Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Nickel-catalysed highly regioselective synthesis of β-acyl naphthalenes under reductive conditions

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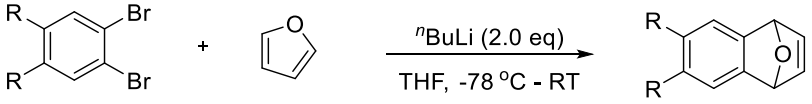
1. General remarks

Substituted substrates **1** were obtained according to the literature reports.[1] Other reagents and solvents were obtained from commercially available and used directly without further purification. All the reactions were monitored by thin-layer chromatography. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR data were obtained on AVANCE III Bruker 500 MHz or 400 MHz nuclear resonance spectrometers unless otherwise noted. Chemical shifts (in ppm) were referenced to tetramethylsilane (TMS) (δ = 0.00 ppm) in $CDCl_3$ or DMSO-d_6. The data of ^{1}H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (J values) in Hz and integration. ^{13}C NMR spectra were obtained by the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.16 ppm) or DMSO-d_6 (δ = 39.50 ppm). Flash chromatography was performed using 300-400 mesh silica gel with the indicated eluent according to standard techniques. Analysis of crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. High-resolution mass spectral (HRMS) data were recorded on Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer using electrospray ionization (ESI) mode.

2. General procedure

2.1 General procedure for the synthesis of oxabenzonorbornadienes[1]



To a stirred solution of substituted 1,2-dibromobenzene (100 mmol) in anhydrous THF (200 mL) and freshly distilled furan (300 mmol) at -78 °C was added ^{n}BuLi (110 mmol, 1.1 equiv, 2.4 M in hexane) dropwise under N_2. The solution was stirred at -78 °C for 1.5 h. Then, 100 mL distillated water was added to the reaction mixture and left to warm up to room temperature. EtOAc was added to the reaction mixture and the organic phase was separated. The aqueous solution was extracted with EtOAc and the combined organic solution was dried over $MgSO_4$. The solvent was then removed in vacuo and the resulting mixture was purified by a flash silica gel column using a mixture of ^{n}hexane/EtOAc as eluent to give the desired pure compounds **1**.

2.2 General procedure for the synthesis of β-acyl naphthalenes

To a 10 mL Schlenk tube was added sequentially $NiBr_2$(DME) (6.2 mg, 0.02 mmol), 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.0 mg, 0.024 mmol), Zn power (39.2 mg, 0.6 mmol) and oxabenzonorbornadiene **1** (0.20 mmol) was added in DMF or DMA (0.50 mL) under N_2. Acyl chloride **2** (0.40 mmol) were added via syringe. The resulting solution was stirred at room temperature or 70 ºC for 12 h. Then, the crude reaction mixture was diluted with ethyl acetate (10 mL) and washed with water (5 mL), extracted with EtOAc (5 mL x 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography to give product **3**.

2.3 Procedure for the synthesis of 4

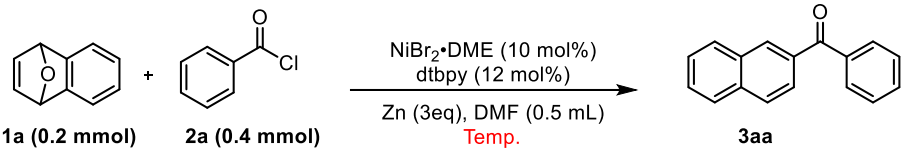
A suspension of zinc (0.205 g, 4.0 eq) in dry THF (12 mL) was stirred under N_2 at 0 °C. Titanium tetrachloride (0.14 mL, 2.0 eq) was added slowly and the ice bath was removed. The mixture was heated to 70 °C for 3.5 hours. Then, 2-benzoylnaphthalene (0.116 g, 0.5 mmol, 1.0 eq) in THF (7 mL) was added. The mixture was stirred at 70 °C for overnight. The solution was cooled to room temperature and quenched with a saturated solution of aqueous ammonium chloride. Then, the mixture was extracted with chloroform, the organic phase dried over $MgSO_4$ and the solvent removed by evaporation. The product was obtained as white solid. The *E*/*Z*-isomers were separated by recrystallization from a mixture of hexane and toluene.

2.5 Procedure for the synthesis of 5

A suspension of ethynyltrimethylsilane (160 uL, 1.5 eq) in dry THF (10 mL) was stirred under N_2 at -78 °C. Then ^{n}BuLi (0.5 mL, 2.0 eq) was added slowly. The mixture was stirred for 1 hours. Then **3aa** (232mg, 1 mmol) was added. The mixture was stirred for another 3.5 hours under room temperature. 0.5 M KOH was added and the reaction was stirred for 15 min. Add the acid until the pH≈7. Then, the mixture was extracted with EA, the organic phase dried over $MgSO_4$ and the solvent removed by evaporation. The product was obtained as oil liquid.

3. Optimization of the reaction conditions

3.1 Table S1. Optimization of the temperature

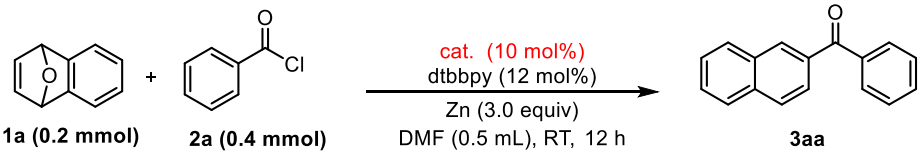


1a (0.2 mmol) **2a (0.4 mmol)** **3aa**

Entry	Temp.	Yield/%
1	**RT**	**78**
2	10 °C	34
3	0 °C	trace
4	40 °C	80
5	50 °C	62
6	RT	38[a]

[a] with 5 mol% of $NiBr_2$•DME and 6 mol% of dtbpy

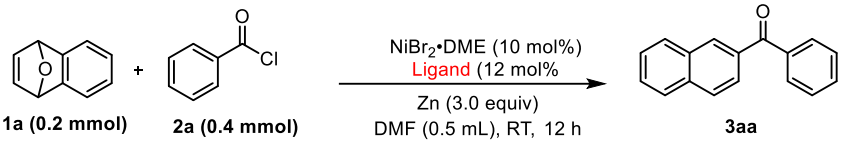
3.2 Table S2. Optimization of the catalyst



1a (0.2 mmol) **2a (0.4 mmol)** **3aa**

Entry	cat.	Yield/%
1	$NiBr_2$	32
2	$NiBr_2$•bipy	trace
3	$NiBr_2$•diglyme	25
4	$NiCl_2$•DME	18
5	$NiCl_2$• $6H_2O$	trace
6	$Ni(acac)_2$	13
7	$NiCl_2$• 4py	<10
8	$NiCl_2$• 1,10-phen	<10
9	$NiCl_2$•dtbbpy	<10
10	$NiBr_2$•dtbbpy	26
11	NiI_2	23
12	$CoCl_2$	trace
13	$Co(acac)_2$	trace
14	$FeCl_3$	trace
15	$Fe(OTf)_3$	trace

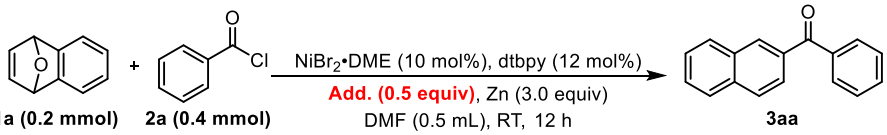
3.3 Table S3. Optimization of the ligand



1a (0.2 mmol) **2a (0.4 mmol)** **3aa**

entry	**Ligand**	Yield/%
1	bipy	49
2	dimebpy	56
3	tripy	23
4	4,4,4-tri-t-Bu-tripy	<10
5	2,9-dimephen	<10
6	1,8-dimephen	<10
7	4,7-dimephen	<10
8	4,7-diph-phen	<10
9	$Ph_2PCH_2PPh_2$	<10

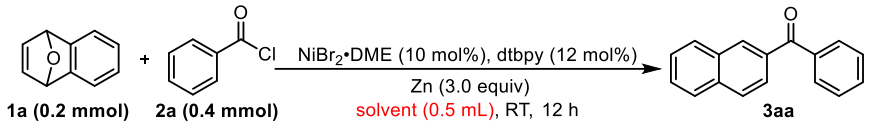
3.4 Table S4. Optimization of the additive



1a (0.2 mmol) **2a (0.4 mmol)** **3aa**

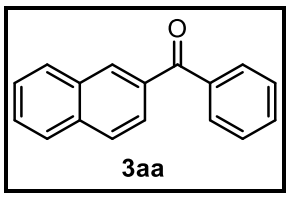
Entry	**Additive**	**Yield/%**
1	LiCl	55
2	LiBr	63
3	LiI	45
4	LiF	60
5	KI	52
6	NaI	52
7	MgF_2	58
8	$MgCl_2$	36
9	pydine	32

3.5 Table S5. Optimization of the solvent



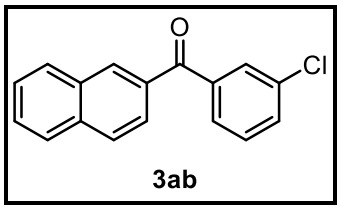
Entry	Solvent	Yield/%
1	DMA	<20
2	DMSO	<10
3	THF	69
4	dioxane	<20
5	CH_3CN	<20
6	NMP	nd
7	DCE	<20
8	DMF:THF/ 1:4	38

4. Characterization data for products



Naphthalen-2-yl(phenyl)methanone (3aa)[2] colorless oil, 78%

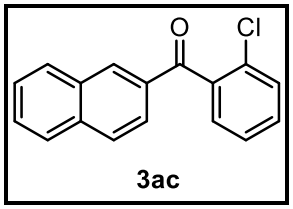
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.31 (s, 1H), 8.09 (t, J = 8.0 Hz, 2H), 8.04 (d, J = 8.0 Hz, 1H), 7.88 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.82 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 2H), 7.73-7.67 (m, 2H), 7.63-7.57 (m, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 195.9, 137.4, 134.9, 134.4, 132.8, 131.9, 131.5, 129.8, 129.6, 128.7, 128.5, 127.8, 127.1, 125.4. **MS** (EI) *m/z* (relative intensity): 232 (M^+, 95), 155 (100), 127 (70).



(3-Chlorophenyl)(naphthalen-2-yl)methanone (3ab)[3] colorless oil, 58%

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.35 (s, 1H), 8.15-8.10 (m, 2H), 8.06 (d, J = 8.0 Hz, 1H), 7.90 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.80-7.76 (m, 2H), 7.74-7.83 (m, 1H), 7.71-7.69 (m, 1H), 7.66-7.61 (m, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 195.0, 139.8, 135.4, 134.2, 134.0, 132.8, 132.3,

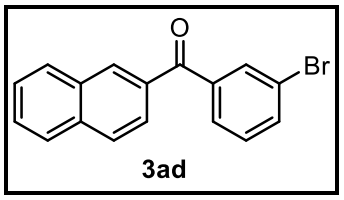
132.2, 131.1, 130.1, 129.5, 129.3, 129.0, 128.9, 128.2, 127.6, 125.6. **MS** (EI) *m/z* (relative intensity): 266 (M^+, 55), 155 (100), 127 (55).



3ac

(2-Chlorophenyl)(naphthalen-2-yl)methanone (3ac)[4] colorless oil, 51%

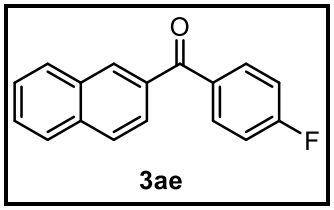
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.22 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 2H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.93 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.73-7.70 (m, 1H), 7.66-7.63 (m, 2H), 7.62-7.60 (m, 1H), 7.59-7.58 (m, 1H), 7.58-7.57 (m, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 194.7, 138.3, 135.5, 133.4, 132.6, 132.1, 131.9, 130.0, 130.0, 129.4, 129.3, 129.0, 127.9, 127.6, 127.3, 124.1. **MS** (EI) *m/z* (relative intensity): 266 (M^+, 55), 155 (100), 127 (55).



3ad

(3-Bromophenyl)(naphthalen-2-yl)methanone (3ad)[5] yellow oil, 49%

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.35 (s, 1H), 8.15-8.10 (m, 2H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.94-7.91 (m, 2H), 7.89 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.80 (dt, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.73-7.69 (m, 1H), 7.65-7.62 (m, 1H), 7.59 (t, *J* = 8.0 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 194.6, 139.7, 135.3, 135.0, 133.8, 131.9, 131.9, 130.9, 129.8, 128.9, 128.8, 128.6, 127.8, 127.2, 125.2, 122.1, 99.6. **MS** (EI) *m/z* (relative intensity): 312 (M^+, 35), 155 (100), 127 (55).

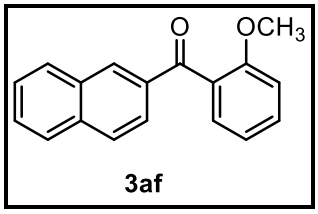


3ae

(4-Fluorophenyl)(naphthalen-2-yl)methanone (3ae)[6] yellow oil, 61%

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.32 (s, 1H), 8.13-8.03 (m, 3H), 7.92-7.84 (m, 3H), 7.71-7.61 (m, 2H), 7.44-7.40 (m, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 194.6, 164.8 (*J* = 252.5 Hz), 134.9,

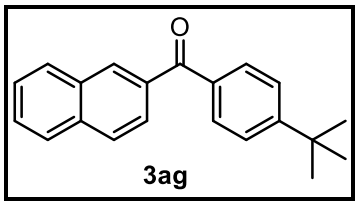
134.3, 134.0, 132.77 (J = 10.1 Hz), 131.9, 131.4, 129.6, 128.7, 128.5, 127.8, 127.2, 125.3, 115.8 (J = 22.2 Hz). **MS** (EI) *m/z* (relative intensity): 250 (M^+, 100), 155 (85), 127 (65).



3af

(2-Methoxyphenyl)(naphthalen-2-yl)methanone (3af)[7] yellow oil, 58%

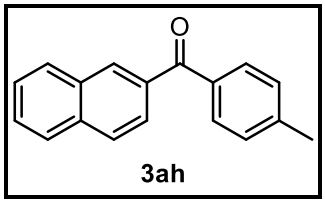
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.22 (s, 1H), 8.08-8.04 (m, 3H), 8.02 (dd, J_1 = 12.0 Hz, J_2 = 2.0 Hz, 1H), 7.86-7.84 (m, 1H), 7.69-7.65 (m, 2H), 7.61-7.56 (m, 1H), 7.41-8.38 (m, 1H), 7.24-7.12 (m, 1H), 3.67 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 196.1, 157.3, 135.6, 135.0, 132.6, 132.5, 131.9, 130.2, 129.4, 129.3, 129.0, 128.8, 128.2, 127.4, 124.9, 121.1, 112.6, 56.1. **MS** (EI) *m/z* (relative intensity): 262 (M^+, 90), 135 (100), 127 (97).



3ag

[4-(*tert*-Butyl)phenyl](naphthalen-2-yl)methanone (3ag)[8] colorless oil, 71%

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.33 (s, 1H), 8.14-8.03 (m, 3H), 7.87 (dd, J_1 = 12.0 Hz, J_2 = 2.0 Hz, 1H), 7.79 (dt, J_1 = 8.4 Hz, J_2 = 2 Hz, 2H), 7.71-7.67 (m, 1H), 7.64-7.61 (m, 3H), 1.35 (s, 9H). **^{13}C NMR** (101 MHz, DMSO) δ 195.5, 155.9, 134.8, 134.7, 134.6, 132.0, 131.2, 130.0, 129.6, 128.6, 128.4, 127.8, 127.1, 125.6, 125.5, 35.0, 31.0. **MS** (EI) *m/z* (relative intensity): 288 (M^+, 65), 273 (100), 161 (75).

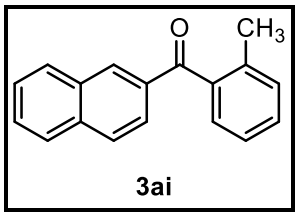


3ah

Naphthalen-2-yl(*p*-tolyl)methanone (3ah)[9] colorless oil, 70%

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 (s, 1H), 8.11-8.02 (m, 3H), 7.86 (dd, J_1 = 12.0 Hz, J_2 = 2.0 Hz, 1H), 7.74-7.72 (m, 2H), 7.70-7.60 (m, 2H), 7.41(d, J = 8.0 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR**

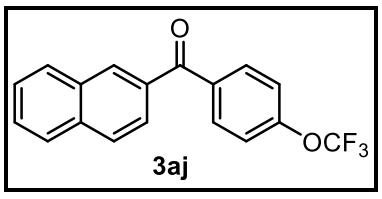
(101 MHz, DMSO-d_6) δ 195.6, 143.2, 134.8, 134.7, 131.9, 131.2, 130.1, 129.6, 129.3, 128.6, 128.4, 127.8, 127.1, 125.4, 39.6, 21.3. **MS** (EI) *m/z* (relative intensity): 245 (M^+, 100), 127 (50), 91 (30).



3ai

Naphthalen-2-yl(*o*-tolyl)methanone (3ai)[7] colorless oil, 69%

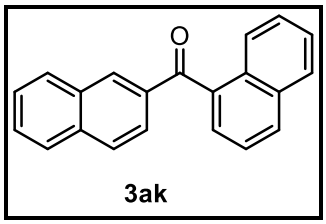
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.95-7.92 (m, 1H), 7.85-7.78 (m, 3H), 7.55 (dt, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.53 (dt, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.37-7.29 (m, 2H), 7.24-7.17 (m, 2H), 2.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.6, 138.8, 136.7, 135.6, 135.0, 132.7, 132.4, 131.0, 130.2, 129.6, 128.6, 128.5, 128.4, 127.8, 126.8, 125.2, 125.0, 77.0, 20.0. **MS** (EI) *m/z* (relative intensity): 245 (M^+, 100), 127 (50), 91 (30).



3aj

Naphthalen-2-yl(4-(trifluoromethoxy)phenyl)methanone (3aj) colorless oil, 67%

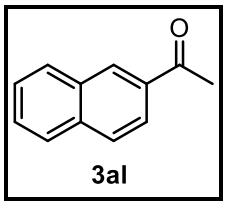
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.35 (s, 1H), 8.14-8.09 (m, 2H), 8.05 (d, J = 4.0 Hz, 1H), 7.97-7.94 (m, 2H), 7.89 (dd, J_1 = 10.0 Hz, J_2 = 1.5 Hz, 1H), 7.71-7.68 (m, 1H), 7.65-7.61 (m, 1H), 7.59 (d, J = 6.8 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 194.6, 151.2, 136.3, 135.0, 133.9, 132.2, 131.9, 131.7, 129.7, 128.8, 128.6, 127.8, 127.2, 125.3, 120.8, 120.3 (q, J = 259.3 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ -56.55. **MS** (EI) *m/z* (relative intensity): 316 (M^+, 90), 189 (65), 155 (100), 127 (65). **HRMS (ESI)** m/z: calcd for [M+H^+] $C_{18}H_{11}F_3O_2$: 317.2867, found: 317.2865.



3ak

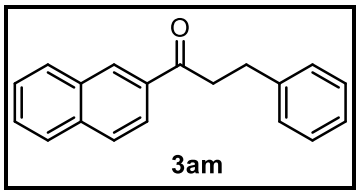
Naphthalen-1-yl(naphthalen-2-yl)methanone (3ak)[10] colorless oil, 50%

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.13-8.04 (m, 3H), 7.97 (t, *J* = 5.5 Hz, 2H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 5.5 Hz, 1H), 7.63-7.49 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.0, 136.7, 135.8, 135.7, 133.8, 132.9, 132.4, 131.2, 131.1, 129.7, 128.7, 128.5, 128.4, 127.8, 127.7, 127.3, 126.8, 126.5, 125.8, 125.4, 124.4. **MS** (EI) *m/z* (relative intensity): 282 (M^+, 85), 155 (95), 127 (100).



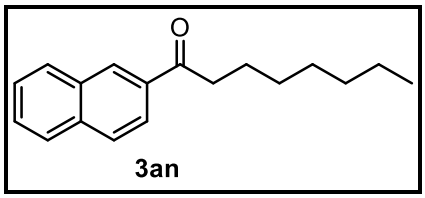
1-(Naphthalen-2-yl)ethan-1-one (3al)[11] colorless oil, 55%

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.92 (dd, J_1 = 9.0 Hz, J_2 = 2.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.77 (m, 2H), 7.49 (m, 2H), 2.60 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.1, 135.6, 134.5, 132.5, 130.2, 129.6, 128.5, 128.4, 127.8, 126.8, 123.9, 26.7. **MS** (EI) *m/z* (relative intensity): 170 (M^+, 65), 155 (95), 127 (100).



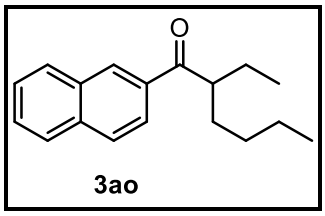
1-(Naphthalen-2-yl)-3-phenylpropan-1-one (3am)[12] colorless oil, 62%

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.88 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 8.5 Hz, 2H), 7.42-7.34 (m, 2H), 7.18-7.13 (m, 4H), 7.08-7.06 (m, 1H), 3.26 (t, *J* = 7.0 Hz, 2H), 2.99 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 199.1, 141.5, 135.6, 134.2, 132.6, 129.8, 129.6, 128.7, 128.6, 128.5, 128.4, 127.9, 126.9, 126.3, 123.9, 40.6, 30.3. **MS** (EI) *m/z* (relative intensity): 260 (M^+, 45), 155 (100), 127 (60).



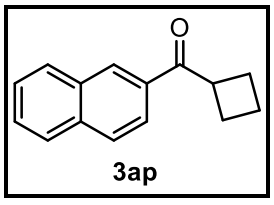
1-(Naphthalen-2-yl)octan-1-one (3an)[13]colorless oil, 65%

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.96 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.80 (t, J = 8.5 Hz, 2H), 7.52-7.45 (m, 2H), 3.02-2.99 (t, J = 7.0 Hz, 2H), 1.75-1.69 (m, 2H), 1.36-1.18 (m, 8H), 0.83-0.80 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 200.6, 135.5, 134.5, 132.6, 129.5, 128.3, 127.7, 126.7, 126.4, 124.0, 118.7, 38.7, 31.7, 29.4, 29.2, 24.6, 22.6, 14.1. **MS** (EI) *m/z* (relative intensity): 254 (M^+, 20), 170 (100), 155 (85), 127 (70).



2-Ethyl-1-(naphthalen-2-yl)hexan-1-one (3ao) colorless oil, 75%

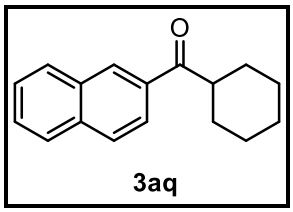
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.96 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.80 (m, 2H), 7.49 (m, 2H), 3.44 (m, 1H), 1.78 (m, 2H), 1.53 (m, 2H), 1.20 (m, 4H), 0.83 3.26 (t, J = 7.5 Hz, 3H), 0.77 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 204.8, 135.7, 135.4, 132.8, 129.8, 129.3, 128.6, 128.5, 127.9, 126.8, 124.4, 47.8, 32.1, 30.0, 25.8, 23.1, 14.1, 12.2. **MS** (EI) *m/z* (relative intensity): 254 (M^+, 15), 155 (100), 127 (60). **HRMS (ESI)** m/z: calcd for [$M+H^+$] $C_{18}H_{23}O$: 255.1743, found: 255.1745.



Cyclobutyl(naphthalen-2-yl)methanone (3ap)[14] colorless oil, 62%

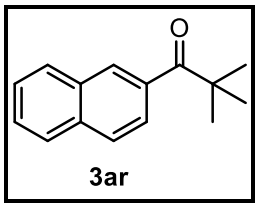
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.00 (dd, J_1 = 10.0 Hz, J_2 = 2 Hz, 2H), 7.89 (t, J = 9.0 Hz, 2H), 7.60-7.53 (m, 2H), 4.20-4.13 (m, 1H), 2.52-2.45 (m, 2H), 2.40-2.34 (m, 2H), 2.18-2.11 (m, 1H), 1.98-1.92 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 201.0, 135.5, 133.0, 132.6, 129.9, 129.5,

128.4, 128.3, 127.8, 126.7, 124.2, 42.3, 25.3, 18.3. **MS** (EI) *m/z* (relative intensity): 210 (M^+, 25), 155 (100), 127 (60).



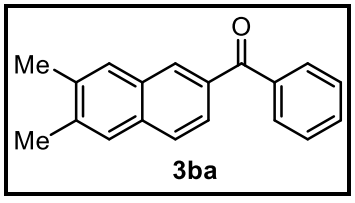
Cyclohexyl(naphthalen-2-yl)methanone (3aq)[15] colorless oil, 52%

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.03 (dd, J_1 = 9.0 Hz, J_2 = 2 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.90 (m, 2H), 7.61 (m, 2H), 3.46 (tt, J_1 = 11.5 Hz, J_2 = 3.5 Hz, 1H), 1.97 (m, 2H), 1.90 (m, 2H), 1.63 (m, 2H), 1.50 (qt, J_1 = 12.5 Hz, J_2 = 3.0 Hz, 2H), 1.35-1.26 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 203.9, 135.5, 133.7, 132.6, 129.6, 129.6, 128.4, 128.3, 127.7, 126.7, 124.4, 45.7, 29.6, 26.0, 25.9. **MS** (EI) *m/z* (relative intensity): 235 (M^+, 25), 155 (100), 127 (55).



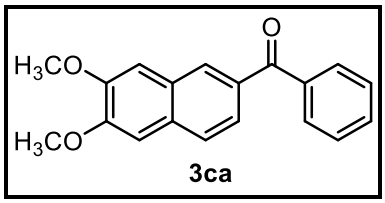
2,2-Dimethyl-1-(naphthalen-2-yl)propan-1-one (**3ar**)[16] colorless oil, 59%

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.94 (dd, J_1 = 9.0 Hz, J_2 = 2.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.78 (m, 2H), 7.48 (m, 2H), 1.14 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.1, 135.6, 134.6, 132.5, 130.2, 129.5, 128.5, 128.4, 127.8, 126.8, 123.9, 46.3, 30.1. **MS** (EI) *m/z* (relative intensity): 212 (M^+, 65), 155 (100), 127 (55).



