Enantioselective Intramolecular Hydroarylation of Alkenes via Directed C–H Bond Activation

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Supporting Information

This material contains experimental details, including synthetic procedures and characterization, to obtain the results in Table 3 − 7. Material for Tables 1 and 2 is in the previous communication.[1]

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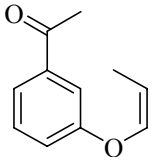
Experimental:

General Procedures. All organic reactions were performed under an atmosphere of N_2 in flame- or oven-dried glassware unless otherwise stated. All imine formation reactions and preparations for all C-H activation experiments were carried out in a N_2-filled inert atmosphere box (glovebox). Microwave reactions were conducted by using a Biotage Initiator microwave reactor. Visualization of the developed chromatograms was performed by fluorescence quenching, $KMnO_4$ stain, or *para*-anisaldehyde stain. Organic extracts were dried over anhydrous $MgSO_4$ or Na_2SO_4 and were concentrated using a rotary evaporator under high vacuum pressure. Unless otherwise noted, ^{1}H, ^{13}C, and ^{31}P NMR measurements were conducted using a 400 MHz spectrometer at room temperature. NMR chemical shifts are reported in ppm and referenced to residual protonated solvent or added internal standard, and coupling constants are reported in Hz. Chiral HPLC analyses were performed using a flow rate of 1 mL/min and *i*-PrOH/hexanes as the mobile phase. A polarimeter with a sodium lamp was used to determine specific rotations and concentrations are reported in g/dL. Circular dichroism spectra were measured in MeOH. IR spectroscopy was conducted using an FT-IR spectrometer equipped with a single-bounce ZnSe attenuated total reflectance plate, and only partial data are listed.

Materials. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Molecular sieves and Celite were heated at approximately 250 °C under vacuum overnight to remove any trace of water and were stored in a glovebox. Tetrahydrofuran (THF), 1,4-dioxane, diethyl ether, benzene, toluene, and methylene chloride were passed through activated alumina columns under nitrogen pressure. Triethylamine was distilled under nitrogen from CaH_2.

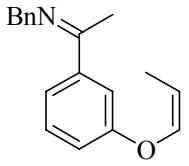
Benzylamine was distilled and was stored over 3 Å or 4 Å molecular sieves. The following compounds were prepared according to referenced literature procedures: $[RhCl(coe)_2]_2$[2] and ligands $FcPCy_2$,[3] and **L8** − **L11**.[4] Tetrahydrofuran-d_8 and 1,4-dioxane-d_8 were dried over sodium/benzophenone ketyl and distilled using vacuum transfer procedures. All liquid reagents and deuterated solvents were thoroughly degassed using three freeze-pump-thaw cycles prior to transfer into the glovebox.

Compounds 1-15. Procedures and analytical characterization for substrates and products reported in Table 2 and equations 1 to 3 have previously been reported.[1]



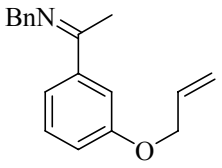
1-{3-[((*Z*)-Propenyl)oxy]phenyl}ethanone (37). A mixture of Cs_2CO_3 (7.98 g, 24.4 mmol), CuCl (406 mg, 4.10 mmol), and acetylacetone (0.82 g, 8.19 mmol) in tetrahydrofuran (50 mL) was stirred at room temperature. After 5 min, 3'-hydroxyacetophenone (2.23 g, 16.3 mmol) and *cis*-1-bromo-1-propene (1.81 mL, 21.2 mmol) were added, and the mixture was heated to reflux. After 17.5 h, *cis*-1-bromo-1-propene (1.81 mL, 21.2 mmol) was added, and reflux was continued for an additional 6 h. After cooling it to room temperature, the reaction mixture was filtered through a Celite pad, and the filtrate was concentrated. The residue was purified by silica gel column chromatography (silica gel: 400 mL, eluted first with hexanes and then 20:1 hexanes/ethyl acetate), to give the title compound as a yellow oil (1.29 g, 45% yield). IR (ZnSe, thin film) ν_{max} (cm^{-1}): 1685, 1583, 1440, 1267, 1206, 1026. ^1H NMR (400 MHz, $CDCl_3$): δ 7.64-7.61 (m, 1H), 7.58-7.56 (m, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.23-7.19 (m, 1H), 6.41 (dq, J = 1.6, 6.0 Hz, 1H), 4.97 (dq, J = 6.0, 6.8 Hz, 1H), 2.61 (s, 3H), 1.73 (dd,

J = 1.6, 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 197.6, 157.7, 140.3, 138.6, 129.8, 122.5, 121.1, 115.2, 108.7, 26.8, 9.4. HRMS (EI): *m*/*z* calcd. for $C_{11}H_{12}O_2$ (M^+): 176.0837, found: 176.0836.

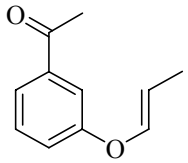


Benzyl-[1-{3-[((*Z*)-propenyl)oxy]phenyl}ethylidene]amine (18).

Representative procedure for imine formation. To a solution of 1-{3-[((*Z*)-propenyl)oxy]phenyl}ethanone (665 mg, 3.77 mmol) in benzene (2.40 mL) was added benzylamine (576 μL, 5.28 mmol). The reaction mixture was stirred over 4Å molecular sieves (1.18 g) for 24 h, after which it was filtered through a Celite pad, and concentrated *in vacuo*. The residue was again reacted over 4 Å molecular sieves (3.08 g) in benzene (2.40 mL) for 21 h because starting ketone still remained as determined by ^1H NMR analysis. The mixture was filtered through a Celite pad and concentrated *in vacuo*. After establishing that no starting material remained as determined by ^1H NMR analysis, the title compound (900 mg, 90% yield) was isolated by Kügelrohr distillation (120-135 °C, 0.05 mm Hg) as a colorless cloudy oil containing a mixture of imine *E*/*Z* isomers (16/1 by ^1H NMR). The product was stored in an inert atmosphere glovebox at -25 °C. Imine **18** prepared and purified in this way was not characterized fully due to hydrolytic lability and was used as obtained in the subsequent reaction. ^1H NMR (400 MHz, $CDCl_3$) reported for *E* isomer: δ 7.54-7.50 (m, 2H), 7.44- 7.39 (m, 2H), 7.38-7.21 (m, 4H), 7.05-7.01 (m, 1H), 6.42 (dq, J = 1.6, 6.0 Hz, 1H), 4.89 (dq, J = 6.0, 6.8 Hz, 1H), 4.74 (s, 2H), 2.33 (s, 3H), 1.72 (dd, J = 1.6, 6.8 Hz, 3H).

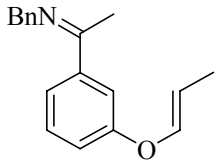


[1-(3-Allyloxyphenyl)ethylidene]benzylamine (16). This compound was prepared in crude form according to the previously reported method[5] and was subjected to Kügelrohr distillation (120 °C, 0.05 mm Hg) to give the title compound as a light yellow oil. Its spectral data agreed with those previously reported.[5]

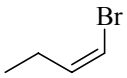


1-{3-[((*E*)-Propenyl)oxy]phenyl}ethanone (38). A mixture of Cs_2CO_3 (8.05 g, 24.7 mmol), CuCl (409 mg, 4.13 mmol), and acetylacetone (0.83 g, 8.3 mmol) in tetrahydrofuran (50 mL) was stirred at room temperature. After 5 min, 3'-hydroxyacetophenone (2.23 g, 16.3 mmol) and *trans*-1-bromo-1-propene (1.83 mL, 21.3 mmol) were added, and the mixture was heated to reflux. After 3 h and 45 min, *trans*-1-bromo-1-propene (1.30 mL, 15.1 mmol) was added, and reflux was continued for an additional 15 h. After cooling to room temperature, the reaction mixture was filtered through a Celite pad and the filtrate was concentrated. The residue was purified by silica gel column chromatography (silica gel: 400 mL, eluted first with hexanes and then 20:1 hexanes/ethyl acetate), to give the title compound as a yellow oil (1.46 g, 51% yield). IR (ZnSe, thin film) ν_{max} (cm^{-1}): 1685, 1582, 1439, 1268, 1209, 1126, 1093. ^1H NMR (400 MHz, $CDCl_3$): δ 7.64-7.60 (m, 1H), 7.56-7.54 (m, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.20-7.16 (m, 1H), 6.45 (dq, J = 1.6, 12.0 Hz, 1H), 5.43 (dq, J = 6.8, 12.0 Hz, 1H), 2.60 (s, 3H), 1.69 (dd, J = 1.6, 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 197.6, 157.7, 141.4,

138.6, 129.8, 122.5, 121.2, 115.1, 109.5, 26.7, 12.3. HRMS (EI): *m*/*z* calcd. for $C_{11}H_{12}O_2$ (M^+): 176.08373, found: 176.08374.

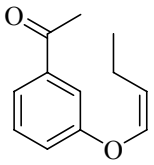


Benzyl-[1-{3-[((*E*)-propenyl)oxy]phenyl}ethylidene]amine (17). This compound was prepared according to the representative procedure for imine formation from 1-{3-[((*E*)-propenyl)oxy]phenyl}ethanone (667 mg, 3.78 mmol). The title compound (706 mg, 70% yield) was isolated by Kügelrohr distillation (160-177 °C, 0.05 mm Hg) as a colorless cloudy oil containing a mixture of imine *E*/*Z* isomers (18/1 by ^{1}H NMR). Imine **17** prepared and purified in this way was not characterized fully due to hydrolytic lability and was used as obtained in the subsequent reaction. ^{1}H NMR (400 MHz, $CDCl_3$) reported for *E* isomer: δ 7.54-7.49 (m, 2H), 7.44- 7.41 (m, 2H), 7.38-7.23 (m, 4H), 7.03-6.99 (m, 1H), 6.46 (dq, *J* = 1.6, 12.0 Hz, 1H), 5.38 (dq, *J* = 6.8, 12.0 Hz, 1H), 4.74 (s, 2H), 2.32 (s, 3H), 1.67 (dd, *J* = 1.6, 6.8 Hz, 3H).



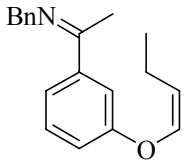
(*Z*)-1-Bromobut-1-ene (39). This compound was prepared in a manner similar to that previously reported for (*Z*)-1-bromo-1-alkenes.[6] To a solution of (*E*)-2-pentenoic acid (2.13 g, 21.3 mmol) in $CHCl_3$ (10 mL) was added bromine (7.67 g, 48.0 mmol) at room temperature. An exothermic reaction occurred. After stirring at room temperature for 17 h, the mixture was concentrated to give *anti*-2,3-dibromopentanoic acid as a reddish oil (5.66 g), which was taken on directly to the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.45 (d, *J* = 11.2 Hz, 1H), 4.40-4.33 (m, 1H),

2.37-2.26 (1H, m), 1.97-1.85 (1H, m), 1.12 (t, J = 7.2 Hz, 3H). A mixture of *anti*-2,3-dibromopentanoic acid (3.02 g, 11.6 mmol) and triethylamine (1.70 mL, 12.2 mmol) in DMF (15 mL) was exposed to microwave irradiation (200W) for 1 min. After cooling to room temperature, the mixture was filtered through a Celite pad and the filtrate was subjected to atmospheric pressure distillation. The fraction collected at 60-90 °C was washed with saturated aqueous NH_4Cl to give the title compound (899 mg, 57% yield, 2 steps) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.13-6.06 (m, 2H), 2.25-2.17 (m, 2H), 1.03 (t, J = 7.6 Hz, 3H). ^{1}H NMR data agree with those previously reported.[7]

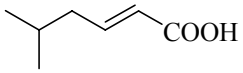


1-{3-[((*Z*)-But-1-enyl)oxy]phenyl}ethanone (40). A mixture of Cs_2CO_3 (2.89 g, 8.87 mmol), CuCl (151 mg, 1.53 mmol), and acetylacetone (302 μL, 2.94 mmol) in tetrahydrofuran (10 mL) was stirred at room temperature. After 5 min, 3'-hydroxyacetophenone (799 mg, 5.87 mmol) and (*Z*)-1-bromobut-1-ene (701 mg, 5.19 mmol) were added, the reaction vessel was sealed, and the mixture was heated to 75 °C for 23 h. After cooling to room temperature, the reaction mixture was diluted with diethyl ether and insoluble material was removed by filtration. The filtrate was concentrated and the residue was purified by silica gel column chromatography (silica gel: 200 mL, eluent: 1-10% gradient of ethyl acetate in hexanes) to give the title compound as a yellow oil (545 mg, 55% yield). IR (ZnSe, thin film) ν_{max} (cm^{-1}): 1686, 1584, 1439, 1267, 1206, 1035. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.0 Hz, 1H), 7.58-7.56 (m, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.22-7.19 (m, 1H), 6.36 (dt, J = 1.4, 6.2 Hz, 1H), 4.92 (dt, J = 6.2, 7.2 Hz, 1H), 2.61 (s, 3H), 2.27-2.18 (m, 2H), 1.03 (t, J = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (100

MHz, $CDCl_3$): δ 197.6, 157.8, 139.0, 138.6, 129.8, 122.4, 121.1, 116.1, 115.2, 26.8, 17.5, 14.2. HRMS (EI): *m*/*z* calcd. for $C_{12}H_{14}O_2$ (M^+): 190.0994, found: 190.0996.

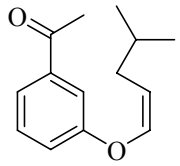


Benzyl-[1-{3-[((*Z*)-but-1-enyl)oxy]phenyl}ethylidene]amine (20). This compound was prepared according to the representative procedure for imine formation from 1-{3-[((*Z*)-but-1-enyl)oxy]phenyl}ethanone (335 mg, 1.76 mmol). The title compound (350 mg, 71% yield) was isolated by Kügelrohr distillation (121-123 °C, 0.05 mm Hg) as a colorless oil containing a mixture of imine *E*/*Z* isomers (11/1 by ^{1}H NMR). Imine **20** prepared and purified in this way was not characterized fully due to hydrolytic lability and was used as obtained in the subsequent reaction. ^{1}H NMR (400 MHz, $CDCl_3$) reported for *E* isomer: δ 7.53-7.51 (m, 2H), 7.44-7.38 (m, 2H), 7.38-7.23 (m, 4H), 7.05-7.01 (m, 1H), 6.37 (dt, *J* = 1.6, 6.0 Hz, 1H), 4.85 (dt, *J* = 6.0, 7.6 Hz, 1H), 4.74 (s, 2H), 2.33 (s, 3H), 2.27-2.18 (m, 2H), 1.03 (t, *J* = 7.6 Hz, 3H).



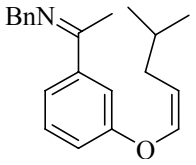
(*E*)-5-Methylhex-2-enoic acid (41). A mixture of methyl 5-methylhexanoate (7.02 g, 49.4 mmol), a solution of NaOH (3.34 g, 83.5 mmol) in H_2O (20 mL), and methanol (50 mL) was stirred at room temperature for 1.5 h. After concentration, the mixture was diluted with H_2O, neutralized with 1N aqueous HCl to adjust the pH to 4-5, and then extracted with $CHCl_3$ three times. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated to provide the title compound (3.60 g, 57% yield) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (dt, *J* = 7.6, 15.6 Hz, 1H), 5.82 (dt,

J = 1.4, 15.6, 1H), 2.15-2.10 (m, 2H), 1.85-1.71 (m, 1H), 0.94 (d, J = 6.4 Hz, 6H). ^{1}H NMR data agree with those previously reported.[8]



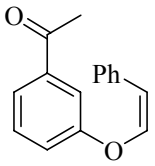
1-[3-((*Z*)-4-Methylpent-1-enyloxy)phenyl]ethanone (42). This compound was prepared in a manner similar to that described above for 1-{3-[((*Z*)-but-1-enyl)oxy]phenyl}ethanone. To a solution of (*E*)-5-methylhex-2-enoic acid (2.31 g, 18.0 mmol) in $CHCl_3$ (15 mL) was added bromine (6.48 g, 40.5 mmol) at room temperature. An exothermic reaction occurred. After stirring at room temperature for 12 h, the mixture was concentrated to give *anti*-2,3-dibromo-5-methylhexanoic acid (4.51 g) as a light yellow solid, which was directly used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.42 (d, J = 10.8 Hz, 1H), 4.36-4.28 (m, 1H), 2.08-1.93 (m, 2H), 1.76-1.64 (m, 1H), 1.12 (d, J = 6.4 Hz, 3H), 0.93 (d, J = 6.0 Hz, 3H). A mixture of *anti*-2,3-dibromo-5-methylhexanoic acid (3.42 g, 11.9 mmol) and triethylamine (1.73 mL, 12.4 mmol) in DMF (10 mL) was exposed to microwave irradiation (200W) for 1 min. After cooling to room temperature, the mixture was diluted with H_2O and the organic layer was washed with saturated aqueous NH_4Cl, H_2O (x2), and brine to give the (*Z*)-1-bromo-4-methylpent-1-ene (982 mg) as a brown oil, which was used directly in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.19 (dt, J = 1.6, 7.2 Hz, 1H), 6.11 (dt, J = 6.8, 7.2 Hz, 1H), 2.12-2.07 (m, 2H), 1.80-1.68 (m, 1H), 0.94 (d, J = 6.8 Hz, 6H). A mixture of Cs_2CO_3 (2.74 g, 8.41 mmol), CuCl (145 mg, 1.46 mmol), and acetylacetone (282 μL, 2.75 mmol) in tetrahydrofuran (10 mL) was stirred at room temperature. After 5 min, 3'-hydroxyacetophenone (752 mg, 5.52 mmol) and (*Z*)-1-

bromo-4-methylpent-1-ene (903 mL, 5.54 mmol) were added, the reaction vessel was sealed, and the mixture was heated to 75 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with diethyl ether and insoluble material was removed by filtration. The filtrate was concentrated and the residue was purified by silica gel column chromatography (silica gel: 200 mL, eluent: 1-5% gradient of ethyl acetate in hexanes) to give the title compound as a yellow oil (387 mg, 14% yield, 3 steps). IR (ZnSe, thin film) ν_{max} (cm^{-1}): 1687, 1584, 1440, 1267, 1206, 1054. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.59 (m, 1H), 7.59-7.56 (m, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.22-7.18 (m, 1H), 6.43 (dt, J = 1.4, 6.2 Hz, 1H), 4.93 (dt, J = 6.2, 6.8 Hz, 1H), 2.61 (s, 3H), 2.13-2.07 (m, 2H), 1.73-1.62 (m, 1H), 0.93 (d, J = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 197.7, 157.8, 140.0, 138.6, 129.8, 122.4, 121.1, 115.3, 113.1, 33.0, 28.4, 26.8, 22.3. HRMS (EI): m/z calcd. for $C_{14}H_{18}O_2$ (M^+): 218.1307, found: 218.1306.

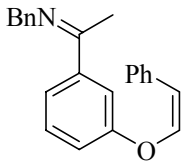


Benzyl-[1-[3-((*Z*)-4-methylpent-1-enyloxy)phenyl]ethylidene]amine (22). This compound was prepared according to the representative procedure for imine formation from 1-[3-((*Z*)-4-methylpent-1-enyloxy)phenyl]ethanone (302 mg, 1.38 mmol). The title compound (269 mg, 63% yield) was isolated by Kügelrohr distillation (135-140 °C, 0.05 mm Hg) as a colorless oil containing a mixture of imine *E*/*Z* isomers (17/1 by ^{1}H NMR). Imine **22** prepared and purified in this way was not characterized fully due to hydrolytic lability and was used as obtained in the subsequent reaction. ^{1}H NMR (400 MHz, $CDCl_3$) reported for *E* isomer: δ 7.53-7.50 (m, 2H), 7.42 (d, J = 7.6 Hz, 2H), 7.38-7.23 (m, 4H),

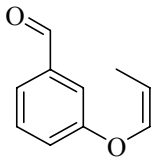
7.04-7.01 (m, 1H), 6.43 (dt, *J* = 1.4, 6.0 Hz, 1H), 4.86 (dt, *J* = 6.0, 7.6 Hz, 1H), 4.74 (s, 2H), 2.33 (s, 3H), 2.13-2.07 (m, 2H), 1.73-1.62 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 6H).



1-[3-((*Z*)-Styryloxy)phenyl]ethanone (43). A mixture of Cs_2CO_3 (3.76 g, 11.5 mmol), CuCl (196 mg, 1.98 mmol), and acetylacetone (392 μL, 3.82 mmol) in tetrahydrofuran (15 mL) was stirred at room temperature. After 5 min, 3'-hydroxyacetophenone (1.03 g, 7.57 mmol) and ((*Z*)-2-bromovinyl)benzene[6] (1.40 g, 7.65 mmol) were added, the reaction vessel was sealed, and the mixture was subjected to microwave irradiation at 110 °C for 4 h. After cooling it to room temperature, the reaction mixture was diluted with diethyl ether and H_2O, and insoluble material was removed by filtration. The organic layer of the filtrate was washed with saturated aqueous NH_4Cl, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (silica gel: 200 mL, eluent: 1-7% gradient of ethyl acetate in hexanes) to give the title compound as a brown oil (214 mg, 12% yield). IR (ZnSe, thin film) ν_{max} (cm^{-1}): 1685, 1585, 1439, 1265, 1208, 1051. ^1H NMR (400 MHz, $CDCl_3$): δ 7.72-7.66 (m, 4H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.37-7.32 (m, 3H), 7.23 (t, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 6.8 Hz, 1H), 5.70 (d, *J* = 6.8 Hz, 1H), 2.63 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 197.4, 157.4, 140.9, 138.7, 134.5, 130.0, 128.8, 128.4, 126.9, 123.4, 121.6, 116.0, 111.5, 26.8. HRMS (EI): *m*/*z* calcd. for $C_{16}H_{14}O_2$ (M^+): 238.0994, found: 238.0999.

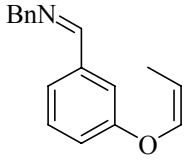


Benzyl-[1-[3-((*Z*)-styryloxy)phenyl]ethylidene]amine (24). This compound was prepared according to the representative procedure for imine formation from 1-[3-((*Z*)-styryloxy)phenyl]ethanone (281 mg, 1.18 mmol). The title compound (224 mg, 58% yield) was isolated by Kügelrohr distillation (158-168 °C, 0.05 mm Hg) as a light yellow oil containing a mixture of imine *E*/*Z* isomers (14/1 by ^{1}H NMR). Imine **24** prepared and purified in this way was not characterized fully due to hydrolytic lability and was used as obtained in the subsequent reaction. ^{1}H NMR (400 MHz, $CDCl_3$) reported for *E* isomer: δ 7.71-7.66 (m, 3H), 7.59 (d, J = 8.0 Hz, 1H), 7.44-7.15 (m, 10H), 6.66 (d, J = 6.8 Hz, 1H), 5.64 (d, J = 6.8 Hz, 1H), 4.76 (s, 2H), 2.35 (s, 3H).

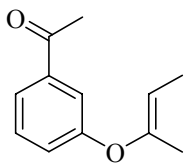


3-[((*Z*)-Propenyl)oxy]benzaldehyde (44). A mixture of Cs_2CO_3 (8.07 g, 24.8 mmol), CuCl (413 mg, 4.17 mmol), and acetylacetone (0.86 g, 8.59 mmol) in tetrahydrofuran (50 mL) was stirred at room temperature. After 15 min, 3-[1,3]dioxolan-2-ylphenol (2.79 g, 16.8 mmol) and *cis*-1-bromo-1-propene (3.62 mL, 42.6 mmol) were added, and the mixture was stirred under reflux for 19 h. After cooling to room temperature, the mixture was filtered through a Celite pad and the filtrate was concentrated. The residue was dissolved in tetrahydrofuran (50 mL), 1N aqueous HCl (20 mL) was added, and the mixture was stirred at room temperature for 30 min. After evaporating the tetrahydrofuran, the mixture was extracted with diethyl ether. The

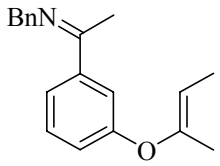
organic layer was washed with H_2O, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (silica gel: 50 mL, eluted with 20:1 hexanes/ethyl acetate), to give the title compound as a yellow oil (1.98 g, 73% yield). IR (ZnSe, thin film) ν_{max} (cm^{-1}): 1697, 1589, 1482, 1256, 1144, 1029. ^1H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.56 (dt, J = 1.2, 7.6 Hz, 1H), 7.52-7.46 (m, 2H), 7.30-7.25 (m, 1H), 6.42 (dq, J = 1.6, 6.0 Hz, 1H), 5.00 (dq, J = 6.0, 6.8 Hz, 1H), 1.73 (dd, J = 1.6, 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 191.7, 158.0, 140.0, 137.9, 130.2, 124.4, 122.6, 115.2, 109.1, 9.4. HRMS (EI): m/z calcd. for $C_{10}H_{10}O_2$ (M^+): 162.0681, found: 162.0684.



Benzyl-[1-{3-[((*Z*)-propenyl)oxy]phenyl}methylidene]amine (26). This compound was prepared according to the representative procedure for imine formation from 3-[((*Z*)-propenyl)oxy]benzaldehyde (545 mg, 3.36 mmol). The title compound (540 mg, 64% yield) was isolated by Kügelrohr distillation (108-110 °C, 0.05 mm Hg) as a colorless oil. Imine **26** prepared and purified in this way was not characterized fully due to hydrolytic lability and was used as obtained in the subsequent reaction. ^1H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.48- 7.45 (1H, m), 7.41-7.22 (m, 7H), 7.08-7.03 (m, 1H), 6.42 (dq, J = 1.6, 6.0 Hz, 1H), 4.91 (dq, J = 6.0, 6.8 Hz, 1H), 4.83 (s, 2H), 1.71 (dd, J = 1.6, 6.8 Hz, 3H).

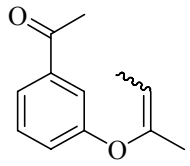


1-[3-((*E*)-1-Methyl-propenyloxy)-phenyl]ethanone (45). A mixture of Cs_2CO_3 (8.05 g, 24.7 mmol), CuCl (414 mg, 4.18 mmol), and acetylacetone (0.83 g, 8.3 mmol) in tetrahydrofuran (50 mL) was stirred at room temperature. After 10 min, 3'-hydroxyacetophenone (2.24 g, 16.5 mmol) and (*E*)-2-bromo-2-butene (2.14 mL, 21.1 mmol) were added, and the mixture was heated to reflux. After 32 h, the reaction mixture was filtered through a Celite pad and the filtrate was concentrated. The residue was purified by silica gel column chromatography (silica gel: 100 mL, eluted first with hexanes and then 20:1 hexanes/ethyl acetate) to give the title compound as a colorless oil (2.13 g, 68% yield). IR (ZnSe, thin film) ν_{max} (cm^{-1}): 1686, 1582, 1437, 1266, 1200, 1176. ^1H NMR (400 MHz, $CDCl_3$): δ 7.62-7.59 (m, 1H), 7.52-7.50 (m, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.17-7.14 (m, 1H), 5.02 (q, J = 7.2 Hz, 1H), 2.59 (s, 3H), 1.87 (s, 3H), 1.65 (d, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 197.3, 156.8, 149.4, 138.4, 129.4, 122.6, 122.1, 116.9, 107.3, 26.4, 14.0, 11.6. HRMS (EI): *m*/*z* calcd. for $C_{12}H_{14}O_2$ (M^+): 190.09938, found: 190.09944.

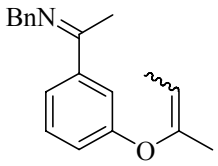


Benzyl-[1-[3-((*E*)-1-methylpropenyloxy)phenyl]ethylidene]amine (28). This compound was prepared according to the representative procedure for imine formation from 1-[3-((*E*)-1-methylpropenyloxy)phenyl]ethanone (714 mg, 3.75 mmol). The title compound (677 mg, 65% yield) was isolated by Kügelrohr distillation (110-120 °C, 0.05 mm Hg) as a colorless oil containing a mixture of imine isomers (*E*/*Z* = 19/1 by ^1H NMR). Imine **28** prepared and purified in this way was not characterized fully due to hydrolytic lability and was used as obtained in the subsequent reaction. ^1H NMR (400

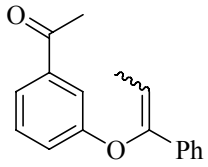
MHz, $CDCl_3$) reported for *E* isomer: δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.47-7.42 (m, 3H), 7.37-7.22 (m, 4H), 7.00-6.96 (m, 1H), 4.96 (q, *J* = 7.2 Hz, 1H), 4.74 (s, 2H), 2.31 (s, 3H), 1.87 (s, 3H), 1.63 (d, *J* = 7.2 Hz, 3H).



1-[3-(1-Methylpropenyloxy)phenyl]ethanone (46). A mixture of Cs_2CO_3 (8.06 g, 24.7 mmol), CuCl (413 mg, 4.17 mmol), and acetylacetone (0.85 g, 8.5 mmol) in tetrahydrofuran (50 mL) was stirred at room temperature. After 30 min, 3'-hydroxyacetophenone (2.24 g, 16.5 mmol) and (*Z*)-2-bromo-2-butene (2.14 mL, 21.1 mmol) were added, and the mixture was heated to reflux. After 13 h, (*Z*)-2-bromo-2-butene (2.14 mL, 21.1 mmol) was added and reflux was continued for an additional 3 days. After cooling to room temperature, the reaction mixture was filtered through a Celite pad and the filtrate was concentrated. The residue was purified by silica gel column chromatography (silica gel: 50 mL, eluent: 0-10% gradient of ethyl acetate in hexanes) to give the title compound as a colorless oil (631 mg, 20% yield) as a mixture of *Z*/*E* isomers (4/1 by ^{1}H NMR). IR (ZnSe, thin film) ν_{max} (cm^{-1}): 1686, 1582, 1437, 1264, 1202. ^{1}H NMR (400 MHz, $CDCl_3$) reported for *Z* isomer: δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.48 (s, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.15-7.10 (m, 1H), 5.12 (q, *J* = 6.8 Hz, 1H), 2.59 (s, 3H), 1.82 (s, 3H), 1.54 (d, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) reported for *Z* isomer: 197.8, 156.7, 147.3, 138.7, 129.7, 121.7, 120.8, 115.0, 111.5, 26.8, 18.4, 10.6. HRMS (EI): *m*/*z* calcd. for $C_{12}H_{14}O_2$ (M^+): 190.0994, found: 190.0991.

