Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

Synthesis of Spirocyclic Orthoesters by 'Anomalous' Rhodium(II)-Catalyzed Intramolecular C–H Insertions

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I. General Experimental Details

Unless otherwise indicated, all reactions were performed under a nitrogen atmosphere and glassware was flame dried under vacuum prior to use. Temperatures quoted as 0 °C and -78 °C were obtained by cooling the reaction vessel in baths of ice/H_2O and dry ice/acetone respectively. Tetrahydrofuran (THF), diethyl ether (Et_2O) and dichloromethane were dried and deoxygenated by passing the nitrogen-purged solvents through activated alumina column under a positive pressure of nitrogen. All other reagents and solvents were used as purchased from commercial suppliers unless otherwise noted. Reaction progress was monitored by thin layer chromatography (TLC) on aluminum backed silica gel plates, visualizing with UV light, and plates were developed using vanillin. Flash chromatography was performed using silica gel (230 – 400 mesh). NMR spectra were acquired on Varian INOVA 500 and 600 MHz NMR spectrometers in $CDCl_3$ (referenced to 7.26 ppm for ^1H and 77.16 for ^{13}C) or C_6D_6 (referenced to 7.16 ppm for ^1H and 128.06 for ^{13}C). Coupling constants (*J*) are in Hz. The multiplicities of the signals are described using the following abbreviations: s = singlet, d = doublet, t = triplet, br = broad. LRESIMS were recorded on an Agilent 6120 quadrupole LCMS system. High resolution mass spectra (HRMS) were recorded on a Bruker MicrOTof-Q spectrometer (Dionex UltiMate 3000 micro LC system, ESI mode).

II. Synthetic Procedures and Characterisation Data

5-Phenyltetrahydrofuran-2-ol (3). A solution of 5-bromopent-1-ene (8.0 mL, 67.1 mmol, 1 eq) in Et_2O was added dropwise to a mixture of Mg turnings (1.96 g, 80.5 mmol, 1.2 eq) in Et_2O. The reaction mixture was refluxed for 1h then cooled down to 0 ºC. Benzaldehyde (7.5 mL, 73.8 mmol, 1.1 eq) was added dropwise and the reaction allowed to warm up to RT and stirred for 2 h. The reaction mixture was quenched with saturated aqueous solution of NH_4Cl and extracted with EtOAc. The combined organic phases were dried over $MgSO_4$, and concentrated. The residue was purified by flash chromatography (SiO_2, 8:92 EtOAc/Pet Spirit) yielding 1-phenylhex-5-en-1-ol (S1) (8.57 g, 73%), which showed NMR spectra identical to those reported.[1] **^{1}H NMR** ($CDCl_3$, 500 MHz) 7.27 (4H, m, 4 × Ar$\underline{H}$), 7.20 (1H m, × Ar$\underline{H}$), 5.70 (1H, m, $C\underline{H}{=}CH_2$), 4.89 (2H, m, $CH{=}C\underline{H}_2$), 4.60 (1H, m, $C\underline{H}(OH)$), 2.00 (2H, m, $CH(OH)C\underline{H}_2$), 1.80-1.58 (4H, m, $C\underline{H}_2$), 1.51-1.26 (2H, m, $C\underline{H}_2$). Subsequently, ozone was bubbled into a solution of 1-phenylhex-5-en-1-ol (8.57 g, 48.6 mmol) in CH_2Cl_2 at −78 ºC until blue color became persistent. Dioxygen was then bubbled until the blue color disappeared. Triphenylphosphine (15 g, 58.0 mmol) was added portionwise and the reaction mixture allowed to warm up to RT and stirred overnight. The solvent was then removed *in vacuo*. The residue was purified by flash chromatography (SiO_2, 2:8 EtOAc/Pet Spirit) yielding the desired lactol **3** (6.48 g, 75%), which showed NMR spectra identical to those reported.[2] **^{1}H NMR** (d_6-DMSO, 500 MHz) 7.33 (4H, m, 4 × Ar$\underline{H}$), 7.24 (1H m, × Ar$\underline{H}$), 6.47 (1H, d, J = 6.1 Hz, OH), 4.72 (1H, m, $OC\underline{H}(OH)$), 4.44 (1H, dd, J = 2.1, 11.4 Hz, $OC\underline{H}Ph$), 1.82 (1H, m, $(OH)CHC\underline{H}_aH_b$), 1.73 - 1.59 (3H, m, $(OH)CHCH_a\underline{H}_b$ + $C\underline{H}_2$), 1.34 - 1.26 (2H, m, $C\underline{H}_2$).