(6,7-Dimethylnaphthalen-2-yl) (phenyl)methanone (3ba) [17]colorless oil, 76%

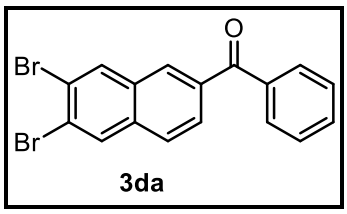
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.78-7.69 (m, 4H), 7.54-7.48 (m, 3H), 7.42-7.38 (m, 2H), 2.35 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.0, 138.7, 138.2, 136.7, 134.3, 134.0, 132.2, 131.3, 131.1, 130.1, 128.9, 128.3, 127.4, 127.3, 125.1, 20.5, 20.2. **MS** (EI) *m/z* (relative intensity): 260 (M^+, 75), 183 (100), 155 (30).



3ca

(6,7-Dimethoxynaphthalen-2-yl) (phenyl)methanone (3ca) colorless oil, 72%

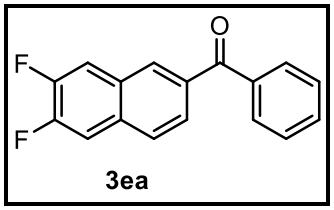
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.79-7.66 (m, 4H), 7.57-7.41 (m, 3H), 7.43-7.36 (m, 2H), 3.73 (s, 3H), 3.71 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.6, 138.8, 136.8, 135.6, 132.6, 131.0, 130.2, 129.6, 128.7, 128.5, 128.4, 127.8, 126.8, 125.2, 125.1, 20.5, 20.2. **HRMS (ESI)** m/z: calcd for [M+H$^+$] $C_{19}H_{16}O_3$ 293.1172, found: 293.1179.



3da

(6,7-Dibromonaphthalen-2-yl) (phenyl)methanone (3da)[17] yellow oil, 51%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.38-8.20 (m, 4H), 8.15-8.08 (m, 3H), 8.04-7.93 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.9, 142.3, 141.9, 137.1, 136.9, 133.8, 132.5, 131.7, 130.6, 128.5, 128.4, 128.1, 127.7, 126.32, 126.1. **HRMS (ESI)** m/z: calcd for [M+H$^+$] $C_{17}H_{10}OBr_2$: 388.9171, found: 388.9191.

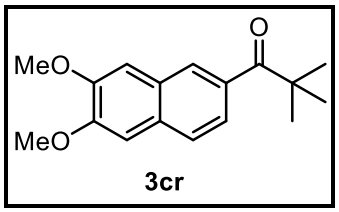


3ea

(6,7-Dibromonaphthalen-2-yl) (phenyl)methanone (3ea)[17] yellow oil, 41%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.46-8.21 (m, 4H), 8.16-8.02 (m, 3H), 8.01-7.94 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.0, 151.1 (*J* = 218.2 Hz), 151.0 (d, *J* = 218.2 Hz), 142.0,

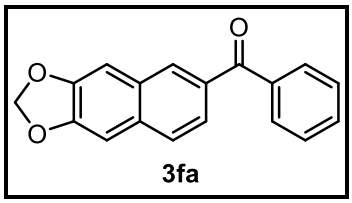
141.9, 139.8 (*J* = 31.3 Hz), 138.9 (*J* = 27.3 Hz), 137.7, 136.8, 136.2, 135.0, 134.4, 133.2, 132.3 (d, *J* = 29.3 Hz), 131.6 (*J* = 29.3 Hz). **MS** (EI) *m/z* (relative intensity): 268 (M^+, 75), 191 (70), 105 (100).



3cr

1-(6,7-Dimethoxynaphthalen-2-yl)-2,2-dimethylpropan-1-one (3cr)[18] colorless oil, 68%

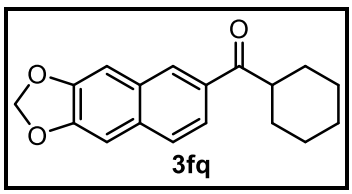
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.73-7.67 (m, 2H), 7.18 (s, 1H), 7.12 (s, 1H), 4.10-4.00 (m, 6H), 1.43 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.5, 151, 150.0, 133.9, 130.69, 128.1, 127.4, 126.0, 123.7, 107.3, 106.0, 56.0, 56.0, 44.3, 28.4. **HRMS (ESI)** m/z: calcd for [M+H^+] $C_{17}H_{20}O_3$ 273.1485, found: 273.1490.



3fa

Naphtho[2,3-d][1,3]dioxol-6-yl(phenyl)methanone (3ea)[18] colorless oil, 75%

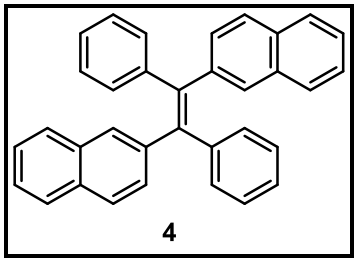
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.85 (d, *J* = 6.0 Hz, 2H), 7.80-7.78 (m, 1H), 7.74-7.72(m, 1H), 7.62-7.59 (m, 1H), 7.52-7.49 (m, 2H), 7.17 (d, *J* = 2.5 Hz, 2H), 6.08 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.7, 149.7, 148.4, 138.2, 133.5, 133.2, 132.2, 130.7, 130.0, 129.4, 128.3, 127.1, 124.9, 105.1, 103.9, 101.5. **MS** (EI) *m/z* (relative intensity): 276 (M^+, 70), 199 (100), 171 (25), 77 (25).



3fq

Cyclohexyl(naphtho[2,3-d][1,3]dioxol-6-yl)methanone (3fq) colorless oil, 65%

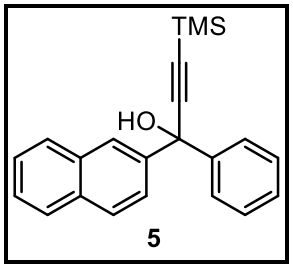
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.87 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.22 (s, 1H), 7.13 (s, 1H), 6.07 (s, 2H), 3.40 (tt, J_1 = 11.0 Hz, J_2 = 3.0 Hz, 1H), 1.94-1.91 (m, 2H), 1.88-1.85 (m, 2H), 1.58-1.51 (m, 2H), 1.48 (qt, J_1 = 9.5 Hz, J_2 = 3.0 Hz, 2H), 1.34-1.25 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 203.8, 149.6, 148.2, 133.3, 132.4, 129.8, 128.4, 127.3, 123.3, 105.2, 103.8, 101.5, 45.6, 29.6, 26.0, 25.9. **MS** (EI) *m/z* (relative intensity): 282 (M^+, 20), 199 (100), 171 (20). **HRMS (ESI)** m/z: calcd for [$M+H^+$] $C_{18}H_{19}O_3$: 283.1329, found: 283.1342.



4

(*E*)-1,2-di(naphthalen-2-yl)-1,2-diphenylethene (4) yellow solid, 68%

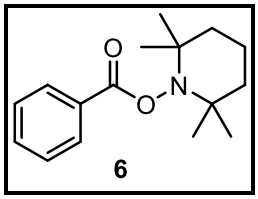
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.50-7.44 (m, 5H), 7.40 (d, J = 9.0 Hz, 1H), 7.30-7.22 (m, 4H), 7.13-7.10 (m, 2H), 7.04-6.97 (m, 10H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.0, 143.8, 141.5, 141.4, 141.4, 141.3, 133.2, 132.2, 131.6, 131.6, 130.6, 129.6, 128.1, 128.1, 127.9, 127.8, 127.5, 127.5, 127.1, 127.0, 126.7, 126.6, 125.8, 125.8, 125.8, 125.7.



5

1-(Naphthalen-2-yl)-1-phenyl-3-(trimethylsilyl) prop-2-yn-1-ol (5) colorless oil, 54%

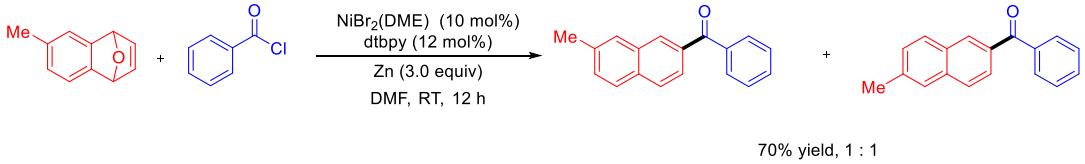
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.74-7.72 (m, 1H), 7.68-7.63 (m, 2H), 7.56-7.54 (m, 2H), 7.48 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 7.37-7.32 (m, 2H), 7.22-7.19 (m, 2H), 7.16-7.12 (m, 1H), 2.88 (s, 1H), 0.15 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 142.0, 132.9, 132.79, 128.49, 128.29, 128.1, 127.7, 127.5, 126.2, 126.1, 124.6, 124.2, 107.65, 92.3, 74.7, -0.1.



2,2,6,6-tetramethylpiperidin-1-yl benzoate (6) colorless oil.

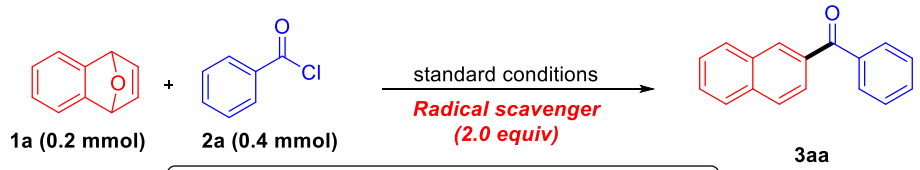
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-8.06 (m, 2H), 7.59-7.55 (m, 1H), 7.48-7.44 (m, 2H), 1.59 (s, 2H), 1.57 (s, 2H), 1.28 (s, 6H), 1.25 (s, 2H), 1.12 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 166.4, 132.8, 129.7, 128.4, 69.0, 60.4, 39.1, 32.0, 20.8, 17.0.

Reaction with monosubstituted oxabicyclic alkene



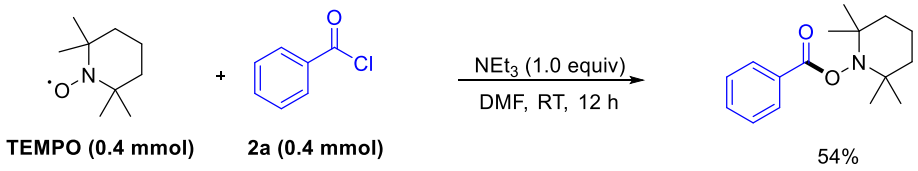
70% yield, 1 : 1

Reactions with TEMPO or BHT as radical inhibitor



1a (0.2 mmol) **2a (0.4 mmol)** **3aa**

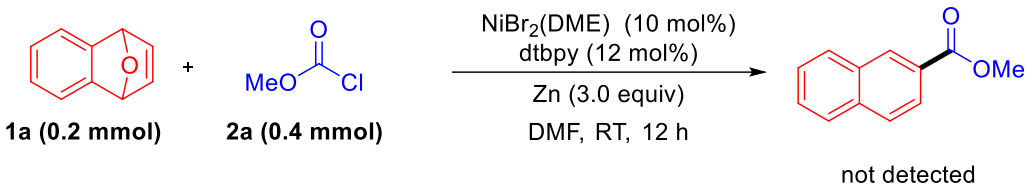
Radical scavenger	GC Yield (%)
none	78%
TEMPO	trace
BHT	36%



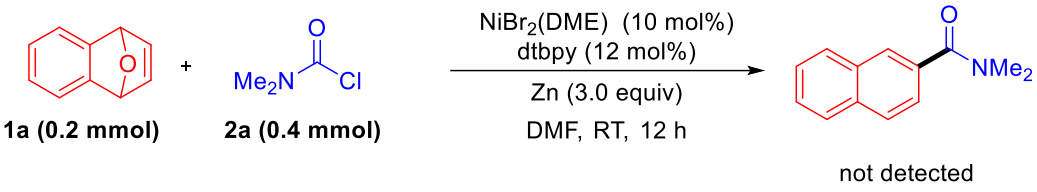
TEMPO (0.4 mmol) **2a (0.4 mmol)** 54%

The reactions with radical inhibitor TEMPO and BHT gave significantly decreased yields. However, the reaction of TEMPO with acid chloride could occur without any catalyst, ligand and reductant. Therefore, the studies with TEMPO or BHT as radical inhibitor is not useful for the understanding of the reaction mechanism.

Reactions with methyl chloroformate or dimethylcarbamoyl chloride

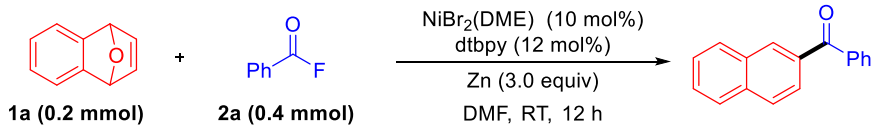


1a (0.2 mmol) **2a (0.4 mmol)** not detected

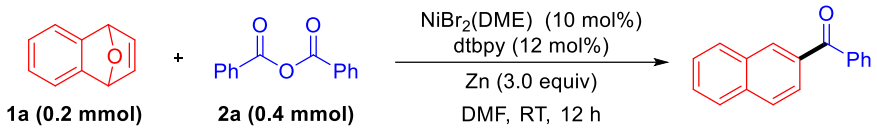


1a (0.2 mmol) **2a (0.4 mmol)** not detected

Reactions with acyl fluoride or acid anhydride instead of acyl chloride



1a (0.2 mmol) **2a (0.4 mmol)** not detected



1a (0.2 mmol) **2a (0.4 mmol)** 52%

Reference

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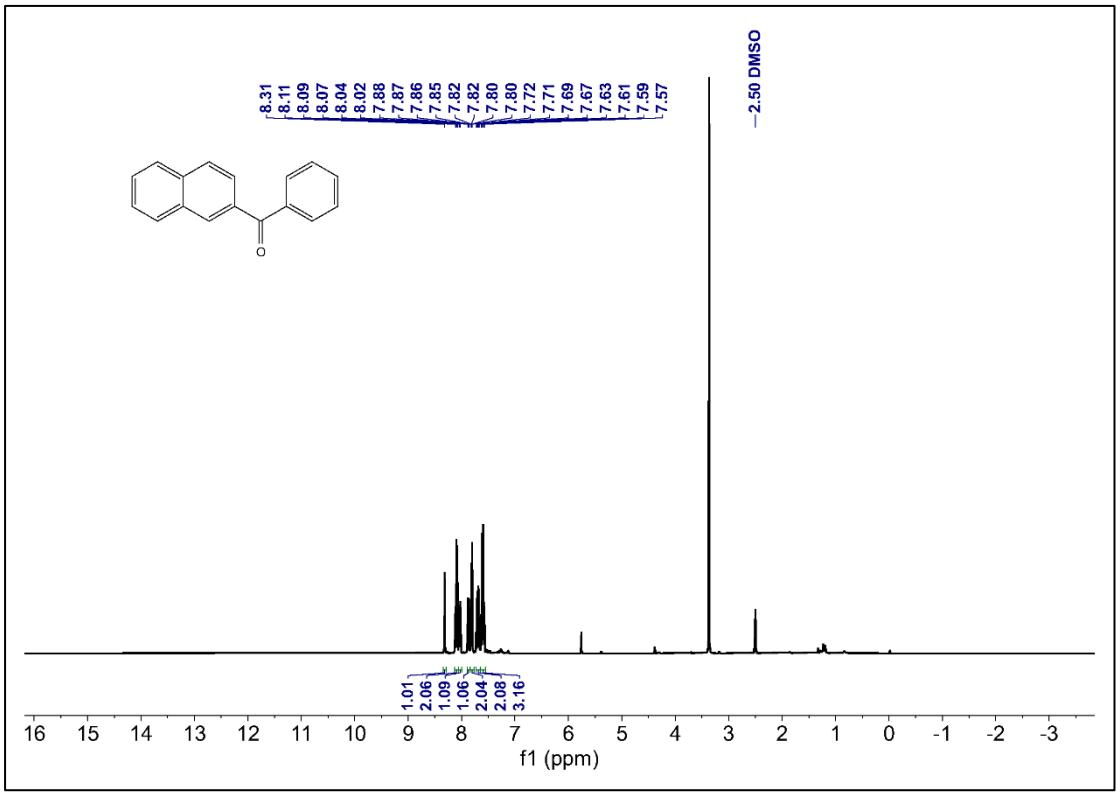
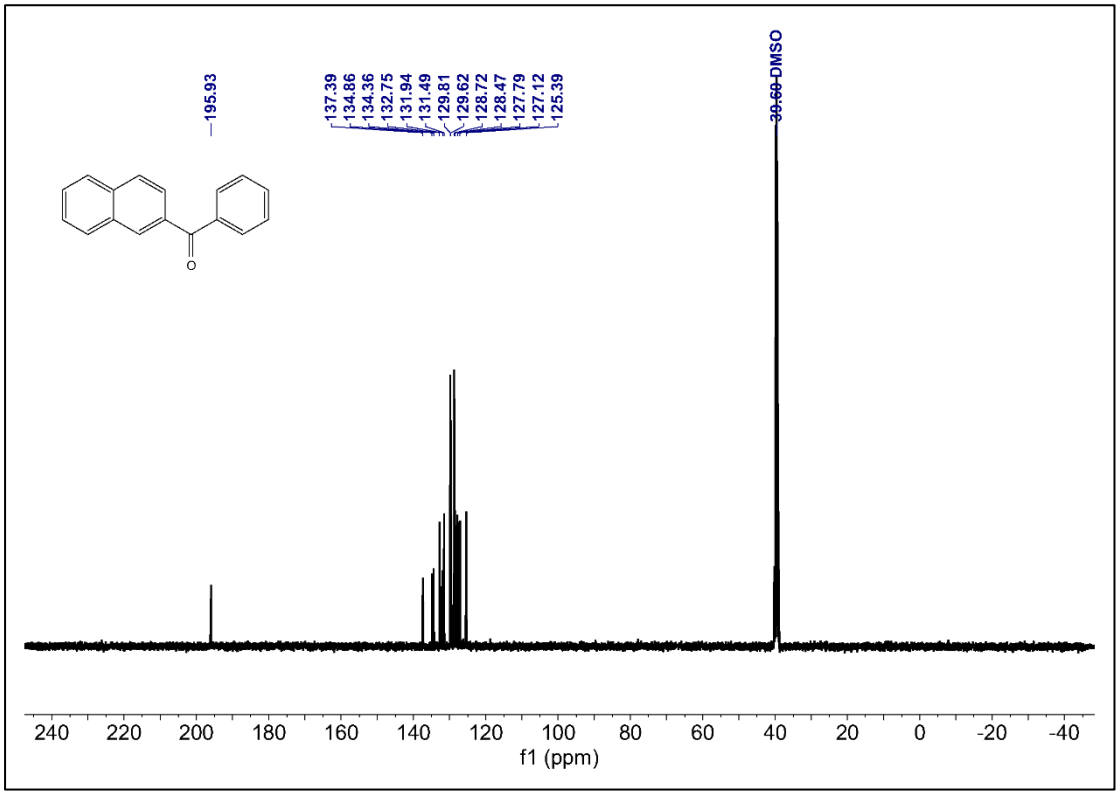
NMR spectrum

3aa





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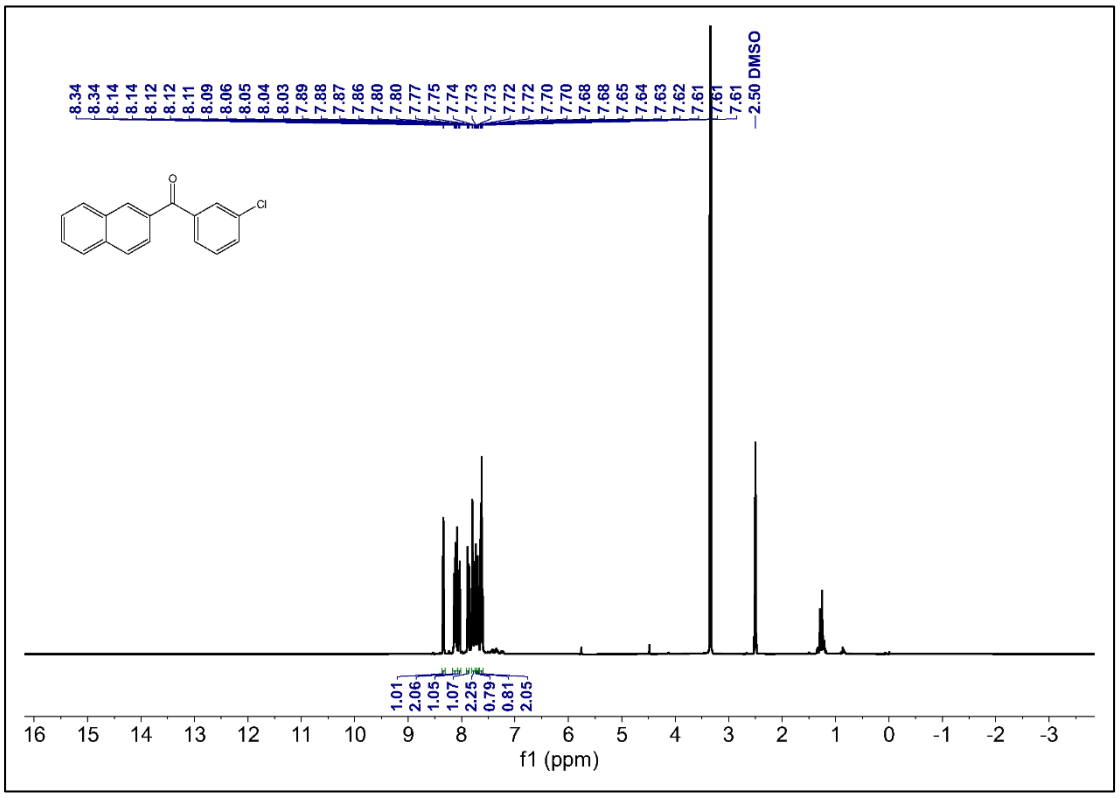
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7.87
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7.77
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7.74
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7.73
7.72
7.72
7.70
7.70
7.68
7.68
7.65
7.64
7.63
7.62
7.61
7.61
7.61
2.50 DMSO
Cl
O
1.01
2.06
1.05
1.07
2.25
0.79
0.81
2.05
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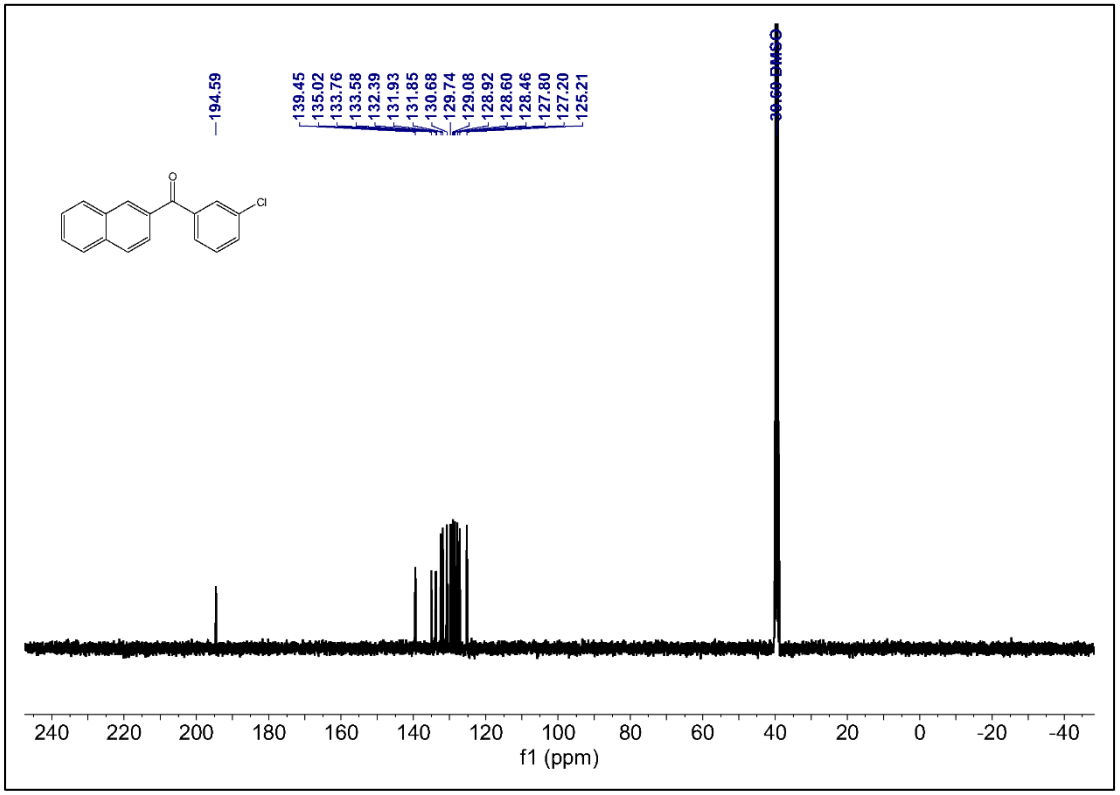
f1 (ppm)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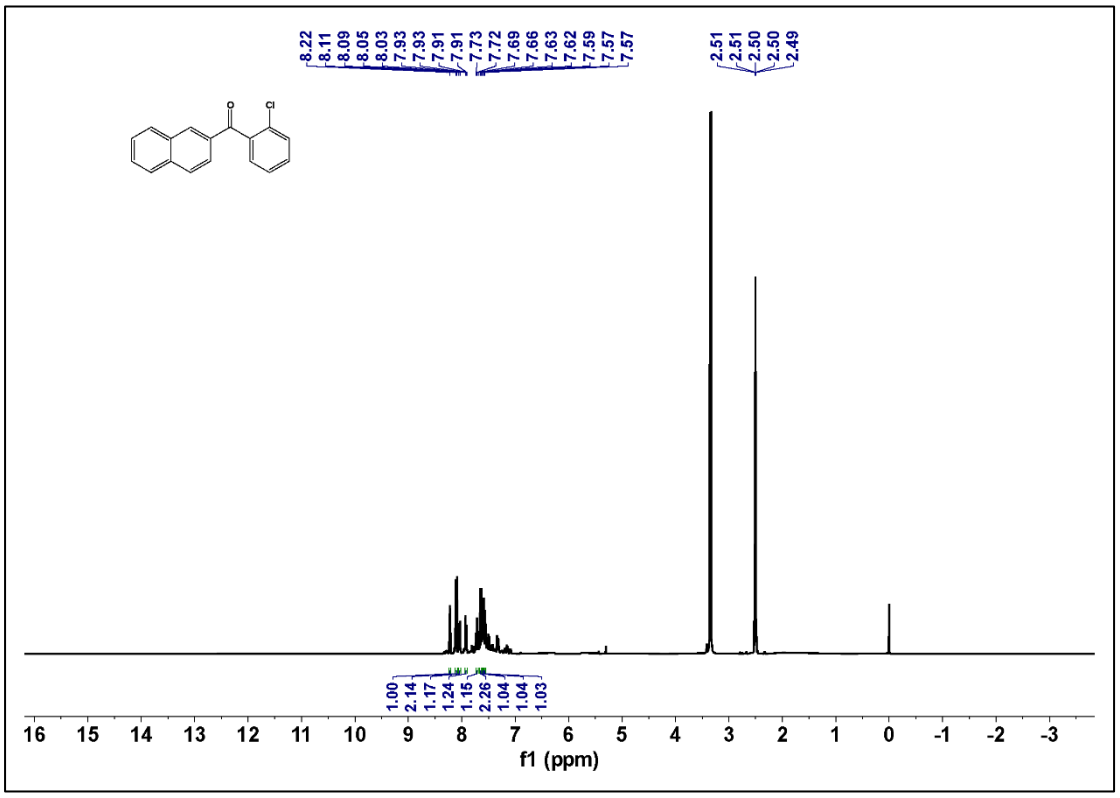
f1 (ppm)

