Transition metal-free homologative cross-coupling of aldehydes and ketones with geminal bis(boron) compounds

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Supporting Information

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General Information

Solvents and commercially available reagents were purchased from standard chemical suppliers (Fisher, Sigma-Aldrich, VWR, Fluorochem) and used as received without further purification or drying. Reactions were performed under an atmosphere of dry nitrogen gas. Thin layer chromatography (TLC) was performed on Merck DF-Alufoilien 60F254 0.2 mm precoated plates. Product spots were visualized by UV light at 254 nm, and subsequently developed using vanillin or potassium permanganate as appropriate. Flash column chromatography was carried out using silica gel (Apollo Scientific 60Å particle size 40-63 micron). Melting points are uncorrected. Infra-red spectra were recorded on a Bruker Alpha-P ATR instrument on the neat compound. NMR spectra were recorded on a Bruker DPX-300, Bruker Avance III HD 300 MHz or Bruker Avance III HD 500 MHz instrument. For ^{1}H NMR spectra, chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using residual protonated solvent as internal standard ($CDCl_3$ at 7.26 ppm, d_6-acetone at 2.05 ppm). Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q, (quartet), app (apparent), br (broad). Coupling constants (J) are quoted to the nearest 0.1 Hz. For proton decoupled ^{13}C NMR spectra, chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using deuterated solvent as internal standard ($CDCl_3$ at 77.16 ppm, d_6-acetone at 29.92 ppm). Assignments were made using DEPT or PENDANT pulse sequences. For proton-decoupled ^{19}F NMR spectra, chemical shifts (δ) are quoted in parts per million (ppm) downfield of $CFCl_3$, using residual protonated solvent as internal standard ($CFCl_3$ at 376.38 MHz with respect to tetramethylsilane at 400.00 MHz). Low resolution mass spectra were recorded using electrospray ionization (ESI) techniques on an Agilent 6130R instrument. High resolution mass spectra were recorded using electrospray ionization (ESI) techniques on a Bruker Maxis instrument

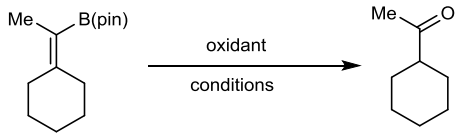
Reaction Optimization

Optimization of hindered base for boron-Wittig

Entry	Hindered Base	Conversion (%)*	E/Z ratio
1	LDA	65 (45% E- & 20% Z-)	2.3:1
2	LiHMDS	Trace	-
3	LiTMP	95 (E-)	>19:1
4	^{t}BuOLi	0	-

Key to successful deprotonation is the use of a strong, sterically hindered base. LiTMP shows high basicity and fast deprotonation kinetics at 0 °C. LDA has similar basicity but is less sterically hindered and likely gives some competing attack at boron. The reason for the lower E/Z selectivity using LDA is not clear. LiHMDS is less basic than LiTMP (pK_a 26 vs. 36) so is not sufficiently basic to deprotonate alpha- to boron. This leads to an estimate of the pK_a of geminal bis(boron) compounds to be between 26 and 36. ^{t}BuOLi gives exclusive attack at boron rather than deprotonation.

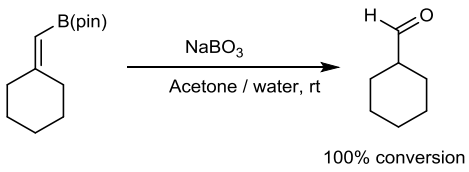
Optimization of oxidizing agent



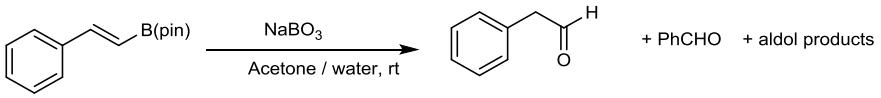
Oxidant	Equiv.	Solvent	Temp	% Vinyl boronate	% Ketone	Notes
Oxone	1.0	Acetone / H_2O, 2:3	25	trace	trace	Significant decomp.
Oxone	2.0	Acetone / H_2O, 1:3	25	66	34	Significant decomp.
Oxone	4.0	Acetone / H_2O, 1:6	25	trace	trace	Significant decomp.
Oxone	4.0	Acetone / H_2O, 1:3	25	73	27	Significant decomp.
Oxone	2.0	Acetone / H_2O, 1:3	50	86	14	Significant decomp.
$NaBO_3$	2.0	Acetone / H_2O, 1:3	25	trace	>95	Little decomp.
$NaBO_3$	1.2	Acetone / H_2O, 3:4	25	0	100	No decomp.
$NaBO_3$	1.2	THF / H_2O, 3:4	25	12	88	Little decomp.
$NaBO_3$	1.2	Dioxane / H_2O, 3:4	25	78	22	Prod. volatility on solvent evaporation
$NaBO_3$	1.2	MeCN / H_2O, 3:4	25	trace	trace	Prod. volatility on solvent evaporation
$NaBO_3$	1.2	DCM / H_2O, 3:4	25	100	0	Oxidant immiscibility
$NaBO_3$	1.2	iPrOH / H_2O, 3:4	25	30	70	Little decomp.

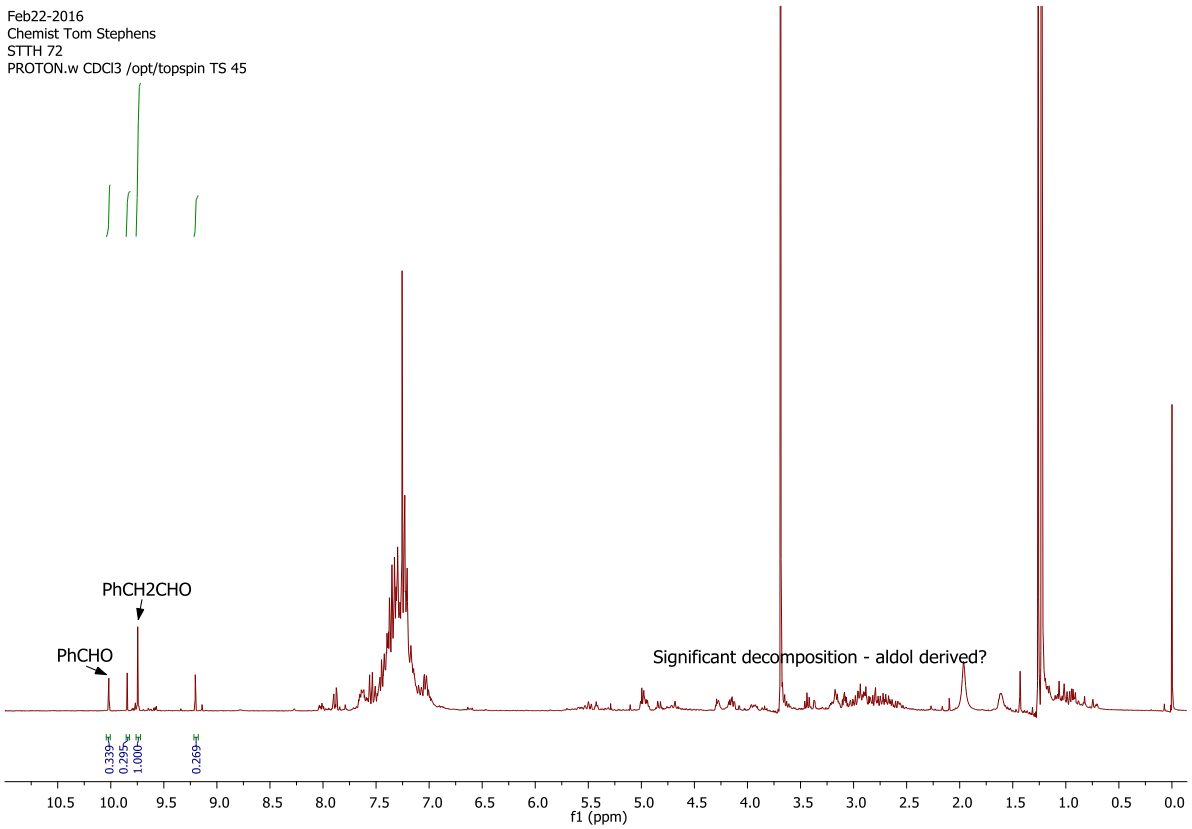
Key to successful oxidation of this tetrasubstituted vinyl-boronate was the use of sodium perborate as oxidant rather than oxone, which gave poorer conversions and often significant decomposition. The use of acetone as solvent gave good mixing of oxidant and substrate and therefore clean oxidation to high conversion.

These conditions also proved very applicable to the oxidation of a trisubstituted vinyl-boronate.

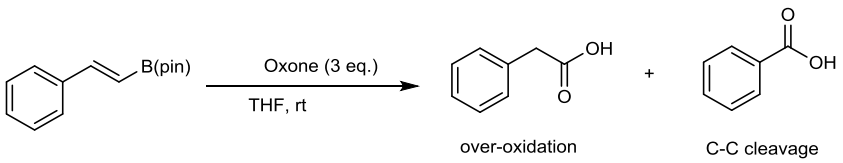


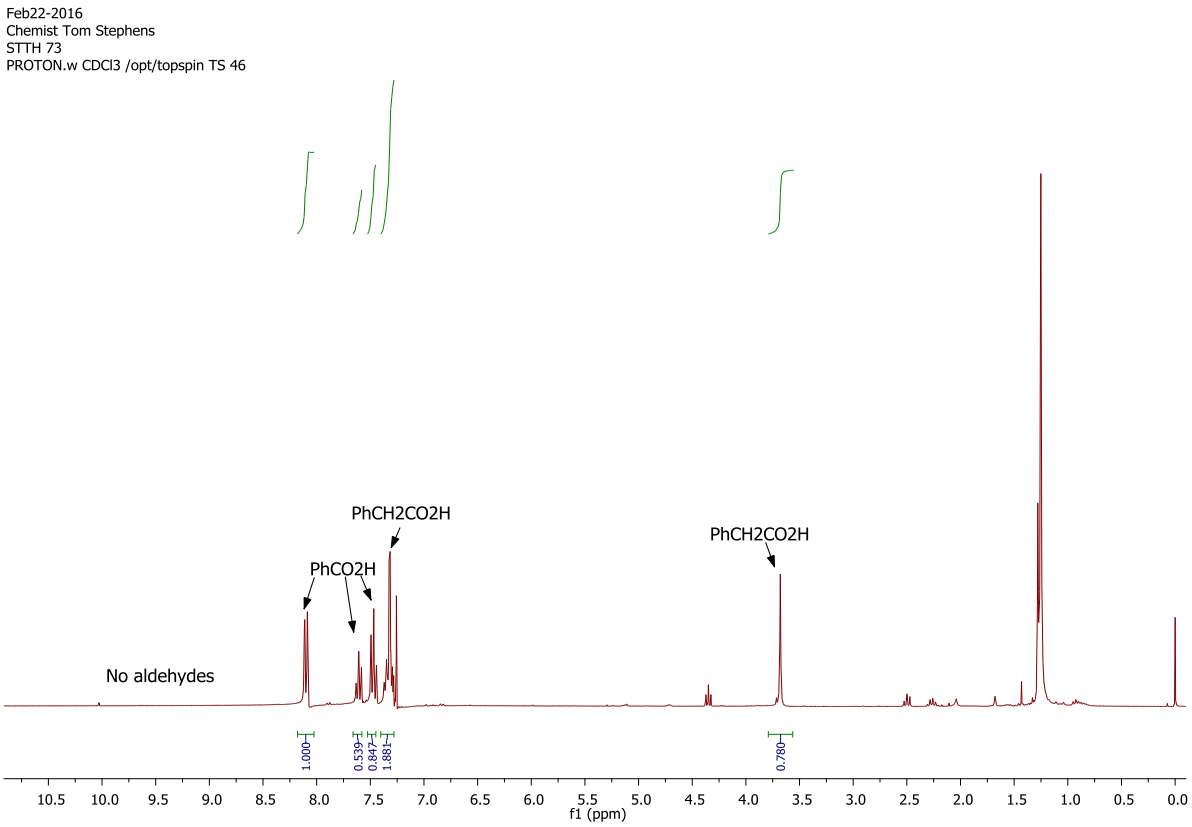
The use of aryl-substituted vinyl boronates derived from boron-Wittig reaction of aromatic aldehydes gave much more significant by-products. Here the use of $NaBO_3$ as oxidant was inappropriate due to aldol side-reactions of the more acidic benzylic aldehyde products under the basic reaction conditions.



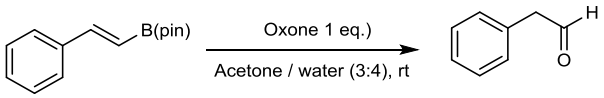


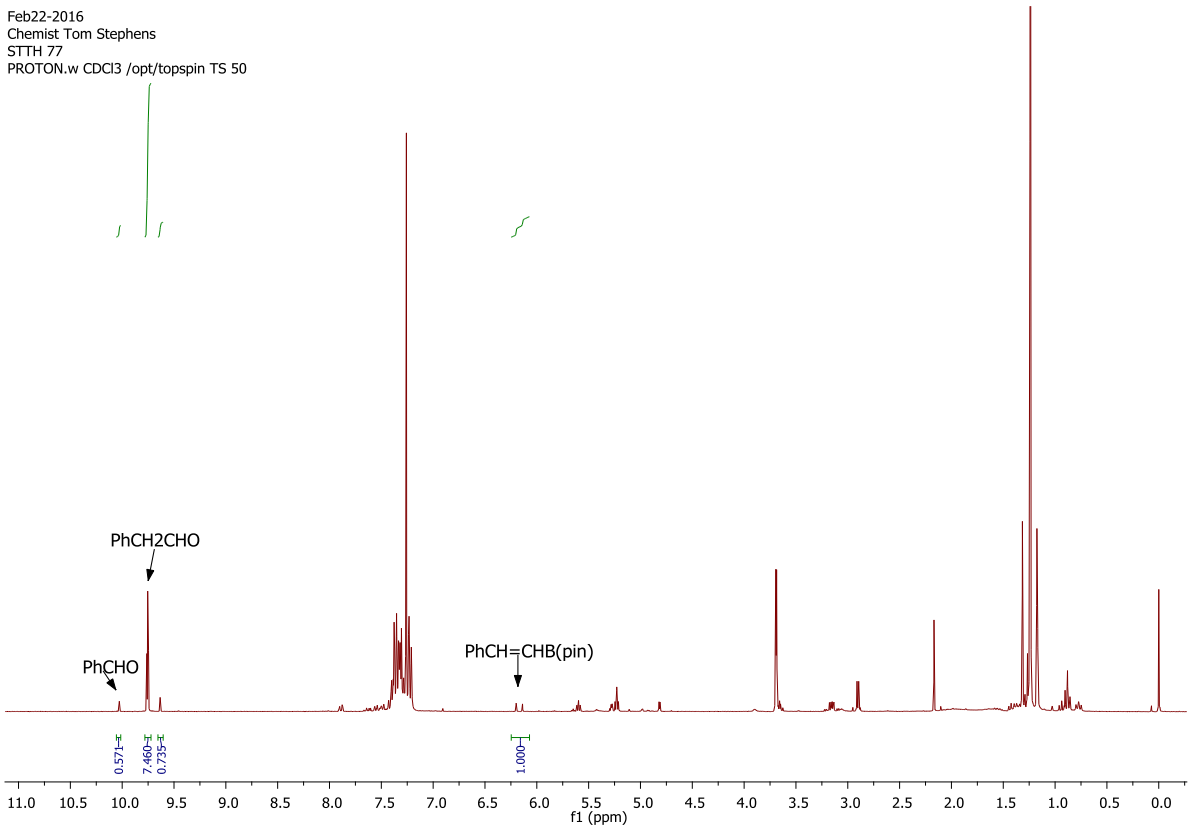
Acidic conditions were therefore required for successful oxidation to prevent aldol side-processes. However, these substrates also proved susceptible to C-C bond-cleavage processes and over oxidation.





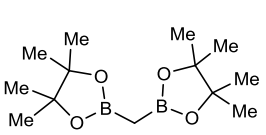
Cleanest oxidation of these substrates that give benzylic aldehydes on oxidation was achieved using 1 equivalent of oxone in acetone / water (3:4).



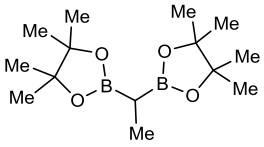


Preparation of geminal bis(boron) compounds

The following geminal bis(boron) compounds were prepared by literature methods. NMR and mass spectral data was in full agreement with the literature.



S1



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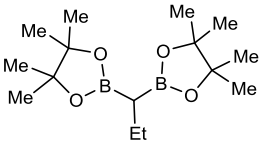

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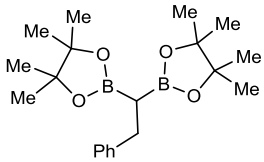

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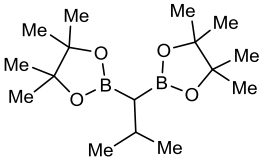

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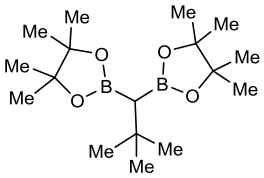
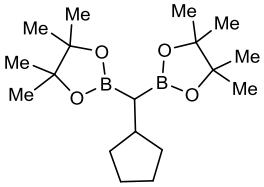
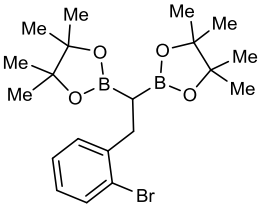


S6



S7

2,2'-(2-(2-bromophenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) – S8



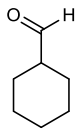
S8

A solution of LiTMP was prepared by the addition of nBuLi (1.32 mL, 2.5 M in hexanes, 3.3 mmol) to 2,2,6,6-tetramethylpiperidine (0.565 mL, 3.3 mmol) in THF (5 mL) at -78 °C. A solution of bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane **S1** in THF (1 mL) was added slowly to the LiTMP solution and stirred for 1 h. After this period a solution of 2-bromobenzyl bromide (0.750 g, 3.0 mmol) in THF (2 mL) was added to the mixture, which was stirred at -78 °C for 2 h before warming to room temperature. The solution was diluted with diethyl ether (10 mL) and water (5 mL) and the organic layer separated. The aqueous layer was extracted with further portions of diethyl ether (3 x 10 mL) and the combined organic extracts were dried ($MgSO_4$), filtered and evaporated. The crude material was purified by flash column chromatography on silica (EtOAc / hexanes, 10%) to give the title compound as a white solid; δ_H (500 MHz, $CDCl_3$) 7.41 (1H, dd, *J* = 7.9, 0.8 Hz, Ar**H**), 7.28 (1H, dd, *J* = 7.5, 1.4 Hz, Ar**H**), 7.10 (1H, td, *J* = 7.5, 0.8 Hz, Ar**H**), 6.93 (1 H, td, *J* = 7.9, 1.4 Hz, Ar**H**), 2.91 (2H, d, *J* = 7.9 Hz ArC**H₂**), 1.23 (1H, t, *J* = 7.9 Hz, C**H**(Bpin)$_2$), 1.13 (12H, s, 4 x CH_3), 1.13 (12H, s, 4 x CH_3); δ_C (125 MHz, $CDCl_3$) 143.5 (C), 132.5 (CH), 130.3 (CH), 127.1 (CH), 126.9 (CH), 124.6 (C), 83.2 (C), 31.7 (CH_2), 24.8 (CH_3), 24.5 (CH_3) (carbon adjacent to boron not visible); HRMS (ES^+) Exact mass calculated for $C_{20}H_{31}{}^{11}B_2{}^{79}BrO_4$ $[M+Na]^+$: 458.1522, found: 458.1526.

General Procedure for homologative cross-coupling

2,2,6,6-tetramethylpiperidine (1.2 equiv.) was dissolved in THF (0.6M) and cooled to 0 °C under dry nitrogen. *n*-Butyllithium solution (2.50 M, 1.2 equiv.) was added dropwise and the solution stirred for 10 minutes. A solution of geminal bis(boron) compound (1.2 equiv.) in THF (1.2 M) was prepared and added dropwise to the LiTMP solution at 0 °C. After stirring for 15 minutes the solution was cooled to -78 °C before the dropwise addition of a solution of aldehyde or ketone (1 equiv.) in THF (1.0 M). After an hour at this temperature, the solution was warmed to 0 °C and stirred for a further 2 hours. The solvent was evaporated under vacuum and replaced with acetone (4.4 mL per mmol of starting carbonyl compound). The solution was cooled to 0 °C and an aqueous solution of sodium perborate (1.5 equiv., 0.9 M) was added dropwise. The solution was stirred at 0 °C for 1 hour. Generally after this period the reaction was complete, however certain cases required the addition of further 0.5 equiv. portions of sodium perborate solution. When fully oxidized, water (5 mL) was added and the mixture extracted with diethyl ether (3 × 5 mL). The combined extracts were dried ($MgSO_4$), filtered and evaporated to yield crude product. The products were purified by flash column chromatography (Et_2O / pentane).

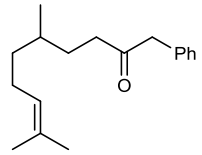
Cyclohexanecarbaldehyde - 1a



The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.570 mL, 3.3 mmol), *n*-butyllithium (1.32 mL, 2.5 M in hexanes, 3.3 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (0.890 g, 3.3 mmol) and cyclohexanone (0.310 mL, 3.0 mmol) in THF (12 mL), followed by oxidation by sodium perborate (0.690 g, 4.5 mmol) in water (9.9 mL) and acetone (13.2 mL). The compound was purified by column chromatography using Et_2O / pentane (5%) as eluent to yield the title compound as a colourless oil (0.240 g, 71%). δ_H (300 MHz, $CDCl_3$) 9.61 (1H, s, C**H**O), 2.29 – 2.17 (1H, m, C**H**CHO), 1.96– 1.82 (2H, m), 1.80 – 1.69 (2H, m), 1.69 – 1.58 (1H, m), 1.45 – 1.17 (5H, m). This data is in agreement with the literature.[1]

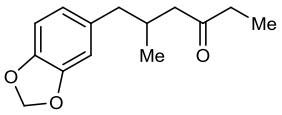
[1] M. Kirihara, T. Noguchi, N. Okajima, S. Naito, Y. Ishizuka, A. Harano, H. Tsukiji, R. Takizawa, *Tetrahedron* **2012**, *68*, 1515.

5,9-dimethyl-1-phenyldec-8-en-2-one - 2a



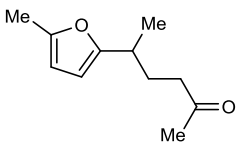
The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and 2,2'-(2-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (215 mg, 0.6 mmol) and citronellal (91.0 µL, 0.5 mmol) in THF (2 mL), followed by oxidation by sodium perborate (115 mg, 0.75 mmol) in water (1.65 mL) and acetone (2.0 mL). The compound was purified by column chromatography using Et_2O / pentane (10%) as eluent to yield the title compound as a colourless oil (84 mg, 65%). ν_{max} (neat): 2969 (CH), 2927 (CH), 1710 (C=O), 1496, 1378, 1271, 1086, 1047, 879, 699 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.35 – 7.30 (2H, m, Ar**H**), 7.28 – 7.23 (1H, m, Ar**H**), 7.20 (2H, d, *J* = 7.0 Hz, Ar**H**), 5.05 (1H, tt, *J* = 7.0, 1.3 Hz, C=C**H**), 3.68 (2H, s, PhC**H₂**), 2.52 – 2.36 (2H, m), 2.01 – 1.84 (2H, m), 1.67 (3H, s, =CC**H₃**), 1.58 (3H, s, =CC**H₃**), 1.42 – 1.20 (4H, m), 1.16 – 1.05 (1H, m, C**H**CH_3), 0.82 (3H, d, *J* = 6.2 Hz, CHC**H₃**); δ_C (100 MHz, $CDCl_3$) 208.8 (**C**=O), 134.4 (**C**), 131.2 (**C**), 129.4 (2 × **C**H), 128.7 (2 × **C**H), 126.9 (**C**H), 124.6 (**C**H), 50.1 (**C**H_2), 39.7 (**C**H_2), 36.8 (**C**H_2), 32.0 (**C**H), 30.6 (**C**H_2), 25.7 (**C**H_3), 25.4 (**C**H_2), 19.2 (**C**H_3), 17.6 (**C**H_3); HRMS (ES^+): Exact mass calculated for $C_{18}H_{26}O$ $[M+Na]^+$: 281.1876, found: 281.1874.

6-(benzo[d][1,3]dioxol-5-yl)-5-methylhexan-3-one - 2b



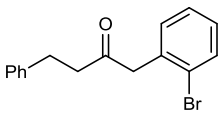
The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and 2,2'-(propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (178 mg, 0.6 mmol) and 2-methyl-3-(3,4-methylenedioxyphenyl)-propanal (83.0 µL, 0.5 mmol) in THF (2 mL), followed by oxidation by sodium perborate (115 mg, 0.75 mmol) in water (1.65 mL) and acetone (2.0 mL). The compound was purified by column chromatography using EtOAc / hexane (5%) as eluent to yield the title compound as a colourless oil (68 mg, 58%). ν_{max} (neat): 2959 (CH), 2929 (CH), 1709 (C=O), 1503, 1488, 1440, 1243, 1188, 1036, 925, 806 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.71 (1H, d, *J* = 7.9 Hz, Ar**H**), 6.65 (1H, d, *J* = 1.5 Hz, Ar**H**), 6.58 (1H, dd, *J* = 7.9, 1.5 Hz, Ar**H**), 5.91 (2H, s, O**CH₂**O), 2.48 (1H, dd, *J* = 13.3, 6.6 Hz, O=CC**H₂**CHMe), 2.42 – 2.32 (4H, m, O=CC**H₂**CHMe and O=CC**H₂**CH_3 and ArC**H₂**), 2.30 – 2.17 (2H, m, ArC**H₂** and CH_3C**H**), 1.02 (3H, t *J* = 7.2 Hz, CH_2C**H₃**), 0.88 (3H, d, *J* = 6.3 Hz, CH_2C**H₃**); δ_C (100 MHz, $CDCl_3$) 211.2 (**C**=O), 147.4 (**C**), 145.6 (**C**), 134.2 (**C**), 121.9 (**C**H), 109.4 (**C**H), 107.9 (**C**H), 100.7 (**C**H_2), 48.7 (**C**H_2), 42.8 (**C**H_2), 36.4 (**C**H_2), 31.2 (**C**H), 19.6 (**C**H_3), 7.6 (**C**H_3); HRMS (ES^+): Exact mass calculated for $C_{14}H_{18}O_3$ $[M+Na]^+$: 257.1148, found: 257.1146.

5-(5-methylfuran-2-yl)hexan-2-one - 2c



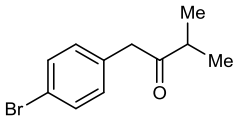
The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and 2,2'-(ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (169 mg, 0.6 mmol) and 3-(5-Methyl-2-furyl)butyraldehyde (75.0 µL, 0.5 mmol) in THF (2 mL), followed by oxidation by sodium perborate (115 mg, 0.75 mmol) in water (1.65 mL) and acetone (2.0 mL). The compound was purified by column chromatography using EtOAc / hexane (10%) as eluent to yield the title compound as a colourless oil (63 mg, 70%). ν_{max} (neat): 2971 (CH), 2930 (CH), 1709 (C=O), 1359, 1165, 1085, 1047 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.83 (2H, s, Ar**H**), 2.27 (1H, sextet, *J* = 6.9 Hz, C**H**CH_3), 2.40 (2H, dd, *J* = 7.4, 8.7 Hz, C$\mathbf{H_2}$C=O), 2.24 (3H, s, C$\mathbf{H_3}$), 2.10 (3H, s, C$\mathbf{H_3}$), 1.89 – 1.78 (2H, m, CHC$\mathbf{H_2}$), 1.21 (3H, d, *J* = 6.9 Hz, CHC$\mathbf{H_3}$); δ_C (100 MHz, $CDCl_3$) 208.8 (**C**=O), 157.6 (**C**), 150.3 (**C**), 105.6 (**C**H), 104.6 (**C**H), 41.3 (**C**H_2), 32.5 (**C**H_3), 29.9 (**C**H), 29.6 (**C**H_2), 19.2 (**C**H_3), 13.5 (**C**H_3); HRMS (ES^+): Exact mass calculated for $C_{11}H_{16}O_2$ $[M+Na]^+$: 203.1043, found: 204.1043.

1-(2-bromophenyl)-4-phenylbutan-2-one - 2d



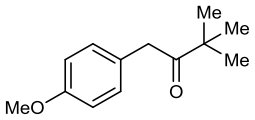
The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and 2,2'-(2-(2-bromophenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (262 mg, 0.6 mmol) and phenylacetaldehyde (66.0 µL, 0.5 mmol) in THF (2 mL), followed by oxidation by sodium perborate (115 mg, 0.75 mmol) in water (1.65 mL) and acetone (2.0 mL). The compound was purified by column chromatography using EtOAc / hexane (5%) as eluent to yield the title compound as a colourless oil (92 mg, 61%). ν_{max} (neat): 3022 (CH), 2953 (CH), 2926 (CH), 1705 (C=O), 1439, 1409, 1359, 1321, 1134, 1023, 1014, 755, 699 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.56 (1H, dd, *J* = 8.0, 0.8 Hz, Ar**H**), 7.30 – 7.23 (3H, m, Ar**H**), 7.21 – 7.10 (5H, m, Ar**H**), 3.83 (2H, s, O=CC$\mathbf{H_2}$Ar), 2.95 – 2.89 (2H, m), 2.85 – 2.79 (2H, m); δ_C (100 MHz, $CDCl_3$) 206.0 (**C**=O), 140.9 (**C**), 134.6 (**C**), 132.8 (**C**H), 131.7 (**C**H), 128.8 (**C**H), 128.5 (2 × **C**H), 128.4 (2 × **C**H), 127.6 (**C**H), 126.1 (**C**H), 125.0 (**C**), 50.2 (**C**H_2), 44.0 (**C**H_2), 29.7 (**C**H_2); HRMS (ES^+): Exact mass calculated for $C_{16}H_{15}O^{79}Br$ $[M+Na]^+$: 325.0198, found: 325.0197.

1-(4-bromophenyl)-3-methylbutan-2-one - 2e



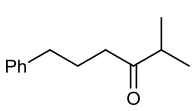
The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and 2,2'-(2-methylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (186 mg, 0.6 mmol) and 4-bromobenzaldehyde (93.0 mg, 0.5 mmol) in THF (2 mL), followed by oxidation by sodium perborate (115 mg, 0.75 mmol) in water (1.65 mL) and acetone (2.0 mL). The compound was purified by column chromatography using Et_2O / hexane (5%) as eluent to yield the title compound as a white solid (73 mg, 60%). m.p. 65 – 67 °C; ν_{max} (neat): 2968, 2933, 2871, 1704 (C=O), 1486, 1465, 1450, 1321, 1068, 1041, 1007, 788 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.44 (2H, d, *J* = 8.3 Hz, Ar**H**), 7.07 (2H, d, *J* = 8.3 Hz, Ar**H**), 3.70 (2H, s, ArC**H₂**), 2.71 (1H, septet, *J* = 6.9 Hz, C**H**$(CH_3)_2$), 1.11 (6H, d, *J* = 6.9 Hz, CH(C**H₃**)$_2$); δ_C (100 MHz, $CDCl_3$) 211.2 (**C**=O), 133.3 (**C**), 131.7 (2 × **C**H), 131.2 (2 × **C**H), 120.9 (**C**), 46.7 (**C**H_2), 40.4 (**C**H), 18.2 (2 × **C**H_3); HRMS (ES^+): Exact mass calculated for $C_{11}H_{13}O^{79}Br$ $[M+Na]^+$: 263.0042, found: 263.0044.

1-(4-methoxyphenyl)-3,3-dimethylbutan-2-one - 2f



The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and 2,2'-(2,2-dimethylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (177 mg, 0.55 mmol) and 4-methoxybenzaldehyde (55.0 µL, 0.46 mmol) in THF (2 mL), followed by oxidation by sodium perborate (115 mg, 0.75 mmol) in water (1.65 mL) and acetone (2.0 mL). A second portion of sodium perborate (57.5 mg, 0.375 mmol) in water (0.8 mL) and acetone (1.0 mL) was added after 2 hours. The compound was purified by column chromatography using EtOAc / hexane (5%) as eluent to yield the title compound as a colourless oil (38 mg, 40%). ν_{max} (neat): 2967 (CH), 1707 (C=O), 1612, 1511, 1464, 1245, 1177, 1033, 1007 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.10 (2H, d, *J* = 8.5 Hz, Ar**H**), 6.86 (2H, d, *J* = 8.5 Hz, Ar**H**), 3.80 (3H, s, OC**H₃**), 3.75 (2H, s, ArC**H₂**), 1.20 (9H, s, C(C**H₃**)$_3$); δ_C (100 MHz, $CDCl_3$) 213.1 (**C**=O), 158.2 (**C**), 130.3 (2 × **C**H), 126.8 (**C**), 113.7 (2 × **C**H), 55.1 (**C**H_3), 44.4 (**C**), 42.2 (**C**H_2), 26.3 (3 × **C**H_3); HRMS (ES^+): Exact mass calculated for $C_{13}H_{18}O_2$ $[M+Na]^+$: 229.1199, found: 229.1201.

