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Manganese Catalyzed α-Alkylation of Ketones with Secondary Alcohols Enables the Synthesis of β-Branched Carbonyl Compounds

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1. General

Unless stated otherwise, all the reactions have been performed under an inert atmosphere (Ar) in well-dried glassware. Reaction temperatures correspond to the temperature of the bath surrounding the vessel.

Analytics: ^{1}H, ^{13}C NMR spectra has been recorded on Bruker (^{1}H: 500 MHz, ^{13}C {^{1}H}: 126 MHz) and JEOL (^{1}H: 400 MHz, ^{13}C {^{1}H}: 101 MHz) and were referenced to the resonances of the solvent used. Multiplicities has been indicated as: br (broad), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet) or m (multiplet). Coupling constants (*J*) are reported in Hertz (Hz). FT-IR spectra were recorded by Perkin–Elmer FT–IR Spectrometer. Mass spectra were recorded on Bruker micrOTOF-Q II Spectrometer. For thin-layer chromatography (TLC) analysis Merck pre-coated TLC plates (silica gel 60 F254 0.25 mm) were used and visualization was accomplished by UV light (254 nm), I_2, $KMnO_4$, and cerium molybdate.

Chemicals. Commercially available chemicals were bought from Sigma–Aldrich, Alfa–Aesar, Avra Synthesis, and used without any further purification. Dry solvents were prepared according to the standard procedure and degassed by freeze–pump–thaw cycles, prior to use. No attempts were made to optimize yields for substrate, catalyst, and ligand.

2. Preparation of ligands and starting materials:

Synthesis of the Ligands

No attempts were made to optimize yields for ligand synthesis.

Ligands **L1** was prepared according to the following procedure previously reported by us.[1] The corresponding ketone (2 mmol), hydrazine (2 mmol) and acetic acid (1 drop) were mixed in ethanol (2 mL) and heated to reflux at 80 ^{o}C for overnight. Reaction mixture was then evaporated and the resulting solid was extracted in dichloromethane and dried over $MgSO_4$. Evaporation of the volatiles yields the corresponding hydrazone **L1**. The crude was then purified by column chromatography on silica gel using ethyl acetate/hexane as eluent.

Ligands (**L2–L3**) were prepared according to the following procedure.[2] The corresponding aldehyde (2 mmol) and 2-(aminomethyl)pyridine (2.2 mmol) were mixed and stirred at room temperature in methanol (20 mL) in the presence of excess Na_2SO_4 (5 mmol) for 5 h. Filtration was done to remove the solid particles from the reaction mixture. After addition of $NaBH_4$ (2 mmol), the mixture was gently warmed at 45 ^{o}C for 1 h. The solvent was then removed under reduced pressure and water (5 mL) was then added and the organic materials were extracted with DCM, washed with brine. The volatiles were then evaporated, and the residue was purified by column chromatography on silica gel using ethyl acetate/hexane as eluent.to obtain the ligands **L2-L3**. **1-(pyridin-2-yl)-N-(thiophen-2-ylmethyl)methanamine (L2):** 360 mg, 88%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.3 Hz, 1H), 7.61 (td, *J* = 7.7, 1.6 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.18 (dd, *J* = 4.4, 2.1 Hz, 1H), 7.13 (dd, *J* = 7.4, 4.8 Hz, 1H), 6.95 – 6.89 (m, 2H), 4.01 (s, 2H), 3.92 (s, 2H), 2.13 (s, 1H). m/z = 204.0. **1-(furan-2-yl)-N-(pyridin-2-ylmethyl)methanamine (L3):** 190 mg, 50%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.63 (td, *J* = 7.7, 1.8 Hz, 1H), 7.35 (d, *J* = 1.6 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.15 (dd, *J* = 7.7, 4.9 Hz, 1H), 6.30 (dd, *J* = 3.1, 2.0 Hz, 1H), 6.19 (d, *J* = 2.9 Hz, 1H), 3.92 (s, 2H), 3.83 (s, 2H), 2.71 (s, 1H). **^{13}C NMR** (101 MHz,$CDCl_3$) δ 159.5, 153.8, 149.4, 142.0, 136.6, 122.5, 122.1, 110.2, 107.3, 54.3, 45.8. m/z = 188.1.

Synthesis of Ligand **L4.**[2] Ligand **L2** (0.5 mmol) and NaH (1.1 eq) in dry THF (3 mL) were stirred for 30 minutes at 0 ^{o}C. Methyl iodide (1.2 eq) in THF (1 mL) was added drop wise at 0 ^{o}C and then left it for overnight at room temperature. The solvent was eliminated under reduced pressure. After the addition of water organic material was extracted with ethyl acetate. The crude was then purified by column chromatography on silica gel using ethyl acetate/hexane as eluent. **N-methyl-1-(pyridin-2-yl)-N-(thiophen-2-ylmethyl)methanamine (L4).** Yield 69% (75 mg, 0.34 mmol), **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.61 – 8.49 (m, 1H), 7.67 (td, *J* = 7.7, 1.7 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.19 –

7.13 (m, 1H), 6.99 – 6.91 (m, 2H), 3.82 (s, 2H), 3.71 (s, 2H), 2.31 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.6, 149.1, 142.6, 136.7, 126.6, 126.0, 125.1, 123.1, 122.1, 62.8, 56.5, 42.5. **HRMS:** Calculated for $[C_{12}H_{15}N_2S]^+$; $[M + H]^+$] 219.0950, found 219.0952.

Synthesis of the ketones.

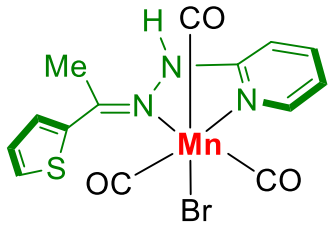
1-(2,3,4,5,6-pentamethylphenyl)ethanone (1a), 1-mesitylethan-1-one (1b) and 1-(2,3,5,6-tetramethylphenyl)ethan-1-one (1c) were prepared according to the following literature.[3] To a solution of pentamethylbenzene (592 mg, 4 mmol), mesitylene (556 µl, 4 mmol) or 1,2,4,5-tetramethylbenzene (537 mg) in DCM (24 mL), acetyl chloride (0.312 mL, 4.4 mmol) was added at 0 °C. Then portion wise aluminium chloride (11.2 g, 84.3 mmol) was added over 10 mins. Resulting mixture was then stirred at RT for 4 h. After completion of reaction, crushed ice (c.a. 30 g) was poured onto the reaction mixture. After the ice had melted, the layers were separated and the aqueous layer was extracted twice with dichloromethane, dried over $MgSO_4$. Purification had been done by column chromatography (hexane:ethylacetatre, 95:5) afforded the title compound **1a**, **1b** or **1c**. Yield **1a** (700 mg, 92%), **1b** (473 mg, 73%), **1c** (564 mg, 80%).

3. Synthesis of Manganese complexes:

Synthesis of Mn1.

Complex **Mn1** were prepared according to our previous published procedure.[1]

Mn1.[1] In a Schlenk tube, **L1** (21.7 mg, 1.0 equiv) and $Mn(CO)_5Br$ (28.0 mg, 1.02 eq) were taken



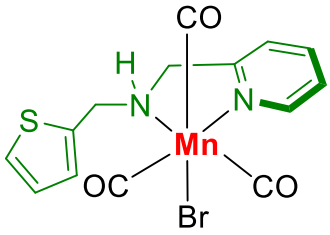
and then THF (2.0 mL) was added and the reaction tube was sealed and heated at 90 °C for 4 h. The color of the solution turns into red during that time. Yellow color crystals started to come out upon cooling. Hexane was added and the yellow crystals are collected upon decanting the solvent from the Schlenk tube, washed with hexane and dried. 40.1 mg, 92% yield. Selected IR (KBr) ν (cm^{-1}): 2026 (C=O), 1934.8 (C=O), 1908.7 (C=O), 1617.4, 1574, 1487, 1104.3. **^{1}H NMR** (400 MHz, DMSO-D_6) δ 11.05 (s, 1H), 8.48 (d, J = 5.5 Hz, 1H), 7.87 – 7.78 (m, 2H), 7.52 (d, J = 2.8 Hz, 1H), 7.20 (dd, J = 8.6, 4.8 Hz, 2H), 7.00 (t, J = 6.4 Hz, 1H), 2.61 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-D_6) δ 224.1, 222.9, 216.8, 156.3, 155.5, 149.7, 142.1, 139.2, 130.3, 129.7, 127.5, 116.6, 108.7, 24.8. Elemental analysis calcd (%) for $C_{14}H_{14}BrMnN_3O_3S$: C 38.29, H 3.21, N 9.57; found: C 37.36, H 3.30, N 9.27.

Synthesis of Mn2-4.

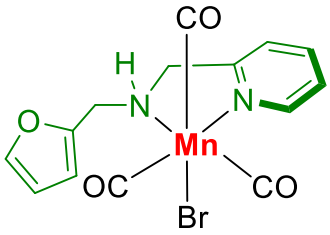
Complex **Mn2-5** were prepared according to previous reported procedure.[2]

In a Schlenk tube, **L2-5** (0.1 mmol), $Mn(CO)_5Br$ (28.0 mg, 1.02 eq), and THF (2.0 mL) were taken and the reaction tube was sealed and heated at 90 ^oC for 4 h. The color of the solution turns into red during that time. After evaporation of solvent under Ar atmosphere it turns amorphous yellow color solids which were washed with hexane (3 x 2 mL) and dried. Brown color solid compounds were obtained with 85 – 96% yields.

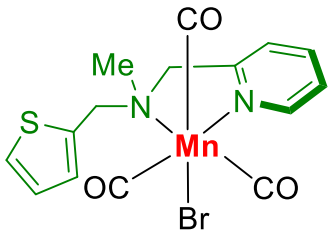
Mn2:[2] Yield 96% (41 mg, 0.96 mmol). Selected **IR** (ATR, cm^{-1}): 3149, 1989 (C=O), 1907 (C=O), 1862 (C=O), 1432, 1238, 1089, 1013, 995, 760. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.10 – 7.60 (s, 1H), 7.56 – 6.69 (m, 5H), 4.94 (s, 1H), 4.58 – 3.46 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 222.7, 221.2, 221.0, 158.4, 154.0, 138.3, 137.7, 128.8, 127.7, 126.9, 124.9, 121.4, 57.3, 53.6. **Elemental analysis** calcd (%) for $C_{14}H_{12}BrMnN_2O_3S$: C 39.74, H 2.86, N 6.92; found: C 39.09, H 2.88, N 5.53. **HRMS:** Calculated for $[C_{14}H_{12}MnN_2O_3S; [M\text{-}Br]^+]$ 342.9949, found 342.9944.



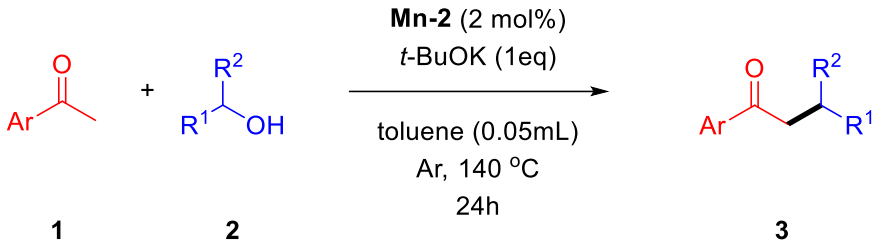
Mn3:[2] Yield 90% (36.6 mg, 0.90 mmol). Selected **IR** (ATR, ν cm^{-1}): 3151 (N-H), 1991 (C=O), 1905 (C=O), 1866 (C=O), 1587, 1466, 1434, 1134, 940, 720, 675. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.75 (s, 1H), 7.51 – 7.22 (m, 3H), 6.49 (s, 1H), 6.42 (s, 1H), 4.59 (d, *J* = 13.3 Hz, 1H), 4.17 – 4.09 (m, 3H), 3.75 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 222.4, 221.3, 221.2, 158.6, 154.0, 149.6, 143.5, 138.3, 124.9, 121.3, 111.1, 110.9, 57.7, 51.4. **HRMS**: Calculated for $[C_{14}H_{12}MnN_2O_4; [M – Br]^+]$ 327.0178, found 343.0182.



Mn4:[2] Yield 91% (39.8 mg, 0.91 mmol). Selected **IR** (ATR, ν cm^{-1}): 1989 (C=O), 1901 (C=O), 1852 (C=O), 1589, 1460, 1427, 1409, 1397, 1221, 755, 701, 679. **Elemental analysis** calcd (%) for $C_{15}H_{14}BrMnN_2O_3S$: C 41.21, H 3.23, N 6.41; found: C 40.71, H 3.05, N 6.29. **HRMS:** Calculated for $[C_{15}H_{14}MnN_2O_3S; [M\text{-}Br]^+]$ 357.0106, found 357.0123.



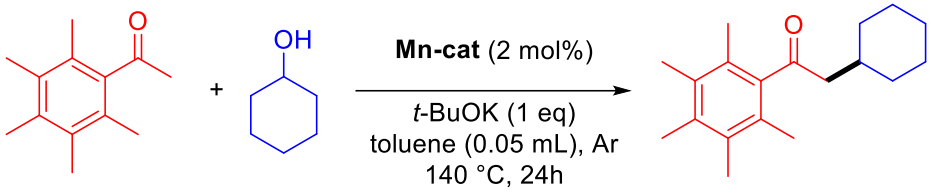
4. General procedure for the Mn-catalyzed alkylation of ketones with secondary alcohols:



In a well-capped reaction tube, *t*-BuOK (22.4 mg, 0.2 mmol), **Mn2** (2 mg, 0.004 mmol, 2 mol%) were suspended in toluene (0.05 mL). To the suspension secondary alcohol **2** (0.4 mmol) followed by the ketone **1** (0.2 mmol) were added under argon atmosphere. The tube was then closed and stirred in a preheated oil bath at 140 °C for 24 h. The reaction was quenched with water (2 mL) and the organics were extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated and was subsequently purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture as eluent.

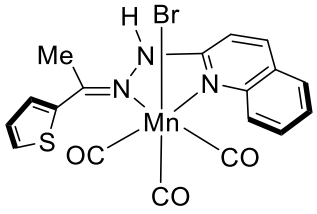
5. Optimization of reaction conditions:

Table S1: Screening of different Mn(I)-catalyst:

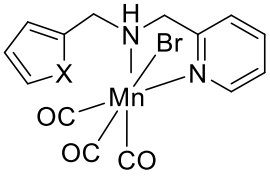


1a **2a** **3aa**

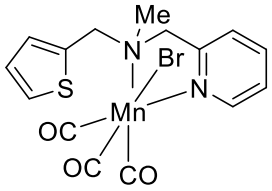
Entry	Mn-Cat	Mn loading (mol%)	Yield of **3aa** (%)
1.	**Mn1**	2.0	10
2.	**Mn2**	2.0	85
3.	**Mn3**	2.0	25
4.	**Mn4**	2.0	5
5.	**$MnBr(CO)_5$**	2.0	5
6.	**Mn2**	1.0	70
7.	**Mn2**	0	10



Mn1



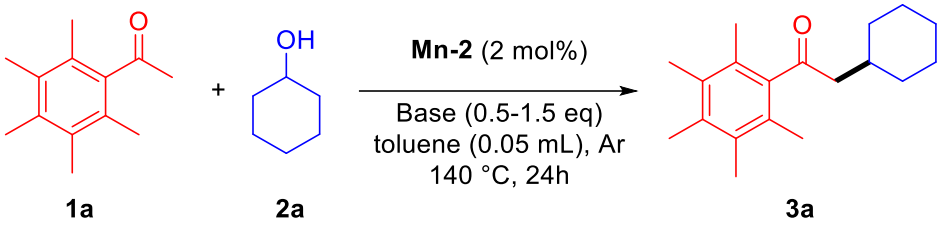
Mn2 (X = S)
Mn3 (X = O)



Mn4

Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Mn-cat, *t*-BuOK (0.2 mmol) under argon atmosphere at 140 °C in toluene (0.05 mL) for 24 h in a screw-capped reaction tube. Isolated yields.

Table S2: Base optimization:

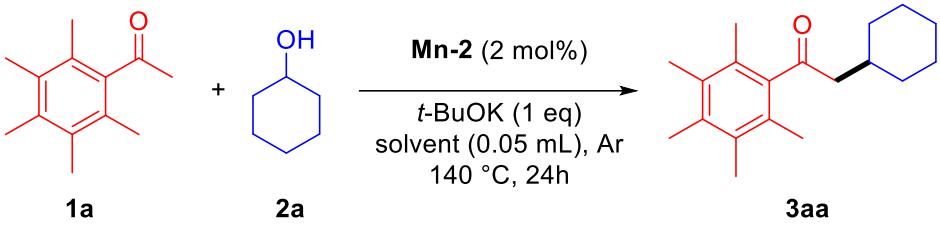


1a **2a** **3a**

Entry	Base	Loading (equiv)	Yield of 3aa (%)[b]
1.	*t*-BuOK	1.0	85
2.	*t*-BuONa	1.0	15
3.	*t*-BuOLi	1.0	<5
4.	Cs_2CO_3	1.0	<5
5.	*t*-BuOK	0.5	50
6.	*t*-BuOK	1.5	67
7.	*t*-BuOK	0	<5

Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), **Mn2** (0.004 mmol), and base under argon atmosphere at 140 °C in toluene (0.05 mL) for 24 h in a screw-capped reaction tube. Isolated yields.

Table S3: Solvent optimization:



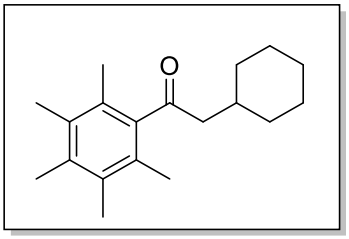
1a **2a** **3aa**

Entry	Solvent	Yield of **3aa** (%)
1.	**toluene**	**85**
2.	*t*-BuOH	51
3.	1,4-dioxane	10
4.	Neat	Irreproducible yields
5.	toluene (0.1 mL)	70

Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), **Mn-2** (2 mol%), *t*-BuOK (0.2 mmol) under argon atmosphere at 140 °C in solvent (0.05 mL) for 24 h in a screw-capped reaction tube. Isolated yields.

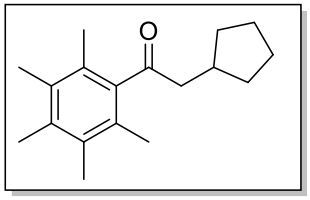
6. Characterization Data:

2-cyclohexyl-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (**3aa**)[4]



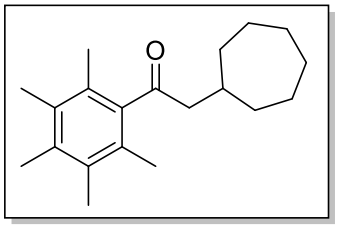
Yield 46.3 mg (0.17 mmol, 85%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.56 (d, *J* = 6.4 Hz, 2H), 2.22 (s, 3H), 2.17 (s, 6H), 2.09 (s, 6H), 1.94 – 1.81 (m, 2H), 1.77 – 1.62 (m, 3H), 1.46 – 1.11 (m, 4H), 1.08 – 0.90 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.2, 140.9, 135.4, 133.2, 127.4, 53.3, 33.5, 32.5, 26.5, 26.3, 17.1, 16.8, 16.1.

2-cyclopentyl-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (**3ab**)[4]



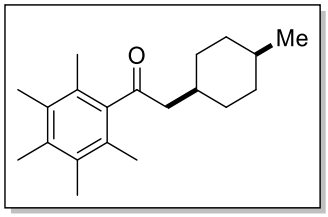
Yield 47.5 mg (0.184 mmol, 92%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate= 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.74 (d, *J* = 6.8 Hz, 2H), 2.47 – 2.36 (m, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.12 (s, 6H), 2.02 – 1.93 (m, 2H), 1.59-1.65 (m, 4H), 1.23 – 1.13 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.9, 140.9, 135.3, 133.1, 127.4, 52.1, 34.7, 32.9, 25.1, 17.2, 16.8, 16.0.

2-cycloheptyl-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one(**3ac**)[5]



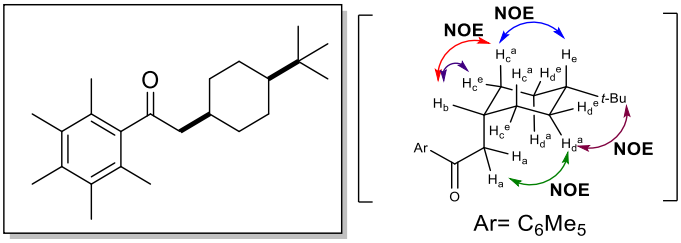
Yield 49.3 mg (0.172 mmol, 86%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.64 (d, *J* = 6.4 Hz, 2H), 2.24- 2.28 (m, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.12 (s, 6H), 1.96 – 1.80 (m, 2H), 1.71 – 1.62 (m, 4H), 1.57 – 1.47 (m, 4H), 1.33 – 1.22 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.4, 140.9, 135.3, 133.1, 127.5, 54.1, 35.0, 34.2, 28.4, 26.5, 17.1, 16.8, 16.0.

2-(4-methylcyclohexyl)-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (**3ad**)



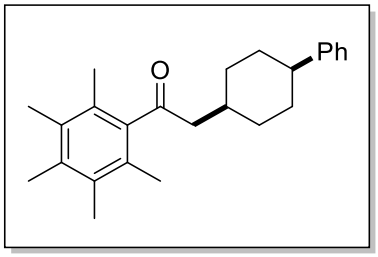
Yield 55.0 mg (0.17 mmol, 85%), d.r. > 99:1. Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.69 (d, *J* = 6.5 Hz, 2H), 2.37 – 2.30 (m, 1H), 2.24 (s, 3H), 2.20 (s, 6H), 2.12 (s, 6H), 1.66-1.58 (m, 4H), 1.61- 1.53 (m, 2H), 1.48 (dd, *J* = 11.0, 4.8 Hz, 2H), 1.20 (dt, *J* = 11.8, 6.3 Hz, 1H), 0.91 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 211.3, 141.0, 135.3, 133.1, 127.4, 53.3,50.2, 35.2, 33.4, 30.9, 29.2, 17.1, 16.7, 16.0. Selected **IR** (ATR) ν (cm^{-1}): 3451, 2915, 2849, 1703, 1455, 1385, 1101. HRMS calcd for $C_{20}H_{30}ONa$ [M + Na] 309.2194, found 309.2190. The *cis* configuration of the product was assigned by analogy with the compound **3ae**.

2-(4-(tert-butyl)cyclohexyl)-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (**3ae**)[4]



Yield 54.7 mg (0.156 mmol, 78%), d.r. >99:1. Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.76 (d, *J* = 6.7 Hz, 2H, 2×H_a), 2.58-2.57 (m, 1H, 1×H_b), 2.25 (s, 3H), 2.21 (s, 6H), 2.13 (s, 6H), 1.75 (d, *J* = 12.1 Hz, 2H, 2×H_c^e), 1.64 – 1.54 (m, 4H, , 2×H_c^a and 2×H_d^e), 1.14 – 1.02 (m, 2H, 2×H_d^a), 1.01 – 0.91 (m, 1H, 1×H_e), 0.84 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.4, 141.1, 135.4, 133.2, 127.4, 53.3, 48.4, 47.8, 33.9, 32.7, 31.0, 27.6, 26.9, 22.1, 17.2, 16.8, 16.1. *Cis* configuration is confirmed by NOE experiments and by comparing the NMR data with previously reported one in Ref 4.

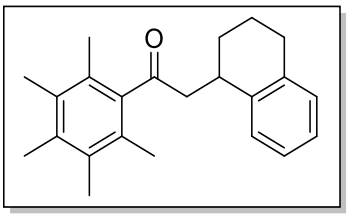
1-(2,3,4,5,6-pentamethylphenyl)-2-(4-phenylcyclohexyl)ethan-1-one(**3af**)



Yield 53.0 mg (0.15 mmol, 76%), d.r.>99:1. Column Chromatography on silica gel (Eluent; hexane:ethyl acetate=49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33- 7.25 (m, 2H), 7.25 – 7.15 (m, 3H), 2.83 (d, *J* = 6.7 Hz, 2H), δ 2.62 (dt, *J* = 6.8, 4.8 Hz, 2H), 2.25 (s, 3H), 2.20 (s, 6H), 2.13 (s, 6H), 1.78 (dt, *J* = 7.2, 4.1 Hz, 6H), 1.70 – 1.56 (m, 2H) .**^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.2, 147.3, 140.9, 135.5, 133.3, 128.4, 127.4, 126.9, 125.9, 53.2, 48.4, 43.5, 33.6, 30.5, 29.2, 27.4, 17.2, 16.8, 16.1. Selected **IR** (ATR) ν (cm^{-1}): 3442, 2922, 1696, 1452, 1386, 1172, 1059. HRMS calcd

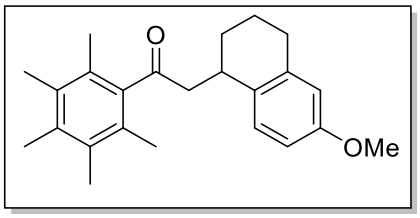
for $C_{25}H_{32}ONa$ [M + Na] 371.2351, found 371.2343. The *cis* configuration of the product was assigned by analogy with the compound **3ae**.

1-(2,3,4,5,6-pentamethylphenyl)-2-(1,2,3,4-tetrahydronaphthalen-1-yl)ethan-1-one (**3ag**)[4]



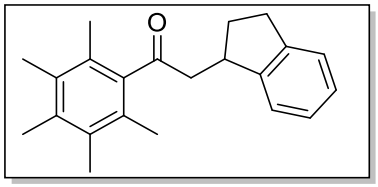
Yield 41.0 mg (0.128 mmol, 64%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 – 7.16 (m, 1H), 7.14 – 7.04 (m, 3H), 3.66 (m, 1H), δ 3.04 (d, *J* = 0.9 Hz, 1H), 3.02 (s, 1H), 2.80- 2.77 (m, 2H), 2.23 (s, 3H), 2.18 (s, 6H), 2.13 (s, 6H), 2.11- 2.07 (m, 1H), 1.91 – 1.74 (m, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.6, 140.5, 140.3, 137.3, 135.5, 133.2, 129.3, 128.5, 127.4, 126.0, 125.9, 53.6, 32.3, 29.7, 28.7, 19.8, 17.2, 16.8, 16.1.

2-(6-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (**3ah**)



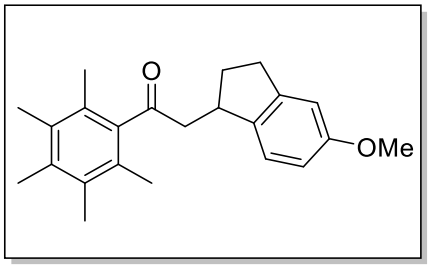
Yield 46.3 mg (0.13 mmol, 66%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.5 Hz, 1H), 6.70-6.67 (m, 1H), 6.59 (d, *J* = 2.6 Hz, 1H), 3.76 (s, 3H), 3.64 – 3.55 (m, 1H), 2.98 (d, *J* = 6.3 Hz, 2H), 2.75 (t, *J* = 6.0 Hz, 2H), 2.22 (s, 3H), 2.17 (s, 6H), 2.11 (s, 6H), 2.09 – 2.02 (m, 1H), 1.83-1.77 (m, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.7, 157.6, 138.4, 135.4, 133.2, 132.4, 129.5, 127.4, 113.6, 112.3, 55.3, 53.6, 31.5, 29.9, 28.9, 19.7, 17.1, 16.7, 16.0. Selected **IR** (ATR) ν (cm^{-1}): 3437, 2928, 2663, 1699, 1498, 1259, 1150. HRMS calcd for $C_{24}H_{30}O_2Na$ [M + Na] 373.2138, found 373.2128.

2-(2,3-dihydro-1H-inden-1-yl)-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (**3ai**)[5]



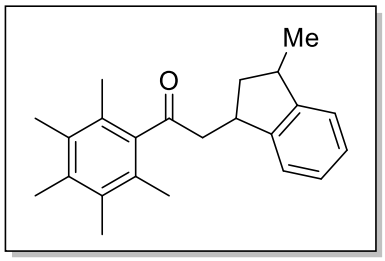
Yield 40.5 mg (0.132 mmol, 66%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.18-7.15 (m, 2H), 3.82 – 3.73 (m, 1H), 3.23-3.17 (m, 1H), 2.97 – 2.90 (m, 2H), 2.89-2.84 (m, 1H), 2.65-2.57 (m, 1H), 2.23 (s, 3H), 2.18 (s, 6H), 2.13 (s, 6H), 1.80-1.71 (m, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 211.1, 146.3, 144.1, 140.6, 135.6, 133.3, 127.5, 126.7, 126.4, 124.7, 123.7, 51.5, 39.9, 33.3, 31.6, 17.3, 16.8, 16.1.

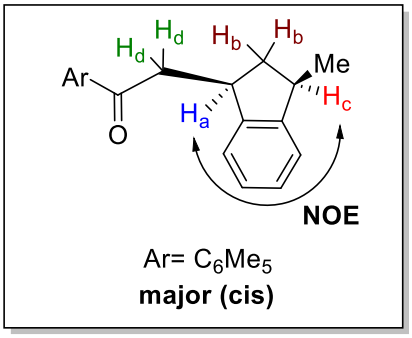
2-(5-methoxy-2,3-dihydro-1H-inden-1-yl)-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (**3aj**)



Yield 60.6 mg (0.18 mmol, 90%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.3 Hz, 1H), 6.81 (d, *J* = 1.8 Hz, 1H), 6.75- 6.71 (m, 1H), 3.80 (s, 3H), 3.78 – 3.70 (m, 1H), 3.22-3.14 (m, 1H), 2.97 – 2.79 (m, 3H), 2.68-2.58 (m, 1H), 2.25 (s, 3H), 2.21 (s, 6H), 2.15 (s, 6H), 1.84- 1.73 (m, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.2, 159.0, 145.6, 140.6, 138.4, 135.5, 133.2, 127.4, 124.2, 112.2, 110.1, 55.5, 51.8, 39.0, 33.6, 31.8, 17.4, 16.8, 16.1. Selected **IR** (ATR) ν (cm^{-1}): 3437, 2937, 2667, 1703, 1494, 1257, 1150. HRMS calcd for $C_{23}H_{28}O_2Na$ [M + Na] 359.1987, found 359.1983.

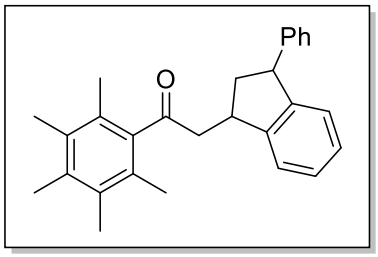
2-(3-methyl-2,3-dihydro-1H-inden-1-yl)-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (**3ak**)





Yield 51.3 mg (0.16 mmol, 80%), d.r. = 78:22. Column Chromatography on silica gel (Eluent; hexane:ethyl acetate=49:1). **(major-cis) ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 11.4, 2.4 Hz, 4H), 3.79-3.69 (m, 1H, 1 × H_a), 3.40 (dd, *J* = 19.0, 4.0 Hz, 1H, 1 × H_d), 3.23 (dt, *J* = 10.1, 6.9 Hz, 1H, 1 × H_c), 2.95- 2.85 (m, 2H, 1 × H_d and 1 × H_b), 2.28 (s, 3H), 2.24 (s, 6H), 2.21 (s, 6 H), 1.39 (d, *J* = 6.8 Hz, 3H, 3 × Me-H) , 1.34 – 1.29 (m, 1H, 1 × H_b). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.1, 148.6, 145.9, 135.6, 133.2, 127.4, 126.8, 126.4, 123.2, 123.0, 51.5, 43.6, 38.6, 38.3, 19.6, 17.3, 16.8, 16.1. Selected **IR** (ATR) ν (cm^{-1}): 3451, 2928, 2863, 1708, 1455, 1389. HRMS calcd for $C_{23}H_{28}ONa$ [M + Na] 343.2038, found 343.2038. Cis configuration assigned by NOE-experiments.

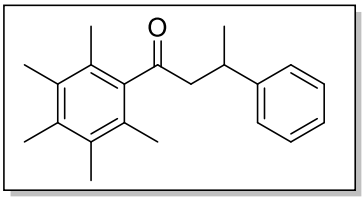
1-(2,3,4,5,6-pentamethylphenyl)-2-(3-phenyl-2,3-dihydro-1H-inden-1-yl)ethan-1-one (**3al**)



Yield 58.9 mg (0.15 mmol, 77%), d.r.= 57:43. Column Chromatography on silica gel (Eluent; hexane:ethyl acetate=49:1). **(major-cis) ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40- 7.17 (m, 14H), 7.05 (d, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 7.3 Hz, 1H), 4.47 (t, *J* = 7.4 Hz, 1H), 4.38 (dd, *J* = 9.9, 7.8 Hz,

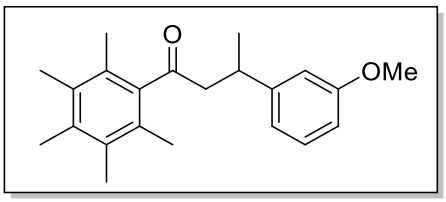
1H), 4.08 – 3.97 (m, 1H), 3.90- 3.81 (m, 1H), 3.42 (dd, *J* = 19.1, 4.0 Hz, 1H), 3.21 – 3.11 (m, 2H), 2.95 (dd, *J* = 18.9, 9.5 Hz, 1H), 2.68 – 2.55 (m, 1H), 2.46- 2.35 (m, 1H), 2.26 (d, *J* = 1.8 Hz, 3H), 2.22 (d, *J* = 2.3 Hz, 7H), 2.15 (d, *J* = 5.3 Hz, 7H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.8, 210.8, 146.9, 146.7, 146.4, 146.4, 145.3, 144.8, 140.4, 135.6, 133.2, 128.6, 128.5, 127.9, 127.4, 127.2, 127.1, 127.1, 126.9, 126.8, 126.5, 126.4, 125.3 , 125.1, 124.2, 123.0, 51.6, 51.2, 50.7, 49.8, 45.3, 43.0, 38.8, 38.6, 17.3, 16.8, 16.1. Selected **IR** (ATR) ν (cm^{-1}): 3438, 2924, 2863, 1699, 1450, 1257, 1115. HRMS calcd for $C_{28}H_{30}ONa$ [M + Na] 405.2194, found 405.2189. The configuration of the major product was assigned as cis by analogy with the compound **3ak**.

1-(2,3,4,5,6-pentamethylphenyl)-3-phenylbutan-1-one(**3am**)[4]



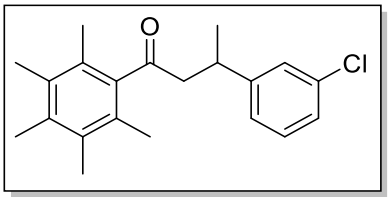
Yield 48.8 mg (0.16 mmol, 83%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 4H), 7.23 – 7.17 (m, 1H), 3.62 – 3.51 (m, 1H), 3.00 (m, 2H), 2.23 (s, 3H), 2.17 (s, 6H), 2.01 (br, 6H), 1.40 (d, *J* = 6.9 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.3, 146.8, 140.5, 135.5, 133.1, 128.6, 127.4, 127.2, 126.3, 53.9, 34.3, 22.5, 16.9, 16.8, 16.0.

3-(3-methoxyphenyl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one(**3an**)[5]



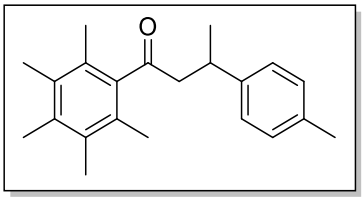
Yield 58.4 mg (0.18 mmol, 90%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.19 (m, 1H), 6.88 – 6.69 (m, 3H), 3.79 (s, 3H), 3.58 – 3.48 (m, 1H), 3.05-2.90 (m,2H), 2.21 (d, *J* = 8.5 Hz, 3H), 2.16 (br, 6H), 2.01 (s, 5H), 1.38 (d, *J* = 7.0 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.2, 159.8, 148.5, 140.5, 135.5, 133.2, 129.5, 127.5, 119.5, 113.1, 111.5, 55.3, 53.8, 34.4, 22.4, 17.0, 16.8, 16.0.

3-(3-chlorophenyl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (**3ao**)[5]



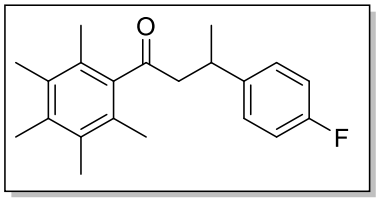
Yield 59.2 mg (0.18 mmol, 90%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 2H), 7.18 – 7.10 (m, 2H), 3.56 – 3.45 (m, 1H), 2.97-2.94 (m, 2H), 2.21 (s, 3H), 2.15 (s, 6H), 1.99 (br, 6H), 1.36 (d, *J* = 7.0 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.9, 148.8, 140.3, 135.6, 133.2, 129.8, 127.4, 127.3, 126.5, 125.6, 53.6, 34.2, 22.3, 17.0, 16.8, 16.0.

1-(2,3,4,5,6-pentamethylphenyl)-3-(p-tolyl)butan-1-one(**3ap**)[5]



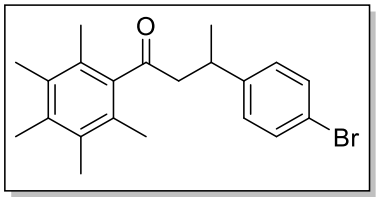
Yield 46.3 mg (0.17 mmol, 84%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate= 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17-7.10 (m, 4H), 3.57 – 3.48 (m, 1H), 3.05-2.91 (m, 2H), 2.33 (s, 3H), 2.23 (s, 3H), 2.17 (s, 6H), 2.02 (br, 6H), 1.38 (d, *J* = 6.9 Hz, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.4, 143.9, 140.6, 135.8, 135.5, 133.1, 129.2, 127.5, 127.0, 53.9, 33.9, 22.6, 21.1, 17.0, 16.8, 16.0.

