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SUPPORTING INFORMATION

Double asymmetric hydrogenation of conjugated dienes: a self-breeding chirality route for C_2 symmetric 1,4-diols

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General Procedures

All reactions and manipulations were performed under nitrogen or argon, either in a Braun Labmaster 100 glovebox or using standard Schlenk-type techniques. All solvents were distilled under nitrogen with the following desiccants: sodium-benzophenone-ketyl for diethyl ether (Et_2O) and tetrahydrofuran (THF); sodium for *n*-hexane and toluene; CaH_2 for dichloromethane (CH_2Cl_2); and NaO^iPr for isopropanol (^{i}PrOH). (Z)-1-Iodo-alken-2-yl acetates **2b-j** were synthesized by procedures described

in the literature,[S1] Complexes [Rh(NBD)(P-OP)]BF_4 (P-OP = phosphine-phosphite; **3a-3c**),[S2] [$NiCl_2(PPh_3)_2$],[S3] and [AuCl(IPr)] (IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene)[S4] were prepared as described previously. All other reagents were purchased from commercial suppliers and used as received. IR spectra were recorded on Perkin-Elmer 1720-XFT or Bruker Vector 22 spectrometers. NMR spectra were obtained on Bruker DPX-300, DRX-400, or DRX-500 spectrometers. $^{31}P\{^1H\}$ NMR shifts were referenced to external 85% H_3PO_4, while $^{13}C\{^1H\}$ and ^1H shifts were referenced to the residual signals of deuterated solvents. All data are reported in ppm downfield from $(CH_3)_4Si$. All NMR measurements were carried out at 25 °C, unless otherwise stated. HPLC analyses were performed by using a Waters 2690 chromatograph. HPLC analyses were performed at 30 ºC. HRMS data were obtained on a JEOL JMS-SX 102A, Thermo Orbitrap Elite or Thermo QExactive mass spectrometers in the General Services of Universidad de Sevilla (CITIUS). Optical rotations were measured on a Perkin-Elmer Model 341 polarimeter.

Synthesis and Characterization of Dienes 1

Synthesis of (*Z*,*Z*)-hexa-2,4-diene-2,5-diyl diacetate (1a): 2,4-Hexadiyne (0.079 g; 1 mmol), acetic acid (0.154 mL; 2 mmol), [AuCl(IPr)] (0.019 g; 0.05 mmol), $AgPF_6$ (0.012 g; 0.05 mmol) and toluene (3 mL) were introduced into a Teflon-capped sealed tube, and the reaction mixture was stirred at 120 ºC for 18 h in the absence of light. The solvent was then removed *in vacuo* and the resulting oily residue purified by flash column chromatography over silica gel using diethyl ether/*n*-hexane (1:5) as eluent. White solid. Yield: 0.059 g (60%). ^1H NMR ($CDCl_3$, 400 MHz): δ = 5.64 (s, 2H, =CH),

2.18 (s, 6H, CH_3), 1.95 (s, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 168.5, 145.9, 109.8, 20.8, 19.8 ppm. IR (KBr): ν = 1738 (s, C=O), 1652 (m, C=C) cm^{-1}. HRMS (ESI): *m/z* 221.0787, $[M+Na^+]$ (calcd for $C_{10}H_{14}O_4Na$: 221.0784).

General procedure for the preparation of the 1,3-diene-1,4-diyl diacetates 1b-j. A suspension of $[NiCl_2(PPh_3)_2]$ (0.065 g, 0.1 mmol), NaI (0.015 g, 0.1 mmol) and Zn dust (0.105 g, 1.6 mmol) in THF (5 mL) was stirred at room temperature for 30 min. After this time, a solution of the corresponding (*Z*)-*β*-iodoenol acetate **2b-j** (1 mmol) in THF (2 mL) was added and the resulting mixture further stirred at r.t. for 16 hours. The solvent was then removed *in vacuo*, and the crude reaction mixture purified by column chromatography over silica gel using *n*-hexane/diethyl ether (10:1) as eluent. The corresponding dienes **1b-j** were obtained as pure *Z,Z* isomers in 71-89% yield.

(*Z*,*Z*)-Deca-4,6-diene-4,7-diyl diacetate (1b): White solid. Yield: 0.104 g (82%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.64 (s, 2H, =CH), 2.24 (t, *J*(H-H) = 7.5 Hz, 4H, CH_2), 2.19 (s, 6H, CH_3), 1.53-1.41 (m, 4H, CH_2), 0.91 (t, *J*(H-H) = 7.2 Hz, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 168.6, 149.7, 109.2, 35.6, 20.7, 19.9, 13.5 ppm. IR (KBr): ν = 1750 (s, C=O), 1645 (m, C=C) cm^{-1}. HRMS (ESI): *m/z* 277.1406, $[M+Na^+]$ (calcd for $C_{14}H_{22}O_4Na$: 277.1410).

(*Z*,*Z*)-Dodeca-5,7-diene-5,8-diyl diacetate (1c): White solid. Yield: 0.126 g (89%). ^1H NMR ($CDCl_3$, 400 MHz): *δ* = 5.63 (s, 2H, =CH), 2.26 (t, *J*(H-H) = 7.2 Hz, 4H, CH_2), 2.19 (s, 6H, CH_3), 1.44-1.40 (m, 4H, CH_2), 1.35-1.31 (m, 4H, CH_2), 0.90 (t, *J*(H-H) = 7.2 Hz, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 168.6, 149.9, 109.0, 33.3, 28.7, 22.1, 20.8, 13.8 ppm. IR (KBr): ν = 1760 (s, C=O), 1647 (m, C=C) cm^{-1}. HRMS (ESI): *m/z* 283.1908, $[M+H^+]$ (calcd for $C_{16}H_{27}O_4$: 283.1904).

(*Z*,*Z*)-Hexadeca-7,9-diene-7,10-diyl diacetate (1d): White solid. Yield: 0.135 g (80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.63 (s, 2H, =CH), 2.25 (t, *J*(H-H) = 7.6 Hz, 4H, CH_2), 2.19 (s, 6H, CH_3), 1.44-1.41 (m, 4H, CH_2), 1.27 (br, 12H, CH_2), 0.88 (t, *J*(H-H) = 6.0 Hz, 6H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 168.6, 149.9, 109.0, 33.6, 31.6, 28.7, 26.6, 22.5, 20.8, 14.0 ppm. IR (KBr): ν = 1754 (s, C=O), 1643 (m, C=C) cm^{-1}. HRMS (ESI): *m/z* 361.2351, [M+Na^{+}] (calcd for $C_{20}H_{34}O_4Na$: 361.2349).

(*Z*,*Z*)-2,11-Dimethyldodeca-5,7-diene-5,8-diyl diacetate (1e): White solid. Yield: 0.116 g (75%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.64 (s, 2H, =CH), 2.27 (t, *J*(H-H) = 7.5 Hz, 4H, CH_2), 2.21 (s, 6H, CH_3), 1.59-1.53 (m, 2H, CH), 1.38-1.30 (m, 4H, CH_2), 0.89 (d, *J*(H-H) = 6.6 Hz, 12H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 168.6, 150.1, 108.9, 35.6, 31.6, 27.6, 22.4, 20.8 ppm. IR (KBr): ν = 1747 (s, C=O), 1650 (m, C=C) cm^{-1}. HRMS (ESI): *m/z* 333.2040, [M+Na^{+}] (calcd for $C_{18}H_{30}O_4Na$: 333.2036).

(*Z*,*Z*)-1,4-Dicyclopentylbuta-1,3-diene-1,4-diyl diacetate (1f): White solid. Yield: 0.124 g (81%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.64 (s, 2H, =CH), 2.75-2.64 (m, 2H, CH), 2.20 (s, 6H, CH_3), 1.81 (br, 4H, CH_2), 1.66-1.42 (m, 12H, CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 168.7, 152.4, 107.8, 44.1, 30.5, 24.8, 20.7 ppm. IR (KBr): ν = 1751 (s, C=O), 1638 (m, C=C) cm^{-1}. HRMS (ESI): *m/z* 329.1726, [M+Na^{+}] (calcd for $C_{18}H_{26}O_4Na$: 329.1723).

(*Z*,*Z*)-1,4-Dicyclohexylbuta-1,3-diene-1,4-diyl diacetate (1g): White solid. Yield: 0.119 g (71%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.58 (s, 2H, =CH), 2.22 (s, 6H, CH_3), 2.19-2.14 (m, 2H, CH), 1.89-.166 (m, 10H, CH_2), 1.32-1.08 (m, 10H, CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ = 168.7, 154.0, 107.3, 42.0, 30.6, 26.0, 25.9, 20.7

ppm. IR (KBr): ν = 1753 (s, C=O), 1635 (m, C=C) cm^{-1}. HRMS (ESI): *m/z* 357.2035, $[M+Na^+]$ (calcd for $C_{20}H_{30}O_4Na$: 357.2036).

(*Z*,*Z*)-1,6-Diphenylhexa-2,4-diene-2,5-diyl diacetate (1h): Pale yellow solid. Yield: 0.135 g (77%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.35-7.21 (m, 10H, Ar-H), 5.68 (s, 2H, =CH), 3.63 (s, 4H, CH_2), 2.06 (s, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 168.5, 149.2, 136.6, 129.2, 128.5, 126.8, 110.7, 39.9, 20.6 ppm. IR (KBr): ν = 1748 (s, C=O), 1635 (m, C=C) cm^{-1}. HRMS (ESI): *m/z* 373.1415, $[M+Na^+]$ (calcd for $C_{22}H_{22}O_4Na$: 373.1410).

(*Z*,*Z*)-1,8-Diphenylocta-3,5-diene-3,6-diyl diacetate (1i): White solid. Yield: 0.140 g (74%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.38-7.19 (m, 10H, Ar-H), 5.67 (s, 2H, =CH), 2.81 (t, *J*(H-H) = 7.8 Hz, 4H, CH_2), 2.62 (t, *J*(H-H) = 7.8 Hz, 4H, CH_2), 2.13 (s, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 168.6, 149.3, 140.8, 128.4, 128.3, 126.1, 109.6, 35.3, 33.1, 20.7 ppm. IR (KBr): ν = 1737 (s, C=O), 1651 (m, C=C) cm^{-1}. HRMS (ESI): *m/z* 401.1725, $[M+Na^+]$ (calcd for $C_{24}H_{26}O_4Na$: 401.1723).

(*Z*,*Z*)-1,10-Diphenyldeca-4,6-diene-4,7-diyl diacetate (1j): White solid. Yield: 0.158 g (78%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.35-7.20 (m, 10H, Ar-H), 5.70 (t, *J*(H-H) = 4.3 Hz, 2H, =CH), 2.67 (t, *J*(H-H) = 7.4 Hz, 4H, CH_2), 2.38-2.35 (m, 4H, CH_2), 2.22 (s, 6H, CH_3), 1.85-1.82 (m, 4H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ = 168.6, 149.4, 141.8, 128.5, 128.4, 125.9, 109.6, 35.1, 33.2, 28.2, 20.8 ppm. IR (KBr): ν = 1746 (s, C=O), 1644 (m, C=C) cm^{-1}. HRMS (ESI): *m/z* 429.2040, $[M+Na^+]$ (calcd for $C_{26}H_{30}O_4Na$: 429.2036).

Synthesis and Characterization of Diesters 6

Representative process for asymmetric hydrogenation. In a glovebox, a solution of **5b** (0.33 mg, 0.50 μmol) and substrate **1c** (14.2 mg, 0.050 mmol) in 1,2-dichloroethane (0.5 mL) was placed in a HEL CAT-18 or in a HEL 16 mL reactors. The reactor was purged with hydrogen and finally pressurized at 20 bar. The reaction was heated at 40 ºC and magnetically stirred for 24 h. Then, the reactor was depressurized and the resulting solution slowly evaporated under vacuum. The remaining residue was readily analyzed by ^{1}H NMR to determine conversion, as hydrogenations cleanly proceeded to products **6**. Then it was dissolved in a *i*-PrOH / *n*-hexane 1:10 mixture and passed through a short pad of silica gel to remove catalyst decomposition products. The solution obtained was carefully evaporated and the residue obtained was analyzed by chiral GC or HPLC to determine enantiomeric excess and diastereomeric ratio, with the exception of **6d**, as described below. Racemic mixtures were obtained by hydrogenation of **1** with [Rh(COD)(DiPFc)]BF_4 [DiPFc = 1,1'-bis(diisopropylphosphino)ferrocene].[S5]

Hexane-2,5-diyl diacetate (6a): GC, Chirasil DEX CB, initial temp = 140 °C (5 min), then 5 °C/min up to 200 °C (15 min), 20 psi (He), t_1= 3.9 min (*S*,*S*), t_2 = 4.3 min (*R*,*S*), t_3 = 4.6 min (*R*,*R*).

Decane-4,7-diyl diacetate (6b): GC, Chirasil DEX CB, initial temp = 140 °C (5 min), then 5 °C/min up to 200 °C (15 min), 20 psi (He), t_1= 9.2 min (*S*,*S*), t_2 = 9.6 min (*R*,*R*), t_3 = 9.7 min (*R*,*S*).

Dodecane-5,8-diyl diacetate (6c): GC, Chirasil DEX CB, initial temp = 140 °C (5 min), then 5 °C/min up to 200 °C (15 min), 20 psi (He), t_1= 16.4 min (*S*,*S*), t_2 = 16.6 min (*R*,*R*), t_3 = 16.9 min (*R*,*S*).

Hexadecan-7,10-diyl diacetate (6d): determined by $^{19}F\{^{1}H\}$ NMR analysis of the Mosher esters of the corresponding hexadecane-7,10-diol (see below).

2,11-Dimethyl-dodecan-5,8-diyl diacetate (6e): GC, Chirasil DEX CB, initial temp = 120 °C (5 min), then 2.5 °C/min up to 200 °C (15 min), 20 psi (He), t_1= 40.2 min (*S*,*S*), t_2 = 40.3 min (*R*,*R*), t_3 = 40.7 min (*R*,*S*).

1,4-Dicyclopentyl-butane-1,4-diyl diacetate (6f): GC, Chirasil DEX CB, initial temp = 140 °C (5 min), then 5 °C/min up to 200 °C (15 min), 20 psi (He), t_1= 20.4 min (*minor*), t_2 = 20.6 min (*major*), t_3 = 20.9 min (*R*,*S*).

1,4-Dicyclohexyl-butane-1,4-diyl diacetate (6g): GC, Chirasil DEX CB, initial temp = 120 °C (5 min), then 2.5 °C/min up to 200 °C (15 min), 20 psi (He), t_1= 44.6 min (*minor*), t_2 = 44.9 min (*major*), t_3 = 45.6 min (*R*,*S*).

1,6-Diphenyl-hexane-2,5-diyl diacetate (6h): HPLC, Chiralcel AD-H, 97:3 *n*-hexane:*i*-PrOH, flow 1.0 mL/min, t_1 = 8.9 min (*R*,*S*), t_2 = 9.4 min (*S*,*S*), t_2 = 10.8 min (*R*,*R*).

1,8-Diphenyl-octane-3,6-diyl diacetate (6i): HPLC, Chiralcel AD-H, 97:3 *n*-hexane: *i*-PrOH, flow 1.0 mL/min, t_1 = 13.2 min (*R*,*S*), t_2 = 14.5 min (*R*,*R*), t_2 = 19.5 min (*S*,*S*).

1,10-Diphenyl-decane-4,7-diyl diacetate (6j): HPLC, Chiralcel AD-H, 97:3 *n*-hexane: *i*-PrOH, flow 0.7 mL/min, t_1 = 13.2 min (*R*,*S*), t_2 = 13.8 min (*S*,*S*), t_2 = 14.7 min (*R*,*R*).

Hexane-2,5-diyl diacetate (6a): obtained according to the general procedure (S/C = 100) as a pale orange oil using **5d** [9.2 mg, 93 % yield; dr = 85:15, 96 % ee, (*R*,*R*)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.91 (m, 2H, CH), 2.03 (s, 6H, CH_3), 1.56 (m,

4H, CH_2), 1.21 (d, *J*(H-H) = 6.3 Hz, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 170.7, 70.6, 31.7, 21.4, 19.9 ppm; HRMS (ESI): *m/z* 225.1098, $[M+Na]^+$ (calcd for $C_{10}H_{18}O_4Na$: 225.1097).

Decane-4,7-diyl diacetate (6b): obtained according to the general procedure (S/C = 100) as a pale orange oil using **5d** [11.6 mg, 90 % yield; dr = 83:17, 94 % ee, (*R*,*R*)]. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.87 (m, 2H, CH), 2.03 (s, 6H, CH_3), 1.53 (m, 8H, CH_2), 1.30 (m, 4H, CH_2), 0.90 (t, *J*(H-H) = 7.5 Hz, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 170.9, 73.7, 36.3, 29.8, 21.2, 18.6, 13.9 ppm; HRMS (ESI): *m/z* 281.1725, $[M+Na]^+$ (calcd for $C_{14}H_{26}O_4Na$: 281.1723).

Dodecane-5,8-diyl diacetate (6c): obtained according to the general procedure (S/C = 100) as a pale orange oil using **5b** [13.5 mg, 94 % yield; dr = 74:26, 96 % ee, (*R*,*R*)]. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.85 (m, 2H, CH), 2.03 (s, 6H, CH_3), 1.52 (m, 8H, CH_2), 1.28 (m, 8H, CH_2), 0.98 (t, *J*(H-H) = 6.9 Hz, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 170.9, 73.9, 33.8, 29.8, 27.5, 22.6, 21.2, 14.0 ppm; HRMS (ESI): *m/z* 309.2039, $[M+Na]^+$ (calcd for $C_{16}H_{30}O_4Na$: 309.2036).

Hexadecan-7,10-diyl diacetate (6d): obtained according to the general procedure (S/C = 100) as a pale orange oil using **5b** [15.2 mg, 89 % yield; dr = 74:26, 95 % ee, (*R*,*R*)]. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.85 (m, 2H, CH), 2.03 (s, 6H, CH_3), 1.52 (m, 8H, CH_2), 1.26 (m, 16H, CH_2), 0.87 (t, *J*(H-H) = 6.8 Hz, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 170.9, 73.9, 34.1, 31.7, 29.8, 29.2. 25.3, 22.6, 21.3, 14.1 ppm; HRMS (ESI): *m/z* 365.2657, $[M+Na]^+$ (calcd for $C_{20}H_{38}O_4Na$: 365.2662).

2,11-Dimethyl-dodecan-5,8-diyl diacetate (6e): obtained according to the general procedure (S/C = 100) as a pale orange oil using **5d** [14.4 mg, 92 % yield; dr = 79:21, 95 % ee, (*R*,*R*)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.85 (m, 2H, CHO), 2.04 (s, 6H, CH_3), 1.52 (m, 10H, CH_2 + $(CH_3)_2CH$), 1.15 (m, 4H, CH_2), 0.87 (d, *J*(H-H) = 6.4 Hz, 12H, $(CH_3)_2CH$) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ = 170.9, 74.2, 34.3, 31.9, 29.8, 27.9, 22.6, 22.5, 21.3 ppm; HRMS (ESI): *m/z* 337.2350, $[M+Na]^+$ (calcd for $C_{18}H_{34}O_4Na$: 337.2349).

1,4-Dicyclopentyl-butane-1,4-diyl diacetate (6f): obtained according to the general procedure (S/C = 100) as a pale orange oil using **5d** [14.3 mg, 92 % yield; dr = 59:41, 60 % ee]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.80 (m, 2H, CH), 2.04 (m, 8H, CH_3 + CH), 1.54 (m, 16H, CH_2), 1.19 (m, 4H, CH_2) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ = 171.0, 77.4, 43.6, 29.2, 29.0, 28.5, 25.5, 25.2, 21.2 ppm; HRMS (ESI): *m/z* 333.2036, $[M+Na]^+$ (calcd for $C_{18}H_{30}O_4Na$: 333.2036).

1,4-Dicyclohexyl-butane-1,4-diyl diacetate (6g): obtained according to the general procedure (S/C = 100) as a pale orange oil using **5c** [15.7 mg, 93 % yield; dr = 36:64, 77 % ee]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.71 (m, 2H, CH), 2.05 (s, 6H, CH_3), 1.55 (m, 16H, CH_2 + CH), 1.10 (m, 10H, CH_2) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ = 171.0, 77.9, 41.2, 29.0, 28.1, 27.2, 26.4, 26.1, 26.0, 21.2 ppm; HRMS (ESI): *m/z* 361.2346, $[M+Na]^+$ (calcd for $C_{20}H_{34}O_4Na$: 361.2349).

1,6-Diphenyl-hexane-2,5-diyl diacetate (6h): obtained according to the general procedure using **5a** but with higher substrate and catalyst concentration (**1h**: 0.035 g, 0.1 mmol; DCE: 0.25 mL; S/C = 100) as a pale orange oil [16.8 mg, 95 % yield; dr = 81:19, 96 % ee, (*S*,*S*)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.25 (m, 5H, Ar-H), 7.20 (m, 2H, Ar-H), 7.15 (m, 3H, Ar-H), 5.04 (m, 2H, CH), 2.85 (m, 2H, C*H*H), 2.73 (m, 2H,

CH*H*), 1.94 (s, 6H, CH_3), 1.55 (m, 4H, CH_2) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 170.6, 137.3, 129.4, 128.4, 126.5, 74.2, 40.5, 29.1, 21.1 ppm; HRMS (ESI): *m/z* 377.1719, $[M+Na]^+$ (calcd for $C_{22}H_{26}O_4Na$: 377.1723).

1,8-Diphenyl-octane-3,6-diyl diacetate (6i): obtained according to the general procedure (S/C = 100) as a pale orange oil using **5a** [17.2 mg, 90 % yield; dr = 64:36, 71 % ee, (*R*,*R*)]. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.28 (m, 4H, Ar-H), 7.17 (m, 6H, Ar-H), 4.92 (m, 2H, CH), 2.61 (m, 4H, CH_2), 2.03 (s, 6H, CH_3), 1.85 (m, 4H, CH_2), 1.59 (m, 4H, CH_2) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 170.8, 141.5, 128.5, 128.3, 126.0, 73.4, 35.8, 31.8, 29.8, 21.2 ppm; HRMS (ESI): *m/z* 405.2029 $[M+Na]^+$ (calcd for $C_{24}H_{30}O_4Na$: 405.2036).

1,10-Diphenyl-decane-4,7-diyl diacetate (6j): obtained according to the general procedure (S/C = 100) as a pale orange oil using **5a** [18.6 mg, 91 % yield; dr = 71:29, 89 % ee, (*R*,*R*)]. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.30 (m, 4H, Ar-H), 7.18 (m, 6H, Ar-H), 4.91 (m, 2H, CH), 2.63 (m, 4H, CH_2), 2.06 (s, 6H, CH_3), 1.55 (m, 12H, CH_2) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 170.9, 142.1, 128.4, 128.3, 125.9, 73.6, 35.7, 33.7, 29.8, 27.1, 21.3 ppm; HRMS (ESI): *m/z* 433.2344 $[M+Na]^+$ (calcd for $C_{26}H_{34}O_4Na$: 433.2349).

Determination of configuration of products 6

Configuration of **6a** was determined by comparison of GC data with an authentic sample of (*S*,*S*)-hexane-2,5-diyl diacetate. For compounds **6b**-**6e** and **6i-6j** configuration was assigned by analogy. For compound **6h**, configuration was determined by

conversion into the corresponding enantiopure alcohol (*S,S*)-**8h** and comparison of optical rotation with that reported in the literature.[S6]

Synthesis and Characterization of Diols 8

(*R,R*)-5,8-Dodecanediol (8c): to a solution of diacetate **6c** (0.268 g, dr = 80:20; 95 % ee, corresponding to 0.69 mmol of the C_2 isomers) in MeOH (5 mL) was added K_2CO_3 (390 mg, 2.8 mmol) and the resulting mixture stirred for 18 h. Deionized water (10 mL) was added and the mixture extracted with Et_2O (3 × 10 mL). Organic phases were collected, dried over $MgSO_4$ and solvent evaporated under reduced pressure, giving a mixture of (*R,R*)- and (*R,S*)-**8c** as a white foamy solid. Subsequent crystallization in a *n*-hexane/*i*-PrOH (90:10) mixture yielded (*R,R*)-**8c** as a white solid (0.102 g, 0.50 mmol, 72 %). $[\alpha]_D^{20}$ = -12.4° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.57 (m, 2H, CH), 3.25 (s, 2H, OH), 1.62 (m, 2H, CH_2), 1.41 (m, 14H, CH_2), 0.89 (t, *J*(H-H) = 7.1 Hz, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 72.4, 37.5, 34.2, 27.9, 22.8, 14.1 ppm; Elem. Anal. Calcd for $C_{12}H_{26}O_2$: C 71.23 %, H 12.95 %; found: C 71.14%, H 12.60%.

(*S,S*)-1,6-Diphenyl-2,5-hexanediol (8h): A sample of **6h** (0.193 g, dr = 74:26, 95 % ee, corresponding to 0.40 mmol of the C_2 isomers), was deacylated as described in the procedure for **8c**. A careful recrystallization of diol **8h** in a *n*-hexane/*i*-PrOH (10:90) mixture, allowed to separate less soluble (*R,S*)-**8h** isomer. Final evaporation of the mother liquor led to (*S,S*)-**8h** as a white solid (0.085 g, 0.31 mmol, 77 %). Spectroscopic data for this compound agree with literature data.[S6]

Mosher ester of diol 8d (9)

This analysis has been performed with two samples (A and B) of **8d**. Sample A was obtained by deprotection of diester **6d** obtained by non-enantioselective hydrogenation of **1d** with [Rh(COD)(DiPFc)]BF_4. Sample B was obtained by deprotection of diester **6d** obtained by the enantioselective hydrogenation of **1d** with **5b** under our standard conditions. Sample A of **8d** (0.020 g, 0.077 mmol) was dried azeotropically with toluene (2 × 5 mL) and the residue obtained dissolved in DCM (2 mL). Over this solution it is added pyridine (0.025 mL, 0.308 mmol) and (*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl chloride (0.047 g, 0.19 mmol). The resulting mixture is stirred for 4 h, evaporated under reduced pressure and the resulting oil dissolved in a Et_2O/*n*-hexane (1:9) mixture and filtered through a short pad of silica. The solution obtained was evaporated to yield the diester *rac*-**9** as a colorless oil (0.047 g, 89 %). For the analysis of product of enantioselective hydrogenation of **1d** with **5d** it was followed an analogous procedure starting with sample B. Below is detailed the characterization of *rac*-**9**, while isomer assignation has been done by comparison with spectra of enantioenriched **9**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.55 (m, 4H, Ar-H), 7.40 (m, 6H, Ar-H), 5.05 (m, 2H, CH), 3.57 (s, 6H, OCH_3), 1.56 (m, 8H, CH_2), 1.23 (m, 16H, CH_2), 0.89 (m, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): Isómer *R,R,R,R*: δ = 166.3 (2 C=O), 132.4 (2 C_q arom), 129.6 (2 CH arom), 128.4 (4 CH arom), 127.3 (4 CH arom), 123.0 (q, *J*(C-F) = 289 Hz, 2 CF_3), 84.4 (q, *J*(C-F) = 28 Hz, 2 C_q-Ph), 76.8 (2 OCH), 55.4 (2 OCH_3), 33.7 (2 CH_2), 31.6 (2 CH_2), 29.0 (2 CH_2), 28.7 (2 CH_2), 25.0 (2 CH_2), 22.5 (2 CH_2), 14.0 (2 CH_3) ppm; Isómer *R,S,S,R*: δ = 166.2 (2 C=O), 132.3 (2 C_q arom), 129.6 (2 CH arom), 128.4 (4 CH arom), 127.3 (4 CH arom), 123.0 (q, *J*(C-F) = 289 Hz, 2 CF_3), 84.5 (q, *J*(C-F) = 28 Hz, 2 C_q-Ph), 55.4 (2 OCH_3), 33.6 (2 CH_2), 31.6 (2 CH_2), 29.6 (2 CH_2), 28.9 (2 CH_2), 24.7 (2 CH_2), 22.5 (2 CH_2),

14.0 (2 CH_3) ppm; signals of methyne carbons of this isomer have not been observed due to overlap with solvent signal; $^{19}F\{^1H\}$ NMR ($CDCl_3$, 565 MHz): δ = -71.11 (*R*,*R*,*S*,*R*), -71.12 (*R*,*R*,*R*,*R*), -71.15 (*R*,*R*,*S*,*R*), -71.20 (*R*,*S*,*S*,*R*) ppm; HRMS (ESI): *m/z* 713.3243 $[M+Na]^+$ (calcd for $C_{36}H_{48}O_6F_6Na$: 713.3247).

(*S*,*S*)-Bis-1,2(2,5-di-*n*-butylphospholane)benzene (11)

*(a) (R,R)-5,8-Dodecanediol cyclic sulphate (**10**):* over a solution of diol (*R*,*R*)-**8c**, (140 mg, 0.69 mmol) in DCM (3 mL) cooled at 0ºC was added NEt_3 (0.290 mL, 2.0 mmol) and $SOCl_2$ (0.060 mL, 1.4 mmol). The mixture was left to warm to room temperature, stirred for 2 h and evaporated under reduced pressure. The residue obtained was dissolved in a *n*-hexane:DCM (4:1) mixture and filtered through a short pad of silica. The solution obtained was evaporated giving an orange residue which was used without further purification for the next step. The mentioned residue was dissolved in a mixture of DCM (2 mL), acetonitrile (2 mL) and water (3 mL). The mixture was cooled down to 0 ºC and hydrated $RuCl_3$ (1.1 mg, 0.005 mmol) and $NaIO_4$ (226.7 mg, 1.1 mmol) were added. The reaction was kept on stirring for 2 h and extracted with Et_2O (3 × 10 mL). Ethereal phases were collected, dried over $MgSO_4$, resulting solution evaporated giving an oily residue which was crystallized in a *n*-hexane:Et_2O (10:90) mixture to give corresponding cyclic sulphate of (*R*,*R*)-**10** as a white solid. $[\alpha]_D^{20}$ = -29° (*c* 0.1, THF). ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.60 (m, 2H, CH), 1.90 (m, 4H, CH_2), 1.70 (m, 2H, CH_2), 1.37 (m, 10H, CH_2), 0.88 (t, *J*(H-H) = 7.8 Hz, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ = 85.3, 35.1, 32.9, 27.2, 22.2, 13.8 ppm; HRMS (ESI): *m/z* 287.1289 $[M+Na]^+$ (calcd for $C_{12}H_{24}O_4NaS$: 287.1288).