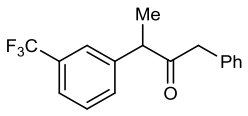
2-methyl-6-phenylhexan-3-one - 2g



The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.570 mL, 3.3 mmol), *n*-butyllithium (1.32 mL, 2.5 M in hexanes, 3.3 mmol) and 2,2'-(2-

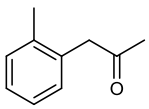
methylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (1.02 g, 3.3 mmol) and hydrocinnamaldehyde (0.400 mL, 3.0 mmol) in THF (12 mL), followed by oxidation by sodium perborate (0.690 g, 4.5 mmol) in water (9.9 mL) and acetone (13.2 mL). The compound was purified by column chromatography using EtOAc / hexane (5%) as eluent to yield the title compound as a colourless oil (0.410 g, 71%). δ_H (400 MHz, $CDCl_3$) 7.30 – 7.24 (2H, m, Ar**H**), 7.21 – 7.15 (3H, m, Ar**H**), 2.61 (2H, t, *J* = 7.4 Hz, ArC**H₂**), 2.56 (1H, septet, *J* = 7.0 Hz, C**H**$(CH_3)_2$), 2.45 (2H, t, *J* = 7.4 Hz, O=CC**H₂**), 1.90 (2H, pent, *J* = 7.4 Hz, $ArCH_2C$**H₂**), 1.07 (6H, d, *J* = 7.0 Hz, CH(C**H₃**)₂); δ_C (100 MHz, $CDCl_3$) 214.5 (**C**=O), 141.7 (**C**), 128.4 (2 × **C**H), 128.3 (2 × **C**H), 125.8 (**C**H), 40.8 (**C**H), 39.4 (**C**H_2), 35.1 (**C**H_2), 25.1 (**C**H_2), 18.2 (2 × **C**H_3); HRMS (ES^+): Exact mass calculated for $C_{13}H_{18}O$ $[M+Na]^+$: 213.1250, found: 213.1250.

1-phenyl-3-(3-(trifluoromethyl)phenyl)butan-2-one - 2h



The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and 2,2'-(2-phenylethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (215 mg, 0.6 mmol) and 3'-trifluoromethylacetophenone (76.0 µL, 0.5 mmol) in THF (2 mL), followed by oxidation by sodium perborate (115 mg, 0.75 mmol) in water (1.65 mL) and acetone (2.0 mL). The compound was purified by column chromatography using EtOAc / hexane (5%) as eluent to yield the title compound as a colourless oil (83 mg, 58%). ν_{max} (neat): 2941 (CH), 1710 (C=O), 1453, 1327, 1164, 1120, 1073, 699 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.52 (1H, d, *J* = 7.8 Hz, Ar**H**), 7.79 (1H, t, *J* = 7.8 Hz, Ar**H**), 7.40 – 7.30 (2H, m, Ar**H**), 7.30 – 7.21 (3H, m, Ar**H**), 7.04 (2H, d, *J* = 6.5 Hz, Ar**H**), 3.93 (1H, q, *J* = 7.0 Hz, C**H**CH_3), 3.66 (1H, d, *J* = 15.3 Hz, C**H₂**Ph), 3.62 (1H, d, *J* = 15.3 Hz, C**H₂**Ph), 1.39 (3H, d, *J* = 7.0 Hz, CHC**H₃**); δ_C (100 MHz, $CDCl_3$) 207.3 (**C**=O), 141.2 (**C**), 133.8 (**C**), 131.3 (**C**H), 131.2 (q, *J* = 32 Hz, **C**), 129.39 (2 x **C**H), 129.36 (2 x **C**H), 128.7 (**C**H), 127.1 (**C**H), 124.9 (q, *J* = 3.8 Hz, **C**H), 124.1 (q, *J* = 3.7 Hz, **C**H), 123.9 (q, *J* = 272 Hz, **C**F_3), 51.5 (**C**H), 48.5 (**C**H_2), 17.9 (**C**H_3); δ_F (282 MHz, $CDCl_3$) -62.6 (3F, s); HRMS (ES^+): Exact mass calculated for $C_{17}H_{15}OF_3$ $[M+Na]^+$: 315.0967, found: 315.0966.

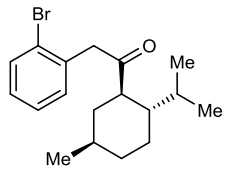
1-(o-tolyl)propan-2-one - 2i



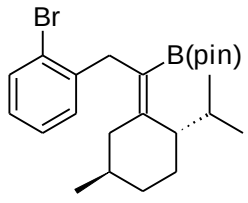
The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and 2,2'-(ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (169 mg, 0.6 mmol) and o-tolylaldehyde (59.0 µL, 0.5 mmol) in THF (2 mL), followed by oxidation by sodium perborate (115 mg, 0.75 mmol) in water (1.65 mL) and acetone (2.0 mL). The compound was purified by column

chromatography using EtOAc / hexane (10%) as eluent to yield the title compound as a colourless oil (72 mg, 97%). δ_H (400 MHz, $CDCl_3$) 7.21 – 7.12 (4H, m, Ar**H**), 3.72 (2H, s, ArC**H₂**), 2.26 (3H, s, ArC**H₃**), 2.15 (3H, s, O=CC**H₃**); δ_C (100 MHz, $CDCl_3$) 206.3 (**C**=O), 136.8 (**C**), 133.1 (**C**), 130.4 (**C**H), 130.3 (**C**H), 127.3 (**C**H), 126.2 (**C**H), 49.1 (**C**H_2), 29.2 (**C**H_3), 19.5 (**C**H_3); m/z (ES^+) 171 $[M+Na]^+$. Data in agreement with the literature[2]

2-(2-bromophenyl)-1-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)ethan-1-one - 2j



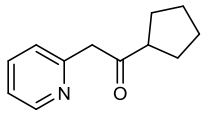
The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and 2,2'-(ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (169 mg, 0.6 mmol) and (L)-menthone (86.0 µL, 0.5 mmol) in THF (2 mL), followed by oxidation by sodium perborate (115 mg, 0.75 mmol) in water (1.65 mL) and acetone (2.0 mL). A second portion of sodium perborate (57.5 mg, 0.375 mmol) in water (0.8 mL) and acetone (1.0 mL) was added after 2 hours. The compound was purified by column chromatography using EtOAc / hexane (10%) as eluent to yield the title compound as a white solid (98 mg, 58%). ν_{max} (neat): 2950 (CH), 2921 (CH), 1705 (C=O), 1470, 1441, 1368, 1306, 1050, 1025, 743 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.55 (1H, d, *J* = 8.0 Hz, Ar**H**), 7.27 – 7.24 (1H, m, Ar**H**), 7.20 – 7.16 (1H, m, Ar**H**), 7.11 (1H, td, *J* = 7.5, 1.8 Hz, Ar**H**), 4.01 (1H, d, *J* = 16.8 Hz, ArC**H₂**), 3.86 (1H, d, *J* = 16.8 Hz, ArC**H₂**), 3.19 – 3.14 (1H, m, O=CC**H**), 2.09 (1H, dq, *J* = 13.6, 2.4 Hz), 1.88 – 1.55 (5H, m), 1.55 – 1.38 (1H, m), 1.31 – 1.21 (1H, m), 0.87 (3H, d, *J* = 7.8 Hz, C**H₃**), 0.85 (3H, d, *J* = 7.6 Hz, C**H₃**), 0.81 (3H, d, *J* = 6.7 Hz, C**H₃**); δ_C (100 MHz, $CDCl_3$) 209.0 (**C**=O), 134.8 (**C**), 132.7 (**C**H), 131.9 (**C**H), 128.6 (**C**H), 127.4 (**C**H), 125.0 (**C**), 49.7 (**C**H_2), 48.2 (**C**H), 47.3 (**C**H), 37.6 (**C**H_2), 35.4 (**C**H_2), 29.7 (**C**H), 27.5 (**C**H), 25.9 (**C**H_2), 22.4 (**C**H_3), 21.6 (**C**H_3); HRMS (ES^+): Exact mass calculated for $C_{18}H_{25}O^{79}Br$ $[M+Na]^+$: 359.0981, found: 359.0977.



Also present was boronate **2j'** δ_H (400 MHz, $CDCl_3$) 7.49 (1H, dd, *J* = 7.9, 0.9 Hz, Ar**H**), 7.24–7.14 (2H, m, Ar**H**), 7.02–6.95 (1H, m, Ar**H**), 3.64 (1H, d, *J* = 16.7 Hz, ArC**H₂**), 3.54 (1H, d, *J* = 16.7 Hz, ArC**H₂**), 2.62 (1H, dt, *J* = 10.3, 3.4 Hz), 2.27–2.19 (1H, m), 2.12–1.75 (4H, m), 1.75–1.65 (2H, m), 1.12 (6H, s, O(C**H₃**)$_2$), 1.11 (6H, s, O(C**H₃**)$_2$), 0.94 (3H, d, *J* = 6.5 Hz, C**H₃**), 0.86 (3H, d, *J* = 7.2 Hz, C**H₃**), 0.85 (3H, d, *J* = 6.7 Hz, C**H₃**); δ_C (100 MHz, $CDCl_3$) 156.2 (**C**), 142.0 (**C**), 132.1 (**C**H), 130.3 (**C**H), 126.9 (**C**H), 126.8 (**C**H), 82.7 (**C**), 36.0 (**C**H_2), 32.4 (**C**H_2), 30.4 (**C**H), 26.89 (**C**H), 26.88 (**C**H_2), 25.8 (**C**H), 24.7 (**C**H_3), 24.6 (**C**H_3), 24.5 (**C**H_2), 21.3 (**C**H_3), 21.2 (**C**H_3), 18.4 (**C**H_3).

[2] C. Liu, G. T. Kelly, C. M. H. Watanabe, *Org. Lett*., **2006**, *8*, 1065.

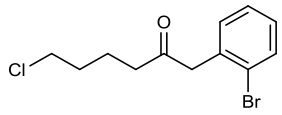
1-cyclopentyl-2-(pyridin-2-yl)ethan-1-one - 2k



The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and 2,2'-(cyclopentylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (202 mg, 0.6 mmol) and pyridine-2-carboxaldehyde (48.0 µL, 0.5 mmol) in THF (2 mL), followed by oxidation by sodium perborate (115 mg, 0.75 mmol) in water (1.65 mL) and acetone (2.0 mL). The compound was purified by column chromatography using EtOAc / hexane (10%) as eluent to yield the title compound as a yellow oil (48 mg, 51%). δ_H (400 MHz, $CDCl_3$) 8.59 (1H, d, *J* = 4.7 Hz, Ar**H**), 7.61 – 7.53 (1H, m, Ar**H**), 7.21 – 7.13 (1H, m, Ar**H**), 7.13 – 7.07 (1H, m, Ar**H**), 4.01 (2H, s, ArC**H₂**), 3.08 (1H, pentet, *J* = 7.9 Hz, O=CC**H**), 1.89 – 1.79 (4H, m), 1.77 – 1.53 (4H, m); δ_C (100 MHz, $CDCl_3$) 209.6 (**C**=O), 155.0 (**C**), 149.3 (**C**H), 136.5 (**C**H), 124.3 (**C**H), 121.9 (**C**H), 51.32 (**C**H), 51.26 (**C**H_2), 28.8 (2 × **C**H_2), 26.0 (2 × **C**H_2); HRMS (ES^+): Exact mass calculated for $C_{12}H_{15}NO$ $[M+Na]^+$: 212.1046, found: 212.1041.

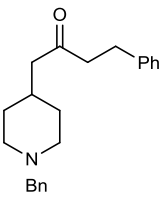
Also present was enol tautomer **2k'** in a keto:enol ratio of approx. 13:1. Diagnostic enol resonances: δ_H (400 MHz, $CDCl_3$) 15.0 (1H, br s, O**H**), 8.23 (1H, d, *J* = 5.1 Hz, Ar**H**), 7.57 (1H, t, *J* = 7.5 Hz, Ar**H**), 6.97–6.89 (2H, m, Ar**H**), 5.40 (1H, s, C=C**H**).

1-(2-bromophenyl)-6-chlorohexan-2-one - **2l**



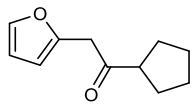
The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and 2,2'-(2-(2-bromophenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (262 mg, 0.6 mmol) and 4-chlorobutanal (65.0 mg, 0.5 mmol) in THF (2 mL), followed by oxidation by sodium perborate (115 mg, 0.75 mmol) in water (1.65 mL) and acetone (2.0 mL). The compound was purified by column chromatography using EtOAc / hexane (10%) as eluent to yield the title compound as a colourless oil (85 mg, 58%). ν_{max} (neat): 2956 (CH), 1715 (C=O), 1568, 1470, 1316, 1125, 1088, 1026, 748 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.57 (1H, dd, *J* = 8.0, 1.1 Hz, Ar**H**), 7.29 (1H, td, *J* = 7.5, 1.1Hz, Ar**H**), 7.21 (1H, dd, *J* = 7.7, 1.7 Hz, Ar**H**), 7.14 (1H, td, *J* = 7.5, 1.7 Hz, Ar**H**), 3.85 (2H, s, ArC**H₂**), 3.51 (2H, t, *J* = 6.1 Hz, C**H₂**Cl), 2.54 (2H, t, *J* = 6.6 Hz, O=CC**H₂**CH_2), 1.81 – 1.70 (4H, m, alkyl C**H₂**C**H₂**); δ_C (100 MHz, $CDCl_3$) 206.3 (**C**=O), 134.6 (**C**), 132.8 (**C**H), 131.7 (**C**H), 128.8 (**C**H), 127.6 (**C**H), 124.9 (**C**), 50.0 (**C**H_2), 44.6 (**C**H_2), 41.4 (**C**H_2), 31.8 (**C**H_2), 20.9 (**C**H_2); HRMS (ES^+): Exact mass calculated for $C_{12}H_{14}O^{35}Cl^{79}Br$ $[M+Na]^+$: 310.9809, found: 310.9810.

1-(1-benzylpiperidin-4-yl)-4-phenylbutan-2-one - **2m**



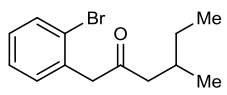
The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and 2,2'-(3-phenylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (223 mg, 0.6 mmol) and 1-benzylpiperidine-4-carboxaldehyde (99.0 µL, 0.5 mmol) in THF (2 mL), followed by oxidation by sodium perborate (115 mg, 0.75 mmol) in water (1.65 mL) and acetone (2.0 mL). The compound was purified by column chromatography using EtOAc / hexane (10 to 20%) as eluent to yield the title compound as a colourless oil (85 mg, 53%). ν_{max} (neat): 2921 (CH), 1709 (C=O), 1495, 1453, 1365, 1114, 1077, 740, 698 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.33 – 7.22 (7H, m, Ar**H**), 7.21 – 7.14 (3H, m, Ar**H**), 3.51 (2H, s, PhC**H₂**N), 2.91 – 2.81 (4H, m, N(C**H₂**)₂), 2.70 (2H, t, *J* = 7.7 Hz, PhC**H₂**), 2.30 (2H, d, *J* = 6.8 Hz, O=CC**H₂**CH), 1.99 (2H, td, *J* = 11.8, 2.3 Hz), 1.88 – 1.76 (2H, m), 1.60 (2H, d, *J* = 12.9 Hz), 1.34 – 1.20 (1H, m); δ_C (100 MHz, $CDCl_3$) 209.4 (**C**=O), 141.0 (**C**), 129.3 (2 x **C**H), 128.5 (2 x **C**H), 128.3 (**C**H), 128.2 (2 x **C**H), 127.1 (**C**H), 126.1 (2 x **C**H), 63.2 (**C**H_2), 53.4 (2 x **C**H_2), 49.6 (**C**H_2), 44.9 (**C**H_2), 31.9 (**C**H_2), 31.6 (**C**H), 29.7 (2 x **C**H_2); HRMS (ES^+): Exact mass calculated for $C_{23}H_{27}NO$ $[M+H]^+$: 322.2165, found: 322.2165.

1-cyclopentyl-2-(furan-2-yl)ethan-1-one - 2n



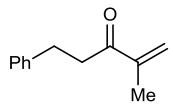
The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and 2,2'-(cyclopentylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (202 mg, 0.6 mmol) and 2-furaldehyde (41.0 µL, 0.5 mmol) in THF (2 mL), followed by oxidation by sodium perborate (115 mg, 0.75 mmol) in water (1.65 mL) and acetone (2.0 mL). The compound was purified by column chromatography using Et_2O / hexane (10%) as eluent to yield the title compound as a colourless oil (75 mg, 84%). δ_H (400 MHz, $CDCl_3$) 7.35 (1H, d, *J* = 1.1 Hz, Ar**H**), 6.34 (1H, dd, *J* = 3.0, 2.1 Hz, Ar**H**), 6.19 (1H, d, *J* = 3.0 Hz, Ar**H**), 3.76 (2H, s, ArC**H₂**), 2.95 (1H, pent, *J* = 8.0 Hz, O=CC**H**), 1.81 – 1.71 (4H, m, CH(C**H₂**)₂), 1.71 – 1.50 (4H, m, CHCH_2(C**H₂**)₂); δ_C (100 MHz, $CDCl_3$) 208.4 (**C**=O), 148.6 (**C**), 141.9 (**C**H), 110.6 (**C**H), 109.1 (**C**H), 50.5 (**C**H), 41.5 (**C**H_2), 28.9 (**C**H_2), 26.0 (**C**H_2); HRMS (ES^+): Exact mass calculated for $C_{11}H_{14}O_2$ $[M+Na]^+$: 201.0886, found: 201.0889.

1-(2-bromophenyl)-4-methylhexan-2-one - 2o



The title compound was prepared from 2,2,6,6-tetramethylpiperidine (20.0 µL, 0.12 mmol), *n*-butyllithium (75.0 µL, 1.6 M in hexanes, 0.12 mmol) and 2,2'-(2-(2-bromophenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (52.0 mg, 0.12 mmol) and 2-methylbutyraldehyde (11.0 µL, 0.1 mmol) in THF (1 mL), followed by oxidation by sodium perborate (23.0 mg, 0.15 mmol) in water (0.4 mL) and acetone (0.5 mL). The compound was purified by column chromatography using EtOAc / hexane (5%) as eluent to yield the title compound as a colourless oil (25 mg, 91%). δ_H (500 MHz, $CDCl_3$) 7.57 (1H, d, *J* = 8.0 Hz, Ar**H**), 7.28 (1H, t, *J* = 7.1 Hz, Ar**H**), 7.23 – 7.19 (1H, m, Ar**H**), 7.14 (1H, td, *J* = 7.8, 1.5 Hz, Ar**H**), 3.85 (2H, s, ArC**H₂**), 2.49 (1H, dd, *J* = 16.2, 5.7 Hz, O=CC**H₂**CH), 2.30 (1H, dd, *J* = 16.2, 8.0 Hz, O=CC**H₂**CH), 2.03 – 1.92 (1H, m), 1.39 – 1.29 (1H, m), 1.26 – 1.14 (1H, m), 0.90 (3H, d, *J* = 6.7 Hz, CHC**H₃**), 0.87 (3H, t, *J* = 7.4 Hz, CH_2C**H₃**); δ_C (125 MHz, $CDCl_3$) 206.9 (**C**=O), 134.8 (**C**), 132.8 (**C**H), 131.7 (**C**H), 128.7 (**C**H), 127.6 (**C**H), 125.0 (**C**), 50.5 (**C**H_2), 49.6 (**C**H_2), 30.6 (**C**H), 29.4 (**C**H_2), 19.4 (**C**H_3), 11.3 (**C**H_3); HRMS (ES^+): Exact mass calculated for $C_{11}H_{14}O_2$ $[M+Na]^+$: 201.0886, found: 201.0889.

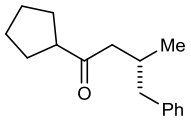
2-methyl-5-phenylpent-1-en-3-one - 3



The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and 2,2'-(3-phenylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (223 mg, 0.6 mmol) and chloroacetone (40.0 µL, 0.5 mmol) in THF (2 mL), followed by oxidation by sodium perborate (115 mg, 0.75 mmol) in water (1.65 mL) and acetone (2.0 mL). The compound was purified by column chromatography using Et_2O / hexane (10%) as eluent to yield the title compound as a colourless oil (57 mg, 65%). δ_H (300 MHz, $CDCl_3$) 7.25 – 7.07 (5H, m, Ar**H**), 5.87 (1H, dq, *J* = 0.9, 0.6 Hz, C=C**H**), 5.68 (1H, dd, *J* = 1.4, 0.6 Hz, C=C**H**), 2.98 – 2.90 (2H, m), 2.90 – 2.82 (2H, m), 1.81 (3H, dd, *J* = 1.4, 0.9 Hz); δ_C (100 MHz, $CDCl_3$) 201.0 (**C**=O), 144.4 (**C**), 141.4 (**C**), 128.5 (2 x **C**H), 128.4 (2 x **C**H), 126.0 (**C**H), 124.6 (**C**H_2), 39.3 (**C**H_2), 30.3 (**C**H_2), 17.6 (**C**H_3); *m/z* (ES^+) 197 $[M+Na]^+$. Data is in full agreement with the literature.[3]

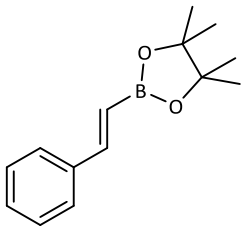
[3] M. Tang, C.-A. Fan, F.-M. Zhang, Y.-Q. Tu*, W.-X. Zhang and A.-X. Wang, *Org. Lett.*, **2008**, *10*, 5585–5588

(R)-1-cyclopentyl-3-methyl-4-phenylbutan-1-one – 4



The title compound was prepared from 2,2,6,6-tetramethylpiperidine (41.0 µL, 0.24 mmol), *n*-butyllithium (0.150 mL, 1.6 M in hexanes, 0.24 mmol) and 2,2'-(cyclopentylmethylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (81.0 mg, 0.24mmol) and (R)-2-methyl-3-phenylpropanal (30.0 mg, 0.2 mmol) in THF (1 mL), followed by oxidation by sodium perborate (46.0 mg, 0.30 mmol) in water (0.8 mL) and acetone (1.0 mL). The compound was purified by column chromatography using Et_2O / hexane (10%) as eluent to yield the title compound as a colourless oil (32 mg, 70%). δ_H (500 MHz, $CDCl_3$) 7.27 (2H, t, *J* = 7.4 Hz, Ar**H**), 7.19 (1H, t, *J* = 7.4 Hz, Ar**H**), 7.16 (2H, d, *J* = 7.4 Hz, Ar**H**), 2.80 (1H, pent, *J* = 7.7 Hz, O=CC**H**), 2.59 (1H, dd, *J* = 13.2, 6.4 Hz, O=CC**H₂**), 2.46 (1H, dd, *J* = 13.2, 7.3 Hz, O=CC**H₂**), 2.43 (1H, dd, *J* = 15.5, 4.8 Hz, PhC**H₂**), 2.40 – 2.32 (1H, m, C**H**CH_3) 2.30 (1H, dd, *J* = 15.5, 7.5 Hz, PhC**H₂**), 1.83 – 1.51 (8H, m, cyclopentylC**H₂**), 0.89 (3H, d, *J* = 6.4 Hz, C**H₃**); δ_C (125 MHz, $CDCl_3$) 212.9 (**C**=O), 140.6 (**C**), 129.2 (2 × **C**H), 128.2 (2 × **C**H), 125.9 (**C**H), 51.8 (**C**H), 48.5 (**C**H_2), 43.2 (**C**H_2), 30.9 (**C**H), 29.0 (**C**H_2), 28.6 (**C**H_2), 26.0 (**C**H_2), 25.9 (**C**H_2), 19.8 (**C**H_3); HRMS (ES^+): Exact mass calculated for $C_{11}H_{14}O_2$ $[M+Na]^+$: 201.0886, found: 201.0889. Enantiomeric excess was determined by HPLC with a Chiralcel IC column (99:1 hexane:*i*-PrOH, 1.0 mL/min, 210 nm, 25 °C); t_r (minor) = 10.4 min, t_r (major) = 10.9 min; 98% ee.

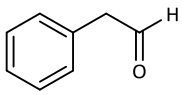
(E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane – 5a'



The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.570 mL, 3.3 mmol), *n*-butyllithium (2.64 mL, 2.5 M in hexanes, 3.3 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (0.885 g, 3.3 mmol) and benzaldehyde (0.300 mL, 3.0 mmol). The compound was purified by column chromatography using EtOAc / hexane (10%) as eluent to yield the title compound as a colourless oil (0.474 g, 69%). δ_H (300 MHz, $CDCl_3$) 7.52 – 7.28 (6H, m, Ar**H** and PhC**H**), 6.17 (1H, d, *J* = 18.4 Hz, C**H**Bpin), 1.32 (12H, s, C**H₃**). δ_C (75 MHz, $CDCl_3$) 149.5 (BC=**C**H), 128.9 (**C**H), 128.6 (**C**H), 127.1 (**C**H), 83.4 (**C**CH_3), 24.8 (C**C**H_3). *m/z* (ES+) 231 $[M+H]^+$. Data in full agreement with the literature.[4]

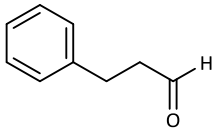
[4] D. S. Matteson and D. Majumdar, *Organometallics*, 1983, **2**, 230–236.

2-phenylacetaldehyde – 5a



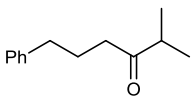
Alkenyl-boronate **5a'** (270 mg, 1.2 mmol) was dissolved in acetone (2.7 mL) and stirred until a homogenous solution was achieved. An Oxone® (360 mg, 1.17 mmol) solution in water (3.6 mL) was added dropwise to the solution of alkenyl boronate at 0 ^{o}C over 5 mins, and stirred for 1 h. Upon completion the reaction was quenched with 1M HCl (1 mL) and extracted with DCM (3 × 25 mL). The combined organics were washed with water, brine, dried over $MgSO_4$ and concentrated *in vacuo.* The compound was purified via column chromatography using EtOAc / hexane (10%) as eluent to yield the title compound as a colourless oil (111 mg, 79%). A second experiment with yield 106 mg (74%) was also performed. δ_H (300 MHz, $CDCl_3$) 9.75 (1H, t, *J* = 2.4 Hz, C**H**O), 7.41 – 7.31 (3H, m, Ar**H**), 7.25 – 7.20 (2H, m, Ar**H**), 3.68 (2H, d, *J* = 2.3 Hz, C**H₂**). Data in full agreement with the literature.[5]

3-phenylpropanal – 5b



The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.324 mL, 1.90 mmol), *n*-butyllithium (0.760 mL, 2.5 M in hexanes, 1.90 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (510 mg, 1.90 mmol) and 2-phenylacetaldehyde (210 mg, 1.75 mmol) in THF (4 mL), followed by oxidation by sodium perborate (250 mg, 2.5 mmol) in water (3.3 mL) and acetone (4.0 mL). The compound was purified by column chromatography using EtOAc / hexane (10%) to yield the title compound as a colourless oil (209 mg, 89%). δ_H (300 MHz, $CDCl_3$) 9.82 (1H, s, C**H**O), 7.33 – 7.17 (5H, m, Ar**H**), 2.96 (2H, t, *J* = 7.7 Hz, C**H₂**), 2.78 (2H, t, *J* = 7.7 Hz, C**H₂**). Data in full agreement with the literature.[6]

2-methyl-6-phenylhexan-3-one – 5c

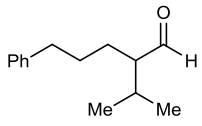


The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.236 mL, 1.4 mmol), *n*-butyllithium (0.560 mL, 2.5 M in hexanes, 1.4 mmol) and 2,2'-(2-methylpropane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.433 g, 1.4 mmol) and 3-phenylpropanal (0.165 mL, 1.25 mmol) in THF (3 mL), followed by oxidation by sodium perborate (0.200 g, 2.00 mmol) in water (3.3 mL) and acetone (4 mL). The compound was purified by column

[5] M. W. C. Robinson, K. S. Pillinger, I. Mabbett, D. A. Timms and A. E. Graham, *Tetrahedron*, 2010, **66**, 8377–8382.
[6] T. D. Beeson and D. W. C. Macmillan, *J. Am. Chem. Soc.*, 2005, **127**, 8826–8.

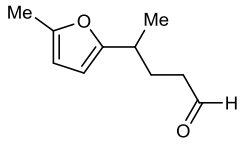
chromatography using EtOAc / hexane (5%) as eluent to yield the title compound as a colourless oil (0.168 g, 71%). δ_H (400 MHz, $CDCl_3$) 7.30 – 7.24 (2H, m, Ar**H**), 7.21 – 7.15 (3H, m, Ar**H**), 2.61 (2H, t, *J* = 7.4 Hz, ArC**H₂**), 2.56 (1H, septet, *J* = 7.0 Hz, C**H**(CH_3)$_2$), 2.45 (2H, t, *J* = 7.4 Hz, O=CC**H₂**), 1.90 (2H, pent, *J* = 7.4 Hz, $ArCH_2C$**H₂**), 1.07 (6H, d, *J* = 7.0 Hz, CH(C**H₃**)$_2$); δ_C (100 MHz, $CDCl_3$) 214.5 (**C**=O), 141.7 (**C**), 128.4 (2 × **C**H), 128.3 (2 × **C**H), 125.8 (**C**H), 40.8 (**C**H), 39.4 (**C**H_2), 35.1 (**C**H_2), 25.1 (**C**H_2), 18.2 (2 × **C**H_3); HRMS (ES^+): Exact mass calculated for $C_{13}H_{18}O$ $[M+Na]^+$: 213.1250, found: 213.1250.

2-isopropyl-5-phenylpentanal – 5d



The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.200 mL, 1.2 mmol), *n*-butyllithium (0.480 mL, 2.5 M in hexanes, 1.2 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (0.320 g, 1.2 mmol) and 2-methyl-6-phenylhexan-3-one (150 mg, 0.79 mmol) in THF (4 mL), followed by oxidation by sodium perborate (0.230 g, 1.5 mmol) in water (3.3 mL) and acetone (4.4 mL). The compound was purified by column chromatography using EtOAc / hexane (5%) as eluent to yield the title compound as a colourless oil (109 mg, 68%). δ_H (400 MHz, $CDCl_3$) 9.60 (1H, d, *J* = 3.5 Hz, C**H**O), 7.26 (2H, t, *J* = 7.5 Hz, Ar**H**), 7.20 – 7.12 (3H, m, Ar**H**), 2.68 – 2.53 (2H, m, PhC**H₂**), 2.10 – 2.02 (1H, m, OHCC**H**), 2.01 – 1.92 (1H, m), 1.74 – 1.44 (4H, m, C**H₂**C**H₂**), 0.94 (3H, d, *J* = 6.8 Hz, C**H₃**), 0.93 (3H, d, *J* = 6.8 Hz, C**H₃**); δ_C (100 MHz, $CDCl_3$) 205.8 (**C**=O), 141.9 (**C**), 128.31 (2 × **C**H), 128.29 (2 × **C**H), 125.8 (**C**H), 58.2 (**C**H), 35.9 (**C**H_2), 29.3 (**C**H_2), 28.3 (**C**H), 25.6 (**C**H_2), 20.2 (**C**H_3), 19.7 (**C**H_3); HRMS (ES^+): Exact mass calculated for $C_{13}H_{18}O$ $[M+Na]^+$: 227.1412, found: 227.1414.