3ac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2.50
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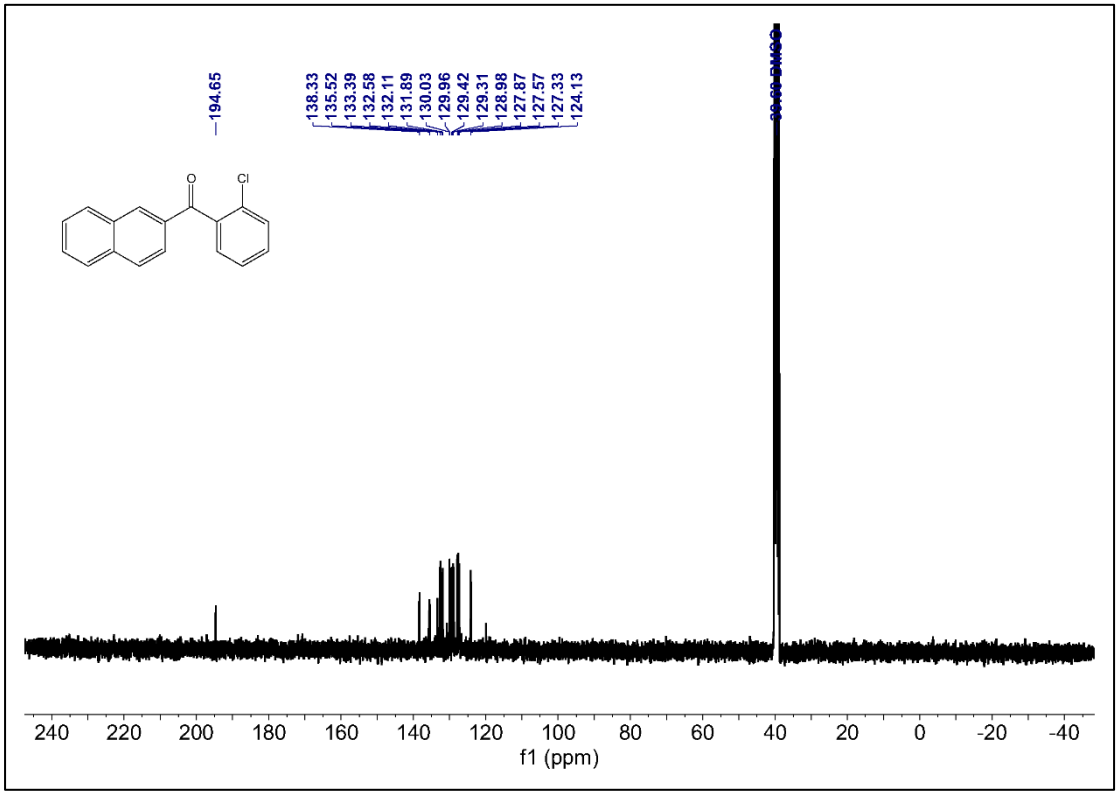
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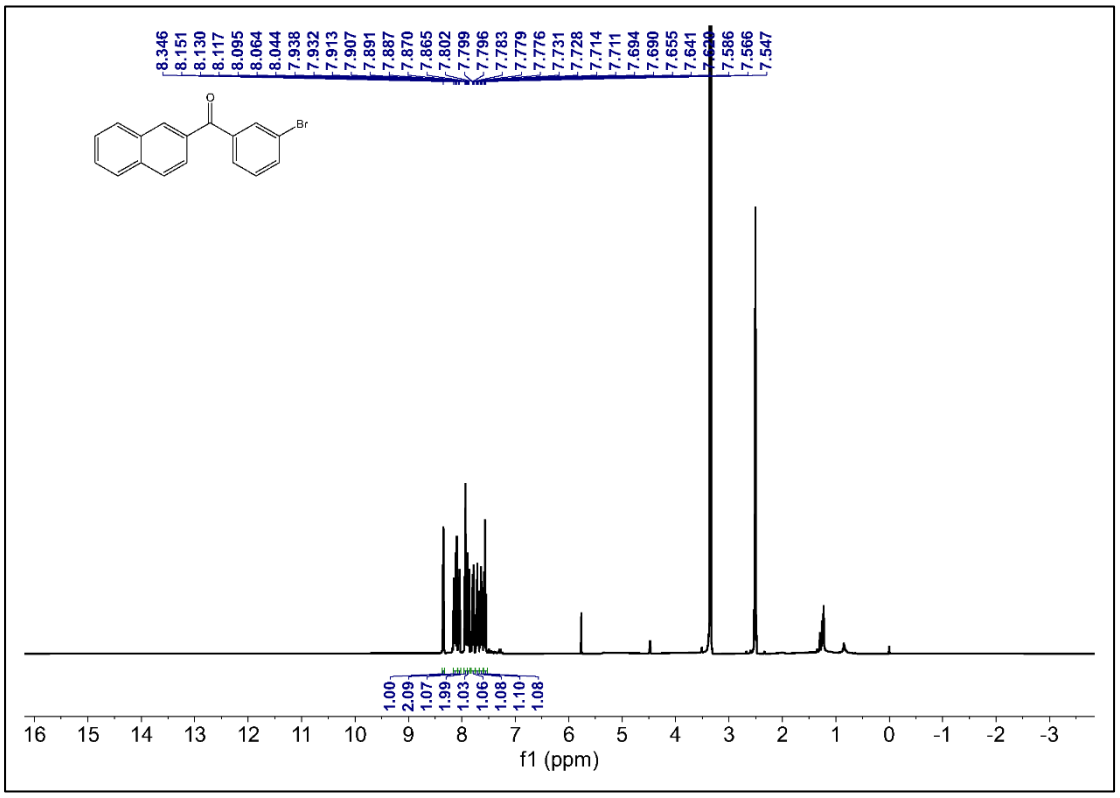
f1 (ppm)

3ad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O
Br
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2.09
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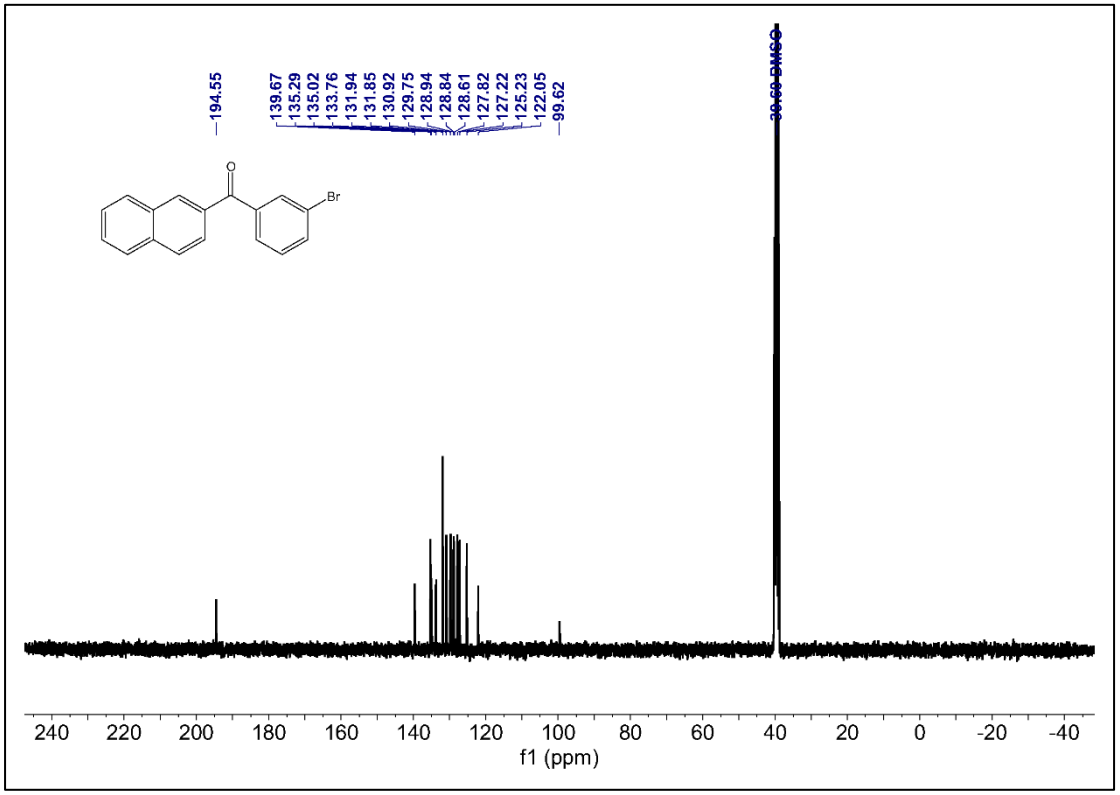
f1 (ppm)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f1 (ppm)

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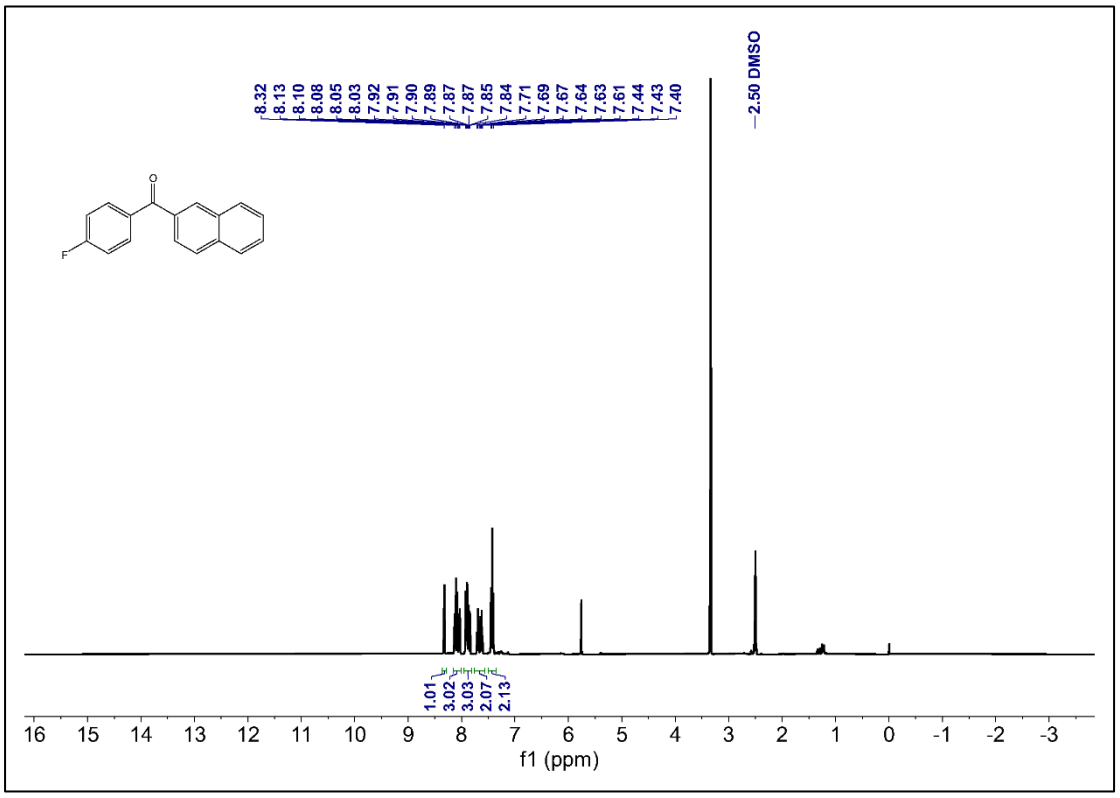
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7.84
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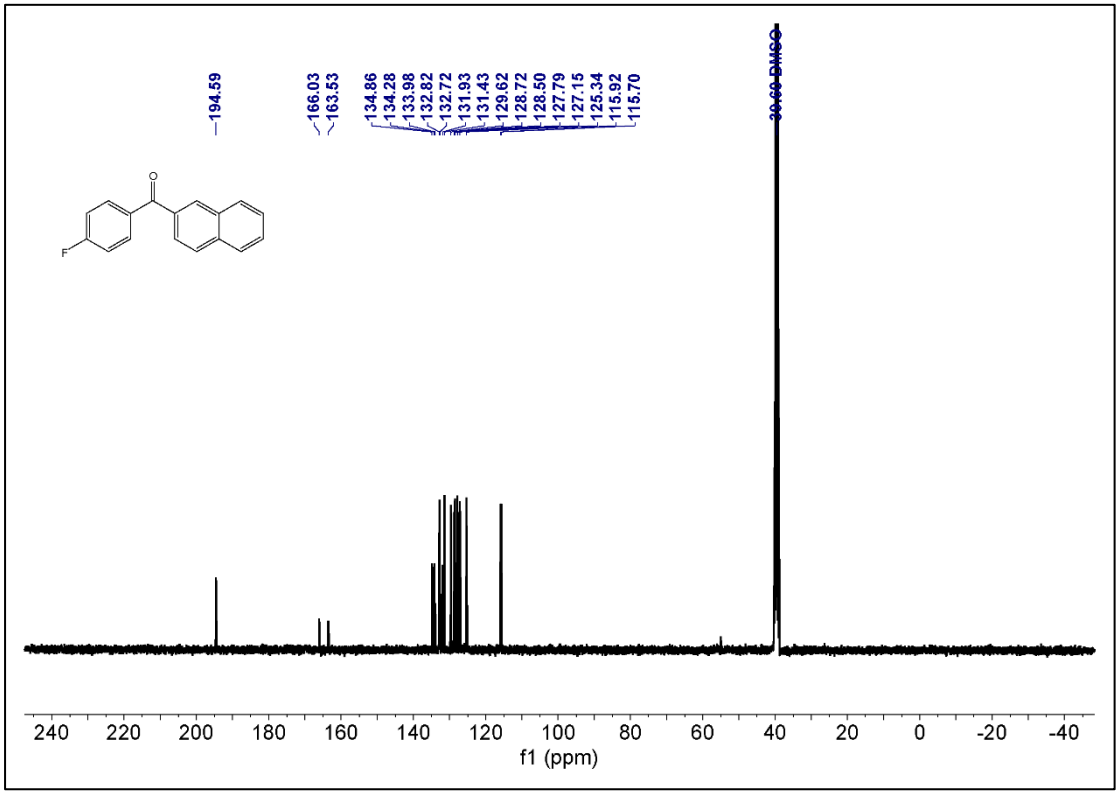
3.03
2.07
2.13
f1 (ppm)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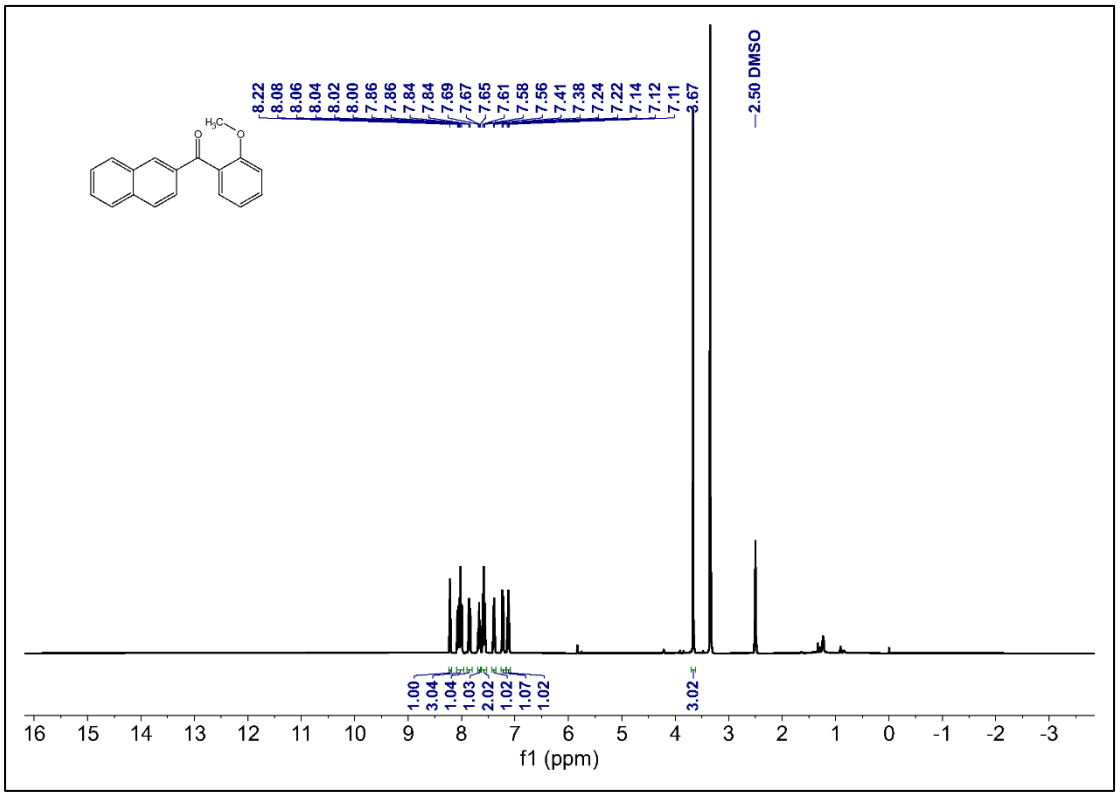
f1 (ppm)

3af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1.07
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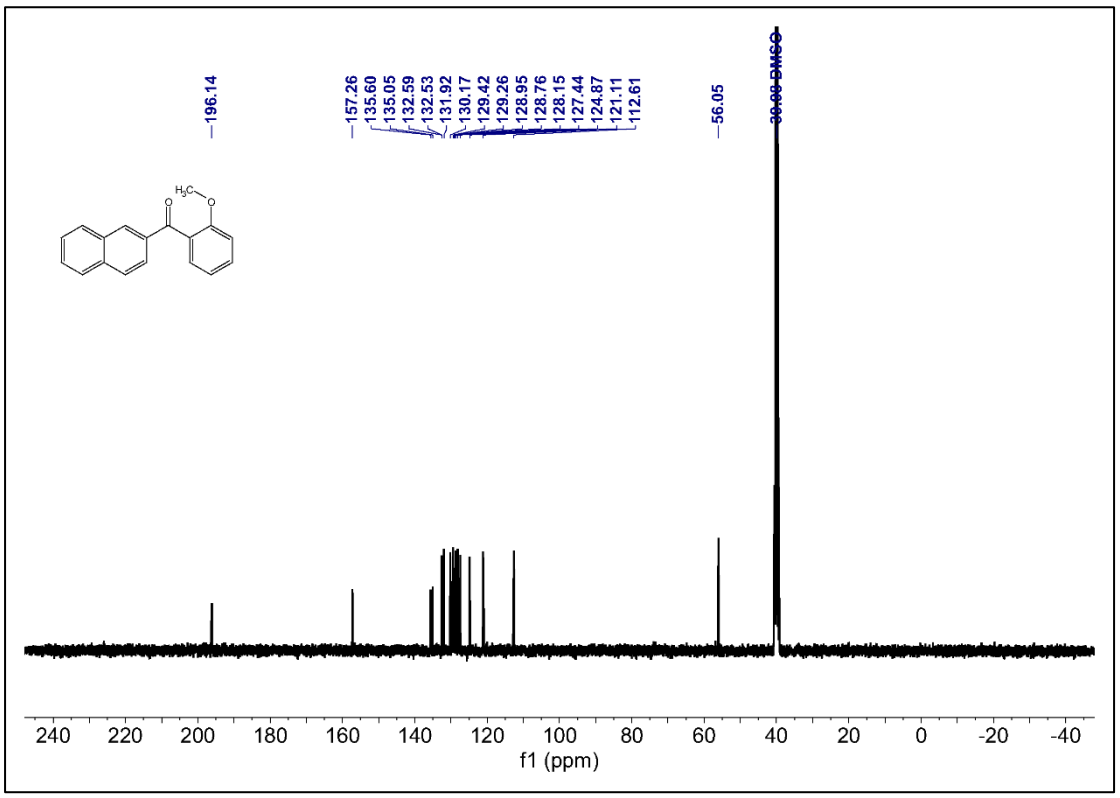
3.02
f1 (ppm)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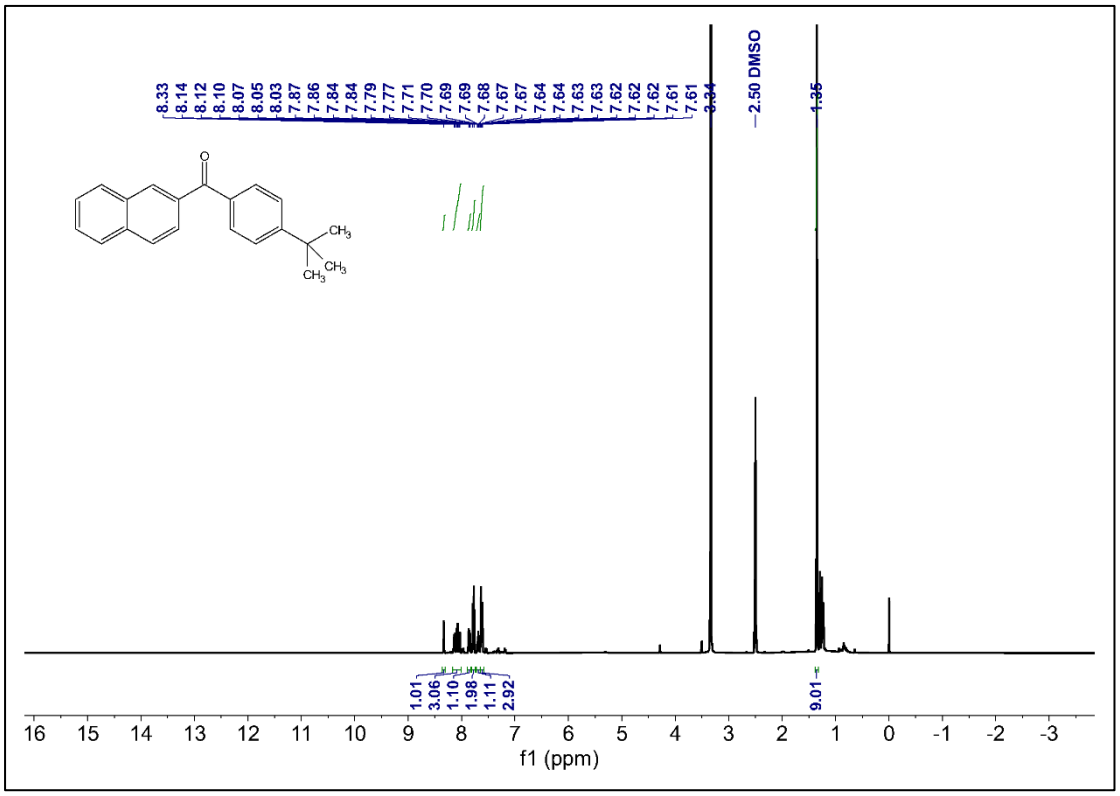
3ag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7.63
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7.61
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CH3
CH3
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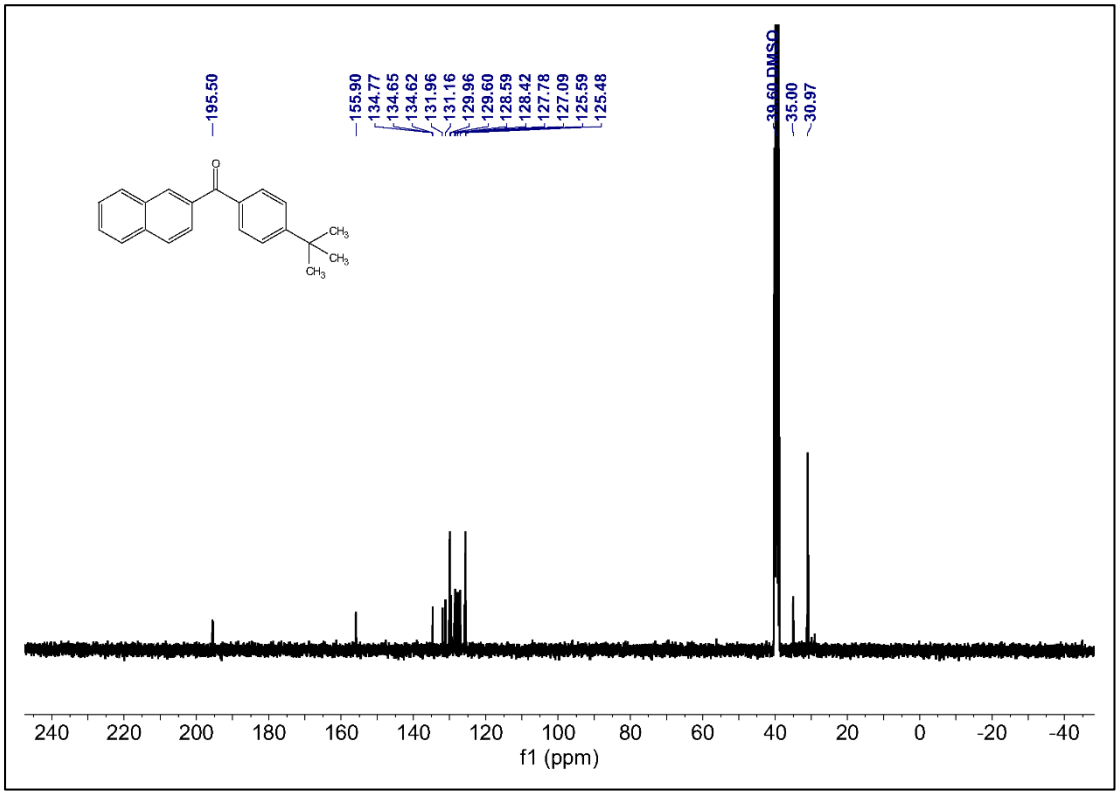
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125.59
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CH3
CH3
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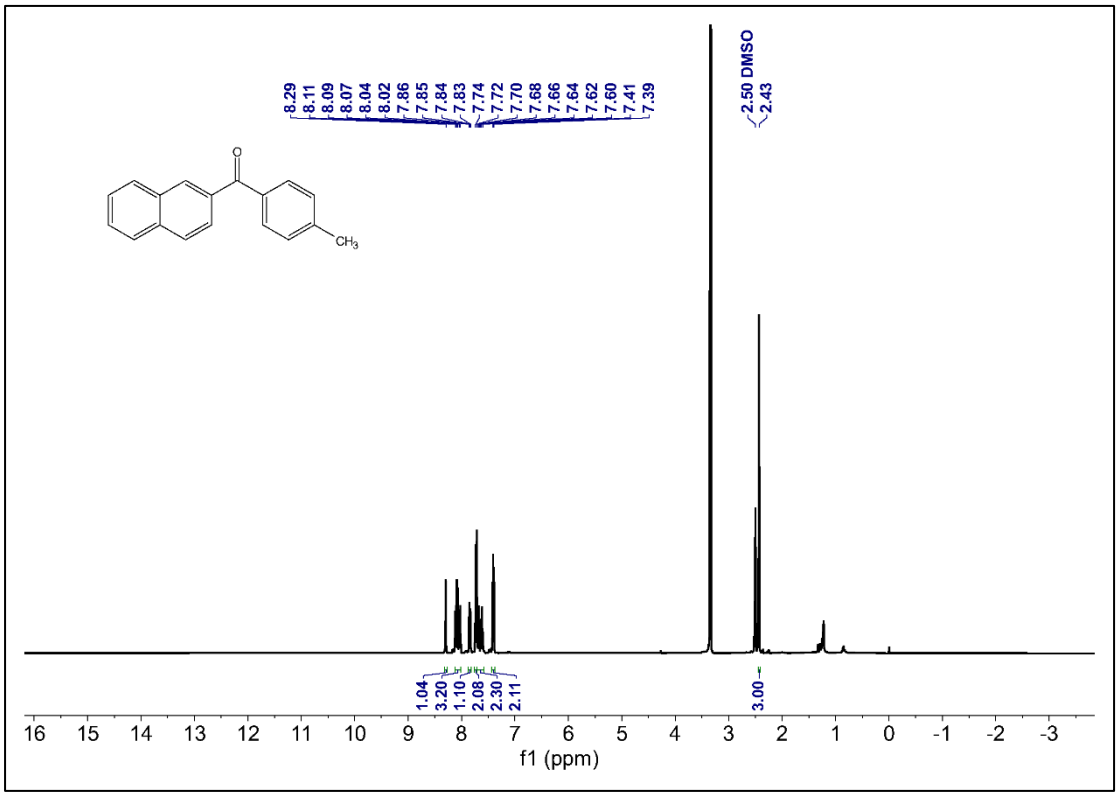
f1 (ppm)

