Supporting Information

Cross-coupling of aryl aldehydes and benzyl chlorides enabled by dual *N*-heterocyclic carbene/cobalt catalysis.

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General methods and materials

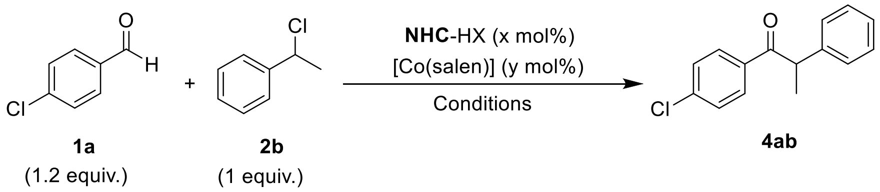
All manipulations were performed -unless otherwise noted- under an atmosphere of dry argon using standard Schlenk or dry box techniques. Catalytic tests were run in Teflon capped 15 mL Schlenk reaction tubes (FengTecEx; Ref.: P260001; Reaction tube P26, heavy wall, with side port). Solvents were dried by standard methods (Na for ethers and CaH_2 for the rest) and distilled under argon. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on the NMR-ICMG platform of Grenoble with Bruker Avance 400 and 500 MHz spectrometers at 298 K. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (^1H, ^{13}C) $CFCl_3$ (^{19}F). Coupling constants *J* are given in Hertz as positive values. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad signal. Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F25 pre-coated silica gel plate (0.2 mm thickness) and visualization were performed using a UV lamp. Silica 60 M (0.04-0.063 mm; Macherey-Nagel GmbH & Co. KG), aluminum oxide 90 basisch (Macherey-Nagel GmbH & Co. KG) for column chromatography was employed.

Infrared (IR) data were recorded on Perkin-Elmer GS2000 IR spectrophotometer with a Golden-Gate ATR unit in the solid state. Mass spectra were recorded on a Waters Gevo X2-S Qtof mass spectrometer or on a Thermo Scientific LTQ Orbitrap XL mass spectrometer.

NHC1-**3**HPF_6,[1] **NHC4**-HI,[2] **NHC5**-**6**HPF_6,[1] **NHC7**-HBF_4,[3] **NHC8**-HI,[4] **NHC9**-HBF_4[5] were synthesized according to reported procedures. *para*-Chlorobenzaldehyde (**1a**) was recrystallized from ethanol/water (9:1) mixture prior to use. Other starting materials were purchased from commercial sources and used without further purification.

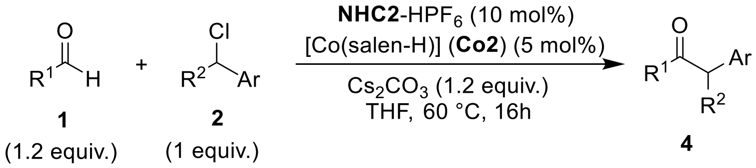
Experimental procedures

Optimization of the methodology



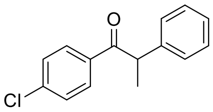
0.25 mmol scale reaction: In an argon filled glove-box, the corresponding [Co(salen)] complex was introduced in a Teflon capped 15 mL Schlenk reaction tube. Then, the flask was sealed and put it out of the glovebox and connected to a Schlenk line. Under argon atmosphere and at room temperature, 4- chlorobenzaldehyde (**1a**; 0.042 g, 0.3 mmol), the corresponding **NHC** precursor, 1 mL of freshly distilled dry solvent, 1-phenylethyl chloride (**2b**; 0.033 mL, 0.25 mmol) and the base (0.3 mmol) were added in this order and the flask was sealed. Then, the mixture was stirred at the given temperature in an oil bath overnight (16 h). The flask was opened to the air, 1,3,5-trimethoxybenzene (TMB) as internal standard (0.042 g, 0.25 mmol) was added, followed by a saturated aqueous solution of ammonium chloride (10 mL). The mixture was extracted with dichloromethane (3 x 10 mL), washed with water (10 mL), dried over anhydrous Na_2SO_4, filtered and volatiles removed in the rotary evaporator. The crude sample including TMB as internal standard was analyzed by ^{1}H NMR spectroscopy employing $CDCl_3$ as solvent. Specific reaction conditions and ^{1}H NMR yields for **4ab** are given in Table 1 and 2 in the manuscript.

Scope of the reaction



1 mmol scale reaction: In an argon filled glove-box [Co(salen-H)] (**Co2**; 0.016 g, 0.05 mmol) was introduced in a Teflon capped 15 mL Schlenk reaction tube. Then, the flask was sealed and put it out of the glovebox and connected to a Schlenk line. Under argon atmosphere and at room temperature, the corresponding aldehyde (**1**, 1.2 mmol), **NHC2**-HPF_6 (0.041 g, 0.1 mmol), 4 mL of freshly distilled dry THF, the corresponding substituted benzyl chloride (**2**, 1 mmol) and Cs_2CO_3 (0.39 g, 1.2 mmol) were added in this order and the flask was sealed. Then, the mixture was stirred at 60 °C in an oil bath overnight (16 h). The flask was opened to the air, add saturated aqueous solution of ammonium chloride (15 mL). The mixture was extracted with dichloromethane (3 x 15 mL), washed with water (15 mL), dried over anhydrous Na_2SO_4, filtered and volatiles removed in the rotary evaporator. Crude samples were purified by silica-gel or aluminum oxide column chromatography. Note: some crude samples were purified by liquid-liquid extraction protocol for the removal of unreacted aldehydes and other impurities employing sodium bisulfite.[6]

Characterization of isolated products:

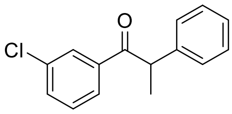


4ab

The residue was purified by silica-gel column chromatography employing cyclohexane/ethyl acetate (99/2) as eluent (Rf = 0.3) to afford the desired product as yellow solid. Isolated mass: 0.18 g; 75% yield. The physical and spectral data were identical to those previously reported for this compound.[7]

^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.87 (m, 2H), 7.36 – 7.31 (m, 2H), 7.30 – 7.22 (m, 5H), 4.61 (q, *J* = 6.9 Hz, 1H), 1.54 (d, *J* = 6.9 Hz, 3H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$): *δ* 199.2, 141.3, 139.3, 135.5, 134.9, 130.3, 129.2, 128.9, 127.8, 127.2, 48.2, 19.6 ppm.

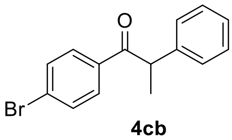


4bb

The residue was purified by the liquid-liquid extraction protocol[6] to afford the desired product as brown solid. Isolated mass: 0.15 g and yield: 61%. The physical and spectral data were identical to those previously reported for this compound.[8]

^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.89 (s, 1H), 7.79 (dd, *J* = 19.8, 7.8 Hz, 1H), 7.42 (d, 1H), 7.30 – 7.09 (m, 6H), 4.59 (q, *J* = 6.8 Hz, 1H), 1.52 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): *δ* 199.2, 141.0, 138.2, 134.9, 132.8, 129.9, 129.2, 128.9, 127.8, 127.6, 127.0, 48.3, 19.5 ppm.

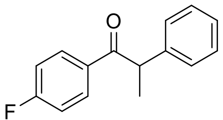


4cb

The residue was purified by the liquid-liquid extraction protocol[6] and by silica gel column chromatography using cyclohexane/EtOAc (65/35) to afford the desired product as light brown oil. Isolated mass: 0.08 g and yield: 27%. The physical and spectral data were identical to those previously reported for this compound.[7]

^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.80 – 7.75 (m, 2H), 7.51 – 7.45 (m, 2H), 7.30 – 7.25 (m, 2H), 7.23 – 7.17 (m, 3H), 4.58 (q, *J* = 6.8 Hz, 1H), 1.50 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): *δ* 199.4, 141.3, 135.3, 131.9, 130.5, 129.3, 127.8, 127.2, 48.2, 19.5 ppm.



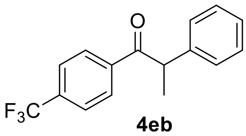
4db

The residue was purified by aluminum oxide column chromatography using cyclohexane/EtOAc (99/1) to obtain yellow oil. Isolated mass: 0.11 g and yield: 48%. The physical and spectral data were identical to those previously reported for this compound.[7]

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.99 – 7.82 (m, 2H), 7.24 (m, 2H), 7.20 – 7.07 (m, 2H), 7.09 – 6.86 (m, 2H), 4.61 (q, J = 6.8 Hz, 1H), 1.5 (d, J = 6.8 Hz 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 198.8, 166.6, 164.6, 141.5, 133.0, 133.0, 131.6, 131.5, 129.2, 127.8, 127.1, 115.8, 115.62, 48.1, 19.6 ppm.

^{19}F NMR (470 MHz, CDCl$_3$): δ -105.6 (s) ppm.



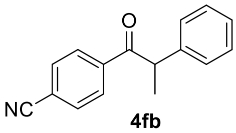
4eb

The residue was purified by the liquid-liquid extraction protocol[6] and by silica gel column chromatography using cyclohexane/EtOAc (90/10) to afford the desired product as orange solid. Isolated mass: 0.07 g and yield: 25%. The physical and spectral data were identical to those previously reported for this compound.[9]

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.02 (d, J = 8.2 Hz, 2H), 7.62 (t, J = 8.2 Hz, 2H), 7.33 – 7.20 (m, 5H), 4.65 (q, J = 6.8 Hz, 1H), 1.55 (d, J = 6.8 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 199.4, 140.9, 139.3, 129.4, 129.2, 127.9, 127.4, 125.7, 125.7, 125.6, 48.7, 19.5 ppm.

^{19}F NMR (470 MHz, CDCl$_3$): δ -63.19 (s) ppm.

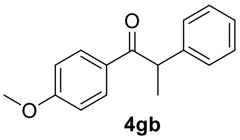


4fb

The residue was purified by silica gel column chromatography using cyclohexane/DCM (60/40) to afford the desired product as orange yellow. Isolated mass: 0.07 g and yield: 30%. The physical and spectral data were identical to those previously reported for this compound.[9]

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.00-7.98 (m, 2H), 7.67-7.65 (m, 2H), 7.34 – 7.2 (m, 5H), 4.61 (q, J = 6.8 Hz, 1H), 1.53 (d, J = 6.8 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 197.0, 145.3, 138.8, 133.2, 131.8, 129.1, 129.1, 127.6, 117.5, 110.1, 46.7, 18.2 ppm.

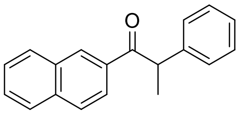


4gb

The residue was purified by the liquid-liquid extraction protocol[6] to afford the desired products brown solid. Isolated mass: 0.1 g and yield: 41%. The physical and spectral data were identical to those previously reported for this compound.[10]

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.94 (m, 2H), 7.28 (m, 2H), 7.22 – 7.17 (m, 2H), 6.85 (m, 3H), 4.64 (q, J = 6.9 Hz, 1H), 3.82 (s, 3H), 1.53 (d, J = 6.9 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 199.0, 163.3, 142.1, 131.2, 129.6, 127.8, 126.9, 113.8, 55.5, 47.7, 19.7 ppm.

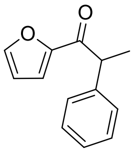


4hb

The residue was purified by the liquid-liquid extraction protocol[6] to afford the desired products brown solid. Isolated mass: 0.25 g and yield: 96%. The physical and spectral data were identical to those previously reported for this compound.[9]

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.48 (s, 1H), 8.01 (dd, J = 8.7, 1.7 Hz, 1H), 7.90 (d, J = 8.7 Hz, 1H), 7.82 (d, J = 8.7 Hz, 2H), 7.53 (m 2H), 7.32 (m, 3H), 7.19 (m, 1H), 4.85 (q, J = 6.9 Hz, 1H), 1.60 (d, J = 6.9 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 200.7, 142.0, 135.7, 134.2, 132.8, 130.8, 130.0, 129.4, 128.7, 128.7, 128.1, 128.0, 127.3, 127.0, 124.9, 48.3, 19.9 ppm.

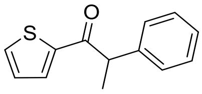


4ib

The residue was purified by aluminum oxide column chromatography using cyclohexane/EtOAc (99/1) to obtain as yellow solid. Isolated mass: 0.12 g and yield: 60%. The physical and spectral data were identical to those previously reported for this compound.[9]

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.53 (d, J = 1.5 Hz, 1H), 7.41 – 7.26 (d, J = 1.5 Hz, 4H), 7.24 – 7.19 (m, 1H), 7.13 (d, J = 3.6 Hz, 1H), 6.46 (dd, J = 3.6, 1.7 Hz, 1H), 4.49 (q, J = 7.0 Hz, 1H), 1.54 (d, J = 7.0 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 189.8, 152.6, 146.7, 141.2, 129.2, 128.3, 128.2, 118.2, 112.55, 48.3, 18.7 ppm.

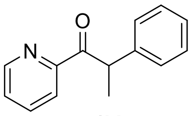


4jb

The residue was purified by the liquid-liquid extraction protocol[6] to afford the desired product as brown oil. Isolated mass: 0.13 g and yield: 60%. The physical and spectral data were identical to those previously reported for this compound.[9]

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.6 (dd, J = 3.8, 1.0 Hz, 1H), 7.5 (dd, J = 3.8, 1.0 Hz, 1H), 7.3 – 7.2 (m, 4H), 7.2 (m, 1H), 7.0 (m, 1H), 4.5 (q, J = 6.9 Hz, 1H), 1.5 (d, J = 6.9 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 193.4, 143.8, 141.4, 133.7, 132.5, 129.1, 128.2, 127.9, 127.2, 49.5, 19.3 ppm.

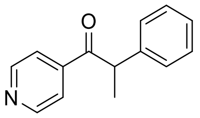


4kb

The residue was purified by the liquid-liquid extraction protocol[6] to afford the desired product as light brown solid. Isolated mass: 0.11 g and yield: 65%. The physical and spectral data were identical to those previously reported for this compound.[7]

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.66 – 8.65 (m, 1H), 8.03 – 7.98 (m, 1H), 7.77 (m, 1H), 7.42 – 7.35 (m, 3H), 7.29 (dd, J = 21.4, 4.6 Hz, 3H), 7.19 – 7.11 (m, 4H), 5.42 (q, J = 7.1 Hz, 1H), 1.57 – 1.54 (d, J = 7.1 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 202.0, 153.1, 148.9, 141.0, 136.9, 128.6, 127.0, 126.8, 122.9, 45.1, 18.3 ppm.



4lb

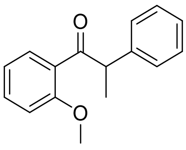
The residue was purified by aluminum oxide column chromatography using cyclohexane/EtOAc (85/15) to obtain yellow oil. Isolated mass: 0.05 g and yield: 23%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.72 (dd, J = 4.5, 1.6 Hz, 2H), 7.68 (dd, J = 4.5, 1.6 Hz, 2H), 7.35 – 7.25 (m, 2H), 4.60 (q, J = 6.8 Hz, 1H), 1.56 (d, J = 6.8 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 200.0, 151.2, 151.24, 151.09, 142.9, 140.6, 129.7, 127.7, 122.1, 49.1, 19.5 ppm.

HRMS (ESI) *m/z* calcd for $[M+H]^+$: 212.1069; found: 212.1065.

IR (neat): 2973, 1680, 1587, 1208, 950, 714 cm^{-1}.

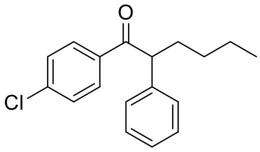


4mb

The residue was purified by the liquid-liquid extraction protocol[6] and by silica gel column chromatography using cyclohexane/EtOAc (97/3) to afford the desired product as light yellow oil. Isolated mass: 0.03 g and yield: 11%. The physical and spectral data were identical to those previously reported for this compound.[11]

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.43 (m, 1H), 7.35 – 7.33 (m, 2H), 7.19 (m, 4H), 6.89 (m, 2H), 4.71 (q, J = 6.9 Hz, 1H), 3.84 (s, 3H), 1.51 (d, J = 6.9 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 204.3, 157.7, 141.5, 132.9, 130.5, 129.1, 128.5, 128.3, 126.7, 120.7, 111.4, 55.5, 51.9, 18.9 ppm.



4ac

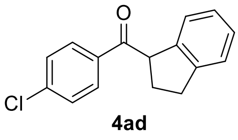
The residue was purified by aluminum oxide column chromatography using cyclohexane/EtOAc (99/1) to obtain yellow oil. Isolated mass: 0.12 g and yield: 42%.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.8 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 7.24 – 7.13 (m, 4H), 4.40 (m, 1H), 2.13 – 2.07 (m, 2H), 1.77-1.73 (m, 2H), 1.29 – 1.09 (m, 5H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 199.0, 139.7, 139.3, 135.4, 130.2, 129.1, 128.9, 128.3, 127.1, 53.9, 33.8, 30.0, 22.8, 14.1 ppm.

HRMS (ESI) *m/z* calcd for [M+H]$^+$: 287.1197; found: 287.1194.

IR (neat): 2930, 2859, 1681, 1453, 1202, 752 cm^{-1}.

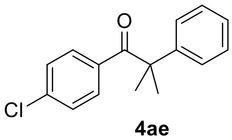


4ad

The residue was purified by silica gel column chromatography using cyclohexane/EtOAc (99/1) to obtain brown oil. Isolated mass: 0.12 g and yield: 47%. The physical and spectral data were identical to those previously reported for this compound.[12]

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.00 – 7.97 (m, 2H), 7.51 – 7.46 (m, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.11 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 7.4 Hz, 1H), 5.02 – 4.96 (m, 1H), 3.25 – 2.94 (m,2H), 2.46 (m, 2H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$) δ 199.4, 144.7, 141.2, 139.8, 135.5, 130.4, 129.2, 127.8, 127.6, 126.5, 125.1, 52.7, 32.1, 29.7 ppm.



4ae

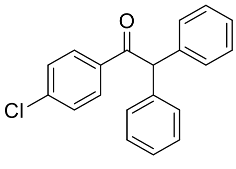
The residue was purified by silica gel column chromatography using cyclohexane/DCM (80/20) to obtain yellow oil. Isolated mass: 0.11 g and yield: 42%.

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.45 – 7.41 (m, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 3H), 7.21 – 7.16 (m, 2H), 1.59 (s, 6H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 202.5, 145.2, 138.2, 134.5, 131.4, 129.5, 128.4, 127.1, 125.8, 51.6, 27.9 ppm.

HRMS (ESI) *m/z* calcd for $[M+H]^+$: 259.0889; found: 259.0881.

IR (neat): 3085, 2929, 1670, 1246, 627 cm^{-1}.

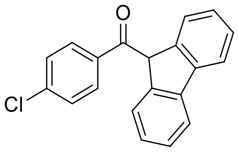


4af

The residue was purified by the liquid-liquid extraction protocol and by silica gel column chromatography using cyclohexane/EtOAc (99/1) to afford the desired product yellow solid. Isolated mass: 0.14 g and yield: 48%. The physical and spectral data were identical to those previously reported for this compound.[13]

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.95 – 7.91 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.31 (m, 6H), 7.24 (m, 4H), 5.96 (s, 1H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 197.0, 142.1, 139.5, 138.8, 135.1, 130.4, 129.1, 129.0, 128.8, 128.4, 127.3, 126.9, 59.6 ppm.

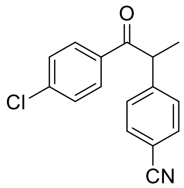


4ag

The residue was purified by the liquid-liquid extraction protocol and by silica gel column chromatography using cyclohexane/EtOAc (99/1), to afford the desired product as yellow solid. Isolated mass: 0.08 g and yield: 26%. The physical and spectral data were identical to those previously reported for this compound.[13]

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.86 (m, 2H), 7.55 (m, 2H), 7.5 – 7.37 (m, 5H), 7.27 (m, 3H), 5.49 (s, 1H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 197.1, 142.2, 141.6, 134.8, 130.6, 129.0, 128.4, 127.8, 125.3, 124.5, 120.8, 59.7 ppm.

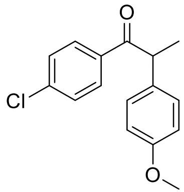


4ah

The residue was purified by the liquid-liquid extraction protocol to afford the desired product as orange oil. Isolated mass: 0.15 g and yield: 56%. The physical and spectral data were identical to those previously reported for this compound.[14]

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.86 – 7.84 (m, 2H), 7.61 – 7.59 (d, J = 5.4 Hz, 2H), 7.38 (d, J = 5.4 Hz, 4H), 4.71 – 4.67 (q, J = 6.8 Hz, 1H), 1.55 (d, J = 6.8 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 199.0, 140.6, 139.7, 132.5, 129.4, 129.3, 127.8, 127.5, 118.1, 116.1, 48.8, 19.4 ppm.

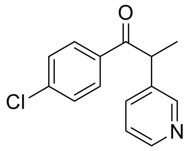


4ai

The residue was purified by the liquid-liquid extraction protocol to afford the desired product as black oil. Isolated mass: 0.05 g and yield: 18%. The physical and spectral data were identical to those previously reported for this compound.[15]

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.88 – 7.85 (d, J = 6.8 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.15 (d, J = 6.8 Hz, 2H), 6.85 – 6.81 (m, 2H), 4.56 (q, J = 6.8 Hz, 1H), 3.76 (s, 3H), 1.45 (d, J = 6.8 Hz, 3H) ppm.

^{13}C NMR (126 MHz, CDCl$_3$): δ 199.4, 158.7, 139.2, 134.9, 133.3, 130.3, 128.9, 128.8, 114.6, 55.3, 47.3, 19.5 ppm.



4aj

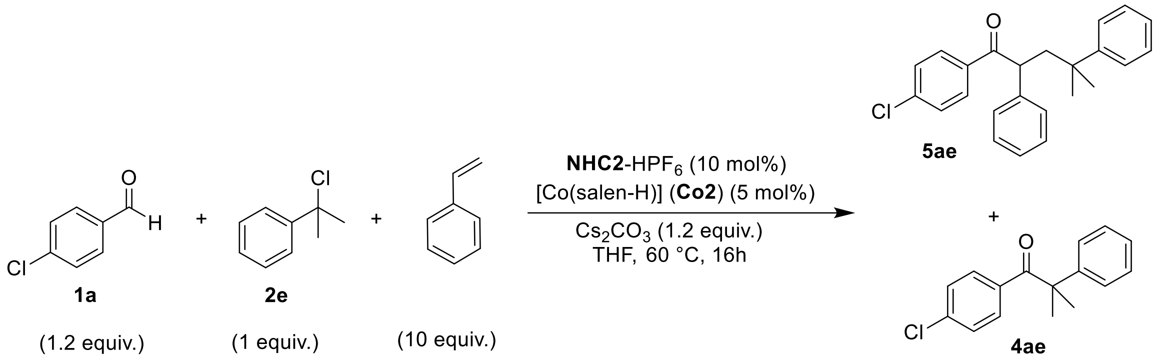
The residue was purified by the liquid-liquid extraction protocol to afford the desired product as black oil. Isolated mass: 0.1 g and yield: 41%. The physical and spectral data were identical to those previously reported for this compound.

^{1}H NMR (400 MHz, CDCl$_3$): δ 8.58 (m, 1H), 8.45 (m, 1H), 7.89– 7.87 (m, 2H), 7.59 – 7.57 (m, 1H), 7.40 – 7.38 (m, 2H), 7.24 – 7.21 (m, 1H), 4.68 (q, J = 6.9 Hz, 1H), 1.56 (d, J = 6.9 Hz, 3H) ppm.