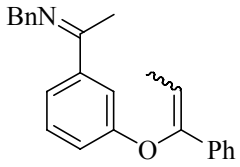


Benzyl-[1-[3-(1-methylpropenyloxy)phenyl]ethylidene]amine (29). This compound was prepared according to the representative procedure for imine formation from 1-[3-(1-methylpropenyloxy)phenyl]ethanone (*Z*/*E* = 4/1) (591 mg, 3.10 mmol). The title compound (620 mg, 72% yield) was isolated by Kügelrohr distillation (110-118 °C, 0.05 mm Hg) as a colorless oil containing a mixture of isomers (*E*/*Z* = 14/1 for imine, *Z*/*E* = 4/1 for olefin by ^{1}H NMR). Imine **29** prepared and purified in this way was not characterized fully due to hydrolytic lability and was used as obtained in the subsequent reaction. ^{1}H NMR (400 MHz, $CDCl_3$) reported for *E*-imine, *Z*-olefin isomer: δ 7.56-7.19 (m, 8H), 6.97-6.90 (m, 1H), 5.08 (q, *J* = 6.4 Hz, 1H), 4.74 (s, 2H), 2.32 (s, 3H), 1.82 (s, 3H), 1.56 (d, *J* = 6.4 Hz, 3H).

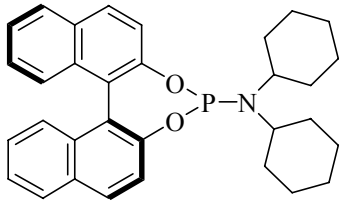


1-[3-(1-Phenylpropenyloxy)phenyl]ethanone (47). A mixture of Cs_2CO_3 (2.95 g, 9.05 mmol), CuCl (157 mg, 1.59 mmol), and acetylacetone (302 μL, 2.94 mmol) in tetrahydrofuran (10 mL) was stirred at room temperature. After 5 min, 3'-hydroxyacetophenone (707 mg, 5.19 mmol) and ((*Z*)-1-bromopropenyl)benzene[9] (1.02 g, 5.20 mmol) were added, the reaction vessel was sealed, and the mixture was heated to 75 °C for 66 h. After cooling to room temperature, the reaction mixture was diluted with diethyl ether and insoluble material was removed by filtration. The filtrate was concentrated and the residue was purified by silica gel column chromatography (silica

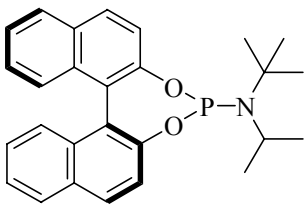
gel: 200 mL, eluent: 1-7% gradient of ethyl acetate in hexanes), to give the title compound as a light yellow oil (411 mg, 31% yield) as a mixture of *Z*/*E* isomers (8/1 by ^{1}H NMR). IR (ZnSe, thin film) ν_{max} (cm^{-1}): 1685, 1582, 1438, 1261, 1200, 1019. ^{1}H NMR (400 MHz, $CDCl_3$) reported for *Z* isomer: δ 7.56-7.44 (4H, m), 7.36-7.19 (m, 4H,), 7.18-7.13 (m, 1H), 5.97 (q, *J* = 6.8 Hz, 1H), 2.55 (s, 3H), 1.76 (d, *J* = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) reported for *Z* isomer: 197.7, 157.5, 149.4, 138.7, 135.0, 129.8, 128.5, 128.0, 125.1, 121.6, 120.1, 114.9, 112.8, 26.7, 11.4. HRMS (EI): *m*/*z* calcd. for $C_{17}H_{16}O_2$ (M^+): 252.1150, found: 252.1149.



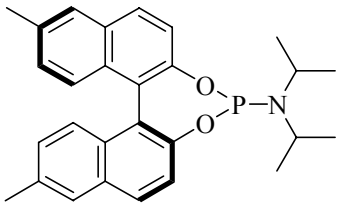
Benzyl-[1-[3-(1-phenylpropenyloxy)phenyl]ethylidene]amine (31). This compound was prepared according to the representative procedure for imine formation from 1-[3-(1-phenylpropenyloxy)phenyl]ethanone (320 mg, 1.27 mmol). The title compound (307 mg, 71% yield) was isolated by Kügelrohr distillation (163-167 °C, 0.05 mm Hg) as a light yellow oil containing a mixture of isomers (*E*/*Z* = 15/1 for imine, *Z*/*E* = 9/1 for olefin by ^{1}H NMR). Imine **31** prepared and purified in this way was not characterized fully due to hydrolytic lability and was used as obtained in the subsequent reaction. ^{1}H NMR (400 MHz, $CDCl_3$) reported for *E*-imine, *Z*-olefin isomer: δ 7.54 (t, *J* = 2.0 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 3H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.32-7.19 (m, 5H), 6.93 (dd, *J* = 2.0, 8.0 Hz, 1H), 5.94 (q, *J* = 6.8 Hz, 1H), 4.71 (s, 2H), 2.28 (s, 3H), 1.76 (d, *J* = 6.8 Hz, 3H).



(*S*)-Dicyclohexyl-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*']dinaphthalen-4-yl)amine (L12).[10] To a solution of dicyclohexylamine (0.40 mL, 2.00 mmol) in tetrahydrofuran (10 mL) was added dropwise *n*-butyllithium (1.6 M in hexanes) (1.25 mL, 2.00 mmol) between -75 °C and -65 °C over 10 min, and the mixture was stirred for 10 min. Phosphorus trichloride (1.74 mL, 19.9 mmol) was added and the mixture was stirred at room temperature for 4 h. The reaction mixture was concentrated and the residue was suspended in toluene. Insoluble material was removed by filtration and the filtrate was concentrated. To the residue was added toluene (10 mL), (*S*)-(-)-1,1'-bi-2-naphthol (526 mg, 2.00 mmol), and triethylamine (1.4 mL, 10.0 mmol), and the mixture was stirred at room temperature. After 14 h, the mixture was diluted with diethyl ether, insoluble material was removed by filtration, and the filtrate was concentrated. The residue was purified by silica gel column chromatography (silica gel: 100 mL, eluted with 40:1 hexanes/ethyl acetate) to give the title compound as a white solid (258 mg, 26% yield). mp 211-214 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.8 Hz, 1H), 7.89 (t, J = 8.8 Hz, 3H), 7.49 (d, J = 8.8 Hz, 1H), 7.43-7.36 (m, 4H), 7.31-7.19 (m, 3H), 2.86-2.72 (m, 2H), 1.93-0.75 (m, 20H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 151.8. HRMS (ESI): m/z calcd. for $C_{32}H_{35}NO_2P$ (MH^+): 496.2405, found: 496.2393.

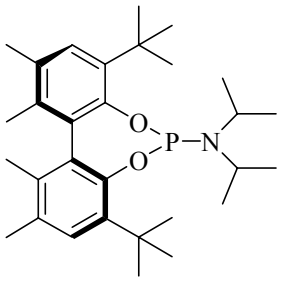


(*S*)-*tert*-Butyl-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*']dinaphthalen-4-yl)isopropylamine (L13). A mixture of (*S*)-(-)-1,1'-bi-2-naphthol (524 mg, 1.83 mmol) and phosphorus trichloride (2.0 mL, 22.9 mmol) was stirred under reflux for 22 h. After cooling to room temperature, the reaction mixture was concentrated and the residue was diluted with toluene and concentrated two times to give crude 4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*']dinaphthalene. A solution of *tert*-butyldiisopropylamine (0.86 mL, 5.43 mmol) in tetrahydrofuran (2.5 mL) was cooled in a dry ice/acetone bath, and *n*-butyllithium (1.6 M in hexanes) (2.50 mL, 4.00 mmol) was added dropwise. The mixture was stirred at room temperature for 30 min and added to a solution of 4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*']dinaphthalene in tetrahydrofuran (2.5 mL) cooled in a dry ice/acetone bath. After stirring it at room temperature for 16 h, the mixture was concentrated and the residue was purified by silica gel column chromatography (silica gel: 70 mL, eluted with 20:1 hexanes/ethyl acetate) to give the title compound as a white solid (183 mg, 23% yield). mp 168-170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.8 Hz, 1H), 7.91-7.86 (m, 3H), 7.49 (d, J = 8.8 Hz, 1H), 7.39-7.30 (m, 4H), 7.30-7.17 (m, 3H), 3.56-3.42 (m, 1H), 1.45 (s, 9H), 1.27 (d, J = 7.2 Hz, 3H), 0.90-0.72 (br, 3H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 159.0. HRMS (FAB): m/z calcd. for $C_{27}H_{29}NO_2P$ (MH^+): 430.1936, found: 430.1935.



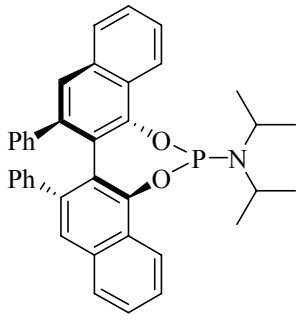
(*S*)-(9,14-Dimethyl-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*']dinaphthalen-4-yl)diisopropylamine (L14). A mixture of (*S*)-6,6'-dimethyl-1,1'-bi-2-naphthol (119

mg, 378 μmol), diisopropylphosphoramidous dichloride (156 mg, 772 μmol), and triethylamine (0.26 mL, 1.87 mmol) in tetrahydrofuran (2.5 mL) was stirred at room temperature for 44 h. Insoluble material was removed by filtration and the filtrate was concentrated. The residue was purified by silica gel column chromatography (silica gel: 30 mL, eluted with 20:1 hexanes/ethyl acetate) to give the title compound as a colorless foam (47.9 mg, 29% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.8 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.66 (s, 2H), 7.45 (d, J = 8.8 Hz, 1H), 7.39 (d, J = 8.8 Hz, 1H), 7.31 (d, J = 8.8 Hz, 1H), 7.20 (d, J = 8.8 Hz, 1H), 7.09 (d, J = 8.8 Hz, 1H), 7.06 (d, J = 8.8 Hz, 1H), 3.42-3.31 (m, 2H), 2.49 (s, 3H), 2.47 (s, 3H), 1.21 (d, J = 6.8 Hz, 6H), 1.16 (d, J = 6.8 Hz, 6H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 151.2. HRMS (FAB): m/z calcd. for $C_{28}H_{31}NO_2P$ (MH^+): 444.20924, found: 444.20917.



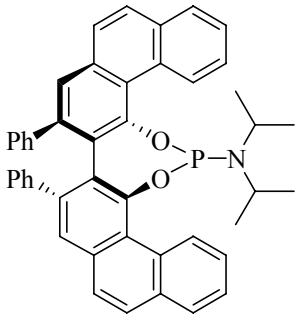
(*S*)-(4,8-Di-*tert*-butyl-1,2,10,11-tetramethyl-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl)diisopropylamine (L15).[11] A mixture of (*S*)-(-)-5,5',6,6'-tetramethyl-3,3'-di-*tert*-butyl-1,1'-biphenyl-2,2'-diol (200 mg, 565 μmol), diisopropylphosphoramidous dichloride (118 mg, 581 μmol), and triethylamine (0.24 mL, 1.72 mmol) in tetrahydrofuran (2 mL) was stirred at room temperature for 26 h. Insoluble material was removed by filtration and the residue was concentrated. The residue was purified by silica gel column chromatography (silica gel: 20 mL, eluted with 40:1 hexanes/ethyl acetate) to give the title compound mixed with the starting diol (145 mg).

This material was treated again with diisopropylphosphoramidous dichloride (242 mg, 1.20 mmol) and triethylamine (0.70 mL, 5.02 mmol) in tetrahydrofuran (2 mL) at room temperature for 22 h. After removal of insoluble material by filtration, the filtrate was concentrated and the residue was purified by silica gel column chromatography (silica gel: 50 mL, eluent: 0-3% gradient of ethyl acetate in hexanes) to give the title compound as a colorless foam (109 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (s, 1H), 7.06 (s, 1H), 3.35-2.97 (br, 2H), 2.25 (s, 3H), 2.22 (s, 3H), 1.87 (s, 3H), 1.69 (s, 3H), 1.55-0.59 (br, 12H), 1.48 (s, 9H), 1.41 (s, 9H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 146.4. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): δ 145.8 (lit. δ 147.5).[11] HRMS (FAB): *m*/*z* calcd. for $C_{30}H_{47}NO_2P$ (MH^+): 484.3344, found: 484.3358.

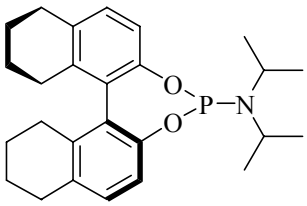


[(6*aS*)-6,7-Diphenyldinaphtho[1,2-*d*:2',1'-*f*][1,3,2]dioxaphosphepine-14-yl]diisopropylamine (L16). A mixture of (2*S*)-(-)-3,3'-diphenyl-(2,2'-binaphthalene)-1,1'-diol (116 mg, 264 μmol), diisopropylphosphoramidous dichloride (146 μL, 791 μmol), and triethylamine (0.37 mL, 2.65 mmol) in tetrahydrofuran (2 mL) was stirred at room temperature for 22 h. The mixture was diluted with ethyl acetate and filtered through a Celite pad. The filtrate was concentrated and the residue was purified by silica gel column chromatography (silica gel: 50 mL, eluent: 1-3% gradient of ethyl acetate in hexanes) to give the title compound as a white solid (109 mg, 73% yield). mp 210-211 °C.

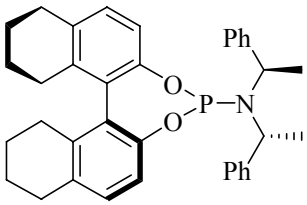
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, J = 7.6 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 7.85-7.72 (m, 2H), 7.63-7.47 (m, 4H), 7.39 (s, 1H), 7.35 (s, 1H), 7.11-7.02 (m, 2H), 6.96-6.83 (m, 4H), 6.55 (d, J = 7.2 Hz, 2H), 6.45 (d, J = 7.2 Hz, 2H), 3.47-3.32 (m, 2H), 1.45-1.16 (br, 6H), 1.16-0.53 (br, 6H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 155.1. HRMS (ESI): m/z calcd. for $C_{38}H_{35}NO_2P$ (MH^+): 568.2405, found: 568.2390.



[(8*aS*)-8,9-Diphenyldiphenanthro[4,3-*d*:3',4'-*f*][1,3,2]dioxaphosphepine-18-yl]diisopropylamine (L17). A mixture of (3*S*)-(+)-2,2'-diphenyl-(3,3'-biphenanthrene)-4,4'-diol (119 mg, 205 μmol), diisopropylphosphoramidous dichloride (89.3 mg, 441 μmol), and triethylamine (0.14 mL, 1.00 mmol) in tetrahydrofuran (2.5 mL) was stirred at room temperature for 24 h. The mixture was diluted with diethyl ether, insoluble material was removed by filtration, and the filtrate was concentrated. The residue was purified by silica gel column chromatography (silica gel: 30 mL, eluted with 20:1 hexanes/ethyl acetate) to give the title compound as a white solid (106 mg, 78% yield). mp 209-211 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97-9.91 (m, 1H), 9.87-9.81 (m, 1H), 7.99-7.89 (m, 2H), 7.82-7.60 (m, 8H), 7.49 (s, 1H), 7.43 (s, 1H), 7.11-7.02 (m, 2H), 6.97-6.86 (m, 4H), 6.59 (d, J = 7.2 Hz, 2H), 6.52 (d, J = 6.8 Hz, 2H), 3.29-3.16 (m, 2H), 1.85-0.75 (br, 12H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 146.1. HRMS (ESI): m/z calcd. for $C_{46}H_{39}NO_2P$ (MH^+): 668.2718 found: 668.2706.

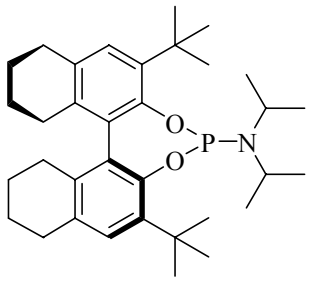


(*S*)-Diisopropyl-(8,9,10,11,12,13,14,15-octahydro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*']dinaphthalen-4-yl)amine (L18).[12] A mixture of (*S*)-(-)-5,5',6,6',7,7',8,8'-octahydro-1,1'-bi-2-naphthol (351 mg, 1.19 mmol), diisopropylphosphoramidous dichloride (657 μL, 3.56 mmol), and triethylamine (1.65 mL, 11.8 mmol) in tetrahydrofuran (5 mL) was stirred at room temperature for 20 h. The mixture was filtered through a Celite pad, the filtrate was concentrated, and the residue was purified by silica gel column chromatography (silica gel: 50 mL, eluent: 1-3% gradient of ethyl acetate in hexanes), to give the title compound as a white solid (252 mg, 50% yield). mp 135-137 °C (lit. 123-125 °C)[11] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, J = 8.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 1H), 3.35-3.20 (m, 2H), 2.88-2.54 (m, 6H), 2.35-2.15 (m, 2H), 1.82-1.75 (m, 6H), 1.75-1.45 (m, 2H), 1.16 (d, J = 6.8 Hz, 6H), 1.15 (d, J = 6.8 Hz, 6H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 146.1. ^{31}P{^{1}H} NMR (162 MHz, toluene-d_8): δ 145.5 (lit. δ 149.4).[12] HRMS (FAB): m/z calcd. for $C_{26}H_{35}NO_2P$ (MH^+): 424.2405, found: 424.2413.

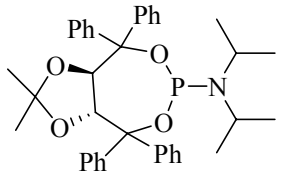


(*S*)-(8,9,10,11,12,13,14,15-Octahydro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*']dinaphthalen-4-yl)-bis((*R*)-1-phenylethyl)amine (L19).[13] A mixture of (*S*)-(-)-5,5',6,6',7,7',8,8'-octahydro-1,1'-bi-2-naphthol (517 mg, 1.76 mmol) and phosphorus

trichloride (2.0 mL, 22.9 mmol) was stirred under reflux for 15 h. After cooling to room temperature, the reaction mixture was concentrated and the residue was diluted with toluene and concentrated two times to give crude 4-chloro-8,9,10,11,12,13,14,15-octahydro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*']dinaphthalene. A solution of [*R*-(*R**,*R*)]-(+)-bis(*α*-methylbenzyl)amine (397 mg, 1.76 mmol) in tetrahydrofuran (5 mL) was cooled in a dry ice/acetone bath and *n*-butyllithium (1.6 M in hexanes) (1.1 mL, 1.76 mmol) was added dropwise. The mixture was stirred at room temperature for 30 min and added to a solution of 4-chloro-8,9,10,11,12,13,14,15-octahydro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*']dinaphthalene in tetrahydrofuran (5 mL) cooled in a dry ice/acetone bath using additional 3 mL of tetrahydrofuran. After stirring it at room temperature for 18 h, the mixture was concentrated and the residue was purified by silica gel column chromatography (silica gel: 50 mL, eluent: 0-3% gradient of ethyl acetate in hexanes, and then silica gel: 50 mL, eluent: 1% ethyl acetate in hexanes) to give the title compound as a colorless foam (308 mg, 32% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.00 (m, 13H), 6.93 (d, J = 8.0 Hz, 1H), 4.47-4.35 (m, 2H), 2.87-2.57 (m, 6H), 2.34-2.17 (m, 2H), 1.81-1.70 (m, 6H), 1.66 (d, J = 7.2 Hz, 6H), 1.60-1.46 (m, 2H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 139.8. HRMS (ESI): *m*/*z* calcd. for $C_{36}H_{39}NO_2P$ (MH^+): 548.2718, found: 548.2703.

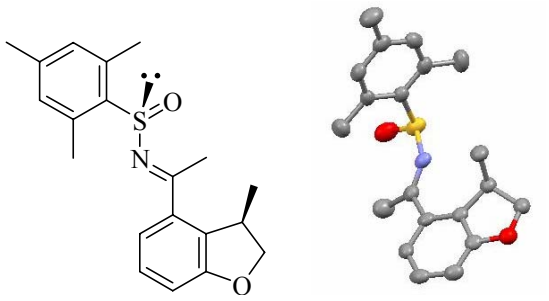


(*S*)-(2,6-Di-*tert*-butyl-8,9,10,11,12,13,14,15-octahydro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*']dinaphthalen-4-yl)diisopropylamine (L20). (*S*)-(+)-5,5',6,6',7,7',8,8'-octahydro-3,3'-di-*tert*-butyl-1,1'-bi-2-naphthol, dipotassium salt (225 mg, 466 μmol) was partitioned between chloroform and saturated aqueous NH_4Cl. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was mixed with tetrahydrofuran (5.0 mL), diisopropylphosphoramidous dichloride (288 mg, 1.42 mmol), and triethylamine (0.50 mL, 3.59 mmol), and the resulting mixture was then stirred at room temperature for 18 h. The reaction mixture was filtered through a Celite pad, the filtrate was concentrated, and the residue was purified by silica gel column chromatography (silica gel: 30 g, eluted with 40:1 hexanes/ethyl acetate) to give the title compound as a light brown foam (35.9 mg, 19% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.19 (s, 1H), 7.16 (s, 1H), 3.40-2.97 (br, 2H), 2.79-2.52 (m, 5H), 2.49-2.32 (m, 2H), 2.13-2.03 (m, 1H), 1.70-0.58 (m, 20H), 1.65 (s, 9H), 1.60 (s, 9H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 148.0. HRMS (ESI): *m*/*z* calcd. for $C_{34}H_{52}NO_2P$ (MH^+): 536.3657, found: 536.3648.



((3*aR*,8*aR*)-2,2-Dimethyl-4,4,8,8-tetraphenyltetrahydro[1,3]dioxolo[4,5-*e*][1,3,2]dioxaphosphepin-6-yl)diisopropylamine (L21).[14] A mixture of (-)-TADDOL (504 mg, 1.08 mmol), diisopropylphosphoramidous dichloride (219 mg, 1.08 mmol), and triethylamine (0.45 mL, 3.23 mmol) in tetrahydrofuran (2.5 mL) was stirred at room temperature for 46 h. The mixture was filtered through a Celite pad, the filtrate was concentrated, and the residue was purified by silica gel column chromatography (silica

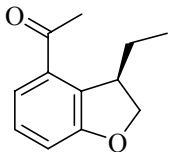
gel: 20 mL, eluted with 40:1 hexanes/ethyl acetate) to give the title compound as a colorless foam (208 mg, 32% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 7.2 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 7.46 (d, J = 7.2 Hz, 2H), 7.43 (d, J = 7.2 Hz, 2H), 7.31-7.12 (m, 12H), 5.21-5.16 (m, 1H), 4.59 (d, J = 8.8 Hz, 1H), 3.98 (sept, J = 6.8 Hz, 2H), 1.43 (s, 3H), 1.24 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 6.8 Hz, 6H), 0.21 (s, 3H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 140.2. HRMS (ESI): m/z calcd. for $C_{37}H_{43}NO_4P$ (MH^+): 596.2930, found: 596.2936.



(S_S, *R*)-2,4,6-Trimethylbenzenesulfinic acid [1-(3-methyl-2,3-dihydrobenzofuran-4-yl)eth-(*E*)-ylidene]amide ((S_S, *R*)-33). To a solution of (*R*)-1-(3-methyl-2,3-dihydrobenzofuran-4-yl)ethanone (90% ee) (30.0 mg, 170 μmol) and (*S*)-(+)-2,4,6-trimethylbenzenesulfinamide[15] (36.7 mg, 200 μmol) in tetrahydrofuran (0.36 mL) was added $Ti(OEt)_4$ (85% solution in isopropanol) (83 μL, 342 μmol), and the mixture was heated to 75 °C. After 16.5 h, an additional amount of $Ti(OEt)_4$ (85% solution in isopropanol) (83 μL, 342 μmol) was added and heating was continued for an additional 23 h. The reaction mixture was diluted with saturated aqueous NaCl and ethyl acetate and insoluble material was removed by filtration. The organic layer of the filtrate was dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography (silica gel: 400 mL, eluted first with 20:1 and then 7:1

hexanes/ethyl acetate) to give the title compound as a light yellow solid (18.1 mg, 31% yield). mp 89-91 °C. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 1604, 1572, 1433, 1274, 1223, 1079. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (t, J = 8.0 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.90-6.80 (m, 3H), 4.52 (t, J = 8.4 Hz, 1H), 4.20 (dd, J = 3.2, 8.4 Hz, 1H), 4.01-3.91 (m, 1H), 2.69 (s, 3H), 2.65 (s, 6H), 2.28 (s, 3H), 1.08 (d, J = 6.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 173.1, 160.3, 141.5, 138.3, 137.9, 135.7, 132.3, 130.6, 128.2, 120.3, 112.5, 78.7, 36.8, 21.5, 21.1, 20.1, 19.4. HRMS (FAB): m/z calcd. for $C_{20}H_{24}NO_2S$ (MH^+): 342.1528, found: 342.1534.

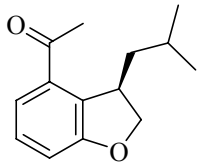
Recrystallization from petroleum ether yielded X-ray quality crystals of **(S_S, *R*)-33**. The crystal structure established the absolute configuration of **(*R*)-48**. The absolute configurations of **(*R*)-49** – **52** were assigned by analogy to this result.



(*R*)-1-(3-Ethyl-2,3-dihydrobenzofuran-4-yl)ethanone ((*R*)-49). In a glovebox, to a medium-walled NMR tube was added a mixture of $[RhCl(coe)_2]_2$ (3.6 mg, 0.0050 mmol) and (*S*)-diisopropyl-(8,9,10,11,12,13,14,15-octahydro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*']dinaphthalen-4-yl)amine (4.3 mg, 0.010 mmol) in 1,4-dioxane (0.40 mL) and a solution of benzyl-[1-{3-[((*Z*)-but-1-enyl)oxy]phenyl}ethylidene]amine (14.1 mg, 0.0505 mmol) in 1,4-dioxane (0.10 mL). The tube was fitted with a Cajon adapter, the mixture was frozen, and then the tube was flame sealed under vacuum. The NMR tube was then placed in oil bath heated to 50 °C for 96 h. After the reaction, the sealed tube was opened and the mixture was concentrated. To the residue were added 1,4-dioxane (0.50 mL) and concentrated HCl/H_2O (1/1) (0.50

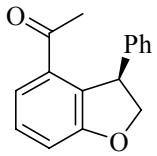
mL). The mixture was stirred at room temperature for 3 h and then was extracted with diethyl ether four times. The combined organic layers were concentrated and the residue was purified by silica gel column chromatography (silica gel: 15 mL, eluted with 20:1 hexanes/ethyl acetate) to give the title compound as a light yellow oil

(5.1 mg, 53% yield). IR (ZnSe, thin film) ν_{max} (cm^{-1}): 1685, 1585, 1446, 1258. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 8.0 Hz, 1H), 7.23 (t, J = 8.0 H, 1H), 6.98 (d, J = 8.0 Hz, 1H), 4.52–4.43 (m, 2H), 3.90–3.83 (m, 1H), 2.60 (s, 3H), 1.71–1.60 (m, 1H), 1.52–1.40 (m, 1H), 0.91 (t, J = 7.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 199.2, 160.9, 134.1, 132.2, 128.3, 122.2, 114.0, 76.3, 43.6, 28.2, 26.8, 11.4. HRMS (EI): *m*/*z* calcd. for $C_{12}H_{14}O_2$ (M^+): 190.09938, found: 190.09943. Chiral HPLC (Chiralcel AS column, 0.5% *i*PrOH/hexanes, 1mL/min): major, 18.0 min; minor, 12.7 min; 92% ee. CD (c = 4 x 10^{-5} M, MeOH): λmax (Δε): 252 (+3.90).



(*R*)-1-(3-Isobutyl-2,3-dihydrobenzofuran-4-yl)ethanone ((*R*)-50). In a glovebox, to a medium-walled NMR tube was added a mixture of $[RhCl(coe)_2]_2$ (3.6 mg, 0.0050 mmol) and (*S*)-diisopropyl-(8,9,10,11,12,13,14,15-octahydro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*']dinaphthalen-4-yl)amine (4.2 mg, 0.0099 mmol) in 1,4-dioxane (0.40 mL) and a solution of benzyl-[1-[3-((*Z*)-4-methylpent-1-enyloxy)phenyl]ethylidene]amine (15.1 mg, 0.0491 mmol) in 1,4-dioxane (0.10 mL). The tube was fitted with a Cajon adapter, the mixture was frozen, and then the tube was flame sealed under vacuum. The NMR tube was then placed in oil bath heated to 75 °C for 67 h. After the reaction, the sealed tube was opened and the mixture was concentrated. To the

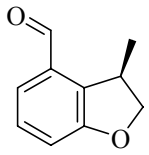
residue were added 1,4-dioxane (0.50 mL) and concentrated HCl/H_2O (1/1) (0.50 mL). The mixture was stirred at room temperature for 3 h and then was extracted with diethyl ether four times. The combined organic layer was concentrated and the residue was purified by silica gel column chromatography (silica gel: 15 mL, eluted with 20:1 hexanes/ethyl acetate). The purified product was contaminated with the vinyl ether ketone **42** and therefore was resubmitted to the reaction in 1,4-dioxane (0.50 mL) and concentrated HCl/H_2O (1/1) (0.50 mL) at room temperature for an additional 24 h. The mixture was extracted with diethyl ether four times. The combined organic layer was concentrated and the residue was purified by silica gel column chromatography (silica gel: 15 mL, eluting with 20:1 hexanes/ethyl acetate) to give the title compound as a colorless oil (5.1 mg, 48% yield). IR (ZnSe, thin film) ν_{max} (cm^{-1}): 1683, 1584, 1444, 1261. ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 4.48–4.44 (m, 2H), 4.00–3.93 (m, 1H), 2.60 (s, 3H), 1.75–1.65 (m, 1H), 1.44–1.30 (m, 2H), 1.05 (d, J = 6.8 Hz, 3H), 0.91 (d, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 198.9, 160.6, 133.7, 133.3, 128.1, 122.2, 113.9, 76.6, 43.1, 40.7, 28.1, 26.5, 23.8, 21.1. HRMS (EI): m/z calcd. for $C_{14}H_{18}O_2$ (M^+): 218.1307, found: 218.1308. Chiral HPLC (Chiralcel AS column, 0.5% *i*PrOH/hexanes, 1mL/min): major, 10.9 min; minor, 9.07 min; 90% ee. CD (c = 9.2 x 10^{-5} M, MeOH): λmax (Δε): 252 (+7.12).