3ah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7.41
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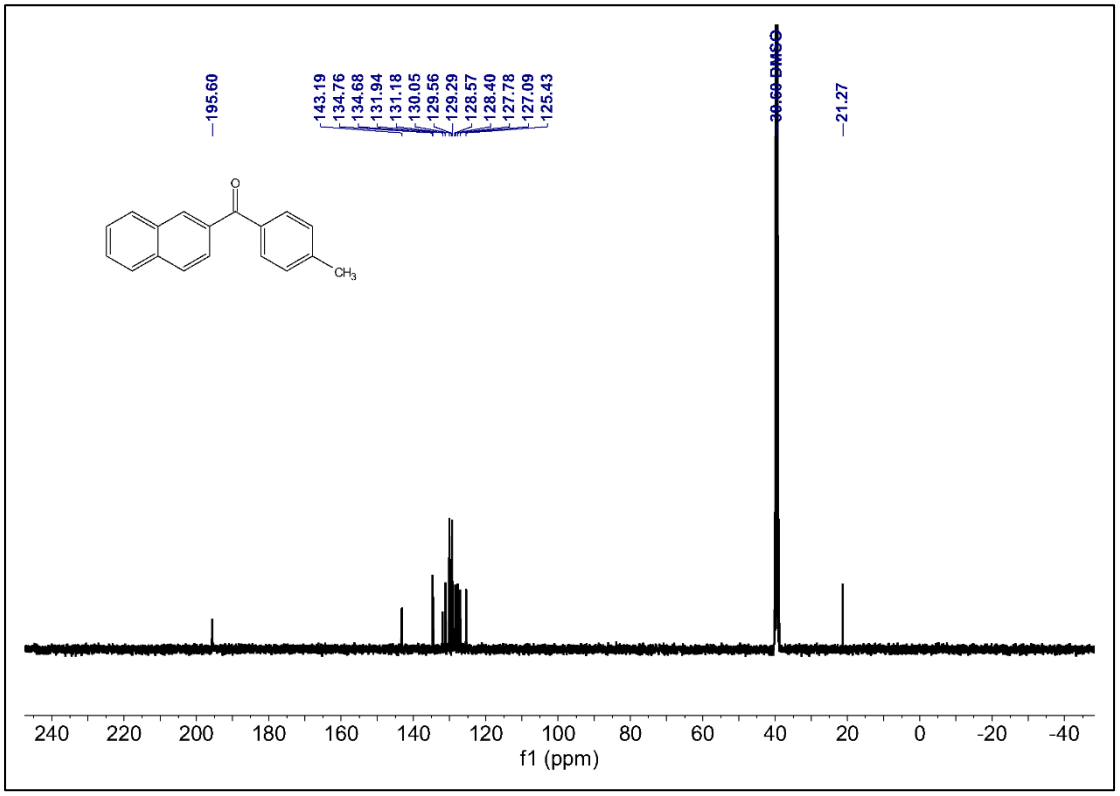
f1 (ppm)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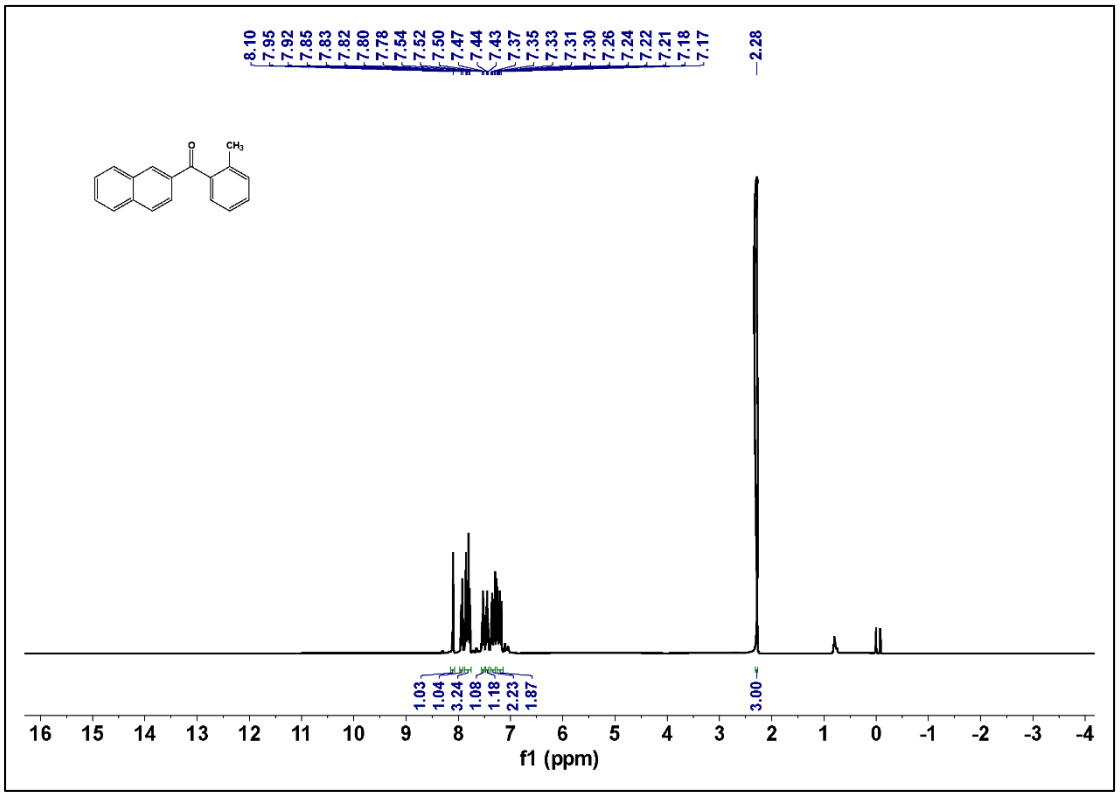
3ai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7.21
7.18
7.17
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1.03
1.04
3.24
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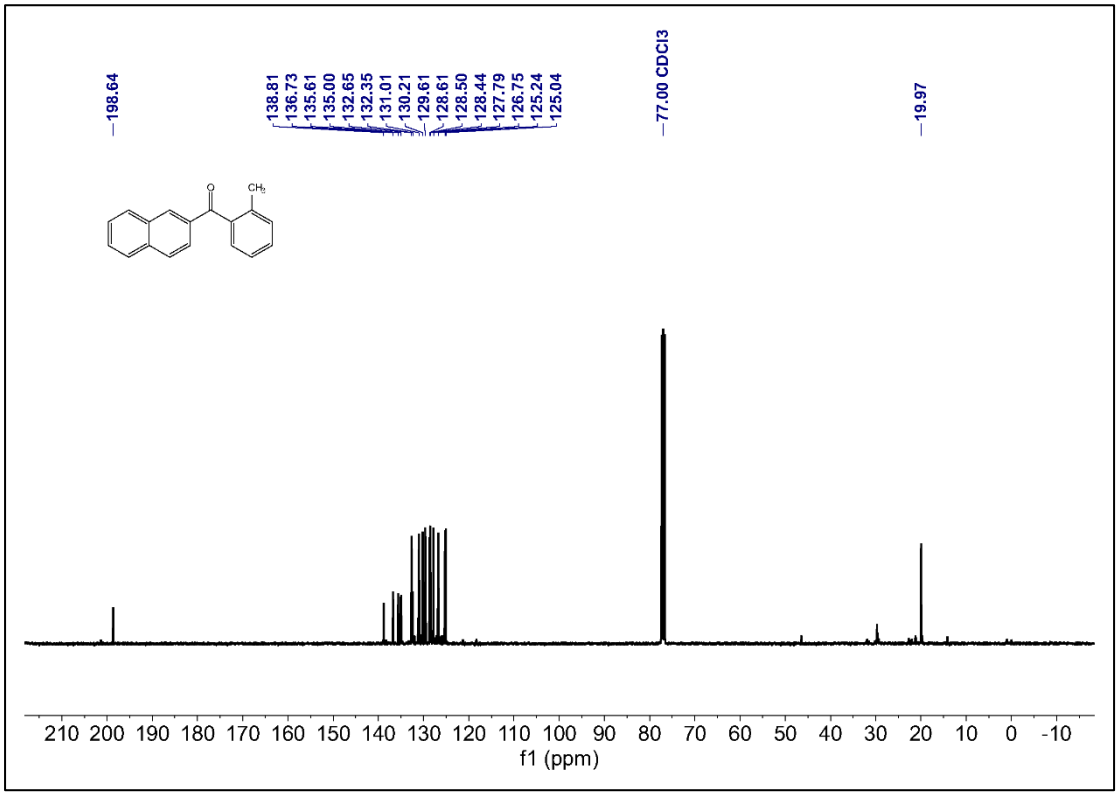
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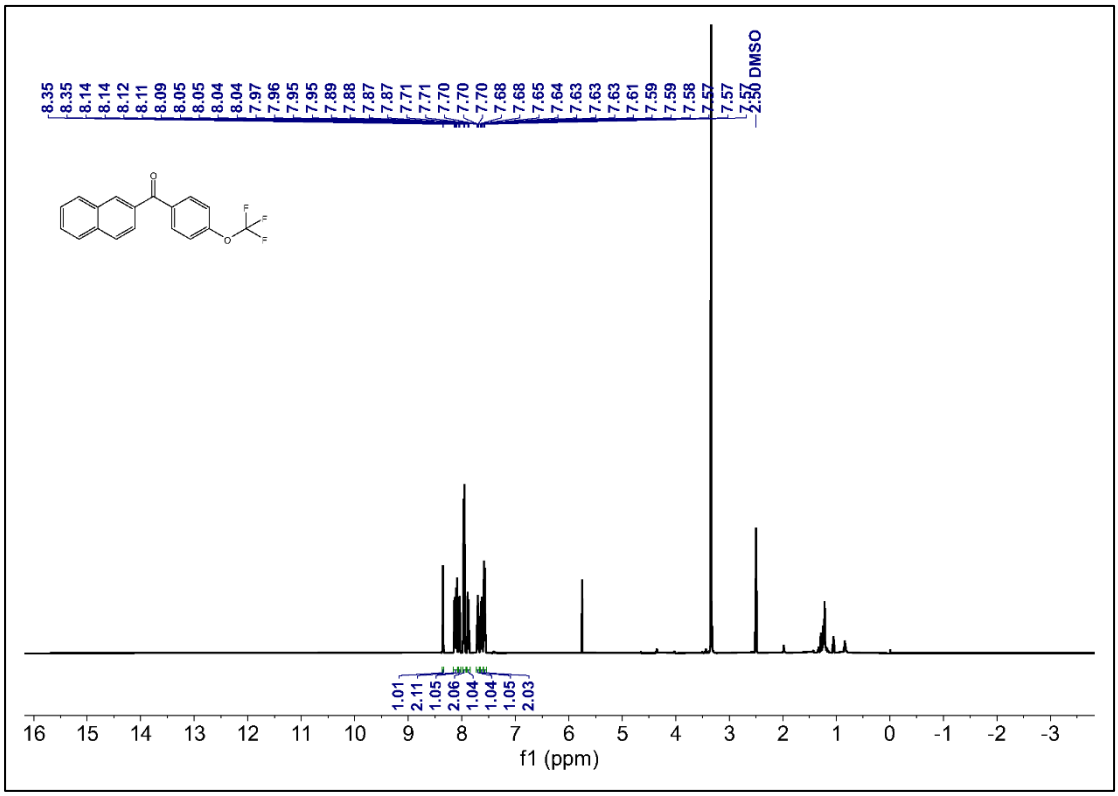
3aj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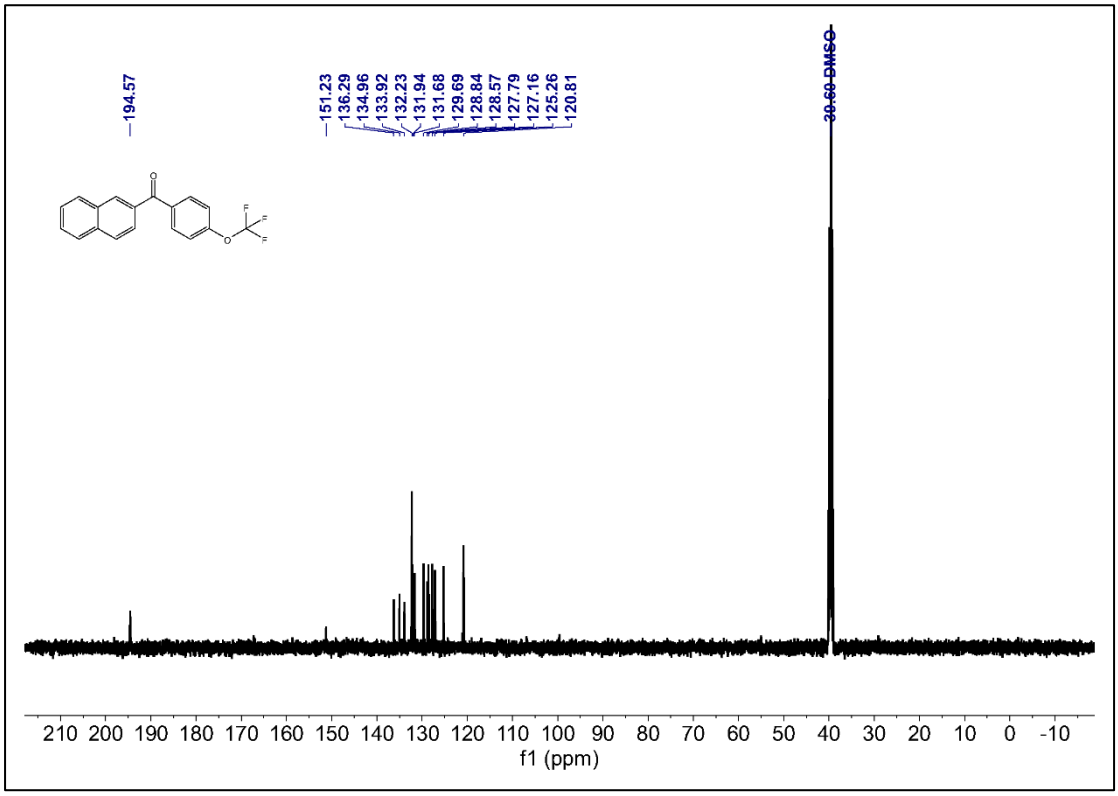
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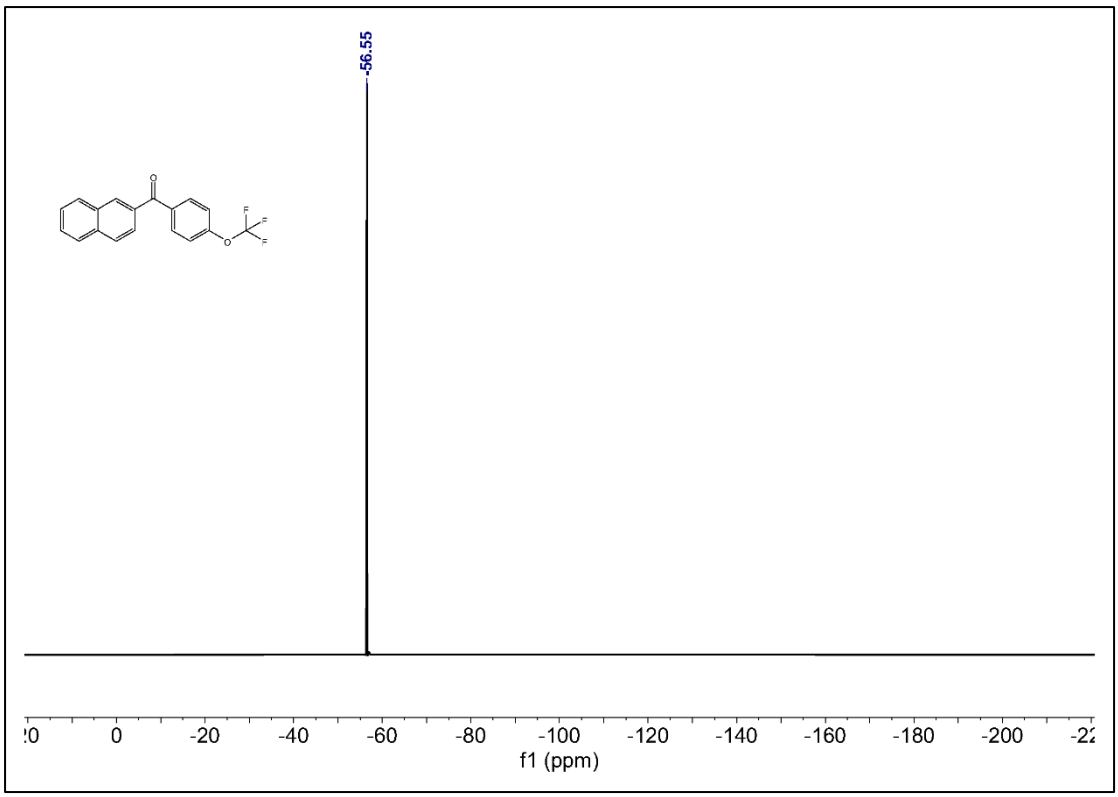
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F
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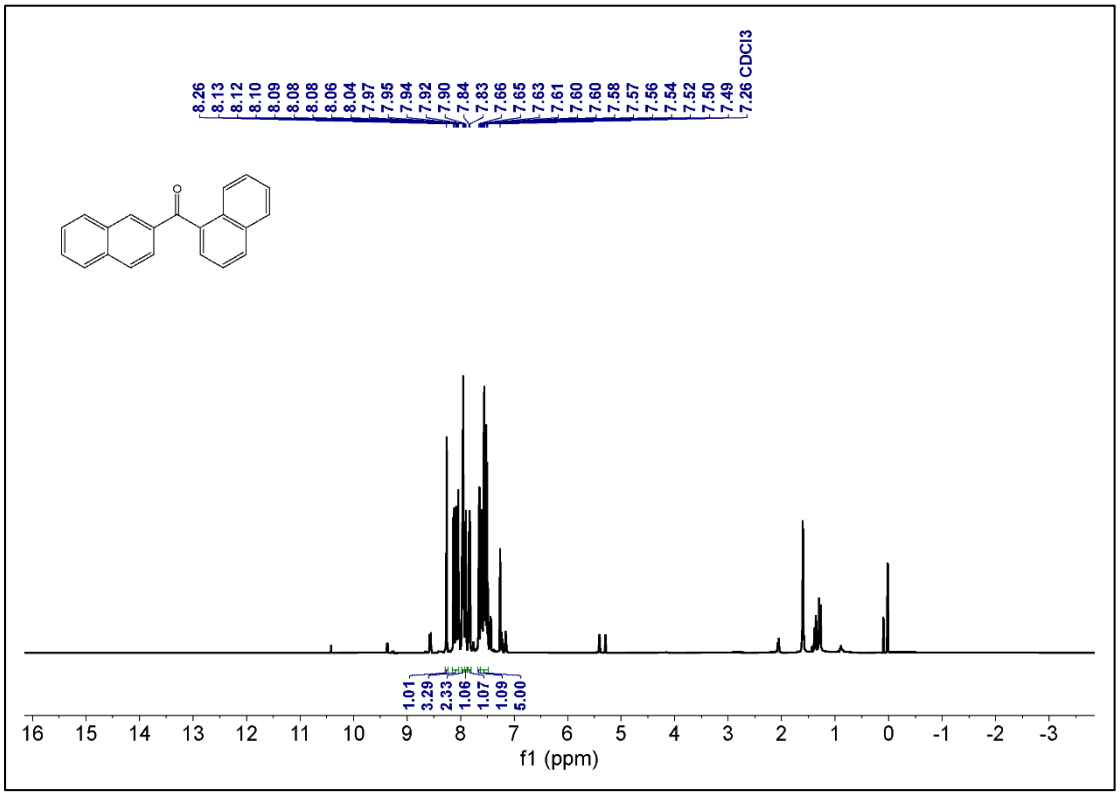
3ak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7.49
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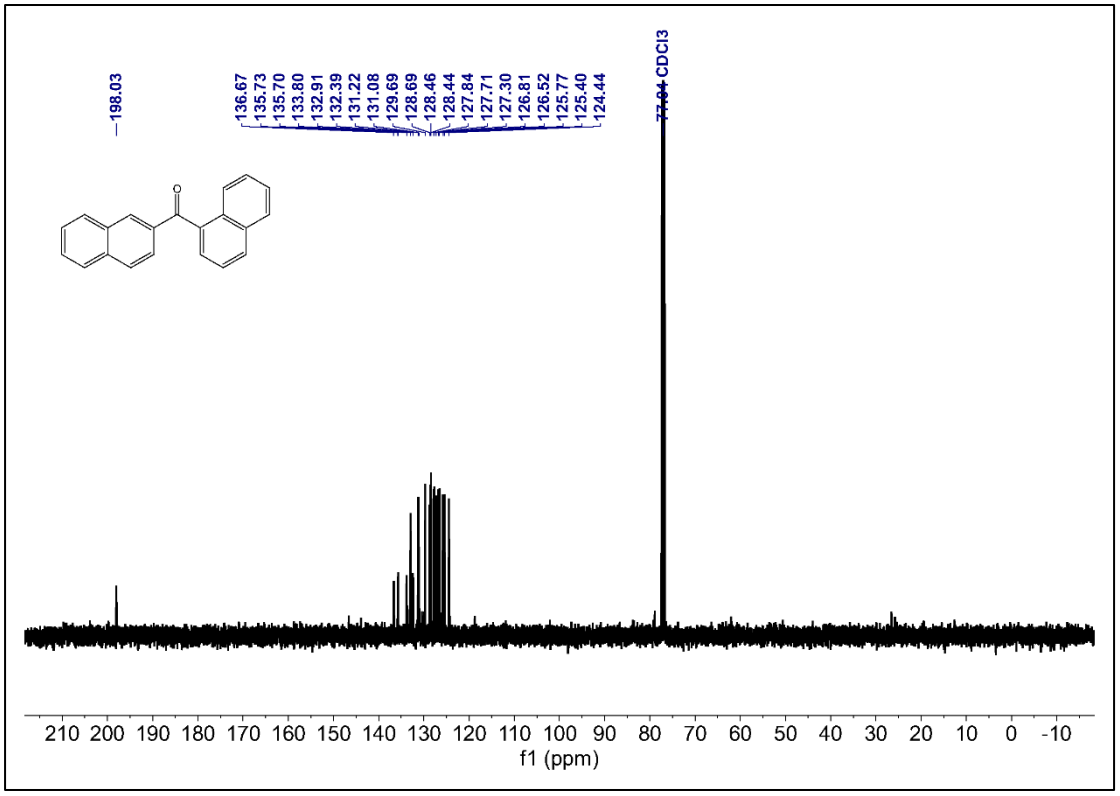
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127.30
126.81
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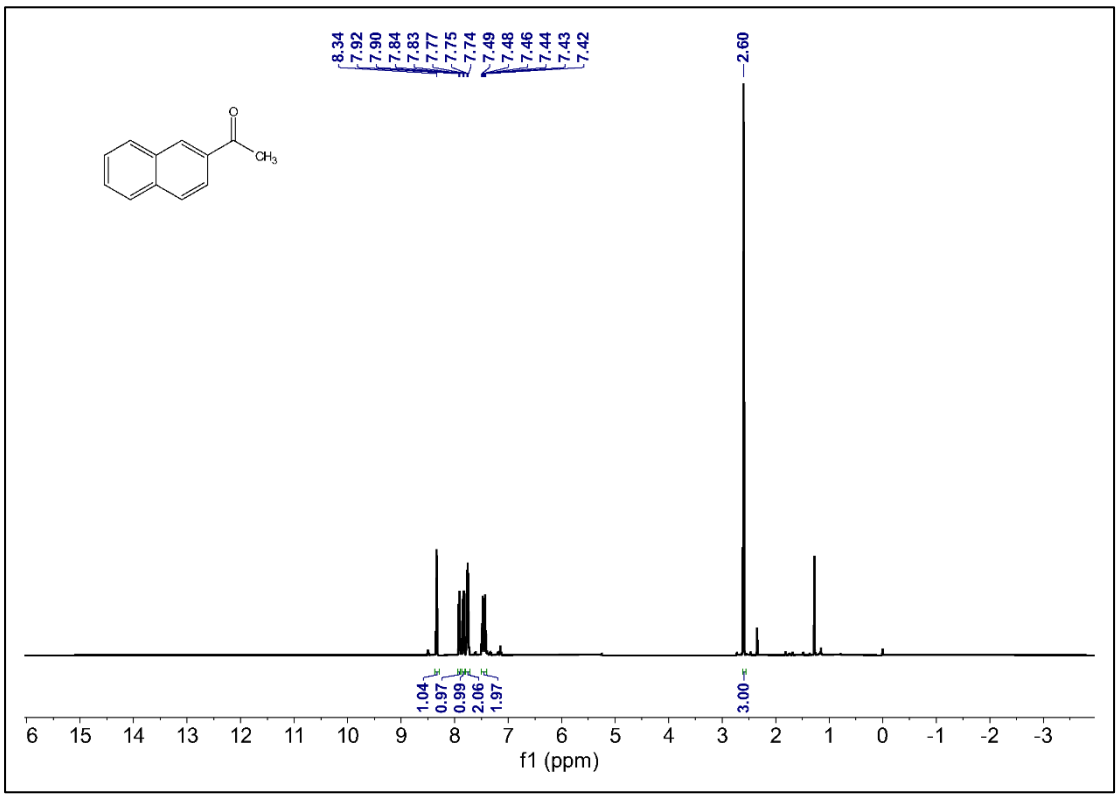
3al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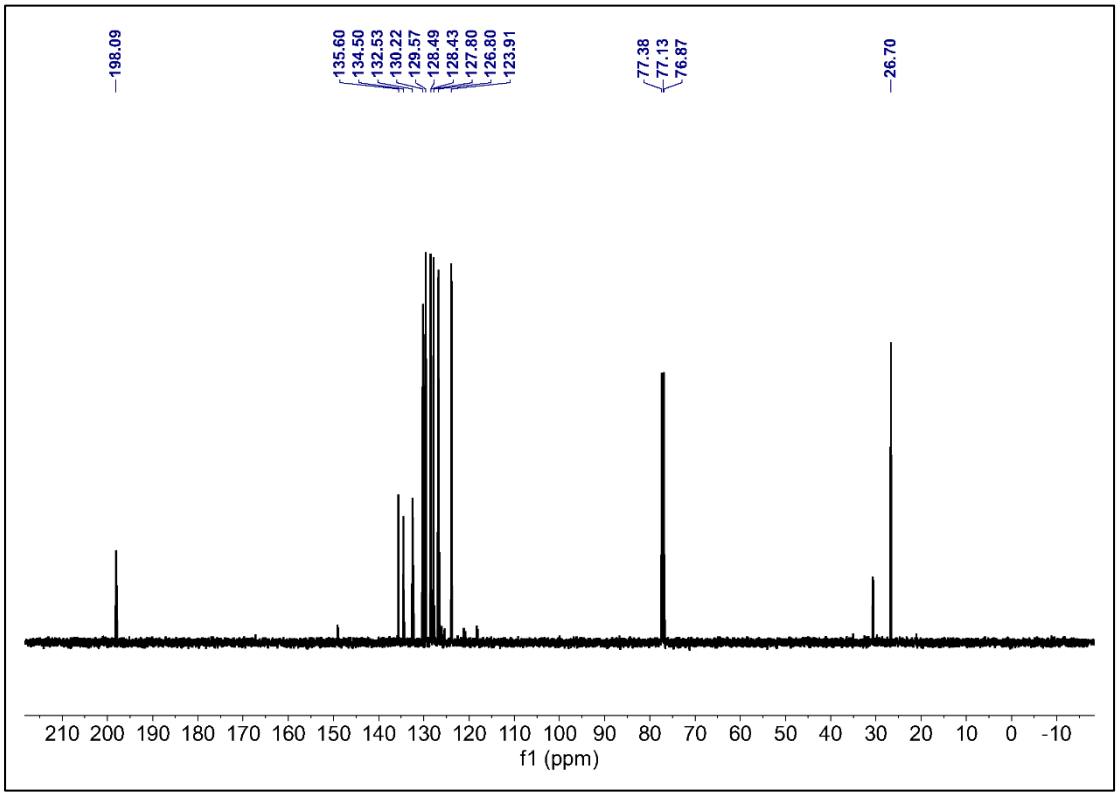
f1 (ppm)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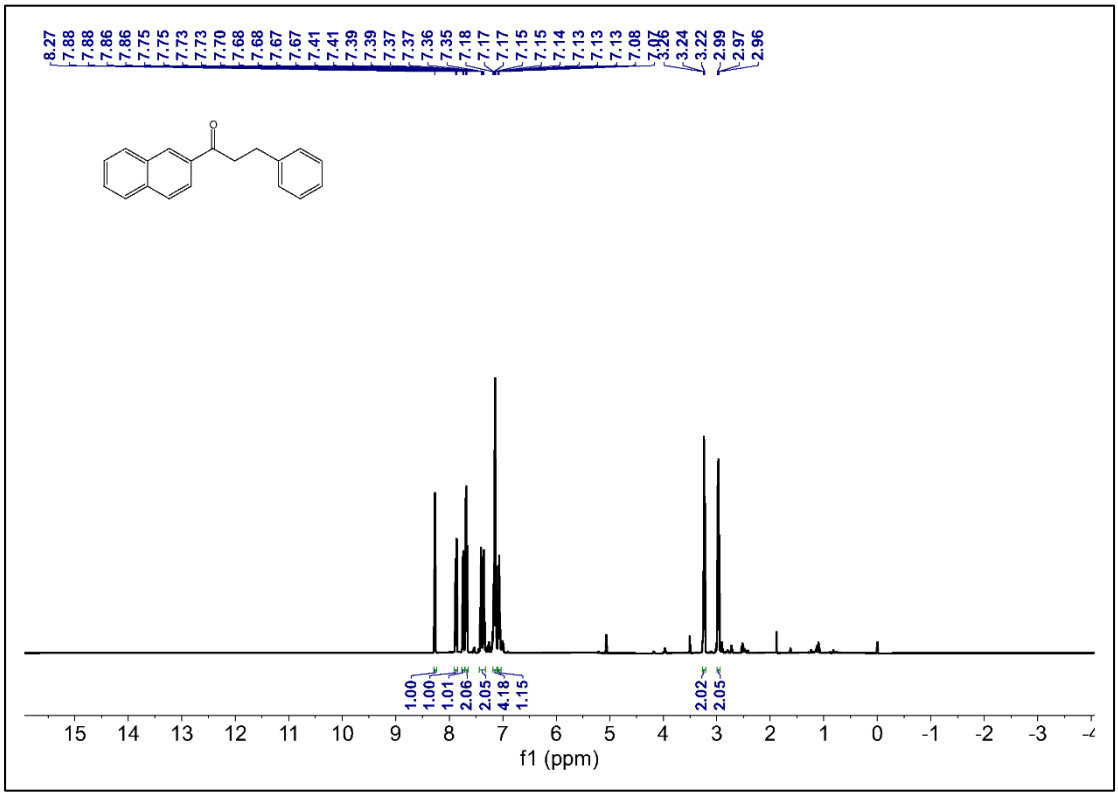
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1.00
1.01
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2.02
2.05
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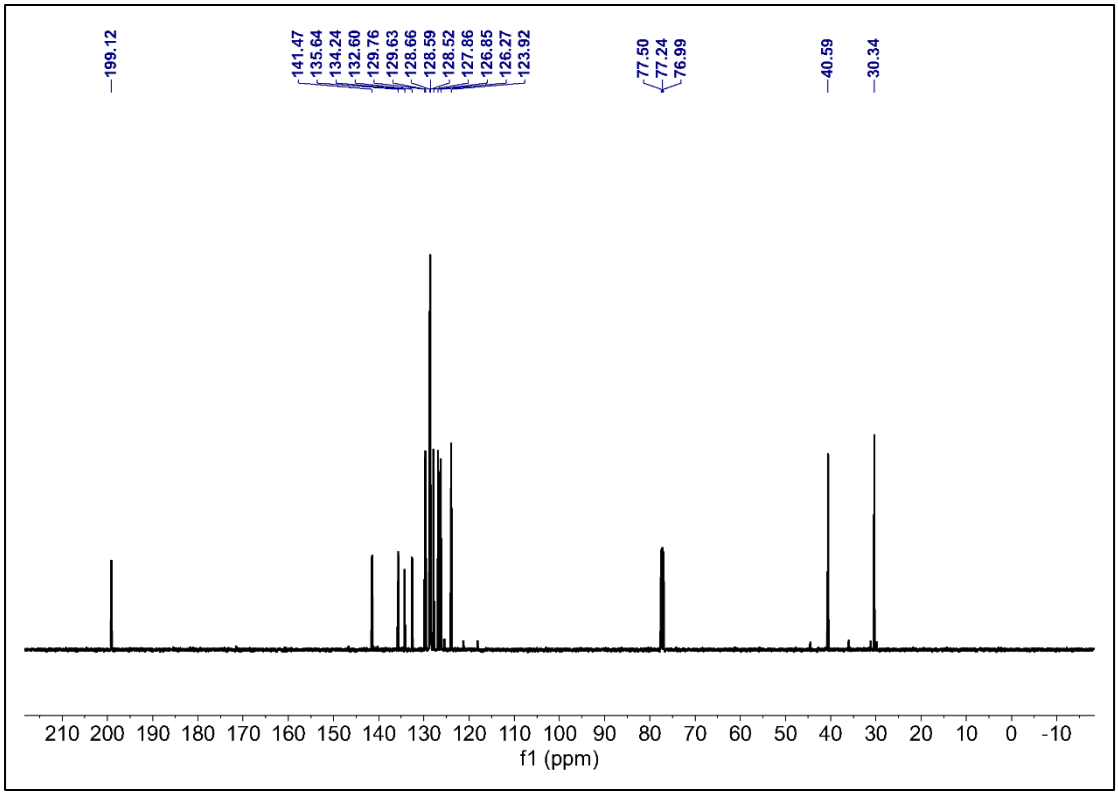
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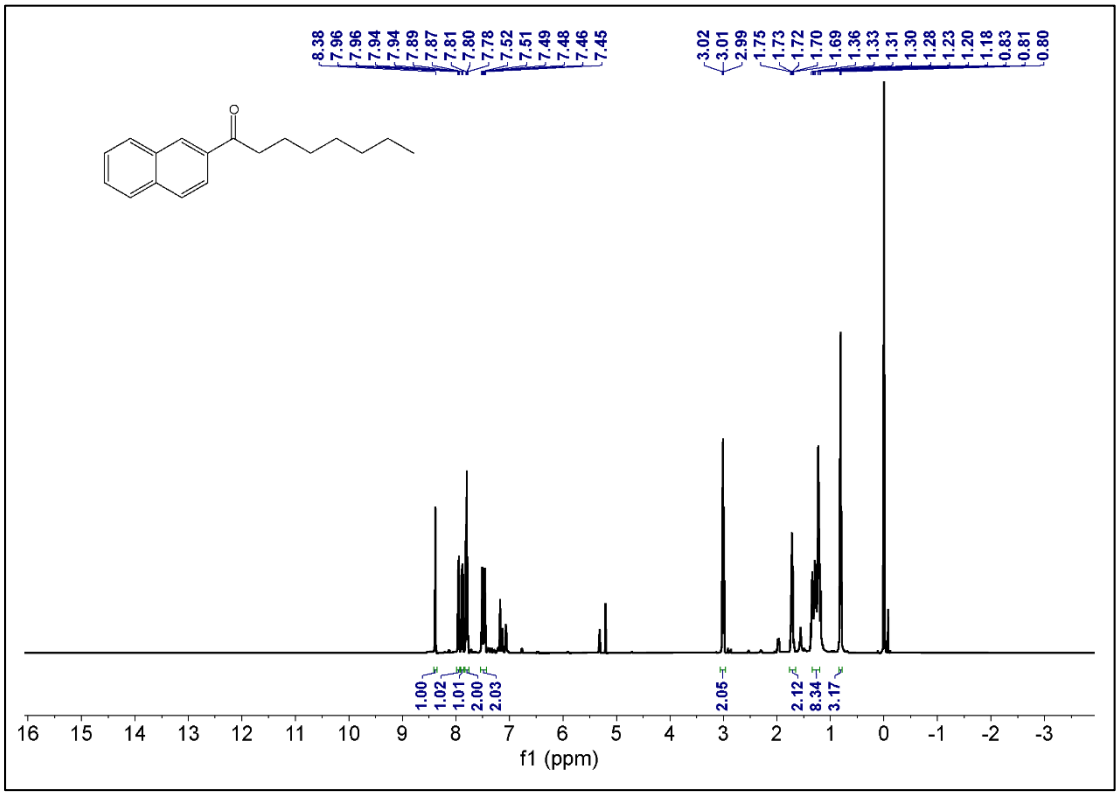
f1 (ppm)

