Electronic Supplementary Material (ESI) for ChemComm.

A Phosphine-Free Iron Complex-Catalyzed Synthesis of Cycloalkanes via the Borrowing Hydrogen Strategy

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Supporting Information

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Part 1: General Considerations

All air- and moisture-sensitive manipulations were carried out using standard vacuum line Schlenk tubes techniques. Dry toluene was dried using a solvent purification system from Innovative Technologies, by passage through towers containing activated alumina. Tert-butanol and alcohol substrates were deglazed prior to use by bubbling argon gas directly in the solvent. Other solvents and chemicals were purchased from different suppliers and used as received. Deuterated solvents for NMR spectroscopy were purchased from Sigma Aldrich and used as received. NMR spectra were recorded on a 600 MHz Brücker spectrometer. Proton (^{1}H) NMR information is given in the following format: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant(s) (*J*) in Hertz (Hz), number of protons, type. The prefix *app* is occasionally applied when the true signal multiplicity was unresolved and *br* indicates the signal in question broadened. Carbon (^{13}C) NMR spectra are reported in ppm (δ) relative to $CDCl_3$ unless noted otherwise. Infrared spectra were recorded over a PerkinElmer Spectrum 100 FT-IR Spectrometer using neat conditions. HRMS analyses were performed by Laboratoire de Chimie Moléculaire et Thioorganique analytical Facilities.

Part 2: General Procedures for the synthesis of starting materials

General Procedure A: Reduction of Diacids Compounds

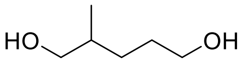
Under argon, in a 250 mL round bottomed flask equipped with a stirring bar, $LiAlH_4$ (40 mmol, 1.513 g) was added in dry THF (75 mL). Then the mixture was cooled down to 0 °C and a solution of the desired carboxylic diacid (10 mmol) in dry THF (25 mL) was dropwise added. After addition, the reaction was stirred and heated to reflux for 16 h. After cooling down to room temperature, the reaction was quenched with saturated Na_2SO_4 solution and filtered over celite. The filtrate was then washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Depending on the crude mixture, the desired product was purified by flash chromatography on silica gel using pentane-ethyl acetate or used without further purification.

General Procedure B: Synthesis of Diesters Compounds

According to a literature procedure, a mixture of the desired benzaldehyde (20 mmol), ethyl acetoacetate (40 mmol), and piperidine (2.8 mmol) was stirred at room temperature for 3 days. During this time, the mixture turned solid and it was filtered off, washed with Et_2O (4 x 10 mL) and dried in vacuo. The solid was dissolved in EtOH (40 mL) and a solution of NaOH (40 g) in water (40 mL) and refluxed for 1 h. Then the organic solvent was evaporated under reduce pressure, and the aqueous phase was acidified to pH 1 with an HCl 37 % solution. The aqueous phase was extracted with AcOEt (3 x 40 mL). The organic phases were combined and dried over $MgSO_4$, then the solvent was evaporated under reduce pressure. The resulting diacid compound was dissolved in EtOH (40 mL) and 10 drops of concentrated H_2SO_4 aqueous solution was added. The solution was refluxed for 3 h. Then, EtOH was evaporated under reduced pressure and the crude product was dissolved in water, extracted with AcOEt (3 x 20 mL). The organic phases were combined and dried over $MgSO_4$, then the solvent was evaporated under reduce pressure. The crude diester was used without further purification.

General Procedure C: Reduction of Diesters Compounds

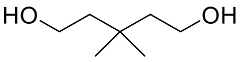
Under argon, in a 250 mL round bottomed flask equipped with a stirring bar, $LiAlH_4$ (40 mmol, 1.513 g) was added in dry Et_2O (75 mL). Then the mixture was cooled down to 0 °C and a solution of the desired diester (10 mmol) in dry Et_2O (25 mL) was dropwise added. After addition, the reaction was stirred at room temperature for 16 h. The reaction was quenched with saturated Na_2SO_4 solution and filtered over celite. The filtrate was then washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Depending on the crude mixture, the desired product was purified by flash chromatography on silica gel using pentane-ethyl acetate or used without further purification.



Chemical Formula: $C_6H_{14}O_2$

- **2-methylpentane-1,5-diol[1] (1a)**

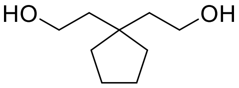
According to general procedure A, reduction of 2-methylpentanedioic acid (10 mmol, 1.461 g) afforded the pure product **1a** as a colorless oil (1.102g, 93 %) without further purification. **^{1}H-NMR (CDCl$_3$, 600 MHz)**: δ 3.63 (t, *J* = 5.8 Hz, 2H), 3.46 (d, *J* = 5.8 Hz, 2H), 2.25-2.18 (m, 2H), 1.65-1.61 (m, 2H), 1.56-1.50 (m, 2H), 1.23-1.17 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 3H) ppm. **^{13}C-NMR (CDCl$_3$, 150 MHz)**: δ 67.9, 62.9, 35.3, 29.8, 29.0, 16.6 ppm.



Chemical Formula: $C_7H_{16}O_2$

- **3,3-dimethylpentane-1,5-diol[1] (1b)**

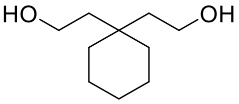
According to general procedure A, reduction of 3,3-dimethylpentanedioic acid (10 mmol, 1.600 g) afforded the pure product **1b** as a colorless oil (1.149 g, 87 %) without further purification. **^{1}H-NMR (CDCl$_3$, 600 MHz)**: δ 3.65 (t, *J* = 7.2 Hz, 4H), 3.53 (br. s, 2H), 1.52 (t, *J* = 7.2 Hz, 4H), 0.90 (s, 6H) ppm. **^{13}C-NMR (CDCl$_3$, 150 MHz)**: δ 59.1, 43.8, 31.5, 28.1 ppm.



Chemical Formula: $C_9H_{18}O_2$

- **2,2'-(cyclopentane-1,1-diyl)bis(ethan-1-ol)[1] (1c)**

According to general procedure A, reduction of 2,2'-(cyclopentane-1,1-diyl)diacetic acid (10 mmol, 1.861 g) afforded the pure product **1c** as a colorless oil (1.233 g, 78 %) without further purification. **^{1}H-NMR (CDCl$_3$, 600 MHz)**: δ 3.72 (t, *J* = 6.9 Hz, 4H), 2.07 (br. s, 2H), 1.63 (t, *J* = 6.9 Hz, 4H), 1.62-1.59 (m, 4H), 1.44-1.41 (m, 4H) ppm. **^{13}C-NMR (CDCl$_3$, 150 MHz)**: δ 59.9, 43.3, 40.8, 38.4, 24.2 ppm.



Chemical Formula: $C_{10}H_{20}O_2$

- **2,2'-(cyclohexane-1,1-diyl)bis(ethan-1-ol)[1] (1d)**

According to general procedure A, reduction of 2,2'-(cyclohexane-1,1-diyl)diacetic acid (10 mmol, 2.001 g) afforded the pure product **1d** as a colorless oil (1.187 g, 69 %) without further purification. **^{1}H-NMR (CDCl$_3$, 600 MHz)**: δ 3.74-3.69 (m, 4H), 2.10 (br. s, 2H), 1.44-1.39 (m, 6H), 1.32-1.31 (m, 4H) ppm. **^{13}C-NMR (CDCl$_3$, 150 MHz)**: δ 58.9, 39.8, 36.5, 34.0, 26.3, 21.5 ppm.

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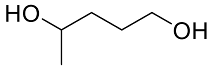
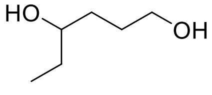
[1] R. J. Armstrong, W. M. Akhtar, J. R. Frost, K. E. Christensen, N. G. Stevenson and T. J. Donohoe, *Tetrahedron*, 2019, **75**, 130680.



Chemical Formula: $C_5H_{12}O_2$

- **pentane-1,4-diol[1] (1e)**

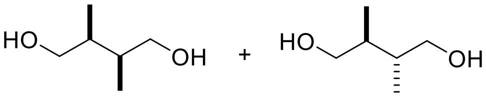
According to a modified general procedure C (2 equiv. of $LiAlH_4$), reduction of 5-methyldihydrofuran-2(3H)-one (10 mmol, 1.000 g) afforded the pure product **1e** as a colorless oil (0.980 g, 94 %) without further purification. **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 3.87-3.83 (m, 1H), 3.72-3.66 (m, 2H), 2.41 (br. s, 2H), 1.71-1.58 (m, 3H), 1.53-1.48 (m, 1H), 1.20 (d, *J* = 6.2 Hz, 3H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 68.0, 63.0, 36.2, 29.2, 23.6 ppm.



Chemical Formula: $C_6H_{14}O_2$

- **hexane-1,4-diol[2] (1f)**

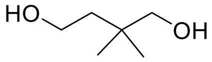
According to a modified general procedure C (2 equiv. of $LiAlH_4$), reduction of 5-ethyldihydrofuran-2(3H)-one (10 mmol, 1.141 g) afforded the pure product **1f** as a colorless oil (1.087 g, 92 %) without further purification. **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 3.72-3.63 (m, 2H), 3.59-3.54 (m, 2H), 2.36 (br. s, 2H), 1.72-1.62 (m, 2H), 1.54-1.43 (m, 3H), 0.93 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 73.2, 63.0, 33.9, 30.3, 29.1, 10.0 ppm.



Chemical Formula: $C_6H_{14}O_2$

- ***rac*-(2S,3S)-2,3-dimethylbutane-1,4-diol[3] and (2R,3S)-2,3-dimethylbutane-1,4-diol[4] (1g)**

According to general procedure A, reduction of 2,3-dimethylsuccinic acid (5 mmol, 0.730 g) afforded the pure product **1g** as a colorless oil (0.520 g, 88 %) without further purification. Product was obtained as a mixture of racemic and *meso* compounds (60:40 d.r.). **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 3.61 (dd, J = 3.9; 10.9 Hz, 2H-rac), 3.55 (dd, J = 6.9; 10.9 Hz, 2H-meso), 3.52-3.48 (m, 4H-rac+meso), 3.00 (br. s, 2H), 1.83-1.80 (m, 2H-meso), 1.71-1.69 (m, 2H-rac), 0.90-0.89 (m, 6H-rac+meso) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 68.0, 65.9, 65.6, 60.4, 38.7, 37.9, 30.3, 26.0, 21.1, 14.2, 14.0, 13.4 ppm.



Chemical Formula: $C_6H_{14}O_2$

- **2,2-dimethylbutane-1,4-diol[5] (1h)**

According to general procedure A, reduction of 2,2-dimethylsuccinic acid (5 mmol, 0.730 g) afforded the pure product **1h** as a colorless oil (0.496 g, 84 %) without further purification. **^{1}H-NMR ($CDCl_3$, 600 MHz)**: 3.71 (app t, *J* = 5.7 Hz, 2H), 3.35 (s, 2H), 2.82 (br. s, 2H), 1.55 (app

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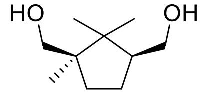
[2] H. Tan, X. Chen, H. Chen, H. Liu and S. Q. *Eur. J. Org. Chem*. 2015, 4976-4963.

[3] M. J. Pelc and A. Zakarian. *Org. Lett*. 2005, **7**, 1629-1631.

[4] A. A. Vasil'ev, L. Engman and E. P. Serebryakov. *J. Chem. Soc.; Perkin Trans 1*. 2000, 2211-2216.

[5] A. Jana, K. Das, A. Kundu, P. Ramdas Thorve, D. Adhikari and B. Maji. *ACS Catal*. 2020, **10**, 2615-2626.

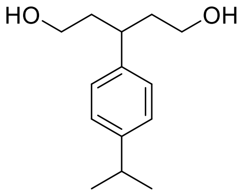
t, *J* = 5.7 Hz, 2H), 0.91 (s, 6H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 71.5, 59.1, 42.7, 34.9, 24.9 ppm.



Chemical Formula: $C_{10}H_{20}O_2$

▪ ((1R,3S)-1,2,2-trimethylcyclopentane-1,3-diyl)dimethanol[1] (1i)

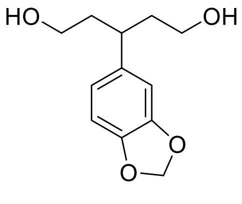
According to general procedure A, reduction of (1R,3S)-1,2,2-trimethylcyclopentane-1,3-dicarboxylic acid (10 mmol, 2.001 g) afforded the pure product **1i** as a white solid (1.515 g, 88 %) without further purification. **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 3.72 (dd, *J* = 5.3, 10.3 Hz, 1H), 3.58 (d, *J* = 10.7 Hz, 1H), 3.51 (dd, *J* = 8.4, 10.3 Hz, 1H), 3.46 (d, *J* = 10.8 Hz, 1H), 2.11-2.04 (m, 1H), 1.98-1.92 (m, 1H), 1.62-1.57 (m, 1H), 1.42-1.33 (m, 4H), 1.02 (s, 3H), 1.01 (s, 3H), 0.78 (s, 3H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 69.2, 65.0, 50.5, 48.8, 44.0, 33.7, 25.5, 24.2, 20.4, 18.5 ppm.



Chemical Formula: $C_{14}H_{22}O_2$

▪ 3-(4-isopropylphenyl)pentane-1,5-diol (1j)

A mixture of 4-isopropylbenzaldehyde (20 mmol, 3.03 mL), ethyl acetoacetate (40 mmol, 5.10 mL), and piperidine (2.8 mmol, 0.277 mL) were subjected to general procedure B to afford crude diethyl 3-(4-isopropylphenyl)pentanedioate (3.639 g, 59 %) which was used without further purification. According to general procedure C, reduction of 3-(4-isopropylphenyl)pentanedioate (3.639, 11.88 mmol) afforded the pure product **1j** as a light brown solid (1.662 g, 63 %) by silica flash column chromatography (ethyl acetate). **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 7.15 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 3.58-3.54 (m, 2H), 3.50-3.46 (m, 2H), 2.90-2.85 (m, 2H), 1.96-1.89 (m, 4H), 1.86-1.80 (m, 2H), 1.23 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 147.0, 141.6, 127.5, 126.7, 61.0, 39.4, 38.4, 33.7, 24.0 ppm. **IR (neat)**: ν 3328, 2958, 2871, 1510, 1382, 1039, 828, 581 cm $^{-1}$. **HRMS (ESI-TOF) m/z [M + Na]$^{+}$**: Calcd for $C_{14}H_{22}O_2Na$ 245.1517; Found 245.1519.

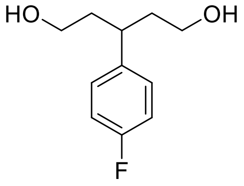


Chemical Formula: $C_{12}H_{16}O_4$

▪ 3-(benzo[d][1,3]dioxol-5-yl)pentane-1,5-diol (1k)

A mixture of benzo[d][1,3]dioxole-5-carbaldehyde (20 mmol, 3.00 g), ethyl acetoacetate (40 mmol, 5.10 mL), and piperidine (2.8 mmol, 0.277 mL) were subjected to general procedure B to afford crude diethyl 3-(benzo[d][1,3]dioxol-5-yl)pentanedioate (3.266 g, 53 %) which was used without further purification. According to general procedure C, reduction of diethyl 3-(benzo[d][1,3]dioxol-5-yl)pentanedioate (3.266, 10.59 mmol) afforded the pure product **1k** as a light yellow solid (1.448 g, 61 %) by silica flash column chromatography (ethyl acetate). **^{1}H-**

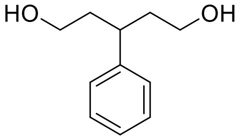
NMR ($CDCl_3$, 600 MHz): δ 6.72 (d, J = 7.8 Hz, 1H), 6.68 (s, 1H), 6.63 (dd, J = 1.1, 7.8 Hz, 1H), 5.93 (s, 2H), 3.58-3.54 (m, 2H), 3.48-3.44 (m, 2H), 2.88-2.84 (m, 1H), 1.96-1.86 (m, 4H), 1.78-1.73 (m, 2H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 147.8, 145.9, 138.2, 120.7, 108.2, 107.5, 100.8, 60.7, 39.4, 38.3 ppm. **IR (neat)**: ν 3271, 2923, 2878, 1609, 1487, 1441, 1242, 1033, 917, 810, 641, 464 cm^{-1}. **HRMS (ESI-TOF) m/z [M + H]$^+$**: Calcd for $C_{12}H_{17}O_4$ 225.1119; Found 225.1127.



Chemical Formula: $C_{11}H_{15}FO_2$

▪ 3-(4-fluorophenyl)pentane-1,5-diol[1] (1l)

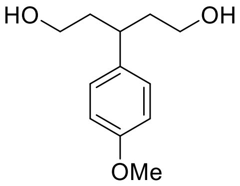
A mixture of 4-fluorobenzaldehyde (20 mmol, 2.44 mL), ethyl acetoacetate (40 mmol, 5.10 mL), and piperidine (2.8 mmol, 0.277 mL) were subjected to general procedure B to afford crude diethyl 3-(4-fluorophenyl)pentanedioate (2.595 g, 46 %) which was used without further purification. According to general procedure C, reduction of 3-(4-fluorophenyl)pentanedioate (2.595 g, 9.20 mmol) afforded the pure product **1l** as a white solid (1.492 g, 82 %) by silica flash column chromatography (ethyl acetate). **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 7.15-7.13 (m, 2H), 6.99-6.96 (m, 2H), 3.57-3.53 (m, 2H), 3.45-3.41 (m, 2H), 2.97-2.92 (m, 1H), 2.19 (br. s, 2H), 1.94-1.89 (m, 2H), 1.80-1.74 (m, 2H) ppm. **^{19}F-NMR ($CDCl_3$, 600 MHz)**: δ -116.8 ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 160.5 (d, J = 243 Hz), 140.0 (d, J = 3.2 Hz), 128.9 (d, J = 7.7 Hz), 128.9 (d, J = 20.9 Hz), 60.4, 39.2, 37.5 ppm.



Chemical Formula: $C_{11}H_{16}O_2$

▪ 3-phenylpentane-1,5-diol[1] (1m)

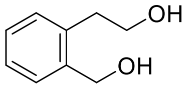
A mixture of 4-fluorobenzaldehyde (20 mmol, 2.44 mL), ethyl acetoacetate (40 mmol, 5.10 mL), and piperidine (2.8 mmol, 0.277 mL) were subjected to general procedure B to afford crude diethyl 3-phenylpentanedioate (2.589 g, 49 %) which was used without further purification. According to general procedure C, reduction of diethyl 3-phenylpentanedioate (2.589 g, 9.80 mmol) afforded the pure product **1m** as a white solid (1.430 g, 81 %) by silica flash column chromatography (ethyl acetate). **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 7.32-7.28 (m, 2H), 7.24-7.18 (m, 3H), 3.58-3.53 (m, 2H), 3.48-3.43 (m, 2H), 2.95-2.89 (m, 1H), 1.99-1.90 (m, 4H), 1.86-1.79 (m, 2H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 144.4, 128.6, 127.6, 126.4, 60.7, 39.2, 38.5 ppm.



Chemical Formula: $C_{12}H_{18}O_3$

- **3-(4-methoxyphenyl)pentane-1,5-diol[1] (1n)**

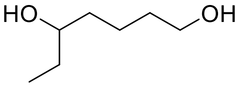
A mixture of 4-fluorobenzaldehyde (20 mmol, 2.44 mL), ethyl acetoacetate (40 mmol, 5.10 mL), and piperidine (2.8 mmol, 0.277 mL) were subjected to general procedure B to afford crude diethyl 3-(4-methoxyphenyl)pentanedioate (2.471 g, 42 %) which was used without further purification. According to general procedure C, reduction of diethyl 3-phenylpentanedioate (2.471 g, 8.40 mmol) afforded the pure product **1n** as a white solid (1.306 g, 74 %) by silica flash column chromatography (ethyl acetate). **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 7.10 (app d, *J* = 8.5 Hz, 2H), 6.84 (app d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 3.58-3.53 (m, 2H), 3.50-3.45 (m, 2H), 2.89-2.83 (m, 1H), 1.96-1.89 (m, 2H), 1.84-1.77 (m, 2H), 1.38 (br. s, 2H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 158.1, 136.2, 128.4, 114.0, 61.0, 55.2, 39.6, 38.1 ppm.



Chemical Formula: $C_9H_{12}O_2$

- **2-(2-(hydroxymethyl)phenyl)ethan-1-ol[1] (1o)**

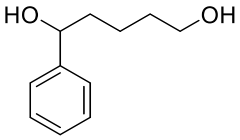
According to general procedure A, reduction of 2-(carboxymethyl)benzoic acid (10 mmol, 1.800 g) afforded the pure product **1o** as a light yellow oil (1.095 g, 72 %) without further purification. **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 7.31-7.28 (m, 2H), 7.23-7.21 (m, 2H), 4.60 (s, 2H), 3.83 (t, *J* = 5.8 Hz, 2H), 3.14 (br. s, 2H), 2.91 (t, *J* = 5.8 Hz, 2H) ppm.**^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 139.2, 138.2, 130.0, 129.8, 128.6, 126.7, 63.4, 63.1, 35.0 ppm.



Chemical Formula: $C_7H_{16}O_2$

- **heptane-1,5-diol[2] (1p)**

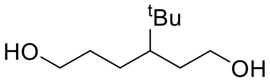
To a solution of 3,4-dihydro-2H-pyran (421 mg, 5 mmol) in water (5 mL) was added a 2.0 M HCl (10 mL) aqueous solution at 0 °C. The reaction was stirred 15 min and then allowed to warm to room temperature and stirred for 1 hour. The reaction was quenched with saturated $NaHCO_3$ solution and the mixture was extracted two times with CH_2Cl_2. The combined organic layers was washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo to afford the crude lactol as a light yellow oil (413 mg, 81 %). Then the crude lactol was dissolved in dry THF (15 mL). At 0 °C, a solution of ethylmagnesium bromide (3.0 M in THF, 3 equiv) was dropwise added for 10 min. Then the reaction was stirred 2 hours at room temperature. The reaction was quenched with saturated NH_4Cl solution and extracted three times with ethyl acetate. The combined organic layers was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduce pressure to afford the crude product. The crude product was purified by silica flash column chromatography (dichloromethane/methanol 95:5) to afford the pure product **1p** as a colorless oil (272 mg, 51 %). **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 3.65 (t, *J* = 6.2 Hz, 2H), 3.54-3.53 (m, 1H), 1.69 (br. s, 2H), 1.61-1.42 (m, 8H), 0.92 (d, *J* = 7.4 Hz, 3H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 73.2, 62.8, 36.4, 32.6, 30.2, 21.8, 9.9 ppm.



Chemical Formula: $C_{11}H_{16}O_2$

- **1-phenylpentane-1,5-diol[1] (1q)**

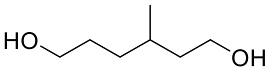
To a solution of 3,4-dihydro-2H-pyran (421 mg, 5 mmol) in water (5 mL) was added a 2.0 M HCl (10 mL) aqueous solution at 0 °C. The reaction was stirred 15 min and then allowed to warm to room temperature and stirred for 1 hour. The reaction was quenched with saturated $NaHCO_3$ solution and the mixture was extracted two times with CH_2Cl_2. The combined organic layers was washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo to afford the crude lactol as a light yellow oil (413 mg, 81 %). Then the crude lactol was dissolved in dry THF (15 mL). At 0 °C, a solution of phenylmagnesium bromide (1.0 M in THF, 3 equiv) was dropwise added for 10 min. Then the reaction was stirred 2 hours at room temperature. The reaction was quenched with saturated NH_4Cl solution and extracted three times with ethyl acetate. The combined organic layers was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduce pressure to afford the crude product. The crude product was purified by silica flash column chromatography (pentane/ethyl actetate 1:1 to pure ethyl acetate) to afford the pure product **1q** as a colorless oil (512 mg, 70 %). **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 7.36-7.33 (m, 4H), 7.29-7.26 (m, 1H), 4.67 (dd, J = 5.6; 7.6 Hz, 1H), 3.62 (t, J = 6.4 Hz, 2H), 1.95 (br. s, 2H), 1.85-1.80 (m, 1H), 1.76-1.70 (m, 1H), 1.62-1.56 (m, 2H), 1.54-1.49 (m, 1H), 1.39-1.35 (m, 1H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 144.7, 128.5, 127.5, 125.8, 62.7, 38.7, 32.4, 22.0 ppm.



Chemical Formula: $C_{10}H_{22}O_2$

- **3-(*tert*-butyl)hexane-1,6-diol[5] (1r)**

To a stirred solution of 4-(*tert*-butyl)cyclohexanone (1.541 g, 10 mmol) in dichloromethane (20 mL), a solution of *m*-chloroperbenzoic acid (3.106 g, 18 mmol) in dichloromethane (10 mL) was dropwise added. The reaction was stirred for 16 hours. Then the excess of *m*-chloroperbenzoic acid was quenched with saturated Na_2SO_3 aqueous solution. The organic layer was separated, washed with saturated $NaHCO_3$ aqueous solution, brine, dried over $MgSO_4$, filtered and concentrated under reduce pressure to afford crude 5-(*tert*-butyl)oxepan-2-one (1.502 g, 88 %). According to a modified general procedure C (2 equiv. of $LiAlH_4$), reduction of 5-(*tert*-butyl)oxepan-2-one (1.502 g, 8.82 mmol) afforded pure product **1r** as a colorless oil (1.167 g, 76 %) without further purification. **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 3.66-3.59 (m, 4H), 2.40 (br. s, 2H), 1.78-1.74 (m, 1H), 1.65-1.63 (m, 1H), 1.56-1.51 (m, 2H), 1.33-1.29 (m, 1H), 1.14-1.11 (m, 1H), 1.02-1.00 (m, 1H), 0.86 (s, 9H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 63.1, 62.9, 44.5, 34.4, 33.8, 32.5, 27.6, 27.4 ppm.

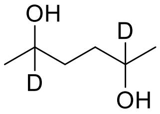


Chemical Formula: $C_7H_{16}O_2$

- **3-methylhexane-1,6-diol[5] (1s)**

To a stirred solution of 4-methylcyclohexanone (1.121 g, 10 mmol) in dichloromethane (20 mL), a solution of *m*-chloroperbenzoic acid (3.106 g, 18 mmol) in dichloromethane (10 mL) was dropwise added. The reaction was stirred for 16 hours. Then the excess of *m*-

chloroperbenzoic acid was quenched with saturated Na_2SO_3 aqueous solution. The organic layer was separated, washed with saturated $NaHCO_3$ aqueous solution, brine, dried over $MgSO_4$, filtered and concentrated under reduce pressure to afford crude 5-methyloxepan-2-one (1.093 g, 85 %). According to a modified general procedure C (2 equiv. of $LiAlH_4$), reduction of 5-methyloxepan-2-one (1.093 g, 8.53 mmol) afforded pure product **1s** as a colorless oil (1.076 g, 95 %) without further purification. **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 3.73-3.67 (m, 2H), 3.64 (t, *J* = 6.6 Hz, 2H), 1.62-1.52 (m, 6H), 1.44-1.38 (m, 2H), 1.23-1.18 (m, 1H), 2.40 (br. s, 2H), 1.78-1.74 (m, 1H), 1.65-1.63 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 3H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 63.1, 61.0, 39.7, 32.9, 30.0, 29.2, 19.6 ppm.



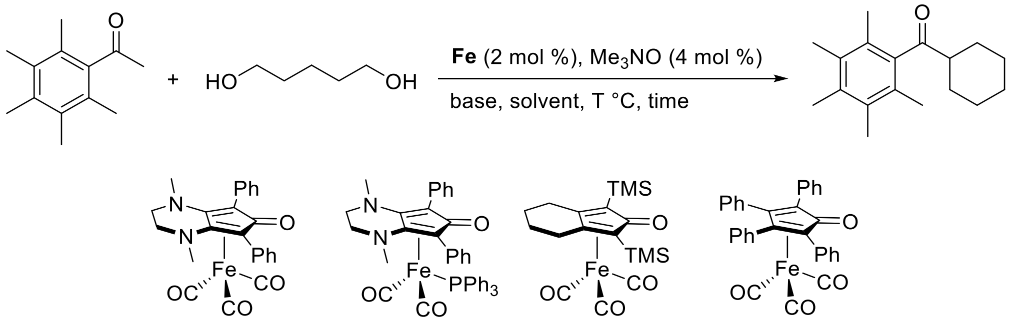
Chemical Formula: $C_6H_{12}D_2O_2$

- **hexane-2,5-*d*$_2$-2,5-diol (1t)**

To a solution of $NaBD_4$ (313 mg, 2.5 eq) in methanol (20 mL) was slowly added hexane-2,5-dione (342 mg, 3 mmol) at 0 °C. The reaction was then stirred at room temperature for one hour. The solution was quenched by slow addition of water (20 mL) and then extracted three times with ethyl acetate (3 x 15 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated under reduce pressure to afford pure product **1t** as a colorless oil (336 mg, 93 %) without further purification. **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 2.16 (br. s, 2H), 1.62-1.51 (m, 4H), 1.20 (br. s, 6H) ppm. **HRMS (ESI-TOF) m/z [M + H]$^+$**: Calcd for $C_6H_{13}OD_2$ 121.1132; Found 121.1136.

Part 3: Optimization of reaction conditions

Table S1: Optimization of reaction conditions[a]



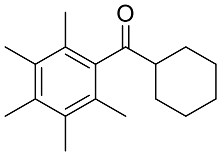
entry	diol (equiv)	catalyst	temperature (°C)	base (equiv)	solvent	time (h)	1a (%)
1	1	Fe1	110	NaO^tBu (2)	toluene (1 M)	24	-
2	2	Fe1	110	NaO^tBu (2)	toluene (1 M)	24	4
3	2	Fe1	120	NaO^tBu (2)	toluene (1 M)	24	12
4	2	Fe1	130	NaO^tBu (2)	toluene (1 M)	24	19
5	2	Fe1	130	NaO^tBu (2)	toluene (2 M)	24	19
6	2	Fe1	130	NaO^tBu (2)	toluene (3 M)	24	20
7	2	Fe1	130	NaO^tBu (2)	toluene (4 M)	24	22
8	2	Fe1	130	NaO^tBu (2)	toluene (5 M)	24	26
9	2	Fe1	130	NaO^tBu (4)	toluene (5 M)	24	36
10	2	Fe1	130	K_3PO_4 (4)	toluene (5 M)	24	18
11	2	Fe1	130	K_2CO_3 (4)	toluene (5 M)	24	10
12	2	Fe1	130	NaOMe (4)	toluene (5 M)	24	27
13[b]	2	Fe1	130	NaOH (4)	toluene (5 M)	24	46
14[b]	**2**	**Fe1**	**130**	**NaOH (4)**	**toluene (5 M)**	**40**	**84**
15[b]	3	Fe1	130	NaOH (4)	toluene (5 M)	40	83
16[b]	2	Fe1	130	NaOH (4)	toluene (5 M)	50	84
17[b]	2	Fe1	140	NaOH (4)	toluene (5 M)	40	82
18[b]	2	-	130	NaOH (4)	toluene (5 M)	40	< 5
19[b]	2	Fe2	130	NaOH (4)	toluene (5 M)	40	61
20[b]	2	Fe3	130	NaOH (4)	toluene (5 M)	40	19
21[b]	2	Fe4	130	NaOH (4)	toluene (5 M)	40	4

[a] Reaction performed using 0.5 mmol of starting material, conversion was determined by ^{1}H-NMR analysis of the crude mixture.
[b] Reaction performed without using Me_3NO.

Part 4: General procedure for the synthesis of cycloalkanes from 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one

General Procedure D:

In a 15 mL flame-dried Schlenk tube equipped with a stirring bar, 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg), the desired diol (2.0 equiv), iron complex **Fe1** (4.56 mg, 2 mol %), NaOH (80 mg, 4 equiv) and toluene (0.1 mL, 5 M) were poured in under an argon atmosphere. The mixture was rapidly stirred at room temperature for 2 min and then placed into a pre-heated oil bath at 130 °C and stirred over 40 hours. The mixture was cooled-down to room temperature, filtrated over celite with diethyl ether and concentrated under reduced pressure. The conversion was determined by ^{1}H-NMR spectroscopy and the residue was purified by flash chromatography on silica gel using pentane-diethyl ether as eluent to afford the desired product.



Chemical Formula: $C_{18}H_{26}O$

- **cyclohexyl(2,3,4,5,6-pentamethylphenyl)methanone[6] (2a)**

According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with pentane-1,5-diol (2.0 equiv, 105 µL) afforded the pure product **2a** as a white solid (102 mg, 79 %) by silica flash column chromatography (pentane/diethyl ether 98:2). **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 2.59 (tt, *J* = 3.4; 11.9 Hz, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.09 (s, 6H), 1.95-1.92 (m, 2H), 1.82-1.80 (m, 2H), 1.69-1.67 (m, 2H), 1.45-1.39 (m, 2H), 1.26-1.19 (m, 3H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 215.0, 140.2, 135.3, 133.0, 128.1, 53.1, 28.21, 26.0, 25.9, 17.9, 16.7, 16.0 ppm.

- **Scale up of the reaction to 5 mmol starting material**

In a 30 mL flame-dried Schlenk tube equipped with a stirring bar, 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (5 mmol, 950 mg), pentane-1,5-diol (2.0 equiv, 1.050 mL), iron complex **Fe1** (45.6 mg, 2 mol %), NaOH (800 mg, 4 equiv) and toluene (1.0 mL, 5 M) were poured in under an argon atmosphere. The mixture was rapidly stirred at room temperature for 2 min and then placed into a pre-heated oil bath at 130 °C and stirred over 40 hours. The mixture was cooled-down to room temperature, filtrated over celite with diethyl ether and concentrated under reduced pressure. The conversion was determined by ^{1}H-NMR spectroscopy and the residue was purified by flash chromatography on silica gel using pentane-diethyl ether (98:2) as eluent to afford the pure product **2a** as a white solid (1.006 g, 78 %). ^{1}H-NMR data was comparable with the previous NMR data.

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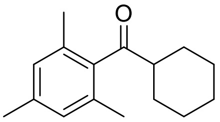
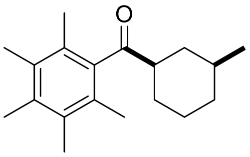
[6] W. M. Akhtar, R. J. Armstrong, J. R. Frost, N. G. Stevenson and T. J. Donohoe, *J. Am. Chem. Soc.* 2018, **140**, 11916-11920.



Chemical Formula: $C_{16}H_{22}O$

- **cyclohexyl(mesityl)methanone[5] (2b)**

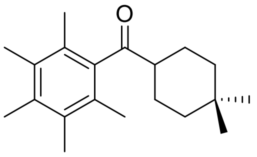
According to general procedure D, alkylation of 1-mesitylethan-1-one (0.5 mmol, 83 µL) with pentane-1,5-diol (2.0 equiv, 105 µL) afforded the pure product **2b** as a light yellow solid (62 mg, 54 %) by silica flash column chromatography (pentane/diethyl ether 98:2). **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 6.83 (s, 2H), 2.65 (tt, *J* = 3.3; 11.8 Hz, 1H), 2.28 (s, 3H), 2.19 (s, 6H), 1.93-1.91 (m, 2H), 1.83-1.80 (m, 2H), 1.70-1.69 (m, 1H), 1.45-1.38 (m, 2H), 1.29-1.19 (m, 3H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 213.7, 139.1, 138.2, 133.2, 128.5, 52.2, 28.2, 25.8, 25.8, 21.0, 19.6 ppm.



Chemical Formula: $C_{19}H_{28}O$

- ***rac*-((1R,3S)-3-methylcyclohexyl)(2,3,4,5,6-pentamethylphenyl)methanone[1] (2c)**

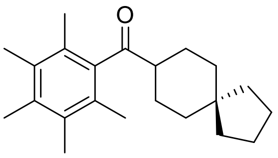
According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1a** (2.0 equiv, 118 mg) afforded the pure product **2c** as a white solid (102 mg, 79 %, 85:15 d.r.) by silica flash column chromatography (pentane/diethyl ether 98:2). The relative stereochemistry is in accordance with the literature. **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 2.65 (tt, *J* = 3.2; 12.0 Hz, 1H), 2.25 (s, 3H), 2.20 (s, 6H), 2.11 (s, 6H), 1.93-1.90 (m, 2H), 1.84-1.81 (m, 1H), 1.71-1.67 (m, 1H), 1.41-1.35 (m, 2H), 1.30-1.25 (m, 1H), 1.14-1.08 (m, 1H), 0.92 (d, *J* = 6.5 Hz), 0.91-0.86 (m, 1H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 214.8, 140.2, 135.3, 133.0, 128.1, 53.2, 36.4, 34.6, 32.4, 27.8, 25.8, 22.7, 17.9, 16.7, 16.0 ppm.



Chemical Formula: $C_{20}H_{30}O$

- **(4,4-dimethylcyclohexyl)(2,3,4,5,6-pentamethylphenyl)methanone[1] (2d)**

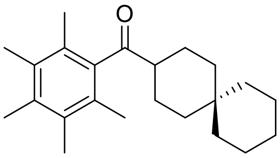
According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1b** (2.0 equiv, 132 mg) afforded the pure product **2d** as a white solid (109 mg, 76 %) by silica flash column chromatography (pentane/diethyl ether 98:2). **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 2.51 (tt, *J* = 3.6; 12.0 Hz, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.10 (s, 6H), 1.77-1.74 (m, 2H), 1.68-1.61 (m, 2H), 1.48-1.44 (m, 2H), 1.14 (td, *J* = 4.0; 13.3 Hz, 2H), 0.93 (s, 3H), 0.90 (s, 3H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 215.3, 140.2, 135.3, 133.0, 128.1, 53.2, 38.7, 32.8, 29.9, 24.2, 24.1, 17.9, 16.7, 16.0. ppm.



Chemical Formula: $C_{22}H_{32}O$

- **(2,3,4,5,6-pentamethylphenyl)(spiro[4.5]decan-8-yl)methanone[1] (2e)**

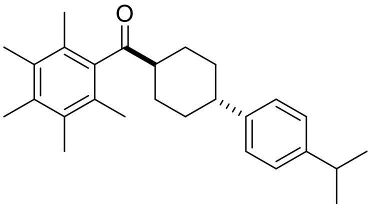
According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1c** (2.0 equiv, 158 mg) afforded the pure product **2e** as a white solid (115 mg, 74 %) by silica flash column chromatography (pentane/diethyl ether 98:2). **^{1}H-NMR (CDCl$_3$, 600 MHz)**: δ 2.56 (tt, *J* = 3.6; 12.2 Hz, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.09 (s, 6H), 1.95-1.92 (m, 2H), 1.82-1.80 (m, 2H), 1.65-1.54 (m, 8H), 1.43 (t, *J* = 7.0 Hz, 2H), 1.32 (t, *J* = 7.0 Hz, 2H), 1.22 (td, *J* = 3.0; 13.2 Hz, 1H) ppm. **^{13}C-NMR (CDCl$_3$, 150 MHz)**: δ 215.2, 140.2, 135.3, 133.0, 128.1, 53.1, 42.1, 41.9, 37.4, 34.4, 25.4, 25.0, 24.00, 17.9, 16.7, 16.0 ppm.



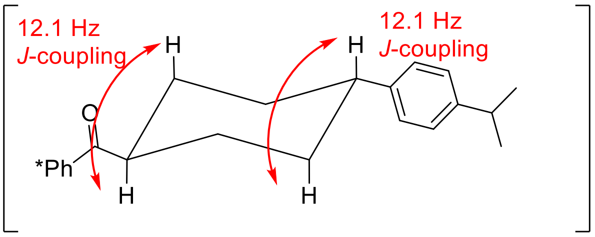
Chemical Formula: $C_{23}H_{34}O$

- **(2,3,4,5,6-pentamethylphenyl)(spiro[5.5]undecan-3-yl)methanone[1] (2f)**

According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1d** (2.0 equiv, 172 mg) afforded the pure product **2f** as a white solid (127 mg, 78 %) by silica flash column chromatography (pentane/diethyl ether 98:2). **^{1}H-NMR (CDCl$_3$, 600 MHz)**: δ 2.55 (tt, *J* = 3.7; 11.8 Hz, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.10 (s, 6H), 1.75-1.69 (m, 2H), 1.67-1.59 (m, 2H), 1.44-1.40 (m, 8H), 1.20-1.18 (m, 2H), 0.99 (td, *J* = 3.7; 13.1 Hz, 2H) ppm. **^{13}C-NMR (CDCl$_3$, 150 MHz)**: δ 215.3, 140.2, 135.3, 133.0, 128.1, 53.6, 41.6, 32.0, 31.7, 26.8, 23.2, 21.7, 21.5, 17.90, 16.7, 16.0 ppm.



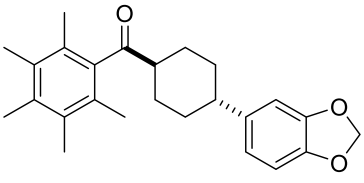
Chemical Formula: $C_{27}H_{36}O$



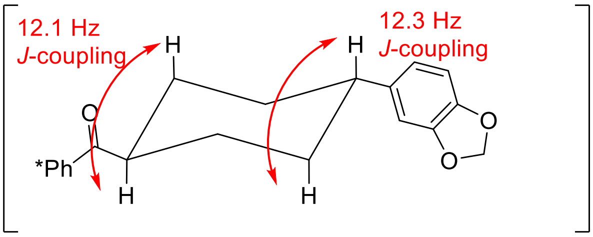
- ***rac*-((1R,4R)-4-(4-isopropylphenyl)cyclohexyl)(2,3,4,5,6-pentamethylphenyl)methanone (2g)**

According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1j** (2.0 equiv, 222 mg) afforded the pure product **2g** as a white solid (135 mg, 72 %, >95:5 d.r.) by silica flash column chromatography (pentane/dichloromethane 1:1). The relative stereochemistry was determined by *J*-coupling constant analysis. **^{1}H-NMR (CDCl$_3$, 600 MHz)**: δ 7.15 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 2.85 (sept, *J* = 6.9 Hz, 1H), 2.68 (tt, *J* = 3.4; 12.1 Hz, 1H), 2.51 (tt, *J* = 3.3; 12.1 Hz, 1H), 2.25 (s, 3H), 2.20 (s, 6H), 2.13 (s, 6H), 2.08-2.05 (m, 2H), 2.01-1.99 (m, 2H), 1.59 (app qd, *J* = 3.2, 13.1 Hz, 2H), 1.42 (qd, *J* = 3.2, 13.0 Hz, 2H), 1.24 (d, J = 6.9 Hz, 6H) ppm. **^{13}C-NMR**

(CDCl$_3$, 150 MHz): δ 214.8, 146.5, 144.2, 140.1, 135.4, 133.1, 128.1, 126.6, 126.3, 52.6, 43.3, 33.6, 33.6, 28.4, 24.0, 18.0, 16.7, 16.1 ppm. **IR (neat)**: ν 2926, 2855, 1685, 1514, 1446, 1260, 1113, 933, 830, 709, 551 cm $^{-1}$. **HRMS (ESI-TOF) m/z [M + Na]$^+$**: Calcd for $C_{27}H_{36}ONa$ 399.2664; Found 399.2663.

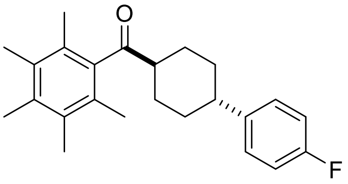


Chemical Formula: $C_{25}H_{30}O_3$



- ***rac*-((1R,4R)-4-(benzo[d][1,3]dioxol-5-yl)cyclohexyl)(2,3,4,5,6-pentamethylphenyl)methanone (2h)**

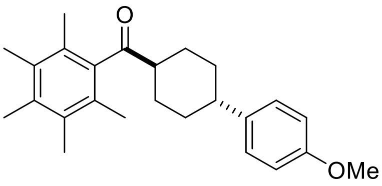
According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1k** (2.0 equiv, 224 mg) afforded the pure product **2h** as a white solid (144 mg, 76 %, >95:5 d.r.) by silica flash column chromatography (pentane/ethyl acetate 7:3). The relative stereochemistry was determined by *J*-coupling constant analysis. **^{1}H-NMR (CDCl$_3$, 600 MHz)**: δ 6.72 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 1.6 Hz, 2H), 6.63 (dd, *J* = 1.6, 8.1 Hz, 1H), 5.91 (s, 2H), 2.66 (tt, *J* = 3.3; 12.1 Hz, 1H), 2.44 (tt, *J* = 3.3; 12.3 Hz, 1H), 2.24 (s, 3H), 2.20 (s, 6H), 2.12 (s, 6H), 2.09-2.05 (m, 2H), 1.98-1.95 (m, 2H), 1.58 (app qd, *J* = 3.3, 13.1 Hz, 2H), 1.36 (qd, *J* = 3.3, 13.1 Hz, 2H) ppm. **^{13}C-NMR (CDCl$_3$, 150 MHz)**: δ 214.7, 147.5, 145.6, 141.0, 140.0, 135.5, 133.1, 128.1, 119.5, 108.1, 107.2, 100.8, 52.6, 43.5, 33.8, 28.4, 18.0, 16.7, 16.0 ppm. **IR (neat)**: ν 2934, 2855, 1687, 1488, 1435, 1238, 1038, 937, 814, 642 cm $^{-1}$. **HRMS (ESI-TOF) m/z [M + H]$^+$**: Calcd for $C_{25}H_{31}O_3$ 379.2273; Found 379.2272.



Chemical Formula: $C_{24}H_{29}FO$

- **(*trans*-4-(4-fluorophenyl)cyclohexyl)(2,3,4,5,6-pentamethylphenyl)methanone[1] (2i)**

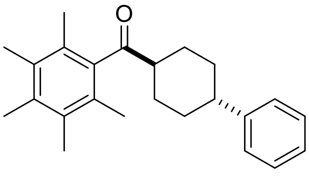
According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1l** (2.0 equiv, 198 mg) afforded the pure product **2i** as a white solid (141 mg, 80 %, >95:5 d.r.) by silica flash column chromatography (pentane/dichloromethane 1:1). The relative stereochemistry is in accordance with the literature. **^{1}H-NMR (CDCl$_3$, 600 MHz)**: δ 7.16-7.13 (m, 2H), 6.99-6.96 (m, 3H), 2.68 (tt, *J* = 3.3; 12.1 Hz, 1H), 2.50 (tt, *J* = 3.3; 12.1 Hz, 1H), 2.25 (s, 3H), 2.21 (s, 6H), 2.13 (s, 6H), 2.11-2.08 (m, 2H), 2.00-1.97 (m, 2H), 1.65-1.61 (m, 2H), 1.46-1.39 (m, 2H) ppm. **^{19}F-NMR (CDCl$_3$, 600 MHz)**: δ – 116.9 ppm. **^{13}C-NMR (CDCl$_3$, 150 MHz)**: δ 214.6, 160.3 (d, *J* = 243.5 Hz), 142.5 (d, *J* = 3.4 Hz), 140.0, 135.5, 133.1, 128.1, 128.1 (d, *J* = 7.7 Hz), 115.0 (d, *J* = 20.8 Hz), 52.5, 43.0, 33.7, 28.4, 17.9, 16.7, 16.0 ppm.



