Supporting Information

DMSO-promoted α-bromination of α-aryl ketones for the construction of 2-aryl-2-bromo-cycloketones

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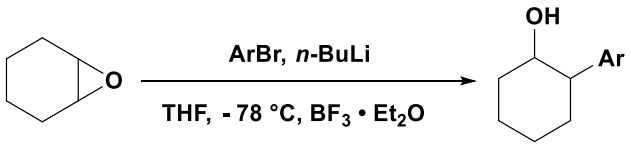
1. General information

Chemicals and solvents were purchased from Energy Chemical (Shanghai, China) unless otherwise stated. All the commercial reagents and solvents were used as such without further purification. Analytical thin-layer chromatography (TLC) and silica gel were purchased from Qingdao Shuoyuan Silicone Technology Co., Ltd. Flash chromatography was purchased from Biotage. Silica gel column was purchased from Changzhou Santai Technology Co., Ltd. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV-300 spectrometer (300 MHz ^{1}H, 75 MHz ^{13}C) using $CDCl_3$ or DMSO-d6 solutions. Chemical shifts (δ) are expressed in ppm recorded using the residual solvent as the internal reference in all cases ($CDCl_3$: ^{1}H 7.26 ppm, ^{13}C 77.16 ppm; DMSO-d6: ^{1}H 2.50 ppm, ^{13}C 39.52 ppm). Signal splitting patterns are described as chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad), coupling constant in hertz (Hz), and integration. DFT calculation was proceeded under M062x/6-31g** scrf(pcm, solvent=chloroform) level by Gaussian09 software. High-resolution mass spectrometry (HRMS) analysis was recorded on an LTQ Orbitrap Velos Pro spectrometer.

2. General procedure for the synthesis of starting material

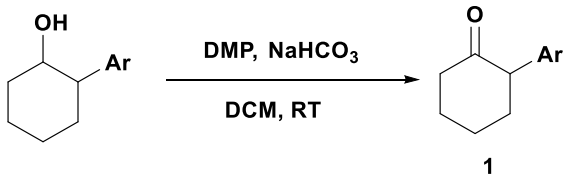
Substrate **1a** is commercially available. Substrate **1b**, **1d**~**1f**, **1h**~**1j**, **1l**, **1m**, **1o**, **1q**, **1r** and **1ab** were synthesized according to Method I[1]. Substrate **1c**, **1g**, **1k** and **1s**~**1u** were synthesized according to Method II[2]. The procedures for the preparation of substrates **1n**, **1v** and **1x** were followed as Method III[3]. Substrates **1y** and **1z** were prepared according to Method IV[4]. Substrate **1p**[5], **1w**[6] and **1ac**[7] were obtained by previously reported methods. The characterization data of **1b**~**1z, 1ab** and **1ac** are in accordance with corresponding references.

2.1 Method I



To a solution of ArBr (16 mmol, 1.14 equiv.) in dried THF (70 mL) *n*-BuLi was added dropwise (10 mL, 1.6 M in hexane, 16 mmol, 1.14 equiv.) at -78 °C under N_2 atmosphere, and the resulting mixture was stirred at this temperature for 1 h. Then cyclohexene oxide (14 mmol, 1.0 equiv.) was added dropwise to the mixture at -78 °C, followed by the addition of $BF_3{\cdot}Et_2O$ (16 mmol, 1.14

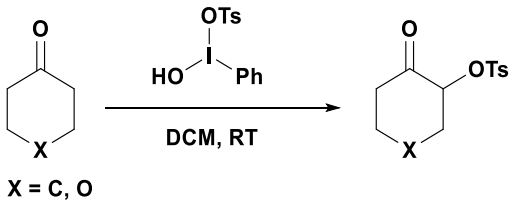
equiv.) dropwise. The reaction mixture was stirred at this temperature for another 1 h, then the reaction was quenched by the addition of saturated aqueous NH_4Cl at -78 °C and was allowed to warm to room temperature. The mixture was extracted with Et_2O (2 × 50 mL), and the combined organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to provide the desired alcohol.



1

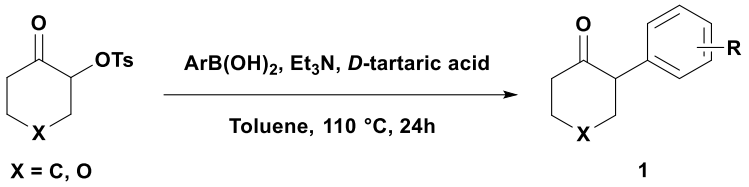
To a stirred solution of alcohol (4.0 mmol, 1.0 equiv.) in DCM (40 mL), $NaHCO_3$ (16.0 mmol, 4.0 equiv.) and Dess-Martin periodinane (DMP) (6.0 mmol, 1.5 equiv.) were added. The reaction mixture was stirred at room temperature until the consumption of starting material (monitored by TLC). Subsequently, saturated aqueous $Na_2S_2O_3$ (10 mL) and H_2O (30 mL) were added and the contents of the flask were transferred to a separatory funnel, then the aqueous layer was extracted with DCM (2 × 30 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the expected ketone **1**.

2.2 Method II



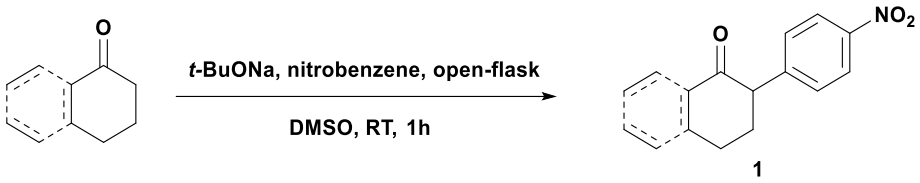
X = C, O

To the ketone (12 mmol, 1.2 equiv.) dissolved in DCM (30 mL), [hydroxy(tosyloxy)iodo]benzene (10 mmol, 1.0 equiv.) was added, and the heterogeneous suspension was stirred at room temperature until the solid was completely dissolved. The mixture was washed with H_2O and the organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude products were cooled for 24 h at -20 °C whereupon *α*-(tosyloxy)cyclohexanone crystallized from the solution. The solid was filtered and washed with petroleum ether, affording the desired *α*-(tosyloxy)cycloketone.



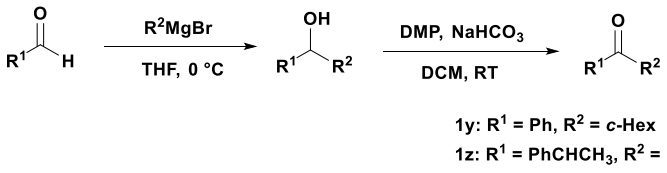
To a solution of *α*-(tosyloxy)cycloketone (3.0 mmol, 1.0 equiv.) and arylboronic acids (6.0 mmol, 2.0 equiv.) in toluene (30 mL), Et_3N (9.0 mmol, 3.0 equiv.) and (*D*)-tartaric acid (0.9 mmol, 0.3 equiv.) were added. The reaction mixture was then stirred at 110 °C for 24 h under N_2 atmosphere. Upon completion, the reaction mixture was concentrated via rotary evaporation. The crude mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to provide the desired product **1**.

2.3 Method III



t-BuONa (6.0 mmol, 1.2 equiv.) was added one portion to the solution of the nitrobenzene (12.0 mmol, 2.0 equiv.) and the ketone (5.0 mmol, 1.0 equiv.) in dry DMSO (50 mL) at room temperature. Once the base dissolved completely, the mixture was stirred at room temperature for 1 h. Next, saturated aqueous NH_4Cl solution (15 mL) was added and the resulting mixture was extracted with ethyl acetate (3 × 40 mL). The organic layers were combined, washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by column chromatography (petroleum ether/ethyl acetate) to give the α-arylated ketone **1**.

2.4 Method IV

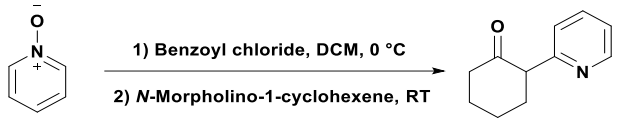


To a solution of the aldehyde (8.0 mmol, 1,0 equiv.) in THF (80 mL), EtMgBr (3 M in Et_2O, 3.34 mL) or *c*-HexMgBr (1 M in Et_2O, 9.0 mL) were added dropwise at -20 °C. The reaction mixture was then stirred at 0 °C for 3 hours under N_2 atmosphere. then the reaction was quenched by addition of saturated aqueous NH_4Cl (10 mL) and H_2O at 0 °C and was allowed to warm to room temperature. The mixture was extracted with Et_2O (2 × 50 mL), and the combined organic phase was dried over

Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to provide the desired alcohol.

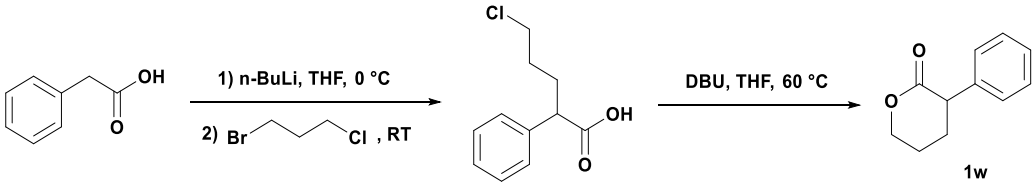
To a stirred solution of alcohol (1.0 equiv.) in DCM, $NaHCO_3$ (4.0 eq) and DMP (1.5 equiv.) were added. The reaction mixture was stirred at room temperature until the consumption of starting material (monitored by TLC). Subsequently, saturated aqueous $Na_2S_2O_3$ and H_2O (15 mL) were added and the contents of the flask were transferred to a separatory funnel, then the aqueous layer was extracted with DCM (2 × 25 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the expected ketone **1**.

2.5 Synthesis of 1p, 1w and 1ac



1p

To a solution of pyridine *N*-oxide (9.0 mmol, 1.12 equiv.) in DCM (30 mL) at 0 ℃, 0.93 mL (8.0 mmol, 1.0 equiv.) of benzoyl chloride was added dropwise with stirring. A white precipitate formed and the mixture was stirred at 0 ℃ for 40 min. A solution of *N*-Morpholino-1-cyclohexene (10.0 mmol, 1.25 equiv.) in DCM (10 mL) was added slowly with stirring. The mixture was allowed to warm to room temperature and stirred for 72 h. The solvent was removed under reduced pressure and 3 M HCl solution (20 mL) was added to the remaining orange oil. The mixture was washed several times with ether. The aqueous solution was adjusted to pH=8 with dilute NaOH solution and the oil which separated was extracted with DCM. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 93:7) to afford **1p** as the yellow liquid in 51% yield (*a mixture of ketone-enol 70:30*).

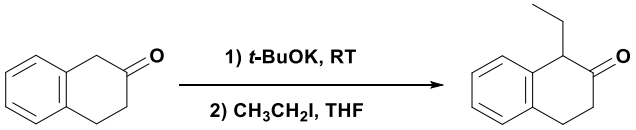


1w

A solution of benzylacetic acid (10.0 mmol, 1.0 equiv.) in dry THF (40 mL) was cooled to -78 ℃ while stirring under an N_2 atmosphere. To this solution *n*-butyllithium (2.0 equiv., 8.0 mL of 2.5 M in hexane) was added dropwise such that the internal temperature was maintained at -78 ℃. Upon

complete addition, the resultant slurry was slowly warmed to 0 °C and stirred at that temperature for 2 h. 1-Bromo-3-chloropropane (1.1 mL, 11.0 mmol, 1.1 equiv.) was then added and the reaction was allowed to warm to room temperature and stirred for 18 h. The reaction was quenched with 1N NaOH (20 mL) and transferred to a separatory funnel. The aqueous layer was collected and the organic was extracted again with 1N NaOH (20 mL). The combined aqueous cuts were re-acidified with 3N HCl (18 mL) and extracted with DCM (3 × 30 mL). The combined organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo to an oil.

The oil was redissolved in THF (25 mL), treated with DBU (1.5 mL, 10.0 mmol) and was heated to 60 °C for 18 h. The resultant slurry was cooled to room temperature and filtered through a sintered glass funnel. The wet cake was rinsed with EtOAc (3 × 10 mL) and the combined filtrates were concentrated in vacuo. The crude lactone was purified by flash chromatography (petroleum ether/ethyl acetate 81:19) to afford **1w** as the white solid in 70% yield.

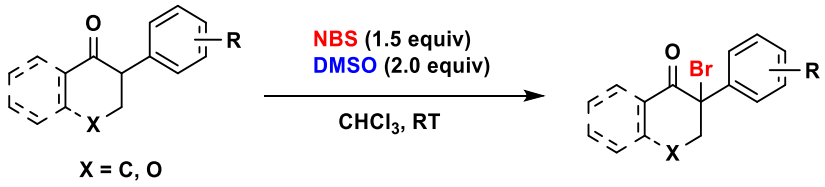


1ac

To a round bottom flask 2-tetralone (0.73 g, 5.0 mmol) and anhydrous THF (0.25 M, 20 mL) were added, followed by *t*-BuOK (0.62 g, 5.5 mmol, 1.1 equiv.). The flask was capped and the reaction stirred at room temperature under N_2. After 40 min, the reaction was cooled to 0 °C and EtI (0.50 mL, 5.5 mmol, 1.1 equiv.) was added dropwise. After EtI addition, the ice bath was removed and the reaction was stirred at room temperature for 2 h. Subsequently, 1 mL of HCl (3 M) and DCM (10 mL) were added and the contents of the flask were transferred to a separatory funnel, then the aqueous layer was extracted with DCM (2 × 20 mL). The combined organic layers were dried (anhydrous Na_2SO_4) and concentrated under reduced pressure. The crude mixture was purified by column chromatography (petroleum ether/ethyl acetate 95:5) to afford **1ac** in 40% yield.

3. General procedure for the preparation of the products

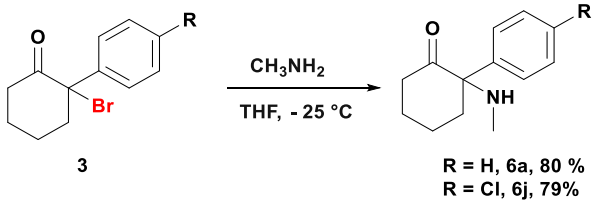
3.1 Synthesis of products 3



To a solution of 2-arylcycloket-1-ones **1** (1.0 mmol, 1.0 equiv.) in $CHCl_3$ (4.0 mL), DMSO (142 μL, 2.0 equiv.) and N-bromosuccinimide (NBS, 267 mg, 1.5 equiv.) were successively added at room temperature, and the mixture was stirred at room temperature until the consumption of starting material (monitored by TLC). Then the reaction was quenched by the addition of saturated 0.5 mL aqueous $Na_2S_2O_3$ and 3 mL water at room temperature, and the aqueous layer was extracted with DCM (2 × 5 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and removed under a vacuum. The resulting crude product was purified by flash chromatography (petroleum ether/ethyl acetate) to afford the 2-aryl-2-bromo-cycloketones **3**.

For the gram-scale bromination, to a solution of 2-phenylcyclohexan-1-one (**1a**, 2.61 g, 15 mmol, 1.0 equiv.) in $CHCl_3$ (60 mL), DMSO (2.13 mL, 2.0 equiv.) and NBS (4.00 g, 1.5 equiv.) were successively added at room temperature, and the mixture was stirred at room temperature until the consumption of starting material (monitored by TLC). Then the reaction was quenched by the addition of saturated 7 mL aqueous $Na_2S_2O_3$ and 50 mL water at room temperature, and the aqueous layer was extracted with DCM (2 × 50 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and removed under a vacuum. The resulting crude product was purified by flash chromatography (petroleum ether/ethyl acetate) to afford the 2-bromo-2-phenylcyclohexan-1-one (**3a**, light yellow oil, 2.68 g, 71% yield).

3.2 Synthesis of ketamine derivatives 6a and 6j



To a solution of **3a** or **3j** (1.0 mmol, 1.0 equiv.) in THF (5.0 mL), methylamine (27 wt% in EtOH, 0.63 mL, 4.0 equiv.) was added dropwise at - 25 °C under N_2 atmosphere. The reaction

mixture was stirred at this temperature until TLC showed full conversion of the substrate, then the reaction was warmed to room temperature then saturated aqueous Na_2CO_3 (1.5 mL) and water (3.0 mL) were added. The mixture was extracted with DCM (3 × 5 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4 and removed under a vacuum. The residue was dissolved in Et_2O (5.0 mL) and DCM (1.0 mL), 1 M HCl (5.0 mL) and H_2O (5.0 mL) were then added and stirred for 15 min. The aqueous layer was separated and washed with Et_2O (5.0 mL) and DCM (1.0 mL) 2 times. Then saturated aqueous Na_2CO_3 (3.0 mL) was added and the aqueous layer was extracted with DCM (3 × 5 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and removed under a vacuum to afford 2-(methylamino)-2-phenylcyclohexan-1-one (**6a**, 163.5 mg, 80%) as brown oil or 2-(4-chlorophenyl)-2-(methylamino)cyclohexan-1-one (**6j**, 186.6 mg, 79%) as yellow oil.

4. DFT calculation

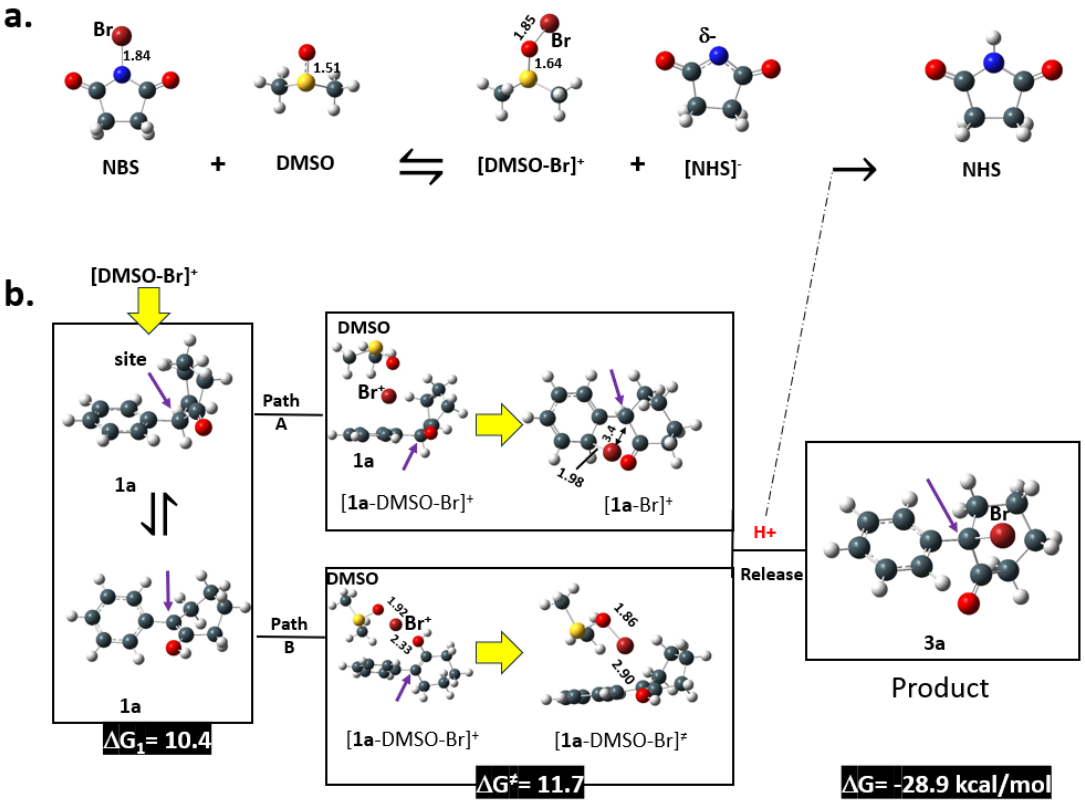


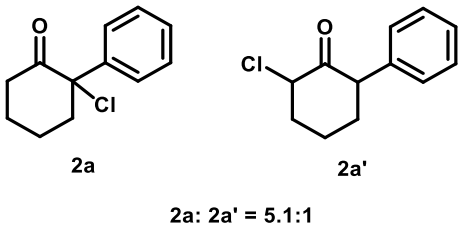
Figure S1. The proposed reaction mechanism from DFT calculation **a**. The transfer of Br^+ from NBS to DMSO. **b**. The keto-enol tautomerism of **1a**, and the corresponding reaction path for each tautomeric isomer. ΔG refers to the free energy for the whole reaction (NBS+**1a**→**3a**+NHS). Path A: the reaction of keto isomer with DMSO-Br^+; Path B: the enol isomer with DMSO-Br^+. Path B is the preferable reaction route owing to lower steric hindrance for attacking the π electrons of enol and the similarity between the conformations of the transition state and product.

Table S1. Calculated free energy for each molecular in reaction.

Molecular	Free energy (Hartree)
1a	-540.518175
NBS	-2931.622860
DMSO	-553.028634
1a-OH (enol)	-540.501520
Br^+	-2571.331905
$[DMSO\text{-}Br]^+$	-3124.563493
NHS^-	-359.977248
$[\mathbf{1a}\text{-}Br]^+$	-3112.052884
INT (path B)	-3665.081764
Possible transition state (path B)	-3665.063148
NHS	-360.470556
3a	-3111.716509

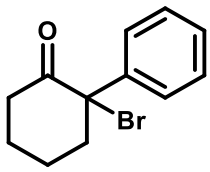
5. Characterization of products

2-chloro-2-phenylcyclohexan-1-one (2a) and 2-chloro-6-phenylcyclohexan-1-one (2a') as a mixture (2a: 2a' = 5.1: 1)



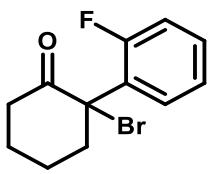
The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 95:5). Colorless oil, 107.1 mg, 51 % yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.45-7.27 (m, 26.6H), 7.20-7.12 (m, 2.0H), 4.43 (t, *J* = 3.2 Hz, 1H, **2a'**), 4.35 (dd, *J* = 11.9, 5.3 Hz, 1.0H, **2a'**)[8], 3.03-2.77 (m, 10.2H, **2a**)[9], 2.44 (ddd, *J* = 14.8, 7.5, 2.5 Hz, 10.1H), 2.37-2.20 (m, 4.3H), 2.10-1.72 (m, 22.8H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 203.6, 161.0, 138.7, 128.9, 128.7, 128.6, 128.6, 127.4, 127.2, 76.8 (**2a**), 61.6 (**2a'**), 51.6 (**2a'**), 41.9 (**2a**), 39.2 (**2a**), 34.6 (**2a'**), 27.5 (**2a**), 22.8 (**2a**), 20.1 (**2a'**). HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{12}H_{14}ClO$, 209.0728; found, 209.0722.

2-bromo-2-phenylcyclohexan-1-one (3a)



The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 95:5). White solid, 195.2 mg, 77% yield, 71% in a gram-scale. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.47-7.28 (m, 5H), 3.08- 2.88 (m, 2H), 2.70-2.56 (m, 1H), 2.48 (dt, *J* = 14.1, 7.2 Hz, 1H), 2.05-1.76 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 203.0, 139.3, 128.9, 128.7, 127.5, 72.7, 42.6, 38.8, 27.4, 23.4. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{12}H_{14}BrO$, 253.0223; found, 253.0217.

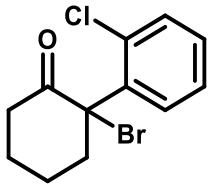
2-bromo-2-(2-fluorophenyl)cyclohexan-1-one (3b)



The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 96:4). Colorless oil, 100.3 mg, 37% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) : δ 7.71 (td, *J* = 7.9, 1.7 Hz, 1H),

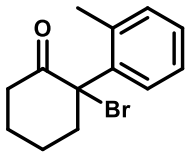
7.35 (tdd, *J* = 7.9, 5.1, 1.7 Hz, 1H), 7.19 (td, *J* = 7.7, 1.2 Hz, 1H), 7.06 (ddd, *J* = 11.5, 8.1, 1.1 Hz, 1H), 3.13 (ddd, *J* = 15.3, 10.7, 5.6 Hz, 1H), 2.82-2.65 (m, 1H), 2.63-2.41 (m, 2H), 2.19-1.97 (m, 2H), 1.97-1.76 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 201.3, 159.4 (d, *J* = 249.2 Hz), 130.6 (d, *J* = 8.9 Hz), 129.9 (d, *J* = 3.2 Hz), 128.0 (d, *J* = 11.4 Hz), 124.6 (d, *J* = 3.4 Hz), 116.2 (d, *J* = 22.5 Hz), 69.9 (d, *J* = 3.2 Hz), 43.3 (d, *J* = 2.0 Hz), 37.5, 26.7, 22.8. HRMS (ESI$^+$) *m/z* $[M + H]^+$ calcd for $C_{12}H_{13}BrFO$, 271.0128; found, 271.0124.

2-bromo-2-(2-chlorophenyl)cyclohexan-1-one (3c)

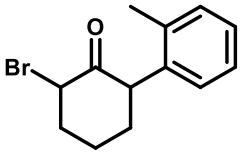


The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 96:4). Colorless oil, 123.4 mg, 43% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.44-7.24 (m, 3H), 3.14-2.99 (m, 1H), 2.93 (ddd, *J* = 15.1, 10.0, 3.8 Hz, 1H), 2.69-2.57 (m, 1H), 2.46-2.33 (m, 1H), 2.14-1.96 (m, 3H), 1.89 (tt, *J* = 14.4, 7.2 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 201.6, 137.9, 132.0, 131.4, 131.1, 129.8, 127.5, 73.7, 43.2, 37.5, 25.7, 22.7. HRMS (ESI$^+$) *m/z* $[M + H]^+$ calcd for $C_{12}H_{13}BrClO$, 286.9833; found, 286.9828.

2-bromo-2-(*o*-tolyl)cyclohexan-1-one (3d) and 2-bromo-6-(*o*-tolyl)cyclohexan-1-one (3d') as a mixture (3d: 3d' = 3.0: 1)



3d

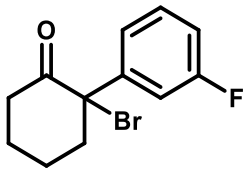


3d'

The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 95:5). Colorless oil, 213.1 mg, 80% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.69-7.60 (m, 2.9H), 7.32-7.24 (m, 6.0H), 7.24-7.15 (m, 6.1H), 7.15-7.08 (m, 1.0H), 4.76 (dd, *J* = 13.1, 5.1 Hz, 1.0H, **3d'**), 4.56-4.48 (m, 1.0H, **3d'**), 3.30-3.11 (m, 3.0H, **3d**)[10], 2.88-2.69 (m, 3.0H), 2.59-2.39 (m, 6.9H), 2.38-2.24 (m, 3.2H), 2.23 (s, 3.0H, **3d'**), 2.20 (s, 9.0H, **3d**), 2.14-2.05 (m, 1.0H), 2.04-1.80 (m, 13.3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 205.0, 203.8, 137.7, 137.4, 137.0, 136.1, 132.9, 130.4, 129.0, 127.3, 127.1, 126.6, 126.5, 126.1, 75.0 (**3d**), 52.9 (**3d'**), 47.4 (**3d'**), 45.0 (**3d**), 38.8 (**3d**), 36.1 (**3d'**), 33.4

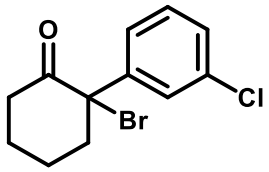
(**3d'**), 29.1 (**3d**), 23.7 (**3d**), 22.0 (**3d**), 21.0 (**3d'**), 19.6 (**3d'**). HRMS (ESI$^+$) *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{16}BrO$, 267.0379; found, 267.0375.

2-bromo-2-(3-fluorophenyl)cyclohexan-1-one (3e)



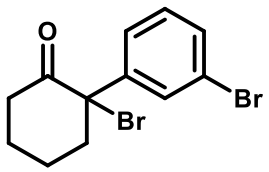
The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 96:4). Yellow oil, 165.6 mg, 61% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.35 (td, *J* = 8.2, 6.1 Hz, 1H), 7.24-7.13 (m, 2H), 7.02 (tdd, *J* = 8.2, 2.3, 0.7 Hz, 1H), 3.06 (ddd, *J* = 13.7, 6.8, 2.9 Hz, 1H), 2.92-2.78 (m, 1H), 2.69-2.56 (m, 1H), 2.54-2.40 (m, 1H), 2.12-1.76 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 202.4, 162.8 (d, *J* = 246.4 Hz), 141.9 (d, *J* = 7.4 Hz), 130.2 (d, *J* = 8.3 Hz), 123.5 (d, *J* = 3.0 Hz), 115.6 (d, *J* = 21.1 Hz), 115.2 (d, *J* = 23.4 Hz), 71.1, 42.5, 38.6, 27.2, 23.2. HRMS (ESI$^+$) *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{13}BrFO$, 271.0128; found, 271.0124.