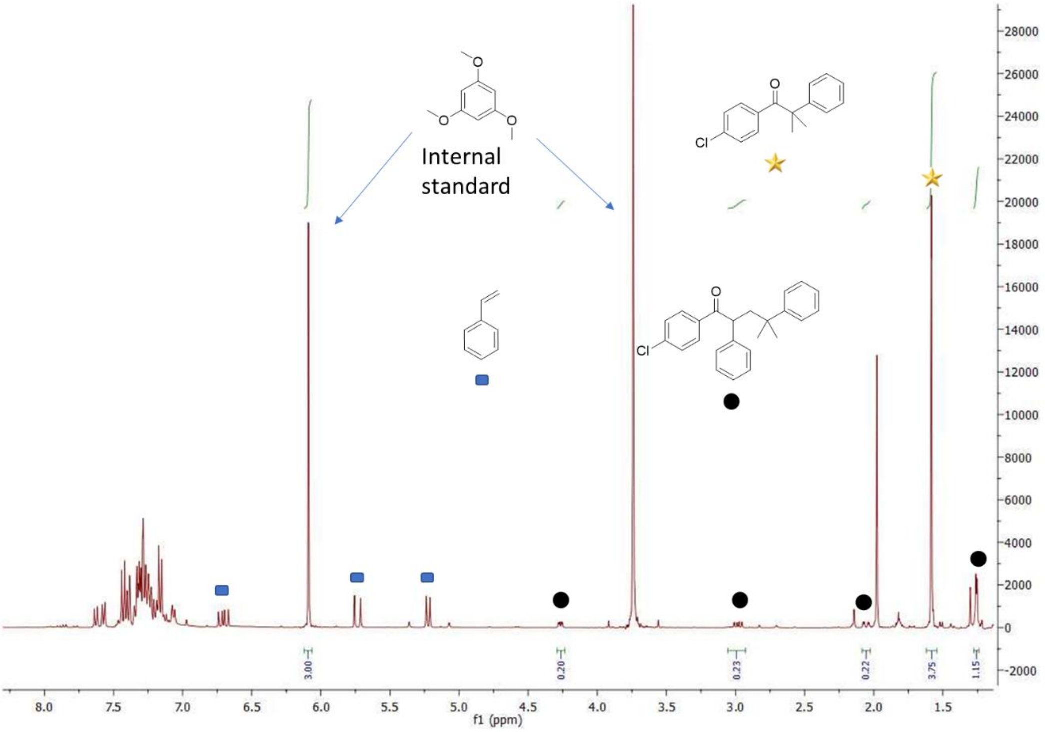
^{13}C NMR (126 MHz, CDCl$_3$): δ 198.4, 149.3, 148.5, 139.8, 135.1, 134.2, 130.1, 129.1, 124.0, 45.0, 19.6 ppm.

HRMS (ESI) *m/z* calcd for $[M+H]^+$: 246.0680; found: 246.0677.

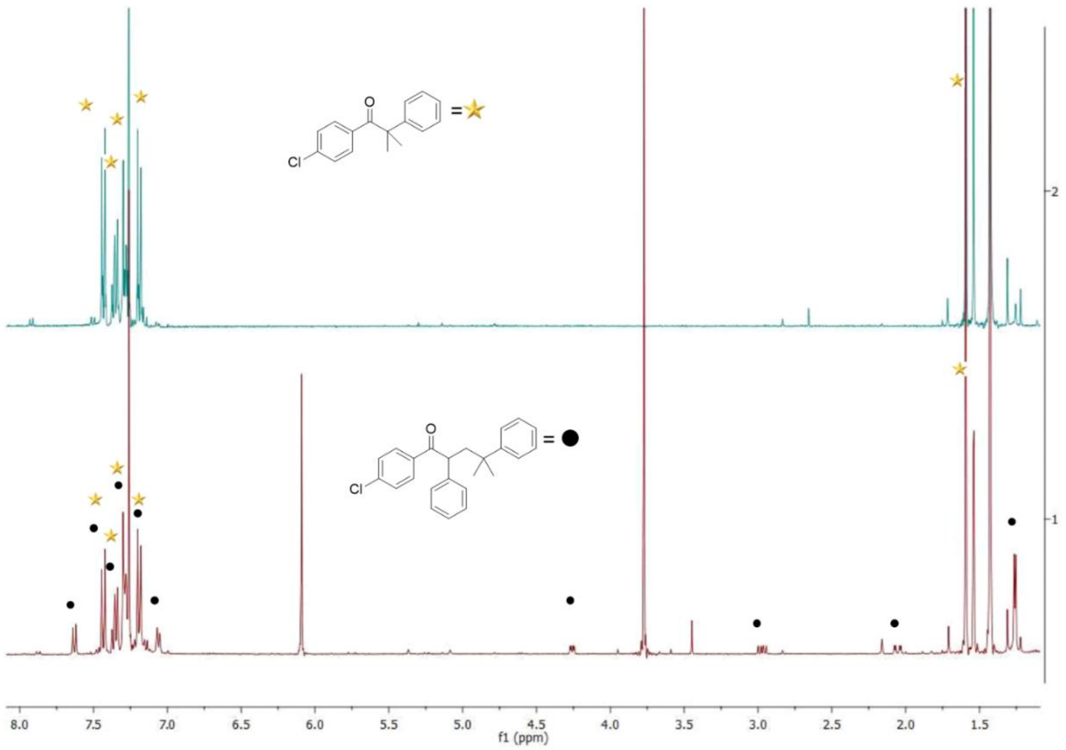
IR (neat): 2960, 2848, 1695, 1090, 1015, 795, 702, 630 cm^{-1}.



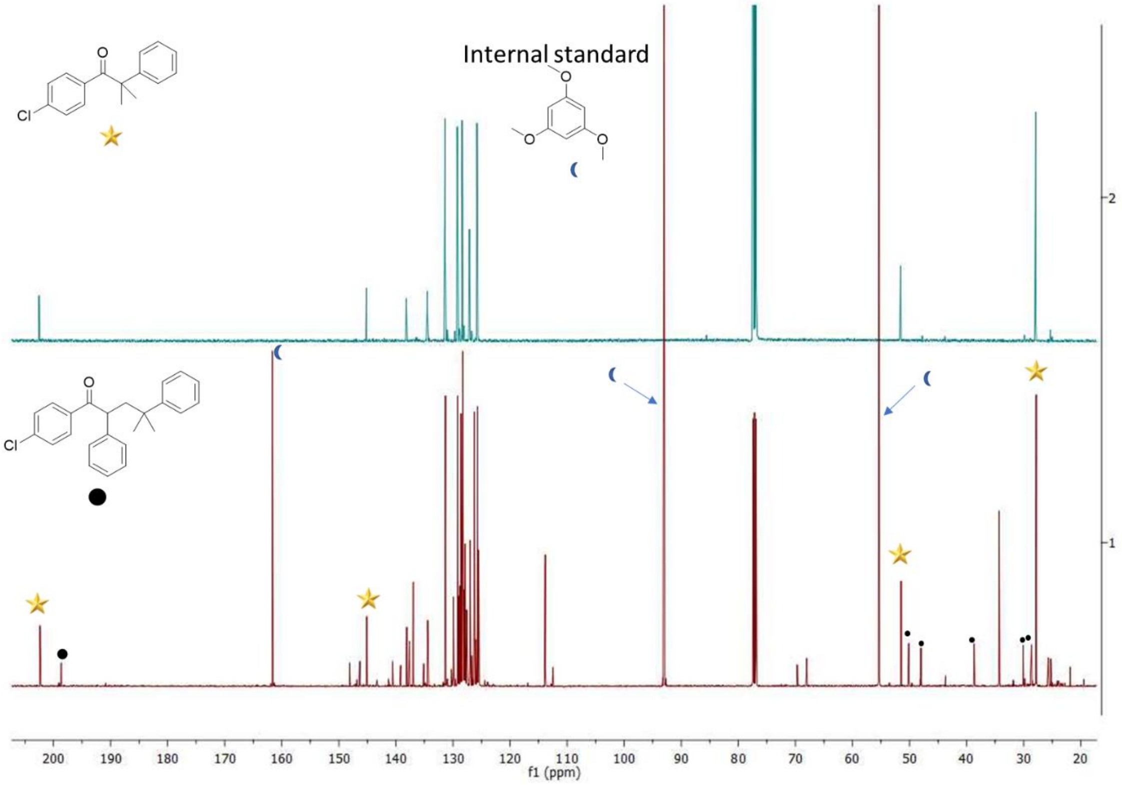
In an argon filled glove-box [Co(salen-H)] (**Co2**; 0.016 g, 0.05 mmol) was introduced in a Teflon capped 15 mL Schlenk reaction tube. Then, the flask was sealed and put it out of the glovebox and connected to a Schlenk line. Under argon atmosphere and at room temperature, aldehyde (**1a**, 1.2 mmol), **NHC2**-HPF$_6$ (0.041 g, 0.1 mmol), 4 mL of freshly distilled dry THF, benzyl chloride (**2e**, 1 mmol), the styrene (1.15 mL, 10 mmol) and Cs$_2$CO$_3$ (0.39 g, 1.2 mmol) were added in this order and the flask was sealed. Then, the mixture was stirred at 60 °C in an oil bath overnight (16 h). The flask was opened to the air, 1,3,5- trimethoxybenzene (TMB) as internal standard (0.168 g, 1 mmol) was added, followed by a saturated aqueous solution of ammonium chloride (15 mL). The mixture was extracted with dichloromethane (3 x 15 mL), washed with water (15 mL), dried over anhydrous Na$_2$SO$_4$, filtered and volatiles removed in the rotary evaporator. The crude mixture contained **4ae** and **5ae** and the ratio was determined with the internal standard by ^{1}H NMR integration. Purification by column chromatography failed. The presence of **5ae** was confirmed from the characteristic peaks found in a similar molecule from the literature.[16]



^{1}H NMR analysis of the crude mixture with TMB in CDCl$_3$



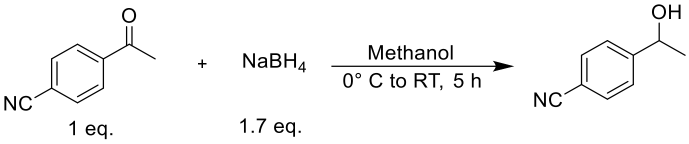
^{1}H NMR of the attempted purification by column chromatography in $CDCl_3$



^{13}C NMR of the attempted purification by column chromatography in $CDCl_3$

Synthesis of starting materials

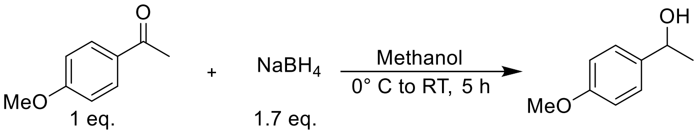
Synthesis of benzyl alcohols



6h

Standard procedure according to a published procedure:[17] The corresponding ketone (1 eq.) was dissolved in 20 mL of methanol, and slowly sodium borohydride (1.7 eq.) was added at 0 °C and the reaction was stirred at room temperature for 5 h. Then, it was quenched by HCl 1M aqueous solution and extracted it by dichloromethane, washed with brine, dried over anhydrous $MgSO_4$, filtered and volatiles removed in the rotary evaporator. Isolated mass: 1.9 g and yield: 95%. The physical and spectral data were identical to those previously reported for this compound.[18]

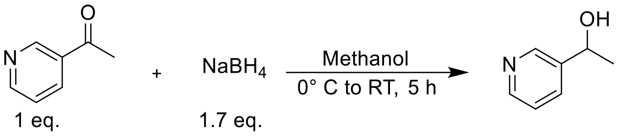
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 5.08 – 4.74 (m, 1H), 1.52 (m, 3H) ppm.



6i

Isolated mass: 0.5 g and yield: 66%. The physical and spectral data were identical to those previously reported for this compound.[18]

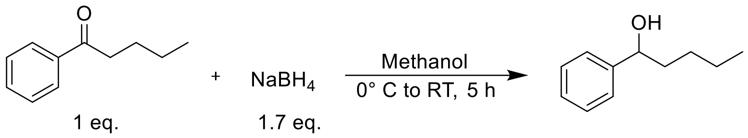
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 – 7.20 (m, 2H), 6.94 – 6.82 (m, 2H), 4.29 – 4.18 (m, 1H), 3.81 (s, 3H), 1.42 (m, 3H) ppm.



6j

Isolated mass: 0.28 g and yield: 45%. The physical and spectral data were identical to those previously reported for this compound.[19]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.81 – 8.27 (m, 2H), 7.69 (m, 1H), 7.30 – 7.19 (m, 1H), 4.92 (m, 1H), 2.75 – 1.85 (m, 1H), 1.68 – 1.42 (m, 3H) ppm.



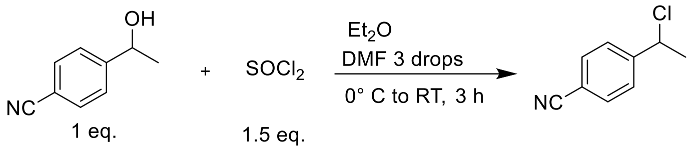
6c

Isolated mass: 1 g and yield: 97%. The physical and spectral data were identical to those previously reported for this compound.[20]

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.33 (d, J = 3.4 Hz, 2H), 7.25 (d, J = 3.4 Hz, 2H), 7.17 (m, 1H), 4.53 (m, 1H), 1.80 – 1.51 (m, 2H), 1.39 – 1.08 (m, 4H), 0.80 (m, 3H) ppm.

Synthesis of benzyl chlorides

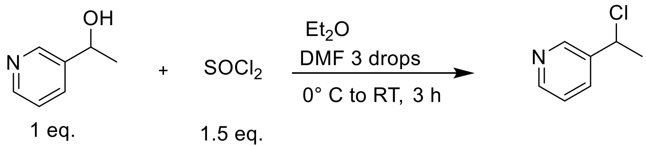
Procedure A:[21]



2h

In a Schlenk reaction tube under argon atmosphere, the corresponding alcohol (1 eq.) was dissolved in 10 mL of diethyl ether and slowly SOCl$_2$ (1.5 eq.) was added at 0 °C followed by 3 drops of DMF. The reaction was stirred at room temperature for 3h. Then, it was quenched by saturated NaHCO$_3$ aqueous solution and extracted with dichloromethane, washed with brine, dried over anhydrous MgSO$_4$, filtered and volatiles removed in the rotary evaporator. Isolated mass: 0.47 g and yield: 91%. The physical and spectral data were identical to those previously reported for this compound.[22]

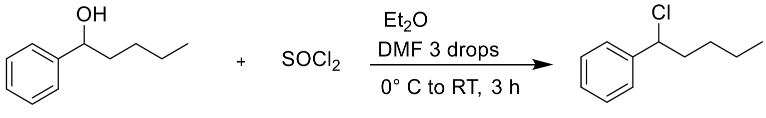
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.76 – 7.65 (m, 2H), 7.58 – 7.54 (m, 2H), 5.10 (q, J = 6.8 Hz, 1H), 1.86 (d, J = 6.8 Hz, 3H) ppm.



2j

According to procedure A. **2j** was obtained with Isolated mass: 0.8 g and yield: 40%. The spectral data were consistent to those previously reported for this compound.[19]

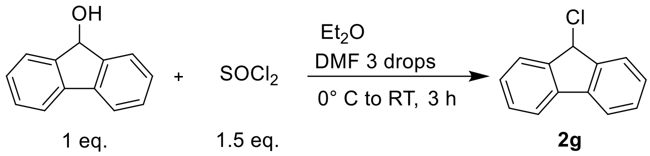
^{1}H NMR (400 MHz, CDCl$_3$): δ 8.62 (m, 1H), 8.60 – 8.51 (m, 1H), 7.84 – 7.72 (m, 1H), 7.30 (m, 1H), 5.11 (q, J = 6.8 Hz, 1H), 1.88 (d, J = 6.8 Hz, 2H) ppm.



2c

According to procedure A**. 2c** was obtained with Isolated mass: 0.2 g and yield: 20%. The spectral data were consistent to those previously reported for this compound.

^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.44 – 7.26 (m, 5H), 4.90 – 4.78 (m, 1H), 2.24 – 1.99 (m, 2H), 1.49 – 1.24 (m, 4H), 0.89 (m, 3H) ppm.

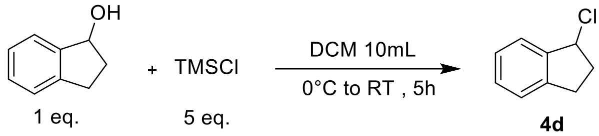


2g

According to procedure **A. 2g** was obtained with Isolated mass: 0.43 g and yield: 82%. The spectral data were consistent to those previously reported for this compound.[23]

^{1}H NMR (500 MHz, CDCl$_3$): *δ* 7.66 (m, 4H), 7.46 – 7.39 (m, 2H), 7.35 (m, 2H), 5.81 (s, 1H) ppm.

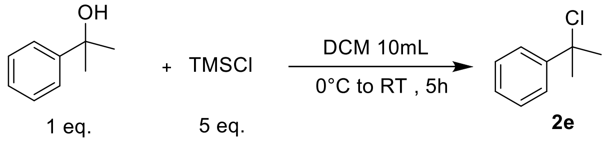
Procedure B:[24]



4d

In a Schlenk reaction tube under argon atmosphere, the corresponding alcohol (1 eq.) was dissolved in 10 mL of dichloromethane, and slowly distilled TMSCl (5 eq.) was added at 0 °C. The reaction was stirred at room temperature for 2 h. Then, it was quenched by water and extracted with dichloromethane, washed with brine, dried over anhydrous MgSO$_4$, filtered and volatiles removed in the rotary evaporator. Isolated mass: 0.55 g and yield: 90%. The spectral data were consistent to those previously reported for this compound.[25]

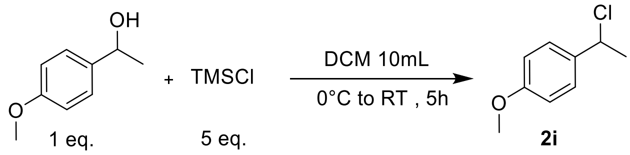
^{1}H NMR (400 MHz, CDCl$_3$): *δ* 7.44 (m, 1H), 7.31 – 7.26 (m, 2H), 7.26 – 7.21 (m, 1H), 5.44 (m, 1H), 3.20 (m, 1H), 2.90 (m, 1H), 2.72 – 2.51 (m, 1H), 2.45 – 2.20 (m, 1H) ppm.



2e

According to procedure B**. 2e** was obtained with Isolated mass: 0.3 g and yield: 55%. The spectral data were consistent to those previously reported for this compound.[25]

^{1}H NMR (500 MHz, CDCl$_3$): *δ* 7.54 – 7.50 (m, 2H), 7.31 – 7.26 (m, 2H), 7.23 – 7.19 (m, 1H), 1.93 (s, 6H) ppm.

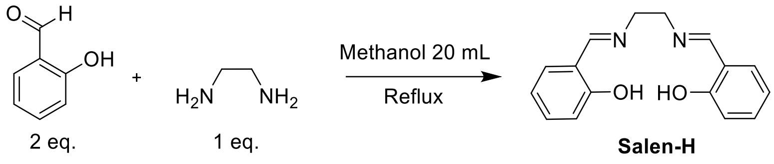


2i

According to procedure **B**. **2i** was obtained with Isolated mass: 0.2 g and yield 60%. The spectral data were consistent to those previously reported for this compound.[22]

^{1}H NMR (400 MHz, CDCl$_3$): δ 7.41 – 7.31 (m, 2H), 6.96 – 6.80 (m, 2H), 5.16 – 5.02 (m, 1H), 3.81 (s, 3H), 1.85 (m, 3H) ppm.

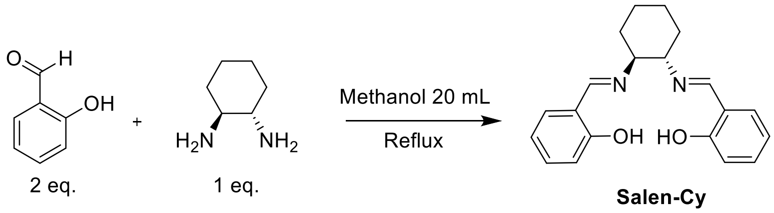
Cobalt(salen) complex synthesis



Salen-H

According to a published procedure. [26] In a round bottom flask salicylaldehyde (2 eq., 40 mmol) was added to 20 mL methanol, followed by slow addition of the corresponding ethylene diamine (1 eq., 20 mmol). Then, the mixture was stirred under reflux for 2h. It was cooled down to 0 °C, filtered and washed with methanol. Finally, it was recrystallized in boiling methanol. **Salen-H** was obtained as yellow crystals. Isolated mass: 5.1 g and yield 94%. The spectral data were consistent to those previously reported for this compound.

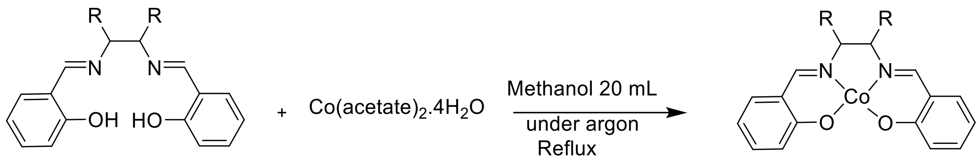
^{1}H NMR (400 MHz, CDCl$_3$): δ 13.19 (s,2H), 8.36 (s, 2H), 7.29 (m 2H), 7.23 (m, 2H), 6.94 (d, J = 7.4 Hz, 2H), 6.86 (t, J = 7.4 Hz, 2H), 3.95 (s, 4H), 1.56 (s, 2H) ppm.



Salen-Cy

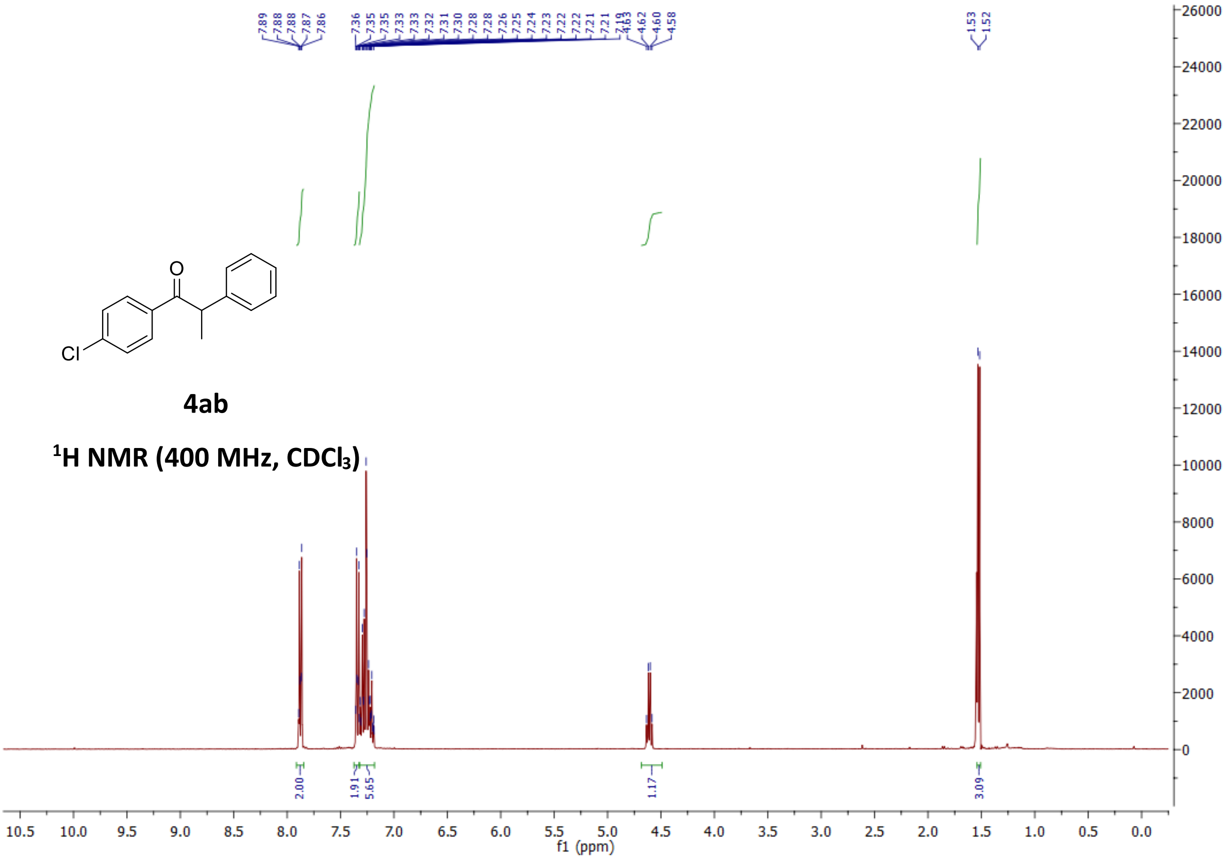
In a round bottom flask salicylaldehyde (2 eq., 40 mmol) was added to 20 mL methanol, followed by slow addition of the corresponding *trans*-1,2-diaminocyclohexane (1 eq., 20 mmol). Then, the mixture was stirred under reflux for 2h. It was cooled down to 0 °C, filtered and washed with methanol. Finally, it was recrystallized in boiling methanol). **Salen-Cy** ligand was obtained as yellow crystals. Isolated mass: 6 g and yield 94%. The spectral data were consistent to those previously reported for this compound.[27]

^{1}H NMR (500 MHz, CDCl$_3$): δ 13.32 (s, 2H), 8.25 (s, 2H), 7.23 (ddd, J = 8.8, 7.5, 1.6 Hz, 2H), 7.14 (dd, J = 7.5, 1.6 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.79 (m, 2H), 3.72 (q, J = 7.0 Hz, 3H), 3.37 – 3.28 (m, 2H), 2.09 – 1.83 (m, 4H), 1.31 – 1.15 (m, 4H) ppm.