Chemical Formula: $C_{25}H_{32}O_2$

- ***rac*-((1R,4R)-4-(4-methoxyphenyl)cyclohexyl)(2,3,4,5,6-pentamethylphenyl)methanone[1] (2j)**

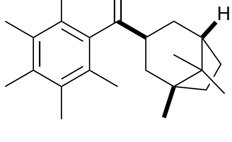
According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1n** (2.0 equiv, 180 mg) afforded the pure product **2j** as a white solid (142 mg, 71 %, >95:5 d.r.) by silica flash column chromatography (pentane/ethyl acetate 8:2). The relative stereochemistry is in accordance with the literature. **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 7.12 (app d, *J* = 8.7 Hz, 2H), 6.84 (app d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.68 (tt, *J* = 3.3; 12.1 Hz, 1H), 2.47 (tt, *J* = 3.3; 12.1 Hz, 1H), 2.26 (s, 3H), 2.21 (s, 6H), 2.14 (s, 6H), 2.10-2.08 (m, 2H), 2.00-1.97 (m, 2H), 1.61 (qd, *J* = 3.3, 13.1 Hz, 2H), 1.40 (qd, *J* = 3.3, 13.1 Hz, 2H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 214.8, 157.8, 140.1, 139.1, 135.4, 133.1, 128.1, 127.5, 113.7, 55.2, 52.6, 42.9, 33.8, 28.4, 17.9, 16.7, 16.0 ppm.



Chemical Formula: $C_{24}H_{30}O$

- **(2,3,4,5,6-pentamethylphenyl)(*trans*-4-phenylcyclohexyl)methanone[1] (2k)**

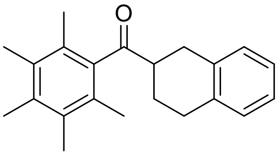
According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1m** (2.0 equiv, 180 mg) afforded the pure product **2k** as a white solid (119 mg, 71 %, >95:5 d.r.) by silica flash column chromatography (pentane/diethyl ether 95:5). The relative stereochemistry is in accordance with the literature. **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 7.31-7.29 (m, 2H), 7.21-7.18 (m, 3H), 2.69 (tt, *J* = 3.3; 12.1 Hz, 1H), 2.52 (tt, *J* = 3.3; 12.1 Hz, 1H), 2.25 (s, 3H), 2.21 (s, 6H), 2.14 (s, 6H), 2.11-2.09 (m, 2H), 2.03-1.99 (m, 2H), 1.69-1.61 (m, 2H), 1.51-1.44 (m, 2H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 214.7, 146.9, 140.0, 135. 5, 133.1, 128.4, 128.1, 126.7, 126.1, 52.6, 43.8, 33.5, 28.4, 18.0, 16.7, 16.0 ppm.



Chemical Formula: $C_{23}H_{34}O$

- **(2,3,4,5,6-pentamethylphenyl)(1,8,8-trimethylbicyclo[3.2.1]octan-3-yl)methanone[1] (2l)**

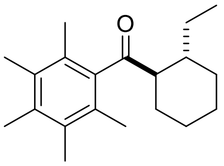
According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1i** (2.0 equiv, 172 mg) afforded the pure product **2l** as a white solid (112 mg, 69 %, >95:5 d.r.) by silica flash column chromatography (pentane/diethyl ether 95:5). The relative stereochemistry is in accordance with the literature and was confirmed by single cristal X-ray crystallographic analysis after crystallization from MeOH. **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 3.02 (tt, *J* = 6.1; 12.3 Hz, 1H) 2.24 (s, 3H), 2.19 (s, 6H), 2.11 (s, 6H), 2.04-1.99 (m, 1H), 1.90-1.82 (m, 2H), 1.78-1.74 (m, 1H), 1.64-1.59 (m, 1H), 1.51-1.44 (m, 2H), 1.33-1.26 (m, 2H), 0.99 (s, 3H), 0.86 (br. s, 6H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 215.4, 140.6, 135.2, 132.9, 127.8, 46.4, 45.4, 42.6, 42.5, 37.1, 35.3, 29.8, 26.4, 24.5, 20.9, 18.5, 17.9, 16.7, 16.0 ppm.

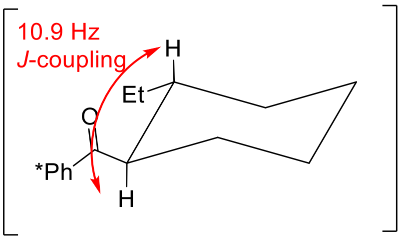


Chemical Formula: $C_{22}H_{26}O$

- **(2,3,4,5,6-pentamethylphenyl)(1,2,3,4-tetrahydronaphthalen-2-yl)methanone[1] (2m)**

According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1o** (2.0 equiv, 152 mg) afforded the pure product **2m** as a white solid (109 mg, 71 %) by silica flash column chromatography (pentane/diethyl ether 95:5). **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 7.13-7.11 (m, 3H), 7.09-7.08 (m, 1H), 3.18-3.13 (m, 1H), 3.11-3.06 (m, 1H), 3.00-2.97 (m, 1H), 2.94-2.90 (m, 1H), 2.86-2.80 (m, 1H), 2.27 (s, 3H), 2.26-2.22 (m, 1H), 2.21 (s, 6H), 2.14 (s, 6H), 1.81-1.74 (m, 1H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 214.0, 139.8, 135.8, 135.7, 135.4, 133.3, 129.3, 128.8, 125.9, 125.8, 49.7, 30.7, 29.4, 25.5, 18.0, 16.8 ppm.

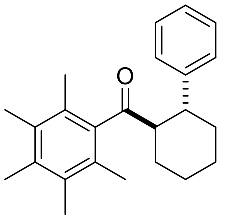




Chemical Formula: $C_{20}H_{30}O$

- ***rac*-((1R,2R)-2-ethylcyclohexyl)(2,3,4,5,6-pentamethylphenyl)methanone (2n)**

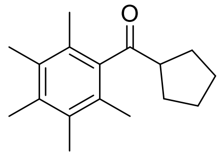
According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1p** (2.0 equiv, 109 mg) afforded the pure product **2n** as a white solid (109 mg, 76 %, 90:10 d.r.) by silica flash column chromatography (pentane/diethyl ether 98:2). The relative stereochemistry was determined by *J*-coupling constant analysis. **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 2.54 (td, J = 3.4; 10.9 Hz, 1H), 2.23 (s, 3H), 2.18 (s, 6H), 2.13 (br. s, 6H), 2.05-2.02 (m, 1H), 1.93-1.89 (m, 1H), 1.83-1.79 (m, 1H), 1.75-1.70 (m, 3H), 1.26-1.14 (m, 3H), 1.06-1.04 (m, 1H), 0.95 (t, J = 7.3 Hz, 3H), 0.91-0.88 (m, 1H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 213.2, 139.7, 135.5, 133.0, 57.9, 38.8, 29.9, 29.4, 27.0, 26.5, 25.5, 17.9, 16.8, 11.7 ppm. **IR (neat)**: ν 2928, 2851, 1682, 1569, 1447, 1260, 1109, 1005, 903, 801, 694, 476 cm^{-1}. **HRMS (ESI-TOF) m/z [M + Na]$^+$**: Calcd for $C_{20}H_{30}ONa$ 309.2194; Found 309.2182.



Chemical Formula: $C_{24}H_{30}O$

- ***rac*-((1R,2R)-2-ethylcyclohexyl)(2,3,4,5,6-pentamethylphenyl)methanone (2o)**

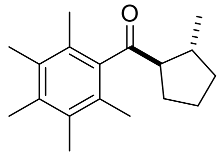
According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1q** (2.0 equiv, 180 mg) afforded the pure product **2o** as a white solid (129 mg, 77 %, >95:5 d.r.) by silica flash column chromatography (pentane/diethyl ether 95:5). The relative stereochemistry was determined by *J*-coupling constant analysis. **^{1}H-NMR (CDCl$_3$, 600 MHz)**: δ 7.34-7.33 (m, 2H), 7.24-7.22 (m, 2H), 7.16-7.13 (m, 1H), 3.09 (td, *J* = 3.9; 12.5 Hz, 1H), 2.97 (td, *J* = 3.3; 11.6 Hz, 1H), 2.17-1.90 (m, 15H), 1.86-1.81 (m, 2H), 1.65-1.58 (m, 2H), 1.42-1.26 (m, 4H) ppm. **^{13}C-NMR (CDCl$_3$, 150 MHz)**: δ 211.7, 145.1, 139.3, 135.4, 132.8, 128.8, 127.8, 126.0, 58.4, 44.2, 33.8, 29.9, 26.3, 26.2, 17.9, 17.8, 16.7, 16.00, 15.9 ppm.



Chemical Formula: $C_{17}H_{24}O$

- **cyclopentyl(2,3,4,5,6-pentamethylphenyl)methanone[5] (2p)**

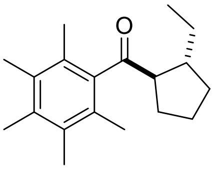
According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with butane-1,4-diol (2.0 equiv, 88 µL) afforded the pure product **2p** as a white solid (68 mg, 56 %) by silica flash column chromatography (pentane/diethyl ether 98:2). **^{1}H-NMR (CDCl$_3$, 600 MHz)**: δ 3.16 (quint, *J* = 8.2 Hz, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.12 (s, 6H), 1.92-1.85 (m, 4H), 1.80-1.73 (m, 2H), 1.63-1.57 (m, 2H) ppm. **^{13}C-NMR (CDCl$_3$, 150 MHz)**: δ 215.1, 141.1, 135.3, 133.1, 127.7, 54.3, 29.7, 25.8, 17.8, 16.7, 16.0 ppm.

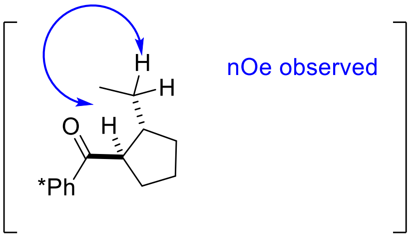


Chemical Formula: $C_{18}H_{26}O$

- ***rac*-((1R,2R)-2-methylcyclopentyl)(2,3,4,5,6-pentamethylphenyl)methanone[1] (2q)**

According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1e** (2.0 equiv, 104 mg) afforded the pure product **2q** as a white solid (62 mg, 48 %) by silica flash column chromatography (pentane/diethyl ether 95:5). **^{1}H-NMR (CDCl$_3$, 600 MHz)**: δ 2.76 (q, *J* = 8.0 Hz, 1H), 2.34 (sept, *J* = 7.3 Hz, 1H), 2.23 (s, 3H), 2.18 (s, 6H), 2.12 (s, 6H), 1.97-1.85 (m, 3H), 1.71-1.59 (m, 2H), 1.29-1.21 (m, 2H), 1.00 (d, *J* = 6.7 Hz, 3H) ppm. **^{13}C-NMR (CDCl$_3$, 150 MHz)**: δ 214.4, 141.0, 135.3, 133.0, 127.8, 61.7, 37.1, 35.1, 30.0, 24.8, 20.6, 17.9, 16.7, 16.0 ppm.

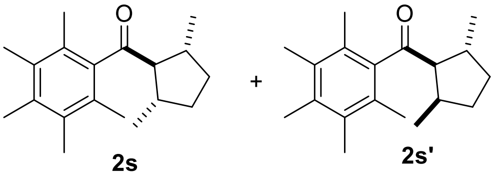




Chemical Formula: $C_{19}H_{28}O$

- ***rac*-((1R,2R)-2-ethylcyclopentyl)(2,3,4,5,6-pentamethylphenyl)methanone (2r)**

According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1f** (2.0 equiv, 118 mg) afforded the pure product **2r** as a yellow solid (89 mg, 65 %) by silica flash column chromatography (pentane/diethyl ether 95:5). The relative stereochemistry was determined by nOe analysis. **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 2.85 (q, *J* = 7.2 Hz, 1H) 2.24 (m, 4H), 2.18 (s, 6H), 2.12 (s, 6H), 1.97-1.89 (m, 2H), 1.85-1.79 (m, 1H), 1.70-1.60 (m, 2H), 1.55-1.50 (m, 1H), 1.32-1.25 (m, 1H), 1.20-1.14 (m, 1H), 0.85 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 214.4, 140.9, 135.2, 133.0, 127.8, 60.0, 43.7, 32.0, 29.8, 28.6, 25.0, 17.9, 16.7, 16.0, 12.7 ppm. **HRMS (ESI-TOF) m/z [M + H]$^+$**: Calcd for $C_{19}H_{29}O$ 273.2132; Found 273.2136.

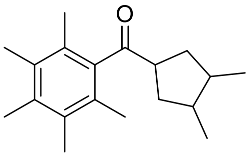


2s **2s'**

Chemical Formula: $C_{19}H_{28}O$

- **(2,5-dimethylcyclopentyl)(2,3,4,5,6-pentamethylphenyl)methanone[1] (2s)**

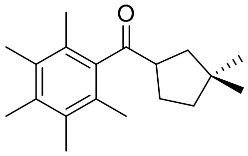
According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol hexane-2,5-diol (2.0 equiv, 118 mg) afforded the pure product **2s** and **2s'** as a white solid (91 mg, 67 %, 70:30 d.r. with **2s** as the major stereoisomer) by silica flash column chromatography (pentane/diethyl ether 95:5) The relative stereochemistry is in accordance with the literature. **^{1}H-NMR (C_6D_6, 600 MHz) of 2s**: δ 2.76-2.70 (m, 2H), 2.58 (t, *J* = 8.0 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 6H), 2.15 (s, 6H), 2.01-1.96 (m, 2H), 1.49-1.40 (m, 2H), 1.16 (d, *J* = 6.8 Hz, 6H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz) of 2s**: δ 212.1, 142.3, 135.4, 133.4, 128.7, 70.1, 38.3, 34.4, 21.8, 18.5, 17.0, 16.4 ppm. **^{1}H-NMR (C_6D_6, 600 MHz) of 2s'**: δ 2.99 (app t, *J* = 7.0 Hz, 1H), 2.54-2.50 (m, 1H), 2.20 (s, 3H), 2.19 (s, 6H), 2.15 (s, 6H), 1.92-1.88 (m, 1H), 1.80-1.75 (m, 2H), 1.47 (d, *J* = 7.0 Hz, 3H), 1.34-1.28 (m, 1H), 1.10 (d, *J* = 6.8 Hz, 3H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz) of 2s'**: δ 212.0, 142.4, 135.5, 133.4, 129.1, 65.4, 38.2, 34.3, 22.1, 18.5, 16.9, 16.4 ppm.



Chemical Formula: $C_{19}H_{28}O$

- **(3,4-dimethylcyclopentyl)(2,3,4,5,6-pentamethylphenyl)methanone (2t)**

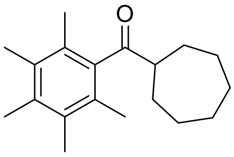
According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1g** (2.0 equiv, 118 mg) afforded the pure product **2t** as a white solid (63 mg, 46 %, 70:17:13 d.r.) by silica flash column chromatography (pentane/diethyl ether 95:5). The relative stereochemistry of the diastereoisomers could not be determined. **^{1}H-NMR ($CDCl_3$, 600 MHz) of the major diastereoisomer**: δ 3.32-3.26 (m, 1H), 2.30-2.25 (m, 1H), 2.24 (s, 3H), 2.20 (s, 6H), 2.12 (s, 6H), 2.09-2.00 (m, 1H), 1.67-1.54 (m, 2H), 1.48-1.38 (m, 2H), 1.02 (d, J = 6.5 Hz, 3H), 0.97 (d, J = 6.5 Hz, 3H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz) of the major diastereoisomer**: δ 215.2, 141.2, 135.3, 133.1, 127.7, 57.9, 43.2, 41.4, 39.1, 37.3, 18.6, 17.9, 17.8, 16.8, 16.1 ppm. **IR (neat)**: ν 2964, 2869, 1687, 1571, 1453, 1109, 926, 864, 689, 499 cm $^{-1}$. **HRMS (ESI-TOF) m/z $[M + H]^+$**: Calcd for $C_{12}H_{29}O$ 273.2133; Found 273.2134.



Chemical Formula: $C_{19}H_{28}O$

- **(3,3-dimethylcyclopentyl)(2,3,4,5,6-pentamethylphenyl)methanone[5] (2u)**

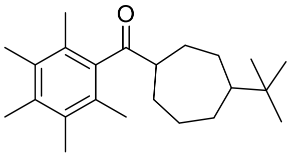
According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1h** (2.0 equiv, 118 mg) afforded the pure product **2u** as a white solid (75 mg, 55 %) by silica flash column chromatography (pentane/diethyl ether 98:2). **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 3.42-3.36 (m, 1H), 2.25 (s, 3H), 2.20 (s, 6H), 2.12 (s, 6H), 2.11-2.05 (m, 1H), 1.97-1.91 (m, 1H), 1.74 (dd, J = 10.0, 12.4 Hz, 1H), 1.66 (dd, J = 8.1, 12.4 Hz, 1H), 1.62-1.7 (m, 1H), 1.48-1.43 (m, 1H), 1.11 (s, 3H), 0.98 (s, 3H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 215.1, 141.3, 135.3, 133.0, 127.6, 53.7, 44.4, 40.6, 39.7, 29.3, 28.6, 28.6, 17.7, 16.7, 16.0 ppm.



Chemical Formula: $C_{19}H_{28}O$

- **cycloheptyl(2,3,4,5,6-pentamethylphenyl)methanone[5] (2v)**

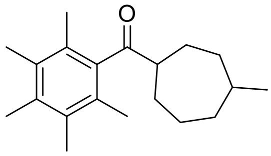
According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with hexane-1,6-diol (2.0 equiv, 118 mg) afforded the pure product **2v** as a white solid (99 mg, 73 %) by silica flash column chromatography (pentane/diethyl ether 98:2). **^{1}H-NMR ($CDCl_3$, 600 MHz)**: δ 2.86-2.80 (m, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.10 (s, 6H), 2.00-1.96 (m, 2H), 1.77-1.74 (m, 2H), 1.69-1.53 (m, 6H), 1.45-1.42 (m, 2H)-1.92 (m, 2H), 1.82-1.80 (m, 2H), 1.69-1.67 (m, 2H), 1.45-1.42 (m, 2H) ppm. **^{13}C-NMR ($CDCl_3$, 150 MHz)**: δ 215.2, 140.2, 135.3, 133.0, 128.3, 54.7, 29.4, 28.4, 26.4, 17.9, 16.7, 16.0 ppm.



Chemical Formula: $C_{23}H_{36}O$

- **(4-(*tert*-butyl)cycloheptyl)(2,3,4,5,6-pentamethylphenyl)methanone[5] (2w)**

According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1r** (2.0 equiv, 174 mg) afforded the pure product **2w** as a white solid (110 mg, 67 %, 55:45 d.r.) by silica flash column chromatography (pentane/diethyl ether 98:2). **^{1}H-NMR (CDCl$_3$, 600 MHz)**: δ 2.85-2.74 (m, 1H), 2.24 (s, 3H), 2.19 (s, 6H), 2.10 (s, 6H), 1.94-1.89 (m, 1H), 1.86-1.80 (m, 2H), 1.74-1.66 (m, 2H), 1.57-1.47 (m, 2H) 1.29-1.21 (m, 2H), 1.13-1.05 (m, 2H), 0.84 (s, 9H) ppm. **^{13}C-NMR (CDCl$_3$, 150 MHz)**: δ 215.3, 215.2, 140.2, 140.2, 135.3, 135.3, 133.0, 133.0, 128.3, 128.3, 55.8, 53.8, 49.6, 49.3, 33.7, 33.7, 30.5, 30.3, 29.4, 28.4, 28.4, 28.4, 27.6, 27.6, 27.4, 27.4, 26.6, 24.6, 17.9, 17.9, 16.7, 16.7, 16.0, 16.0 ppm.



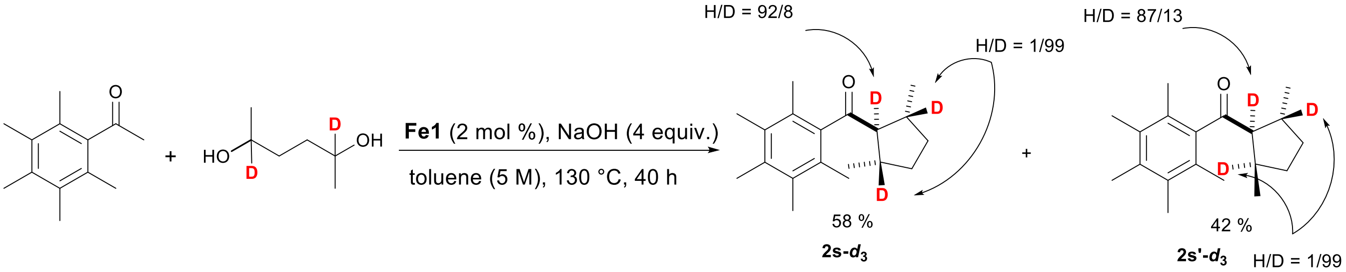
Chemical Formula: $C_{20}H_{30}O$

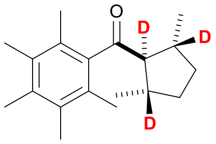
- **(4-(methyl-butyl)cycloheptyl)(2,3,4,5,6-pentamethylphenyl)methanone[5] (2x)**

According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol **1s** (2.0 equiv, 132 mg) afforded the pure product **2x** as a white solid (92 mg, 64 %, 57:43 d.r.) by silica flash column chromatography (pentane/diethyl ether 9:1). **^{1}H-NMR (CDCl$_3$, 600 MHz)**: δ 2.90-2.80 (m, 1H), 2.24 (s, 3H), 2.18 (s, 6H), 2.09 (s, 6H), 2.03-1.97 (m, 1H), 1.88-1.70 (m, 4H), 1.66-1.55 (m, 4H), 1.34-1.26 (m, 1H) 1.18-1.04 (m, 2H), 0.89 (t, *J* = 6.7 Hz, 3H) ppm. **^{13}C-NMR (CDCl$_3$, 150 MHz)**: δ 215.1, 215.1, 140.2, 140.20, 135.4, 133.0, 133.0, 128.3, 55.0, 54.2, 38.1, 36.4, 35.9, 35.1, 34.3, 33.1, 30.0, 29.0, 28.3, 26.2, 26.1, 23.9, 23.7, 23.5, 17.9, 16.7, 16.0 ppm.

Part 5: Mechanistic studies

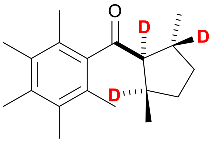
Scheme S1: Deuterium-labeling experiment





2s-d_3

+

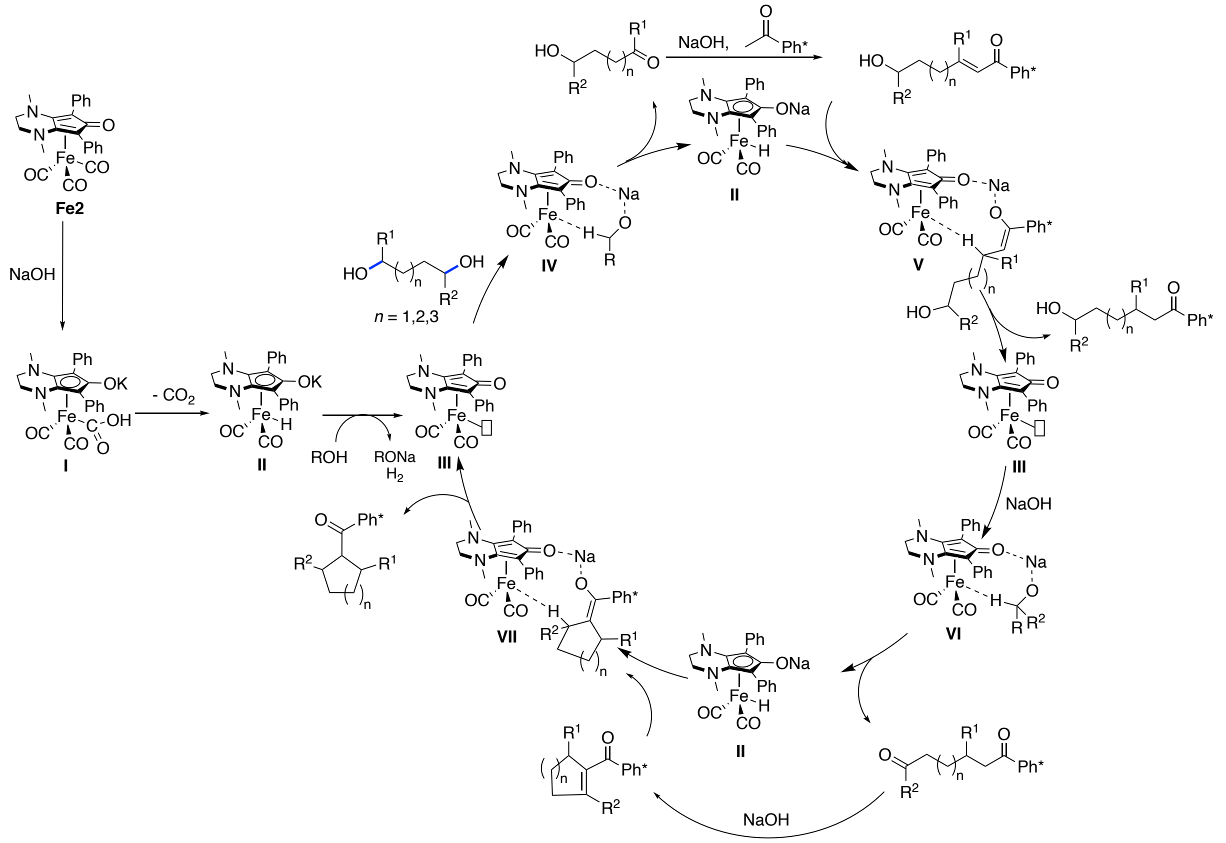


2s'-d_3

(3,4-dimethylcyclopentyl)(2,3,4,5,6-pentamethylphenyl)methanone (2s-d_3)

According to general procedure D, alkylation of 1-(2,3,4,5,6-pentamethylphenyl)ethan-1-one (0.5 mmol, 95 mg) with diol hexane-2,5-d_2-diol (2.0 equiv, 118 mg) afforded the pure product **2s-d_3** and **2s'-d_3** as a white solid (98 mg, 71 %, 58:42 d.r. with **2s-d_3** as the major stereoisomer) by silica flash column chromatography (pentane/diethyl ether 95:5). Attribution was determined by comparison with non-deuterated product (Figure **S2**). **^{1}H-NMR (C_6D_6, 600 MHz) of 2s-d_3**: δ 2.59 (s, 1H), 2.34 (s, 3H), 2.30 (s, 6H), 2.15 (s, 6H), 1.99-1.96 (m, 2H), 1.44-1.40 (m, 2H), 1.15 (s, 6H) ppm. **^{1}H-NMR (C_6D_6, 600 MHz) of 2s'-d_3**: δ 3.00 (s, 1H), 2.20 (br. s, 9H), 2.15 (s, 6H), 1.89-1.88 (m, 1H), 1.78-1.77 (m, 1H), 1.47 (s, 3H), 1.32-1.28 (m, 1H), 1.09 (s, 3H) ppm.