3-(4-fluorophenyl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (**3aq**)[5]



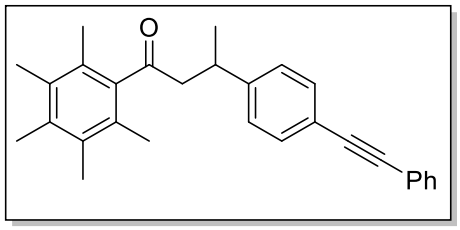
Yield 29.9 mg (0.096 mmol, 48%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 8.6, 5.5 Hz, 2H), 6.97 (t, *J* = 8.7 Hz, 2H), 3.63 – 3.48 (m, 1H), 2.94 (m, 2H), 2.22 (s, 3H), 2.15 (s, 6H), 1.97 (br, 6H), 1.36 (d, *J* = 7.1 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.1, 162.9 , 160.3, 142.4, 140.4, 133.2, 128.7, 128.6, 127.4, 115.4, 115.2, 54.1, 33.7, 22.6, 17.0, 16.8, 16.0.**^{19}F NMR** (471 MHz, $CDCl_3$) δ -117.20.

3-(4-bromophenyl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (**3ar**)[5]



Yield 37.3 mg (0.10 mmol, 50%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 1H), 7.29 – 7.17 (m, 2H), 7.13 (d, *J* = 8.3 Hz, 8H), 3.57 – 3.45 (m, 1H), 3.06 – 2.83 (m, 1H), 2.21 (s, 3H), 2.15 (s, 6H), 1.97 (br, 6H), 1.34 (d, *J* = 7.1 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.9, 145.7, 140.3, 135.6, 133.2, 131.6, 129.0, 128.6, 127.4, 126.3, 119.9, 53.7, 33.9, 22.4, 17.0, 16.8, 16.0.

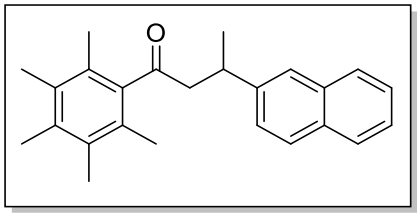
1-(2,3,4,5,6-pentamethylphenyl)-3-(4-(phenylethynyl)phenyl)butan-1-one (**3as**)[5]



Yield 23.6 mg (0.060 mmol, 30%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.01 (m, 10H), 3.48 (dd, *J* = 13.5, 6.8 Hz,

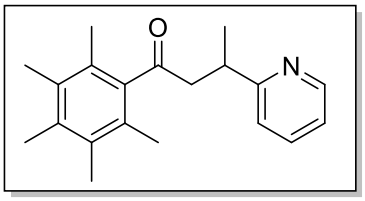
1H), 3.03- 2.82 (m, 2H), 2.20 (s, 3H), 2.14 (s, 6H), 1.97 (br, 6H), 1.33 (d, *J* = 6.9 Hz, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.0, 145.6, 140.4, 137.4, 135.4, 135.1, 133.0, 130.1, 129.8, 128.9, 128.8, 128.2, 127.3, 127.0, 126.9, 53.8, 33.9, 22.1, 16.9, 16.7, 15.9.

3-(naphthalen-2-yl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one(**3at**)[5]



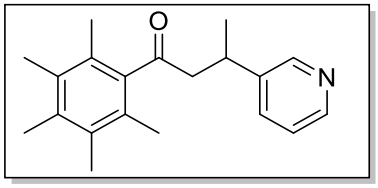
Yield 39.2 mg (0.114 mmol, 57%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81- 7.76 (m, 3H), 7.67 (s, 1H), 7.49 – 7.35 (m, 3H), 3.78 – 3.64 (m, 1H), 3.18- 2.99 (m, 2H), 2.21 (s, 3H), 2.14 (s, 6H), 2.00 (br, 6H), 1.47 (d, *J* = 6.9 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.3, 144.2, 140.5, 135.5, 133.7, 133.2, 132.3, 128.2, 127.7, 127.7, 127.5, 126.1, 125.9, 125.4, 125.3, 53.7, 34.5, 22.6, 17.1, 16.8, 16.0.

1-(2,3,4,5,6-pentamethylphenyl)-3-(pyridin-2-yl)butan-1-one (**3au**)[5]



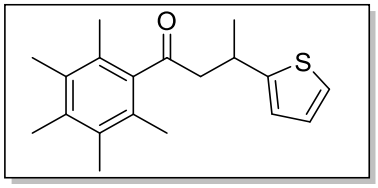
Yield 54.3 mg (0.184 mmol, 92%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44- 8.42 (m, 1H), 7.53- 7.49 (m, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.05 – 6.94 (m, 1H), 3.57- 3.52 (m, 1H), 3.33-3.27 (m, 1H), 2.91- 2.85 (m, 1H), 2.12 (s, 3H), 2.06 (s, 6H), 1.92 (br, 6H), 1.30 (d, *J* = 7.0 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.5, 165.1, 149.1, 140.4, 136.5, 135.3, 133.0, 127.5, 122.8, 121.4, 52.0, 36.3, 21.2, 16.9, 16.7, 15.9.

1-(2,3,4,5,6-pentamethylphenyl)-3-(pyridin-3-yl)butan-1-one (**3av**)[5]



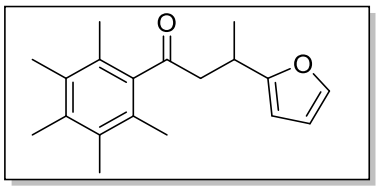
Yield 54.9 mg (0.186 mmol, 93%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.51- 8.50 (m, 1H), 7.60- 7.56 (m, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.10-7.06 (m, 1H), 3.67- 3.58 (m, 1H), 3.41- 3.34 (m, 1H), 2.99- 2.92 (m, 1H), 2.19 (s, 3H), 2.14 (s, 6H), 1.99 (br, 6H), 1.38 (d, *J* = 6.9 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.5, 165.1, 149.1, 140.4, 136.5, 135.3, 132.9, 127.4, 122.8, 121.4, 51.9, 36.3, 21.2, 16.9, 16.7, 15.9.

1-(2,3,4,5,6-pentamethylphenyl)-3-(thiophen-2-yl)butan-1-one (**3aw**)[5]



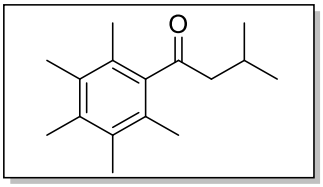
Yield 36.1 mg (0.12 mmol, 60%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 4.9, 1.0 Hz, 1H), 6.92- 6.86 (m, 2H), 3.90- 3.81 (m, 1H), 3.12- 2.89 (m, 2H), 2.21 (s, 3H), 2.16 (s, 5H), 2.02 (br, 6H), 1.46 (d, *J* = 7.0 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.7, 150.8, 140.3, 135.6, 133.2, 127.5, 126.7, 123.2, 122.9, 54.7, 29.9, 23.3, 17.0, 16.8, 16.1.

3-(furan-2-yl)-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (**3ax**)



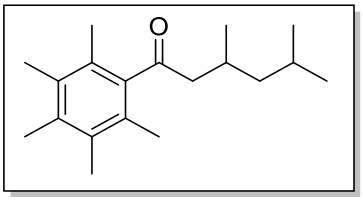
Yield 30.1 mg (0.106 mmol, 53%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 6.27- 6.26 (m, 1H), 6.03 (d, *J* = 3.3 Hz, 1H), 3.65- 3.57 (m, 1H), 3.16- 3.10 (m, 1H), 2.85- 2.78 (m, 1H), 2.22 (s, 3H), 2.17 (s, 6H), 2.05 (s, 6H), 1.38 (d, *J* = 6.9 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.7, 159.3, 140.9, 140.3, 135.5, 133.2, 127.5, 110.1, 104.1, 51.1, 28.0, 19.2, 16.9, 16.8, 16.0. Selected **IR** (ATR) ν (cm^{-1}): 3447, 2919, 2663, 1694, 1455, 1376, 1150. HRMS calcd for $C_{19}H_{24}O_2Na$ [M + Na] 307.1674, found 307.1673.

3-methyl-1-(2,3,4,5,6-pentamethylphenyl)butan-1-one (**3ay**)



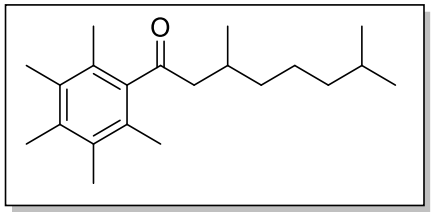
Yield 31.1 mg (0.134 mmol, 67%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.57 (d, *J* = 6.4 Hz, 2H), 2.35- 2.29 (m, 1H), 2.22 (s, 3H), 2.18 (s, 6H), 2.10 (s, 6H), 1.02 (d, *J* = 6.7 Hz, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.4, 140.9, 135.4, 133.2, 127.4, 54.6, 23.4, 22.9, 17.1, 16.8, 16.1. Selected **IR** (ATR) ν (cm^{-1}): 3451, 2954, 2871, 1694, 1455, 1402, 1363, 1263. HRMS calcd for $C_{16}H_{24}ONa$ [M + Na] 255.1725, found 255.1722.

3,5-dimethyl-1-(2,3,4,5,6-pentamethylphenyl)hexan-1-one (**3az**)



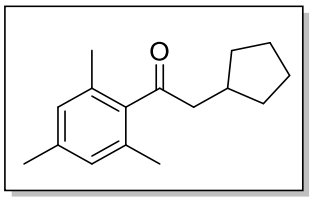
Yield 47.2 mg (0.172 mmol, 86%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.72- 2.46 (m, 2H), 2.24 (s, 3H), 2.19 (s, 6H), 2.12 (s, 6H), 1.72- 1.62 (m, 1H), 1.25 – 1.09 (m, 2H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.95-0.88 (m, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.4, 140.9, 135.4, 133.2, 127.4, 53.4, 46.5, 25.8, 25.4, 23.5, 22.3, 20.3, 17.2, 16.8, 16.1. Selected **IR** (ATR) ν (cm^{-1}): 3449, 2958, 2867, 1708, 1459, 1385, 1097. HRMS calcd for $C_{19}H_{30}ONa$ [M + Na] 297.2189, found 297.2195.

3,7-dimethyl-1-(2,3,4,5,6-pentamethylphenyl)octan-1-one (**3aza**)



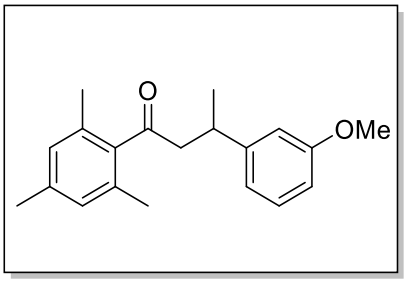
Yield 33.9 mg (0.112 mmol, 56%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.70-2.47 (m, 2H), 2.22 (s, 3H), 2.17 (s, 6H), 2.10 (s, 6H), 1.56 – 1.48 (m, 1H), 1.43 – 1.21 (m, 4H), 1.22 – 1.12 (m, 3H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 211.4, 140.9, 135.3, 133.1, 127.4, 53.0, 39.2, 37.1, 28.1, 27.9, 24.7, 22.8, 22.7, 20.1, 17.1, 16.7, 16.0. Selected **IR** (ATR) ν (cm^{-1}): 3416, 2928, 2871, 1699, 1459, 1381. HRMS calcd for $C_{21}H_{34}ONa$ [M + Na] 325.2507, found 325.2512.

2-cyclopentyl-1-mesitylethan-1-one (**3bb**)



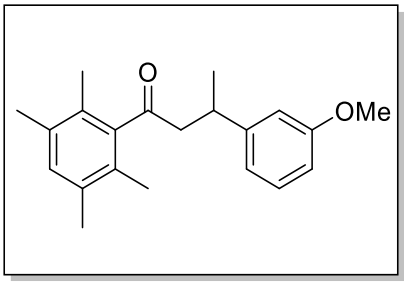
Yield 37.7 mg (0.164 mmol, 82%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.81 (s, 2H), 2.72 (d, *J* = 7.0 Hz, 2H), 2.43 – 2.32 (m, 1H), 2.25 (s, 3H), 2.18 (s, 6H), 1.99 – 1.84 (m, 2H), 1.70 – 1.59 (m, 2H), 1.56- 1.45 (m, 2H), 1.19 – 1.08 (m, 2H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.8, 139.9, 138.2, 132.6, 128.6, 51.4, 40.4, 35.0, 32.9, 30.9, 29.5, 25.1, 21.2, 19.3. Selected **IR** (ATR) ν (cm^{-1}): 3451, 2954, 2867, 1699, 1612, 1455, 1257. HRMS calcd for $C_{16}H_{22}ONa$ [M + Na] 253.1563, found 253.1573.

1-mesityl-3-(3-methoxyphenyl)butan-1-one (**3bn**)



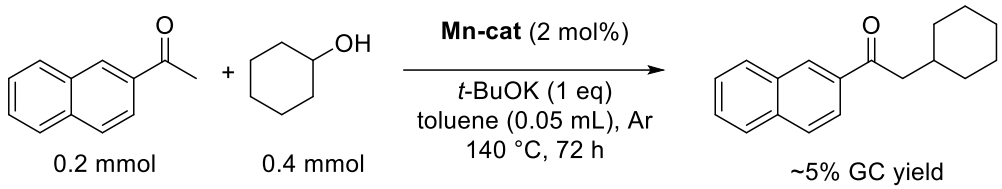
Yield 47.4 mg (0.16 mmol, 80%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate = 49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25- 7.17 (m, 1H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.80 – 6.77 (m, 3H), 6.75 – 6.70 (m, 1H), 3.78 (s, 3H), 3.55- 3.44 (m, 1H), 3.07- 2.89 (m, 2H), 2.25 (s, 3H), 2.07 (s, 6H), 1.35 (d, *J* = 7.0 Hz, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 209.1, 159.8, 148.3, 139.6, 138.4, 132.7, 129.6, 128.7, 119.5, 113.1, 111.6, 55.3, 53.1, 34.7, 22.4, 21.1, 19.1. Selected **IR** (ATR) ν (cm^{-1}): 3438, 2928, 2849, 1686, 1594, 1272, 1041. HRMS calcd for $C_{20}H_{24}O_2Na$ [M + Na] 319.1669, found 319.1671.

3-(3-methoxyphenyl)-1-(2,3,5,6-tetramethylphenyl)butan-1-one (**3cn**)

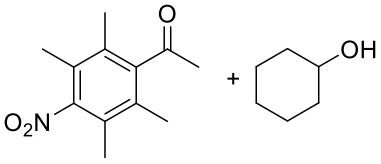


Yield 50.2 mg (0.162 mmol, 81%). Column Chromatography on silica gel (Eluent; hexane:ethyl acetate=49:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 15.8, 7.9 Hz, 1H), 6.93 (s, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.81 – 6.78 (m, 1H), 6.76 – 6.71 (m, 1H), 3.79 (s, 3H), 3.52 (dd, *J* = 13.1, 7.1 Hz, 1H), 3.07- 2.87 (m, 2H), 2.17 (s, 6H), 1.96 (s, 6H), 1.37 (d, *J* = 6.8 Hz, 3H).**^{13}C NMR** (101 MHz,$CDCl_3$) δ 210.1, 159.8, 148.5, 142.6, 134.5, 131.7, 129.6, 128.1, 119.5, 113.1, 111.5, 55.3, 53.5, 34.4, 22.4, 19.6, 15.8. Selected **IR** (ATR) ν (cm^{-1}): 3451, 2928, 1699, 1599, 1463, 1259. HRMS calcd for $C_{21}H_{26}O_2Na$ [M + Na] 333.1830, found 333.1865.

7. Unsuccessful reactions:

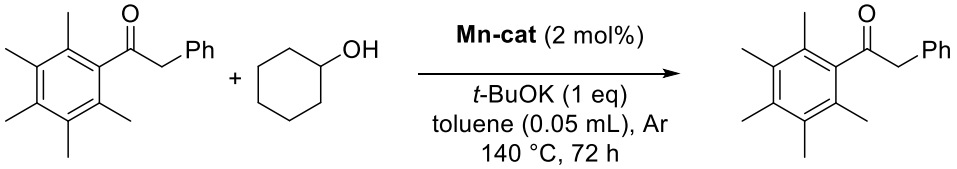


0.2 mmol 0.4 mmol ~5% GC yield



complex reaction mixture

0.2 mmol 0.4 mmol

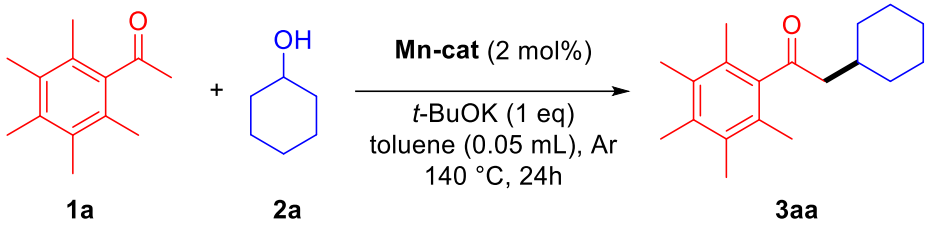


0.2 mmol 0.4 mmol recovered >95% yield

0.2 mmol 0.4 mmol 11%

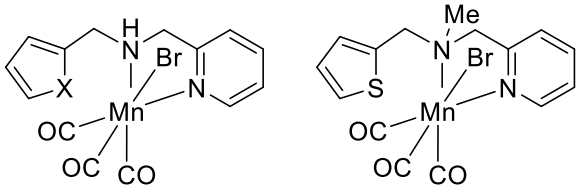
8. Mechanistic experiments:

8.1. M-L cooperation:



1a **2a** **3aa**

Entry	Mn-Cat	Mn loading (mol%)	Yield of **3aa** (%)
1.	**Mn2**	2.0	85
3.	**Mn3**	2.0	25
4.	**Mn4**	2.0	<5

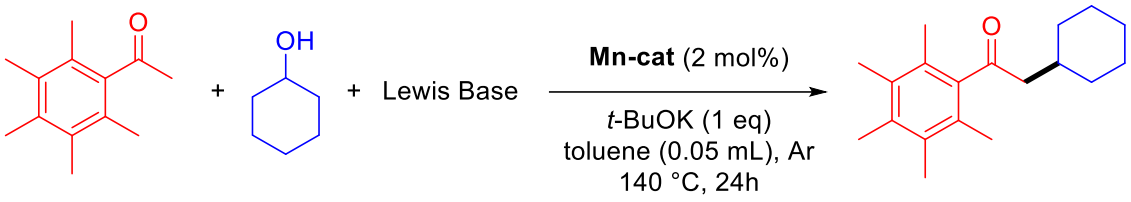


Mn2 (X = S)
Mn3 (X = O)

Mn4

In an oven dried, well-capped reaction tube, *t*-BuOK (22.4 mg, 0.2 mmol), **Mn-cat** (0.002 mmol, 2 mol%) were suspended in toluene (0. 5 mL). To the suspension secondary alcohol **2a** followed by ketone **1a** were added under inert atmosphere. The tube was then closed and stirred in a preheated oil bath at 140 ^{o}C for 24 h. The reaction was quenched with water (2 mL) and the organics were extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated and was subsequently purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate (49:1) mixture as eluent affording the corresponding product.

8.2. Effect of added Lewis base:

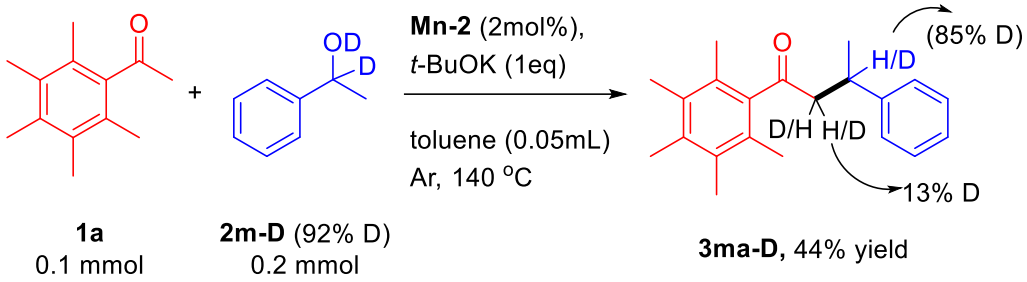


1a **2a** **3aa**

Lewis Base	Mol %	Yield of 3a
Pyridine	20	45%
2-Me Pyridine	20	3%
4-Me Pyridine	20	11%

In an oven dried, screw-cap reaction tube, *t*-BuOK (22.4 mg, 0.2 mmol), **Mn2** (2 mg, 0.004 mmol, 2 mol%) were suspended in toluene (0.05 mL). To the suspension, alcohol **2a** was added followed by ketone **1a** under inert atmosphere. To the reaction mixture Lewis base was added. The tube was then closed and stirred in a preheated oil bath at 140 °C for 24 h. The respective yields were then estimated using GC analysis with mesitylene as standard.

8.3.a. Deuterium labelling experiment:



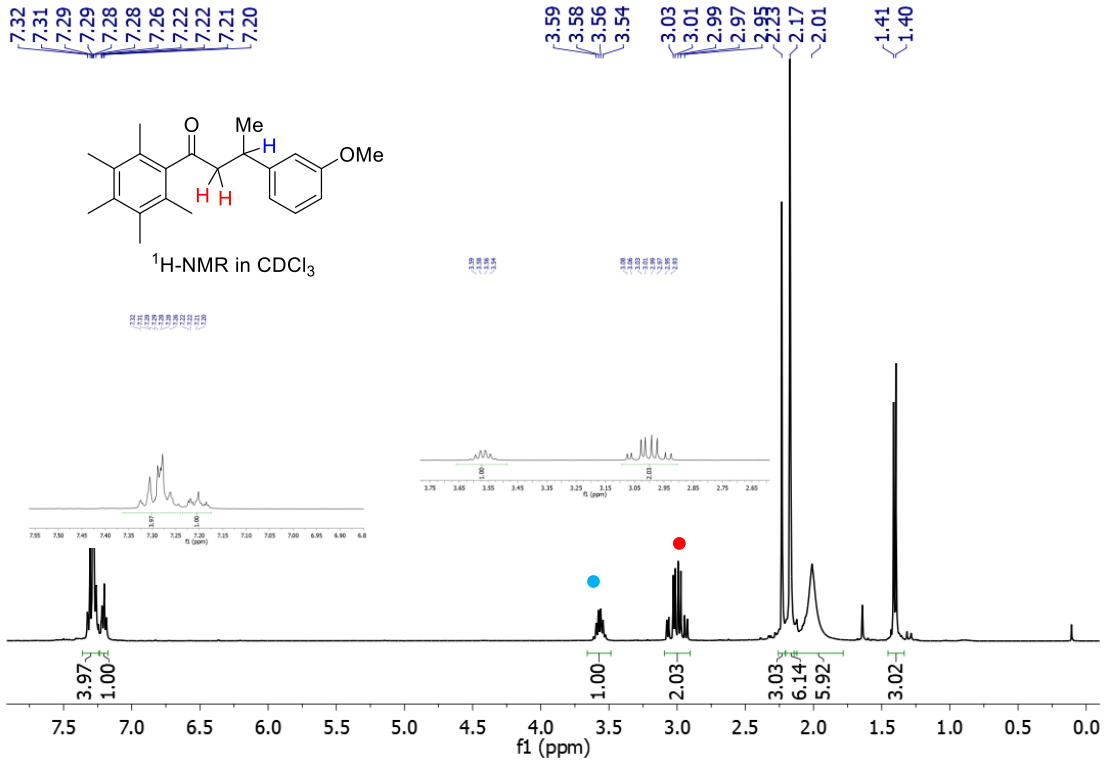
1a
0.1 mmol

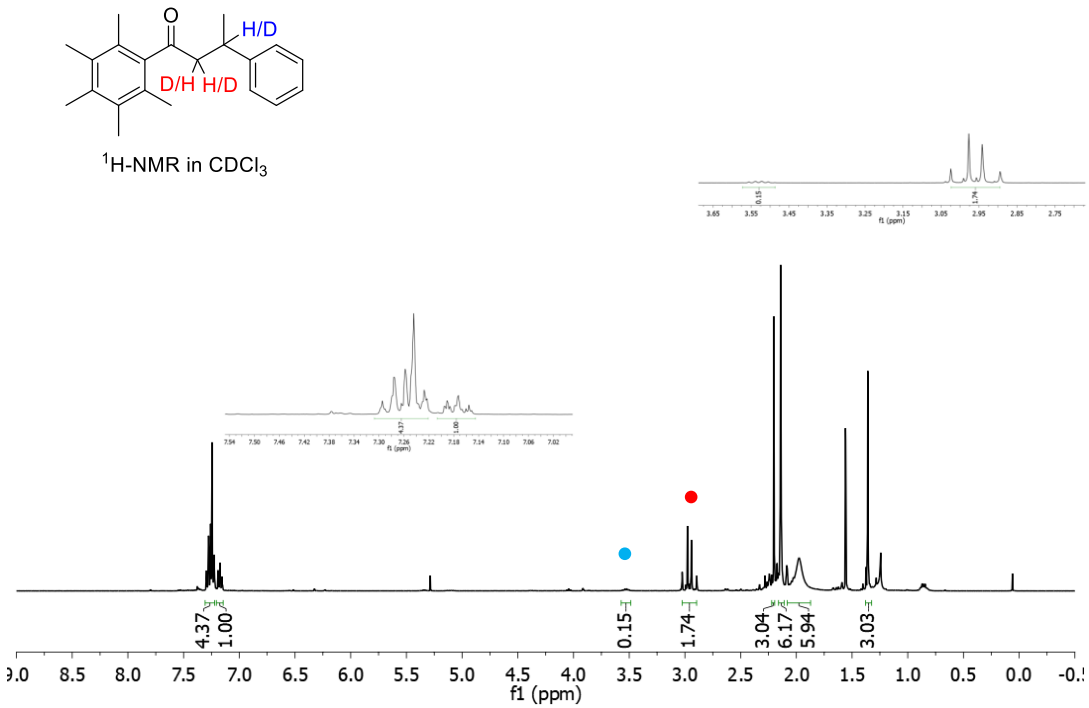
2m-D (92% D)
0.2 mmol

3ma-D, 44% yield

In an oven dried, well-capped reaction tube, *t*-BuOK (11.2 mg, 0.1 mmol), **Mn2** (1 mg, 0.002 mmol, 2 mol%) were suspended in toluene (0.025 mL). To the suspension secondary alcohol **2m-D** (92% D) followed by ketone **1a** were added under inert atmosphere. The tube was then closed and stirred in a preheated oil bath at 140 °C for 48 h. The reaction was quenched with water (2 mL) and the organics were extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated and was subsequently purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate (49:1) mixture as eluent

affording the corresponding product **3m-D** in 44% yield. The deuterium labelling was calculated by 1H NMR analysis of the product.

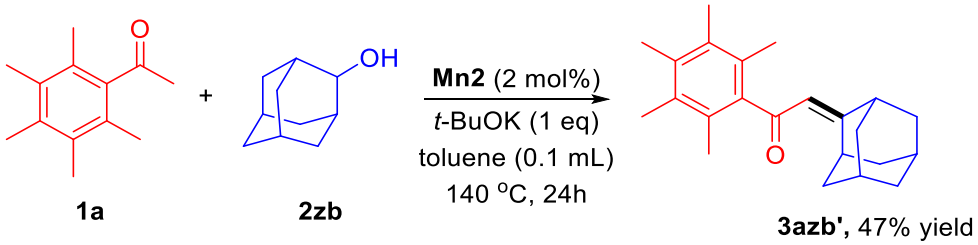




8.3.b. Kinetic isotope effect:

In two separate oven dried, well-capped reaction tube, *t*-BuOK (11.2 mg, 0.1 mmol), **Mn2** (1 mg, 0.002 mmol, 2 mol%) were suspended in toluene (0.025 mL). To the suspension secondary alcohol **2m** in one reaction tube and **2m-D** in another were added followed by ketone **1a** under inert atmosphere. The tubes were then closed and stirred in a preheated oil bath at 140 °C for 4 h. The reaction was quenched with water (2 mL). The respective yields were determined by GC analysis using mesitylene as the internal standard and KIE value k_H/k_D = 16.7/7.8 = 2.14 was determined.

8.4. Isolation of the chalcone intermediate:

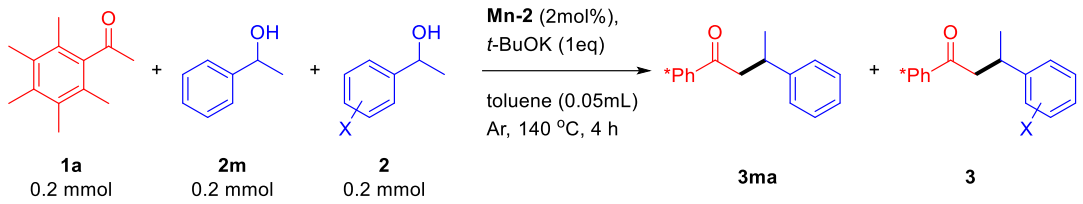


In an oven dried, well-capped reaction tube, *t*-BuOK (22.4 mg, 0.2 mmol), **Mn2** (2 mg, 0.002 mmol, 2 mol%) were suspended in toluene (0.1 mL). To the suspension secondary alcohol **2zb** followed by ketone **1a** were added under inert atmosphere. The tube was then closed and stirred in a preheated oil bath at 140 °C for 24 h. The reaction was quenched with water (2 mL) and the organics were extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated and was subsequently purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate (49:1) mixture as eluent affording the corresponding chalcone **3azb'**. Yield 30.3 mg (0.094 mmol, 47%)

2-(adamantan-2-ylidene)-1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (3azb'): **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.14 (s, 1H), 3.71 (s, 1H), 2.39 (br, 1H), 2.23 (s, 3H), 2.18 (s, 6H), 2.15 (s, 6H), 2.00 (d, *J* = 2.4 Hz, 1H), 1.97 (br, 3H), 1.91 – 1.77 (m, 8H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.3, 171.3, 141.8, 135.1, 133.1, 127.9, 120.4, 41.9, 40.5, 39.5, 36.9, 33.2, 28.0, 17.3, 16.8, 16.1. Selected **IR** (ATR) ν (cm^{-1}): 3450, 2909, 2852, 1670, 1609, 1447, 1386, 1268, 1124. HRMS calcd for $C_{23}H_{30}ONa$ [M + Na] 345.2189, found 345.2191.

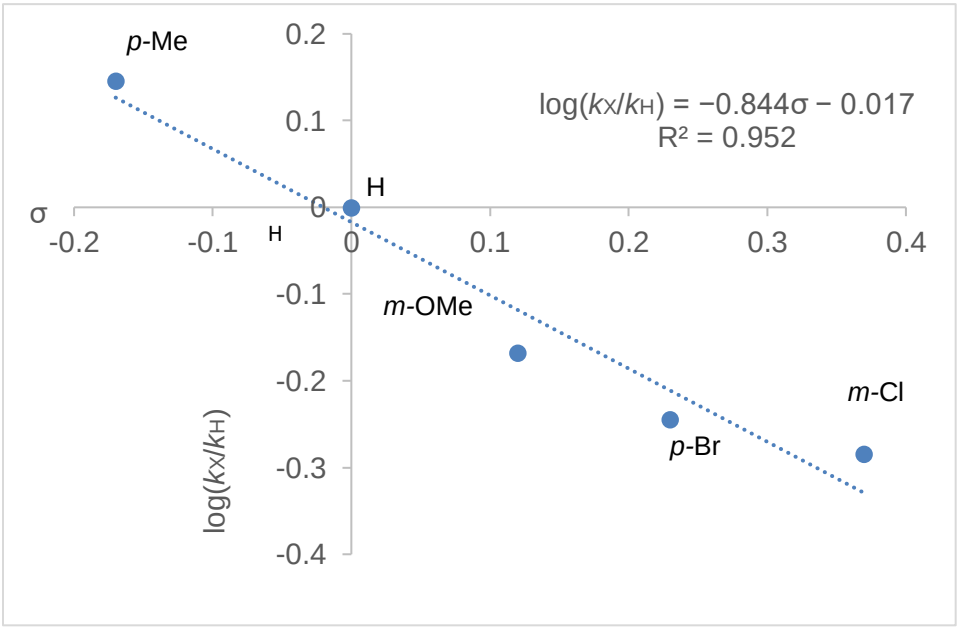
8.5. Hammett studies:

In four different oven dried, screw-cap reaction tube, *t*-BuOK (22.4 mg, 0.2 mmol), **Mn-2** (2 mg, 0.004 mmol, 2 mol%) were suspended in toluene (0.05 mL). To the suspension, alcohol **2m** was added under inert atmosphere. To the four different reaction tubes different alcohols **2n**, **2o**, **2q**, **2r** were added respectively followed by ketone **1a**. The tube was then closed and stirred in a preheated oil bath at 140 ^{o}C for 4 h. The ratio of yields (**3m: 3n**), (**3m: 3o**), (**3m: 3q**) and (**3m: 3r**) were estimated using GC analysis with mesitylene as standard.



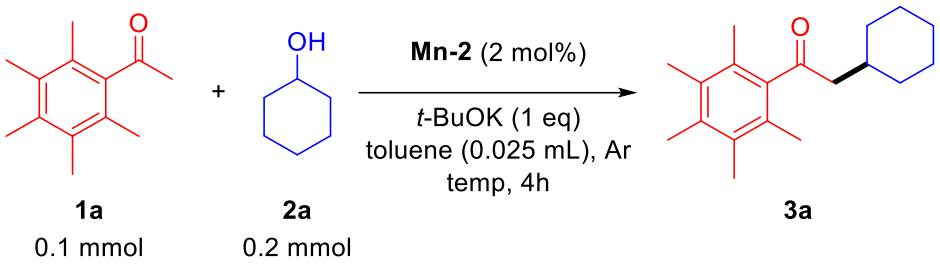
1a 0.2 mmol | **2m** 0.2 mmol | **2** 0.2 mmol | **3ma** | **3**

X	σ	k_x/k_H	$\log(k_x/k_H)$
p-Me	-0.17	1.40	0.1461
H	0	0	0
m-OMe	0.12	0.68	-0.1675
p-Br	0.23	0.57	-0.2441
m-Cl	0.37	0.52	-0.2840



8.6. Eyring analysis:

In an oven dried, screw-cap reaction tube, *t*-BuOK (11.2 mg, 0.1 mmol), **Mn2** (1 mg, 0.002 mmol, 2 mol%) were suspended in toluene (0.025 mL). To the suspension, alcohol **2a** was added followed by ketone **1a** under inert atmosphere. The tube was then closed and stirred in a preheated oil bath at respective temperature for 4 h. The respective rates were calculated from the measured yield of **3aa** using GC analysis with mesitylene as an internal standard.

