Electronic and bite angle effects in catalytic C-O bond cleavage of a lignin model compound using ruthenium xantphos complexes

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Electronic supporting information.

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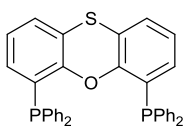
General experimental

All reactions were carried out using standard Schlenk techniques under an argon atmosphere or in an inert atmosphere glove-box at ambient temperature. Toluene and TMEDA were distilled from sodium, THF and diethyl ether were distilled from sodium/benzophenone, hexanes from sodium/benzophenone/triglyme and dichloromethane from CaH_2. 2-Phenoxy-1-phenylethanol,[1] 6,7-bis(diphenyl-phosphino)benzo[k,l]xanthene (**14e**)[2] and (10,10-di-methyl-10H-dibenzo[b,e][1,4]oxasiline-4,6-diyl)bis(diphenyl-phosphane) (**14b**)[3] were synthesised according to literature procedures. The intermediate (9,9-dimethyl-9H-xanthene-4,5-diyl)bis(dichlorophosphane) (**18**) was synthesised by modifying literature proceedures.[4-8] All reagents were purchased from commercial suppliers and used as received, unless otherwise noted. NMR spectra were obtained on a Bruker AVANCE III 500 spectrometer. For ^{1}H and ^{13}C NMR the chemical shifts were referenced to the residual solvent signal. All NMR shifts are reported as δ in parts per million (ppm). Mass spectrometry was carried out at National Mass Spectrometry Facility (NMSF-Swansea). Infrared spectra were measured on a Perkin Elmer 2000 FT-IR system and elemental analysis was carried out in the facility at London Metropolitan University. Gas chromatography was performed on a Thermo Scientific Trace GC Ultra equipment (split/splitless injector, Restek Rtx®-1, 100 % dimethyl polysiloxane column with 30 m × 0.25 mm × 0.25 µm dimensions, carrier gas – He, F.I.D. detector). Data was analysed using Chromeleon data system.

Synthesis of Xantphos-type ligands

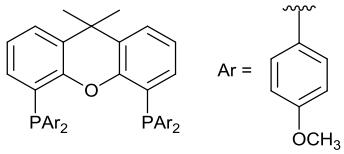
4,5-bis(diphenylphosphanyl)phenoxathiine (Thixantphos) – (14c)



At – 78 °C, *sec*-butyllithium (1.4 M in cyclohexane, 10.7 mL, 14.97 mmol) was added drop-wise to a stirred solution of phenoxathiin (1.00 g, 4.99 mmol) and TMEDA (2.25 mL, 14.97 mmol) in dry diethyl ether (50 mL). The reaction mixture was allowed to reach room temperature and stirred for 16 h. Then a solution of chlorodiphenylphosphine (2.92 mL, 14.97 mmol) in hexanes (15 mL) was added drop-wise to the reaction mixture, which was cooled to – 78 °C and stirred for 16 h. Solvents were removed *in vacuo* and the resulting

solid was dissolved in dichloromethane. This solution was washed with water (3 × 10 mL) and the organic fraction was dried with $MgSO_4$, filtered and the volatiles were removed *in vacuo*. Resulting solid was crystallised by dichloromethane to give a white crystalline solid. Yield = 2.2 g (77.5%). Mp 244-246 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24-7.34 (m, 12H), 7.23-7.17 (m, 8H), 7.10 (dd, *J* = 7.6, 1.5 Hz, 2H), 6.90 (t, *J* = 7.6 Hz, 2H), 6.50 (dq, *J* = 7.6, 1.6 Hz, 2H). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ – 17.86 (s). ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.2 (t, *J* = 10.1), 136.9 (t, *J* = 6.3), 133.9 (t, *J* = 10.6 Hz), 132.5, 128.3, 128.2 (t, *J* = 3.4 Hz), 128.0 (t, *J* = 12.6), 127.2, 124.6, 119.9. IR (KBr, cm^{-1}) 3052 (m), 2851 (w), 1565 (m), (1477 (m), 1433 (s), 1394 (s), 1227 (s), 1204 (m), 1089 (m), 1025 (m). MS: APCI $[M+H]^+$ Calcd.: 569.1252 Found: 569.1242 (%). Anal. Calcd. For $C_{36}H_{26}OP_2S$: C, 76.04; H, 4.61. Found: C, 75.97; H, 4.52.

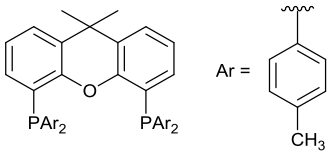
(9,9-dimethyl-9H-xanthene-4,5-diyl)bis(bis(4-methoxyphenyl)phosphane)–(5a)



At room temperature, a solution of 4-bromoanisole (0.75 mL, 6 mmol) in THF (4 mL) was added drop-wise to a stirred mixture of magnesium turnings (350 mg, 12 mmol) activated with 1,2-dibromoethane (0.05 mL, 0.06 mmol) in THF (3 mL). The reaction mixture was stirred for 3 h, filtered and added dropwise to a stirred solution of (9,9-dimethyl-9H-xanthene-4,5-diyl) bis(dichloro-phosphane) (**18**) (0.5 g, 1.2 mmol) in THF (10 mL) at 0 °C and allowed to warm to room temperature and stirred for another 3 h. The resulting mixture was hydrolysed with water (5 mL) and the solvents were removed *in vacuo*. The residue obtained was dissolved in dichloromethane and washed with dilute hydrochloric acid. The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 10 mL). Combined organic fractions were dried with $MgSO_4$, filtered and the dichloromethane removed to give a white crystalline solid. Yield = 0.52 g (62%). Mp 211-212 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.05 (dt, *J* = 8.7, 3.5 Hz, 8H), 6.92 (t, *J* = 7.6 Hz, 2H), 6.75 – 6.68 (m, 8H), 6.50 (dq, *J* = 7.6, 1.8 Hz, 2H), 3.76 (s, 12H), 1.61 (s, 6H). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ -20.46 (s). ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.6 (s), 142.6 (s), 135.1 (t, *J* =11.3 Hz), 131.8 (s), 129.88 (s), 128.5 (t, *J* = 5.0 Hz), 125.9 (s), 123.2 (s), 113.7 (t, *J* = 3.8 Hz), 54.9 (s), 31.7 (s). IR (KBr, cm^{-1}) 2961 (m), 2836 (w), 1593 (s), 1565 (m), 1495 (s), 1460 (m), 1459 (s), 1401 (s),

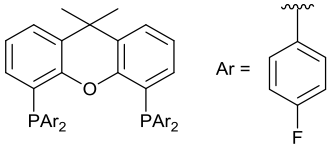
1285 (m), 1237 (s), 1176 (m), 1093 (m), 1028 (m), APCI $[M+H]^+$ Calcd.: 699.2424 Found: 699.2423. Anal. Calcd. For $C_{43}H_{40}O_5P_2$: C, 73.92; H, 5.77. Found: C, 73.86; H, 5.72.

(9,9-dimethyl-9H-xanthene-4,5-diyl)bis(di-p-tolylphosphane)–(5b)



This compound was synthesised similarly to **5a** using 4-bromotoluene (0.75 mL, 6.0 mmol). The white crude product was purified by flash column chromatography (eluent: 10% dichloromethane/hexanes) and crystallised from eluents. White crystalline solid; Yield = 0.45 g (59%). Mp 238-239 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.03 (dt, *J* = 7.4, 3.6 Hz, 8H), 6.98 (d, *J* = 7.7 Hz, 8H), 6.91 (t, *J* = 7.6 Hz, 2H), 6.52 (dq, *J* = 7.6, 1.7 Hz, 2H), 2.29 (s, 12H), 1.61 (s, 6H). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ -19.57 (s). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.2 (s), 141.9 (s), 133.5 (t, *J* =11.3 Hz), 130.0 (s), 129.0 (s), 128.5 (t, *J* = 5.0 Hz), 125.99 (s), 122.3 (s), 113.75 (t, *J* = 3.8 Hz), 54.99 (s), 31.2 (s), 21.3 (s). IR (KBr, cm^{-1}) 3012 (m), 2966 (m), 2920 (m), 1562 (m), 1494 (m), 1439 (m), 1405 (s), 1286 (m), 1241 (s), 1185 (m), 1109 (m), 1091 (m), 1019 (m). APCI $[M+H]^+$ Calcd.: 635.2627 Found: 635.2623. Anal. Calcd. For $C_{43}H_{40}OP_2$: C, 81.37; H, 6.35. Found: C, 81.33; H, 6.30.

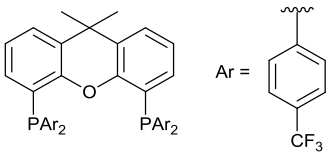
(9,9-dimethyl-9H-xanthene-4,5-diyl)bis(bis(4-fluorophenyl)phosphane)-(5c)



This compound was synthesised similarly to **5a** using 4-bromofluorobenzene (0.66 mL, 6.0 mmol). The white crude product was purified by flash column chromatography (eluent: 20% ethyl acetate/petroleum ether 40:60) and crystallised from the eluents. White crystalline solid; Yield = 0.36 g (46%). Mp 196-198 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.13 (m, 8H), 7.01 (t, *J* = 7.7 Hz, 2H), 6.99 – 6.91 (m, 8H), 6.49 (dq, *J* = 7.6, 1.8 Hz, 2H), 1.68 (s, 6H). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ -19.15 (s). ^{19}F {^{1}H} NMR (471 MHz, chloroform-*d*) δ -112.98 (s). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.2 (s), 141.9 (s), 133.5 (t, *J* =11.3 Hz), 130.0 (s), 129.0 (s), 128.5 (t, *J* = 5.0 Hz), 125.99 (s), 122.3 (s), 113.75 (t, *J* = 3.8 Hz), 54.99 (s), 31.2 (s), 21.3 (s). IR (KBr, cm^{-1}) 3066 (m), 2961 (m), 1896 (w), 1587 (s), 1493 (s), 1402 (s), 1296

(m), 1224 (s), 1158 (s), 1089 (m), 1031 (m), APCI $[M+H]^+$ Calcd.: 651.1624 Found: 651.1618. Anal. Calcd. For $C_{39}H_{28}OF_4P_2$: C, 72.00; H, 4.34. Found: C, 71.90; H, 4.40.