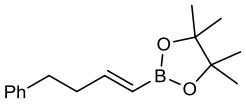
4-(5-methylfuran-2-yl)pentanal – 6



The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (161 mg, 0.6 mmol) and 3-(5-methyl-2-furyl)butyraldehyde (75.0 µL, 0.5 mmol) in THF (2 mL), followed by oxidation by sodium perborate (115 mg, 0.75 mmol) in water (1.65 mL) and acetone (2.0 mL). The compound was purified by column chromatography using EtOAc / hexane (10%) as eluent to yield the title compound as a colourless oil (68 mg, 82%). δ_H (300 MHz, $CDCl_3$) 9.70 (1H, s, C**H**O), 5.84 (2H, s, Ar**H**), 2.91 – 2.70 (1H, m, ArC**H**), 2.42 (2H, t, *J* = 7.5 Hz, HOCC**H₂**), 2.24 (3H, s, ArC**H₃**), 1.99 – 1.81 (2H, m, CHC**H₂**), 1.24 (3H, d, *J* = 8.6 Hz, CHC**H₃**); δ_C (100 MHz, $CDCl_3$) 202.3 (**C**=O), 157.1 (**C**), 150.4 (**C**),

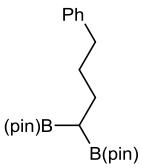
105.6 (**C**H), 104.9 (**C**H), 41.6 (**C**H_2), 32.5 (**C**H), 28.0 (**C**H_2), 19.1 (**C**H_3), 13.5 (**C**H_3); HRMS (ES^+): Exact mass calculated for $C_{10}H_{14}O_2$ $[M+Na]^+$: 189.0886, found: 189.0884.

(E)-4,4,5,5-tetramethyl-2-(4-phenylbut-1-en-1-yl)-1,3,2-dioxaborolane - 7



The title compound was prepared from 2,2,6,6-tetramethylpiperidine (0.101 mL, 0.6 mmol), *n*-butyllithium (0.240 mL, 2.5 M in hexanes, 0.6 mmol) and bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (161 mg, 0.6 mmol) and hydrocinnamaldehyde (66.0 µL, 0.5 mmol) in THF (2 mL). The compound was purified by column chromatography using EtOAc / hexane (10%) as eluent to yield the title compound as a colourless oil (83 mg, 64%). δ_H (400 MHz, $CDCl_3$) 7.31 – 7.25 (2H, m, Ar**H**), 7.22 – 7.16 (3H, m, Ar**H**), 6.71 (1H, dt, *J* = 18.0, 6.2 Hz, CH_2C**H**=), 5.51 (1H, dt, *J* = 18.0, 1.4 Hz, =C**H**B(pin)), 2.78 – 2.71 (2H, m, PhC**H₂**), 2.52 – 2.44 (2H, m, =CHC**H₂**), 1.27 (12H, s, 4 × C**H₃**); δ_C (100 MHz, $CDCl_3$) 153.4 (**C**H), 141.7 (**C**), 128.3 (4 × **C**H), 125.8 (**C**H), 83.0 (**C**), 37.5 (**C**H_2), 34.6 (**C**H_2), 24.8 (4 × **C**H_3). Data in full agreement with the literature.[7]

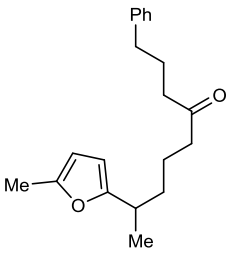
2,2'-(4-phenylbutane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) - 8



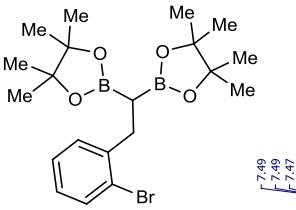
To a mixture of $[Rh(cod)Cl]_2$ (6.2 mg, 0.0125 mmol) and 1,4-bis(diphenylphosphino)butane (12.8 mg, 0.03 mmol) and (E)-4,4,5,5-tetramethyl-2-(4-phenylbut-1-en-1-yl)-1,3,2-dioxaborolane **7** (112 mg, 0.43 mmol) in 1,2-dichloroethane (0.5 mL) was added pinacolborane (87.0 µL, 0.6 mmol). The mixture was stirred at room temperature for 16 h then passed through a short column of silica using Et_2O as eluent. After evaporation, the crude mixture was purified by column chromatography using EtOAc / hexane (5%) to give the title compound as a colourless oil (95 mg, 57%); δ_H (400 MHz, $CDCl_3$) 7.28 – 7.22 (2H, m, Ar**H**), 7.21 – 7.12 (3H, m, Ar**H**), 2.60 (2H, t, *J* = 7.0 Hz, PhC**H₂**), 1.67 – 1.59 (4H, m, C**H₂**C**H₂**CH), 1.23 (12H, s, 4 × C**H₃**), 1.22 (12H, s, 4 × C**H₃**) 0.77 (1H, t, *J* = 6.0 Hz, C**H**$(Bpin)_2$).; δ_C (100 MHz, $CDCl_3$) 143.0 (**C**), 128.3 (2 × **C**H), 128.1 (2 × **C**H), 125.4 (**C**H), 82.9 (**C**), 36.0 (**C**H_2), 34.3 (**C**H_2), 25.5 (**C**H_2), 28.8 (**C**H_3), 24.5 (**C**H_3). Data in full agreement with the literature.[8]

[7] K. Takai, Y. Kunisada, Y. Tachibana, N. Yamaji, E. Nakatani*, Bull. Chem. Soc. Jpn*., **2004**, *77*, 1581–1586
[8] C. Sun, B. Potter, J. P. Morken *J. Am. Chem. Soc.*, **2014**, *136*, 6534–6537

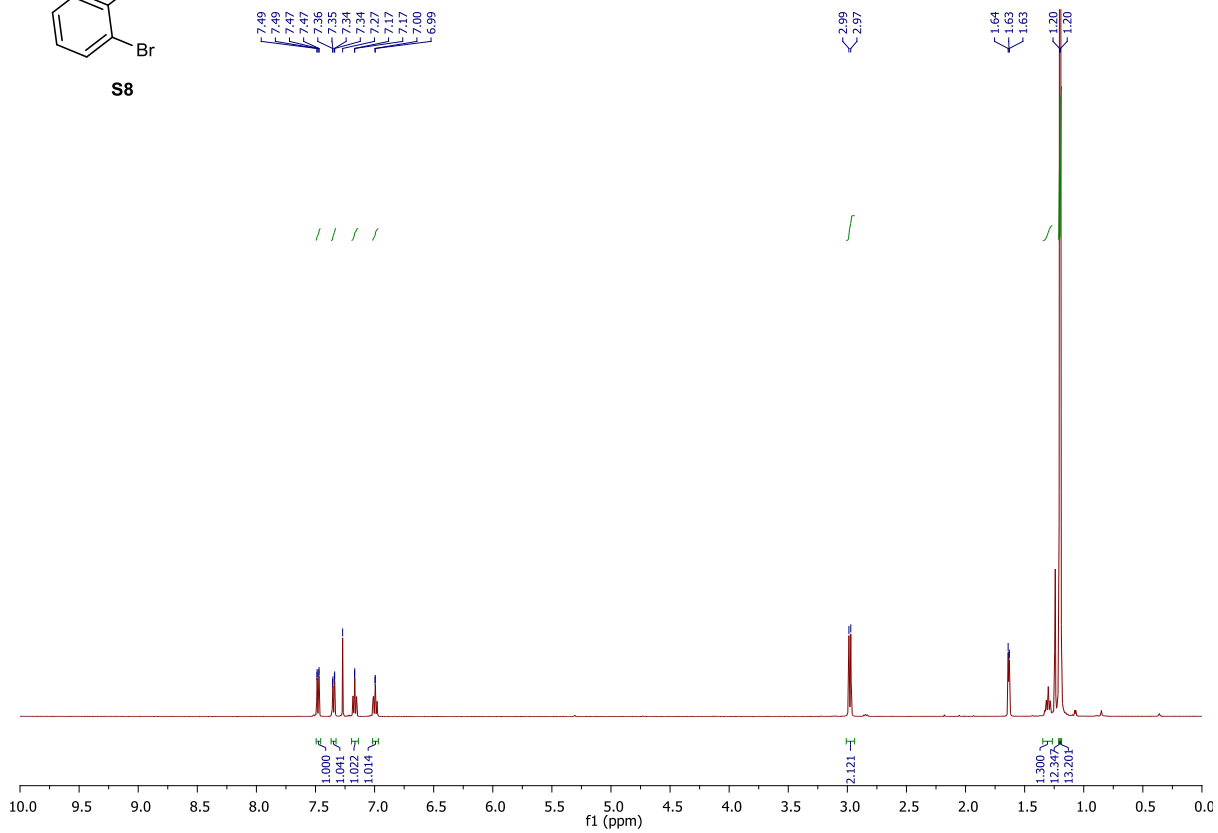
8-(5-methylfuran-2-yl)-1-phenylnonan-4-one - 9



The title compound was prepared from 2,2,6,6-tetramethylpiperidine (44.0 µL, 0.26 mmol), *n*-butyllithium (0.104 mL, 2.5 M in hexanes, 0.26 mmol) and 2,2'-(4-phenylbutane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **8** (100 mg, 0.26 mmol) and 4-(5-methylfuran-2-yl)pentanal **6** (28.0 mg, 0.168 mmol) in THF (1 mL), followed by oxidation by sodium perborate (50.0 mg, 0.32 mmol) in water (0.82 mL) and acetone (1.1 mL). The compound was purified by column chromatography using Et_2O / hexane (10%) as eluent to yield the title compound as a colourless oil (26 mg, 53%). ν_{max} (neat): 2970, 2926, 2875 (CH), 1708 (C=O), 1453, 1375, 1219, 1088, 1048 754 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.31 – 7.25 (2H, m, Ar**H**), 7.21 – 7.14 (3H, m, Ar**H**), 5.83 (2H, s, Ar**H**), 2.78 – 2.68 (1H, m, ArC**H**), 2.61 (2H, t, *J* = 7.6 Hz, O=CC**H₂**), 2.43 – 2.31 (4H, m, PhC**H₂** and O=CC**H₂**), 2.24 (3H, s, ArC**H₃**), 1.89 (2H, pent, *J* = 7.6 Hz, $PhCH_2C$**H₂**), 1.68 – 1.39 (4H, m, MeCHC**H₂**C**H₂**), 1.20 (3H, d, *J* = 7.0 Hz, CHC**H₃**); δ_C (100 MHz, $CDCl_3$) 210.8 (**C**=O), 158.4 (**C**), 150.0 (**C**), 141.6 (**C**), 128.5 (2 × **C**H), 128.4 (2 × **C**H), 125.9 (**C**H), 105.6 (**C**H), 104.1 (**C**H), 42.8 (**C**H_2), 41.8 (**C**H_2), 35.3 (**C**H_2), 3.1 (**C**H_2), 33.0 (**C**H), 25.2 (**C**H_2), 21.4 (**C**H_2), 19.1 (**C**H_3), 13.5 (**C**H_3); HRMS (ES^+): Exact mass calculated for $C_{19}H_{24}O_2$ $[M+Na]^+$: 307.1669, found: 307.1671.


Me
Me
Me
Me
O
B
O
B
O
O
Me
Me
Me
Me
Br

S8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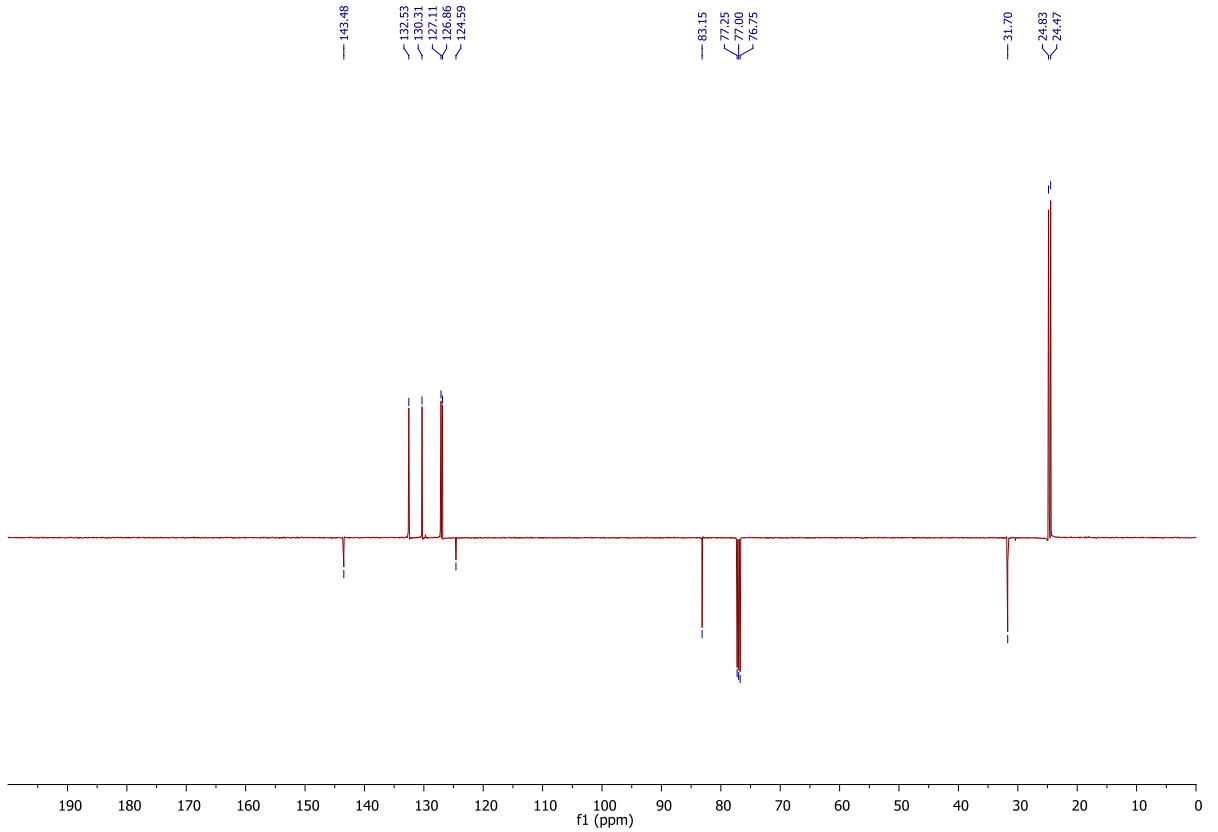
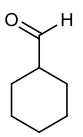
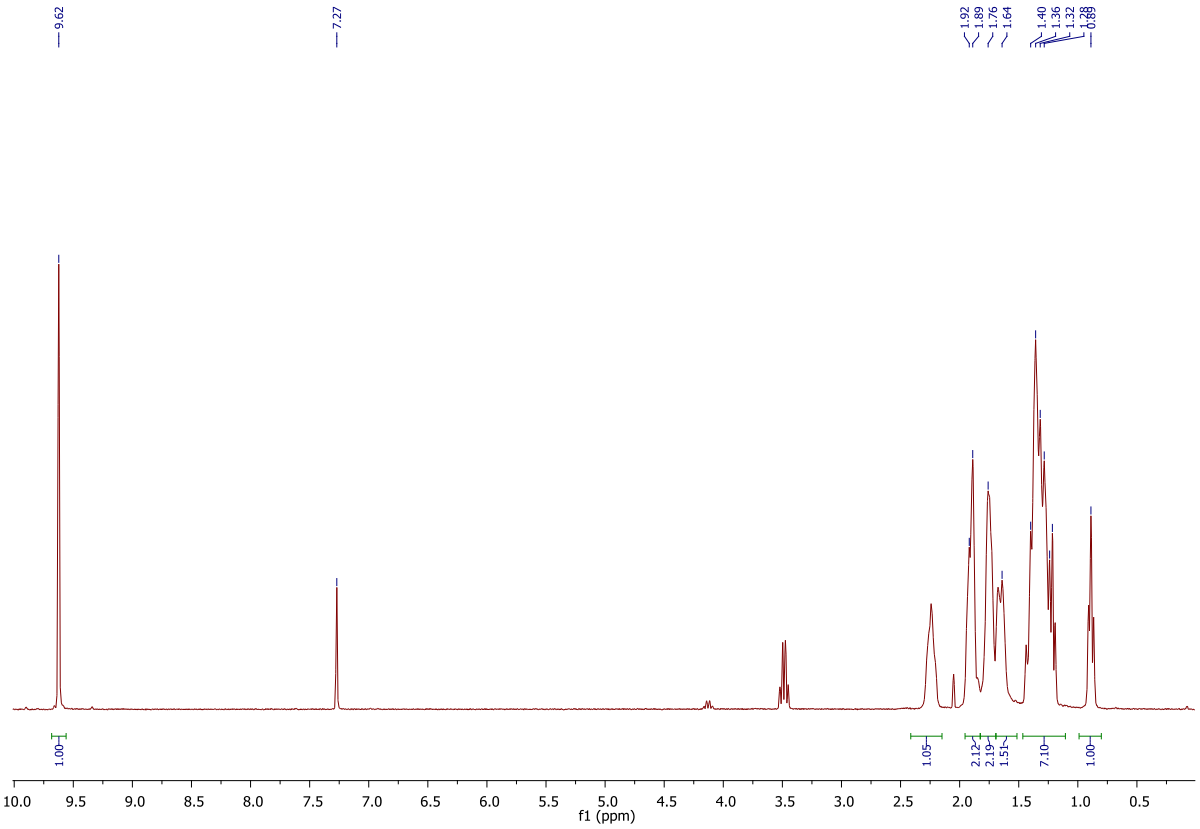
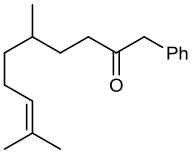
7.49
7.47
7.47
7.36
7.35
7.34
7.34
7.27
7.17
7.17
7.00
6.99
2.99
2.97
1.64
1.63
1.63
1.20
1.20
1.000
1.041
1.022
1.014
2.121
1.300
12.34
13.20
f1 (ppm)


143.48
132.53
130.31
127.11
126.86
124.59
83.15
77.25
77.00
76.75
31.70
24.83
24.47
f1 (ppm)

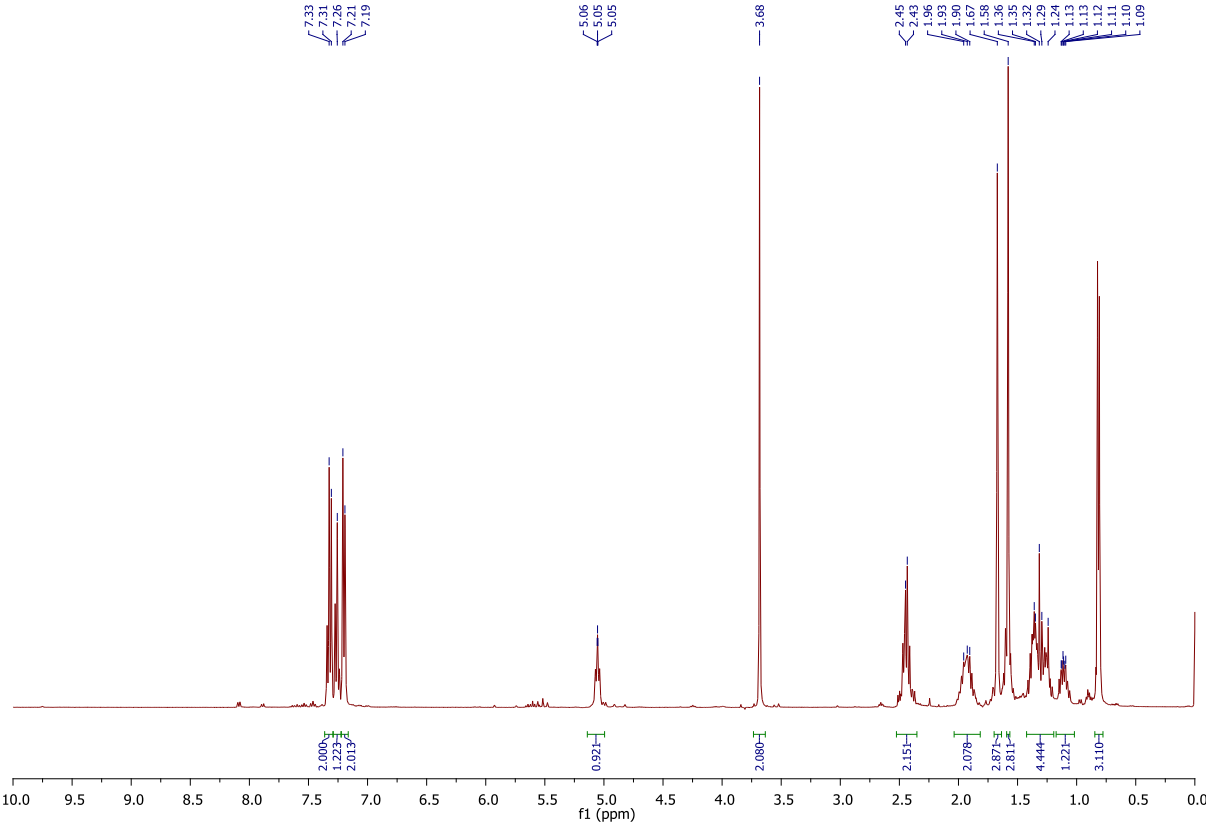

O
H

1a


9.62
7.27
1.92
1.89
1.76
1.64
1.40
1.36
1.32
1.00
1.05
2.12
2.19
1.51
7.10
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Ph
O

2a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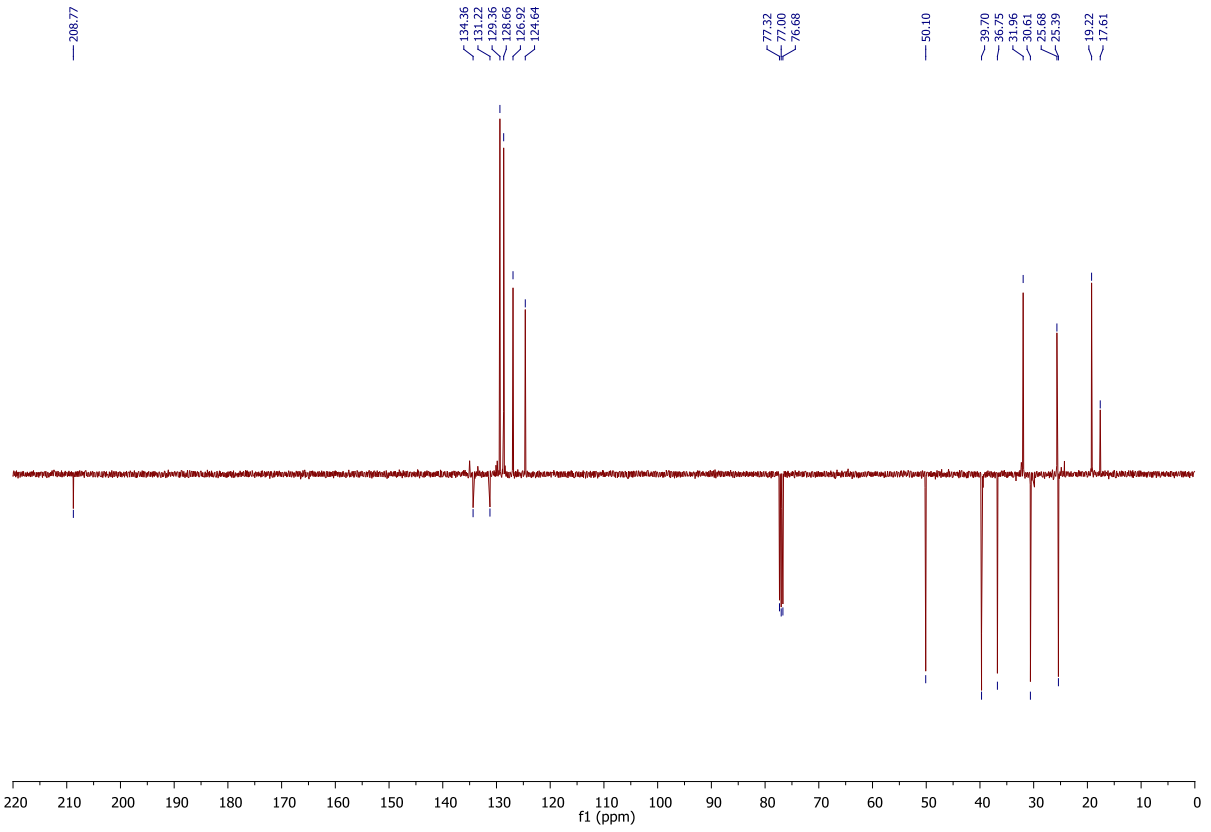
7.31
7.26
7.21
7.19
5.06
5.05
5.05
3.68
2.45
2.43
1.96
1.93
1.90
1.67
1.58
1.36
1.35
1.32
1.29
1.24
1.13
1.12
1.11
1.10
1.09
2.000
1.223
2.013
0.921
2.080
2.151
2.078
2.871
2.811
4.444
1.221
3.110
f1 (ppm)


208.77
134.36
131.22
129.36
128.66
126.92
124.64
77.32
77.00
76.68
50.10
39.70
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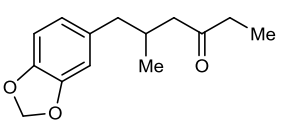
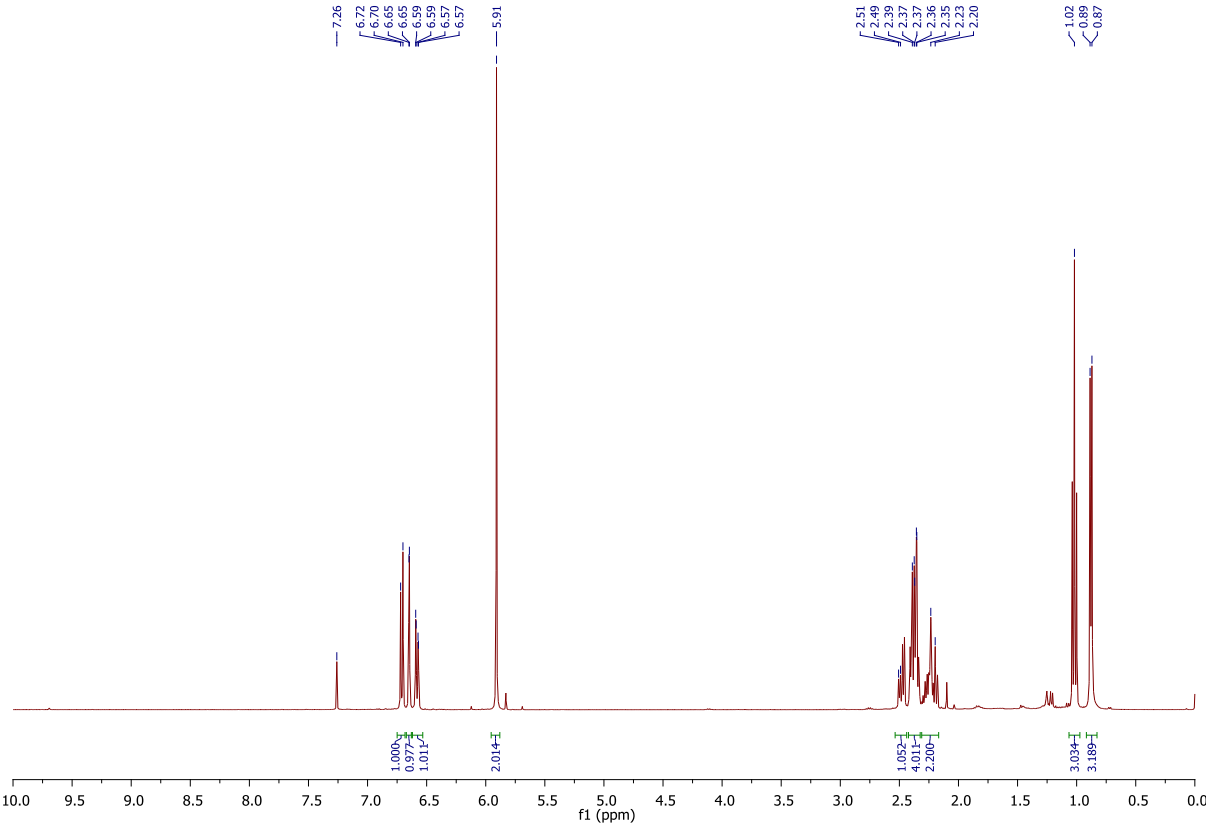
25.68
25.39
19.22
17.61
f1 (ppm)


Me
Me
O
O
O

2b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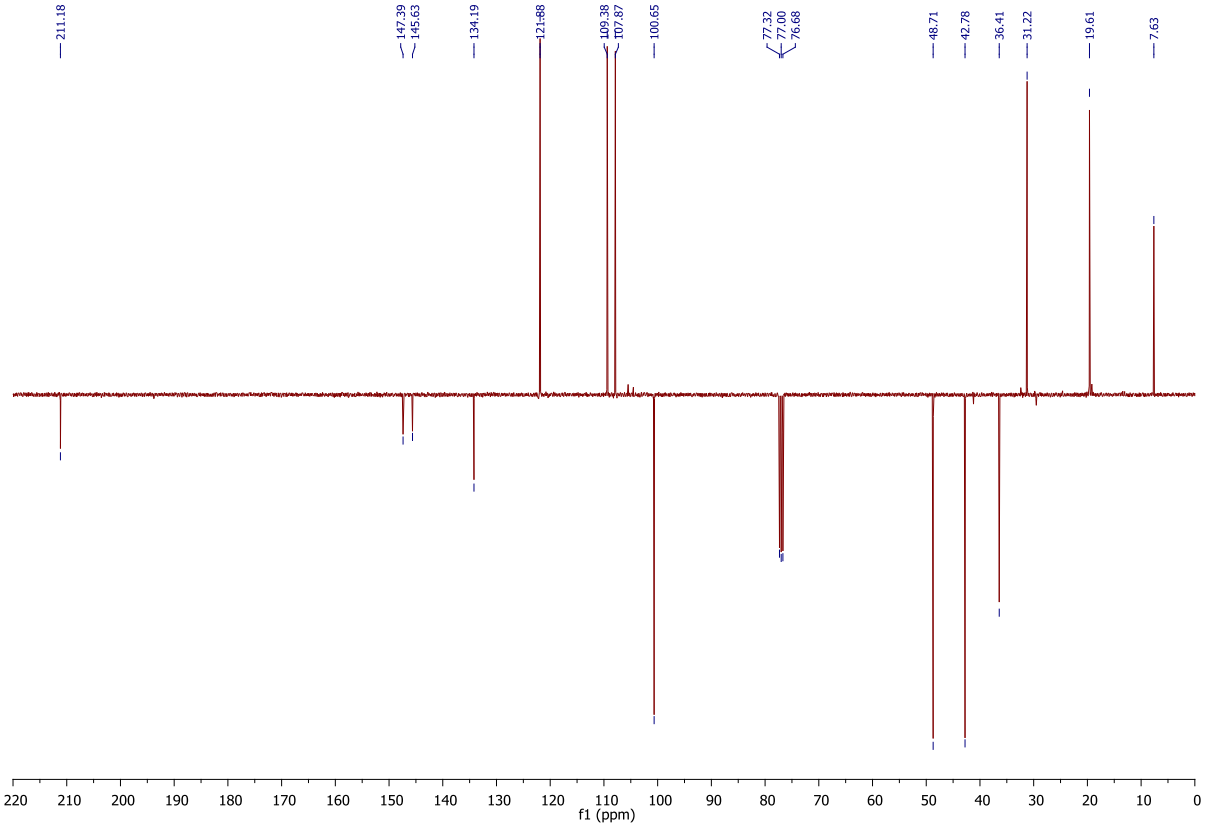
6.72
6.70
6.65
6.65
6.59
6.59
6.57
6.57
5.91
2.51
2.49
2.39
2.37
2.37
2.36
2.35
2.23
2.20
1.02
0.99
0.87
1.000
0.977
1.011
2.014
1.052
4.011
2.200
3.034
3.189
f1 (ppm)