***cis*-*N*-methoxy-*N*-methyl-2-(6-phenyltetrahydro-2*H*-pyran-2-yloxy)acetamide (5).** A solution of lactol **3** (1 g, 5.61 mmol) in THF (15 mL) was cooled down to -78 ºC. KHMDS

(0.5 M in toluene, 12 mL, 5.89 mmol) was added dropwise and the resulting mixture was stirred for 30 min, warmed up to 0 ºC then cooled down again to -78 ºC. A solution in THF (6 mL) of freshly distilled α-bromo amide **4** (1.55 g, 8.52 mmol) was then added dropwise and the mixture stirred at -78 ºC for 2h. The yellow reaction mixture was then quenched with aqueous NH_4Cl (10 mL) and H_2O (20mL). The layers were then separated and the aqueous layer was extracted with Et_2O (2 x 40 mL). The combined organic extracts were washed with a saturated NaCl solution, dried over anhydrous $MgSO_4$, and concentrated. Purification by flash column chromatography (SiO_2, 3:7 EtOAc/Pet spirit) yielded the single *cis* diastereoisomer **5** (1.15 g, 74%) as a white solid (m.p. 62 – 64 ºC). **R***f* 0.33 (30% EtOAc/Pet spirit); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.39 - 7.32 (4H, m, 4 × Ar$\underline{H}$), 7.28 - 7.25 (1H, m, Ar$\underline{H}$), 4.73 (1H, dd, *J* = 1.8, 9.6 Hz, OC$\underline{H}$(CH_2)O), 4.53 (2H, ABq, $\Delta\nu_{AB}$ = 16.6 Hz, J_{AB} = 16.0 Hz, OC$\underline{H}_2$C=O), 4.44 (1H, dd, *J* = 2.2, 11.5 Hz, ArC$\underline{H}$(CH_2)O), 3.64 (3H, s, OC$\underline{H}_3$), 3.18 (3H, s, NC$\underline{H}_3$), 2.03 (1H, m, C$\underline{H}_2$), 1.97 (1H, m, C$\underline{H}_2$), 1.80 - 1.77 (1H, m, C$\underline{H}_2$), 1.71 (1H, app. qt , *J* = 3.8, 13.3 Hz, C$\underline{H}_2$), 1.62 - 1.45 (2H, m, C$\underline{H}_2$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.1 (C), 142.5 (C), 128.4 (CH), 127.4 (CH), 126.0 (CH), 102.5 (CH), 78.3 (CH), 64.7 (CH_2), 61.5 (CH_3), 33.3 (CH_2), 32.4 (CH_3), 30.9 (CH_2), 22.7 (CH_2); **MS** (+ESI) *m/z* 302 ($[M + Na]^+$, 100); **HRMS** (ESI+) *m/z* calculated for $C_{15}H_{21}NNaO_4$ 302.1363 $[M + Na]^+$ found 302.1362.

trans*-2-(allyloxy)-6-phenyltetrahydro-2H-pyran (7).** A mixture of lactol **3** (11 g, 64 mmol), allyl alcohol (15 g, 258 mmol) and $Sc(OTf)_3$ (~ 300 mg, 1 mol%) was refluxed overnight. The allyl alcohol was then evaporated and the crude product purified by flash column chromatography (SiO_2, 5:95 CH_2Cl_2/Pet spirit). Two isomers were isolated and separated: the desired *trans* diastereoisomer **7** (10.2 g, 73%) along with the *cis* diastereoisomer (3.0 g, 23%) both as pale yellow oils. **Rf* 0.50 (2:8 CH_2Cl_2/Pet spirit); **^{1}H**