Scheme S2: Proposed mechanism



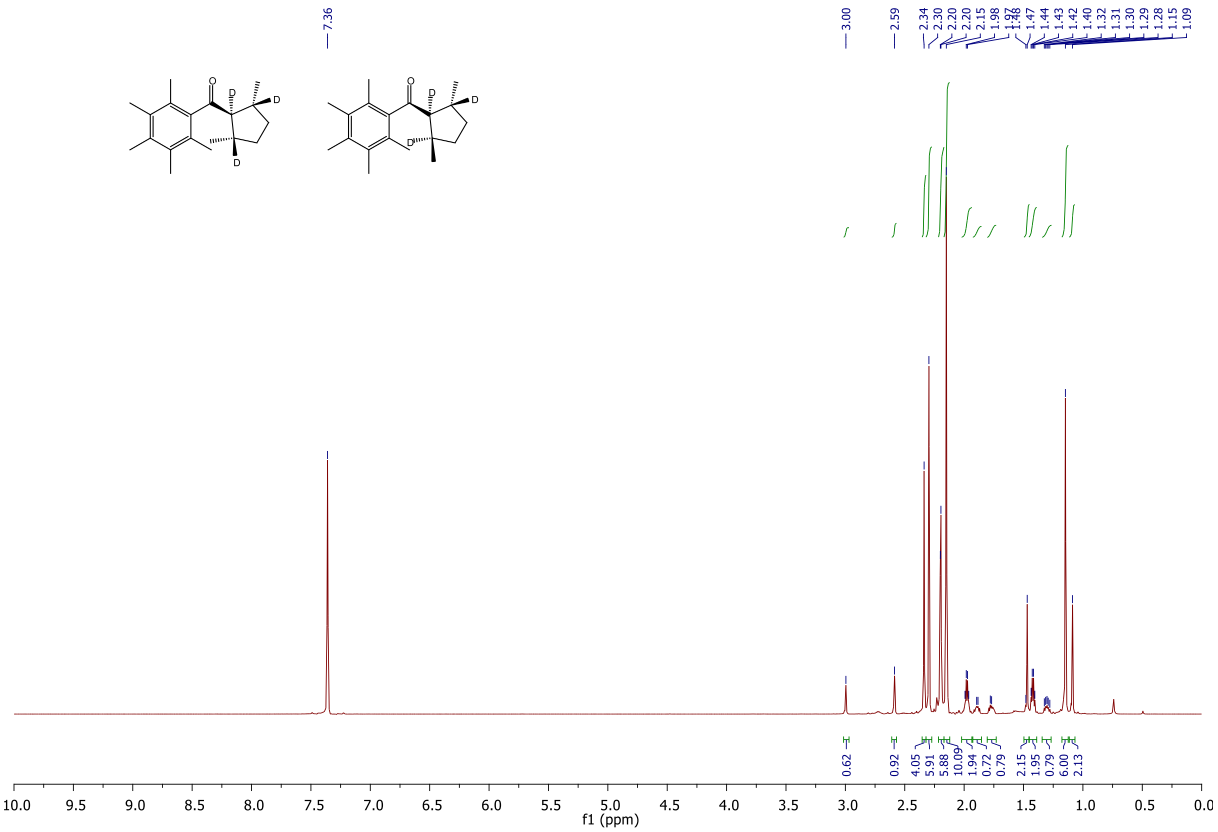


Figure S1: ^{1}H-NMR (600 MHz) in C_6D_6 of 2s-d_3 and 2s‘-d_3

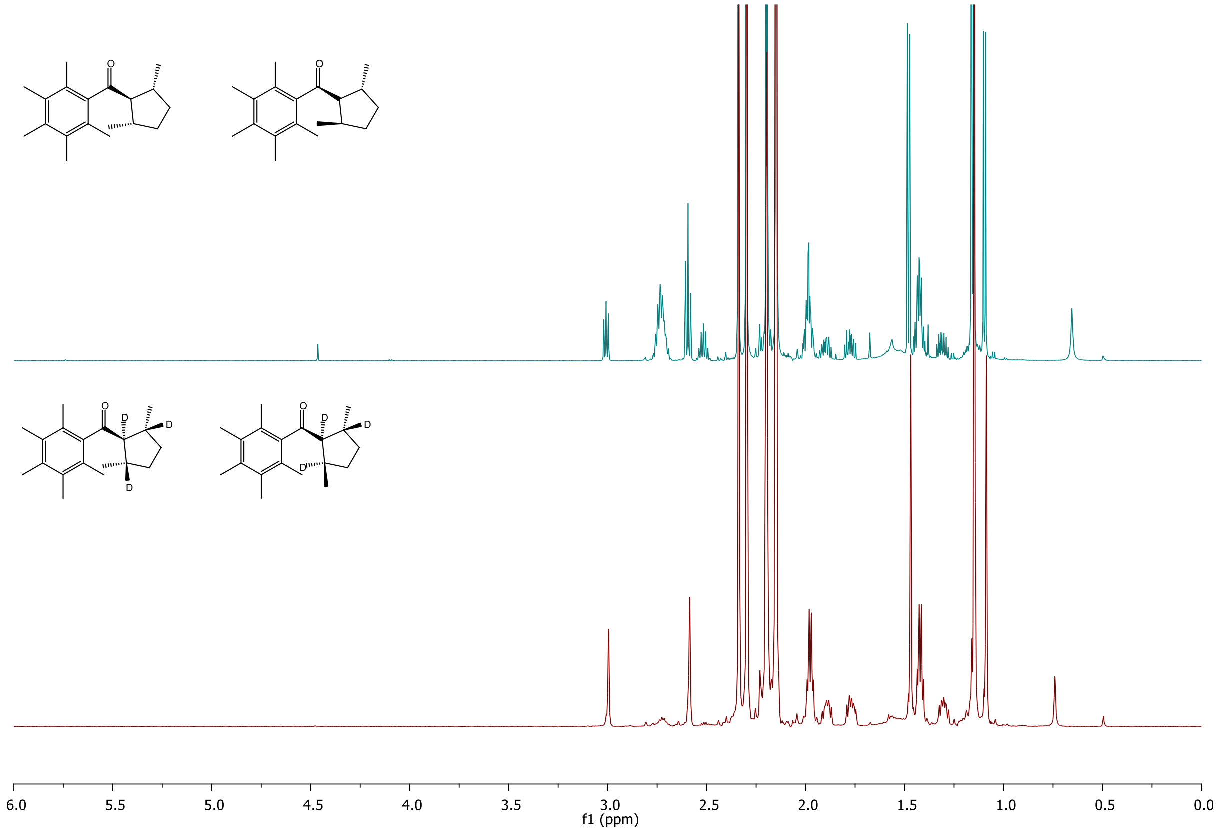


Figure S2: Stacked NMR Spectra of 2s and 2s-d_3

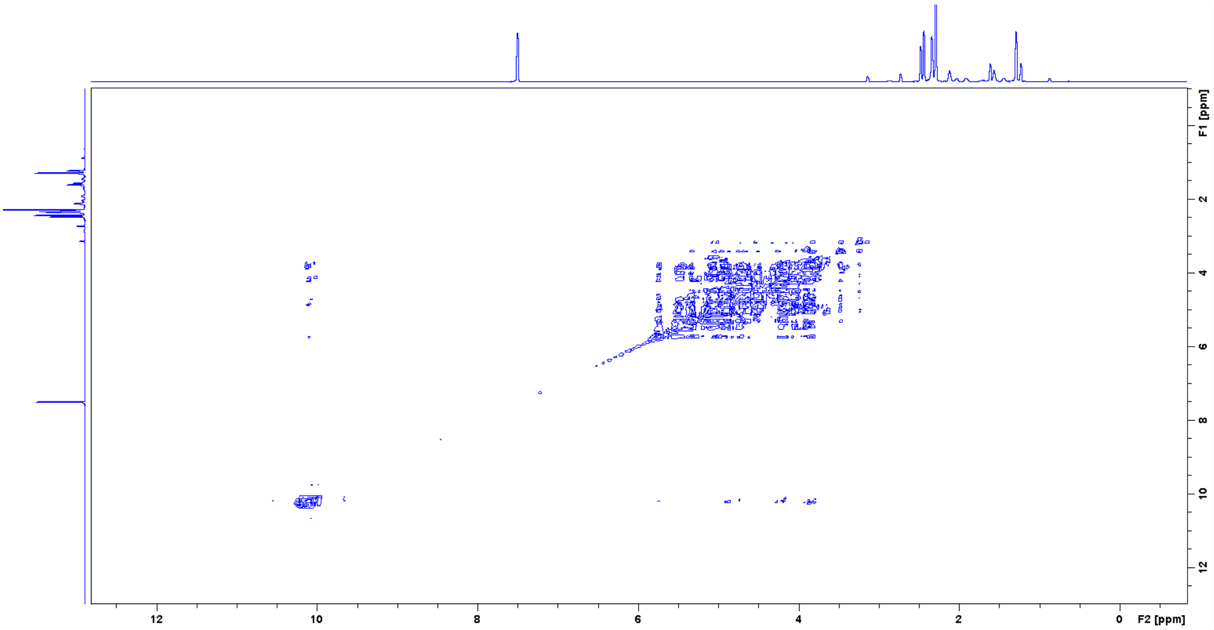


Figure S3: COSY (600 MHz) in C_6D_6 of 2s-d_3 and 2s'-d_3

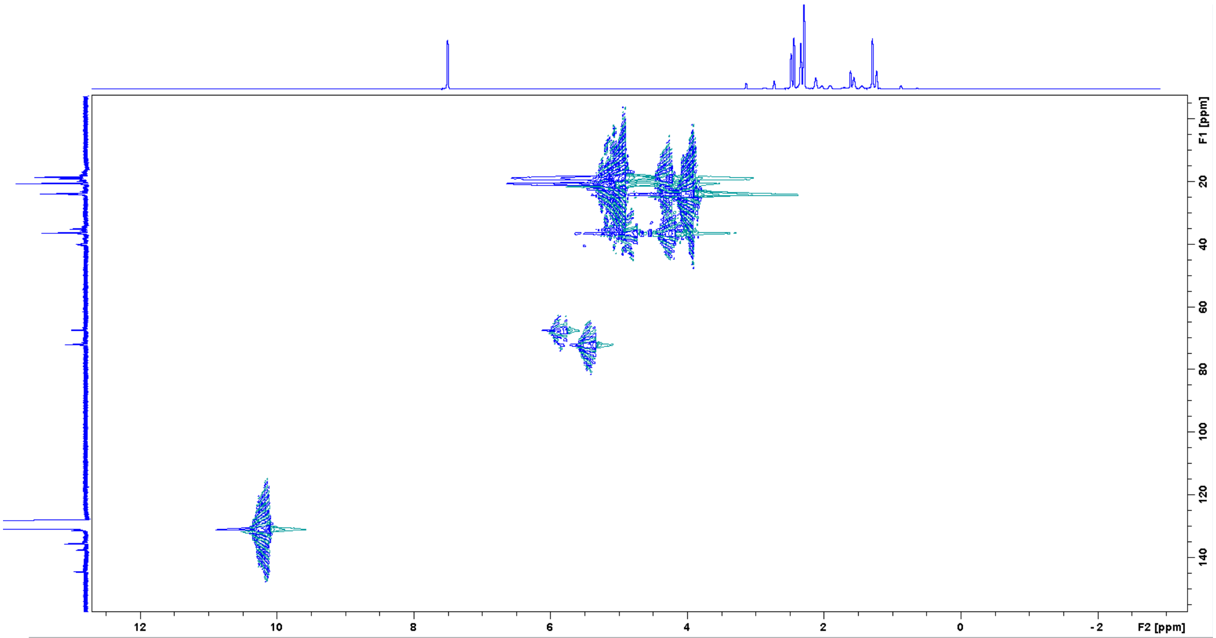


Figure S4: HSQC (600 MHz) in C_6D_6 of 2s-d_3 and 2s'-d_3

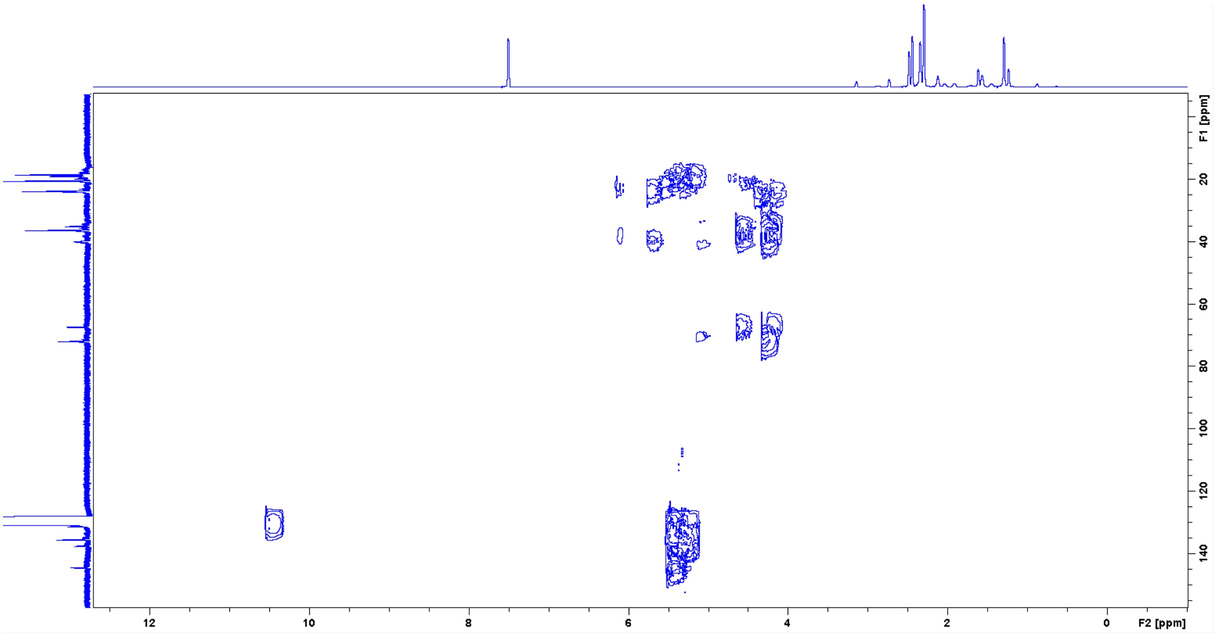


Figure S5: HMBC (600 MHz) in C_6D_6 of 2s-d_3 and 2s‘-d_3

Part 6: NMR spectra of starting materials

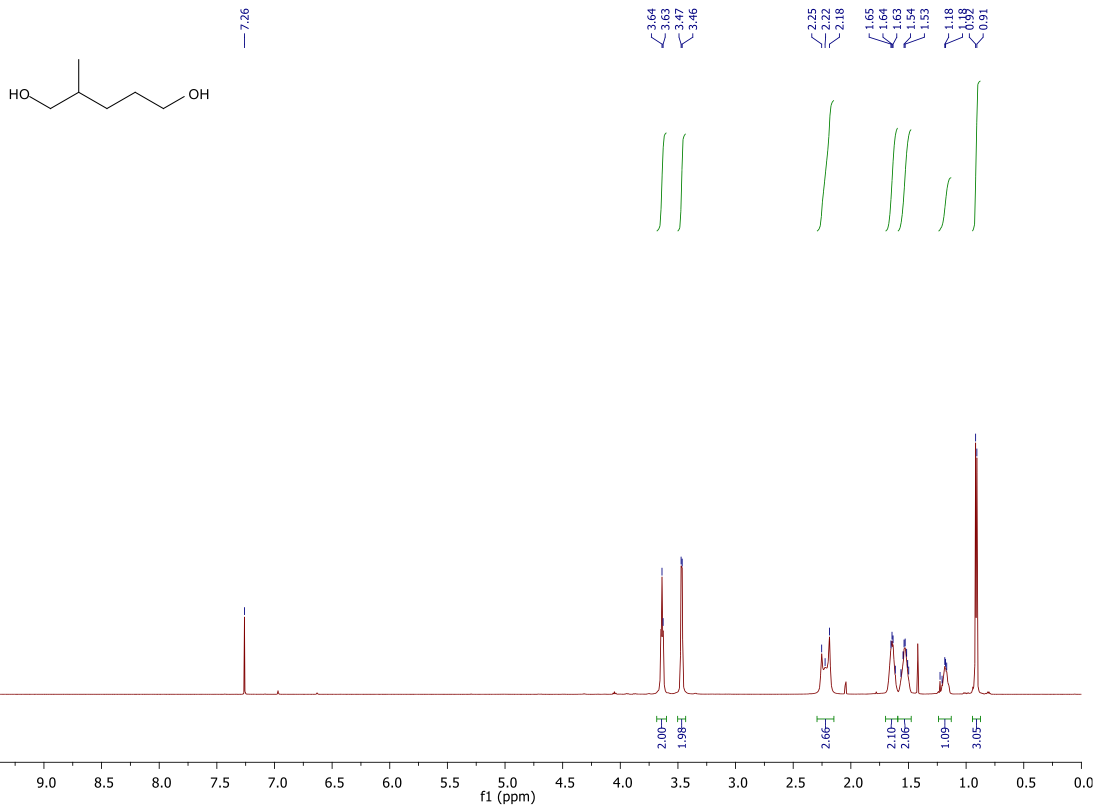


Figure S6: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 1a

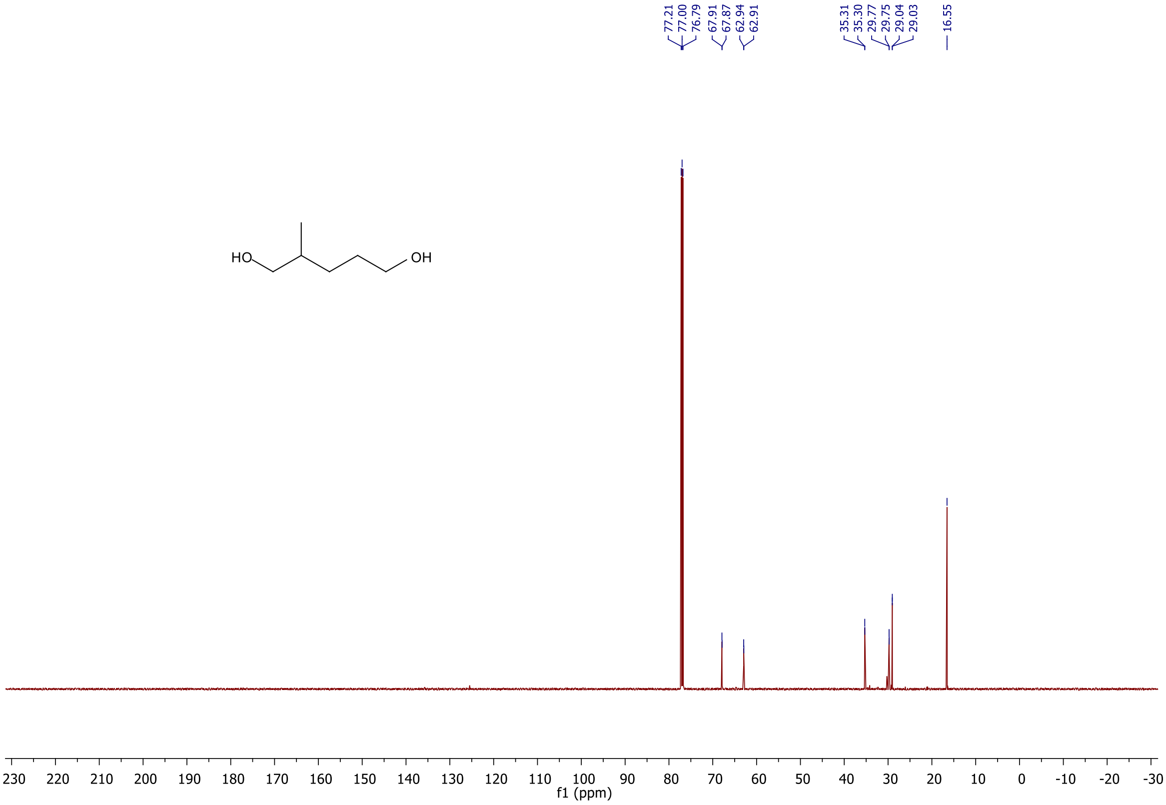


Figure S7: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 1a

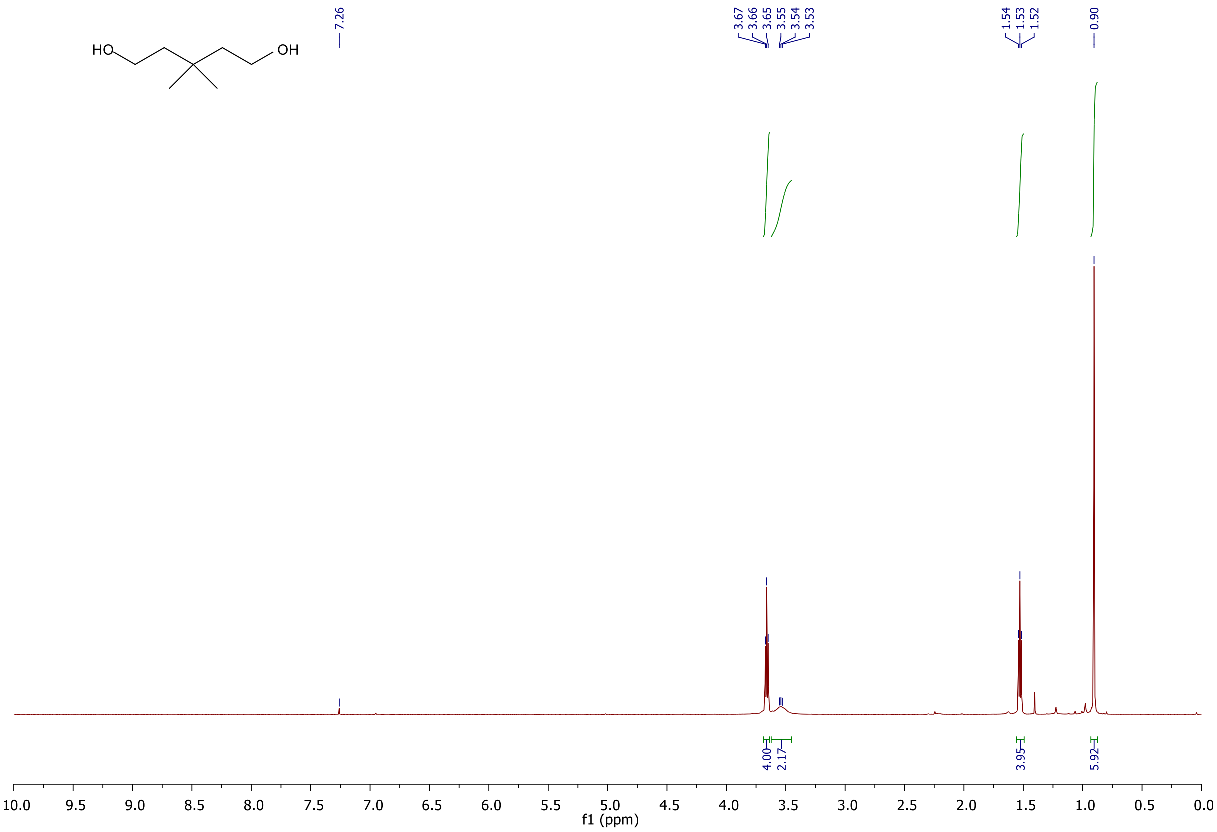


Figure S8: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 1b

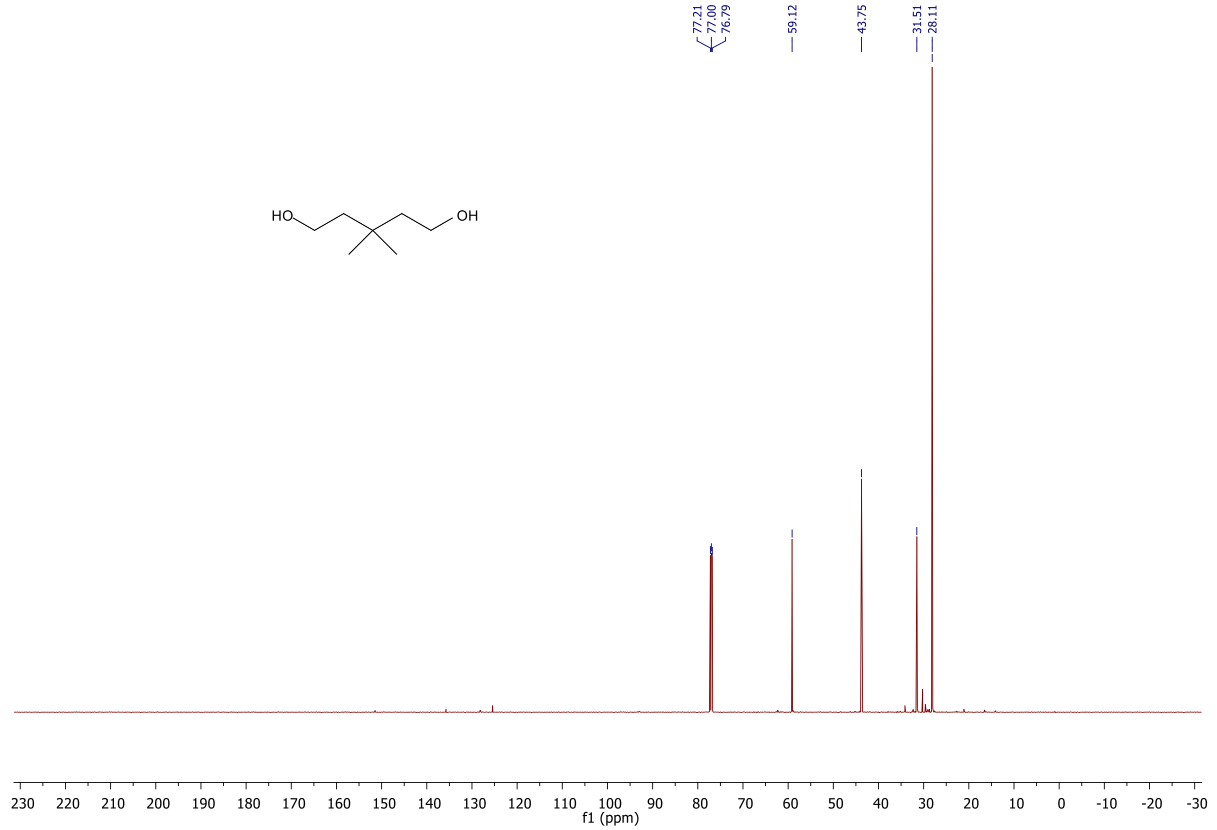


Figure S9: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 1b

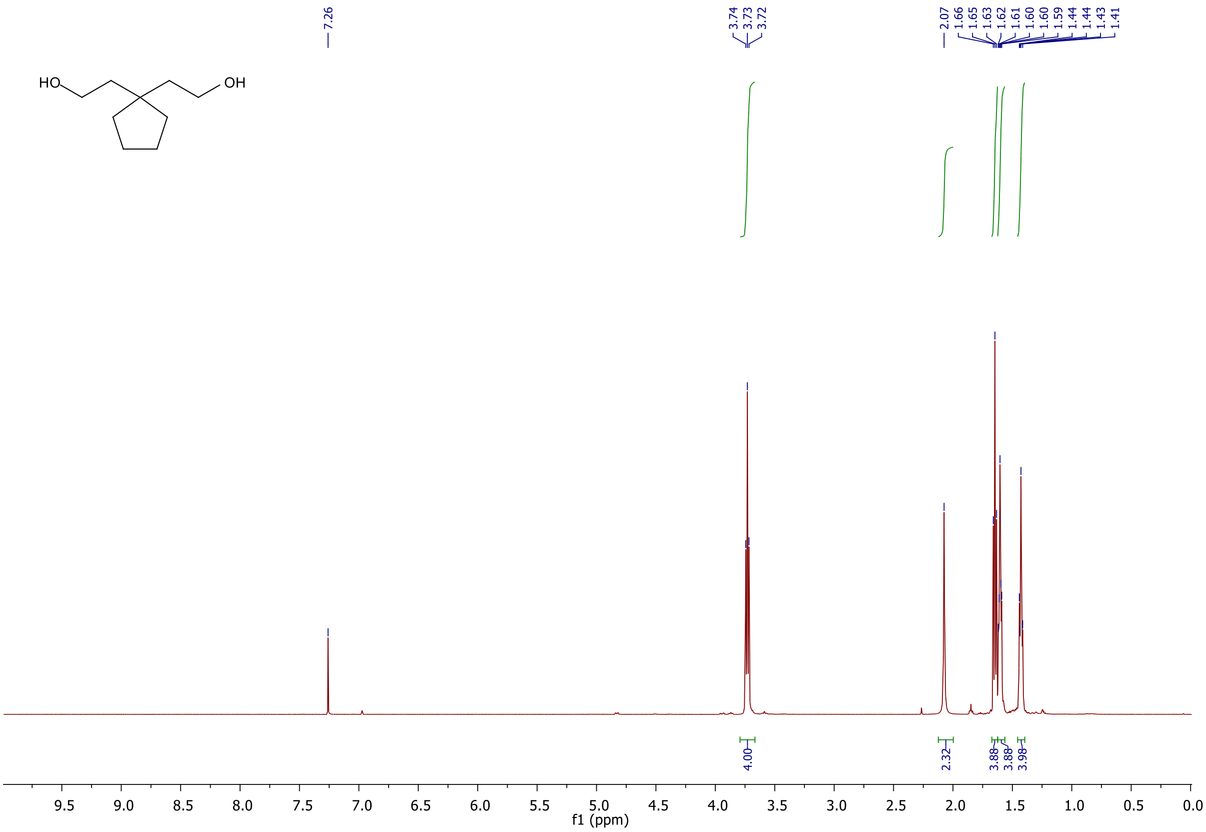


Figure S10: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 1c

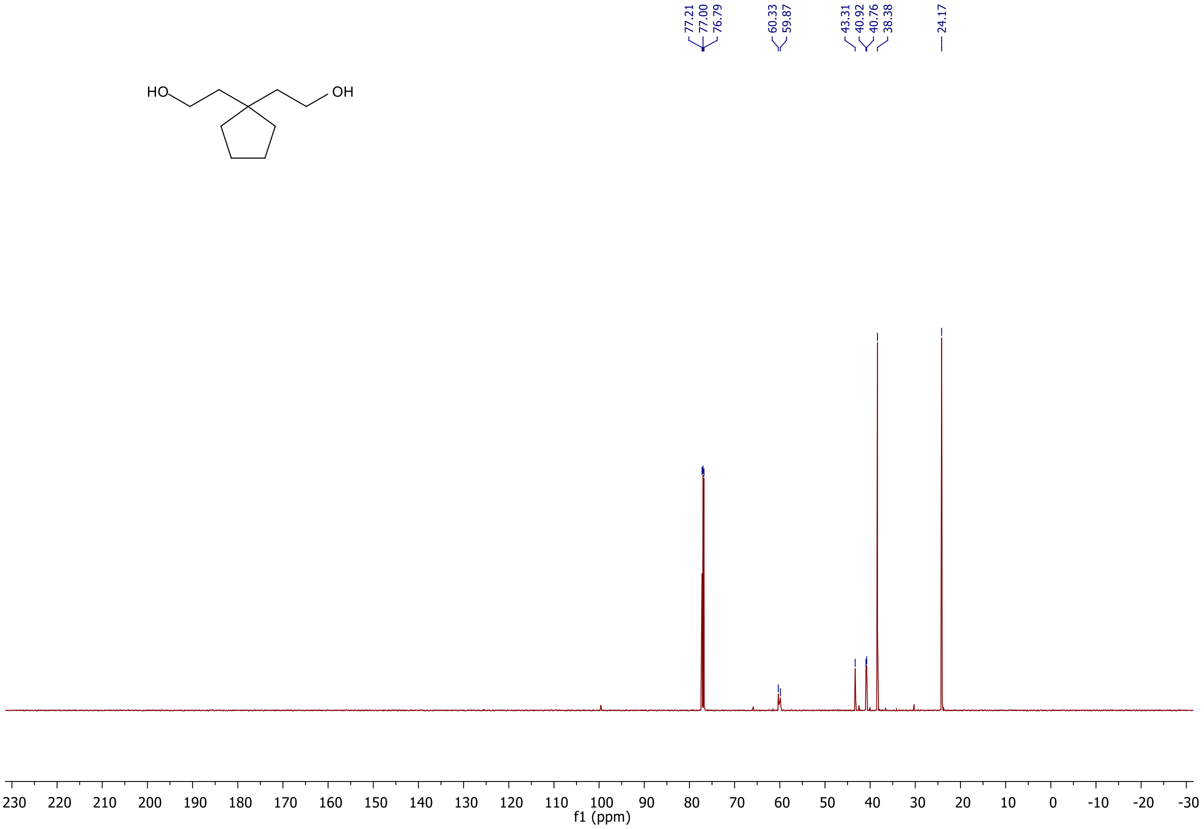


Figure S11: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 1c

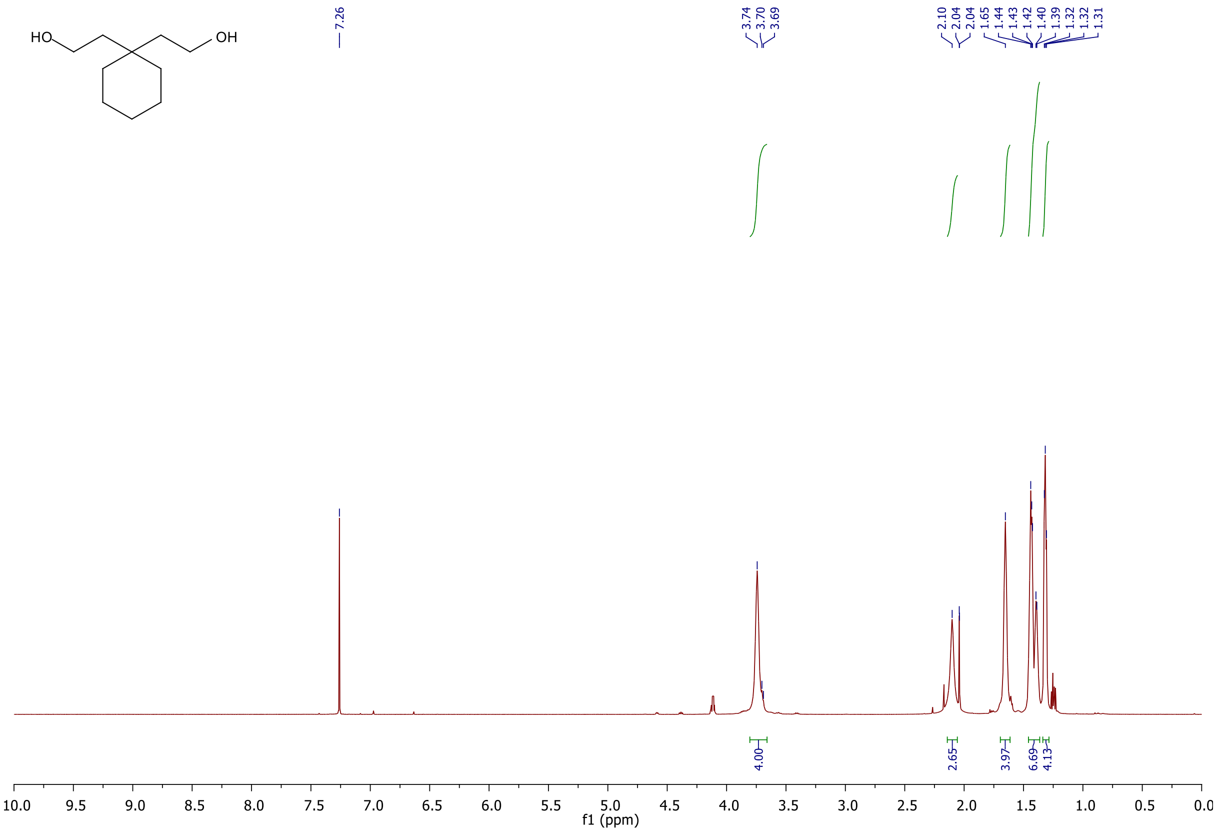


Figure S12: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 1d

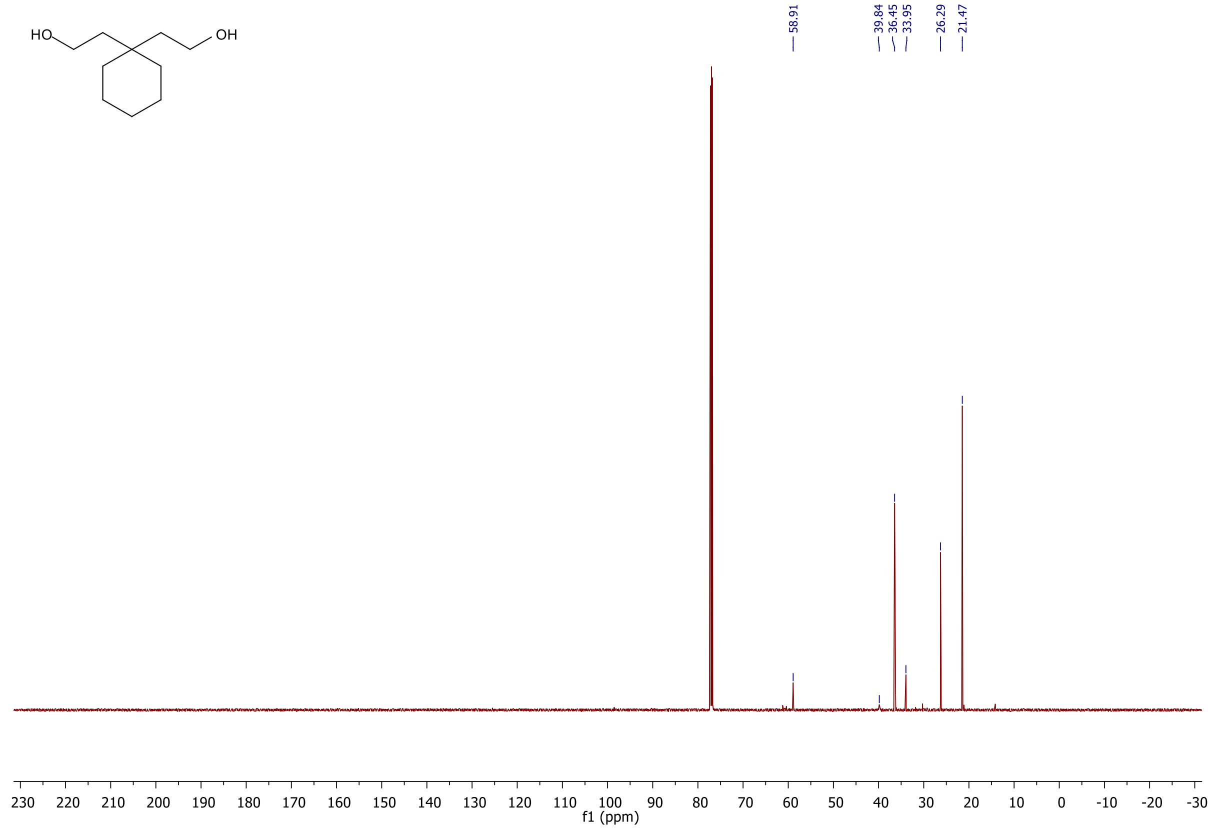


Figure S13: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 1d

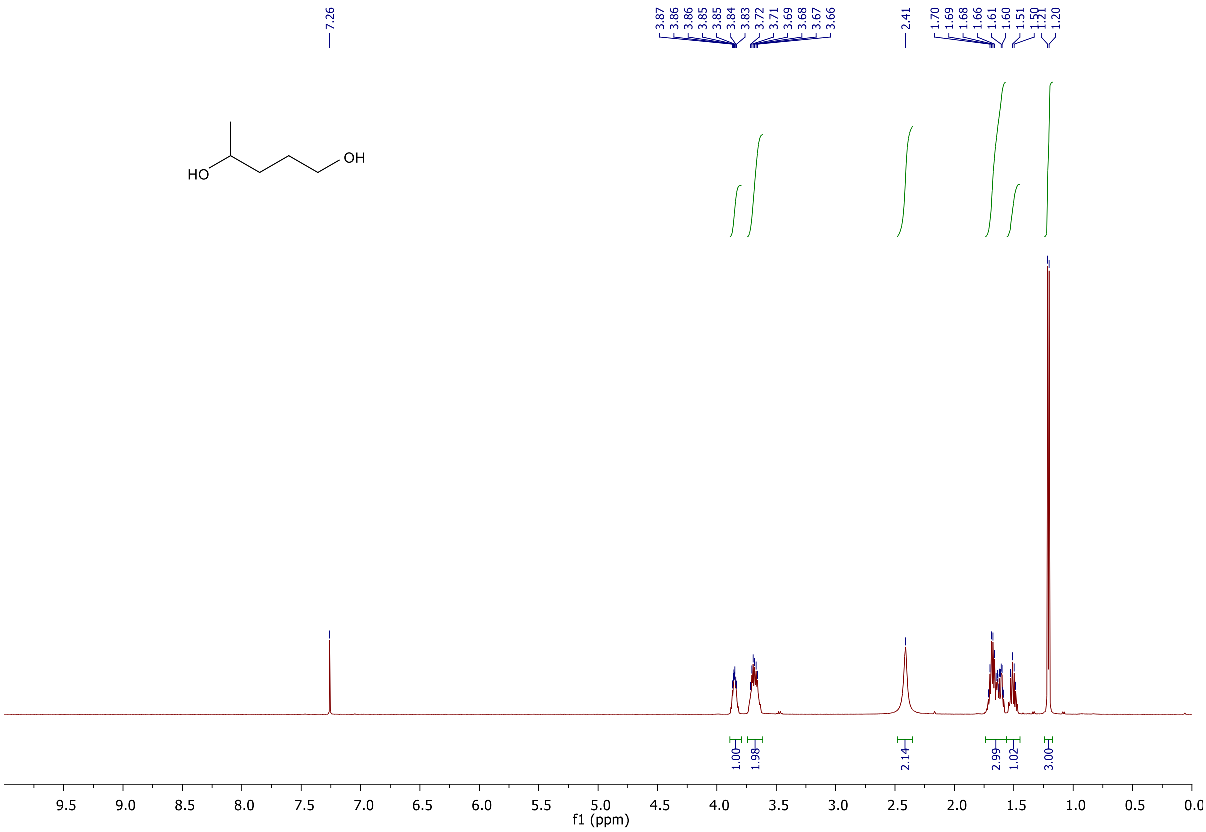


Figure S14: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 1e

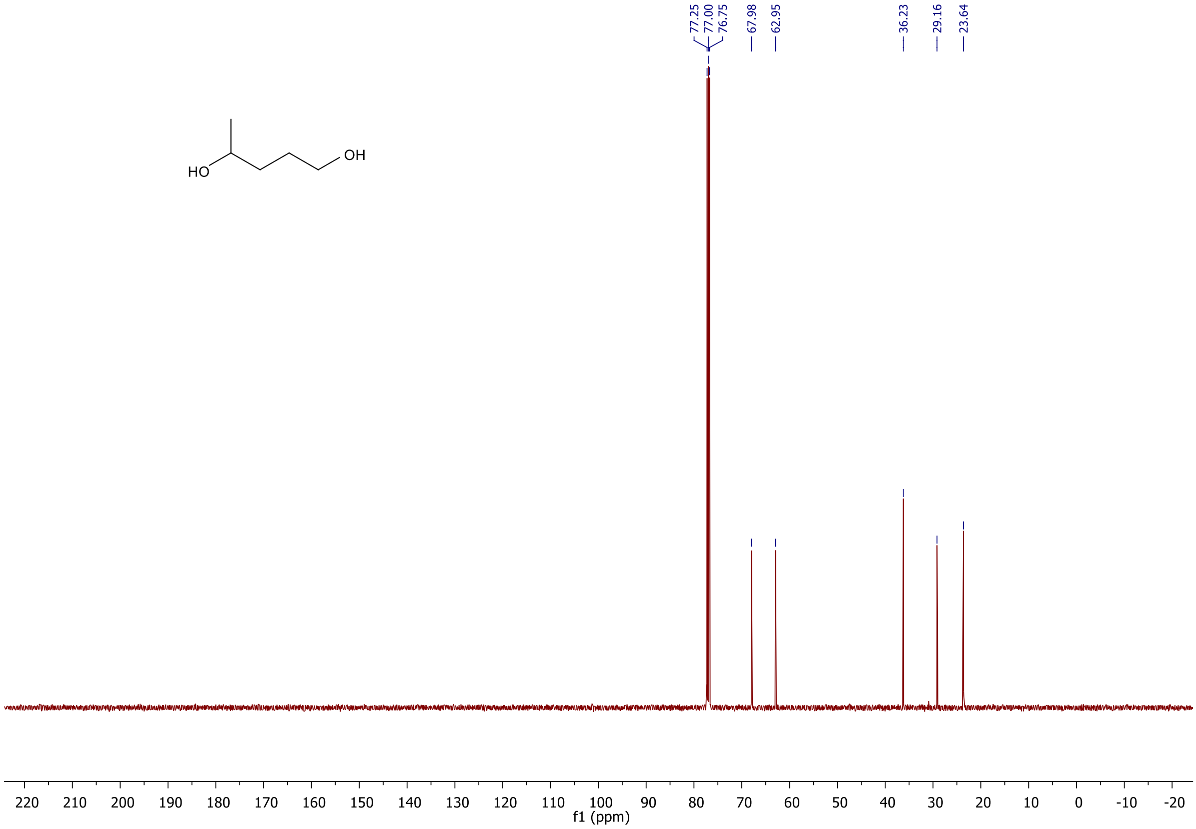


Figure S15: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 1e

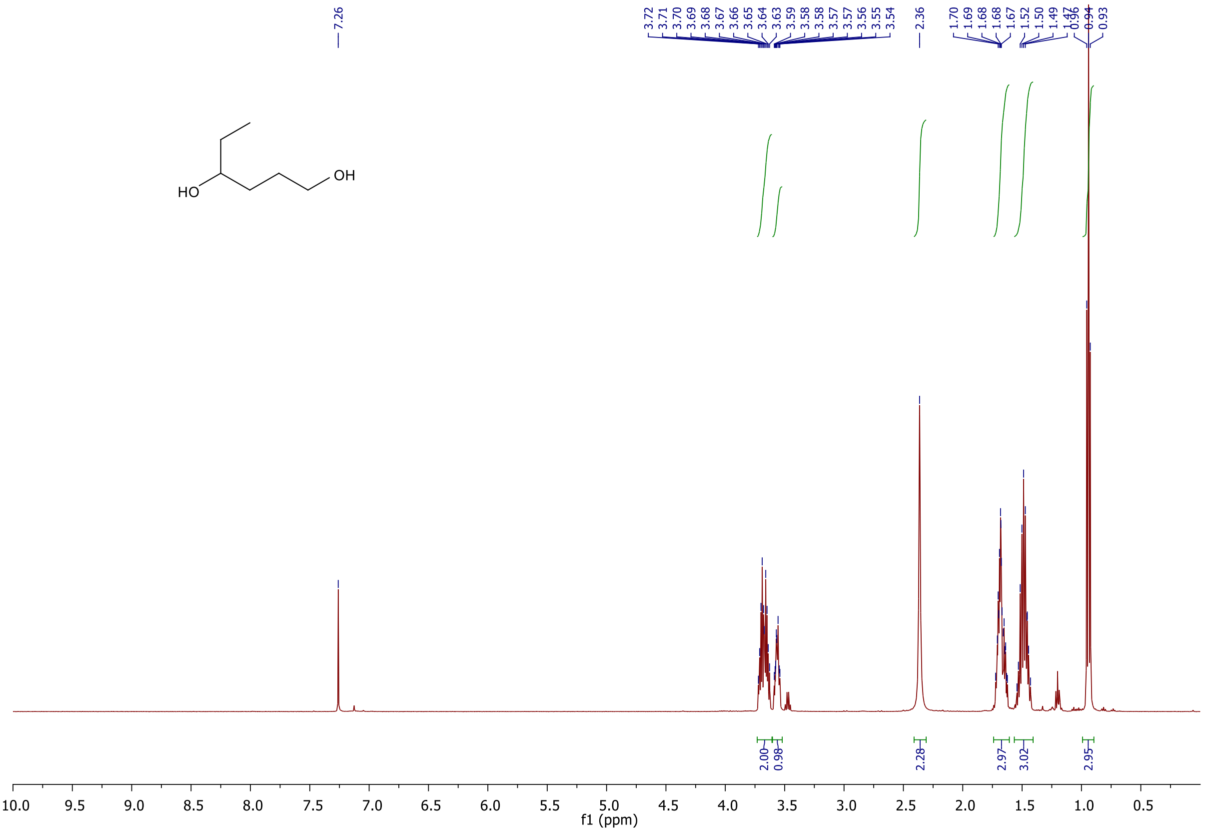


Figure S16: ^{1}H-NMR (600 MHz) in CDCl$_3$ of 1f

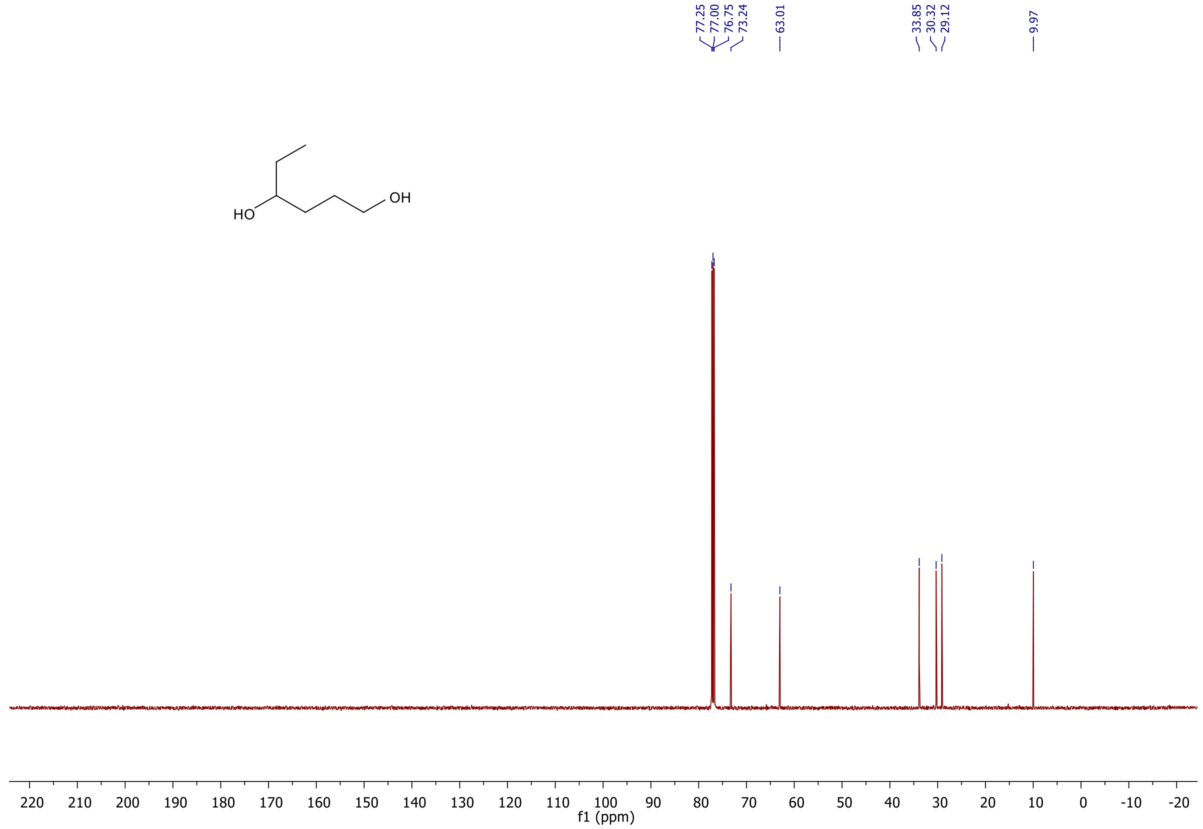


