 7.53-7.40 (m, 4H), 7.40-7.28 (m, 3H), 4.35 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 140.9, 140.0, 136.7, 133.7, 133.4, 130.0, 128.9, 128.82, 128.76, 127.6, 127.4, 127.2, 45.2; IR (KBr, cm^{-1}) 3056, 3028, 2922, 1685, 1595, 1565, 1487, 1447, 1408, 1208, 1000, 991, 825, 750, 687, 658, 567.



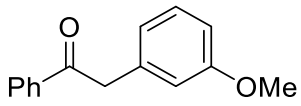
2-([1,1'-biphenyl]-2-yl)-1-phenylethan-1-one (3ak) [6]. Colorless oil, 136.2 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.56-7.51 (m, 1H), 7.48-7.23 (m, 11H), 4.28 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 142.5, 141.4, 136.7, 133.1, 132.5, 130.8, 130.3, 129.2, 128.6, 128.39, 128.36, 127.7, 127.3, 127.1, 43.4; IR (liquid film, cm^{-1}) 3059, 3024, 2907, 1683, 1597, 1580, 1480, 1448, 1332, 1215, 1010, 992, 776, 704, 691, 666, 552.



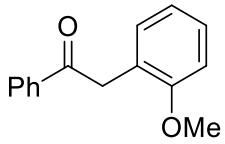
2-(naphthalen-2-yl)-1-phenylethan-1-one (3al) [12]. White solid, 126.8 mg, 87% yield, m.p. 119-121 ℃ (Lit. 122-124 ℃ [12]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.82-7.67 (m, 4H), 7.55-7.48 (m, 1H), 7.48-7.30 (m, 5H), 4.41 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 136.7, 133.7, 133.3, 132.5, 132.2, 128.8, 128.4, 128.2, 127.8, 127.74, 127.69, 126.2, 125.8, 45.8; IR (KBr, cm^{-1}) 2955, 2924, 2854, 1685, 1596, 1579, 1447, 1408, 1377, 1331, 1209, 1017, 802, 754, 741, 689, 665, 519.



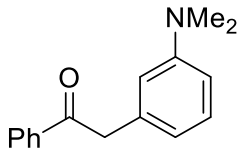
2-(naphthalen-1-yl)-1-phenylethan-1-one (3am) [2]. White solid, 113.4 mg, 76% yield, m.p. 100-103 ℃ (Lit. 102-103 ℃ [13]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.6 Hz, 2H), 7.96-7.86 (m, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.63-7.57 (m, 1H), 7.57-7.41 (m, 5H), 7.38 (d, *J* = 6.8 Hz, 1H), 4.75 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 136.8, 134.0, 133.4, 132.4, 131.5, 128.9, 128.8, 128.6, 128.1, 128.0, 126.4, 125.9, 125.6, 124.0, 43.2; IR (KBr, cm^{-1}) 3049, 2902, 1682, 1594, 1578, 1448, 1418, 1332, 1212, 1176, 1001, 982, 787, 769, 755, 687, 586, 569, 539.



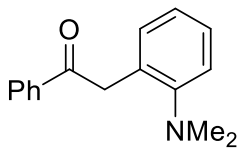
2-(3-methoxyphenyl)-1-phenylethan-1-one (3an) [14]. Colorless oil, 119.8 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-8.95 (m, 2H), 7.62-7.51 (m, 1H), 7.50-7.39 (m, 2H), 7.30-7.19 (m, 1H), 6.92-6.72 (m, 3H), 4.26 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 159.9, 136.7, 136.1, 133.3, 129.8, 128.8, 121.9, 115.2, 112.5, 55.3, 45.7; IR (liquid film, cm^{-1}) 3059, 2938, 2836, 1679, 1597, 1585, 1494, 1449, 1318, 1265, 1211, 1153, 1050, 1001, 755, 692, 607, 574.



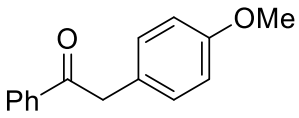
2-(2-methoxyphenyl)-1-phenylethan-1-one (3ao) [6]. White solid, 118.1 mg, 86% yield, m.p. 60-62 ℃ (Lit. 59-61 ℃ [6]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 6.8 Hz, 2H), 7.57-7.49 (m, 1H), 7.49-7.39 (m, 2H), 7.29-7.21 (m, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 6.96-6.90 (m, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 4.27 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 157.3, 137.1, 133.0, 131.1, 128.6, 128.54, 128.49, 123.9, 120.8, 110.7, 55.5, 40.1; IR (KBr, cm^{-1}) 2996, 2970, 2929, 2901, 2837, 1691, 1601, 1588, 1579, 1520, 1461, 1449, 1332, 1249, 1216, 1180, 1026, 990, 937, 761, 692, 573, 538.



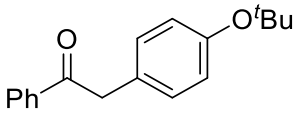
2-(3-(dimethylamino)phenyl)-1-phenylethan-1-one (3ap). White solid, 85.3 mg, 60% yield, m.p. 54-56 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.60-7.51 (m, 1H), 7.51-7.37 (m, 2H), 7.24-7.13 (m, 1H), 6.65-6.64 (m, 3H), 4.24 (s, 2H), 2.93 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 150.9, 136.8, 135.5, 133.1, 129.5, 128.8, 128.7, 117.8, 113.5, 111.3, 46.3, 40.7; IR (KBr, cm^{-1}) 2923, 2905, 2848, 2800, 1691, 1602, 1578, 1498, 1447, 1348, 1332, 1205, 1182, 999, 853, 768, 755, 688, 670, 571; HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{18}NO$ $[M + H]^+$ 240.1383, found: 240.1384.



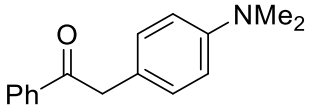
2-(2-(dimethylamino)phenyl)-1-phenylethan-1-one (3aq). Colorless oil, 117.4 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-7.88 (m, 2H) 7.51-7.42 (m, 1H), 7.42-7.32 (m, 2H), 7.26-7.18 (m, 2H), 7.15-7.08 (m, 1H), 7.08-6.97 (m, 1H), 4.30 (s, 2H), 2.54 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 152.3, 137.1, 132.6, 131.8, 130.7, 128.4, 128.3, 128.0, 124.1, 120.5, 44.6, 42.0; IR (liquid film, cm^{-1}) 3061, 2940, 2863, 2831, 2789, 1675, 1595, 1581, 1320, 1276, 1248, 1207, 1099, 1071, 945, 866, 768, 756, 716, 641, 560; HRMS (ESI): *m*/*z* calcd. for $C_{16}H_{18}NO$ $[M + H]^+$ 240.1383, found: 240.1385.



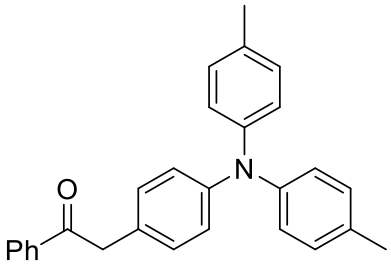
2-(4-methoxyphenyl)-1-phenylethan-1-one (**3ar**) [2]. White solid, 44.0 mg, 32% yield, m.p. 83-86 ℃ (Lit. 86.2-88 ℃ [15]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16-7.88 (m, 2H), 7.60-7.52 (m, 1H), 7.52-7.40 (m, 2H), 7.27-7.12 (m, 2H), 6.91-6.77 (m, 2H), 4.23 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 158.6, 136.7, 133.2, 130.6, 128.74, 128.71, 126.6, 114.3, 55.4, 44.7; IR (KBr, cm^{-1}) 2953, 2934, 1691, 1596, 1586, 1514, 1447, 1411, 1334, 1244, 1218, 1204, 1177, 1106, 997, 792, 756, 691, 655, 570, 541.



2-(4-(tert-butoxy)phenyl)-1-phenylethan-1-one (3as). White solid, 109.0 mg, 68% yield, m.p. 83-85 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-7.96 (m, 2H), 7.60-7.51 (m, 1H), 7.50-7.41 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 4.24 (s, 2H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 154.4, 136.8, 133.2, 130.0, 129.4, 128.8, 124.4, 78.5, 44.9, 29.0; IR (KBr, cm^{-1}) 3067, 2976, 2931, 2903, 1684, 1594, 1578, 1508, 1449, 1407, 1387, 1365, 1339, 1230, 1218, 1205, 1159, 1101, 994, 923, 897, 860, 796, 753, 690, 655, 583, 567; HRMS (EI): *m*/*z* calcd. for $C_{18}H_{20}O_2$ $[M]^+$ 268.1458, found: 268.1456.

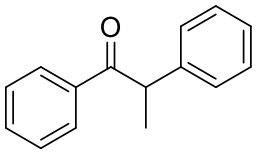


2-(4-(dimethylamino)phenyl)-1-phenylethan-1-one (3at) [15]. White solid, 16.1 mg, 14% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.56-7.51 (m, 1H), 7.47-7.41 (m, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8.0 Hz, 2H), 4.19 (s, 2H), 2.92 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 136.9, 133.1, 130.2, 128.8, 128.73, 128.69, 113.4, 44.8, 41.0; IR (KBr, cm^{-1}) 2920, 2892, 2850, 2802, 1687, 1615, 1595, 1523, 1447, 1339, 1229, 1204, 1180, 993, 946, 814, 787, 755, 690, 651.

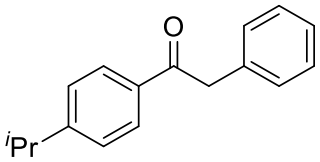


2-(4-(di-p-tolylamino)phenyl)-1-phenylethan-1-one (3au). Pale yellow oil, 185.0 mg, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.00 (m, 2H), 7.63-7.54 (m, 1H), 7.53-7.44 (m, 2H), 7.14-7.10 (m, 2H), 7.08-7.04 (m, 4H), 7.02-6.97 (m, 6H), 4.23 (s, 2H), 2.32 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0, 147.2, 145.5, 136.8, 133.2, 132.5, 130.2, 129.9, 128.8, 127.6, 124.6, 123.0, 44.8, 20.9; IR (KBr, cm^{-1}) 3057, 3027, 2920, 2861, 1899, 1679, 1606, 1581, 1507, 1448, 1320, 1275, 1220, 1203, 1180, 1109, 1018,

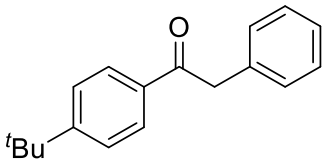
992, 910, 815, 753, 733, 719, 692, 629; HRMS (ESI): *m*/*z* calcd. for $C_{28}H_{26}NO$ $[M + H]^+$ 392.2009, found: 392.2011.



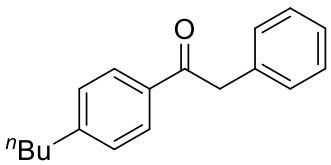
1,2-diphenylpropan-1-one (**3av**) [16]. Colorless oil, 23.7 mg, 19% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.50-7.45 (m, 1H), 7.42-7.35 (m, 2H), 7.33-7.27 (m, 4H), 7.23-7.18 (m, 1H), 4.69 (q, *J* = 6.8Hz, 2H), 1.54 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.5, 141.6, 136.6, 132.9, 129.1, 128.9, 128.6, 127.9, 127.0, 48.0, 19.6; IR (liquid film, cm^{-1}) 2966, 2933, 2875, 1679, 1595, 1578, 1490, 1453, 1446, 1280, 1233, 1209, 1007, 752, 734, 704, 696, 660, 566, 512.



1-(4-isopropylphenyl)-2-phenylethan-1-one (3ba) [17]. White solid, 108.9 mg, 82% yield, m.p. 39-40 ℃ (Lit. 36-38 ℃ [18]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.38-7.14 (m, 7H), 4.24 (s, 2H), 3.11-2.78 (m, 1H), 1.24 (d, *J* = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 154.8, 134.9, 134.6, 129.5, 129.0, 128.7, 126.9, 126.8, 45.5, 34.3, 23.7; IR (KBr, cm^{-1}) 2961, 2928, 2870, 1683, 1605, 1497, 1454, 1411, 1333, 1222, 1202, 1057, 994, 827, 757, 716, 697, 580, 560.

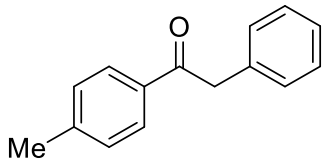


1-(4-(tert-butyl)phenyl)-2-phenylethan-1-one (3ca) [19]. White solid, 142.8 mg, 96% yield, m.p. 39-40 ℃ (Lit. 43-44 ℃ [20]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.36-7.20 (m, 5H), 4.26 (s, 2H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 157.0, 134.9, 134.2, 129.6, 128.79, 128.76, 127.0, 125.7, 45.6, 35.3, 31.2; IR (KBr, cm^{-1}) 2963, 2867, 1690, 1604, 1496, 1453, 1434, 1291, 1281, 1222, 1109, 991, 825, 815, 734, 708, 576, 550.

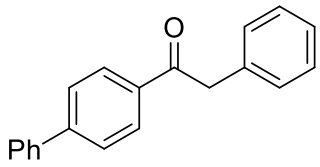


1-(4-butylphenyl)-2-phenylethan-1-one (3da). White solid, 72.7 mg, 47% yield, m.p. 56-59 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8 Hz, 2H), 7.35-7.29 (m, 2H), 7.29-7.19 (m, 5H), 4.25 (s, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.65-1.54 (m, 2H), 1.34 (qt, *J* = 14.4, 7.2 Hz, 2H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 149.0, 134.9, 134.4, 129.6, 128.9, 128.8, 128.7, 126.9, 45.5, 35.8, 33.3,

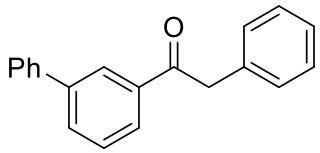
22.4, 14.0; IR (KBr, cm^{-1}) 2958, 1682, 1603, 1567, 1463, 1436, 1353, 1315, 1007, 993, 822, 783, 737, 727, 697, 638, 567; HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{20}NaO$ $[M + Na]^+$ 275.1406, found: 275.1410.



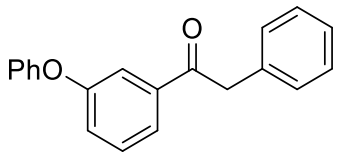
2-phenyl-1-(p-tolyl)ethan-1-one (3ea) [2]. White solid, 19.5 mg, 15% yield, m.p. 102-104 ℃ (Lit. 102-105 ℃ [21]); ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.38-7.31 (m, 2H), 7.31-7.23 (m, 5H), 4.28 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 144.1, 134.9, 134.3, 129.6, 129.5, 128.9, 128.8, 127.0, 45.6, 21.8; IR (KBr, cm^{-1}) 2905, 2854, 1682, 1606, 1497, 1406, 1335, 1223, 1199, 1173, 997, 815, 731, 696, 569.



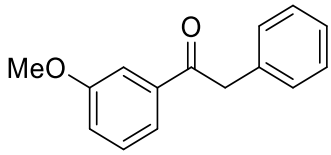
1-([1,1'-biphenyl]-4-yl)-2-phenylethan-1-one (3fa) [2]. White solid, 137.0 mg, 83% yield, m.p. 139-142 ℃ (Lit. 144-145 ℃ [22]); ^1H NMR (400 MHz, $CDCl_3$): δ 8.17-8.01 (m, 2H), 7.72-7.64 (m, 2H), 7.64-7.57 (m, 2H), 7.51-7.44 (m, 2H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.38-7.21 (m, 5H), 4.31 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 145.9, 139.9, 135.4, 134.7, 129.6, 129.3, 129.1, 128.8, 128.4, 127.38, 127.36, 127.0, 45.7; IR (KBr, cm^{-1}) 3036, 2926, 2682, 1601, 1498, 1452, 1398, 1334, 1201, 1075, 991, 830, 761, 752, 717, 686, 570.



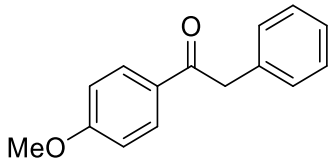
1-([1,1'-biphenyl]-3-yl)-2-phenylethan-1-one (3ga). White solid, 138.9 mg, 85% yield, m.p. 88-89 ℃; ^1H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.62-7.55 (m, 2H), 7.55-7.49 (m, 1H), 7.49-7.42 (m, 2H), 7.41-7.20 (m, 6H), 4.33 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 141.8, 140.2, 137.2, 134.6, 131.9, 129.6, 129.2, 129.0, 128.8, 127.9, 127.6, 127.4, 127.3 ,127.0, 45.8; IR (KBr, cm^{-1}) 3027, 2908, 1687, 1597, 1496, 1449, 1419, 1404, 1338, 1320, 1290, 1187, 1030, 997, 801, 754, 729, 694, 666, 569; HRMS (ESI): *m*/*z* calcd. for $C_{18}H_{17}O$ $[M + H]^+$ 273.1274, found: 273.1276.



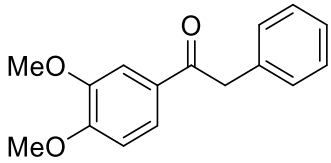
1-(3-phenoxyphenyl)-2-phenylethan-1-one (3ha). White solid, 140.8 mg, 80% yield, m.p. 66-69 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.66 (m, 1H), 7.59 (t, *J* = 2.0 Hz, 1H), 7.39-7.25 (m, 5H), 7.24-7.09 (m, 5H), 7.03-6.92 (m, 2H), 4.18 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 157.9, 156.5, 138.3, 134.4, 130.10, 130.06, 129.5, 128.8, 127.0, 124.0, 123.34, 123.33, 119.4, 118.3, 45.7; IR (KBr, cm^{-1}) 3060, 3034, 1690, 1579, 1493, 1480, 1434, 1322, 1244, 1218, 1147, 1074, 895, 812, 754, 731, 691, 661, 563; HRMS (ESI): *m*/*z* calcd. for $C_{20}H_{17}O_2$ $[M + H]^+$ 289.1223, found: 289.1228.



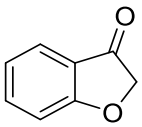
1-(3-methoxyphenyl)-2-phenylethan-1-one (3ia) [17]. Colorless oil, 121.4 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 2.4 Hz, 1H), 7.38-7.29 (m, 3H), 7.29-7.19 (m, 3H), 7.09 (dd, *J* = 8.0, 2.4, 1H), 4.26 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 159.9, 138.0, 134.7, 129.7, 129.5, 128.8, 127.0, 121.4, 119.8, 112.9, 55.5, 45.7; IR (liquid film, cm^{-1}) 3030, 2940, 2836, 1683, 1597, 1583, 1488, 1454, 1432, 1335, 1277, 1259, 1031, 787, 725, 698.



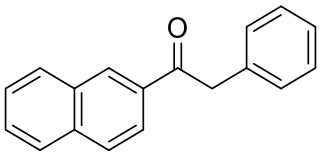
1-(4-methoxyphenyl)-2-phenylethan-1-one (3ja) [2]. White solid, 117.0 mg, 81% yield, m.p. 67-69 ℃ (Lit. 67-68.1 ℃ [15]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-7.96 (m, 2H), 7.39-7.21 (m, 5H), 6.99-6.90 (m, 2H), 4.25 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 163.6, 135.1, 131.0, 129.7, 129.5, 128.7, 126.9, 113.9, 55.6, 45.4; IR (KBr, cm^{-1}) 3033, 2904, 2837, 1679, 1601, 1576, 1506, 1452, 1411, 1335, 1264, 1172, 1111, 1030, 991, 831, 721, 697, 566.



1-(3,4-dimethoxyphenyl)-2-phenylethan-1-one (3ka) [23]. White solid, 121.9 mg, 80% yield, m.p. 87-89 ℃ (Lit. 86-87 ℃ [24]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 1H), 7.56 (s, 1H), 7.40-7.17 (m, 5H), 6.87 (d, *J* = 8.4 Hz, 1H), 4.24 (s, 2H), 3.93 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 153.4, 149.2, 135.2, 129.9, 129.4, 128.8, 126.9, 123.6, 110.8, 110.1, 56.2, 56.1, 45.3; IR (KBr, cm^{-1}) 2940, 2907, 1675, 1600, 1584, 1518, 1451, 1420, 1315, 1282, 1263, 1238, 1158, 1142, 1027, 864, 813, 722, 627, 547.

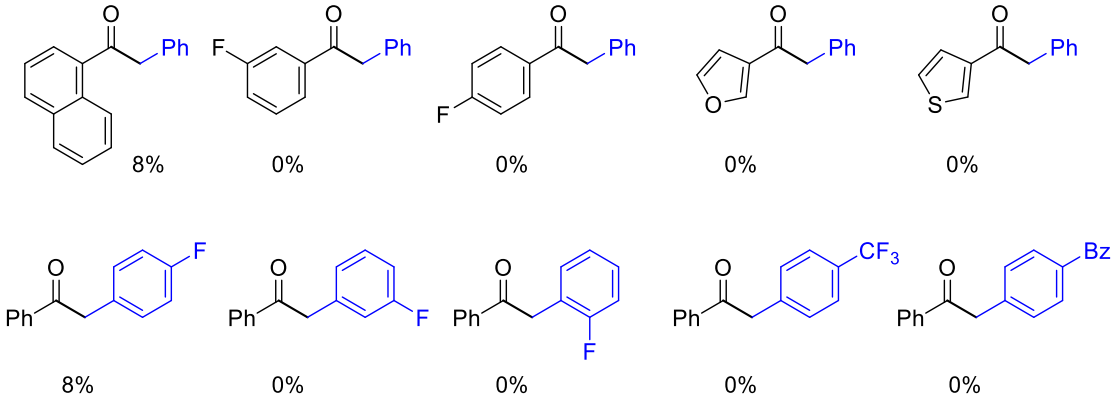


benzofuran-3(2H)-one (3l) [25]**.** Yellow solid, 35.8 mg, 45% yield, m.p. 101-103 ℃ (Lit. 100-102 ℃ [26]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.6 Hz, 1H), 7.64-7.57 (m, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.12-7.05 (m, 1H), 4.62 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 174.1, 138.0, 124.2, 122.1, 121.3, 113.8, 74.8.

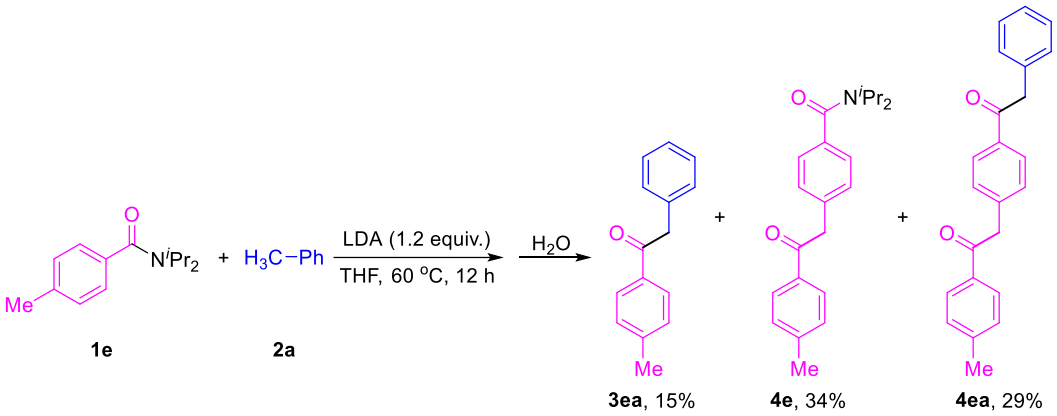


1-(naphthalen-2-yl)-2-phenylethan-1-one (3ma) [2]. White solid, 120.5 mg, 80% yield, m.p. 88-90 ℃ (Lit. 95-97 ℃ [27]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H), 8.06 (dd, *J* = 8.8, 4.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.91-7.83 (m, 2H), 7.63-7.52 (m, 2H), 7.40-7.29 (m, 4H), 7.28-7.23 (m, 1H), 4.41 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 135.7, 134.8, 134.1, 132.6, 130.5, 129.7, 129.6, 128.8, 128.7, 128.6, 127.9, 127.0, 126.9, 124.4, 45.7; IR (KBr, cm^{-1}) 3058, 3027, 2934, 1679, 1626, 1596, 1435, 1351, 1325, 1275, 1184, 1122, 994, 941, 825, 775, 741, 729, 697, 474.

Scheme S1. Additional products of benzylic benzoylation of toluenes



The reaction of toluene with 4-methyl benzamide 1e



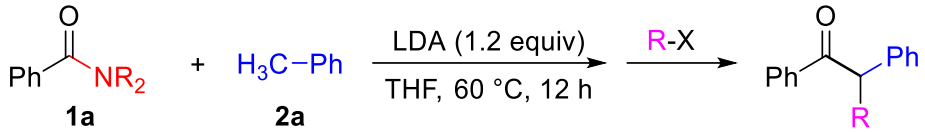
To a 25 mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added tertiary benzamide **1e** (135.0 mg, 0.62 mmol), LDA (77.2 mg, 0.72 mmol), THF (1.0 mL) and toluene **2a** (192 μL, 1.8 mmol). The tube was sealed and stirred at 60 ℃ for 12 hours. The mixture was then cooled to room temperature and quenched by adding H_2O and diluted by ethyl acetate (EtOAc, 10 mL). The aqueous solution was extracted with EtOAc (10 mL × 3) and the combined organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration by rotary evaporation, the mixture was purified by silica gel column chromatography (PE/EtOAc = 40/1 to 2/1) to afford **3ea** (19.5 mg, 0.092 mmol, 15% yield), **4e** (35.6 mg, 0.105 mmol, 34% yield) and **4ea** (29.7 mg, 0.090 mmol, 29% yield).

***N,N*-diisopropyl-4-(2-oxo-2-(p-tolyl)ethyl)benzamide (4e).** White solid, 35.6 mg, 34% yield, m.p. 121-123 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.36-7.22 (m, 6H), 4.27 (s, 2H), 4.02-3.34 (m, 2H), 2.42 (s, 3H), 1.58-1.07 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 171.0, 144.4, 137.5, 135.5, 134.1, 129.7, 129.5, 128.9, 126.2, 45.2, 29.8, 21.8, 20.9; IR (KBr, cm^{-1}) 3000, 2960, 2926, 2851, 1688, 1632, 1605, 1446, 1406, 1382, 1366, 1344, 1224, 1200, 1192, 1133, 1081, 1038, 1005, 814, 612, 568; HRMS (ESI): *m/z* calcd. for $C_{22}H_{28}NO_2$ $[M + H]^+$ 338.2115, found: 338.2118.

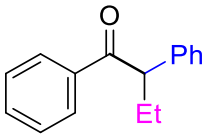
1-(4-(2-oxo-2-(p-tolyl)ethyl)phenyl)-2-phenylethan-1-one (4ea). White solid, 29.7 mg, 29% yield, m.p. 163-165 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.39-7.22 (m, 9H), 4.31 (s, 2H), 4.26 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 196.5, 144.5, 140.5, 135.4, 134.7, 134.0, 130.0, 129.6, 129.1, 128.8, 127.0, 45.6, 45.4, 21.8; IR (KBr, cm^{-1}) 3031, 2957, 2925, 2855, 1684, 1605, 1499, 1455, 1408, 1339, 1226, 1196, 1187, 1081, 1006, 993, 815, 769, 724, 697, 573; HRMS (ESI): *m/z* calcd. for $C_{23}H_{21}O_2$ $[M + H]^+$ 329.1536, found: 329.1540.

4. Control Experiments

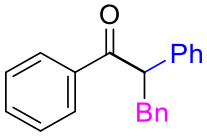
The reactions quenched with ethyl iodide and benzyl bromide



To a 25 mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added tertiary benzamide **1a** (122.0 mg, 0.59 mmol), LDA (77.1 mg, 0.72 mmol), THF (1.0 mL) and toluene **2a** (192 μL, 1.8 mmol). The tube was sealed and stirred at 60 ℃ for 12 h. After being cooled to room temperature, EtI (141.0 mg, 0.90 mmol) was added and then stirred under nitrogen for another 12 hours. Then the mixture was quenched by adding H_2O and diluted by ethyl acetate (EtOAc, 10 mL). The aqueous solution was extracted with EtOAc (10 mL × 3) and the combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After filtration and concentration by rotary evaporation, the mixture was purified by silica gel column chromatography (PE/EtOAc = 40/1) to afford the desired product **5aa**.

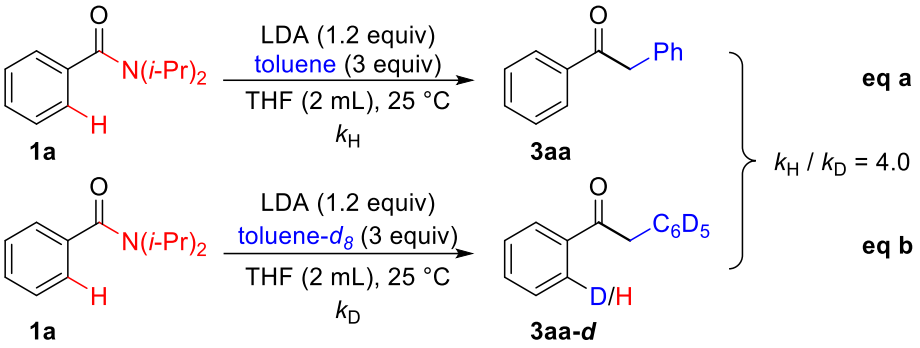


1,2-diphenylbutan-1-one (**5aa**) [28]. Colorless oil, 118.6 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.40-7.34 (m, 2H), 7.33-7.23 (m, 4H), 7.22-7.15 (m, 1H), 4.44 (dd, *J* = 7.6, 7.2 Hz, 1H), 2.27-2.13 (m, 1H), 1.93-1.79 (m, 1H), 0.90 (dd, *J* = 7.2, 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 139.7, 137.1, 132.9, 129.0, 128.8, 128.6, 128.4, 127.1, 55.6, 27.3, 12.4; IR (liquid film, cm^{-1}) 3081, 3057, 3025, 2966, 2933, 2875, 1679, 1595, 1578, 1490, 1464, 1446, 1357, 1280, 1233, 1209, 1178, 1070, 1027, 1007, 906, 828, 753, 739, 704, 696, 685, 660, 566.



1,2,3-triphenylpropan-1-one (**6aa**) [29]. The title compound was synthesis following the same procedure as **5aa** but quenching with BnBr (107 μL, 0.90 mmol). White solid, 150.3 mg, 88% yield, m.p. 116-118 ℃ (Lit. 122-124 ℃ [29]; 120-121 ℃[30]); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.35-7.28 (m, 2H), 7.28-6.96 (m, 10H), 4.81 (dd, *J* = 7.2, 7.2 Hz, 1H), 3.57 (dd, *J* = 13.6, 7.2 Hz, 1H), 3.07 (dd, *J* = 13.6, 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 139.9, 139.2, 136.8, 132.9, 129.2, 129.0, 128.8, 128.6, 128.4, 128.3, 127.2, 126.2, 56.0, 40.2; IR (KBr, cm^{-1}) 3083, 3059, 3027, 2920, 1676, 1596, 1580, 1495, 1454, 1448, 1363, 1341, 1245, 1213, 1175, 1073, 1053, 1029, 950, 757, 734, 696, 543.

5. Kinetic Isotope Effect Experiment



For **eq a**: To a 25 mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added LDA (77.1 mg, 0.72 mmol), tertiary benzamide **1a** (123.0 mg, 0.6 mmol), THF (2 mL), toluene (192 μL, 1.8 mmol) and *n*-tridecane (internal standard, 32.0 mg). The tube was sealed and stirred at 25 ℃. Samples were taken and analyzed by GC for every 10 minutes.

For **eq b**: To a 25 mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added LDA (77.1 mg, 0.72 mmol), tertiary benzamide **1a** (123.0 mg, 0.6 mmol), THF (2 mL), toluene-d_8 (192 μL, 1.8 mmol) and *n*-tridecane (internal standard, 31.0 mg). The tube was sealed and stirred at 25 ℃. Samples were taken and analyzed by GC for every 30 minutes.

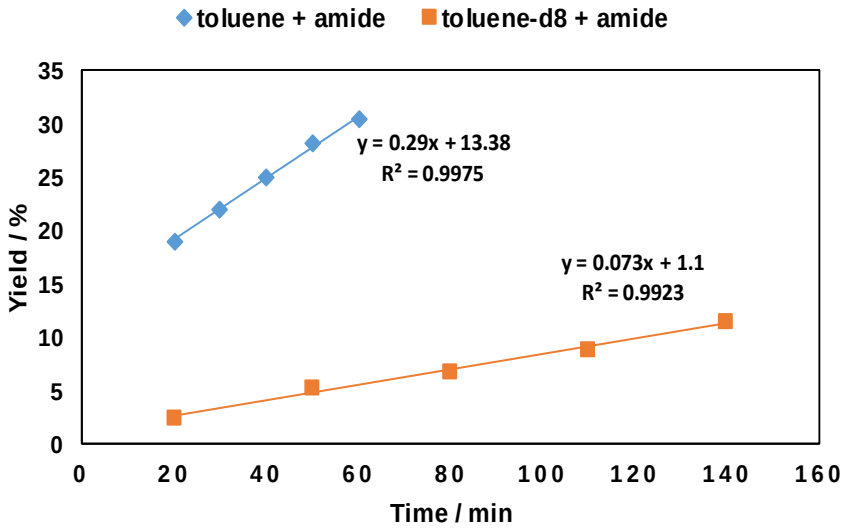
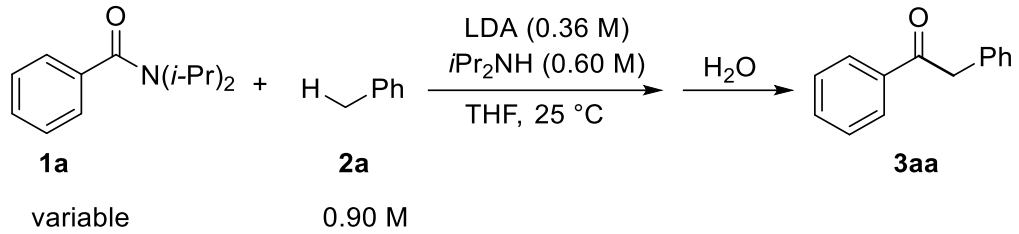


Figure S1 Initial Reaction Rates of Benzylic Benzoylation of Toluene and Toluene-d_8

6. Kinetic Experiments

6.1 Kinetic studies: variable benzamide **1a** (from 0.1198 M to 0.4213 M).



Reaction condition: tolouene [**2a**] = 0.90 M, [LDA] = 0.36 M, [iPr$_2$NH] = 0.60 M, 25 ℃.

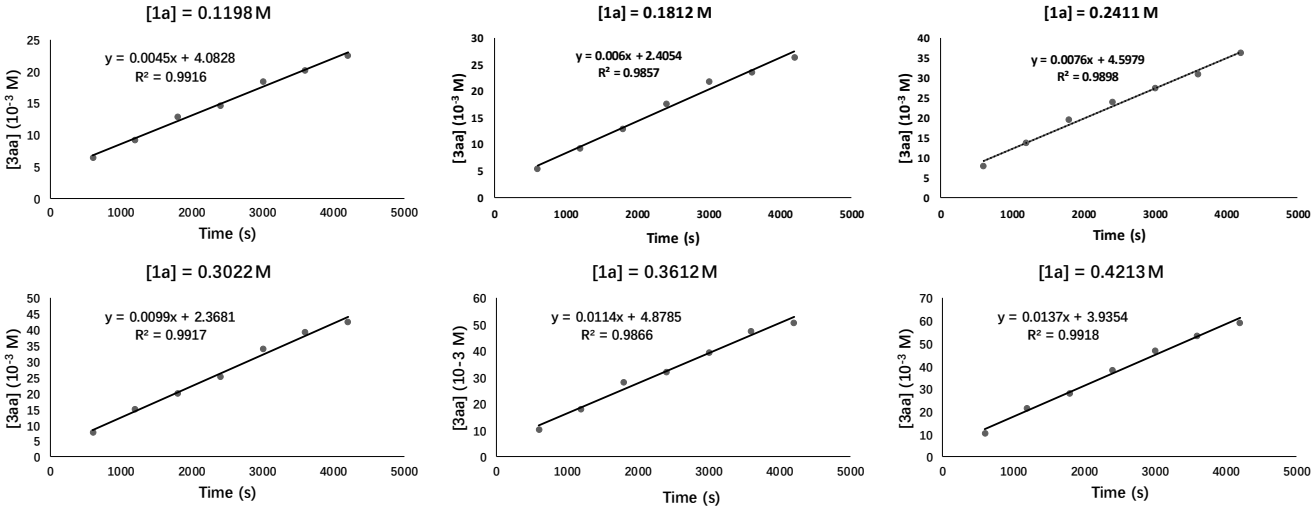


Figure S2 Initial Reaction Rates with Various Concentrations of Benzamide **1a**

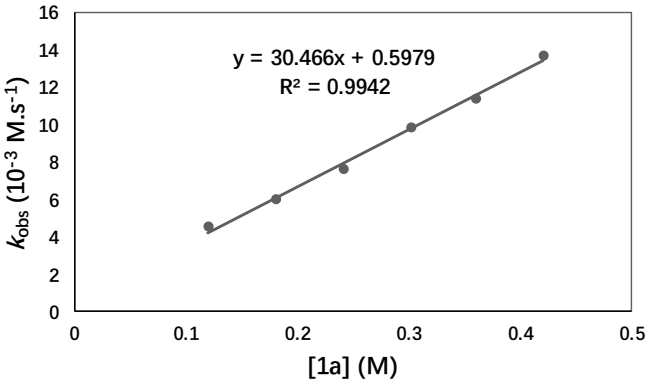
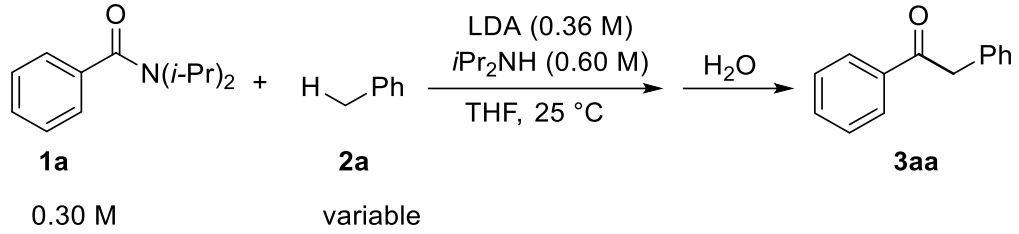


Figure S3 Effect of Benzamide **1a** Concentration on the Initial Rate

6.2 Kinetic studies: variable toluene **2a** (from 0.1786 M to 0.3008 M).



Reaction condition: benzamide [**1a**] = 0.30 M, [LDA] = 0.36 M, [iPr$_2$NH] = 0.60 M, 25 ℃.