211.18
147.39
145.63
134.19
121.88
109.38
107.87
100.65
77.32
77.00
76.68
48.71
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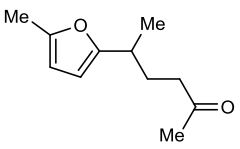
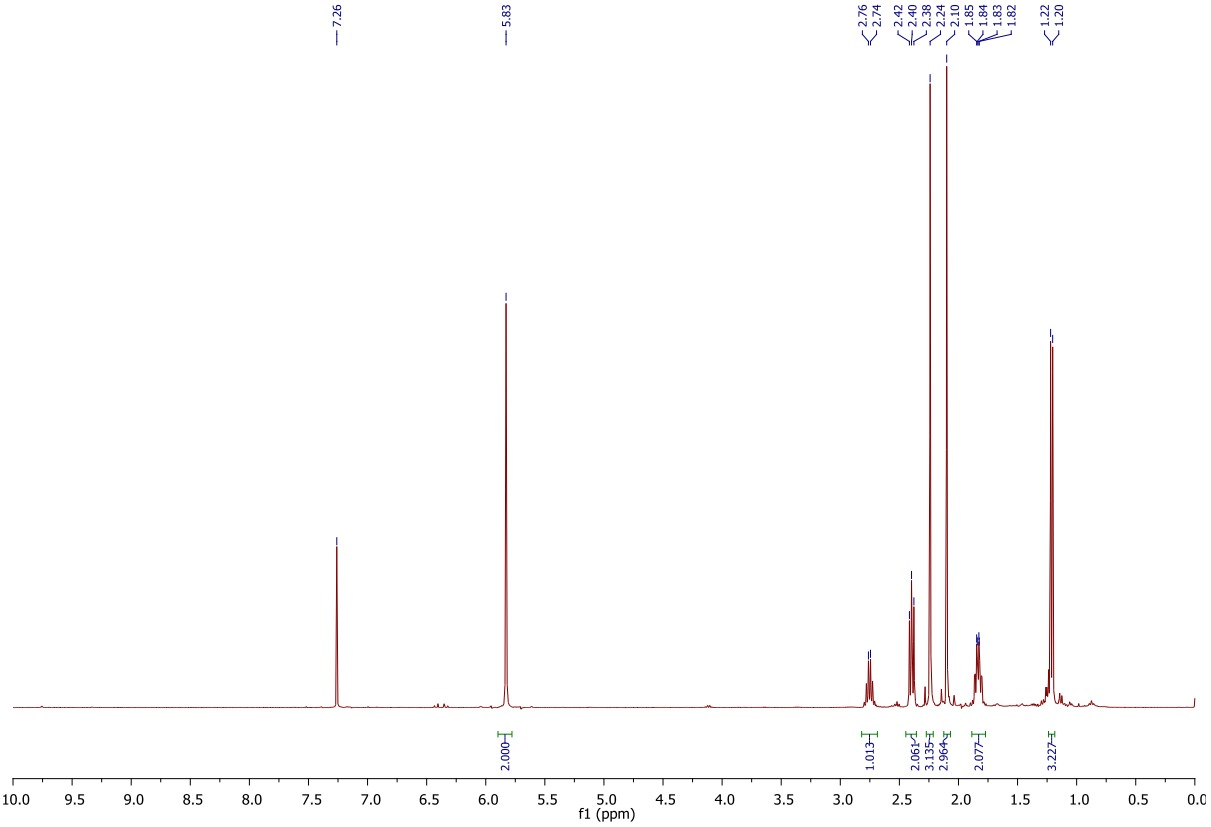
36.41
31.22
19.61
7.63
f1 (ppm)


Me
O
Me
O
Me

2c


7.26
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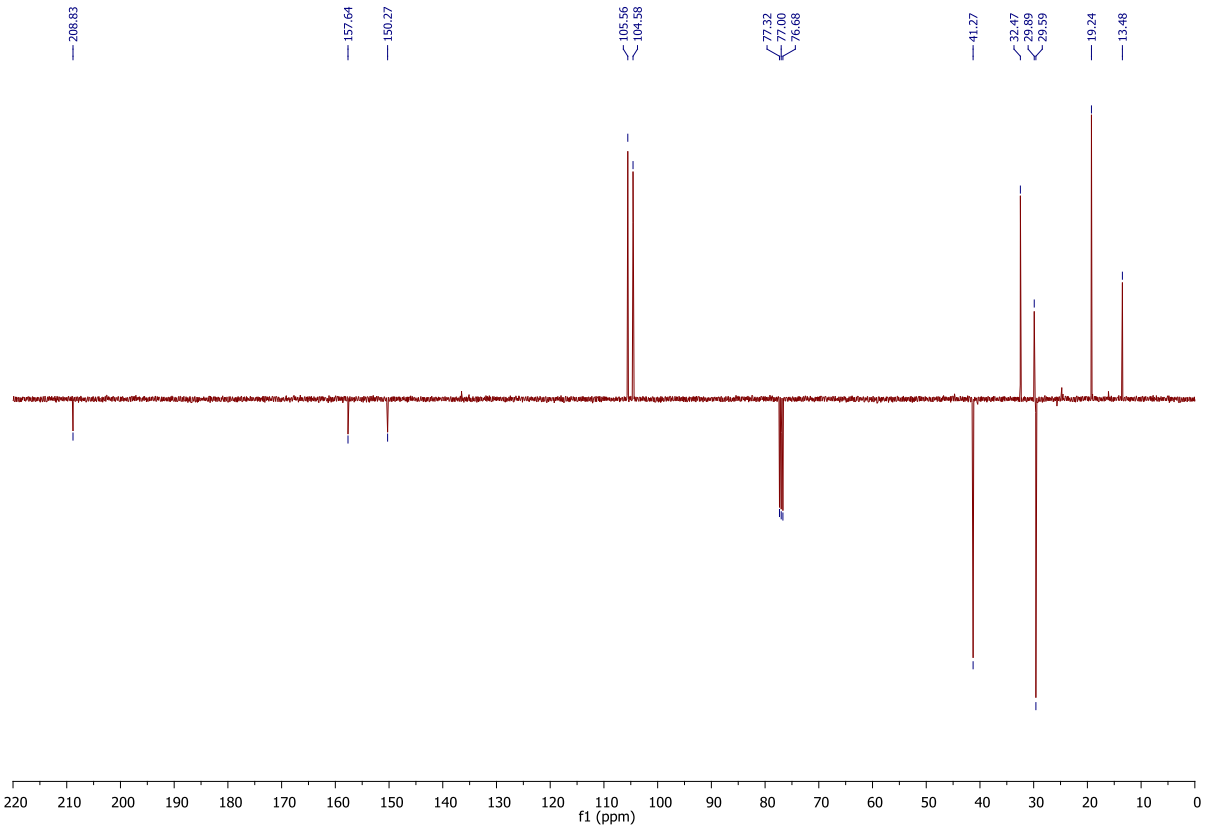
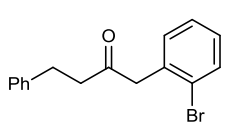
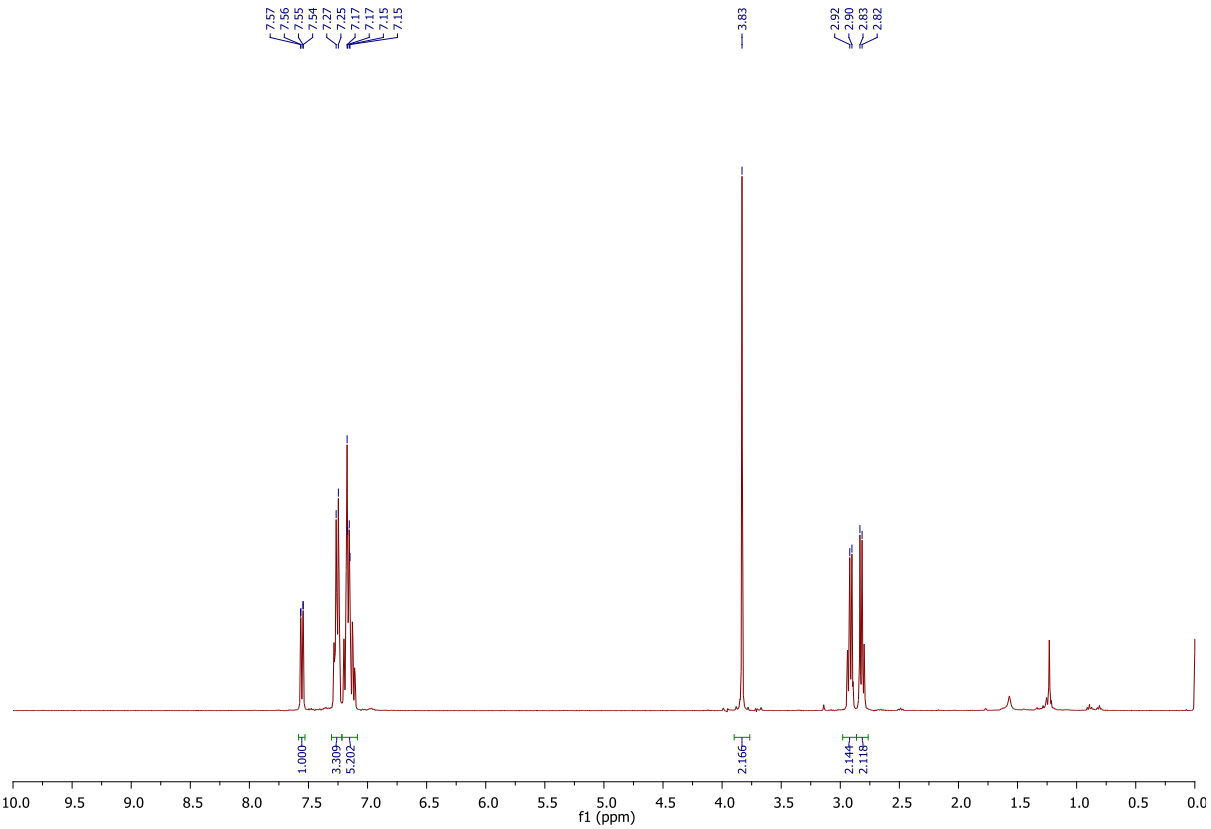
2.76
2.74
2.42
2.40
2.38
2.24
2.10
1.85
1.84
1.83
1.82
1.22
1.20
2.000
1.013
2.061
3.135
2.964
2.077
3.227
f1 (ppm)


208.83
157.64
150.27
105.56
104.58
77.32
77.00
76.68
41.27
32.47
29.89
29.59
19.24
13.48
f1 (ppm)

2d


O
Ph
Br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7.55
7.54
7.27
7.25
7.17
7.17
7.15
7.15
3.83
2.92
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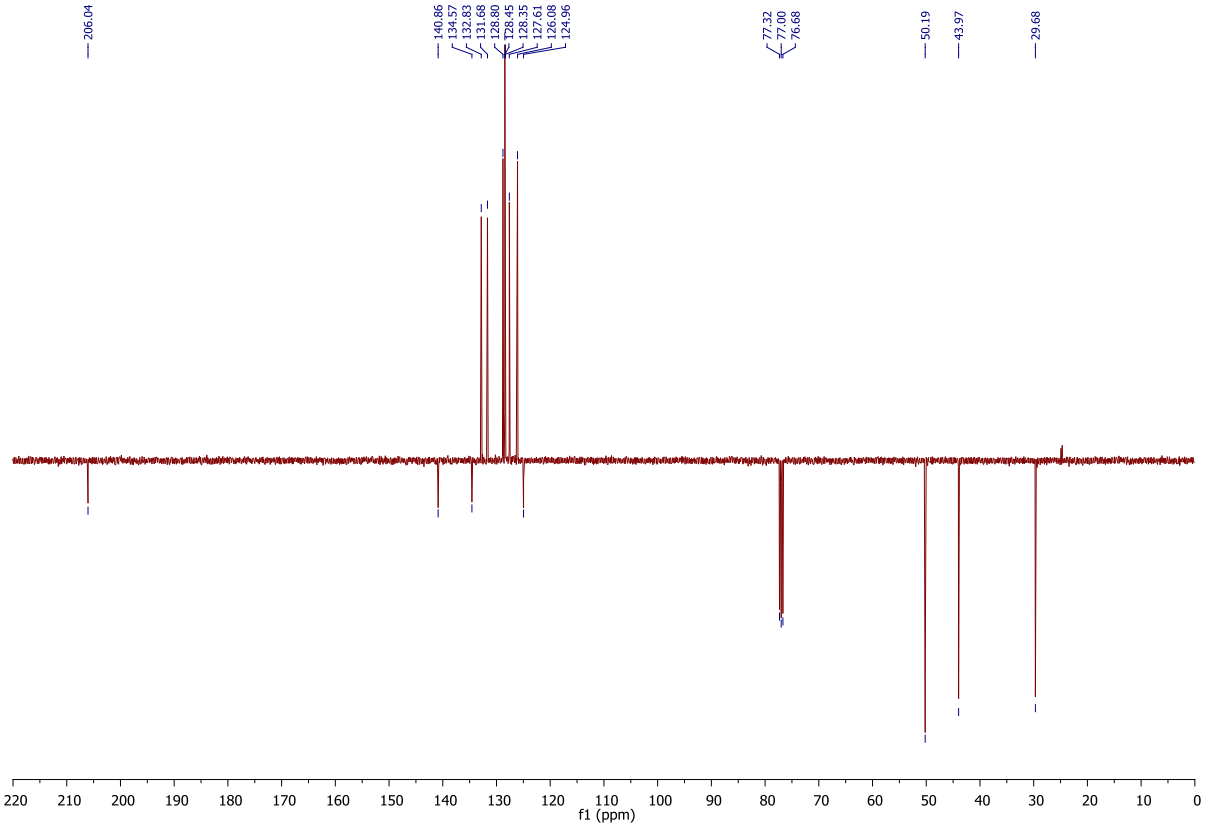
2.83
2.82
1.000
3.309
5.202
2.166
2.144
2.118
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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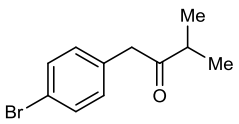
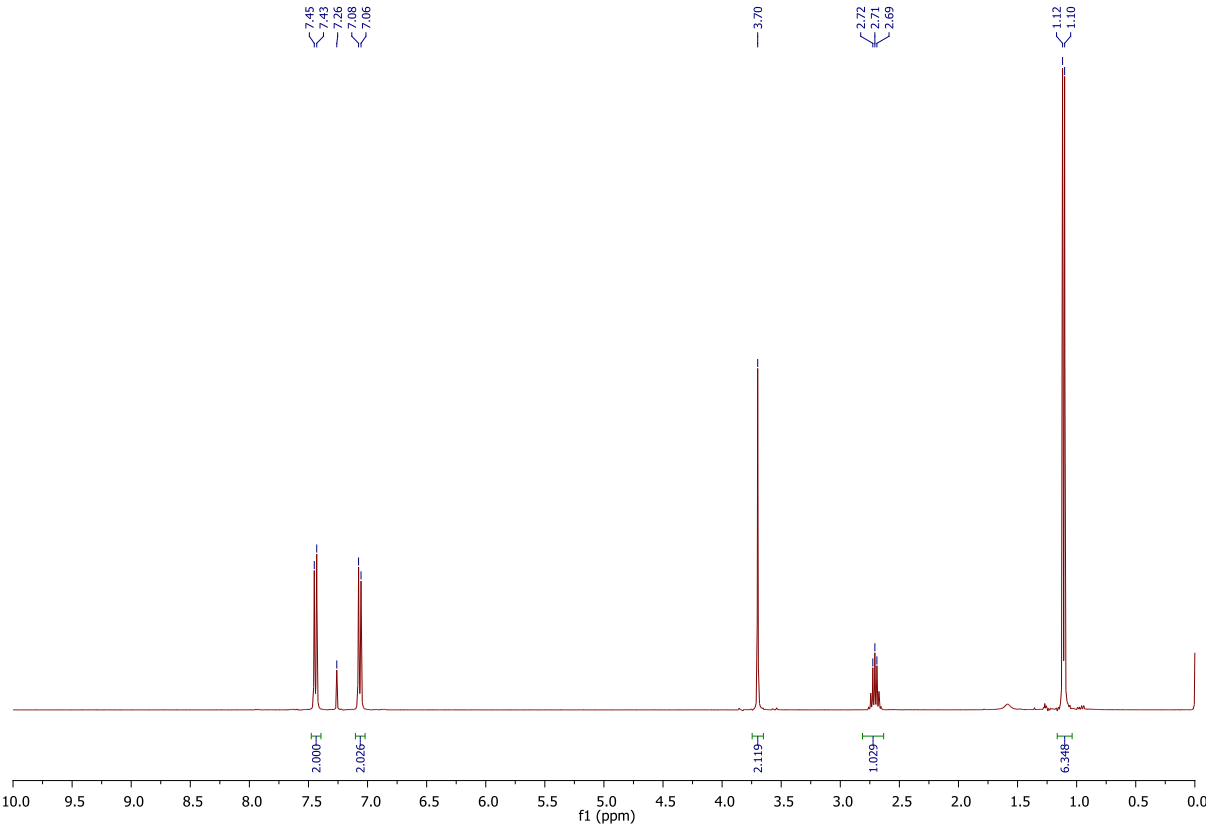
131.68
128.80
128.45
128.35
127.61
126.08
124.96
77.32
77.00
76.68
50.19
43.97
29.68
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
Me
O
Br

2e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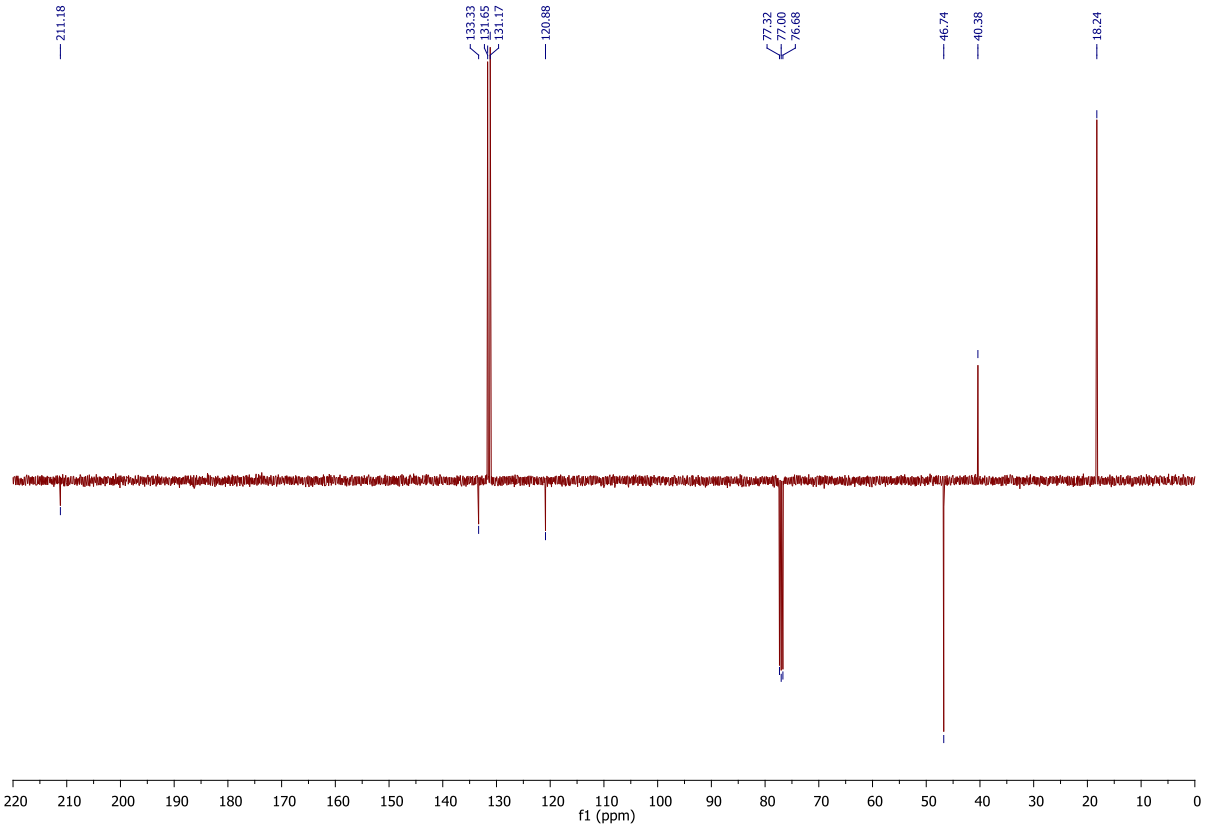
7.43
7.26
7.08
7.06
3.70
2.72
2.71
2.69
1.12
1.10
2.000
2.026
2.119
1.029
6.348
f1 (ppm)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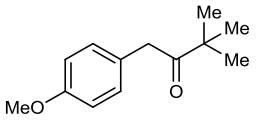
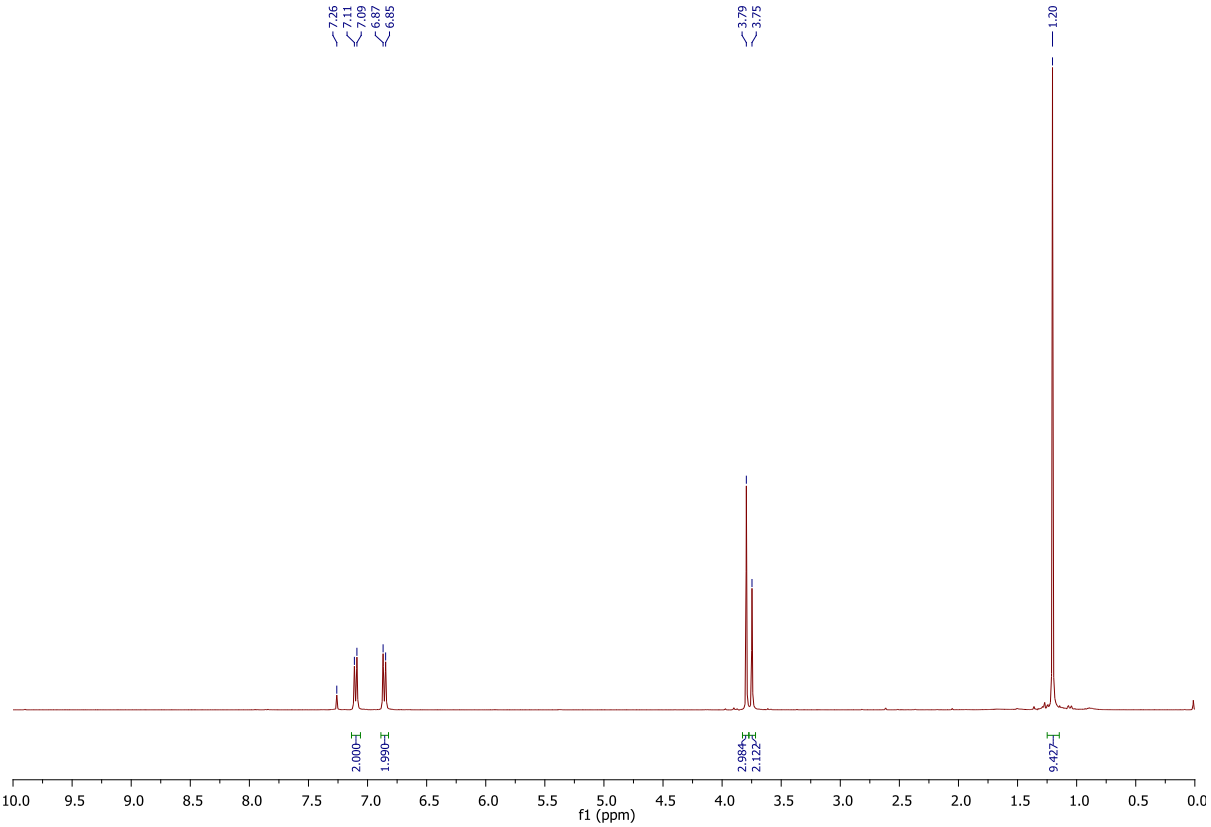
133.33
131.65
131.17
120.88
77.32
77.00
76.68
46.74
40.38
18.24
f1 (ppm)

2f


Me
Me
Me
O
MeO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6.85
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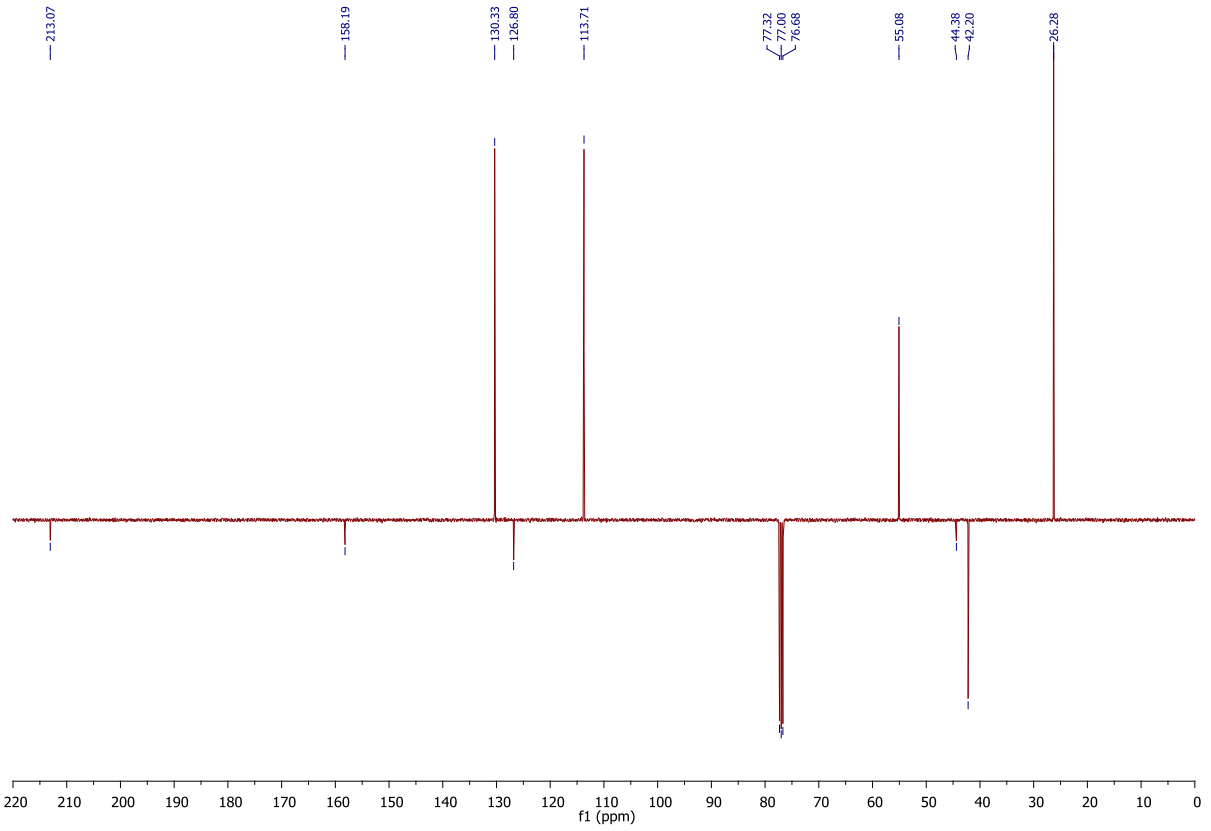
1.20
2.000
1.990
2.984
2.122
9.427
f1 (ppm)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126.80
113.71
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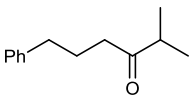
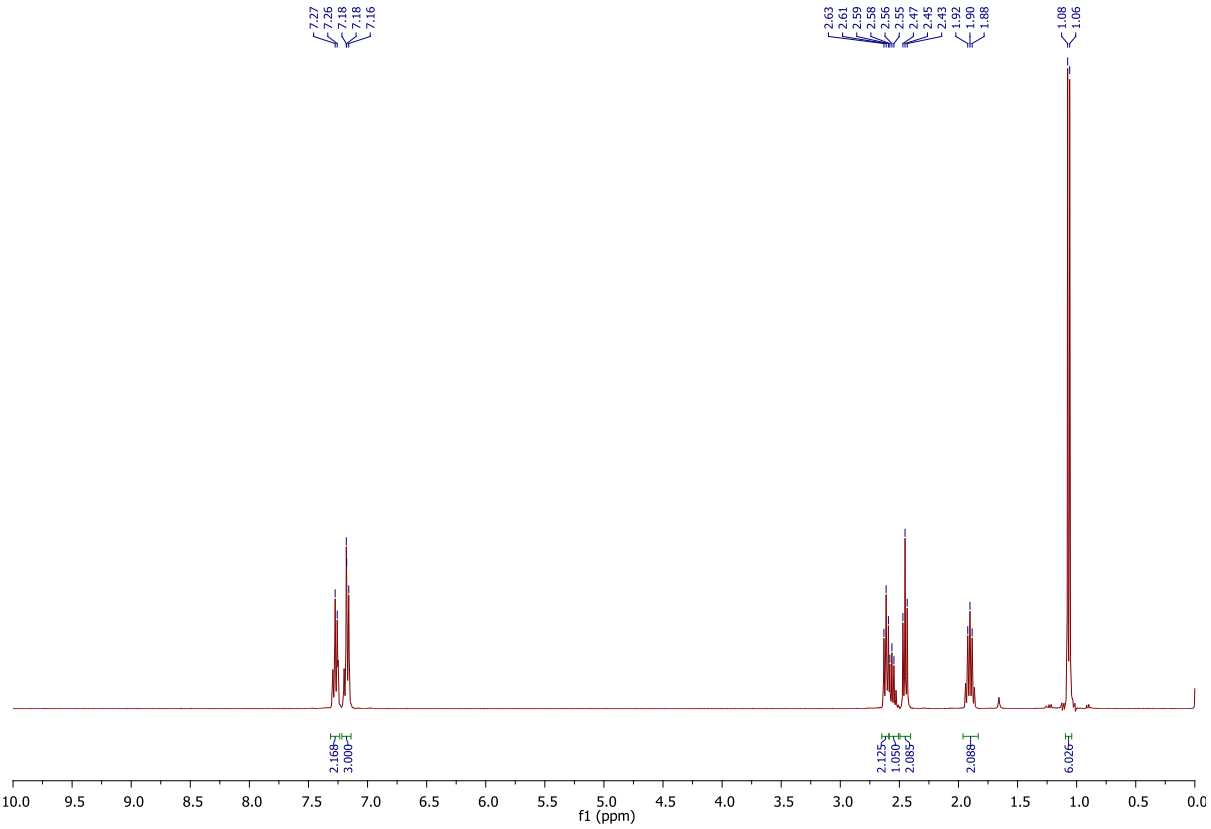
77.00
76.68
55.08
44.38
42.20
26.28
f1 (ppm)