2-bromo-2-(3-chlorophenyl)cyclohexan-1-one (3f)



The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 95:5). Light yellow oil, 198.7 mg, 69% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.47-7.40 (m, 1H), 7.34-7.27 (m, 3H), 3.15-2.98 (m, 1H), 2.89-2.76 (m, 1H), 2.68-2.55 (m, 1H), 2.53-2.40 (m, 1H), 2.13-1.93 (m, 2H), 1.92-1.77 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 202.4, 141.4, 134.6, 129.9, 128.8, 127.9, 126.3, 71.0, 42.4, 38.5, 27.2, 23.2. HRMS (ESI$^+$) *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{13}BrClO$, 286.9833; found, 286.9828.

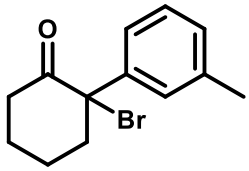
2-bromo-2-(3-bromophenyl)cyclohexan-1-one (3g)



The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 97:3). Light yellow oil, 191.3 mg, 58% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.62-7.55 (m, 1H), 7.49-7.41 (m,

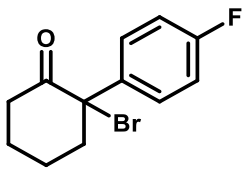
1H), 7.36 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.25 (t, *J* = 7.9 Hz, 1H), 3.16-2.99 (m, 1H), 2.82 (ddd, *J* = 13.4, 7.3, 3.7 Hz, 1H), 2.68-2.55 (m, 1H), 2.54-2.41 (m, 1H), 2.14-1.77 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 202.4, 141.6, 131.7, 130.7, 130.2, 126.9, 122.7, 70.9, 42.4, 38.5, 27.2, 23.2. HRMS (ESI^+) *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{13}Br_2O$, 330.9328; found, 330.0923.

2-bromo-2-(*m*-tolyl)cyclohexan-1-one (3h)



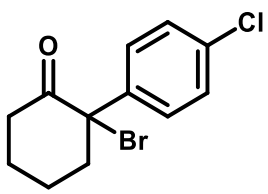
The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 97:3). Light yellow oil, 220.1 mg, 82% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.33-7.18 (m, 3H), 7.16-7.06 (m, 1H), 3.06 (ddd, *J* = 14.6, 6.6, 2.9 Hz, 1H), 2.96-2.84 (m, 1H), 2.68-2.42 (m, 2H), 2.36 (s, 3H), 2.01-1.75 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 203.1, 139.2, 138.7, 129.5, 128.8, 128.1, 124.4, 73.2, 42.7, 39.0, 27.5, 23.6, 21.7. HRMS (ESI^+) *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{16}BrO$, 267.0379; found, 267.0376.

2-bromo-2-(4-fluorophenyl)cyclohexan-1-one (3i)



The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 97:3). White solid, 183.6 mg, 68 % yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.52-7.33 (m, 2H), 7.14-6.95 (m, 2H), 3.17-2.97 (m, 1H), 2.92-2.77 (m, 1H), 2.69-2.56 (m, 1H), 2.54-2.38 (m, 1H), 2.13-1.94 (m, 2H), 1.94-1.77 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 202.8, 162.5 (d, *J* = 249.1 Hz), 135.3 (d, *J* = 3.5 Hz), 129.8 (d, *J* = 8.3 Hz), 115.6 (d, *J* = 21.6 Hz), 71.3, 42.4, 38.5, 27.3, 23.2. HRMS (ESI^+) *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{13}BrFO$, 271.0128; found, 271.0124.

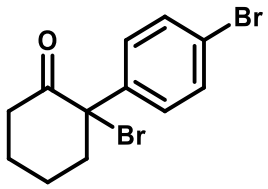
2-bromo-2-(4-chlorophenyl)cyclohexan-1-one (3j)



The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 97:3). Light

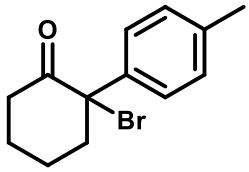
yellow solid, 208.1 mg, 72% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.41-7.29 (m, 4H), 3.12-2.99 (m, 1H), 2.88-2.74 (m, 1H), 2.67- 2.55 (m, 1H), 2.51-2.38 (m, 1H), 2.11-1.91 (m, 2H), 1.91-1.76 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 202.5, 137.9, 134.5, 129.3, 128.8, 71.1, 42.2, 38.4, 27.2, 23.1. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{12}H_{13}BrClO$, 286.9833; found, 286.9828.

2-bromo-2-(4-bromophenyl)cyclohexan-1-one (3k)



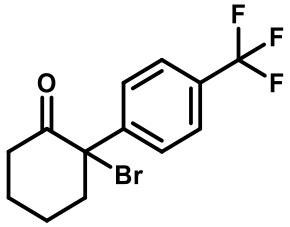
The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 98:2). Light yellow solid, 237.0 mg, 71% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.56-7.44 (m, 2H), 7.36-7.27 (m, 2H), 3.16-3.00 (m, 1H), 2.88-2.72 (m, 1H), 2.70-2.54 (m, 1H), 2.52-2.38 (m, 1H), 2.15-1.74 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 202.5, 138.5, 131.8, 129.6, 122.9, 71.1, 42.3, 38.5, 27.2, 23.2. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{12}H_{13}Br_2O$, 330.9328; found, 330.9324.

2-bromo-2-(*p*-tolyl)cyclohexan-1-one (3l)



The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 97:3). White solid, 206.1 mg, 77% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.25 (dd, *J* = 36.3, 7.9 Hz, 4H), 3.14-2.97 (m, 1H), 2.97-2.83 (m, 1H), 2.69-2.54 (m, 1H), 2.48 (dt, *J* = 14.0, 7.0 Hz, 1H), 2.34 (s, 3H), 2.02-1.69 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 203.1, 138.7, 136.4, 129.7, 127.4, 73.0, 42.6, 38.9, 27.5, 23.5, 21.2. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{13}H_{16}BrO$, 267.0379; found, 267.0375.

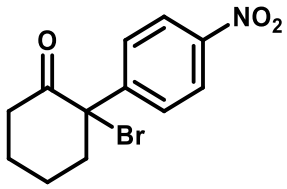
2-bromo-2-(4-(trifluoromethyl)phenyl)cyclohexan-1-one (3m)



The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 96:4). Light yellow oil, 224.1 mg, 70% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.60 (q, *J* = 8.6 Hz, 4H), 3.15 (ddd,

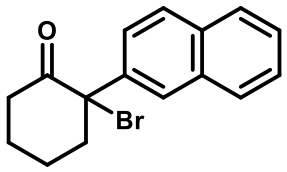
J = 14.4, 9.4, 5.2 Hz, 1H), 2.86-2.72 (m, 1H), 2.70-2.57 (m, 1H), 2.54-2.39 (m, 1H), 2.18-1.95 (m, 2H), 1.95-1.77 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 202.4, 143.3 (d, *J* = 1.2 Hz), 130.5 (d, *J* = 32.7 Hz), 128.5, 125.5 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 272.2 Hz), 70.5, 42.3, 38.3, 27.1, 23.0. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{13}H_{13}BrF_3O$, 321.0096; found, 321.0093.

2-bromo-2-(4-nitrophenyl)cyclohexan-1-one (3n)



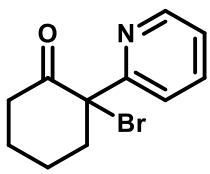
The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 95:5). Light brown solid, 196.5 mg, 66% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.28-8.16 (m, 2H), 7.70-7.58 (m, 2H), 3.27 (ddd, *J* = 14.5, 10.8, 5.9 Hz, 1H), 2.68 (dd, *J* = 6.4, 5.3 Hz, 2H), 2.49 (dt, *J* = 11.3, 5.4 Hz, 1H), 2.26-2.01 (m, 2H), 1.99-1.75 (m, 2H).**^{13}C NMR** (75 MHz, $CDCl_3$): δ 202.0, 147.6, 146.5, 129.5, 123.5, 69.3, 42.2, 38.1, 27.0, 22.9. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{12}H_{13}BrNO_3$, 298.0073; found, 298.0067.

2-bromo-2-(naphthalen-2-yl)cyclohexan-1-one (3o)



The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 96:4). Yellow oil, 207.4 mg, 68% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.94-7.76 (m, 4H), 7.64-7.42 (m, 3H), 3.25-2.94 (m, 2H), 2.83-2.64 (m, 1H), 2.58 -2.43 (m, 1H), 2.15-1.79 (m, 4H).**^{13}C NMR** (75 MHz, $CDCl_3$): δ 203.2, 136.8, 133.1, 133.1, 128.6, 128.5, 127.7, 127.1, 126.7, 126.0, 125.9, 72.9, 42.4, 38.9, 27.5, 23.5. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{16}H_{16}BrO$, 303.0379; found, 303.0373.

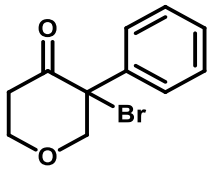
2-bromo-2-(pyridin-2-yl)cyclohexan-1-one (3p)



The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 93:7). Yellow solid, 247.5 mg, 97% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.68-8.45 (m, 1H), 7.73 (td, *J*

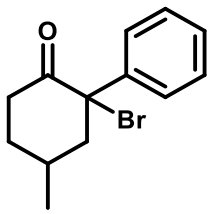
= 7.8, 1.8 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.22 (ddd, *J* = 7.5, 4.8, 1.0 Hz, 1H), 3.26 (ddd, *J* = 14.7, 7.1, 3.0 Hz, 1H), 3.04-2.91 (m, 1H), 2.63-2.43 (m, 2H), 2.04 -1.85 (m, 3H), 1.85-1.71 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 202.7, 158.6, 148.9, 137.0, 123.9, 123.2, 73.4, 41.9, 39.3, 27.3, 23.3. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{11}H_{13}BrNO$, 254.0175; found, 254.0171.

3-bromo-3-phenyltetrahydro-4*H*-pyran-4-one (3s)



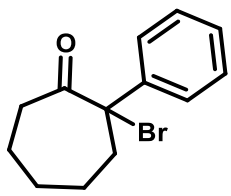
The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 95:5). Light yellow oil, 195.9 mg, 77% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.51 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.44-7.29 (m, 3H), 4.89 (dd, *J* = 12.5, 1.3 Hz, 1H), 4.24-4.15 (m, 1H), 4.13 (d, *J* = 12.5 Hz, 1H), 3.92 (ddd, *J* = 11.3, 8.4, 5.7 Hz, 1H), 2.79-2.66 (m, 2H).**^{13}C NMR** (75 MHz, $CDCl_3$): δ 198.5, 137.0, 129.2, 129.2, 127.8, 76.5, 70.0, 69.0, 40.6. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{11}H_{12}BrO_2$, 255.0015; found, 255.0010.

2-bromo-4-methyl-2-phenylcyclohexan-1-one (3t)



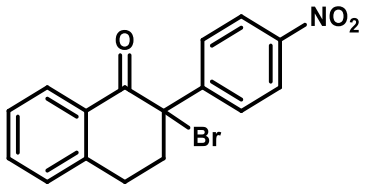
The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 96:4). Yellow oil, 200.1 mg, 75% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.58-7.45 (m, 2H), 7.41-7.27 (m, 3H), 3.54 (td, *J* = 14.6, 6.3 Hz, 1H), 2.71-2.55 (m, 2H), 2.50 (ddd, *J* = 14.9, 4.4, 2.5 Hz, 1H), 2.19 -1.98 (m, 2H), 1.49 (tdd, *J* = 13.6, 12.2, 4.4 Hz, 1H), 1.11 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 203.0, 139.5, 129.0, 128.4, 127.9, 69.7, 50.1, 37.0, 34.7, 28.9, 21.1. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{13}H_{16}BrO$, 267.0379; found, 267.0375.

2-bromo-2-phenylcycloheptan-1-one (3u)



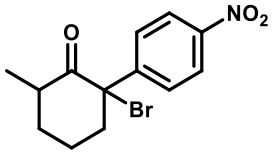
The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 97:3). Light yellow oil, 209.4 mg, 78% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.48-7.40 (m, 2H), 7.40-7.27 (m, 3H), 3.00 (dd, *J* = 15.5, 9.0 Hz, 1H), 2.74-2.51 (m, 3H), 1.99-1.79 (m, 3H), 1.79-1.48 (m, 3H).**^{13}C NMR** (75 MHz, $CDCl_3$): δ 205.3, 140.3, 128.9, 128.7, 127.3, 76.3, 41.2, 39.6, 29.8, 27.1, 25.2. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{13}H_{16}BrO$, 267.0379; found, 267.0376.

2-bromo-2-(4-nitrophenyl)-3,4-dihydronaphthalen-1(2*H*)-one (3v)

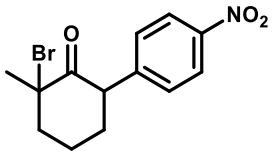


The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 94:6). Red brown solid, 276.6 mg, 80% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.28-8.14 (m, 3H), 7.85-7.75 (m, 2H), 7.57 (td, *J* = 7.5, 1.2 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 3.38 (ddd, *J* = 17.1, 8.4, 5.7 Hz, 1H), 3.02 (dt, *J* = 17.4, 4.6 Hz, 1H), 2.91-2.74 (m, 2H).**^{13}C NMR** (75 MHz, $CDCl_3$): δ 189.7, 147.7, 146.6, 142.4, 134.5, 130.1, 129.7, 129.6, 128.9, 127.6, 123.4, 67.4, 39.8, 27.8. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{16}H_{13}BrNO_3$, 346.0073; found, 346.0068.

2-bromo-6-methyl-2-(4-nitrophenyl)cyclohexan-1-one (3x) and 2-bromo-2-methyl-6-(4-nitrophenyl)cyclohexan-1-one (3x') as a mixture (3x: 3x' = 0.7: 1)



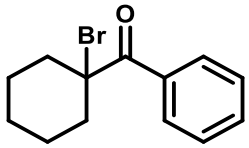
3x



3x'

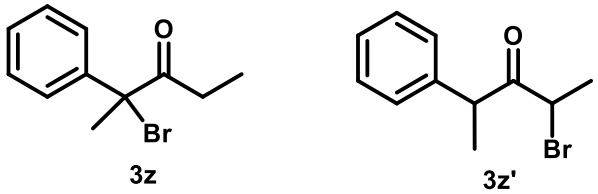
The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 94:6). Light yellow oil, 226.1 mg, 72% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.31-8.17 (m, 5.2H), 7.56-7.48 (m, 1.9H), 7.37-7.30 (m, 3.2H), 4.81 (dd, *J* = 13.5, 5.3 Hz, 1.4H, **3x'**), 3.41 (dd, *J* = 14.6, 3.1 Hz, 1.0H, **3x**), 2.73-2.59 (m, 1.1H), 2.59-2.45 (m, 2.6H), 2.40-2.25 (m, 3.3H), 2.13-1.92 (m, 6.8H), 1.90 (s, 4.3H, **3x'**), 1.86-1.74 (m, 2.2H), 1.15 (d, *J* = 6.4 Hz, 3H, **3x**).**^{13}C NMR** (75 MHz, $CDCl_3$): δ 203.5, 203.0, 147.6, 147.2, 146.7, 145.8, 129.9, 127.5, 124.7, 123.6, 72.1 (**3x**), 65.9 (**3x'**), 51.3 (**3x'**), 44.1 (**3x'**), 43.5 (**3x**), 43.0 (**3x**), 36.5 (**3x**), 34.8 (**3x'**), 28.5 (**3x'**), 23.8 (**3x**), 22.5 (**3x'**), 15.5 (**3x**). HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{13}H_{15}BrNO_3$, 312.0230; found, 312.0223.

(1-bromocyclohexyl)(phenyl)methanone (3y)



The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 97:3). Colorless oil, 237.2 mg, 89% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.14-8.01 (m, 2H), 7.56-7.48 (m, 1H), 7.47-7.36 (m, 2H), 2.45-2.27 (m, 2H), 2.25-2.08 (m, 2H), 1.89-1.70 (m, 2H), 1.64-1.46 (m, 3H), 1.44-1.32 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 197.6, 135.9, 132.2, 129.9, 128.2, 68.0, 38.4, 25.1, 23.7. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{13}H_{16}BrO$, 267.0379; found, 267.0375

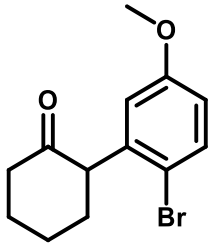
2-bromo-2-phenylpentan-3-one (3z) and 2-bromo-4-phenylpentan-3-one (3z') as a mixture (3z: 3z' = 2.3: 1)



3z: 3z' = 2.3:1

The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 98:2). Colorless oil, 107.1 mg, 45% yield. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50-7.43 (m, 4.3H), 7.41 – 7.24 (m, 10.4H), 7.24-7.17 (m, 1.9H), 4.38 (dq, *J* = 19.2, 6.8 Hz, 2H, **3z'**), 2.78 (dq, *J* = 17.2, 7.3 Hz, 2.2H, **3z**), 2.35 (dq, *J* = 17.3, 7.3 Hz, 2.4H, **3z**), 2.14 (s, 6.9H, **3z**), 1.60 (d, *J* = 6.7 Hz, 3.8H, **3z'**), 1.45 (d, *J* = 6.9 Hz, 3.3H, **3z'**), 1.06 (t, *J* = 7.3 Hz, 6.9H, **3z**). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 205.3, 203.6, 140.3, 140.1, 129.4, 128.9, 128.4, 128.1, 127.7, 126.9, 71.1 (**3z**), 49.5 (**3z'**), 45.1 (**3z'**), 31.1 (**3z**), 31.0 (**3z**), 19.8 (**3z'**), 18.2 (**3z'**), 9.6 (**3z**). HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{11}H_{14}BrO$, 241.0223; found, 241.0220.

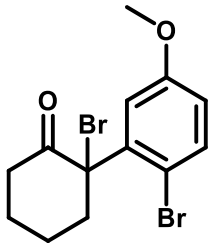
2-(2-bromo-5-methoxyphenyl)cyclohexan-1-one (1aa)



The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 94:6). Colorless oil, 202.2 mg, 71% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.7 Hz, 1H), 6.76

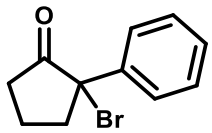
(d, *J* = 3.0 Hz, 1H), 6.69 (dd, *J* = 8.7, 3.0 Hz, 1H), 4.05 (dd, *J* = 12.4, 5.1 Hz, 1H), 3.78 (s, 3H), 2.60-2.50 (m, 2H), 2.24 (tdt, *J* = 12.5, 5.5, 3.1 Hz, 2H), 2.09-1.75 (m, 4H).**^{13}C NMR** (75 MHz, $CDCl_3$): δ 209.0, 159.0, 139.5, 133.2, 115.8, 115.8, 113.9, 56.9, 55.5, 42.6, 34.3, 27.9, 25.8. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{13}H_{16}BrO_2$, 283.0328; found, 283.0322.

2-bromo-2-(2-bromo-5-methoxyphenyl)cyclohexan-1-one (3aa)



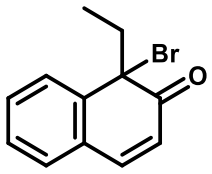
The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 94:6). Light yellow oil, 60.1 mg, 17% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.62 (d, *J* = 3.0 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 6.73 (dd, *J* = 8.7, 3.0 Hz, 1H), 3.82 (s, 3H), 3.14-2.85 (m, 2H), 2.72-2.58 (m, 1H), 2.43-2.29 (m, 1H), 2.18-1.85 (m, 4H).**^{13}C NMR** (75 MHz, $CDCl_3$): δ 201.5, 159.3, 140.4, 135.3, 119.3, 114.8, 111.9, 75.1, 55.7, 43.1, 37.6, 25.1, 22.6. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{13}H_{15}Br_2O_2$, 360.9433; found, 360.9429.

2-bromo-2-phenylcyclopentan-1-one (3ab)



The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 97:3). Only crude product was gained. **^{1}H NMR** (300 MHz, DMSO-d6): δ 7.31-7.08 (m, 2H), 6.97-6.73 (m, 3H), 2.24-2.04 (m, 2H), 2.04-1.95 (m, 1H), 1.85 (dt, *J* = 19.2, 9.4 Hz, 1H), 1.67-1.40 (m, 2H).**^{13}C NMR** (75 MHz, DMSO-d6): δ 208.3, 138.1, 128.6, 128.3, 126.8, 67.9, 35.2, 18.9. HRMS (ESI^+) *m/z* $[M + H]^+$ calcd for $C_{11}H_{12}BrO$, 239.0066; found, 239.0062.

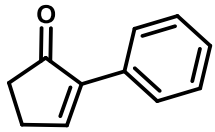
1-bromo-1-ethylnaphthalen-2(1*H*)-one (3ac)



The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 95:5). Yellow oil, 164.3 mg, 65% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.8 Hz, 1H), 7.51-

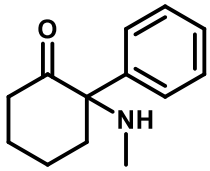
7.30 (m, 4H), 6.32 (d, J = 9.9 Hz, 1H), 2.99 (dq, J = 14.6, 7.3 Hz, 1H), 2.66 (dq, J = 14.8, 7.4 Hz, 1H), 0.63 (t, J = 7.4 Hz, 3H).**^{13}C NMR** (75 MHz, $CDCl_3$): δ 193.4, 144.3, 140.6, 130.8, 130.1, 129.4, 129.1, 128.5, 124.6, 60.9, 32.8, 10.8. HRMS (ESI^+) m/z $[M + H]^+$ calcd for $C_{12}H_{12}BrO$, 251.0066; found, 251.0061.

2-phenylcyclopent-2-en-1-one (5)



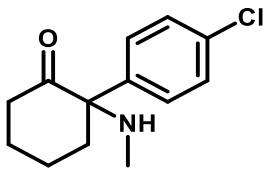
The crude product was purified by flash chromatography (petroleum ether/ethyl acetate 96:4). Yellow solid, 50.9 mg, 32% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.83 (t, J = 2.9 Hz, 1H), 7.72-7.65 (m, 2H), 7.43-7.29 (m, 3H), 2.76-2.67 (m, 2H), 2.64-2.55 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 207.8, 159.1, 143.6, 131.8, 128.6, 128.5, 127.2, 35.9, 26.3. HRMS (ESI^+) m/z $[M + Na]^+$ calcd for $C_{11}H_{10}NaO$, 181.0624; found, 181.0623.

2-(methylamino)-2-phenylcyclohexan-1-one (6a)



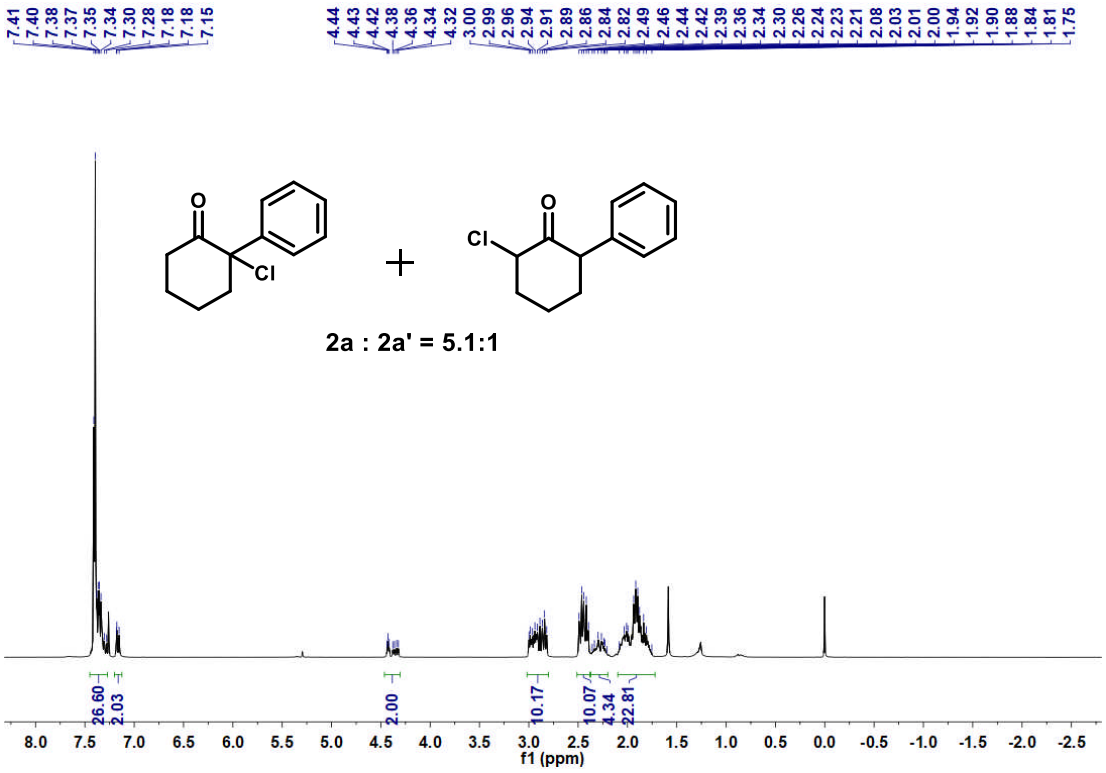
Brown oil, 163.5 mg, 80% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.45-7.13 (m, 5H), 2.99-2.75 (m, 1H), 2.49-2.13 (m, 3H), 2.02 (s, 3H), 1.99-1.89 (m, 1H), 1.79 (dt, J = 20.1, 12.6 Hz, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 211.6, 138.9, 128.9, 127.6, 127.2, 69.9, 39.9, 35.5, 29.0, 27.9, 22.4. HRMS (ESI^+) m/z $[M + H]^+$ calcd for $C_{13}H_{18}NO$, 204.1383; found, 204.1379.

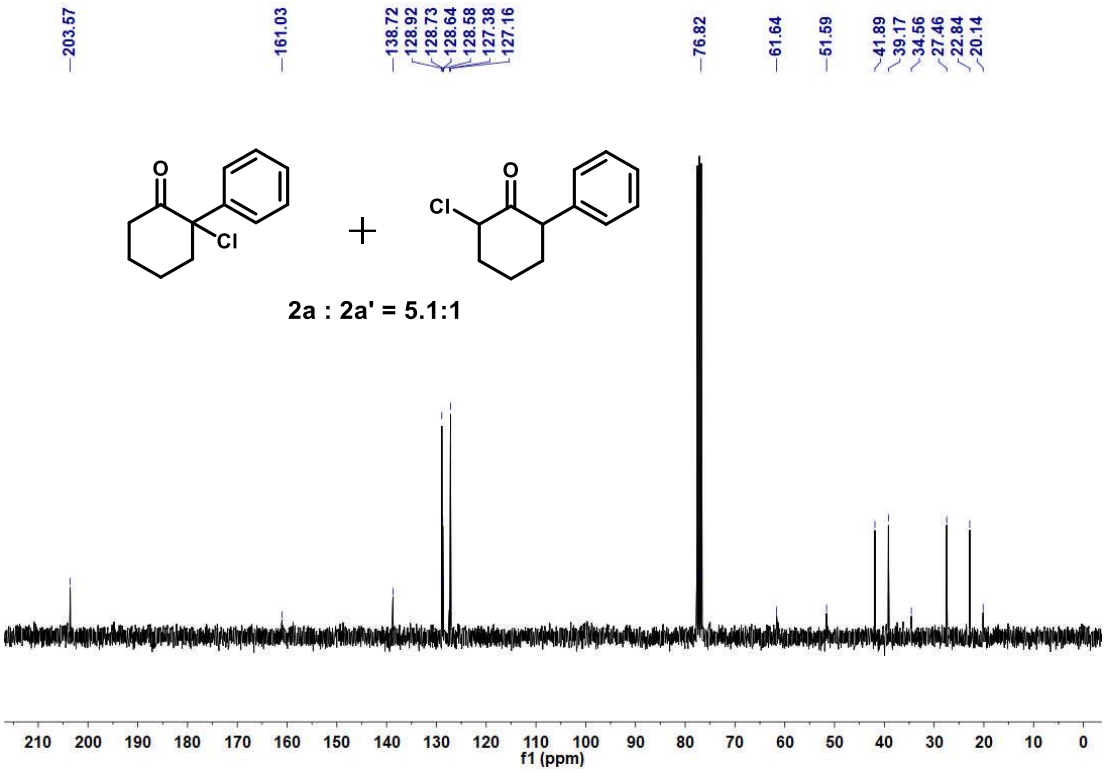
2-(4-chlorophenyl)-2-(methylamino)cyclohexan-1-one (6j)

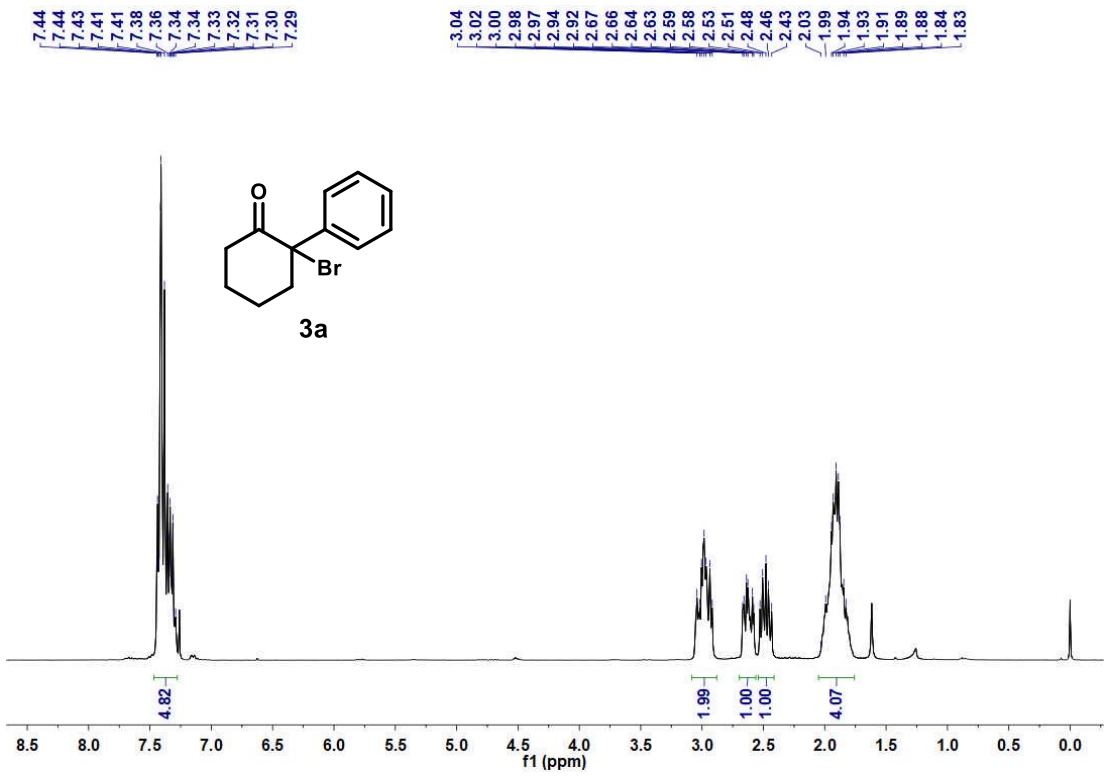


Yellow oil, 186.6 mg, 79% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.19 (dd, J = 49.4, 8.5 Hz, 4H), 2.78-2.63 (m, 1H), 2.41-2.30 (m, 1H), 2.28-2.13 (m, 2H), 1.95 (s, 3H), 1.92-1.83 (m, 1H), 1.82-1.51 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 210.9, 137.6, 133.3, 128.9, 128.6, 69.4, 39.7, 35.7, 28.8, 27.6, 22.2. HRMS (ESI^+) m/z $[M + H]^+$ calcd for $C_{13}H_{17}ClNO$, 238.0993; found, 238.0988.

