Electronic Supporting Information

Ligand-Redox Assisted Nickel Catalysis toward Stereoselective Synthesis of (n+1)-membered Cycloalkanes from 1,n-Diols with Methyl Ketones

Amreen K. Bains, Abhishek Kundu, Debabrata Maiti* and Debashis Adhikari*

Table of contents

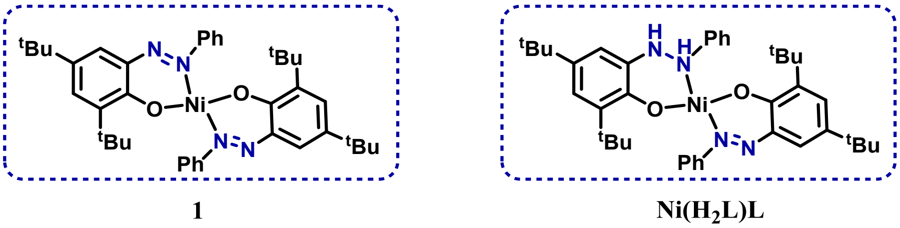
1. General Information

Reagent Information. All starting compounds employed in this study were procured from commercial suppliers. Potassium *tert*-butoxide, potassium hydroxide, potassium carbonate, sodium hydroxide, chalcone were purchased from Avra Synthesis Pvt. Ltd., India. 1,4-Butanediol; 1,5-pentanediol; 2,5-hexanediol; 3-methylpentane-1,5-diol and 1,6-hexanediol were purchased from TCI, India. These chemicals were used without further purification. Aryl ketones (**2a-2f**) were prepared according to reported procedures[S2-S6]. Glassware were dried overnight at 160 °C. Solvents such as acetonitrile, ethanol, and dichloromethane were used as received from the suppliers (Finar Chemicals). The solvent toluene was dried by heating over sodium with benzophenone as an indicator. For thin layer chromatography (TLC), aluminium foil coated with silica and fluorescent indicator @254 nm (from Merck) was used. Column chromatography was performed using SD Fine silica gel 60-120 mesh using a gradient of hexane and ethyl acetate or diethyl ether as mobile phase.

Analytical Information. All isolated compounds were characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, and HRMS. IR spectra were recorded on a Perkin–Elmer FTIR spectrometer as a KBr pellet. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker Biospin Advance III FT-NMR spectrometer. NMR shifts are reported as delta (δ) units in parts per million (ppm), and coupling constants (J) are reported in Hertz (Hz). Chemical shifts (δ) are quoted to the nearest 0.01 ppm relative to the residual protons in $CDCl_3$ (δ 7.26 ppm). Carbon chemical shifts are internally referenced to the deuterated solvent signals in $CDCl_3$ (δ 77.1 ppm). High-resolution mass spectra (HRMS) were recorded on a Waters QTOF mass spectrometer.

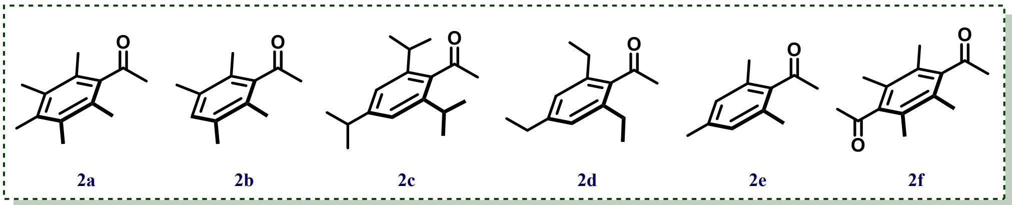
2. Experimental section

2.1. Preparation of 1, Ni(H_2L)L



The nickel complex **1, Ni(H_2L)L** was synthesized according to the reported literature[S1].

2.2. Synthesis of aryl ketone (2a-2f):



a) 1-(2,3,4,5,6-Pentamethylphenyl) ethan-1-one (2a), 1-(2,3,5,6-Tetramethylphenyl) ethan-1-one (2b), 1-(2,4,6-Triethylphenyl)ethan-1-one (2d), 1-Mesitylethan-1-one (2e) were prepared according to the following literature[S2-S4]. To a solution of pentamethylbenzene (741.2 mg, 5 mmol) or 1,2,4,5- tetramethylbenzene (671.1 mg, 5 mmol) or 1,3,5-triethylbenzene (811.3 mg, 5 mmol) or mesitylene (600.9 mg, 5 mmol) in DCM (50 mL), acetyl chloride (0.475 mL, 6 mmol) was added and cooled to 0 °C. Later, $AlCl_3$ (723.8 mg, 5.42 mmol) was added portion-wise over the course of 10 minutes. The resulting mixture was then warmed up to room temperature. The reaction mixture was stirred for 4 h. After completion of the reaction (checked via TLC), crushed ice was added to the reaction mixture. The final product was extracted with dichloromethane (50 mL × 3 times) and dried over sodium sulphate. The pure products **2a**, **2b, 2d,** or **2e** were obtained through flash column chromatographic (hexane/ethyl acetate, 100:5) separation. Yield of the products; **2a** (855 mg, 90%), **2b** (740 mg, 84%), **2d** (867 mg, 85%), **2e** (714 mg, 88%).

b) 1-(2,4,6-Triisopropylphenyl) ethan-1-one (2c): was prepared according to the reported procedure in literature[S5]. A 100 mL round bottom flask was charged with 2,4,6-triisopropylbenzene (1.02 g, 5 mmol) in 50 mL of CS_2, and acetyl chloride (0.475 mL, 6 mmol) was added to it, after which the mixture was cooled to 0 °C. Later, $AlCl_3$ (723.8 mg, 5.42 mmol) was added portion-wise over the course of 10 minutes. The reaction mixture was stirred and refluxed for 16 h. After completion of the reaction (checked via TLC), crushed ice was added to the reaction mixture. The final product was extracted with dichloromethane (50 mL × 3 times) and dried over sodium sulphate. The pure product was obtained after flash column chromatography (hexane/ethyl acetate, 100:5) to afford the title compound **2c** (1 g, 86%) as a white solid.

c) 1,1'-(2,3,5,6-Tetramethyl-1,4-phenylene) bis(ethan-1-one) (2f): was prepared according to the reported procedure in literature[S6]. A 100 mL round bottom flask was charged with 1,2,4,5- tetramethylbenzene (335.5 mg, 2.5 mmol) in 50 mL of CS_2, acetyl chloride (0.475 mL, 6 mmol) was added to it after which the mixture was cooled to 0 °C. Later, $AlCl_3$ (723.8 mg, 5.42 mmol) was added portion-wise over the course of 10 minutes. The resulting mixture was refluxed for 16 h. After completion of the reaction (checked via TLC), crushed ice was added to the reaction mixture. The final product was extracted with dichloromethane (50 mL × 3 times) and dried over sodium sulphate. The pure product was obtained after flash column chromatography (hexane/ethyl acetate, 100:5) to afford the title compound **2f** (474 mg, 87%) as a white solid.

2.3. Synthesis of diols:

General reduction procedure: A 100 mL Schleck flask was charged with 1,n-dicarboxylic acids (10 mmol). To it, 60 mL of THF was added. The flask was cooled down to 0 °C. Next, 30 mmol of $LiAlH_4$ was added portion-wise with vigorous evolution of hydrogen. After the complete evolution of hydrogen, the flask was warmed to room temperature. The mixture was heated to refluxed for 16 h and then cooled to room temperature. A solution of 15% aqueous NaOH (20 mL) was added. The solution was stirred for 1 hour and extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$. Purification had been done by column chromatography on silica gel with hexane: ethyl acetate (1:1) as eluent.

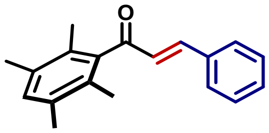
1) **2, 2-Dimethyl pentane-1,5-diol:** 3,3-Dimethyldihydro-2H-pyran-2,6(3*H*)-dione (1.42 g, 10 mmol), $LiAlH_4$ (1.12 g, 30 mmol) and THF (60 mL) were subjected to general reduction procedure. Yield (1.06 g, 81%).
2) **3,3-Dimethyl pentane-1,5-diol:** 3,3-Dimethylpentanedioic acid (1.6 g, 10 mmol), $LiAlH_4$ (1.12 g, 30 mmol) and THF (60 mL) were subjected to general reduction procedure. Yield (1.04 g, 79 %).
3) **1,1-Cyclohexanediethanol:** 1,1-Cyclohexanediacetic acid (2 g, 10 mmol), $LiAlH_4$ (1.12 g, 30 mmol) and THF (60 mL) were subjected to general reduction procedure. Yield (1.42 g, 83%).
4) **((1S,3R)-1,2,2-Trimethylcyclopentane-1,3-diyl)dimethanol:** Camphoric acid (2 g, 10 mmol), $LiAlH_4$ (1.12 g, 30 mmol) and THF (60 mL) were subjected to general reduction procedure. Yield (1.2 g, 70%).
5) **Pentane-1,4-diol:** 5-Methyldihydrofuran-2(3H)-one (1 g, 10 mmol), $LiAlH_4$ (1.12 g, 30 mmol) and THF (60 mL) were subjected to general reduction procedure. (681 mg, 65%).
6) **3-(*p*-Tolyl)pentane-1,5-diol:**[S16] A mixture of 4-methyl benzaldehyde (20.0 mmol), ethyl acetoacetate (40.0 mmol), and piperidine (2.8 mmol) was stirred at room temperature for 3 days. A yellow solid started forming over time. After which, EtOH (5 mL) was added to the mixture, heated to reflux for 3 hours, and cooled. The resulting precipitate was collected and washed with Et_2O (4 x 50 mL). The dried solid was dissolved in EtOH (80 mL) and then aq. NaOH (50% w/v) was then added. The resulting mixture was heated to reflux for 1 hr and then cooled to room temperature. The solution was diluted and acidified to pH 1 using conc. HCl. The resulting mixture was extracted three times with EtOAc. The combined organics were dried (Na_2SO_4) and concentrated *in-vacuo*. Diacid was obtained as a pure product in (930 mg, 21 %) yield. Diacid (10 mmol), $LiAlH_4$ (30 mmol) and THF (60 mL) were subjected to general reduction procedure. Yield (1.3 g, 69 %).
7) **3-(4-Methoxyphenyl)pentane-1,5-diol:**[S8] A mixture of 4-methoxy benzaldehyde (20.0 mmol), ethyl acetoacetate (40.0 mmol), and piperidine (2.8 mmol) was stirred at room temperature for 3 days. A yellow solid started forming over time. After which, EtOH (5 mL) was added to the mixture, heated to reflux for 3 hours, and cooled. The resulting precipitate was collected and washed with Et_2O (4 x 50 mL). The dried solid was dissolved in EtOH (80 mL) and then aq. NaOH (50%

w/v) was then added. The resulting mixture was heated to reflux for 1 hr and then cooled to room temperature. The solution was diluted and acidified to pH 1 using conc. HCl. The resulting mixture was extracted three times with EtOAc. The combined organics were dried (Na_2SO_4) and concentrated *in-vacuo.* Diacid was obtained as a pure product in (1.5 g, 32 %) yield. Diacid (10 mmol), $LiAlH_4$ (30 mmol) and THF (60 mL) were subjected to general reduction procedure. Yield (1.5 g, 74 %).

8) **3-(3-Bromophenyl)pentane-1,5-diol:**[S15] A mixture of 3-bromo benzaldehyde (20.0 mmol), ethyl acetoacetate (40.0 mmol), and piperidine (2.8 mmol) was stirred at room temperature for 3 days. A yellow solid started forming over time. After which, EtOH (5 mL) was added to the mixture, heated to reflux for 3 hours, and cooled. The resulting precipitate was collected and washed with Et_2O (4 x 50 mL). The dried solid was dissolved in EtOH (80 mL) and then aq. NaOH (50% w/v) was then added. The resulting mixture was heated to reflux for one h and then cooled to room temperature. The solution was diluted and acidified to pH 1 using conc. HCl. The resulting mixture was extracted three times with EtOAc. The combined organics were dried (Na_2SO_4) and concentrated *in-vacuo*. Diacid was obtained as a pure product in (1.5 g, 26 %) yield. Diacid (10 mmol), $LiAlH_4$ (30 mmol) and THF (60 mL) were subjected to general reduction procedure. Yield (1.8 g, 71 %).

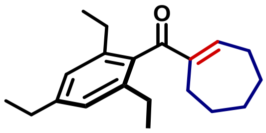
2.4. Synthesis of 3-phenyl-1-(2,3,5,6-tetramethylphenyl) prop-2-en-1-one (5a): To a solution of NaOH (1 mmol) in H_2O (3 mL), ethanolic solution of 1-(2,3,5,6-tetramethylphenyl) ethan-1-one (1mmol, **2b**) was added at 0 °C. To it, benzaldehyde (1 mmol) was introduced drop-wise. The mixture was then allowed to warm to room temperature and stirred for 2 h after which a precipitate of the product formed. Finally, the obtained product was filtered and recrystallized using ethanol. The desired product 3-phenyl-1-(2,3,5,6-tetramethylphenyl) prop-2-en-1-one **(5a)** is fully characterized by ^1H, ^{13}C NMR spectroscopies.

3-Phenyl-1-(2,3,5,6-tetramethylphenyl) prop-2-en-1-one (5a):



White solid (222 mg, 84%), ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.51 (m, 2H), 7.41 – 7.37 (m, 3H), 7.17 (d, J = 16.3 Hz, 1H), 7.03 – 6.94 (m, 2H), 2.25 (s, 6H), 2.08 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 147.0, 140.2, 134.5, 134.3, 131.8, 130.9, 129.7, 129.0, 128.7, 19.6, 16.3 ppm; IR (KBr pellet): 2914, 2831, 1683, 1610, 1310, 1149, 1030, 914, 782, 634 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{20}O$ 265.1592; Found 265.1581.

Cycloheptyl-(2,4,6-triethylphenyl) methanone (8a): was isolated as a minor product during column separation of **4cc** and was accumulated to a sizable amount after multiple batches of reaction.

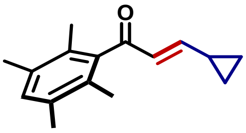


Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 2H), 6.18 (d, J = 1.7 Hz, 1H), 2.66- 2.60 (m, 2H), 2.41 – 2.34 (m, 6H), 1.72 – 1.69 (m, 2H), 1.49 – 1.46 (m, 2H), 1.26-1.23 (m, 3H), 1.14-1.10 (m, 5H), 0.99 (s, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9, 154.5, 144.5, 140.4, 138.8, 136.5, 125.3, 36.7, 33.1, 28.9, 26.2, 22.8, 19.2, 15.7, 15.55 ppm; IR (KBr pellet): 3018, 2987, 2786,1702, 1503, 1293, 1023, 923, 765 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{28}O$ 285.2218; Found 285.2205.

2.5. Synthesis of radical-probe substrate

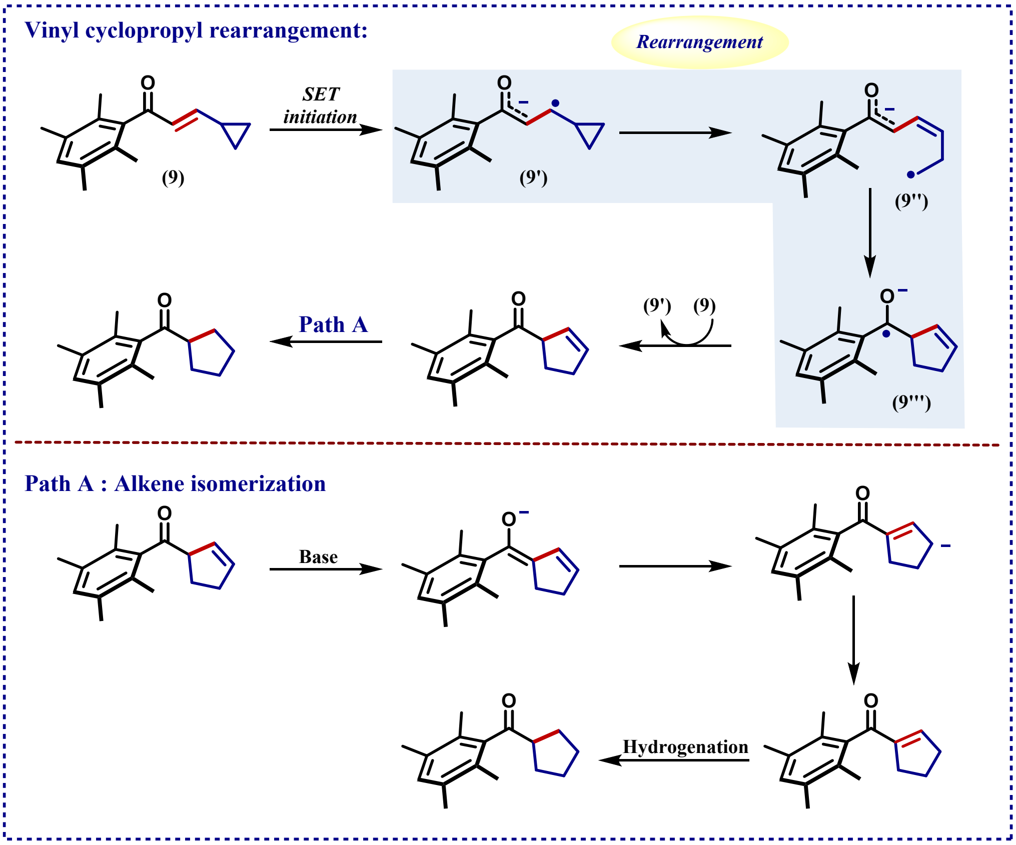
Procedure: To a solution of NaOH (1 mmol) in H_2O (3 mL), ethanolic solution of 1-(2,3,5,6-tetramethylphenyl) ethan-1-one was added at 0 °C. To it, cyclopropane carboxaldehyde (1 mmol) was introduced drop-wise. The mixture was then allowed to warm to room temperature and stirred for 2 h after which a precipitate of the product formed. Finally, the obtained product was filtered and recrystallized using ethanol. The desired product 3-cyclopropyl-1-(2,3,5,6-tetramethylphenyl) prop-2-en-1-one **(9)** is fully characterized by ^1H, ^{13}C NMR spectroscopies.

3-Cyclopropyl-1-(2,3,5,6-tetramethylphenyl) prop-2-en-1-one (9):



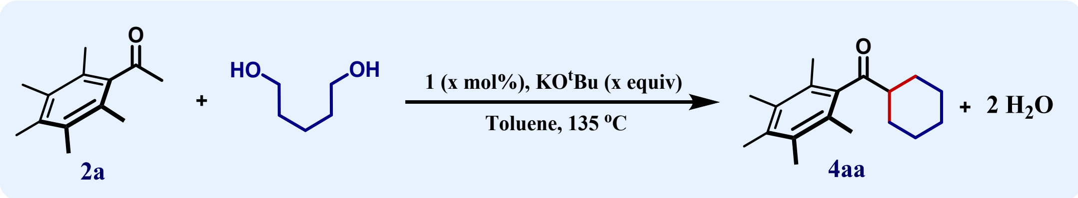
White solid (164 mg, 72%), mp: 95-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.41 (d, J = 15.6 Hz, 1H), 5.95 (m, 1H), 2.20 (s, 6H), 2.02 (s, 6H), 1.65 – 1.59 (m, 1H), 1.02 – 0.95 (m, 2H), 0.62 – 0.55 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 157.8, 140.5, 134.1, 131.55, 130.0, 129.6, 19.6, 19.5, 16.3, 15.2, 9.5 ppm; IR (KBr pellet): 2823, 2810, 1690, 1645, 1573, 1401, 1310, 1223, 1174, 1061, 1029, 1001, 914, 871, 782, 639 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{20}O$ 229.1592; Found 229.1587.

Scheme S1. Plausible pathway for formation of ring opened product[S7]:



3. Optimization of the reaction condition

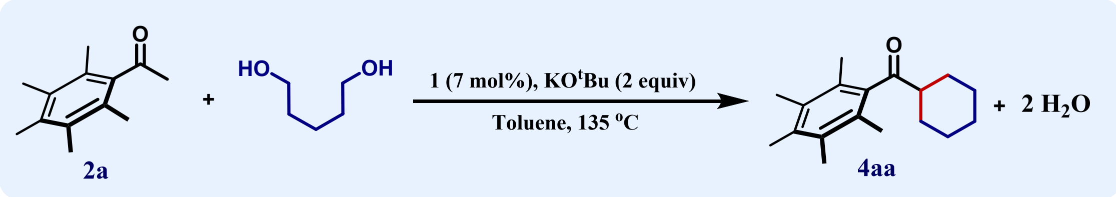
Table S1: Catalyst loading and base optimization



entry	catalyst loading	base loading	4aa (yield %)
1	7 mol%	KO^{t}Bu (2 equiv)	87
2	-	KO^{t}Bu (2 equiv)	n.r
3	6 mol%	KO^{t}Bu (2 equiv)	56
4	5 mol%	KO^{t}Bu (2 equiv)	41
5	7 mol%	KO^{t}Bu (1.5 equiv)	62
6	7 mol%	KO^{t}Bu (1 equiv)	39
7	7 mol%	K_2CO_3 (2 equiv)	n.r
8	7 mol%	KOH (2 equiv)	n.r
9	7 mol%	NaOH (2 equiv)	n.r
10	7 mol%	-	n.r

Reaction conditions: **1** (x mol %, with respect to **2a**), **2a** (0.5 mmol), 1,5-pentanediol (1.5 mmol), KO^{t}Bu (x equiv, with respect to **2a**), toluene (5 mL), 135 °C, 24 h (isolated yield).

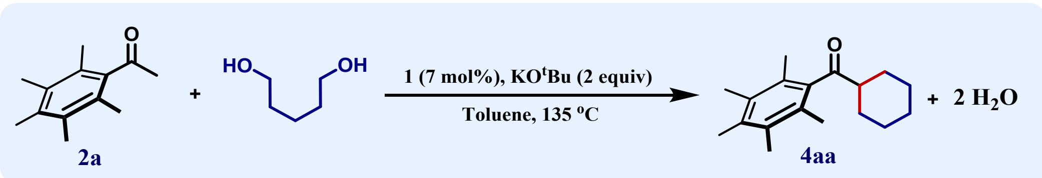
Table S2: Dilution optimization



entry	amount of solvent	solvent	4aa (yield %)
1	2 mL	Toluene	20
2	4 mL	Toluene	51
3	5 mL	Toluene	87
4	6 mL	Toluene	62
5	-	neat	-
6	5 mL	^{t}AmOH	n.r
7	5 mL	Xylene	59

Reaction conditions: **1** (7 mol %, with respect to **2a**), **2a** (0.5 mmol), 1,5-pentanediol (1.5 mmol), KO^{t}Bu (2 equiv, with respect to **2a**), solvent (x mL), 135 °C, 24 h (isolated yield).

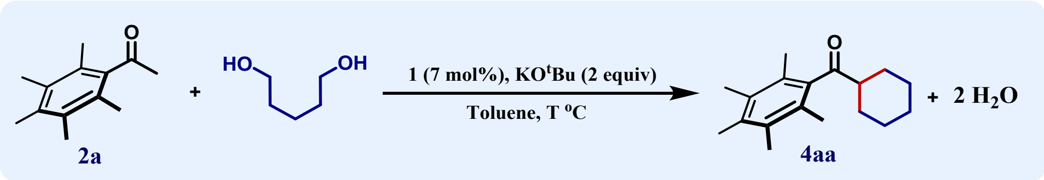
Table S3: Optimization of alcohol equivalent



entry	alcohol amount (mmol)	4aa (yield %)
1	0.5	16
2	1	42
3	1.5	87

Reaction conditions: **1** (7 mol %, with respect to **2a**), **2a** (0.5 mmol), 1,5-pentanediol (x mmol), KO^{t}Bu (2 equiv, with respect to **2a**), toluene (5 mL), 135 °C, 24 h (isolated yield).

Table S4: Dependence of yield on the temperature of reaction:



entry	temp (°C)	4aa (yield %)
1	110	31
2	120	65
3	135	87

Reaction conditions: **1** (7 mol %, with respect to **2a**), **2a** (0.5 mmol), 1,5-pentanediol (1.5 mmol), KO^{t}Bu (2 equiv, with respect to **2a**), toluene (5 mL), T °C, 24 h (isolated yield).

4. **General Procedure for the synthesis of (1+*n*)-membered cycloalkanes from methyl ketones and diols**.

Disclaimer: In a typical reaction, all the required components were loaded in an aerobic atmosphere, and then the reaction flask was purged with an inert gas for only two minutes before closing the flask tightly.

a) **General procedure for the synthesis of (1+n)-membered cycloalkanes from methyl ketones (2a-2e) and diols**.

A 15 mL pressure tube was charged with 7 mol% of **1,** 0.5 mmol of aryl ketone **(2a-2e)**, KO^{t}Bu (1 mmol) in 5 mL toluene. To it, 1.5 mmol of diols was added under constant stirring of the reaction mixture. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 135 °C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The residue was purified by column chromatography using hexane/diethyl ether (100:1) as eluent to afford pure products. The desired products were fully characterized by ^{1}H, ^{13}C NMR spectroscopies.

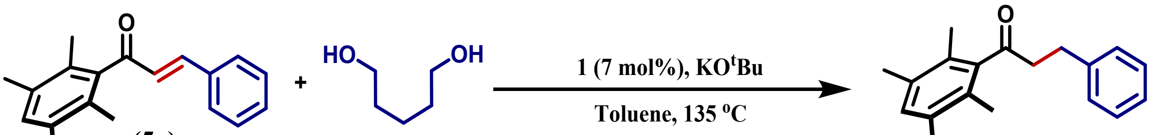
b) **General procedure for the synthesis of (1+n) membered cycloalkanes from bis-methyl ketone (2f) and diols**.

A 15 mL pressure tube was charged with 7 mol% of **1,** 0.25 mmol of bis-ketone **(2f)**, KO^{t}Bu (1 mmol), in 5 mL toluene. To it, 1.5 mmol of diols was added under constant stirring of the reaction mixture. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 135 °C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The residue was purified by column chromatography using hexane/diethyl ether (100:1) as eluent to afford pure products. The desired products were fully characterized by ^{1}H, ^{13}C NMR spectroscopies.

5. Mechanistic studies

5.1. Hydrogenation of intermediate

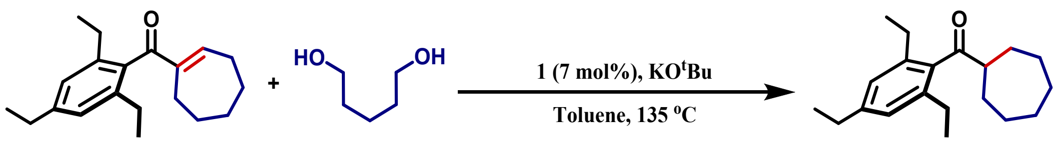
5.1.1.



(5a) **(74% yield)**

A 15 mL pressure tube was charged with 7 mol% of **1,** 0.5 mmol of 3-phenyl-1-(2,3,5,6-tetramethylphenyl)prop-2-en-1-one **(5a),** 1 mmol of 1,5-pentanediol, KO^{t}Bu (1 mmol) in 5 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. This reaction mixture was refluxed at 135 °C for 24 h. The desired product 3-phenyl-1-(2,3,5,6-tetramethylphenyl) propan-1-one was observed as the desired product in (98 mg) 74% yield. The isolated compound was characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, and HRMS.

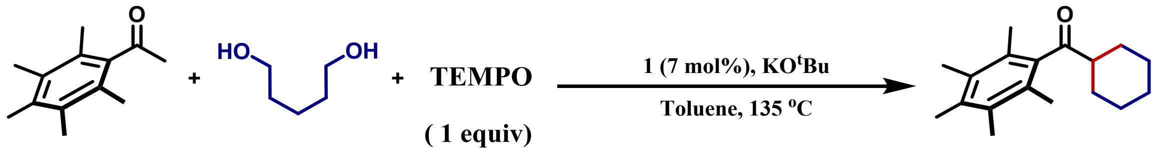
5.1.2.



(8a) **(4cc, 78% yield)**

A 15 mL pressure tube was charged with 7 mol% of **1,** 0.5 mmol of cyclohex-1-en-1-yl(2,4,6-triethylphenyl) methanone **(8a)**, 1 mmol of 1,5-pentanediol, KO^{t}Bu (1 mmol) in 5 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. This reaction mixture was refluxed at 135 °C for 24 h. Cyclohexyl-(2,4,6-triethylphenyl) methanone **(4cc)** was observed as the desired product in (105 mg) 78% yield. The isolated compound was characterized by ^{1}H NMR, ^{13}C NMR spectroscopy, and HRMS.

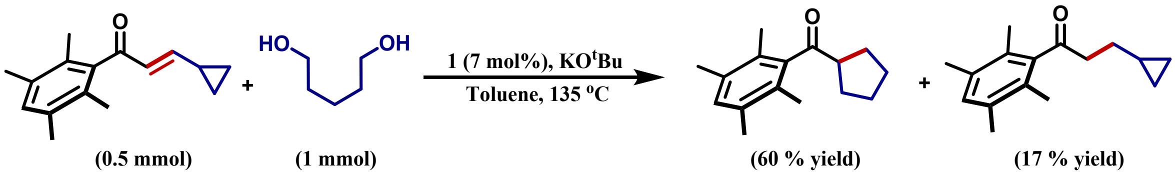
5.2. Radical quenching experiments



No product

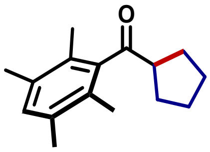
A 15 mL pressure tube was charged with 7 mol% of **1,** 0.5 mmol of **2a**, KO^{t}Bu (1 mmol) in 5 mL toluene. To this mixture 1.5 mmol of 1,5-pentanediol and 1 equiv of TEMPO was added. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 135 °C for 24 h. The reaction mixture was cooled to room temperature and concentrated *in vacuo.* The complete quenching of reaction was observed.

5.3. Experiment with a radical-probe substrate



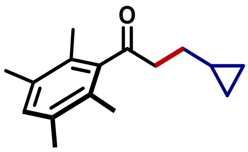
A 15 mL pressure tube was charged with 7 mol% of **1,** 0.5 mmol of 3-cyclopropyl-1-(2,3,5,6-tetramethylphenyl) prop-2-en-1-one (**9**), 1 mmol of 1,5-pentanediol, KO^{t}Bu (0.5 mmol) in 5 mL toluene. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. This reaction mixture was refluxed at 135 °C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The residue was purified by column chromatography using hexane/diethyl ether (100:1) as an eluent to afford pure products. The desired products are characterized by ^{1}H, ^{13}C NMR spectroscopies.

Cyclopentyl(2,3,5,6-tetramethylphenyl)methanone (4bb):



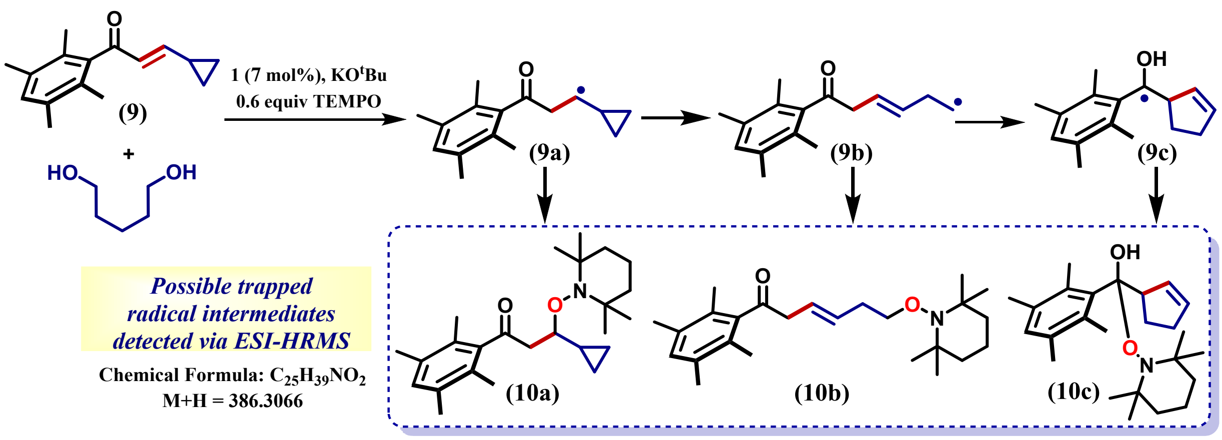
White solid (69 mg, 60%), mp: 76 °C, eluent combination: hexane/diethyl ether (100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 3.19 (m, 1H), 2.21 (s, 6H), 2.08 (s, 6H), 1.89 (m, 4H), 1.80 – 1.72 (m, 2H), 1.66 – 1.57 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.0, 143.3, 134.5, 131.6, 128.4, 54.1, 29.7, 26.0, 19.6, 16.6 ppm. The NMR spectroscopic data is in agreement with the literature[S8].

3-Cyclopropyl-1-(2,3,5,6-tetramethylphenyl)propan-1-one (4bb'):



White solid (20 mg, 17%), mp: 65-66 °C, eluent combination: hexane/ethyl acetate (100:5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 1H), 2.80 (m, 2H), 2.20 (s, 6H), 2.06 (d, J = 4.5 Hz, 6H), 1.64 – 1.60 (m, 2H), 0.84 – 0.73 (m, 1H), 0.45 (m, 2H), 0.09 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.0, 143.0, 134.4, 131.5, 128.0, 77.4, 77.1, 76.8, 45.4, 28.3, 19.6, 16.0, 10.7, 4.7 ppm; IR (KBr pellet): 2963, 2910, 2863, 2121, 1700, 1501, 1401, 1286, 1121, 980, 702 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{22}O$ 231.1749; Found 231.1742.

5.4. Detection of radical intermediate arrested by TEMPO



A 15 mL pressure tube was charged with 7 mol% of **1,** 0.5 mmol of **3**-cyclopropyl-1-(2,3,5,6-tetramethylphenyl)prop-2-en-1-one (**10**), 1 mmol of 1,5-pentanediol, KO^{t}Bu (0.5 mmol) in 5 mL toluene. To it, added 0.6 equiv TEMPO. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. This reaction mixture was refluxed at 135 °C for 12 h. The reaction mixture was subjected to HRMS (ESI) for characterization. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{39}NO_2$ 386.3059; Found 386.3066.

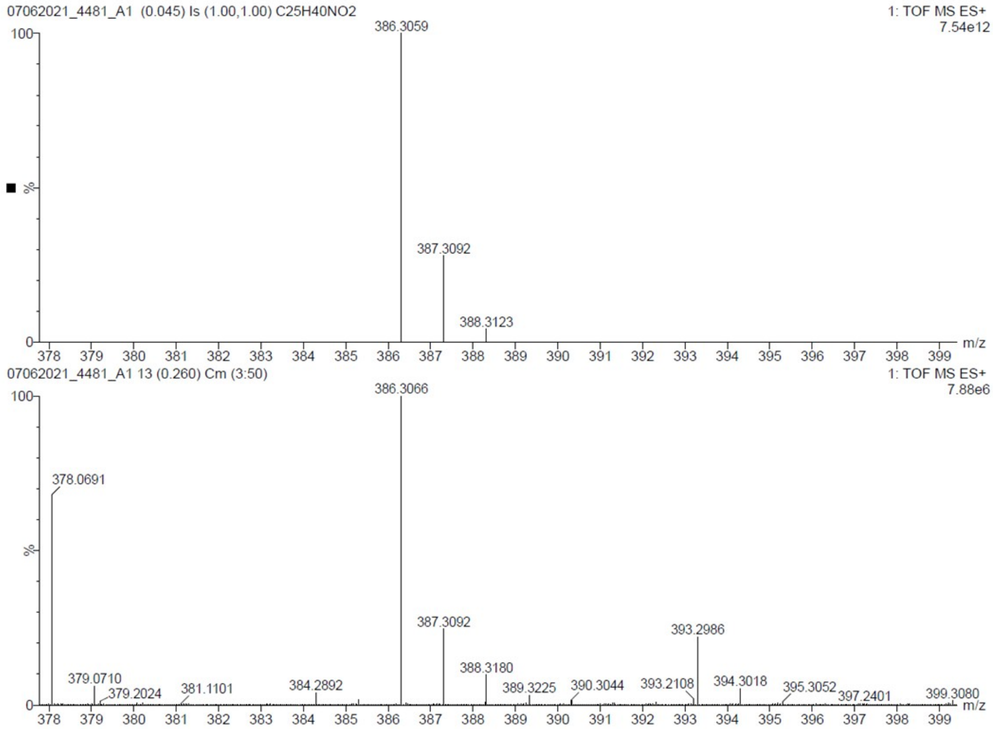


Figure S1. Mass spectrum of radical arrested TEMPO intermediate. (Bottom spectrum is experimentally observed and top one is simulated.)

5.5. Procedure for the ketyl-TEMPO adduct formation

a) A 15 mL pressure tube was charged with 0.5 mmol of **$Ni(H_2L)L$,** 0.5 mmol of chalcone, KO^tBu (1 mmol) in 5 mL toluene. To it, 0.5 equiv TEMPO was added under constant stirring of the reaction mixture. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 135 ^oC for 12 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The reaction mixture was subjected to ESI-HRMS for further characterization.

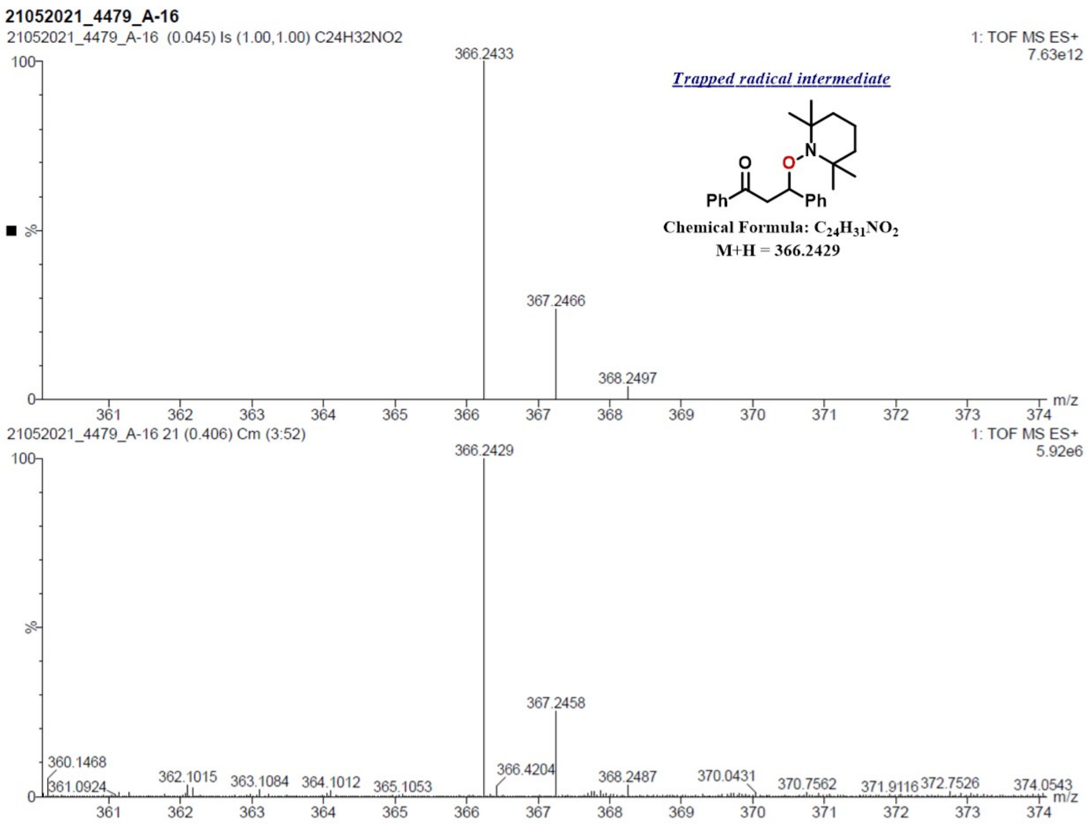


Figure S2. Mass spectrum of ketyl-TEMPO adduct. ESI-HRMS m/z: $[M + H]^+$ Calcd for $C_{24}H_{11}NO_2$ 366.2433; Found 366.2429; (Bottom spectrum is experimentally observed and top one is simulated.)

b) A 15 mL pressure tube was charged with 0.5 mmol of **Ni(H$_2$L)L,** 0.5 mmol of 3-phenyl-1-(2,3,5,6-tetramethylphenyl) prop-2-en-1-one **(5a)**, KO^{t}Bu (1 mmol) in 5 mL toluene. To it, 0.5 equiv TEMPO was added under constant stirring of the reaction mixture. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 135 ^{o}C for 12 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The reaction mixture was subjected to HRMS (ESI) for further characterization.

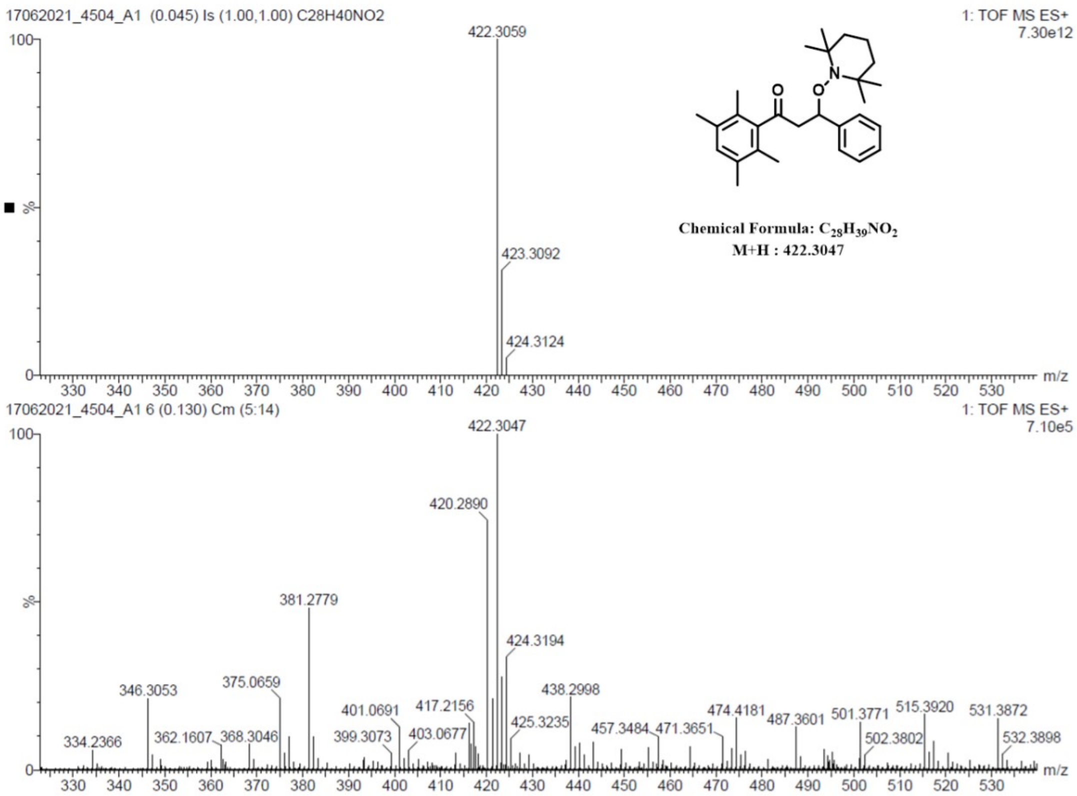
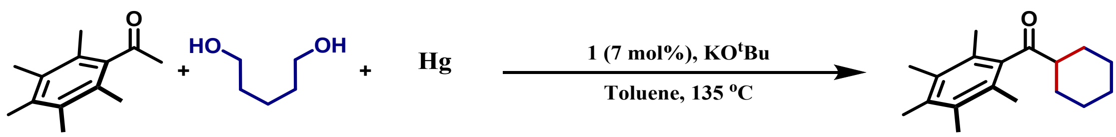


Figure S3. Mass spectrum of ketyl-TEMPO adduct. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{28}H_{39}NO_2$ 422.3059; Found 422.3047; (Bottom spectrum is experimentally observed and top one is simulated.)

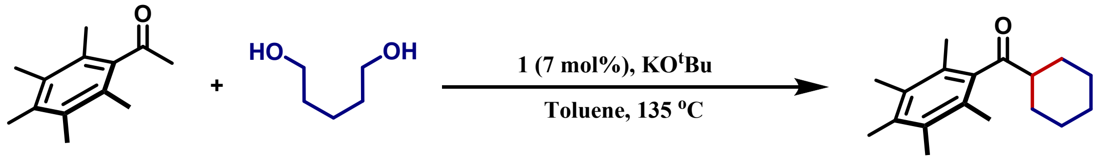
5.6. Mercury drop test



To establish the homogeneity of the **1,** we have carried out a mercury drop experiment.

A 15 mL pressure tube was charged with 7 mol% of **1,** 0.5 mmol of aryl ketone **(2a)**, KO^{t}Bu (1 mmol) in 5 mL toluene. To this mixture 1.5 mmol of 1,5-pentanediol and 1 drop of mercury was added. The reaction flask was purged with an inert gas for few minutes before closing the flask tightly. The reaction mixture was stirred at 135 °C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated *in vacuo.* The isolation of the product **4aa** (in 81% yield) after 24 h confirmed the homogeneous behaviour of the catalyst.

5.7. Synthetic application: Gram-Scale synthesis



2a **4aa, 69% yield**

a typical reaction, 25 mL Schleck flask was charged with 7 mol% of **1,** 1 g (5.26 mmol) of 1-(2,3,4,5,6-pentamethylphenyl) ethan-1-one **(2a)**, KO^{t}Bu (1.17 g, 10.52 mmol), in 40 mL toluene. To this mixture, 1.6 g (15.8 mmol) of 1,5-pentanediol was charged under constant stirring of the reaction mixture. The reaction flask was connected to condenser under nitrogen flow. The reaction mixture was stirred at 135 °C for 24 h. The reaction mixture was cooled to room temperature upon completion and concentrated further *in vacuo.* The desired product was purified by column chromatography using hexane/diethyl ether (100:1) as an eluent to afford pure product **4aa** (936 mg, 69% yield).

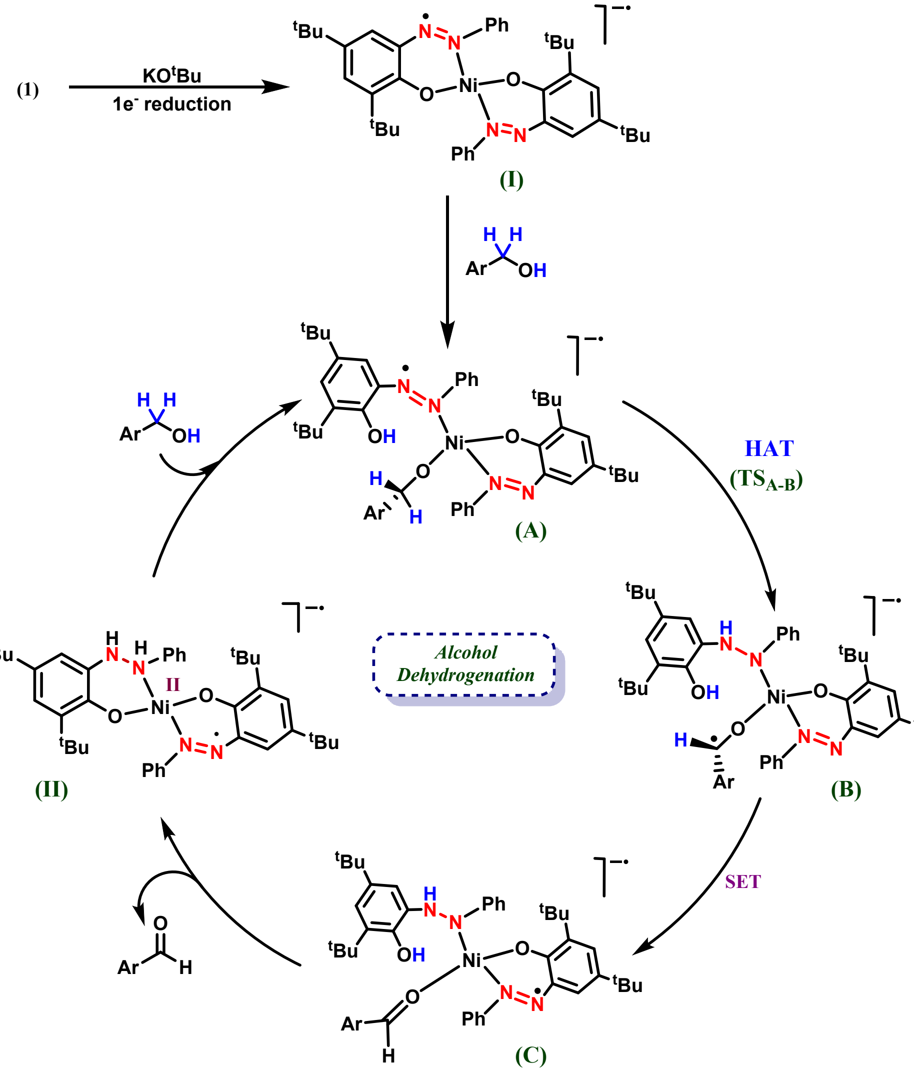
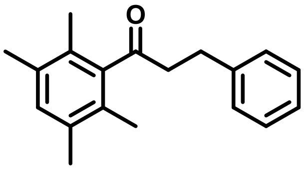


Figure S4. Proposed mechanism for dehydrogenation of alcohol by **1**

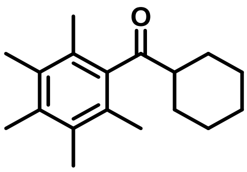
6. **Analytical data**

3-Phenyl-1-(2,3,5,6-tetramethylphenyl)propan-1-one: White solid (98 mg, 74%), eluent combination: hexane/diethyl ether (100:1).



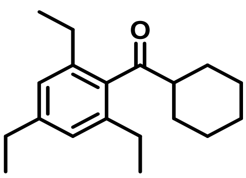
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 5H), 6.99 (s, 1H), 3.14 – 3.10 (m, 2H), 3.07 – 3.03 (m, 2H), 2.24 (s, 6H), 2.05 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.8, 142.6, 141.0, 134.4, 131.6, 128.6, 128.5, 126.2, 46.8, 29.3, 19.5, 15.9 ppm; IR (KBr pellet): 3054, 2938, 2831, 2219, 1622, 1445, 1254, 1121, 737 cm^{-1}; HRMS (ESI) m/z: [M-H]$^{+}$ Calcd for $C_{19}H_{22}O$ 265.1592; Found 265.1581.

Cyclohexyl(2,3,4,5,6-pentamethylphenyl)methanone (4aa): White solid (112 mg, 87%), eluent combination: hexane/diethyl ether (100:1).



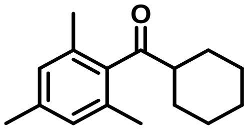
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 - 2.60 (m, 1H), 2.24 (s, 3H), 2.20 (s, 6H), 2.11 (s, 6H), 1.96 – 1.93 (m, 2H), 1.83 – 1.81 (m, 2H), 1.70 – 1.69 (m, 1H), 1.48 – 1.39 (m, 2H), 1.27 – 1.19 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.1, 140.2, 135.4, 133.1, 128.2, 53.2, 28.3, 26.0, 18.0, 16.8, 16.1 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

Cyclohexyl(2,4,6-triethylphenyl)methanone (4ab): Yellow oil (104 mg, 77%), eluent combination: hexane/diethyl ether (100:1).



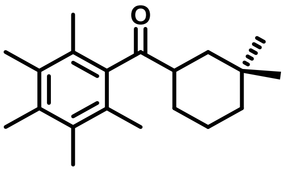
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 2H), 2.65 - 2.59 (m, 3H), 2.49 – 2.43 (m, 4H), 1.96-1.91 (m, 2H), 1.84 – 1.80 (m, 2H), 1.69 - 1.67 (m, 1H), 1.42 – 1.39 (m, 2H), 1.25 – 1.19 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.3, 149.3, 143.5, 138.3, 121.1, 54.1, 34.4, 33.3, 32.5, 30.8, 26.4, 26.2, 24.0 ppm; IR (KBr pellet): 3109, 2893, 2234, 1709, 1563, 1402, 1198, 1002, 945, 721 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{28}O$ 273.2218; Found 273.2203.

Cyclohexyl(mesityl)methanone (4ac): Yellow oil (96 mg, 84%), eluent combination: hexane/diethyl ether (100:1).



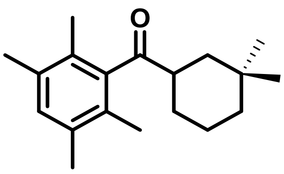
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 2.72 - 2.64 (m, 1H), 2.28 (s, 3H), 2.19 (s, 6H), 1.95 – 1.89 (m, 2H), 1.83 – 1.79 (m, 2H), 1.70 - 1.68 (m, 1H), 1.44 – 1.37 (m, 2H), 1.29 – 1.21 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.8, 139.3, 138.3, 133.4, 128.6, 52.4, 28.3, 26.0, 21.1, 19.7 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

(3,3-Dimethylcyclohexyl)(2,3,4,5,6-pentamethylphenyl) methanone (4ad): White solid (121 mg, 85%), eluent combination: hexane/diethyl ether (100:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90 - 2.82 (m, 1H), 2.26 (s, 3H), 2.21 (s, 6H), 2.12 (s, 6H), 1.94 - 1.93 (m, 1H), 1.68 – 1.61 (m, 2H), 1.50 – 1.37 (m, 3H), 1.34 – 1.13 (m, 2H), 0.99 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.2, 140.4, 135.3, 133.0, 128.1, 49.2, 40.5, 38.7, 33.3, 30.6, 28.4, 24.3, 22.0, 17.9, 16.7, 16.0 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

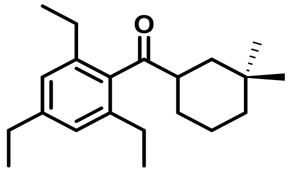
(3,3-Dimethylcyclohexyl)(2,3,5,6-tetramethylphenyl)methanone (4ae): White solid (100 mg, 75%), eluent combination: hexane/diethyl ether (100:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 2.88 – 2.80 (m, 1H), 2.21 (d, J = 3.5 Hz, 6H), 2.06 (s, 6H), 1.97 – 1.87 (m, 1H), 1.66 – 1.58 (m, 2H), 1.45 – 1.37 (m, 3H), 1.34 – 1.24 (m, 1H), 1.19- 1.14 (m, 1H), 0.97 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.1, 142.4, 134.4, 131.6, 128.7, 48.9, 40.5, 38.6, 33.3, 30.6, 28.4, 24.3, 21.9, 19.6, 16.7 ppm; IR

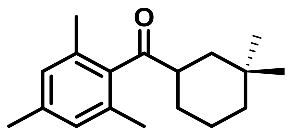
(KBr pellet): 3098, 2876, 2678, 1693, 1543, 1109, 908, 762 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{28}O$ 273.2218; Found 273.2203.