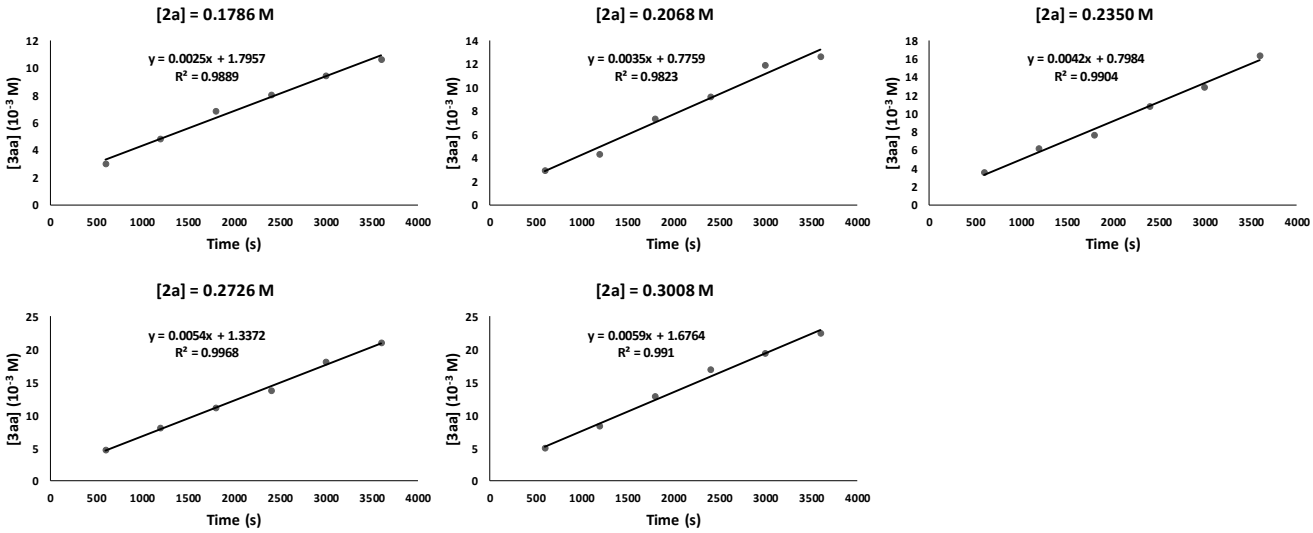


Figure S4 Initial Reaction Rates with Various Concentrations of Toluene **2a**

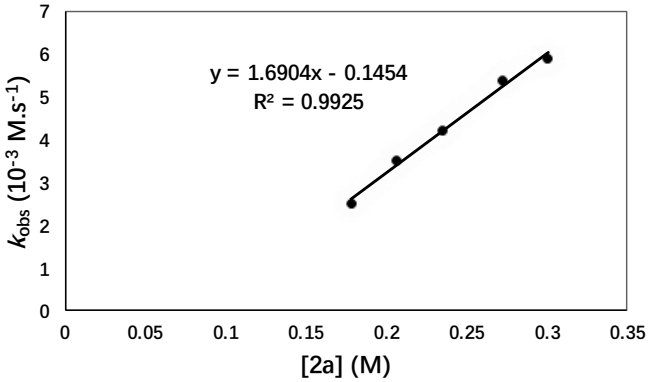
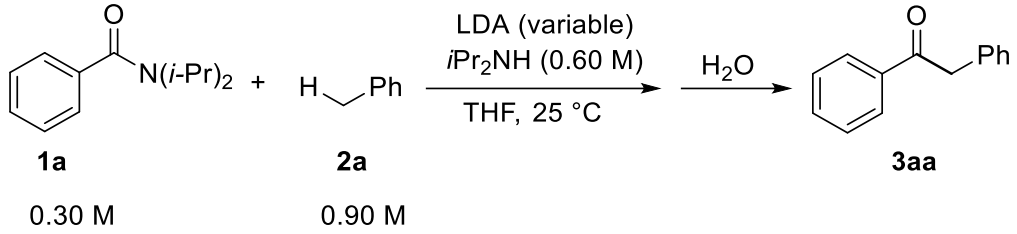


Figure S5 Effect of Toluene **2a** Concentration on the Initial Rate

6.3 Kinetic studies: variable LDA (from 0.1209 M to 0.3622 M).



Reaction condition: benzamide [**1a**] = 0.30 M, toluene [**2a**] = 0.90 M, [*i*Pr$_2$NH] = 0.60 M, 25 ℃.

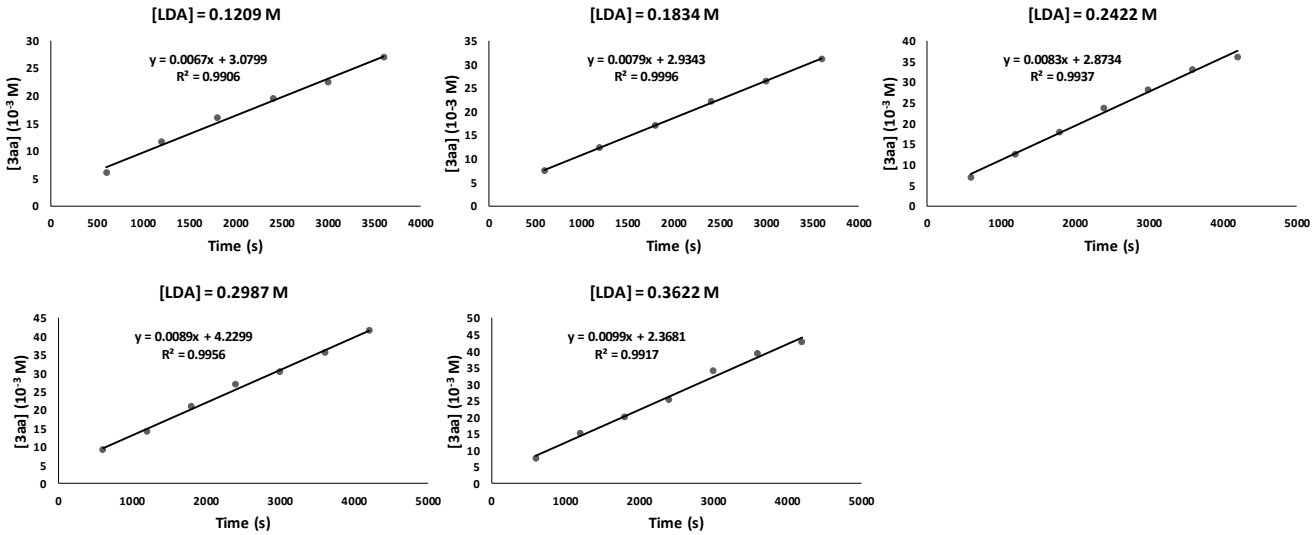


Figure S6 Initial Reaction Rates with Various Concentrations of LDA

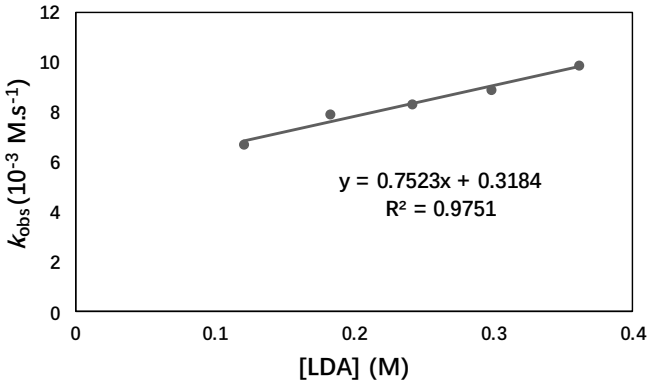
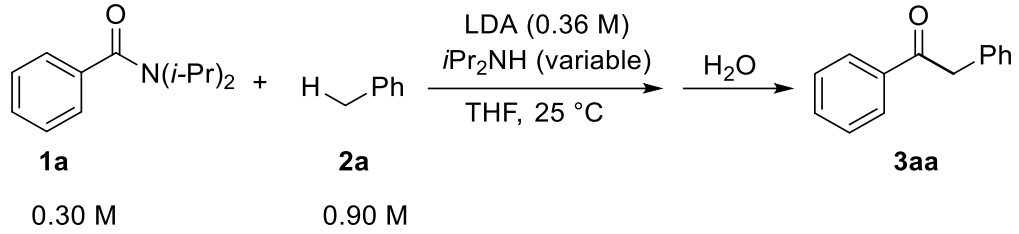


Figure S7 Effect of LDA Concentration on the Initial Rate

6.4 Kinetic studies: variable *i*Pr$_2$NH (from 0.1498 M to 0.7492 M).



Reaction condition: benzamide [**1a**] = 0.30 M, toluene [**2a**] = 0.90 M, [LDA] = 0.36 M, 25 ℃.

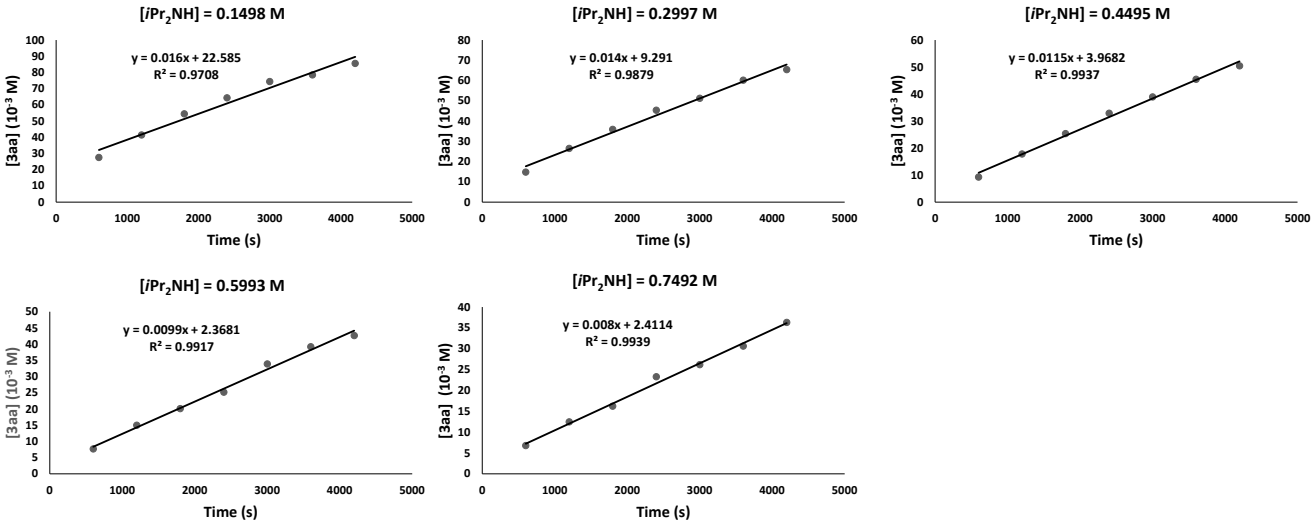


Figure S8 Initial Reaction Rates with Various Concentrations of *i*Pr$_2$NH

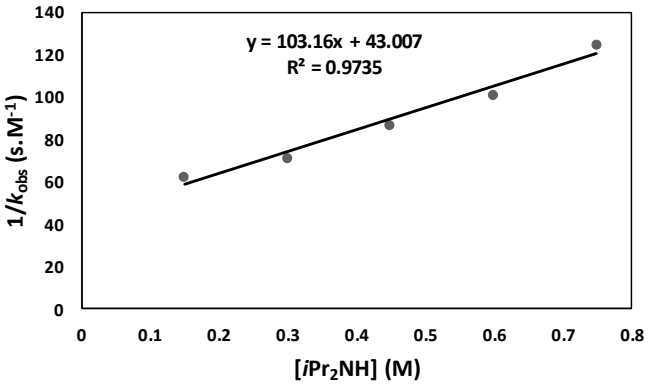
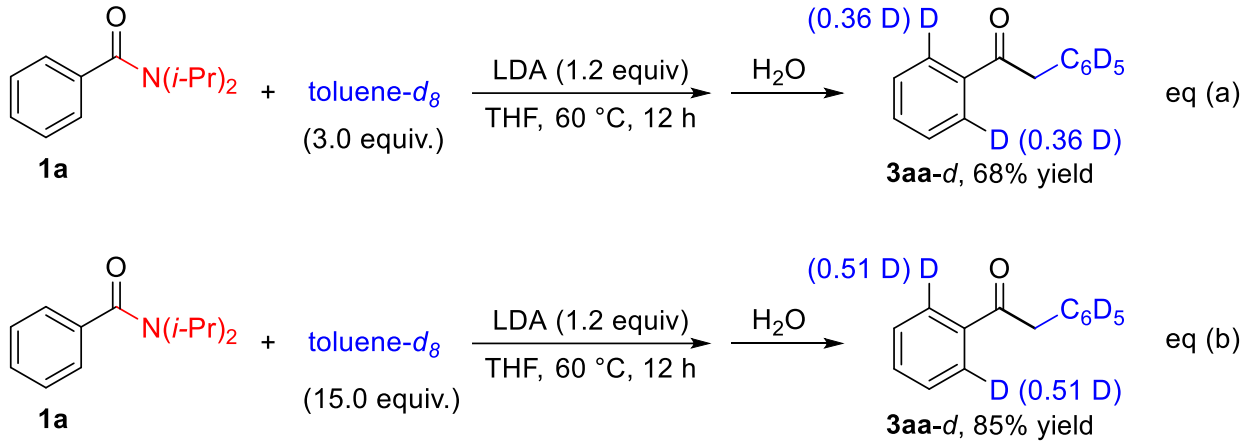


Figure S9 Effect of *i*Pr$_2$NH Concentration on the Initial Rate

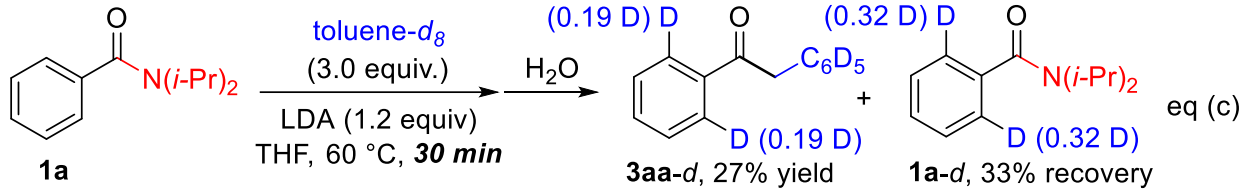
The above kinetic analyses suggest that this benzylic benzoylation reaction of toluene with benzamide promoted by LDA is first order in benzamide, first order in LDA, first order in toluene and minus one order in HDA.

$$k_{obs} = k[1a]^1[LDA]^1[Toluene]^1[HDA]^{-1}$$

7. Deuterium Labeling Studies

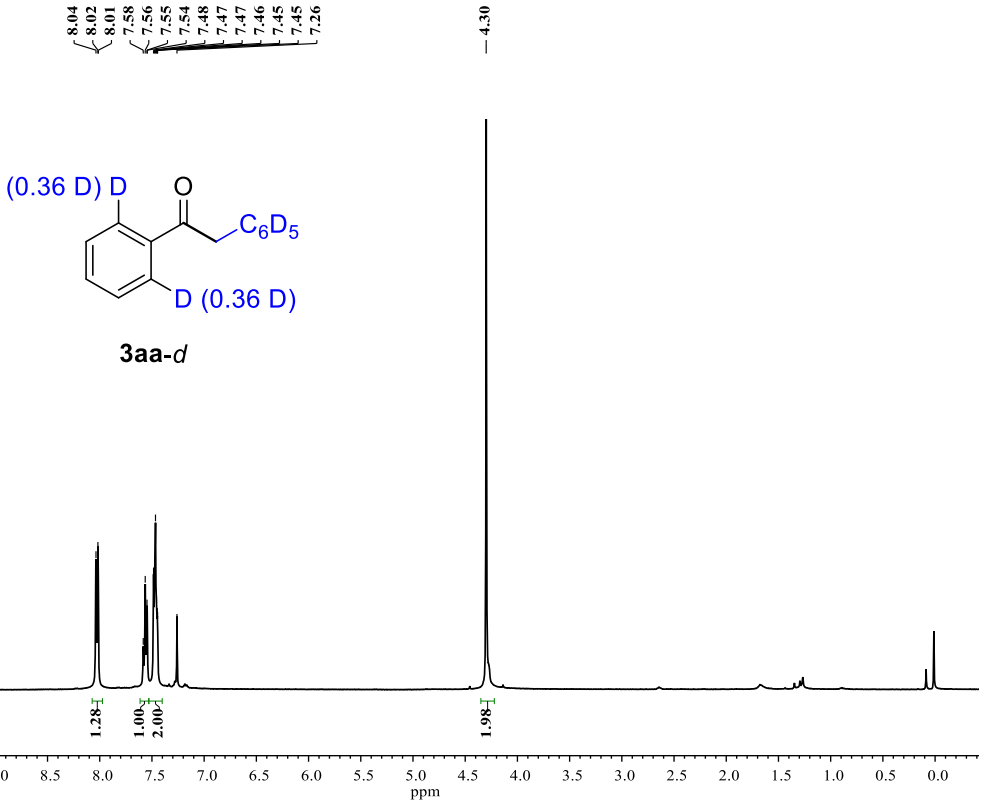


To a 25 mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added LDA (77.1 mg, 0.72 mmol), tertiary benzamide **1a** (123.2 mg, 0.60 mmol), THF (1.0 mL) and toluene-d_8. The tube was sealed and stirred at 60 ℃ for 12 hours. The mixture was then cooled to room temperature, quenched by adding H_2O and diluted by EtOAc (ethyl acetate, 10 mL). The aqueous solution was extracted with EtOAc (10 mL × 3) and the combined organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration by rotary evaporation, the mixture was purified by silica gel column chromatography (PE/EtOAc = 40/1) to afford the desired product **3aa**-*d*. The deuterium incorporation on the *orhto*-position of benzoyl group of **3aa**-*d* was detected by ^{1}H NMR.



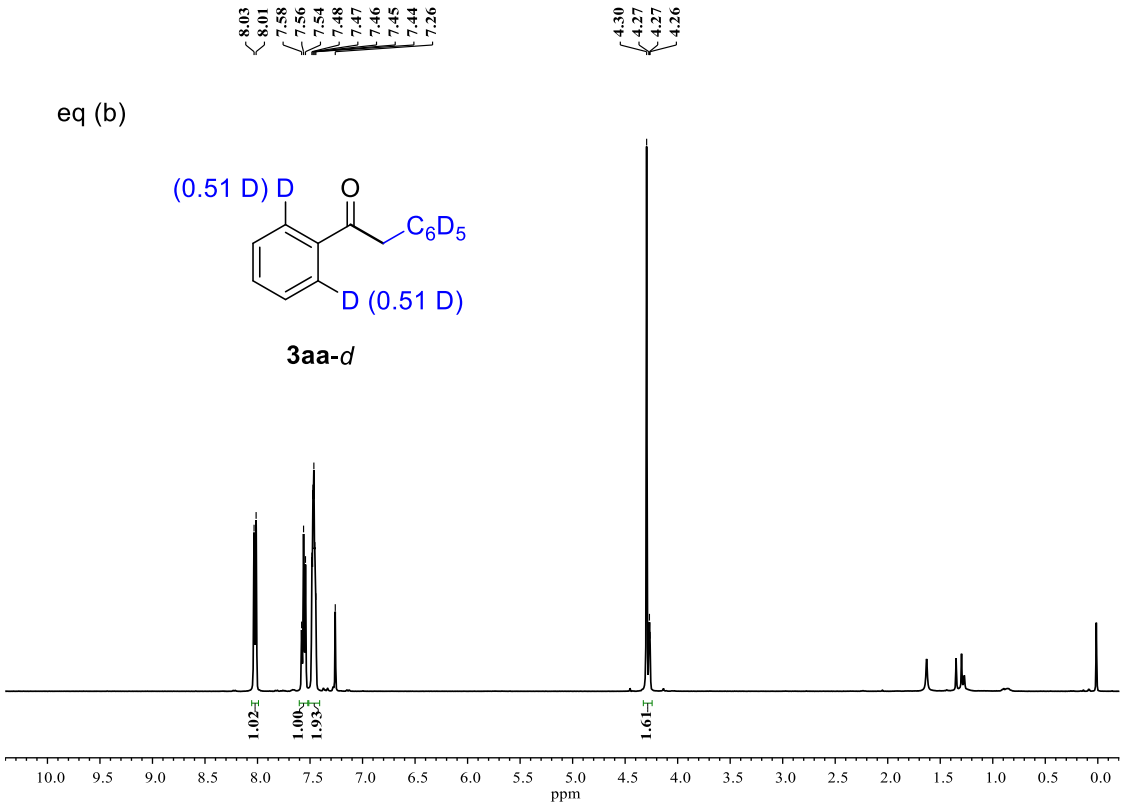
To a 25 mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added LDA (77.1 mg, 0.72 mmol), tertiary benzamide **1a** (123.7 mg, 0.60 mmol), THF (1.0 mL) and toluene-d_8 (192 μL, 1.80 mmol). The tube was sealed and stirred at 60 ℃ for 30 min. The mixture was then cooled to room temperature, quenched by adding H_2O and diluted by EtOAc (ethyl acetate, 10 mL). The aqueous solution was extracted with EtOAc (10 mL × 3) and the combined organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration by rotary evaporation, the mixture was purified by silica gel column chromatography (PE/EtOAc = 40/1 to 10/1) to afford **3aa**-*d* (32.4 mg, 27% yield) and **1a**-*d* (40.5 mg, 33% recovery). The deuterium incorporations on the *orhto*-position of benzoyl group of **3aa**-*d* and **1a**-*d* were detected by ^{1}H NMR.

eq (a)



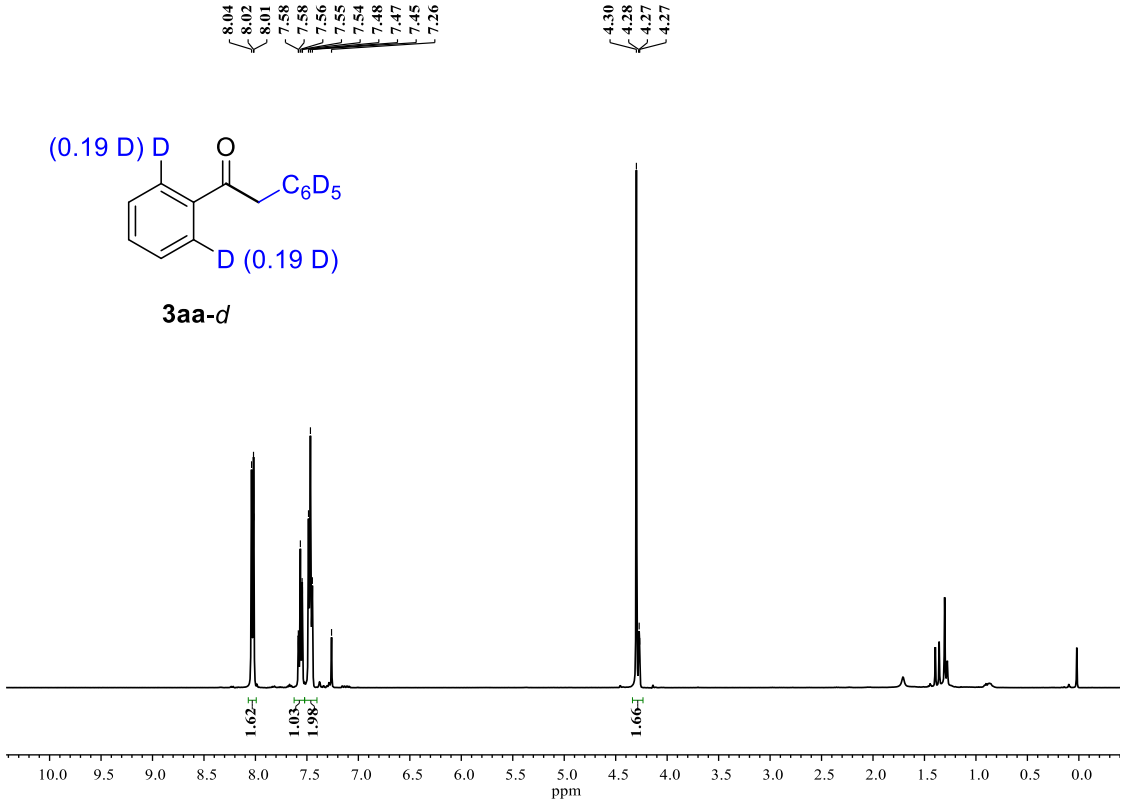
3aa-*d*

eq (b)

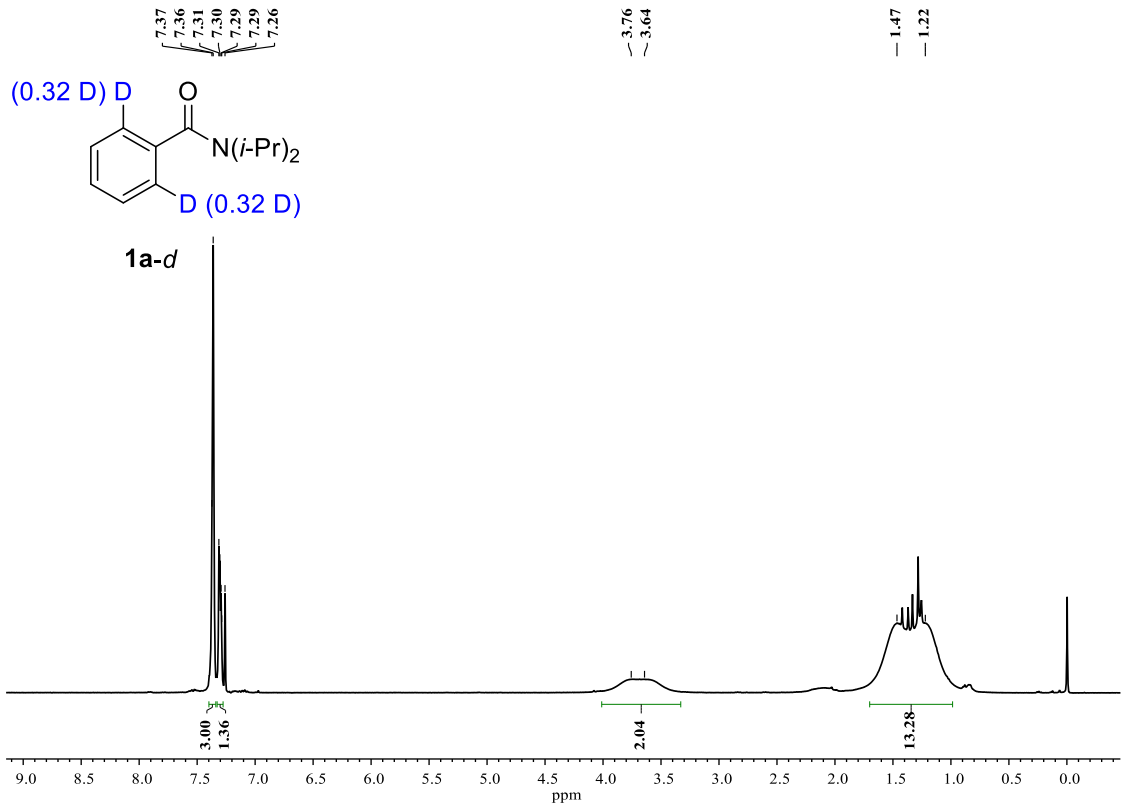


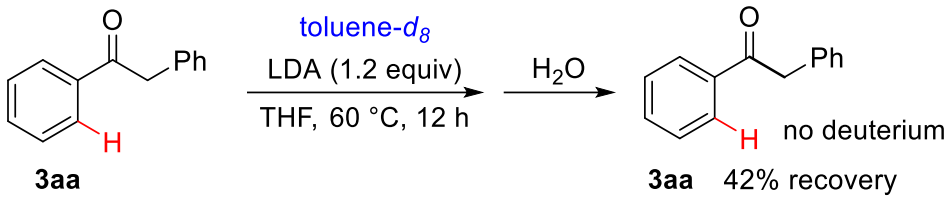
3aa-*d*

eq (c) **3aa**-*d*

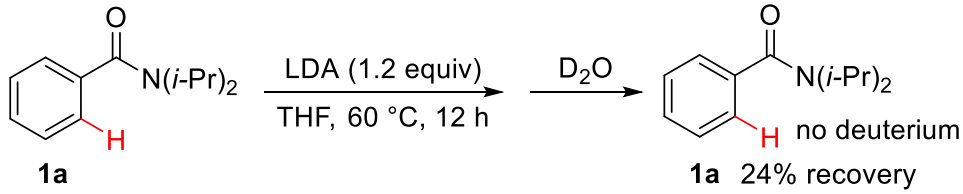


eq (c) **1a**-*d*

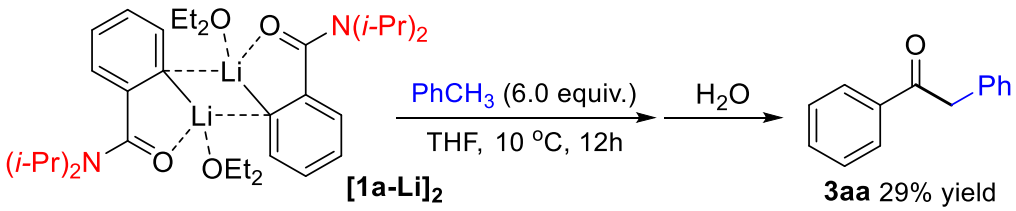




To a 25 mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added LDA (77.1 mg, 0.72 mmol), ketone **3aa** (118.0 mg, 0.6 mmol), THF (1.0 mL) and toluene-d_8 (192 μL, 1.8 mmol). The tube was sealed and stirred at 60 ℃ for 12 hours. The mixture was then cooled to room temperature and quenched by adding H_2O and diluted by ethyl acetate (EtOAc, 10 mL). The aqueous solution was extracted with EtOAc (10 mL × 3) and the combined organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration by rotary evaporation, the mixture was purified by silica gel column chromatography (PE/EtOAc = 40/1) to afford **3aa** (49.3 mg, 42% recovery). No deuterium incorporation was detected on the *ortho*-position of benzoyl group in the recovered **3aa** by ^{1}H NMR.



To a 25 mL Schlenk tube equipped with a Teflon septum and magnetic stir bar were added LDA (77.2 mg, 0.72 mmol), tertiary benzamide **1a** (122.0 mg, 0.59 mmol) and THF (1.0 mL). The tube was sealed and stirred at 60 ℃ for 12 hours. The mixture was then cooled to room temperature and quenched by adding D_2O (1 mL) and diluted by ethyl acetate (EtOAc, 10 mL). The aqueous solution was extracted with EtOAc (10 mL × 3) and the combined organic layer was dried over anhydrous Na_2SO_4. After filtration and concentration by rotary evaporation, the mixture was purified by silica gel column chromatography (PE/EtOAc = 10/1) to recovered **1a** (28.9 mg, 24% recovery). No deuterium incorporation was detected on the *ortho*-position of amide group in the recovered tertiary benzamide **1a** by ^{1}H NMR.



We prepared the *ortho*-lithiated amides **[1a-Li]$_2$** according reported procedure.[31] Treating **[1a-Li]$_2$** with 6.0 equiv. of toluene afforded ketone product **3aa** with 29% yield. The above outcomes suggest intermediate **A**, as proposed, could be involved in the reaction pathway.