6. The spectra of ^{1}H and ^{13}C NMR



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7.33
7.32
7.31
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7.29
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3.02
3.00
2.98
2.97
2.94
2.92
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2.66
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2.59
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2.48
2.46
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2.03
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1.83
O
Br
3a
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1.00
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7.0
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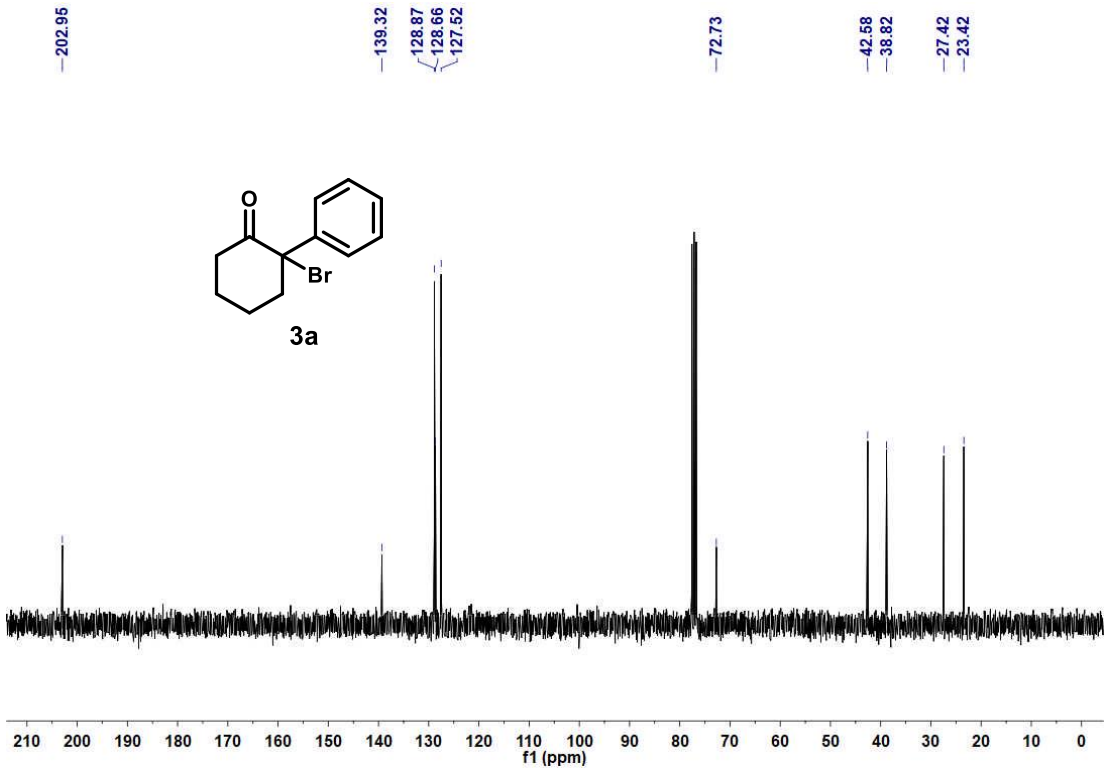
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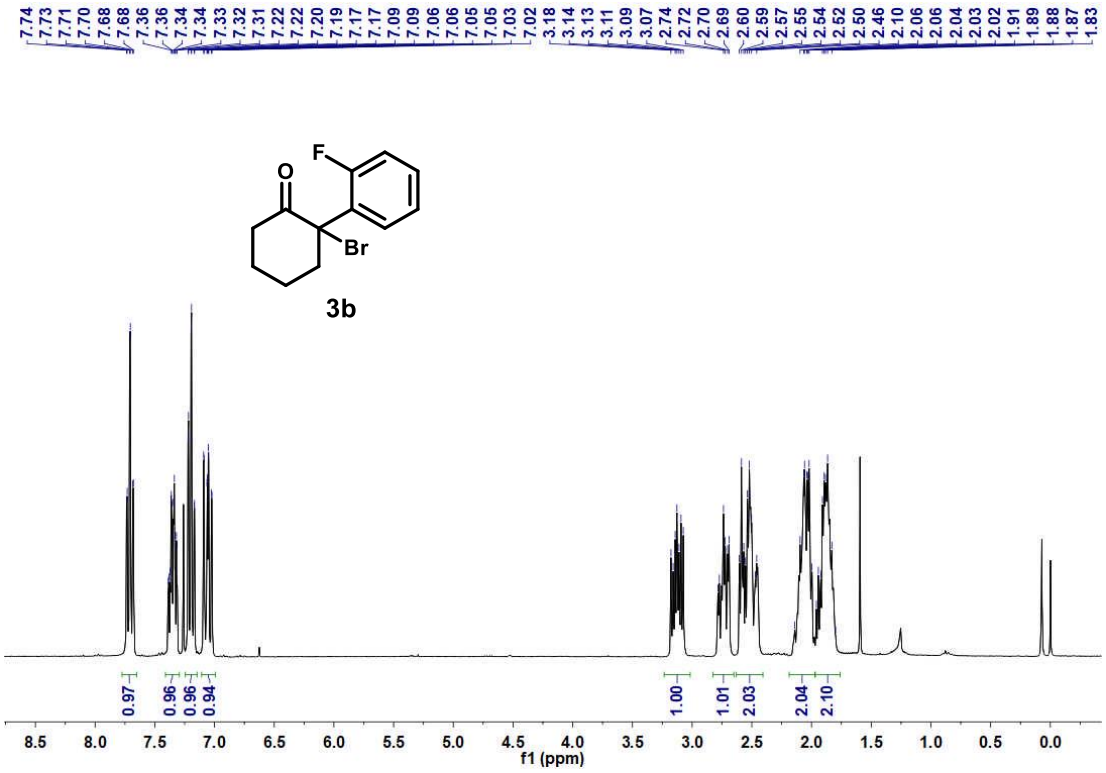
f1 (ppm)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3.18 3.14 3.13 3.11 3.09 3.07 2.74 2.72 2.70 2.69 2.60 2.59 2.57 2.55 2.54 2.52 2.50 2.46 2.10 2.06 2.06 2.04 2.03 2.02 1.91 1.89 1.88 1.87 1.83
F
O
Br
3b
0.97 0.96 0.96 0.94 1.00 1.01 2.03 2.04 2.10
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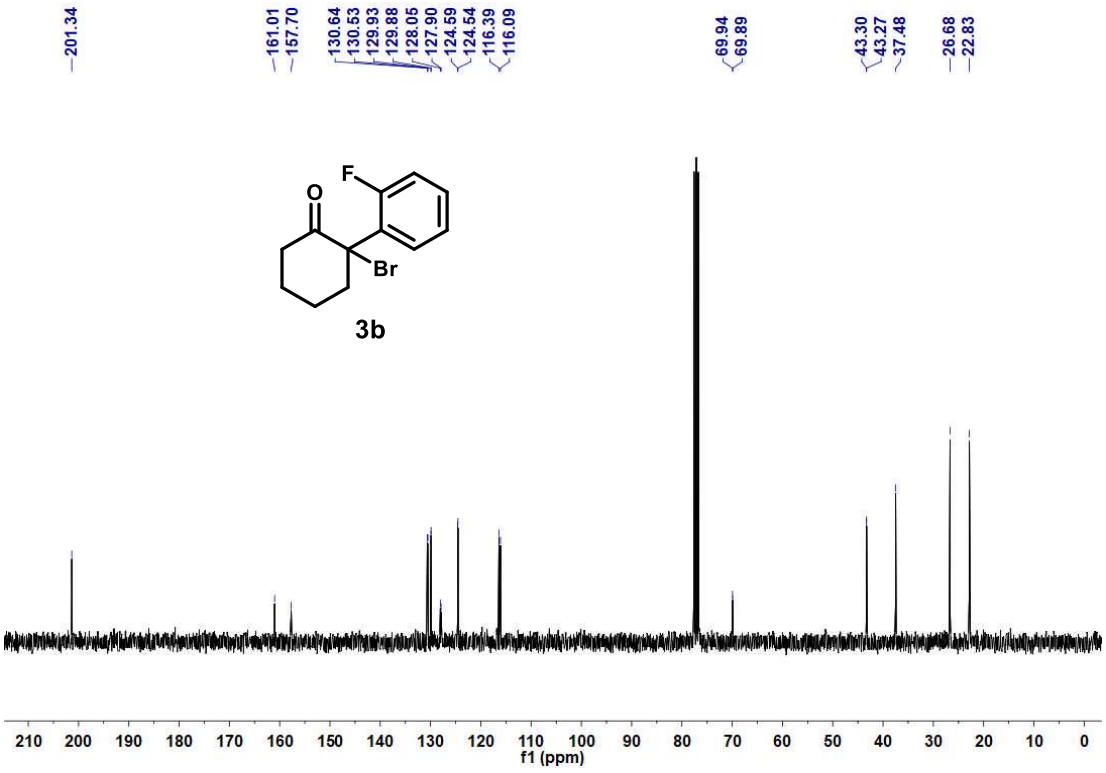
f1 (ppm)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69.94 69.89
43.30 43.27 37.48
26.68 22.83
F
O
Br
3b
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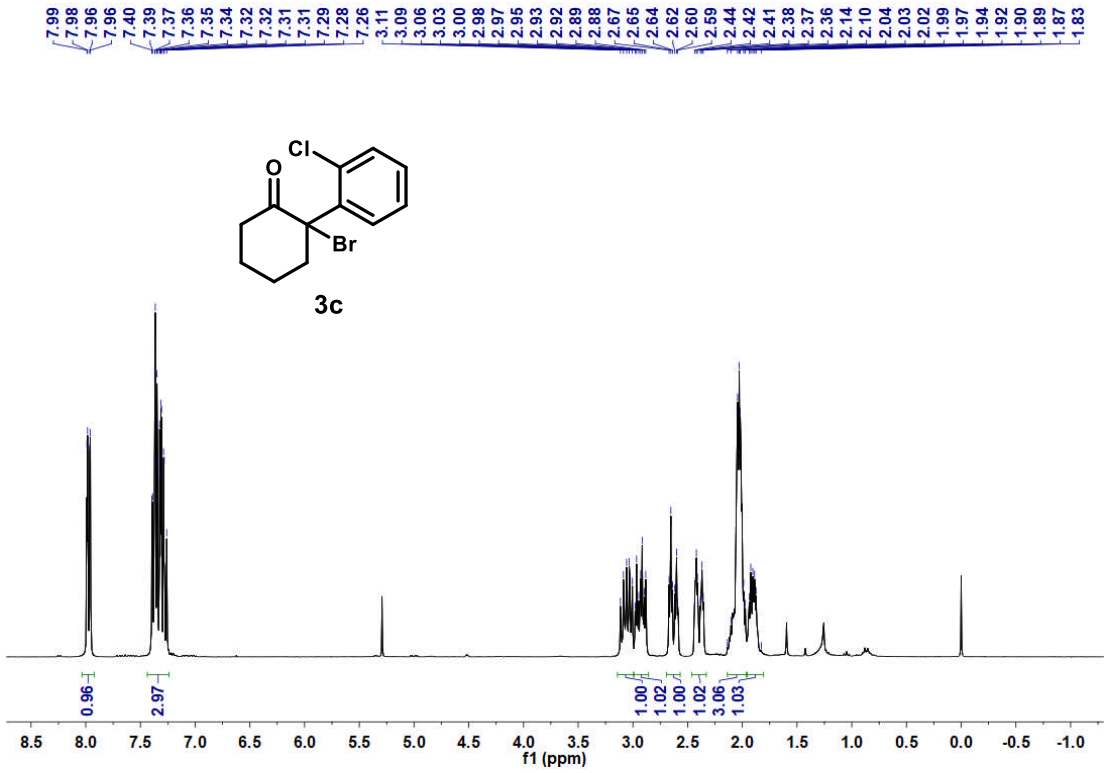
f1 (ppm)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2.02
1.99
1.97
1.94
1.92
1.90
1.89
1.87
1.83
Cl
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Br
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1.00
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3.06
1.03
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6.0
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5.0
4.5
4.0
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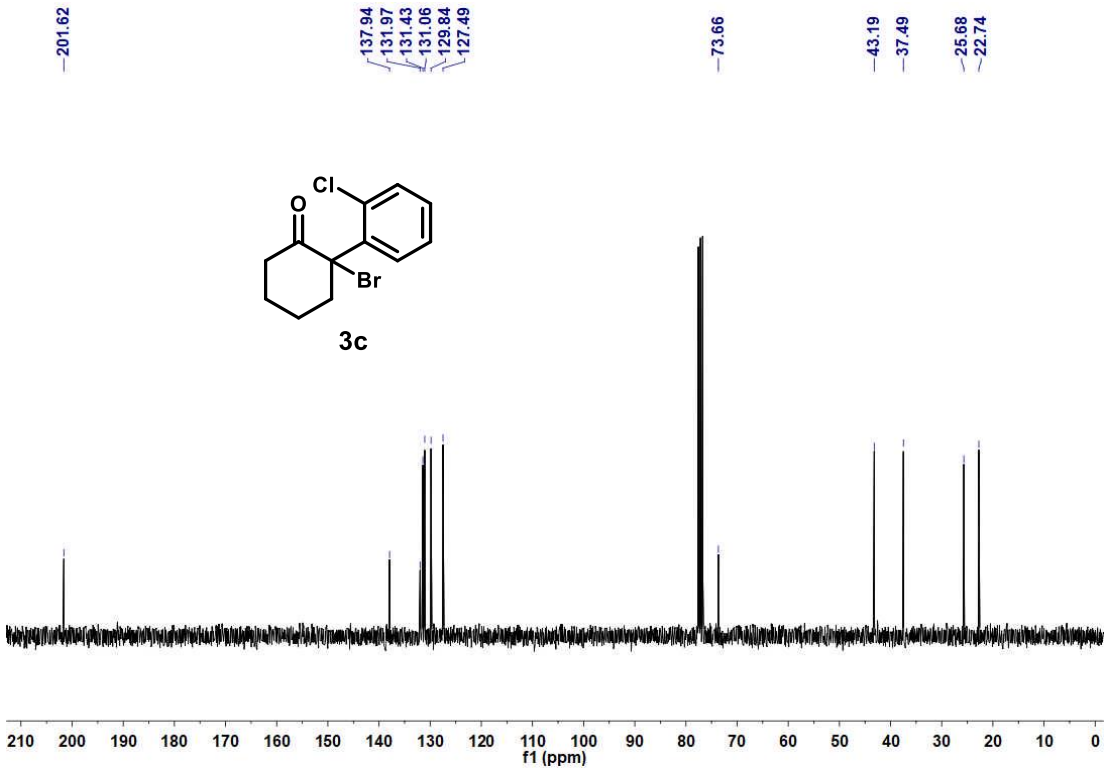
f1 (ppm)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131.06
129.84
127.49
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43.19
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25.68
22.74
Cl
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Br
3c
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200
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90
80
70
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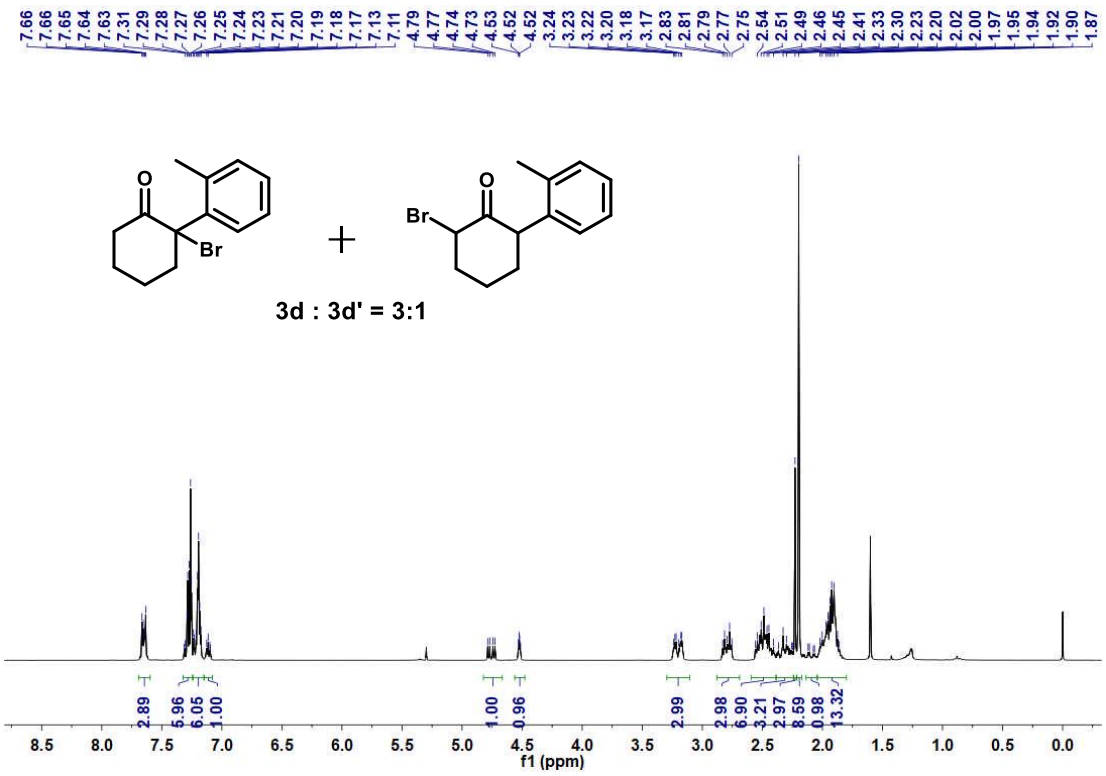
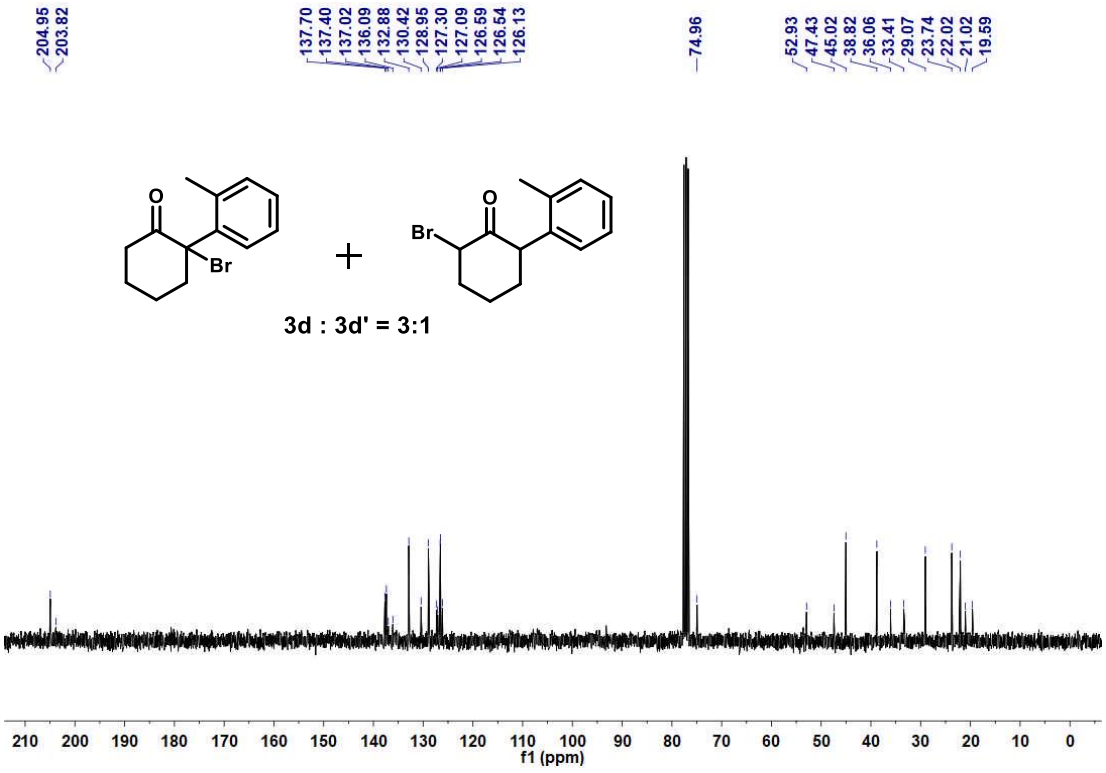
50
40
30
20
10
0
f1 (ppm)


7.66 7.66 7.65 7.64 7.63 7.31 7.29 7.28 7.27 7.26 7.25 7.24 7.23 7.21 7.20 7.19 7.18 7.17 7.13 7.11 4.79 4.77 4.74 4.73 4.53 4.52 4.52 3.24 3.23 3.22 3.20 3.18 3.17 2.83 2.81 2.79 2.77 2.75 2.54 2.51 2.49 2.46 2.45 2.41 2.33 2.30 2.23 2.20 2.02 2.00 1.97 1.95 1.94 1.92 1.90 1.87
O
Br
Br
O
3d : 3d' = 3:1
2.89 6.96 6.05 1.00 1.00 0.96 2.99 2.98 6.90 3.21 2.97 8.59 0.98 13.32
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