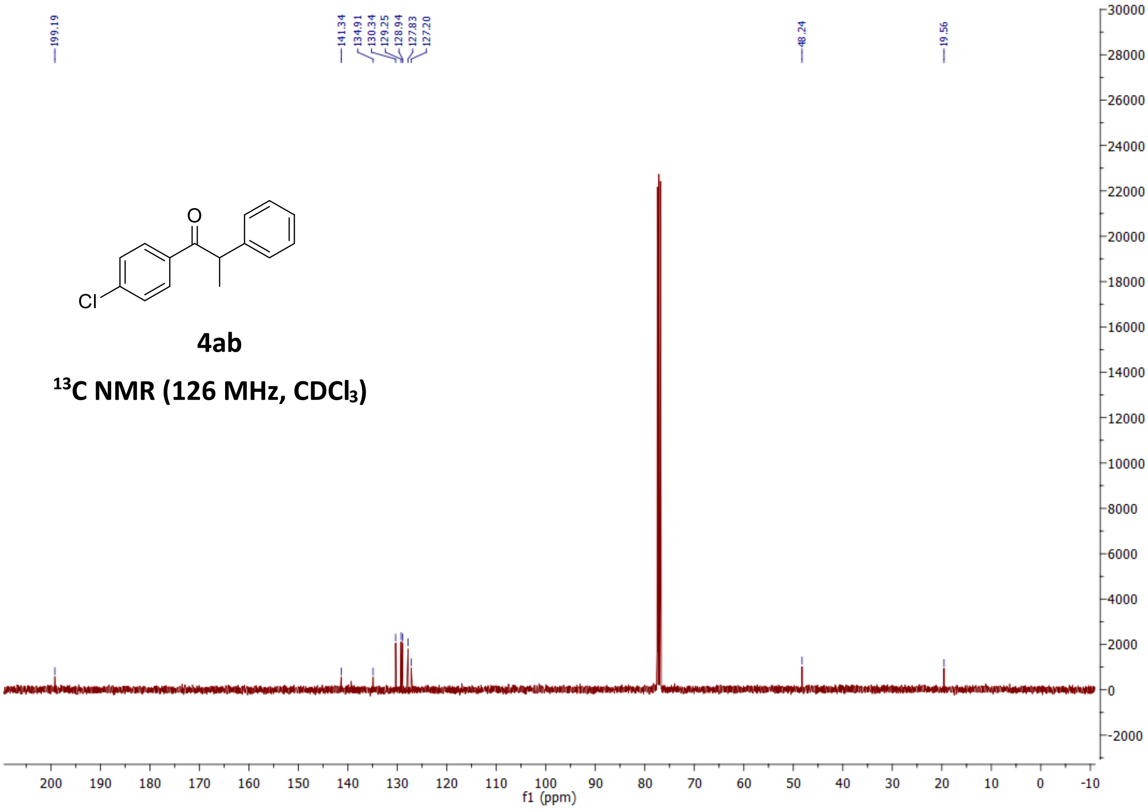
According to a published procedure,[27] in a Schlenk reaction tube under argon atmosphere, the corresponding salen (1.05 eq.) was dissolved in degassed methanol followed by the addition of cobalt acetate (1 eq.). Then, the mixture was stirred under reflux. It was cooled to 0 °C, filtered by canula under argon atmosphere and dried under vacuum. The solid was stored in the glovebox. A brown complex was obtained with Isolated mass: 0.5 g and yield: 90% for [Co(salen-H)] (**Co2**). A dark purple complex was obtained with Isolated mass: 1.28 g and yield: 90% for [Co(salen-Cy)] (**Co1**).

NMR spectra



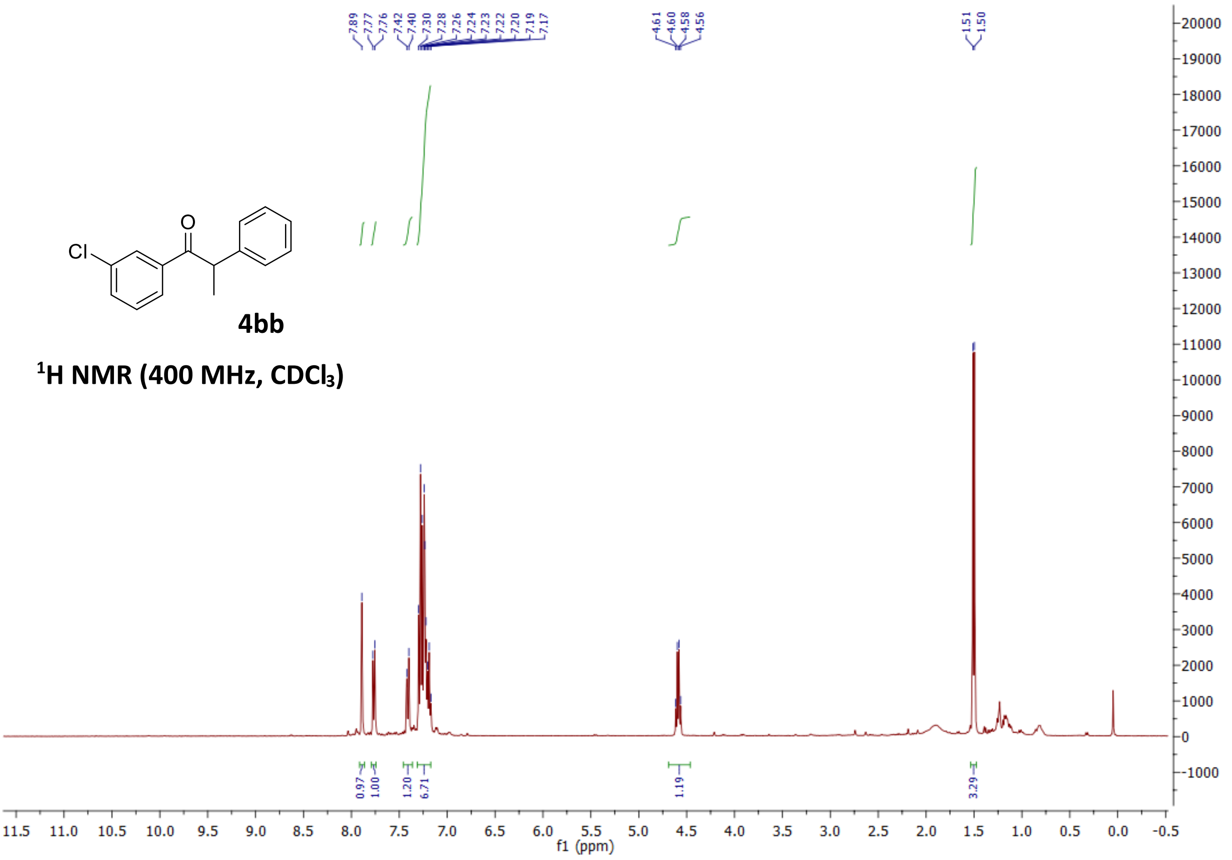
4ab

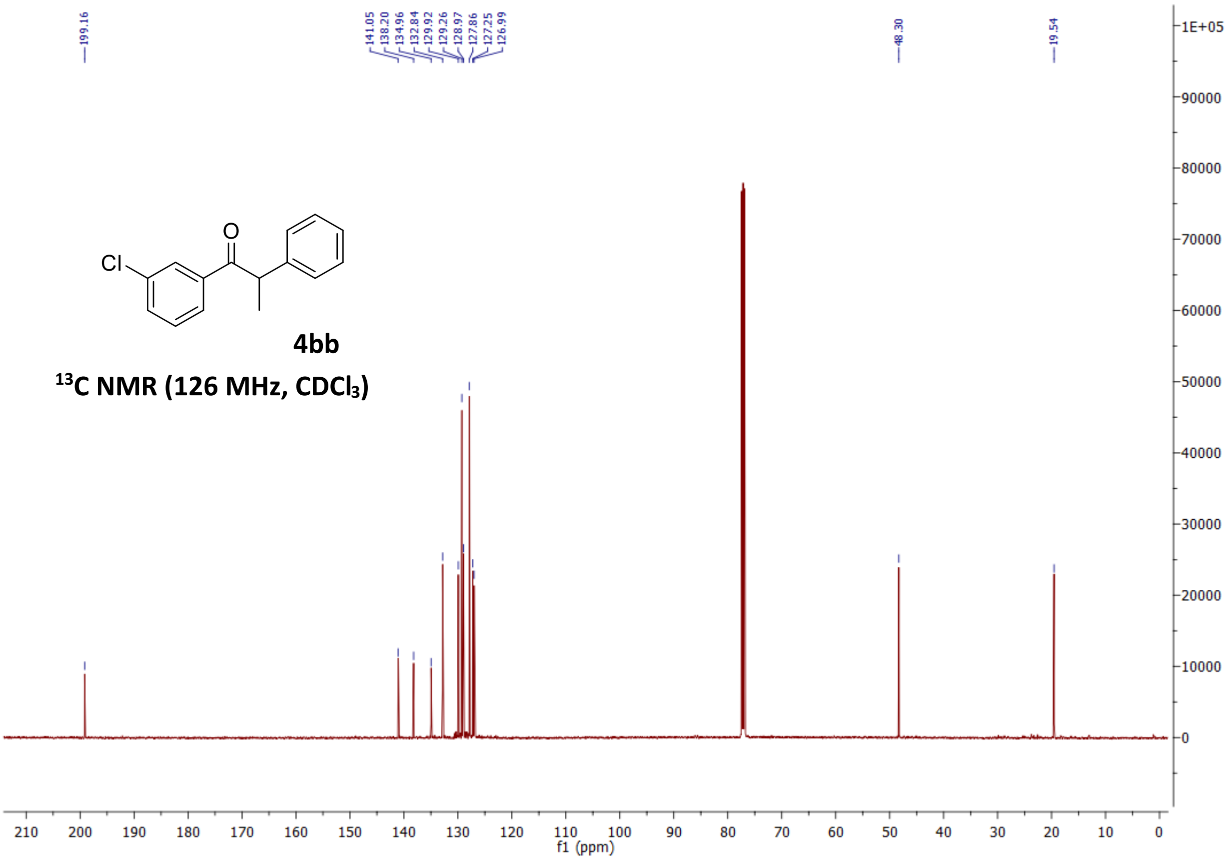
^{1}H NMR (400 MHz, CDCl$_3$)

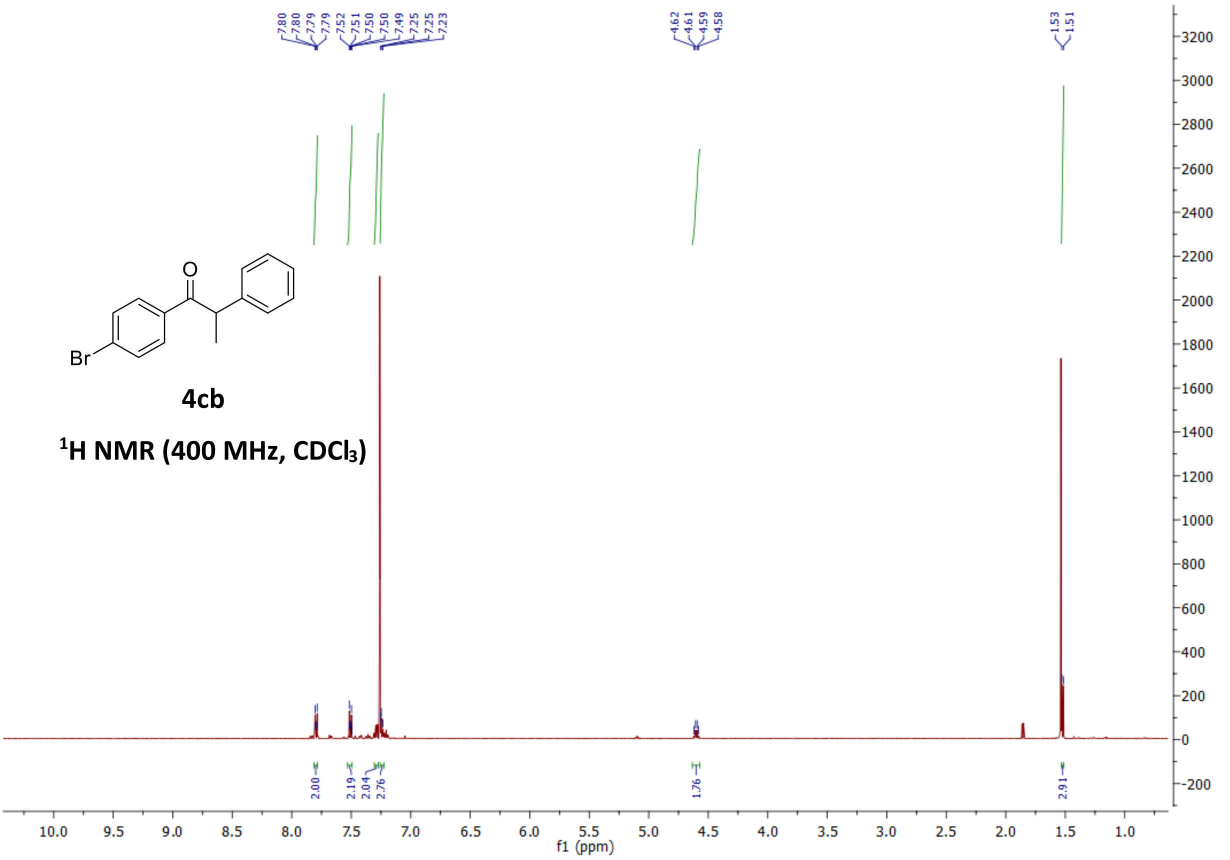


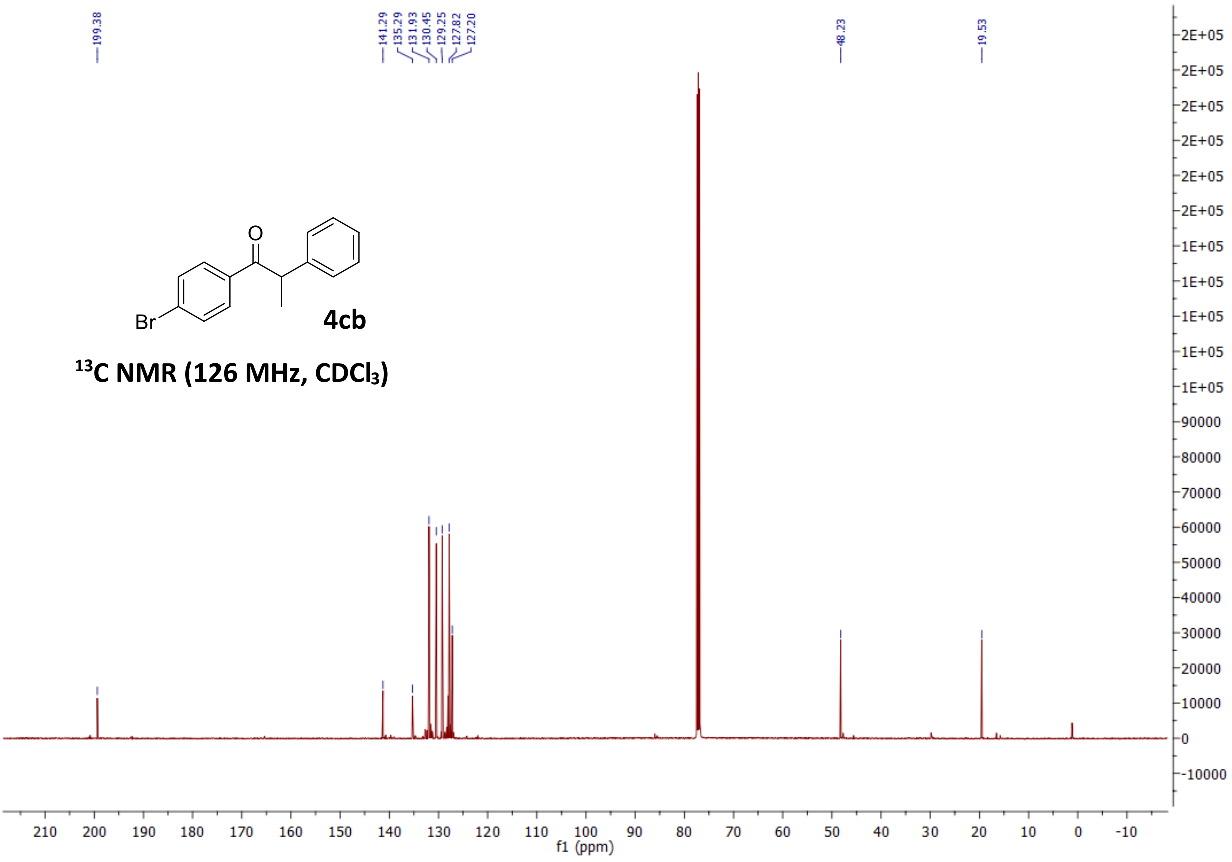
4ab

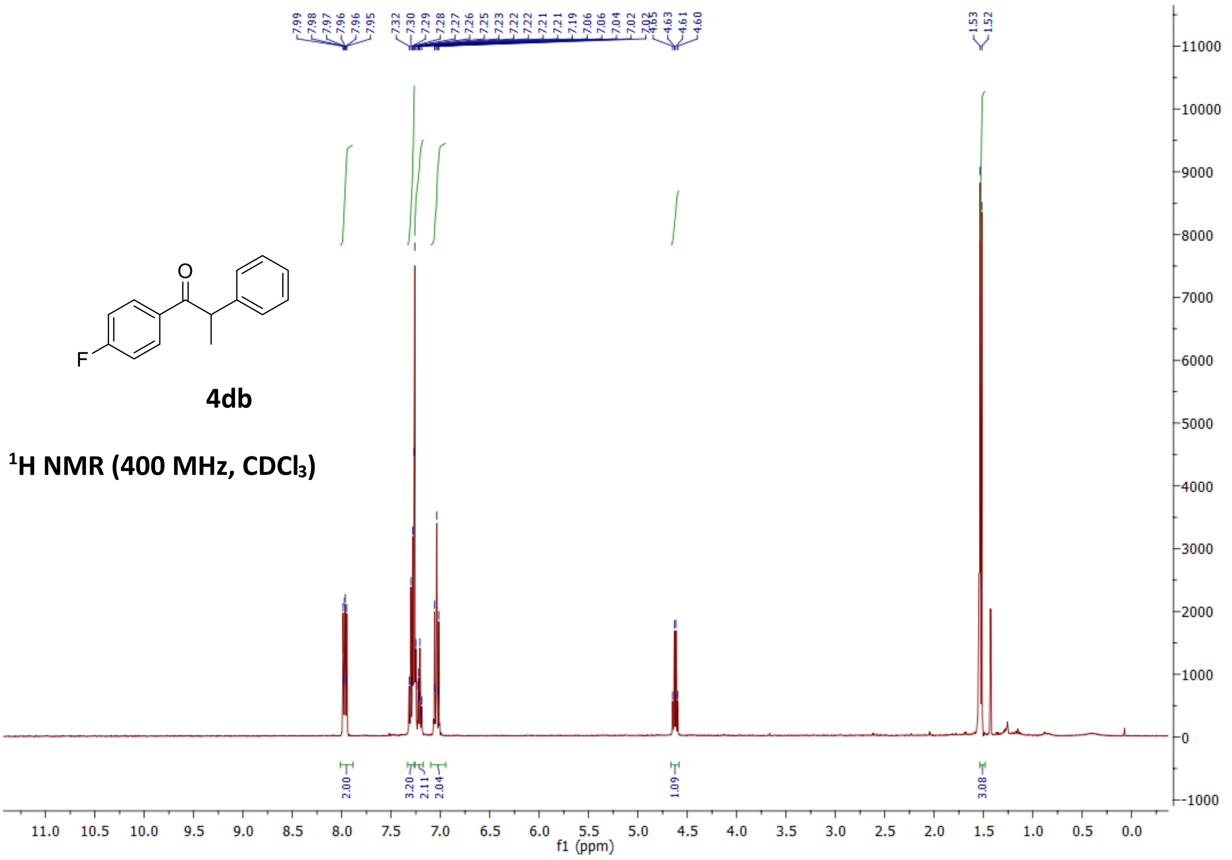
^{13}C NMR (126 MHz, CDCl$_3$)


7.89
7.77
7.76
7.42
7.40
7.30
7.28
7.26
7.24
7.23
7.22
7.20
7.19
7.17
4.61
4.60
4.58
4.56
1.51
1.50
Cl
O
4bb
^{1}H NMR (400 MHz, CDCl$_3$)
0.97
1.00
1.20
6.71
1.19
3.29
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


199.16
141.05
138.20
134.96
132.84
129.92
129.26
128.97
127.86
127.25
126.99
48.30
19.54
Cl
O
4bb
^{13}C NMR (126 MHz, CDCl$_3$)
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