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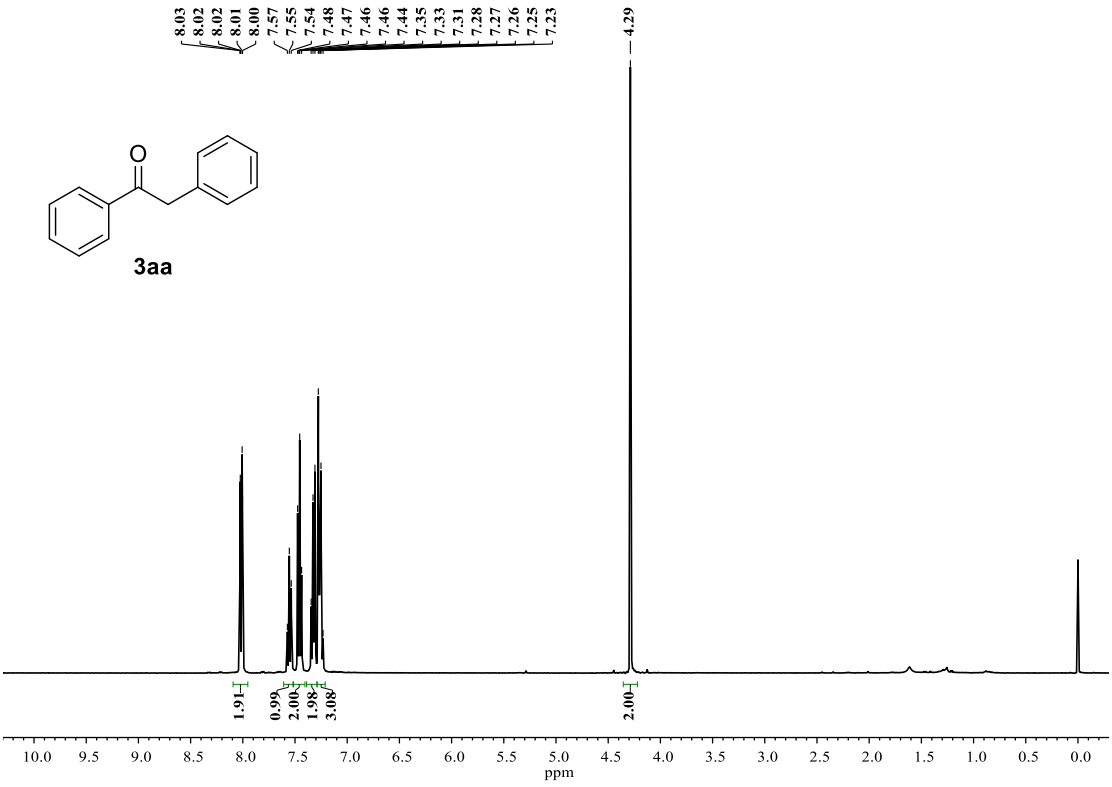
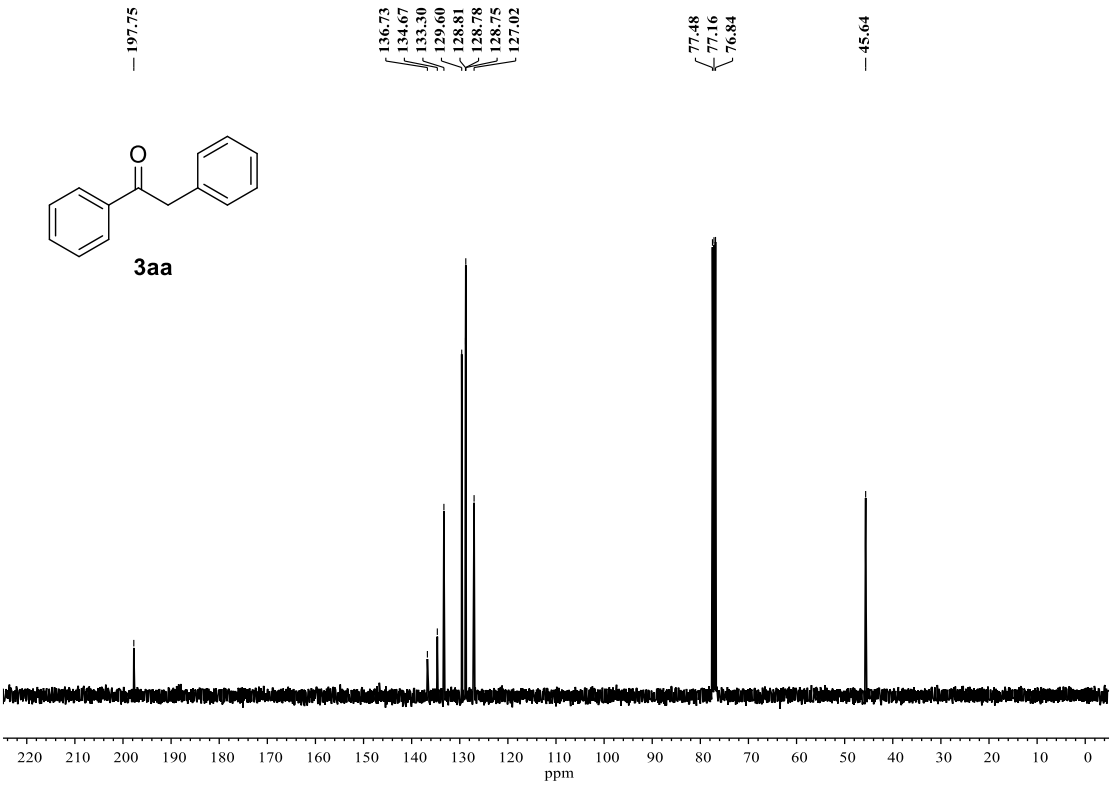
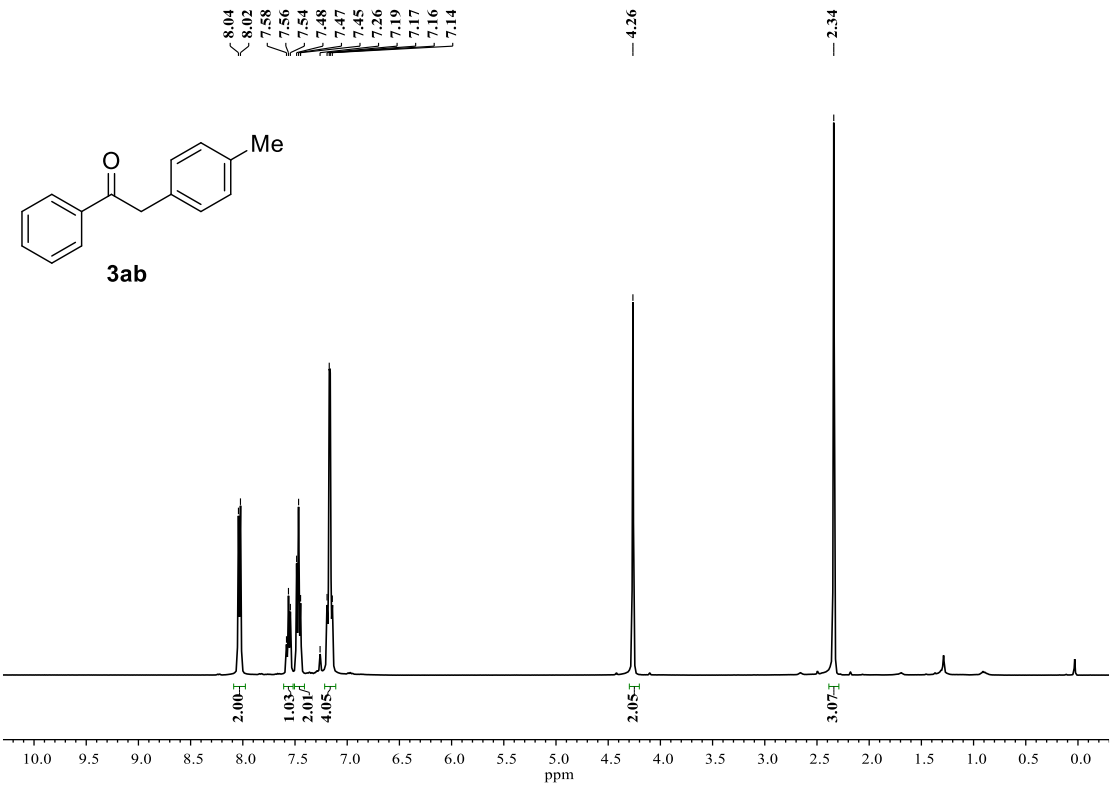
8. ^{1}H and ^{13}C NMR Spectra