204.95 203.82 137.70 137.40 137.02 136.09 132.88 130.42 128.95 127.30 127.09 126.59 126.54 126.13 74.96 52.93 47.43 45.02 38.82 36.06 33.41 29.07 23.74 22.02 21.02 19.59
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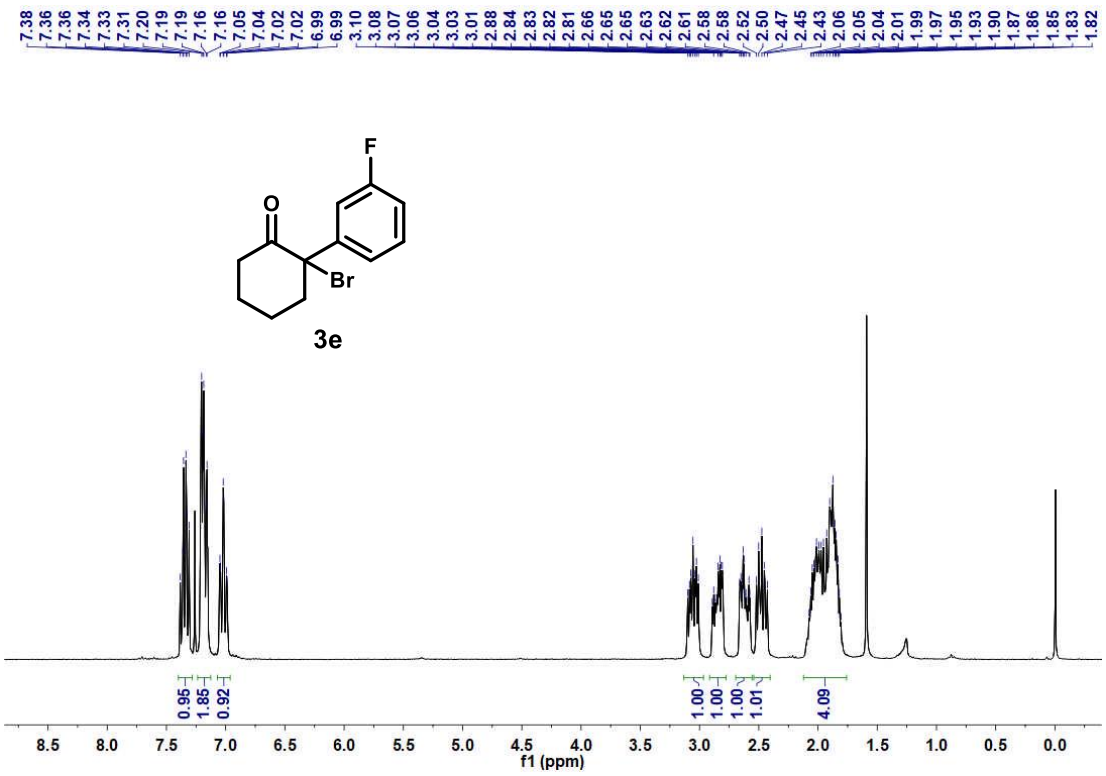
f1 (ppm)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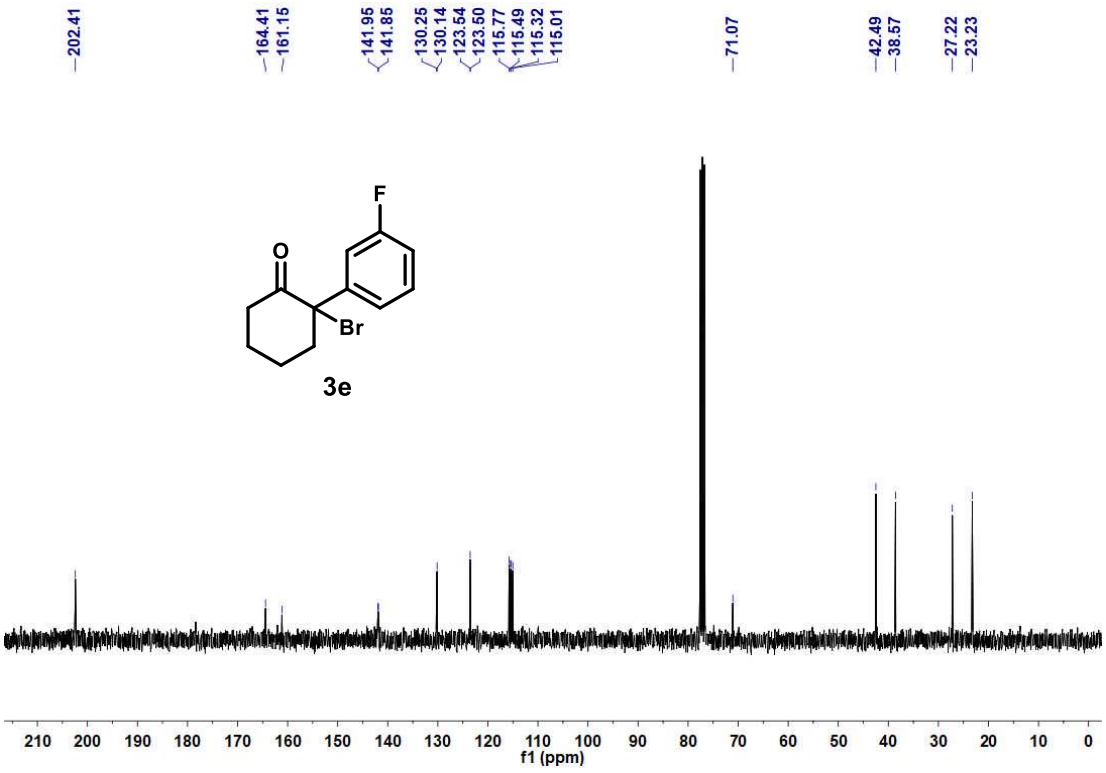
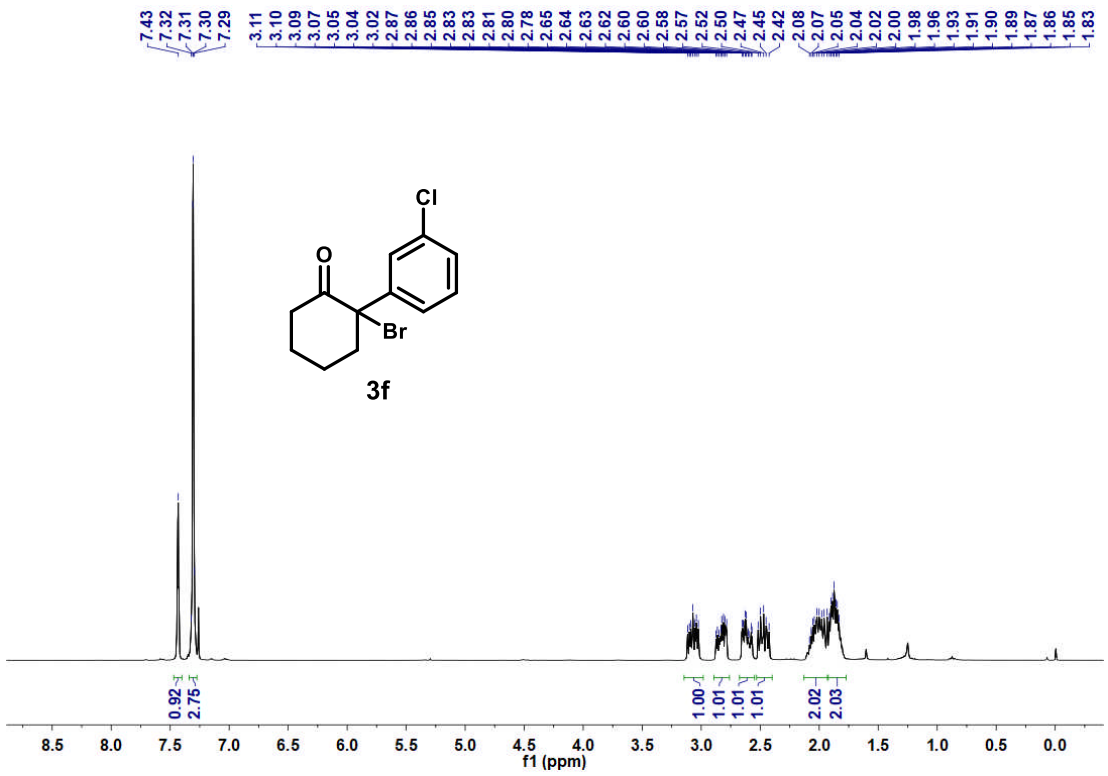
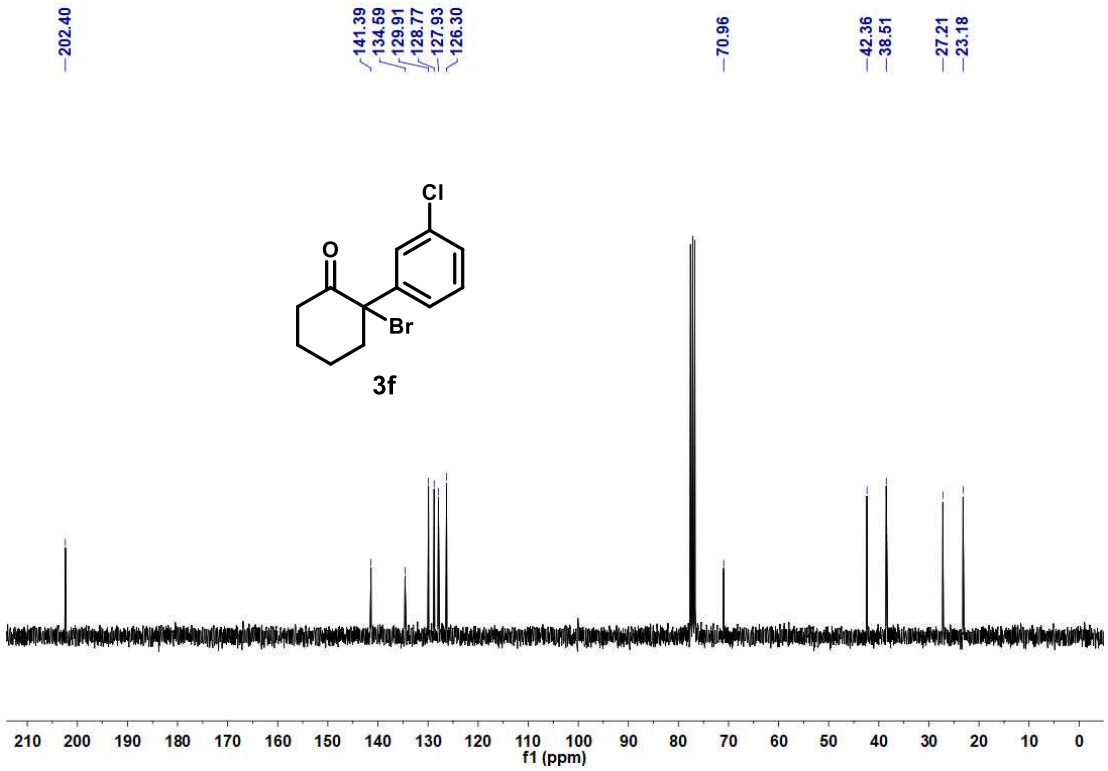
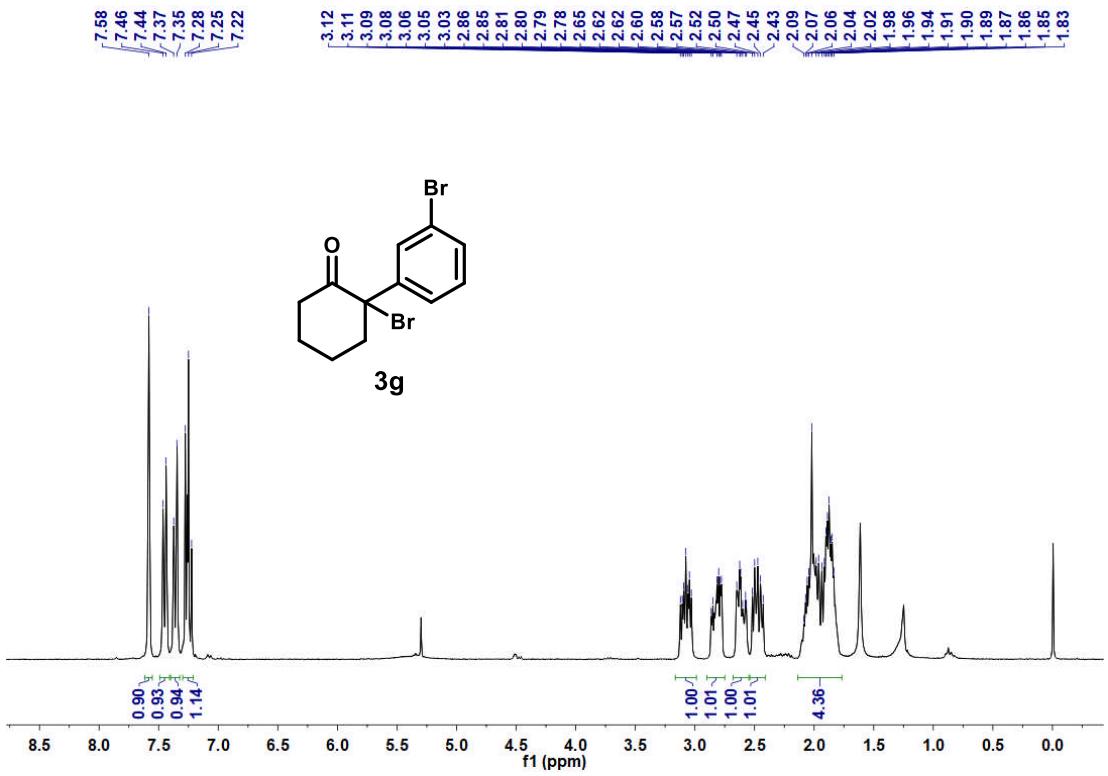
F
O
Br
3e
0.95 1.85 0.92 1.00 1.00 1.00 1.01 4.09
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


202.41
164.41 161.15
141.95 141.85 130.25 130.14 123.54 123.50 115.77 115.49 115.32 115.01
71.07
42.49 38.57
27.22 23.23
F
O
Br
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.43 7.32 7.31 7.30 7.29 3.11 3.10 3.09 3.07 3.05 3.04 3.02 2.87 2.86 2.85 2.83 2.83 2.81 2.80 2.78 2.65 2.64 2.63 2.62 2.60 2.60 2.58 2.57 2.52 2.50 2.47 2.45 2.42 2.08 2.07 2.05 2.04 2.02 2.00 1.98 1.96 1.93 1.91 1.90 1.89 1.87 1.86 1.85 1.83
Cl
O
Br
3f
0.92 2.75 1.00 1.01 1.01 1.01 2.02 2.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


202.40 141.39 134.59 129.91 128.77 127.93 126.30 70.96 42.36 38.51 27.21 23.18
Cl
O
Br
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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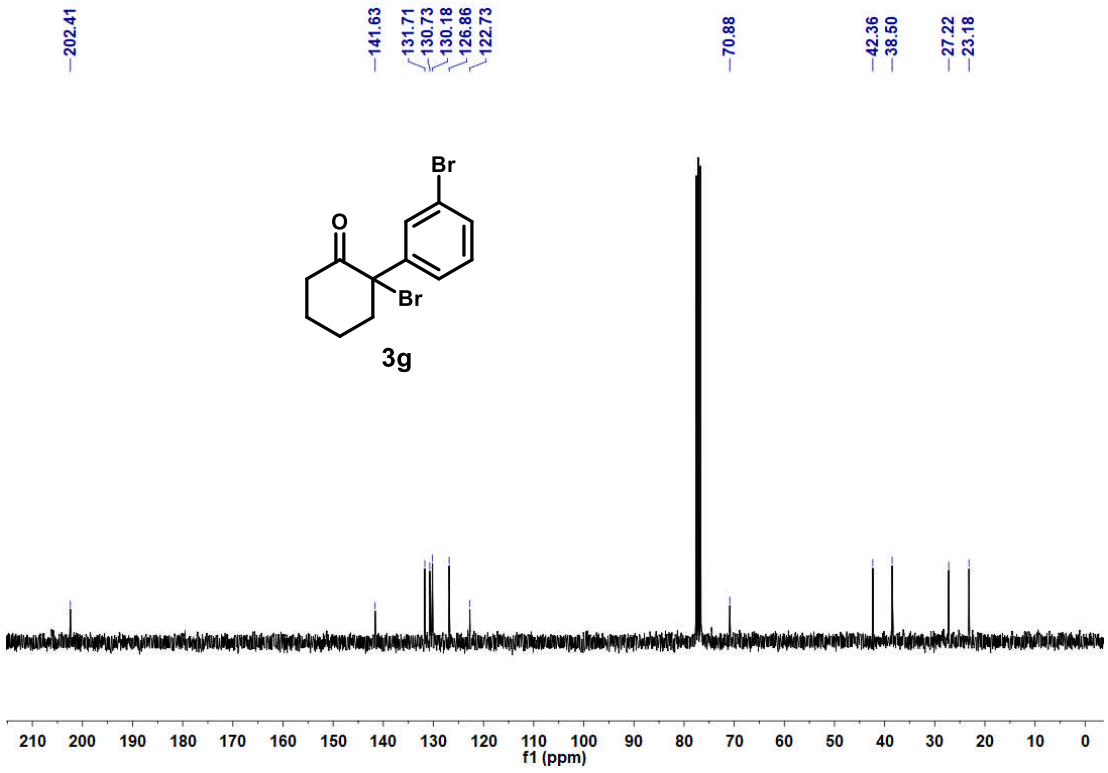
7.46
7.44
7.37
7.35
7.28
7.25
7.22
3.12
3.11
3.09
3.08
3.06
3.05
3.03
2.86
2.85
2.81
2.80
2.79
2.78
2.65
2.62
2.62
2.60
2.58
2.57
2.52
2.50
2.47
2.45
2.43
2.09
2.07
2.06
2.04
2.02
1.98
1.96
1.94
1.91
1.90
1.89
1.87
1.86
1.85
1.83
Br
O
Br
3g
0.90
0.93
0.94
1.14
1.00
1.01
1.00
1.01
4.36
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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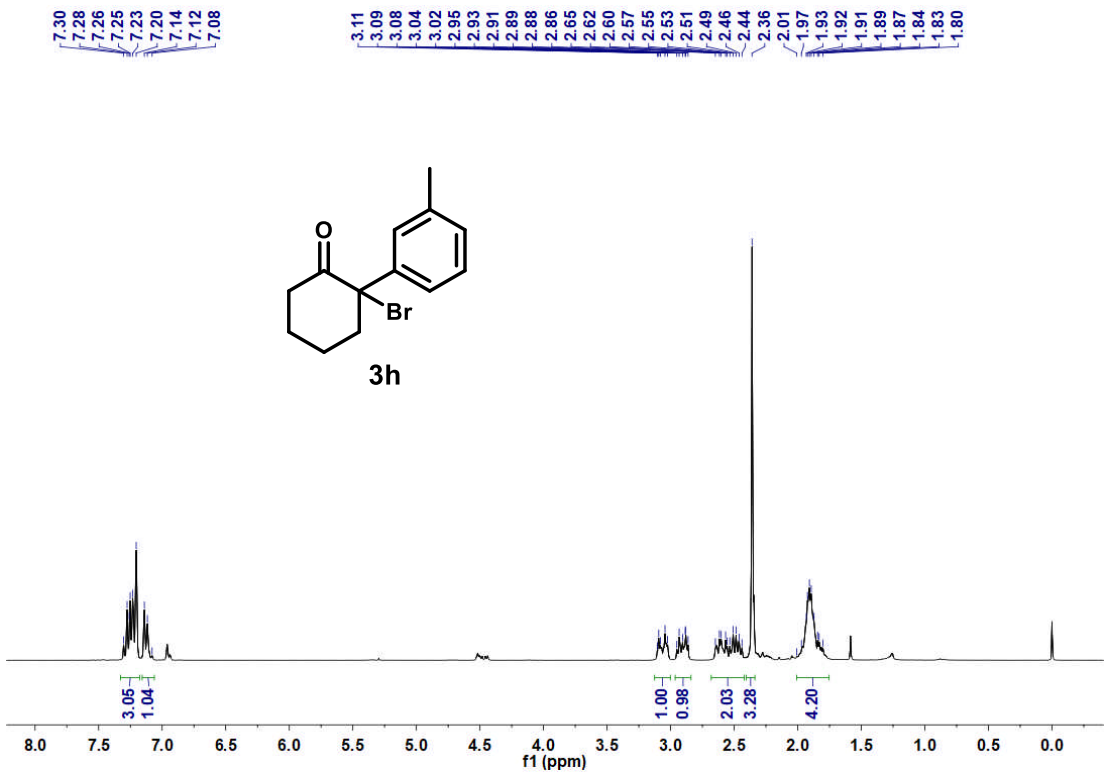
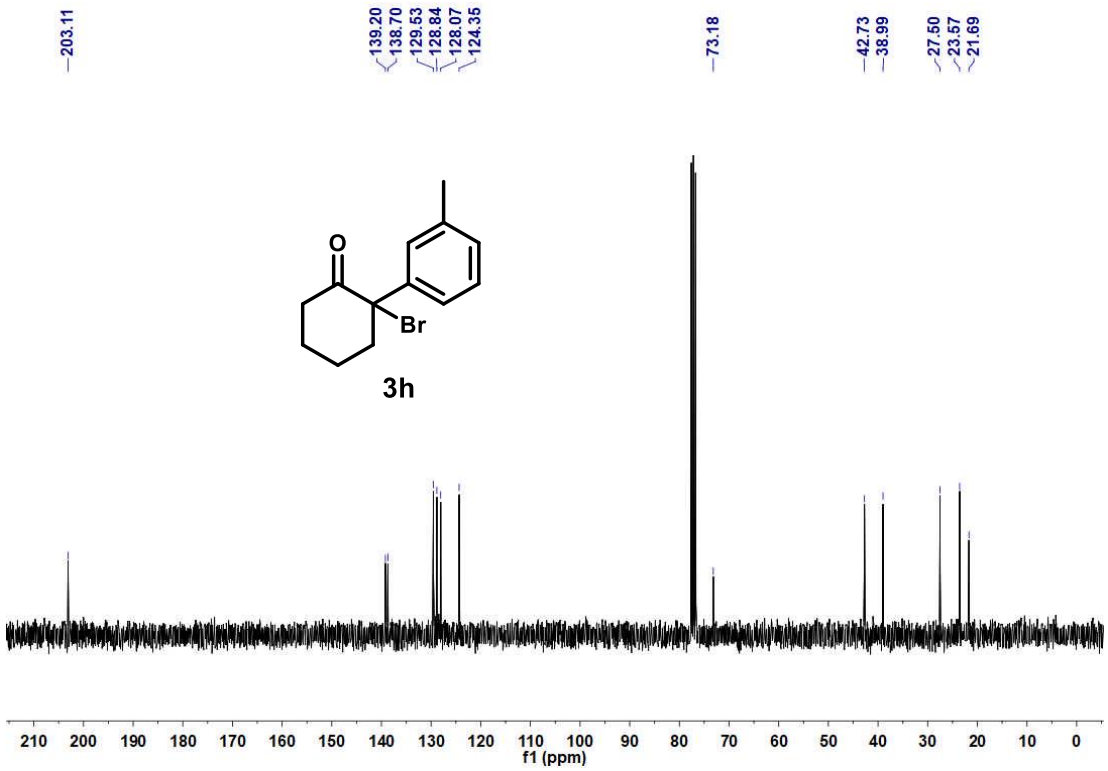
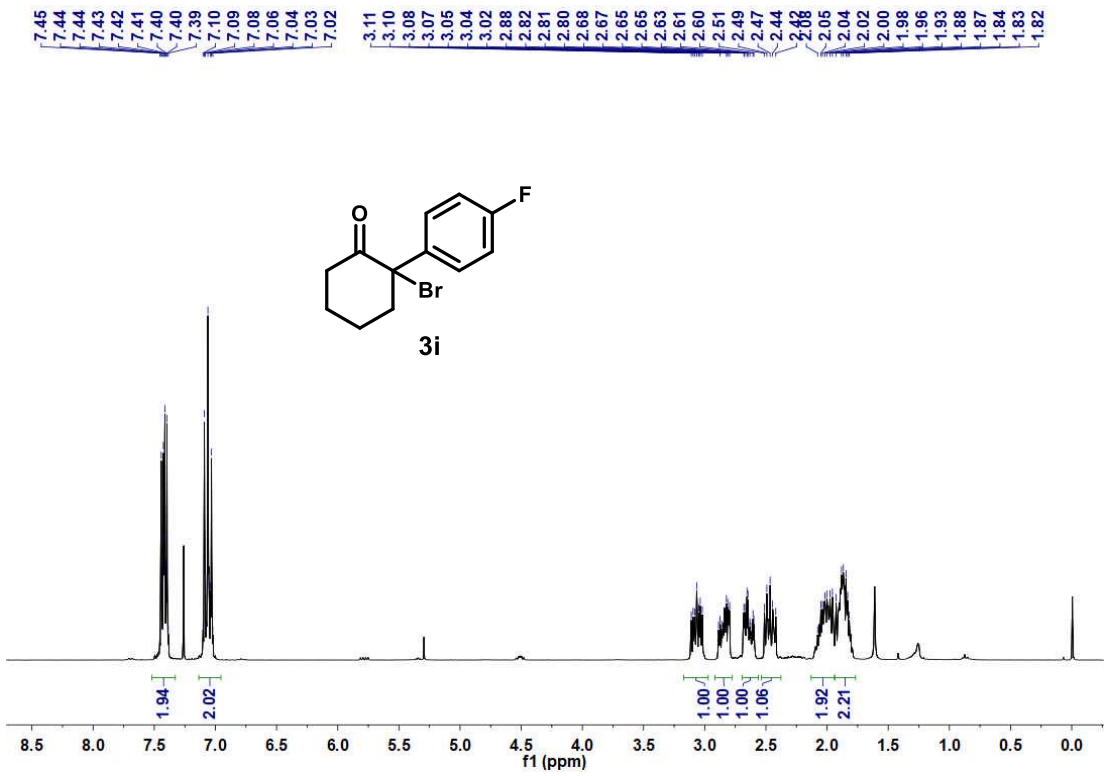
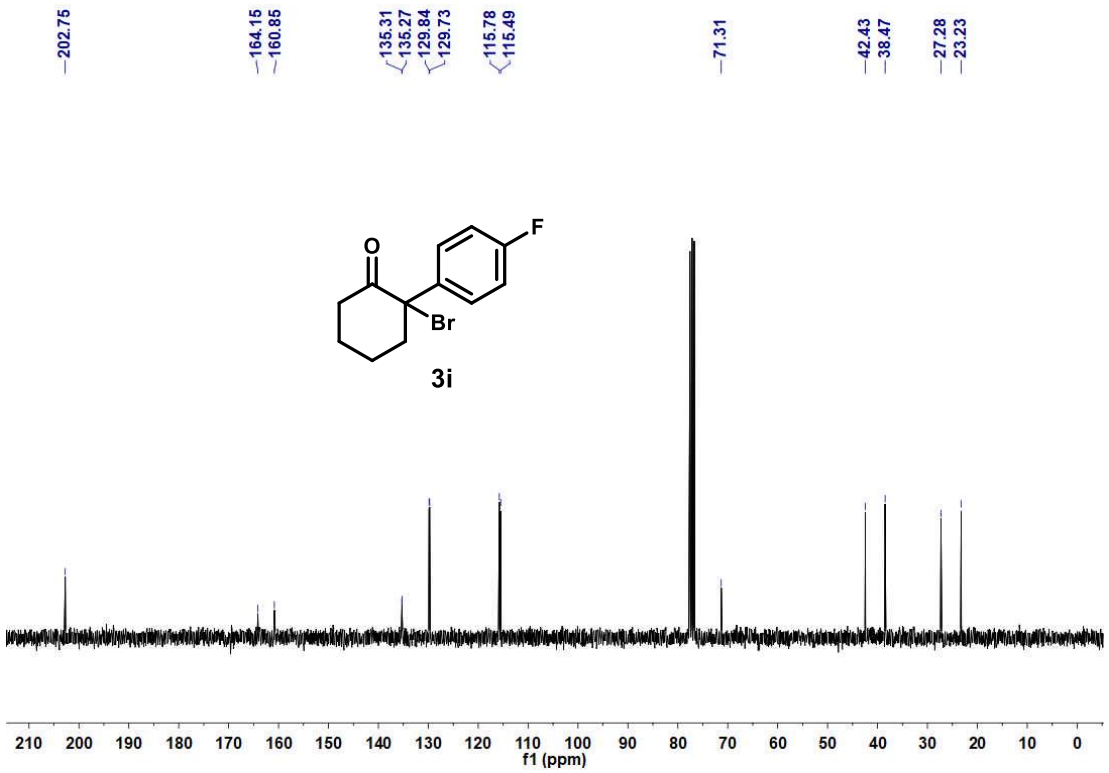
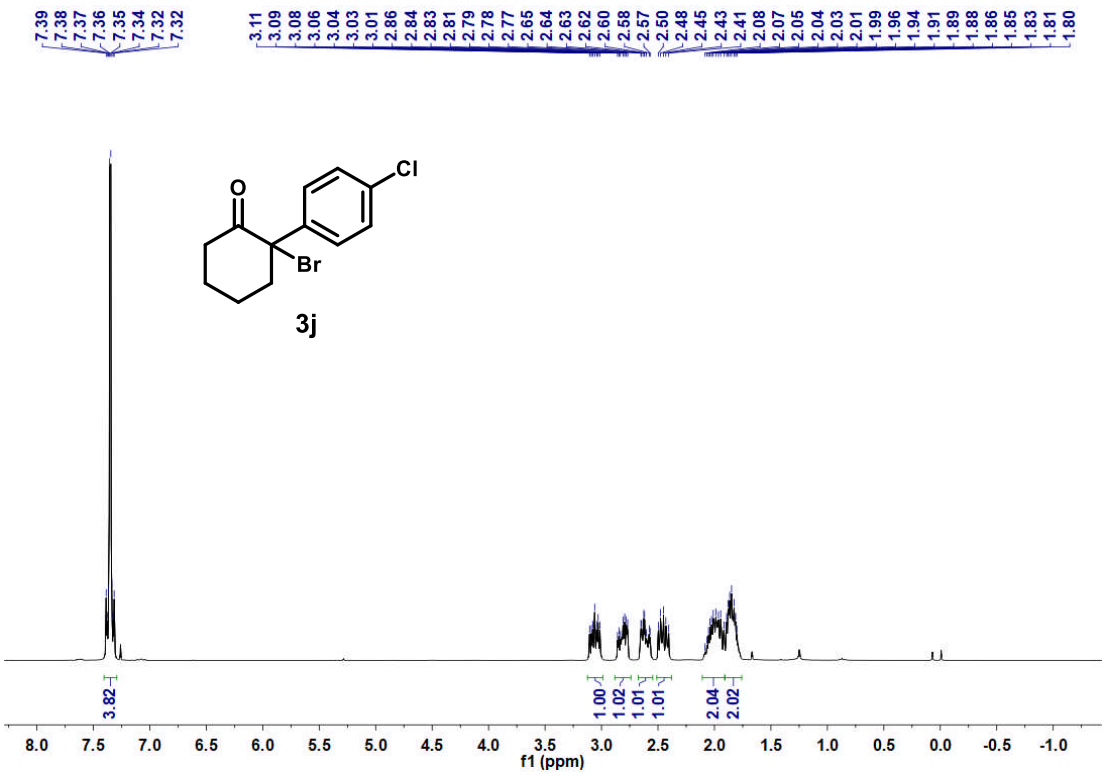
141.63
131.71
130.73
130.18
126.86
122.73
70.88
42.36
38.50
27.22
23.18
Br
O
Br
3g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

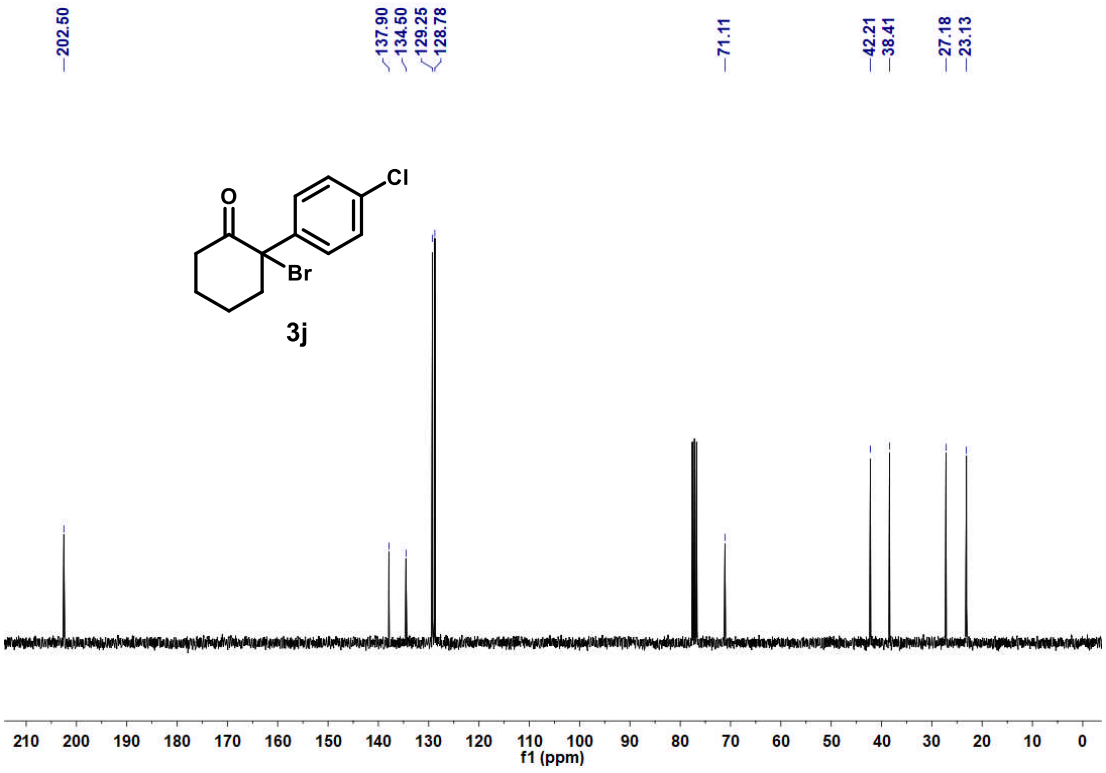

7.30
7.28
7.26
7.25
7.23
7.20
7.14
7.12
7.08
3.11
3.09
3.08
3.04
3.02
2.95
2.93
2.91
2.89
2.88
2.86
2.65
2.62
2.60
2.57
2.55
2.53
2.51
2.49
2.46
2.44
2.36
2.01
1.97
1.93
1.92
1.91
1.89
1.87
1.84
1.83
1.80
O
Br
3h
3.05
1.04
1.00
0.98
2.03
3.28
4.20
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