(3,3-Dimethylcyclohexyl)(2,4,6-triethylphenyl)methanone (4af): Yellow oil (118 mg, 79%), eluent combination: hexane/diethyl ether (100:1).



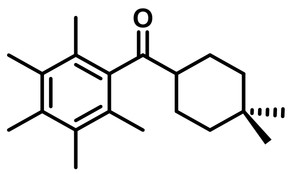
^1H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 2H), 2.89 – 2.81 (m, 1H), 2.66 – 2.60 (m, 2H), 2.50 – 2.44 (m, 4H), 1.93 (d, J = 12.6 Hz, 1H), 1.63 – 1.58 (m, 2H), 1.45 – 1.33 (m, 3H), 1.28 – 1.19 (m, 11H), 0.97 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.1, 140.8, 135.1, 133.0, 127.2, 53.3, 46.3, 25.6, 25.3, 23.3, 22.1, 20.1, 17.0, 16.6, 15.9 ppm; IR (KBr pellet): 3209, 2902, 2765, 1694, 1502, 1109, 953, 690 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{32}O$ 301.2531; Found 301.2518.

(3,3-Dimethylcyclohexyl)(mesityl)methanone (4ag): Yellow oil (110 mg, 86%), eluent combination: hexane/diethyl ether (100:1).



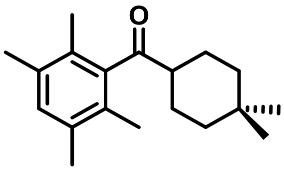
^1H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 2.93 – 2.85 (m, 1H), 2.28 (s, 3H), 2.19 (s, 6H), 1.94 – 1.89 (m, 1H), 1.65 – 1.54 (m, 2H), 1.42 – 1.25 (m, 4H), 1.18 – 1.11 (m, 1H), 0.95 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.0, 139.4, 138.4, 133.4, 128.7, 48.4, 40.6, 38.7, 33.3, 30.7, 28.4, 24.4, 21.9, 21.1, 19.8 ppm; IR (KBr pellet): 3103, 2984, 2209, 1709, 1398, 1252, 1098, 789 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{26}O$ 259.2061; Found 259.2046.

(4,4-Dimethylcyclohexyl)(2,3,4,5,6-pentamethylphenyl)methanone (4ah): White solid (105 mg, 74%), eluent combination: hexane/diethyl ether (100:1).



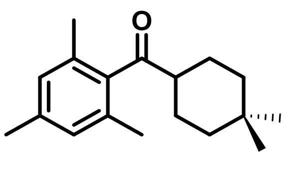
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 – 2.53 (m, 1H), 2.26 (s, 3H), 2.21 (s, 6H), 2.13 (s, 6H), 1.81 – 1.77 (m, 2H), 1.73 – 1.62 (m, 2H), 1.52 – 1.48 (m, 2H), 1.23 – 1.16 (m, 2H), 0.96 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.1, 140.3, 135.3, 133.0, 128.1, 53.2, 38.7, 32.8, 29.9, 24.2, 17.9, 16.7, 16.0 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

(4,4-Dimethylcyclohexyl)(2,3,5,6-tetramethylphenyl)methanone (4ai): White solid (99 mg, 73%), eluent combination: hexane/diethyl ether (100:1).



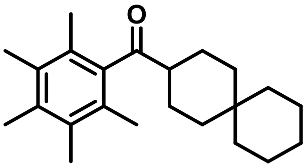
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 2.59 – 2.52 (m, 1H), 2.21 (s, 6H), 2.08 (s, 6H), 1.79 – 1.75 (m, 2H), 1.71 – 1.64 (m, 2H), 1.50 – 1.47 (m, 2H), 1.22 – 1.15 (m, 2H), 0.94 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.9, 142.4, 134.4, 131.6, 128.7, 52.9, 38.7, 32.8, 29.9, 24.2, 24.1, 19.6, 16.7 ppm; IR (KBr pellet): 3123, 2980, 2781, 2109, 1702, 1440, 1302, 1120, 952, 701 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{28}O$ 273.2218; Found 273.2203.

(4,4-Dimethylcyclohexyl)(mesityl)methanone (4aj): Yellow oil (91 mg, 71%), eluent combination: hexane/diethyl ether (100:1).



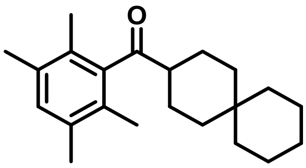
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 2.64 – 2.56 (m, 1H), 2.28 (s, 3H), 2.20 (s, 6H), 1.77 – 1.71 (m, 2H), 1.69 – 1.58 (m, 2H), 1.49 – 1.45 (m, 2H), 1.22 – 1.14 (m, 2H), 0.93 (d, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.0, 139.3, 138.3, 133.3, 128.7, 52.4, 38.7, 32.8, 30.0, 24.3, 24.2, 21.1, 19.7 ppm; IR (KBr pellet): 3029, 2987, 2878, 2301, 1710, 1309, 1109, 1092, 987, 723 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{26}O$ 259.2061; Found 259.2046.

(2,3,4,5,6-Pentamethylphenyl)(spiro[5.5]undecan-3-yl)methanone (4ak): White solid (132 mg, 81%), eluent combination: hexane/diethyl ether (100:1).



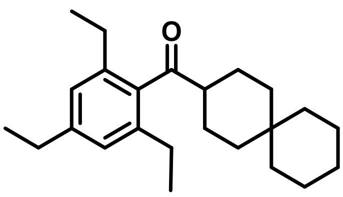
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 - 2.54 (m, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.10 (s, 6H), 1.76 – 1.63 (m, 4H), 1.62-1.59 (m, 2H), 1.42 – 1.40 (m, 8H), 1.21- 1.18 (m, 2H), 1.05 – 0.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.3, 140.4, 135.4, 133.1, 128.2, 53.7, 41.7, 36.2, 32.1, 31.9, 27.0, 23.4, 21.8, 21.6, 18.0, 16.8, 16.1 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

Spiro[5.5]undecan-3-yl(2,3,5,6-tetramethylphenyl)methanone (4al): White solid (129 mg, 83%), eluent combination: hexane/diethyl ether (100:1).



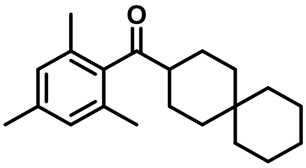
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 2.64 – 2.56 (m, 1H), 2.21 (s, 6H), 2.07 (s, 6H), 1.77 – 1.69 (m, 4H), 1.66-1.60 (m, 2H), 1.43 (m, 8H), 1.22 – 1.19 (m, 2H), 1.06 – 0.99 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.0, 142.5, 134.4, 131.6, 128.7, 53.4, 41.6, 36.2, 32.1, 31.8, 27.0, 23.3, 21.7, 21.6, 19.6, 16.7 ppm; IR (KBr pellet): 3046, 2981, 2745, 2290, 1720, 1453, 1267, 1093, 946, 673 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{32}O$ 313.2531; Found 313.2519.

Spiro[5.5]undecan-3-yl(2,4,6-triethylphenyl)methanone (4am): Yellow oil (120 mg, 71%), eluent combination: hexane/diethyl ether (100:1).



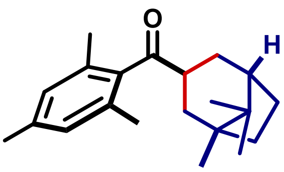
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 2H), 2.65 – 2.59 (m, 3H), 2.50 – 2.44 (m, 4H), 1.76 – 1.69 (m, 4H), 1.64 – 1.60 (m, 2H), 1.41 (s, 8H), 1.26 – 1.19 (m, 11H), 1.05 – 0.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.2, 144.8, 139.6, 138.6, 125.6, 53.4, 41.7, 36.3, 32.1, 31.9, 28.8, 27.0, 26.6, 23.6, 21.8, 21.6, 16.0, 15.5 ppm; IR (KBr pellet): 3024, 2934, 2765, 1654, 1450, 1109, 952, 726 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{36}O$ 341.2845; Found 341.2832.

Mesityl(spiro[5.5]undecan-3-yl)methanone (4an): Yellow oil (114 mg, 77%), eluent combination: hexane/diethyl ether (100:1).



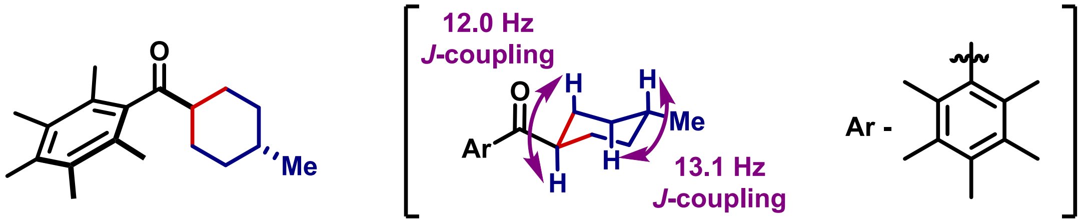
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 2.67 – 2.61 (m, 1H), 2.28 (s, 3H), 2.19 (s, 6H), 1.76 – 1.68 (m, 4H), 1.64 – 1.61 (m, 2H), 1.42 (m, 8H), 1.21 – 1.19 (m, 2H), 1.06 – 1.00 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.0, 139.4, 138.3, 133.3, 128.6, 52.9, 41.6, 36.2, 32.1, 31.9, 27.0, 23.4, 21.8, 21.6, 21.1, 19.7 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

Mesityl (1,8,8-trimethylbicyclo[3.2.1]octan-3-yl)methanone (4ao): Yellow oil (90 mg, 61%), eluent combination: hexane/diethyl ether (100:1).



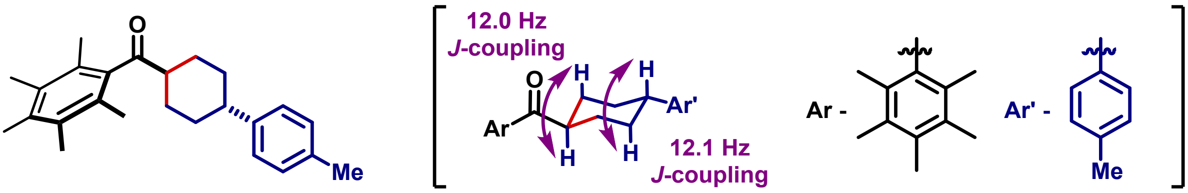
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 3.09 (tt, *J* = 12.3, 6.1 Hz, 1H), 2.28 (s, 3H), 2.20 (s, 6H), 1.98 (tdd, *J* = 12.4, 2.5, 1.3 Hz, 1H), 1.91 – 1.72 (m, 3H), 1.61 (dt, *J* = 7.2, 2.7 Hz, 1H), 1.50 – 1.41 (m, 2H), 1.35 – 1.22 (m, 3H), 0.98 (s, 3H), 0.85 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.1, 139.7, 138.3, 133.2, 128.7, 45.7, 45.5, 42.8, 42.7, 37.3, 35.5, 30.0, 26.6, 24.7, 21.1, 21.0, 19.8, 18.6 ppm; IR (KBr pellet): 3098, 2987, 2803, 1694, 1540, 1392, 1103, 987, 764, 682 cm^{-1}; HRMS (ESI) m/z: $[M - H]^+$ Calcd for $C_{21}H_{30}O$ 297.2218; Found 297.2214.

(4-Methylcyclohexyl)(2,3,4,5,6-pentamethylphenyl)methanone (4ap): White solid (100 mg, 75%), eluent combination: hexane/diethyl ether (100:1).



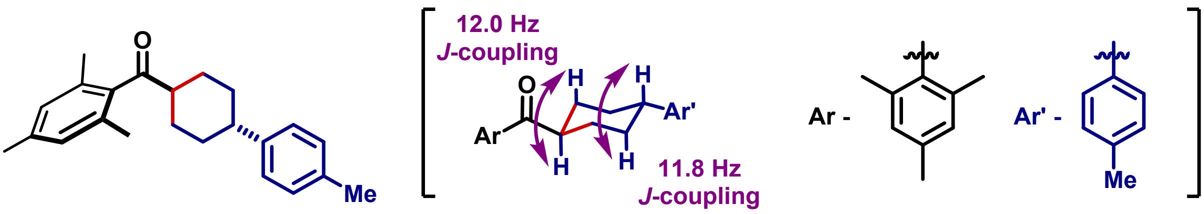
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (tt, J = 12.1, 3.2 Hz, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.09 (s, 6H), 1.94 (d, J = 12.1 Hz, 2H), 1.79-1.75 (m, 2H), 1.47 (ddd, J = 13.1, 3.3 Hz, 2H), 1.40 – 1.30 (m, 1H), 0.98 – 0.85 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.3, 140.3, 135.4, 133.1, 128.2, 53.0, 34.7, 32.3, 28.3, 22.6, 18.0, 16.8, 16.1 ppm. The NMR spectroscopic data is in agreement with the literature [S15].

(2,3,4,5,6-Pentamethylphenyl)((1r,4r)-4-(p-tolyl)cyclohexyl)methanone (4aq): White solid (120 mg, 69%), eluent combination: hexane/diethyl ether (100:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.08 (m, 4H), 2.73 (ddd, J = 12.0, 7.7, 3.3 Hz, 1H), 2.53 (ddd, J = 12.1, 7.8, 3.4 Hz, 1H), 2.34 (s, 3H), 2.27 (s, 3H), 2.23 (s, 6H), 2.16 (s, 6H), 2.13-2.10 (m, 1H), 2.06 – 1.98 (m, 2H), 1.72-1.61 (m, 2H), 1.53-1.42 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.8, 144.0, 140.1, 135.6, 133.1, 129.1, 128.2, 126.7, 52.7, 43.4, 33.7, 28.5, 21.0, 18.0, 16.8, 16.1 ppm; IR (KBr pellet): 2985, 2874, 2741, 1678, 1498, 1401, 1107, 987, 630 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{25}H_{32}O$ 349.2531; Found 349.2519.

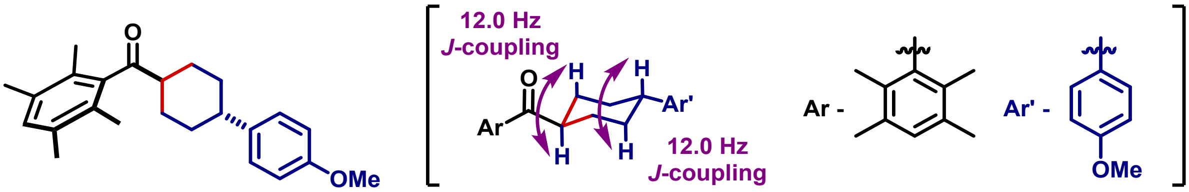
Mesityl (4-(p-tolyl)cyclohexyl)methanone (4ar): White solid (117 mg, 74%), eluent combination: hexane/diethyl ether (100:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.11 (m, 4H), 6.89 (s, 2H), 2.80 (ddd, J = 12.0, 8.8, 3.1 Hz, 1H), 2.54 (ddd, J = 11.8, 7.5, 3.1 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 2.26 (s, 6H), 2.13-

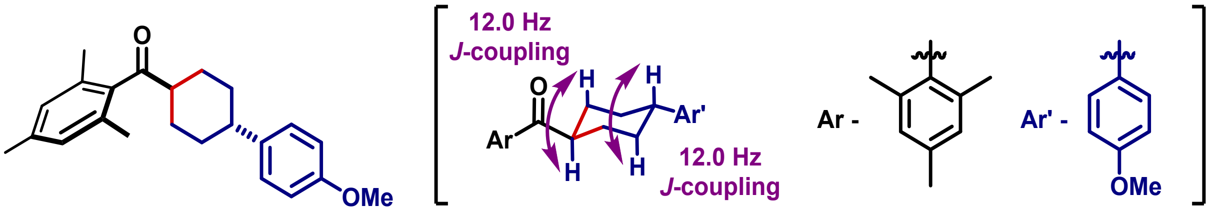
2.10 (m, 2H), 2.06 – 1.99 (m, 2H), 1.75 – 1.61 (m, 2H), 1.55-1.48 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.5, 143.9, 139.1, 138.4, 135.6, 133.3, 129.1, 128.7, 126.7, 51.9, 43.4, 33.7, 28.5, 21.1, 19.7 ppm; IR (KBr pellet): 3012, 2987, 2784, 2674, 1702, 1530, 1414, 987, 714, 621 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{23}H_{28}O$ 321.2218; Found 321.2205.

(4-(4-Methoxyphenyl)cyclohexyl)(2,3,5,6-tetramethylphenyl)methanone (4as): White solid (130 mg, 78%), eluent combination: hexane/diethyl ether (100:1).



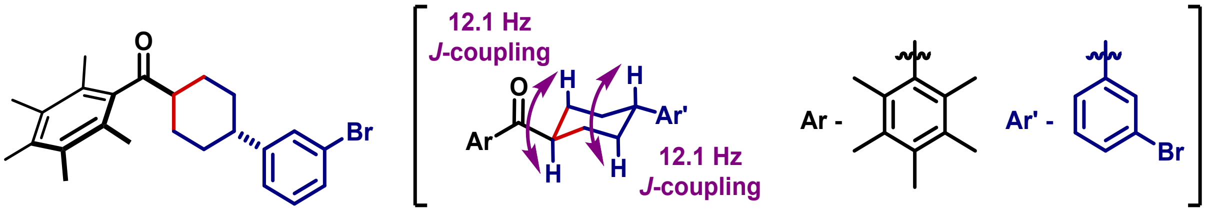
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.13 (m, 2H), 7.00 (s, 1H), 6.89 – 6.84 (m, 2H), 3.80 (s, 3H), 2.74 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.52 (tt, *J* = 12.0, 3.2 Hz, 1H), 2.25 (s, 6H), 2.13-2.10 (m, 8H), 2.03-1.99 (m, 2H), 1.72 – 1.60 (m, 2H), 1.52-1.41 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.5, 157.9, 142.2, 139.1, 134.4, 131.7, 128.7, 127.6, 113.8, 55.2, 52.4, 42.9, 33.8, 28.5, 19.6, 16.8 ppm; IR (KBr pellet): 3074, 2981, 2843, 2658, 1703, 1642, 1403, 1008, 953, 702 cm^{-1}; HRMS (ESI) m/z: $[M]^+$ Calcd for $C_{24}H_{30}O_2$ 350.2245; Found 350.2232.

Mesityl (4-(4-methoxyphenyl)cyclohexyl)methanone (4at): White solid (135 mg, 82%), eluent combination: hexane/diethyl ether (100:1).



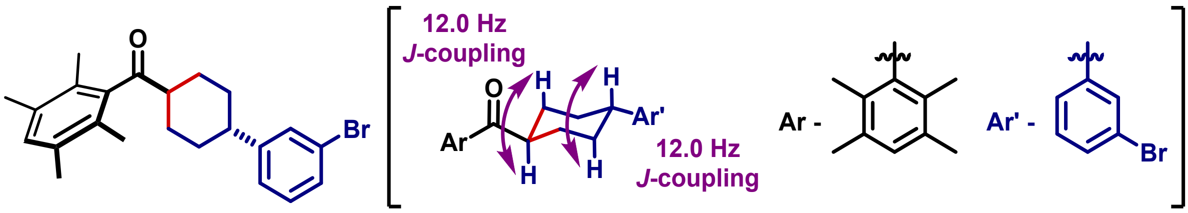
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.6 Hz, 2H), 6.90 – 6.84 (m, 4H), 3.80 (s, 3H), 2.79 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.52 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.31 (s, 3H), 2.25 (s, 6H), 2.13-2.10 (m, 2H), 2.06 – 1.97 (m, 2H), 1.73-1.62 (m, 2H), 1.53 – 1.40 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.5, 157.9, 139.1, 138.4, 133.3, 128.7, 127.6, 113.8, 55.2, 51.8, 42.9, 33.8, 28.5, 21.1, 19.7 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

(4-(3-Bromophenyl)cyclohexyl)(2,3,4,5,6-pentamethylphenyl)methanone (4au): White solid (146 mg, 72%), eluent combination: hexane/diethyl ether (100:1).



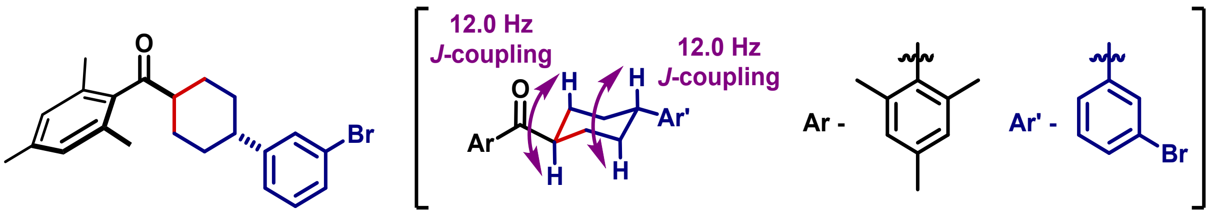
1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.33 (m, 2H), 7.24-7.22 (m, 2H), 2.76 (t, J = 12.1 Hz, 1H), 2.58 (t, J = 12.1 Hz, 1H), 2.29 (s, 3H), 2.24 (s, 6H), 2.18 (s, 6H), 2.13-2.11 (m, 1H), 2.05 (d, J = 11.8 Hz, 2H), 1.69 (dd, J = 13.2 Hz, 2H), 1.51 (q, J = 12.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.8, 146.9, 140.1, 135.5, 133.1, 128.4, 128.1, 126.8, 126.1, 52.7, 43.8, 33.6, 28.5, 18.0, 16.8, 16.1 ppm. The NMR spectroscopic data is in agreement with the literature [S15].

(4-(3-Bromophenyl)cyclohexyl)(2,3,5,6-tetramethylphenyl)methanone (4av): White solid (150 mg, 77%), eluent combination: hexane/diethyl ether (100:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.24-7.22 (m, 2H), 7.01 (s, 1H), 2.76 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.57 (tt, *J* = 12.0, 3.3 Hz, 1H), 2.25 (s, 6H), 2.15-2.13 (m, 8H), 2.08 – 2.00 (m, 2H), 1.74 – 1.63 (m, 2H), 1.56-1.46 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.5, 146.9, 142.2, 134.5, 131.7, 128.8, 128.4, 126.8, 126.1, 52.4, 43.8, 33.6, 28.4, 19.6, 16.8 ppm; IR (KBr pellet): 3017, 2982, 256, 1703, 1598, 1432, 1068, 785 cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{23}H_{27}BrO$ 341.3015; Found 341.3010.

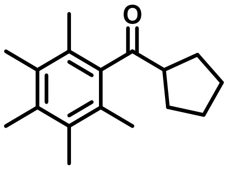
(4-(3-Bromophenyl)cyclohexyl)(mesityl)methanone (4aw): White solid (152 mg, 79%), eluent combination: hexane/diethyl ether (100:1).



1H NMR (400 MHz, CDCl3) δ 7.34 – 7.28 (m, 2H), 7.22-7.20 (m, 3H), 6.87 (s, 2H), 2.79 (tt, J = 12.0, 3.3 Hz, 1H), 2.55 (tt, J = 12.0, 3.4 Hz, 1H), 2.30 (s, 3H), 2.24 (s, 6H), 2.16 – 2.08 (m, 2H), 2.01-2.00 (m, 2H), 1.70 – 1.60 (m, 2H), 1.55-1.44 (m, 2H); ^{13}C NMR (101 MHz,

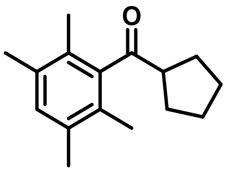
$CDCl_3$) δ 213.5, 146.9, 139.1, 138.5, 133.3, 128.7, 128.5, 126.8, 126.2, 51.9, 43.9, 33.6, 28.5, 21.1, 19.8 ppm; IR (KBr pellet): 2987, 2854, 2713, 1703, 1584, 1103, 875, 625 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{25}BrO$ 385.1167; Found 385.1161.

Cyclopentyl(2,3,4,5,6-pentamethylphenyl)methanone (4ba): White solid (67 mg, 55%), eluent combination: hexane/diethyl ether (100:1).



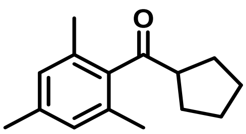
^1H NMR (400 MHz, $CDCl_3$) δ 3.22 – 3.16 (m, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.12 (s, 6H), 1.93 – 1.83 (m, 4H), 1.79 – 1.72 (m, 2H), 1.65 – 1.58 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.3, 141.4, 135.5, 133.2, 127.9, 54.5, 29.8, 26.0, 17.9, 16.8, 16.1 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

Cyclopentyl(2,3,5,6-tetramethylphenyl)methanone (4bb): White solid (70 mg, 60%), eluent combination: hexane/diethyl ether (100:1).



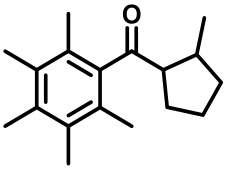
^1H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 3.23 – 3.15 (m, 1H), 2.21 (s, 6H), 2.08 (s, 6H), 1. 94 – 1.85 (m, 4H), 1.79 – 1.75 (m, 2H), 1.64 – 1.59 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.0, 143.3, 134.5, 131.6, 128.4, 54.1, 29.7, 26.0, 19.6, 16.6 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

Cyclopentyl(mesityl)methanone (4bc): Yellow oil (60 mg, 54%), eluent combination: hexane/diethyl ether (100:1).



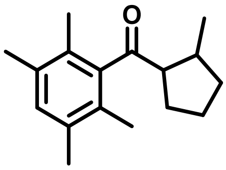
^1H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 3.27 – 3.19 (m, 1H), 2.27 (s, 3H), 2.21 (s, 6H), 1.89 – 1.84 (m, 4H), 1.78 – 1.74 (m, 2H), 1.63 – 1.58 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.2, 140.2, 138.3, 133.0, 128.7, 53.4, 29.9, 26.1, 21.1, 19.7 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

(2-Methylcyclopentyl)(2,3,4,5,6-pentamethylphenyl)methanone (4bd): White solid (85 mg, 66%), eluent combination: hexane/diethyl ether (100:1).

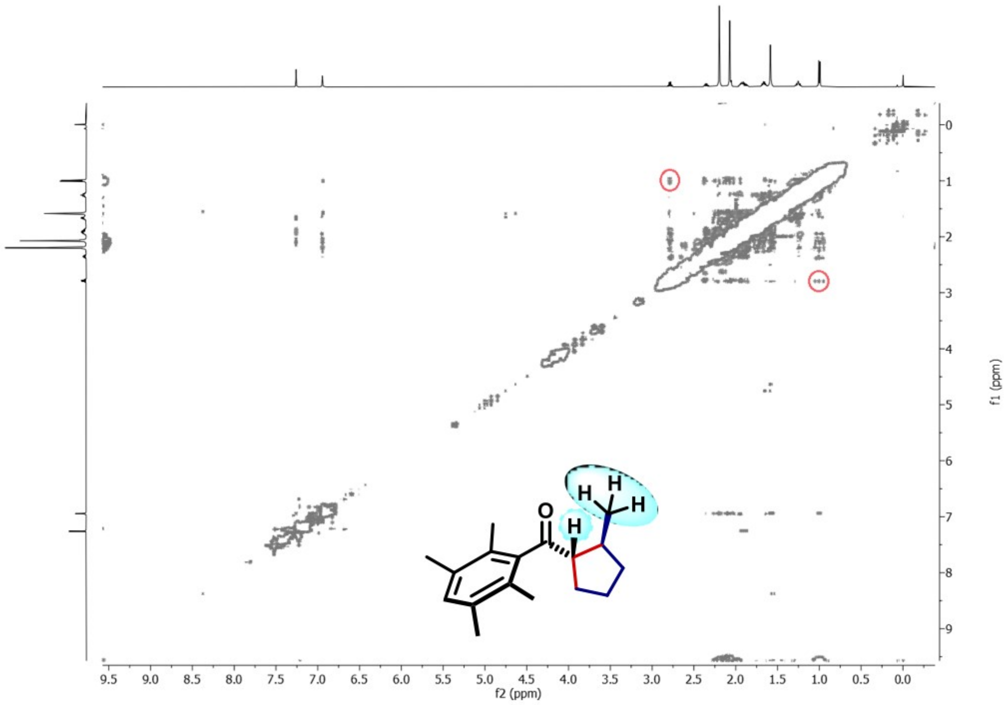


^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 – 2.77 (m, 1H), 2.42 – 2.35 (m, 1H), 2.24 (s, 3H), 2.20 (s, 6H), 2.13 (s, 6H), 1.98 – 1.87 (m, 3H), 1.72 - 1.63 (m, 2H), 1.31 – 1.22 (m, 1H), 1.02 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.5, 141.1, 135.3, 133.1, 127.9, 61.8, 37.1, 35.2, 30.1, 24.8, 20.7, 17.9, 16.8, 16.1 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

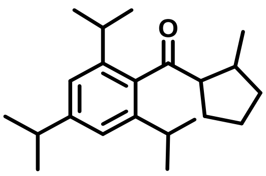
(2-Methylcyclopentyl)(2,3,5,6-tetramethylphenyl)methanone (4be): White solid (65 mg, 54%), eluent combination: hexane/diethyl ether (100:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 1H), 2.83 – 2.77 (m, 1H), 2.41 – 2.32 (m, 1H), 2.21 (s, 6H), 2.09 (s, 6H), 1.93 – 1.87 (m, 3H), 1.72 – 1.64 (m, 2H), 1.29 – 1.22 (m, 1H), 1.02 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.2, 143.1, 134.4, 131.6, 128.5, 61.5, 37.2, 35.2, 30.0, 24.9, 20.7, 19.6, 16.7 ppm; IR (KBr pellet): 3109, 2876, 2709. 2249, 1701, 1234, 1109, 782, 671 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{24}O$ 245.1905; Found 245.1885.

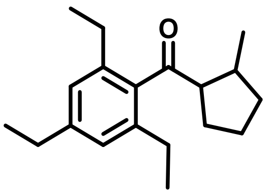


(2-Methylcyclopentyl)(2,4,6-triisopropylphenyl)methanone (4bf): Yellow oil (108 mg, 69%), eluent combination: hexane/diethyl ether (100:1).



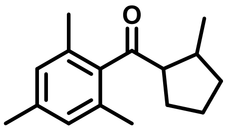
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 2H), 2.93 – 2.85 (m, 1H), 2.81 – 2.73 (m, 1H), 2.66 – 2.64 (m, 2H), 2.43 – 2.35 (m, 1H), 1.99 – 1.85 (m, 3H), 1.71 – 1.63 (m, 2H), 1.32 – 1.19 (m, 19H), 1.02 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.7, 149.4, 138.3, 121.2, 62.0, 37.2, 35.2, 34.3, 31.2, 30.4, 24.9, 24.0, 20.7 ppm; IR (KBr pellet): 3123, 2987, 2781, 2192, 1701, 1502, 1398, 1221, 1101, 739 cm^{-1}; HRMS (ESI) m/z: $[M - H]^+$ Calcd for $C_{22}H_{34}O$ 313.2531; Found 313.2519.

(2-Methylcyclopentyl)(2,4,6-triethylphenyl)methanone (4bg): Yellow oil (88 mg, 65%), eluent combination: hexane/diethyl ether (100:1).

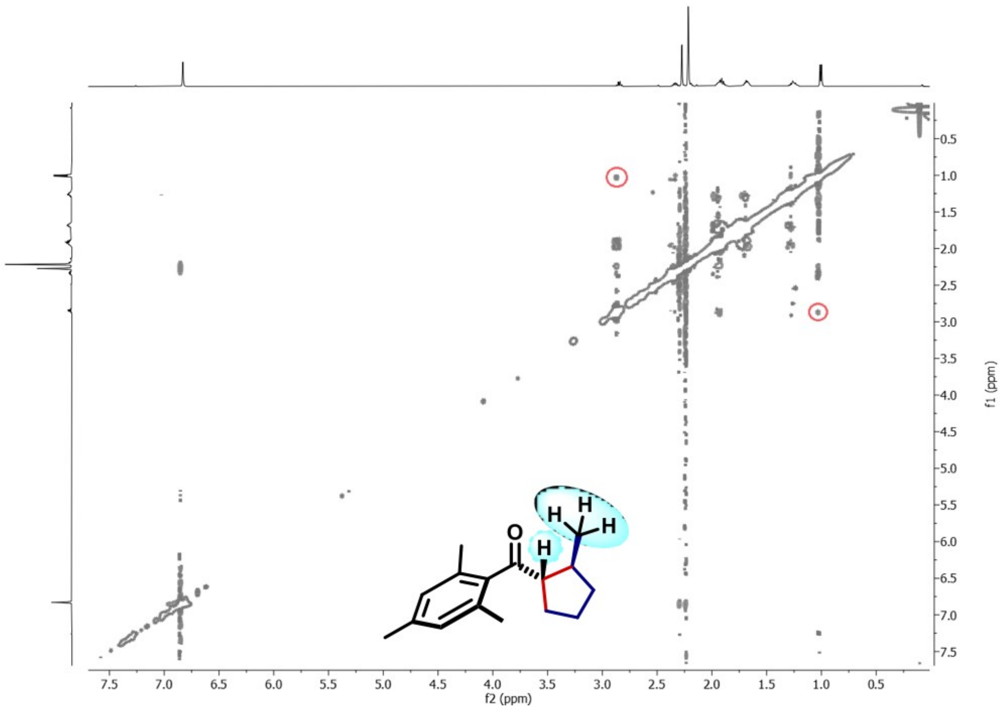


^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (s, 2H), 2.84 – 2. 78 (m, 1H), 2.65 – 2.59 (m, 2H), 2.49-2.46 (m, 4H), 2.37 – 2.33 (m, 1H), 1.97 – 1.87 (m, 3H), 1.69 – 1.63 (m, 1H), 1.25 - 1.19 (m, 11H), 1.00 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.5, 144.8, 139.5, 139.3, 125.8, 61.4, 37.7, 35.3, 30.4, 28.8, 26.5, 24.9, 20.7, 16.0, 15.5 ppm; IR (KBr pellet): 3109, 2899, 2298, 1698, 1501, 1302, 1101, 923, 731 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{28}O$ 273.2218; Found 273.2207.

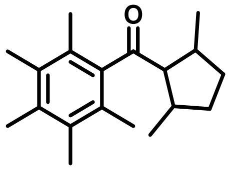
Mesityl(2-methylcyclopentyl)methanone (4bh): Yellow oil (80 mg, 70%), eluent combination: hexane/diethyl ether (100:1).



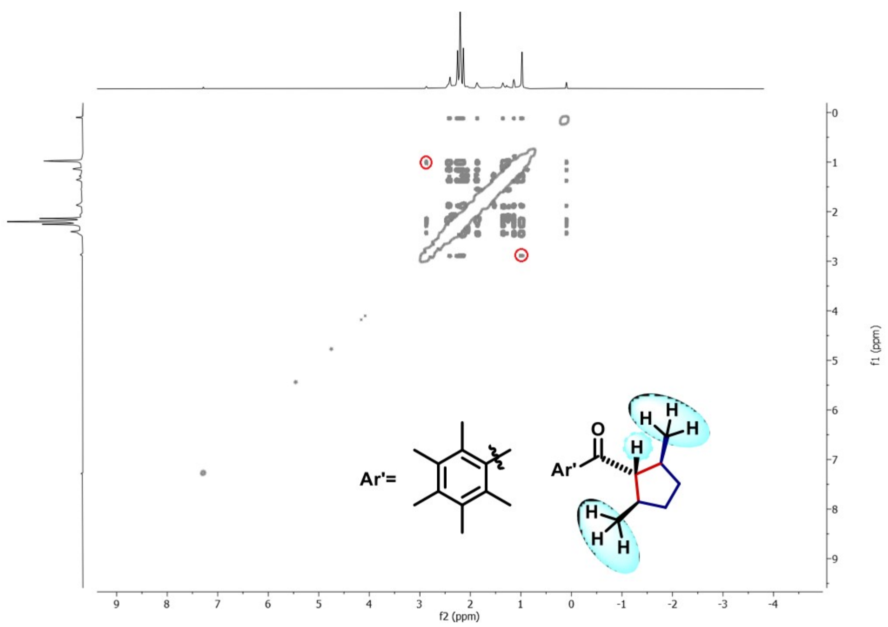
^1H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 2.88 – 2.82 (m, 1H), 2.38 – 2.32 (m, 1H), 2.28 (s, 3H), 2.22 (s, 6H), 1.99 – 1.88 (m, 3H), 1.73 – 1.65 (m, 2H), 1.31 – 1.20 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.2, 140.0, 138.3, 133.1, 128.8, 60.9, 37.8, 35.3, 30.1, 24.9, 21.1, 20.6, 19.8 ppm; IR (KBr pellet): 3201, 2903, 2365, 1701, 1503, 1329, 1211, 902, 723 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{22}O$ 231.1748; Found 231.1723.



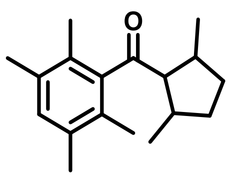
(2,5-dimethylcyclopentyl)(2,3,4,5,6-pentamethylphenyl)methanone (4bi): White solid (100 mg, 74%), eluent combination: hexane/diethyl ether (100:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 2.87 – 2.84 (m, 1H), 2.47 – 2.37 (m, 4H), 2.24 (d, J = 2.3 Hz, 4H), 2.19 – 2.17 (m, 12H), 2.12 (s, 4H), 2.09 – 1.99 (m, 1H), 1.84 (m, 2H), 1.53 (m, 1H), 1.41 – 1.30 (m, 2H), 1.29 – 1.18 (m, 1H), 1.12 (d, J = 7.0 Hz, 2H, minor isomer), 0.96 (d, J = 6.3 Hz, 6H, major isomer);^{13}C NMR (101 MHz, $CDCl_3$) δ 214.0, 213.4, 141.3, 141.1, 135.5, 135.3, 133.1, 133.1, 128.5, 127.8, 69.4, 64.9, 37.8, 37.6, 35.7, 33.9, 33.7, 32.3, 21.5, 18.0, 16.8, 16.4, 16.1 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

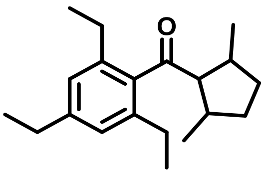


(2,5-dimethylcyclopentyl)(2,3,5,6-tetramethylphenyl)methanone (4bj): White solid (89 mg, 69%), eluent combination: hexane/diethyl ether (100:1).



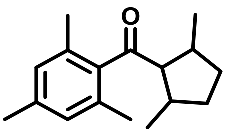
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 1H), 2.49 – 2.31 (m, 3H), 2.20 (s, 7H), 2.13 (d, J = 4.5 Hz, 2H), 2.09 (s, 5H), 1.85 (m, 2H), 1.35 (m, 2H), 1.29 – 1.19 (m, 1H), 1.13 (d, J = 7.0 Hz, 1H,minor isomer), 0.96 (d, *J* = 6.3 Hz, 6H, major isomer); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.5, 213.1, 143.3, 143.2, 134.5, 134.4, 131.8, 131.7, 129.1, 128.5, 69.2, 64.6, 37.7, 37.6, 35.9, 33.9, 33.8, 32.4, 21.5, 21.4, 19.8, 19.7, 16.8, 16.4 ppm; IR (KBr pellet): 3199, 2903, 2454, 1692, 1552, 1298, 876, 701 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{26}O$ 259.2061; Found 259.2055.

(2,5-dimethylcyclopentyl)(2,4,6-triethylphenyl)methanone (4bk): Yellow oil (87 mg, 61%), eluent combination: hexane/diethyl ether (100:1).

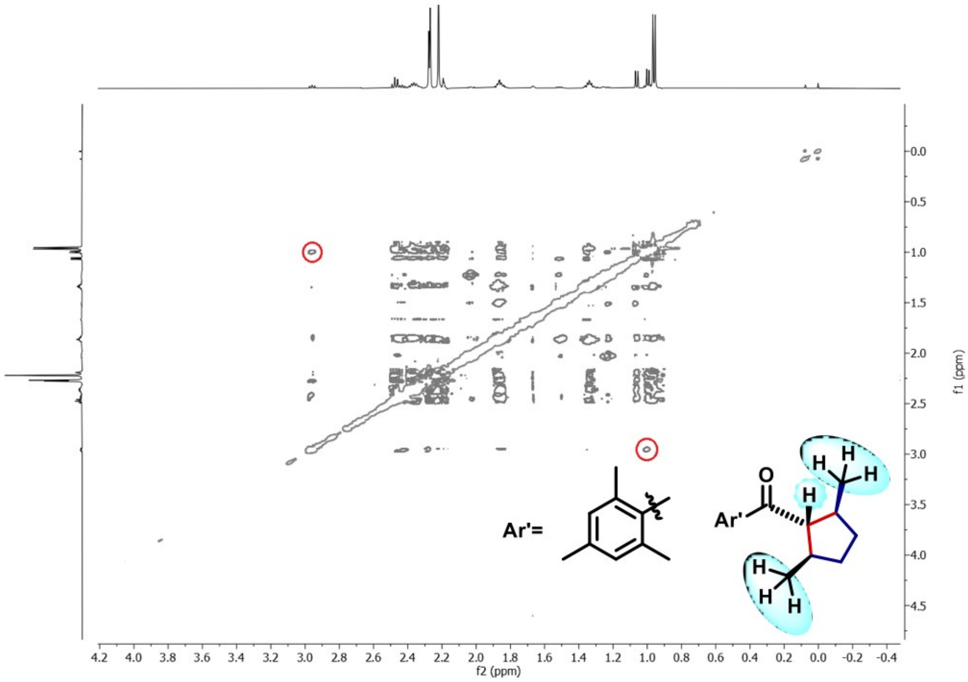


^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (s, 2H), 2.62 (q, *J* = 7.7 Hz, 4H), 2.56 (d, *J* = 7.5 Hz, 1H), 2.50 (m, 5H), 2.45 – 2.30 (m, 4H), 1.86 (m, 3H), 1.42 – 1.28 (m, 4H), 1.23 (m, 14H), 1.08 (d, *J* = 7.0 Hz, 1H, minor isomer), 0.95 (d, *J* = 6.6 Hz, 6H, major isomer);^{13}C NMR (101 MHz, $CDCl_3$) δ 212.6, 144.9, 140.2, 139.6, 139.3, 126.1, 125.8, 125.6, 69.3, 64.6, 38.1, 37.9, 36.6, 34.1, 33.9, 32.6, 28.8, 28.7, 26.6, 26.5, 21.3, 16.5, 16.3, 16.1, 15.5, 15.4 ppm; IR (KBr pellet): 3109, 3001, 2443, 1698, 1492, 1220, 891, 695 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{30}O$ 287.2374; Found 287.2382.

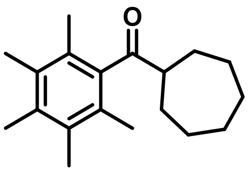
(2,5-dimethylcyclopentyl)(mesityl)methanone (4bl): Yellow oil (89 mg, 73%), eluent combination: hexane/diethyl ether (100:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 2H), 2.50 – 2.31 (m, 3H), 2.27 (d, *J* = 4.8 Hz, 5H), 2.22 (s, 3H), 2.19 (d, *J* = 2.6 Hz, 1H), 2.09 – 1.98 (m, 1H), 1.91 – 1.79 (m, 2H), 1.41 – 1.17 (m, 2H), 1.06 (d, *J* = 7.0 Hz, 1H, minor isomer), 1.00 (d, *J* = 6.7 Hz, 1H, minor isomer), 0.96 (d, *J* = 6.7 Hz, 3H, major isomer);^{13}C NMR (101 MHz, $CDCl_3$) δ 212.5, 212.1, 140.0, 140.0, 138.5, 138.3, 133.9, 133.1, 129.2, 128.9, 68.7, 64.0, 38.1, 37.8, 36.8, 34.1, 33.8, 32.6, 21.2, 21.1, 20.3, 19.9, 16.7 ppm; IR (KBr pellet): 3197, 2981, 2456, 1710, 1612, 1342, 1199, 924, 710 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{24}O$ 245.1905; Found 245.1911.

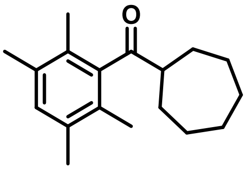


Cycloheptyl(2,3,4,5,6-pentamethylphenyl)methanone (4ca): White solid (91 mg, 67%), eluent combination: hexane/diethyl ether (100:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 2.86 – 2.79 (m, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.10 (s, 6H), 1.99 - 1.95 (m, 2H), 1.75 – 1.73 (m, 2H), 1.71 – 1.62 (m, 2H), 1.59 – 1.54 (m, 4H), 1.48 – 1.39 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.3, 140.3, 135.5, 133.1, 128.4, 54.8, 29.5, 28.5, 26.5, 18.0, 16.8, 16.1 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

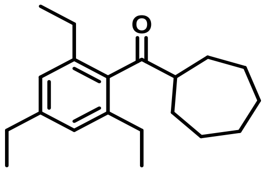
Cycloheptyl(2,3,5,6-tetramethylphenyl)methanone (4cb): White solid (83 mg, 65%), eluent combination: hexane/diethyl ether (100:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 1H), 2.86 – 2.81 (m, 1H), 2.20 (s, 6H), 2.06 (s, 6H), 1.99 – 1.94 (m, 2H), 1.77 – 1.71 (m, 2H), 1.69 - 1.65 (m, 2H), 1.59 – 1.55 (m, 4H), 1.44 (d, *J*

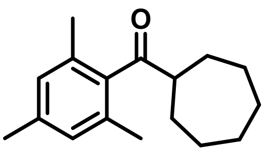
= 9.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.0, 142.4, 134.5, 131.7, 129.1, 54.5, 29.4, 28.5, 26.5, 19.7, 16.8 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

Cycloheptyl(2,4,6-triethylphenyl)methanone (4cc): Yellow oil (84 mg, 59%), eluent combination: hexane/diethyl ether (100:1).



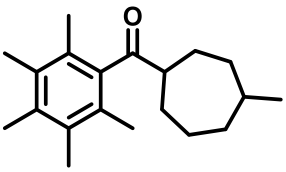
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 2H), 2.90 – 2.85 (m, 1H), 2.66 – 2.60 (m, 2H), 2.51 – 2.45 (m, 4H), 2.02 - 1.97 (m, 2H), 1.79 – 1.74 (m, 2H), 1.69 – 1.55 (m, 6H), 1.46 – 1.43 (m, 2H), 1.27 – 1.21 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.1, 144.8, 139.6, 138.5, 125.7, 48.8, 40.7, 38.7, 33.3, 30.6, 28.7, 28.5, 26.6, 24.3, 22.0, 16.0, 15.4 ppm; IR (KBr pellet): 3099, 2974, 2735, 1698, 1518, 1392, 1106, 1098, 912, 734 cm^{-1}; HRMS (ESI) m/z: $[M - H]^+$ Calcd for $C_{20}H_{30}O$ 285.2218; Found 285.2205.

Cycloheptyl(mesityl)methanone (4cd): Yellow oil (91 mg, 75%), eluent combination: hexane/diethyl ether (100:1).



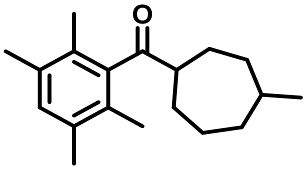
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 2H), 2.93 – 2.86 (m, 1H), 2.28 (s, 3H), 2.20 (s, 6H), 1.97 – 1.92 (m, 2H), 1.78 – 1.71 (m, 2H), 1.68 – 1.63 (m, 2H), 1.61 – 1.55 (m, 4H), 1.46 - 1.43 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.9, 139.3, 138.4, 133.6, 128.7, 53.9, 29.6, 28.5, 26.6, 21.1, 19.8 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

(4-methylcycloheptyl)(2,3,4,5,6-pentamethylphenyl)methanone (4ce): White solid (92 mg, 65%), eluent combination: hexane/diethyl ether (100:1).



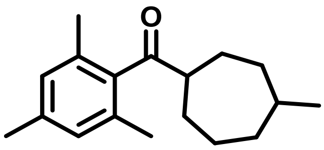
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.92 – 2.81 (m, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.10 (s, 6H), 2.03 – 2.00 (m, 1H), 1.86 – 1.74 (m, 4H), 1.66 – 1.57 (m, 4H), 1.50 – 1.15 (m, 1H), 1.15 – 1.10 (m, 2H), 1.07 - 0.89 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.2, 140.3, 135.4, 133.1, 128.4, 55.1, 54.3, 38.2, 36.5, 36.0, 35.2, 34.4, 33.2, 30.1, 29.1, 28.4, 26.3, 26.2, 23.9, 23.8, 23.6, 18.0, 16.8, 16.1 ppm. The NMR spectroscopic data is in agreement with the literature [S8].

(4-methylcycloheptyl)(2,3,5,6-tetramethylphenyl)methanone (4cf): White solid (94 mg, 69%), eluent combination: hexane/diethyl ether (100:1).



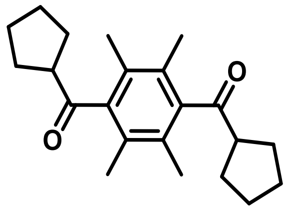
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (s, 1H), 2.96 – 2.84 (m, 1H), 2.22 (s, 6H), 2.09 (s, 6H), 1.92 – 1.76 (m, 4H), 1.70 – 1.57 (m, 4H), 1.48 – 1.31 (m, 1H), 1.26 – 1.05 (m, 2H), 0.95 – 0.92 (m, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 214.6, 214.5, 142.3, 134.3, 131.5, 128.9, 128.8, 54.6, 53.8, 38.2, 36.5, 35.9, 35.1, 34.3, 33.2, 30.0, 28.9, 28.2, 26.2, 26.1, 23.8, 23.7, 23.5, 19.5, 16.6 ppm; IR (KBr pellet): 3098, 2987, 2786, 1682, 1503, 1398, 1102, 932, 656 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{28}O$ 273.2218; Found 273.2203.

Mesityl(4-methylcycloheptyl)methanone (4cg): Yellow oil (77 mg, 60%), eluent combination: hexane/diethyl ether (100:1).



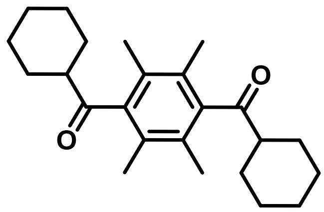
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 2H), 2.98 – 2.86 (m, 1H), 2.28 (s, 3H), 2.20 (s, 6H), 2.04 – 1.95 (m, 1H), 1.90 – 1.73 (m, 5H), 1.66 – 1.58 (m, 3H), 1.20 – 1.17 (m, 1H), 1.13 – 1.11(m, 2H), 0.93 – 0.9 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.8, 213.7, 139.3, 139.3, 138.3, 133.6, 133.5, 128.7, 54.1, 53.4, 38.2, 36.5, 36.1, 35.2, 34.3, 33.3, 30.2, 29.1, 28.5, 26.4, 26.3, 23.9, 23.8, 23.7, 21.1, 19.8 ppm; IR (KBr pellet): 3109, 2987, 2765, 1634, 1512, 1109, 967, 736 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{26}O$ 259.2061; Found 259.2046.

(2,3,5,6-Tetramethyl-1,4-phenylene)bis(cyclopentylmethanone) (4da): White solid (44 mg, 54%), eluent combination: hexane/diethyl ether (100:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19 – 3.11 (m, 2H), 2.17 (s, 3H), 2.07 (s, 9H), 1.86 (d, *J* = 5.1 Hz, 4H), 1.58 (s, 4H), 1.26 (d, *J* = 3.7 Hz, 4H), 0.90 - 0.85 (dd, *J* = 7.3, 3.6 Hz, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.4, 143.0, 128.8, 77.4, 77.1, 76.8, 54.1, 23.3, 22.7, 16.1 ppm ;IR (KBr pellet): 3098, 2891, 1703, 1590, 1209, 1098, 965, 739 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{30}O_2$ 327.2324; Found 327.2319.

(2,3,5,6-Tetramethyl-1,4-phenylene)bis(cyclohexylmethanone) (4db): White solid (62 mg, 71%), eluent combination: hexane/diethyl ether (100:1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 – 2.55 (m, 2H), 2.05 (s, 12H), 1.91 (d, *J* = 12.8 Hz, 4H), 1.81 (d, *J* = 6.2 Hz, 4H), 1.69 (d, *J* = 6.6 Hz, 2H), 1.40 (d, *J* = 11.6 Hz, 4H), 1.24 – 1.19 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.4, 142.6, 129.6, 52.9, 28.2, 26.0, 26.0, 17.1 ppm; IR (KBr pellet): 3103, 2963, 1692, 1579, 1192, 983, 702 cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{34}O_2$ 355.2637; Found 355.2621.