3an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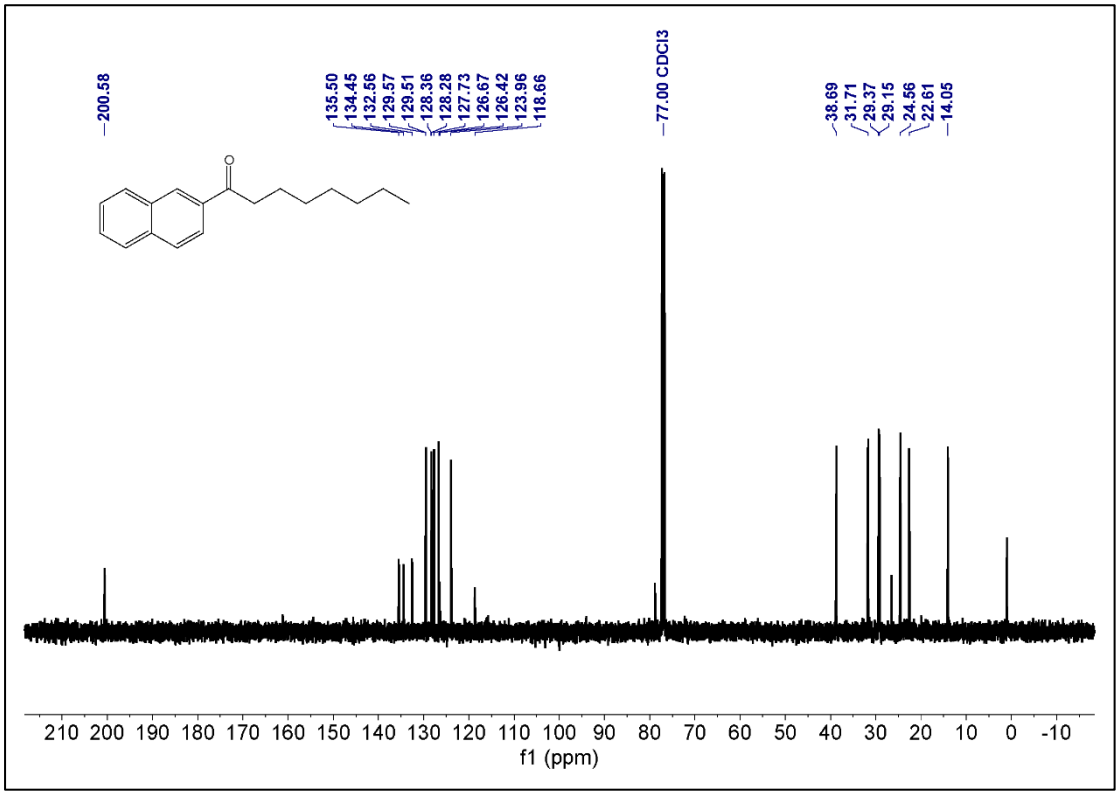
7.52
7.51
7.49
7.48
7.46
7.45
3.02
3.01
2.99
1.75
1.73
1.72
1.70
1.69
1.36
1.33
1.31
1.30
1.28
1.23
1.20
1.18
0.83
0.81
0.80
1.00
1.02
1.01
2.00
2.03
2.05
2.12
8.34
3.17
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


200.58
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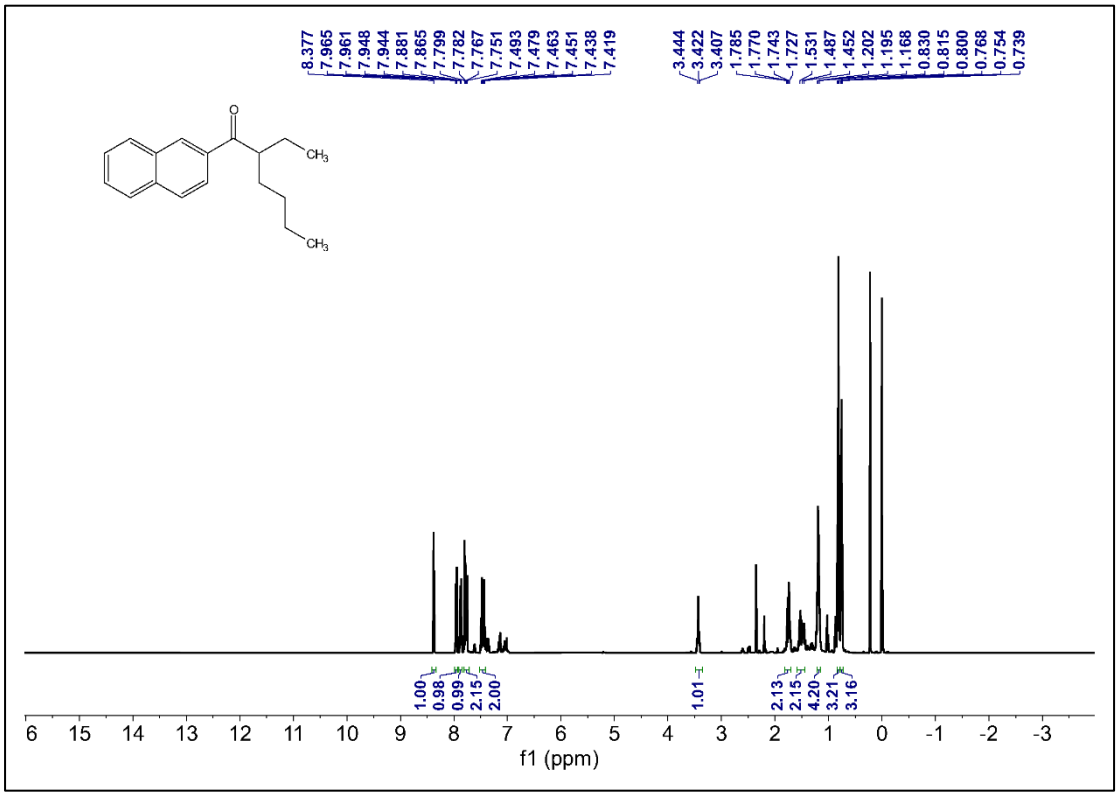
134.45
132.56
129.57
129.51
128.36
128.28
127.73
126.67
126.42
123.96
118.66
77.00 CDCl3
38.69
31.71
29.37
29.15
24.56
22.61
14.05
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3ao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7.944
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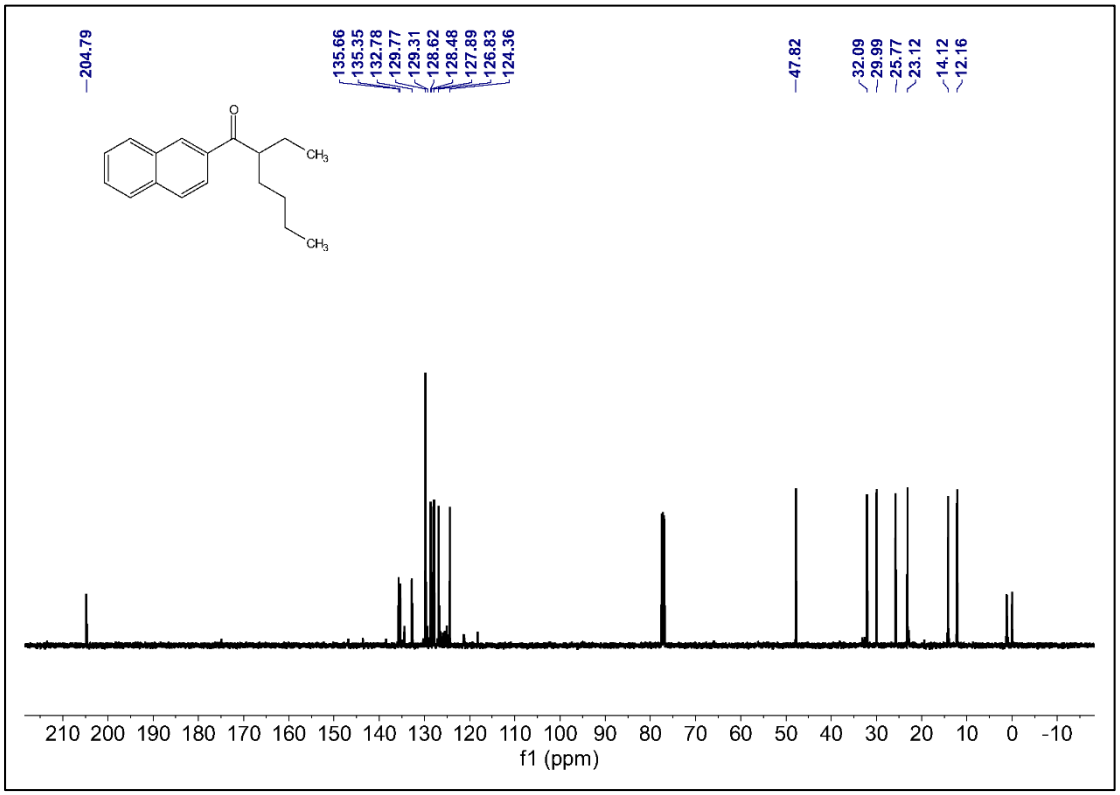
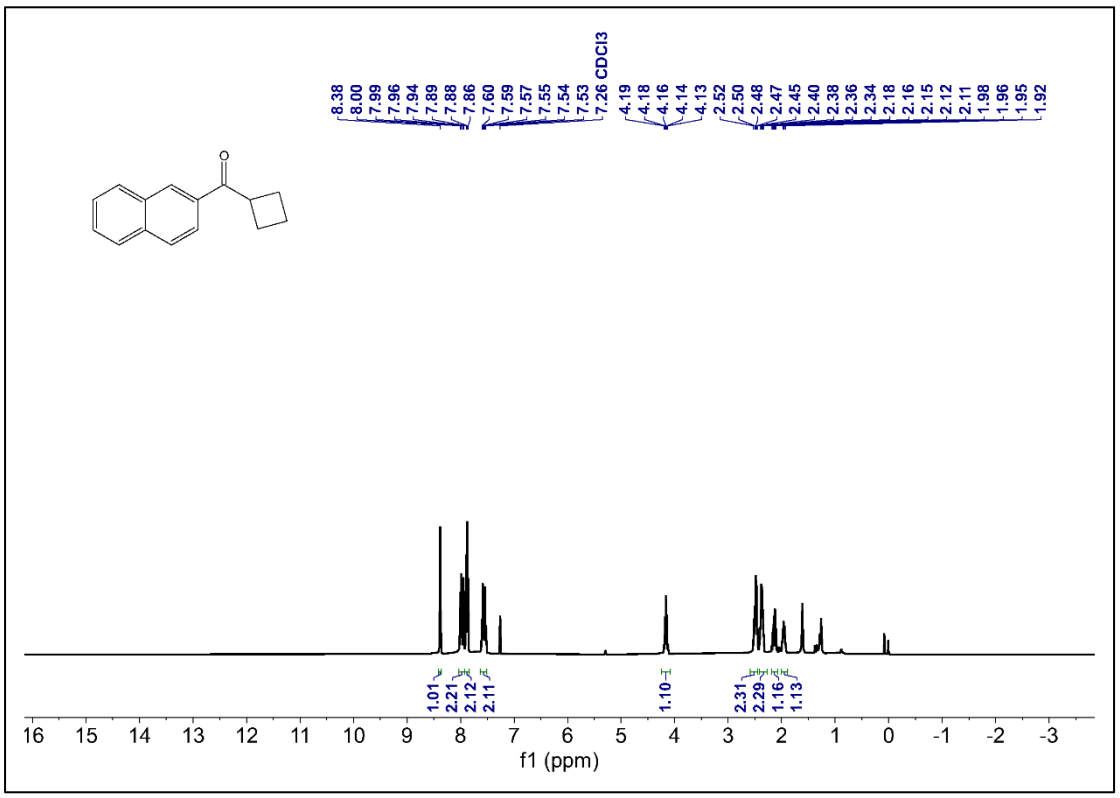
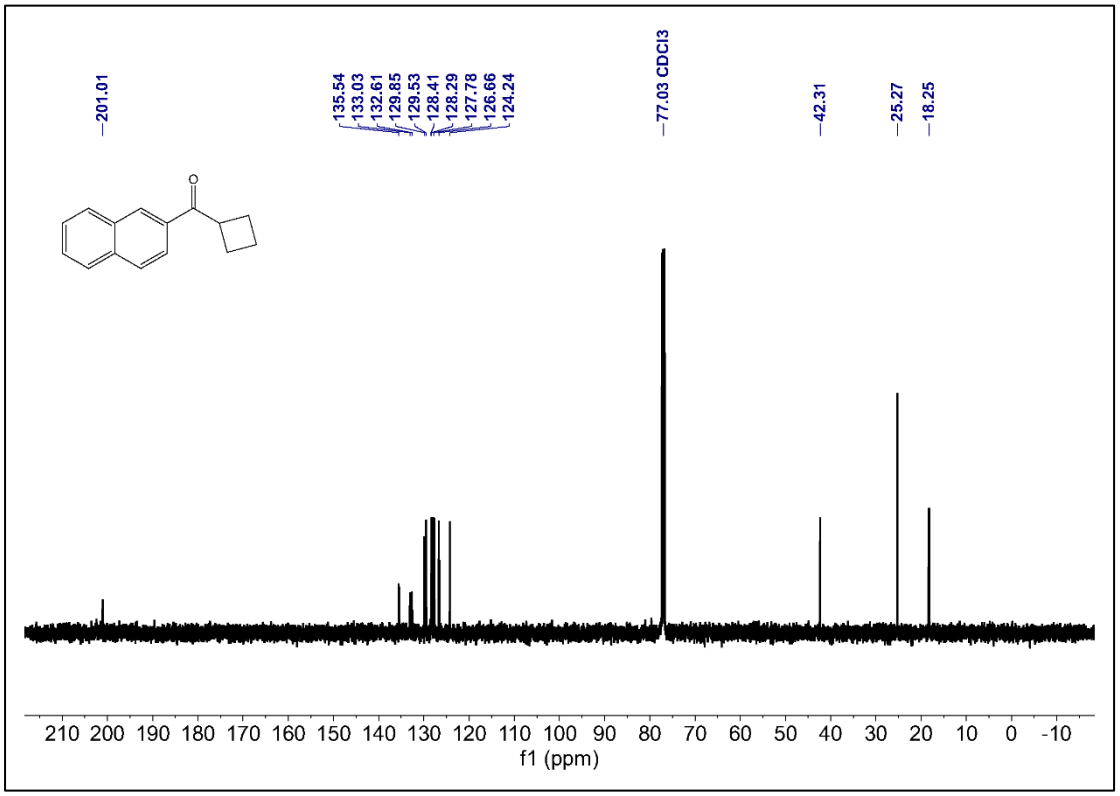
7.865
7.799
7.782
7.767
7.751
7.493
7.479
7.463
7.451
7.438
7.419
3.444
3.422
3.407
1.785
1.770
1.743
1.727
1.531
1.487
1.452
1.202
1.195
1.168
0.830
0.815
0.800
0.768
0.754
0.739
CH3
CH3
1.00
0.98
0.99
2.15
2.00
1.01
2.13
2.15
4.20
3.21
3.16
f1 (ppm)