*(b) (S,S)-Bis-1,2(2,5-di-n-butylphospholane)benzene (**11**):* over a solution of 1,2-bisphosphinobenzene (26.9 mg, 0.19 mmol) in THF (3 mL) was added *n*-BuLi (0.230 mL 1.6 M solution in hexanes, 0.368 mmol) and the reaction was stirred for 1.5 h. Then, the cyclic sulphate obtained in the previous step (*R*,*R*)-**10** (100 mg, 0.36 mmol) was added, the mixture stirred for 2 h, followed by addition of *n*-BuLi (0.230 mL 1.6 M solution in hexanes, 0.368 mmol) and further stirring for 2 h. The mixture obtained was evaporated resulting a residue which was treated with pentane (20 mL) and filtered through a short pad of silica. Further elution with Et_2O afforded a solution, which upon evaporation yielded **11** as a colorless oil (115 mg, 89 %). $[\alpha]_D^{20}$ = +255° (*c* 0.2, THF). ^{1}H NMR (C_6D_6, 500 MHz): δ = 7.40 (m, 2H, Ar-H), 7.10 (m, 2H, Ar-H), 2.52 (m, 2H, CH), 2.31 (m, 2H, CH), 2.15 (m, 2H, CH_2), 1.99 (m, 2H, CH_2), 1.75 (m, 6H, CH_2), 1.36 (m, 20H, CH_2), 0.98 (m, 2H, CH_2), 0.94 (t, *J*(H-H) = 7.0 Hz, 6H, CH_3), 0.84 (t, *J*(H-H) = 7.0 Hz, 6H, CH_3) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): δ = -3.8 ppm; $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ = 144.9 (2 C_q), 132.0 (2 CH arom), 127.7 (2 CH arom), 40.0 (virt t, J_{app}(C-P) = 8 Hz, 2 CH), 39.4 (2 CH), 36.1(virt t, J_{app}(C-P) = 16 Hz, 2 CH_2), 33.6 (2 CH_2), 33.3 (2 CH_2), 32.4 (2 CH_2), 32.0 (virt t, J_{app}(C-P) = 6 Hz, 2 CH_2), 31.8 (virt t, J_{app}(C-P) = 4 Hz, 2 CH_2), 23.1 (2 CH_2), 22.8 (2 CH_2), 14.0 (4 CH_3) ppm; HRMS (ESI) *m*/*z*: 475.3615 $[M+H]^+$ (calcd for $C_{30}H_{53}P_2$: 475.3617).

[Rh(COD)(11)]BF_4 (12): over a stirred solution of $[Rh(COD)_2]BF_4$ (81.5 mg, 0.2 mmol) in DCM (3 mL) was added diphosphine **11** (100 mg, 0.21 mmol) dropwise. After 2 h, the mixture was evaporated and the oily residue thoroughly washed with n-pentane (4 × 20 mL), yielding **12** as an orange powder (82 mg, 53%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 7.73 (br m, 4H, Ar-H), 5.63 (br s, 2H, CH-COD), 4.98 (br s, 2H, CH-COD), 2.47 (m, 13H, 4 CH+C*H*H), 1.89 (m, 5H, C*H*H), 1.32 (m, 23H, C*H*H), 0.87 (t, *J*(H-H) = 6.8 Hz, 6H, CH_3), 0.81 (m, 3H, C*H*H), 0.75 (t, *J*(H-H) = 6.8 Hz, 6H,

CH_3) ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz): δ = 70.4 (d, *J*(P-Rh) = 149 Hz) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ = 141.9 (virt dt, J_{app}(C-P) = 36 Hz, *J*(C-Rh) = 4 Hz, 2 C_q arom), 132.9 (t virt, J_{app}(C-P) = 9 Hz, 2 CH arom), 132.0 (2 CH arom), 105.9 (brm, 2 =CH COD), 92.0 (brm, 2 =CH COD), 51.0 (virt t, J_{app}(C-P) = 13 Hz, 2 CH), 43.1 (virt t, J_{app}(C-P) = 12 Hz, 2 CH), 34.7 (2 CH_2 COD), 34.3 (2 CH_2 COD), 33.3 (brs, 2 CH_2), 33.0 (virt t, J_{app}(C-P) = 5 Hz, 2 CH_2), 32.9 (2 CH_2), 31.5 (virt t, J_{app}(C-P) = 4 Hz, 2 CH_2), 29.1 (2 CH_2), 27.9 (2 CH_2), 22.8 (2 CH_2), 22.4 (2 CH_2), 13.6 (2 CH_3), 13.4 (2 CH_3) ppm; HRMS (ESI) *m*/*z*: 685.3533, $[M\text{-}BF_4]^+$ (calcd for: $C_{38}H_{64}P_2Rh$: 685.3533).

Generation and Characterization of complex [Rh(1a){(*S*,*S*)-Me-Duphos}]$^+$

In a Wilmad quick pressure valve NMR tube was introduced a solution of [Rh(COD){(*S*,*S*)-Me-Duphos}]BF_4 in MeOH (0.5 mL). The tube was pressurized with 4 bar H_2 and heated at 40 ºC for 1 h. At this point full conversion was observed by $^{31}P\{^1H\}$ NMR. The tube was then depressurized introduced in a glove-box and the solution transferred to an ampoule. Then was added **1a** (10 mg, 0.05 mmol) and the resulting solution stirred for 15 min and evaporated. The residue was further dried with additional portions of DCM (3 × 2 mL). Finally, the residue obtained was dissolved in CD_2Cl_2 and the solution transferred to a NMR tube.

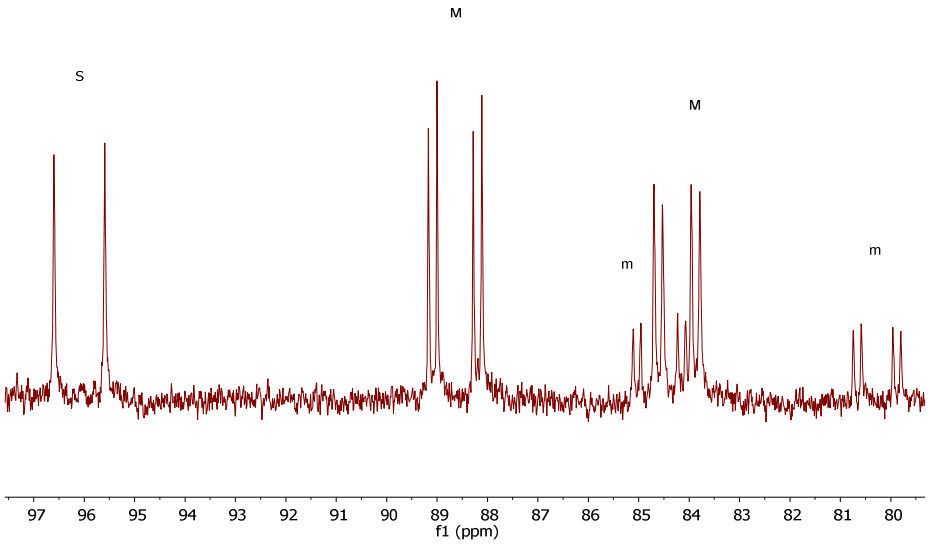


Figure S1. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2) of [Rh(**1a**){(S,S)-Me-Duphos}]BF_4. M and m denote major and minor isomers, respectively, while S corresponds to remaining [Rh{(S,S)-Me-Duphos}$(MeOH)_2$]BF_4.

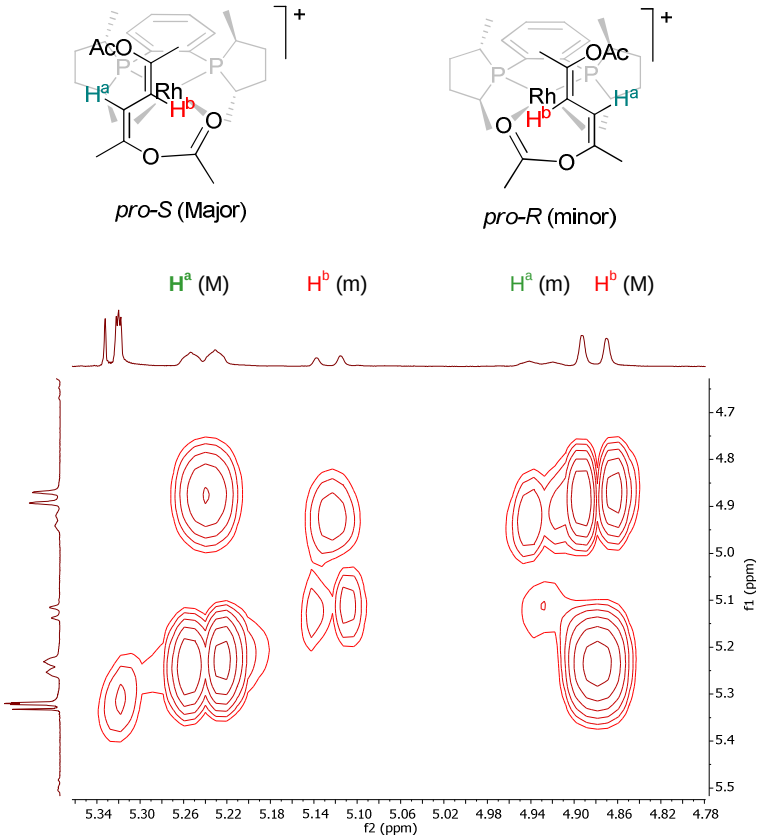


Figure S2. Region of the olefinic protons of the ^{1}H-^{1}H COSY experiment (500 MHz, CD_2Cl_2, 263 K) of [Rh(**1a**){(S,S)-Me-Duphos}]BF_4. M and m denote signals corresponding to major and minor isomers, respectively.

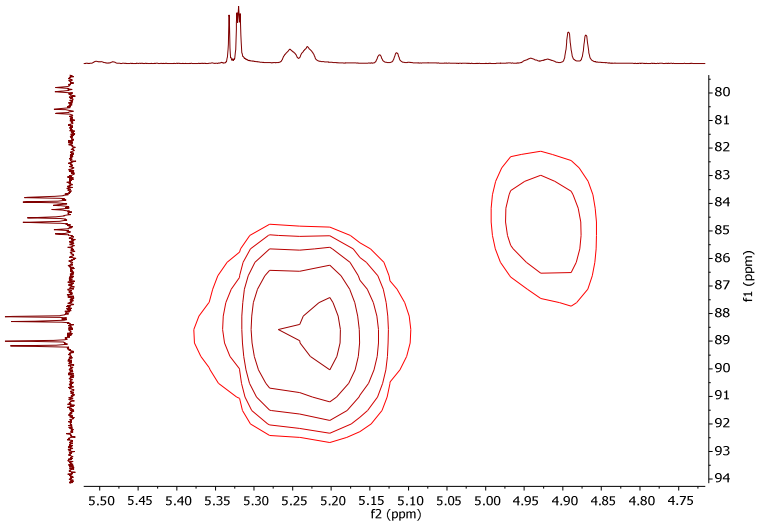


Figure S3. Region of the olefinic protons of the ^{1}H-^{31}P HMQC experiment (CD_2Cl_2, 263 K) of [Rh(**1a**){(S,S)-Me-Duphos}]BF_4.

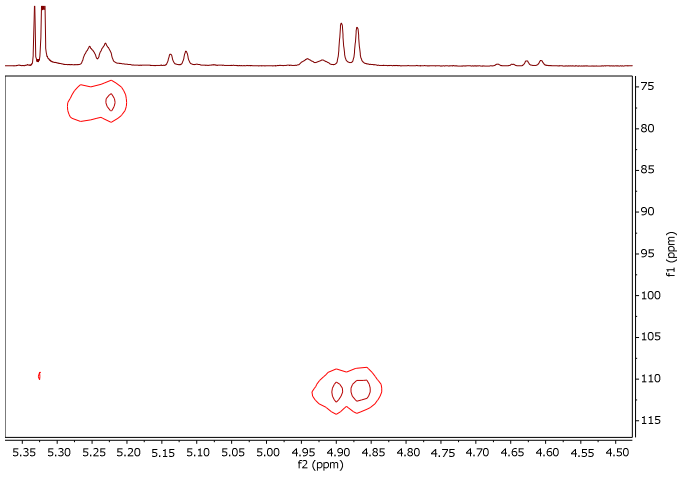


Figure S4. Region of the olefinic protons of the ^{1}H-^{13}C HMQC experiment (CD_2Cl_2, 263 K) of [Rh(**1a**){(S,S)-Me-Duphos}]BF_4.

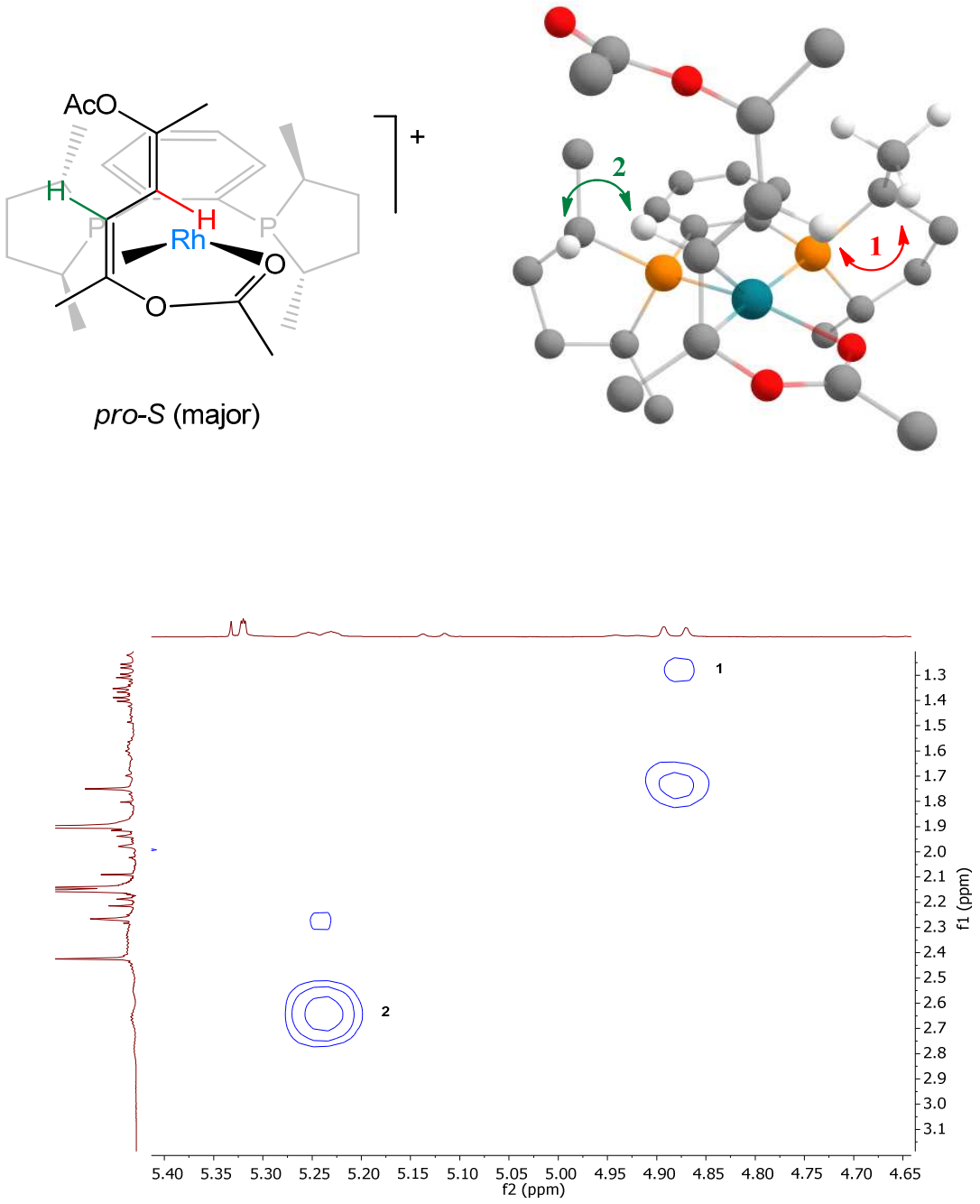


Figure S5. Selected region of the ^{1}H-^{1}H NOESY experiment (500 MHz, CD_2Cl_2, 263 K) of [Rh(**1a**){(S,S)-Me-Duphos}]BF_4. Structurally meaningful signals are marked with 1 and 2.

X-Ray crystal structure determination of diene 1f

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a saturated solution of **1f** in ethyl acetate. The most relevant crystal and refinement data are collected in Table S1, and an ORTEP-type view of the structure with selected structural parameters is given in Figure S6. Diffraction data were recorded on an Oxford Diffraction Xcalibur Nova single-crystal diffractometer, using Cu-Kα radiation (λ = 1.5418 Å), with a crystal-to-detector distance fixed at 62 mm and using the oscillation method, with 1º oscillation and variable exposure time per frame of 2.0-9.0 s. The data collection strategy was calculated with the program CrysAlis Pro CCD.[S7] Data reduction and cell refinement was performed with the program CrysAlis Pro RED.[S7] Empirical absorption correction was applied by means of SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[S7] The software package WINGX was used for space group determination, structure solution and refinement.[S8] The structure was solved by direct methods using SHELXL97.[S9] Isotropic least-squares refinement on F^2 using SHELXL97 was performed.[S9] During the final stages of the refinement, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined. The coordinates of the H atoms were found from different Fourier maps, and included in the refinement with isotropic parameters. The function minimized was $[\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)]^{½}$ where $w = 1/[\sigma^2(F_o^2) + (0.0532P)^2 + 0.2099P]$ with $\sigma(F_o^2)$ from counting statistics and $P = (\text{Max}\ (F_o^2,0) + 2F_c^2)/3$. Supplementary crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC-1869873.

Table S1. Crystal Data and Structure Refinement Details for Compound **1f**

chemical formula	$C_{18}H_{26}O_4$
fw	306.39
T (K)	140(2)
cryst syst	monoclinic
space group	$P2_1/n$
cryst size mm^3	0.18 x 0.18 x 0.11
a, Å	5.4153(2)
b, Å	16.4548(4)
c, Å	9.6656(3)
α, deg	90
β, deg	104.990(3)
γ, deg	90
Z	4
V, $Å^3$	831.97(5)
ρ_{calcd}, g cm^{-3}	1.223
μ, mm^{-1}	0.685
F(000)	332
θ range, deg	5.376 to 69.516
index ranges	$-6 \le h \le 6$; $-19 \le k \le 14$; $-11 \le l \le 11$
completeness to θ_{max}	98.3%
no. of data collected	3657
no. of unique data	1532
no. of params/restrains	109/0
refinement method	full-matrix least-squares on F^2
goodness of fit on F^2	1.041
R1[a] [I > 2σ(I)]	0.0388
wR2[a] [I > 2σ(I)]	0.1003
R1 (all data)	0.0465
wR2 (all data)	0.1080
largest diff peak and hole, e $Å^3$	0.212 and -0.176

a $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)\sum]/\sum[w(F_o^2)^2]\}^{½}$

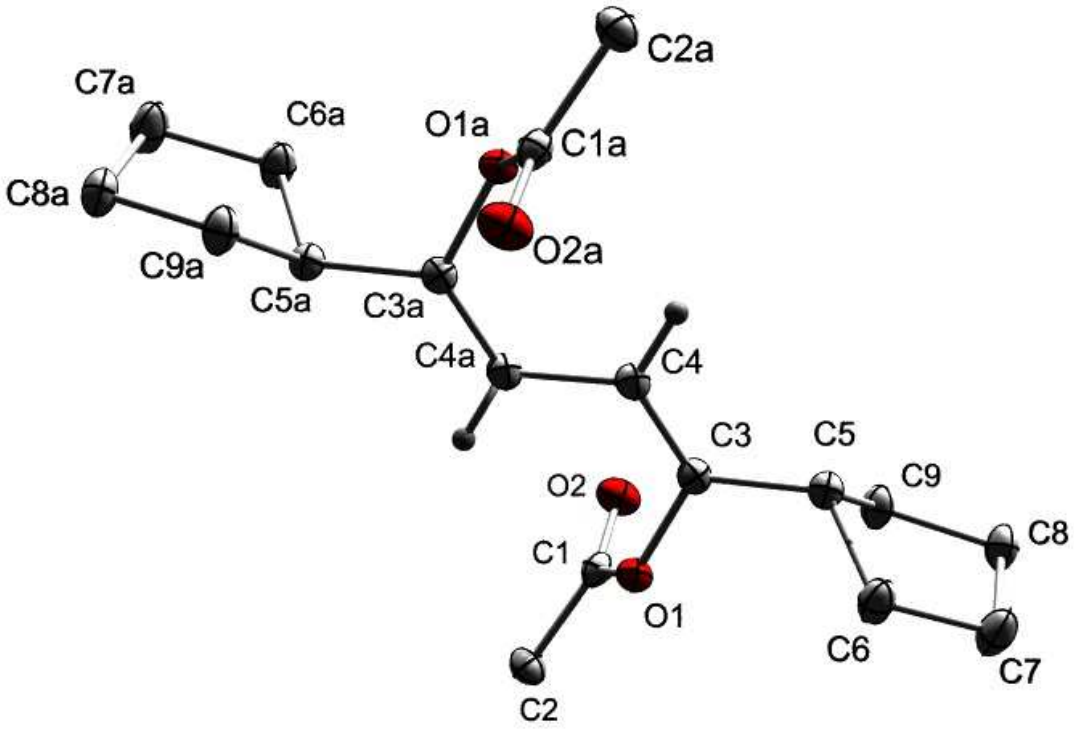


Figure S6. ORTEP-type view of the structure of compound **1f** showing the crystallographic labelling scheme. Hydrogen atoms, except those on C(4) and C(4a), have been omitted for clarity. Those atoms labelled with "a" are generated by symmetry. Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (Å): C(1)-O(1) 1.365(2), C(1)-O(2) 1.199(2), C(1)-C(2) 1.488(2), C(3)-O(1) 1.410(2), C(3)-C(4) 1.330(2), C(3)-C(5) 1.493(2), C(4)-C(4a) 1.449(3). Selected bond angles (˚): O(1)-C(1)-O(2) 122.7(2), O(1)-C(1)-C(2) 110.7(2), O(2)-C(1)-C(2) 126.6(2), C(1)-O(1)-C(3) 117.9(1), O(1)-C(3)-C(4) 119.3(1), O(1)-C(3)-C(5) 114.3(1), C(3)-C(5)-C(6) 114.5(1), C(3)-C(5)-C(9) 116.1(1), C(3)-C(4)-C(4a) 125.3(2).

Computational details

Calculations were performed with Gaussian 09[S10] at the DFT level, using the Becke Three-Parameter functional[S11] with the non-local correlation by Perdew and Wang[S12] (B3PW91) and the D3 version of Grimme's dispersion with Becke-Johnson damping (GD3BJ).[S13] H, C, P and O atoms were represented with the 6-31G(d,p) basis set[S14] whereas Rh atoms were described by the Stuttgart/Dresden Effective Core Potential and the associated basis set as implemented in Gaussian 09.[S15] All molecular geometries were optimized within the SMD continuum solvent (1,2-dichloroethane) model[S16] without any geometry constrains. Frequency calculations were performed at the same level of theory to characterize the stationary points as minima (no imaginary frequencies) or saddle points (transition states, one imaginary frequency), as well as to calculate the Zero-point energy, enthalpy (H) and free energy (G) corrections. The two minima connected by a given transition state were confirmed from vibrational analysis. Energies of calculated structures are given in the Table below:

Coord. Mode	E (RB3PW91) a.u.	Free Energy (298 K), a.u.
A	-2186,166901	-2185,581922
B	-2186,166189	-2185,581116
C	-2186,154027	-2185,568504
D	-2186,14196	-2185,557408
E	-2186,142411	-2185,555756
F	-2186,148372	-2185,560916
G	-2186,149938	-2185,564282

References

S1. (a) P. J. González-Liste, F. León, I. Arribas, M. Rubio, S. E. García-Garrido, V. Cadierno and A. Pizzano, *ACS Catal.*, 2016, **6**, 3056; (b) P. J. González-Liste, J. Francos, S. E. García-Garrido and V. Cadierno, *J. Org. Chem.*, 2017, **82**, 1507.

S2. P. Kleman, P. J. González-Liste, S. E. García-Garrido, V. Cadierno and A. Pizzano, *Chem. Eur. J.*, 2013, **19**, 16209.

S3. K. W. Barnett, *J. Chem. Educ.*, 1974, **51**, 422.

S4. A. Collado, A. Gómez-Suárez, A. R. Martin, A. M. Z. Slawin and S. P. Nolan, *Chem. Commun.*, 2013, **49**, 5541.

S5. M. J. Burk, T. G. P. Harper, J. R. Lee and C. Kalberg, *Tetrahedron Lett.*, 1994, **35**, 4963.

S6. K. T. Sprott and E. J. Corey, *Org. Lett.*, 2003, **5**, 2465.

S7. *CrysAlis*^{Pro} 1.171.38.43, Rigaku Oxford Diffraction, Yarnton, UK, 2015.

S8. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

S9. G. M. Sheldrick, *SHELXL97: Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.

S10. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E.

Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

S11. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

S12. (a) J. P. Perdew, K. Burke and Y. Wang, *Phys. Rev. B.*, 1996, **54**, 533; (b) K. Burke, J. P. Perdew and Y. Wang, in *Electronic Density Functional Theory: Recent Progress and New Directions*, Ed. J. F. Dobson, G. Vignale, and M. P. Das (Plenum, 1998).

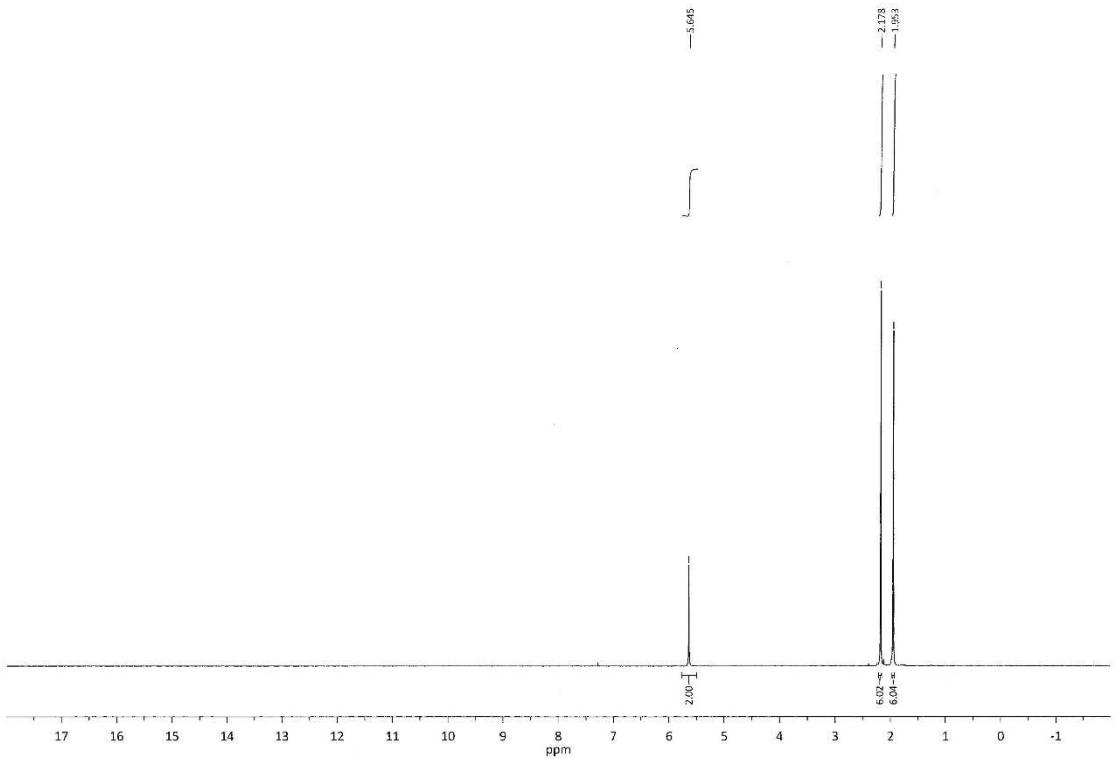
S13. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comp. Chem*., 2011, **32**, 1456.