Ph
O

2g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7.18
7.16
2.63
2.61
2.59
2.58
2.56
2.55
2.47
2.45
2.43
1.92
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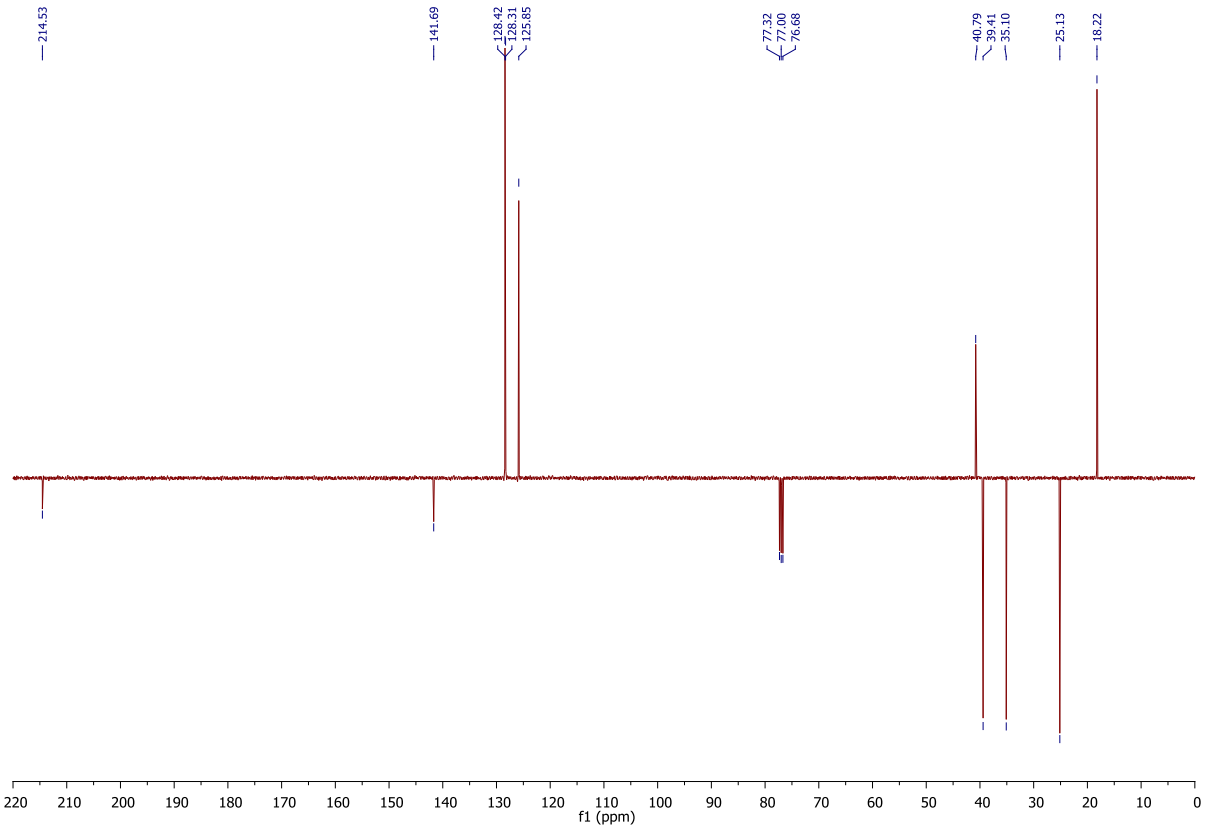
1.050
2.089
2.088
6.026
f1 (ppm)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125.85
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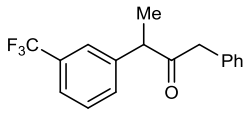
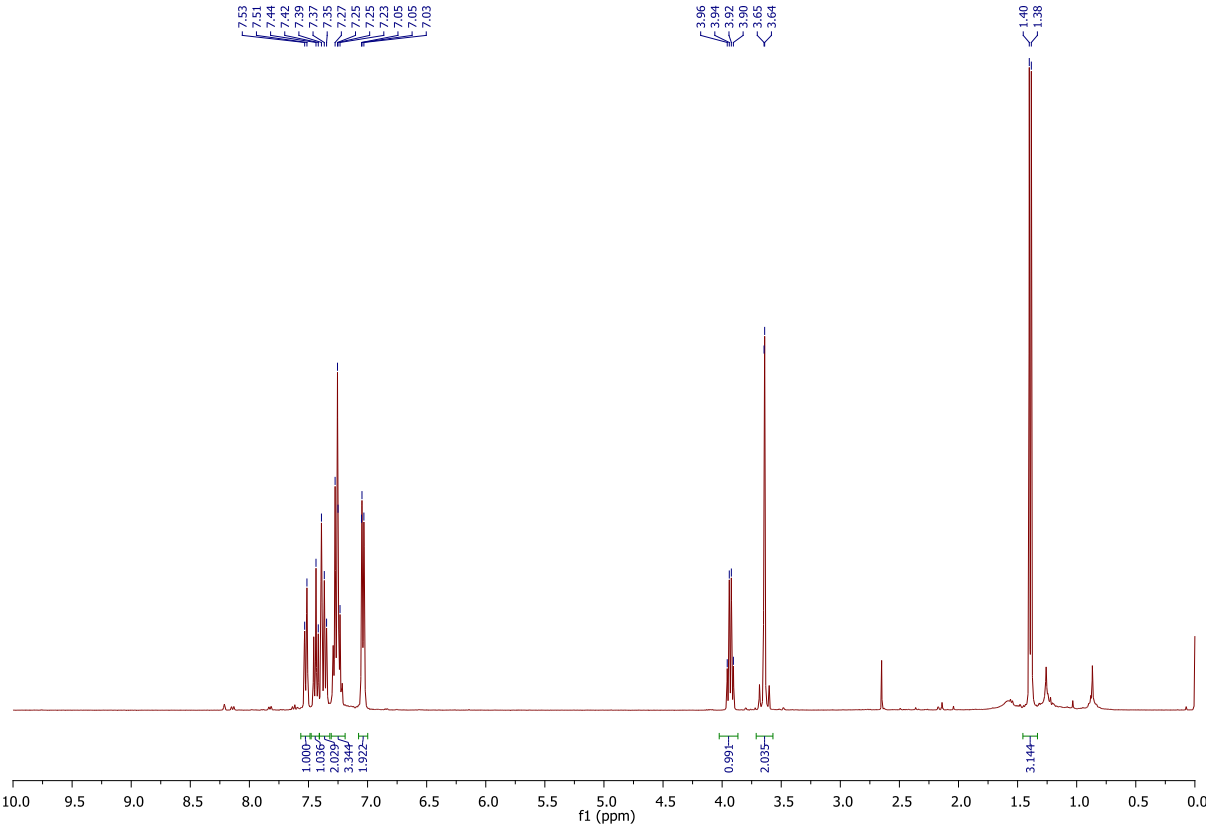
77.00
76.68
40.79
39.41
35.10
25.13
18.22
f1 (ppm)

2h


Me
F3C
Ph
O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7.35
7.27
7.25
7.25
7.23
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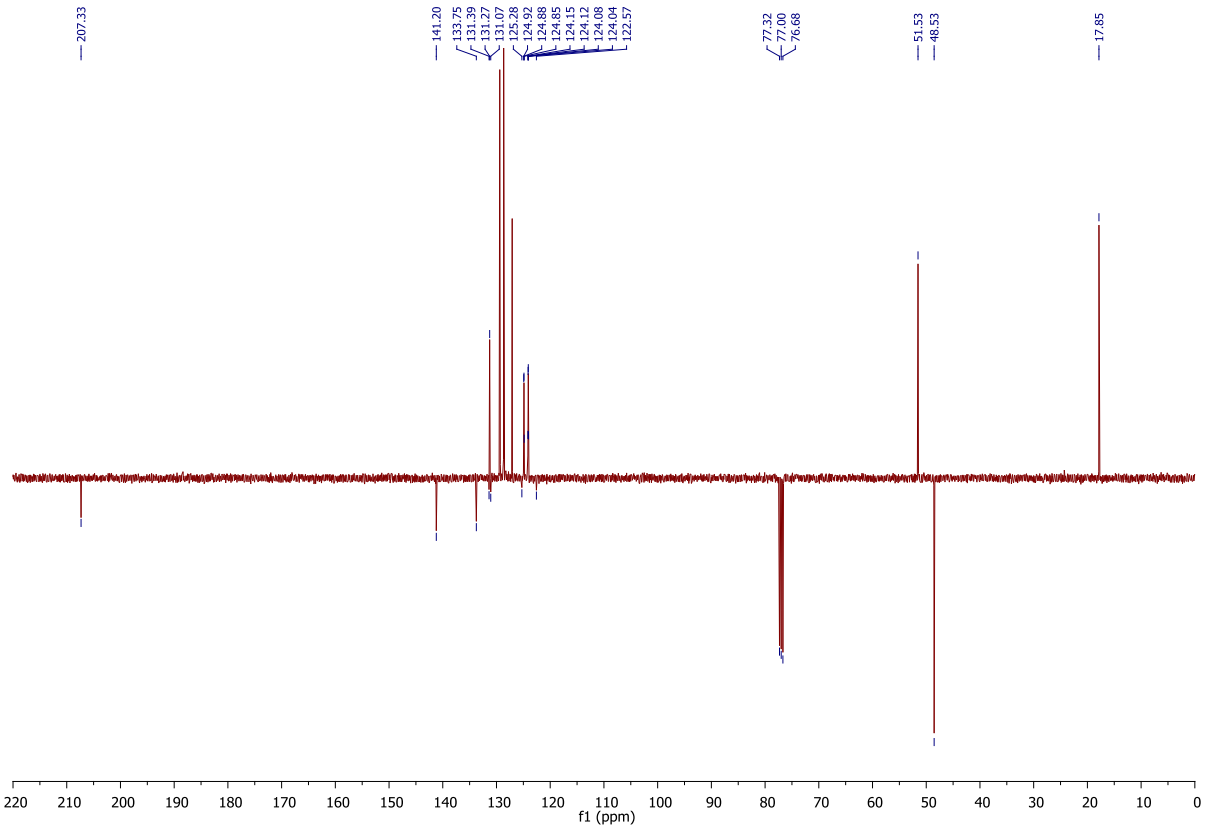
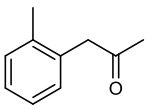
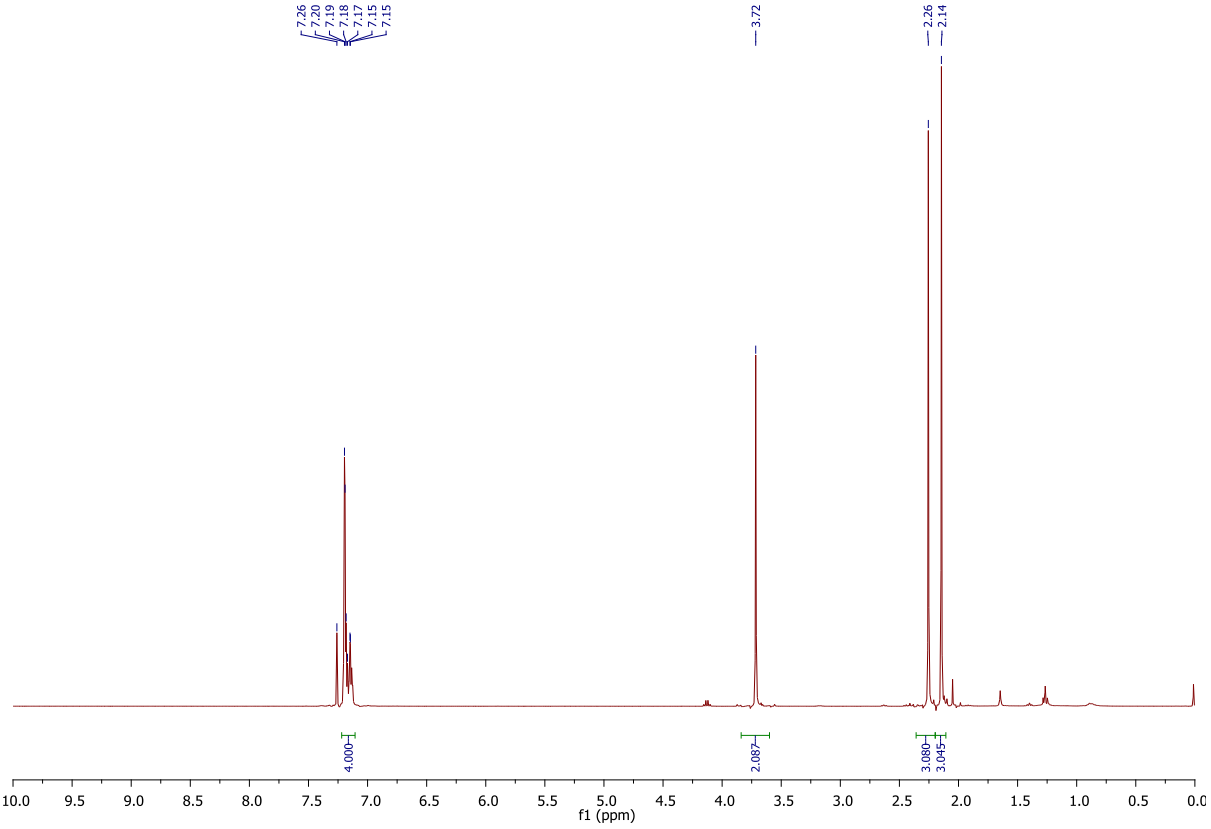
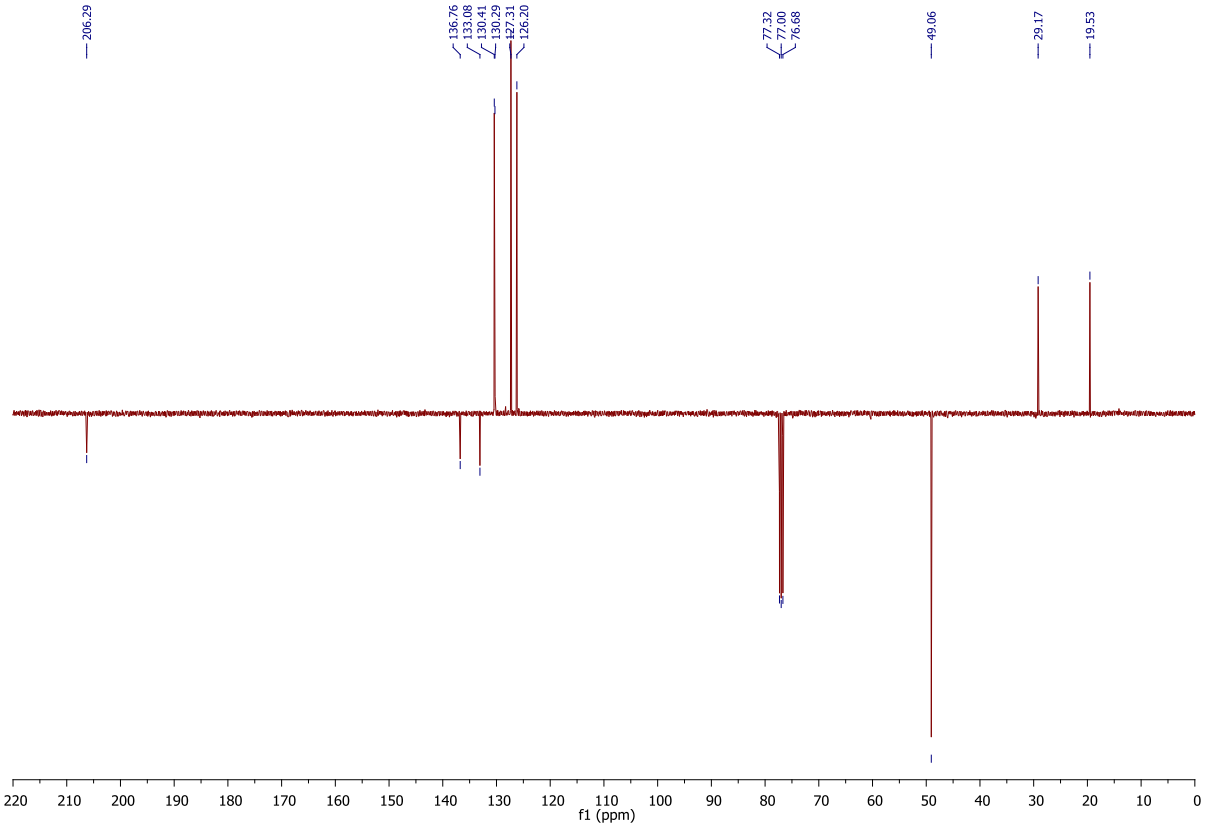
7.03
3.96
3.94
3.92
3.90
3.65
3.64
1.40
1.38
1.000
1.036
2.029
3.344
1.922
0.991
2.035
3.144
f1 (ppm)


207.33
141.20
133.75
131.39
131.27
131.07
125.28
124.92
124.88
124.85
124.15
124.12
124.08
124.04
122.57
77.32
77.00
76.68
51.53
48.53
17.85
f1 (ppm)

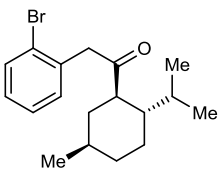
2i

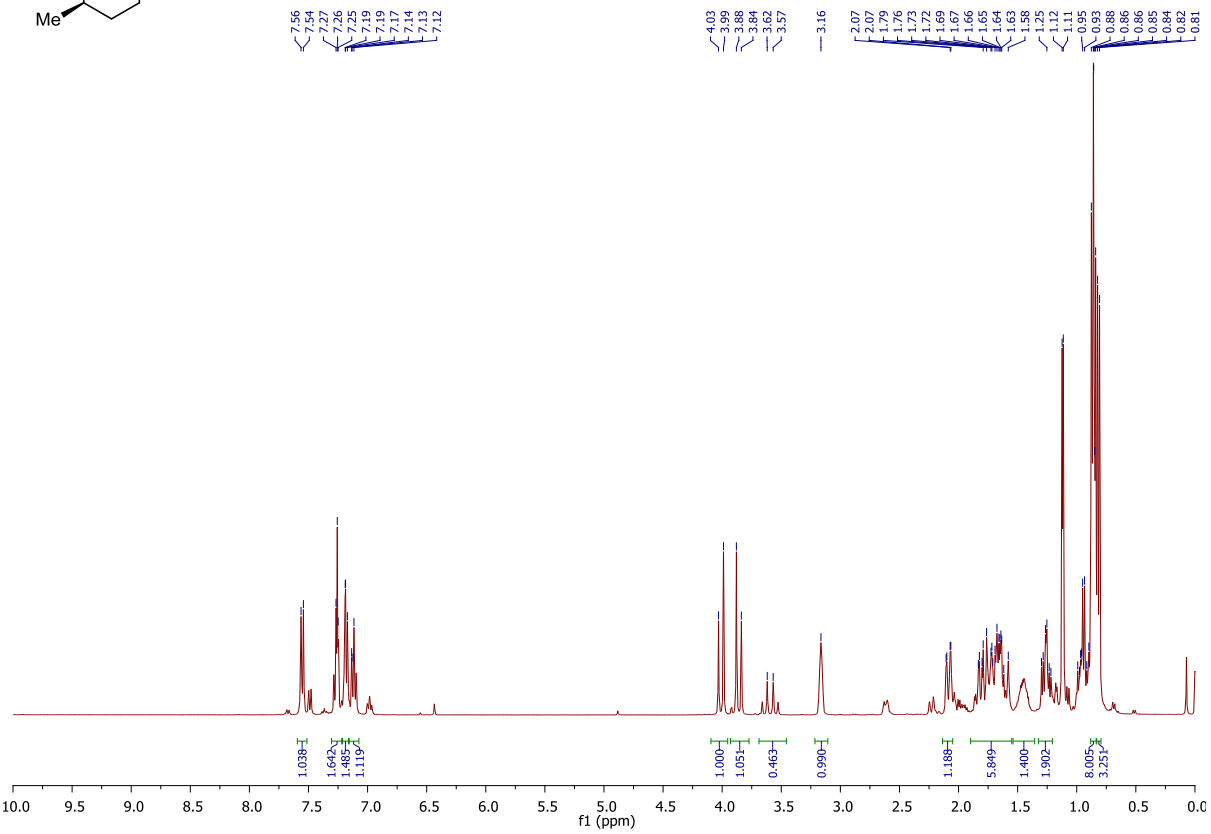



7.26
7.20
7.19
7.18
7.17
7.15
7.15
3.72
2.26
2.14
4.000
2.087
3.080
3.045
f1 (ppm)


206.29
136.76
133.08
130.41
130.29
127.31
126.20
77.32
77.00
76.68
49.06
29.17
19.53
f1 (ppm)

2j


Br
O
Me
Me
Me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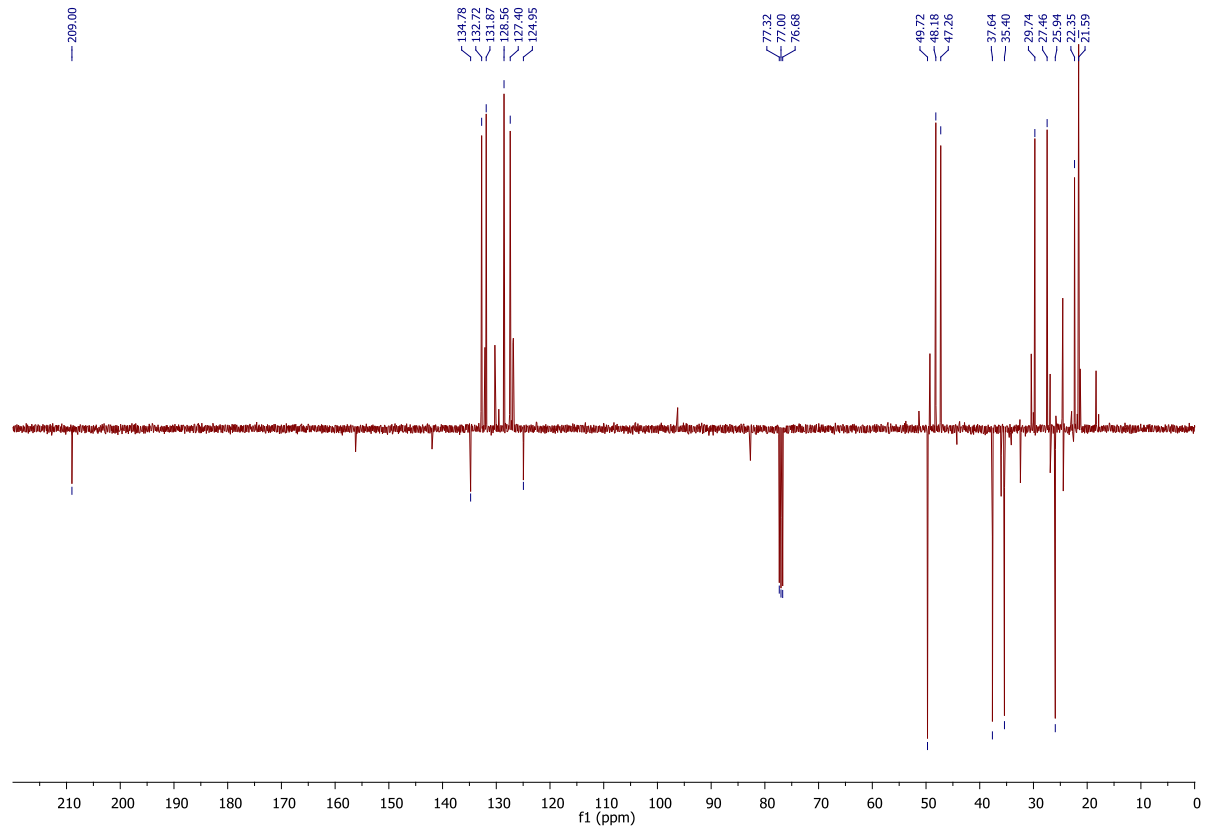
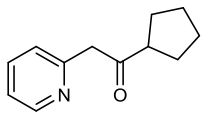
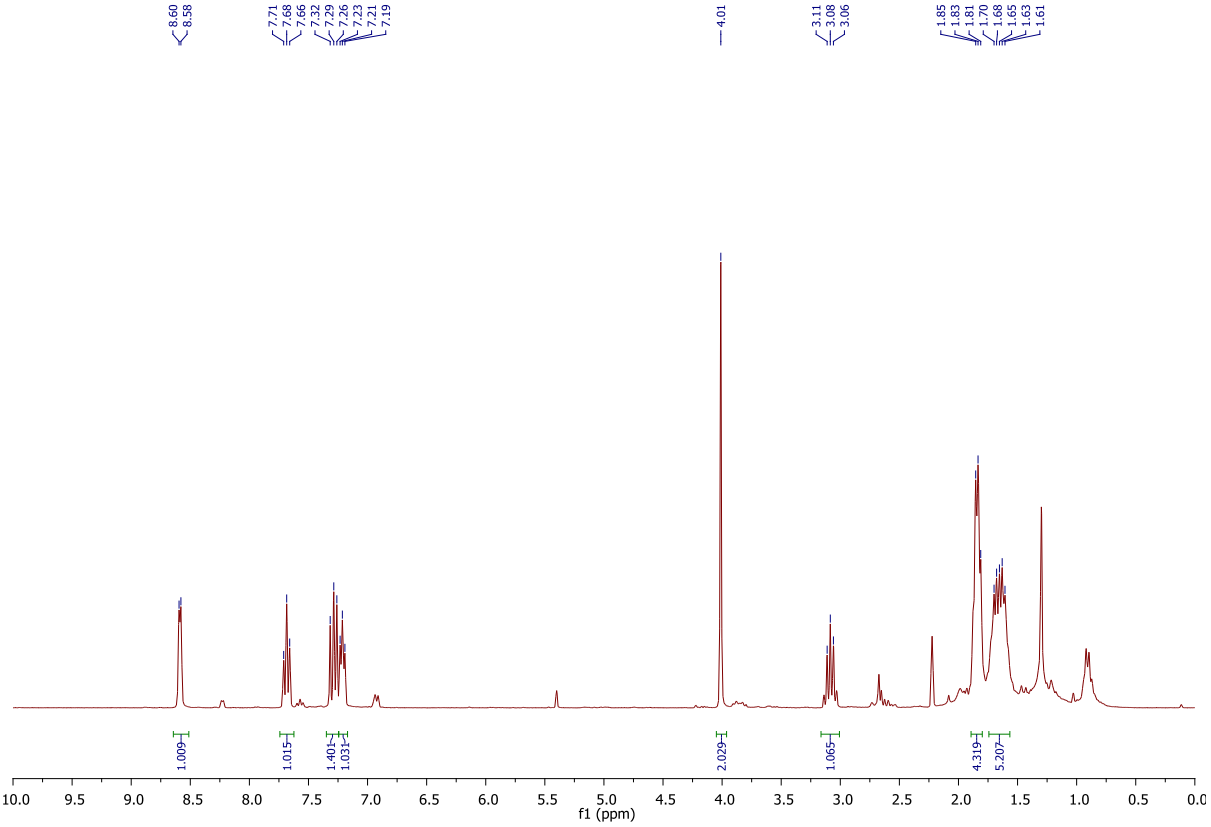
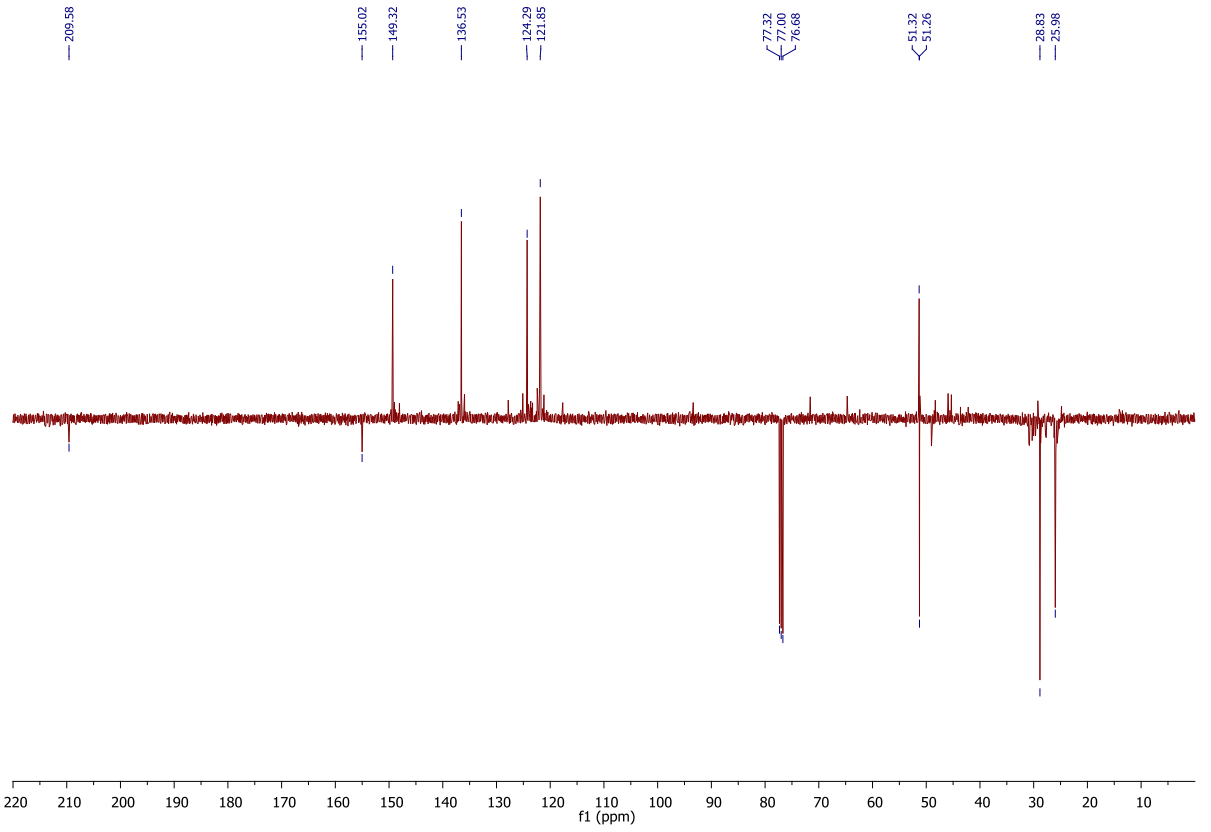
7.54
7.27
7.26
7.25
7.19
7.17
7.14
7.13
7.12
4.03
3.99
3.88
3.84
3.62
3.57
3.16
2.07
2.07
1.79
1.76
1.73
1.72
1.69
1.67
1.66
1.65
1.64
1.63
1.58
1.25
1.12
1.11
0.95
0.93
0.88
0.86
0.85
0.84
0.82
0.81
1.038
1.642
1.485
1.119
1.000
1.051
0.463
0.990
1.188
5.849
1.400
1.902
8.005
3.251
f1 (ppm)


209.00
134.78
132.72
131.87
128.56
127.40
124.95
77.32
77.00
76.68
49.72
48.18
47.26
37.64
35.40
29.74
27.46
25.94
22.35
21.59
f1 (ppm)

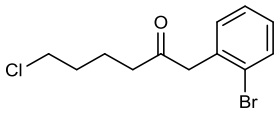
2k

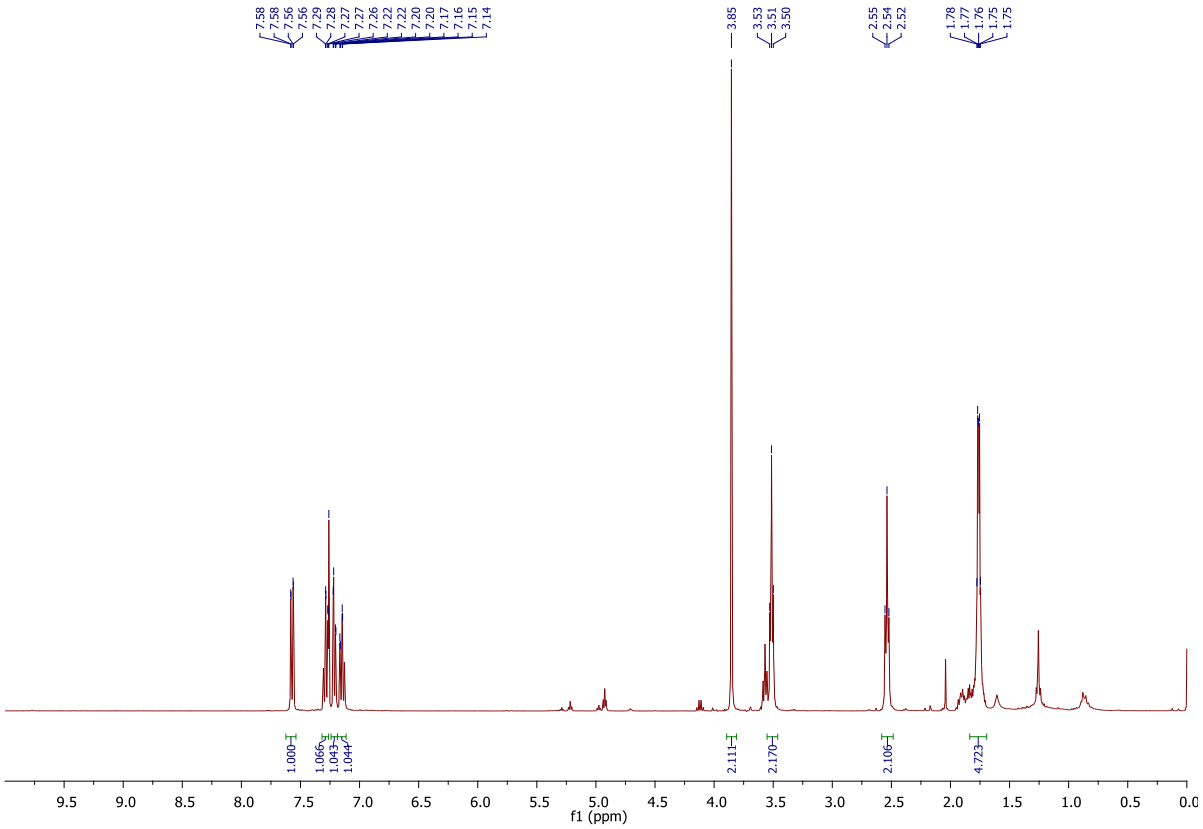

N
O

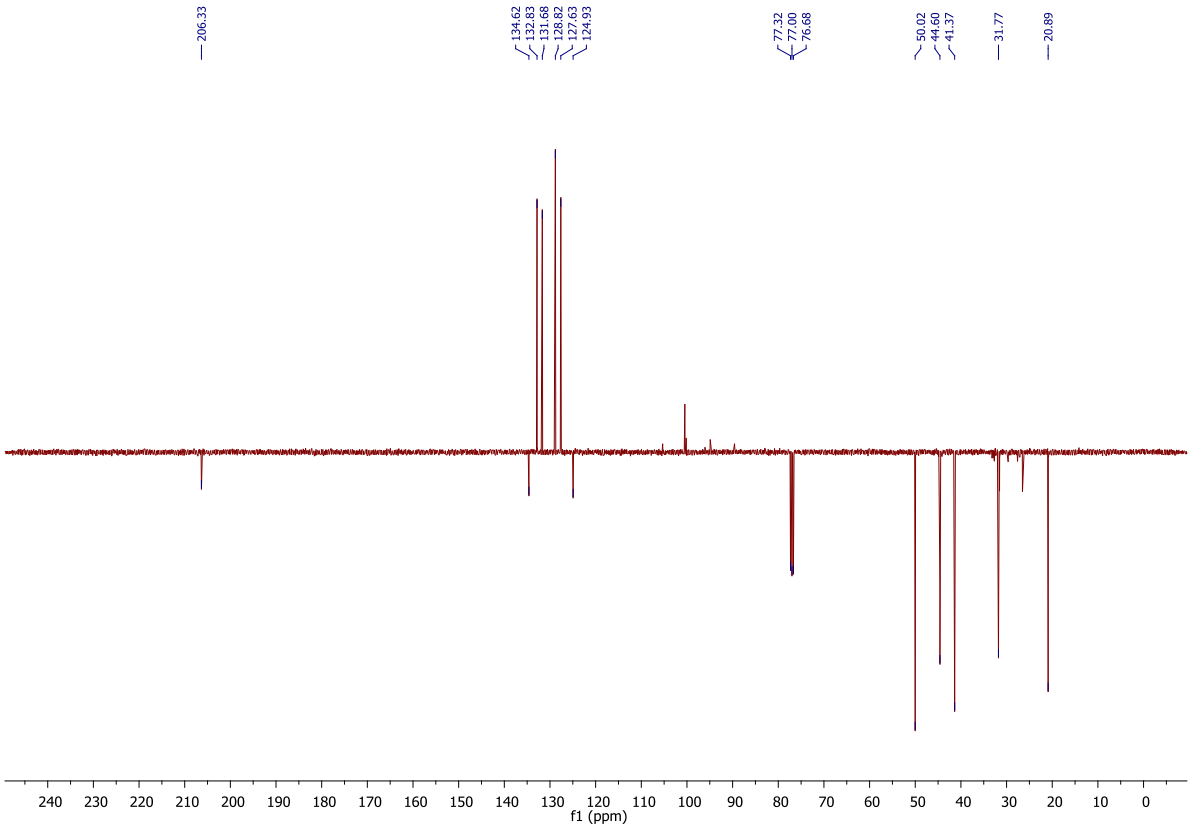

8.60
8.58
7.71
7.68
7.66
7.32
7.29
7.26
7.23
7.21
7.19
4.01
3.11
3.08
3.06
1.85
1.83
1.81
1.70
1.68
1.65
1.63
1.61
1.009
1.015
1.401
1.031
2.029
1.065
4.319
5.207
f1 (ppm)