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4.26
2.34
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O
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2.00
1.03
2.01
4.05
2.05
3.07
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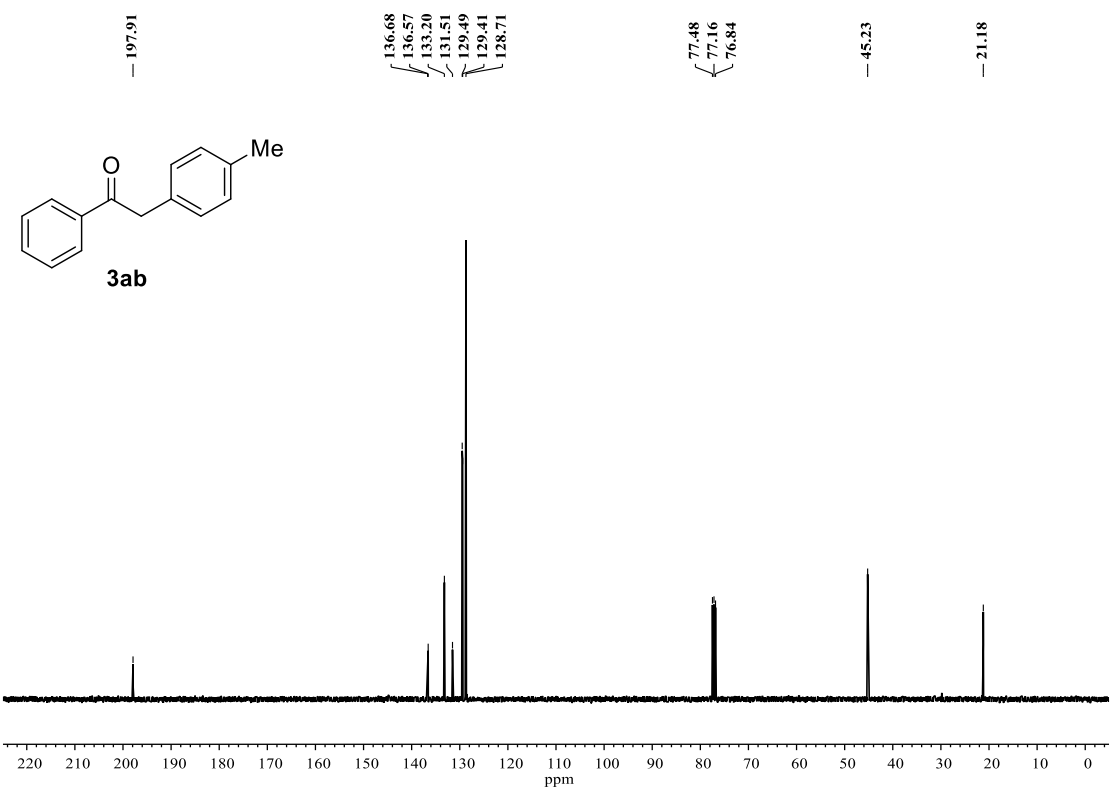
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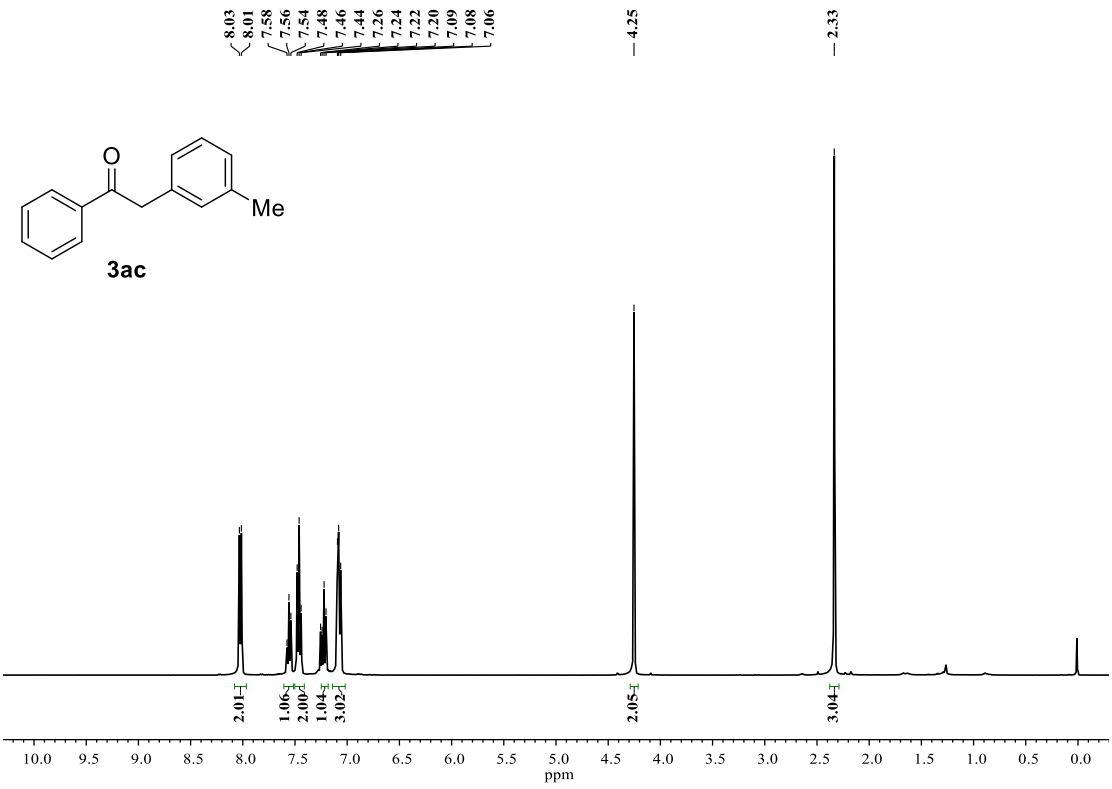
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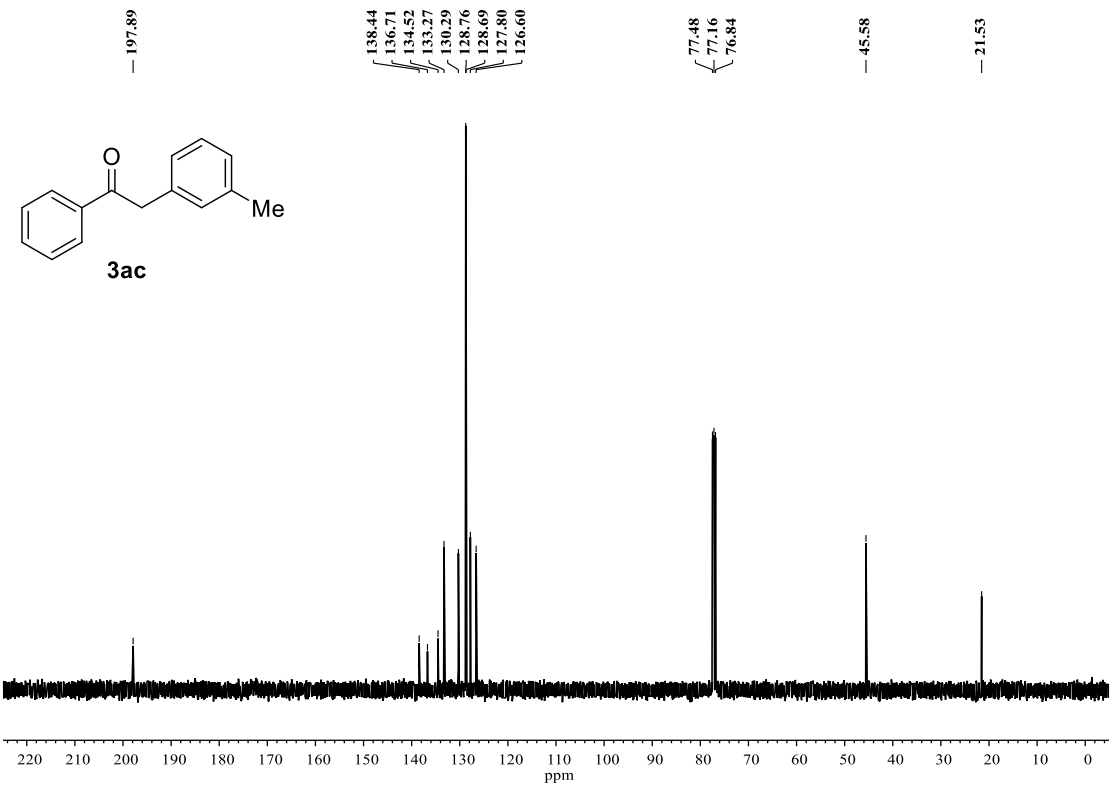
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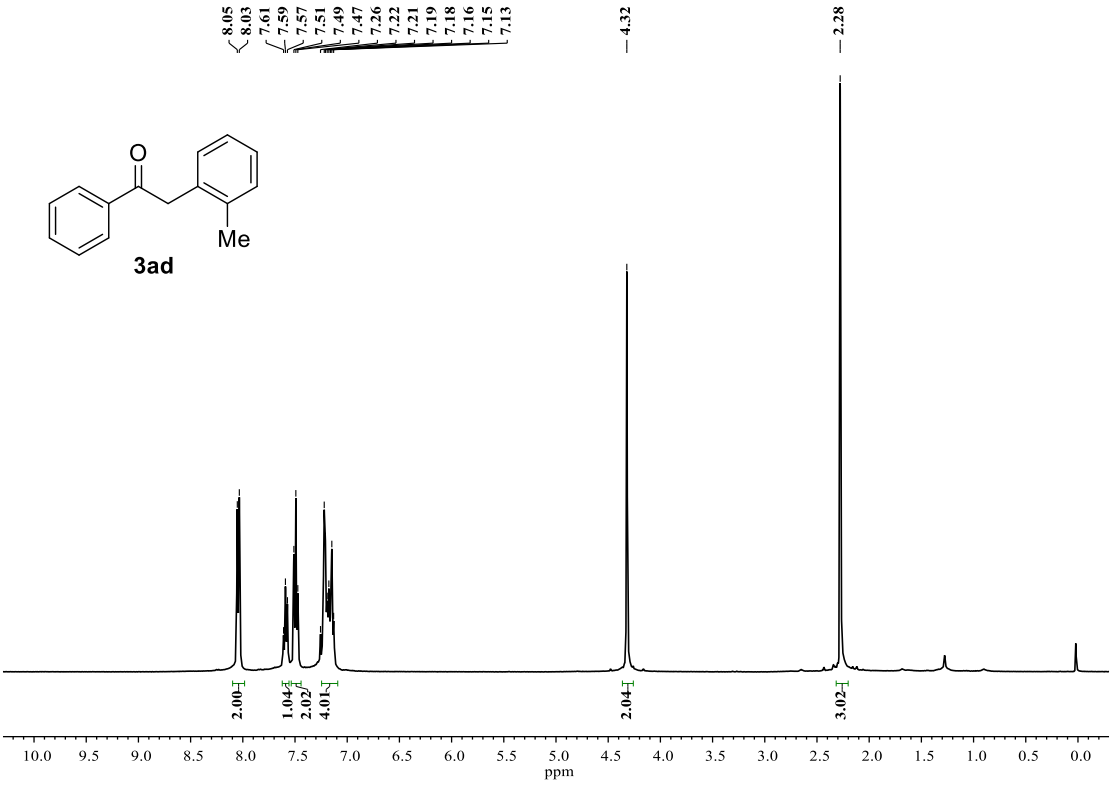
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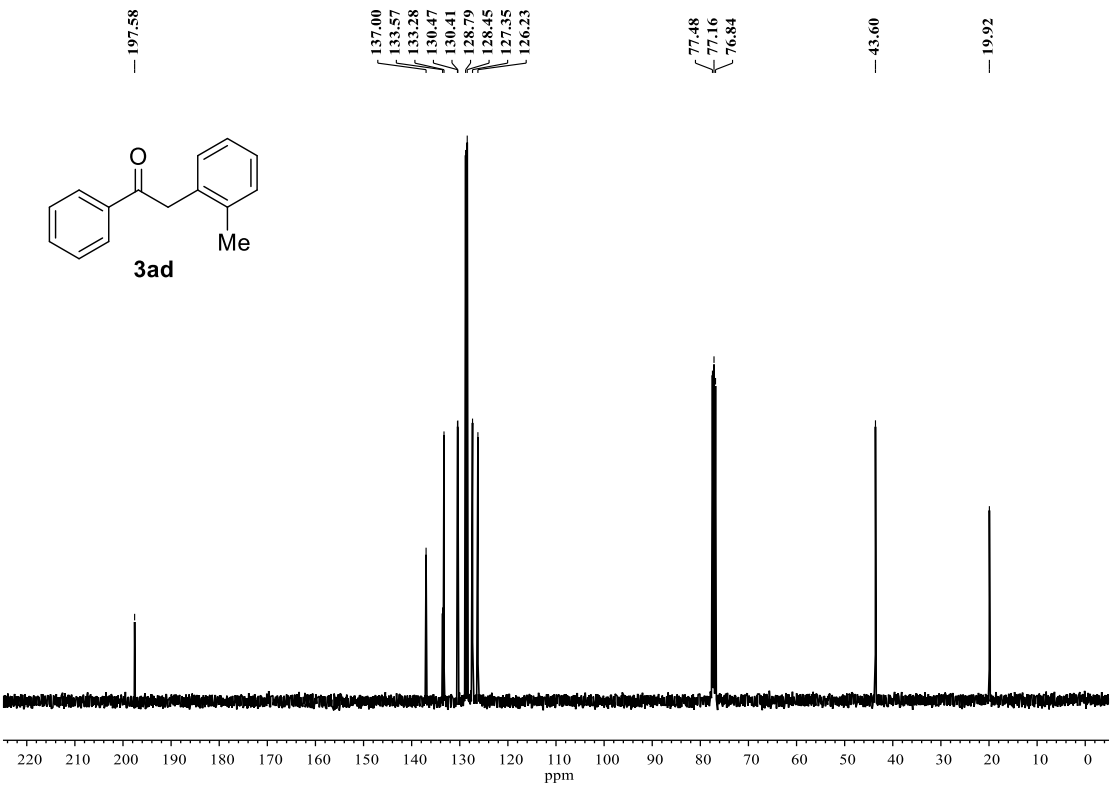
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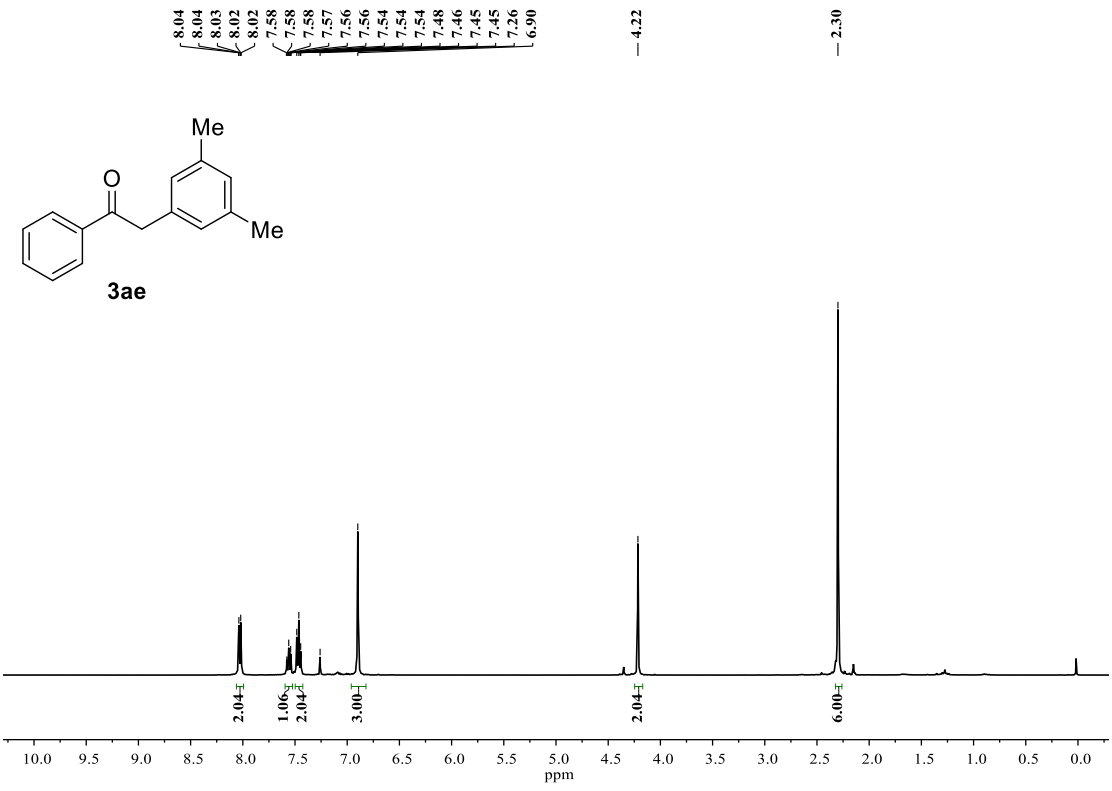
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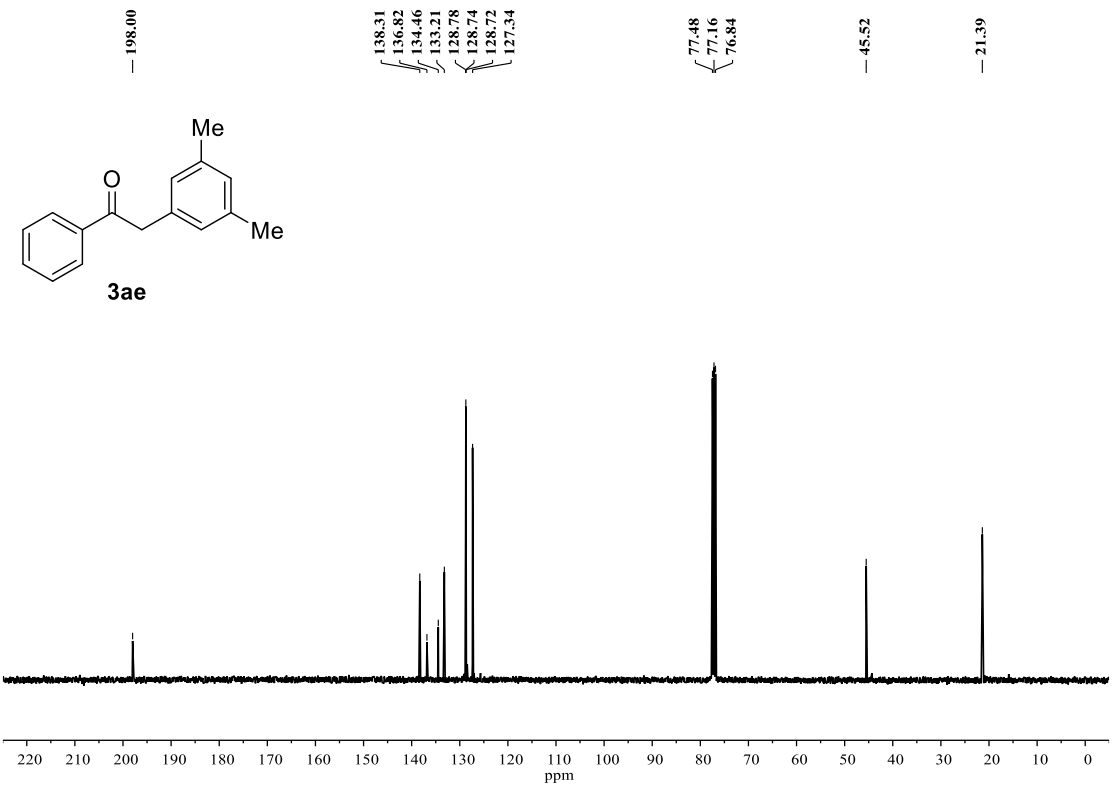
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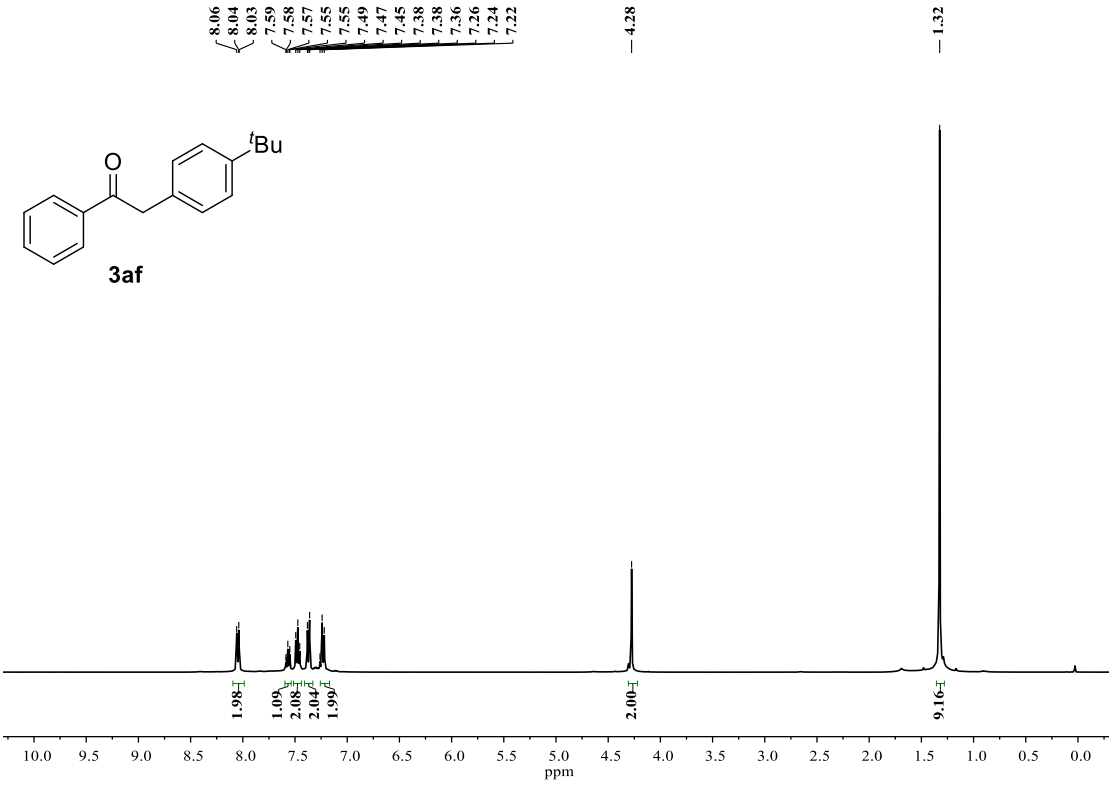
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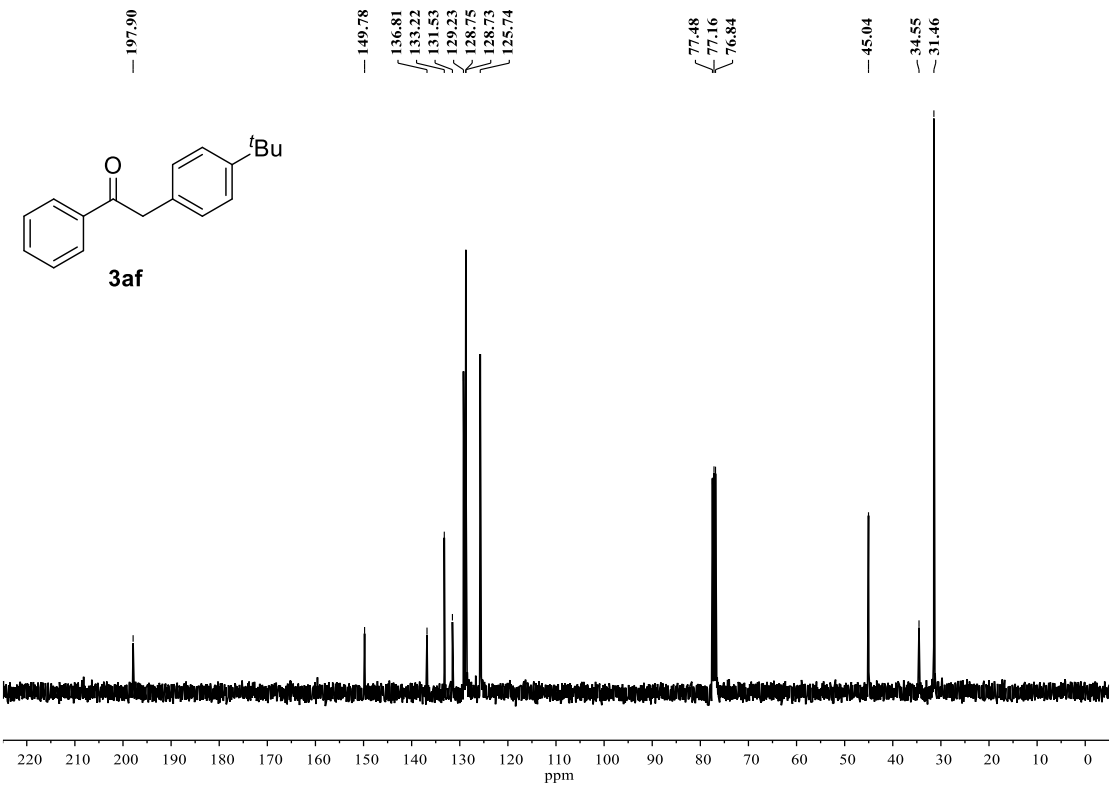
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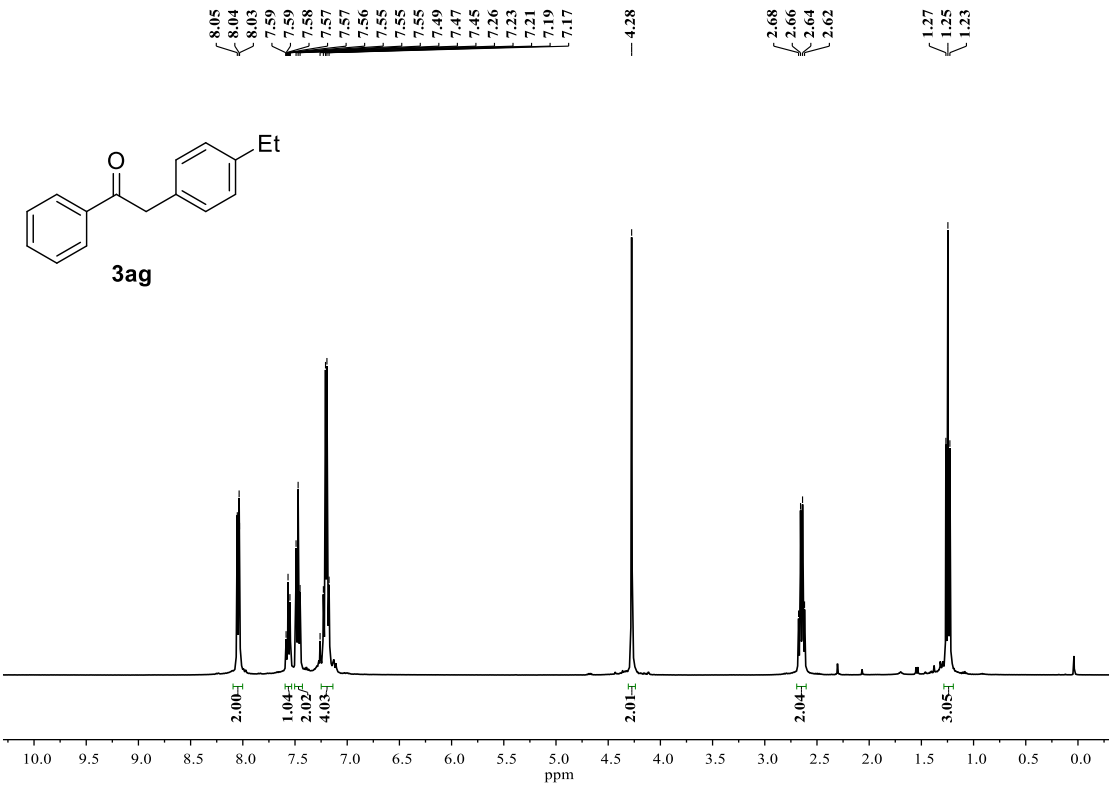
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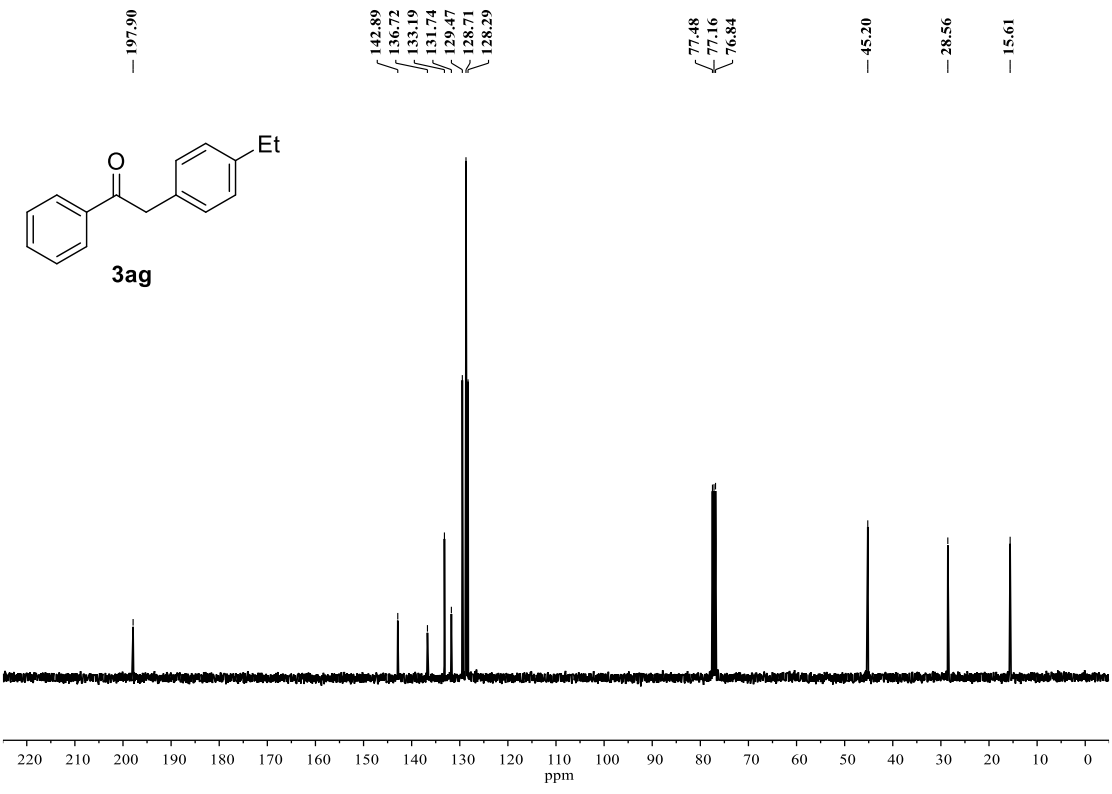
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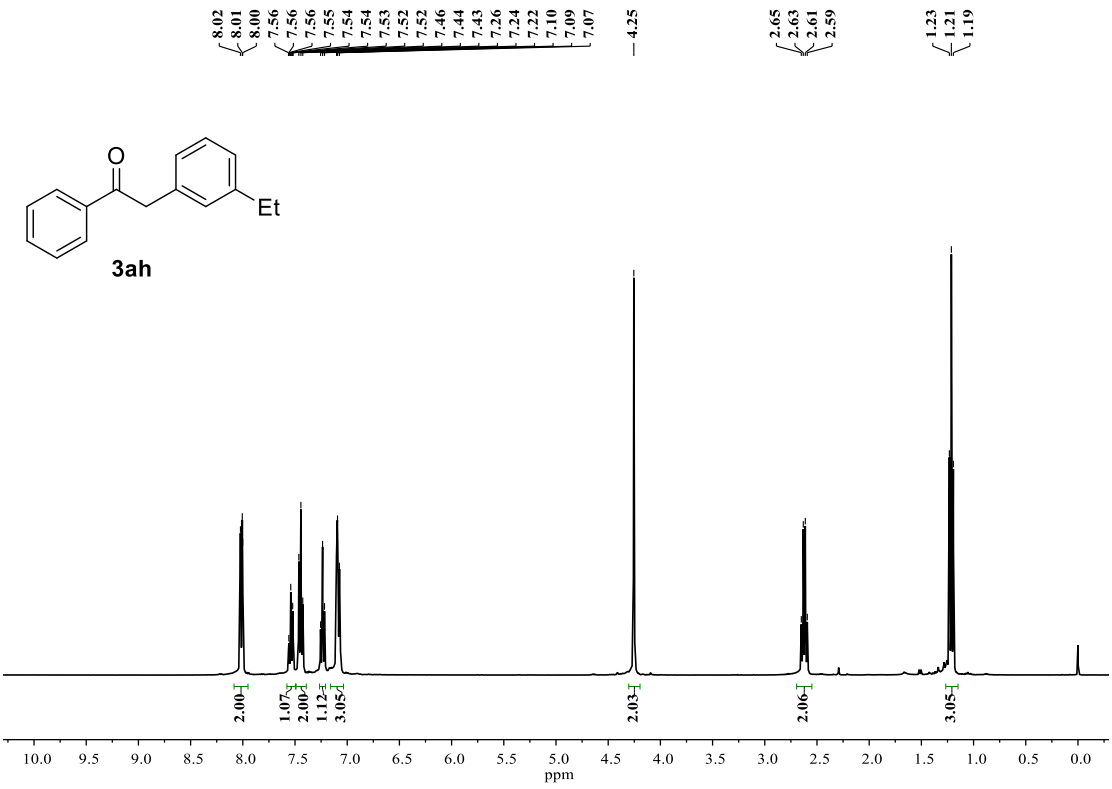
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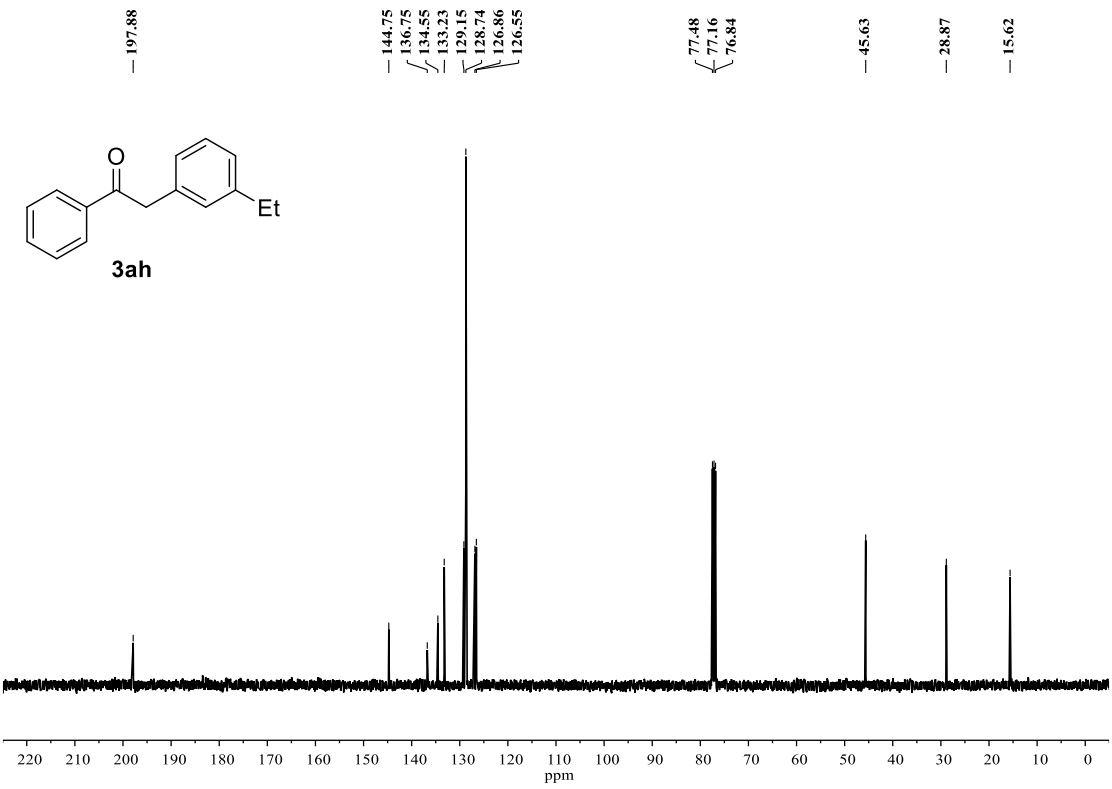
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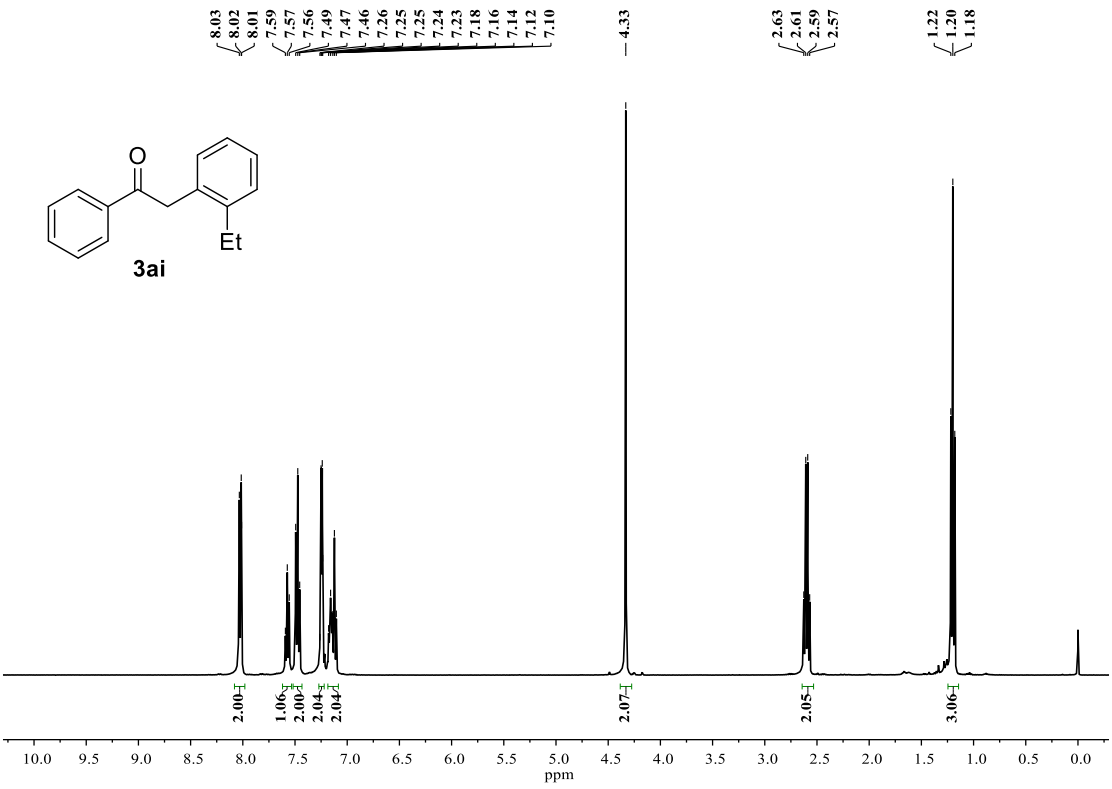
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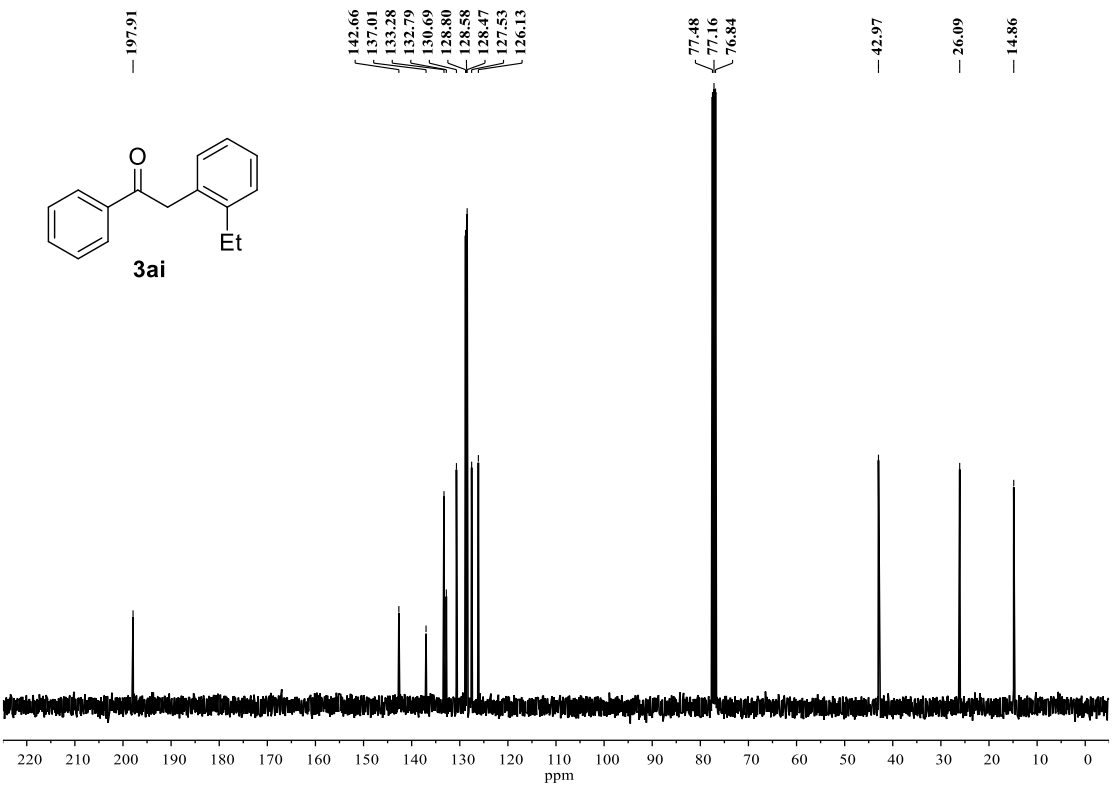
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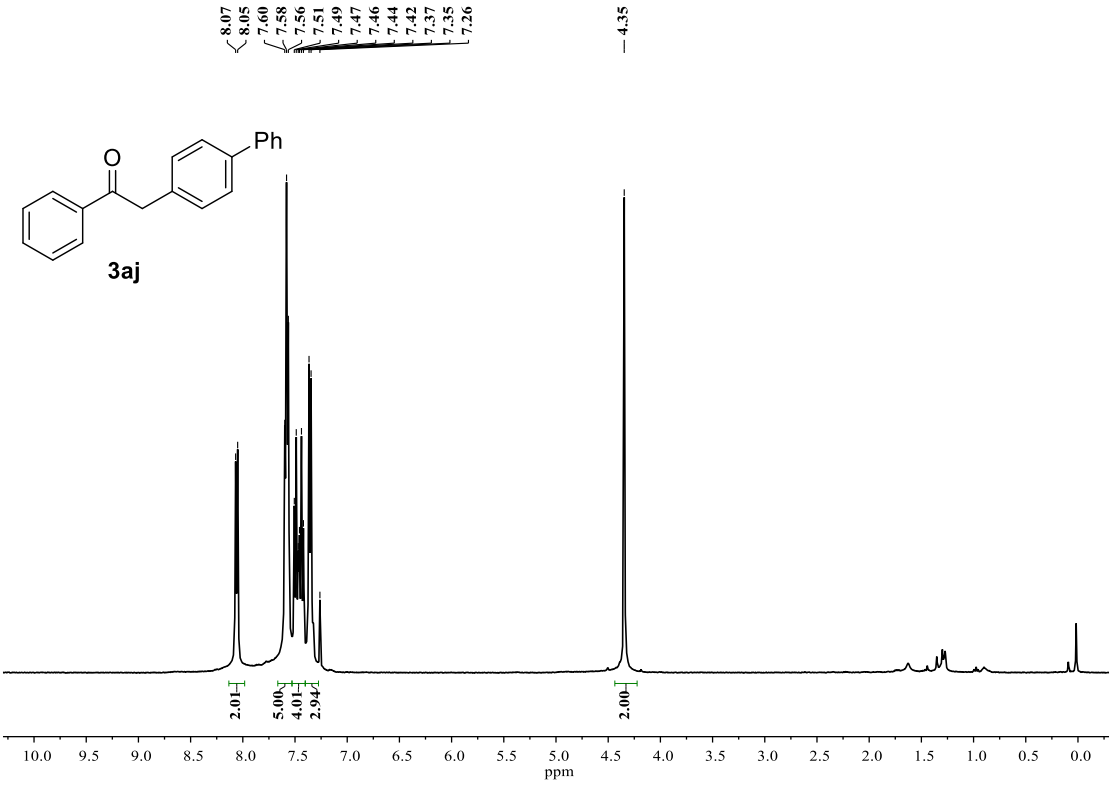
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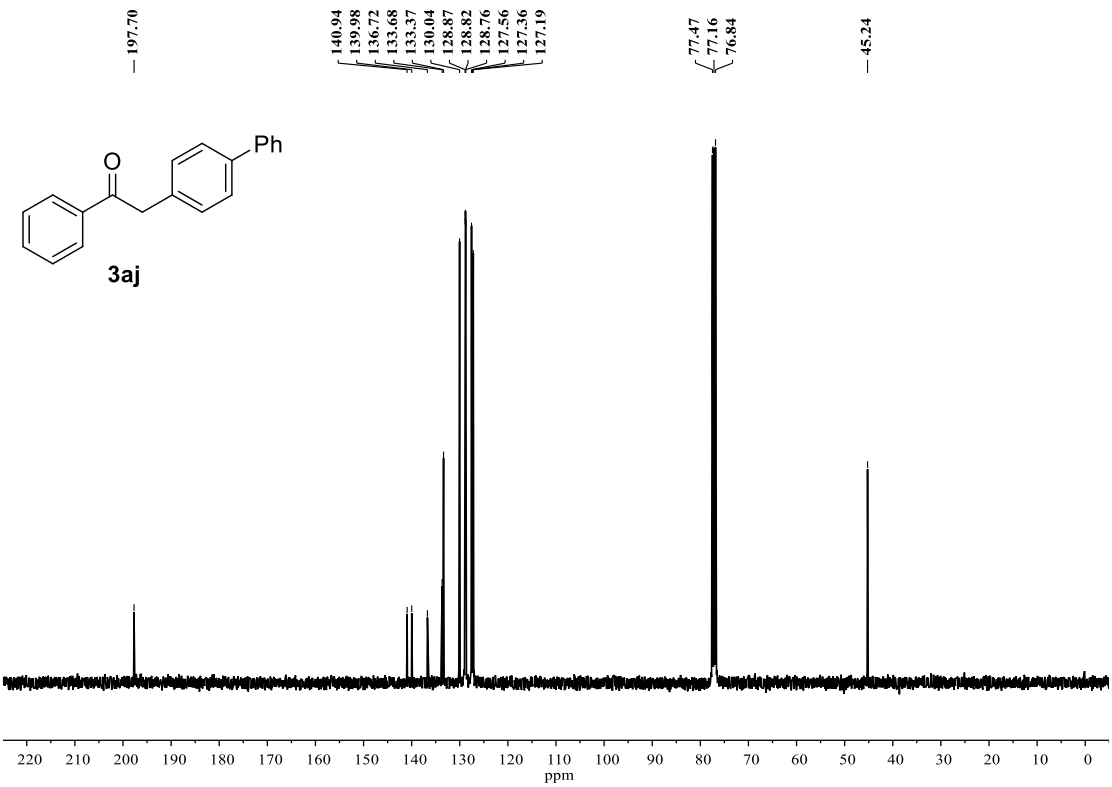
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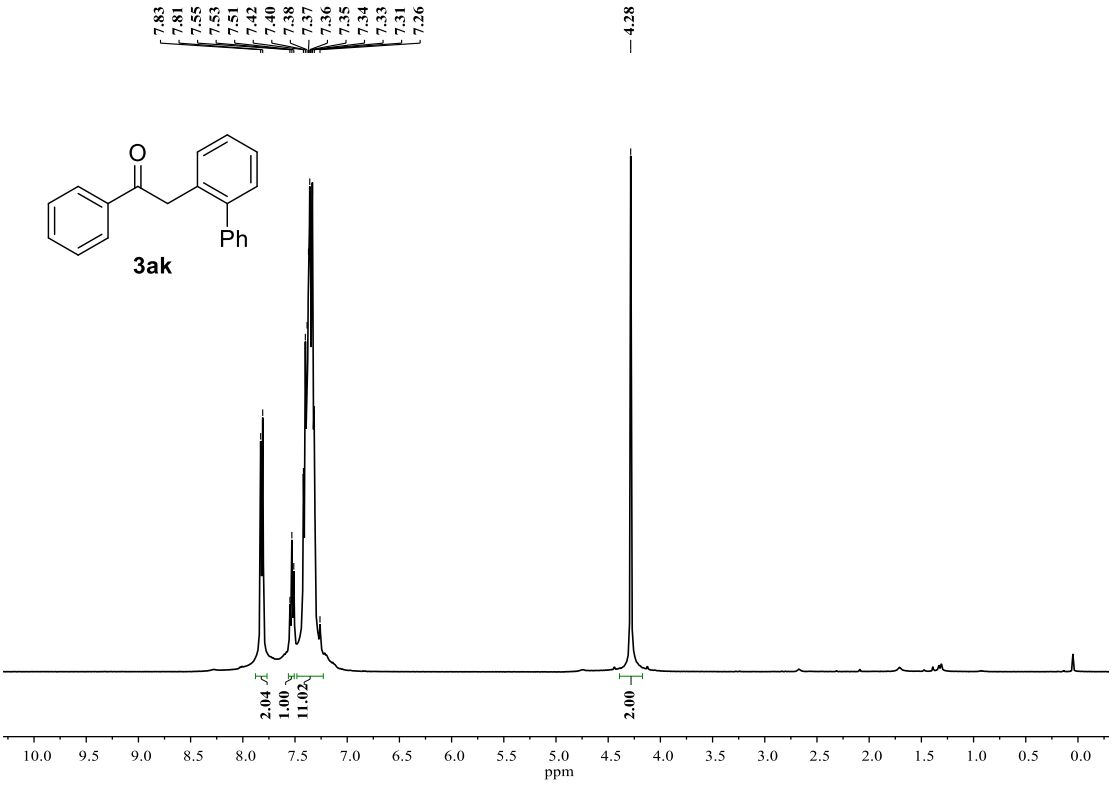
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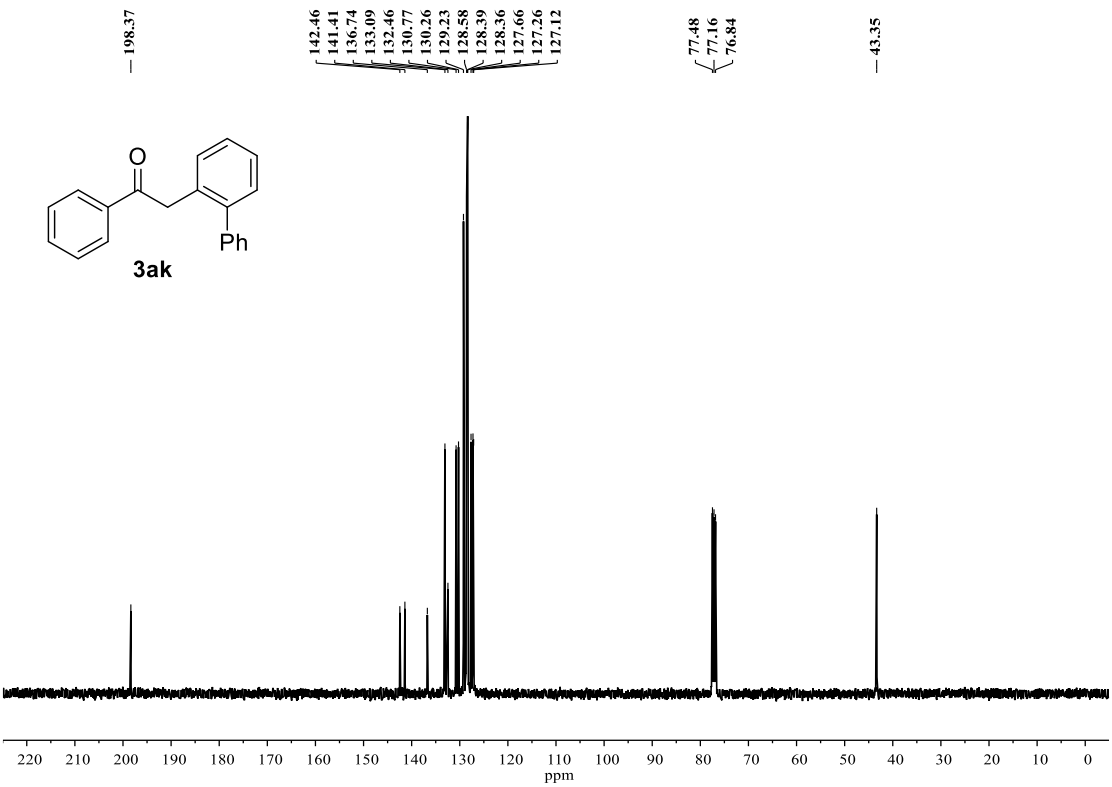
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130.26
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128.39
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127.26
127.12
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76.84
43.35
O
Ph
3ak
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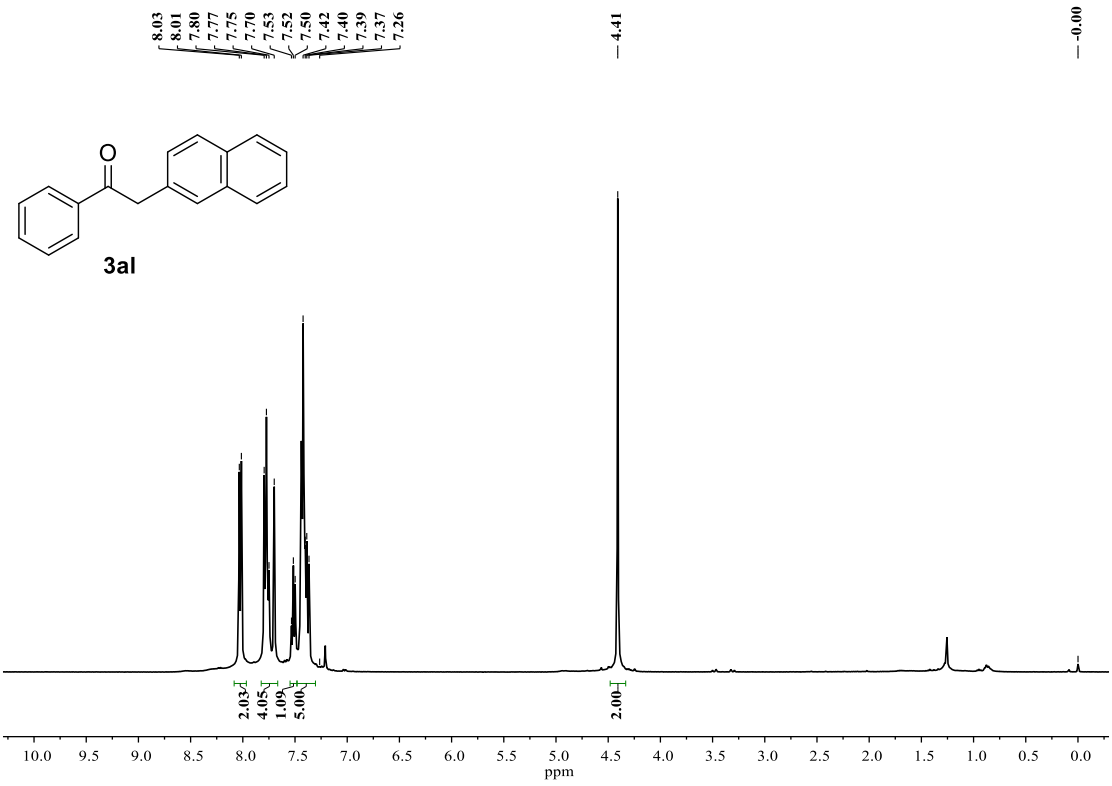
ppm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7.52
7.50
7.42
7.40
7.39
7.37
7.26
4.41
-0.00
O
3al
2.03
4.05
1.09
5.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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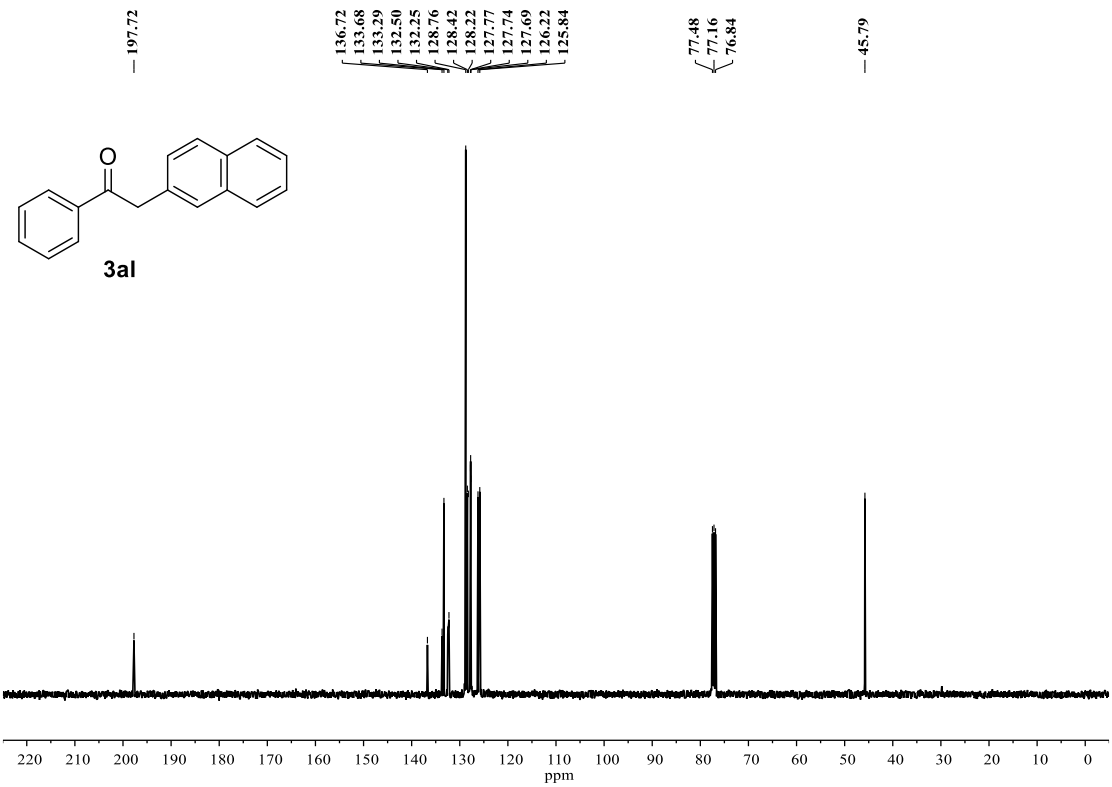
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127.69
126.22
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77.16
76.84
45.79
O
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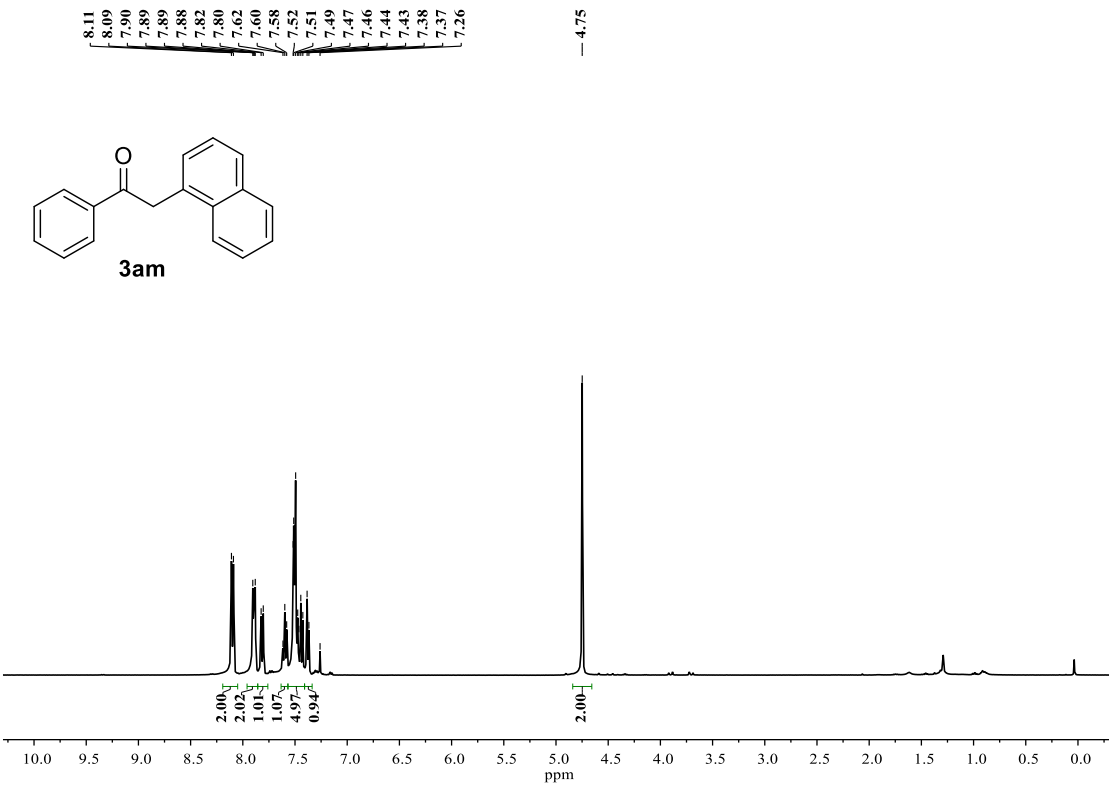
ppm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7.52
7.51
7.49
7.47
7.46
7.44
7.43
7.38
7.37
7.26
4.75
O
3am
2.00
2.02
1.01
1.07
4.97
0.94
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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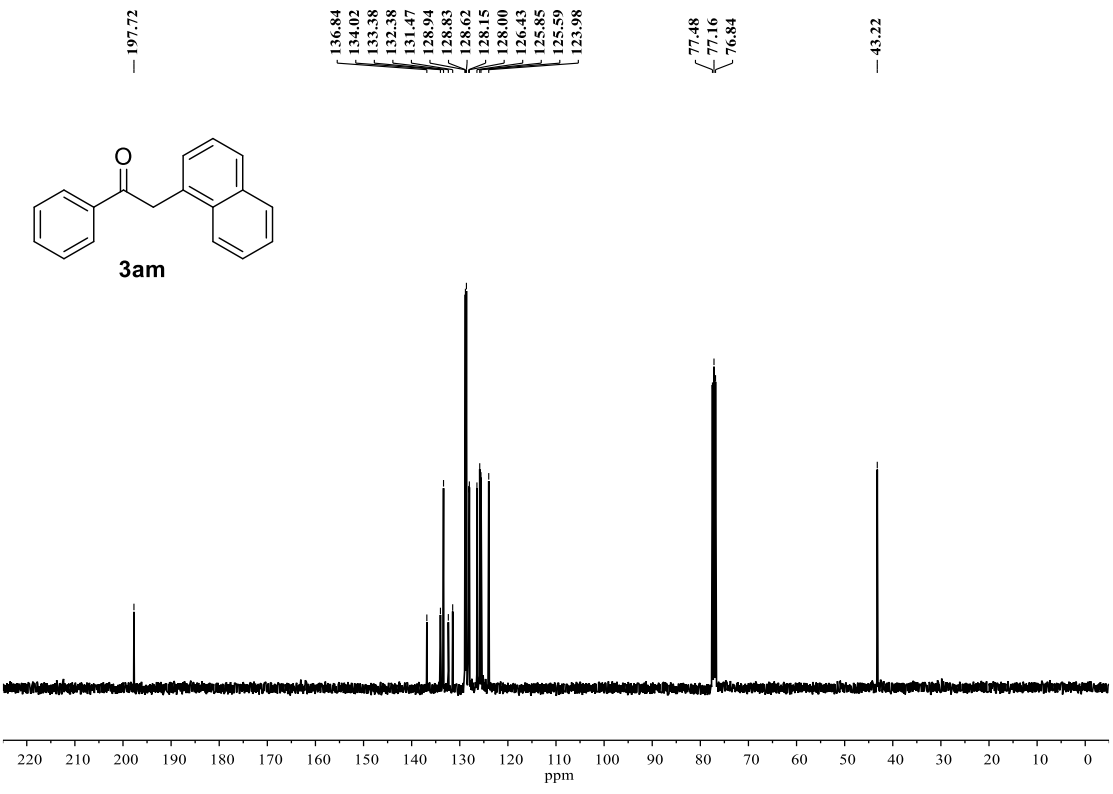
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125.59
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77.16
76.84
43.22
O
3am
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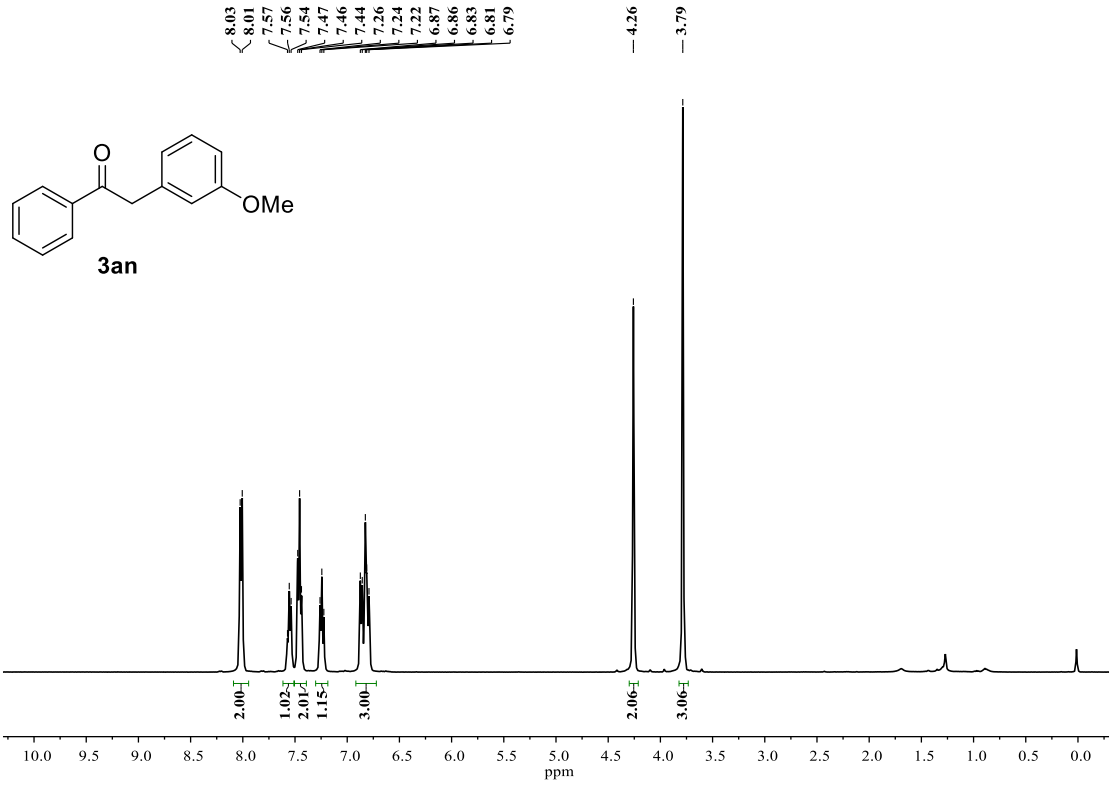
ppm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7.44
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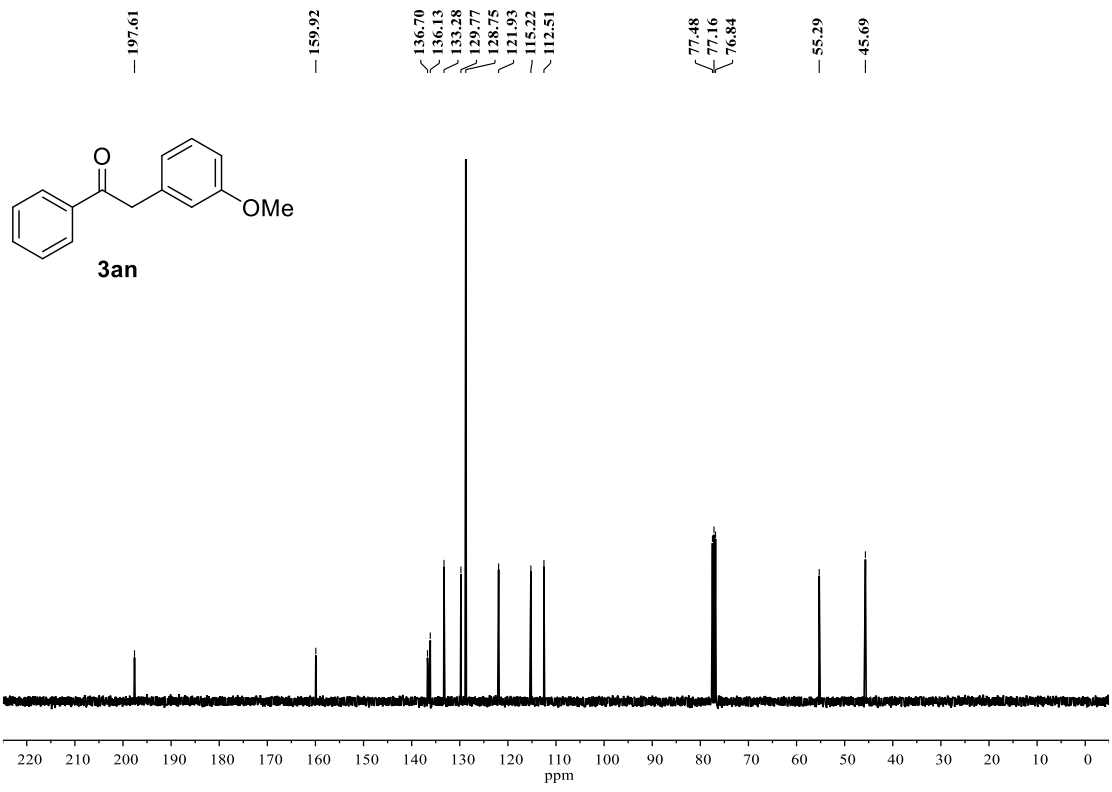
7.24
7.22
6.87
6.86
6.83
6.81
6.79
4.26
3.79
O
OMe
3an
2.00
1.02
2.01
1.15
3.00
2.06
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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45.69
O
OMe
3an
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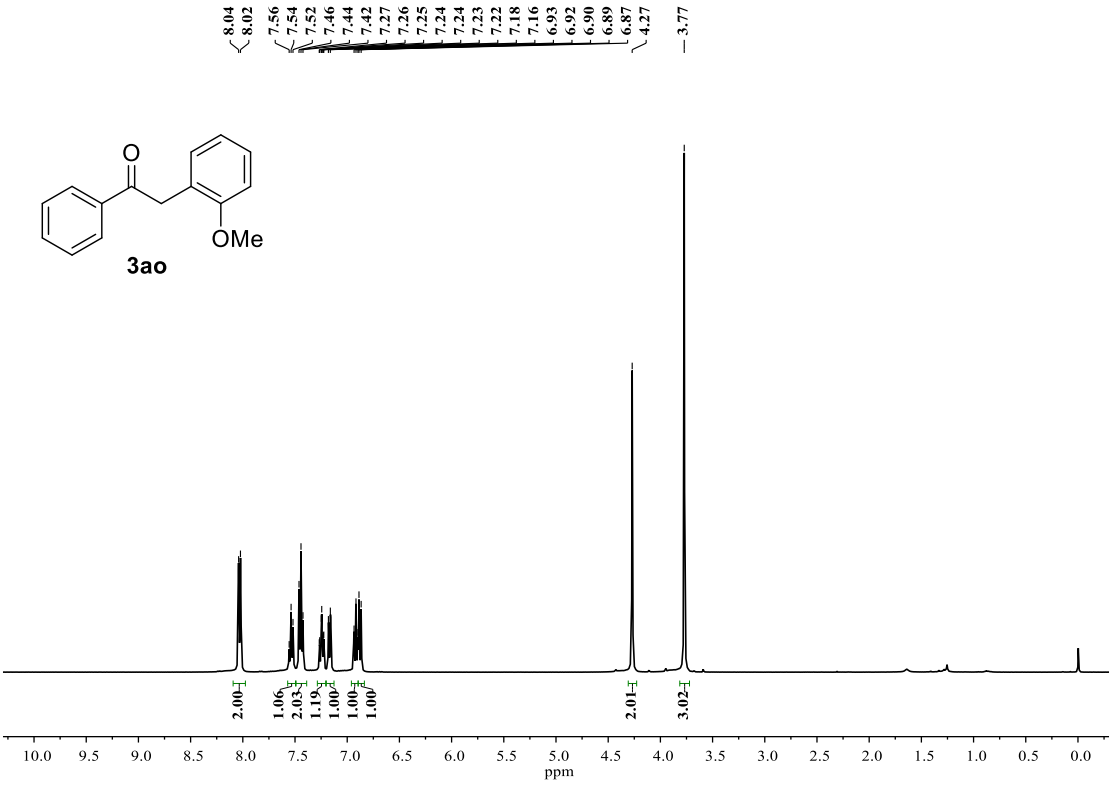
ppm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8.02
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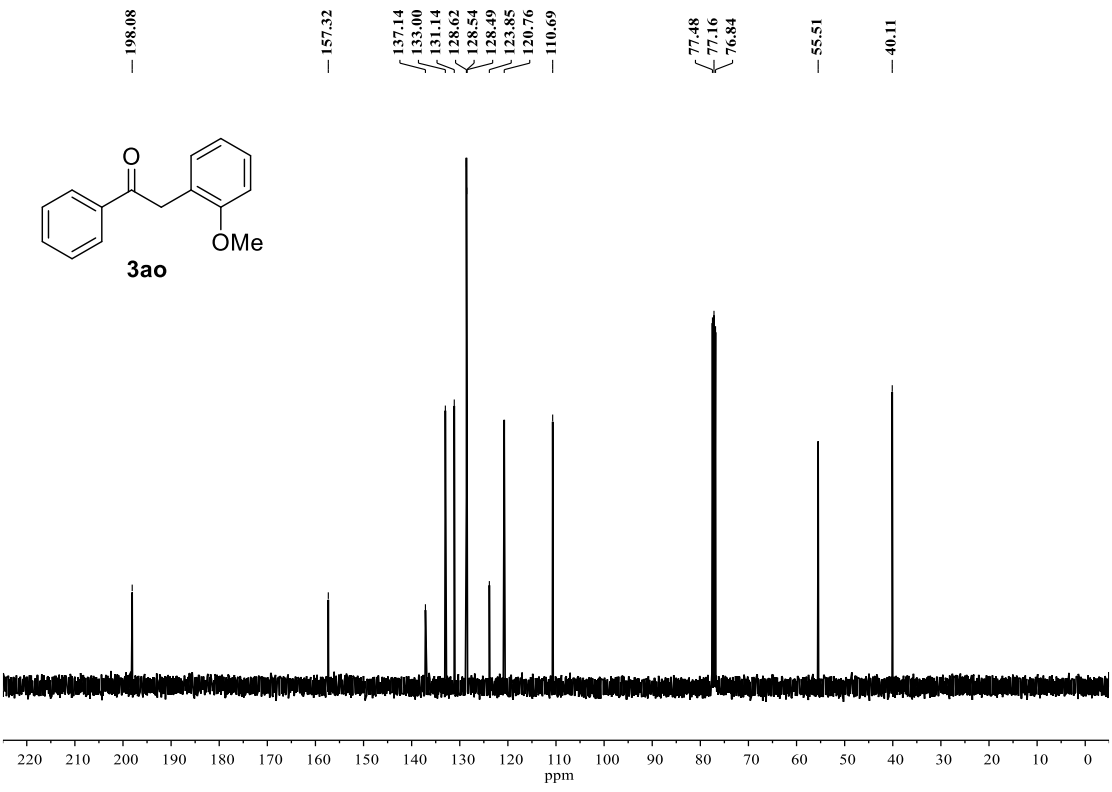
7.46
7.44
7.42
7.27
7.26
7.25
7.24
7.24
7.23
7.22
7.18
7.16
6.93
6.92
6.90
6.89
6.87
4.27
3.77
O
OMe
3ao
2.00
1.06
2.03
1.19
1.00
1.00
1.00
2.01
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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128.49
123.85
120.76
110.69
77.48
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76.84
55.51
40.11
O
OMe
3ao
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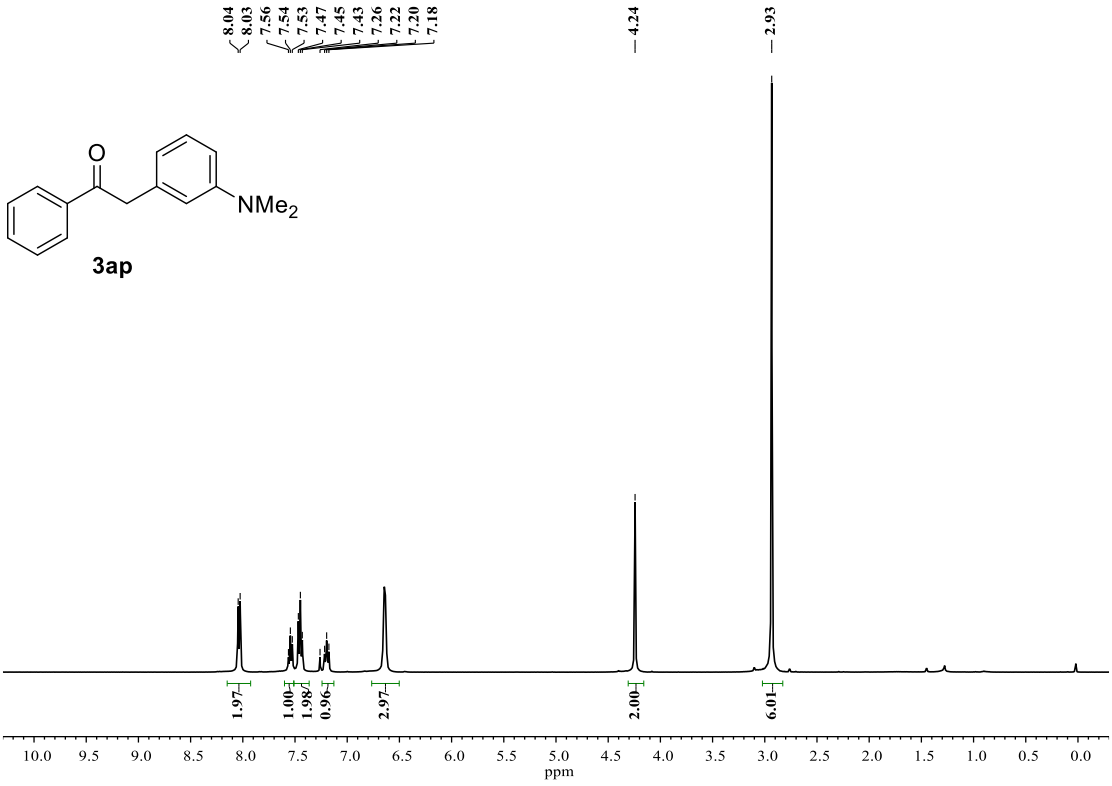
ppm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8.03
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7.43
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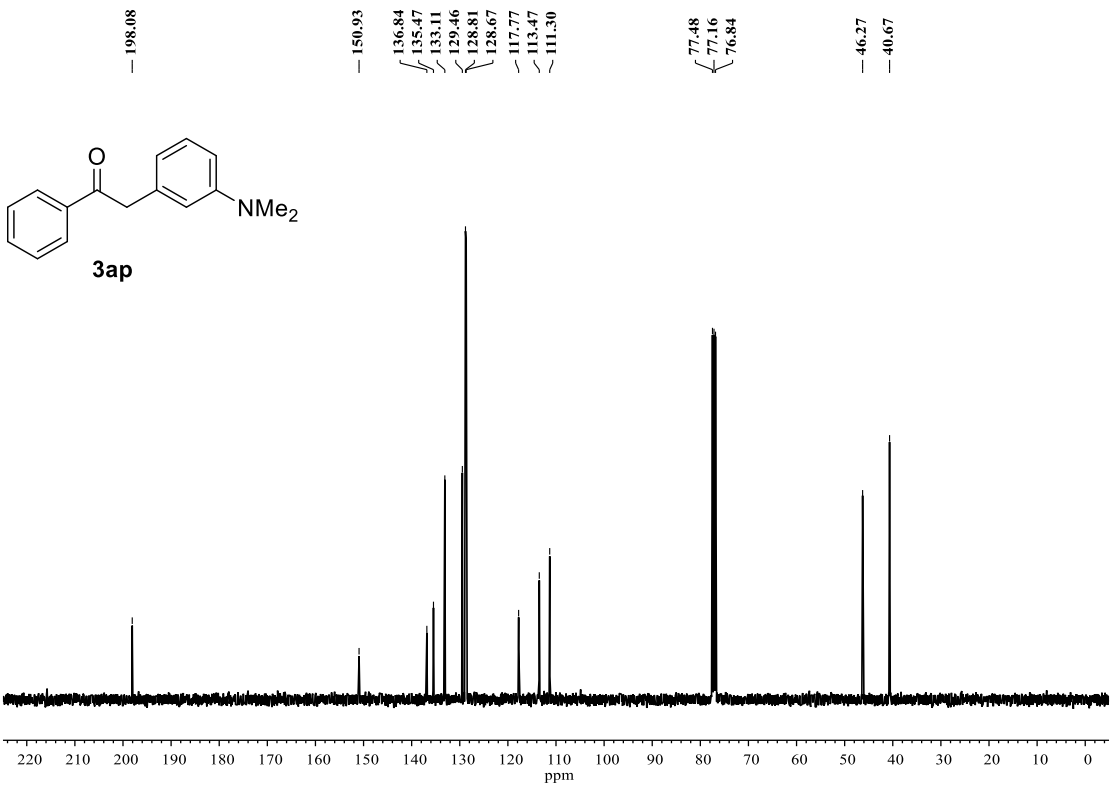
7.22
7.20
7.18
4.24
2.93
O
NMe2
3ap
1.97
1.00
1.98
0.96
2.97
2.00
6.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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129.46
128.81
128.67
117.77
113.47
111.30
77.48
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46.27
40.67
O
NMe2
3ap
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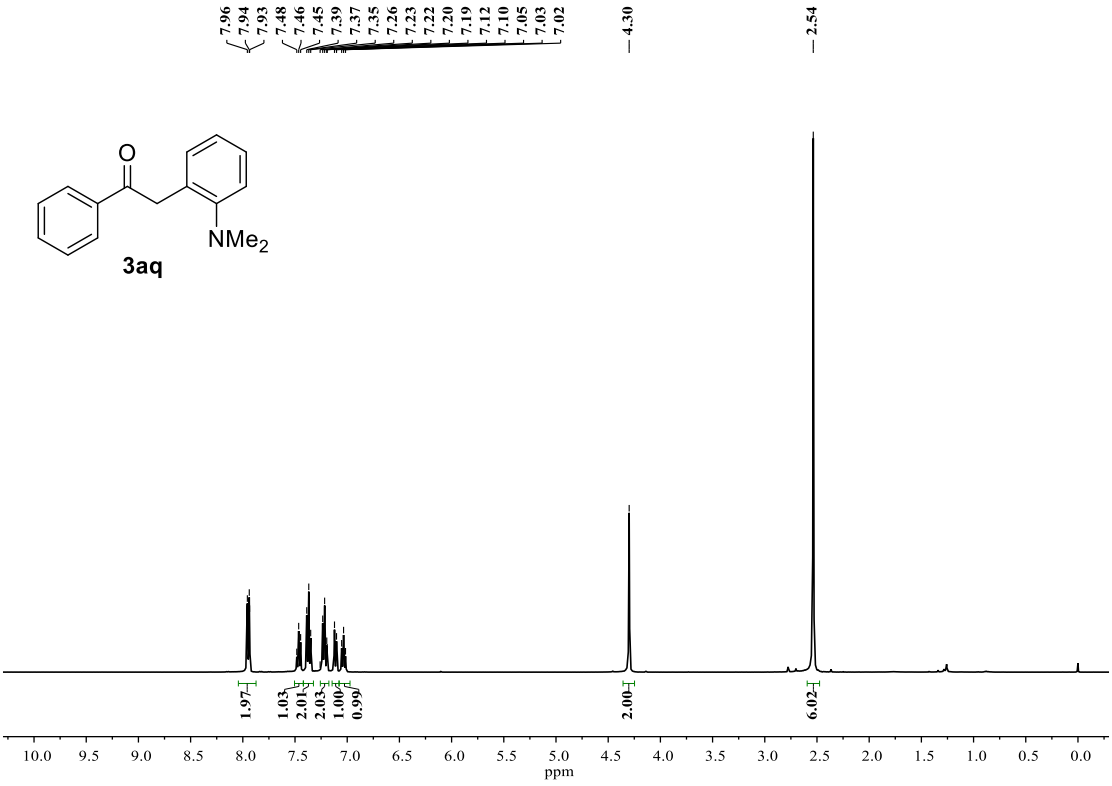
ppm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7.39
7.37
7.35
7.26
7.23
7.22
7.20
7.19
7.12
7.10
7.05
7.03
7.02
4.30
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O
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3aq
1.97
1.03
2.01
2.03
1.00
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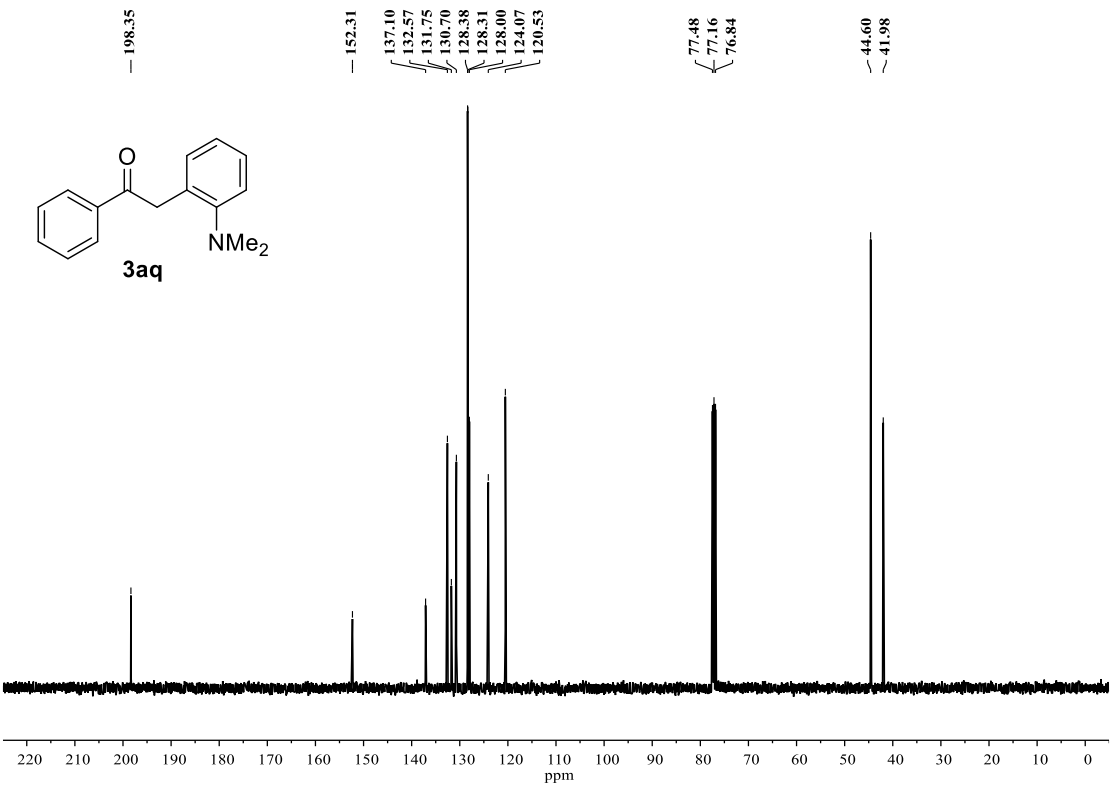
2.00
6.02
ppm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120.53
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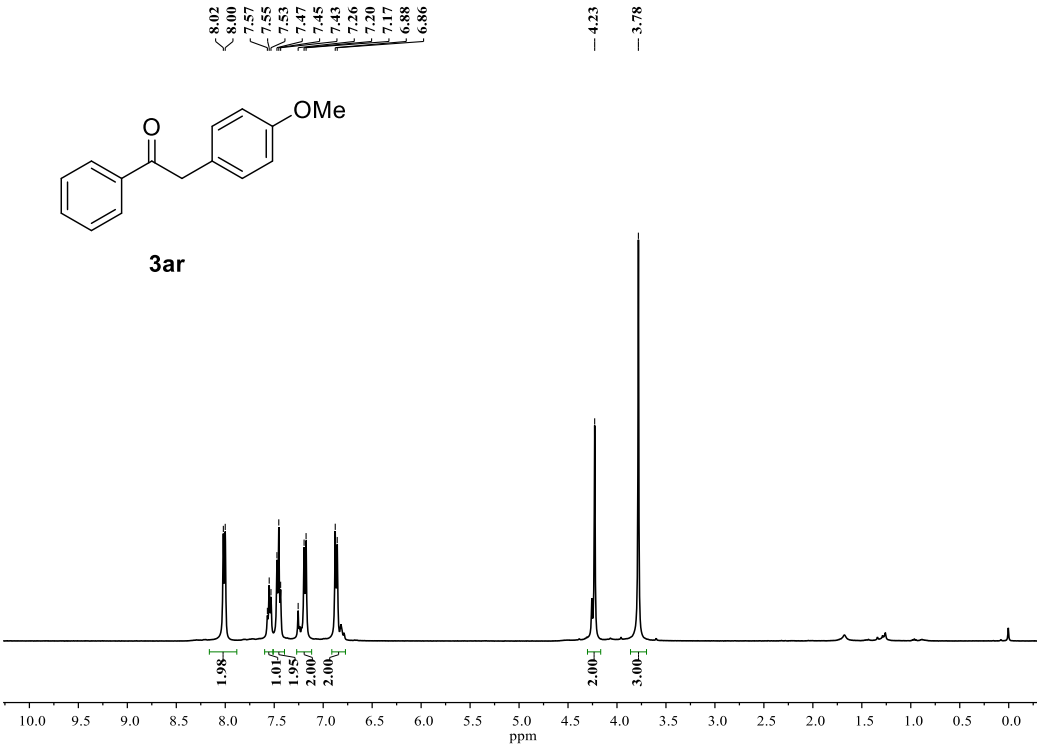
77.16
76.84
44.60
41.98
O
NMe2
3aq
ppm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7.43
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7.20
7.17
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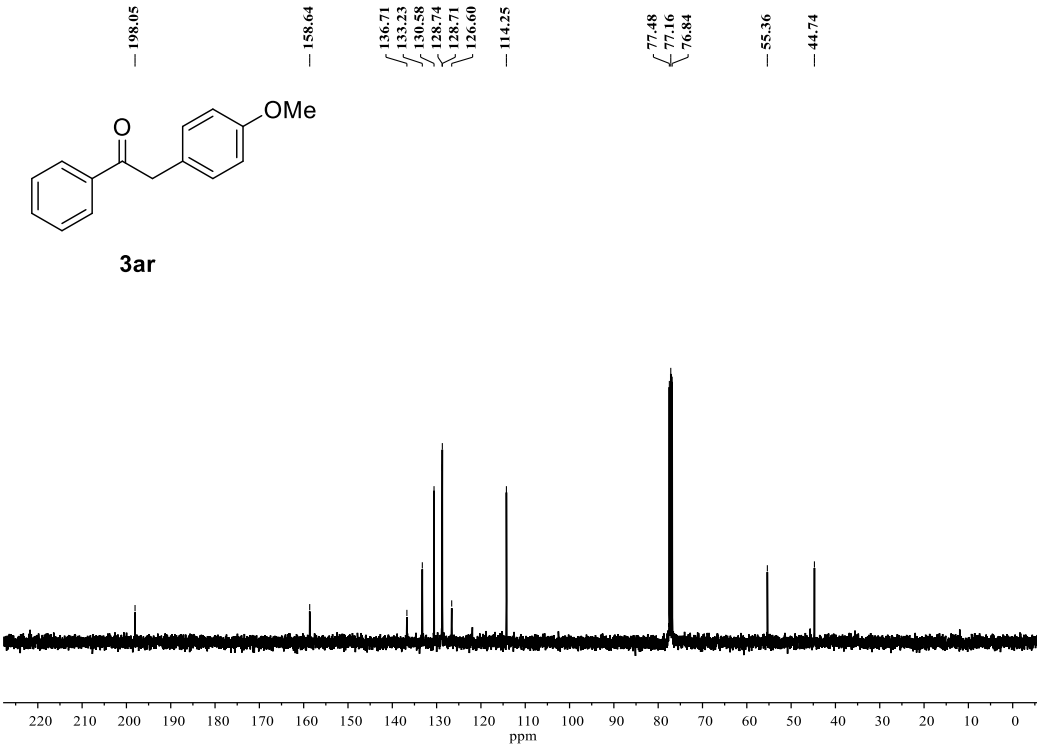
6.86
4.23
3.78
O
OMe
3ar
1.98
1.01
1.95
2.00
2.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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126.60
114.25
77.48
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55.36
44.74
O
OMe
3ar
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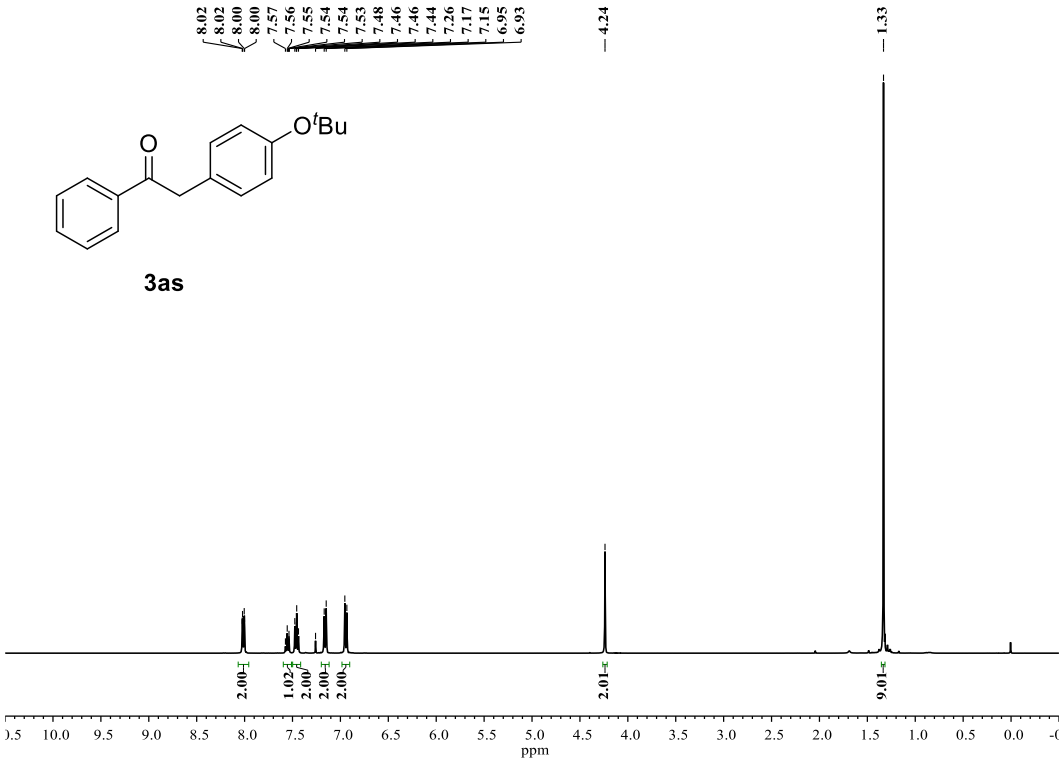
ppm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8.02
8.00
8.00
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7.54
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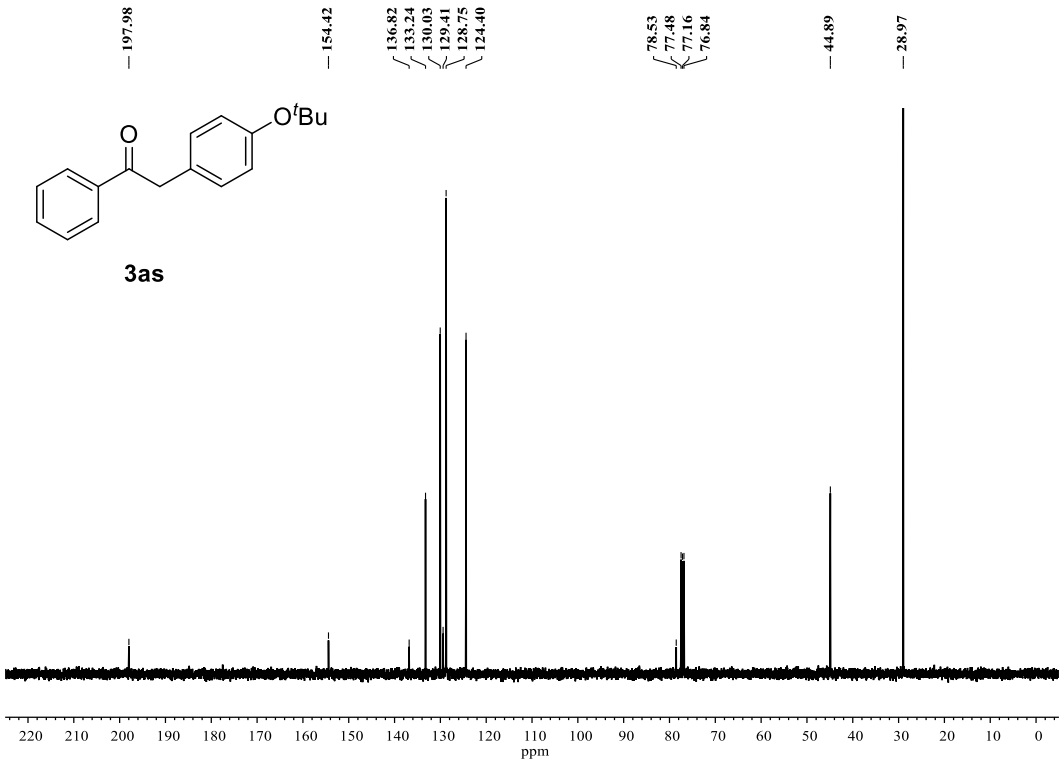
7.53
7.48
7.46
7.46
7.44
7.26
7.17
7.15
6.95
6.93
4.24
1.33
O
O^{t}Bu
2.00
1.02
2.00
2.00
2.00
2.01
9.01
ppm