(9,9-dimethyl-9H-xanthene-4,5-diyl)bis(bis(4-(trifluoromethyl)phenyl)phosphane)-(5d)



This compound was synthesised similarly to **5a** using 4-bromobenzotrifluoride (0.85 mL, 6.0 mmol). The white crude product was purified by flash column chromatography (eluent: 20% dichloromethane/hexanes) and crystallised from the eluents. White crystalline solid; Yield = 0.53 g (52%). Mp 184-186 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 - 7.49 (m, 10H), 7.31 – 7.24 (m, 8H), 7.05 (t, *J* = 7.7 Hz, 2H), 6.49 (dq, *J* = 7.6, 1.8 Hz, 2H), 1.56 (s, 6H). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ -17.64 (s). ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$): δ -62.78 (s). ^{13}C NMR (126 MHz, $CDCl_3$): δ 152.3 (t, *J* =10.1 Hz), 141.29 (t, *J* = 8.8 Hz), 134.3 – 133.6 (m), 131.84 (s), 130.68 (t, *J* = 37.8 Hz), 127.38 (s), 125.14, 124.13, 123.34 (t, *J* = 8.8 Hz), 122.89 (s), 120.73 (s), 34.59 (s), 31.61(s). IR (KBr, cm^{-1}) 3066 (m), 2978 (m), 1925 (m), 1607 (m), 1407 (s), 1326 (s), 1238 (s), 1169 (s), 1133 (s), 1060 (s), 1015 (m). APCI $[M+H]^+$ Calcd.: 851.1497 Found: 851.1487. Anal. Calcd. For $C_{43}H_{28}OF_{12}P_2$: C, 60.72; H, 3.32. Found: C, 60.83; H, 3.39.

GC analysis details

Split ratio	10
Injector temperature	300
Carrier gas	He
Flow control	Flow rate
Flow rate	2.0 mL min^{-1}
Oven temperature programme	50 - 170 °C at 8 °C min^{-1}, then hold 2 min, then 170 – 300 °C at 20 °C min^{-1}, then hold 1 min
Column type	RXi – 1ms
Column dimensions	30 m x 0.25 mm x 0.25 µm
Detector type	Flame Ionisation Detector
Detector temp	300 °C

Representative GC chromatogram

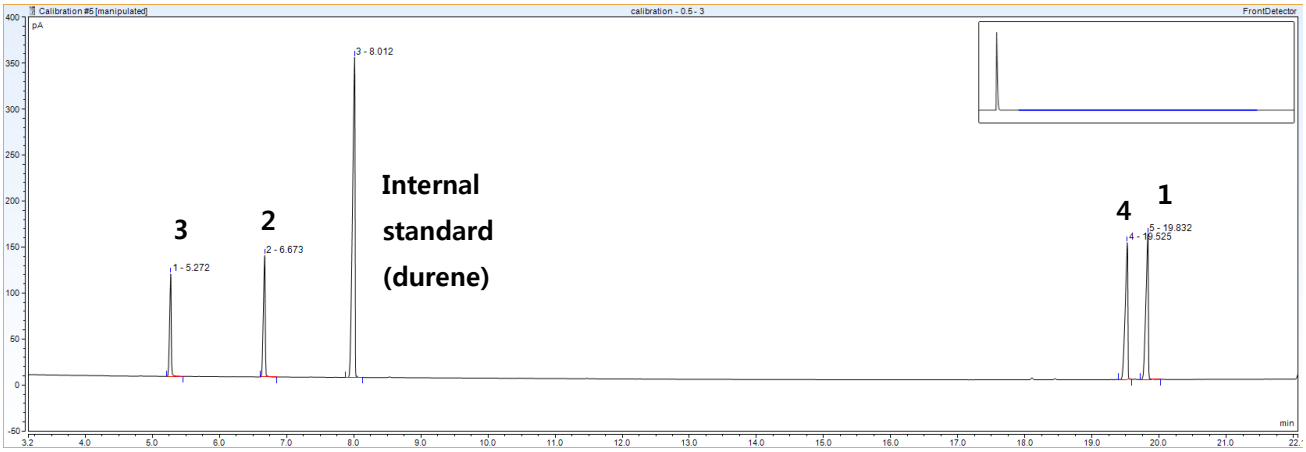


Figure S1. Representative GC chromatogram.

Kinetic profiles for rate dependence of (1) showing initial rates

Graphs showing conversion (%) vs. time (h) for the C-O cleavage of 2-phenoxy-1-phenylethanol (**1**) at varying substrate concentrations. Initial TOF (h^{-1}) taken from the gradient of the graphs and plotted in the text (Figure 2) and corrected for the given catalyst loading. The following plots show reactions during the initial rates period and are not full reaction profiles.

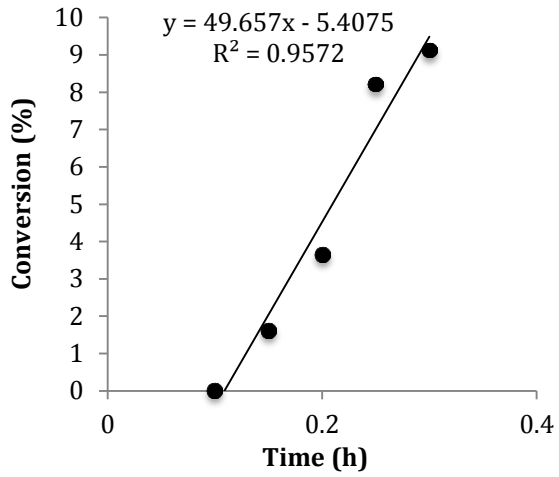


Figure S2. C-O cleavage rate dependence on the concentration of **1** (0.5 mmol). Conversion (%) vs. Time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol by $Ru(H)_2(CO)(PPh_3)_3$ and Xantphos (ligand **5**). Conditions: 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading and 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

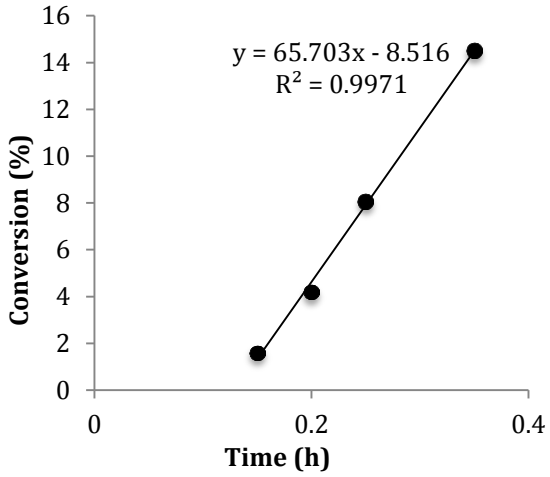


Figure S3. C-O cleavage rate dependence on the concentration of **1** (0.75 mmol). Conversion (%) vs. Time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol by $Ru(H)_2(CO)(PPh_3)_3$ and Xantphos (ligand **5**). Conditions: 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading and 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

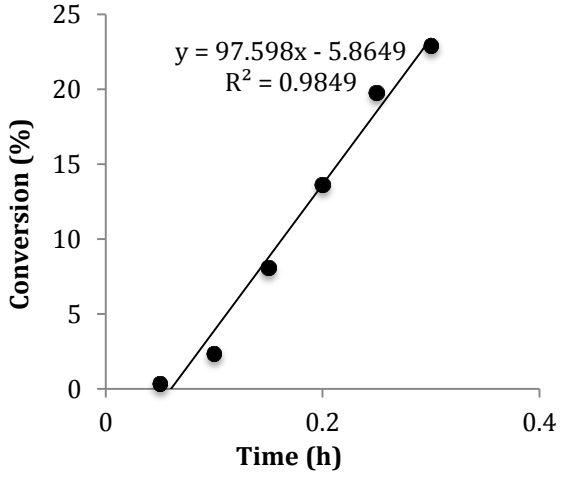


Figure S4. C-O cleavage rate dependence on the concentration of **1** (1.0 mmol). Conversion (%) vs. Time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol by $Ru(H)_2(CO)(PPh_3)_3$ and Xantphos (ligand **5**). Conditions: 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading and 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

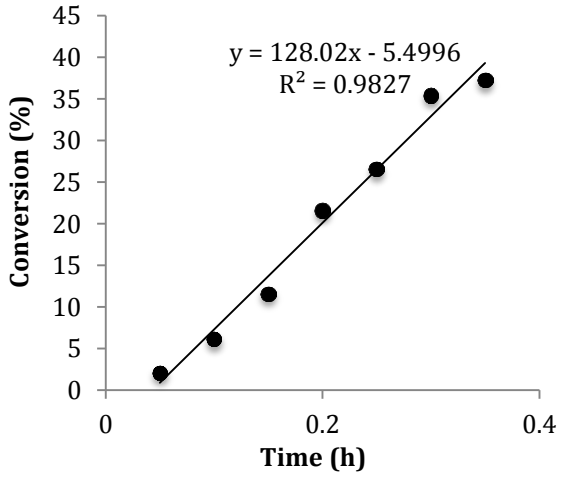


Figure S5. C-O cleavage rate dependence on the concentration of **1** (1.5 mmol). Conversion (%) vs. Time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol by $Ru(H)_2(CO)(PPh_3)_3$ and Xantphos (ligand **5**). Conditions: 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading and 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

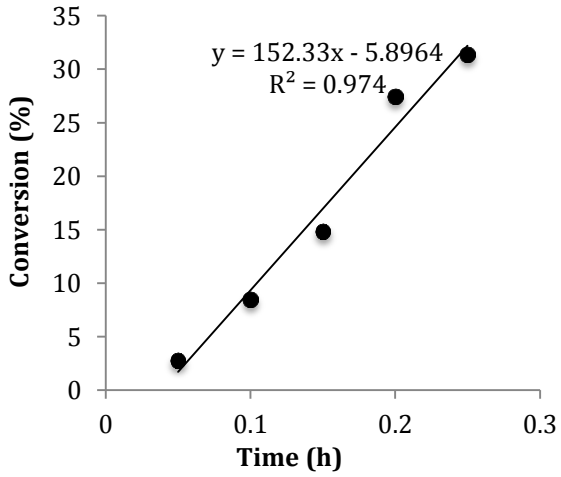


Figure S6. C-O cleavage rate dependence on the concentration of **1** (2.0 mmol). Conversion (%) vs. Time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol by $Ru(H)_2(CO)(PPh_3)_3$ and Xantphos (ligand **5**). Conditions: 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading and 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

Kinetic profiles for rate dependence of catalyst loading showing initial rates

Graphs showing conversion (%) vs. time (h) for the C-O cleavage of 2-phenoxy-1-phenylethanol (**1**) at varying substrate concentrations. Initial TOF (h^{-1}) taken from the gradient of the graphs and plotted in the text (Figure 3.) and corrected for the given catalyst loadings. The following plots show reactions during the initial rates period and are not full reaction profiles.