NMR ($CDCl_3$, 600 MHz) δ 7.38 - 7.33 (4H, m, 4 × Ar$\underline{H}$), 7.28 - 7.25 (1H, m, Ar$\underline{H}$), 5.97 (1H, dddd, *J* = 5.2, 5.9, 10.5, 17.2 Hz, $CH_2C\underline{H}=CH_2$), 5.32 (1H, app. dq, *J* = 1.2, 17.2 Hz, $CH=C\underline{H}_aH_b$), 5.18 (1H, app. dq, *J* = 1.5, 10.4 Hz, $CH=CH_a\underline{H}_b$), 5.03 (1H, app. d, *J* = 2.3 Hz, $OC\underline{H}(CH_2)O$), 4.81 (1H, dd, *J* = 2.4, 11.6 Hz, $ArC\underline{H}(CH_2)O$), 4.24 (1H, ddt, *J* = 1.6, 5.2, 13.1 Hz, $OC\underline{H}_aH_bCH=$), 4.01 (1H, ddt, *J* = 1.5, 5.9, 13.2 Hz, $OCH_a\underline{H}_bCH=$), 2.06 (1H, m, $C\underline{H}_aH_b$), 1.87 – 1.62 (5H, m, $CH_a\underline{H}_b$ + $C\underline{H}_2$); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.2 (C), 134.9 (CH), 128.5 (CH), 127.5 (CH), 126.3 (CH), 116.7 (CH_2) 97.3 (CH), 71. 2 (CH), 67.7 (CH_2), 33.3 (CH_2), 29.7 (CH_2), 18.8 (CH_2); **MS** (+ESI) *m/z* 241 ([M + Na]$^+$, 100), 161 (70); **HRMS** (ESI+) *m/z* calculated for $C_{14}H_{18}NaO_2$ 241.1199 [M + Na]$^+$ found 241.1194.

***trans*-*N*-methoxy-*N*-methyl-2-(6-phenyltetrahydro-2*H*-pyran-2-yloxy)acetamide (8).** Ozone was bubbled into a solution of compound **7** (1.88 g, 8.6 mmol) in CH_2Cl_2 at −78°C until blue color became persistent. Dioxygen was then bubbled until the blue color disappeared. Triphenylphosphine (2.5 g, 9.5 mmol) was added in one portion and the reaction mixture allowed to warm up to RT and stirred overnight. The solvent was then removed *in vacuo*. The residue was suspended in Et_2O and filtered (4 x 50 mL). The filtrate was then evaporated to give the crude aldehyde **S2** that was used into the next step without further purification.

To a solution of the crude aldehyde **S2** (2.3 mmol) in tBuOH (30 mL) and H_2O (10 mL) at 0 ºC was added 2-methyl-2-butene (1.5 mL, 13.8 mmol), followed by the dropwise addition of a solution of $NaClO_2$ (~ 80%, 416 mg, 4.6 mmol) and $NaH_2PO_4•2H_2O$ (1.4 g, 9.2 mmol) in H_2O (20 mL). The resulting mixture was warmed up to RT and stirred overnight. The mixture was diluted with H_2O (90 mL) then extracted with EtOAc (4 x 50 mL), the combined extracts were dried over $MgSO_4$ and concentrated to give the corresponding carboxylic acid **S3** that was also used in the next step without any further purification. **MS** (+ESI) *m/z* 280 ([M + H]$^+$, 20), 161 (30), 119 (100).

To a solution of carboxylic acid **S3** (8.6 mmol) in pyridine (15 mL) was added N,O-dimethylhydroxylamine hydrochloride (1.3 mg, 12.9 mmol) and EDC hydrochloride (5 g, 25.8 mmol). The resulting mixture was stirred overnight. Pyridine was removed *in vacuo* and the crude was adsorbed on silica. Purification by flash column chromatography (SiO_2, 3:7 EtOAc/Pet spirit) yielded the single *trans* diastereoisomer **8** (1.05 g, 42% over 3 steps) as a pale brown solid (m.p. 78 – 79 ºC). **R$_f$** 0.27 (3:7 EtOAc/Pet spirit); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.38 - 7.33 (4H, m, 4 × Ar$\underline{H}$), 7.28 - 7.25 (1H, m, Ar$\underline{H}$), 5.10 (1H, app. d, *J* = 3.5 Hz, OC$\underline{H}$(CH_2)O), 4.84 (1H, dd, *J* = 2.4, 11.6 Hz, ArC$\underline{H}$(CH_2)O), 4.41 (2H, ABq, $\Delta\nu_{AB}$ = 20.8 Hz, J_{AB} = 15.9 Hz, OC$\underline{H}_2$C=O), 3.63 (3H, s, OC$\underline{H}_3$), 3.17 (3H, s, NC$\underline{H}_3$), 2.11 (1H, app. qt, *J* = 3.7, 12.9 Hz C$\underline{H}_a$H$_b$), 1.97 (1H, m, C$\underline{H}_c$H$_d$), 1.86 - 1.60 (4H, m, C$\underline{H}_2$ + CH$_a\underline{H}_b$ + CH$_c\underline{H}_d$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.3 (C), 143.1 (C), 128.5 (CH), 127.5 (CH), 126.3 (CH), 98.2 (CH), 71.6 (CH), 63.7 (CH_2), 61.6 (CH_3), 33.5 (CH_2), 32.4 (CH_3), 29.4 (CH_2), 18.6 (CH_2); **MS** (+ESI) *m/z* 280 ([M + H]$^+$, 20), 161 (30), 119 (100); **HRMS** (ESI+) *m/z* calculated for $C_{15}H_{21}NNaO_4$ 302.1363 [M + Na]$^+$ found 302.1367.