3as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77.16
76.84
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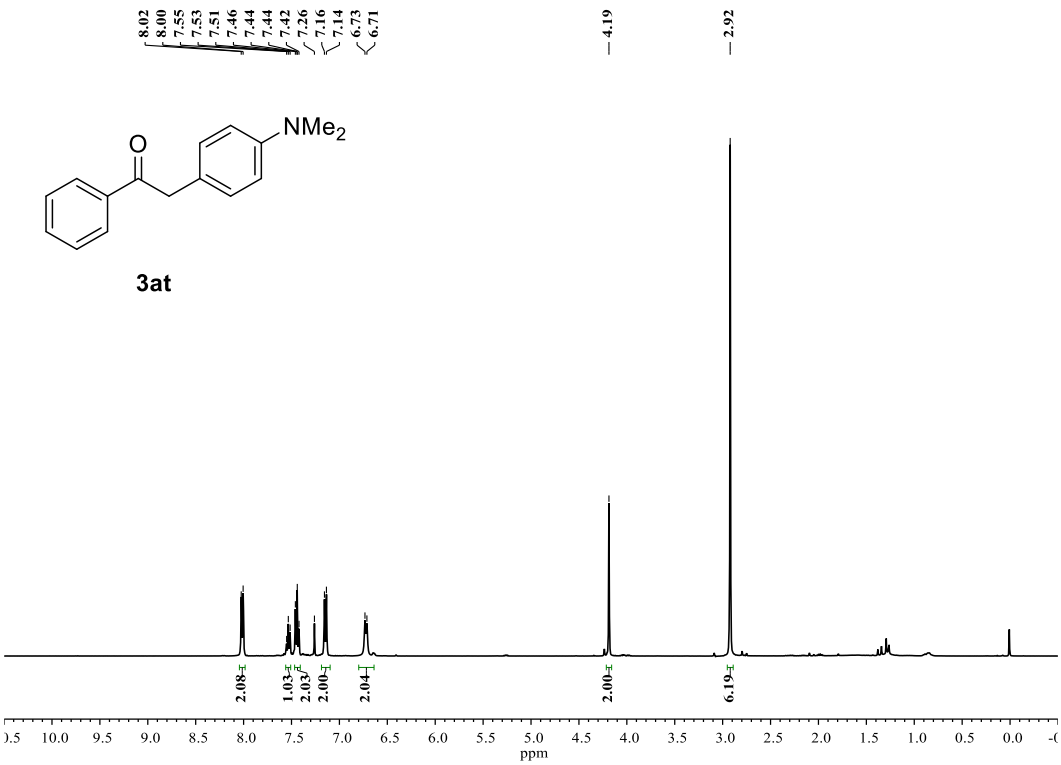
28.97
O
O^{t}Bu
ppm