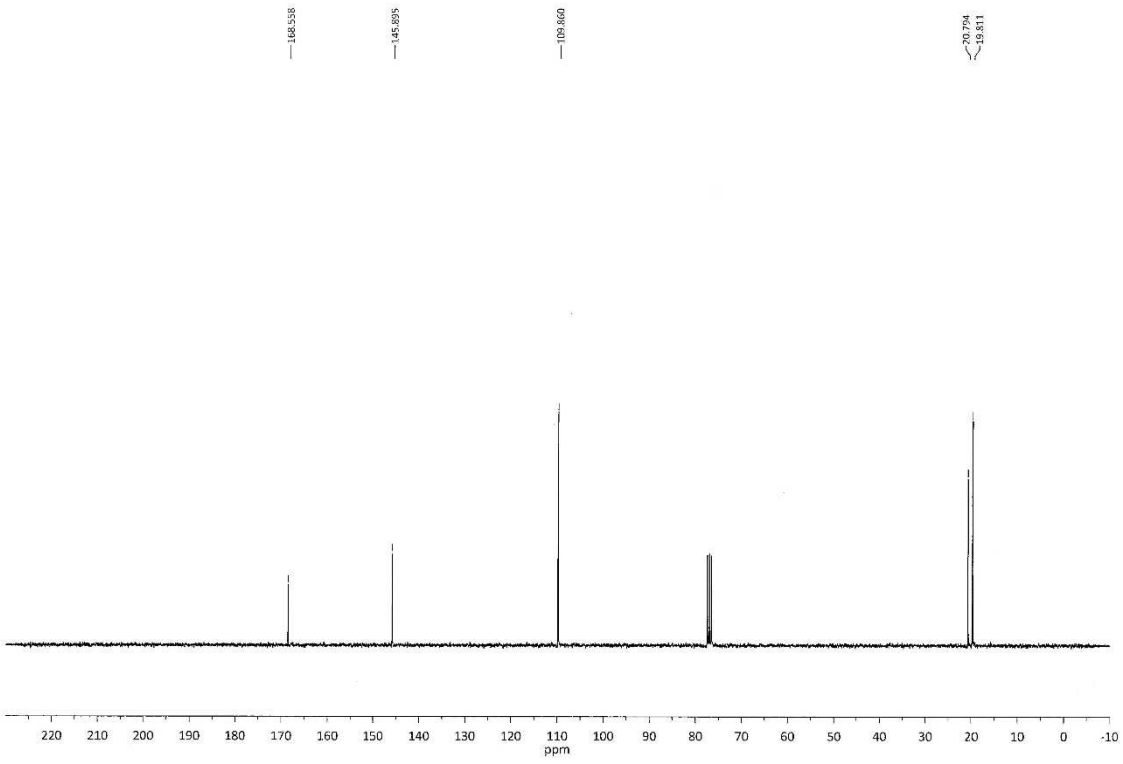
S14. (a) W. J. Hehre, K. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; (b) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213; (c) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.

S15. D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. T. Preuß, *Theor. Chim. Acta*, 1990, **77**, 123.

S16. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B.*, 2009, **113**, 6378.

(*Z*,*Z*)-Hexa-2,4-diene-2,5-diyl diacetate (1a)





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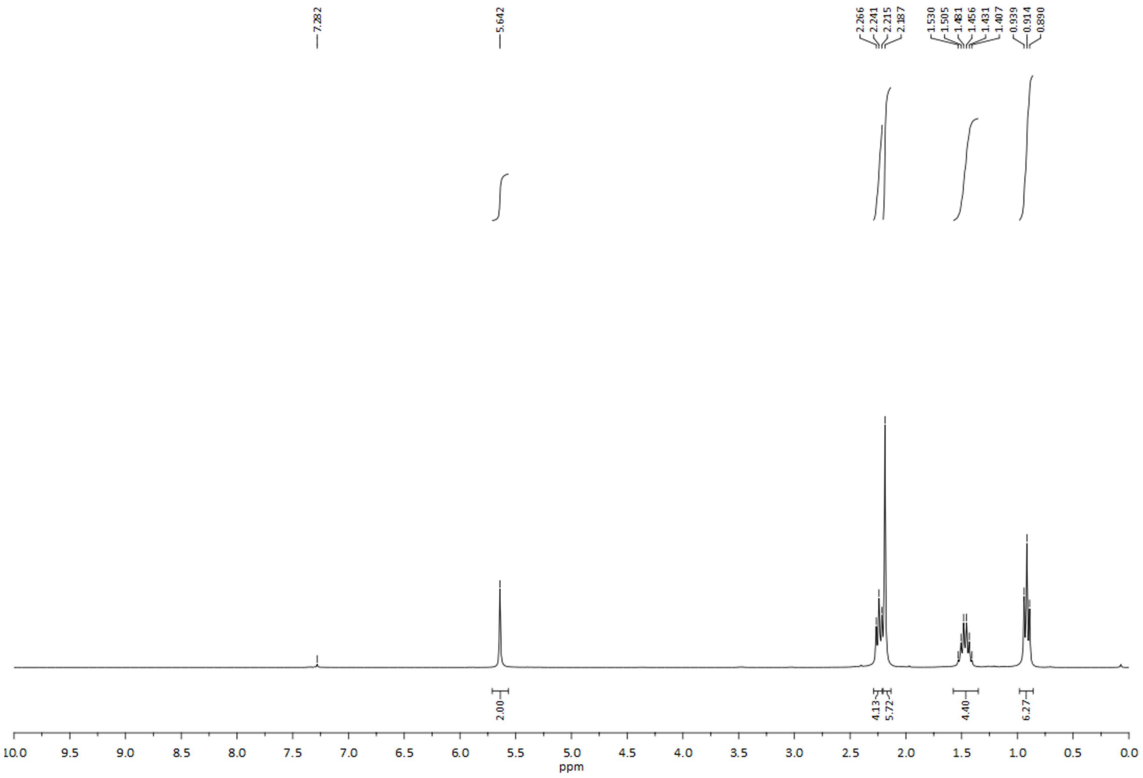

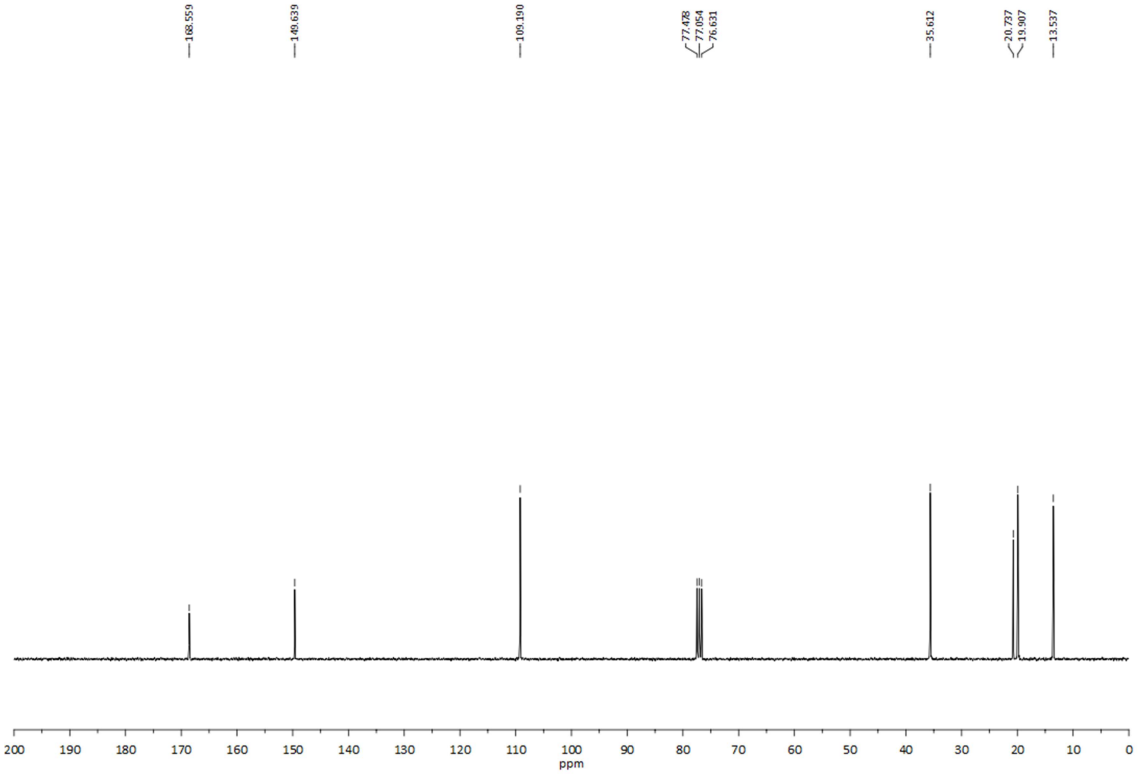

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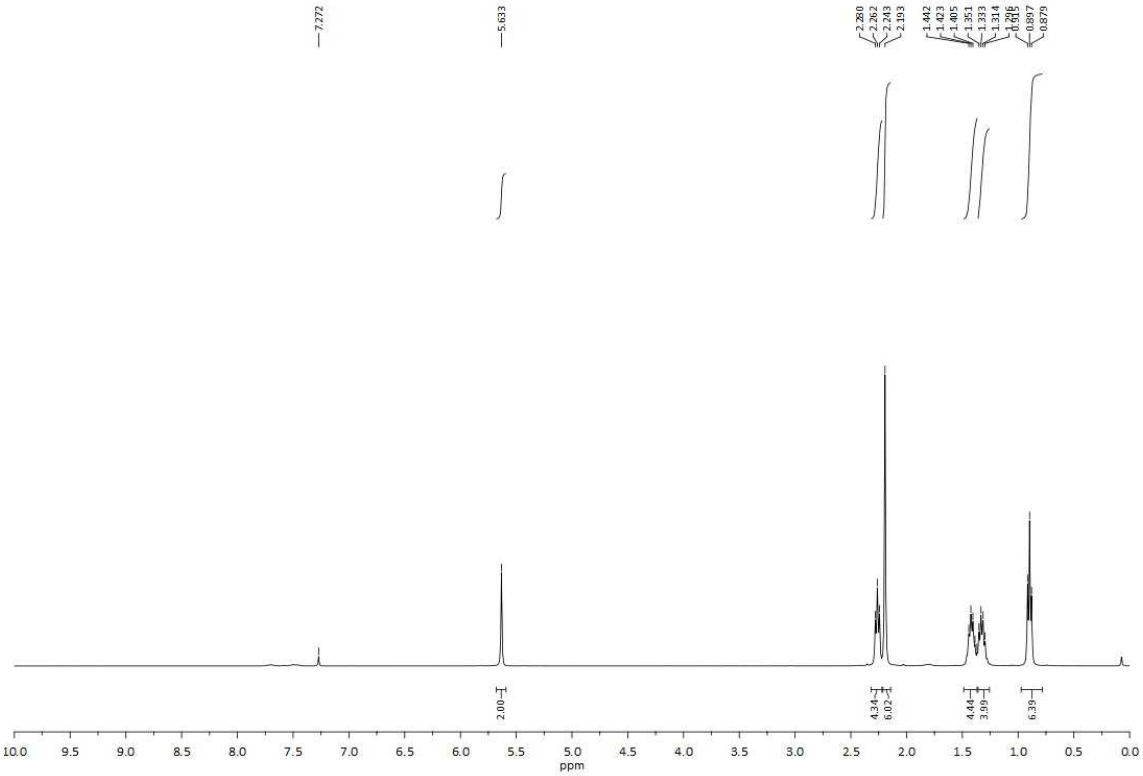

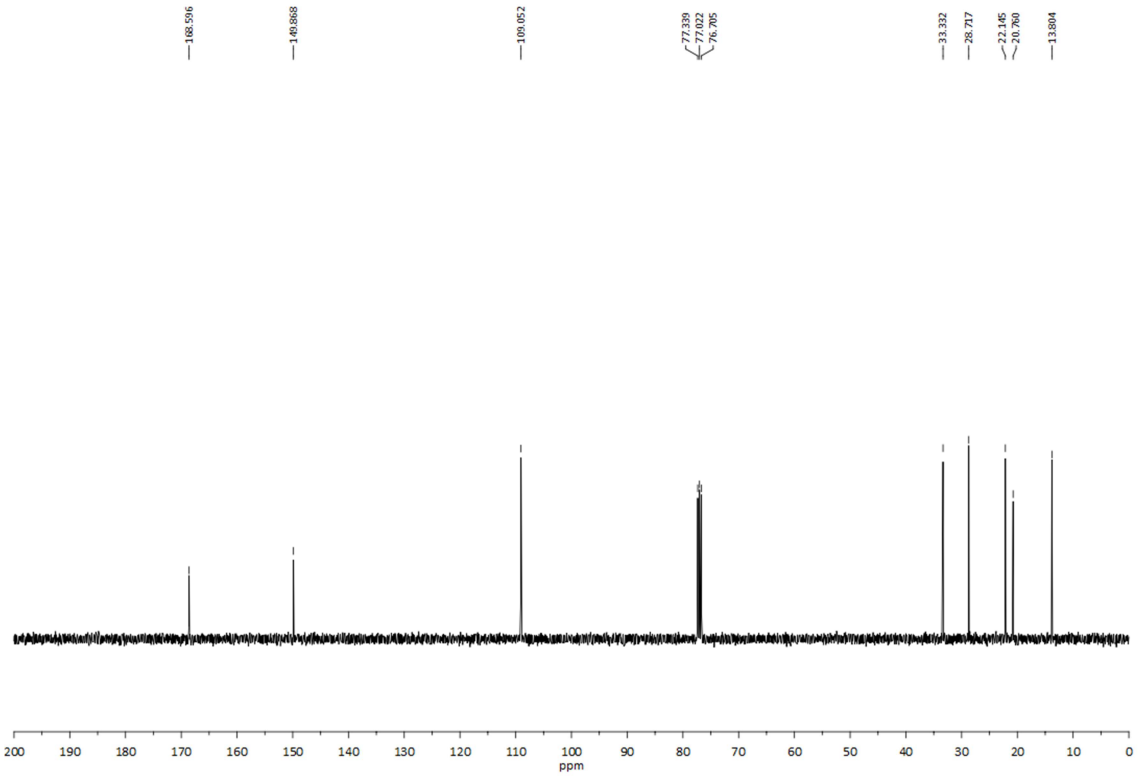

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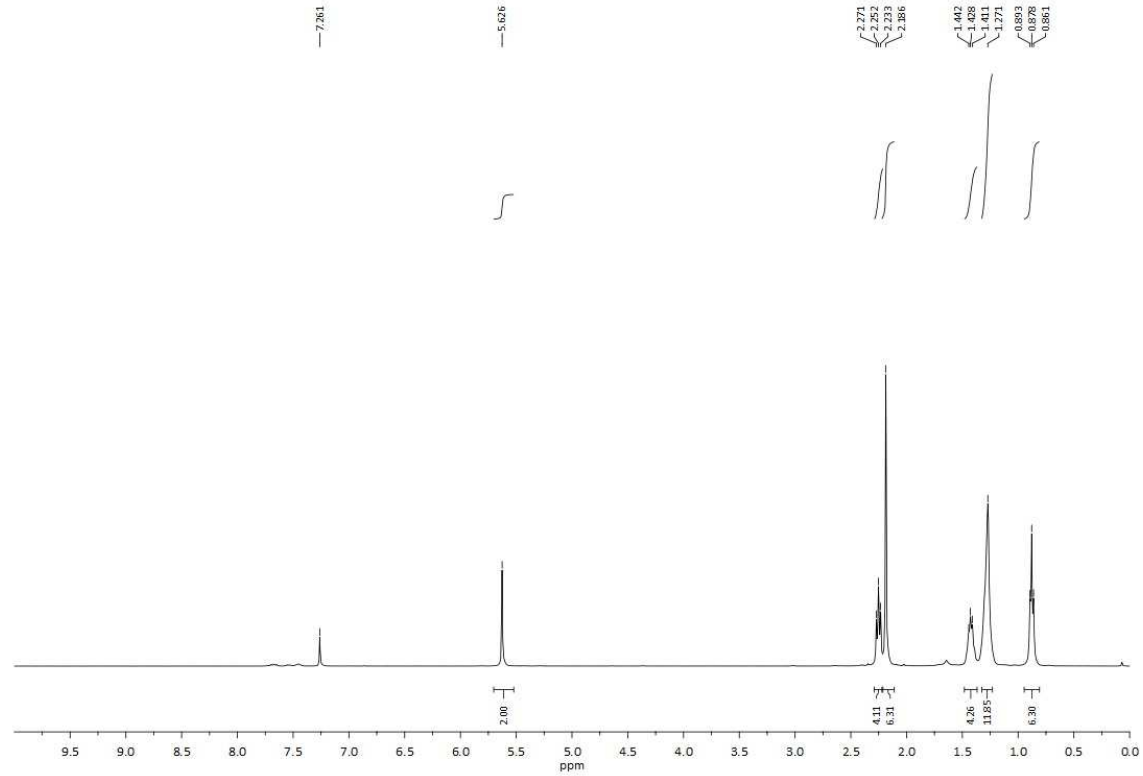

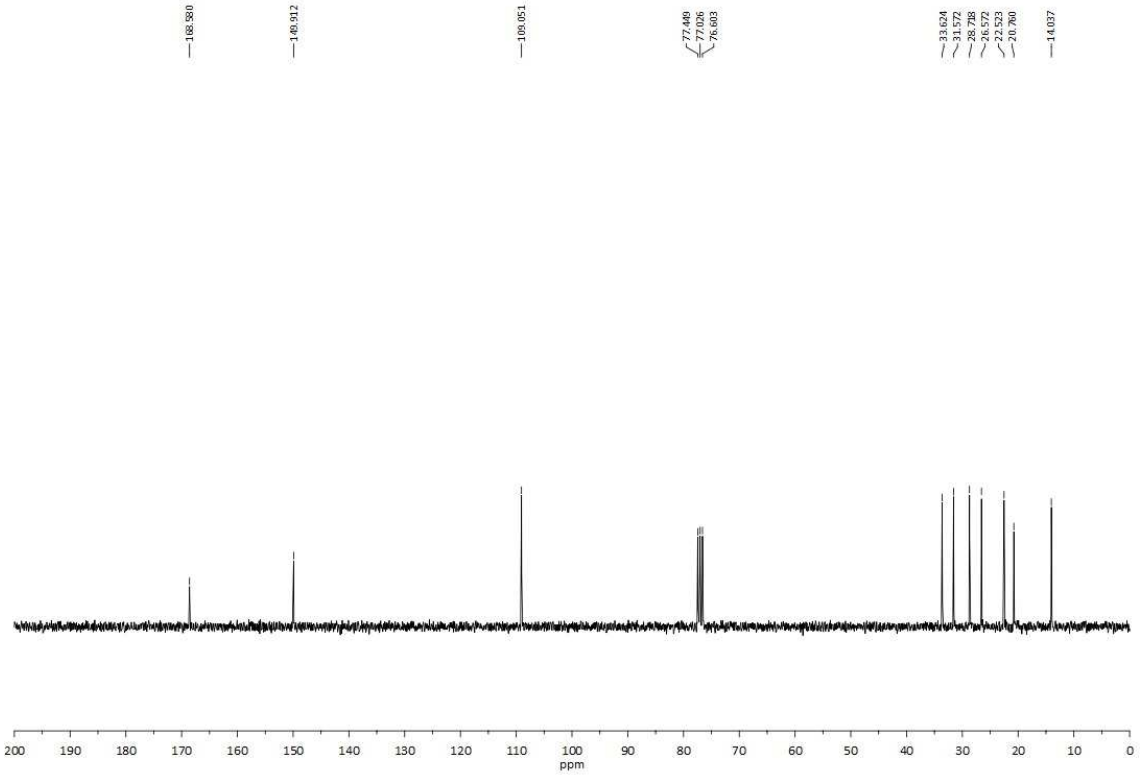

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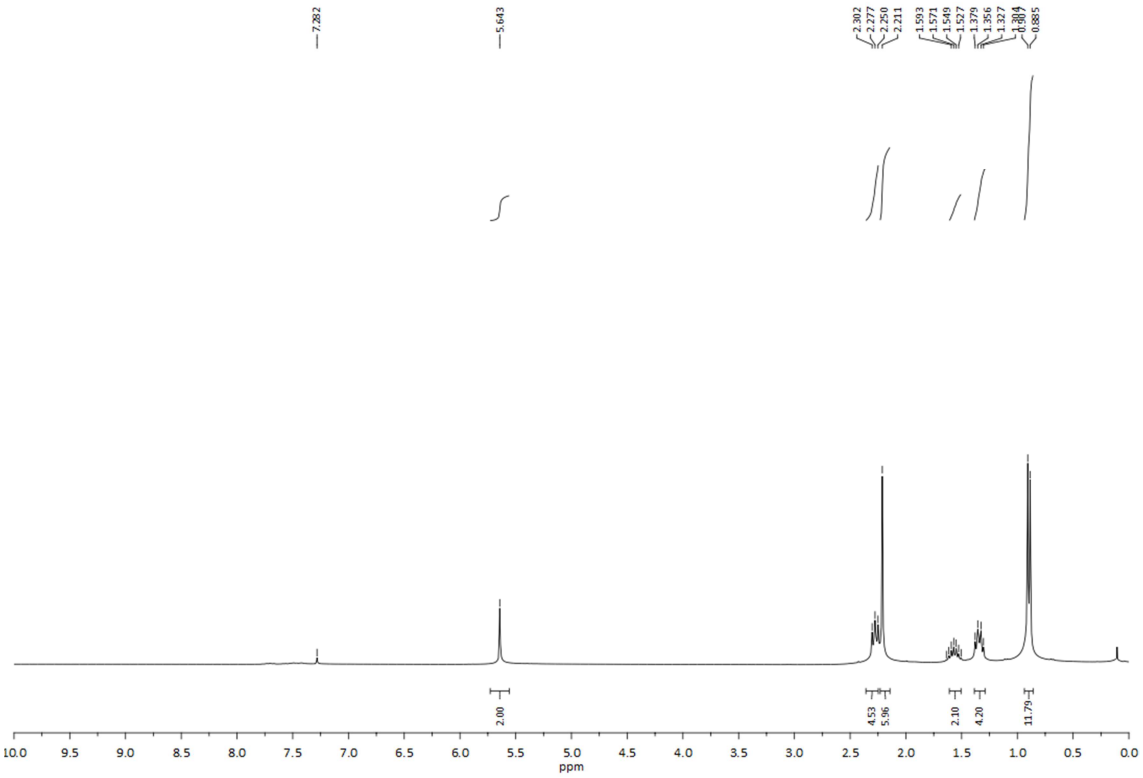

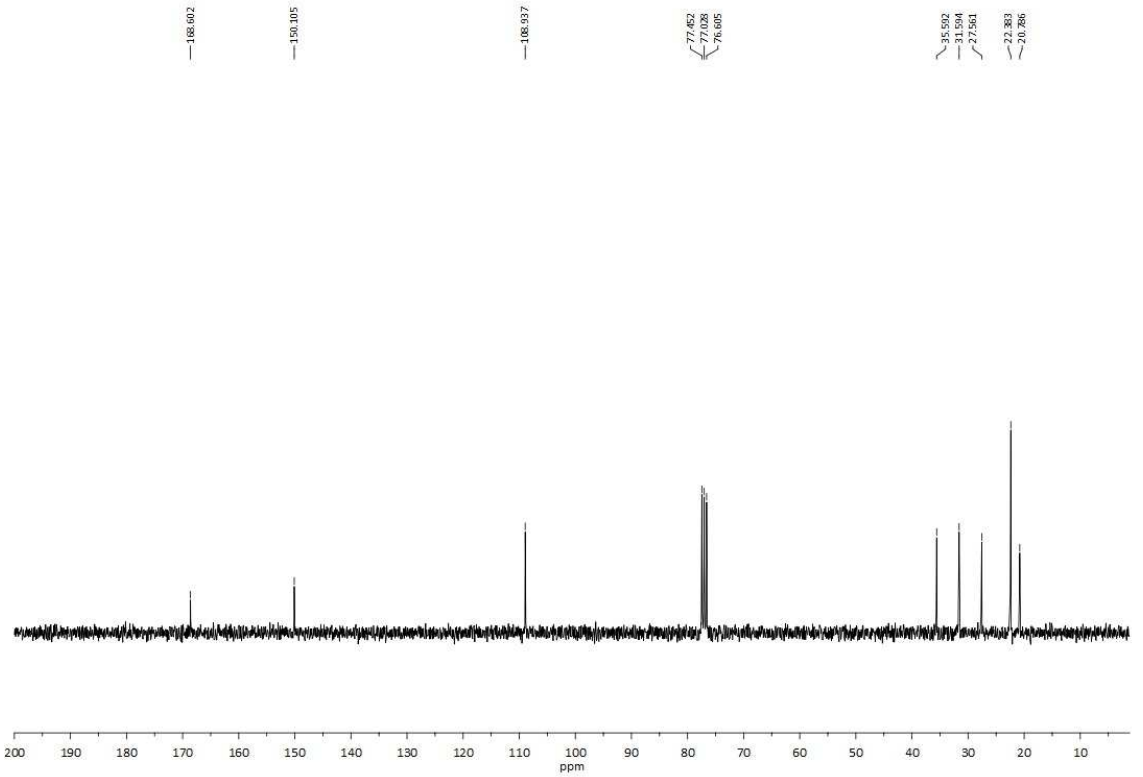

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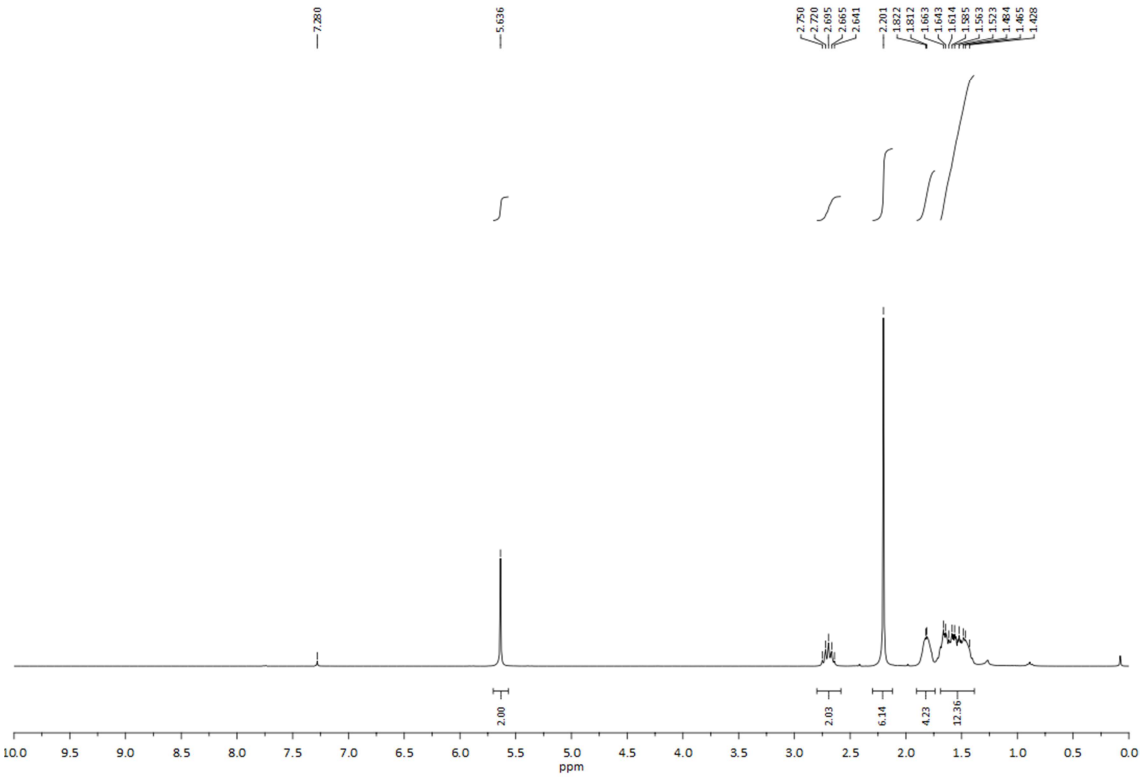

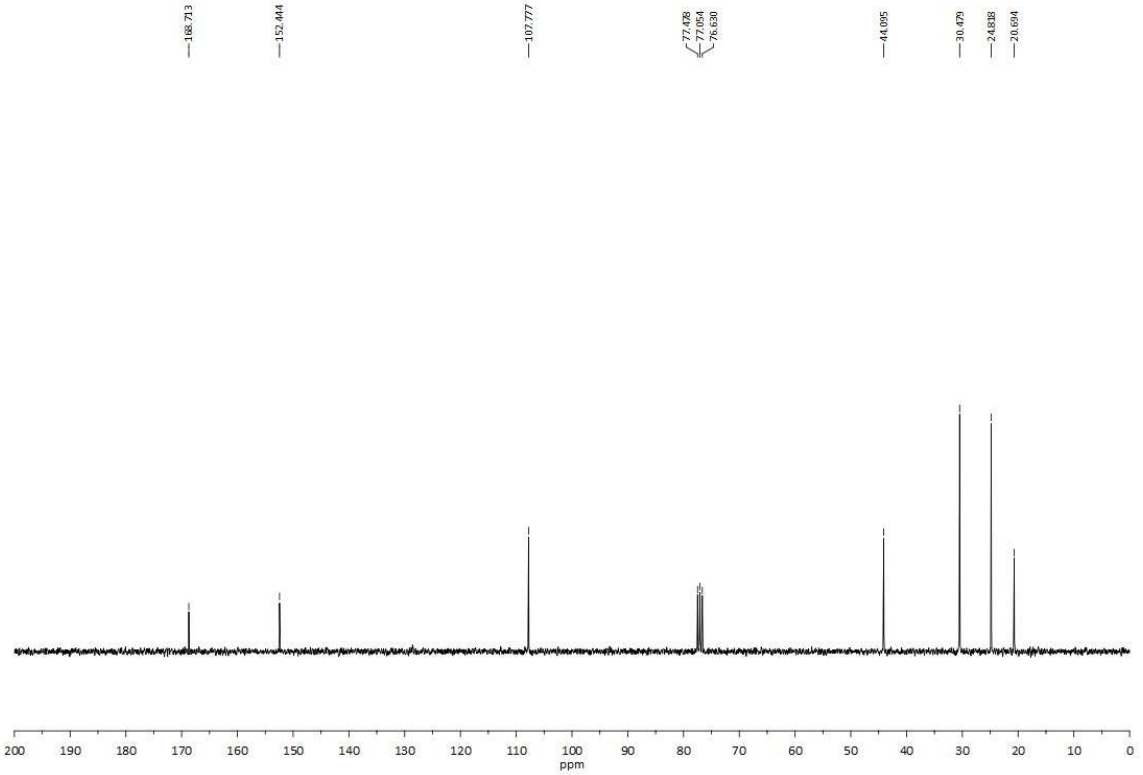

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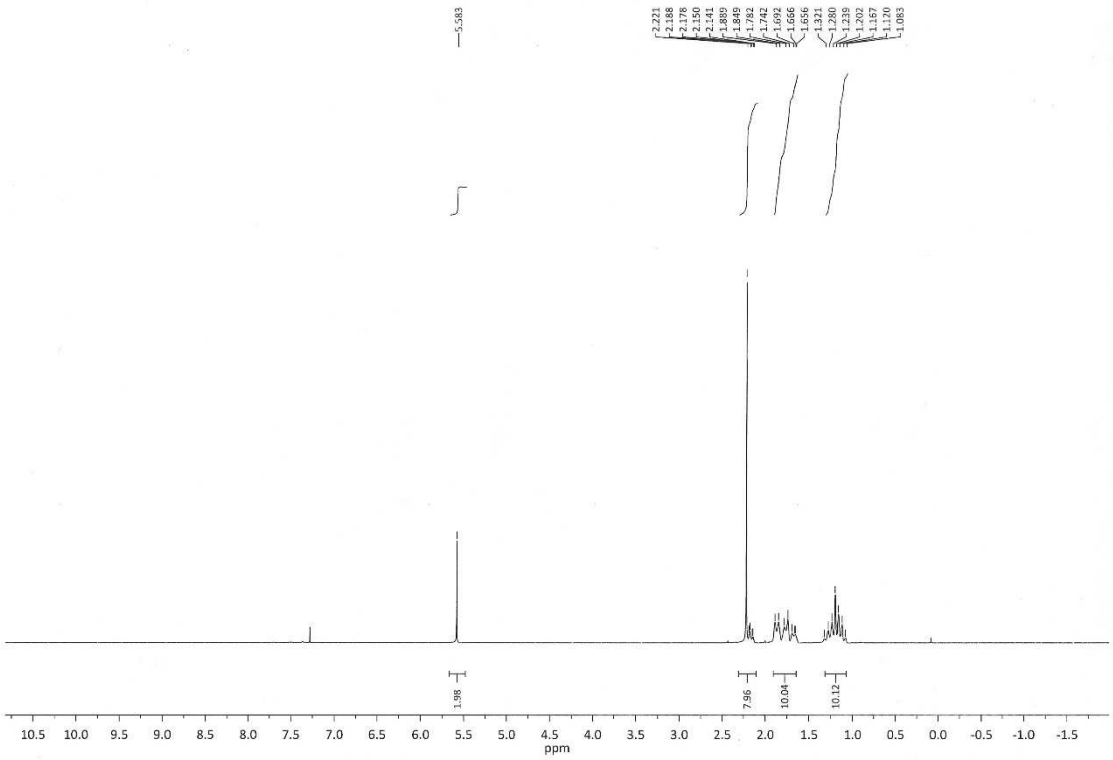