General procedure for Grignard reaction: Formation of *cis*-1-phenyl-3-(6-phenyltetrahydro-*2H*-pyran-2-yloxy)propan-2-one (S4).

The Grignard reagent was prepared from benzyl chloride (620 µL, 5.37 mmol) and magnesium turnings (157 mg, 6.44 mmol) in 5 mL Et_2O. The Grignard reagent was then cooled down to -40 ºC and the Weinreb amide **5** (500 mg, 1.79 mmol) in Et_2O (5 mL) was added dropwise using a dropping funnel. The solution was stirred at -40 ºC for 30 min then allowed to warm to RT and stirred for a further 30 min. The reaction mixture was quenched with sat. NH_4Cl (10 mL) and the layers were separated. The aqueous layer was then extracted with Et_2O (3 x 15 mL). The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, and concentrated. Purification by flash column chromatography (SiO_2, 5:95 EtOAc/Pet spirit) yielded the desired benzyl ketone **S4** (330 mg, 59%) as a pale yellow oil. **R***f* 0.44 (5% EtOAc/Pet spirit); ^{1}**H NMR** ($CDCl_3$, 500 MHz): δ 7.27 (4H, m, 4 × $Ar\underline{H}$), 7.22 - 7.19 (4H, m, 4 × $Ar\underline{H}$), 7.11 (2H, m, 2 × $Ar\underline{H}$), 4.52 (1H, dd, *J* = 2.1, 9.4 Hz, $OC\underline{H}(CH_2)O$), 4.35 (1H, dd, *J* = 2.3, 11.2 Hz, $ArC\underline{H}(CH_2)O$), 4.32 (1H, d, *J* = 17.1 Hz, $OC\underline{H}_aH_bCO$), 4.22 (1H, d, *J* = 17.1 Hz, $OCH_a\underline{H}_bCO$), 3.78 (2H, s, $ArC\underline{H}_2CO$), 1.94 – 1.88 (2H, m, $C\underline{H}_2$), 1.74 (1H, m, $C\underline{H}_2$), 1.67 - 1.58 (1H, m, $C\underline{H}_2$), 1.56 - 1.40 (2H, m, $C\underline{H}_2$); ^{13}**C NMR** ($CDCl_3$, 126 MHz) δ 206.5 (C), 142.1 (C), 133.8 (C), 129.7 (CH), 128.7 (CH), 128.4 (CH), 127.6 (CH), 127.1 (CH), 126.0 (CH), 103.0 (CH), 78.4 (CH), 72.9 (CH_2), 46.4 (CH_2), 33.0 (CH_2), 30.9 (CH_2), 22.6 (CH_2); **MS** (+ESI) *m/z* 333 ($[M+Na]^+$, 100); **HRMS** (ESI+) *m/z* calculated for $C_{20}H_{22}NaO_3$ 333.1461 $[M + Na]^+$ found 333.1466.