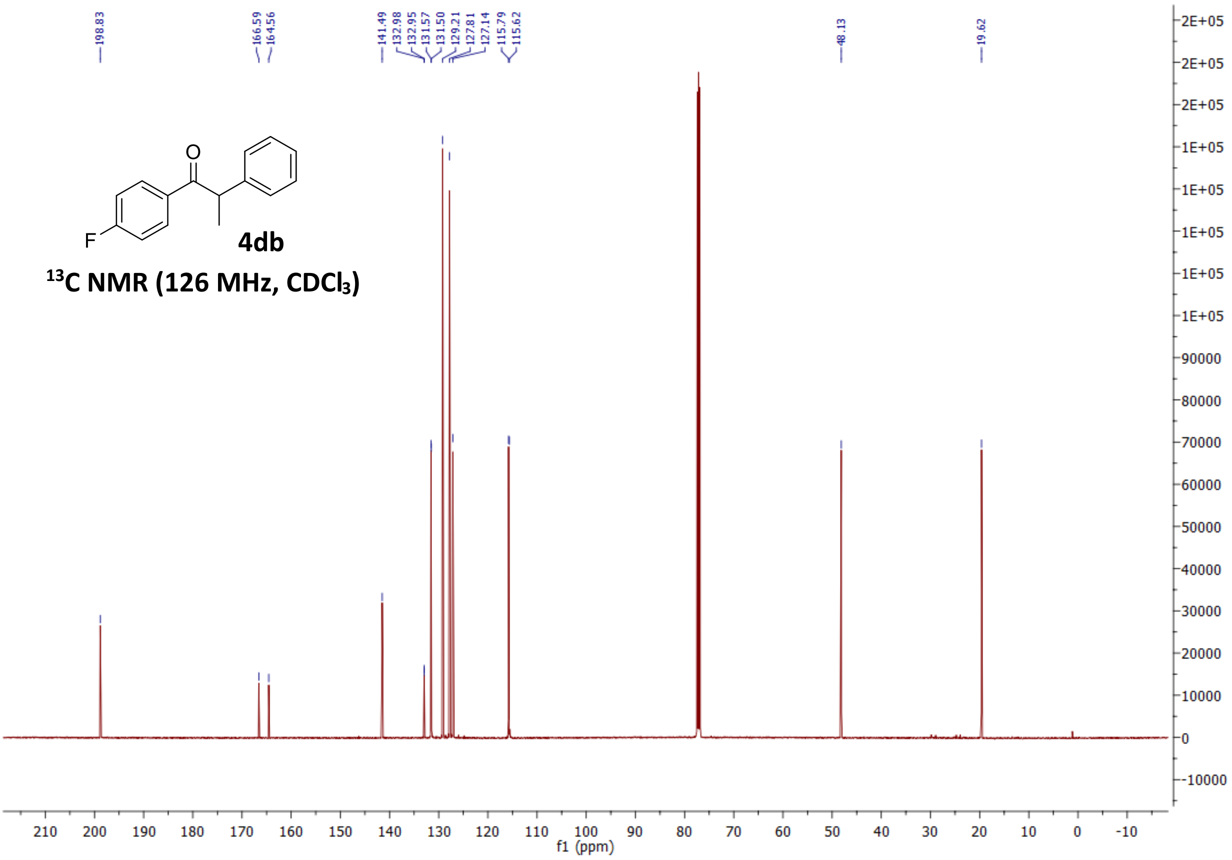

7.80
7.80
7.79
7.79
7.52
7.51
7.50
7.50
7.49
7.25
7.25
7.23
4.62
4.61
4.59
4.58
1.53
1.51
O
Br
4cb
^{1}H NMR (400 MHz, CDCl$_3$)
2.00
2.19
2.04
2.76
1.76
2.91
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


199.38
141.29
135.29
131.93
130.45
129.25
127.82
127.20
48.23
19.53
O
Br
4cb
^{13}C NMR (126 MHz, CDCl$_3$)
2E+05
2E+05
2E+05
2E+05
2E+05
2E+05
1E+05
1E+05
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



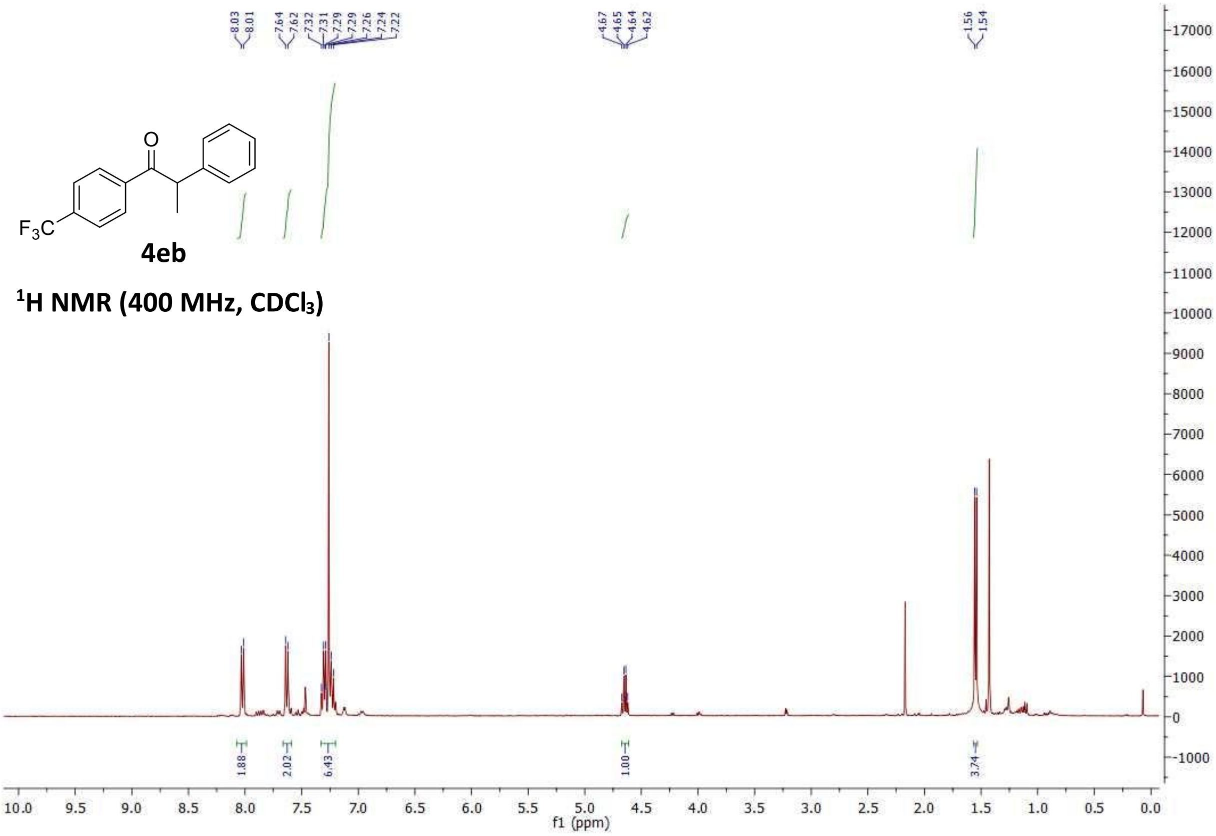
4db

^{1}H NMR (400 MHz, CDCl$_3$)



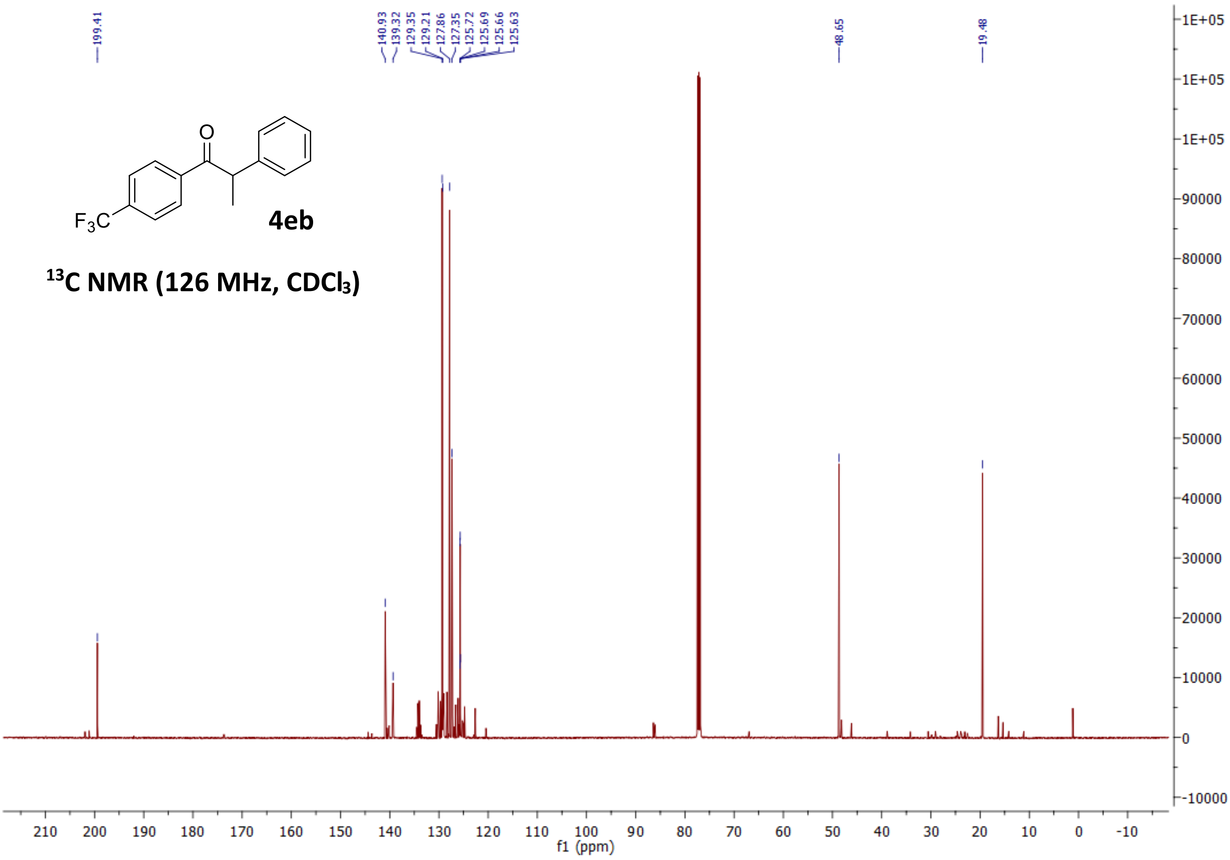
4db

^{13}C NMR (126 MHz, CDCl$_3$)



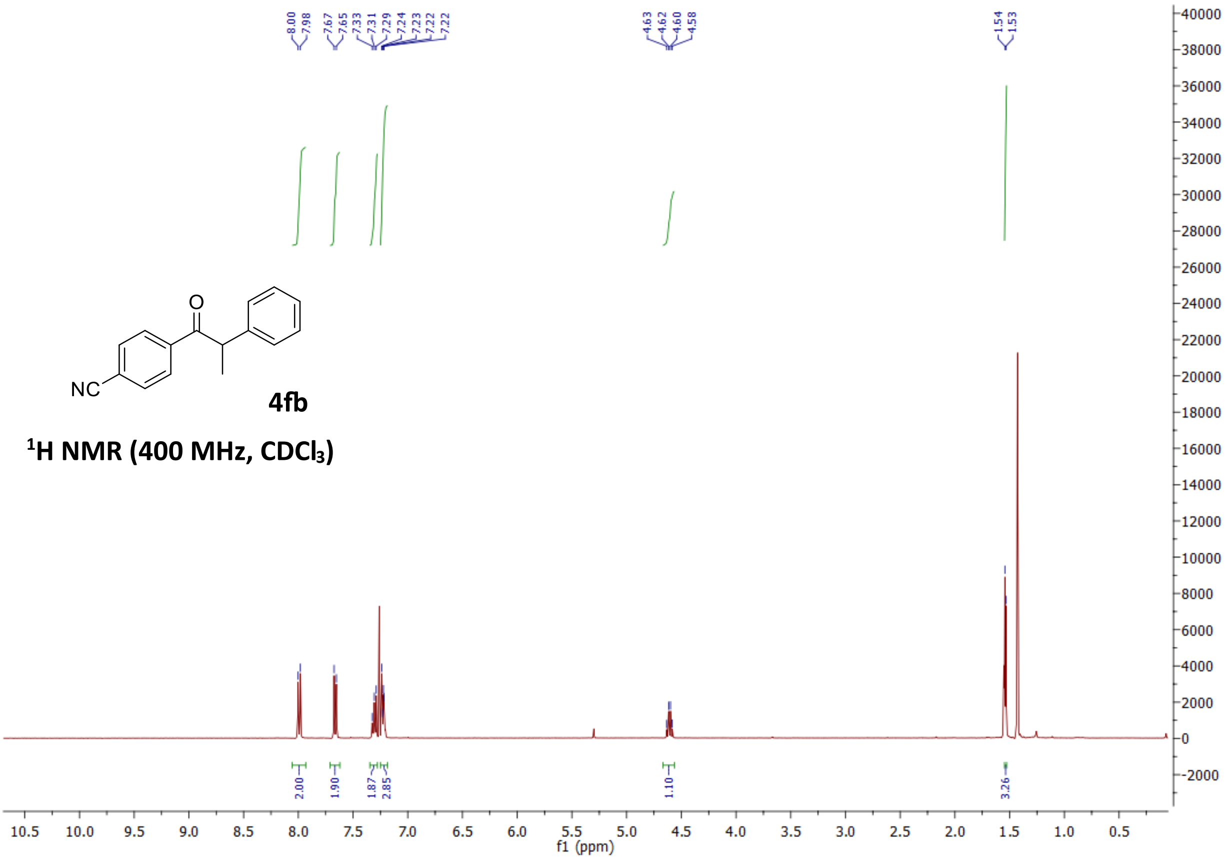
4eb

^{1}H NMR (400 MHz, CDCl$_3$)



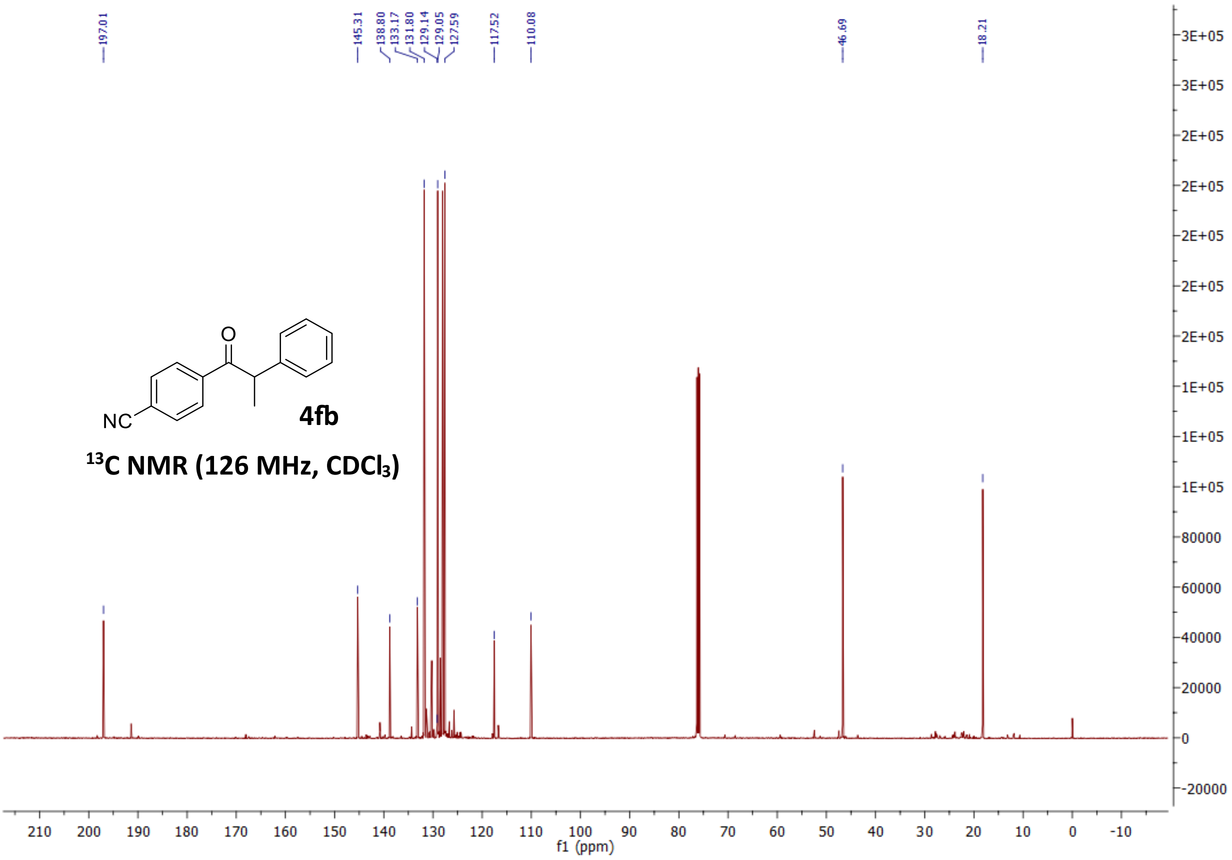
4eb

^{13}C NMR (126 MHz, CDCl$_3$)



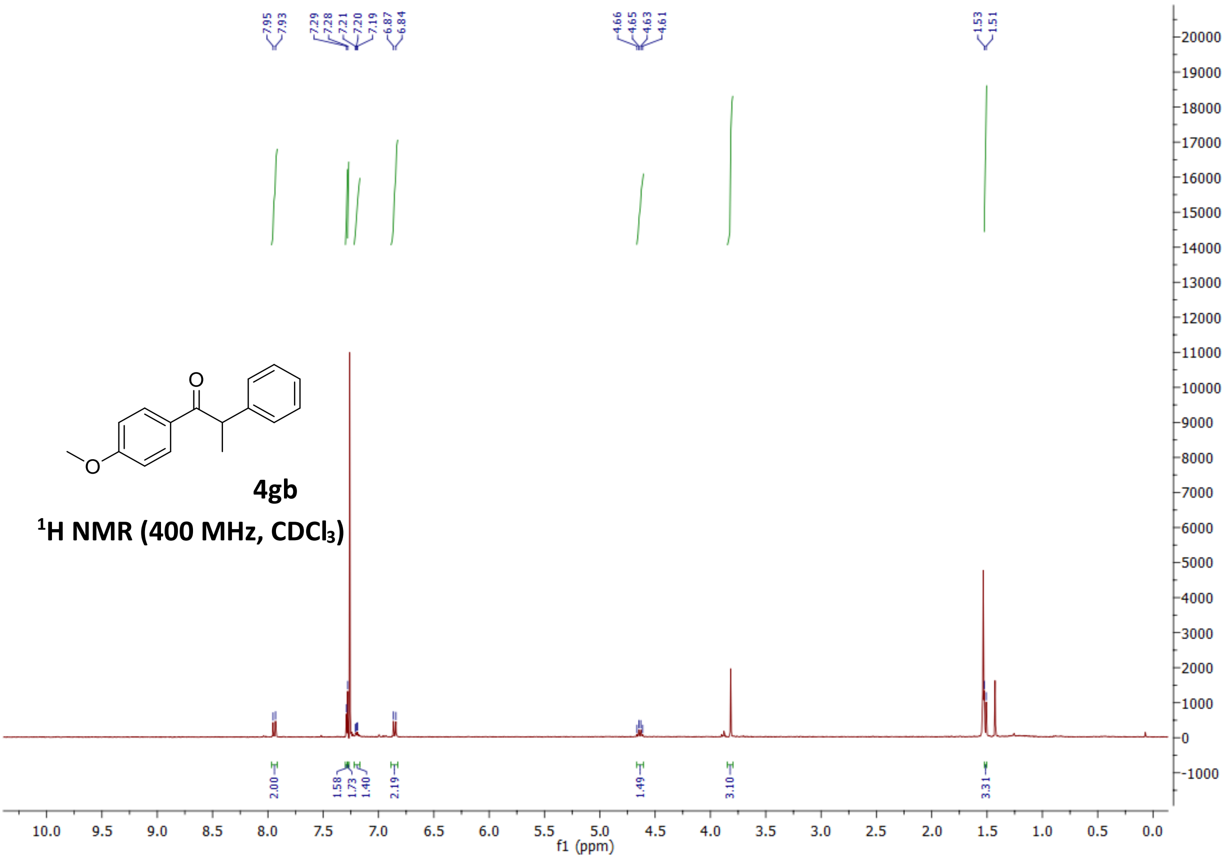
4fb

^{1}H NMR (400 MHz, CDCl$_3$)



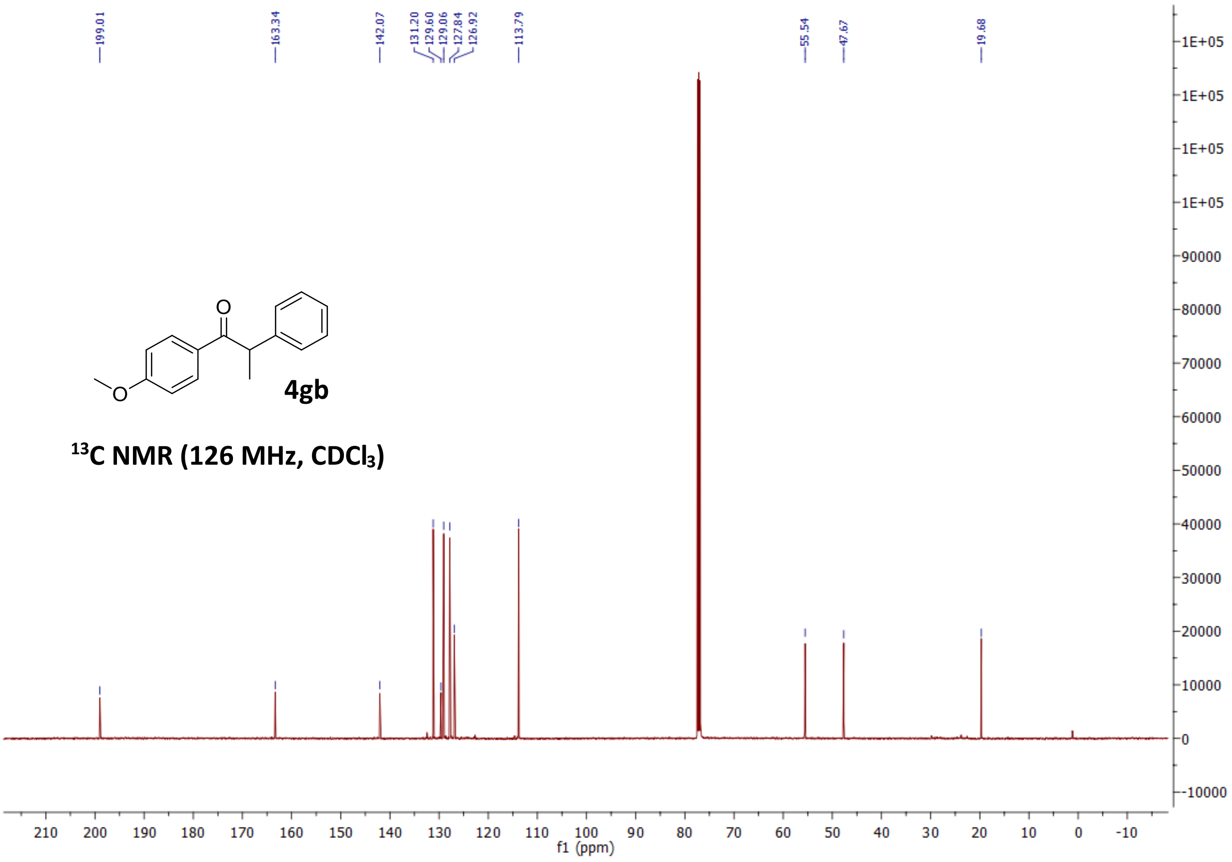
4fb

^{13}C NMR (126 MHz, CDCl$_3$)