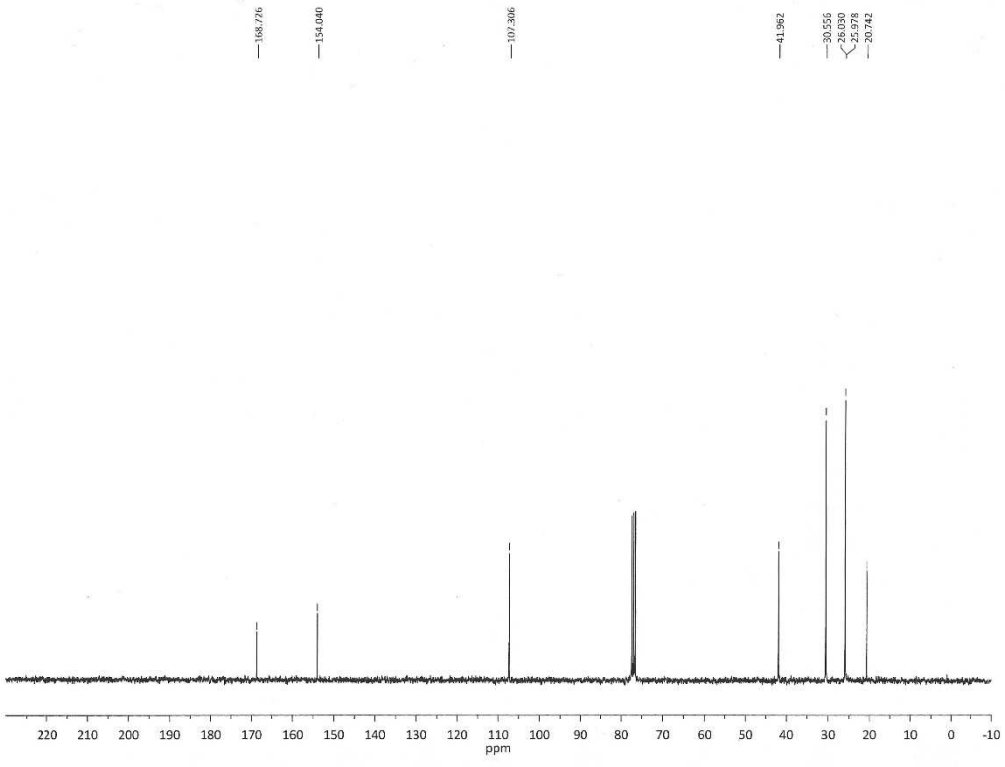

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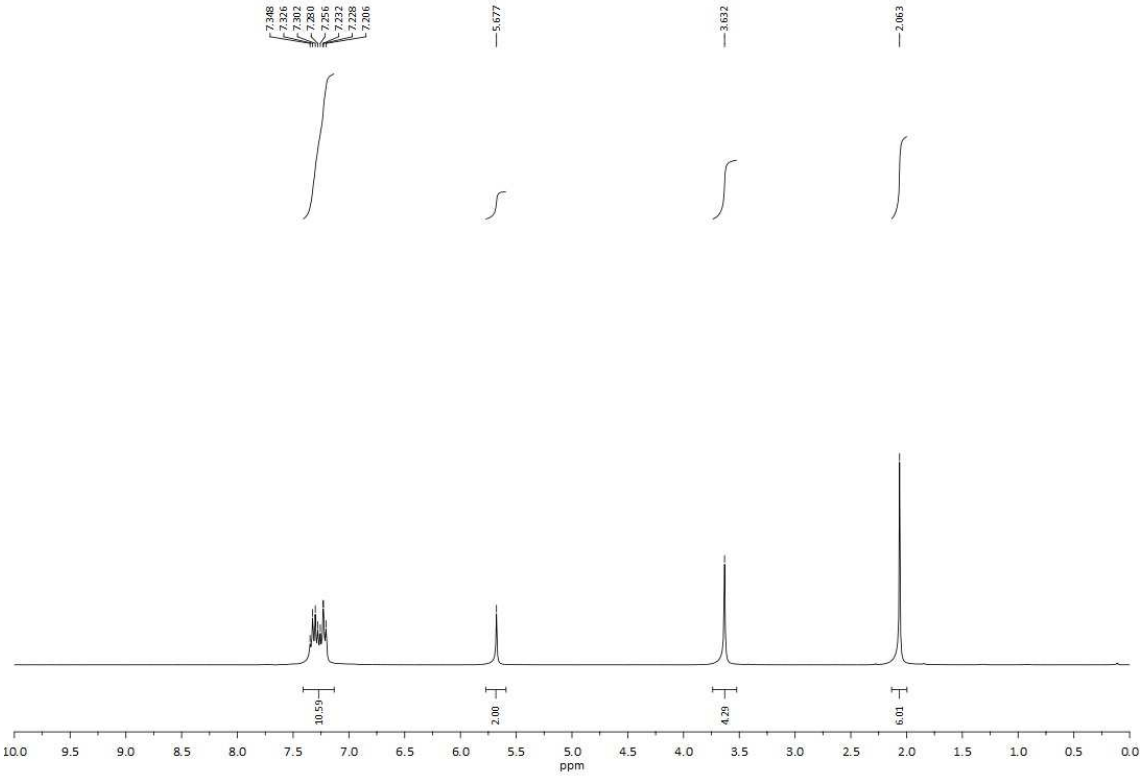

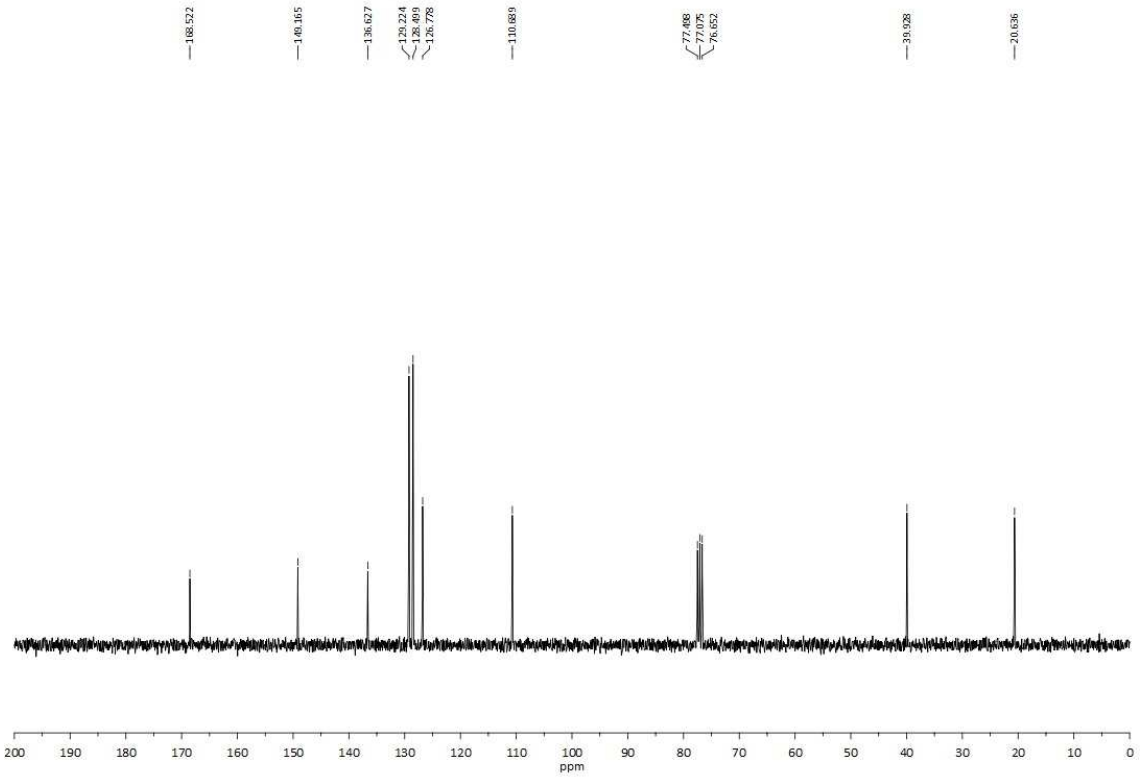

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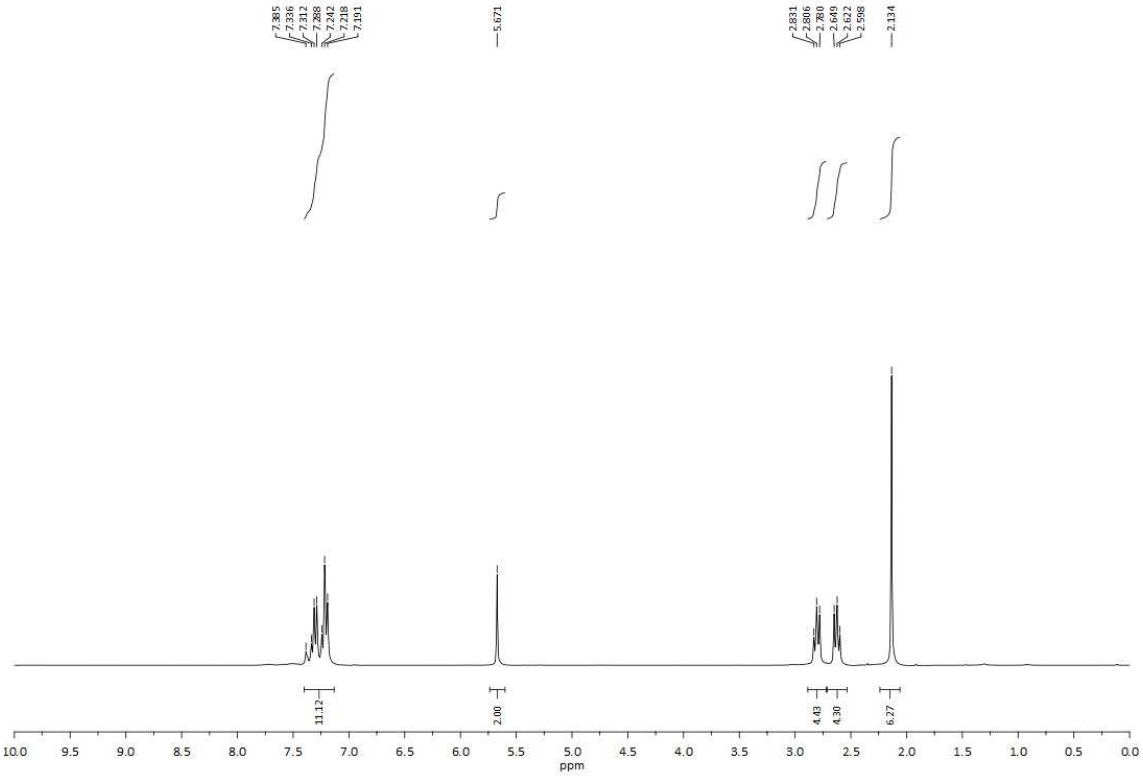

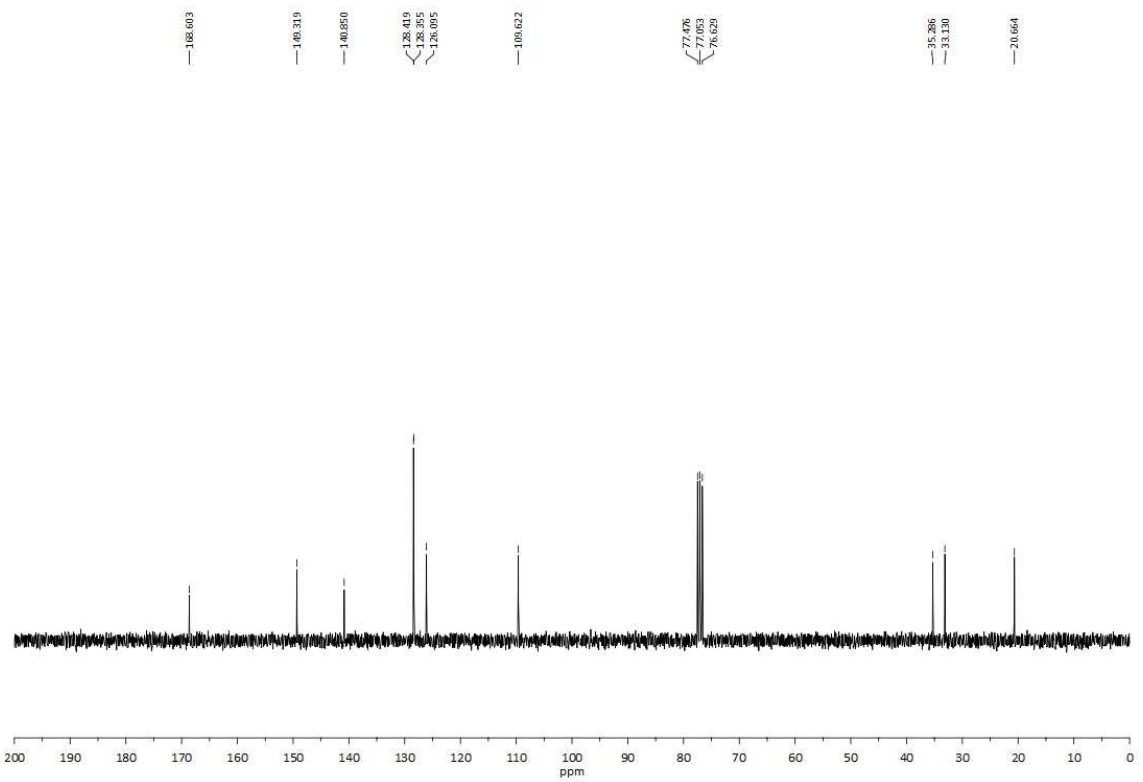

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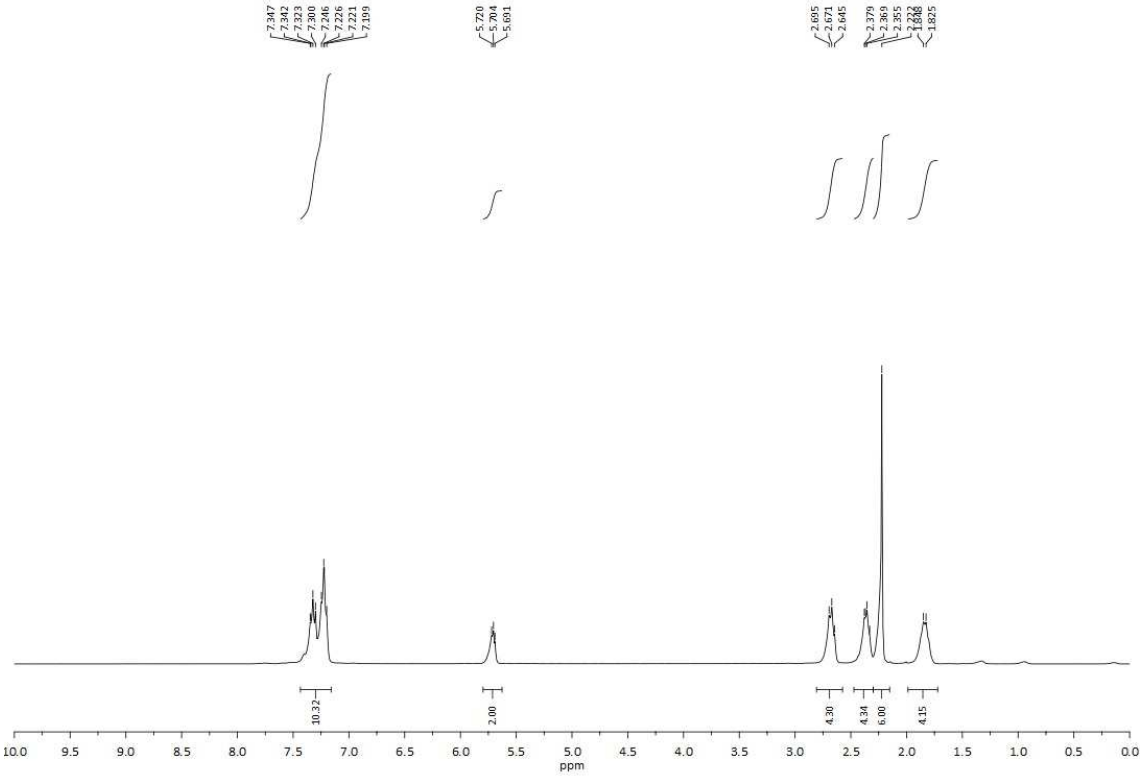

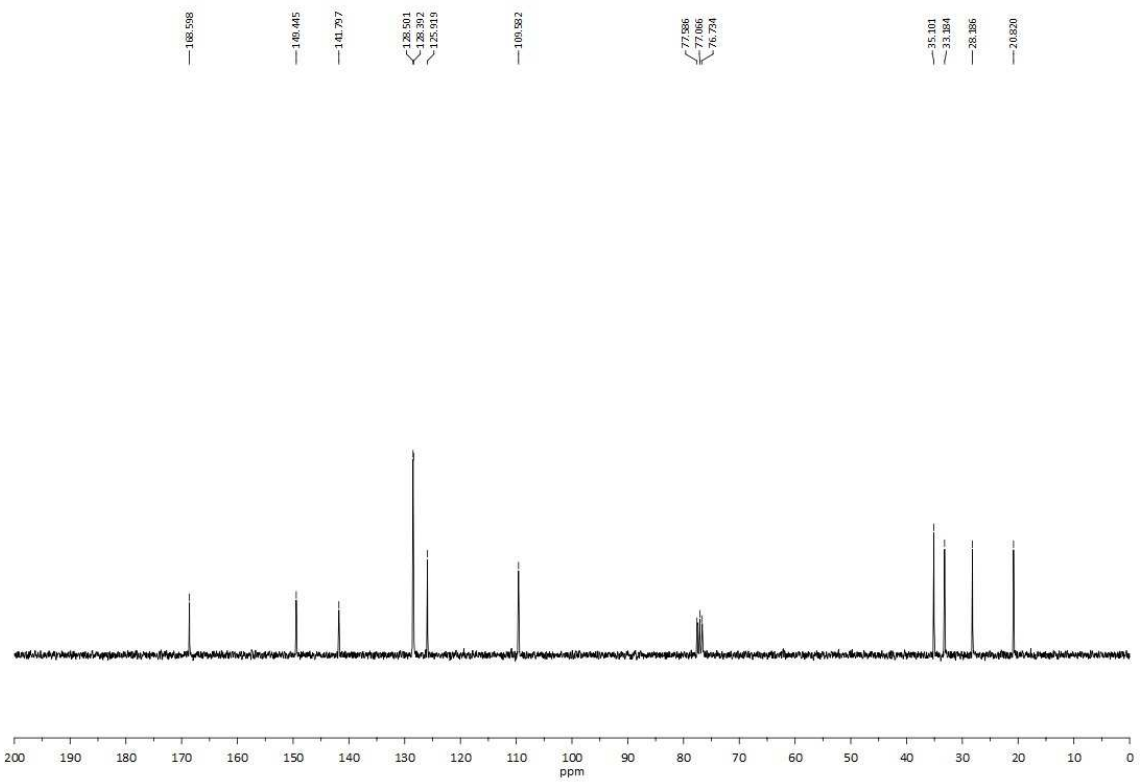

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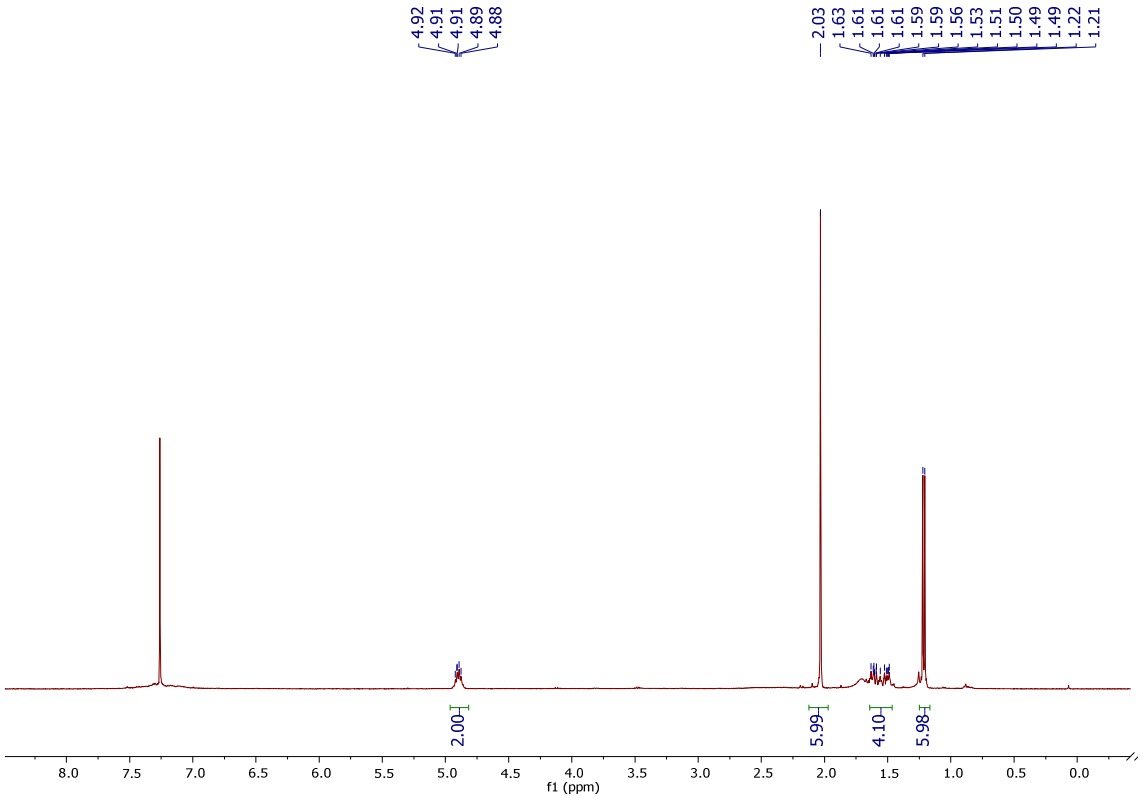

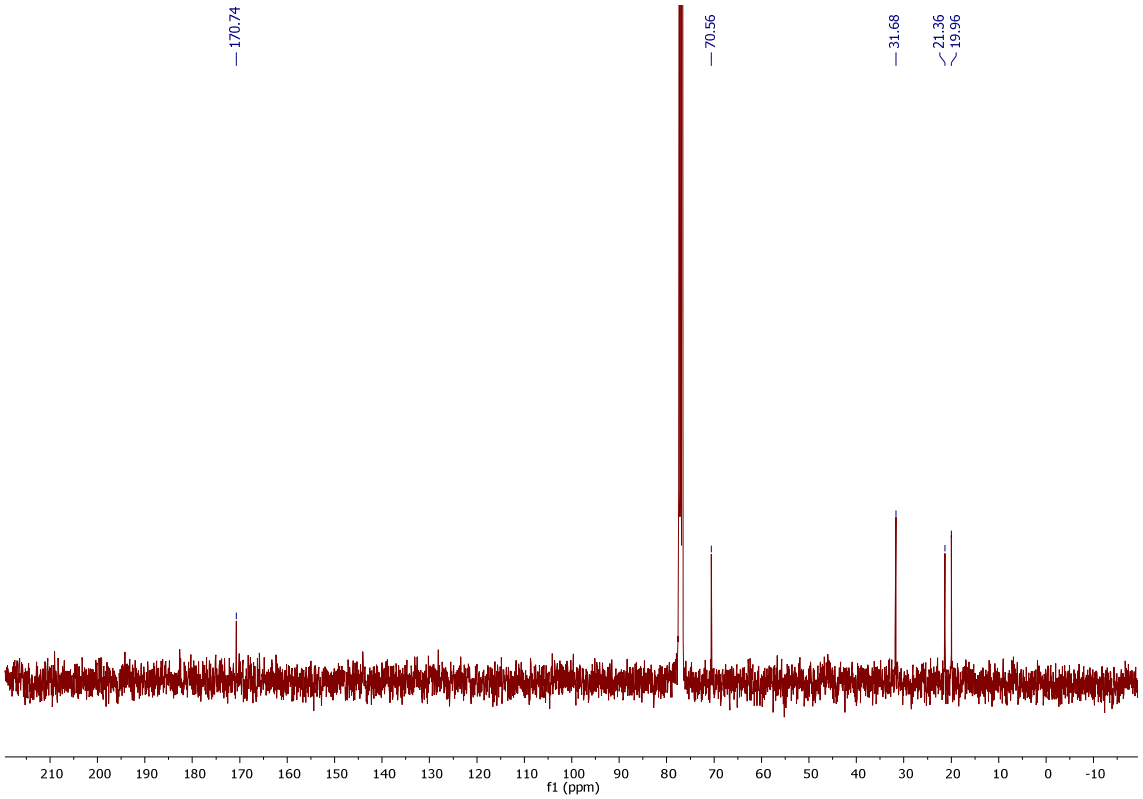

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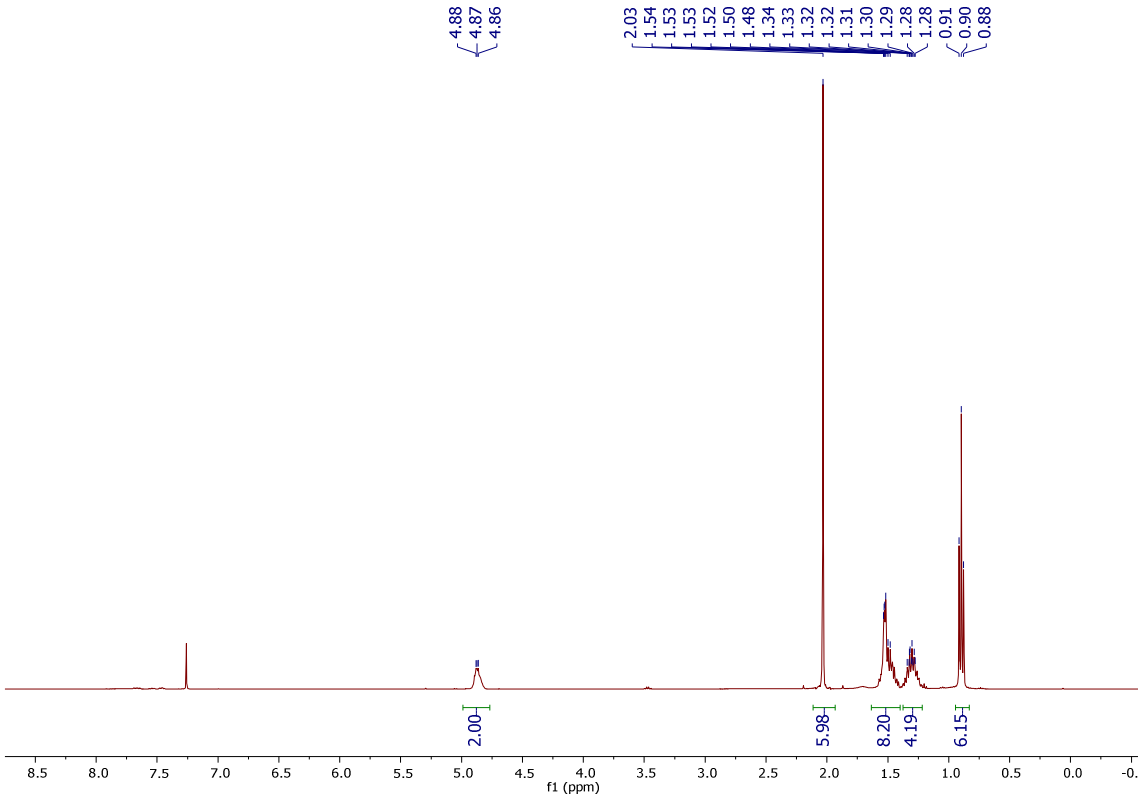