***trans*-1-phenyl-3-(6-phenyltetrahydro-*2H*-pyran-2-yloxy)propan-2-one (S5).**

Following the general procedure described for compound **S4**, the reaction was performed using benzylmagnesium chloride generated from benzyl chloride (1.25 mL, 10.7 mmol) and Mg turnings (314 mg, 12.9 mmol), and Weinreb amide **8** (1 g, 3.6 mmol) in Et_2O. Purification by flash column chromatography (SiO_2, 5:95 EtOAc/Pet spirit) yielded the desired benzyl ketone **S5** (511 mg, 46%) as a pale yellow oil. **R***f* 0.24 (5:95 EtOAc/Pet spirit); ^{1}**H NMR** ($CDCl_3$, 600 MHz): δ 7.34 – 7.25 (8H, m, 8 × $Ar\underline{H}$), 7.21 (2H, m, 2 × $Ar\underline{H}$) 4.96 (1H, app. d, *J* = 3.5 Hz, $OC\underline{H}(CH_2)O$), 4.66 (1H, dd, *J* = 2.4, 11.6 Hz, $ArC\underline{H}(CH_2)O$), 4.34 (1H, d, *J* = 17.4 Hz, $OC\underline{H}_aH_bCO$), 4.20 (1H, d, *J* = 17.4 Hz, $OCH_a\underline{H}_bCO$), 3.77 (2H, ABq, $\Delta\nu_{AB}$ = 7.2 Hz, J_{AB} = 15.1 Hz, $ArC\underline{H}_2CO$) 2.07 (1H, m, $C\underline{H}_aH_b$), 1.91 (1H, m, $C\underline{H}_cH_d$), 1.85 - 1.71 (3H, m, $CH_a\underline{H}_b + CH_c\underline{H}_d + C\underline{H}_eH_f$), 1.64 (1H, m, $CH_e\underline{H}_f$); ^{13}**C NMR** ($CDCl_3$, 151 MHz) δ 205.8 (C), 142.7 (C), 133.6 (C), 129.6 (CH), 128.9 (CH), 128.5 (CH), 127.6 (CH), 127.2 (CH), 126.2 (CH), 98.2 (CH), 71.6 (CH), 71.2 (CH_2), 46.6 (CH_2), 33.2 (CH_2), 29.3 (CH_2), 18.6 (CH_2); **MS** (+ESI) *m/z* 333 ($[M+Na]^+$, 18), 161 (100); **HRMS** (ESI+) *m/z* calculated for $C_{20}H_{22}NaO_3$ 333.1461 $[M + Na]^+$ found 333.1462.

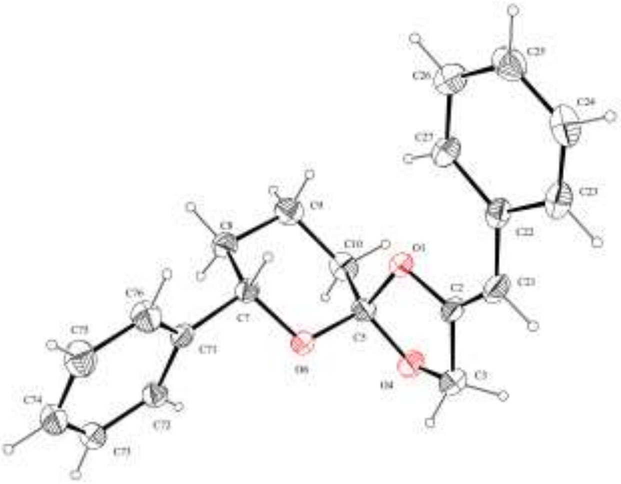
General procedure for diazo transfer: Formation of *cis*-1-phenyl-1-diazo-3-(6-phenyltetrahydro-*2H*-pyran-2-yloxy)propan-2-one (6). To a cool (0 ºC) solution of ketone **S4** in acetonitrile (0.1 M) was added *p*-ABSA (1.2 eq) in one portion. DBU (1.2 eq) was added dropwise by srynge and the solution quickly became bright yellow. The reaction mixture was then quickly filtered through a pad of buffered silica (pH 7), which was then rinsed with 1:9 EtOAc/Pet Spirit. Concentration of the crude *in vacuo,* yielded the corresponding characteristically bright yellow diazoketone **6** in high yields (70 – 82%). Due to the unstable nature of this compound, it was carried forward to the next reaction without further purification or characterization. **R*f*** 0.27 (1:9 EtOAc/Pet spirit); **MS**(+ESI) *m/z* 359 ($[M+Na]^+$, 12), 331 ($[M\text{-}N_2\text{+}Na]^+$, 100).