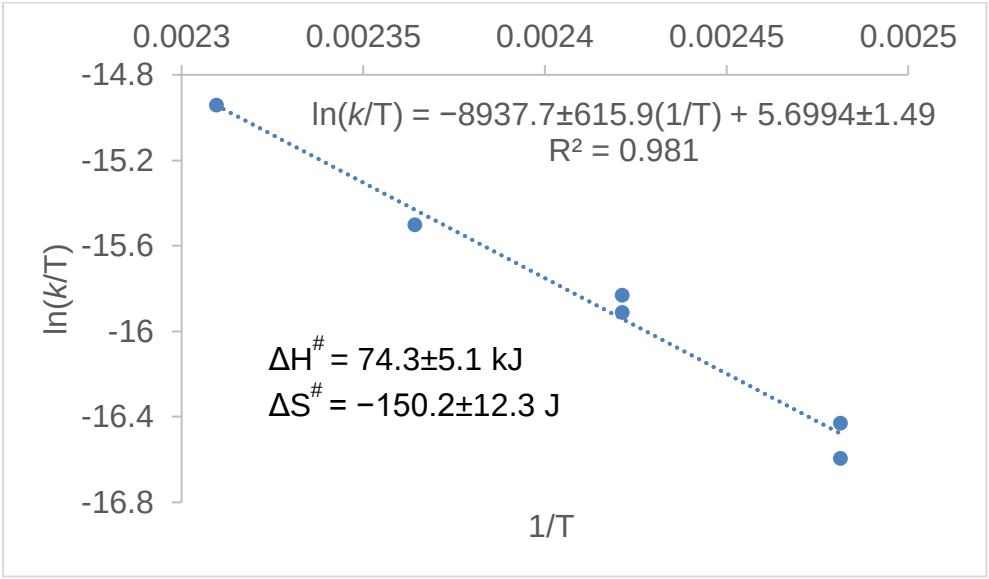


1a 0.1 mmol

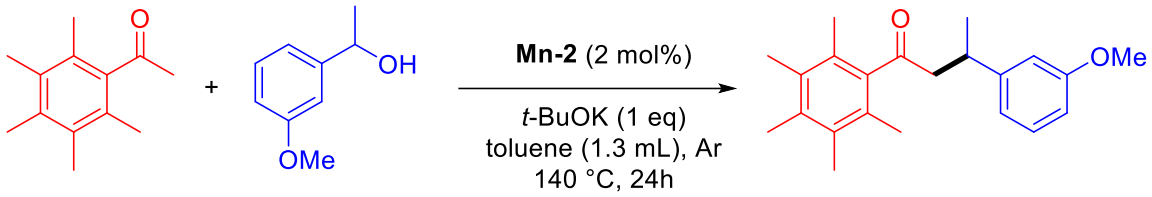
2a 0.2 mmol

3a

Temp	*k*	1/T	ln(*k*/T)
433 K (160°C)	14.04×10^{-5}	0.002309	-14.9418
423 K (150°C)	7.83×10^{-5}	0.002364	-15.5023
413 K (140°C)	5.08×10^{-5}	0.002421	-15.9111
413 K (140°C)	5.50×10^{-5}	0.002421	-15.8316
403 K (130°C)	2.50×10^{-5}	0.002481	-16.5956
403 K (130°C)	2.95×10^{-5}	0.002481	-16.4301



9. Gram-Scale synthesis:



1a 5.26 mmol

2n 10.52 mmol

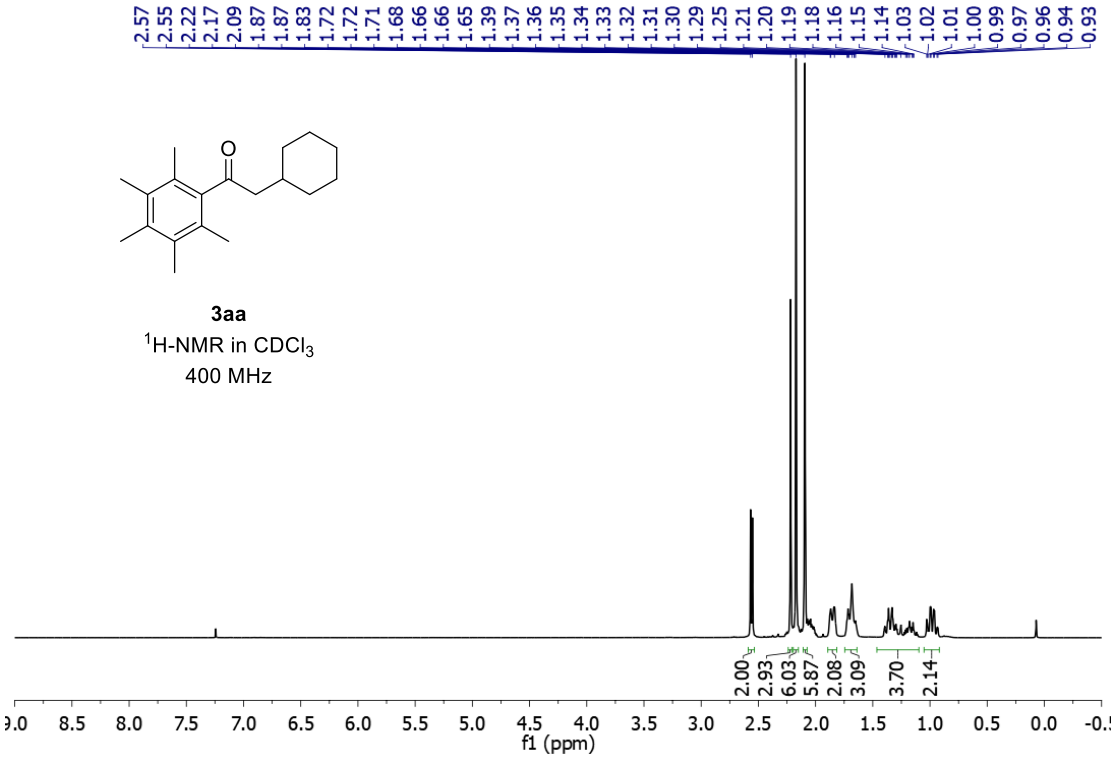
3an 4.58 mmol, 1.48 g 87%

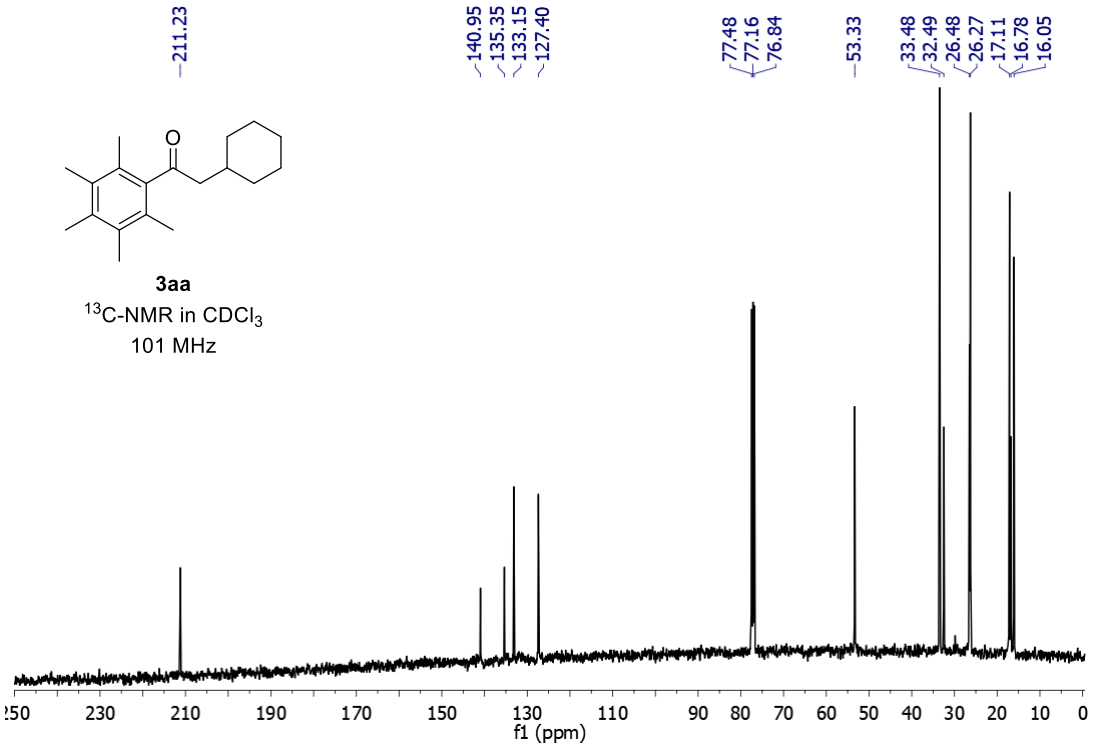
In an oven dried 50 mL Schlenk tube, *t*-BuOK (589 mg, 5.26 mmol), **Mn-2** (50 mg, 0.105 mmol, 2 mol%) were suspended in toluene (1.3 mL). To the suspension, alcohol **2n** (1.46 mL, 10.52 mmol) was added followed by ketone **1a** (1 g, 5.26 mmol) under inert atmosphere. The tube was then closed and stirred in a preheated oil bath at 140 ^{o}C for 24 h. The reaction was quenched with water (5 mL) and the organics were extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated and was subsequently purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate mixture as eluent giving the desired product **3an** in 87% yield (1.48 g, 4.58 mmol).

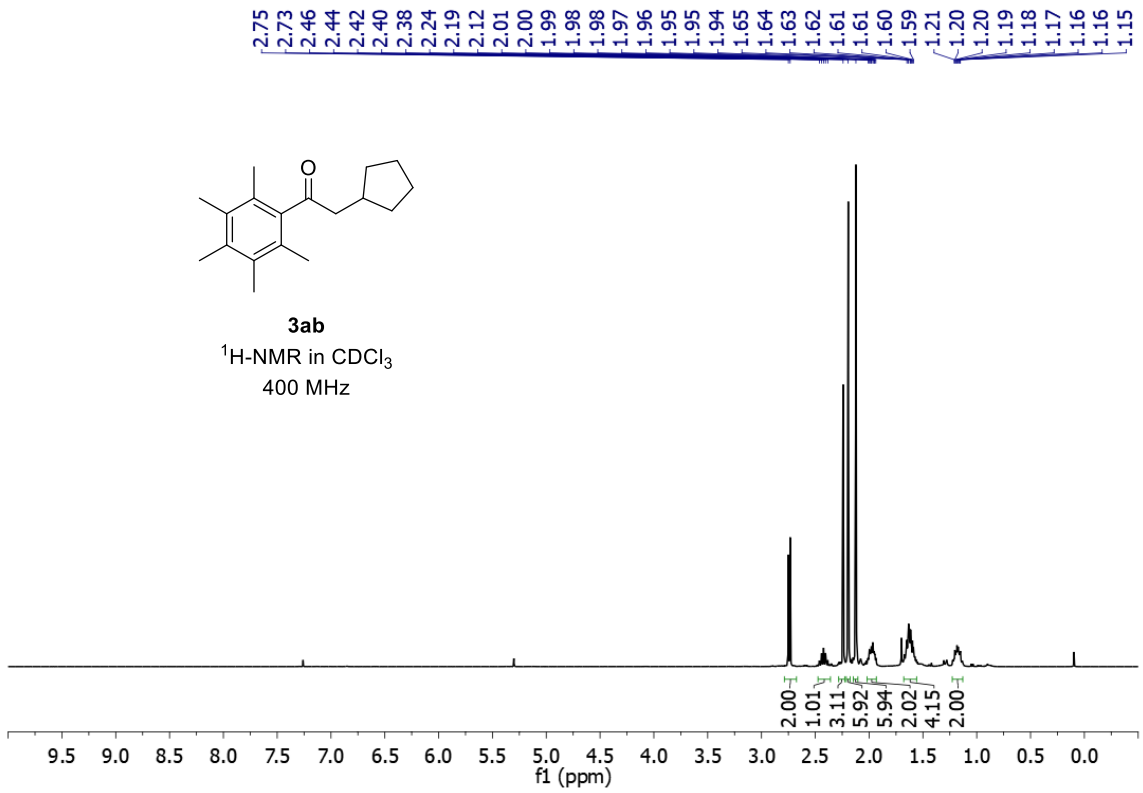
10. References:

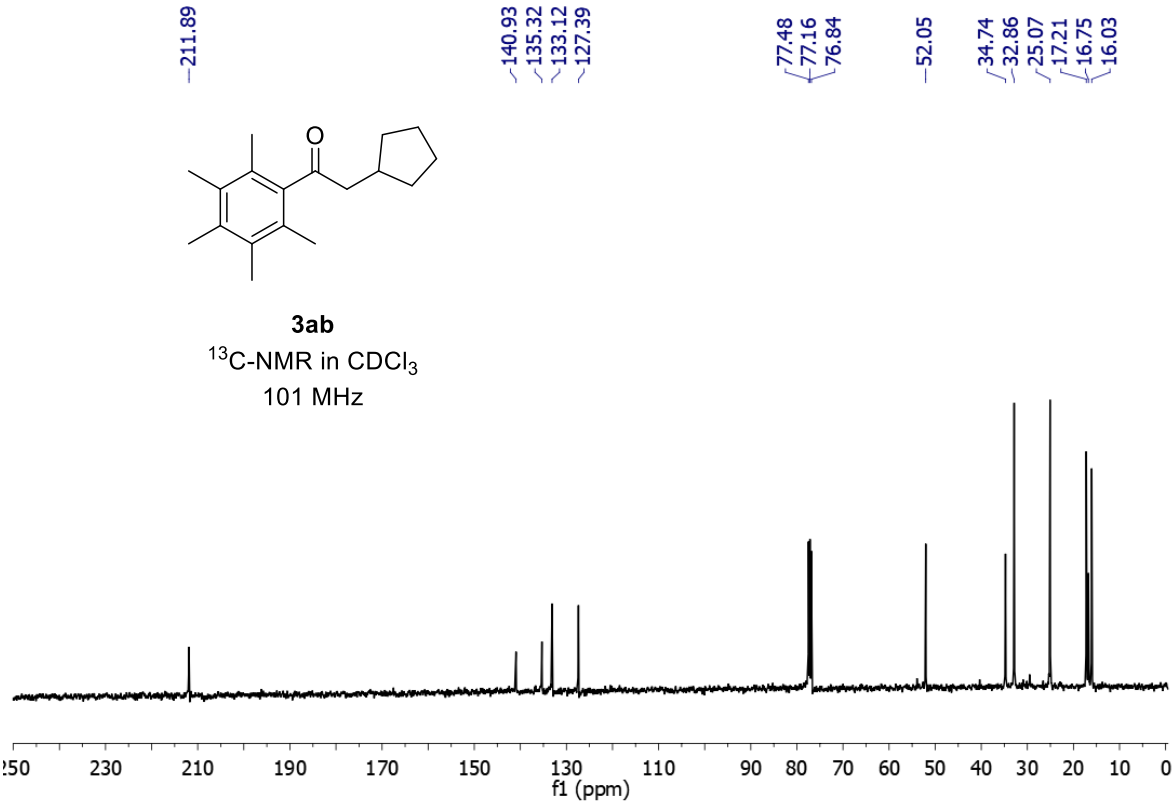
1. A. Jana, C. B. Reddy and B. Maji, *ACS Catal.*, 2018, **8**, 9226-9231.
2. A. Jana, K. Das, A. Kundu, P. R. Thorve, D. Adhikari and B. Maji, *ACS Catal.*, 2020, **10**, 2615-2626.
3. W. M. Akhtar, R. J. Armstrong, J. R. Frost, N. G. Stevenson and T. J. Donohoe, *J. Am. Chem. Soc.*, 2018, **140**, 11916-11920.
4. W. M. Akhtar, C. B. Cheong, J. R. Frost, K. E. Christensen, N. G. Stevenson and T. J. Donohoe, *J. Am. Chem. Soc.*, 2017, **139**, 2577-2580.
5. P. Chakraborty, M. K. Gangwar, B. Emayavaramban, E. Manoury, R. Poli and B. Sundararaju, *ChemSusChem*, 2019, **12**, 3463-3467.

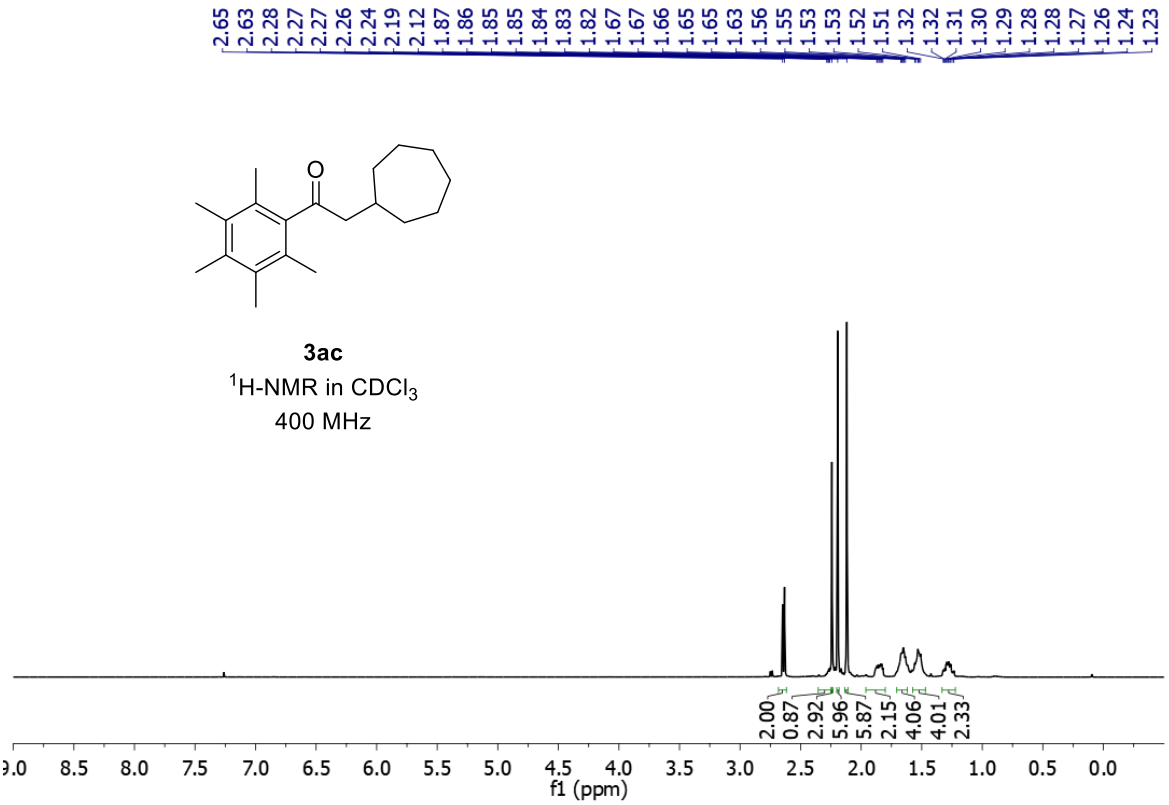
11. Copies of NMR-spectra:

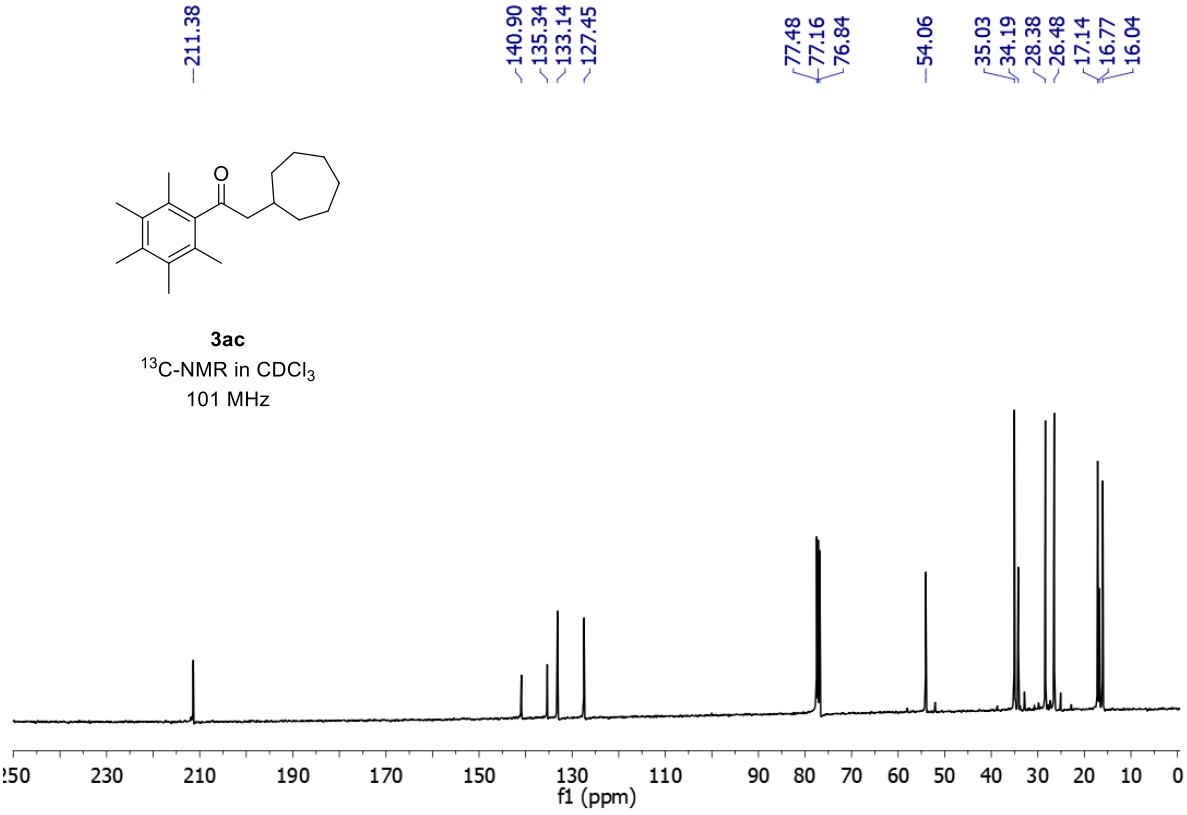


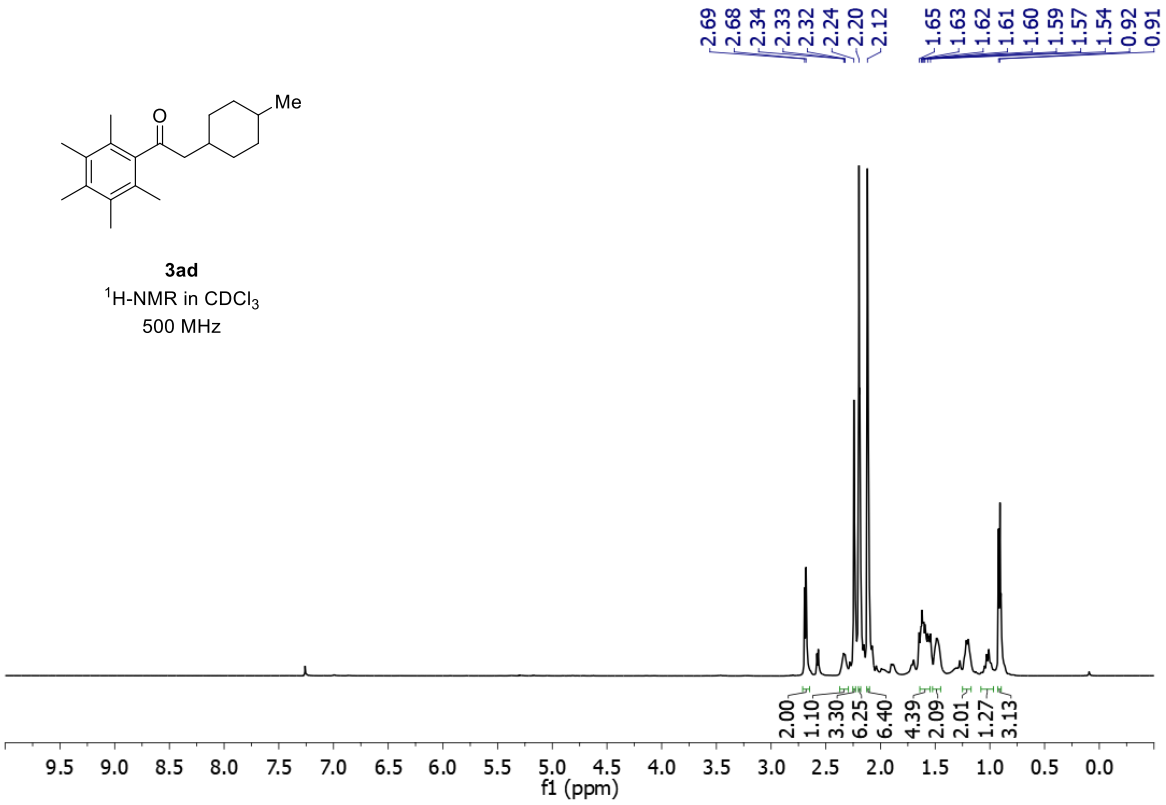



2.75 2.73 2.46 2.44 2.42 2.40 2.38 2.24 2.19 2.12 2.01 2.00 1.99 1.98 1.98 1.97 1.96 1.95 1.95 1.94 1.65 1.64 1.63 1.62 1.61 1.61 1.60 1.59 1.21 1.20 1.20 1.19 1.18 1.17 1.16 1.16 1.15
O
3ab
1H-NMR in CDCl3
400 MHz
2.00 1.01 3.11 5.92 5.94 2.02 4.15 2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


211.89
140.93 135.32 133.12 127.39
77.48 77.16 76.84
52.05
34.74 32.86 25.07 17.21 16.75 16.03
O
3ab
13C-NMR in CDCl3
101 MHz
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


2.65 2.63 2.28 2.27 2.27 2.26 2.24 2.19 2.12 1.87 1.86 1.85 1.85 1.84 1.83 1.82 1.67 1.67 1.66 1.65 1.65 1.63 1.56 1.55 1.53 1.53 1.52 1.51 1.32 1.32 1.31 1.30 1.29 1.28 1.28 1.27 1.26 1.24 1.23
O
3ac
1H-NMR in CDCl3
400 MHz
2.00 0.87 2.92 5.96 5.87 2.15 4.06 4.01 2.33
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

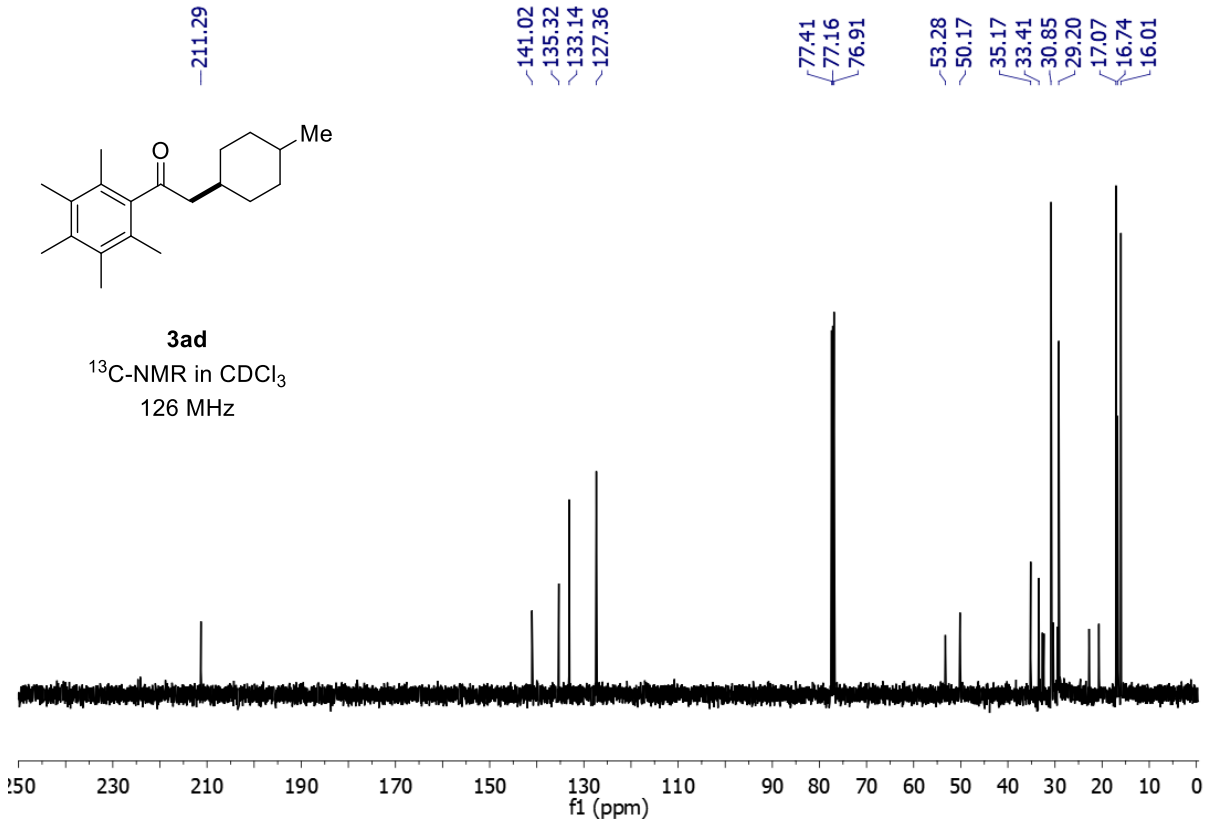

211.38
140.90 135.34 133.14 127.45
77.48 77.16 76.84
54.06
35.03 34.19 28.38 26.48 17.14 16.77 16.04
O
3ac
13C-NMR in CDCl3
101 MHz
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3ad