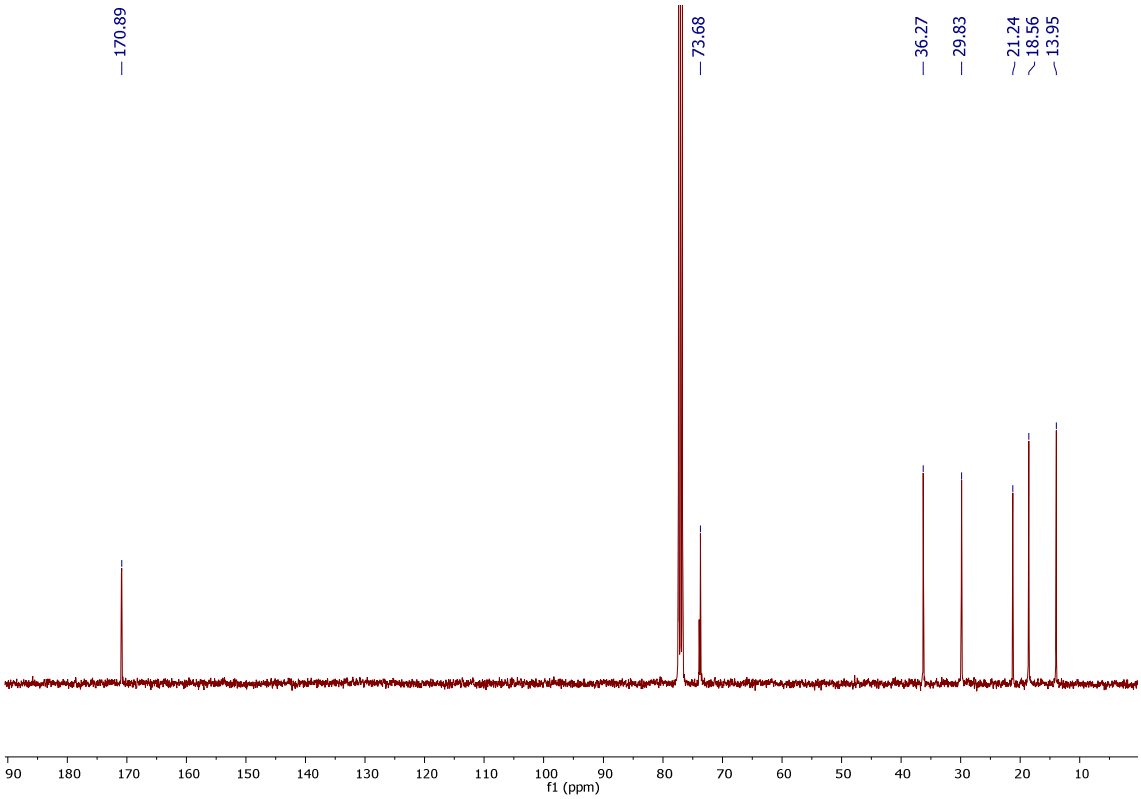

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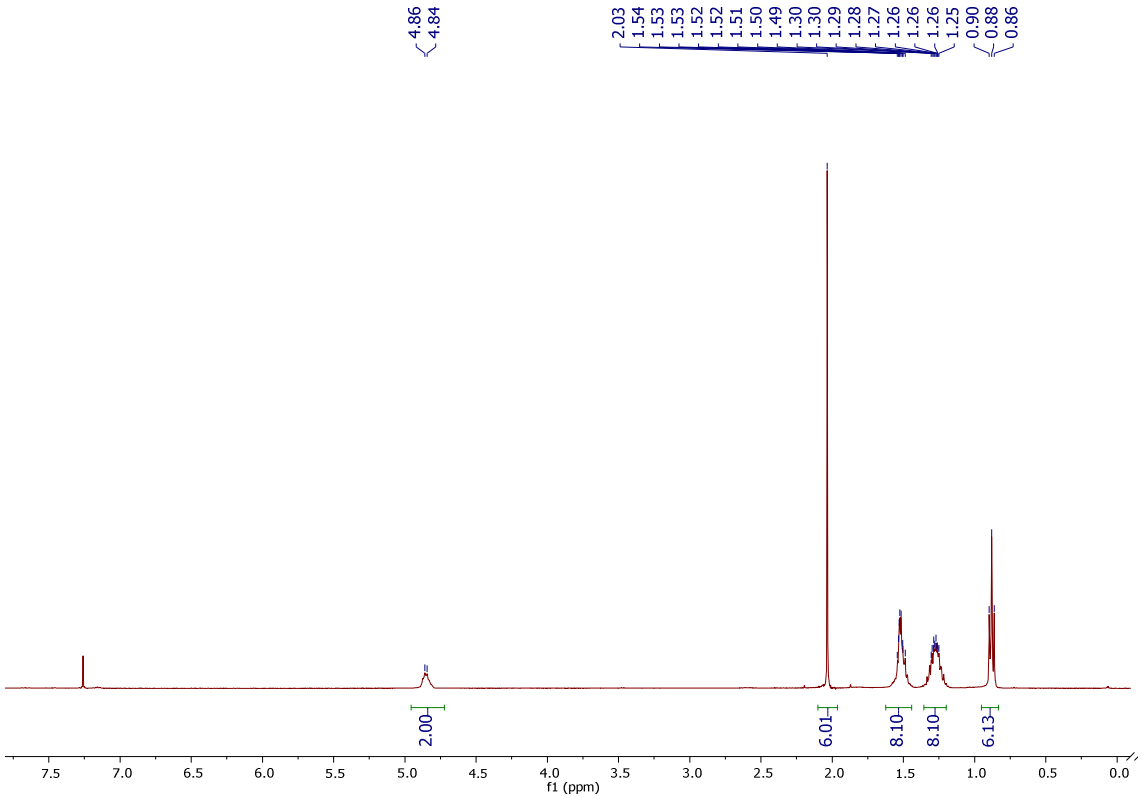

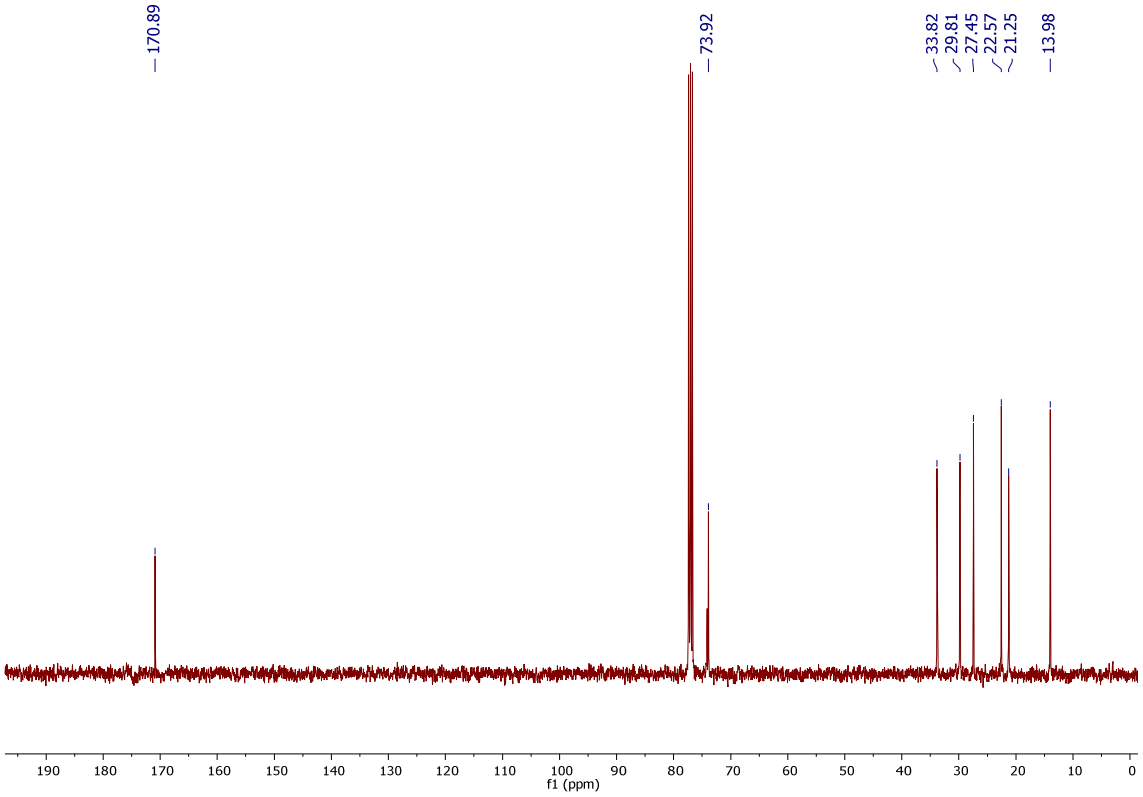

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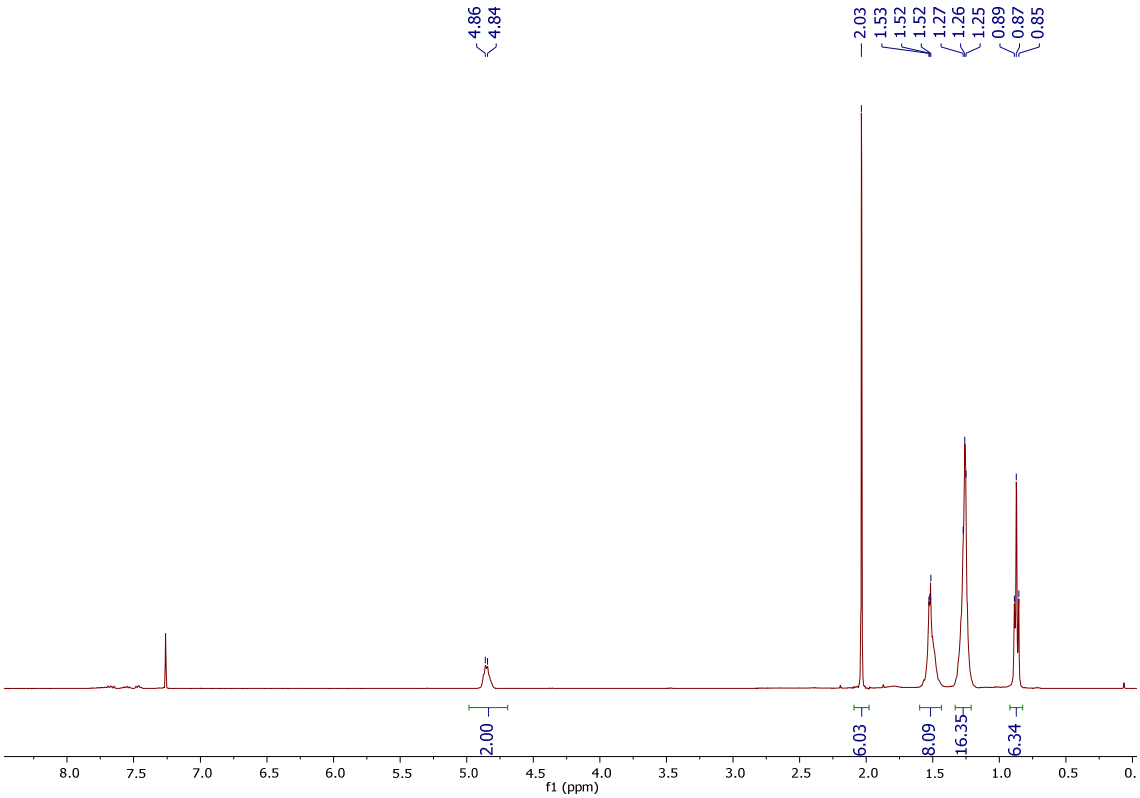

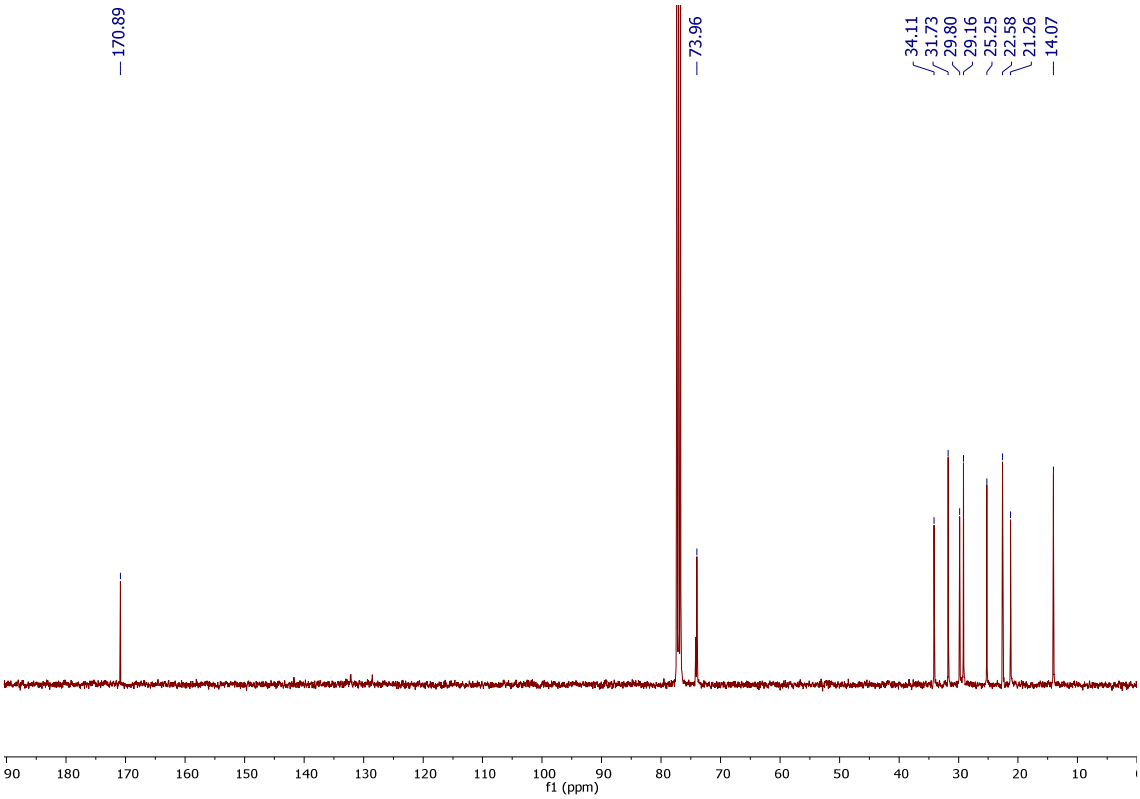

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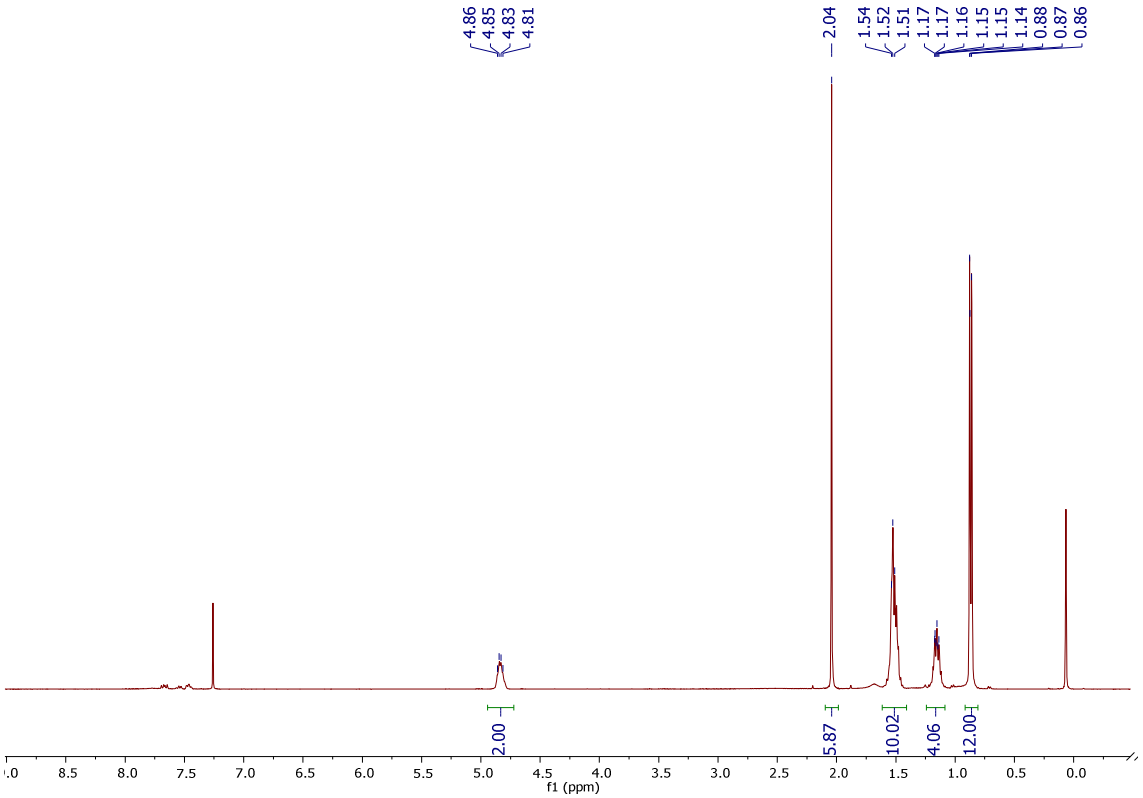
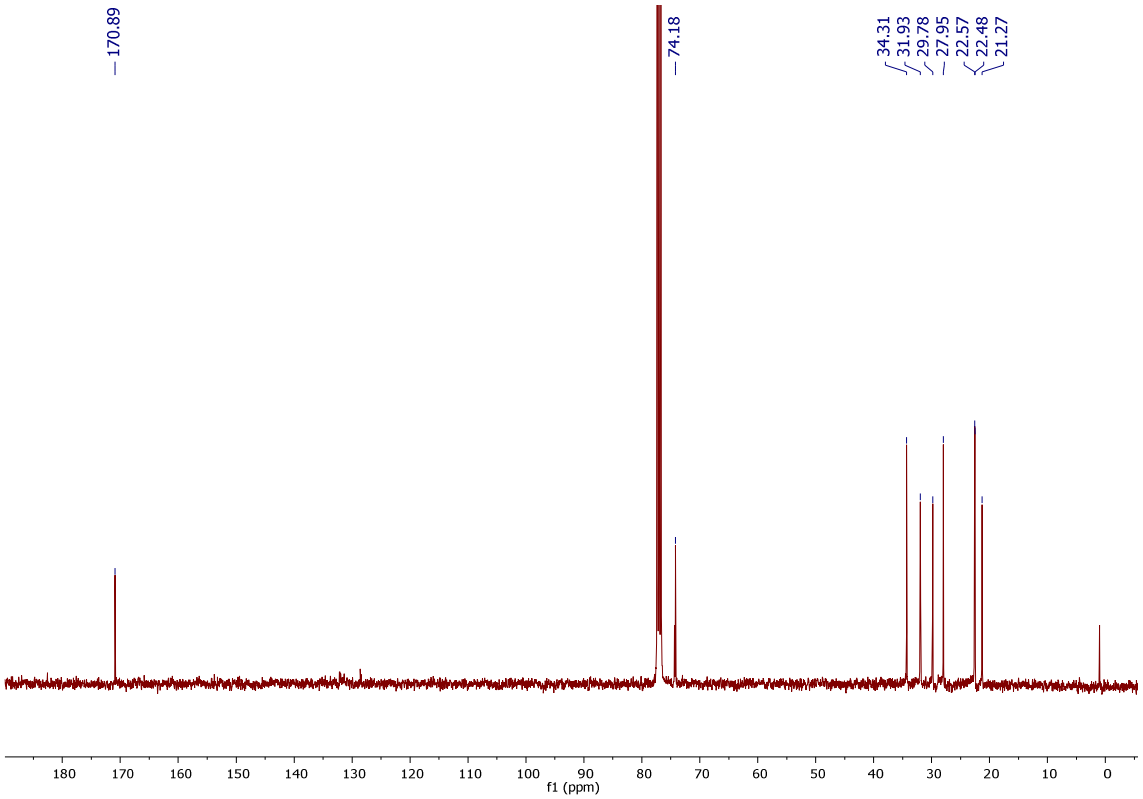
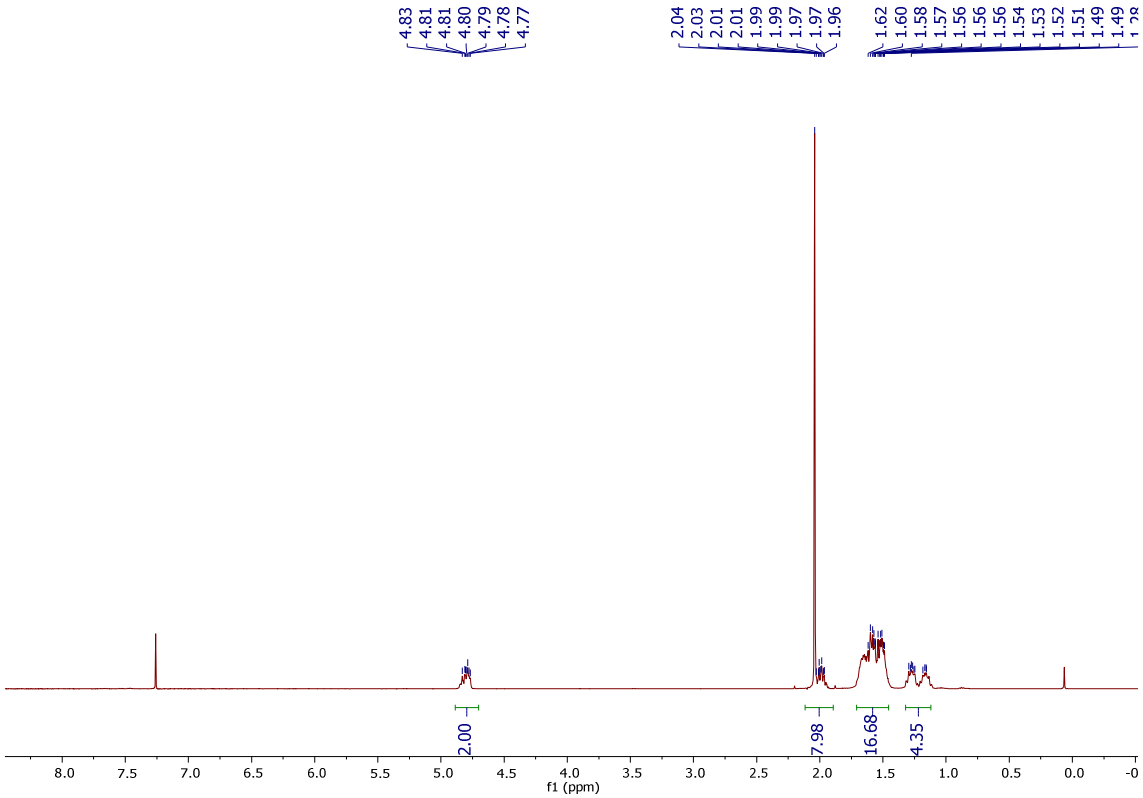
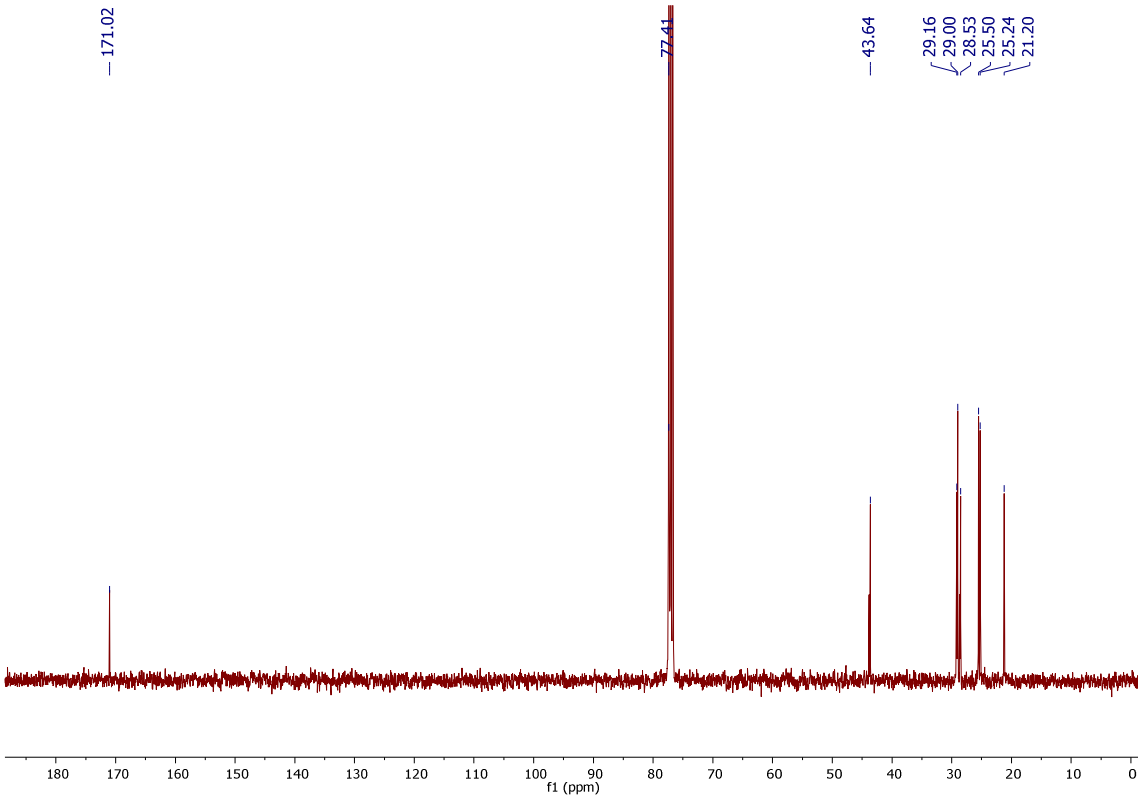




1,4-Dicyclopentyl-butane-1,4-diyl diacetate (6f)





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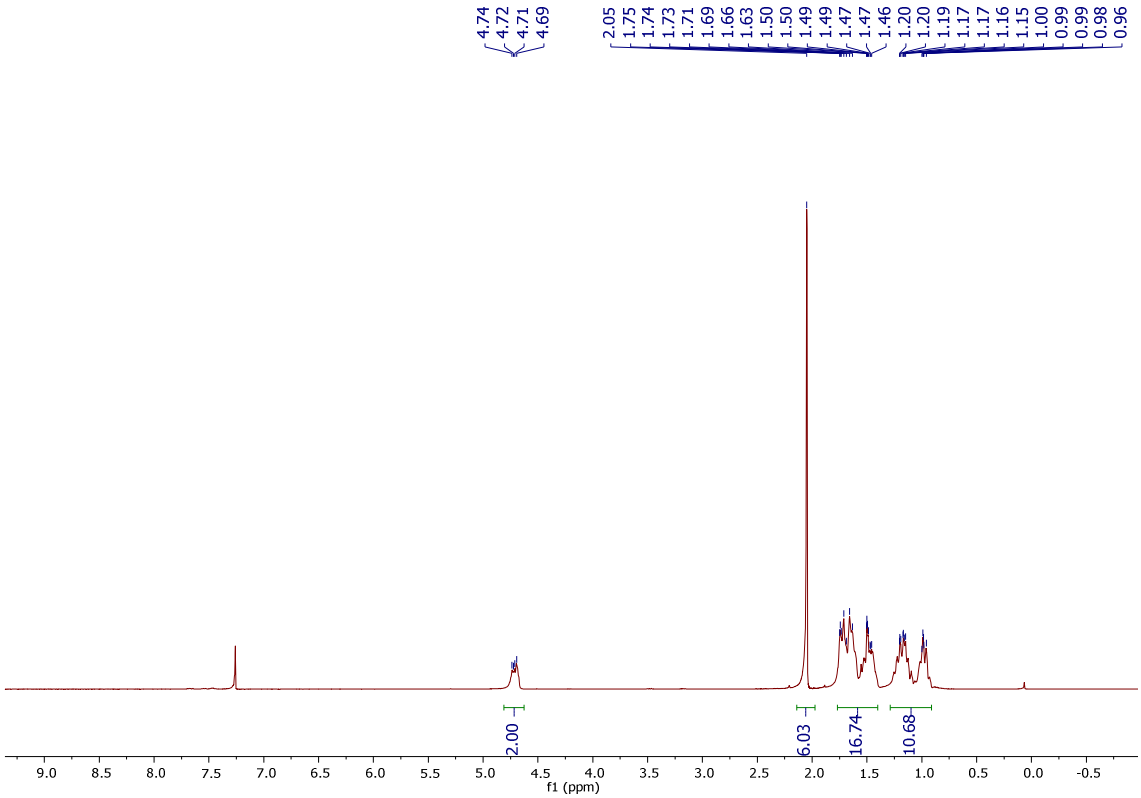