3as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7.44
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7.26
7.16
7.14
6.73
6.71
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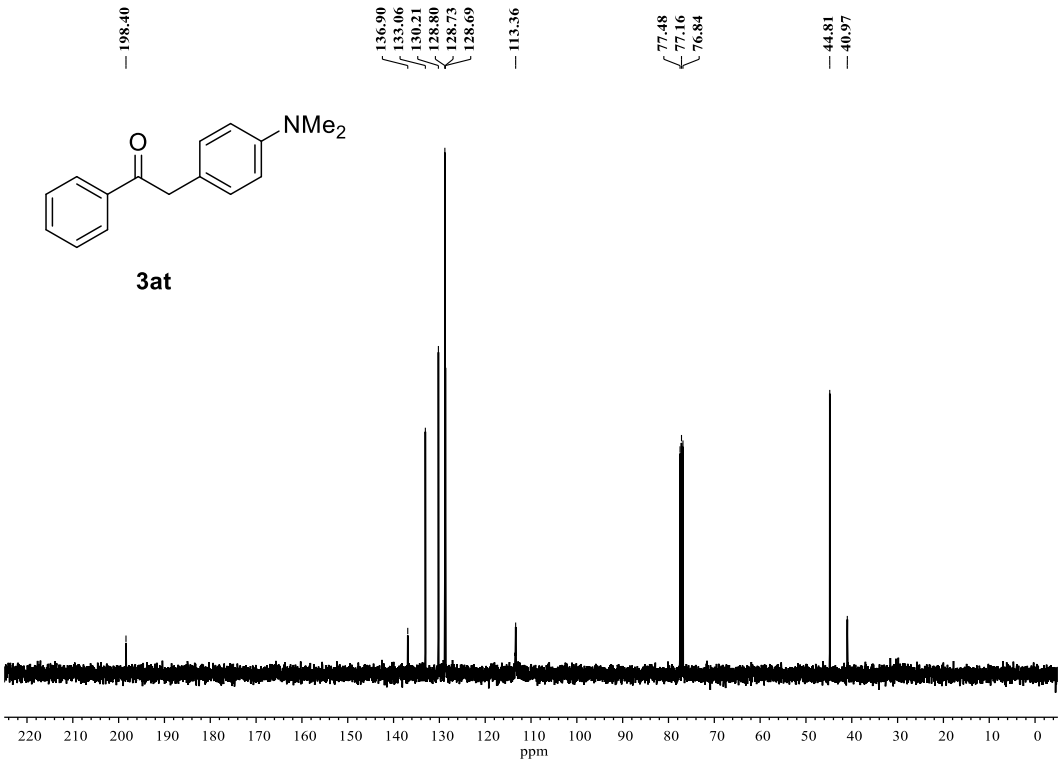
NMe2
O
3at
2.08
1.03
2.03
2.00
2.04
2.00
6.19
ppm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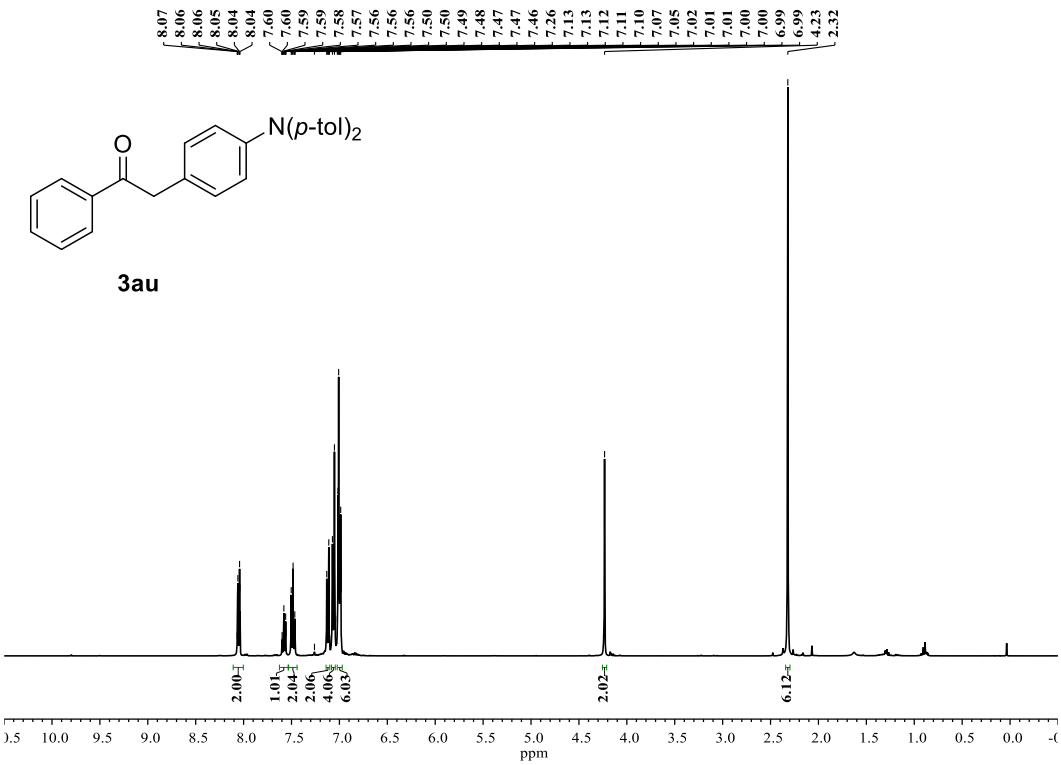
NMe2
O
3at
ppm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8.06
8.05
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7.59
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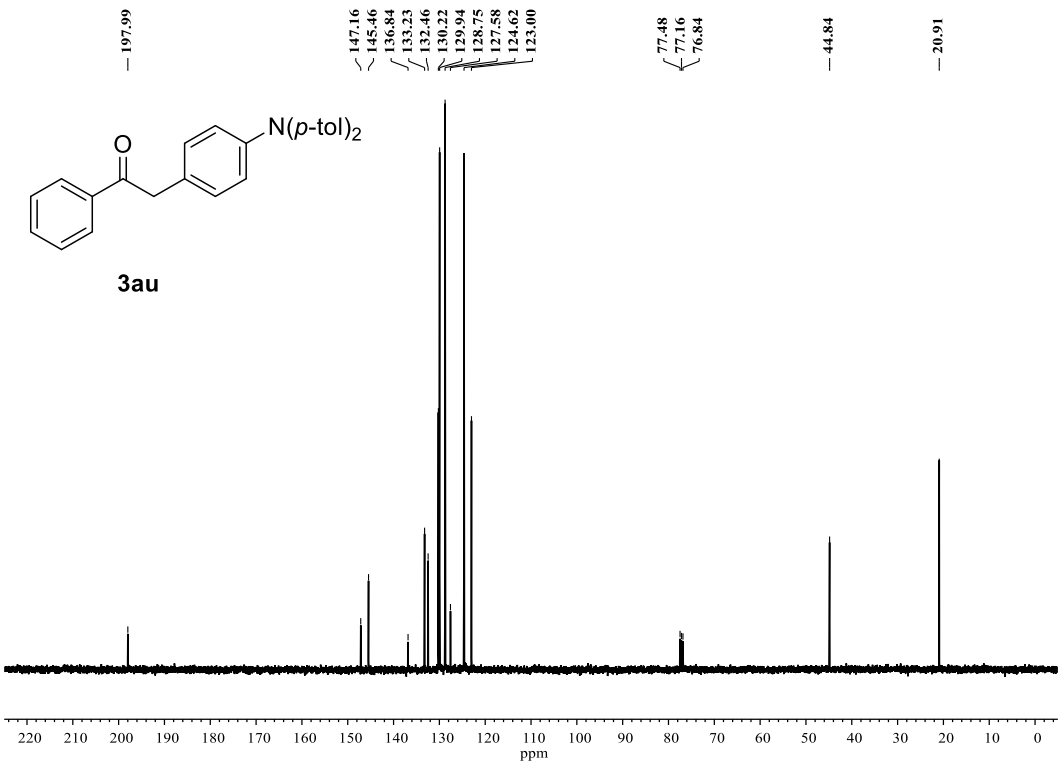
7.56
7.56
7.56
7.50
7.50
7.49
7.48
7.47
7.47
7.46
7.26
7.13
7.13
7.12
7.11
7.10
7.07
7.05
7.02
7.01
7.01
7.00
7.00
6.99
6.99
4.23
2.32
O
N(p-tol)2
2.00
1.01
2.04
2.06
4.06
6.03
2.02
6.12
ppm

3au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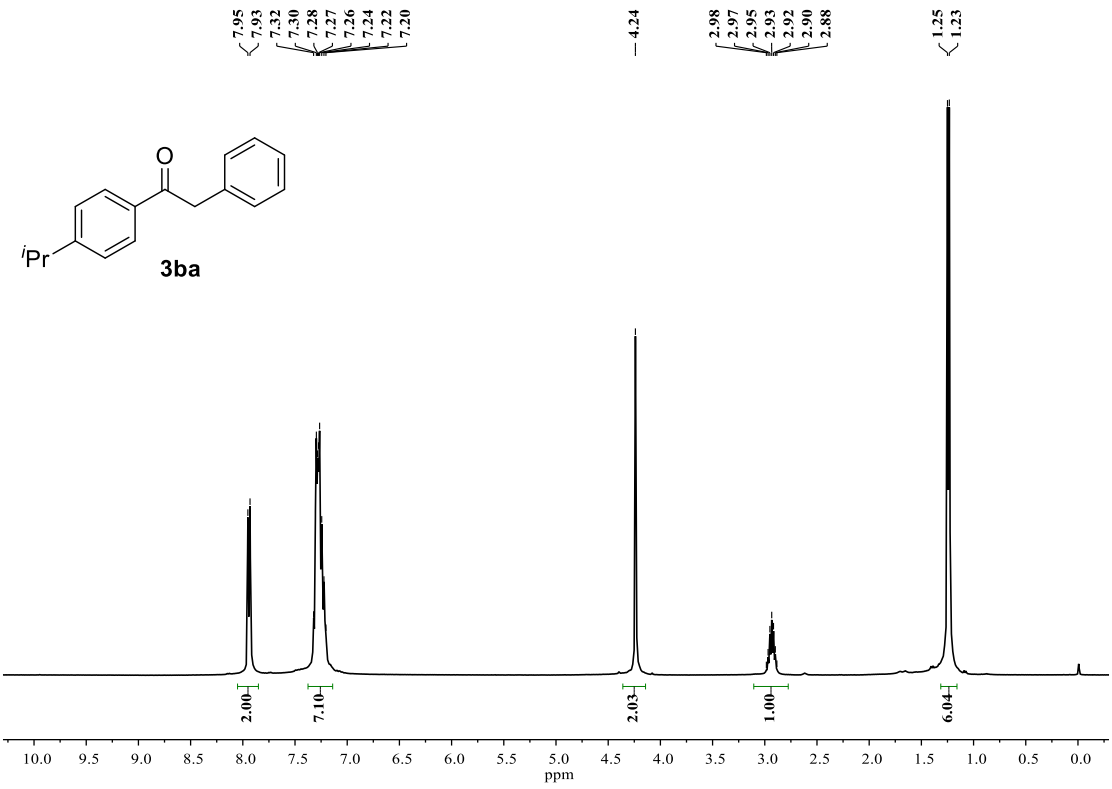
76.84
44.84
20.91
O
N(p-tol)2
ppm