^{1}H-NMR in $CDCl_3$

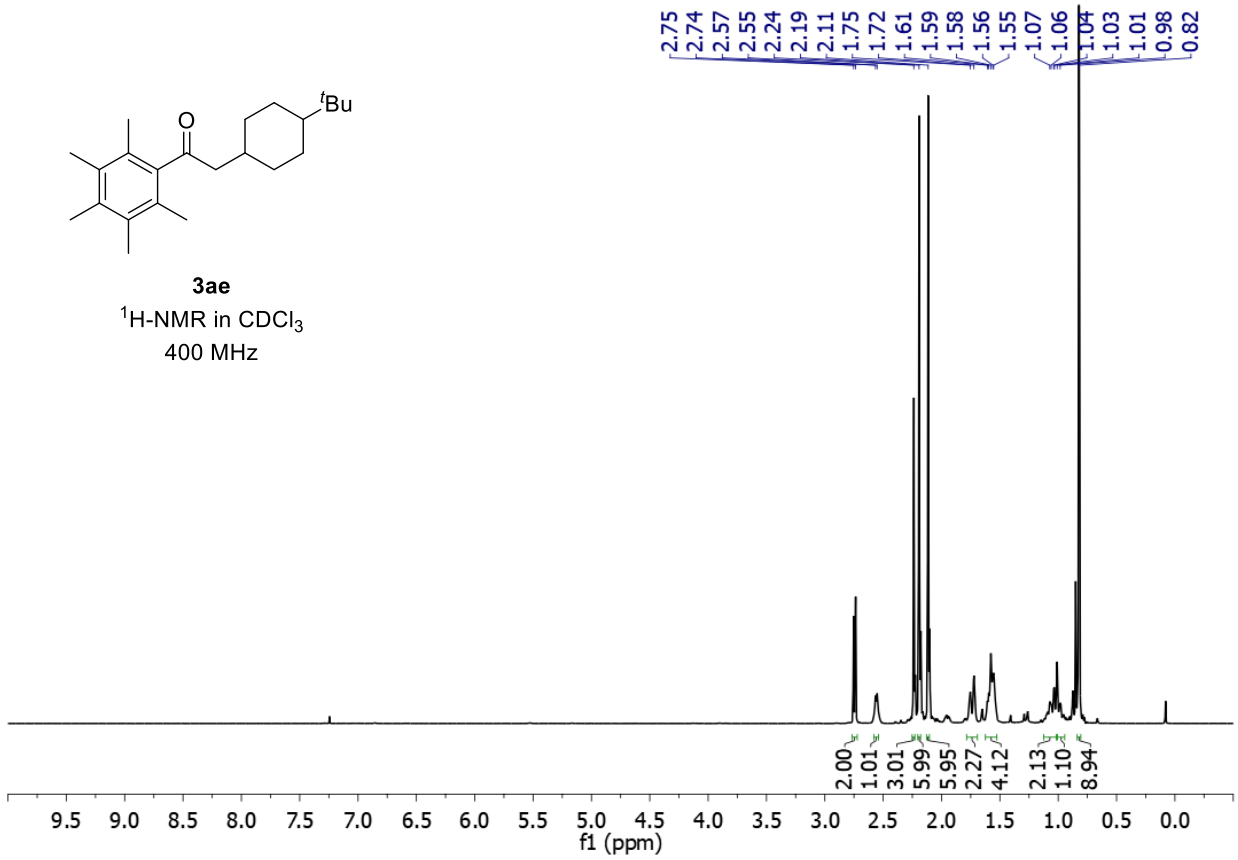
500 MHz



3ad

^{13}C-NMR in $CDCl_3$

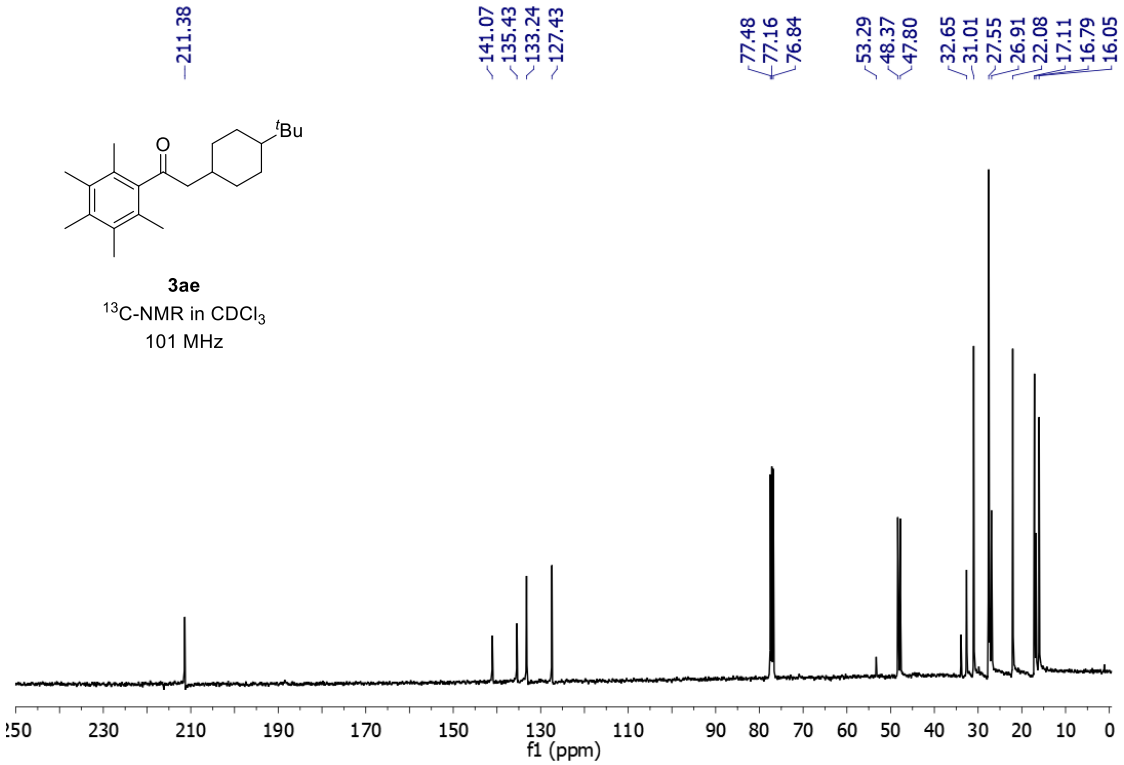
126 MHz



3ae

^{1}H-NMR in $CDCl_3$

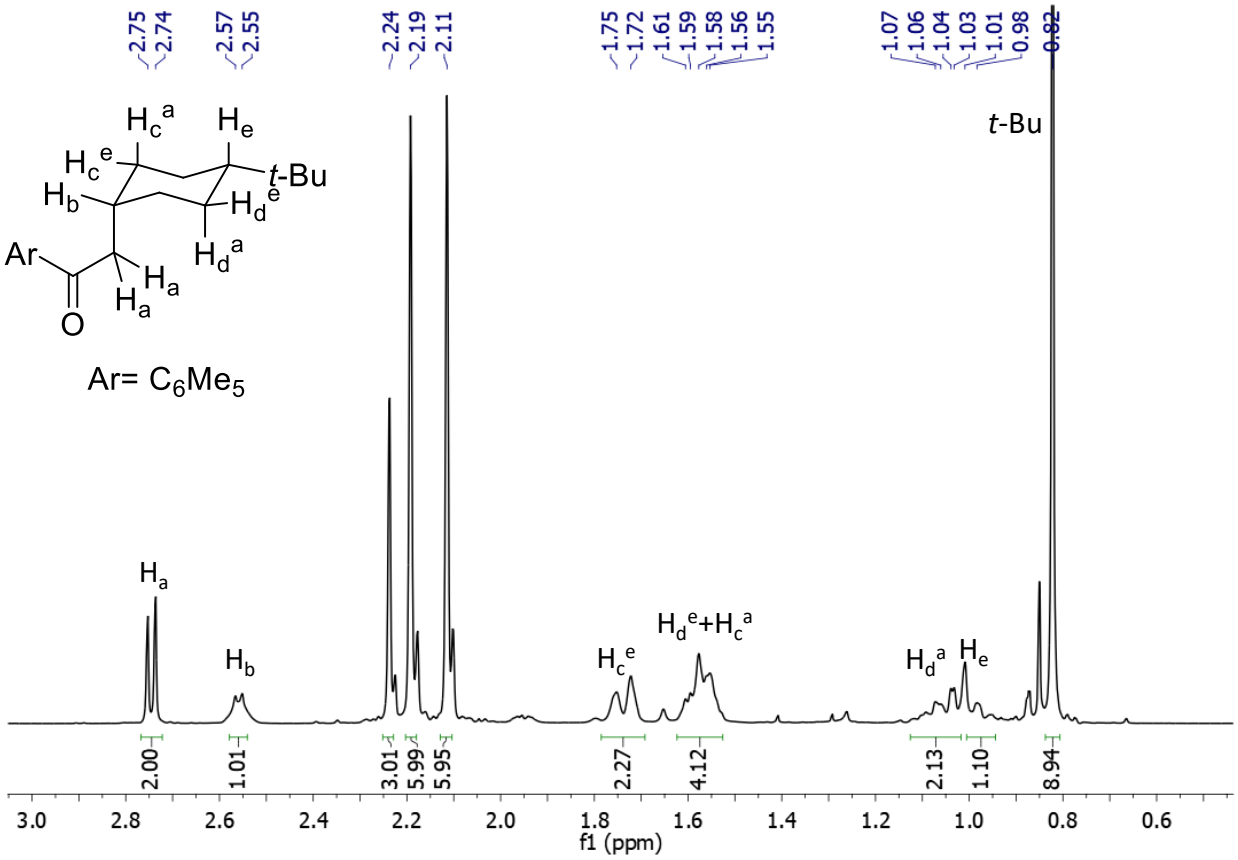
400 MHz



3ae

^{13}C-NMR in $CDCl_3$

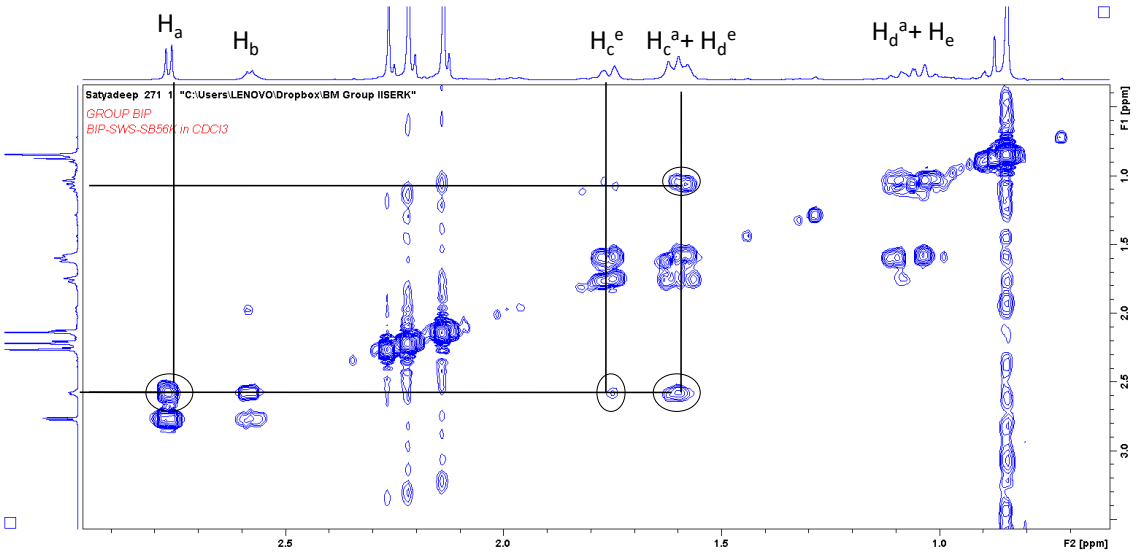
101 MHz

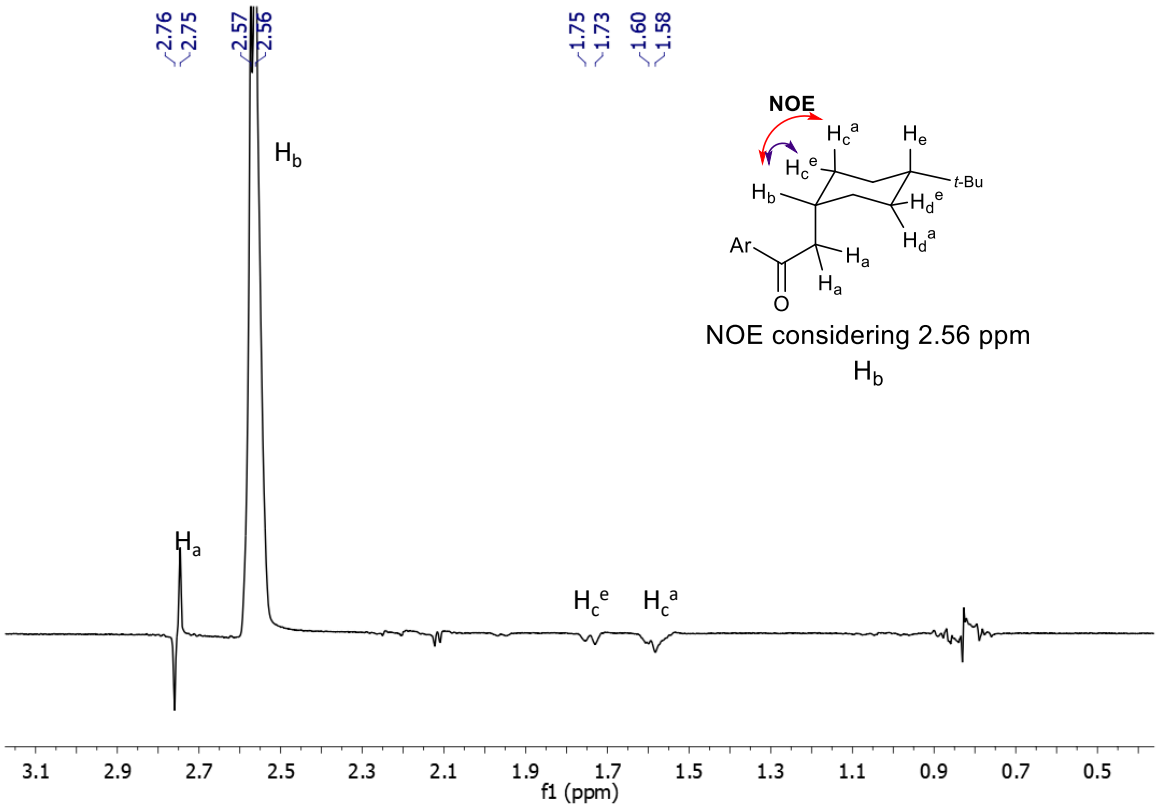


Ar= C_6Me_5

3ae

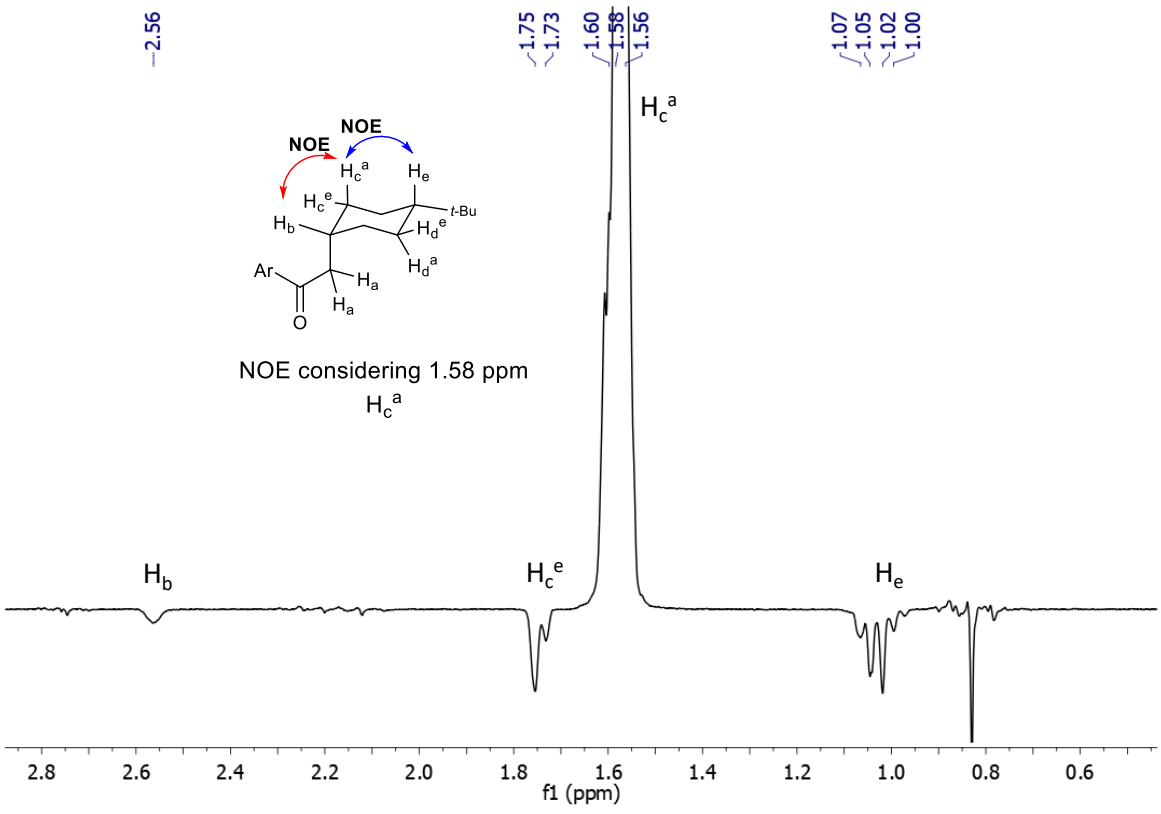
COSY in $CDCl_3$





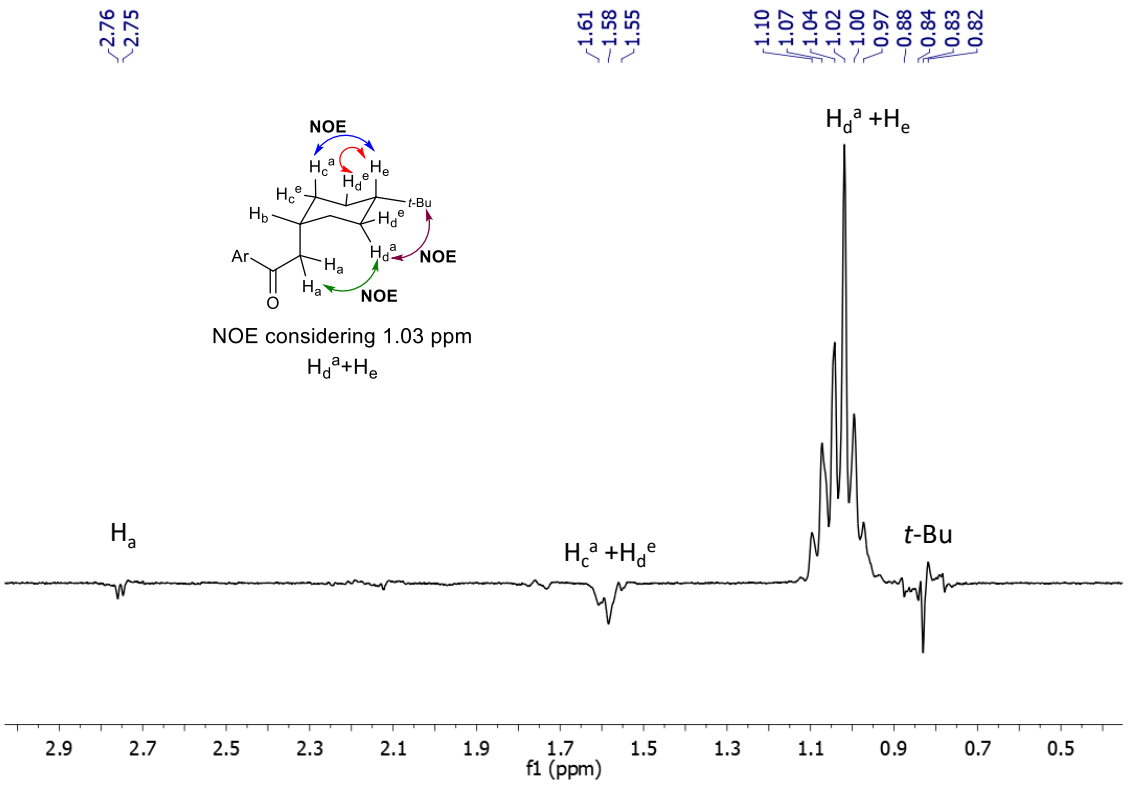
NOE considering 2.56 ppm

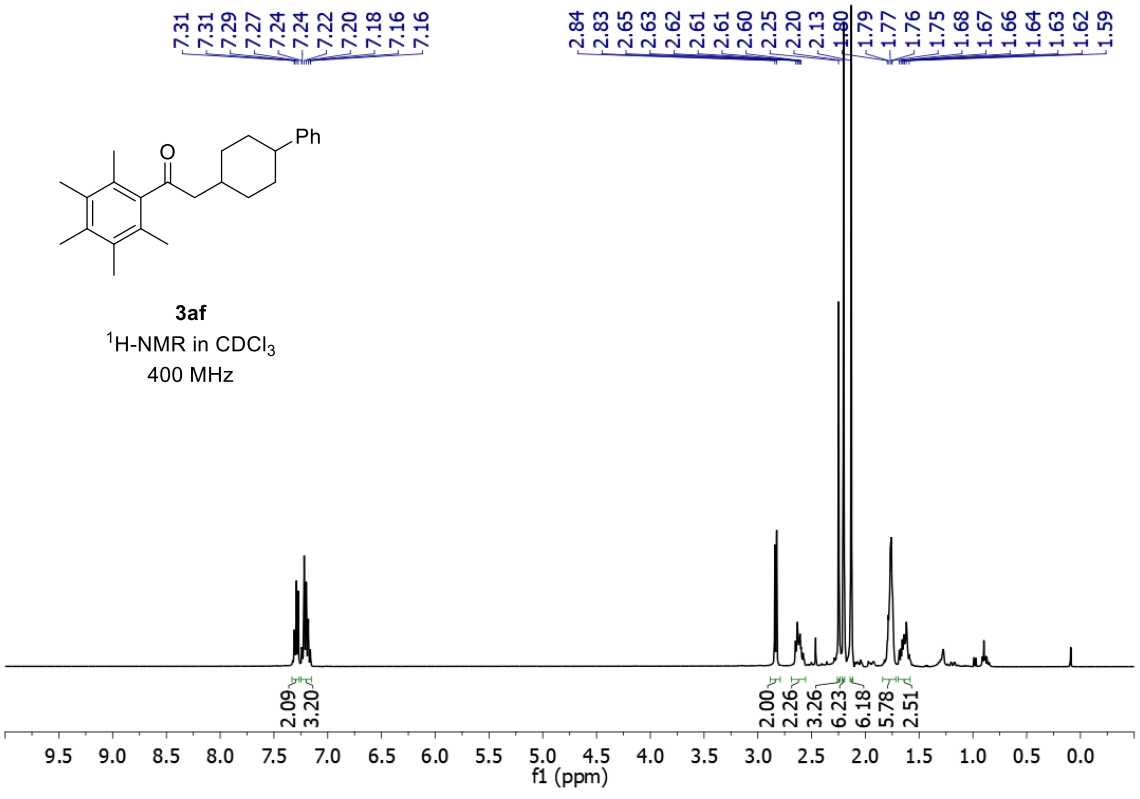
H_b

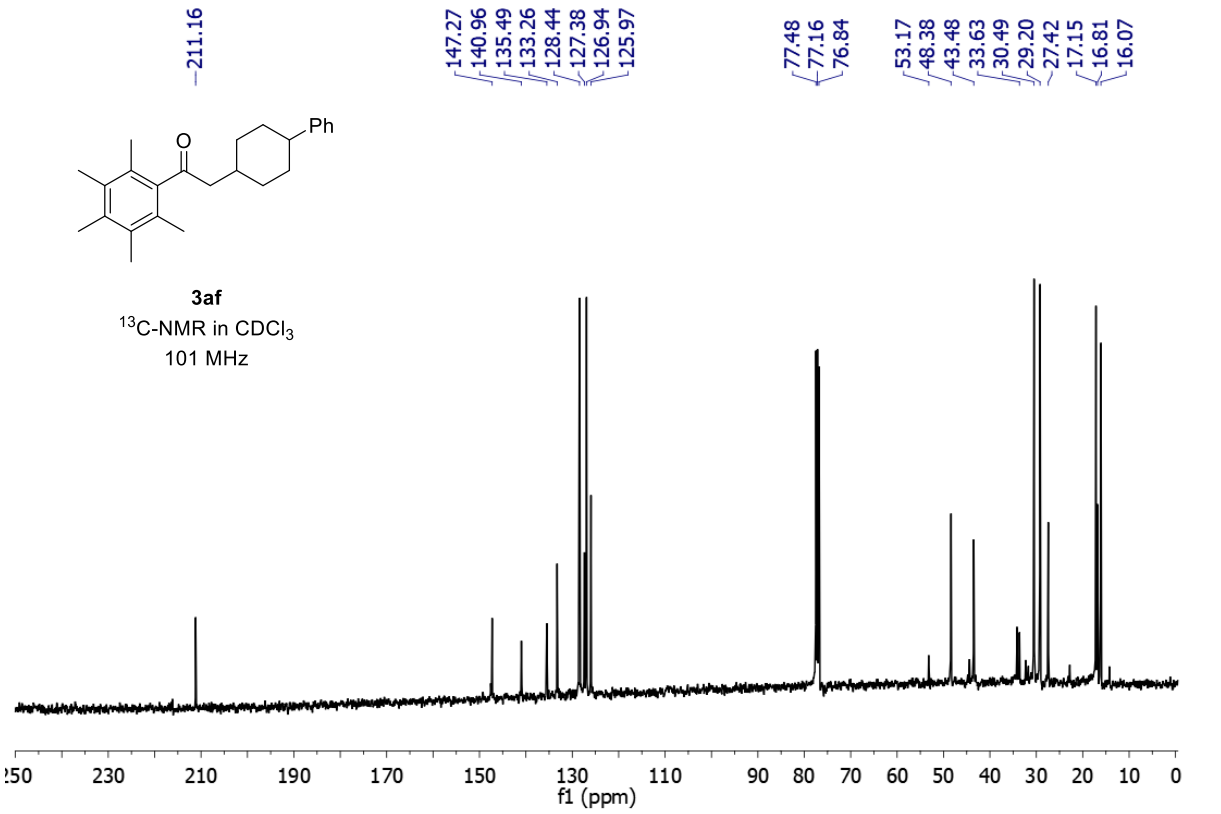


NOE considering 1.58 ppm

H_c^a


2.76
2.75
1.61
1.58
1.55
1.10
1.07
1.04
1.02
1.00
0.97
0.88
0.84
0.83
0.82
NOE
NOE
NOE
NOE considering 1.03 ppm
Hd^a+He
Hd^a +He
Ha
Hc^a +Hd^e
t-Bu
2.9
2.7
2.5
2.3
2.1
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
f1 (ppm)

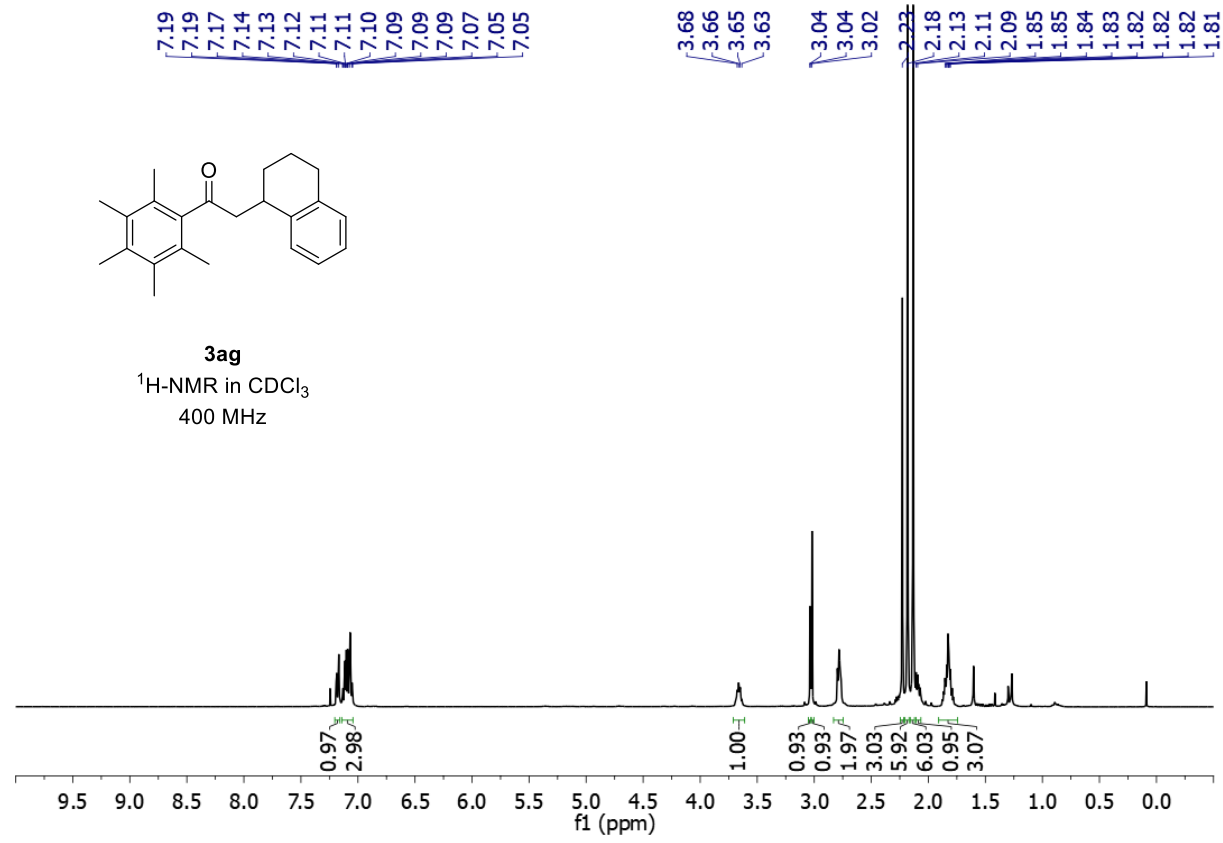

7.31
7.31
7.29
7.27
7.24
7.24
7.22
7.20
7.18
7.16
7.16
2.84
2.83
2.65
2.63
2.62
2.61
2.61
2.60
2.25
2.20
2.13
1.80
1.79
1.77
1.76
1.75
1.68
1.67
1.66
1.64
1.63
1.62
1.59
Ph
O
3af
1H-NMR in CDCl3
400 MHz
2.09
3.20
2.00
2.26
3.26
6.23
6.18
5.78
2.51
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