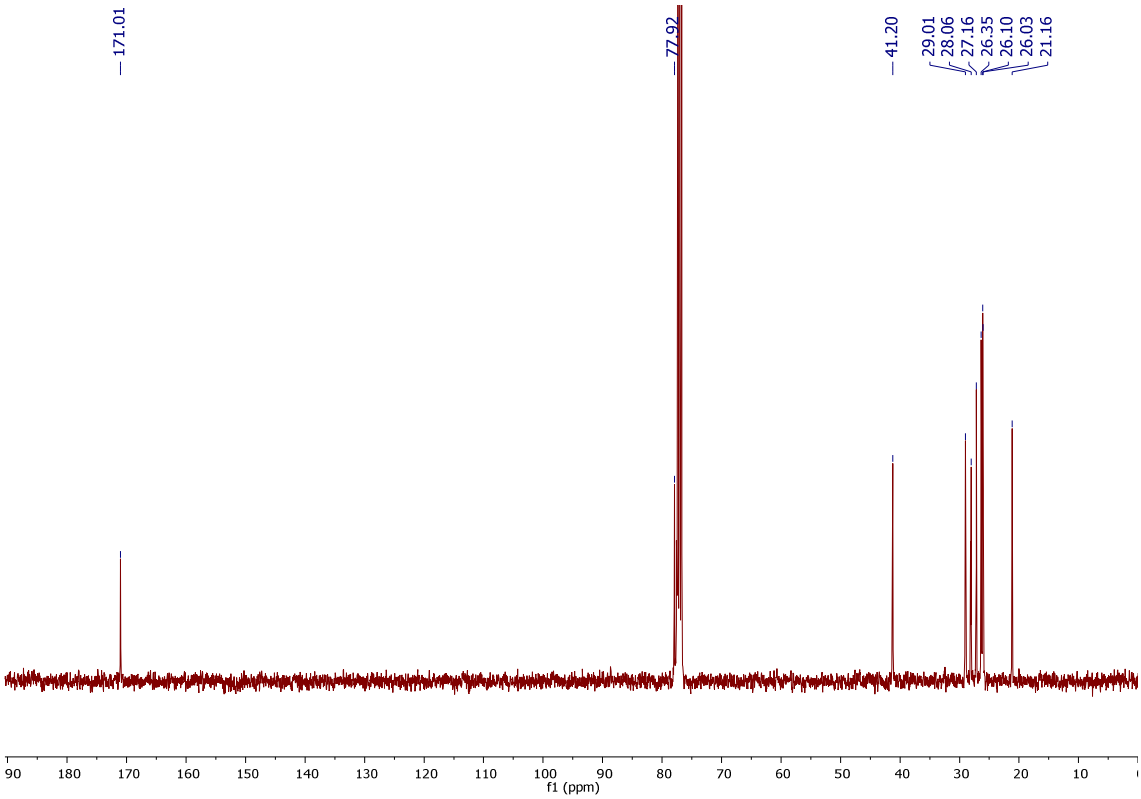

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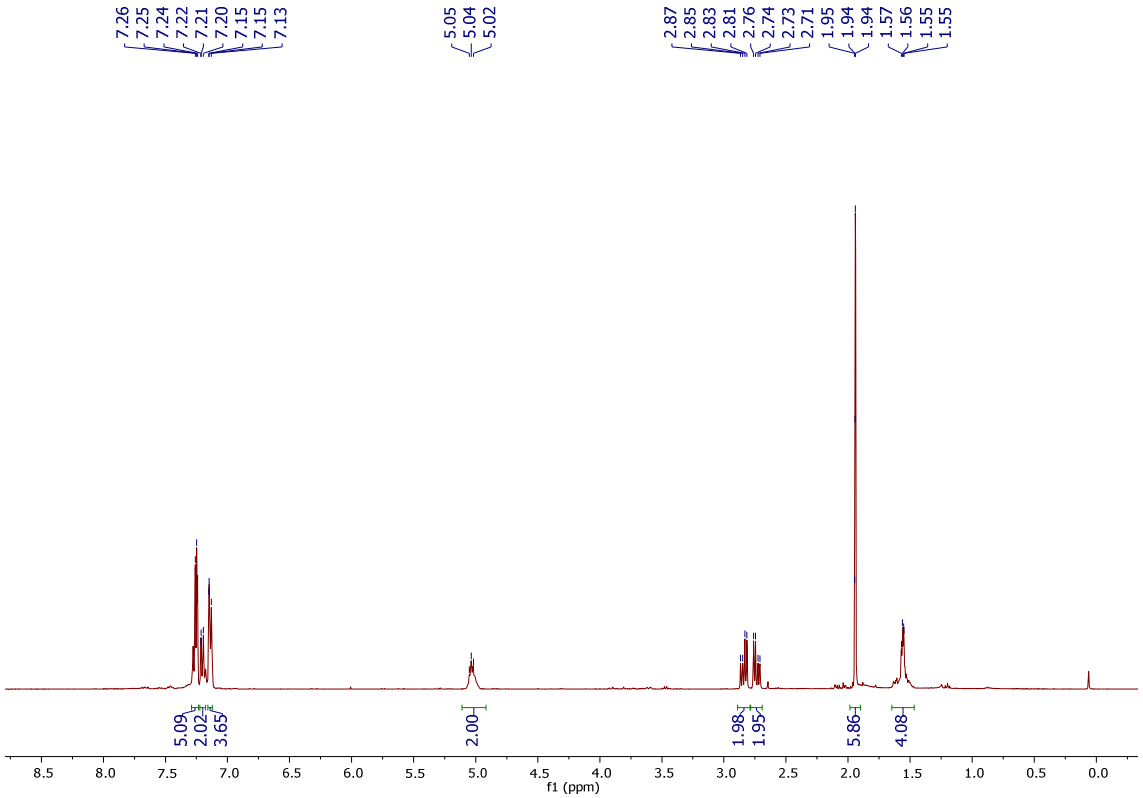

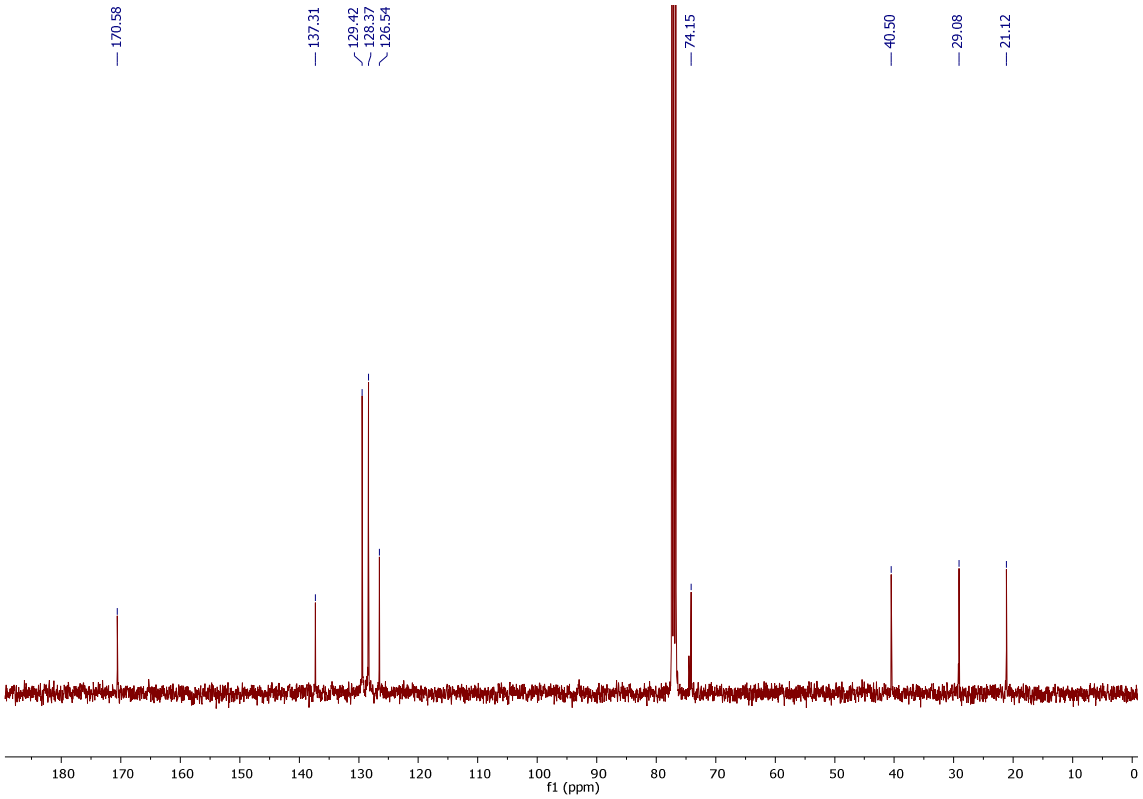

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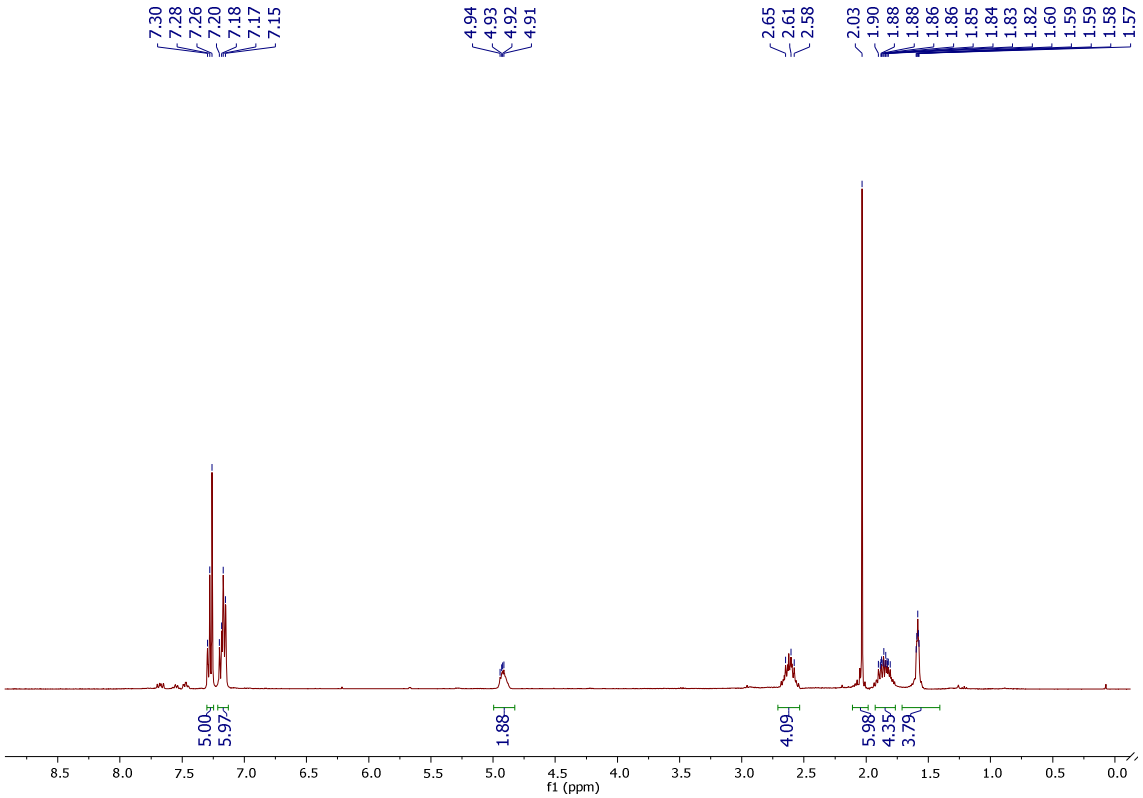

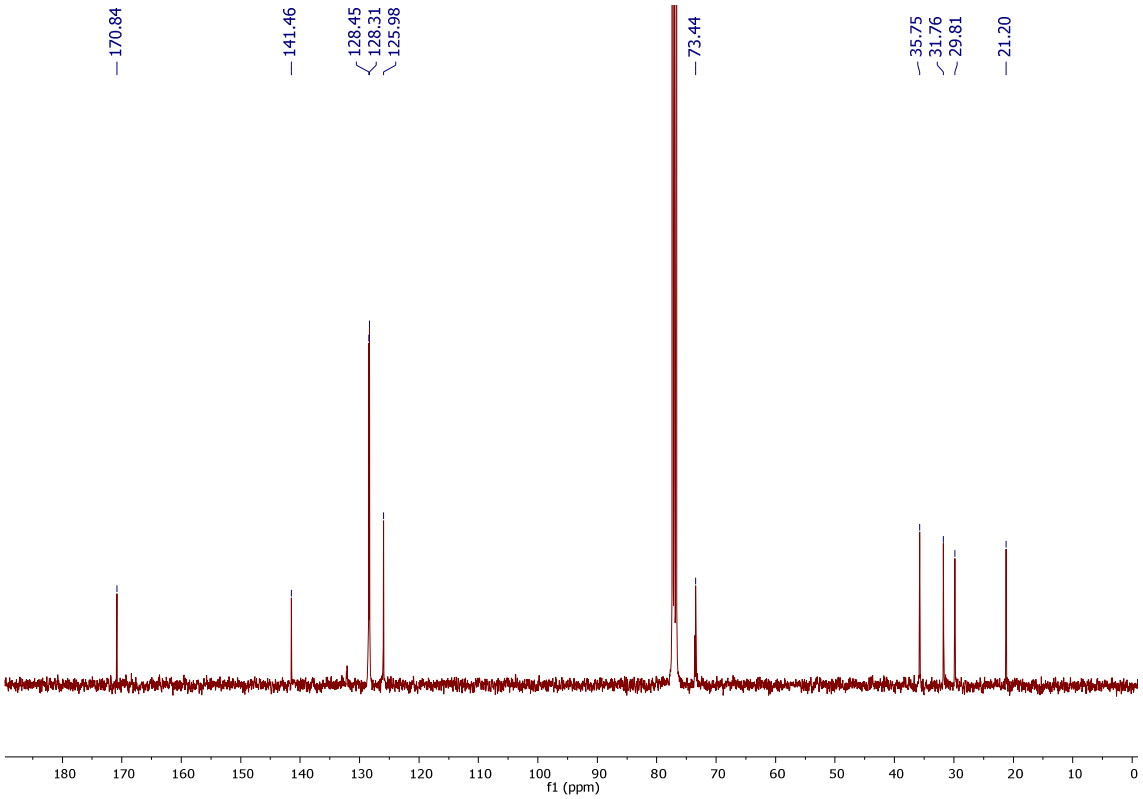

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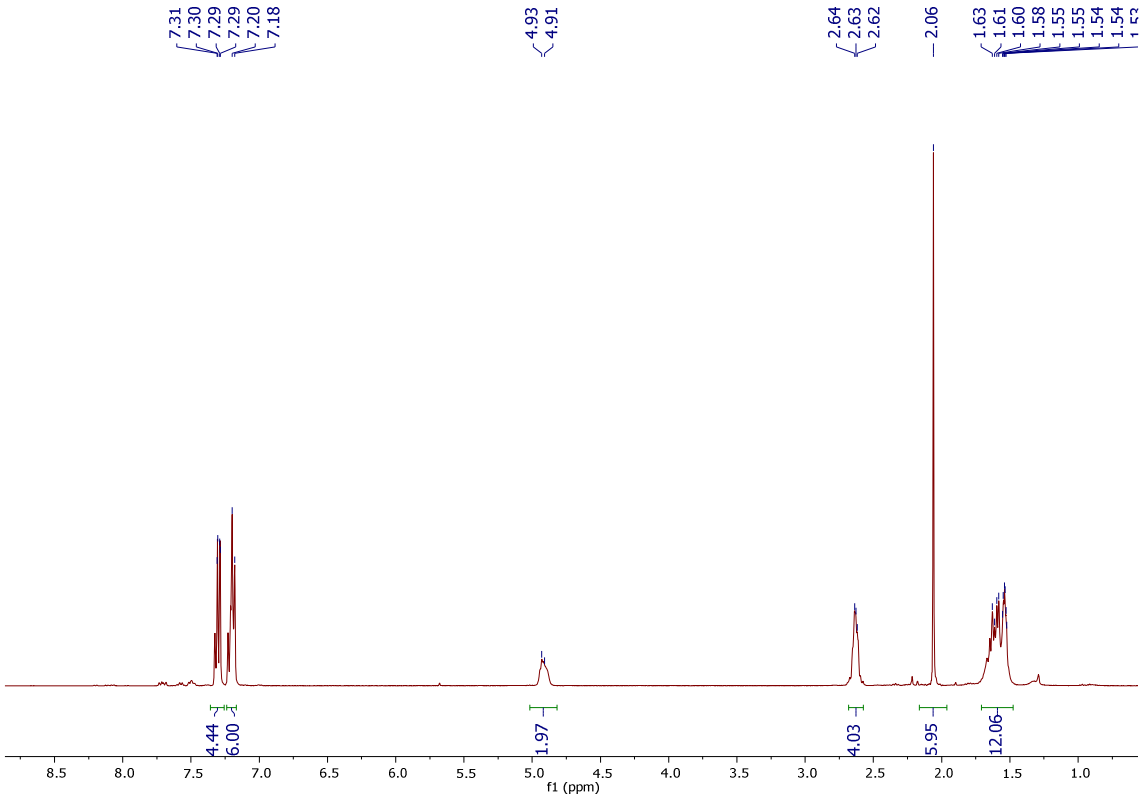
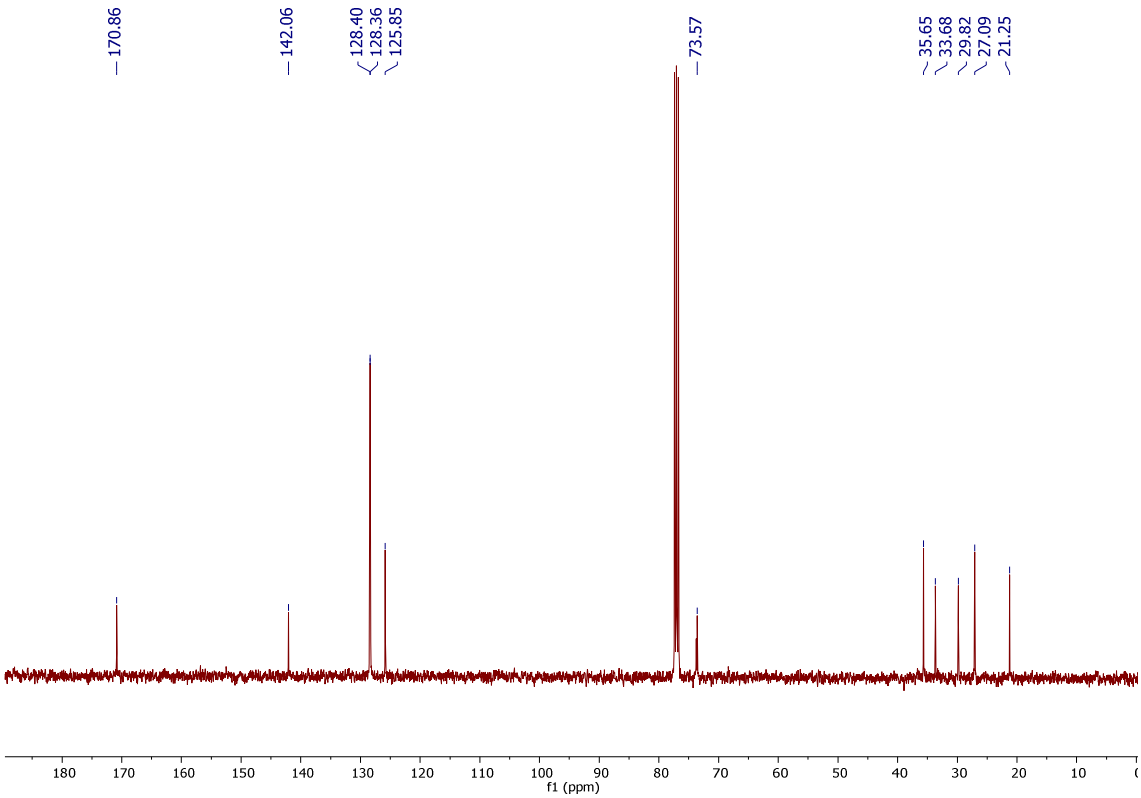
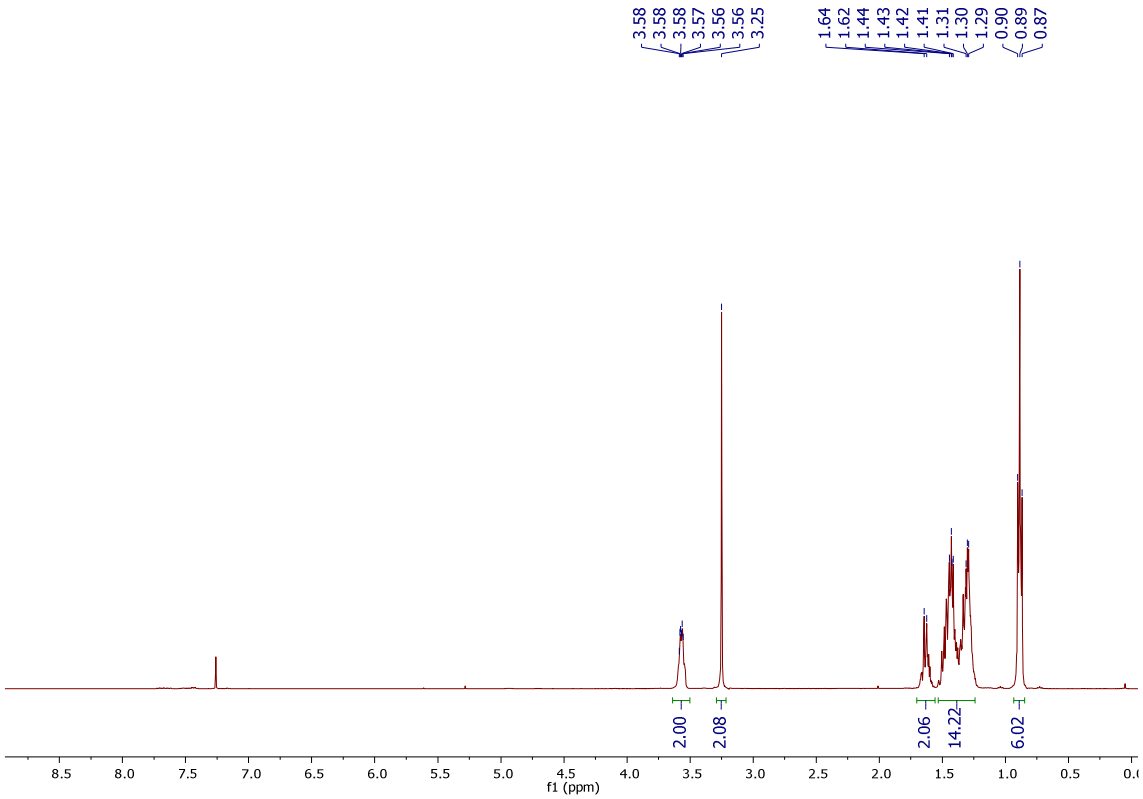
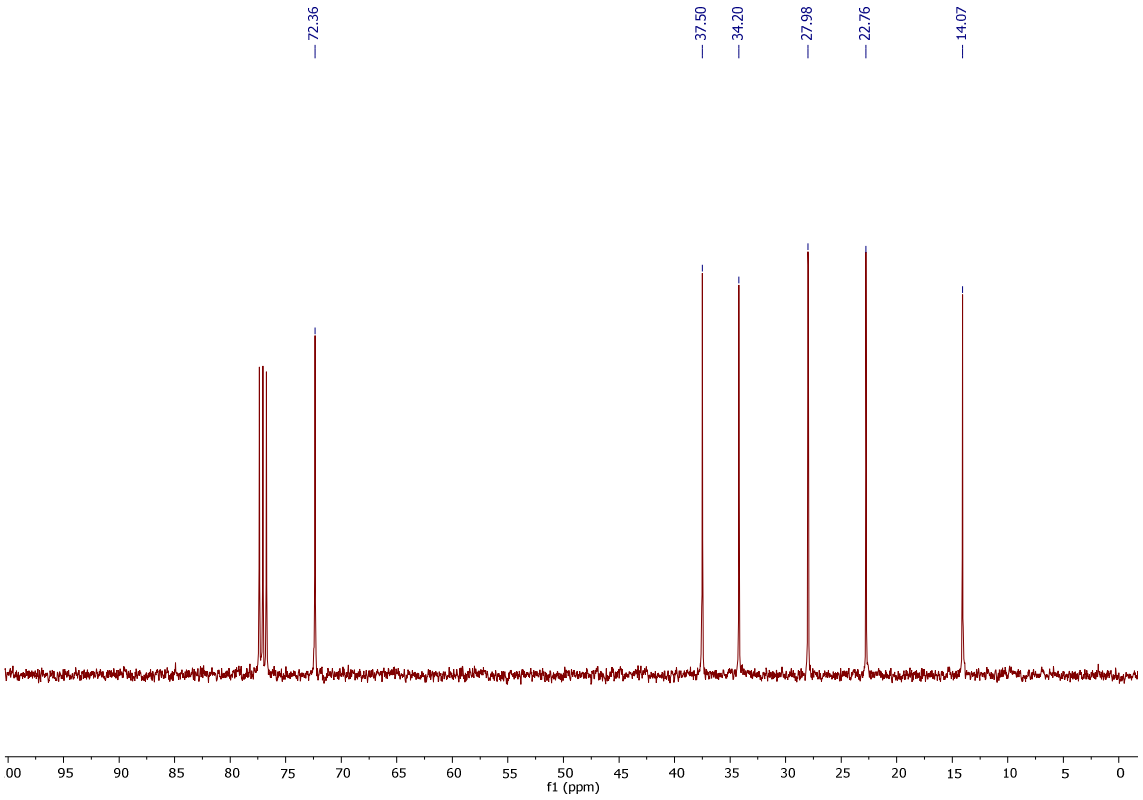


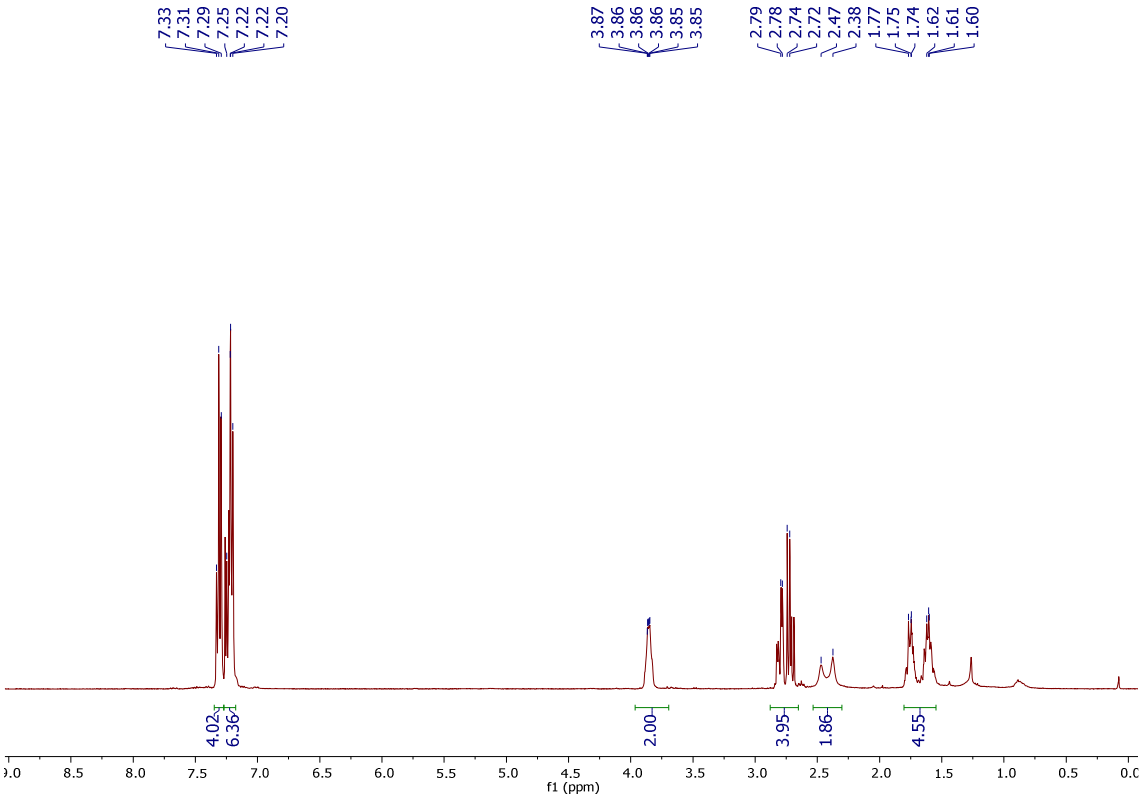


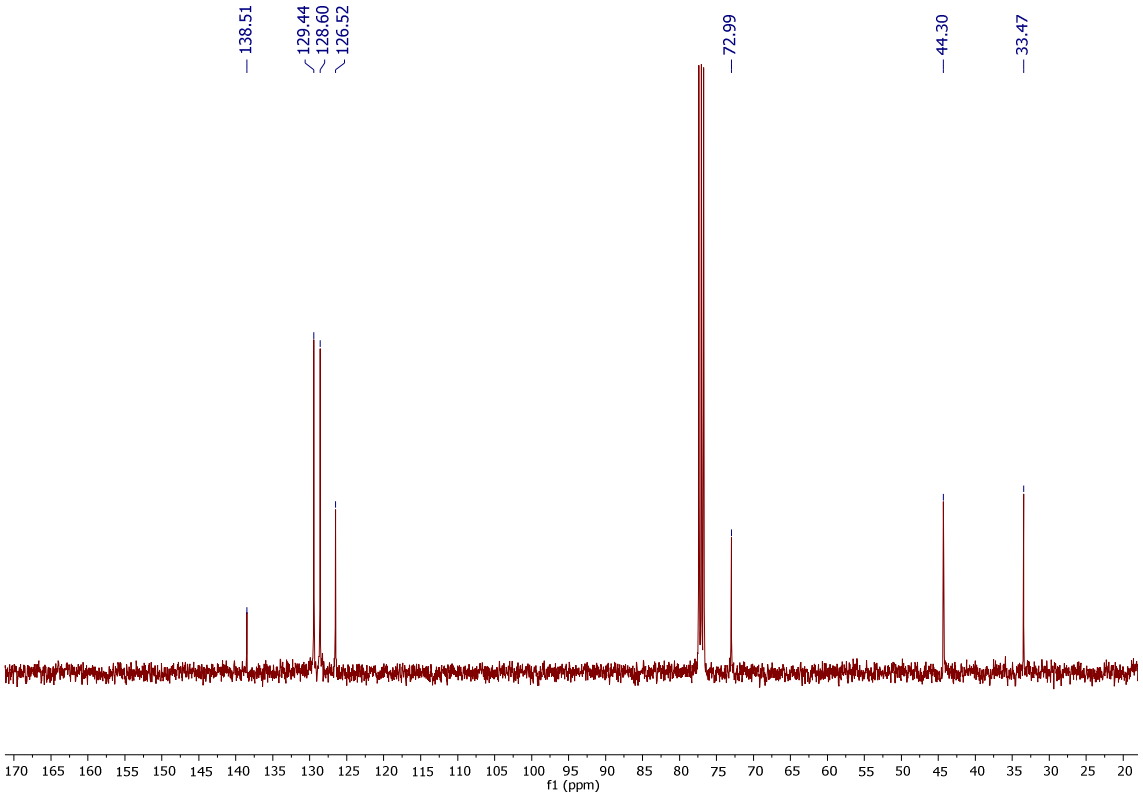
(*R*,*R*)-5,8-Dodecanediol (8c)