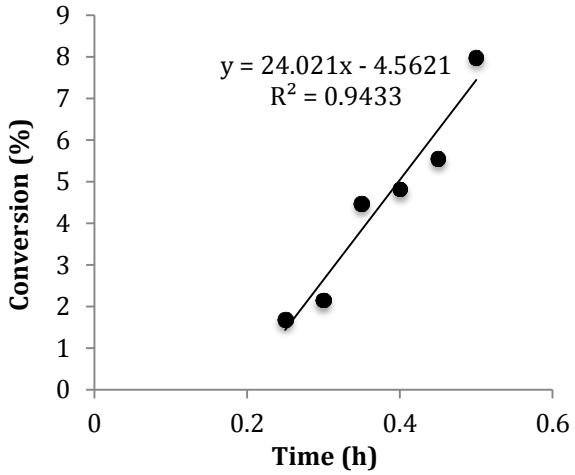


Figure S7. C-O cleavage rate dependence on the concentration of $Ru(H)_2(CO)(PPh_3)_3$/Xantphos catalyst (1 mol%). Conversion (%) vs. Time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with 0.01 mmol catalyst loading, 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

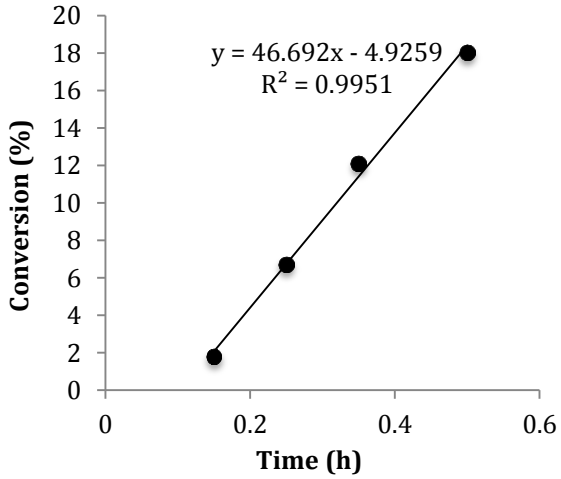


Figure S8. C-O cleavage rate dependence on the concentration of $Ru(H)_2(CO)(PPh_3)_3$/Xantphos catalyst (1.5 mol%). Conversion (%) vs. Time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.015 mmol catalyst loading, 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

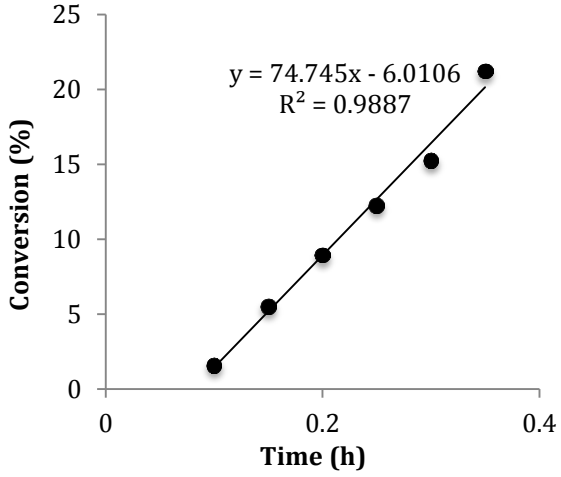


Figure S9. C-O cleavage rate dependence on the concentration of $Ru(H)_2(CO)(PPh_3)_3$/Xantphos catalyst (2 mol%) Conversion (%) vs. catalyst loading for C-O bond cleavage of 2-phenoxy-1-phenylethanol. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading, 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

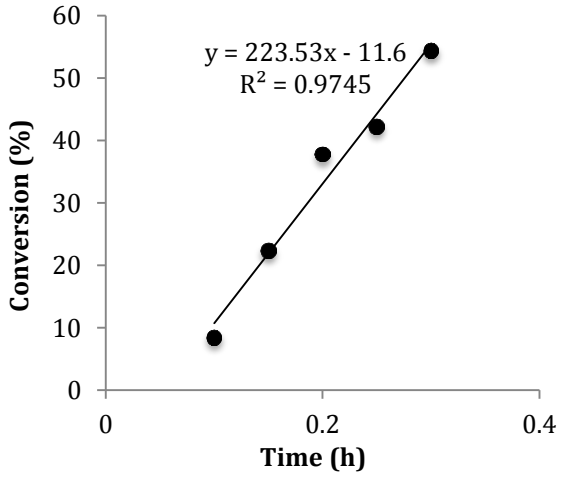


Figure S10. C-O cleavage rate dependence on the concentration of $Ru(H)_2(CO)(PPh_3)_3$/Xantphos catalyst (3 mol%). Conversion (%) vs. catalyst loading for C-O bond cleavage of 2-phenoxy-1-phenylethanol. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.03 mmol catalyst loading, 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

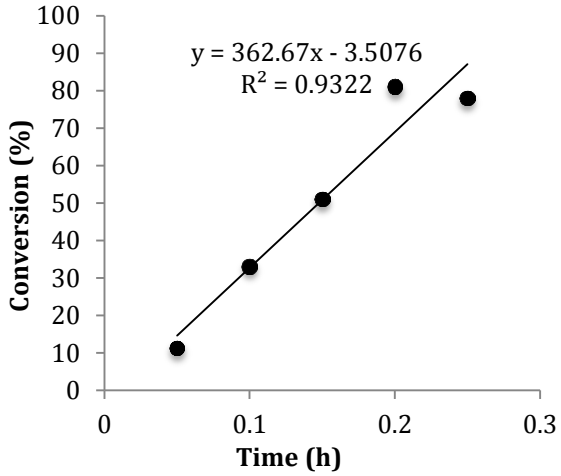


Figure S11. C-O cleavage rate dependence on the concentration of $Ru(H)_2(CO)(PPh_3)_3$/Xantphos catalyst (4 mol%). Conversion (%) vs. catalyst loading for C-O bond cleavage of 2-phenoxy-1-phenylethanol. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.04 mmol catalyst loading, 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

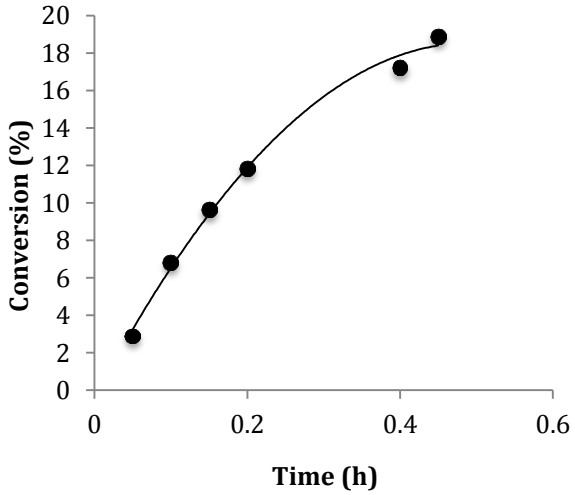


Figure S12. C-O cleavage of 2-phenoxy-phenylethanol with 2% 2-phenoxyacetophenone (**4**) by $Ru(H)_2(CO)(PPh_3)_3$ and Xantphos (ligand **5**). Conversion (%) vs. time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

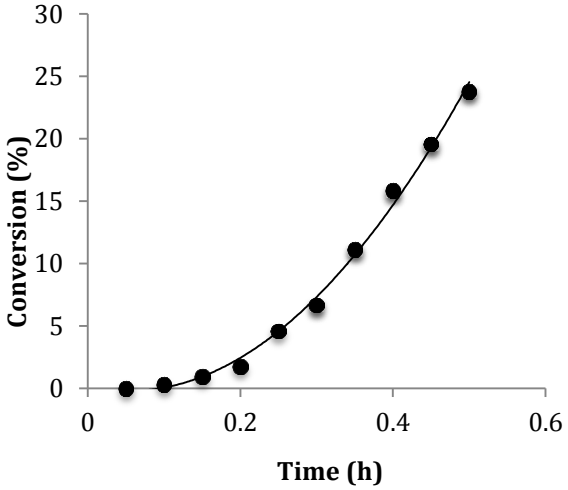


Figure S13. Conversion (%) vs. time (h) for C-O bond cleavage of 2-phenoxy-1-phenylethanol by $Ru(H)_2(CO)(PPh_3)_3$ and Xantphos (ligand **5**) under H_2. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading of 2 mol% 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 135 °C under a H_2 atmosphere. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

Eyring plot for the formation of acetophenone (2)

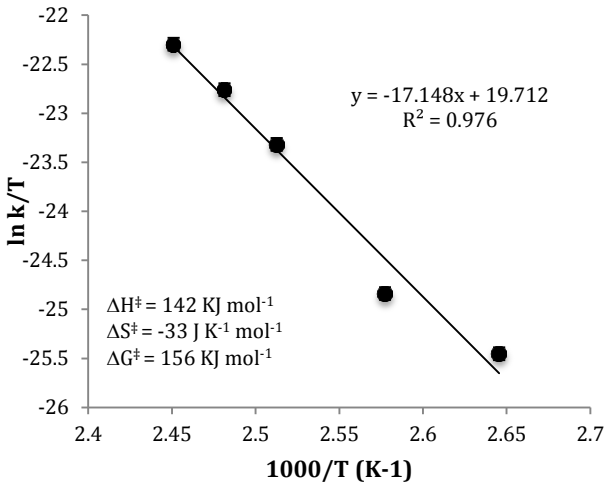


Figure S14. Eyring plot for the formation of acetophenone (**2**) by $Ru(H)_2(CO)(PPh_3)_3$ and Xantphos. Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with 0.02 mmol catalyst loading and 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes. Samples were analysed by gas chromatography, results from duplicate experiments. Error bars were calculated by standard deviation based on quadruple measurements on T = 130 °C.