Figure S17: ^{13}C-NMR (600 MHz) in CDCl$_3$ of 1f

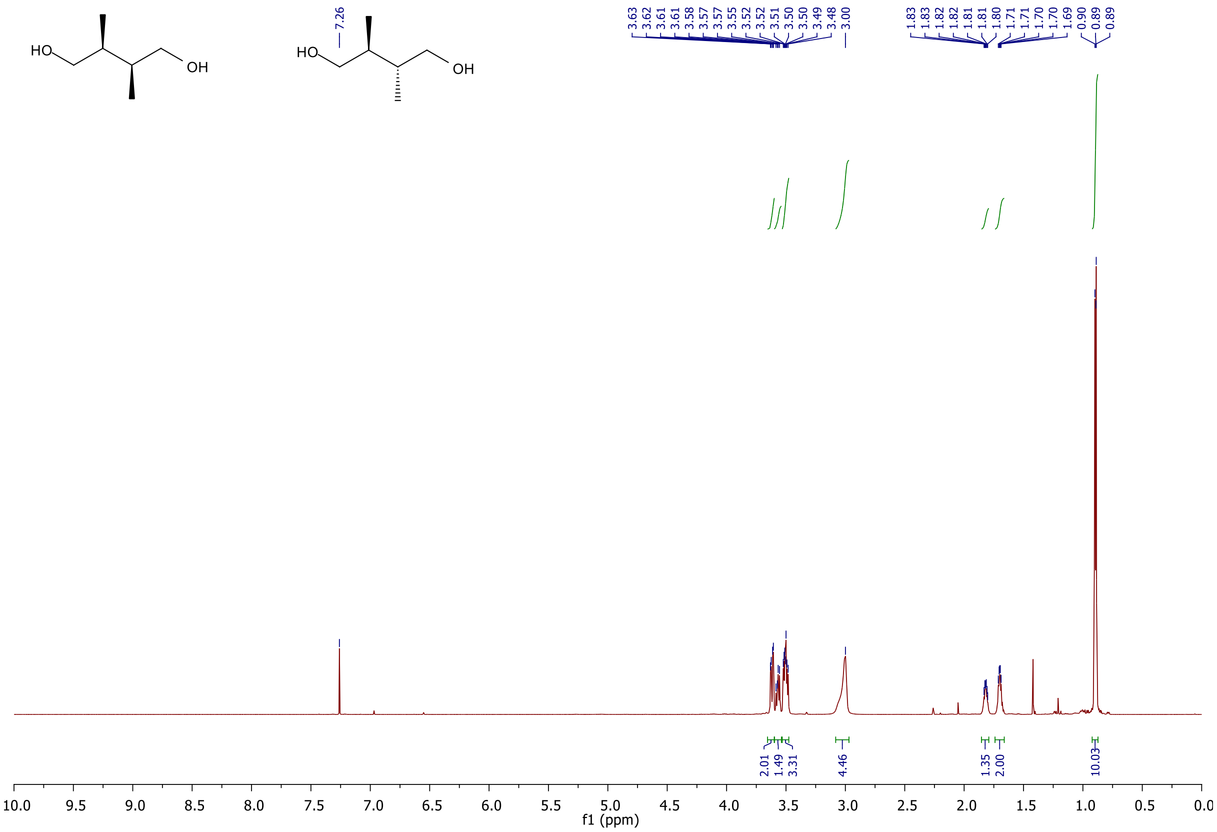


Figure S18: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 1g

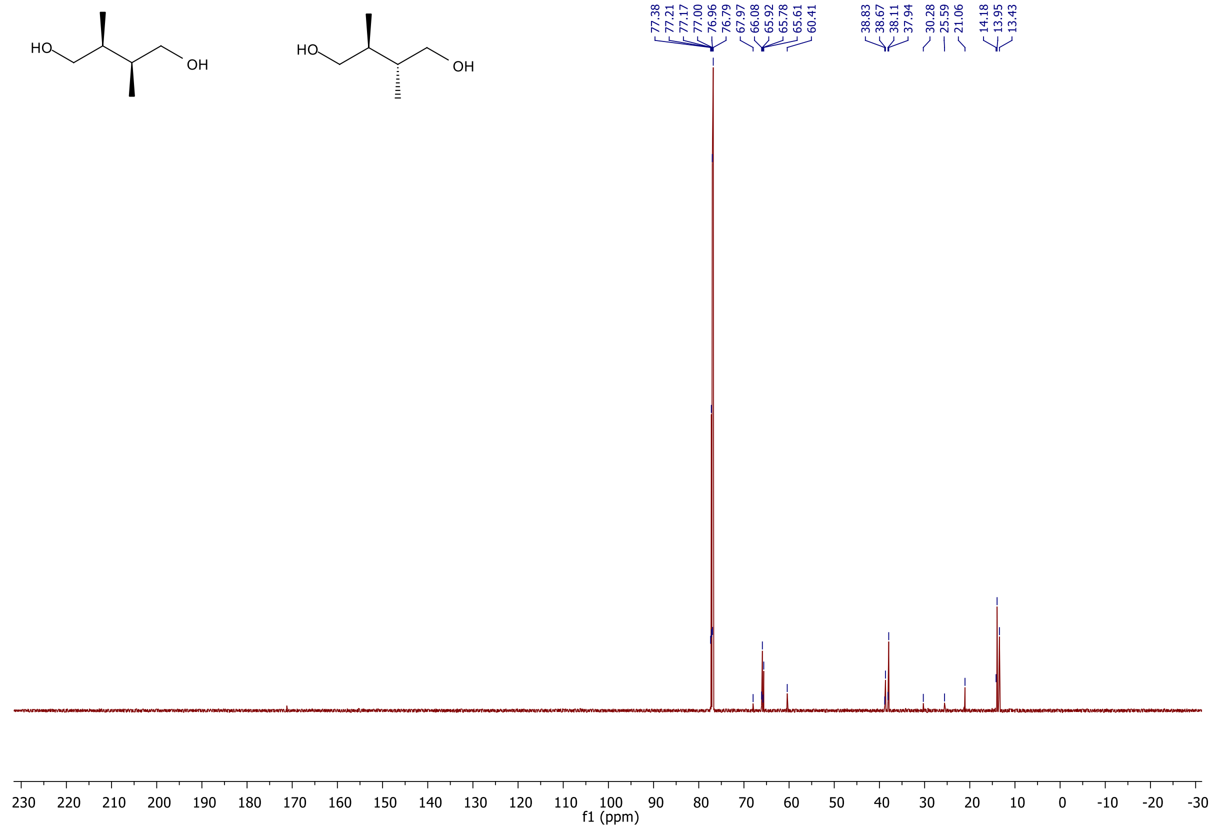


Figure S19: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 1g

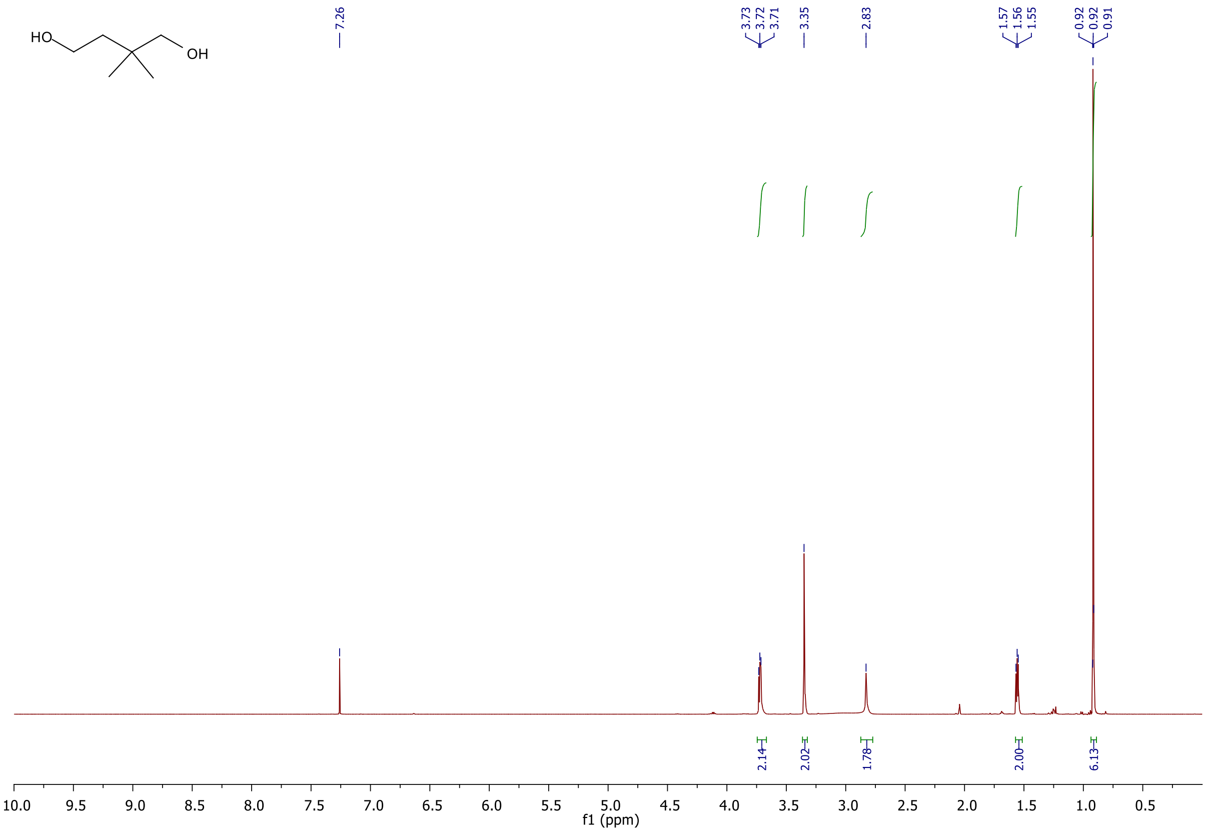


Figure S20: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 1h

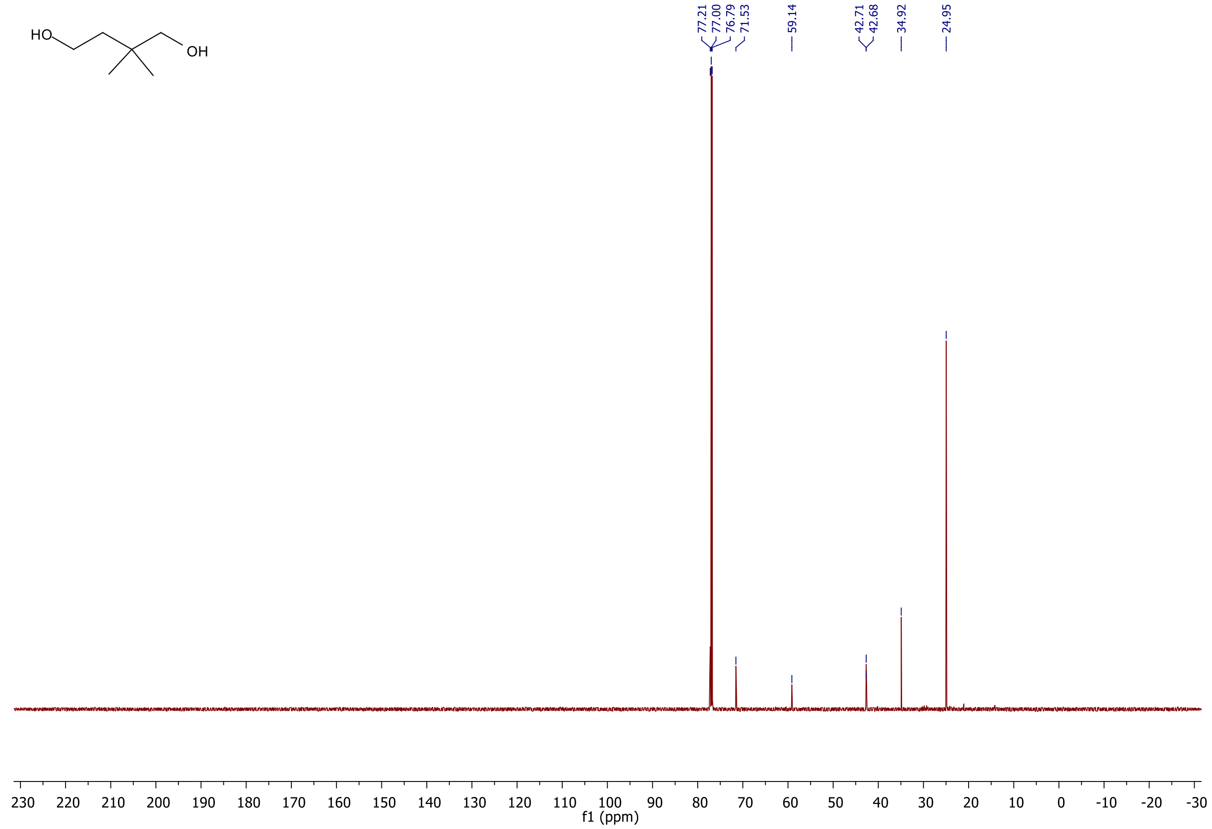


Figure S21: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 1h

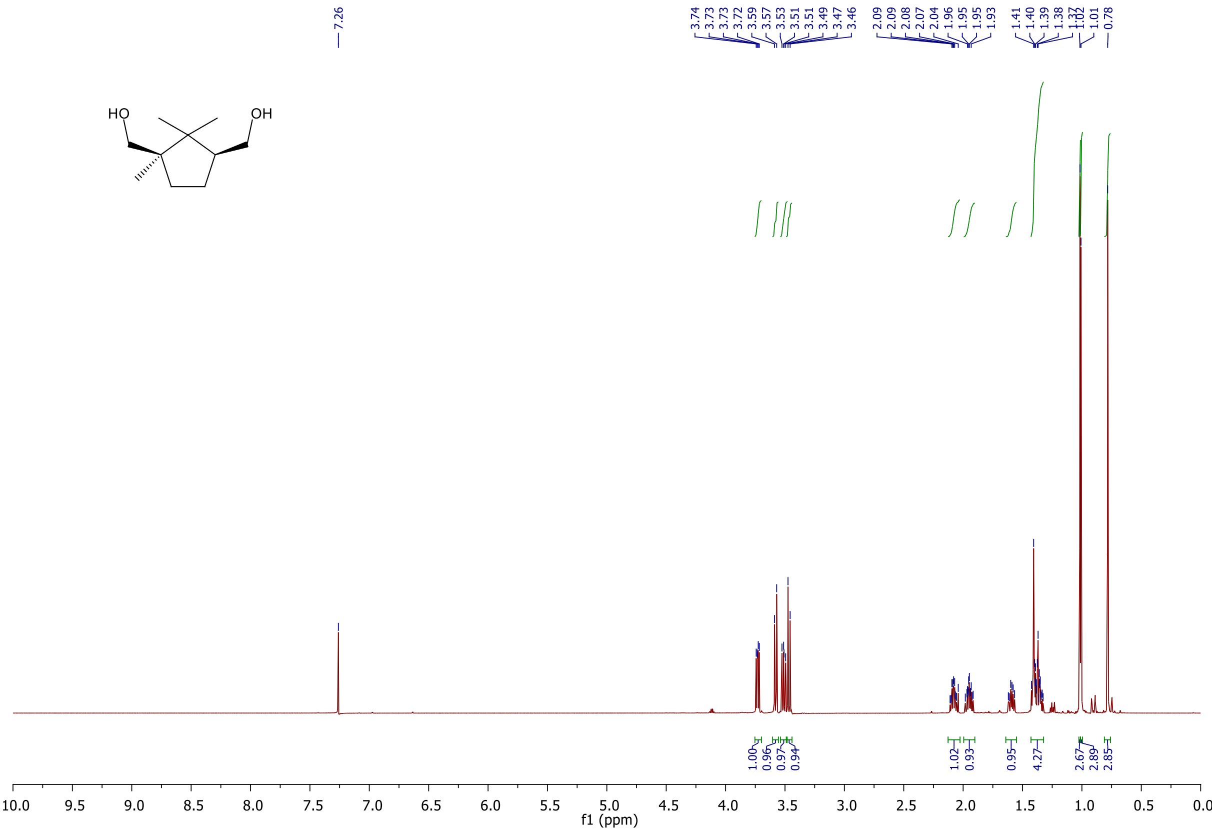


Figure S22: ^{1}H-NMR (600 MHz) in CDCl$_3$ of 1i

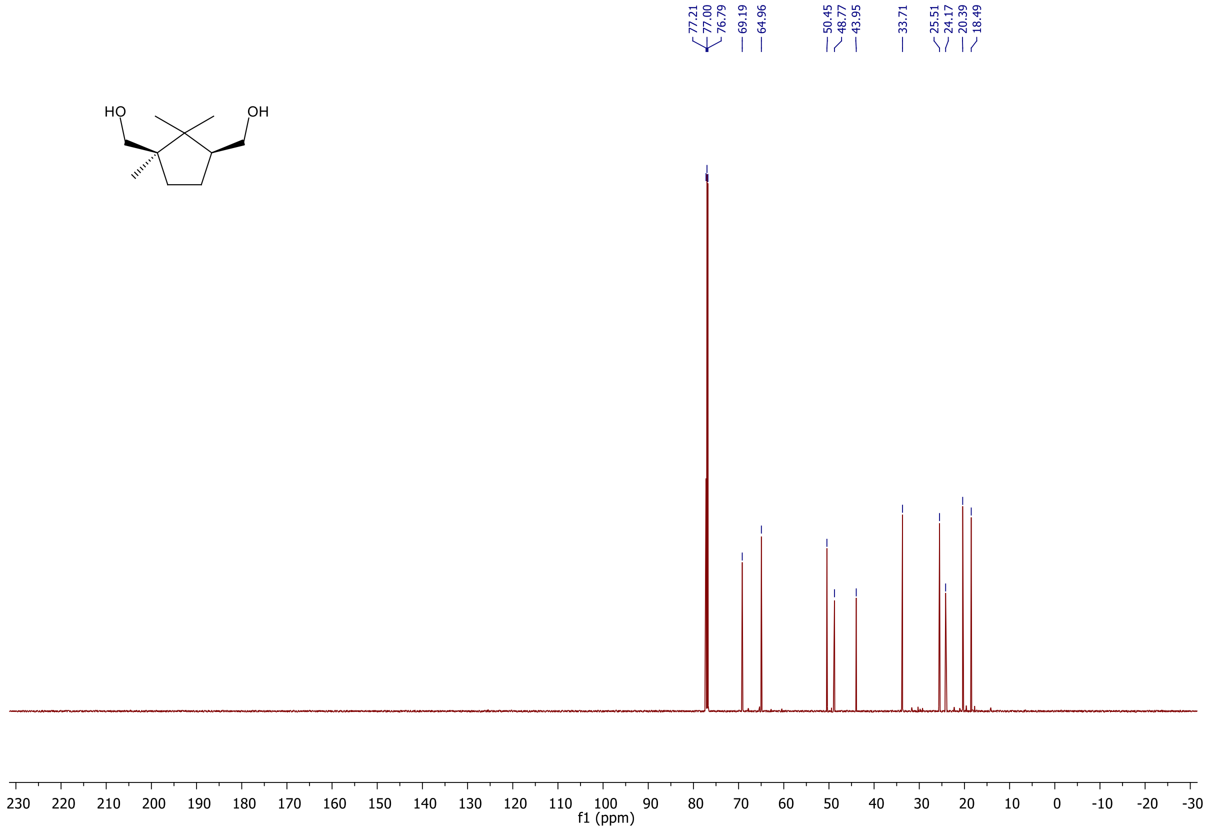


Figure S23: ^{13}C-NMR (150 MHz) in CDCl$_3$ of 1i

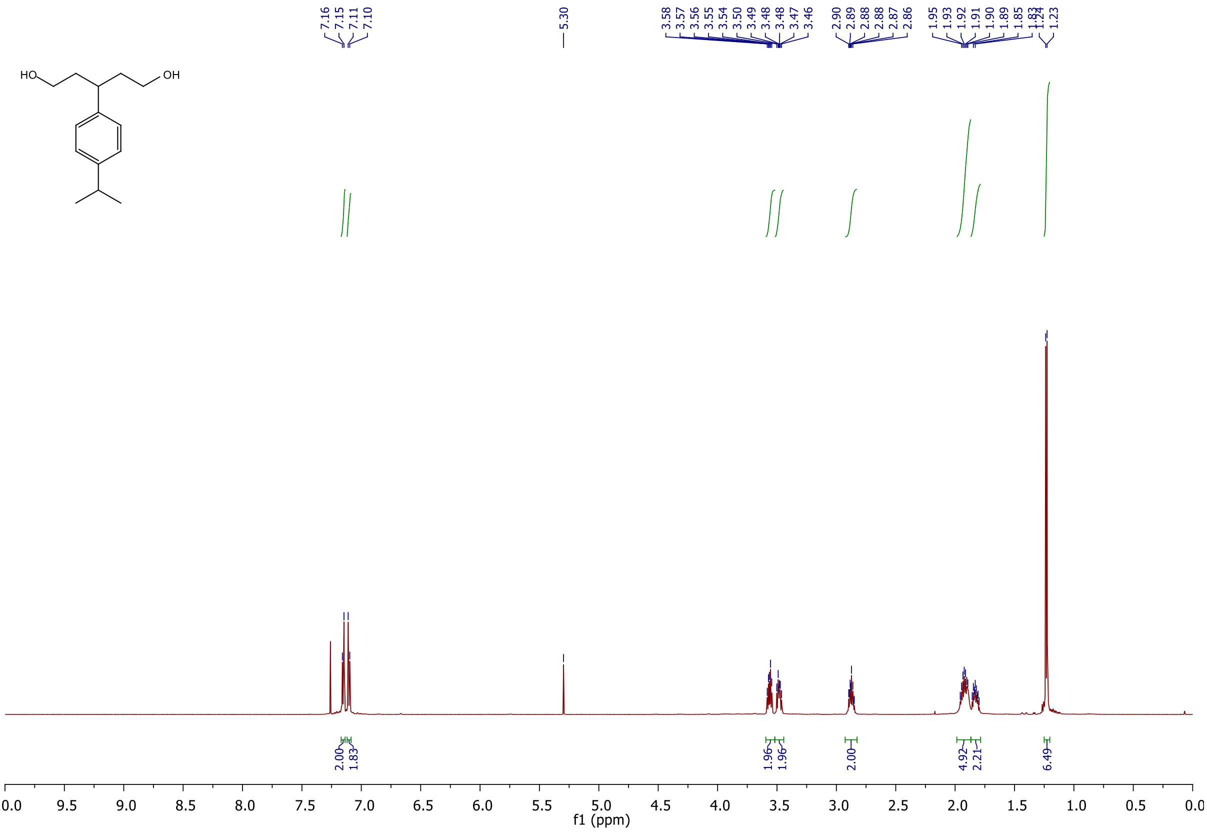


Figure S24: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 1j

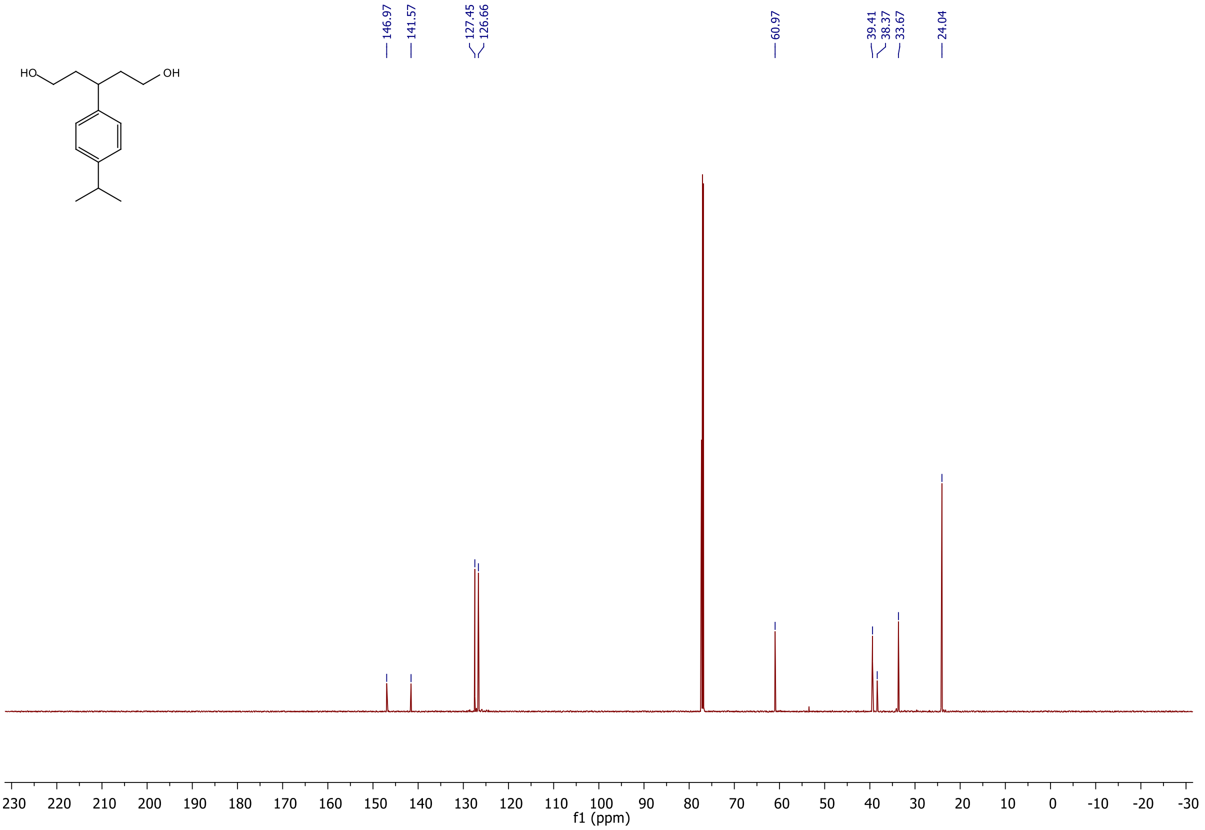


Figure S25: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 1j

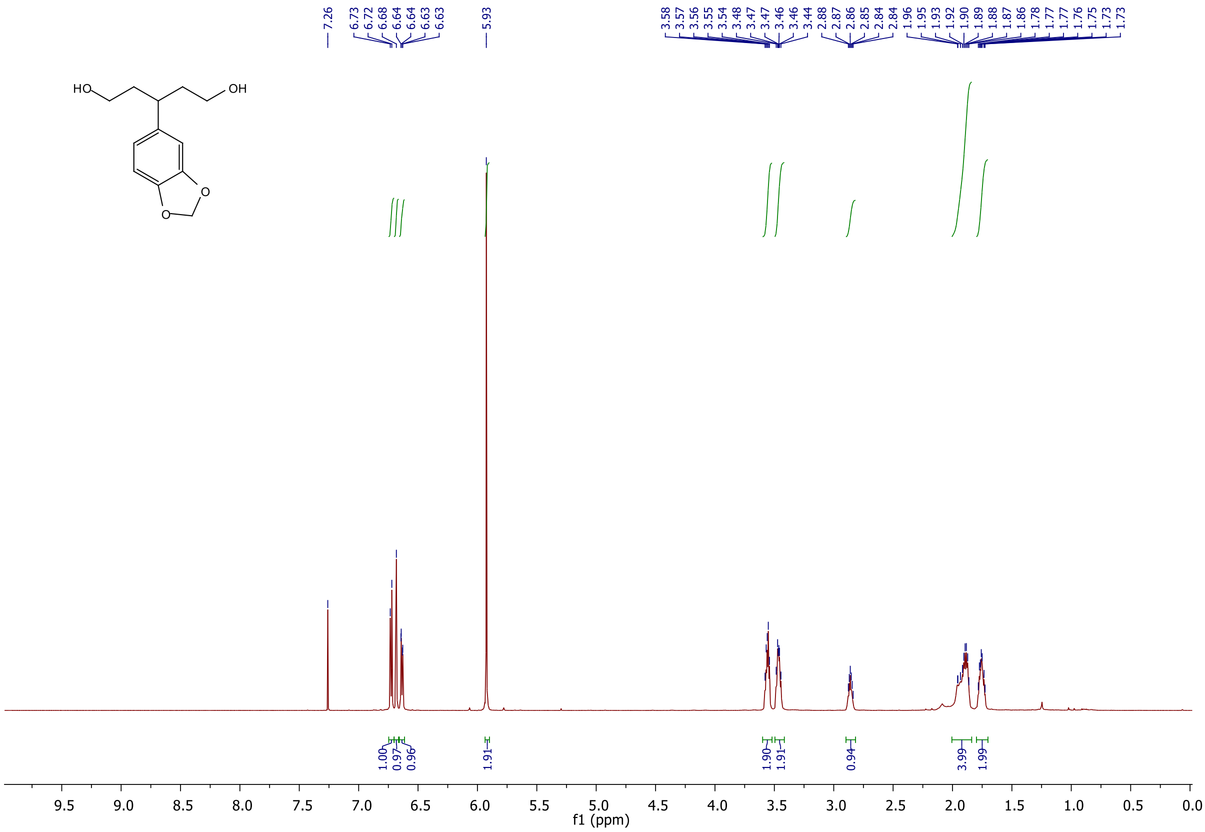


Figure S26: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 1k

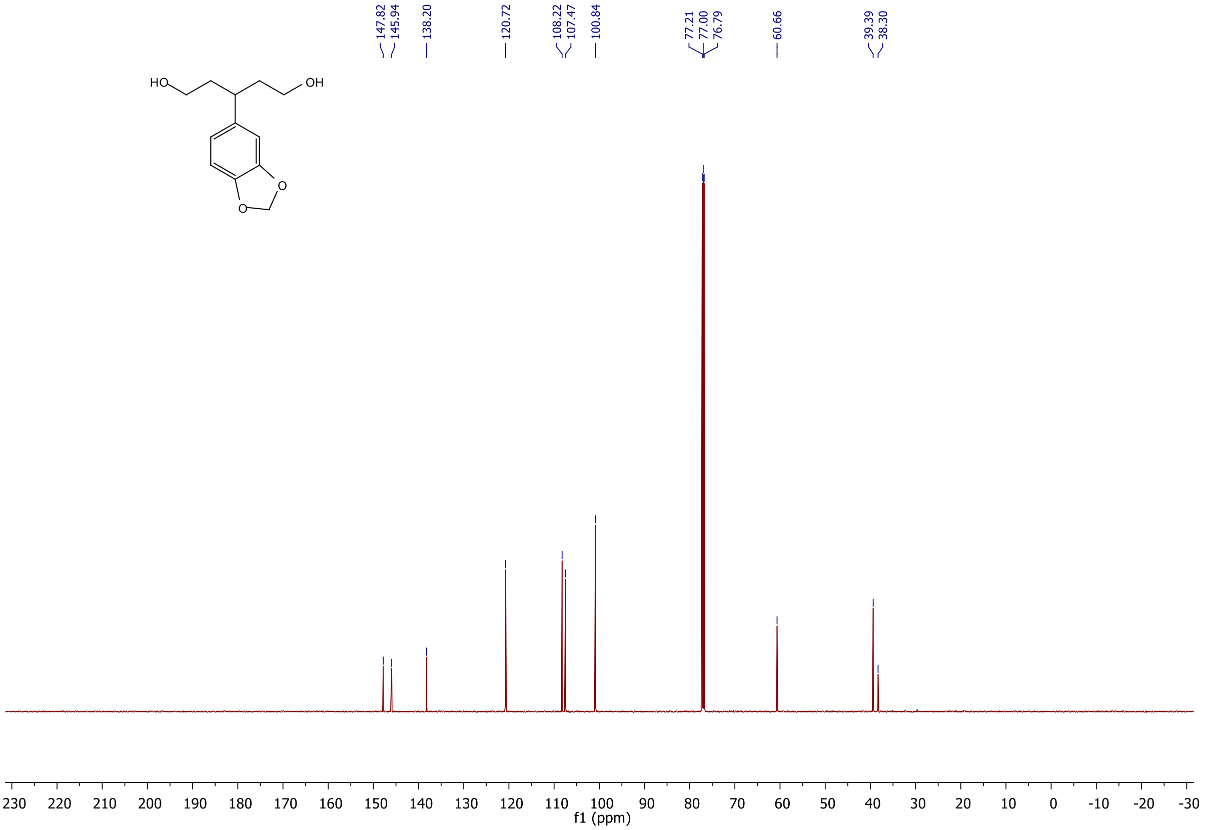


Figure S27: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 1k

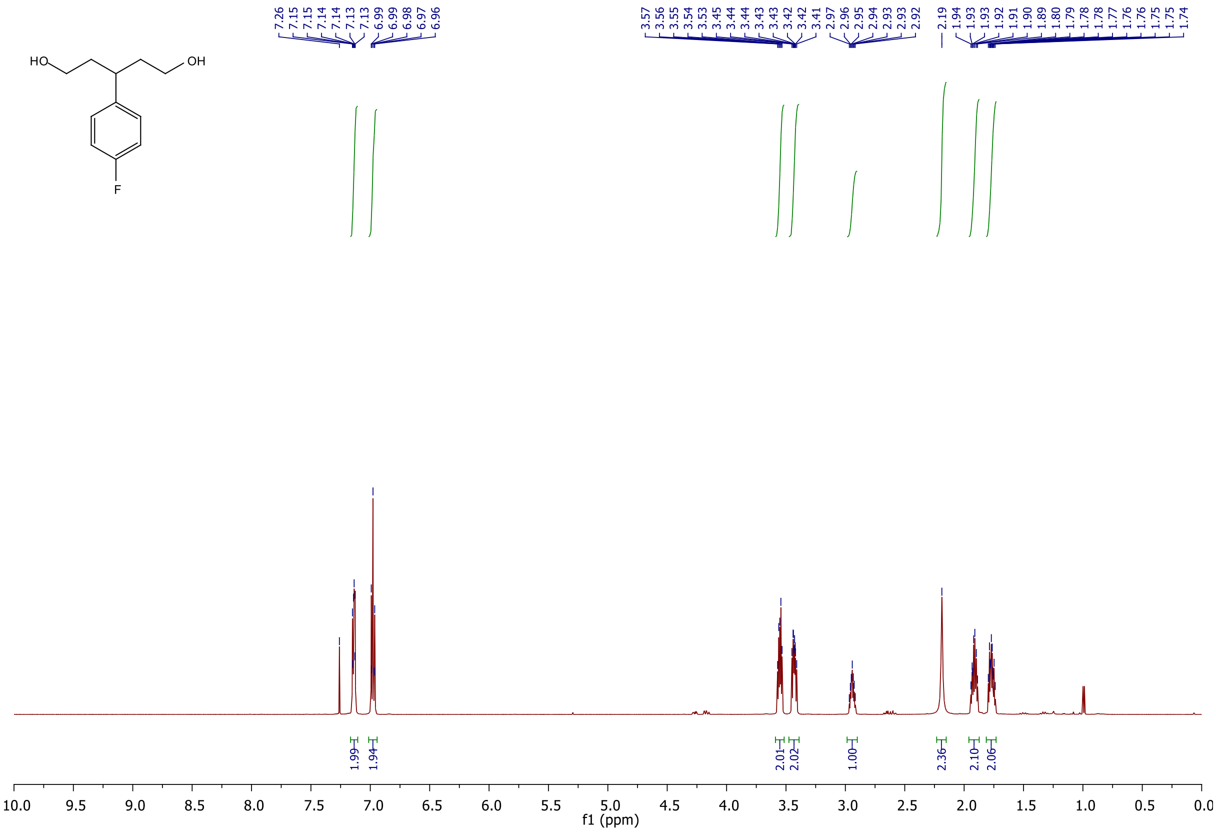


Figure S28: ^{1}H-NMR (600 MHz) in CDCl$_3$ of 1l

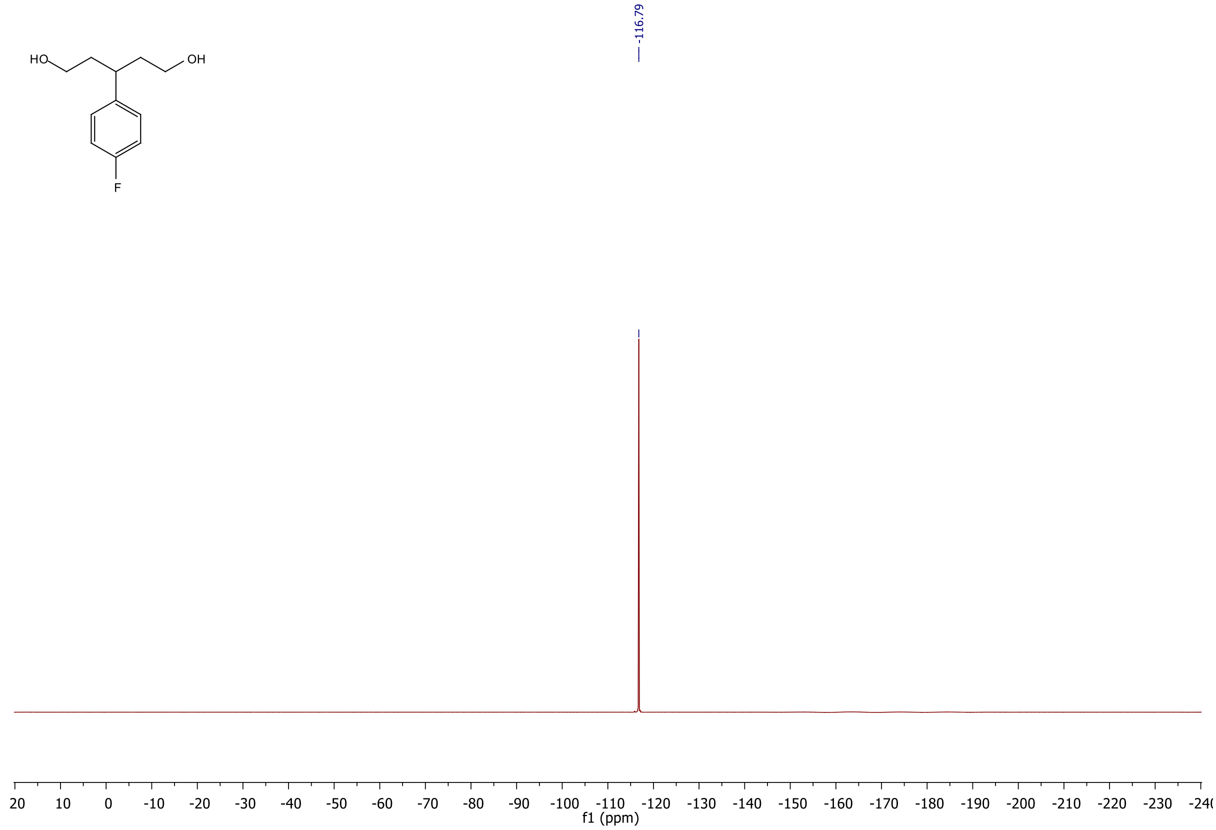


Figure S29: ^{19}F-NMR (600 MHz) in CDCl$_3$ of 1l

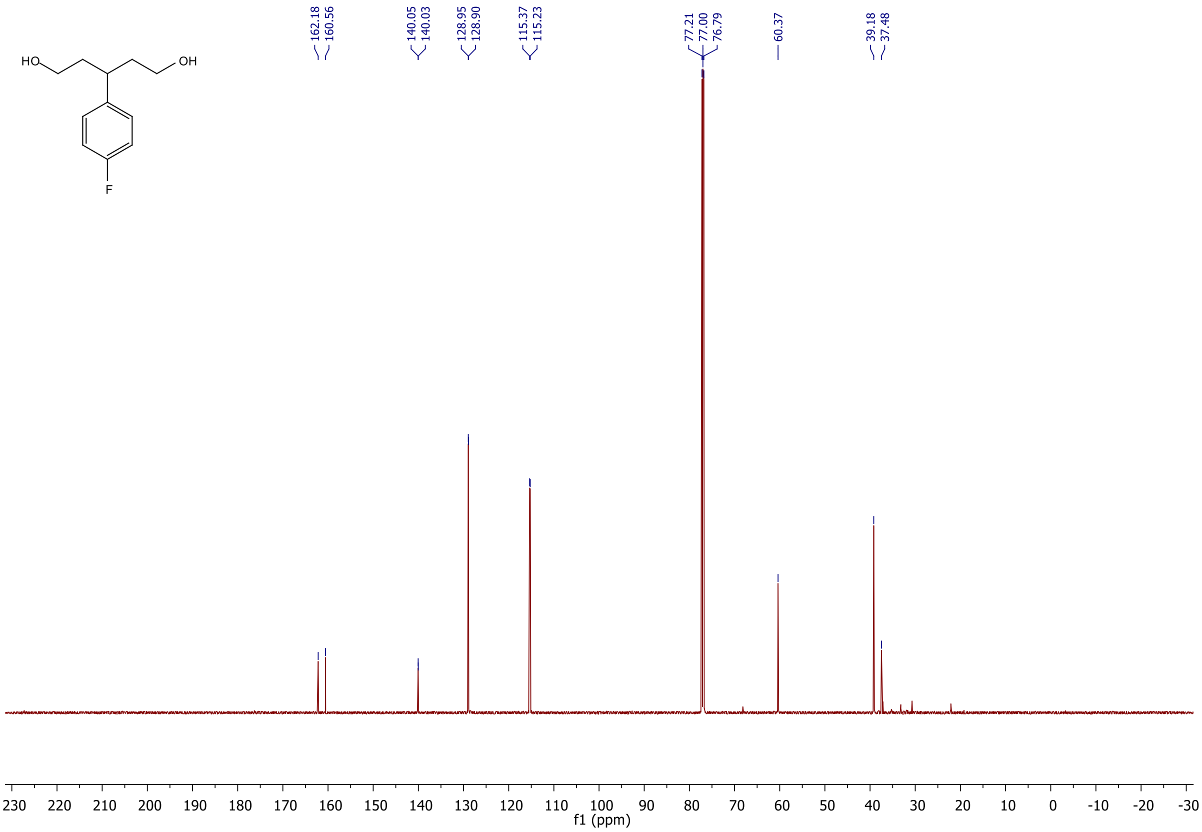


Figure S30: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 1l

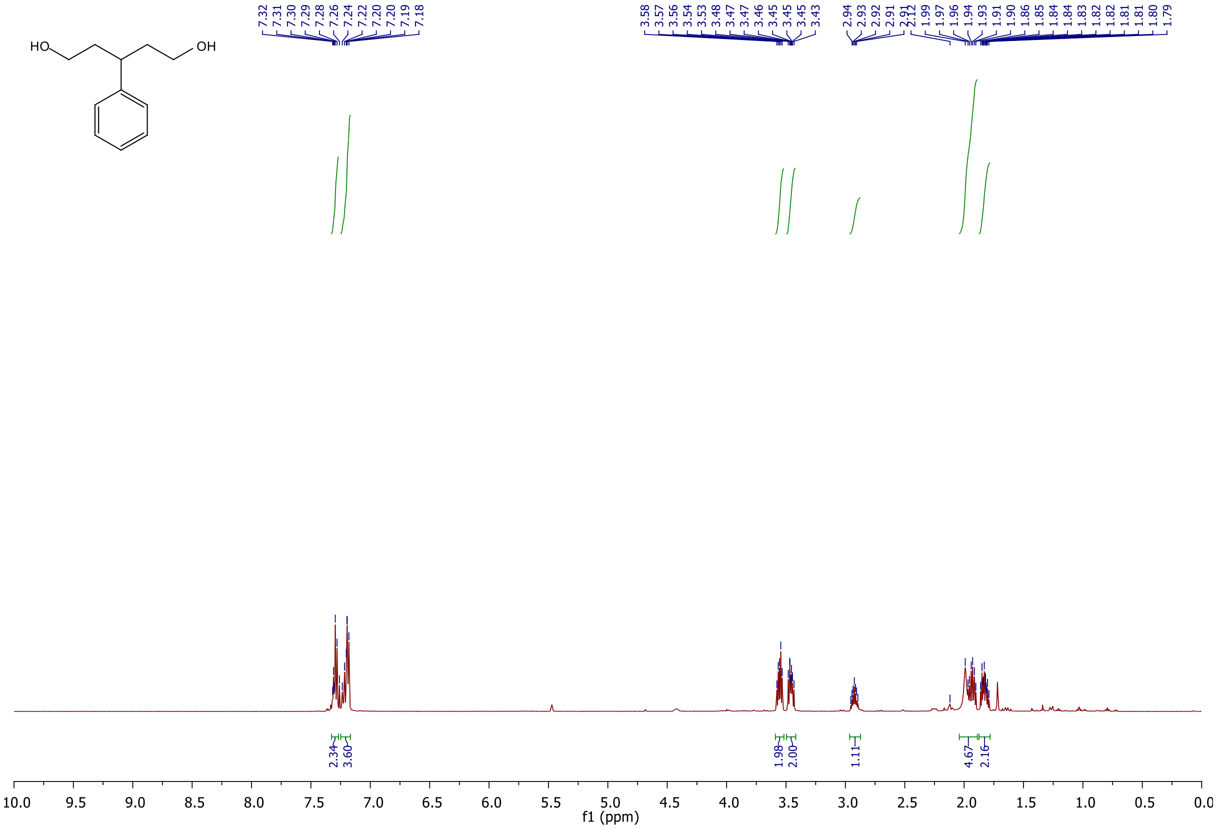


Figure S31: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 1m

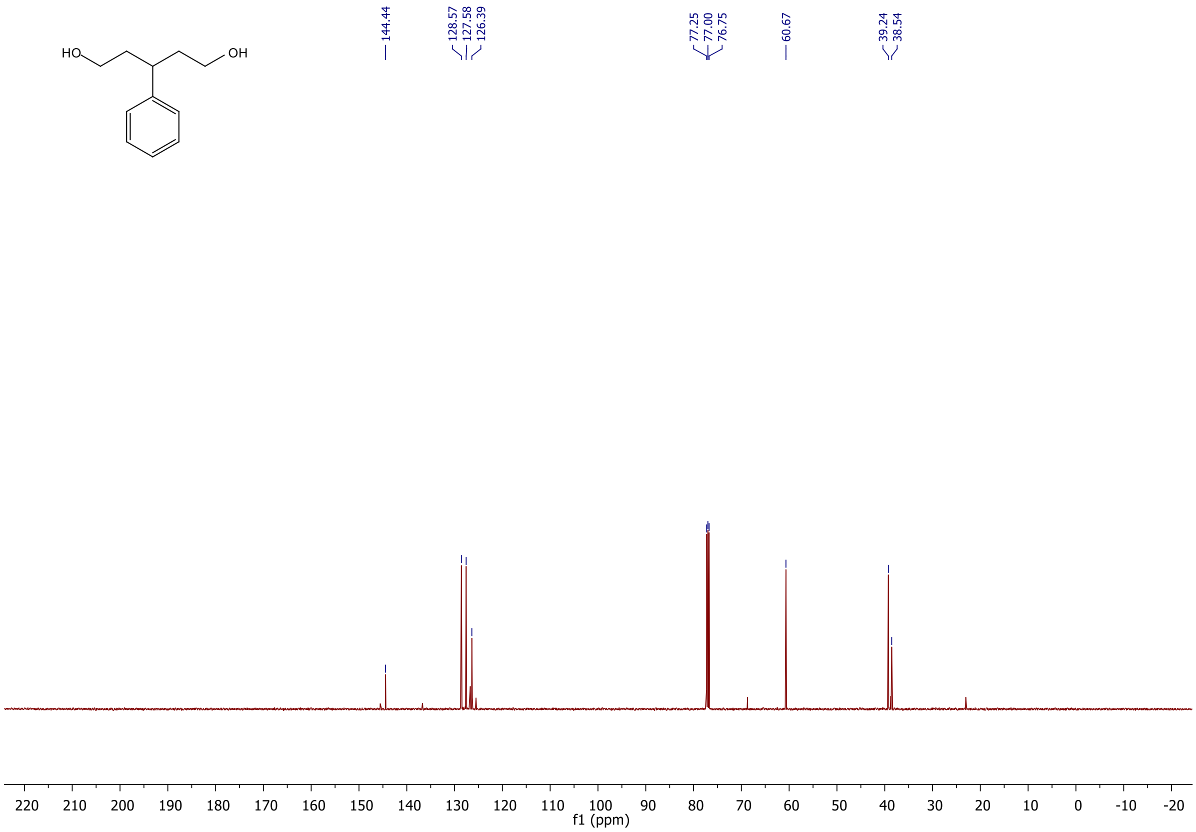


Figure S32: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 1m

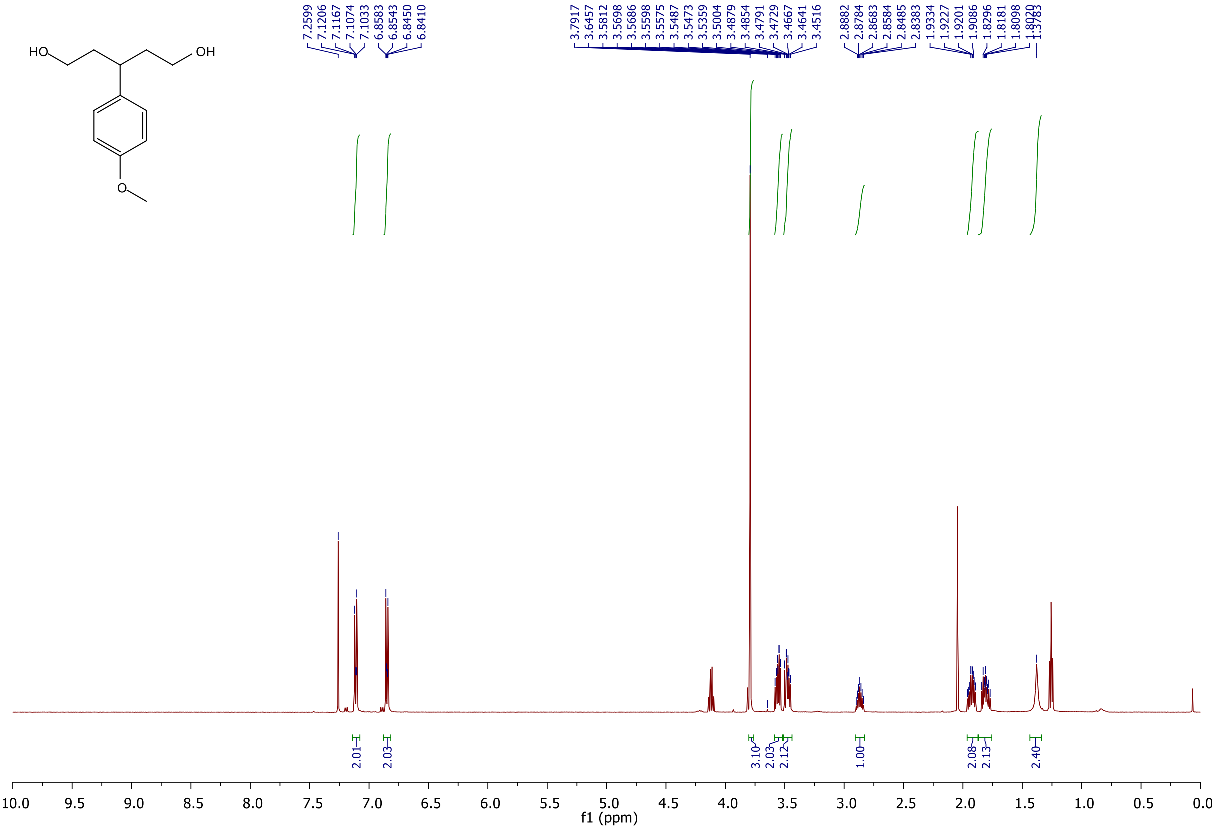


Figure S33: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 1n

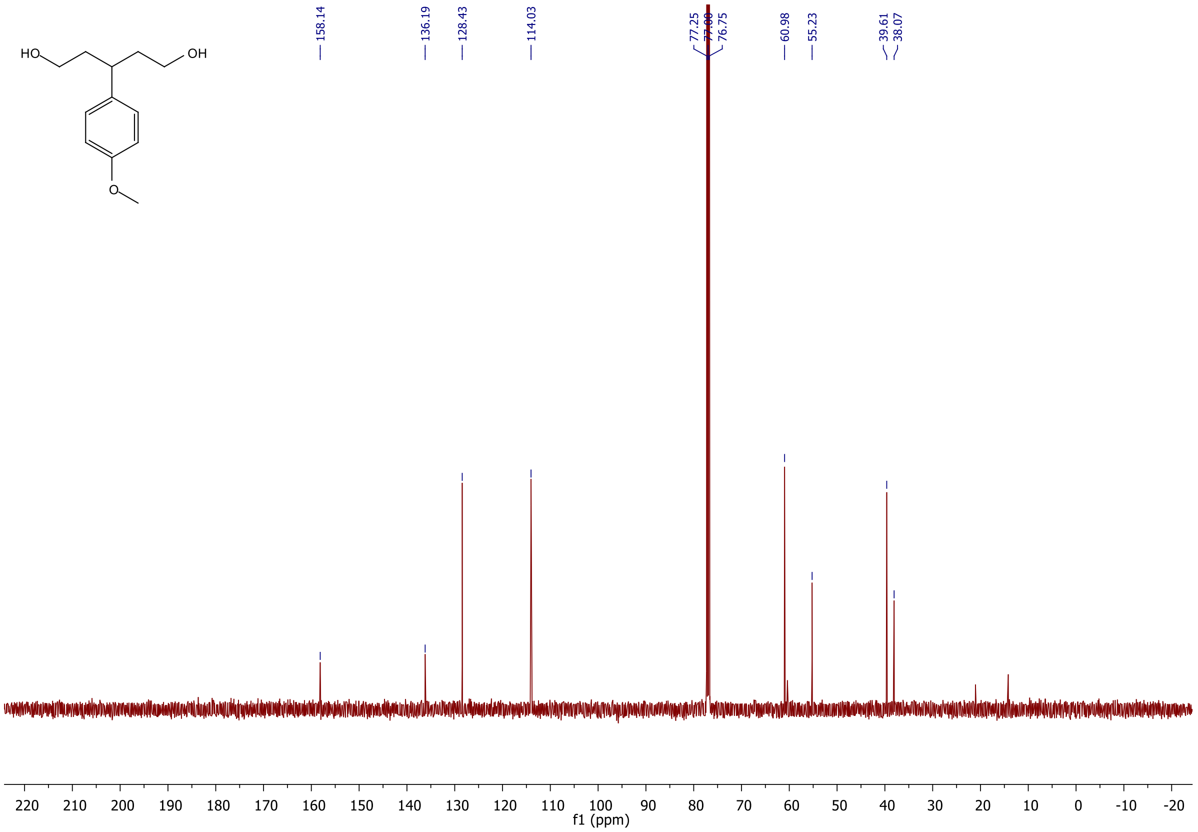