(*R*)-1-(3-Phenyl-2,3-dihydrobenzofuran-4-yl)ethanone ((*R*)-51). In a glovebox, to a medium-walled NMR tube was added a mixture of $[RhCl(coe)_2]_2$ (3.6 mg, 0.0050

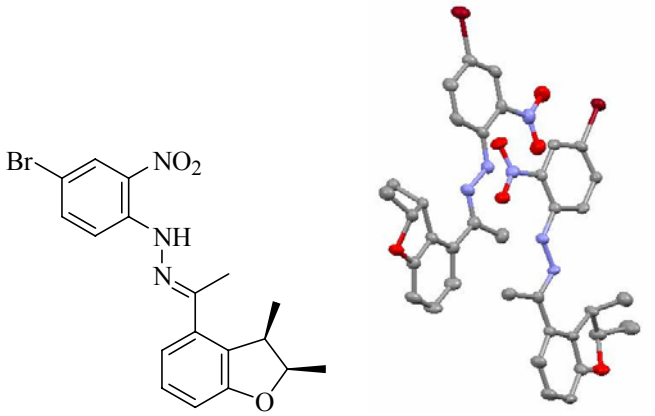
mmol) and (*S*)-diisopropyl-(8,9,10,11,12,13,14,15-octahydro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*']dinaphthalen-4-yl)amine (4.2 mg, 0.0099 mmol) in 1,4-dioxane (0.40 mL) and a solution of benzyl-[1-[3-((*Z*)-styryloxy)phenyl]ethylidene]amine (16.4 mg, 0.0501 mmol) in 1,4-dioxane (0.10 mL). The tube was fitted with a Cajon adapter, the mixture was frozen, and then the tube was flame sealed under vacuum. The NMR tube was then placed in oil bath heated to 75 °C for 22 h. After the reaction, the sealed tube was opened and the mixture was concentrated. To the residue were added 1,4-dioxane (0.50 mL) and concentrated HCl/H_2O (1/1) (0.50 mL). The mixture was stirred at room temperature for 3.5 h and then was extracted with diethyl ether four times. The combined organic layer was concentrated and the residue was purified by silica gel column chromatography (silica gel: 15 mL, eluted with 20:1 hexanes/ethyl acetate). The purified product was contaminated with the vinyl ether ketone **43** and therefore was resubmitted to the reaction in 1,4-dioxane (0.50 mL) and concentrated HCl/H_2O (1/1) (0.50 mL) at 75 °C for an additional 5 h. The mixture was extracted with diethyl ether five times. The combined organic layer was concentrated and the residue was purified by silica gel column chromatography (silica gel: 15 mL, eluted with 20:1 hexanes/ethyl acetate) to give the title compound as a white solid (7.8 mg, 65% yield). mp 91-93 °C. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 1689, 1589, 1440, 1268. ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.27–7.20 (m, 2H), 7.20–7.08 (m, 4H), 5.15 (dd, J = 3.6, 8.8 Hz, 1H), 4.88 (t, J = 8.8 Hz, 1H), 4.57 (dd, J = 3.6, 8.8 Hz, 1H), 2.44 (s, 3H) $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 198.2, 161.3, 143.8, 134.5, 131.1, 129.0, 128.4, 127.3, 126.6, 122.2, 114.2, 84.9, 48.0, 27.8. HRMS (EI): *m*/*z* calcd. for $C_{16}H_{14}O_2$ (M^+): 238.0994, found: 238.0993. Chiral HPLC (Chiralcel AS column, 1%

*i*PrOH/hexanes, 1mL/min): major, 10.3 min; minor, 12.9 min; 87% ee. $[\alpha]_D^{25}$ +11.49 (c 0.31, $CHCl_3$). Maximum value based upon sample enantiomeric purity: $[\alpha]_D^{25}$ +13.21 (c 0.31, $CHCl_3$).



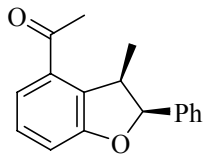
(*R*)-3-Methyl-2,3-dihydrobenzofuran-4-carbaldehyde ((*R*)-52). In a glovebox, to a medium-walled glass reaction vessel was added a mixture of $[RhCl(coe)_2]_2$ (7.2 mg, 0.010 mmol) and (*S*)-(8,9,10,11,12,13,14,15-octahydro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*']dinaphthalen-4-yl)-bis((*R*)-1-phenylethyl)amine (11.1 mg, 0.0203 mmol) in 1,4-dioxane (0.80 mL) and a solution of benzyl-[1-{3-[((*Z*)-propenyl)oxy]phenyl}methylidene]amine (25.0 mg, 0.0995 mmol) in 1,4-dioxane (0.20 mL), and the mixture was stirred at 75 °C for 72 h. After the reaction, the mixture was concentrated and the residue was purified by silica gel column chromatography (silica gel: 15 mL, eluted with 40:1 hexanes/ethyl acetate),[16] which was then treated in 1,4-dioxane (1.0 mL) with concentrated HCl/H_2O (1/1) (1.0 mL) at room temperature for 14 h. The mixture was extracted with diethyl ether four times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography (silica gel: 15 mL, eluted with 40:1 hexanes/ethyl acetate) to give the title compound as a light yellow oil (4.4 mg, 27% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.07 (s, 1H), 7.36–7.30 (m, 2H), 7.05 (dd, J = 2.2, 6.6 Hz, 1H), 4.62 (t, J = 8.6 Hz, 1H), 4.34 (dd, J = 2.8, 8.6 Hz, 1H), 4.00–3.90 (m, 1H), 1.32 (d, J = 6.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 192.2, 160.6, 133.5, 132.7, 128.7, 124.9, 115.3, 79.3, 36.1, 20.6. HRMS (EI): *m*/*z* calcd. for $C_{10}H_{10}O_2$ (M^+): 162.0681,

found: 162.0676. Chiral HPLC (Chiralcel AS column, 0.7% *i*PrOH/hexanes, 1mL/min): major, 10.7 min; minor, 12.3 min; 89% ee.



(2*R*,3*R*)-*N*-(4-Bromo-2-nitrophenyl)-*N*'-[1-(2,3-dimethyl-2,3-dihydrobenzofuran-4-yl)eth-(*E*)-ylidene]hydrazine ((2*R*,3*R*)-34). A mixture of (2*R*,3*R*)-1-(2,3-dimethyl-2,3-dihydrobenzofuran-4-yl)ethanone (93% ee) (27.4 mg, 144 μmol) and 4-bromo-2-nitrohydrazine hydrochloride (39.1 mg, 146 μmol) in absolute ethanol (0.40 mL) was stirred at 80 °C for 1 h. After cooling to room temperature, the precipitated solid was collected by filtration and was washed with absolute ethanol to give a red solid (33.6 mg, 58% yield). mp 158-160 °C. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 1608, 1499, 1479, 1431, 1346, 1307, 1290, 1259, 1209, 1140. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.98 (s, 1H), 8.36 (d, J = 2.4 Hz, 1H), 7.78 (d, J = 9.2 Hz, 1H), 7.62 (dd, J = 2.4, 9.2 Hz, 1H), 7.19 (t, J = 8.0 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 4.86 (quint, J = 6.8 Hz, 1H), 3.86 (quint, J = 6.8 Hz, 1H), 2.43 (s, 3H), 1.51 (d, J = 6.8 Hz, 1H) 1.09 (d, J = 6.8 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 159.7, 149.5, 141.1, 139.2, 135.2, 131.9, 131.6, 128.3, 128.2, 120.2, 117.6, 110.6, 109.8, 82.5, 40.1, 15.2, 13.9. HRMS (FAB): *m*/*z* calcd. for $C_{18}H_{18}N_3O_3Br$ (M^+): 403.0532, found: 403.0535.

Recrystallization from absolute ethanol yielded X-ray quality crystals of **(2*R*,3*R*)-34**. The crystal structure identified the absolute configuration of **(2*R*,3*R*)-53**. The absolute configurations of **(2*S*,3*R*)-54** was assigned by analogy to this result.



(2*S*,3*R*)-1-(3-Methyl-2-phenyl-2,3-dihydrobenzofuran-4-yl)ethanone ((2*S*,3*R*)-54). In a glovebox, to a medium-walled glass reaction vessel was added a mixture of $[RhCl(coe)_2]_2$ (7.2 mg, 0.010 mmol) and (*S*)-(8,9,10,11,12,13,14,15-octahydro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*']dinaphthalen-4-yl)-bis((*R*)-1-phenylethyl)amine (11.0 mg, 0.0201 mmol) in 1,4-dioxane (0.80 mL) and a solution of benzyl-[1-[3-(1-phenylpropenyloxy)phenyl]ethylidene]amine (*Z*/*E* = 9/1 for olefin) (34.0 mg, 0.0996 mmol) in 1,4-dioxane (0.20 mL), and the mixture was stirred at 75 °C for 92 h. After the reaction, the mixture was concentrated. To the residue were added 1,4-dioxane (1.0 mL) and concentrated HCl/H_2O (1/1) (1.0 mL). The mixture was stirred at room temperature for 5 h and then was extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (silica gel: 15 mL, eluted with hexanes and then 40:1 hexanes/ethyl acetate). The purified product was contaminated with the vinyl ether ketone **47** and therefore was resubmitted to the reaction in 1,4-dioxane (1.0 mL) and concentrated HCl/H_2O (1/1) (1.0 mL) at room temperature for an additional 13 h. The mixture was extracted with diethyl ether four times. The combined organic layer was concentrated and the residue was purified by silica gel column chromatography (silica

gel: 15 mL, eluted with 20:1 hexanes/ethyl acetate) to give the title compound as a white solid (11.2 mg, 45% yield). mp 82-84 °C. IR (ZnSe, thin film) ν_{max} (cm^{-1}): 1603, 1572, 1433, 1273, 1079. ^1H NMR (400 MHz, $CDCl_3$): δ 7.45–7.36 (m, 5H), 7.36–7.25 (m, 2H), 7.12 (d, J = 8.0 Hz, 1H), 5.75 (d, J = 7.2 Hz, 1H), 4.16 (quint, J = 7.2 Hz, 1H), 2.61 (s, 3H), 0.72 (d, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 198.9, 159.8, 137.3, 134.9, 133.7, 128.2, 127.5, 126.1, 122.6, 114.5, 88.5, 41.5, 28.1, 15.6. HRMS (EI): *m*/*z* calcd. for $C_{17}H_{16}O_2$ (M^+): 252.1152, found: 252.1150. Chiral HPLC (Chiralcel AS column, 0.5% *i*PrOH/hexanes, 1mL/min): major, 15.9 min; minor, 22.0 min; 90% ee. $[\alpha]_D^{25}$ -62.12 (c 0.47, $CHCl_3$). Maximum value based upon sample enantiomeric purity: $[\alpha]_D^{25}$ -69.02 (c 0.47, $CHCl_3$). A ^1H-^1H NOESY spectrum of **(2*S*,3*R*)-54** indicated that the geometry of the two protons on the dihydrofuran ring was *cis*.

Enantioselective Intramolecular Hydroarylation of Alkenes via Directed C–H Bond Activation

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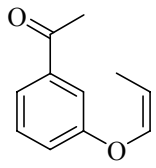
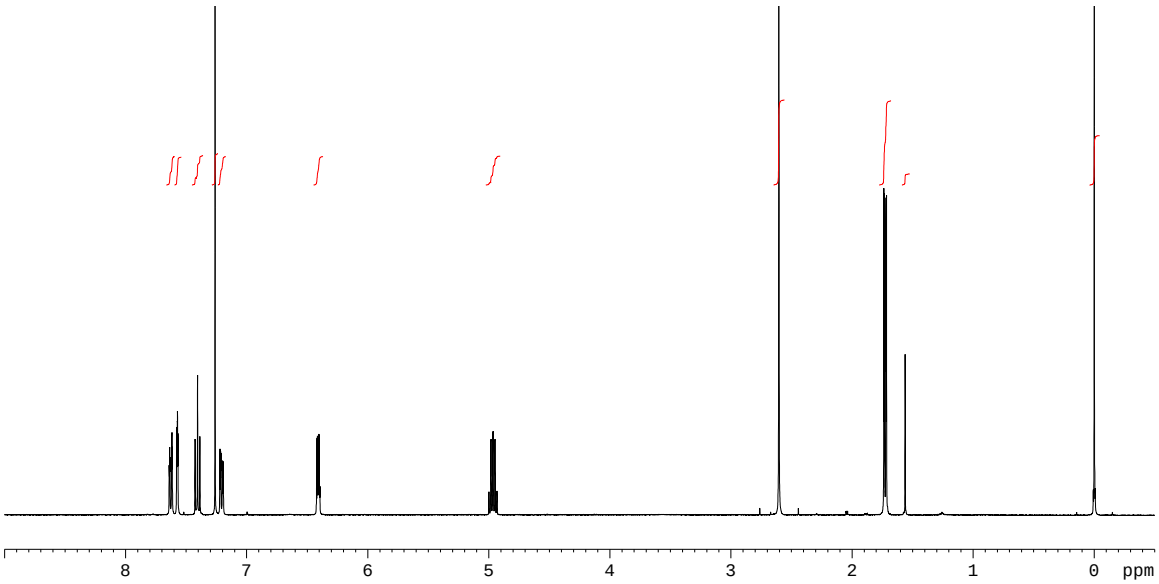
Department of Chemistry, University of California and Division of Chemical Sciences, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Supporting Information (Spectral Data)



^{1}H NMR (Compound **37**)



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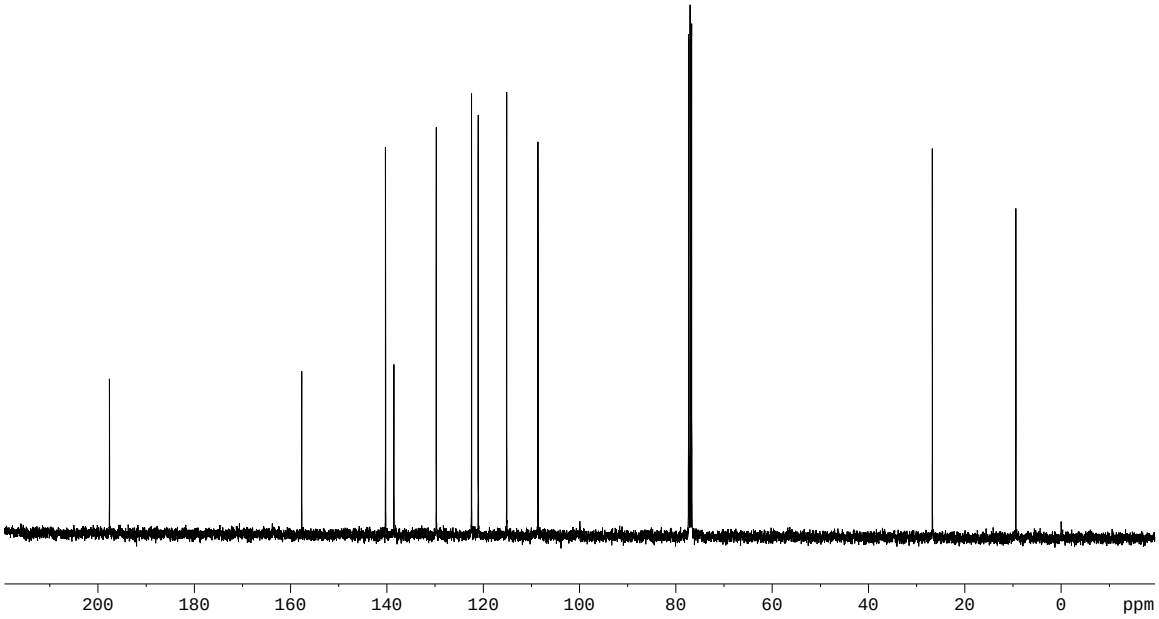
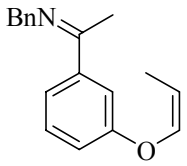
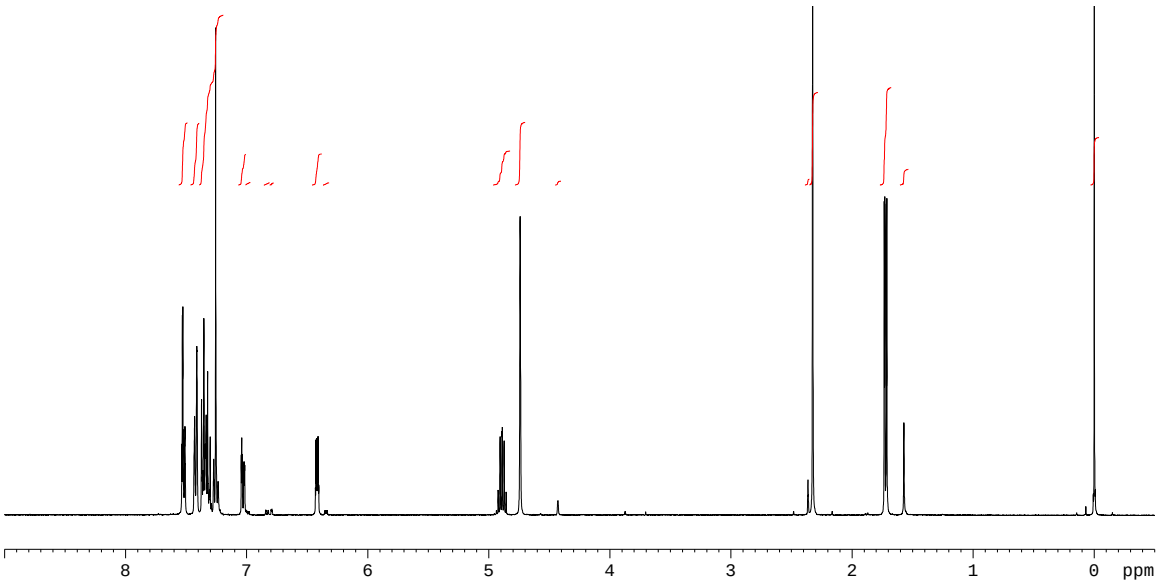
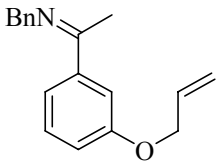


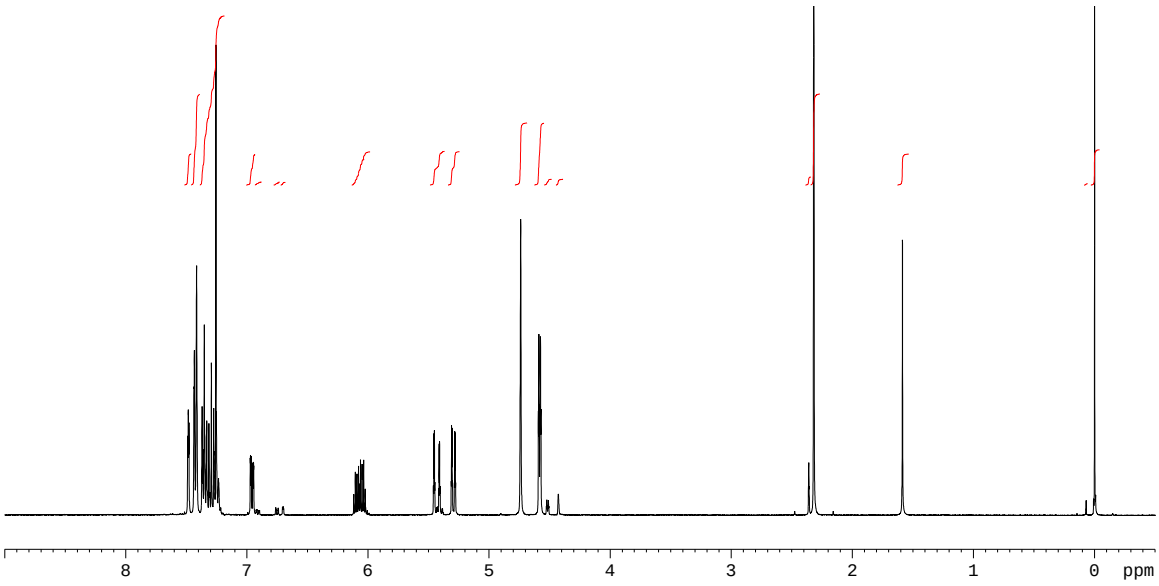


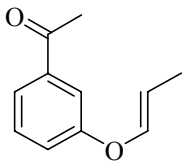
^{1}H NMR (Compound **18**)



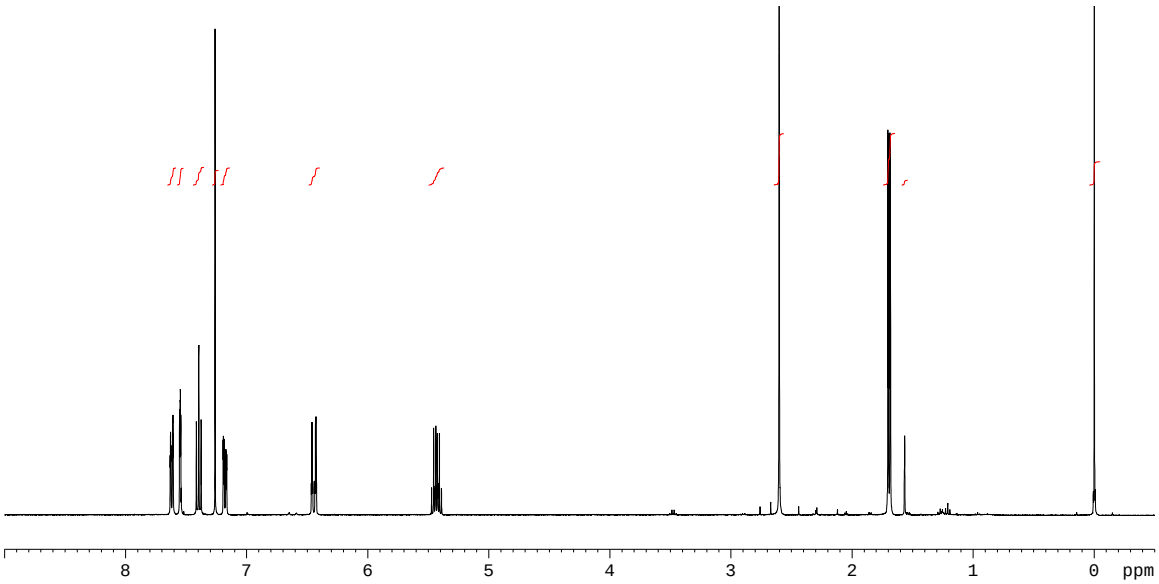


^{1}H NMR (Compound **16**)

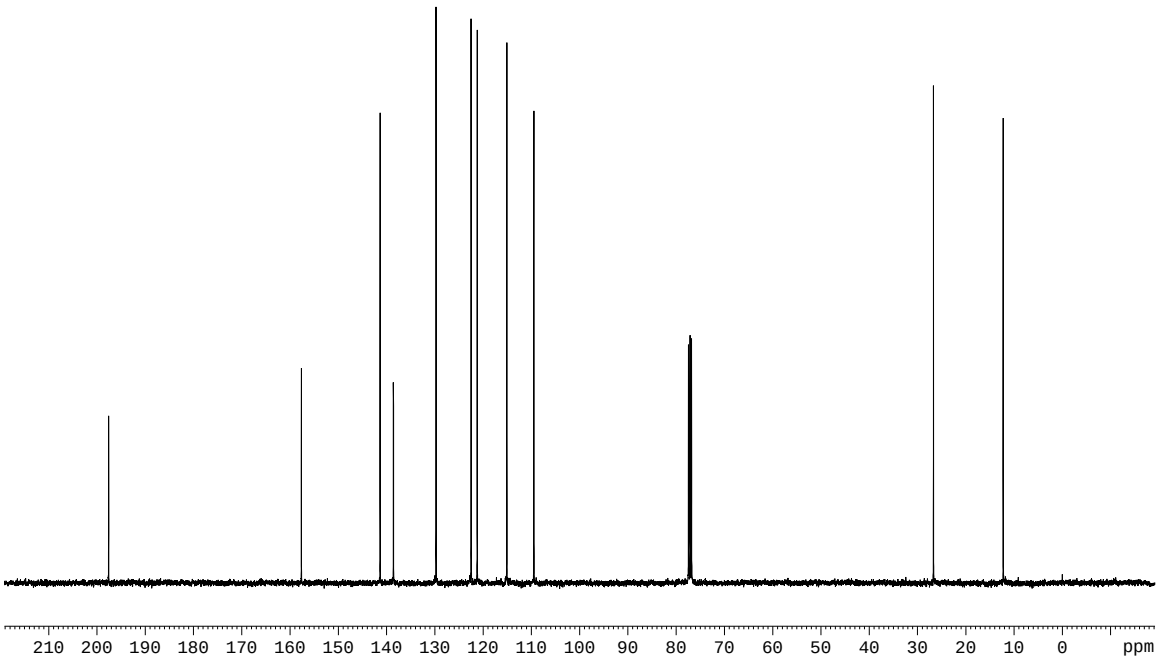


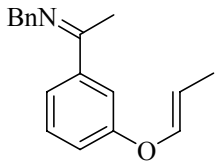


^{1}H NMR (Compound **38**)

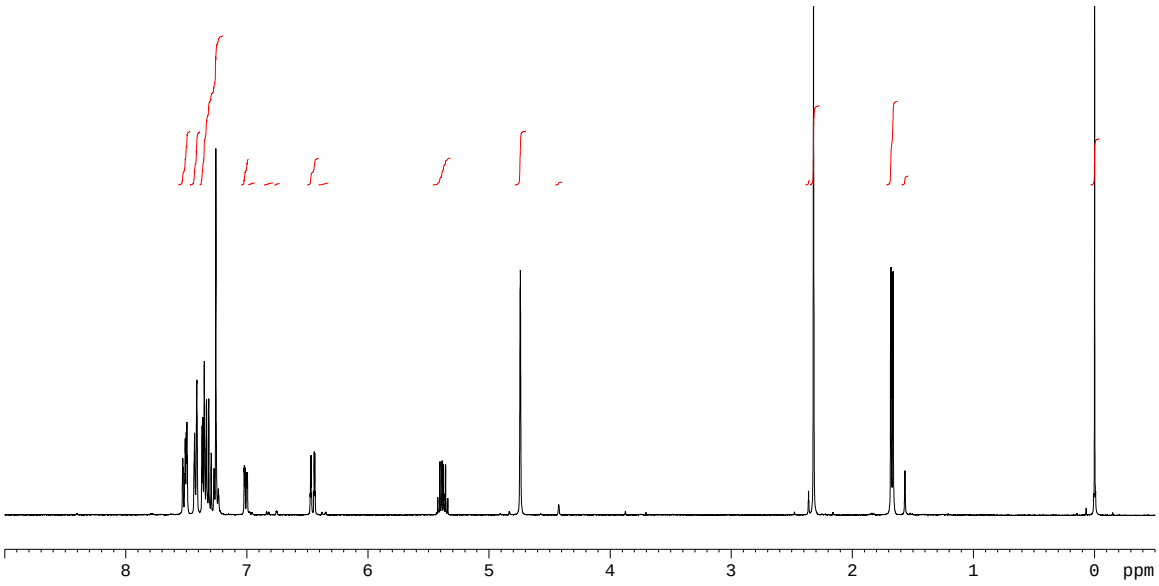


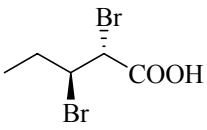
^{13}C NMR (Compound **38**)



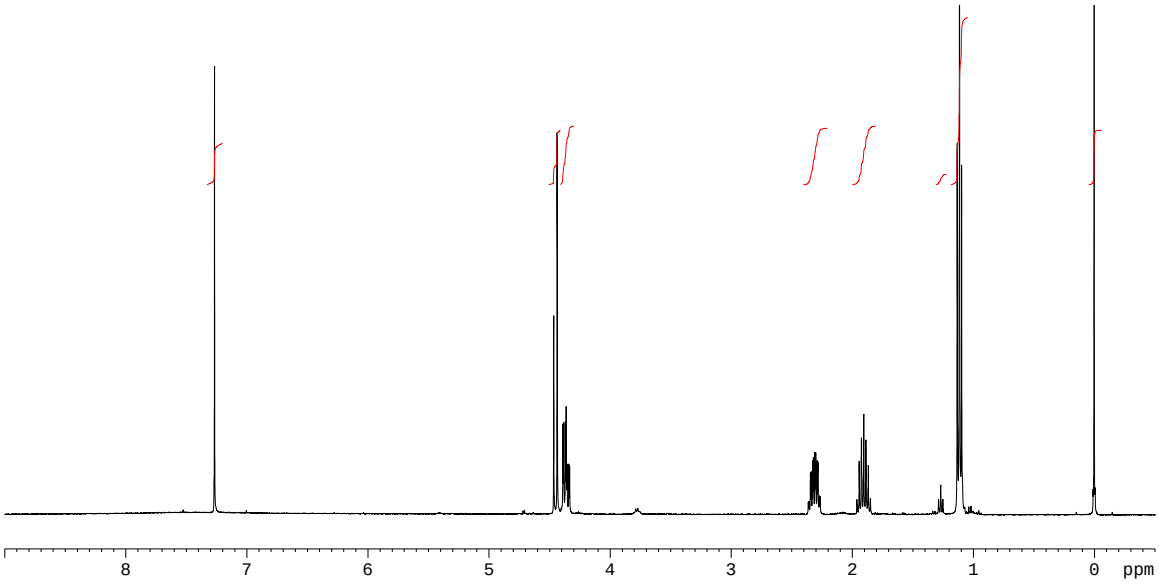


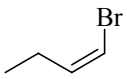
^{1}H NMR (Compound **17**)



