Supporting Information

Additions of Aldehyde derived Radicals and Nucleophilic *N*-Alkylindoles to Styrenes by Photoredox-Catalysis

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Experimental details

Unless otherwise indicated, all reagents and solvents were purchased from commercial distributors and are used as received. Tris[2-phenylpyridinato-*C2,N*]iridium(III) was purchased from STREM Chemicals, Inc..

Solvents (toluene, hexanes, ethyl acetate, dichloromethane) used for column chromatography were of technical grade and used after distillation in a rotary evaporator. THF was dried over sodium/benzophenone then distilled and stored under Ar gas for moisture sensitive reactions.

Substrates α-methylstyrenes[1], *N*-methylindoles[2] and photocatalyst 2,4,6-tris(diphenylamino)-3,5-difluorobenzonitrile[3] were prepared according to reported procedures.

TLC was used to check the reactions for full conversion and was performed on Macherey-Nagel Polygram Sil G/UV_{254} thin layer plates. TLC spots were visualized by UV-light irradiation and/or where stained with ceric ammonium molybdate (Indol-3-yl products are visualized as green to dark blue spot) or vanillin (some imide products are visualized as dark spot) dips.

Routine GC-MS analyses were performed with an Agilent Technologies 7890A GC System equipped with a MN Optima® 5 Accent capillary column (0.32 mm × 30 m × 0.25 μm) and coupled with an Agilent Technologies 5975C VL MSD mass detector.

Flash column chromatography was carried out using Merck Silica Gel 60 (40-63 μm). Yields refer to pure isolated compounds.

^{1}H and ^{13}C NMR spectra were measured with Bruker AV 500, AV 400 and AV 300 spectrometers. All chemical shifts are given in ppm downfield relative to TMS and were referenced to the solvent residual peaks.[4] All ^{1}H NMR chemical shifts are designated using the following abbreviations as well as their combinations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal, app. = apparent. For ^{13}C NMR data the following abbreviations are used: p = primary (*CH_3*), s = secondary (*CH_2*), t = tertiary (*CH*), q = quaternary (*C*).

High resolution mass spectra were recorded with a Bruker APEX III FTICR-MS or a Finnigan SSQ 7000 quadrupole MS or a Finnigan MAT 95 double focusing sector field MS instrument.

High performance liquid chromatography (HPLC) was performed on a Shimadzu LC-20AP HPLC-System.

GC analysis was performed on an Agilent Technologies 6890N Network GC System equipped with a MN Optima® 5 Accent capillary column (0.32 mm × 30 m × 0.25 μm) and flame ionization detector using *n*-Heptadecane as internal standard. GC-samples were prepared by diluting 3-5 μL of the reaction mixture with dichloromethane to 1.0 mL (approx. 0.01 M substrate conc.) and for analysis 1 μL was injected by autosampler.

Luminescence measurings were conducted on an Edinburgh Instruments FS5 Spectrofluorometer equipped with a Xenon arc lamp (150 W CW ozone-free) as light source, Czerny-Turner design monochromators with plane gratings and a Photomultiplier R928P as emission detector, arranged in a 90° angle with the sample and light source. Samples were measured as solutions in a square quartz cuvette (dimensions:10 mm x 10 mm).

Abbreviations: MsOH: methanesulfonic acid; TfOH: trifluormethanesulfonic acid; Me: methyl; Et: ethyl; Bn: benzyl; Bz: benzoyl; *t*Bu: *tert*-butyl; Cbz: benzyloxycarbonyl; DCM: dichloromethane; DMF: *N*,*N*-dimethylformamide; EtOAc: ethyl acetate; Et_2O: diethyl ether; MeOH: methanol; TBPB: *tert*-butyl perbenzoate; THF: tetrahydrofurane.

Synthesis of starting materials

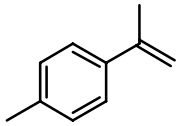
α-Methylstyrenes

Synthesized following a reported method.[1] The isolated styrenes' NMR match the known NMR data.[5-9]

Methyltriphenylphosphonium bromide (4.29 g, 12 mmol, 1.2 equiv.) was dispersed in dry Et_2O (20 mL, 0.6 M – easier removal *in vacuo*, compared with the originally used THF) under argon gas atmosphere. At 0°C a solution of *n*-butyllithium (2.5 M in hexanes, 4.8 mL, 12 mmol, 1.2 equiv.) was added slowly while rigorous stirring of the mixture. The yellow-orange dispersion was stirred at 0°C for 1 h before a solution of the corresponding methylarylketone (10 mmol, 1.0 equiv.) in dry Et_2O (20 mL, 0.5 M) was added dropwisely. The reaction mixture was stirred overnight while warming up

to room temperature. The reaction was quenched by the addition of a saturated aqueous solution of sodium chloride. The aqueous layer was extracted with Et_2O (3x). The combined organic layers were washed with a saturated solution of sodium chloride and dried over sodium sulfate. The solvent was removed under reduced pressure (after addition of silica). The residue was purified by column chromatography using hexanes/Et_2O mixtures as eluent.

1-Methyl-4-(prop-1-en-2-yl)benzene

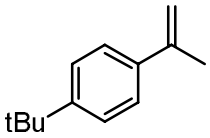


The olefin was synthesized according to the general procedure and isolated using solvent mixture of hexanes/Et_2O (v/v = 95/5) as eluent in column chromatography as colourless oil (631 mg, 4.8 mmol, 48%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 5.34 (s,1 H), 5.04 (s, 1H), 2.35 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.2, 138.5, 137.3, 129.0, 125.5, 111.7, 22.0, 21.2.

1-(*Tert*-butyl)-4-(prop-1-en-2-yl)benzene

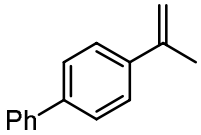


The olefin was synthesized according to the general procedure and isolated using a solvent mixture of hexanes/Et_2O (v/v = 99/1) as eluent in column chromatography as colourless oil (684 mg, 3.9 mmol, 39%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 – 7.40 (m, 2H), 7.40 – 7.34 (m, 2H), 5.37 (s, 1H), 5.06 (s, 1H), 2.17 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 150.5, 143.1, 138.5, 125.3, 125.3, 111.8, 34.6, 31.5, 21.9.

4-(Prop-1-en-2-yl)-1,1'-biphenyl

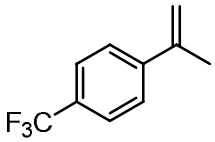


The olefin was synthesized according to the general procedure and isolated using a solvent mixture of hexanes/Et_2O (v/v = 96/4) as eluent in column chromatography as colourless solid (716 mg, 3.7 mmol, 37%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 – 7.53 (m, 6H), 7.49 – 7.41 (m, 2H), 7.38 – 7.31 (m, 1H), 5.44 (s, 1H), 5.12 (s, 1H), 2.20 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 142.9, 140.9, 140.4, 140.3, 128.9, 127.4, 127.1, 127.1, 126.1, 112.6, 22.0.

1-(Prop-1-en-2-yl)-4-(trifluoromethyl)benzene



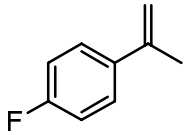
The olefin was synthesized according to the general procedure and isolated using a solvent mixture of hexanes/Et_2O (v/v = 99.5/0.5) as eluent in column chromatography as colourless oil (321 mg, 1.7 mmol, 17%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 – 7.49 (m, 4H), 5.44 (s, 1H), 5.31 – 5.01 (m, 1H), 2.17 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 144.9, 142.4, 129.5 (q, *J* = 32.5 Hz), 125.9, 125.3 (q, *J* = 3.8 Hz), 122.6, 114.7, 21.8.

^{19}F NMR (282 MHz, $CDCl_3$): δ -62.5.

1-Fluoro-4-(prop-1-en-2-yl)benzene



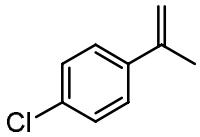
The olefin was synthesized according to the general procedure and isolated using hexanes as eluent in column chromatography as colourless oil (360 mg, 2.6 mmol, 26%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 – 7.38 (m, 2H), 7.06 – 6.96 (m, 2H), 5.33 – 5.27 (m, 1H), 5.09 – 5.04 (m, 1H), 2.14 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 162.5 (d, *J* = 246.2 Hz), 142.4, 137.5 (d, *J* = 3.3 Hz), 127.2 (d, *J* = 7.9 Hz), 115.1 (d, *J* = 21.3 Hz), 112.4 (d, *J* = 1.6 Hz), 22.1.

^{19}F NMR (282 MHz, $CDCl_3$): δ -115.4.

1-Chloro-4-(prop-1-en-2-yl)benzene

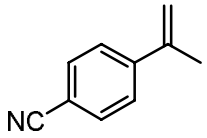


The olefin was synthesized according to the general procedure and isolated using a solvent mixture of hexanes/Et_2O (v/v = 99/1) as eluent in column chromatography as colourless oil (322 mg, 2.1 mmol, 21%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 – 7.36 (m, 2H), 7.33 – 7.27 (m, 2H), 5.39 – 5.33 (m, 1H), 5.13 – 5.08 (m, 1H), 2.14 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 142.3, 139.8, 133.3, 128.5, 127.0, 113.1, 21.9.

4-(Prop-1-en-2-yl)benzonitrile

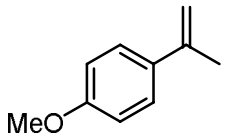


The olefin was synthesized according to the general procedure and isolated using a solvent mixture of hexanes/Et_2O (v/v = 99.5/0.5) as eluent in column chromatography as colourless oil (449 mg, 3.1 mmol, 31%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 – 7.56 (m, 2H), 7.59 – 7.48 (m, 2H), 5.51 – 5.42 (m, 1H), 5.28 – 5.20 (m, 1H), 2.16 (dd, *J* = 1.5, 0.8 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 145.8, 141.9, 132.2, 126.2, 119.1, 115.8, 111.0, 21.6.

1-Methoxy-4-(prop-1-en-2-yl)benzene

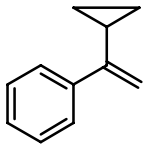


The olefin was synthesized according to the general procedure and isolated using a solvent mixture of hexanes/Et_2O (v/v = 98/2) as eluent in column chromatography as colourless oil (673 mg, 4.5 mmol, 45%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 – 7.36 (m, 2H), 6.93 – 6.80 (m, 2H), 5.32 – 5.25 (m, 1H), 5.03 – 4.96 (m, 1H), 3.82 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.3, 142.8, 134.0, 126.8, 113.7, 110.8, 55.4, 22.1.

(1-Cyclopropylvinyl)benzene



The olefin was synthesized according to the general procedure and isolated using a solvent mixture of hexanes/Et_2O (v/v = 99/1) as eluent in column chromatography as colourless oil (1.27 g, 8.8 mmol, 88%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 – 7.48 (m, 2H), 7.30 – 7.25 (m, 1H), 7.25 – 7.16 (m, 2H), 5.19 (d, *J* = 0.9 Hz, 1H), 4.86 (t, *J* = 1.2 Hz, 1H), 1.63 – 1.52 (m, 1H), 0.80 – 0.71 (m, 2H), 0.56 – 0.47 (m, 2H).

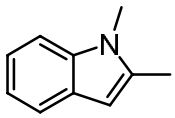
^{13}C NMR (75 MHz, $CDCl_3$): δ 149.5, 141.8, 128.3, 127.6, 126.3, 109.1, 15.8, 6.8.

1-Methylindoles

Synthesized following a reported method.[2] The isolated indoles' NMR spectra match the known NMR data.[10,11]

To NaH (60*wt%*, 430 mg, 10.75 mmol, 1.08 equiv.) in a 100mL-Schlenk round-bottom with stirring bar, a solution of N-H indole (10 mmol) in dry THF (20 mL) was slowly added at 0°C under Ar gas atmosphere and rigorous stirring. The dispersion was stirred for 20 min at 0°C before the addition of methyliodide (622 μL, 10 mmol, 1.0 equiv.) in THF (10 mL). The reaction mixture was stirred over night while warming up to room temperature. The reaction was ended by the addition of a saturated aqueous solution of ammonium chloride. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with a saturated aqueous solution of sodium chloride and dried over magnesium sulfate. The solvent was removed under reduced pressure (after adding some silica) followed by the purification of the residue by column chromatography using eluent mixtures of hexanes/EtOAc.

1,2-Dimethyl-1H-indole

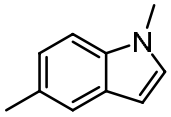


The indole was synthesized according to the general procedure and isolated using a solvent mixture of hexanes/EtOAc (v/v = 98/2) as eluent in column chromatography as pale yellow solid (433 mg, 3.0 mmol, 30%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.52 (d, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.09 – 7.04 (m, 1H), 6.24 (br, 1H), 3.67 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 137.4, 136.9, 128.1, 120.6, 119.7, 119.4, 108.8, 99.7, 29.5, 12.9.

1,5-Dimethyl-1H-indole

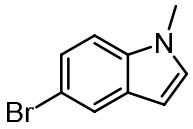


The indole was synthesized according to the general procedure and isolated using a solvent mixture of hexanes/DCM (v/v = 11/1) as eluent in column chromatography as pale yellow solid (481 mg, 3.3 mmol, 33%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.51 (dt, *J* = 1.6, 0.8 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.14 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.07 (d, *J* = 3.1 Hz, 1H), 6.49 (dd, *J* = 3.1, 0.8 Hz, 1H), 3.81 (s, 3H), 2.55 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 135.3, 128.9, 128.8, 128.5, 123.2, 120.6, 109.0, 100.4, 32.9, 21.5.

5-Bromo-1-methylindole



The indole was synthesized according to the general procedure and isolated using a solvent mixture of hexanes/EtOAc (v/v = 95/5) as eluent in column chromatography as colourless solid (1.56 g, 7.4 mmol, 74%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, *J* = 2.2 Hz, 1H), 7.30 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 7.05 (d, *J* = 3.1 Hz, 1H), 6.47 – 6.37 (m, 1H), 3.78 (s, 3H).

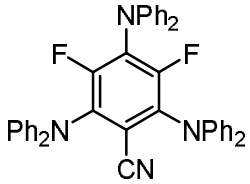
^{13}C NMR (75 MHz, $CDCl_3$): δ 135.5, 130.3, 130.1, 124.5, 123.4, 112.8, 110.8, 100.7, 33.1.

2,4,6-Tris(diphenylamino)-3,5-difluorobenzonitrile (DPA_3F_2BN)

Synthesized following a reported procedure; the isolated photocatalyst's spectra match the reported ones.[3]

In a Schlenk flask diphenylamine (159 mg, 0.94 mmol, 3.8 equiv.) was dissolved in dry THF (5 mL) under Ar gas atmosphere. Sodium hydride (60% in paraffin oil, 57 mg, 1.43 mmol, 5.7 equiv.) was added in little portions to the solution under rigorous stirring. After full addition the pale yellow suspension was stirred for 40 min at 50°C. At room temperature under rigorous stirring pentafluorobenzonitrile (31.5 µL, 0.25 mmol, 1.0 equiv.) was added before stirring the beige reaction mixture for 24 h at room temperature.

The reaction was quenched by the addition of water. After the removal of THF, the residue was extracted with DCM. The organic layer was washed with water and brine before drying over $MgSO_4$. All volatiles were removed *in vacuo* (after the addition of some silica) and the resulting residue was purified by column chromatography using a solvent mixture of hexanes/DCM (10/1 -> 1/1). 2,4,6-tris(diphenylamino)-3,5-difluorobenzonitrile was obtained as yellow solid (128 mg, 0.20 mmol, 80%).



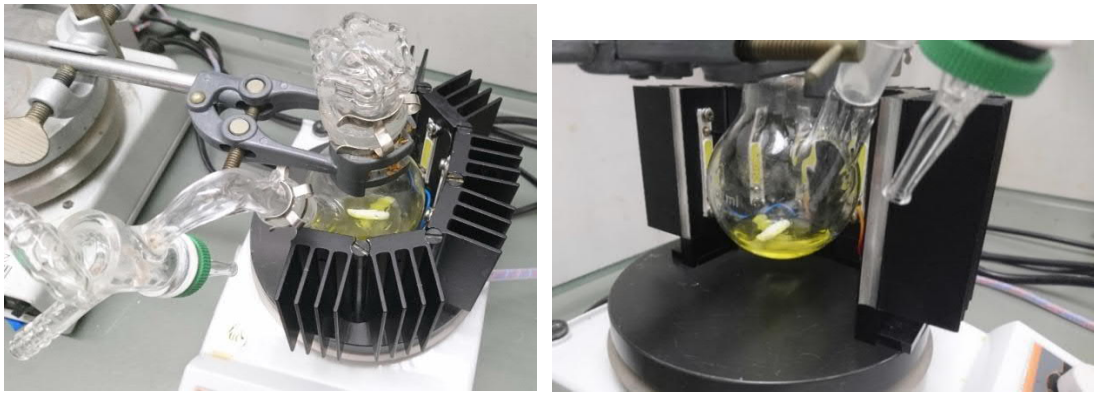
^{1}H NMR (501 MHz, CD_2Cl_2): δ 7.32 – 7.24 (m, 12H), 7.09 – 7.02 (m, 6H), 7.02 – 6.97 (m, 12H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 155.1 (dd, *J* = 258.0, 5.8 Hz), 146.1, 145.9, 135.6 (dd, *J* = 12.1, 4.8 Hz), 130.7 (t, *J* = 12.7 Hz), 129.7, 124.4, 123.8, 122.1, 122.0, 113.7 (t, *J* = 4.1 Hz), 110.9 (t, *J* = 4.2 Hz).

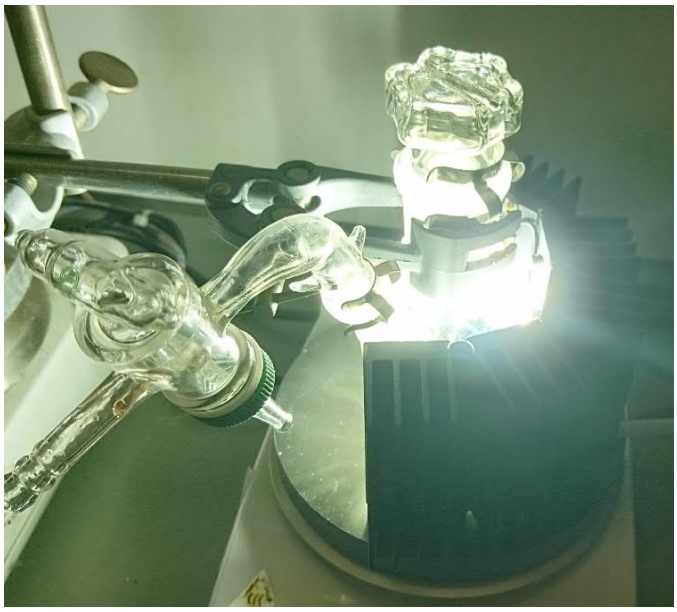
^{19}F NMR (471 MHz, CD_2Cl2): δ -121.18.

Synthesis of products

Reaction set-up for photocatalytic reactions

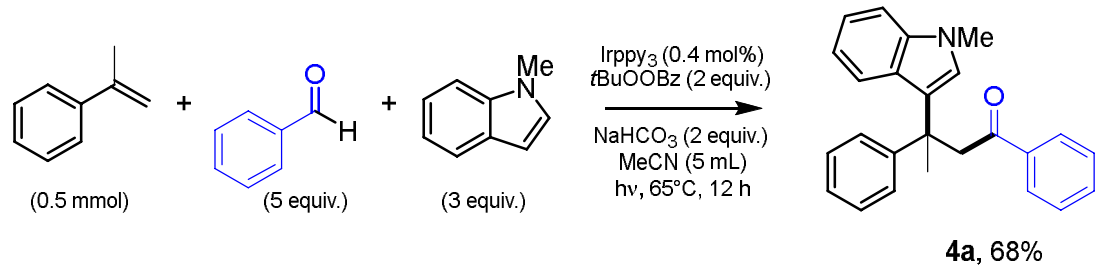


Supplementary Figure S1: Reaction set-up, before the start of the reaction, top and side view



Supplementary Figure S2: Reaction set-up, during the reaction, top view

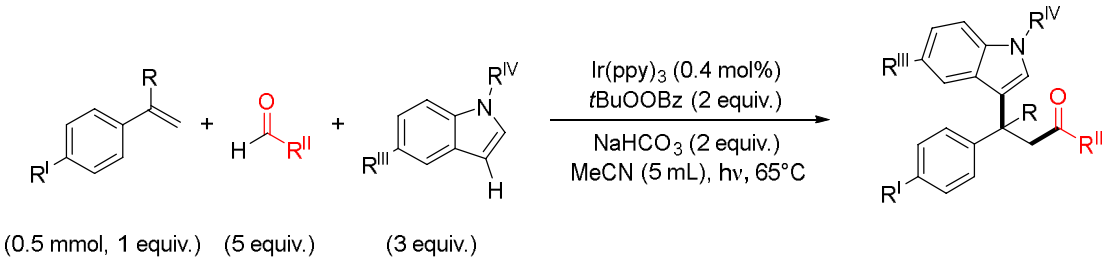
Synthesis of 3-(1-methyl-1H-indol-3-yl)-1,3-diphenylbutan-1-one (4a)



In a Schlenk-round-bottom-flask (100 mL), tris(2-phenylpyridinato-*C2,N*-)iridium (III) (1.3 mg, 2.0 µmol, 0.004 equiv.) and sodium hydrogencarbonate (84 mg, 1.0 mmol, 2 equiv.) were dispersed in dry acetonitrile (5 mL) under Ar gas atmosphere. Subsequently α-methylstyrene (65 µL, 0.5 mmol, 1 equiv.), *N*-methylindole (187 µL, 1.5 mmol, 3 equiv.), benzaldehyde (253 µL, 2.5 mmol, 5 equiv.) and TBPB (187 µL, 1 mmol, 2 equiv.) were added to the yellow dispersion. The reaction mixture was stirred while irradiated with white light (40 W white LED) for 12 h. The irradiation produces a reaction temperature of around 65°C.

The cooled down reaction mixture was diluted, dried under reduced pressure (after addition of some silica) and the obtained residue was purified by column chromatography using a solvent mixture of hexanes/EtOAc (v/v = 40/1 -> 25/1) as eluent. 3-(1-methyl-1H-indol-3-yl)-1,3-diphenylbutan-1-one (**4a**) was obtained as yellow oil (120 mg, 0.34 mmol, 68%).

Difunctionalization reactions with indole nucleophiles



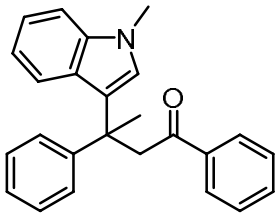
In a Schlenk-round-bottom-flask (100 mL, 0.5 mmol scale), tris(2-phenylpyridinato-*C2,N*-)iridium (III) (1.3 mg, 0.004 equiv.) and sodium hydrogencarbonate (84 mg, 1 mmol, 2 equiv.) were dispersed in dry acetonitrile (5 mL) under Ar gas atmosphere. Subsequently the corresponding styrene (0.5 mmol, 1 equiv.), *N*-methylindole

(1.5 mmol, 3 equiv.), aldehyde (2.5 mmol, 5 equiv.) and TBPB (1 mmol, 2 equiv.) were added to the yellow dispersion. The reaction mixture was stirred while irradiated with white light (40 W white LED) for 12 h. The irradiation produces a reaction temperature of around 65°C.

The reaction mixture was diluted, dried under reduced pressure (after addition of some silica) and the residue was purified by column chromatography using eluent mixtures of hexanes/EtOAc.

These indole compounds often have showed to decompose when stored in solution containing oxygen.

3-(1-Methyl-1H-indol-3-yl)-1,3-diphenylbutan-1-one (4a)



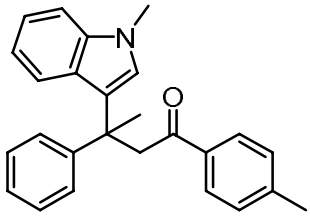
The general procedure using a solvent mixture of hexanes/EtOAc (v/v = 40/1 -> 25/1) as eluent in column chromatography lead to the isolation of this product as yellow oil (120 mg, 0.34 mmol, 68%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.61 – 7.55 (m, 2H), 7.42 – 7.35 (m, 2H), 7.39 – 7.31 (m, 1H), 7.29 – 7.21 (m, 2H), 7.21 – 7.13 (m, 4H), 7.15 – 7.08 (m, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.91 – 6.83 (m, 1H), 6.86 (s, 1H), 4.01 (d, *J* = 14.1 Hz, 1H), 3.73 (d, *J* = 14.1 Hz, 1H), 3.66 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 200.1, 148.3, 138.3, 137.8, 132.2, 128.2, 127.9, 127.9, 126.9, 126.7, 126.3, 126.1, 122.3, 121.4, 121.3, 118.7, 109.3, 48.5, 42.2, 32.7, 28.3.

HRMS (ESI): calculated for $[C_{25}H_{23}NONa]^+$: 376.1672; found: 376.1671.

3-(1-Methyl-1*H*-indol-3-yl)-3-phenyl-1-(*p*-tolyl)butan-1-one (4b)



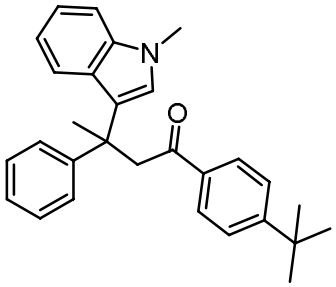
The general procedure using a solvent mixture of hexanes/EtOAc (v/v = 40/1 -> 25/1) lead to the isolation of this product as yellow oil (99 mg, 0.27 mmol, 54%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.34 (m, 2H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.12 (m, 2H), 7.15 – 7.08 (m, 1H), 7.02 – 6.95 (m, 3H), 6.89 – 6.84 (m, 1H), 6.86 (s, 1H), 3.94 (d, *J* = 14.3 Hz, 1H), 3.72 (d, *J* = 14.3 Hz, 1H), 3.67 (s, 3H), 2.30 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.5, 148.3, 143.0, 137.8, 135.9, 128.6, 128.2, 128.1, 126.9, 126.7, 126.4, 126.0, 122.5, 121.31, 121.30, 118.6, 109.3, 48.5, 42.2, 32.7, 28.3, 21.6.

HRMS (ESI): calculated for $[C_{26}H_{25}NONa]^+$: 390.1828; found: 390.1825

1-(4-(*Tert*-butyl)phenyl)-3-(1-methyl-1*H*-indol-3-yl)-3-phenylbutan-1-one (4c)



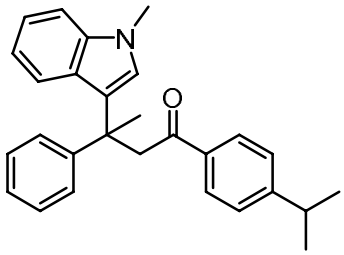
The general procedure using a solvent mixture of hexanes/EtOAc (v/v = 40/1 -> 22/1) lead to the isolation of this product as yellow oil (79 mg, 0.29 mmol, 39%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.54 – 7.48 (m, 2H), 7.39 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.19 – 7.13 (m, 4H), 7.13 – 7.08 (m, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.89 – 6.85 (m, 1H), 6.84 (s, 1H), 4.01 (d, *J* = 14.0 Hz, 1H), 3.67 (d, *J* = 14.0 Hz, 1H), 3.63 (s, 3H), 1.96 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.8, 155.7, 148.5, 137.8, 135.8, 128.2, 127.8, 126.9, 126.8, 126.4, 126.0, 124.7, 122.2, 121.31, 121.30, 118.6, 109.2, 48.4, 42.2, 35.0, 32.6, 31.2, 28.4.

HRMS (ESI): calculated for $[C_{29}H_{31}NONa]^+$: 432.2298; found: 432.2296.

1-(4-Isopropylphenyl)-3-(1-methyl-1*H*-indol-3-yl)-3-phenylbutan-1-one (4d)



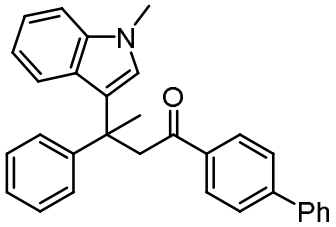
The general procedure using a solvent mixture of hexanes/EtOAc (v/v = 40/1 -> 22/1) for column chromatography and a solvent mixture of hexanes/DCM (v/v = 50/50) for a subsequent thin layer chromatography lead to the isolation of this product as white solid (132 mg, 0.36 mmol, 67%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.17 – 7.13 (m, 2H), 7.11 – 7.07 (m, 1H), 6.97 (dd, *J* = 14.5, 8.2 Hz, 3H), 6.87 – 6.83 (m, 1H), 6.83 (s, 1H), 3.97 (d, *J* = 14.1 Hz, 1H), 3.66 (d, *J* = 14.1 Hz, 1H), 3.64 (s, 3H), 2.82 (h, *J* = 6.9 Hz, 1H), 1.95 (s, 3H), 1.18 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.8, 153.6, 148.4, 137.8, 136.3, 128.2, 128.1, 126.9, 126.8, 126.4, 126.0, 125.9, 122.3, 121.3 (2C), 118.6, 109.3, 48.4, 42.2, 34.2, 32.7, 28.4, 23.84, 23.80.

HRMS (ESI): calculated for $[C_{28}H_{29}NONa]^+$: 418.2141; found: 418.2140.

1-([1,1'-Biphenyl]-4-yl)-3-(1-methyl-1*H*-indol-3-yl)-3-phenylbutan-1-one (4e)



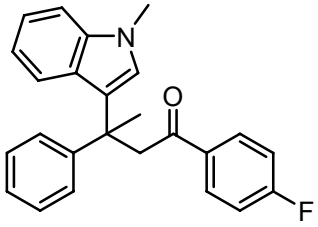
The general procedure using a solvent mixture of hexanes/EtOAc (v/v = 40/1 -> 25/1) for column chromatography lead to the isolation of this product as yellow oil (68 mg, 0.l6 mmol, 31%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.62 – 7.56 (m, 2H), 7.55 – 7.49 (m, 2H), 7.48 – 7.41 (m, 2H), 7.42 – 7.36 (m, 3H), 7.36 – 7.31 (m, 2H), 7.29 – 7.22 (m, 2H), 7.21 – 7.14 (m, 1H), 7.16 – 7.08 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.88 (ddd, *J* = 8.0, 6.4, 1.6 Hz, 1H), 6.85 (s, 1H), 4.05 (d, *J* = 13.7 Hz, 1H), 3.69 (d, *J* = 13.7 Hz, 1H), 3.62 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 200.0, 148.4, 144.8, 140.2, 137.8, 137.0, 129.0, 128.4, 128.2, 128.1, 127.3, 126.9, 126.8, 126.44, 126.43, 126.1, 122.1, 121.4, 121.3, 118.7, 109.3, 48.5, 42.4, 32.7, 28.5.

HRMS (ESI): calculated for $[C_{28}H_{29}NONa]^+$: 452.1985; found: 452.1986.

1-(4-Fluorophenyl)-3-(1-methyl-1*H*-indol-3-yl)-3-phenylbutan-1-one (4f)



The general procedure using a solvent mixture of hexanes/EtOAc (v/v = 40/1 -> 13/1) for column chromatography and a solvent mixture of hexanes/EtOAc (v/v = 70/1) for a subsequent thin layer chromatography lead to the isolation of this product as white solid (124 mg, 0.33 mmol, 67%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.55 – 7.49 (m, 2H), 7.38 – 7.32 (m, 2H), 7.27 – 7.19 (m, 2H), 7.19 – 7.13 (m, 2H), 7.14 – 7.07 (m, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.86 (ddd,

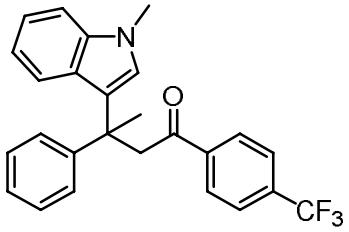
J = 8.0, 6.9, 1.0 Hz, 1H), 6.84 (s, 1H), 6.81 – 6.72 (m, 2H), 3.96 (d, *J* = 13.6 Hz, 1H), 3.65 (s, 3H), 3.63 (d, (*J* = 13.6 Hz), 1H), 1.93 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 198.8, 165.2 (d, *J* = 253.8 Hz), 148.2, 137.8, 134.7 (d, *J* = 3.1 Hz), 130.4 (d, *J* = 9.1 Hz), 128.3, 126.8, 126.7, 126.3, 126.2, 122.0, 121.4 (d, *J* = 28.6 Hz), 118.8, 114.8, 114.7, 109.3, 48.4, 42.4, 32.7, 28.5.

^{19}F NMR (471 MHz, $CDCl_3$): δ -106.85.

HRMS (ESI): calculated for $[C_{25}H_{22}NOFNa]^+$: 394.1578; found: 394.1576.

3-(1-Methyl-1*H*-indol-3-yl)-3-phenyl-1-(4-(trifluoromethyl)phenyl)butan-1-one (4g)



The general procedure using a solvent mixture of hexanes/EtOAc (v/v = 100/1 ->15/1) as eluent in column chromatography followed by a preparative thin layer chromatography with an eluent of hexanes/EtOAc (v/v = 70/1) lead to the isolation of the product as colourless oil (127 mg, 0.30 mmol, 60%).

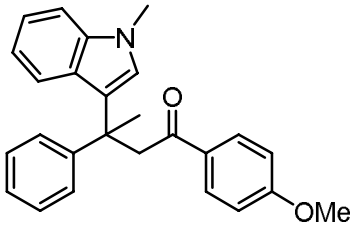
^{1}H NMR (501 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 8.5 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.13 – 7.05 (m, 1H), 6.91 – 6.83 (m, 1H), 6.78 (s, 0H), 4.09 (d, *J* = 12.9 Hz, 0H), 3.59 (d, *J* = 15.1 Hz, 1H), 1.89 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 200.4, 148.2, 140.9, 137.8, 133.2 (q, *J* = 32.5 Hz), 128.46, 127.87, 126.9, 126.8, 126.41, 126.40, 124.5 (q, *J* = 3.7 Hz), 121.7, 121.3 (2C), 119.0, 109.4, 48.7, 42.5, 32.7, 28.8

^{19}F NMR (282 MHz, $CDCl_3$): δ -63.09.

HRMS (ESI): calculated for $[C_{26}H_{22}F_3NONa]^+$: 444.1546; found: 444.1546.

1-(4-Methoxyphenyl)-3-(1-methyl-1*H*-indol-3-yl)-3-phenylbutan-1-one (4h)



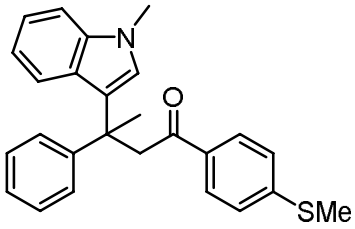
The general procedure using a solvent mixture of hexanes/EtOAc (v/v = 40/1 -> 9/1) as eluent in column chromatography lead to the isolation of the product as white solid (150 mg, 0.39 mmol, 78%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.9 Hz, 2H), 7.38 – 7.34 (m, 3H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.19 – 7.13 (m, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.88 – 6.83 (m, 2H), 6.63 (d, *J* = 8.9 Hz, 3H), 3.91 (d, *J* = 14.0 Hz, 1H), 3.77 (s, 3H), 3.66 (s, 3H), 3.65 (d, *J* = 14.0 Hz, 1H), 1.95 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 198.5, 162.9, 148.4, 137.8, 131.5, 130.2, 128.2, 126.9, 126.7, 126.4, 126.0, 122.5, 121.35, 121.34, 118.7, 113.0, 109.3, 55.5, 48.2, 42.3, 32.7, 28.3.

HRMS (ESI): calculated for $[C_{26}H_{25}NO_2Na]^+$: 406.1777; found: 406.1773.

3-(1-Methyl-1H-indol-3-yl)-1-(4-(methylthio)phenyl)-3-phenylbutan-1-one (4i)



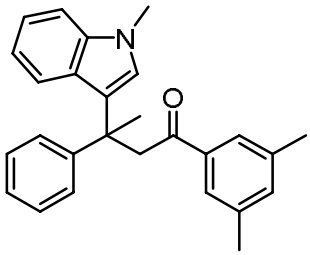
The general procedure using a solvent mixture of hexanes/EtOAc (v/v = 40/1 -> 9/1) as eluent in column chromatography lead to the isolation of the product as white solid (142 mg, 0.36 mmol, 71%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 – 7.42 (m, 2H), 7.41 – 7.32 (m, 2H), 7.28 – 7.20 (m, 2H), 7.20 – 7.14 (m, 2H), 7.14 – 7.07 (m, 1H), 6.98 – 6.91 (m, 3H), 6.89 – 6.83 (m, 1H), 6.83 (s, 1H), 3.94 (d, *J* = 13.8 Hz, 1H), 3.64 (s, 3H), 3.64 (d, *J* = 13.8 Hz, 1H), 2.43 (s, 3H), 1.94 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 199.2, 148.3, 144.6, 137.8, 134.7, 128.3, 128.2, 126.9, 126.8, 126.4, 126.1, 124.4, 122.2, 121.4, 121.3, 118.7, 109.3, 48.3, 42.4, 32.7, 28.4, 14.9.

HRMS (ESI): calculated for $[C_{26}H_{25}NOSNa]^+$: 422.1549; found: 422.1546.

1-(3,5-Dimethylphenyl)-3-(1-methyl-1*H*-indol-3-yl)-3-phenylbutan-1-one (4j)



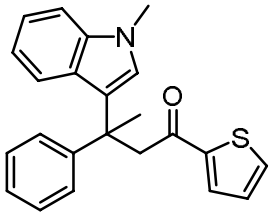
The general procedure using a solvent mixture of hexanes/EtOAc (v/v = 40/1 -> 20/1) for column chromatography and a solvent mixture of hexanes/DCM (v/v = 70/30) for a subsequent thin layer chromatography lead to the isolation of this product as yellow oil (101 mg, 0.26 mmol, 53%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.40 – 7.35 (m, 2H), 7.28 – 7.21 (m, 2H), 7.21 – 7.13 (m, 2H), 7.14 – 7.07 (m, 3H), 7.00 – 6.94 (m, 2H), 6.87 (ddd, *J* = 8.0, 7.0, 0.9 Hz, 1H), 6.82 (s, 1H), 4.00 (d, *J* = 13.7 Hz, 1H), 3.64 (s, 3H), 3.63 (d, *J* = 13.7 Hz, 1H), 2.13 (s, 6H), 1.94 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 200.8, 148.5, 138.4, 137.8, 137.5, 133.8, 128.2, 126.9, 126.8, 126.5, 126.0, 125.8, 122.2, 121.4, 121.3, 118.7, 109.2, 48.6, 42.2, 32.7, 28.4, 21.1.

HRMS (GC-CI): calculated for $[C_{27}H_{28}NO+H]^+$: 382.2165; found: 382.2166.

3-(1-Methyl-1H-indol-3-yl)-3-phenyl-1-(thiophen-2-yl)butan-1-one (4k)



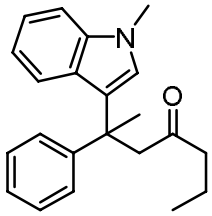
The general procedure using a solvent mixture of hexanes/EtOAc (v/v = 40/1 -> 9/1) as eluent in column chromatography lead to the isolation of the product as white solid (133 mg, 0.37 mmol, 75%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.41 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.25 – 7.18 (m, 3H), 7.18 – 7.13 (m, 1H), 7.13 – 7.09 (m, 1H), 7.04 (dd, *J* = 3.8, 1.0 Hz, 1H), 6.94 – 6.92 (m, 1H), 6.92 (s, 1H), 6.89 – 6.82 (m, 1H), 6.73 (dd, *J* = 4.9, 3.9 Hz, 1H), 3.85 (d, *J* = 13.4 Hz, 1H), 3.68 (s, 3H), 3.61 (d, *J* = 13.4 Hz, 1H), 1.96 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 192.6, 148.1, 145.9, 137.9, 133.2, 131.9, 128.3, 127.6, 126.9, 126.8, 126.4, 126.1, 122.1, 121.4, 121.3, 118.7, 109.3, 49.6, 42.6, 32.8, 28.5.

HRMS (ESI): calculated for $[C_{23}H_{21}NOS+H]^+$: 360.1417; found: 360.1413.

2-(1-Methyl-1*H*-indol-3-yl)-2-phenylheptan-4-one (4l)



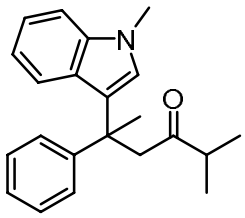
The general procedure using a solvent mixture of hexanes/EtOAc (v/v = 40/1 -> 22/1) as eluent in column chromatography lead to the isolation of the product as yellow oil (84 mg, 0.26 mmol, 53%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.33 – 7.29 (m, 2H), 7.28 – 7.23 (m, 3H), 7.21 – 7.14 (m, 2H), 7.16 – 7.11 (m, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.94 (s, 1H), 6.89 – 6.84 (m, 1H), 3.75 (s, 3H), 3.38 (d, *J* = 12.8 Hz, 1H), 3.15 (d, *J* = 12.8 Hz, 1H), 1.88 (s, 3H), 1.79 (dt, *J* = 17.4, 7.0 Hz, 1H), 1.69 (dt, *J* = 17.4, 7.1 Hz, 1H), 1.31 – 1.23 (m, 2H), 0.57 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 210.9, 148.2, 137.8, 128.2, 126.7, 126.6, 126.3, 126.1, 121.8, 121.5, 121.2, 118.7, 109.4, 52.8, 46.7, 42.0, 32.8, 28.4, 16.8, 13.5.

HRMS (ESI): calculated for $[C_{22}H_{25}NONa]^+$: 342.1828; found: 342.1823.

2-Methyl-5-(1-methyl-1*H*-indol-3-yl)-5-phenylhexan-3-one (4m)



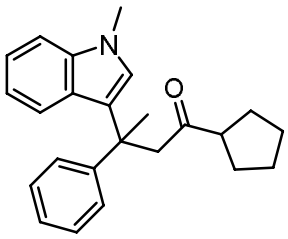
The general procedure using a solvent mixture of hexanes/EtOAc (v/v = 40/1 -> 25/1) as eluent in column chromatography lead to the isolation of the product as yellow oil (54 mg, 0.17 mmol, 34%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.32 – 7.28 (m, 1H), 7.28 – 7.21 (m, 3H), 7.18 – 7.14 (m, 1H), 7.14 – 7.10 (m, 1H), 6.95 – 6.90 (m, 2H), 6.87 – 6.82 (m, 1H), 3.76 (s, 3H), 3.43 (d, *J* = 13.4 Hz, 1H), 3.23 (d, *J* = 13.4 Hz, 1H), 1.94 – 1.83 (m, 4H), 0.78 (d, *J* = 6.9 Hz, 3H), 0.70 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 214.4, 148.3, 137.8, 128.2, 126.8, 126.5, 126.3, 126.1, 122.2, 121.4, 121.2, 118.7, 109.4, 51.1, 42.0, 32.8, 28.3, 18.1, 17.6.

HRMS (ESI): calculated for $[C_{22}H_{25}NONa]^+$: 342.1828; found: 342.1827.

1-Cyclopentyl-3-(1-methyl-1*H*-indol-3-yl)-3-phenylbutan-1-one (4n)



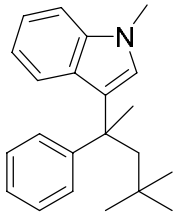
The general procedure using a solvent mixture of hexanes/EtOAc (v/v = 50/1-> 25/1) as eluent in column chromatography lead to the isolation of the product as pale yellow oil (65 mg, 0.19 mmol, 38%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.34 – 7.30 (m, 2H), 7.28 – 7.23 (m, 3H), 7.21 – 7.13 (m, 1H), 7.13 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.94 (s, 1H), 6.86 (ddd, *J* = 8.0, 7.0, 0.9 Hz, 1H), 3.76 (s, 3H), 3.44 (d, *J* = 13.7 Hz, 1H), 3.26 (d, *J* = 13.7 Hz, 1H), 2.25 – 2.15 (m, 1H), 1.90 (s, 3H), 1.53 – 1.43 (m, 5H), 1.39 – 1.27 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 212.9, 148.2, 137.8, 128.2, 126.5, 126.3, 126.0, 122.3, 121.4, 121.2, 118.6, 109.3, 52.7, 52.5, 42.0, 32.8, 29.0, 28.4, 28.3, 26.0.

HRMS (ESI): calculated for $[C_{24}H_{27}NONa]^+$: 368.1985; found: 368.1982.

3-(4,4-Dimethyl-2-phenylpentan-2-yl)-1-methyl-1H-indole (5)



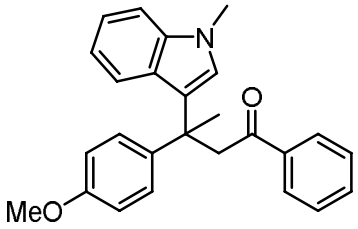
The general procedure using pivaldehyde in the reaction and a solvent mixture of hexanes/EtOAc (v/v = 200/1) as eluent in column chromatography, and a mixture of hexanes/DCM (v/v = 30/1) for a subsequent thin layer chromatography lead to the isolation of this product as pale yellow oil (584 mg, 0.27 mmol, 55%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.44 – 7.40 (m, 2H), 7.28 – 7.22 (m, 3H), 7.19 – 7.10 (m, 2H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.93 (s, 1H), 6.86 (ddd, *J* = 8.1, 7.1, 0.9 Hz, 1H), 3.77 (s, 3H), 2.43 (d, *J* = 14.1 Hz, 1H), 2.34 (d, *J* = 14.1 Hz, 1H), 1.92 (s, 3H), 0.79 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 149.8, 137.9, 127.9, 127.7, 126.8, 126.11, 126.05, 125.6, 121.9, 121.2, 118.4, 109.2, 53.7, 43.3, 32.9, 32.8, 32.1, 28.8.

HRMS (GC-EI): calculated for $[C_{22}H_{27}N]^+$: 305.2138; found: 305.2138.

3-(4-Methoxyphenyl)-3-(1-methyl-1*H*-indol-3-yl)-1-phenylbutan-1-one (6a)



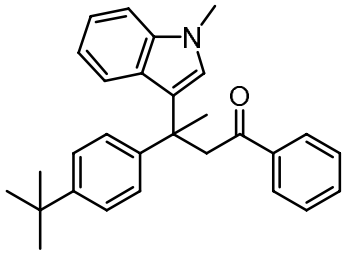
The general procedure using mixtures of hexanes/EtOAc (v/v = 40/1 -> 20/1) as eluent for column chromatography lead to the isolation of the product as yellow oil (144 mg, 0.38 mmol, 75%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.50 – 7.44 (m, 2H), 7.28 – 7.21 (m, 1H), 7.19 – 7.13 (m, 2H), 7.10 – 7.03 (m, 3H), 7.05 – 6.98 (m, 1H), 6.98 – 6.90 (m, 3H), 6.78 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 6.73 (s, 1H), 3.90 (d, *J* = 14.1 Hz, 1H), 3.59 (d, *J* = 14.1 Hz, 1H), 3.55 (s, 3H), 2.20 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 200.2, 145.3, 138.4, 137.8, 135.4, 132.2, 128.9, 127.9 (2C), 126.7, 126.70, 126.4, 122.4, 121.4, 121.3, 118.6, 109.3 48.6, 41.9, 32.7, 28.4, 21.1.

HRMS (ESI): calculated for $[C_{26}H_{25}NO_2Na]^+$: 406.1777; found: 406.1776.

3-(4-(*Tert*-butyl)phenyl)-3-(1-methyl-1*H*-indol-3-yl)-1-phenylbutan-1-one (6b)



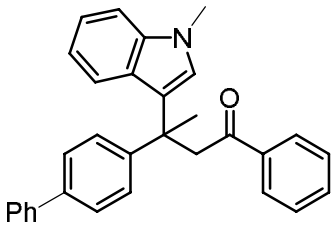
The general procedure using solvent mixtures of hexanes/EtOAc (v/v = 40/1 -> 25/1) for column chromatography and a solvent mixture of DCM/hexanes (v/v = 70/30) for subsequent preparative thin layer chromatography lead to the isolation of the product as white solid (154 mg, 0.38 mmol, 75%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.56 – 7.51 (m, 2H), 7.35 – 7.31 (m, 1H), 7.28 – 7.25 (m, 2H), 7.24 – 7.20 (m, 2H), 7.19 – 7.14 (m, 2H), 7.14 – 7.10 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.90 – 6.85 (m, 2H), 3.95 (d, *J* = 13.8 Hz, 1H), 3.72 (d, *J* = 13.8 Hz, 1H), 3.67 (s, 3H), 1.96 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 200.4, 148.6, 145.0, 138.4, 137.8, 132.1, 127.9, 127.8, 126.7, 126.47, 126.45, 125.0, 122.4, 121.5, 121.3, 118.5, 109.3, 48.8, 42.0, 34.4, 32.7, 31.5, 28.3.

HRMS (ESI): calculated for $[C_{29}H_{31}NONa]^+$: 432.2298; found: 432.2298.

3-([1,1'-Biphenyl]-4-yl)-3-(1-methyl-1*H*-indol-3-yl)-1-phenylbutan-1-one (6c)



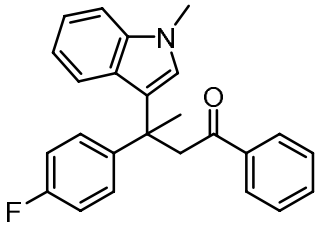
The general procedure using solvent mixtures of hexanes/EtOAc (v/v = 40/1->25/1) as eluent in column chromatography and a mixture of hexanes/DCM (v/v = 80/20) in a subsequent preparative thin layer chromatography lead to the isolation of the product as white solid (150 mg, 0.35 mmol, 70%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.63 – 7.54 (m, 4H), 7.51 – 7.42 (m, 4H), 7.45 – 7.38 (m, 2H), 7.39 – 7.29 (m, 2H), 7.21 – 7.15 (m, 3H), 7.15 – 7.10 (m, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.93 – 6.86 (m, 1H), 6.89 (s, 1H), 4.02 (d, *J* = 14.1 Hz, 1H), 3.78 (d, *J* = 14.1 Hz, 1H), 3.68 (s, 3H), 2.02 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 200.1, 147.3, 141.0, 138.7, 138.3, 137.8, 132.2, 128.8, 127.9, 127.9, 127.3, 127.1, 127.1, 126.8, 126.7, 126.3, 122.2, 121.41, 121.36, 118.7, 109.3, 48.7, 42.1, 32.7, 28.3.

HRMS (ESI): calculated for $[C_{31}H_{27}NONa]^+$: 452.1985; found: 452.1984.

3-(4-Fluorophenyl)-3-(1-methyl-1*H*-indol-3-yl)-1-phenylbutan-1-one (6d)



The general procedure using solvent mixtures of hexanes/EtOAc (v/v = 40/1->22/1) as eluent in column chromatography lead to the isolation of the product as yellow oil (80 mg, 0.23 mmol, 43%).

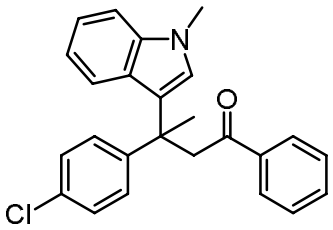
^{1}H NMR (501 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.40 – 7.35 (m, 1H), 7.35 – 7.30 (m, 2H), 7.22 – 7.16 (m, 3H), 7.16 – 7.11 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.94 – 6.86 (m, 4H), 3.95 (d, *J* = 14.2 Hz, 1H), 3.72 (d, *J* = 14.2 Hz, 1H), 3.67 (s, 3H), 1.97 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.8, 162.2, 160.3, 143.8 (d, ^{4}J = 3.2 Hz), 138.0 (d, ^{1}J = 50.6 Hz), 132.4, 128.5 (d, ^{3}J = 7.9 Hz), 128.0, 127.9, 126.5, 126.1, 122.3, 121.5, 121.2, 118.8, 114.8 (d, ^{2}J = 20.9 Hz), 109.4, 48.7, 41.8, 32.7, 28.3.

^{19}F NMR (471 MHz, $CDCl_3$): δ -117.7.

HRMS (ESI): calculated for $[C_{25}H_{22}NOFNa]^{+}$: 394.1578; found: 394.1574.

3-(4-Chlorophenyl)-3-(1-methyl-1*H*-indol-3-yl)-1-phenylbutan-1-one (6e)



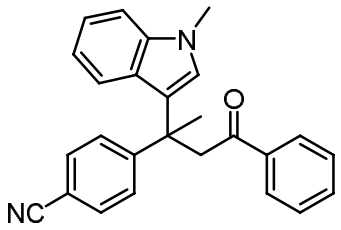
The general procedure using solvent mixtures of hexanes/EtOAc (v/v = 40/1->25/1) as eluent in column chromatography lead to the isolation of the product as yellow oil (107 mg, 0.28 mmol, 54%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 – 7.57 (m, 2H), 7.42 – 7.35 (m, 1H), 7.34 – 7.28 (m, 2H), 7.24 – 7.17 (m, 5H), 7.17 – 7.10 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.95 – 6.88 (m, 1H), 6.86 (s, 1H), 3.97 (d, *J* = 14.4 Hz, 1H), 3.71 (d, *J* = 14.4 Hz, 1H), 3.67 (s, 3H), 1.96 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 199.5, 146.8, 138.2, 137.8, 132.4, 131.8, 128.5, 128.3, 128.0, 127.9 126.6, 126.1, 122.0, 121.5, 121.1, 118.8, 109.4, 48.5, 41.9, 32.7, 28.2.

HRMS (ESI): calculated for $[C_{25}H_{22}NOClNa]^+$: 410.1282; found: 410.1282.

4-(2-(1-Methyl-1H-indol-3-yl)-4-oxo-4-phenylbutan-2-yl)benzonitrile (6f)



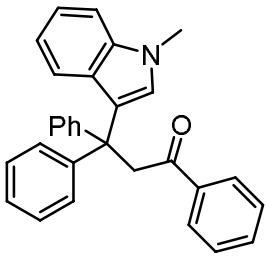
The general procedure using mixtures of hexanes/EtOAc (v/v = 9/1 -> 4/1) as eluent for column chromatography and a mixture of hexanes/DCM (v/v = 30/70) in a subsequent preparative thin layer chromatography lead to the isolation of the product as yellow oil (22 mg, 0.058 mmol, 12%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 – 7.60 (m, 2H), 7.54 – 7.45 (m, 4H), 7.43 – 7.38 (m, 1H), 7.26 – 7.18 (m, 3H), 7.14 (ddd, *J* = 8.2, 5.2, 2.9 Hz, 1H), 6.93 – 6.84 (m, 3H), 3.97 (d, *J* = 14.9 Hz, 1H), 3.75 (d, *J* = 14.9 Hz, 1H), 3.70 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 198.0, 152.8, 137.02, 136.95, 131.9, 131.1, 127.3, 127.1, 127.0, 125.6, 124.9, 120.9, 120.6, 119.9, 118.3, 118.2, 109.0, 108.7, 47.5, 41.6, 31.9, 26.8.

HRMS (ESI): calculated for $[C_{26}H_{22}N_2ONa]^+$: 401.1624; found: 401.1622.

3-(1-Methyl-1H-indol-3-yl)-1,3,3-triphenylpropan-1-one (7a)



The general procedure using mixtures of hexanes/EtOAc (v/v = 17/1 -> 12/1) as eluent for column chromatography lead to the isolation of the product as white solid (128 mg,

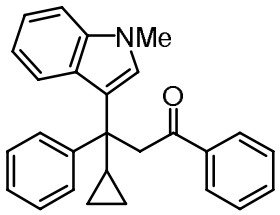
0.31 mmol, 63%). By recrystallization from THF/pentane suitable crystals for X-ray diffractometry analysis were obtained.

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.81 – 7.76 (m, 2H), 7.50 – 7.42 (m, 1H), 7.37 – 7.29 (m, 6H), 7.28 – 7.20 (m, 5H), 7.22 – 7.14 (m, 2H), 7.11 (ddd, *J* = 8.1, 6.7, 0.9 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.83 (ddd, *J* = 8.0, 6.8, 1.0 Hz, 1H), 6.75 (s, 1H), 4.49 (s, 2H), 3.70 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 197.8, 146.5, 138.2, 137.7, 132.7, 129.6, 128.9, 128.4, 127.9 (2C), 127.2, 126.1, 121.8, 121.2, 121.2, 118.8, 109.4, 51.5, 49.6, 32.9.

HRMS (ESI): calculated for $[C_{30}H_{25}NONa]^+$: 438.1828; found: 438.1832.

3-Cyclopropyl-3-(1-methyl-1H-indol-3-yl)-1,3-diphenylpropan-1-one (7b)



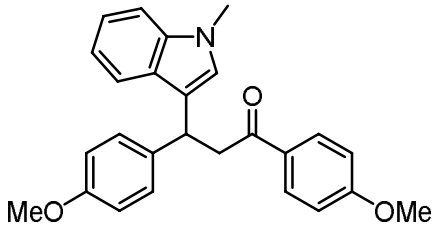
The general procedure a solvent mixture of hexanes/EtOAc (v/v = 200/1) as eluent in column chromatography lead to the isolation of this product as pale yellow oil (50 mg, 0.13 mmol, 26%).

1H NMR (501 MHz, $CDCl_3$): δ 7.62 – 7.58 (m, 2H), 7.38 – 7.31 (m, 3H), 7.24 – 7.19 (m, 2H), 7.19 – 7.14 (m, 3H), 7.11 (d, J = 8.2 Hz, 1H), 7.05 (s, 1H), 7.06 – 7.02 (m, 1H), 6.76 (td, J = 7.5, 6.9, 1.0 Hz, 1H), 6.68 (d, J = 8.2 Hz, 1H), 4.12 (d, J = 13.8 Hz, 1H), 3.83 (d, J = 13.8 Hz, 1H), 3.68 (s, 3H), 2.14 – 2.06 (m, 1H), 0.51 – 0.38 (m, 2H), 0.04 – -0.05 (m, 2H).+

^{13}C NMR (126 MHz, $CDCl_3$): δ 200.2, 144.3, 138.7, 137.4, 132.1, 128.8, 127.87, 127.85, 127.6, 127.2, 126.3, 121.7, 121.1, 119.2, 118.6, 109.2, 48.8, 46.3, 32.8, 18.8, 2.1.

HRMS (ESI): calculated for $[C_{27}H_{25}NONa]^+$: 402.1828; found: 402.1833.

1,3-Bis(4-methoxyphenyl)-3-(1-methyl-1H-indol-3-yl)propan-1-one (8)



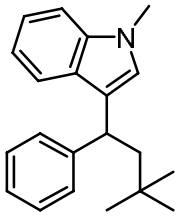
The general procedure using solvent mixtures of hexanes/EtOAc (v/v = 30/1 -> 7/3) for column chromatography lead to the isolation of the product as white solid (71 mg, 0.18 mmol, 35%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.95 – 7.90 (m, 2H), 7.48 – 7.42 (m, 1H), 7.29 – 7.23 (m, 3H), 7.21 – 7.15 (m, 1H), 7.05 – 6.99 (m, 1H), 6.93 – 6.88 (m, 2H), 6.84 – 6.77 (m, 3H), 5.01 (t, *J* = 7.2 Hz, 1H), 3.86 (s, 3H), 3.75 (s, 3H), 3.72 (s, 3H), 3.75 – 3.62 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 197.3, 163.5, 158.0, 137.5, 136.8, 130.5, 130.4, 128.9, 127.1, 126.3, 121.8, 119.8, 118.9, 118.4, 113.9, 113.8, 109.3, 55.6, 55.3, 45.3, 37.6, 32.8.

HRMS (ESI): calculated for $[C_{26}H_{25}NO_3Na]^+$: 422.1727; found: 422.1725.

3-(3,3-Dimethyl-1-phenylbutyl)-1-methyl-1H-indole (9)



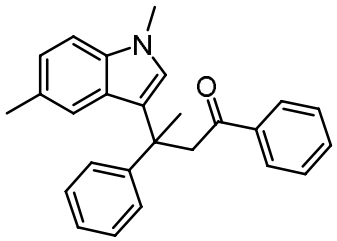
The general procedure using pivaldehyde in the reaction and a solvent mixture of hexanes/EtOAc (v/v = 200/1) as eluent in column chromatography lead to the isolation of this product as pale yellow oil (57 mg, 0.20 mmol, 39%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.28 – 7.23 (m, 3H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.77 (s, 1H), 4.34 (dd, *J* = 7.9, 5.3 Hz, 1H), 3.71 (s, 3H), 2.19 (dd, *J* = 14.1, 5.3 Hz, 1H), 2.09 (dd, *J* = 14.1, 7.9 Hz, 1H), 0.88 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 147.0, 137.3, 128.4, 128.2, 127.2, 126.1, 125.8, 121.6, 120.9, 119.5, 118.7, 109.3, 50.1, 39.6, 32.8, 31.7, 30.4.

HRMS (ESI): calculated for $[C_{21}H_{25}N+H]^+$: 292.2060; found: 292.2060.

3-(1,5-Dimethyl-1*H*-indol-3-yl)-1,3-diphenylbutan-1-one (10a)



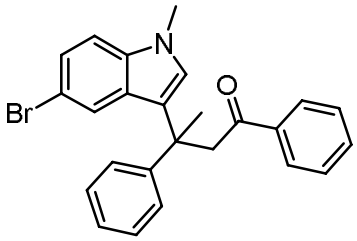
The general procedure using column chromatography with an eluent of hexanes/EtOAc (v/v = 40/1 -> 27/1), followed by a preparative thin layer chromatography with eluent hexanes/DCM (v/v = 75/25) lead to the isolation of the product as yellow oil (112 mg, 0.30 mmol, 61%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.40 – 7.32 (m, 3H), 7.27 – 7.20 (m, 2H), 7.20 – 7.13 (m, 3H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.93 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.80 – 6.75 (m, 2H), 3.96 (d, *J* = 14.3 Hz, 1H), 3.73 (d, *J* = 14.3 Hz, 1H), 3.63 (s, 3H), 2.27 (s, 3H), 1.96 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 200.1, 148.2, 138.4, 136.3, 132.2, 128.2, 127.9, 127.9, 127.7, 126.9, 126.8, 126.5, 126.0, 123.0, 121.8, 121.0, 109.0, 48.7, 42.2, 32.7, 28.2, 21.7.

HRMS (ESI): calculated for $[C_{26}H_{25}NONa]^+$: 390.1828; found: 390.1822.

3-(5-Bromo-1-methyl-1*H*-indol-3-yl)-1,3-diphenylbutan-1-one (10b)



The general procedure using column chromatography with an eluent of hexanes/EtOAc (v/v = 40/1 -> 18/1), followed by a preparative thin layer chromatography with eluent

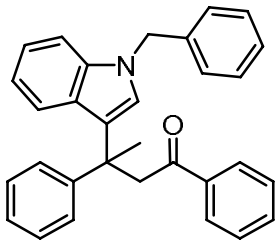
hexanes/DCM (v/v = 75/25) lead to the isolation of the product as yellow oil (114 mg, 0.26 mmol, 53%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.59 – 7.53 (m, 1H), 7.37 – 7.31 (m, 2H), 7.28 – 7.23 (m, 2H), 7.20 – 7.14 (m, 4H), 7.05 (d, *J* = 1.8 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 6.85 (s, 1H), 3.96 (d, *J* = 14.1 Hz, 1H), 3.66 (d, *J* = 14.1 Hz, 1H), 3.62 (s, 2H), 1.93 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.9, 147.8, 138.3, 136.4, 132.3, 128.4, 128.04, 128.01, 127.95, 127.85, 126.7, 126.3, 124.3, 123.6, 121.7, 112.1, 110.8, 48.3, 42.1, 32.9, 28.5.

HRMS (ESI): calculated for $[C_{25}H_{22}BrNONa]^+$: 454.0777; found: 454.0773.

3-(1-Benzyl-1H-indol-3-yl)-1,3-diphenylbutan-1-one (10c)



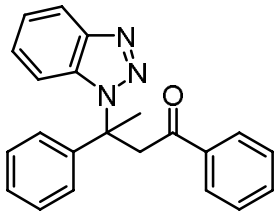
The general procedure using mixtures of hexanes/EtOAc (v/v = 40/1 -> 27/1) as eluent for column chromatography lead to the isolation of the product as white solid (93 mg, 0.21 mmol, 44%).

^{1}H NMR (501 MHz, CD_2Cl_2): δ 7.68 – 7.62 (m, 2H), 7.43 – 7.37 (m, 3H), 7.34 – 7.23 (m, 5H), 7.26 – 7.14 (m, 2H), 7.14 (d, *J* = 8.3 Hz, 1H), 7.07 (s, 1H), 7.06 – 6.97 (m, 4H), 6.87 – 6.80 (m, 1H), 5.25 (s, 2H), 4.03 (d, *J* = 14.2 Hz, 1H), 3.76 (d, *J* = 14.2 Hz, 1H), 1.96 (s, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2): δ 199.7, 148.8, 138.6, 138.3, 137.7, 132.6, 129.1, 128.37, 128.35, 128.2, 127.8, 127.2, 127.0, 126.9, 126.5, 126.3, 123.2, 121.8, 121.5, 119.1, 110.2, 50.3, 48.3, 42.4, 28.4.

HRMS (ESI): calculated for $[C_{31}H_{27}NONa]^+$: 452.1985; found: 452.1989.

3-(1H-benzo[d][1,2,3]triazol-1-yl)-1,3-diphenylbutan-1-one (10d)



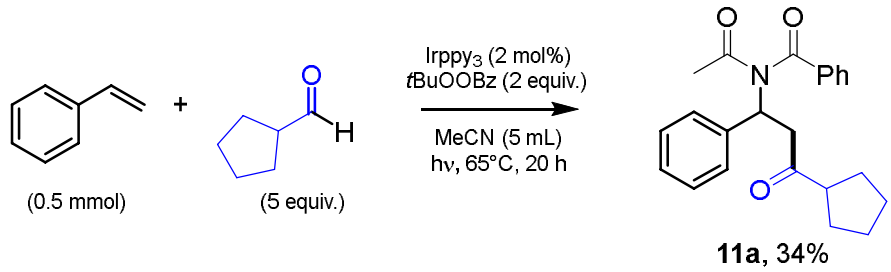
The general procedure using benzotriazole as nucleophile instead of an indole and mixtures of hexanes/EtOAc (v/v = 9/1 -> 4/1) as eluent for column chromatography, followed by a preparative thin layer chromatography with eluent DCM lead to the isolation of the product as white solid (83 mg, 0.24 mmol, 49%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.4 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.53 – 7.48 (m, 1H), 7.41 – 7.36 (m, 2H), 7.34 – 7.28 (m, 3H), 7.28 – 7.24 (m, 3H), 7.18 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.72 (d, *J* = 8.5 Hz, 1H), 4.61 (d, *J* = 16.7 Hz, 1H), 4.32 (d, *J* = 16.7 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 196.1, 146.9, 142.4, 137.5, 133.3, 132.1, 128.9, 128.6, 128.3, 128.1, 127.0, 126.4, 123.9, 120.1, 112.3, 66.7, 49.2, 26.1.

HRMS (ESI): calculated for $[C_{22}H_{19}N_3ONa]^+$: 364.1420; found: 364.1421.

Synthesis of *N*-Acetyl-*N*-(3-cyclopentyl-3-oxo-1-phenylpropyl)benzamide (11a)

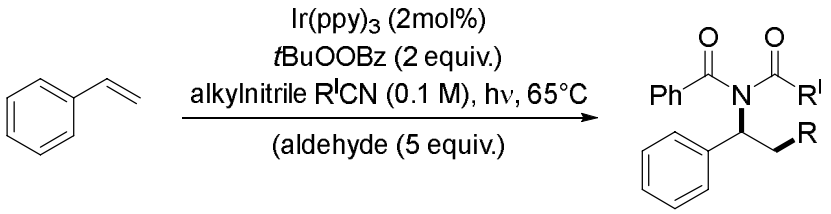


In a Schlenk-round-bottom-flask (100 mL), tris(2-phenylpyridinato-*C2,N*-)iridium (III) (1.3 mg, 2.0 µmol, 0.004 equiv.) was dissolved in dry acetonitrile (5 mL) under Ar gas atmosphere. Subsequently styrene (57 µL, 0.5 mmol, 1 equiv.), cyclopentylcarboxaldehyde (267 µL, 2.5 mmol, 5 equiv.) and TBPB (187 µL, 1.0 mmol, 2 equiv.) were added to the yellow solution. The reaction mixture was stirred while irradiated with white light (40 W white LED) for 20 h. The irradiation produces a reaction temperature of around 65°C.

The cooled down reaction mixture was diluted, dried under reduced pressure (after addition of some silica) and the obtained residue was purified by column chromatography using a solvent mixture of hexanes/EtOAc (v/v = 100/10 -> 85/15) as eluent. After a further purification step on preparative thin layer chromatography with a mixture of DCM/hexanes (v/v = 95/5) as eluent *N*-acetyl-*N*-(3-cyclopentyl-3-oxo-1-phenylpropyl)benzamide (**11a**) was obtained as colourless oil (62 mg, 0.17 mmol, 34%).

Difunctionalization with nitriles as nucleophiles

General procedure:

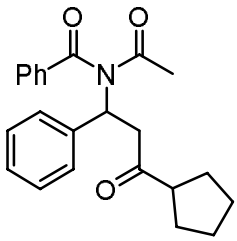


In a Schlenk-tube (10 mL, 0.1 mmol scale)/Schlenk-round-bottom-flask (100 mL, 0.5 mmol scale), respectively, Tris(2-phenylpyridinato-*C2,N*-)iridium (III)

(0.02 equiv.) was dispersed in dry alkylnitrile (1 mL/5 mL) under Ar gas atmosphere. Subsequently styrene (1 equiv.), (aldehyde if required (5 equiv.)) and TBPB (2 equiv.) were added to the yellow dispersion. The reaction mixture was stirred while irradiated with white light (40 W white LED) for 20 h. The irradiation produces a reaction temperature of around 65°C.

The reaction mixture was diluted, dried under reduced pressure (after addition of some silica) and the residue was purified by column chromatography using eluent mixtures of hexanes/EtOAc.

***N*-Acetyl-*N*-(3-cyclopentyl-3-oxo-1-phenylpropyl)benzamide (11a)**



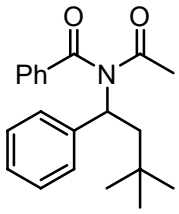
The general procedure using for column chromatography an eluent of hexanes/EtOAc (v/v = 100/10 -> 85/15), combined with a further purification by preparative thin layer chromatography an eluent of DCM/hexanes (v/v = 95/5) lead to the isolation of the product. The substance was obtained as colourless oil (62 mg, 0.17 mmol, 34%)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 – 7.56 (m, 3H), 7.55 – 7.48 (m, 1H), 7.48 – 7.36 (m, 7H), 7.35 – 7.28 (m, 3H), 7.27 – 7.20 (m, 1H), 3.87 (dd, *J* = 18.0, 9.5 Hz, 1H), 3.25 (dd, *J* = 18.0, 5.3 Hz, 1H), 2.98 – 2.81 (m, 1H), 1.89 (s, 3H), 1.82 – 1.65 (m, 3H), 1.64 – 1.49 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 132.8, 129.1, 128.9, 128.6, 127.8, 127.7, 56.3, 51.8, 44.4, 29.1, 28.9, 27.7, 26.1, 26.0.

HRMS (ESI): calculated for $[C_{23}H_{25}NO_3Na]^+$: 386.1727; found: 386.1726.

***N*-Acetyl-*N*-(3,3-dimethyl-1-phenylbutyl)benzamide (11b)**



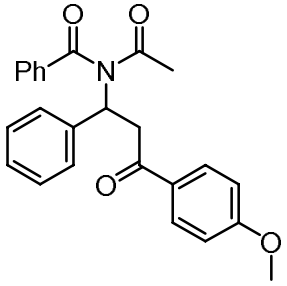
The general procedure using pivaldehyde in the reaction, acetonitrile as solvent and a mixtures of hexanes/EtOAc (v/v = 95/5 -> 85/15) as eluent in chromatography lead to the isolation of this substance as white solid (0.1 mmol scale: 17 mg, 0.053 mmol, 53%; 0.5 mmol scale: 79 mg, 0.24 mmol, 49%)

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.53 – 7.44 (m, 5H), 7.38 – 7.31 (m, 2H), 7.28 – 7.21 (m, 2H), 7.21 – 7.14 (m, 1H), 5.85 (dd, *J* = 7.0, 5.4 Hz ,1H), 2.44 (dd, *J* = 14.7, 7.0 Hz, 1H), 2.17 (dd, *J* = 14.7, 5.4 Hz, 1H), 1.73 (s, 3H), 0.90 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.7, 172.9, 141.0, 137.3, 132.9, 129.0, 128.92, 128.87, 128.3, 127.6, 57.9, 45.8, 31.0, 20.0, 28.1.

HRMS (ESI): calculated for $[C_{21}H_{25}N_1O_2Na]+$: 346.1777; found: 346.1776.

***N*-Acetyl-*N*-(3-(4-methoxyphenyl)-3-oxo-1-phenylpropyl)benzamide (11c)**



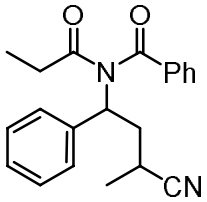
The general procedure using for column chromatography an eluent of hexanes/EtOAc (v/v = 6/1 -> 7/3) lead to the isolation of the product. The substance was obtained as pale yellow oil (104 mg, 0.26 mmol, 52%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 8.01 – 7.94 (m, 2H), 7.62 – 7.57 (m, 2H), 7.55 – 7.47 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.21 (m, 1H), 6.95 – 6.88 (m, 2H), 6.26 (dd, *J* = 9.2, 5.3 Hz, 1H), 4.39 (dd, *J* = 17.6, 9.2 Hz, 1H), 3.85 (s, 3H), 3.72 (dd, *J* = 17.6, 5.3 Hz, 1H), 1.88 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 196.2, 174.7, 173.9, 163.8, 139.7, 136.8, 132.8, 130.6, 129.9, 129.0, 128.9, 128.6, 127.8, 127.7, 113.9, 56.7, 55.6, 40.9, 27.7.

HRMS (ESI): calculated for $[C_{25}H_{23}NO_4Na]^+$: 424.1519; found: 424.1520.

***N*-(3-Cyano-1-phenylbutyl)-*N*-propionylbenzamide (11d)**



After first isolation d.r. ~1.4/1

The general procedure using propionitrile as solvent and a mixture of hexanes/EtOAc (v/v = 19/1 -> 6/1) as eluent in column chromatography lead to the isolation of this substance as colourless oil (0.5 mmol scale: d.r. 1.4/1, 80 mg, 0.24 mmol, 50%).

Via preparative HPLC (Chiralpak IA 5 µm, IA00CG-QD002, 250 mm Chiralpak, 10 mm diameter, eluent: n-heptane/ethanol (v/v = 99/1)) the major diastereoisomer was separated as colourless oil (19 mg, 0.057 mmol, 11%).

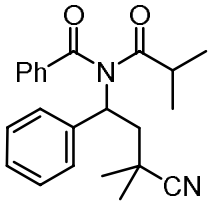
Major Diastereoisomer:

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.55 – 7.51 (m, 3H), 7.49 – 7.44 (m, 2H), 7.42 – 7.37 (m, 2H), 7.34 – 7.29 (m, 2H), 7.29 – 7.23 (m, 1H), 5.86 (dd, *J* = 10.1, 6.0 Hz, 1H), 2.84 (ddd, *J* = 13.9, 10.1, 5.6 Hz, 1H), 2.76 – 2.67 (m, 1H), 2.44 (ddd, *J* = 13.9, 9.4, 6.0 Hz, 1H), 2.13 – 1.99 (m, 2H), 1.40 (d, *J* = 7.0 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 177.9, 174.5, 138.5, 136.6, 133.3, 129.2, 128.9, 128.8, 128.29, 128.25, 122.4, 58.5, 37.2, 33.5, 23.4, 18.2, 9.9.

HRMS (ESI): calculated for $[C_{21}H_{22}N_2O_2Na]^+$: 357.1573; found: 357.1574.

***N*-(3-Cyano-3-methyl-1-phenylbutyl)-*N*-isobutyrylbenzamide (11e)**



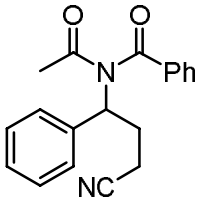
The general procedure using isobutyronitrile as solvent and a mixture of DCM/hexanes (v/v = 95/5) as eluent in column chromatography lead to the isolation of this substance as colourless oil (0.5 mmol scale: 64 mg, 0.18 mmol, 35%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 – 7.48 (m, 5H), 7.43 – 7.36 (m, 2H), 7.34 – 7.21 (m, 3H), 5.96 (dd, *J* = 7.5, 5.6 Hz, 1H), 2.77 (dd, *J* = 14.8, 7.5 Hz, 1H), 2.62 (dd, *J* = 14.8, 5.6 Hz, 1H), 2.16 (hept, *J* = 6.6 Hz, 1H), 1.42 (s, 3H), 1.29 (s, 3H), 0.73 (d, *J* = 6.6 Hz, 3H), 0.71 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 181.9, 173.9, 139.0, 137.0, 133.0, 129.3, 129.1, 128.9, 128.6, 128.4, 124.6, 57.7, 43.7, 39.0, 31.6, 28.0, 26.9, 19.6, 18.9.

HRMS (ESI): calculated for $[C_{11}H_{12}Cl_4Na]^+$: 385.1886; found: 385.1887.

***N*-Acetyl-*N*-(3-cyano-1-phenylpropyl)benzamide (11f)**



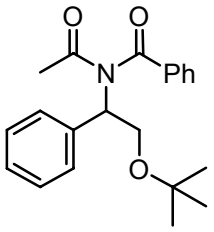
The general procedure using acetonitrile as solvent and a mixture of hexanes/EtOAc (v/v = 95/5 -> 80/20) as eluent in column chromatography lead to the isolation of this substance as colourless oil (0.1 mmol scale: 7.4 mg, 0.024 mmol, 24%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.48 (m, 3H), 7.46 – 7.41 (m, 2H), 7.41 – 7.36 (m, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 5.78 (dd, *J* = 8.8, 7.0 Hz, 1H), 2.90 – 2.75 (m, 1H), 2.68 – 2.54 (m, 1H), 2.50 – 2.36 (m, 2H), 1.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.6, 171.8, 136.8, 135.3, 132.5, 128.2, 128.0, 127.8, 127.4, 118.1, 58.1, 27.3, 26.5, 14.3.

HRMS (ESI): calculated for $[C_{19}H_{18}N_2O_2Na]^+$: 329.1260; found: 329.1257.

***N*-Acetyl-*N*-(2-(*tert*-butoxy)-1-phenylethyl)benzamide (11g)**



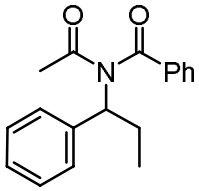
The general procedure using acetonitrile as solvent and a mixture of hexanes/EtOAc (v/v = 95/5) as eluent in column chromatography, and a mixture of hexanes/EtOAc (v/v = 98/2) for a subsequent preparative thin layer chromatography lead to the isolation of this substance as colourless oil (0.1 mmol scale: 3.1 mg, 0.009 mmol, 9%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 7.77 – 7.71 (m, 2H), 7.51 – 7.44 (m, 3H), 7.39 – 7.34 (m, 2H), 7.29 – 7.24 (m, 2H), 7.23 – 7.16 (m, 1H), 5.62 (dd, *J* = 10.5, 5.1 Hz, 1H), 4.08 (dd, *J* = 10.5, 9.2 Hz, 1H), 3.66 (dd, *J* = 9.2, 5.1 Hz, 1H), 1.80 (s, 3H), 0.97 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.3, 173.1, 138.4, 137.1, 132.8, 129.7, 128.7, 128.5, 128.2, 127.7, 73.7, 61.6, 61.4, 27.4, 27.2

HRMS (ESI): calculated for $[C_{21}H_{25}N_1O_3Na]^+$: 362.1727; found: 362.1727.

***N*-Acetyl-*N*-(1-phenylpropyl)benzamide (11h)**



The general procedure using acetonitrile as solvent and a mixture of hexanes/EtOAc (v/v = 95/5) as eluent in column chromatography, and a mixture of hexanes/EtOAc (v/v = 98/2) for a subsequent preparative thin layer chromatography lead to the isolation of this substance as colourless solid (0.1 mmol scale: 6.6 mg, 0.23 mmol, 23%).

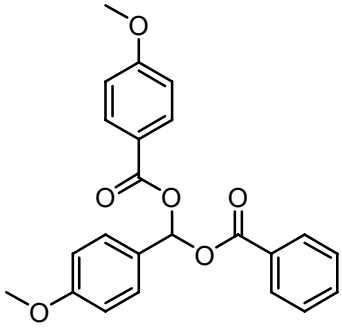
^{1}H NMR (501 MHz, $CDCl_3$): δ 7.63 – 7.57 (m, 2H), 7.56 – 7.49 (m, 1H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.33 – 7.26 (m, 2H), 7.26 – 7.18 (m, 1H), 5.67 – 5.59 (m, 1H), 2.46 – 2.33 (m, 1H), 2.33 – 2.20 (m, 1H), 1.84 (s, 3H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.6, 173.4, 139.9, 137.0, 133.0, 129.0 (2C), 128.39, 128.38, 127.6, 62.3, 27.7, 25.3, 11.9.

HRMS (ESI): calculated for $[C_{18}H_{19}N_1O_2Na]^+$: 304.1308; found: 304.1306.

Other products

(Benzoyloxy)(4-methoxyphenyl)methyl 4-methoxybenzoate (14)



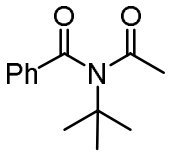
The product was isolated as a side product in the synthesis of **11c**. It was obtained using column chromatography with a mixture of hexanes/EtOAc (v/v = 13/1-> 6/1) as eluent. The substance is a yellow oil (24 mg, 0.061 mmol, 6%).

^{1}H NMR (501 MHz, $CDCl_3$): δ 8.14 (s, 1H), 8.12 – 8.08 (m, 2H), 8.07 – 8.02 (m, 2H), 7.65 (d, *J* = 8.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 6.97 (dd, *J* = 9.3, 2.2 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H), 3.83 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 164.6, 164.3, 164.0, 160.8, 133.6, 132.3, 130.2, 129.5, 128.6, 128.4 (2C), 121.7, 114.2, 113.9, 90.7, 55.6, 55.5.

HRMS (ESI): calculated for $[C_{23}H_{20}O_6Na]^+$: 415.1152; found: 415.1157.

***N*-Acetyl-*N*-(*tert*-butyl)benzamide (15)**



This product was detected in attempted difunctionalization reactions with 1,3,5-trimethoxybenzene as nucleophile instead of indoles. For a detailed discussion, see the chapter “Experiment 6: Isolation of an alternative product” below.

In a Schlenk-round-bottom-flask (100 mL, 0.5 mmol scale), Tris(2-phenylpyridinato-*C2,N*-)iridium (III) (1.4 mg, , 0.02 equiv.) was dispersed in dry acetonitrile (5 mL) under Ar gas atmosphere. Subsequently α-methylstyrene (65 µL, 0.5 mmol, 1 equiv.), 1,3,5-trimethoxybenzene (252 mg, 1.5 mmol, 3 equiv.), pivaldehyde (271 µL, 2.5 mmol, 5 equiv.) and TBPB (196 µL, 1.03 mmol, 2 equiv.) were added to the yellow dispersion. The reaction mixture was stirred while irradiated with white light (40 W white LED) for 20 h. The irradiation produces a reaction temperature of around 65°C.

The reaction mixture was diluted, dried under reduced pressure (after addition of some silica) and the residue was purified by column chromatography using eluent mixtures of hexanes/EtOAc (v/v = 19/1-> 4/1). The product was yielded as colourless oil (118 mg, 0.54 mmol, 52%)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 – 7.95 (m, 2H), 7.71 – 7.59 (m, 1H), 7.58 – 7.46 (m, 2H), 1.84 (s, 2H), 1.50 (s, 7H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 176.5, 168.5, 135.8, 134.6, 130.6, 129.4, 58.6, 28.6, 26.0.

^{15}N NMR (HMBC, 51 MHz, $CDCl_3$): δ -212.8.

HRMS (ESI): calculated for $[C_{13}H_{17}NO_2+H]^+$: 220.1332; found: 220.1333.

Evaluation of reaction conditions

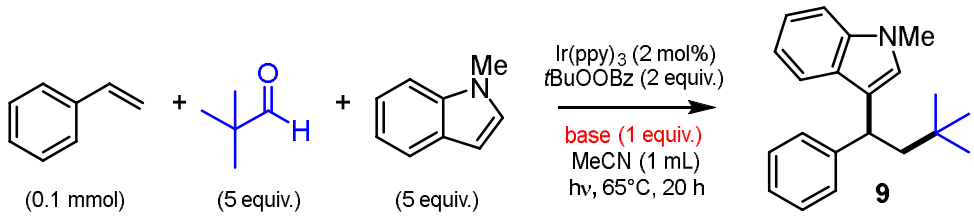
The optimization of adding aldehyde derived radicals asides *N*-methylindole to olefins was carried out for a system containing a peroxide (predominantly perester *t*BuOOBz (TBPB)), a photocatalyst (predominantly $Ir(ppy)_3$), and olefin styrene. The aldehyde used for optimization was pivaldehyde, leading to decarbonylated product **9**. The screening was executed on a 0.1 mmol scale referring to styrene.

Initially the screening showed that styrene should be kept as limiting reagent. The amount of *t*BuOOBz, pivaldehyde and *N*-methylindole were kept each higher than 1 equiv.. The amount of these reagents did not show a striking impact on NMR yield of the obtained product **9**. Also the amount of solvent/acetonitrile plays a minor role in reaction impact. *t*BuOOAc was found as only alternative to *t*BuOOBz under this reaction conditions, but with minor product NMR yield (*t*BuOO*t*Bu, $Na_2S_2O_8$, .*t*BuOOH, *t*BuONO, *t*BuOCl, lauroyl peroxide, and BzOOBz were employed unsuccessfully).

Many metal catalysts (+ ligands) (as single catalyst: $FeCl_2$, CuCl, $CoCl_2$, as co-catalyst: $NiCl_2$ glyme, $CoCl_2$, $Fe(OTf)_3$, $Fe(OAc)_2$, $Cu(OAc)_2$, $PdCl_2$, $In(OTf)_3$, $In(OAc)_3$, $Mg(OAc)_2$, $Sc(OTf)_3$ etc., ligands: phen, bpy) and additives were tested in regard of optimizing electron transfer reactions and stabilization of supposed reaction intermediates (cationic). Only the use of some photocatalysts showed potential of allowing a reaction path to yield **9**.

Light sources of blue light (reaction in 4mL vial under Ar, blue LED, 40W, ~30°C reaction temperature), and reactor with the use of blue light (reaction in 4mL vial under Ar, blue LED, 140W, cooling system -> 20°C) as well as low power white light sources (bulb or LED) showed inferior reaction outcome compared to the use of a high power white LED surrounding to the reaction flask (reaction in 10mL-Schlenk-tube or 100mL-Schlenk-flask under Ar, white LED surrounding, 40W, ~65°C reaction temperature).