7. [1]H and [13]C NMR spectra for synthesized compounds

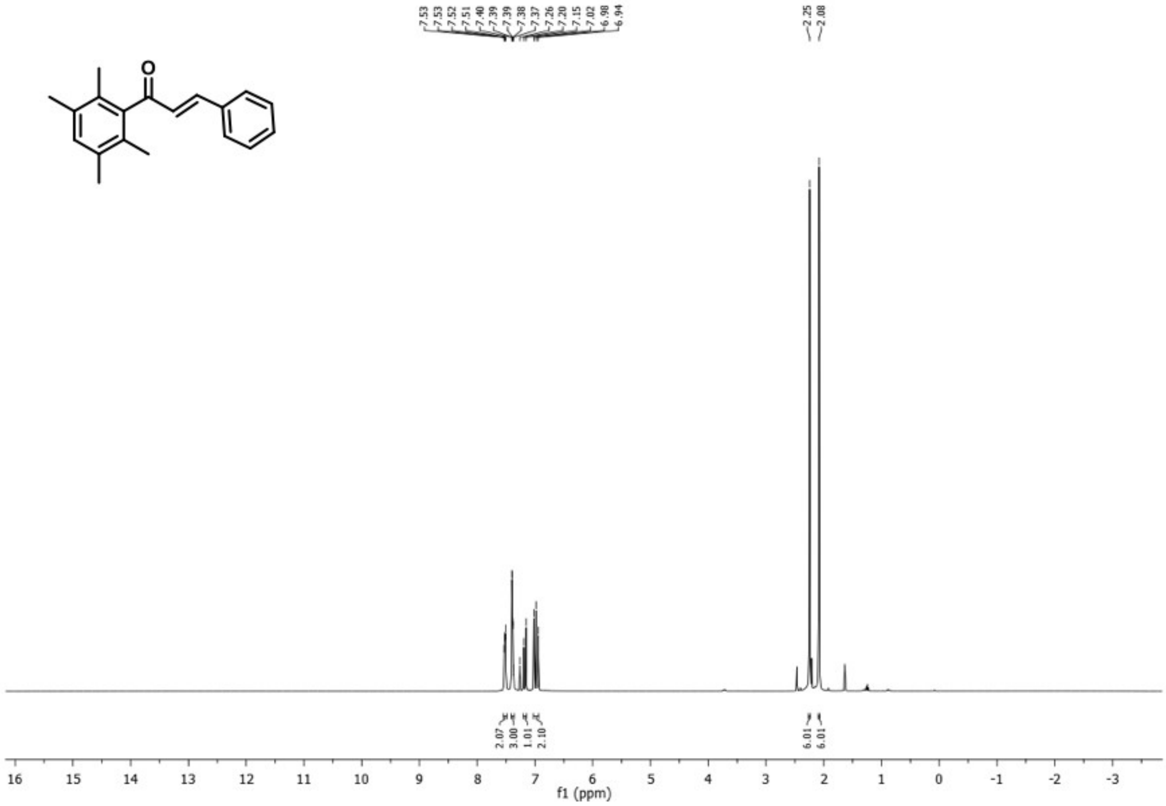


Figure S5. ^{1}H NMR spectrum (400 MHz) of **5a** in $CDCl_3$

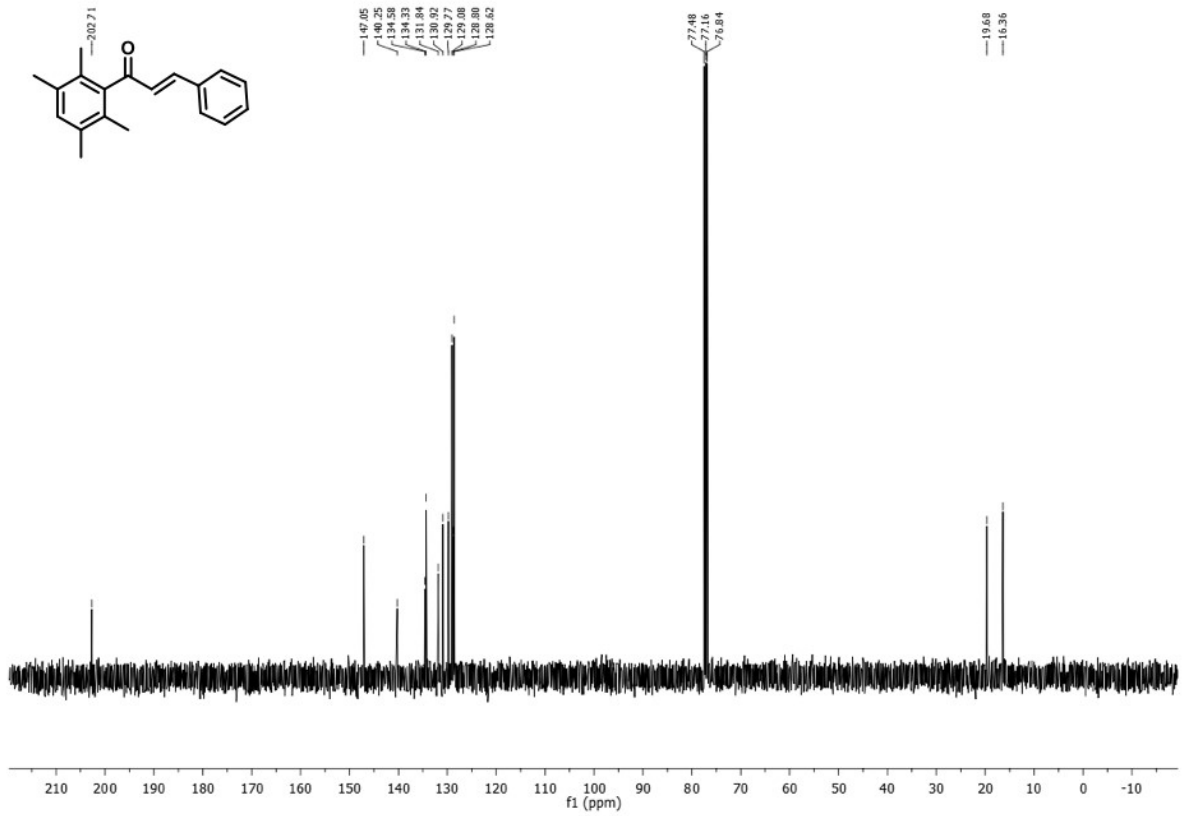


Figure S6. ^{13}C NMR spectrum (100 MHz) of **5a** in $CDCl_3$

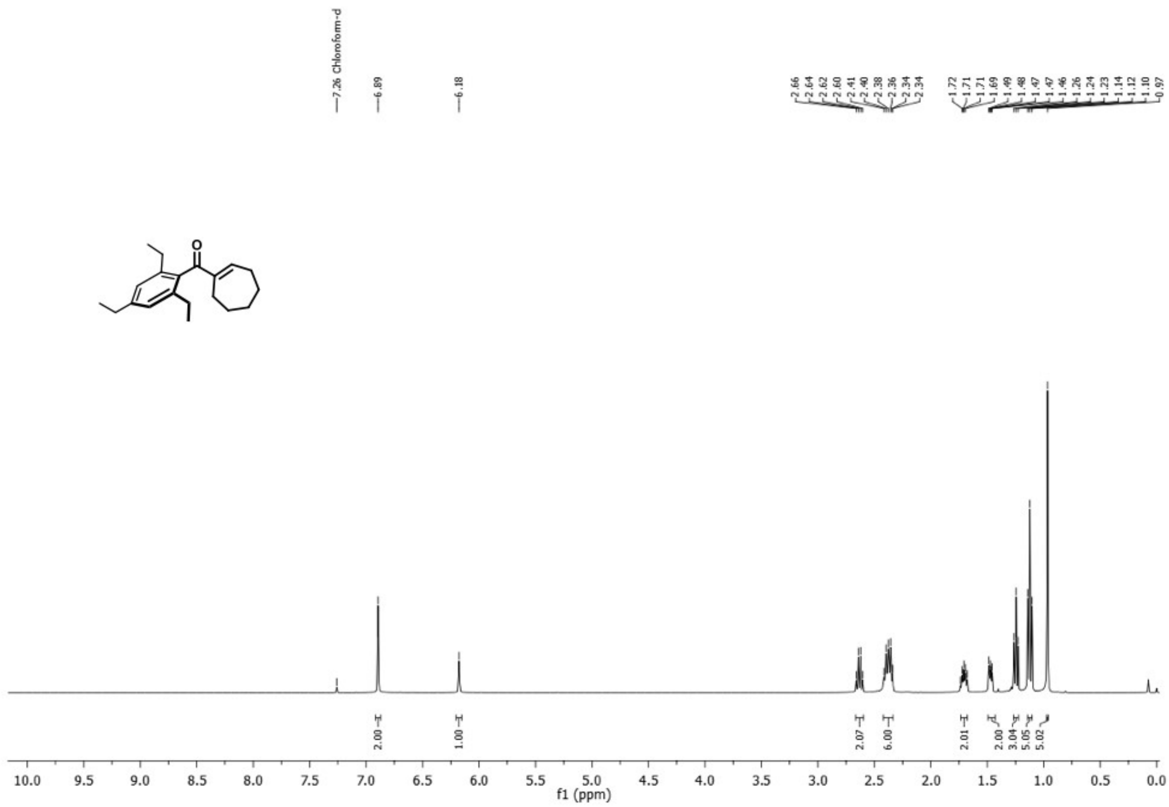


Figure S7. ^{1}H NMR spectrum (400 MHz) of **8a** in $CDCl_3$

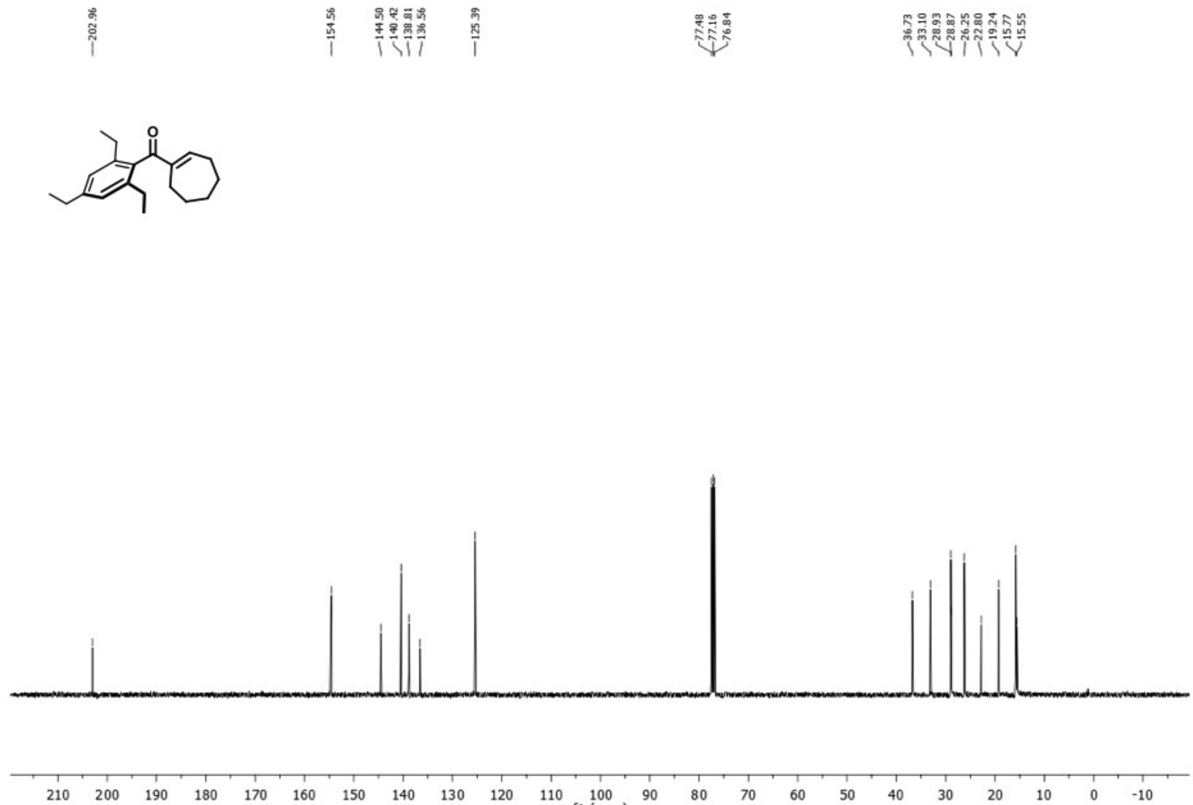


Figure S8. ^{13}C NMR spectrum (100 MHz) of **8a** in $CDCl_3$

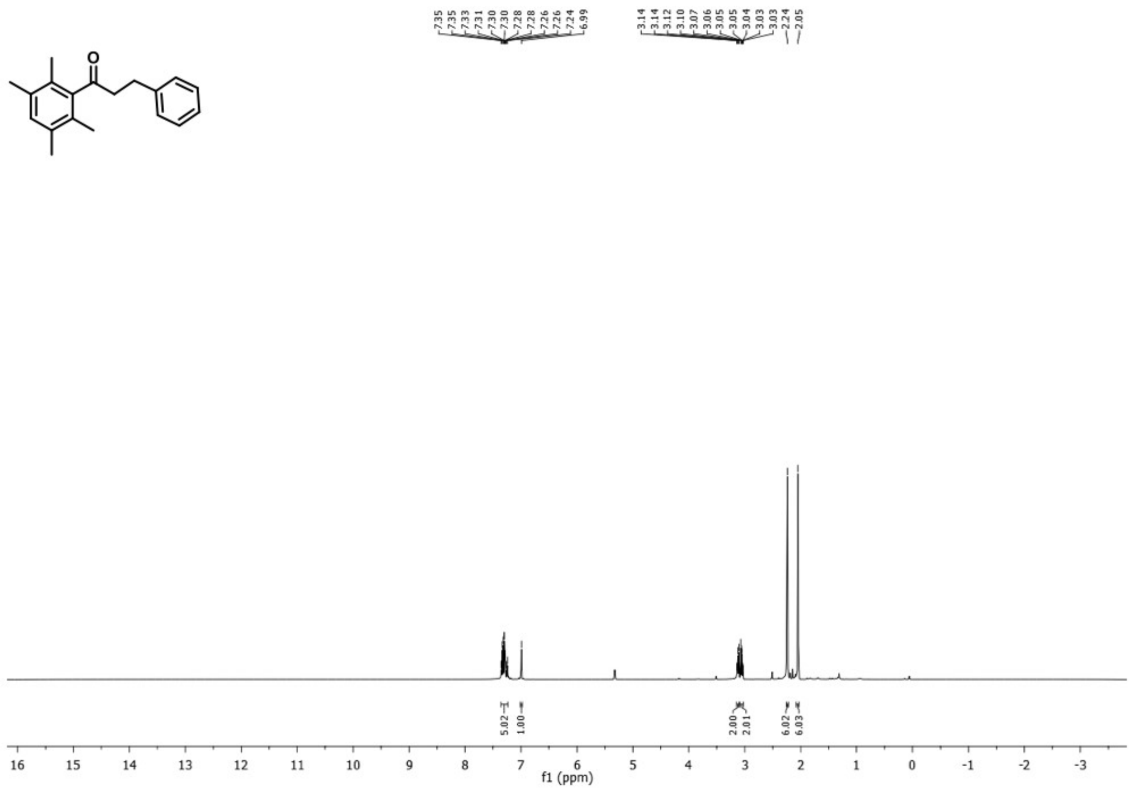


Figure S9. ^{1}H NMR spectrum (400 MHz) of **3-Phenyl-1-(2,3,5,6-tetramethylphenyl)propan-1-one** in $CDCl_3$

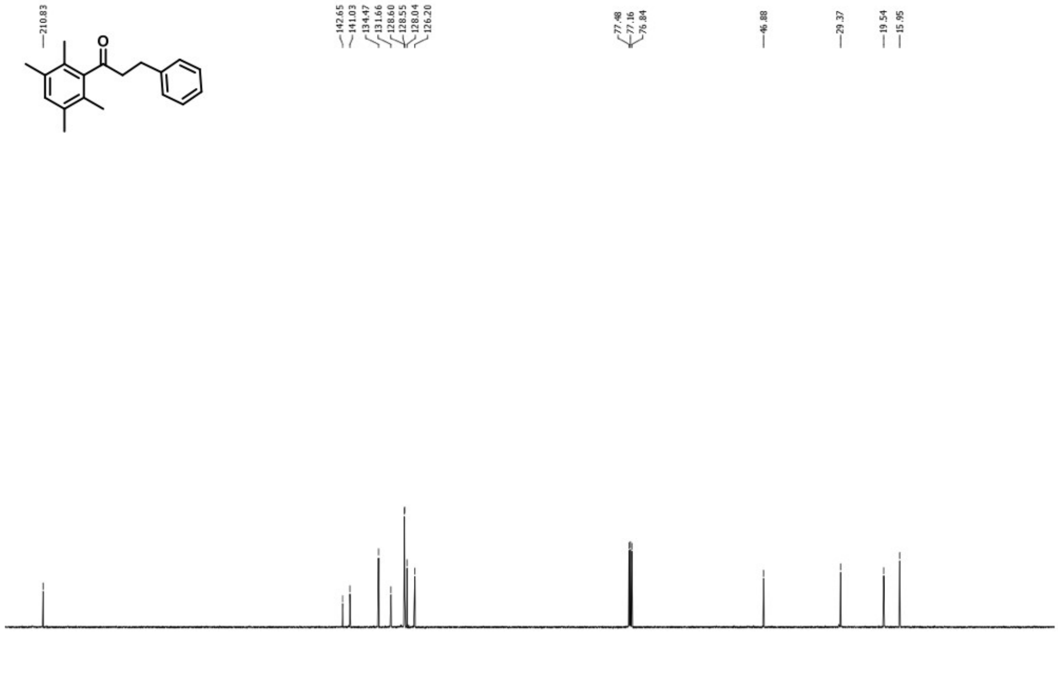


Figure S10. ^{13}C NMR spectrum (100 MHz) of **3-Phenyl-1-(2,3,5,6-tetramethylphenyl)propan-1-one** in $CDCl_3$

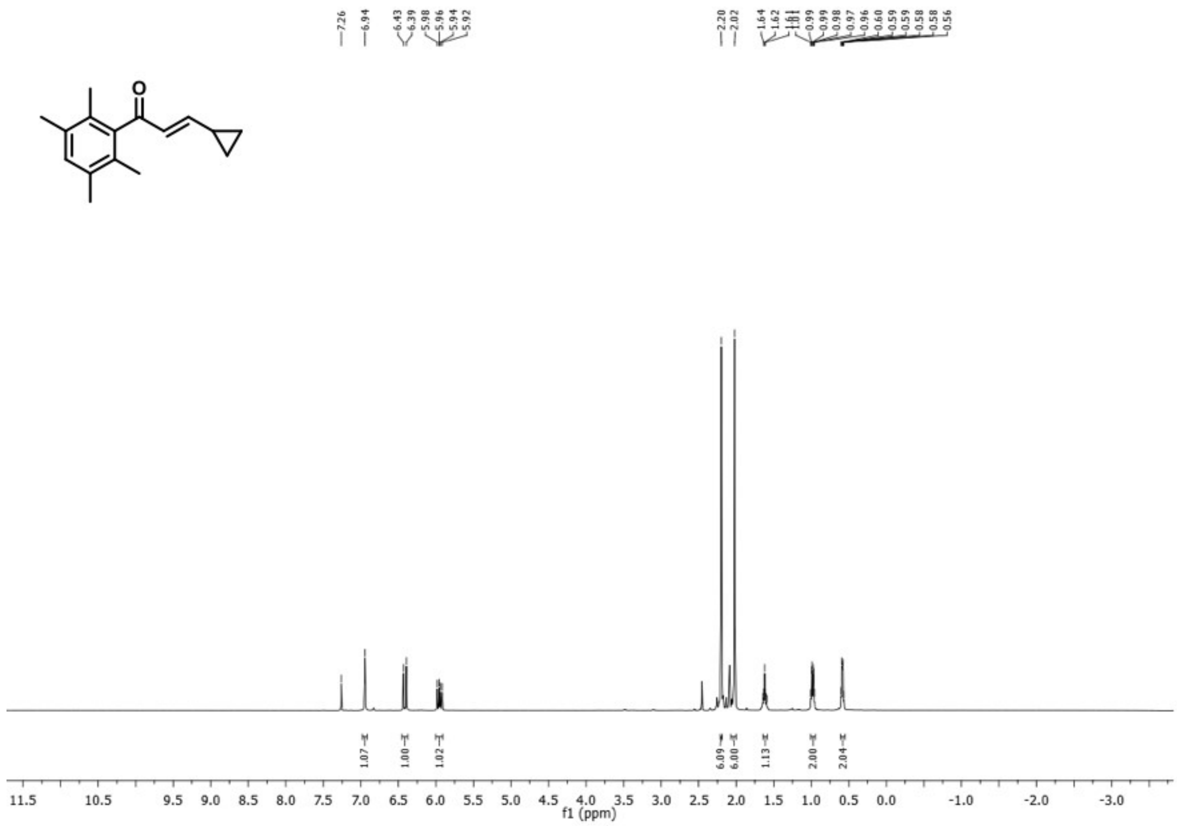


Figure S11. ^{1}H NMR spectrum (400 MHz) of **9** in $CDCl_3$

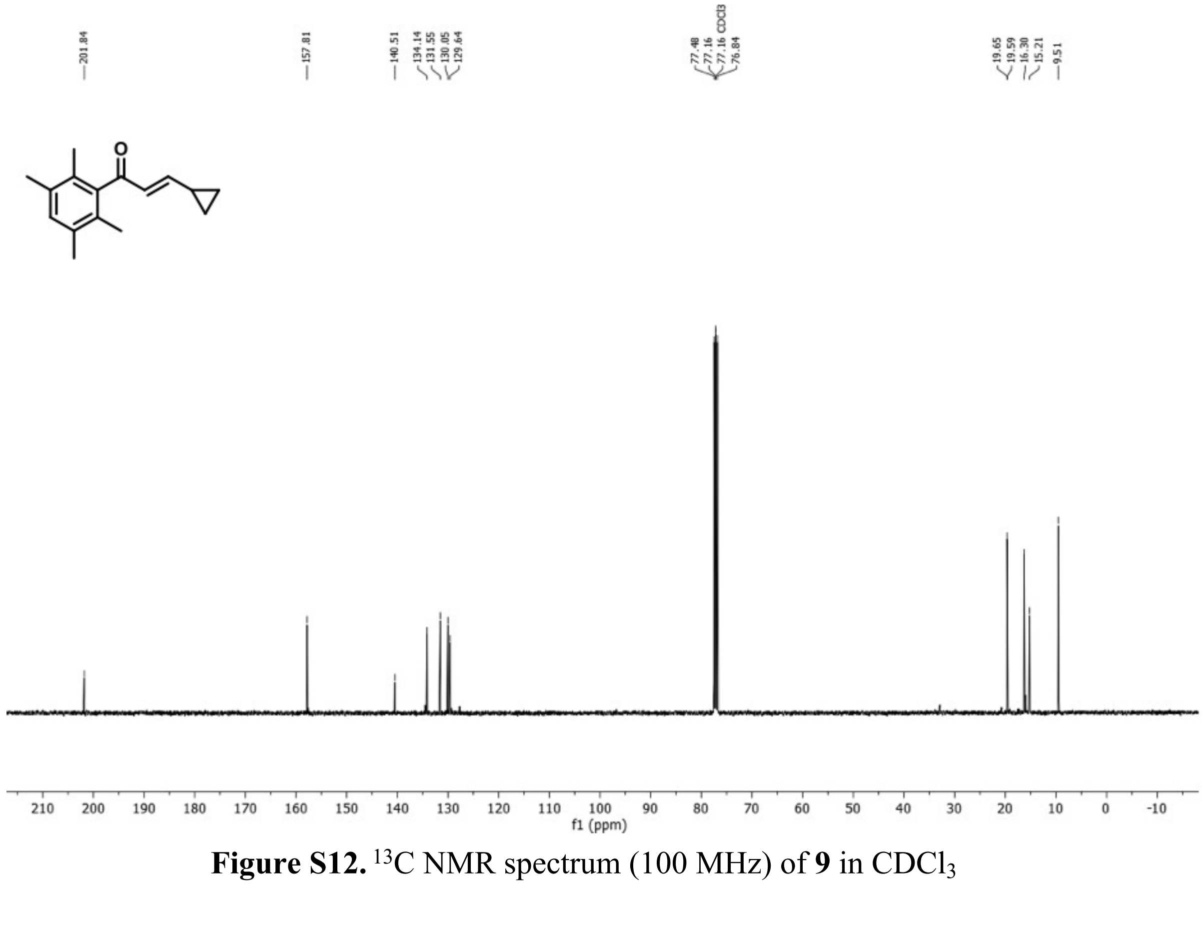


Figure S12. ^{13}C NMR spectrum (100 MHz) of **9** in $CDCl_3$

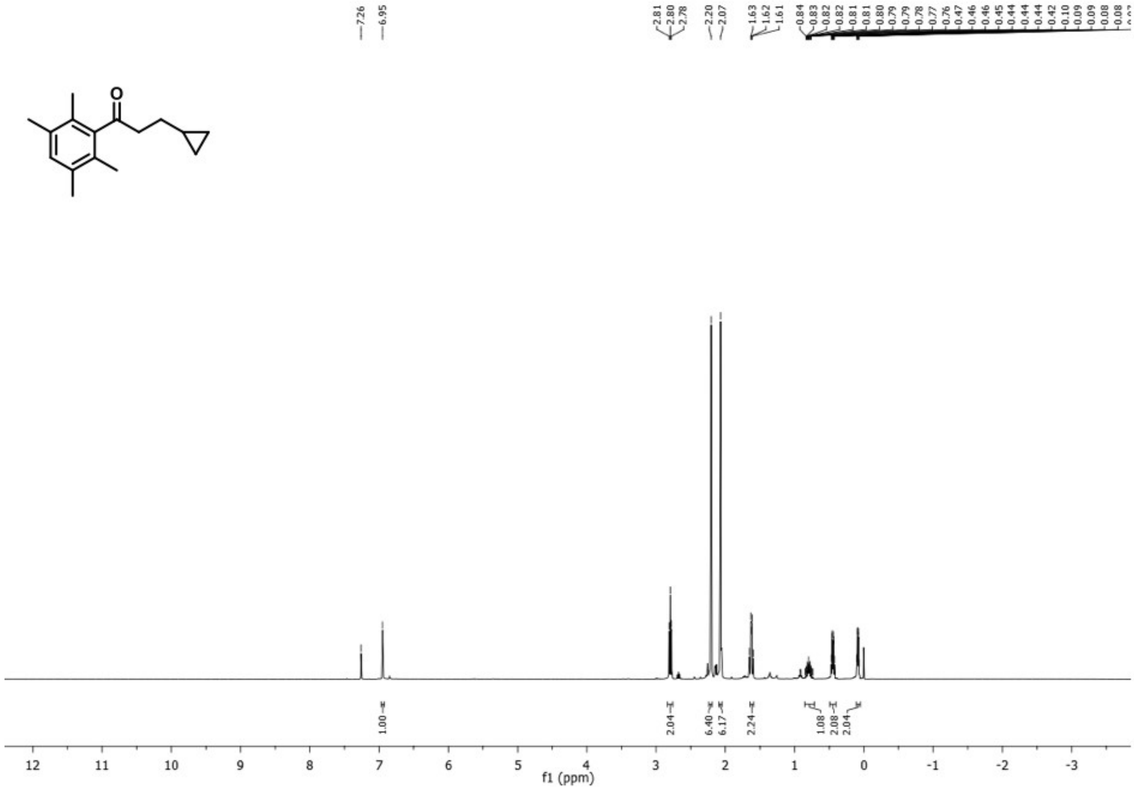


Figure S13. ^{1}H NMR spectrum (400 MHz) of **3-cyclopropyl-1-(2,3,5,6-tetramethylphenyl)propan-1-one (4bb')** in $CDCl_3$

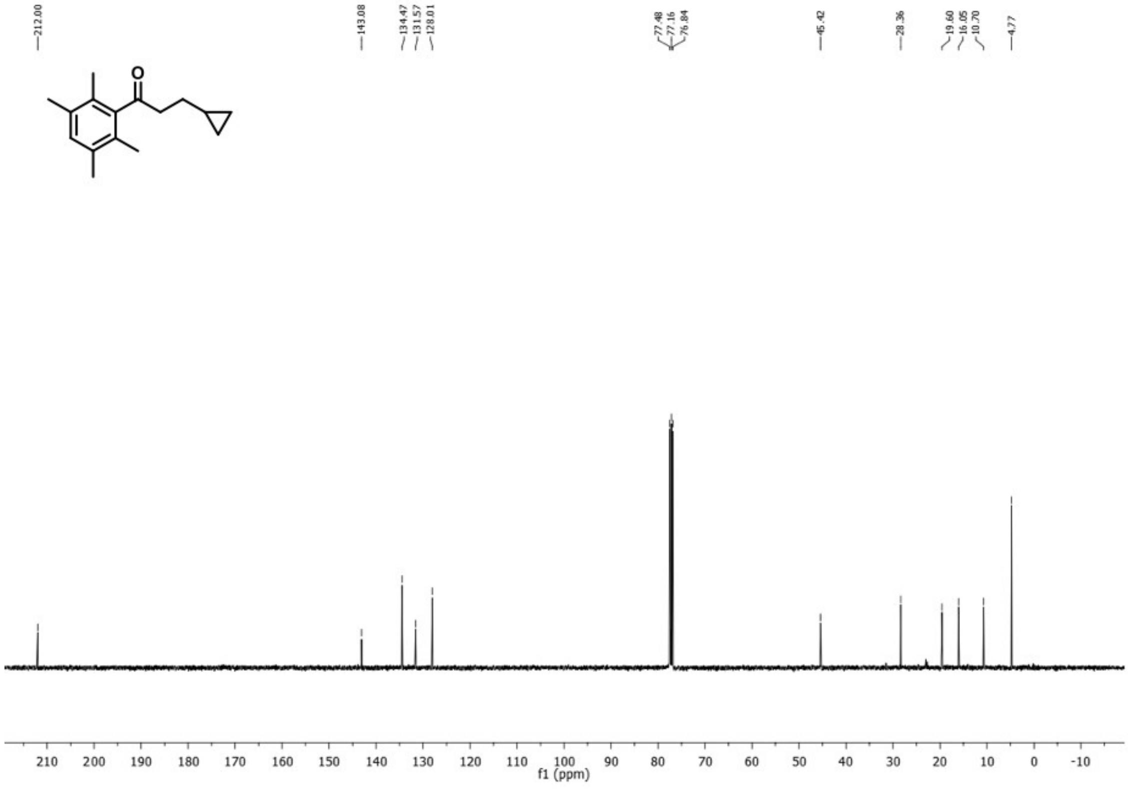


Figure S14. ^{13}C NMR spectrum (100 MHz) of **3-cyclopropyl-1-(2,3,5,6-tetramethylphenyl)propan-1-one (4bb')** in $CDCl_3$