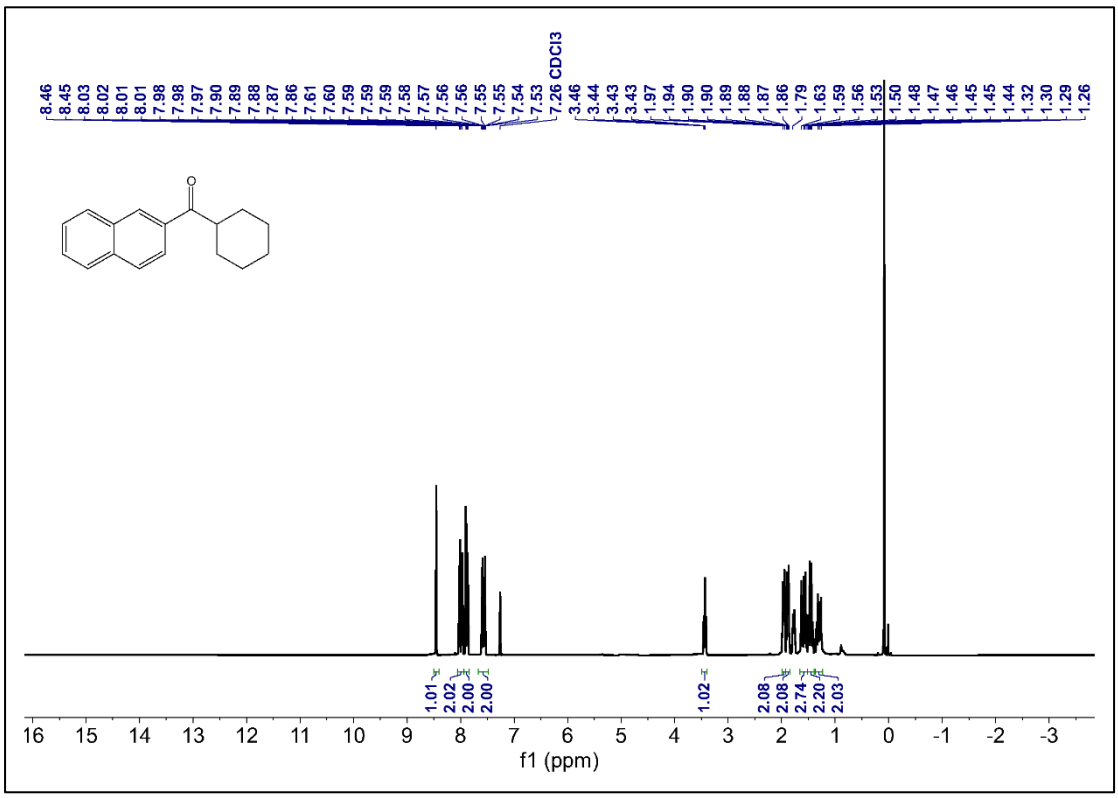

204.79
135.66
135.35
132.78
129.77
129.31
128.62
128.48
127.89
126.83
124.36
47.82
32.09
29.99
25.77
23.12
14.12
12.16
CH3
CH3
f1 (ppm)

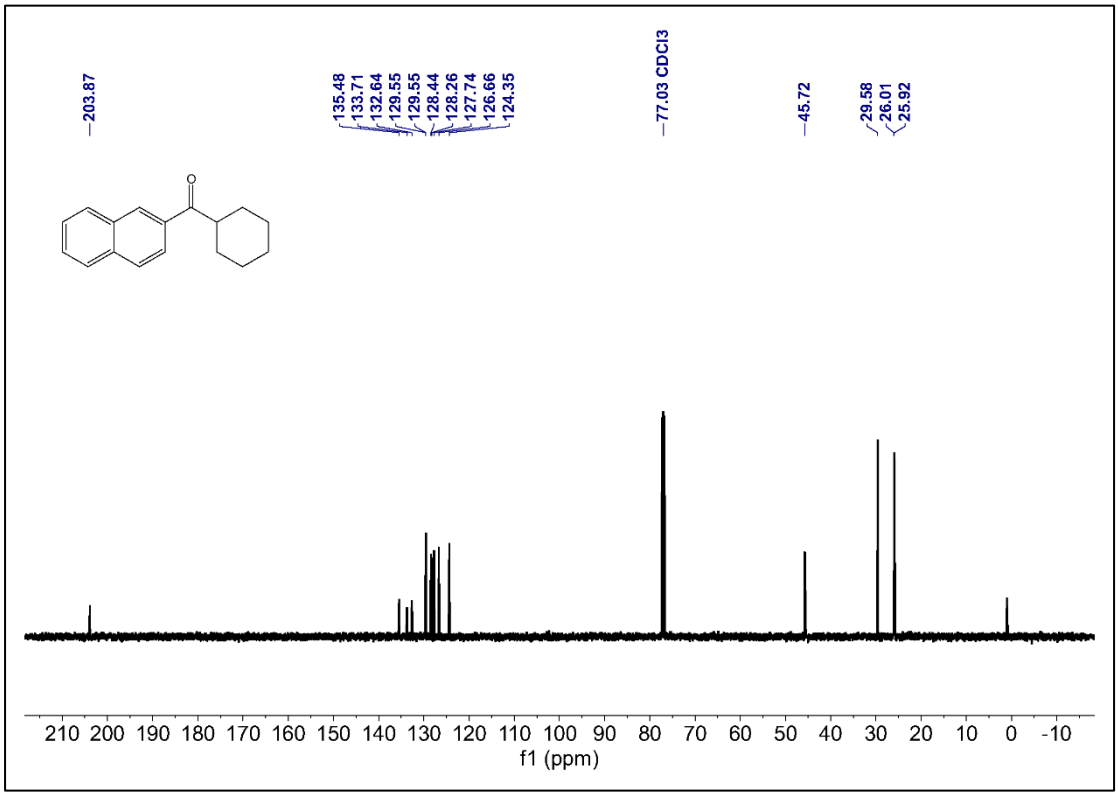
3ap


8.38
8.00
7.99
7.96
7.94
7.89
7.88
7.86
7.60
7.59
7.57
7.55
7.54
7.53
7.26 CDCl3
4.19
4.18
4.16
4.14
4.13
2.52
2.50
2.48
2.47
2.45
2.40
2.38
2.36
2.34
2.18
2.16
2.15
2.12
2.11
1.98
1.96
1.95
1.92
1.01
2.21
2.12
2.11
1.10
2.31
2.29
1.16
1.13
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

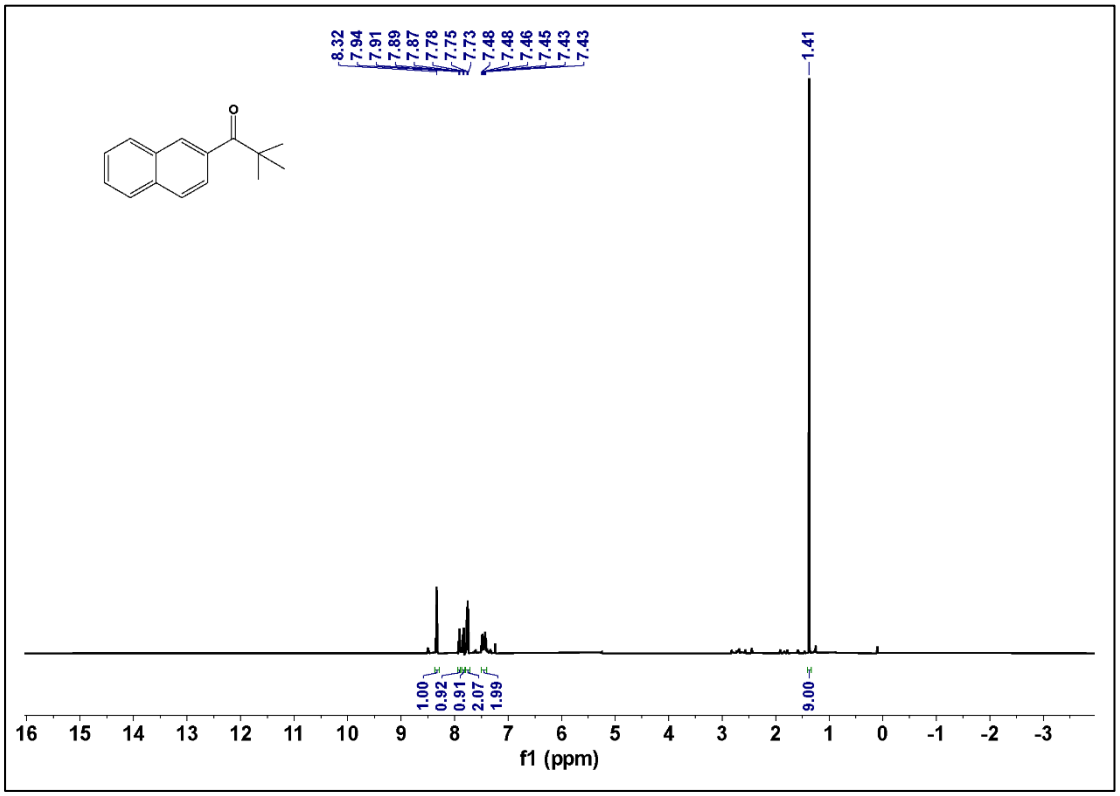

201.01
135.54
133.03
132.61
129.85
129.53
128.41
128.29
127.78
126.66
124.24
77.03 CDCl3
42.31
25.27
18.25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

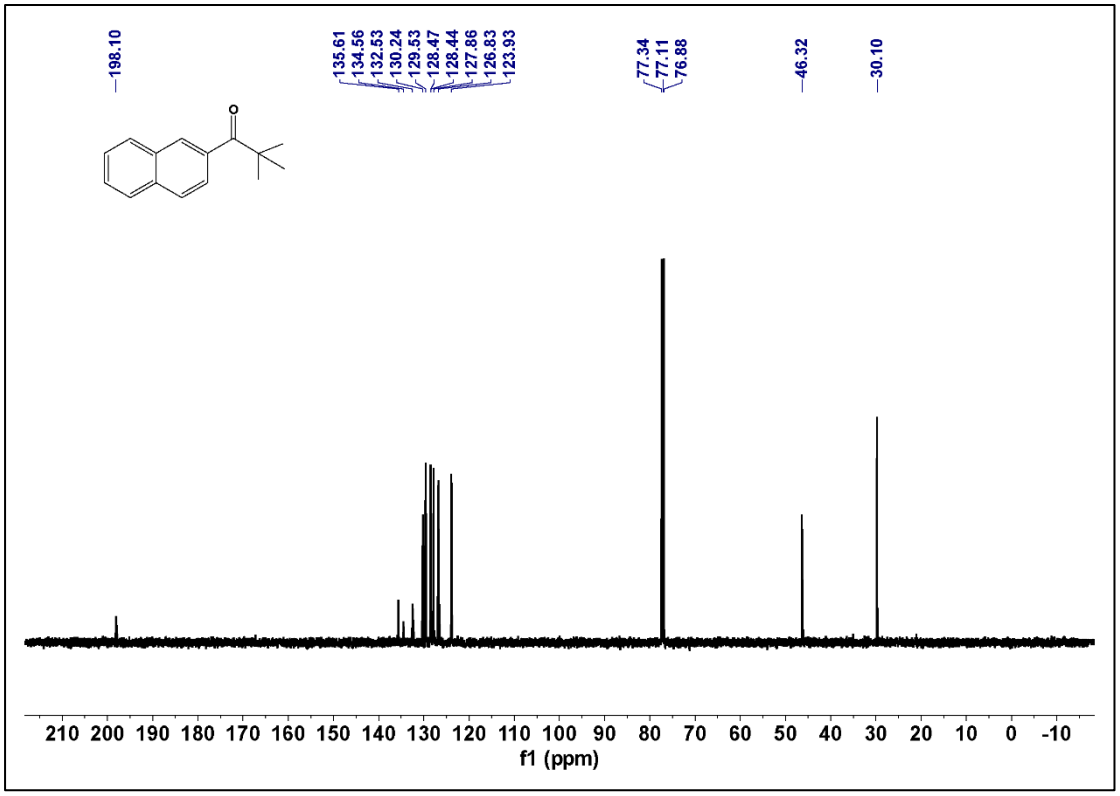
3aq


8.46 8.45 8.03 8.02 8.01 8.01 7.98 7.98 7.97 7.90 7.89 7.88 7.87 7.86 7.61 7.60 7.59 7.59 7.59 7.58 7.57 7.56 7.56 7.55 7.55 7.54 7.53 7.26 CDCl3 3.46 3.44 3.43 3.43 1.97 1.94 1.90 1.90 1.89 1.88 1.87 1.86 1.79 1.63 1.59 1.56 1.53 1.50 1.48 1.47 1.46 1.45 1.45 1.44 1.32 1.30 1.29 1.26
1.01 2.02 2.00 2.00 1.02 2.08 2.08 2.74 2.20 2.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

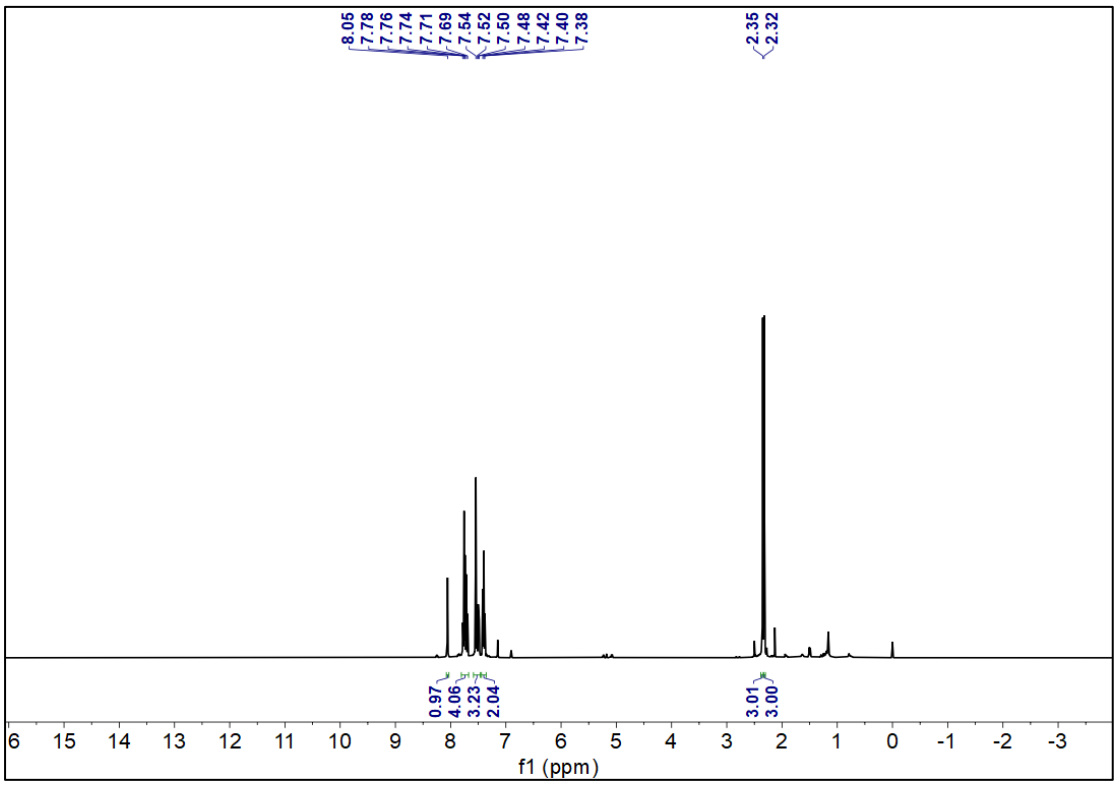

203.87
135.48 133.71 132.64 129.55 129.55 128.44 128.26 127.74 126.66 124.35
77.03 CDCl3
45.72
29.58 26.01 25.92
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

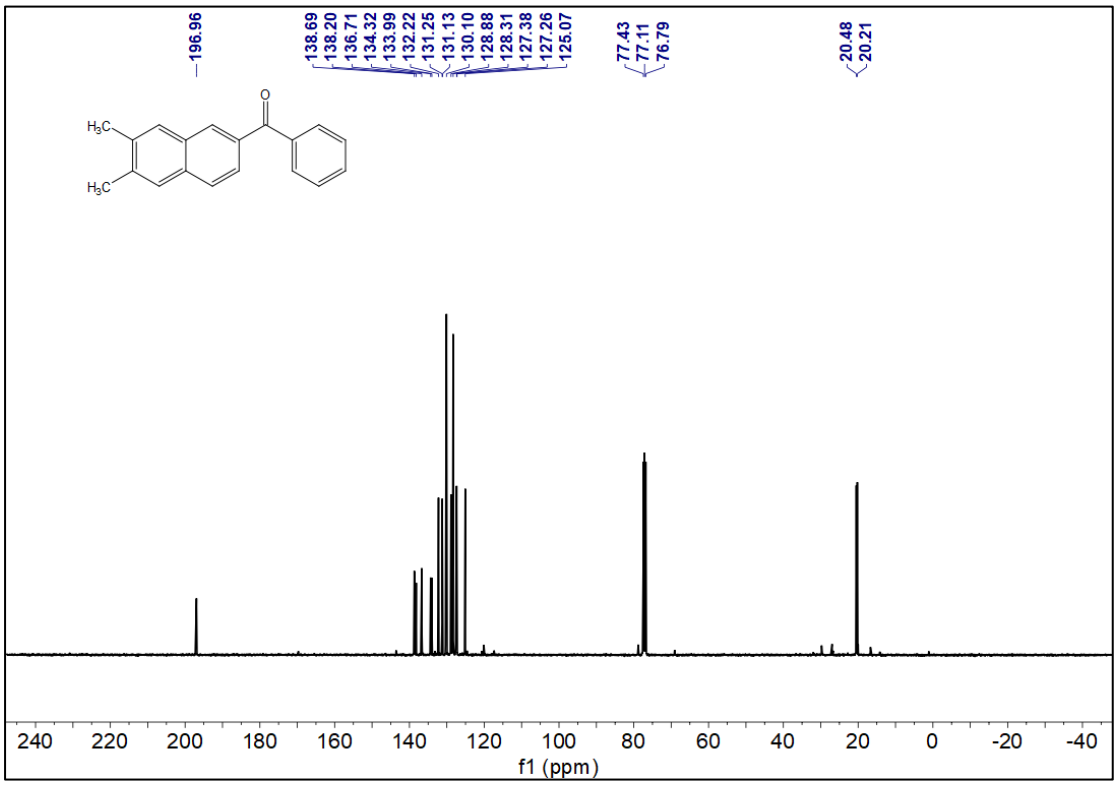
3ar


8.32
7.94
7.91
7.89
7.87
7.78
7.75
7.73
7.48
7.48
7.46
7.45
7.43
7.43
1.41
1.00
0.92
0.91
2.07
1.99
9.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

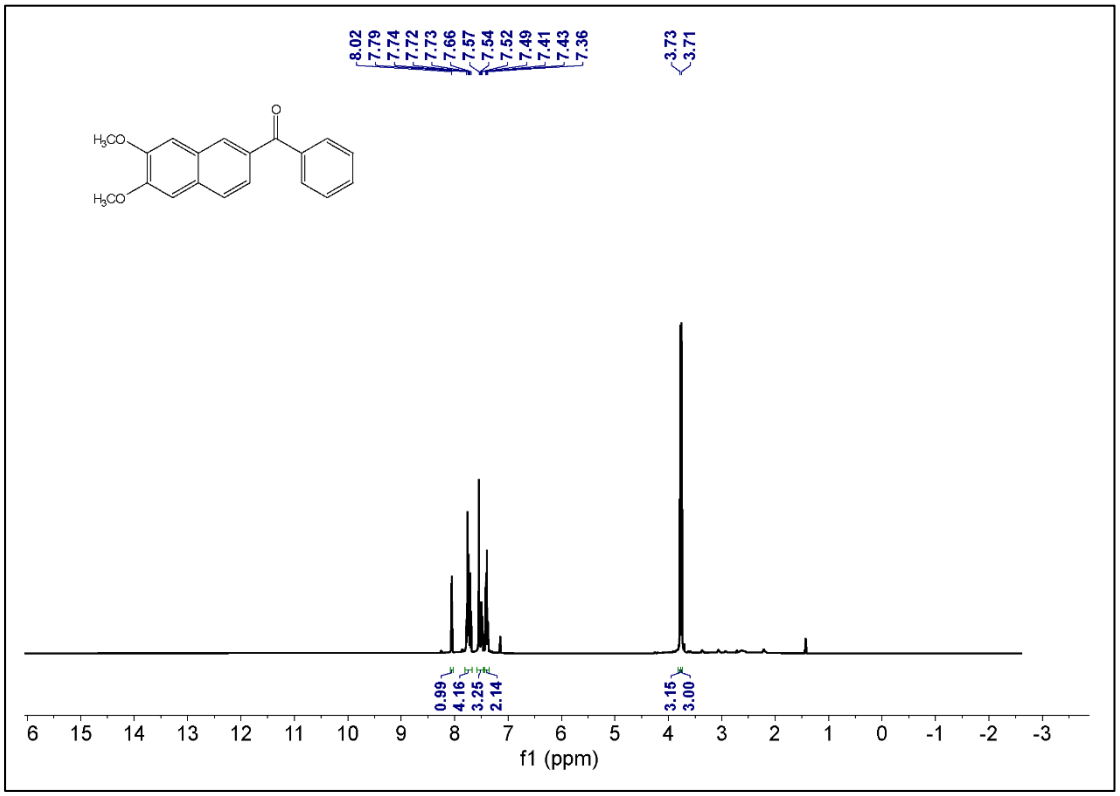

198.10
135.61
134.56
132.53
130.24
129.53
128.47
128.44
127.86
126.83
123.93
77.34
77.11
76.88
46.32
30.10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