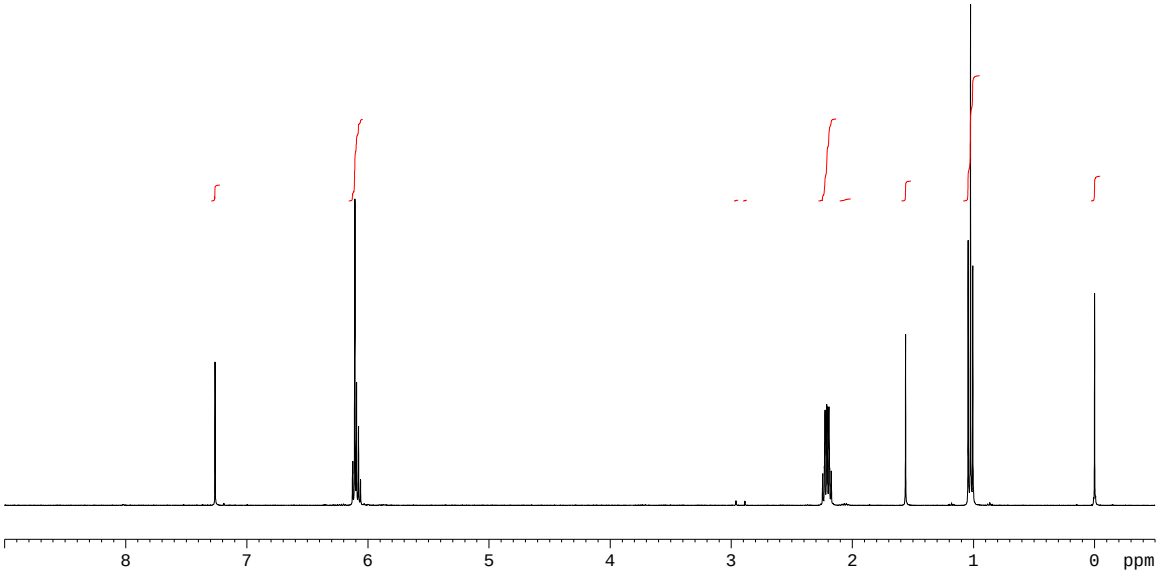


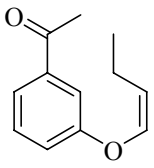
^{1}H NMR



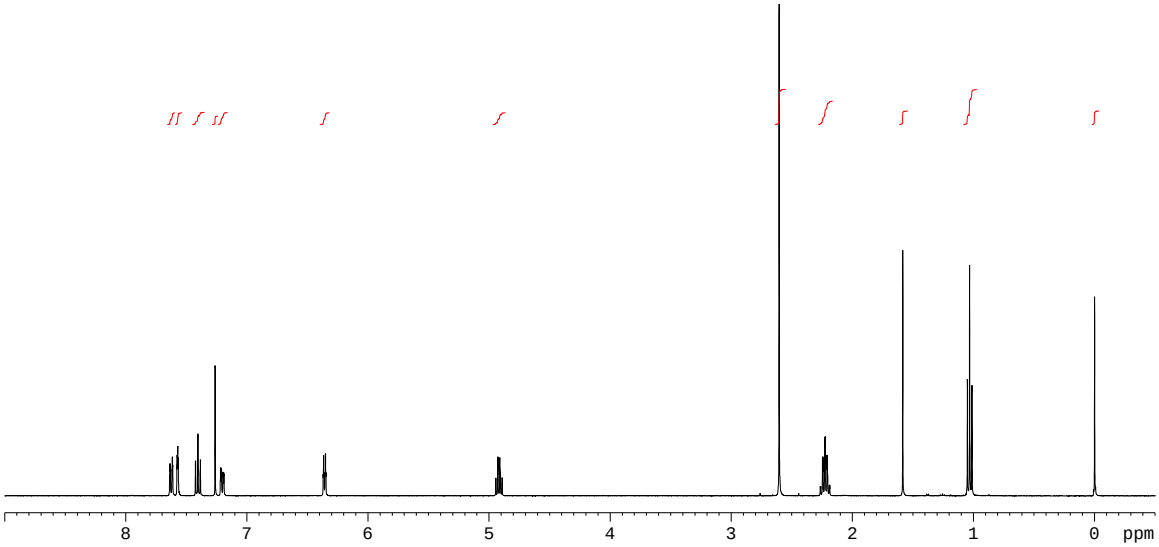


^{1}H NMR (Compound **39**)

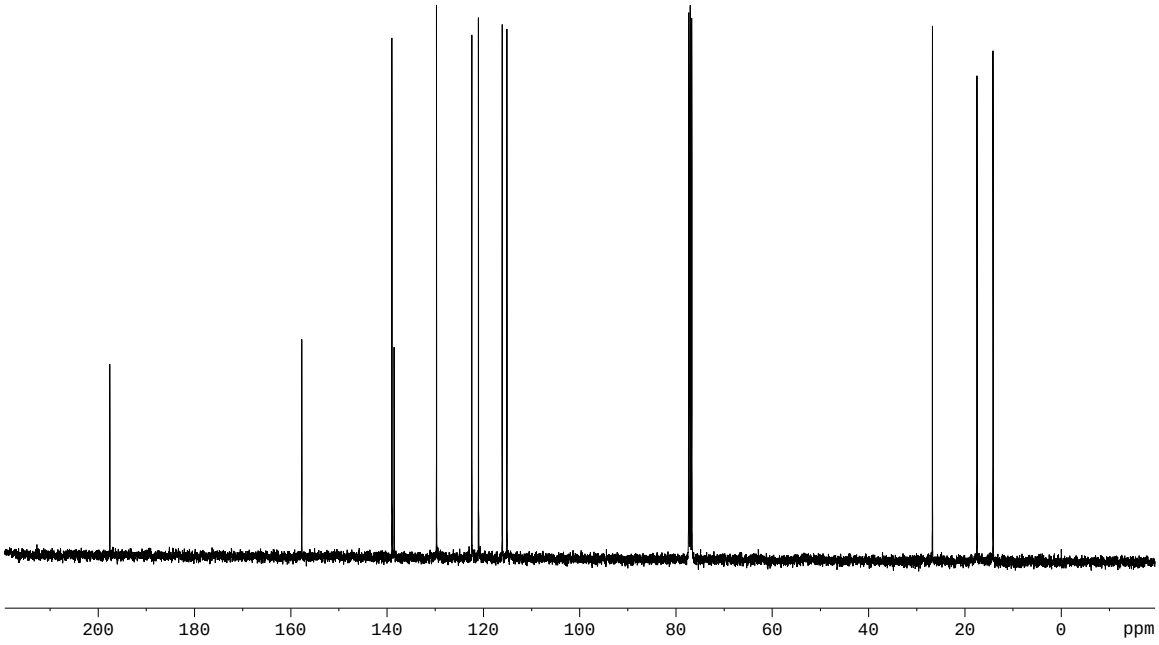


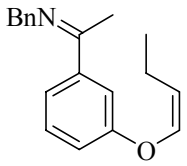


^{1}H NMR (Compound **40**)



^{13}C NMR (Compound **40**)





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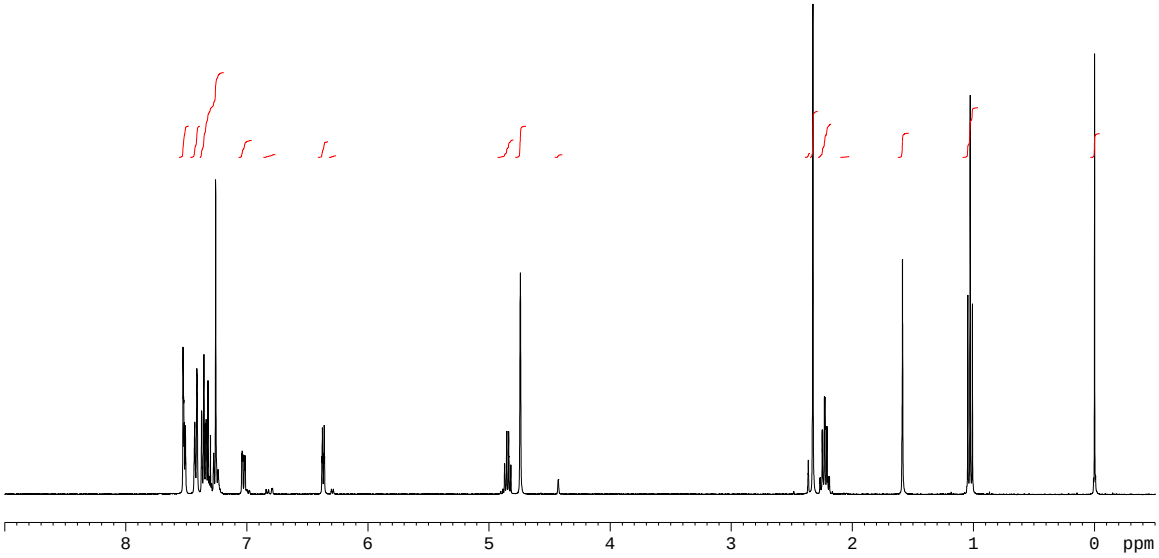
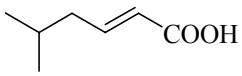
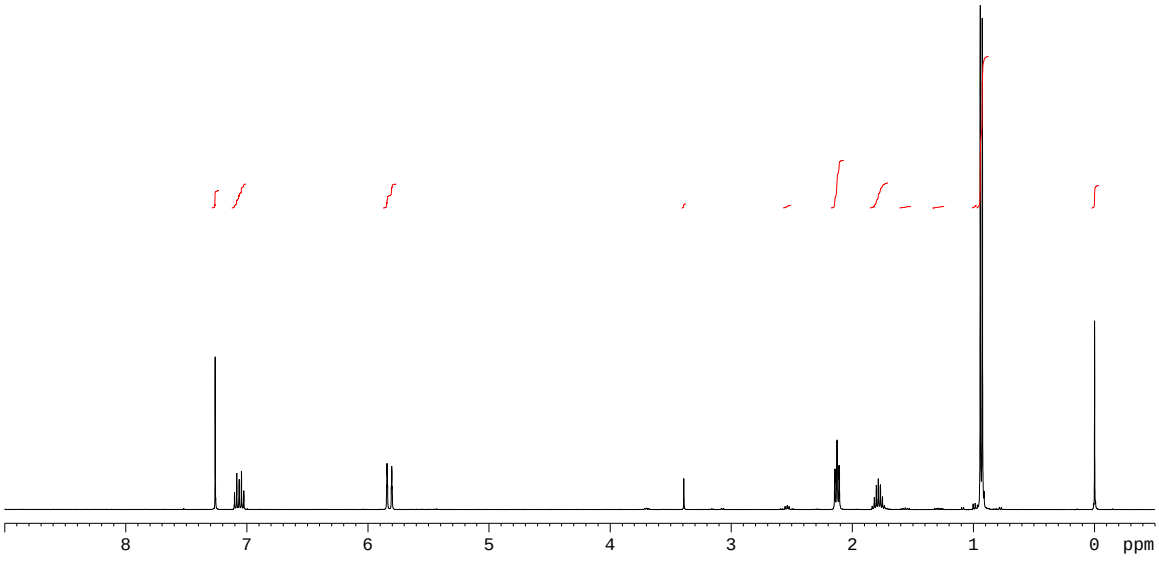
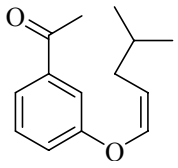


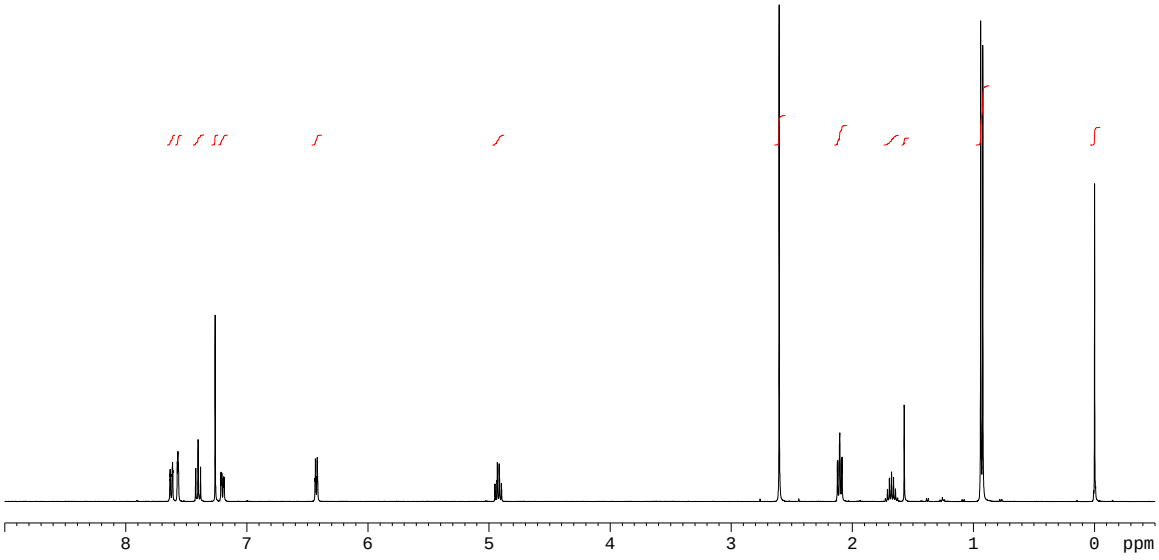


^{1}H NMR (Compound **41**)

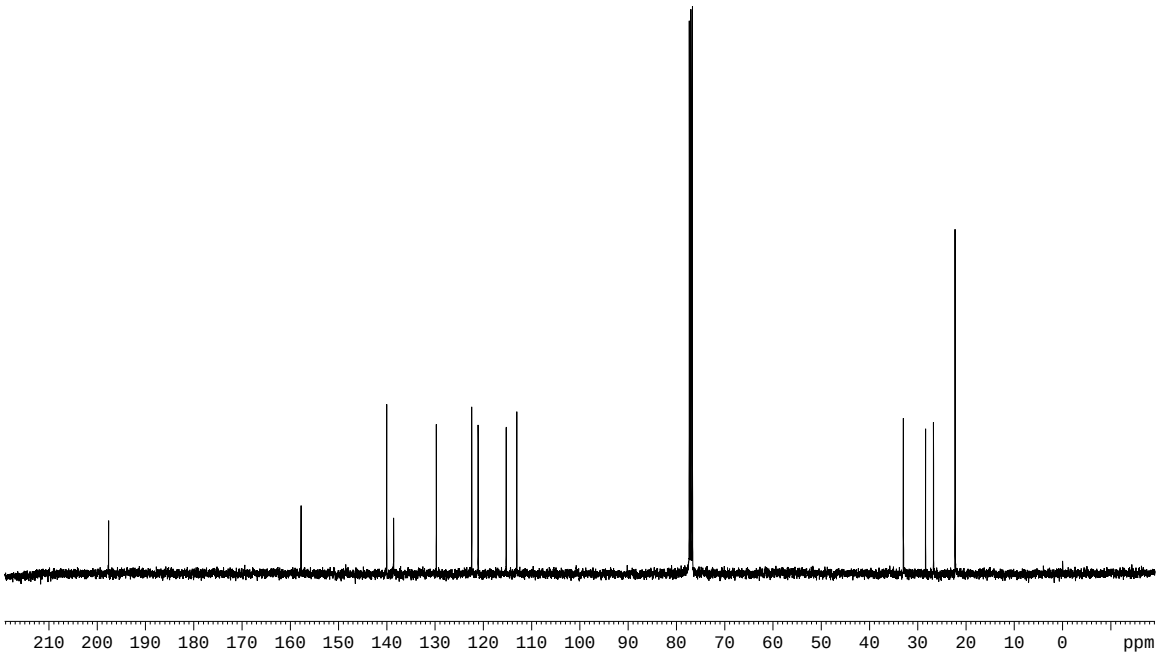


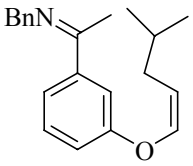


^{1}H NMR (Compound **42**)



^{13} CNMR (Compound **42**)





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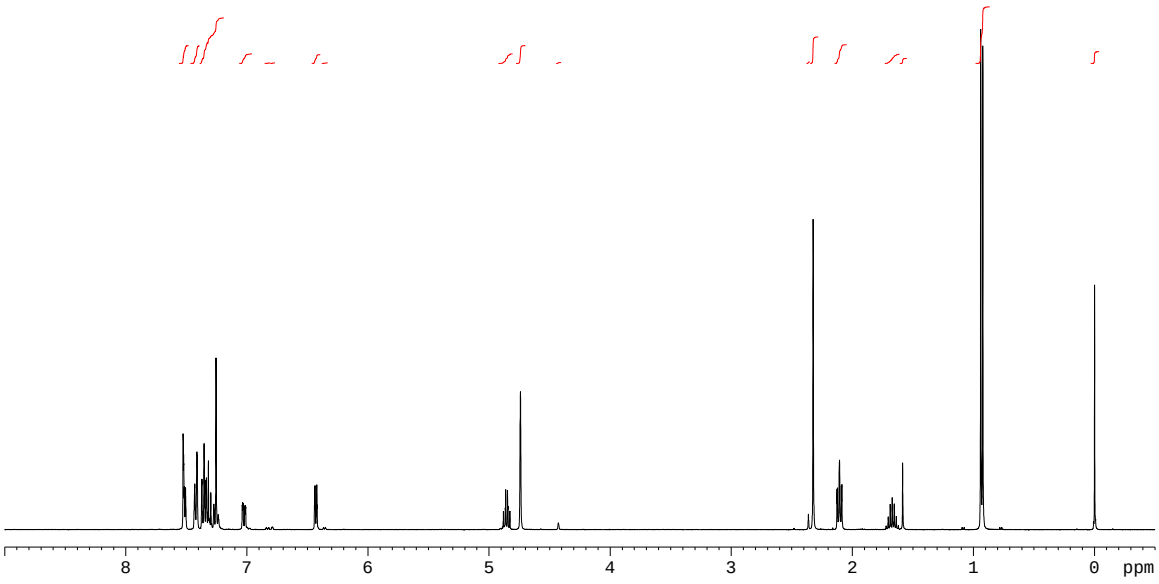

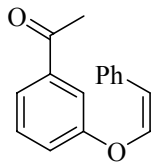

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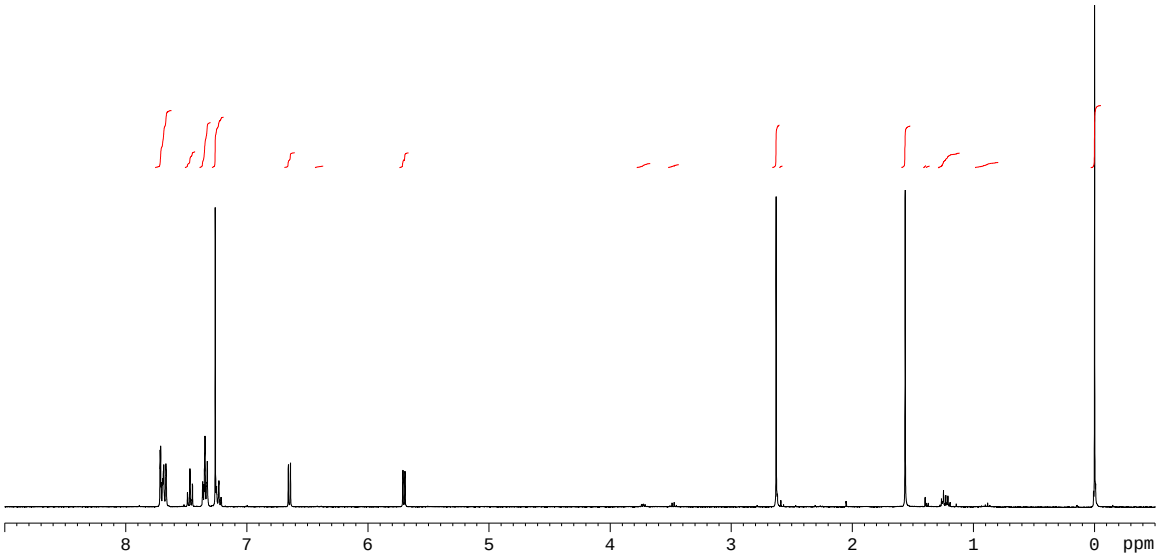
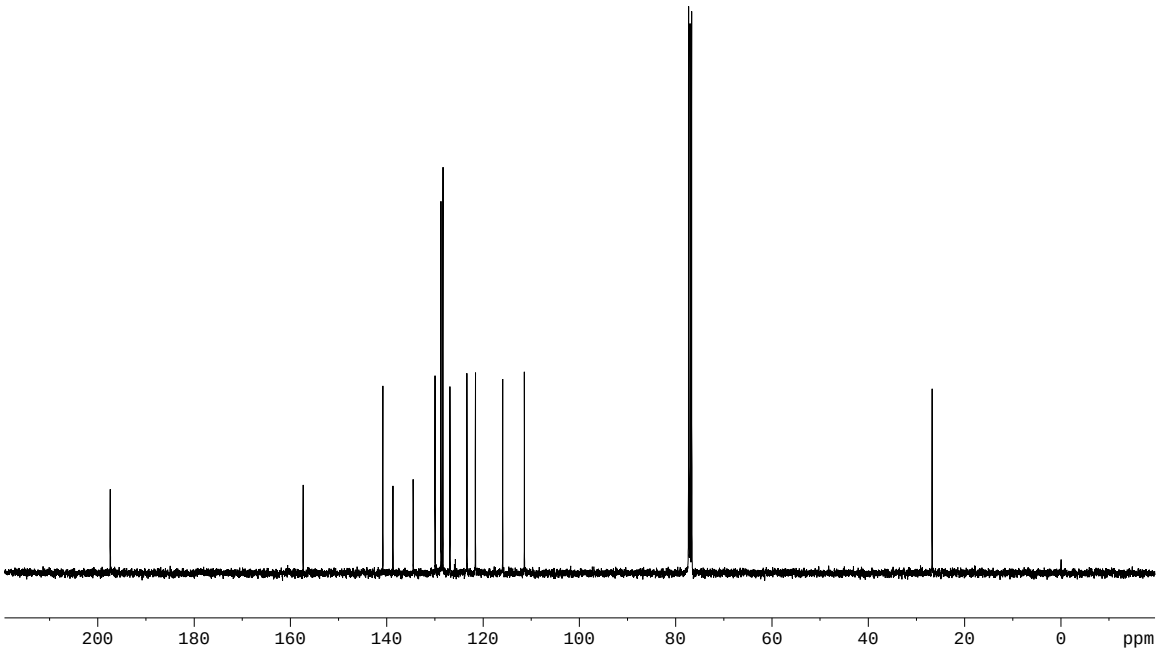
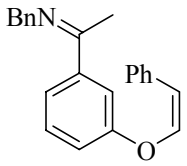
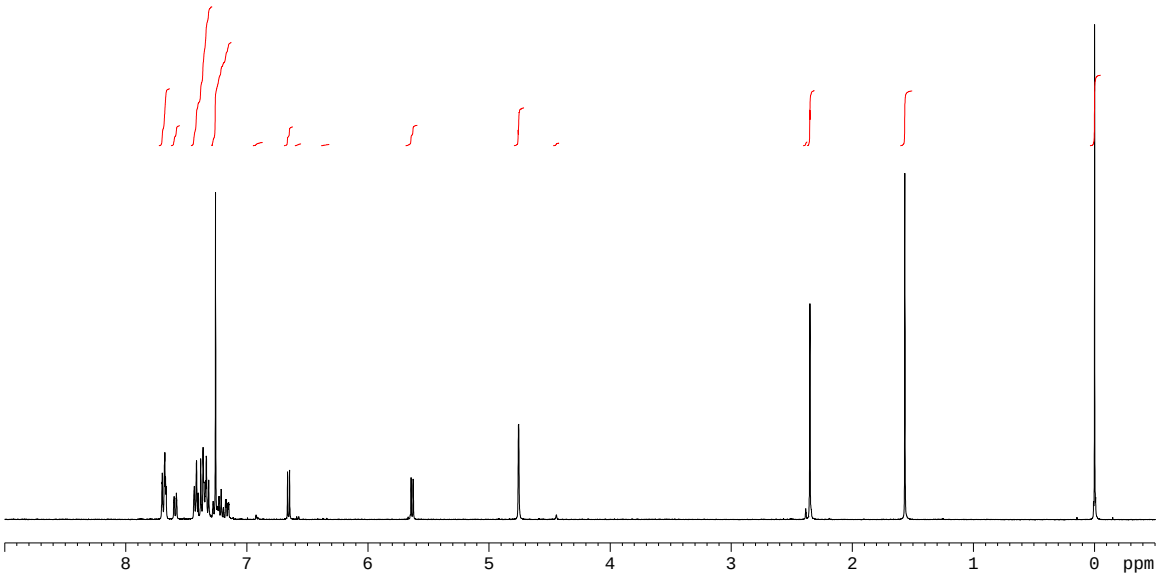


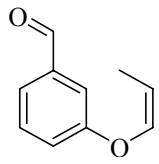
^{13} CNMR (Compound **43**)



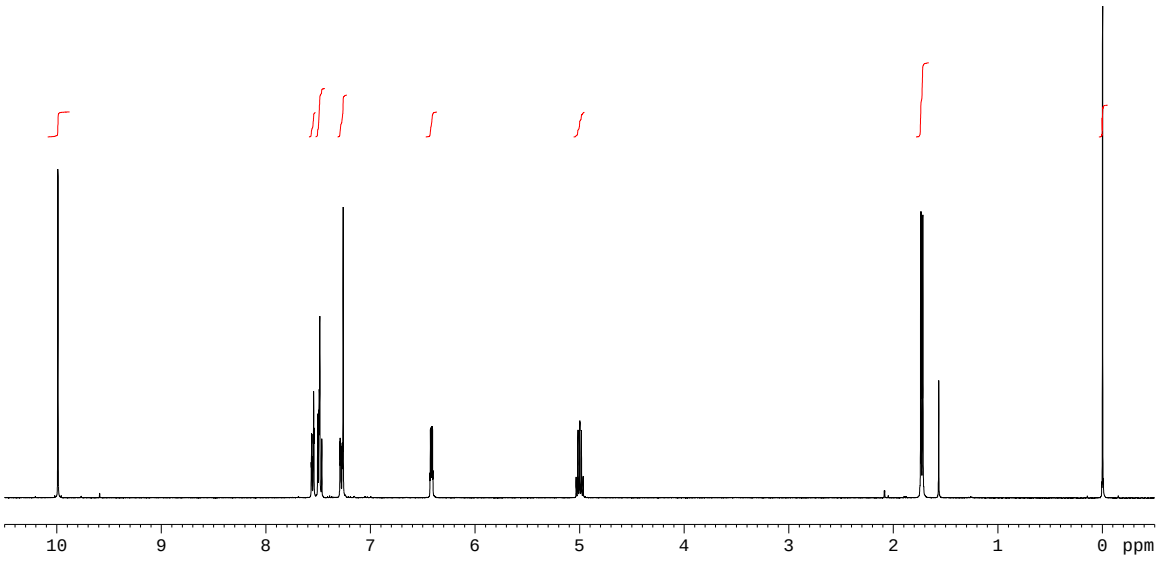


^{1}H NMR (Compound **24**)

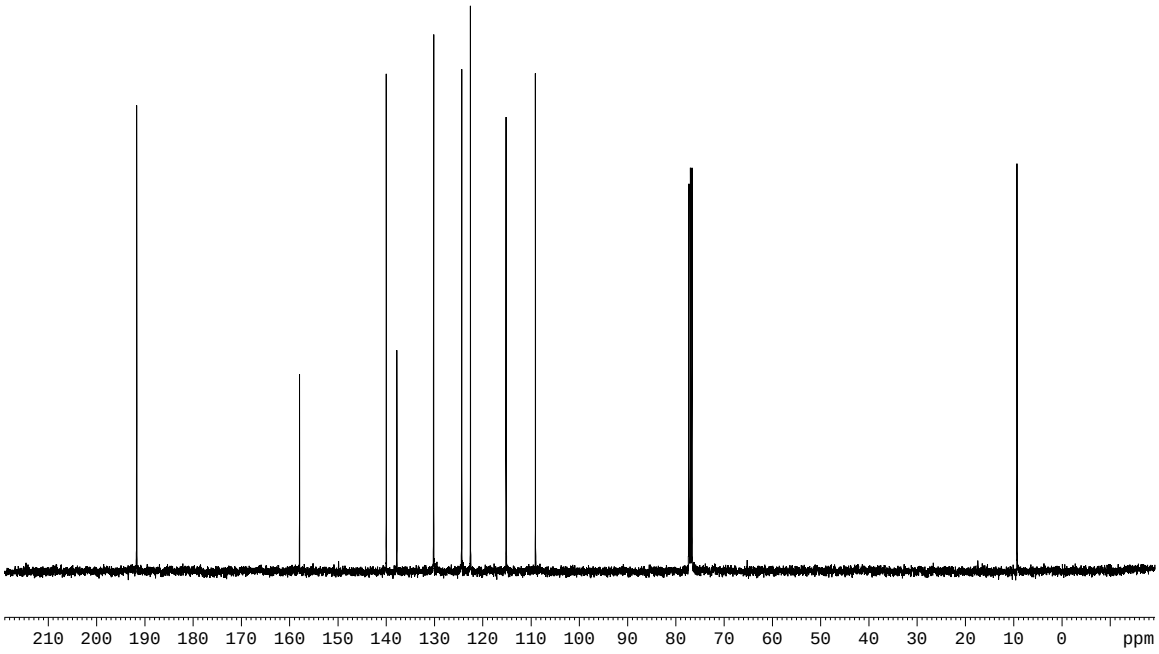


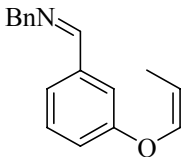


^{1}H NMR (Compound **44**)

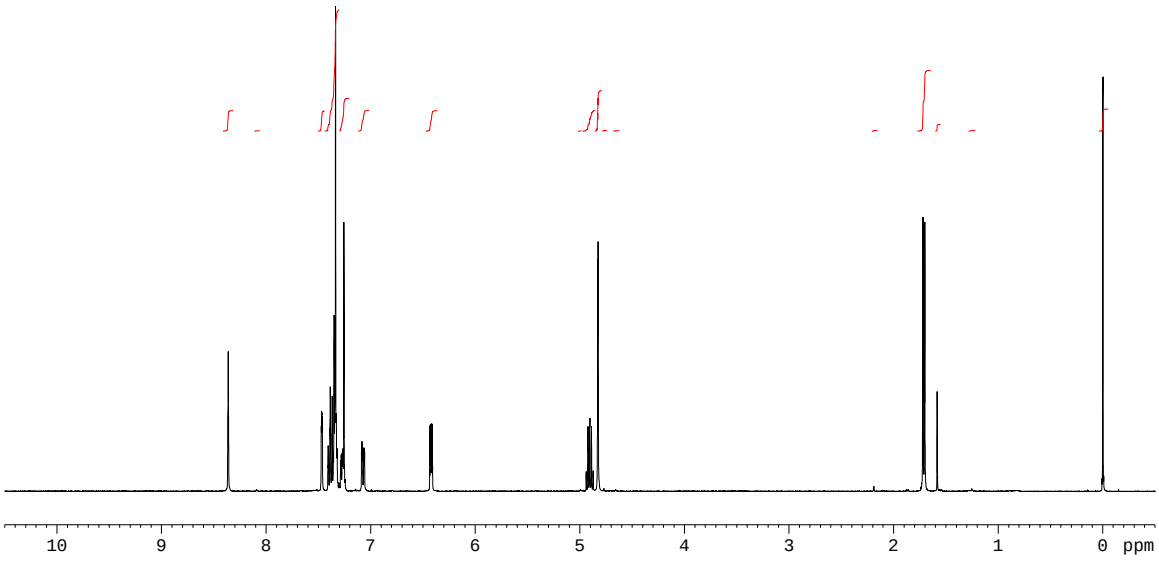


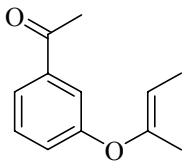
^{13} CNMR (Compound **44**)