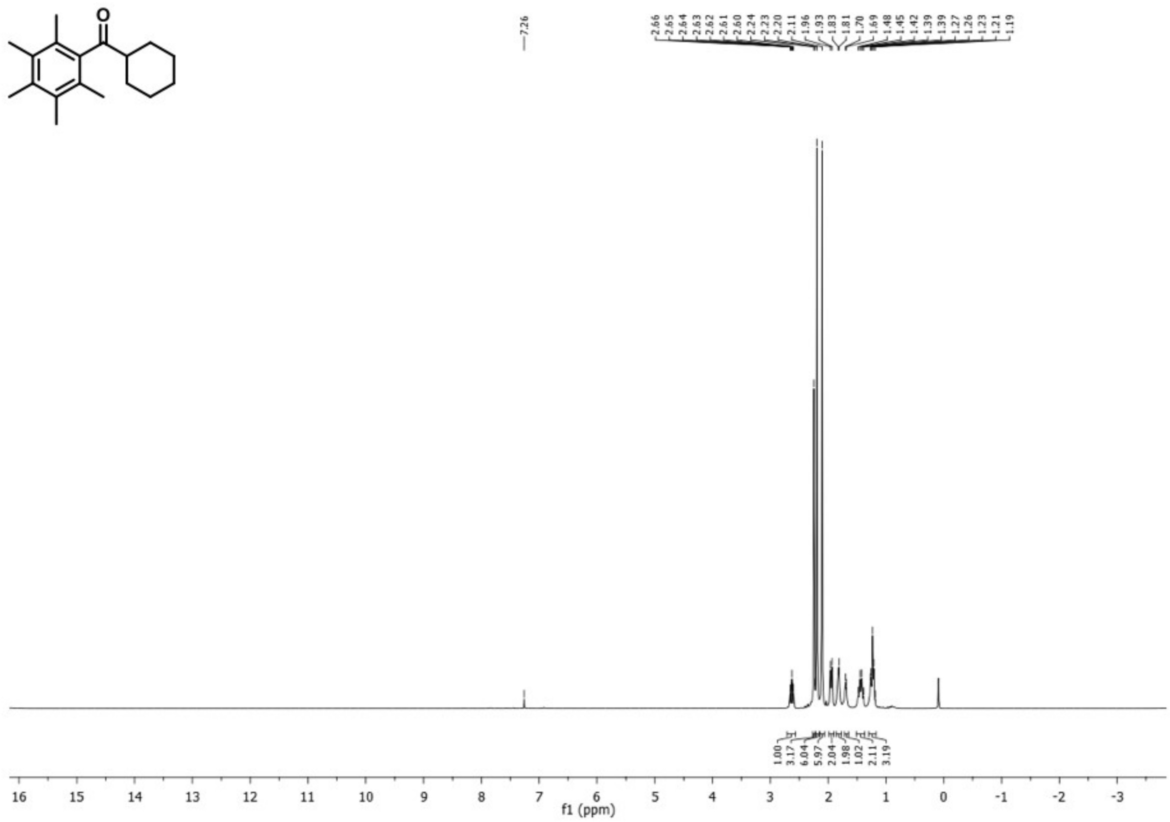


Figure S15. ^{1}H NMR spectrum (400 MHz) of **(4aa)** in $CDCl_3$

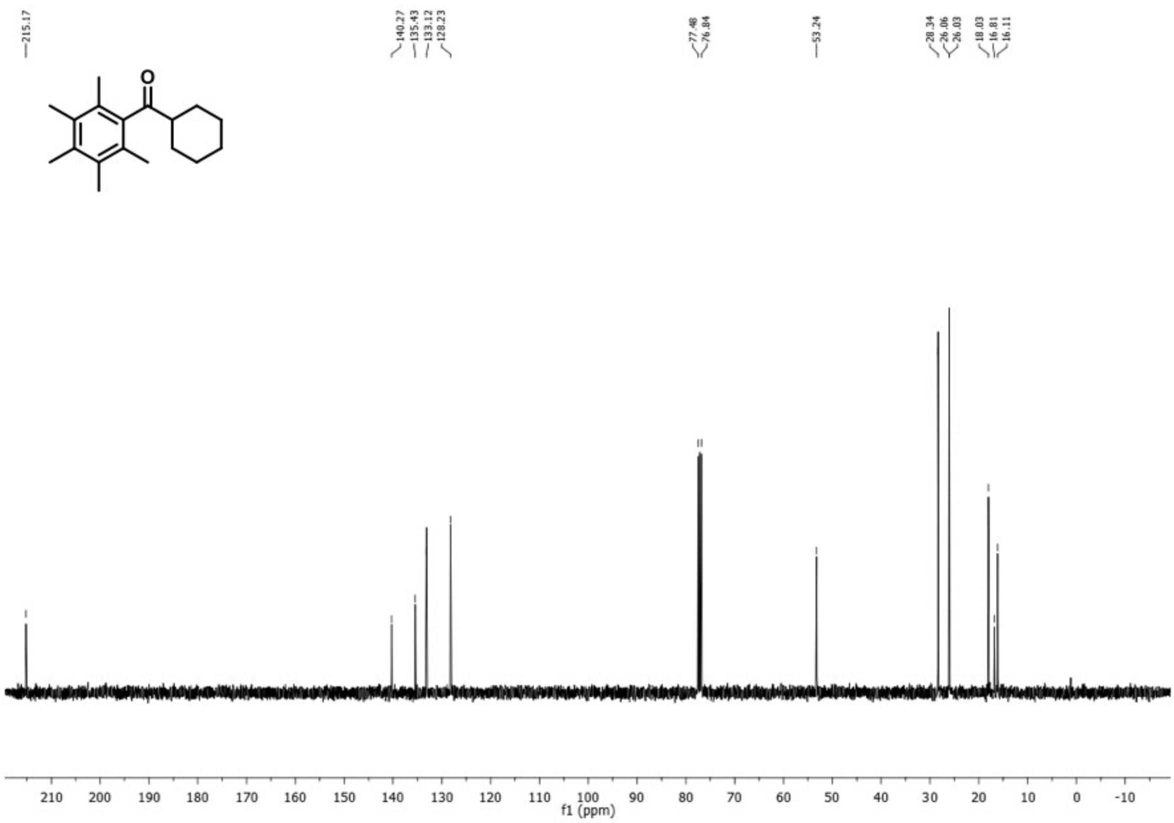


Figure S16. ^{13}C NMR spectrum (100 MHz) of **(4aa)** in $CDCl_3$

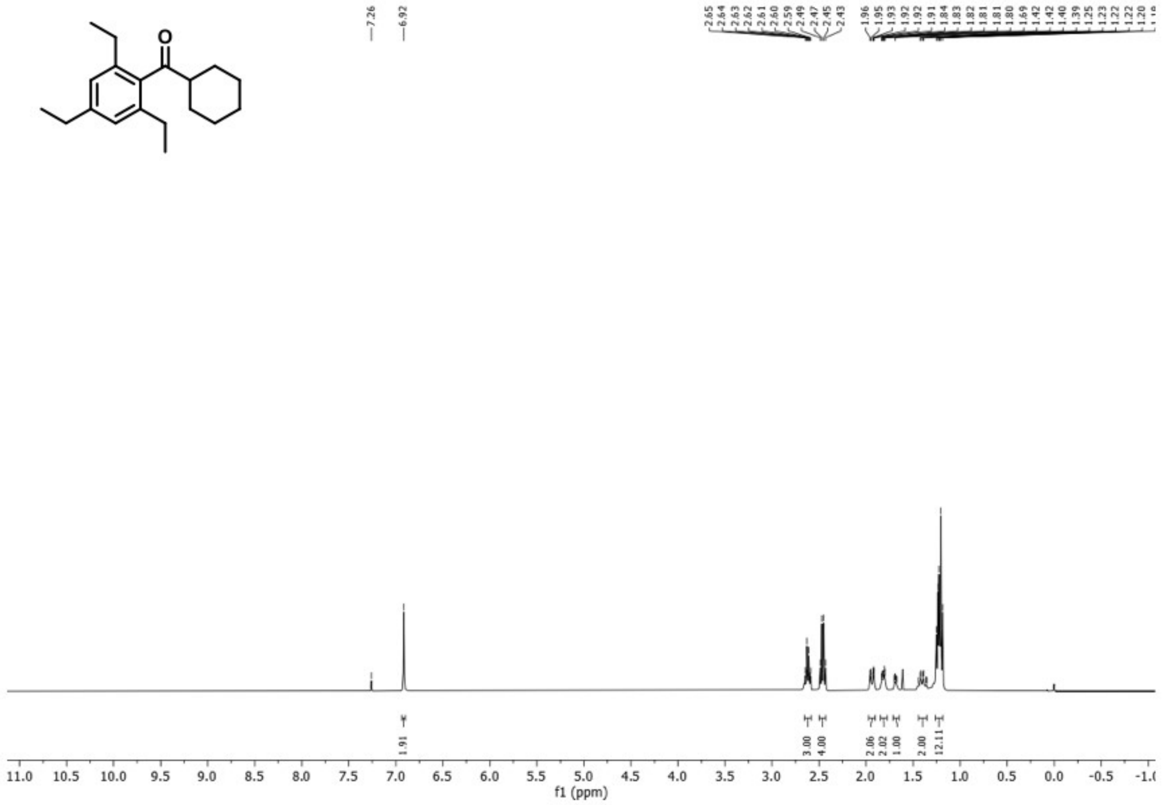


Figure S17. ^{1}H NMR spectrum (400 MHz) of **(4ab)** in $CDCl_3$

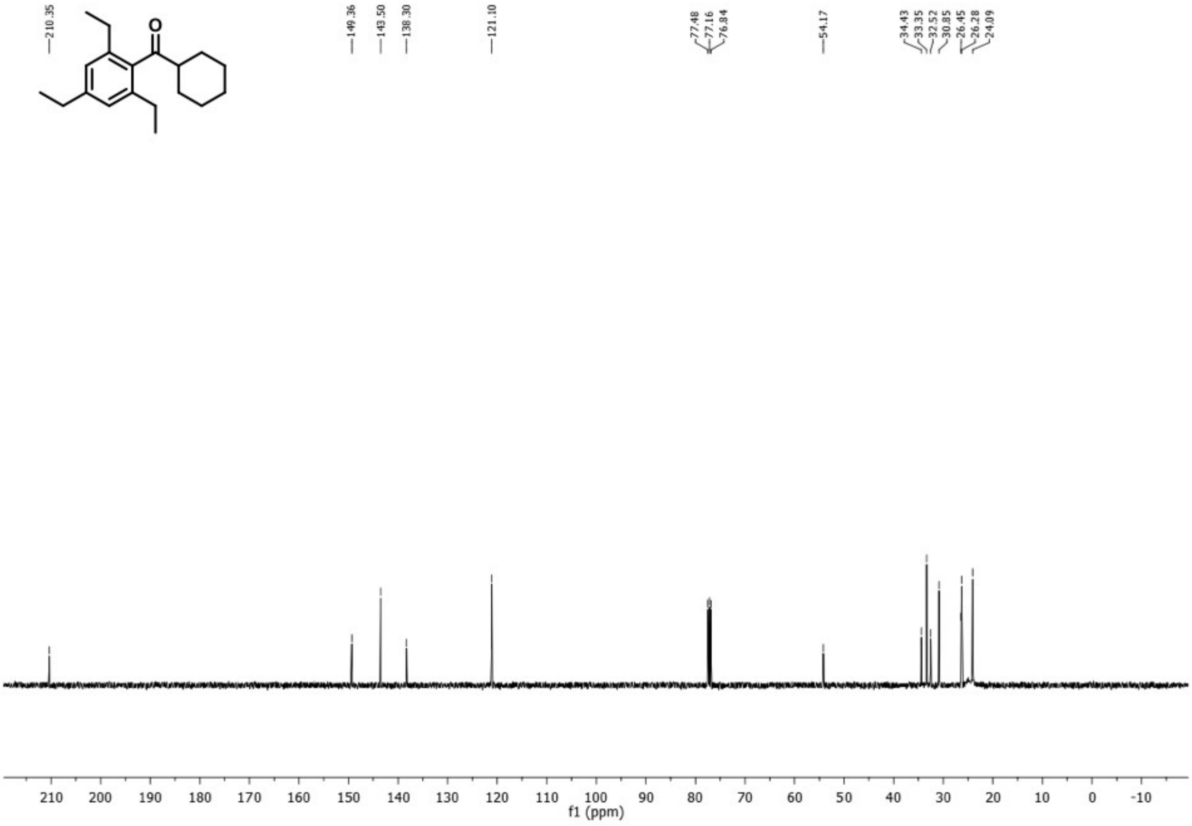


Figure S18. ^{13}C NMR spectrum (100 MHz) of **(4ab)** in $CDCl_3$

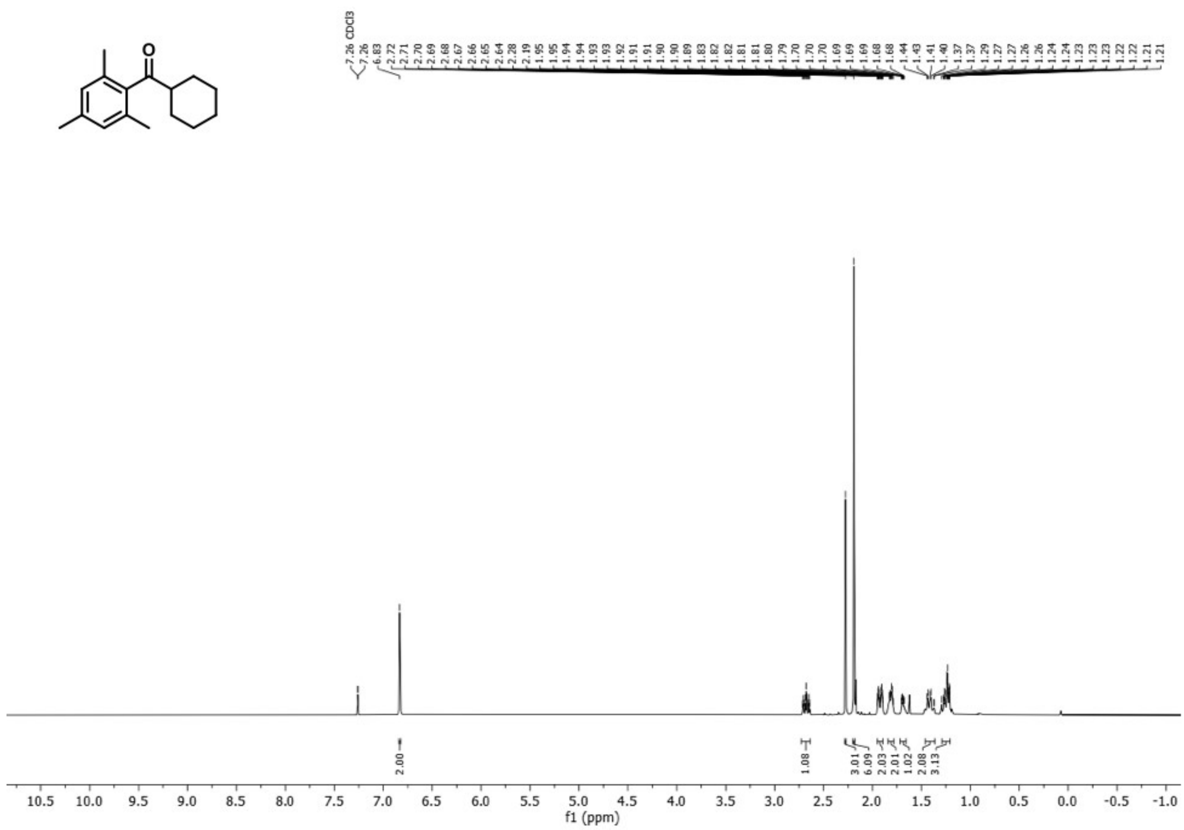


Figure S19. ^{1}H NMR spectrum (400 MHz) of **(4ac)** in $CDCl_3$

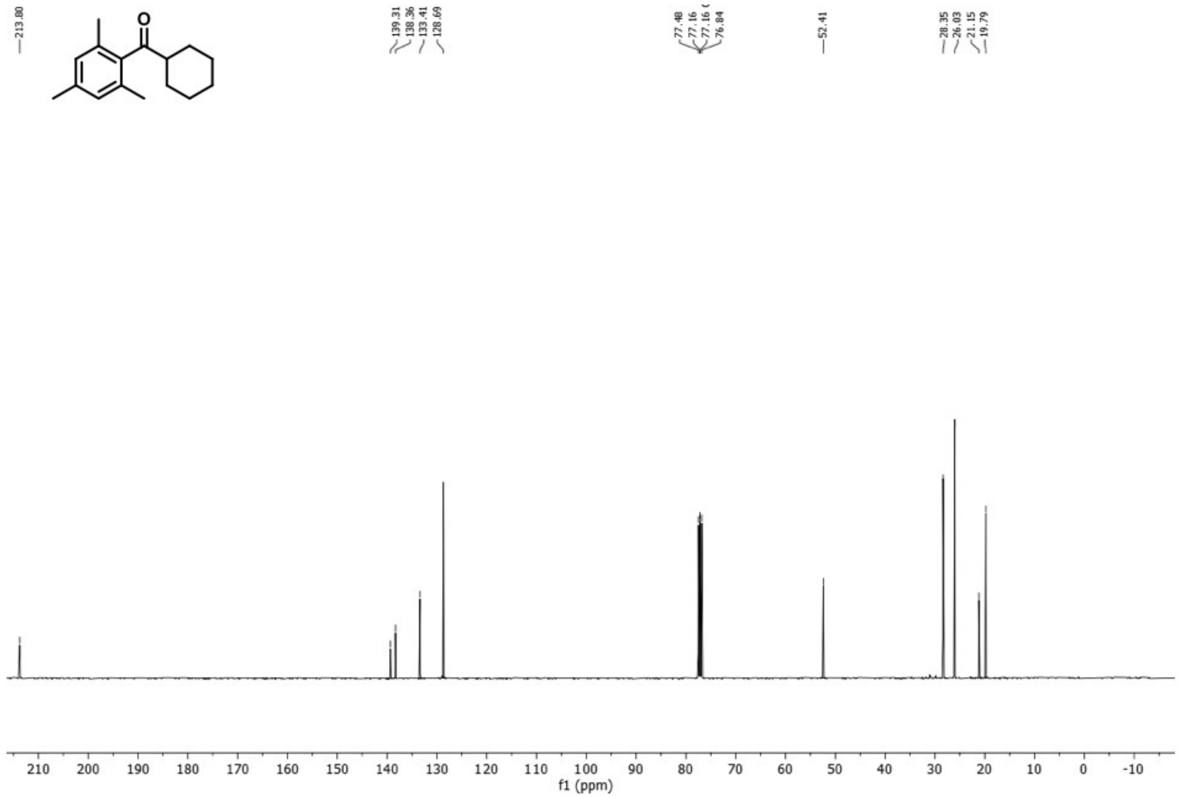


Figure S20. ^{13}C NMR spectrum (100 MHz) of **(4ac)** in $CDCl_3$

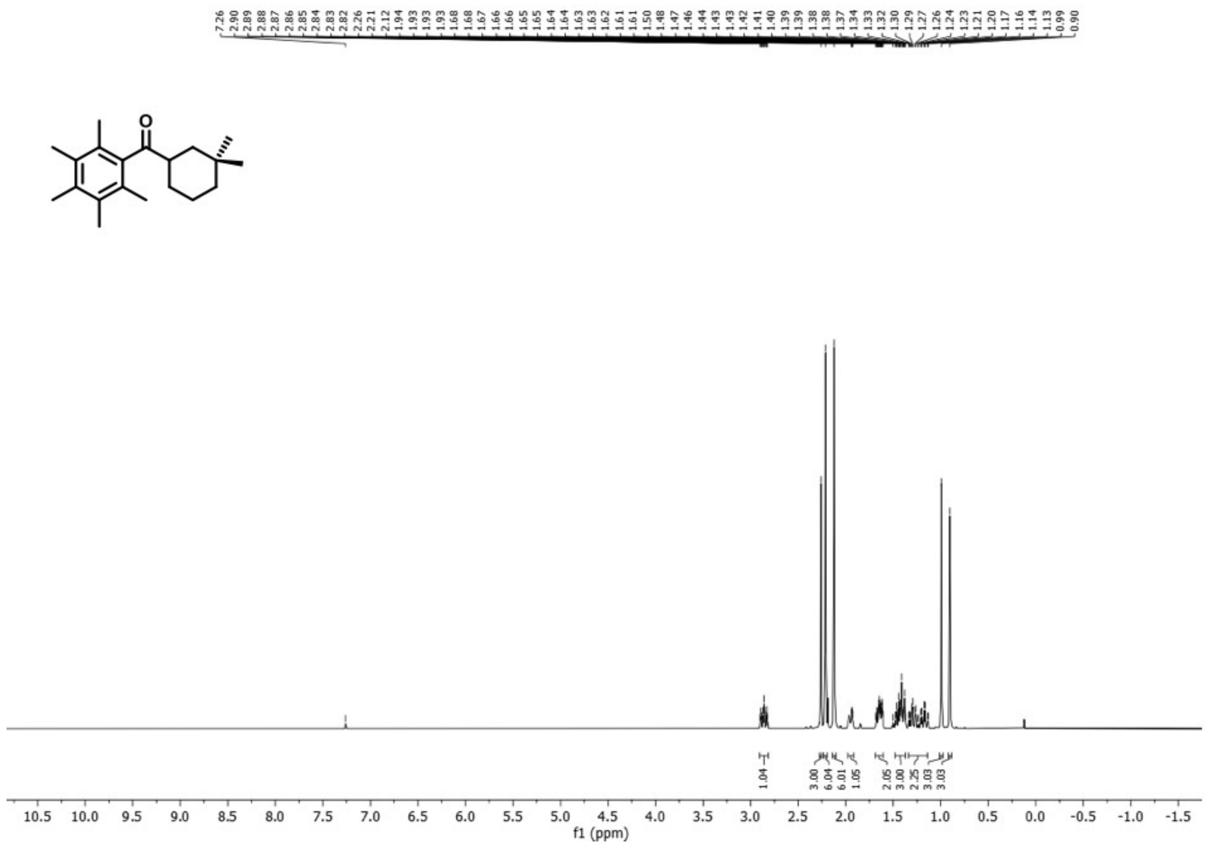


Figure S21. ^{1}H NMR spectrum (400 MHz) of **(4ad)** in $CDCl_3$

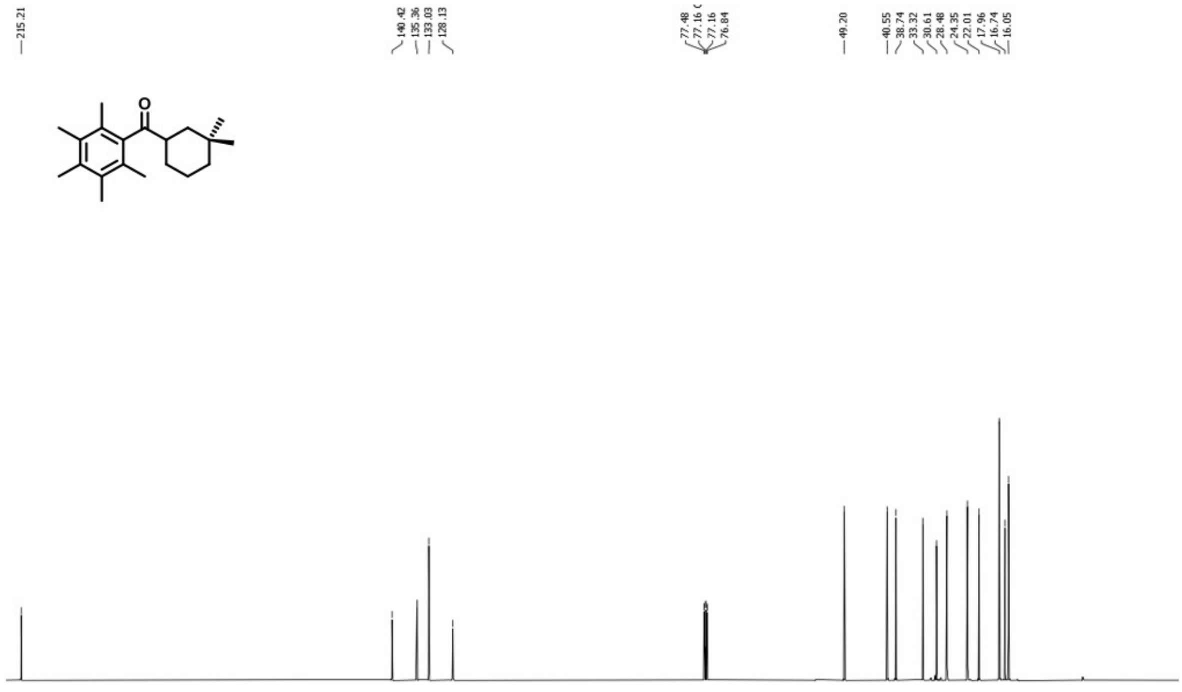


Figure S22. ^{13}C NMR spectrum (100 MHz) of **(4ad)** in $CDCl_3$

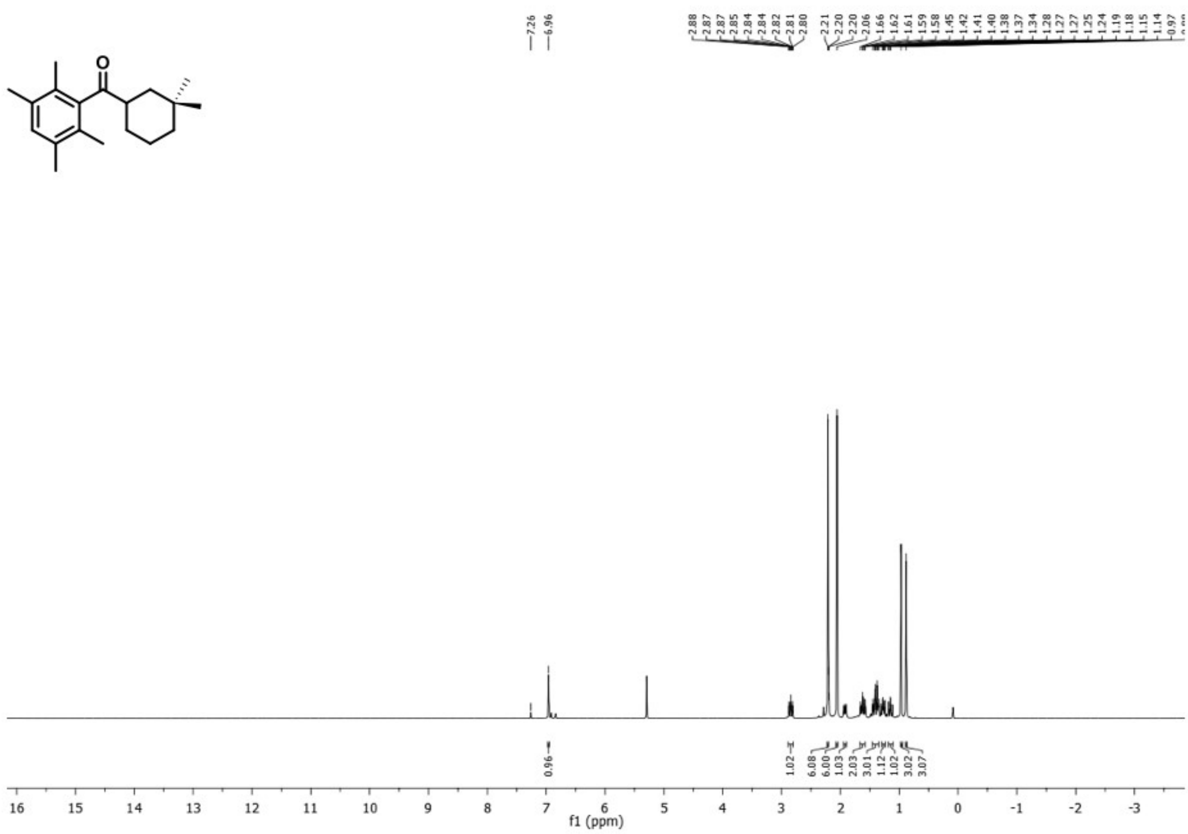


Figure S23. ^{1}H NMR spectrum (400 MHz) of **(4ae)** in $CDCl_3$

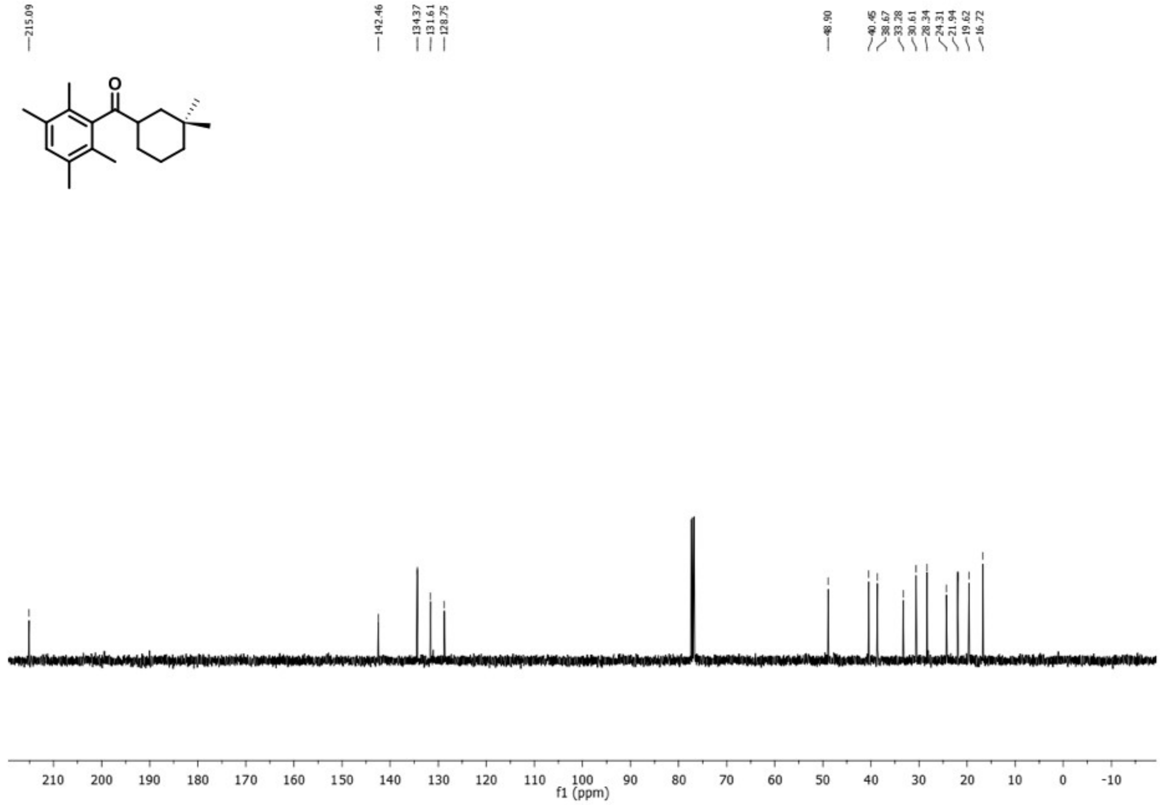


Figure S24. ^{13}C NMR spectrum (100 MHz) of **(4ae)** in $CDCl_3$

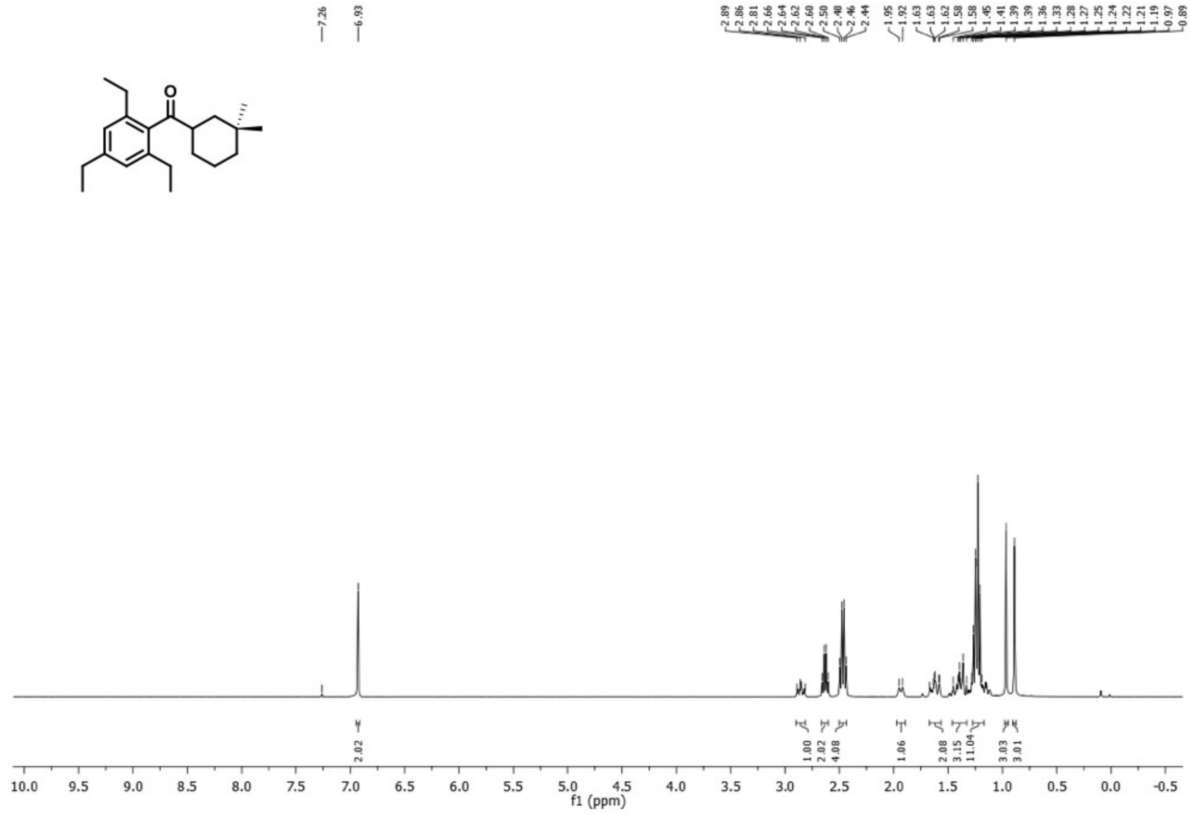


Figure S25. ^{1}H NMR spectrum (400 MHz) of **(4af)** in $CDCl_3$

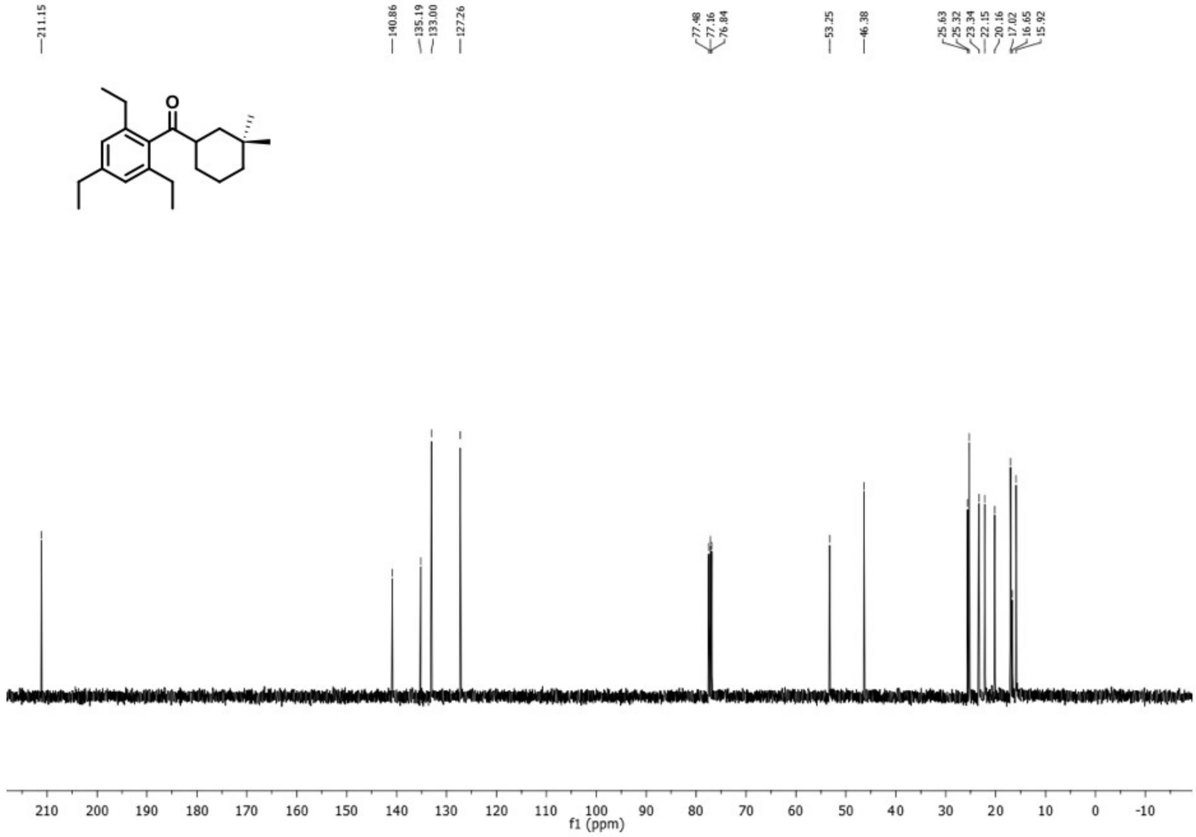


Figure S26. ^{13}C NMR spectrum (100 MHz) of **(4af)** in $CDCl_3$

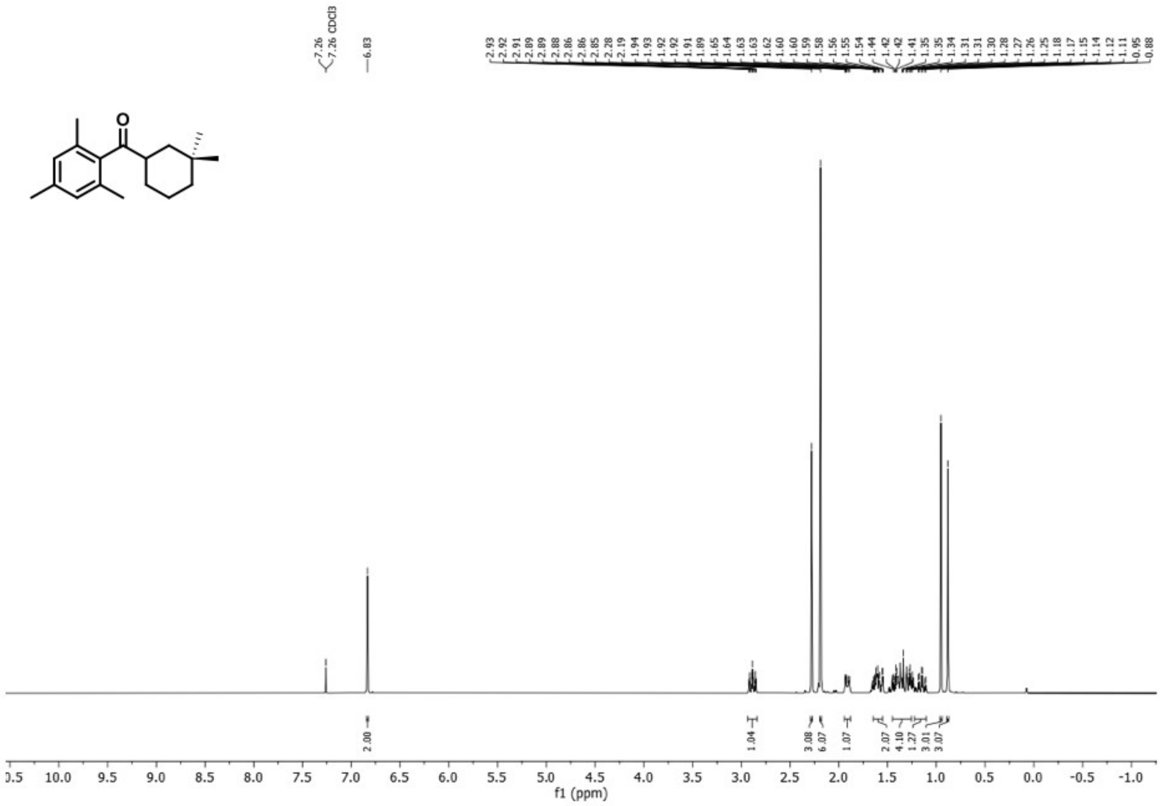


Figure S27. ^{1}H NMR spectrum (400 MHz) of **(4ag)** in $CDCl_3$

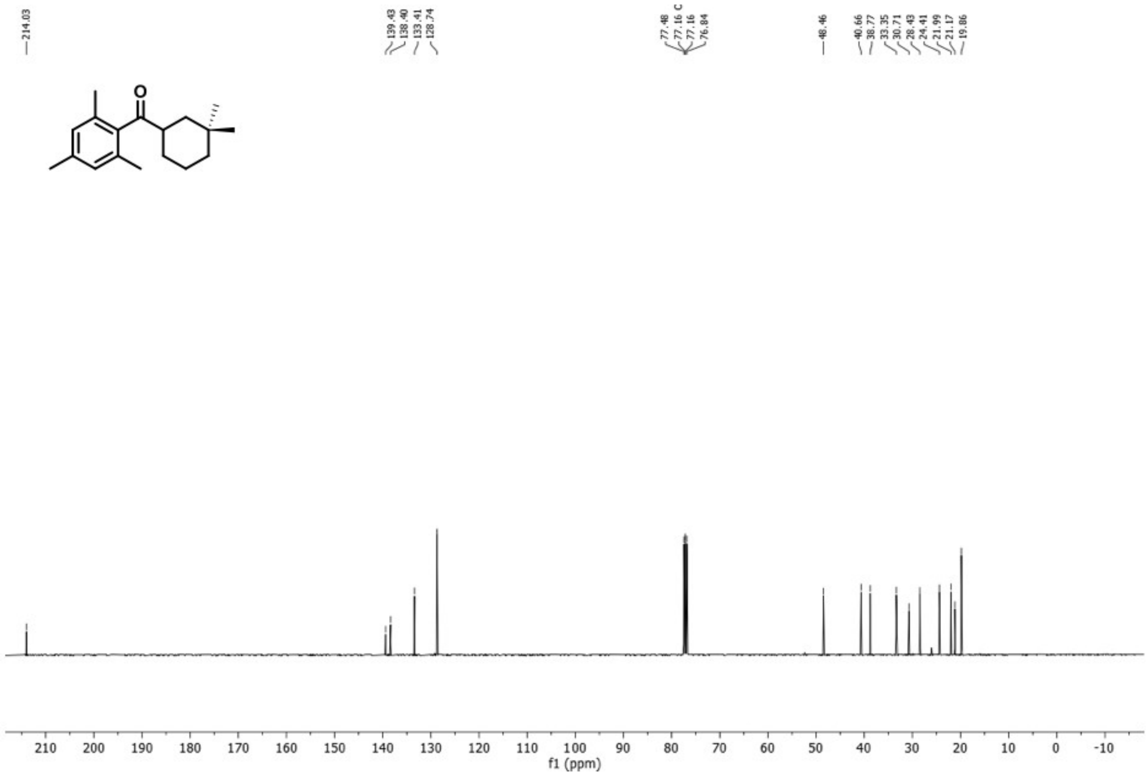


Figure S28. ^{13}C NMR spectrum (100 MHz) of **(4ag)** in $CDCl_3$

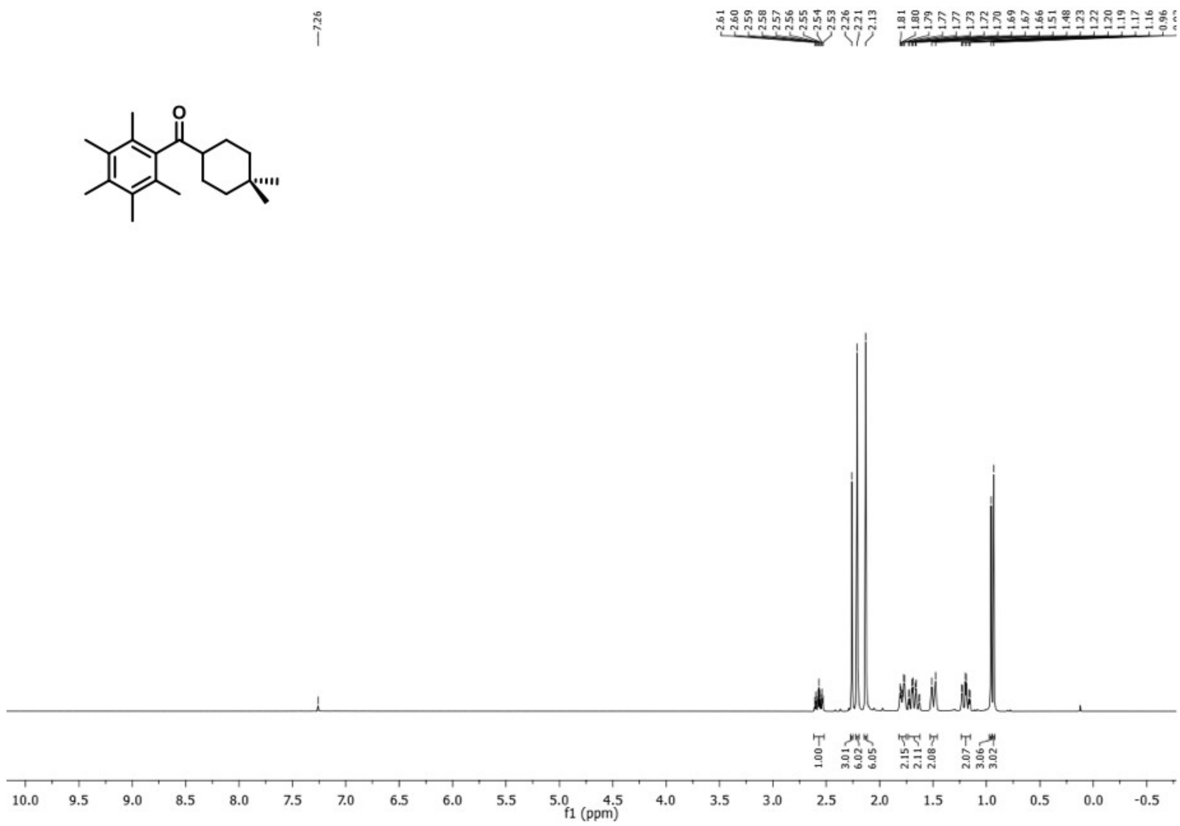


Figure S29. ^{1}H NMR spectrum (400 MHz) of **(4ah)** in $CDCl_3$

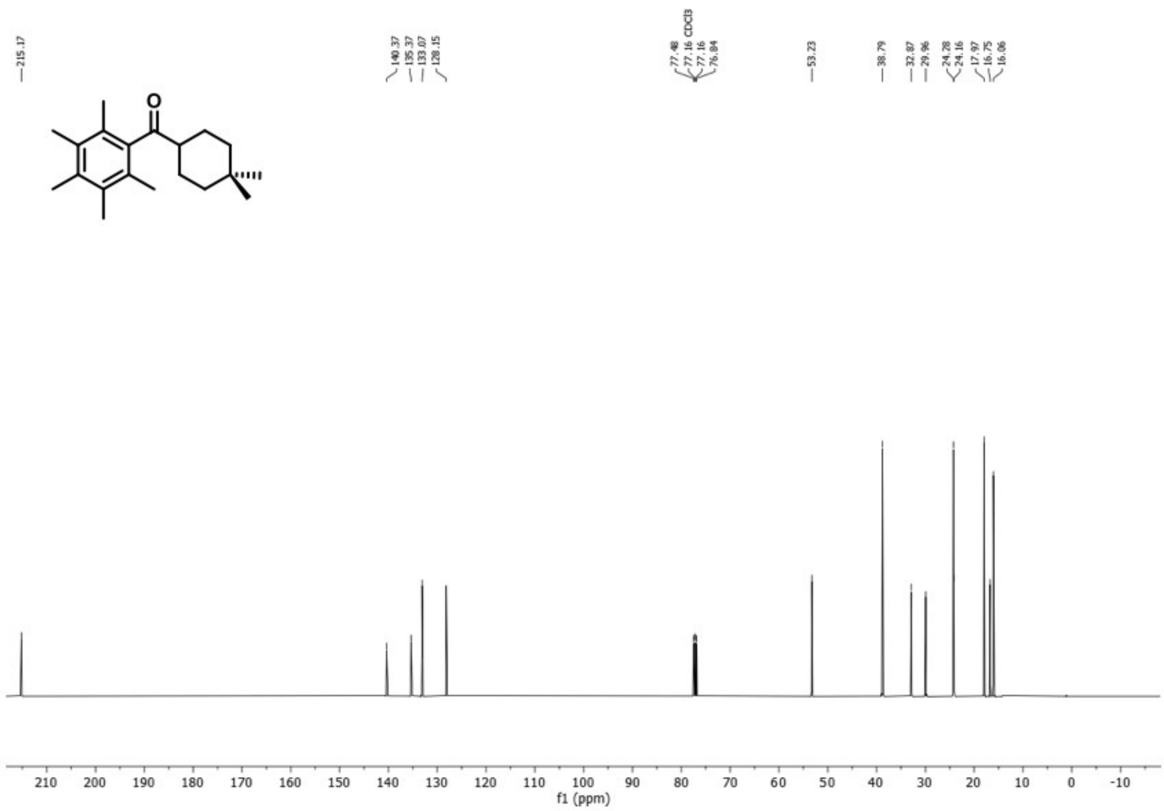


Figure S30. ^{13}C NMR spectrum (100 MHz) of **(4ah)** in $CDCl_3$

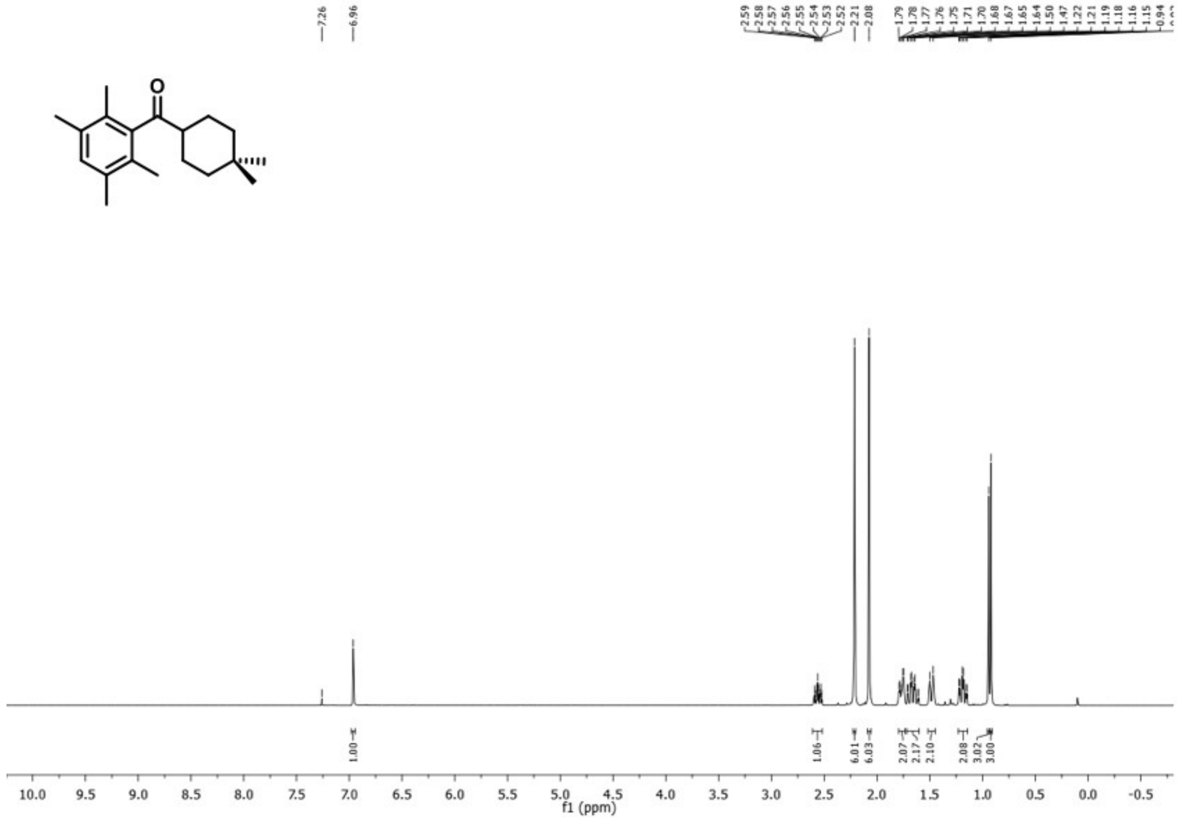


Figure S31. ^{1}H NMR spectrum (400 MHz) of **(4ai)** in $CDCl_3$

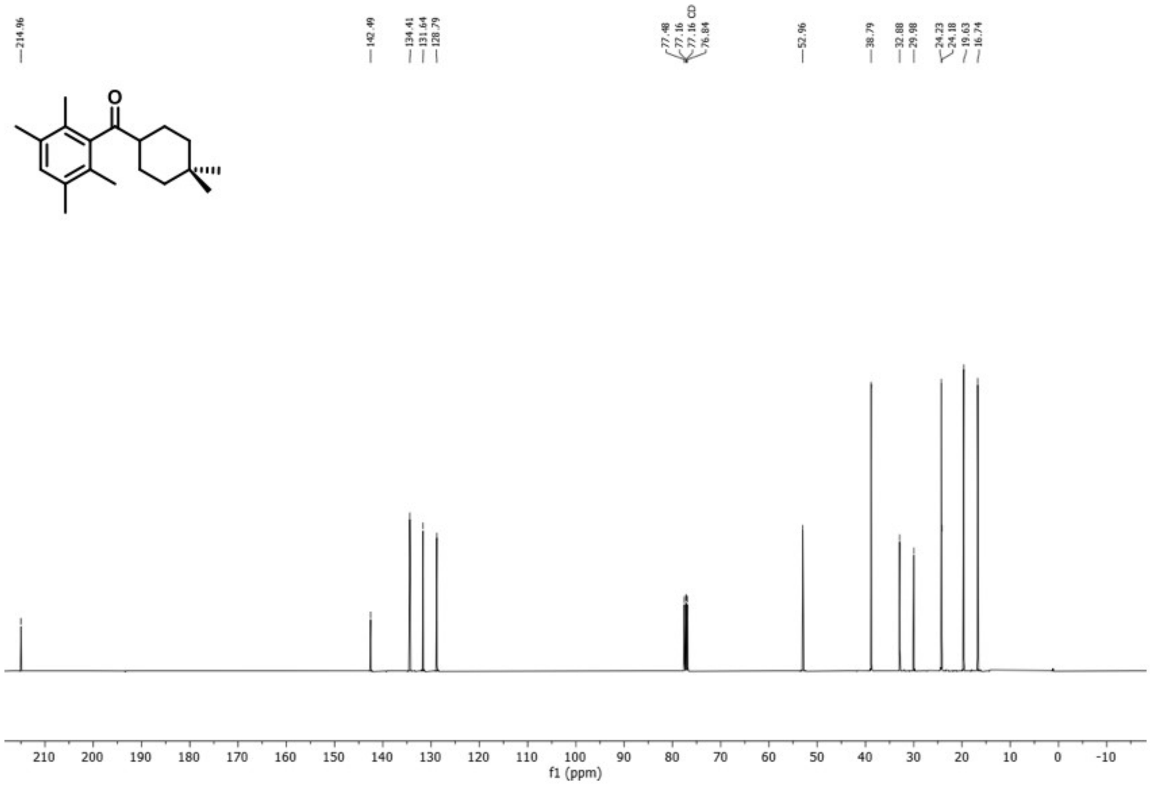


Figure S32. ^{13}C NMR spectrum (100 MHz) of **(4ai)** in $CDCl_3$

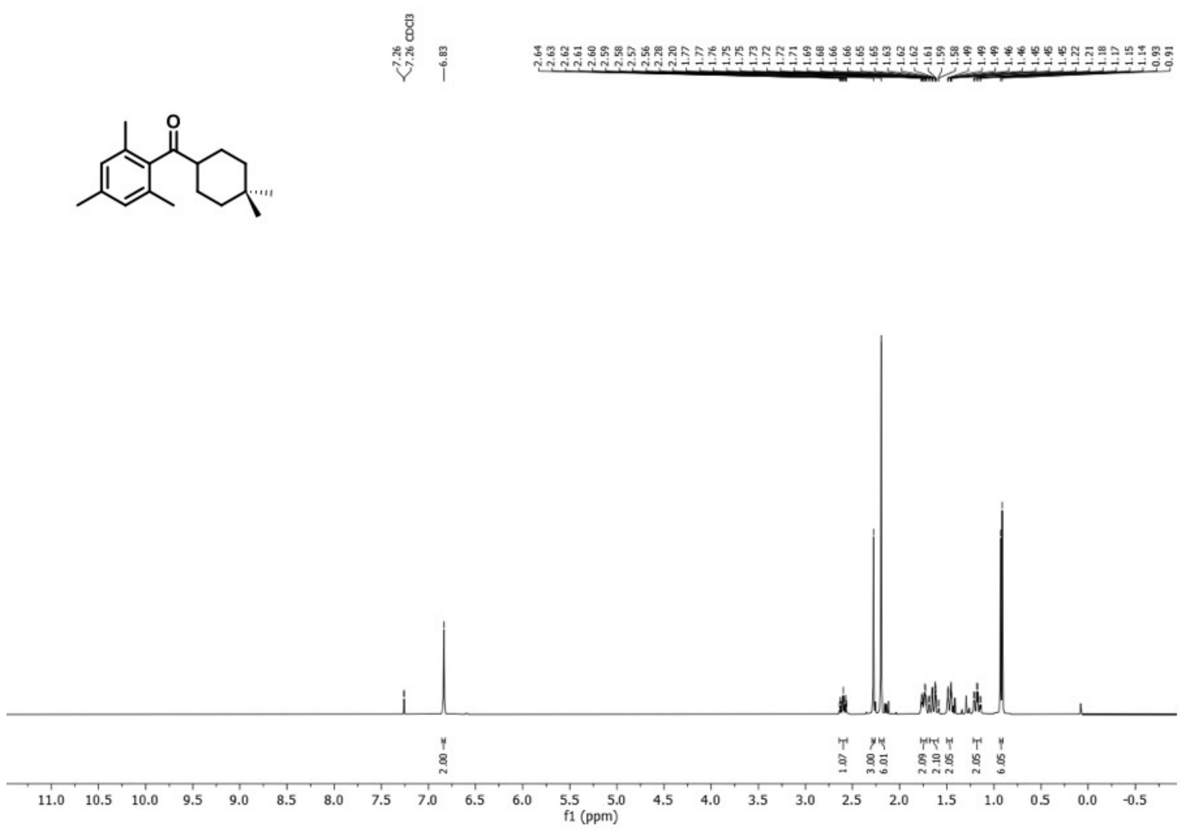


Figure S33. ^{1}H NMR spectrum (400 MHz) of **(4aj)** in $CDCl_3$

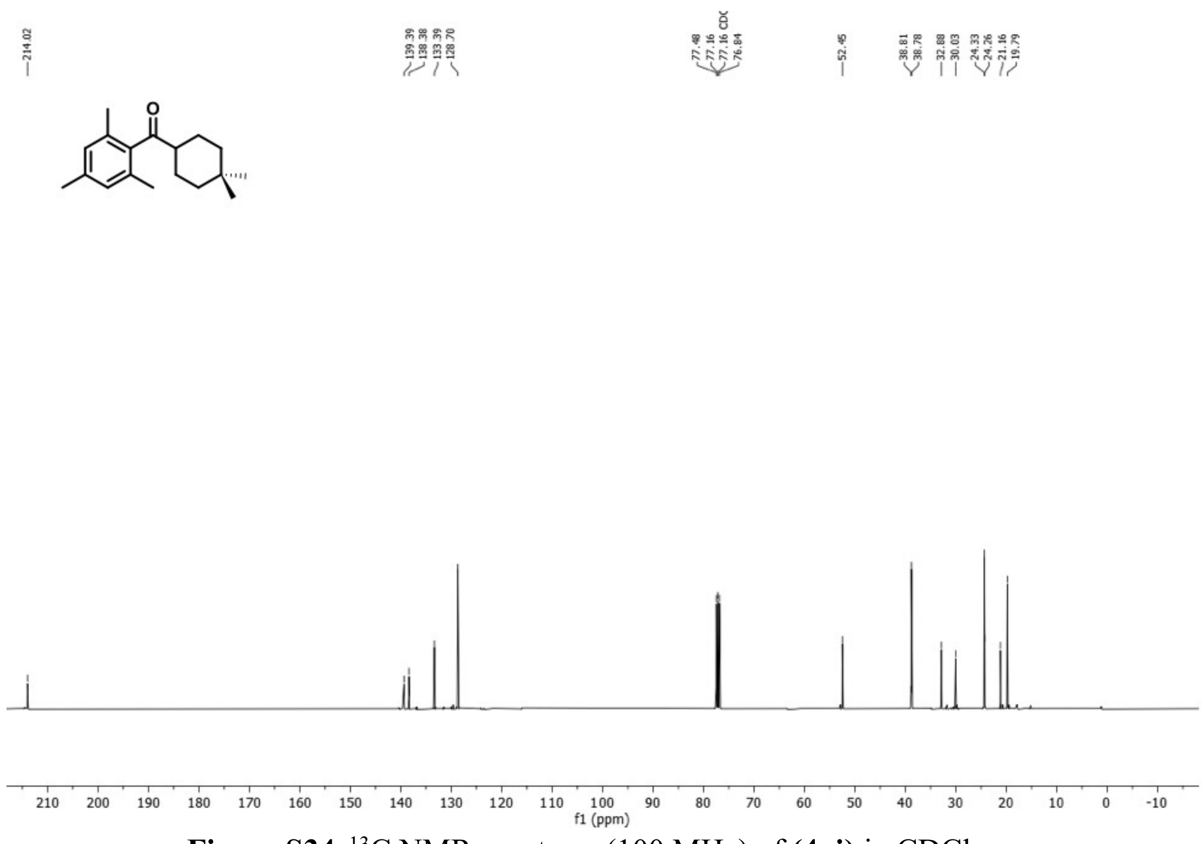


Figure S34. ^{13}C NMR spectrum (100 MHz) of **(4aj)** in $CDCl_3$

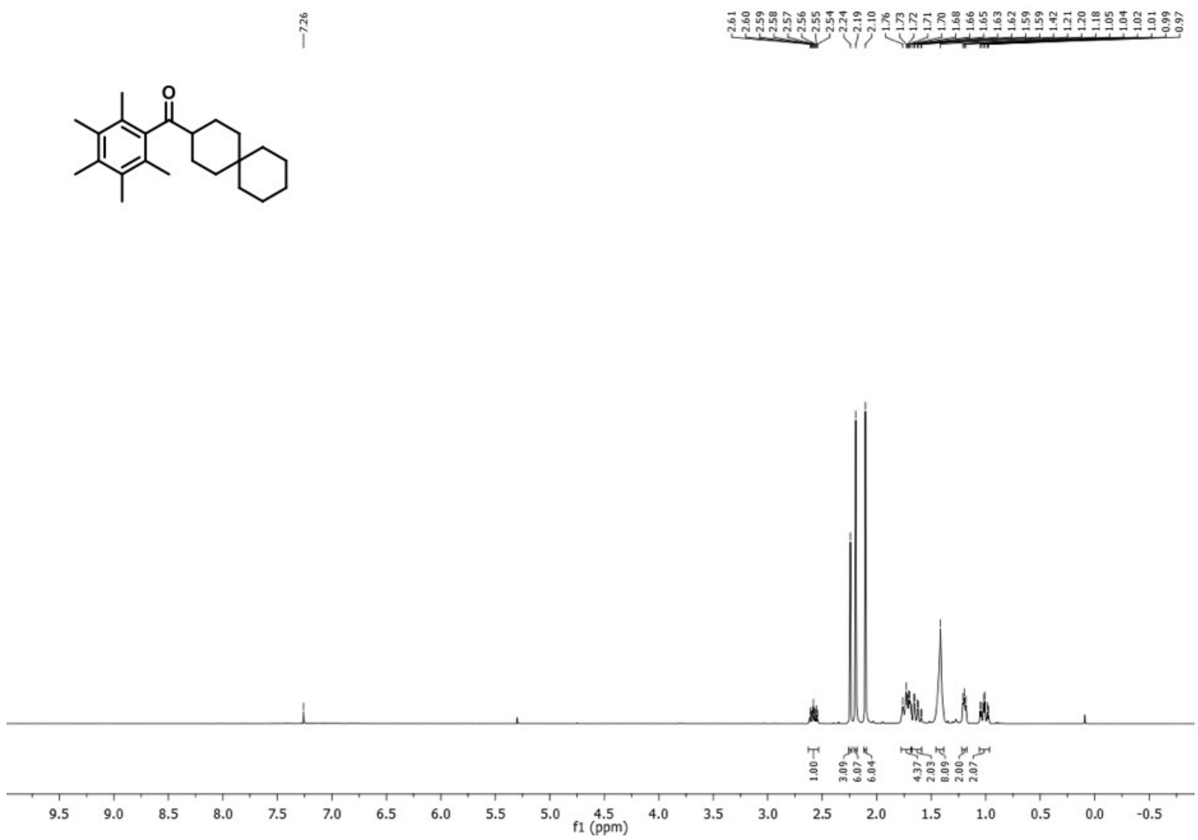


Figure S35. ^{1}H NMR spectrum (400 MHz) of **(4ak)** in $CDCl_3$

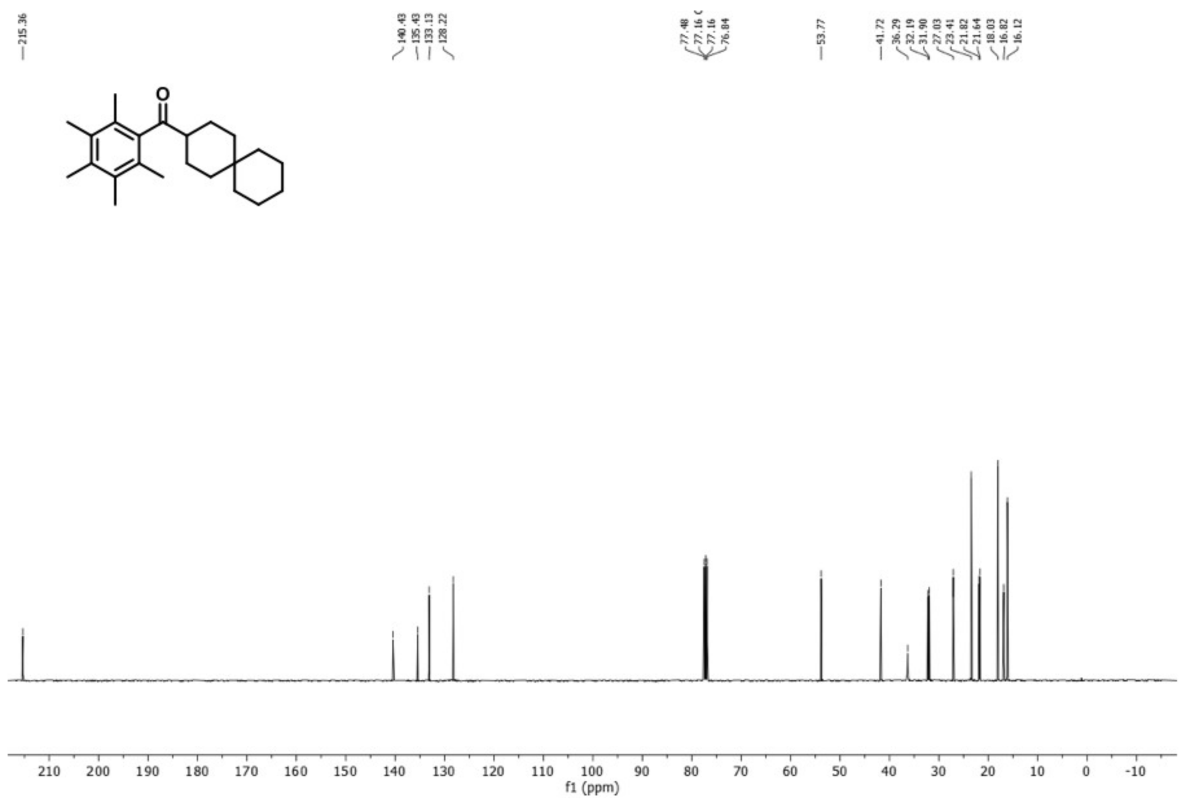


Figure S36. ^{13}C NMR spectrum (100 MHz) of **(4ak)** in $CDCl_3$

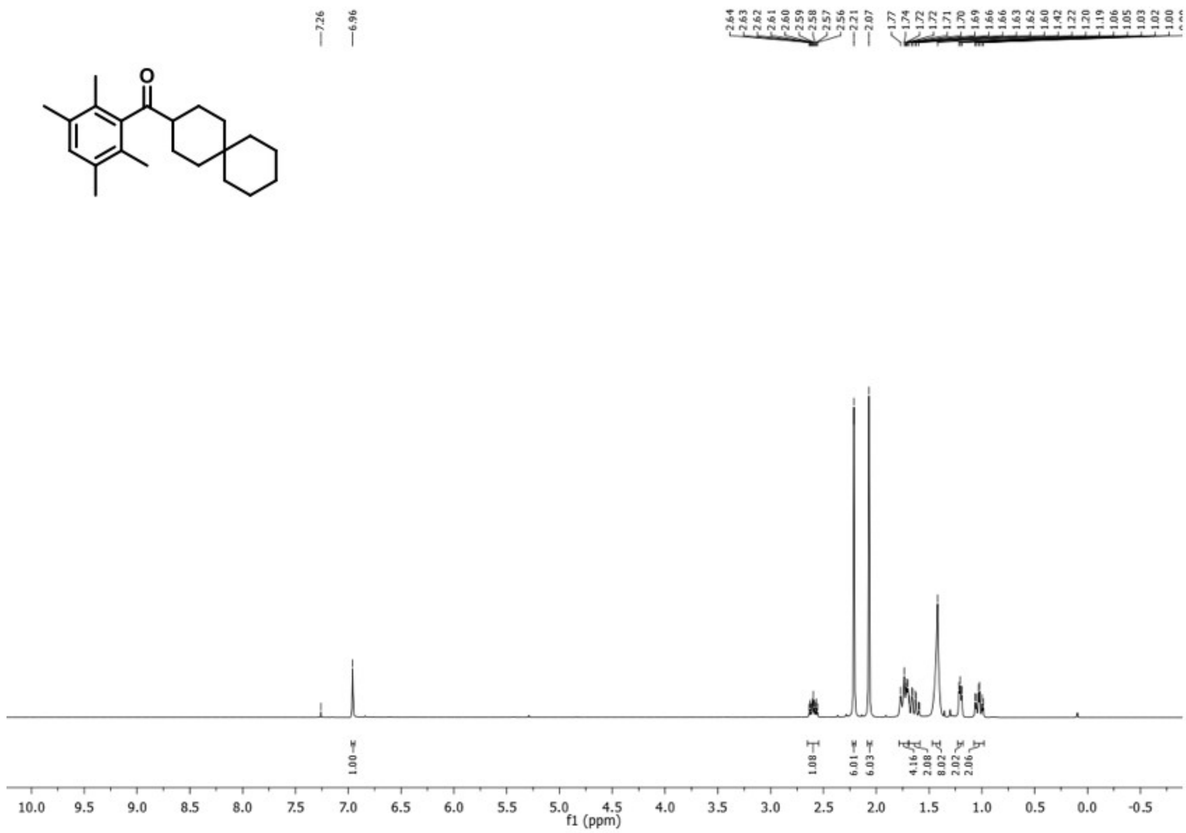


Figure S37. ^{1}H NMR spectrum (400 MHz) of **(4al)** in $CDCl_3$

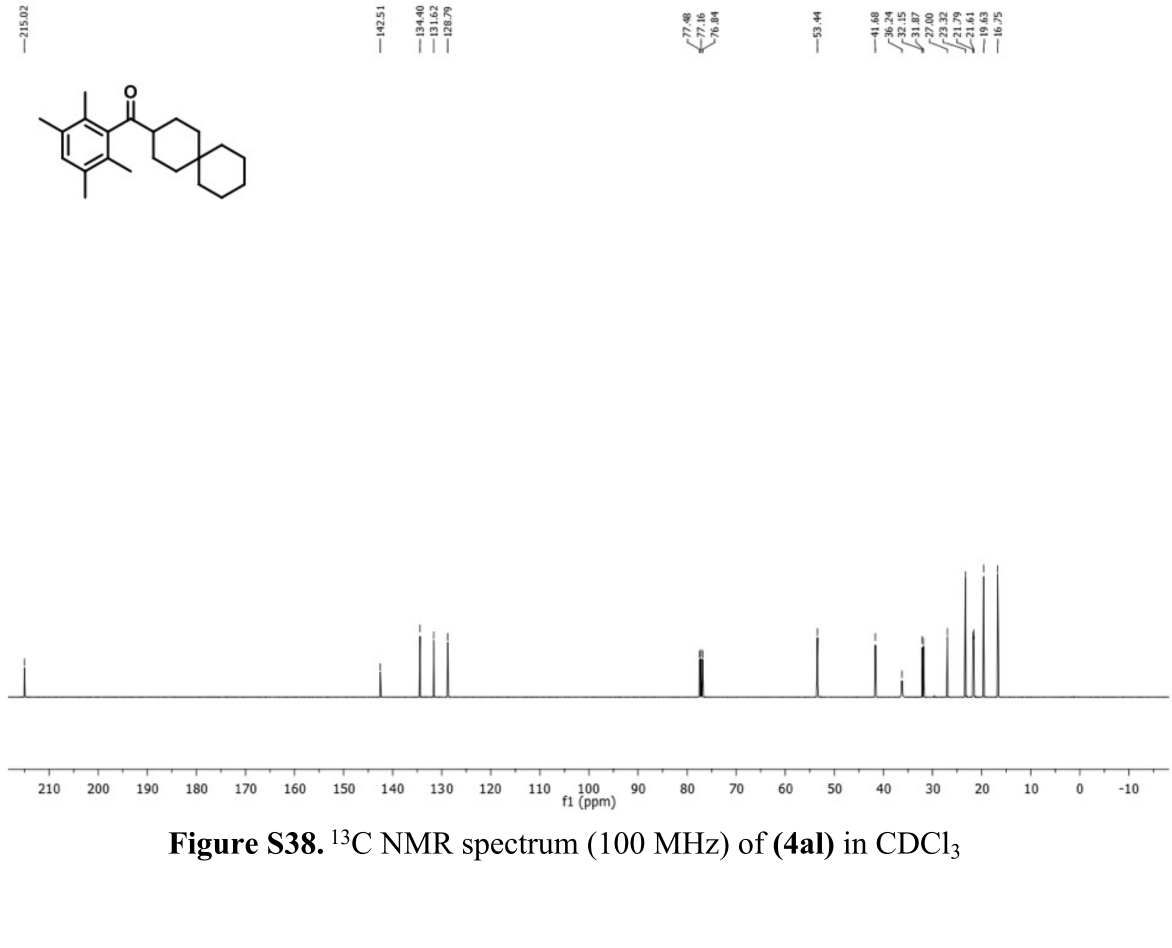


Figure S38. ^{13}C NMR spectrum (100 MHz) of **(4al)** in $CDCl_3$

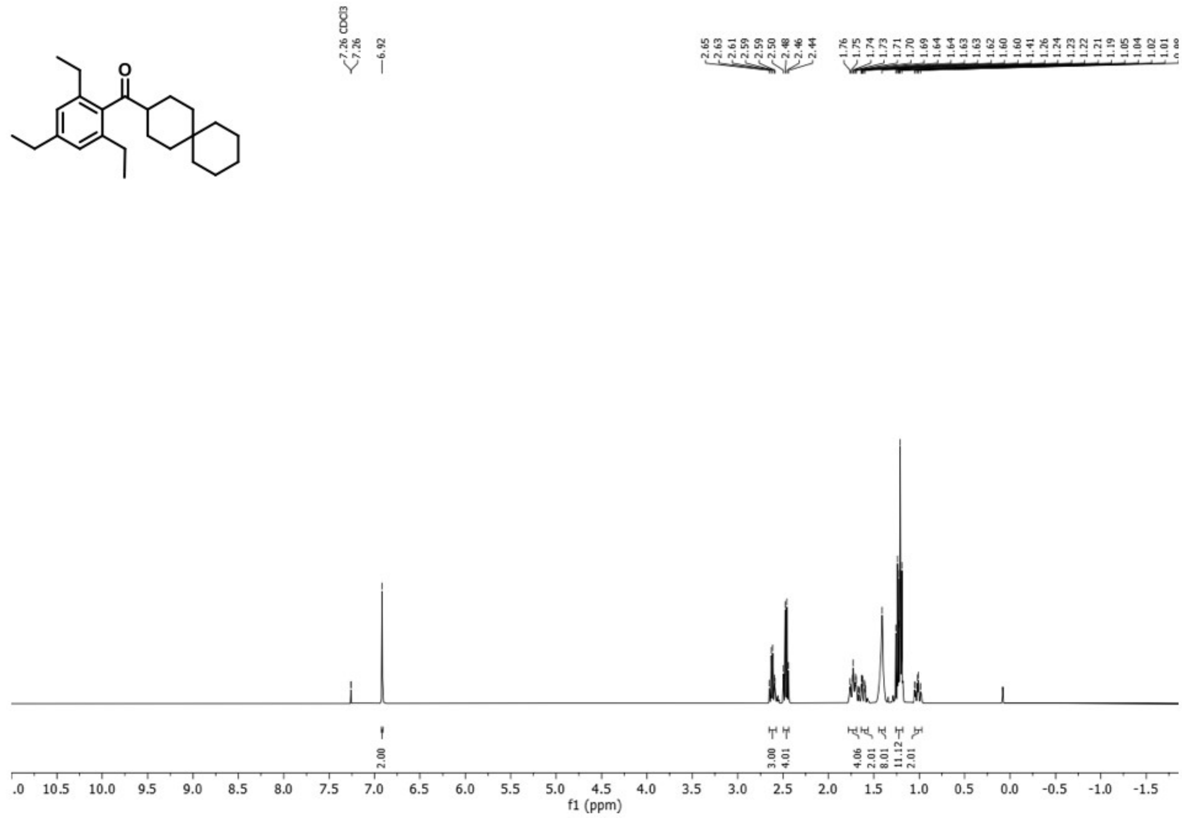


Figure S39. ^{1}H NMR spectrum (400 MHz) of **(4am)** in $CDCl_3$

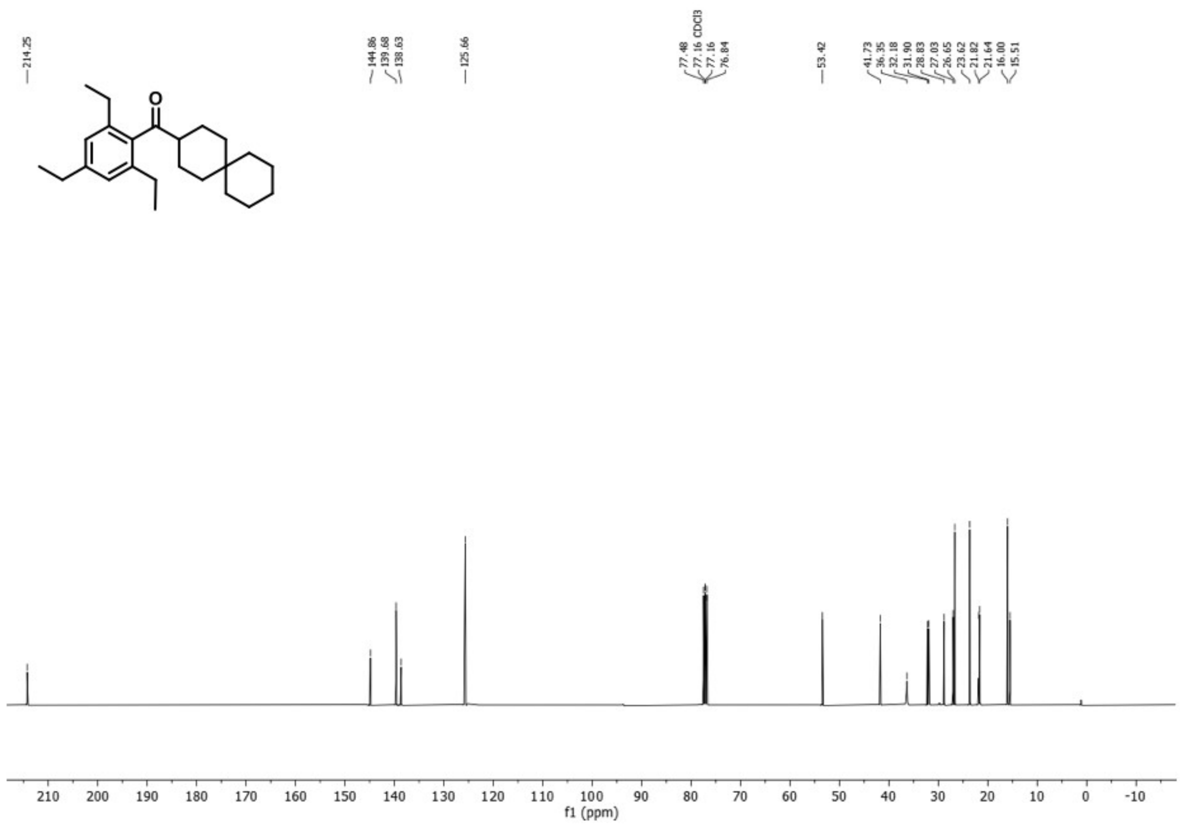


Figure S40. ^{13}C NMR spectrum (100 MHz) of **(4am)** in $CDCl_3$

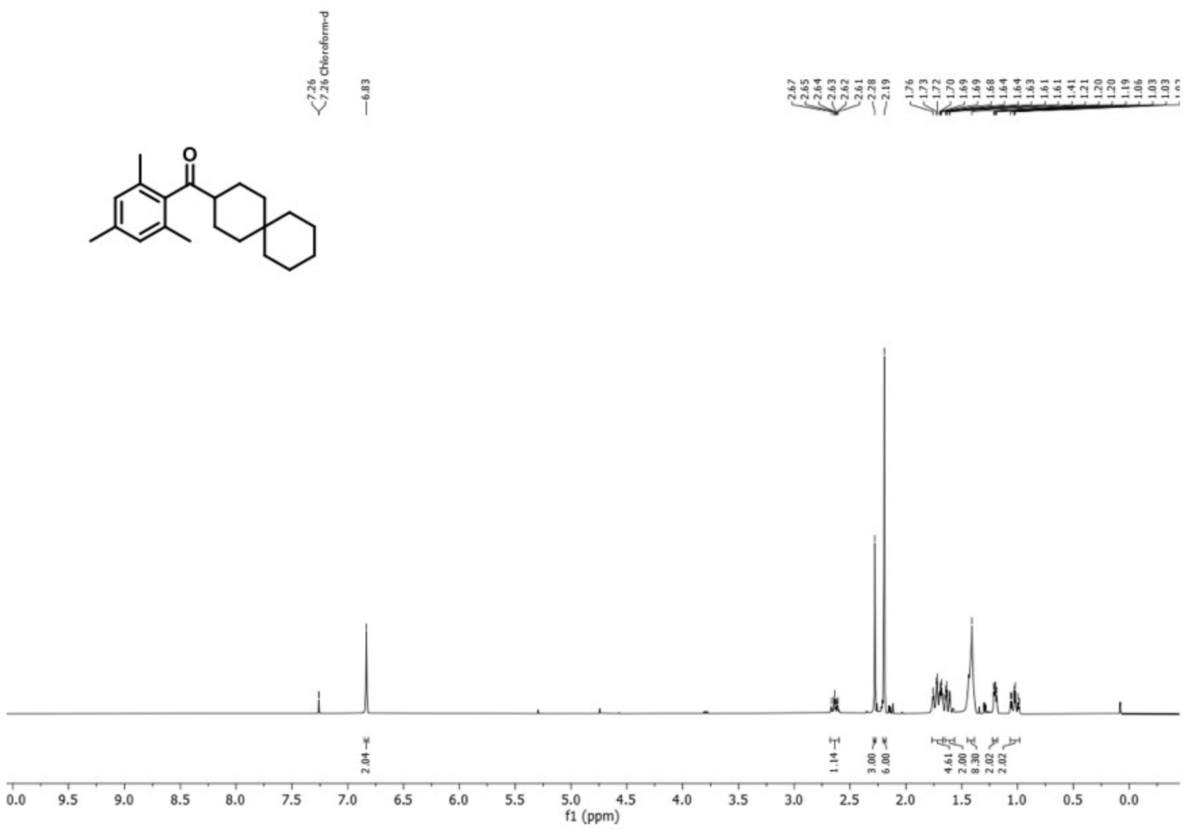


Figure S41. ^{1}H NMR spectrum (400 MHz) of **(4an)** in $CDCl_3$

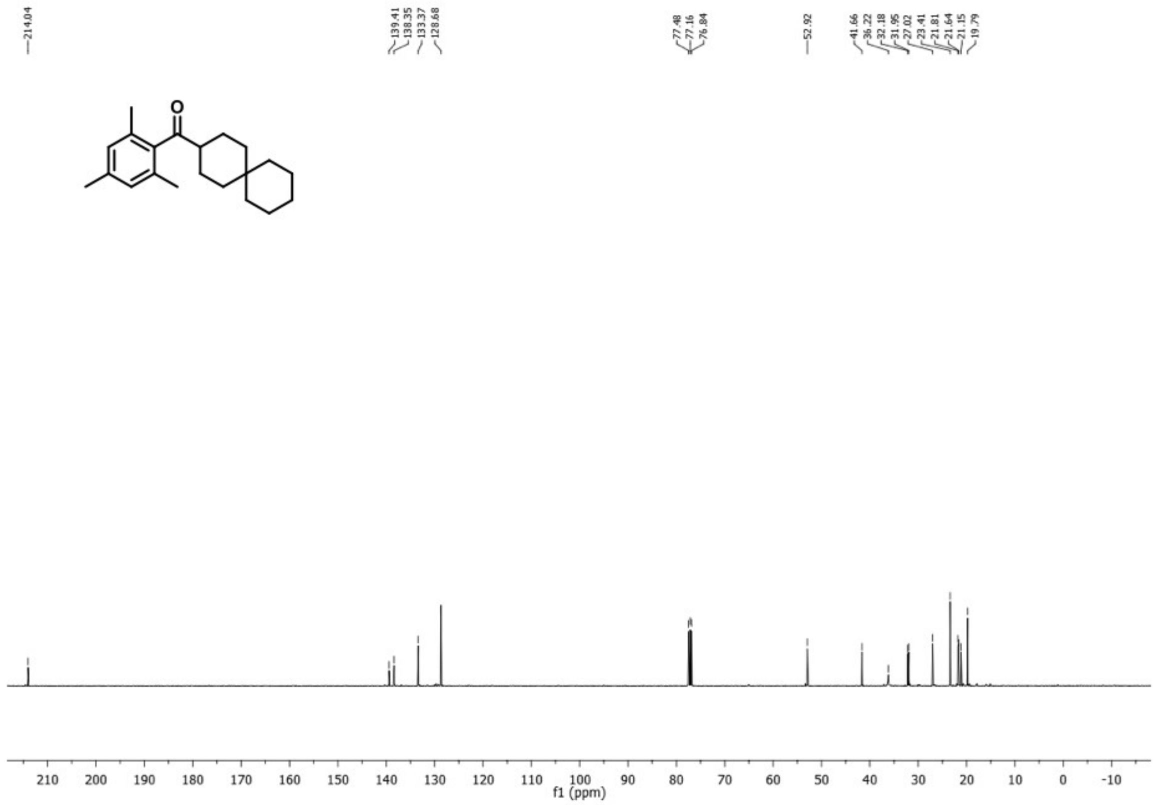


Figure S42. ^{13}C NMR spectrum (100 MHz) of **(4an)** in $CDCl_3$

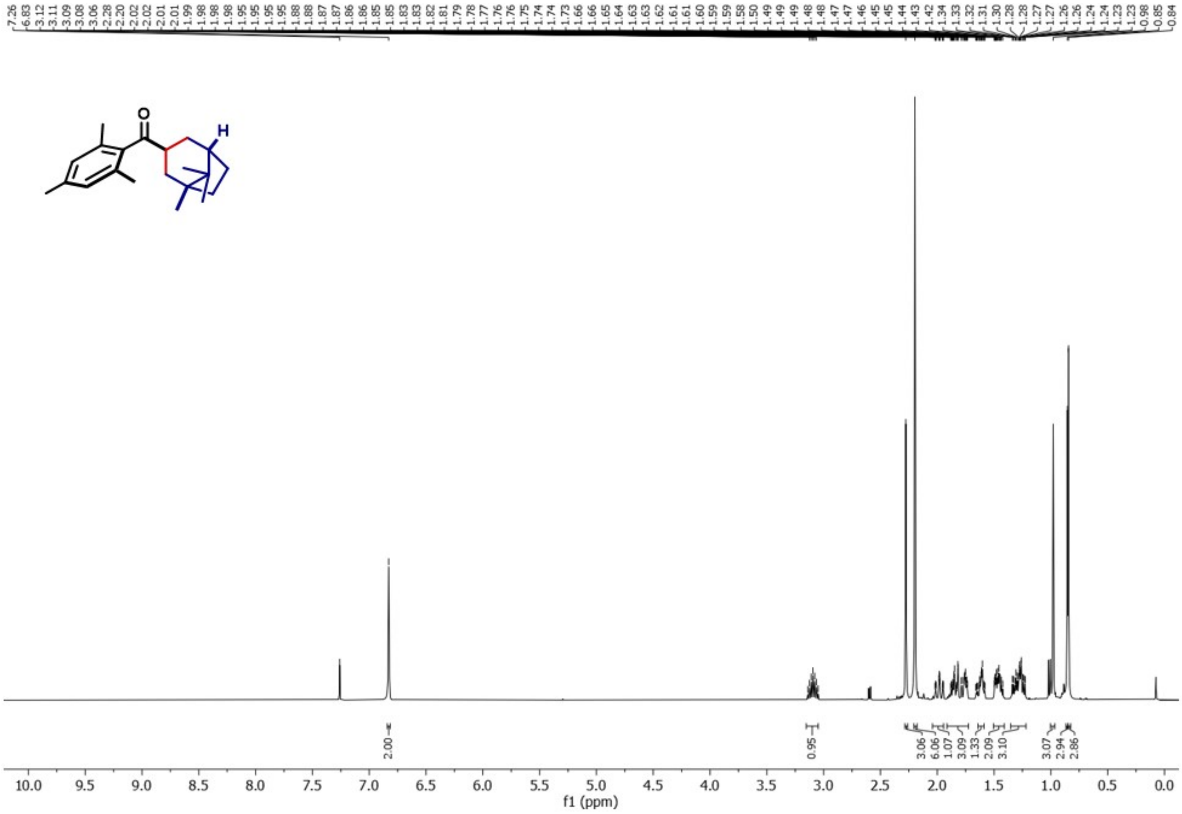


Figure S43. ^{1}H NMR spectrum (400 MHz) of **(4ao)** in $CDCl_3$

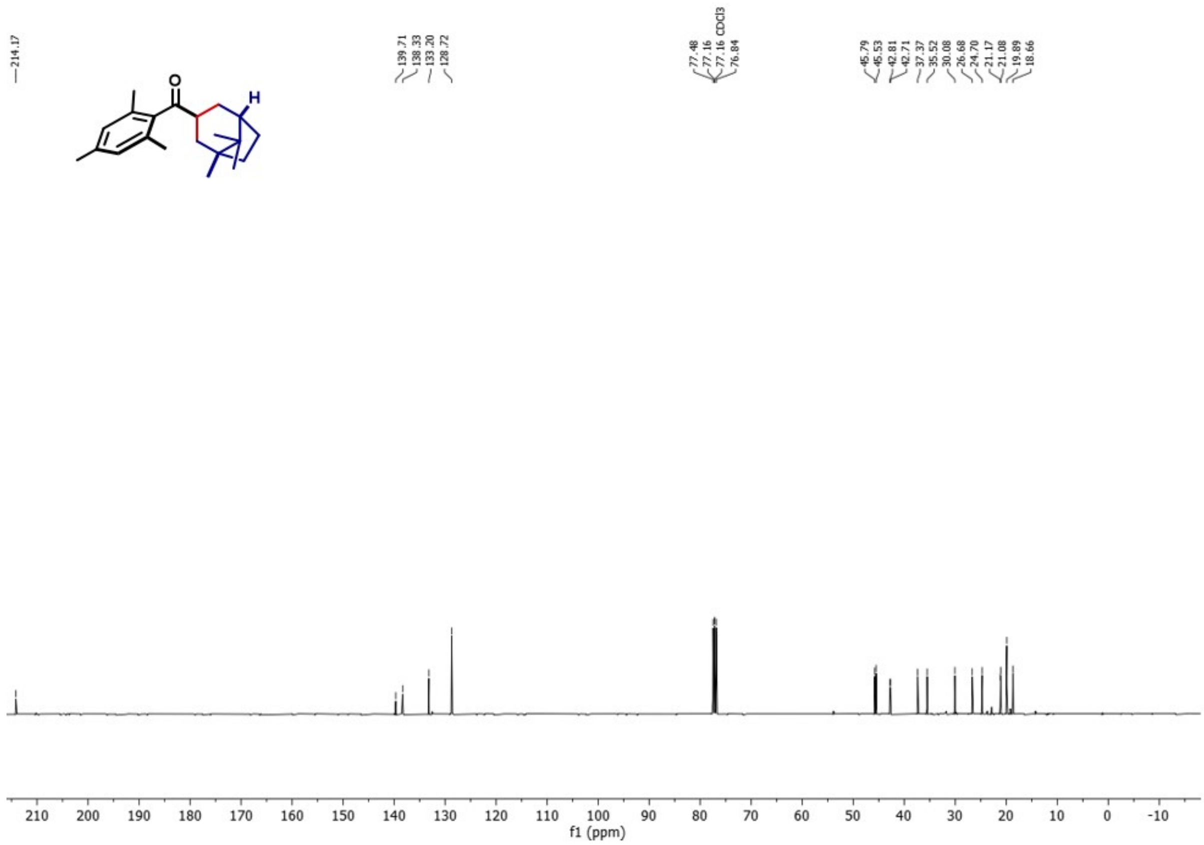


Figure S44. ^{13}C NMR spectrum (100 MHz) of **(4ao)** in $CDCl_3$

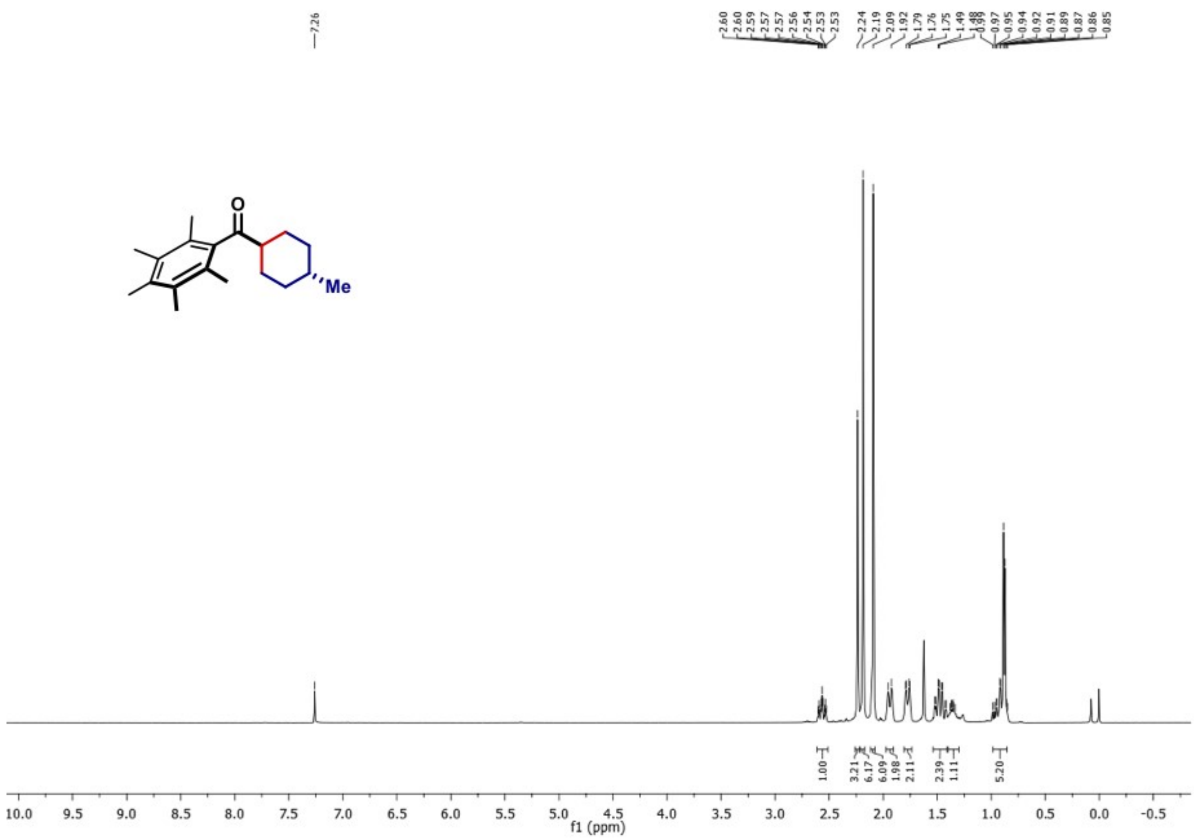


Figure S45. ^{1}H NMR spectrum (400 MHz) of **(4ap)** in $CDCl_3$

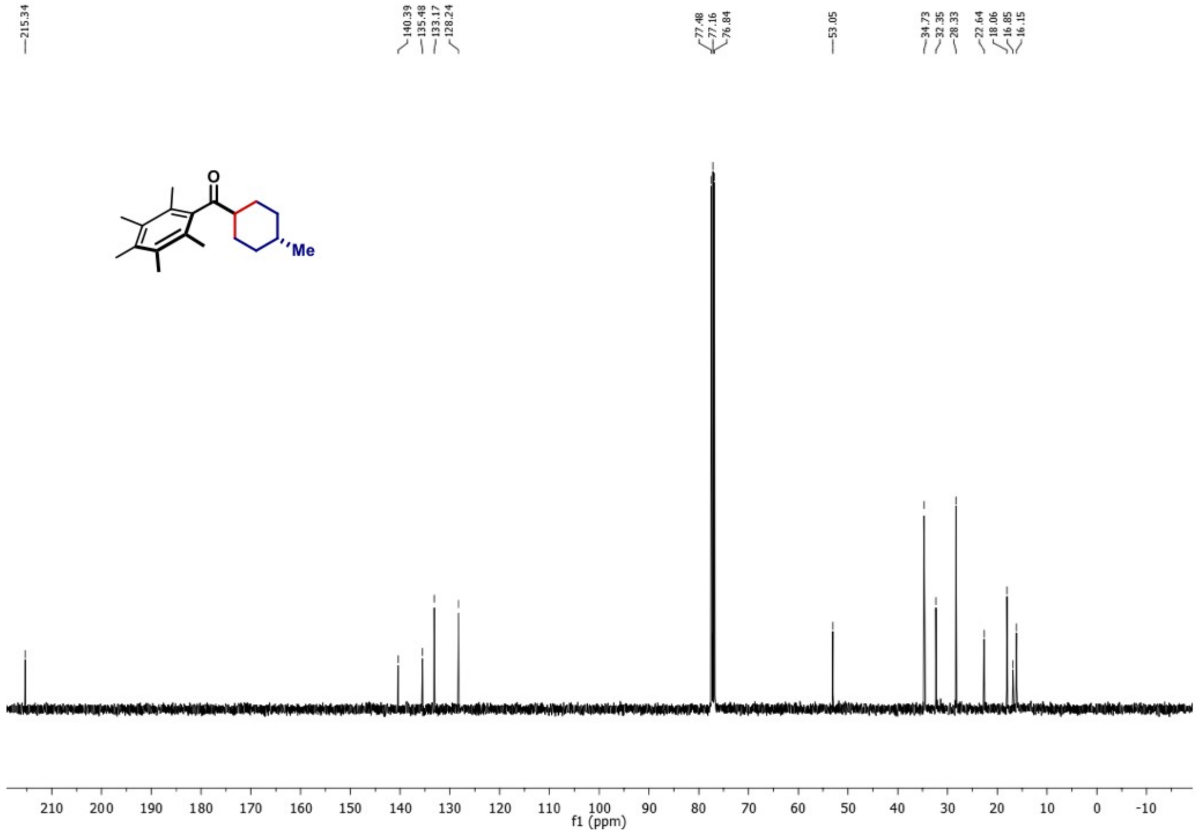


Figure S46. ^{13}C NMR spectrum (100 MHz) of **(4ap)** in $CDCl_3$

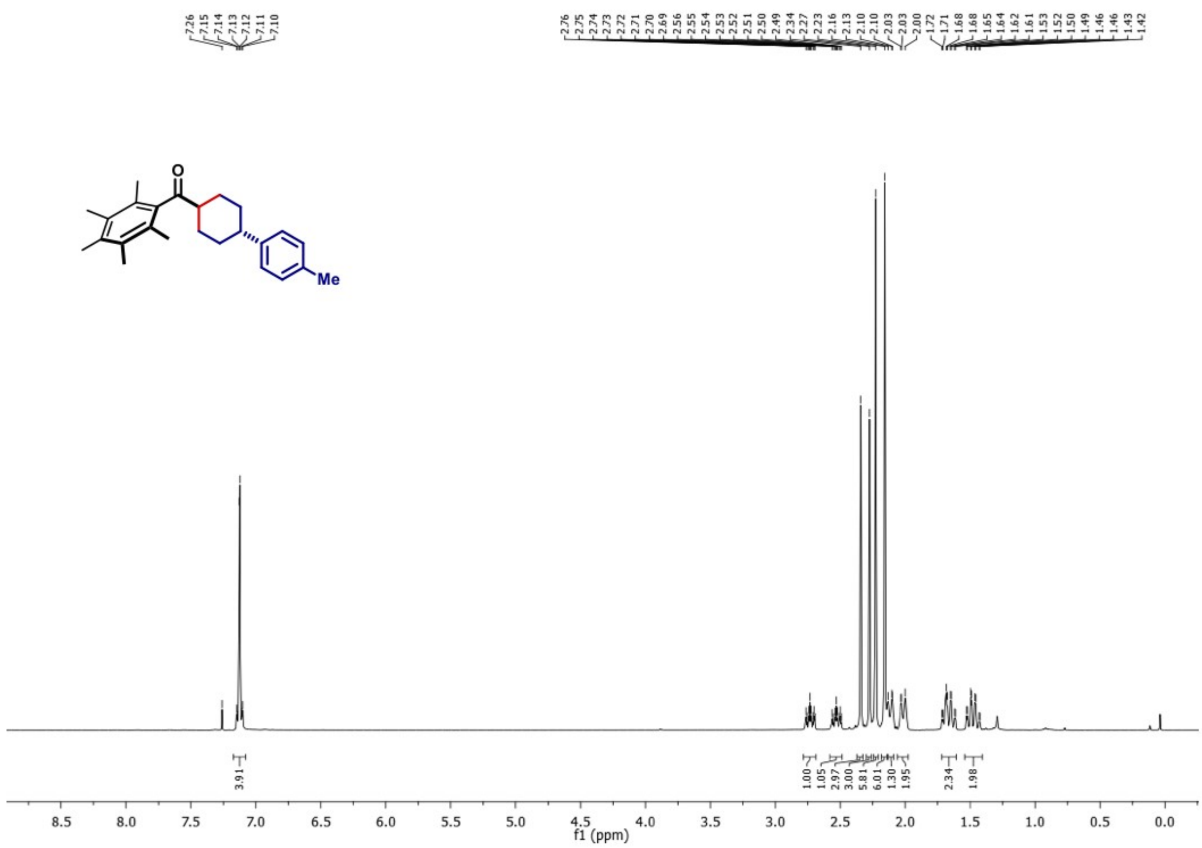


Figure S47. ^{1}H NMR spectrum (400 MHz) of **(4aq)** in $CDCl_3$

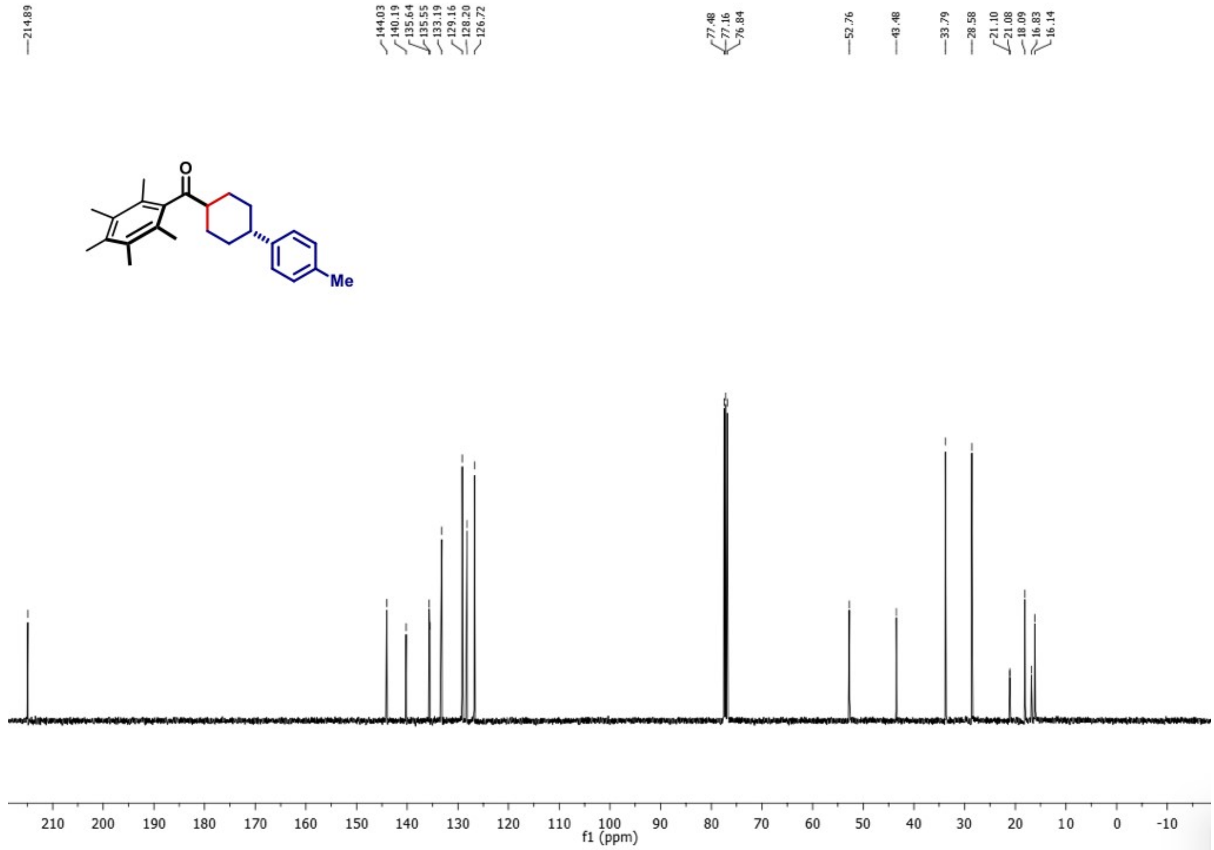


Figure S48. ^{13}C NMR spectrum (100 MHz) of **(4aq)** in $CDCl_3$

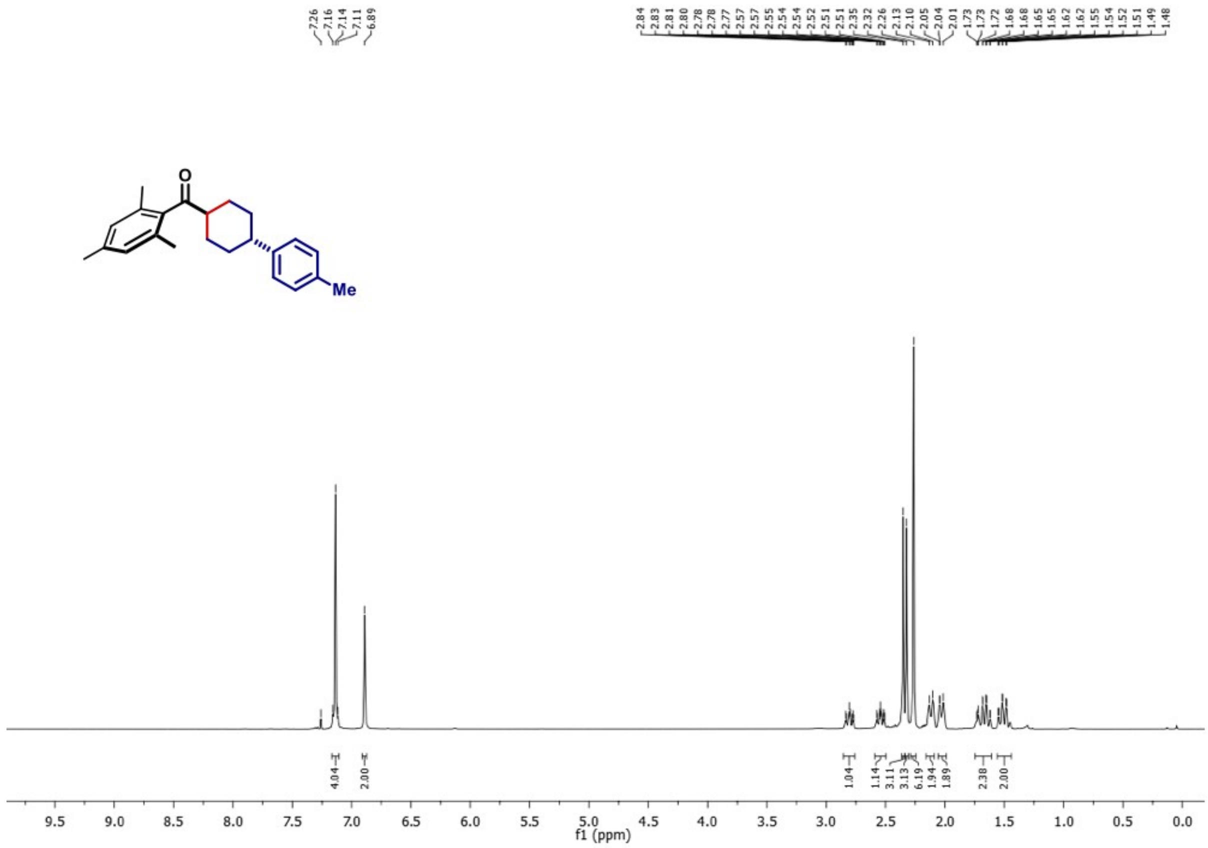


Figure S49. ^{1}H NMR spectrum (400 MHz) of **(4ar)** in $CDCl_3$

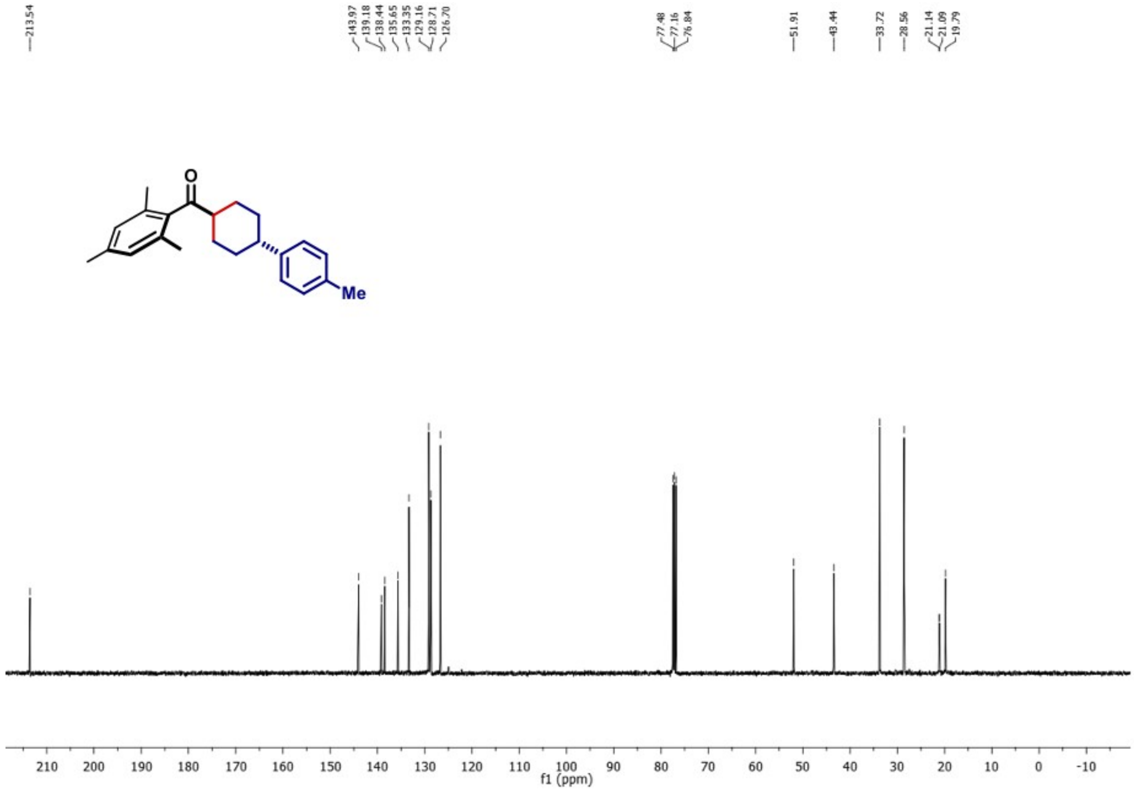


Figure S50. ^{13}C NMR spectrum (100 MHz) of **(4ar)** in $CDCl_3$

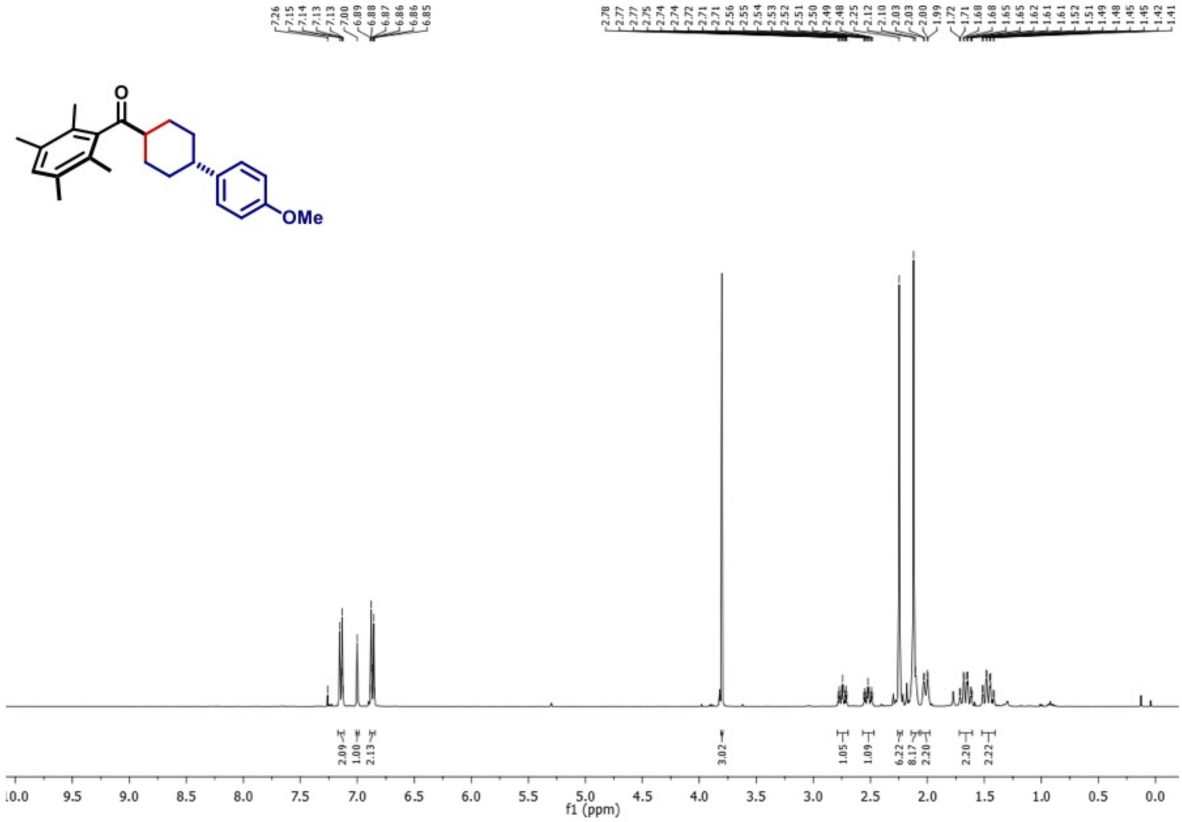


Figure S51. ^{1}H NMR spectrum (400 MHz) of **(4as)** in $CDCl_3$

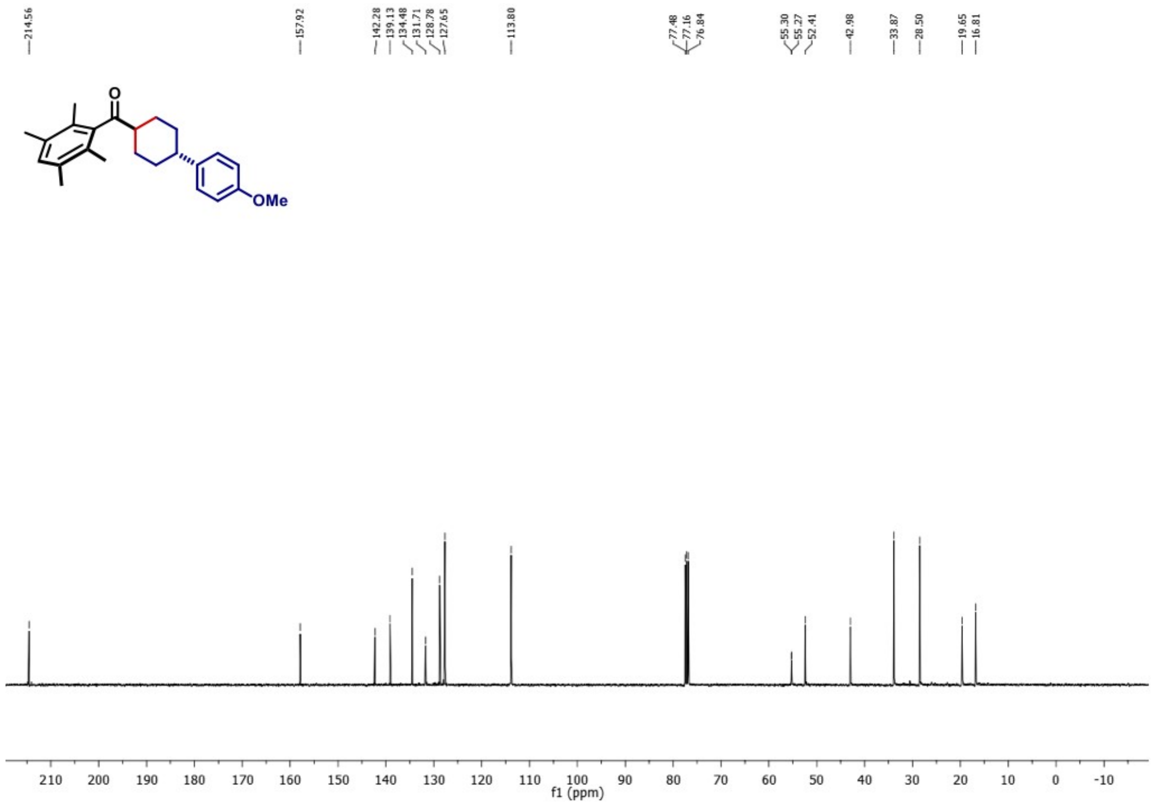


Figure S52. ^{13}C NMR spectrum (100 MHz) of **(4as)** in $CDCl_3$

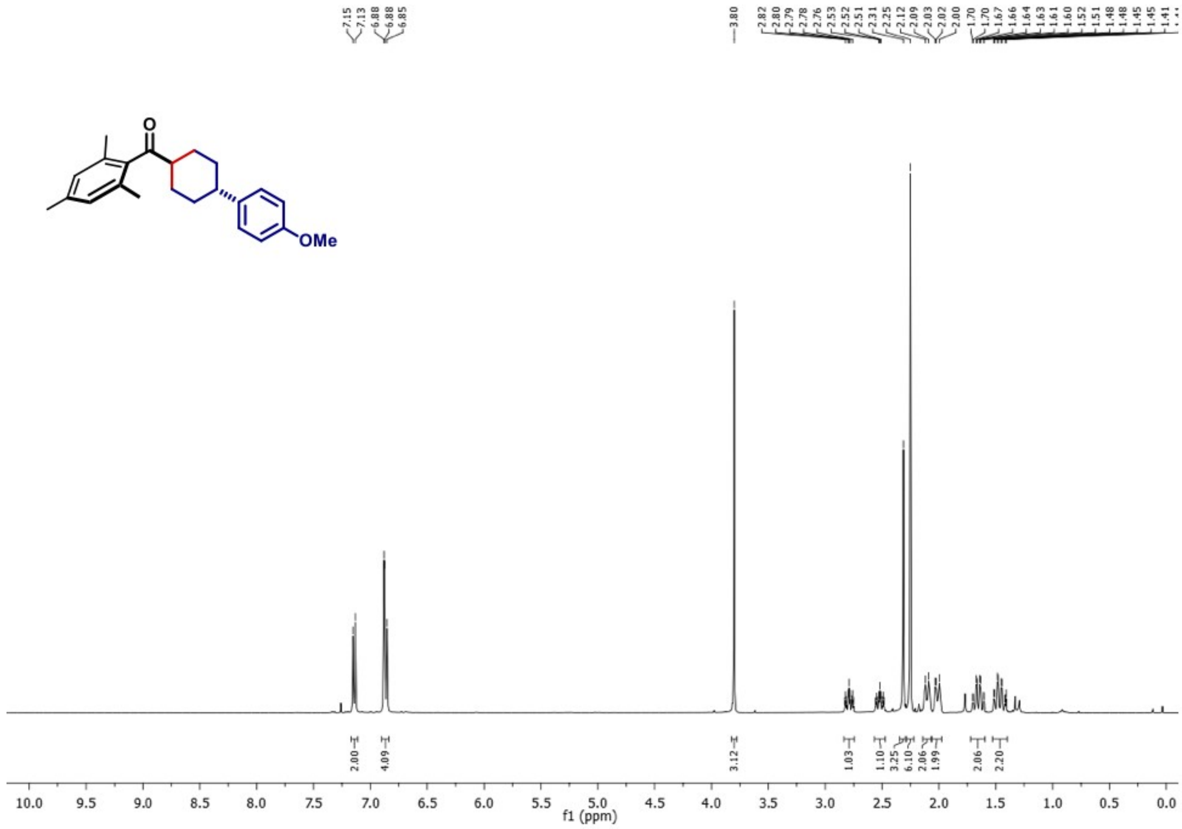


Figure S53. ^{1}H NMR spectrum (400 MHz) of **(4at)** in $CDCl_3$

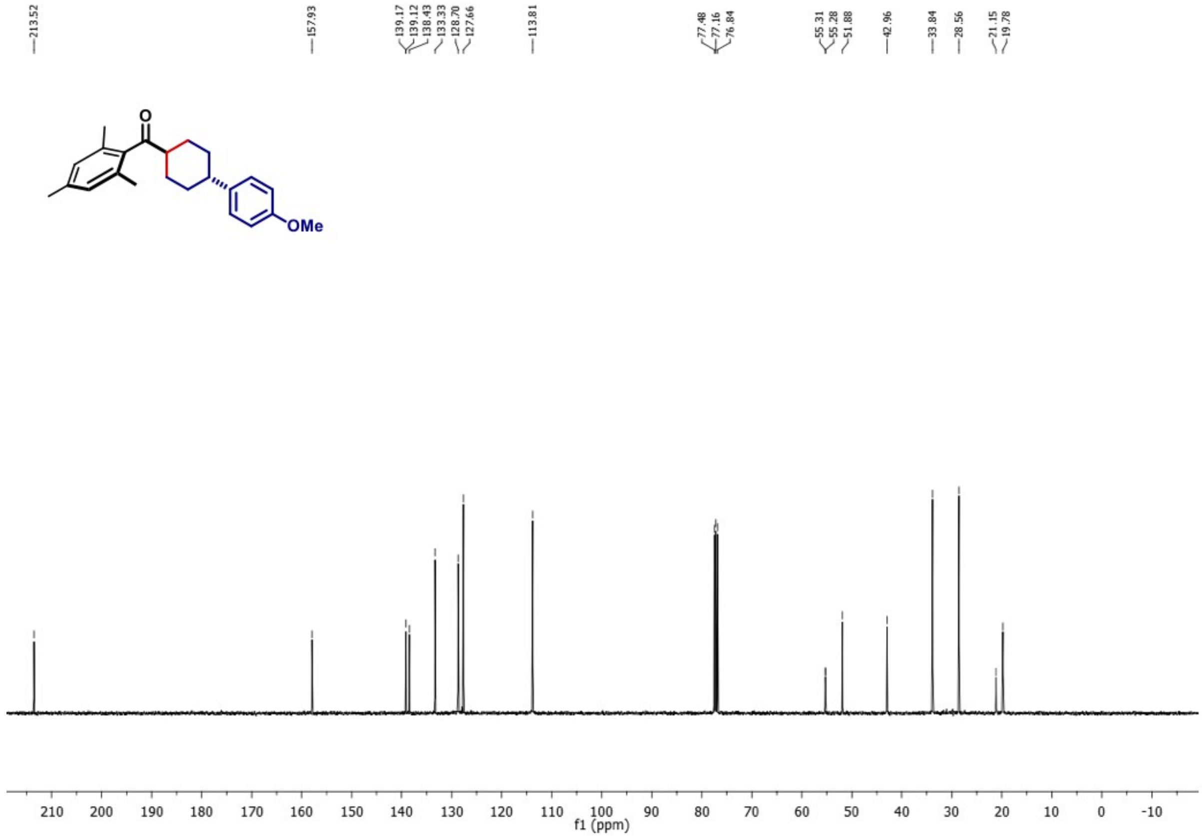


Figure S54. ^{13}C NMR spectrum (100 MHz) of **(4at)** in $CDCl_3$

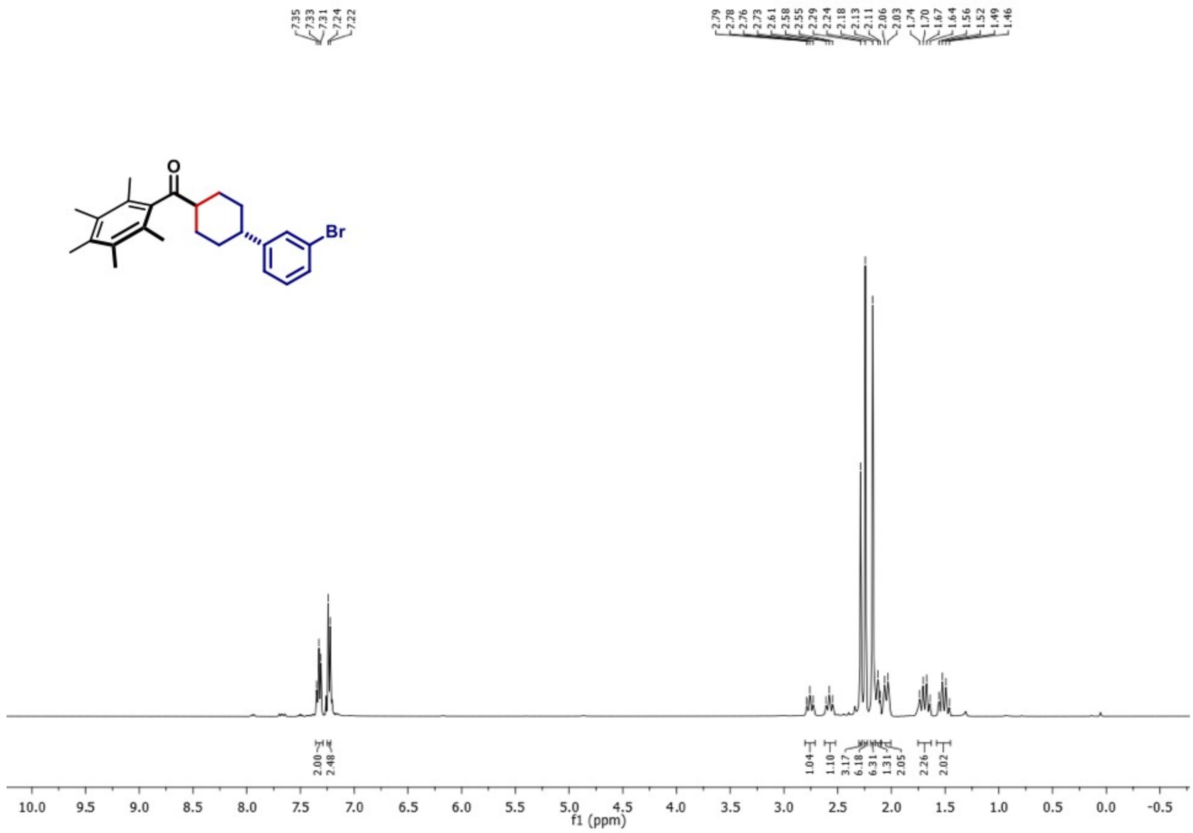


Figure S55. ^{1}H NMR spectrum (400 MHz) of **(4au)** in $CDCl_3$

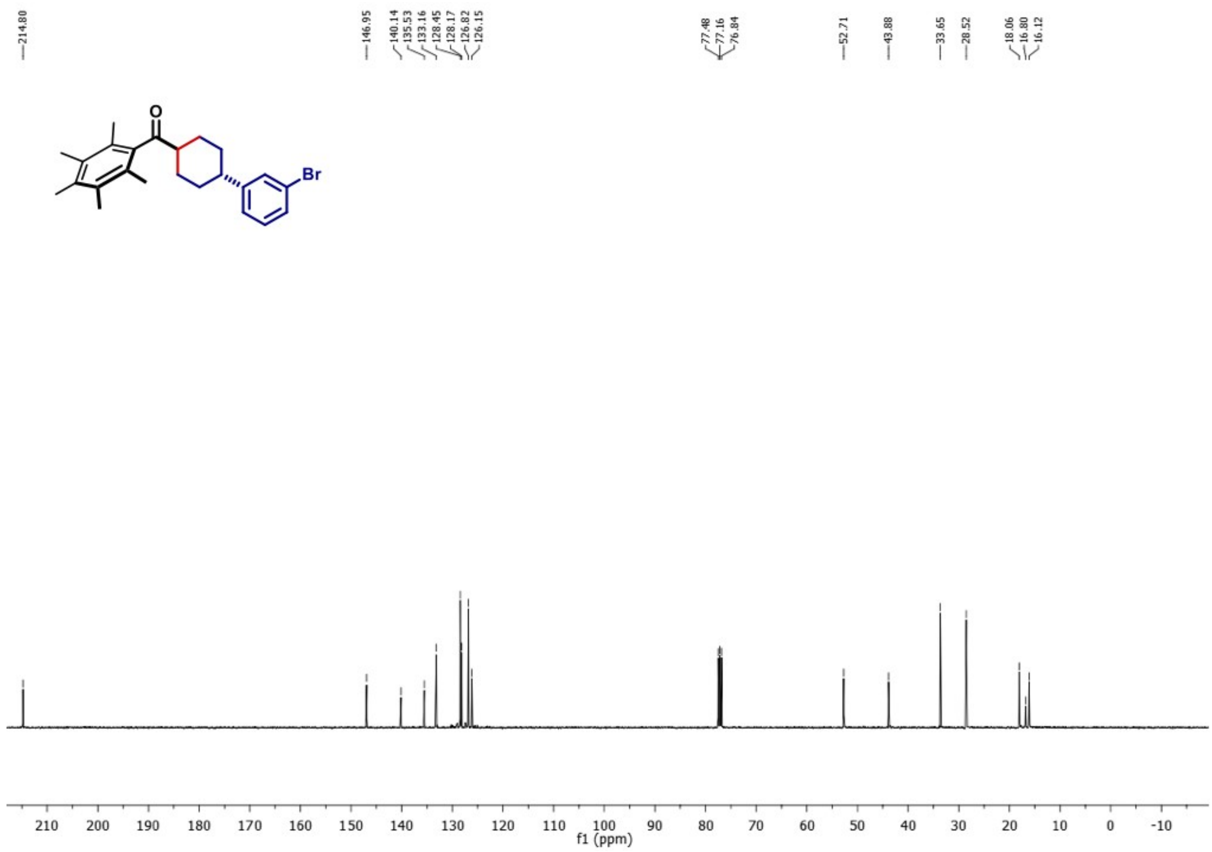


Figure S56. ^{13}C NMR spectrum (100 MHz) of **(4au)** in $CDCl_3$

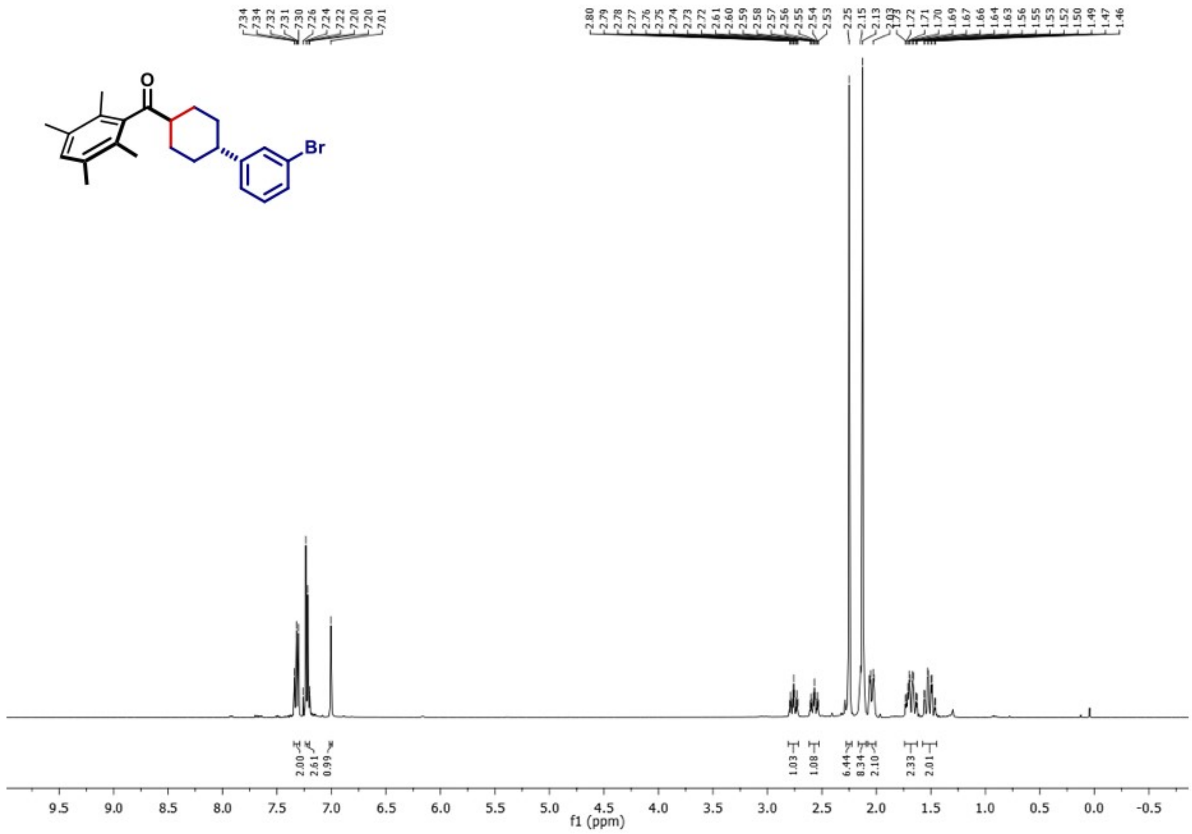


Figure S57. ^{1}H NMR spectrum (400 MHz) of **(4av)** in $CDCl_3$

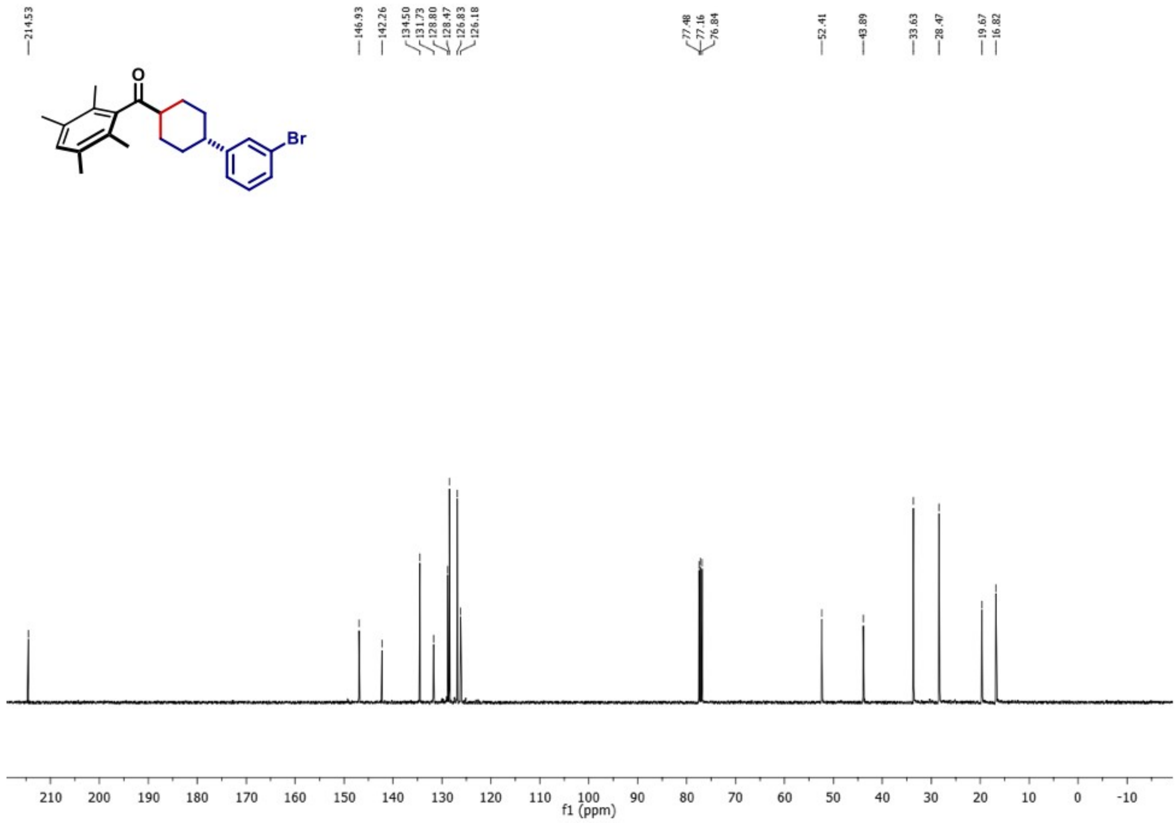


Figure S58. ^{13}C NMR spectrum (100 MHz) of **(4av)** in $CDCl_3$

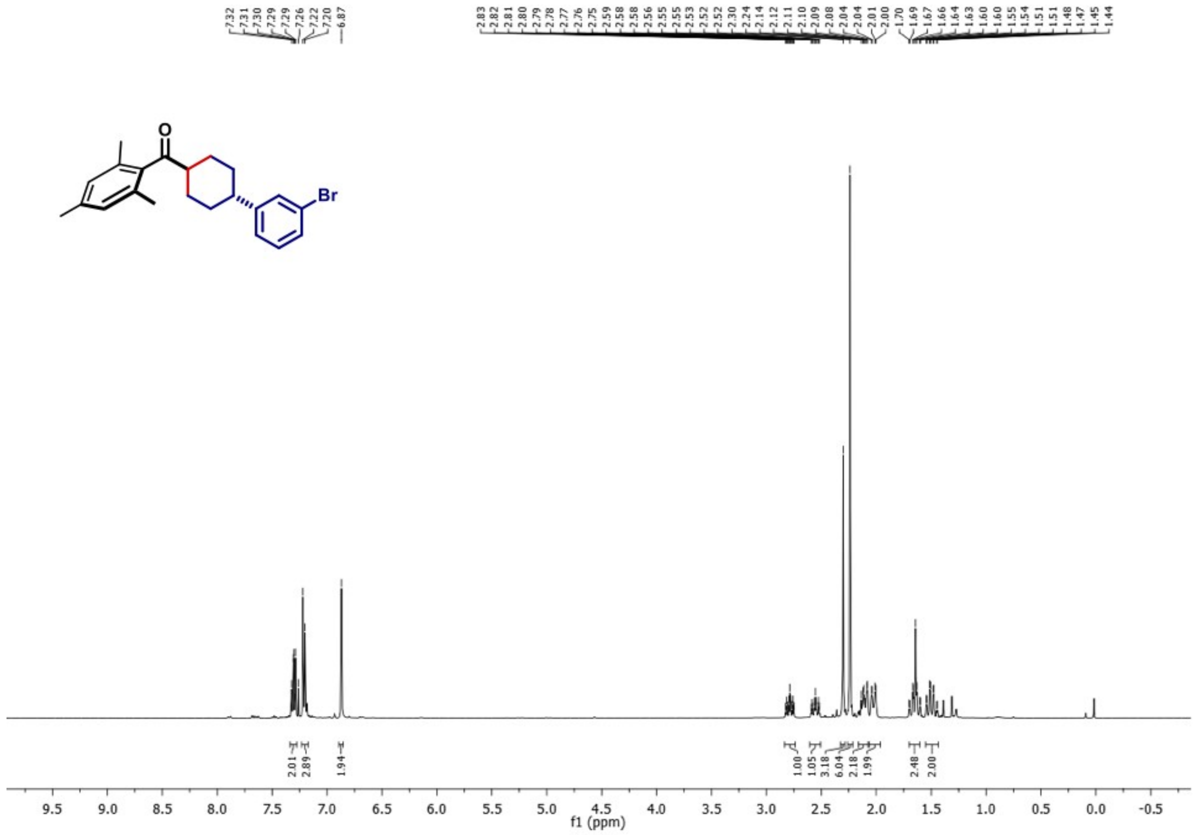


Figure S59. ^{1}H NMR spectrum (400 MHz) of **(4aw)** in $CDCl_3$

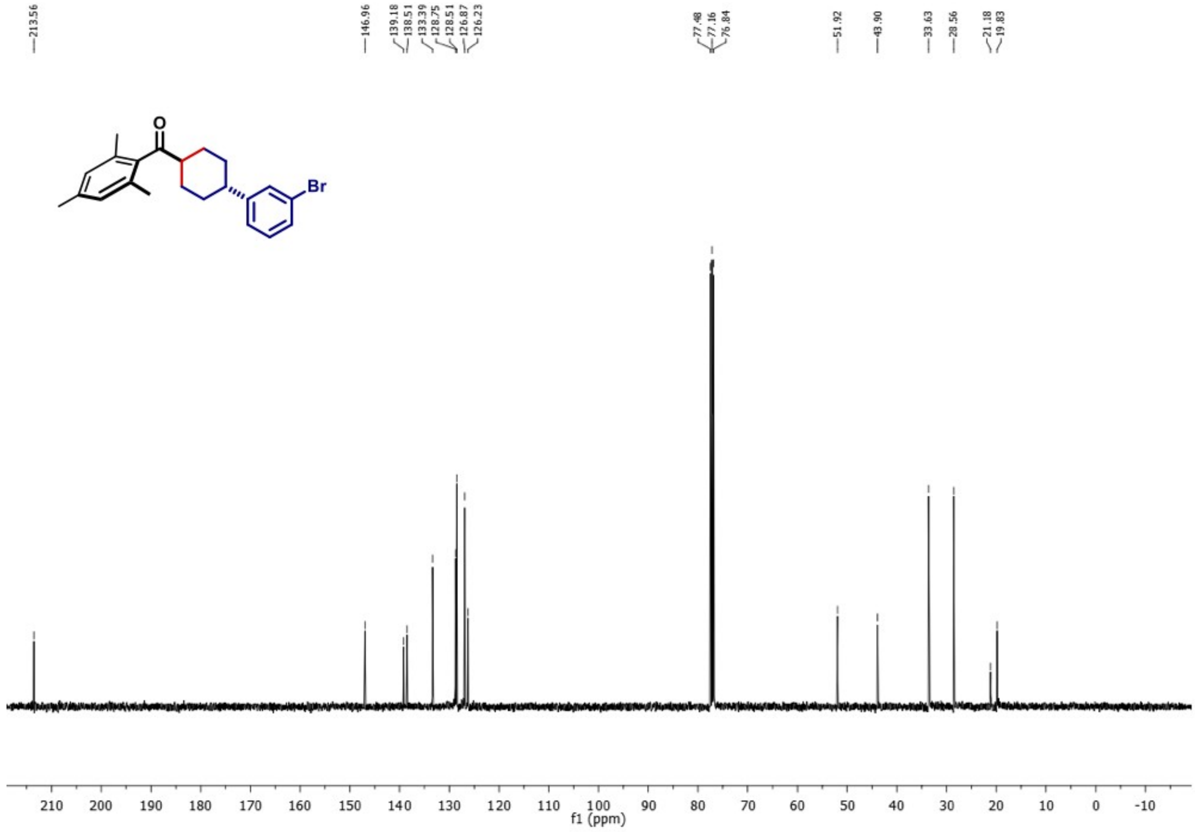


Figure S60. ^{13}C NMR spectrum (100 MHz) of **(4aw)** in $CDCl_3$

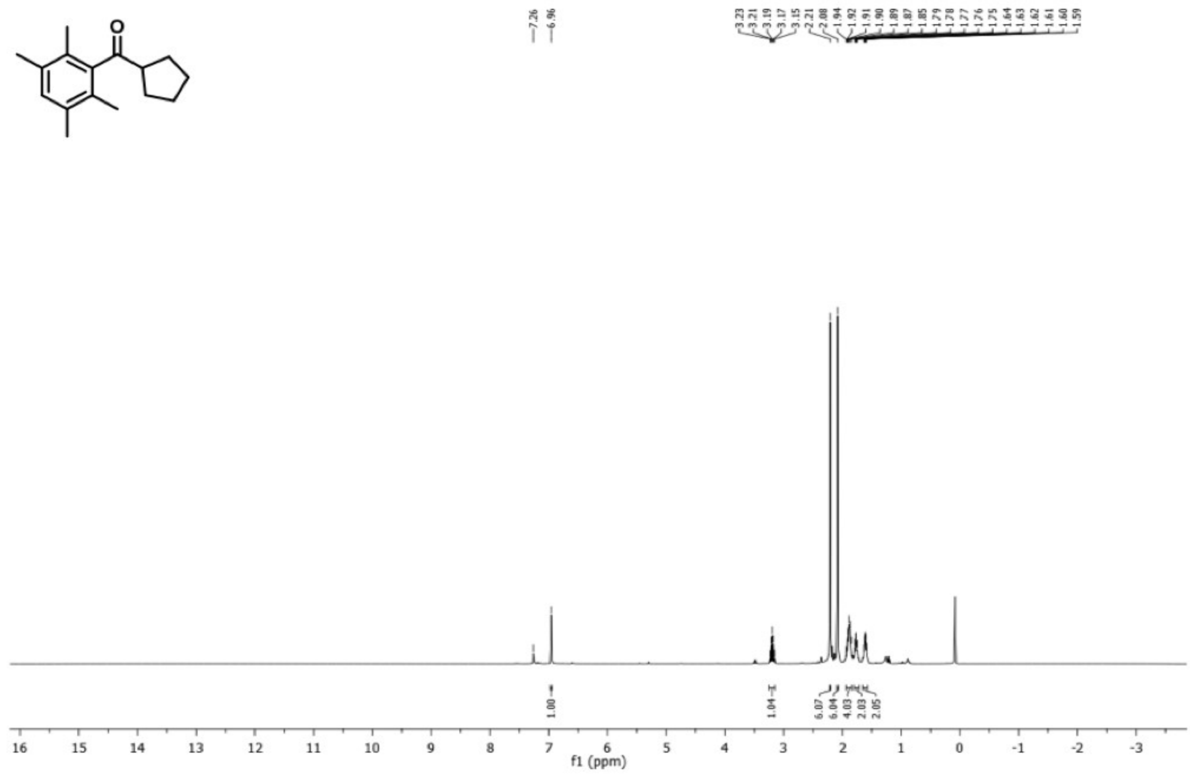


Figure S61. ^{1}H NMR spectrum (400 MHz) of **(4bb)** in $CDCl_3$

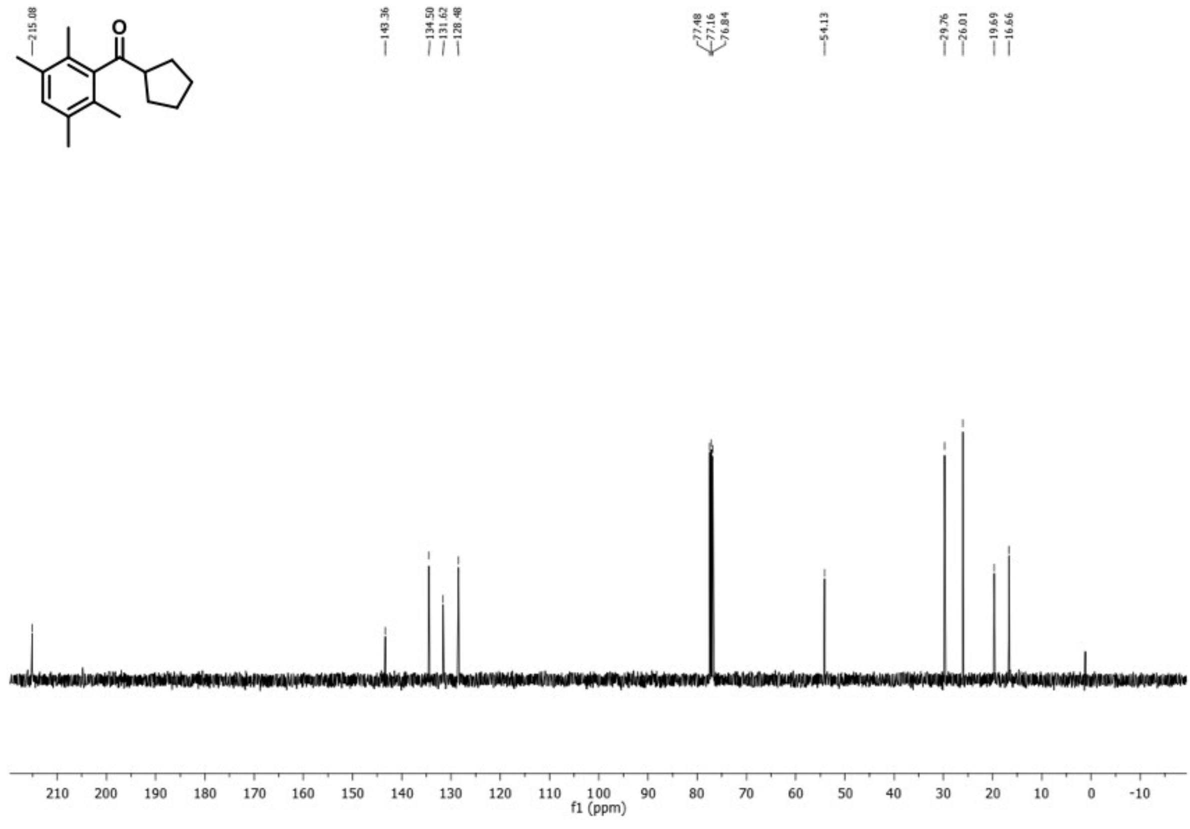


Figure S62. ^{13}C NMR spectrum (100 MHz) of **(4bb)** in $CDCl_3$

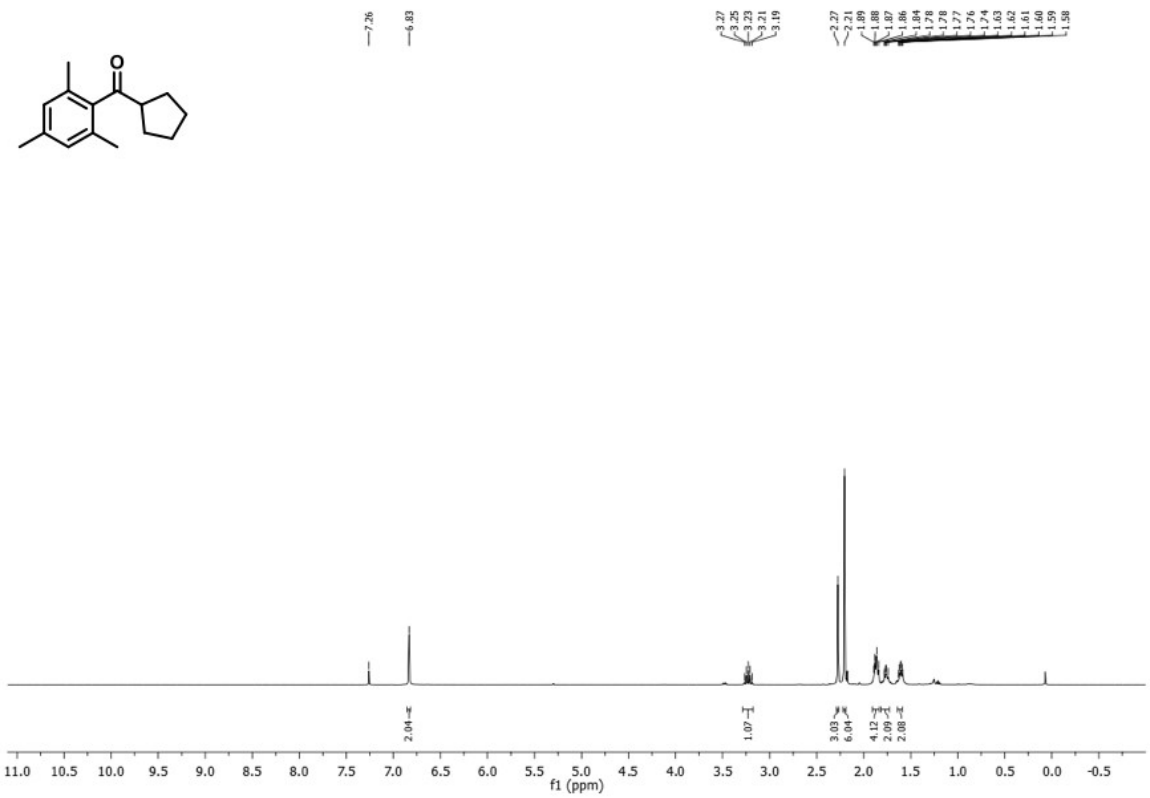


Figure S63. ^{1}H NMR spectrum (400 MHz) of **(4bc)** in $CDCl_3$

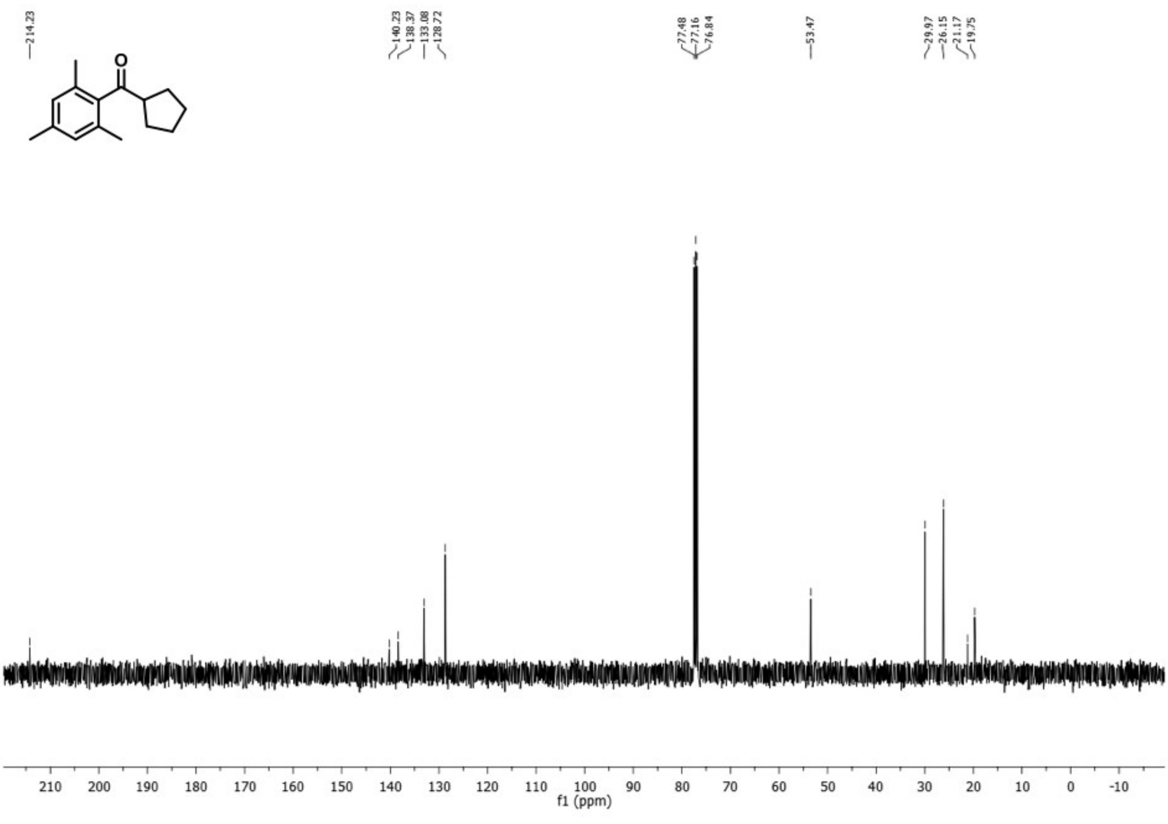


Figure S64. ^{13}C NMR spectrum (100 MHz) of **(4bc)** in $CDCl_3$

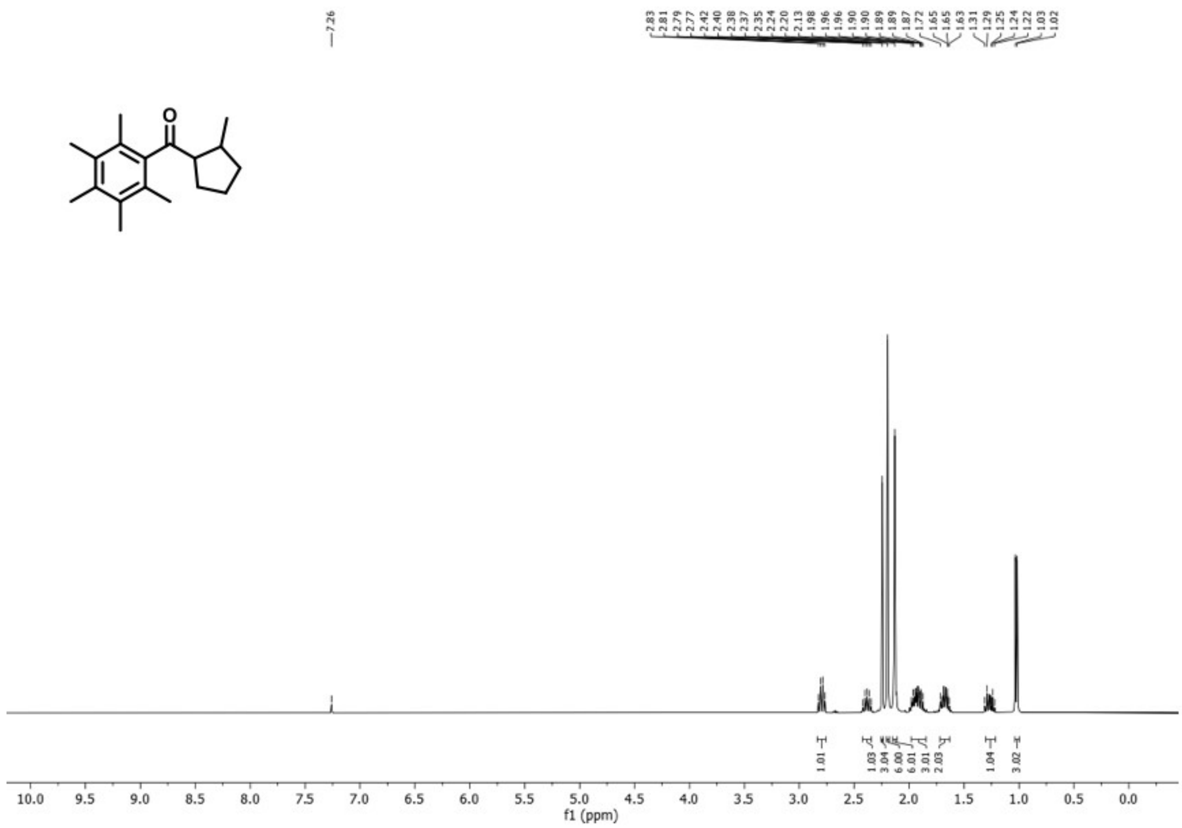


Figure S65. ^{1}H NMR spectrum (400 MHz) of **(4bd)** in $CDCl_3$

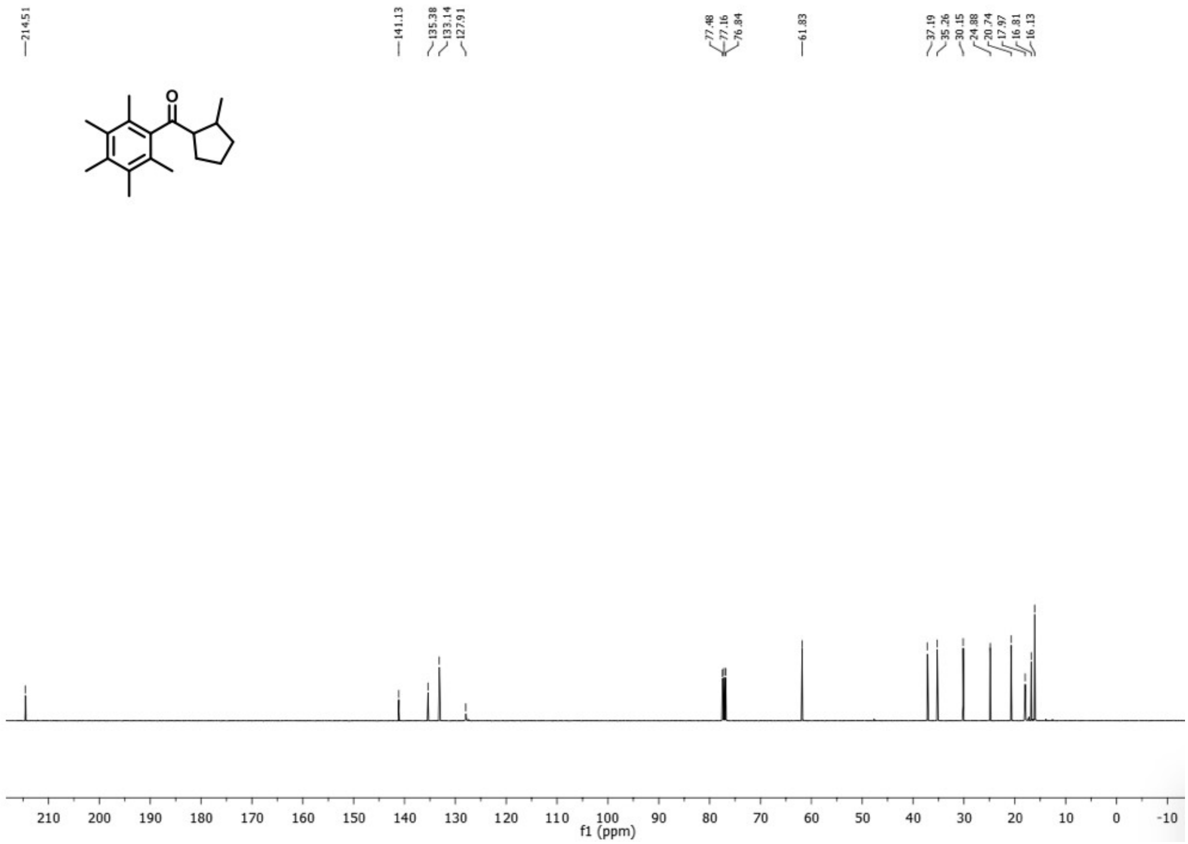


Figure S66. ^{13}C NMR spectrum (100 MHz) of **(4bd)** in $CDCl_3$

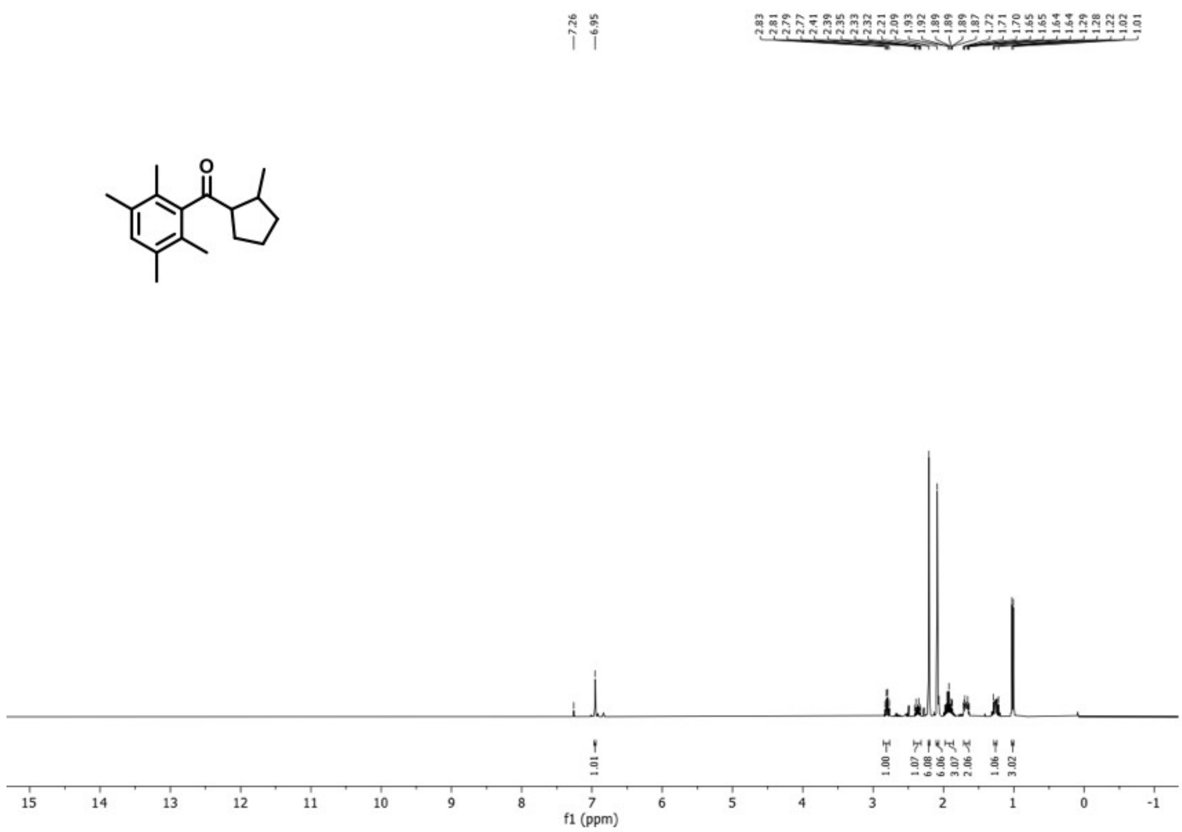


Figure S67. ^{1}H NMR spectrum (400 MHz) of **(4be)** in $CDCl_3$

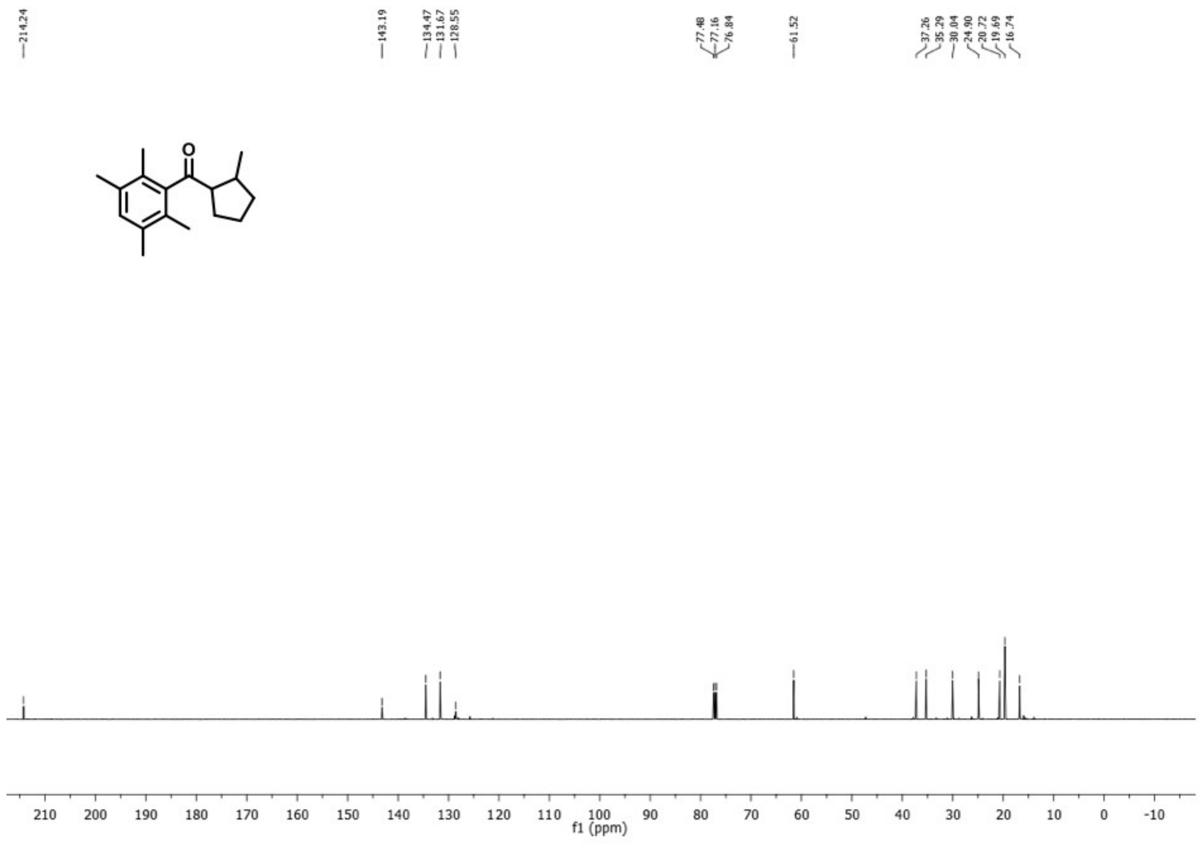


Figure S68. ^{13}C NMR spectrum (100 MHz) of **(4be)** in $CDCl_3$