Kinetic profile for the formation of 2-phenoxyacetophenone (4) at 25 °C and acetophenone (2) at 105 °C

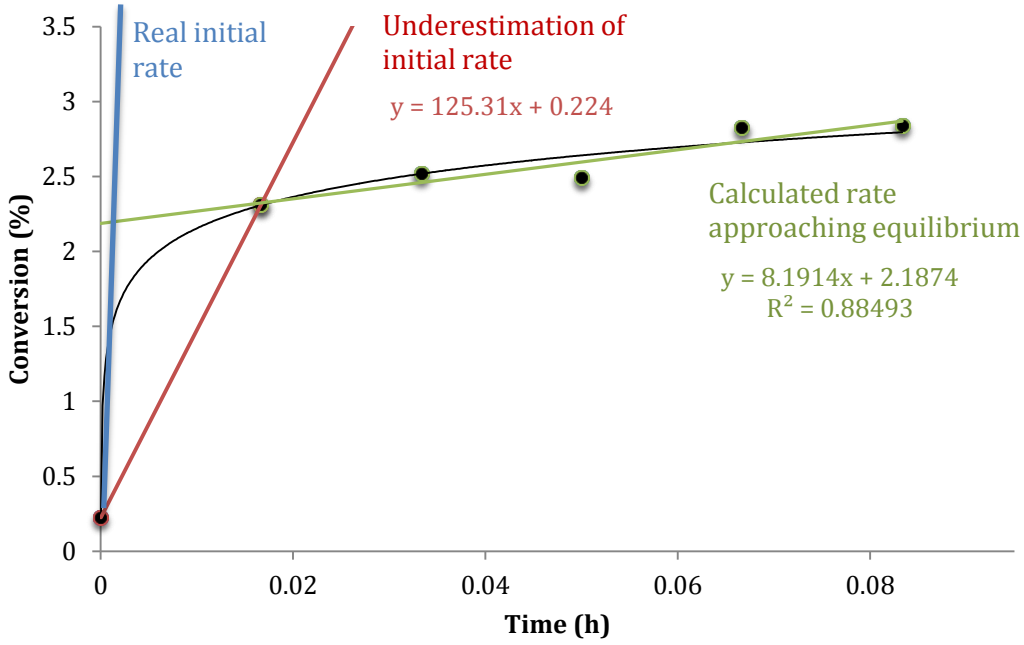


Figure S15. Conversion (%) vs. time (h) for dehydrogenation of 2-phenoxy-1-phenylethanol by $Ru(H)_2(CO)(PPh_3)_3$ and Xantphos (ligand **5**). Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 25 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

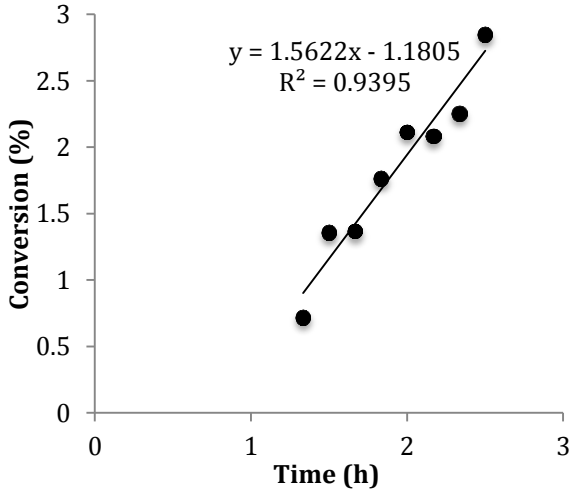


Figure S16. Conversion (%) vs. time for ether cleavage of 2-phenoxy-1-phenylethanol by $Ru(H)_2(CO)(PPh_3)_3$ and Xantphos (ligand **5**). Conditions: 1 mmol of 2-phenoxy-1-phenylethanol with a 0.02 mmol catalyst loading 0.125 mmol of 1,2,4,5-tetramethylbenzene as the internal standard in anhydrous xylenes at 105 °C. Samples withdrawn at regular intervals and were analysed by gas chromatography. Results from duplicates of experiments.