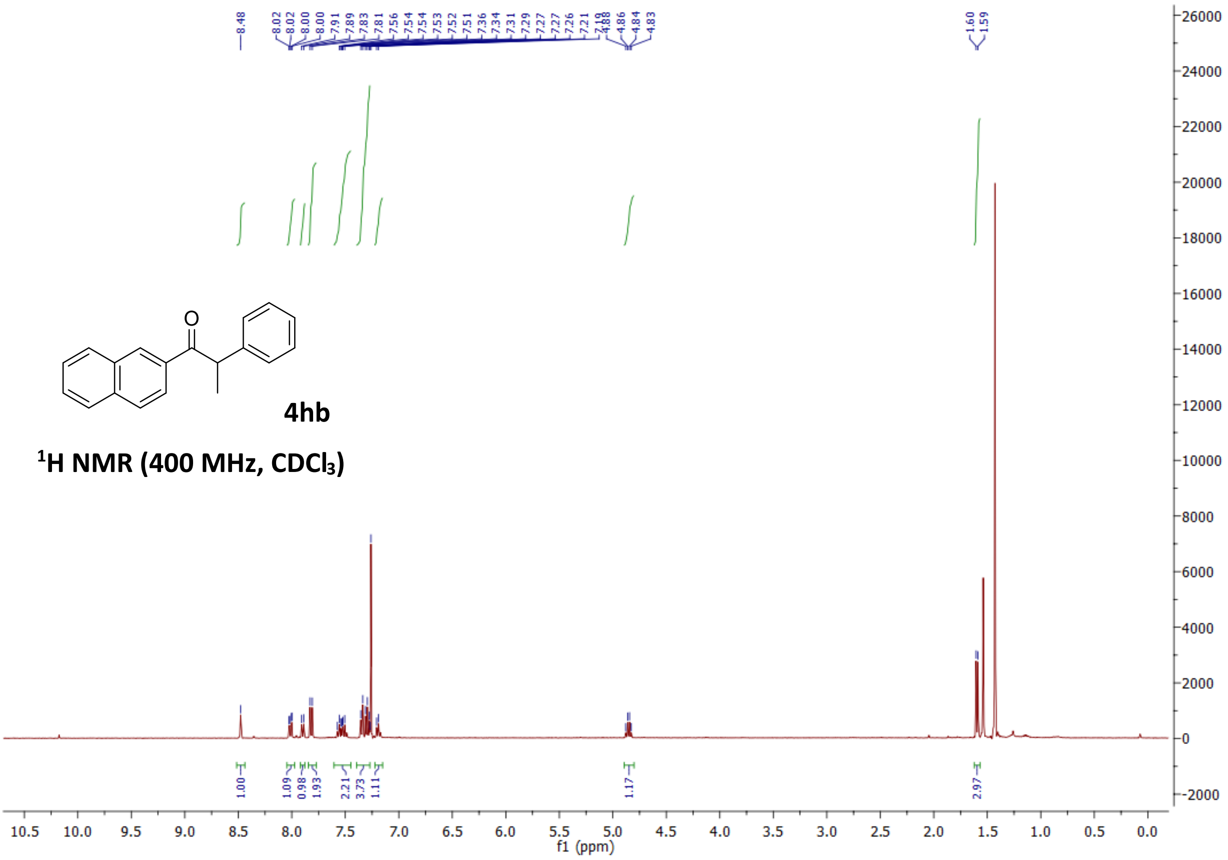
4gb

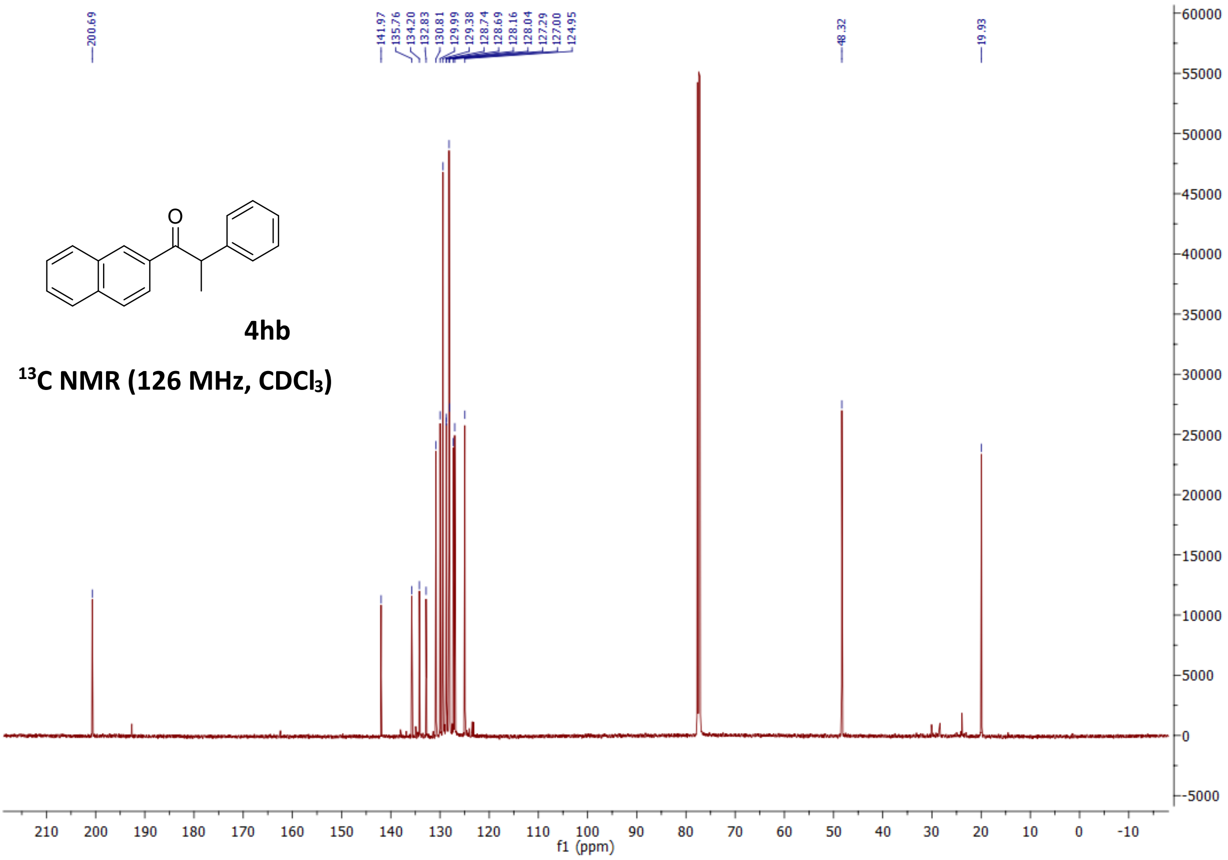
^{1}H NMR (400 MHz, CDCl$_3$)

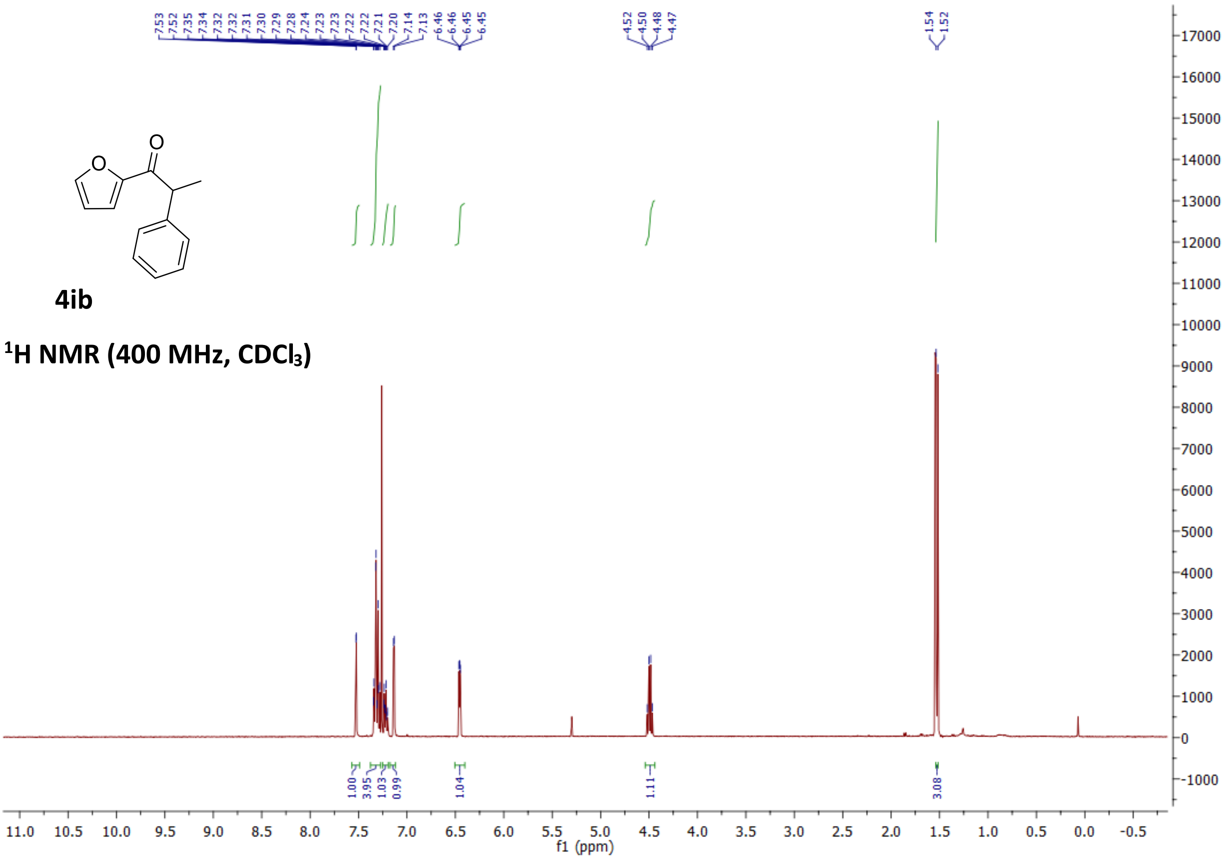


4gb

^{13}C NMR (126 MHz, CDCl$_3$)

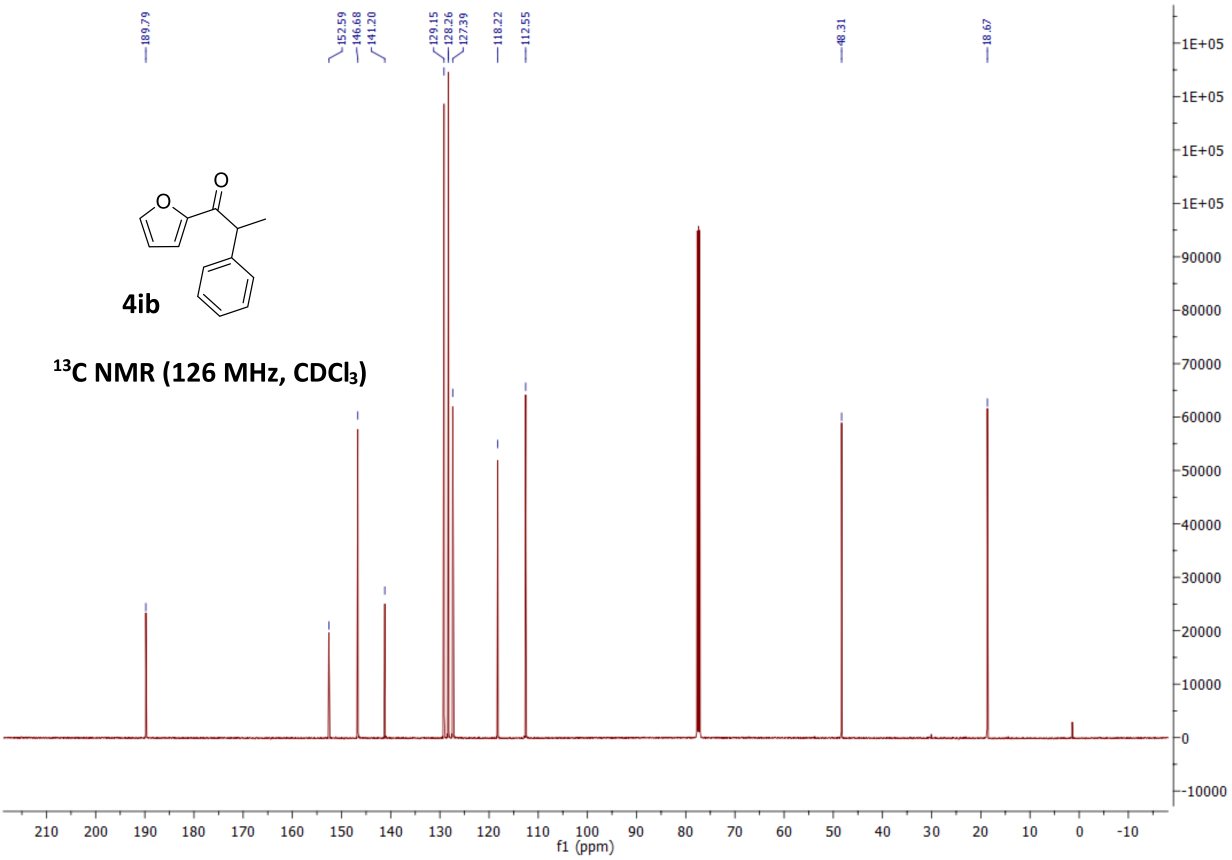

8.48
8.02
8.02
8.00
8.00
7.91
7.89
7.83
7.81
7.56
7.54
7.54
7.53
7.52
7.51
7.36
7.34
7.31
7.29
7.27
7.27
7.26
7.21
7.19
4.88
4.86
4.84
4.83
1.60
1.59
O
4hb
^{1}H NMR (400 MHz, CDCl$_3$)
1.00
1.09
0.98
1.93
2.21
3.73
1.11
1.17
2.97
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000


200.69
141.97
135.76
134.20
132.83
130.81
129.99
129.38
128.74
128.69
128.16
128.04
127.29
127.00
124.95
48.32
19.93
O
4hb
^{13}C NMR (126 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000



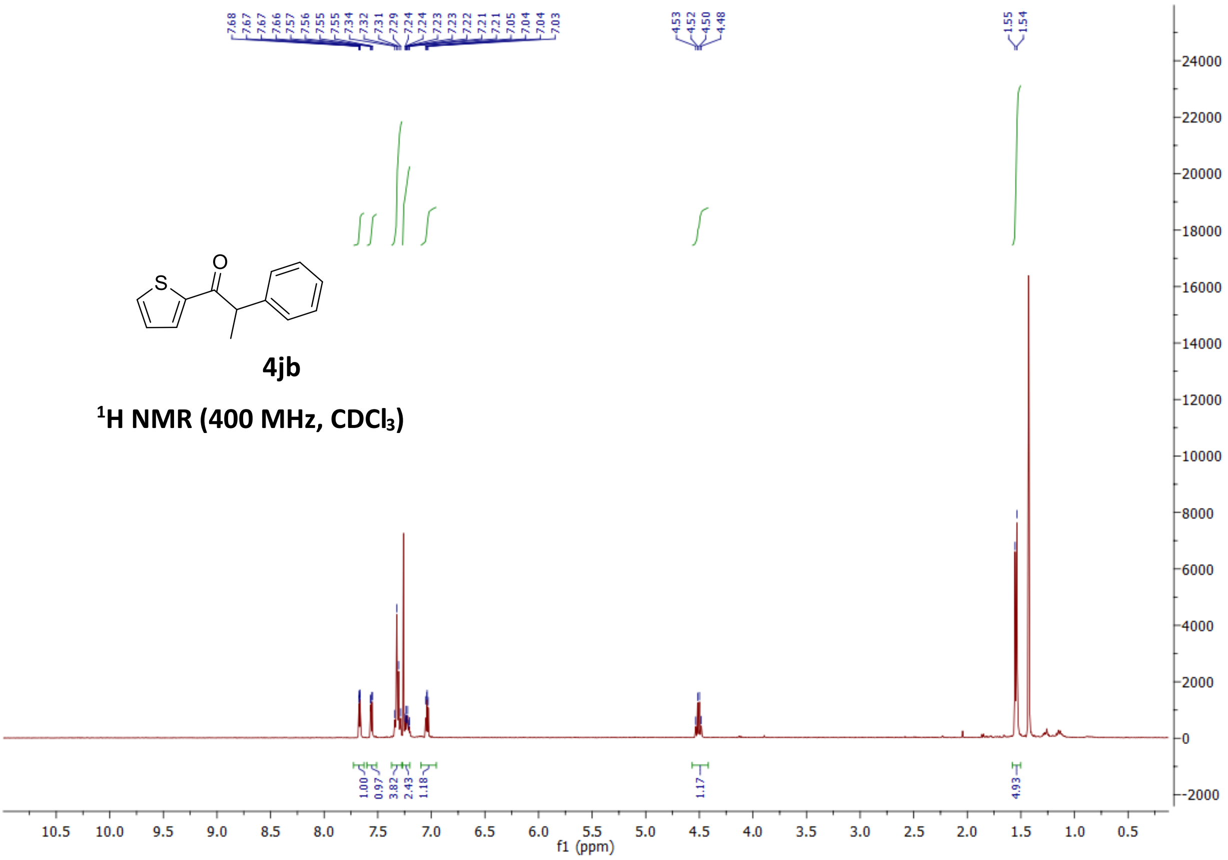
4ib

^{1}H NMR (400 MHz, $CDCl_3$)



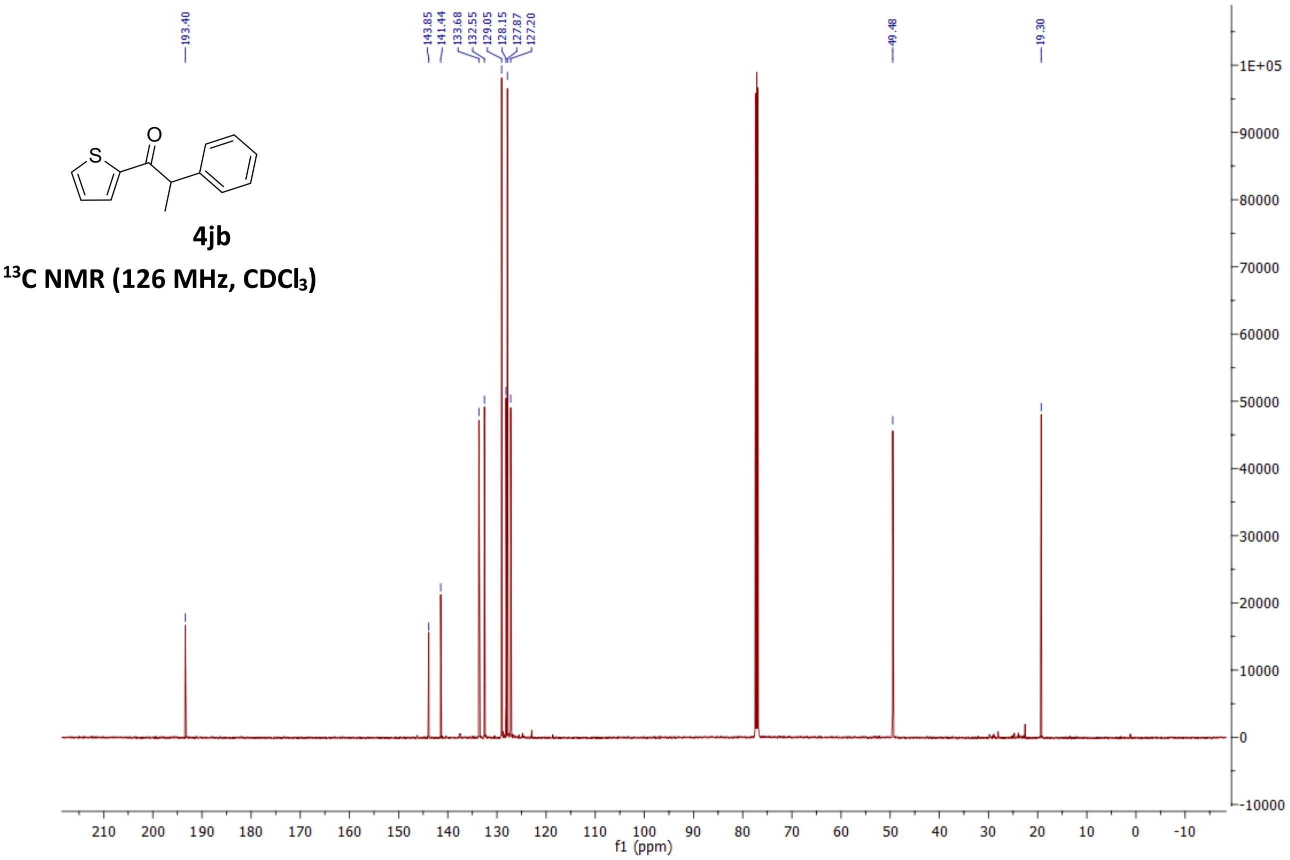
4ib

^{13}C NMR (126 MHz, $CDCl_3$)



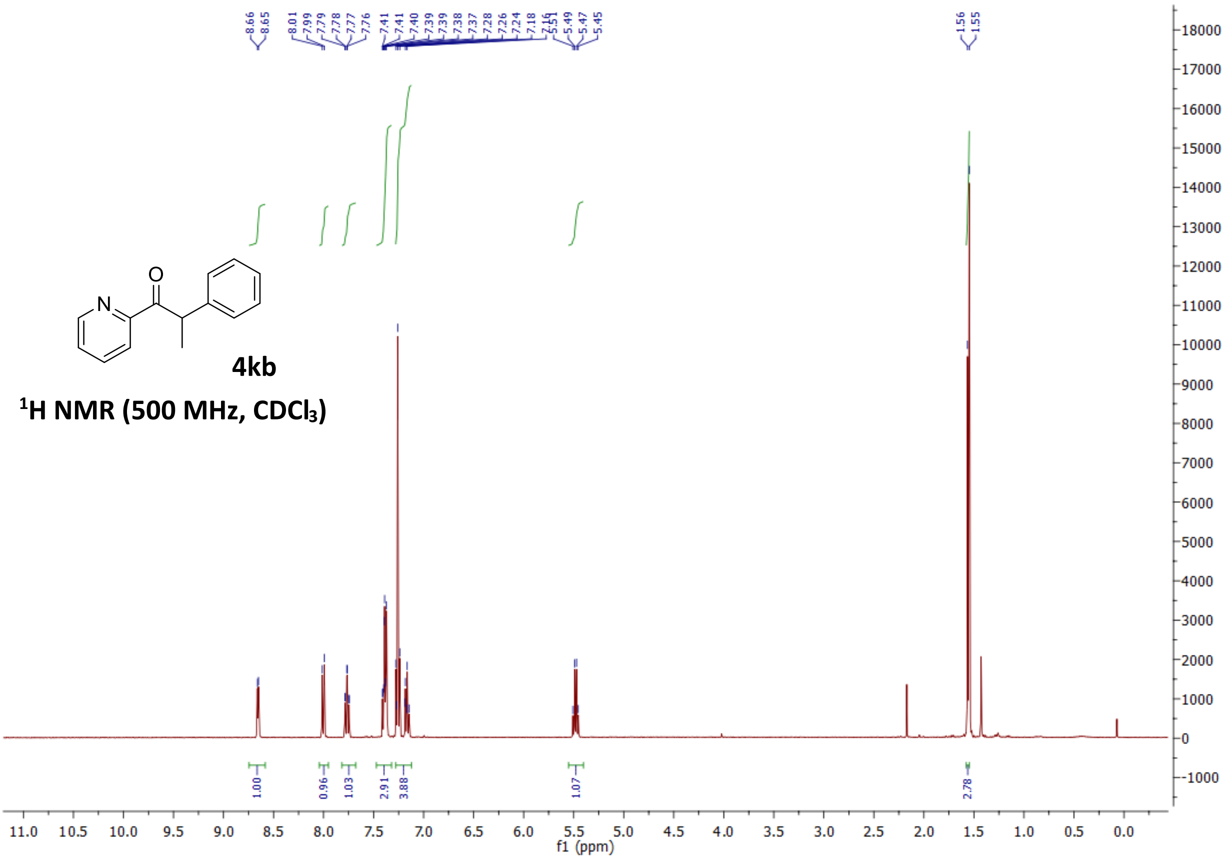
4jb

^{1}H NMR (400 MHz, $CDCl_3$)