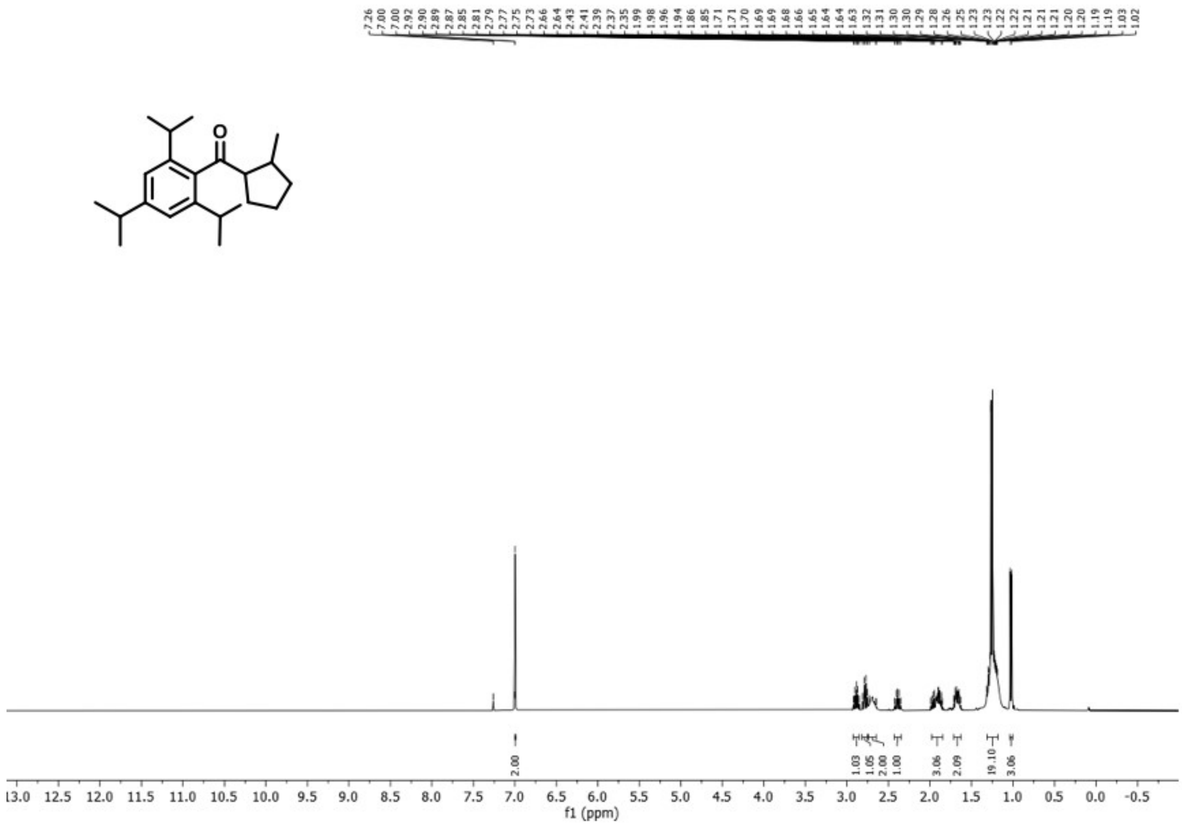


Figure S69. ^{1}H NMR spectrum (400 MHz) of **(4bf)** in $CDCl_3$

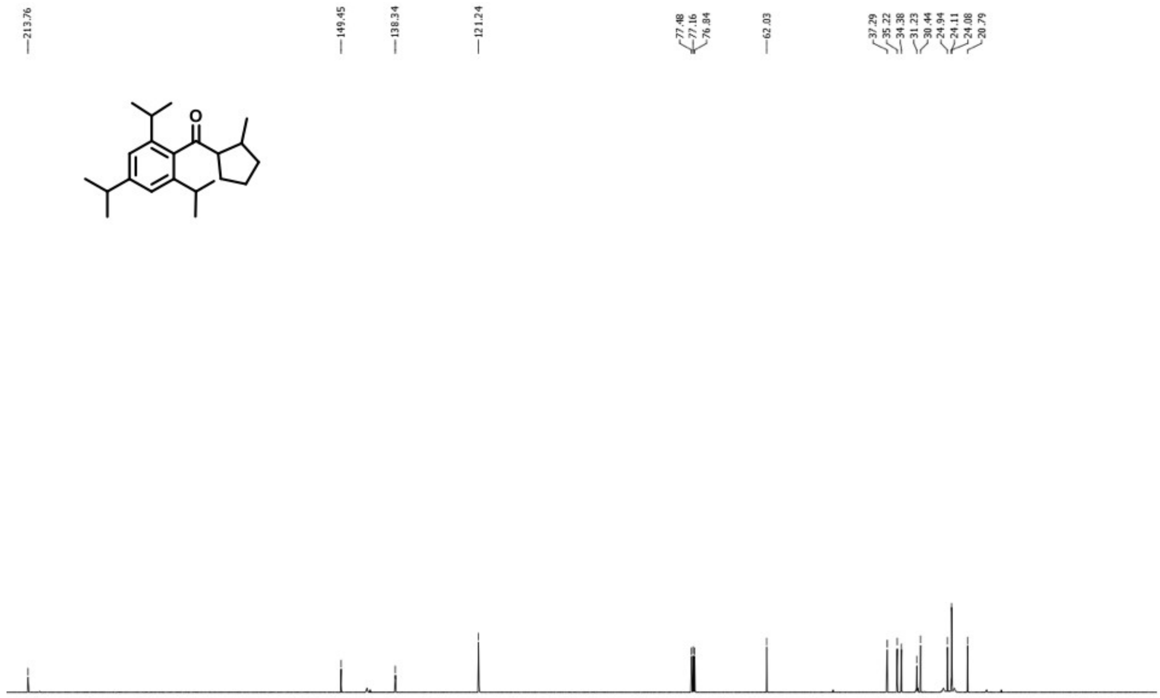


Figure S70. ^{13}C NMR spectrum (100 MHz) of **(4bf)** in $CDCl_3$

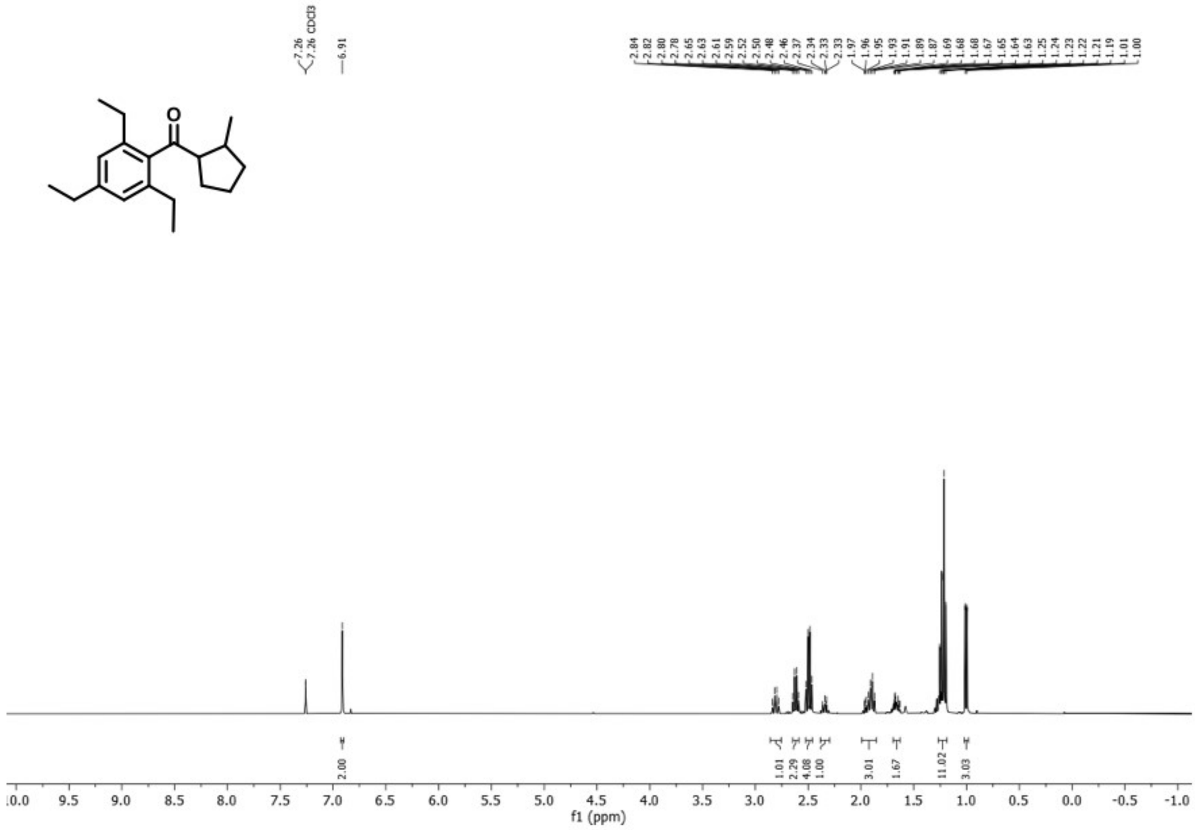


Figure S71 ^{1}H NMR spectrum (400 MHz) of **(4bg)** in $CDCl_3$

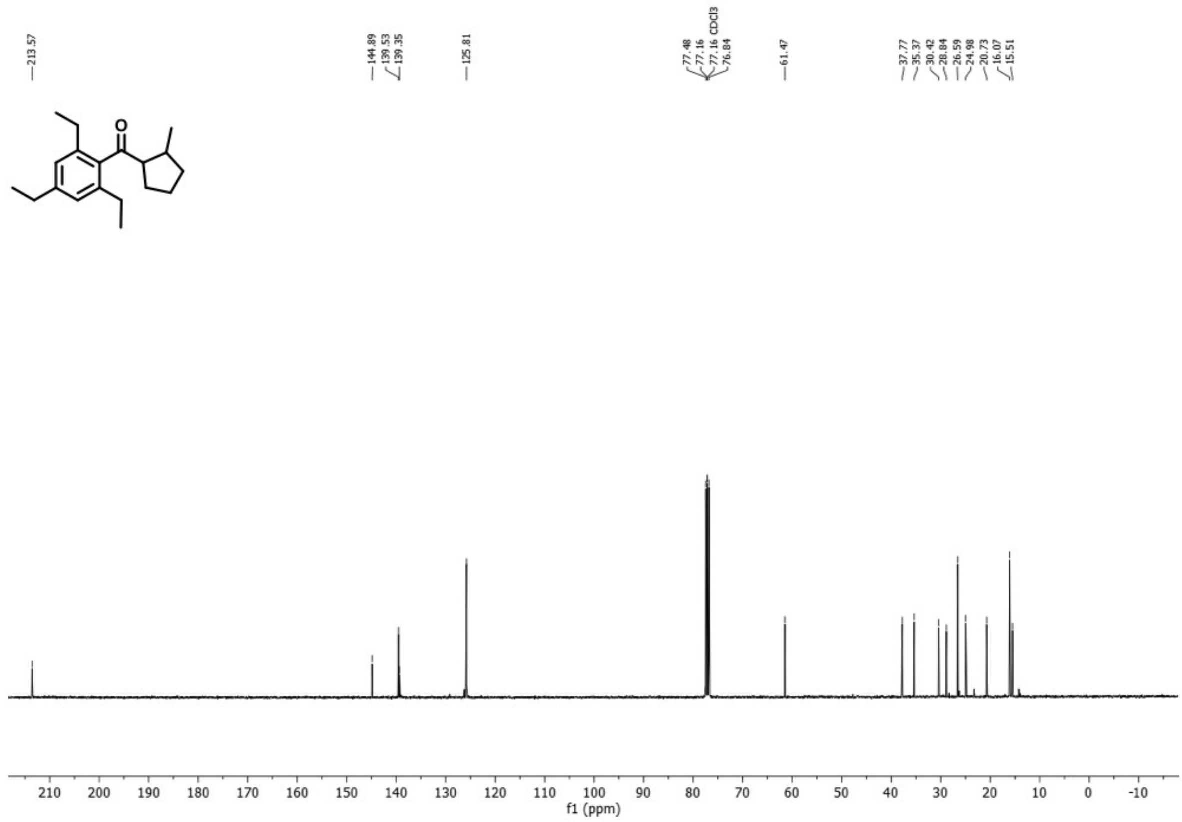


Figure S72. ^{13}C NMR spectrum (100 MHz) of **(4bg)** in $CDCl_3$

Figure S73. ^{1}H NMR spectrum (400 MHz) of **(4bh)** in $CDCl_3$

Figure S74. ^{13}C NMR spectrum (100 MHz) of **(4bh)** in $CDCl_3$

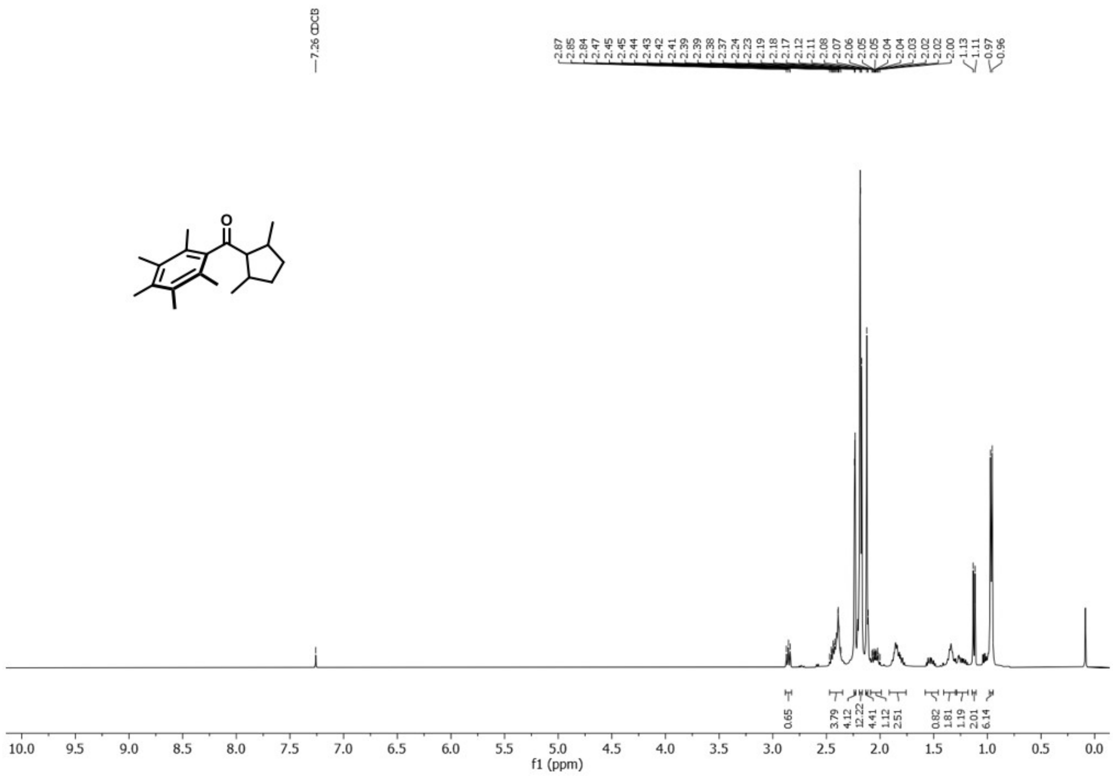


Figure S75. ^{1}H NMR spectrum (400 MHz) of **(4bi)** in $CDCl_3$

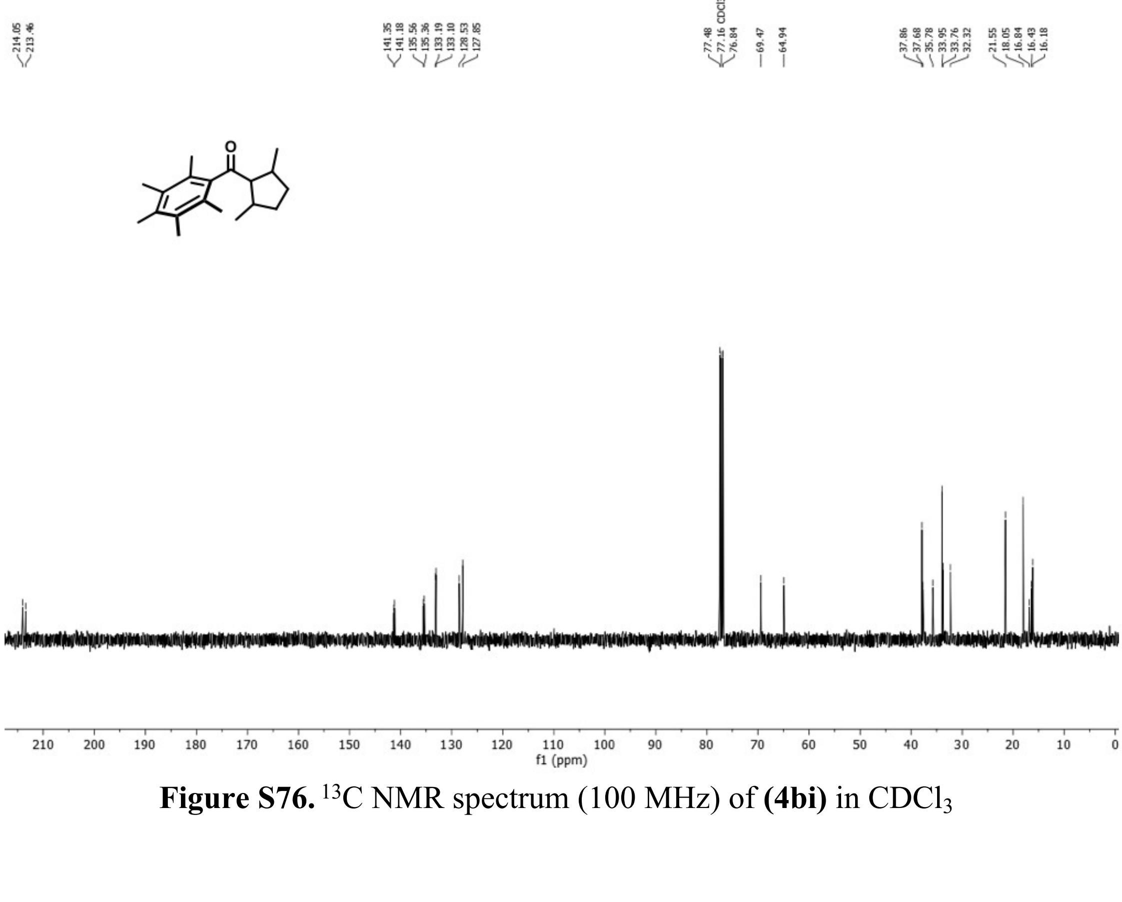


Figure S76. ^{13}C NMR spectrum (100 MHz) of **(4bi)** in $CDCl_3$

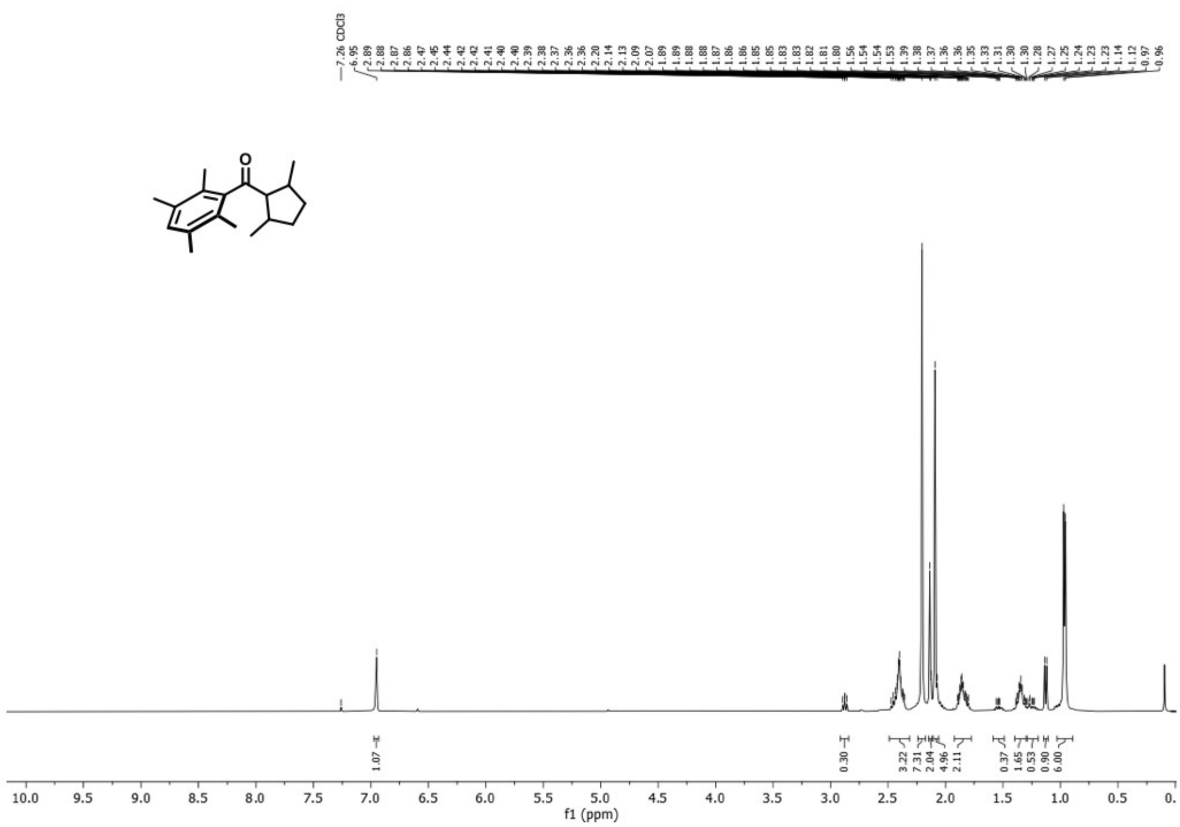


Figure S77. ^{1}H NMR spectrum (400 MHz) of **(4bj)** in $CDCl_3$

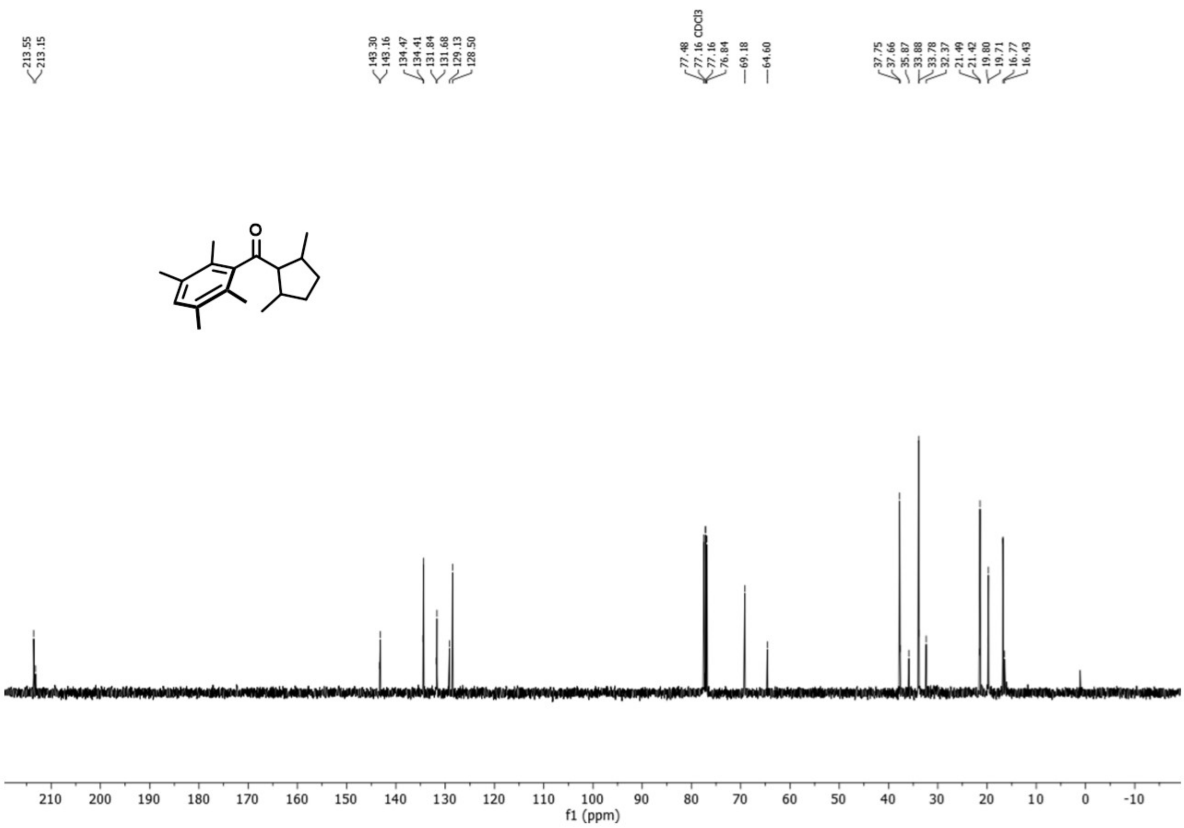


Figure S78. ^{13}C NMR spectrum (100 MHz) of **(4bj)** in $CDCl_3$

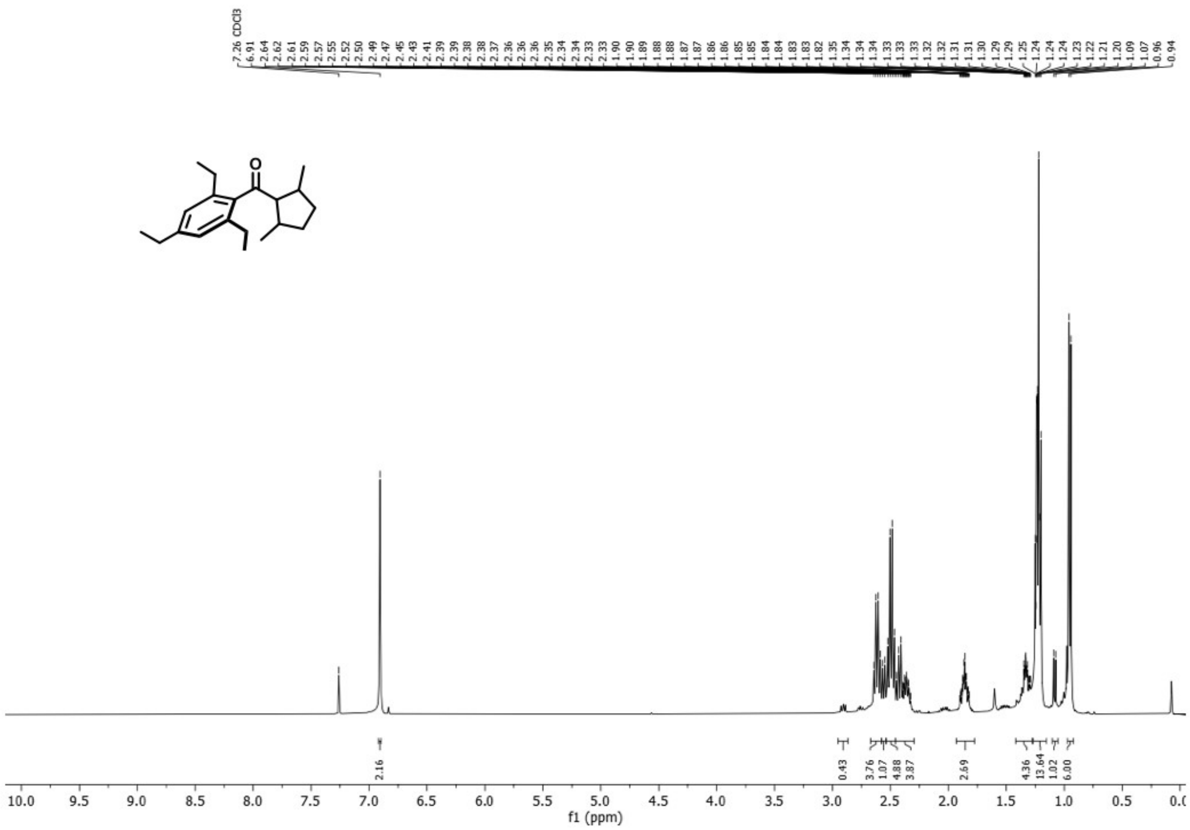


Figure S79. ^{1}H NMR spectrum (400 MHz) of **(4bk)** in $CDCl_3$

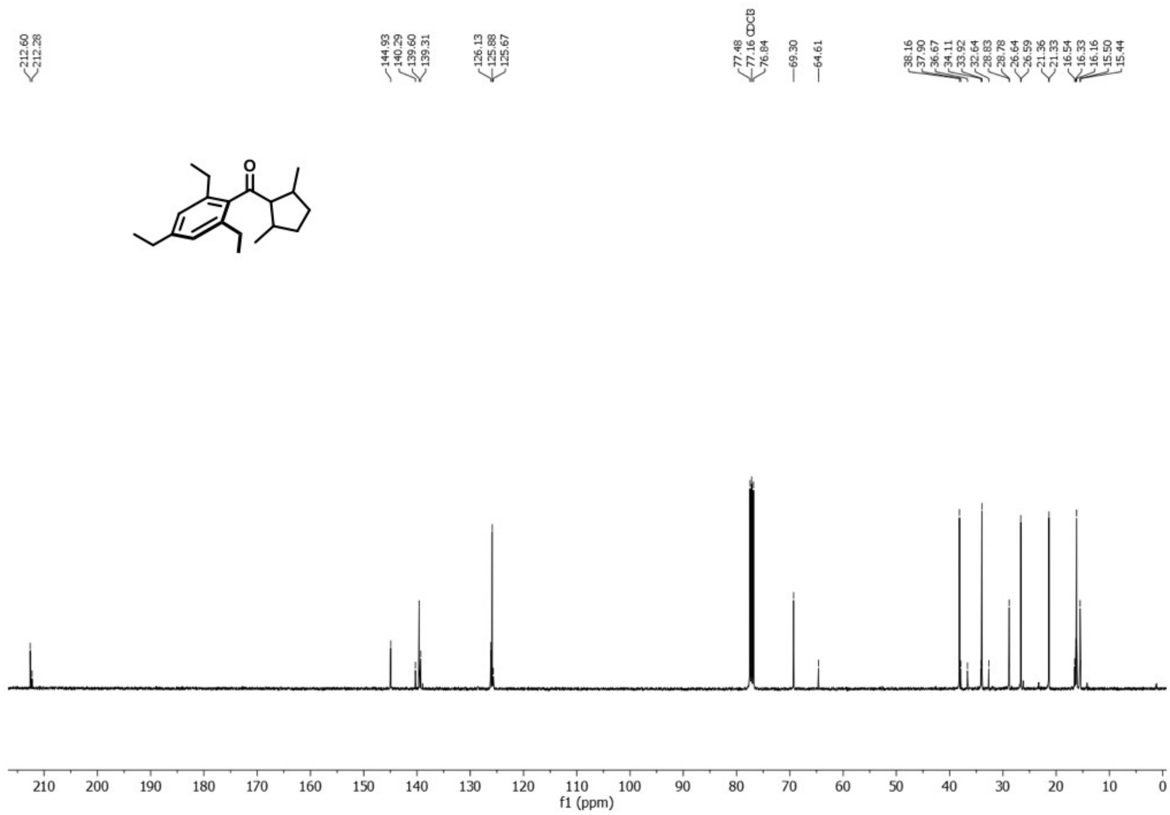


Figure S80. ^{13}C NMR spectrum (100 MHz) of **(4bk)** in $CDCl_3$

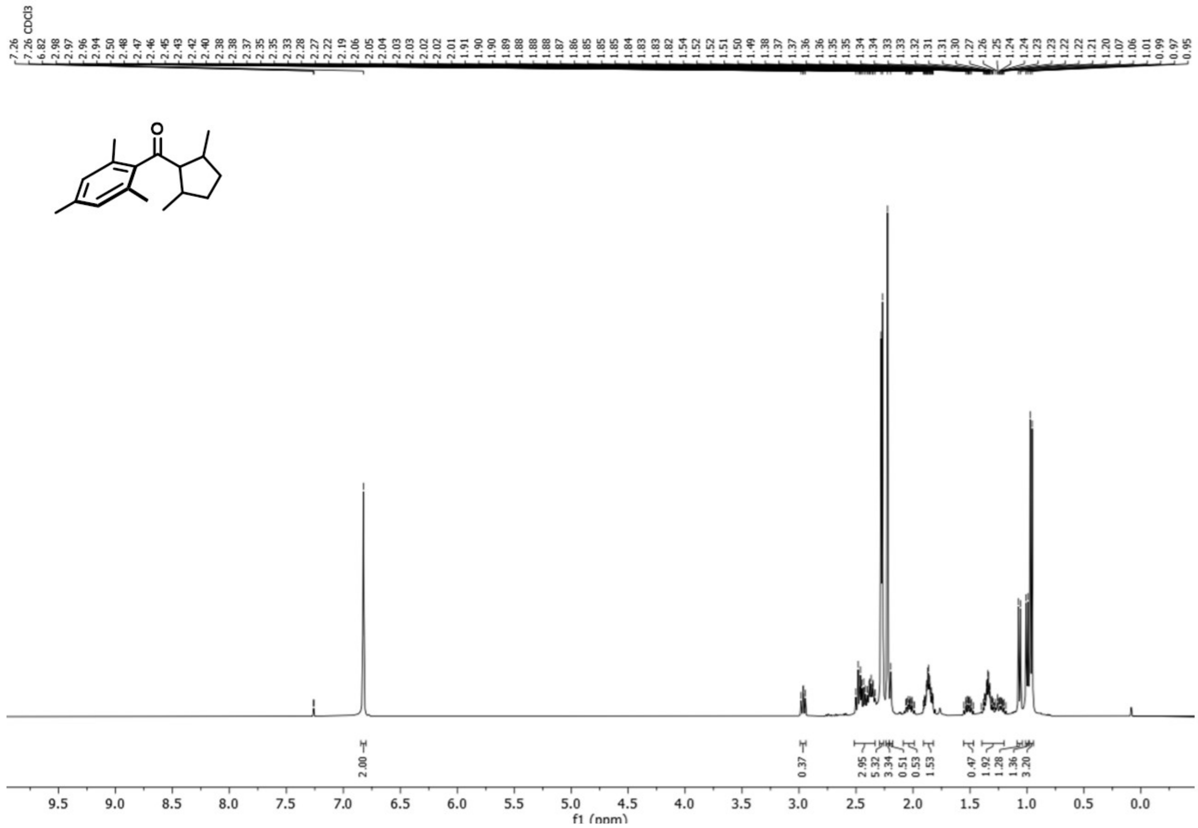


Figure S81. ^{1}H NMR spectrum (400 MHz) of **(4bl)** in $CDCl_3$

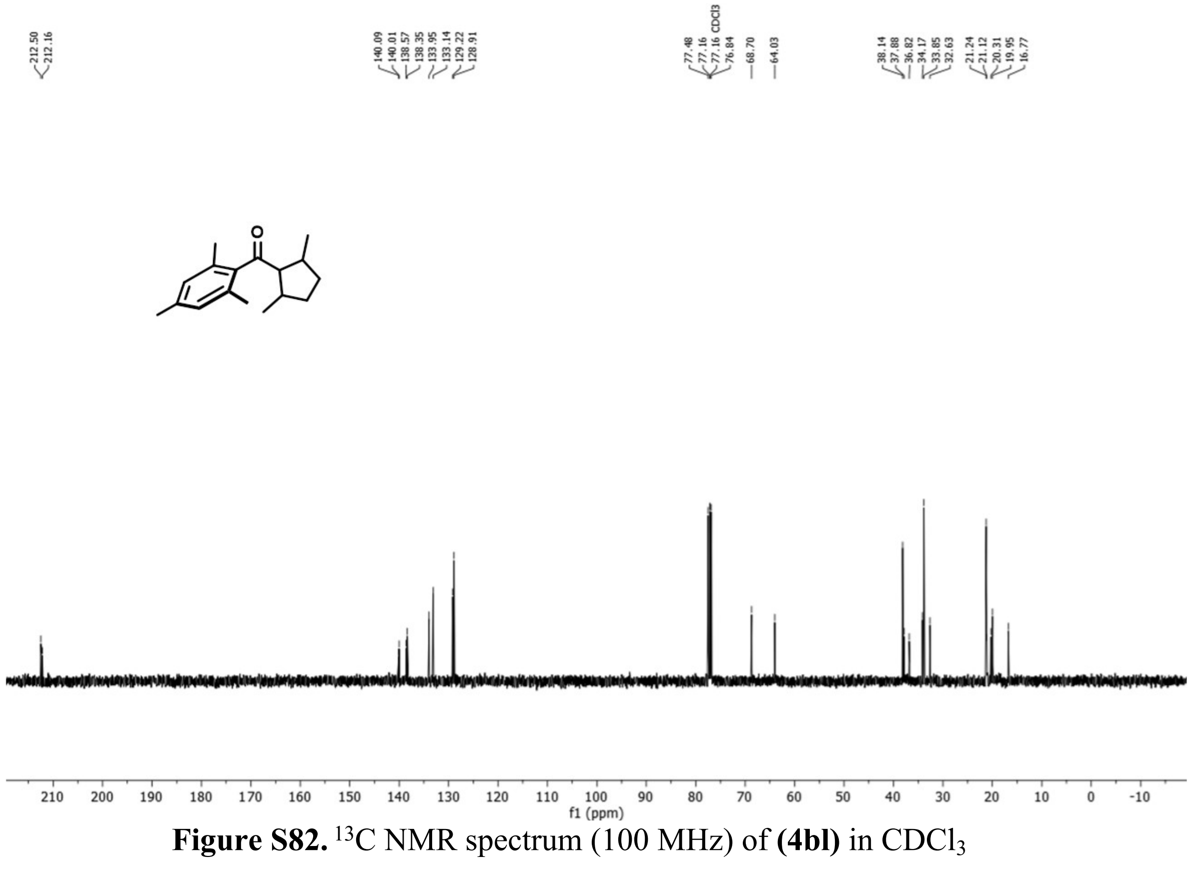


Figure S82. ^{13}C NMR spectrum (100 MHz) of **(4bl)** in $CDCl_3$

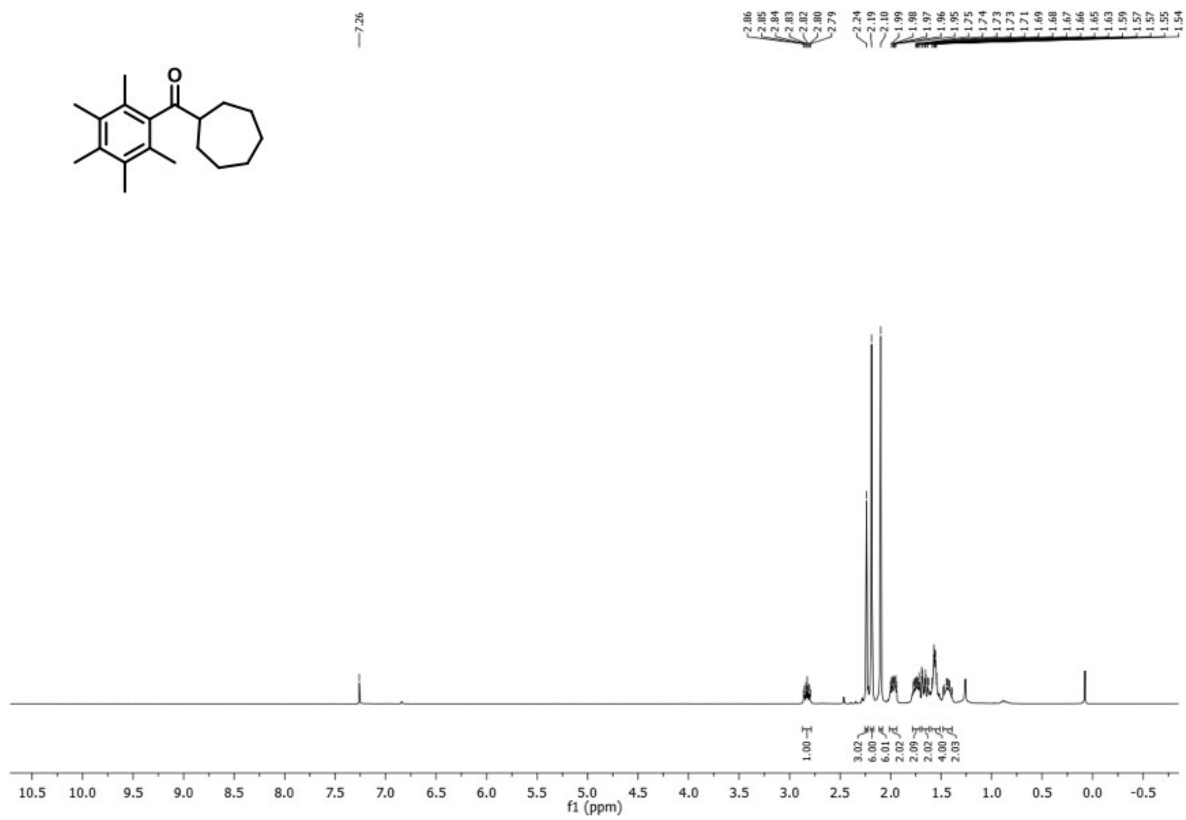


Figure S83. ^{1}H NMR spectrum (400 MHz) of **(4ca)** in $CDCl_3$

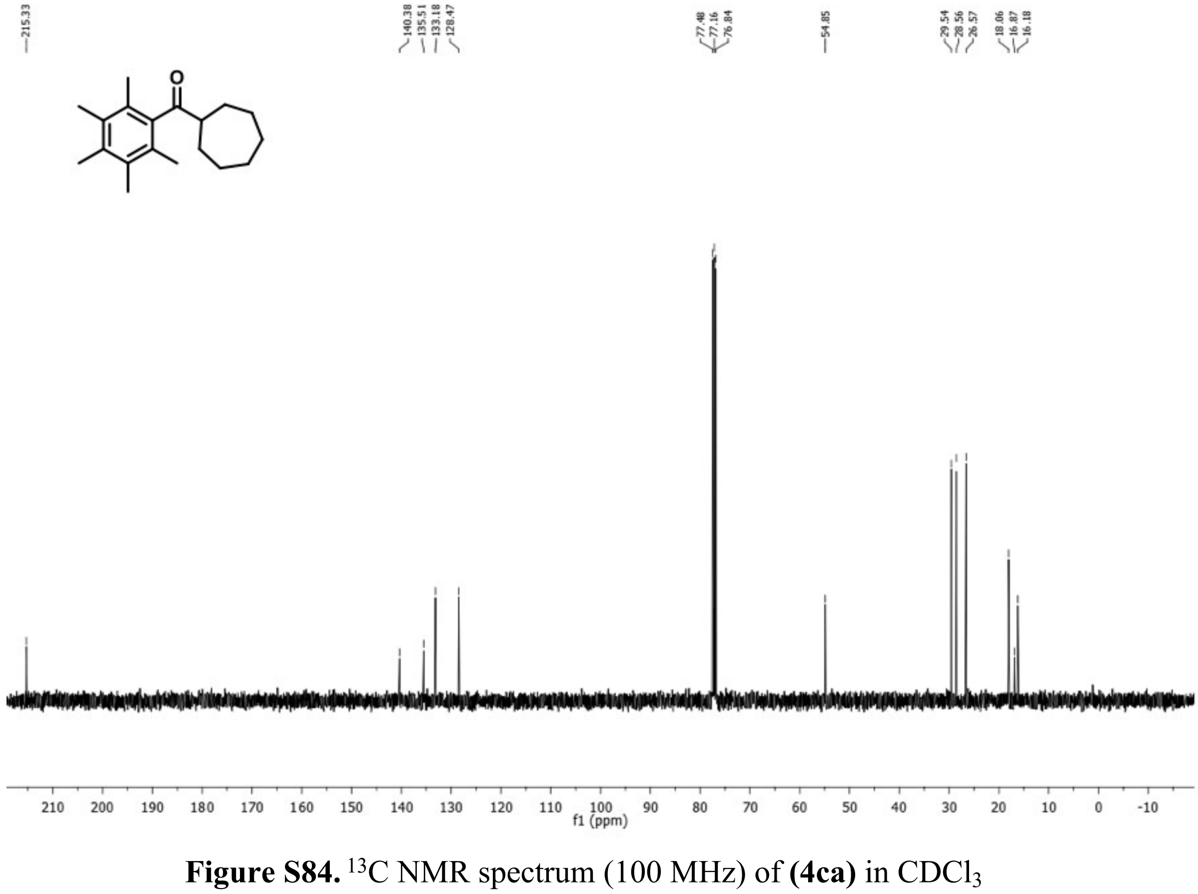


Figure S84. ^{13}C NMR spectrum (100 MHz) of **(4ca)** in $CDCl_3$

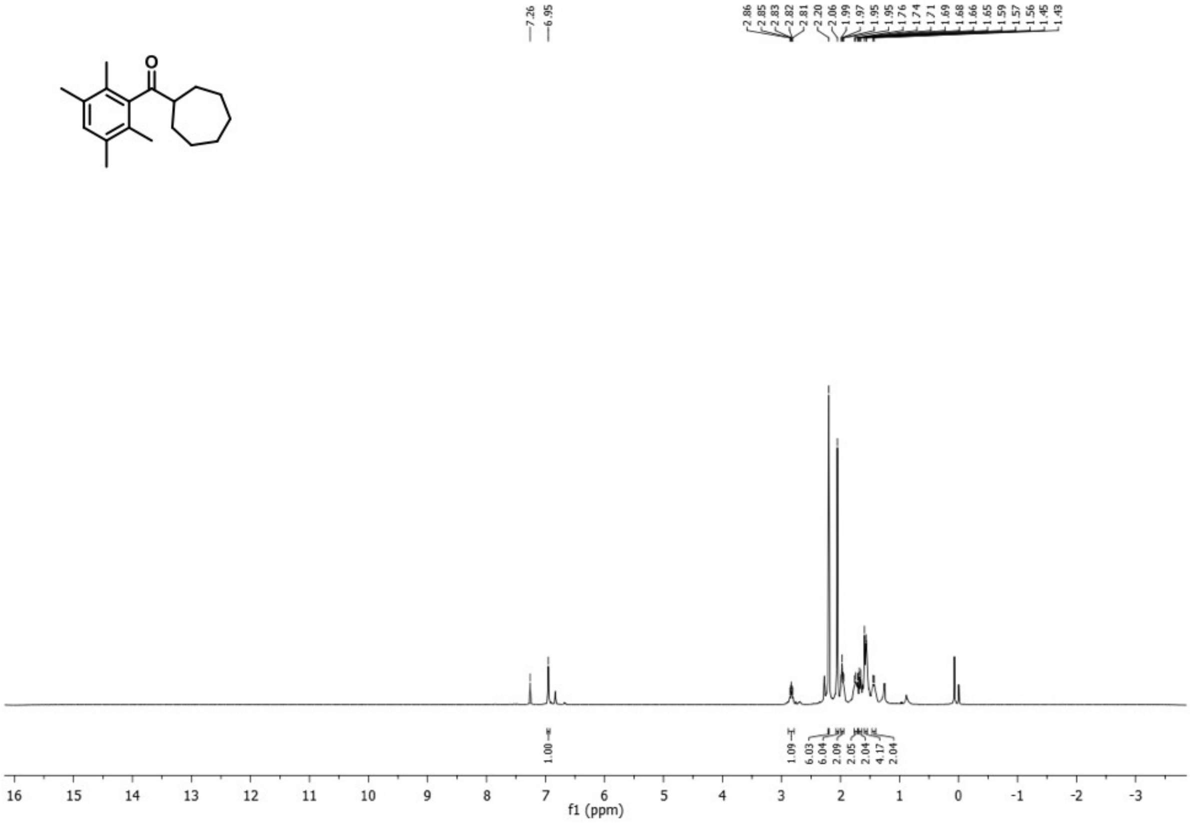


Figure S85. ^{1}H NMR spectrum (400 MHz) of **(4cb)** in $CDCl_3$

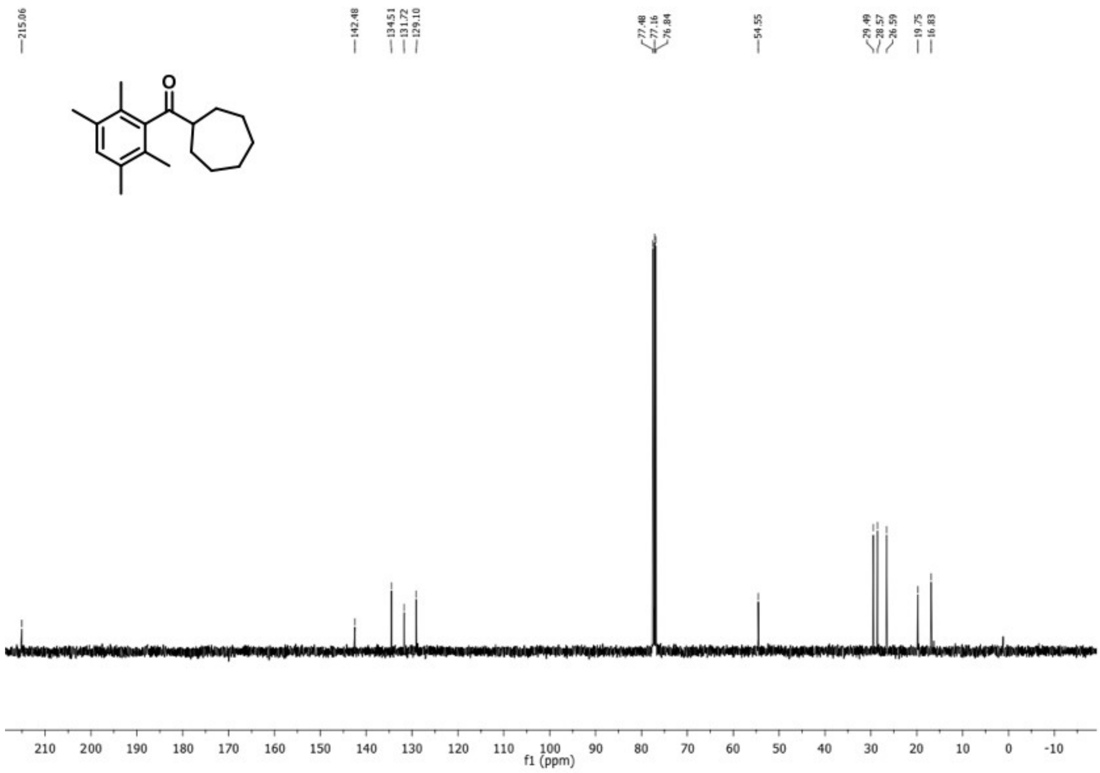


Figure S86. ^{13}C NMR spectrum (100 MHz) of **(4cb)** in $CDCl_3$

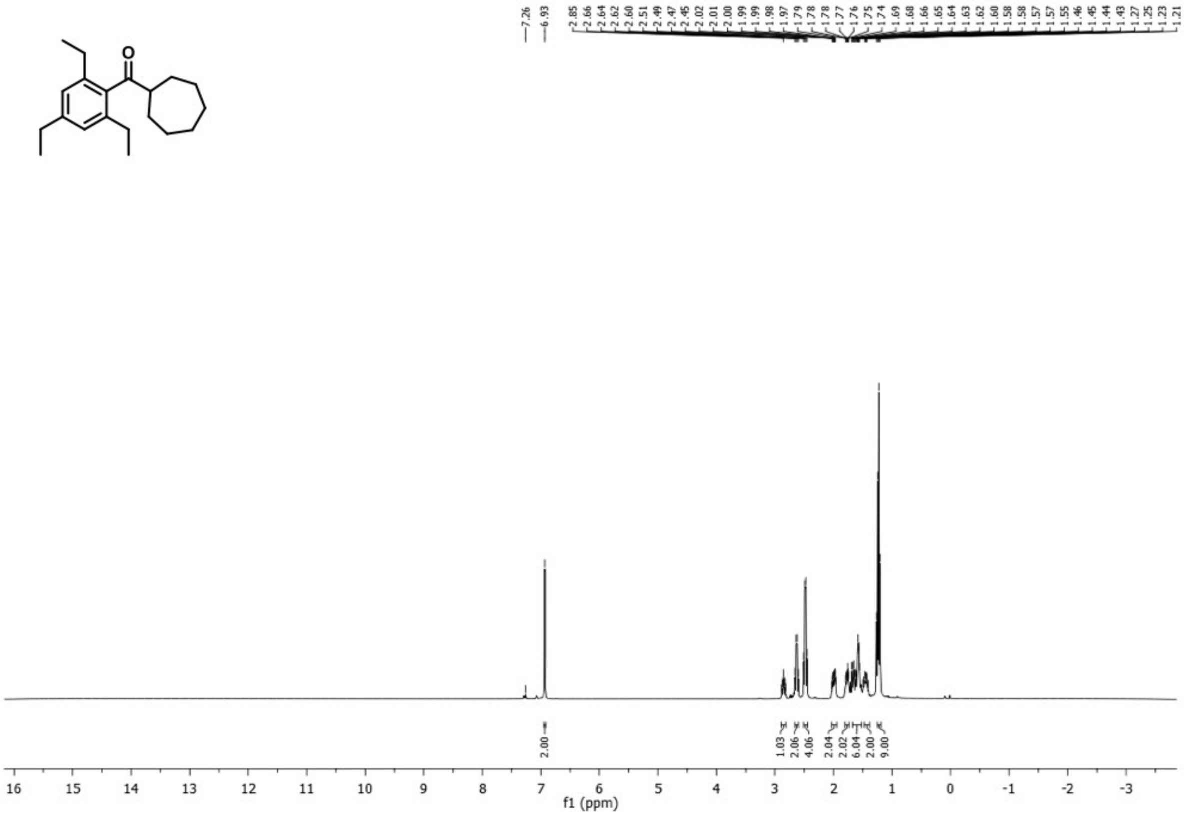


Figure S87. ^{1}H NMR spectrum (400 MHz) of **(4cc)** in $CDCl_3$

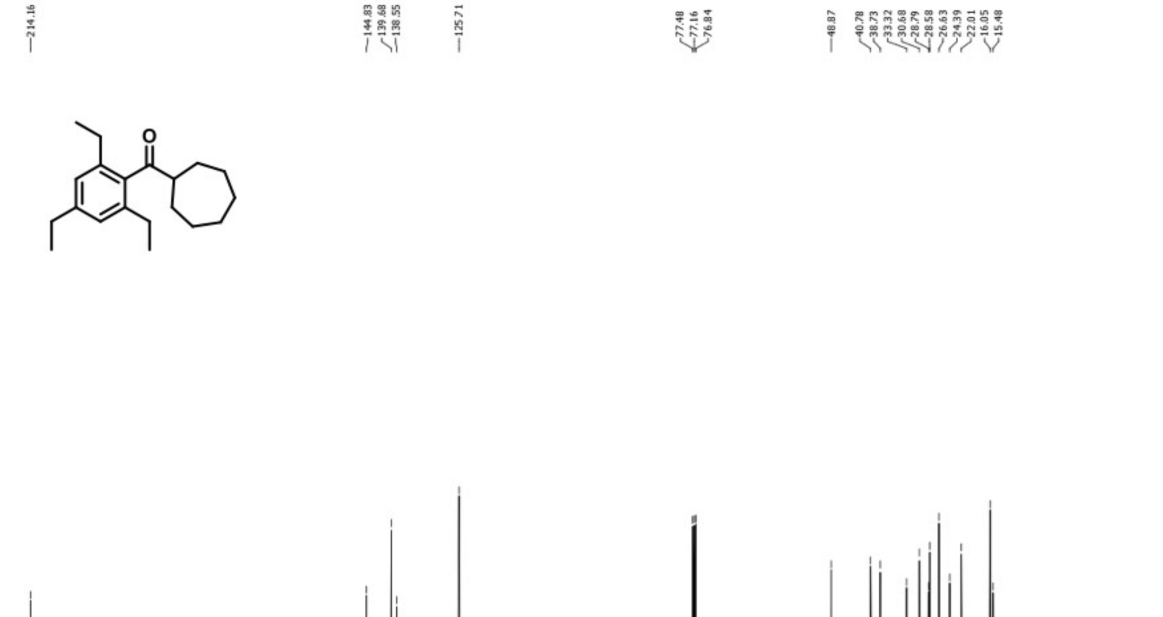


Figure S88. ^{13}C NMR spectrum (100 MHz) of **(4cc)** in $CDCl_3$

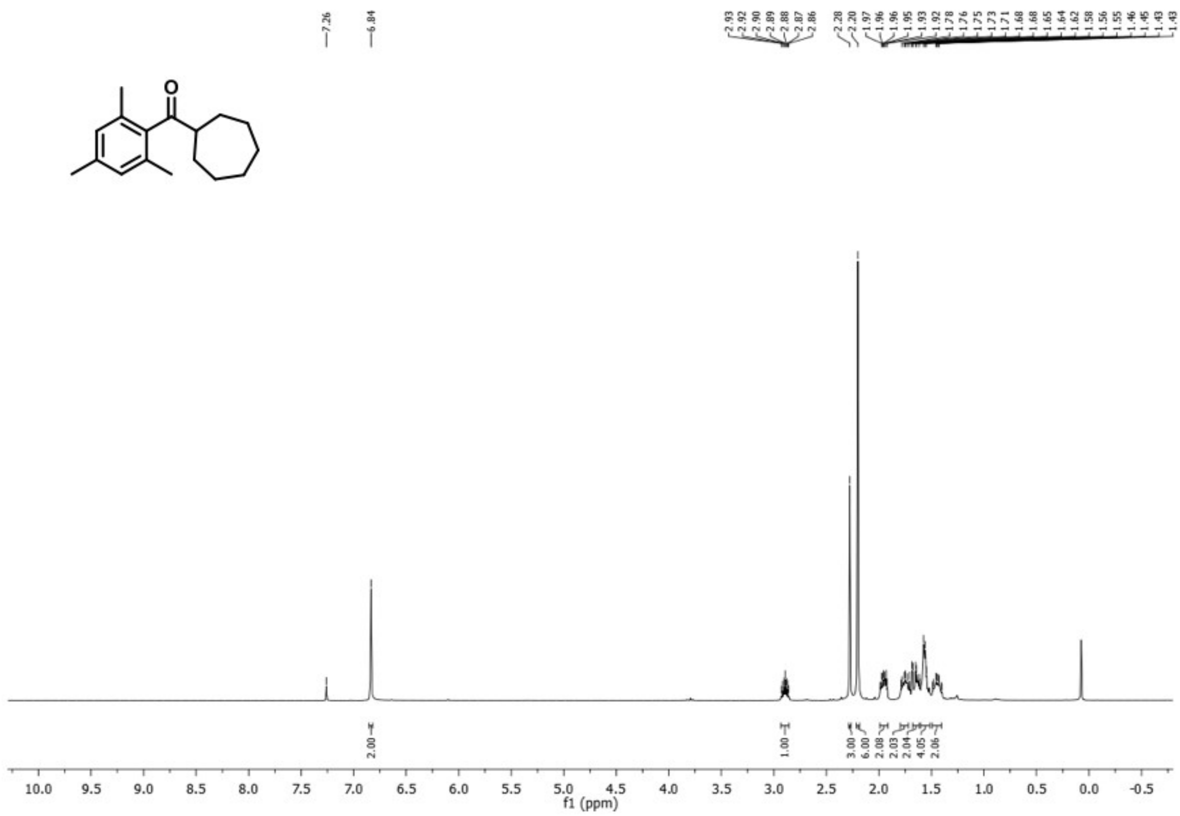


Figure S89. ^{1}H NMR spectrum (400 MHz) of **(4cd)** in $CDCl_3$

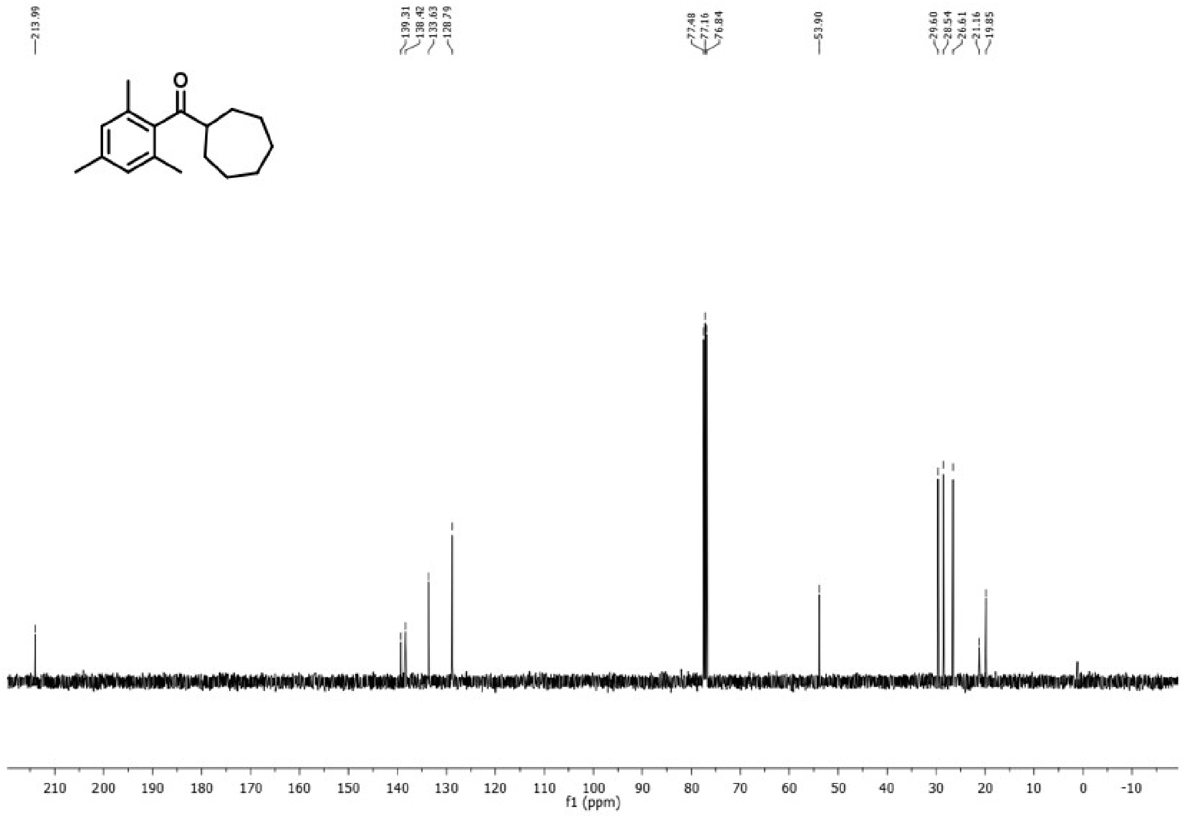


Figure S90. ^{13}C NMR spectrum (100 MHz) of **(4cd)** in $CDCl_3$

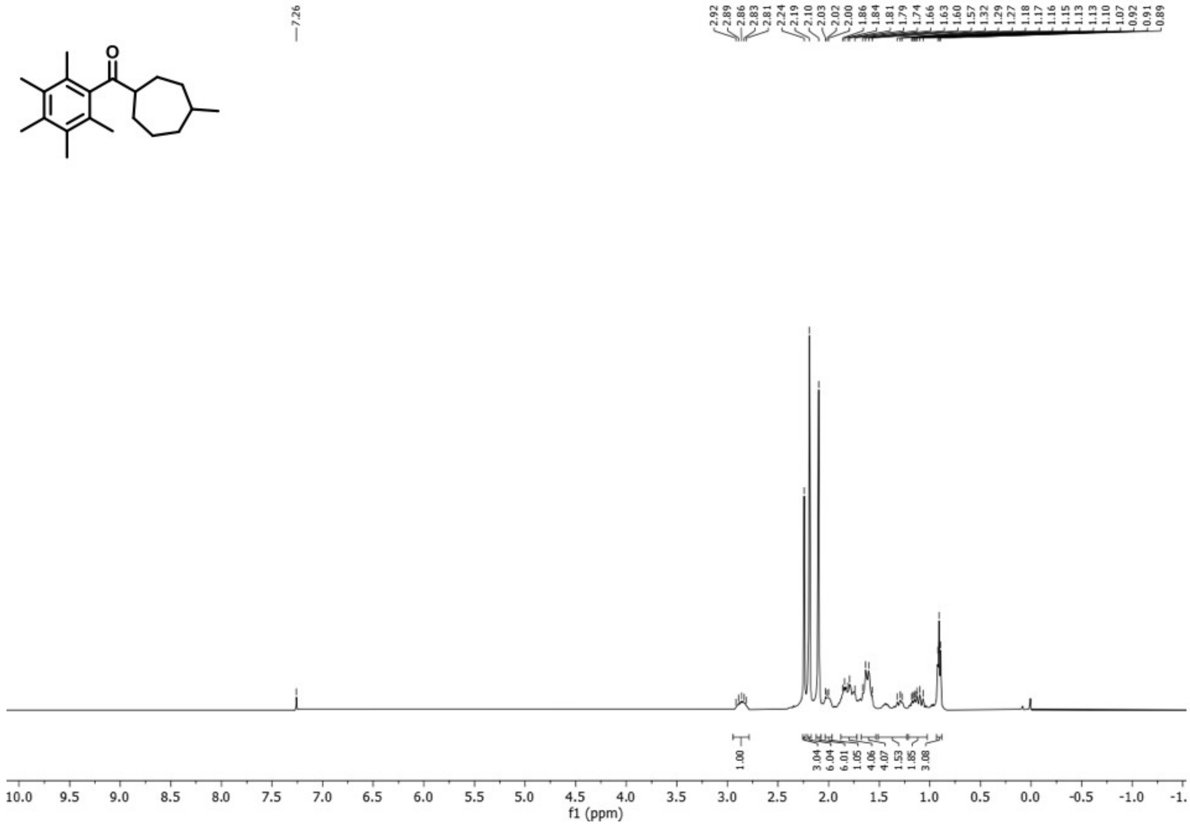


Figure S91. ^{1}H NMR spectrum (400 MHz) of **(4ce)** in $CDCl_3$

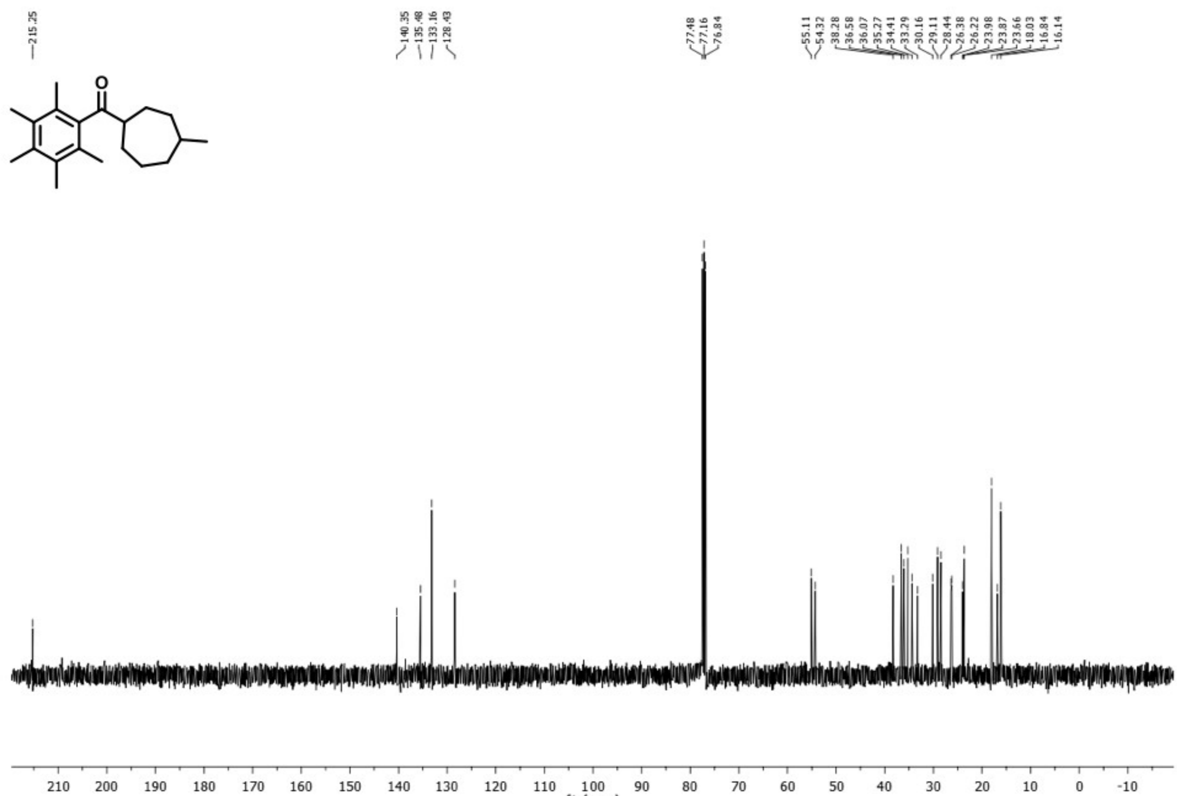


Figure S92. ^{13}C NMR spectrum (100 MHz) of **(4ce)** in $CDCl_3$

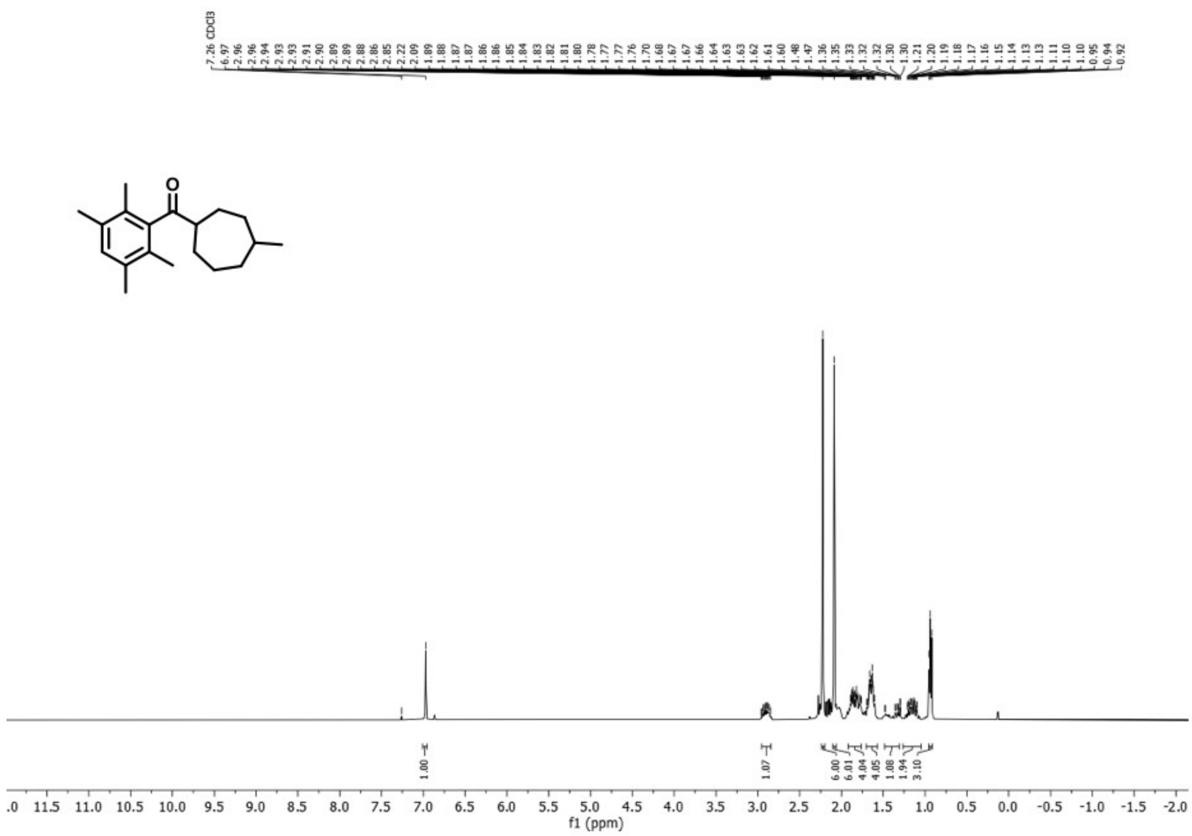


Figure S93. ^{1}H NMR spectrum (400 MHz) of **(4cf)** in $CDCl_3$

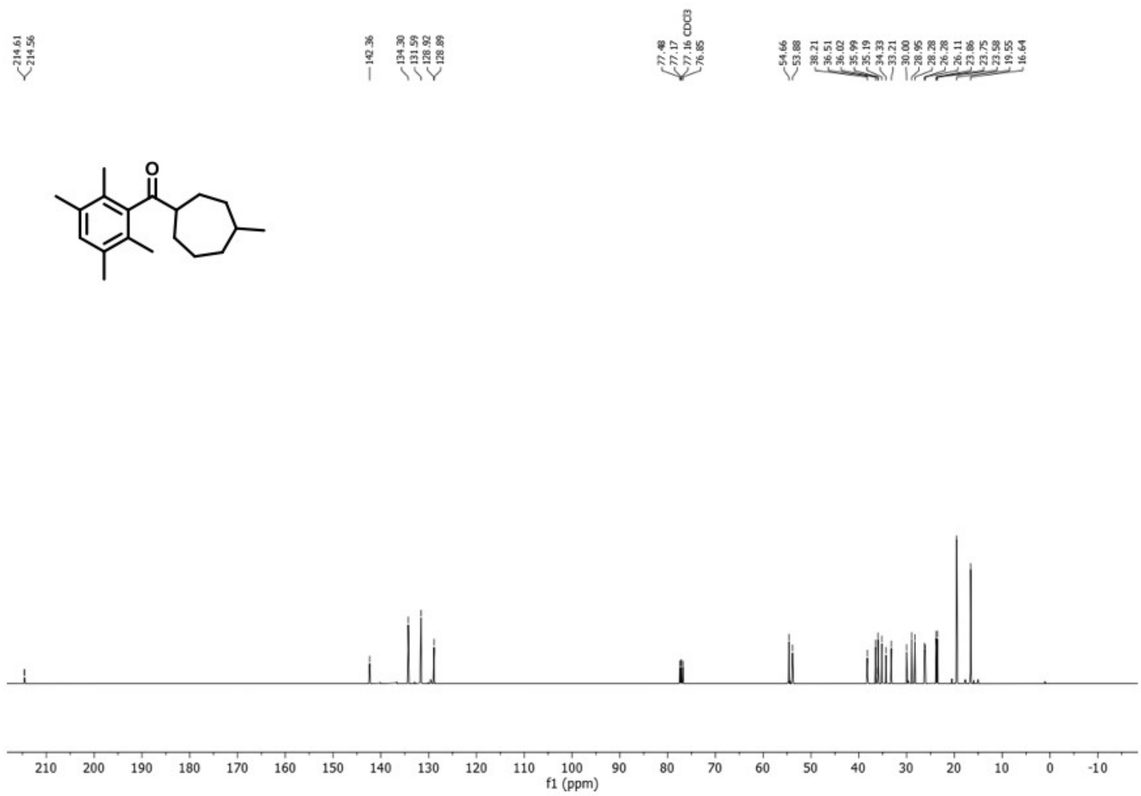


Figure S94. ^{13}C NMR spectrum (100 MHz) of **(4cf)** in $CDCl_3$

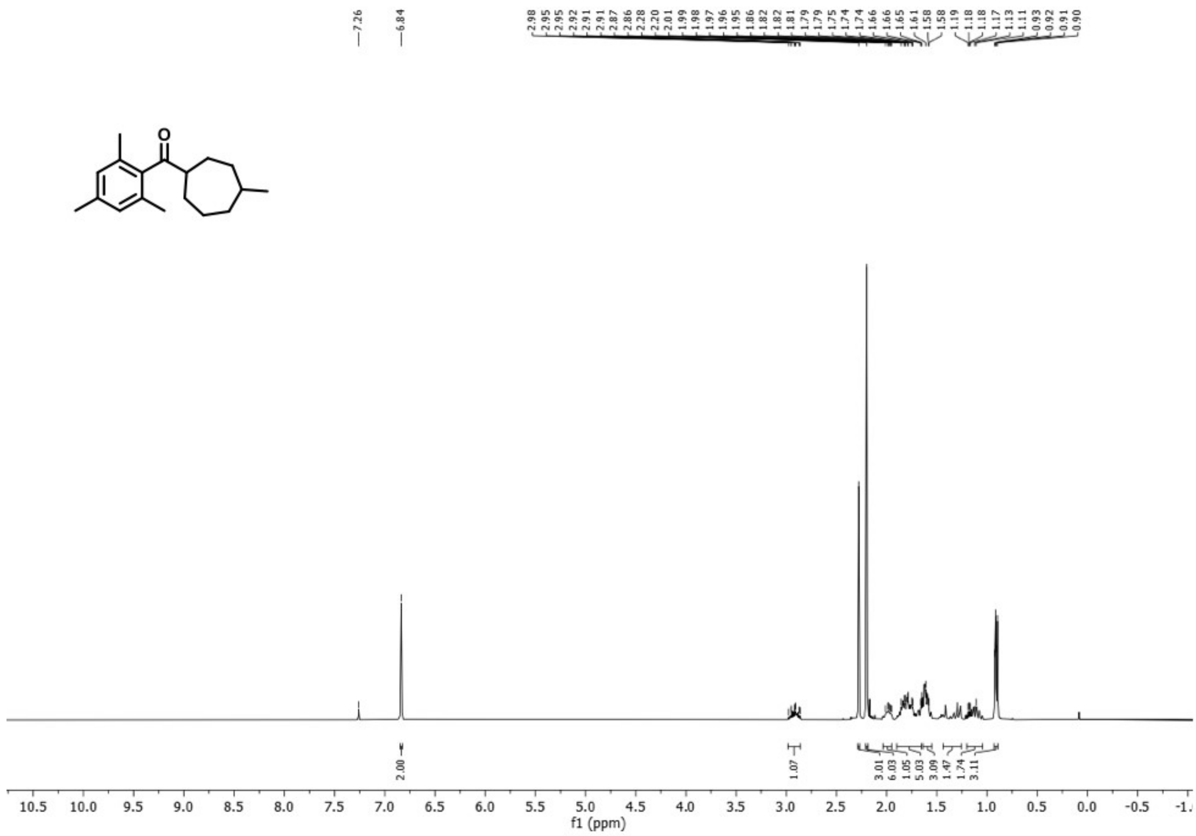


Figure S95. ^{1}H NMR spectrum (400 MHz) of **(4cg)** in $CDCl_3$

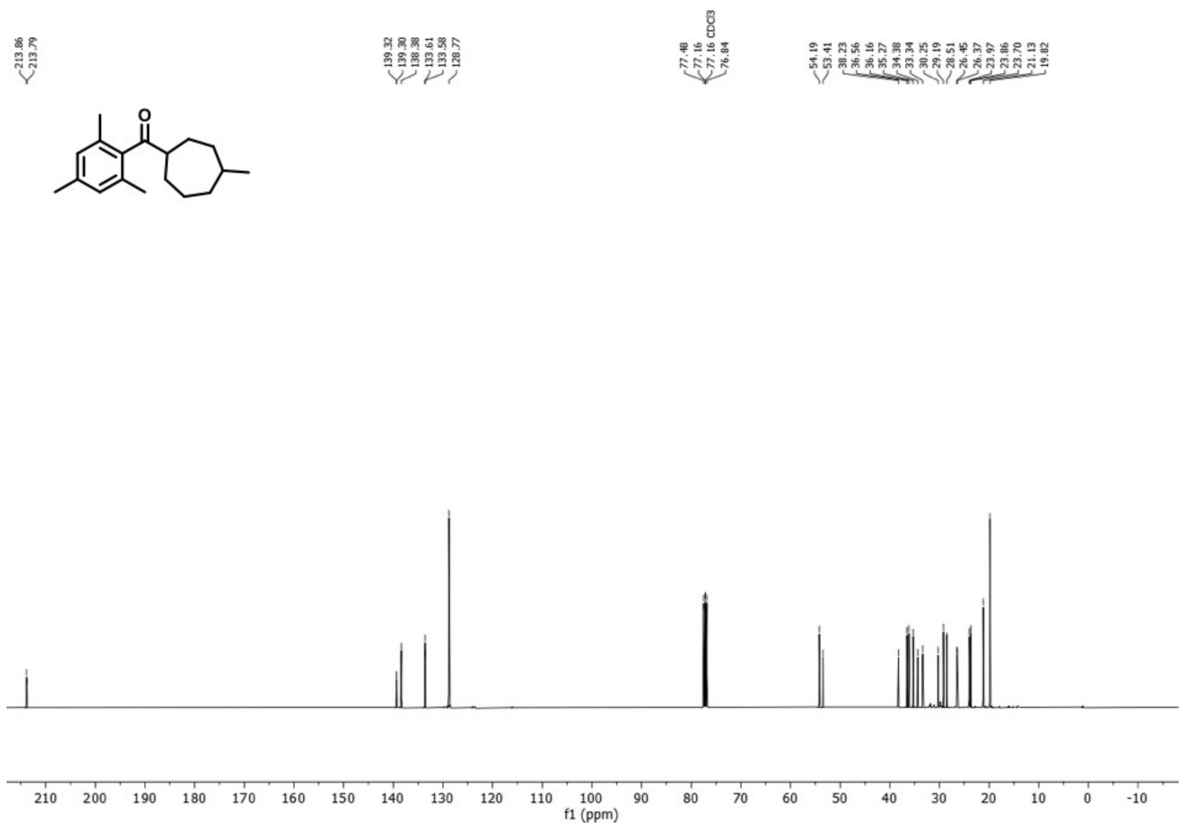


Figure S96. ^{13}C NMR spectrum (100 MHz) of **(4cg)** in $CDCl_3$

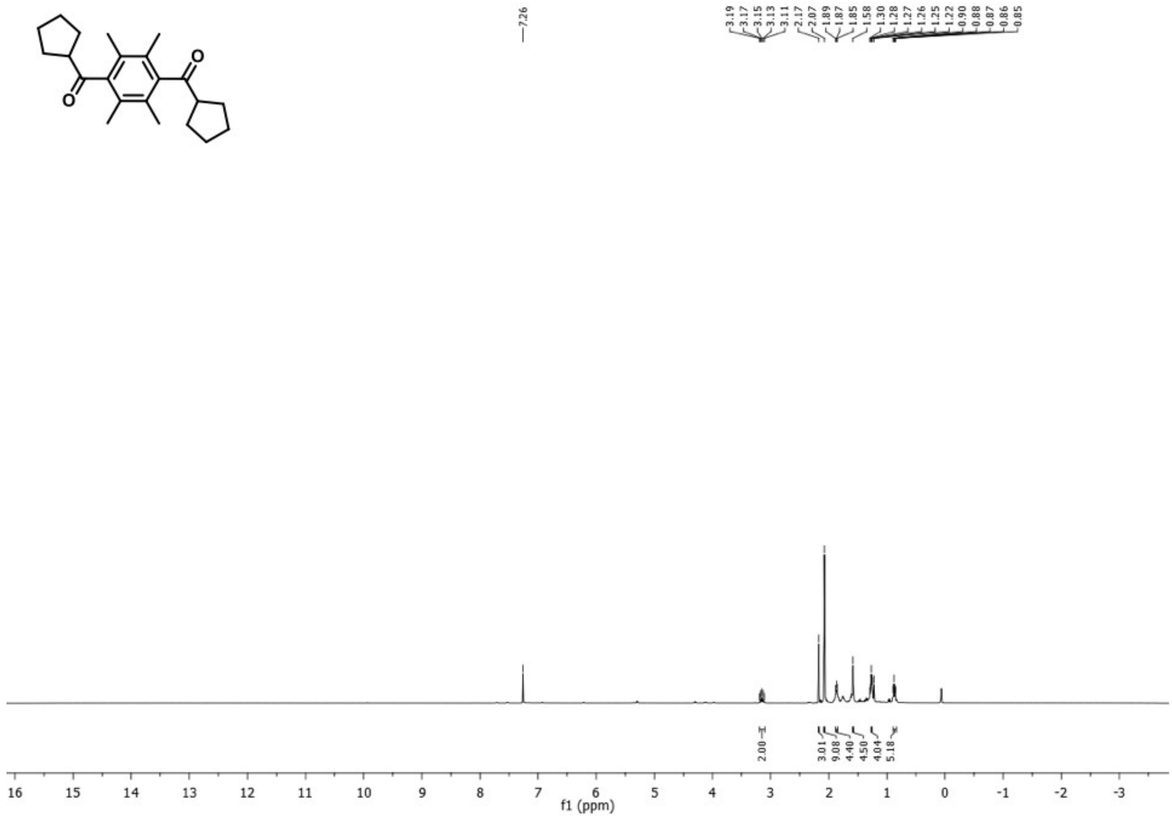


Figure S97. ^{1}H NMR spectrum (400 MHz) of **(4da)** in $CDCl_3$

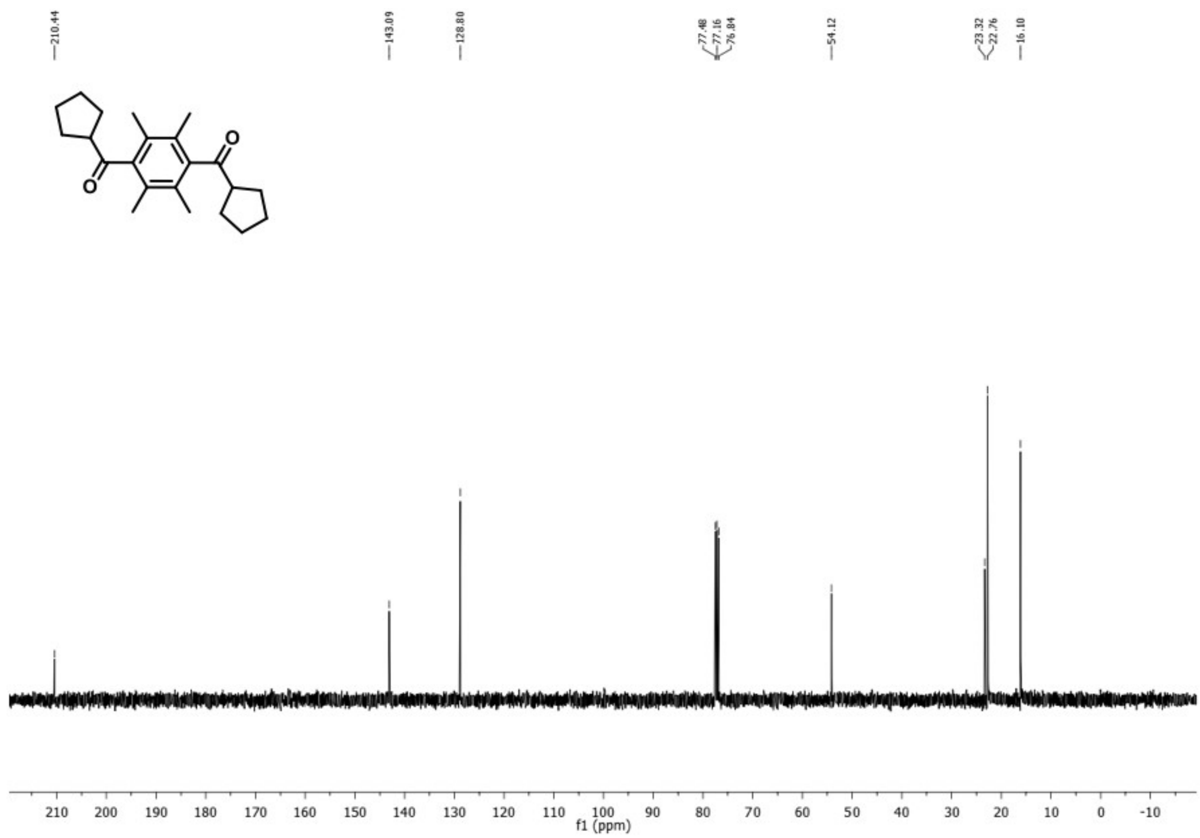


Figure S98. ^{13}C NMR spectrum (100 MHz) of **(4da)** in $CDCl_3$

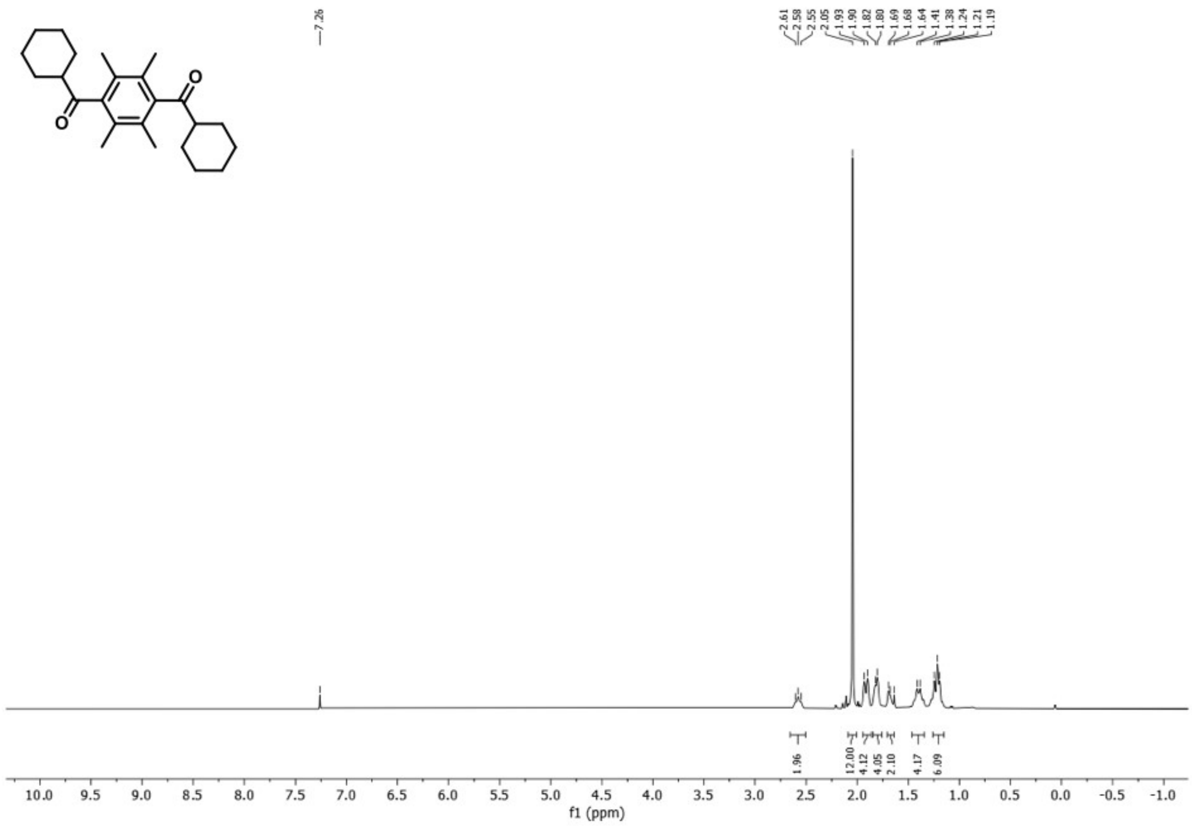


Figure S99. ^{1}H NMR spectrum (400 MHz) of **(4db)** in $CDCl_3$

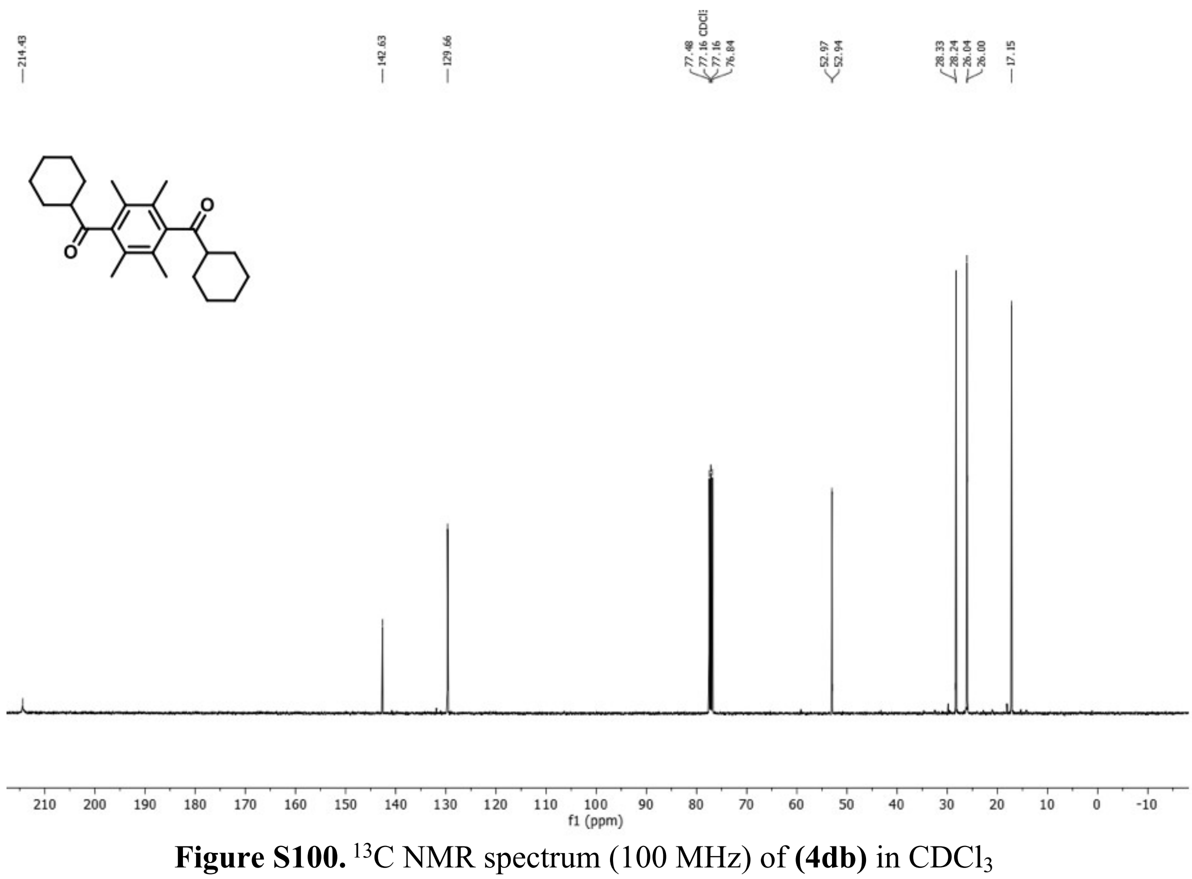


Figure S100. ^{13}C NMR spectrum (100 MHz) of **(4db)** in $CDCl_3$

8. Computational Details

All calculations were carried out using Density Functional Theory as implemented in the Gaussian09[S9] quantum chemistry programs. The geometries of stationary points and transition states (TS) were optimized with M062X functional.[S10] We used double-ζ basis set with the relativistic effective core potential of Hay and Wadt (LANL2DZ)[S11-S12] for the Nickel atom and 6-31G* basis set for other elements (H, C, O and N). The geometries were optimized without any symmetry constraints. Harmonic force constants were computed at the optimized geometries to characterize the stationary points as minima or saddle points. The zero-point vibrational corrections were determined from the harmonic vibrational frequencies to convert the total energies E^e to E^0. The rigid-rotor harmonic-oscillator approximation was applied for evaluating the thermal and entropic contribution that were necessary to obtain the enthalpies, H_{298} and Gibbs free energies, G_{298} at 298 K. To get accurate energies of the optimized structures were revaluated by additional single point energy calculations of each optimized geometry using 6-311G* triple-ζ basis set[S13] for light atoms (H, C, N, O). Implicit solvent effects of toluene were considered and solvent correction was done using the polarized continuum model. [S14]

To decrease the computational cost, (i) tert-butyl groups in the ligand were replaced by methyl and (ii) the methyl groups in the phenyl substituent of pentamethyl acetophenone were replaced with hydrogens and all the calculations were carried out with this truncated framework.

Coordinates of optimised geometries of intermediates and transition states

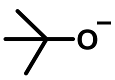
1 [Ni(azo)$_2$]

0 1

C	0.77803000	-2.82150800	0.22593200
C	1.77076900	-2.48289800	1.14508700
C	2.83600900	-3.35000500	1.35736600
H	3.60404400	-3.08991400	2.07845100
C	2.92255400	-4.53968500	0.63579100
C	1.93313500	-4.86315200	-0.29132400

H	2.00160500	-5.78537200	-0.85942400
C	0.85234800	-4.01143000	-0.49478000
C	-2.59674200	-1.73825900	-0.05205400
C	-2.67031700	-0.42643200	0.50752200
C	-3.97011600	0.10424300	0.78152500
C	-5.08121200	-0.60946200	0.39493100
C	-5.01833300	-1.88745400	-0.21982900
C	-3.77791100	-2.44325400	-0.39793300
N	-0.32147200	-1.91881700	0.07615300
N	-1.43829100	-2.47578800	-0.09101900
O	-1.63367200	0.27967000	0.82832900
Ni	-0.00006400	0.00006600	-0.00031300
C	-0.77790100	2.82173800	-0.22639200