NMR data for ligands 5a – c and 14c

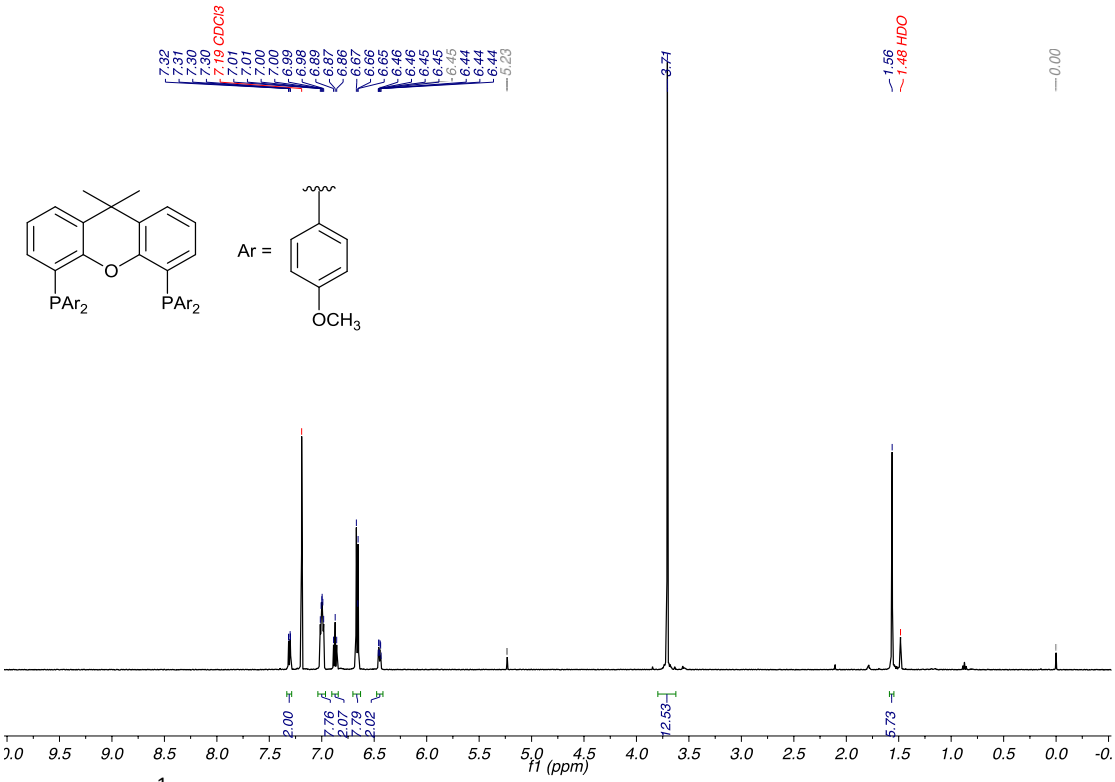


Figure S17. ^{1}H NMR spectra of **5a**

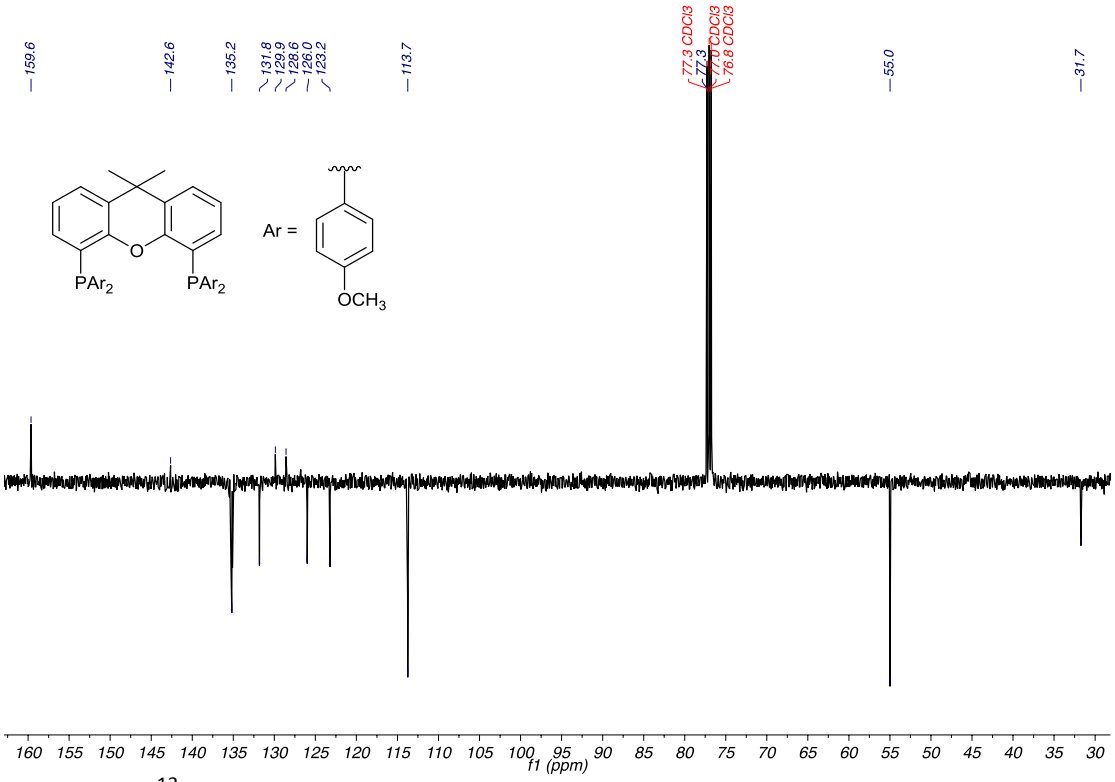


Figure S18. ^{13}C DEPTQ NMR spectra of **5a**

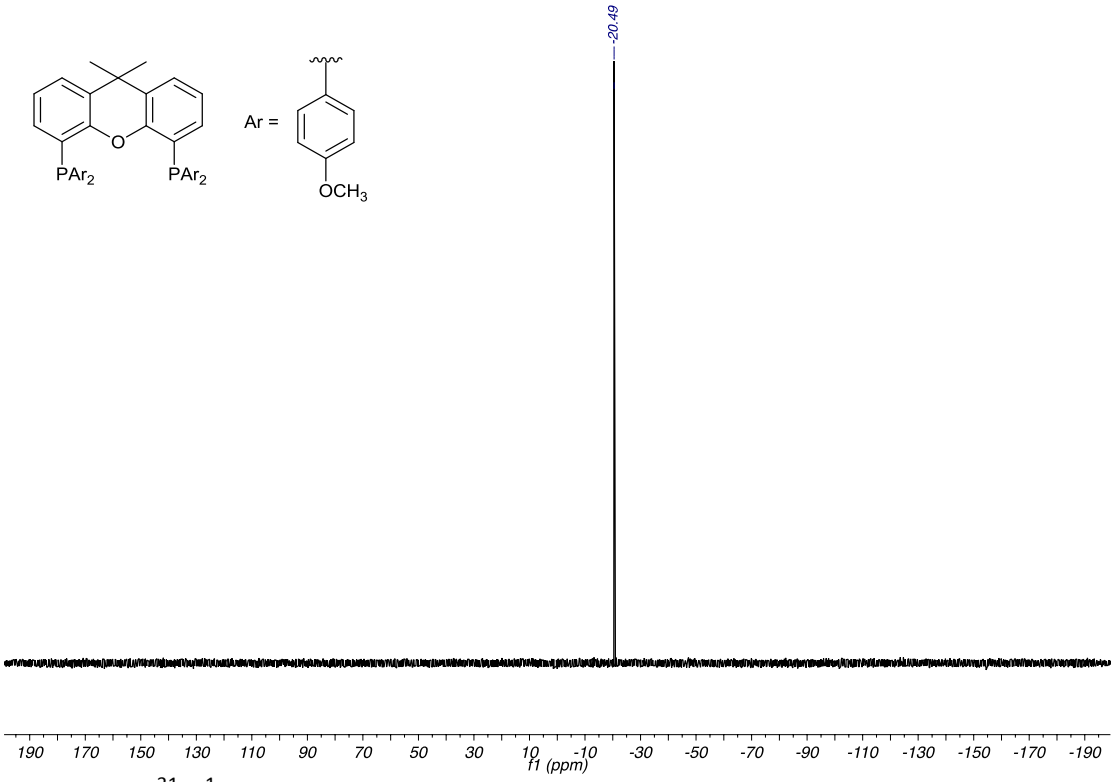


Figure S19. $^{31}P\{^{1}H\}$ NMR spectra of **5a**

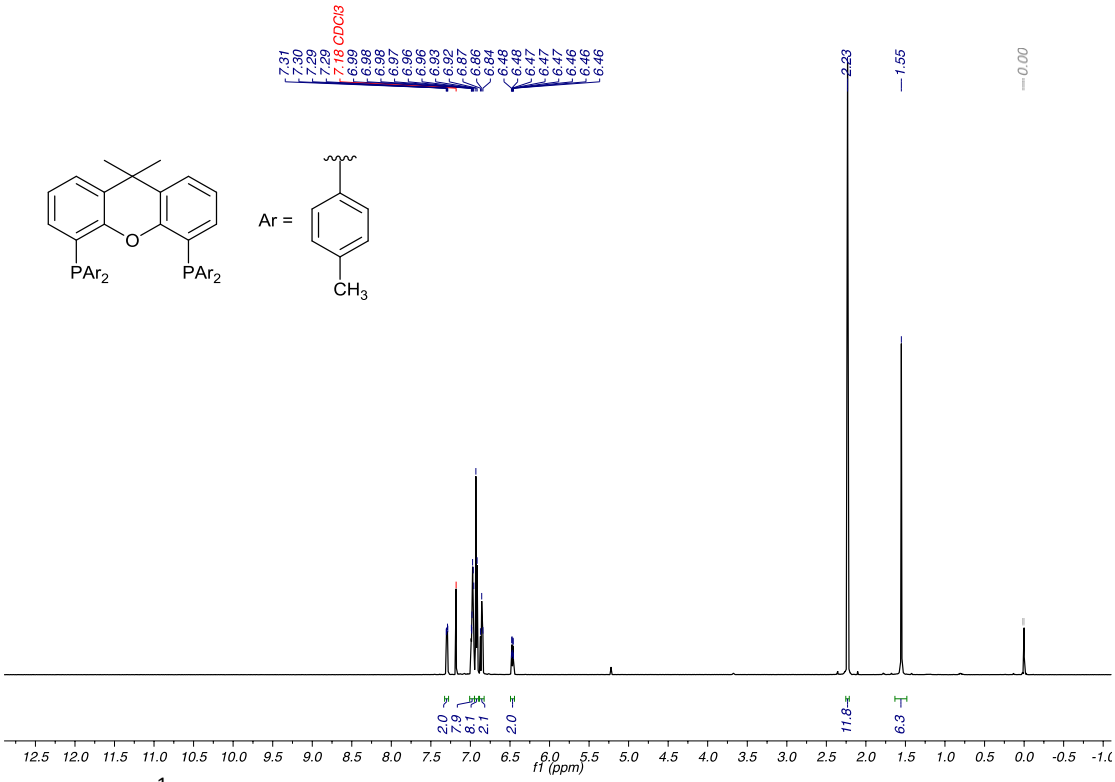


Figure S20. ^{1}H NMR spectra of **5b**