209.58
155.02
149.32
136.53
124.29
121.85
77.32
77.00
76.68
51.32
51.26
28.83
25.98
f1 (ppm)

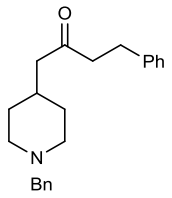
2l

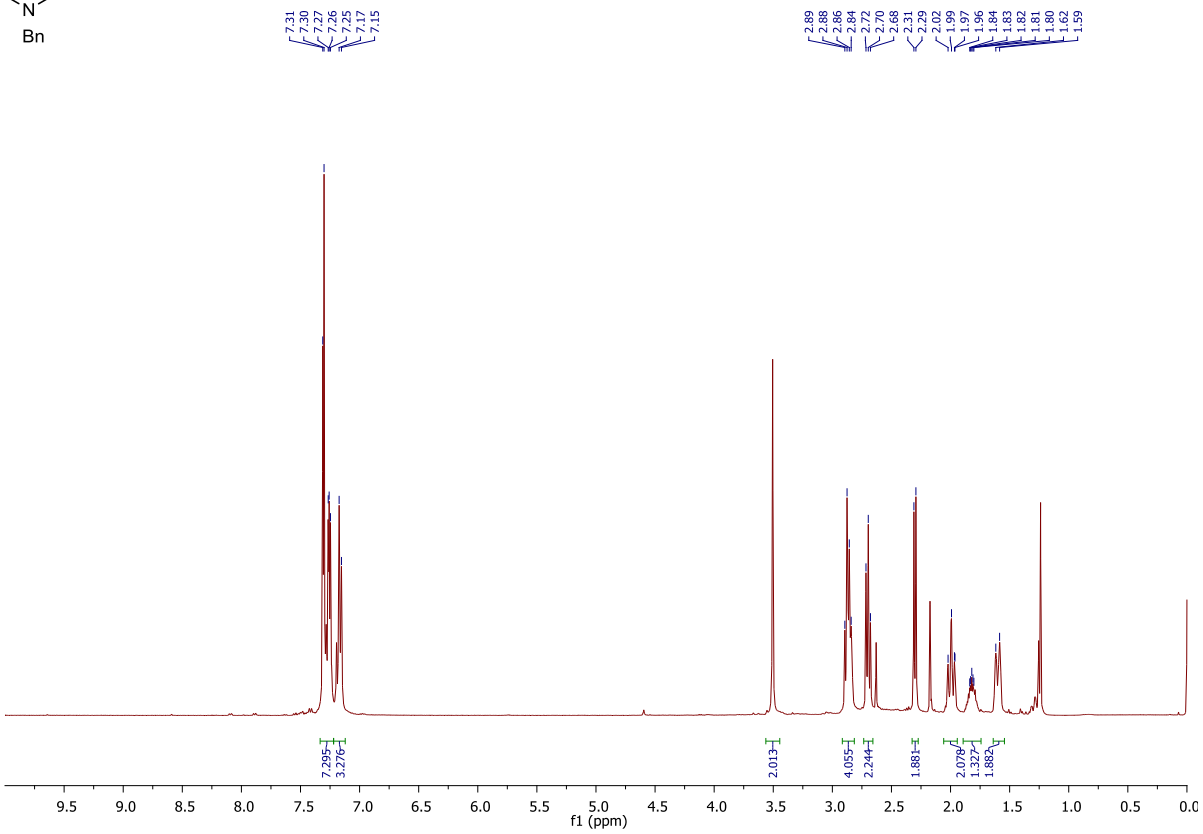

O
Cl
Br

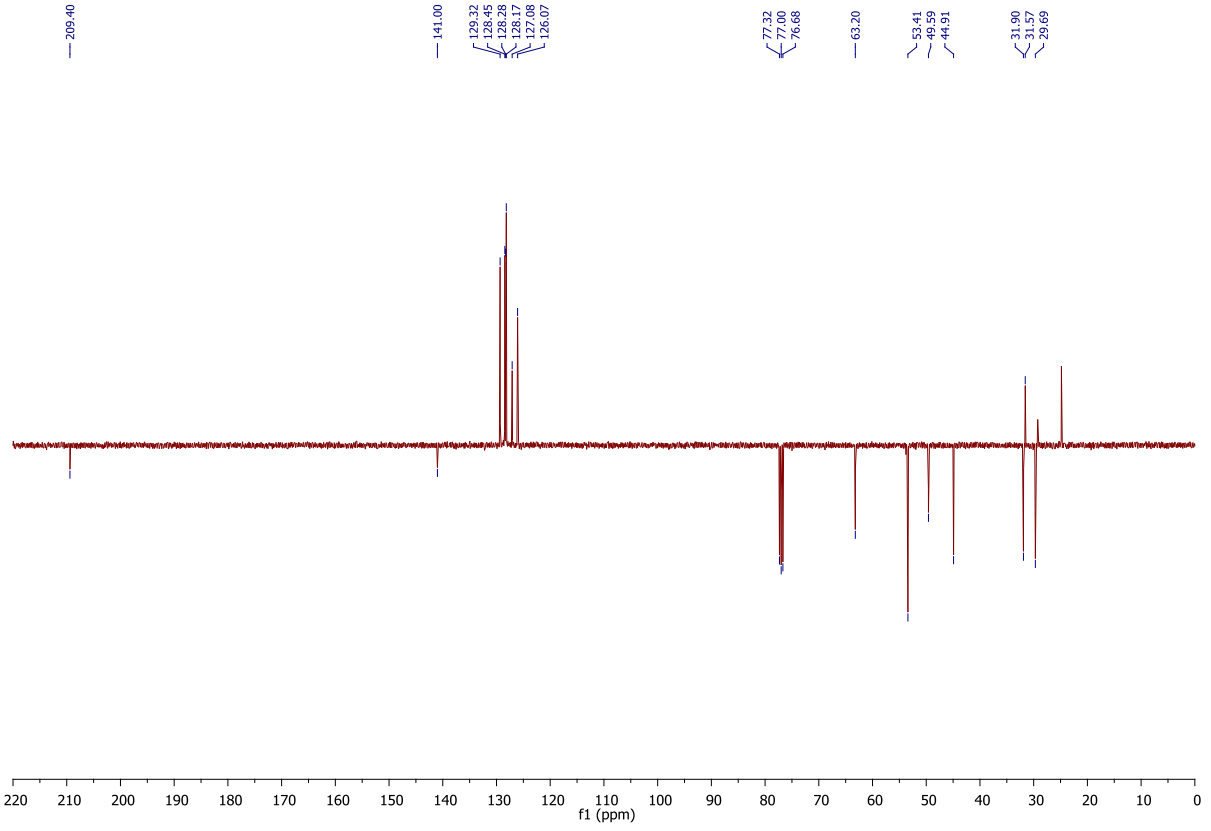

7.58
7.58
7.56
7.56
7.29
7.28
7.27
7.27
7.26
7.22
7.20
7.20
7.17
7.16
7.15
7.14
3.85
3.53
3.51
3.50
2.55
2.54
2.52
1.78
1.77
1.76
1.75
1.75
1.000
1.066
1.043
1.044
2.111
2.170
2.106
4.723
f1 (ppm)

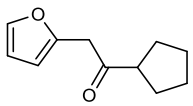

206.33
134.62
132.83
131.68
128.82
127.63
124.93
77.32
77.00
76.68
50.02
44.60
41.37
31.77
20.89
f1 (ppm)

2m

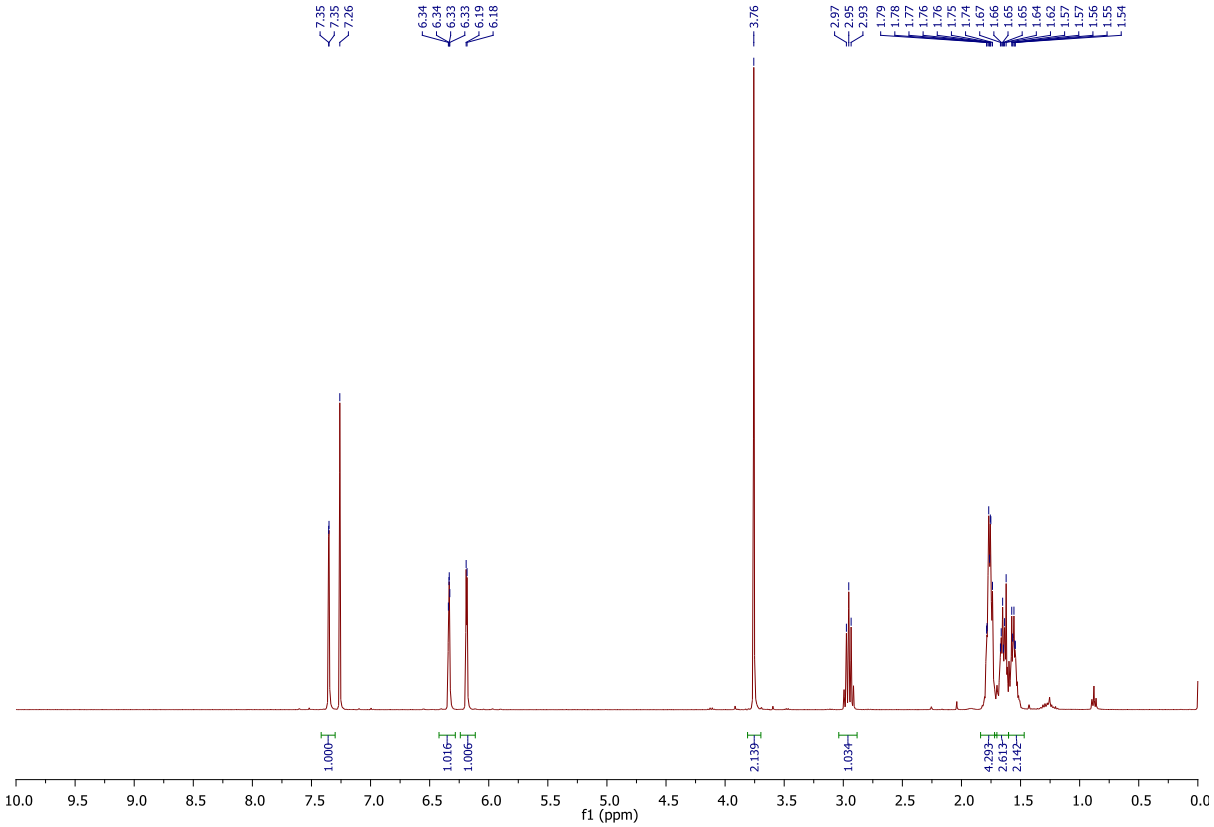

O
Ph
N
Bn

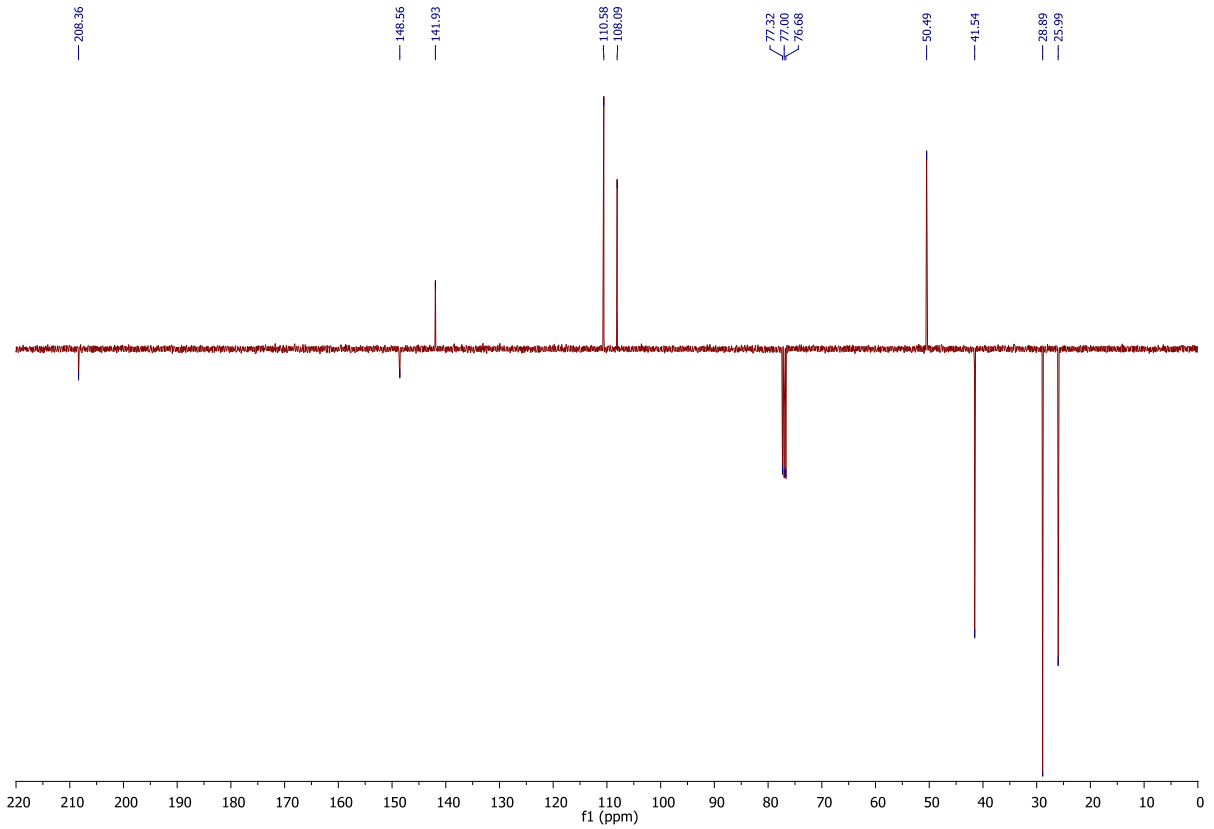

7.31
7.30
7.27
7.26
7.25
7.17
7.15
2.89
2.88
2.86
2.84
2.72
2.70
2.68
2.31
2.29
2.02
1.99
1.97
1.96
1.84
1.83
1.82
1.81
1.80
1.62
1.59
7.295
3.276
2.013
4.055
2.244
1.881
2.079
1.327
1.882
f1 (ppm)

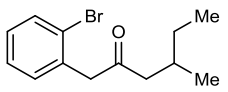

209.40
141.00
129.32
128.45
128.28
128.17
127.08
126.07
77.32
77.00
76.68
63.20
53.41
49.59
44.91
31.90
31.57
29.69
f1 (ppm)



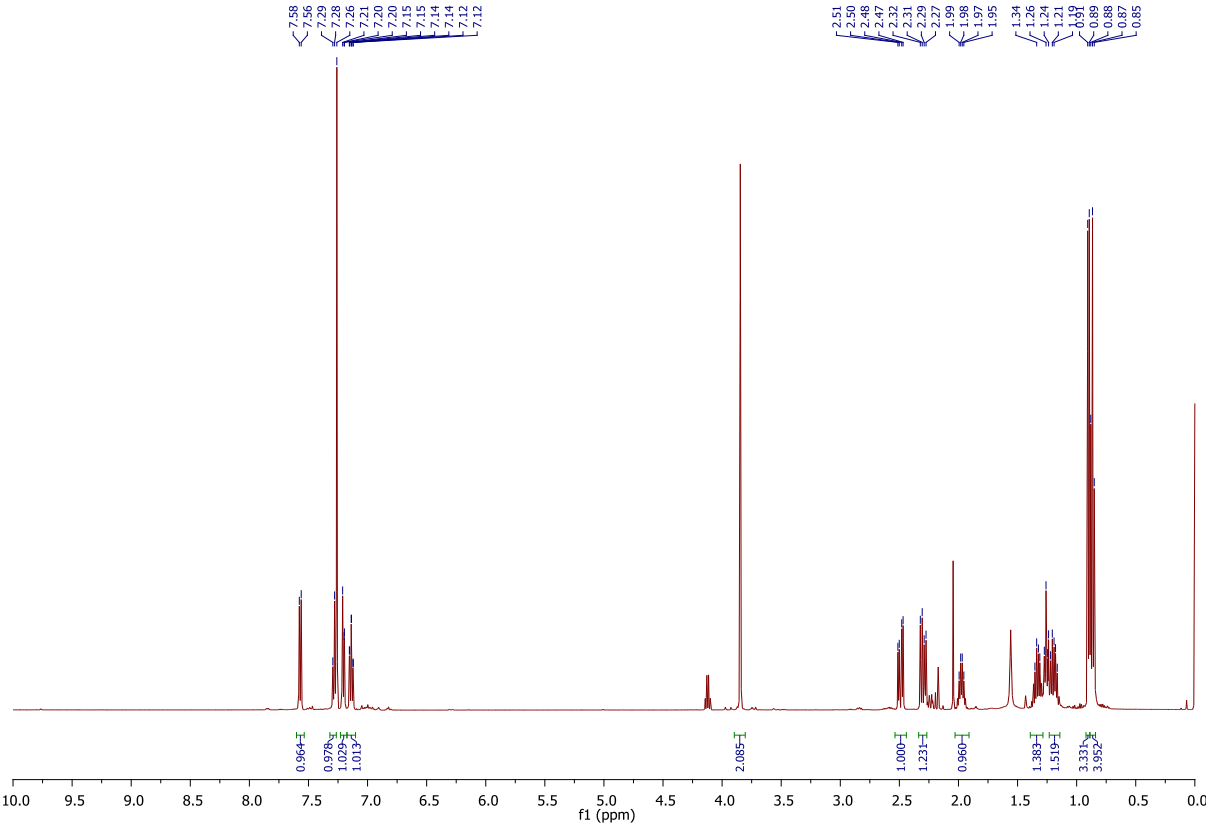
2n


7.35
7.35
7.26
6.34
6.34
6.33
6.33
6.19
6.18
3.76
2.97
2.95
2.93
1.79
1.78
1.77
1.76
1.76
1.75
1.74
1.67
1.66
1.65
1.65
1.64
1.62
1.57
1.57
1.56
1.55
1.54
1.000
1.016
1.006
2.139
1.034
4.293
2.613
2.142
f1 (ppm)


208.36
148.56
141.93
110.58
108.09
77.32
77.00
76.68
50.49
41.54
28.89
25.99
f1 (ppm)


Br
O
Me
Me

2o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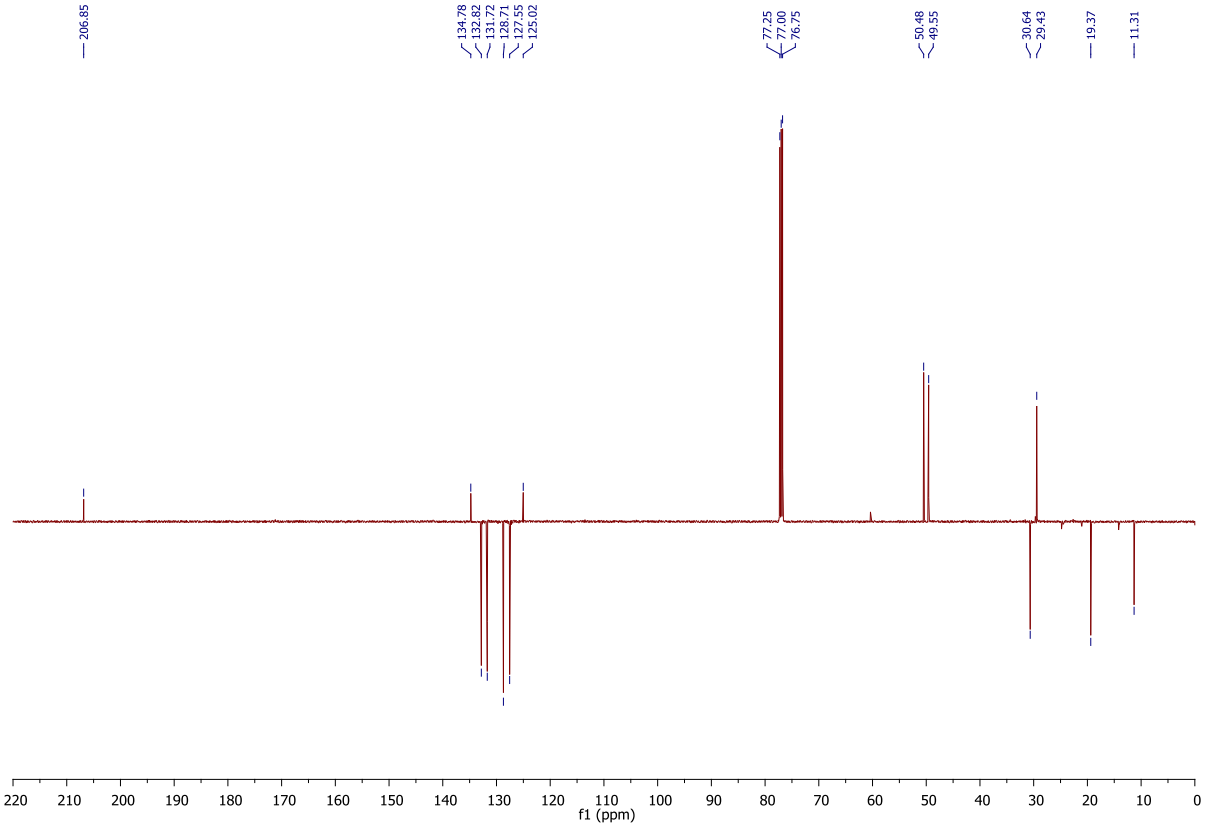
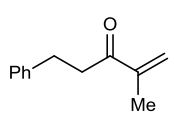
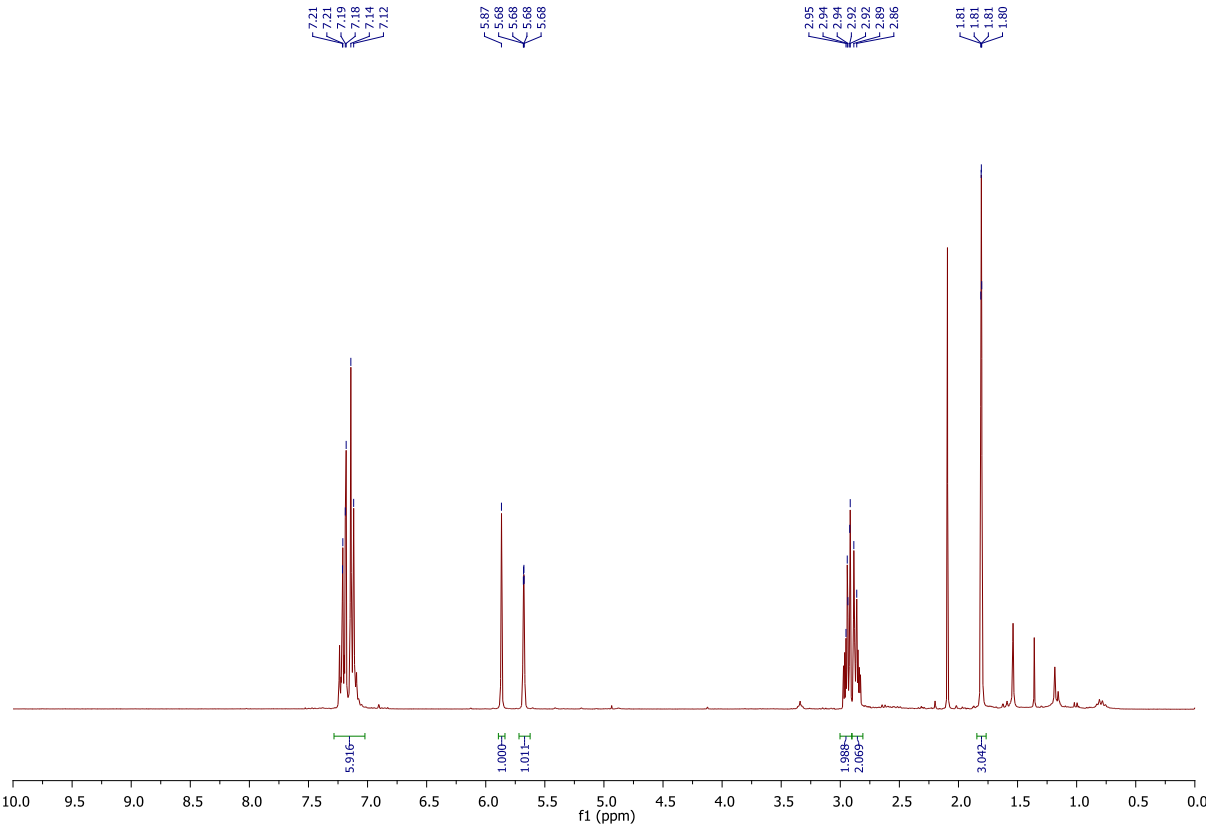
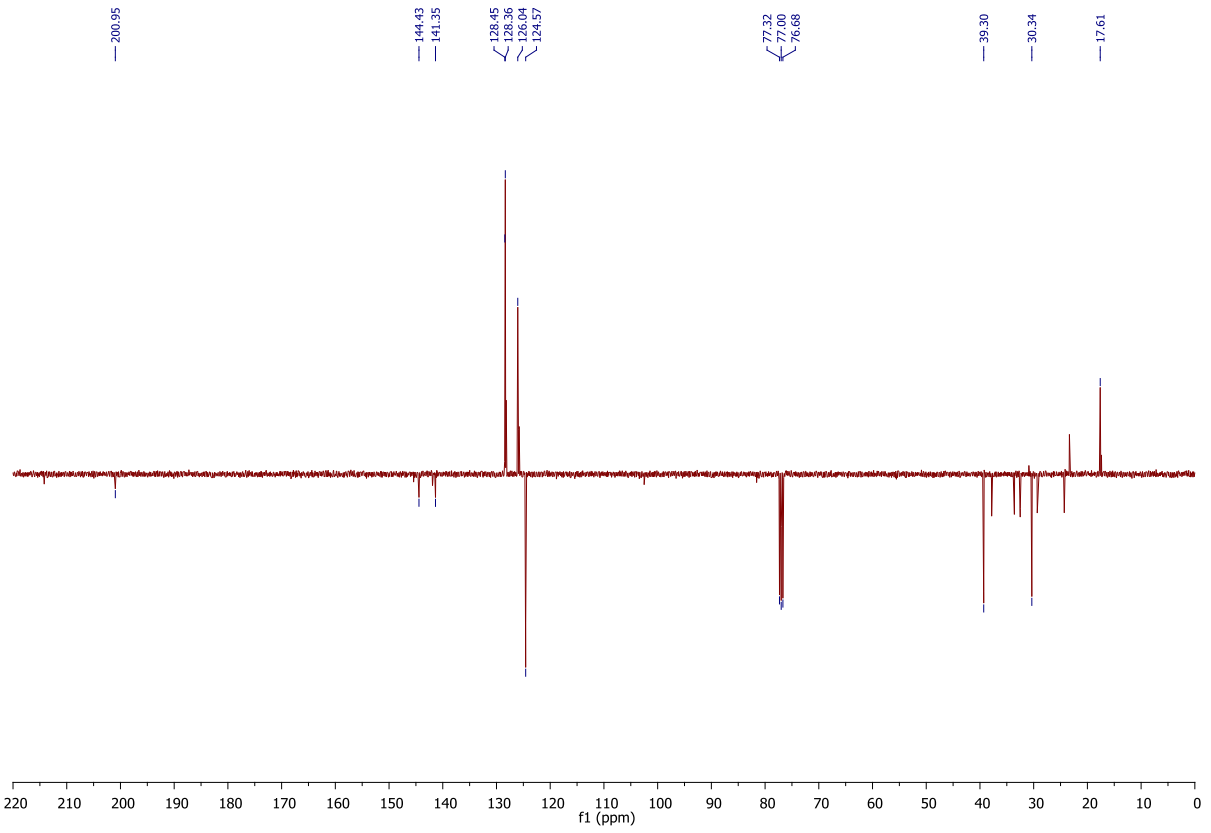
7.56
7.29
7.28
7.26
7.21
7.20
7.20
7.15
7.15
7.14
7.14
7.12
7.12
2.51
2.50
2.48
2.47
2.32
2.31
2.29
2.27
1.99
1.98
1.97
1.95
1.34
1.26
1.24
1.21
0.91
0.89
0.88
0.87
0.85
0.964
0.978
1.029
1.013
2.085
1.000
1.231
0.960
1.383
1.519
3.331
3.952
f1 (ppm)

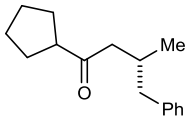

206.85
134.78
132.82
131.72
128.71
127.55
125.02
77.25
77.00
76.75
50.48
49.55
30.64
29.43
19.37
11.31
f1 (ppm)