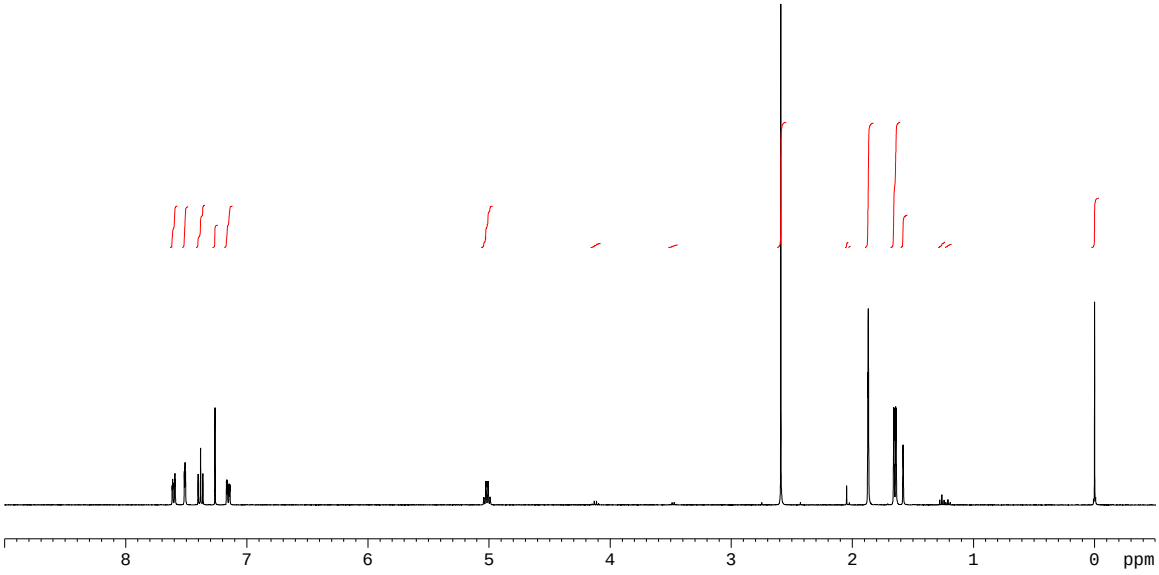


^{1}H NMR (Compound **26**)

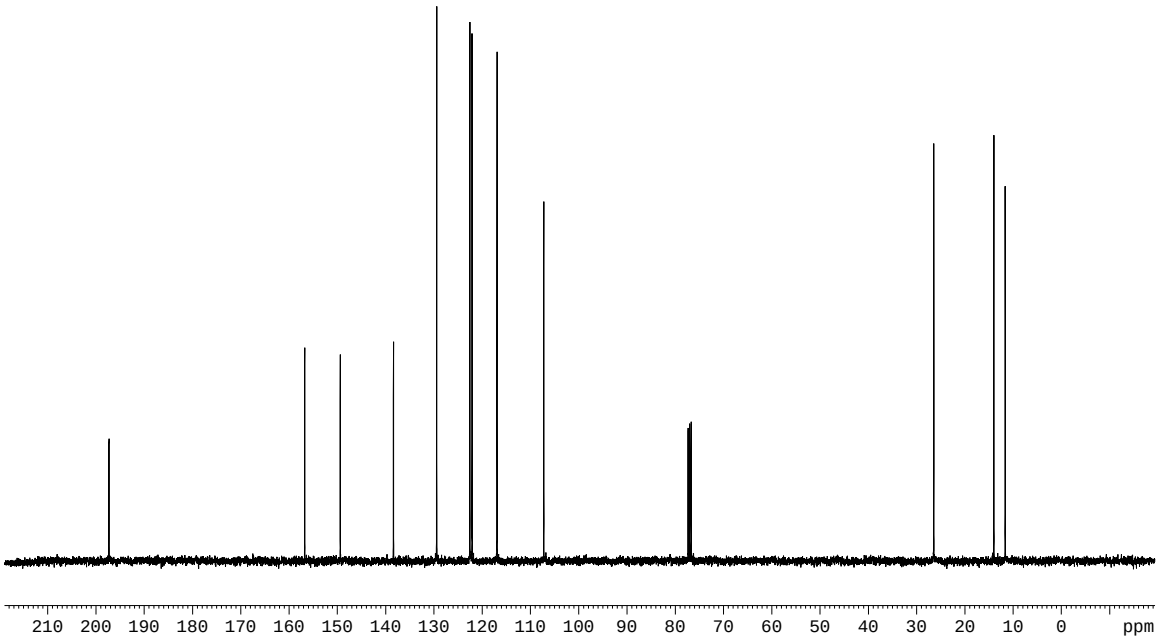


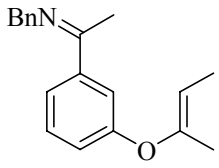


^{1}H NMR (Compound **45**)

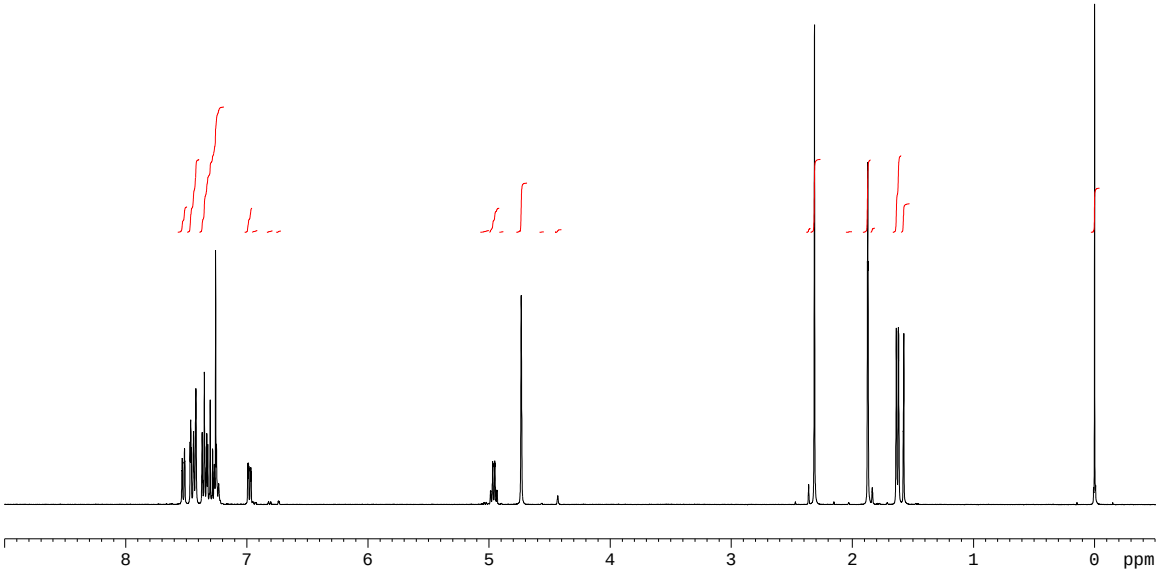


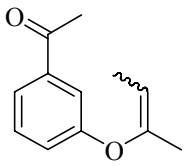
^{13} CNMR (Compound **45**)



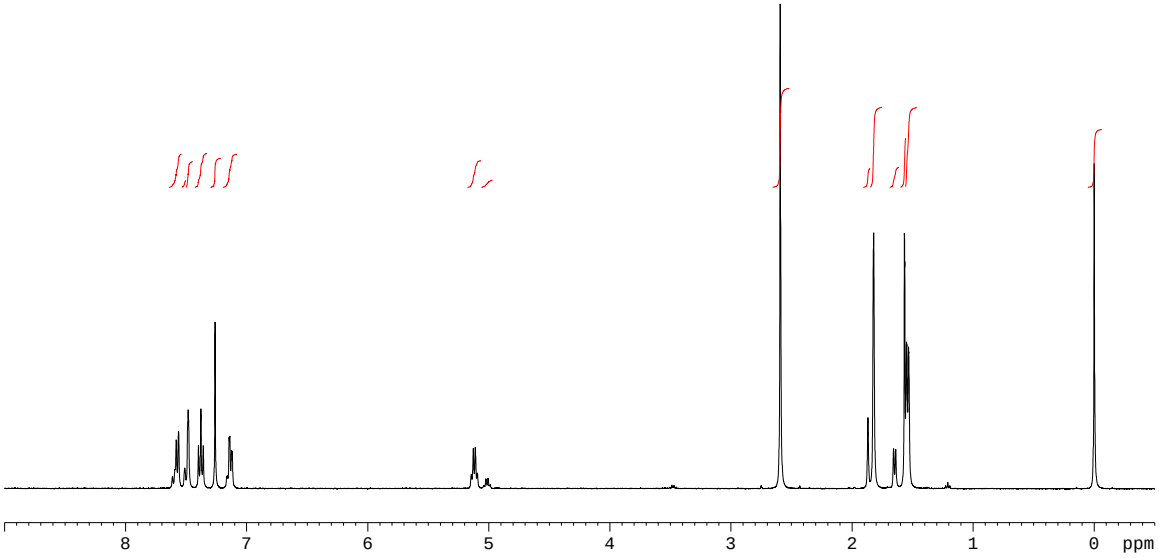


^{1}H NMR (Compound **28**)

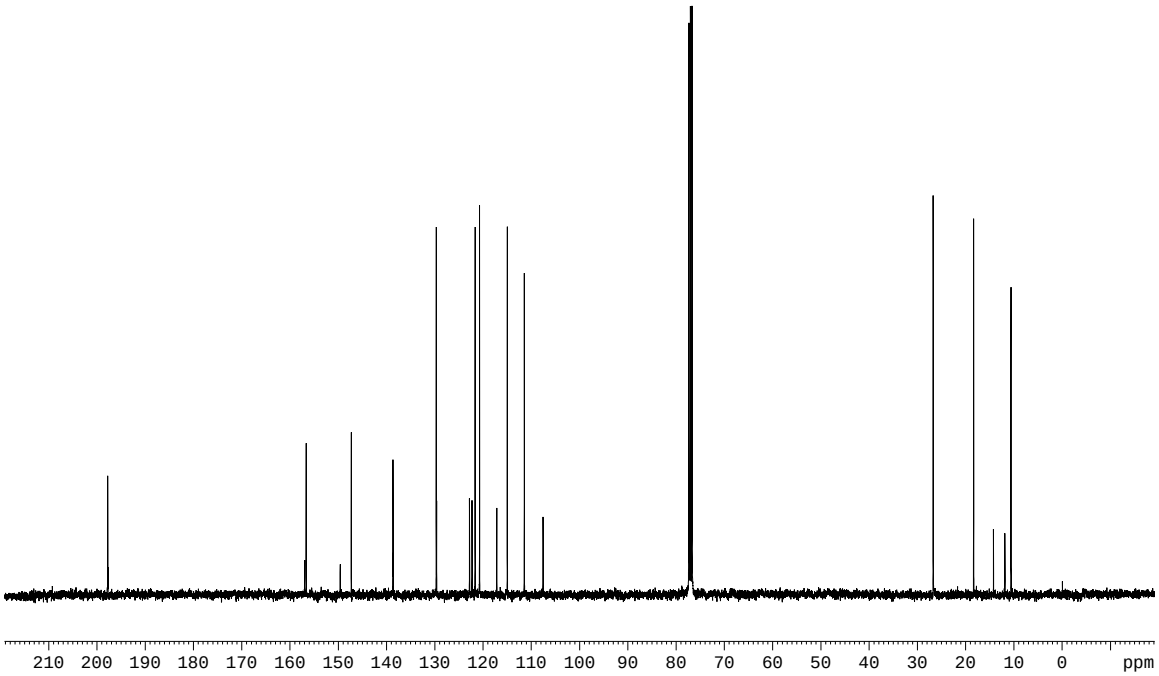


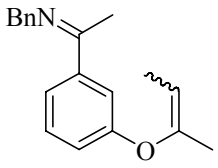


^{1}H NMR (Compound **46**)

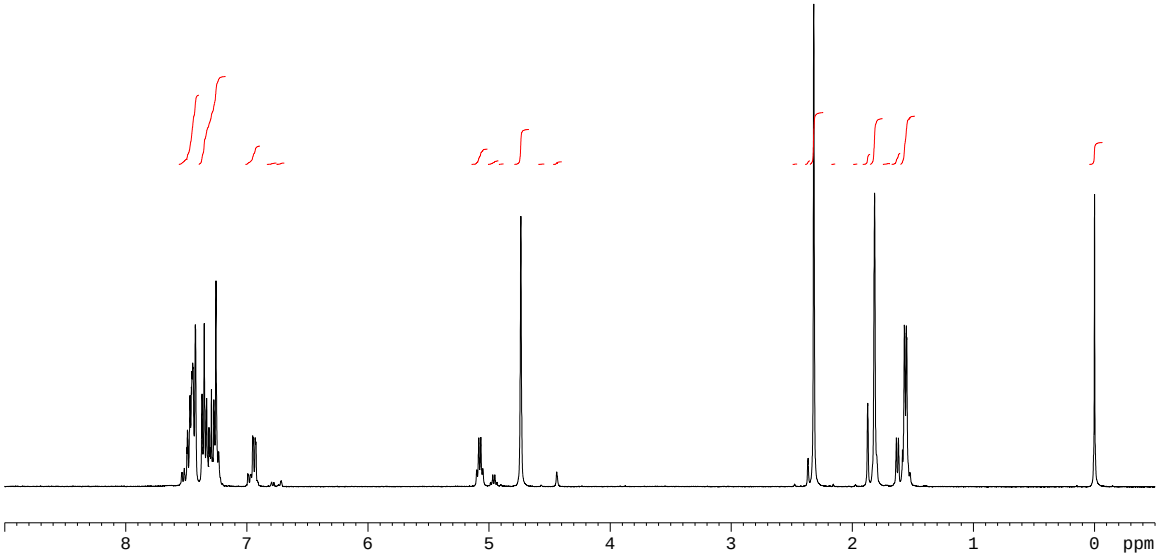


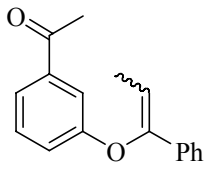
^{13} CNMR (Compound **46**)



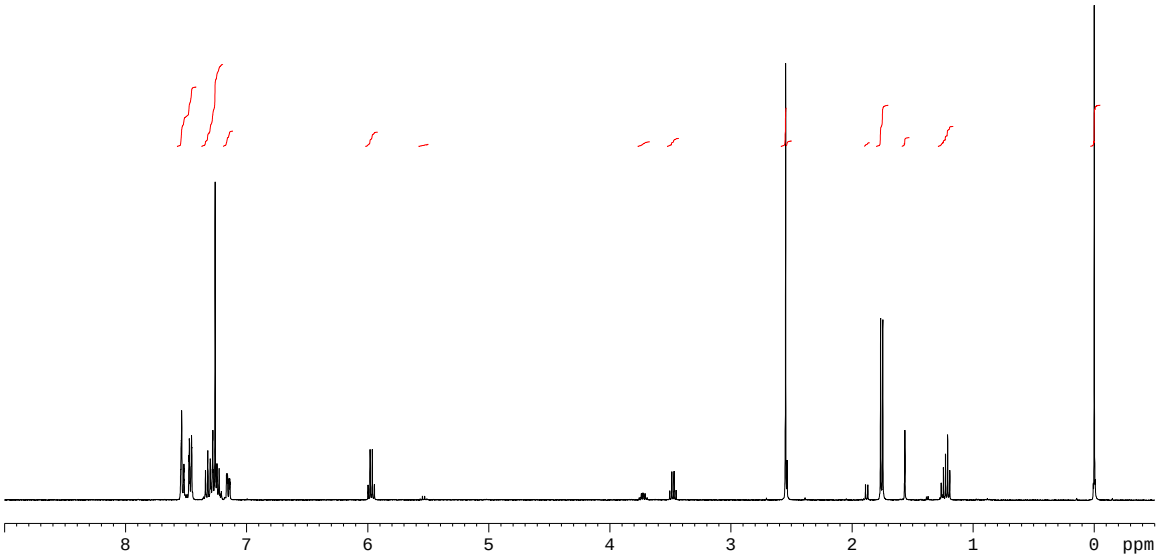


^{1}H NMR (Compound **29**)

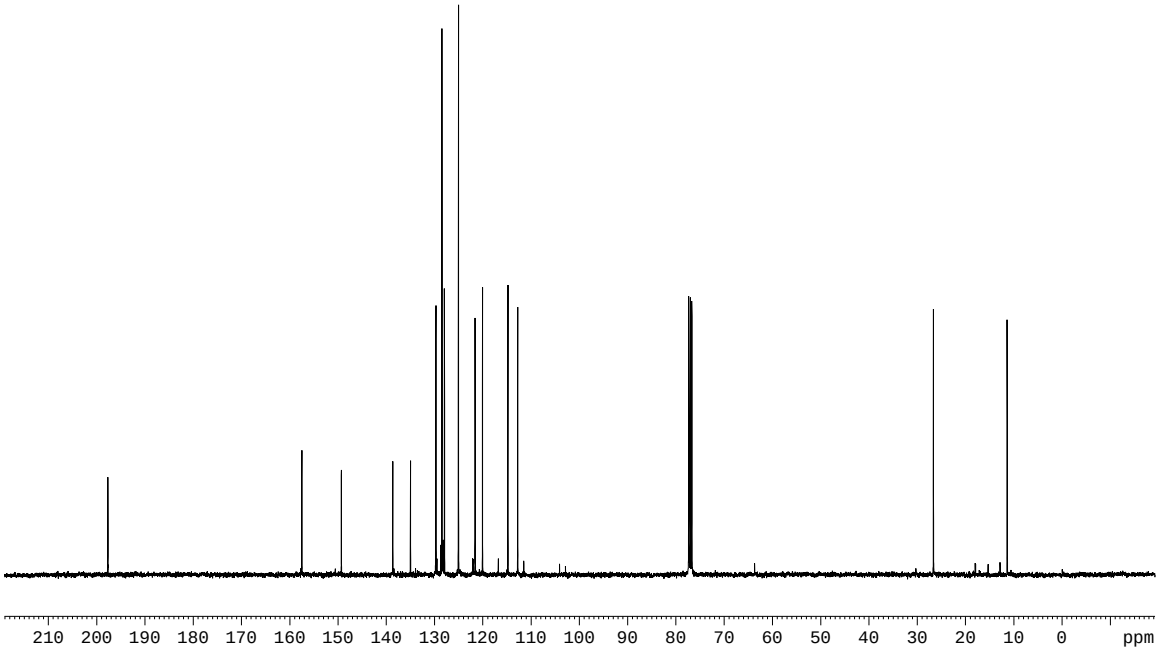


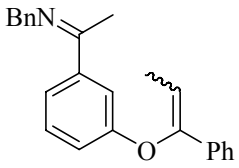


^{1}H NMR (Compound **47**)

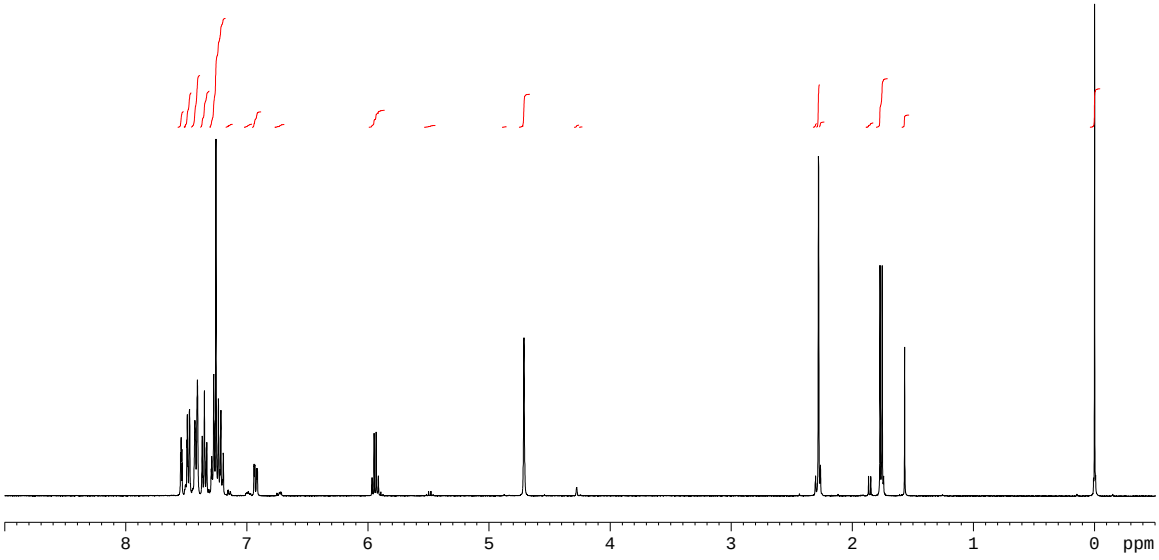


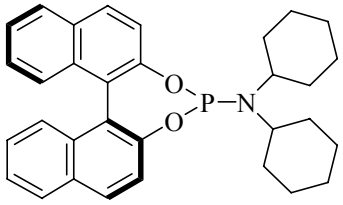
^{13} CNMR (Compound **47**)



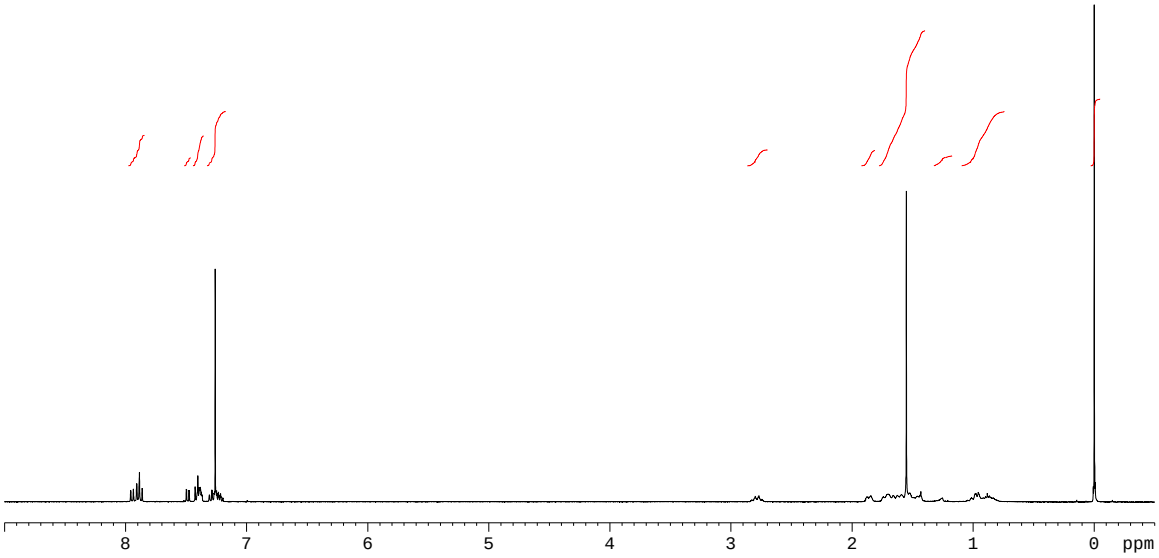


^{1}H NMR (Compound **31**)

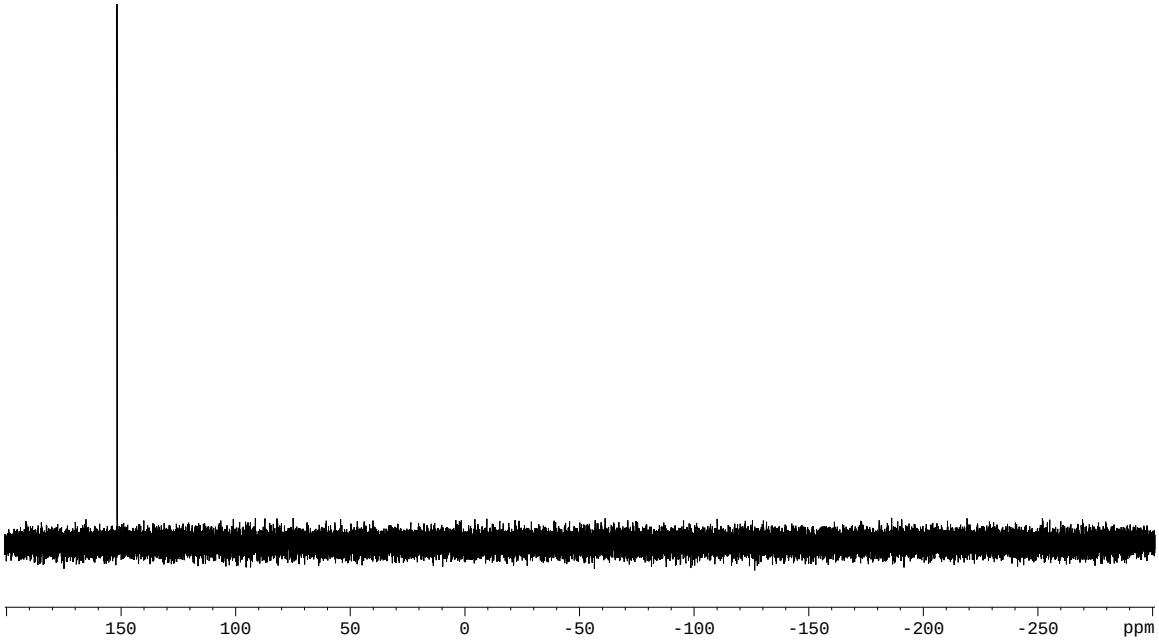


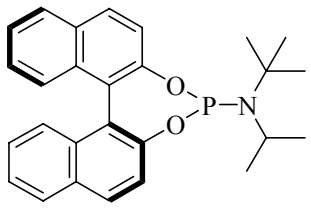


^{1}H NMR (Ligand **L12**)

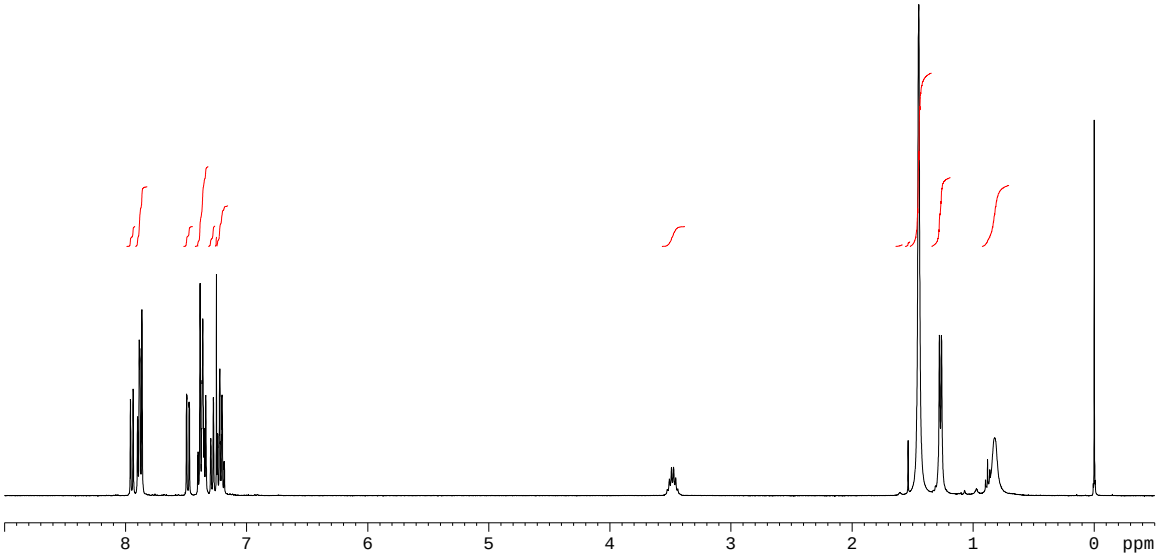


^{31}P NMR (Ligand **L12**)

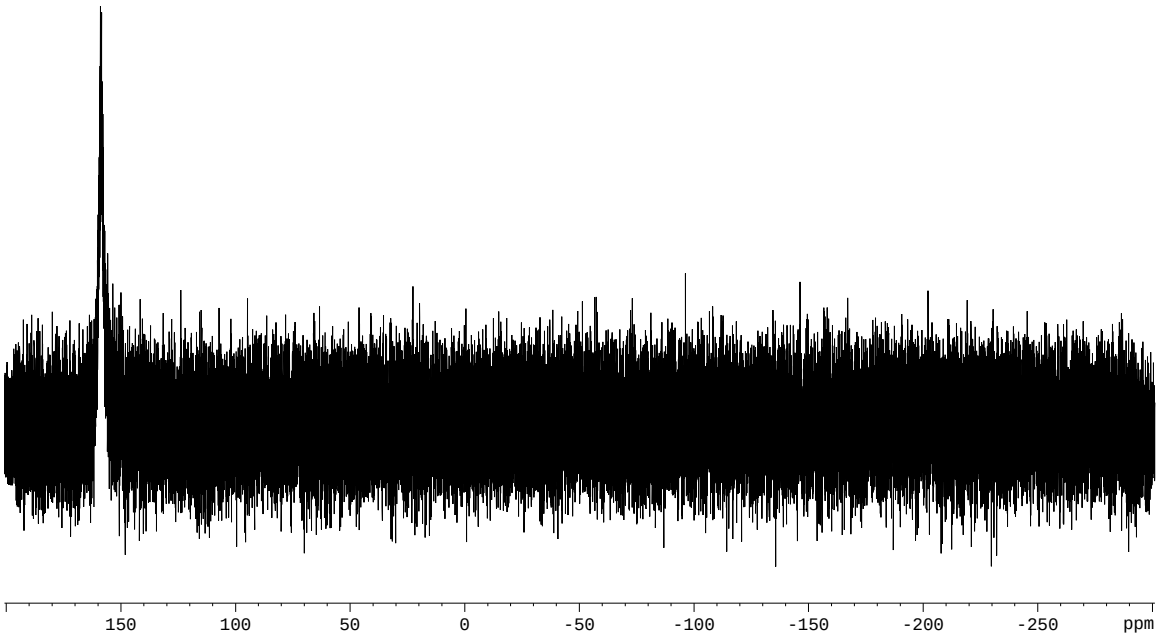


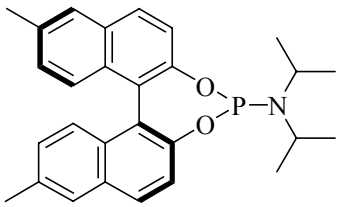


^{1}H NMR (Ligand **L13**)