4jb

^{13}C NMR (126 MHz, $CDCl_3$)



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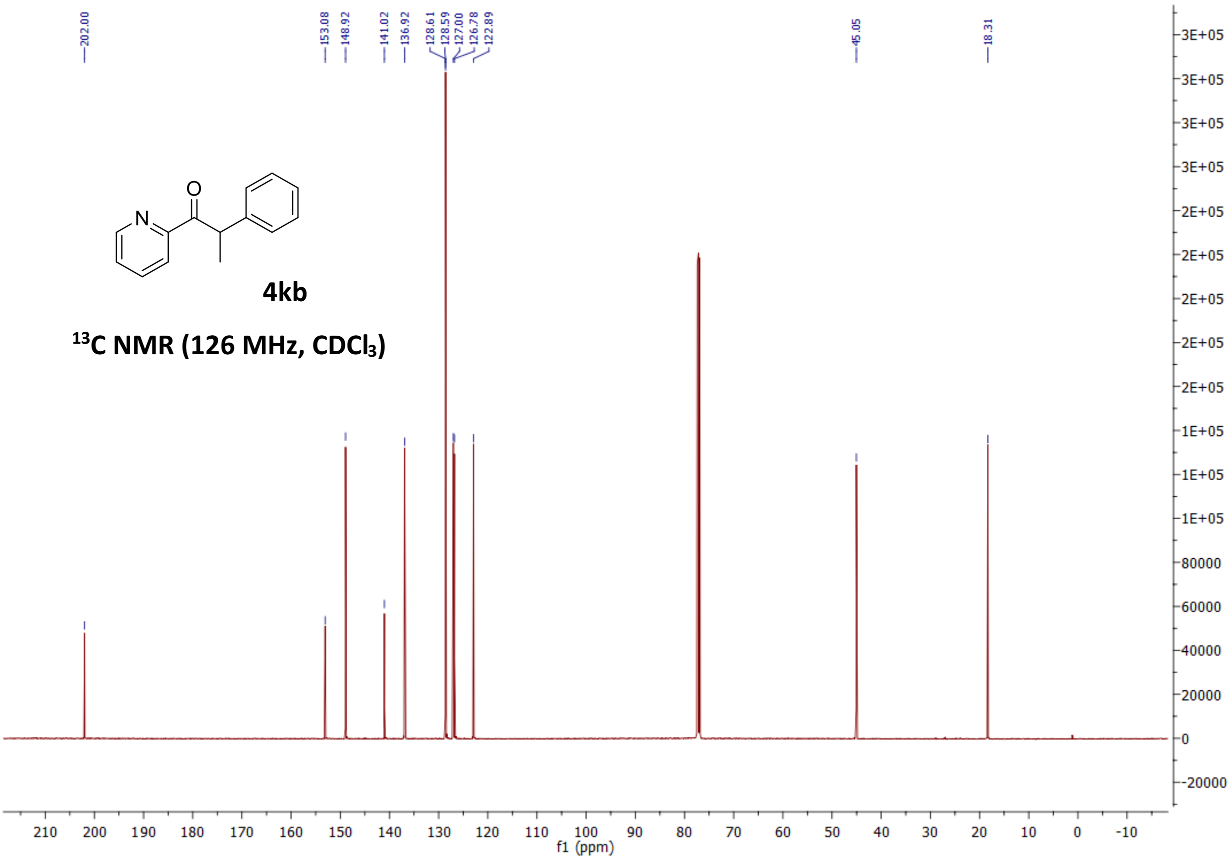
^{1}H NMR (500 MHz, CDCl$_3$)



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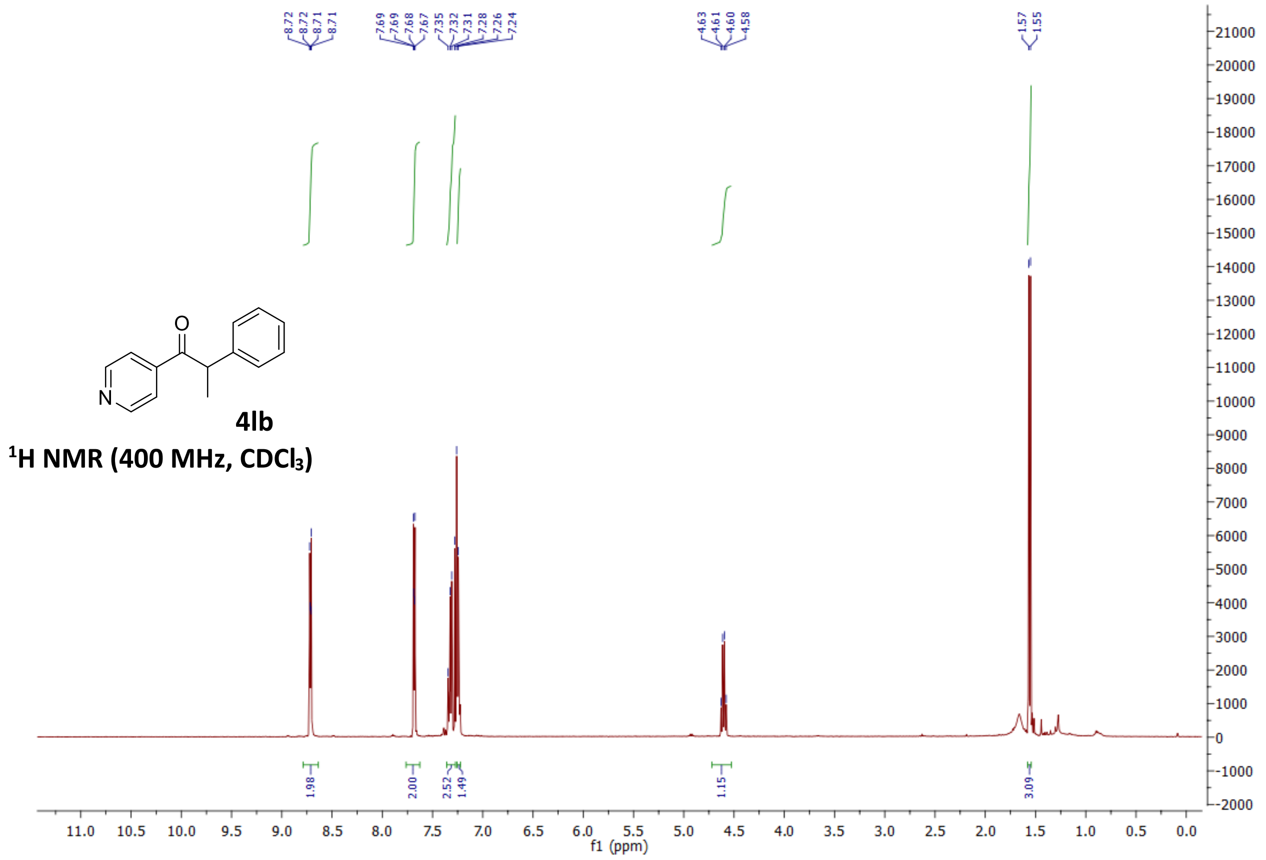
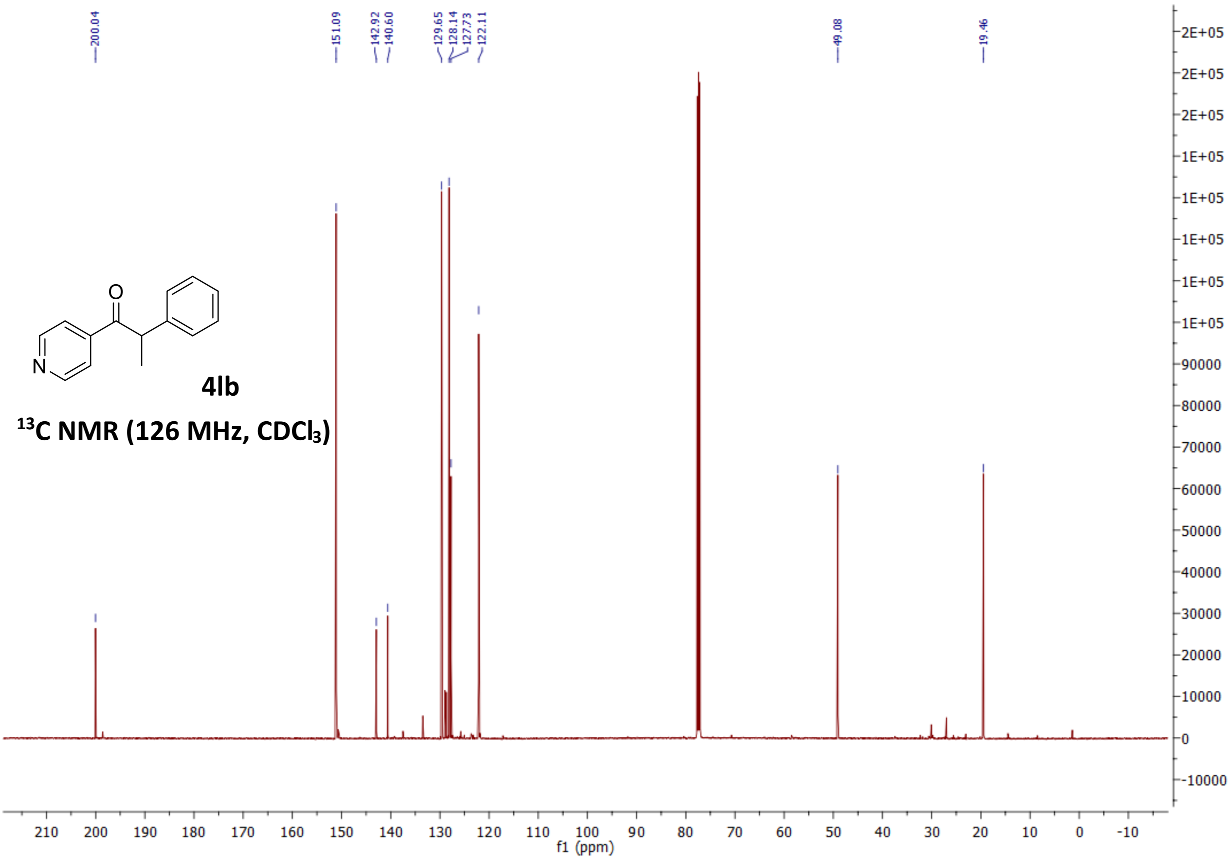
^{13}C NMR (126 MHz, CDCl$_3$)



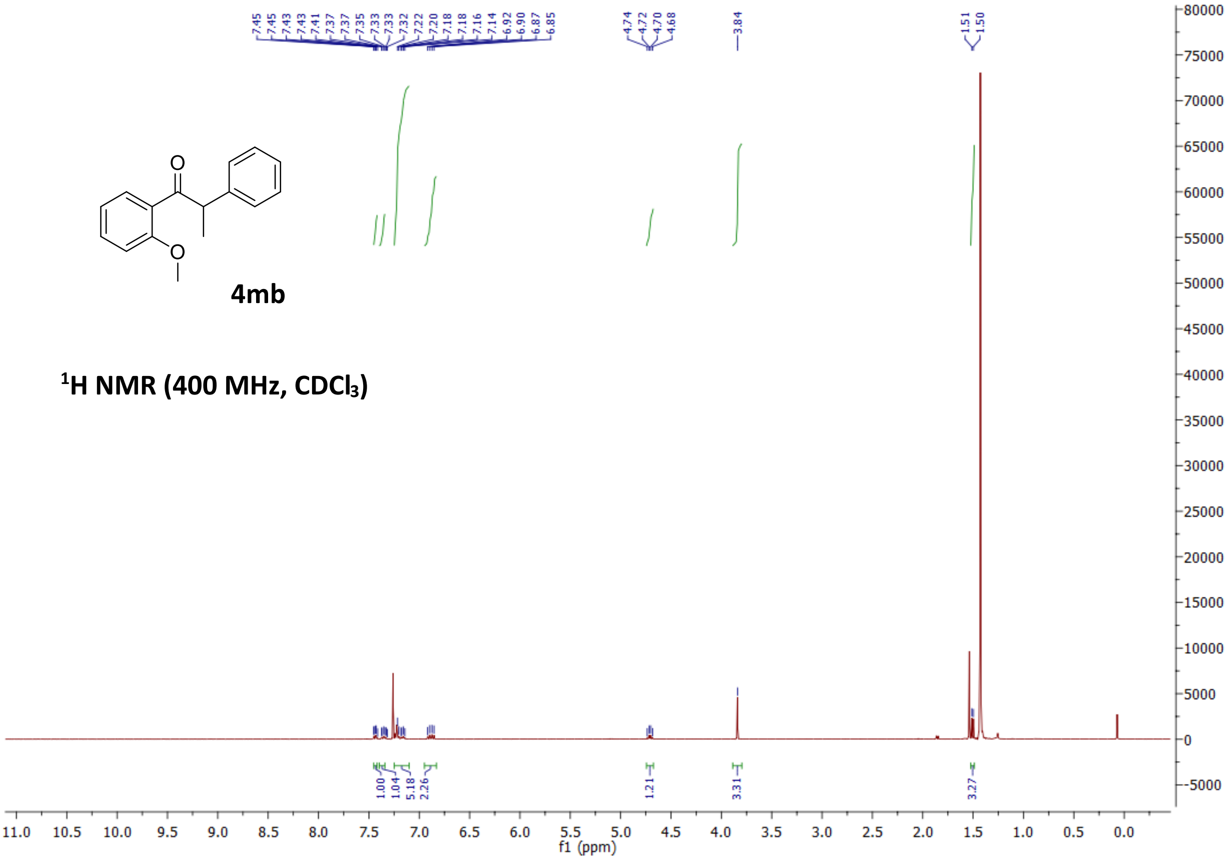
4lb

^{1}H NMR (400 MHz, $CDCl_3$)

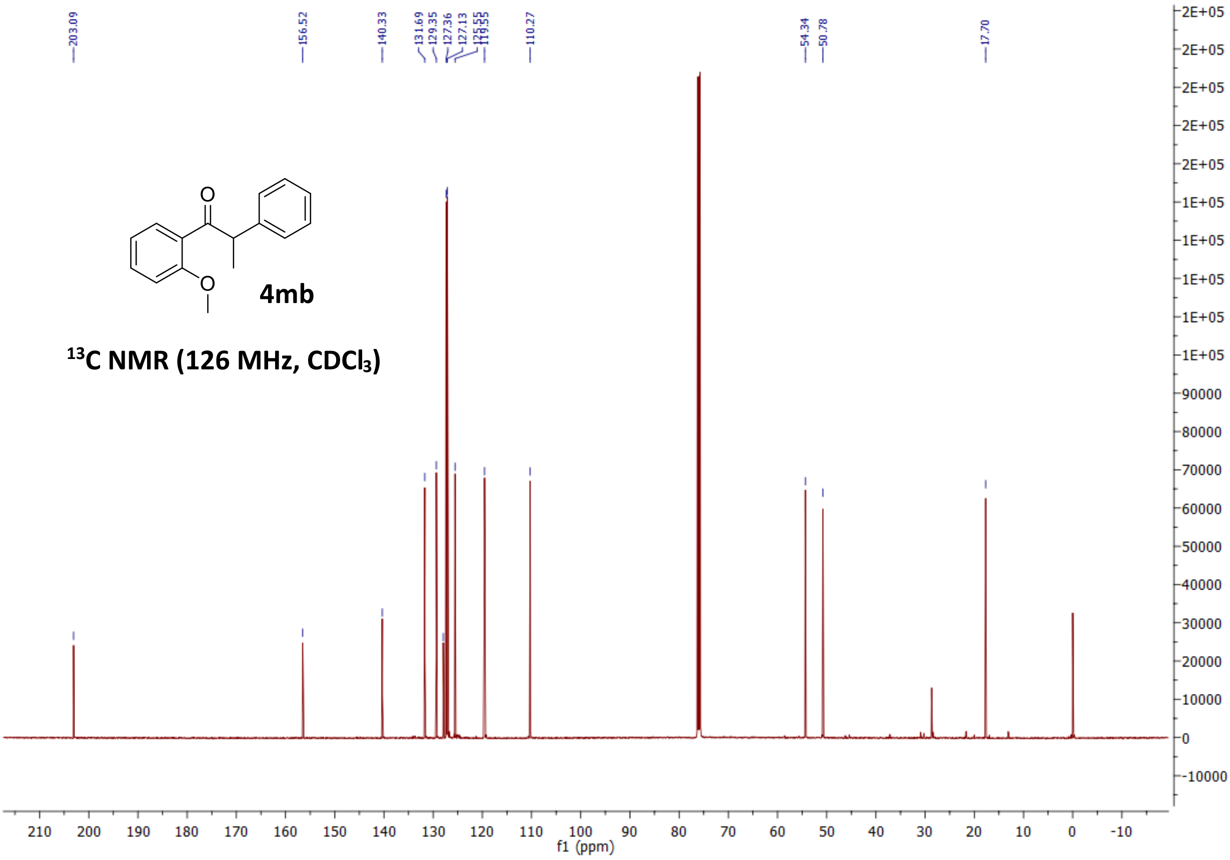


4lb

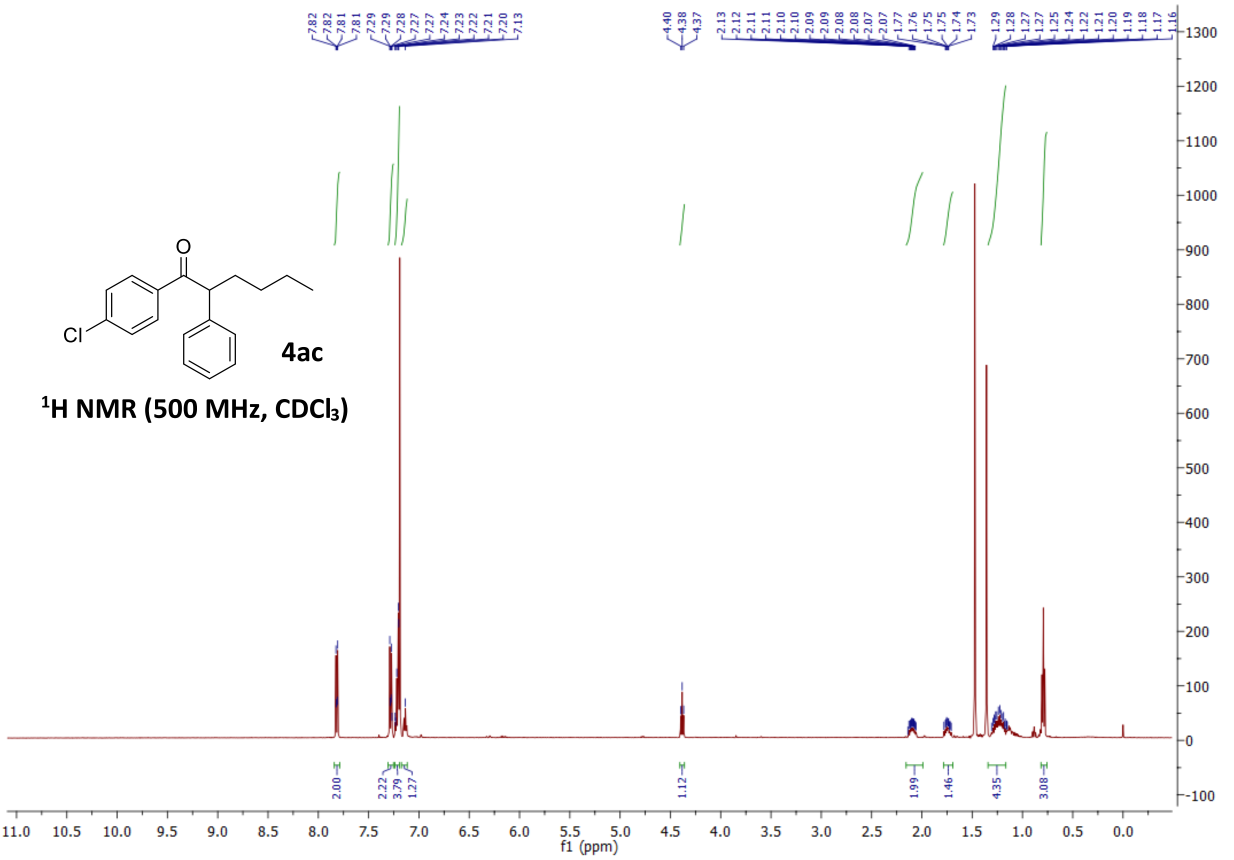
^{13}C NMR (126 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, CDCl$_3$)

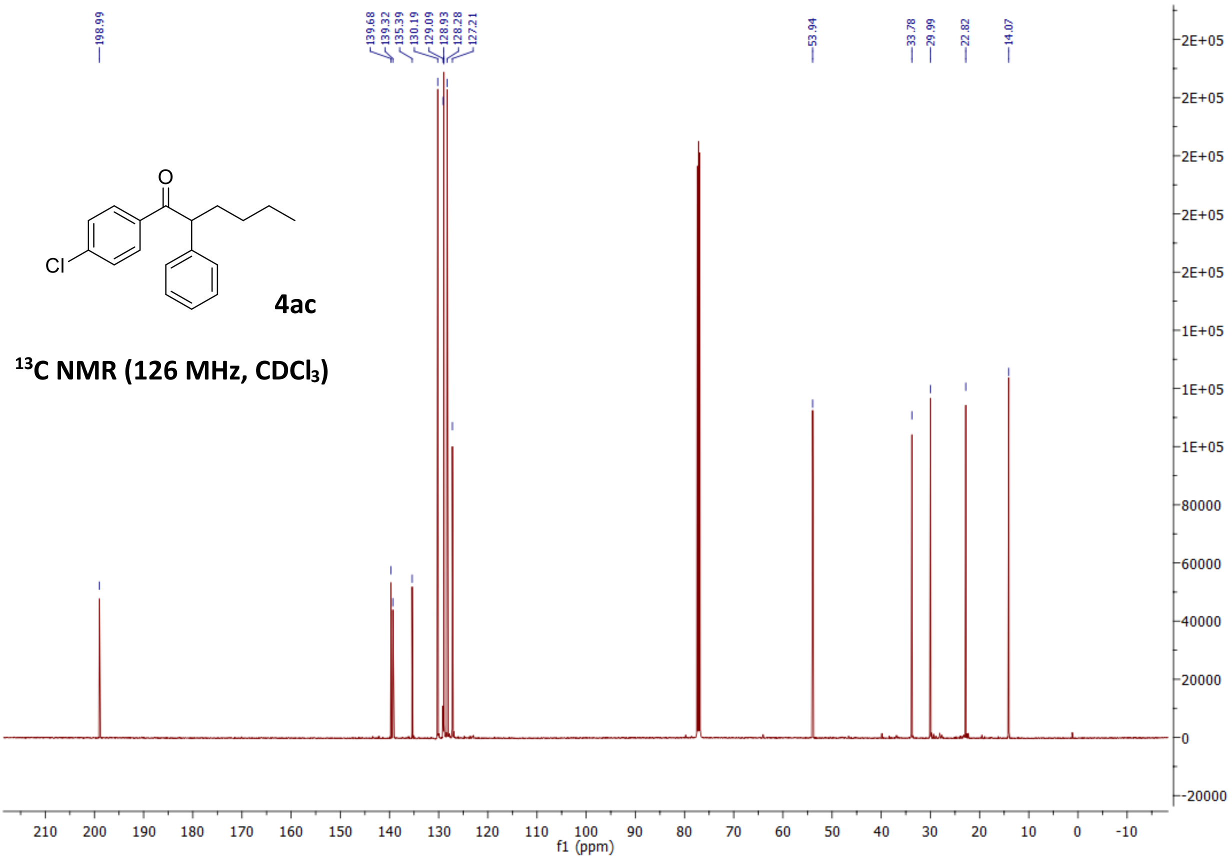


^{13}C NMR (126 MHz, CDCl$_3$)