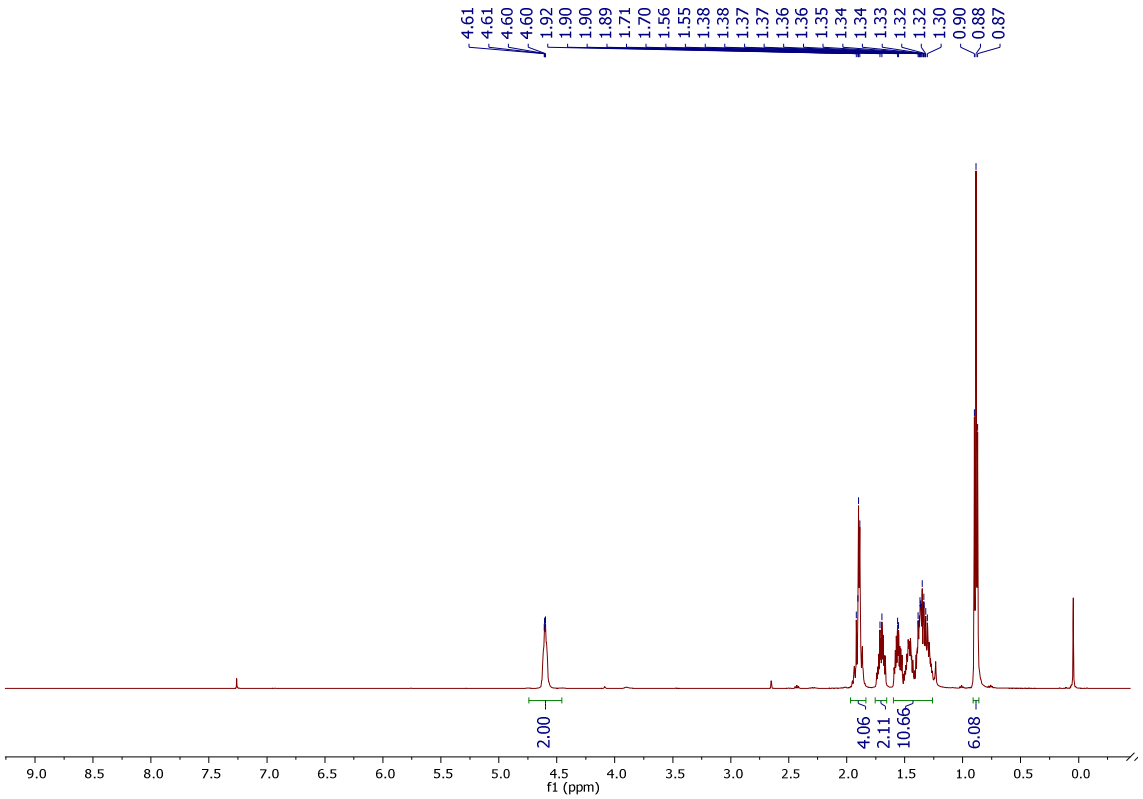


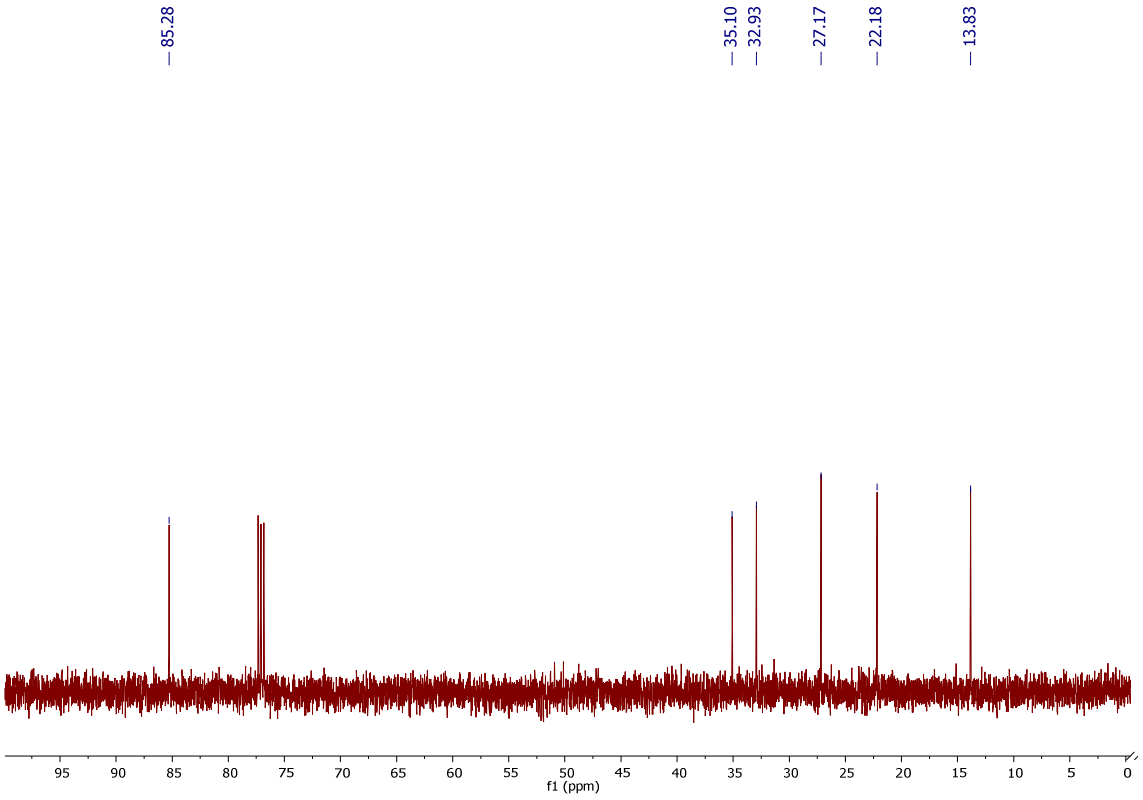
1,6-Diphenyl-2,5-hexanediol (8h)



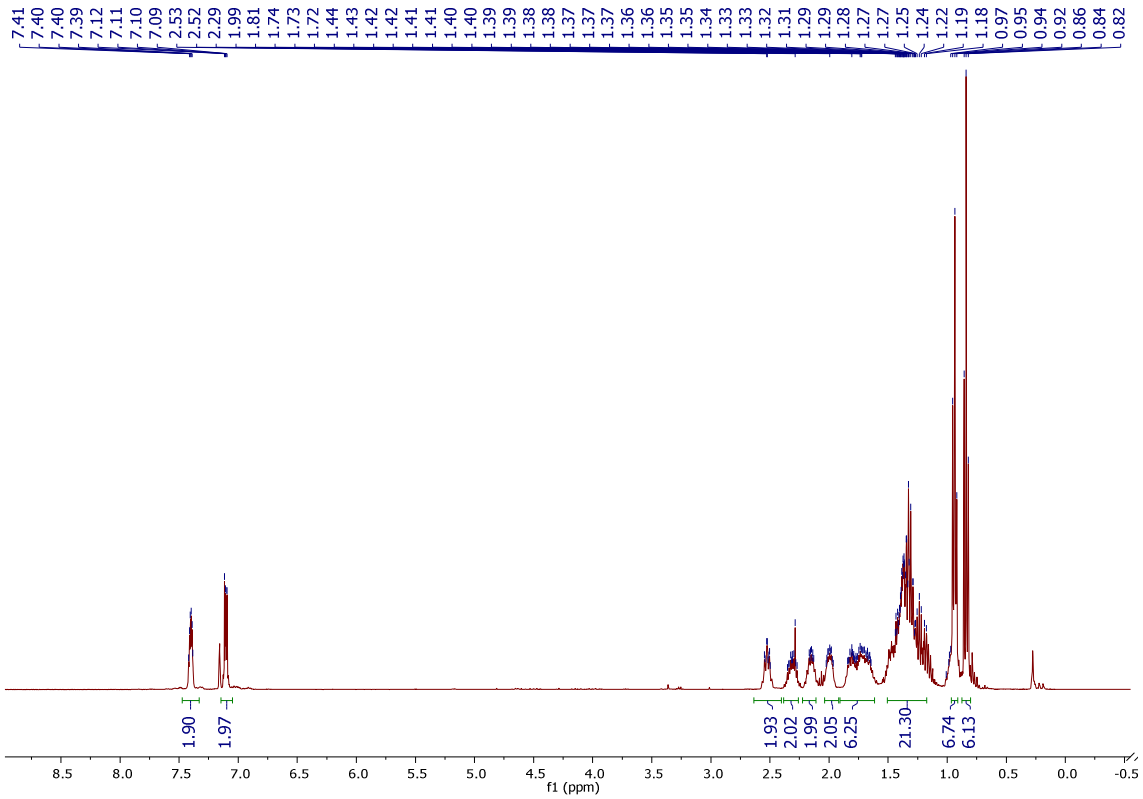


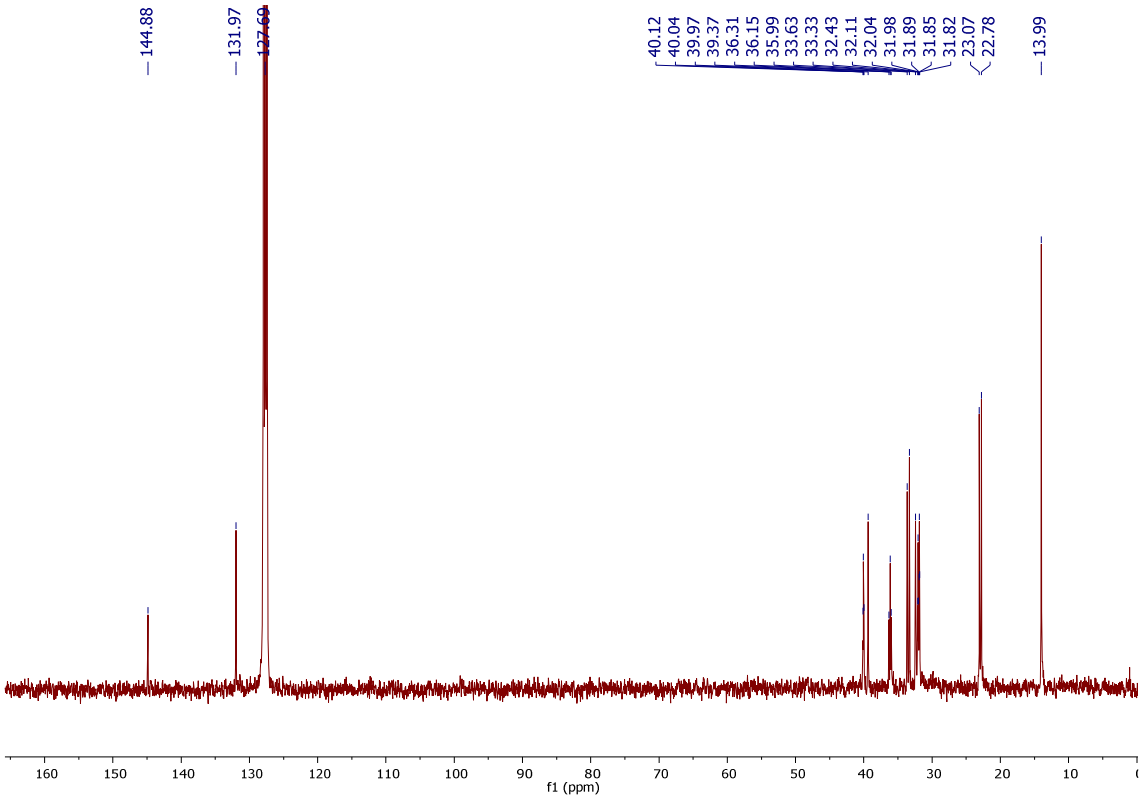
(R,R)-5,8-Dodecanediol cyclic sulphate (10)

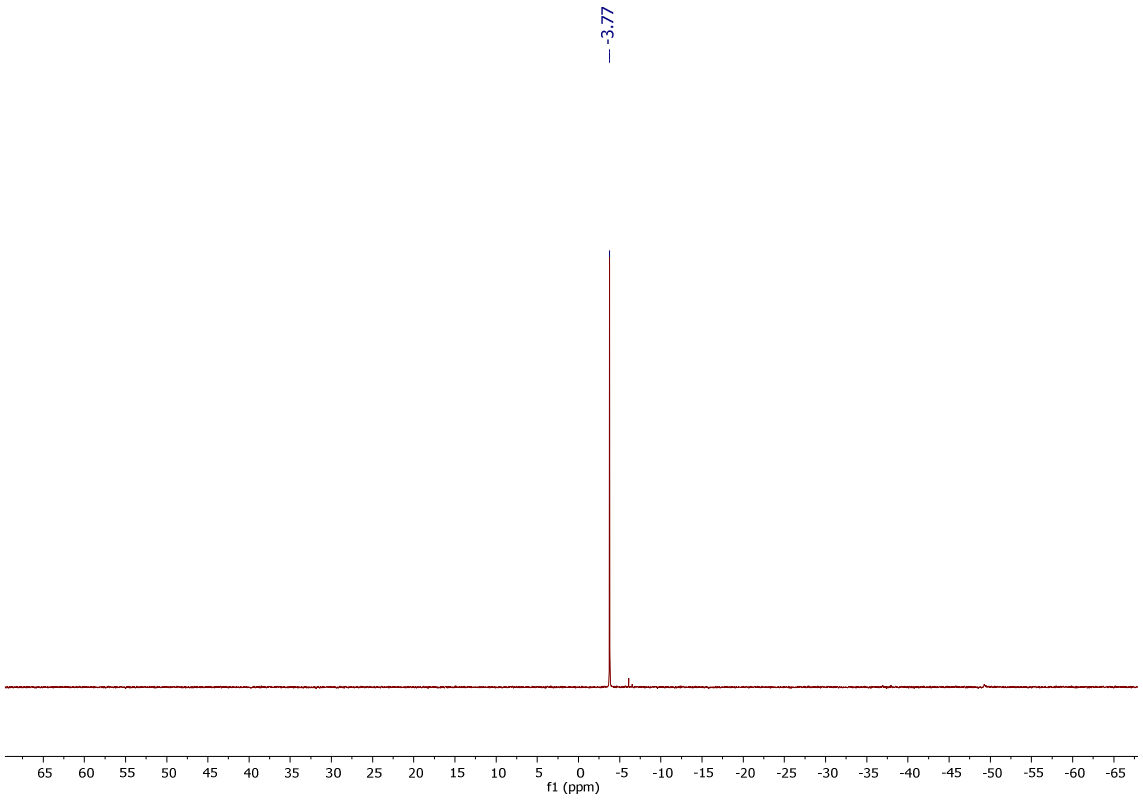




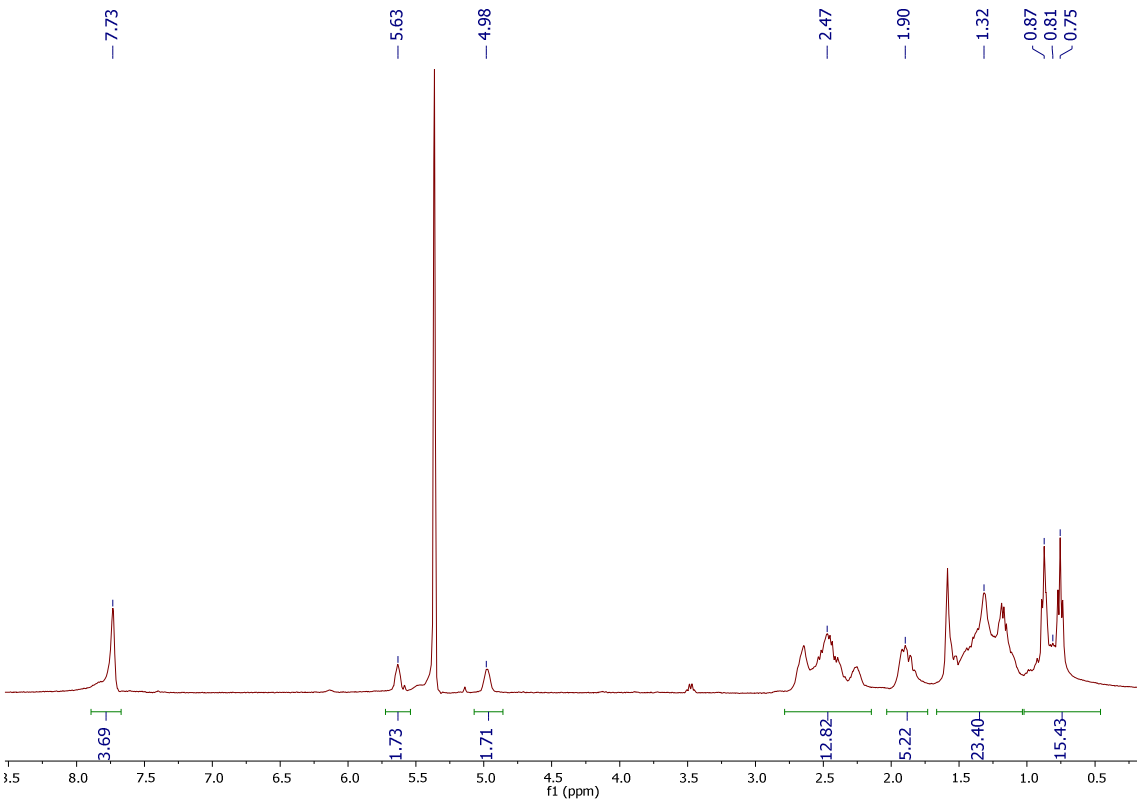
(*S*,*S*)-Bis-1,2(2,5-di-n-butylphospholane)benzene (11)

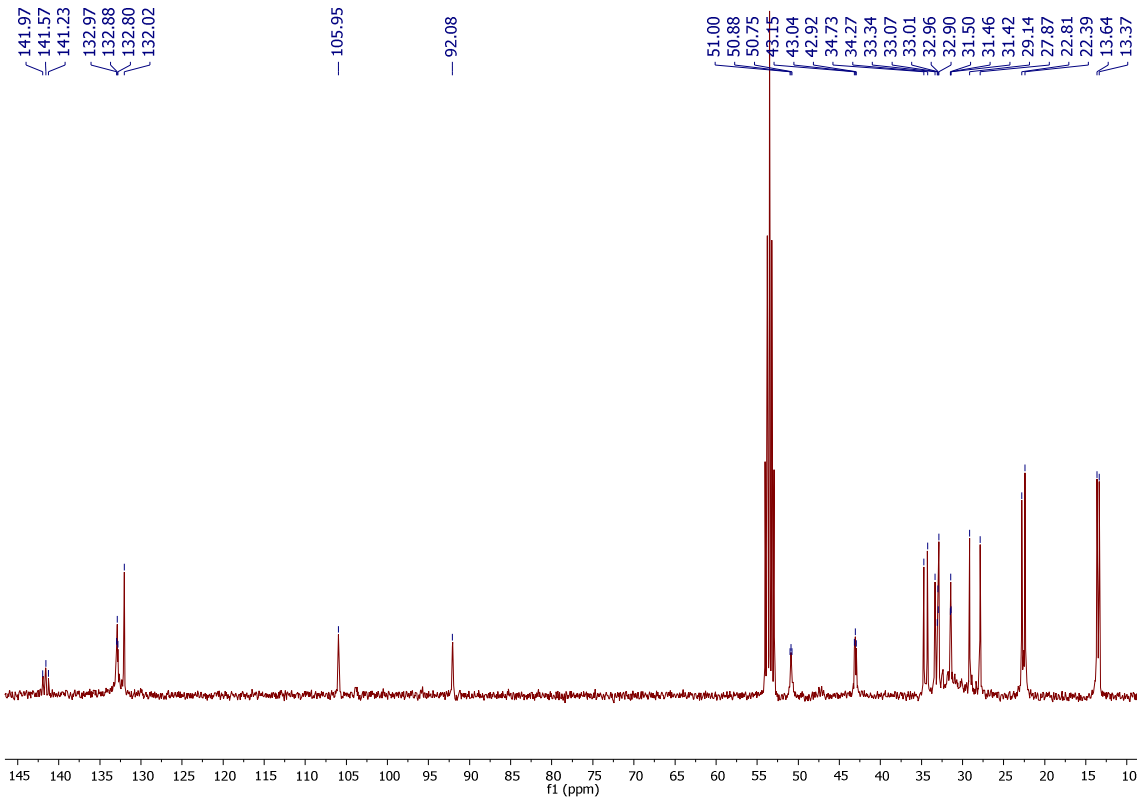


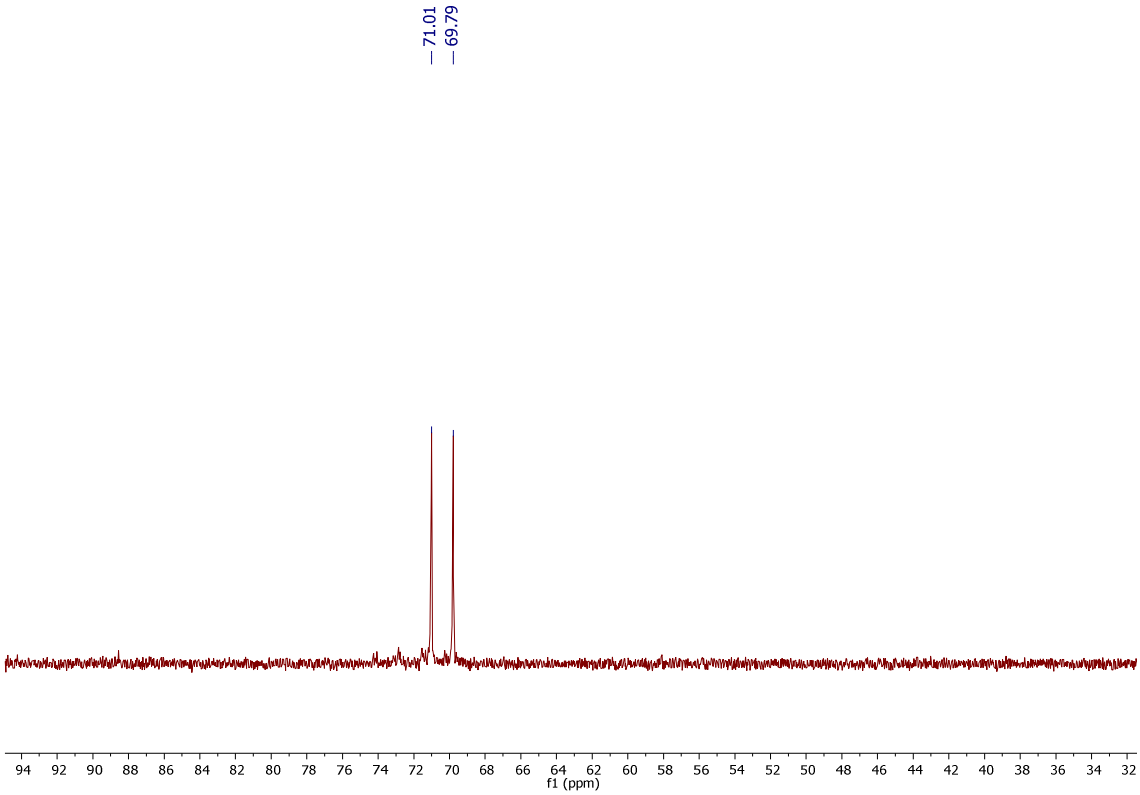




[Rh(COD)(11)]BF_4 (12)

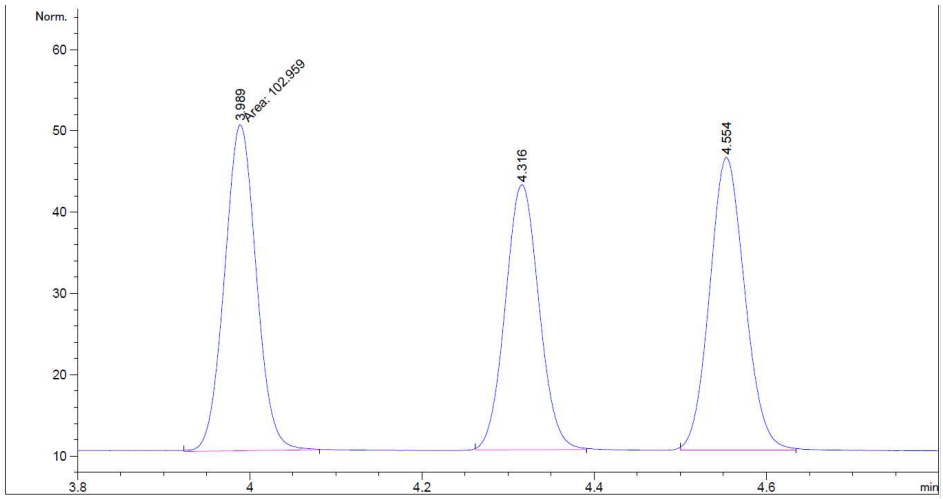



141.97
141.57
141.23
132.97
132.88
132.80
132.02
105.95
92.08
51.00
50.88
50.75
43.15
43.04
42.92
34.73
34.27
33.34
33.07
33.01
32.96
32.90
31.50
31.46
31.42
29.14
27.87
22.81
22.39
13.64
13.37
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)


71.01
69.79
94 92 90 88 86 84 82 80 78 76 74 72 70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32
f1 (ppm)

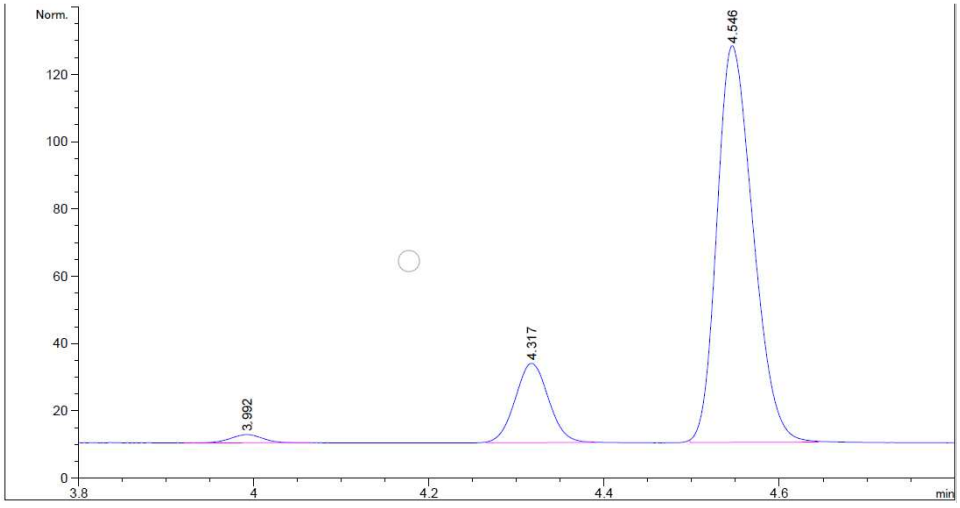
Hexane-2,5-diyl diacetate (6a)

Hydrogenation with achiral catalyst



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %
1	3.989	MM	0.0427	102.95870	35.05620
2	4.316	BB	0.0429	88.90480	30.27101
3	4.554	BB	0.0441	101.83265	34.67279

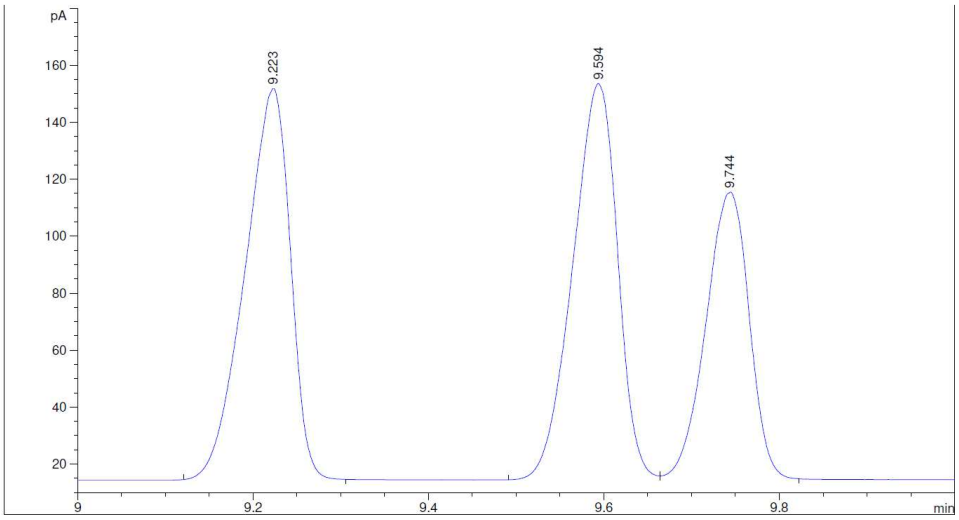
Hydrogenation with **5d** (96 % ee; C_2:meso = 85:15)



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	3.992	MM	0.0419	6.07087	2.41372	1.49533
2	4.317	BB	0.0421	62.62760	23.50888	15.42599
3	4.546	BB	0.0445	337.28909	117.60484	83.07868