3af

^{13}C-NMR in $CDCl_3$

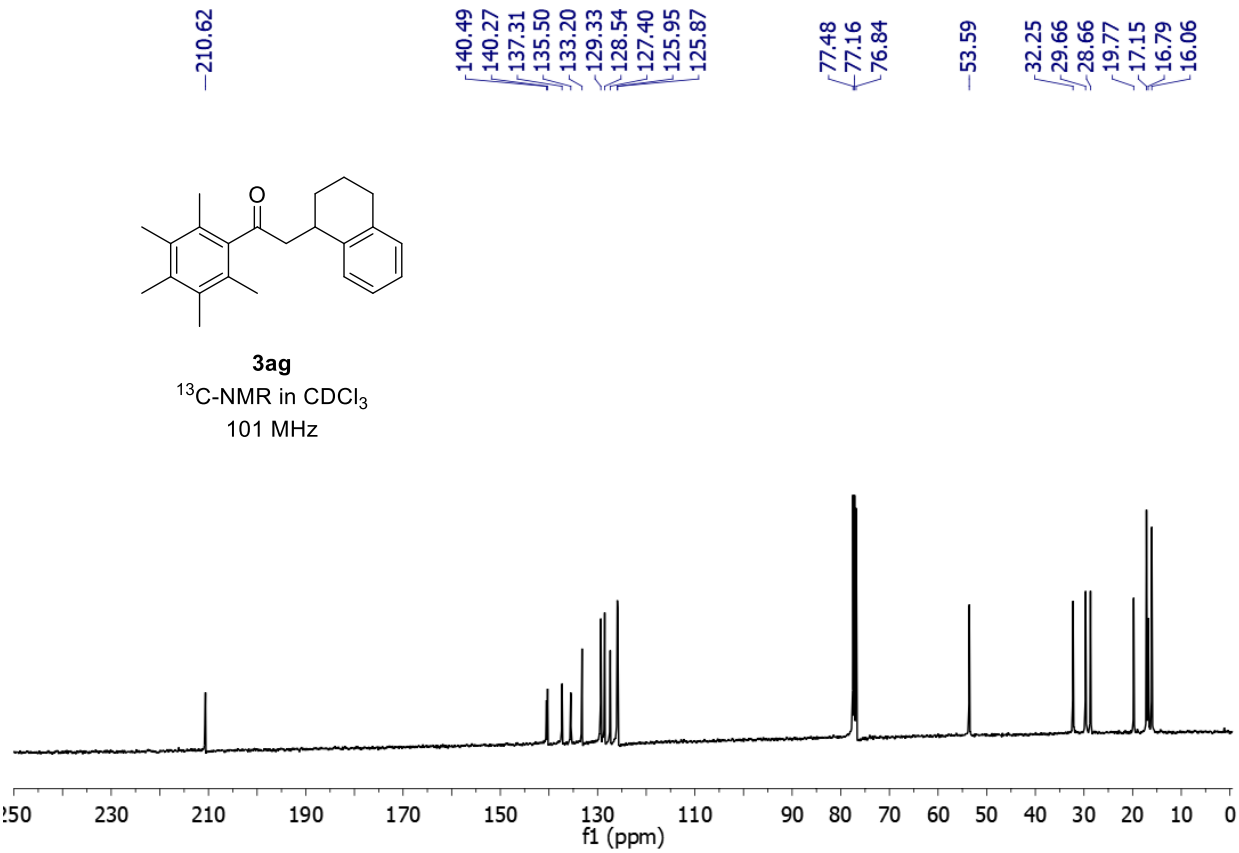
101 MHz



3ag

^{1}H-NMR in $CDCl_3$

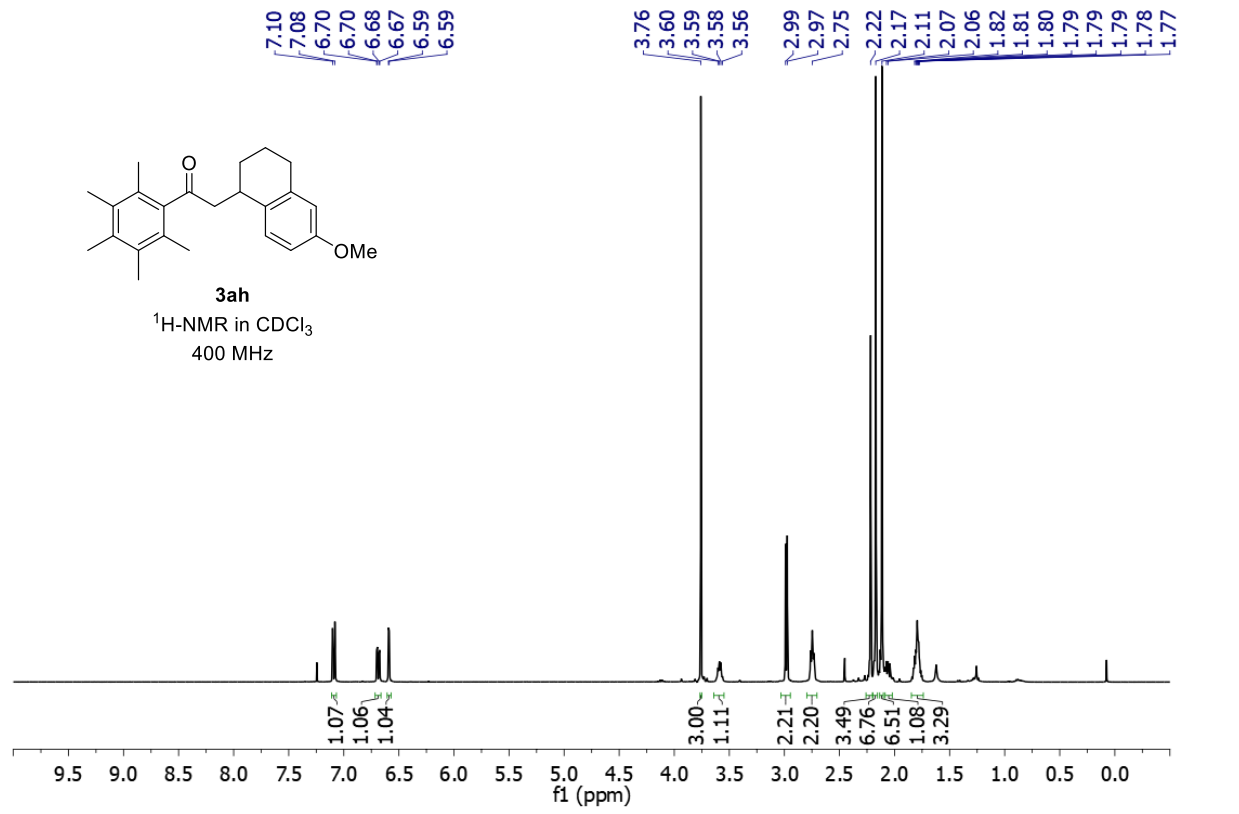
400 MHz



3ag

^{13}C-NMR in $CDCl_3$

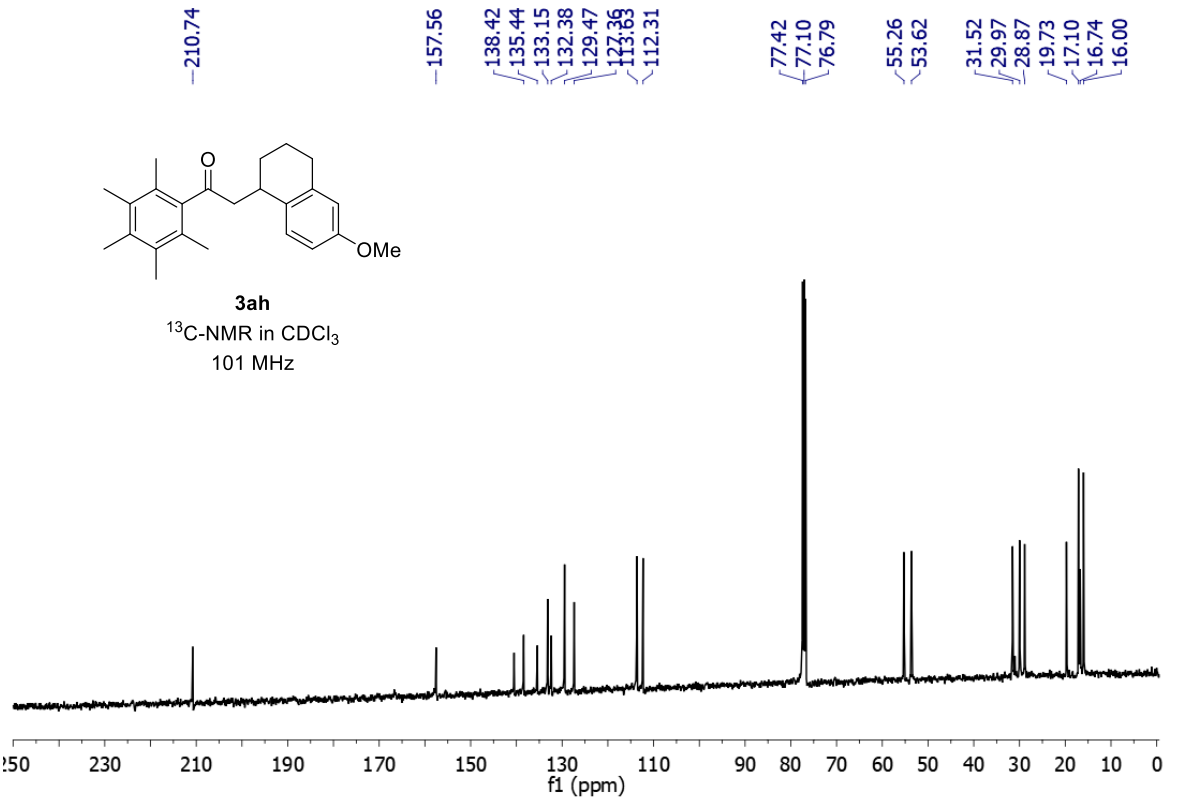
101 MHz



3ah

^{1}H-NMR in $CDCl_3$

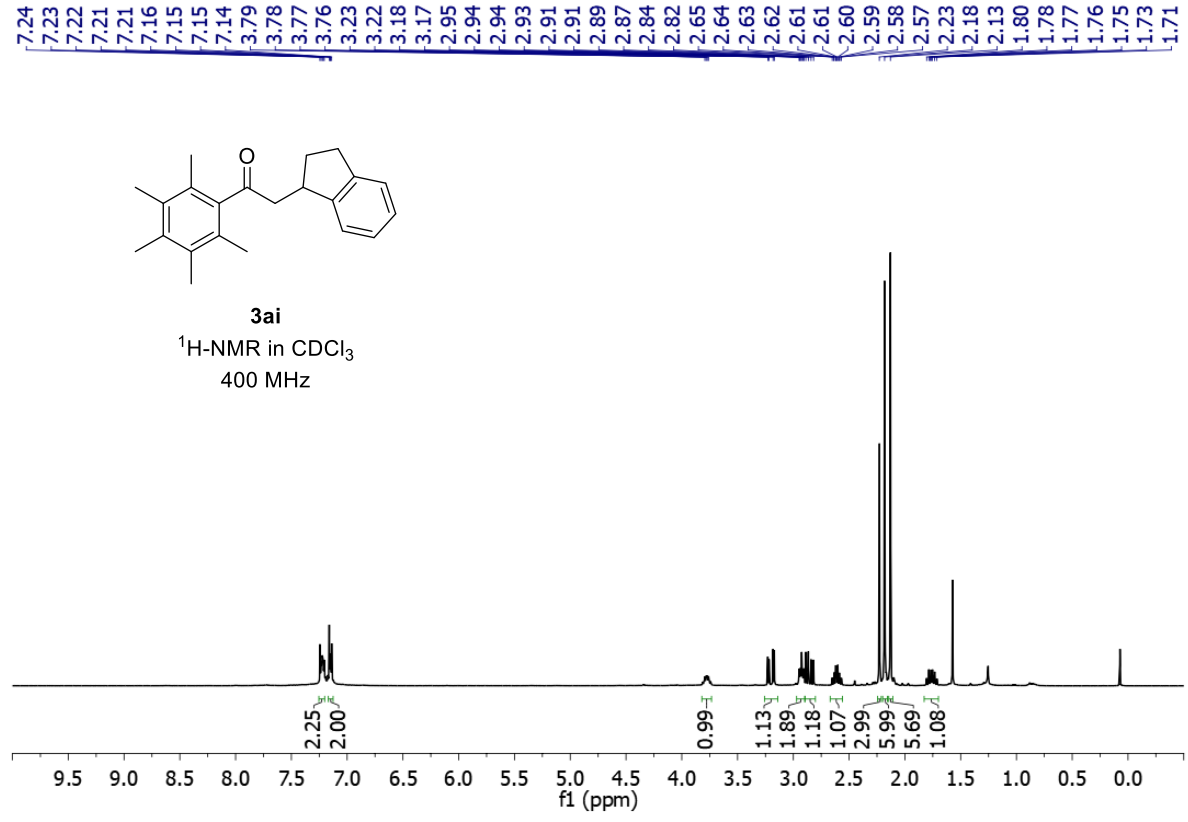
400 MHz



3ah

^{13}C-NMR in $CDCl_3$

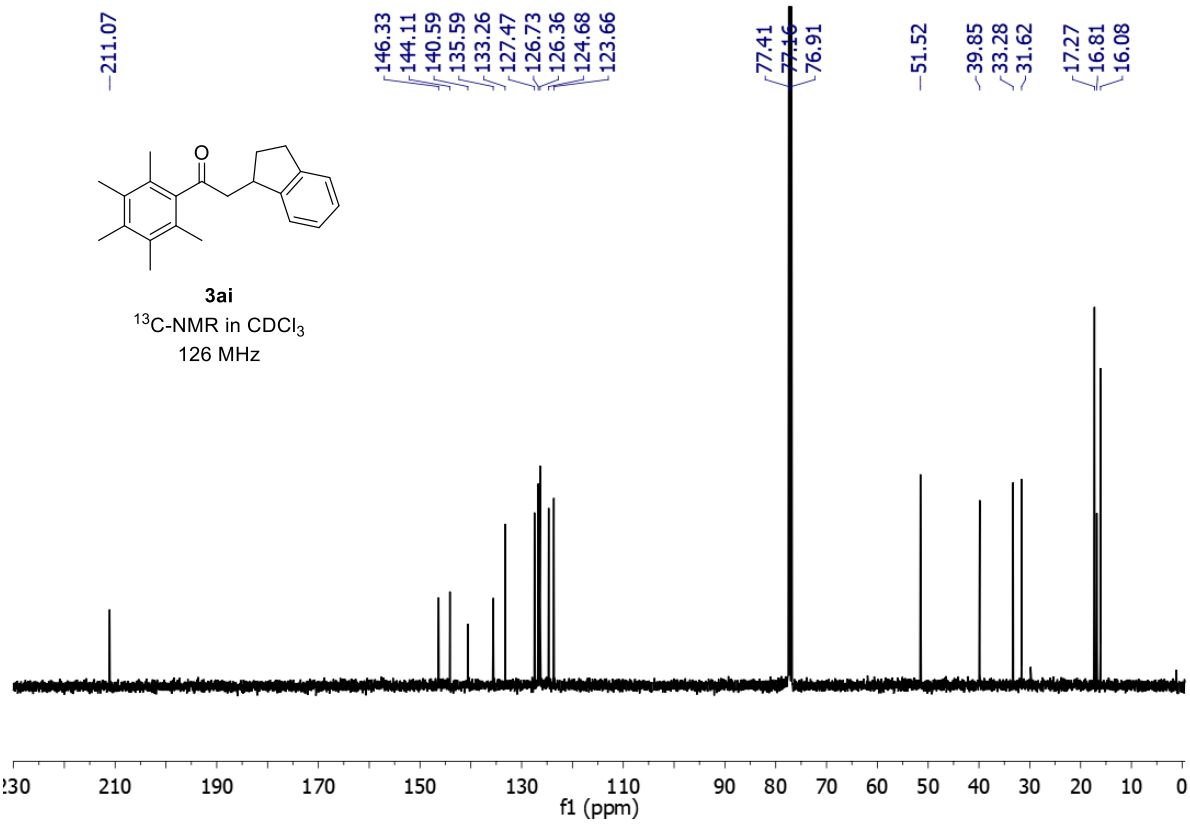
101 MHz

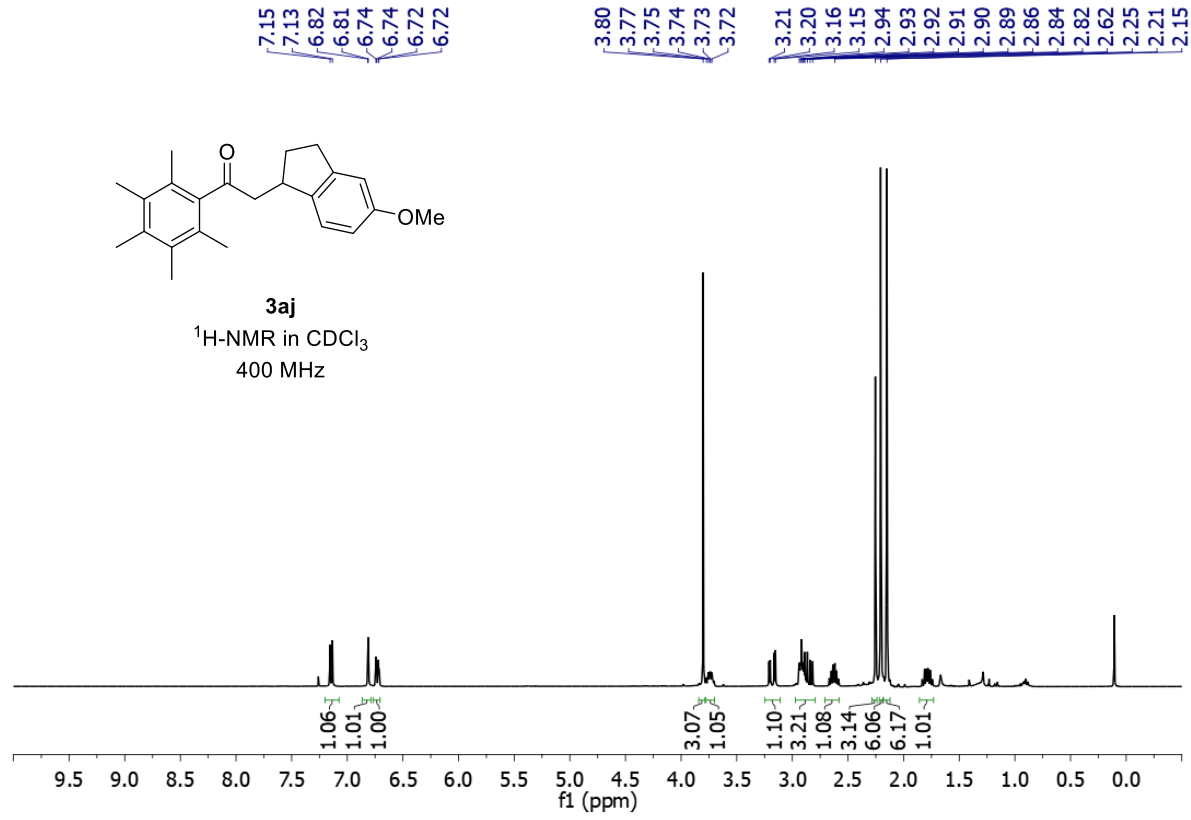


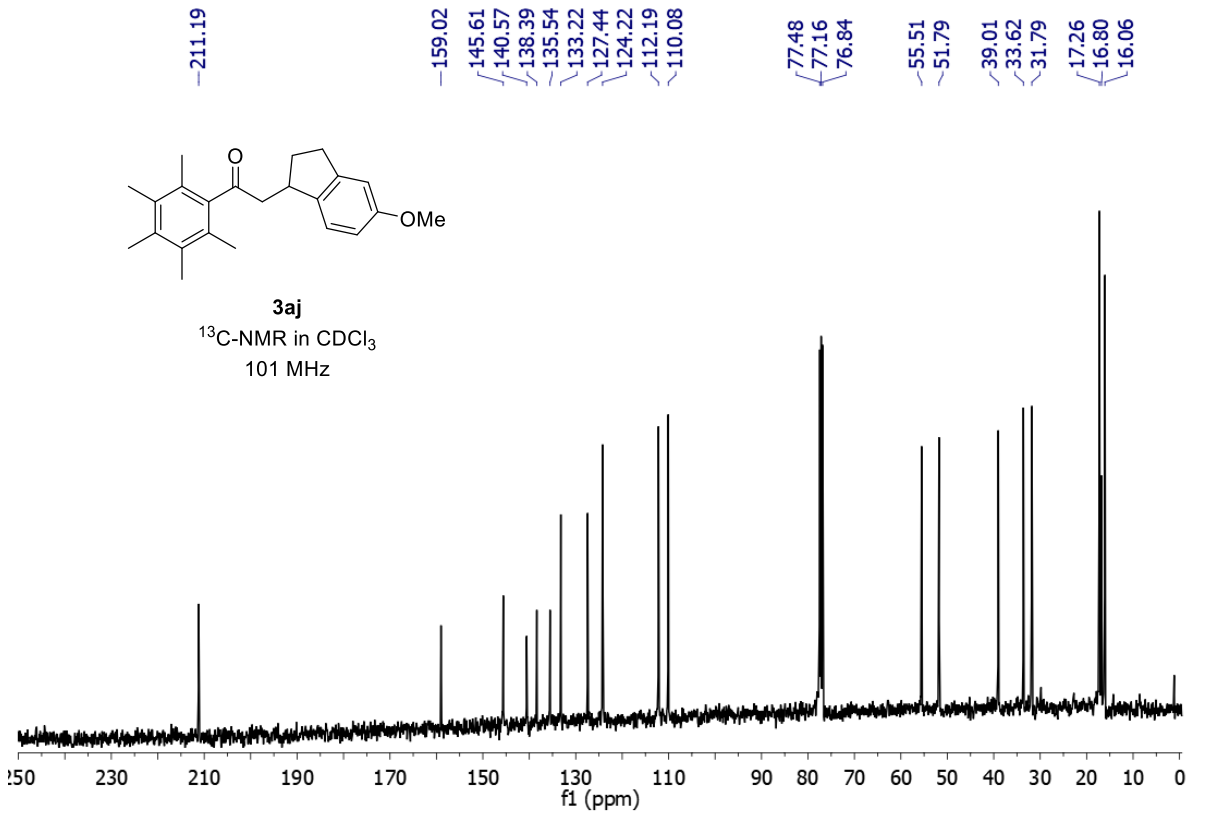
3ai

^{1}H-NMR in $CDCl_3$

400 MHz


211.07
146.33
144.11
140.59
135.59
133.26
127.47
126.73
126.36
124.68
123.66
77.41
77.16
76.91
51.52
39.85
33.28
31.62
17.27
16.81
16.08
O
3ai
13C-NMR in CDCl3
126 MHz
f1 (ppm)

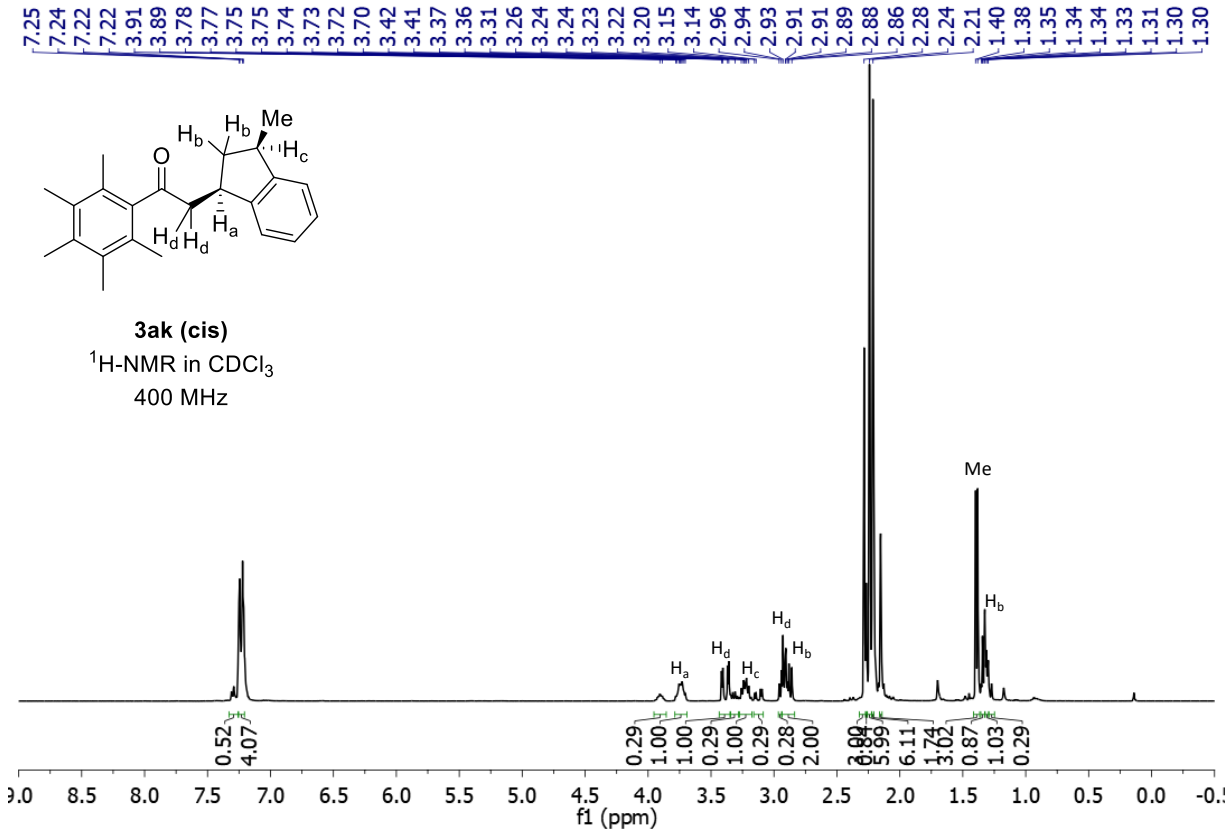

7.15
7.13
6.82
6.81
6.74
6.74
6.72
6.72
3.80
3.77
3.75
3.74
3.73
3.72
3.21
3.20
3.16
3.15
2.94
2.93
2.92
2.91
2.90
2.89
2.86
2.84
2.82
2.62
2.25
2.21
2.15
O
OMe
3aj
1H-NMR in CDCl3
400 MHz
1.06
1.01
1.00
3.07
1.05
1.10
3.21
1.08
3.14
6.06
6.17
1.01
f1 (ppm)



3aj

^{13}C-NMR in $CDCl_3$

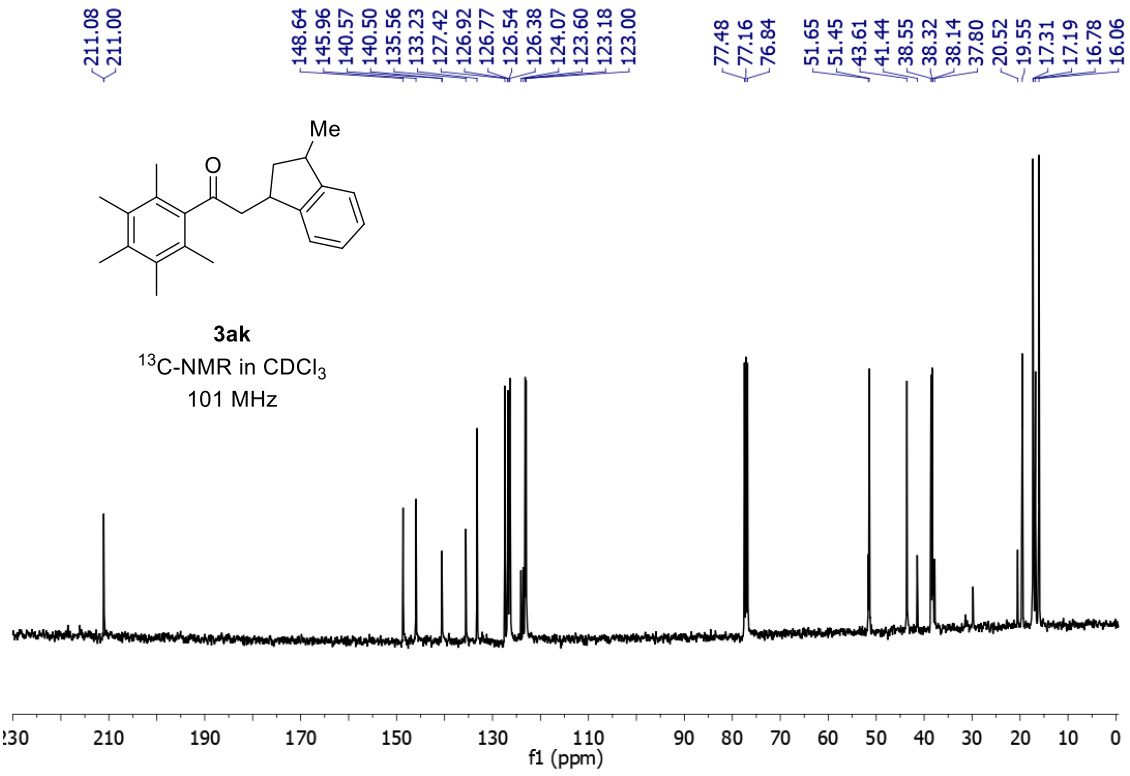
101 MHz



3ak (cis)

^{1}H-NMR in $CDCl_3$

400 MHz


211.08
211.00
148.64
145.96
140.57
140.50
135.56
133.23
127.42
126.92
126.77
126.54
126.38
124.07
123.60
123.18
123.00
77.48
77.16
76.84
51.65
51.45
43.61
41.44
38.55
38.32
38.14
37.80
20.52
19.55
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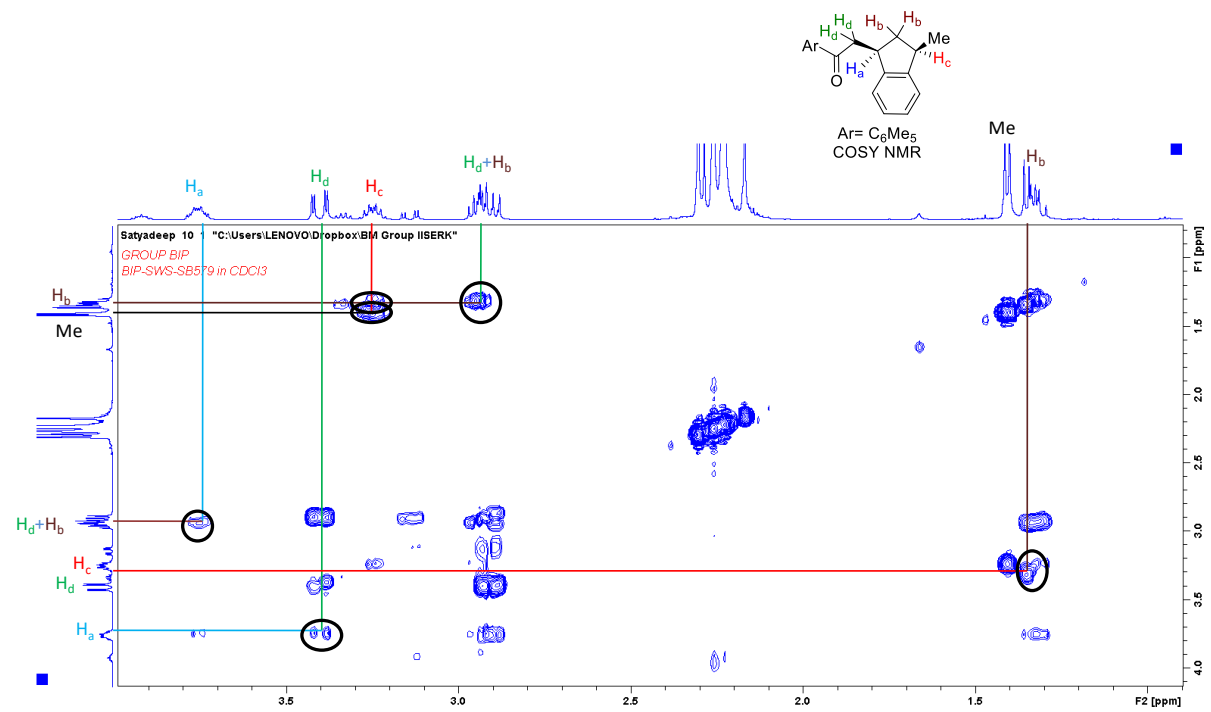
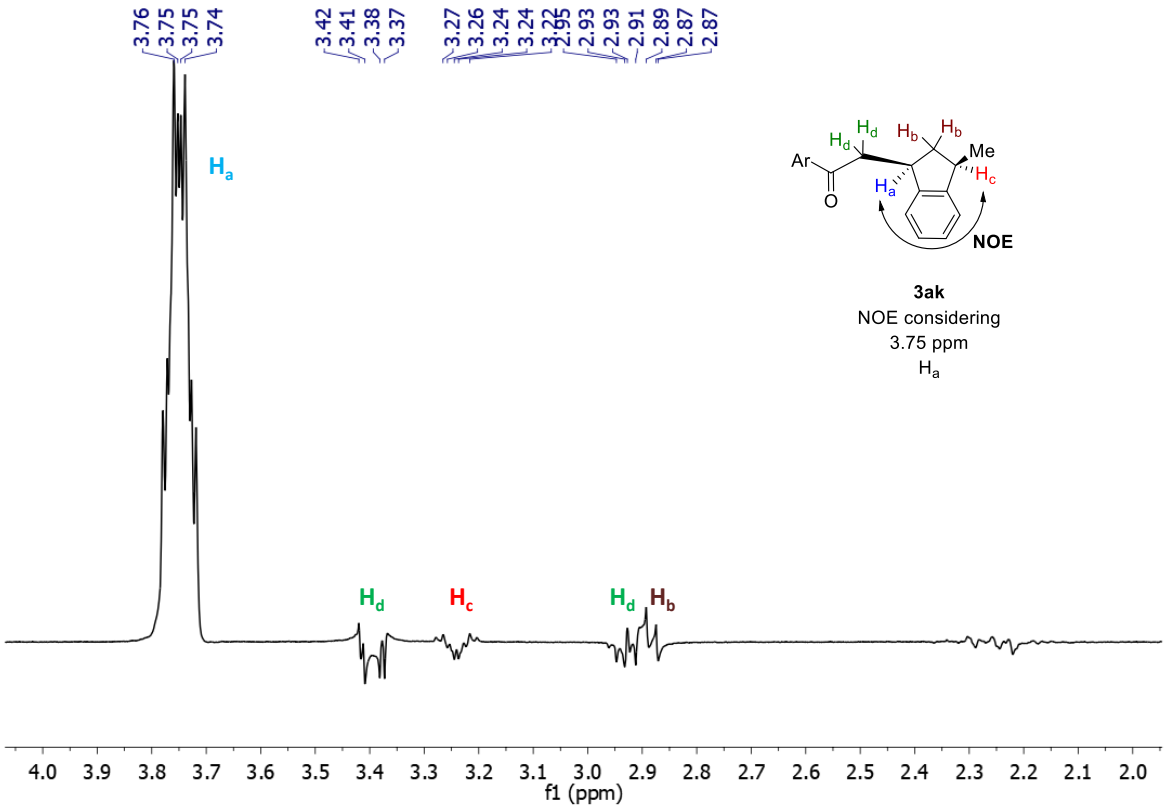
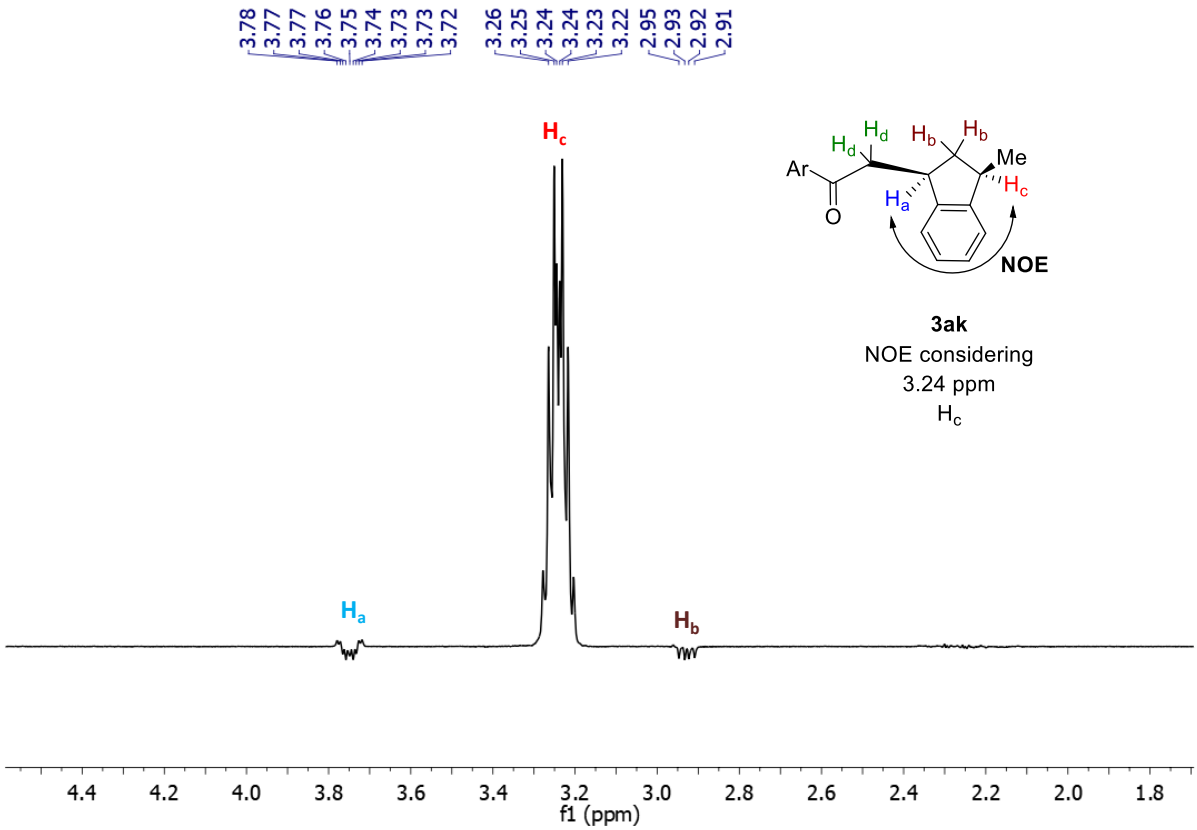
17.19
16.78
16.06
Me
O
3ak
13C-NMR in CDCl3
101 MHz
f1 (ppm)

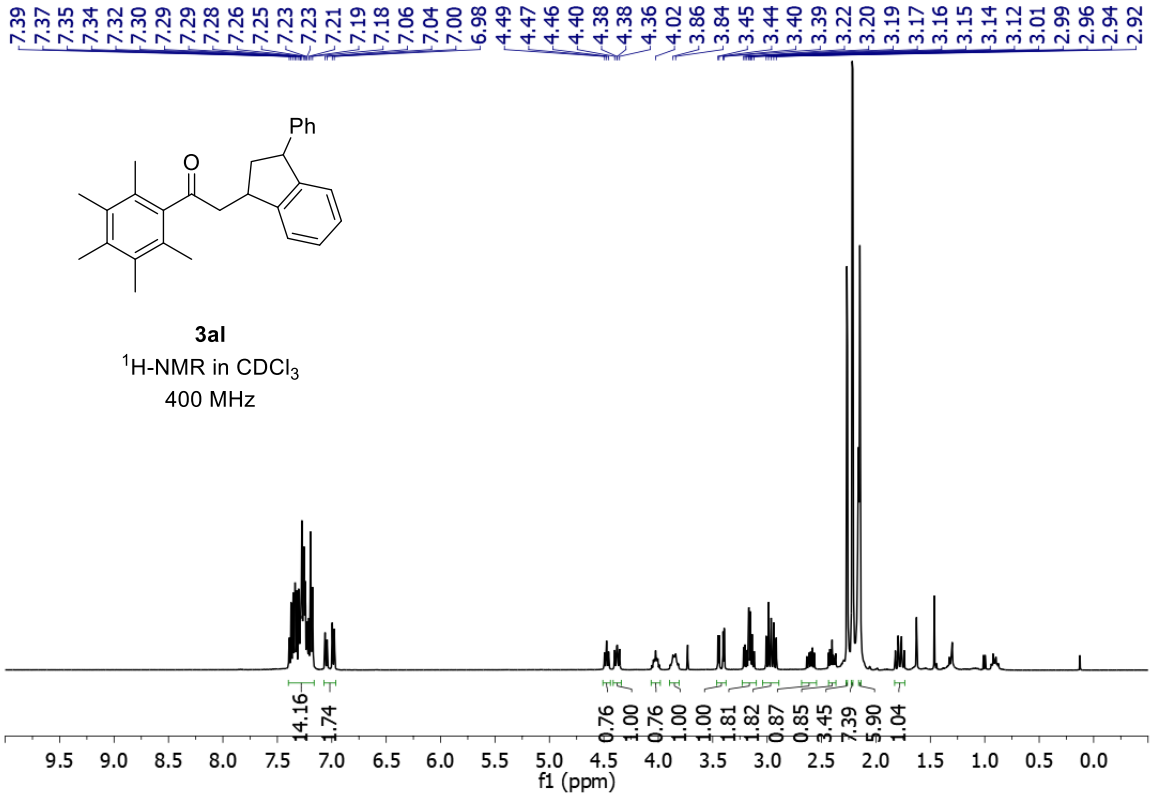

Ar= C6Me5
COSY NMR
Satyadeep 10 "C:\Users\LENOVO\Dropbox\BM Group IISERK"
GROUP BIP
BIP-SWS-SB579 in CDCl3
F2 [ppm]
F1 [ppm]



3ak
NOE considering
3.75 ppm
H_a



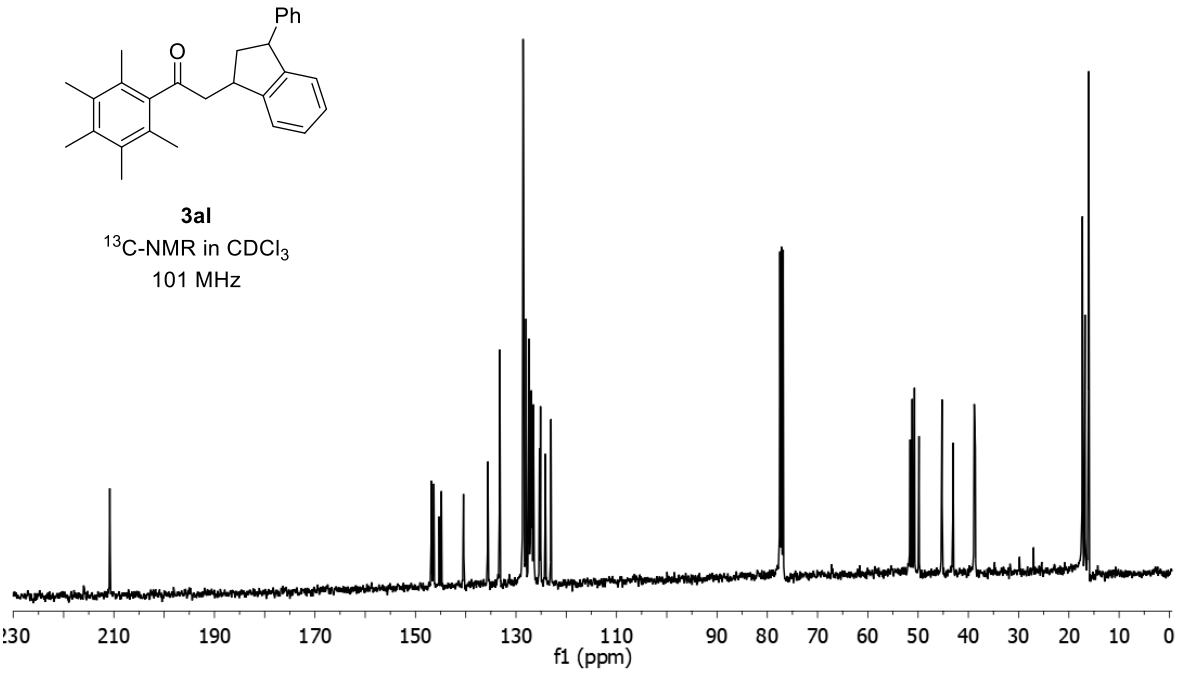
3ak
NOE considering
3.24 ppm
H_c



3al

^{1}H-NMR in $CDCl_3$

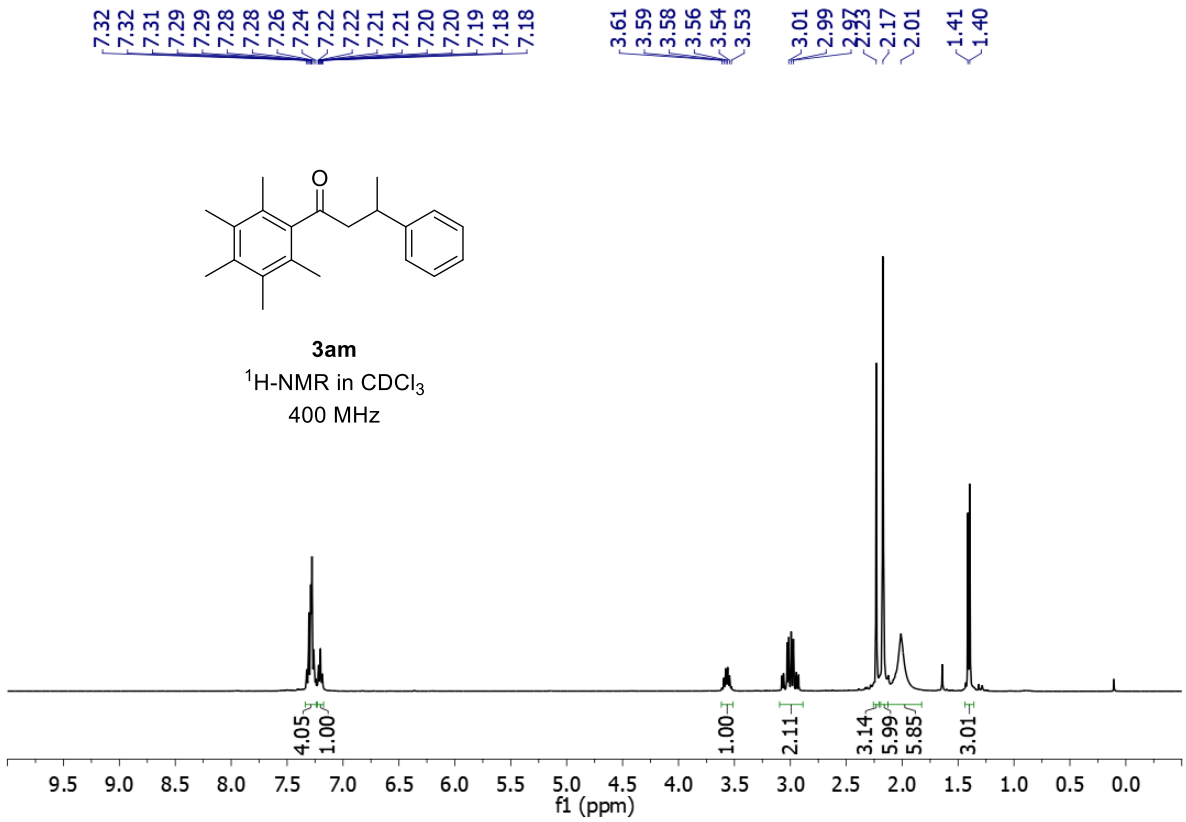
400 MHz

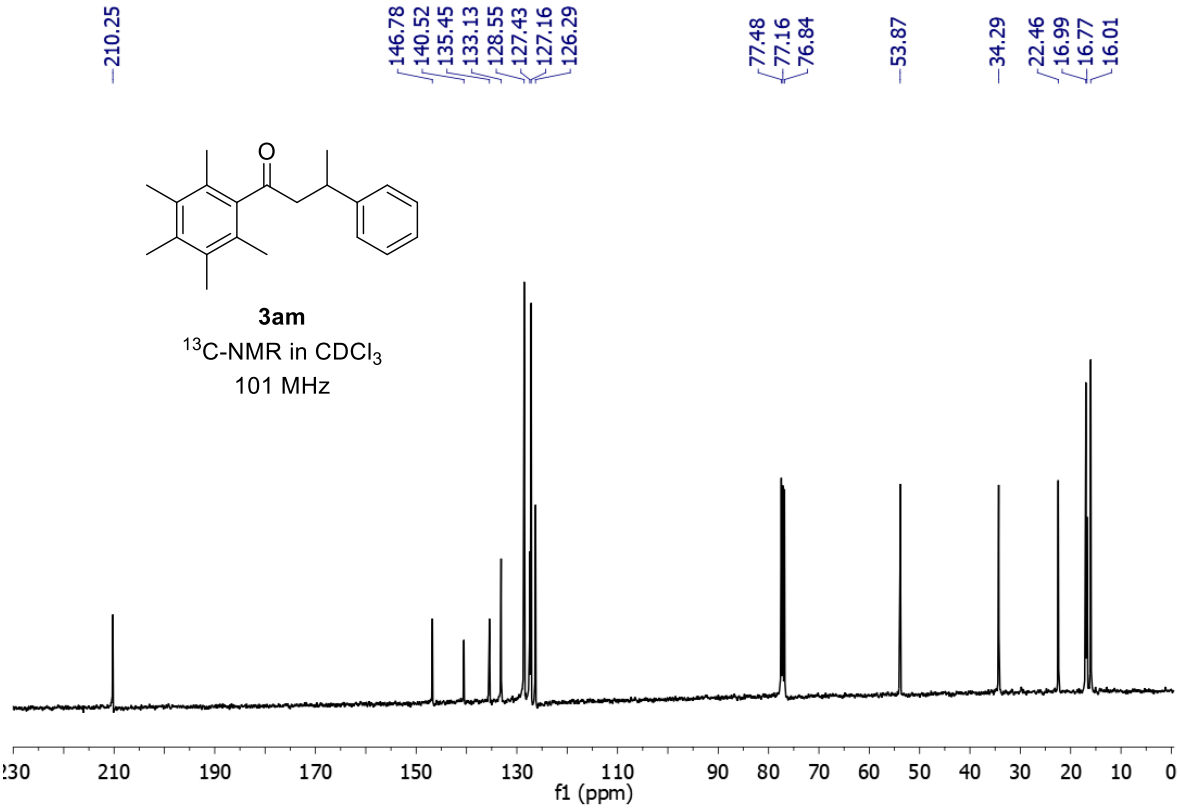


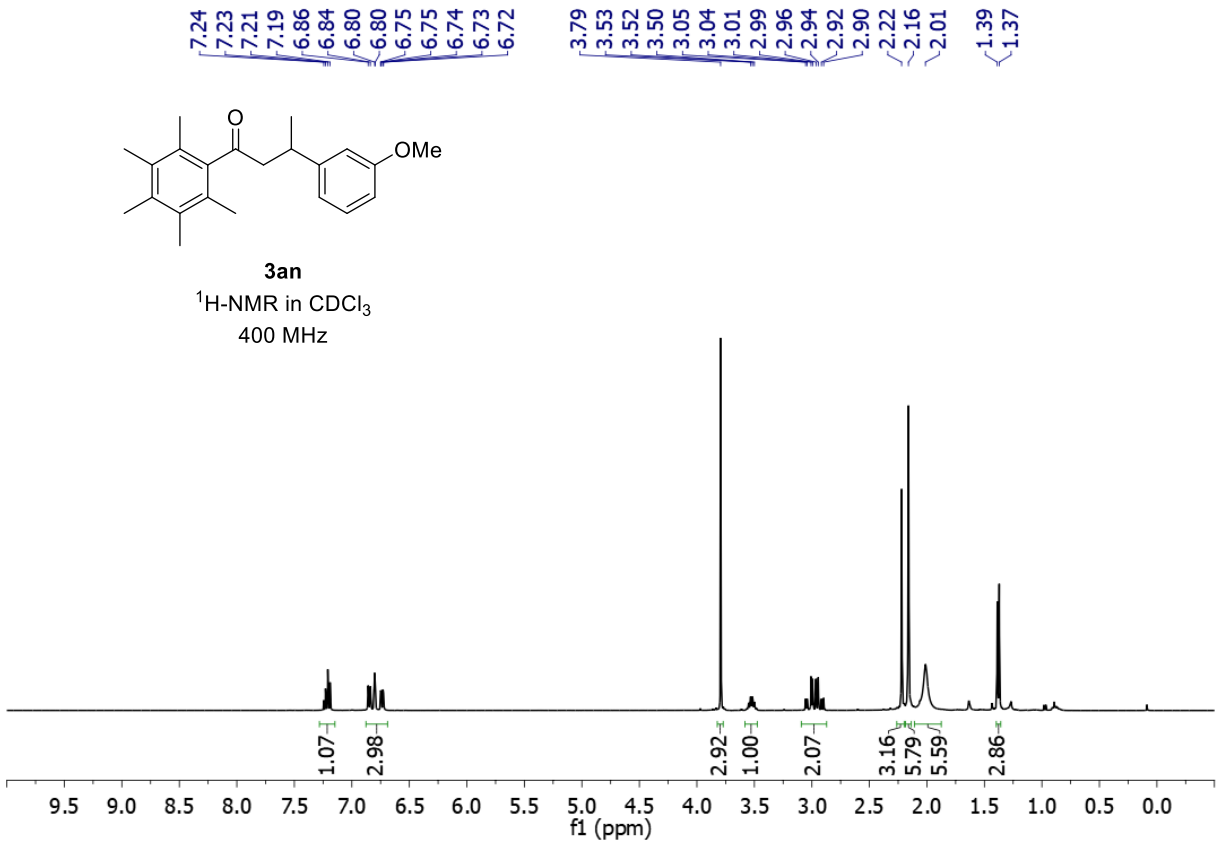
3al

^{13}C-NMR in $CDCl_3$

101 MHz


7.32
7.32
7.31
7.29
7.29
7.28
7.28
7.26
7.24
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.18
7.18
3.61
3.59
3.58
3.56
3.54
3.53
3.01
2.99
2.97
2.93
2.17
2.01
1.41
1.40
O
3am
1H-NMR in CDCl3
400 MHz
4.05
1.00
1.00
2.11
3.14
5.99
5.85
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