C	-1.77052800	2.48321800	-1.14570500
C	-2.83568300	3.35039500	-1.35812400
H	-3.60362900	3.09035900	-2.07932300
C	-2.92225300	4.54007100	-0.63654400
C	-1.93294300	4.86345300	0.29072000
H	-2.00143200	5.78566500	0.85883000
C	-0.85224100	4.01166100	0.49431800
C	2.59662800	1.73804100	0.05254500
C	2.67020200	0.42643500	-0.50755200
C	3.97003400	-0.10426300	-0.78143500
C	5.08109800	0.60912000	-0.39418400
C	5.01819000	1.88685600	0.22113000
C	3.77779400	2.44274300	0.39906600
N	0.32145000	1.91892600	-0.07641900
N	1.43826800	2.47571400	0.09137400
O	1.63357900	-0.27942200	-0.82896100
H	0.06722700	-4.25134100	-1.20292300
H	1.69574200	-1.54728700	1.69282100
H	3.76064500	-5.21098900	0.79239900
H	-3.76027000	5.21144000	-0.79326300
H	-0.06722500	4.25150700	1.20260000

H	-1.69549200	1.54760800	-1.69343800
H	-6.06286700	-0.17744900	0.58666200
H	-3.65869100	-3.44477400	-0.80195000
H	6.06275800	0.17706100	-0.58578000
H	3.65857000	3.44410700	0.80347400
C	4.05393900	-1.41899700	-1.50442700
H	3.46422200	-2.18989800	-1.00089200
H	3.64429400	-1.32206300	-2.51601500
H	5.09122400	-1.75506200	-1.58094400
C	6.28545800	2.59866200	0.61627900
H	6.82354800	2.04971300	1.39699500
H	6.96579200	2.70211400	-0.23576100
H	6.07059300	3.59963200	0.99902800
C	-6.28562600	-2.59960800	-0.61426900
H	-6.96570200	-2.70275100	0.23801500
H	-6.82401100	-2.05109400	-1.39508800
H	-6.07074300	-3.60072800	-0.99661500
C	-4.05397500	1.41930200	1.50392600
H	-3.64378200	1.32298100	2.51534800
H	-3.46470300	2.19011000	0.99971700
H	-5.09130100	1.75515800	1.58078000

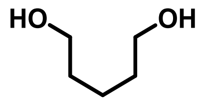


Tert-butoxide anion

-1 1

C	0.12550300	0.13337900	-0.00003700
C	0.72012000	0.85893400	1.25664100
H	0.34122300	1.88895600	1.27061900
H	0.34093100	0.35638500	2.15572000
H	1.82164600	0.88671400	1.30518300
C	0.71983700	-1.31783500	0.00008800
H	0.34065500	-1.84492200	0.88500700

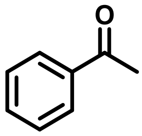
H	0.34078700	-1.84502000	-0.88482800
H	1.82135800	-1.37392000	0.00017300
C	0.72030900	0.85879500	-1.25670500
H	0.34125500	0.35614800	-2.15578700
H	0.34141500	1.88881600	-1.27085300
H	1.82184300	0.88656900	-1.30508400
O	-1.19688200	0.13359300	-0.00013700



pentane-1,5-diol

0 1

O	1.15972100	-3.68828000	0.10783300
C	3.49861700	-3.32506100	-0.02582800
H	3.49116300	-3.07463700	1.04168600
H	3.63361900	-4.41101500	-0.09533700
H	0.29380600	-3.46966700	-0.26053400
C	2.14423600	-2.97101900	-0.61177500
H	2.12508100	-3.23195700	-1.68181100
H	1.98124300	-1.88426300	-0.53535100
C	4.64730200	-2.60526400	-0.72800700
H	4.49383100	-1.51893400	-0.66147100
H	4.63494800	-2.85368600	-1.79863700
C	6.00932000	-2.96349700	-0.13874700
H	6.03945300	-2.70873000	0.92733800
H	6.18050600	-4.04415800	-0.21097400
C	7.15203100	-2.24864000	-0.83602500
H	7.00848100	-1.15922500	-0.75853800
H	7.14946100	-2.50529900	-1.90726600
O	8.35817400	-2.65156900	-0.21596000
H	9.09134800	-2.20097500	-0.65492800



Acetophenone

0 1

O	1.94496600	-3.85771300	0.17903400
C	2.20053100	-3.00415900	-0.64441800
C	2.11595600	-3.30915800	-2.11139800
C	2.40192300	-2.35615300	-3.09198300
C	1.73554100	-4.59909100	-2.49366200
C	2.30843000	-2.68951600	-4.44035100
H	2.69866900	-1.35041900	-2.81003300
C	1.64220700	-4.93157000	-3.83854900
H	1.51847800	-5.32219500	-1.71420700
C	1.92884100	-3.97609500	-4.81358000
H	2.53175600	-1.94571800	-5.19863600
H	1.34639400	-5.93424900	-4.13090100
H	1.85610000	-4.23544100	-5.86544900
C	2.61078700	-1.60925400	-0.21864800
H	1.91125000	-0.86352200	-0.60983900
H	2.61932000	-1.56671600	0.87014900
H	3.60583000	-1.36388900	-0.60358000

III

-1 2

C	-1.01666700	-1.47687100	2.30634200
C	0.15988400	-2.20874800	2.61562000
C	0.09090000	-3.52998700	3.02353100
H	1.01568800	-4.05750400	3.24980600
C	-1.13652100	-4.19067300	3.15404300
C	-2.29680100	-3.47646000	2.87674500
H	-3.26671900	-3.95745600	2.98653600
C	-2.25300500	-2.14642300	2.46156800

C	-2.11408300	1.81767600	1.51632700
C	-1.36324700	2.55714800	2.45942500
C	-1.38764600	3.95325800	2.42740200
C	-2.17662300	4.60858100	1.47655300
C	-2.92834300	3.90002700	0.54235100
C	-2.86684500	2.50660100	0.56513100
N	-0.88123400	-0.18507700	1.85683100
N	-2.15002800	0.41670000	1.56982900
O	-0.62846700	1.94808400	3.41948800
Ni	0.65261100	0.53531000	0.72878900
C	1.07875000	2.38937000	-1.57067500
C	0.17338000	3.27001800	-0.97860100
C	-0.45650900	4.23798900	-1.75819000
H	-1.13224500	4.93956000	-1.27909000
C	-0.21370200	4.30679900	-3.12676700
C	0.66959700	3.40187600	-3.71831600
H	0.84644500	3.43628000	-4.78962900
C	1.32067000	2.45010900	-2.94670100
C	3.72583200	0.30912000	-0.44107700
C	3.45744200	-0.32680800	0.82322100
C	4.52574100	-1.13838500	1.37224400
C	5.70412800	-1.30122400	0.69245900
C	5.96188100	-0.68636500	-0.56275200
C	4.97589700	0.10970800	-1.08415300
N	1.73352200	1.43756000	-0.73060600
N	2.90401300	1.16822700	-1.12972400
O	2.37301000	-0.23044300	1.47660000
H	-3.17192500	-1.59883700	2.28721200
H	1.11577500	-1.69998000	2.51319800
H	-1.18104800	-5.22798200	3.47066200
H	-0.71367500	5.05700500	-3.73287000
H	2.00531200	1.73330100	-3.38454000
H	-0.01455100	3.21470500	0.09219700
C	-2.56382400	-0.96882200	-1.56775800

H	-2.49840600	0.05611900	0.67926700
H	-0.52031800	1.00343700	3.11586800
C	-1.34239600	-1.38100900	-1.20915200
H	-1.21587600	-2.04257300	-0.35548000
C	-0.16343300	-1.01107200	-2.05143700
O	-0.27969400	-0.22156000	-2.97512800
C	1.13869800	-1.71337500	-1.81733700
C	1.41377100	-2.43696000	-0.65467500
C	2.10404000	-1.63827200	-2.82857200
C	2.64068200	-3.08174200	-0.51297400
H	0.70426000	-2.47649200	0.16656300
C	3.31836300	-2.29579800	-2.69030900
H	1.87288300	-1.05492300	-3.71416600
C	3.58885000	-3.02008700	-1.52923700
H	2.85608500	-3.61797700	0.40679400
H	4.06757900	-2.22662700	-3.47372400
H	4.55092900	-3.50864100	-1.40428800
H	5.11080100	0.61708800	-2.03703500
H	6.47747500	-1.93363200	1.13137500
H	-3.41424400	1.93002500	-0.18034200
H	-2.19197100	5.69713300	1.46644300
C	4.24666300	-1.80614600	2.68749200
H	3.95873400	-1.06995700	3.44509500
H	3.39686200	-2.49461700	2.59957000