trans*-1-phenyl-1-diazo-3-(6-phenyltetrahydro-*2H*-pyran-2-yloxy)propan-2-one (9).** The reaction was performed following the general procedure described for diazoketone **6** using ketone **S5**. Concentration of the crude *in vacuo,* yielded the corresponding characteristically bright yellow diazoketone **9** in high yields (70 – quantitative). **R*f 0.60 (1:9 EtOAc/Pet spirit); ^{1}**H NMR** ($CDCl_3$, 600 MHz): δ 7.42 (2H, m, 2 × Ar$\underline{H}$), 7.32 (2H, m, 2 × Ar$\underline{H}$), 7.27 – 7.16 (6H, m, 6 × Ar$\underline{H}$), 4.99 (1H, app. d, *J* = 3.4 Hz, OC$\underline{H}$(CH_2)O), 4.68 (1H, dd, *J* = 11.7, 2.4 Hz, ArC$\underline{H}$(CH_2)O), 4.43 (1H, d, *J* = 14.9 Hz, OC$\underline{H}_aH_b$CO), 4.30 (1H, d, *J* = 14.9 Hz, OC$H_a\underline{H}_b$CO), 1.96 (1H, app. qt, *J* = 13.1, 3.9 Hz, C$\underline{H}_aH_b$), 1.82 – 1.53 (5H, m, C$\underline{H}_{2}$ + C$H_a\underline{H}_b$); ^{13}**C NMR** ($CDCl_3$, 151 MHz) δ 142.6 (C), 129.2 (CH), 128.5 (CH), 127.7 (CH), 127.2 (C), 126.2 (CH), 125.6 (C), 110.2 (C), 98.8 (CH), 71.9 (CH), 71.1 (CH_2), 33.2 (CH_2), 29.4 (CH_2), 18.6 (CH_2), 2 x (C) not observed.

General procedure for Rh(II) catalysed spirocyclisation: Formation of 2-benzylidene-7-phenyl-1,4,6-trioxaspiro[4.5]decane (11). A solution of diazoketone **6** in CH_2Cl_2 (0.03 M) was added dropwise over 10 to 15 minutes to a suspension of rhodium(II) catalyst (2 mol%) in CH_2Cl_2 (0.002 M) at RT. The reaction mixture was stirred for 15 min, adsorbed on silica and purified by flash chromatography (SiO_2, 1:99 EtOAc/Pet spirit) to give the spiroorthoester **11** as a mixture of 2 isomers. **Major isomer 11a:** White solid (m.p 112 – 114 ºC); **R**$_f$ 0.13 (1:99 EtOAc/Pet spirit); ^{1}**H NMR** ($CDCl_3$, 400 MHz): δ 7.56 (2H, app. d, *J* = 7.8 Hz, 2 × Ar$\underline{H}$), 7.36 - 7.30 (6H, m, 6 × Ar$\underline{H}$), 7.26 (1H, m, Ar$\underline{H}$), 7.17 (1H, m, Ar$\underline{H}$), 5.28 (1H, br. s, ArC$\underline{H}$=CO), 4.94 -4.91 (2H, m, ArC$\underline{H}$(CH_2)CO + OC$\underline{H}_a$H$_b$CO), 4.72 (1H, dd, *J* = 1.4, 12.0 Hz, OCH$_a\underline{H}_b$CO), 2.23 – 1.95 (5H, m, C$\underline{H}_2$), 1.68 (1H, m, C$\underline{H}_2$); ^{13}**C NMR** ($CDCl_3$, 126 MHz) δ 148.7 (C), 141.6 (C), 135.7 (C), 128.6 (CH), 128.4 (CH), 127.7 (CH), 127.6 (CH), 126.2 (CH), 125.7 (CH), 123.4 (C), 96.7 (CH), 77.5 (CH), 68.2 (CH_2), 32.4 (CH_2), 31.3 (CH_2), 21.7 (CH_2); **HRMS** (ESI+) *m/z* calculated for $C_{20}H_{20}NaO_3$ 331.1305 [M + Na]$^+$ found 331.1306. **Minor isomer 11b:** White solid (m.p 100 – 102 ºC); **R**$_f$ 0.18 (1:99 EtOAc/Pet spirit); ^{1}**H NMR** (C_6D_6, 500 MHz): δ 7.76 (2H, app. d, *J* = 7.7 Hz, 2 × Ar$\underline{H}$), 7.30 (2H, app. d, *J* = 7.5 Hz, 2 × Ar$\underline{H}$), 7.25 (2H, m, 2 × Ar$\underline{H}$), 7.15 - 7.11 (2H, m, 2 × Ar$\underline{H}$), 7.06 (2H, m, 2 × Ar$\underline{H}$), 5.00 (1H, br. s, ArC$\underline{H}$=CO), 4.87 (1H, dd, *J* = 2.3, 11.7 Hz, ArC$\underline{H}$(CH_2)CO), 4.41 (1H, dd, *J* = 1.9, 12.1 Hz, OC$\underline{H}_a$H$_b$CO), 4.19 (1H, dd, *J* = 1.3, 12.0 Hz, OCH$_a\underline{H}_b$CO), 2.04 – 1.93 (2H, m, C$\underline{H}_2$), 1.86 (1H, m, C$\underline{H}_2$), 1.51 (2H, m, C$\underline{H}_2$), 1.38 (1H, m, C$\underline{H}_2$); ^{13}**C NMR** (C_6D_6, 126 MHz) δ 149.5 (C), 142.3 (C), 136.1 (C), 128.7 (CH), 128.6 (CH), 128.3 (CH), 127.6 (CH), 126.3 (CH), 126.1 (CH), 123.2 (C), 97.3 (CH), 77.4 (CH), 66.7 (CH_2), 33.0 (CH_2), 31.7 (CH_2), 21.6 (CH_2); **MS**(+ESI) *m/z* 331 ([M+Na]$^+$, 85), 217 (80), 117 (100).