O
Ph
Me

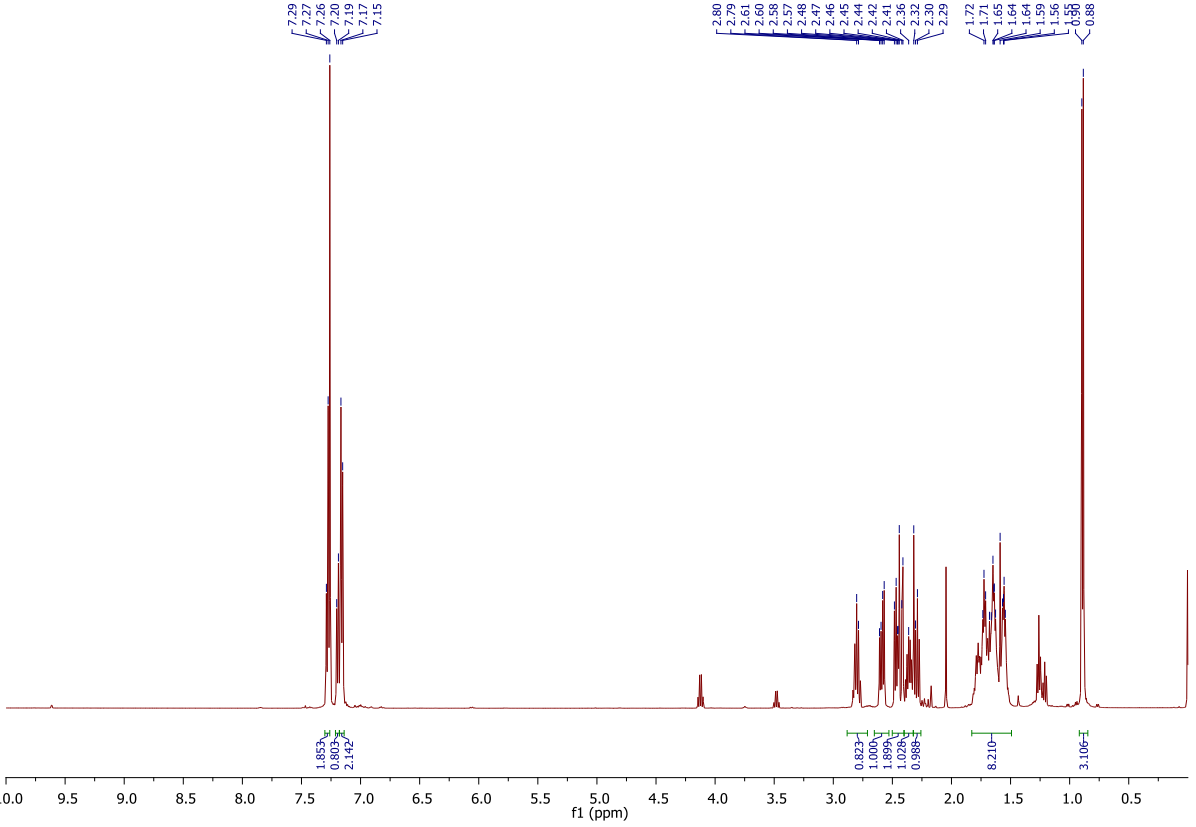
3

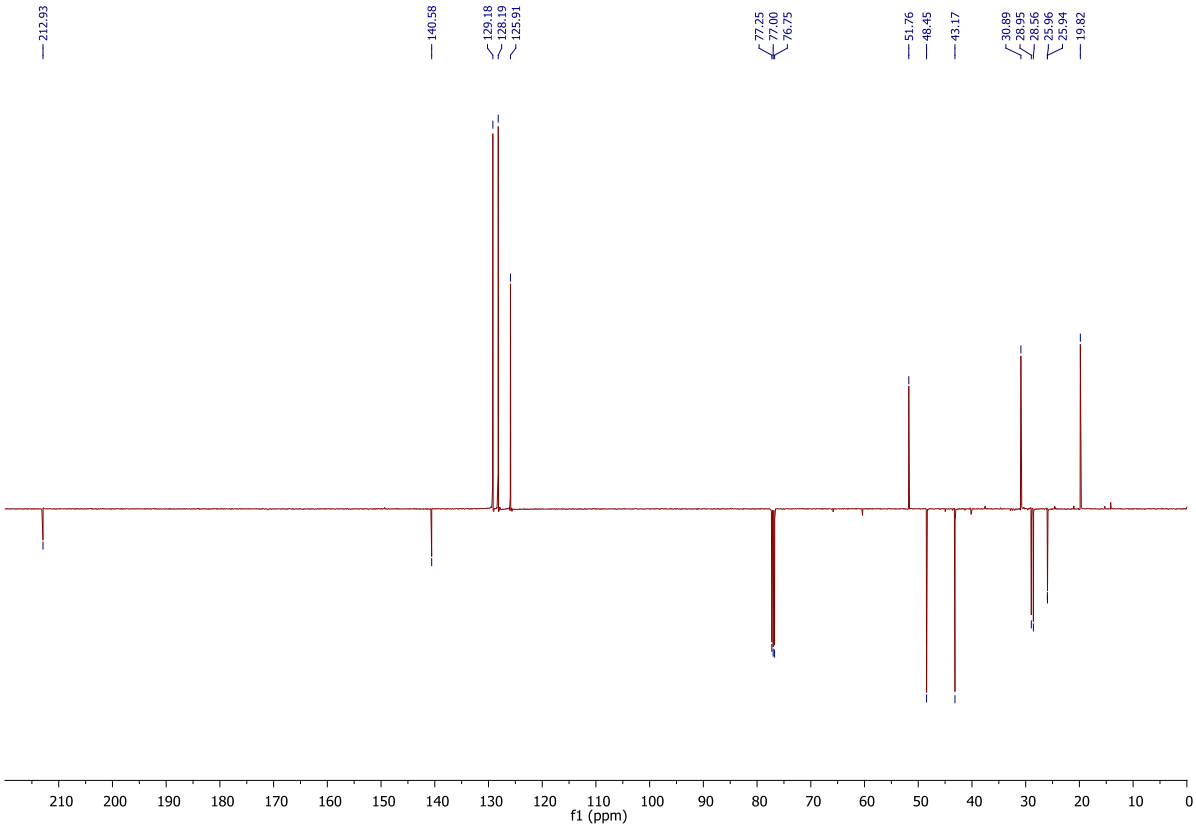

7.21
7.21
7.19
7.18
7.14
7.12
5.87
5.68
5.68
5.68
5.68
2.95
2.94
2.94
2.92
2.92
2.89
2.86
1.81
1.81
1.81
1.80
5.916
1.000
1.011
1.988
2.069
3.042
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


200.95
144.43
141.35
128.45
128.36
126.04
124.57
77.32
77.00
76.68
39.30
30.34
17.61
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

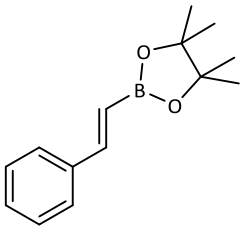

Me
O
Ph

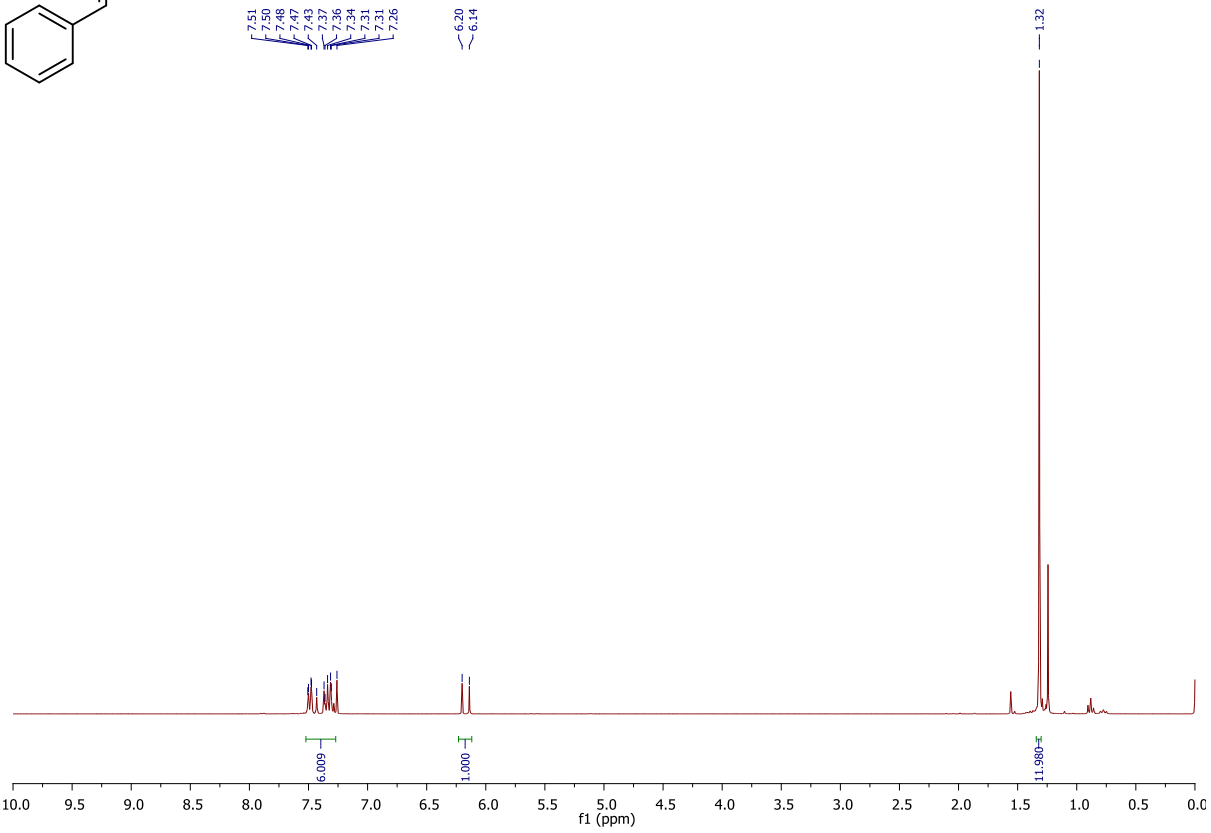
4

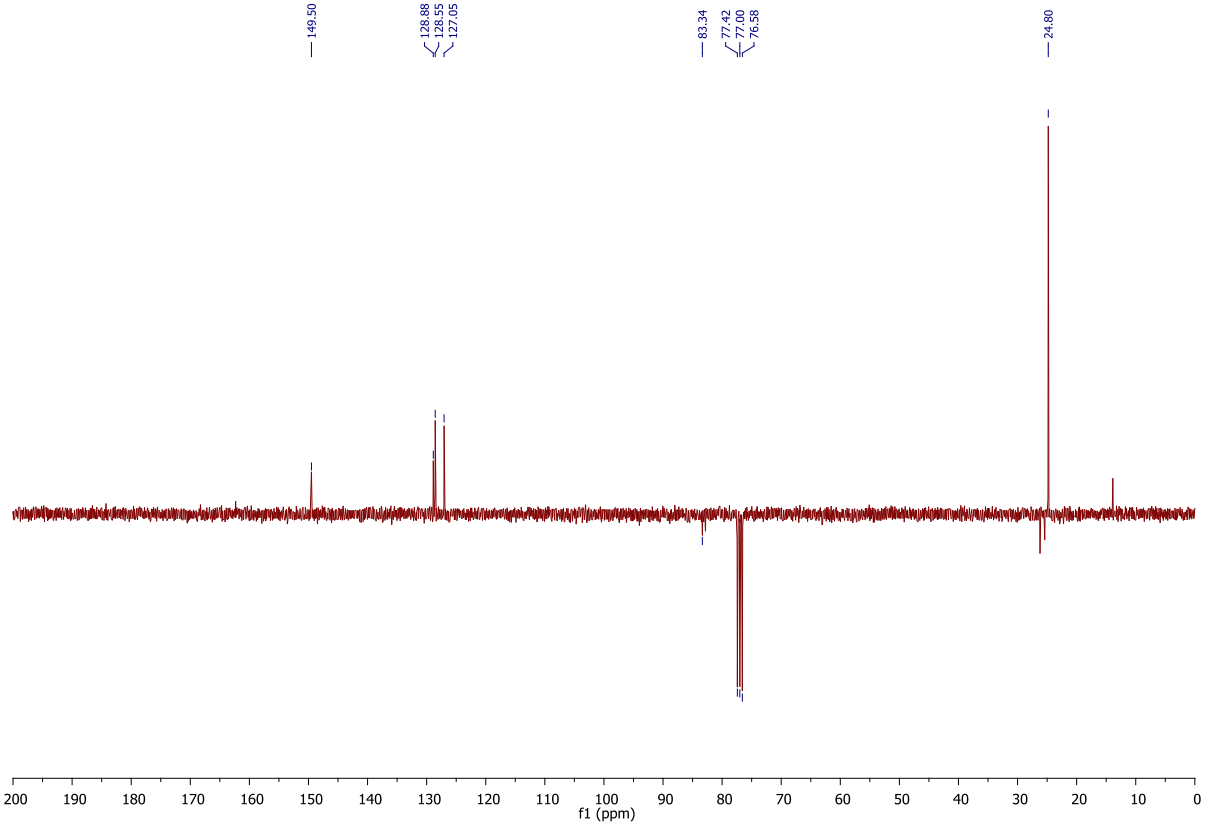

7.29
7.27
7.26
7.20
7.19
7.17
7.15
2.80
2.79
2.61
2.60
2.58
2.57
2.48
2.47
2.46
2.45
2.44
2.42
2.41
2.36
2.32
2.30
2.29
1.72
1.71
1.65
1.64
1.64
1.59
1.56
0.90
0.88
1.853
0.803
2.142
0.823
1.000
1.899
1.028
0.988
8.210
3.106
f1 (ppm)

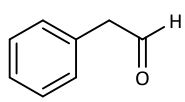

212.93
140.58
129.18
128.19
125.91
77.25
77.00
76.75
51.76
48.45
43.17
30.89
28.95
28.56
25.96
25.94
19.82
f1 (ppm)

5a'

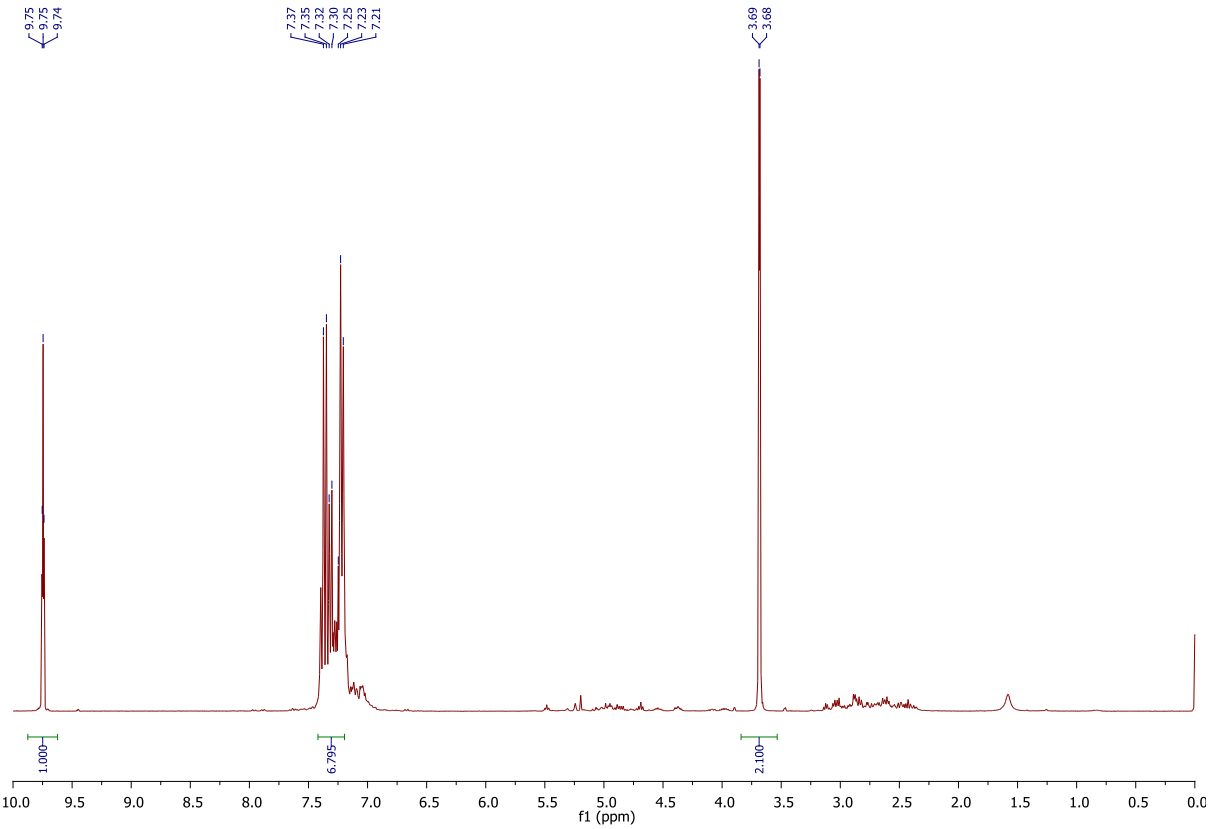

O
B
O

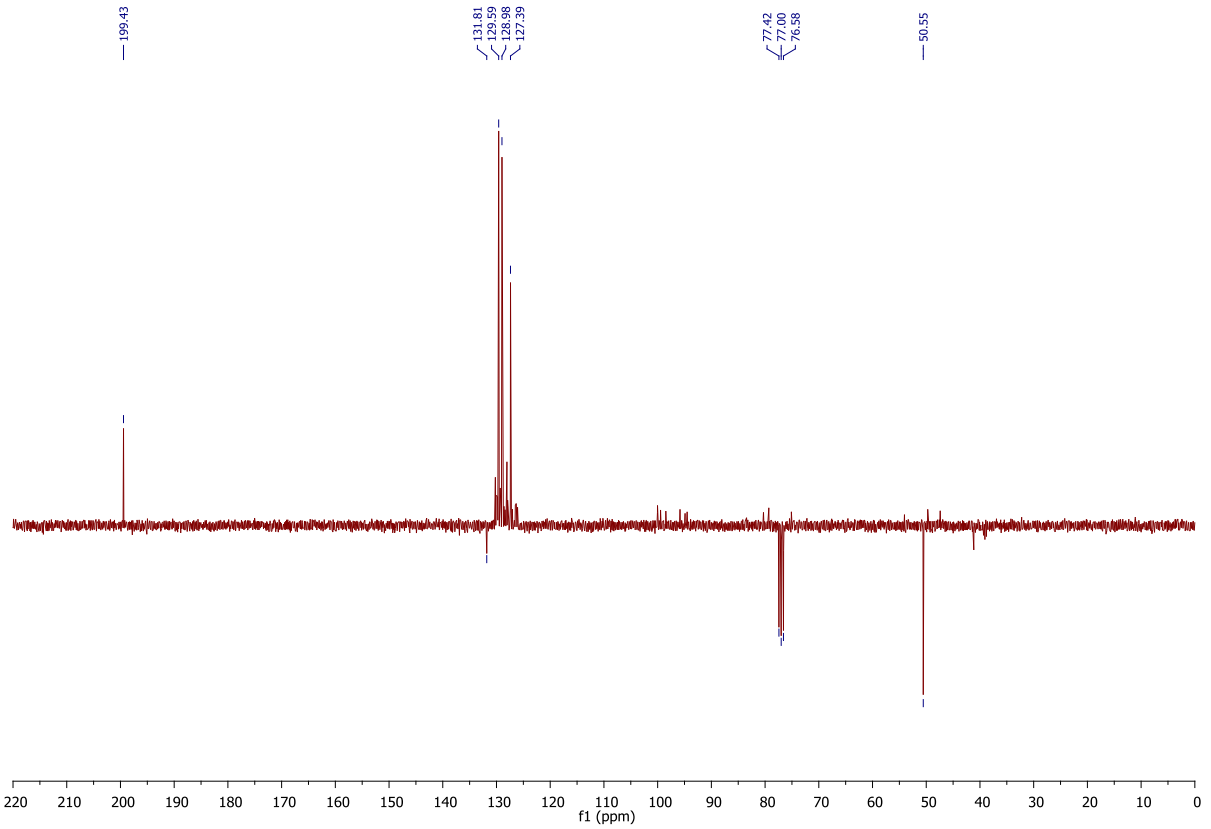

7.51
7.50
7.48
7.47
7.43
7.37
7.36
7.34
7.31
7.31
7.26
6.20
6.14
1.32
6.009
1.000
11.980
f1 (ppm)


149.50
128.88
128.55
127.05
83.34
77.42
77.00
76.58
24.80
f1 (ppm)

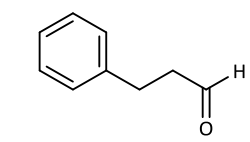

H
O

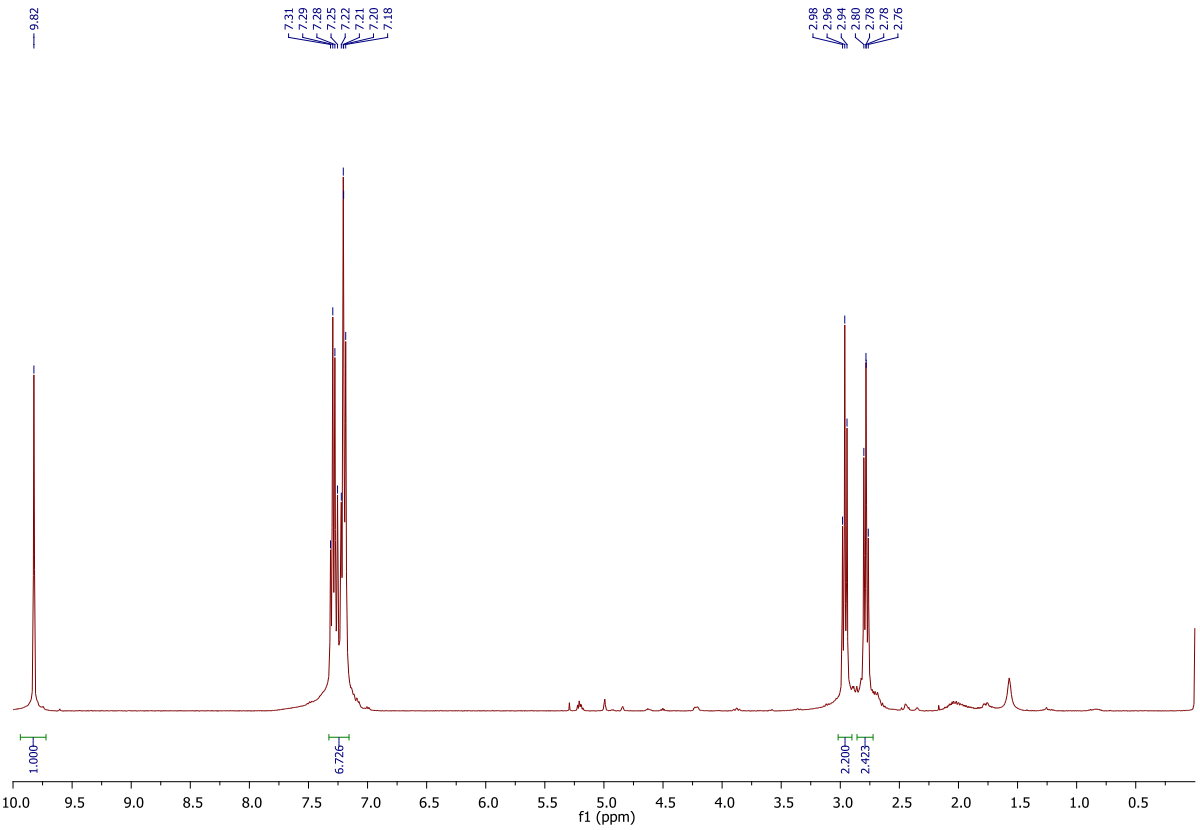
5a


9.75
9.75
9.74
7.37
7.35
7.32
7.30
7.25
7.23
7.21
3.69
3.68
1.000
6.795
2.100
f1 (ppm)


199.43
131.81
129.59
128.98
127.39
77.42
77.00
76.58
50.55
f1 (ppm)

5b


H
O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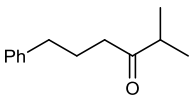
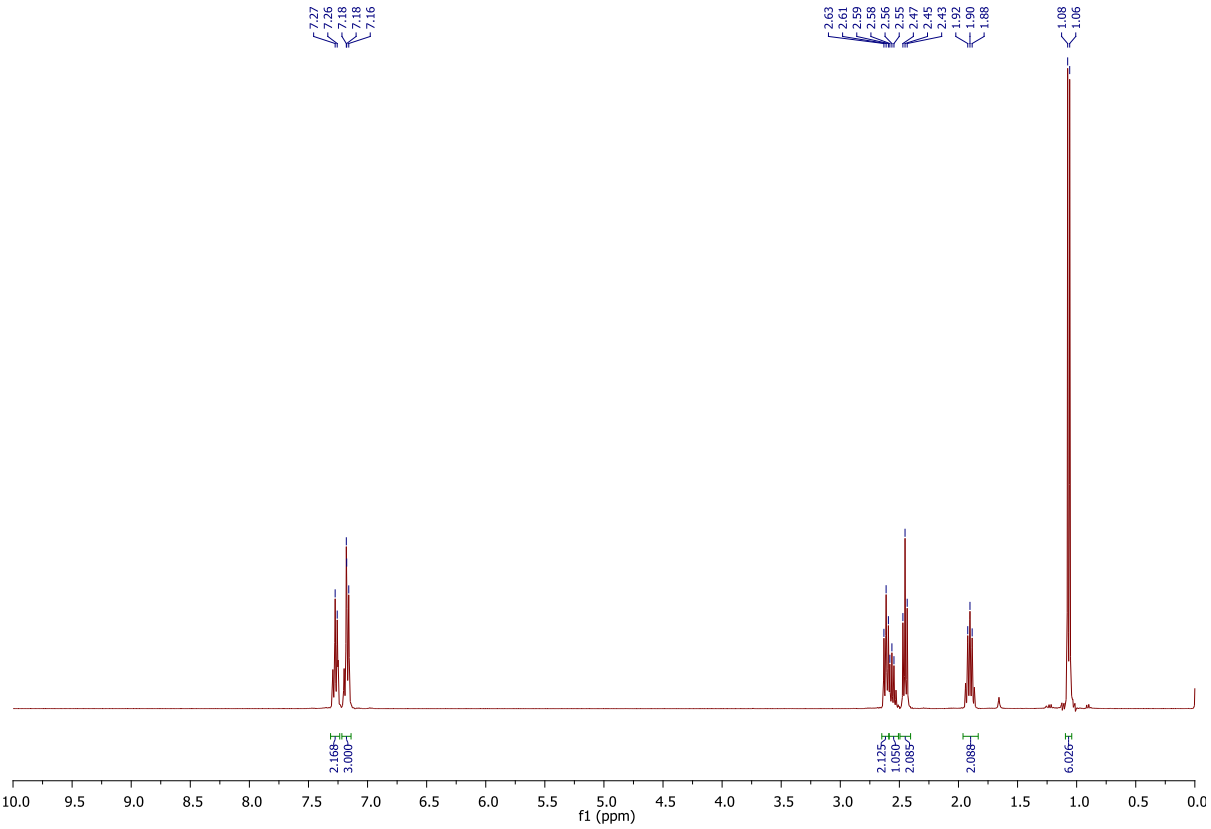
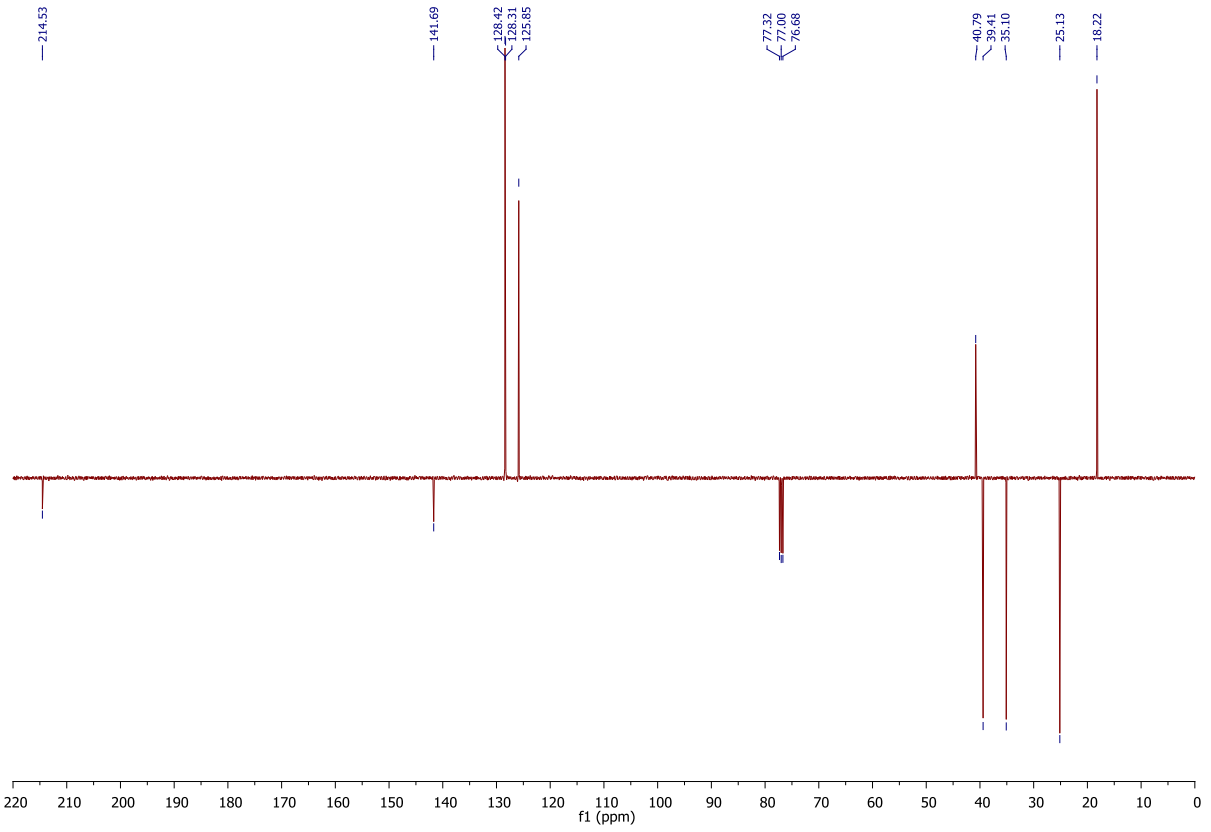
7.28
7.25
7.22
7.21
7.20
7.18
2.98
2.96
2.94
2.80
2.78
2.78
2.76
1.000
6.726
2.200
2.423
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

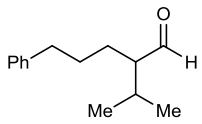

Ph
O

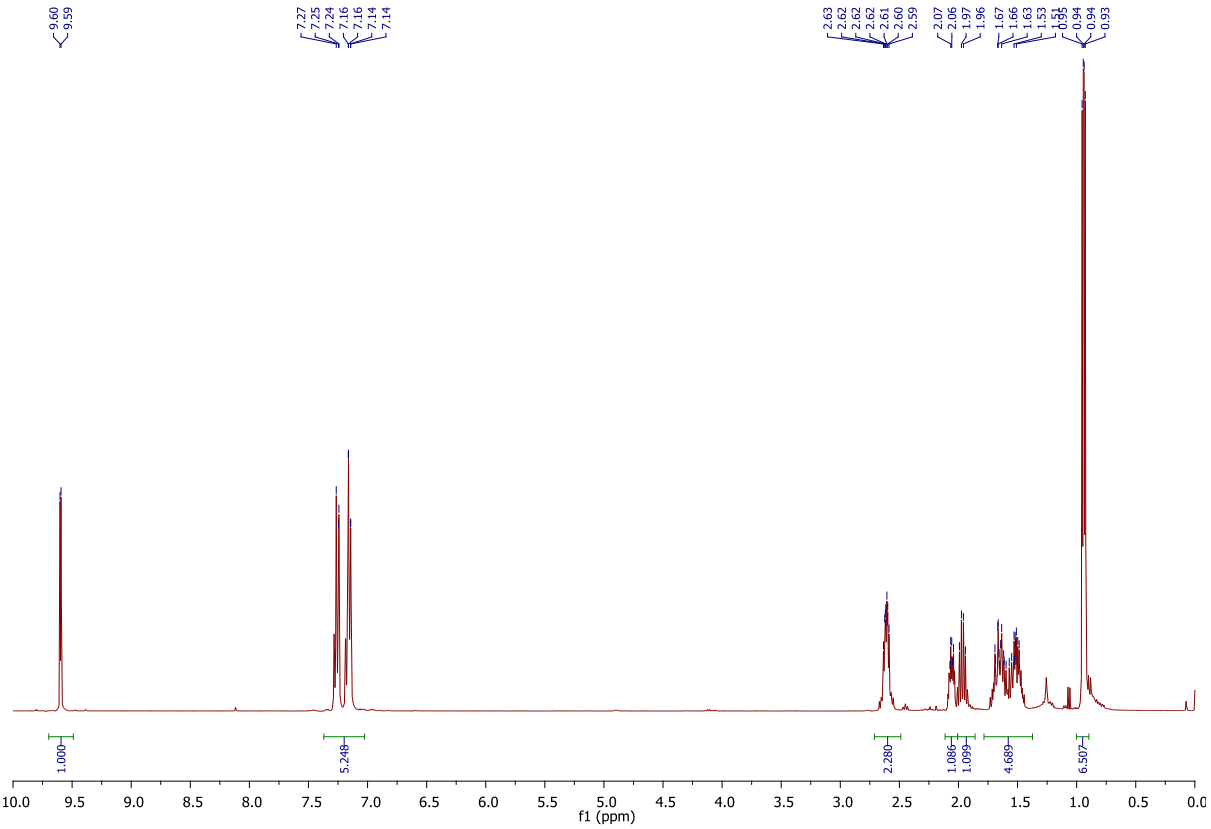
5c

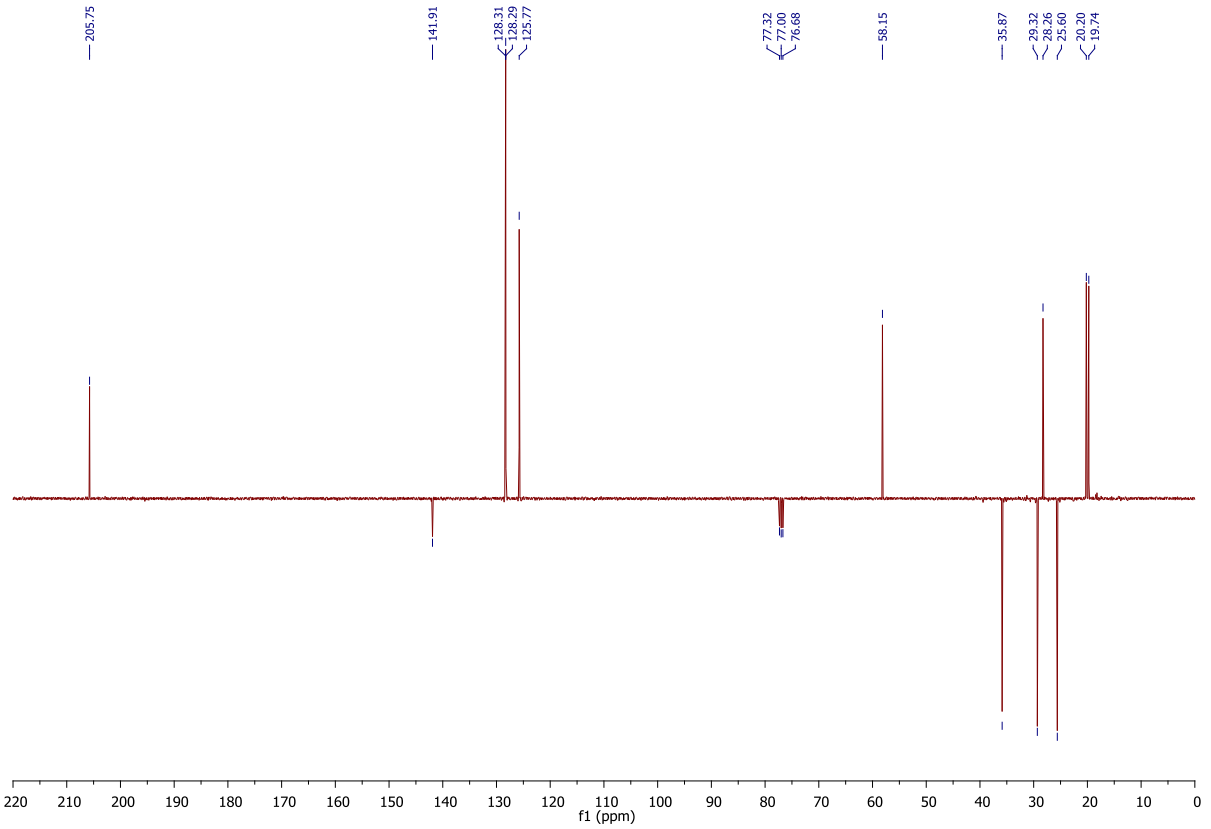

7.27
7.26
7.18
7.18
7.16
2.63
2.61
2.59
2.58
2.56
2.55
2.47
2.45
2.43
1.92
1.90
1.88
1.08
1.06
2.168
3.000
2.125
1.050
2.089
2.088
6.026
f1 (ppm)