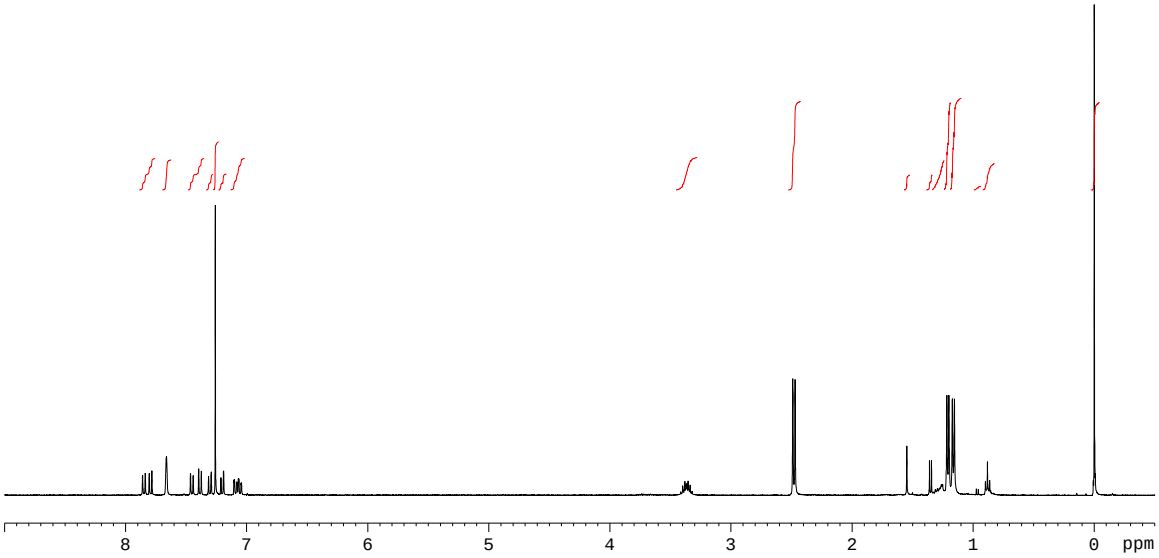


^{31}P NMR (Ligand **L13**)

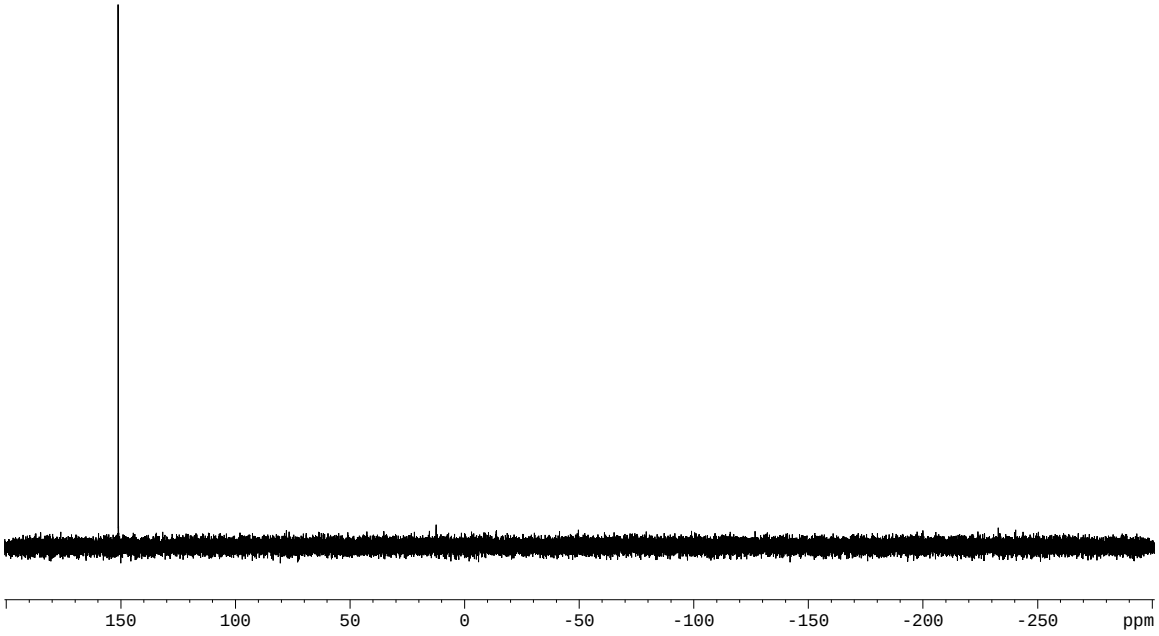


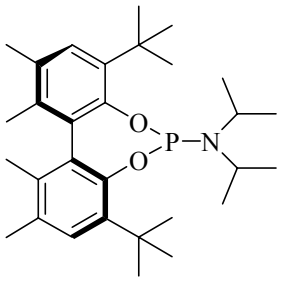


^{1}H NMR (Ligand **L14**)

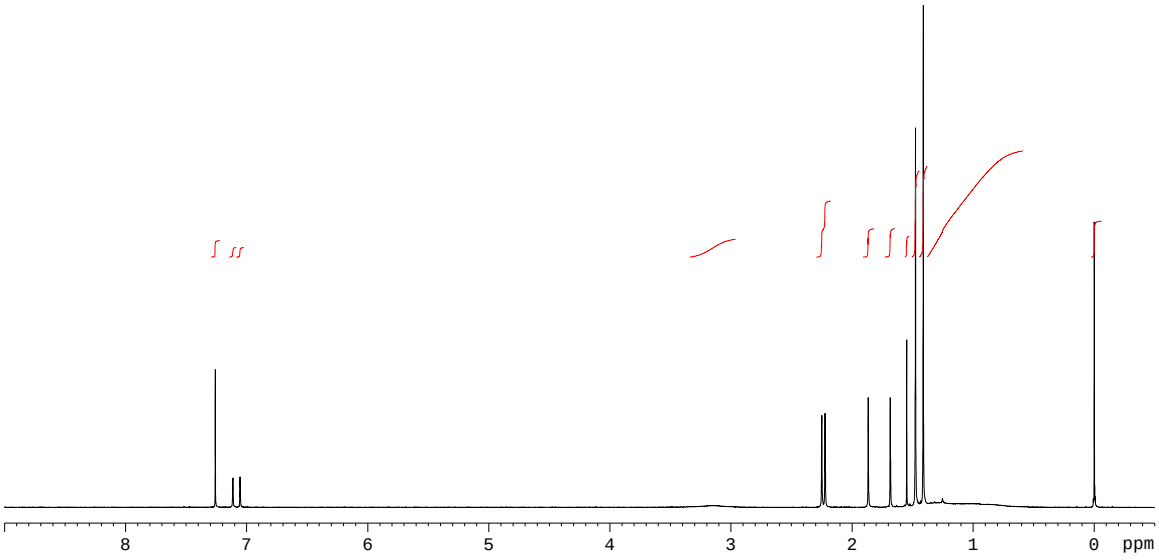


^{31}P NMR (Ligand **L14**)

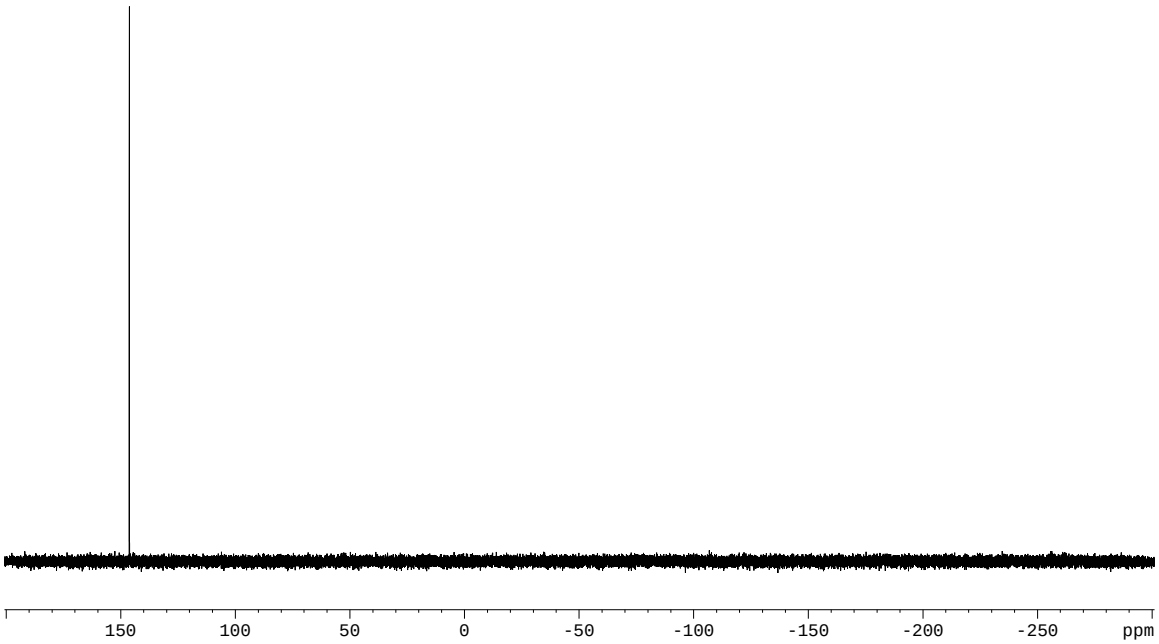




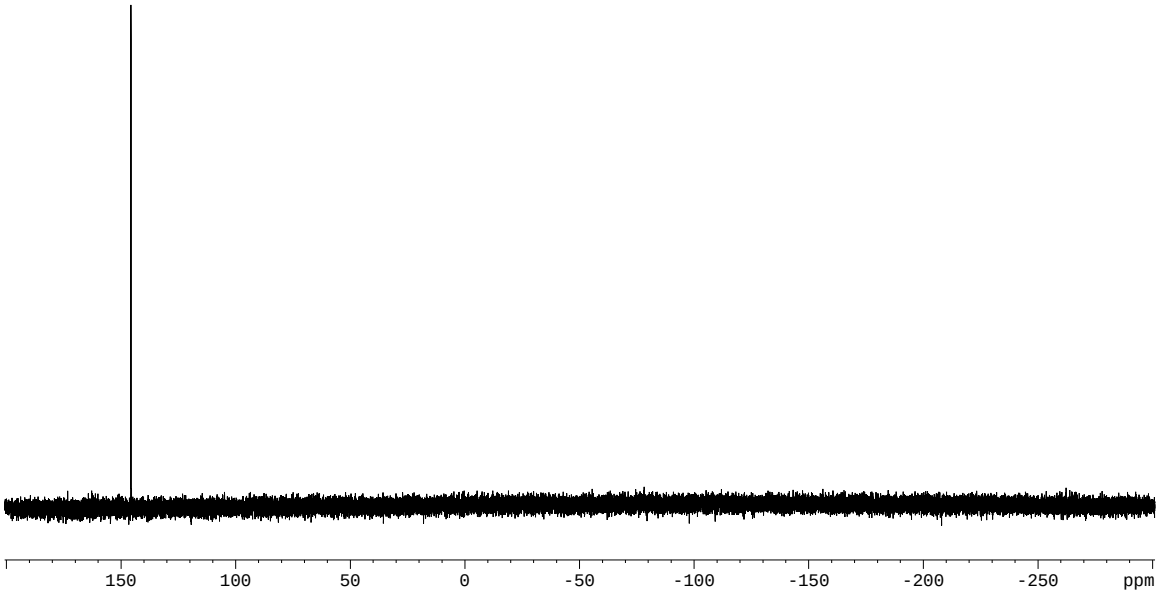
^{1}H NMR (Ligand **L15**)

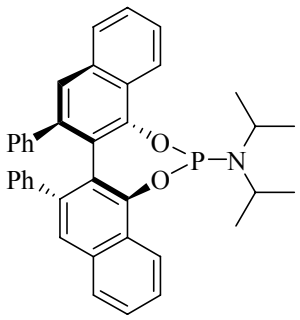


^{31}P NMR ($CDCl_3$) (Ligand **L15**)

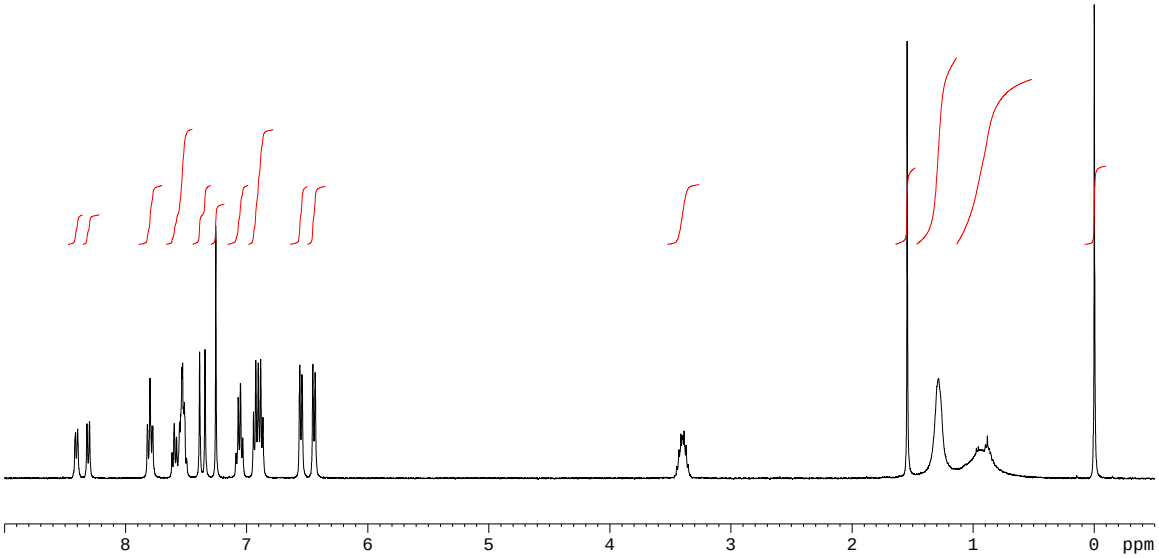


^{31}P NMR (C_6D_6) (Ligand **L15**)

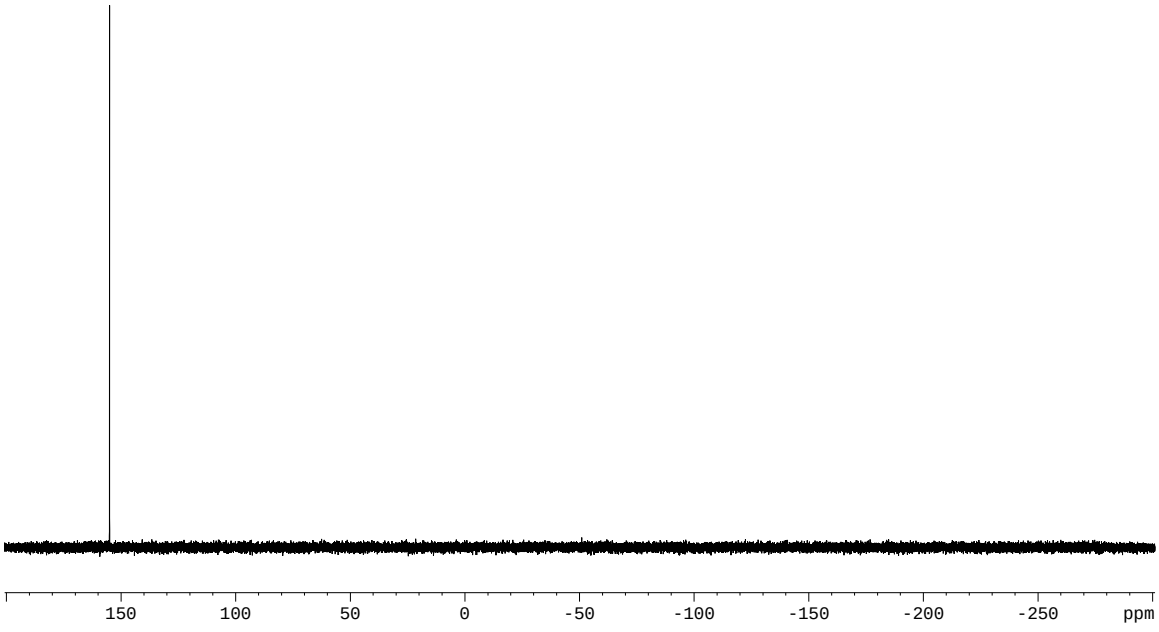


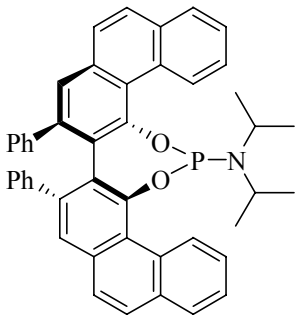


^{1}H NMR (Ligand **L16**)

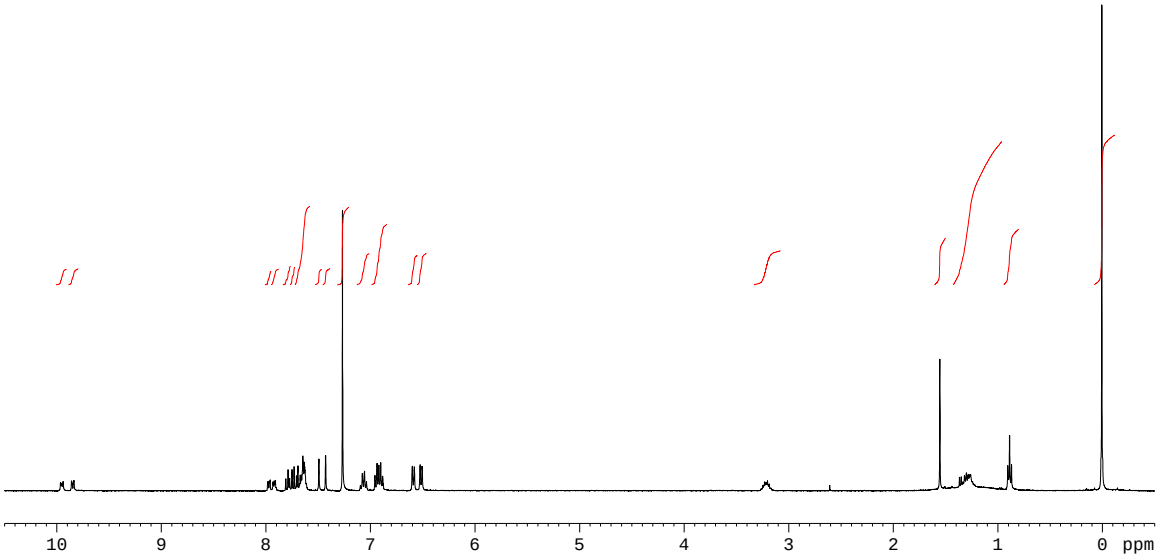


^{31}P NMR (Ligand **L16**)

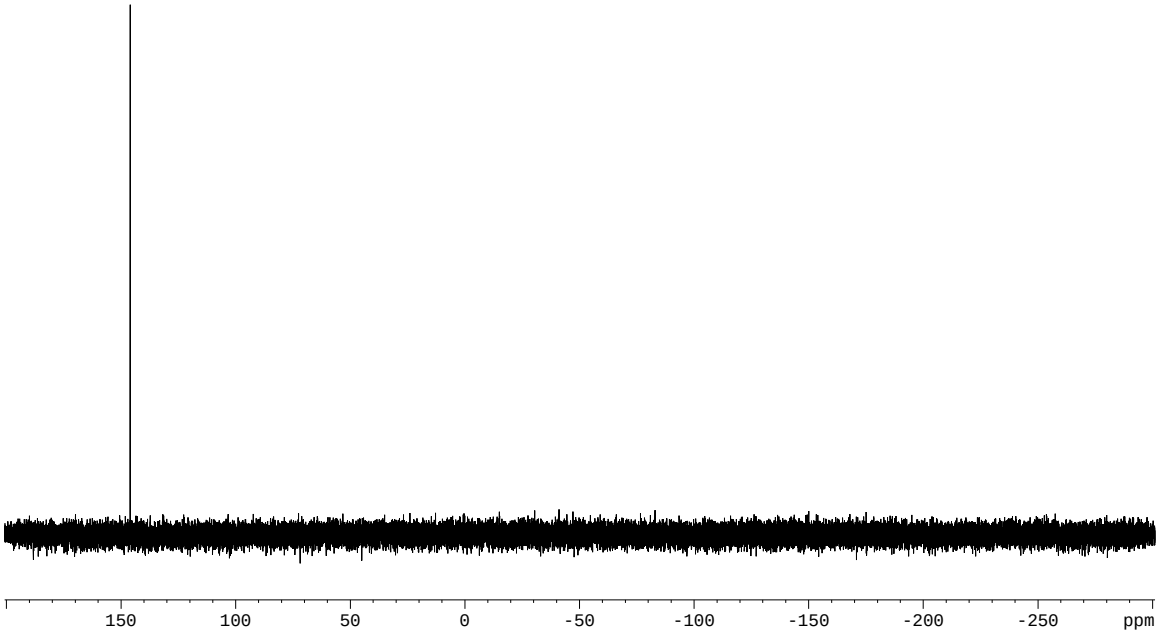


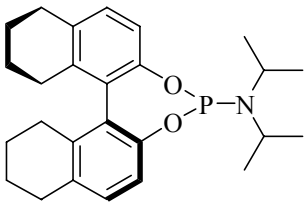


^{1}H NMR (Ligand **L17**)

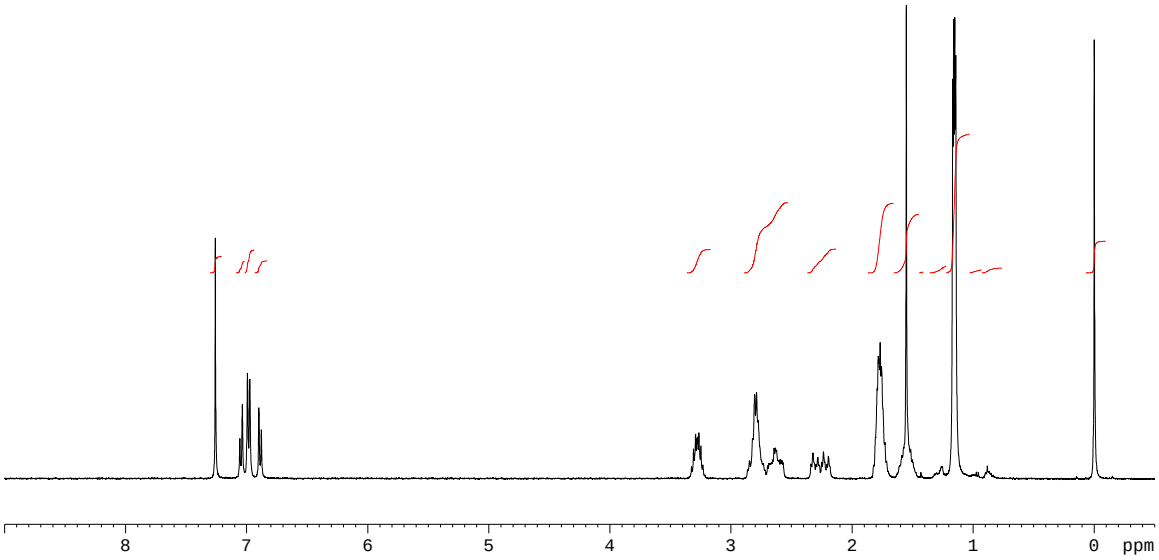


^{31}P NMR (Ligand **L17**)

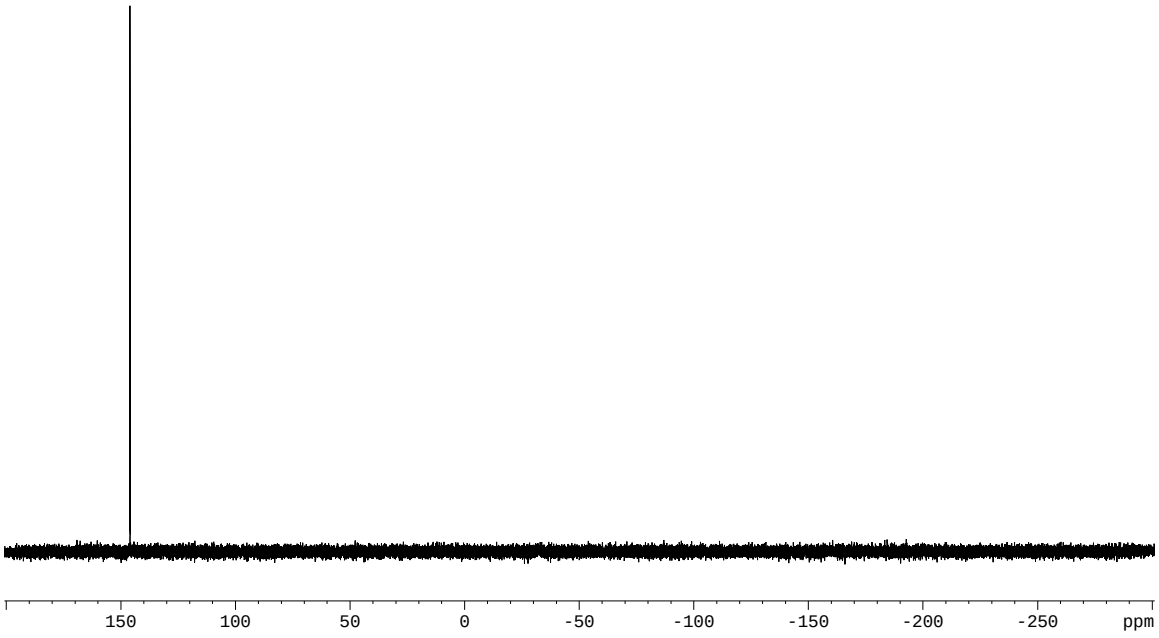




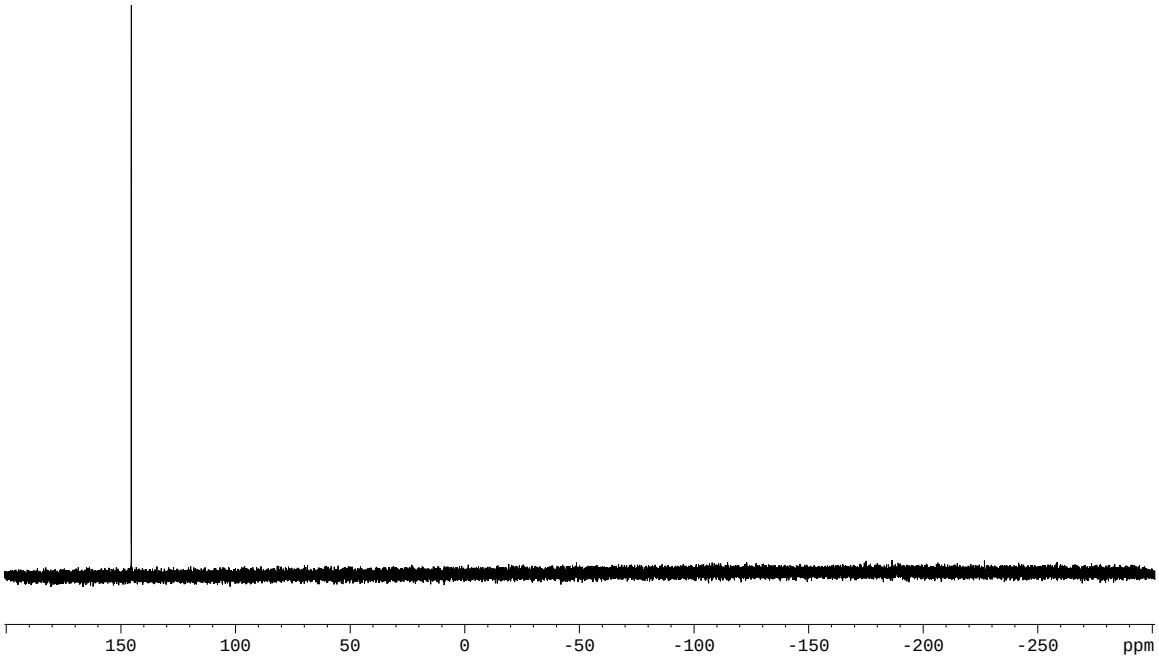
^{1}H NMR (Ligand **L18**)

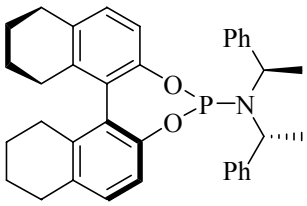


^{31}P NMR ($CDCl_3$) (Ligand **L18**)

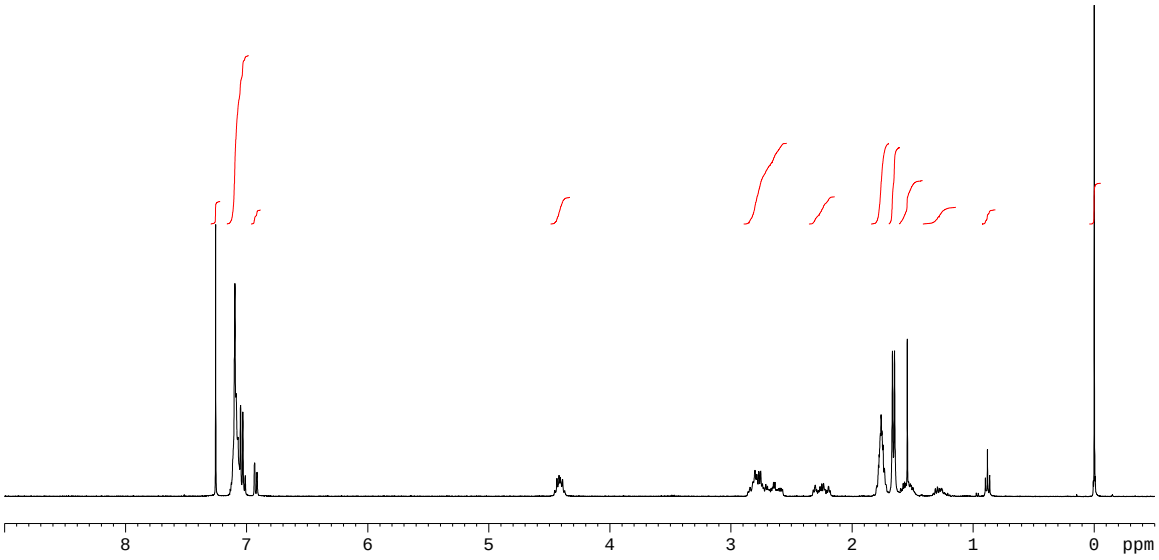


^{31}P NMR (toluene-d_8) (Ligand **L18**)