III. Experimental Details: X-ray Crystallography

A unique data set for compound **11a** was measured at 223 K respectively on an Oxford-Diffraction GEMINI S Ultra CCD diffractometer (Mo-K_{α} radiation) utilizing CrysAlis software.[3] The structures were solved by direct methods and refined by full matrix least squares refinement on F^2. Anisotropic thermal parameters were refined for non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included and constrained at estimated values. Conventional residuals at convergence are quoted; statistical weights were employed. Computation used, SIR-92,[4] SHELX97,[5] ORTEP-3 [6] and PLATON [7] programs.



Thermal ellipsoid plot of **11a**. Ellipsoids are at the 30% probability level.

Crystal data $C_{20}H_{20}O_3$, M_r = 308.36. Orthorhombic, space group *Pbca*, a = 19.6052(7), b = 6.8504(2), c = 24.8223(9) Å. V = 3333.7(2) Å^3. D_c (Z = 8) = 1.30 g cm^{-3}. μ_{Mo} = 0.08 mm^{-1}; crystal size: 0.32 x 0.27 x 0.19 mm. $T_{min/max}$ = 0.99, 1.00. 10970 reflections collected, 4549 unique (R_{int} = 0.029), N_o 3103; R = 0.066 [3103 reflections with $I > 2\square(I)$], wRF^2 = 0.117 (all data). S = 1.12.

Full .cif deposition resides with the Cambridge Crystallographic Data Centre (CCDC No1476765). Copies can be obtained free of charge on application at the following address: http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi).

IV. Computed Geometries and Energies

Cartesian coordinates and associated energies of the species modeled computationally are given below. Geometry optimizations and harmonic vibrational frequency calculations used the M06 functional in the gas phase with a mixed basis set consisting of LANL2DZ on Rh and 6-31G(d,p) on all other atoms. Single-point energies were subsequently computed in SMD implicit dichloromethane with the SDD basis set on Rh and 6-311+G(d,p) on other atoms. Gibbs free energies in solution were calculated by adding the thermochemical corrections derived from the vibrational frequency calculation to the solution-phase potential energy, and are reported a standard state of 298.15 K and 1 mol/L.

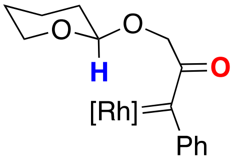
Underneath the coordinates of each species are listed the following energies (all in Hartree):

E: M06/6-31G(d,p)-LANL2DZ total potential energy (excluding zero-point energy) at 0 K

G: M06/6-31G(d,p)-LANL2DZ Gibbs free energy at 298.15 K and 1 mol/L

E_{soln}: M06/6-311+G(d,p)-SDD potential energy plus solvation energy in SMD dichloromethane