Figure S34: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 1n

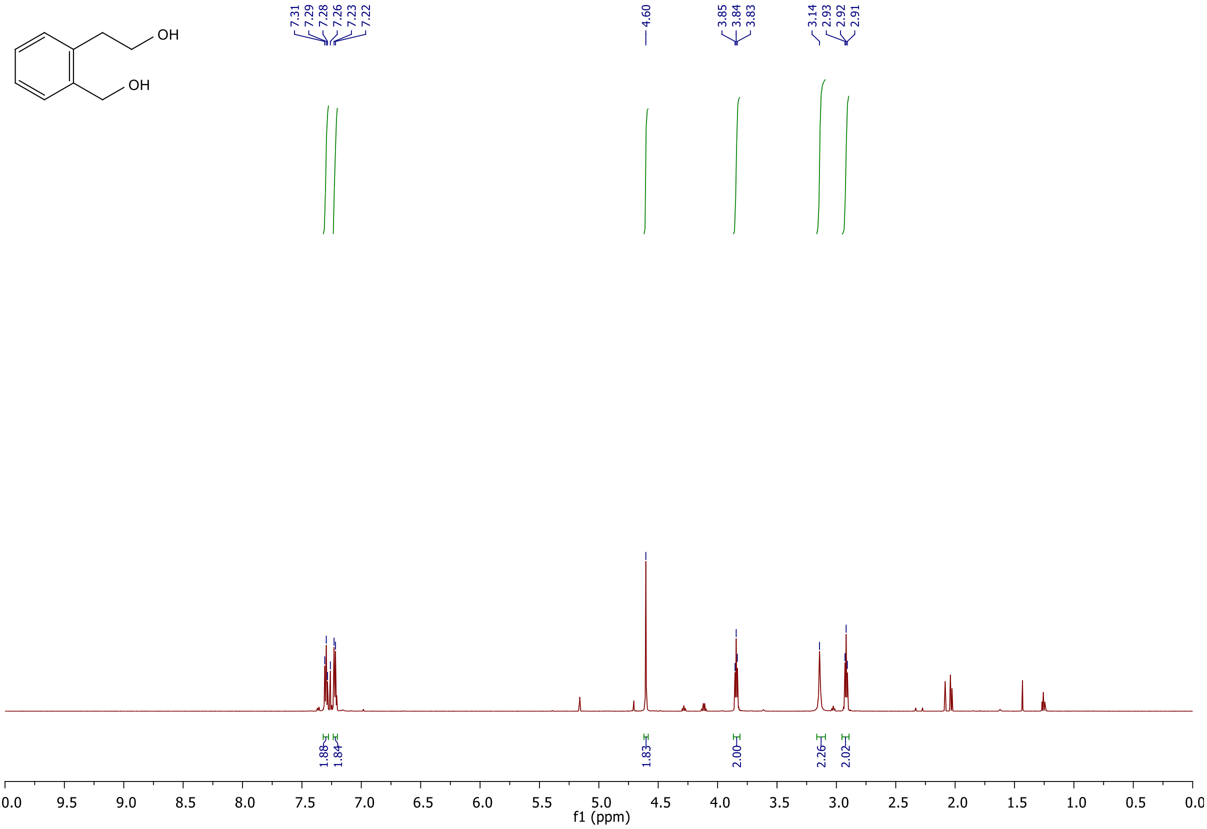


Figure S35: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 1o

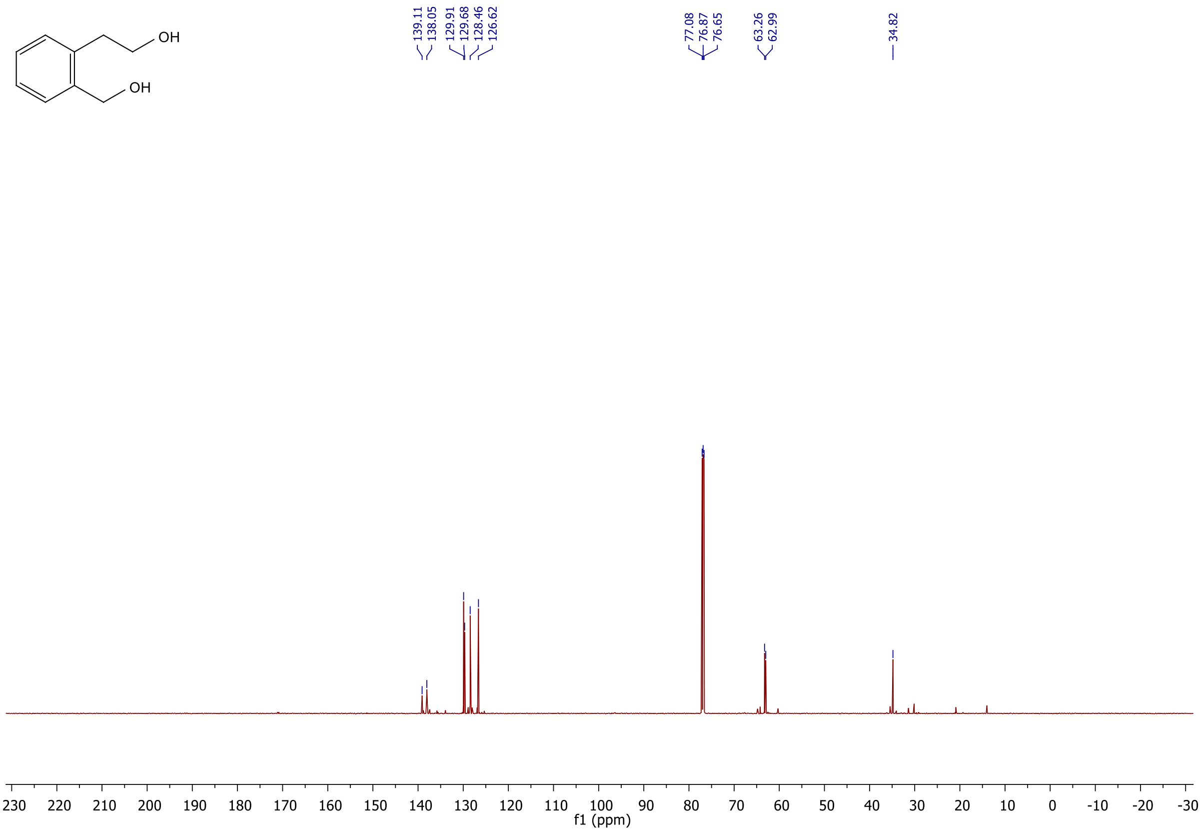


Figure S36: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 1o

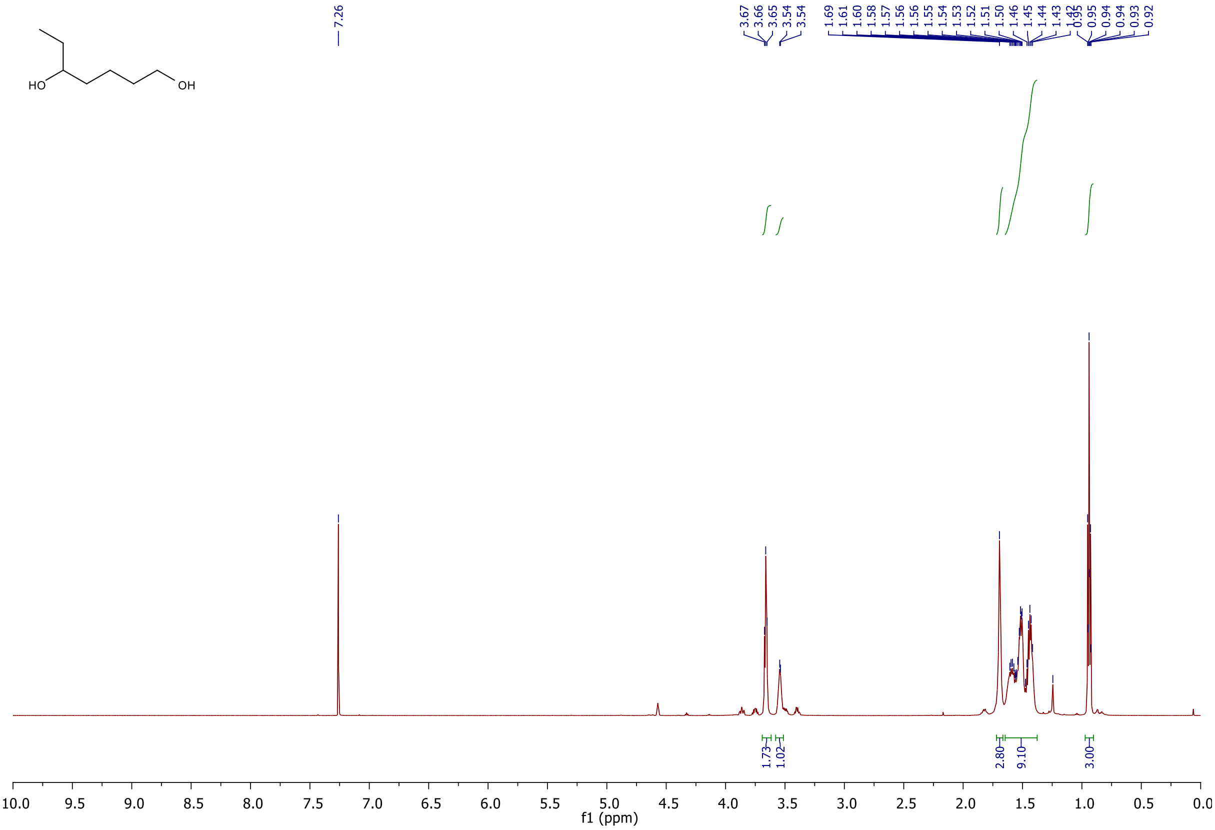


Figure S37: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 1p

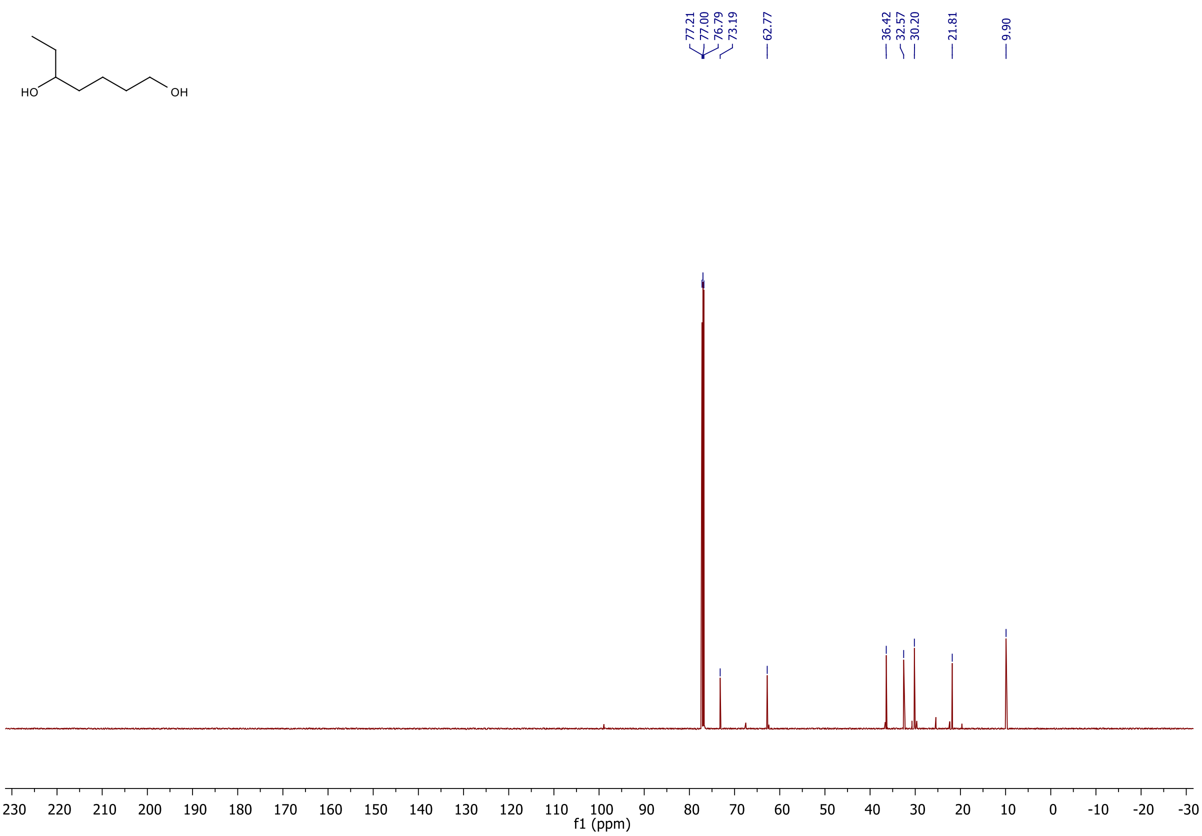


Figure S38: ^{13}C-NMR (150 MHz) in CDCl$_3$ of 1p

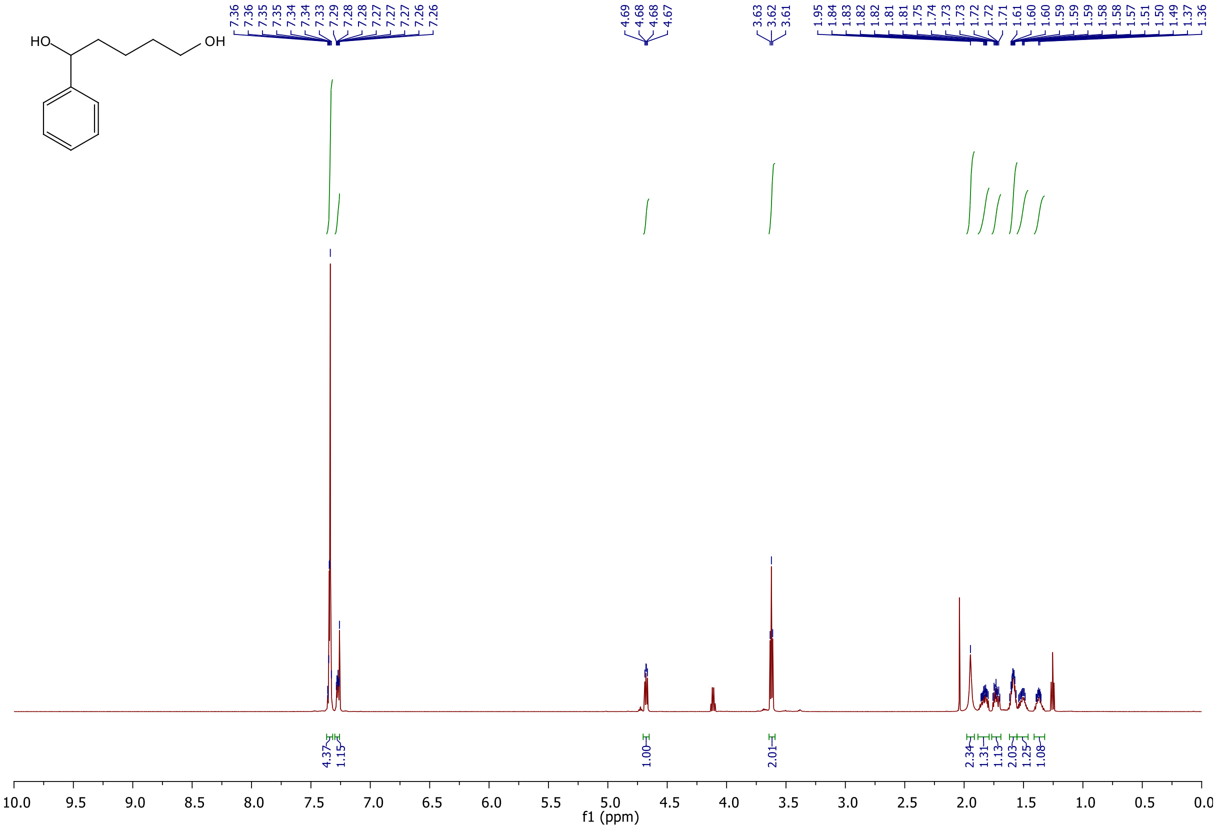


Figure S39: ^{1}H-NMR (600 MHz) in CDCl$_3$ of 1q

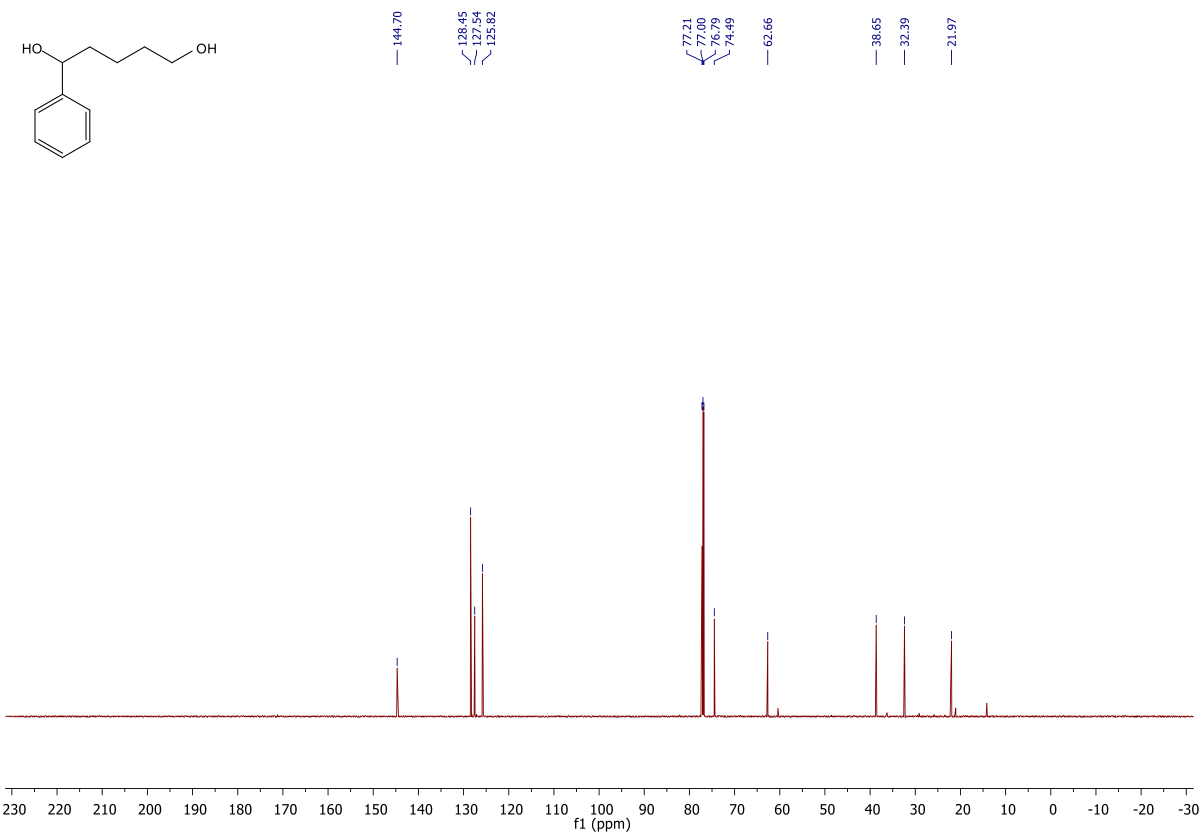


Figure S40: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 1q

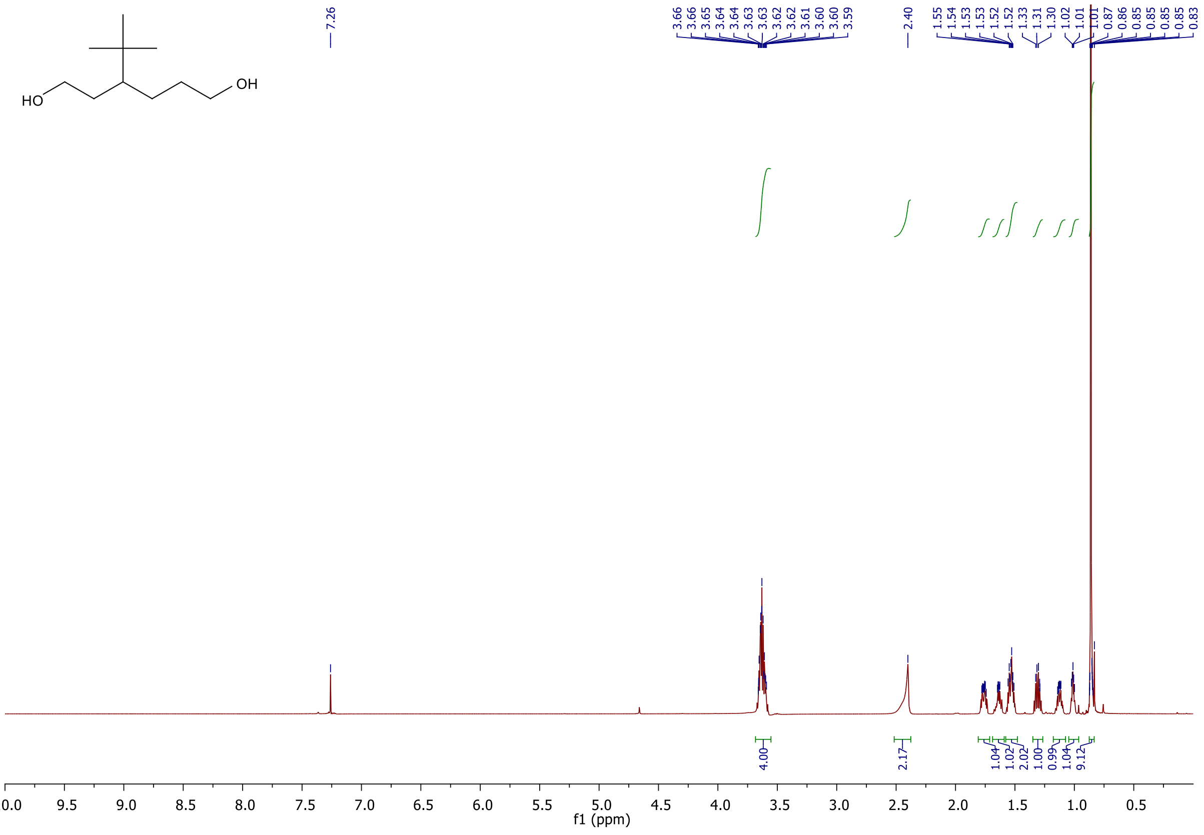


Figure S41: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 1r

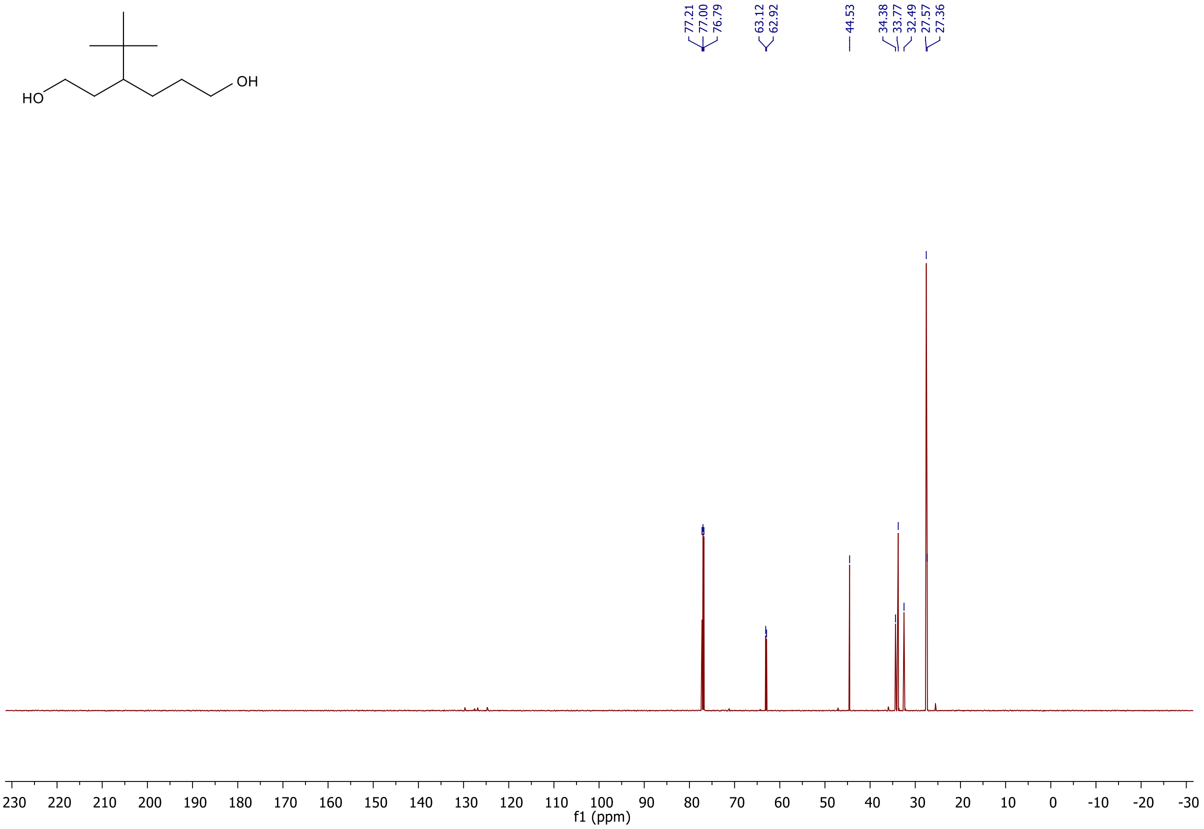


Figure S42: ^{13}C-NMR (150 MHz) in CDCl$_3$ of **1r**

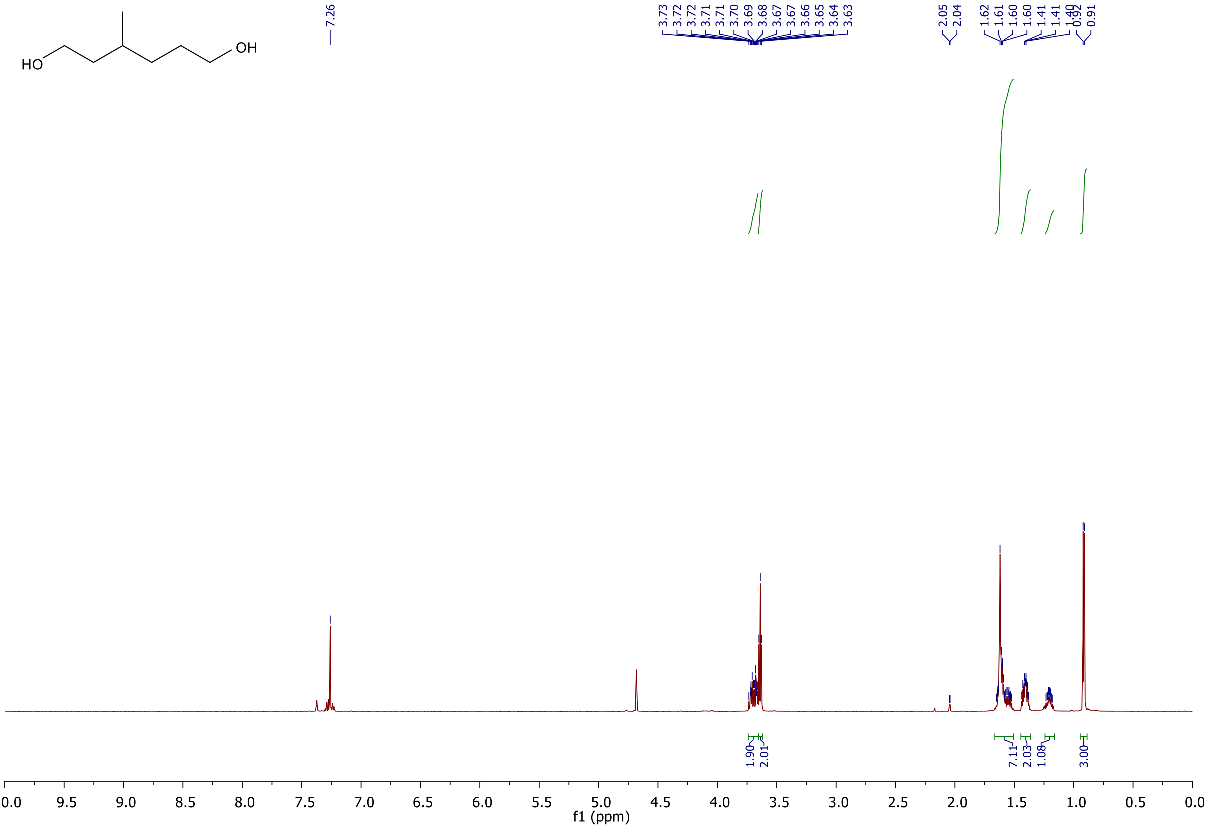


Figure S43: ^{1}H-NMR (600 MHz) in CDCl$_3$ of **1s**

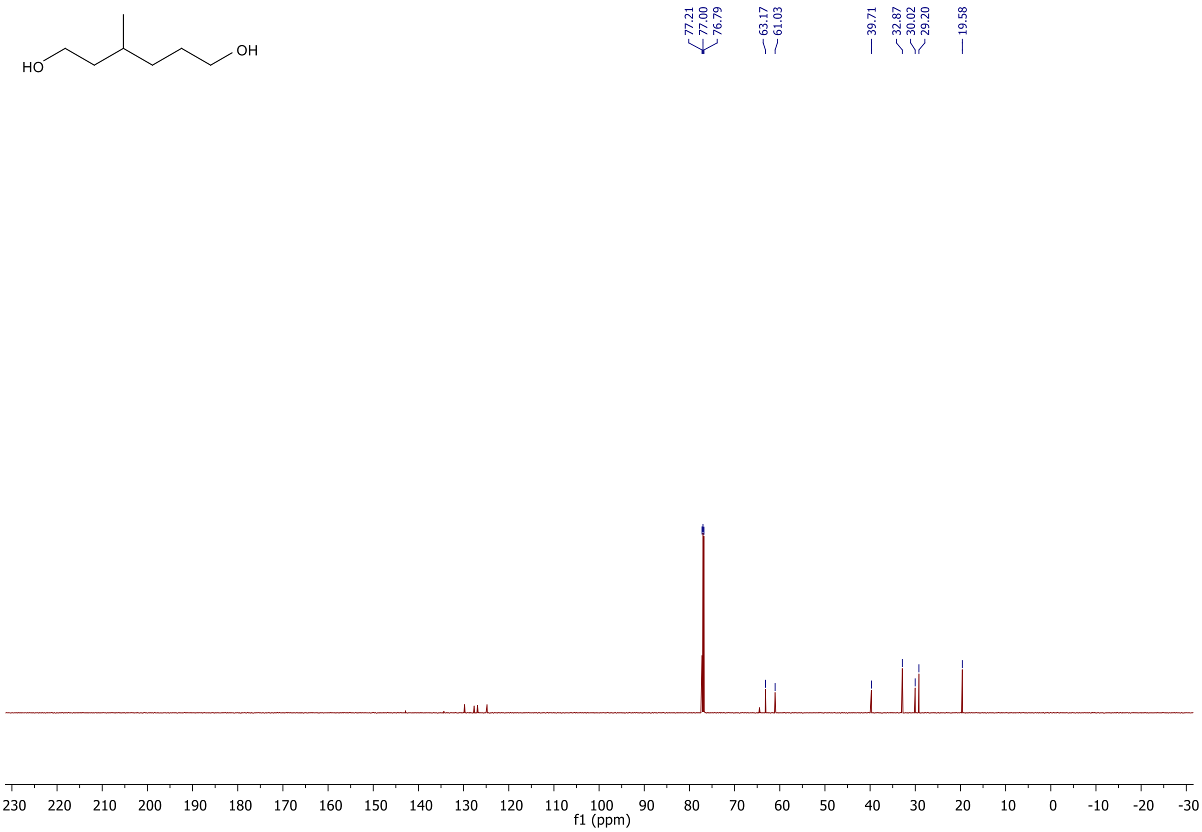


Figure S44: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 1s

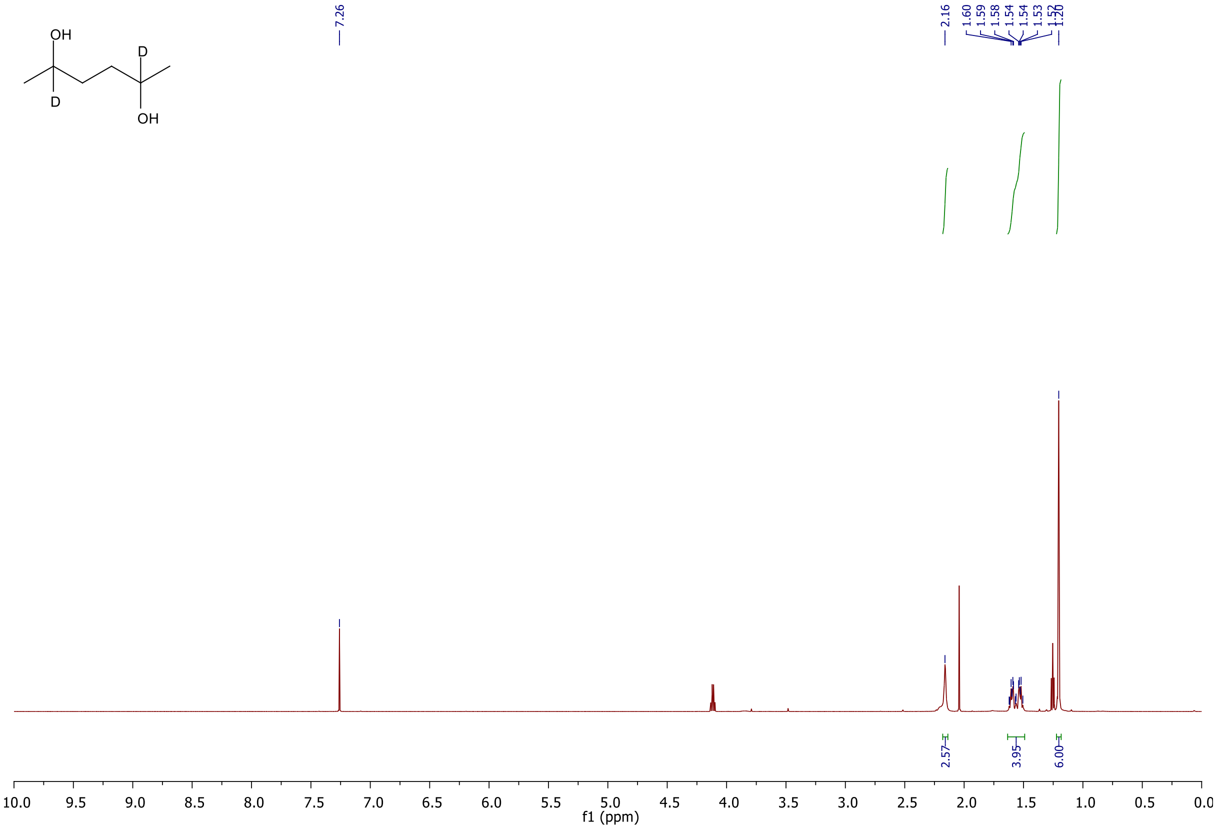


Figure S45: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 1t

Part 7: NMR spectra of products

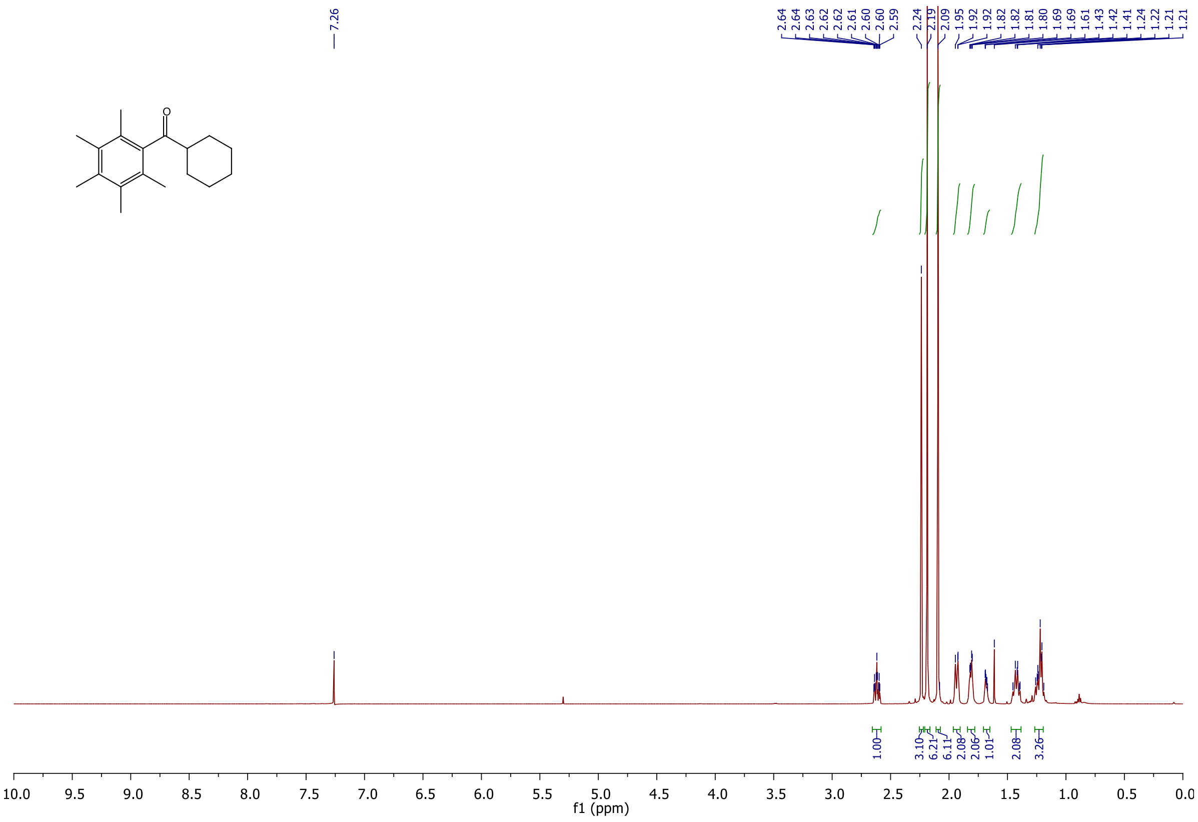


Figure S46: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 2a

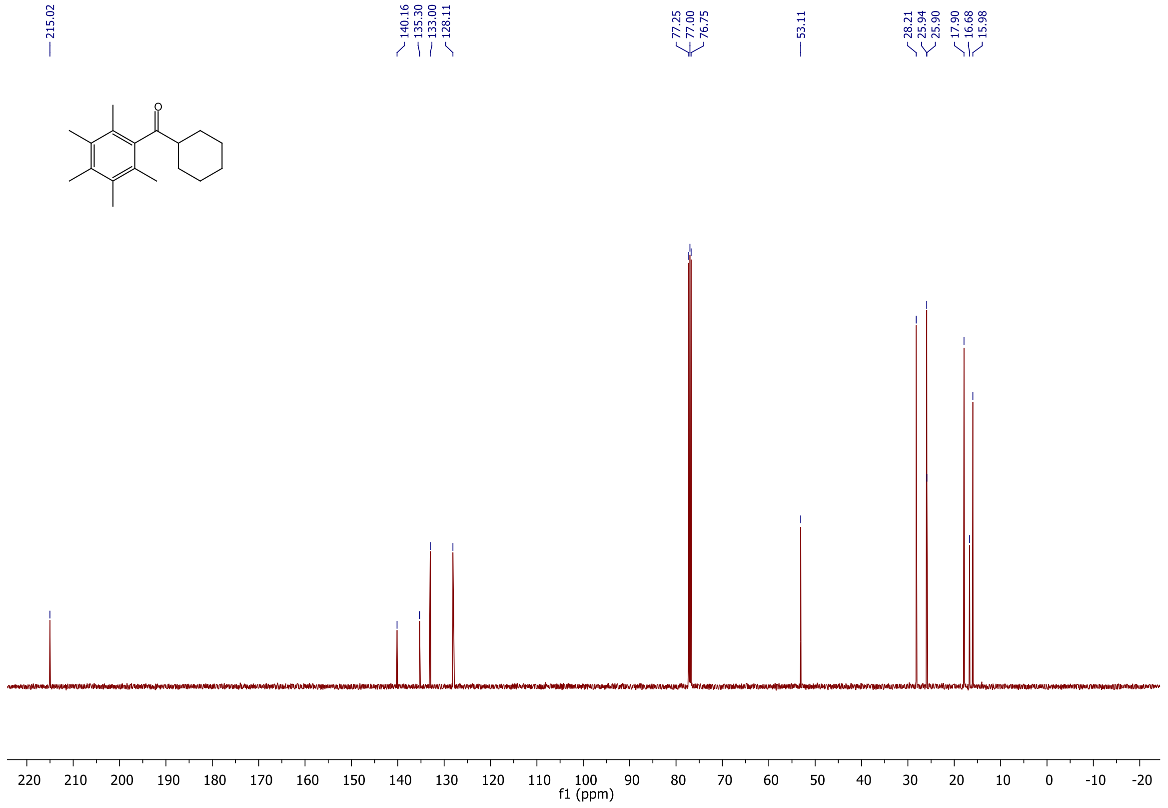


Figure S47: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 2a

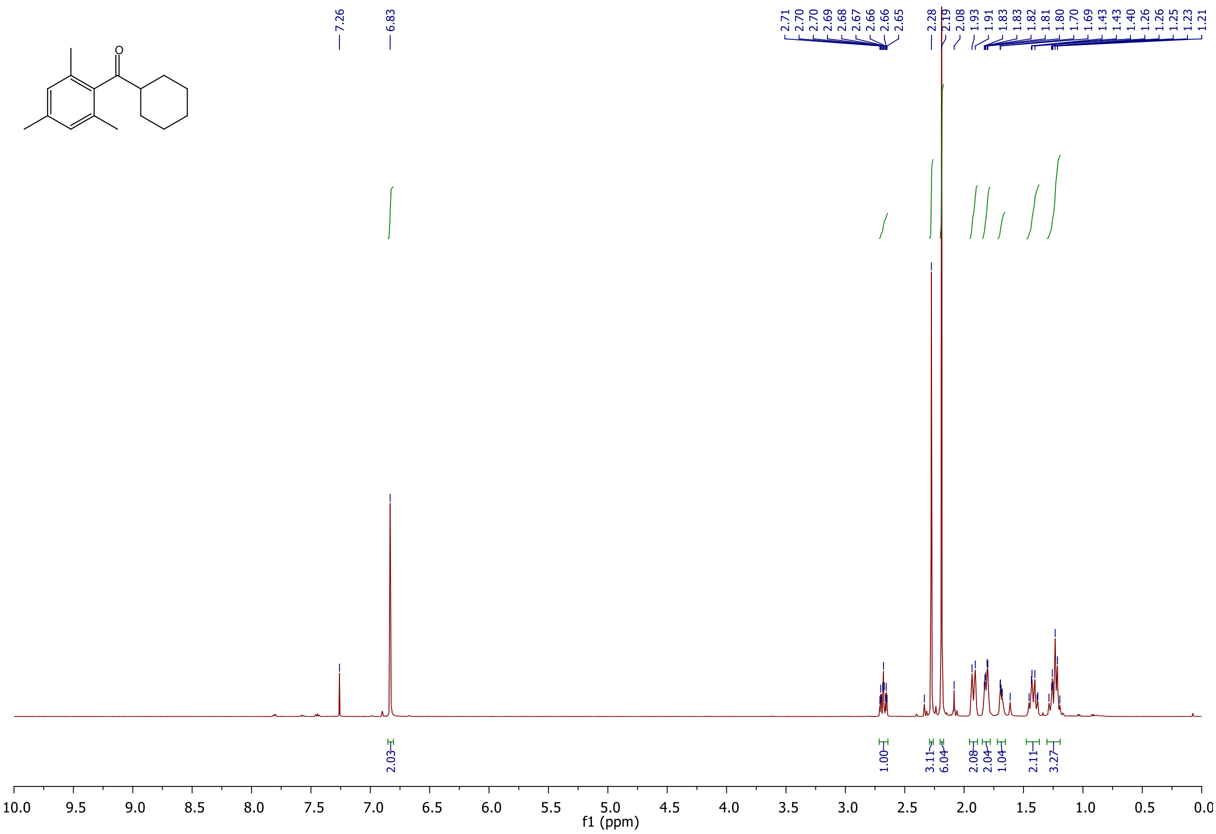


Figure S48: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 2b

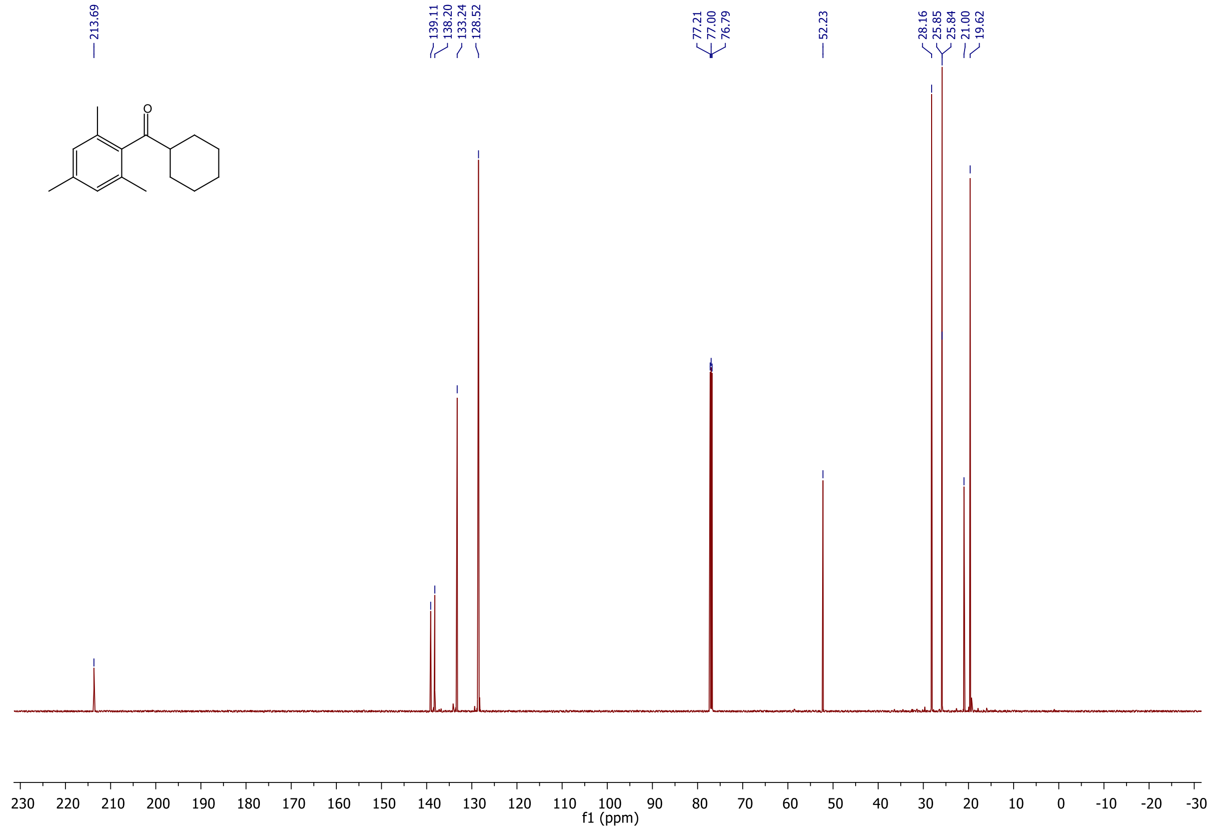


Figure S49: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 2b

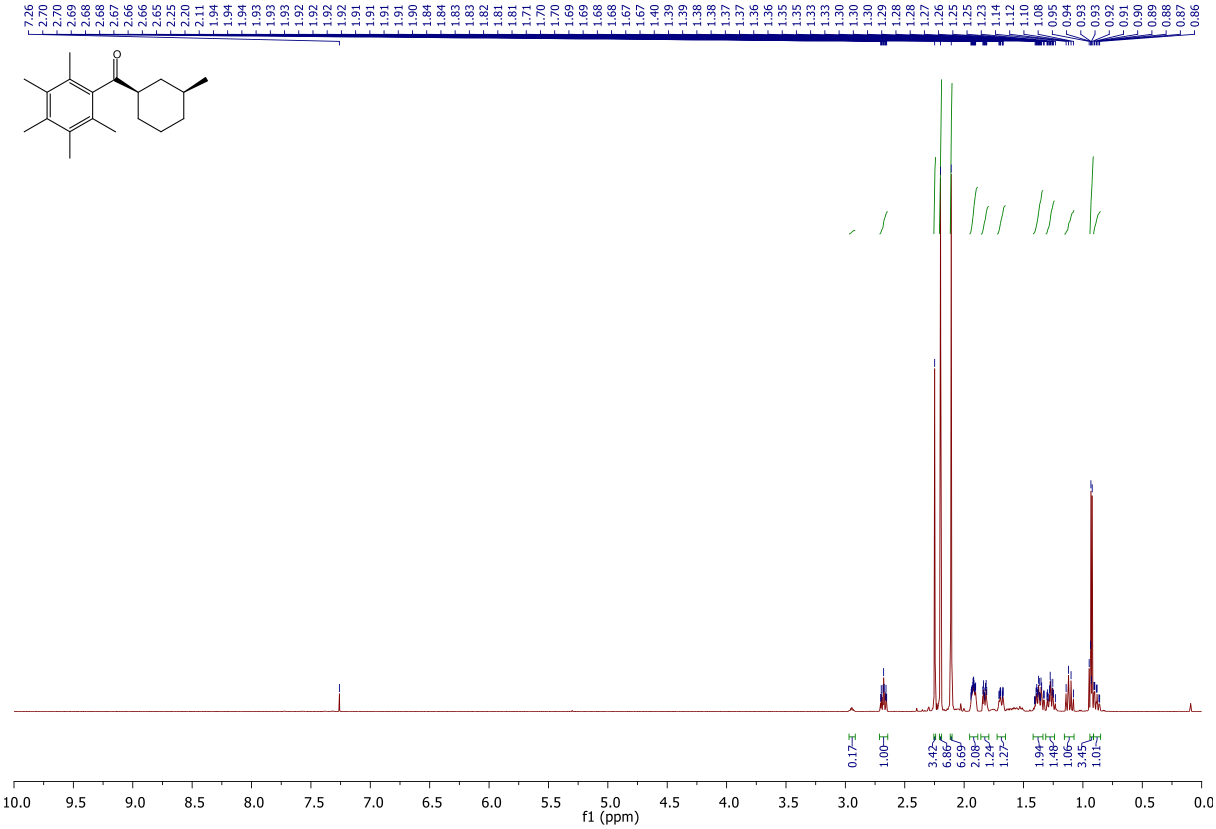


Figure S50: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 2c

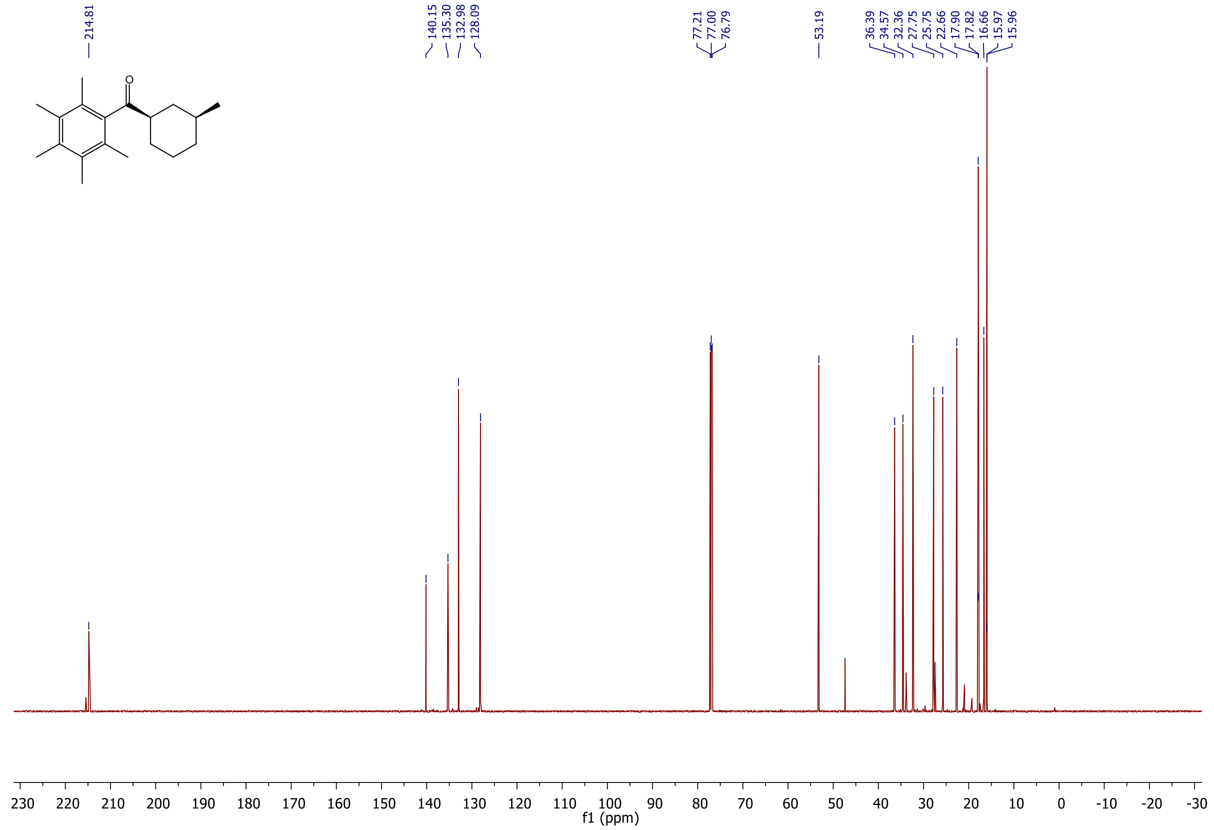