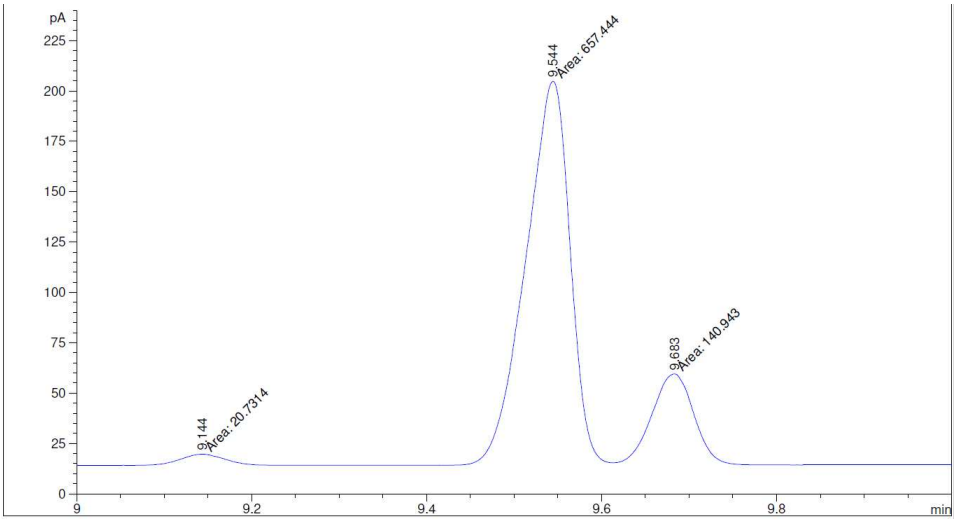
Decane-4,7-diyl diacetate (6b)

Hydrogenation with achiral catalyst



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	9.223	BB	0.0550	490.75806	137.21536	36.93435
2	9.594	BV	0.0541	492.65393	138.94101	37.07703
3	9.744	VB	0.0527	345.31870	100.75025	25.98861

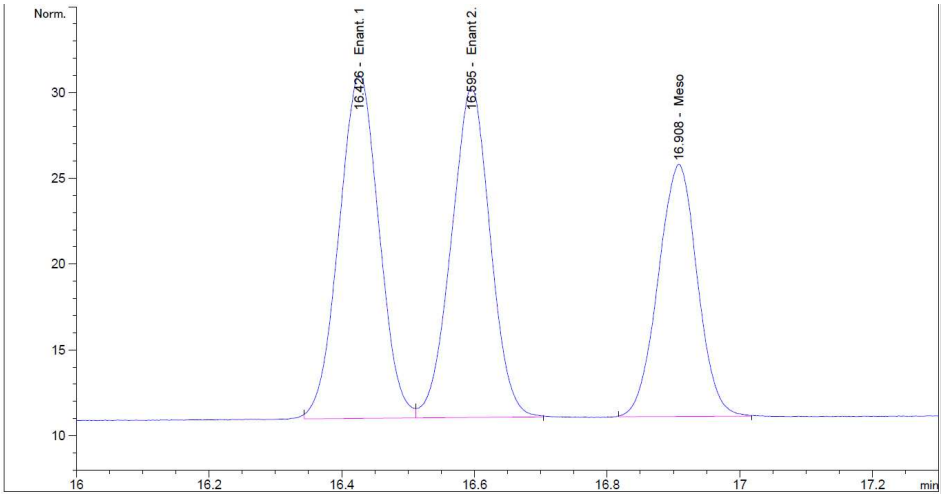
Hydrogenation with **5d** (94 % ee; C_2:meso = 83:17)



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	9.144	MM	0.0603	20.73137	5.72649	2.53094
2	9.544	MM	0.0579	657.44391	189.11534	80.26238
3	9.683	MM	0.0534	140.94305	43.97676	17.20668

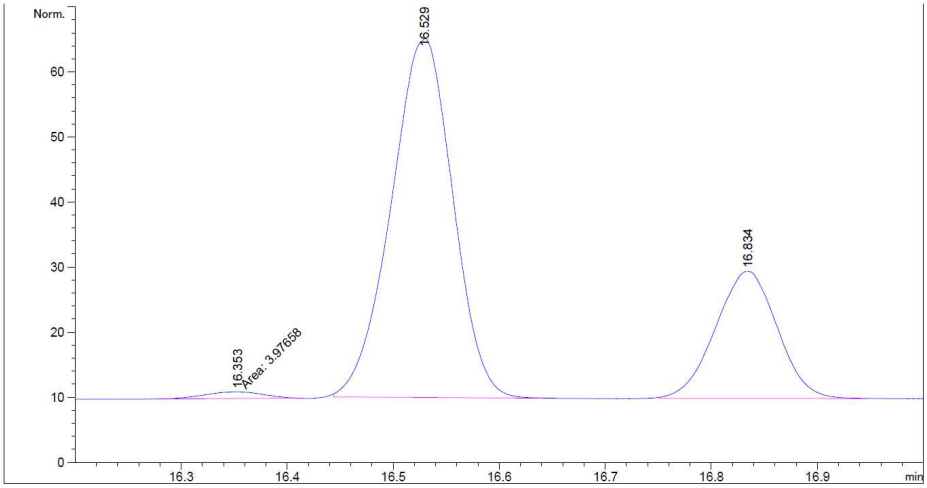
Dodecane-5,8-diyl diacetate (6c)

Hydrogenation with achiral catalyst



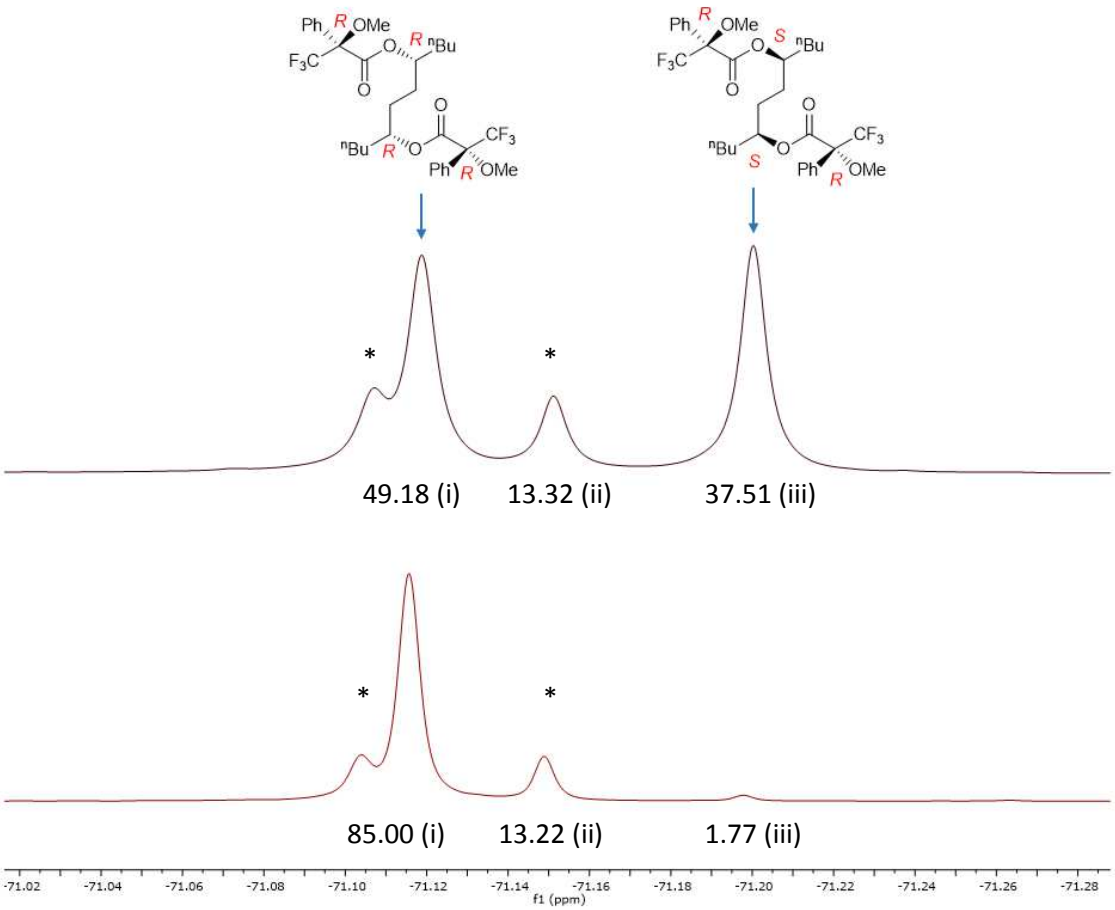
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %
1	16.426	BV	0.0649	83.74672	37.65620
2	16.595	VB	0.0638	78.44142	35.27070
3	16.908	BB	0.0638	60.21009	27.07310

Hydrogenation with **5b** (96 % ee; C_2:meso = 74:26)



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %
1	16.353	MM	0.0625	3.97658	1.29809
2	16.529	BB	0.0634	223.18689	72.85567
3	16.834	BB	0.0642	79.17769	25.84625

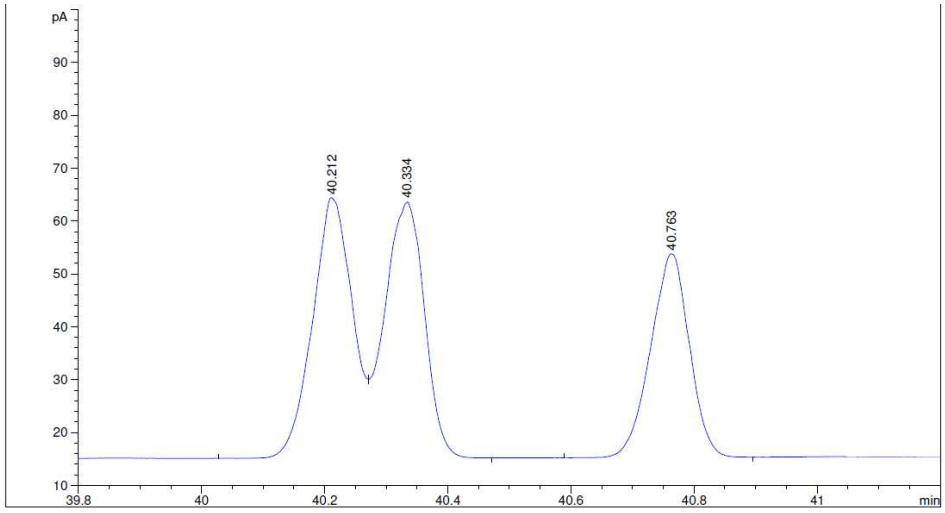
Hexadecan-7,10-diyl diacetate (6d)



Comparison of $^{19}F\{^{1}H\}$ NMR spectra of Mosher esters of diols resulting from deprotection of product of non asymmetric hydrogenation of **1d** (top) and of hydrogenation of **1d** with **5b** (bottom). Signals marked with an asterisk (*) correspond to Mosher diester of *meso*-**10d**, characterized by two unequivalent CF_3 groups. Numerical values correspond to integrals of signals: (i) *R,R,R,R* isomer overlapped with one of the signals of the *meso* isomer, (ii) second signal of the *meso* isomer and (iii) *R,S,S,R* isomer. From data of the bottom spectrum a value of (*R,R,R,R*)/(*R,S,S,R*) = (85.00-13.22)/1.77 = 40.55 can be obtained, corresponding to a 95 % ee of the parent ester **6d**.

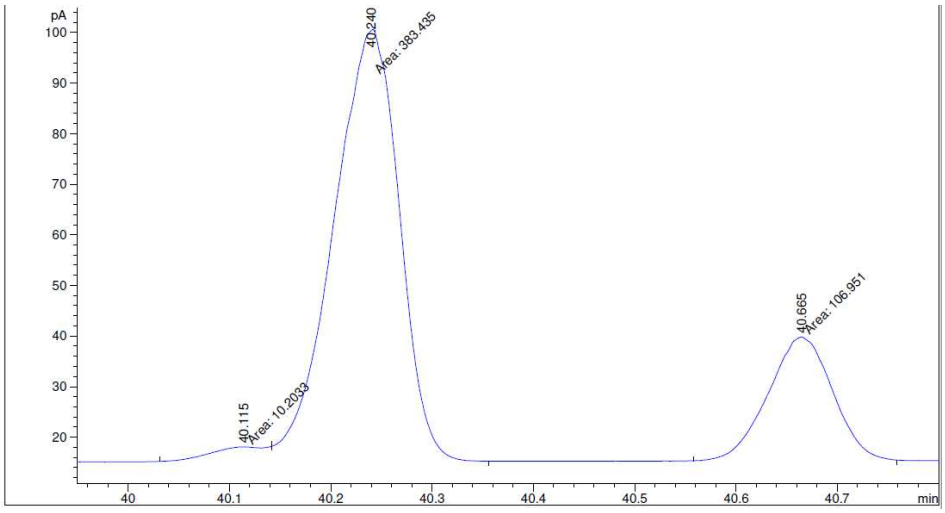
2,11-Dimethyl-dodecan-5,8-diyl diacetate (6e)

Hydrogenation with achiral catalyst



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	40.212	BV	0.0658	221.31906	49.15368	36.46331
2	40.334	VB	0.0693	217.43726	48.47878	35.82377
3	40.763	BB	0.0621	168.20734	38.44756	27.71292

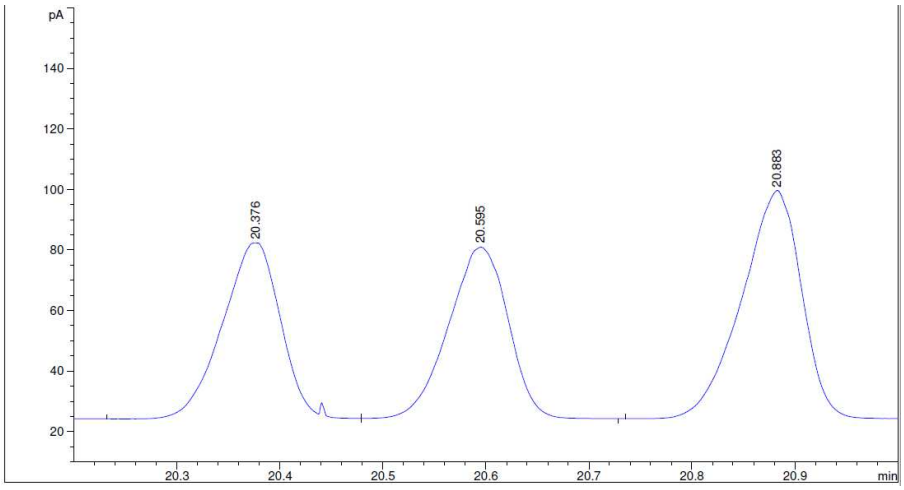
Hydrogenation with **5d** (95 % ee; C_2:meso = 79:21)



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	40.115	MF	0.0630	10.20328	2.70049	2.03825
2	40.240	FM	0.0751	383.43488	85.08346	76.59672
3	40.665	MM	0.0731	106.95099	24.39391	21.36502

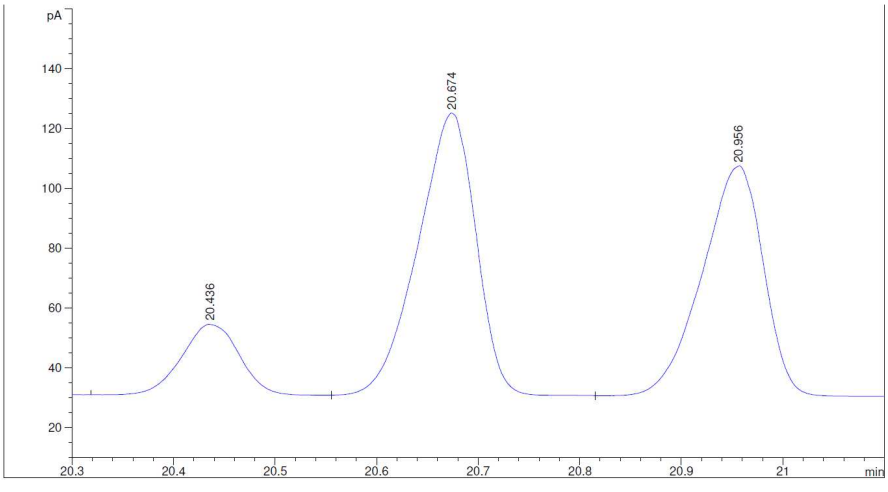
1,4-dicyclopentyl-butane-1,4-diyl diacetate (6f)

Hydrogenation with achiral catalyst



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %
1	20.376	BV	0.0599	228.37314	30.02703
2	20.595	VB	0.0598	228.09204	29.99007
3	20.883	BB	0.0603	304.09332	39.98290

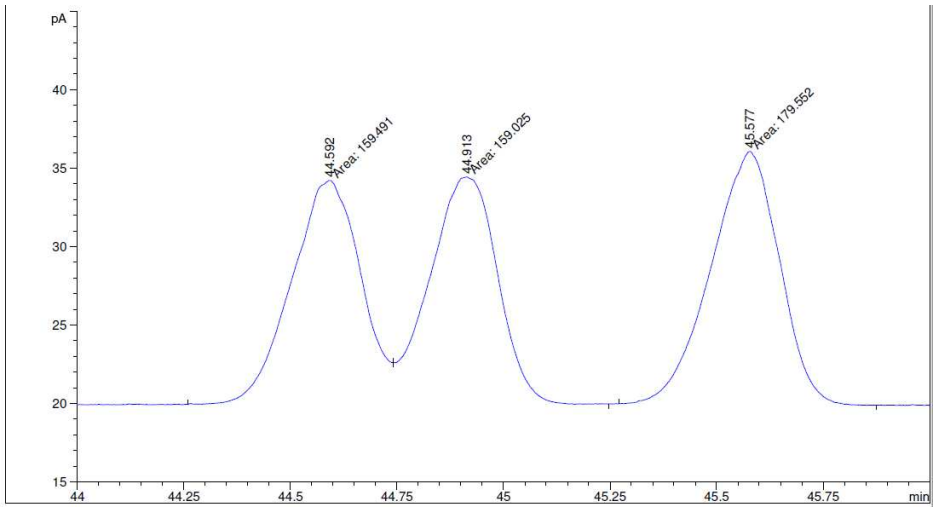
Hydrogenation with **5d** (60 % ee; C_2:meso = 59:41)



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %
1	20.436	BV	0.0616	92.76181	11.76943
2	20.674	PB	0.0593	374.28931	47.48908
3	20.956	BB	0.0624	321.10748	40.74148

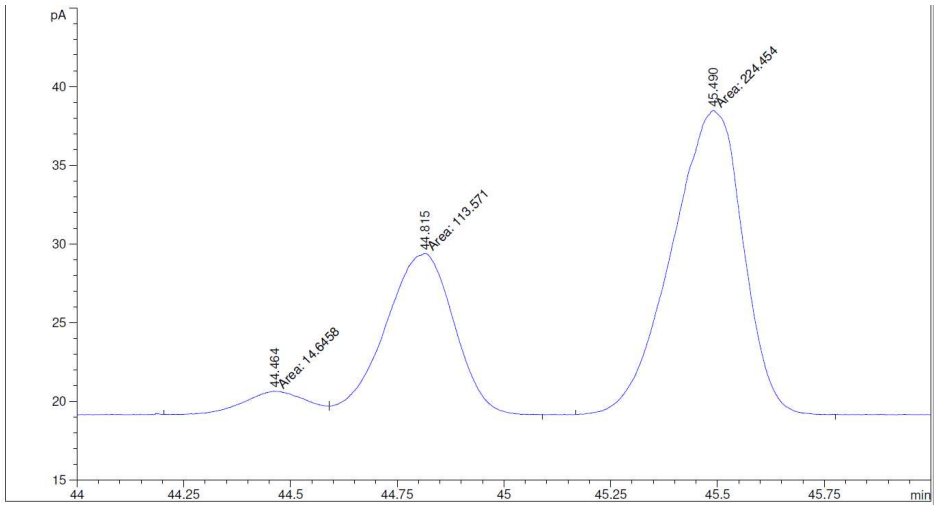
1,4-dicyclohexyl-butane-1,4-diyl diacetate (6g)

Hydrogenation with achiral catalyst



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	44.592	MF	0.1873	159.49078	14.18996	32.02190
2	44.913	FM	0.1838	159.02496	14.41645	31.92838
3	45.577	MM	0.1857	179.55206	16.11417	36.04972

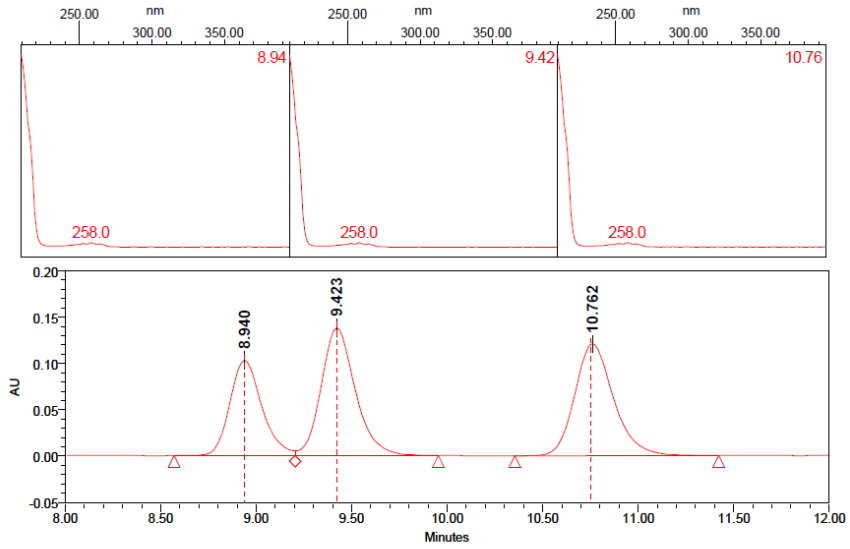
Hydrogenation with **5c** (77 % ee; C_2:meso = 36:64)



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	44.464	MF	0.1687	14.64577	1.44677	4.15281
2	44.815	FM	0.1855	113.57124	10.20436	32.20316
3	45.490	MM	0.1934	224.45407	19.33996	63.64402

1,6-Diphenyl-hexane-2,5-diyl diacetate (6h)

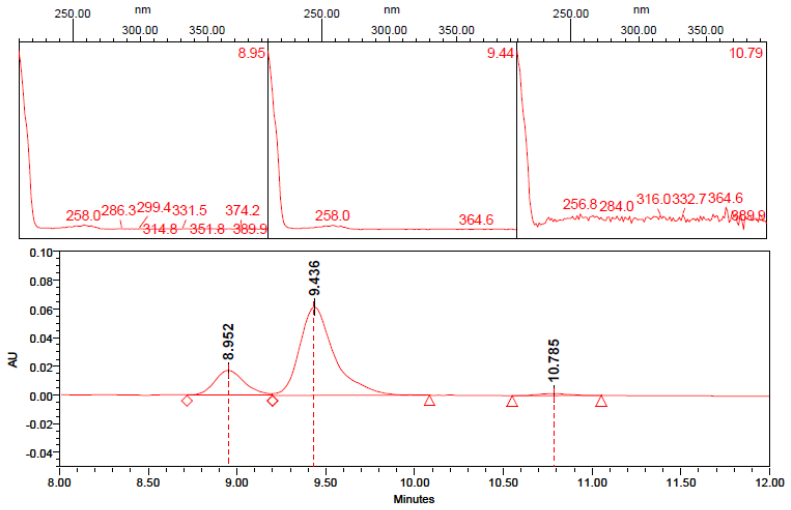
Hydrogenation with achiral catalyst



Peak Results

	RT	Area	% Area
1	8.940	1195111	25.92
2	9.423	1706692	37.02
3	10.762	1708246	37.05

Hydrogenation with **5a** (96 % ee; C_2:meso = 81:19)

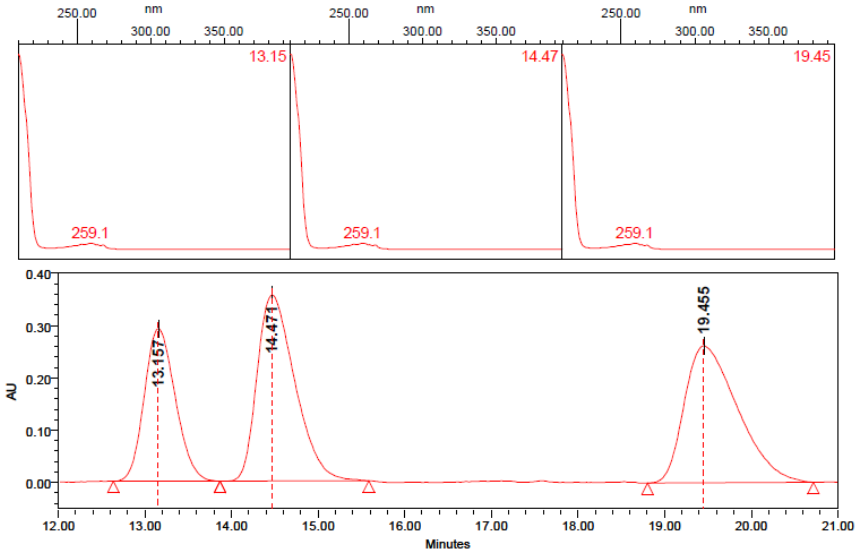


Peak Results

	RT	Area	% Area
1	8.952	204666	19.42
2	9.436	832835	79.03
3	10.785	16373	1.55

1,8-Diphenyl-octane-3,6-diyl diacetate (6i)

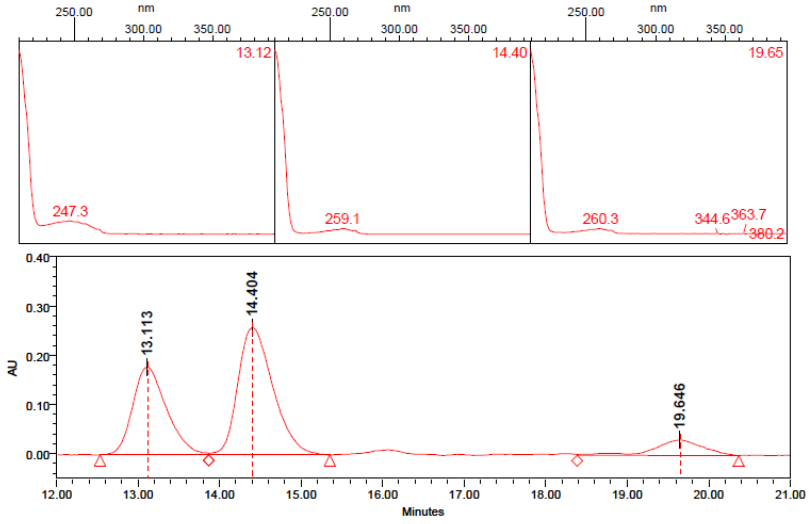
Hydrogenation with achiral catalyst



Peak Results

	RT	Area	% Area
1	13.157	7276737	24.88
2	14.471	10777514	36.85
3	19.455	11189177	38.26

Hydrogenation with **5a** (71 % ee; C_2:meso = 64:36)

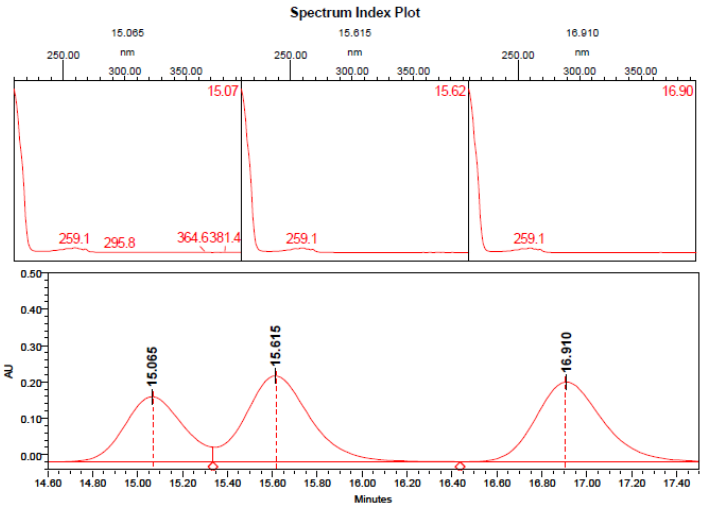


Peak Results

	RT	Area	% Area
1	13.113	5161050	36.32
2	14.404	7741560	54.49
3	19.646	1305563	9.19

1,10-Diphenyl-decane-4,7-diyl diacetate (6j)

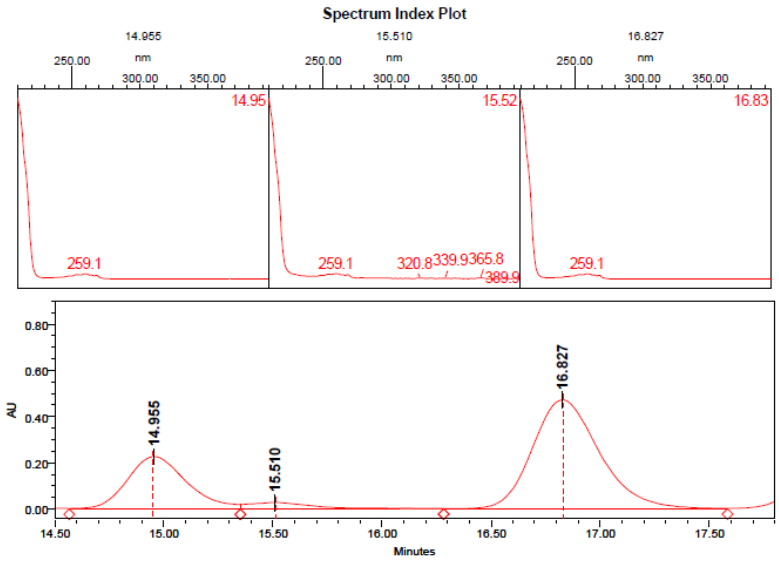
Hydrogenation with achiral catalyst



Peak Results

	RT	Area	% Area
1	15.065	3241747	25.84
2	15.615	4730461	37.71
3	16.910	4572818	36.45

Hydrogenation with **5a** (89 % ee; C_2:meso = 71:29)



Peak Results

	RT	Area	% Area
1	14.955	4255091	28.53
2	15.510	567691	3.81
3	16.827	10089147	67.66