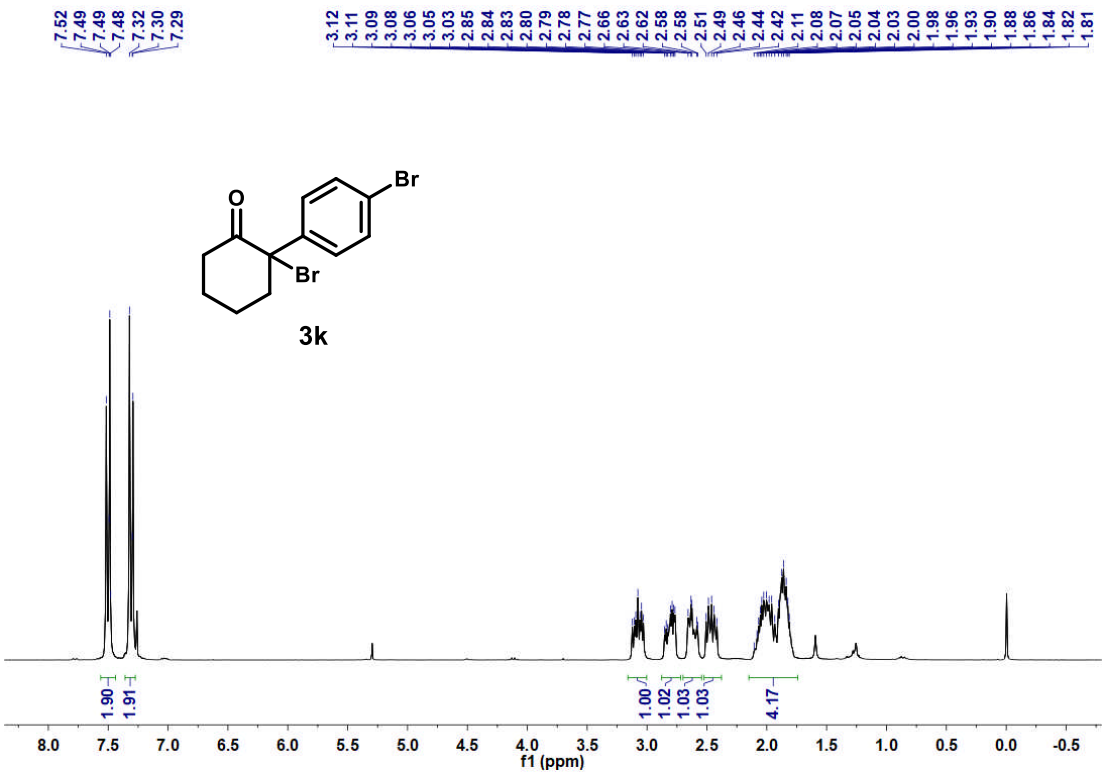

203.11
139.20
138.70
129.53
128.84
128.07
124.35
73.18
42.73
38.99
27.50
23.57
21.69
O
Br
3h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

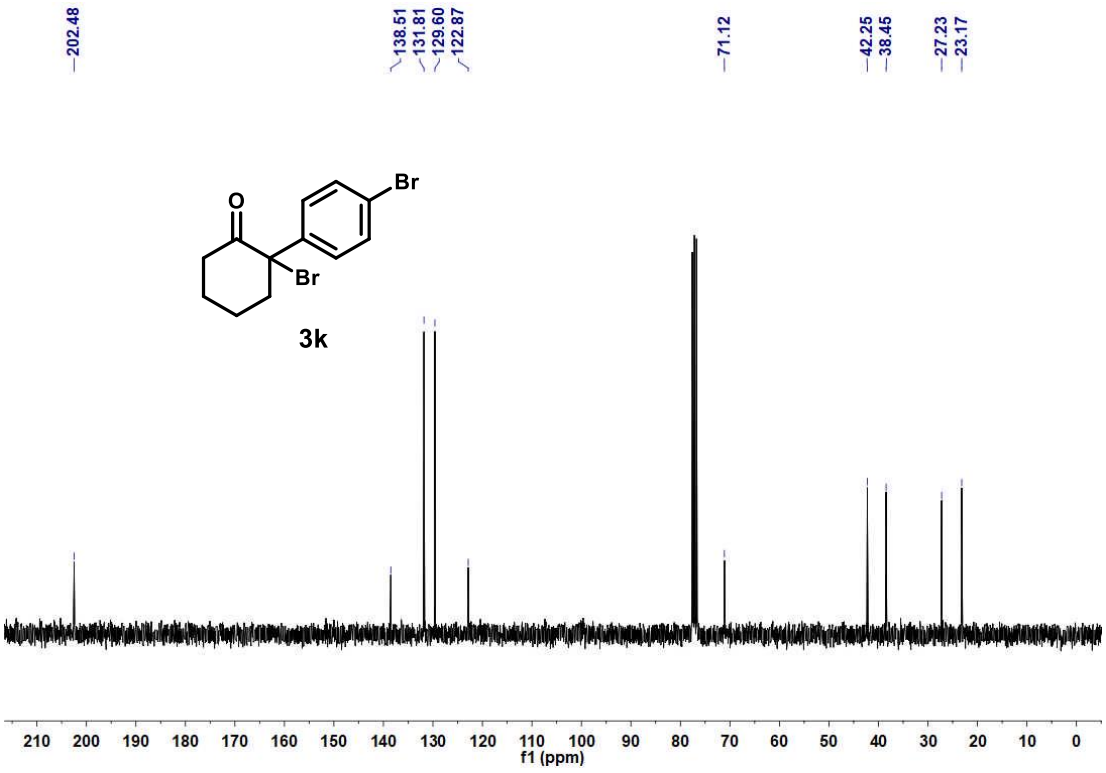

7.45 7.44 7.44 7.43 7.42 7.41 7.40 7.40 7.39 7.10 7.09 7.08 7.06 7.04 7.03 7.02
3.11 3.10 3.08 3.07 3.05 3.04 3.02 2.88 2.82 2.81 2.80 2.68 2.67 2.65 2.65 2.63 2.61 2.60 2.51 2.49 2.47 2.44
2.05 2.04 2.02 2.00 1.98 1.96 1.93 1.88 1.87 1.84 1.83 1.82
O
F
Br
3i
1.94 2.02 1.00 1.00 1.00 1.06 1.92 2.21
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

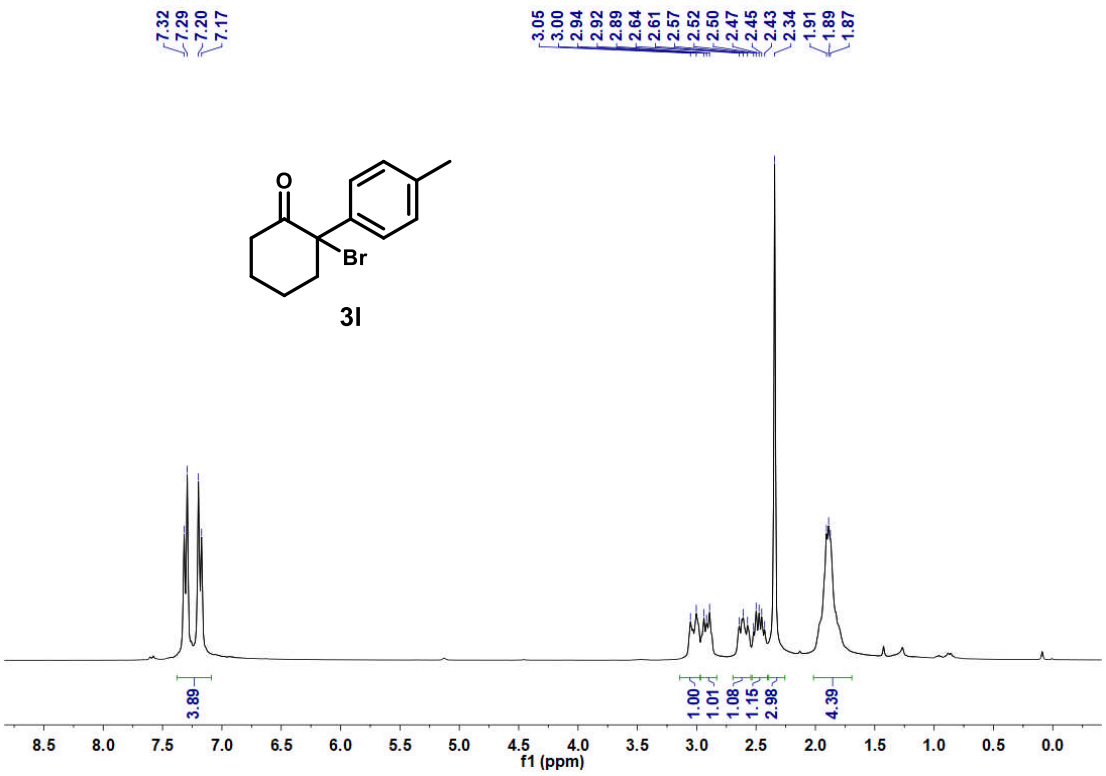

202.75
164.15 160.85
135.31 135.27 129.84 129.73
115.78 115.49
71.31
42.43 38.47
27.28 23.23
O
F
Br
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

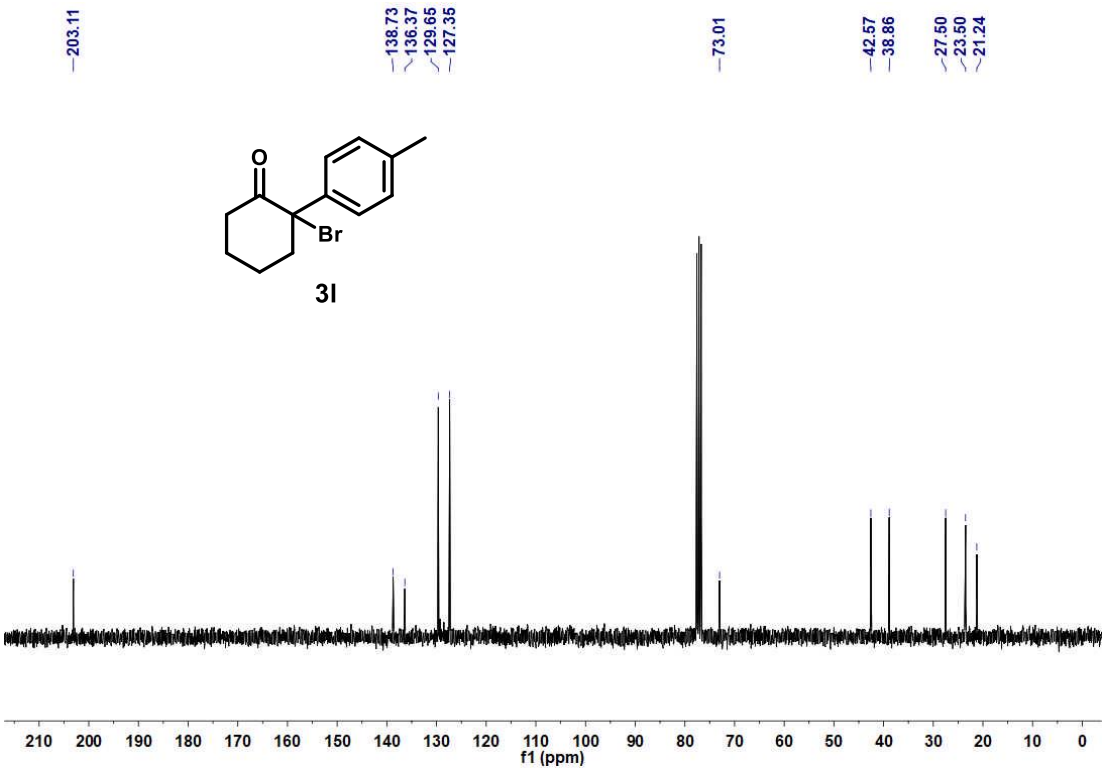

7.39 7.38 7.37 7.36 7.35 7.34 7.32 7.32
3.11 3.09 3.08 3.06 3.04 3.03 3.01 2.86 2.84 2.83 2.81 2.79 2.78 2.77 2.65 2.64 2.63 2.62 2.60 2.58 2.57 2.50 2.48 2.45 2.43 2.41 2.08 2.07 2.05 2.04 2.03 2.01 1.99 1.96 1.94 1.91 1.89 1.88 1.86 1.85 1.83 1.81 1.80
O
Cl
Br
3j
3.82
1.00 1.02 1.01 1.01 2.04 2.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

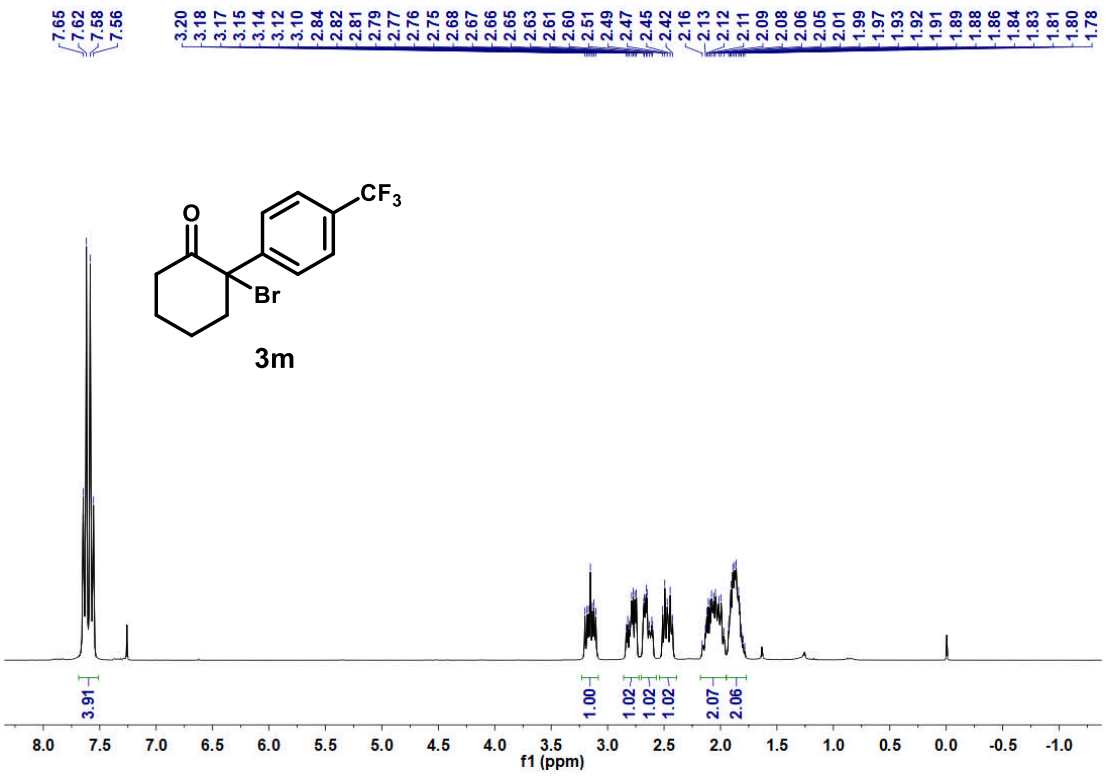

202.50
137.90 134.50 129.25 128.78
71.11
42.21 38.41
27.18 23.13
O
Cl
Br
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

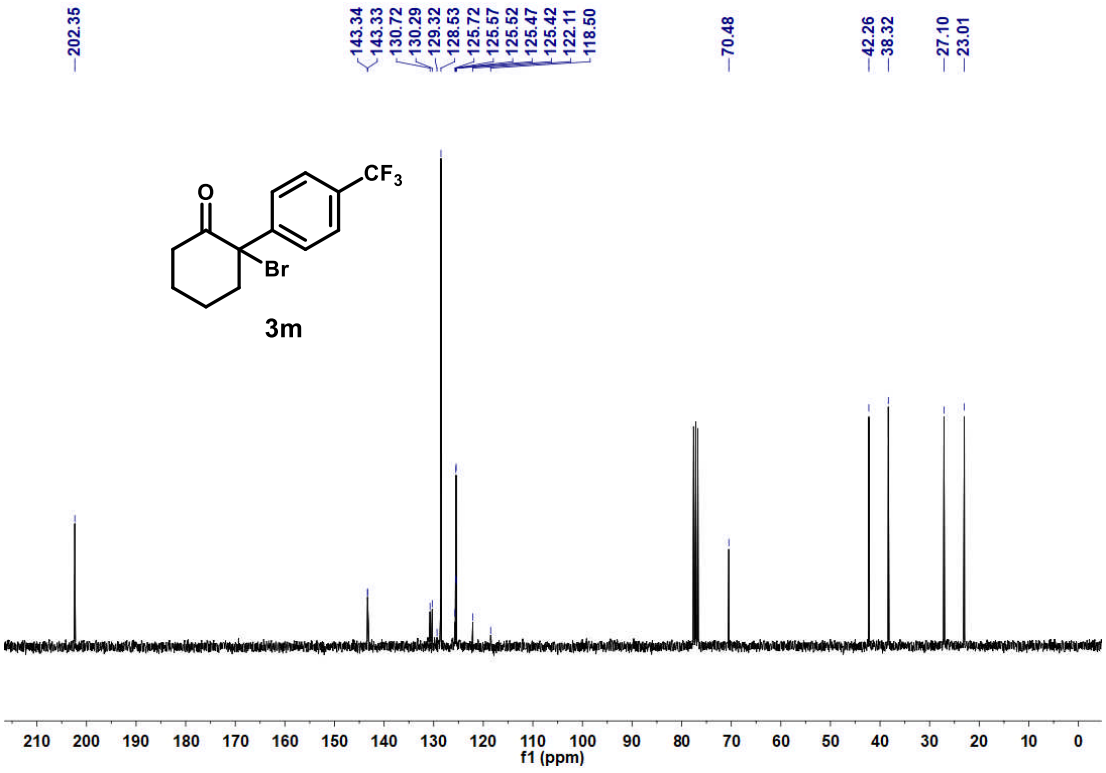

7.52
7.49
7.49
7.48
7.32
7.30
7.29
3.12
3.11
3.09
3.08
3.06
3.05
3.03
2.85
2.84
2.83
2.80
2.79
2.78
2.77
2.66
2.63
2.62
2.58
2.58
2.51
2.49
2.46
2.44
2.42
2.11
2.08
2.07
2.05
2.04
2.03
2.00
1.98
1.96
1.93
1.90
1.88
1.86
1.84
1.82
1.81
Br
O
Br
3k
1.90
1.91
1.00
1.02
1.03
1.03
4.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


202.48
138.51
131.81
129.60
122.87
71.12
42.25
38.45
27.23
23.17
Br
O
Br
3k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.32
7.29
7.20
7.17
3.05
3.00
2.94
2.92
2.89
2.64
2.61
2.57
2.52
2.50
2.47
2.45
2.43
2.34
1.91
1.89
1.87
O
Br
3l
3.89
1.00
1.01
1.08
1.15
2.98
4.39
f1 (ppm)


203.11
138.73
136.37
129.65
127.35
73.01
42.57
38.86
27.50
23.50
21.24
O
Br
3l
f1 (ppm)


7.65
7.62
7.58
7.56
3.20
3.18
3.17
3.15
3.14
3.12
3.10
2.84
2.82
2.81
2.79
2.77
2.76
2.75
2.68
2.67
2.66
2.65
2.63
2.61
2.60
2.51
2.49
2.47
2.45
2.42
2.16
2.13
2.12
2.11
2.09
2.08
2.06
2.05
2.01
1.99
1.97
1.93
1.92
1.91
1.89
1.88
1.86
1.84
1.83
1.81
1.80
1.78
CF3
O
Br
3m
3.91
1.00
1.02
1.02
1.02
2.07
2.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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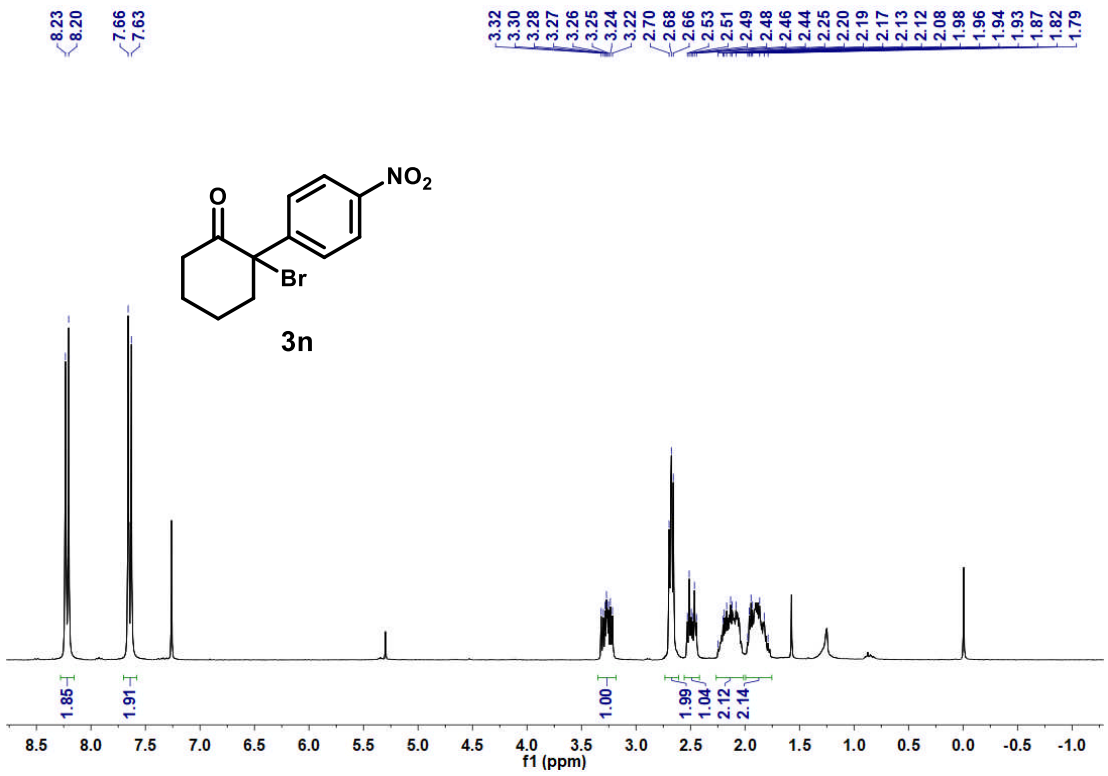
143.34
143.33
130.72
130.29
129.32
128.53
125.72
125.57
125.52
125.47
125.42
122.11
118.50
70.48
42.26
38.32
27.10
23.01
CF3
O
Br
3m
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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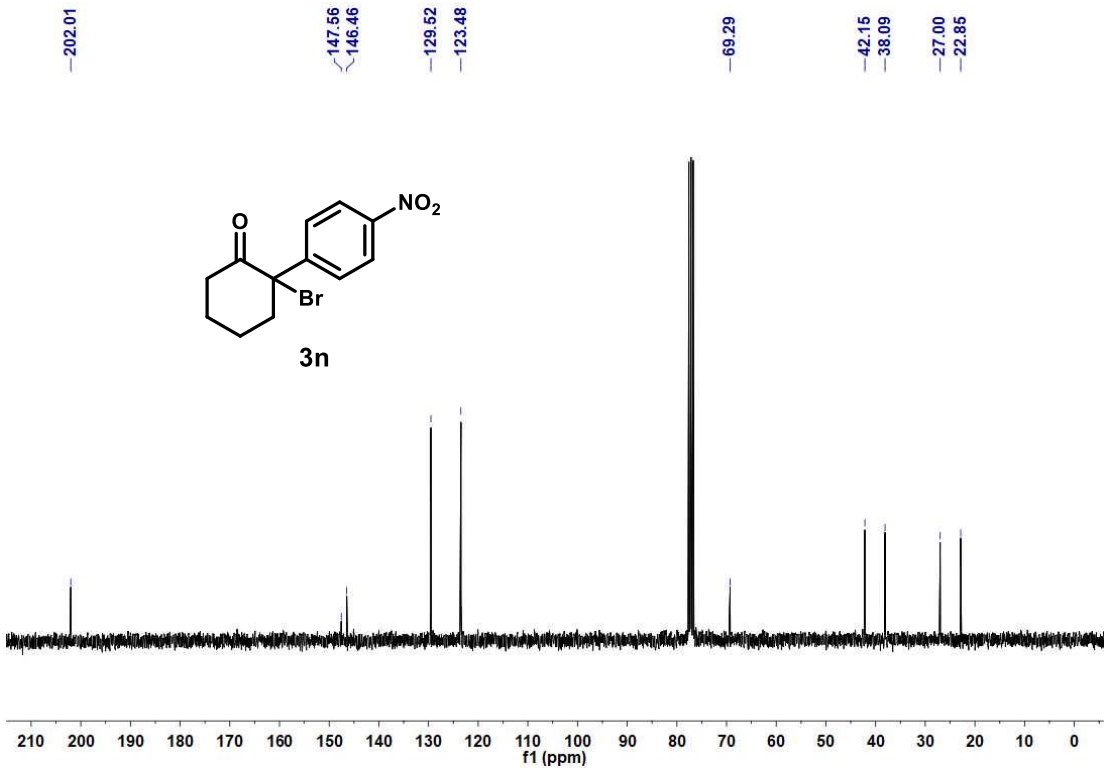
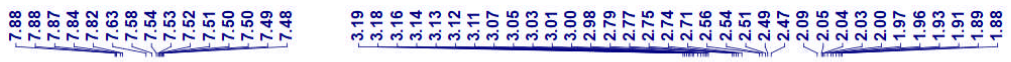
7.63
3.32
3.30
3.28
3.27
3.26
3.25
3.24
3.22
2.70
2.68
2.66
2.53
2.51
2.49
2.48
2.46
2.44
2.25
2.20
2.19
2.17
2.13
2.12
2.08
1.98
1.96
1.94
1.93
1.87
1.82
1.79
O
NO2
Br
3n
1.85
1.91
1.00
1.99
1.04
2.12
2.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


202.01
147.56
146.46
129.52
123.48
69.29
42.15
38.09
27.00
22.85
O
NO2
Br
3n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.88
7.88
7.87
7.84
7.82
7.63
7.58
7.54
7.53
7.52
7.51
7.50
7.50
7.49
7.48
3.19
3.18
3.16
3.14
3.13
3.12
3.11
3.07
3.05
3.03
3.01
3.00
2.98
2.79
2.77
2.75
2.74
2.71
2.56
2.54
2.51
2.49
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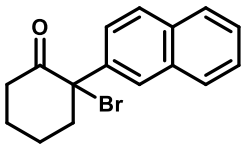
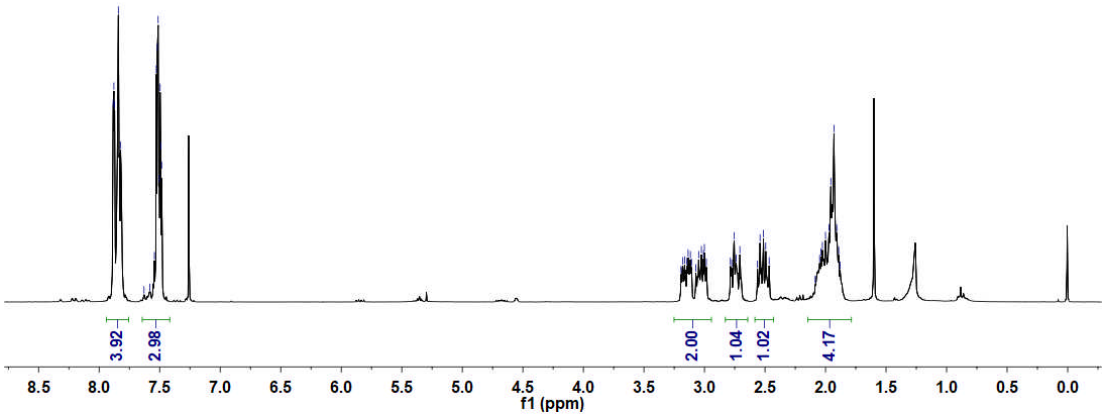
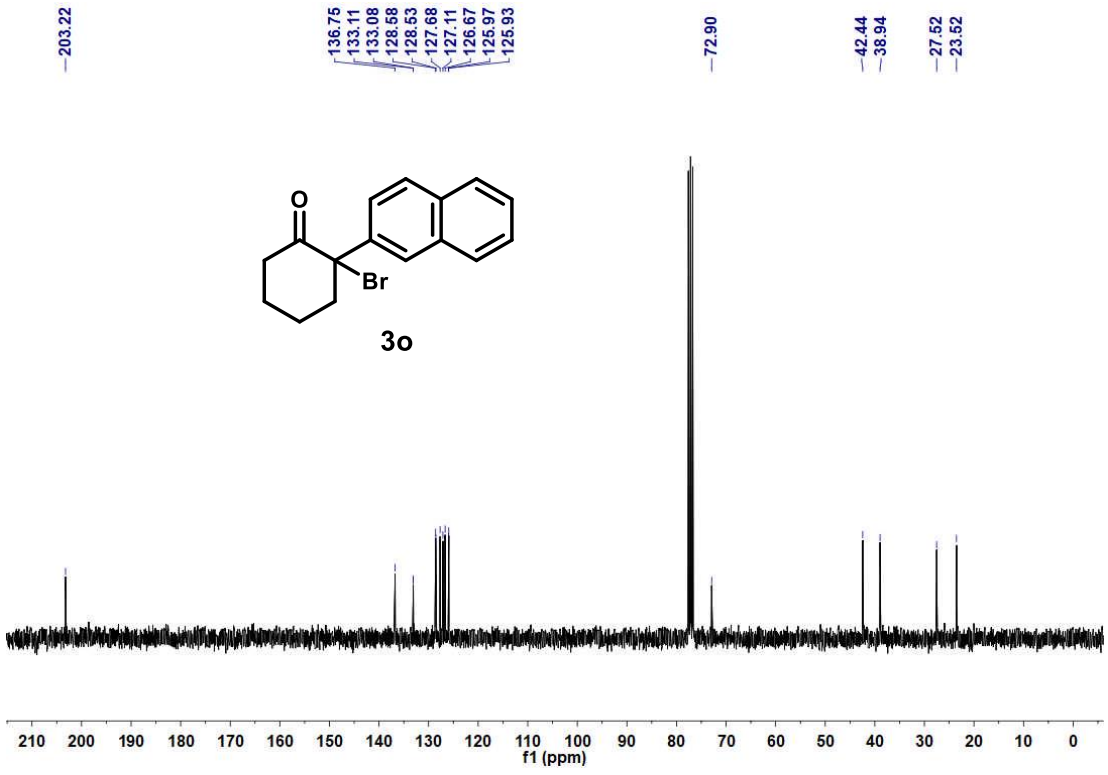
1.97
1.96
1.93
1.91
1.89
1.88