Supplementary Table S1: Variation of Bases



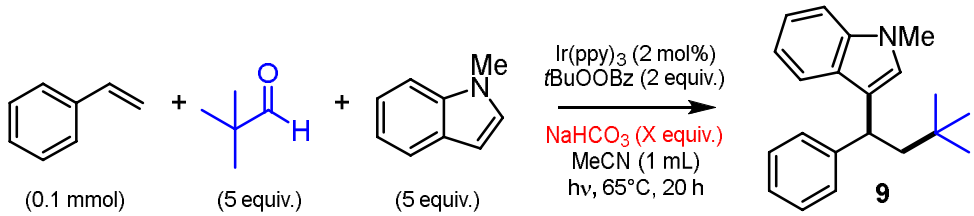
base (1 equiv.)	yield 9 (%)[a]
-	0
*t*BuOK	16
$NaHCO_3$	30 (21)
Cs_2CO_3	27
Ag_2CO_3	29
TMG	25
$NaHCO_3$[b]	35
$KHCO_3$[b]	42
Na_2CO_3[b]	31
$NaHCO_3$[c]	45
$KHCO_3$[c]	37

[a] ^{1}H NMR yield (isolated yield in parentheses);

[b] 0.4 mol% $Ir(ppy)_3$; [c] 0.4 mol% $Ir(ppy)_3$, 2 equiv. base.

TMG = 1,1,3,3-tetramethylguanidine

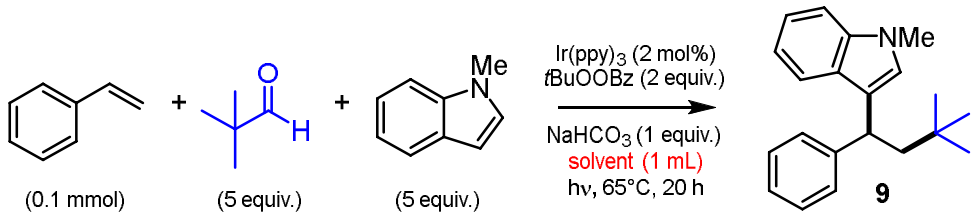
Supplementary Table S2: Variation of the amount of $NaHCO_3$



$NaHCO_3$ equiv.	yield 9 (%)[a]
1.0	30 (21)
1.5	34
2.0	33
3.0	31

[a] ^{1}H NMR yield (isolated yield in parentheses)

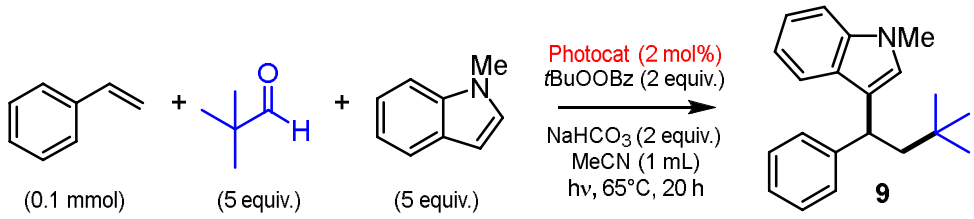
Supplementary Table S3: Variation of Solvents



Solvent (0.1 M)	yield 9 (%)[a]
MeCN	**30 (21)**
DMA	0
PhCl	0
acetone	0
EtOAc	0
DCM	13
$CHCl_3$	0
DMF	0
PhH	0
DMSO	0
MTBE	0
MeOH	0
THF	0
1,4-dioxane	0
DCE	8

[a] ^{1}H NMR yield (isolated yield in parentheses)

Supplementary Table S4: Variation of Photocatalysts



Catalyst (2-3 mol%)	yield 9 (%)[a]
$Ir(ppy)_3$	33
$Ru(bpy)_3(PF_6)_2$	13
Eosin Y	12
Riboflavin	7
$Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbpy)PF_6$	39
$Ir(ppy)_2(dtbpy)PF_6$	41
Fluorescein	3
$TPPBF_4$	0
$Ru(bpy)_3Cl_2$	0
DPA_3F_2BN (5 mol%)	16
DPA_3F_2BN (0.5 mol%)	15
$Ir(dF\text{-}ppy)_3$	0
$Ir(4,5'\text{-}dtbppy)_2(dtbpy)PF_6$	17
$Ir(dF\text{-}ppy)_2(dtbpy)PF_6$	34
$Ir(5'\text{-}F\text{-}ppy)_3$	43

[a] ^{1}H NMR yield (isolated yield in parentheses)

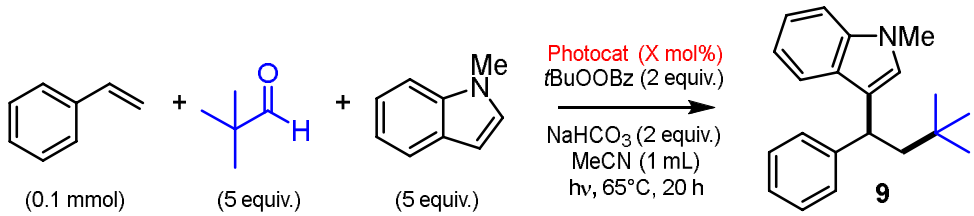
ppy = “2-phenylpyridinate”(*C2, N*)

bpy = 2,2’-bipyridine

TPP = triphenylpyrylium

DPA_3F_2BN = 2,4,6-Tris(diphenylamino)-3,5-difluorobenzonitrile

Supplementary Table S5: Loading of Photocatalyst Ir(ppy)$_3$



Ir(ppy)$_3$ (mol%)	yield 9 (%)[a]
0.1	33
0.2	41
0.4	**45 (39%)**
0.7	40
1.0	39
2.0	33

[a]^{1}H NMR yield (isolated yield in parentheses)

Supplementary Table S6: Loading of Photocatalyst Ir(dF-CF$_3$-ppy)$_2$(dtbpy)PF$_6$

Ir(dF-CF$_3$-ppy)$_2$(dtbpy)PF$_6$ (mol%)	yield 9 (%)[a]
0.1	26
0.2	25
0.7	20
1.0	29
2.0	39

[a]^{1}H NMR yield (isolated yield in parentheses)

Supplementary Table S7: Loading of Photocatalyst $Ir(ppy)_2(dtbpy)PF_6$

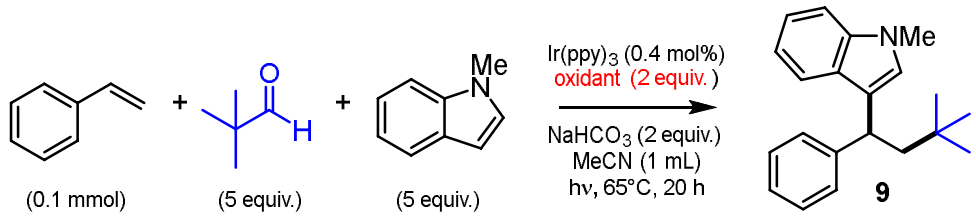
$Ir(ppy)_2(dtbpy)PF_6$ (mol%)	yield 9 (%)[a]
0.1	22
0.2	32
0.4	32
0.7	36
1.0	38
2.0	41

[a] ^{1}H NMR yield (isolated yield in parentheses)

Supplementary Table S8: Loading of Photocatalyst $Ir(5'\text{-}F\text{-}ppy)_3$

$Ir(5'\text{-}F\text{-}ppy)_3$ (mol%)	yield 9 (%)[a]
0.4	37
0.7	40
1.0	39
2.0	43

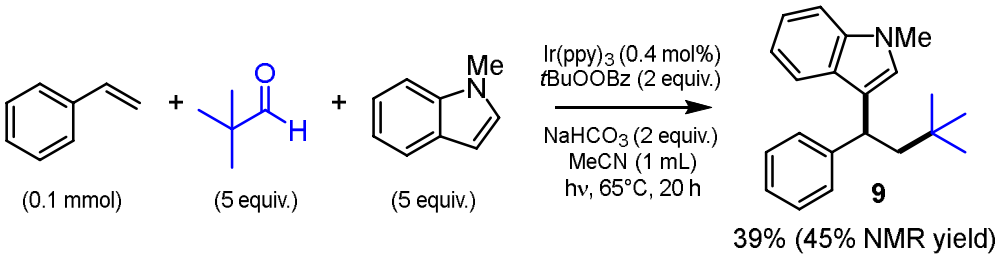
Supplementary Table S9: Variation of oxidant.



oxidant (2 equiv.)	**yield 9 (%)[a]**
*t*BuOOBz	45 (39)
*t*BuOOAc	38
*t*BuOOH (decane)	0
*t*BuOOBz, *t*BuOOH (decane)	26
*t*BuOOBz, *t*BuOOH (H_2O)	23
lauroyl peroxide	0
*t*BuOCl	0
*t*BuONO	0
$Na_2S_2O_8$	0
*t*BuOO*t*Bu	0
BzOOBz	0

In cases of two oxidants, each was conducted in the amount of 2 equiv..

Supplementary Table S10: Variation of further reaction paramaters



Control exp.	yield 9 (%)[a]
no base	0
no catalyst	16
no light/ 65°C	0
no peroxide	0
no cat, no irradiation, 100°C	0
no cat, no irradiation, 120°C for 1h, then 12 h 65°C	0
no cat, no irradiation, 65°C, BPO (4 mol%)[b]	0
no cat, no irradiation, 65°C, AIBN (4 mol%)[b]	0
no cat, **irradiation**, 65°C, BPO (4 mol%)[c]	0
no cat, **irradiation**, 65°C, AIBN (4 mol%)[c]	0
no cat, **irradiation**, 65°C, CBr_4 (5 mol%)[c]	17

[a] ^{1}H NMR yield (isolated yield in parentheses); [b] 12 h reaction time;
[c] 14 h reaction time; BPO = Benzoyl peroxide; AIBN = Azobis(isobutyronitrile)

The reaction lead to no isolatable product (e.g. no **9**) without the presence of a base in the reaction medium. After the attack of *N*-methylindole to the supposed benzylic cationic intermediate a proton has to be removed from the resulting species to obtain the final product. The deprotonation should proceed in theory readily regaining the aromaticity of the indole system and a base should not be needed. But intuitively the release of free protons into a reaction mixture containing aldehyde (, ketone) and olefin molecules (as well as acylated benzylic radical and cation intermediates for other

aldehyde than pivaldehyde) could lead to undesired reactions and even product consumption, so that a buffering system with the present base seems an important factor for a successful reaction conduction.

Also at a reaction temperature of 65°C the absence of powerful white light irradiation does prevent the product formation, arguably by inhibiting electron transfers from unactivated photocatalyst.

In addition the absence of the perester in the reaction mixture leads to no product formation.

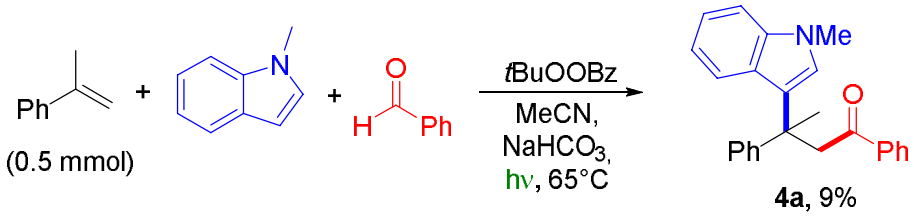
In absence of irradiation and catalyst an oil bath temperature of 100°C, 120°C does not lead to sufficient perester cleavage, nor product formation in a refluxing acetonitrile media. However styrene and aldehyde could be converted quite substantially to unknown products.

With low temperature radical initiators like benzoyl peroxide (BPO) or Azobis(isobutyronitrile) (AIBN) present instead of $Ir(ppy)_3$ in the reaction mixture heating as well as irradiating lead not to a difunctionalization. For BPO as initiator 14 h of irradiation lead to 71% conversion of styrene, 50% conversion of aldehyde and 14% conversion of TBPB (to benzoic acid) with no clear reaction outcomes. When the same mixture is only heated for 12 h at 65°C no styrene was converted, only traces of TBPB and 40% of aldehyde were converted.

For AIBN as initiator in the irradiated and heated mixture after 14 h 39% styrene, 20% aldehyde but no TBPB were converted. The same mixture only heated to 65°C lead after 12 h to no styrene, nor TBPB conversion and 20% conversion for the aldehyde. No clear products were observed via ^{1}H NMR.

In the view of the fact that pivaldehyde and *t*BuOOBz are each on their own not converted in an irradiated acetonitrile solution (see experiments in section Mechanistic Studies and Discussion), but the absence of a catalyst in the above pictured reaction lead anyway to a product formation (16% vs 45% with catalyst), it seems possible that electron transfers to perester molecules are also possible (when also less effectively) from other molecules in this reaction mixture than from Ir species. Furthermore product **4a** could be formed in a reaction mixture containing no Ir-catalyst in low yield.

Reaction without photocatalyst

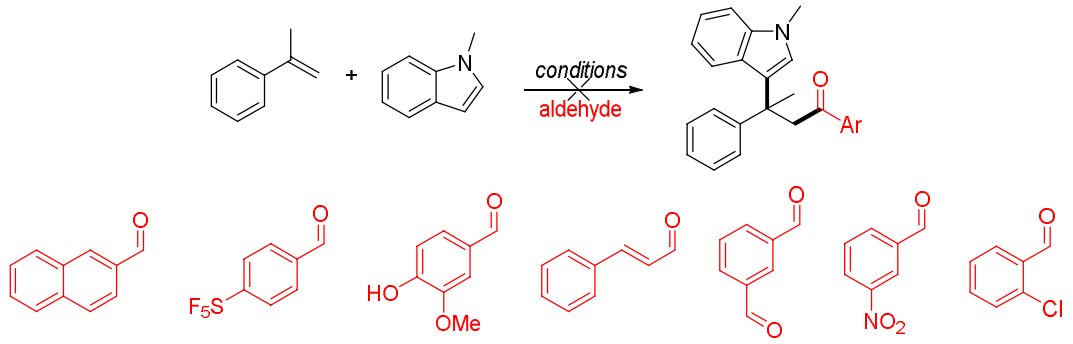


Without the use of catalyst in the reaction, product **4a** was isolated in a 9% yield (0.5 mmol scale). With catalyst $Ir(ppy)_3$ present and otherwise to general procedure unchanged reaction conditions product **4a** was isolated in 68% yield.

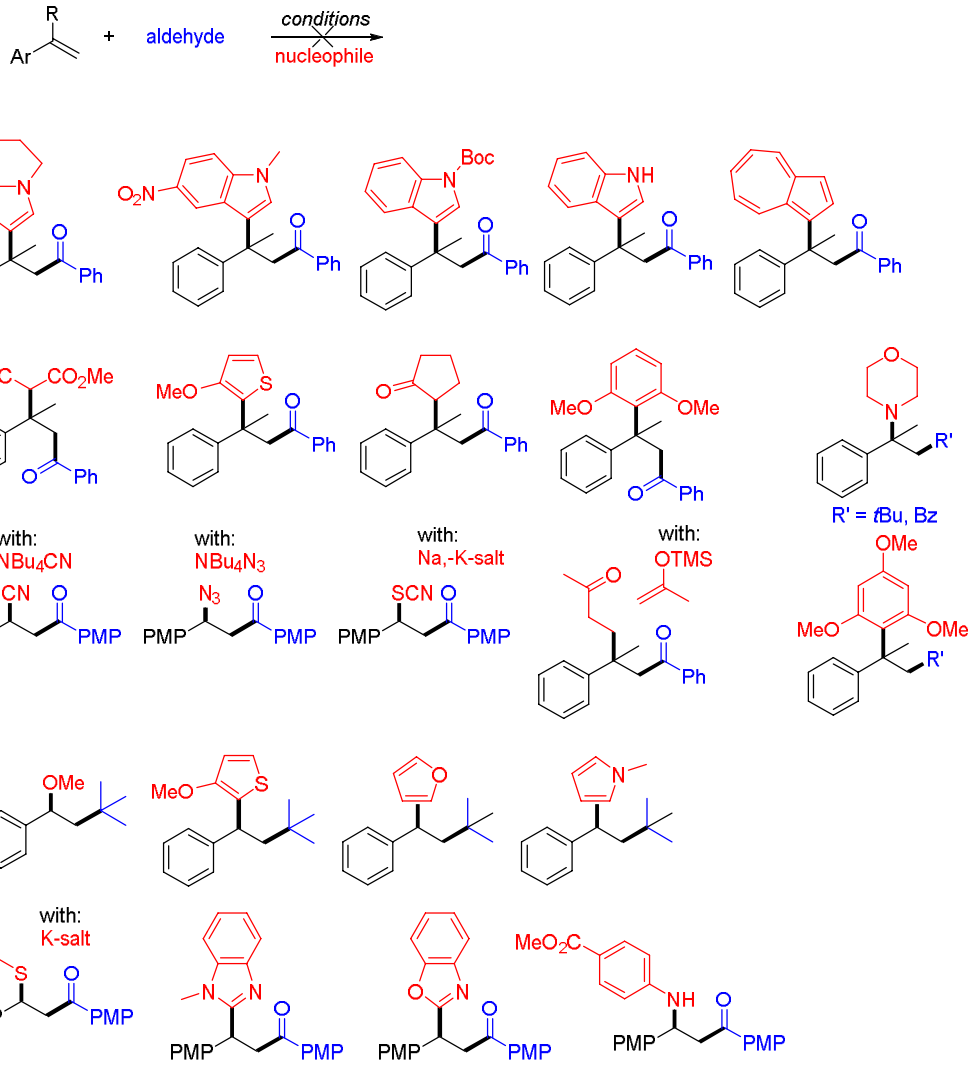
Incompatible substrate combinations

In the following section, products that could not be obtained by the above mentioned procedure are listed.

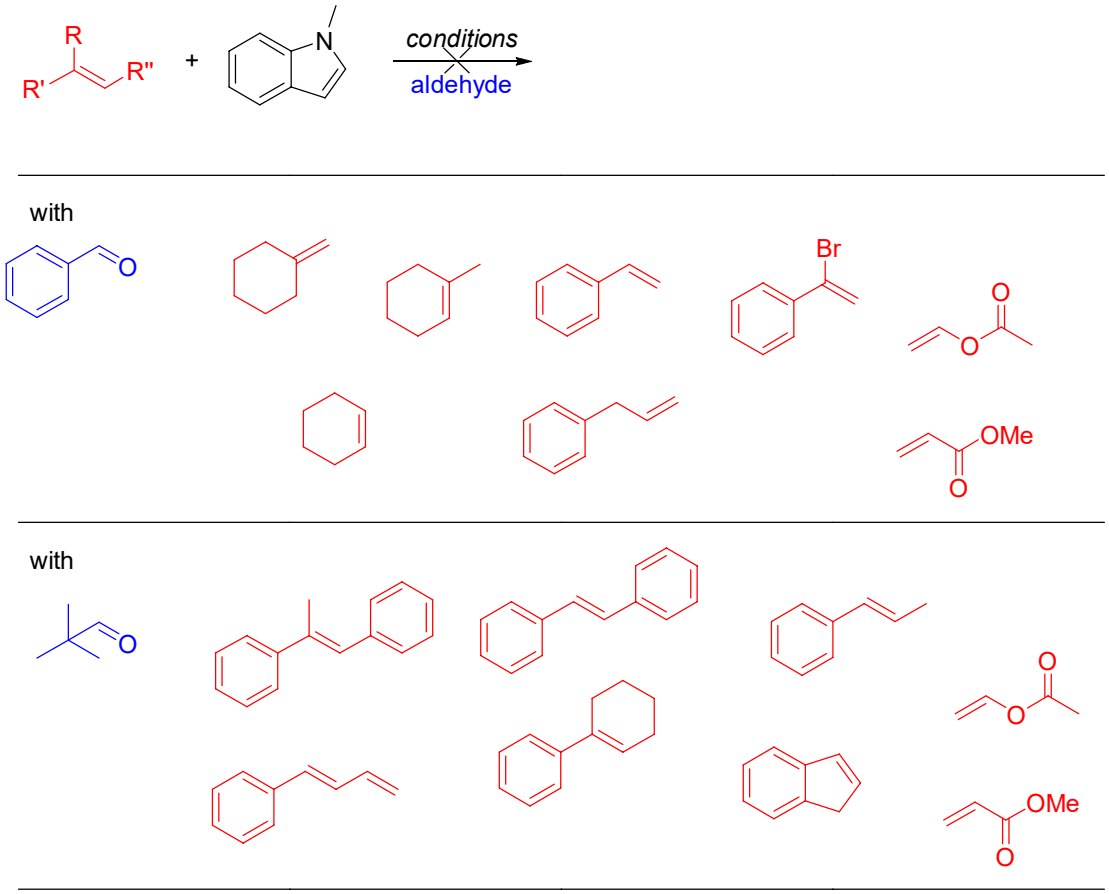
Supplementary Scheme S1: Unsuccessful Aldehydes in the reaction



Supplementary Scheme S2: Unsuccessful Nucleophiles in the reaction

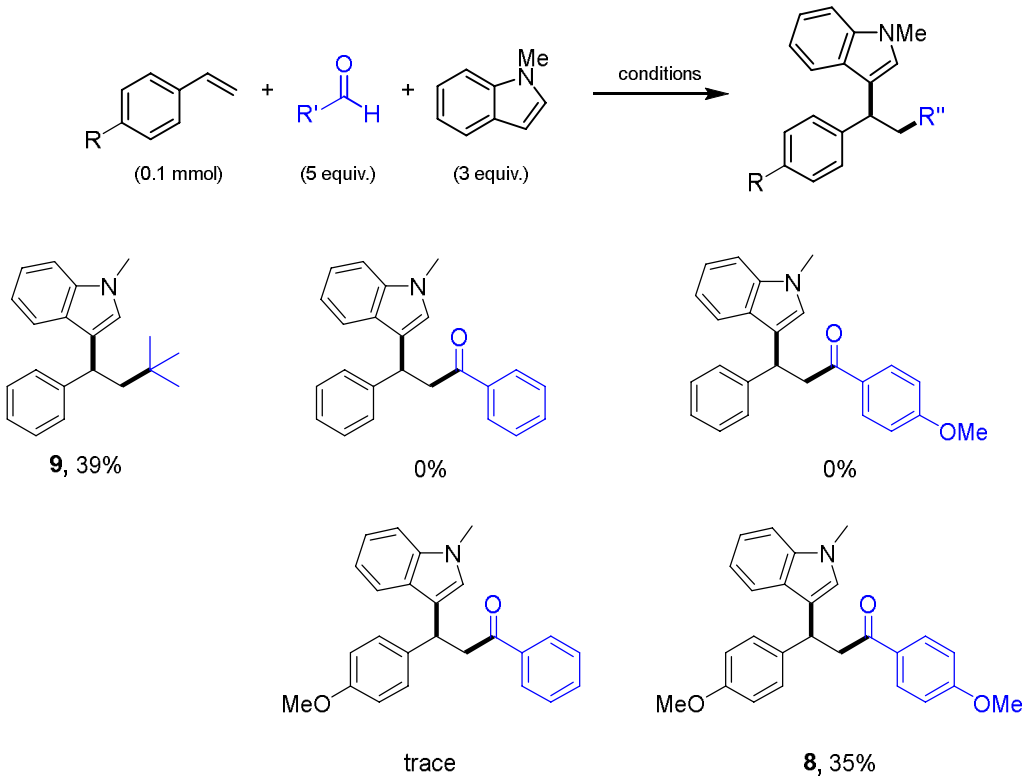


Supplementary Scheme S3: Unsuccessful Olefins in the reaction



Difunctionalizations of styrenes involving indoles as nucleophile show strong impact of the olefin's electronic features. In many previous publications, only electron-rich styrenes were used, showcasing the need to stabilize the cationic reaction intermediate (see the manuscript for references). In general, our synthetic method also requires α-substituted styrenes which result in an increased stabilization of the presumed carbocation intermediate. For α-unsubstituted styrenes the results shown in Supplementary Scheme S4 were obtained.

Supplementary Scheme S4: Unsuccessful combinations of substituted styrenes and aldehydes in reactions with *N*-methyl indole.



Comparing the products derived from *N*-methyl indole and aromatic aldehydes presented here, both an electron-rich olefin as well as an electron-rich aldehyde seem to be required for the reaction to occur – **8** is the only product that could be isolated, with *p*-methoxy-substituents on both styrene and aldehyde. The only other product derived from α-unsubstituted styrene, **9**, also derives from an electron-rich radical (*tert*-butyl radical, formed from pivaldehyde by decarbonylation).

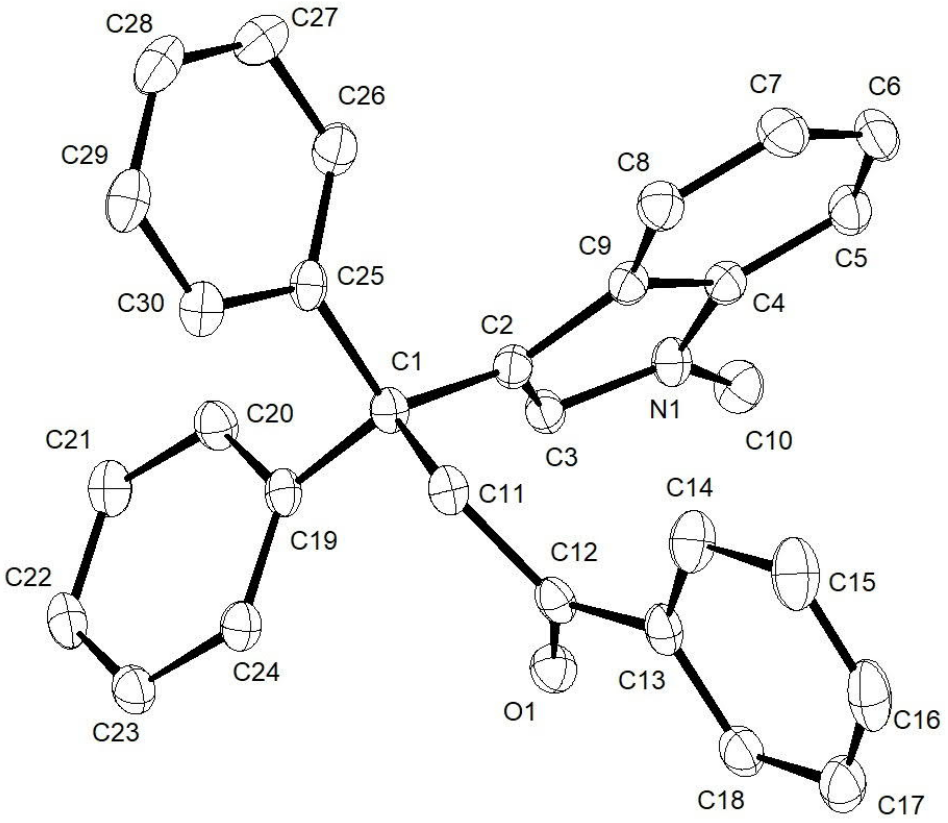
If in these cases the stabilization of the cation intermediate can also be considered as crucial for the reaction to yield a product, it is remarkable that also the aldehyde's electronics seem to be influential. Of course, there could be another explanation for these observations.

Additional structural analysis

X-Ray Crystal Analysis

Product **7a** was recrystallized from THF/pentane (see above) and the resulting crystals were suitable for a XRD experiment, giving the following data:

Structure:



In addition the structure contained disordered solvent molecules which could not be refined satisfactorily. With the squeeze application the accessible solvent voids were deleted from the structure.

The structure shows with the C1–C2 bond a connectivity of an indol-3-yl moiety with the benzylic position of the former styrene (1,1-diphenylethylene).

Crystal data and structure refinement

Identification code	CCDC/CSD No.: 1978887
Empirical formula	$C_{30}H_{25}NO$

Color	colourless	
Formula weight	415.51 $g \cdot mol^{-1}$	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	TRICLINIC	
Space group	**$P\bar{1}$, (no. 2)**	
Unit cell dimensions	a = 8.0782(3)	α=84.7090(10)°.
	b = 12.2475(4) Å	β=76.419(2)°.
	c = 13.2367(4) Å	γ =75.461(2)°.
Volume	1231.46(7) $Å^3$	
Z	2	
Density (calculated)	1.121 $Mg \cdot m^{-3}$	
Absorption coefficient	0.518 mm^{-1}	
F(000)	440 e	
Crystal size	0.230 x 0.142 x 0.034 mm^3	
θ range for data collection	5.800 to 61.163°.	
Index ranges	$-9 \le h \le 9$, $-13 \le k \le 13$, $-15 \le l \le 15$	
Reflections collected	30886	
Independent reflections	3638 [R_{int} = 0.0498]	
Reflections with $I>2\sigma(I)$	3136	
Completeness to θ = 61.163°	96.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.94	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3638 / 0 / 290	
Goodness-of-fit on F^2	1.083	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0337	wR^2 = 0.0903
R indices (all data)	R_1 = 0.0384	wR^2 = 0.0922
Largest diff. peak and hole	0.1 and -0.2 e $\cdot Å^{-3}$	

Supplementary Table S8: bond lengths [Å] and angles [°].

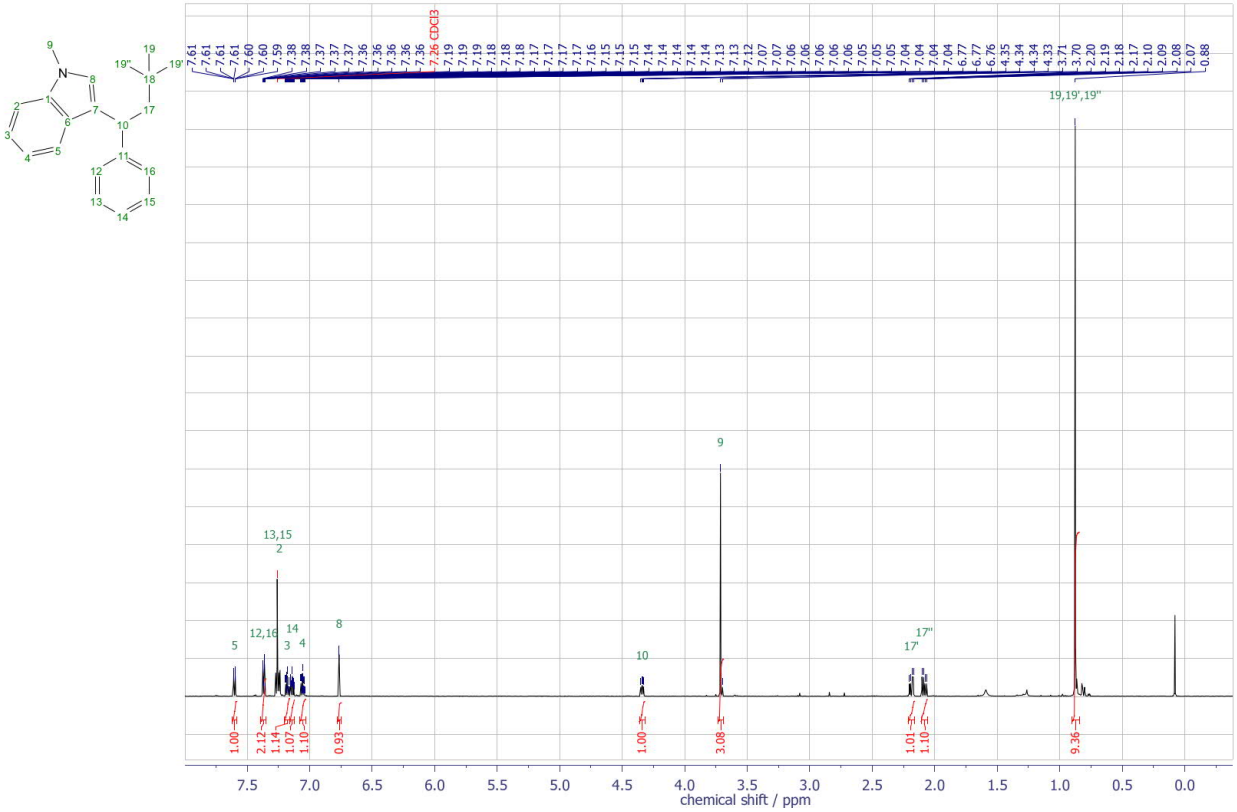
O(1)-C(12)	1.2228(15)	N(1)-C(3)	1.3749(16)
N(1)-C(4)	1.3780(17)	N(1)-C(10)	1.4518(16)
C(1)-C(2)	1.5231(16)	C(1)-C(11)	1.5642(16)
C(1)-C(19)	1.5379(17)	C(1)-C(25)	1.5500(17)

C(2)-C(3)	1.3683(17)	C(2)-C(9)	1.4448(18)
C(4)-C(5)	1.3928(18)	C(4)-C(9)	1.4180(17)
C(5)-C(6)	1.377(2)	C(6)-C(7)	1.4033(19)
C(7)-C(8)	1.3820(19)	C(8)-C(9)	1.4090(18)
C(11)-C(12)	1.5137(17)	C(12)-C(13)	1.5001(18)
C(13)-C(14)	1.3975(19)	C(13)-C(18)	1.4000(19)
C(14)-C(15)	1.387(2)	C(15)-C(16)	1.381(2)
C(16)-C(17)	1.388(2)	C(17)-C(18)	1.3826(19)
C(19)-C(20)	1.3989(18)	C(19)-C(24)	1.3911(17)
C(20)-C(21)	1.3835(19)	C(21)-C(22)	1.3893(18)
C(22)-C(23)	1.3851(19)	C(23)-C(24)	1.3868(18)
C(25)-C(26)	1.3886(18)	C(25)-C(30)	1.3996(18)
C(26)-C(27)	1.3916(19)	C(27)-C(28)	1.383(2)
C(28)-C(29)	1.388(2)	C(29)-C(30)	1.3848(19)

C(3)-N(1)-C(4)	108.43(10)	C(3)-N(1)-C(10)	126.45(11)
C(4)-N(1)-C(10)	125.12(11)	C(2)-C(1)-C(11)	106.73(10)
C(2)-C(1)-C(19)	111.75(10)	C(2)-C(1)-C(25)	112.75(10)
C(19)-C(1)-C(11)	114.02(10)	C(19)-C(1)-C(25)	105.51(10)
C(25)-C(1)-C(11)	106.07(9)	C(3)-C(2)-C(1)	126.91(11)
C(3)-C(2)-C(9)	105.98(11)	C(9)-C(2)-C(1)	126.69(11)
C(2)-C(3)-N(1)	110.92(11)	N(1)-C(4)-C(5)	129.19(11)
N(1)-C(4)-C(9)	107.81(11)	C(5)-C(4)-C(9)	122.99(12)
C(6)-C(5)-C(4)	117.35(12)	C(5)-C(6)-C(7)	121.29(13)
C(8)-C(7)-C(6)	121.31(13)	C(7)-C(8)-C(9)	119.16(12)
C(4)-C(9)-C(2)	106.86(11)	C(8)-C(9)-C(2)	135.22(12)
C(8)-C(9)-C(4)	117.90(12)	C(12)-C(11)-C(1)	116.77(10)
O(1)-C(12)-C(11)	121.70(11)	O(1)-C(12)-C(13)	119.55(11)
C(13)-C(12)-C(11)	118.70(11)	C(14)-C(13)-C(12)	123.68(12)
C(14)-C(13)-C(18)	118.43(12)	C(18)-C(13)-C(12)	117.88(11)
C(15)-C(14)-C(13)	120.78(13)	C(16)-C(15)-C(14)	119.92(14)
C(15)-C(16)-C(17)	120.18(13)	C(18)-C(17)-C(16)	120.01(14)
C(17)-C(18)-C(13)	120.67(13)	C(20)-C(19)-C(1)	118.13(11)
C(24)-C(19)-C(1)	123.80(11)	C(24)-C(19)-C(20)	117.80(12)
C(21)-C(20)-C(19)	121.33(12)	C(20)-C(21)-C(22)	120.07(12)
C(23)-C(22)-C(21)	119.24(12)	C(22)-C(23)-C(24)	120.49(12)
C(23)-C(24)-C(19)	121.05(12)	C(26)-C(25)-C(1)	122.89(11)
C(26)-C(25)-C(30)	117.82(12)	C(30)-C(25)-C(1)	119.27(11)

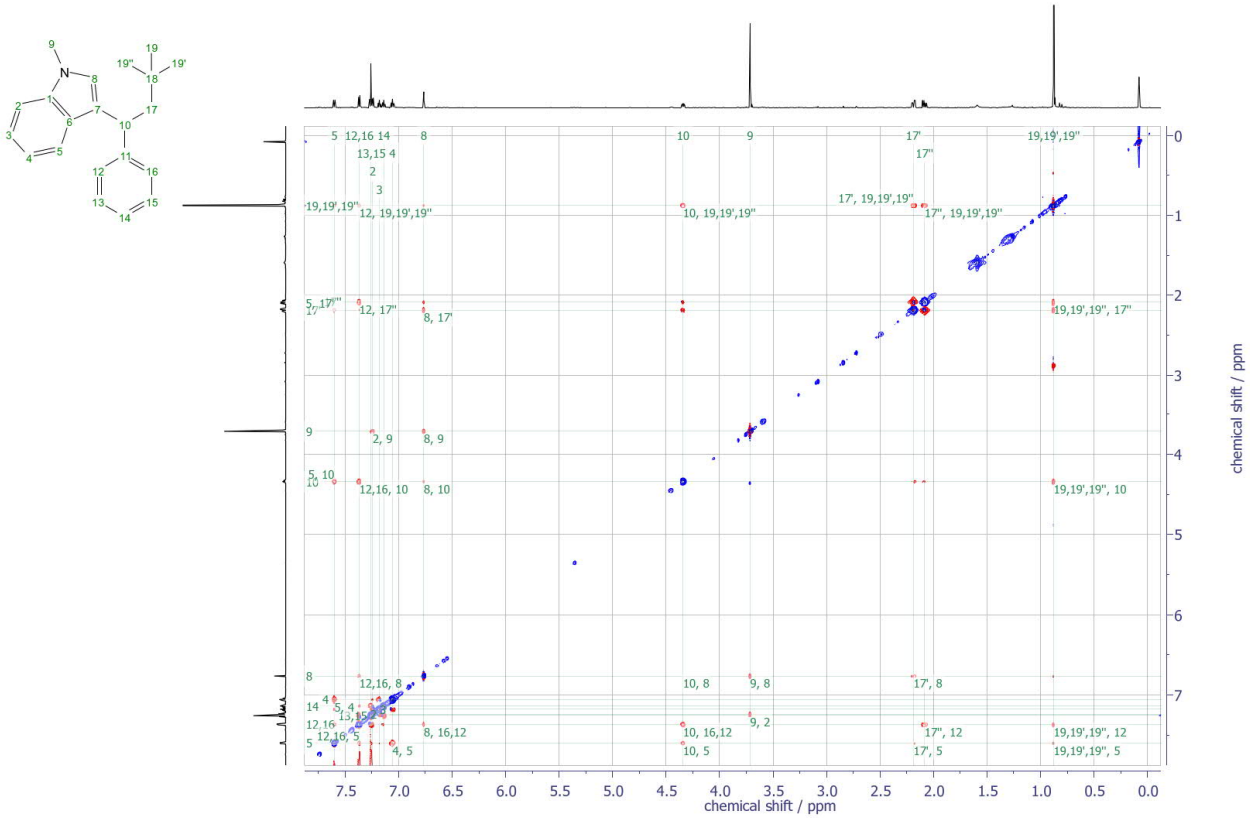
C(25)-C(26)-C(27)	121.08(12)	C(28)-C(27)-C(26)	120.23(13)
C(27)-C(28)-C(29)	119.55(12)	C(30)-C(29)-C(28)	119.89(12)
C(29)-C(30)-C(25)	121.35(12)		

Additional 2D NMR experiments



^{1}H NMR of **9** shows on a first sight a sharp signal for proton 8. Compared to an indole with substitution on C2 like above 1,2-dimethylindole with a broad signal for free C3 proton, it resembles more a C3 substituted indole.

More profound proof is given by the following NOESY NMR experiment data of **9** (with the same atom numbering):



Cross signals of proton 8 with proton 10 as well as protons 9 indicate a spatial positioning of this proton 8 in between benzylic position and the *N*-methyl group which is possible for a C3-substituted indole, not a C2 substituted one.

Mechanistic Studies

Experiment 1: Effect of light on pivaldehyde

A solution of pivaldehyde (0.5 mmol) in acetonitrile (1 mL) under Ar gas atmosphere in a 10mL-Schlenk-tube was stirred and irradiated with white light (white LED, 40 W, 65°C) for 12 h. The ^{1}H NMR analysis of the irradiated solution showed no decomposition of aldehyde during this periode.

Experiment 2: Effect of light on TBPB

A solution of *t*BuOOBz (TBPB, 0.2 mmol) in acetonitrile (1 mL) under Ar gas atmosphere in a 10mL-Schlenk-tube was stirred and irradiated with white light (white LED, 40 W, 65°C) for 12 h. The ^{1}H NMR analysis of the irradiated solution showed no decomposition of peroxide during this periode.

Experiment 3: Effect of Ir(ppy)$_3$ on TBPB

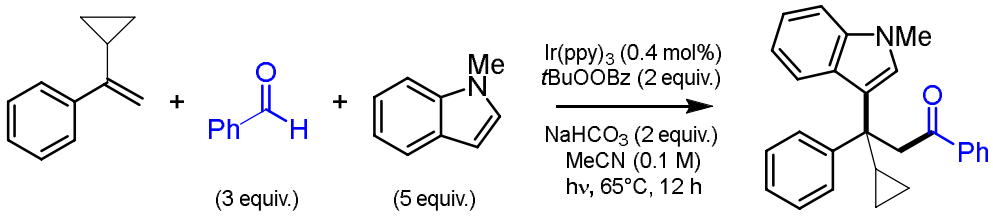
In a NMR tube a dispersion of *t*BuOOBz (TBPB, 0.04 mmol) and Ir(ppy)$_3$ (0.01 mmol) in acetonitrile-d$_3$ (0.5 mL) was irradiated with white light (white LED, 40 W). ^{1}H NMR analysis showed after 25 min of irradiation 29% of the perester was converted to benzoic acid (~28% of *tert*-butoxyl groups were converted to acetone, ~2% to *t*BuOH). After an irradiation time of 13.5 h the perester was fully converted (benzoic acid (>95%), acetone (93%), *t*BuOH(7%)). Remarkably 4 equiv. of TBPB referred to Ir(ppy)$_3$ could be cleaved, showing that in this NMR experiment *t*BuOOBz molecules were not exclusively cleaved by electron transfer from the Ir(III) species. Whether a heterogeneous perester activation is involved could not be excluded. When conducting the same experiment in the dark at the same reaction temperature after 13.5 h only 6% of perester were converted.

Experiment 4: Effect of 1-methylindole on TBPB

In a NMR tube a solution of *t*BuOOBz (TBPB, 0.1 mmol) and *N*-methylindole (0.15 mmol) in acetonitrile-d_3 (0.5 mL) was irradiated with white light (white LED, 40 W). After 2h 20 min of irradiation less than 1% of the perester was converted to benzoic acid, acetone and *t*BuOH. After 13 h benzoic acid (25%), acetone (~8%) and *t*BuOH (~10%) were formed in greater amounts. In a parallel experiment the same mixture was wrapped into dark in the NMR tube while undergoing the heating of the light source. In this experiment after 13 h amounts of *t*BuOH and acetone correspond to less than 1% conversion could be observed. The *N*-methylindole induced slow cleavage of *t*BuOOBz could explain a minor product formation in the absence of Ir catalyst as described in the above sections of "Evaluation of reaction conditions" and "Reaction without catalyst".

Experiment 5: Radical clock experiment

(1-Cyclopropylvinyl)benzene was employed in the procedure and reacted with benzaldehyde and *N*-methylindole to the difunctionalization product **7b**.



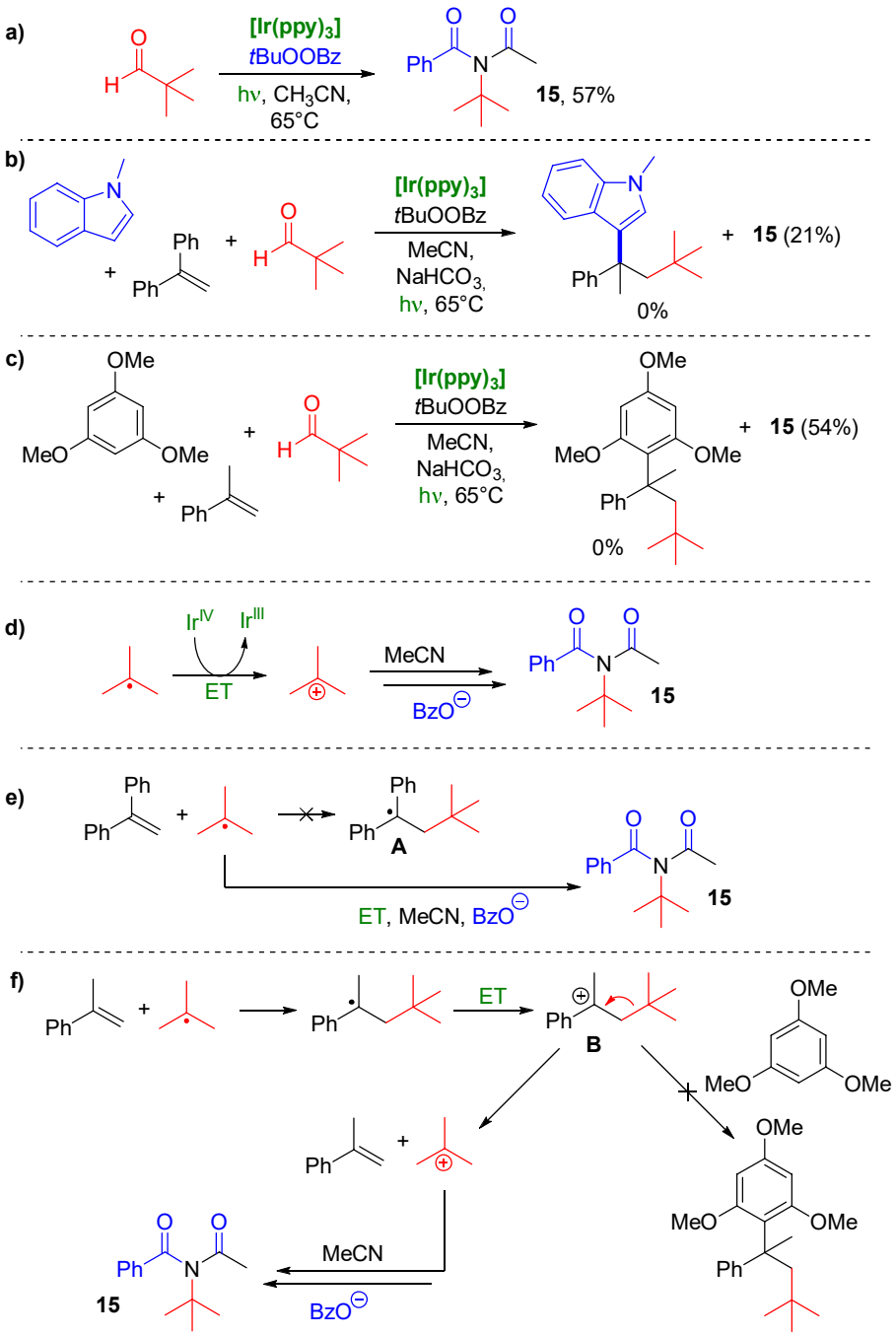
7b (26%)

A lower yield could be due to kinetic competition between ring opening of the radical-adduct intermediate and sequential oxidation and functionalization with *N*-methylindole of the closed form. The radical ring-opening proceeds on a rate scale of 6.1 x 10^4 s^{-1} at room temperature.[12] Additionally, the low yield could be due to decomposition in irradiated reaction medium as well as during work up. The product is relatively sensitive. It quickly decomposes in solution under air atmosphere.

Experiment 6: Isolation of an alternative product

A reaction mixture of pivaldehyde with the irradiated $Ir(ppy)_3$ and TBPB present in acetonitrile yielded **15** from direct oxidation of the formed *tert*-butyl radical (57% yield, Supplementary Scheme S5a).

Supplementary Scheme S5: Isolation of product 15.



[c]Conditions: Olefin (0.5 mmol, 1 equiv.), TBPB (2 equiv.), $Ir(ppy)_3$ (0.4 mol%), pivaldehyde (5 equiv.), nucleophile (3 equiv.), $NaHCO_3$ (2 equiv.), MeCN (5 mL), white LED light, 65°C, 12 h.

Upon examination of the successful difunctionalizations with pivaldehyde closely (reactions giving products **5**, **9** and **11b**), product **15** was not observed on thin layer chromatography even though aldehyde and perester are employed in excess relative to styrene.

However, product **15** was formed in reactions with nucleophiles that failed to give the desired products of styrene difunctionalization. It was formed in 21% yield when reacting 1,1-diphenylethylene with pivaldehyde and *N*-methylindole under the optimized arylalkylation conditions (see Supplementary Scheme S5b), and in 54% yield when investigating the reaction of α-methylstyrene with pivaldehyde and 1,3,5-trimethoxybenzene (see Supplementary Scheme S5c).

These observation can be rationalized as follows:

The oxidation potentials indicate that the oxidation of the benzylic radical intermediate ($PhC•HCH_3$: $E_{1/2}$ = 0.37 V vs SCE in MeCN[13]) is thermodynamical less facile than oxidation of the *tert*-butyl radical ($E_{1/2}$ = 0.09 V vs SCE in MeCN[13]). However, since in successful olefin difunctionalizations with *tert*-butyl radicals (products **5**, **9**, **11b**), **15** was not observed as side product, the addition to the double bond apparently proceeds on a higher rate than the direct oxidation of the *tert*-butyl radical under the presented reaction conditions.

If no olefin is present, oxidation to the *tert*-butyl cation is occurring, giving product **15** by subsequent attack of acetonitrile and a benzoate anion in relatively high yield (Supplementary Scheme S5d).

In the reaction of 1,1-diphenylethylene with pivaldehyde, the expected product did not form, possibly because steric reasons prevented the attack of the *tert*-butyl radical to 1,1-diphenylethylene (since otherwise, all the compounds used in the reaction did react in other combinations, e.g. see products **5** and **7a**). Due to the failure (or low rate) of forming the radical intermediate **A**, the *tert*-butyl radical is oxidized, ultimately forming **15** (Supplementary Scheme S5e).

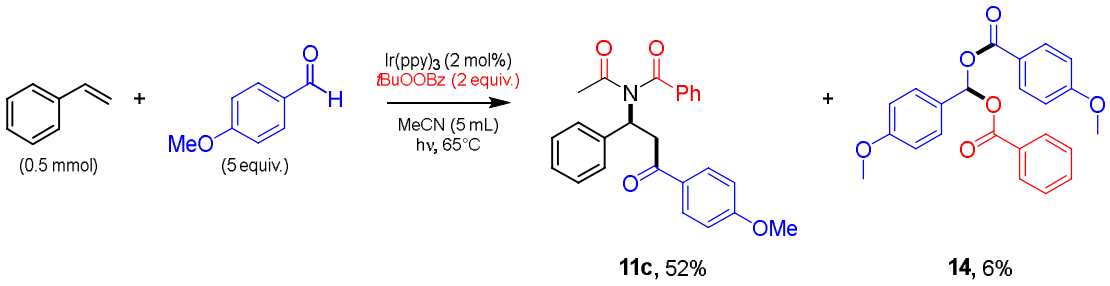
In the reaction of α-methylstyrene, pivaldehyde and 1,3,5-trimethoxybenzene, attack of the *tert*-butyl radical to α-methylstyrene as well as oxidation of the radical intermediate should occur, as indicated by the successful isolation of product **5** in 55% yield, which incorporated *N*-methylindole. The failure of the reaction with 1,3,5-trimethoxybenzene suggests that, for whatever reason, this nucleophile does not attack the carbocation **B**

(Supplementary Scheme S5f). Attack of the solvent acetonitrile also does not occur, as we could not isolate any imide products with α-methylstyrene. Intermediate **B** could then fragment, releasing α-methylstyrene and a *tert*-butyl carbocation, which is subsequently forming **15** by attack of acetonitrile and a benzoate anion.

Experiment 5: Isolation of a side product

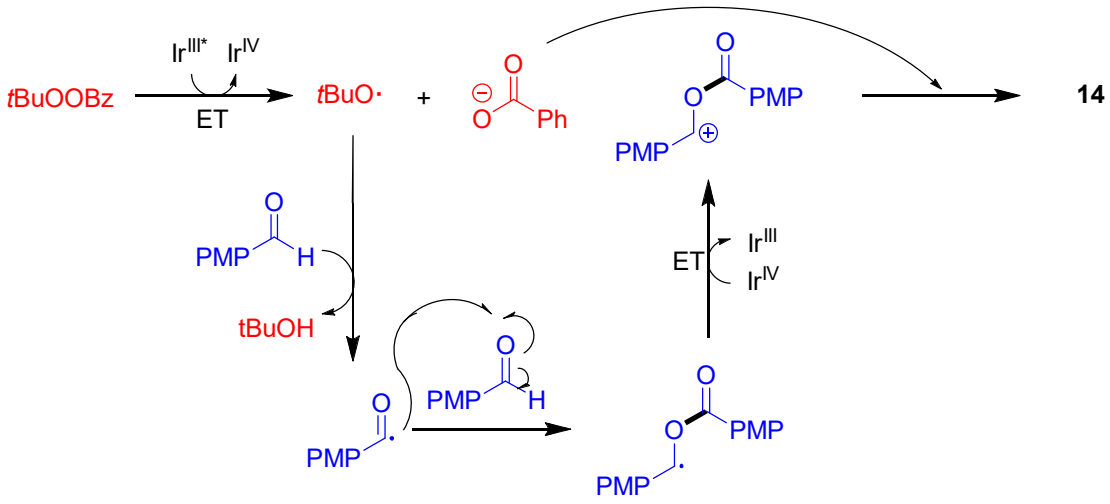
Conducting the general procedure for imide formation in the presence of 4-methoxybenzaldehyde lead to two isolatable products (**11c**, **14**).

Supplementary Scheme S6: Isolation of product 14

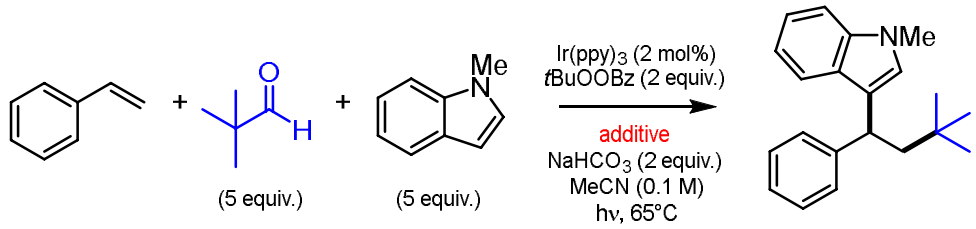


Besides the desired imide product **11c**, a different reaction path for electron-rich 4-methoxybenzaldehyde showed to be possible. Rationalizing the formation of **14**, it could be summarized as difunctionalization of the aldehyde's C–O double bond.

The scheme below shows a possible reaction mechanism to yield product **14** (PMP = *p*-methoxyphenyl). An electron donation from photoexcited $Ir(ppy)_3^*$ to *tert.*-butylperbenzoate (TBPB) leads to the oxidized $Ir(ppy)_3^+$ species and after O–O bond cleavage to the H-acceptor tert.-butyl radical (*t*BuO·) and the benzoate anion. Hydrogen atom transfer (HAT) from 4-methoxybenzaldehyde (PMPCHO) to *t*BuO· generates *tert.*-butanol and the aldehyde's corresponding benzoyl radical. The benzoyl radical is known to be able to attack a further aldehyde molecule at the carbonyl-O atom.[14] The resulting species is an electron-rich benzylic radical which can undergo an oxidation process with the present $Ir(ppy)_3^+$ species to obtain the corresponding benzylic cation as well as recycling the photocatalyst $Ir(ppy)_3$. Nucleophilic attack of the present benzoate anion would lead to the isolated side product **14**.



Experiment 6: Addition of radical inhibitor and trap, resp.



additive (1 equiv.)	yield 9 (%)[a]
no	45
BHT	0
TEMPO	19

[a] ^{1}H NMR yield

BHT = 3,5-Di-*tert*-butyl-4-hydroxytoluene

TEMPO = 2,2,6,6-Tetramethylpiperidinyloxyl

No trapped radicals could be isolated.

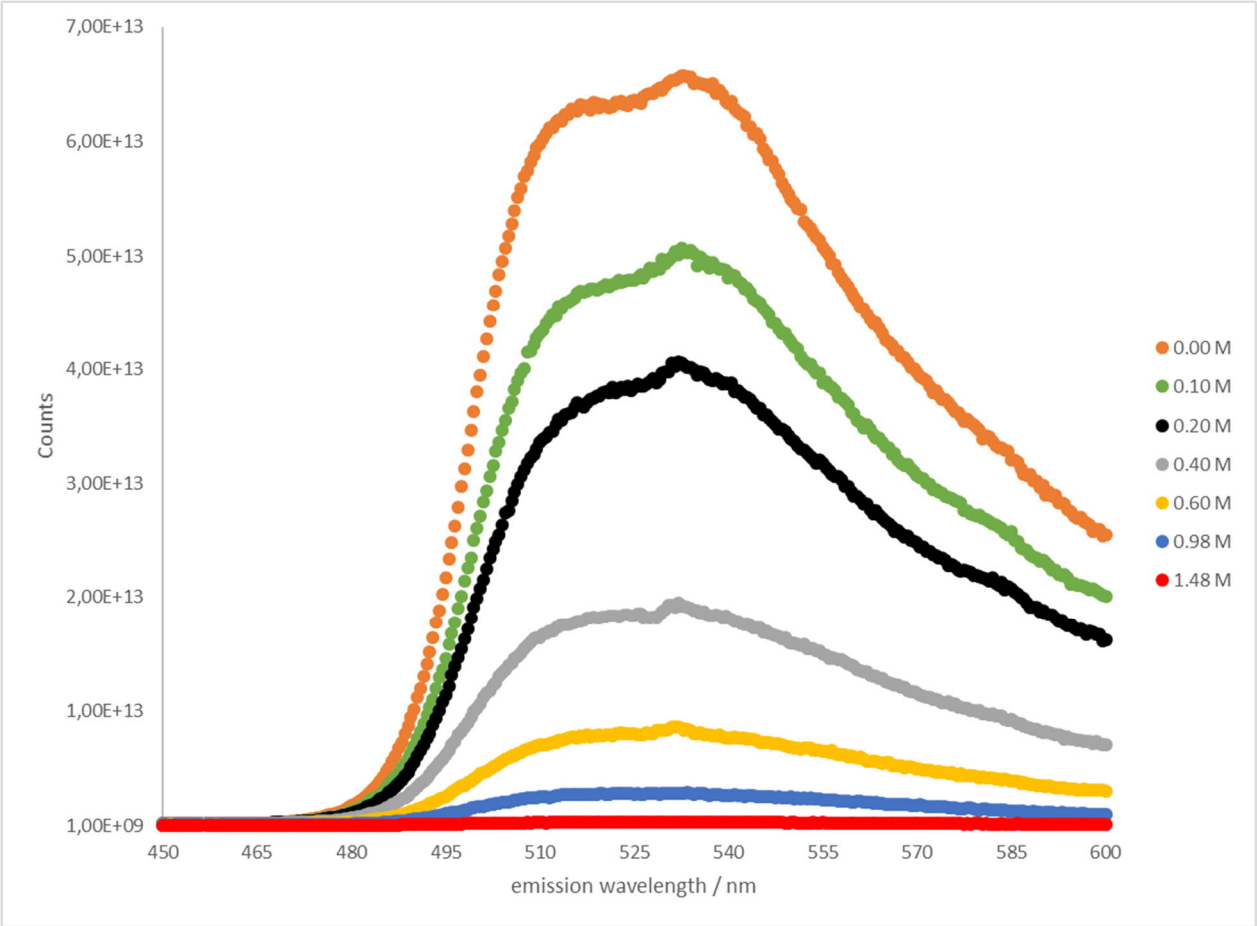
Experiment 7: Luminescence quenching

Luminescence measurements for freshly prepared $Ir(ppy)_3$ stock solutions in acetonitrile were carried out with an excitation irradiation of λ_{ex}= 315 nm and observed

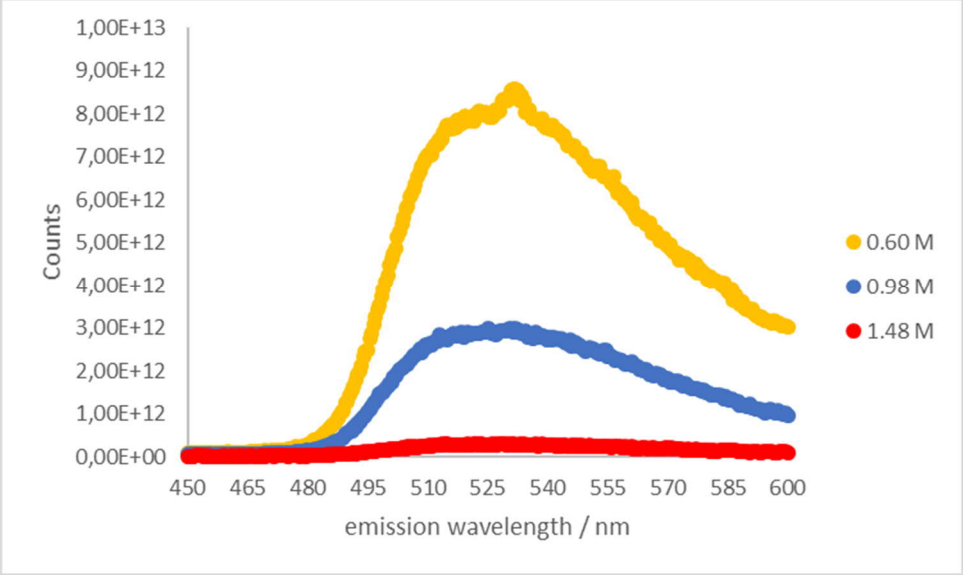
for a luminescence emission of around λ_{em} = 525 nm and an excitation as well as measuring bandwidth of 2 nm.

For a Ir concentration of c = $2 \cdot 10^{-5}$ M there is no luminescence quenching observed in the presence of *tert*-butyl perbenzoate (TBPB), ranging its concentration from c = $1 - 4 \cdot 10^{-3}$ M. This result is similar to the one of experiments carried out by the Knowles group with Ir(dF-CF_3-ppy)$_2$(dtbbpy)(PF_6) and TBPB in DMA.[15]

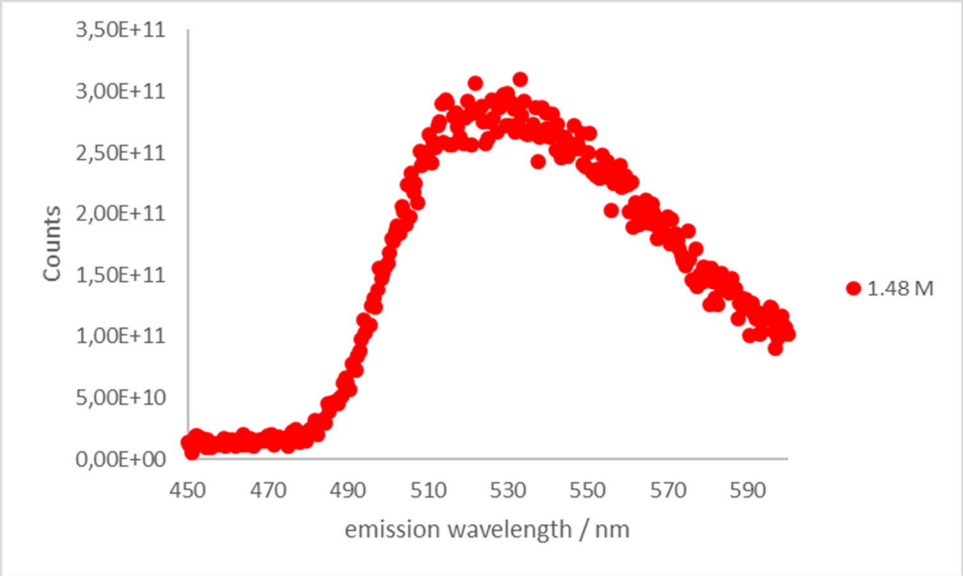
From that point we turned to Ir and TBPB concentrations that resemble more the ones in the synthetic procedure. The following luminescence data were received with measurements of $Ir(ppy)_3$ stock solutions of c = $4.6 \cdot 10^{-4}$ M containing TBPB in a range of c = 0.1-1.5 M. I_0 corresponds to the detector signal of a $Ir(ppy)_3$ stock solution in acetonitrile (c = $4.6 \cdot 10^{-4}$ M) containing no additive (of TBPB).



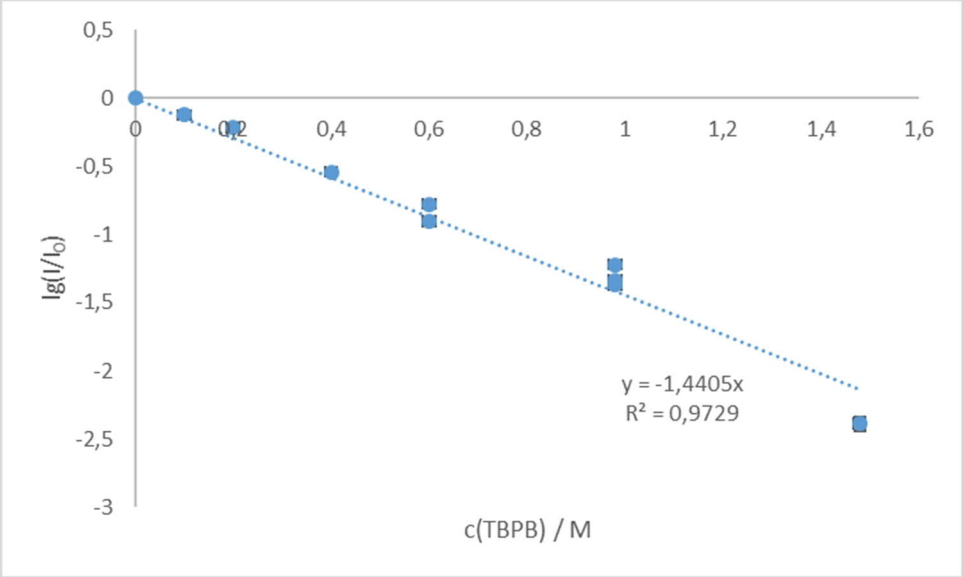
Supplementary Figure S3: Emission spectrum between 450 and 600 nm of $Ir(ppy)_3$ (c = $4.6 \cdot 10^{-4}$ M) stock solutions in acetonitrile containing different concentrations of *tert*-butyl perbenzoate (c = 0-1.48 M).



Supplementary Figure S4: Emission spectrum between 450 and 600 nm of $Ir(ppy)_3$ ($c = 4.6 \cdot 10^{-4}$ M) stock solutions in acetonitrile containing different concentrations of *tert*-butyl perbenzoate (c = 0.60-1.48 M).



Supplementary Figure S5: Emission spectrum between 450 and 600 nm of $Ir(ppy)_3$ ($c = 4.6 \cdot 10^{-4}$ M) stock solutions in acetonitrile containining *tert*-butyl perbenzoate (c = 1.48 M).



Supplementary Figure S6: Luminescence attenuation at λ_{em} = 525 nm of $Ir(ppy)_3$ (c = 4.6 · 10^{-4} M) stock solutions in acetonitrile containining *tert*-butyl perbenzoate (c = 0-1.48 M).

Supplementary Table S11: Error estimation of luminescence attenuation of $Ir(ppy)_3$ (c = 4.6 · 10^{-4} M) stock solutions in acetonitrile containining *tert*-butyl perbenzoate (c = 0-1.48 M).

c(TBPB) / M	error indicator c / M	Counts@525nm	u_I / Counts	lg (I/I_0)	error indicator lg (I/I_0)	error indicator (I_0/I)
0	0	6,36E+13	4E+11	0	0,002731063	0,006288506
0.1	0,012655681	4,78E+13	4E+11	-0,123637601	0,003630525	0,013905993
0.2	0,012655943	3,85E+13	90000000000	-0,218498782	0,001016279	0,011097048
0.4	0,012656516	1,84E+13	2E+11	-0,539054522	0,004724505	0,043474045
0.6	0,01200849	7,97E+12	40000000000	-0,901852787	0,002178636	0,064171209
0.6	0,01200849	1,07E+13	2E+11	-0,773852725	0,008112497	0,1170942
0.98	0,012010082	2,71E+12	80000000000	-1,370360338	0,012815104	0,707852798
0.98	0,012010082	3,87E+12	70000000000	-1,215771955	0,007854921	0,314709881
0.98	0,012010082	2,99E+12	1,1E+11	-1,328365441	0,015996683	0,795884238
1.48	0,011327378	2,61E+11	32000000000	-2,386573151	0,053210205	29,87824351

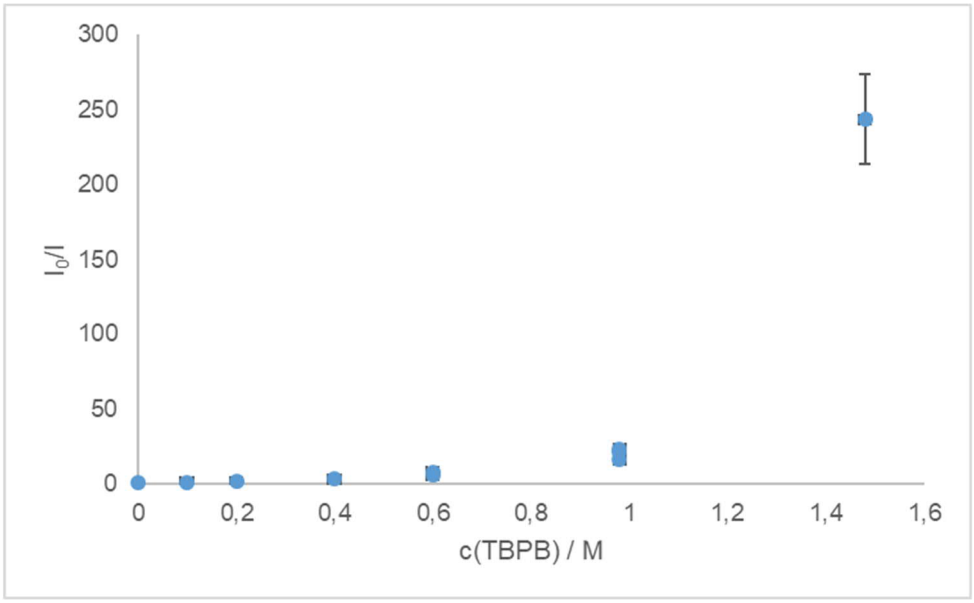
Since the error indicators are not visible in the diagrams of lg (I/I_0), I_0/I, resp. vs c(TBPB) (Supplementary Figure S6-S8), they are listed in the above table (see Supplementary Table S11). The measuring inaccuracy of the used Eppendorf pipette (u_{mL} = 0.004 mL) lead to the error indicators for concentrations via the equations:

$$c(TBPB) = \frac{\frac{\rho}{M}\ V(TBPB)}{V_{ges}} \quad ; \quad u_c = \sqrt{\sum_x \left(\frac{\partial c(TBPB)}{\partial V_x}\ u_{mL} \right)^2}$$

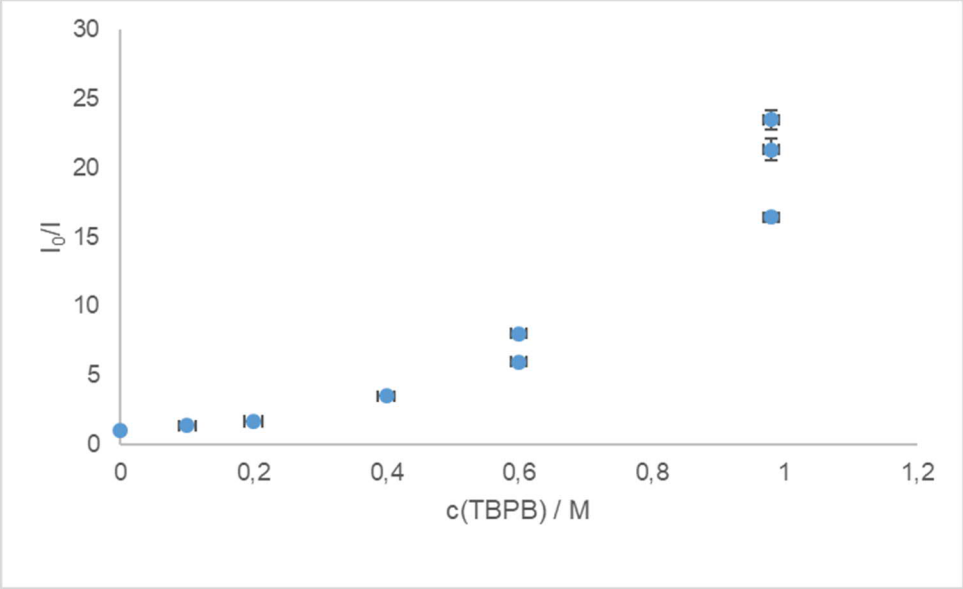
Analogously the errors for values of lg (I/I_0) and I_0/I, resp., were estimated using measuring inaccuracies u_I (see table S11) that were estimated by comparing detector signals at λ_{em} = 525 nm with the signals at λ_{em} = 524-526 nm.

$$attenuation = \ lg\left(\frac{I}{I_0}\right) ; \quad u_{att} = \sqrt{\sum_x \left(\frac{\partial lg\left(\frac{I}{I_0}\right)}{\partial I_x} u_I\right)^2}$$

$$Stern - Volmer\ equation = \frac{I_o}{I} \quad ; u_{SV} = = \sqrt{\sum_x \left(\frac{\partial\left(\frac{I_0}{I}\right)}{\partial I_x} u_I\right)^2}$$



Supplementary Figure S7: Stern-Volmer analysis for luminescence attenuation at λ_{em} = 525 nm of $Ir(ppy)_3$ (c = 4.6 · 10^{-4} M) stock solutions in acetonitrile containining *tert*-butyl perbenzoate (c = 0-1.48 M).



Supplementary Figure S7 Stern-Volmer analysis for luminescence attenuation at λ_{em} = 525 nm of $Ir(ppy)_3$ (c = 4.6 · 10^{-4} M) stock solutions in acetonitrile containining *tert*-butyl perbenzoate (c = 0-0.98 M).

A TBPB concentration of c = 0.2 M is closest to the application in this synthetic study. In conclusion, the obtained data suggest that with rising concentration of TBPB (from 0.1-1.48 M) a less high emission intensity is measured for the $Ir(ppy)_3$ solution. Furthermore, plotting I_0/I vs. [TBPB] after Stern-Volmer shows a non-linear curve for the obtained data. This positive deviation from linear regression is evidence for a more complex behavior with different contemporary quenching modes in this system, like a static one (TBPB and $Ir(ppy)_3$ form a non-luminescent complex) as well as a dynamic one (the excited state $Ir(ppy)_3^*$ is quenched by TBPB).[16,17] In regard of the redox potentials, this dynamic quenching could be an electron transfer from $Ir(ppy)_3^*$ ($E_{1/2}$ = −1.73 V vs SCE in MeCN)[18] to TBPB ($E_{1/2}$ = −1.40 V vs SCE in DMF),[19] forming $Ir^{IV}(ppy)_3^+$, benzoate anion and *tert*-butoxyl radical.

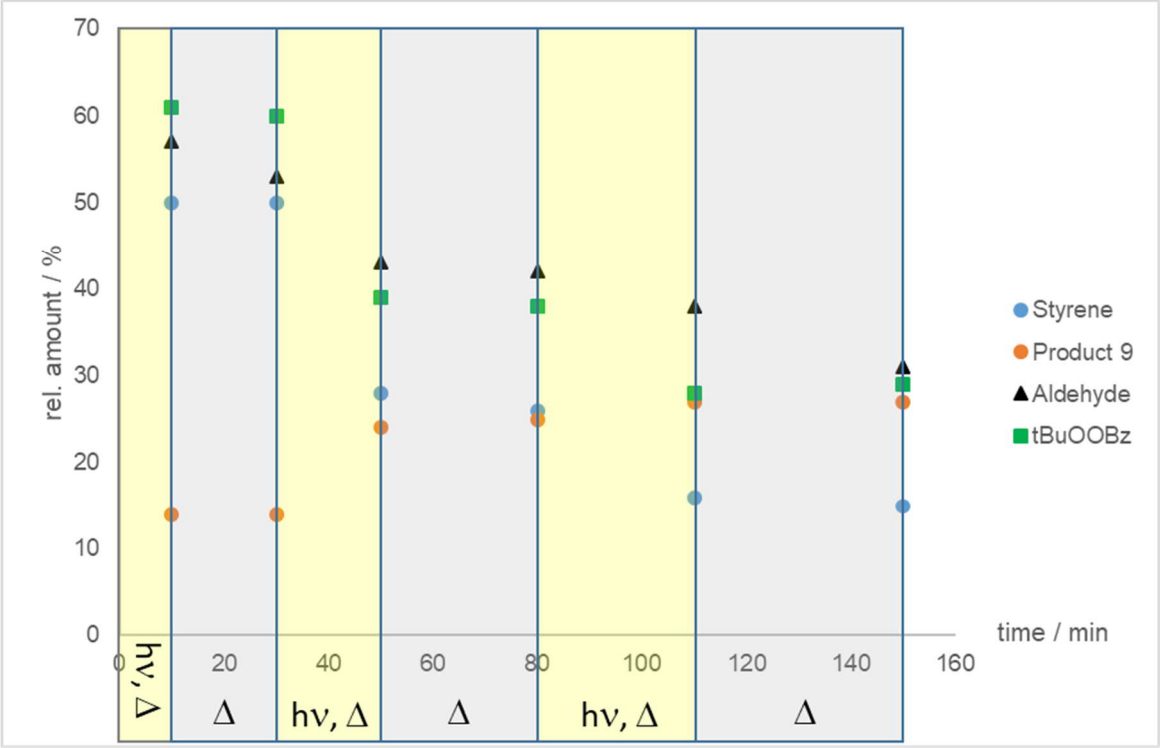
Experiment 8: Light-switches

In a NMR tube $Ir(ppy)_3$ (0.3 mg) and $NaHCO_3$ (16.6 mg) were dispersed in acetonitrile-d_3 (1.0 mL). Styrene (11 µL), *N*-methylindole (62 µL), pivaldehyde (54 µL) and *t*BuOOBz (38 µL) were given into the NMR tube. The reaction mixture was shaken before irradiating the mixture (white LED, 40 W, Δ) and before NMR measurements. The dispersion was alternately irradiated and then kept in the dark by

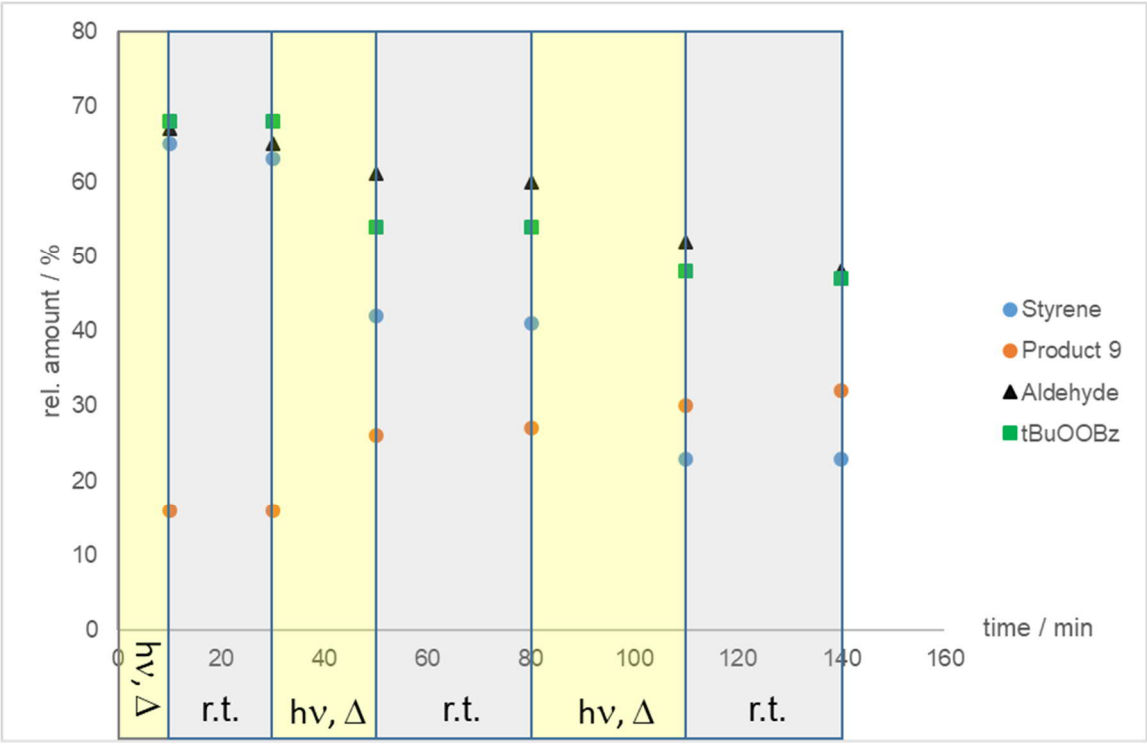
wrapping the tube with aluminum foil before irradiating again. After each light and dark period a ^{1}H NMR of the sample was conducted. The light source heated the reaction mixture (Δ), whereas the actual reaction temperature for these NMR reactions was not determined. The experiment was conducted in two different variants which differ in the dark period treatment:

Variant 1: light period (white LED, 40 W, Δ), alternately with dark period: NMR tube wrapped in aluminum foil while the tube was placed in the photo reactor (Δ).

Variant 2: light period (white LED, 40 W, Δ), alternately with dark period: NMR tube wrapped in aluminum foil and stored at room temperature.



Supplementary Figure S9: Light-Switch Experiment of the difunctionalization of styrene with pivaldehyde and *N*-methylindole in which light and dark period are conducted at the same temperature (Δ) (variant 1).



Supplementary Figure S10: Light-Switch Experiment of the difunctionalization of styrene with pivaldehyde and *N*-methylindole in which dark periods are conducted at room temperature (variant 2).

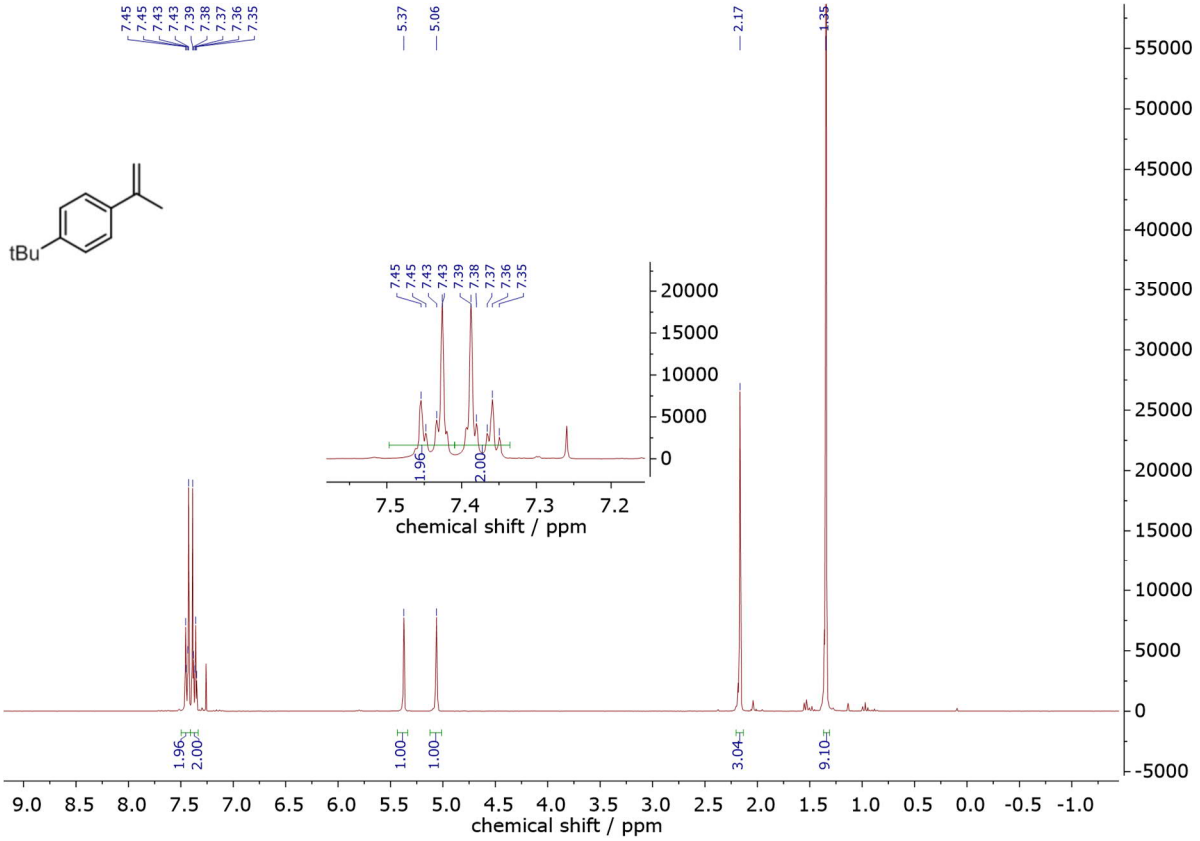
The experiments were performed without stirring a heterogeneous reaction mixture in a NMR tube. Also the reaction vessel therefore varies compared to the synthetic application so that the here obtained data are not in total conformity with the conversions and product amounts at same reaction times that could be obtained in a reaction conducted in a stirred round bottom flask. Also the reaction temperature might be changed a bit compared to the reaction in a round bottom flask (65°C).

In fact also the substrates conversions vary already a bit comparing these two experiments at similar irradiation times. Anyway we like to qualitatively state that these experiments show more ore less no formation of the product and no conversion of *t*BuOOBz (TBPB) in the dark periods, the periods without irradiating the reaction mixture. This is further evidence for a catalytic driven reaction path rather than a radical chain reaction after an initiated perester cleavage.