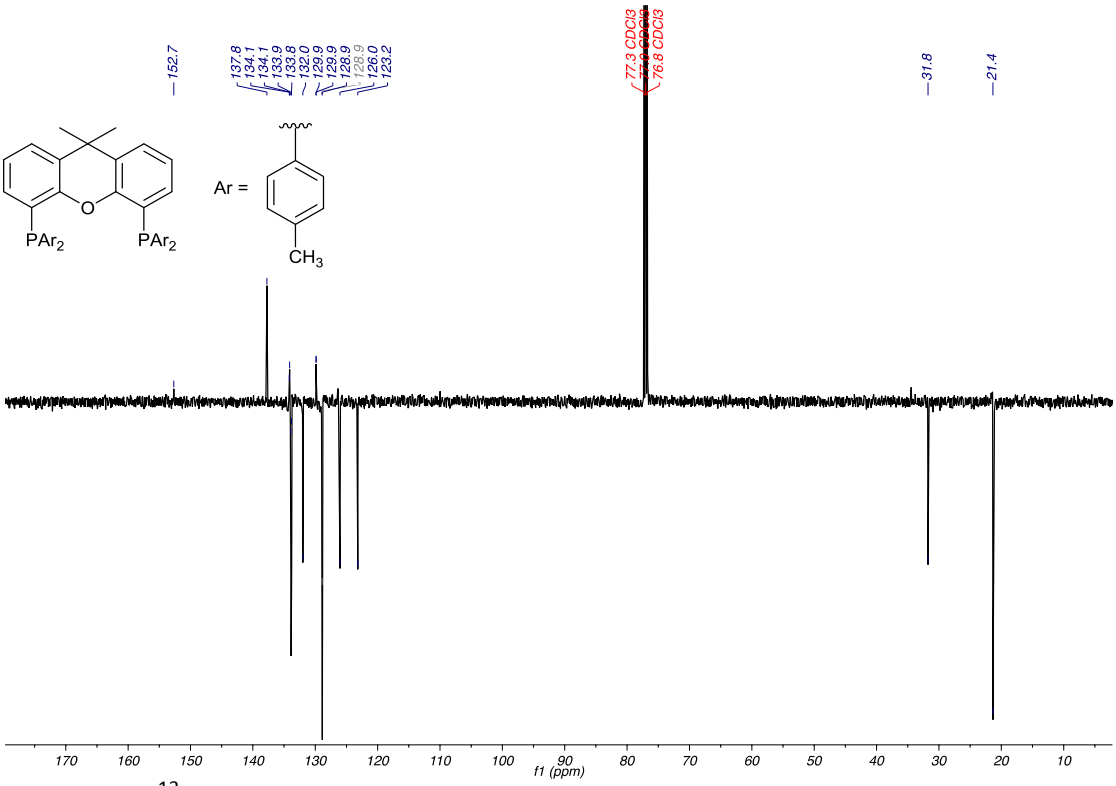


Figure S21. ^{13}C DEPTQ NMR spectra of **5b**

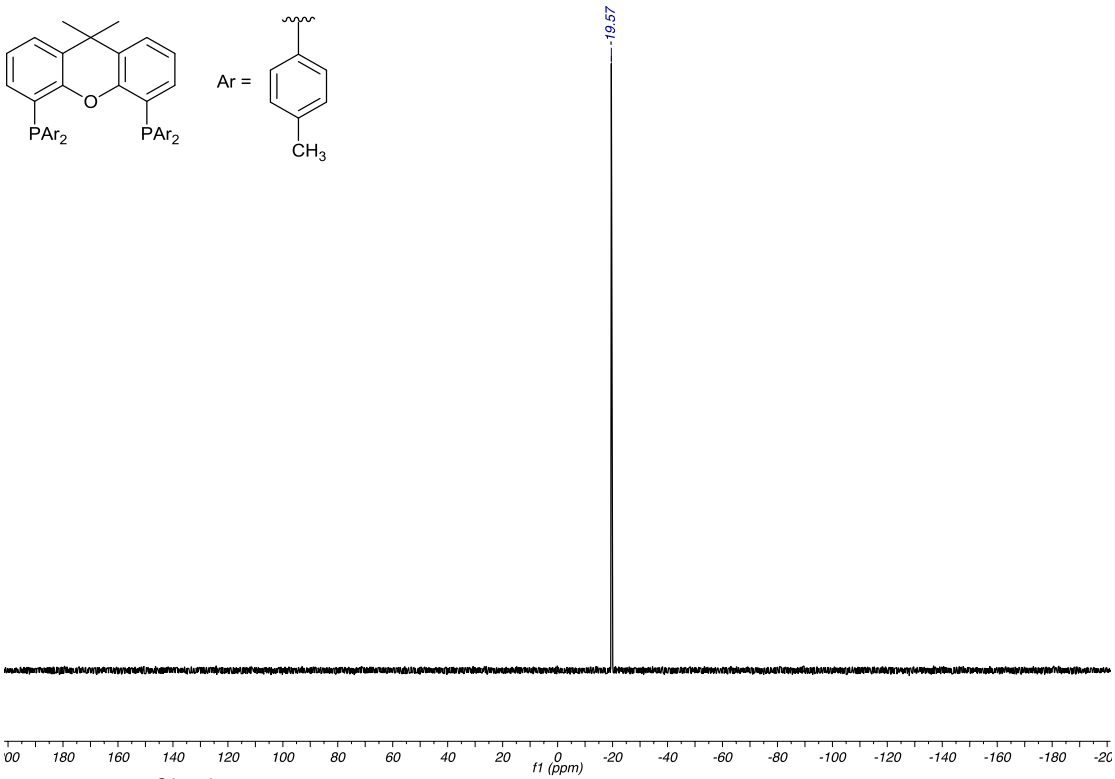


Figure S22. $^{31}P\{^{1}H\}$ NMR spectra of **5b**

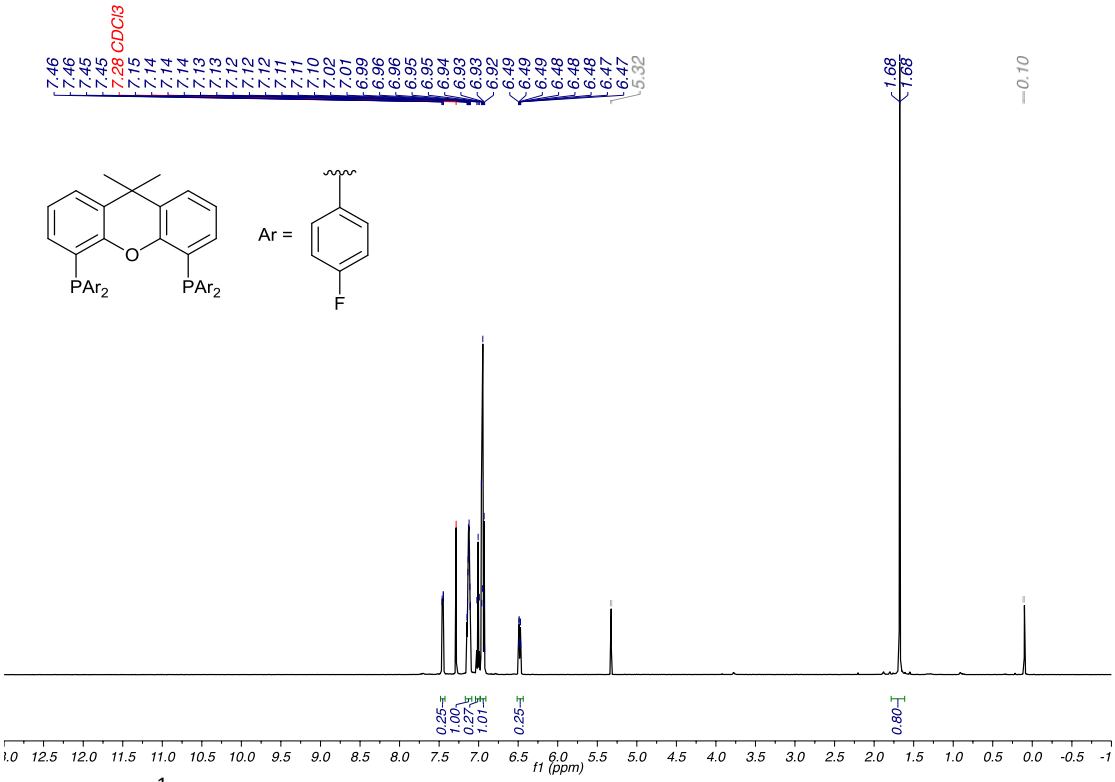


Figure S23. ^{1}H NMR spectra of **5c**

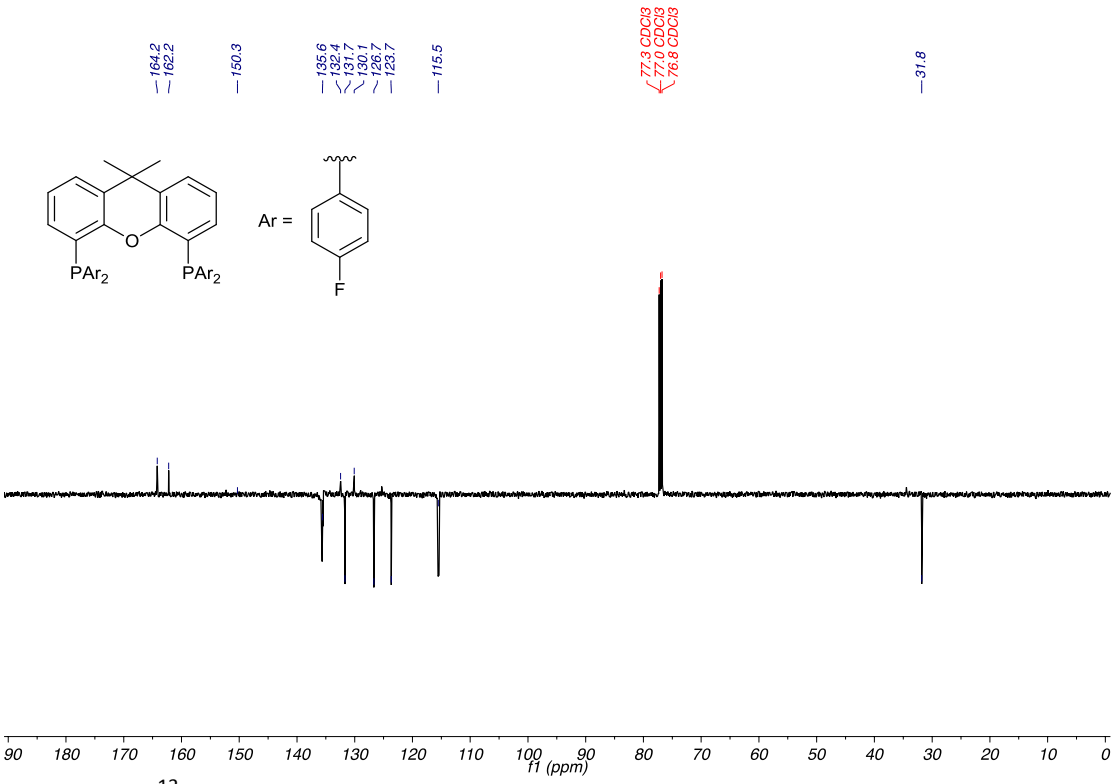


Figure S24. ^{13}C DEPTQ NMR spectra of **5c**

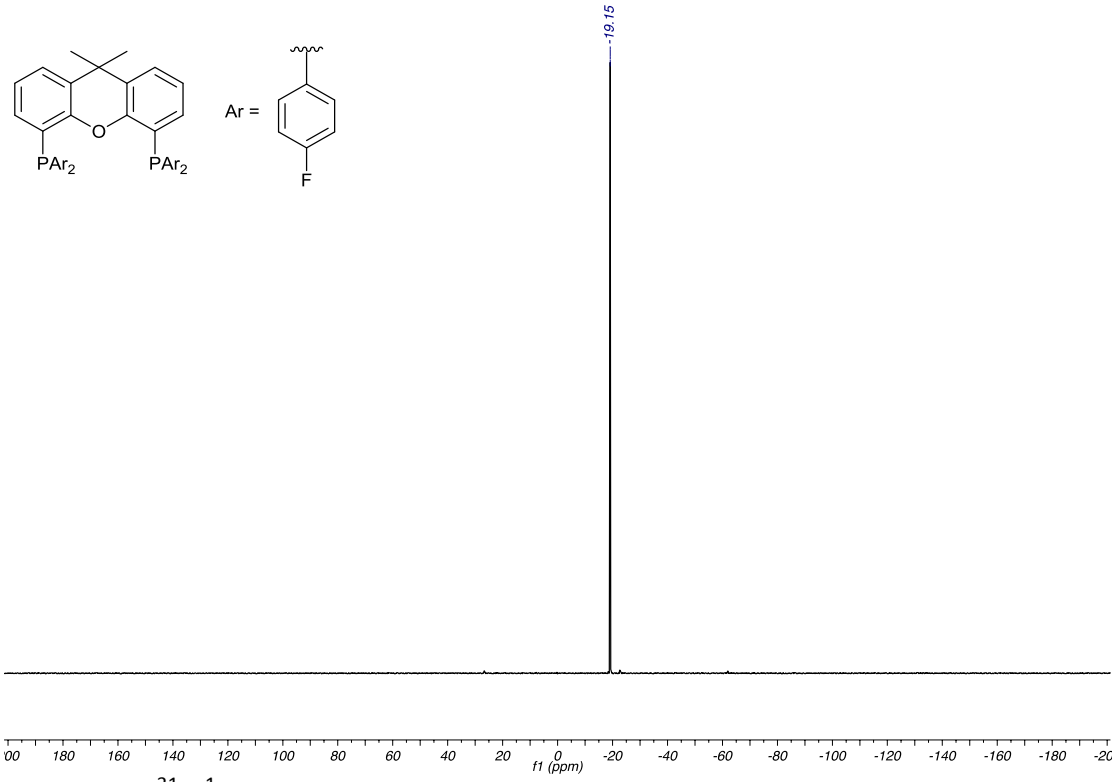