Figure S51: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 2c

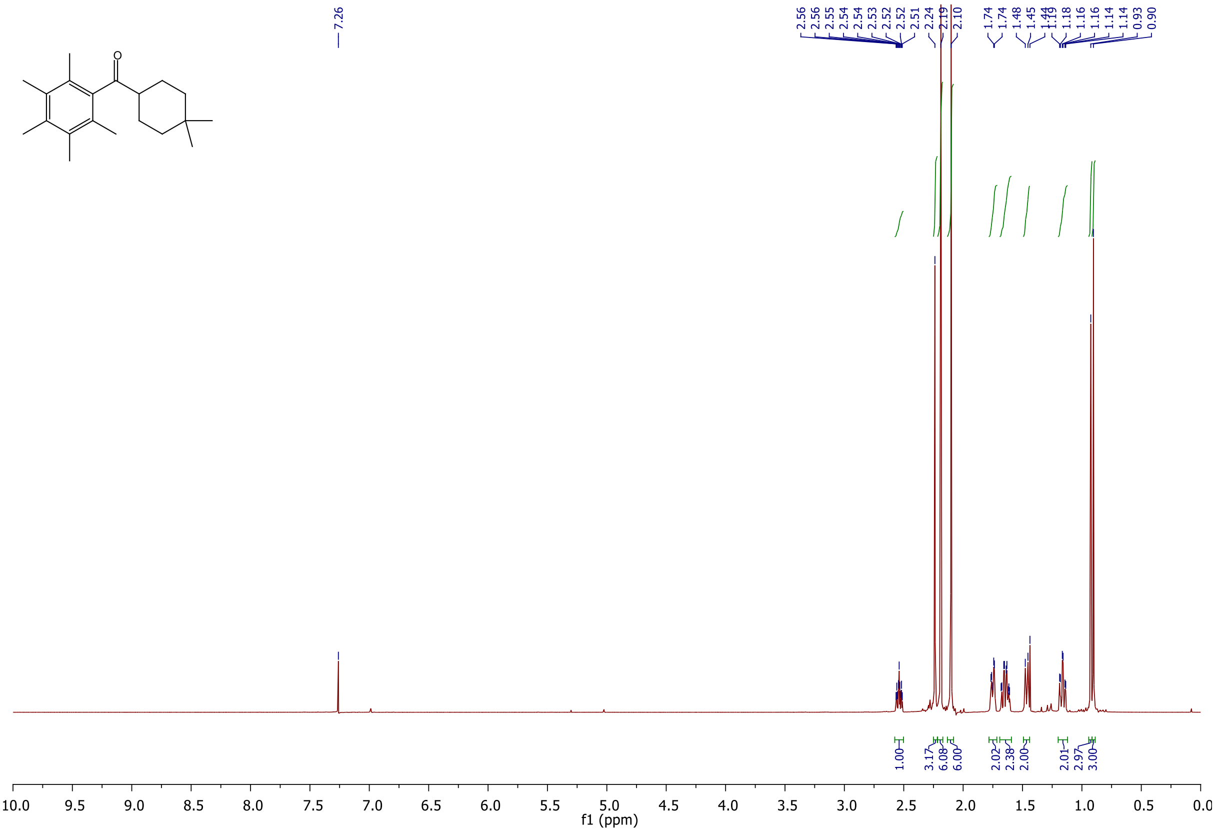


Figure S52: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 2d

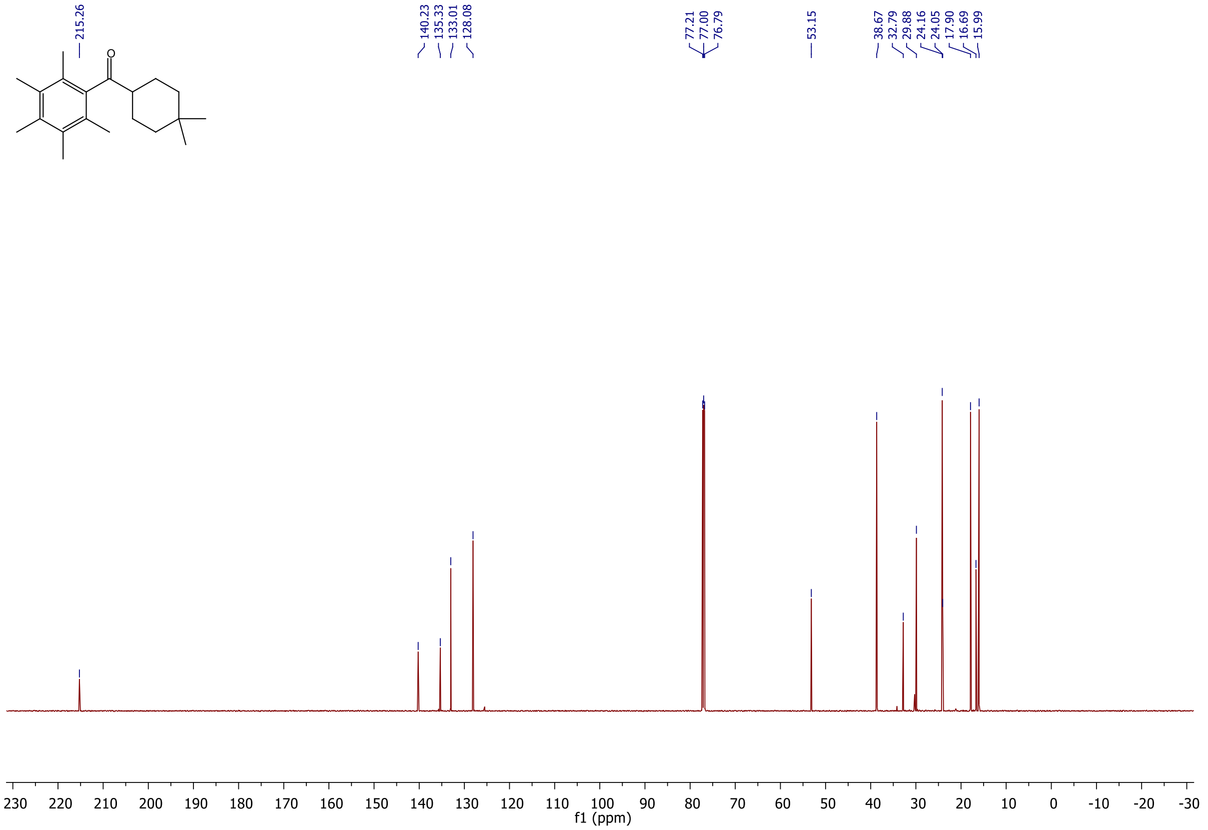


Figure S53: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 2d

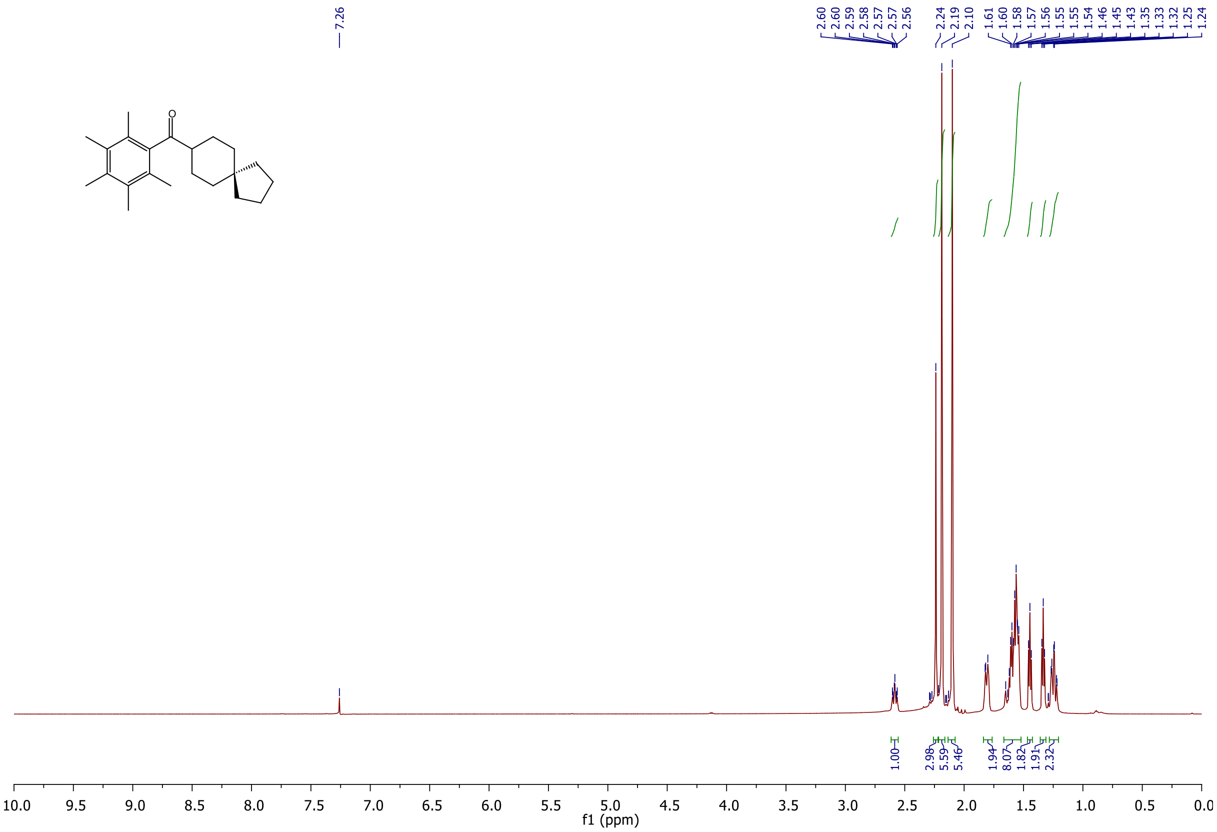


Figure S54: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 2e

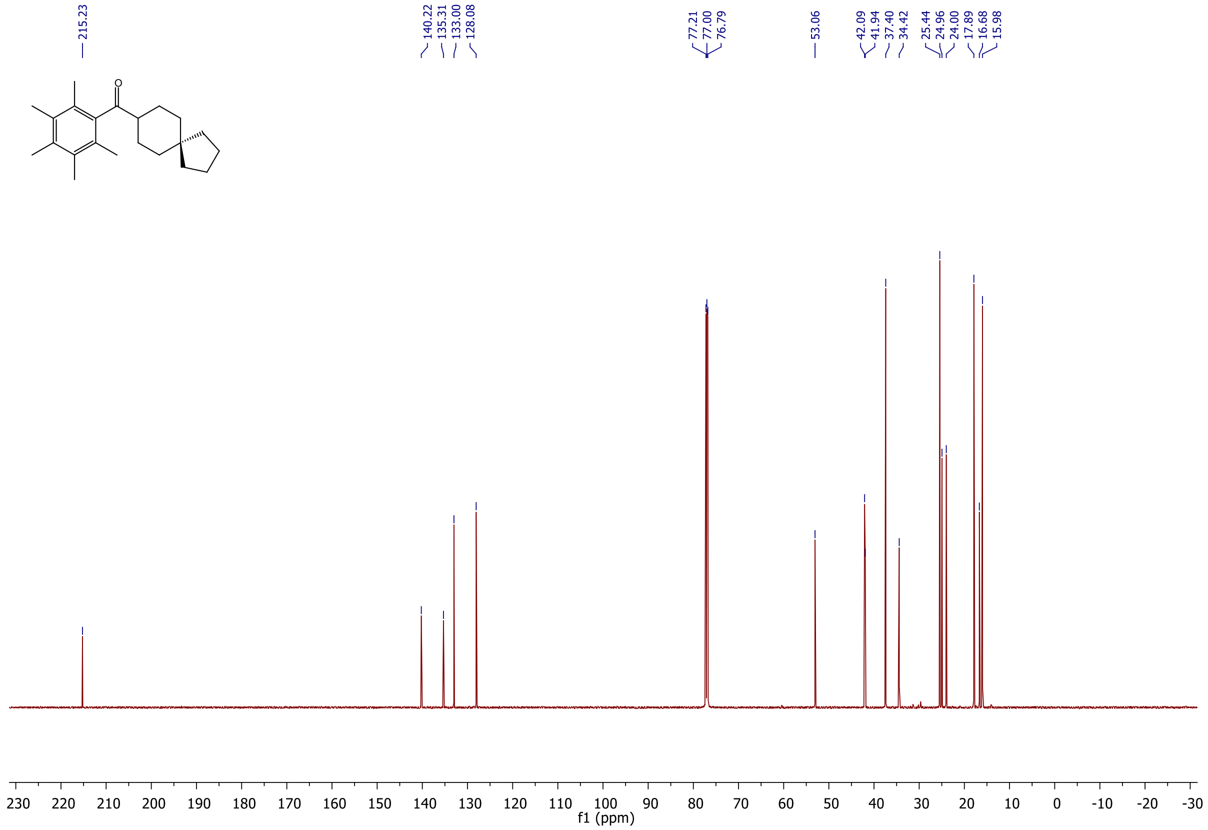


Figure S55: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 2e

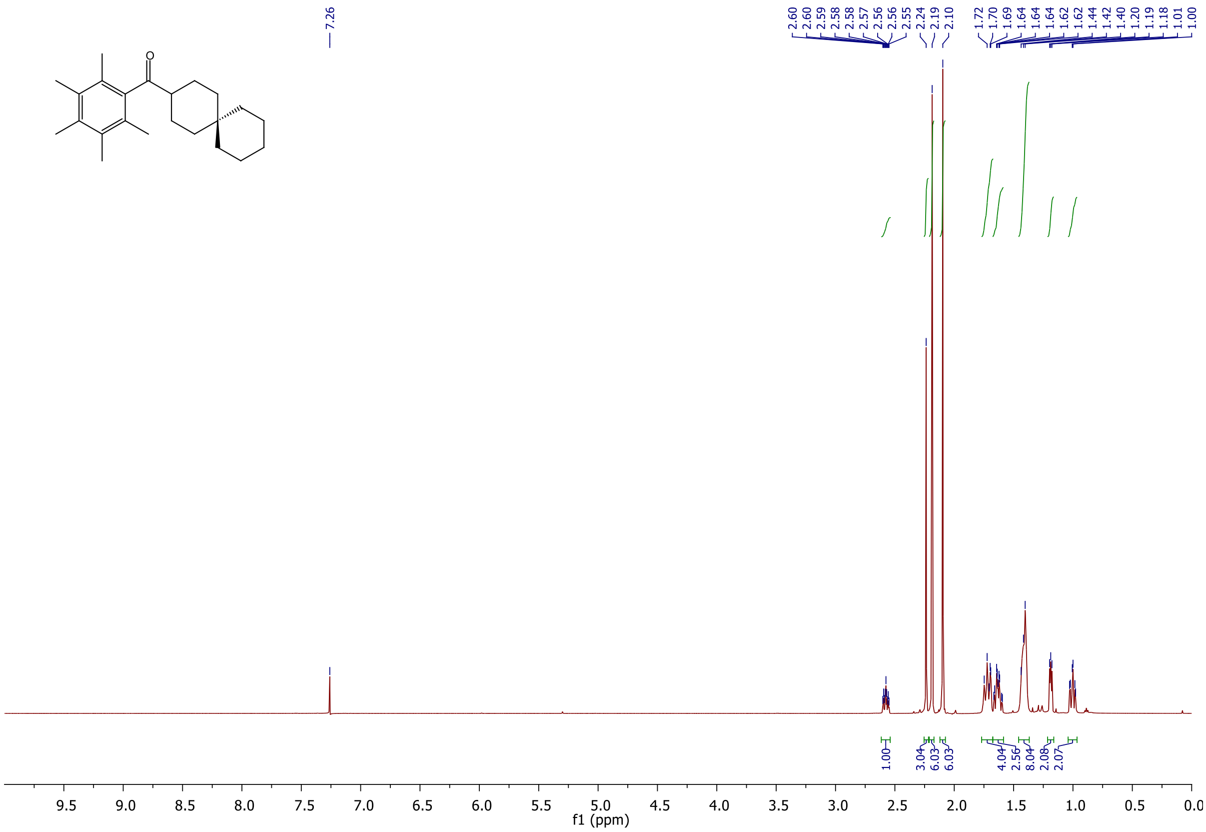


Figure S56: ^{1}H-NMR (600 MHz) in CDCl$_3$ of 2f

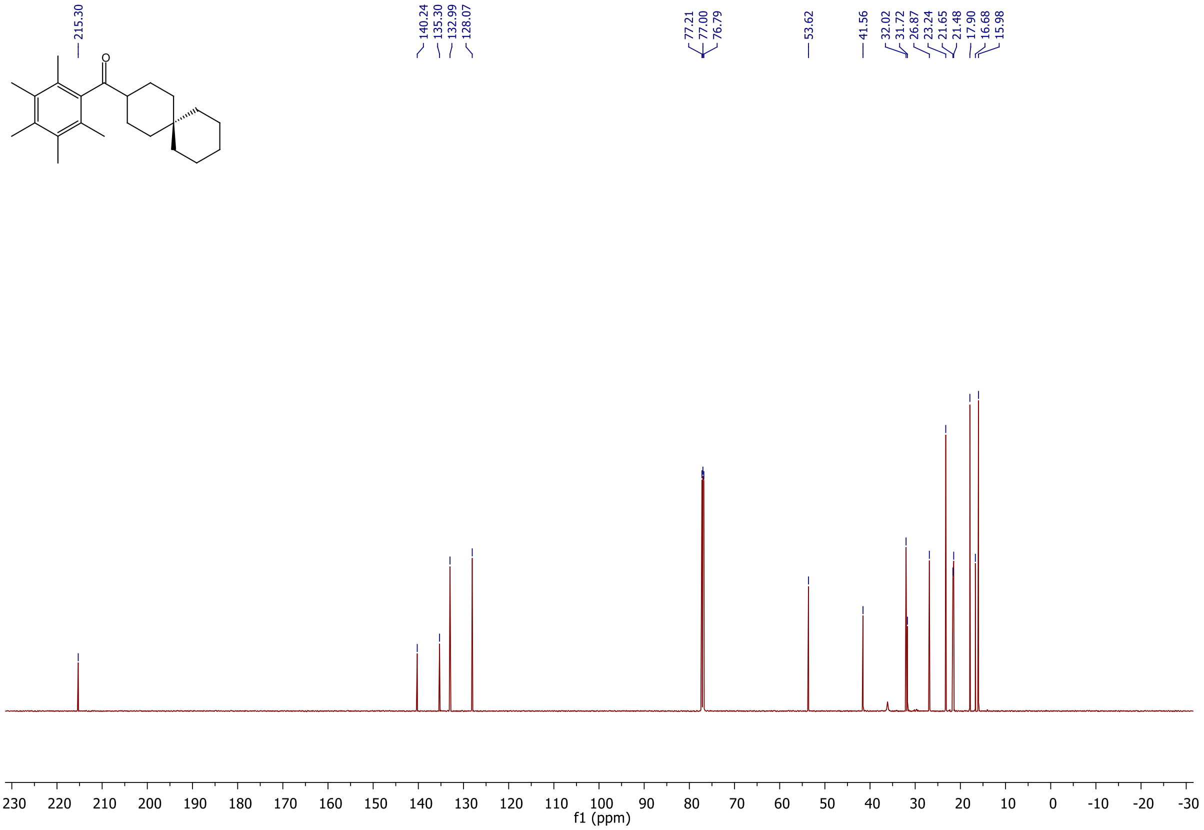


Figure S57: ^{13}C-NMR (150 MHz) in CDCl$_3$ of 2f

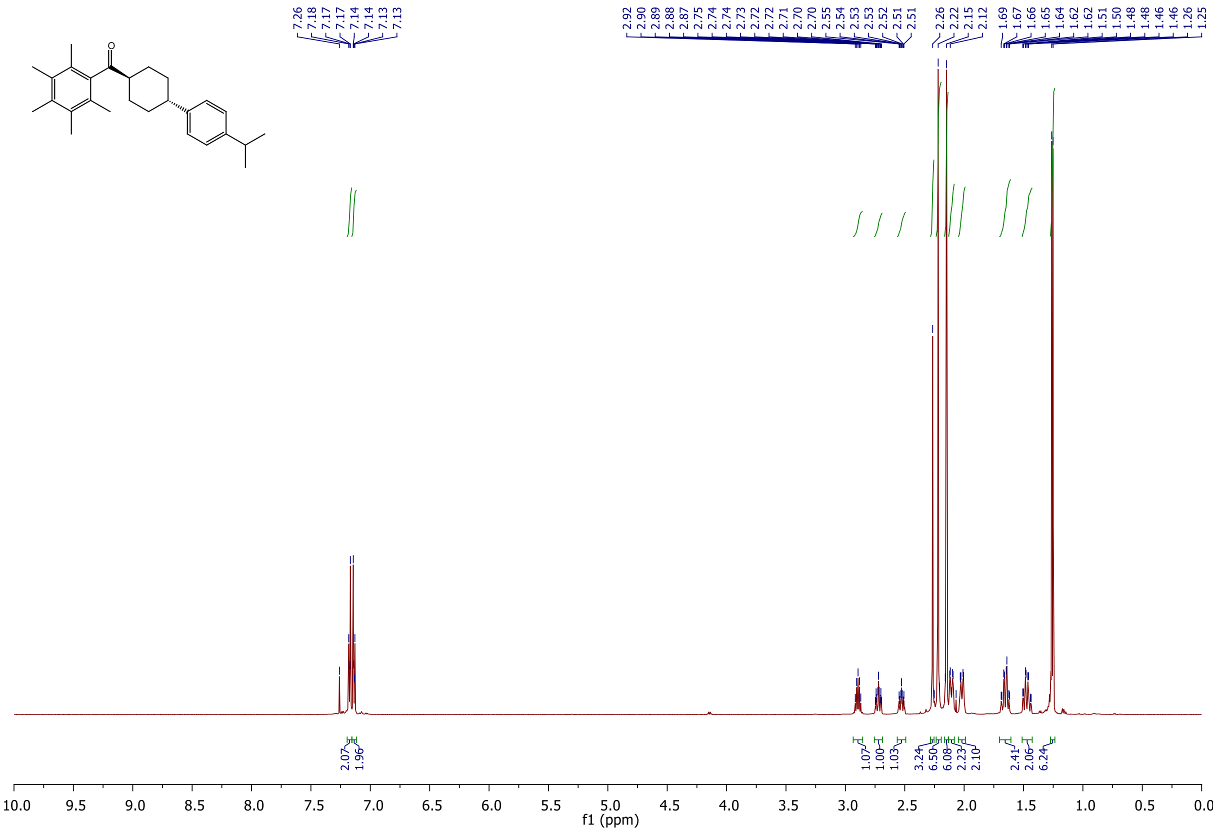


Figure S58: ^{1}H-NMR (600 MHz) in CDCl$_3$ of 2g

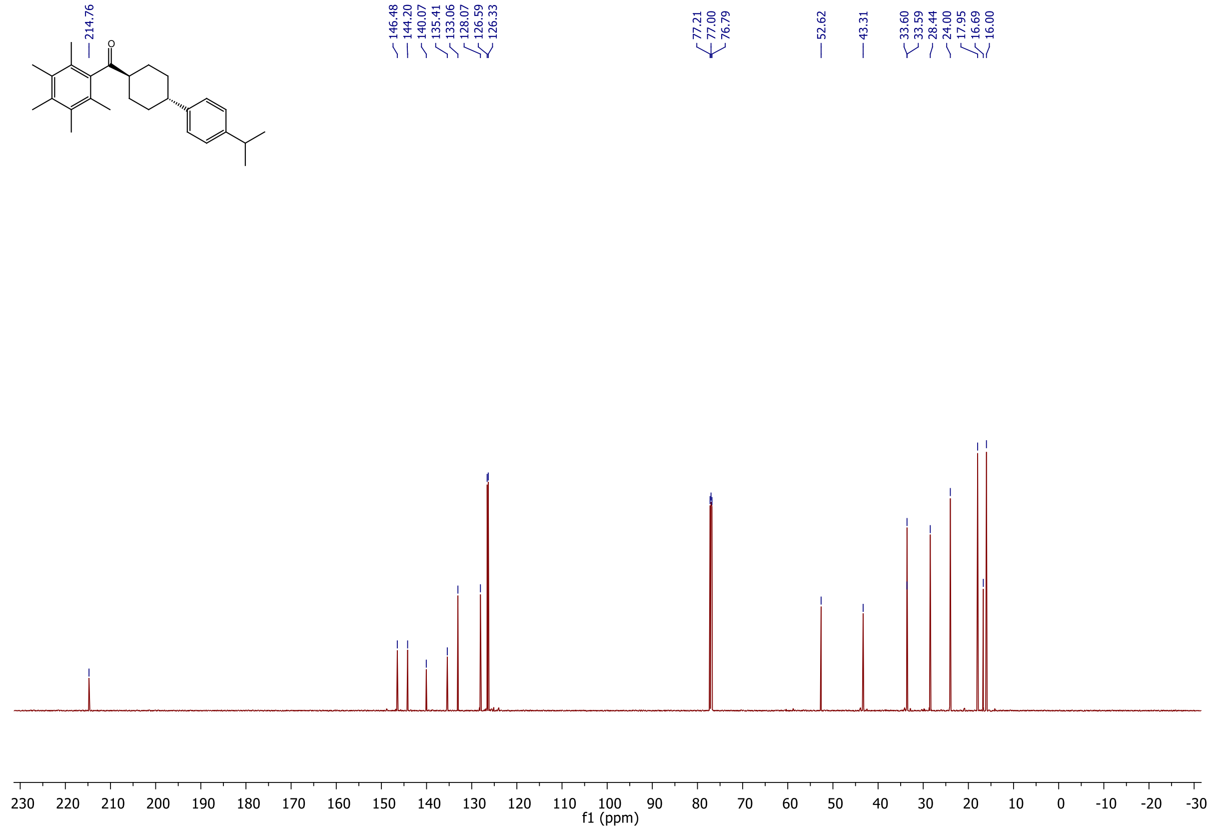


Figure S59: ^{13}C-NMR (150 MHz) in CDCl$_3$ of 2g

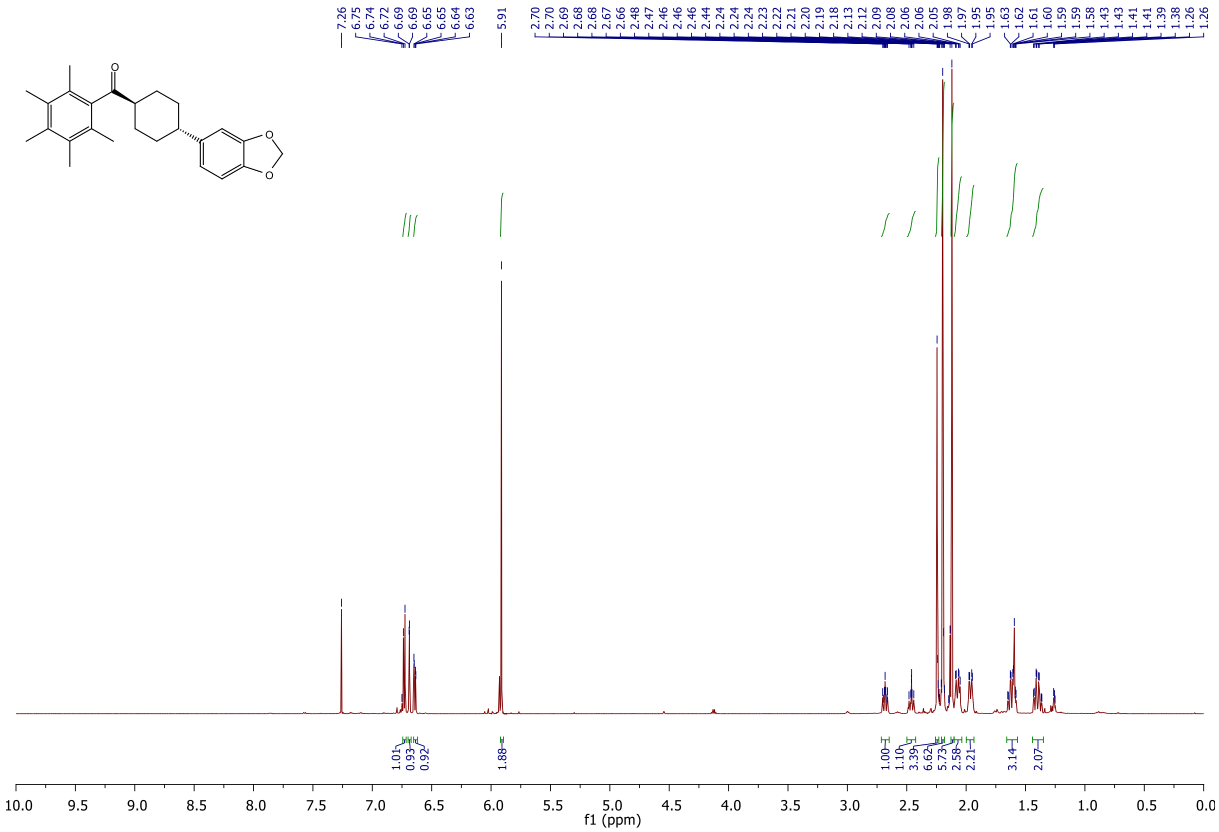


Figure S60: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 2h

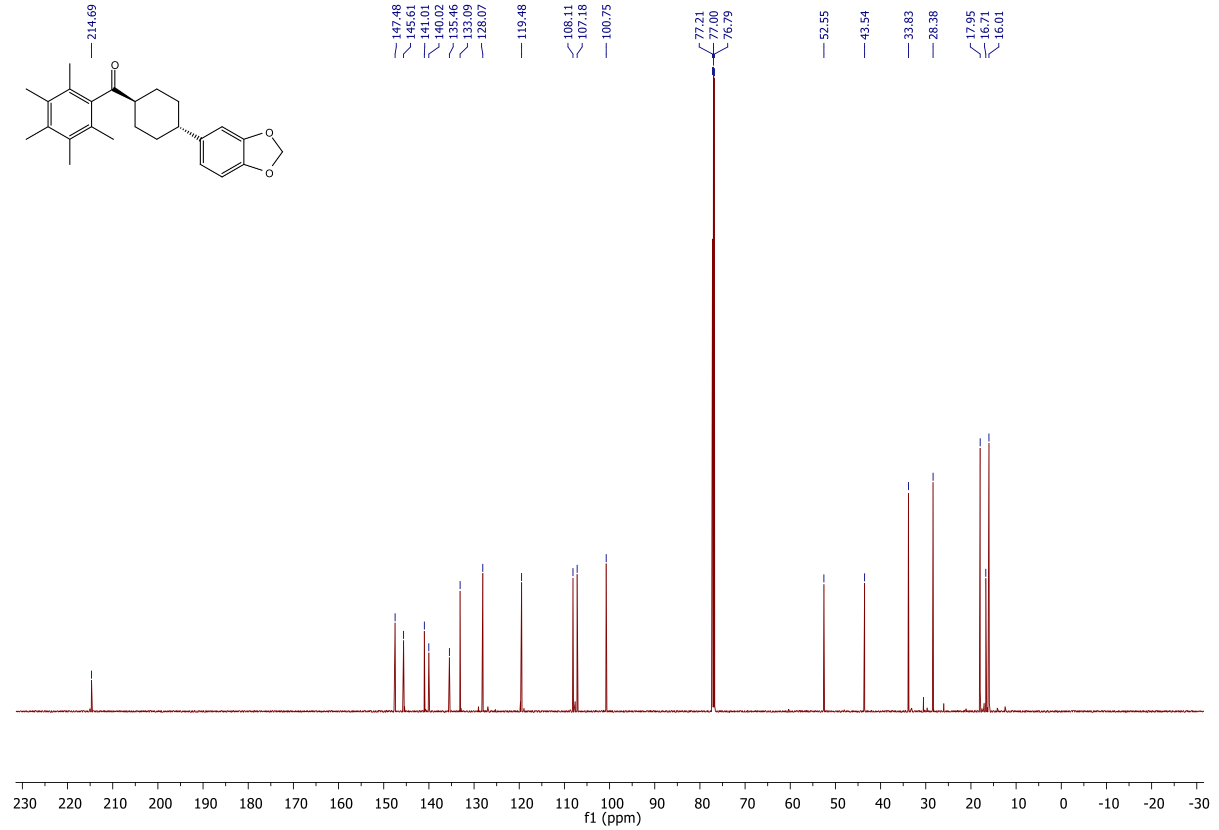


Figure S61: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 2h

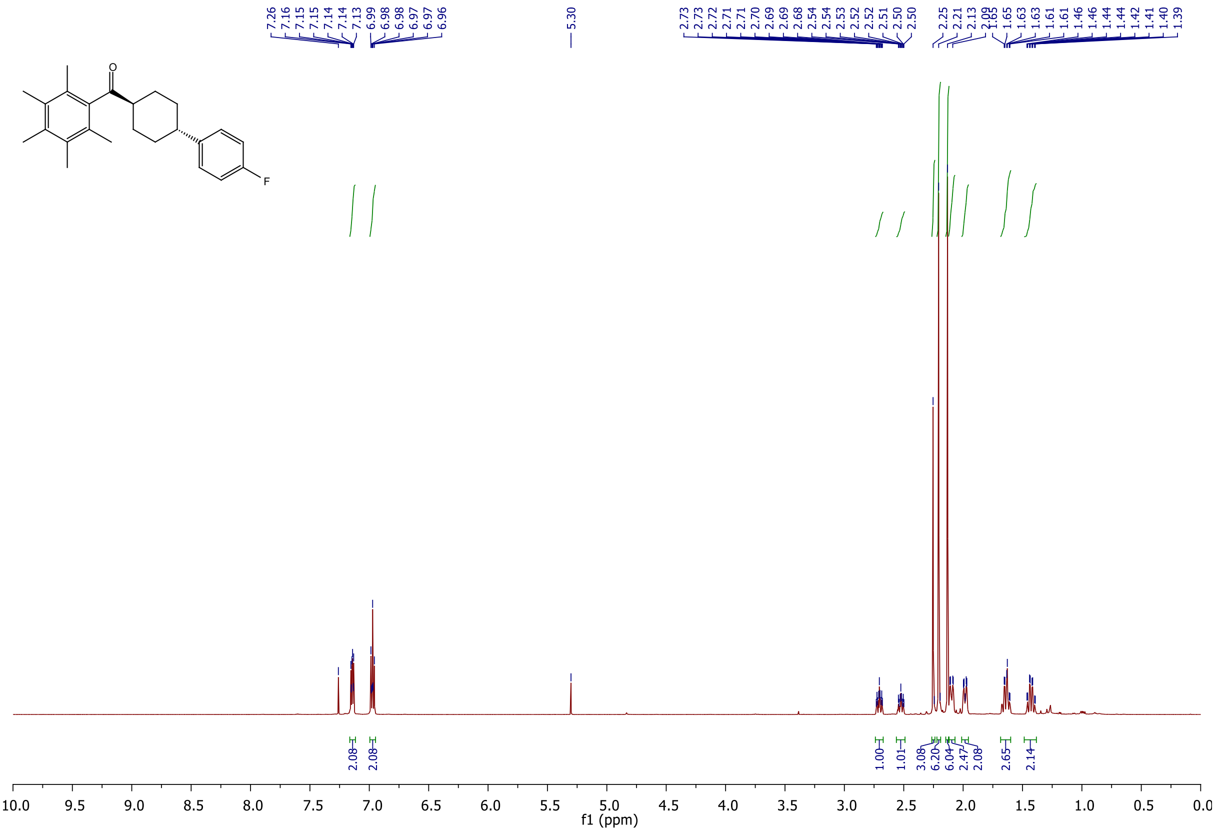


Figure S62: ^{1}H-NMR (600 MHz) in CDCl$_3$ of 2i

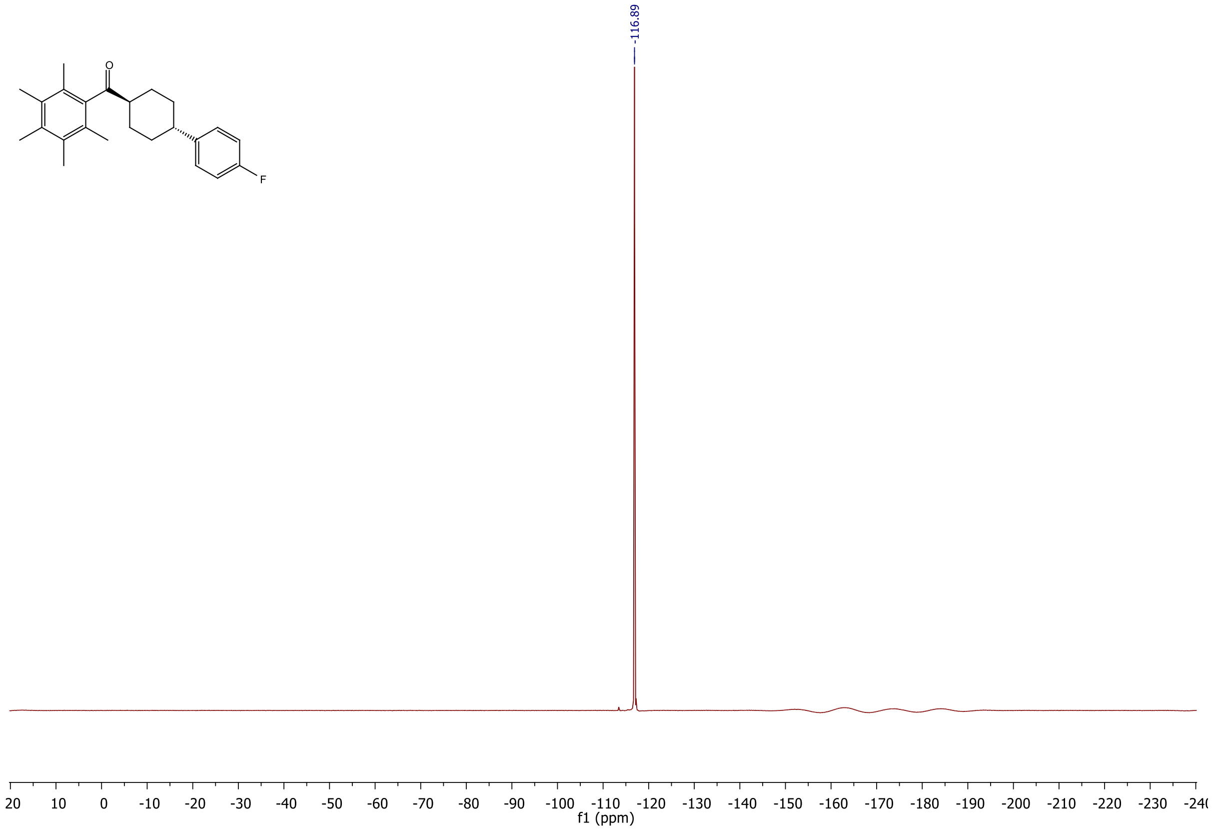


Figure S63: ^{19}F-NMR (600 MHz) in CDCl$_3$ of 2i

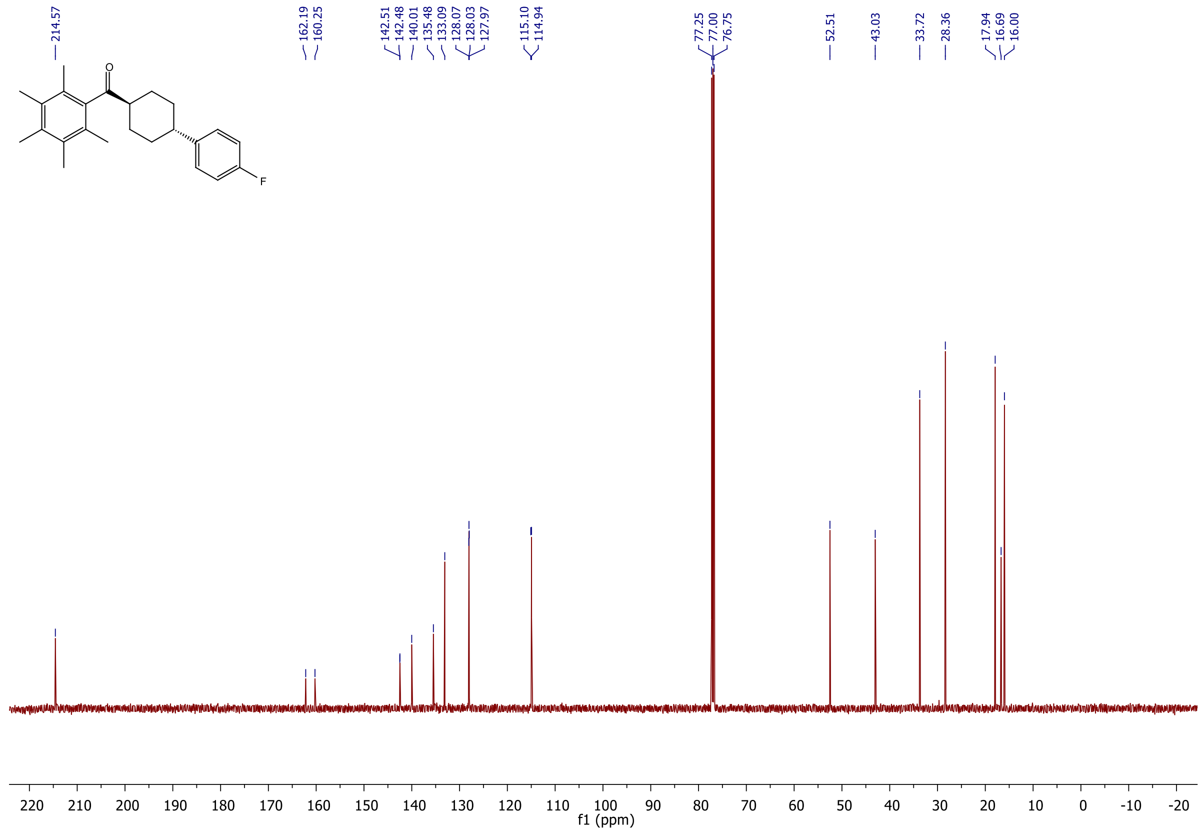


Figure S64: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 2i

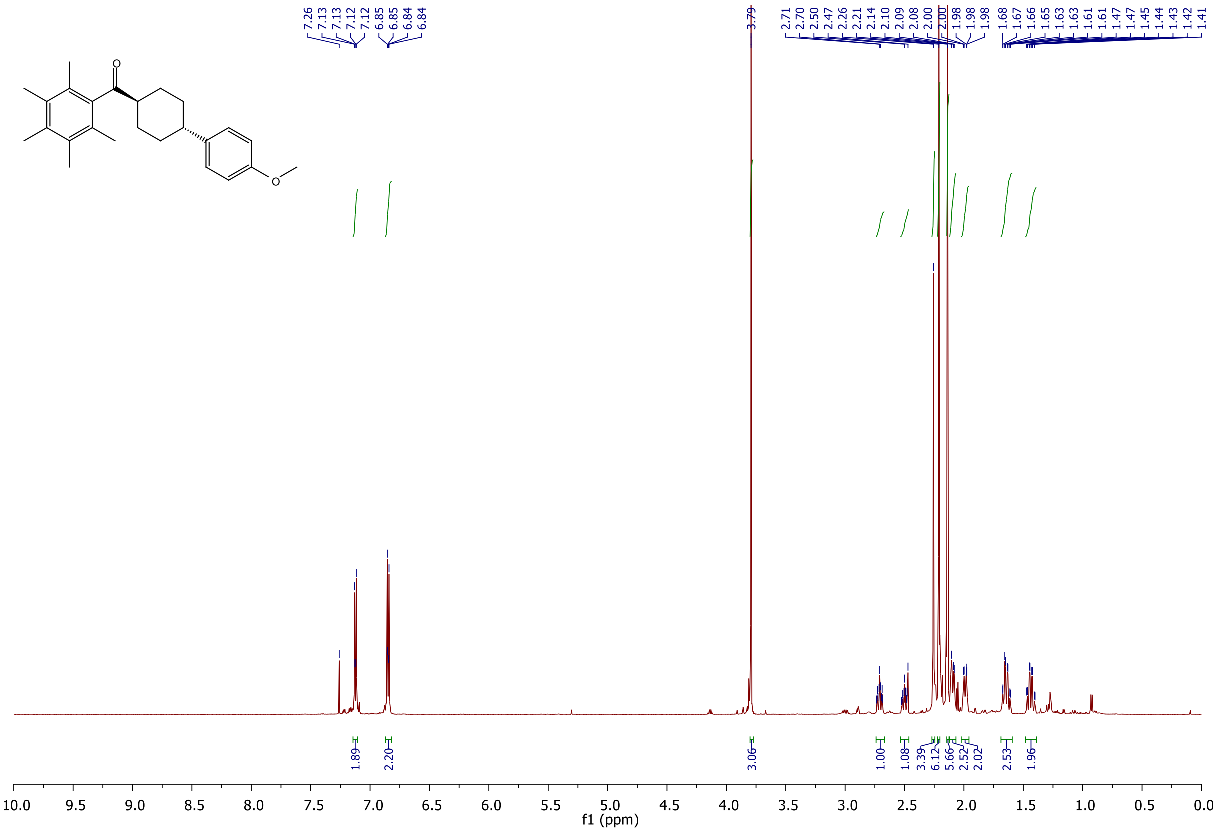


Figure S65: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 2j

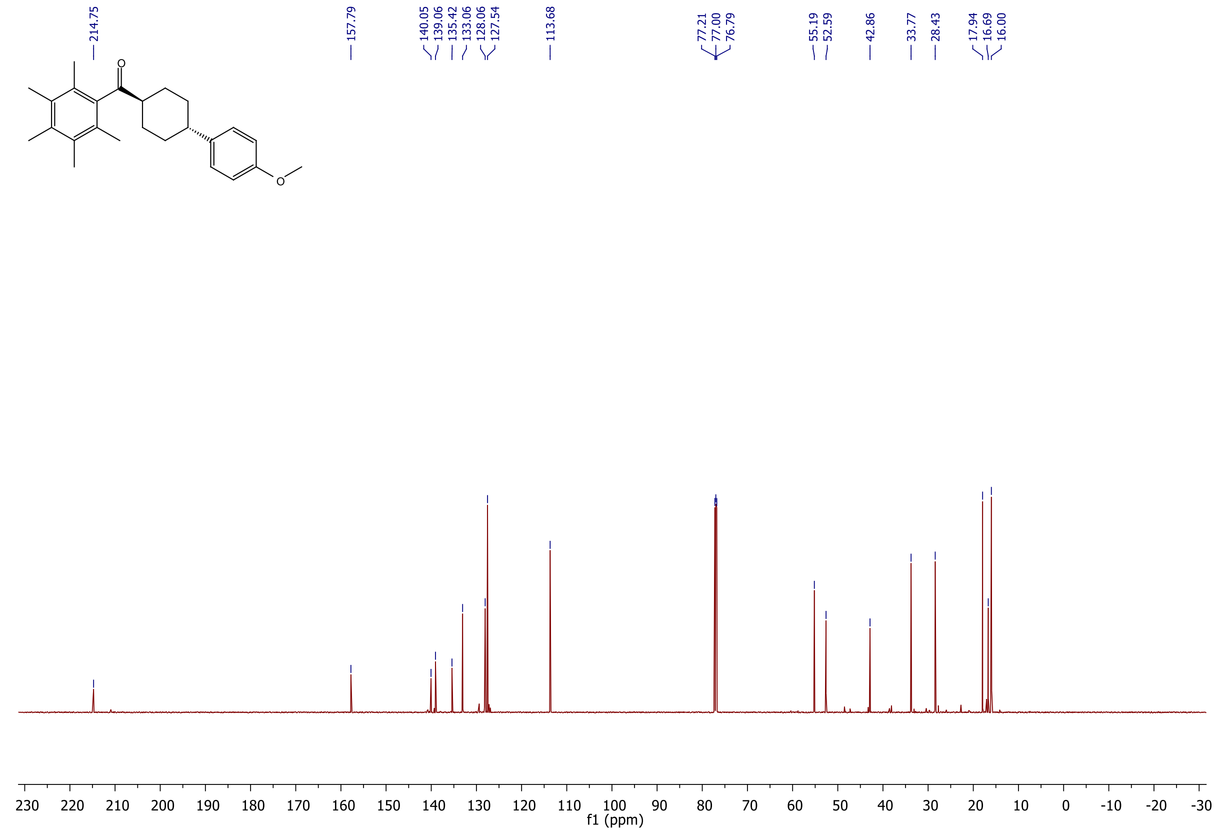


Figure S66: ^{13}C-NMR (150 MHz) in CDCl$_3$ of 2j

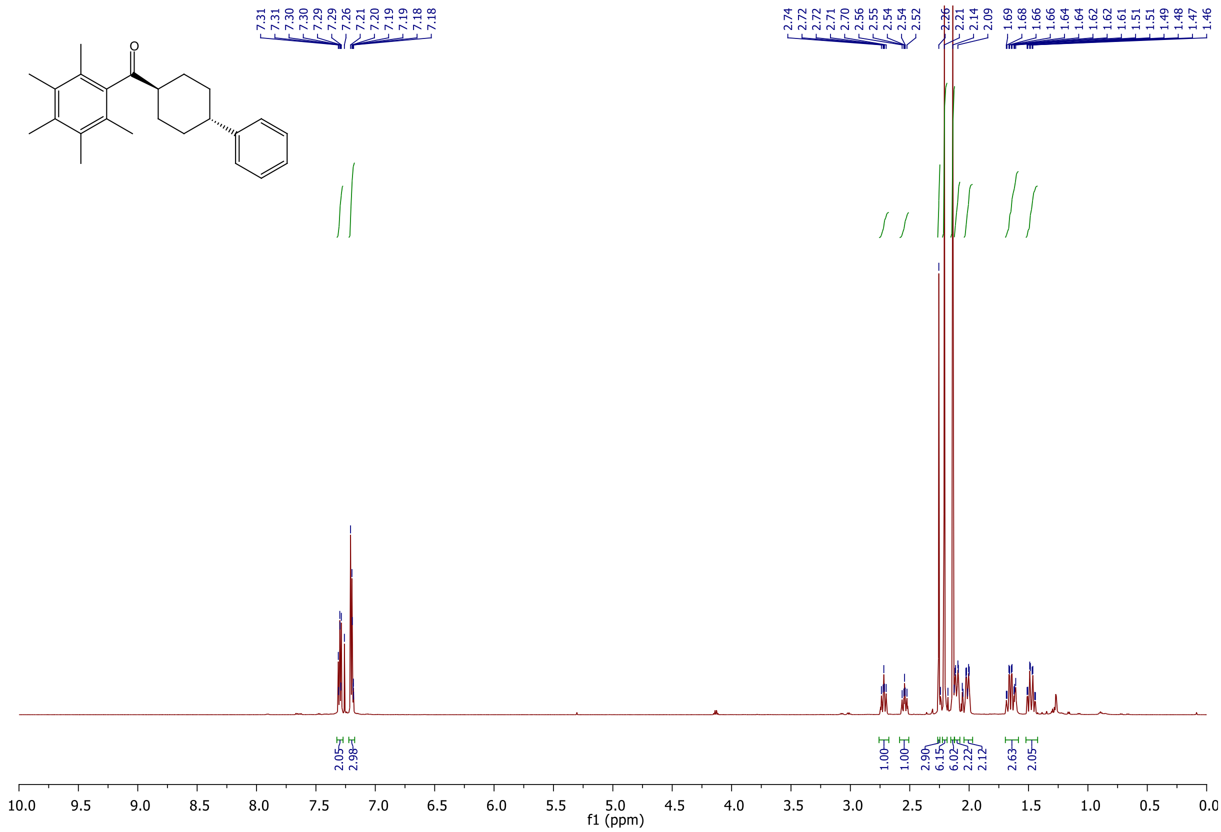


Figure S67: ^{1}H-NMR (600 MHz) in CDCl$_3$ of 2k

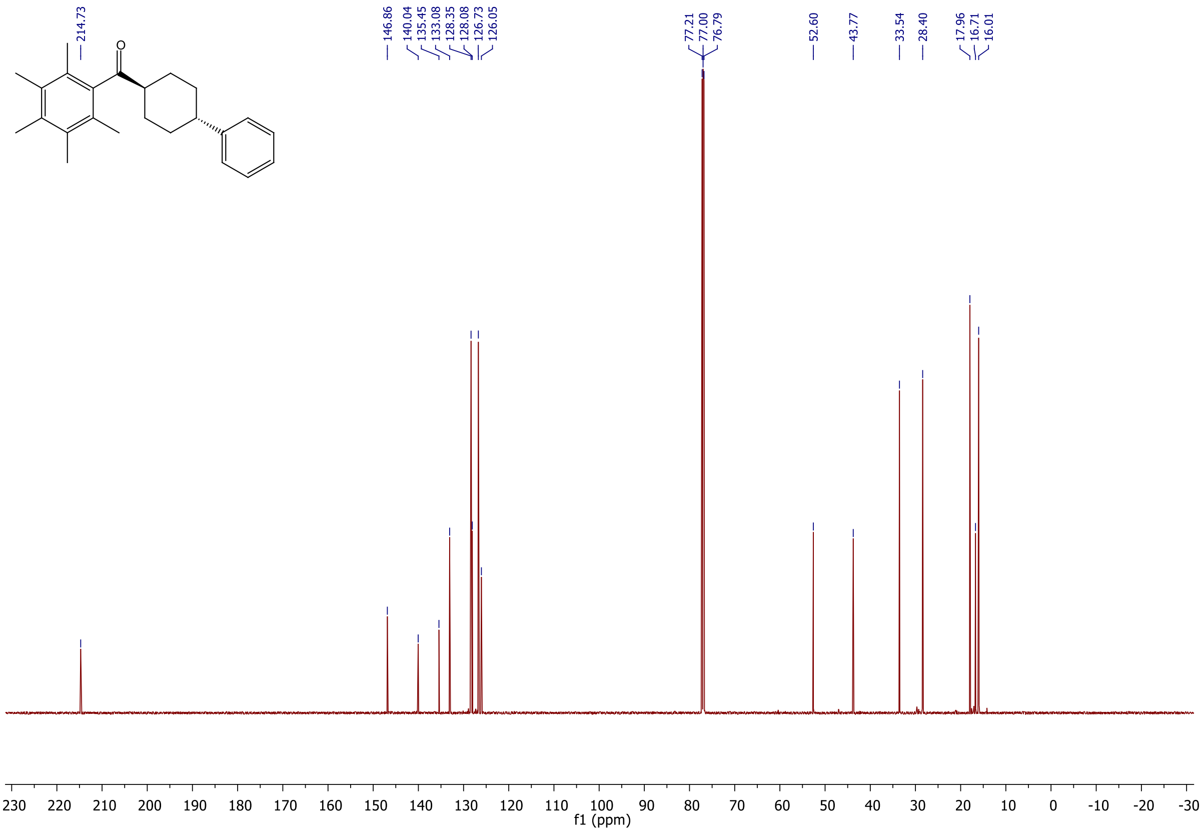


Figure S68: ^{13}C-NMR (150 MHz) in CDCl$_3$ of 2k