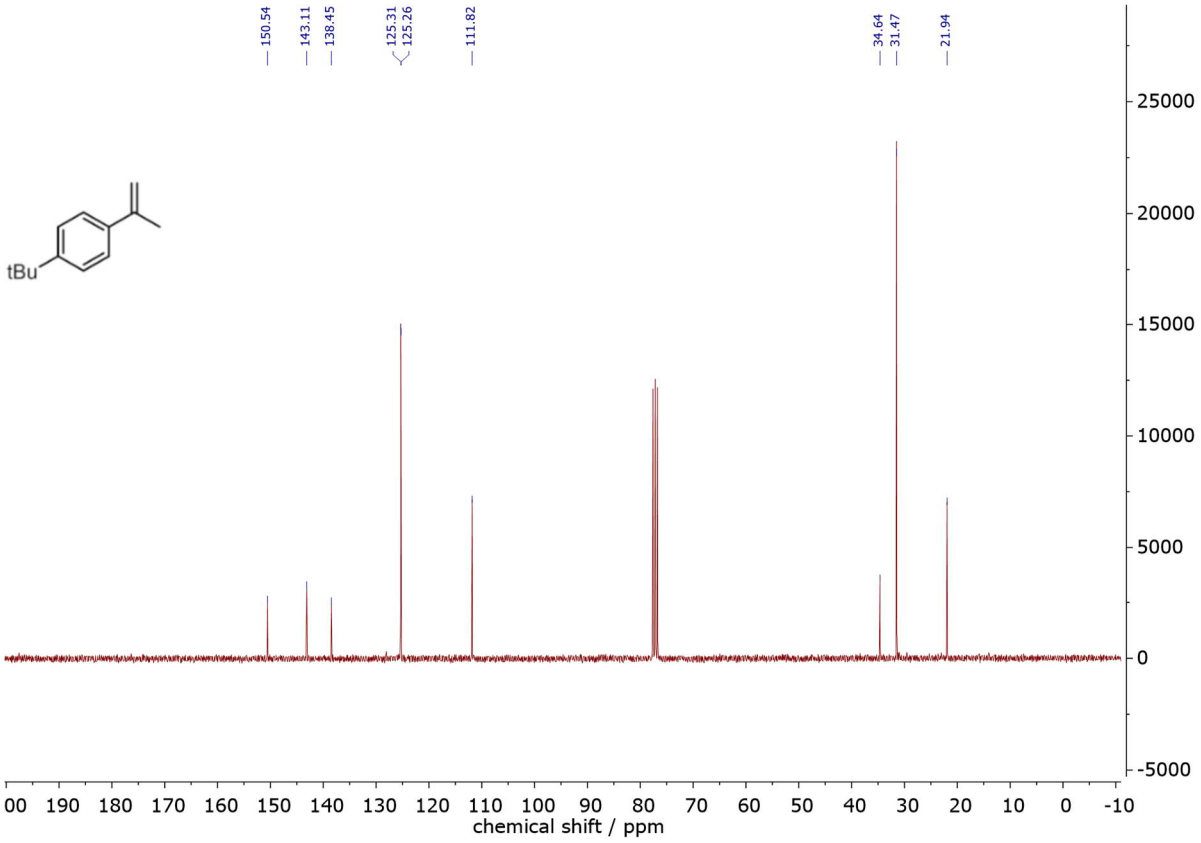
NMR spectra

Starting materials

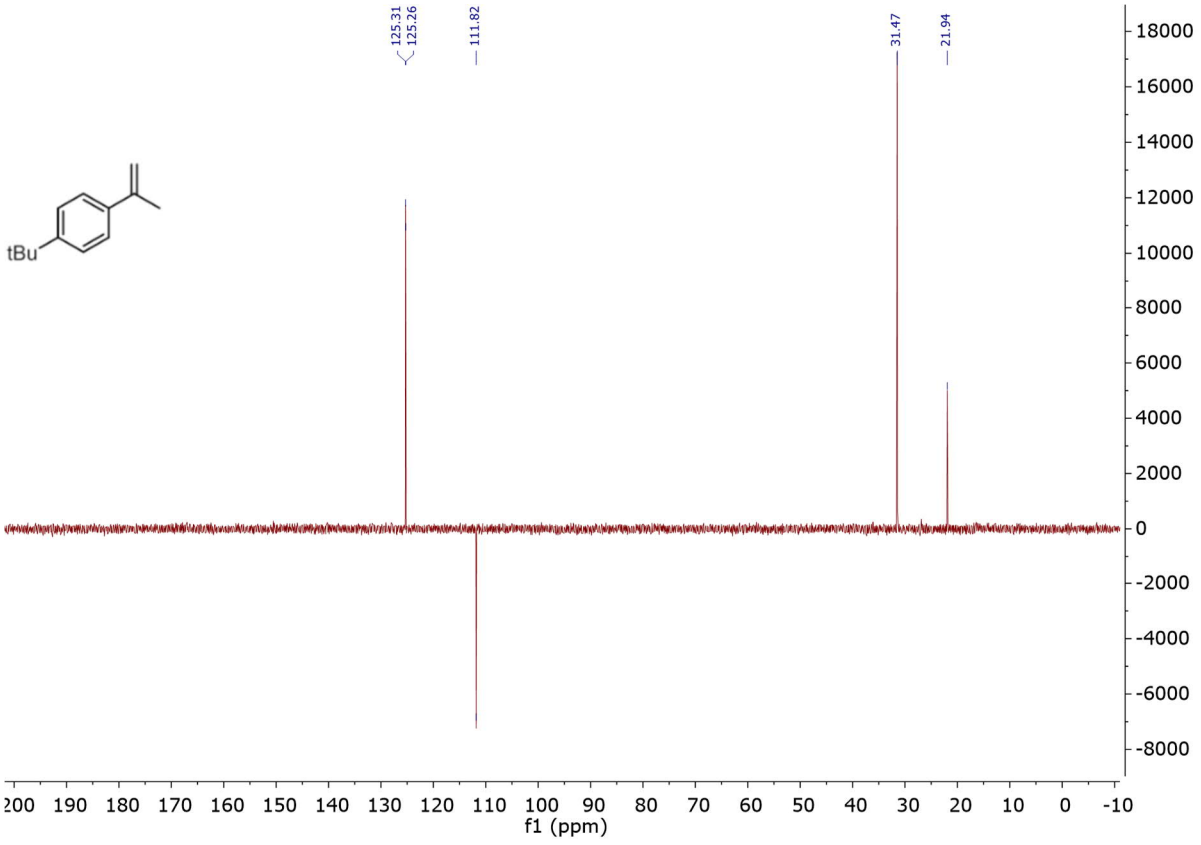
^{1}H (300 MHz, $CDCl_3$) of 4-*tert*-butyl-α-methylstyrene:



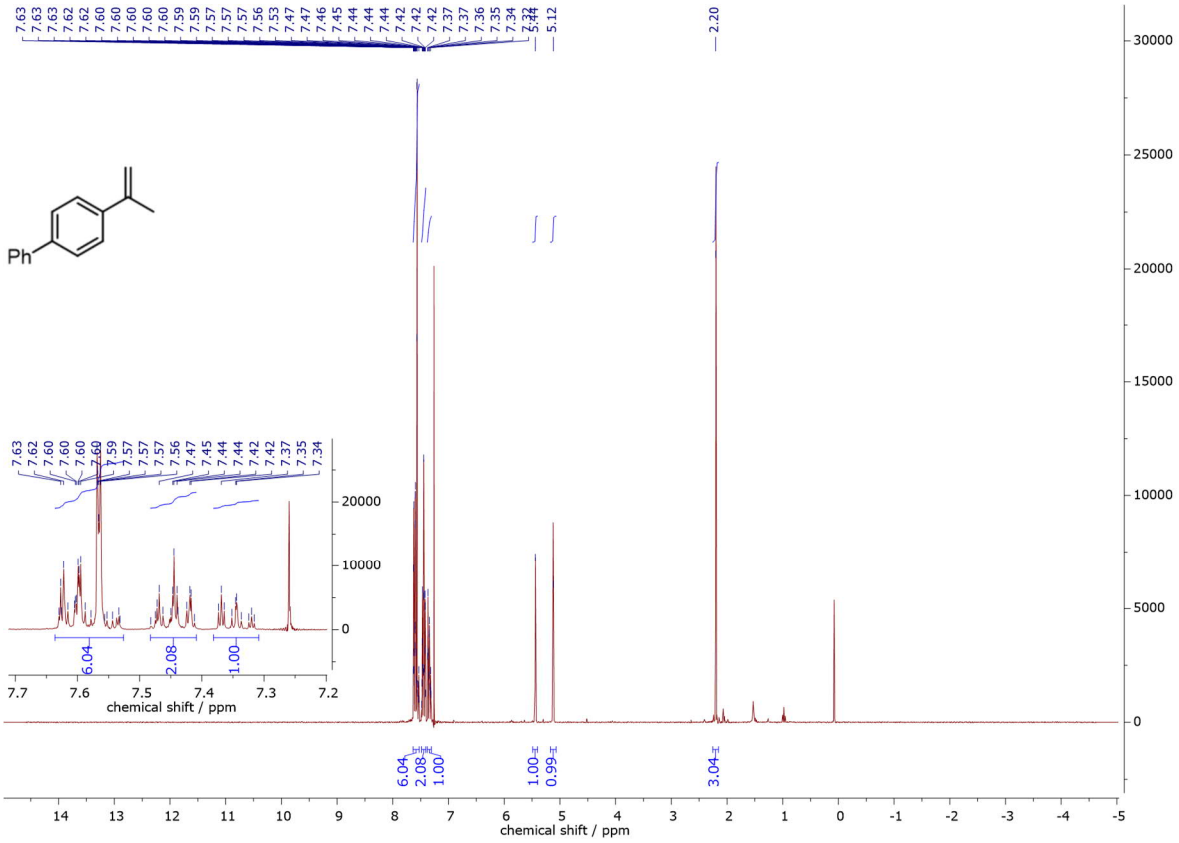
^{13}C {H} (75 MHz, $CDCl_3$) of 4-*tert*-butyl-α-methylstyrene:



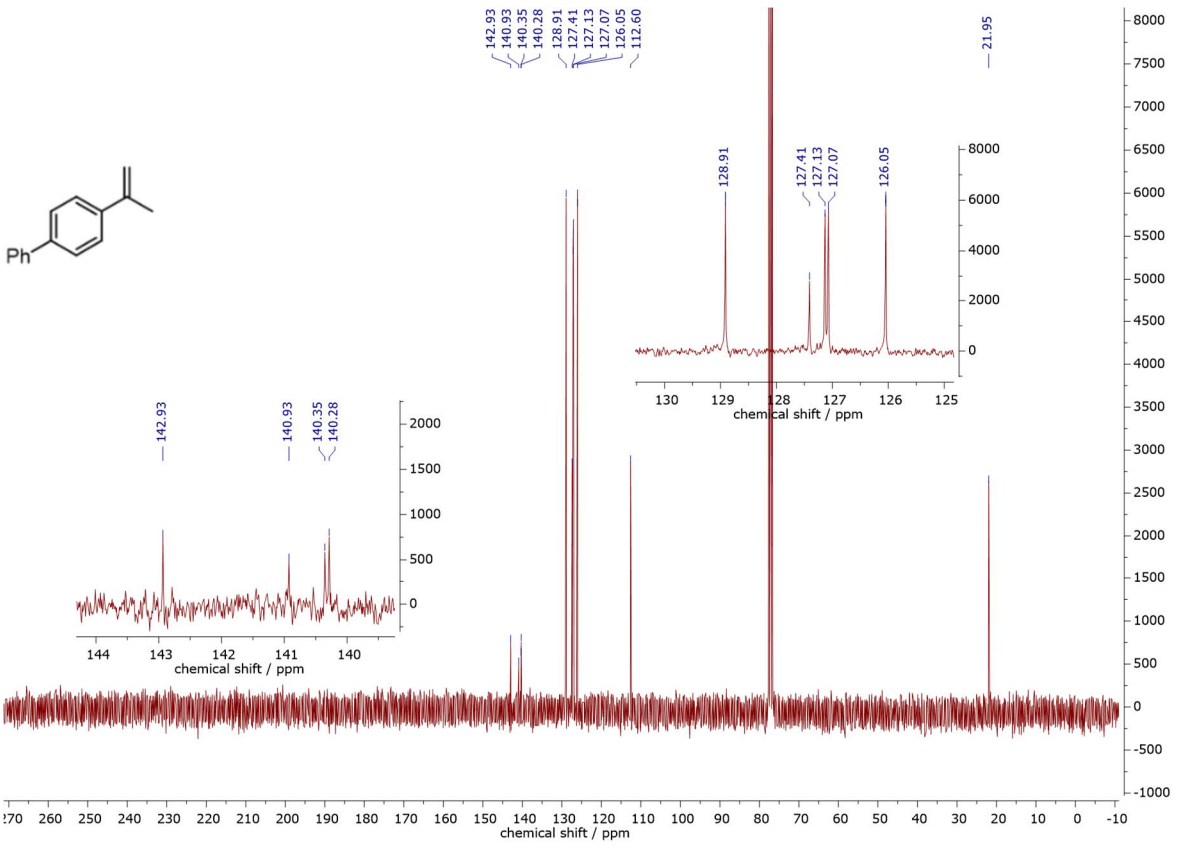
^{13}C DEPT135 {H} (75 MHz, $CDCl_3$) of 4-*tert*-butyl-α-methylstyrene:



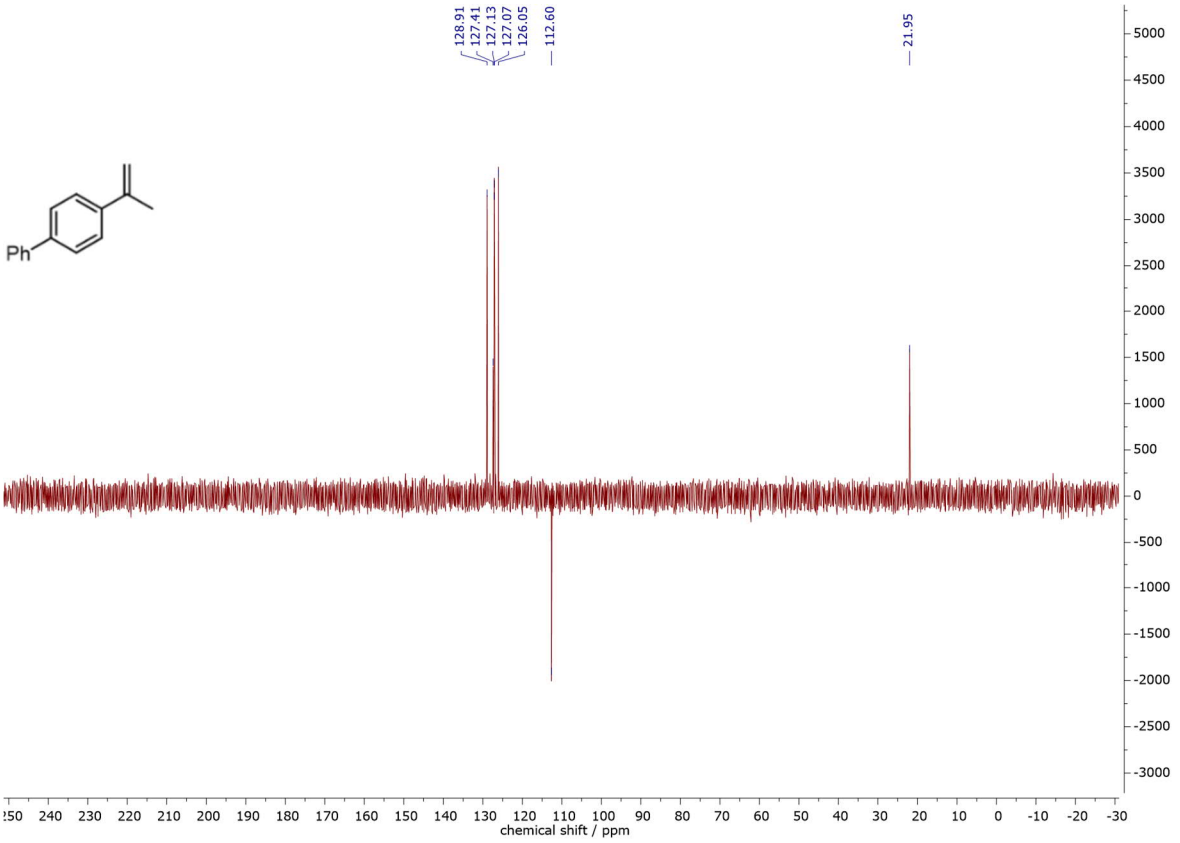
^{1}H (300 MHz, $CDCl_3$) of 4-phenyl-α-methylstyrene:



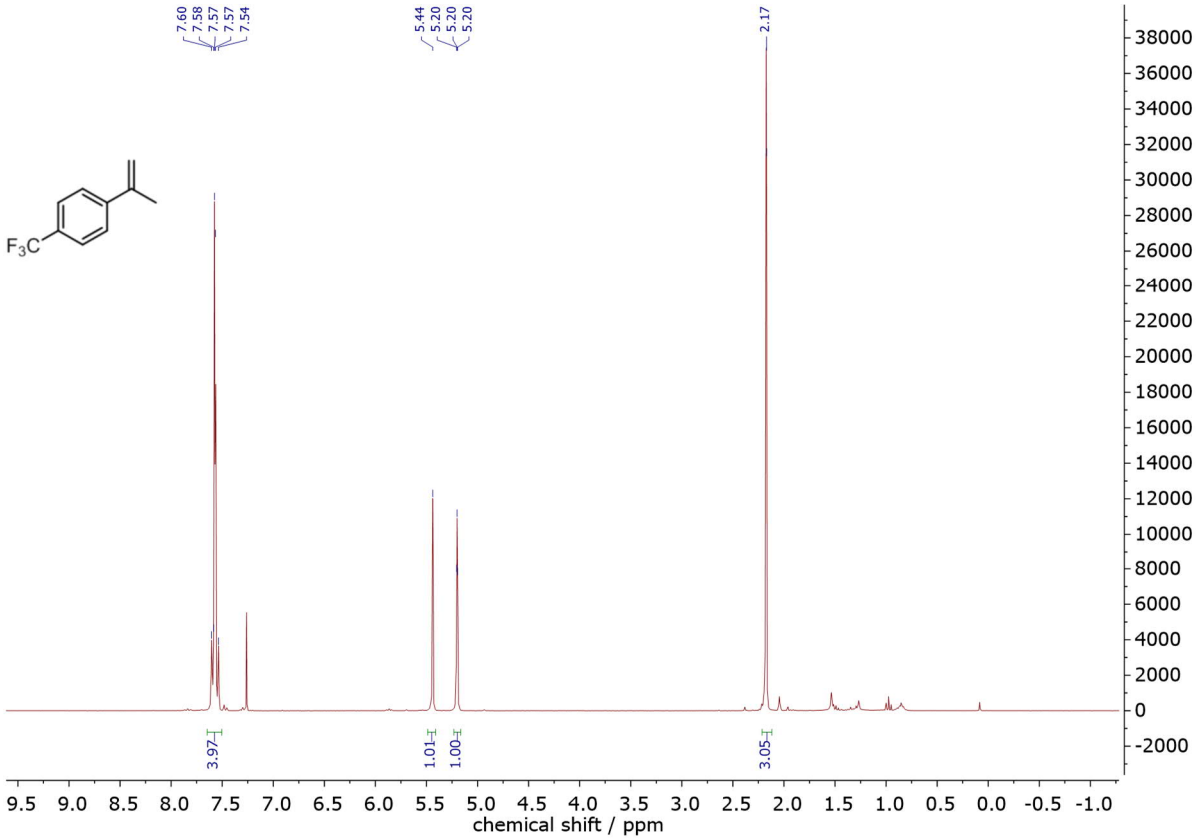
^{13}C {H} (75 MHz, $CDCl_3$) of 4-phenyl-α-methylstyrene:



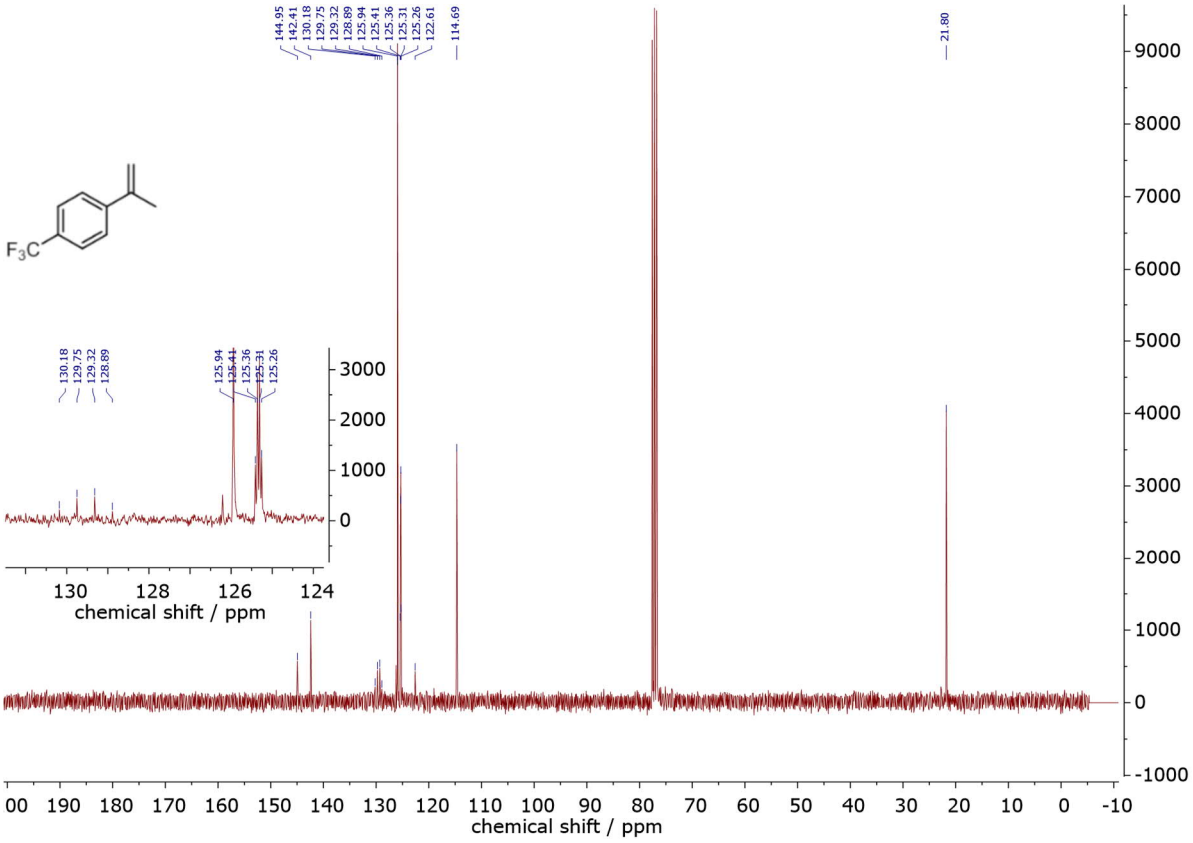
^{13}C DEPT135 {H} (75 MHz, $CDCl_3$) of 4-phenyl-α-methylstyrene:



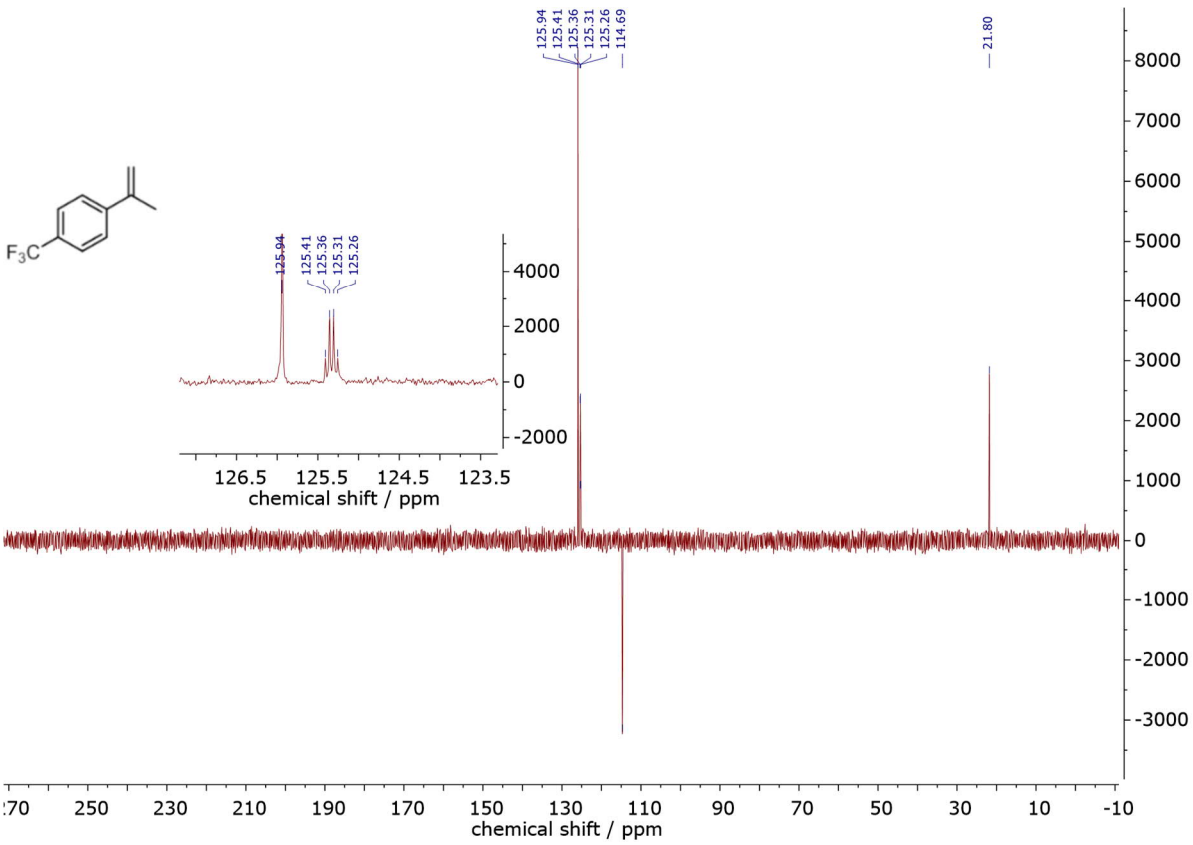
^{1}H (300 MHz, $CDCl_3$) of 4-trifluoromethyl-α-methylstyrene:



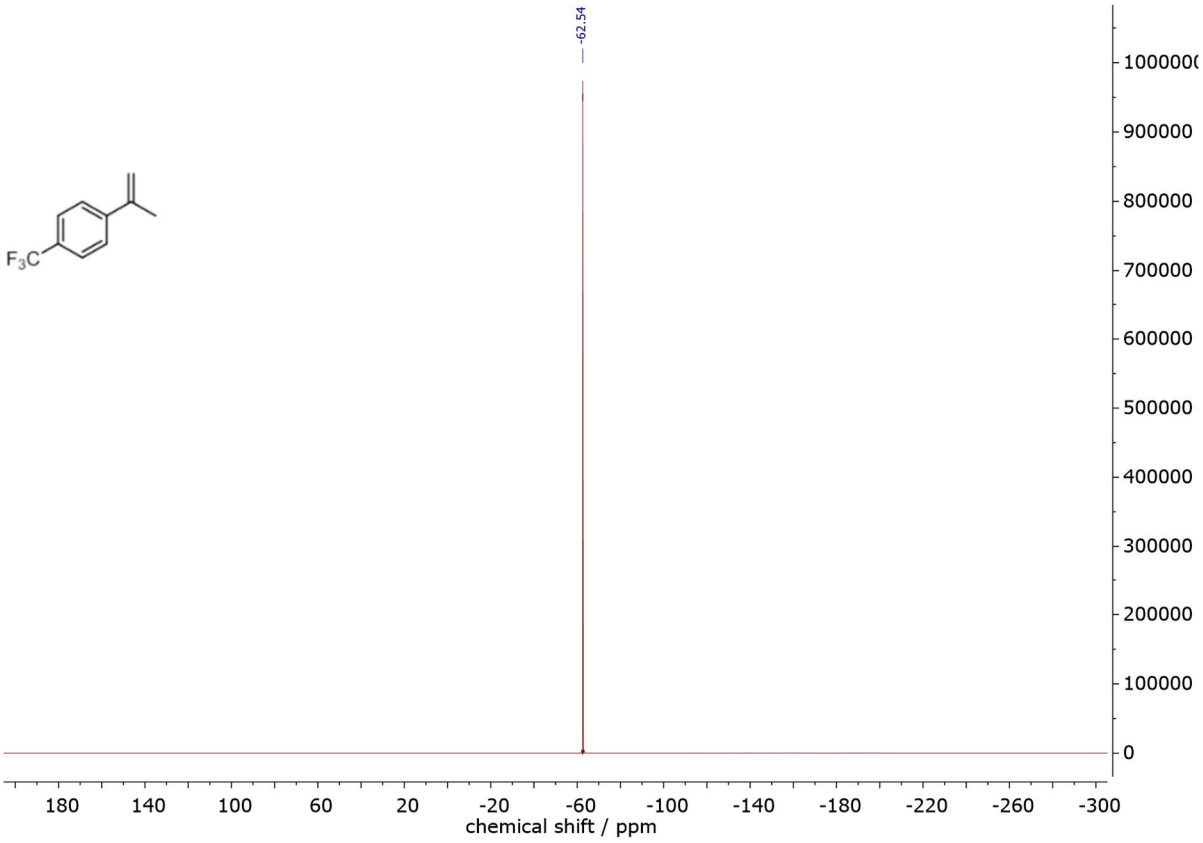
^{13}C {H} (75 MHz, $CDCl_3$) of 4-trifluoromethyl-α-methylstyrene:



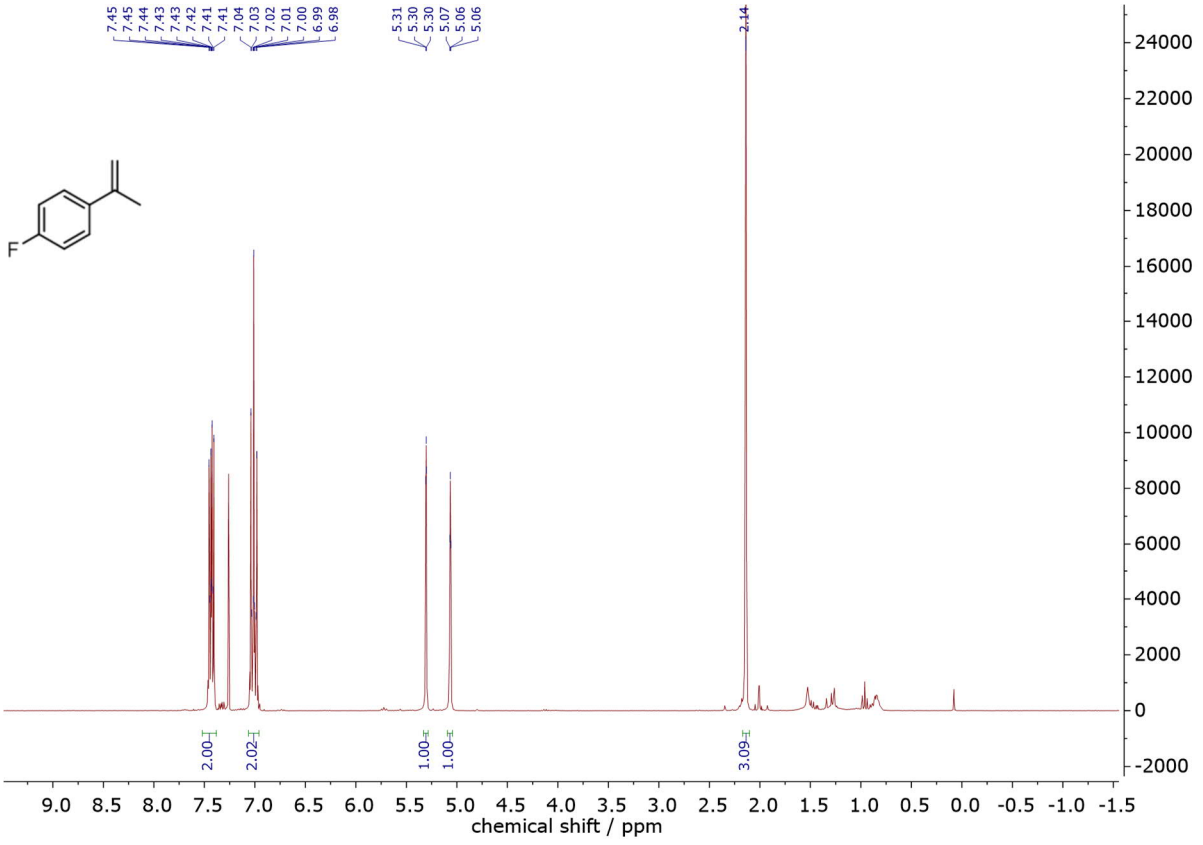
^{13}C DEPT135 {H} (75 MHz, $CDCl_3$) of 4-trifluoromethyl-α-methylstyrene:



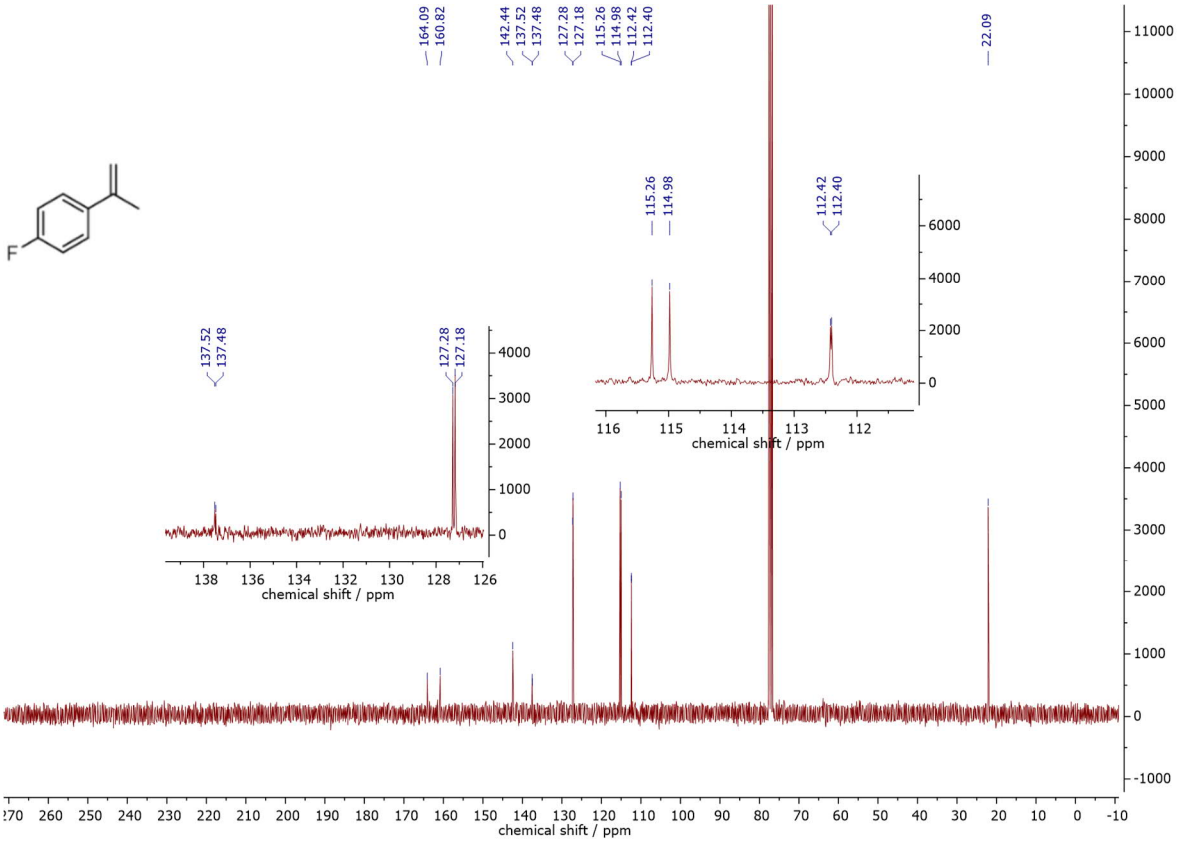
^{19}F (282 MHz, $CDCl_3$) of 4-trifluoromethyl-α-methylstyrene:



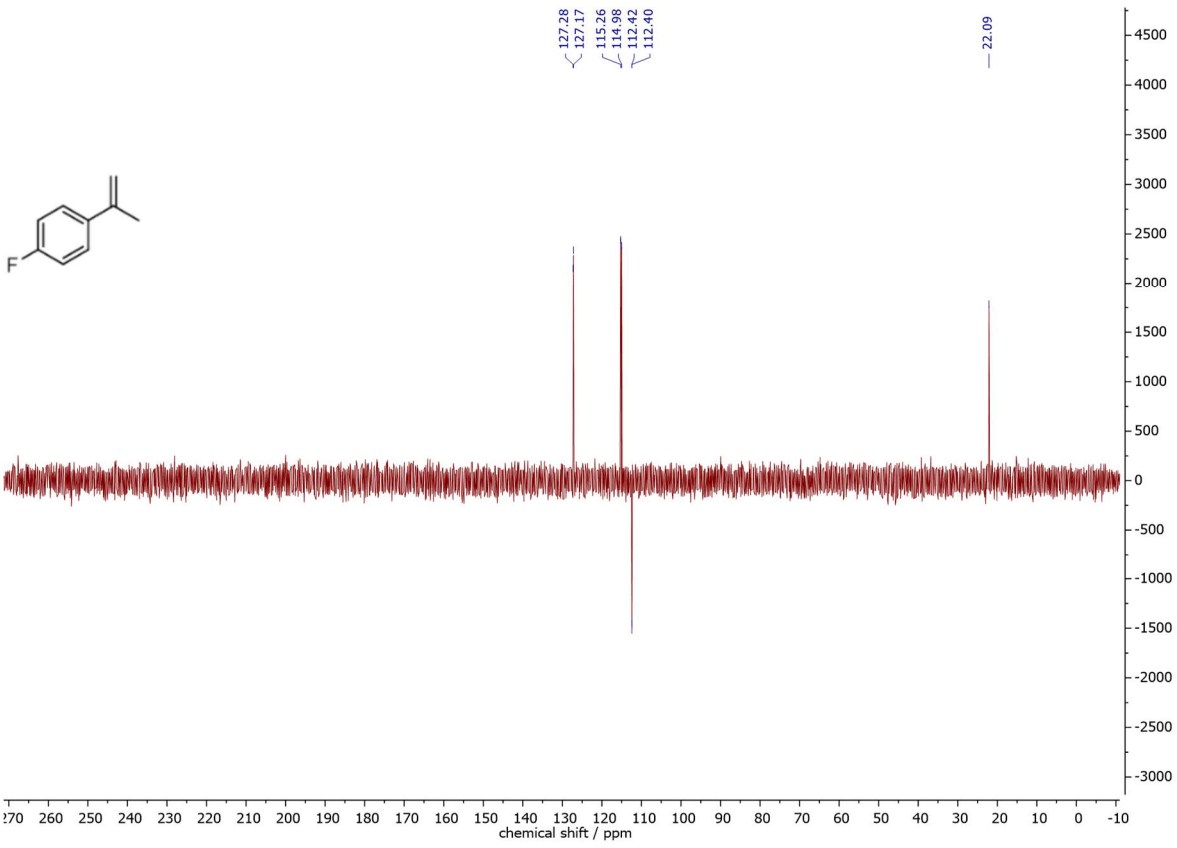
^{1}H (300 MHz, $CDCl_3$) of 4-fluoro-α-methylstyrene:



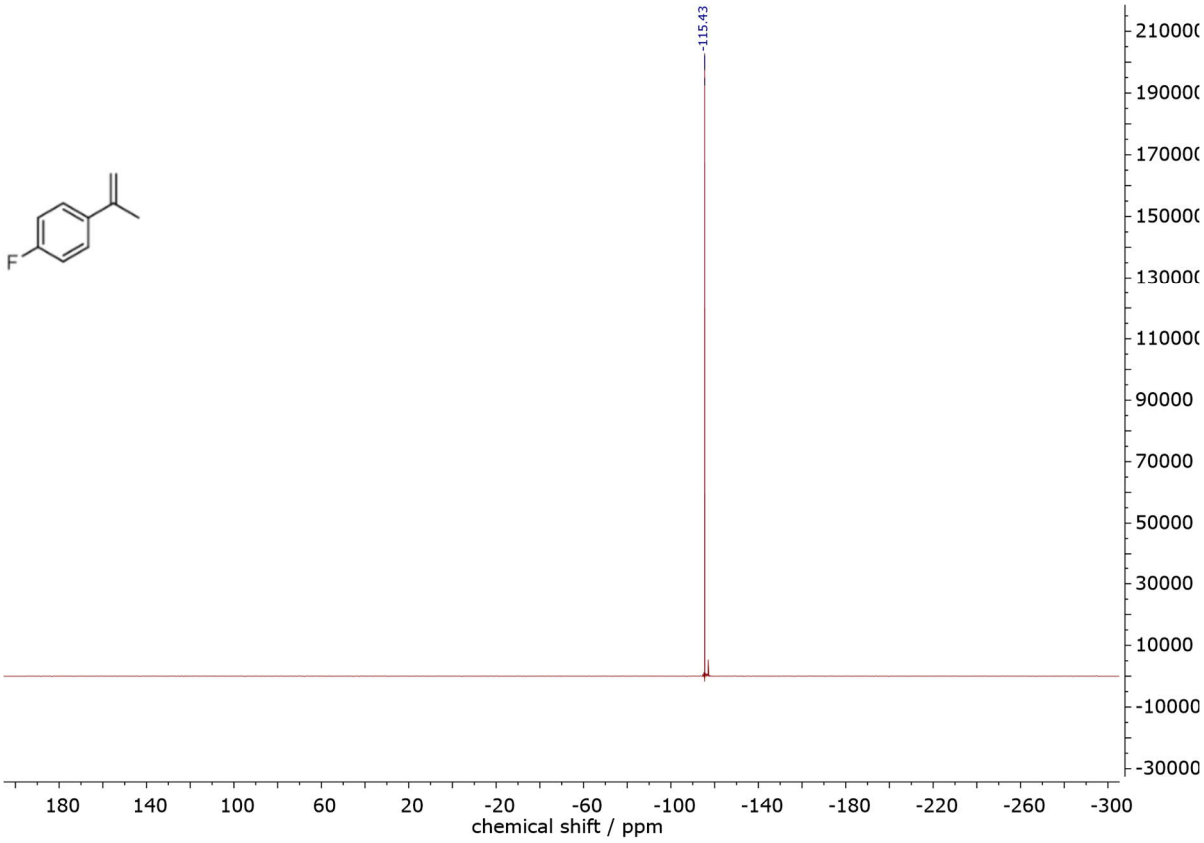
^{13}C {H} (75 MHz, $CDCl_3$) of 4-fluoro-α-methylstyrene:



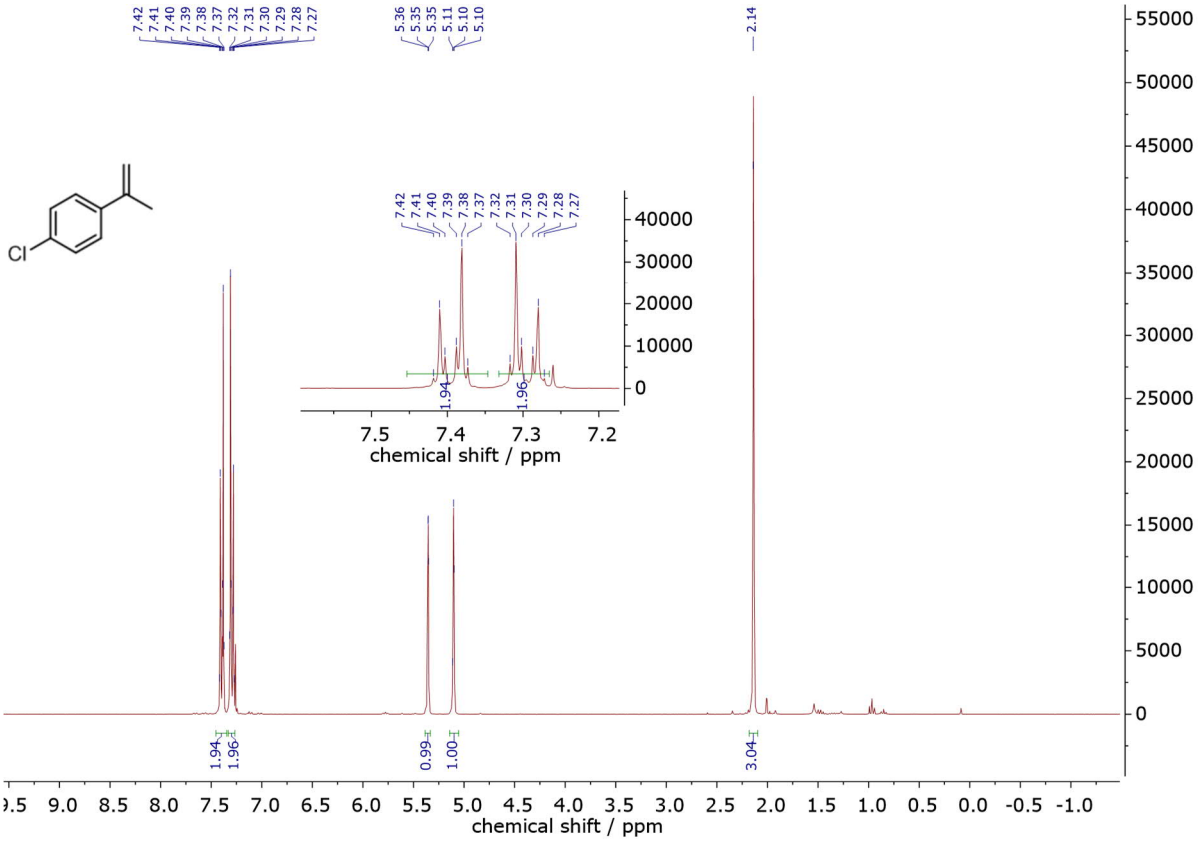
^{13}C DEPT135 {H} (75 MHz, $CDCl_3$) of 4-fluoro-α-methylstyrene:



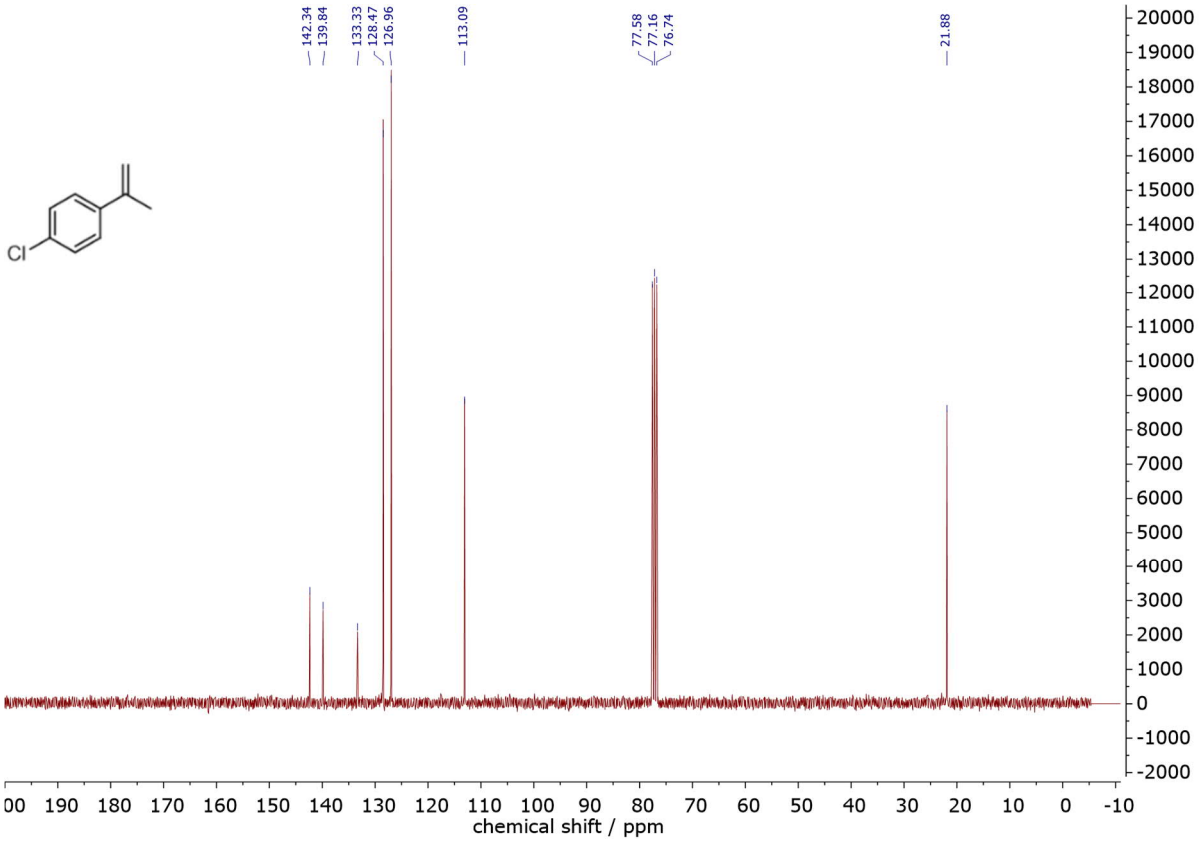
^{19}F (282 MHz, $CDCl_3$) of 4-fluoro-α-methylstyrene:



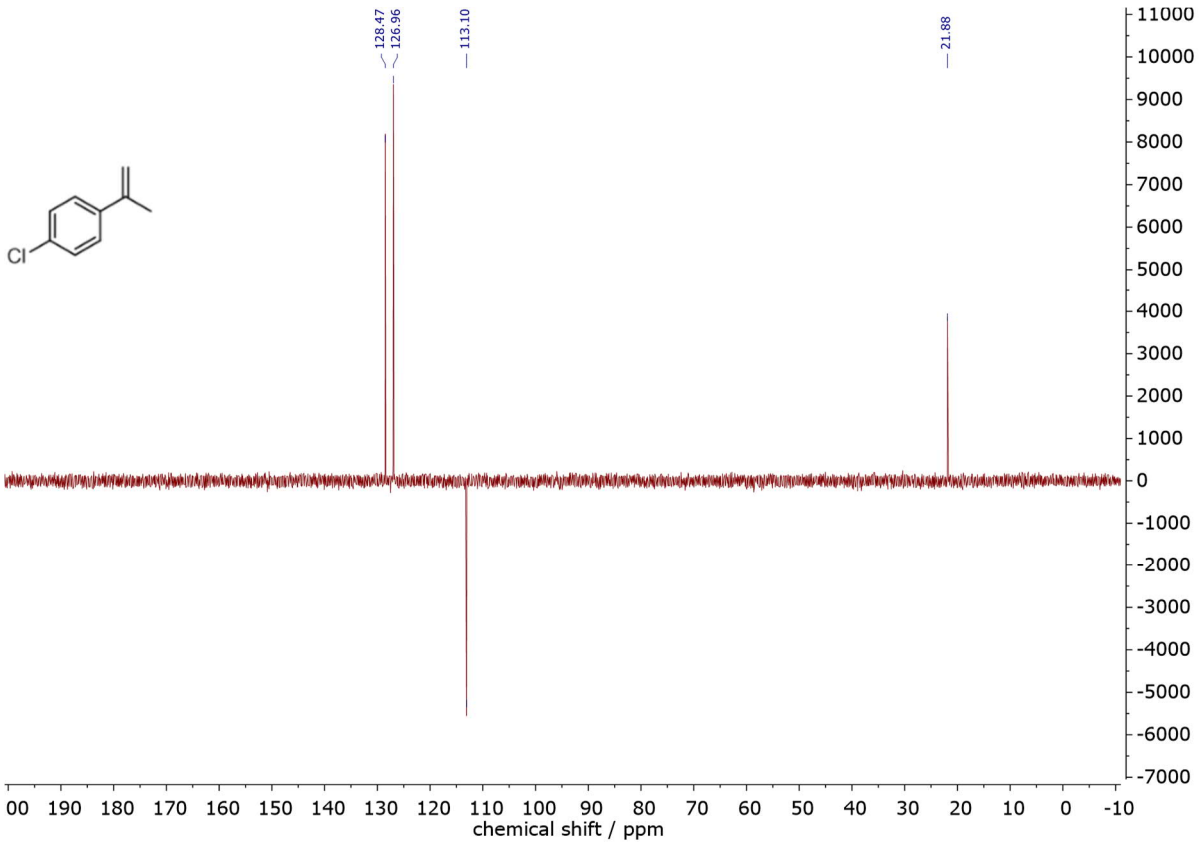
^{1}H (300 MHz, $CDCl_3$) of 4-chloro-α-methylstyrene:



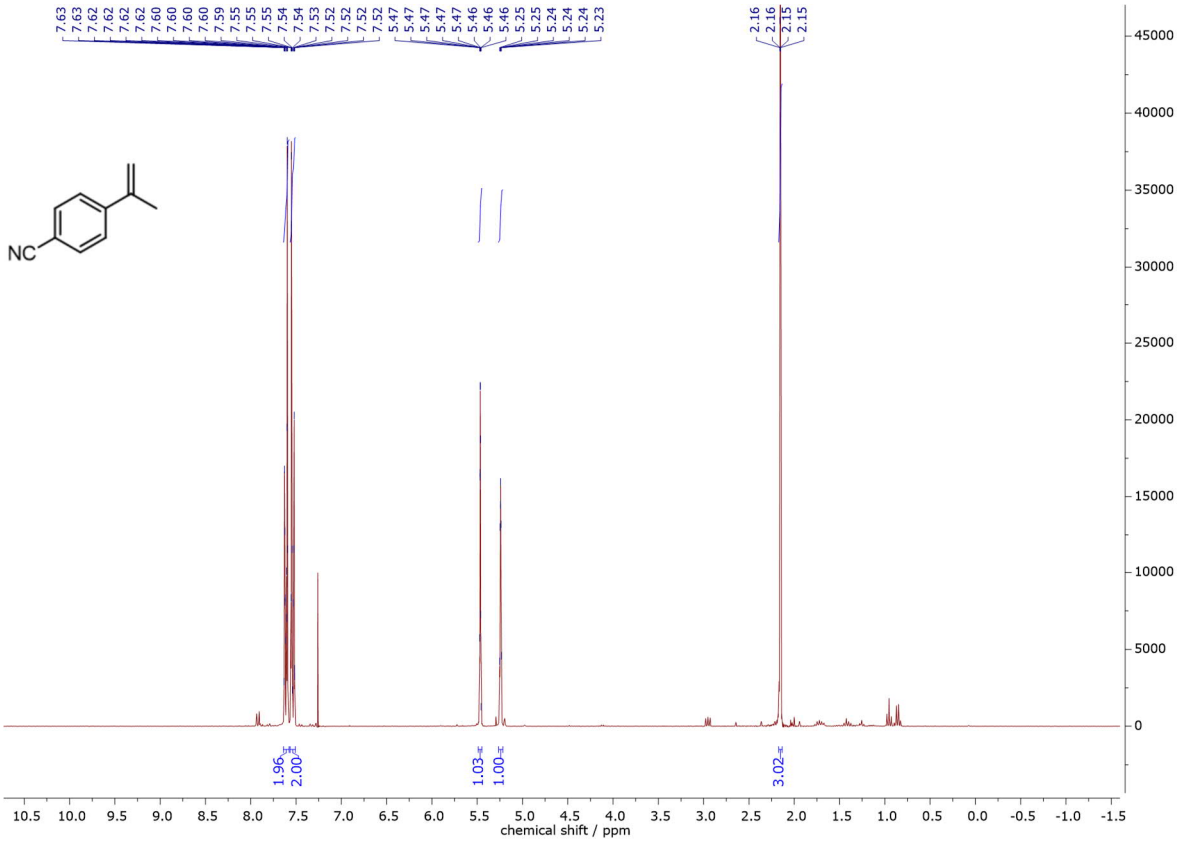
^{13}C {H} (75 MHz, $CDCl_3$) of 4-chloro-α-methylstyrene:



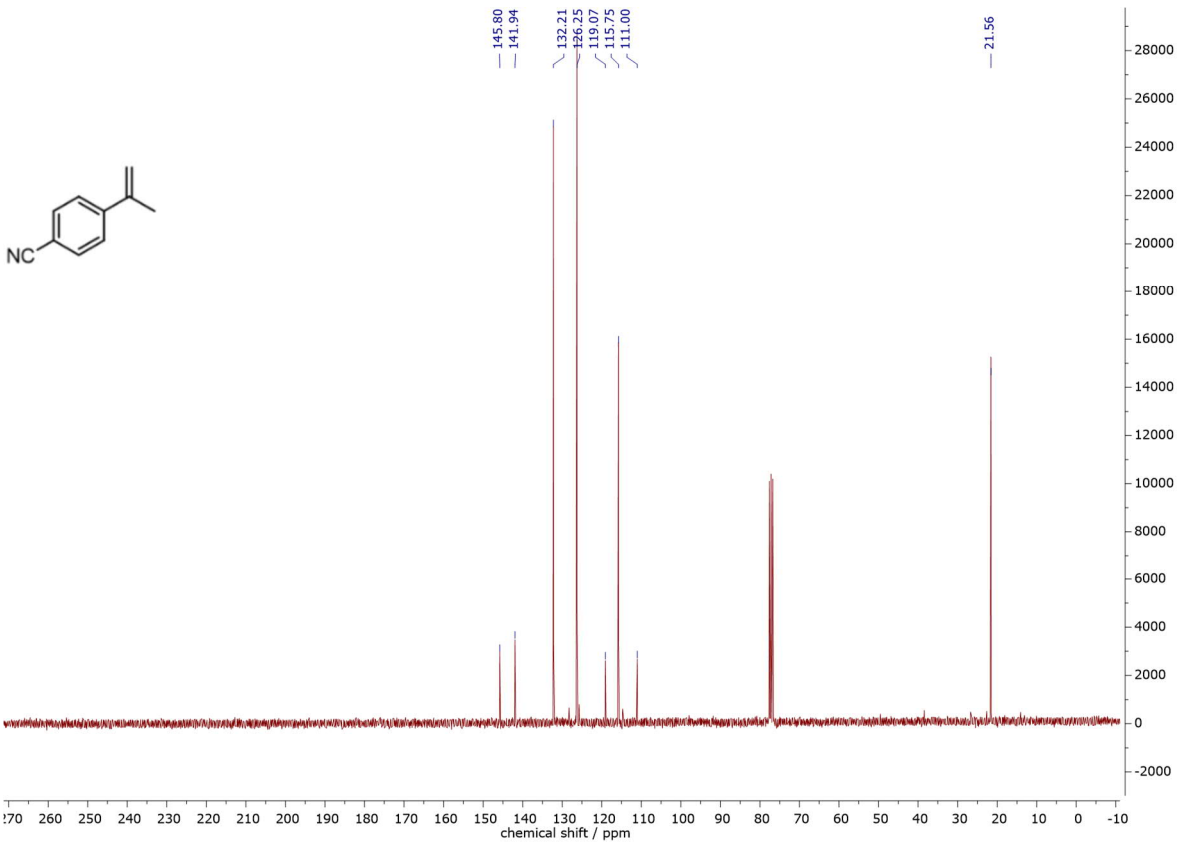
^{13}C DEPT135 {H} (75 MHz, $CDCl_3$) of 4-chloro-α-methylstyrene:



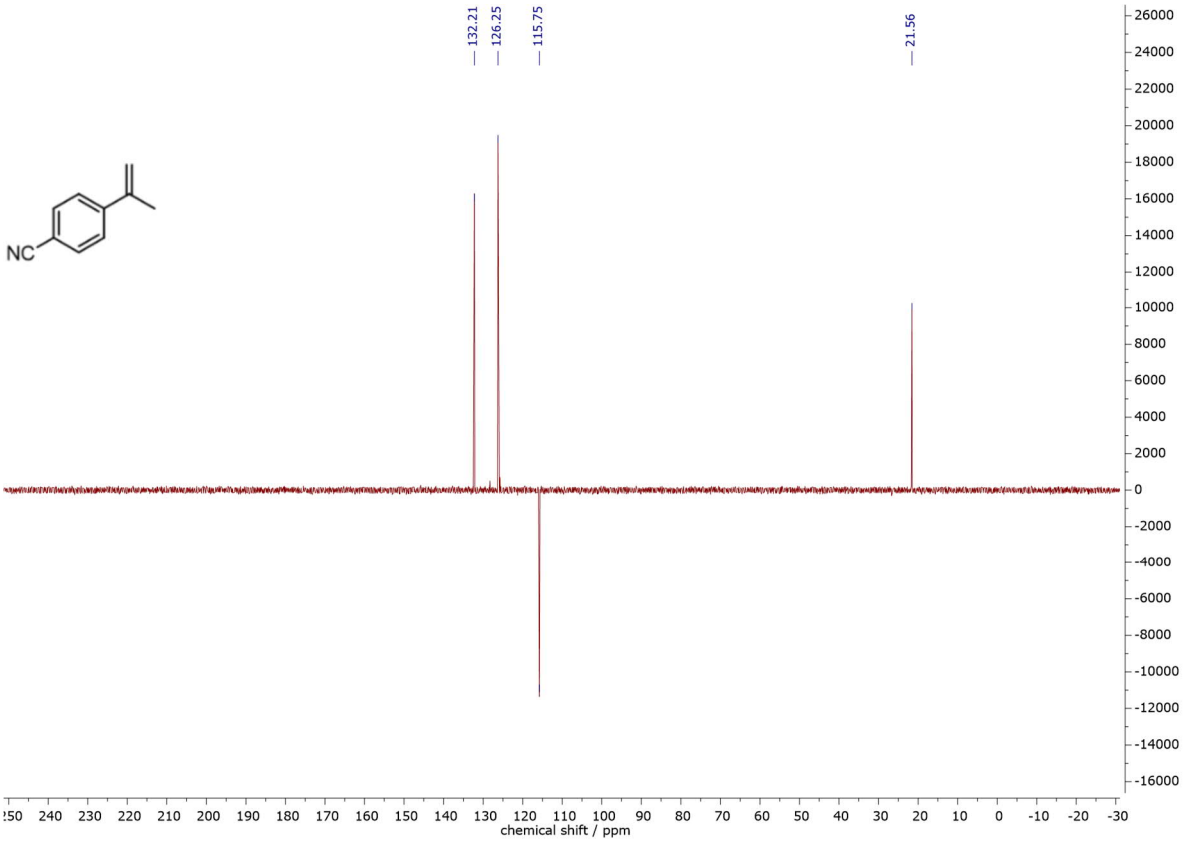
^{1}H (300 MHz, $CDCl_3$) of 4-cyano-α-methylstyrene:



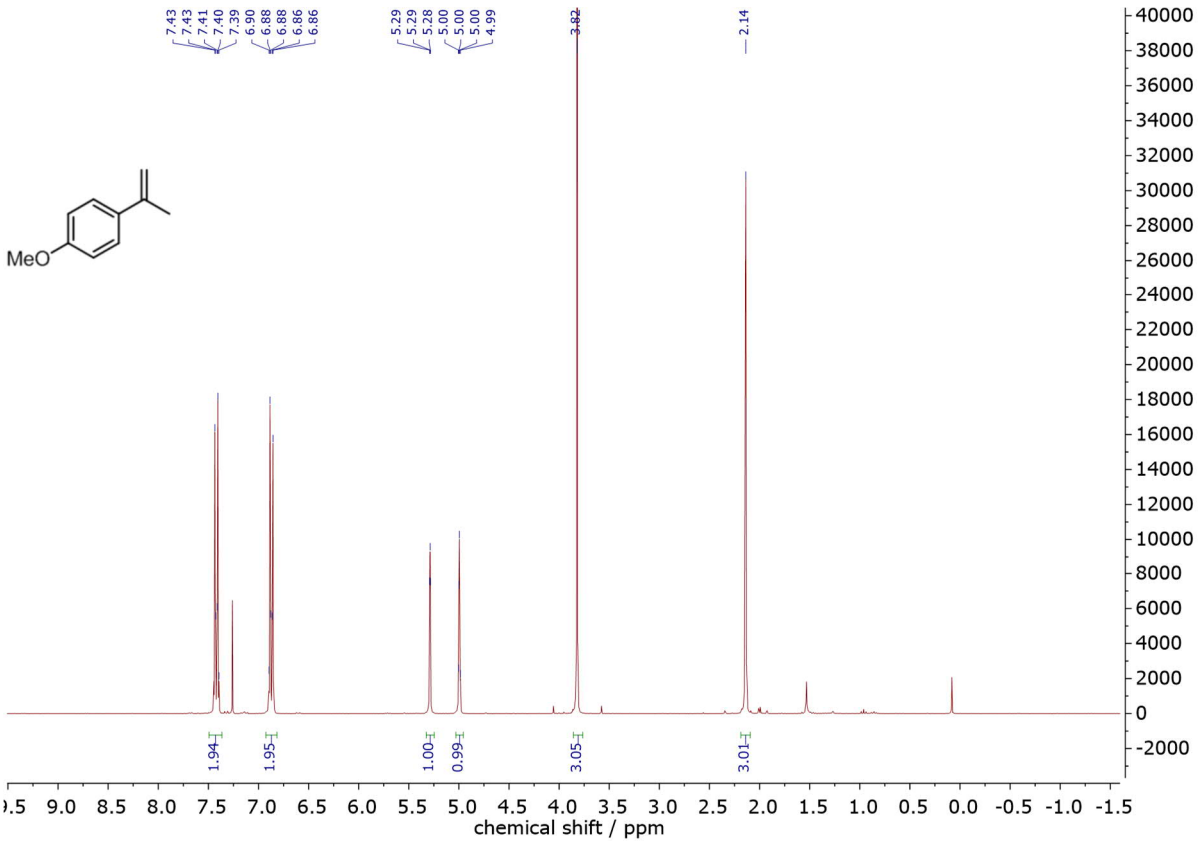
^{13}C {H} (75 MHz, $CDCl_3$) of 4-cyano-α-methylstyrene:



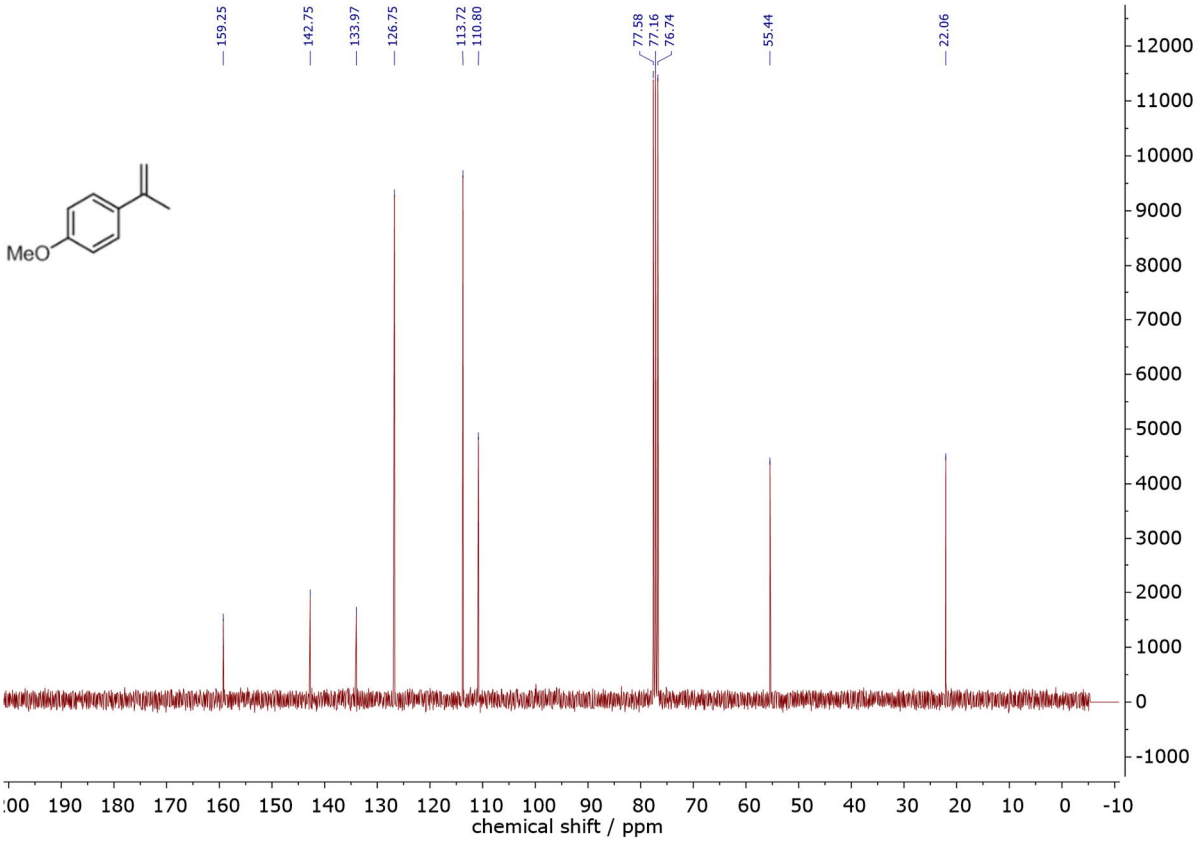
^{13}C DEPT135 {H} (75 MHz, $CDCl_3$) of 4-cyano-α-methylstyrene:



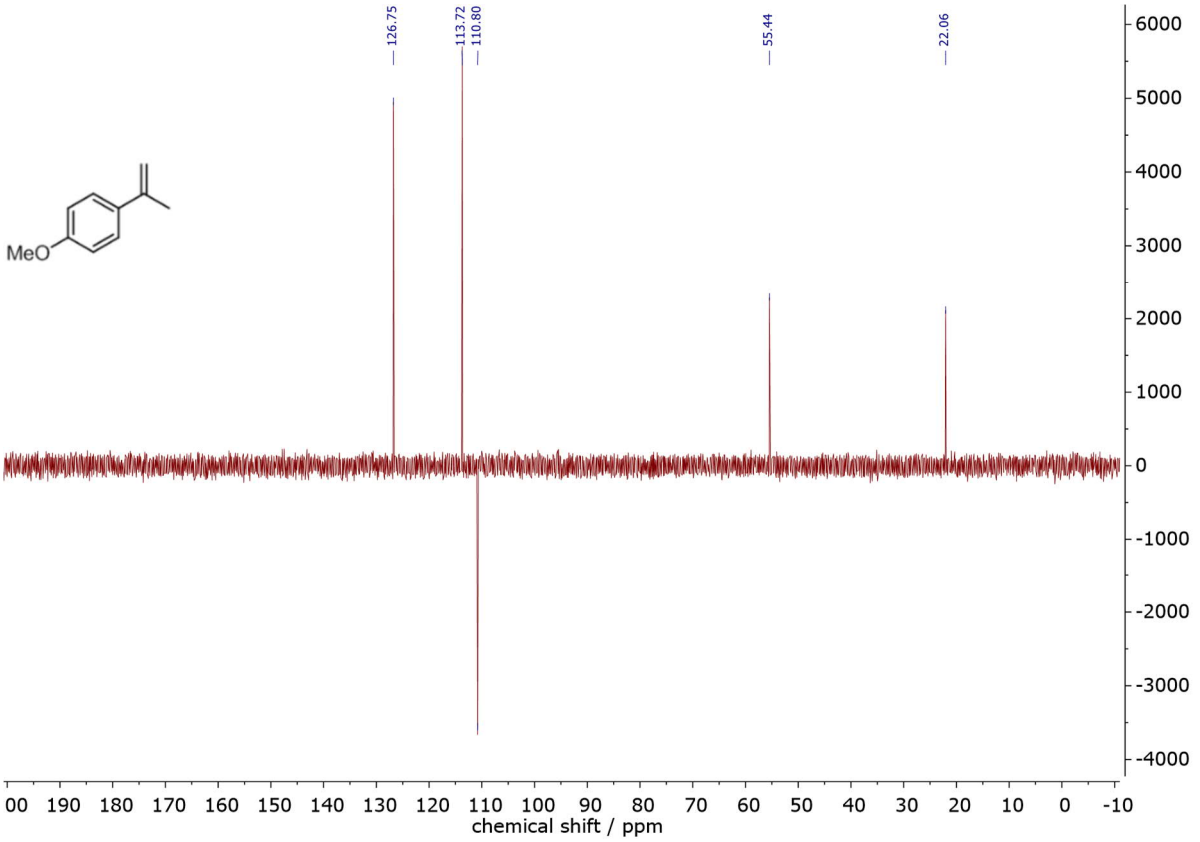
^{1}H (300 MHz, $CDCl_3$) of 4-methoxy-α-methylstyrene:



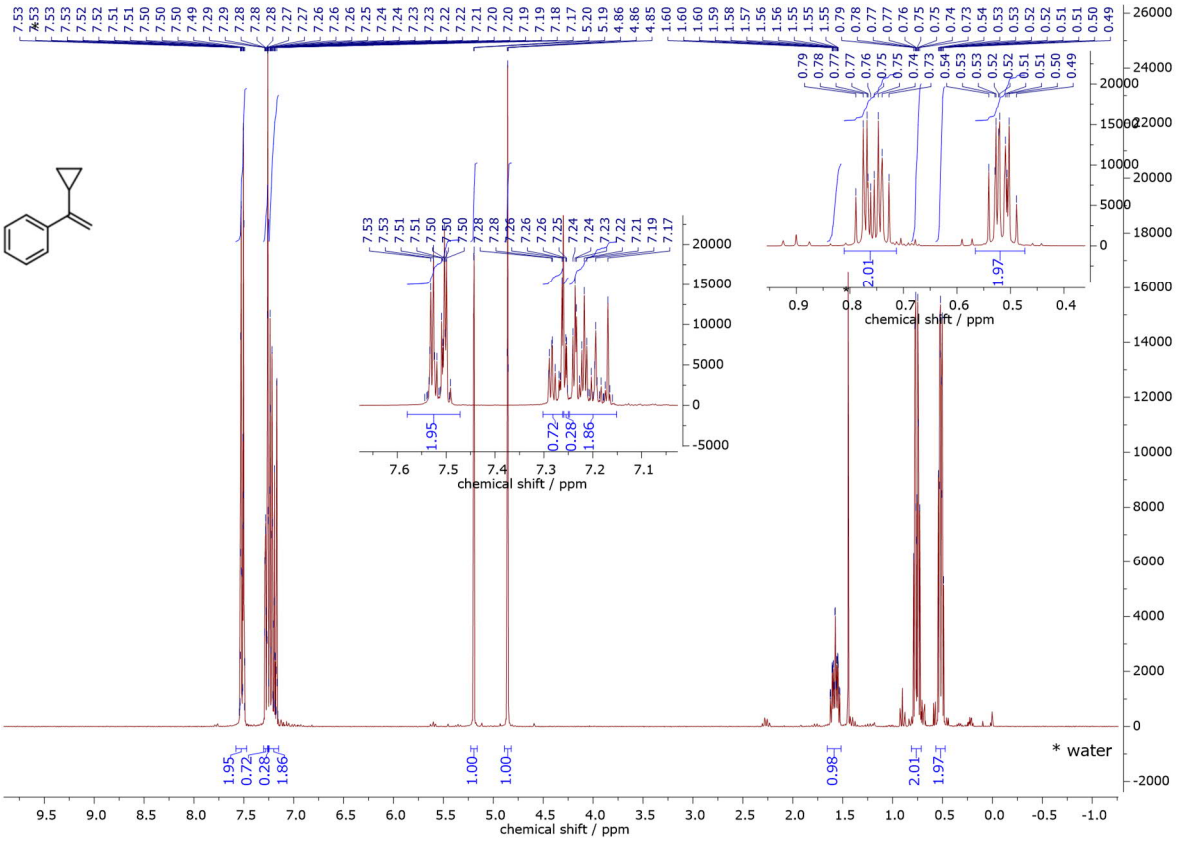
^{13}C {H} (75 MHz, $CDCl_3$) of 4-methoxy-α-methylstyrene:



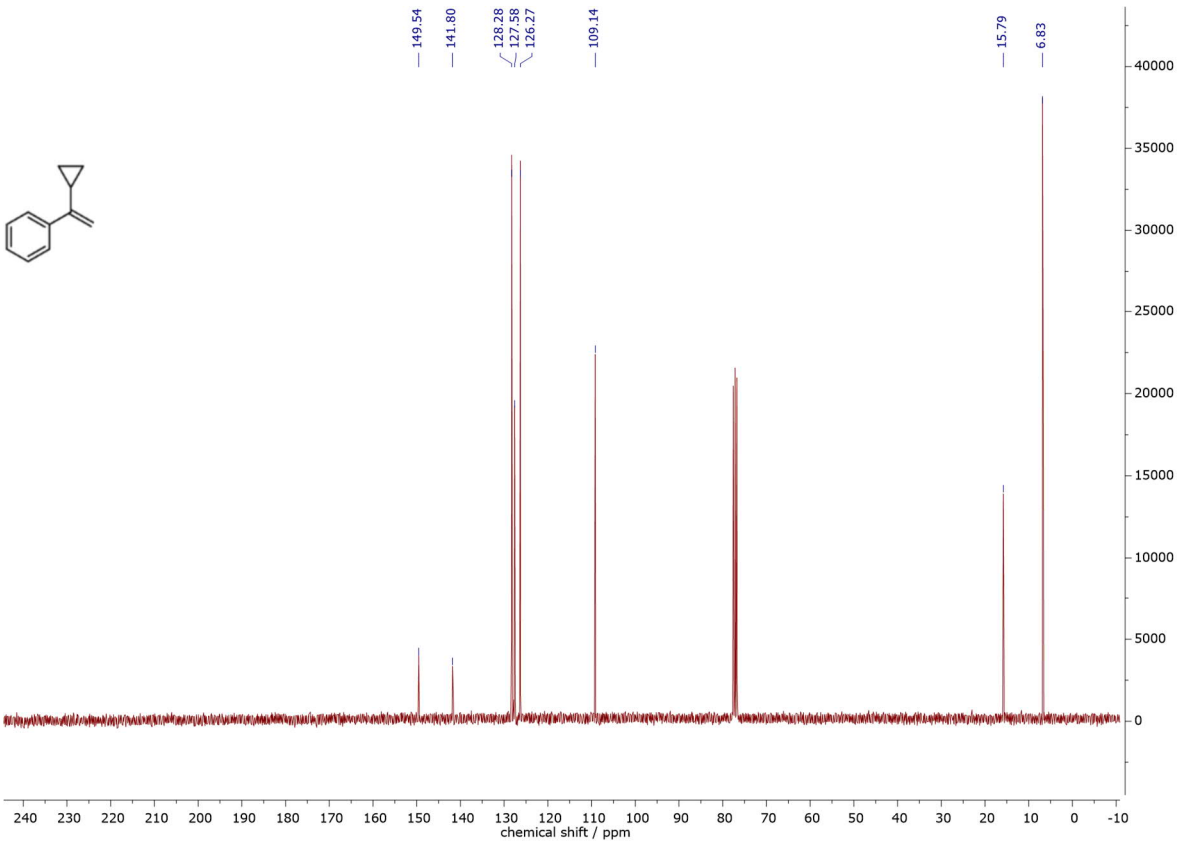
^{13}C DEPT135 {H} (75 MHz, $CDCl_3$) of 4-methoxy-α-methylstyrene:



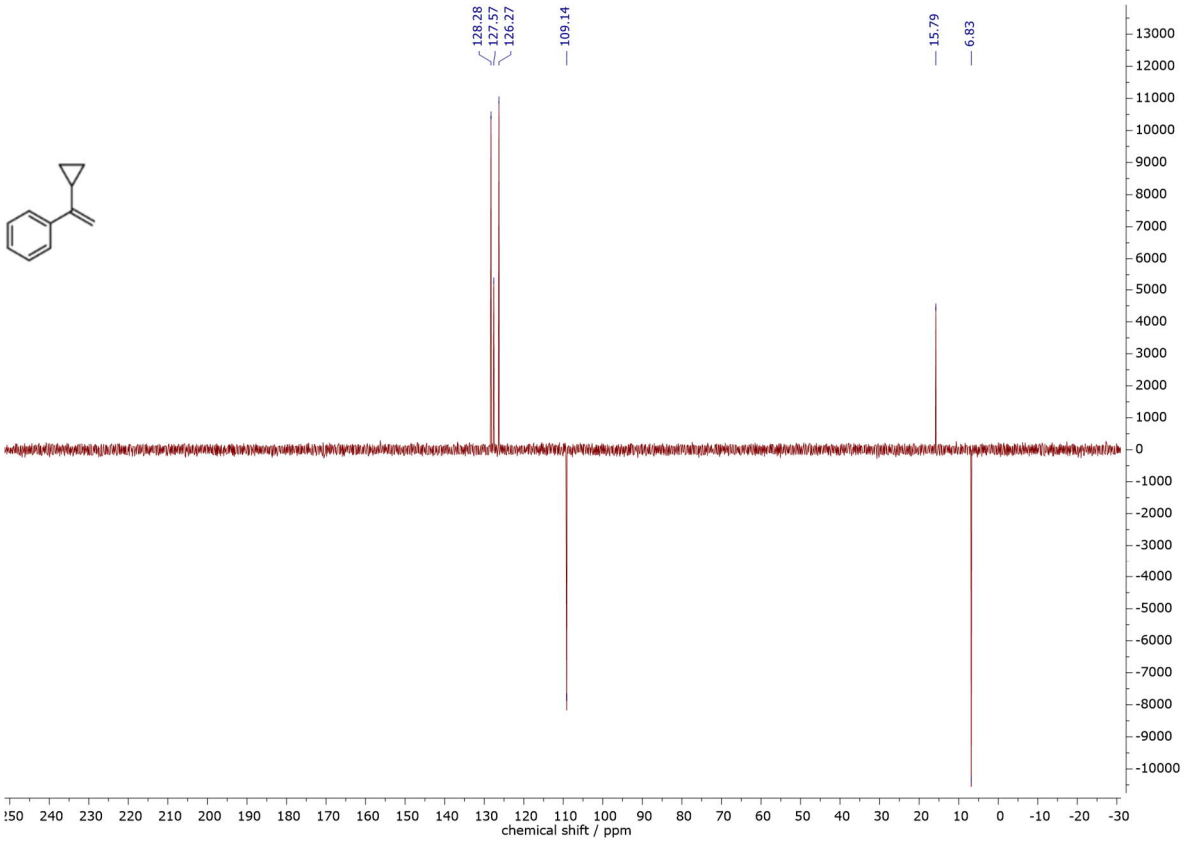
^{1}H (300 MHz, $CDCl_3$) of α-cyclopropylstyrene:



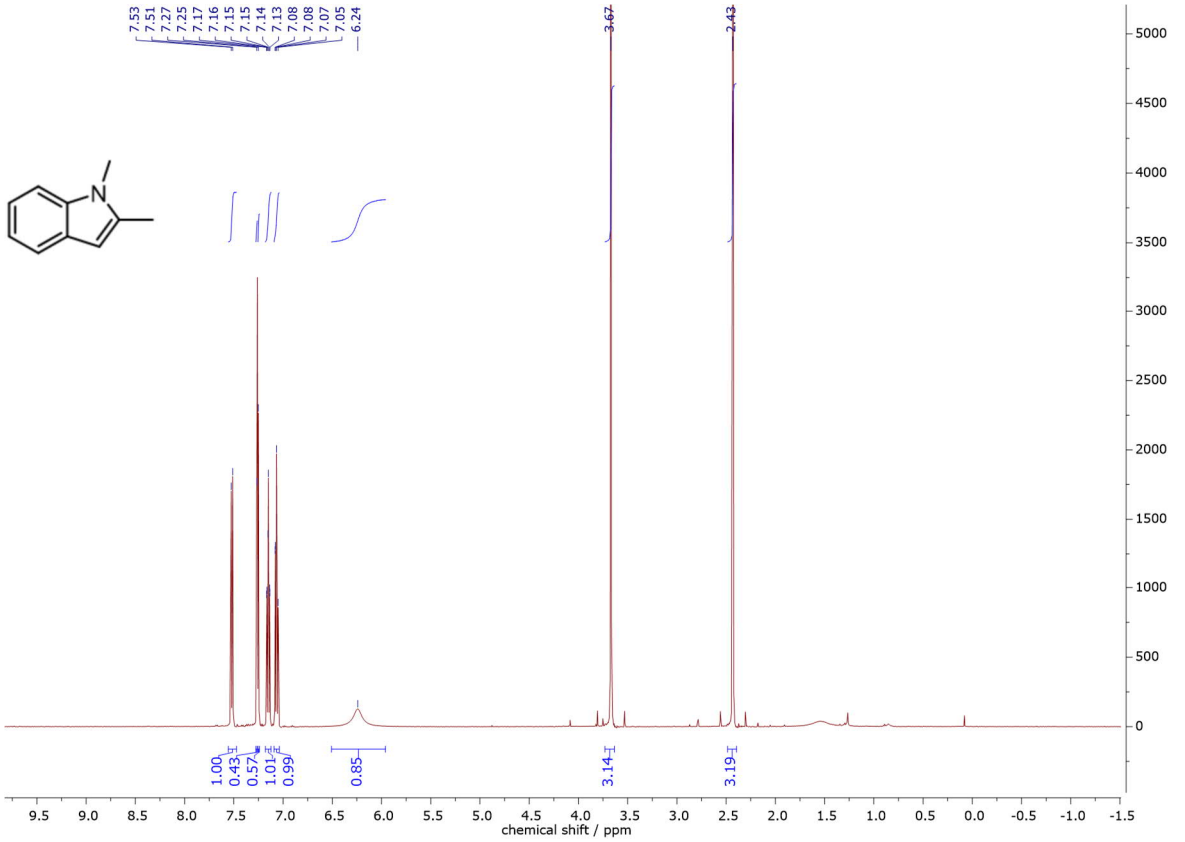
^{13}C {H} (75 MHz, $CDCl_3$) of α-cyclopropylstyrene:



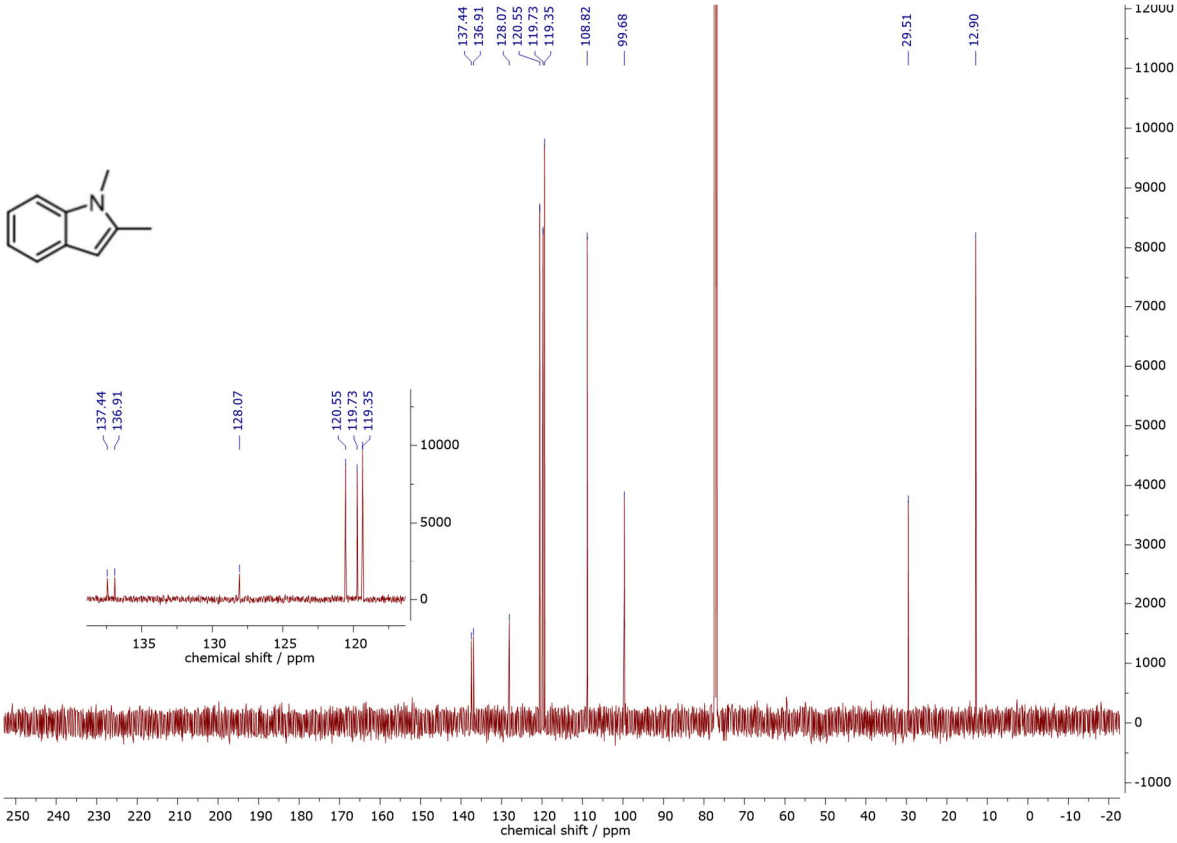
^{13}C DEPT135 {H} (75 MHz, $CDCl_3$) of α-cyclopropylstyrene:



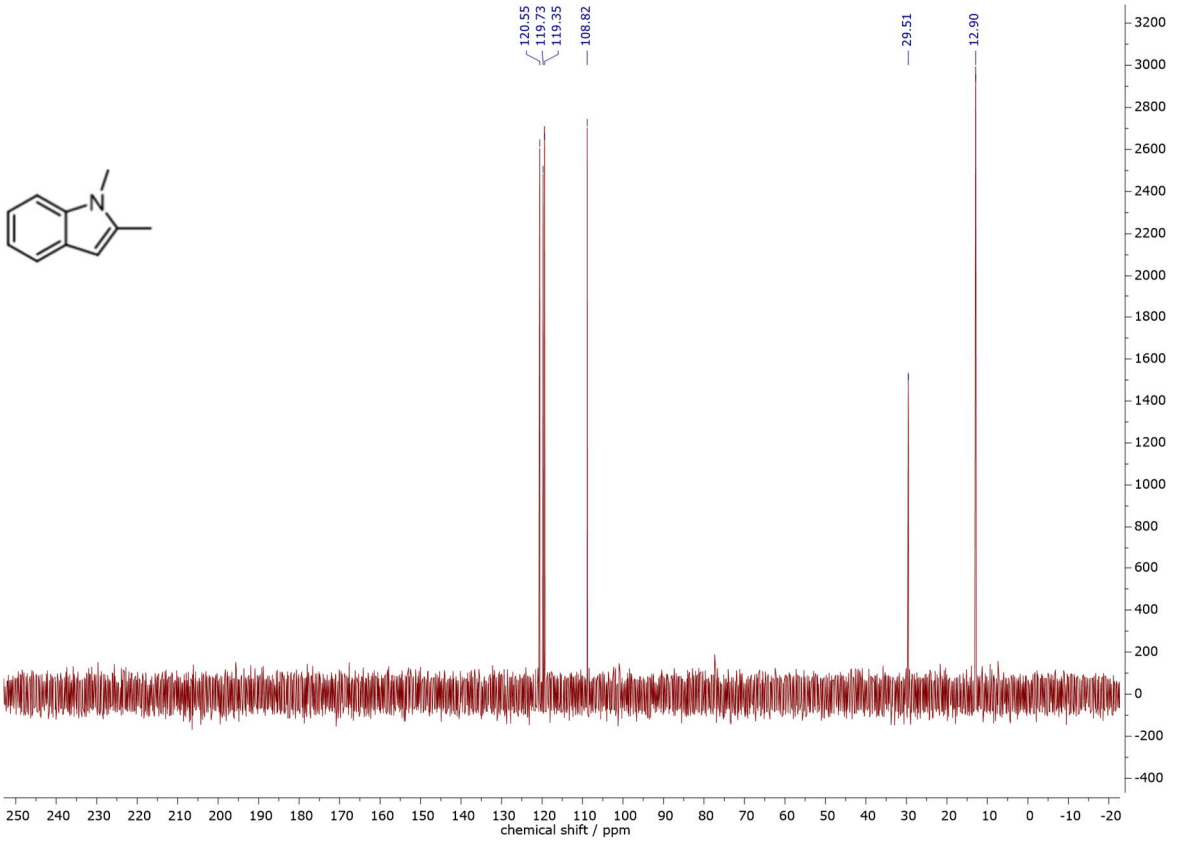
^{1}H (501 MHz, $CDCl_3$) of 1,2-dimethylindole:



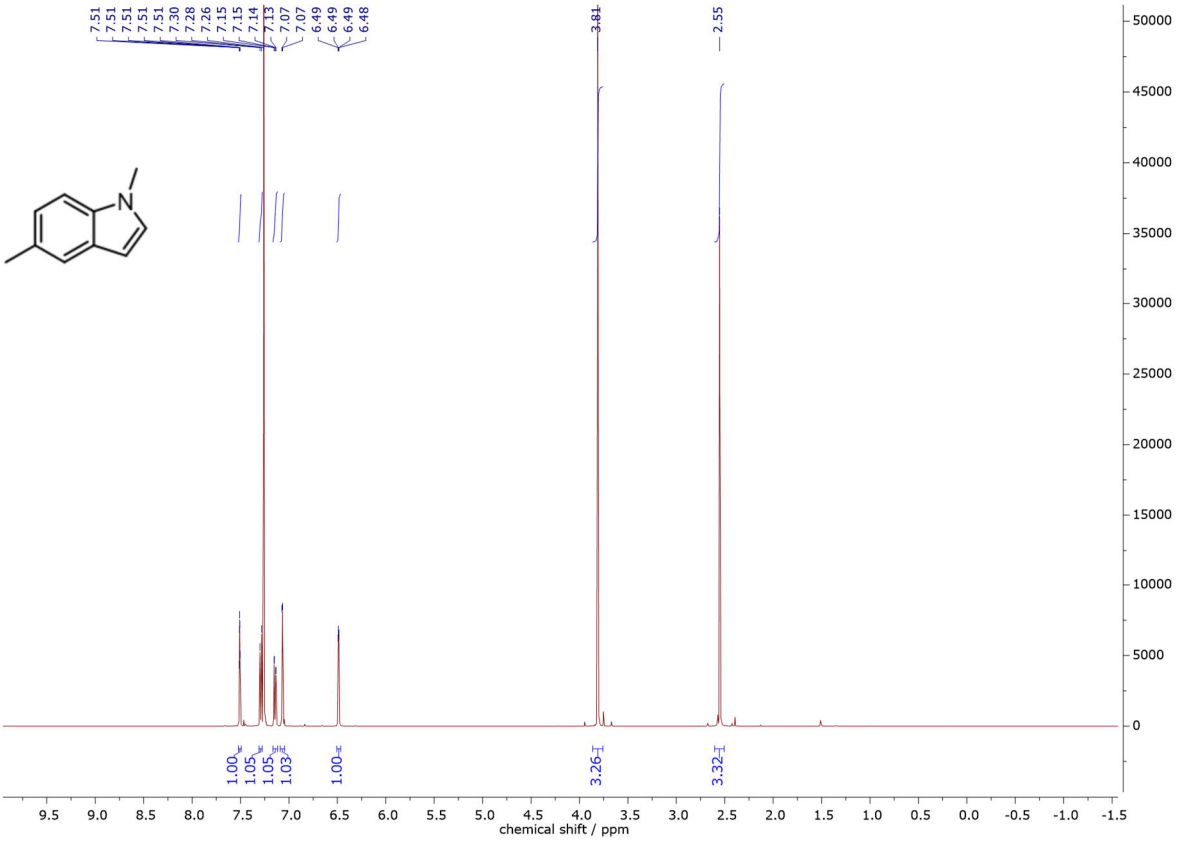
^{13}C {H} (126 MHz, $CDCl_3$) of 1,2-dimethylindole:



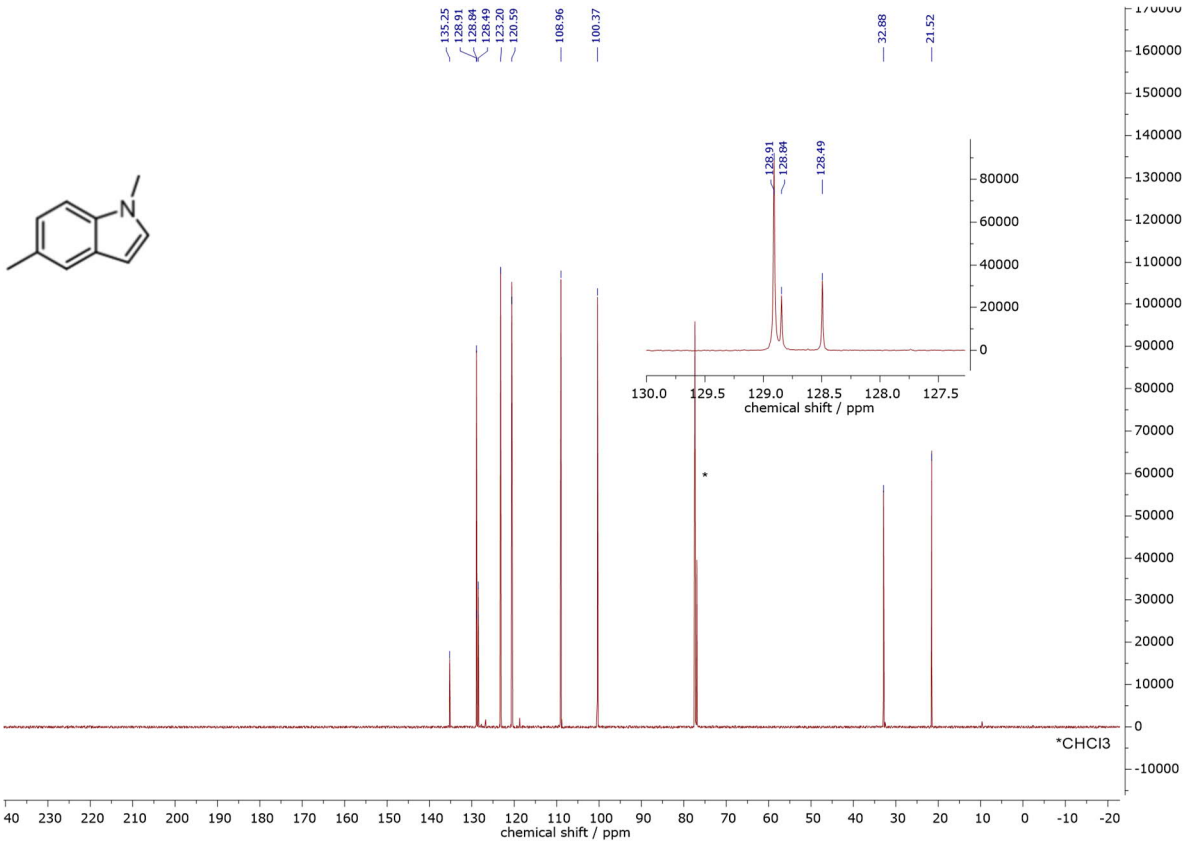
^{13}C DEPT135 {H} (126 MHz, $CDCl_3$) of 1,2-dimethylindole:



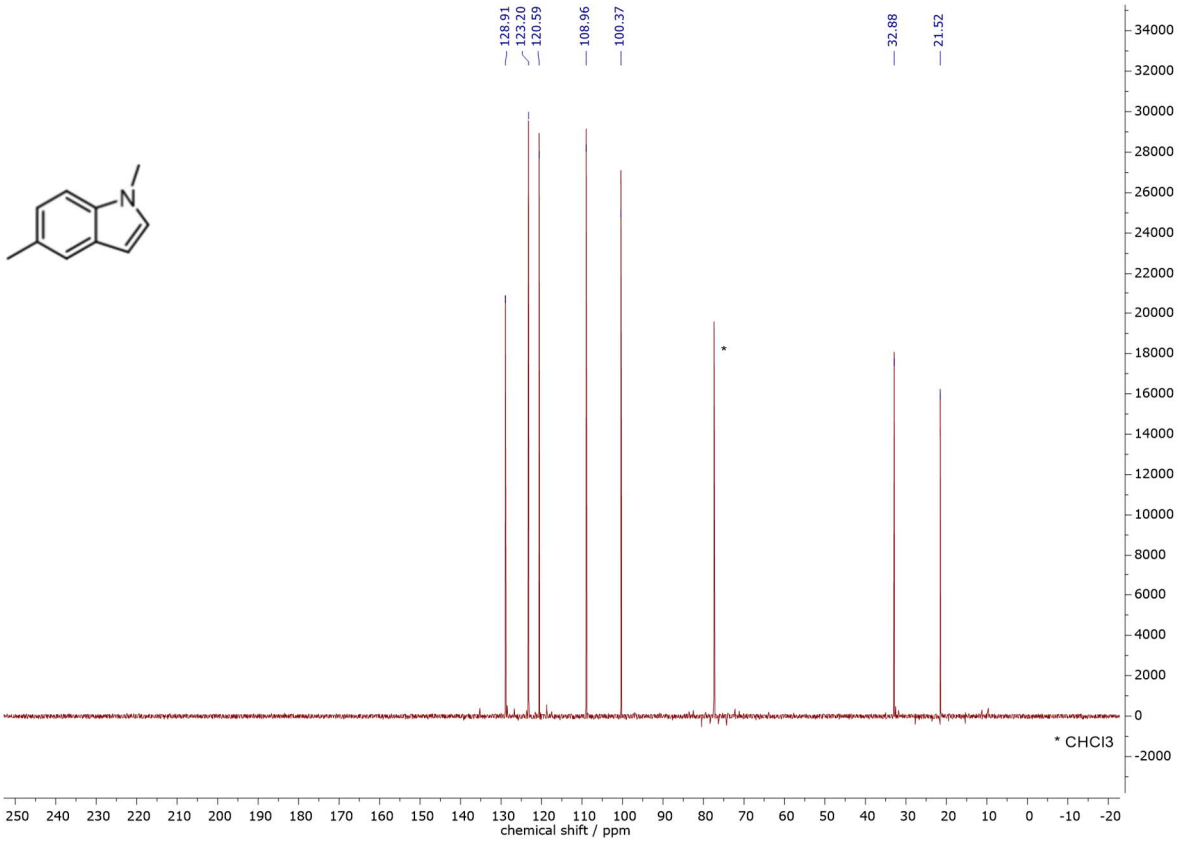
^{1}H (501 MHz, $CDCl_3$) of 1,5-dimethylindole:



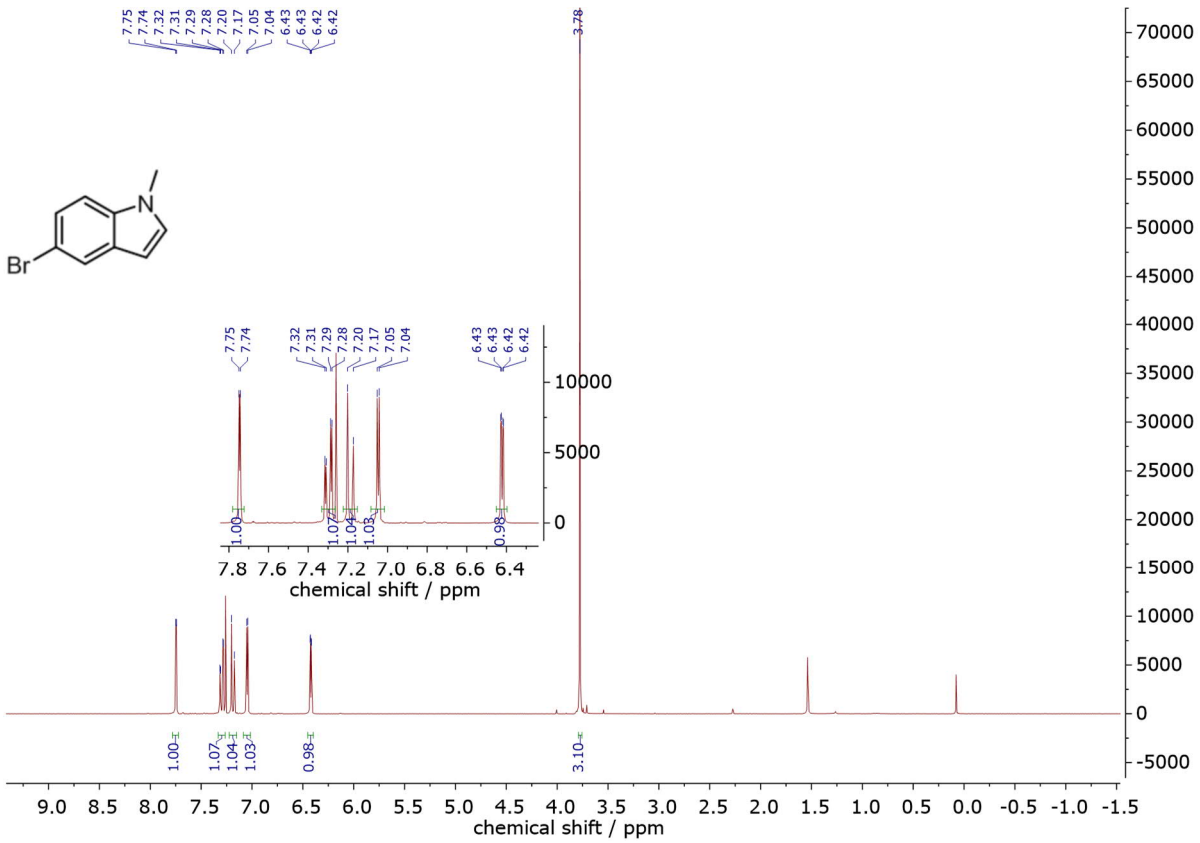
^{13}C {H} (126 MHz, $CDCl_3$) of 1,5-dimethylindole:



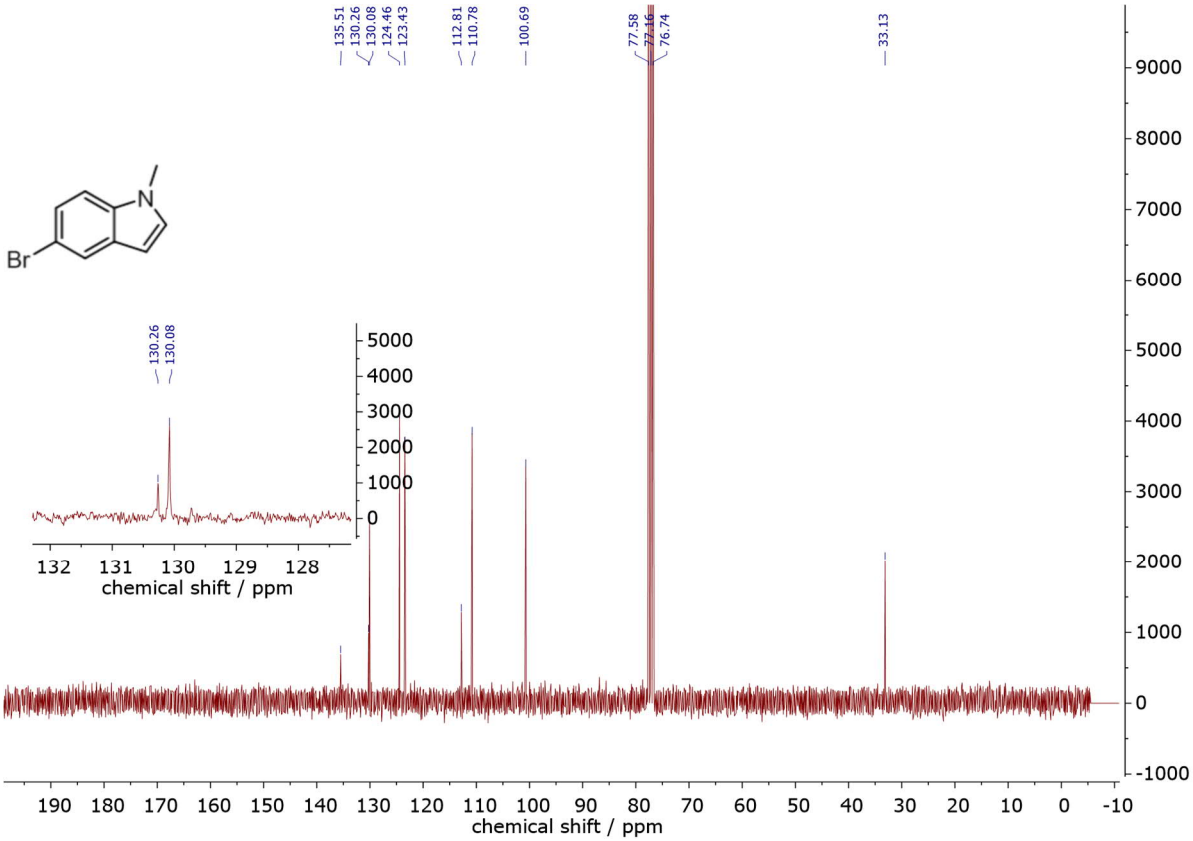
^{13}C DEPT135 {H} (126 MHz, $CDCl_3$) of 1,5-dimethylindole:



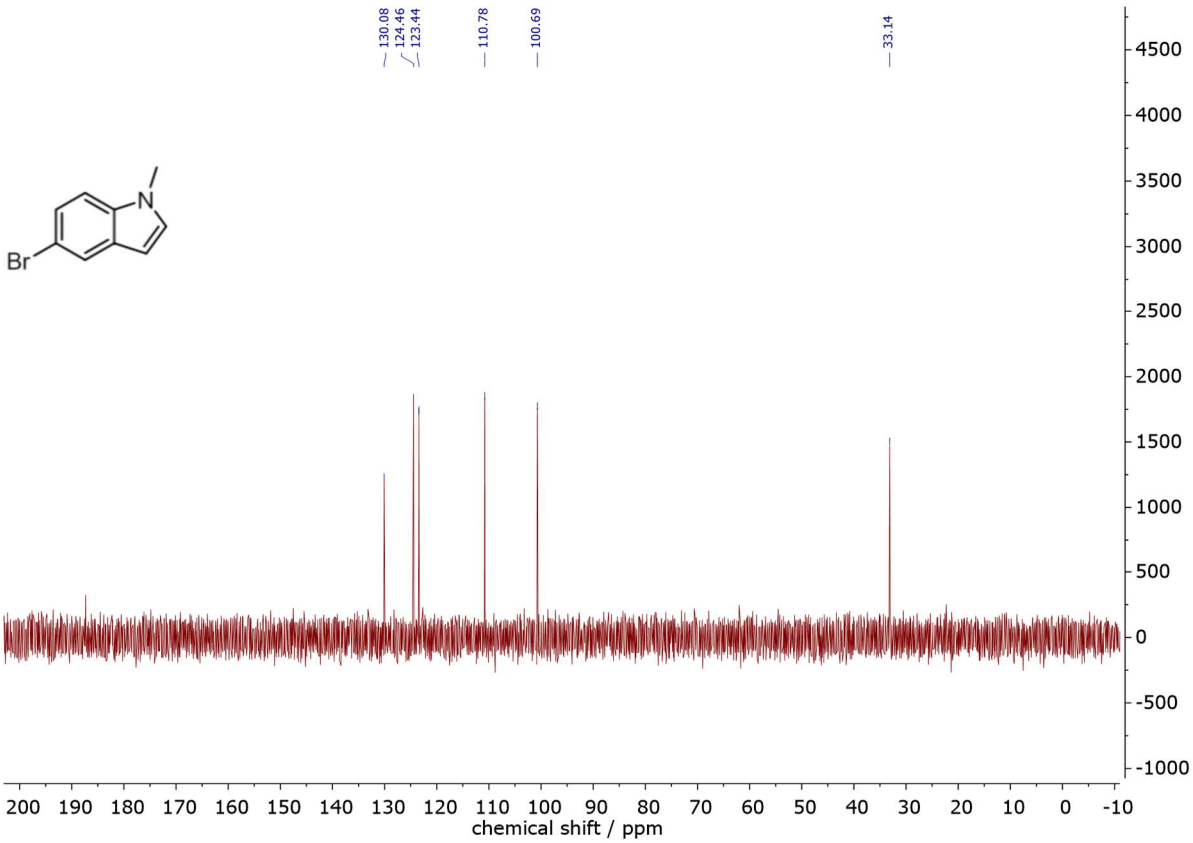
^{1}H (300 MHz, $CDCl_3$) of 5-bromo-1-methylindole:



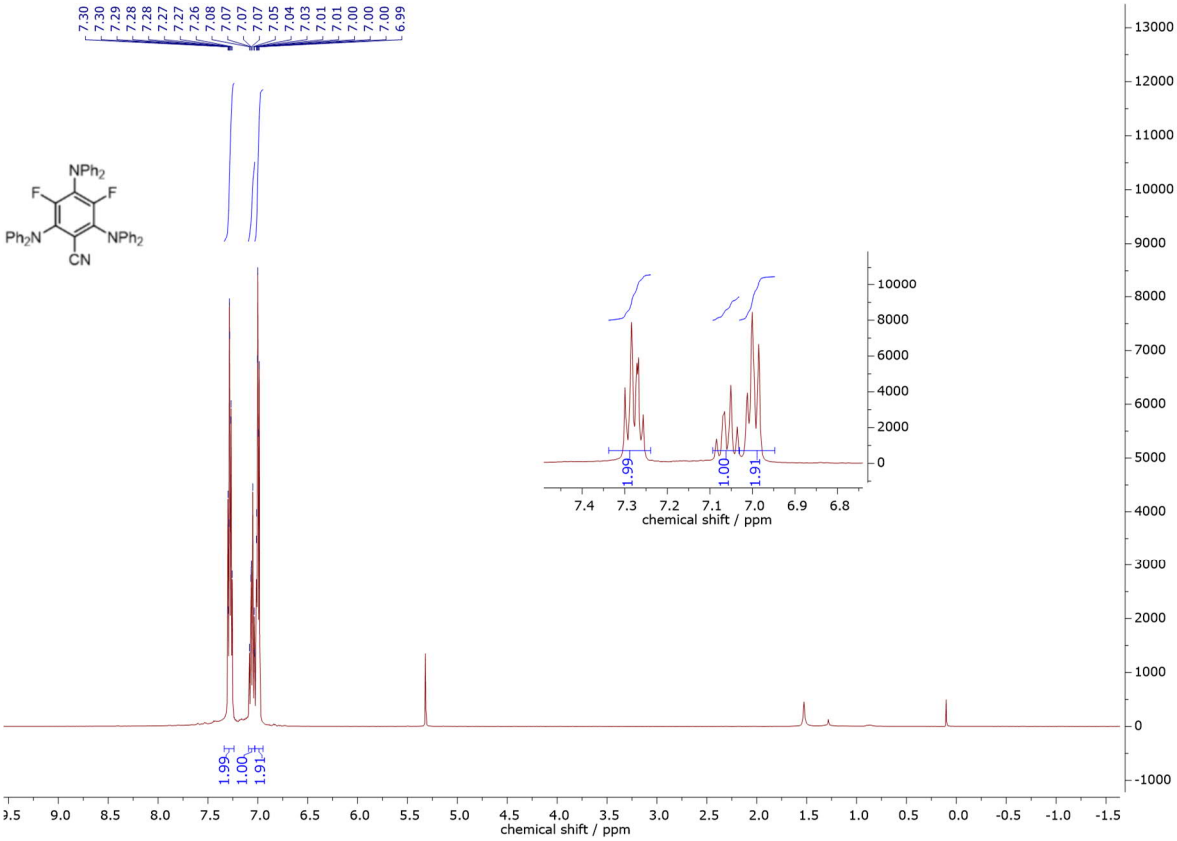
^{13}C {H} (126 MHz, $CDCl_3$) of 5-bromo-1-methylindole:



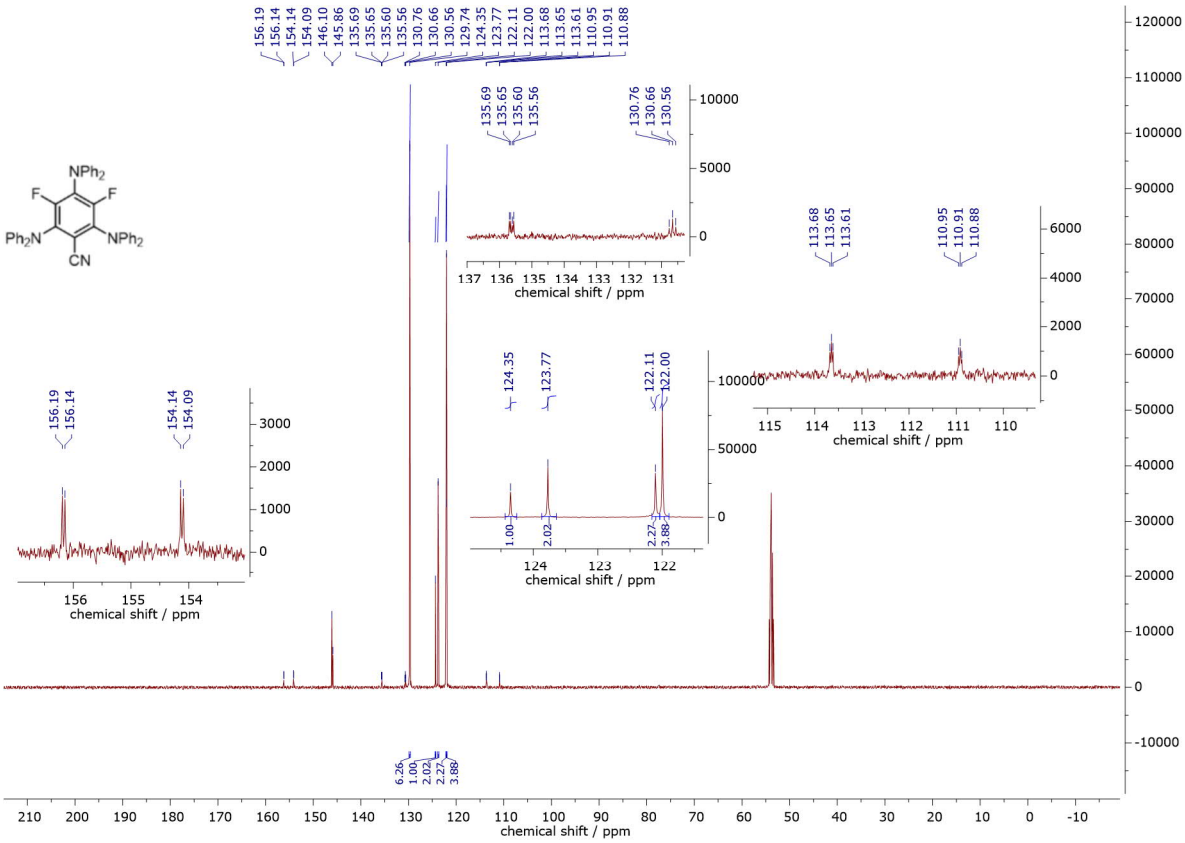
^{13}C DEPT135 {H} (126 MHz, $CDCl_3$) of 5-bromo-1-methylindole:



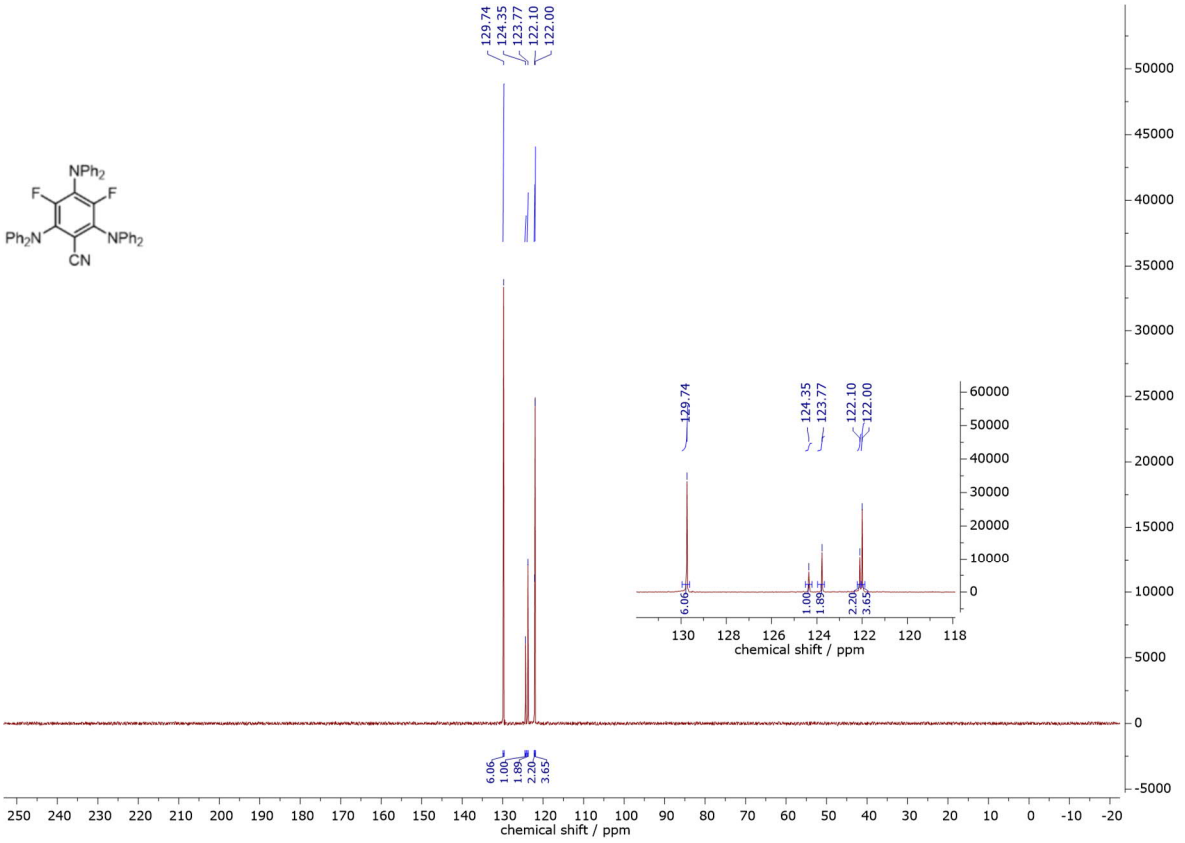
^{1}H (501 MHz, CD_2Cl_2) of 2,4,6-Tris(diphenylamino)-3,5-difluorobenzonitrile (DPA_3F_2BN):



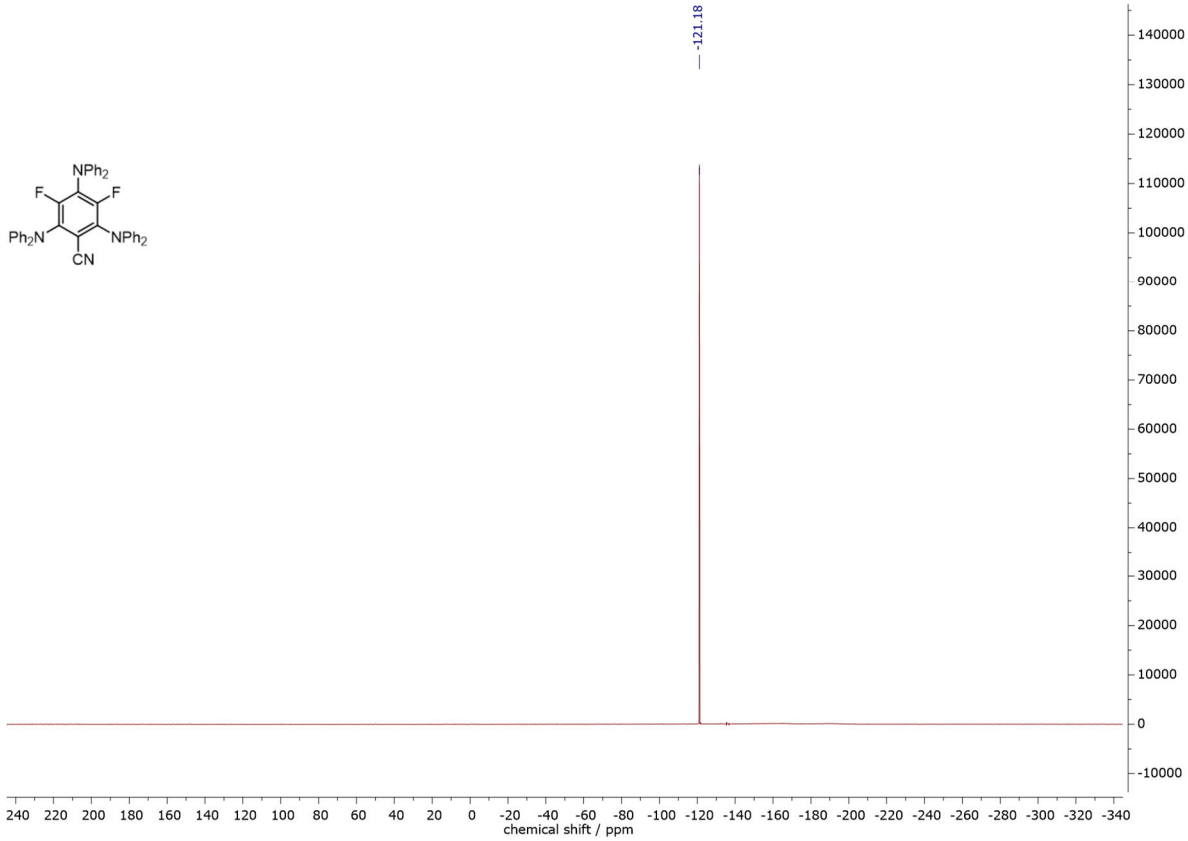
^{13}C {H} (126 MHz, CD_2Cl_2) of 2,4,6-Tris(diphenylamino)-3,5-difluorobenzonitrile (DPA_3F_2BN):



^{13}C DEPT135 {H} (126 MHz, CD_2Cl_2) of 2,4,6-Tris(diphenylamino)-3,5-difluorobenzonitrile (DPA_3F_2BN):

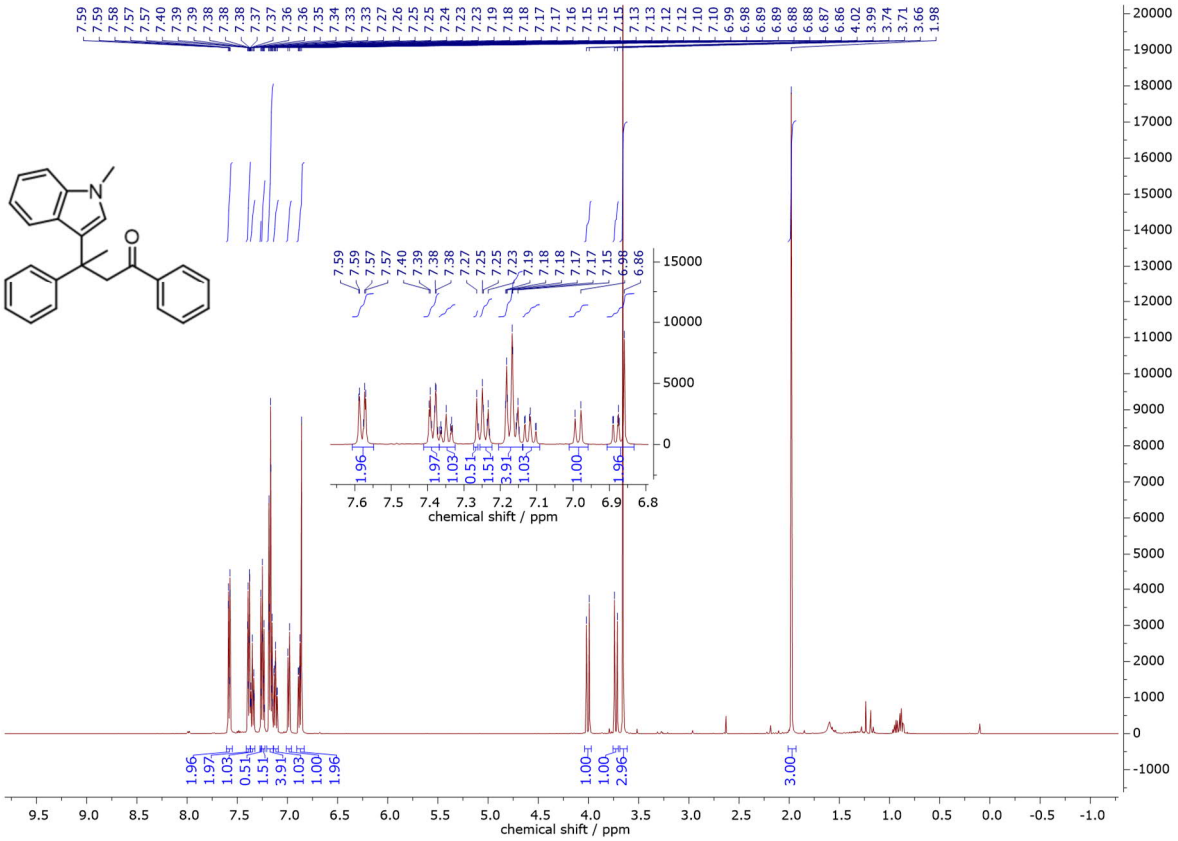


^{19} F (471 MHz, CD_2Cl_2) of 2,4,6-Tris(diphenylamino)-3,5-difluorobenzonitrile (DPA_3F_2BN):

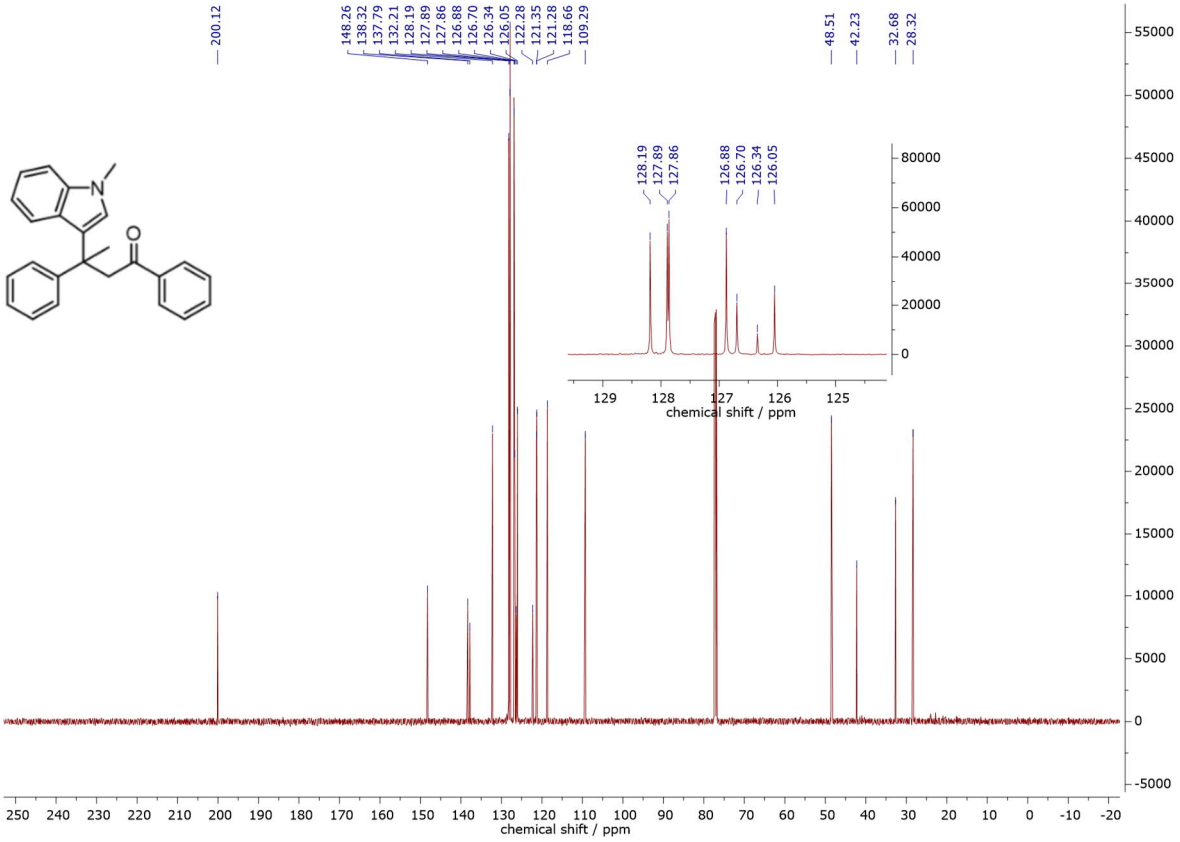


Indole and benzotriazole products

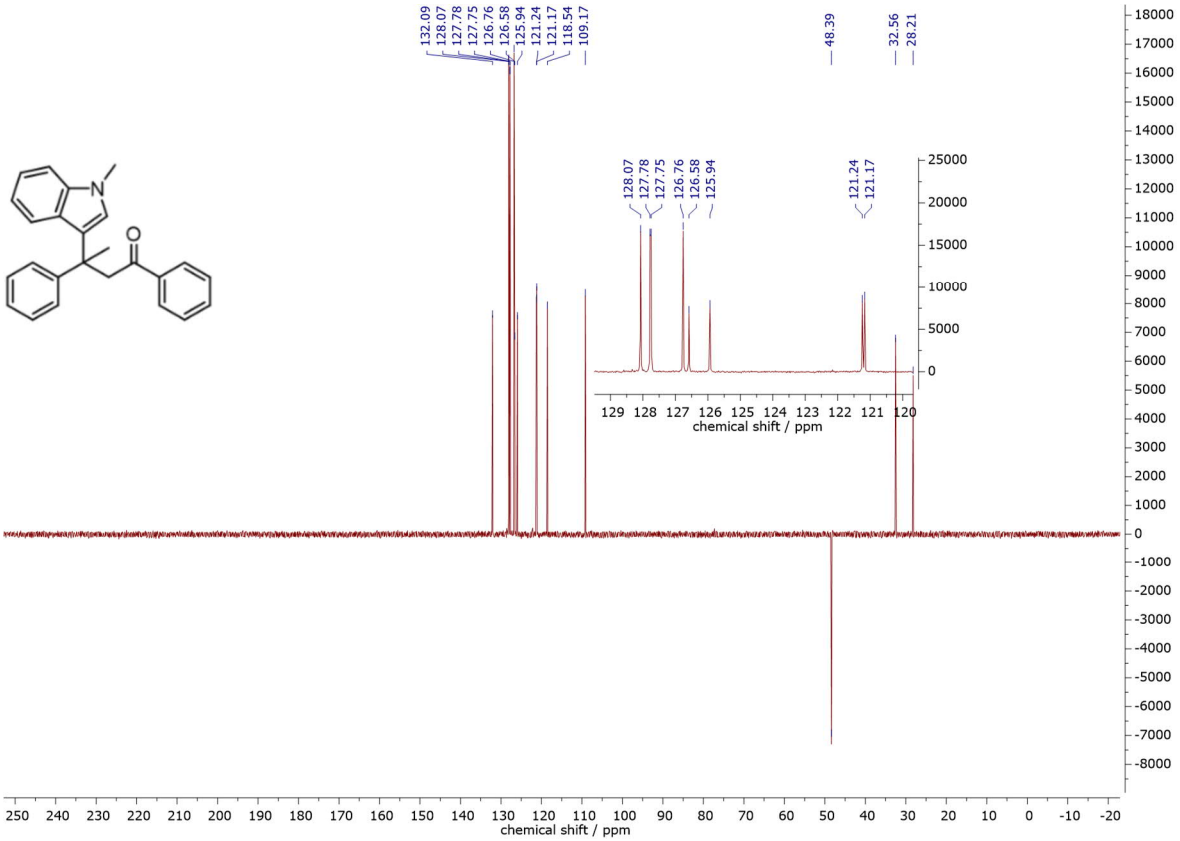
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **4a**:



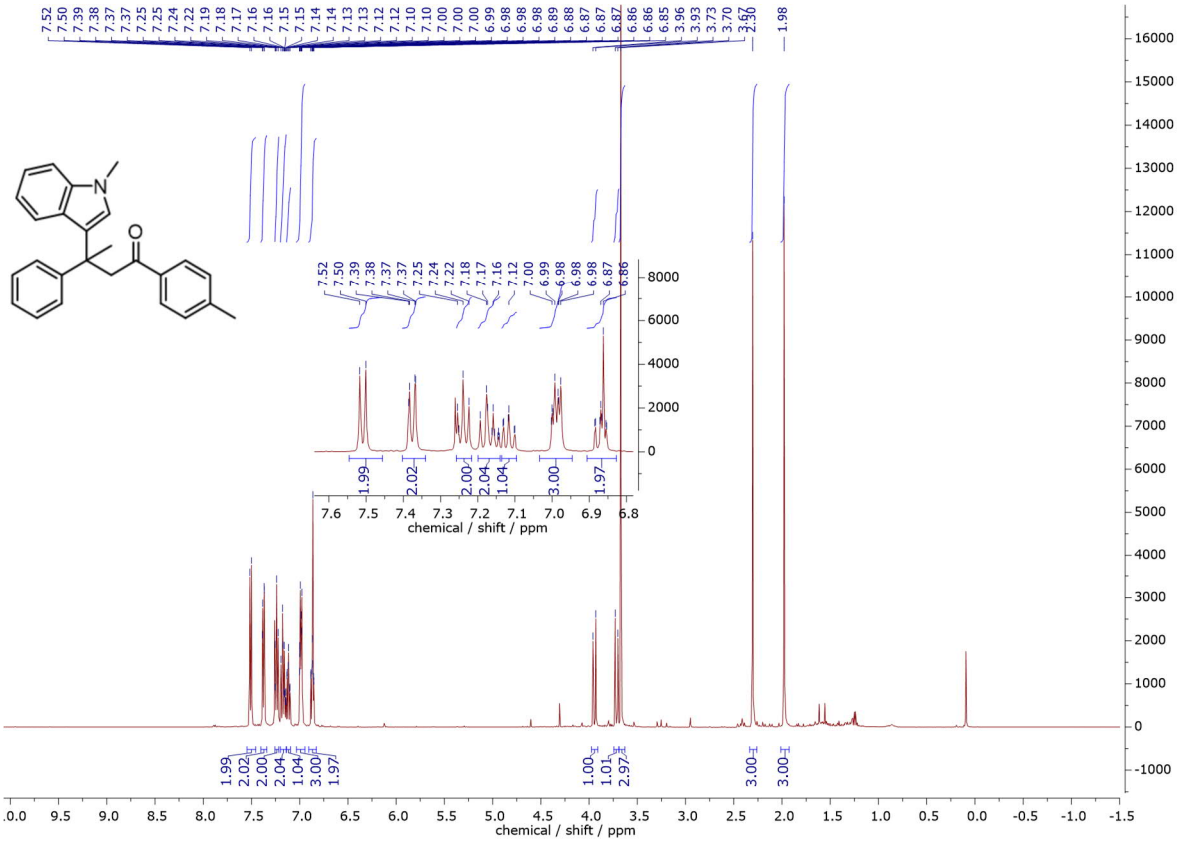
$^{13}C\{H\}$ (126 MHz, $CDCl_3$) NMR spectrum of product **4a**:



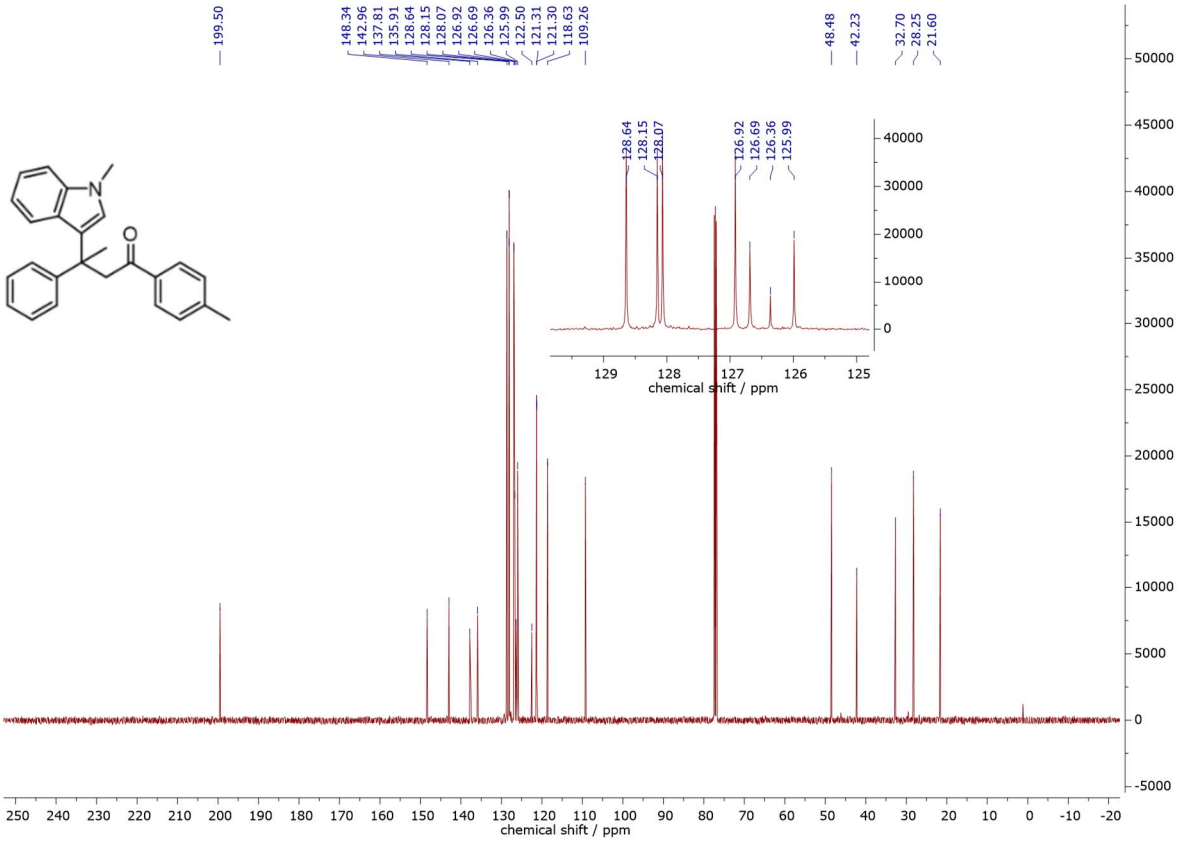
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **4a**:



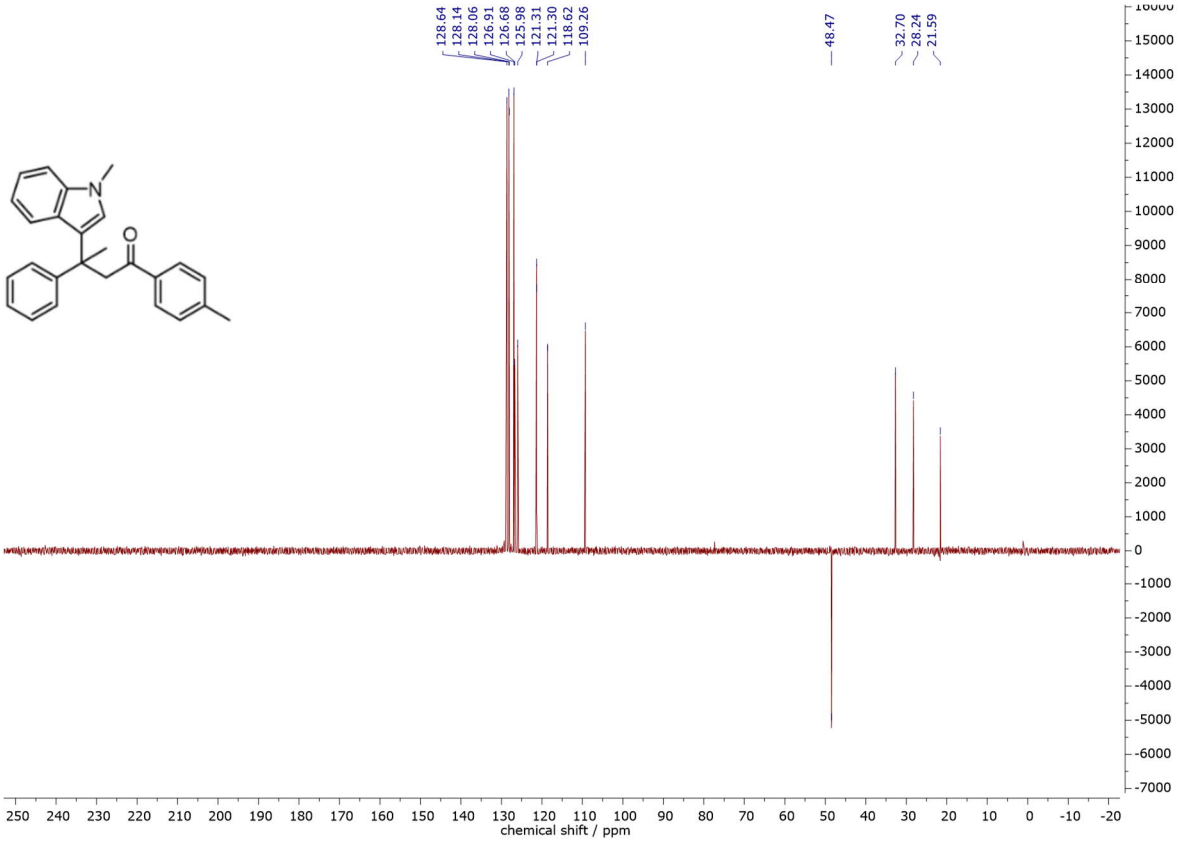
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **4b**:



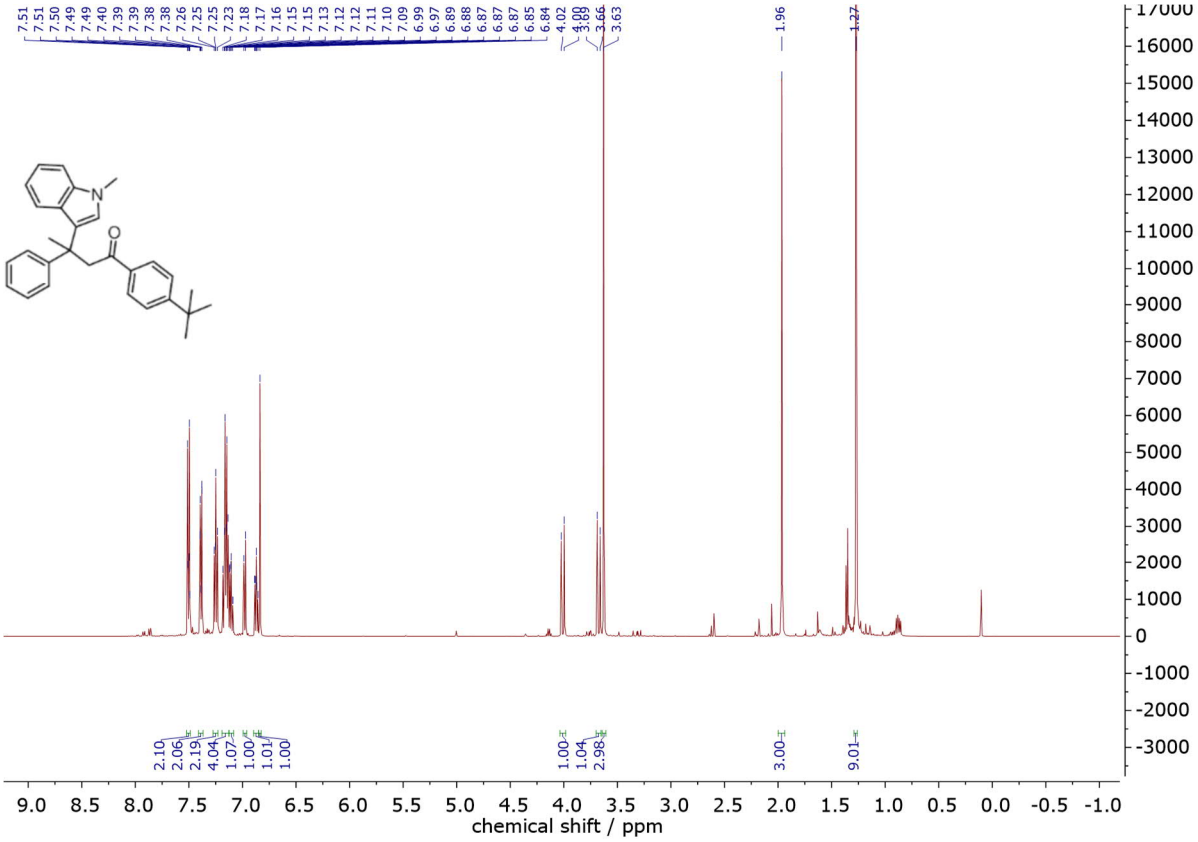
$^{13}C\{H\}$ (126 MHz, $CDCl_3$) NMR spectrum of product **4b**:



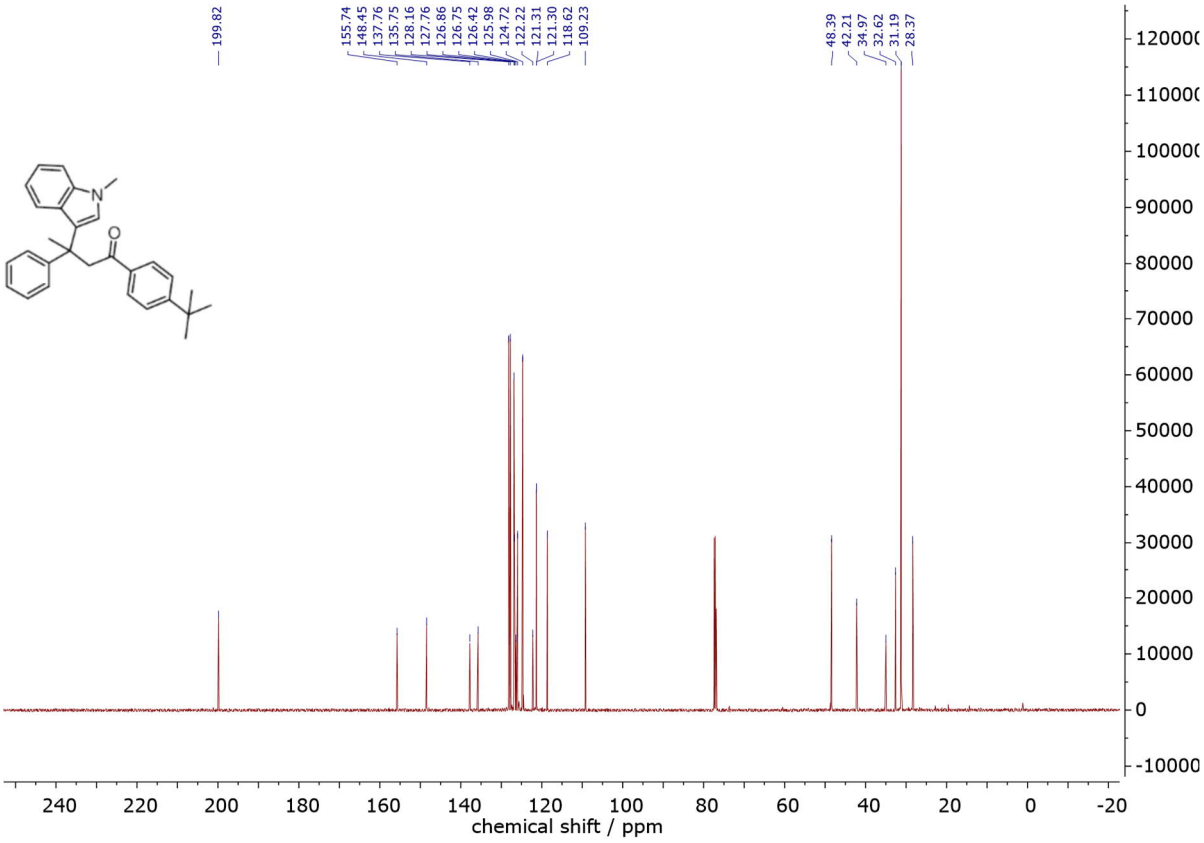
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **4b**:



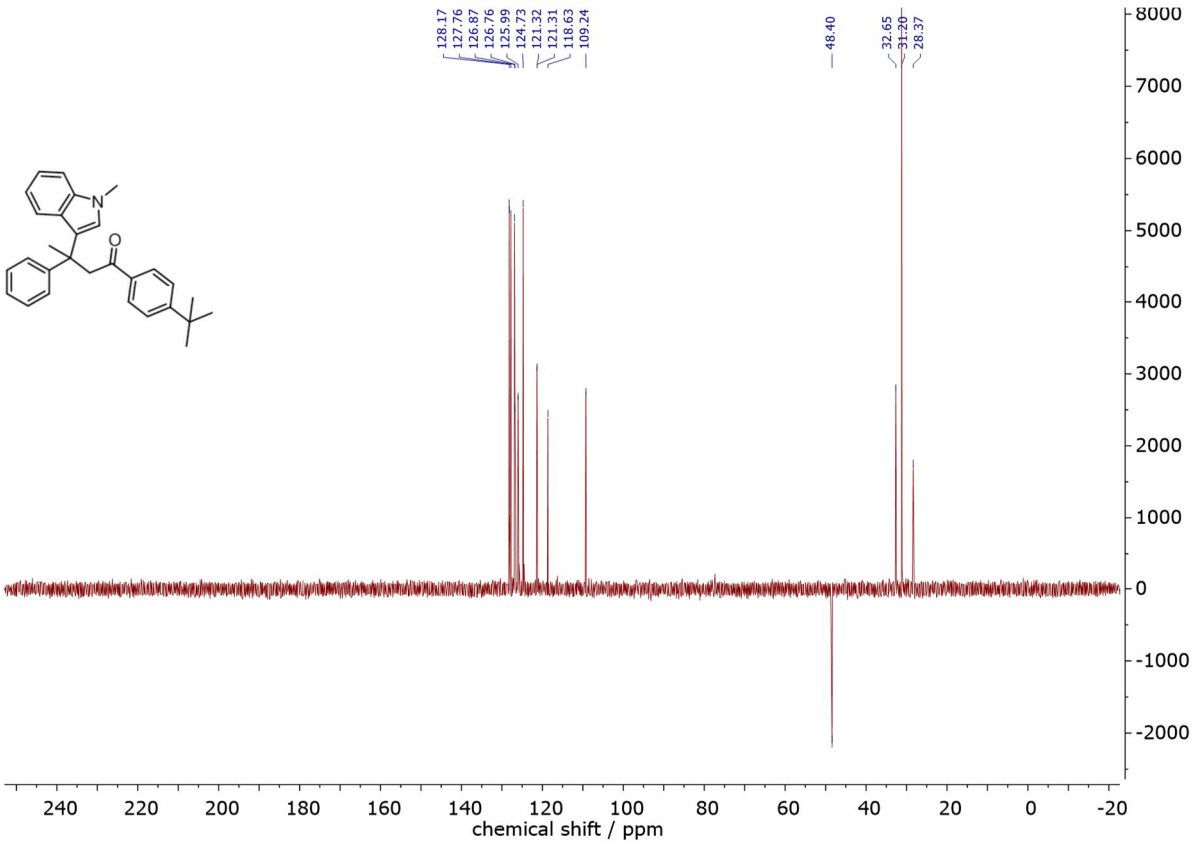
^1H (501 MHz, $CDCl_3$) NMR spectrum of product **4c**:



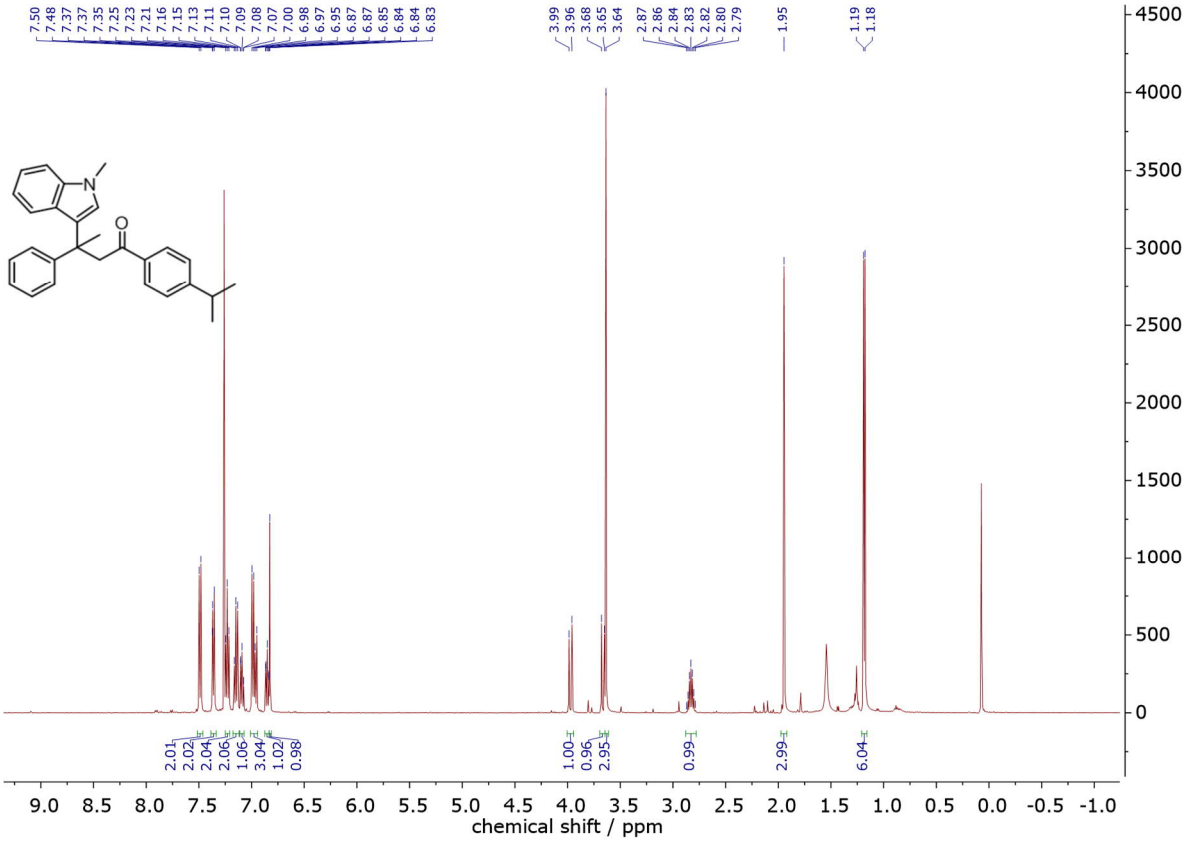
$^{13}C\{H\}$ (126 MHz, $CDCl_3$) NMR spectrum of product **4c**:



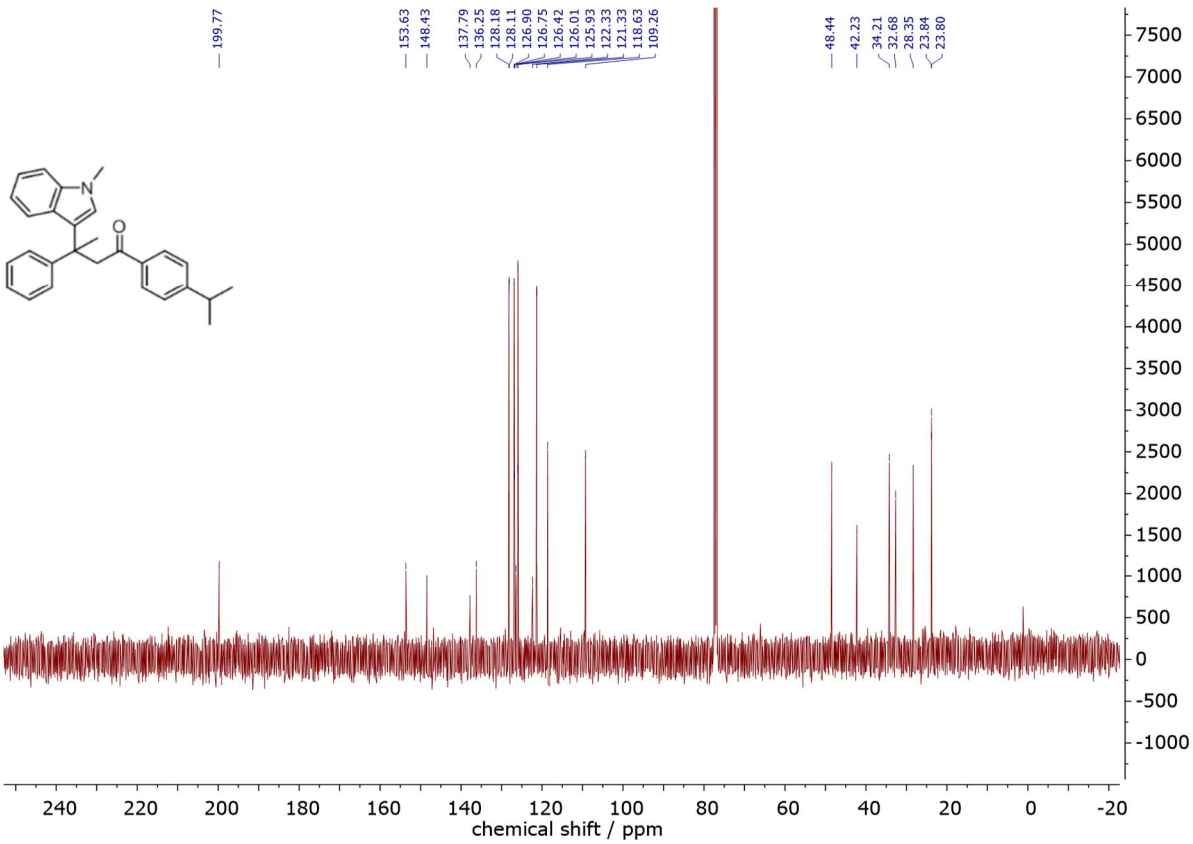
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **4c**:



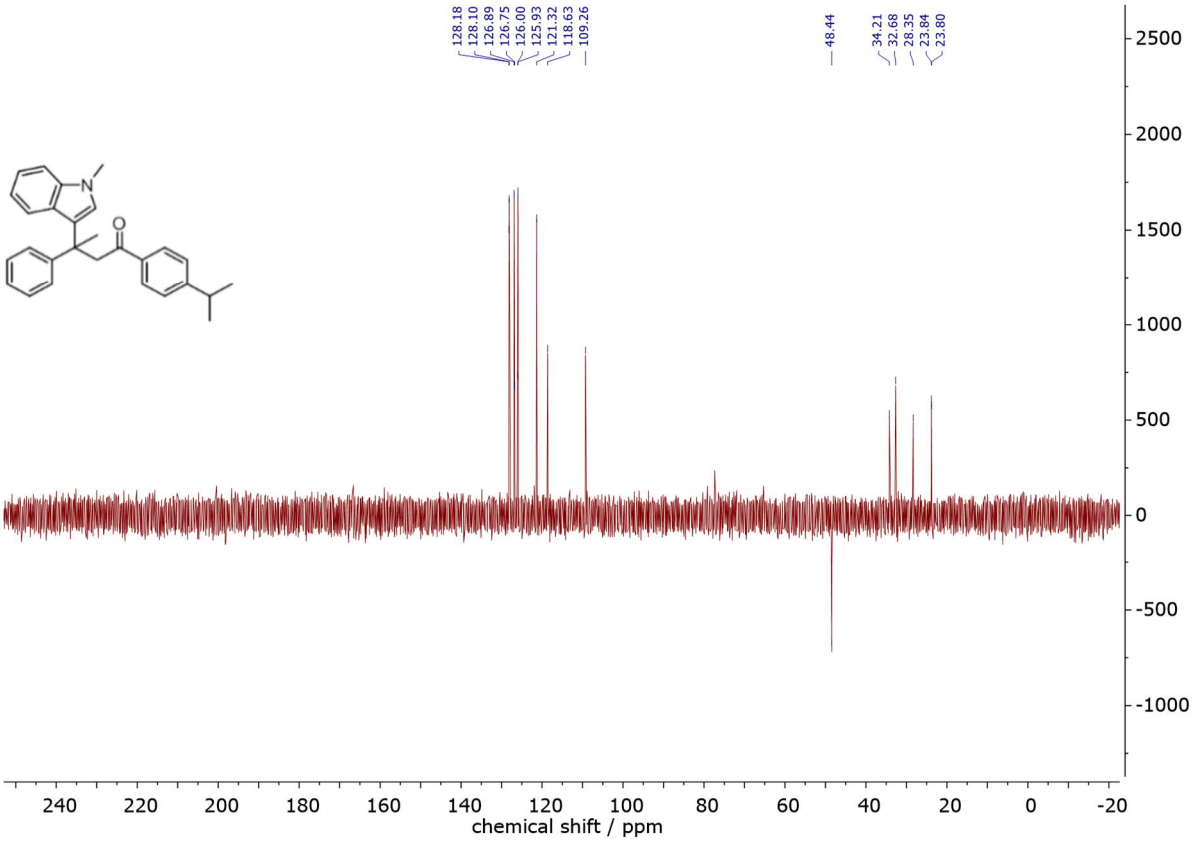
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **4d**:



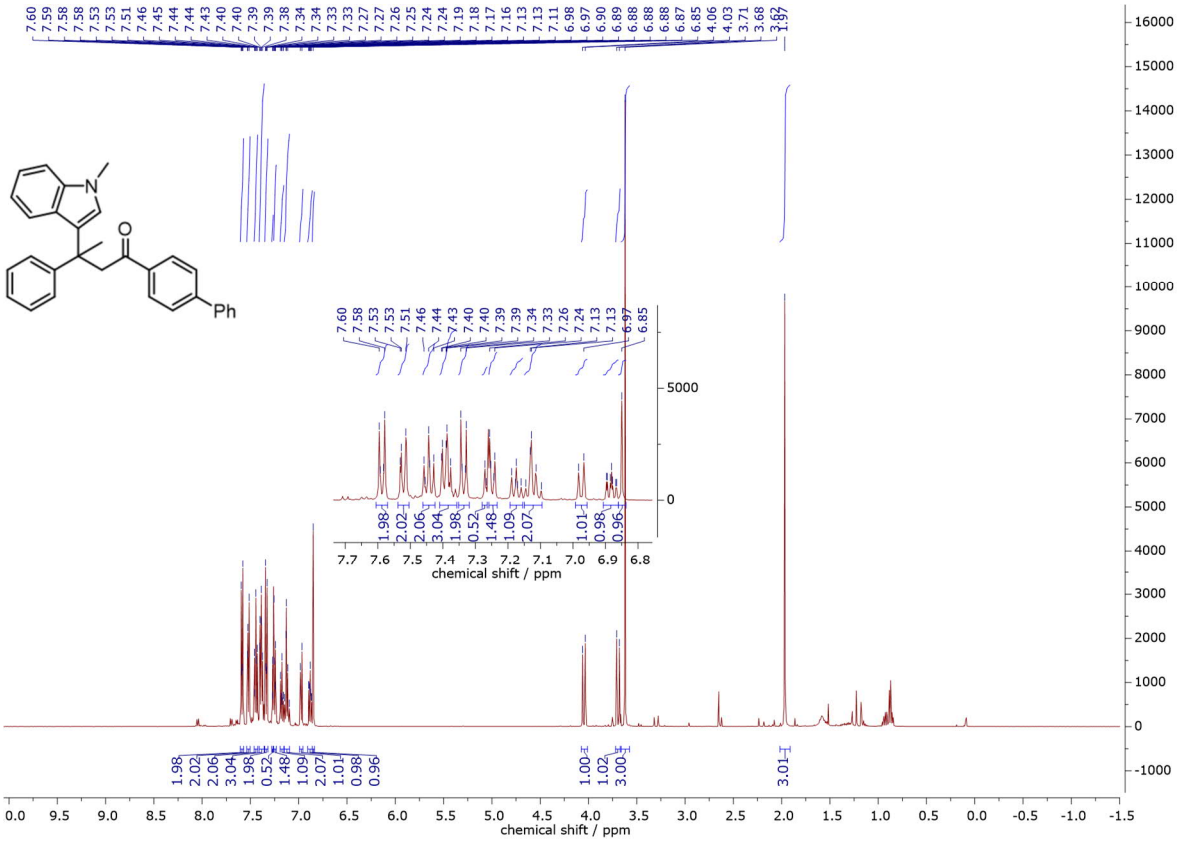
^{13}C{H} (126 MHz, $CDCl_3$) NMR spectrum of product **4d**:



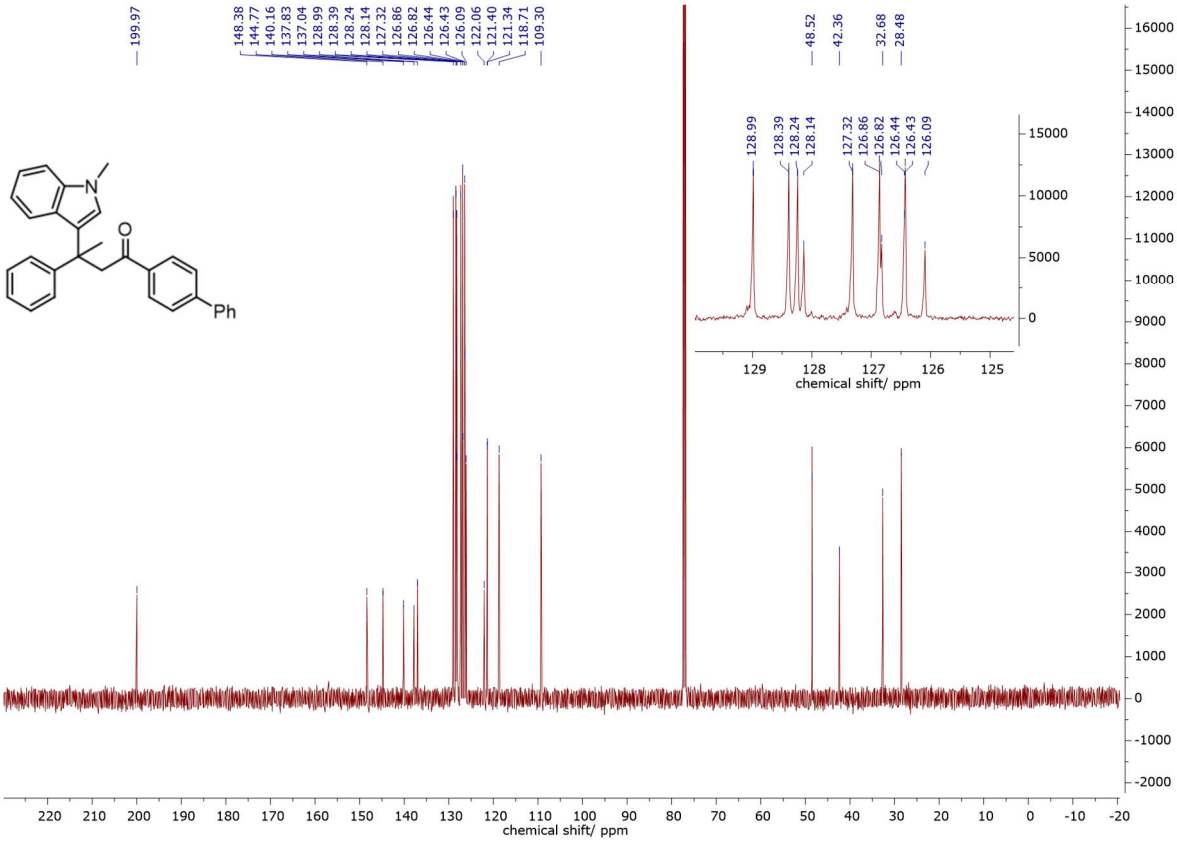
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **4d**:



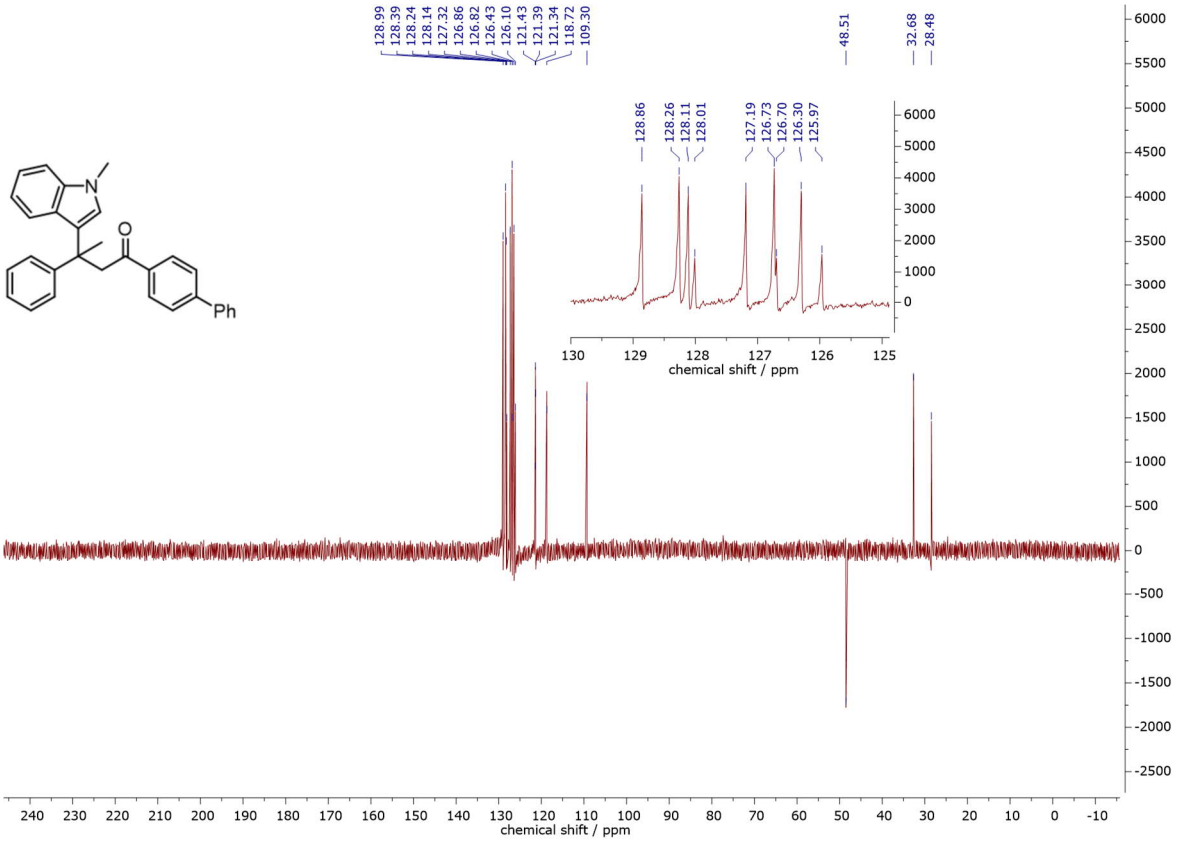
^1H (501 MHz, $CDCl_3$) NMR spectrum of product **4e**:



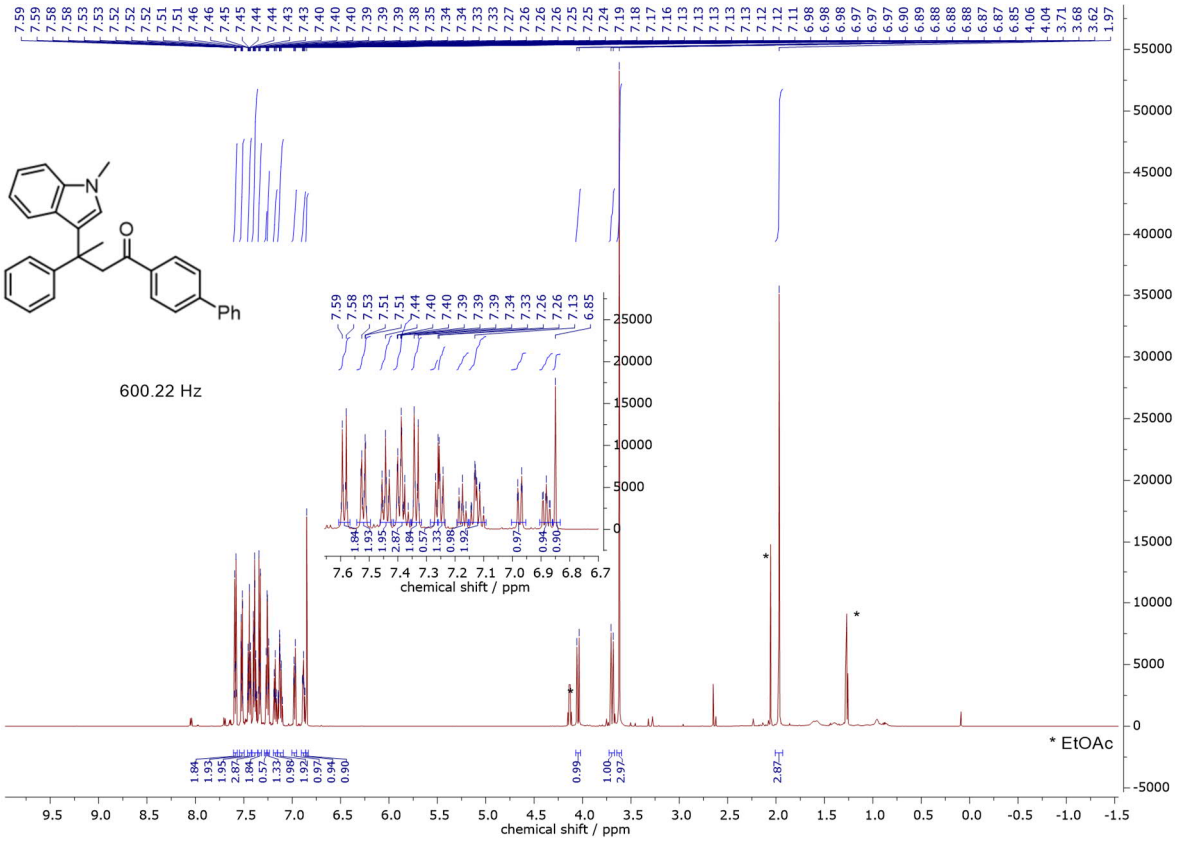
$^{13}C\{H\}$ (126 MHz, $CDCl_3$) NMR spectrum of product **4e**:



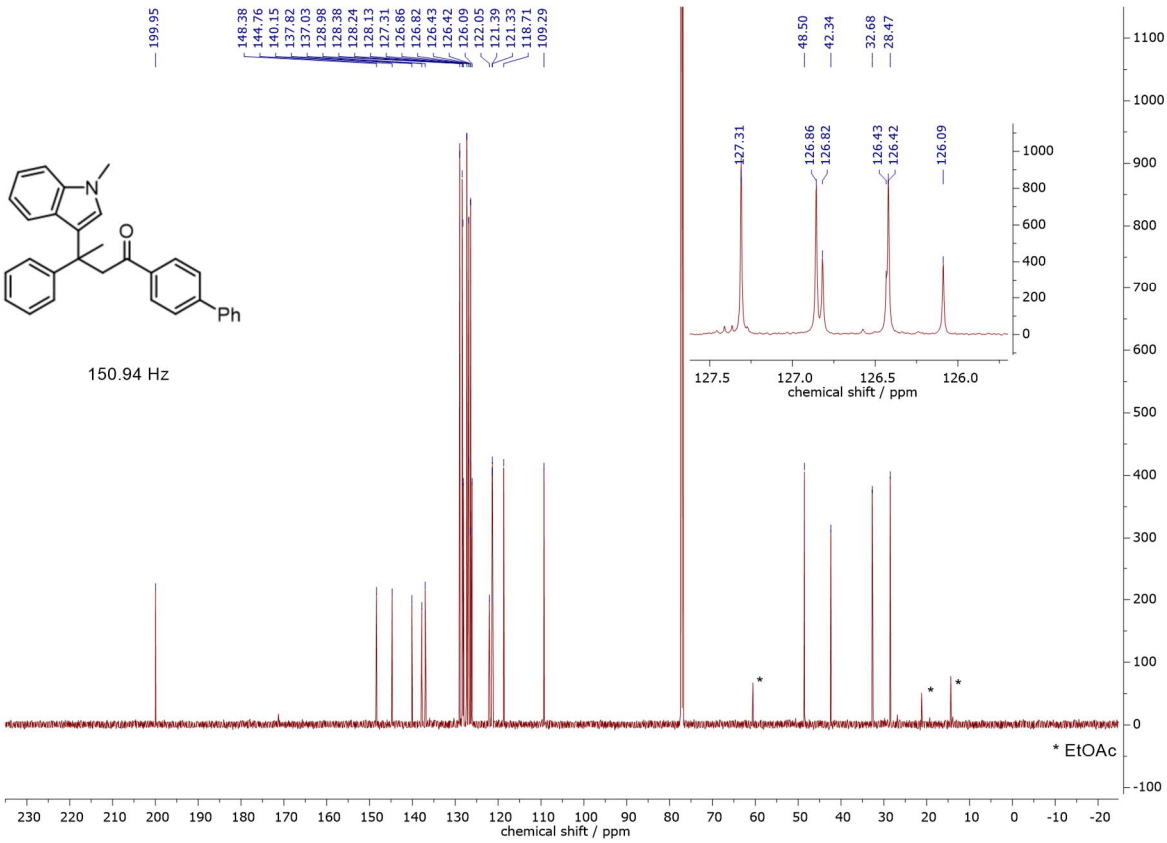
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **4e**:



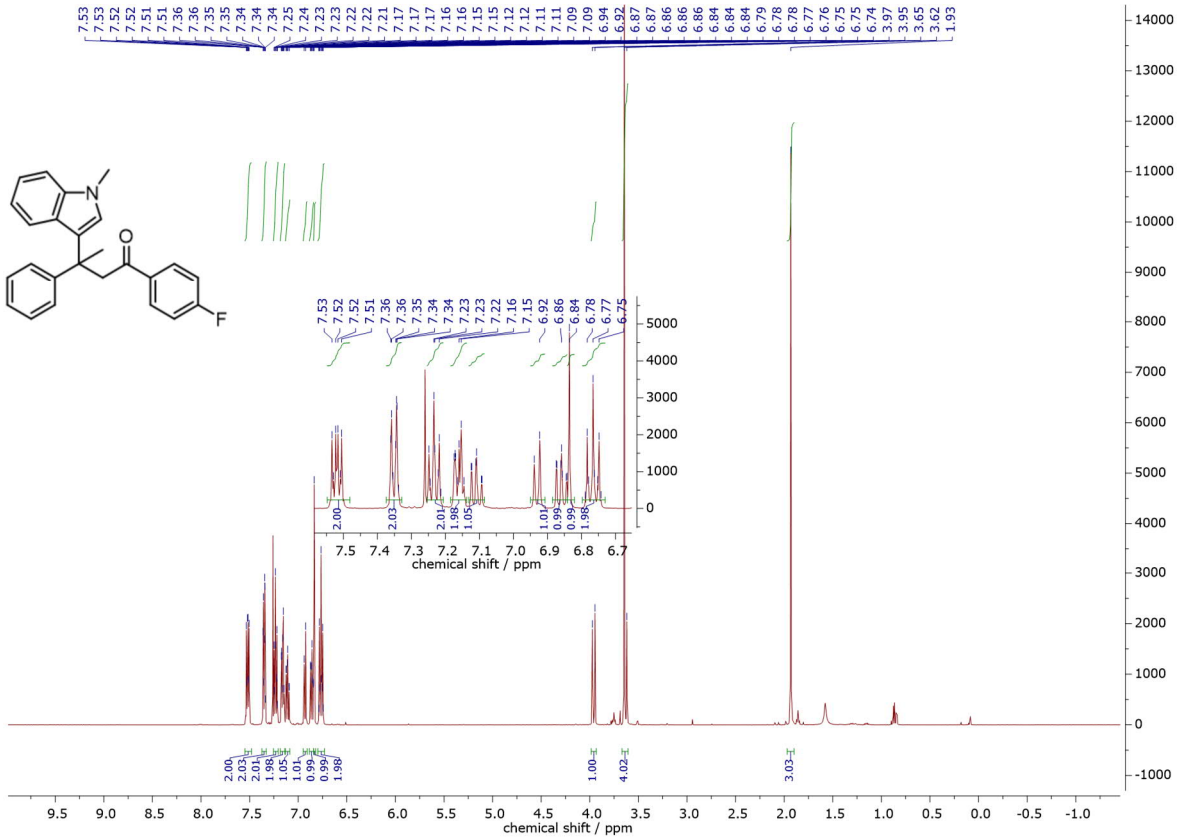
^{1}H (600 MHz, $CDCl_3$) NMR spectrum of product **4e**:



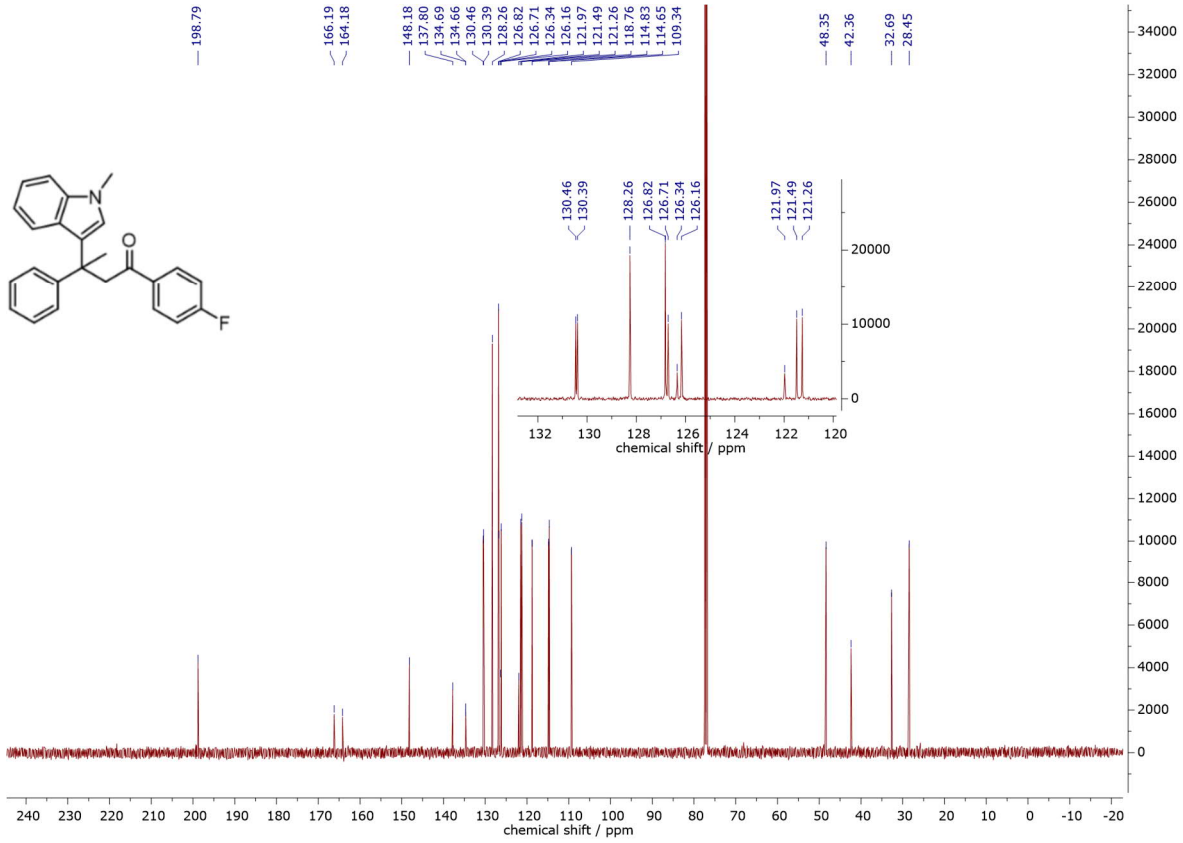
^{13}C{H} (151 MHz, $CDCl_3$) NMR spectrum of product **4e** for clear resolution:



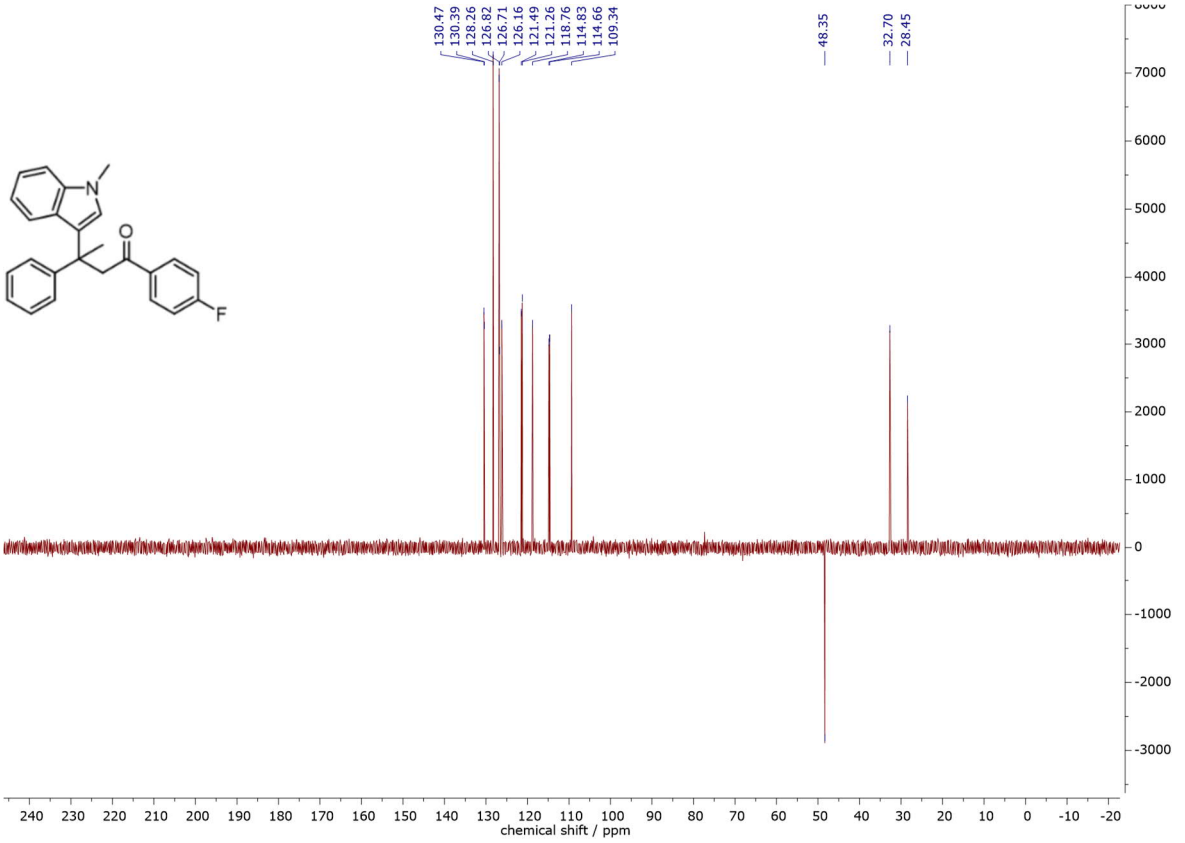
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **4f**:



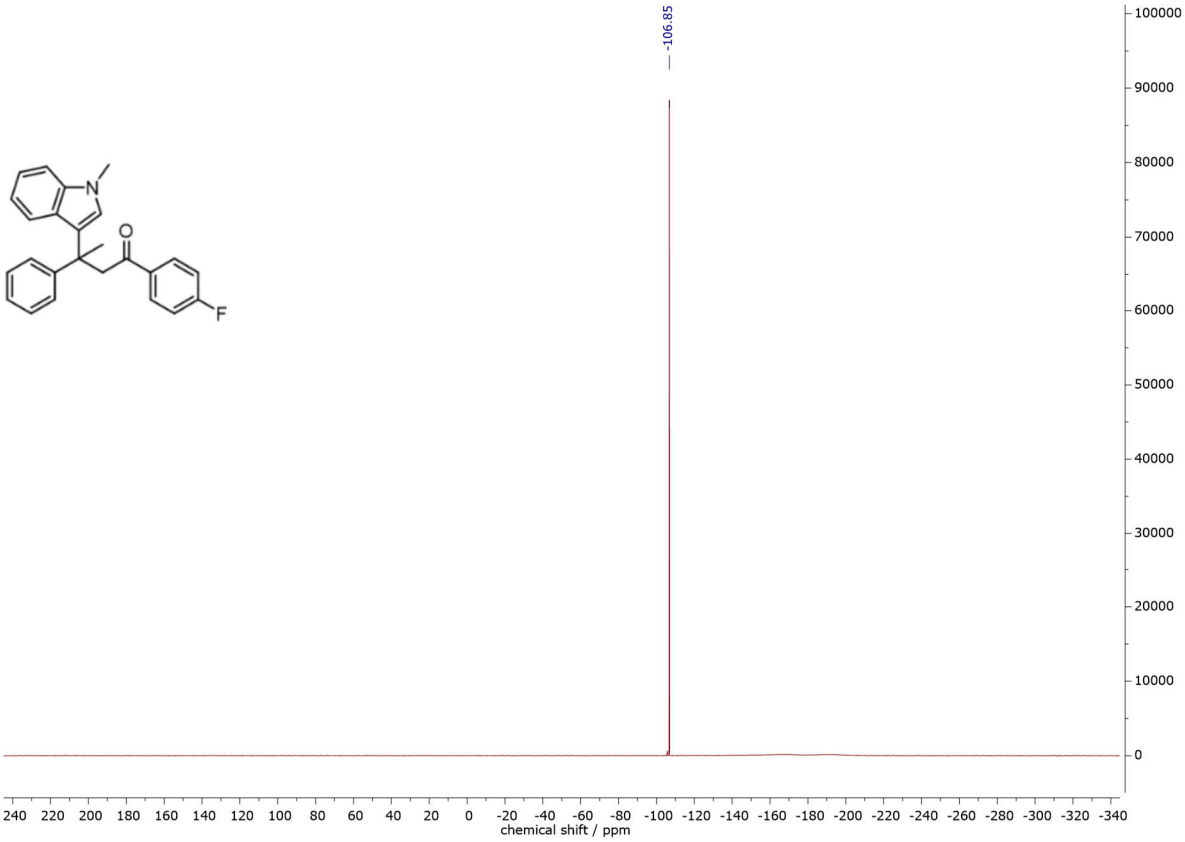
^{13}C{H} (126 MHz, $CDCl_3$) NMR spectrum of product **4f**:



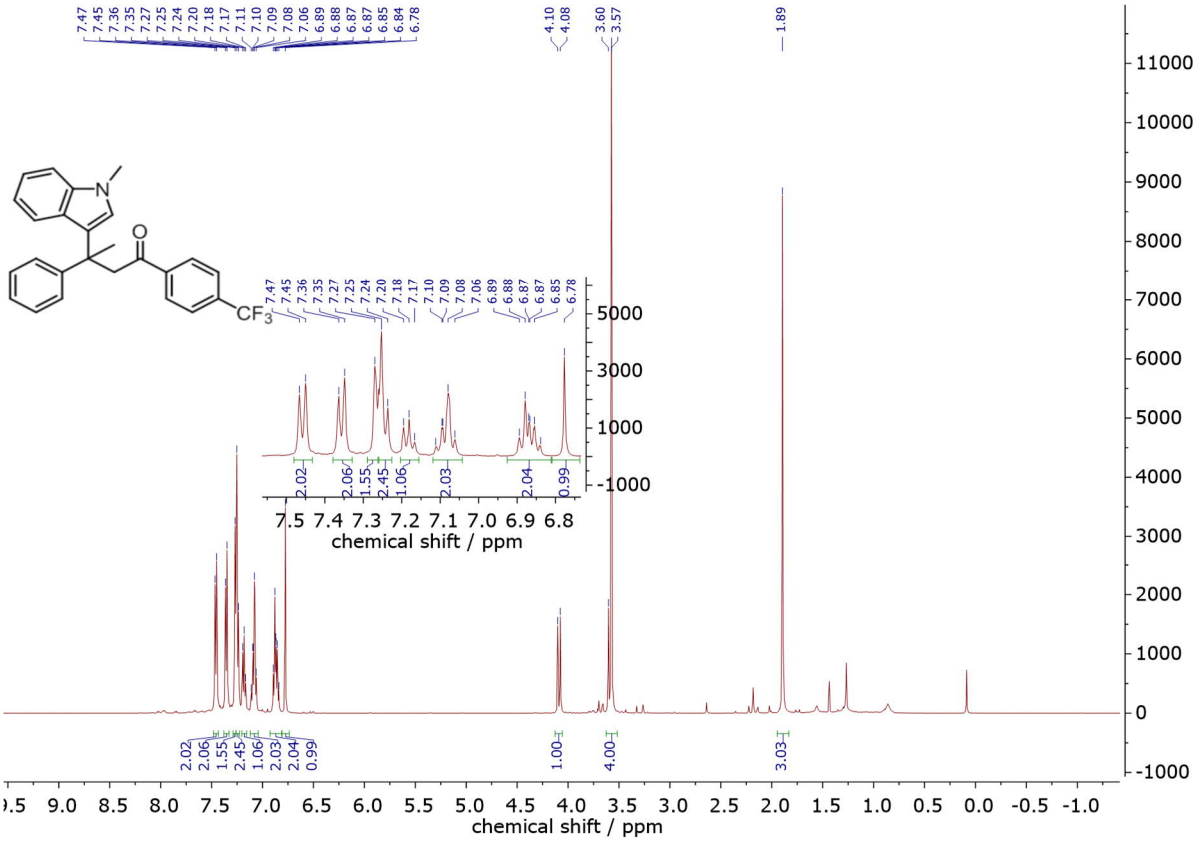
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **4f**:



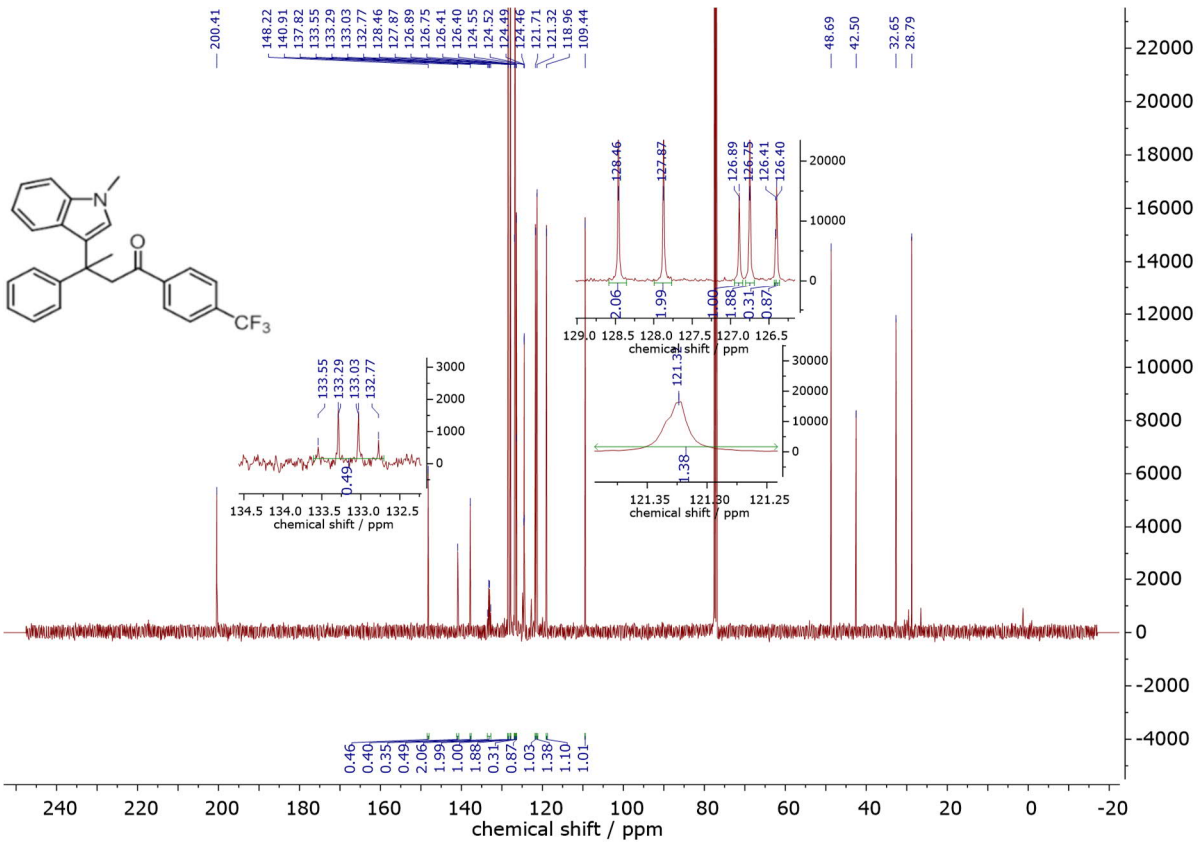
^{19}F (471 MHz, $CDCl_3$) NMR spectrum of product **4f**:



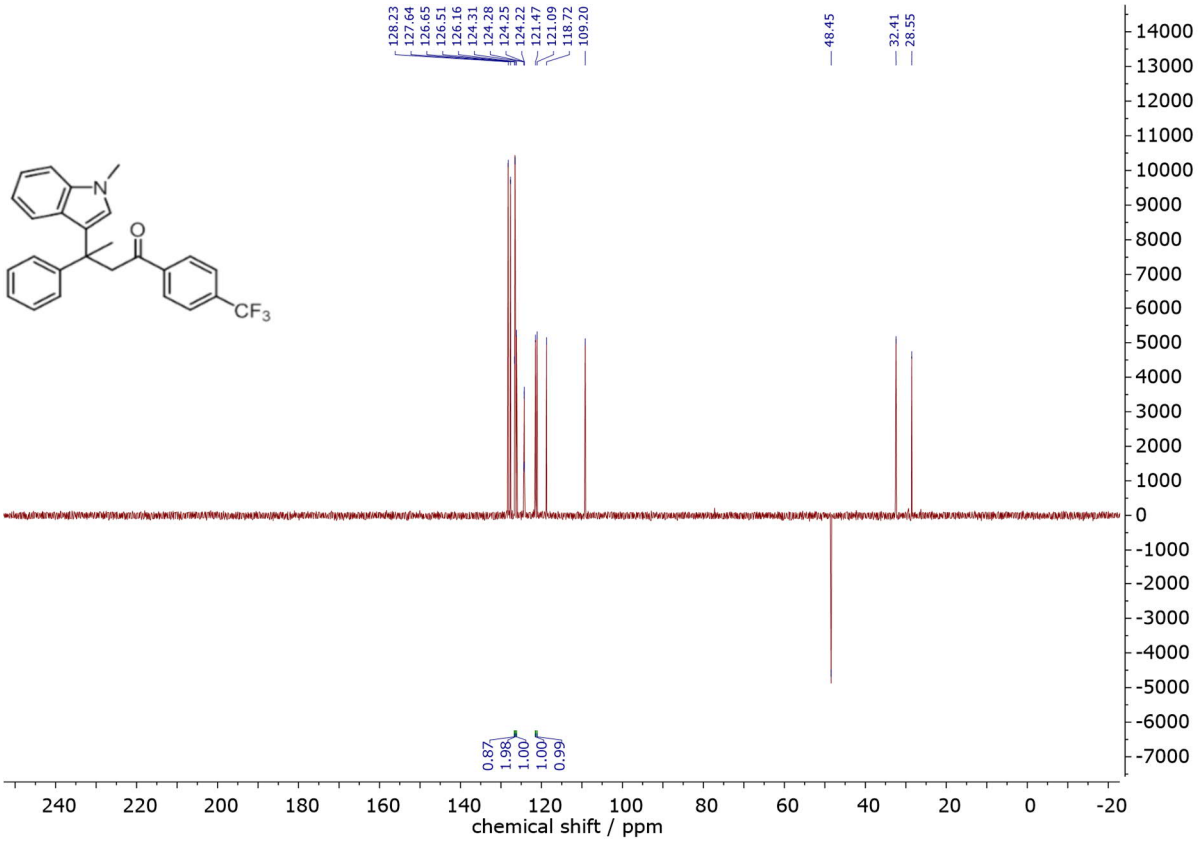
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **4g**:



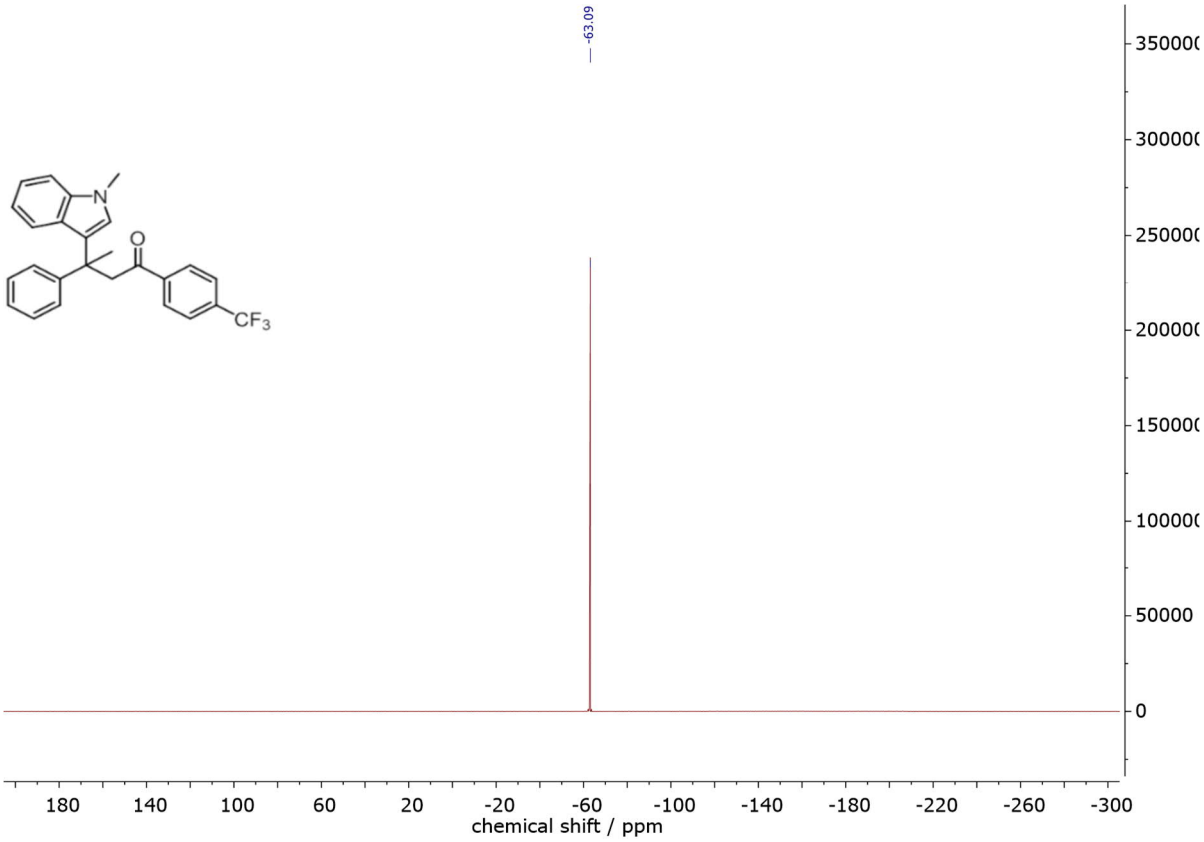
^{13}C{H} (126 MHz, $CDCl_3$) NMR spectrum of product **4g**:



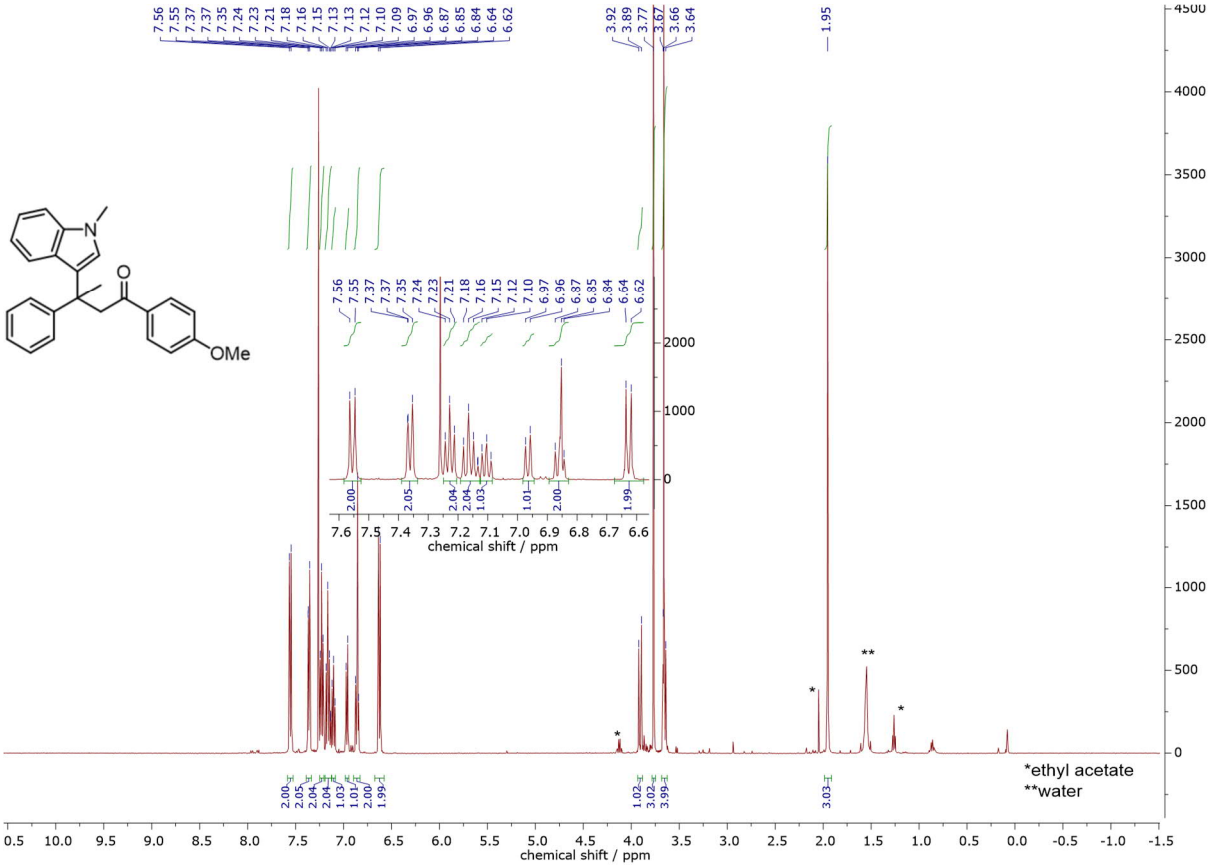
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **4g**:



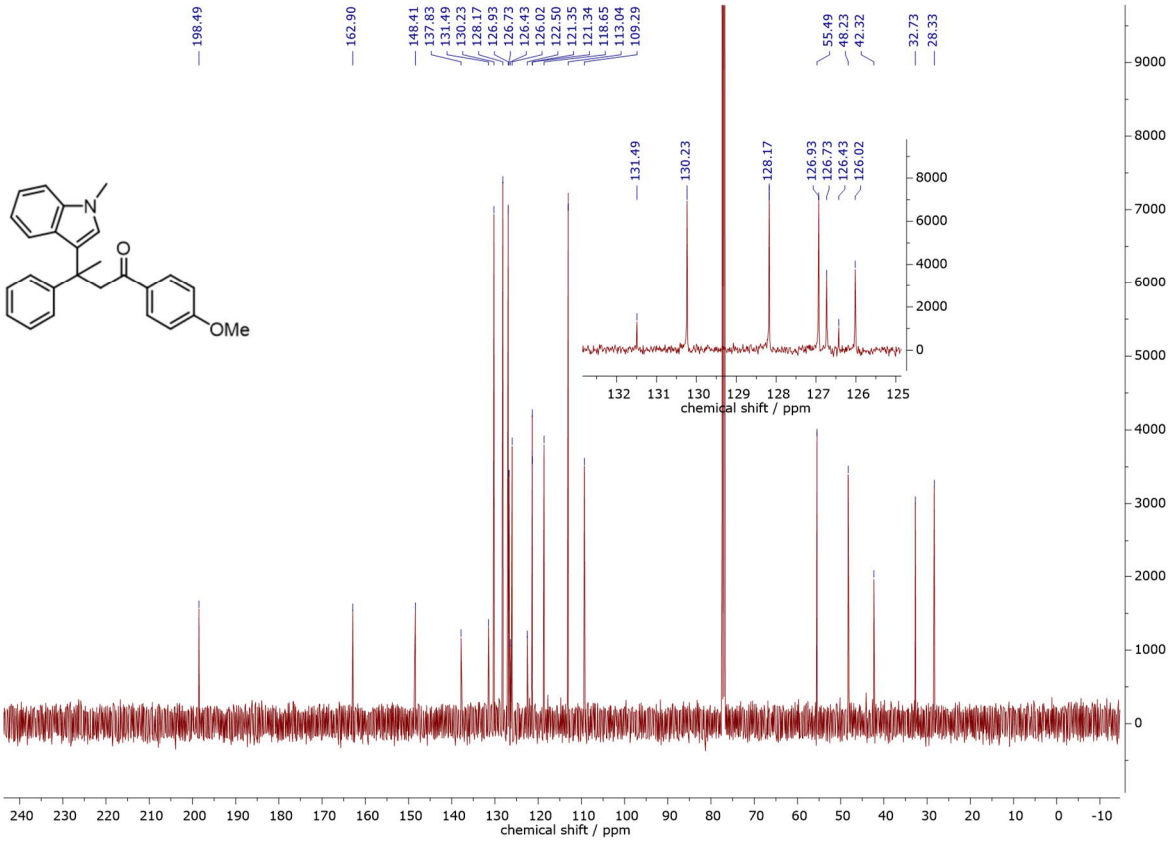
^{19}F (282 MHz, $CDCl_3$) NMR spectrum of product **4g**:



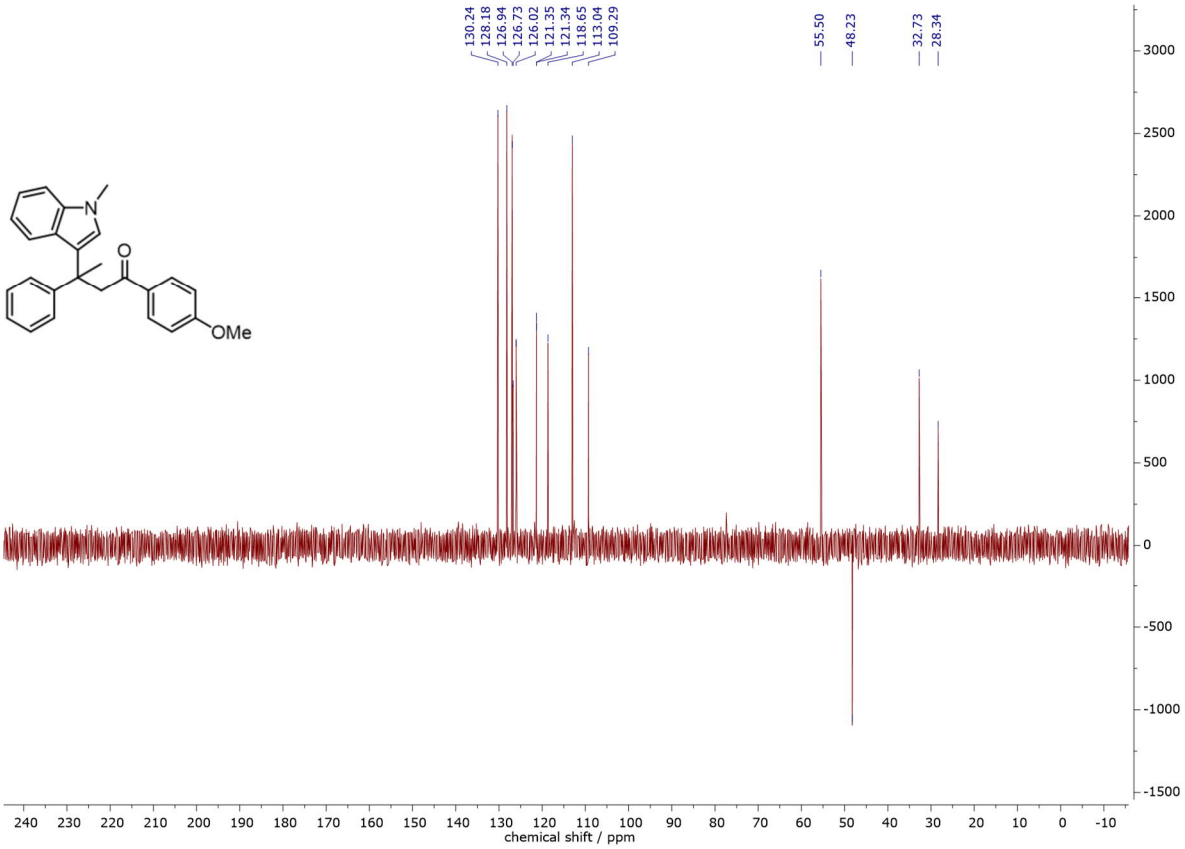
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **4h**:



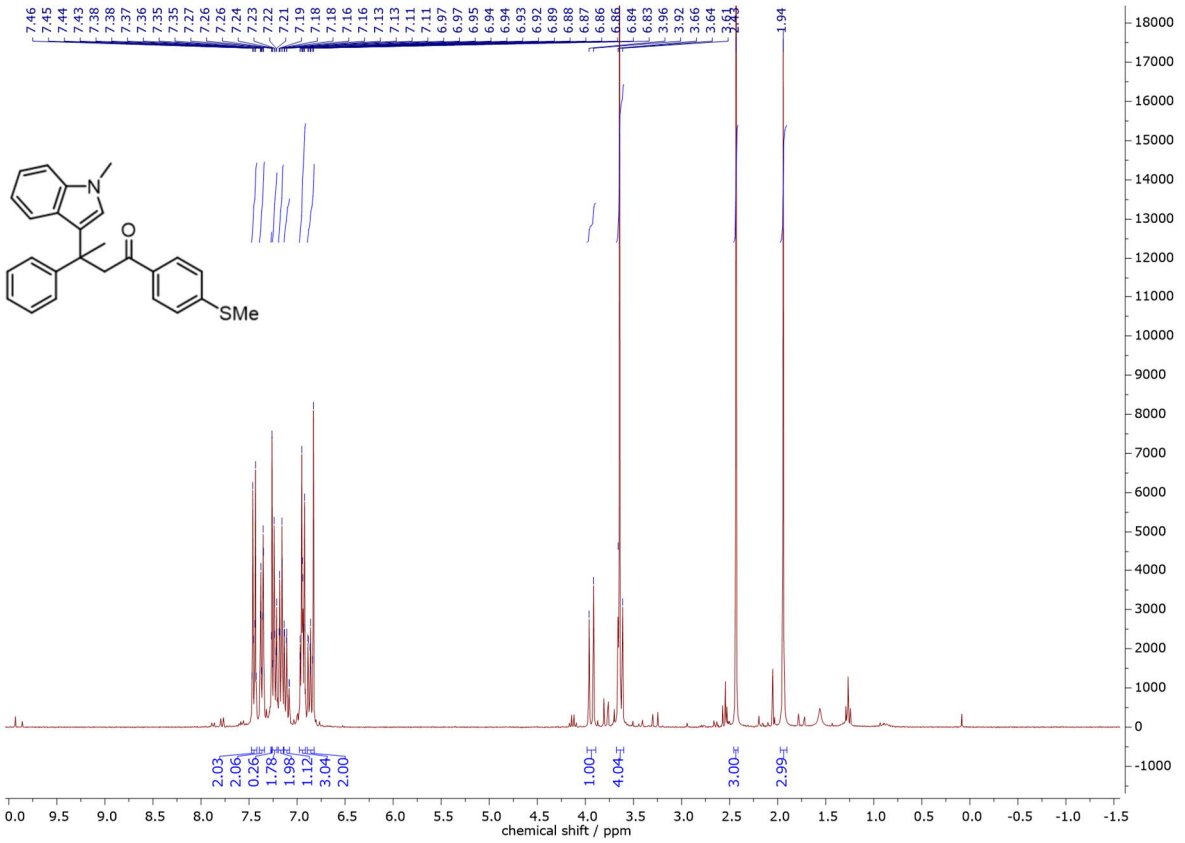
^{13}C{H} (126 MHz, $CDCl_3$) NMR spectrum of product **4h**:



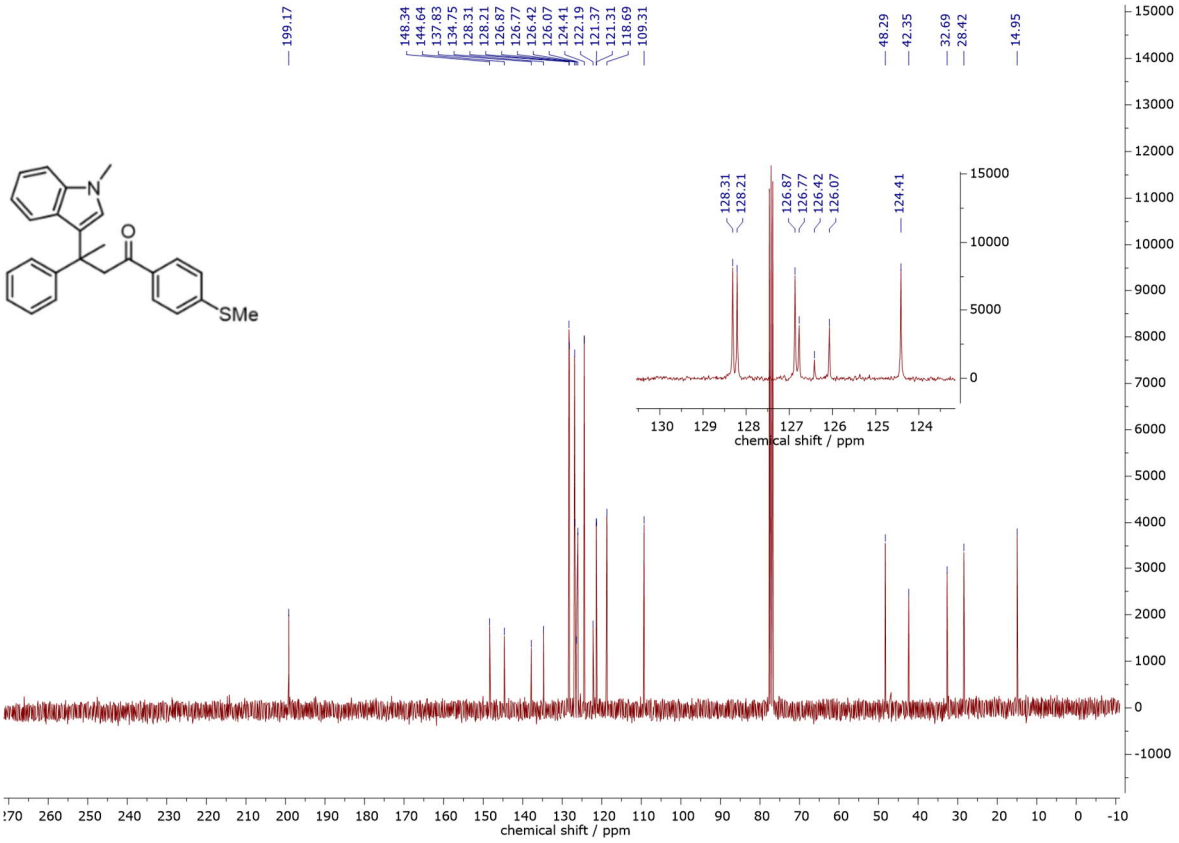
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **4h**:



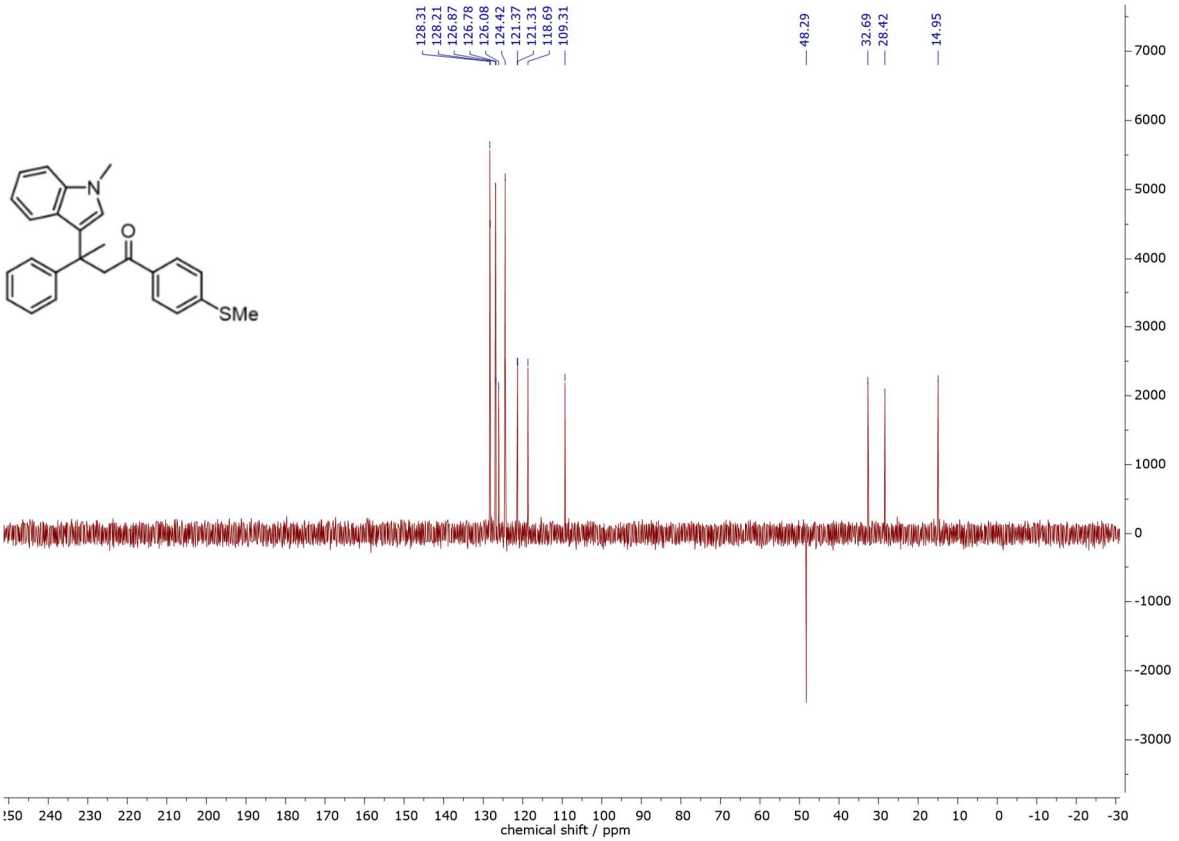
^1H (300 MHz, $CDCl_3$) NMR spectrum of product **4i**:



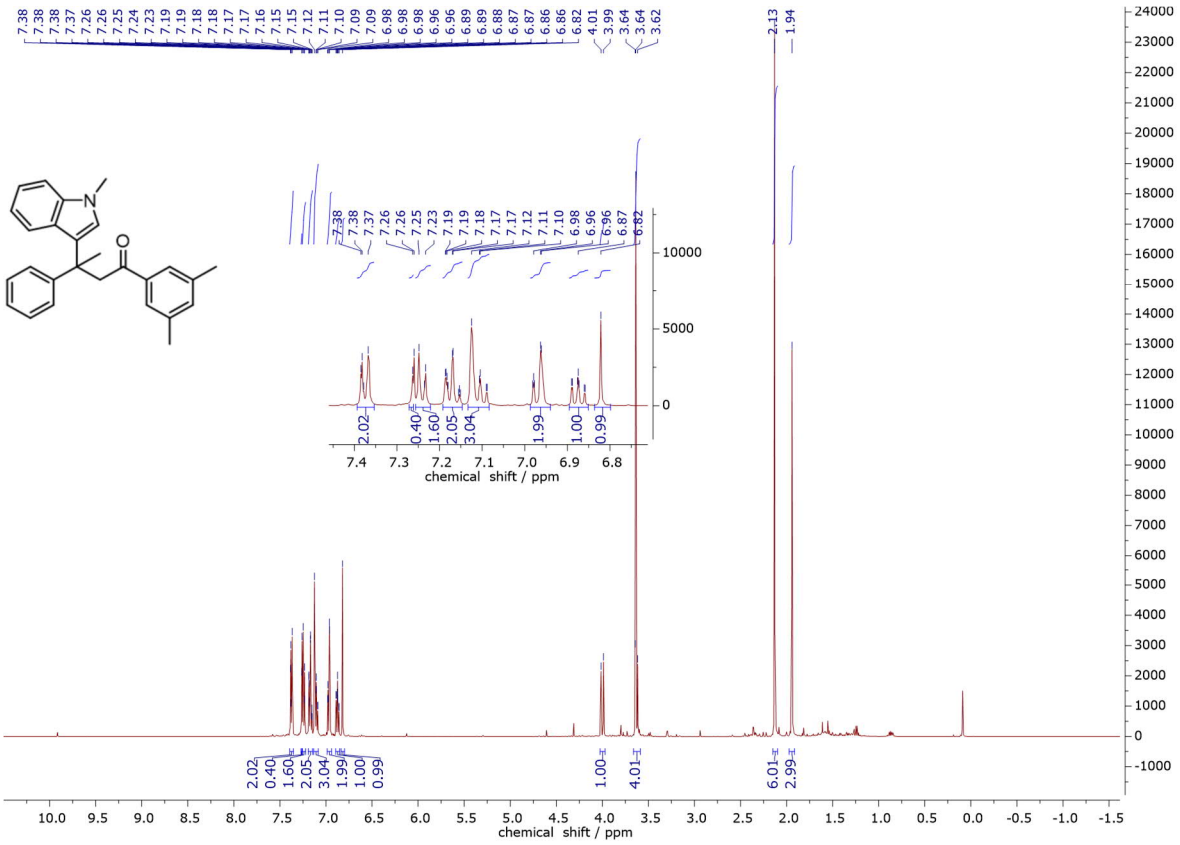
$^{13}C\{H\}$ (75 MHz, $CDCl_3$) NMR spectrum of product **4i**:



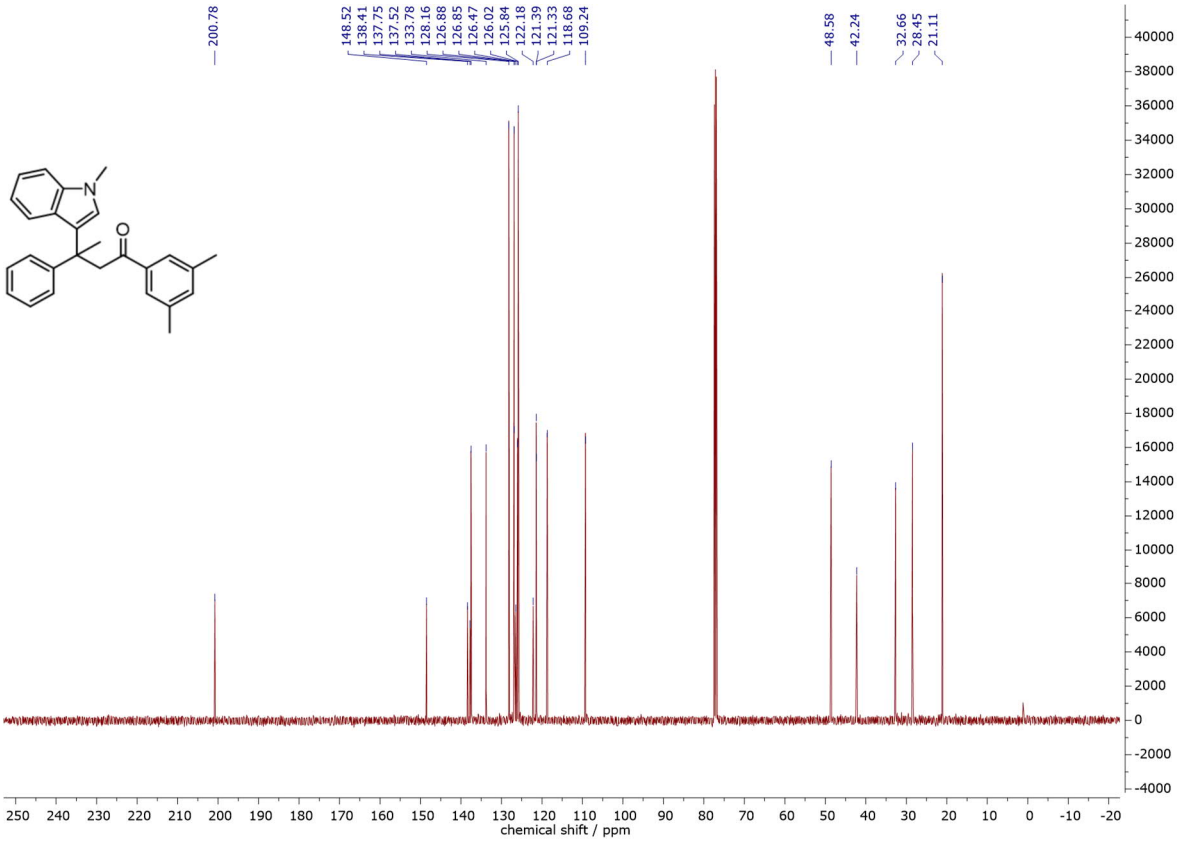
DEPT135 {H} (75 MHz, $CDCl_3$) NMR spectrum of product **4i**:



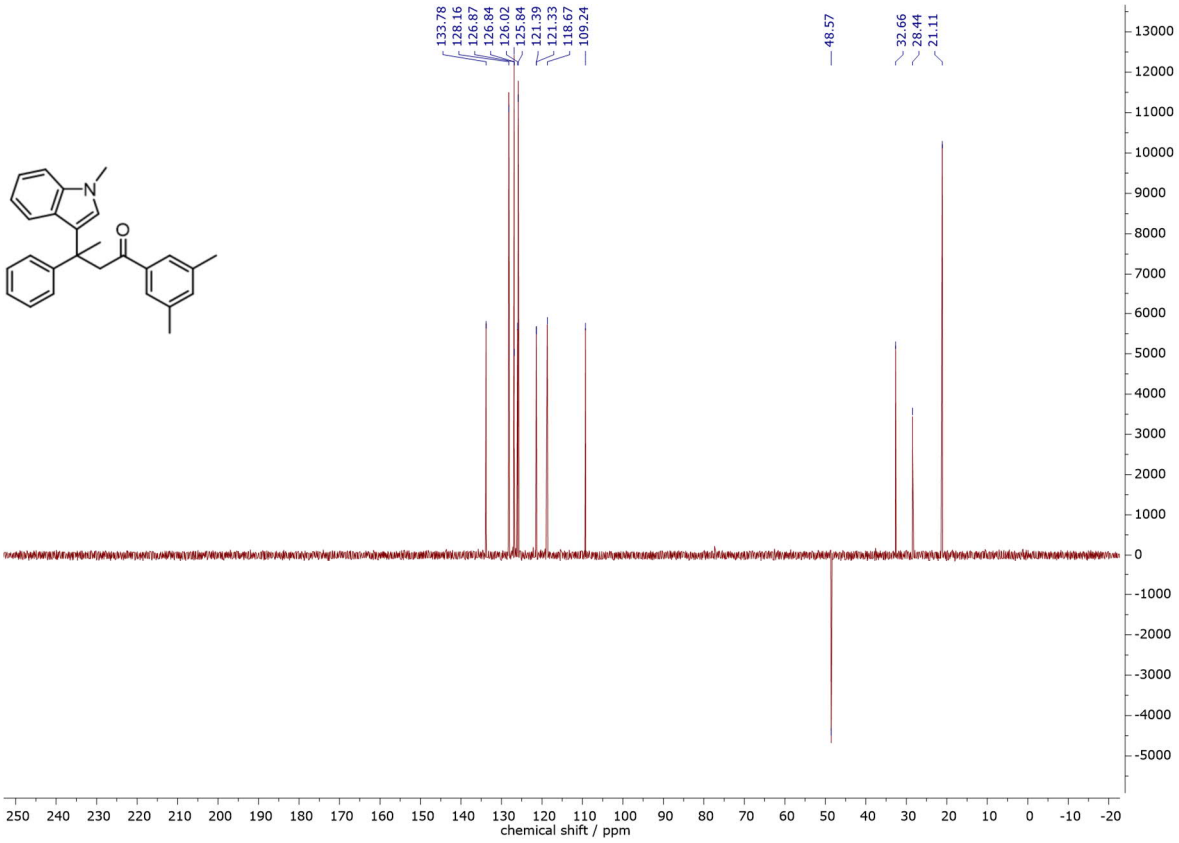
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **4j**:



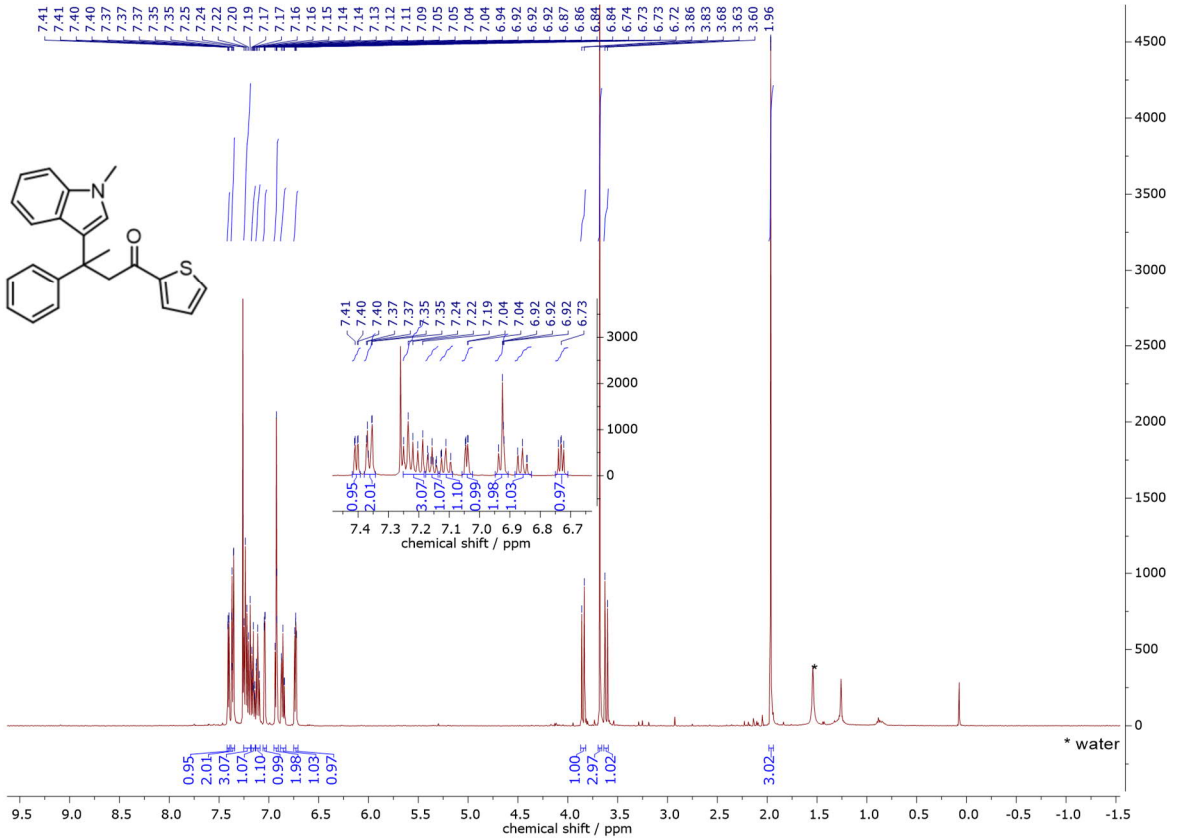
^{13}C{H} (126 MHz, $CDCl_3$) NMR spectrum of product **4j**:



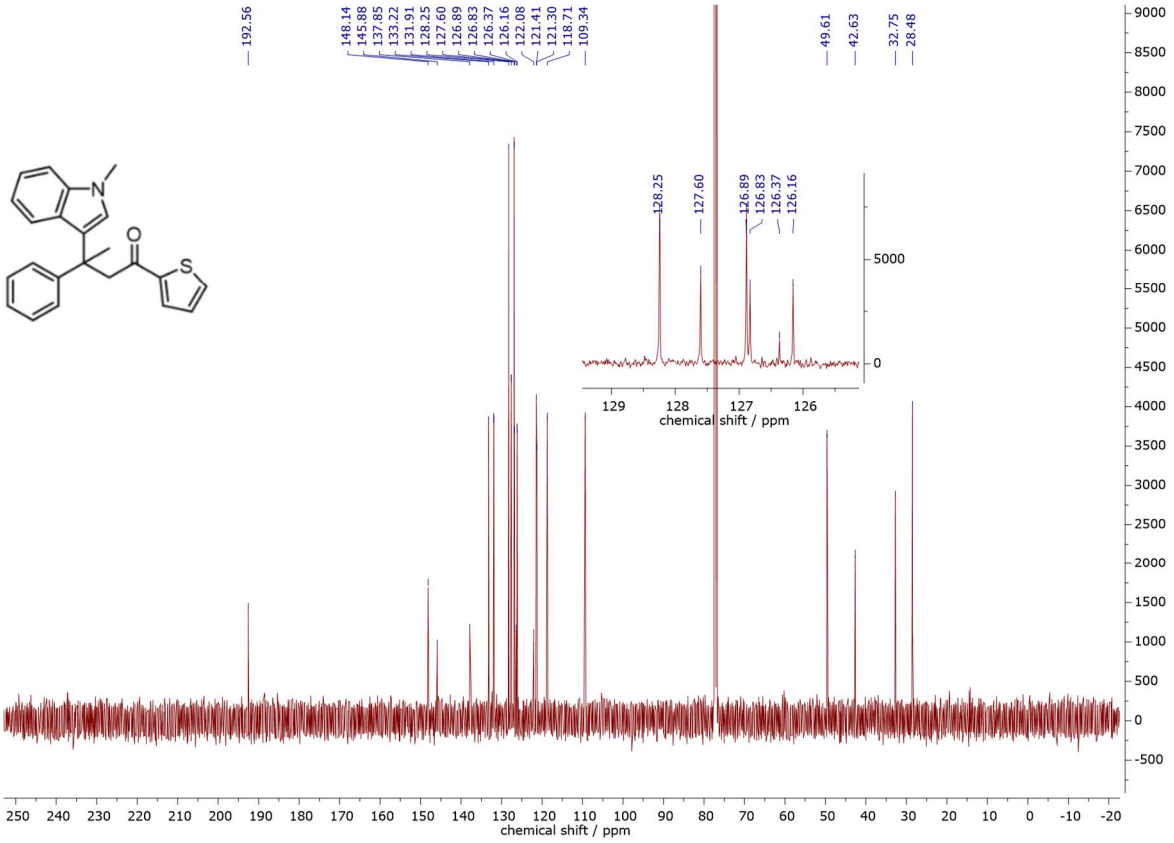
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **4j**:



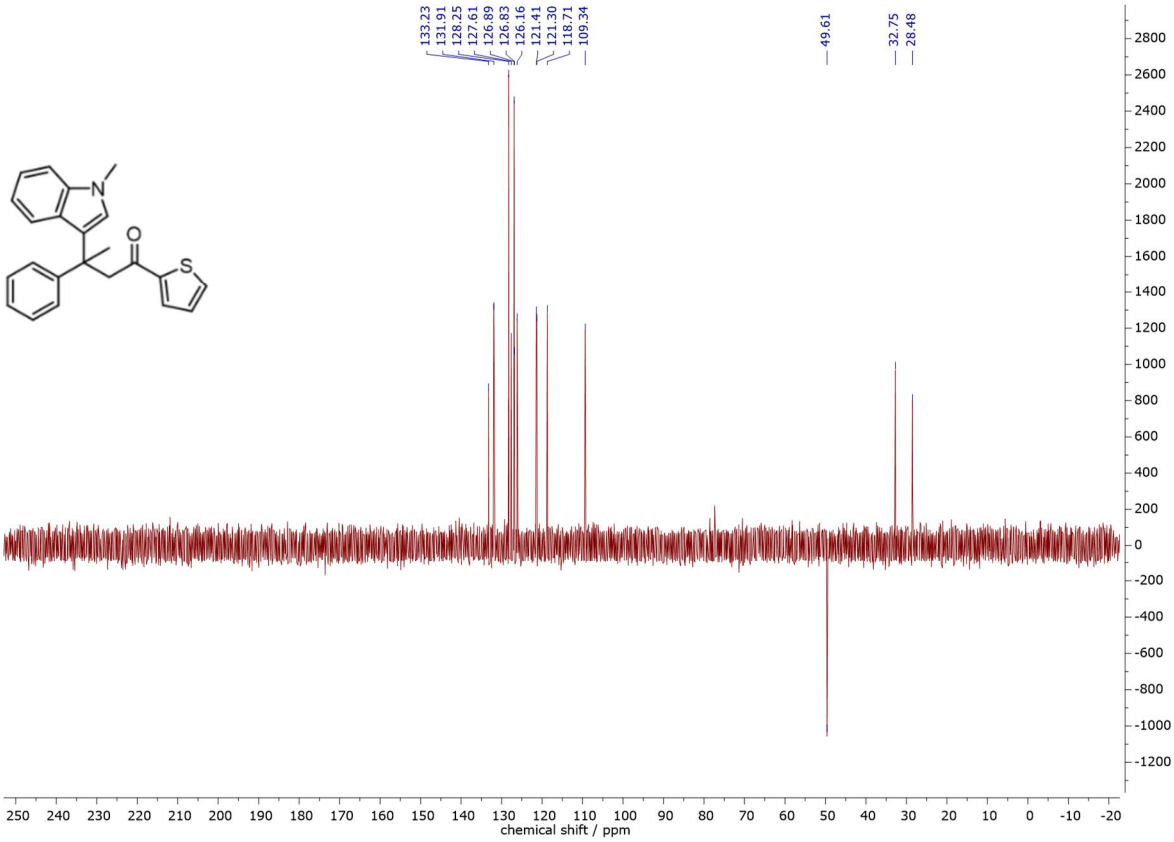
^1H (501 MHz, $CDCl_3$) NMR spectrum of product **4k**:



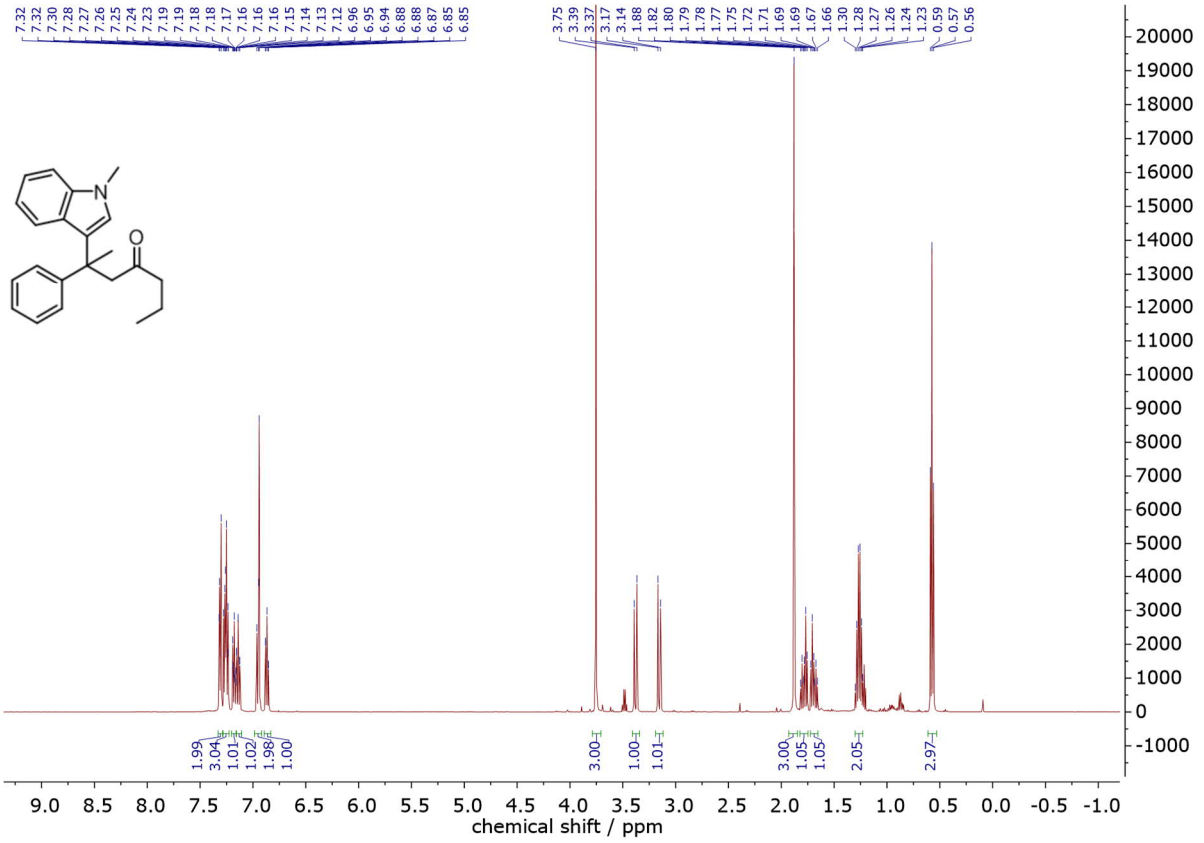
$^{13}C\{H\}$ (126 MHz, $CDCl_3$) NMR spectrum of product **4k**:



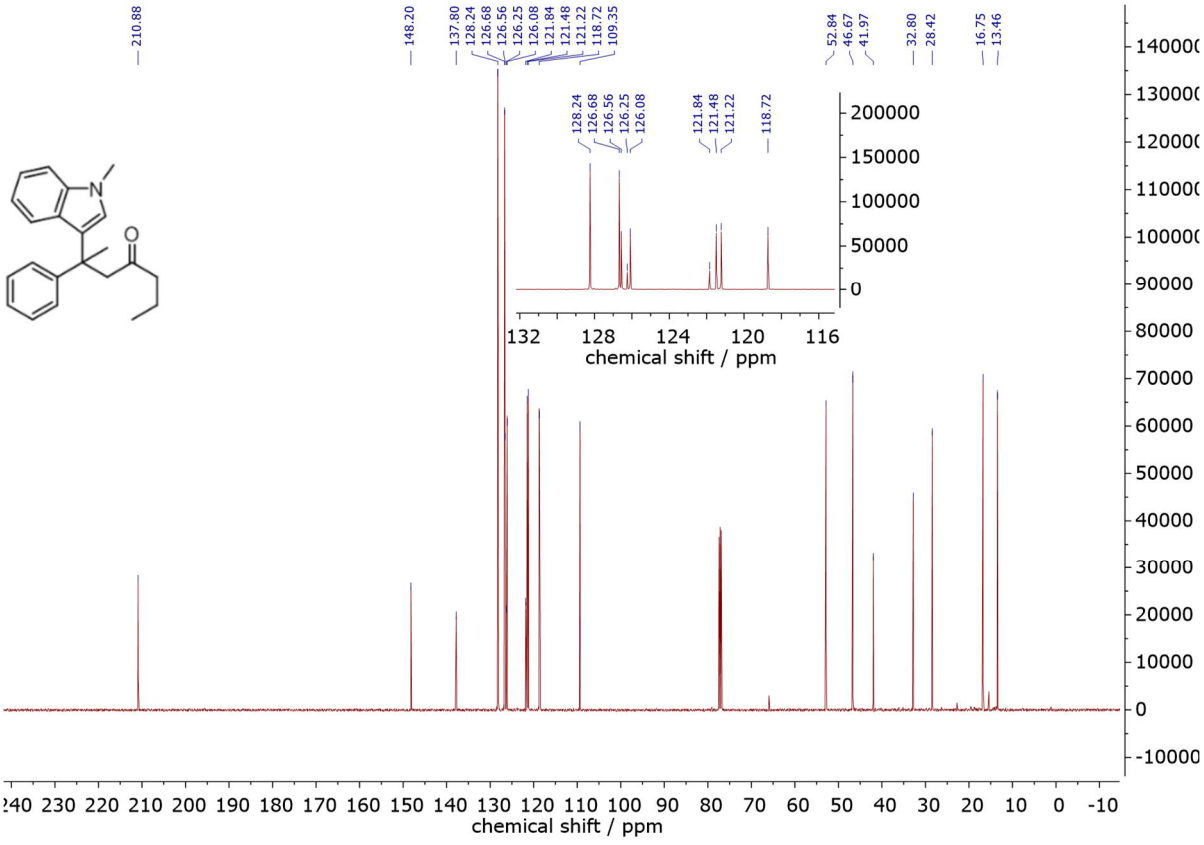
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **4k**:



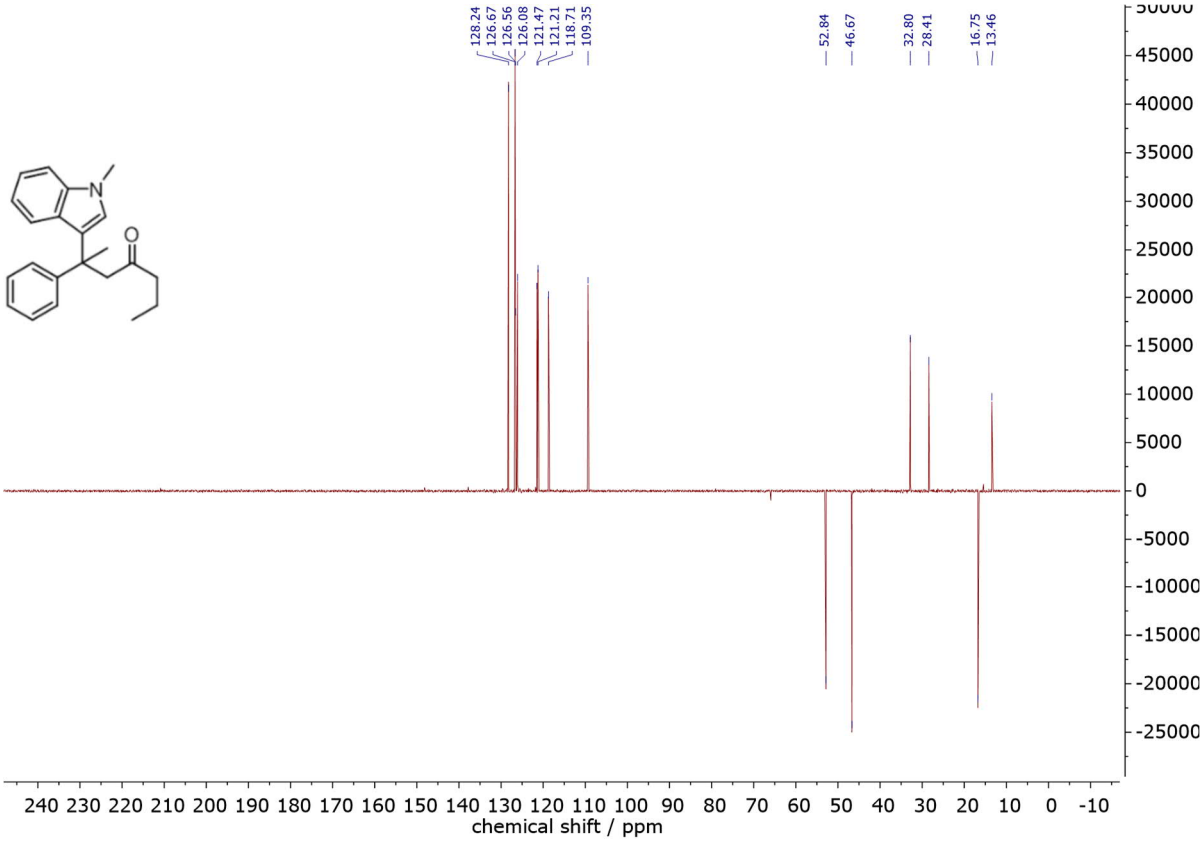
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **4l**:



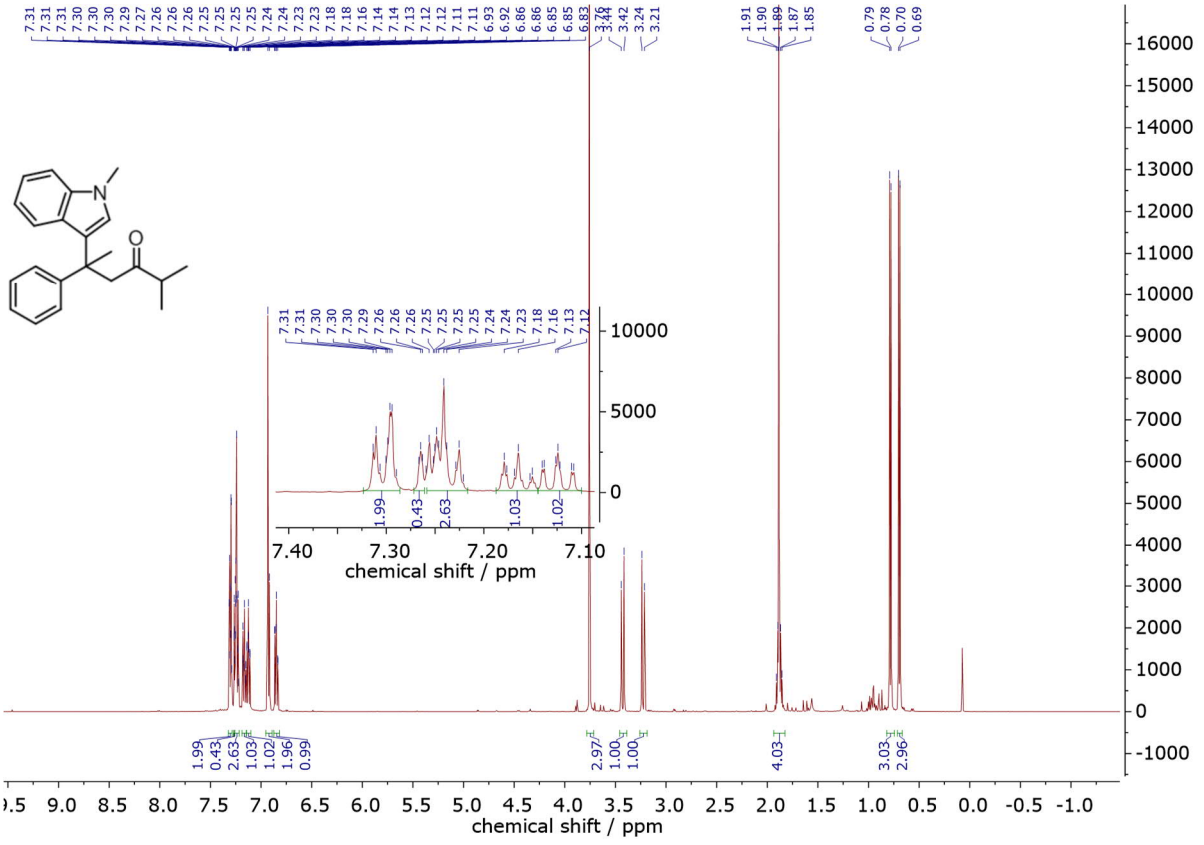
^{13}C{H} (126 MHz, $CDCl_3$) NMR spectrum of product **4l**:



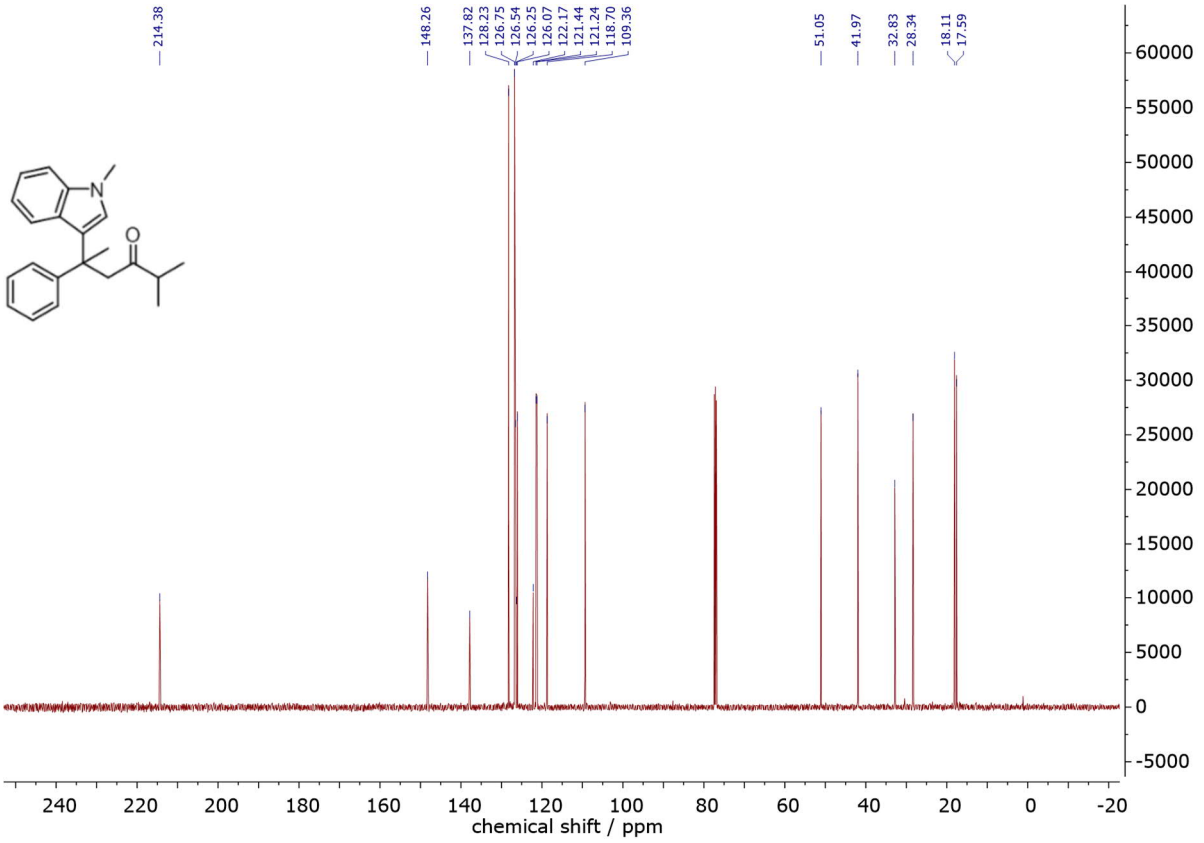
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **4l**:



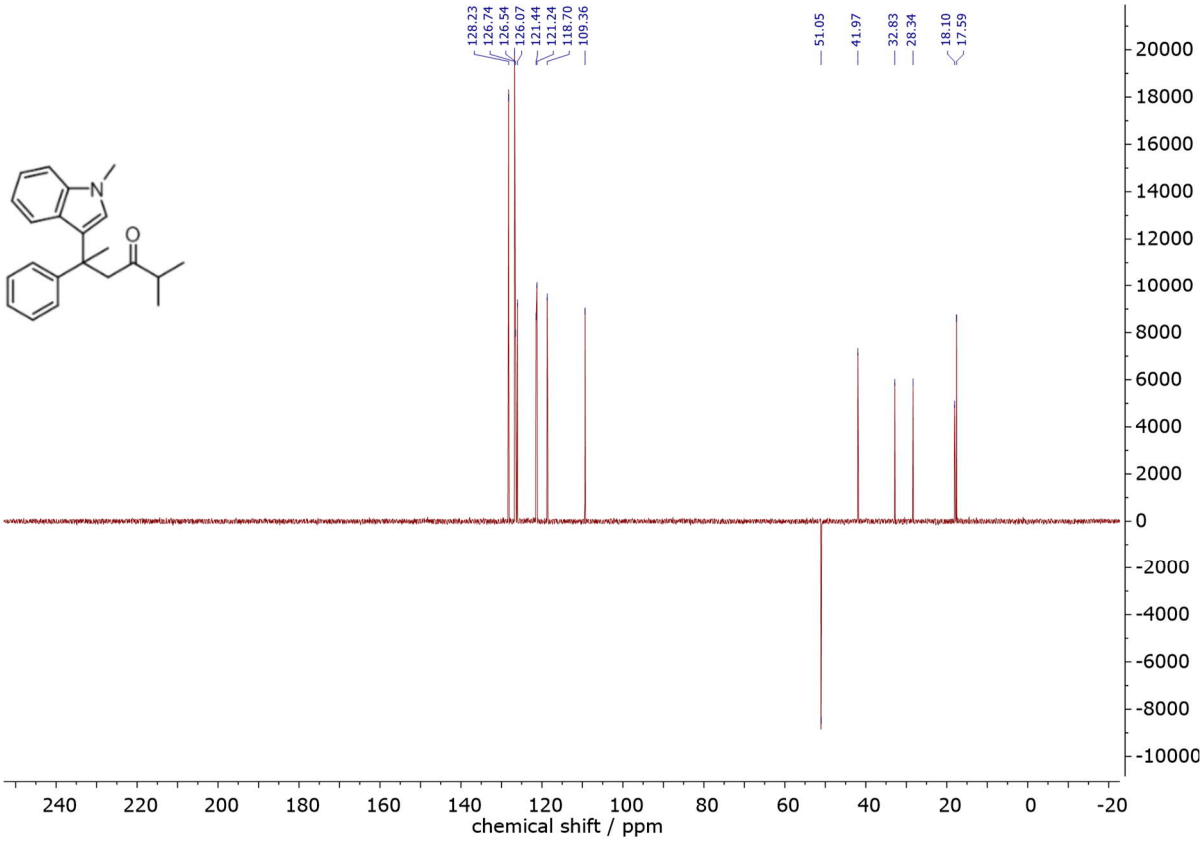
^1H (501 MHz, $CDCl_3$) NMR spectrum of product **4m**:



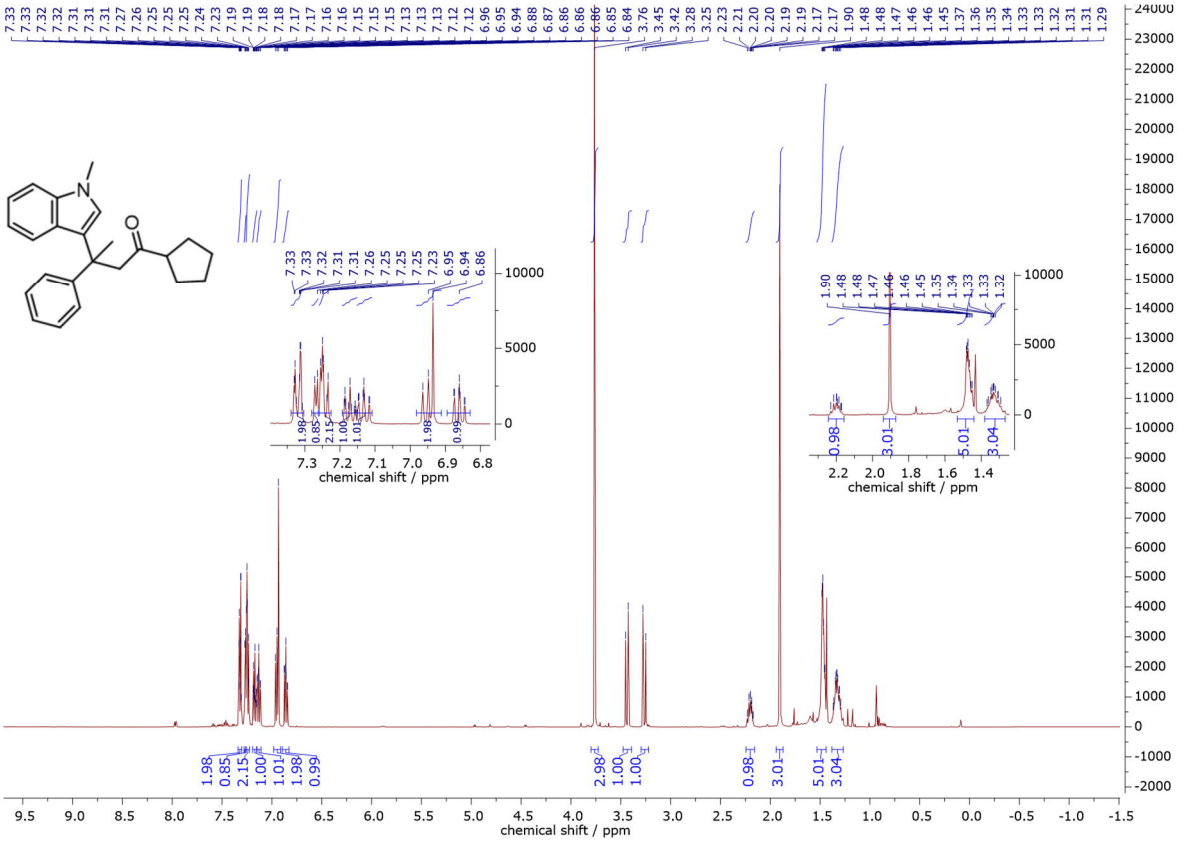
$^{13}C\{H\}$ (126 MHz, $CDCl_3$) NMR spectrum of product **4m**:



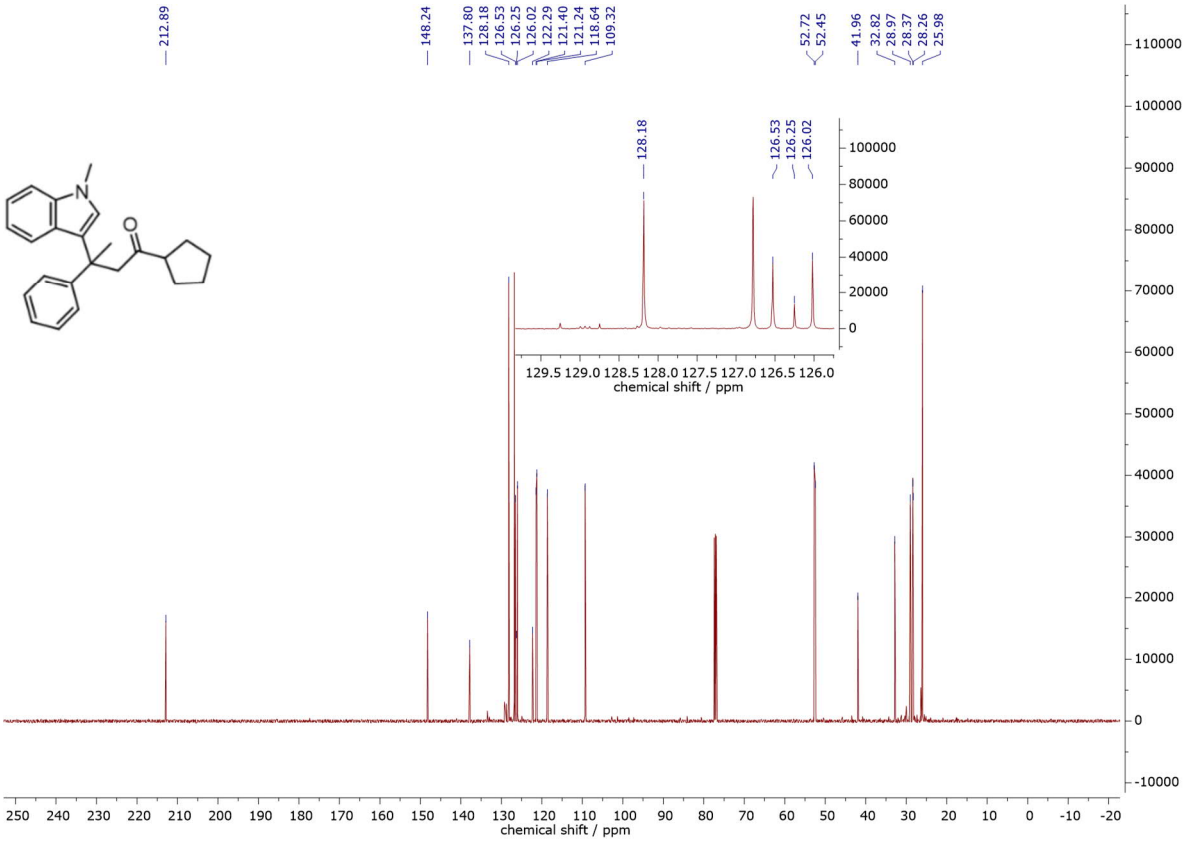
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **4m**:



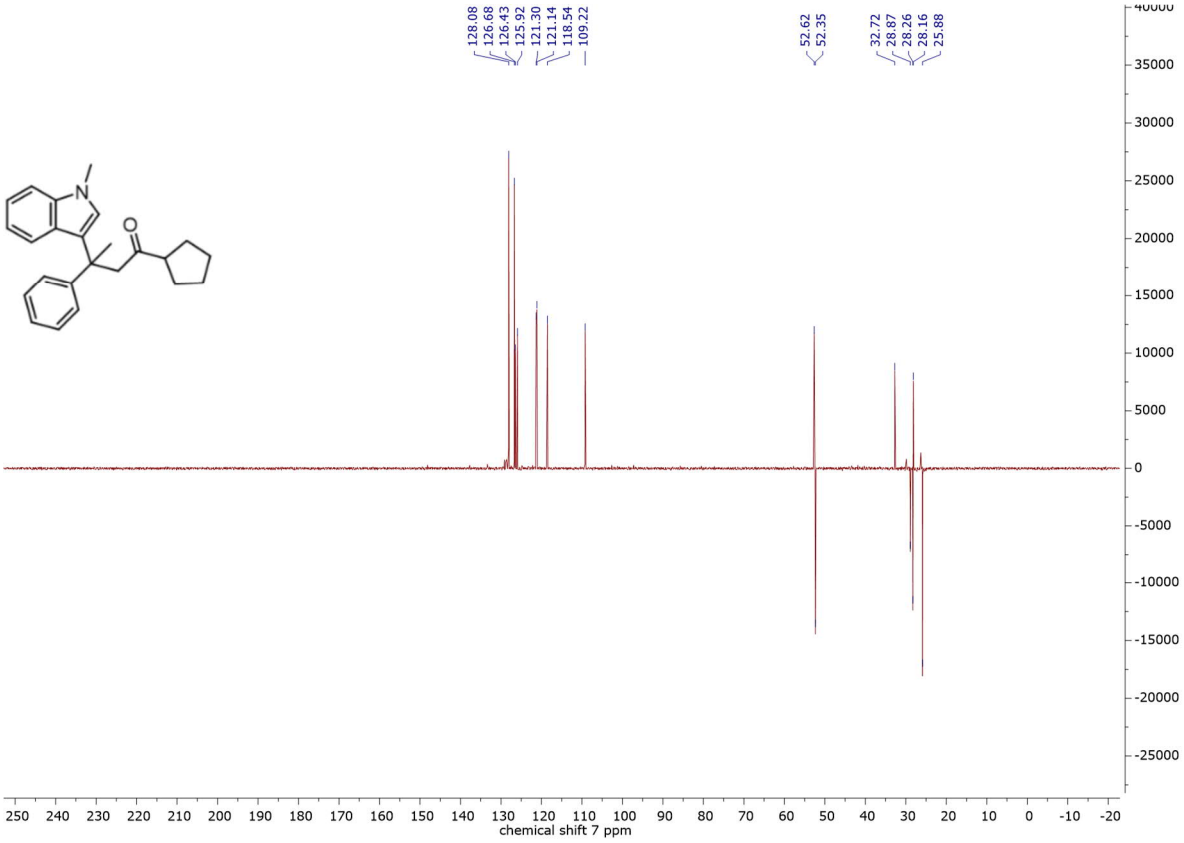
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **4n**:



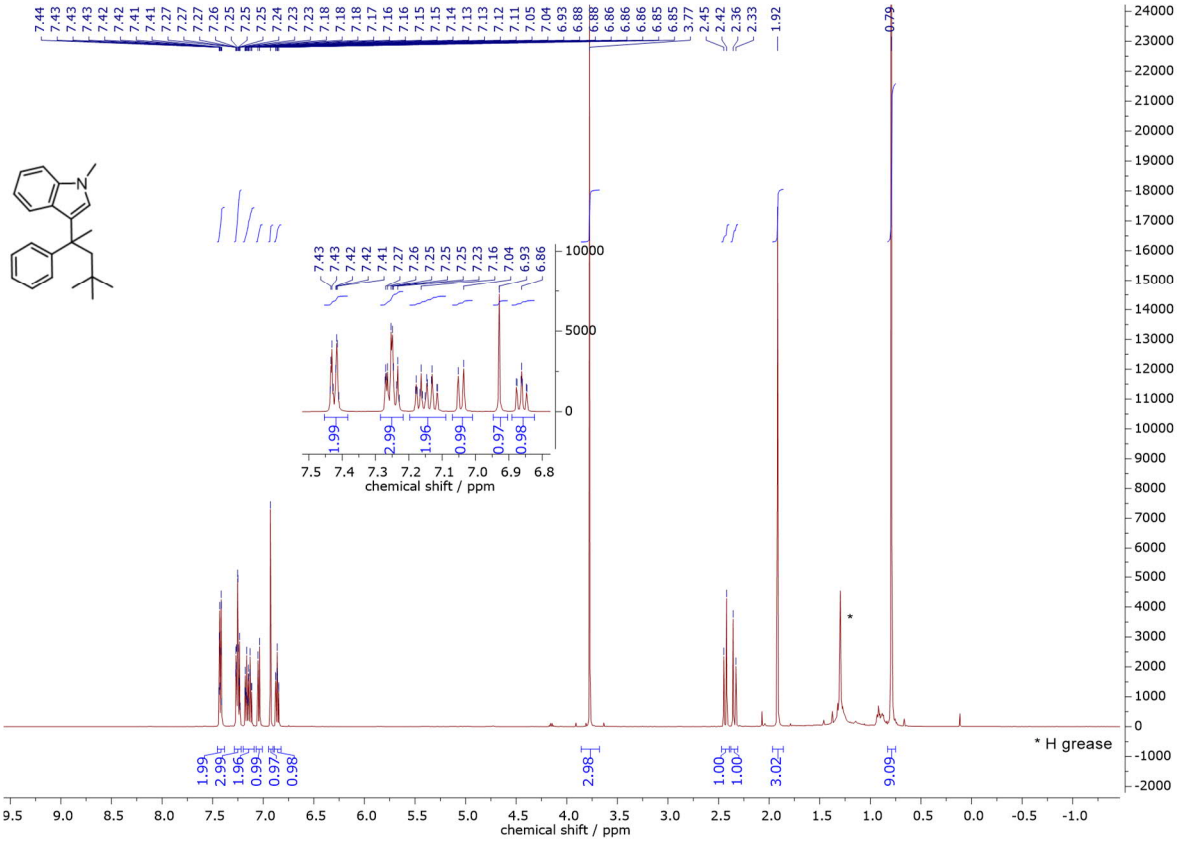
^{13}C{H} (126 MHz, $CDCl_3$) NMR spectrum of product **4n**:



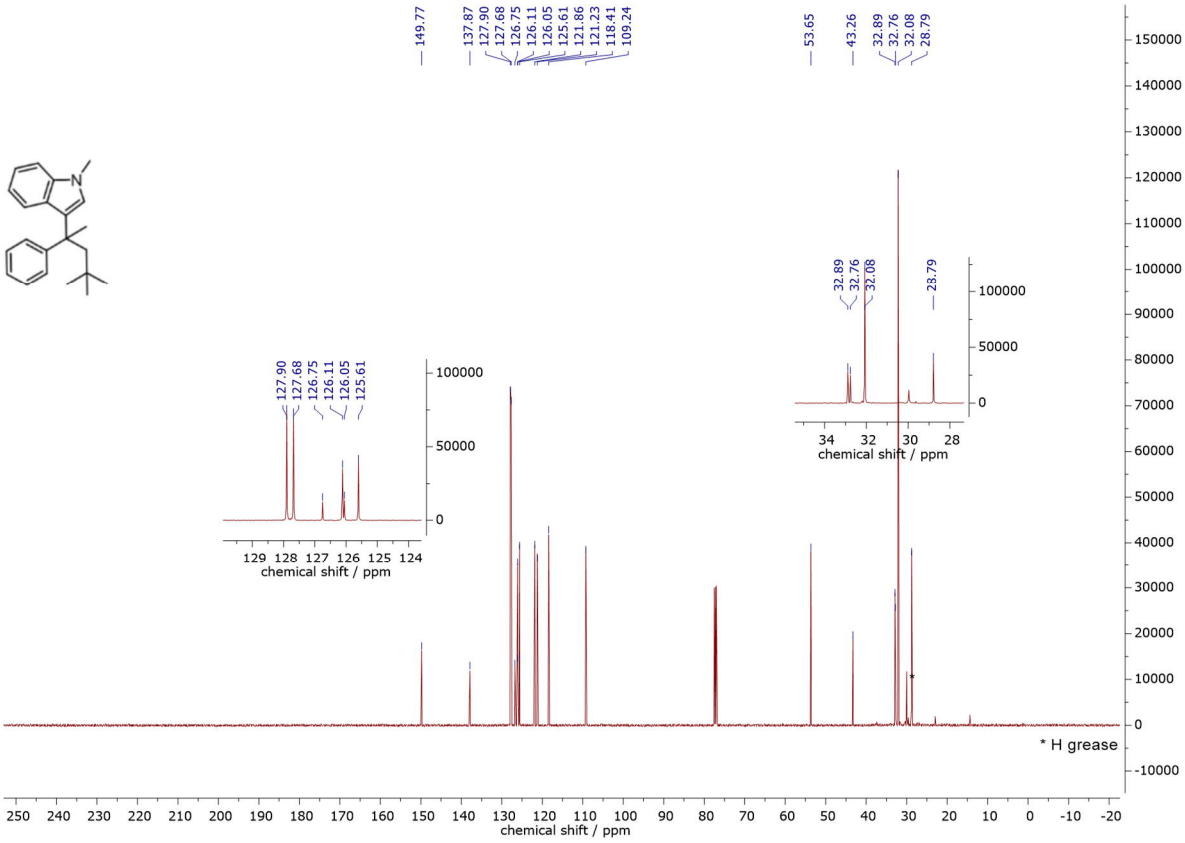
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **4n**:



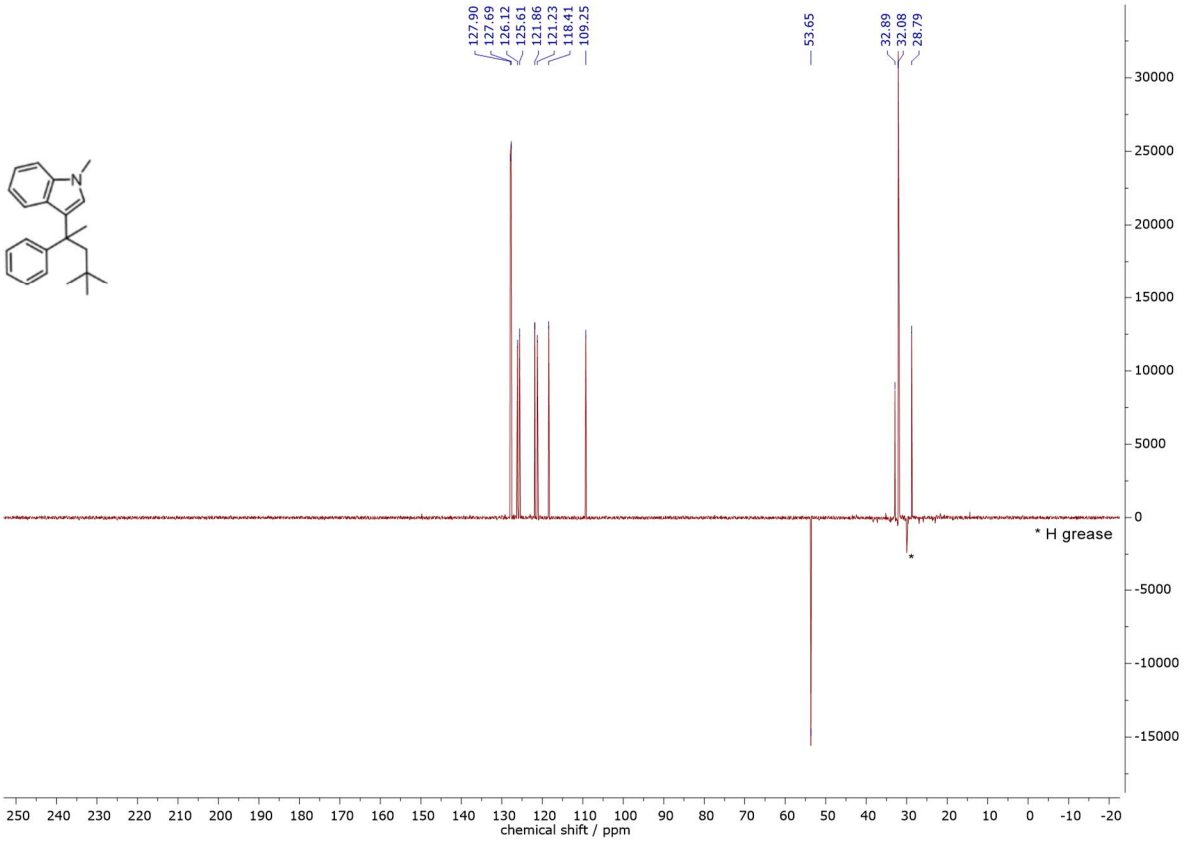
^1H (501 MHz, $CDCl_3$) NMR spectrum of product **5**:



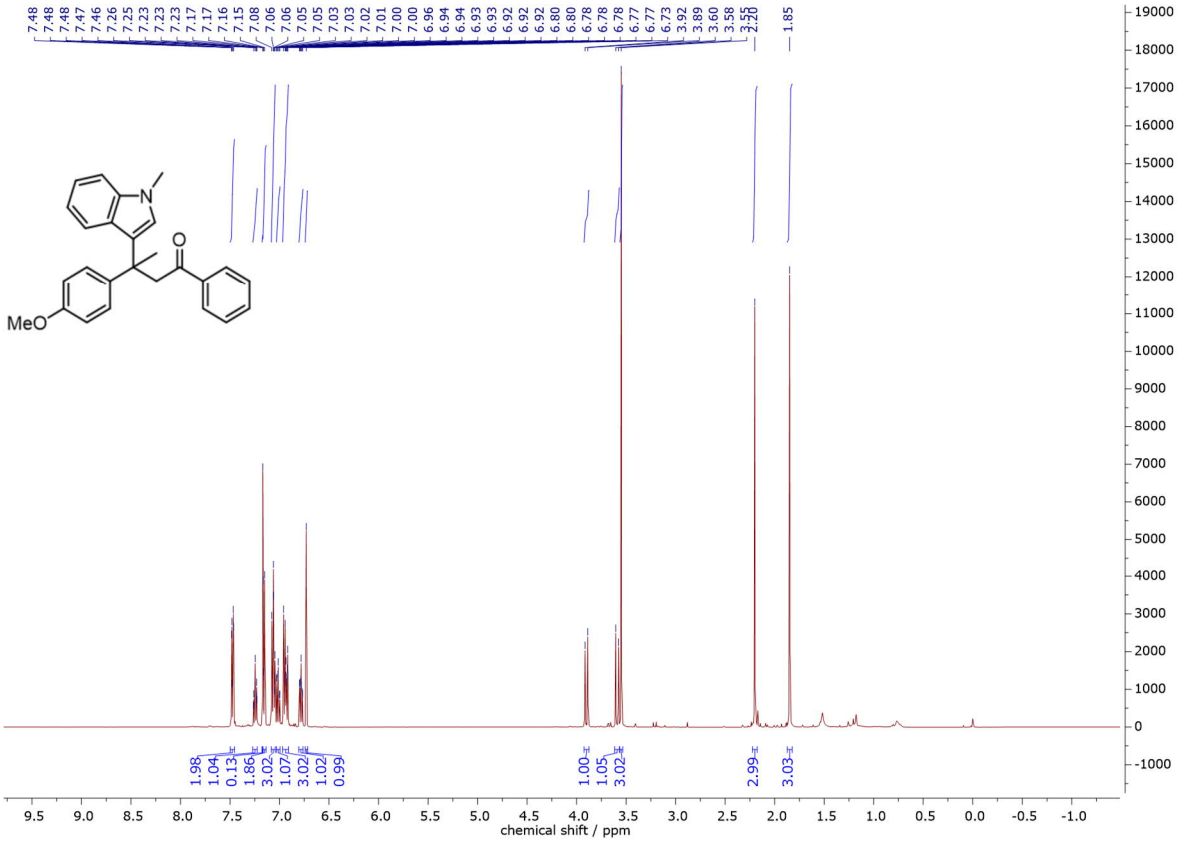
$^{13}C\{H\}$ (126 MHz, $CDCl_3$) NMR spectrum of product **5**:



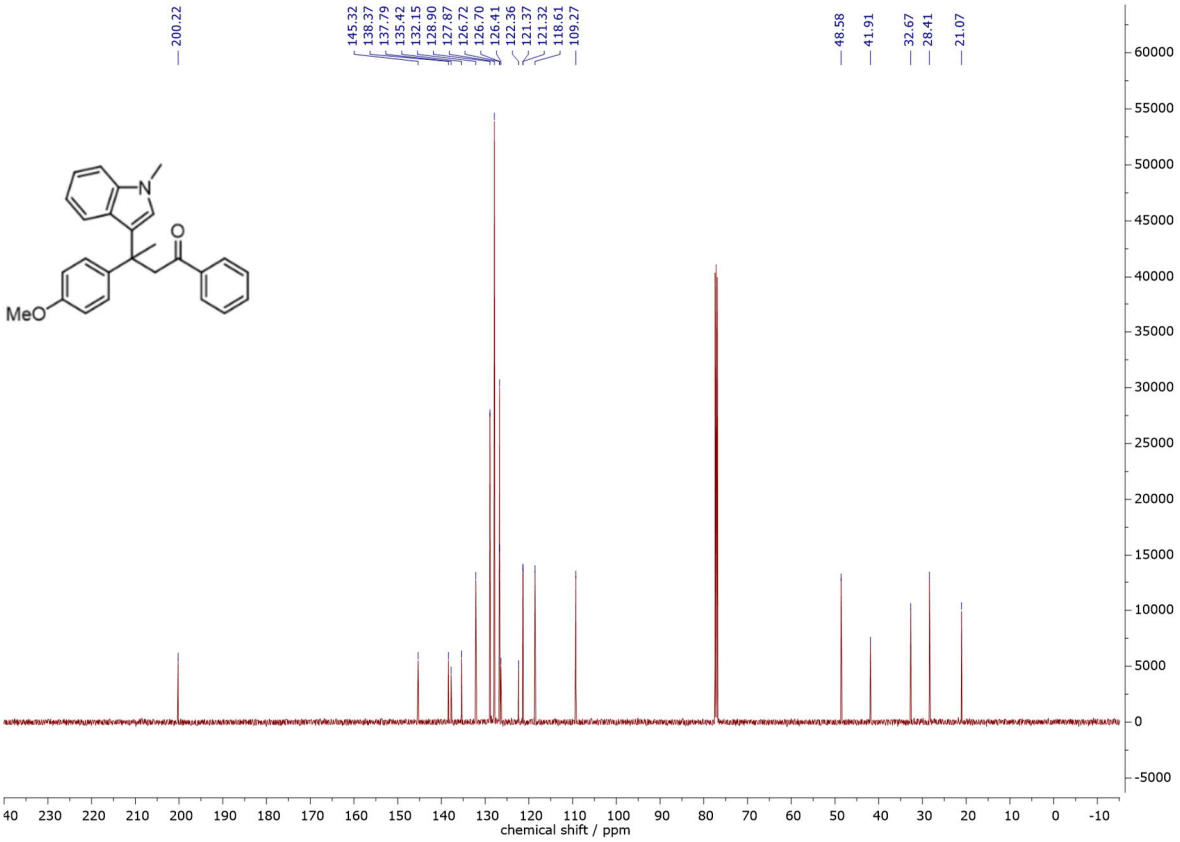
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **5**:



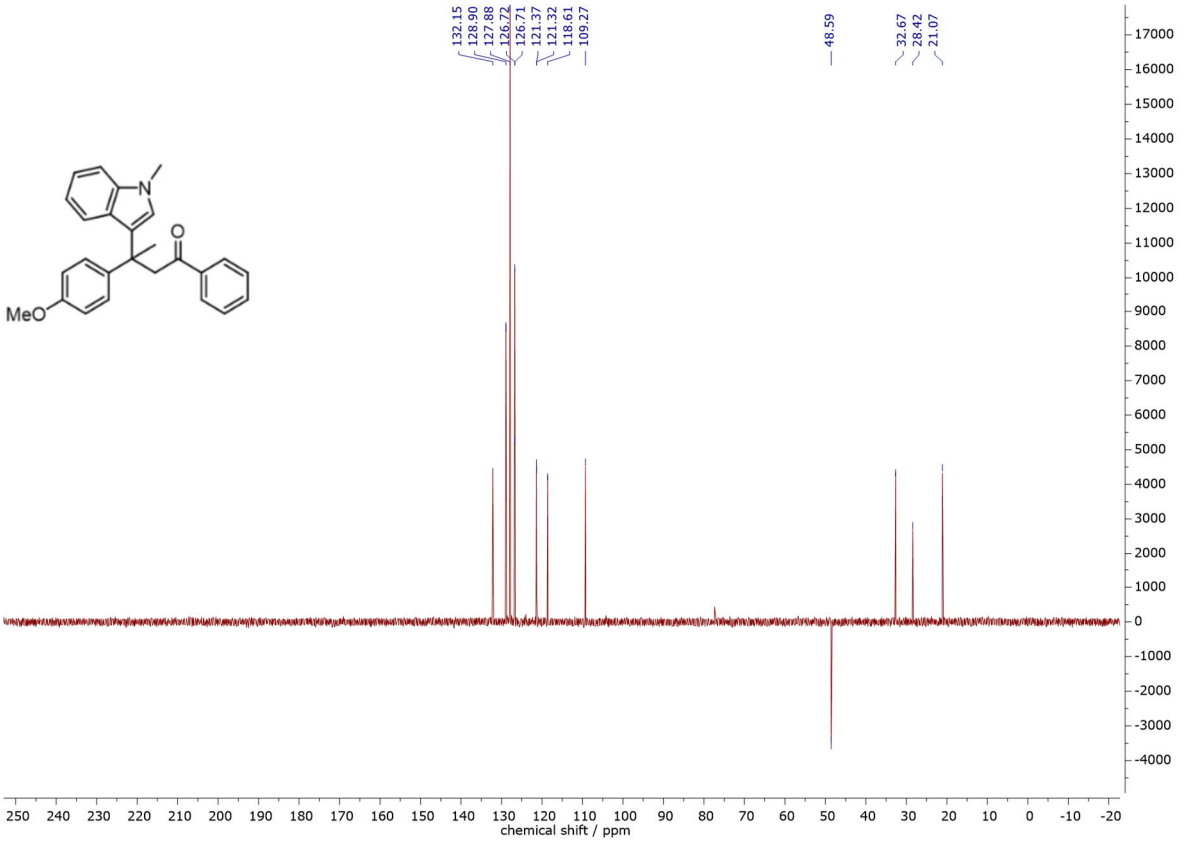
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **6a**:



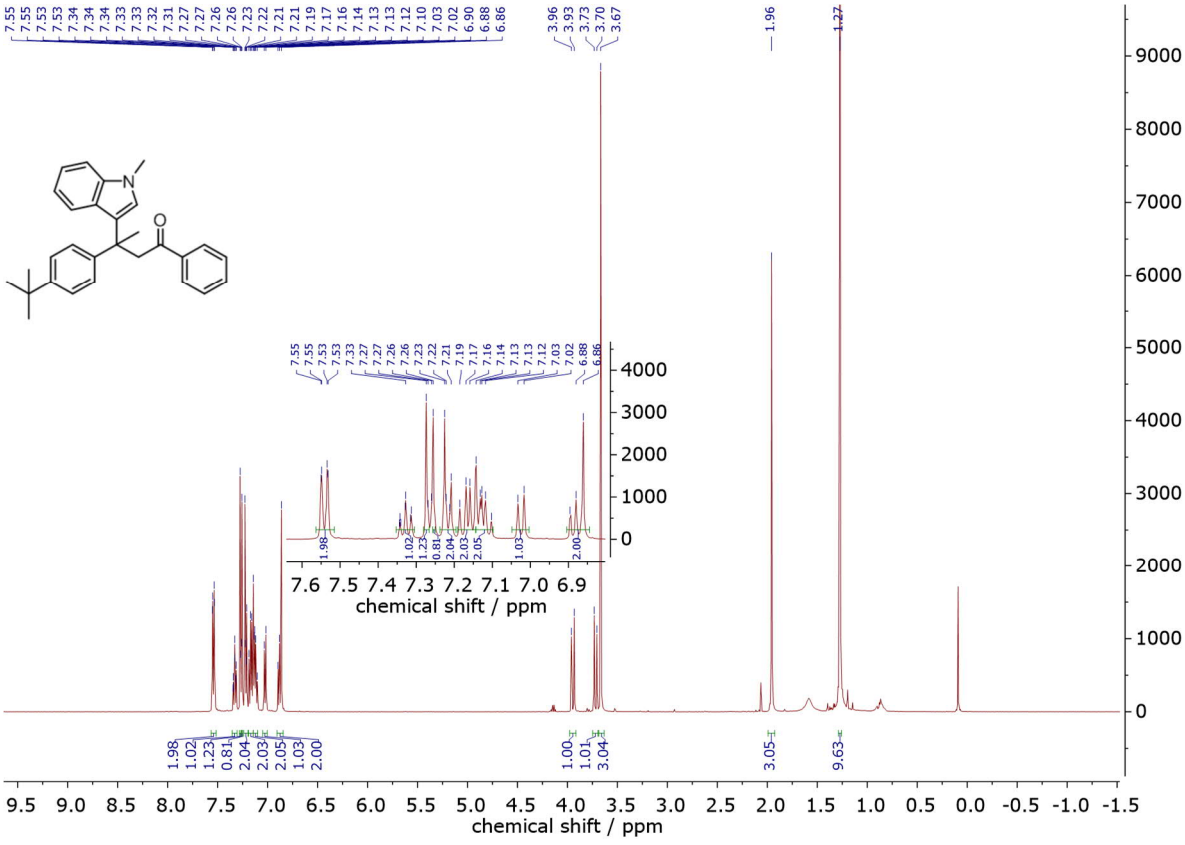
^{13}C{H} (126 MHz, $CDCl_3$) NMR spectrum of product **6a**:



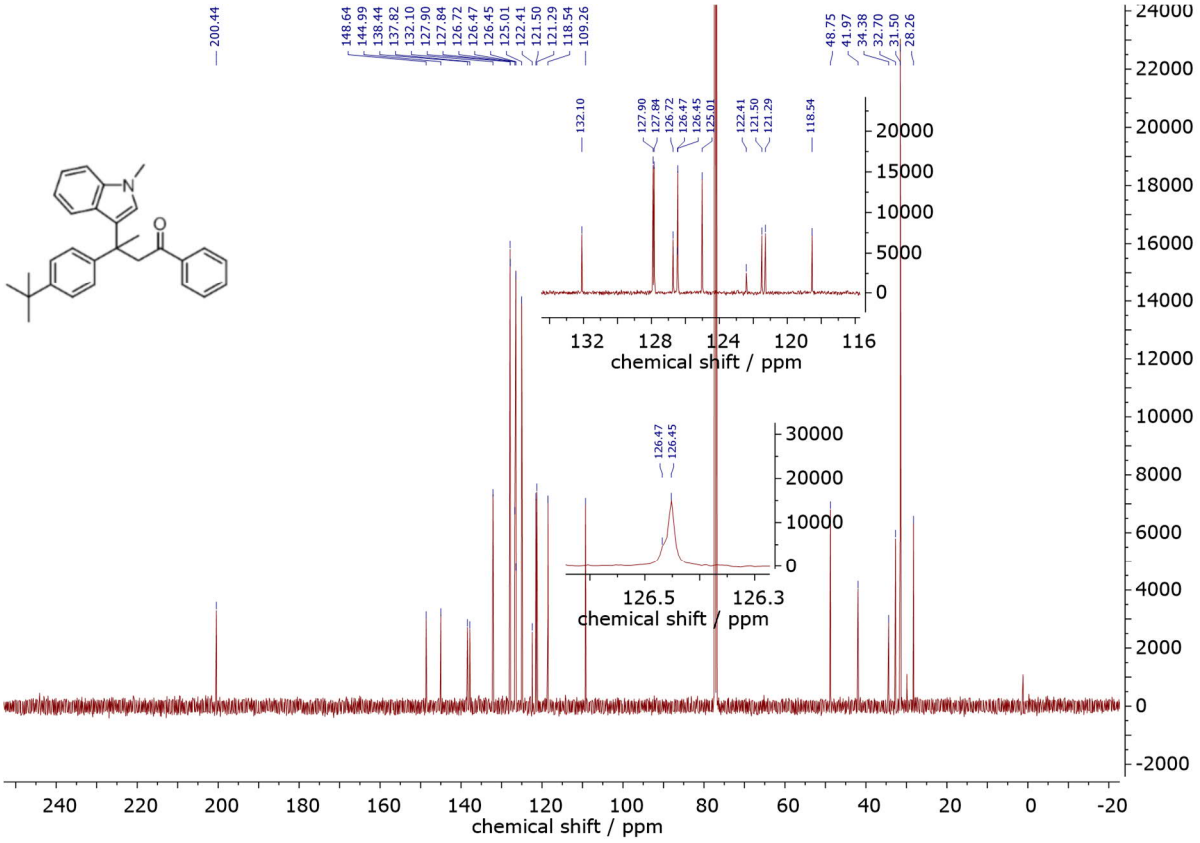
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **6a**:



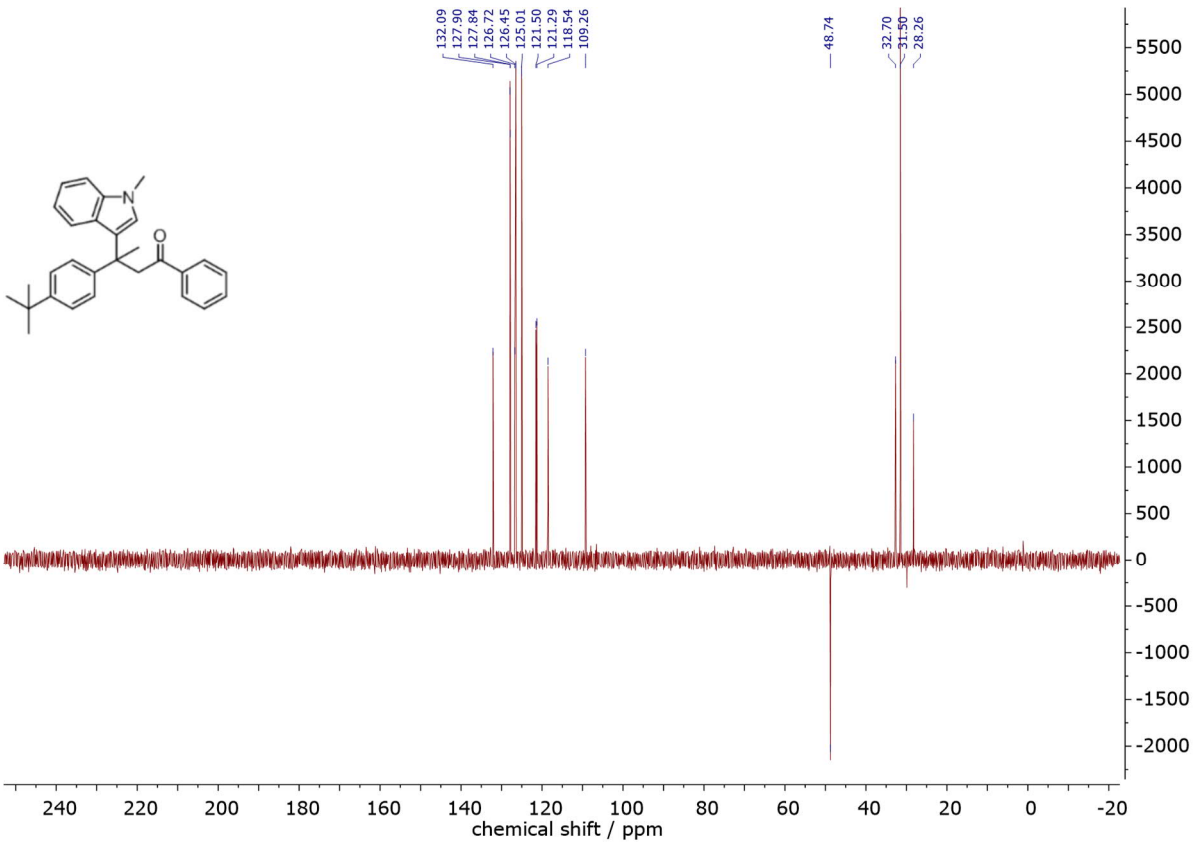
^1H (501 MHz, $CDCl_3$) NMR spectrum of product **6b**:



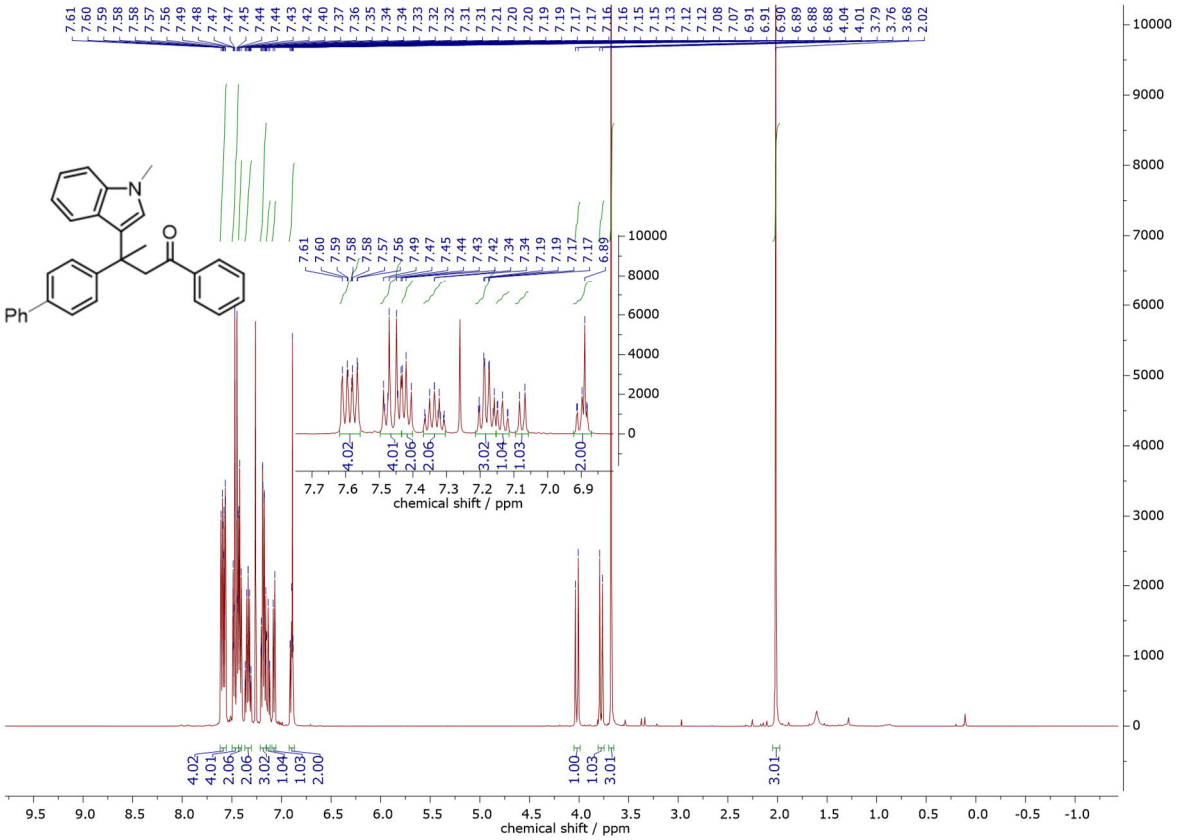
$^{13}C\{H\}$ (126 MHz, $CDCl_3$) NMR spectrum of product **6b**:



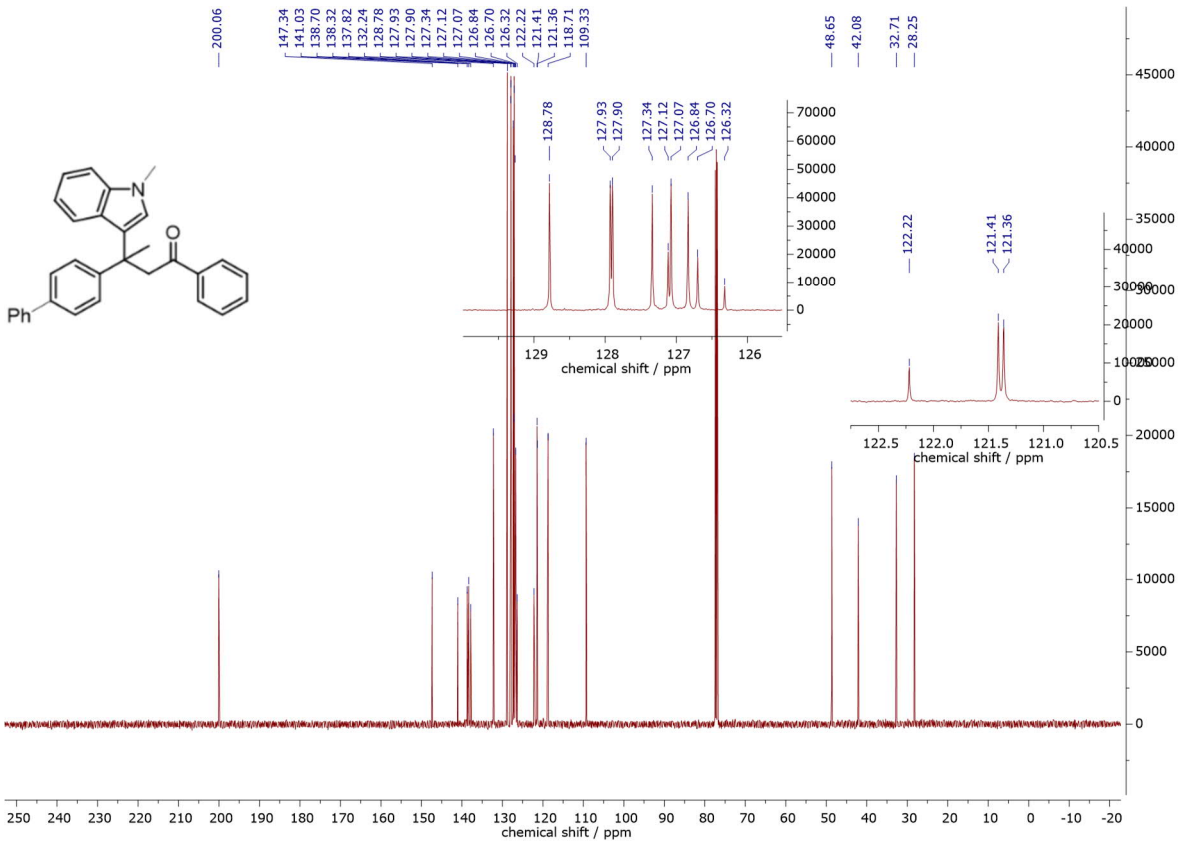
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **6b**:



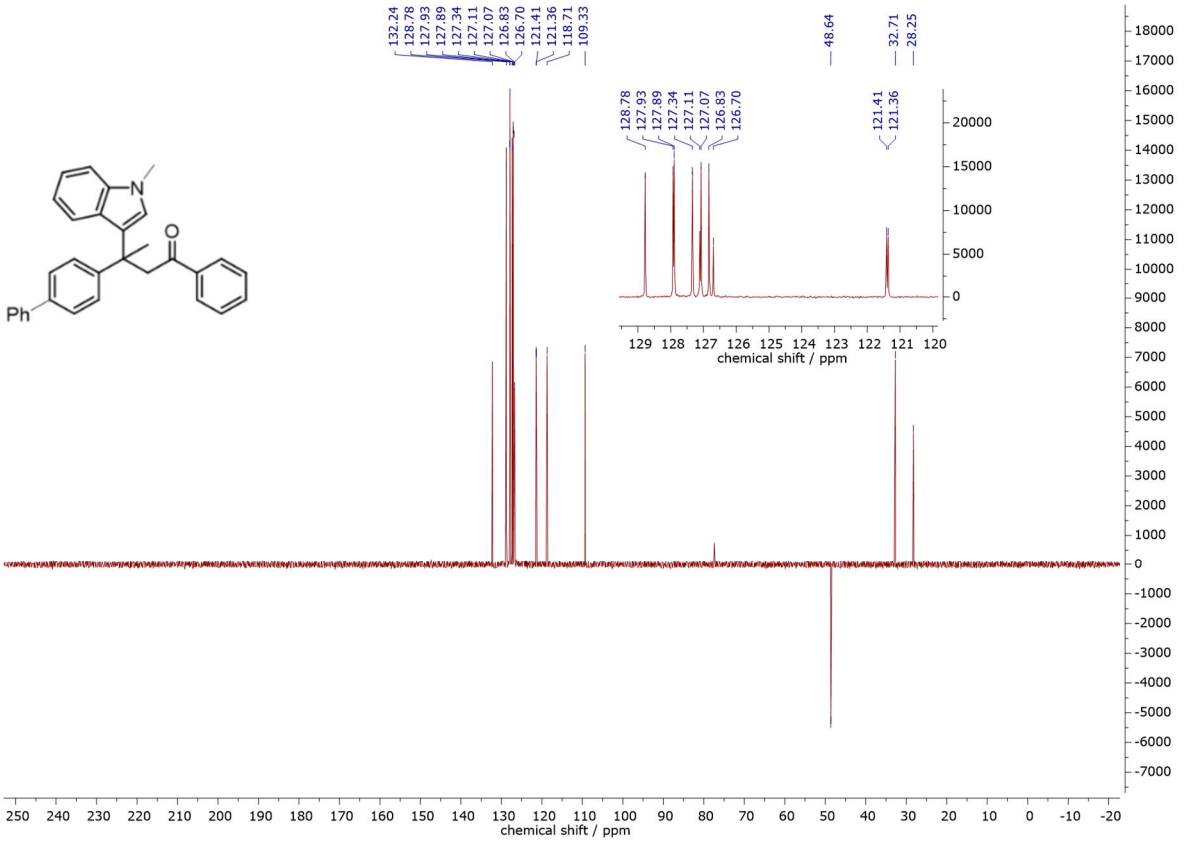
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **6c**:



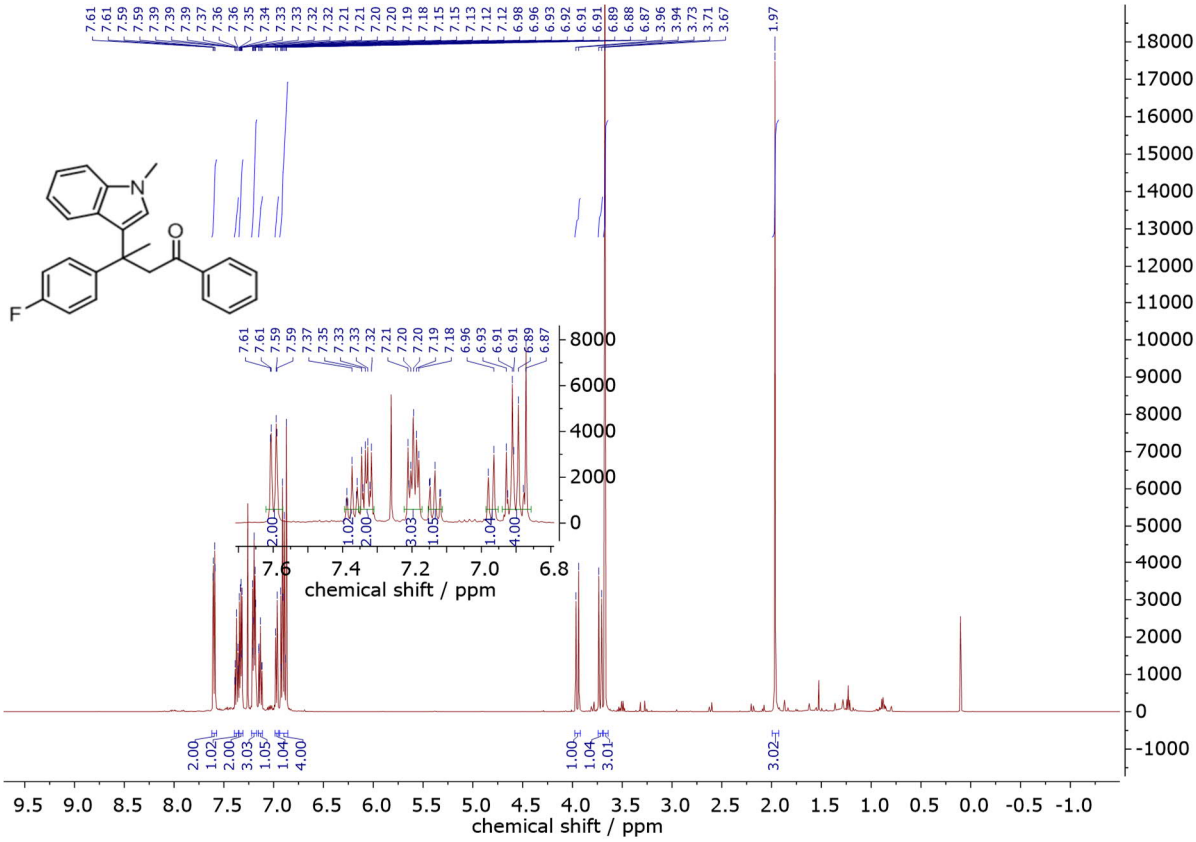
^{13}C{H} (126 MHz, $CDCl_3$) NMR spectrum of product **6c**:



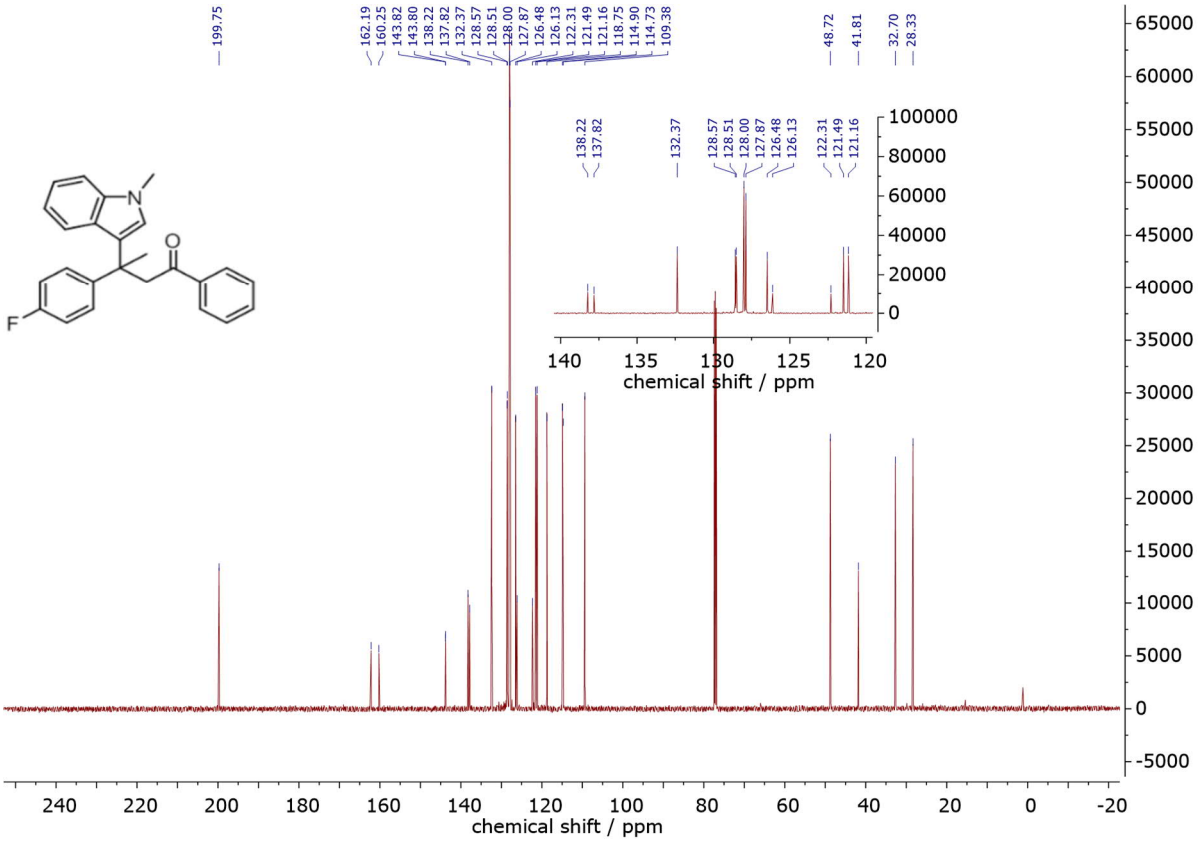
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **6c**:



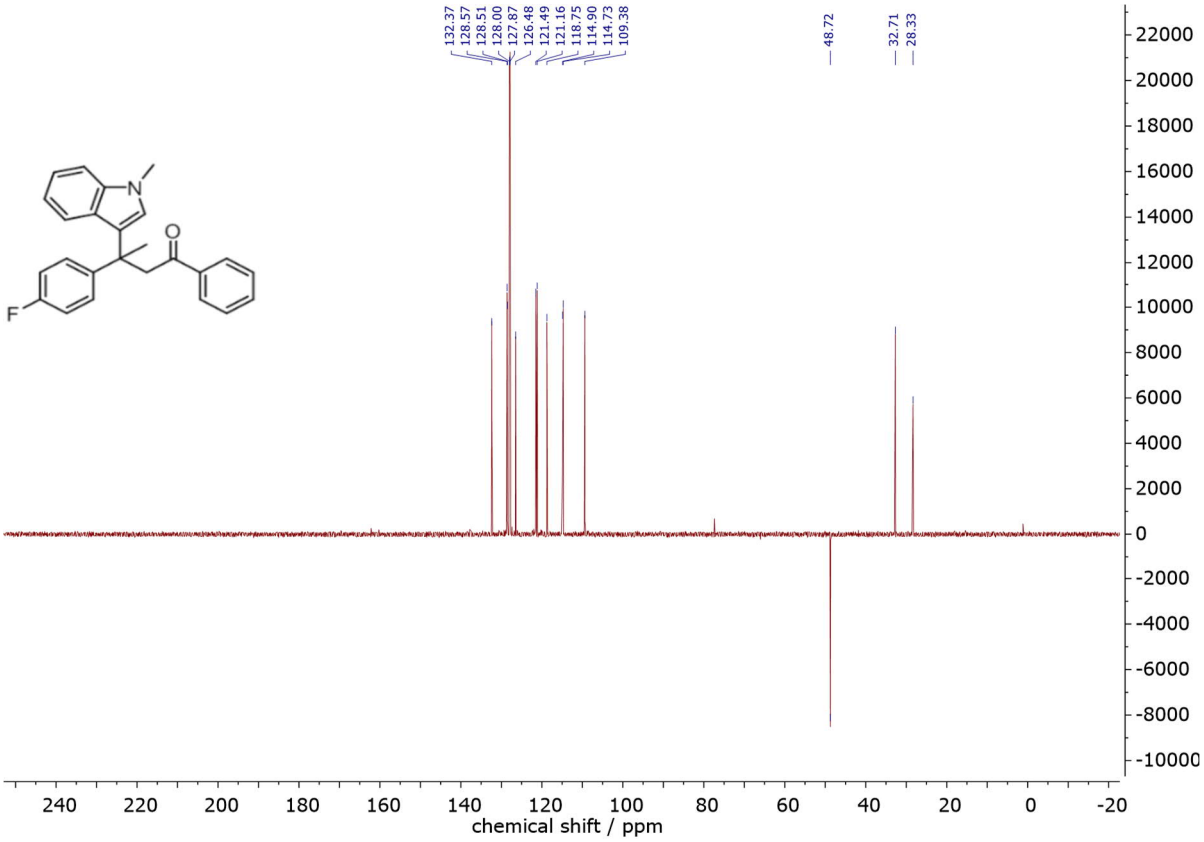
^1H (501 MHz, $CDCl_3$) NMR spectrum of product **6d**:



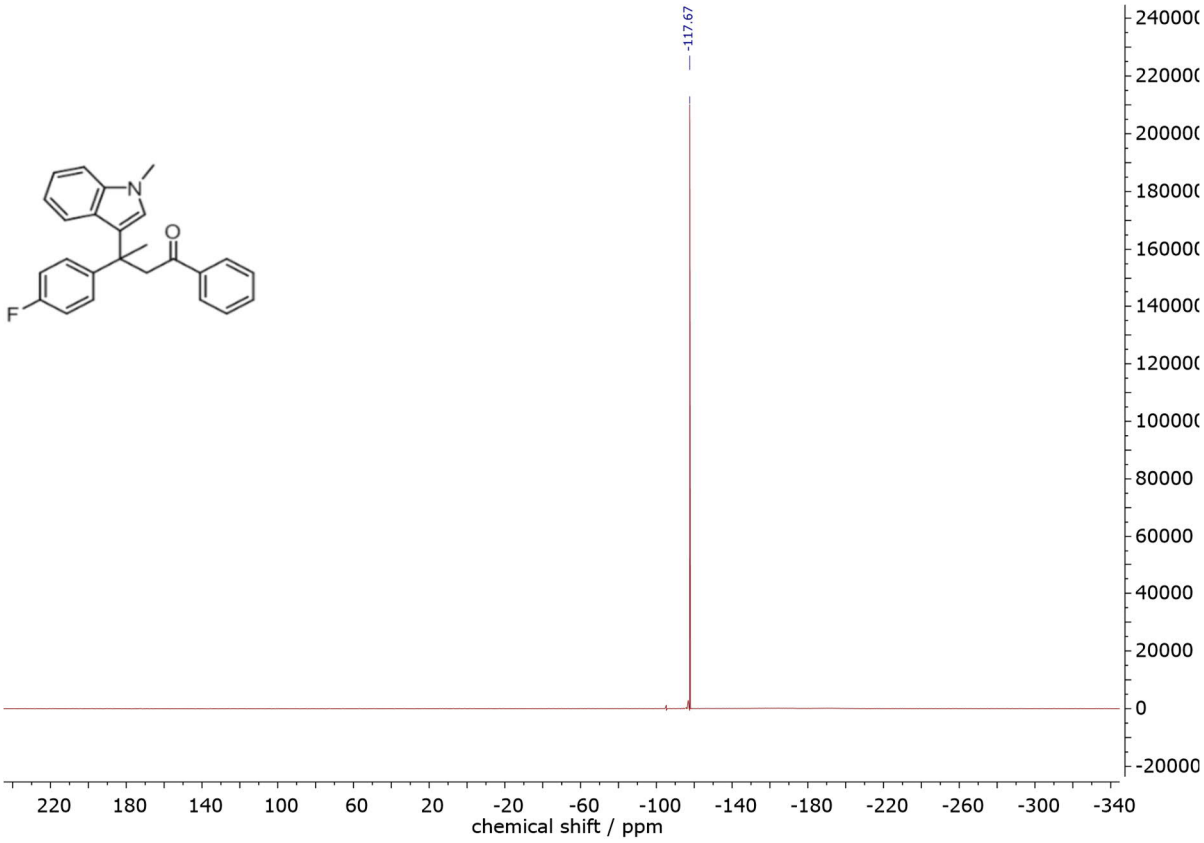
$^{13}C\{H\}$ (126 MHz, $CDCl_3$) NMR spectrum of product **6d**:



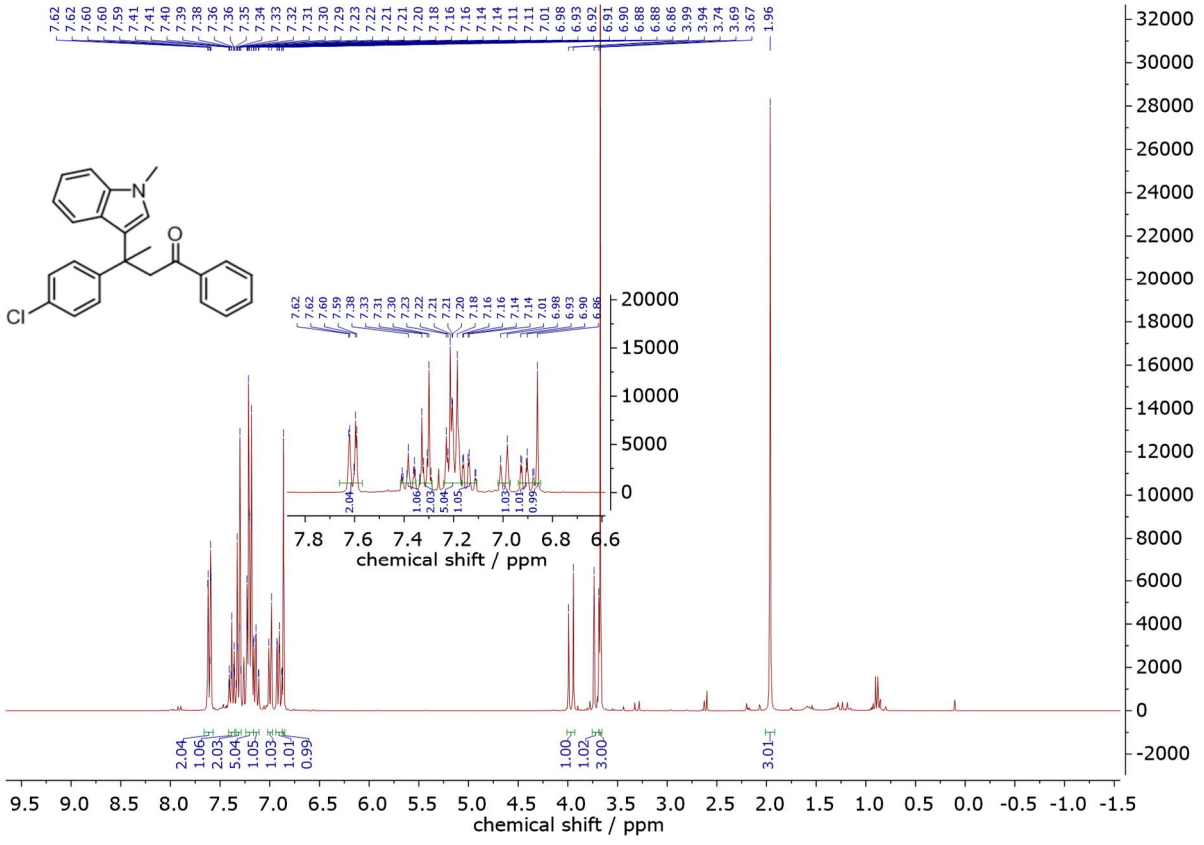
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **6d**:



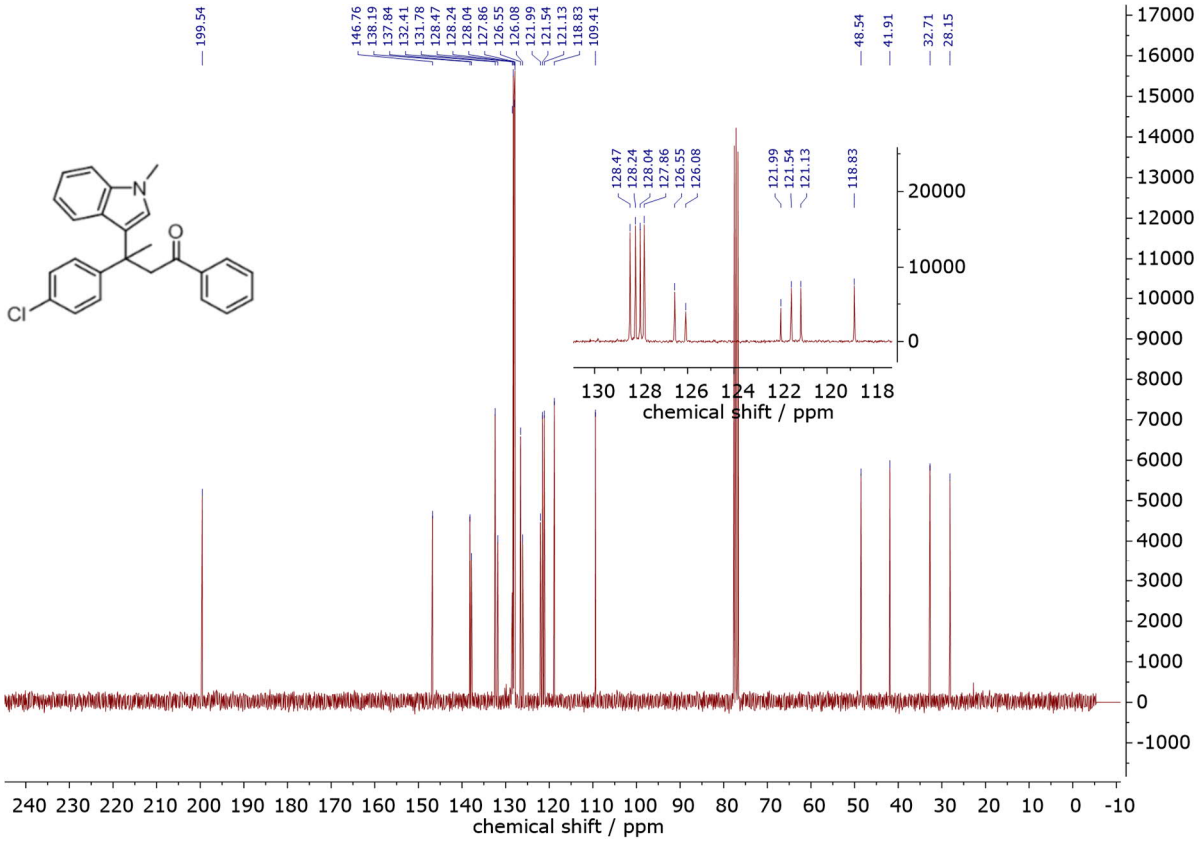
^{19}F (471 MHz, $CDCl_3$) NMR spectrum of product **6d**:



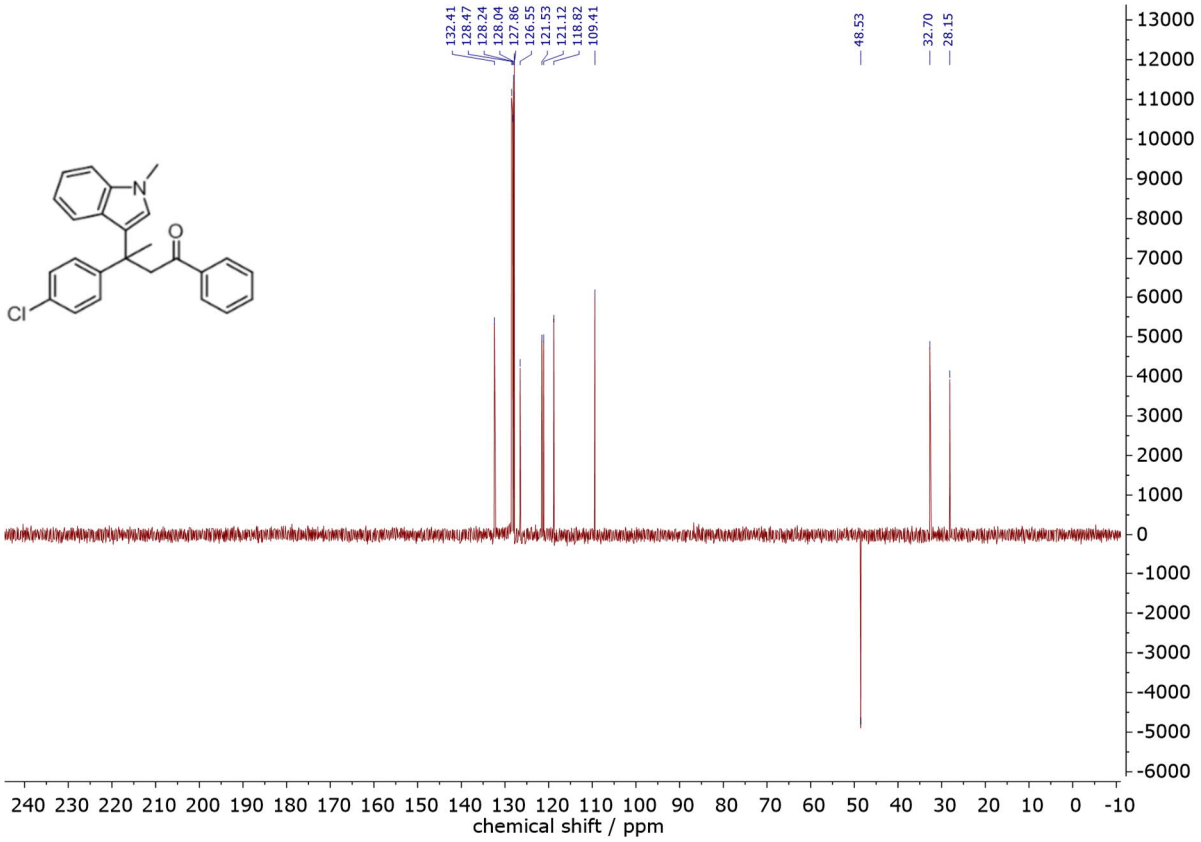
^{1}H (300 MHz, $CDCl_3$) NMR spectrum of product **6e**:



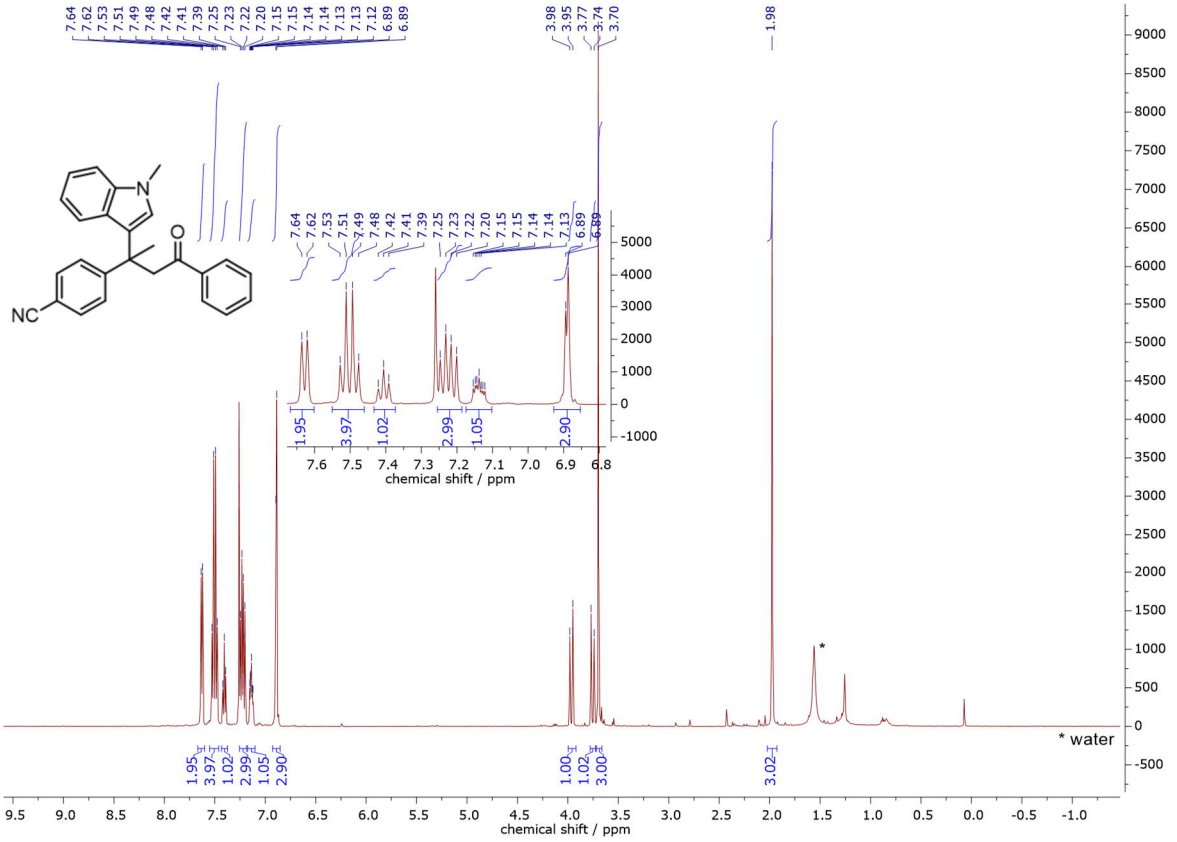
$^{13}C\{H\}$ (75 MHz, $CDCl_3$) NMR spectrum of product **6e**:



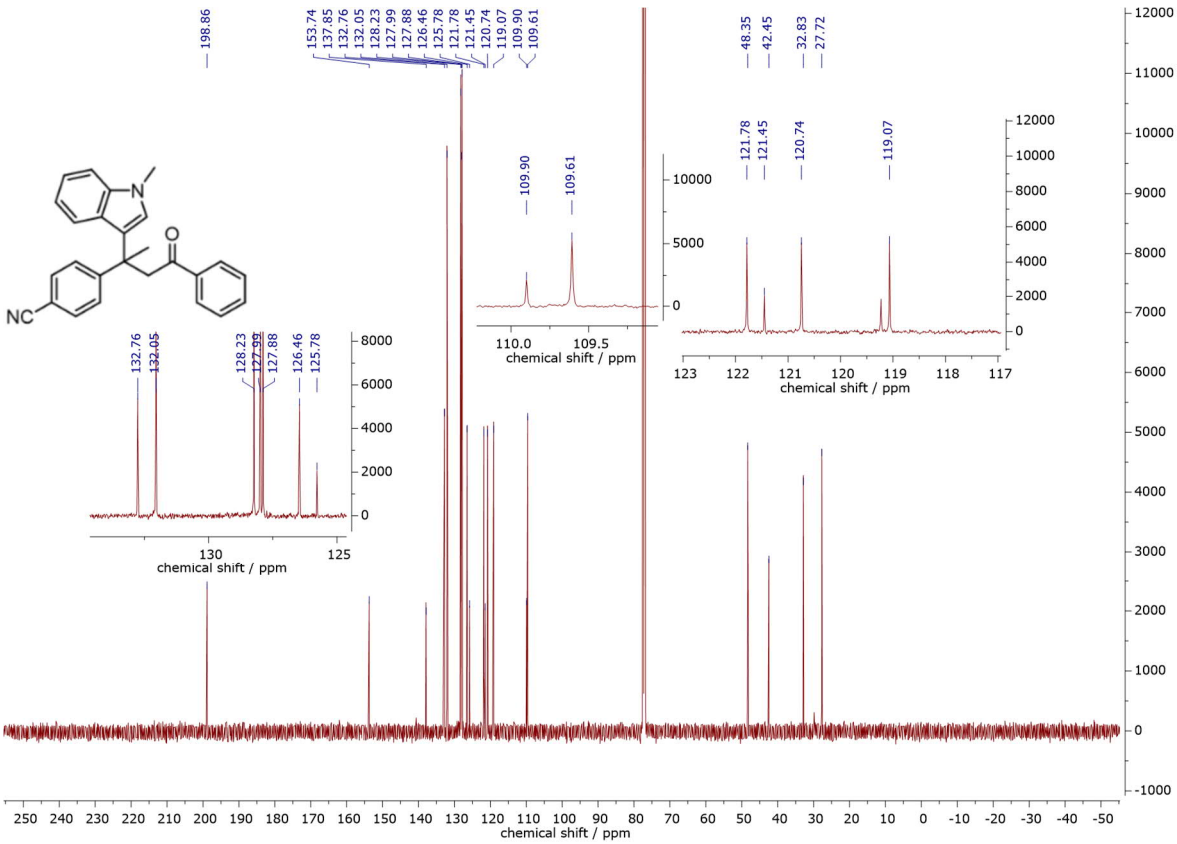
DEPT135 {H} (75 MHz, $CDCl_3$) NMR spectrum of product **6e**:



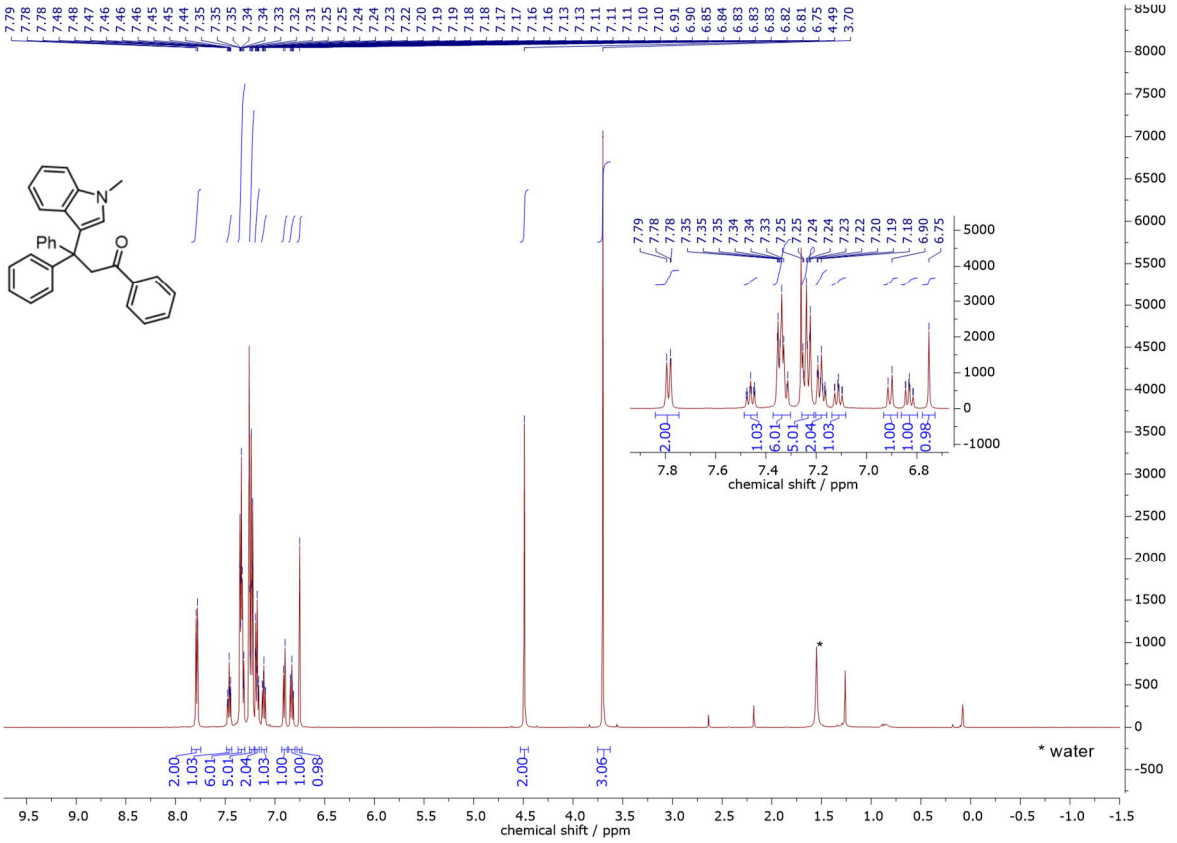
^{1}H (500 MHz, $CDCl_3$) NMR spectrum of product **6f**:



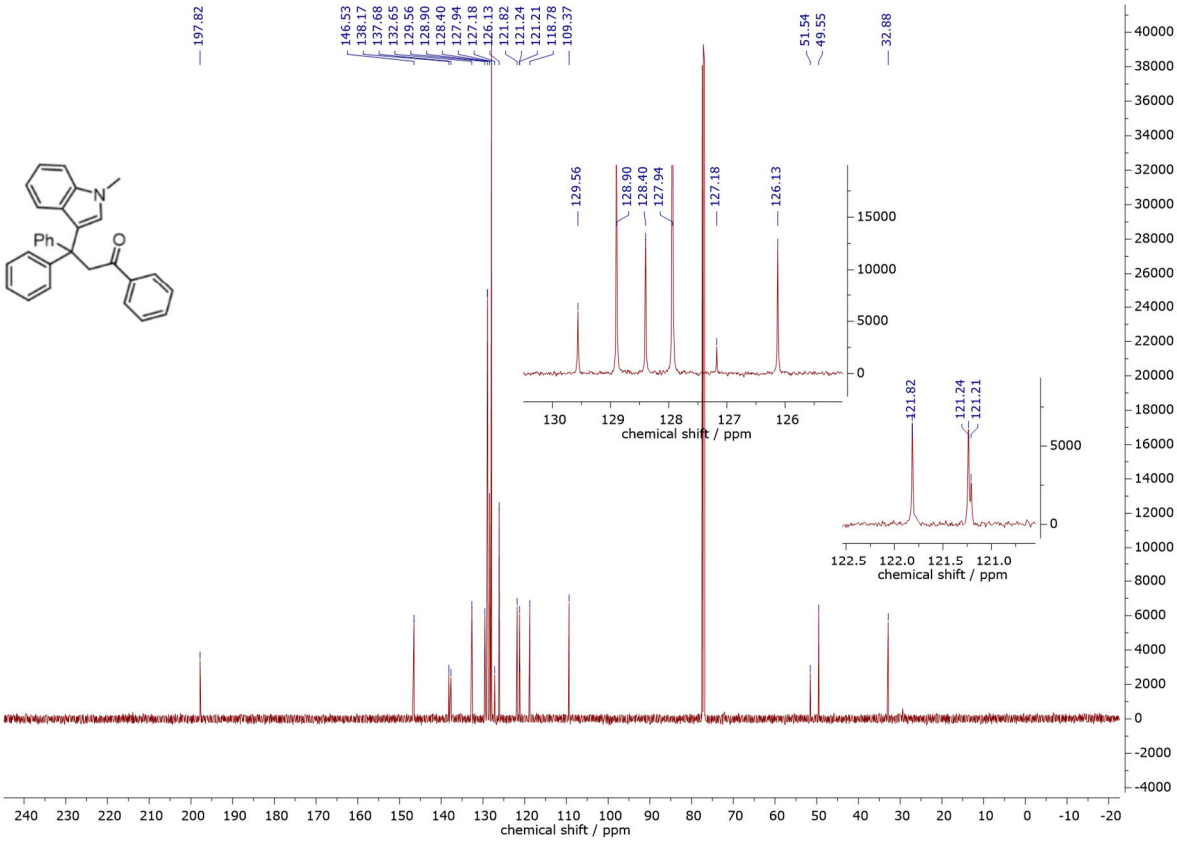
^{13}C{H} (126 MHz, $CDCl_3$) NMR spectrum of product **6f**:



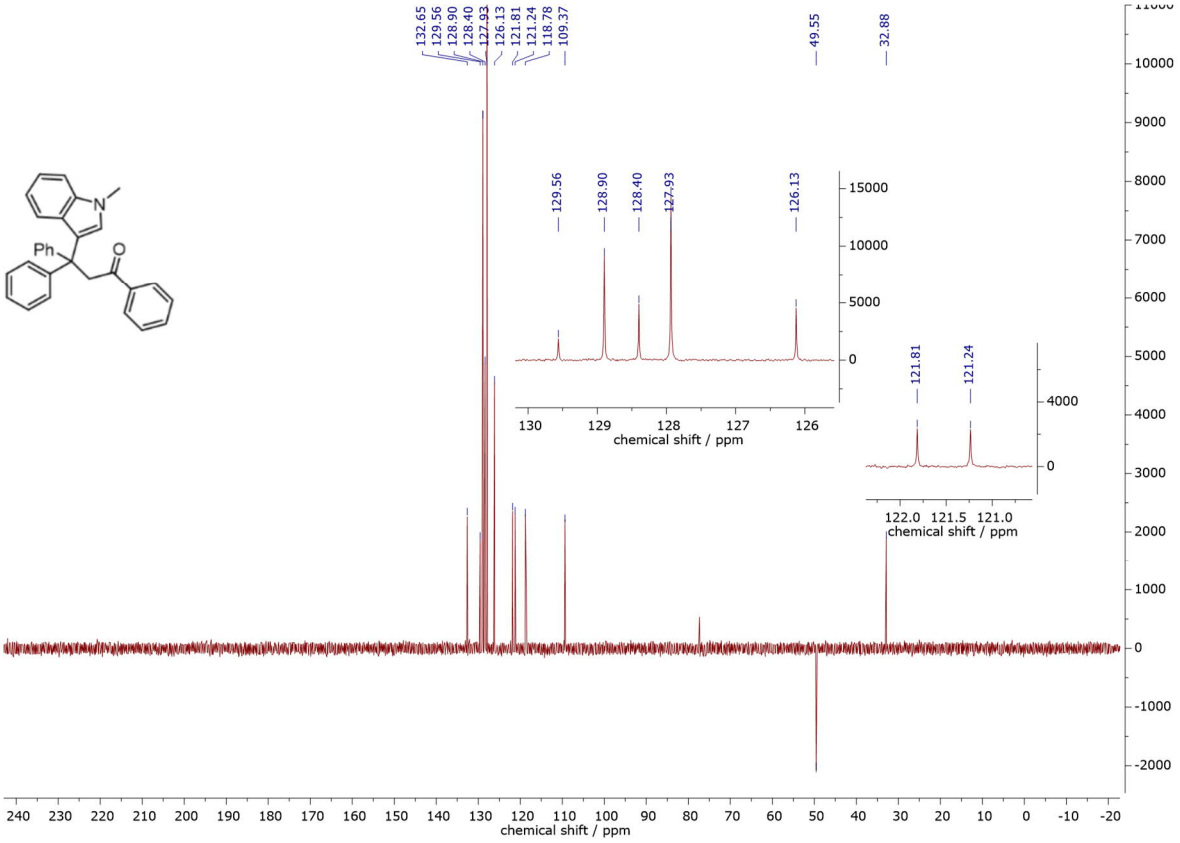
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **7a**:



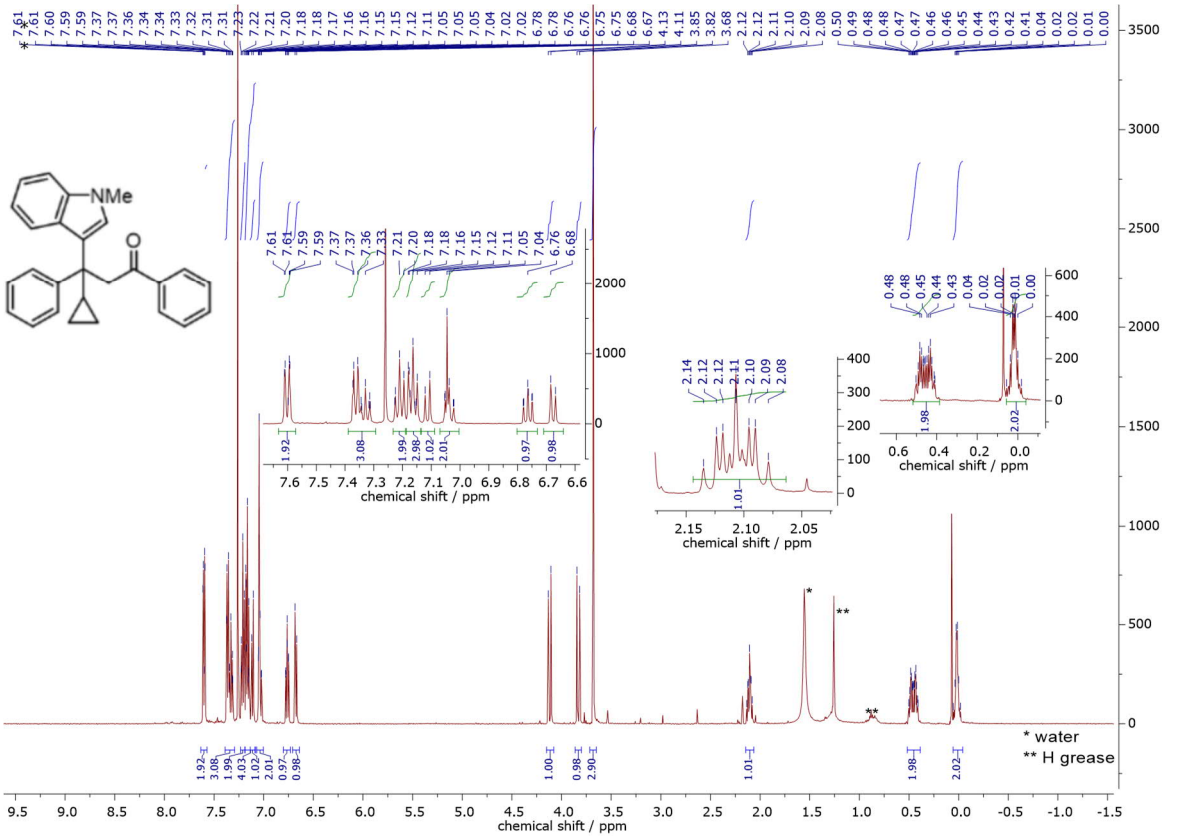
^{13}C{H} (126 MHz, $CDCl_3$) NMR spectrum of product **7a**:



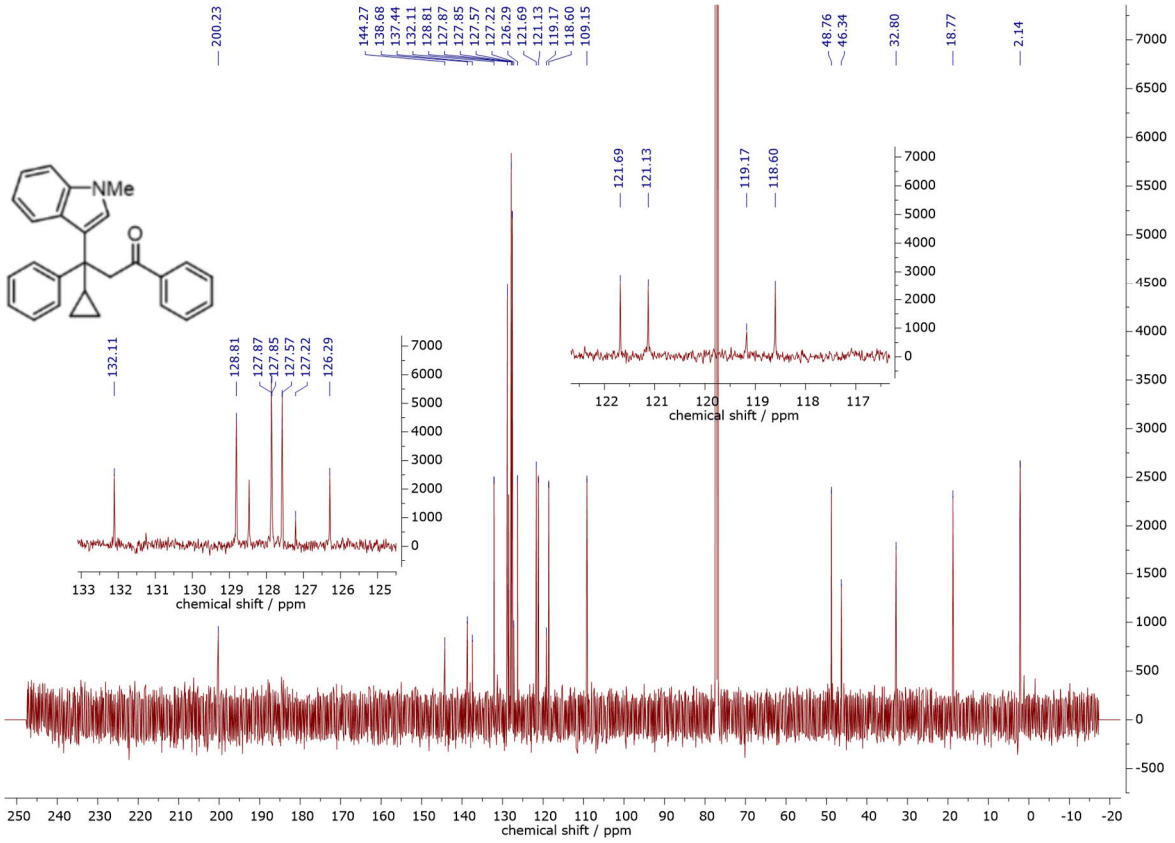
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **7a**:



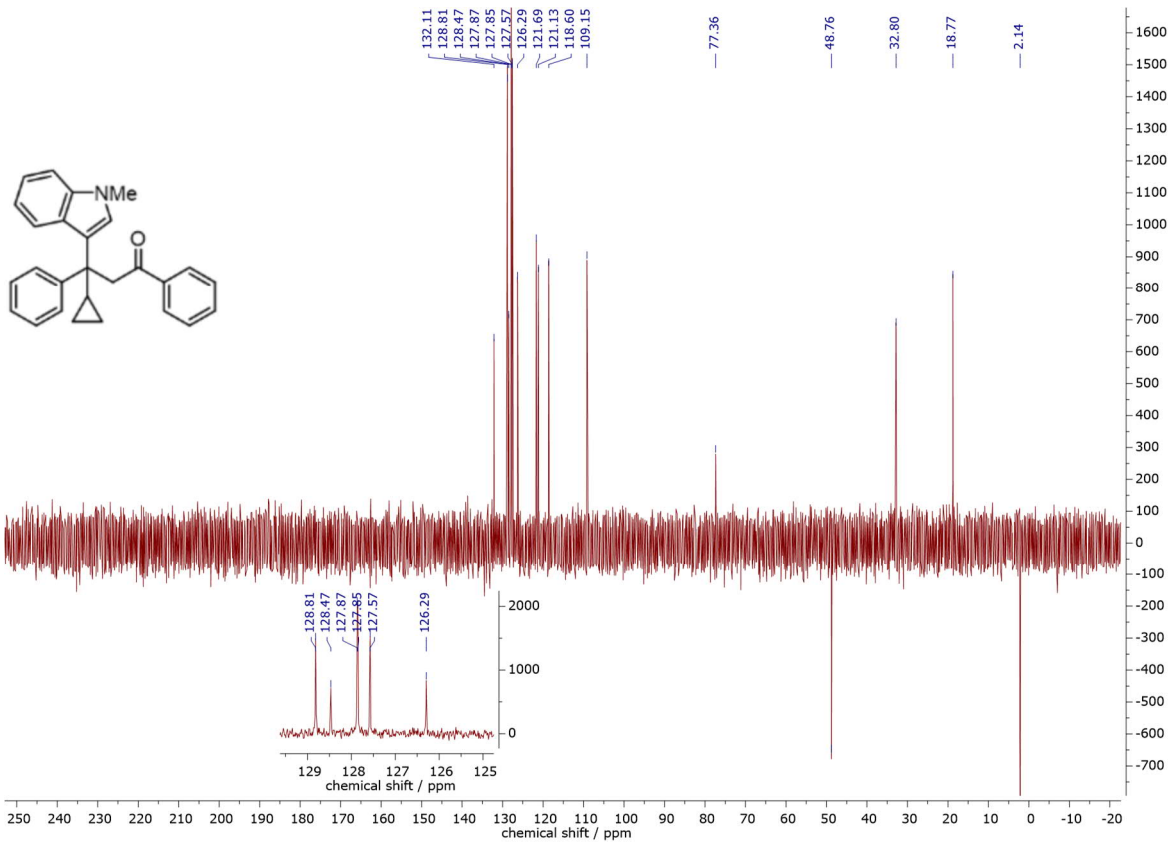
^1H (501 MHz, $CDCl_3$) NMR spectrum of product **7b**:



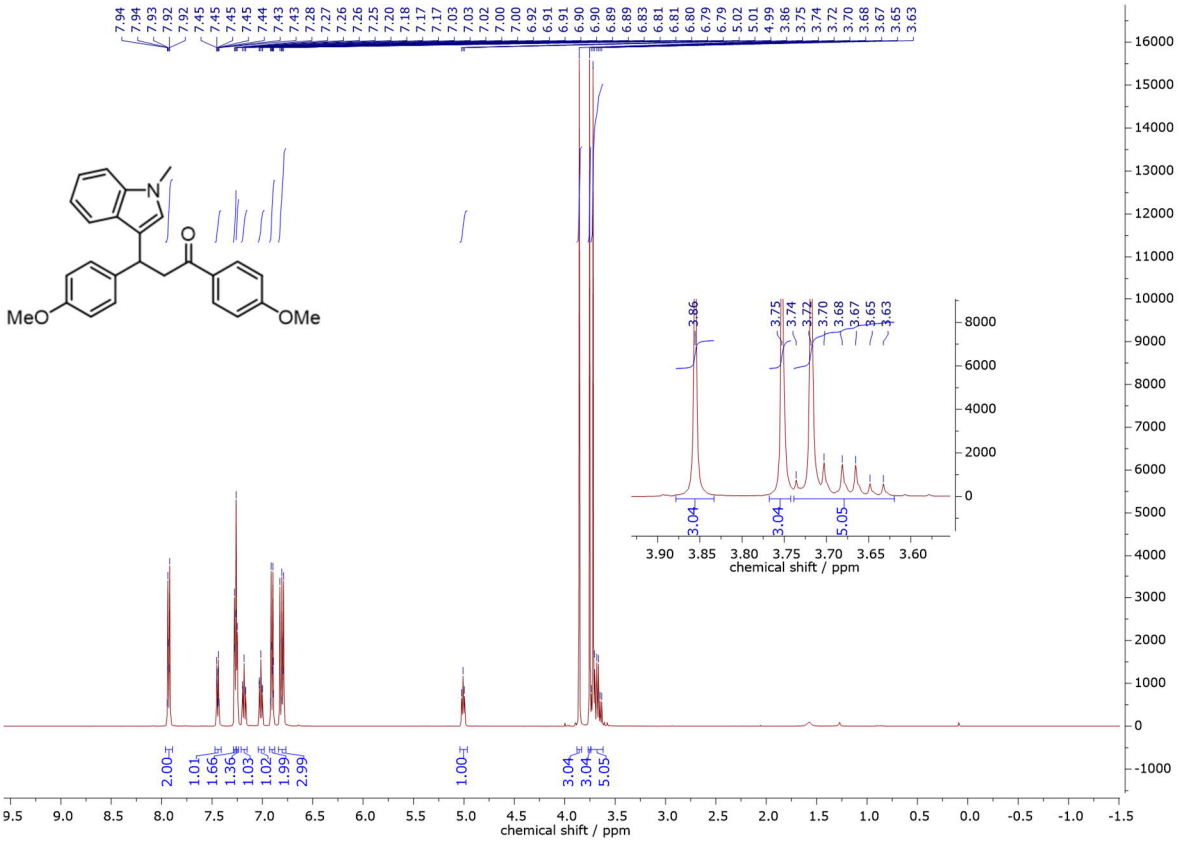
$^{13}C\{H\}$ (126 MHz, $CDCl_3$) NMR spectrum of product **7b**:



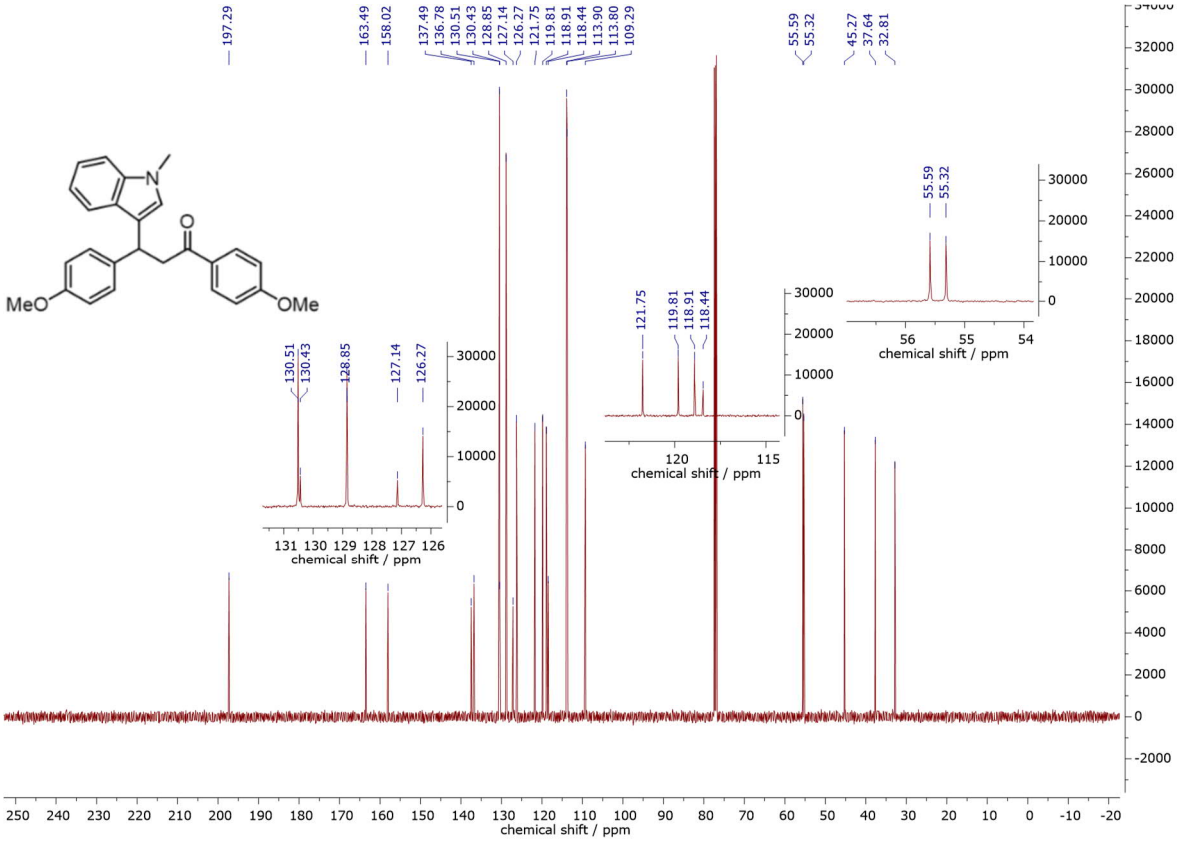
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **7b**:



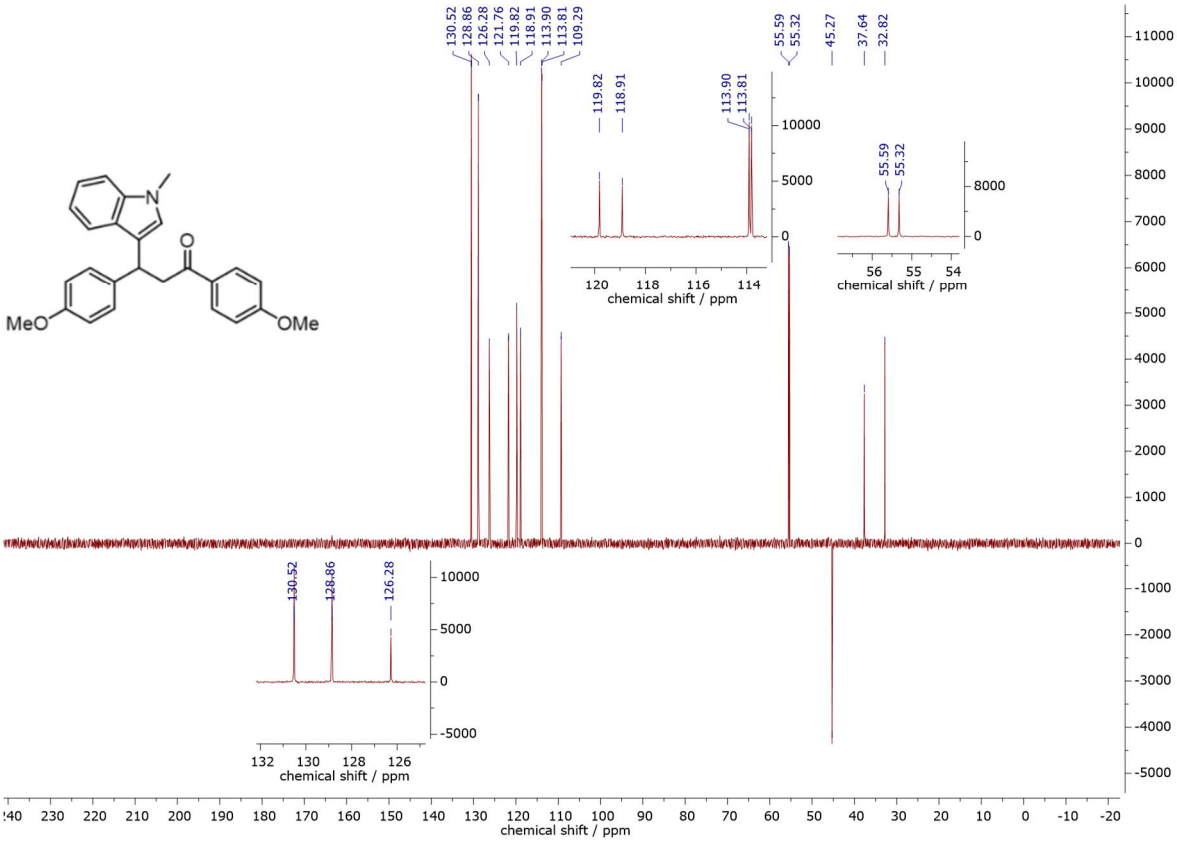
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **8**:



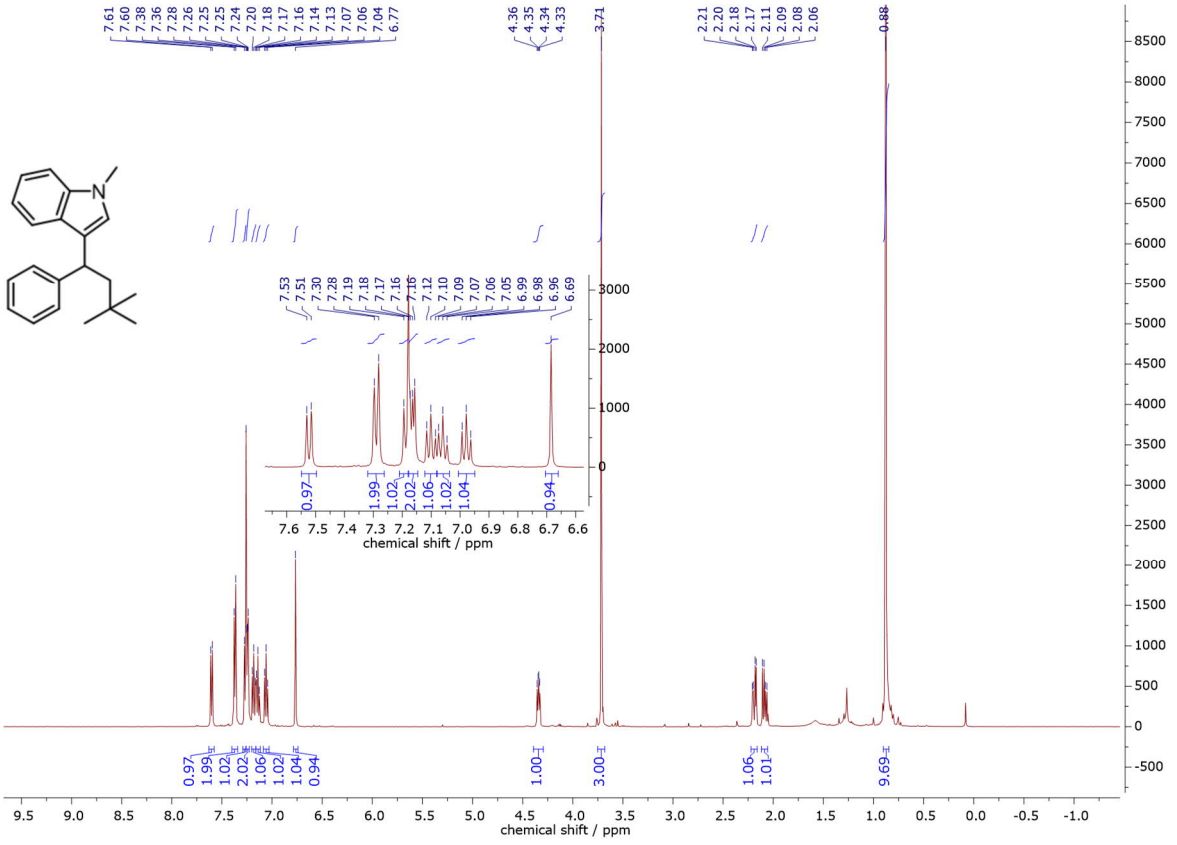
^{13}C{H} (126 MHz, $CDCl_3$) NMR spectrum of product **8**:



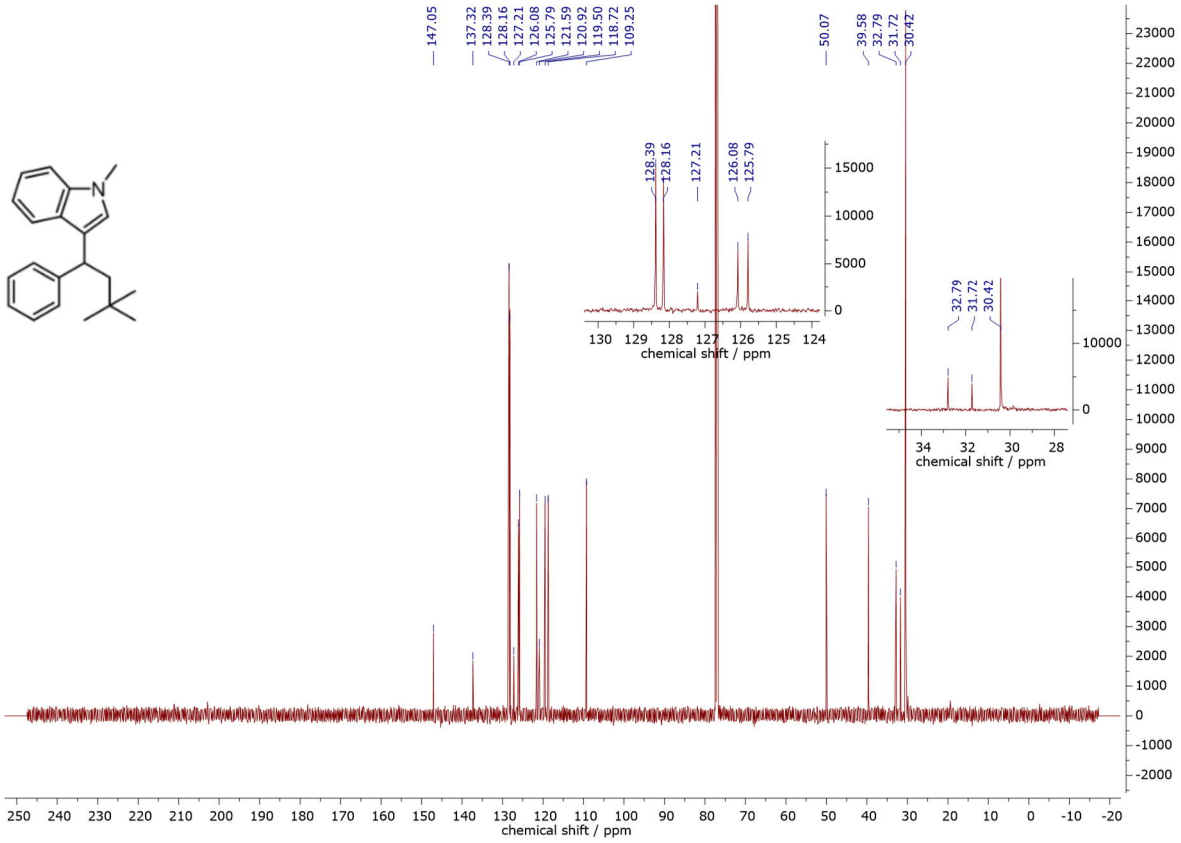
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **8**:



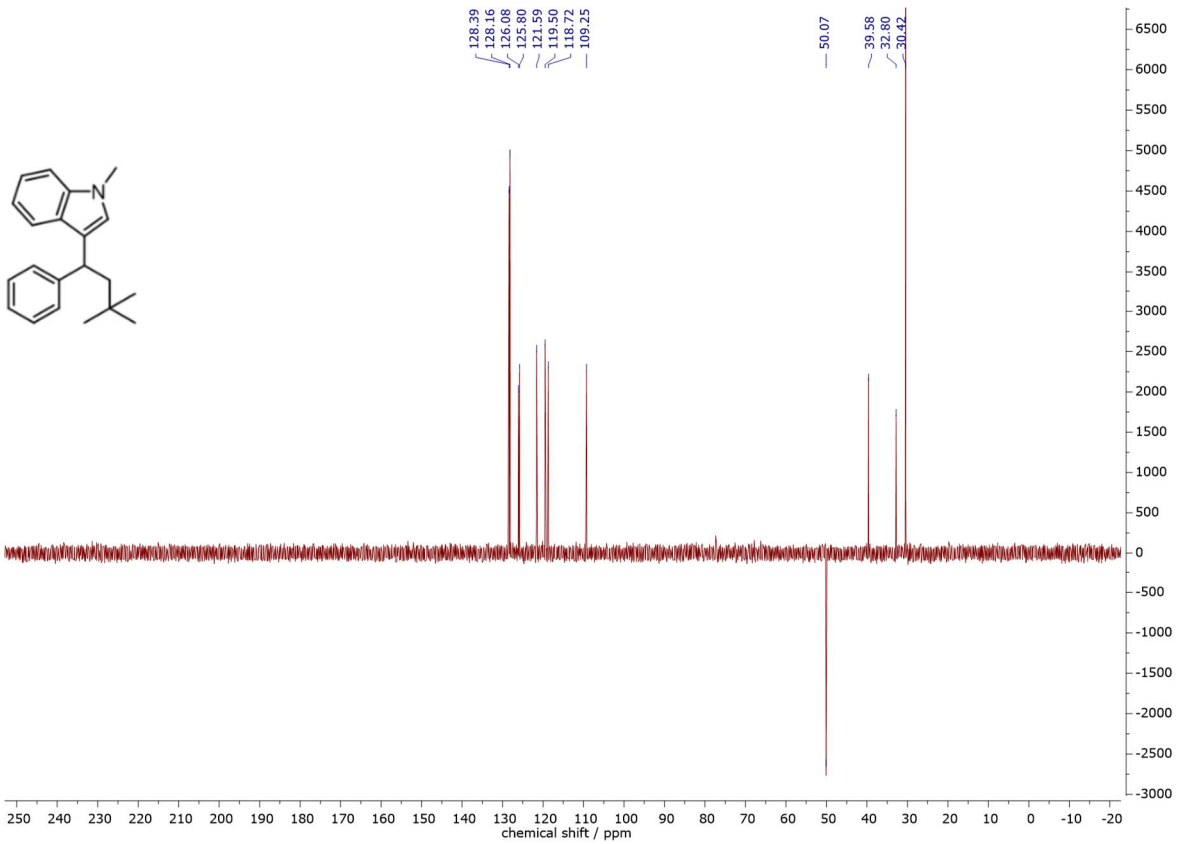
^1H (501 MHz, $CDCl_3$) NMR spectrum of product **9**:



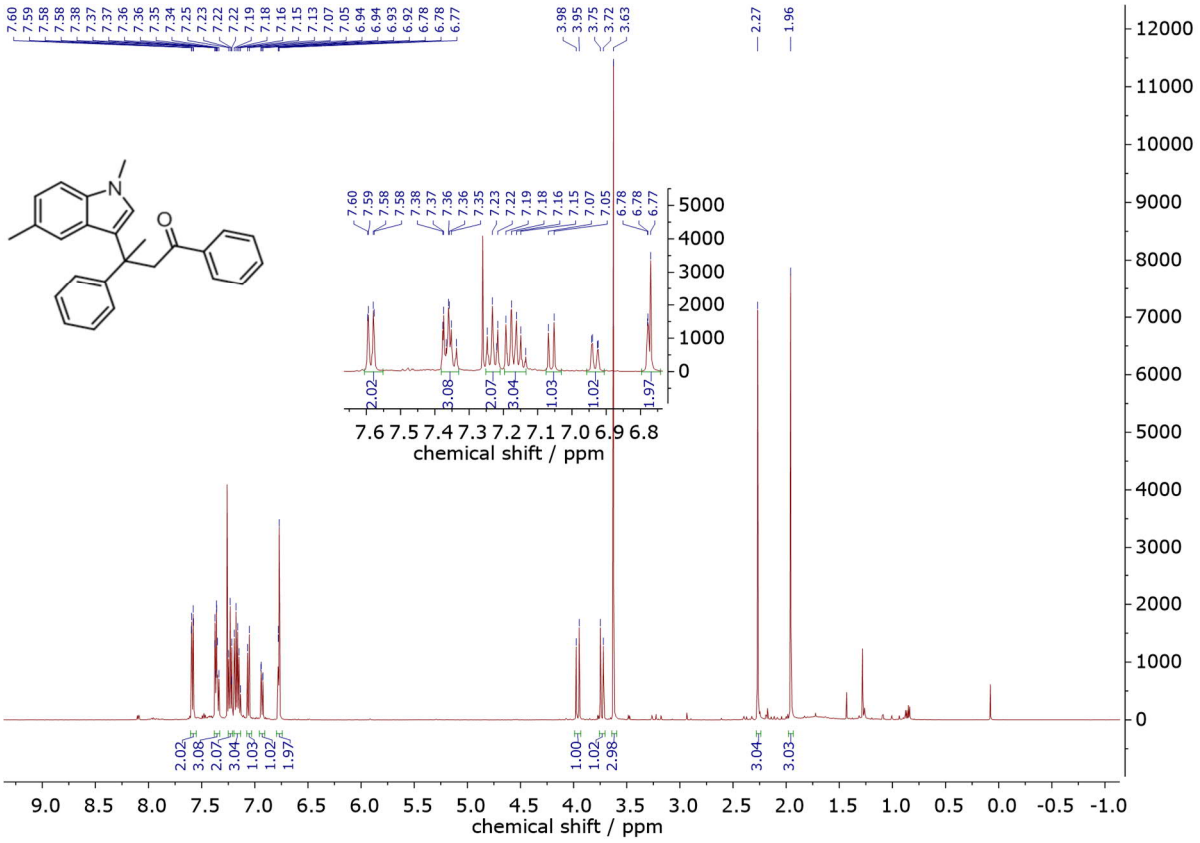
$^{13}C\{H\}$ (126 MHz, $CDCl_3$) NMR spectrum of product **9**:



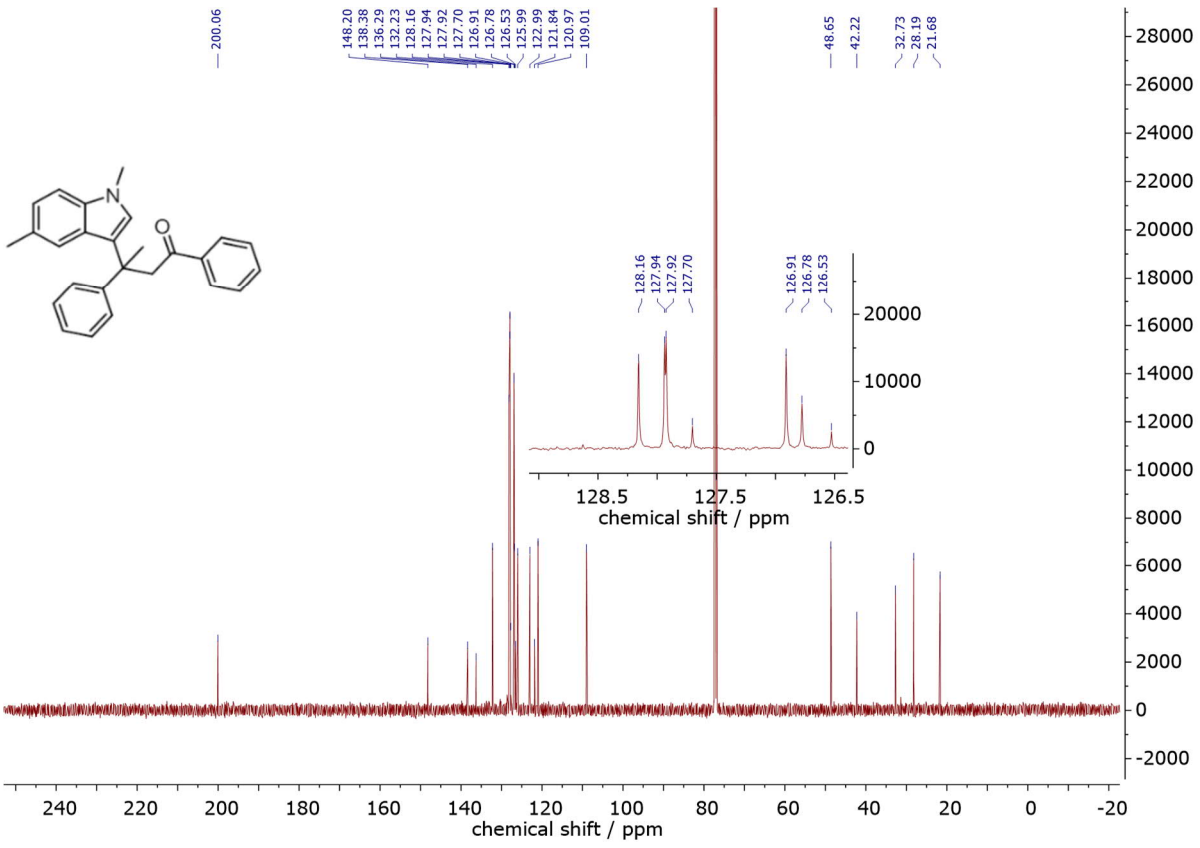
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **9**:



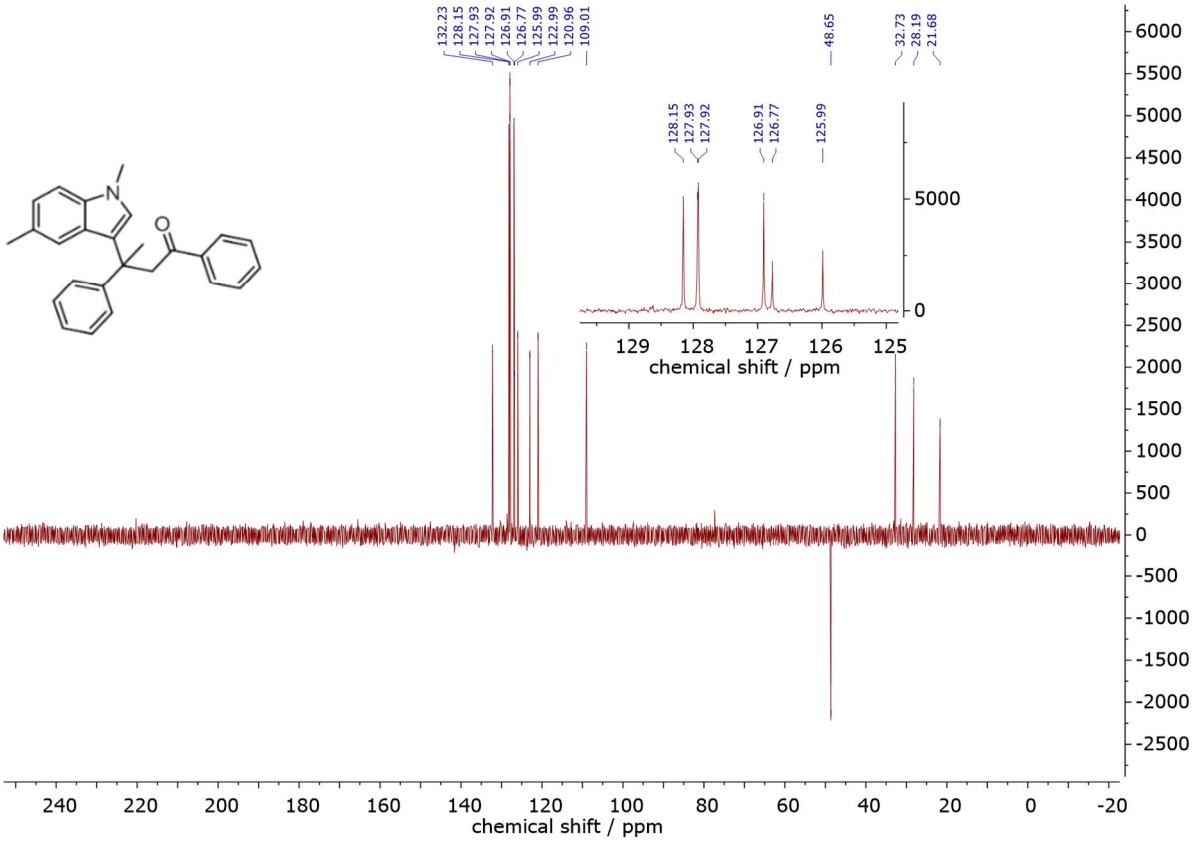
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **10a**:



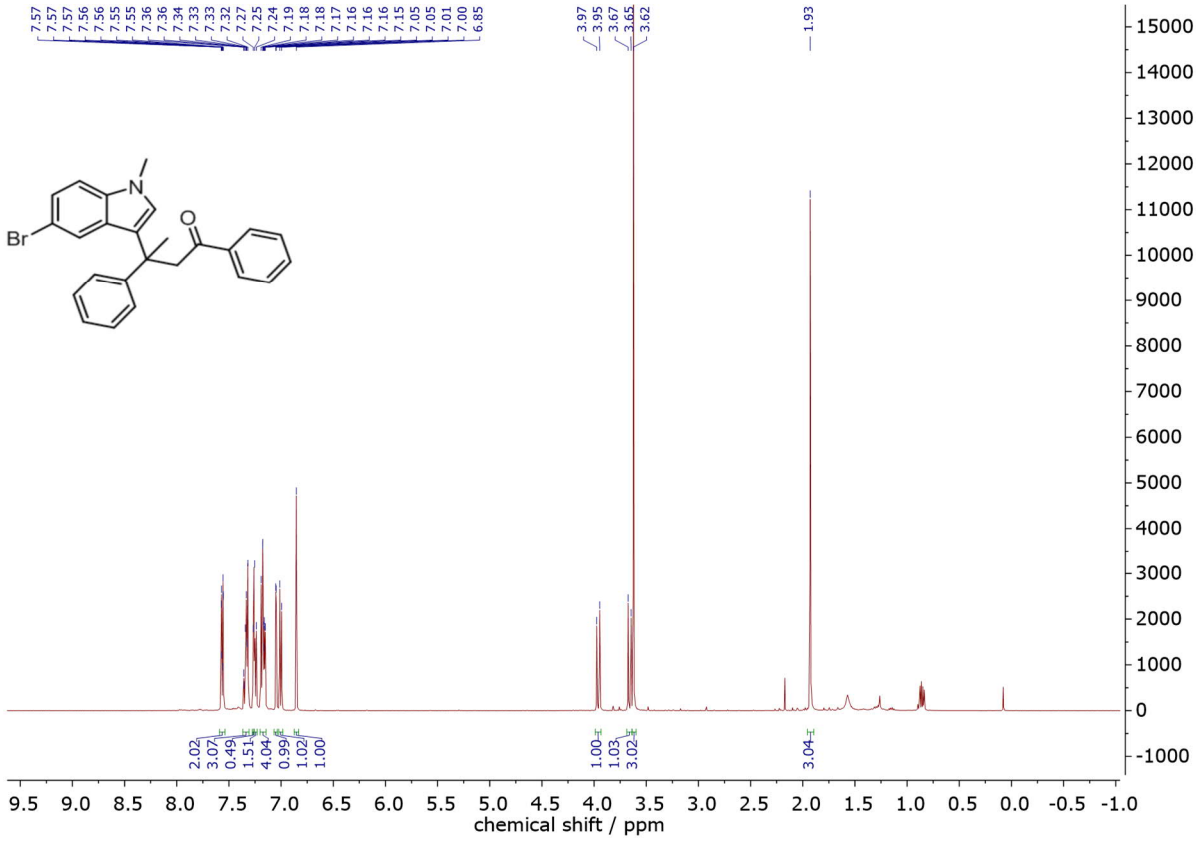
^{13}C{H} (126 MHz, $CDCl_3$) NMR spectrum of product **10a**:



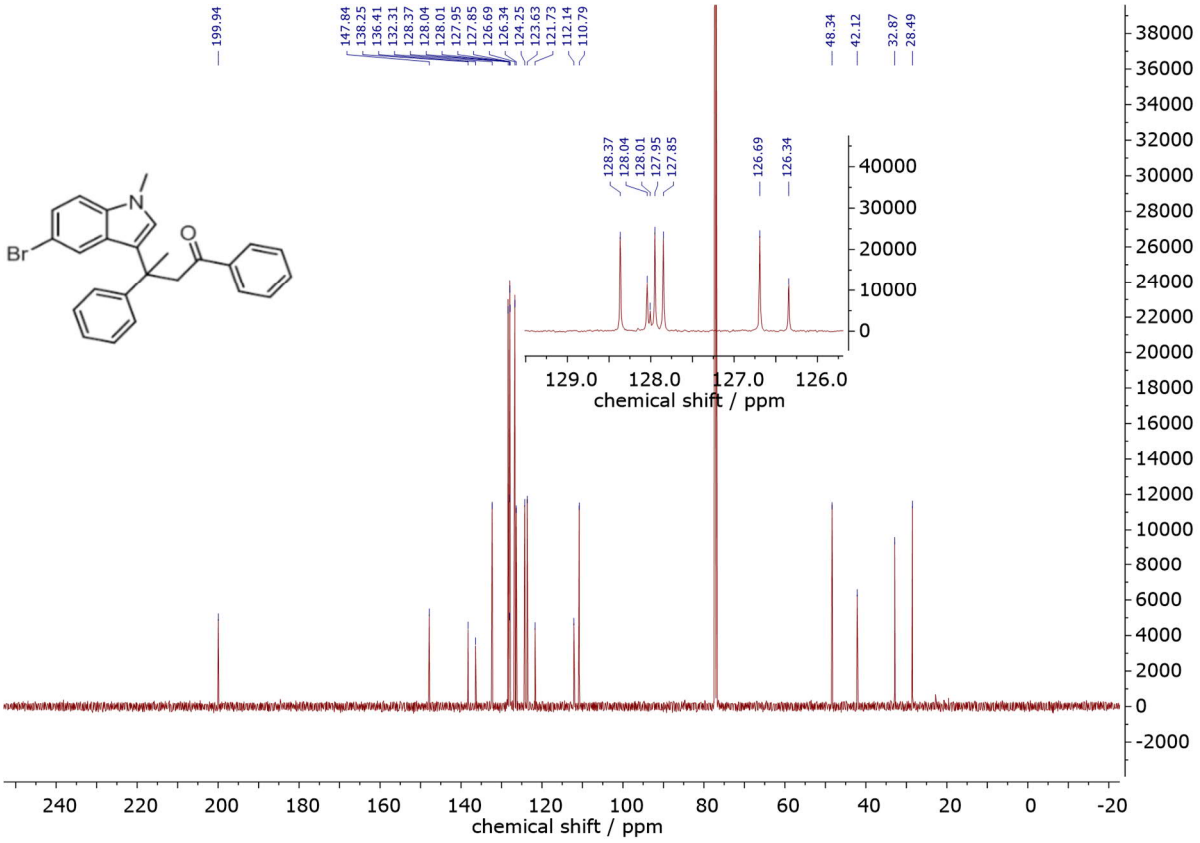
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **10a**:



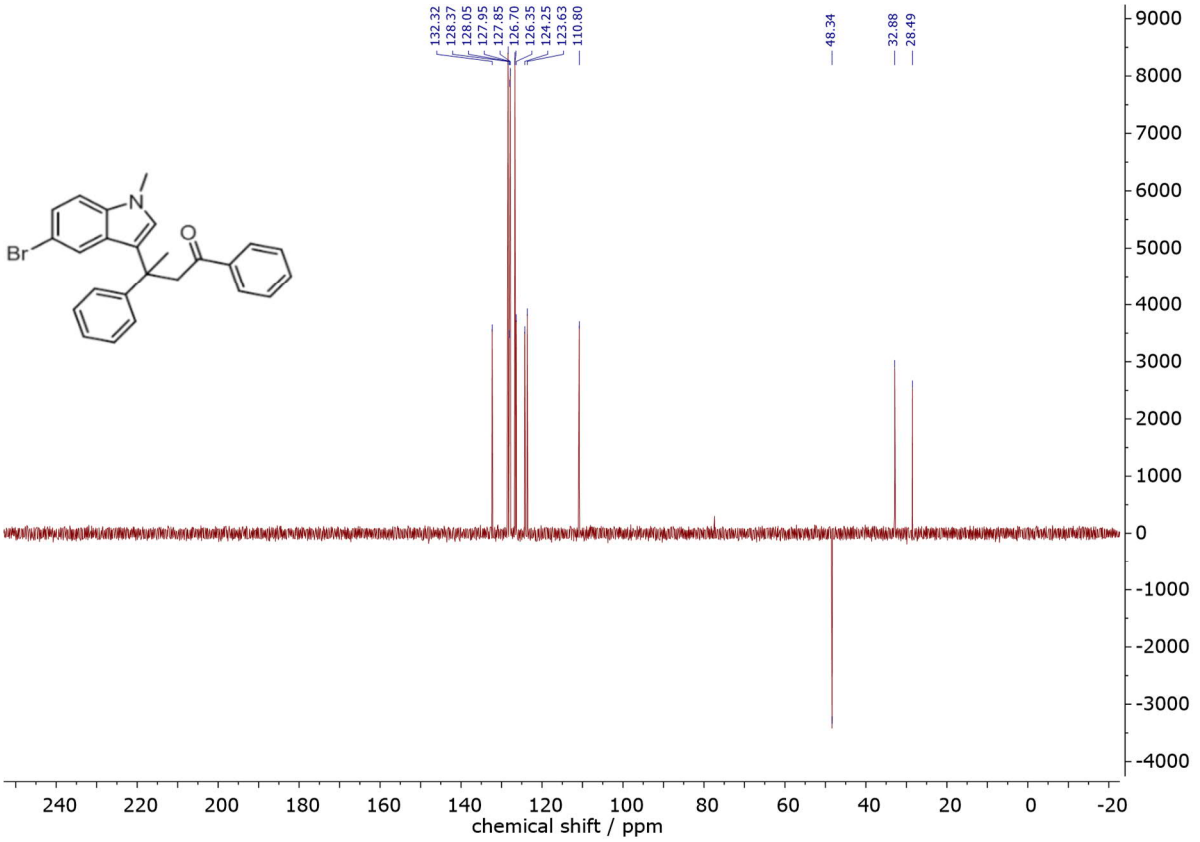
^1H (501 MHz, $CDCl_3$) NMR spectrum of product **10b**:



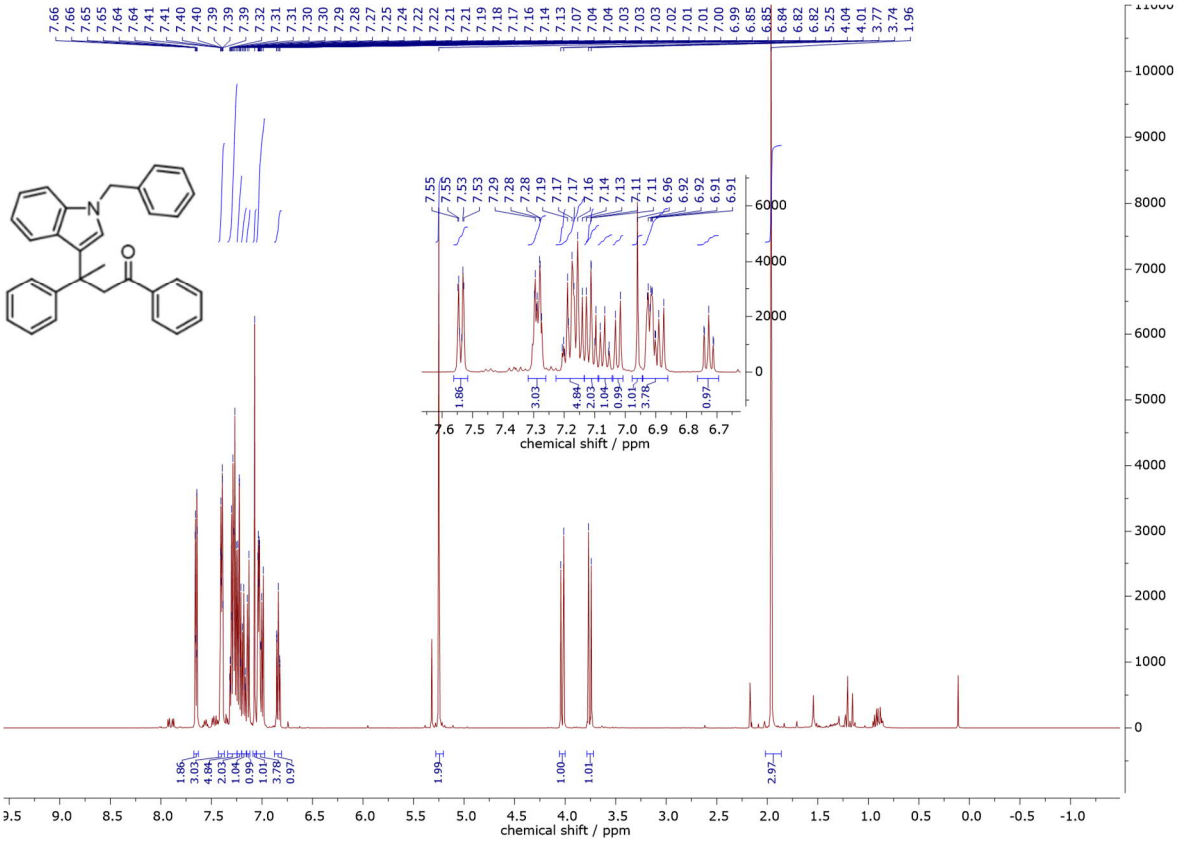
$^{13}C\{H\}$ (126 MHz, $CDCl_3$) NMR spectrum of product **10b**:



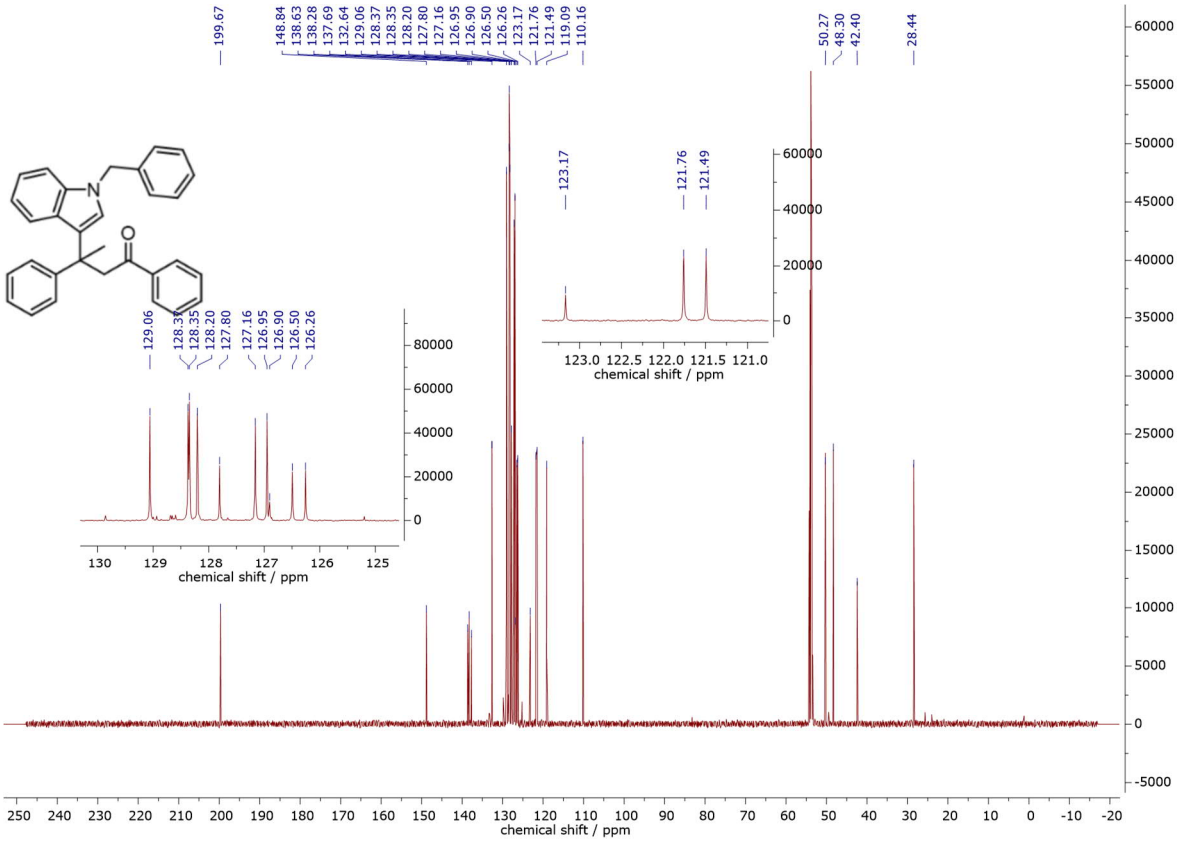
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **10b**:



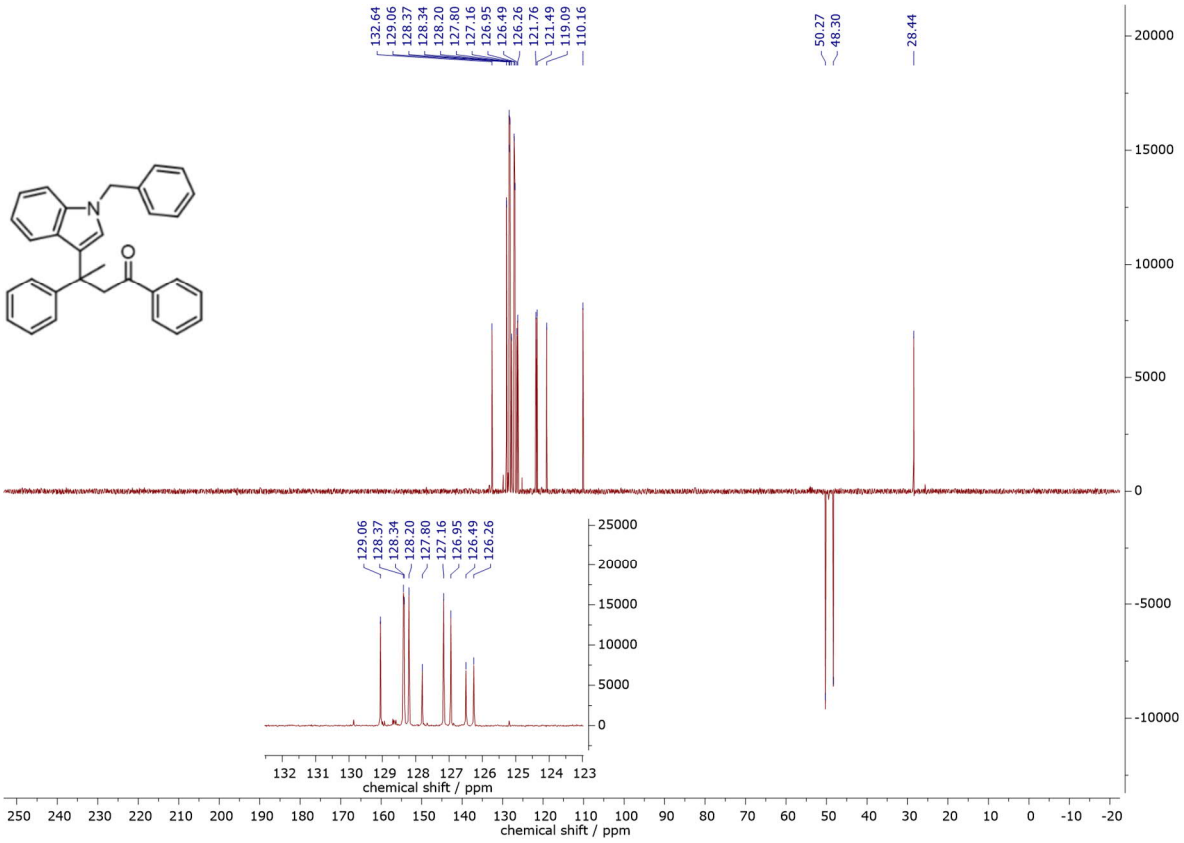
^{1}H (501 MHz, CD_2Cl_2) NMR spectrum of product **10c**:



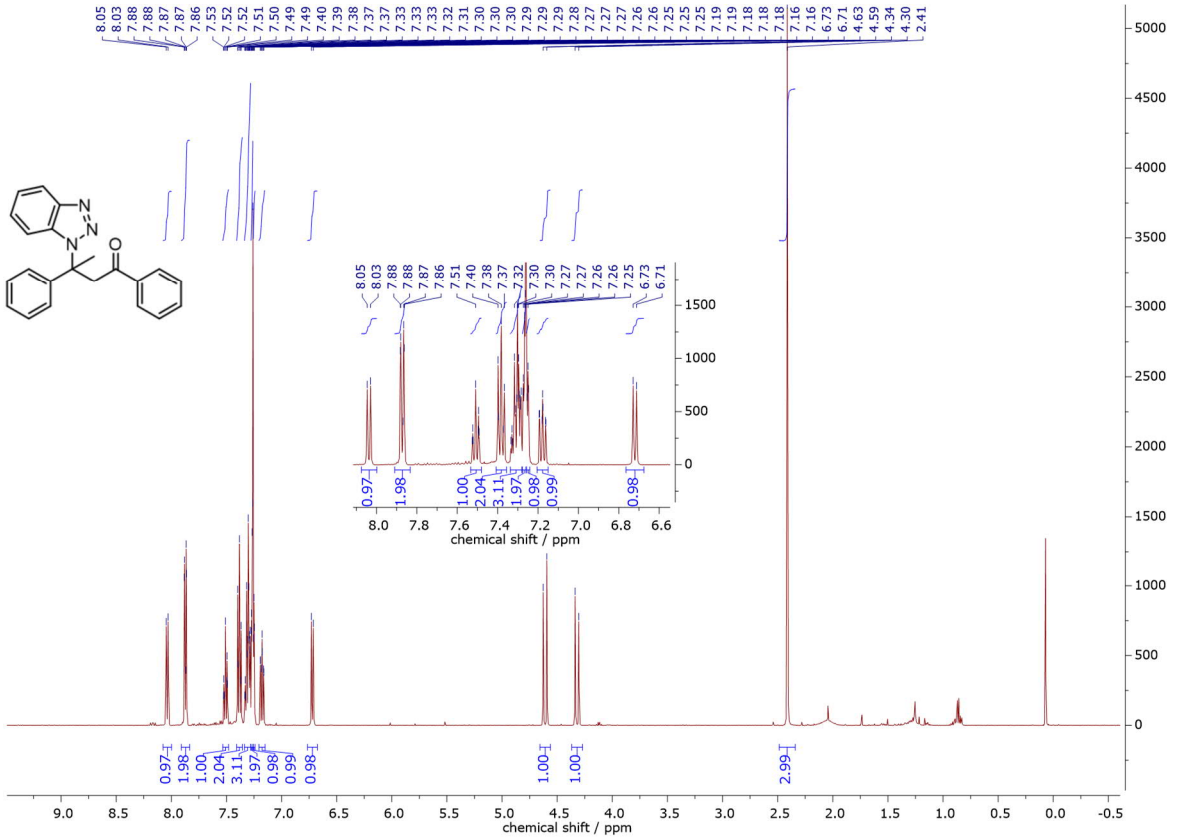
^{13}C{H} (126 MHz, CD_2Cl_2) NMR spectrum of product **10c**:



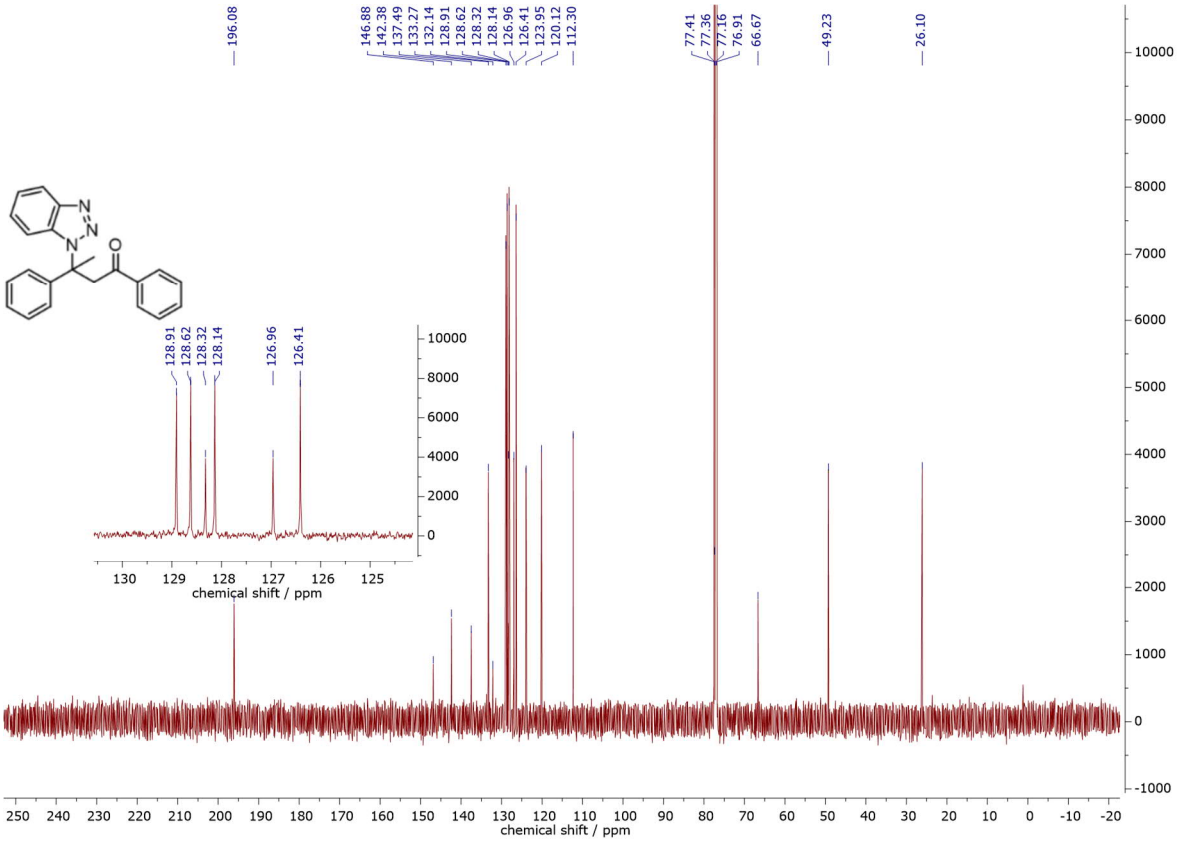
DEPT135 {H} (126 MHz, CD_2Cl_2) NMR spectrum of product **10c**:



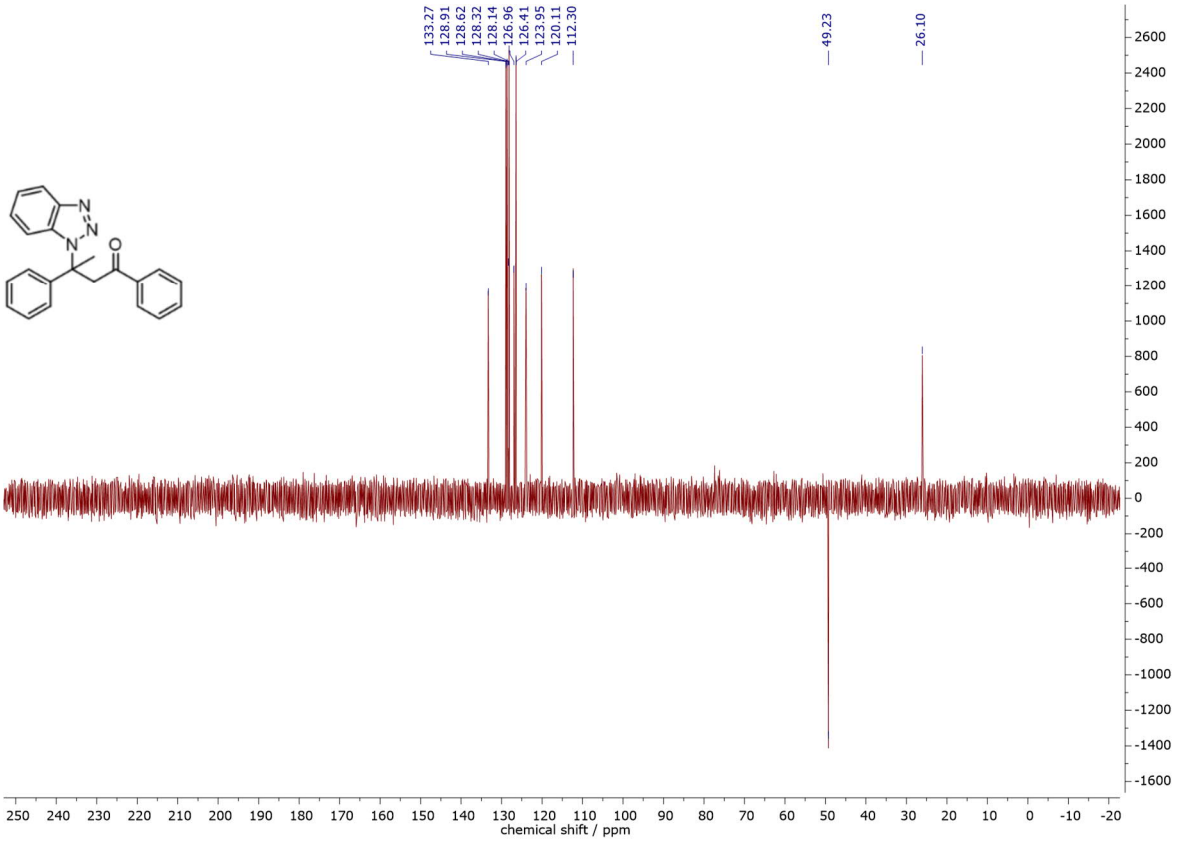
^1H (501 MHz, $CDCl_3$) NMR spectrum of product **10d**:



$^{13}C\{H\}$ (126 MHz, $CDCl_3$) NMR spectrum of product **10d**:

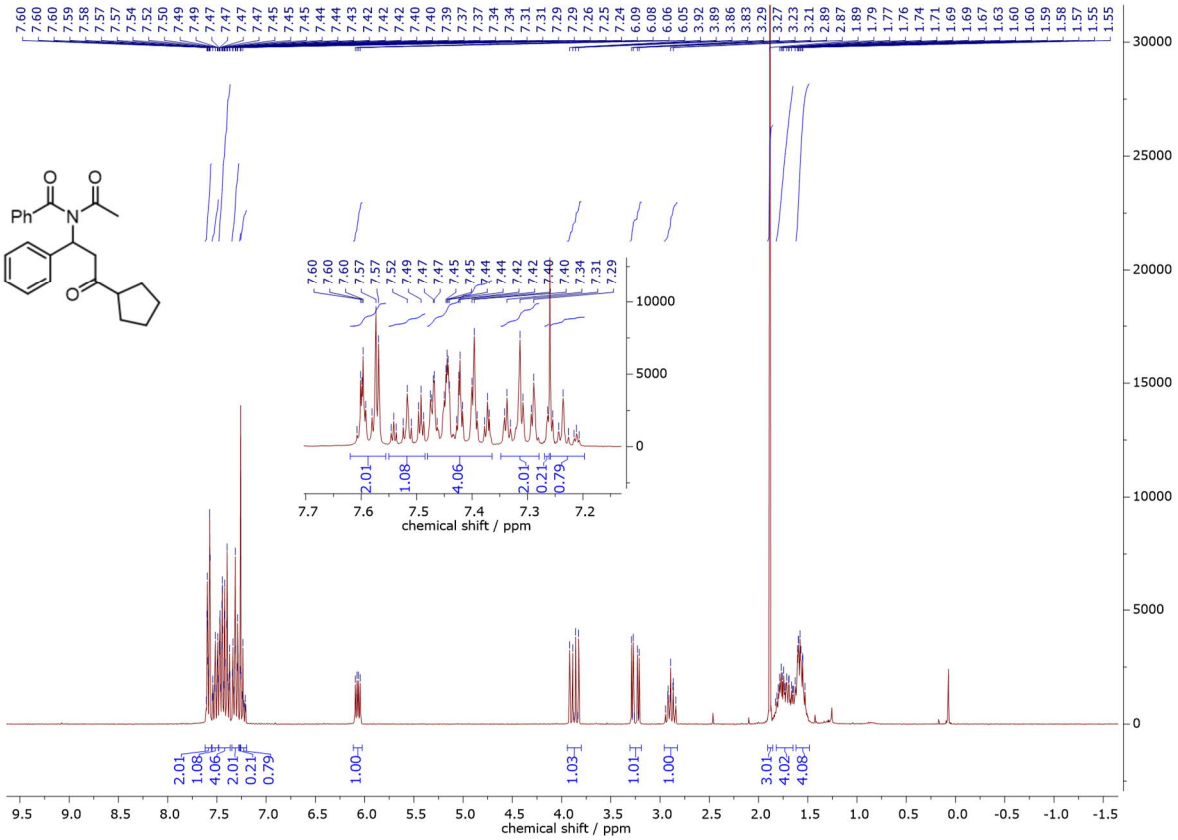


DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **10d**:

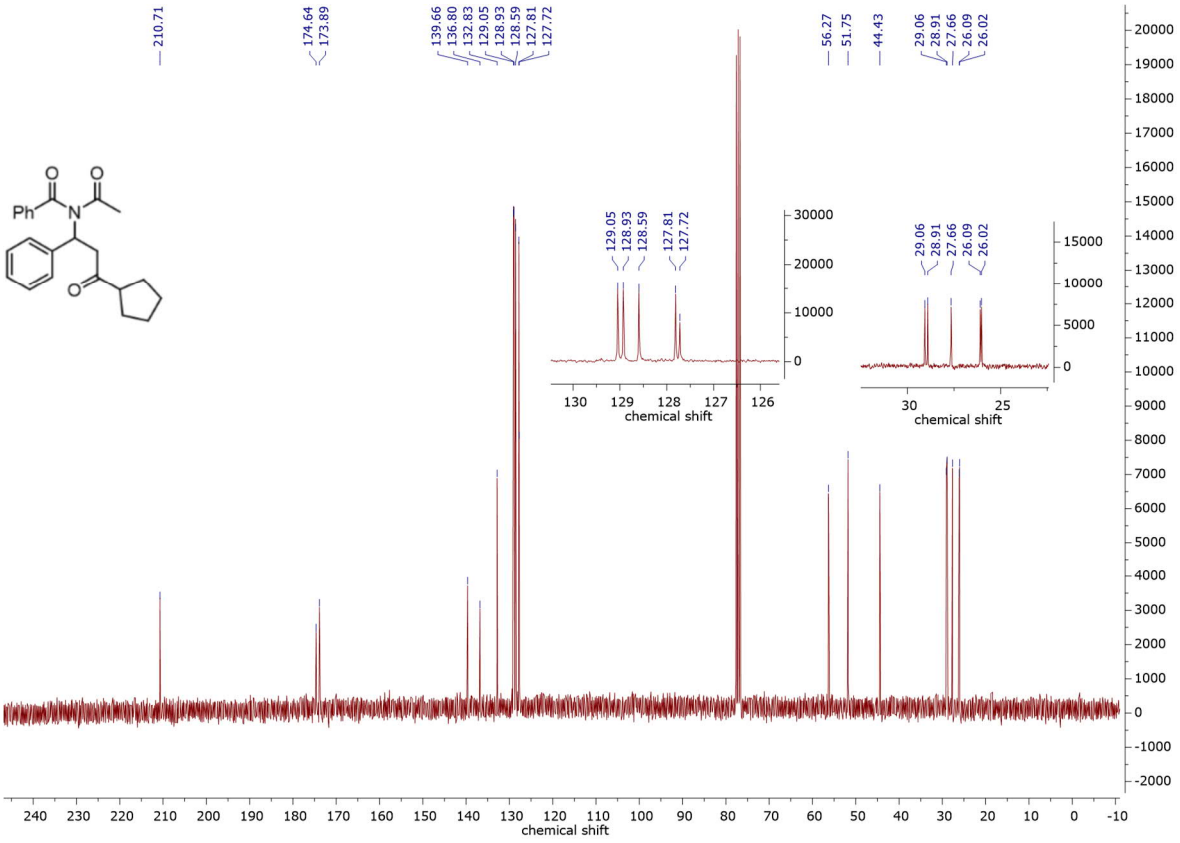


Imide products

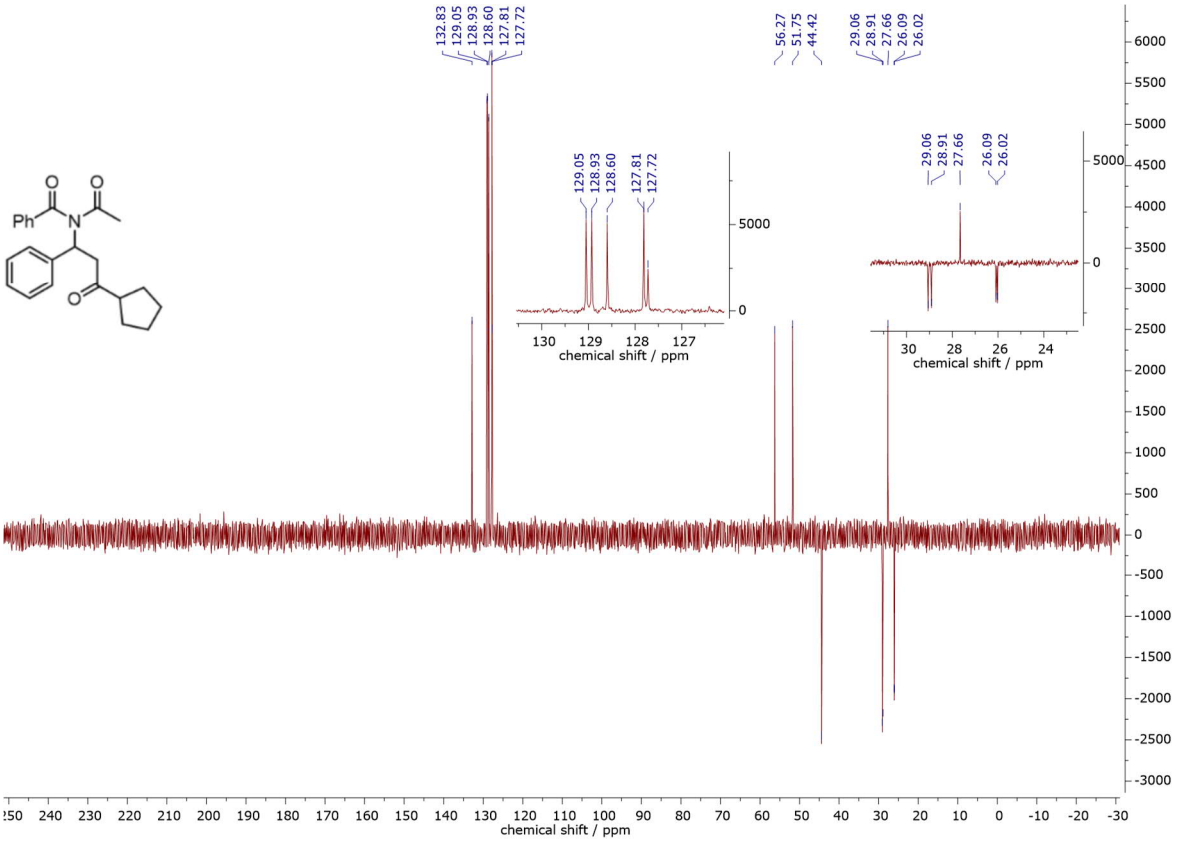
^{1}H (300 MHz, $CDCl_3$) NMR spectrum of product **11a**:



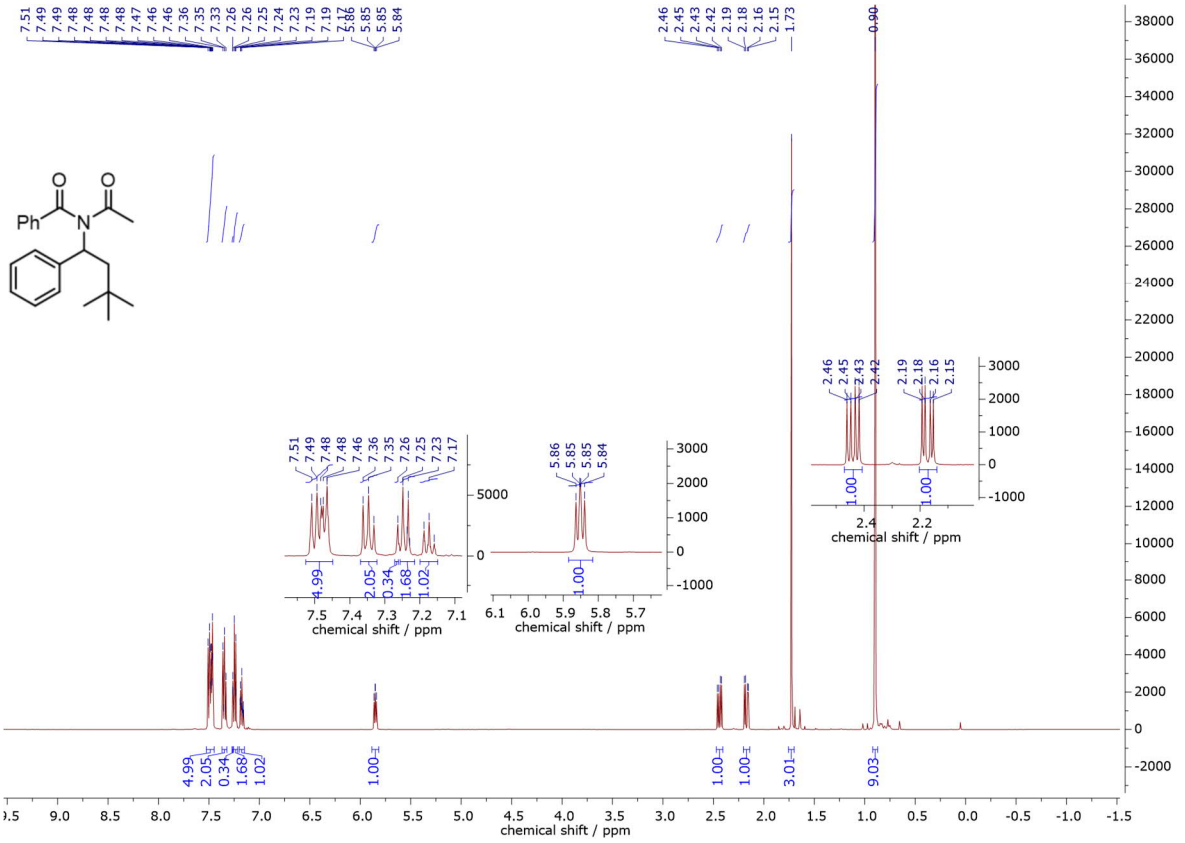
$^{13}C\{H\}$ (75 MHz, $CDCl_3$) NMR spectrum of product **11a**:



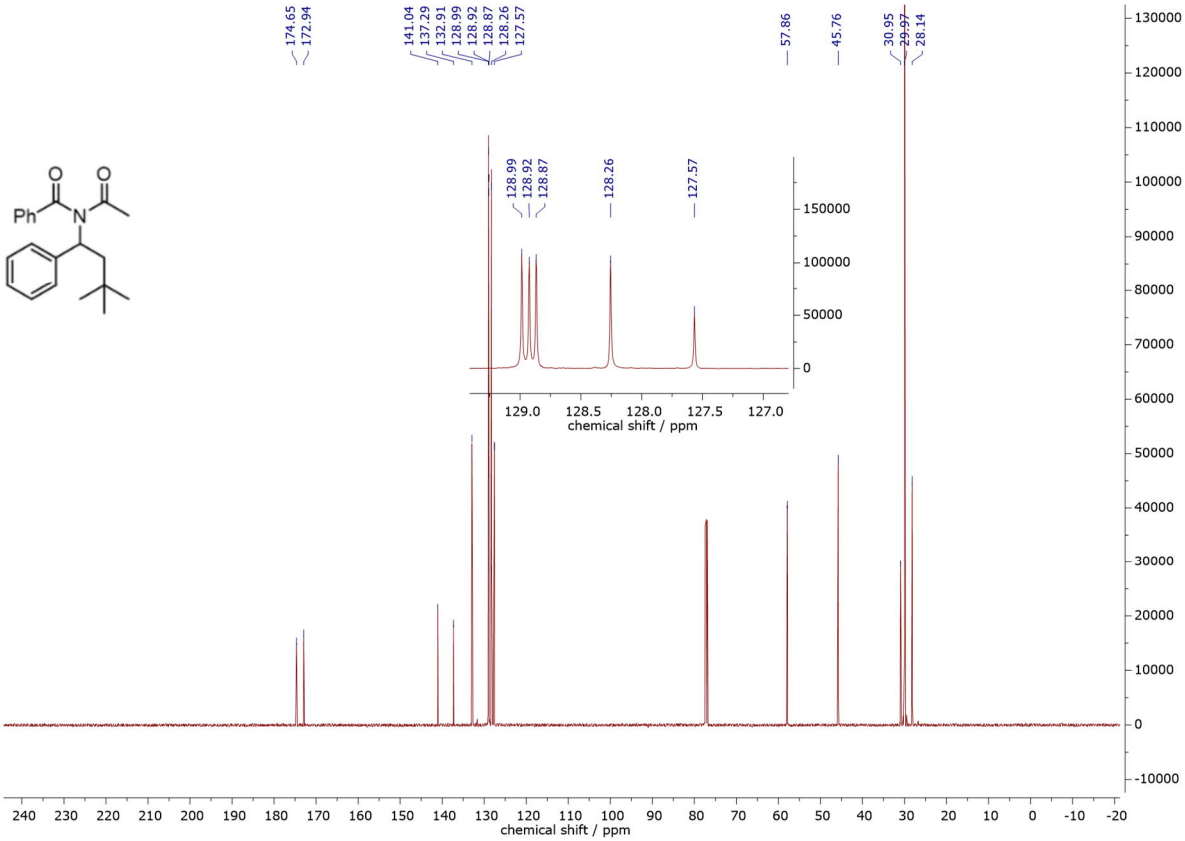
DEPT135 {H} (75 MHz, $CDCl_3$) NMR spectrum of product **11a**:



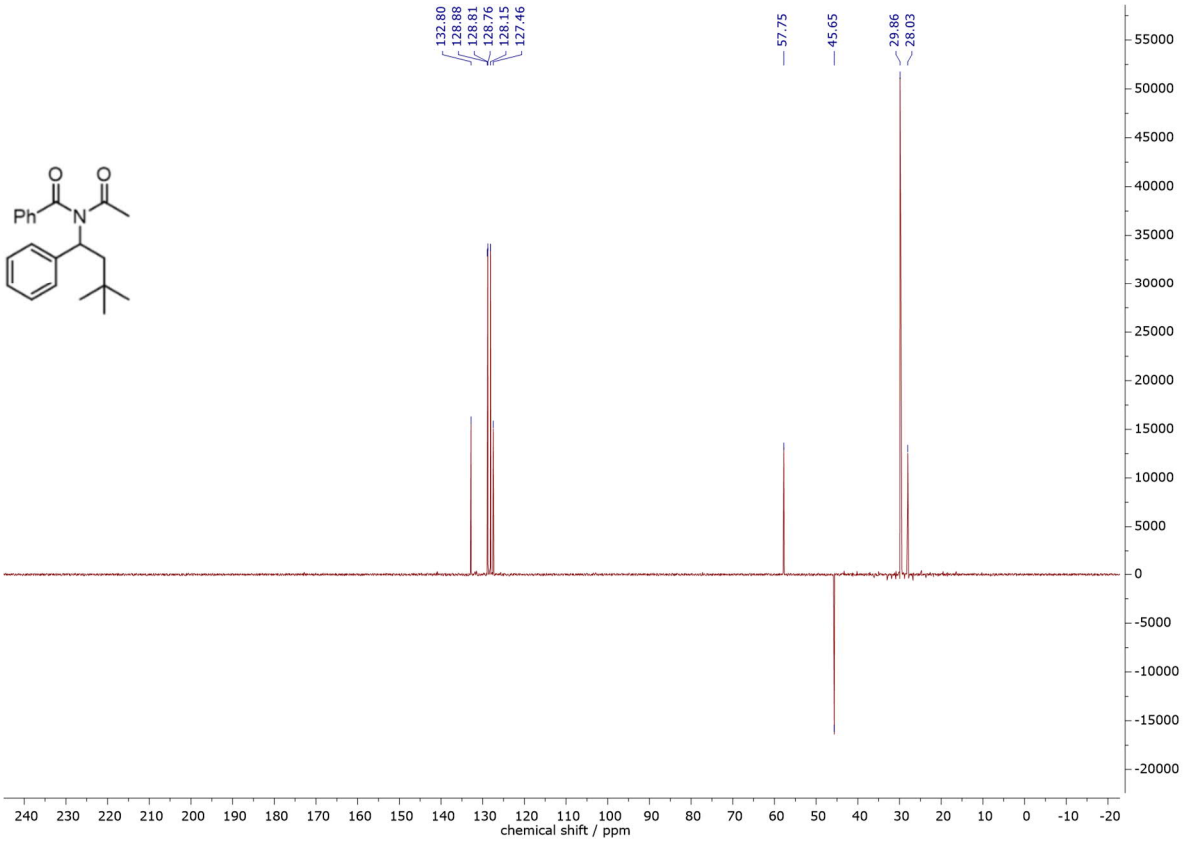
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **11b**:



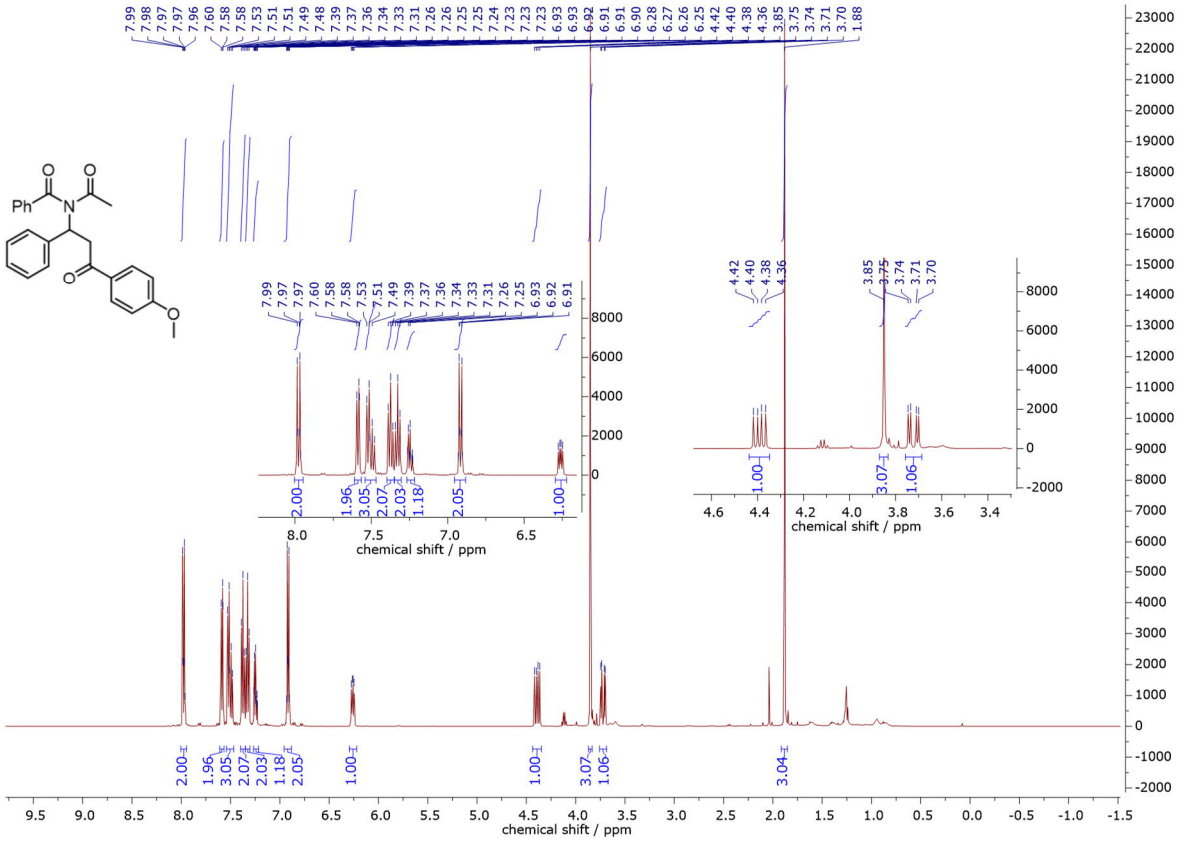
^{13}C{H} (126 MHz, $CDCl_3$) NMR spectrum of product **11b**:



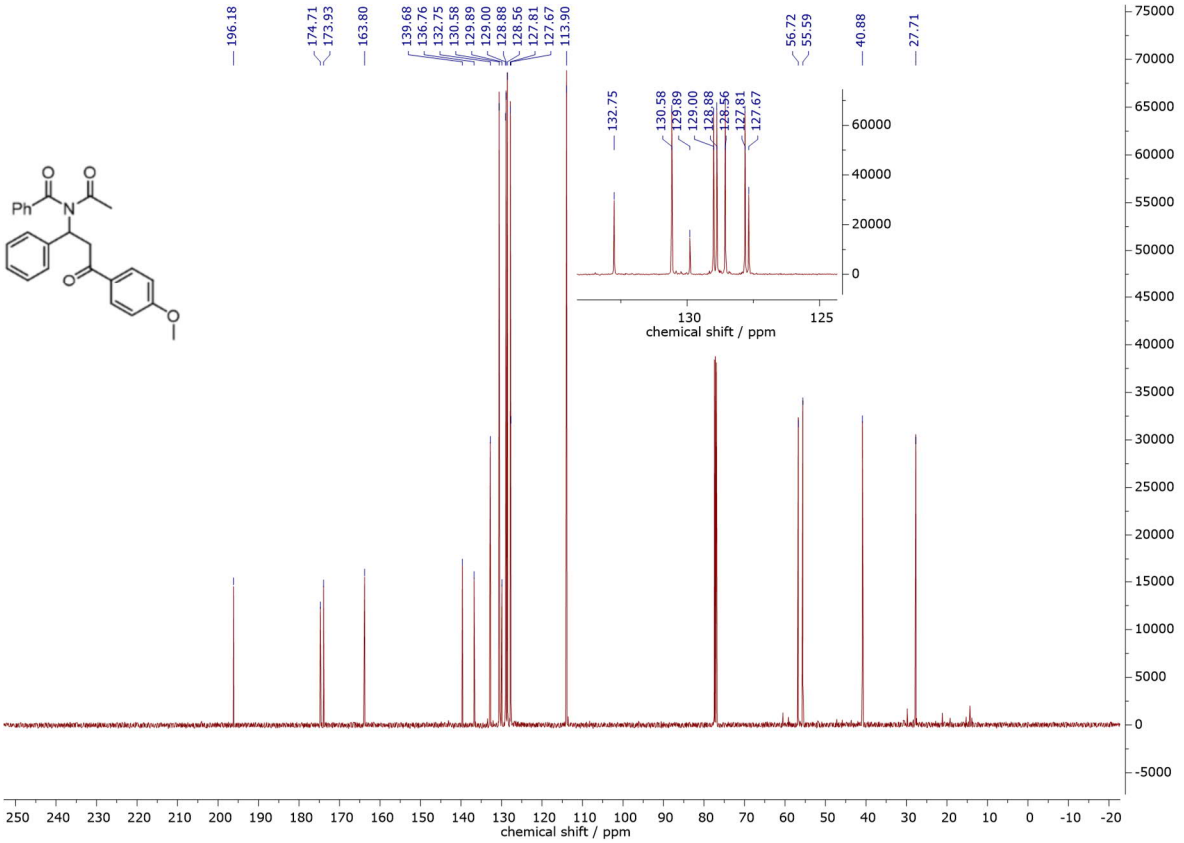
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **11b**:



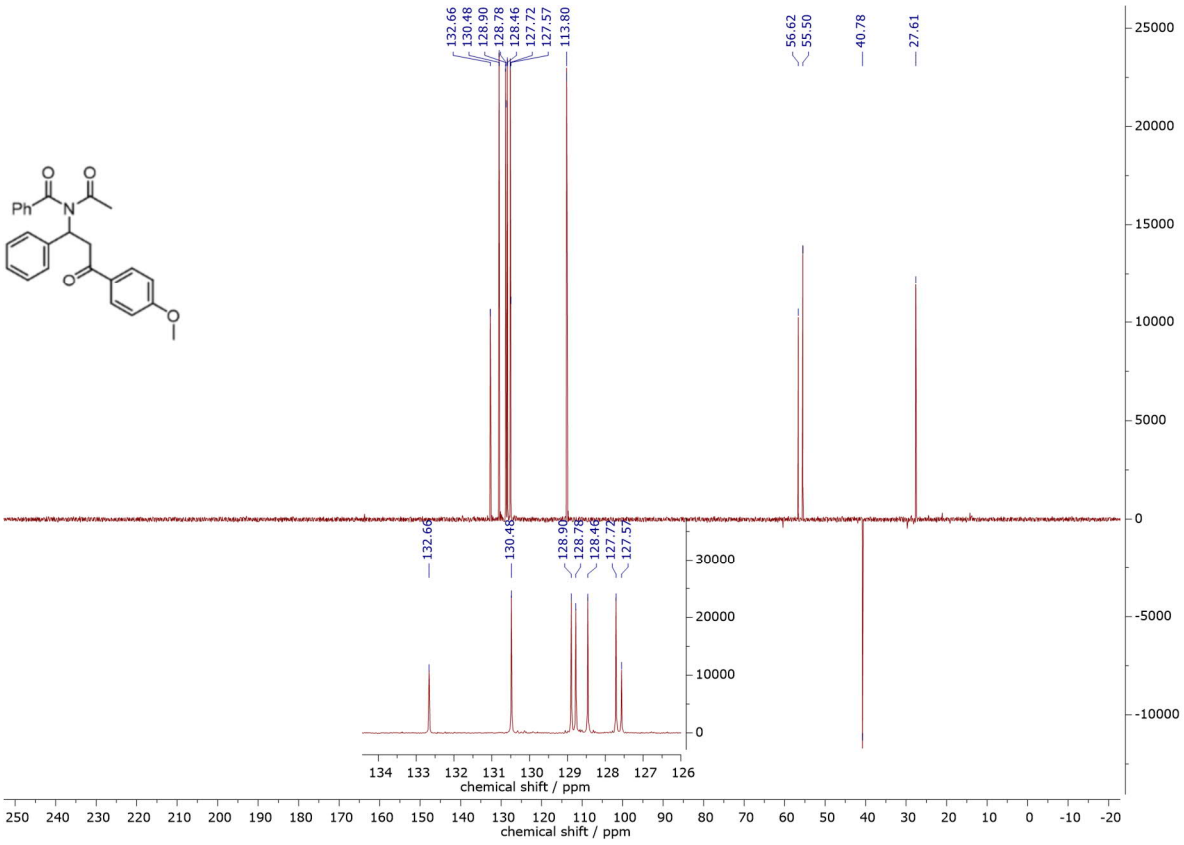
^1H (501 MHz, $CDCl_3$) NMR spectrum of product **11c**:



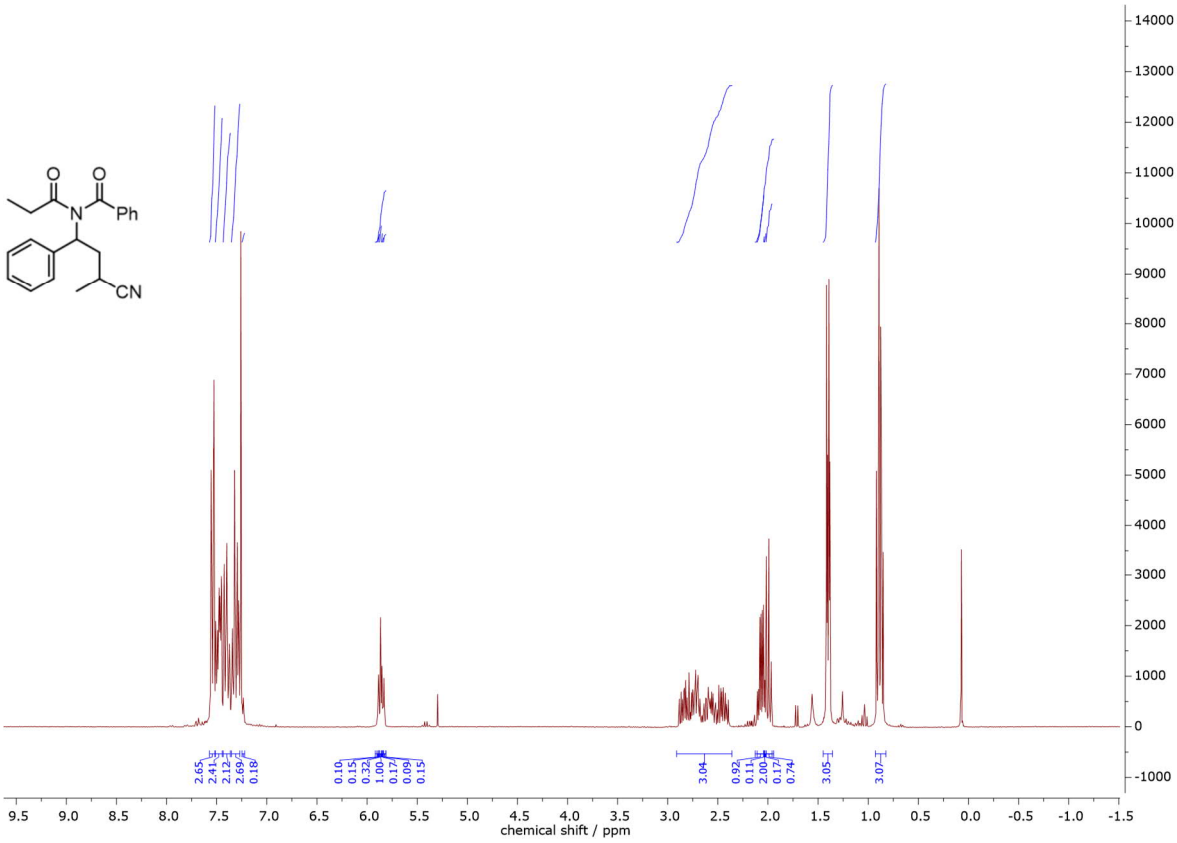
$^{13}C\{H\}$ (126 MHz, $CDCl_3$) NMR spectrum of product **11c**:



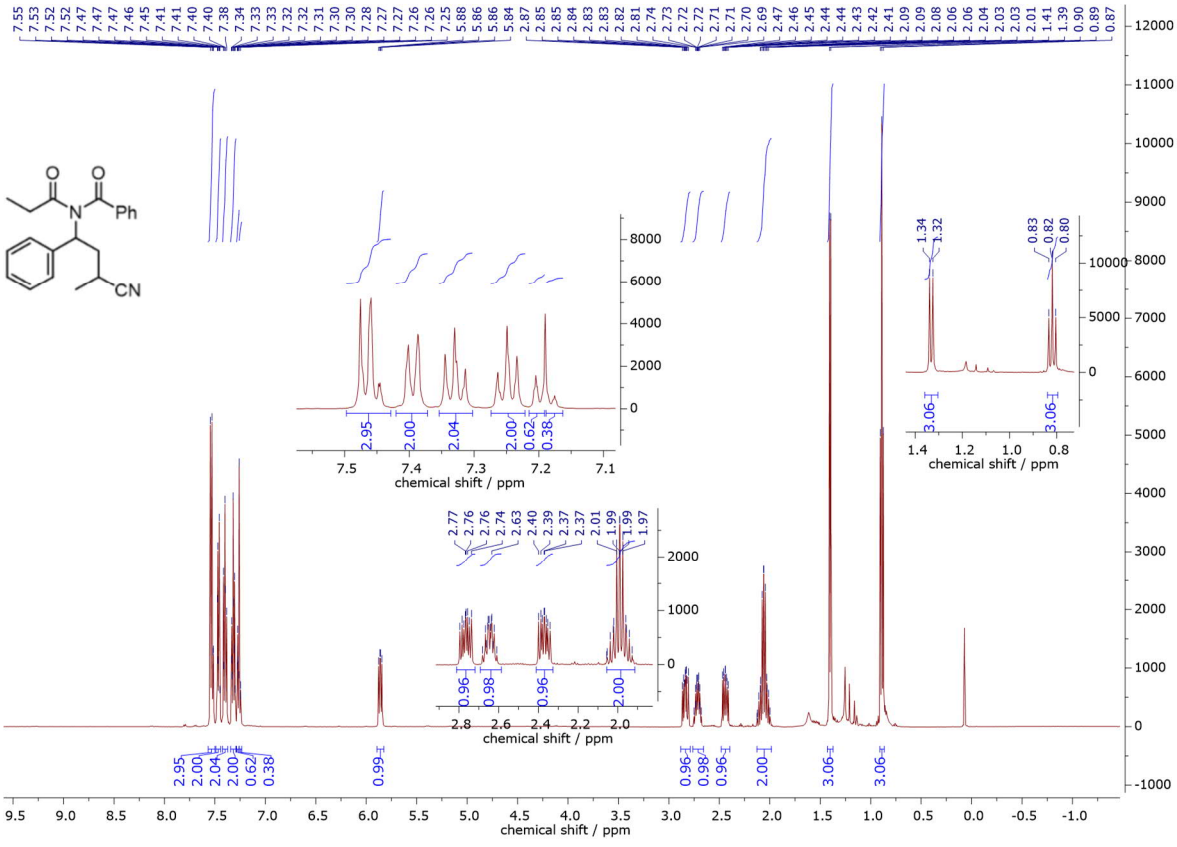
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **11c**:



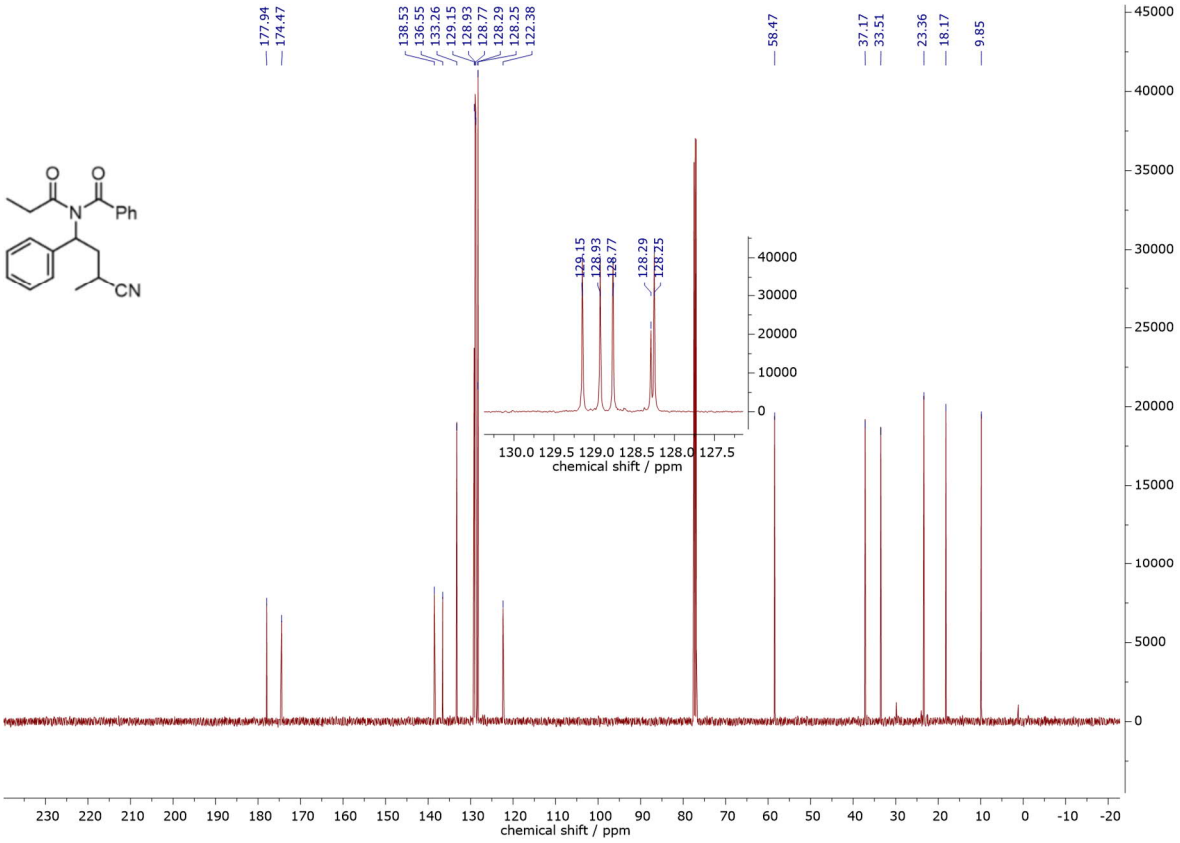
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of diastereomer mixture of structure **11d**:



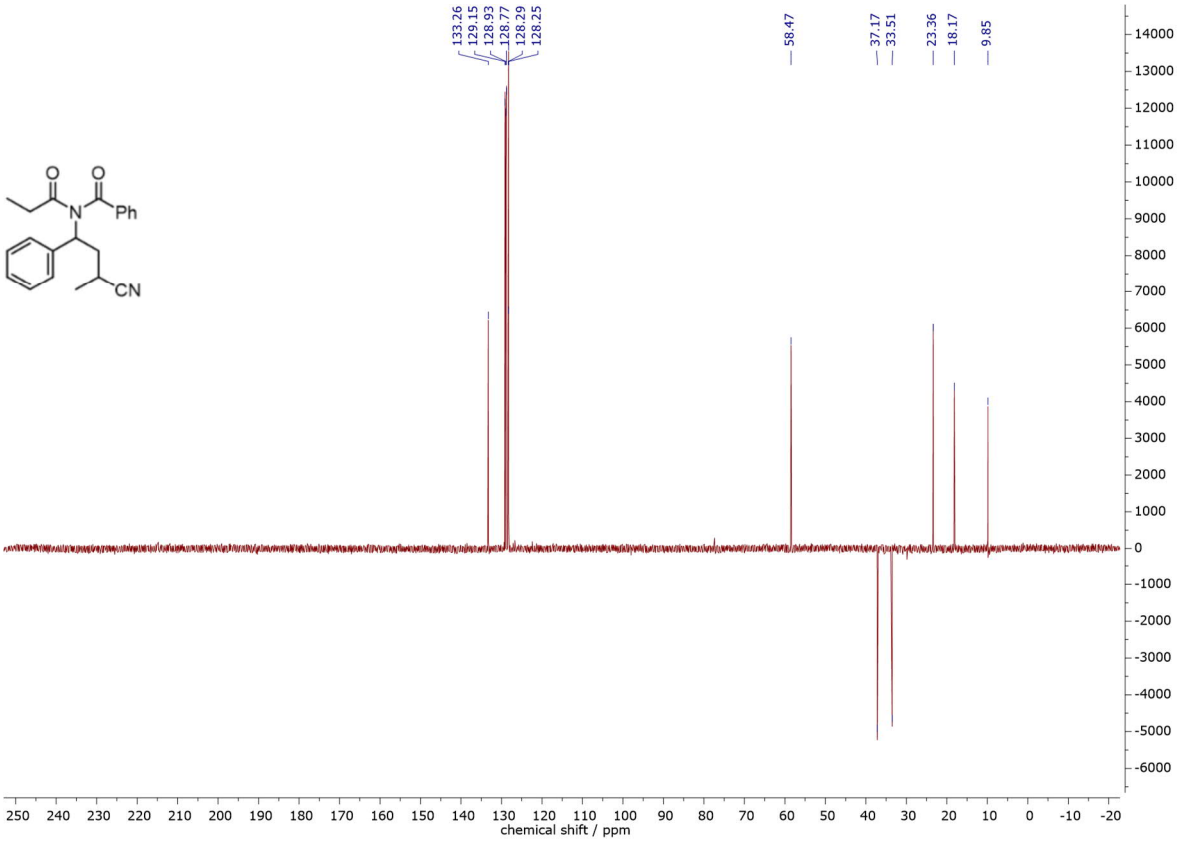
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of major diastereomer **11d**:



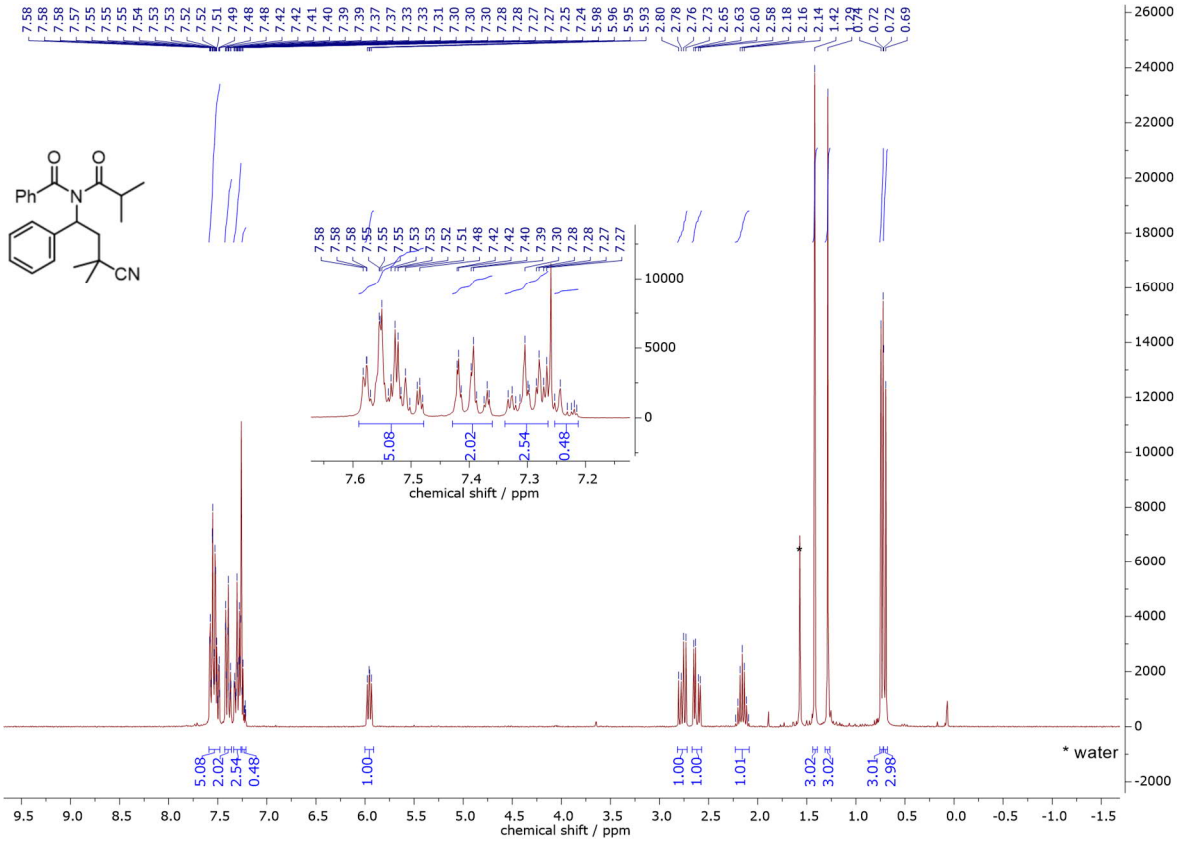
^{13}C {H} (126 MHz, $CDCl_3$) NMR spectrum of major diastereomer **11d**:



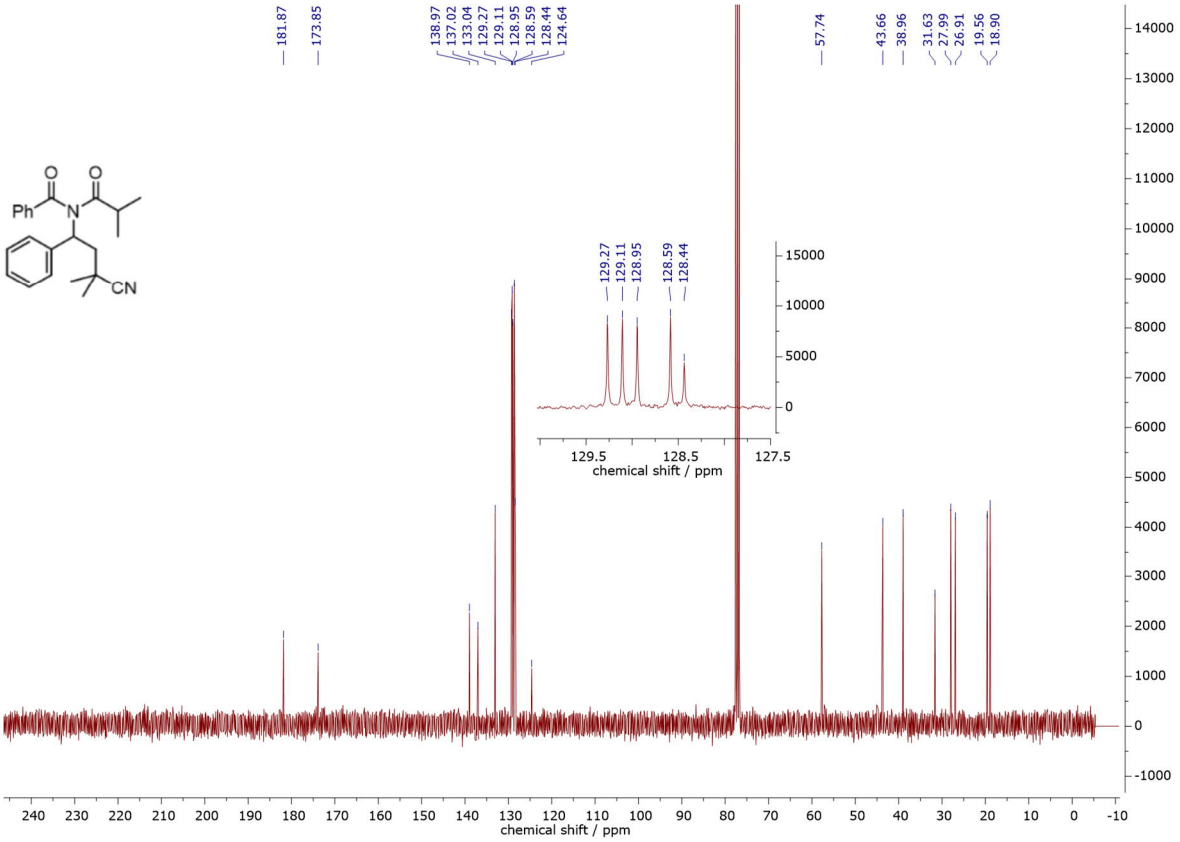
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of major diastereomer **11d**:



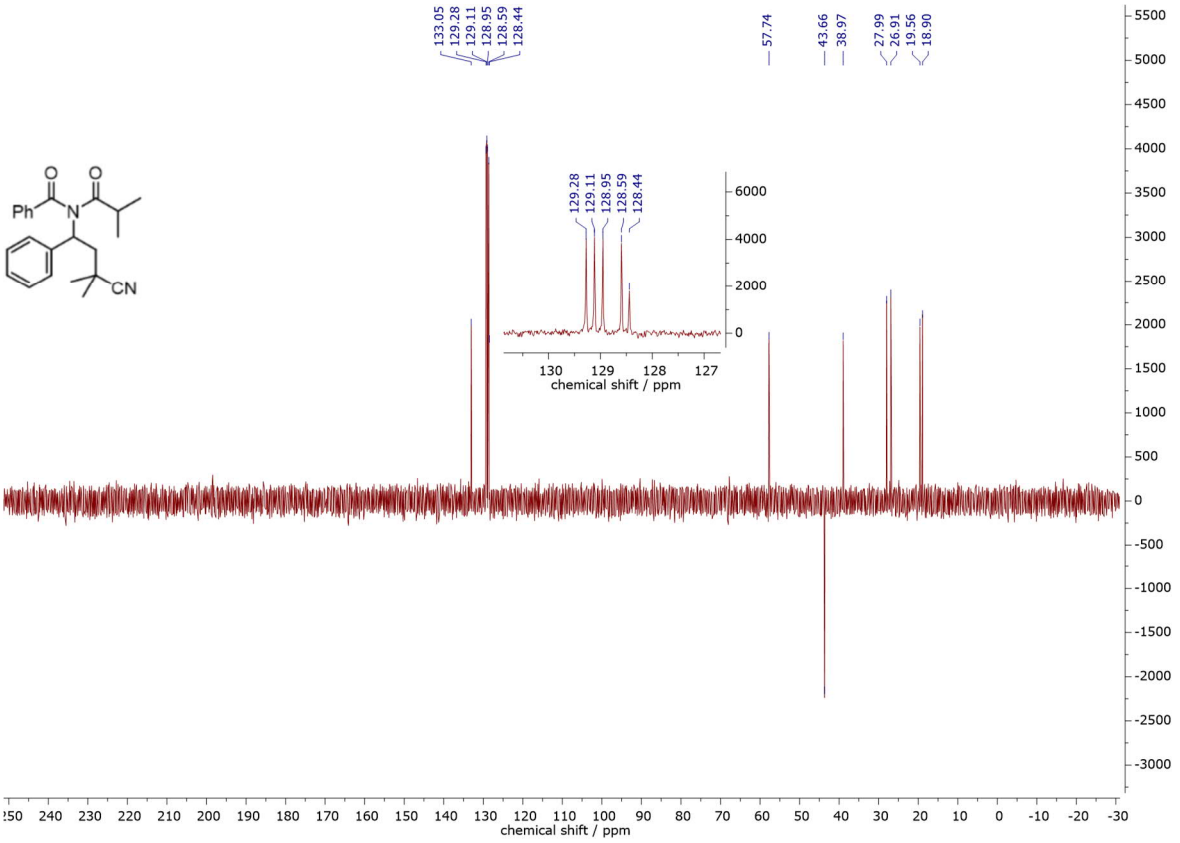
^{1}H (300 MHz, $CDCl_3$) NMR spectrum of product **11e**:



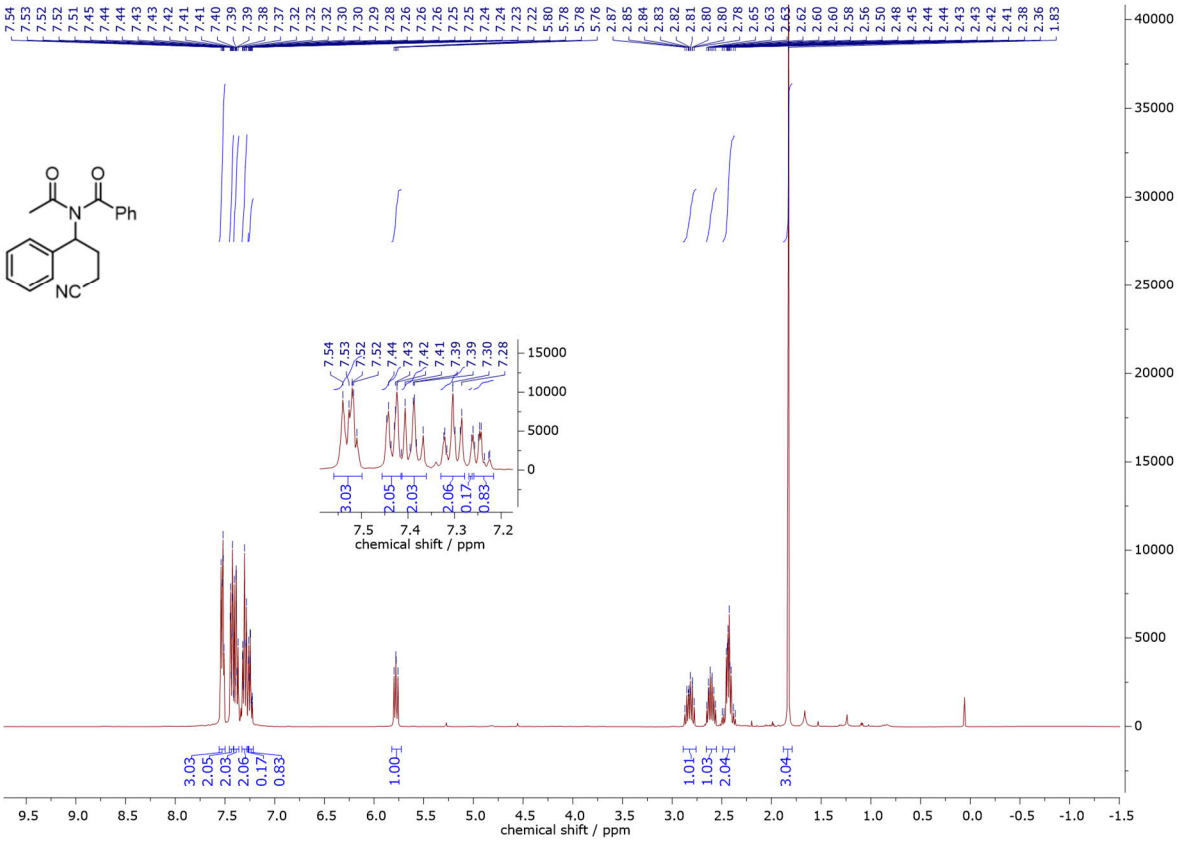
^{13}C {H} (75 MHz, $CDCl_3$) NMR spectrum of product **11e**:



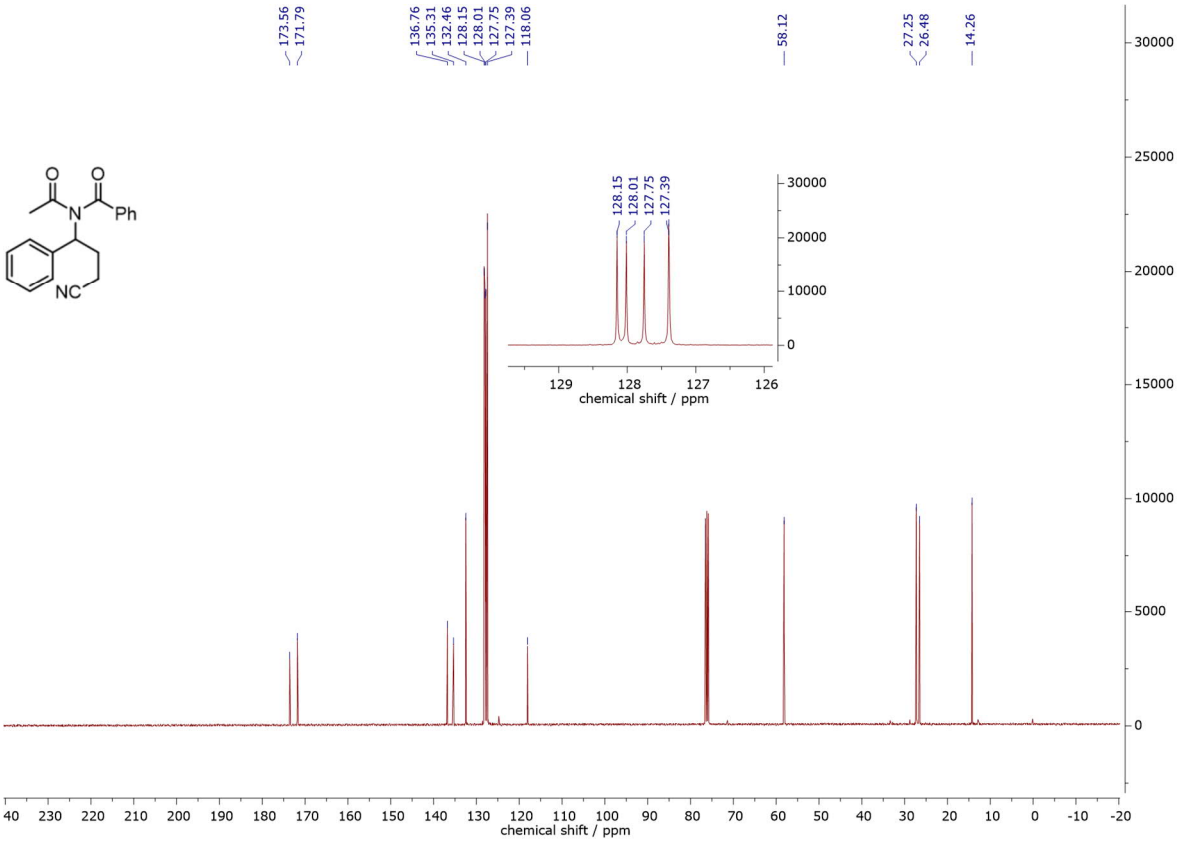
DEPT135 {H} (75 MHz, $CDCl_3$) NMR spectrum of product **11e**:



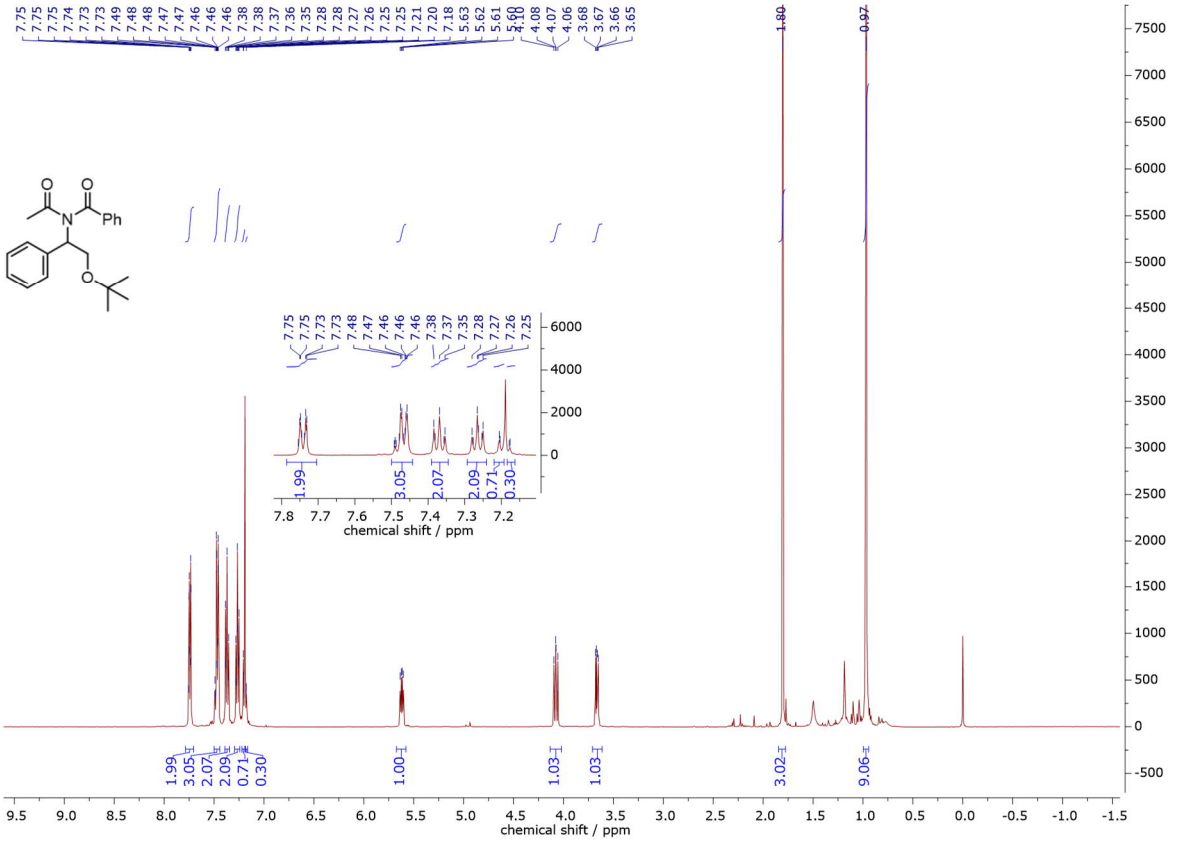
^1H (400 MHz, $CDCl_3$) NMR spectrum of product **11f**:



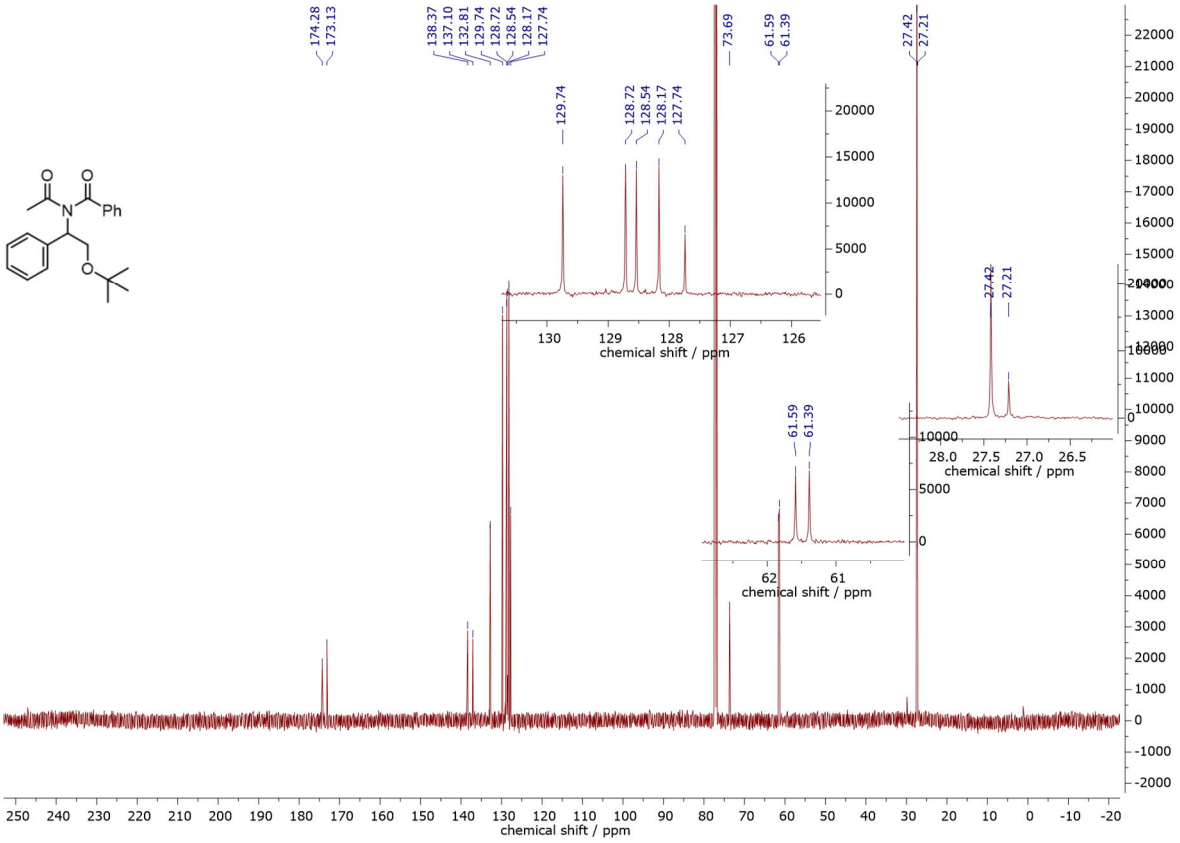
^{13}C {H} (101 MHz, $CDCl_3$) NMR spectrum of product **11f**:



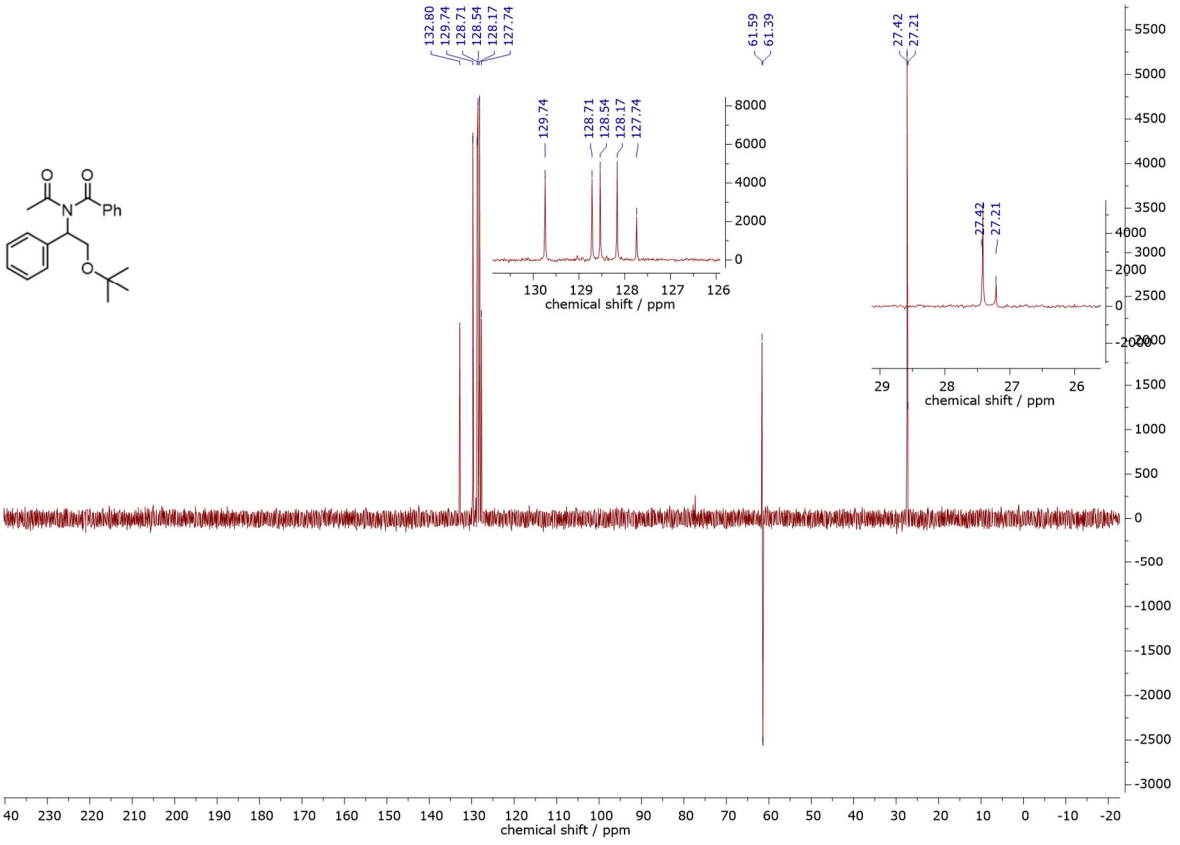
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **11g**:



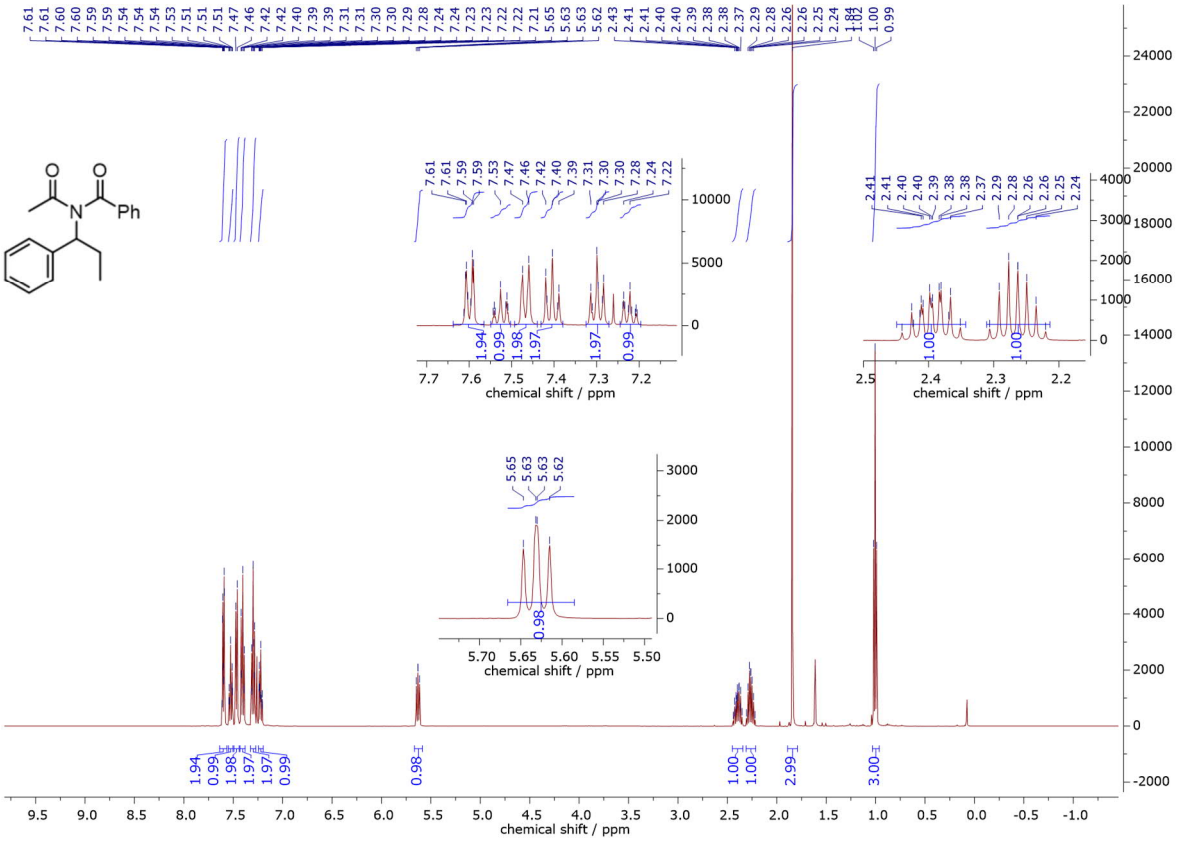
^{13}C {H} (126 MHz, $CDCl_3$) NMR spectrum of product **11g**:



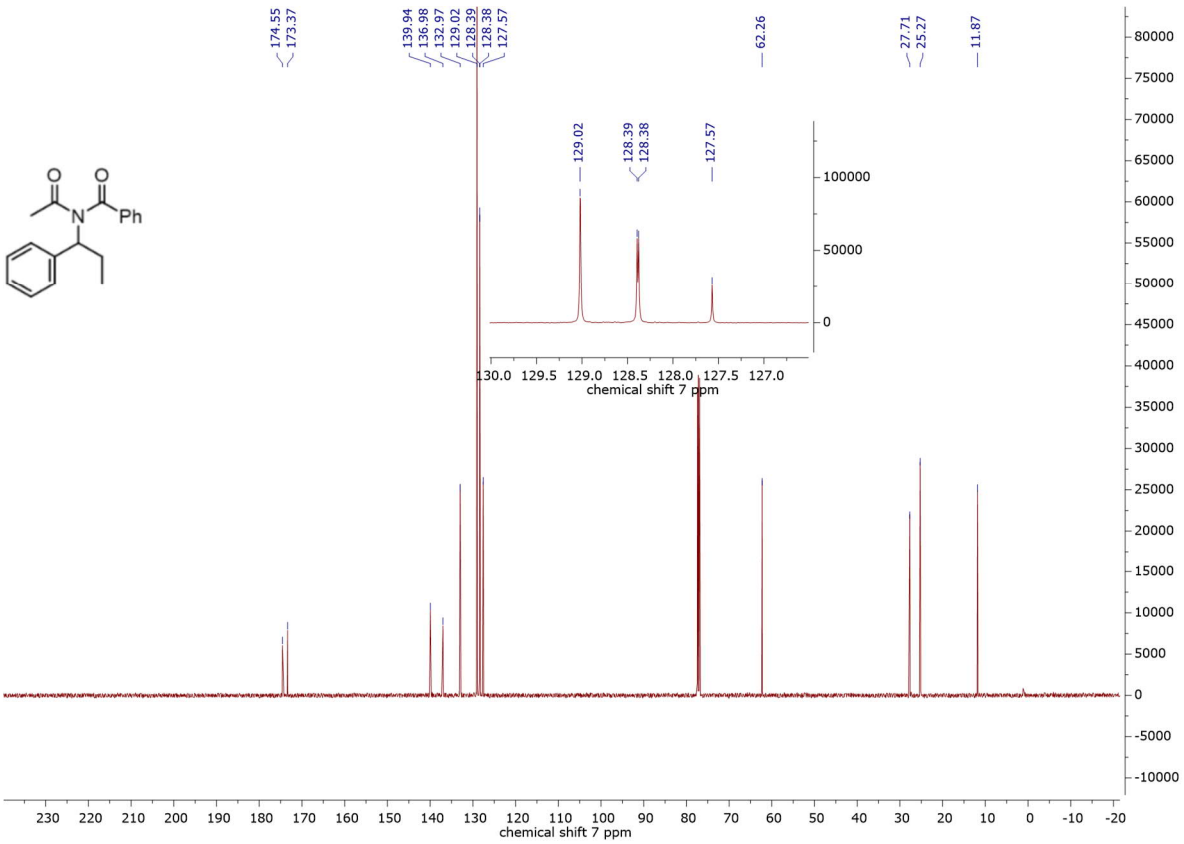
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **11g**:



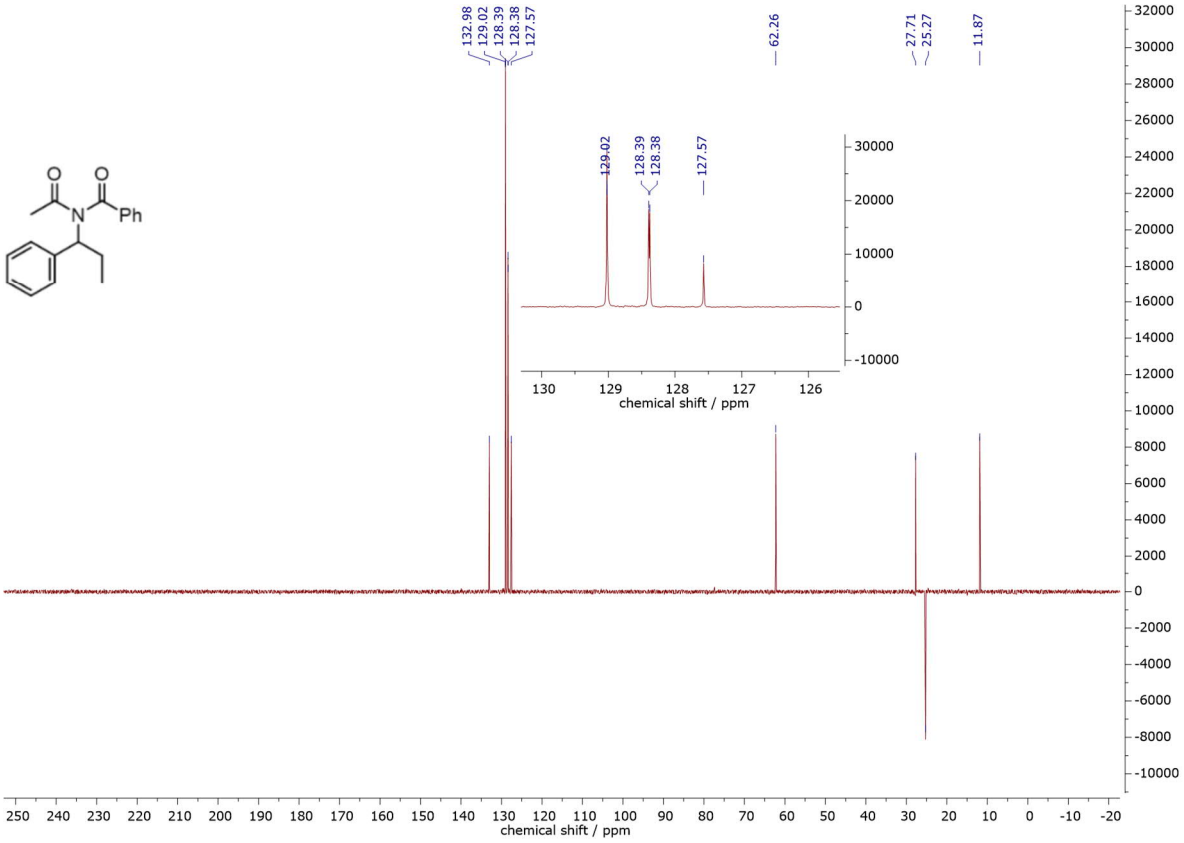
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **11h**:



^{13}C {H} (126 MHz, $CDCl_3$) NMR spectrum of product **11h**:

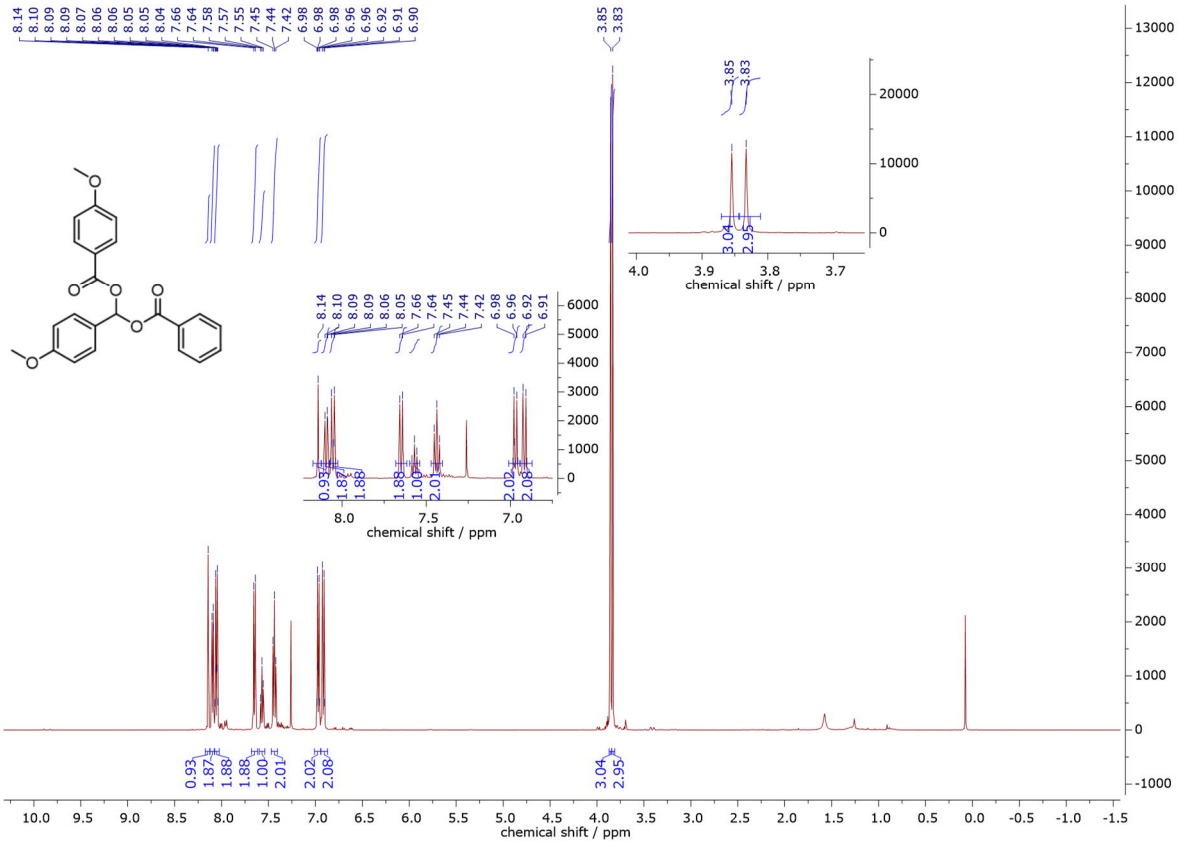


DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **11h**:

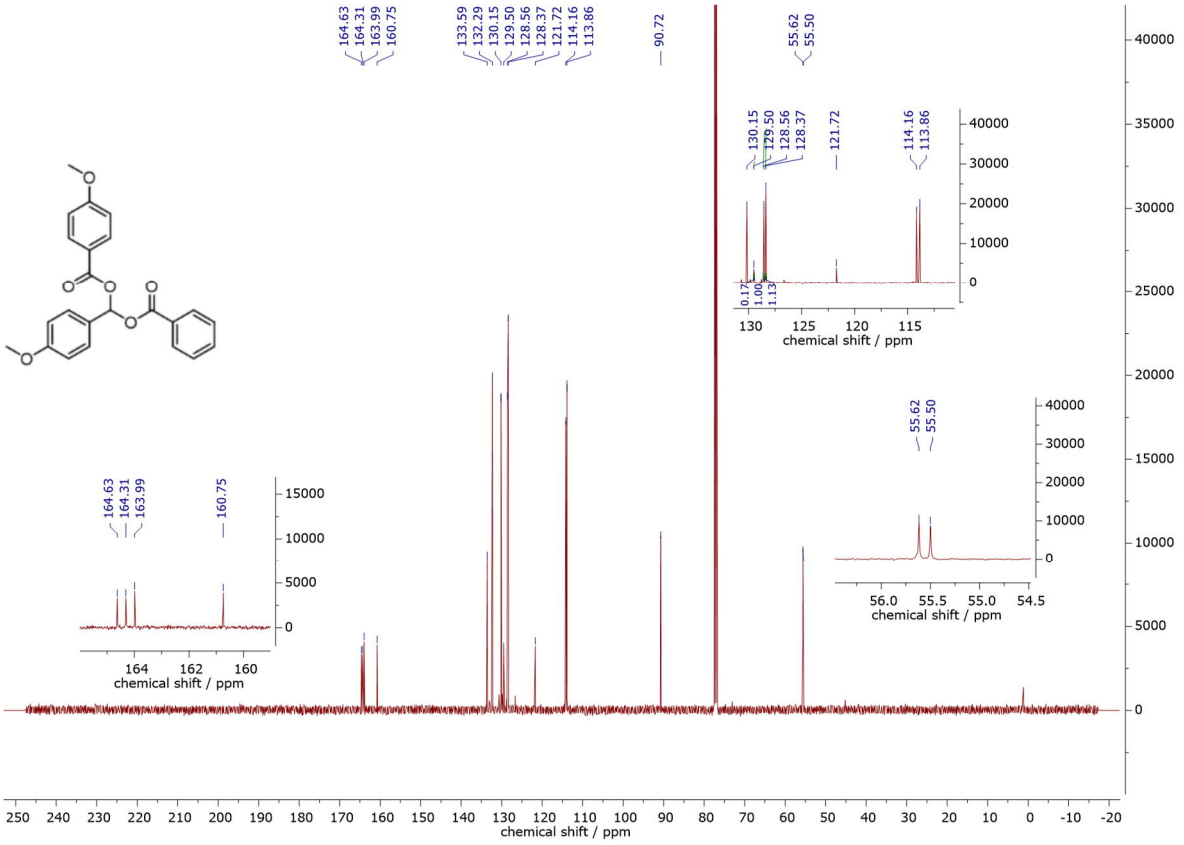


Other products

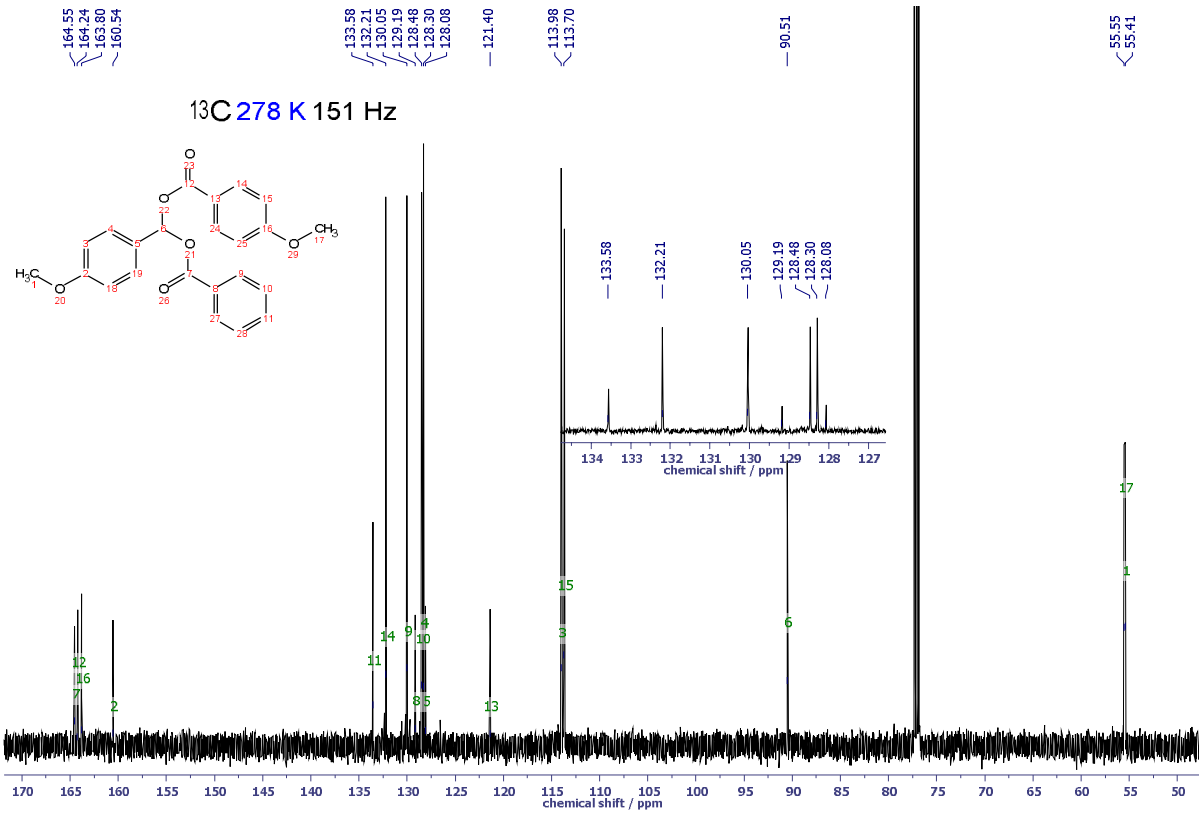
^{1}H (501 MHz, $CDCl_3$) NMR spectrum of product **14**:



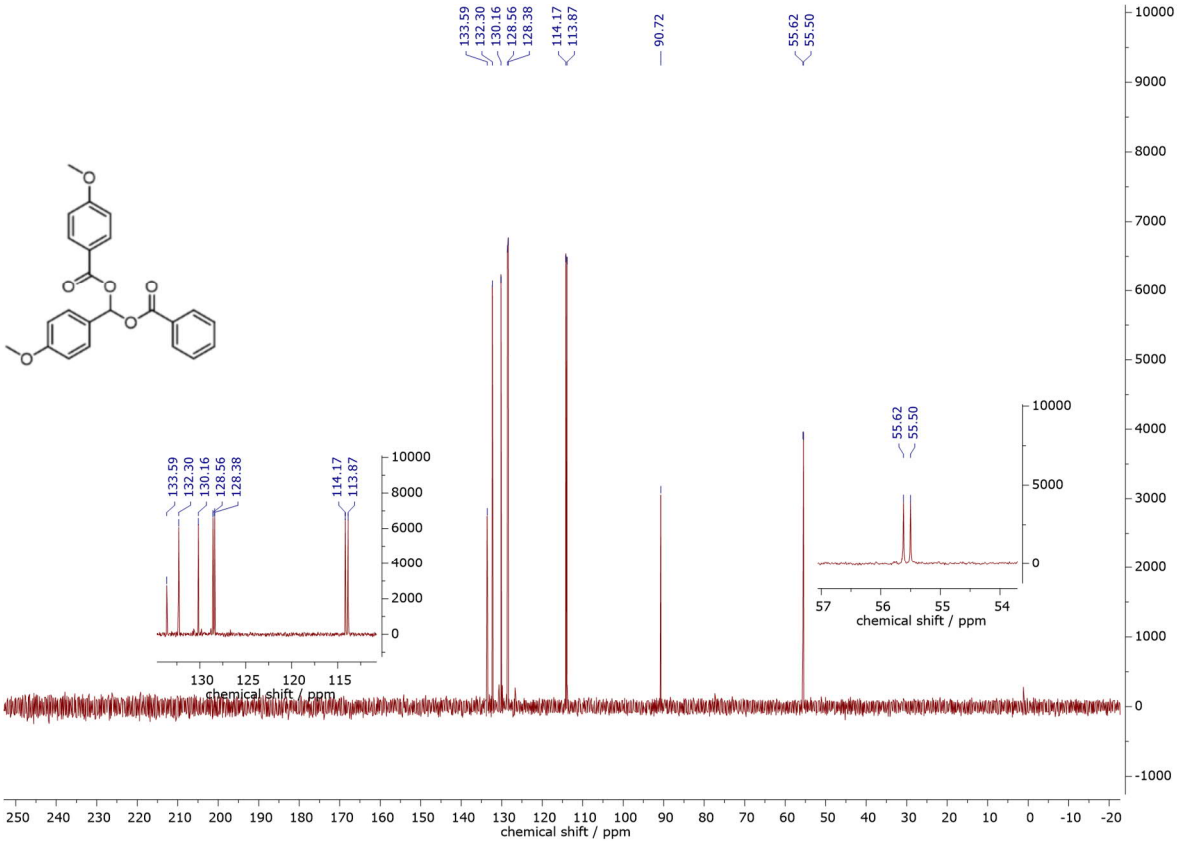
$^{13}C\{H\}$ (126 MHz, $CDCl_3$) NMR spectrum of product **14**:



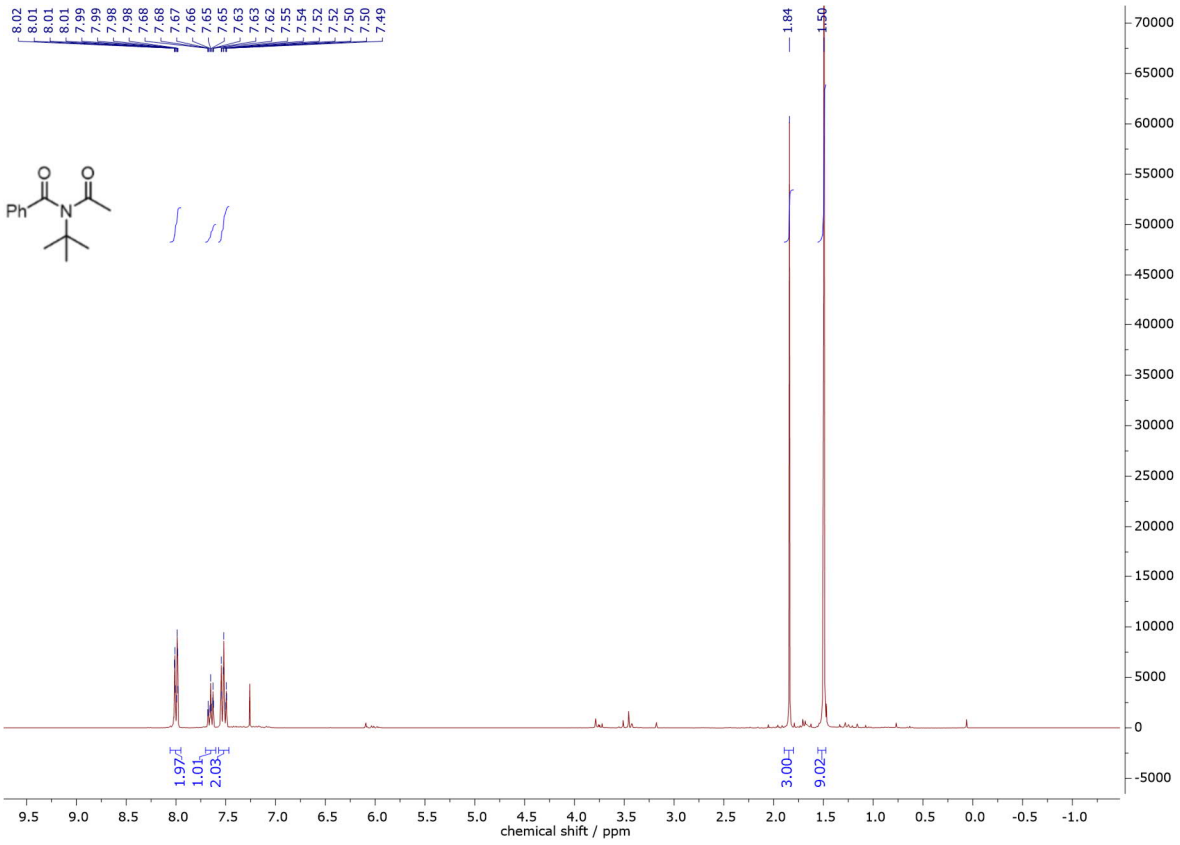
$^{13}C\{H\}$ (151 MHz, 278 K, $CDCl_3$) NMR spectrum of product **14**:



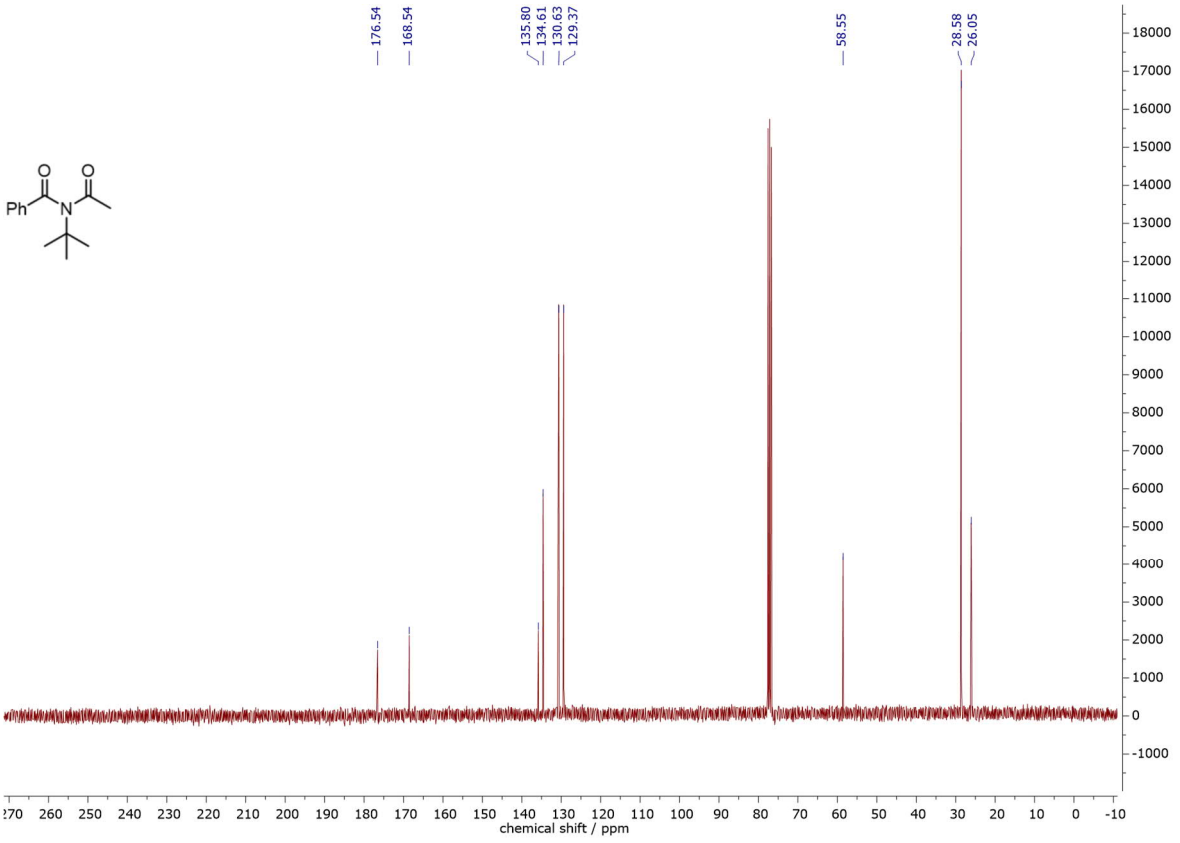
DEPT135 {H} (126 MHz, $CDCl_3$) NMR spectrum of product **14**:



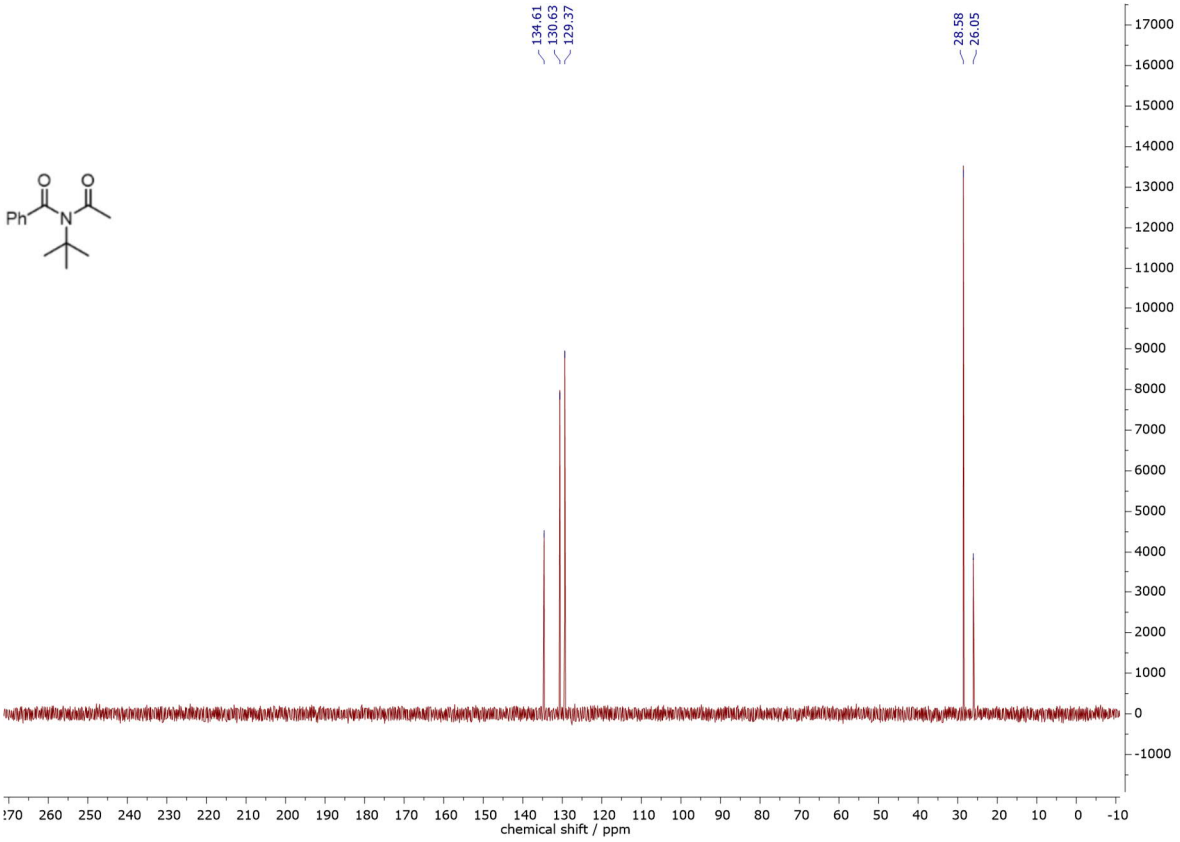
^1H (300 MHz, $CDCl_3$) NMR spectrum of product **15**:



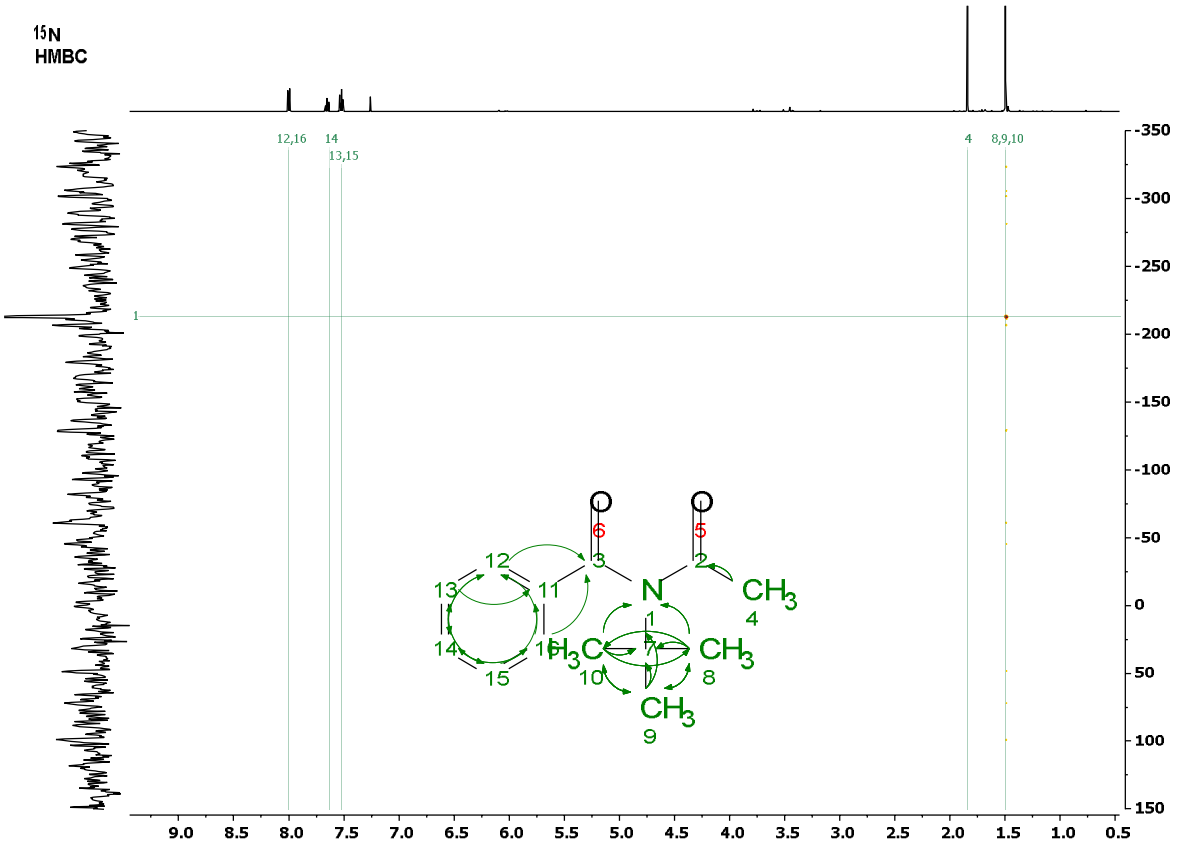
^{13}C {H} (75 MHz, $CDCl_3$) NMR spectrum of product **15**:



DEPT135 {H} (75 MHz, $CDCl_3$) NMR spectrum of product **15**:



^{15}N (HMBC, 51 MHz, $CDCl_3$) NMR spectrum of product **15**:



Supplementary References

(1) Zhang, M.-M.; Liu, F. *Org. Chem. Front.* **2018**, *5*, 3443.

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