O
Br

3o


3.92
2.98
2.00
1.04
1.02
4.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


203.22
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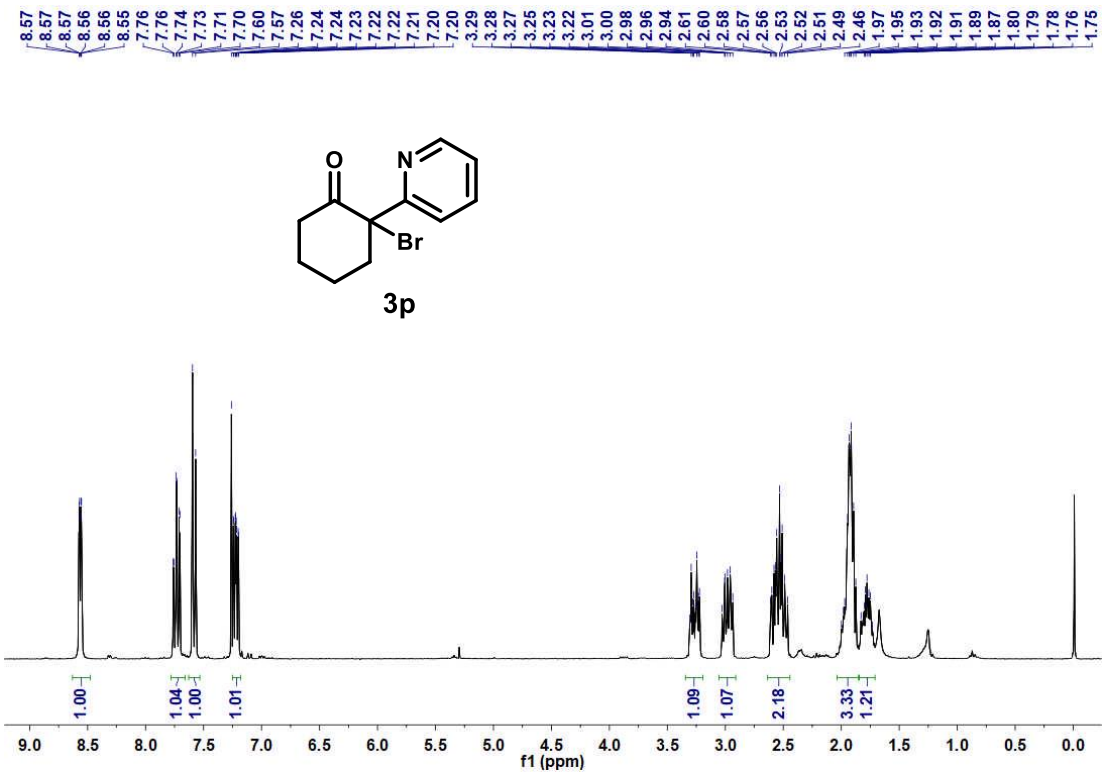
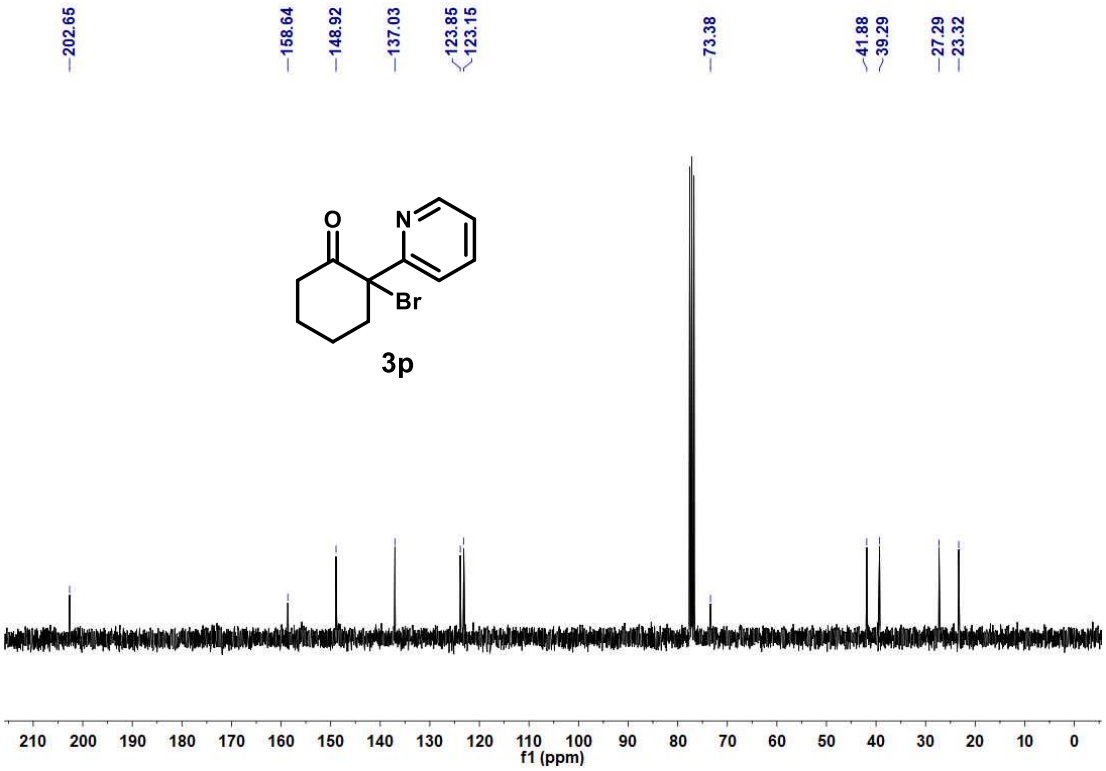
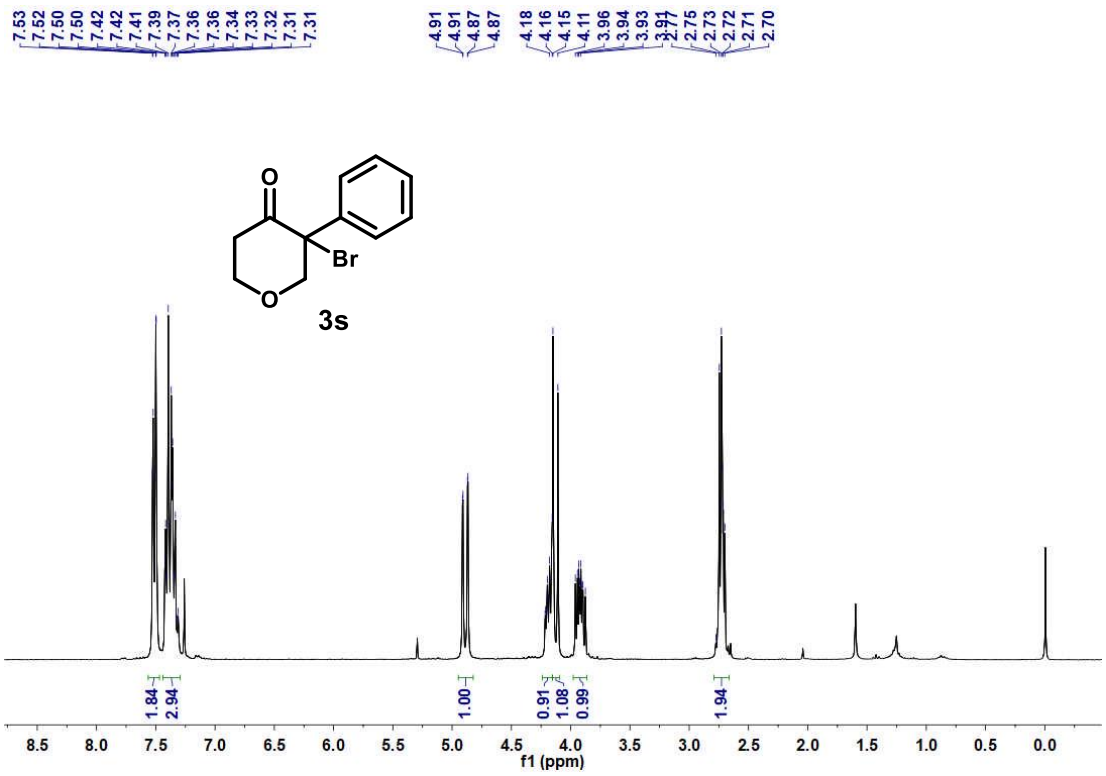
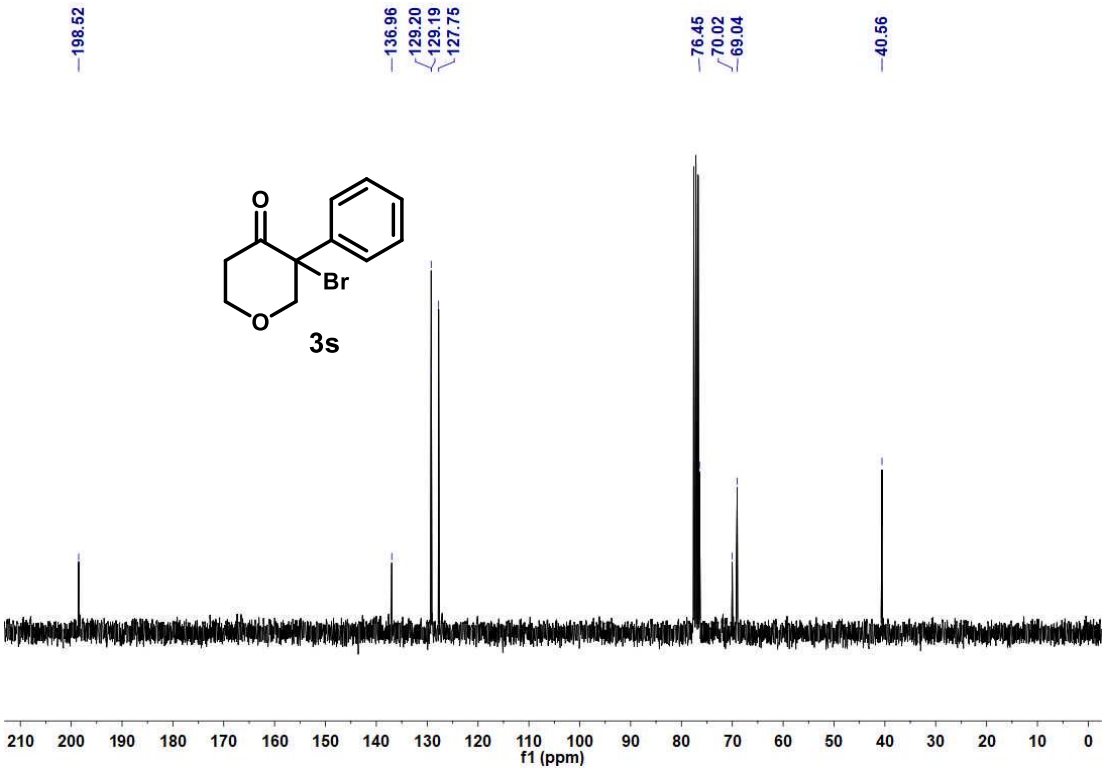
133.11
133.08
128.58
128.53
127.68
127.11
126.67
125.97
125.93
72.90
42.44
38.94
27.52
23.52
O
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

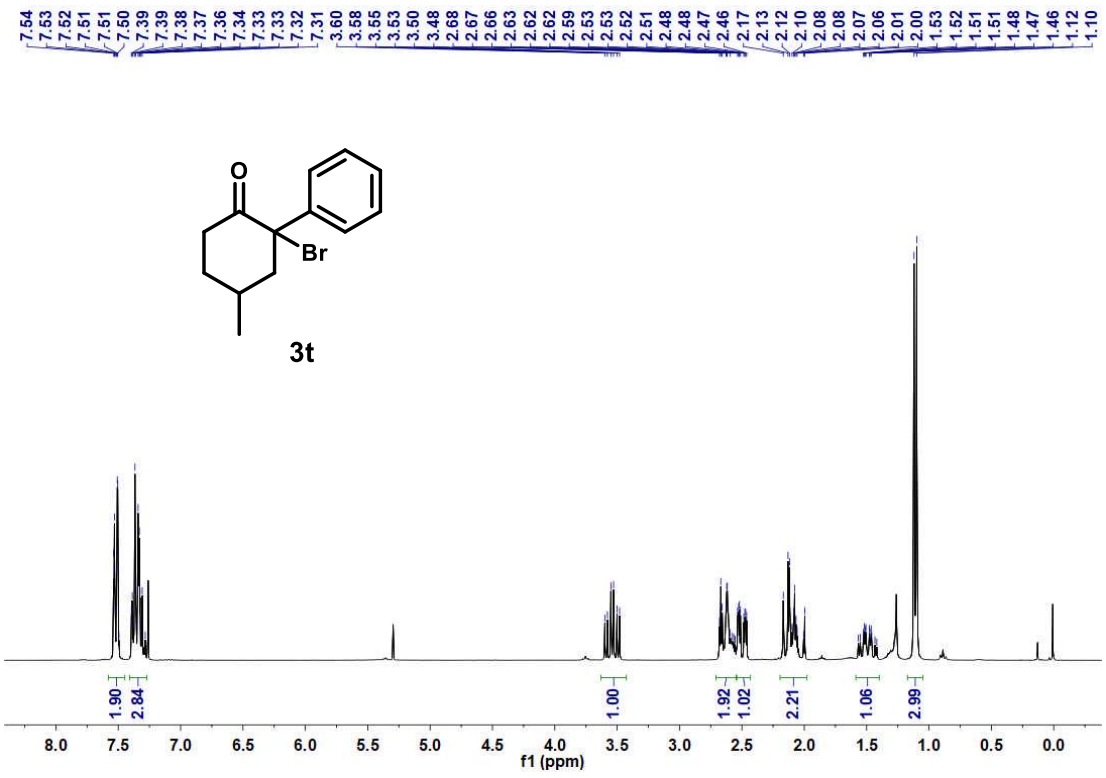
3o

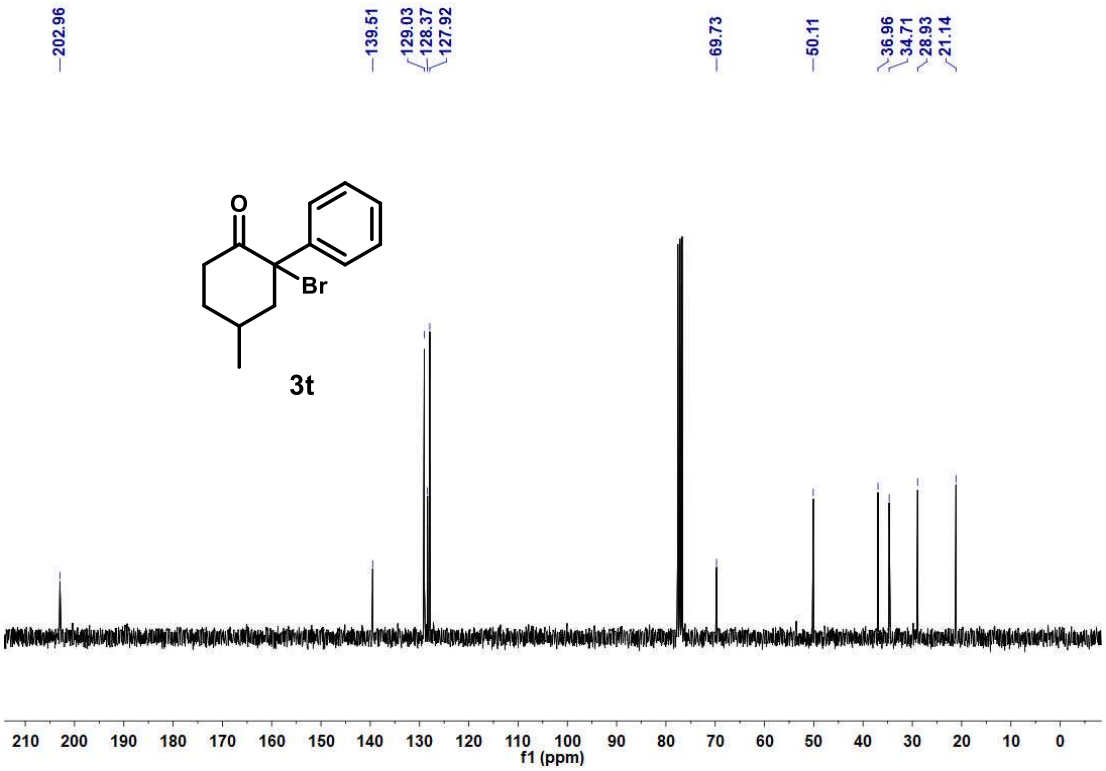

8.57 8.57 8.57 8.56 8.56 8.55 7.76 7.76 7.74 7.73 7.71 7.70 7.60 7.57 7.26 7.24 7.24 7.23 7.22 7.22 7.21 7.20 7.20 3.29 3.28 3.27 3.25 3.23 3.22 3.01 3.00 2.98 2.96 2.94 2.61 2.60 2.58 2.57 2.56 2.53 2.52 2.51 2.49 2.46 1.97 1.95 1.93 1.92 1.91 1.89 1.87 1.80 1.79 1.78 1.76 1.75
O
N
Br
3p
1.00 1.04 1.00 1.01 1.09 1.07 2.18 3.33 1.21
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

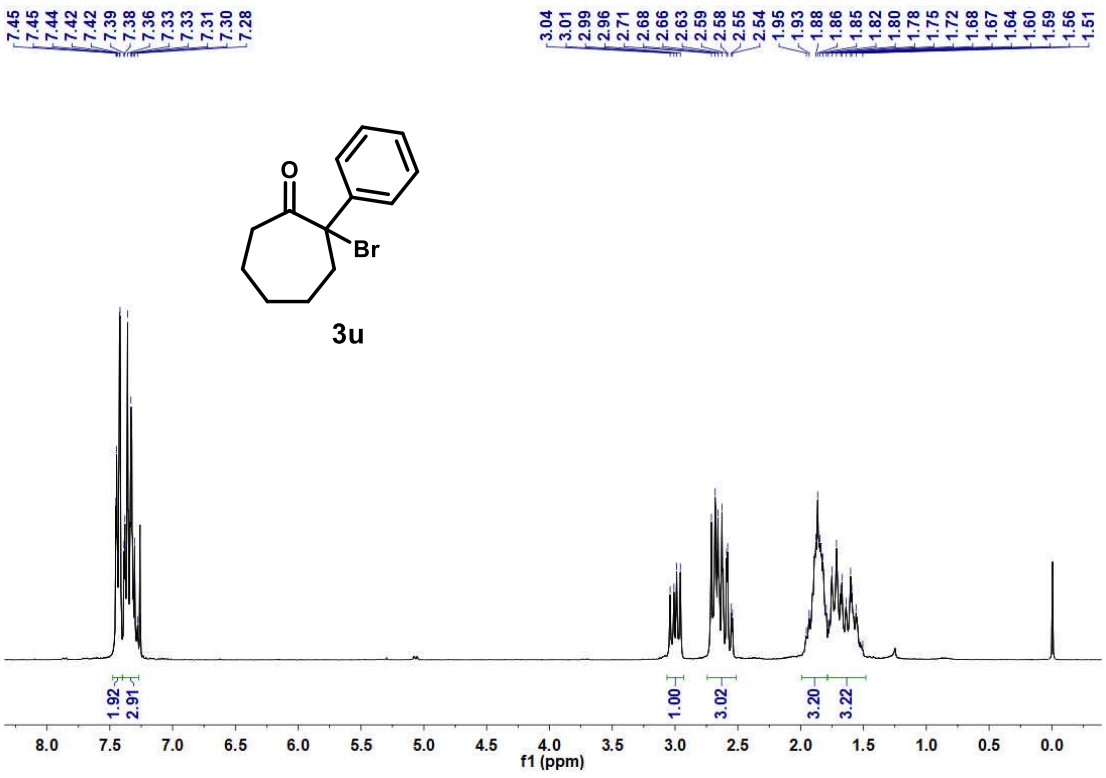

202.65 158.64 148.92 137.03 123.85 123.15 73.38 41.88 39.29 27.29 23.32
O
N
Br
3p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

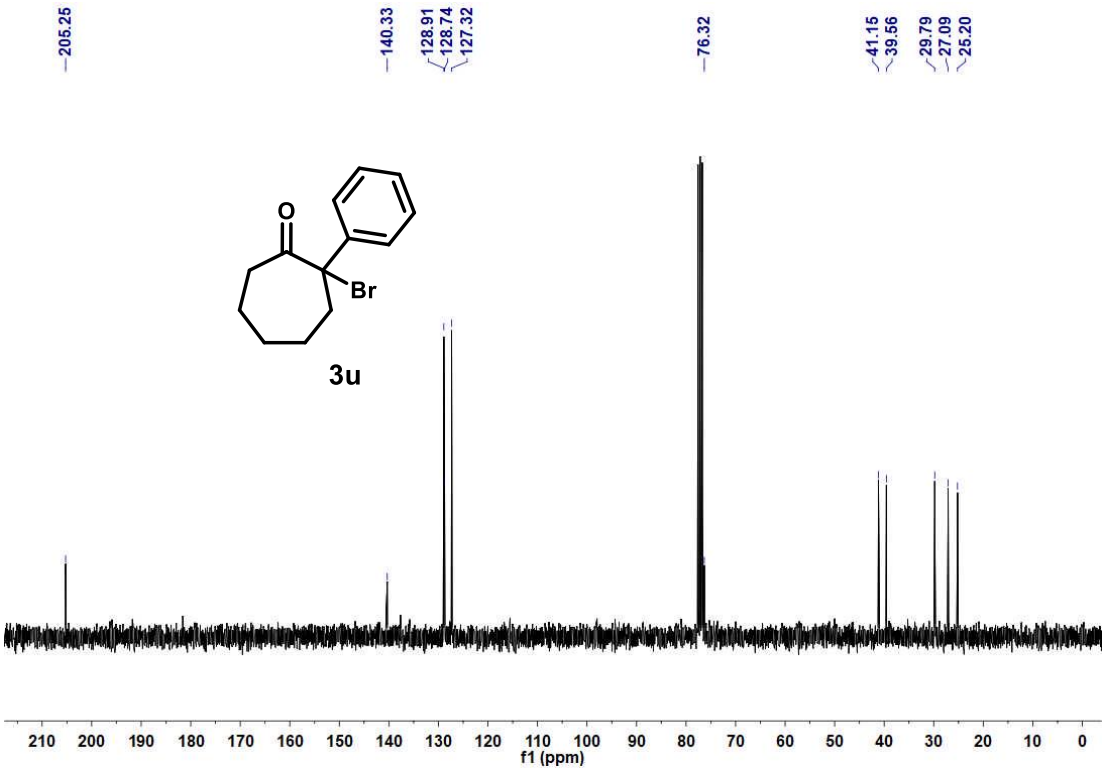

7.53
7.52
7.50
7.50
7.42
7.42
7.41
7.39
7.37
7.36
7.36
7.34
7.33
7.32
7.31
7.31
4.91
4.91
4.87
4.87
4.18
4.16
4.15
4.11
3.96
3.94
3.93
2.77
2.75
2.73
2.72
2.71
2.70
O
Br
O
3s
1.84
2.94
1.00
0.91
1.08
0.99
1.94
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.52
136.96
129.20
129.19
127.75
76.45
70.02
69.04
40.56
O
Br
O
3s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

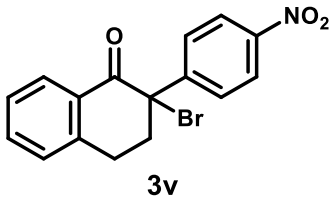

7.54 7.53 7.52 7.51 7.51 7.50 7.39 7.39 7.38 7.37 7.36 7.34 7.33 7.33 7.32 7.31 3.60 3.58 3.55 3.53 3.50 3.48 2.68 2.67 2.66 2.63 2.62 2.62 2.59 2.53 2.53 2.52 2.51 2.48 2.48 2.47 2.46 2.17 2.13 2.12 2.10 2.08 2.08 2.07 2.06 2.01 2.00 1.53 1.52 1.51 1.51 1.48 1.47 1.46 1.12 1.10
O
Br
3t
1.90
2.84
1.00
1.92
1.02
2.21
1.06
2.99
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


202.96
139.51
129.03
128.37
127.92
69.73
50.11
36.96
34.71
28.93
21.14
O
Br
3t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

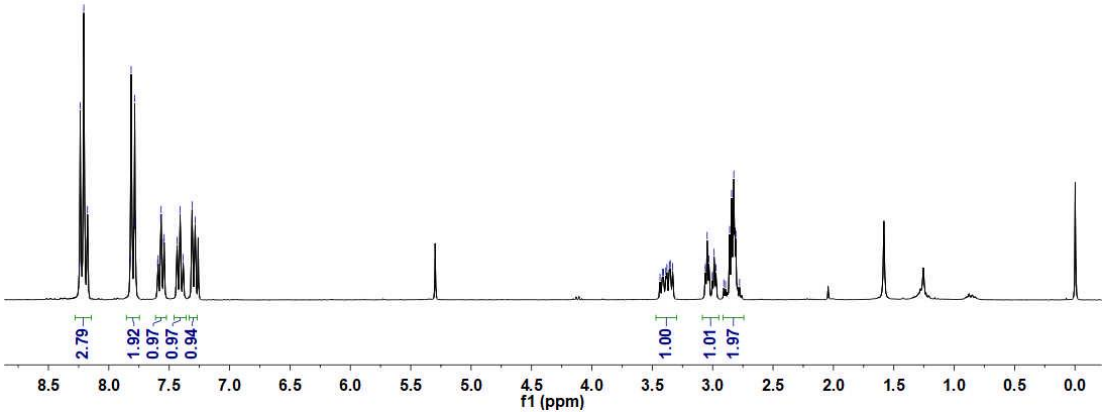

7.45
7.45
7.44
7.42
7.42
7.39
7.38
7.36
7.33
7.33
7.31
7.30
7.28
3.04
3.01
2.99
2.96
2.71
2.68
2.66
2.63
2.59
2.58
2.55
2.54
1.95
1.93
1.88
1.86
1.85
1.82
1.80
1.78
1.75
1.72
1.68
1.67
1.64
1.60
1.59
1.56
1.51
O
Br
3u
1.92
2.91
1.00
3.02
3.20
3.22
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