Figure S25. $^{31}P\{^{1}H\}$ NMR spectra of **5c**

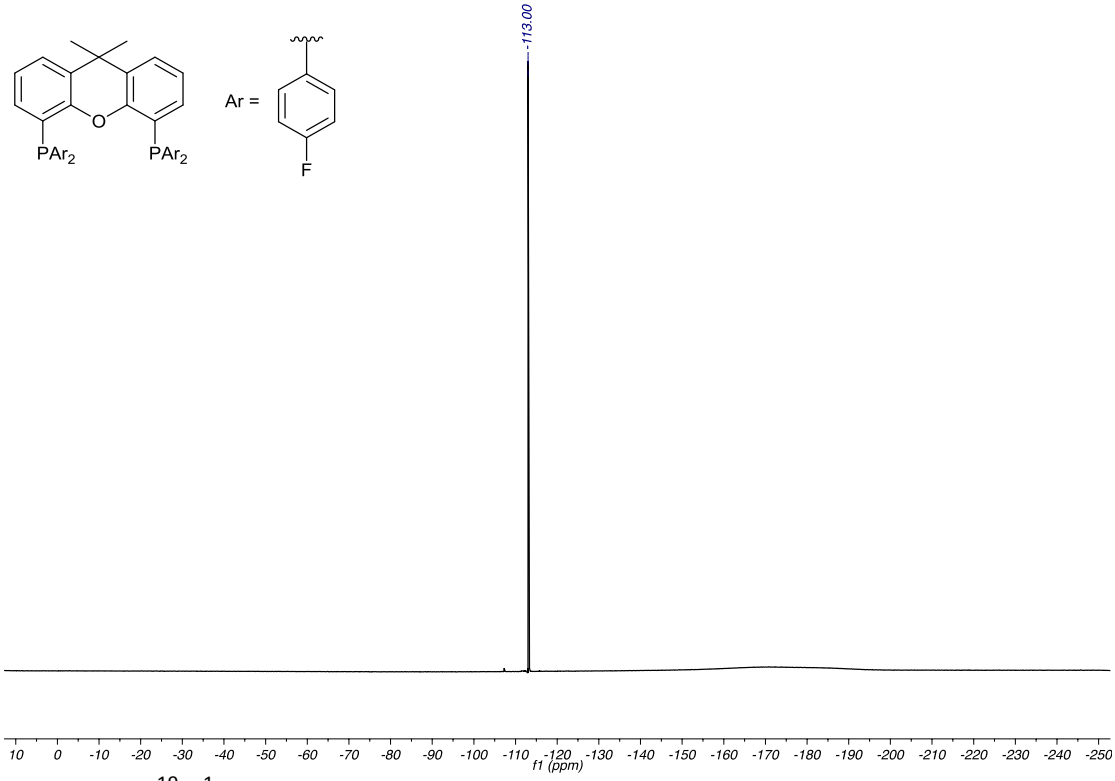


Figure S26. $^{19}F\{^{1}H\}$ NMR spectra of **5c**

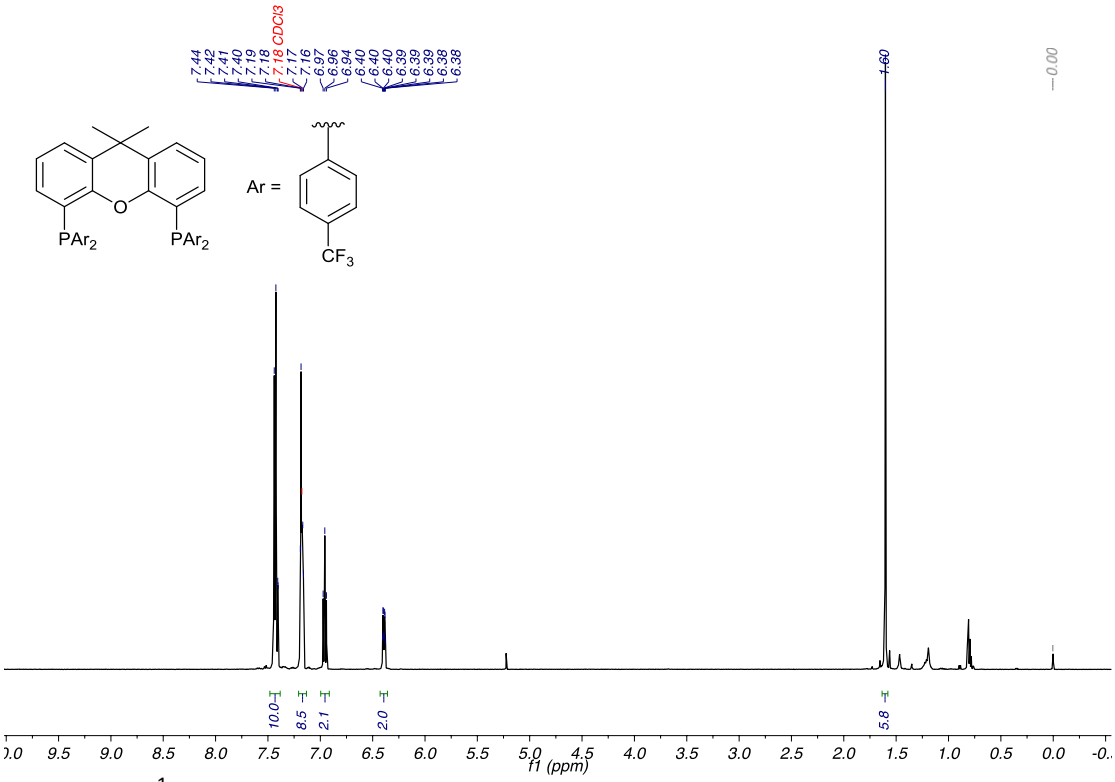


Figure S27. ^{1}H NMR spectra of **5d**

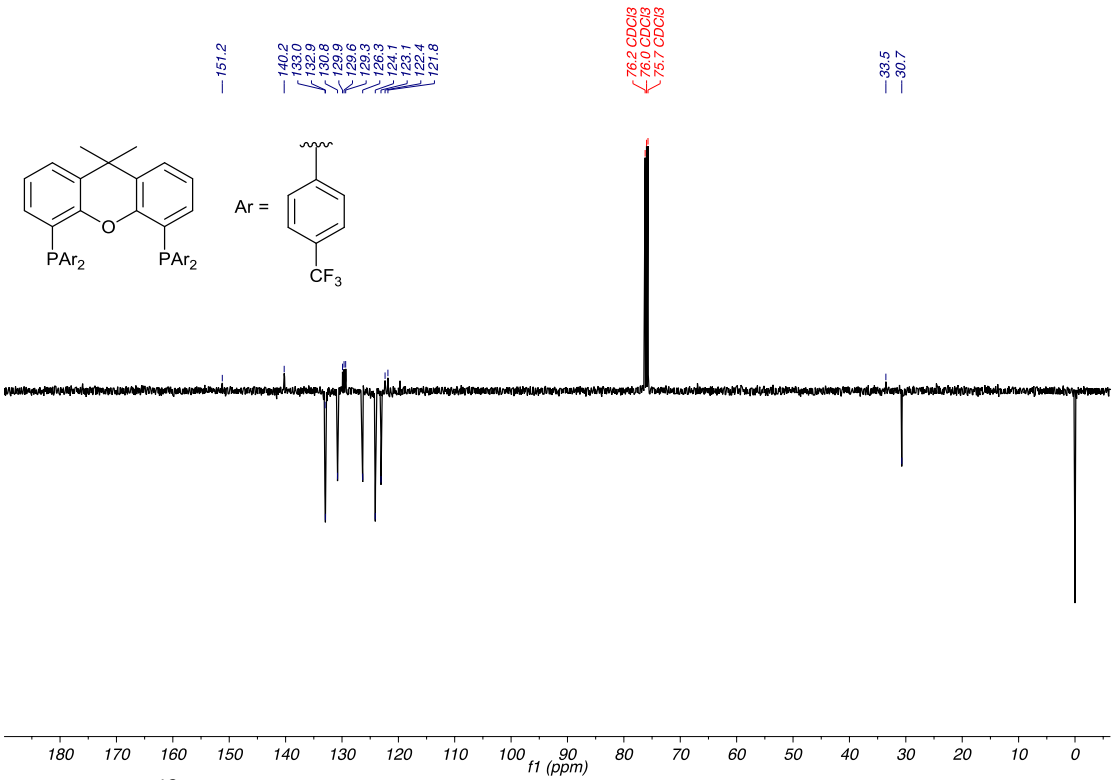


Figure S28. ^{13}C DEPTQ NMR spectra of **5d**

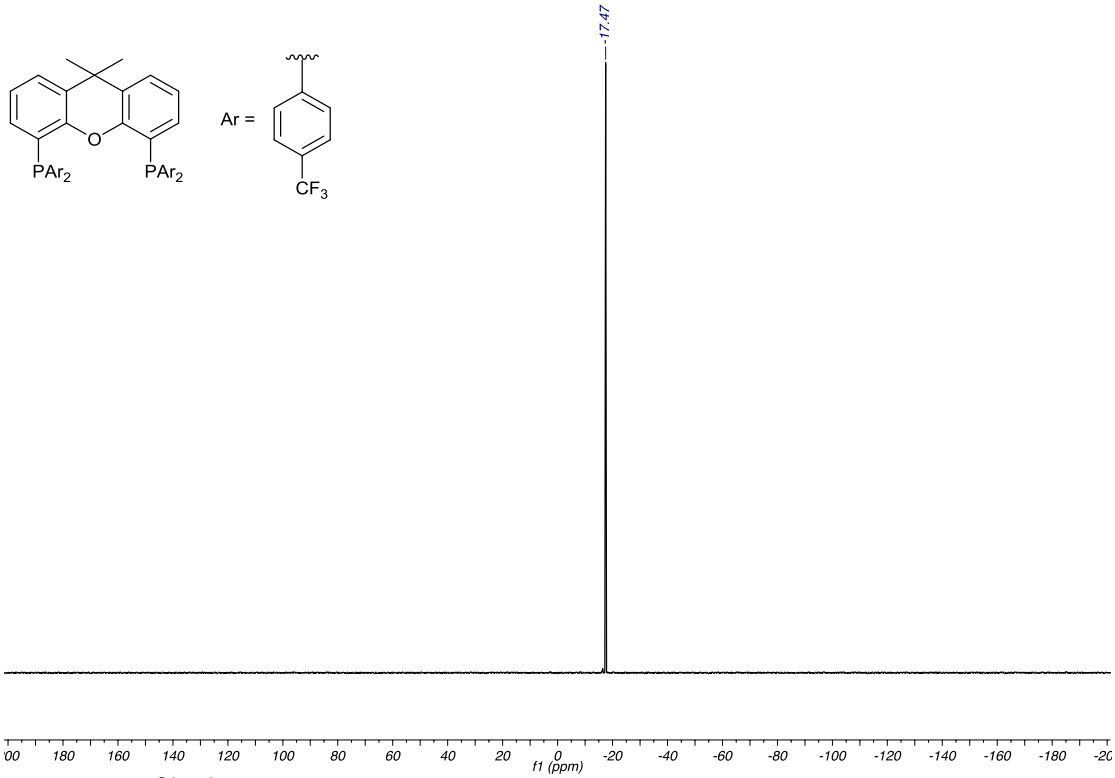


Figure S29. $^{31}P\{^{1}H\}$ NMR spectra of **5d**