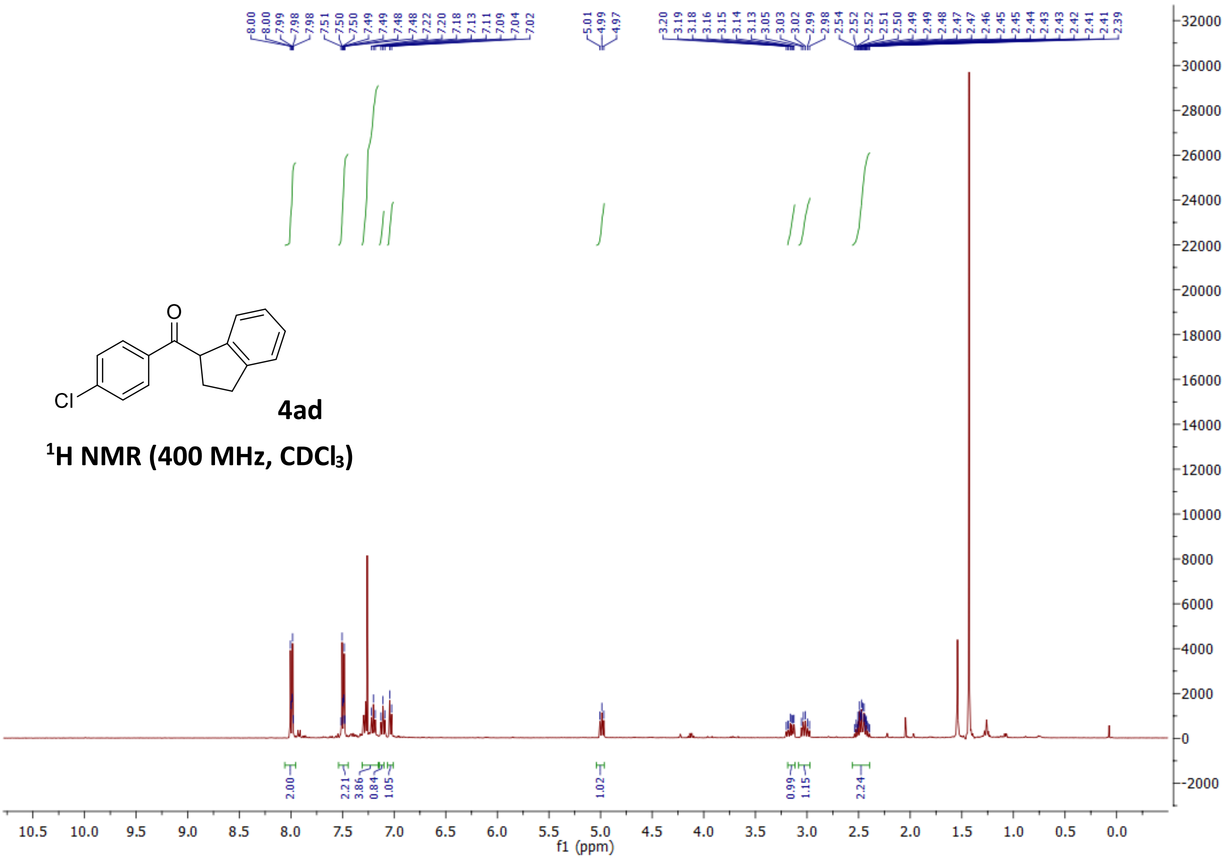
4ac

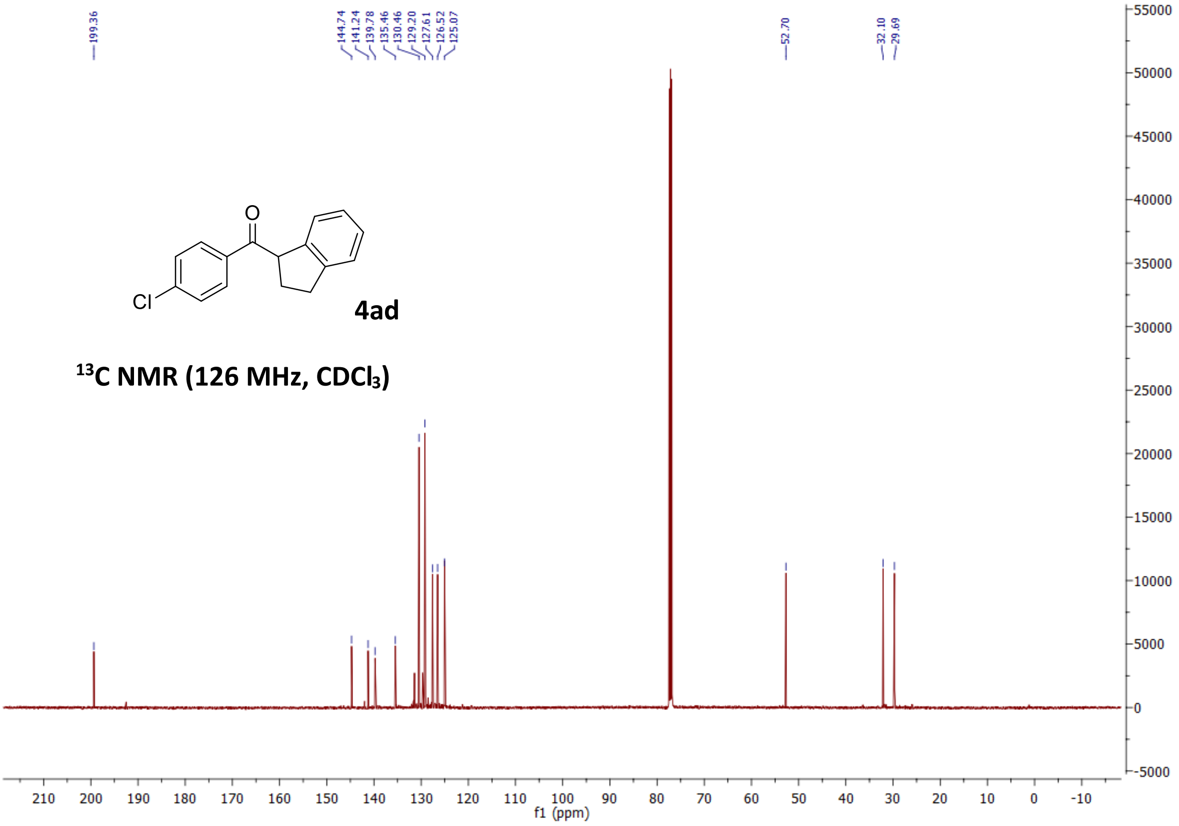
^{1}H NMR (500 MHz, CDCl$_3$)

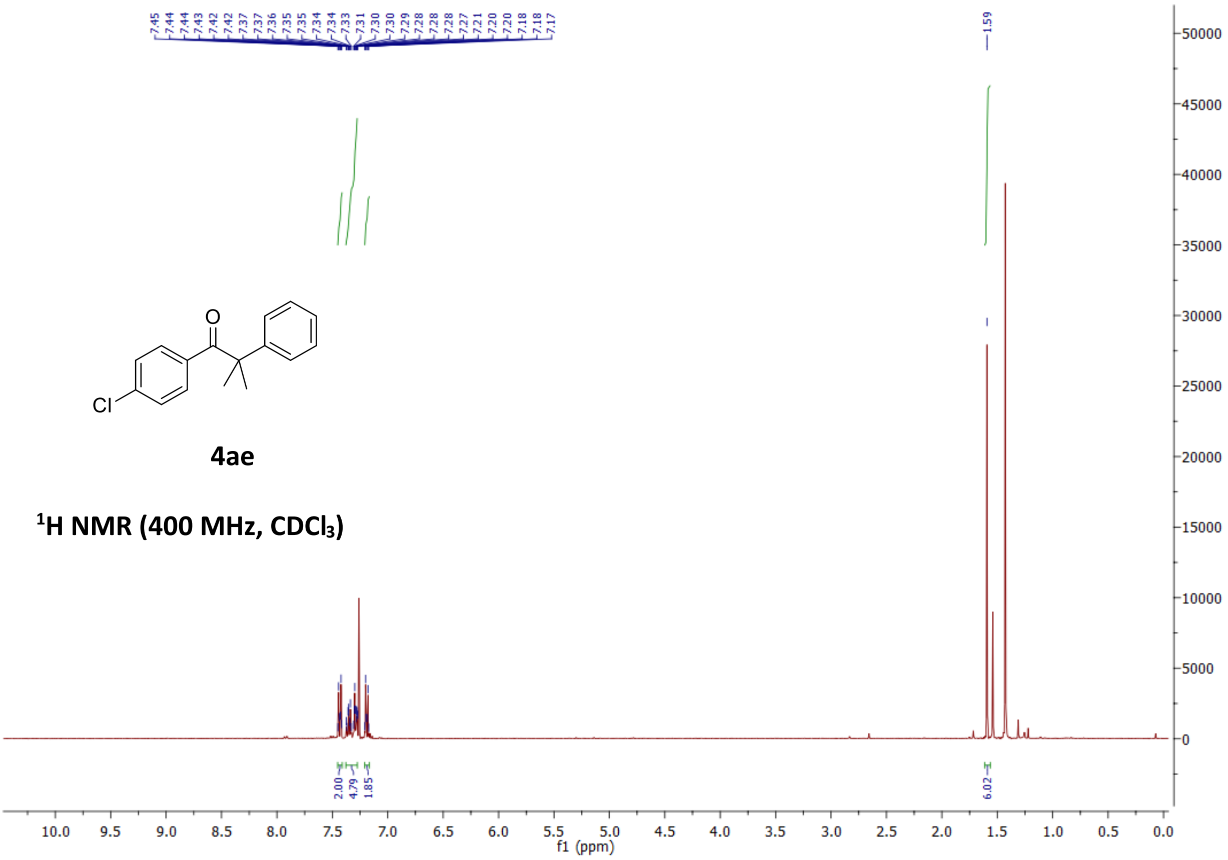


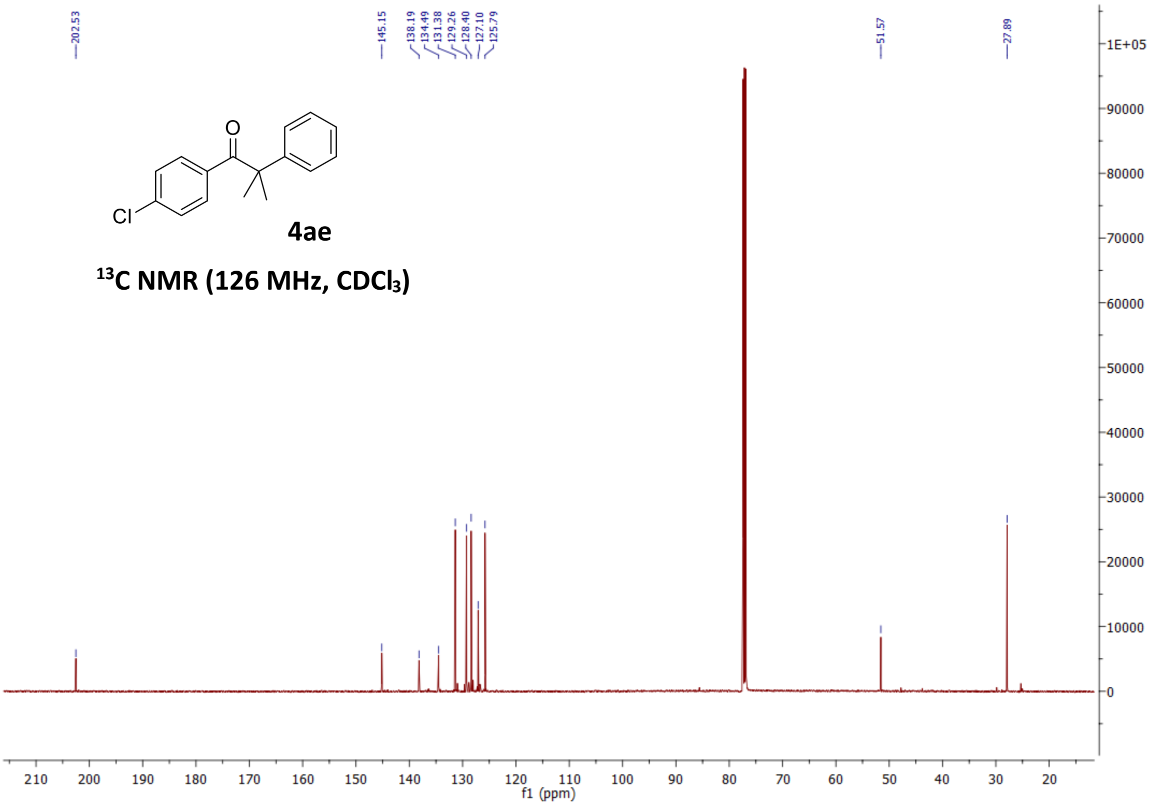
4ac

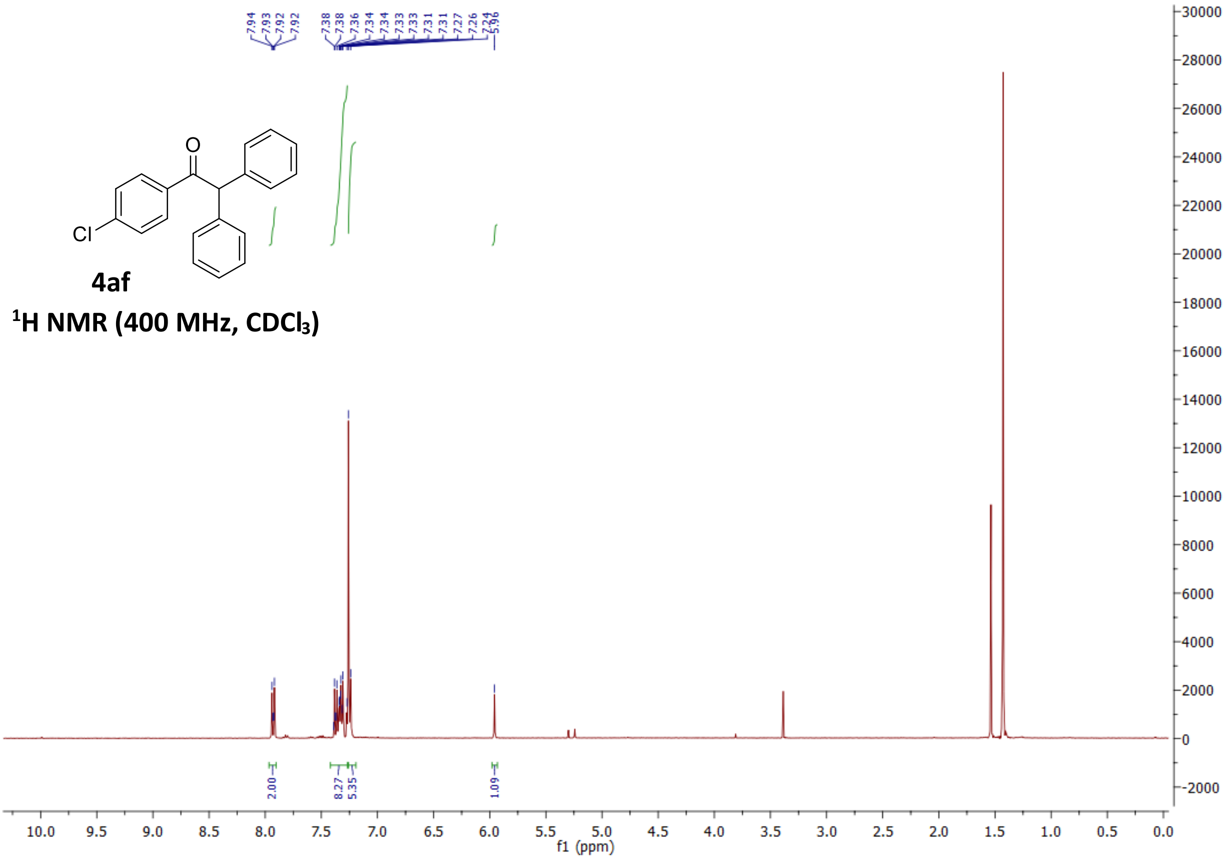
^{13}C NMR (126 MHz, CDCl$_3$)


4ad
^{1}H NMR (400 MHz, CDCl$_3$)
Cl
O
8.00
8.00
7.99
7.98
7.98
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.22
7.20
7.18
7.13
7.11
7.09
7.04
7.02
5.01
4.99
4.97
3.20
3.19
3.18
3.16
3.15
3.14
3.13
3.05
3.03
3.02
2.99
2.98
2.54
2.52
2.52
2.51
2.50
2.49
2.49
2.48
2.47
2.47
2.46
2.45
2.45
2.44
2.43
2.43
2.42
2.41
2.41
2.39
2.00
2.21
3.86
0.84
1.05
1.02
0.99
1.15
2.24
f1 (ppm)


4ad
^{13}C NMR (126 MHz, CDCl$_3$)
Cl
O
199.36
144.74
141.24
139.78
135.46
130.46
129.20
127.61
126.52
125.07
52.70
32.10
29.69
f1 (ppm)

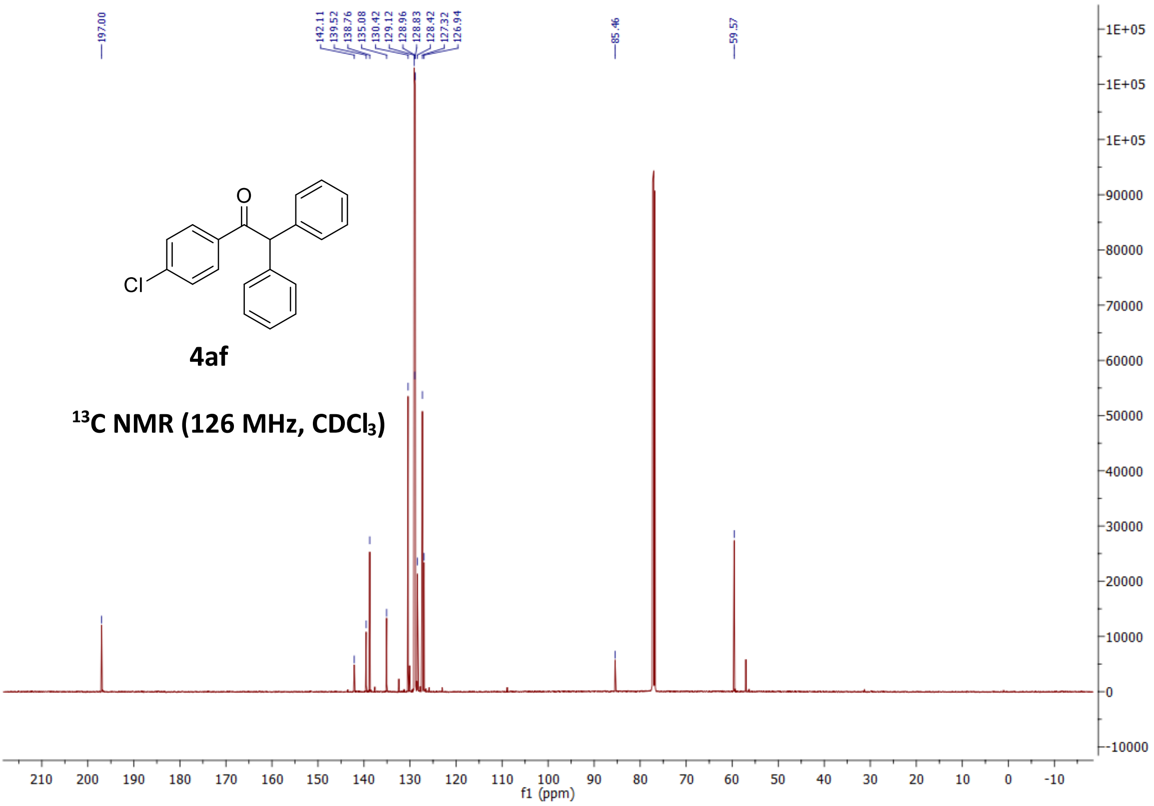

4ae
^{1}H NMR (400 MHz, CDCl$_3$)
Cl
O
7.45
7.44
7.44
7.43
7.42
7.42
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.31
7.30
7.30
7.29
7.28
7.28
7.28
7.27
7.21
7.20
7.20
7.18
7.18
7.17
1.59
2.00
4.79
1.85
6.02
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


4ae
^{13}C NMR (126 MHz, CDCl$_3$)
Cl
O
202.53
145.15
138.19
134.49
131.38
129.26
128.40
127.10
125.79
51.57
27.89
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)



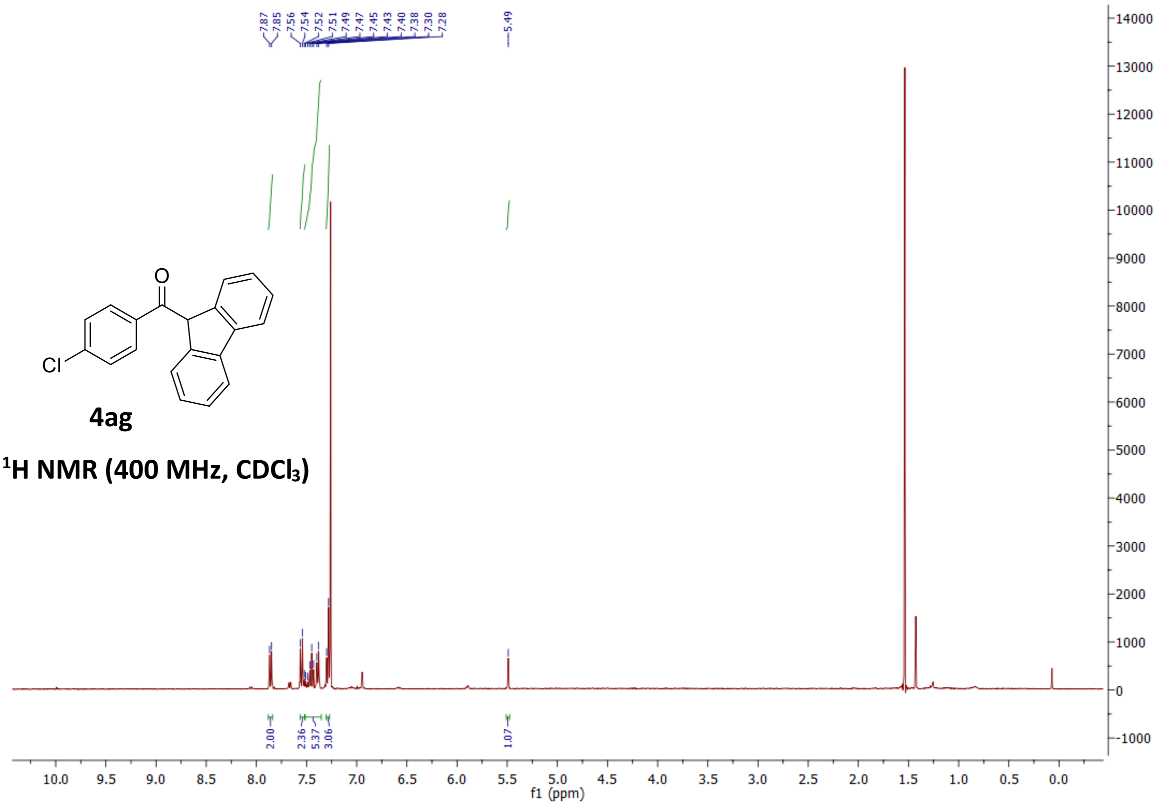
4af

^{1}H NMR (400 MHz, CDCl$_3$)