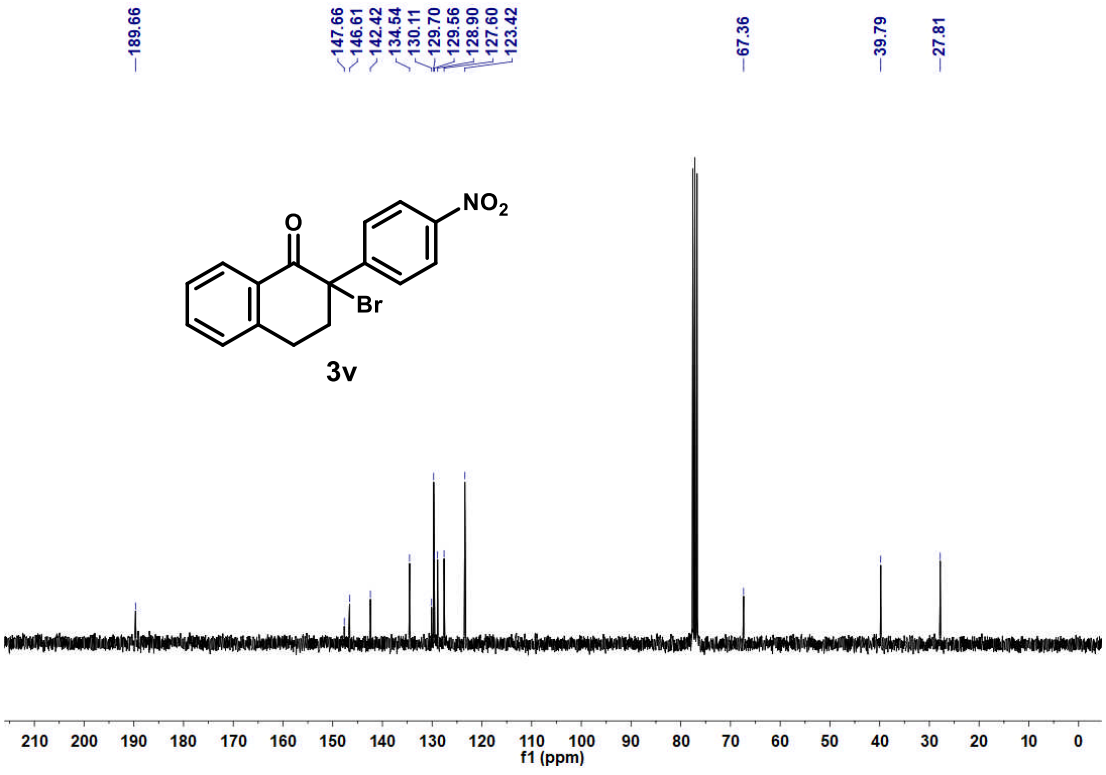

205.25
140.33
128.91
128.74
127.32
76.32
41.15
39.56
29.79
27.09
25.20
O
Br
3u
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.25
8.24
8.21
8.18
7.82
7.82
7.79
7.79
7.60
7.59
7.57
7.57
7.55
7.54
7.43
7.41
7.38
7.31
7.29
3.44
3.42
3.41
3.39
3.38
3.36
3.35
3.33
3.06
3.05
3.03
3.00
2.99
2.97
2.91
2.89
2.86
2.84
2.83
2.81
2.78

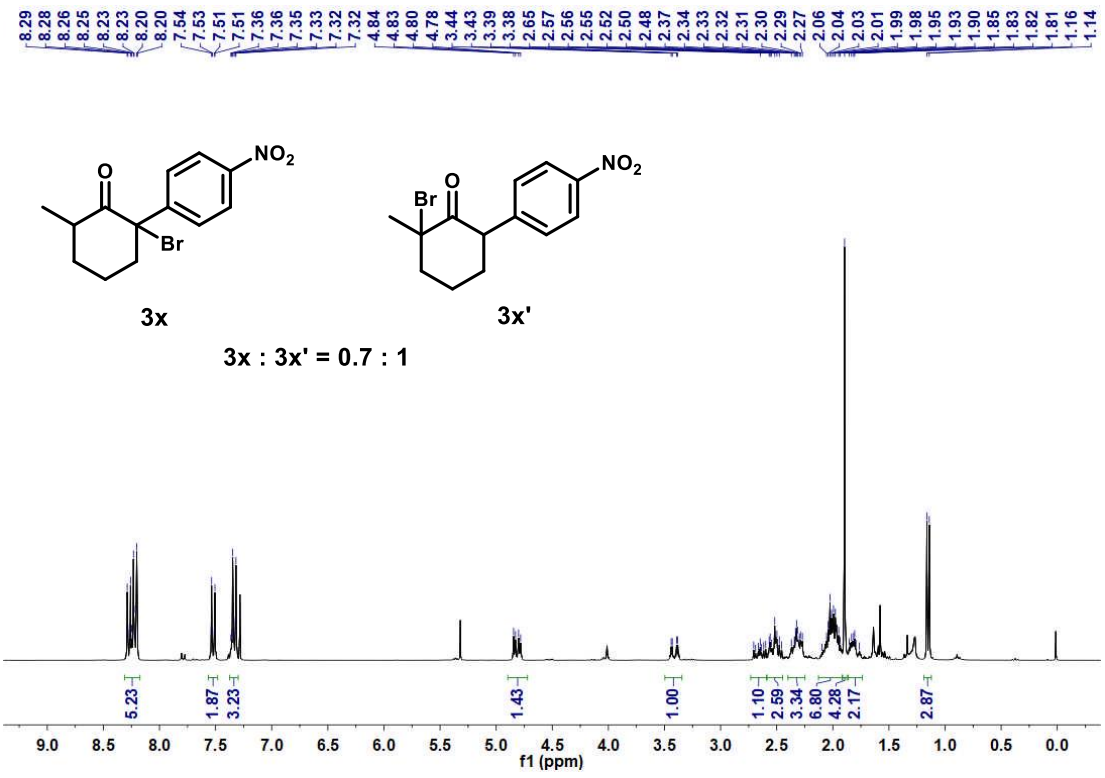

O
NO2
Br

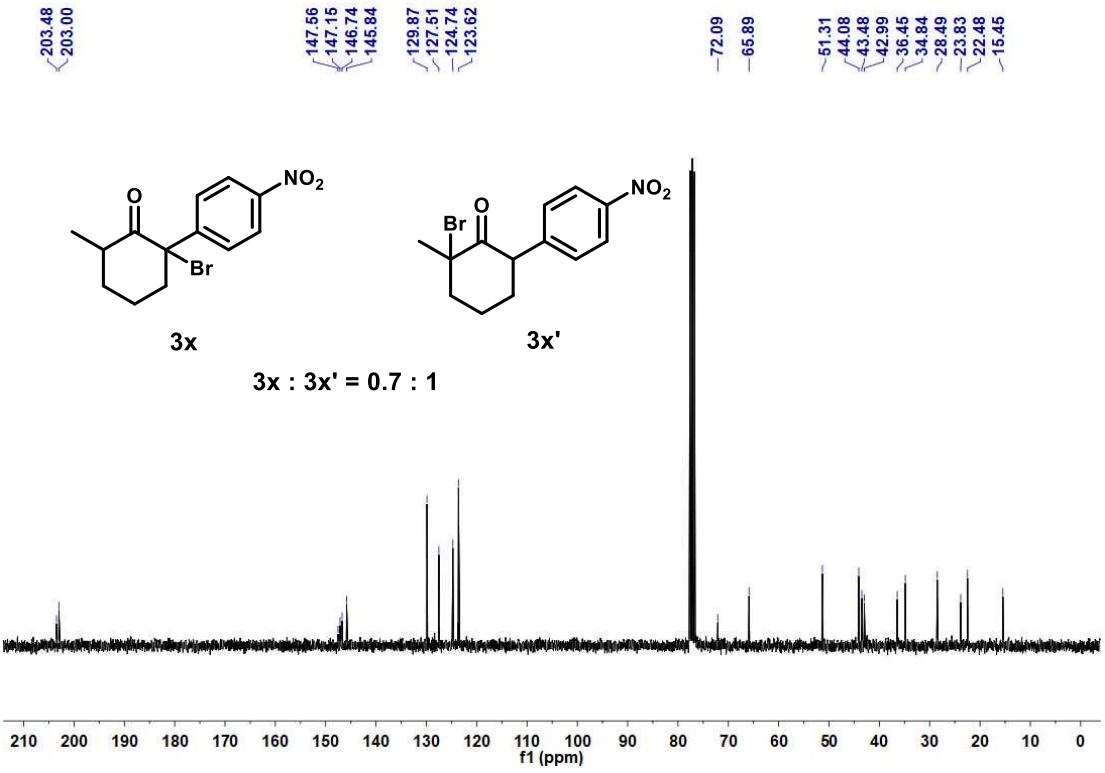
3v

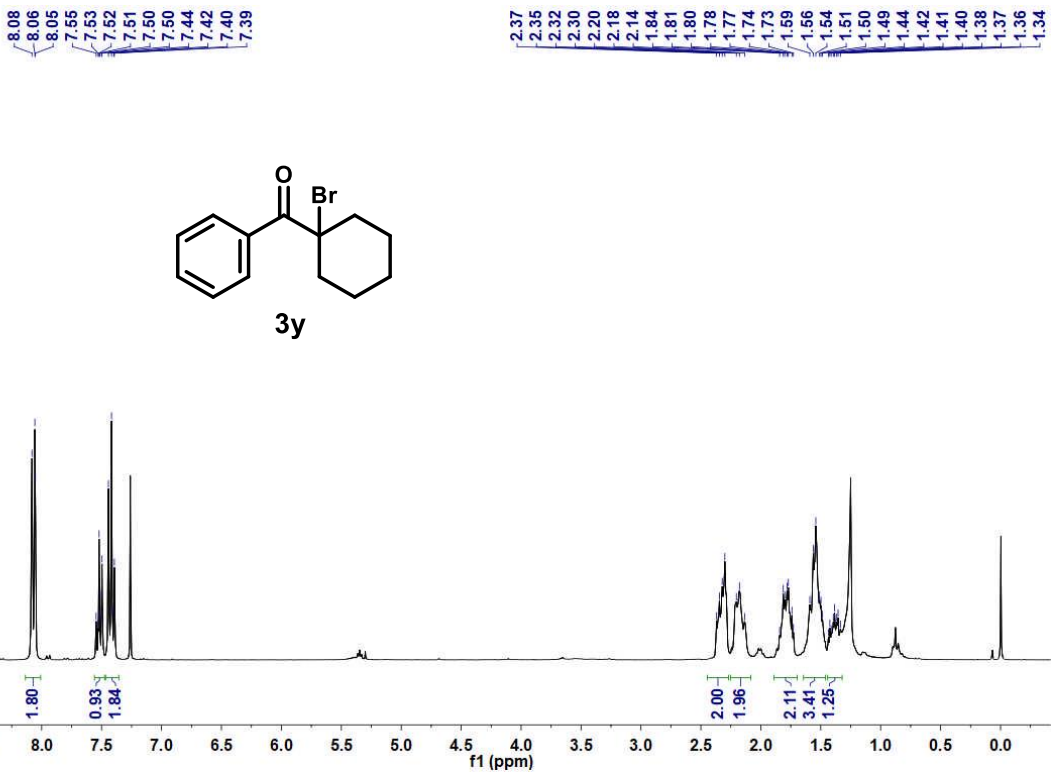

2.79
1.92
0.97
0.97
0.94
1.00
1.01
1.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

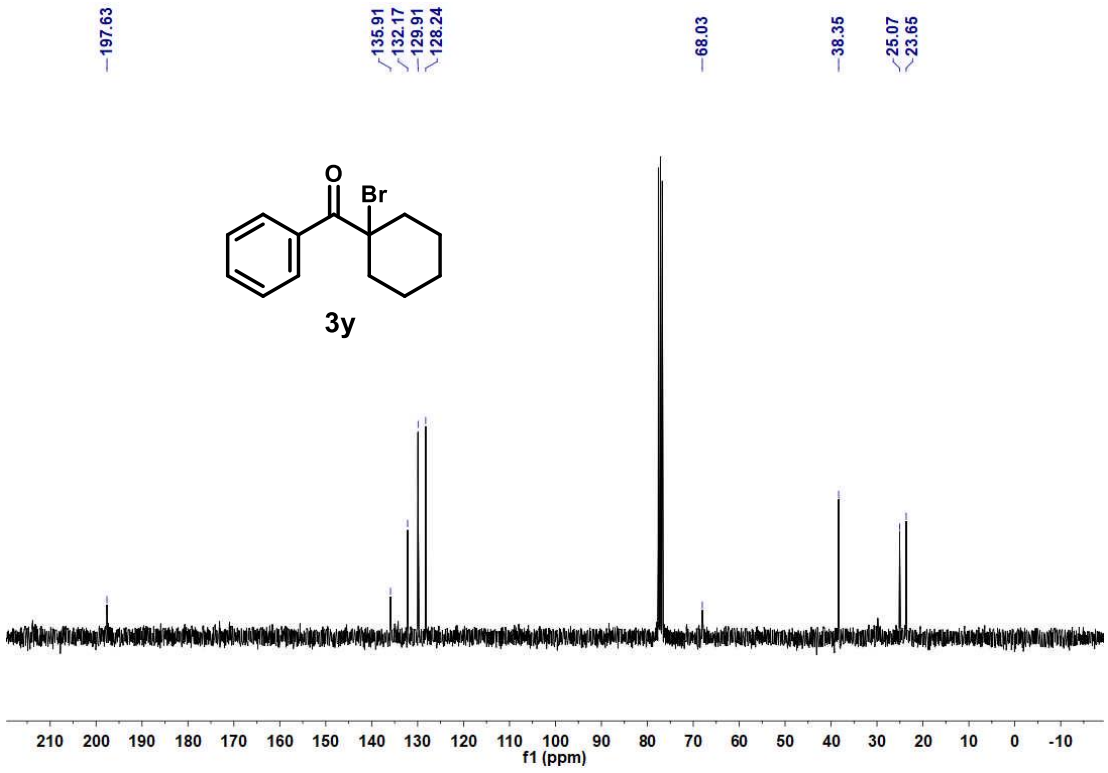

189.66
147.66
146.61
142.42
134.54
130.11
129.70
129.56
128.90
127.60
123.42
67.36
39.79
27.81
O
NO2
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

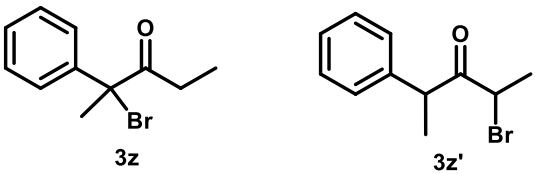
3v


8.29 8.28 8.26 8.25 8.23 8.23 8.20 8.20 7.54 7.53 7.51 7.51 7.36 7.36 7.35 7.33 7.32 7.32 4.84 4.83 4.80 4.78 3.44 3.43 3.39 3.38 2.65 2.57 2.56 2.55 2.52 2.50 2.48 2.37 2.34 2.33 2.32 2.31 2.30 2.29 2.27 2.06 2.04 2.03 2.01 1.99 1.98 1.95 1.93 1.90 1.85 1.83 1.82 1.81 1.16 1.14
NO2
O
Br
3x
3x'
3x : 3x' = 0.7 : 1
5.23 1.87 3.23 1.43 1.00 1.10 2.59 3.34 6.80 4.28 2.17 2.87
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

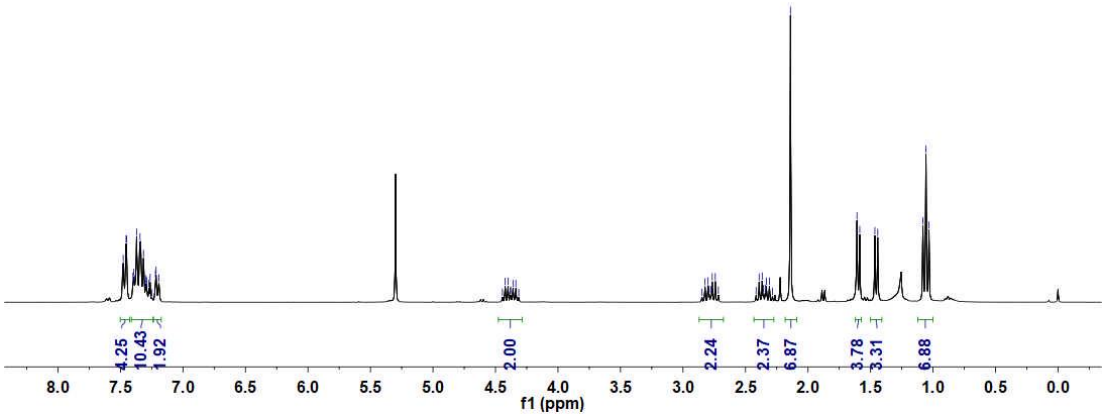

203.48 203.00 147.56 147.15 146.74 145.84 129.87 127.51 124.74 123.62 72.09 65.89 51.31 44.08 43.48 42.99 36.45 34.84 28.49 23.83 22.48 15.45
NO2
O
Br
3x
3x'
3x : 3x' = 0.7 : 1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

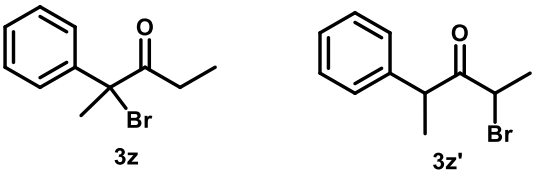

8.08
8.06
8.05
7.55
7.53
7.52
7.51
7.50
7.50
7.44
7.42
7.40
7.39
2.37
2.35
2.32
2.30
2.20
2.18
2.14
1.84
1.81
1.80
1.78
1.77
1.74
1.73
1.59
1.56
1.54
1.51
1.50
1.49
1.44
1.42
1.41
1.40
1.38
1.37
1.36
1.34
O
Br
3y
1.80
0.93
1.84
2.00
1.96
2.11
3.41
1.25
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


197.63
135.91
132.17
129.91
128.24
68.03
38.35
25.07
23.65
O
Br
3y
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)

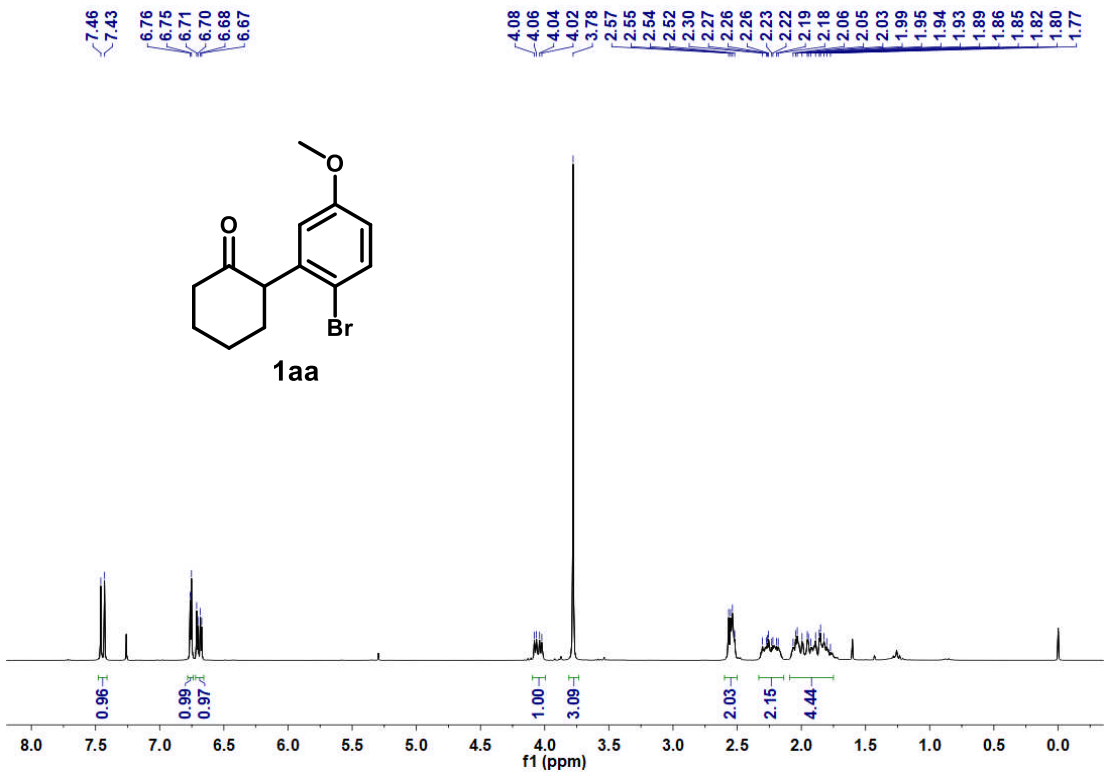


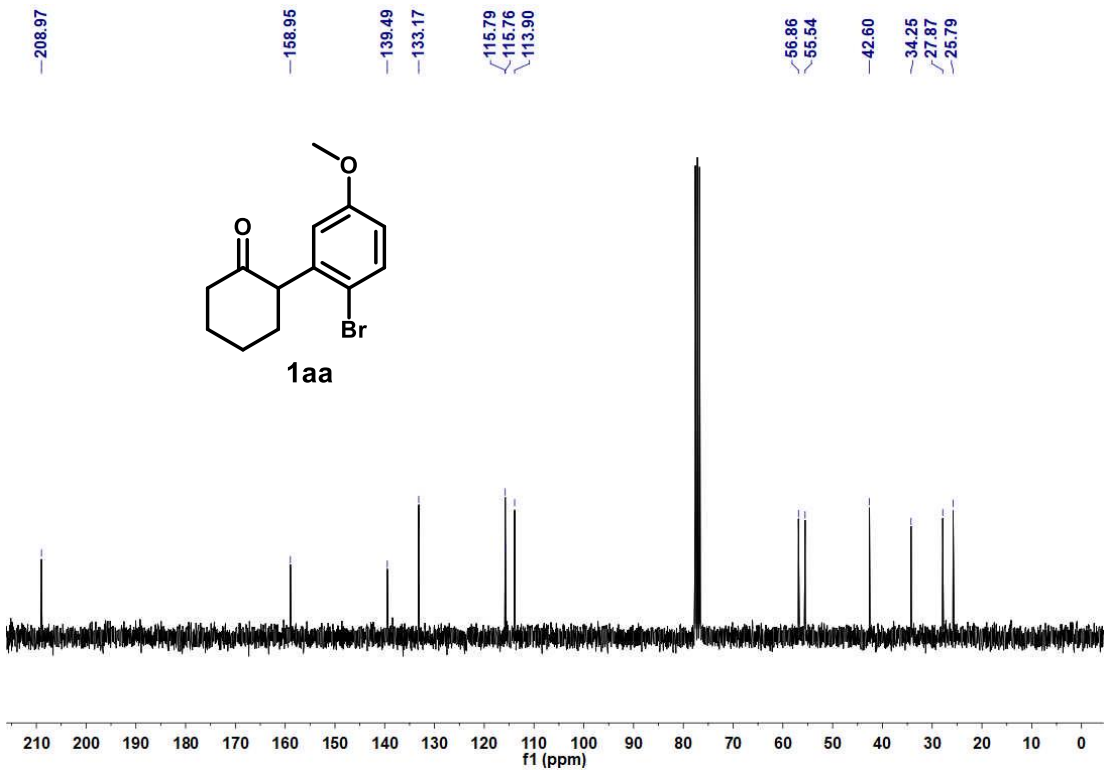
3z: 3z' = 2.3:1

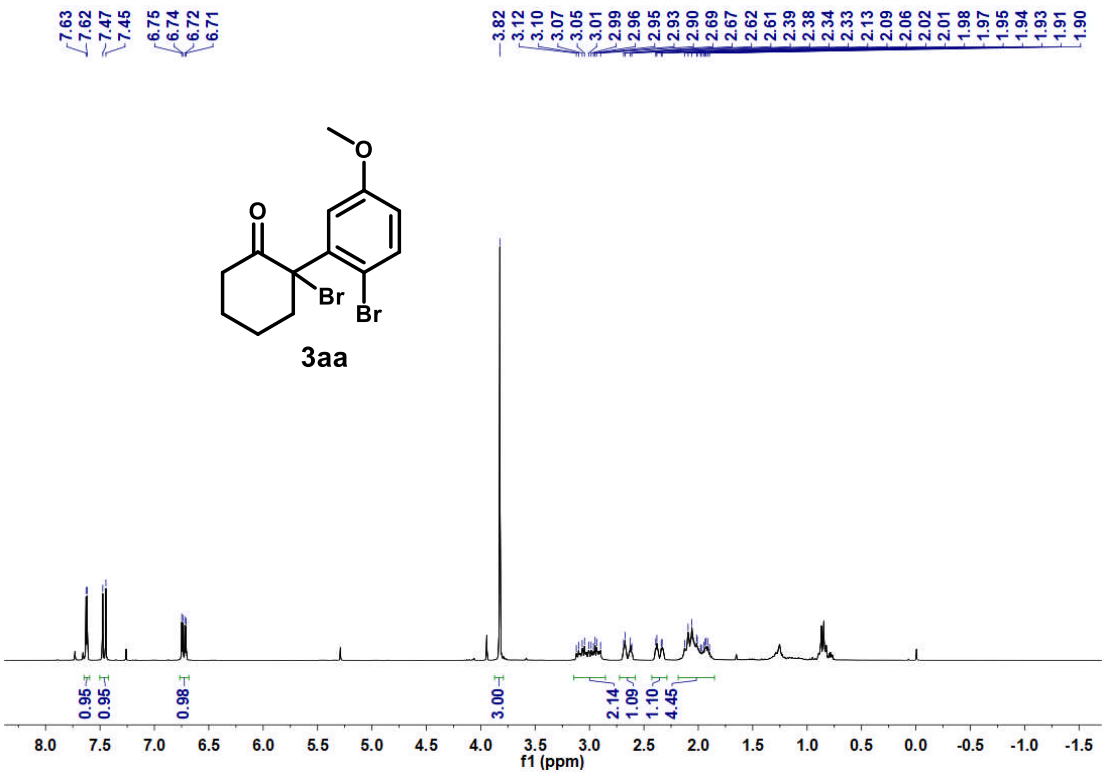


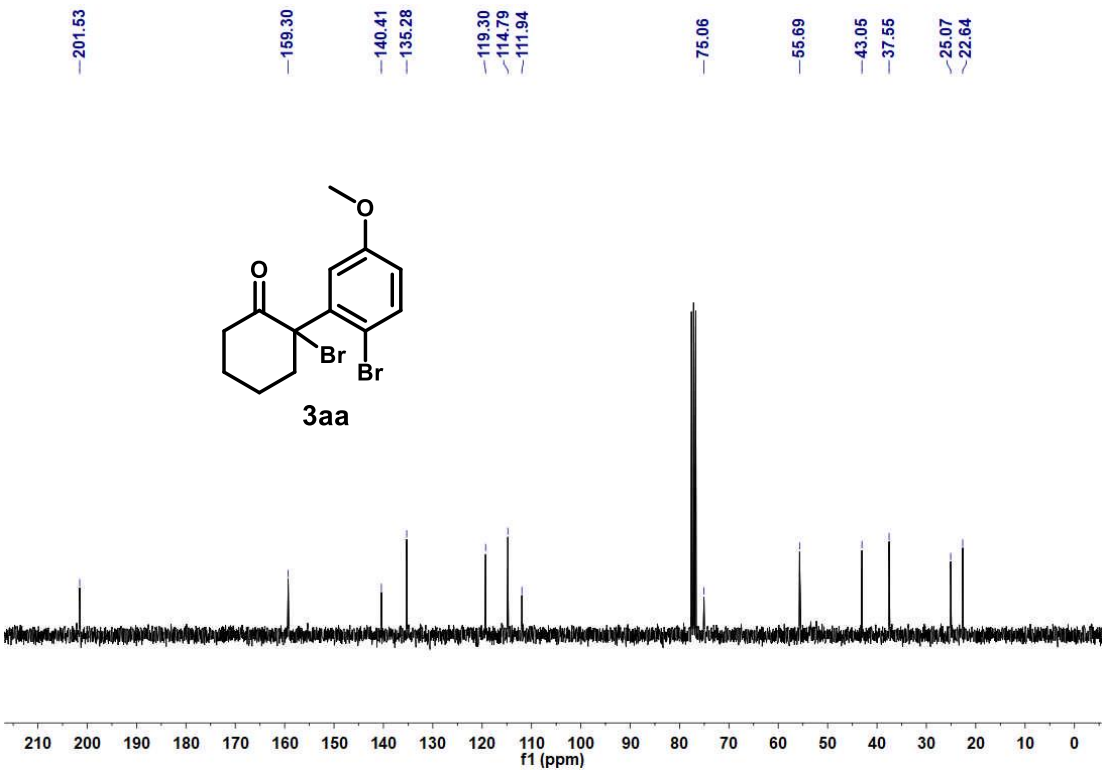


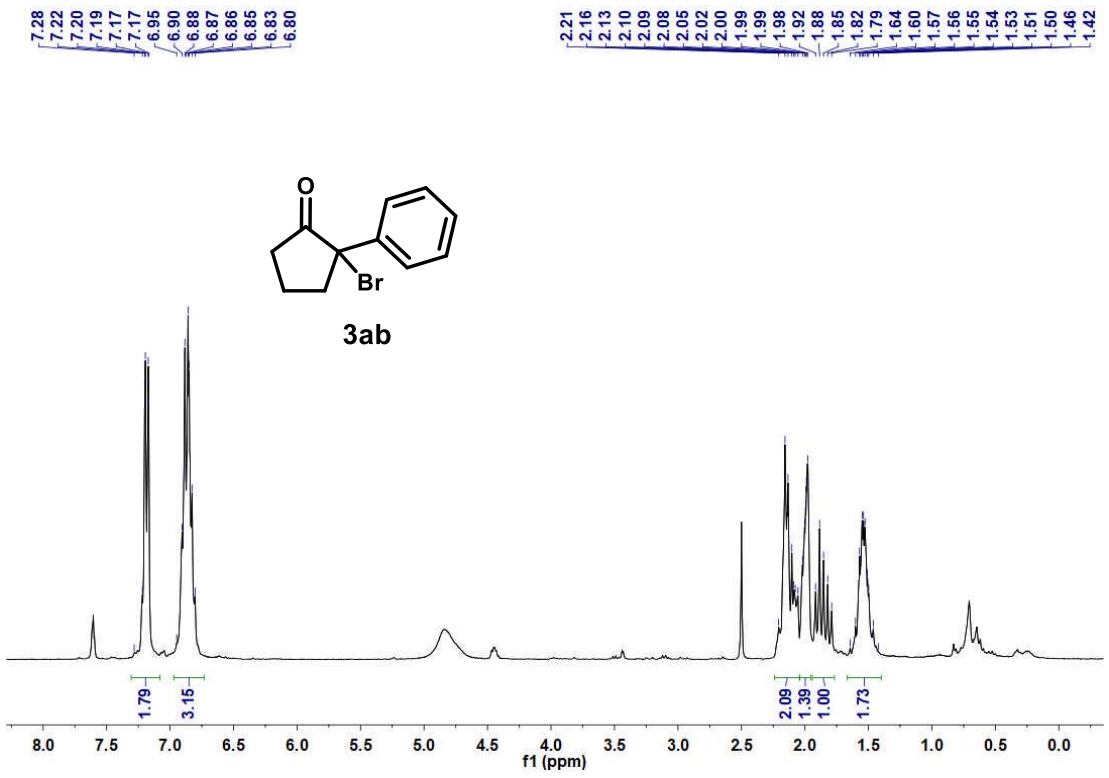
3z: 3z' = 2.3:1

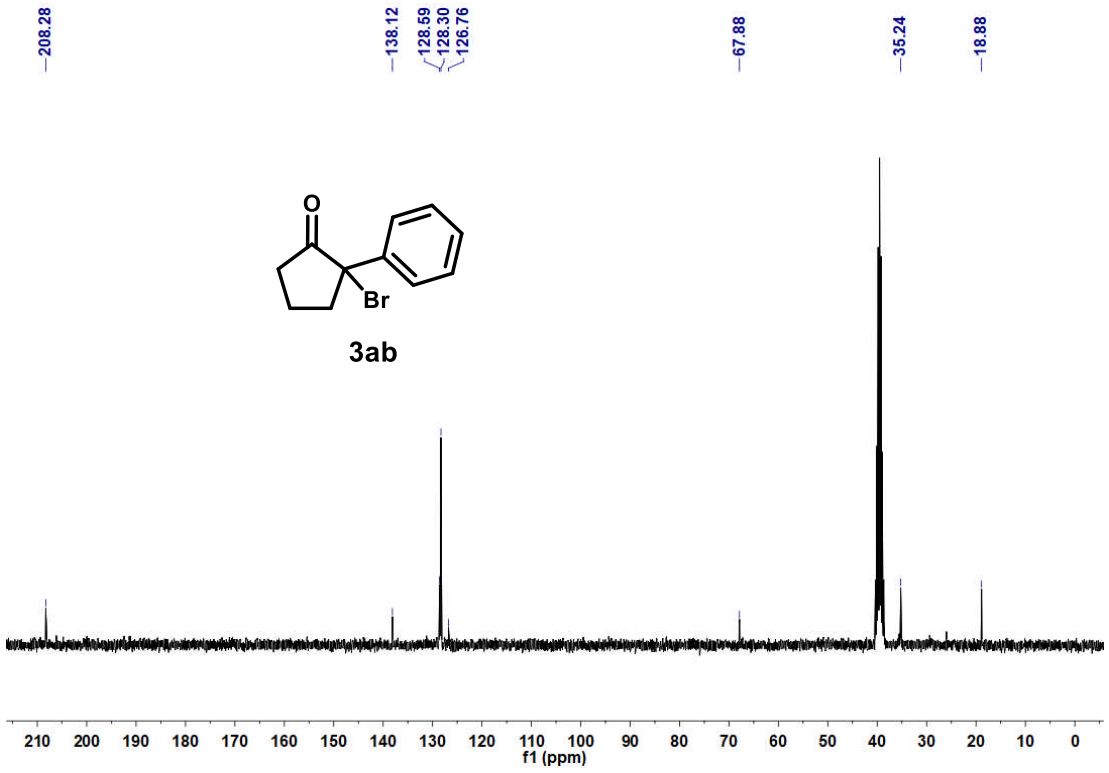

7.46
7.43
6.76
6.75
6.71
6.70
6.68
6.67
4.08
4.06
4.04
4.02
3.78
2.57
2.55
2.54
2.52
2.30
2.27
2.26
2.26
2.23
2.22
2.19
2.18
2.06
2.05
2.03
1.99
1.95
1.94
1.93
1.89
1.86
1.85
1.82
1.80
1.77
O
O
Br
1aa
0.96
0.99
0.97
1.00
3.09
2.03
2.15
4.44
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