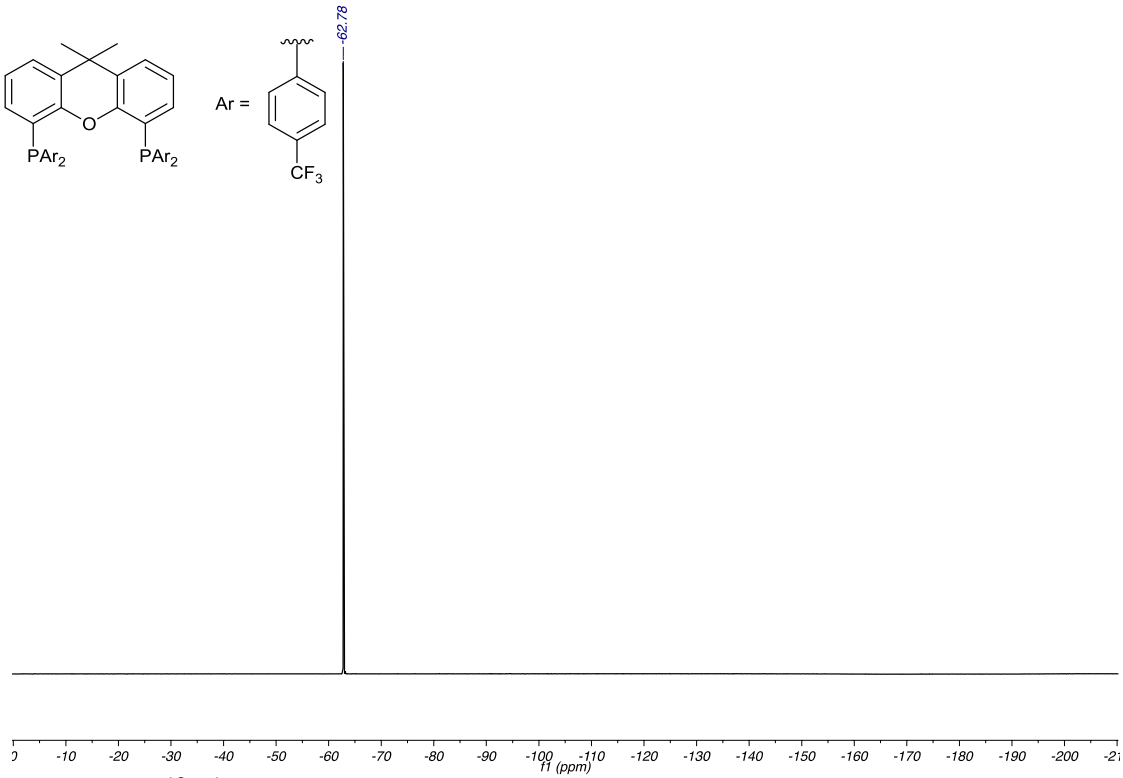


Figure S30. $^{19}F\{^{1}H\}$ NMR spectra of **5d**

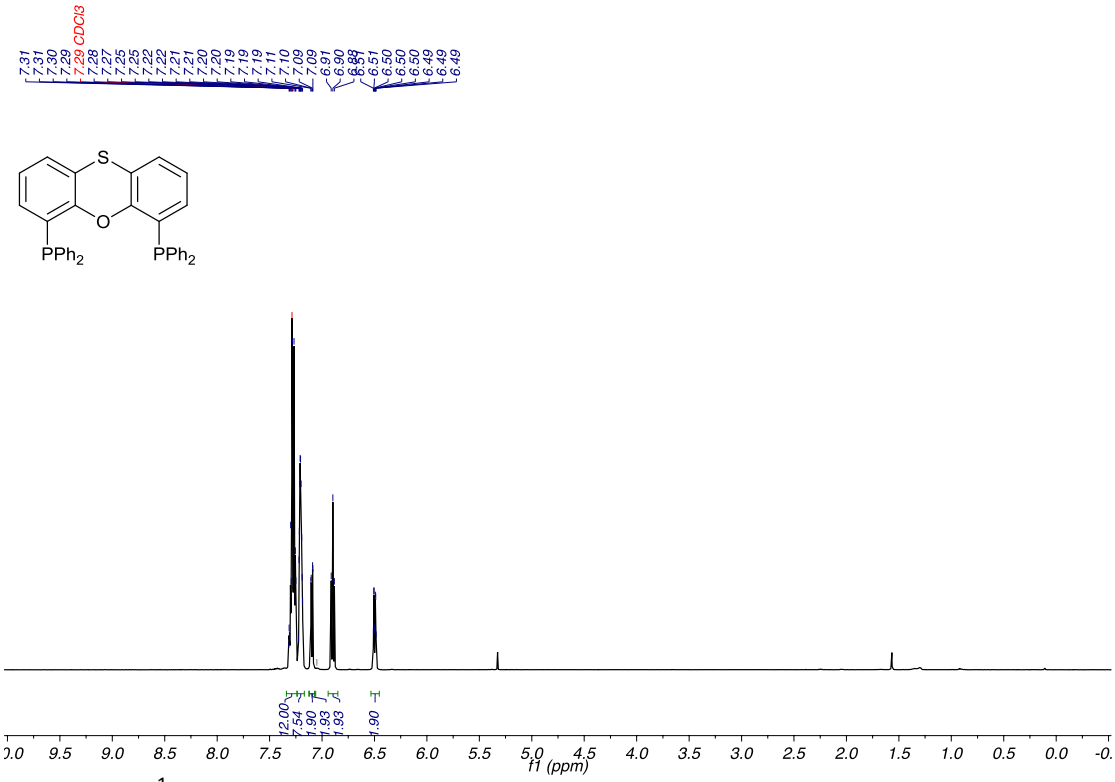


Figure S31. ^{1}H NMR spectra of **14c**

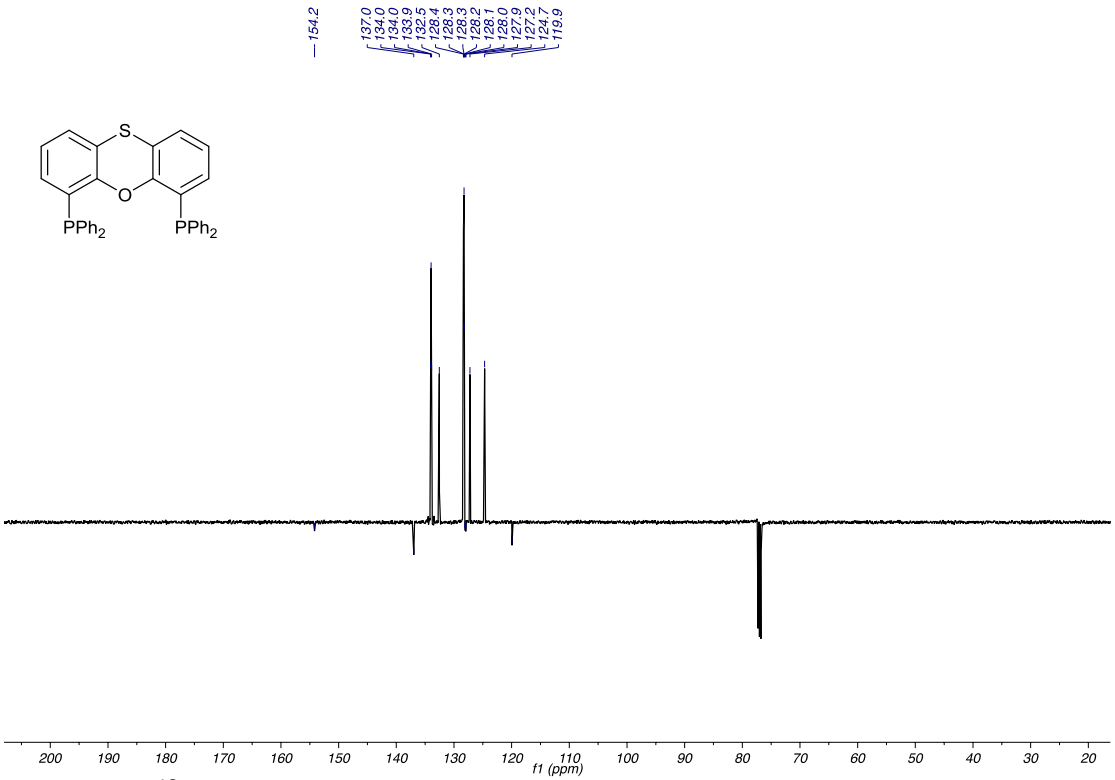


Figure S32. ^{13}C DEPTQ NMR spectra of **14c**

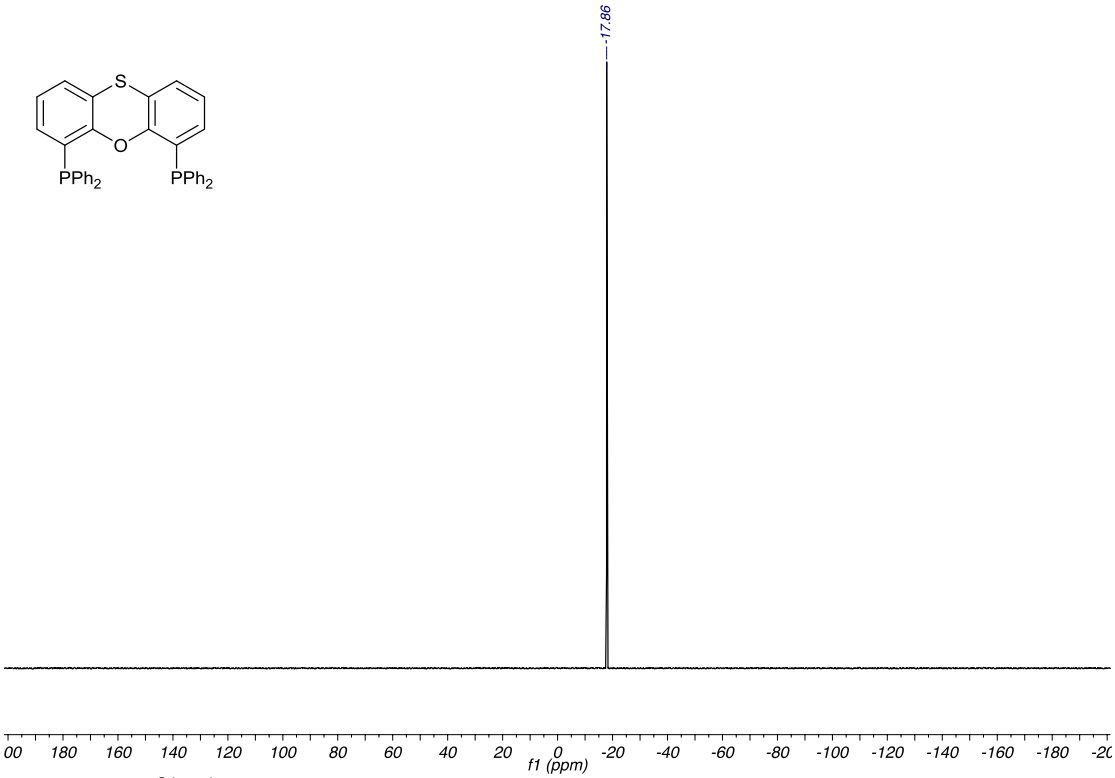


Figure S33. $^{31}P\{^{1}H\}$ NMR spectra of **14c**

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