H	5.11810700	-2.36550000	3.04113500
C	7.26861300	-0.92401200	-1.27375800
H	7.32254800	-0.33866200	-2.19652700
H	8.12804000	-0.64612300	-0.65142700
H	7.39746600	-1.98036600	-1.54326200
C	-0.55968800	4.70228600	3.43550900
H	-0.88770600	4.48082500	4.45683300
H	0.49032600	4.39849900	3.37369600
H	-0.62717500	5.78166200	3.27210200
C	-3.76714500	4.60397900	-0.49523500

H	-4.83434900	4.39098800	-0.36303800
H	-3.63487000	5.68920700	-0.43735900
H	-3.49181300	4.28576600	-1.50751300
H	-2.63905000	-0.31439300	-2.43731600
C	-3.84082400	-1.40035800	-0.90944300
H	-3.61697300	-2.01058600	-0.02615100
H	-4.40381700	-0.52185000	-0.55962400
C	-4.72790200	-2.19086100	-1.88022700
H	-4.91528300	-1.58370600	-2.77664300
H	-4.17712000	-3.07895500	-2.21599800
C	-6.05601800	-2.60799900	-1.25393700
H	-6.62150900	-1.72291000	-0.93815900
H	-5.87852400	-3.20933300	-0.35447400
C	-6.91280900	-3.41192300	-2.21391200
H	-6.36949300	-4.32030300	-2.51838800
H	-7.09985200	-2.82039400	-3.12447800
O	-8.12639500	-3.73826800	-1.56113400
H	-8.65996800	-4.26937300	-2.16642700

TS_{III-IV}

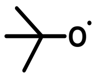
-1 2

C	1.14245900	0.73441500	2.81949000
C	-0.07860600	1.28918200	3.24095600
C	-0.09107200	2.39481900	4.08006200
H	-1.04516000	2.81042500	4.39481100
C	1.10159100	2.97028100	4.52387200
C	2.31089000	2.40869700	4.12306600
H	3.24835100	2.83703700	4.46855800
C	2.34118900	1.29774200	3.28404000
C	2.29370700	-2.12932400	1.07592700
C	1.39817400	-3.13899400	1.50177800
C	1.50579300	-4.43414000	0.97632100
C	2.48924200	-4.71280800	0.03193500
C	3.38911800	-3.73594700	-0.40079400

C	3.27562300	-2.45854500	0.13473800
N	1.09426500	-0.38144300	1.96223100
N	2.30383600	-0.82521900	1.62562000
O	0.42949300	-2.94368300	2.42790600
Ni	-0.40749100	-0.64219900	0.52150400
C	-0.90134400	-1.94221200	-2.18328000
C	0.29739600	-2.61582600	-1.95712700
C	0.97468100	-3.20756000	-3.01925700
H	1.90093000	-3.73999200	-2.82318000
C	0.46701200	-3.11863900	-4.31169200
C	-0.72886100	-2.43476100	-4.53599000
H	-1.12338600	-2.34910000	-5.54483200
C	-1.41458300	-1.84965900	-3.48116300
C	-3.59719400	-0.55776600	-0.32580100
C	-3.25867100	-0.19322700	1.02294600
C	-4.30696700	0.43230800	1.79858100
C	-5.54837500	0.65071000	1.25750700
C	-5.88720900	0.27565800	-0.06804700
C	-4.90758600	-0.32558300	-0.81633000
N	-1.54804900	-1.33605300	-1.06172800
N	-2.78178900	-1.15387300	-1.26000800
O	-2.12254500	-0.37760900	1.56910200
H	3.28147900	0.85139000	2.98288100
H	-1.00029100	0.83069900	2.88939800
H	1.08643900	3.83740100	5.17729000
H	0.99997400	-3.57293600	-5.14208600
H	-2.33794600	-1.30417500	-3.63704700
H	0.68864100	-2.68733500	-0.94670500
C	2.53070200	0.88418800	-0.35373500
H	2.62936500	-0.01979700	0.56122800
H	0.33015500	-1.97328300	2.54540400
C	1.19443000	1.35183300	-0.25643600
H	0.95680500	2.08236300	0.51185700
C	0.26332800	1.18054700	-1.36077700

O	0.56043800	0.59030100	-2.40373000
C	-1.11152500	1.80909200	-1.25571200
C	-1.63508200	2.34654300	-0.07618300
C	-1.90625700	1.79983500	-2.40656300
C	-2.92834200	2.86610300	-0.05333600
H	-1.05873200	2.32267100	0.84514100
C	-3.19401000	2.32132200	-2.38394900
H	-1.48659000	1.35396100	-3.30309400
C	-3.71020700	2.85758300	-1.20489700
H	-3.33375300	3.25558900	0.87622300
H	-3.80565700	2.29503200	-3.28179800
H	-4.72588300	3.24207800	-1.17602500
H	-5.09609100	-0.63155800	-1.84301400
H	-6.30621900	1.14017100	1.87122900
H	3.95089100	-1.66936500	-0.18897800
H	2.54402300	-5.71596700	-0.38684500
C	-3.94061400	0.87536100	3.18569600
H	-3.50410000	0.05162700	3.75978800
H	-3.17409200	1.66099200	3.14594900
H	-4.81119000	1.26715800	3.72046400
C	-7.26527300	0.55005200	-0.61171400
H	-8.04498600	0.06889700	-0.00850100
H	-7.48910500	1.62431000	-0.62639200
H	-7.36086200	0.17843800	-1.63625800
C	0.51596500	-5.47061600	1.43184200
H	0.57341900	-5.62109900	2.51484300
H	-0.50668400	-5.14498500	1.21485500
H	0.69677100	-6.42639000	0.93256400
C	4.44836900	-4.04491800	-1.43012000
H	4.43073900	-3.31543700	-2.24700300
H	5.45337200	-4.02239700	-0.99309800
H	4.29654100	-5.03844000	-1.86314800
H	2.71679000	0.34390100	-1.28889700
C	3.66993400	1.81067300	0.06080200

H	3.39166100	2.33366100	0.98404700
H	4.57314900	1.22619400	0.28955300
C	3.99064600	2.83715700	-1.02803900
H	4.22899200	2.30994800	-1.96226300
H	3.08460500	3.42354300	-1.23030300
C	5.14297500	3.76580200	-0.65160900
H	6.05694400	3.18586300	-0.47176700
H	4.91450300	4.29494700	0.28169700
C	5.42849500	4.79182800	-1.73155100
H	4.52891700	5.40301500	-1.90355100
H	5.66046800	4.27604900	-2.67685000
O	6.51837400	5.59750500	-1.31292100
H	6.67679000	6.26153500	-1.99642400



0 2

C	0.22719300	0.15660400	-0.00003000
C	0.71494000	0.86385500	1.26883900
H	0.34254200	1.89233400	1.29283200
H	0.34429000	0.34121300	2.15457800
H	1.80857000	0.89335000	1.30297900
C	0.68740500	-1.31927000	0.00008600
H	0.31768000	-1.83300700	0.89054900
H	0.31781500	-1.83310600	-0.89037700
H	1.78113800	-1.34318900	0.00017000
C	0.71512900	0.86371400	-1.26890600
H	0.34461300	0.34097400	-2.15464200
H	0.34273500	1.89219100	-1.29306800
H	1.80876500	0.89320600	-1.30288400
O	-1.15281300	0.05772300	-0.00012800

H_2O

0 1

O	0.69426800	-0.42197200	-0.12853300
H	1.65877000	-0.37813200	-0.12853300
H	0.41363700	0.50184000	-0.12853300

IV

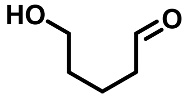
-1 2

C	-1.62786800	1.47032900	2.61160500
C	-2.10488900	0.18132100	2.91337800
C	-3.39261000	0.00500000	3.39969800
H	-3.74461400	-0.99965900	3.62005300
C	-4.23411100	1.10074200	3.60498900
C	-3.75934300	2.37887100	3.31742100
H	-4.40345400	3.24118300	3.47077500
C	-2.47202600	2.57275100	2.82693800
C	1.31414200	2.96417800	1.30732400
C	2.36923100	2.03677500	1.50320400
C	3.62394100	2.23272200	0.91449100
C	3.84747200	3.37682500	0.15903000
C	2.84581300	4.34178200	-0.01913900
C	1.60738400	4.12506700	0.55941200
N	-0.33189100	1.58313100	2.09367900
N	0.02162300	2.84153100	1.79001800
O	2.21901500	0.89453300	2.24280000
Ni	0.24346400	0.24355600	0.58937900
C	2.35583000	0.49720000	-1.57605900
C	1.59648900	1.61245000	-1.93184300
C	2.14404500	2.58266600	-2.76429400