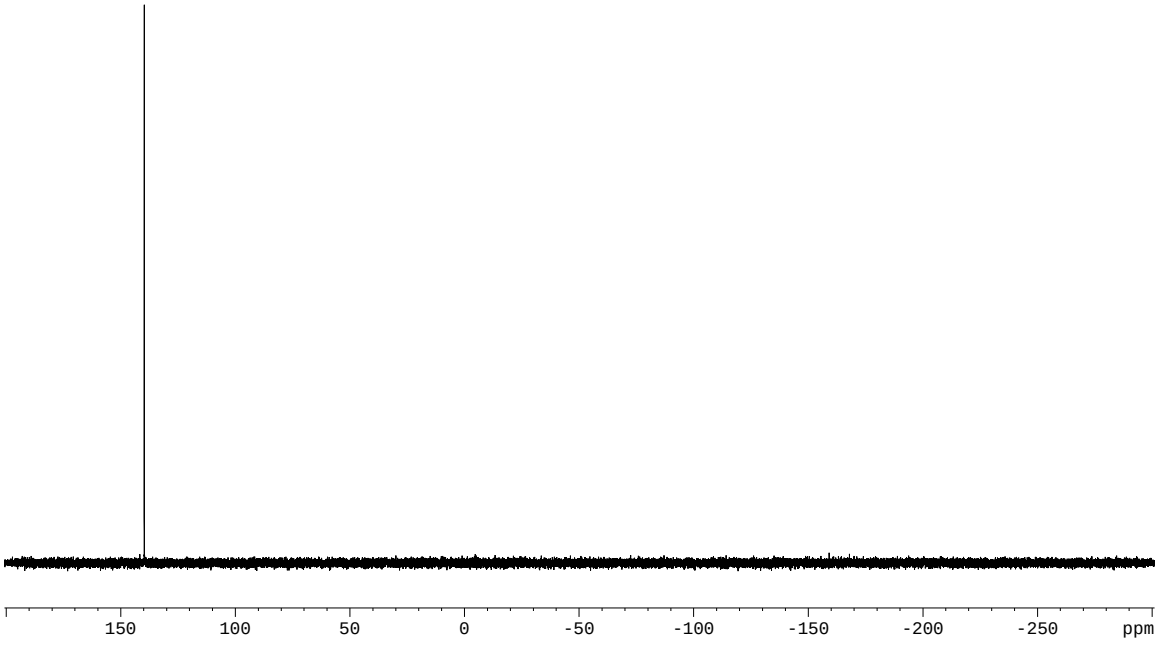


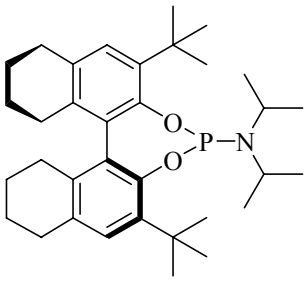


^{1}H NMR (Ligand **L19**)

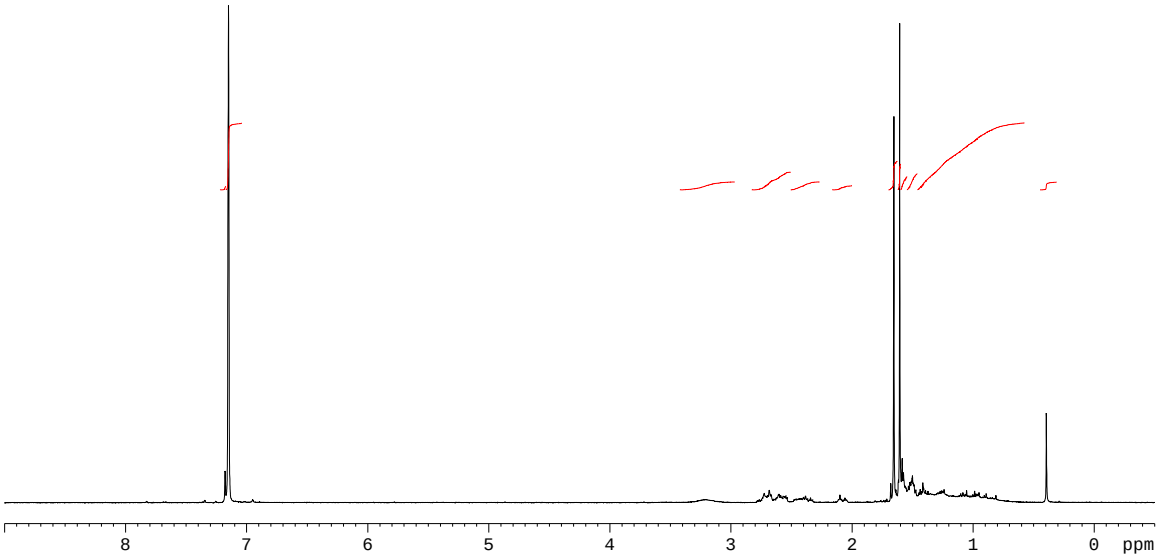


^{31}P NMR (Ligand **L19**)

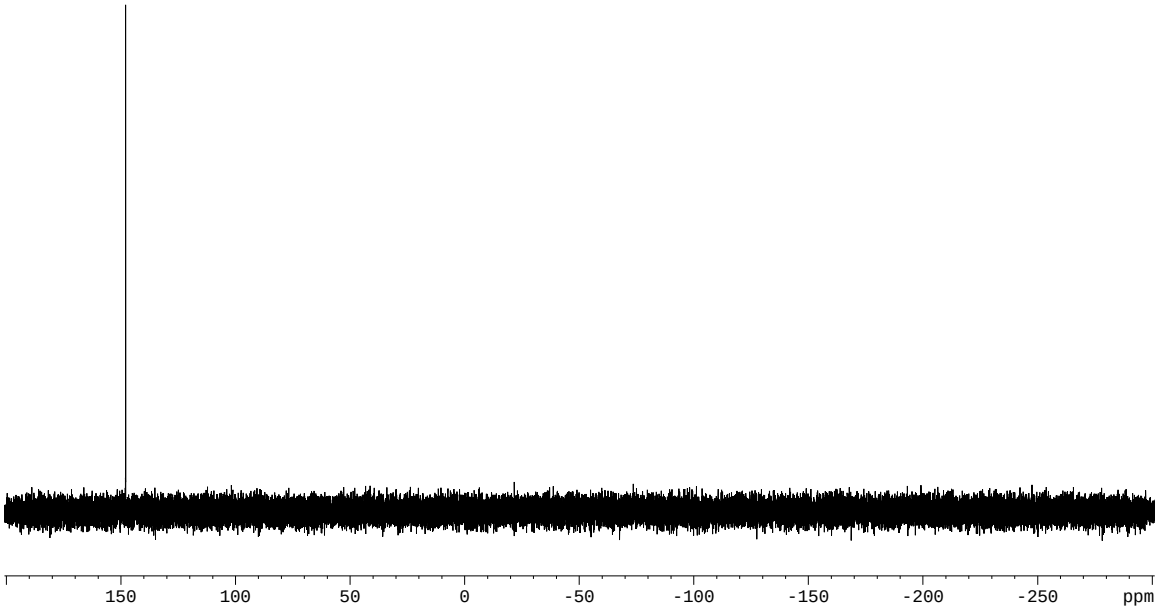


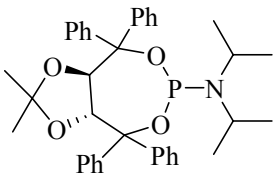


^{1}H NMR (Ligand **L20**)

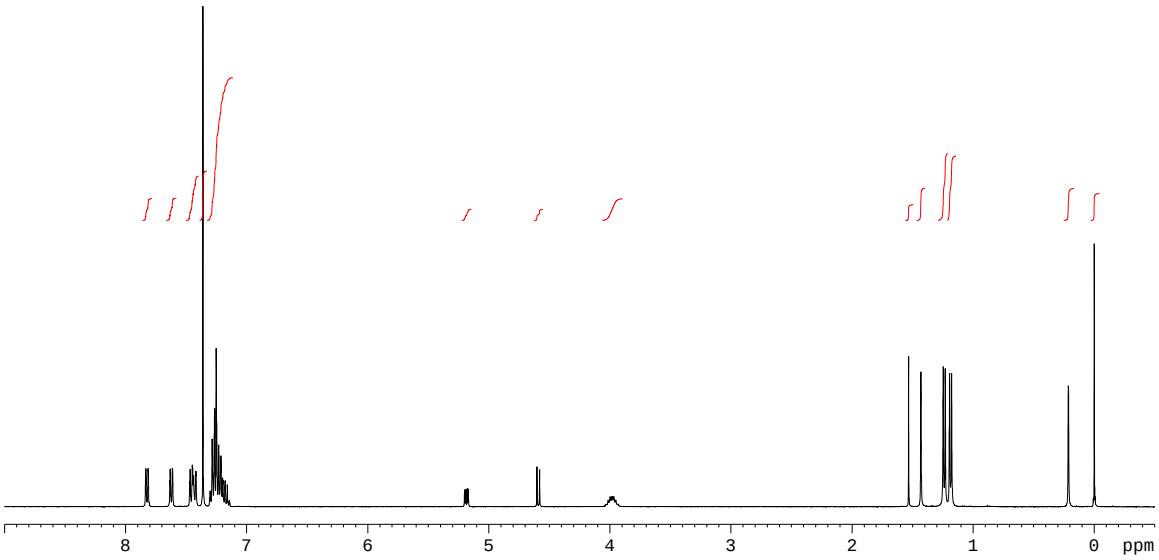


^{31}P NMR (Ligand **L20**)

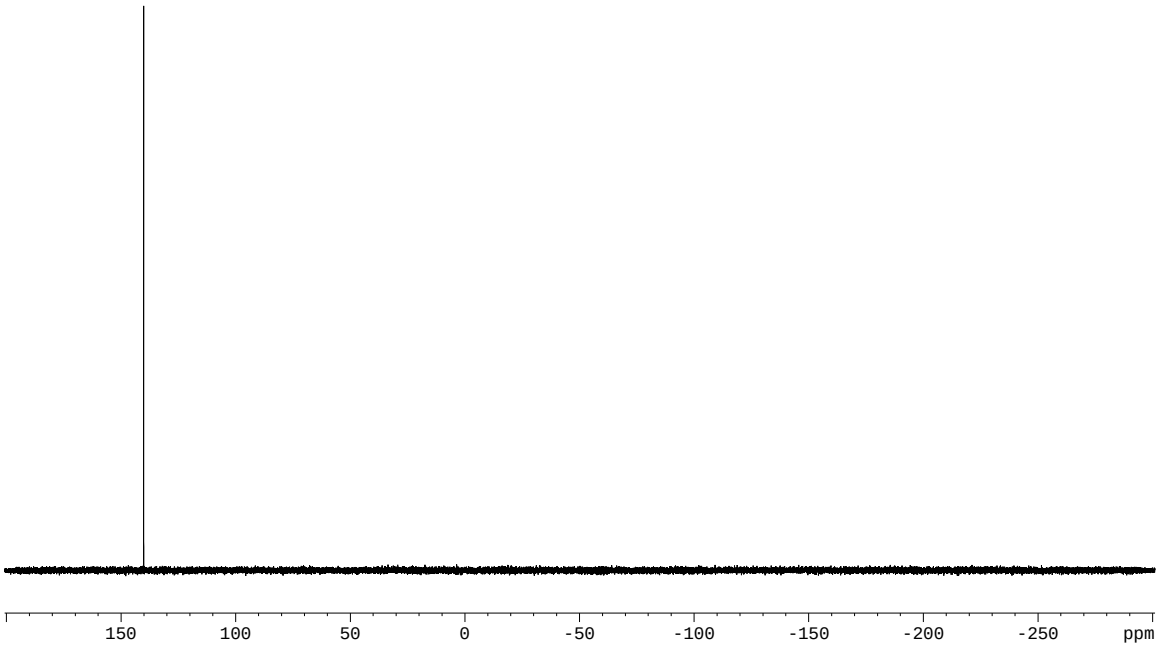


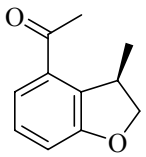


^{1}H NMR (Ligand **L21**)

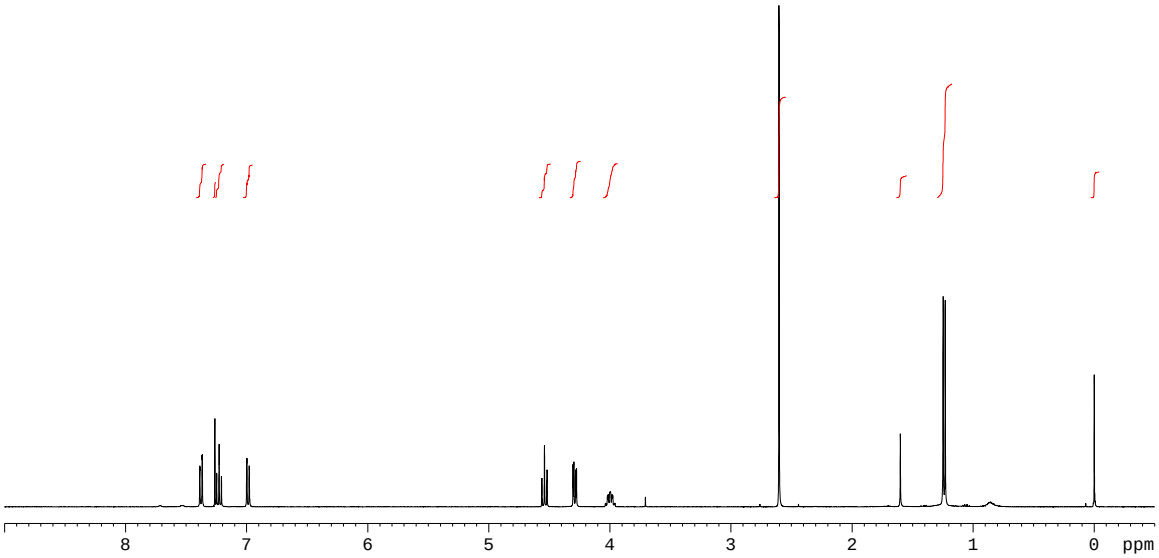


^{31}P NMR (Ligand **L21**)

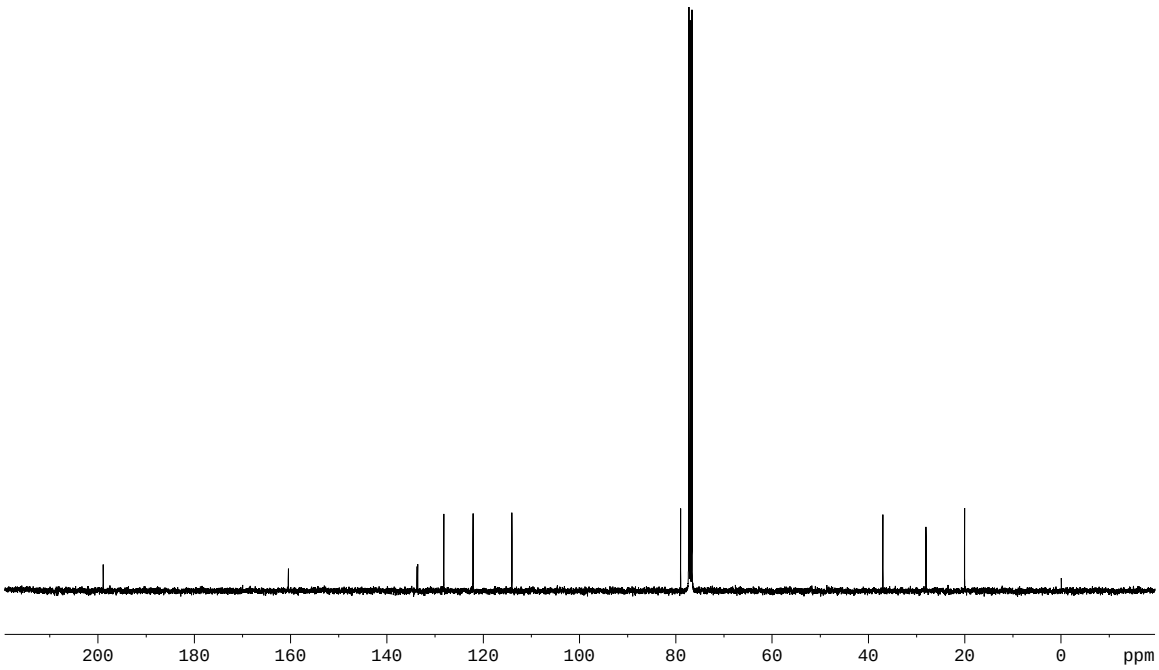


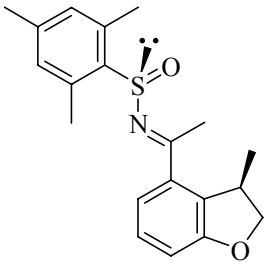


^{1}H NMR (Table 6, entry 1, Compound **48**)

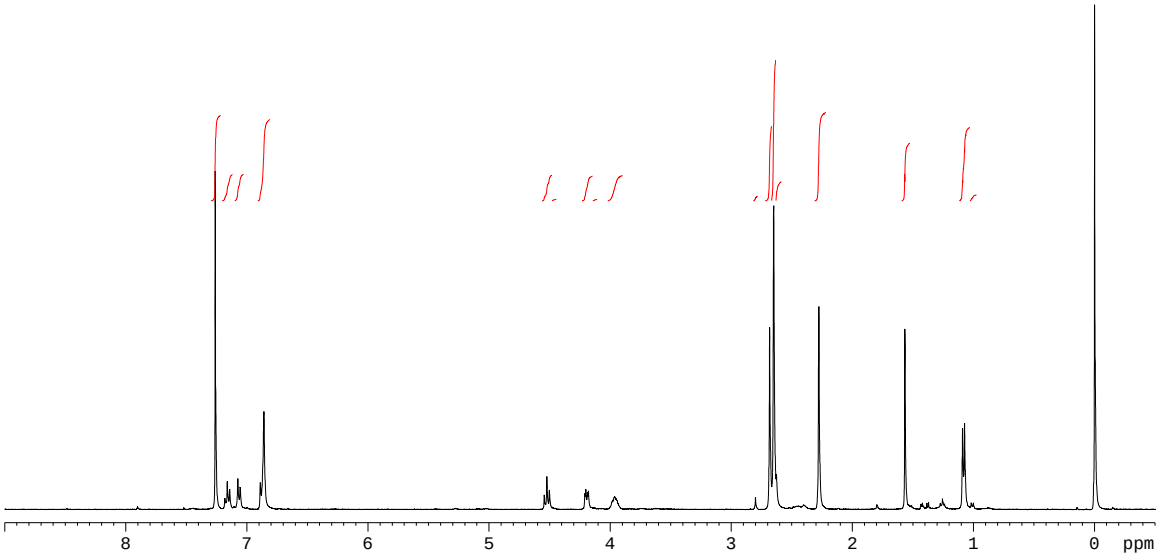


^{13}C NMR (Table 6, entry 1, Compound **48**)

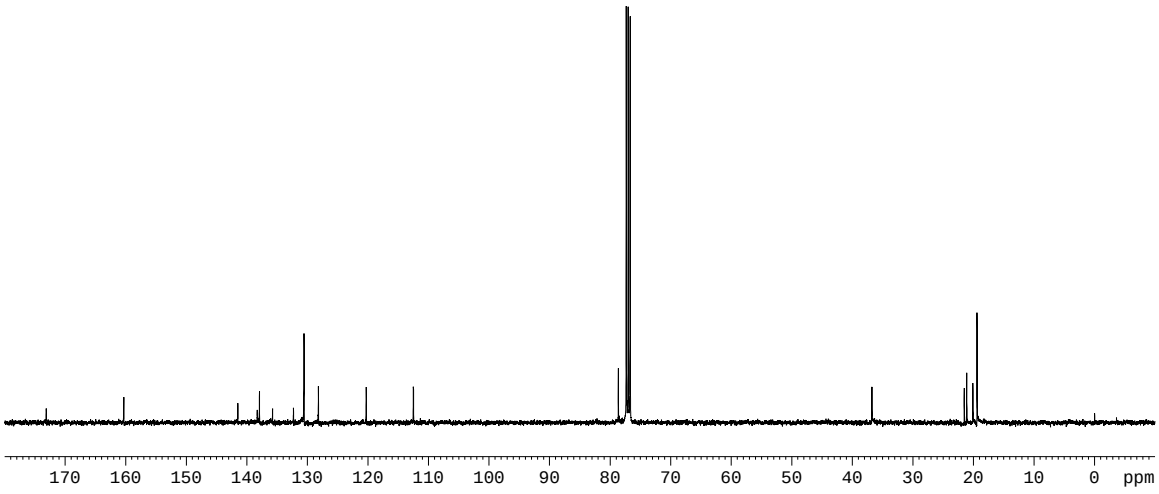


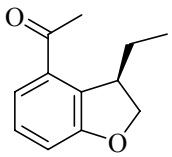


^{1}H NMR (Compound **33**)

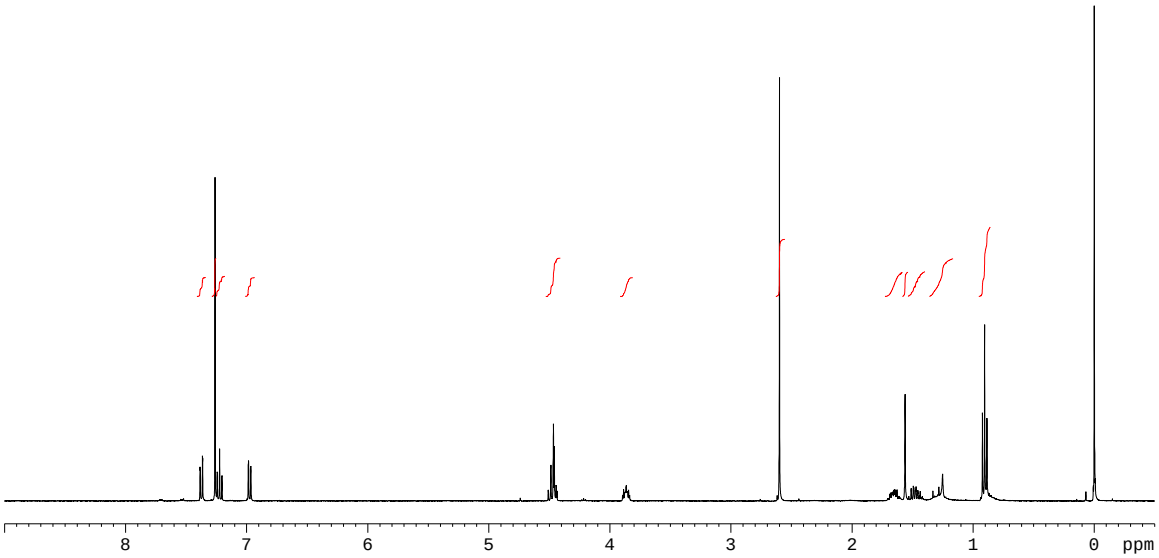


^{13}C NMR (Compound **33**)

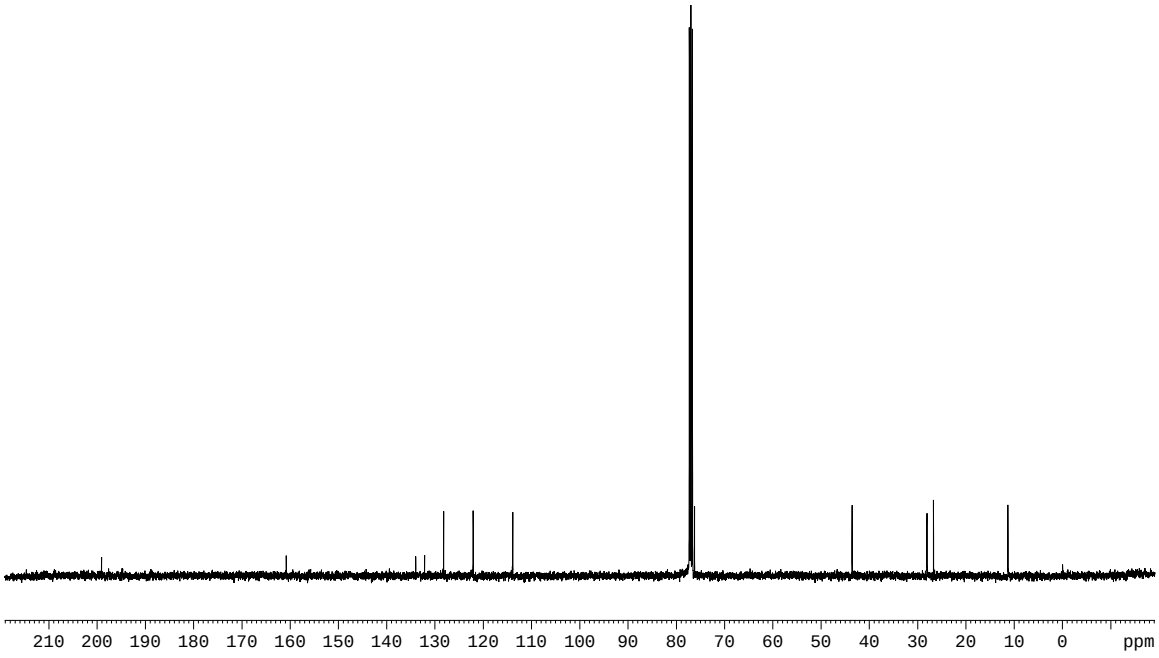


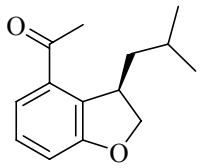


^{1}H NMR (Table 6, entry 2, Compound **49**)

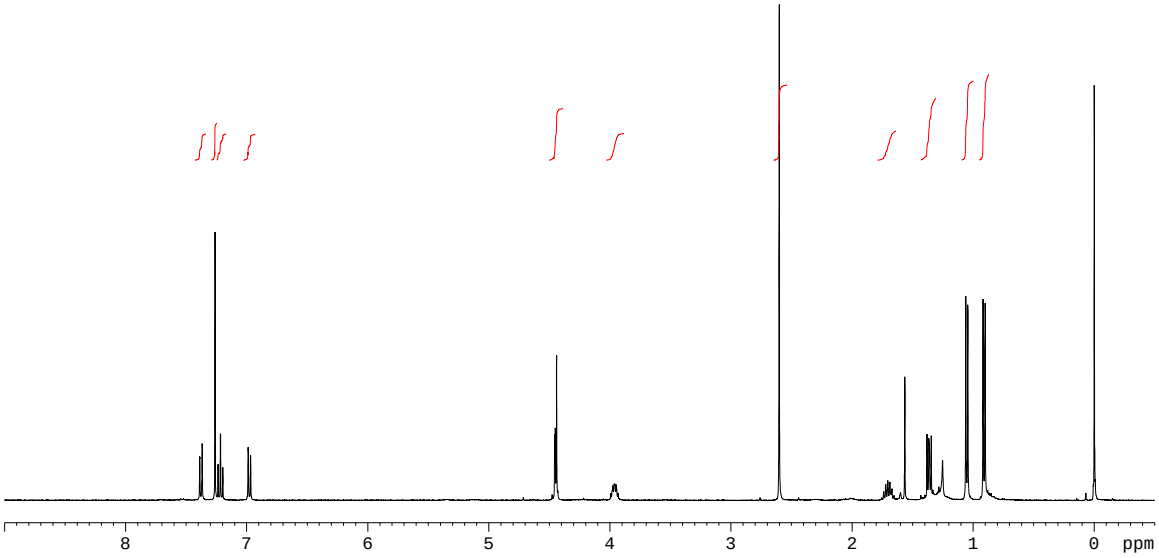


^{13}C NMR (Table 6, entry 2, Compound **49**)

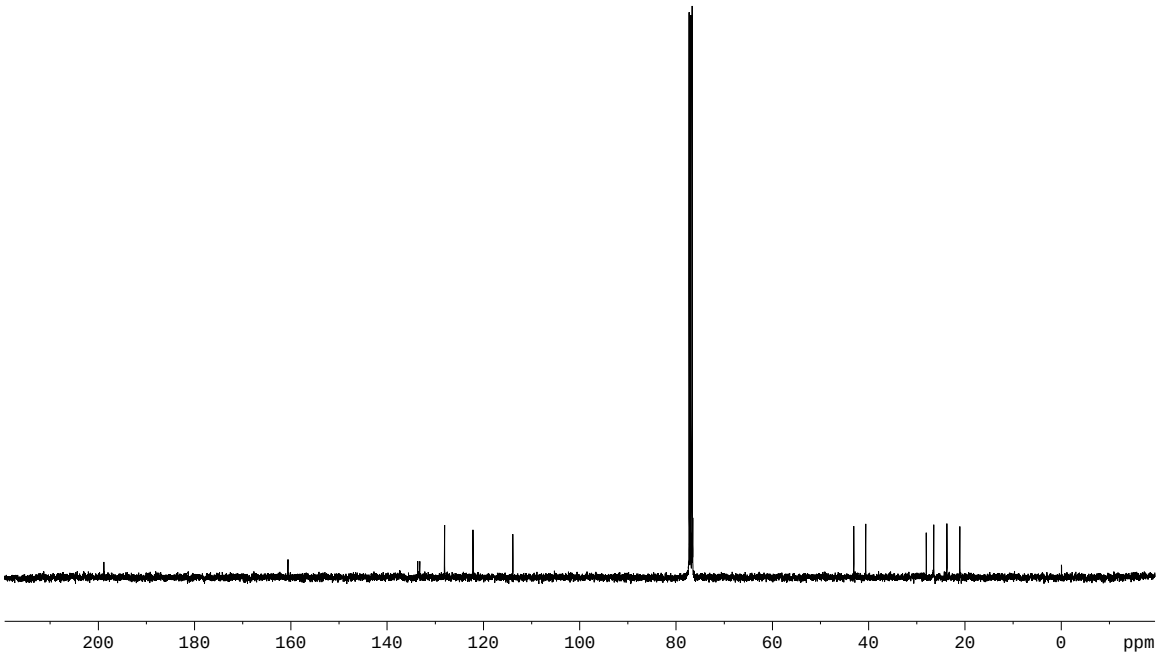


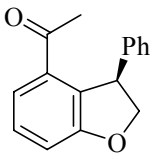


^{1}H NMR (Table 6, entry 3, Compound **50**)