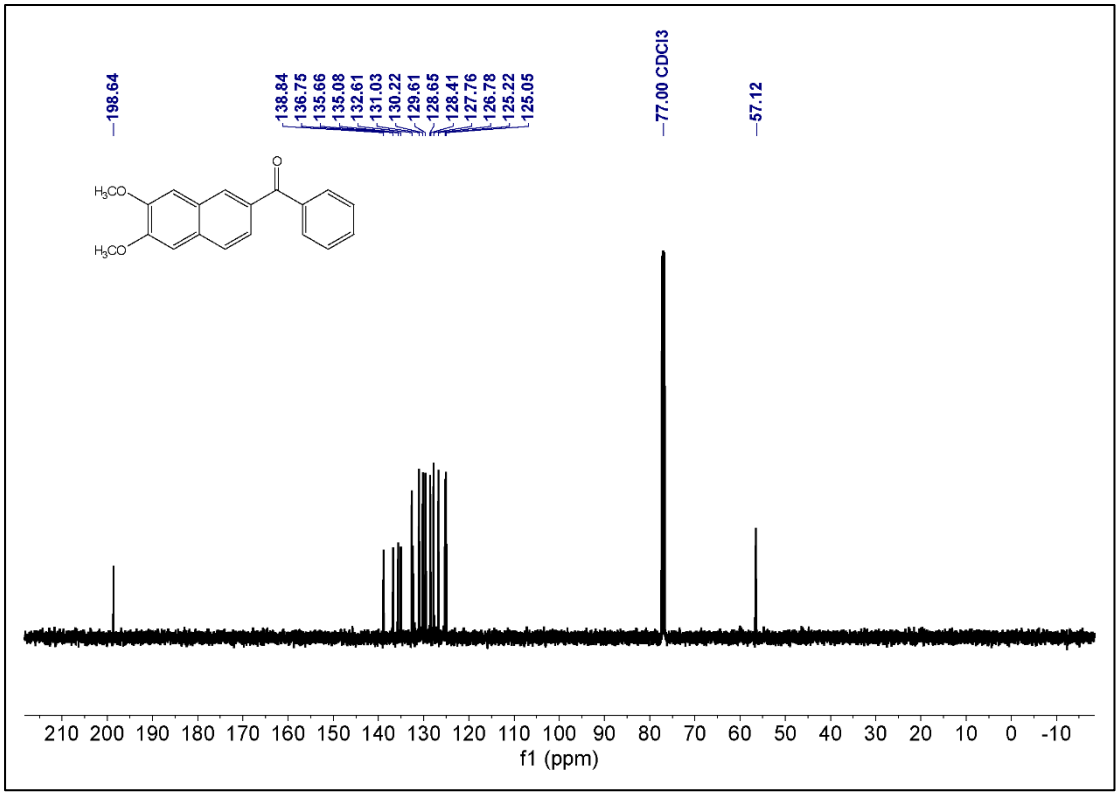
3ba


8.05
7.78
7.76
7.74
7.71
7.69
7.54
7.52
7.50
7.48
7.42
7.40
7.38
2.35
2.32
0.97
4.06
3.23
2.04
3.01
3.00
f1 (ppm)

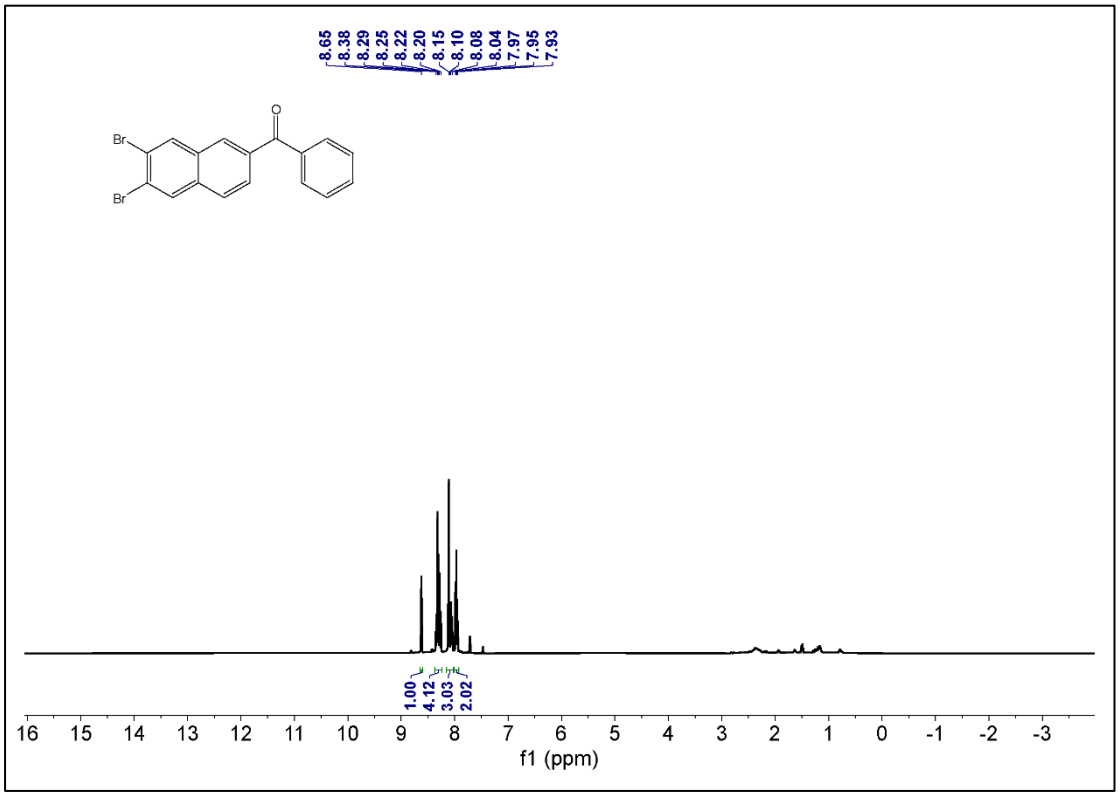

196.96
138.69
138.20
136.71
134.32
133.99
132.22
131.25
131.13
130.10
128.88
128.31
127.38
127.26
125.07
77.43
77.11
76.79
20.48
20.21
O
H3C
H3C
f1 (ppm)

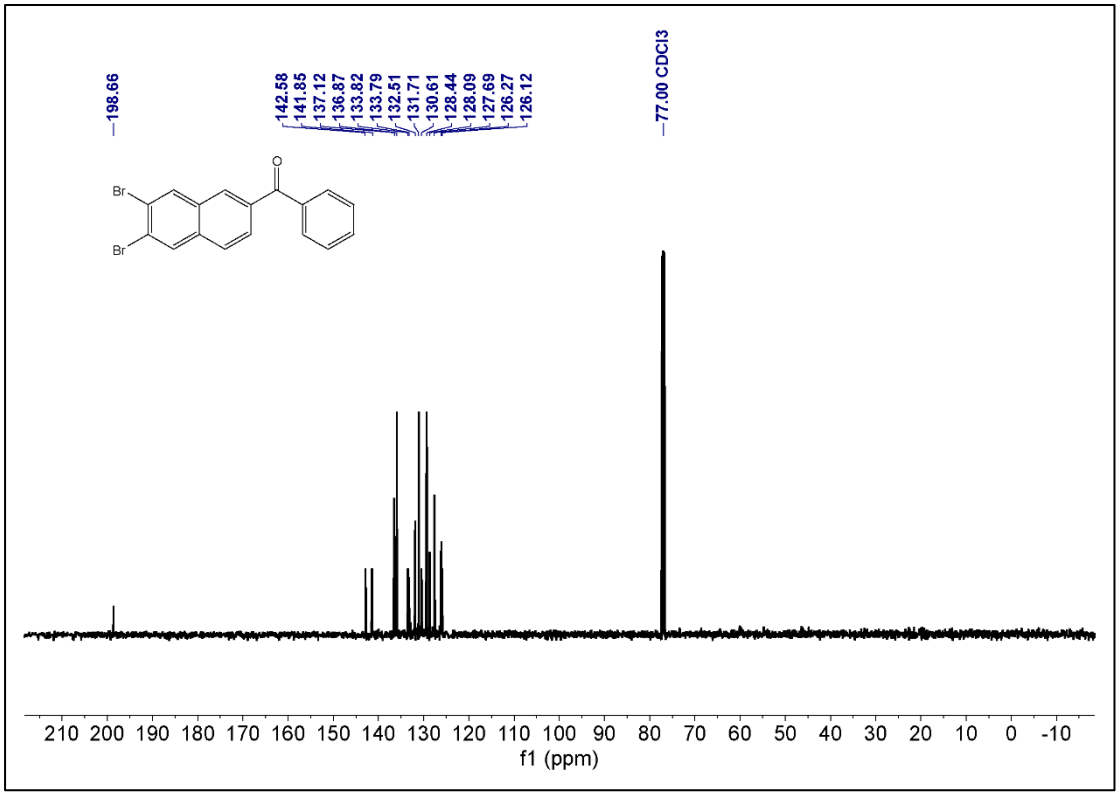
3ca


8.02
7.79
7.74
7.72
7.73
7.66
7.57
7.54
7.52
7.49
7.41
7.43
7.36
3.73
3.71
O
H3CO
H3CO
0.99
4.16
3.25
2.14
3.15
3.00
6 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

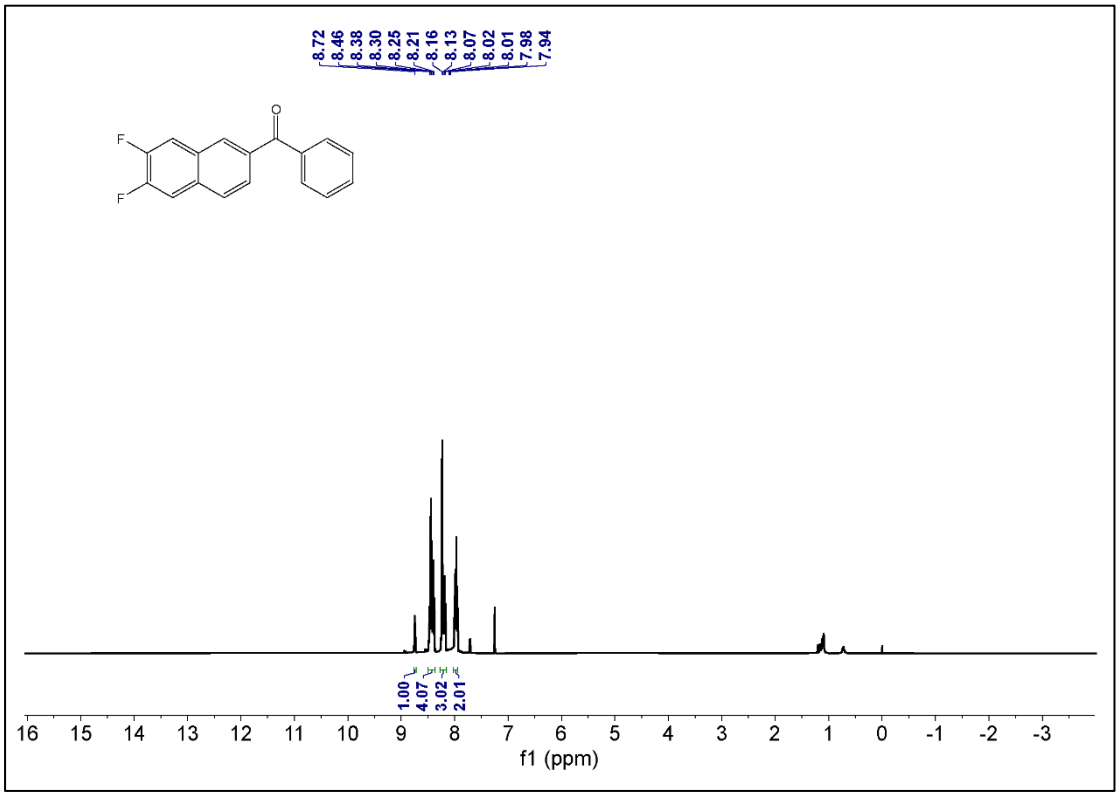

198.64
138.84
136.75
135.66
135.08
132.61
131.03
130.22
129.61
128.65
128.41
127.76
126.78
125.22
125.05
77.00 CDCl3
57.12
O
H3CO
H3CO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

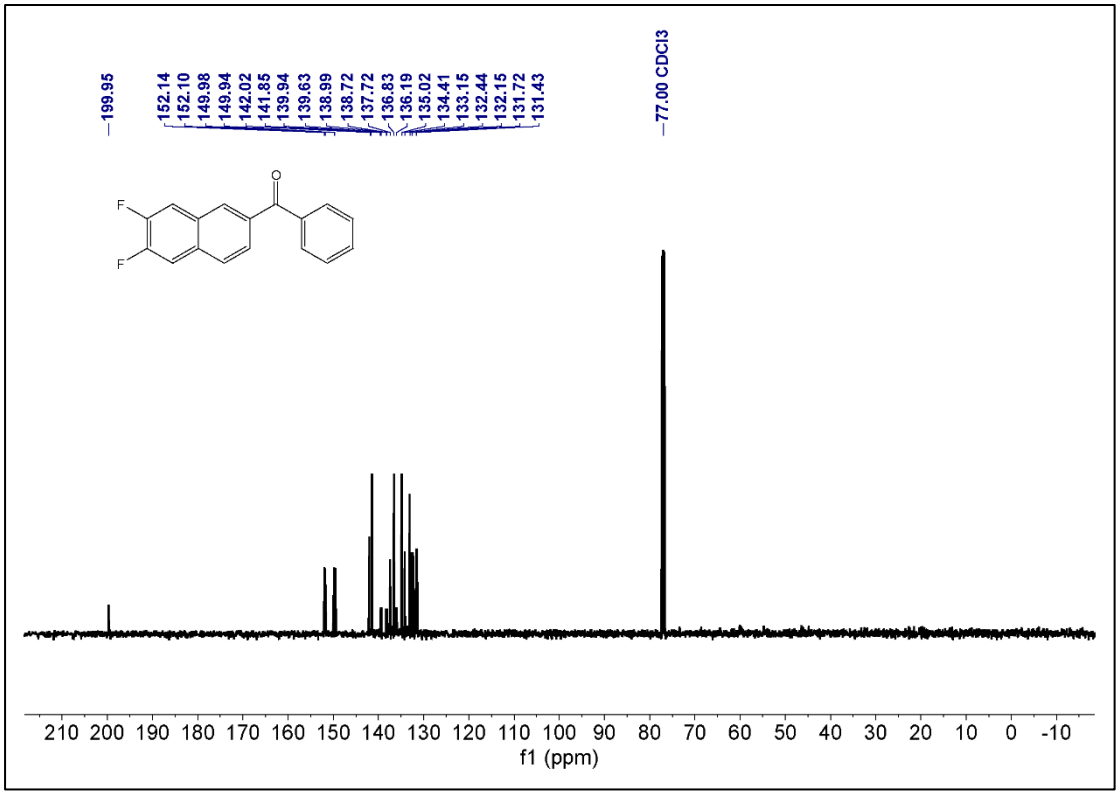
3da


8.65
8.38
8.29
8.25
8.22
8.20
8.15
8.10
8.08
8.04
7.97
7.95
7.93
Br
Br
O
1.00
4.12
3.03
2.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

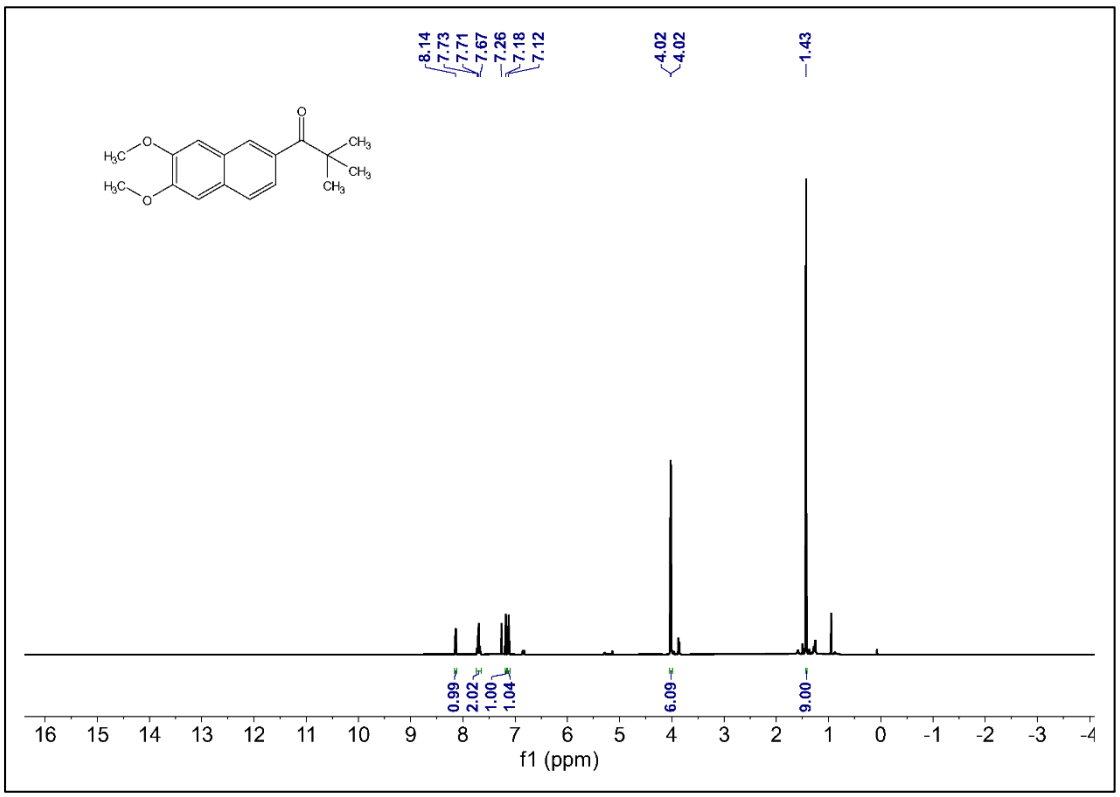

198.66
142.58
141.85
137.12
136.87
133.82
133.79
132.51
131.71
130.61
128.44
128.09
127.69
126.27
126.12
77.00 CDCl3
Br
Br
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

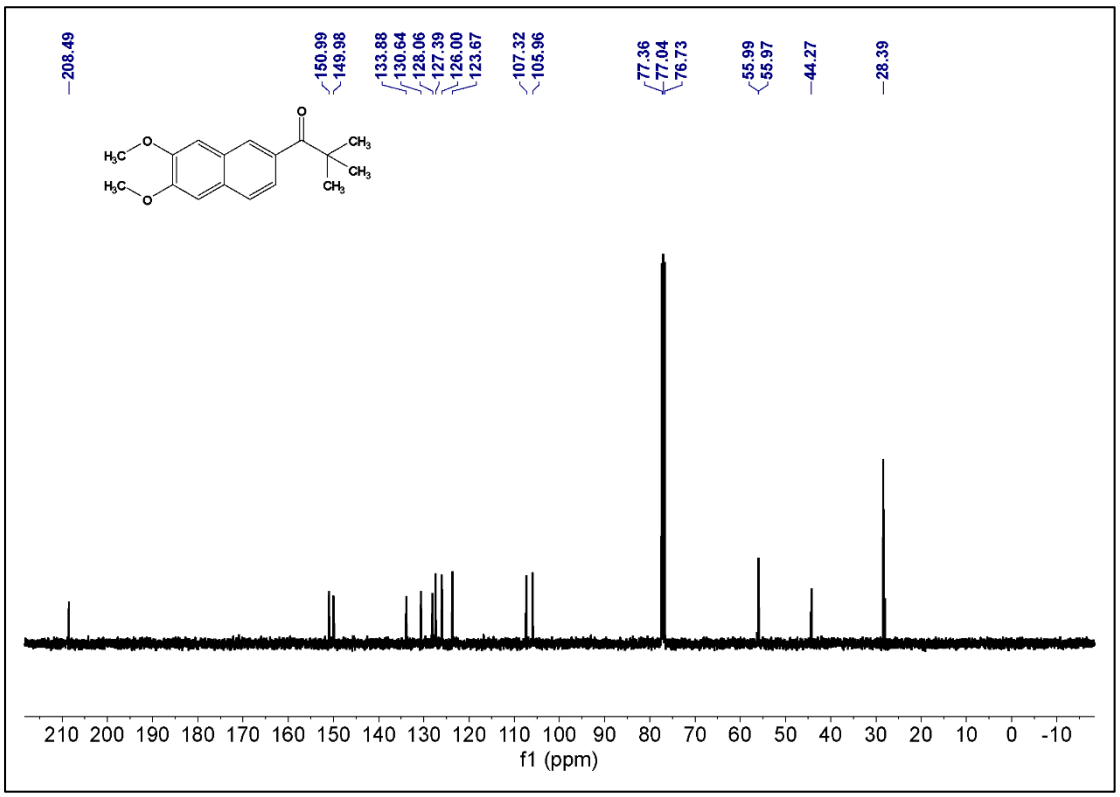
3ea


8.72
8.46
8.38
8.30
8.25
8.21
8.16
8.13
8.07
8.02
8.01
7.98
7.94
F
F
O
1.00
4.07
3.02
2.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

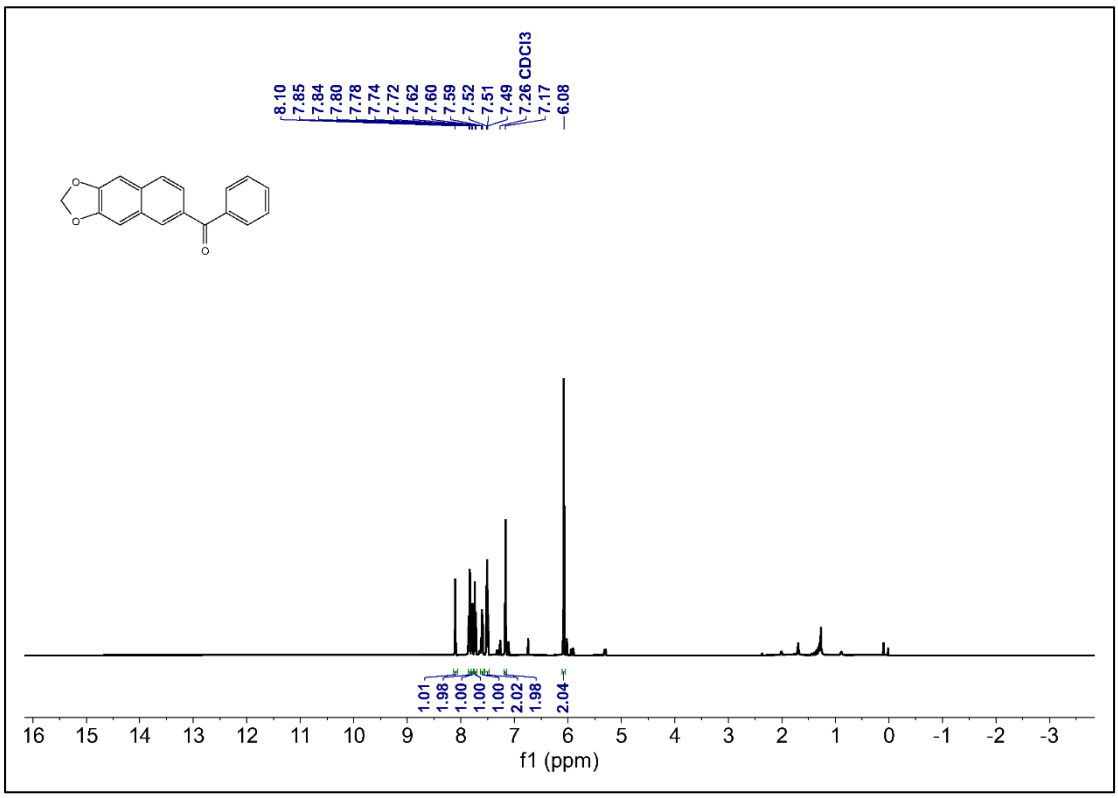

199.95
152.14
152.10
149.98
149.94
142.02
141.85
139.94
139.63
138.99
138.72
137.72
136.83
136.19
135.02
134.41
133.15
132.44
132.15
131.72
131.43
77.00 CDCl3
F
F
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

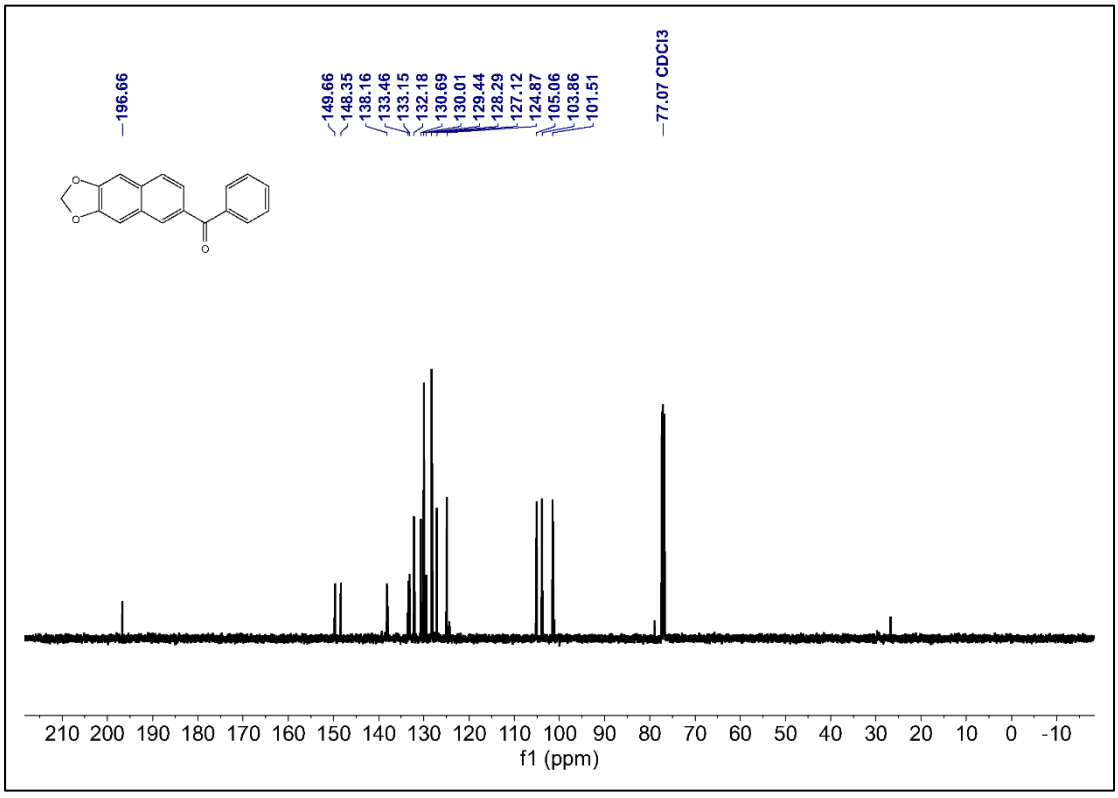
3cr


8.14
7.73
7.71
7.67
7.26
7.18
7.12
4.02
4.02
1.43
0.99
2.02
1.00
1.04
6.09
9.00
f1 (ppm)