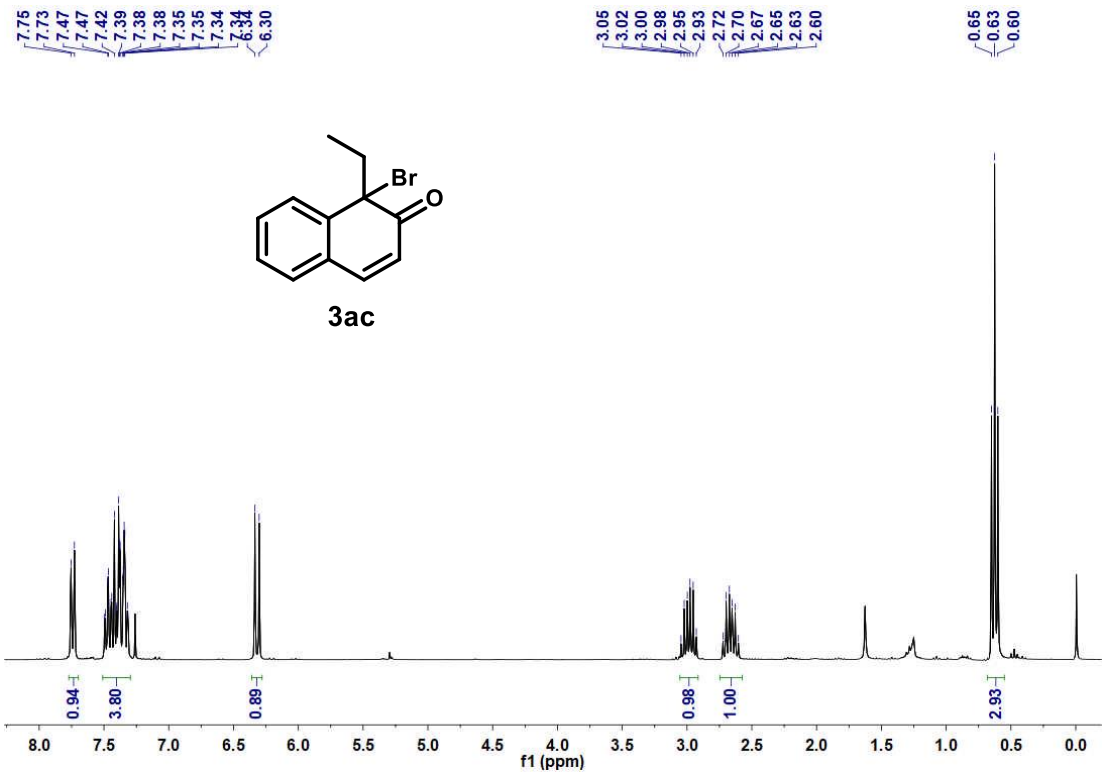

208.97
158.95
139.49
133.17
115.79
115.76
113.90
56.86
55.54
42.60
34.25
27.87
25.79
O
O
Br
1aa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

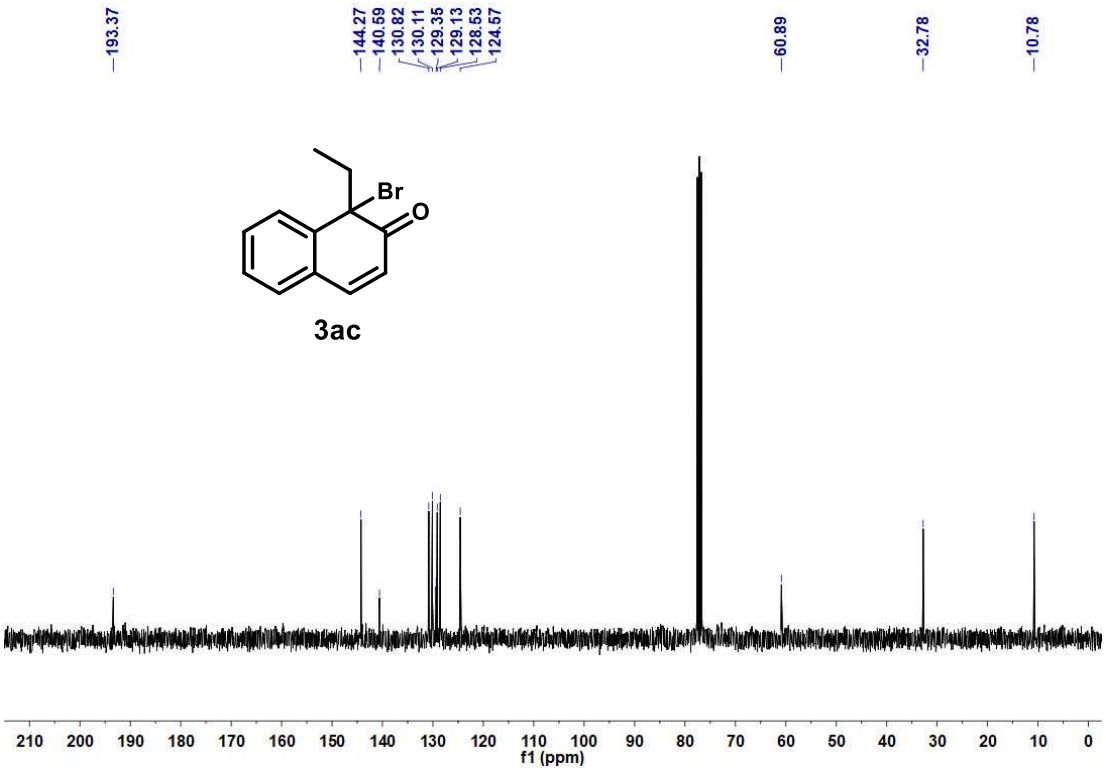

7.63
7.62
7.47
7.45
6.75
6.74
6.72
6.71
3.82
3.12
3.10
3.07
3.05
3.01
2.99
2.96
2.95
2.93
2.90
2.69
2.67
2.62
2.61
2.39
2.38
2.34
2.33
2.13
2.09
2.06
2.02
2.01
1.98
1.97
1.95
1.94
1.93
1.91
1.90
O
O
Br
Br
3aa
0.95
0.95
0.98
3.00
2.14
1.09
1.10
4.45
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

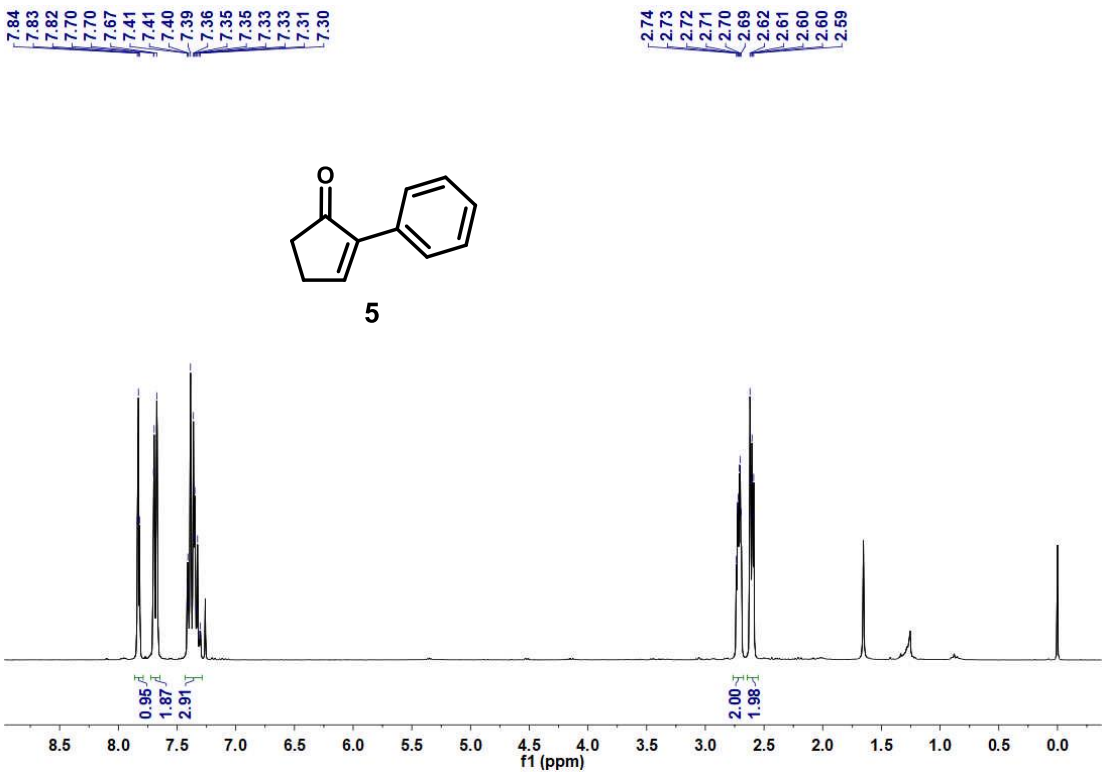

201.53
159.30
140.41
135.28
119.30
114.79
111.94
75.06
55.69
43.05
37.55
25.07
22.64
O
O
Br
Br
3aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

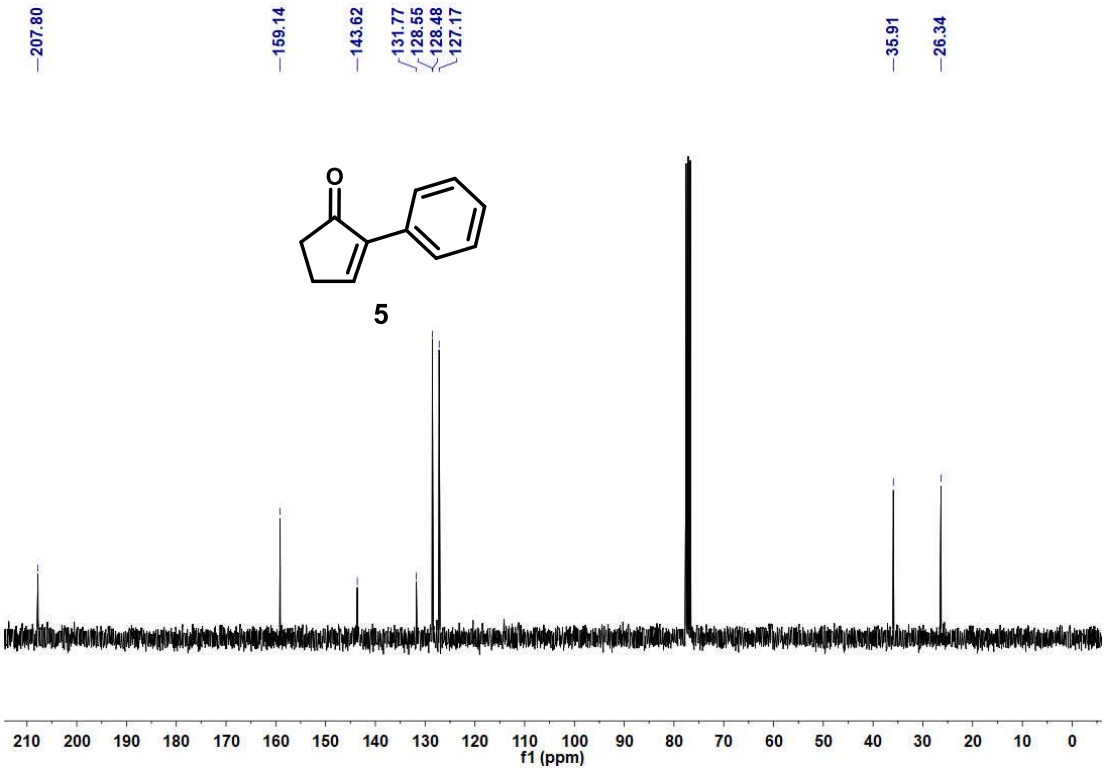

7.28
7.22
7.20
7.19
7.17
7.17
6.95
6.90
6.88
6.87
6.86
6.85
6.83
6.80
2.21
2.16
2.13
2.10
2.09
2.08
2.05
2.02
2.00
1.99
1.99
1.98
1.92
1.88
1.85
1.82
1.79
1.64
1.60
1.57
1.56
1.55
1.54
1.53
1.51
1.50
1.46
1.42
O
Br
3ab
1.79
3.15
2.09
1.39
1.00
1.73
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

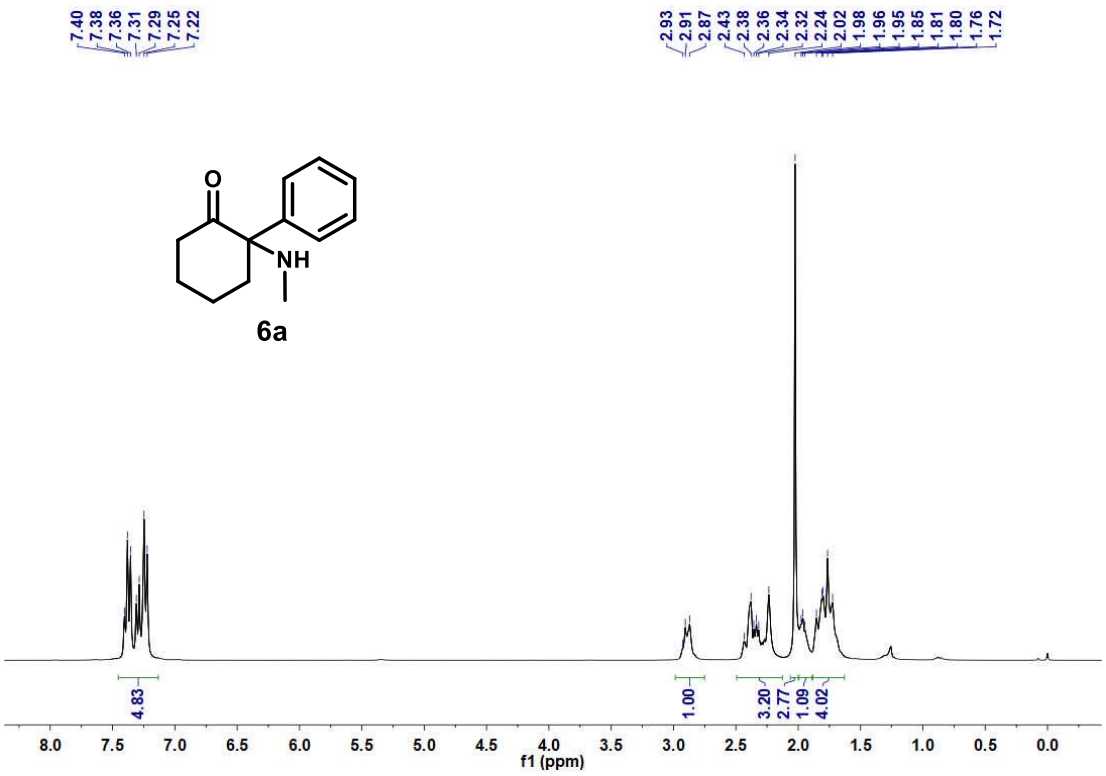

208.28
138.12
128.59
128.30
126.76
67.88
35.24
18.88
O
Br
3ab
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

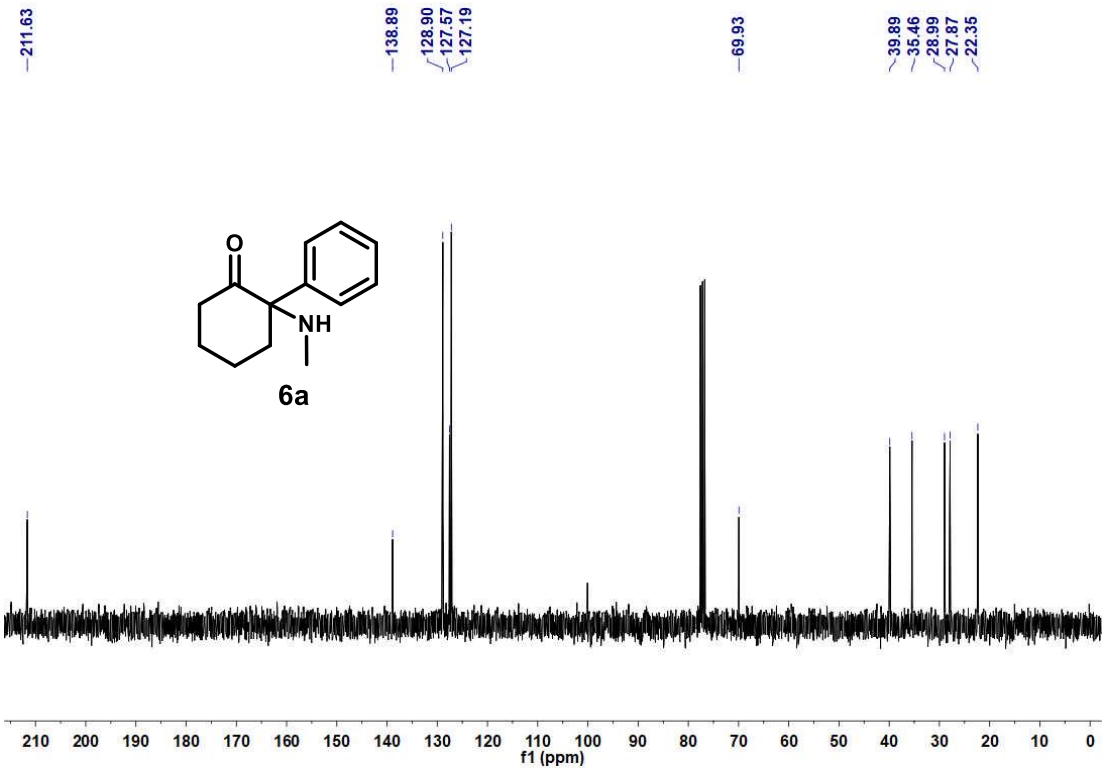

7.75
7.73
7.47
7.47
7.42
7.39
7.38
7.38
7.35
7.35
7.34
7.34
6.34
6.30
3.05
3.02
3.00
2.98
2.95
2.93
2.72
2.70
2.67
2.65
2.63
2.60
0.65
0.63
0.60
Br
O
3ac
0.94
3.80
0.89
0.98
1.00
2.93
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

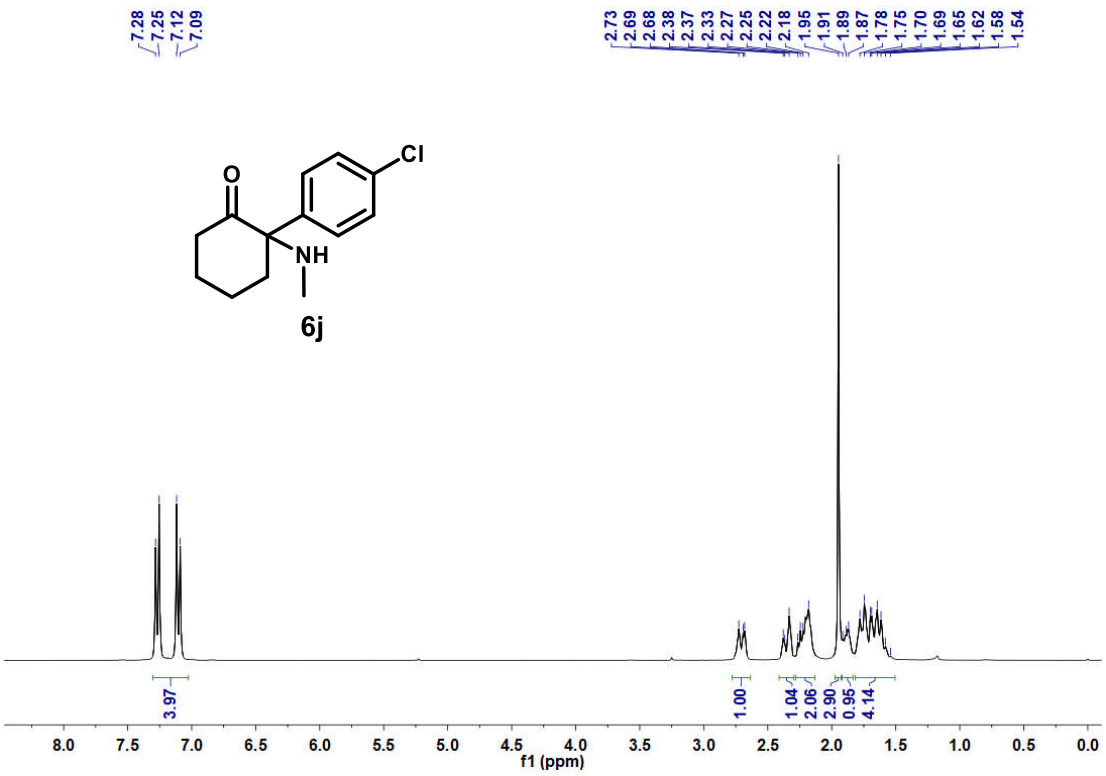

193.37
144.27
140.59
130.82
130.11
129.35
129.13
128.53
124.57
60.89
32.78
10.78
Br
O
3ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

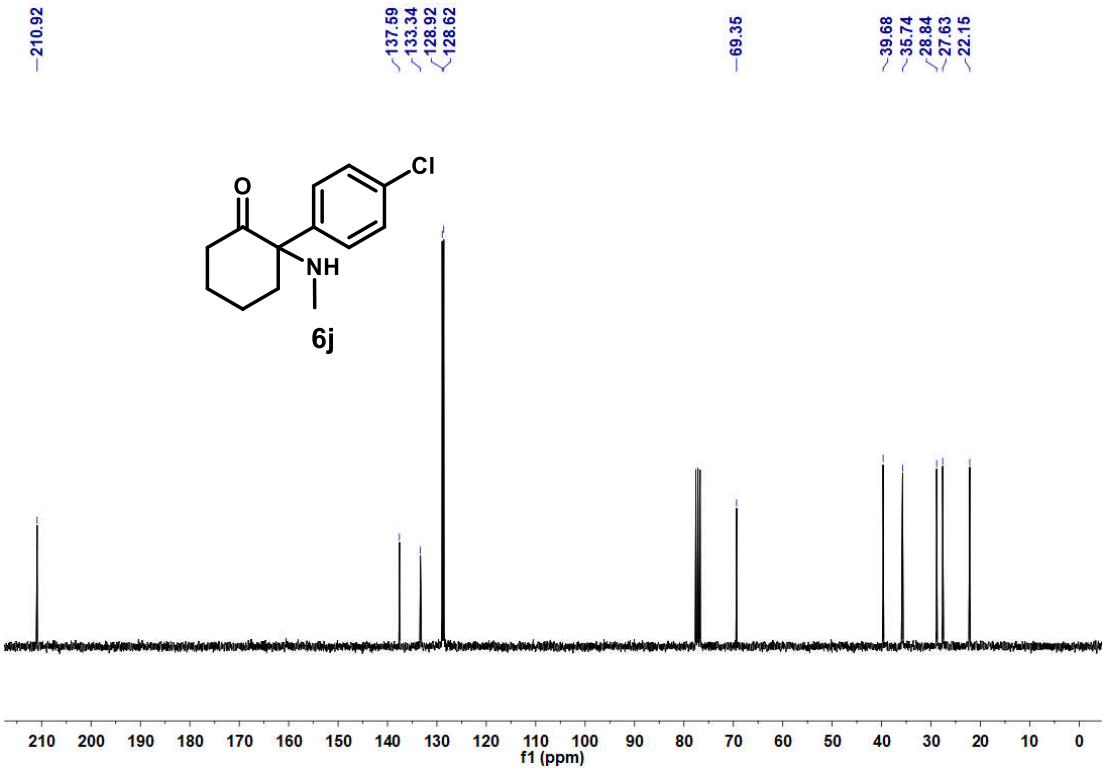

7.84
7.83
7.82
7.70
7.70
7.67
7.41
7.41
7.40
7.39
7.36
7.35
7.35
7.33
7.33
7.31
7.30
2.74
2.73
2.72
2.71
2.70
2.69
2.62
2.61
2.60
2.60
2.59
O
5
0.95
1.87
2.91
2.00
1.98
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


207.80
159.14
143.62
131.77
128.55
128.48
127.17
35.91
26.34
O
5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.40
7.38
7.36
7.31
7.29
7.25
7.22
2.93
2.91
2.87
2.43
2.38
2.36
2.34
2.32
2.24
2.02
1.98
1.96
1.95
1.85
1.81
1.80
1.76
1.72
O
NH
6a
4.83
1.00
3.20
2.77
1.09
4.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


211.63
138.89
128.90
127.57
127.19
69.93
39.89
35.46
28.99
27.87
22.35
O
NH
6a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.28
7.25
7.12
7.09
2.73
2.69
2.68
2.38
2.37
2.33
2.27
2.25
2.22
2.18
1.95
1.91
1.89
1.87
1.78
1.75
1.70
1.69
1.65
1.62
1.58
1.54
O
Cl
NH
6j
3.97
1.00
1.04
2.06
2.90
0.95
4.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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137.59
133.34
128.92
128.62
69.35
39.68
35.74
28.84
27.63
22.15
O
Cl
NH
6j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

7. Supplementary references

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