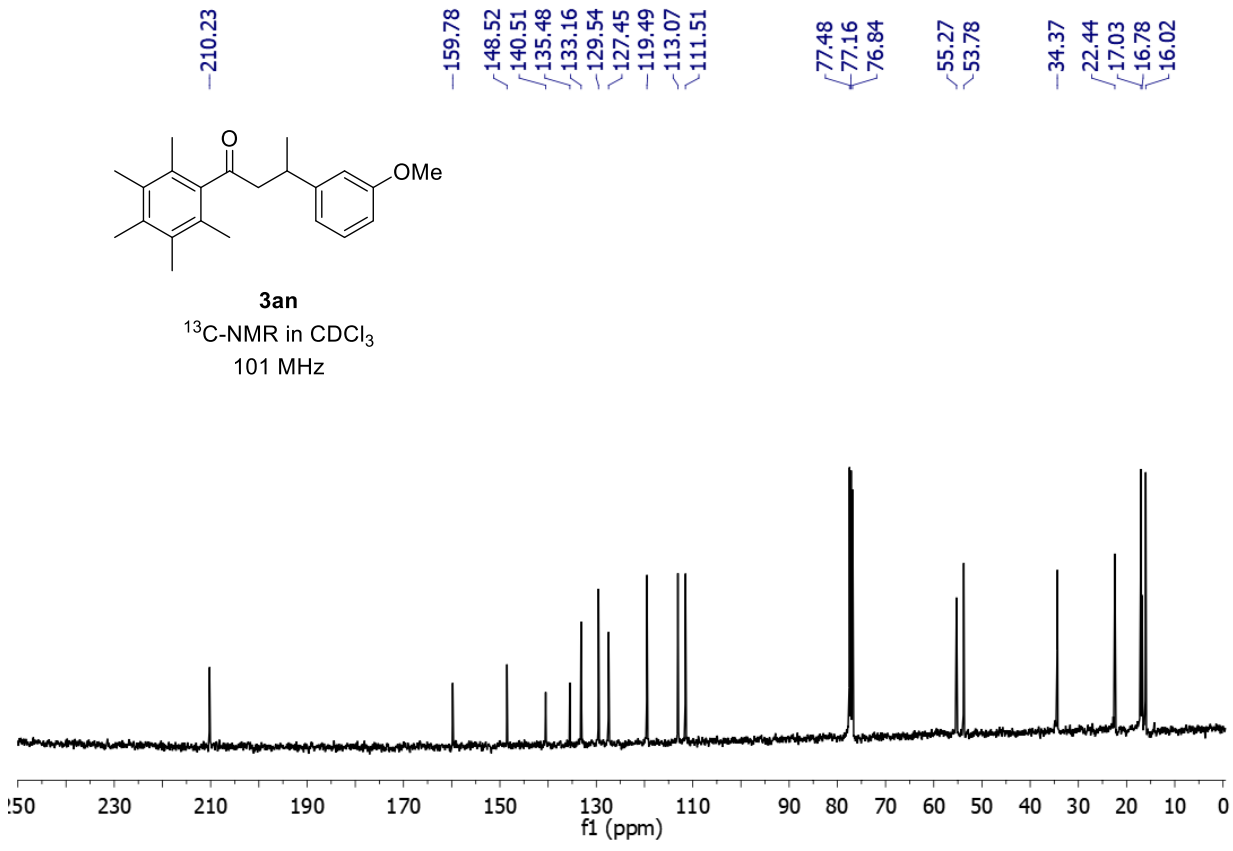

210.25
146.78
140.52
135.45
133.13
128.55
127.43
127.16
126.29
77.48
77.16
76.84
53.87
34.29
22.46
16.99
16.77
16.01
O
3am
13C-NMR in CDCl3
101 MHz
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3an

^{1}H-NMR in $CDCl_3$

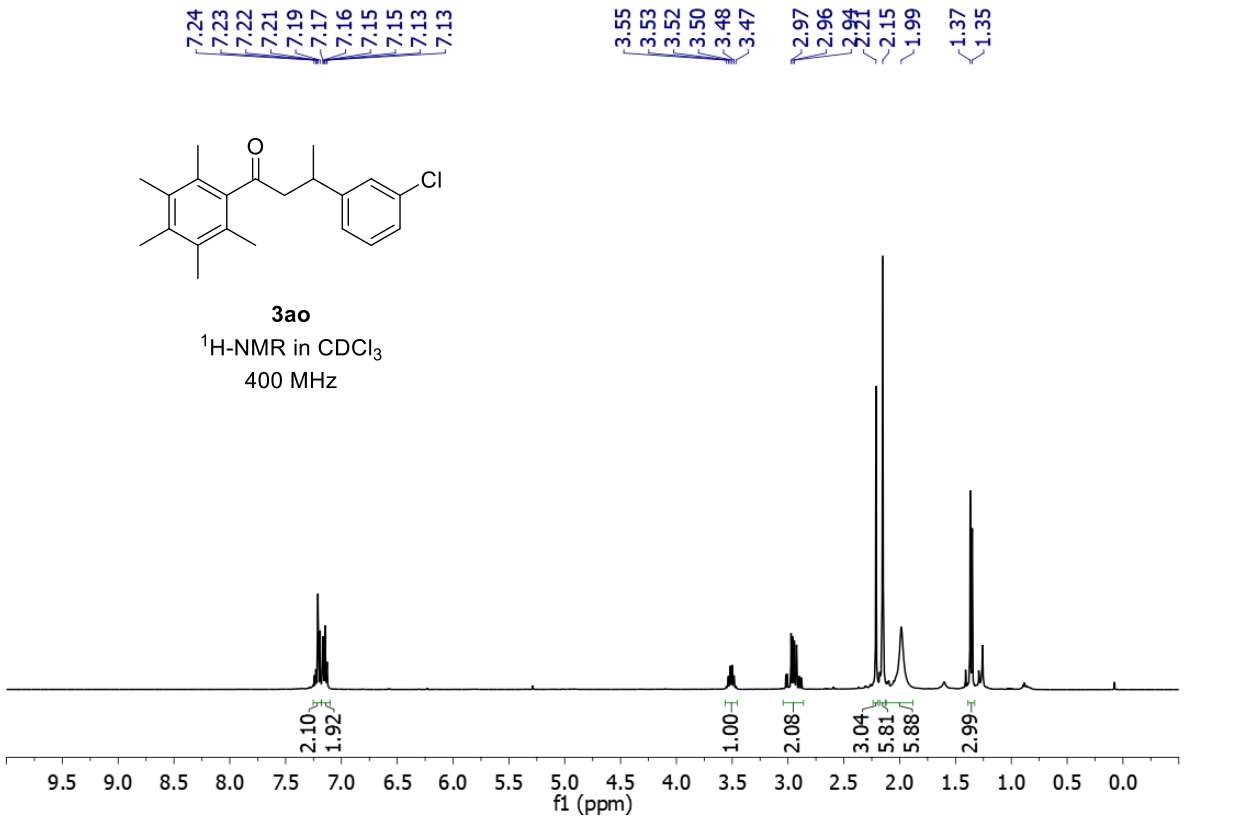
400 MHz



3an

^{13}C-NMR in $CDCl_3$

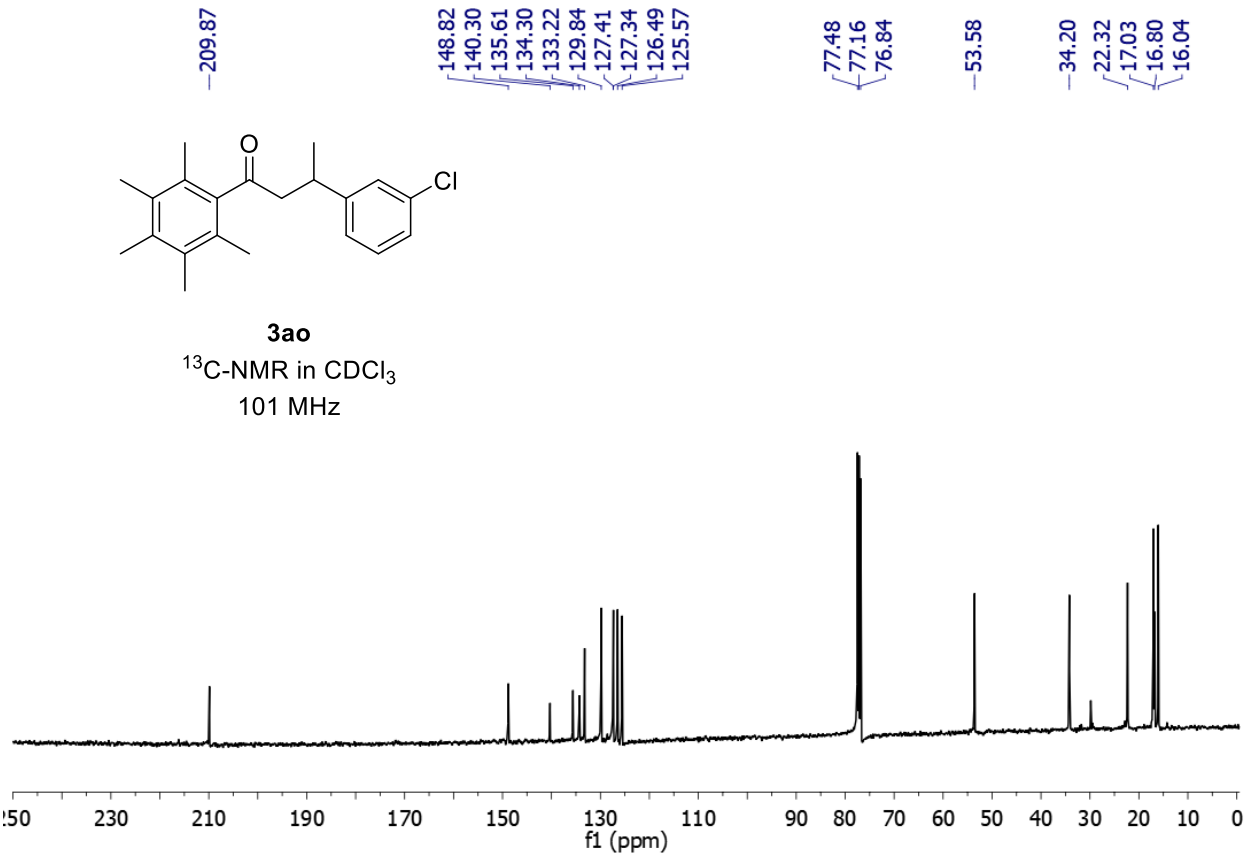
101 MHz



3ao

^{1}H-NMR in $CDCl_3$

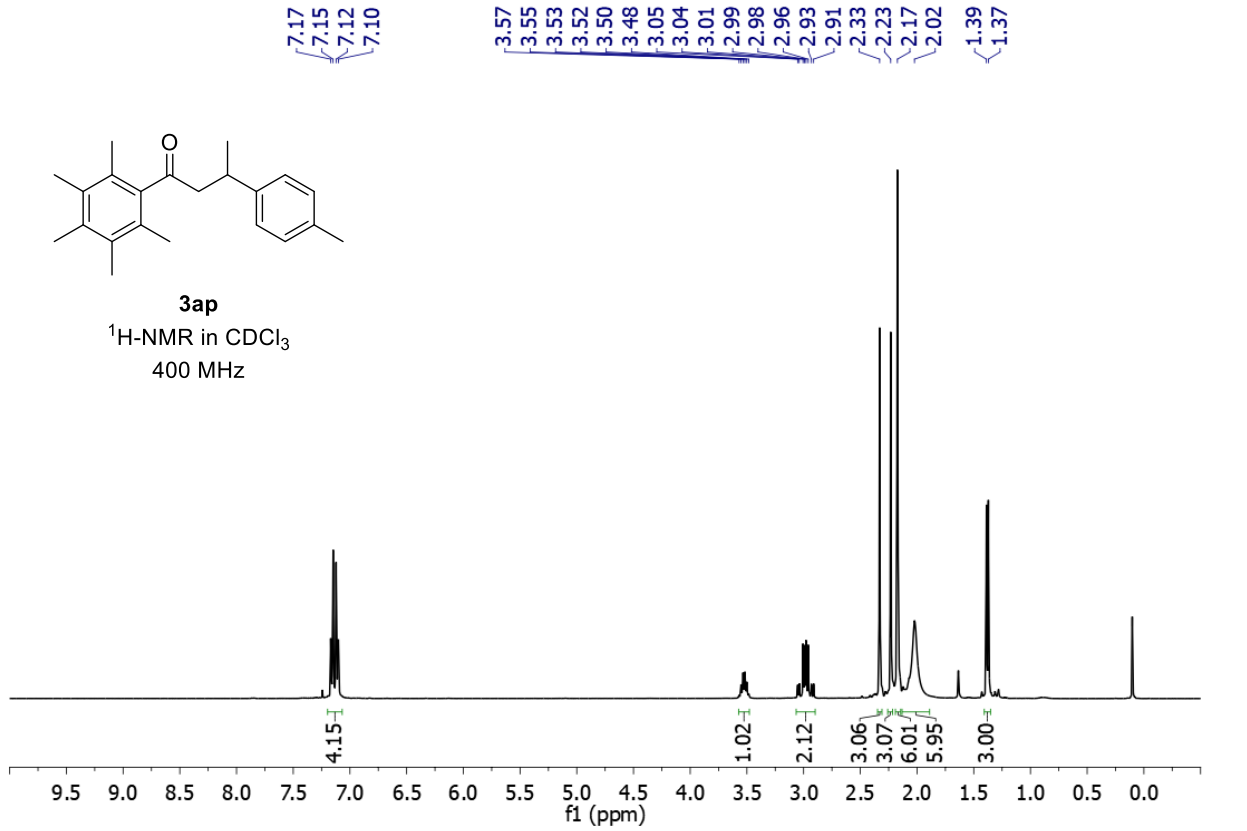
400 MHz

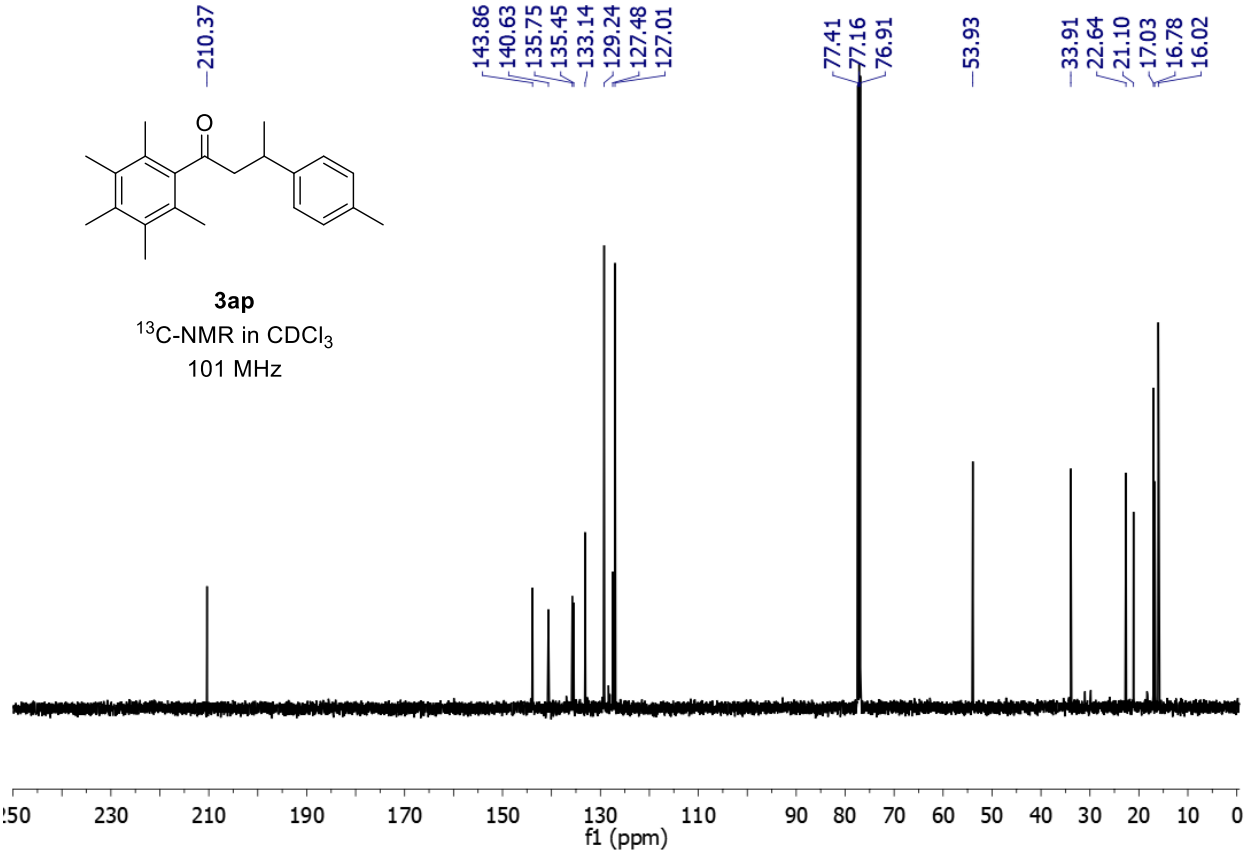


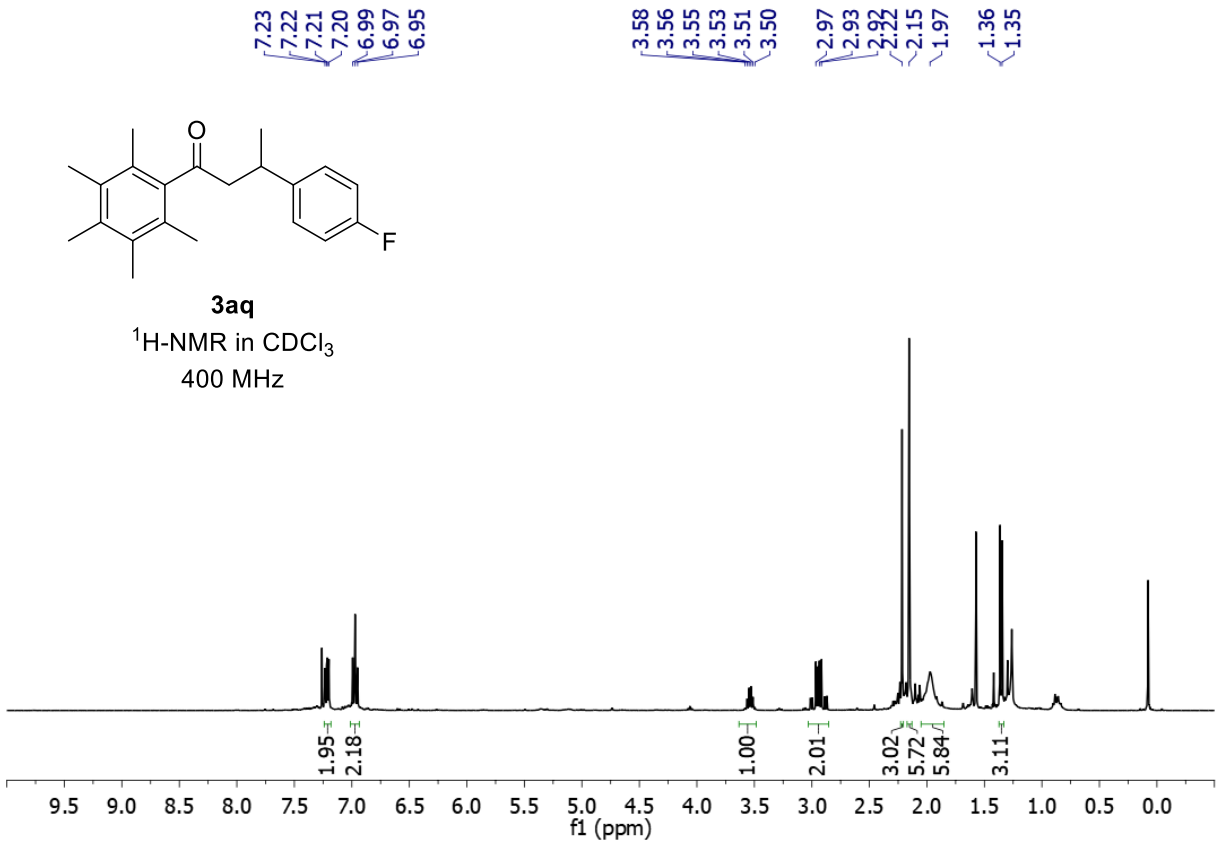
3ao

^{13}C-NMR in $CDCl_3$

101 MHz


7.17
7.15
7.12
7.10
3.57
3.55
3.53
3.52
3.50
3.48
3.05
3.04
3.01
2.99
2.98
2.96
2.93
2.91
2.33
2.23
2.17
2.02
1.39
1.37
O
3ap
1H-NMR in CDCl3
400 MHz
4.15
1.02
2.12
3.06
3.07
6.01
5.95
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

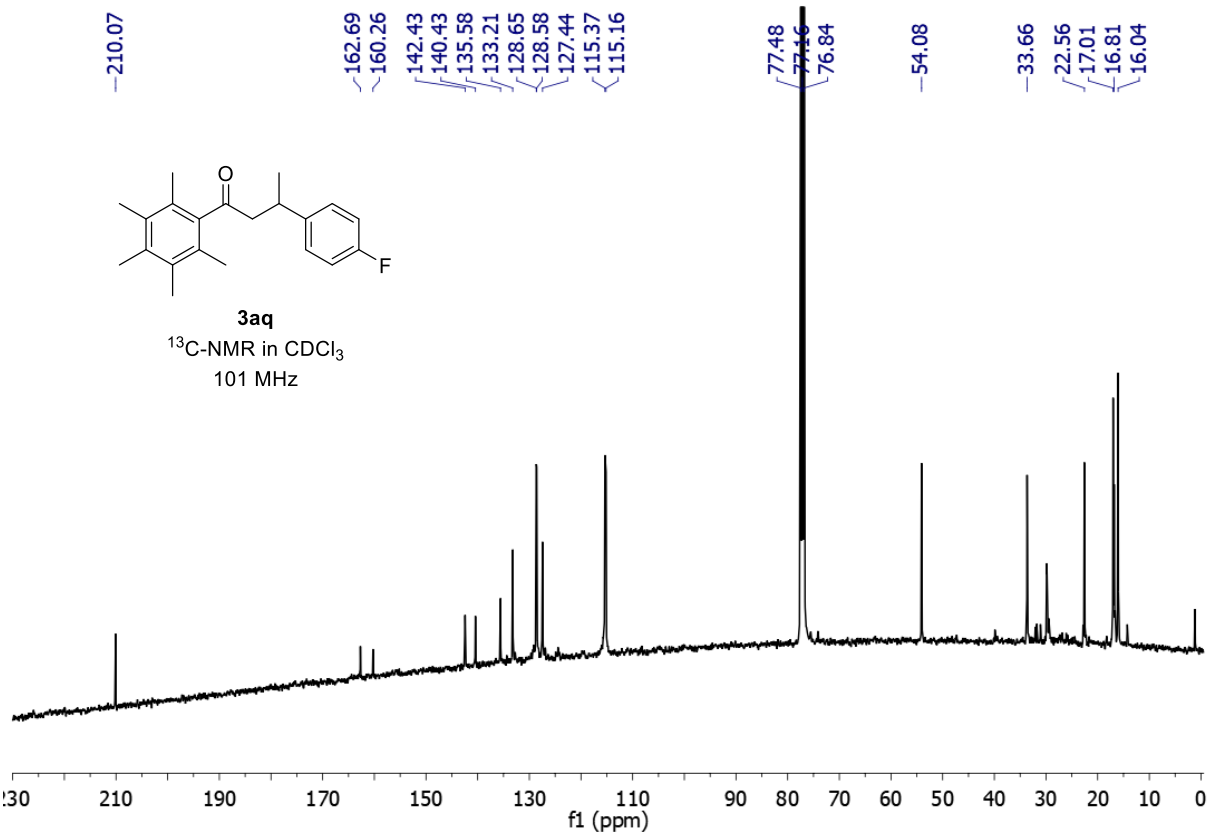

210.37
143.86
140.63
135.75
135.45
133.14
129.24
127.48
127.01
77.41
77.16
76.91
53.93
33.91
22.64
21.10
17.03
16.78
16.02
O
3ap
13C-NMR in CDCl3
101 MHz
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3aq