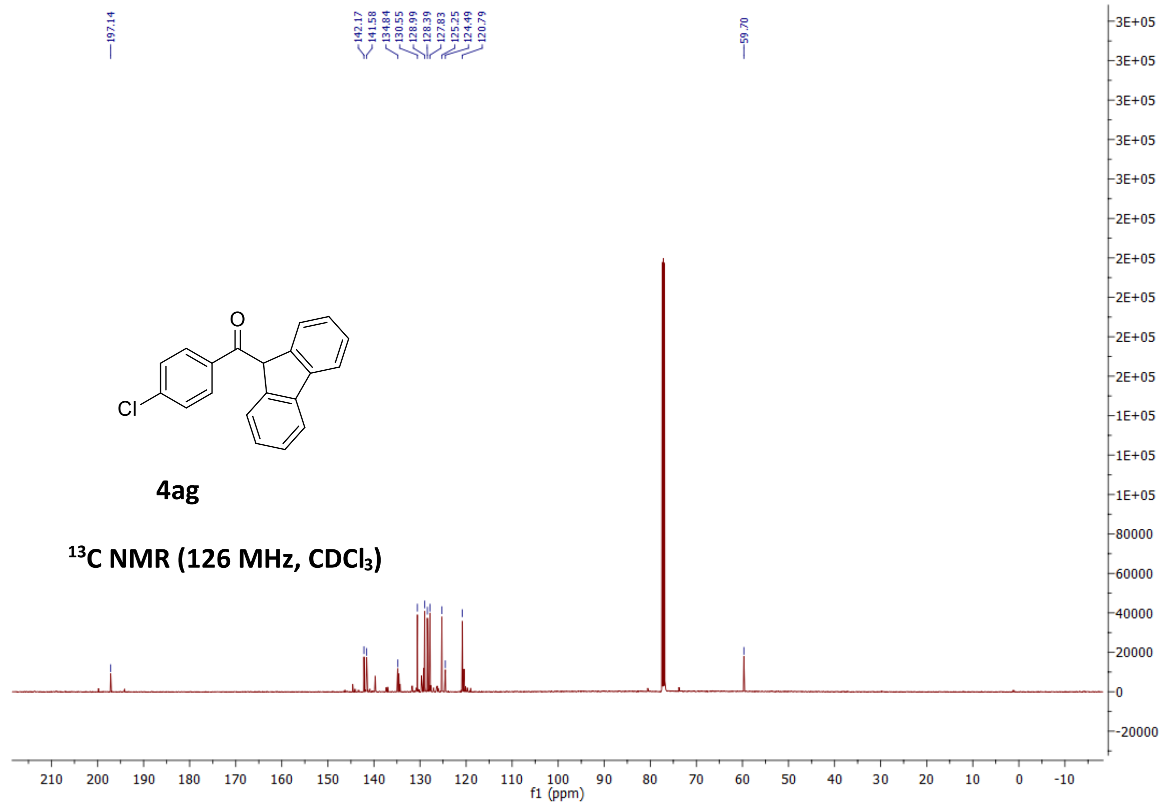
4af

^{13}C NMR (126 MHz, CDCl$_3$)



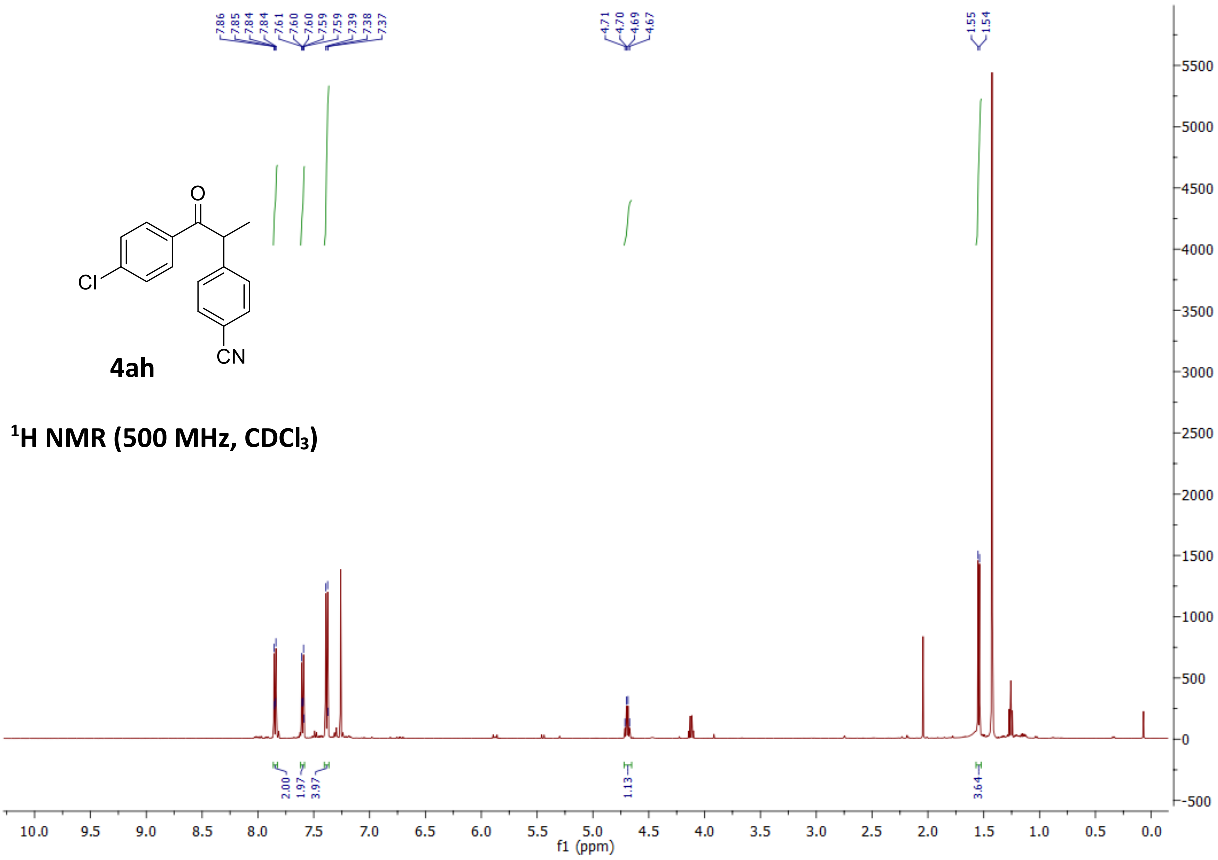
4ag

^{1}H NMR (400 MHz, $CDCl_3$)



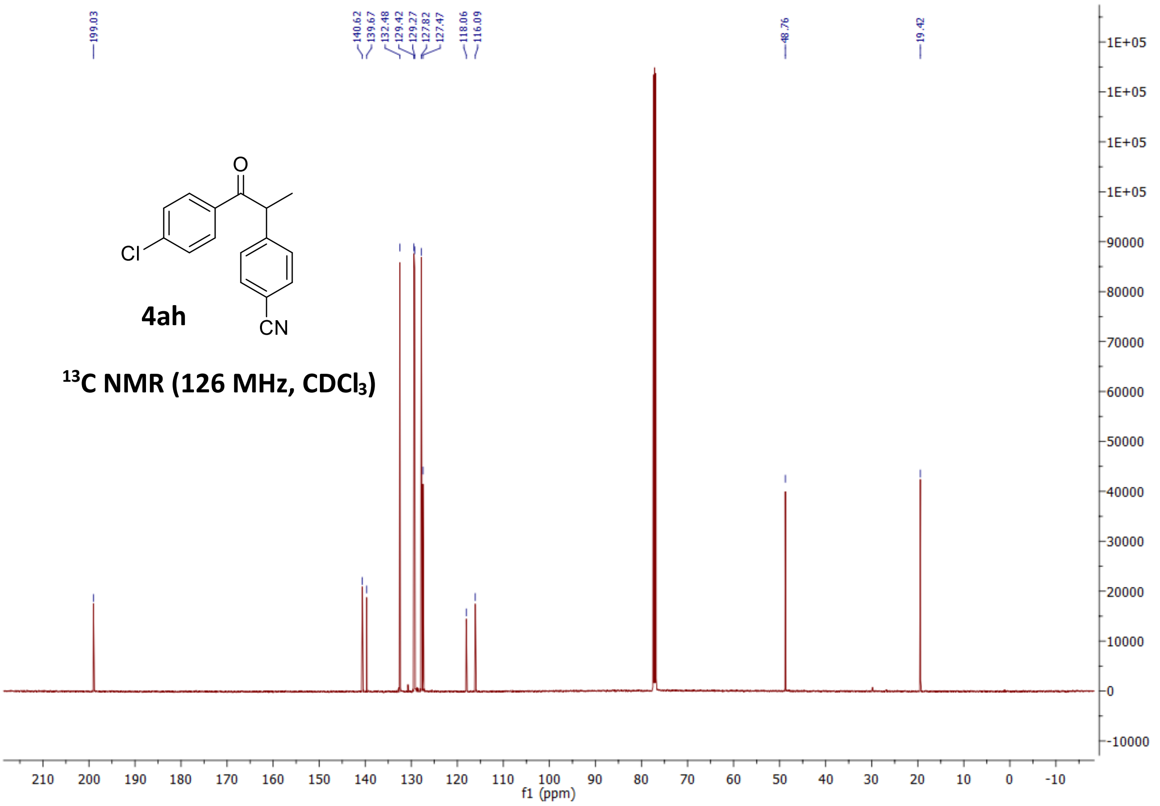
4ag

^{13}C NMR (126 MHz, $CDCl_3$)



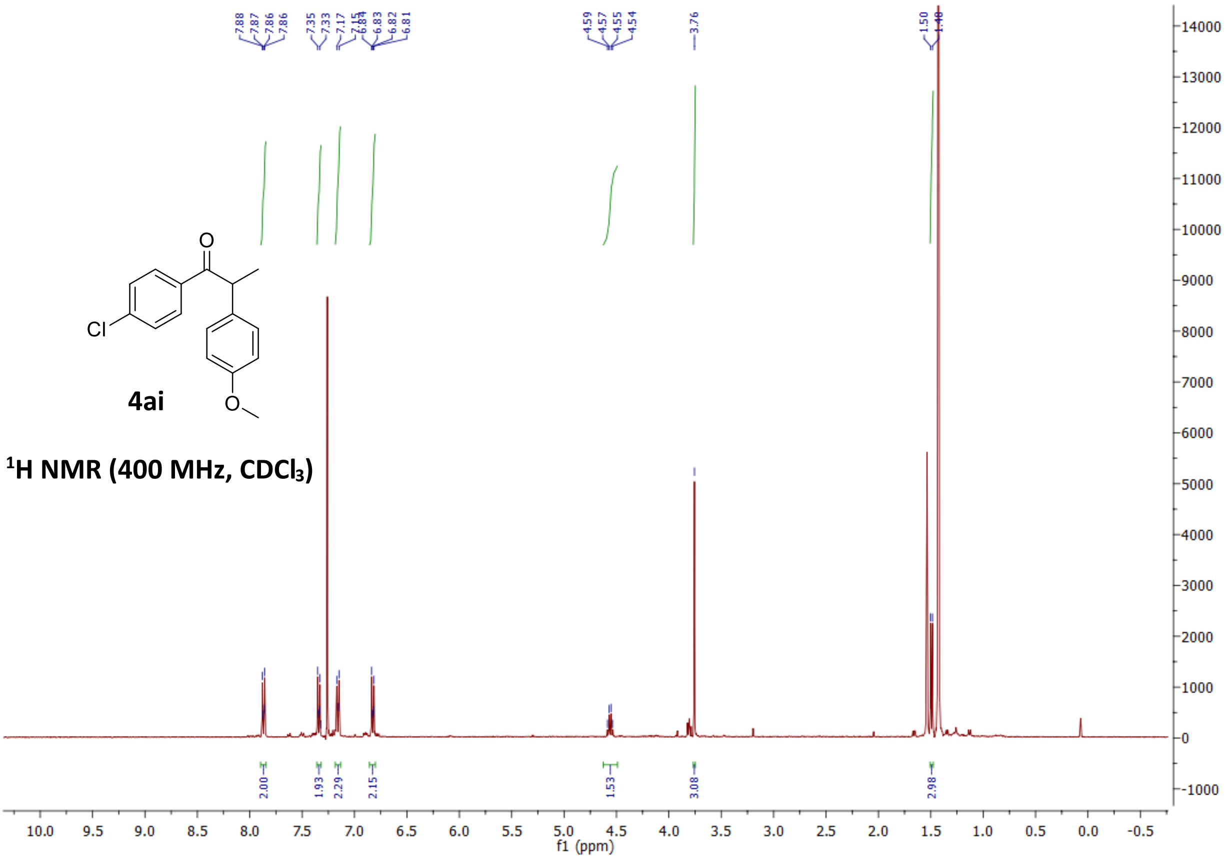
4ah

^{1}H NMR (500 MHz, CDCl$_3$)



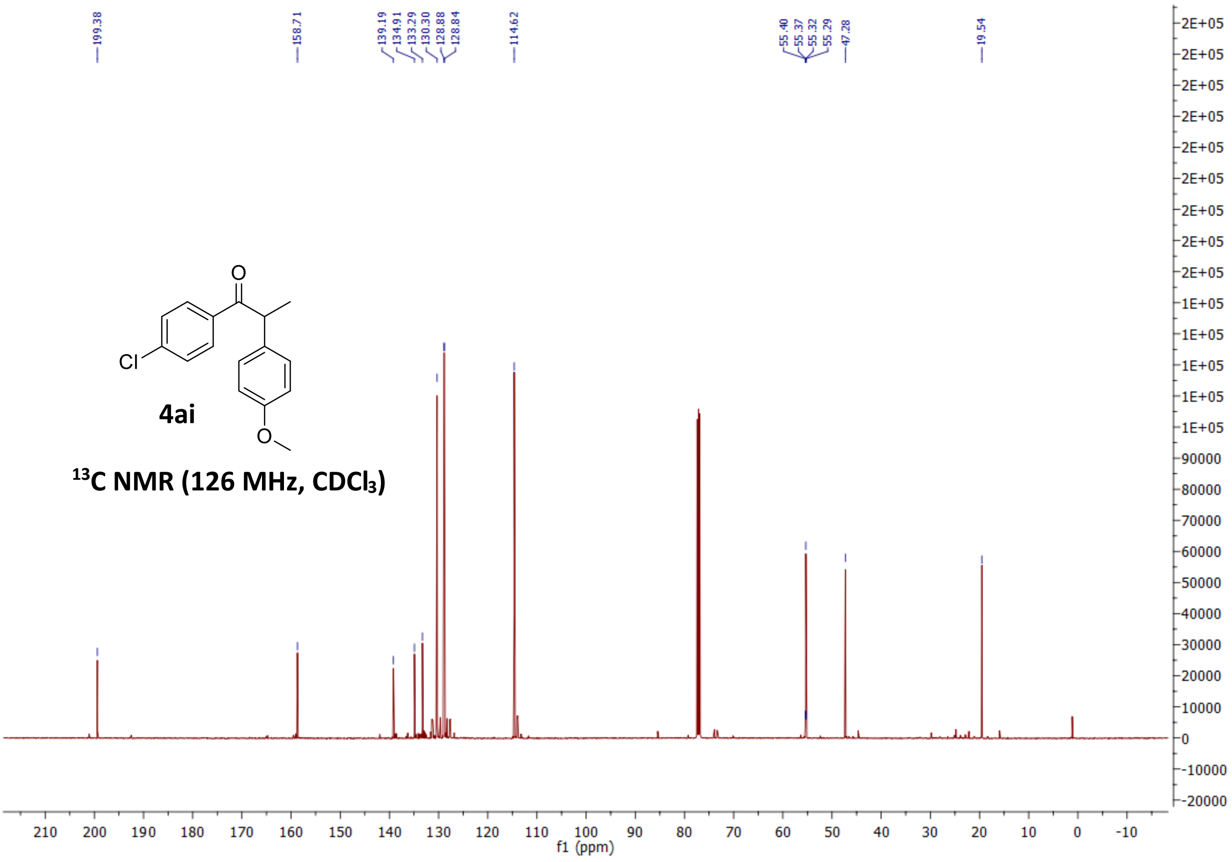
4ah

^{13}C NMR (126 MHz, CDCl$_3$)



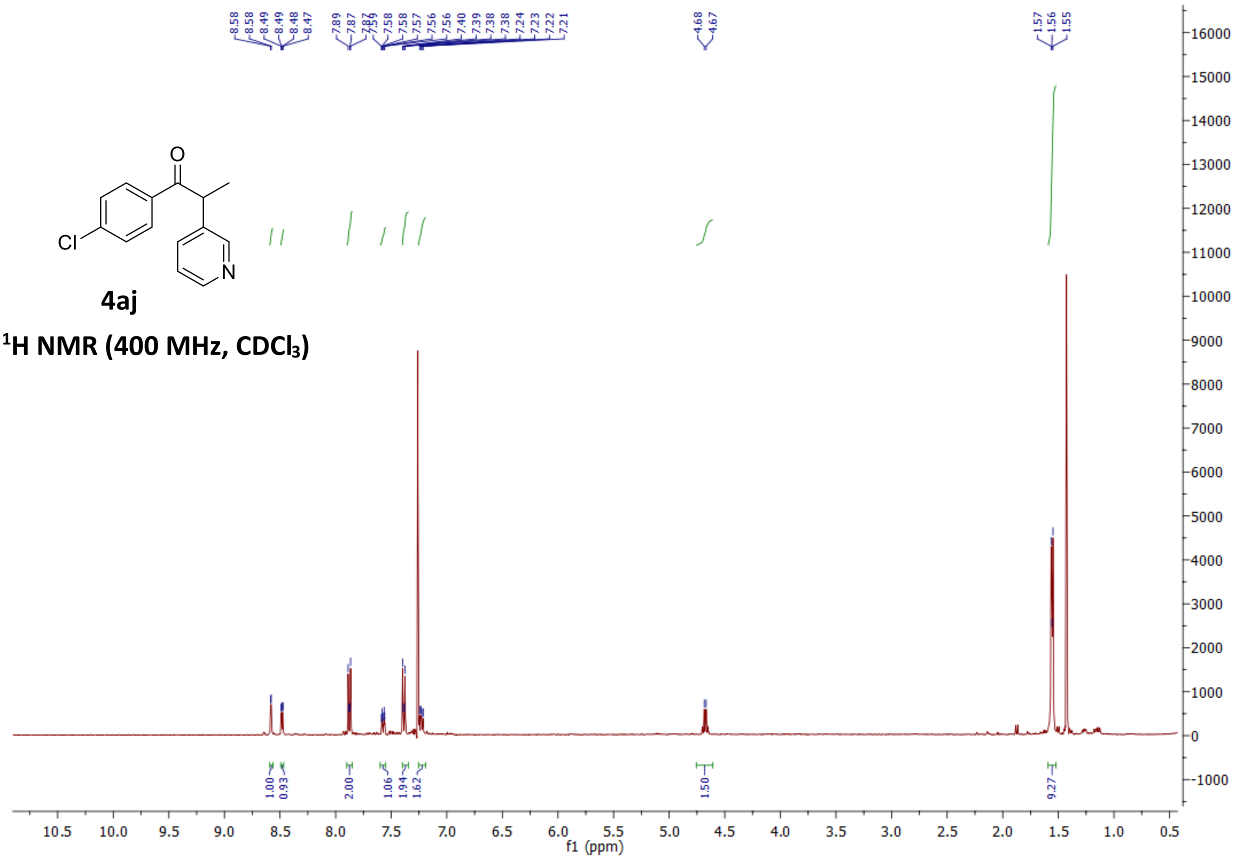
4ai

^{1}H NMR (400 MHz, $CDCl_3$)



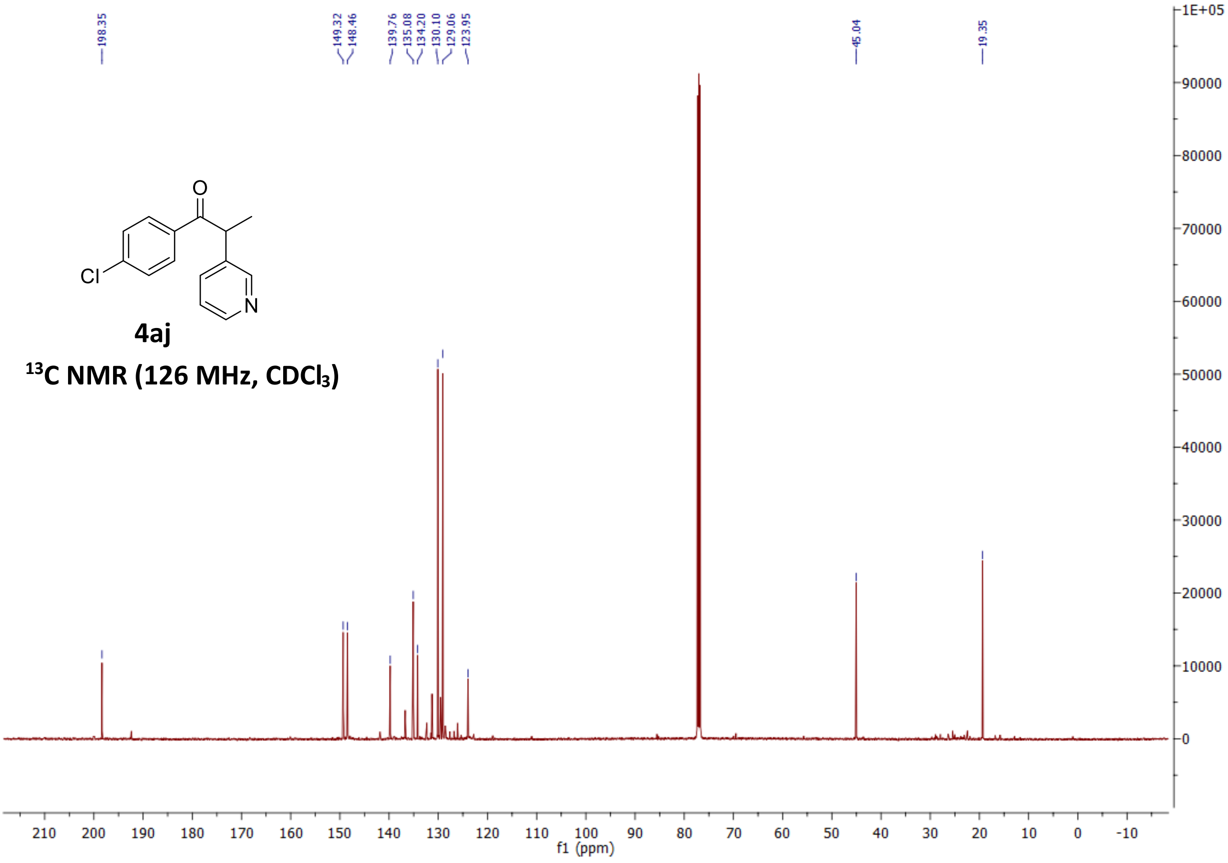
4ai

^{13}C NMR (126 MHz, $CDCl_3$)



4aj

^{1}H NMR (400 MHz, CDCl$_3$)



4aj

^{13}C NMR (126 MHz, CDCl$_3$)

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