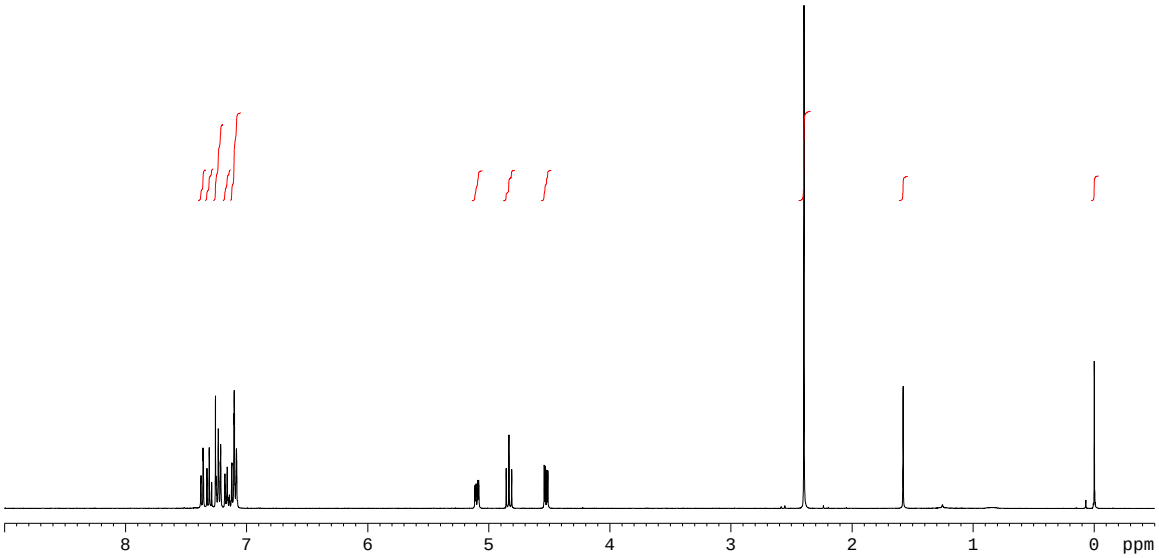


^{13}C NMR (Table 6, entry 3, Compound **50**)

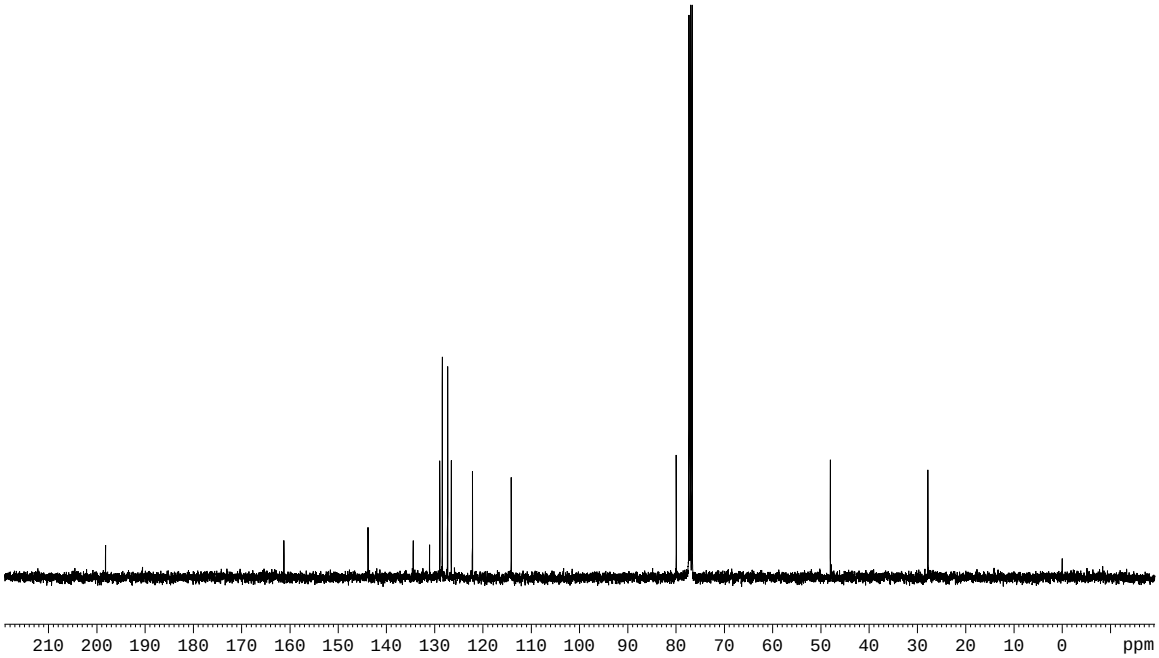


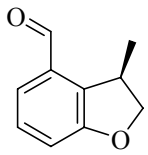


^{1}H NMR (Table 6, entry 4, Compound **51**)

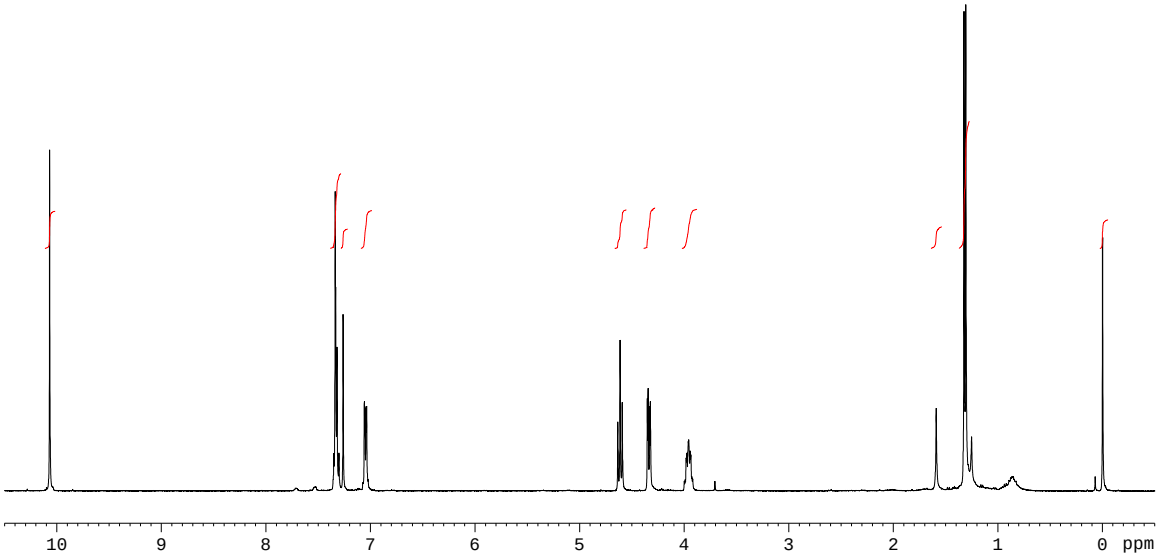


^{13}C NMR (Table 6, entry 4, Compound **51**)

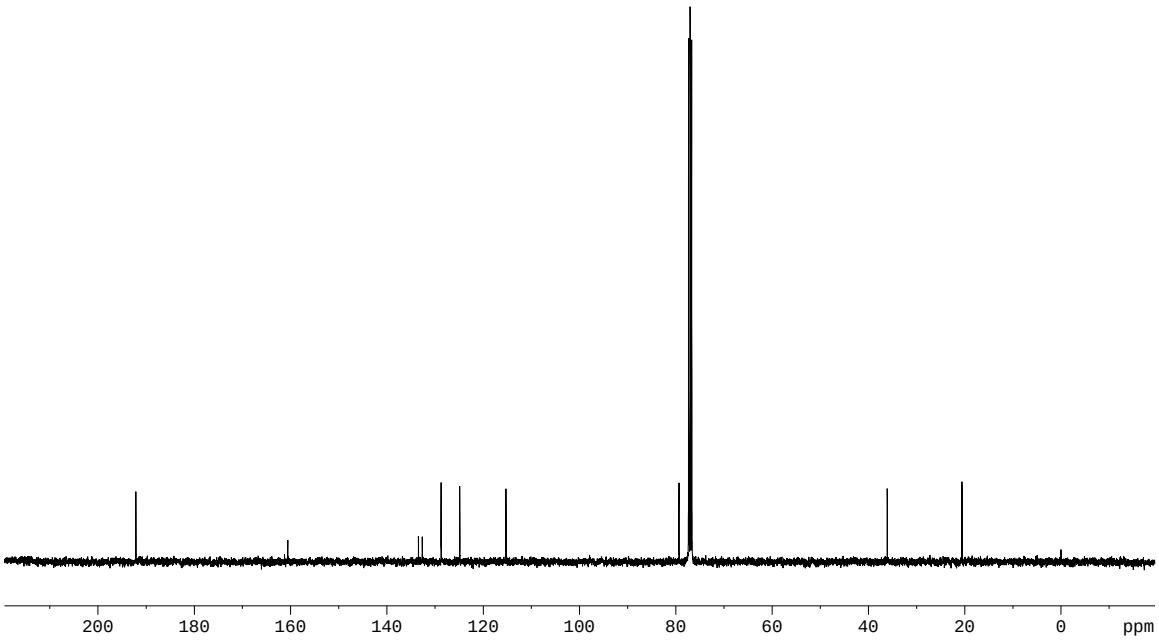


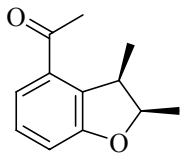


^{1}H NMR (Table 6, entry 7, Compound **52**)

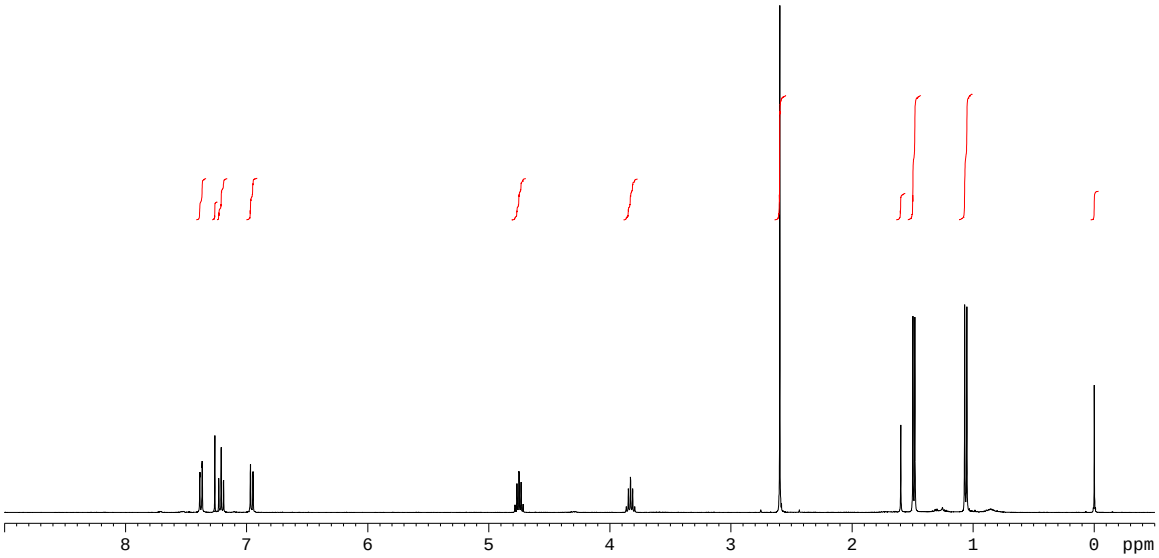


^{13}C NMR (Table 6, entry 7, Compound **52**)

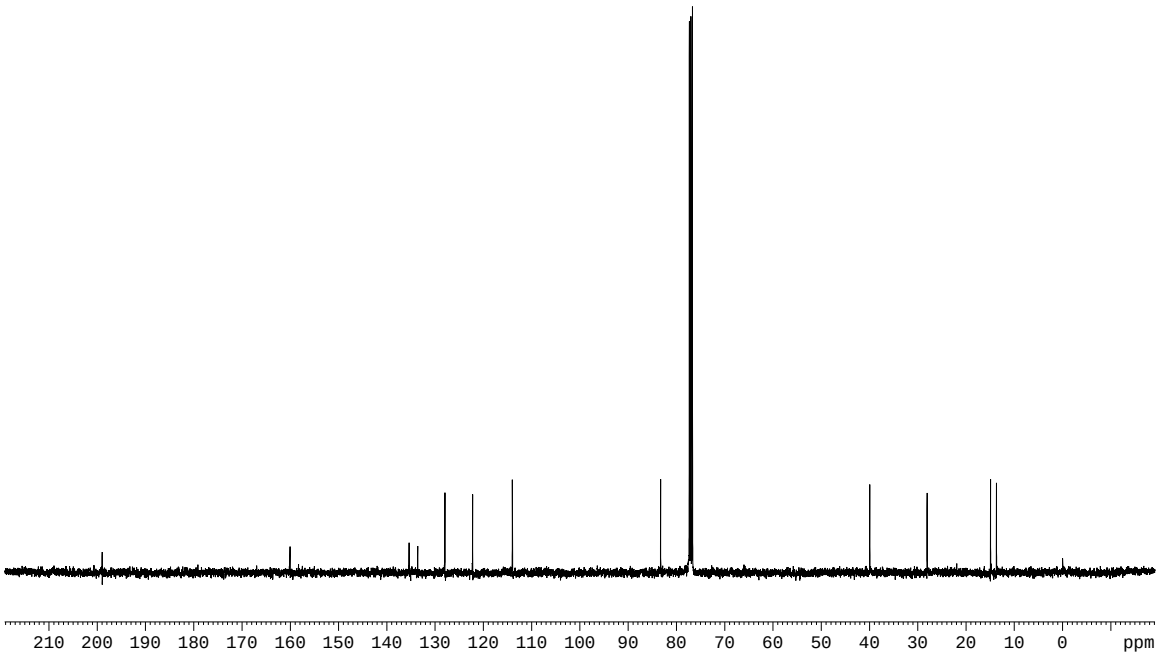




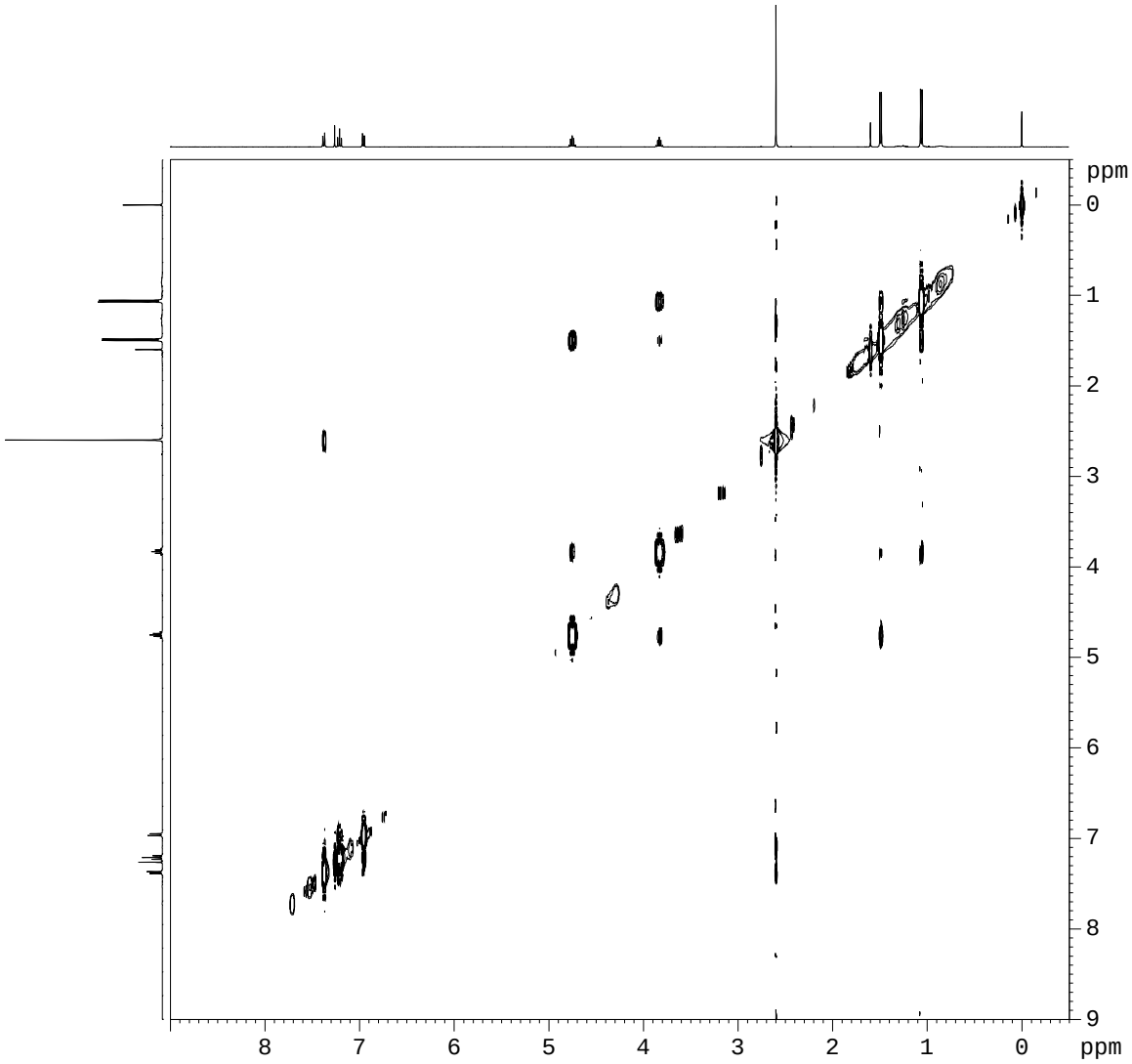
^{1}H NMR (Table 6, entry 8, Compound **53**)

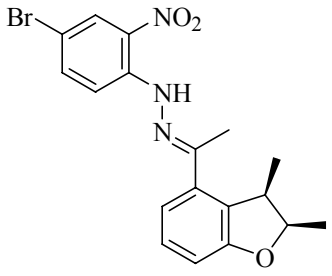


^{13}C NMR (Table 6, entry 8, Compound **53**)

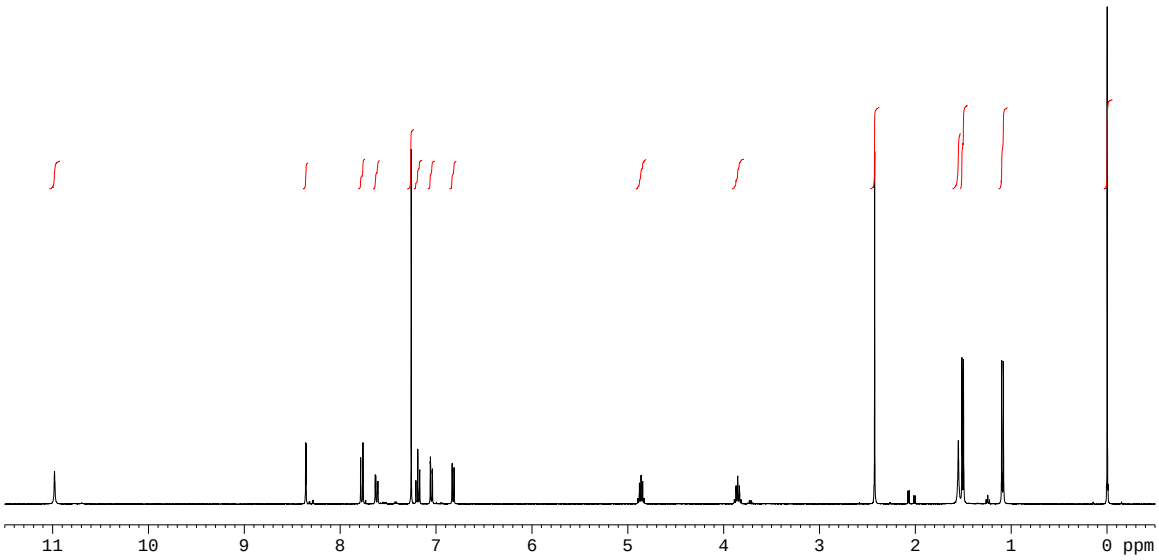


NOESY (Table 6, entry 8, Compound **53**)

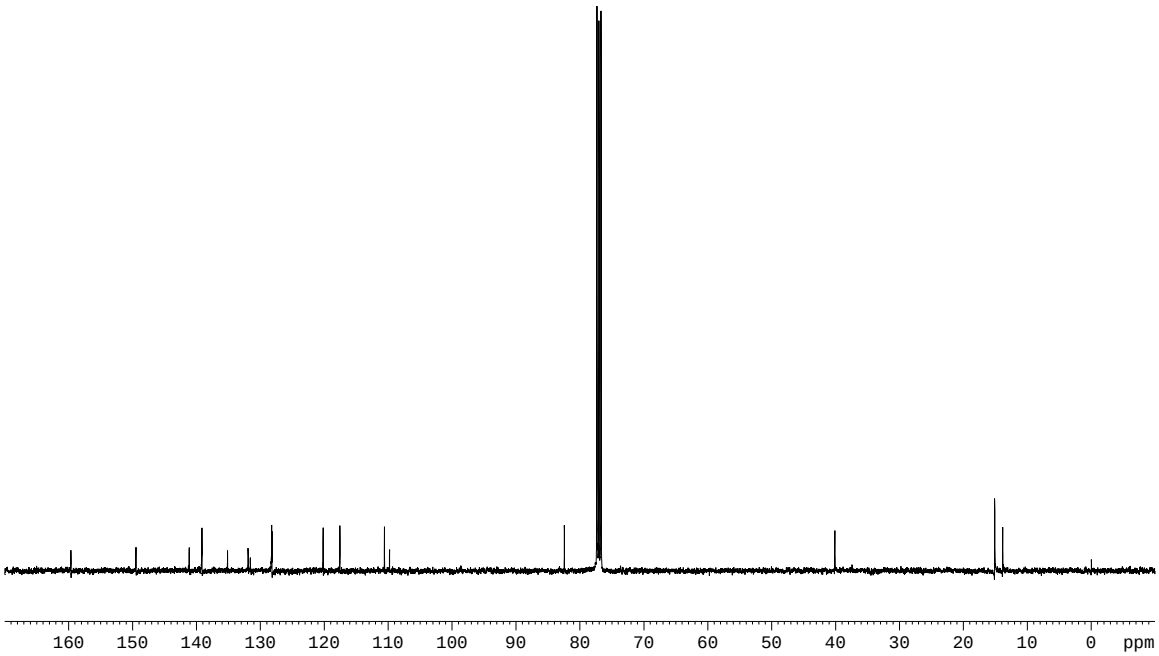


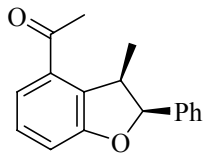


^{1}H NMR (Compound **34**)

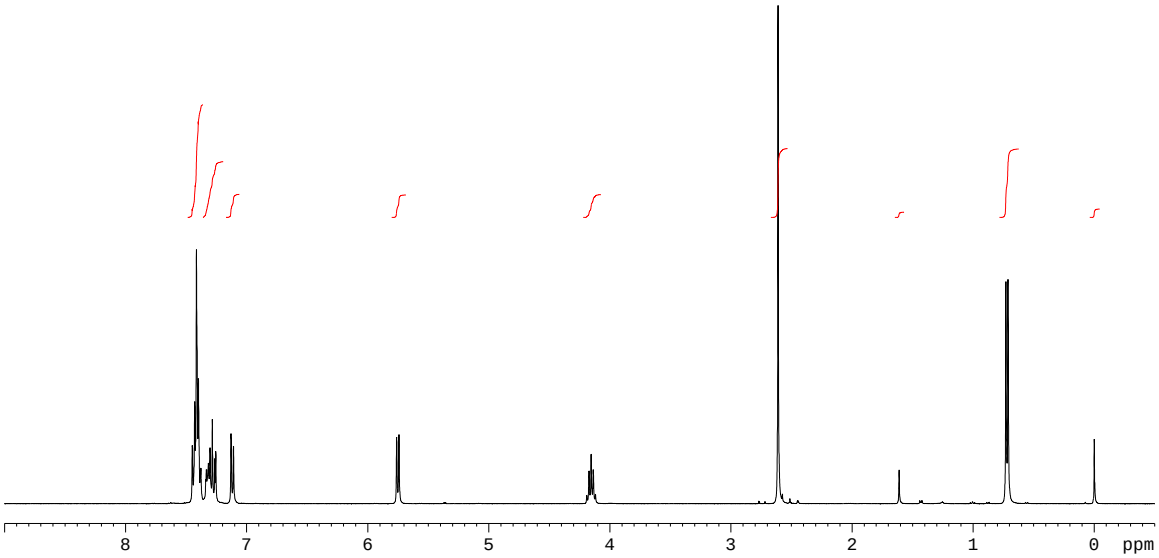


^{13}C NMR (Compound **34**)

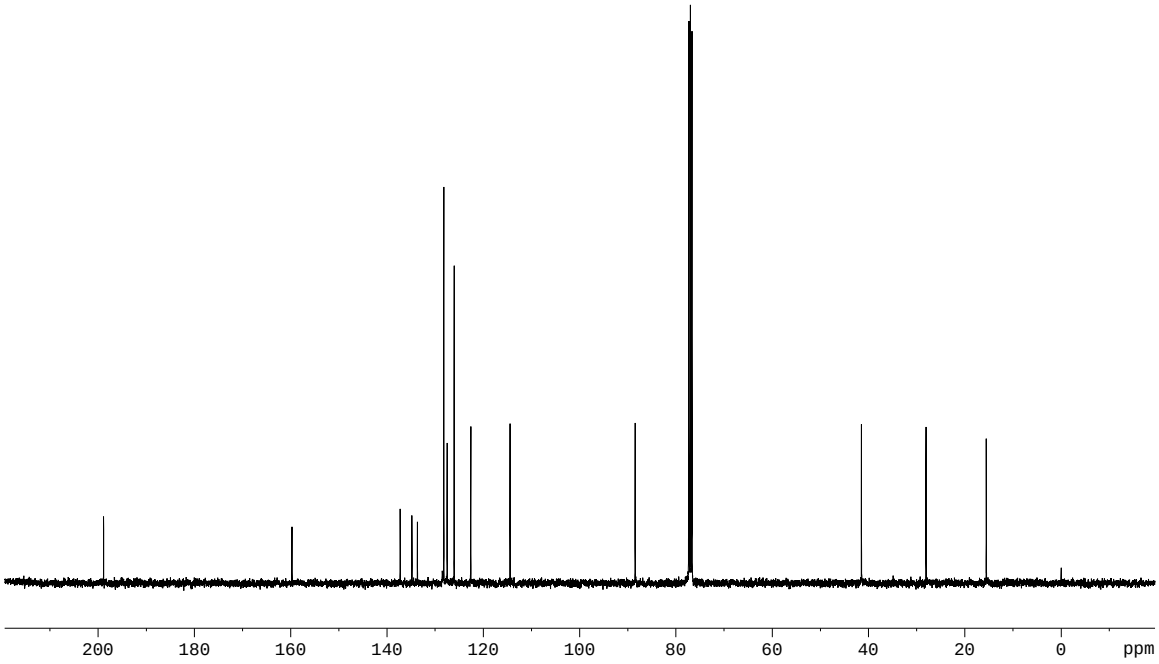




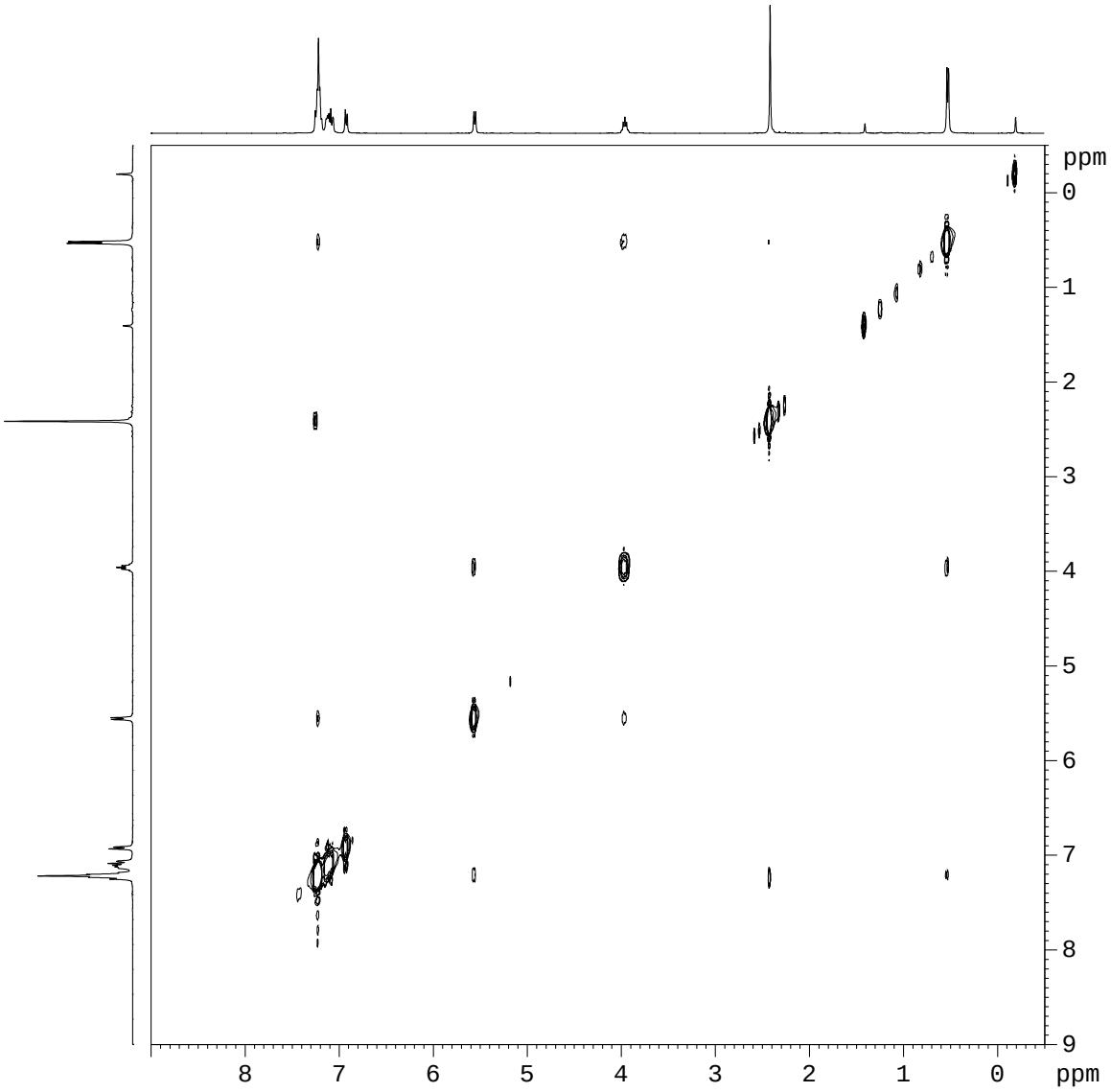
^{1}H NMR (Table 6, entry 9, Compound **54**)



^{13}C NMR (Table 6, entry 9, Compound **54**)



NOESY (Table 6, entry 9, Compound **54**)



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(15) Prepared in > 99% ee as described in Han, Z.; Krishnamurthy, D.; Grover, P; Fang, Q. K.; Pflum, D. A.; Senanayake, C. H. *J. Am. Chem. Soc.* **2002**, *124*, 7880–7001 and Schenkel, L. B.; Ellman, J. A. *J. Org. Chem.* **2004**, *69*, 1800–1802.
(16) Column chromatography was necessary in this case, otherwise the product was contaminated with the propyl ether aldehyde.