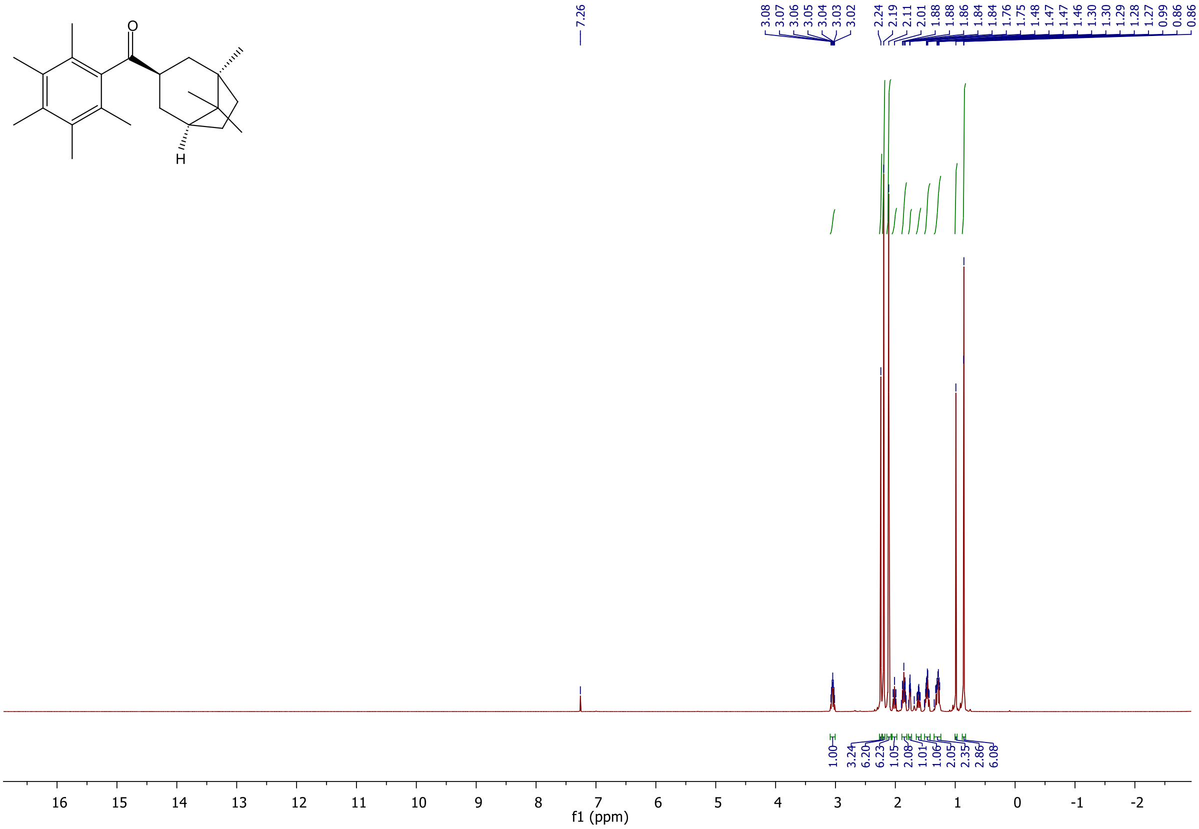


Figure S69: ^{1}H-NMR (600 MHz) in CDCl$_3$ of 2l

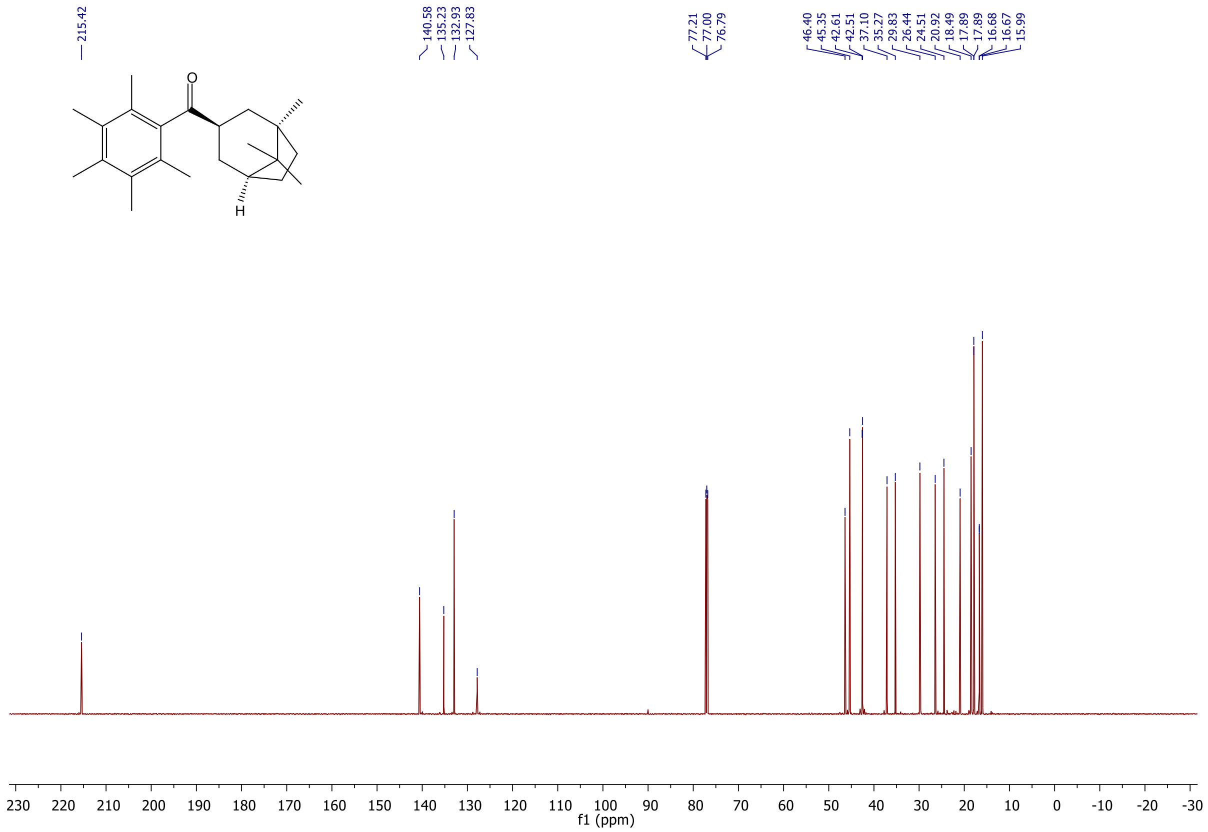


Figure S70: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 2l

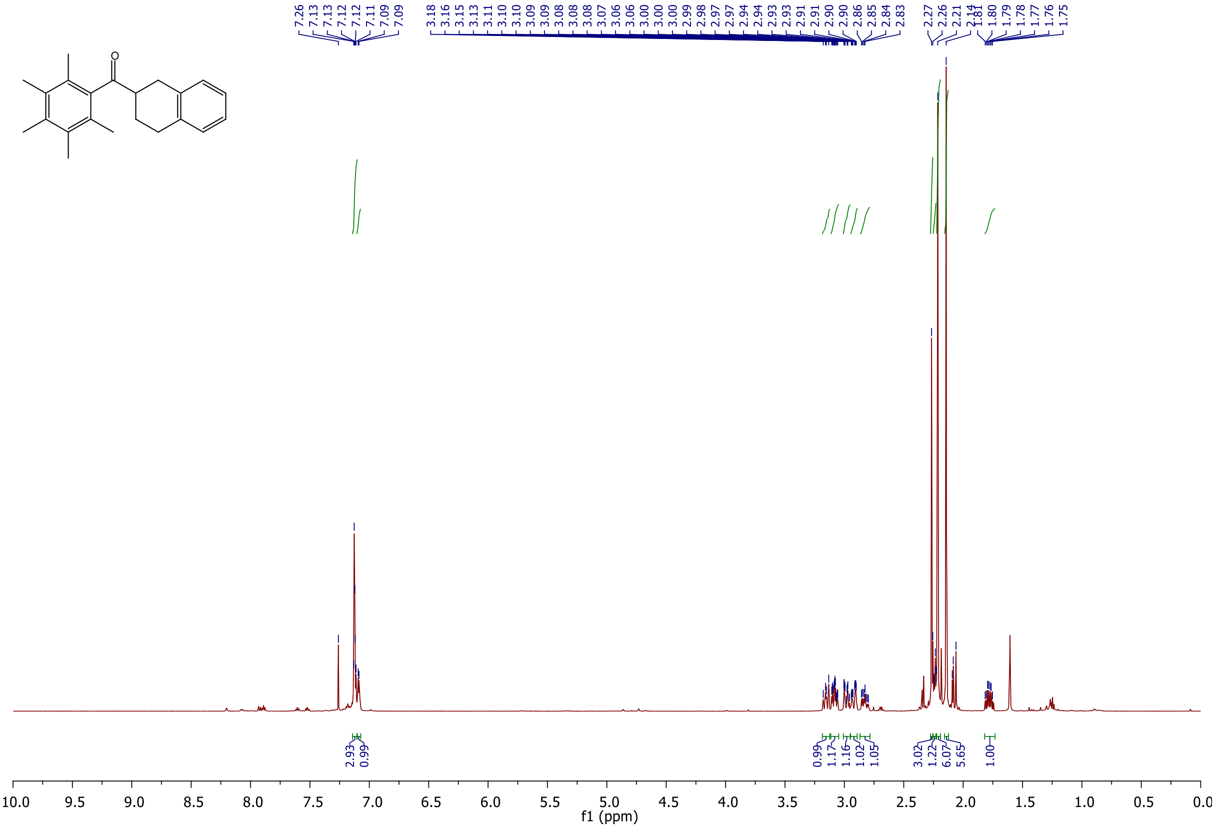


Figure S71: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 2m

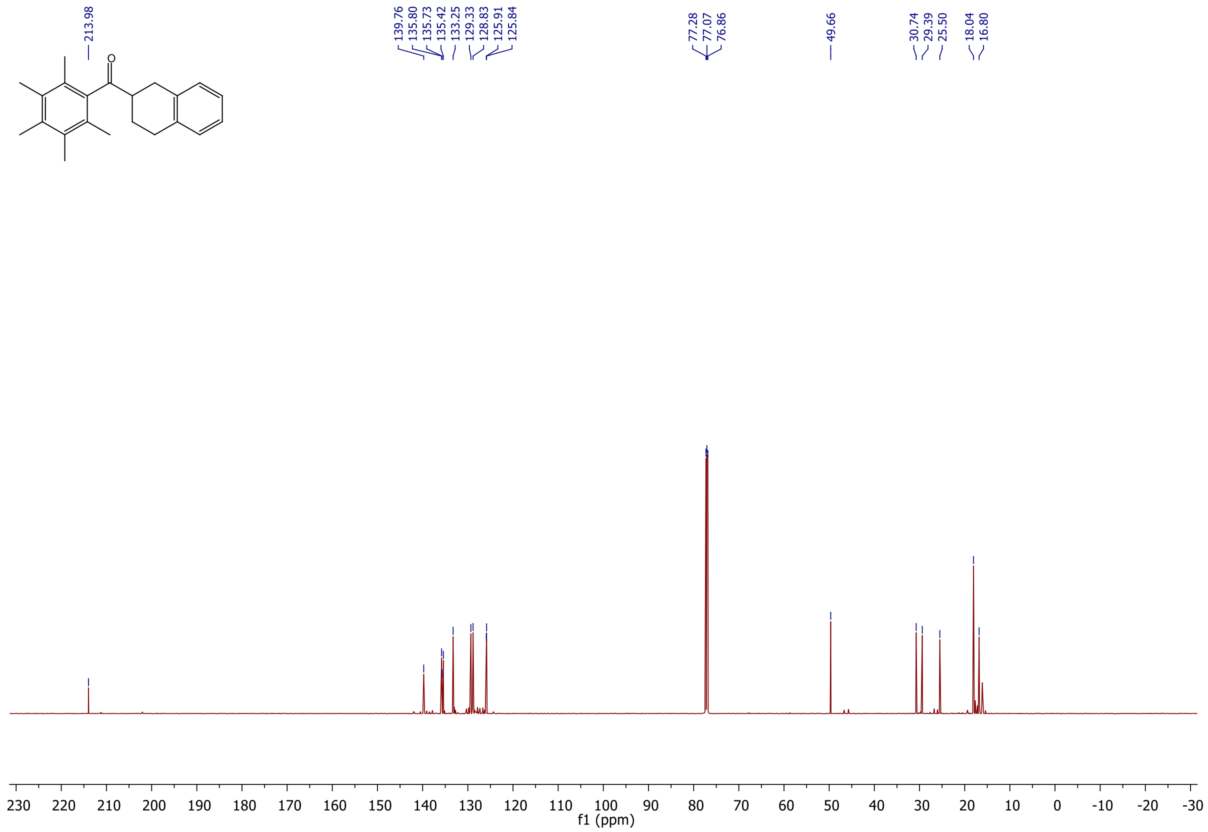


Figure S72: ^{13}C-NMR (150 MHz) in CDCl$_3$ of 2m

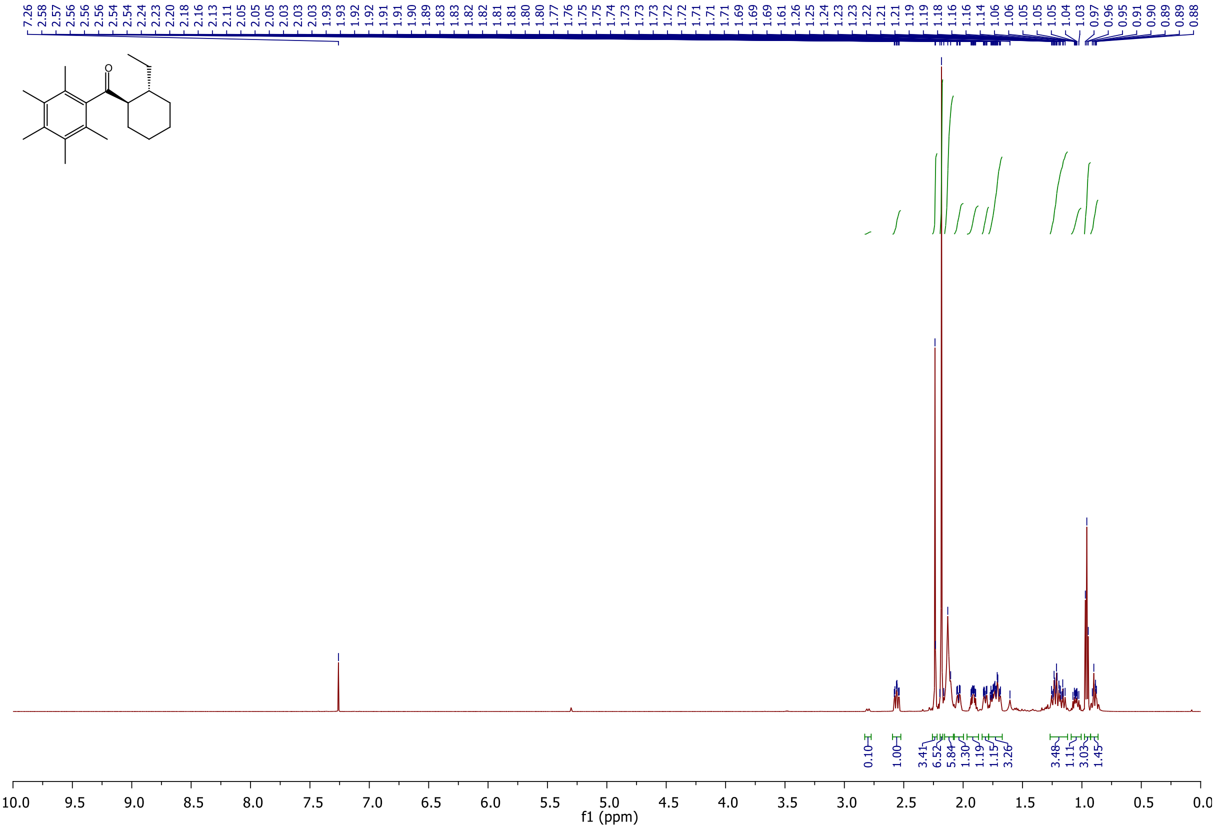


Figure S73: ^{1}H-NMR (600 MHz) in CDCl$_3$ of 2n

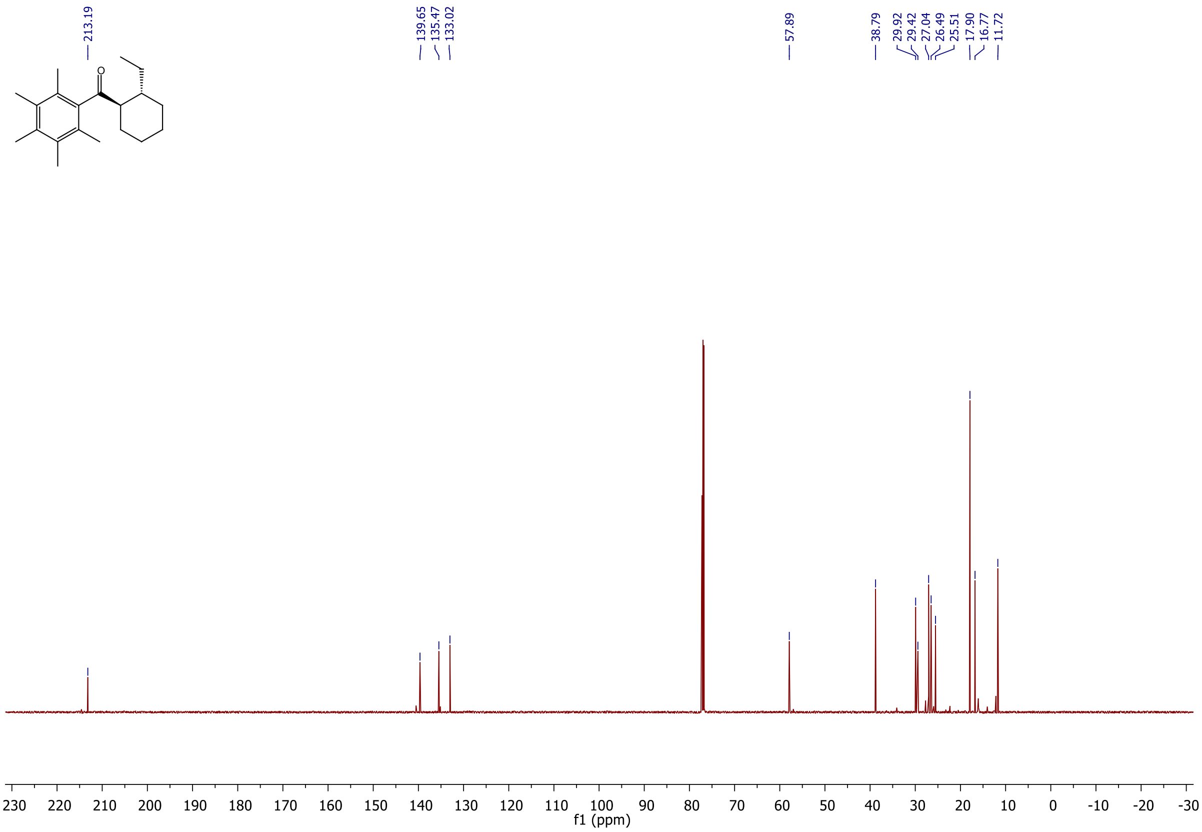


Figure S74: ^{13}C-NMR (150 MHz) in CDCl$_3$ of 2n

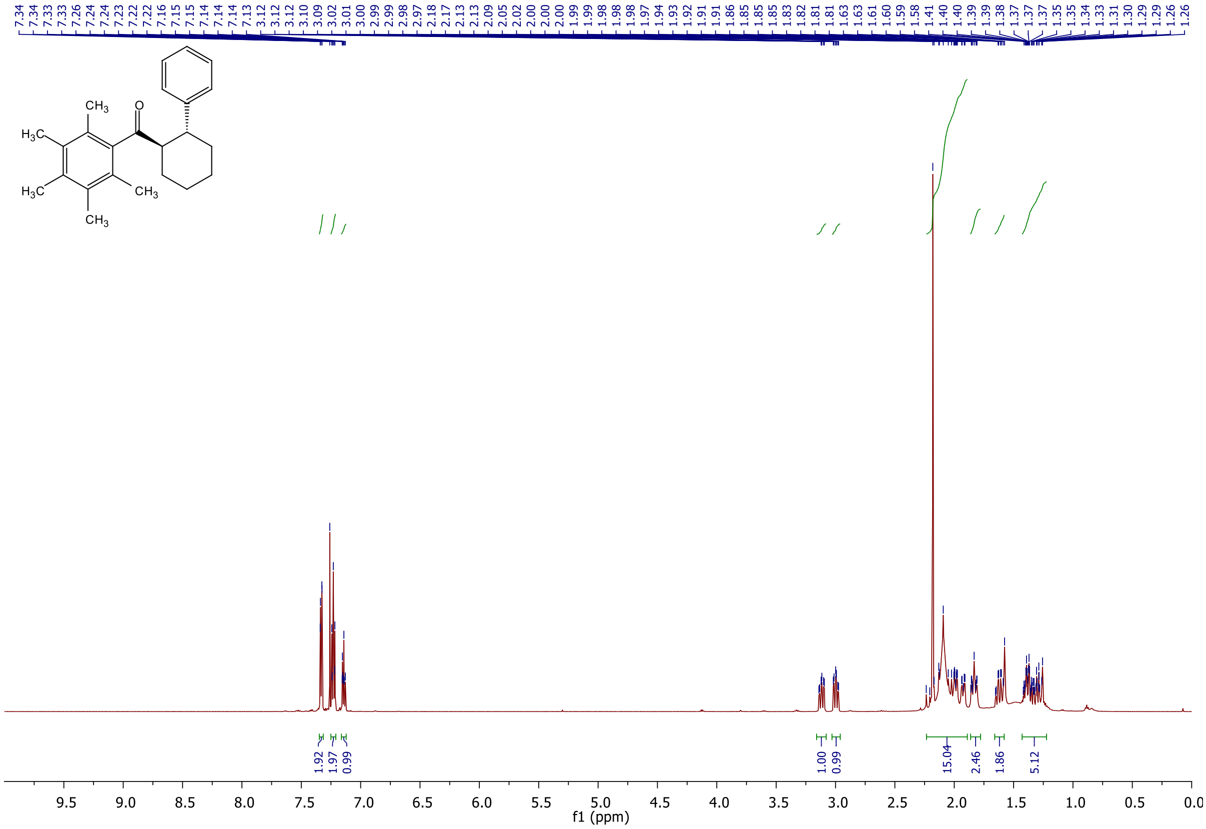


Figure S75: ^{1}H-NMR (600 MHz) in CDCl$_3$ of 2o

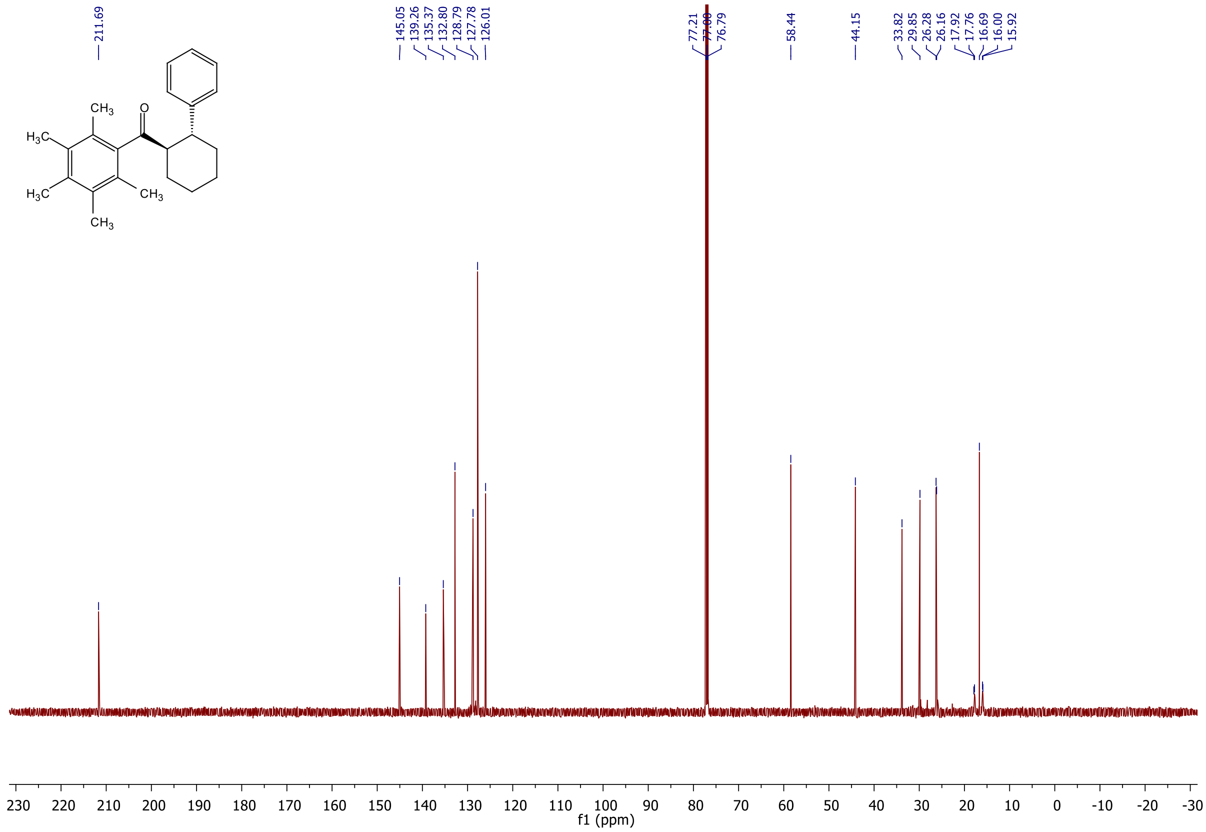


Figure S76: ^{13}C-NMR (150 MHz) in CDCl$_3$ of 2o

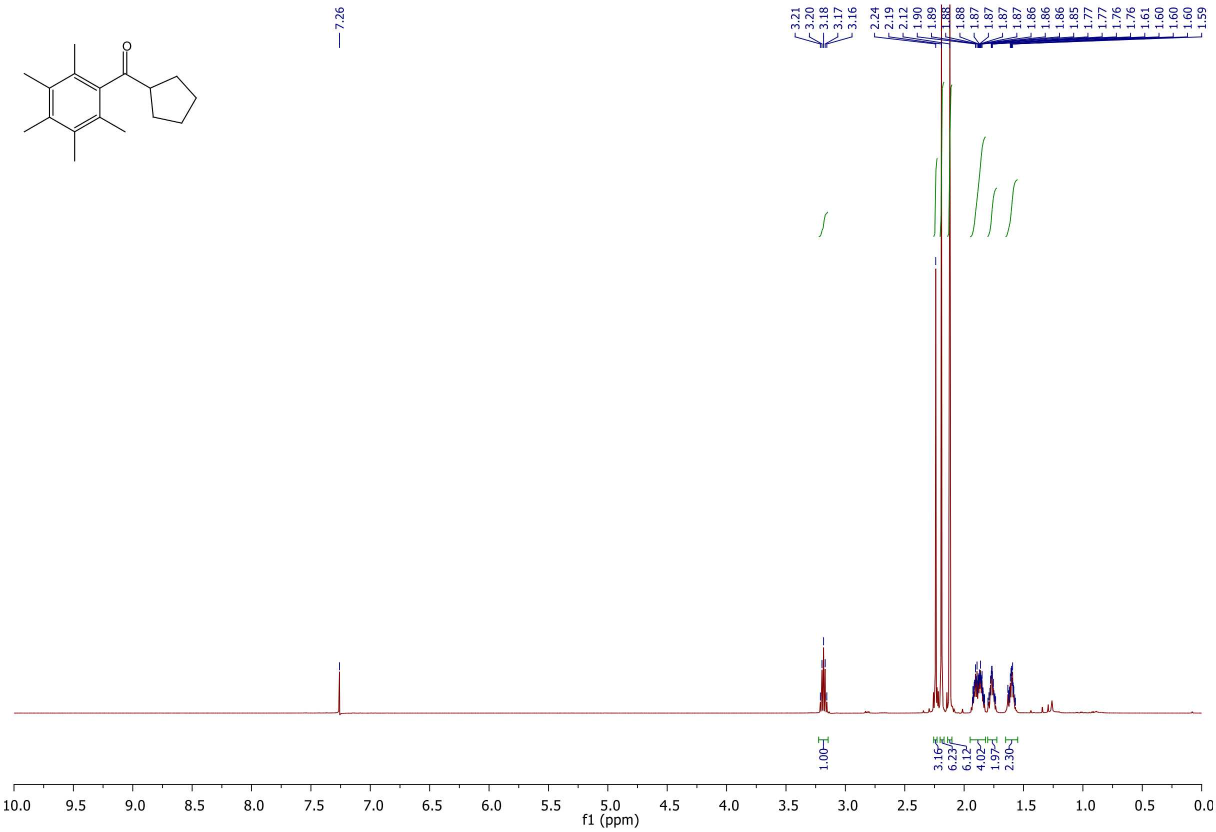


Figure S77: ^{1}H-NMR (600 MHz) in CDCl$_3$ of 2p

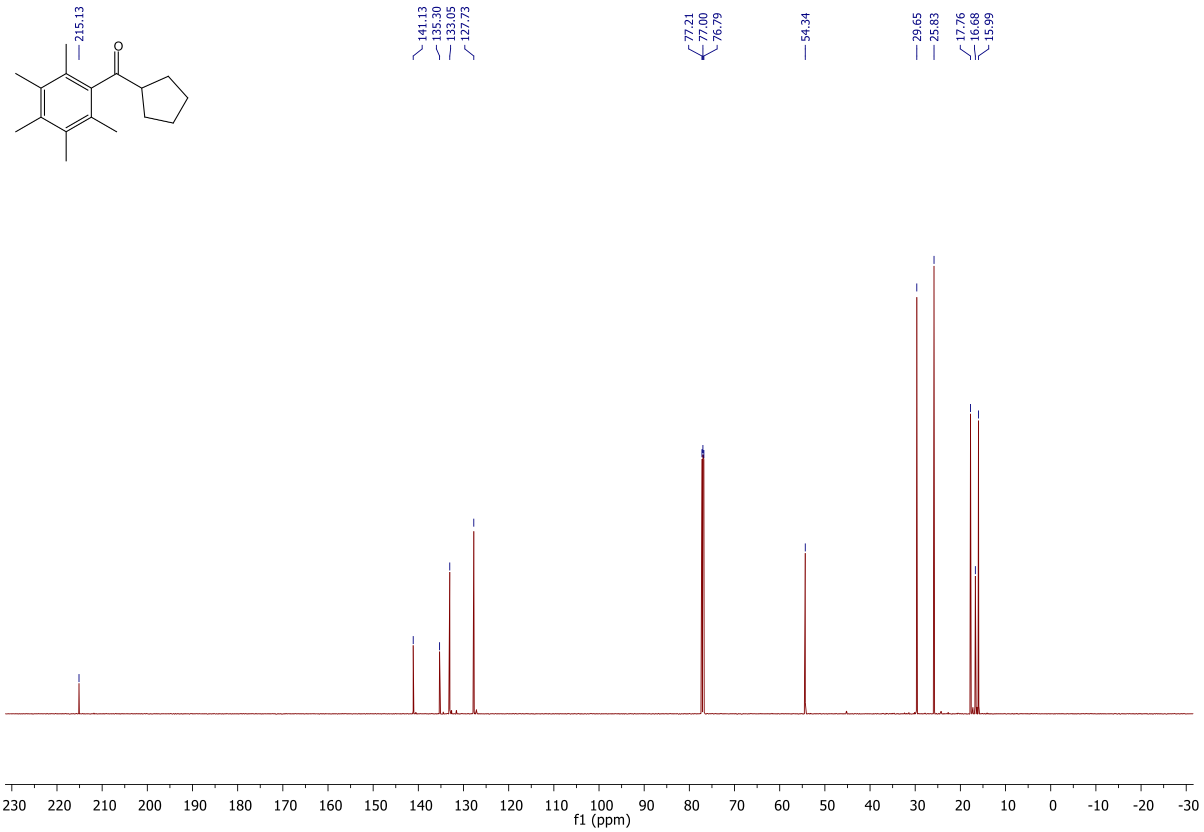


Figure S78: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 2p

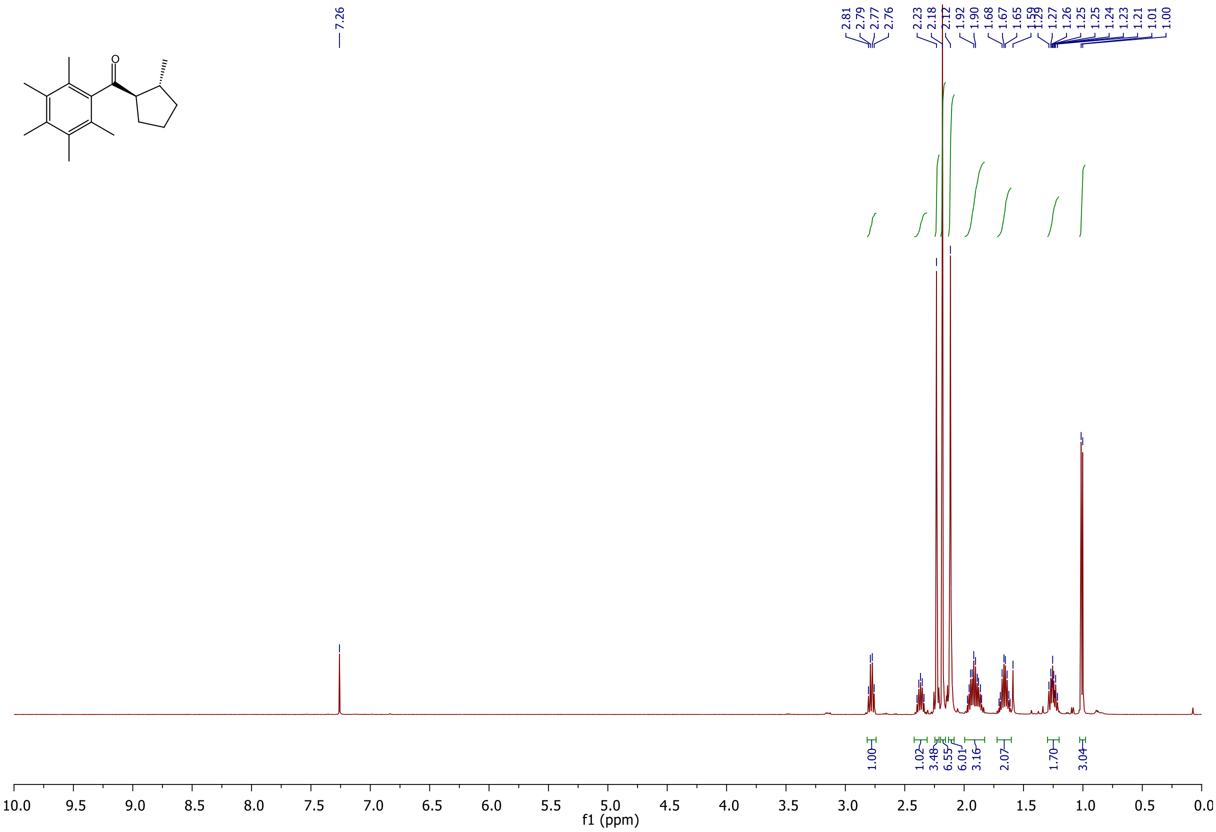


Figure S79: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 2q

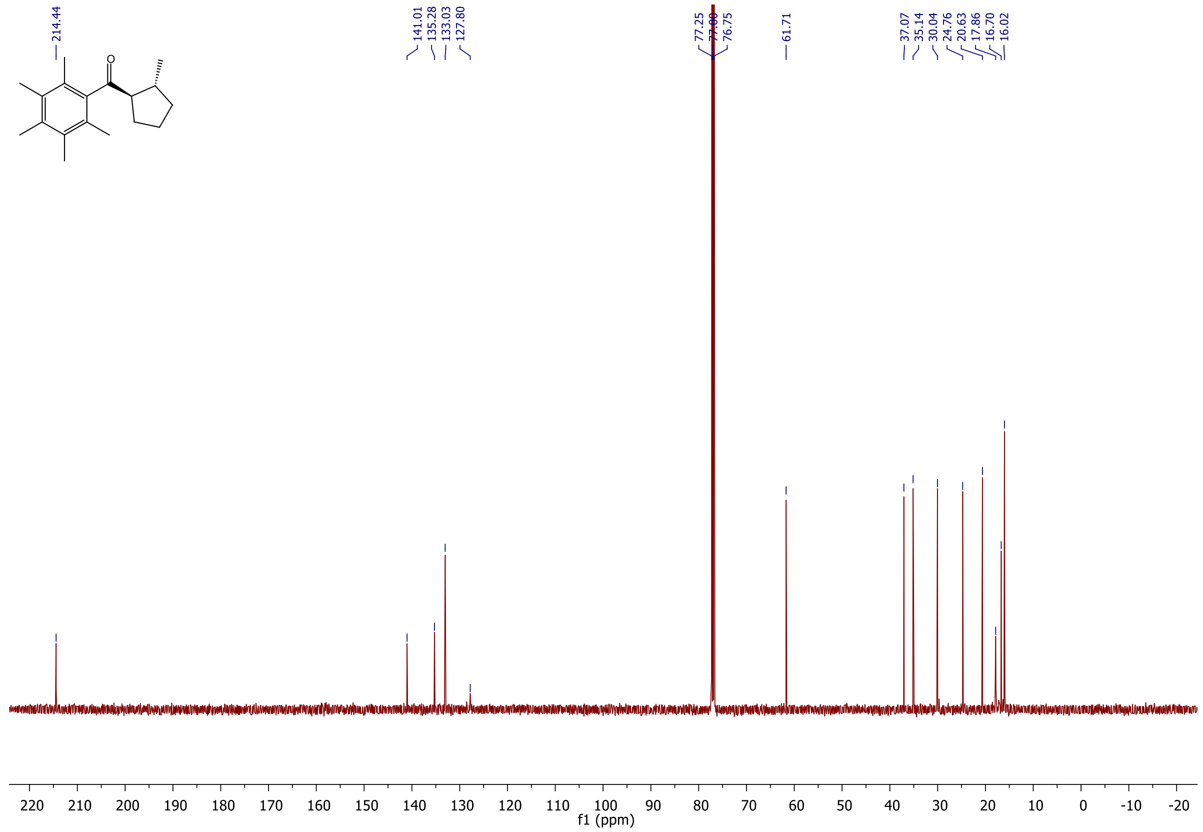


Figure S80: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 2q

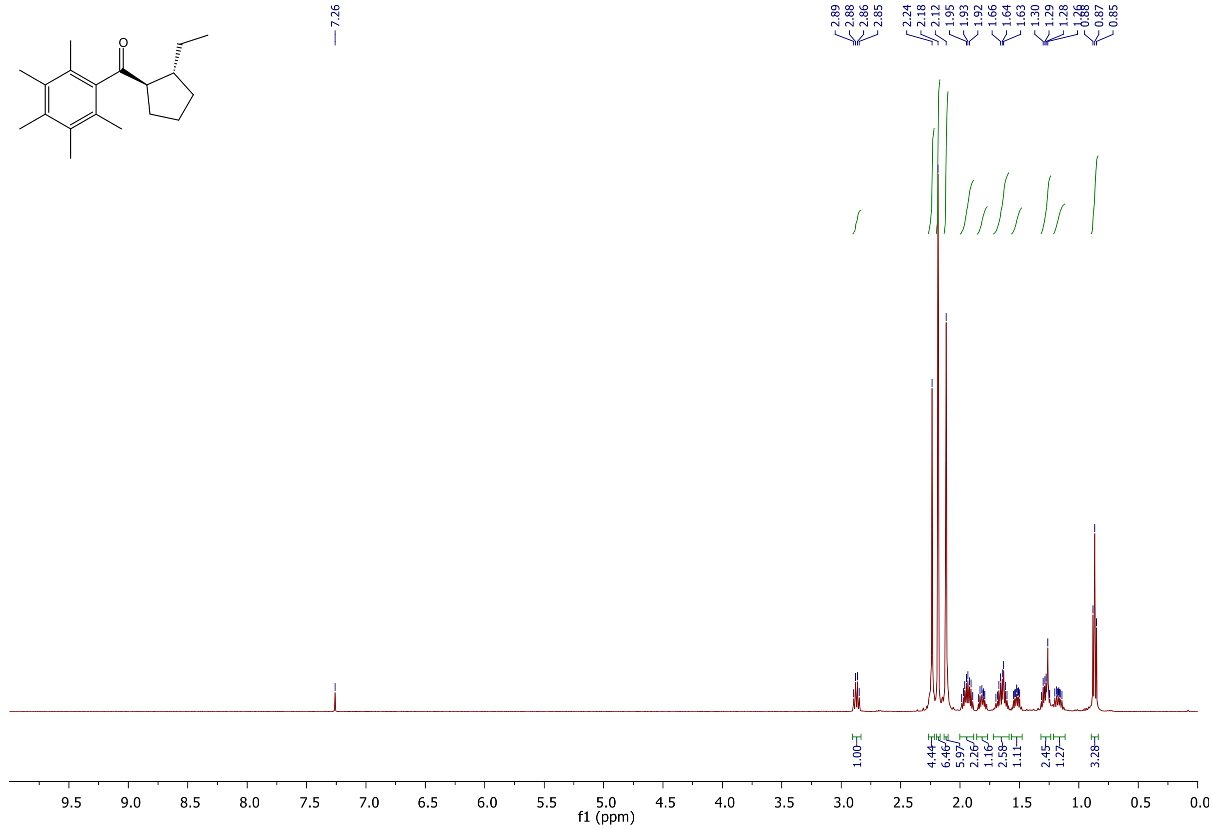


Figure S81: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 2r

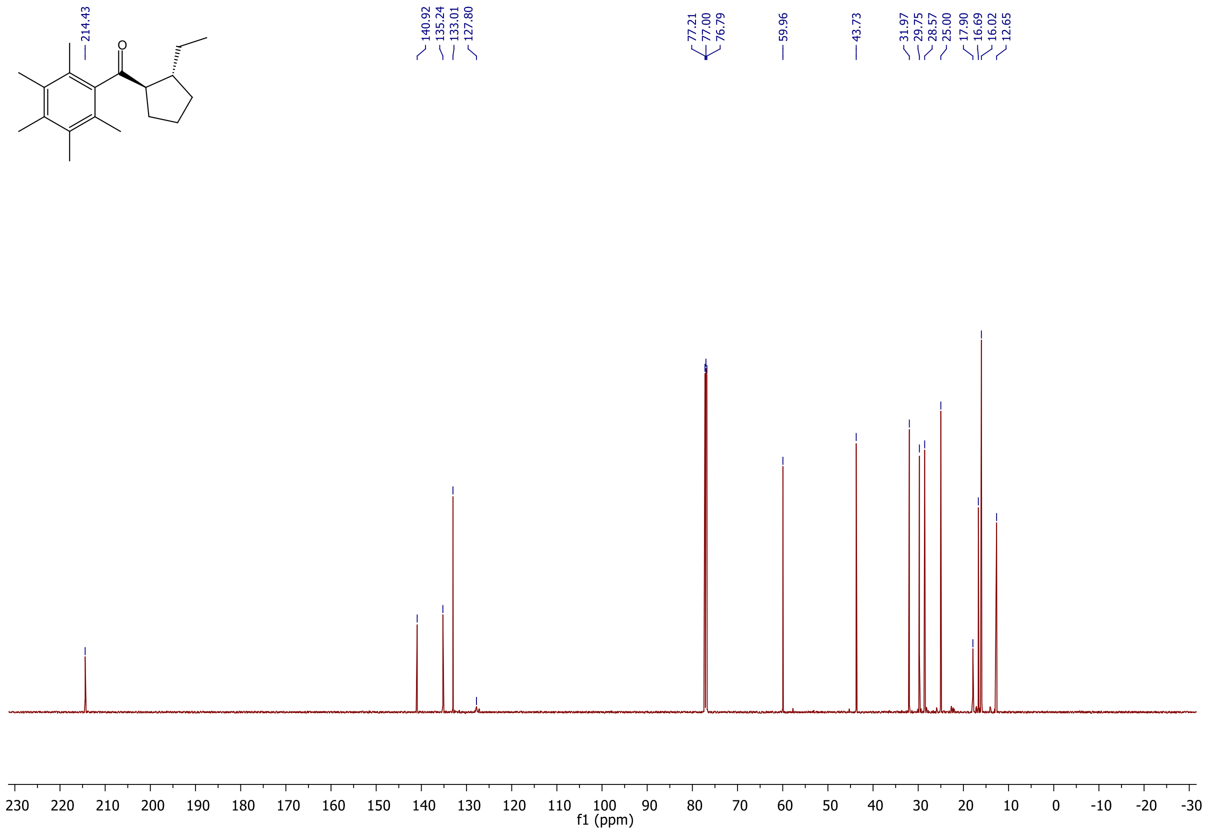


Figure S82: ^{13}C-NMR (150 MHz) in CDCl$_3$ of 2r

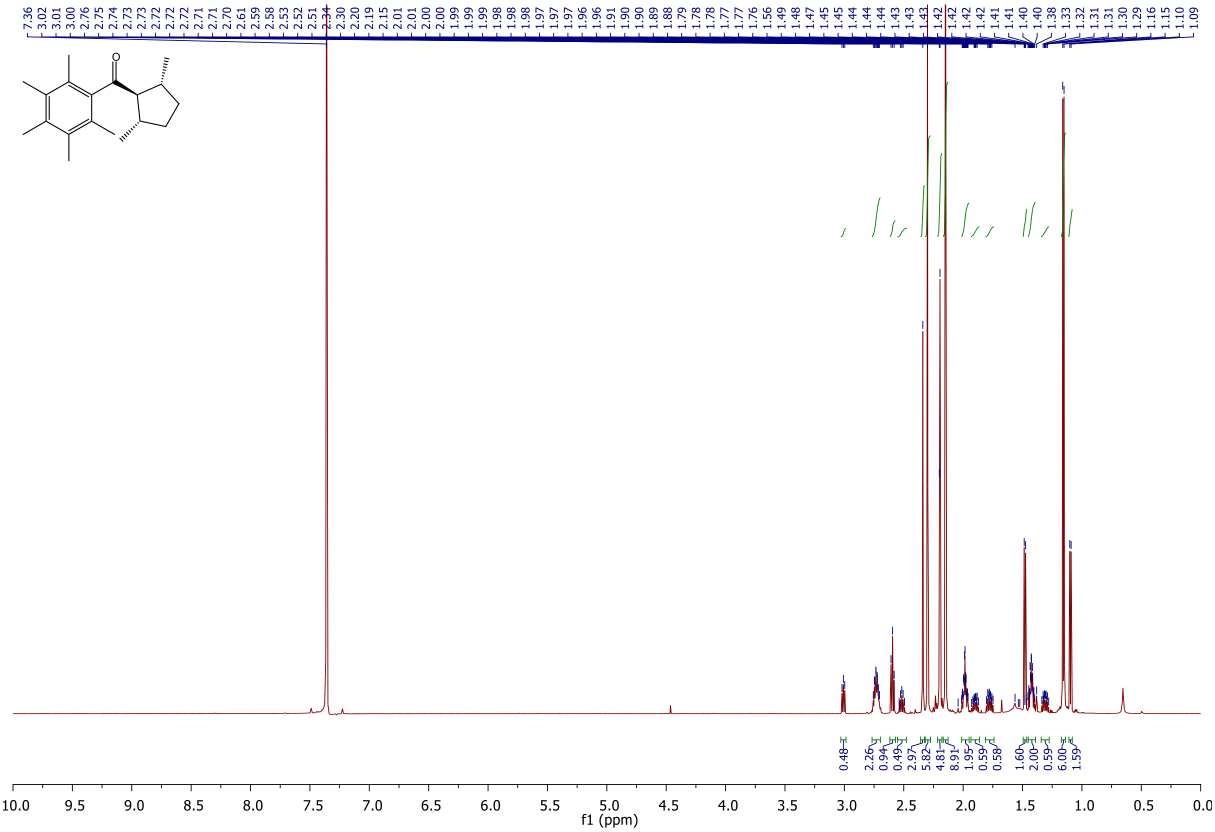


Figure S83: ^{1}H-NMR (600 MHz) in C$_6$D$_6$ of 2s

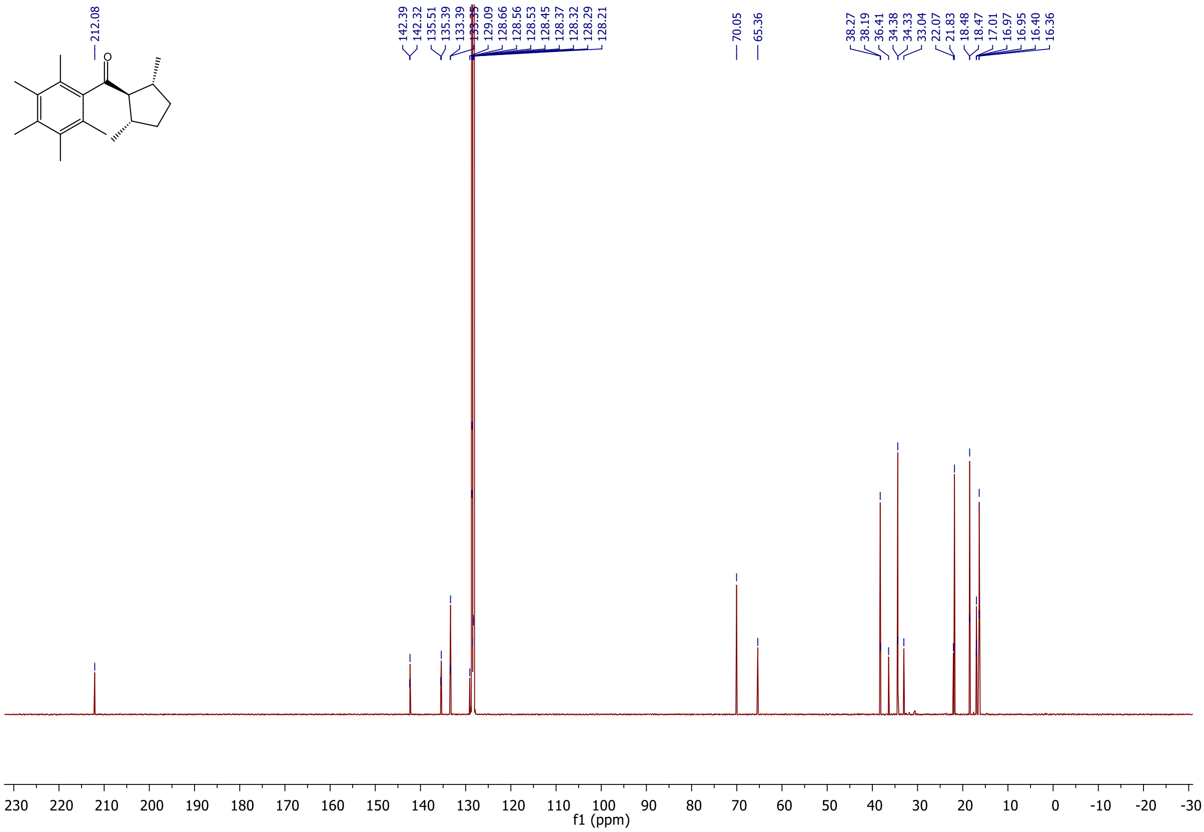


Figure S84: ^{13}C-NMR (150 MHz) in C_6D_6 of 2s

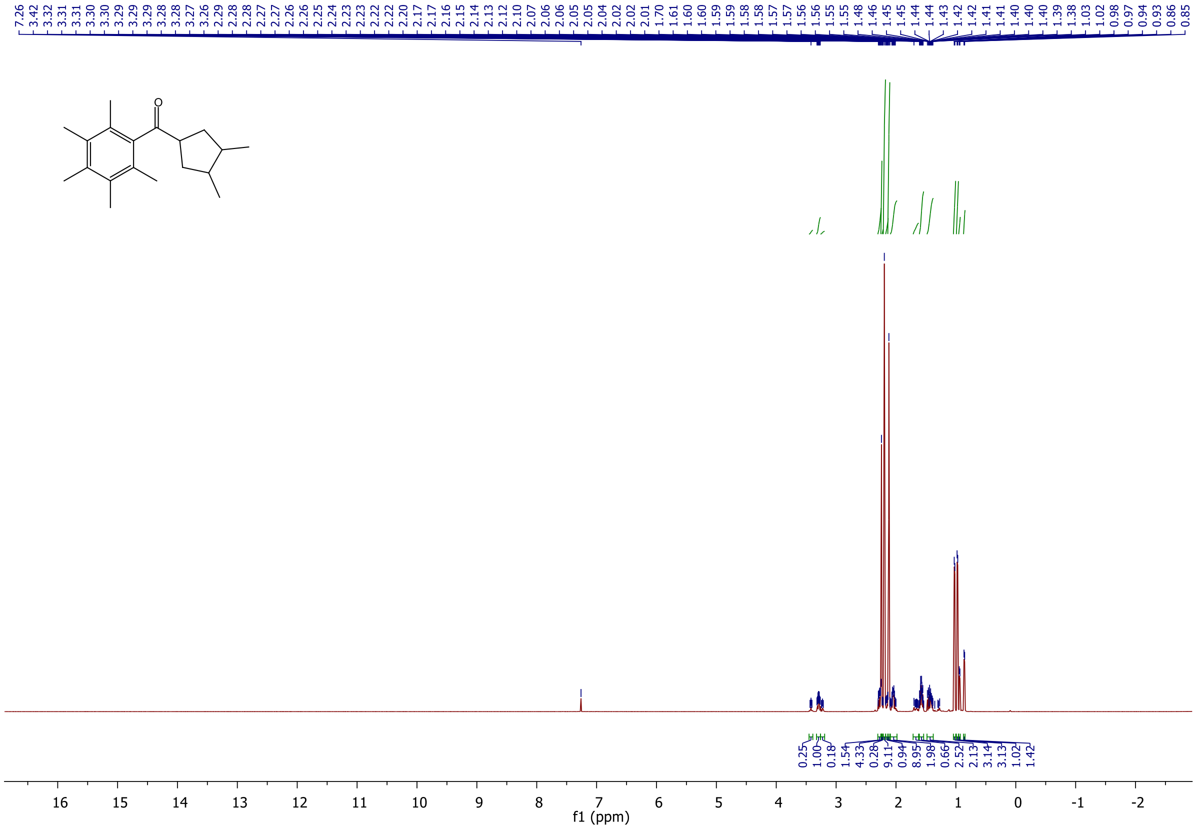


Figure S85: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 2t

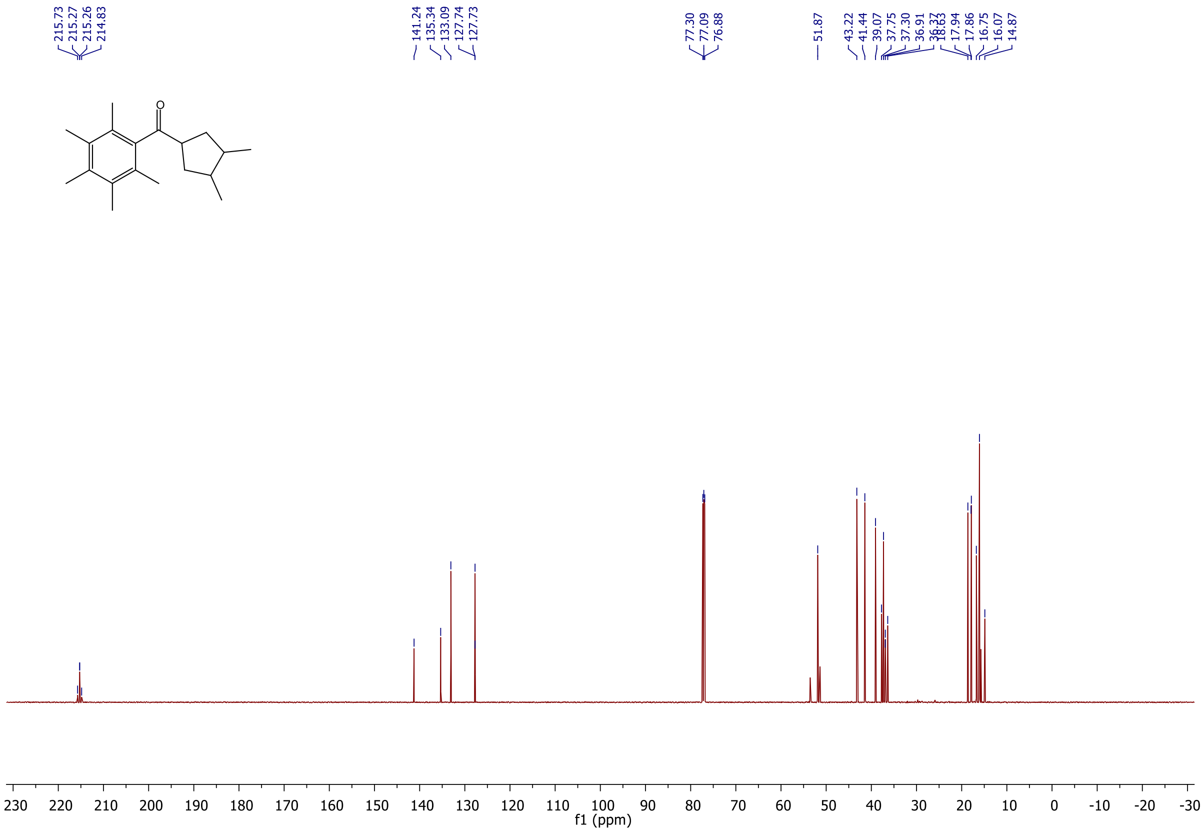


Figure S86: ^{13}C-NMR (150 MHz) in CDCl$_3$ of 2t