^{1}H-NMR in $CDCl_3$

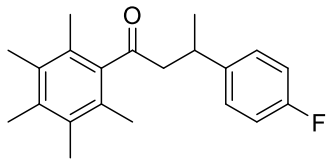
400 MHz



3aq

^{13}C-NMR in $CDCl_3$

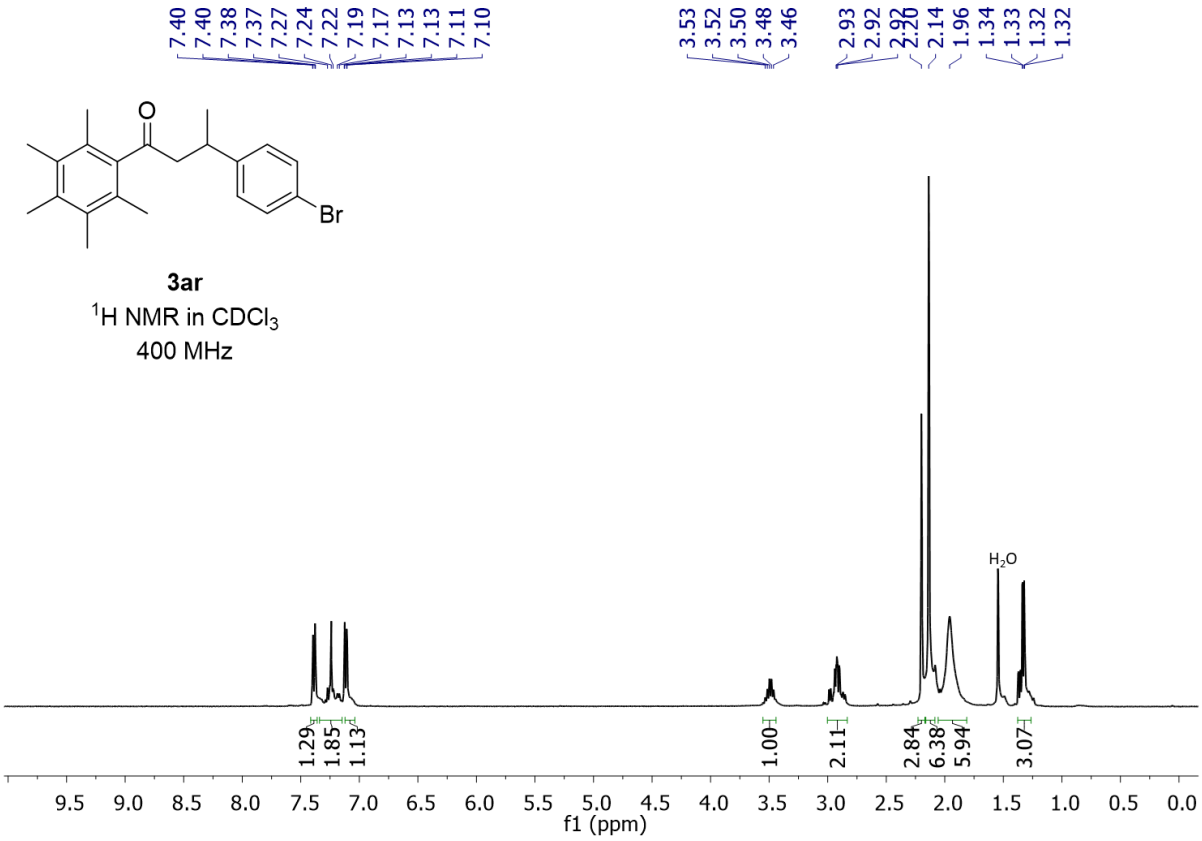
101 MHz

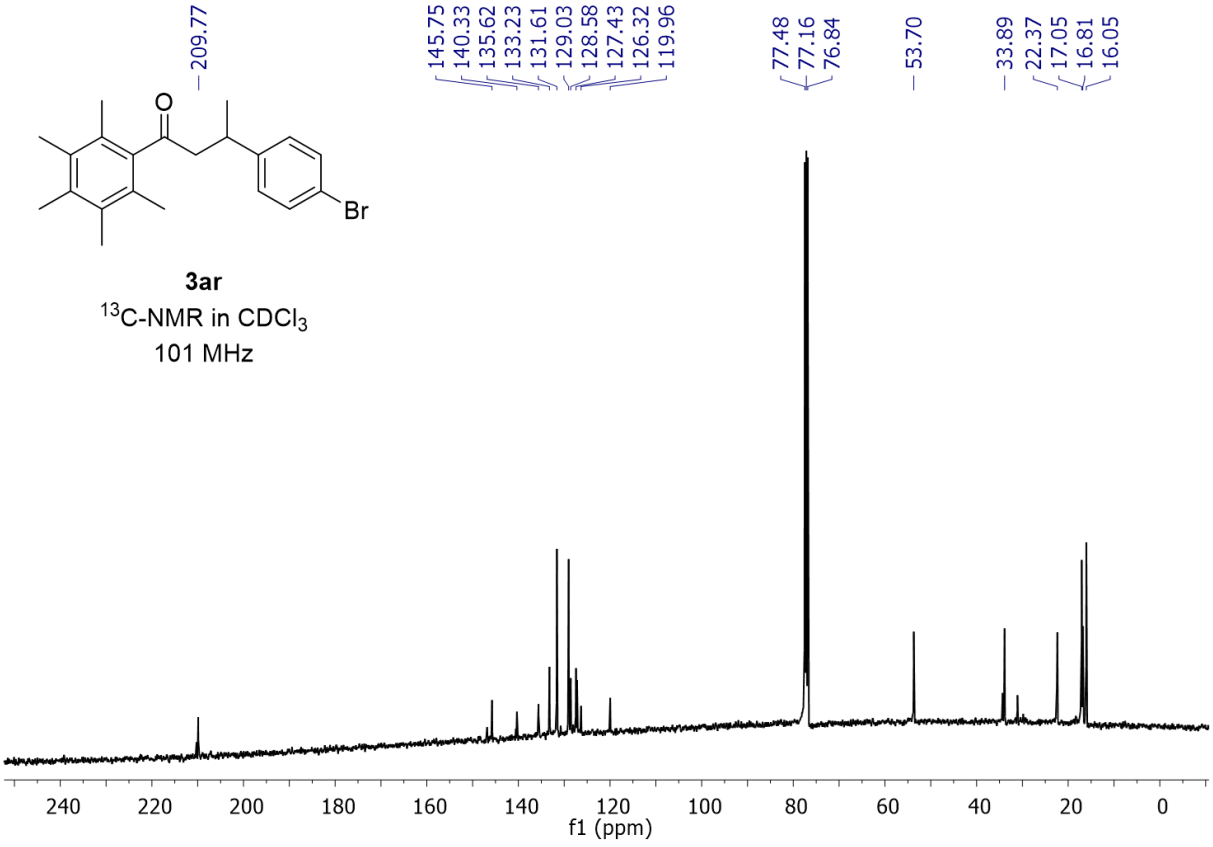


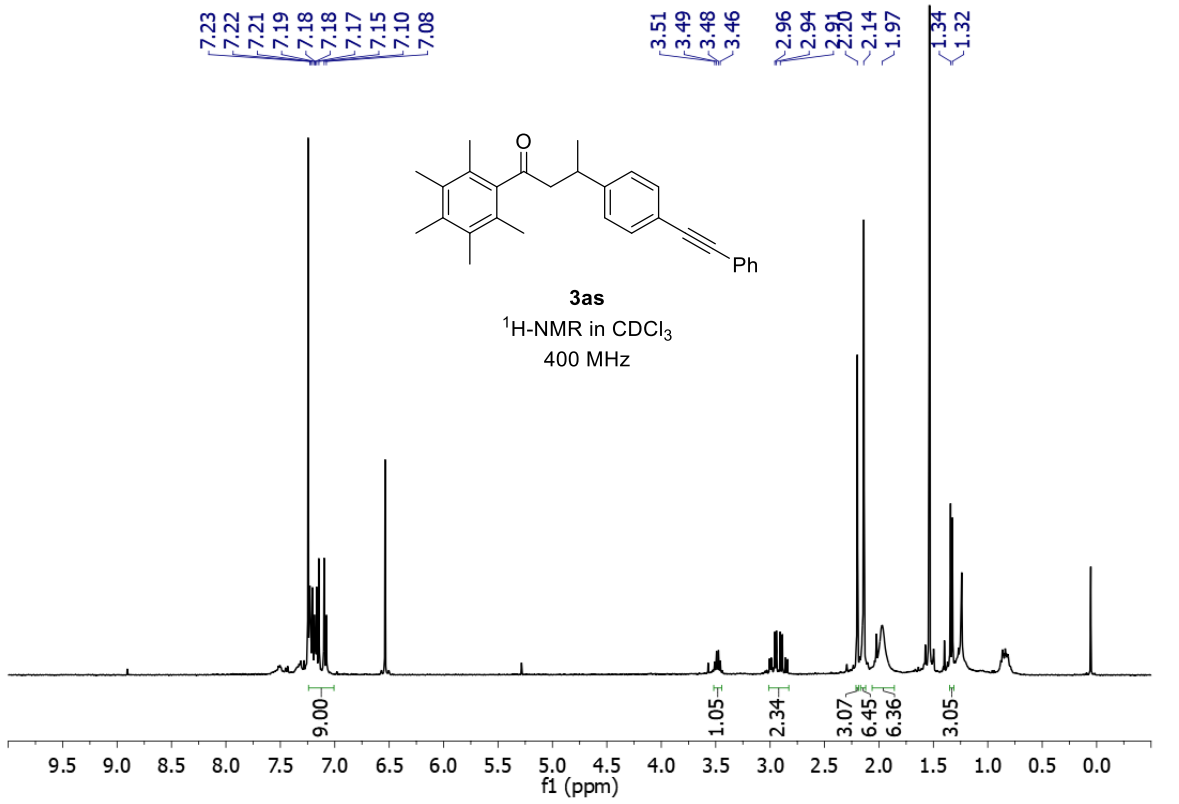
3aq

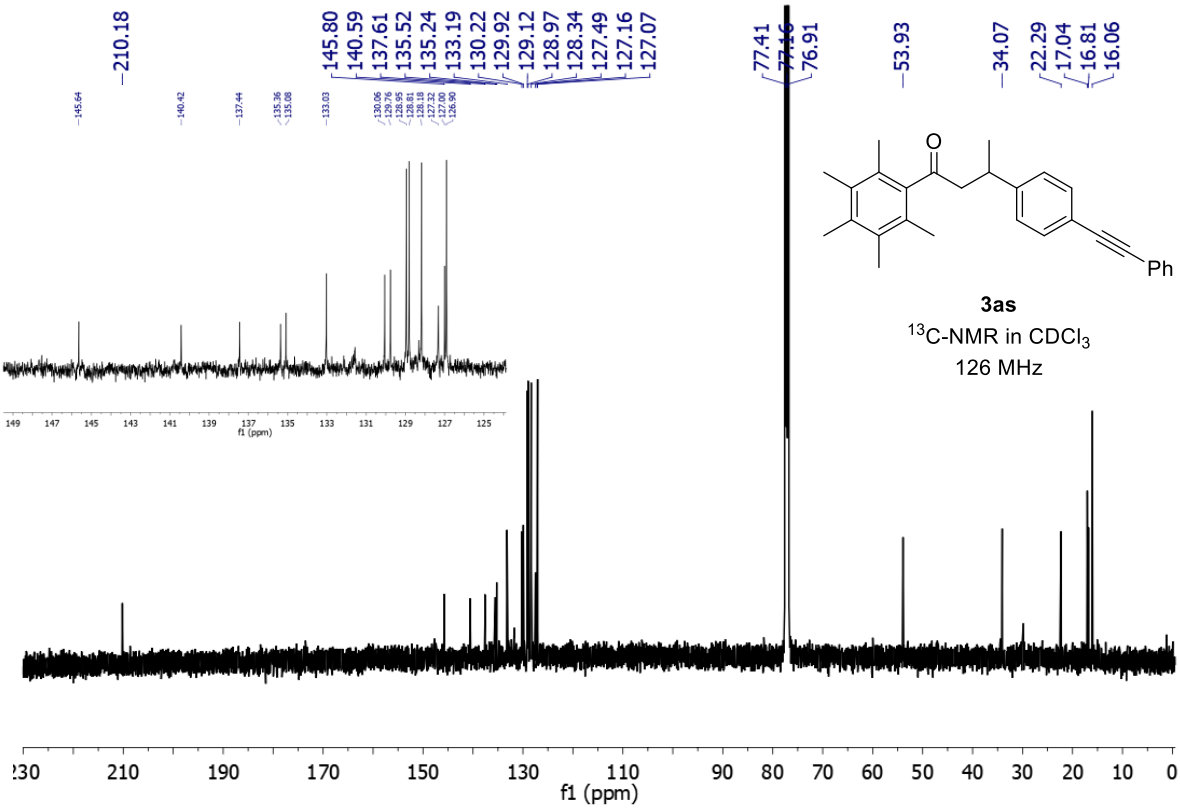
^{19}F-NMR in $CDCl_3$

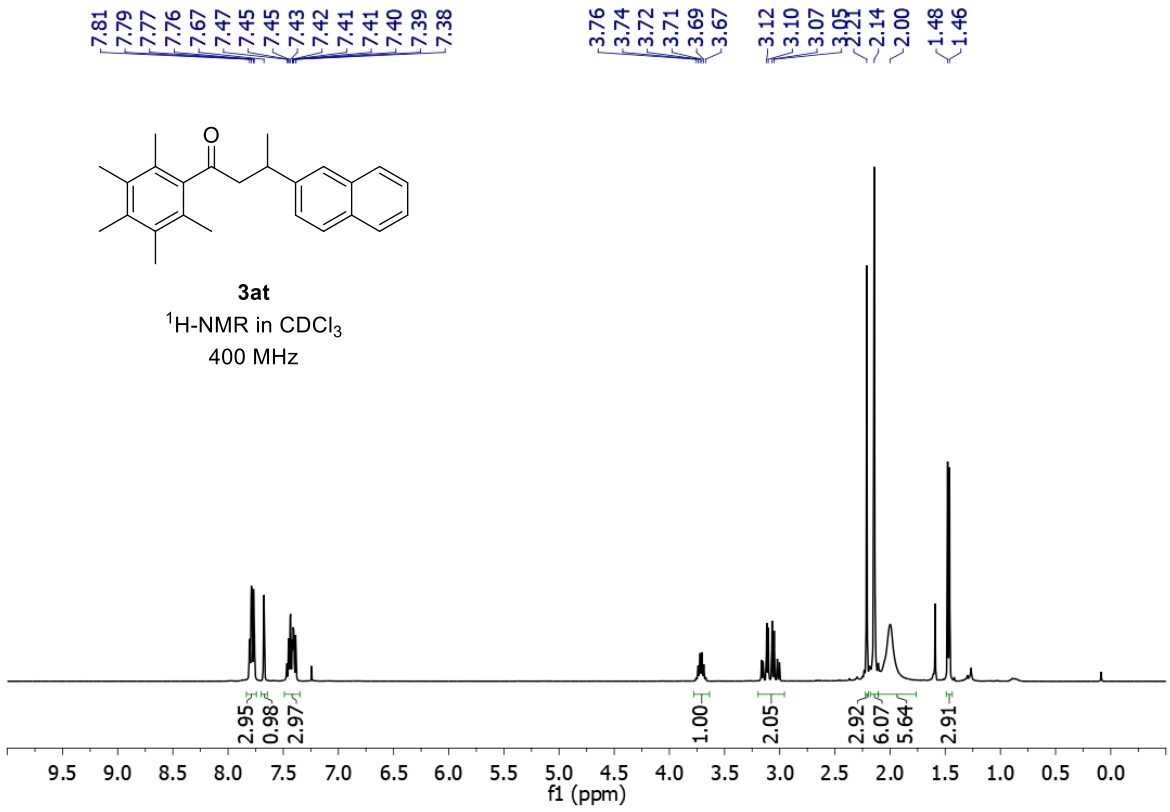
471 MHz

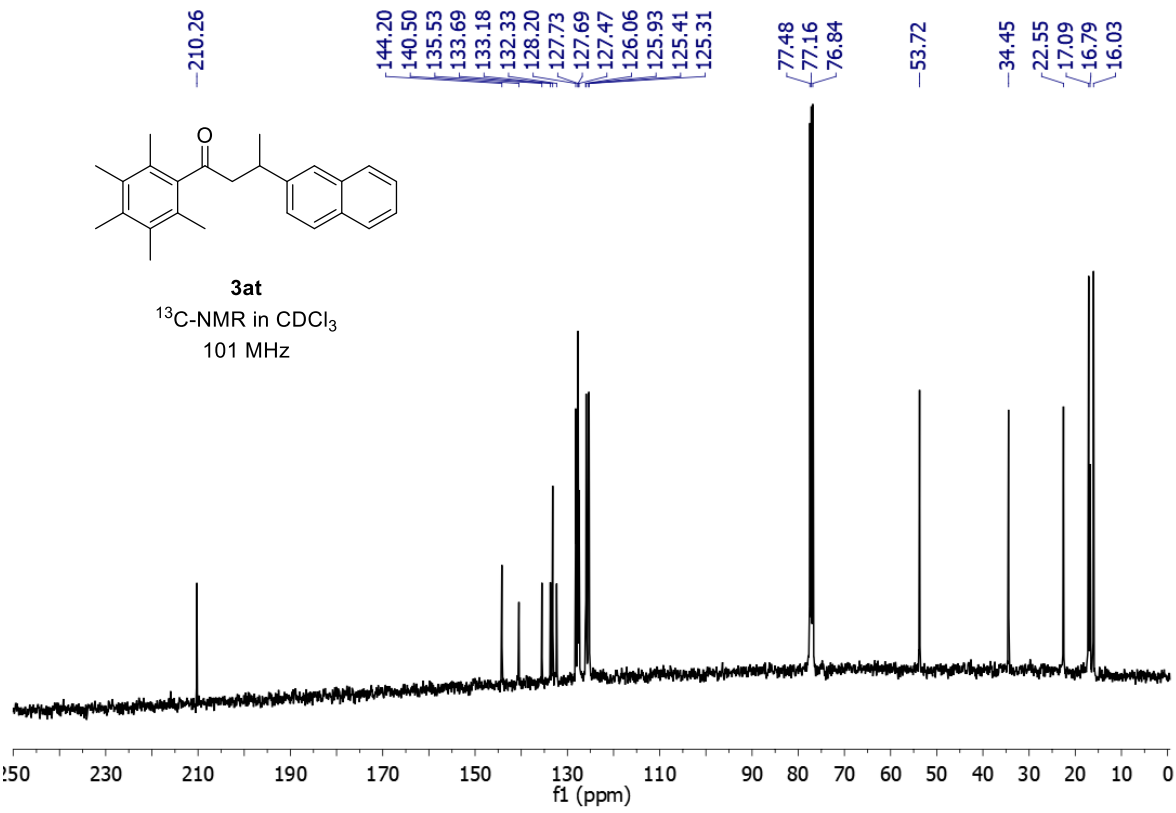

7.40
7.40
7.38
7.37
7.27
7.24
7.22
7.19
7.17
7.13
7.13
7.11
7.10
3.53
3.52
3.50
3.48
3.46
2.93
2.92
2.20
2.14
1.96
1.34
1.33
1.32
1.32
O
Br
3ar
1H NMR in CDCl3
400 MHz
H2O
1.29
1.85
1.13
1.00
2.11
2.84
6.38
5.94
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


209.77
145.75
140.33
135.62
133.23
131.61
129.03
128.58
127.43
126.32
119.96
77.48
77.16
76.84
53.70
33.89
22.37
17.05
16.81
16.05
O
Br
3ar
13C-NMR in CDCl3
101 MHz
240 220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


7.23
7.22
7.21
7.19
7.18
7.18
7.17
7.15
7.10
7.08
3.51
3.49
3.48
3.46
2.96
2.94
2.91
2.20
2.14
1.97
1.34
1.32
O
Ph
3as
1H-NMR in CDCl3
400 MHz
9.00
1.05
2.34
3.07
6.45
6.36
3.05
f1 (ppm)


210.18
145.80
140.59
137.61
135.52
135.24
133.19
130.22
129.92
129.12
128.97
128.34
127.49
127.16
127.07
77.41
77.16
76.91
53.93
34.07
22.29
17.04
16.81
16.06
O
Ph
3as
13C-NMR in CDCl3
126 MHz
f1 (ppm)


7.81
7.79
7.77
7.76
7.67
7.47
7.45
7.45
7.43
7.42
7.41
7.41
7.40
7.39
7.38
3.76
3.74
3.72
3.71
3.69
3.67
3.12
3.10
3.07
3.05
2.21
2.14
2.00
1.48
1.46
O
3at
1H-NMR in CDCl3
400 MHz
2.95
0.98
2.97
1.00
2.05
2.92
6.07
5.64
2.91
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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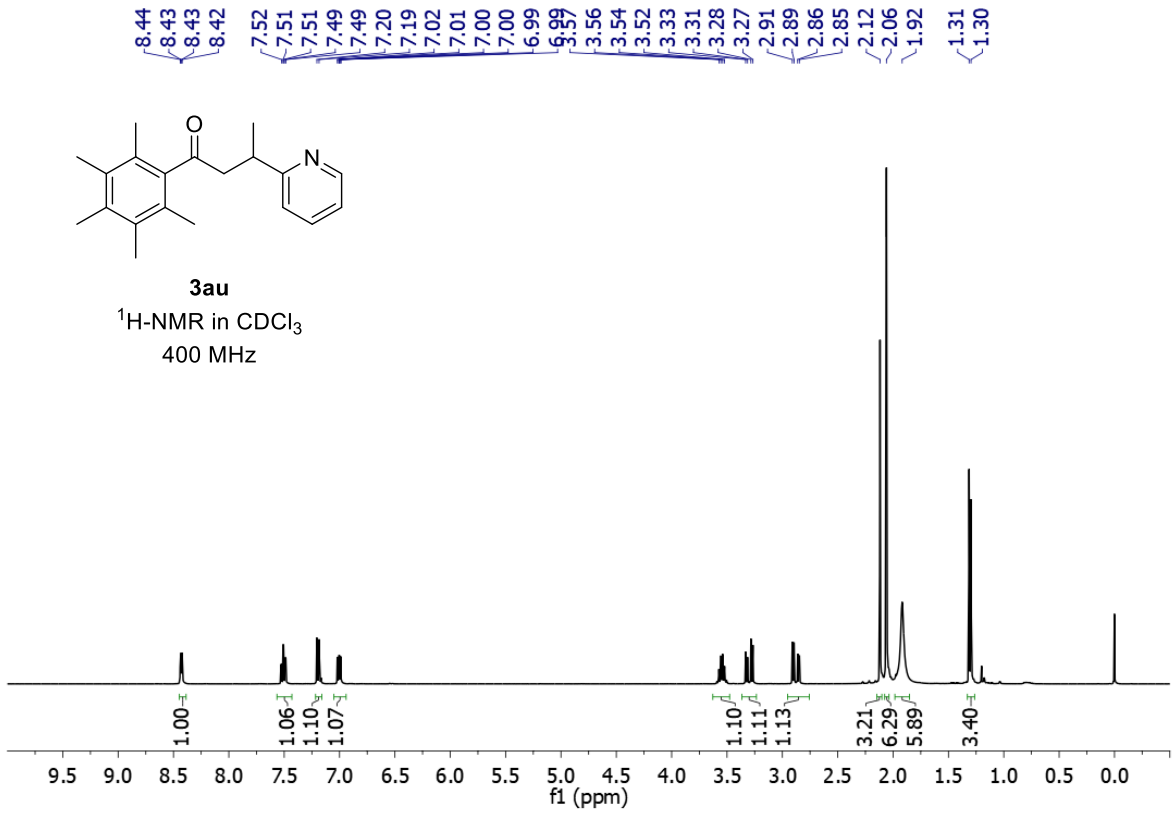
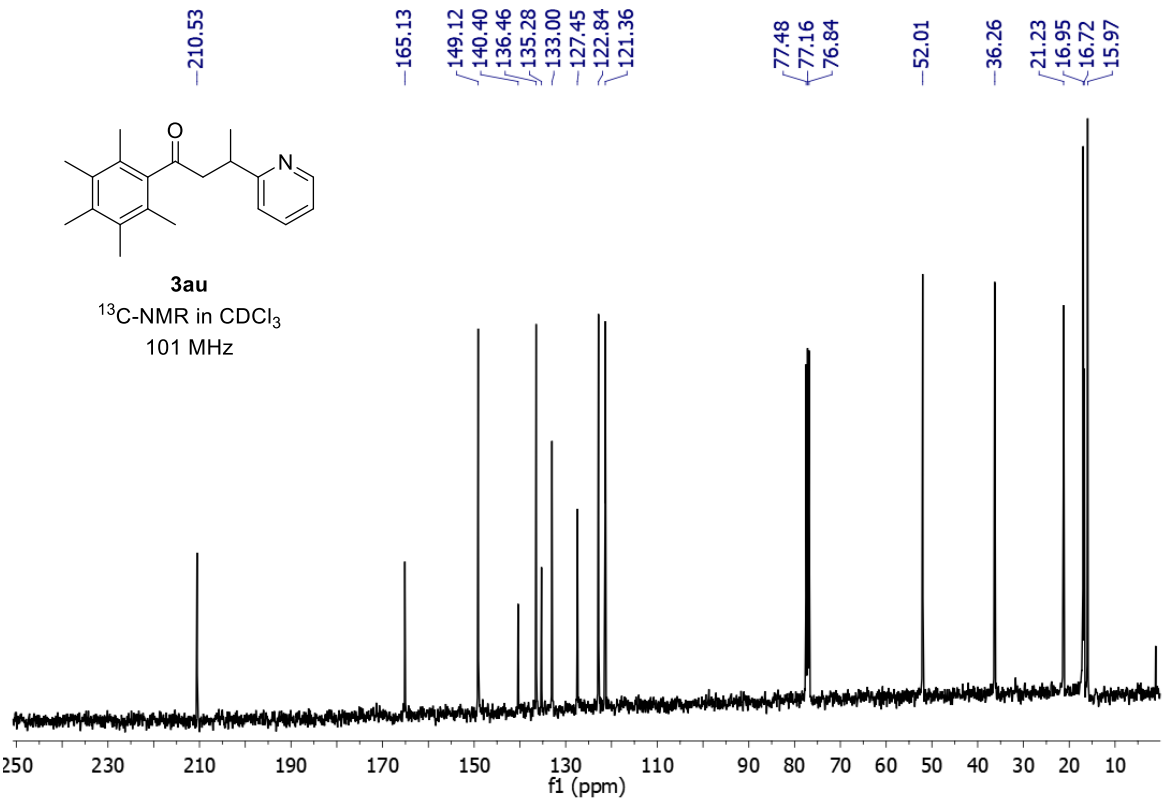
144.20
140.50
135.53
133.69
133.18
132.33
128.20
127.73
127.69
127.47
126.06
125.93
125.41
125.31
77.48
77.16
76.84
53.72
34.45
22.55
17.09
16.79
16.03
O
3at
13C-NMR in CDCl3
101 MHz
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.44
8.43
8.43
8.42
7.52
7.51
7.51
7.49
7.49
7.20
7.19
7.02
7.01
7.00
7.00
6.99
6.99
3.57
3.56
3.54
3.52
3.33
3.31
3.28
3.27
2.91
2.89
2.86
2.85
2.12
2.06
1.92
1.31
1.30
O
N
3au
1H-NMR in CDCl3
400 MHz
1.00
1.06
1.10
1.07
1.10
1.11
1.13
3.21
6.29
5.89
3.40
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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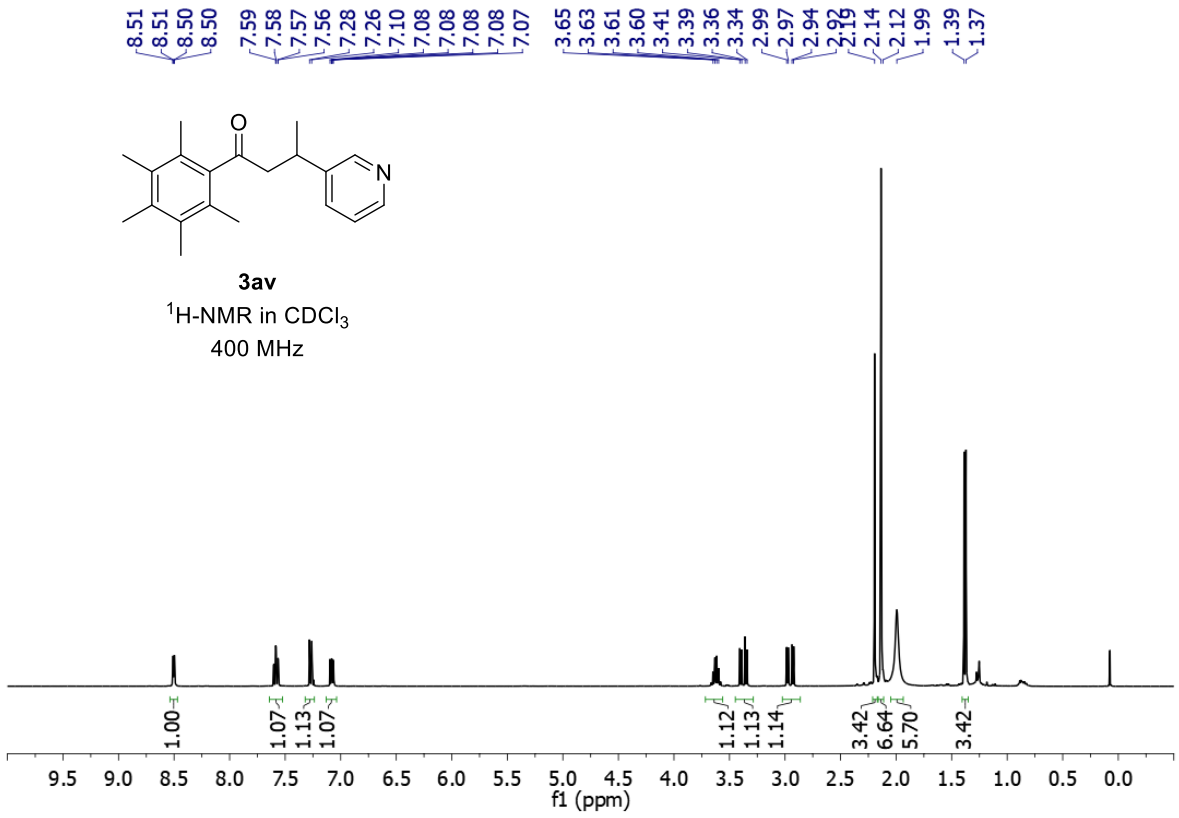
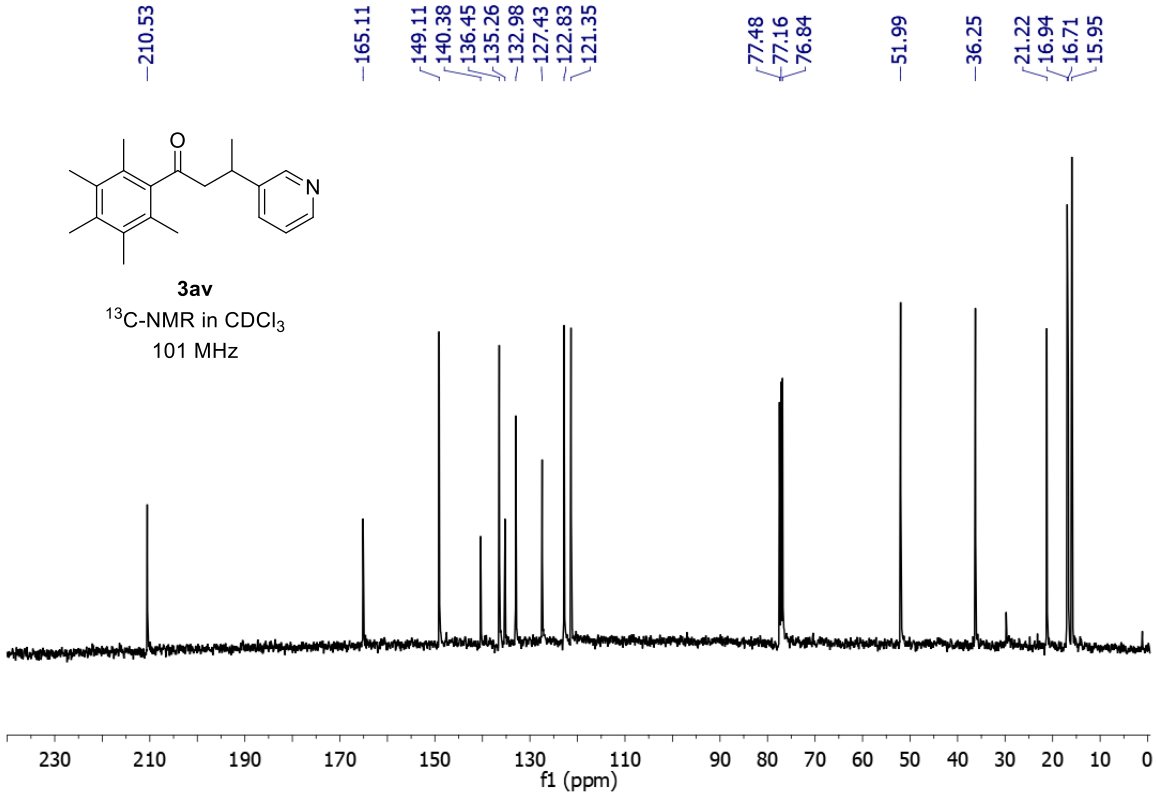
140.40
136.46
135.28
133.00
127.45
122.84
121.36
77.48
77.16
76.84
52.01
36.26
21.23
16.95
16.72
15.97
O
N
3au
13C-NMR in CDCl3
101 MHz
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10
f1 (ppm)


8.51
8.51
8.50
8.50
7.59
7.58
7.57
7.56
7.28
7.26
7.10
7.08
7.08
7.08
7.08
7.07
3.65
3.63
3.61
3.60
3.41
3.39
3.36
3.34
2.99
2.97
2.94
2.92
2.19
2.14
2.12
1.99
1.39
1.37
O
N
3av
1H-NMR in CDCl3
400 MHz
1.00
1.07
1.13
1.07
1.12
1.13
1.14
3.42
6.64
5.70
3.42
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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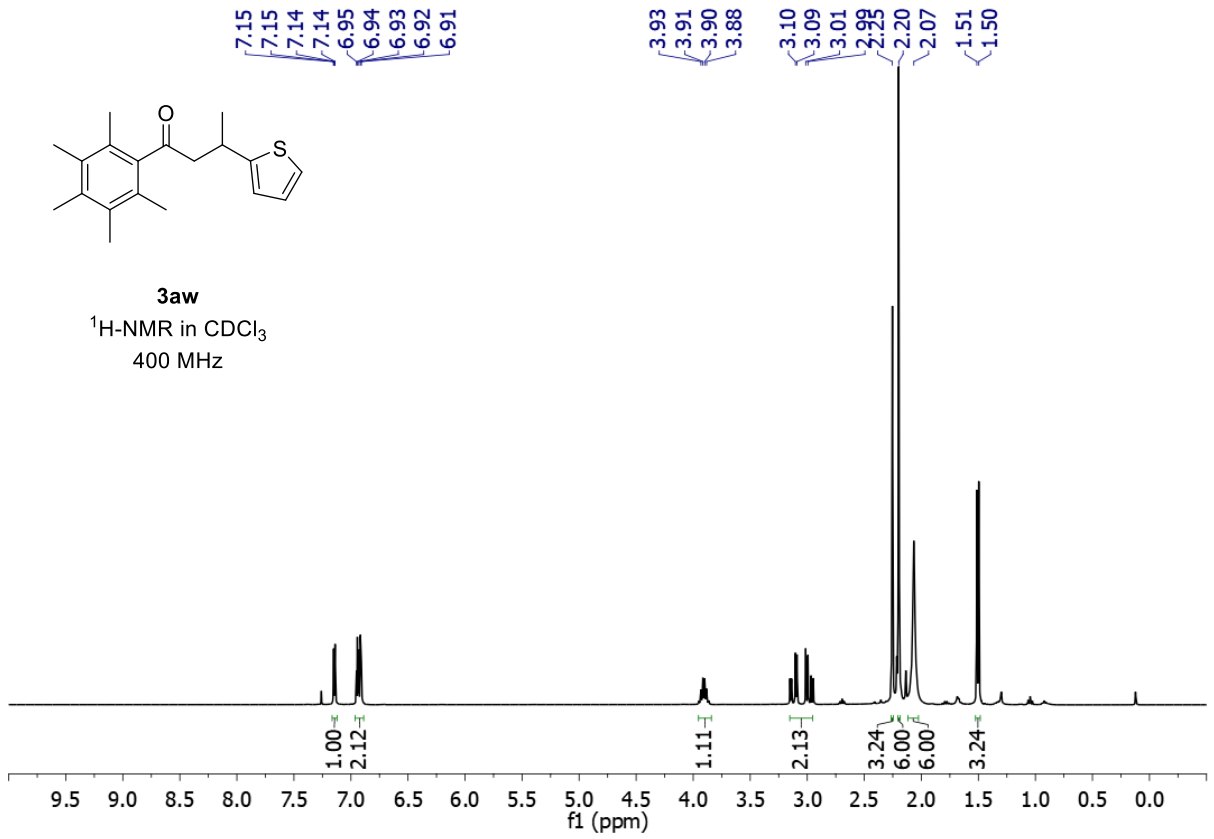
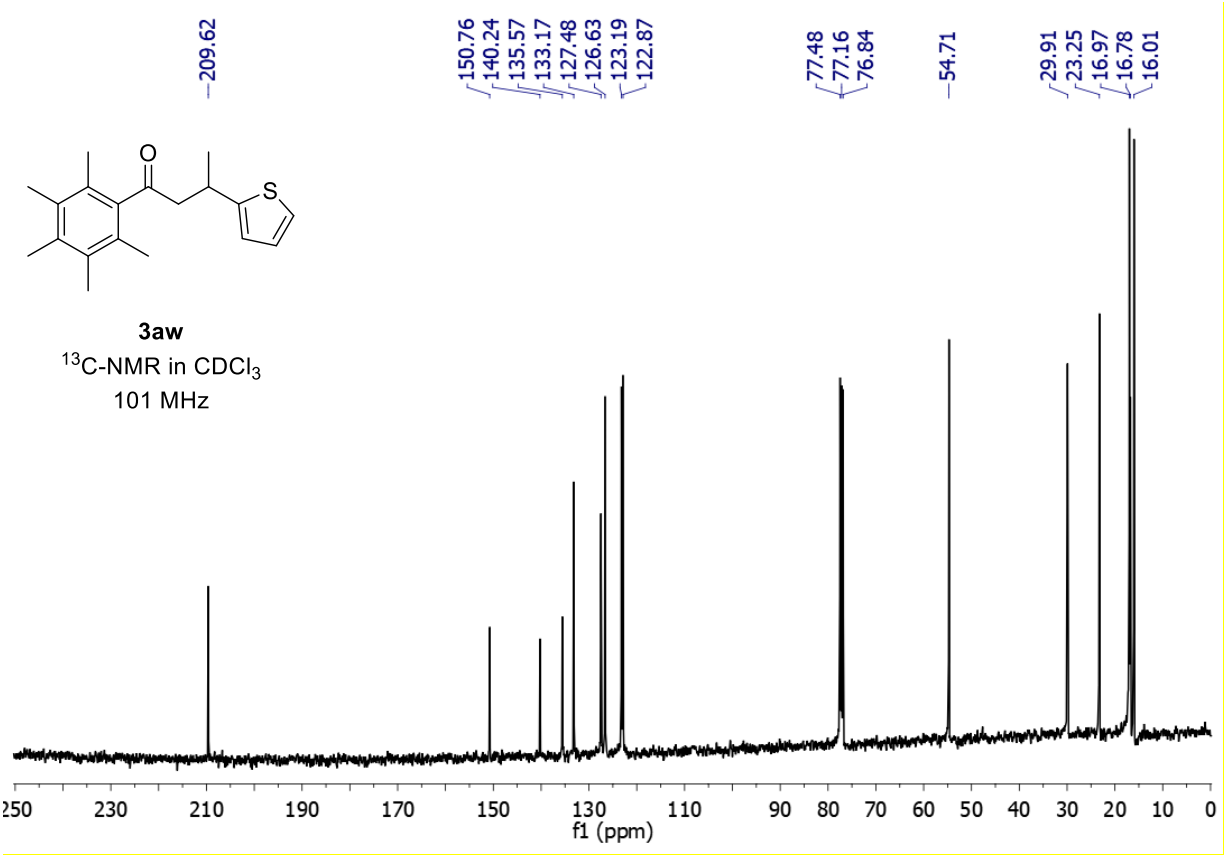
165.11
149.11
140.38
136.45
135.26
132.98
127.43
122.83
121.35
77.48
77.16
76.84
51.99
36.25
21.22
16.94
16.71
15.95
O
N
3av
13C-NMR in CDCl3
101 MHz
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3aw