214.53
141.69
128.42
128.31
125.85
77.32
77.00
76.68
40.79
39.41
35.10
25.13
18.22
f1 (ppm)

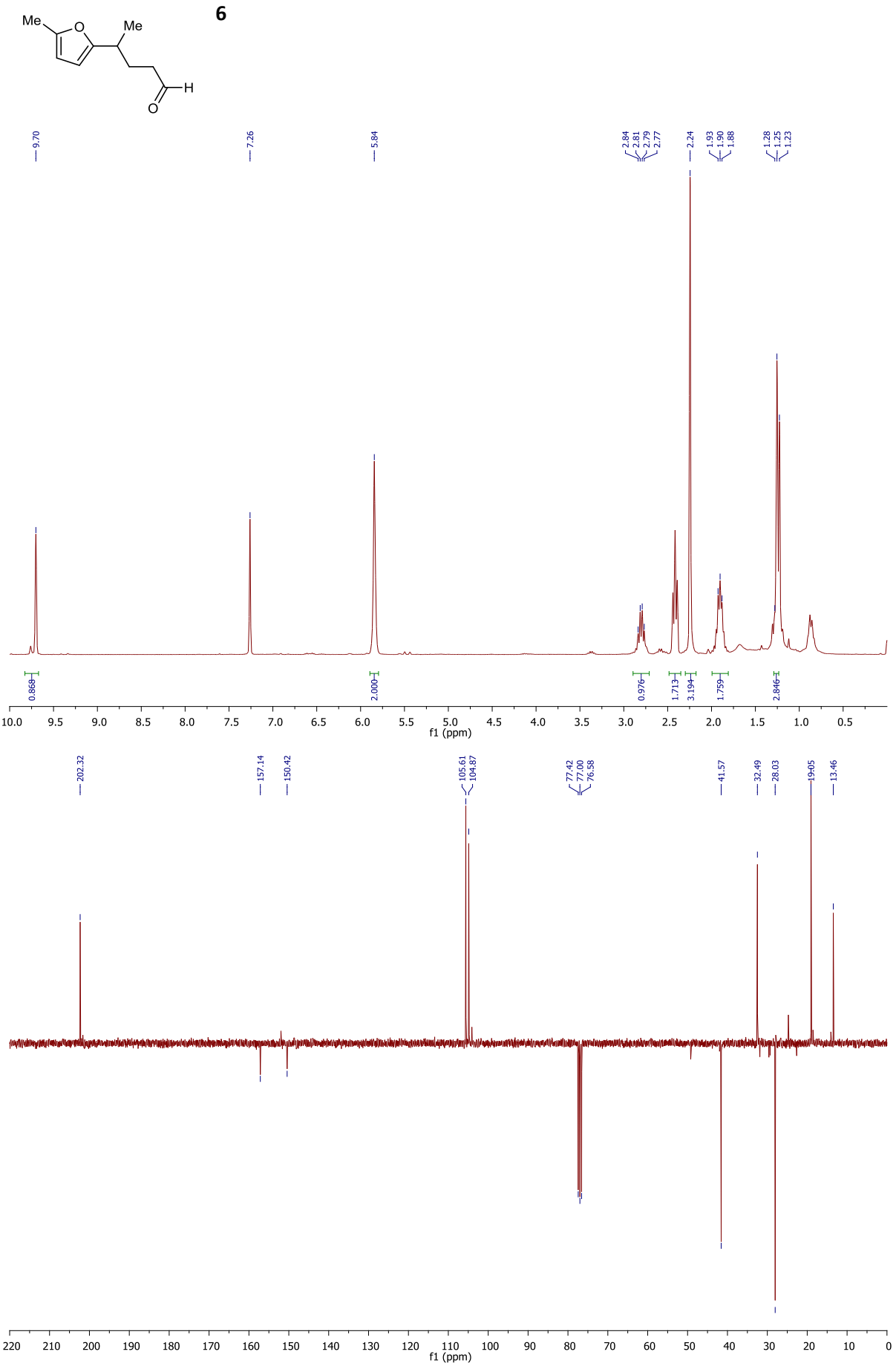
5d

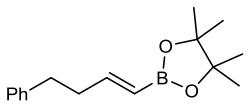

O
H
Ph
Me
Me


9.60
9.59
7.27
7.25
7.24
7.16
7.16
7.14
7.14
2.63
2.62
2.62
2.62
2.61
2.60
2.59
2.07
2.06
1.97
1.96
1.67
1.66
1.63
1.53
0.95
0.94
0.94
0.93
1.000
5.248
2.280
1.086
1.099
4.689
6.507
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

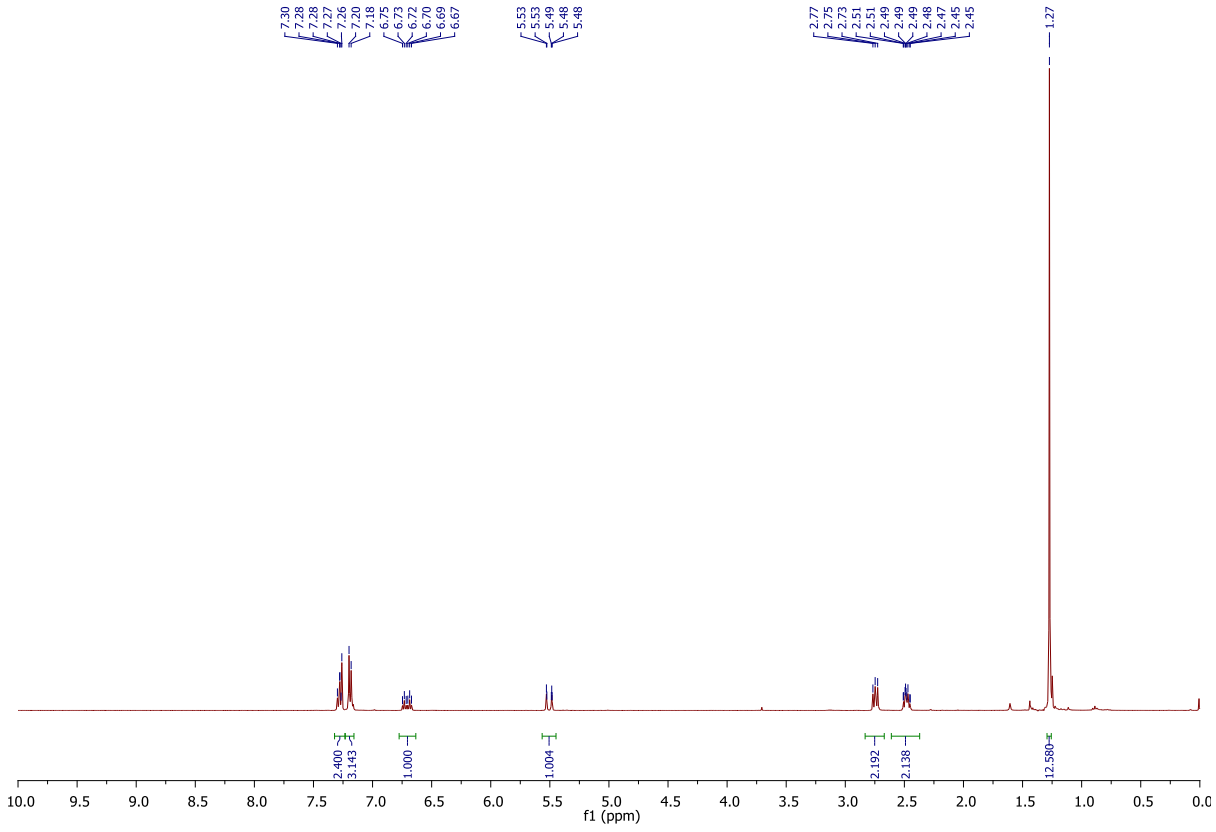

205.75
141.91
128.31
128.29
125.77
77.32
77.00
76.68
58.15
35.87
29.32
28.26
25.60
20.20
19.74
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

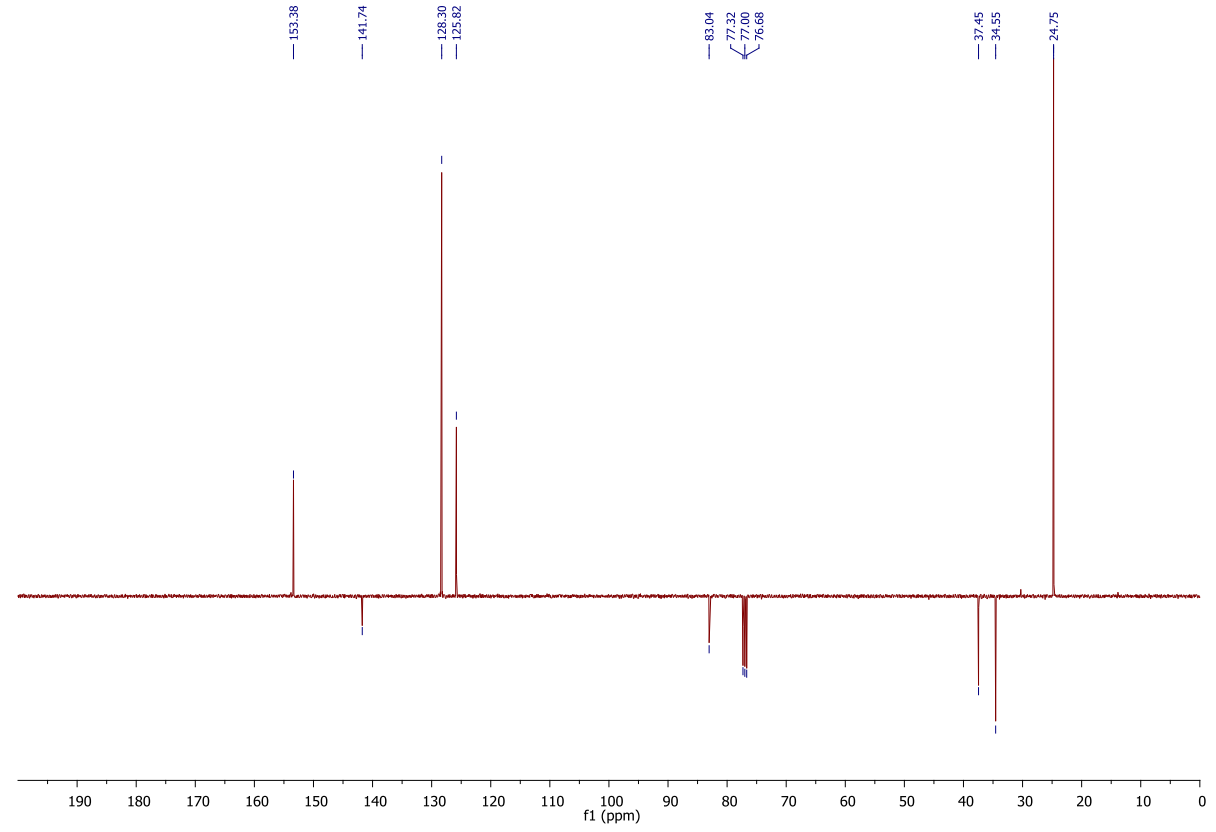
6

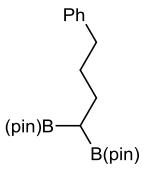

9.70
7.26
5.84
2.84
2.81
2.79
2.77
2.24
1.93
1.90
1.88
1.28
1.25
1.23
0.869
2.000
0.976
1.713
3.194
1.759
2.846
f1 (ppm)
202.32
157.14
150.42
105.61
104.87
77.42
77.00
76.58
41.57
32.49
28.03
19.05
13.46
f1 (ppm)


Ph
O
B
O

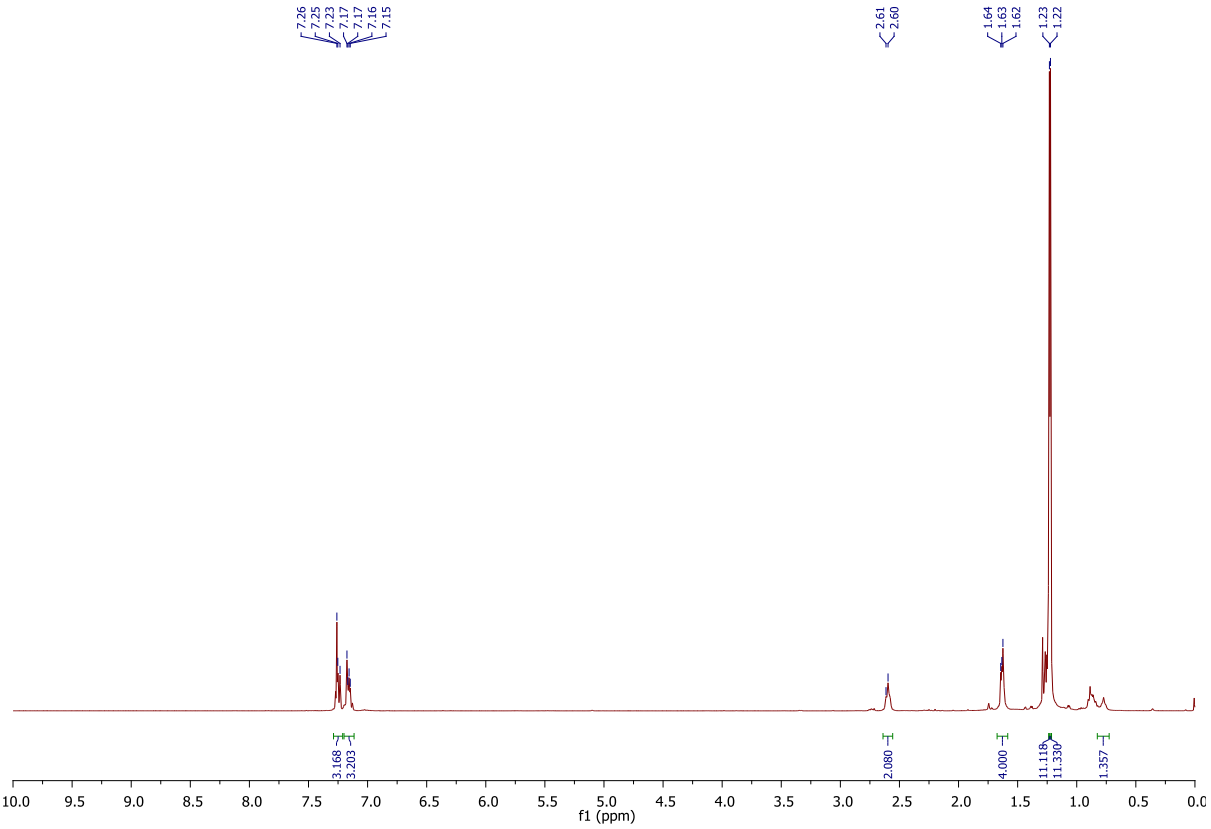
7

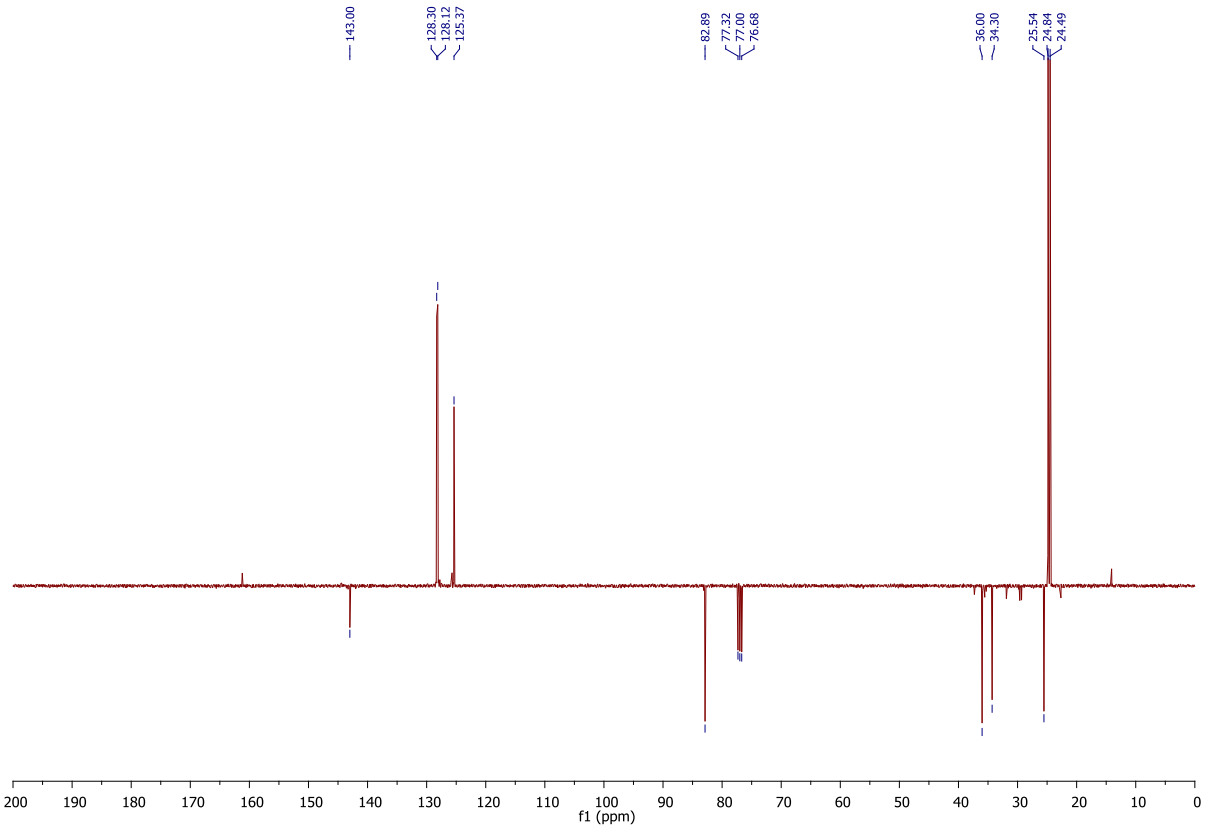

7.30
7.28
7.28
7.28
7.27
7.26
7.20
7.18
6.75
6.73
6.72
6.70
6.69
6.67
5.53
5.53
5.49
5.48
5.48
2.77
2.75
2.73
2.51
2.51
2.49
2.49
2.49
2.48
2.47
2.45
2.45
1.27
2.400
3.143
1.000
1.004
2.192
2.138
12.580
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


153.38
141.74
128.30
125.82
83.04
77.32
77.00
76.68
37.45
34.55
24.75
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

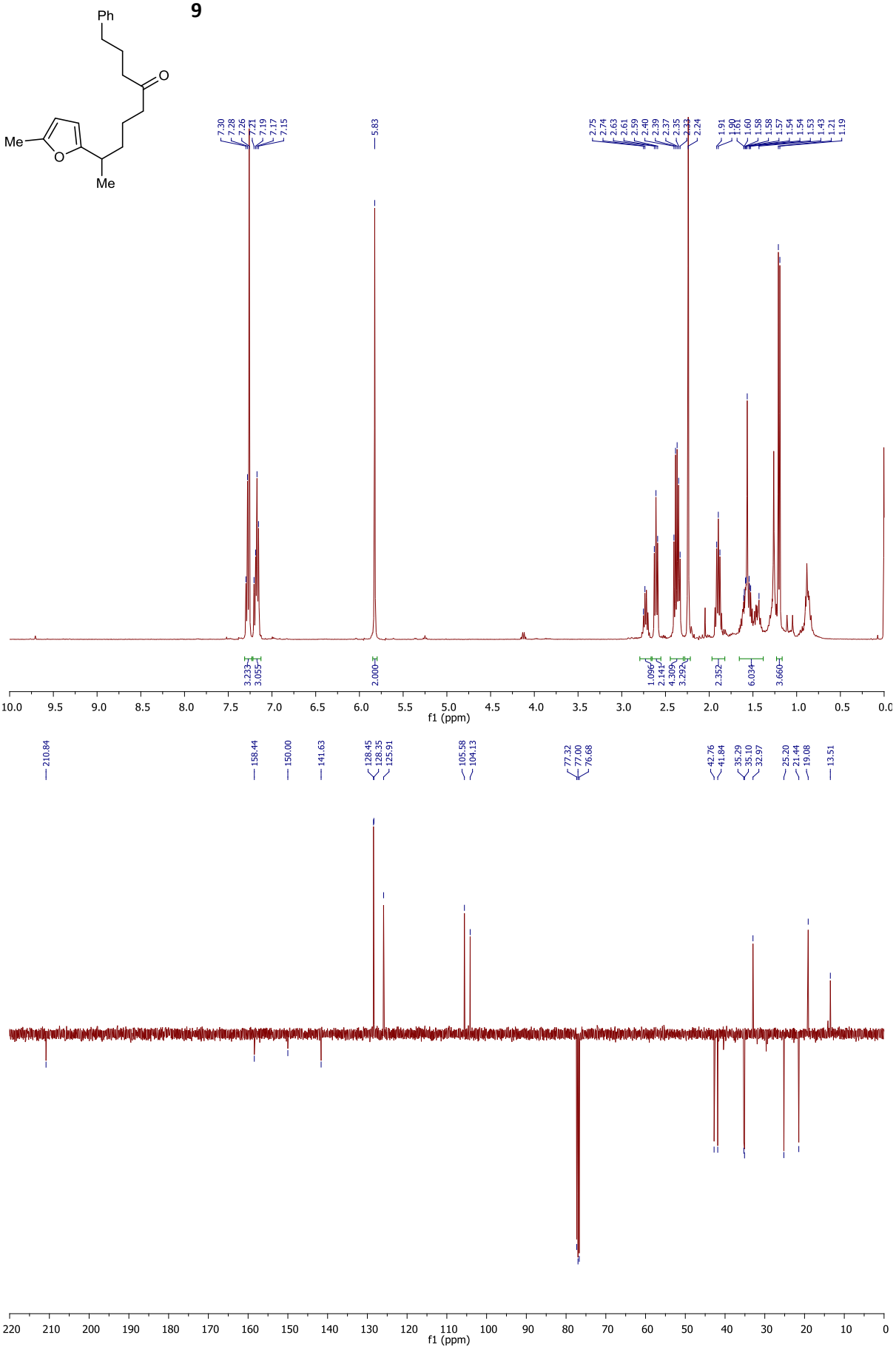

Ph
(pin)B
B(pin)

8

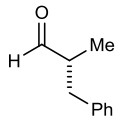

7.26
7.25
7.23
7.17
7.17
7.16
7.15
2.61
2.60
1.64
1.63
1.62
1.23
1.22
3.168
3.203
2.080
4.000
11.118
11.330
1.357
f1 (ppm)

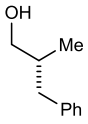

143.00
128.30
128.12
125.37
82.89
77.32
77.00
76.68
36.00
34.30
25.54
24.84
24.49
f1 (ppm)

9


Ph
O
Me
O
Me
7.30
7.28
7.26
7.21
7.19
7.17
7.15
5.83
2.75
2.74
2.63
2.61
2.59
2.40
2.39
2.37
2.35
2.33
2.24
1.91
1.60
1.58
1.58
1.57
1.54
1.54
1.53
1.43
1.21
1.19
3.233
3.055
2.000
1.096
2.142
4.309
3.292
2.352
6.034
3.660
f1 (ppm)
210.84
158.44
150.00
141.63
128.45
128.35
125.91
105.58
104.13
77.32
77.00
76.68
42.76
41.84
35.29
35.10
32.97
25.20
21.44
19.08
13.51
f1 (ppm)

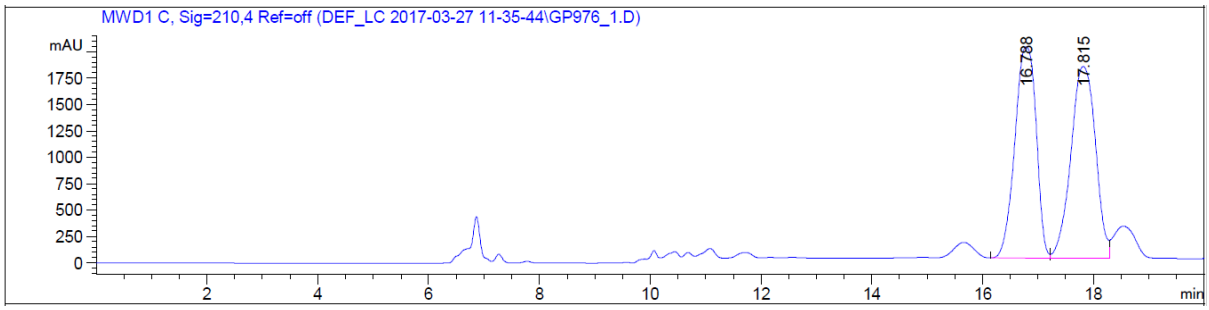
HPLC analysis for enantioenriched homologative cross-coupling (compound 4)



(ee determined via reduction to alcohol


)

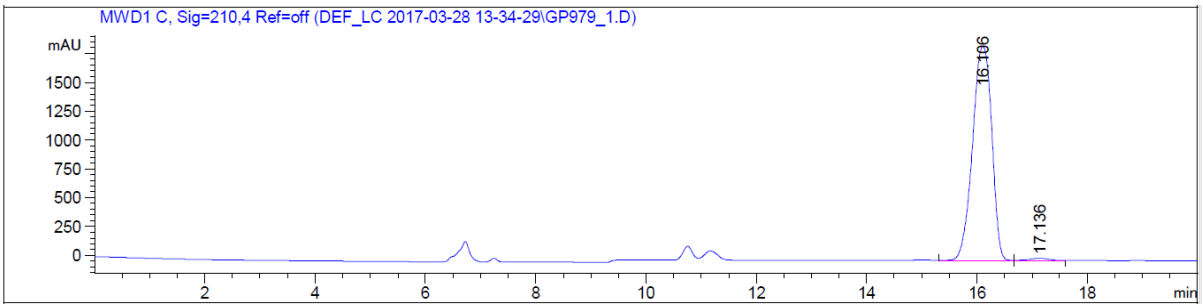
Racemic



Signal 3: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.788	BV	0.4261	5.36029e4	2003.68298	48.8088
2	17.815	VV	0.4906	5.62193e4	1818.95410	51.1912
Totals :				1.09822e5	3822.63708	

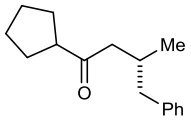
Enantioenriched



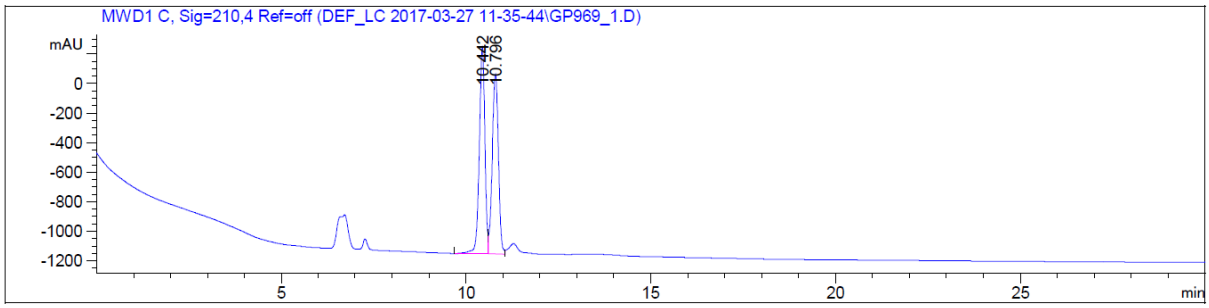
Signal 3: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.106	VV	0.3847	4.49985e4	1857.30615	98.9117
2	17.136	VB	0.4125	495.10760	18.96846	1.0883
Totals :				4.54937e4	1876.27461	

Enantiomeric excess = 98%



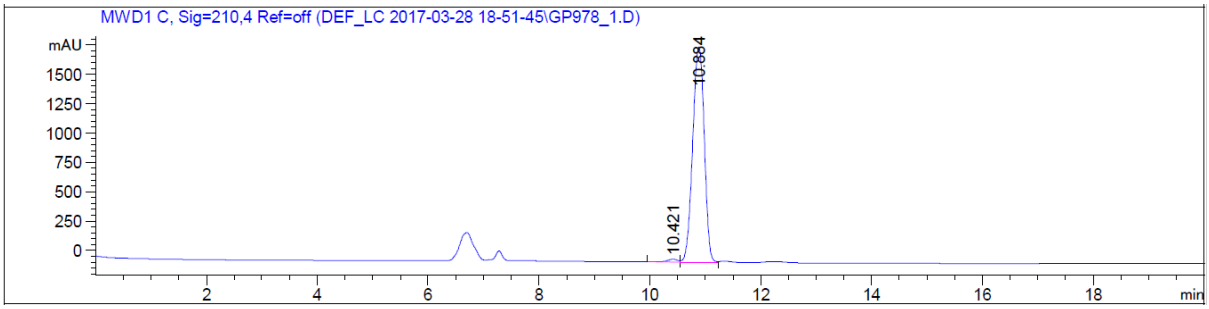
Racemic



Signal 3: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.442	BV	0.1665	1.50503e4	1409.99048	51.6538
2	10.796	VV	0.1809	1.40866e4	1218.03223	48.3462
Totals :				2.91368e4	2628.02271	

Enantioenriched



Signal 3: MWD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.421	BV	0.1945	308.30527	23.90030	1.1479
2	10.884	VV	0.2312	2.65499e4	1830.76086	98.8521
Totals :				2.68582e4	1854.66117	

Enantiomeric excess = 98%