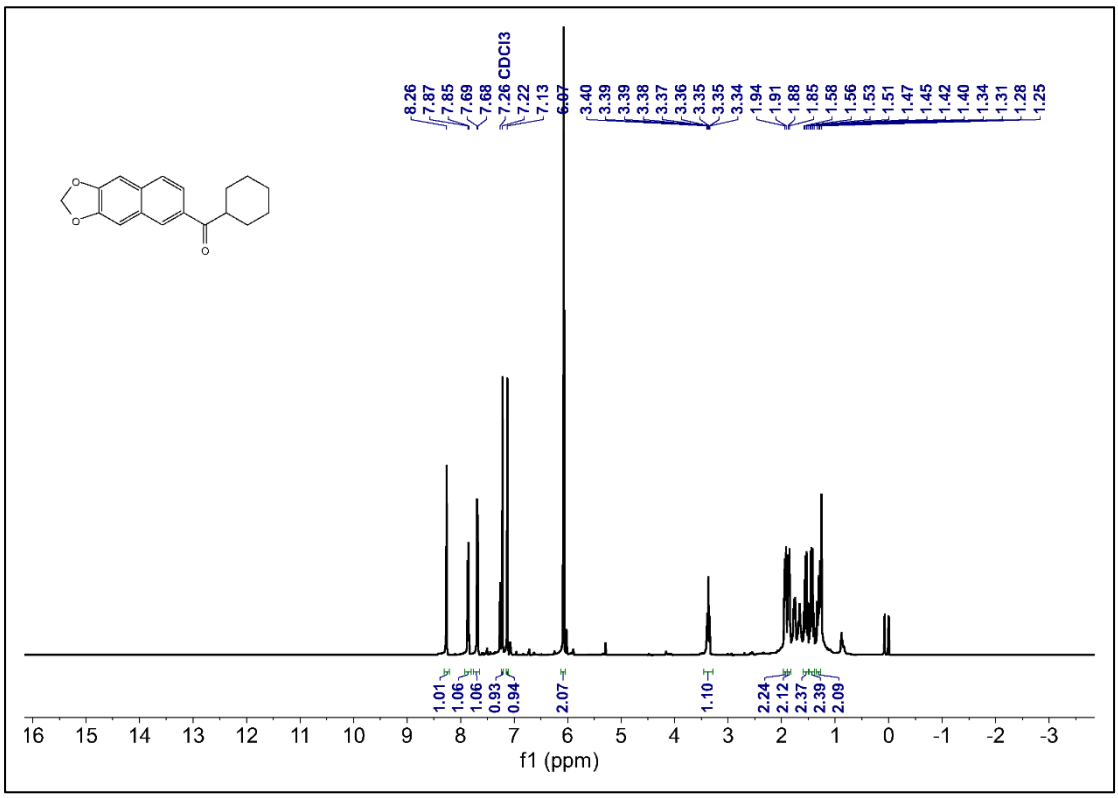

208.49
150.99
149.98
133.88
130.64
128.06
127.39
126.00
123.67
107.32
105.96
77.36
77.04
76.73
55.99
55.97
44.27
28.39
f1 (ppm)

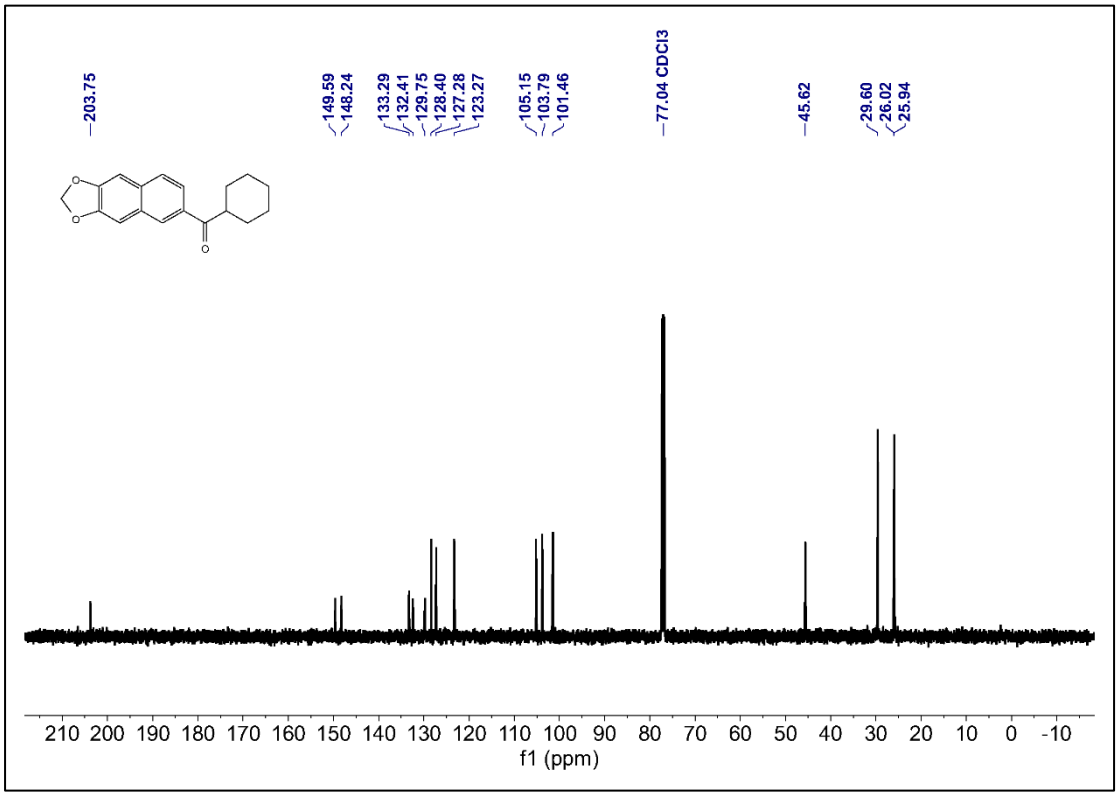
3fa


8.10
7.85
7.84
7.80
7.78
7.74
7.72
7.62
7.60
7.59
7.52
7.51
7.49
7.26 CDCl3
7.17
6.08
1.01
1.98
1.00
1.00
1.00
2.02
1.98
2.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

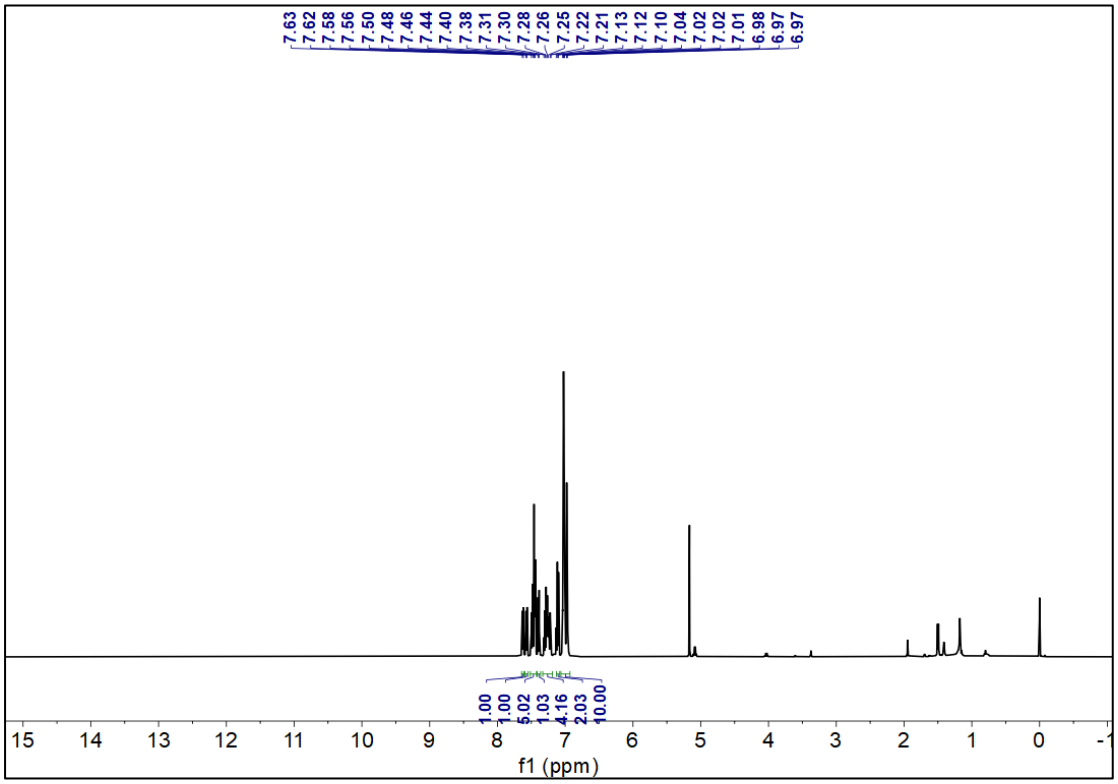

196.66
149.66
148.35
138.16
133.46
133.15
132.18
130.69
130.01
129.44
128.29
127.12
124.87
105.06
103.86
101.51
77.07 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

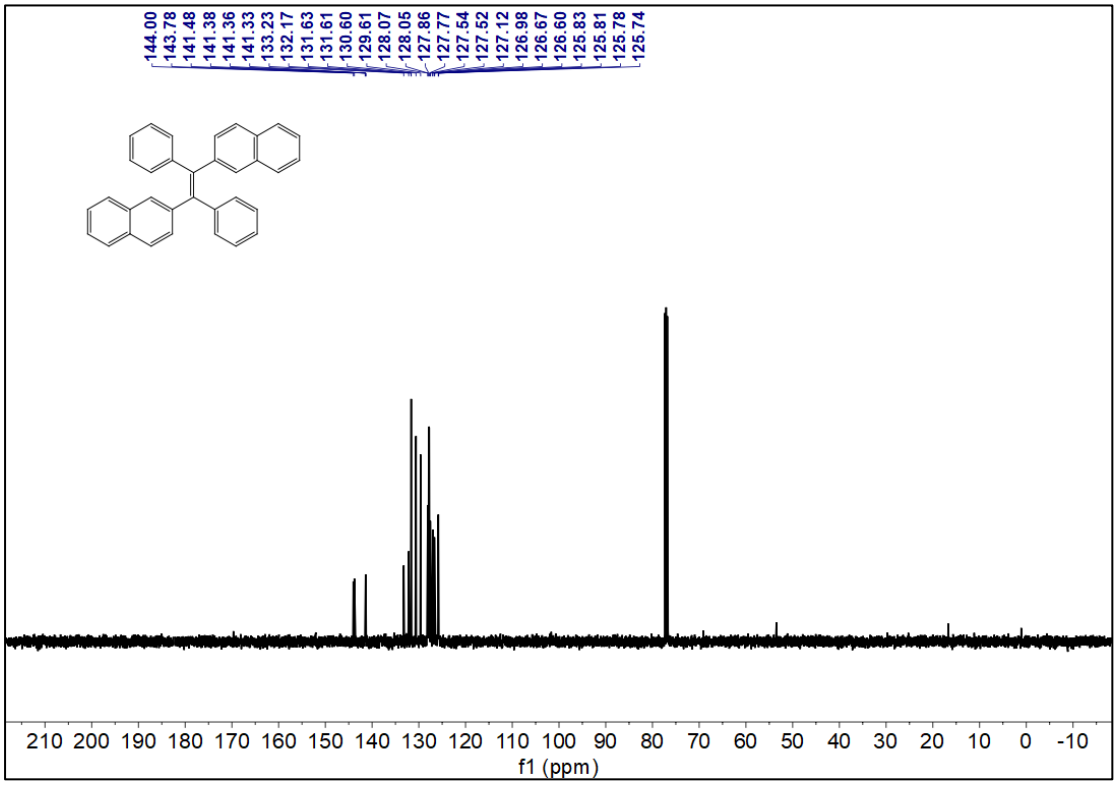
3fq


8.26
7.87
7.85
7.69
7.68
7.26 CDCl3
7.22
7.13
6.87
3.40
3.39
3.39
3.38
3.37
3.36
3.35
3.35
3.34
1.94
1.91
1.88
1.85
1.58
1.56
1.53
1.51
1.47
1.45
1.42
1.40
1.34
1.31
1.28
1.25
1.01
1.06
1.06
0.93
0.94
2.07
1.10
2.24
2.12
2.37
2.39
2.09
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

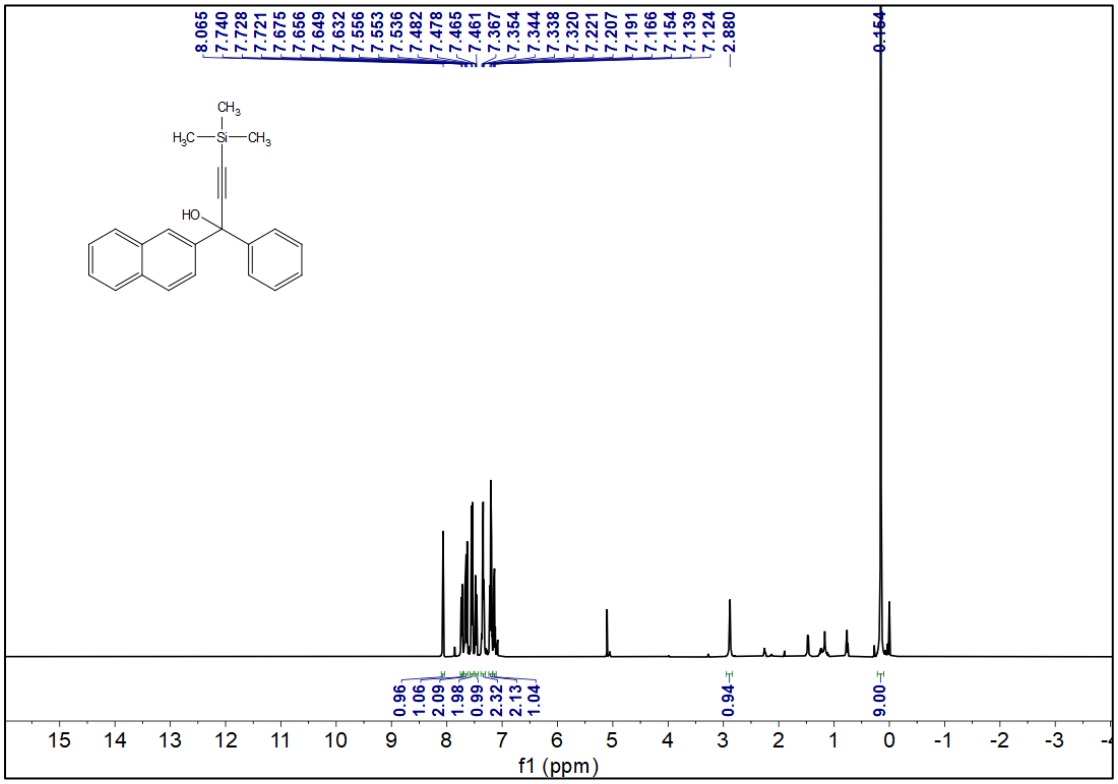

203.75
149.59
148.24
133.29
132.41
129.75
128.40
127.28
123.27
105.15
103.79
101.46
77.04 CDCl3
45.62
29.60
26.02
25.94
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4


7.63
7.62
7.58
7.56
7.50
7.48
7.46
7.44
7.40
7.38
7.31
7.30
7.28
7.26
7.25
7.22
7.21
7.13
7.12
7.10
7.04
7.02
7.02
7.01
6.98
6.97
6.97
1.00
1.00
6.02
1.03
4.16
2.03
10.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


144.00
143.78
141.48
141.38
141.36
141.33
133.23
132.17
131.63
131.61
130.60
129.61
128.07
128.05
127.86
127.77
127.54
127.52
127.12
126.98
126.67
126.60
125.83
125.81
125.78
125.74
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

5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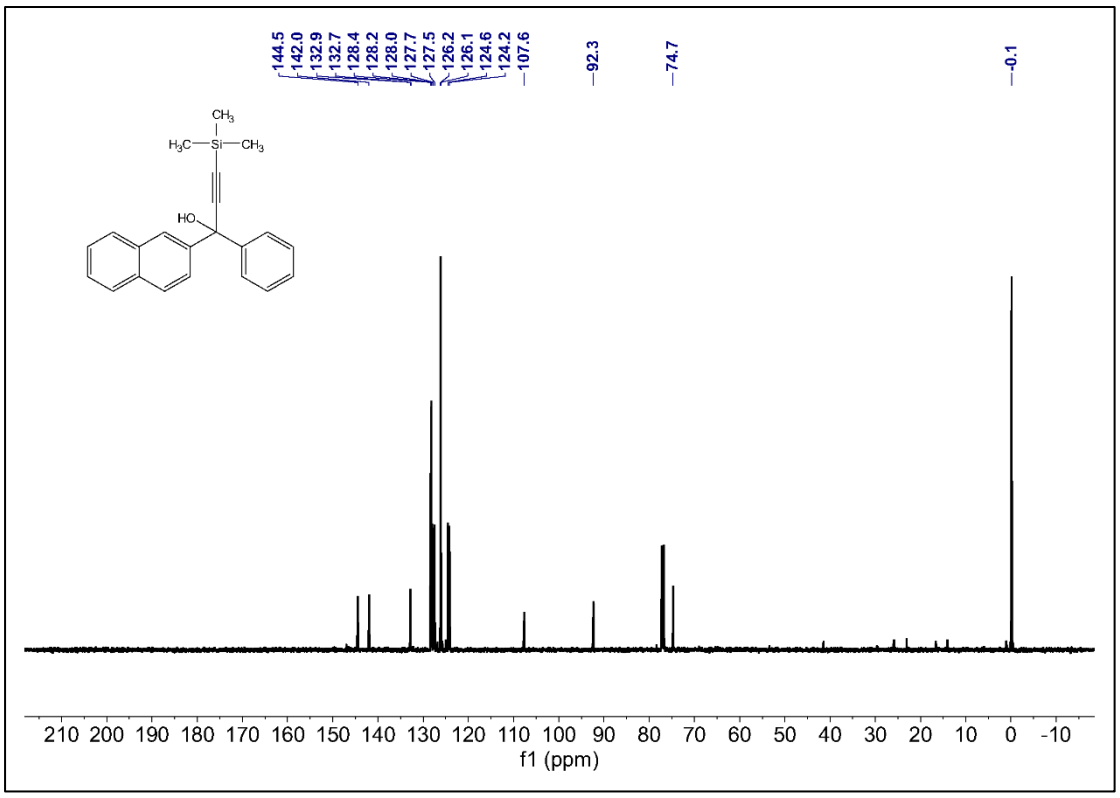
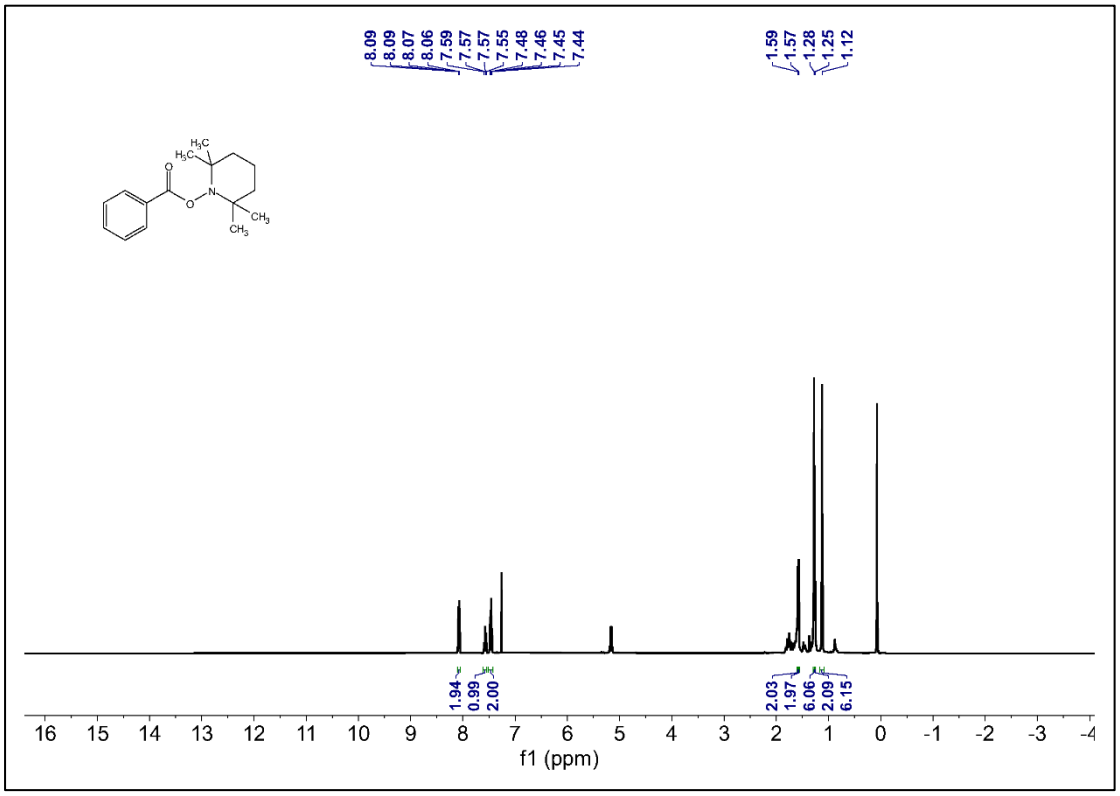
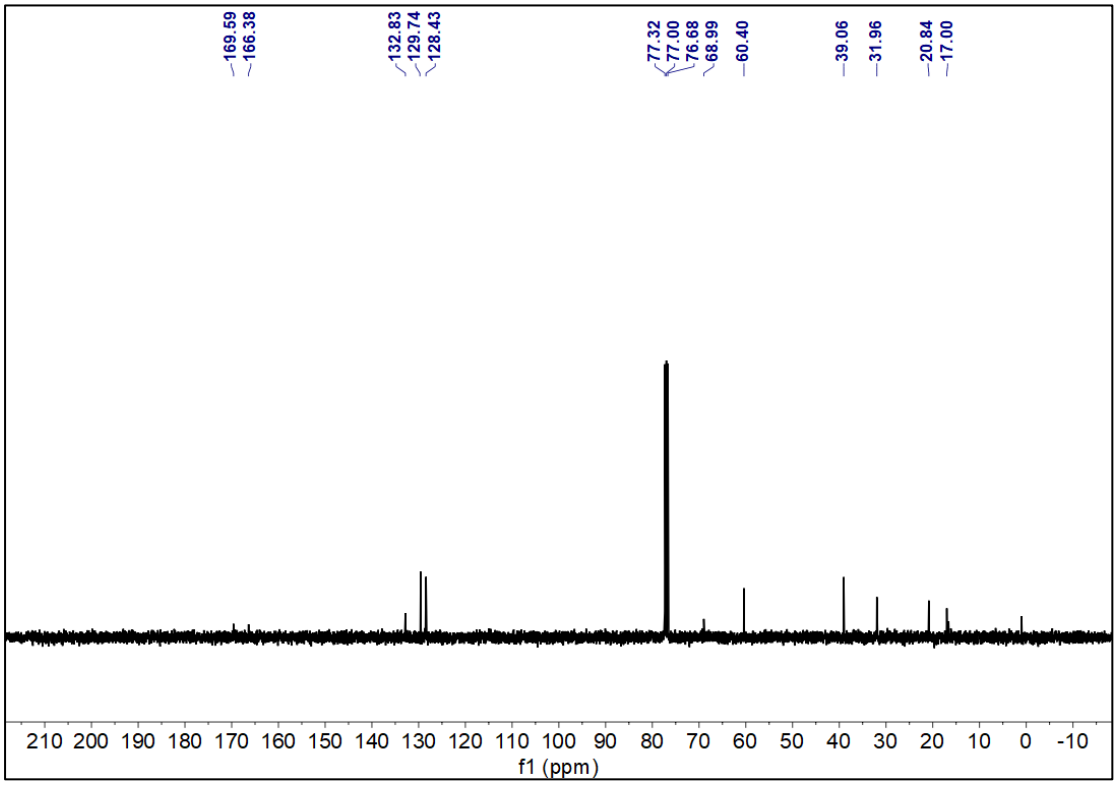
7.728
7.721
7.675
7.656
7.649
7.632
7.556
7.553
7.536
7.482
7.478
7.465
7.461
7.367
7.354
7.344
7.338
7.320
7.221
7.207
7.191
7.166
7.154
7.139
7.124
2.880
0.154
CH3
H3C—Si—CH3
HO
0.96
1.06
2.09
1.98
0.99
2.32
2.13
1.04
0.94
9.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


144.5
142.0
132.9
132.7
128.4
128.2
128.0
127.7
127.5
126.2
126.1
124.6
124.2
107.6
92.3
74.7
-0.1
CH3
H3C—Si—CH3
HO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

6


8.09
8.09
8.07
8.06
7.59
7.57
7.57
7.55
7.48
7.46
7.45
7.44
1.59
1.57
1.28
1.25
1.12
1.94
0.99
2.00
2.03
1.97
6.06
2.09
6.15
f1 (ppm)


169.59
166.38
132.83
129.74
128.43
77.32
77.00
76.68
68.99
60.40
39.06
31.96
20.84
17.00
f1 (ppm)