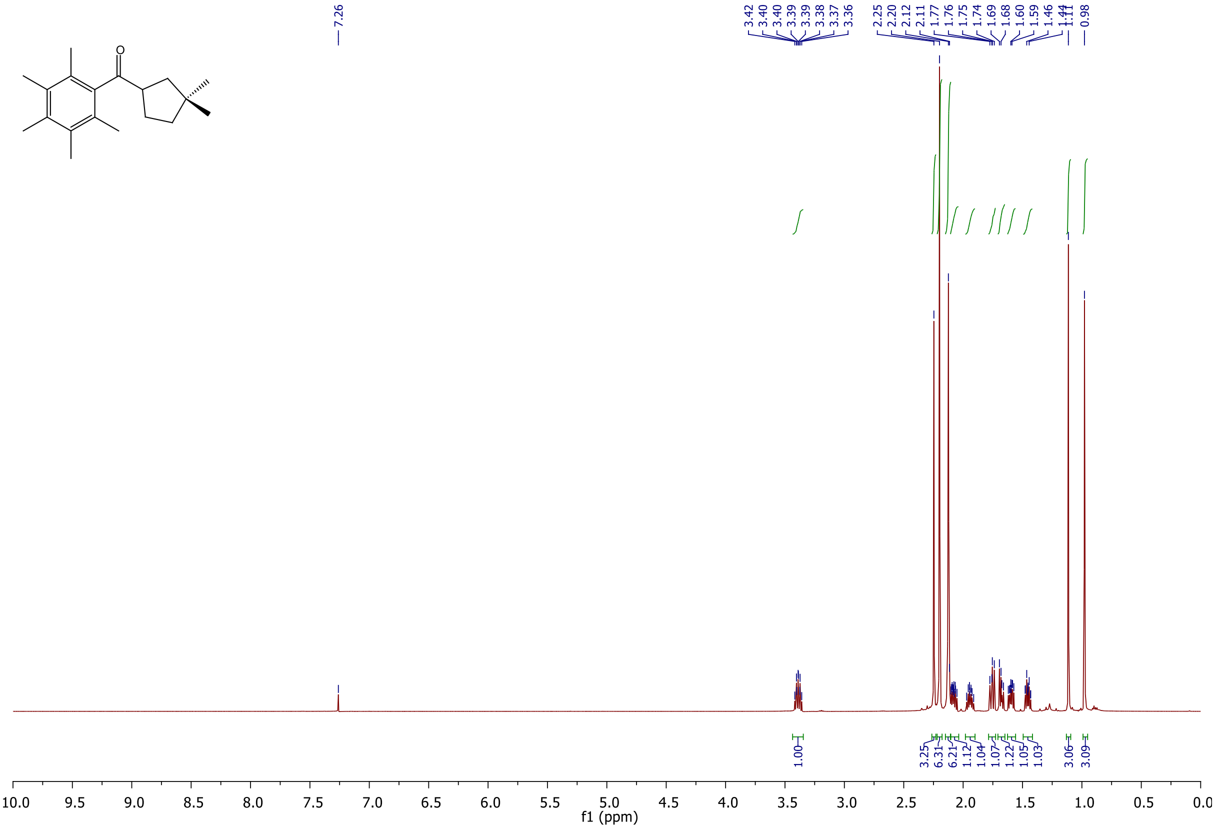


Figure S87: ^{1}H-NMR (600 MHz) in CDCl$_3$ of 2u

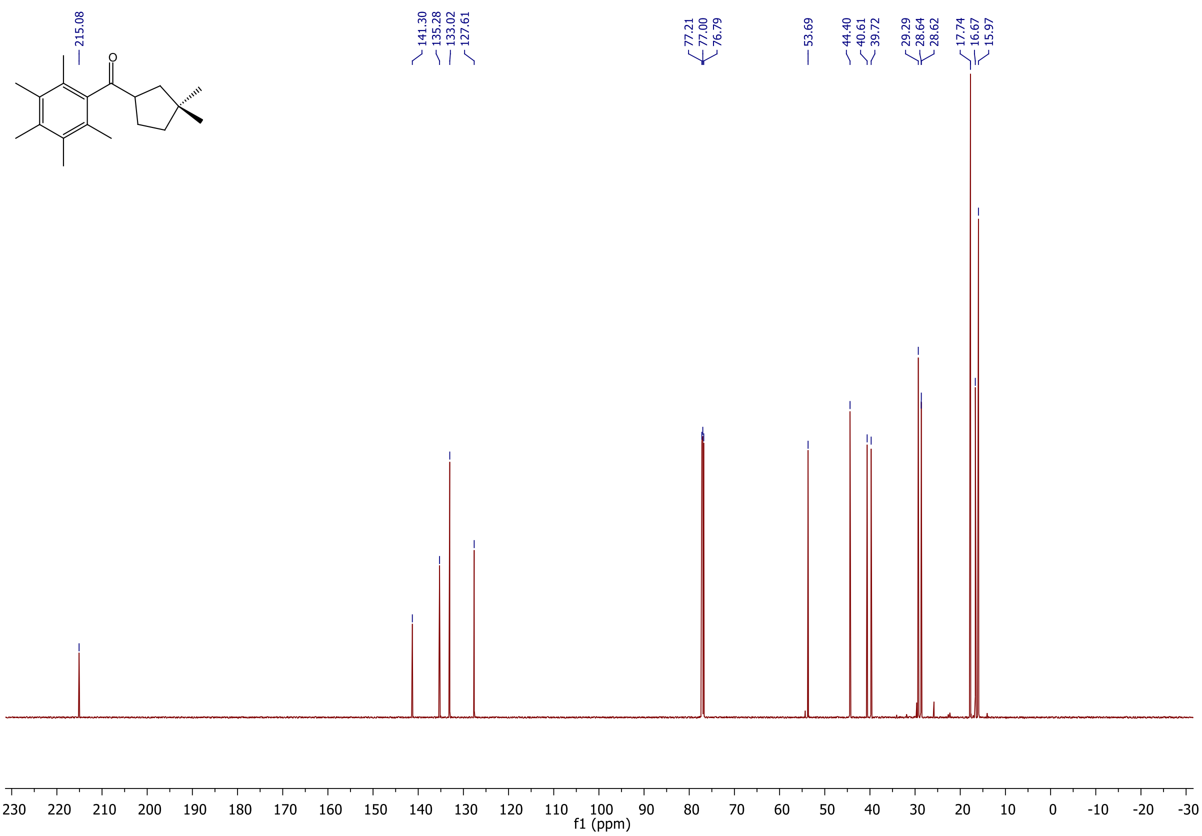


Figure S88: ^{13}C-NMR (150 MHz) in CDCl$_3$ of 2u

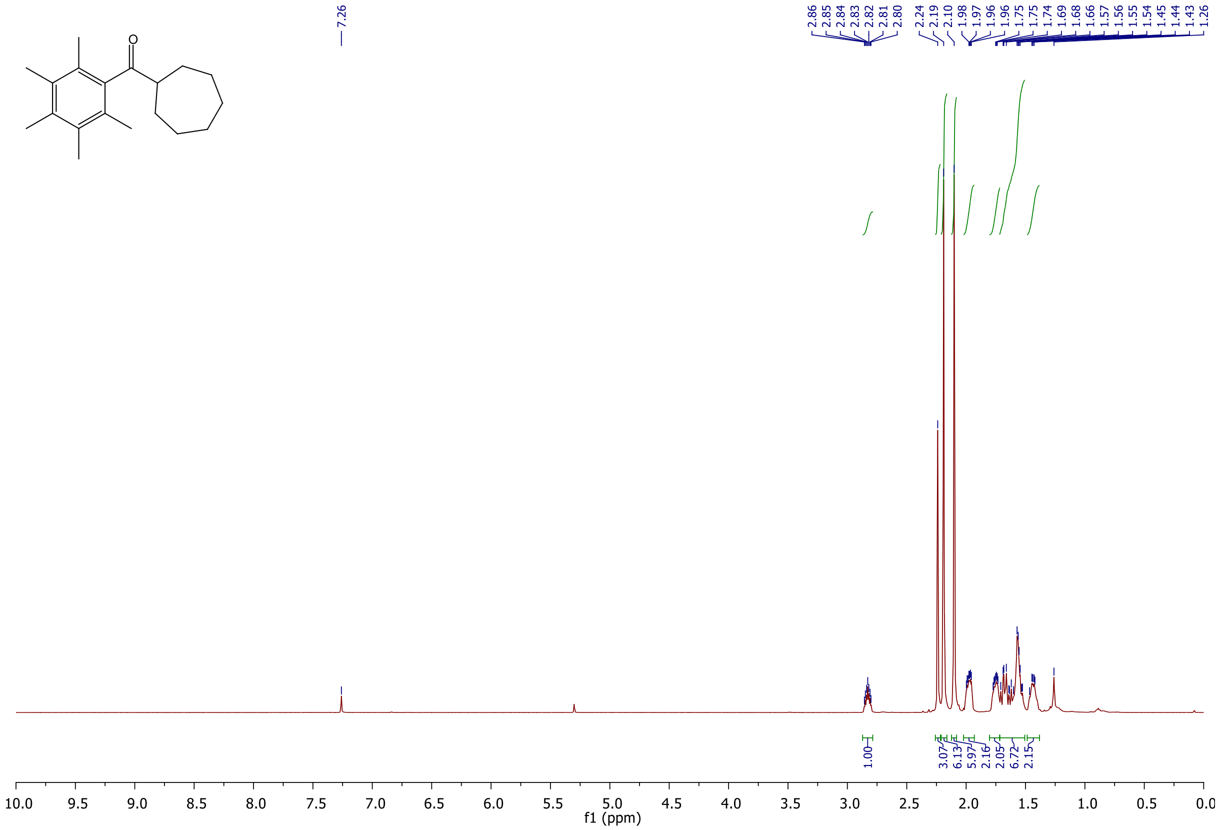


Figure S89: ^{1}H-NMR (600 MHz) in CDCl$_3$ of 2v

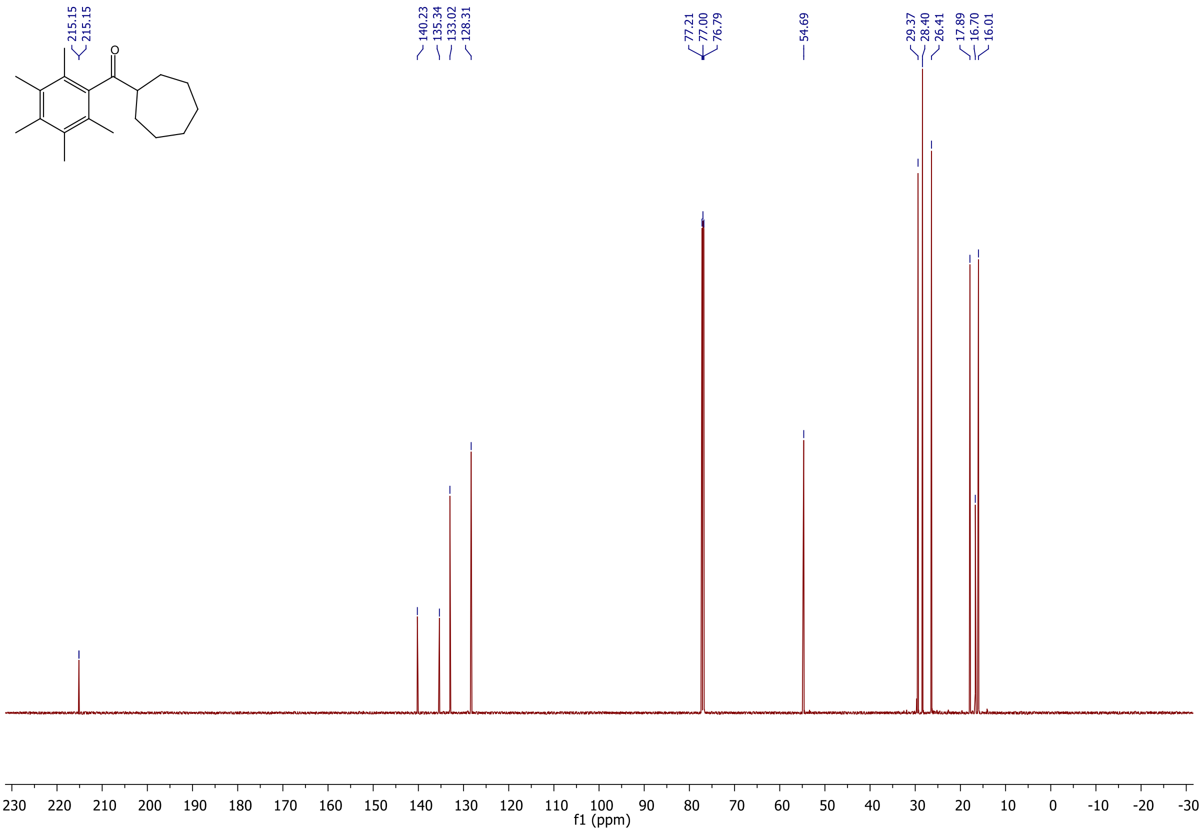


Figure S90: ^{13}C-NMR (150 MHz) in CDCl$_3$ of 2v

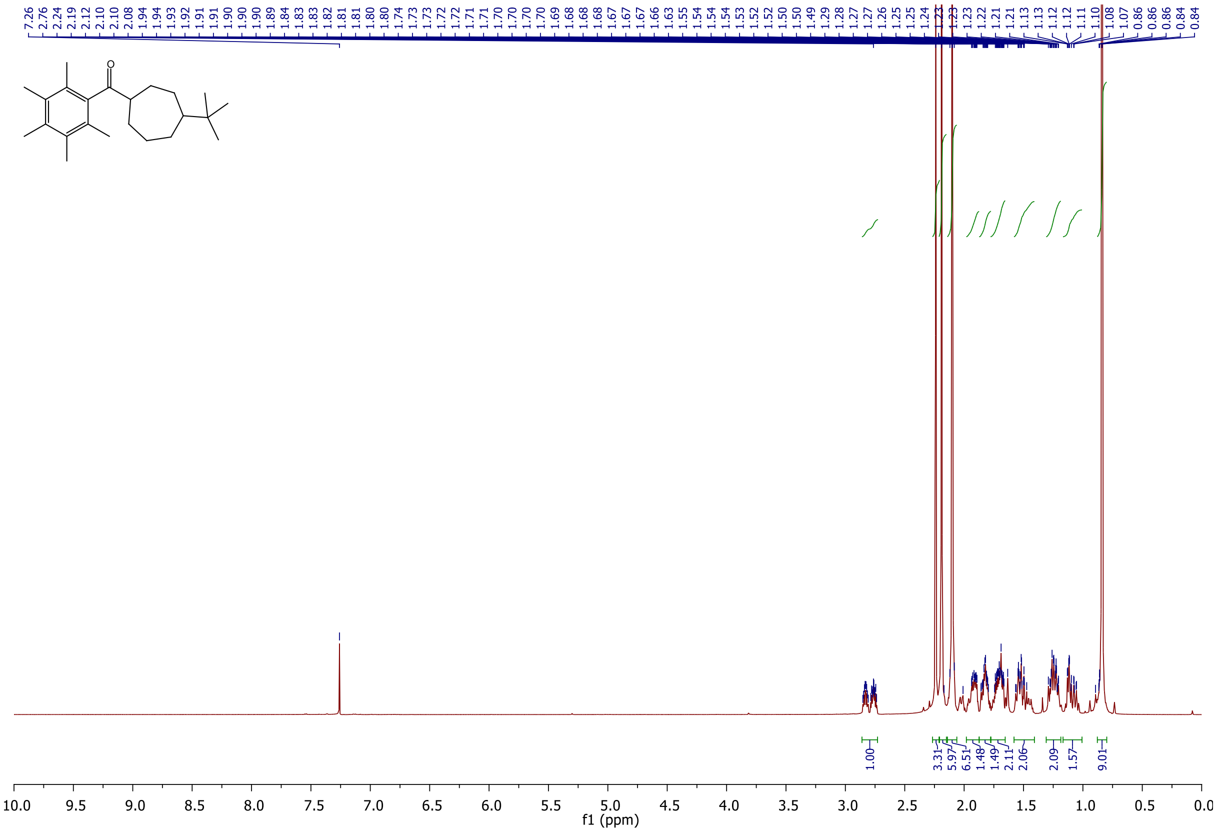


Figure S91: ^{1}H-NMR (600 MHz) in CDCl$_3$ of 2w

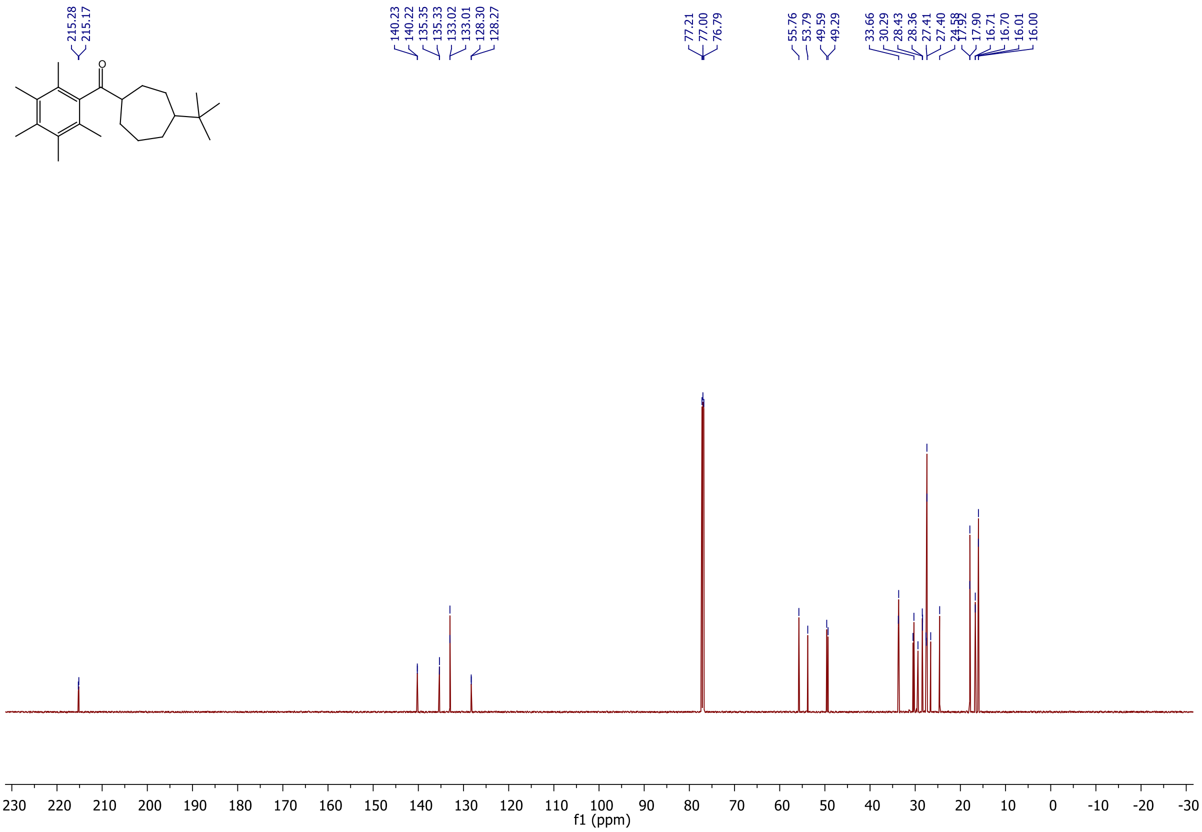


Figure S92: ^{13}C-NMR (150 MHz) in $CDCl_3$ of 2w

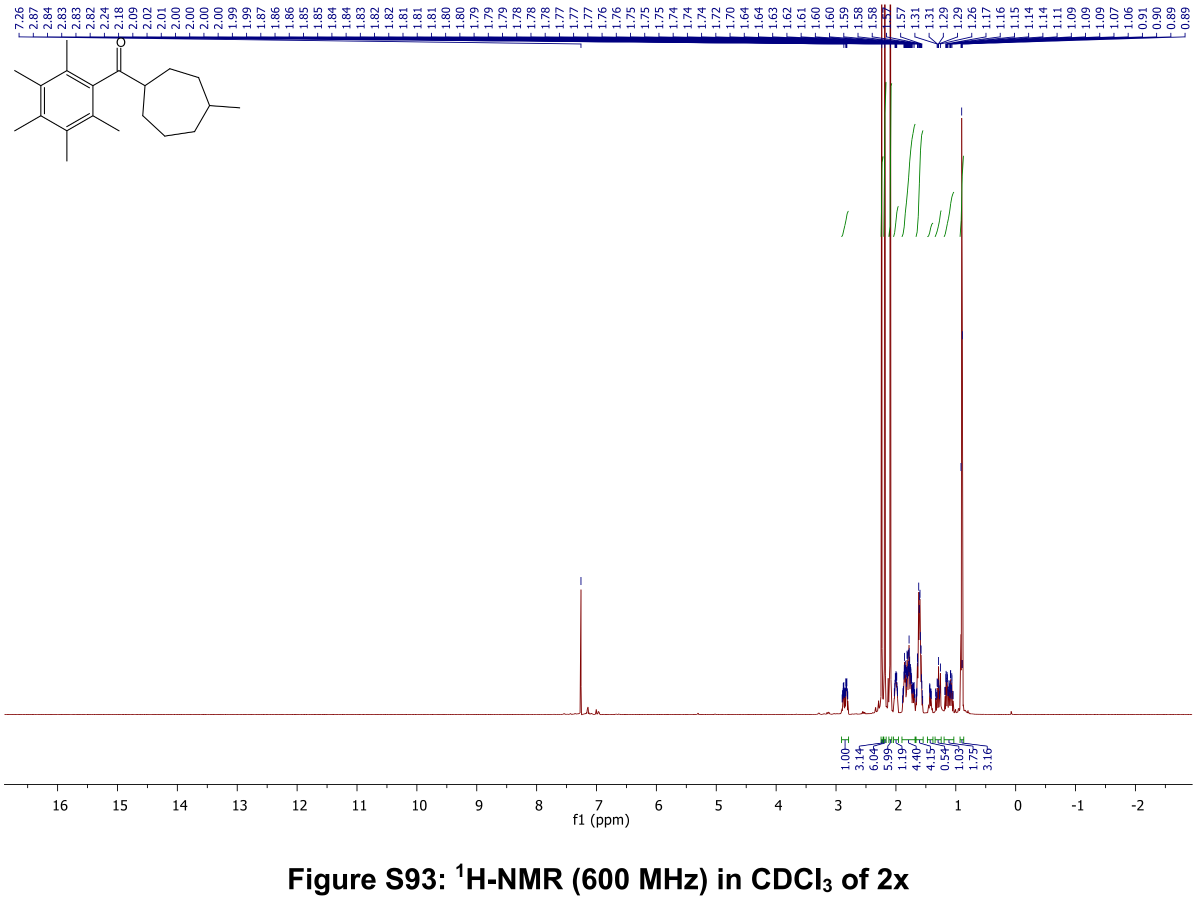


Figure S93: ^{1}H-NMR (600 MHz) in $CDCl_3$ of 2x

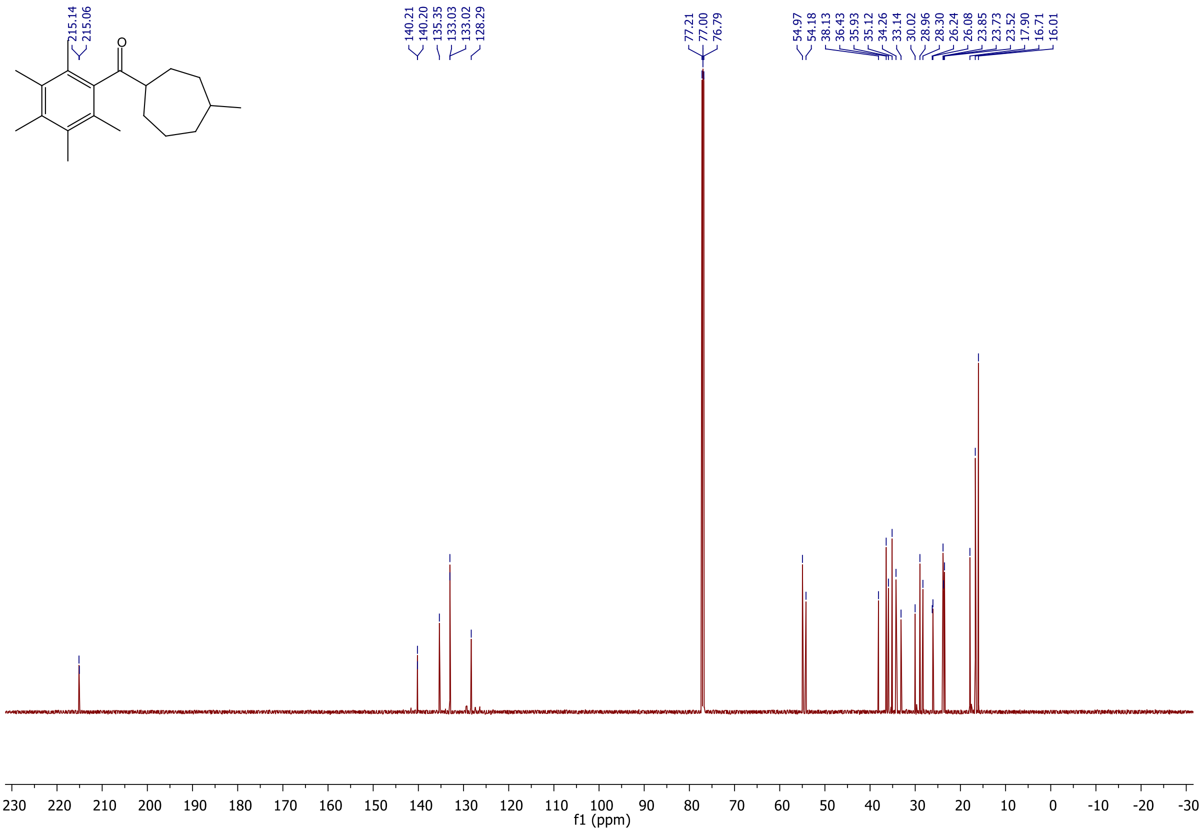
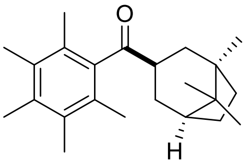
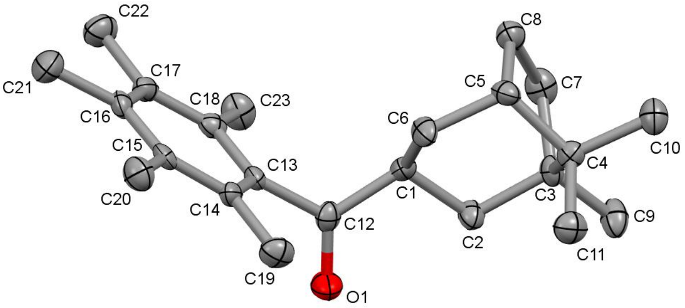


Figure S94: ^{13}C-NMR (150 MHz) in CDCl$_3$ of 2x

Part 7: Crystallographic Data of Compound 2l





Single crystals of **2l** suitable for X–ray crystallographic analysis were obtained by slow evaporation of methanol. X–ray diffraction experiments for monocrystal of **X** were performed at 150 K with graphite–monochromatized Mo K_α radiation (λ = 0.71073 Å) on a Bruker D8Quest diffractometer. Formula $C_{23}H_{34}O$, formula weight 326.50, crystal system monoclinic, space group $P2_1$, a = 6.689(4) Å, b = 10.950(6) Å, c = 13.040(10) Å, $\alpha = \gamma = 90°$, β = 94.67(5)°, V = 952.0(11) Å^3, Z = 2, calculated density = 1.139 g/cm^3, μ = 0.067 mm^{-1}, R_{int} = 0.0711, $R[F^2>2\sigma(F^2)]$ = 0.0575, $wR(F^2)$ = 0.1227. Reflections measured = 6469, independent reflections = 3024, observed reflections $[I > 2\sigma(I)]$ = 1928. Program(s) used to solve structure: SHELXT 2014/5. Program(s) used to refine structure: SHELXL-2018/3. Program used for absorption correction: SADABS 2016/2. Software used to prepare material for publication: SHELXTL.