3au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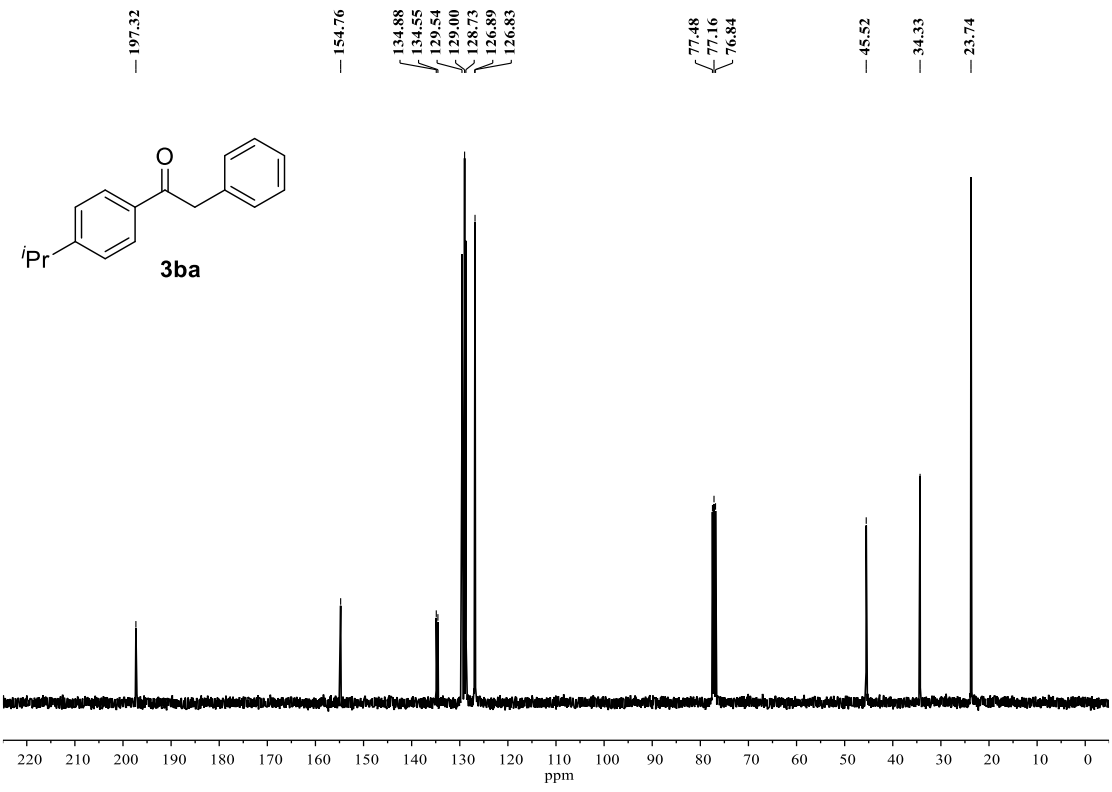
7.27
7.26
7.24
7.22
7.20
4.24
2.98
2.97
2.95
2.93
2.92
2.90
2.88
1.25
1.23
O
iPr
3ba
2.00
7.10
2.03
1.00
6.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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77.48
77.16
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34.33
23.74
O
iPr
3ba
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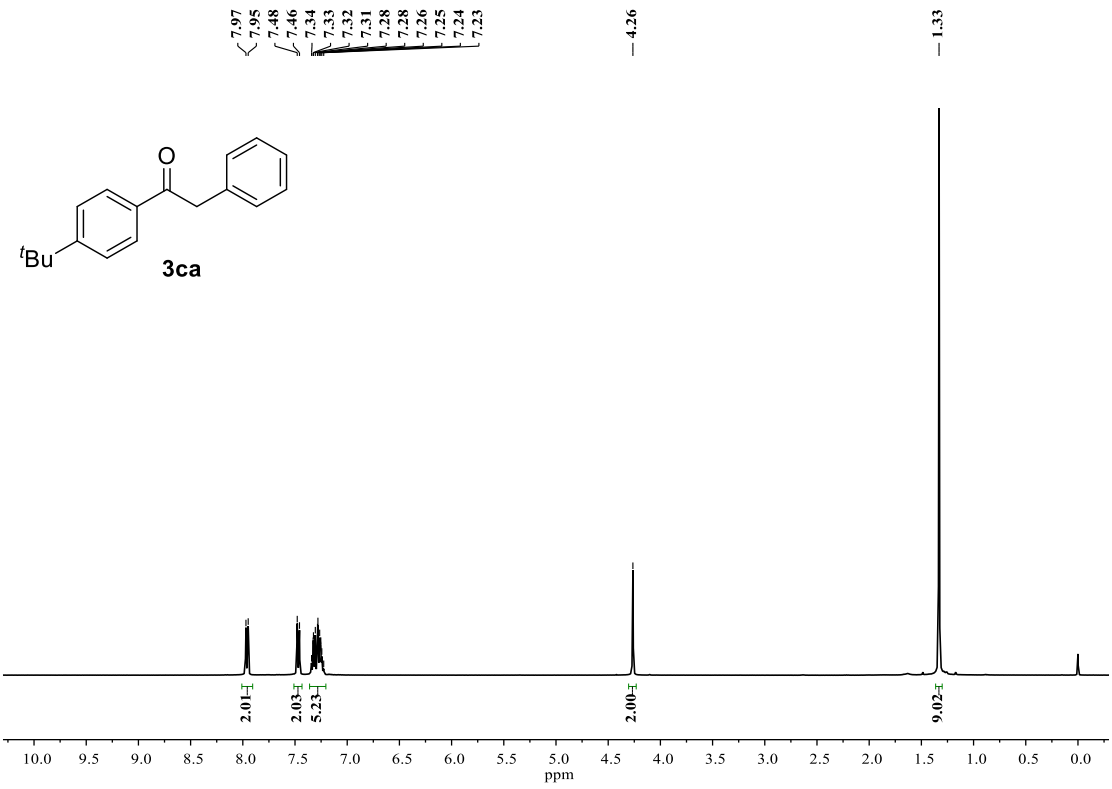
ppm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7.28
7.26
7.25
7.24
7.23
4.26
1.33
O
tBu
3ca
2.01
2.03
5.23
2.00
9.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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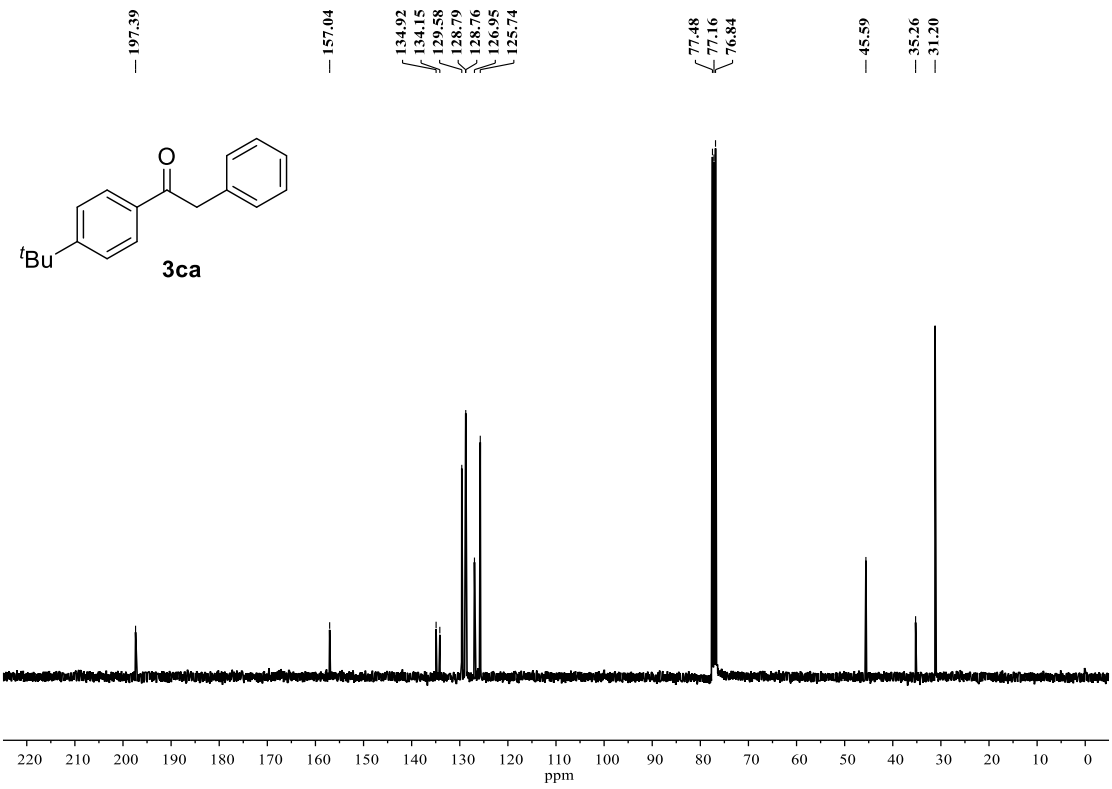
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125.74
77.48
77.16
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35.26
31.20
O
tBu
3ca
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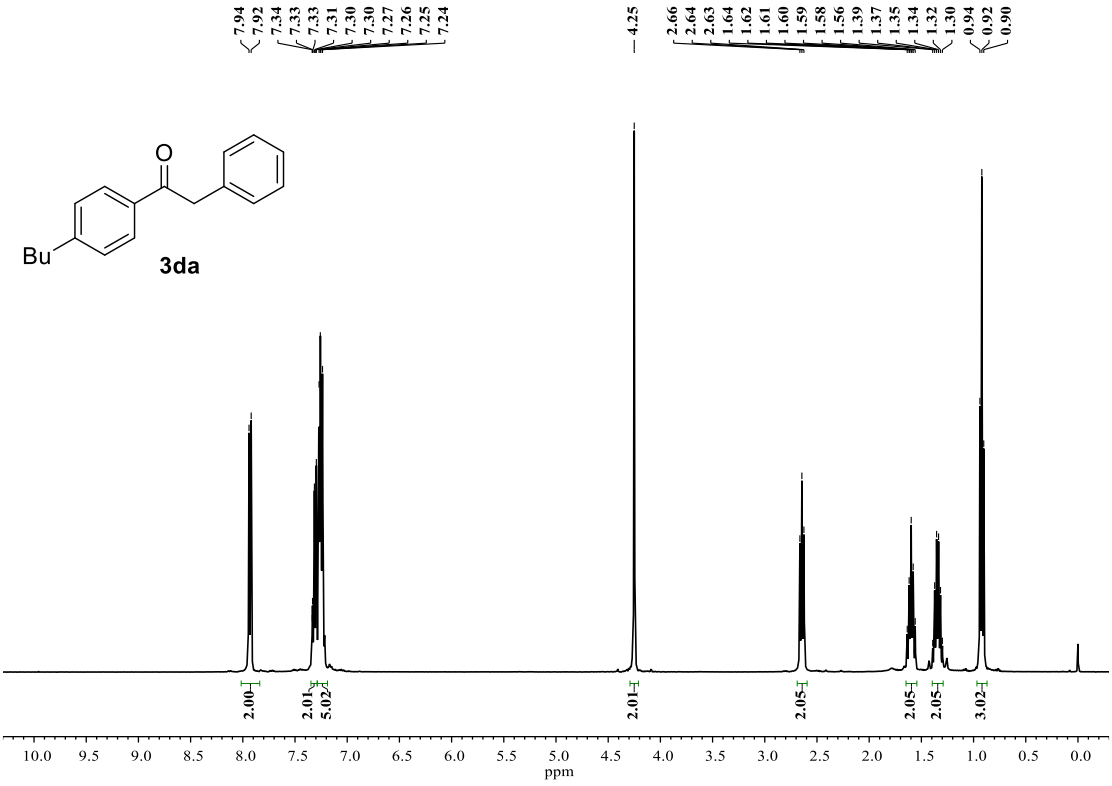
ppm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7.31
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7.30
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7.26
7.25
7.24
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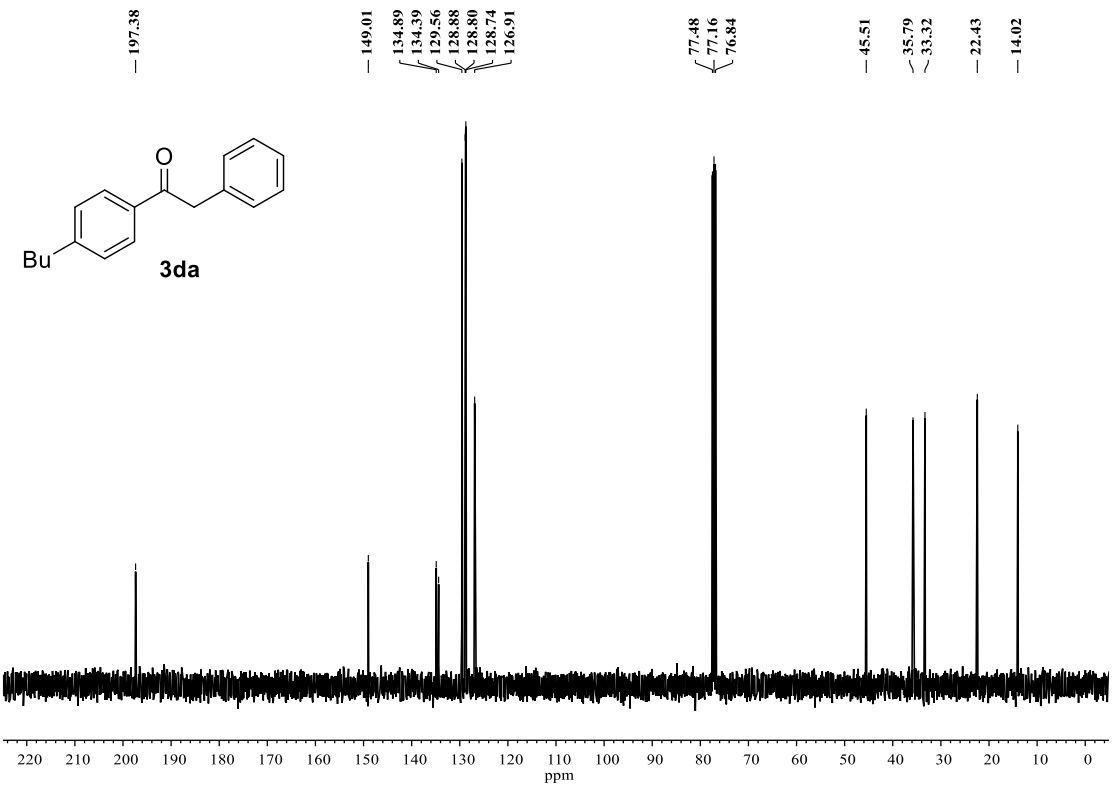
1.62
1.61
1.60
1.59
1.58
1.56
1.39
1.37
1.35
1.34
1.32
1.30
0.94
0.92
0.90
O
Bu
3da
2.00
2.01
5.02
2.01
2.05
2.05
2.05
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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126.91
77.48
77.16
76.84
45.51
35.79
33.32
22.43
14.02
O
Bu
3da
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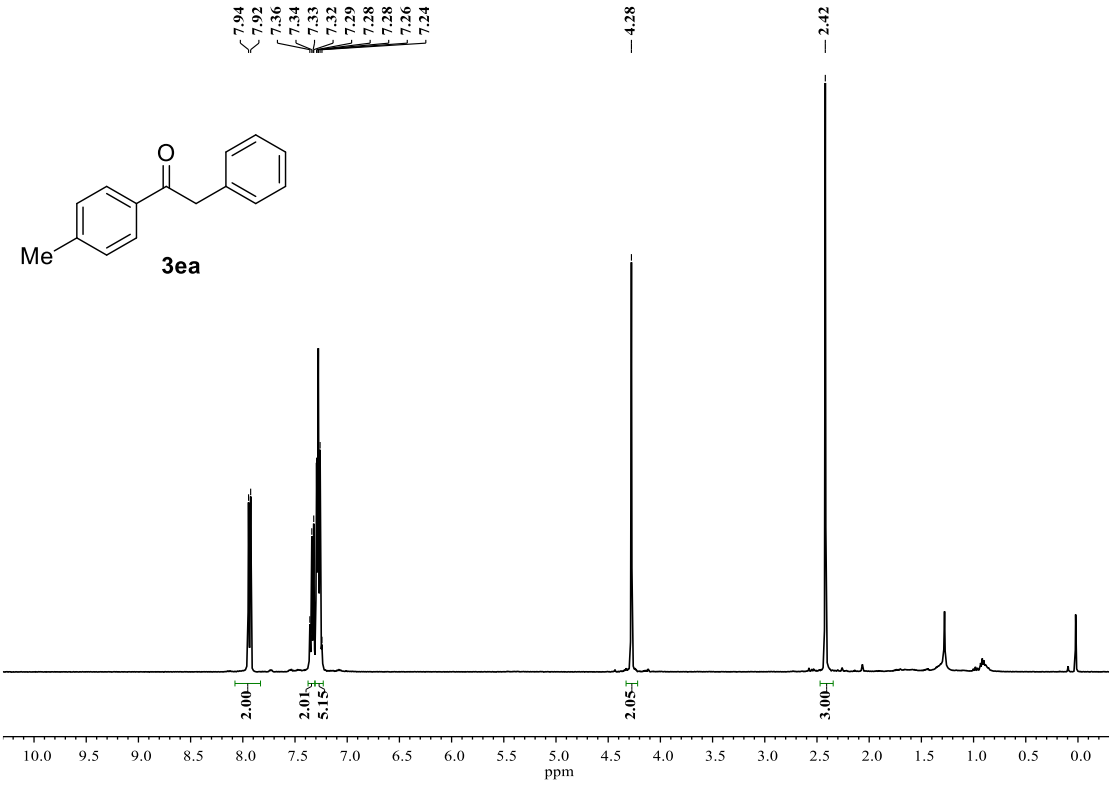
ppm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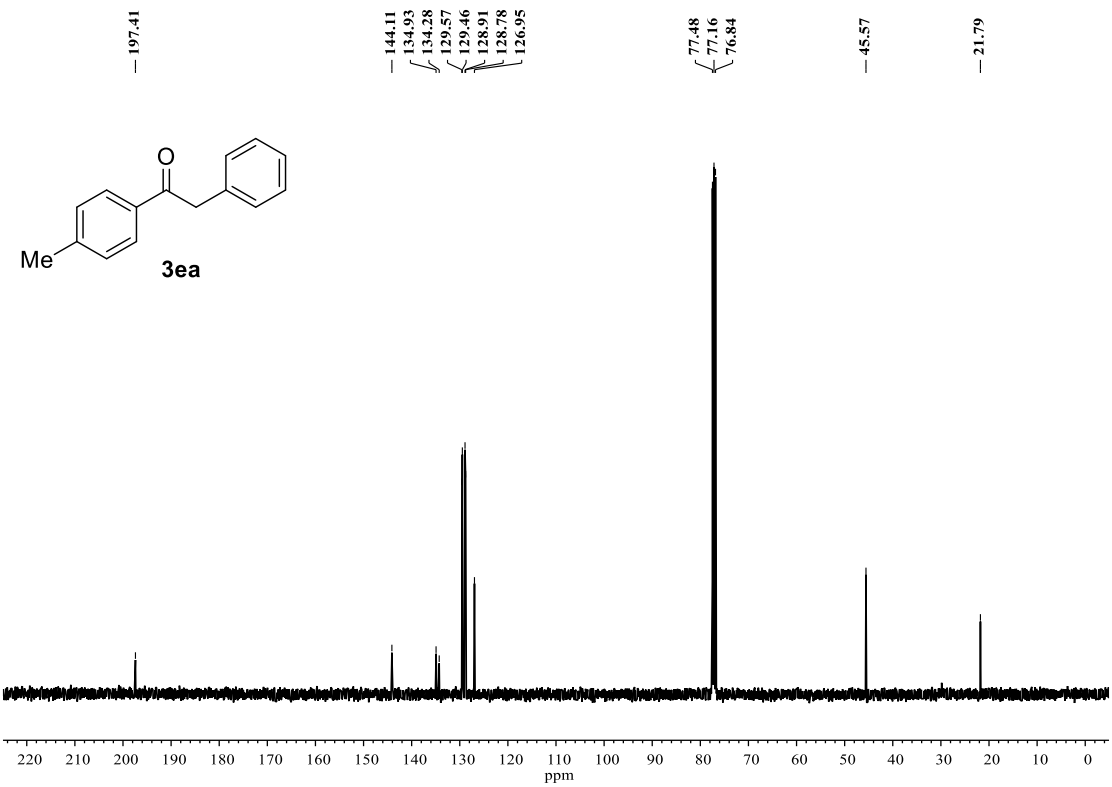
7.32
7.29
7.28
7.28
7.26
7.24
4.28
2.42
O
Me
3ea
2.00
2.01
5.15
2.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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Me
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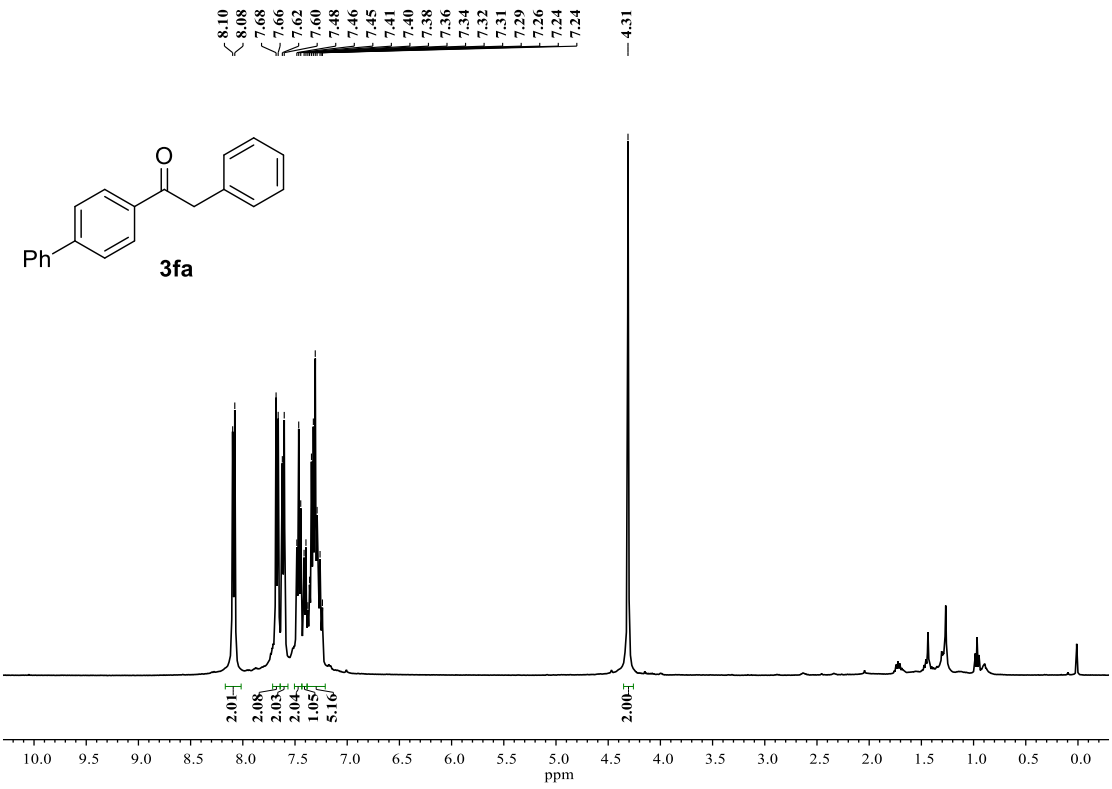
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7.38
7.36
7.34
7.32
7.31
7.29
7.26
7.24
7.24
4.31
O
Ph
3fa
2.01
2.08
2.03
2.04
1.05
5.16
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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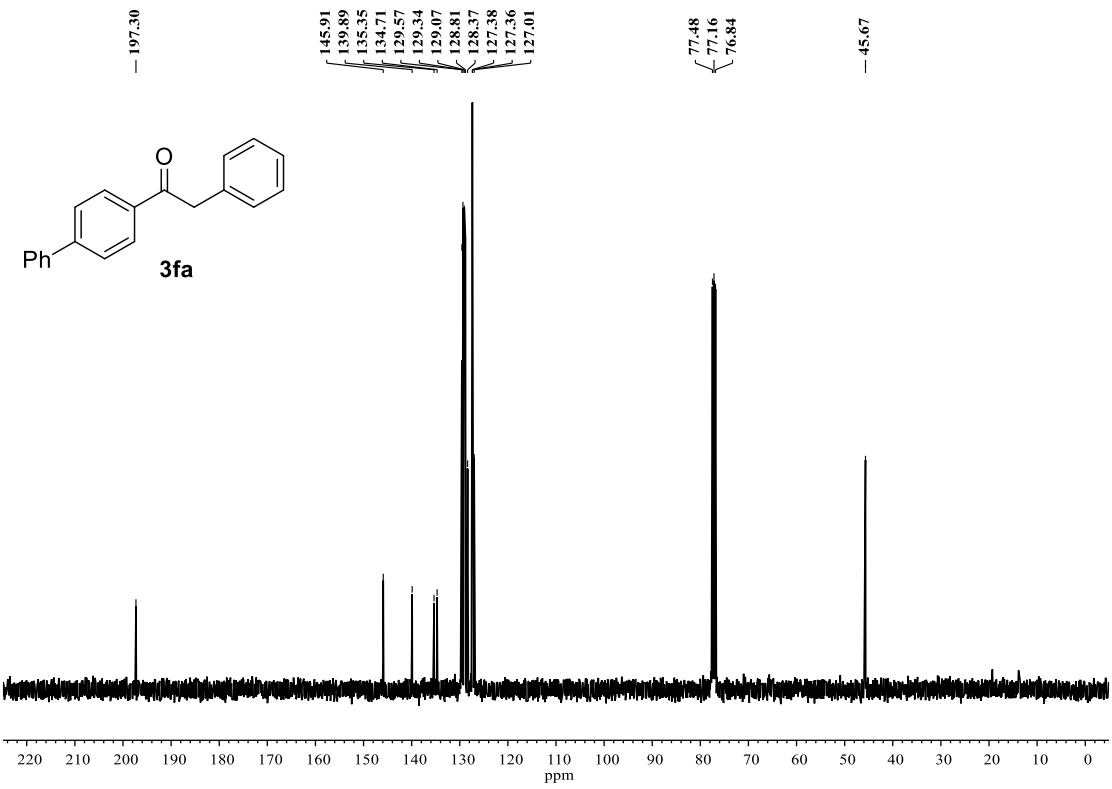
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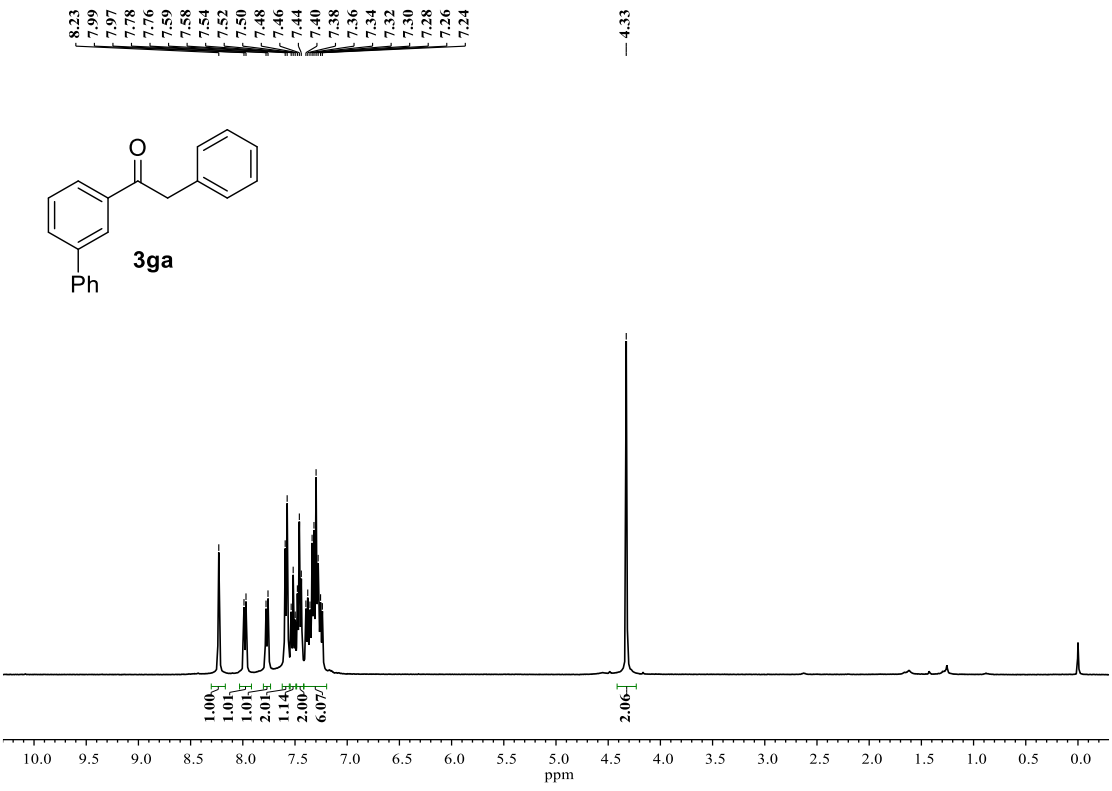
ppm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7.38
7.36
7.34
7.32
7.30
7.28
7.26
7.24
4.33
O
Ph
3ga
1.00
1.01
1.01
2.01
1.14
2.00
6.07
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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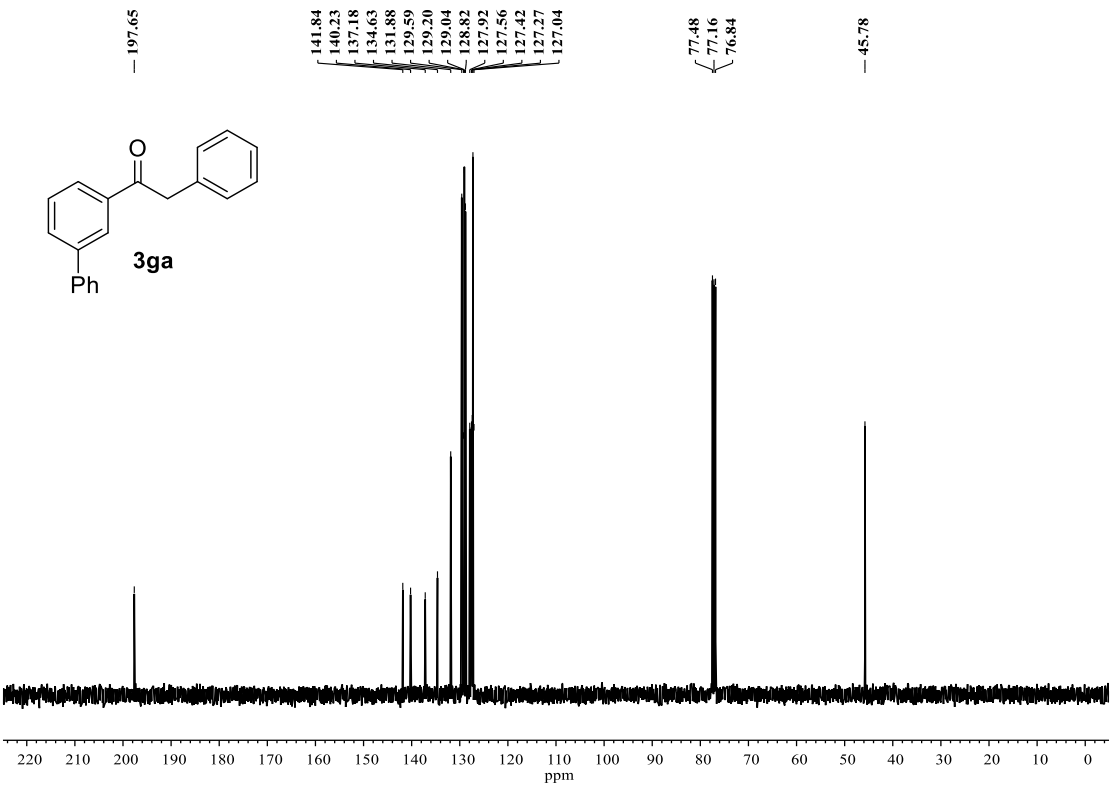
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127.27
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76.84
45.78
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Ph
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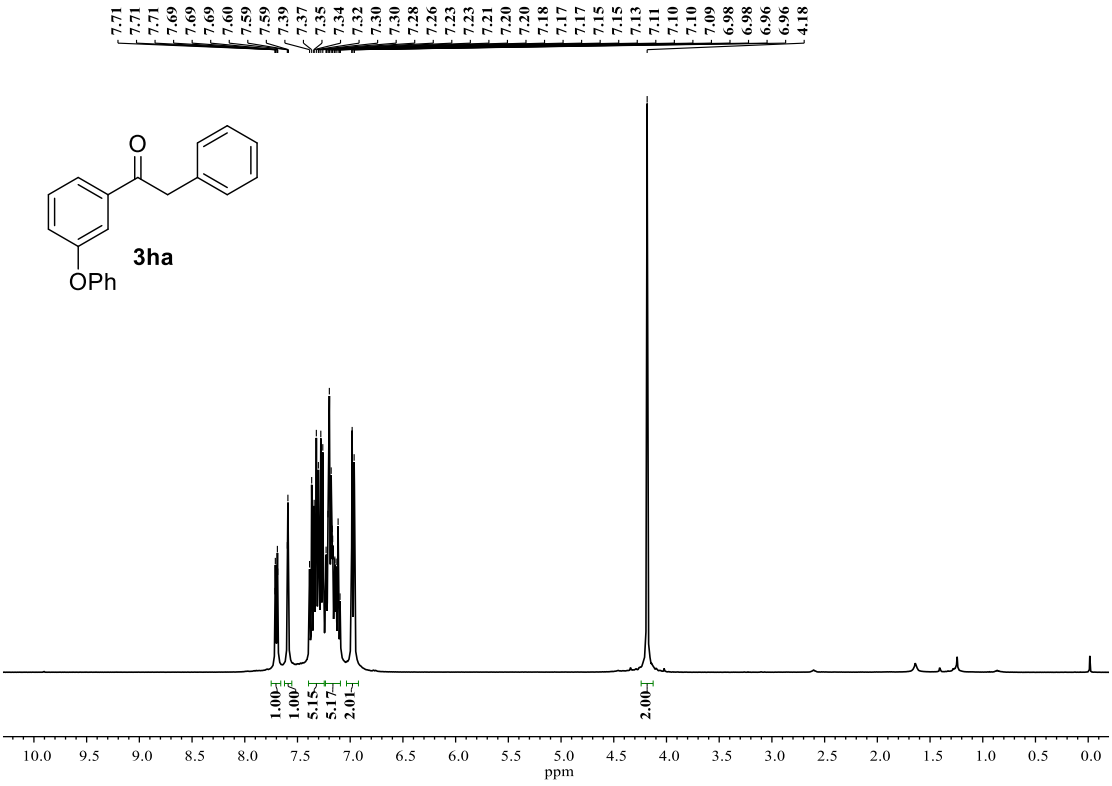
ppm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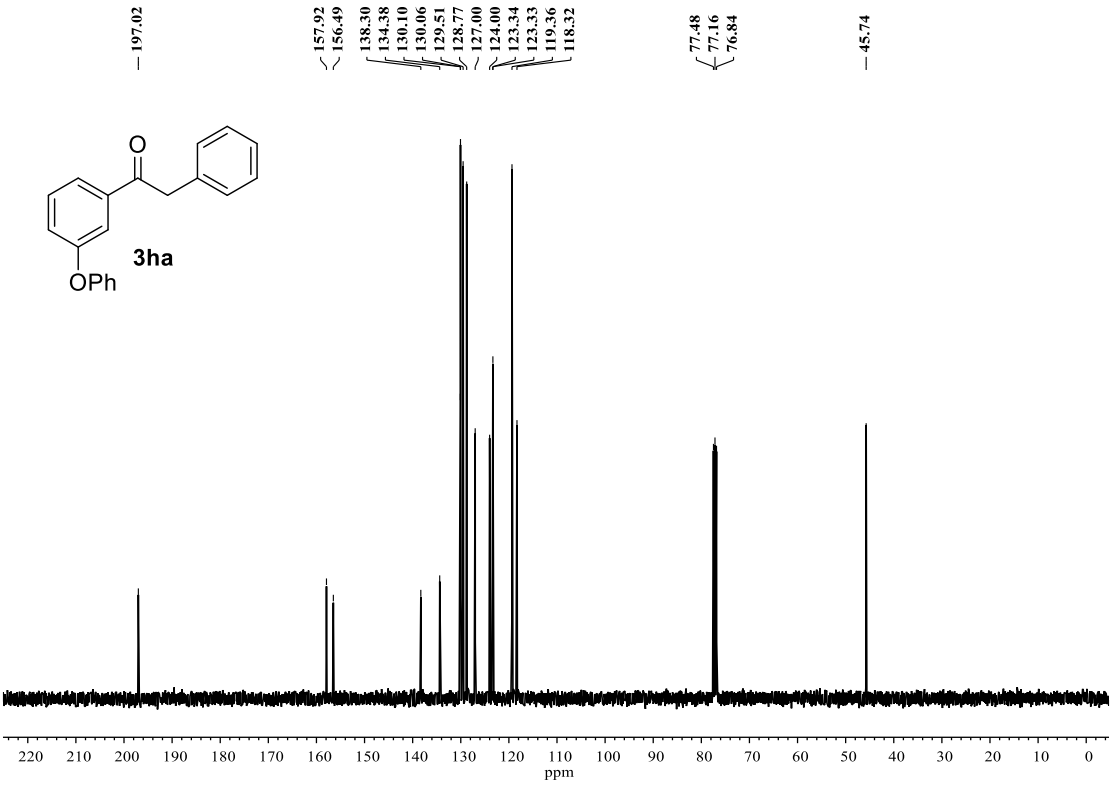
7.20
7.20
7.18
7.17
7.17
7.15
7.15
7.13
7.11
7.10
7.10
7.09
6.98
6.98
6.96
6.96
4.18
O
3ha
OPh
1.00
1.00
5.15
5.17
2.01
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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124.00
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123.33
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118.32
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76.84
45.74
O
3ha
OPh
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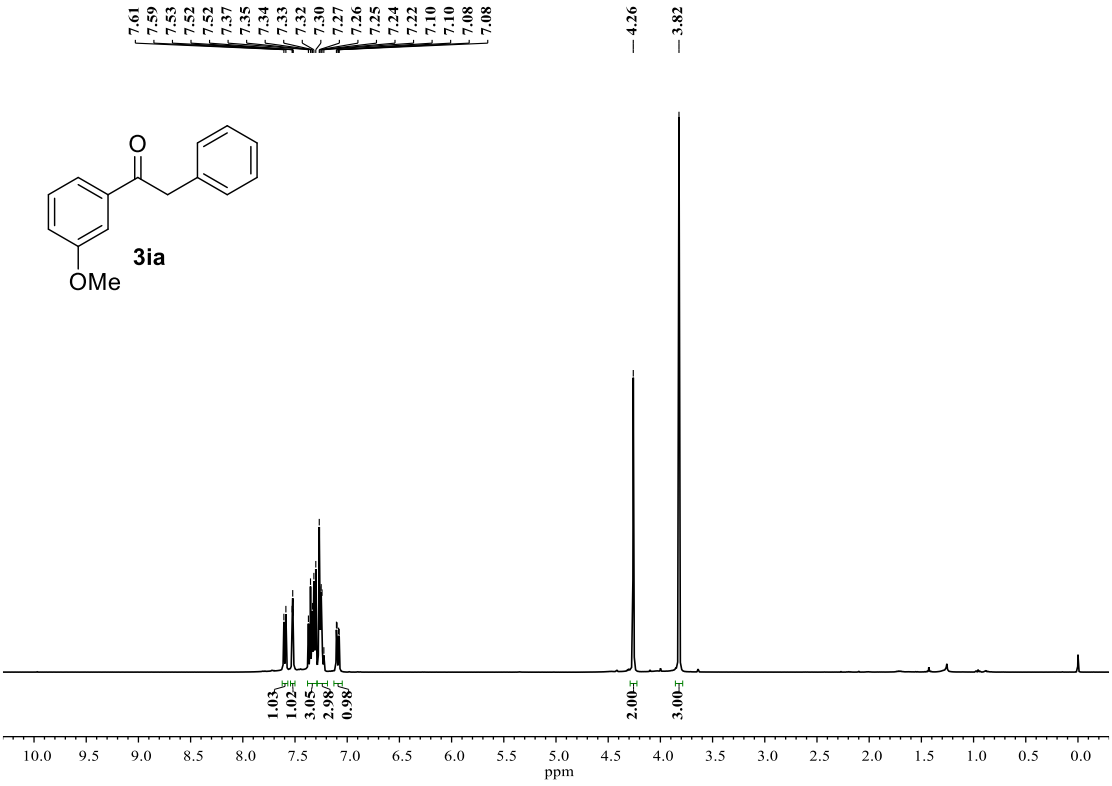
ppm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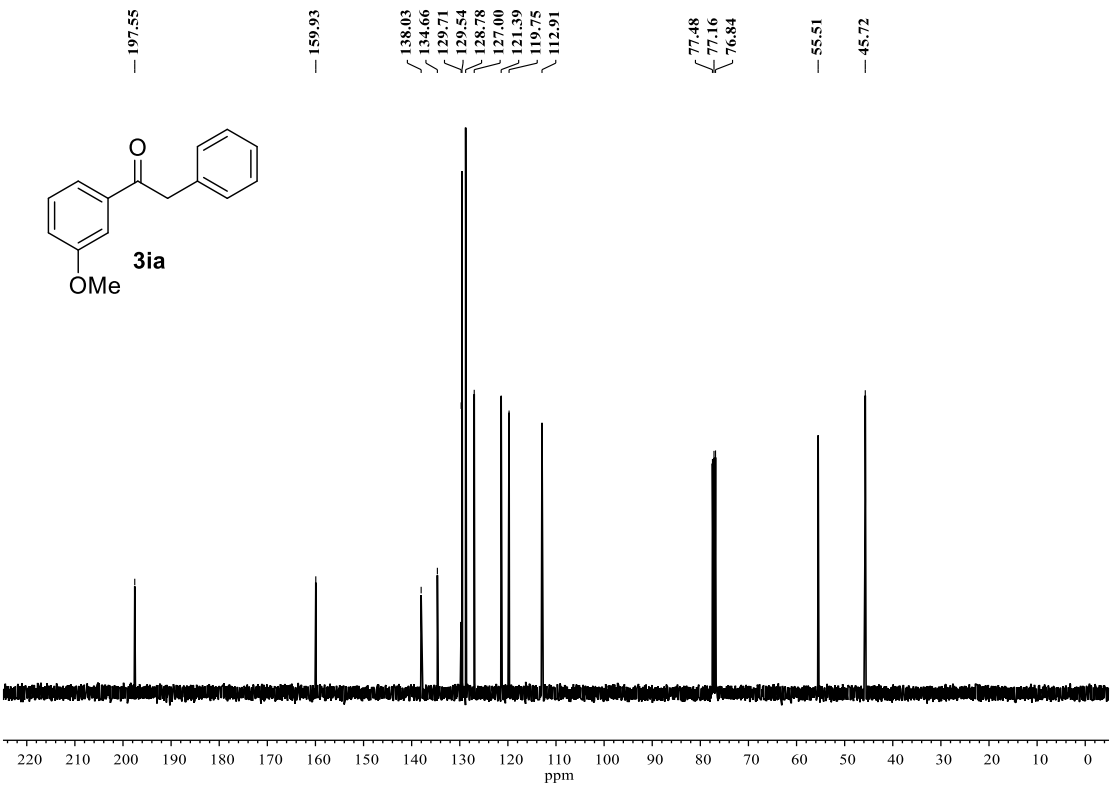
7.27
7.26
7.25
7.24
7.22
7.10
7.10
7.08
7.08
4.26
3.82
O
3ia
OMe
1.03
1.02
3.05
2.98
0.98
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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127.00
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112.91
77.48
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76.84
55.51
45.72
O
3ia
OMe
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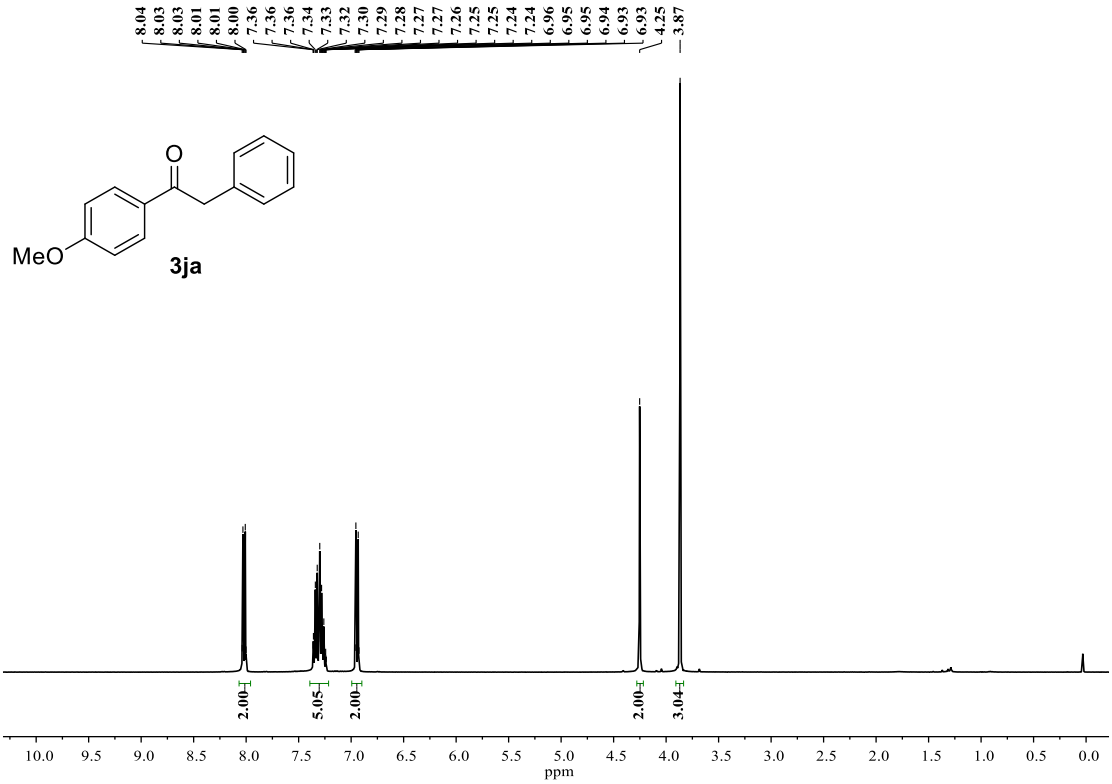
ppm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8.03
8.03
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7.27
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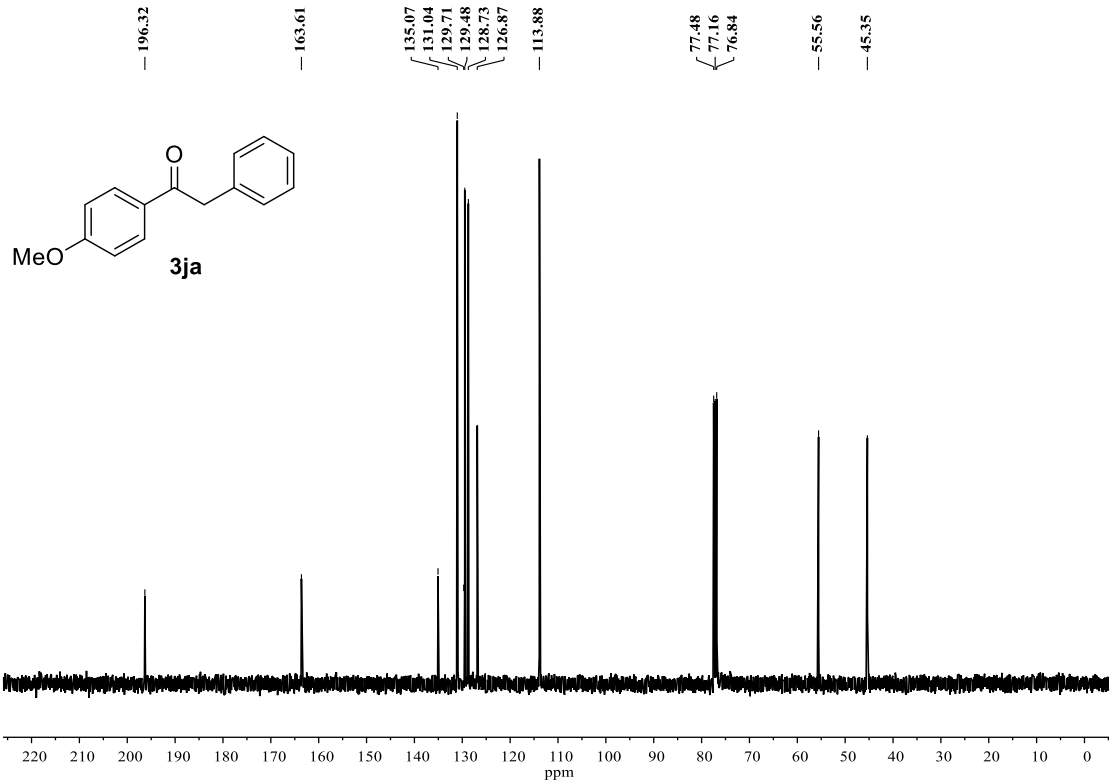
7.25
7.25
7.24
7.24
6.96
6.95
6.95
6.94
6.93
6.93
4.25
3.87
O
MeO
3ja
2.00
5.05
2.00
2.00
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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126.87
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77.48
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55.56
45.35
O
MeO
3ja
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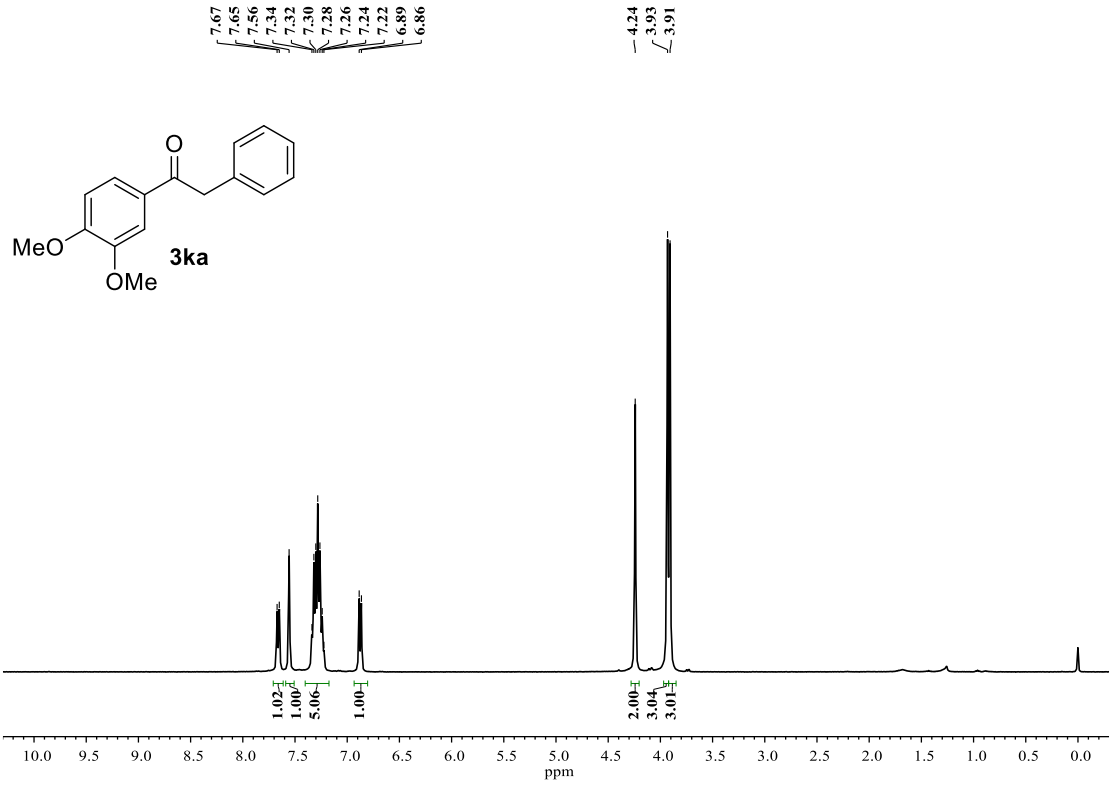
ppm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7.26
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7.22
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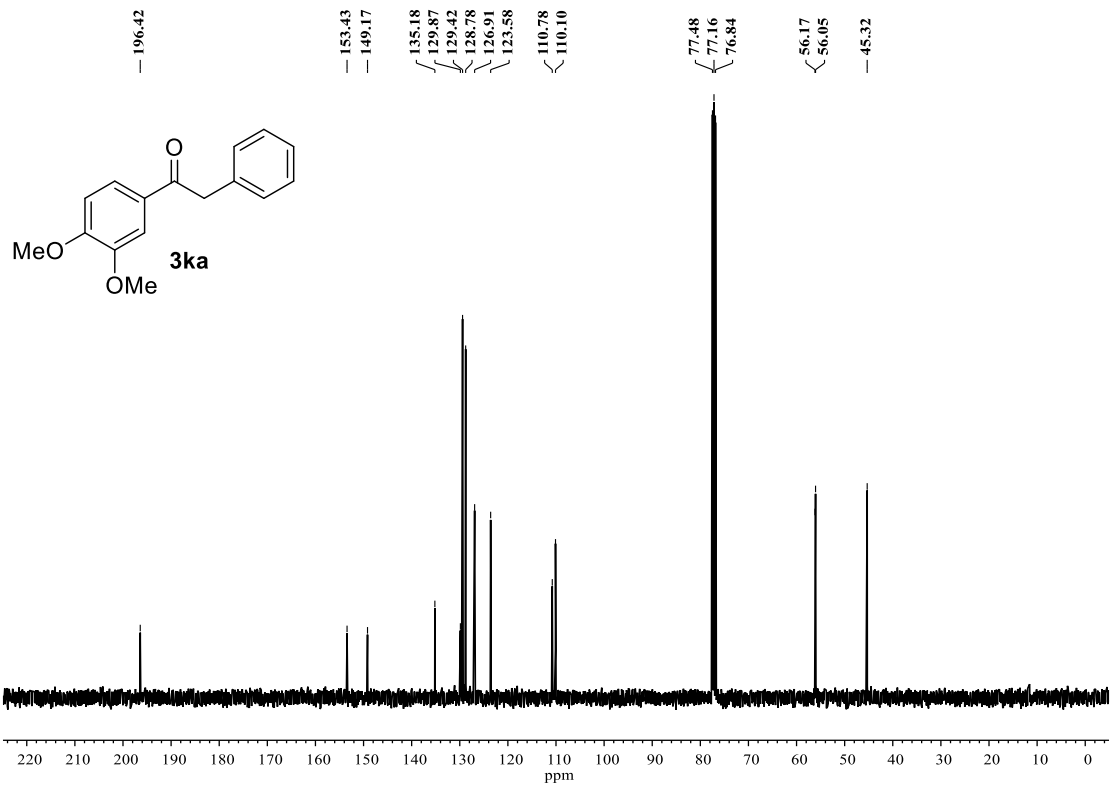
6.86
4.24
3.93
3.91
MeO
OMe
3ka
1.02
1.00
5.06
1.00
2.00
3.04
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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77.48
77.16
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56.05
45.32
MeO
OMe
3ka
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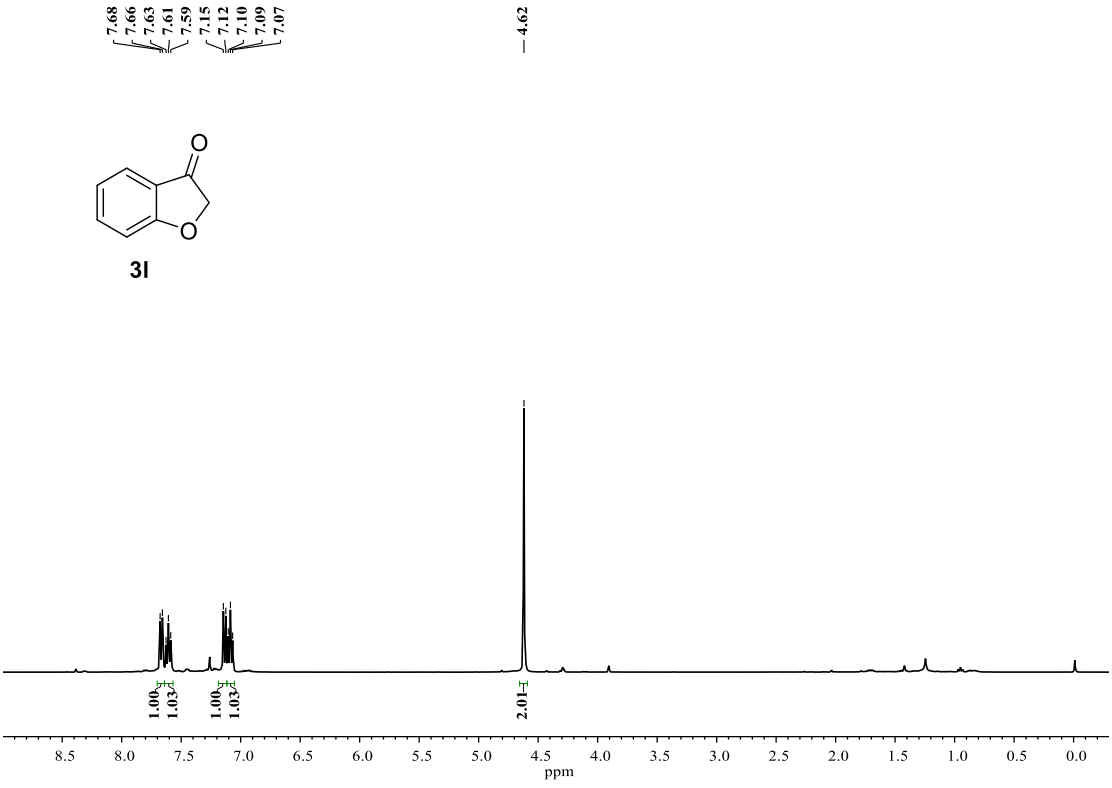
ppm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7.10
7.09
7.07
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O
O
3l
1.00
1.03
1.00
1.03
2.01
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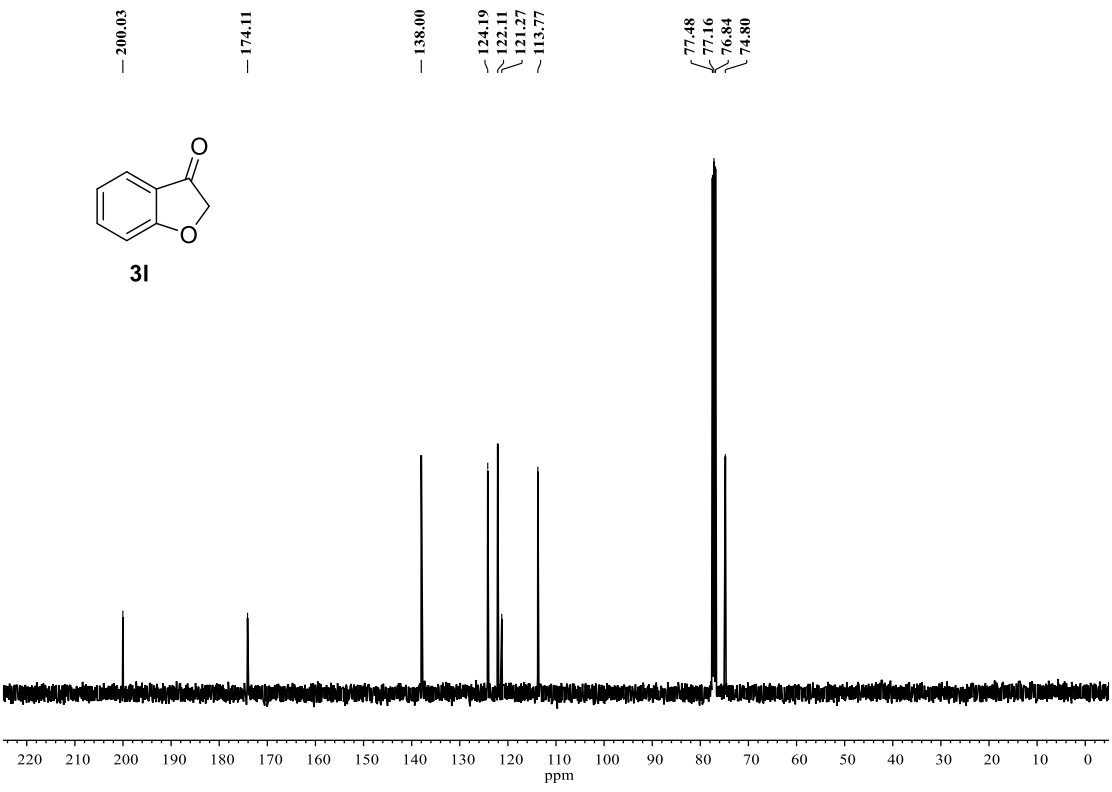
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76.84
74.80
O
O
3l
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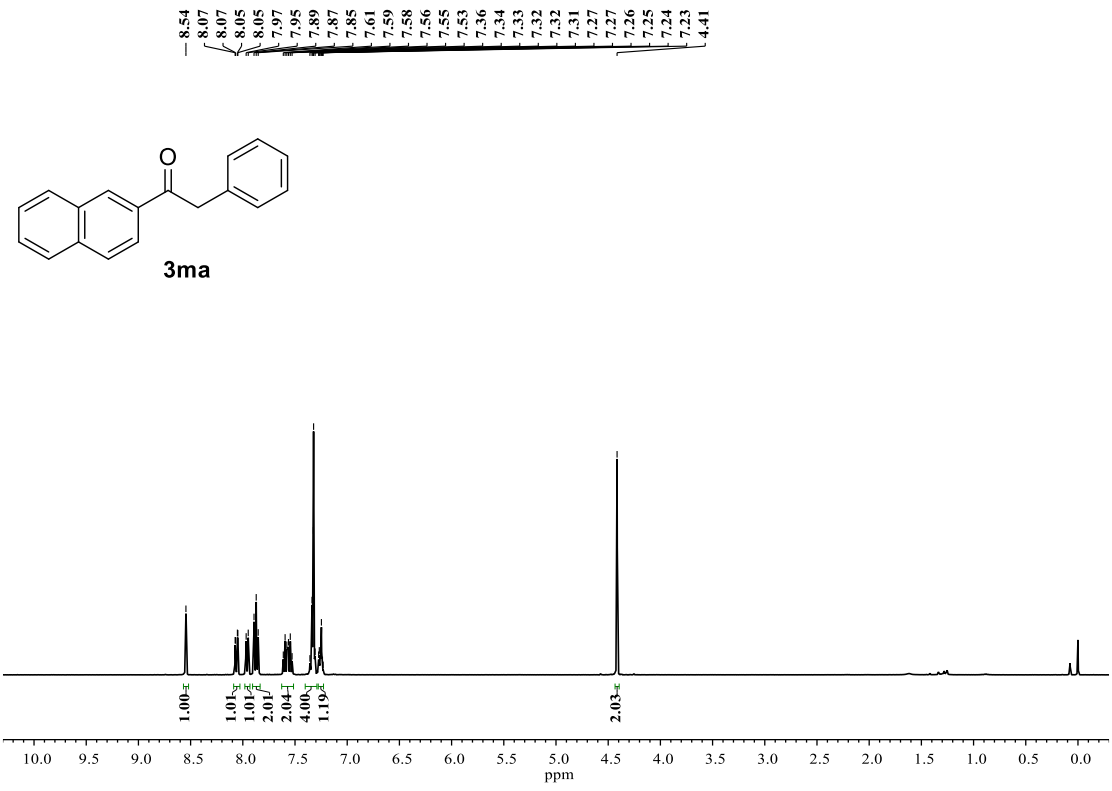
ppm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7.89
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7.58
7.56
7.55
7.53
7.36
7.34
7.33
7.32
7.32
7.31
7.27
7.27
7.26
7.25
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3ma
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1.01
1.01
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2.04
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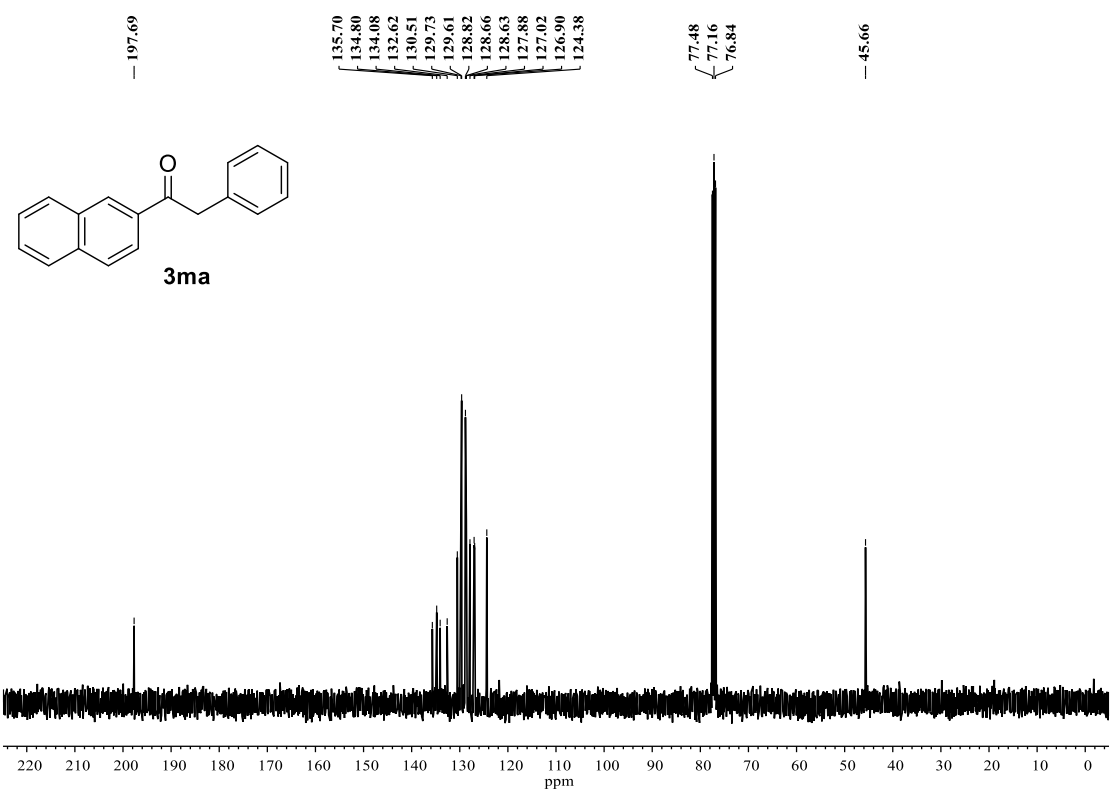
2.03
ppm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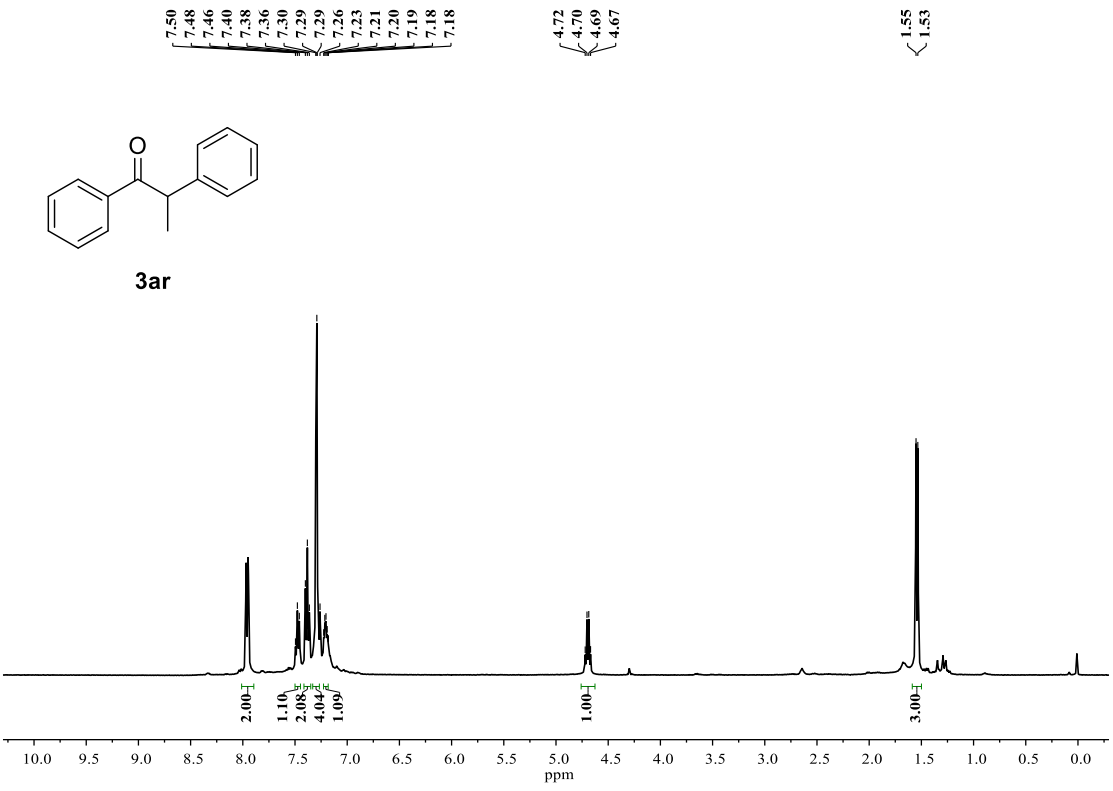
77.16
76.84
45.66
3ma
ppm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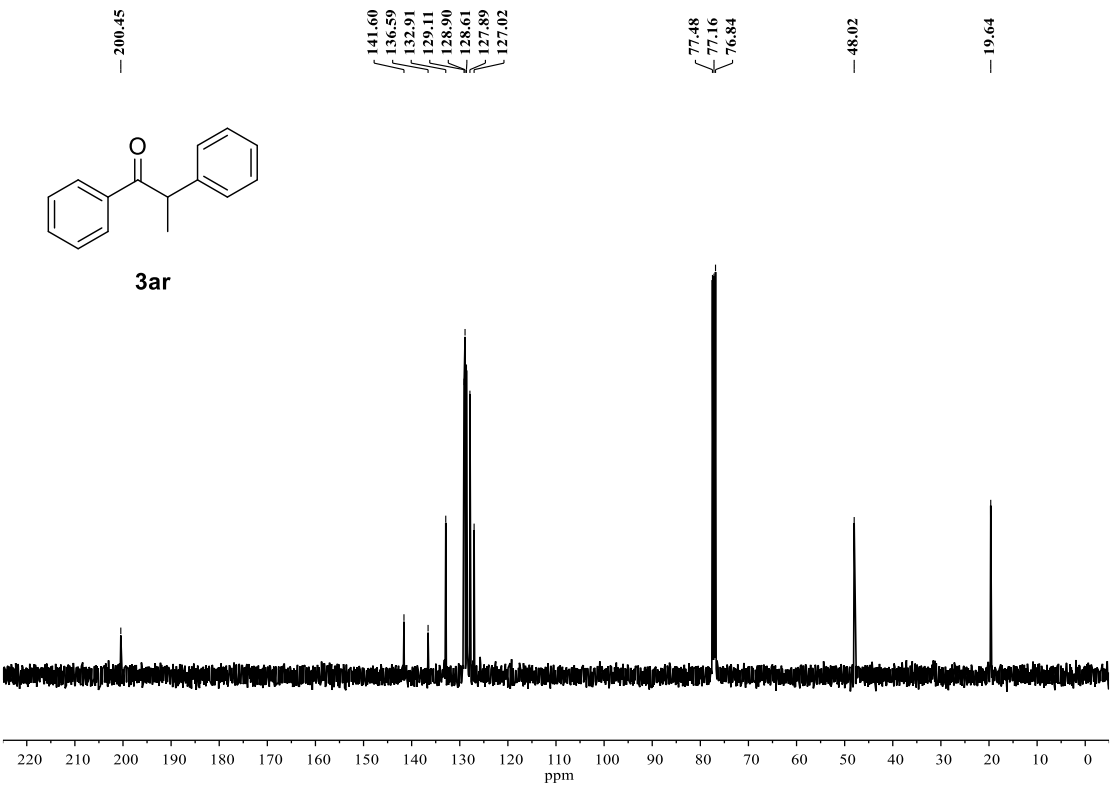
7.20
7.19
7.18
7.18
4.72
4.70
4.69
4.67
1.55
1.53
O
3ar
2.00
1.10
2.08
4.04
1.09
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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128.61
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127.02
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48.02
19.64
O
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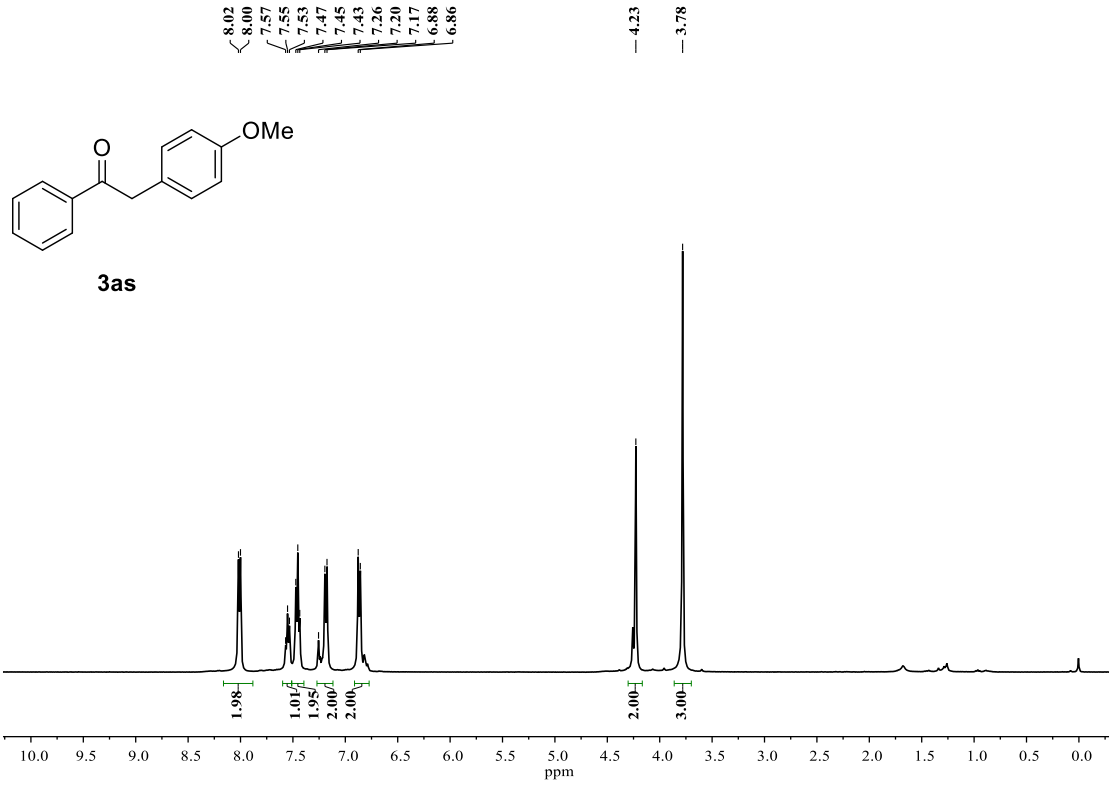
ppm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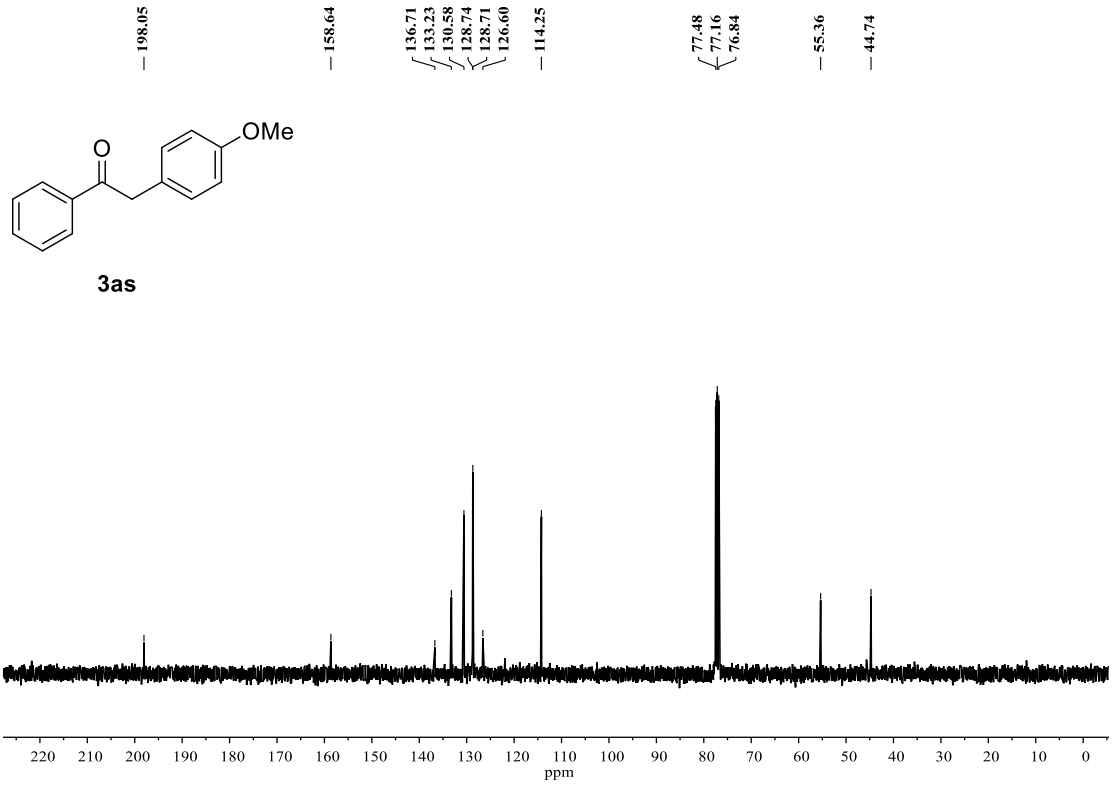
7.17
6.88
6.86
4.23
3.78
O
OMe
1.98
1.01
1.95
2.00
2.00
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