H	1.54462100	3.44606200	-3.03667100
C	3.44742200	2.45313600	-3.23519800
C	4.20386000	1.33668100	-2.87553700
H	5.22419000	1.23240600	-3.23386100

C	3.66424100	0.35802500	-2.05191400
C	1.90148100	-2.60128200	0.12904700
C	0.94176500	-2.52590900	1.19159900
C	0.69634100	-3.73773200	1.93025800
C	1.35337900	-4.89825600	1.60693700
C	2.30152200	-4.97871000	0.55557600
C	2.55585500	-3.82974100	-0.14767900
N	1.76706200	-0.44505700	-0.67771600
N	2.31311200	-1.58132800	-0.69885300
O	0.29291100	-1.47606400	1.53616600
H	-2.09938300	3.56207600	2.59280900
H	-1.44698000	-0.66772500	2.74090500
H	-5.24240800	0.95873200	3.98215000
H	3.87476300	3.21813800	-3.87746400
H	4.23949900	-0.51119200	-1.75482100
H	0.56769800	1.70201000	-1.59329700
C	-2.07677500	1.78660900	-0.71244800
H	-1.66636900	2.47791200	0.03625100
H	1.31750000	0.91086400	2.63745900
C	-1.54838300	0.37305300	-0.52749800
H	-2.12113500	-0.19775100	0.20895000
C	-1.23443300	-0.36196400	-1.73611900
O	-0.99591600	0.16920000	-2.82704400
C	-1.05894500	-1.86825300	-1.64144900
C	-1.62983500	-2.65993000	-0.64199200
C	-0.25878400	-2.48004300	-2.61138400
C	-1.38946400	-4.03255200	-0.60535300
H	-2.24850400	-2.20698100	0.12731700
C	-0.00737600	-3.84611600	-2.56866100
H	0.16898400	-1.84599900	-3.38174100
C	-0.57010300	-4.62761100	-1.56055900
H	-1.82554300	-4.63470200	0.18729600
H	0.64039600	-4.30249200	-3.31224100
H	-0.35983900	-5.69252800	-1.51063800

H	3.26827600	-3.82021600	-0.96906200
H	1.12970800	-5.79996300	2.17821600
H	0.79442500	4.83361100	0.42223200
H	4.81535300	3.51049700	-0.32065600
C	-0.33856200	-3.66282500	3.01495400
H	-0.07614100	-2.90184000	3.75751500
H	-1.30638400	-3.35985000	2.59558400
H	-0.45653200	-4.62743400	3.51723500
C	2.97490100	-6.28735600	0.23391400
H	3.70134200	-6.16422600	-0.57448300
H	3.50616600	-6.69459300	1.10238300
H	2.24892300	-7.04574800	-0.08428600
C	4.67599200	1.17437700	1.10265200
H	4.96992200	1.08923100	2.15461300
H	4.29242900	0.19203500	0.80365100
H	5.56246800	1.40125300	0.50364100
C	3.11098600	5.55399700	-0.87515800
H	3.96220700	6.13450400	-0.50134500
H	3.34697600	5.25571600	-1.90428900
H	2.23976500	6.21453800	-0.90701600
H	-1.75083700	2.14532300	-1.69774300
C	-3.60851400	1.85121000	-0.63731100
H	-3.93113300	1.52433800	0.36258000
H	-3.93841500	2.89494700	-0.74427900
C	-4.29490100	0.99433700	-1.69977800
H	-3.89958500	1.26068000	-2.69003300
H	-4.02348900	-0.05845700	-1.54154400
C	-5.81572200	1.13327400	-1.68939200
H	-6.10639300	2.17090900	-1.89741400
H	-6.21200400	0.88686100	-0.69631300
C	-6.47911900	0.23303300	-2.71341000
H	-6.22642000	-0.81642500	-2.49678400
H	-6.08579900	0.46434800	-3.71584500
O	-7.88353000	0.43780900	-2.66116100

H	-8.29240700	-0.16049800	-3.29988800



5-hydroxypentanal

0 1

O	1.08988800	-3.49283200	0.25975500
C	3.43693100	-3.32429700	-0.03360800
H	3.54335400	-3.33092600	1.05803800
H	3.44014100	-4.37202300	-0.35809700
H	0.22794600	-3.11260000	0.04555800
C	2.08836300	-2.72025700	-0.37930000
H	1.95337600	-2.71973600	-1.47248100
H	2.05680700	-1.67160600	-0.04376500
C	4.59925500	-2.56948000	-0.67317700
H	4.57835000	-1.51862900	-0.35275100
H	4.47756900	-2.56028400	-1.76519300
C	5.95905700	-3.17194400	-0.32573300
H	6.08194600	-3.18082900	0.76636200
H	5.98078500	-4.22338800	-0.64483600
C	7.12085500	-2.41729800	-0.96655900
H	7.10644600	-1.36697300	-0.65343600
H	7.00688500	-2.40534700	-2.05666300
C	8.47250100	-3.02403600	-0.61347200
H	8.51974800	-4.07573400	-0.92915500
H	8.61988700	-3.03478700	0.47562200
C	9.63423200	-2.27879400	-1.24859800
O	9.44312500	-1.30839500	-1.95273200
C	11.03025400	-2.76668000	-0.98862900
C	11.30052400	-3.87764800	-0.18551000
C	12.08883600	-2.07130700	-1.58070200
C	12.61428600	-4.28781000	0.02257800
H	10.49001900	-4.42863400	0.28155800

C	13.39936100	-2.48059300	-1.37304300
H	11.85509900	-1.21161000	-2.20027800
C	13.66329300	-3.59033800	-0.57046200
H	12.81862800	-5.15153700	0.64735100
H	14.21757200	-1.93714000	-1.83511600
H	14.68768600	-3.91125600	-0.40754700

9. References

S1. A. K. Bains, A. Kundu, S. Yadav, D. Adhikari, *ACS Catal*. **2019**, *9*, 9051−9059.

S2. S. Waiba, S. K. Jana, A. Jati, A. Jana, B. Maji, *Chem. Commun.*, **2020**, *56*, 8376- 8379.

S3. W. Zhang, J. Wu, P. Zhou, Y. Wang, A. Hou, *Tetrahedron*, **2013**, *69*, 5850-5858.

S4. I. N. Cvijetić, M. Tanc, I. O. Juranić, T. Ž. Verbić, C. T. Supuran, B. J. Drakulić, *Bioorg. Med. Chem.* **2015**, *23*, 4649–4659.

S5. P. Delair, A. M. Kanazawa, M. B. M. de. Azevedo, A. E. Greene, *Tetrahedron: Asymmetry*. **1996**, *7*, 2702-2710.

S6. M. B. Dambatta, J. Santos, R. R. A. Bolt, L. C. Morrill, *Tetrahedron*, **2020**, *76*, 1315714.

S7. S. Wübbolt, C. B. Cheong, J. R. Frost, K. E. Christensen, T. J. Donohoe, *Angew. Chem. Int. Ed.* **2020**, *59*, 11339 –11344.

S8. A. Jana, K. Das, A. Kundu, P. R. Thorve, D. Adhikari, B. Maji, *ACS Catal.* **2020**, *10*, 2615–2626.

S9. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, Jr., J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.;

Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Gaussian Inc.,Wallingford, CT, 2010.

S10. (a) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215-241. (b) Y. Zhao, D. G. Truhlar, *Acc.Chem. Res.* **2008**, *41*, 157-167.

S11. P. J. Hay, W. R. Wadt, *J. Chem. Phys*. **1985**, *82*, 270-283.

S12. W. R. Wadt, P. J. Hay, *J. Chem. Phys*. **1985**, *82*, 284-298.

S13. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

S14. (a) J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999– 3093. (b) M. Cossi, V. Barone, R. Cammi, J. Tomasi, *Chem. Phys. Lett.* **1996**, *255*, 327– 335. (c) E. Cances, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *107*, 3032– 3041. (d) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995– 2001.

S15. R. J. Armstrong, W. M. Akhtar, J. R. Frost, K. E. Christensen, N. G. Stevenson, T. J. Donohoe, *Tetrahedron,* **2019**, *75*, 130680.

S16. N. R. Lombardıa, V. G. Fernandez, V. Gotor, *J. Org. Chem.* **2011**, *76*, 811–819.