^{1}H-NMR in $CDCl_3$

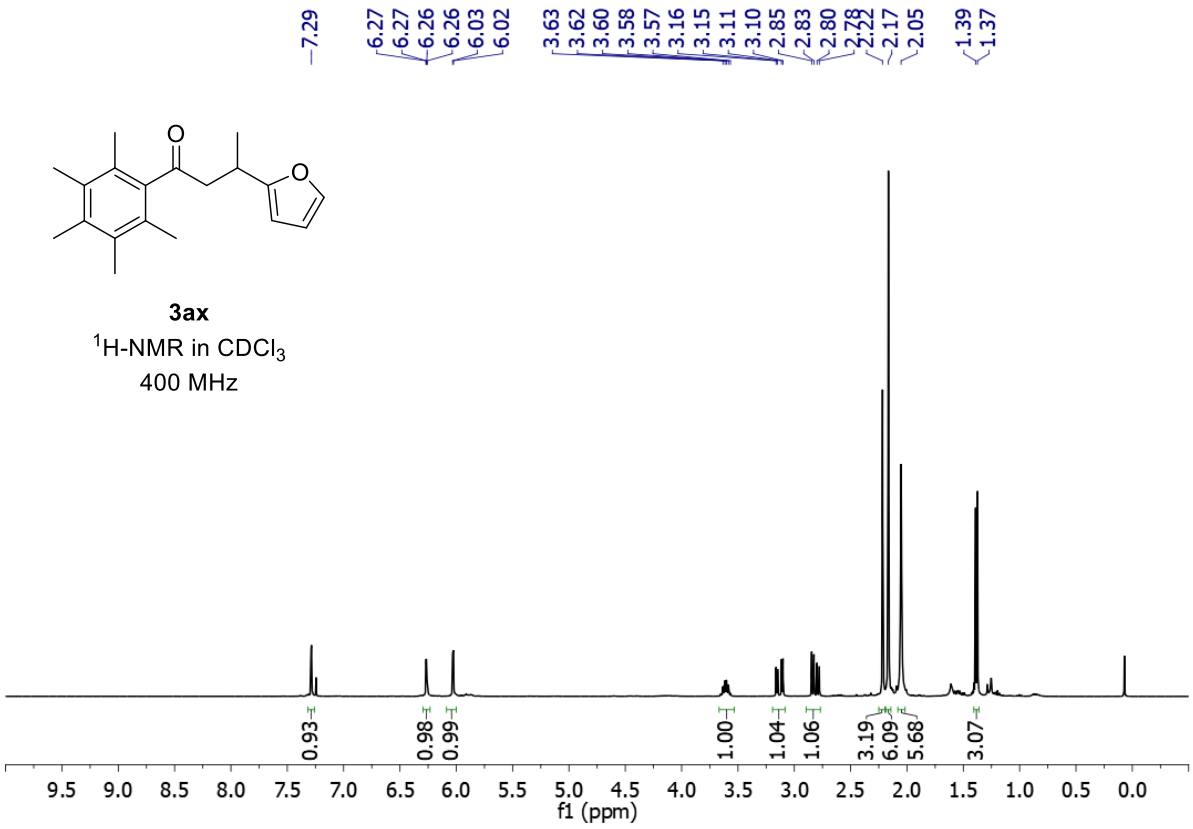
400 MHz



3aw

^{13}C-NMR in $CDCl_3$

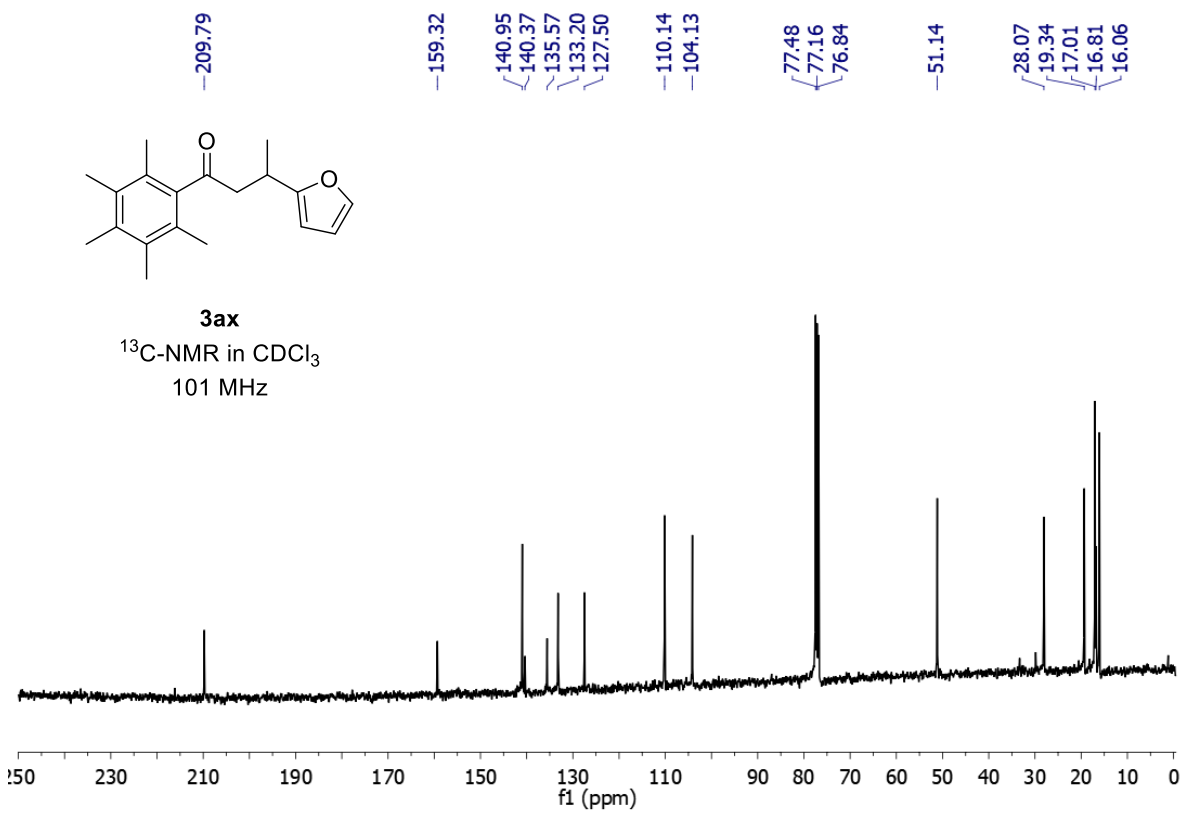
101 MHz



3ax

^{1}H-NMR in $CDCl_3$

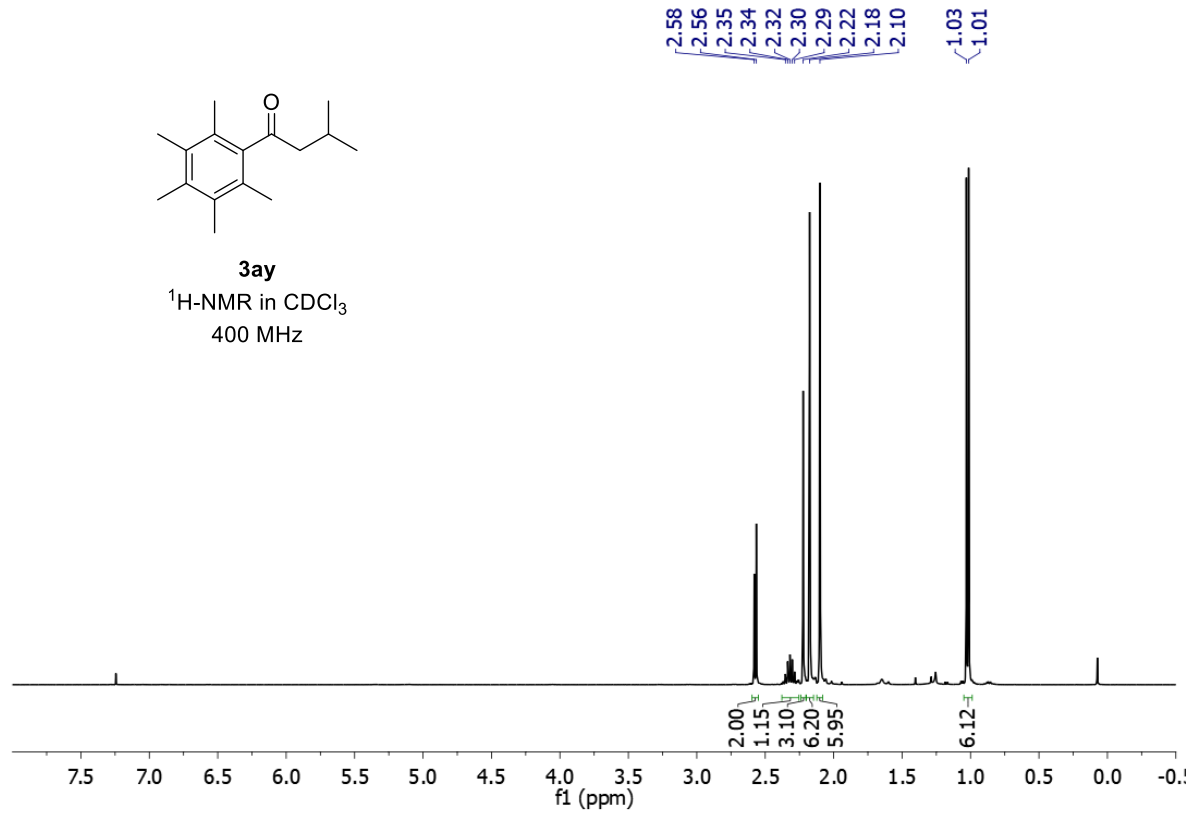
400 MHz



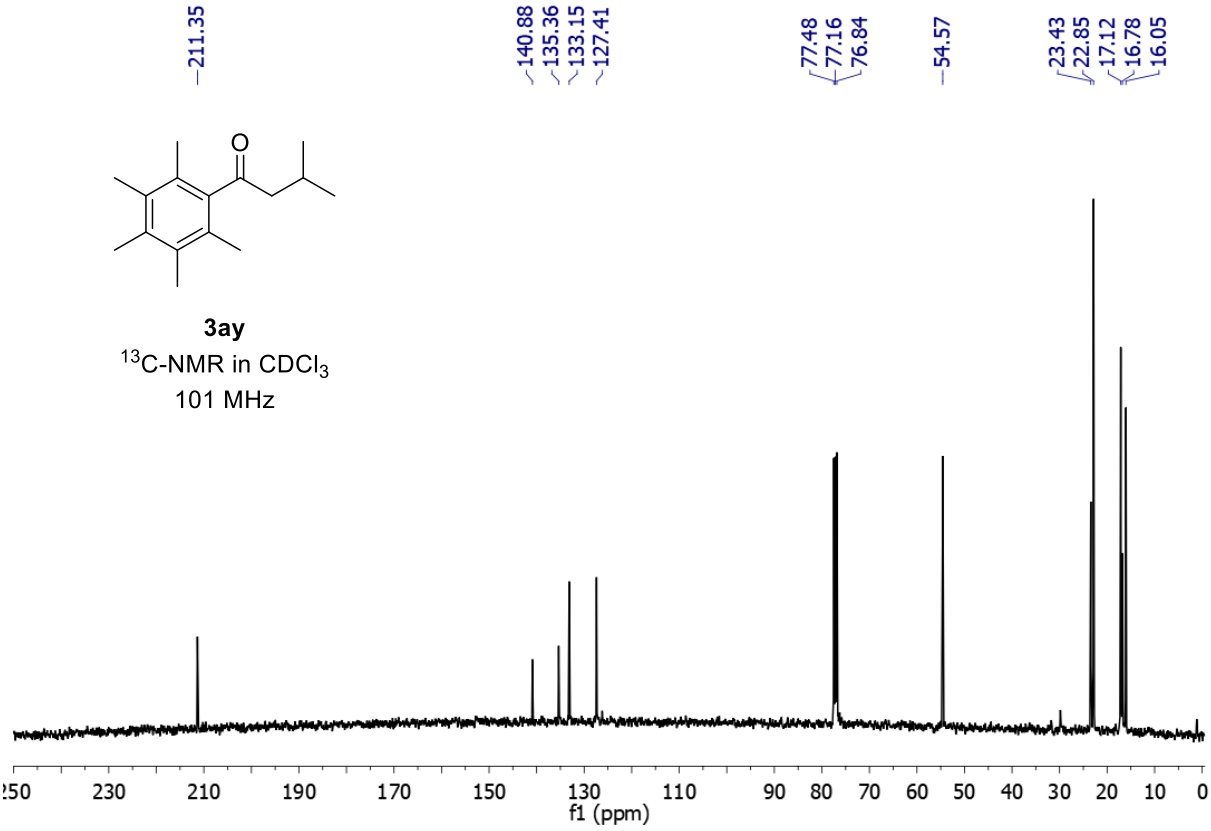
3ax

^{13}C-NMR in $CDCl_3$

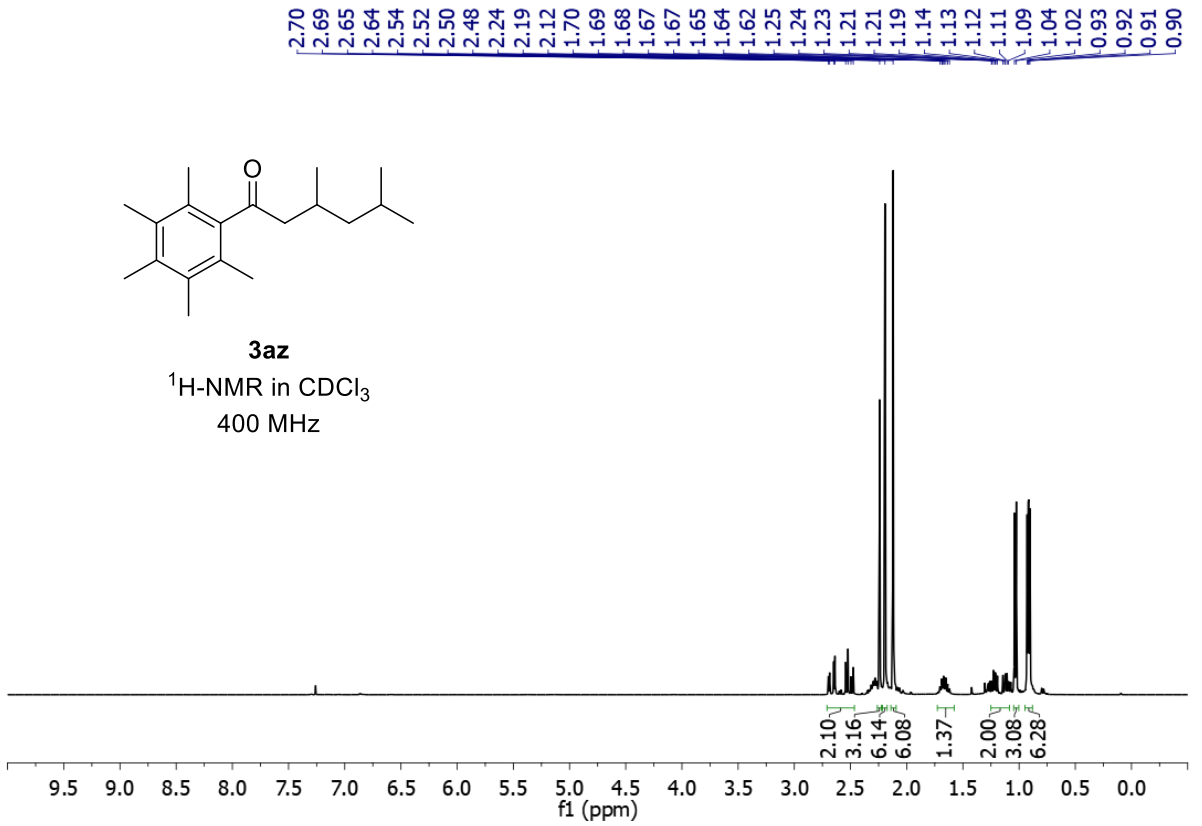
101 MHz

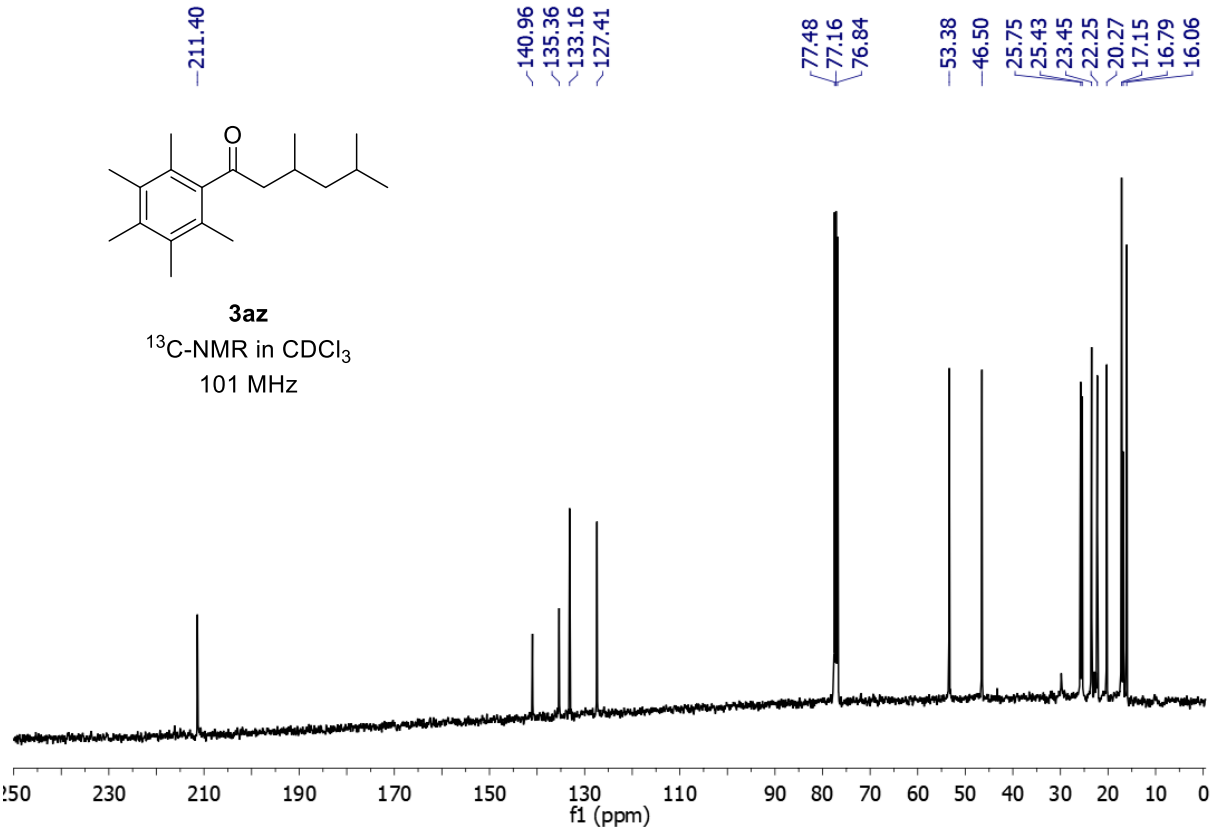


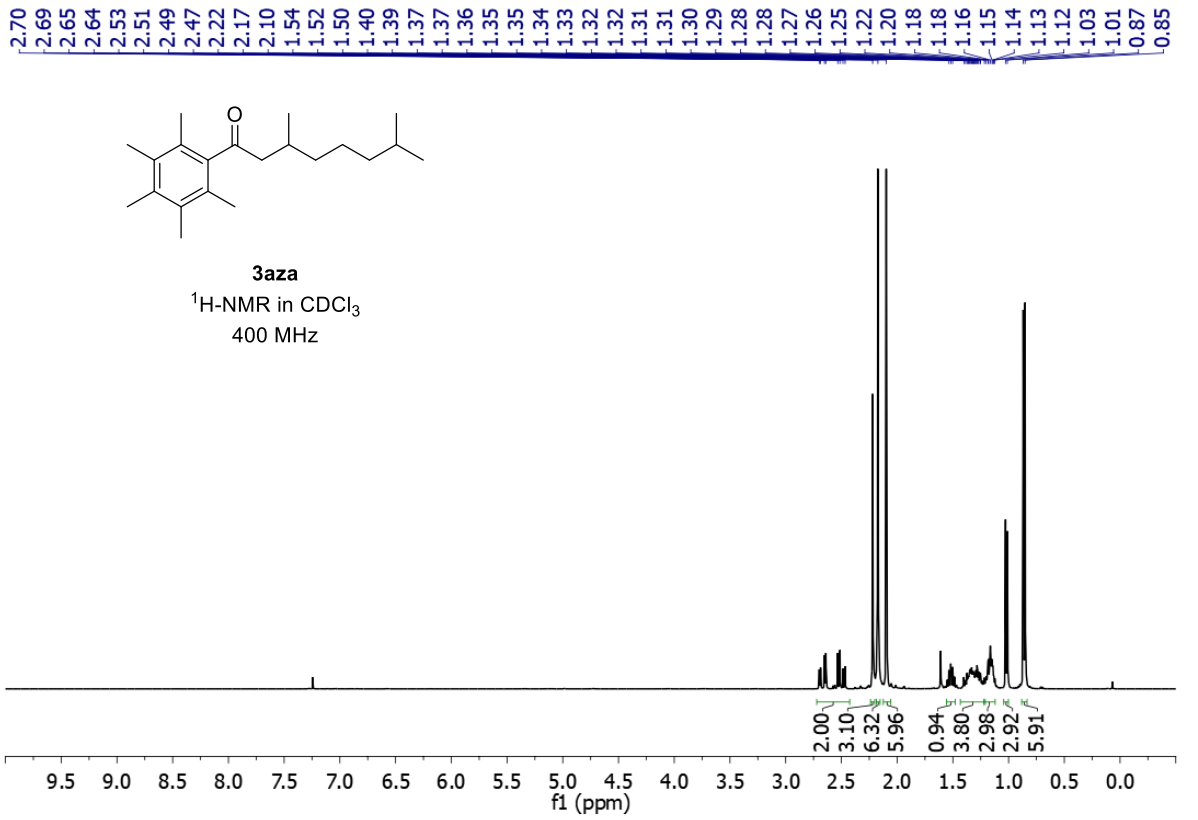
3ay
^{1}H-NMR in $CDCl_3$
400 MHz

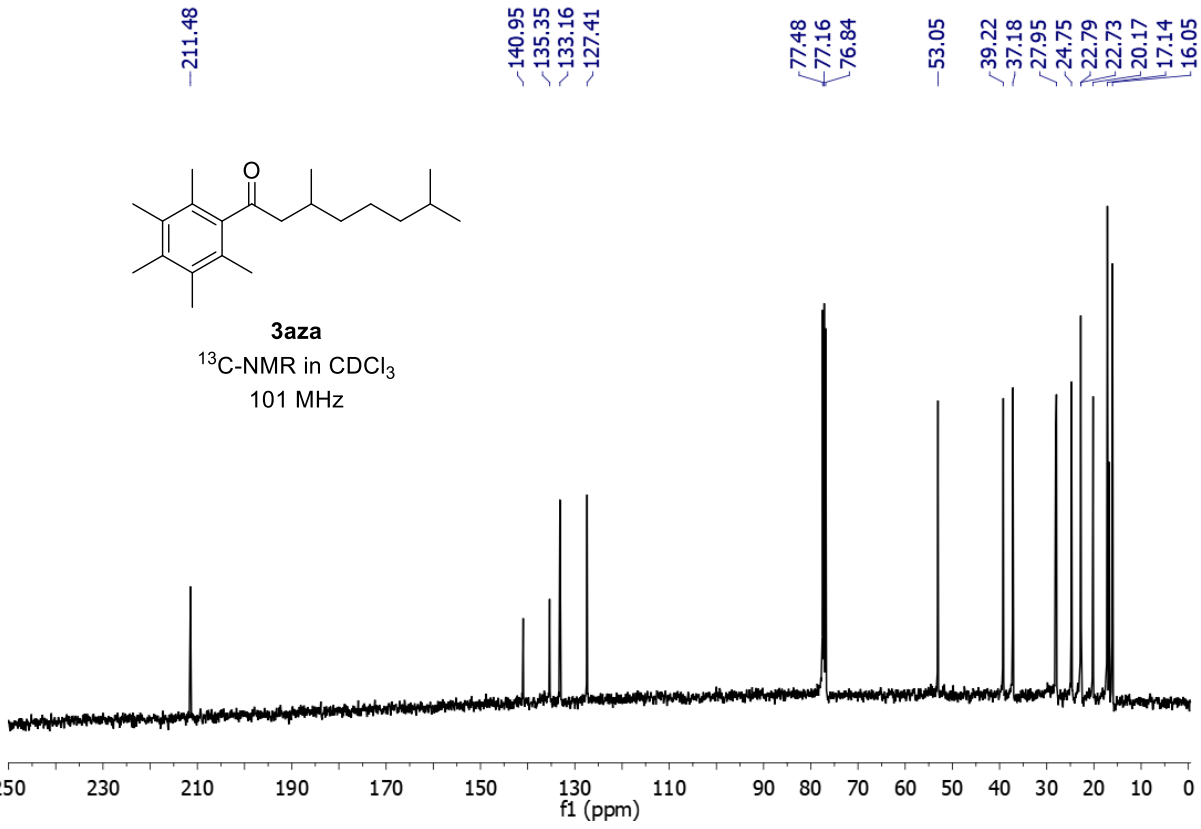


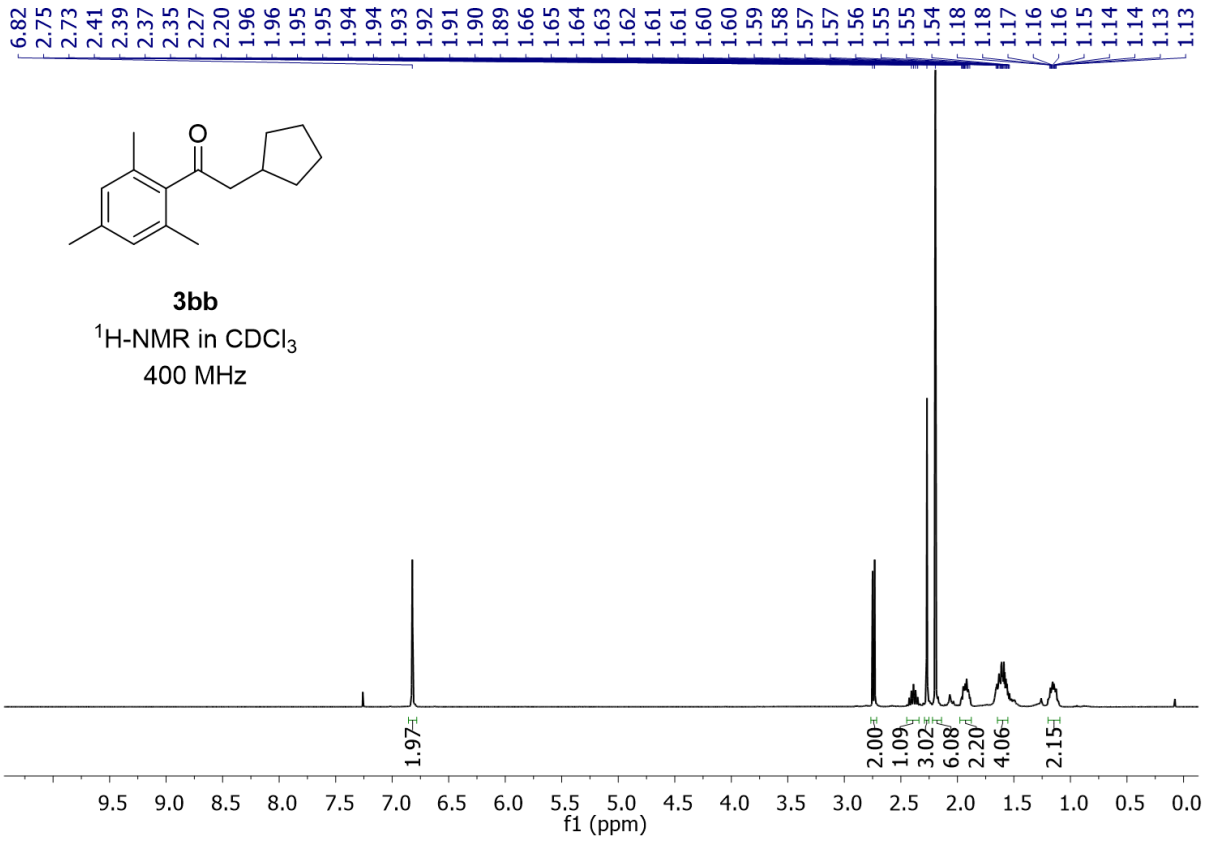
3ay
^{13}C-NMR in $CDCl_3$
101 MHz

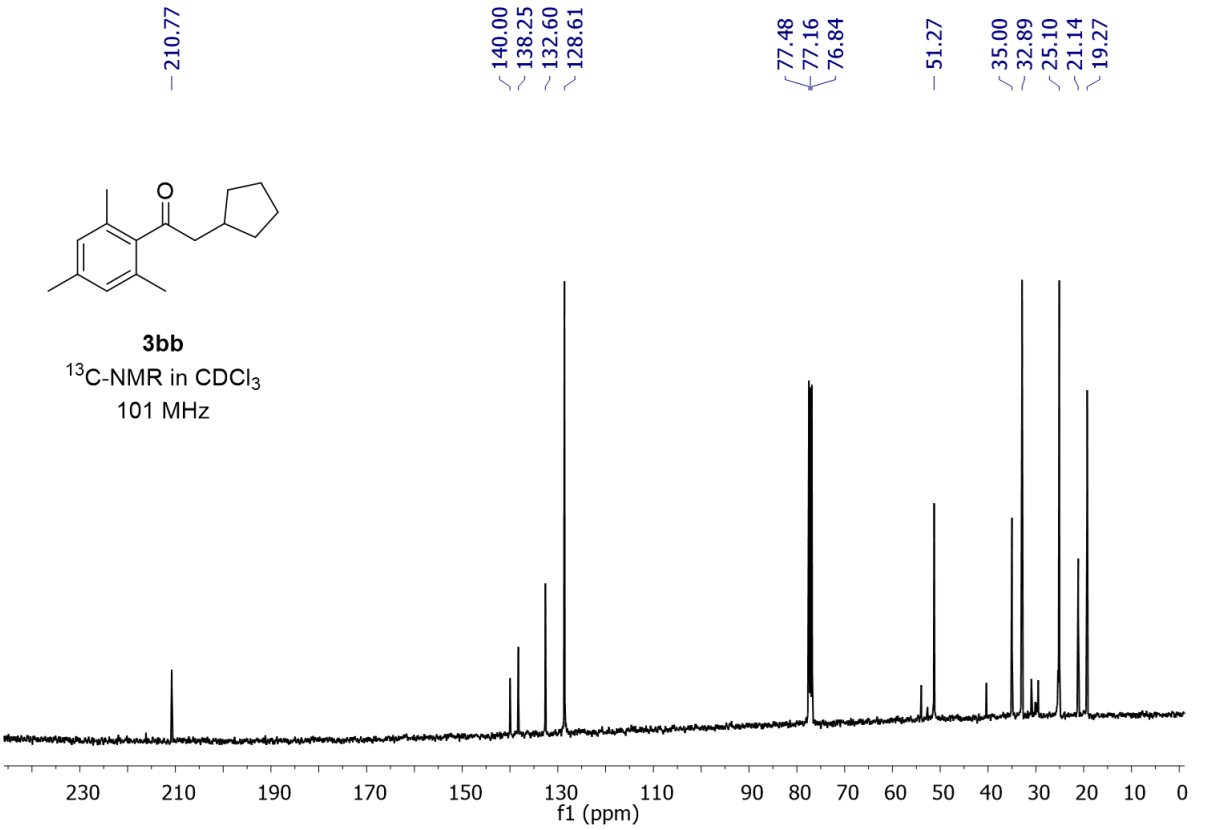

2.70 2.69 2.65 2.64 2.54 2.52 2.50 2.48 2.24 2.19 2.12 1.70 1.69 1.68 1.67 1.67 1.65 1.64 1.62 1.25 1.24 1.23 1.21 1.21 1.19 1.14 1.13 1.12 1.11 1.09 1.04 1.02 0.93 0.92 0.91 0.90
O
3az
1H-NMR in CDCl3
400 MHz
2.10 3.16 6.14 6.08 1.37 2.00 3.08 6.28
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


211.40
140.96 135.36 133.16 127.41
77.48 77.16 76.84
53.38 46.50
25.75 25.43 23.45 22.25 20.27 17.15 16.79 16.06
O
3az
13C-NMR in CDCl3
101 MHz
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


2.70 2.69 2.65 2.64 2.53 2.51 2.49 2.47 2.22 2.17 2.10 1.54 1.52 1.50 1.40 1.39 1.37 1.37 1.36 1.35 1.35 1.34 1.33 1.32 1.32 1.31 1.31 1.30 1.29 1.28 1.28 1.27 1.26 1.25 1.22 1.20 1.18 1.18 1.16 1.15 1.14 1.13 1.12 1.03 1.01 0.87 0.85
O
3aza
1H-NMR in CDCl3
400 MHz
2.00 3.10 6.32 5.96 0.94 3.80 2.98 2.92 5.91
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


211.48
140.95 135.35 133.16 127.41
77.48 77.16 76.84
53.05
39.22 37.18 27.95 24.75 22.79 22.73 20.17 17.14 16.05
O
3aza
13C-NMR in CDCl3
101 MHz
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


6.82 2.75 2.73 2.41 2.39 2.37 2.35 2.27 2.20 1.96 1.96 1.95 1.95 1.94 1.94 1.93 1.92 1.91 1.90 1.89 1.66 1.65 1.64 1.63 1.62 1.61 1.61 1.60 1.60 1.59 1.58 1.57 1.57 1.56 1.55 1.55 1.54 1.18 1.18 1.17 1.16 1.16 1.15 1.14 1.14 1.13 1.13
O
3bb
1H-NMR in CDCl3
400 MHz
1.97
2.00
1.09
3.02
6.08
2.20
4.06
2.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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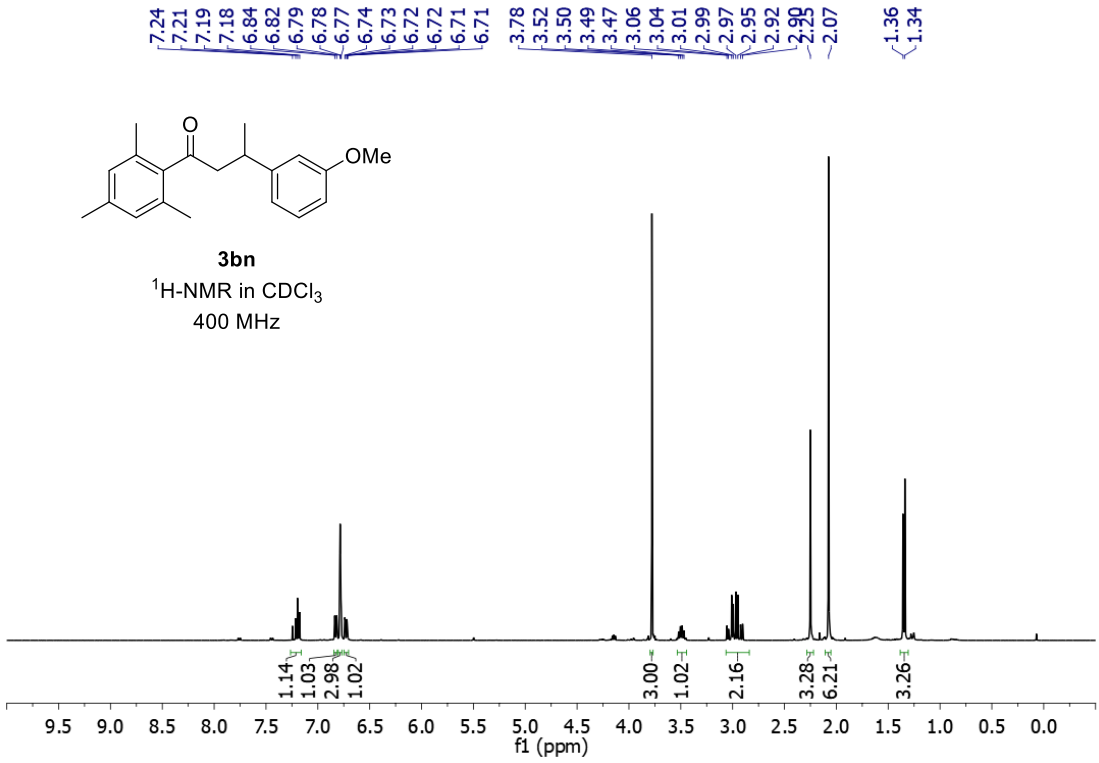
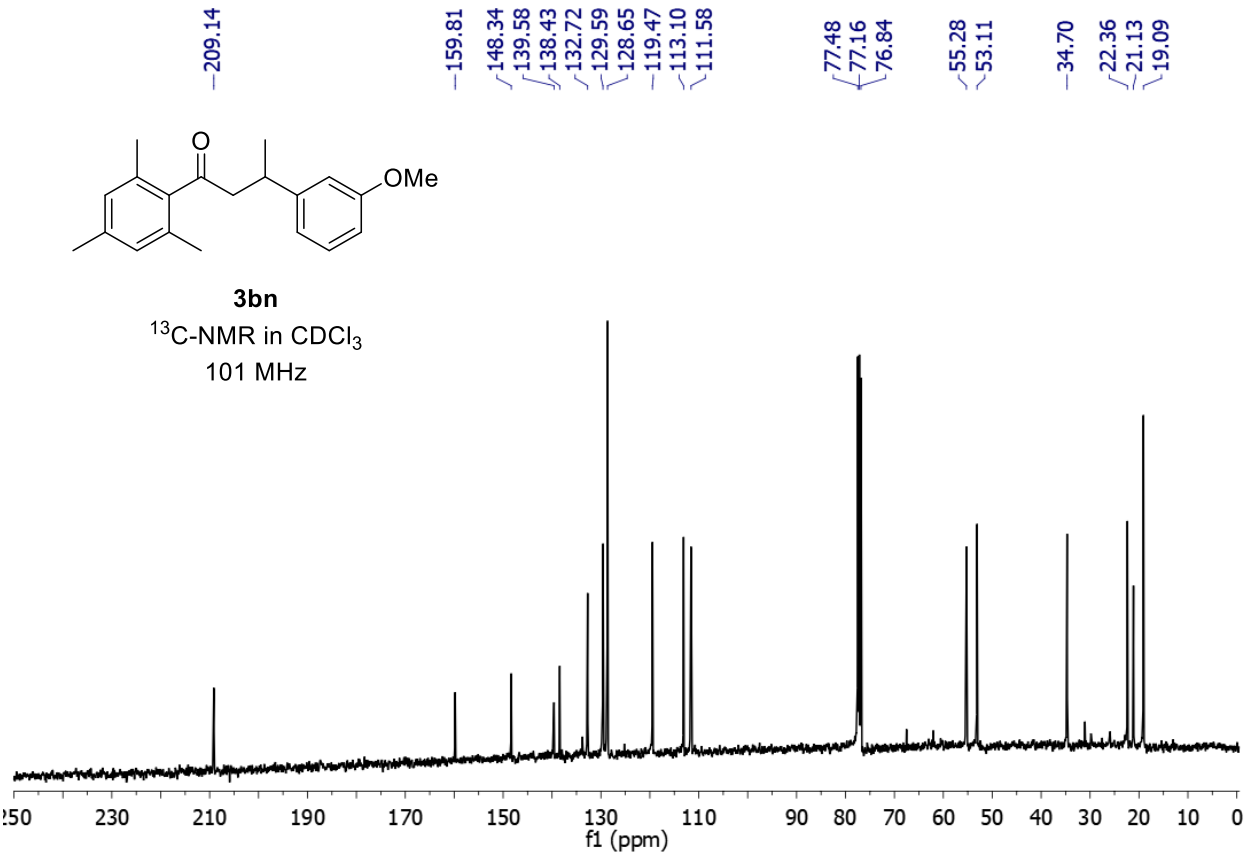
140.00
138.25
132.60
128.61
77.48
77.16
76.84
51.27
35.00
32.89
25.10
21.14
19.27
O
3bb
13C-NMR in CDCl3
101 MHz
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.24
7.21
7.19
7.18
6.84
6.82
6.79
6.78
6.77
6.74
6.73
6.72
6.72
6.71
6.71
3.78
3.52
3.50
3.49
3.47
3.06
3.04
3.01
2.99
2.97
2.95
2.92
2.90
2.25
2.07
1.36
1.34
O
OMe
3bn
1H-NMR in CDCl3
400 MHz
1.14
1.03
2.98
1.02
3.00
1.02
2.16
3.28
6.21
3.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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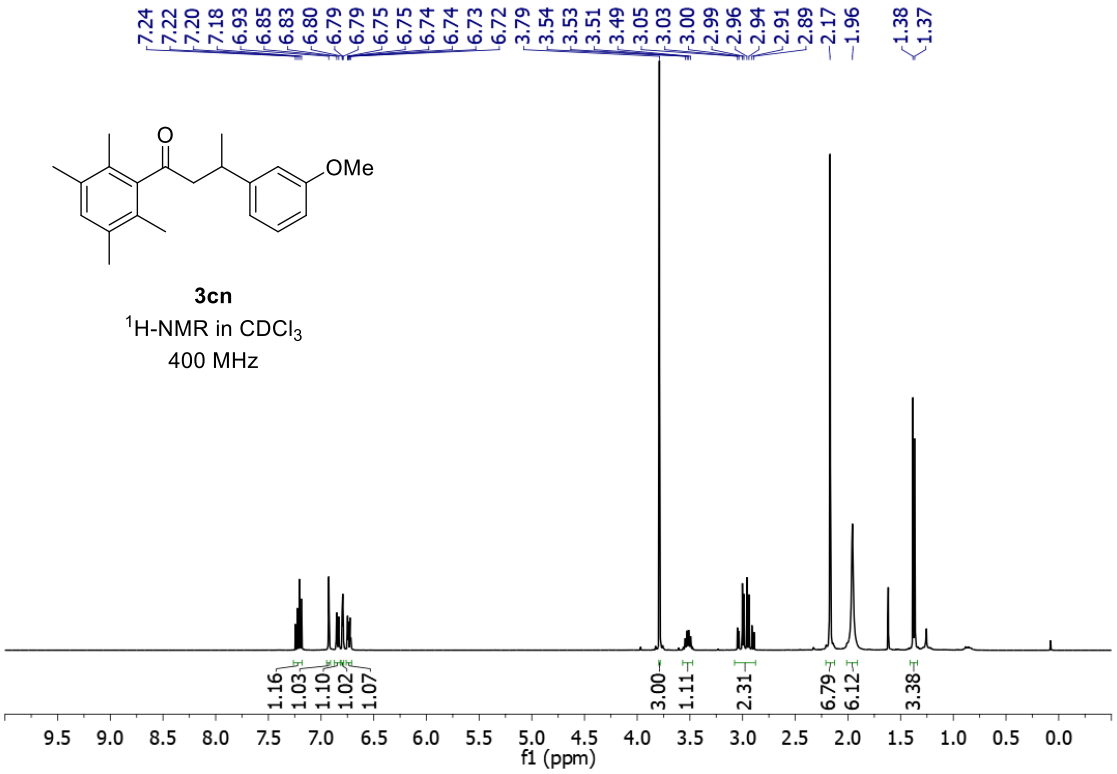
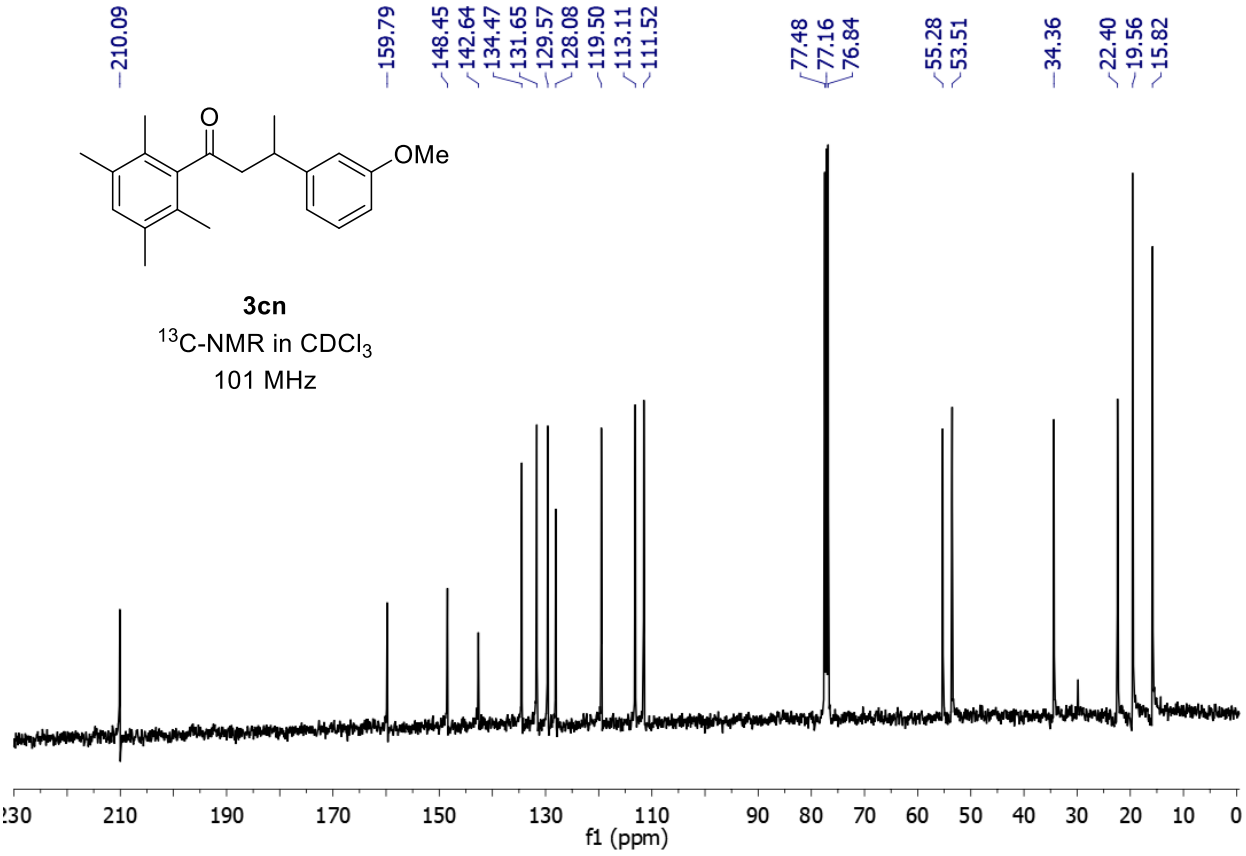
139.58
138.43
132.72
129.59
128.65
119.47
113.10
111.58
77.48
77.16
76.84
55.28
53.11
34.70
22.36
21.13
19.09
O
OMe
3bn
13C-NMR in CDCl3
101 MHz
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3cn

^{1}H-NMR in $CDCl_3$

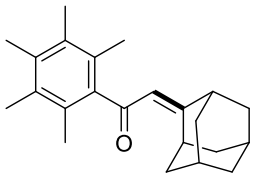
400 MHz



3cn

^{13}C-NMR in $CDCl_3$

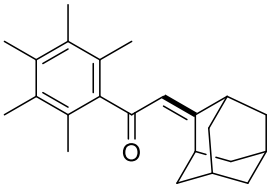
101 MHz



3azb'

^{1}H-NMR in $CDCl_3$

400 MHz



3azb'

^{13}C-NMR in $CDCl_3$

101 MHz