3as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126.60
114.25
77.48
77.16
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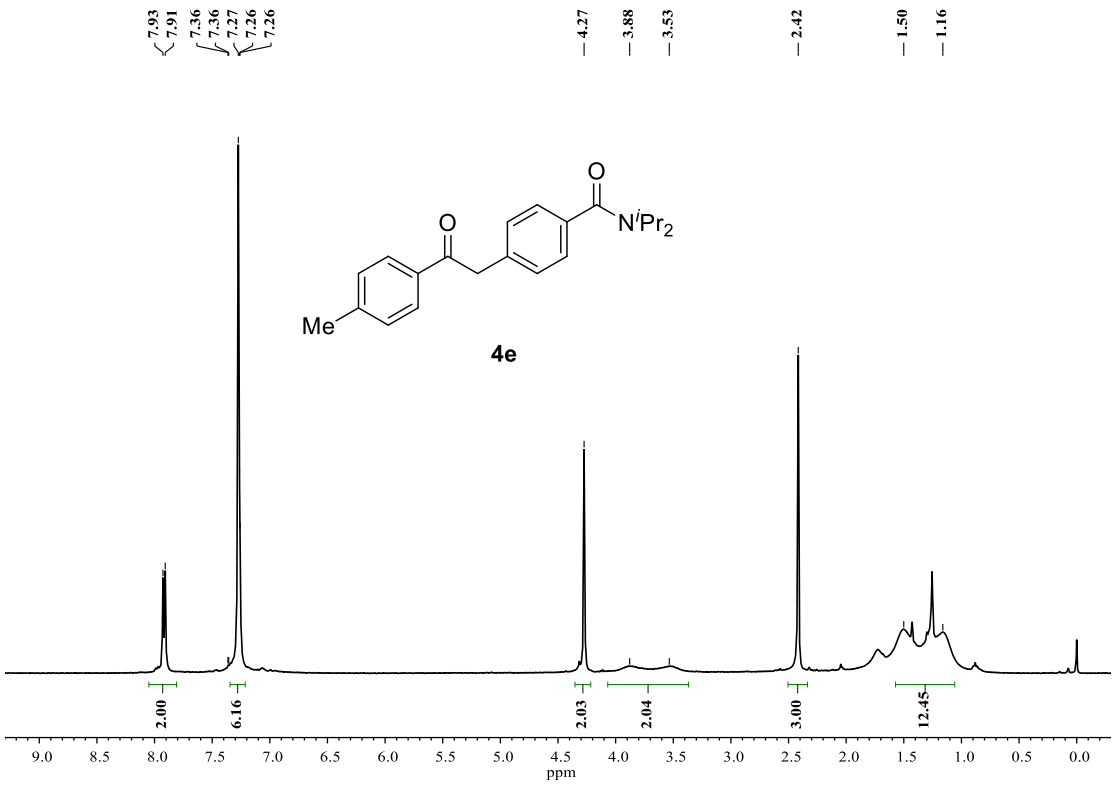
55.36
44.74
O
OMe
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

3as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7.26
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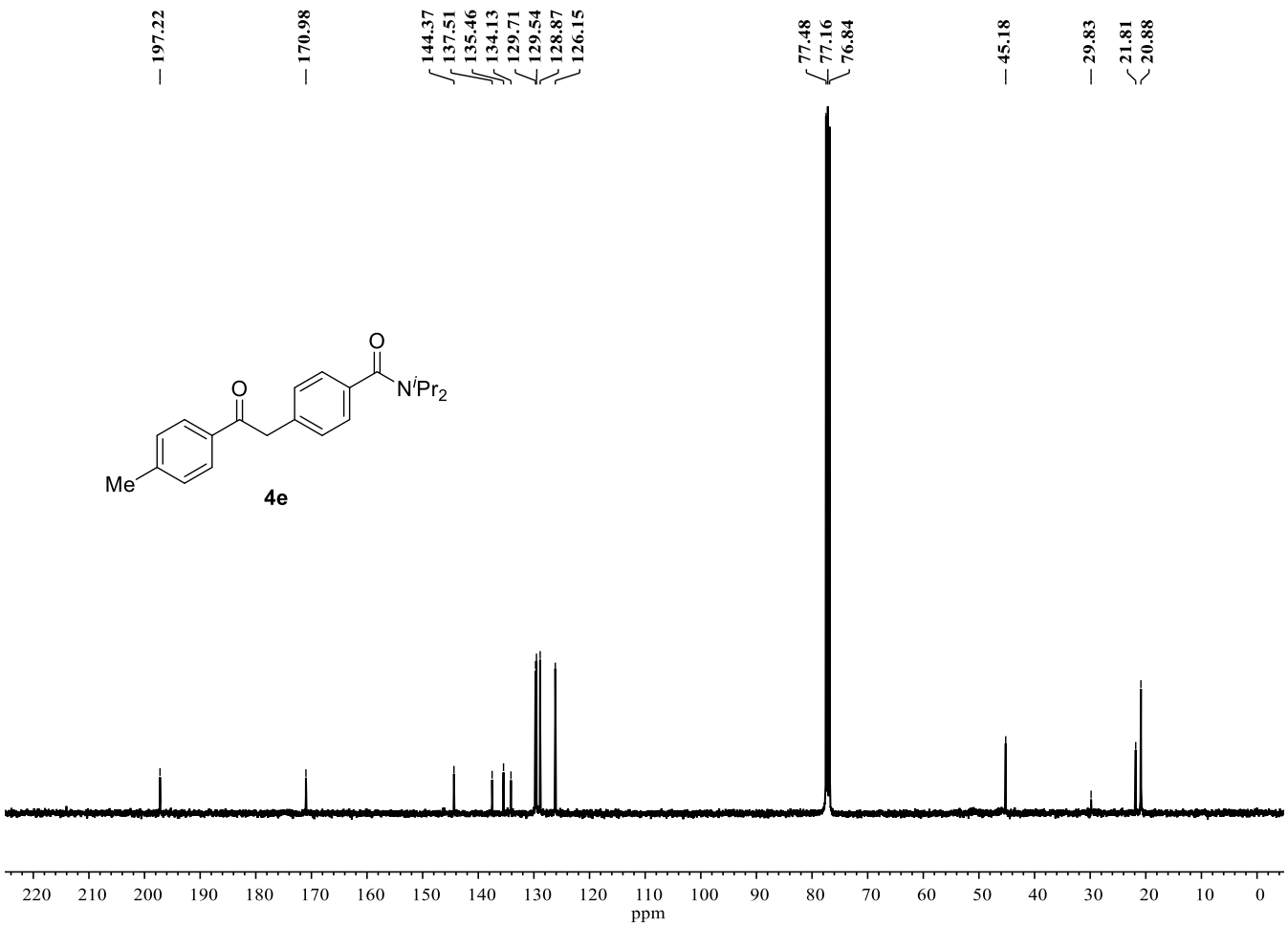
3.53
2.42
1.50
1.16
O
O
N^{i}Pr$_2$
Me
4e
2.00
6.16
2.03
2.04
3.00
12.45
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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76.84
45.18
29.83
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O
N^{i}Pr$_2$
Me
4e
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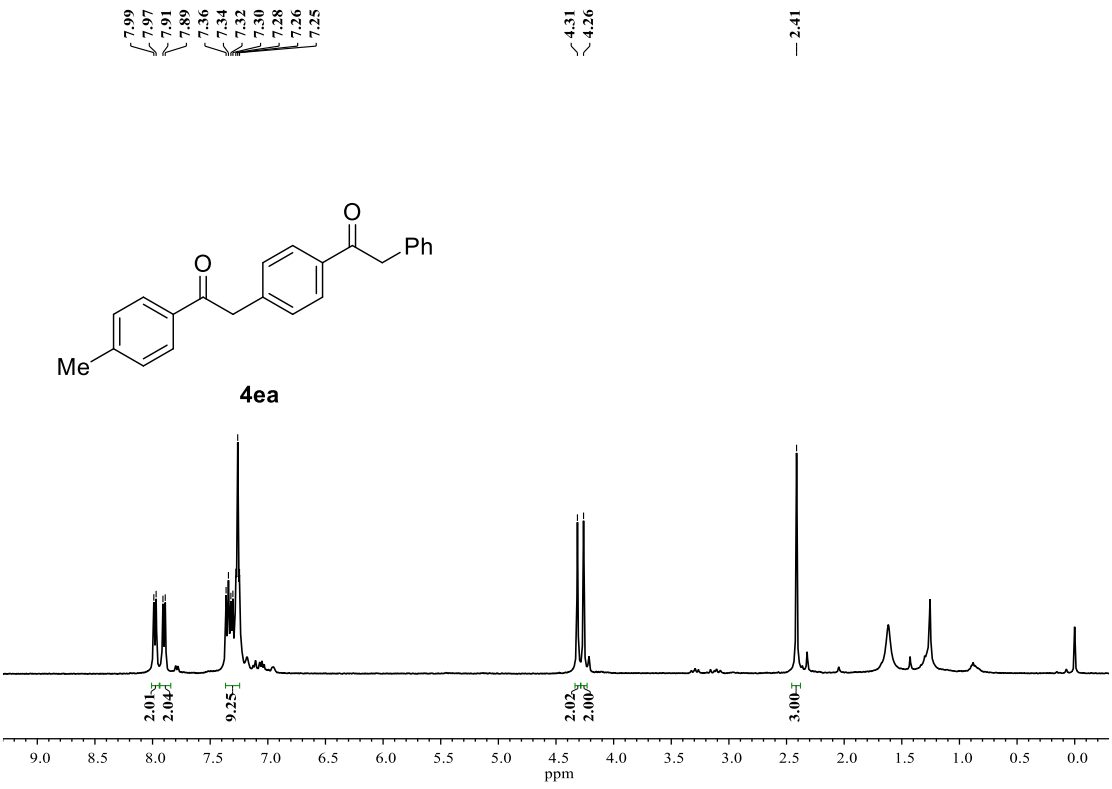
ppm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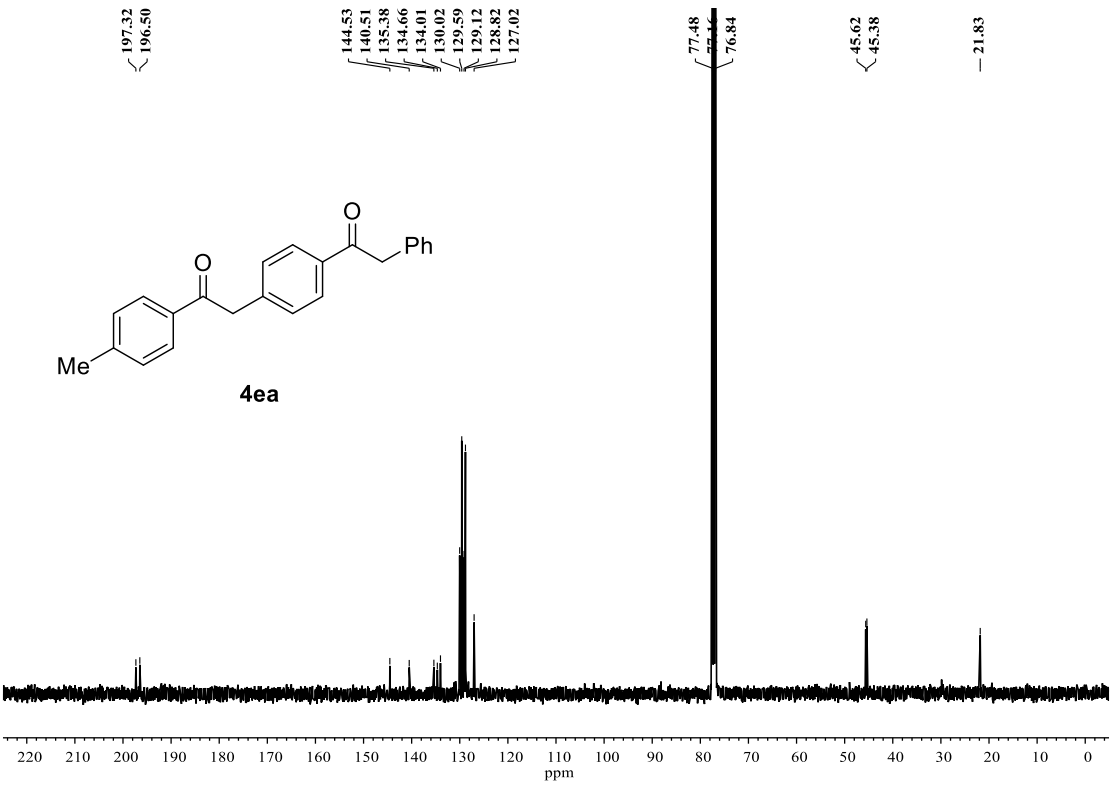
7.26
7.25
4.31
4.26
2.41
O
O
Ph
Me
4ea
2.01
2.04
9.25
2.02
2.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm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130.02
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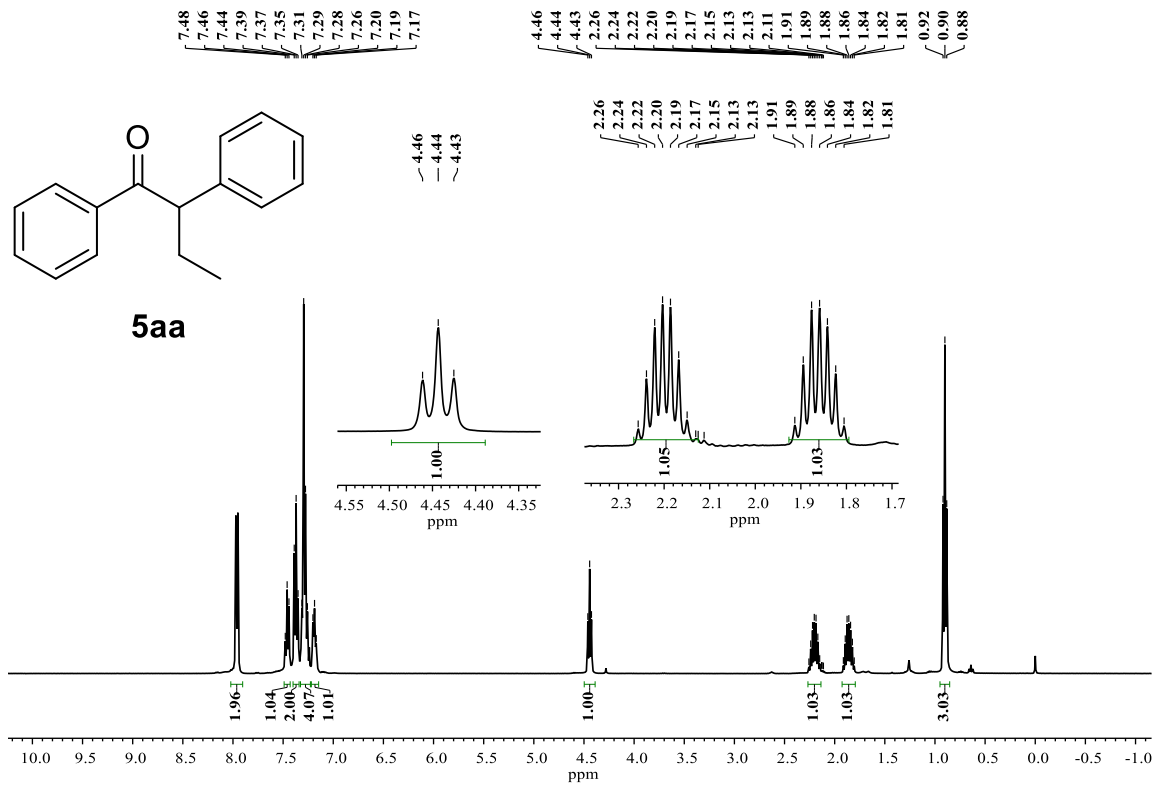
129.12
128.82
127.02
77.48
76.84
45.62
45.38
21.83
O
O
Ph
Me
4ea
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm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7.19
7.17
4.46
4.44
4.43
2.26
2.24
2.22
2.20
2.19
2.17
2.15
2.13
2.13
2.11
1.91
1.89
1.88
1.86
1.84
1.82
1.81
0.92
0.90
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O
5aa
1.00
1.05
1.03
1.96
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2.00
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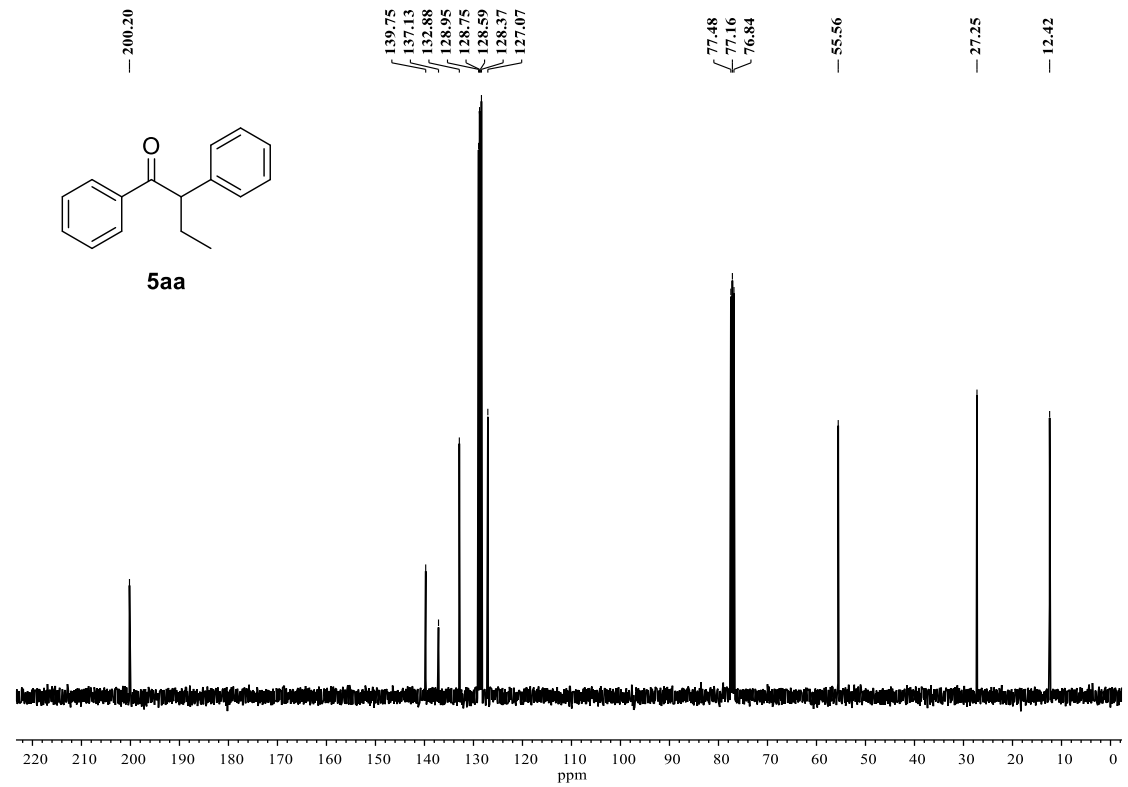
1.01
3.03
ppm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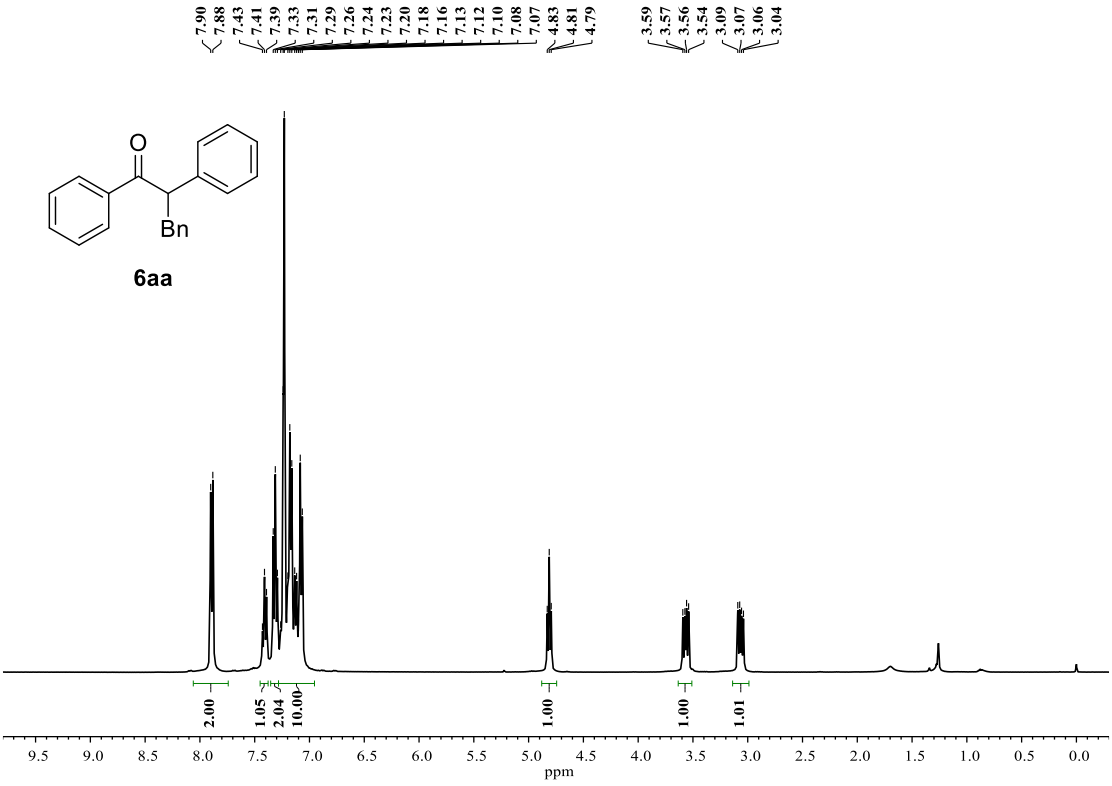
55.56
27.25
12.42
O
5aa
ppm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7.13
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7.10
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7.07
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3.56
3.54
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3.07
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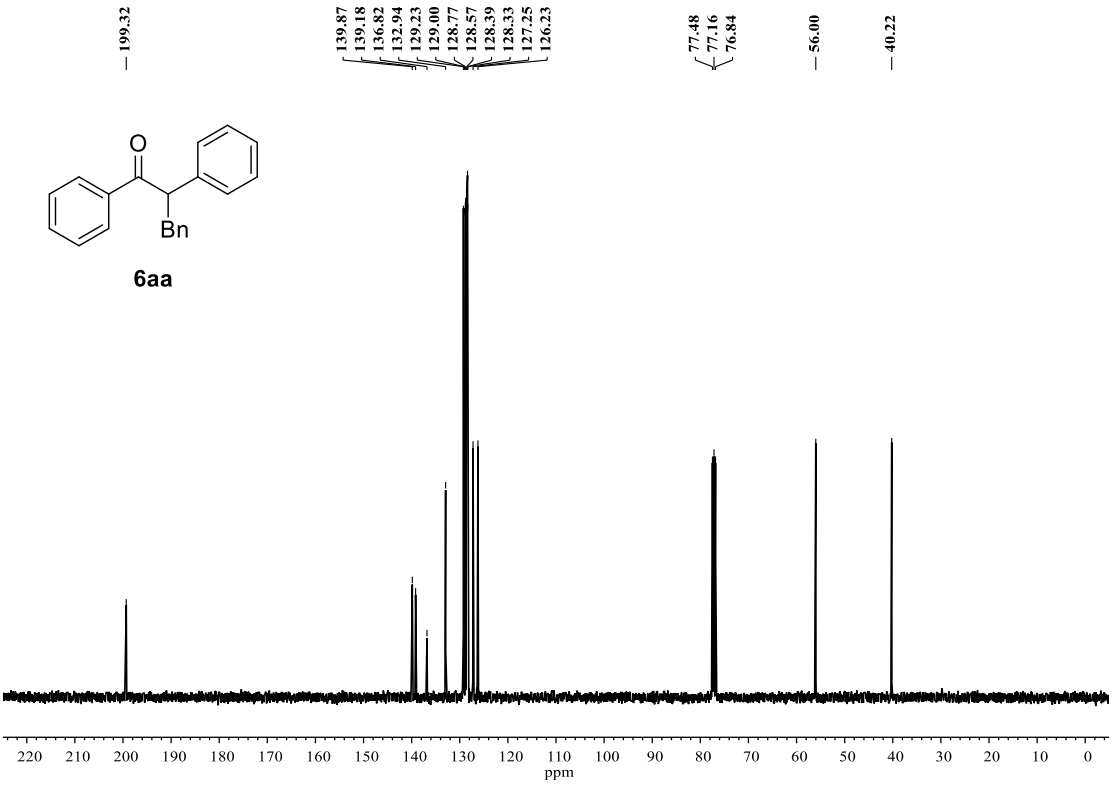
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