Rhodium carbene 18

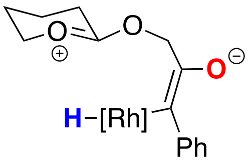


Rh	-0.671947	0.245064	-0.232376
O	0.255101	-1.327053	-1.218748
C	-0.126253	-2.523753	-0.992361
O	-1.096748	-2.881407	-0.280704
Rh	-2.304933	-1.422636	0.581201
C	0.673973	-3.601639	-1.668381
H	1.642711	-3.219066	-2.002764
H	0.118204	-3.964772	-2.539057
H	0.807190	-4.445322	-0.986342
O	0.409082	-0.160252	1.502858
C	-0.091732	-0.928216	2.392420
O	-1.176638	-1.555541	2.322015
C	0.725783	-1.073198	3.645712
H	0.220949	-1.724448	4.360486
H	1.708885	-1.487602	3.396375
H	0.894789	-0.087052	4.089324
O	-1.914013	0.492968	-1.858633
C	-2.915831	-0.278957	-2.007404
O	-3.303593	-1.175913	-1.213637
C	-3.721477	-0.055091	-3.254326
H	-3.064900	0.205783	-4.087044
H	-4.314718	-0.941665	-3.485691
H	-4.401048	0.787215	-3.087442
O	-1.772976	1.669791	0.785571
C	-2.879687	1.329080	1.321918
O	-3.364048	0.171303	1.383102

C	-3.682717	2.452623	1.912493
H	-4.212118	2.968434	1.104440
H	-4.414863	2.064795	2.622724
H	-3.023406	3.180168	2.391834
C	0.661329	1.578110	-0.909560
C	1.039923	2.810058	-0.294145
C	1.715281	3.807959	-1.038259
C	2.088700	4.997536	-0.443923
C	1.832942	5.204241	0.911879
C	1.192059	4.226365	1.669445
C	0.782078	3.045581	1.075169
H	0.282042	2.274300	1.649412
H	1.909674	3.644102	-2.095352
H	2.589458	5.764948	-1.027826
H	2.140083	6.135930	1.381641
H	1.005801	4.394261	2.726927
C	1.245330	1.245489	-2.229561
O	0.736220	1.642985	-3.259126
C	2.489501	0.391404	-2.187762
O	3.052686	0.476743	-0.896611
H	2.203014	-0.637442	-2.445437
H	3.193463	0.750259	-2.950257
C	3.304885	-0.735048	-0.265559
O	4.314525	-1.400734	-0.995868
C	3.735381	-0.461315	1.156208
H	2.391847	-1.367437	-0.272961
H	2.917112	0.052859	1.677130
H	4.604305	0.210547	1.118447
C	4.101836	-1.779913	1.828379
H	3.192797	-2.399873	1.918936
H	4.471024	-1.611443	2.847371
C	5.127326	-2.529837	0.985380
H	6.074365	-1.971986	0.970000
H	5.336862	-3.523056	1.402171
C	4.617241	-2.663783	-0.439137
H	5.359699	-3.123845	-1.099528
H	3.714408	-3.307155	-0.448143

0 imaginary frequencies
E = -1900.865418
G = -1900.443008
E_{soln} = -1903.438781

Rhodium hydride 19

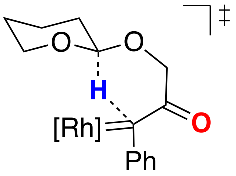


C	-3.342121	-0.079806	-0.201224
C	-4.663361	-0.228811	0.273452
C	-5.731167	-0.223175	-0.608537
C	-5.517785	-0.015992	-1.969188
C	-4.223021	0.171973	-2.445714
C	-3.142560	0.124076	-1.579901
C	-2.237190	-0.133083	0.733416
C	-2.456089	0.518073	2.034280
O	-3.077168	0.027155	2.956270
Rh	-0.432276	-0.770541	0.411601
Rh	1.952321	-0.976249	-0.341050
O	1.829922	-2.986698	0.122881

C	0.884581	-3.429992	0.842017
C	0.930771	-4.889828	1.203471
O	0.367012	0.022588	2.198012
C	1.607033	-0.186261	2.447586
C	2.022399	0.097864	3.864725
O	-0.914933	-1.665081	-1.391122
C	-0.032343	-1.739033	-2.309122
C	-0.530871	-2.277761	-3.620953
O	-0.090270	-2.759995	1.270117
O	2.482828	-0.566390	1.638849
O	2.110604	1.036695	-0.804183
O	1.181613	-1.421122	-2.225307
C	-1.825182	1.891959	2.246725
O	-1.698916	2.573077	0.975253
C	-0.586669	3.013121	0.492694
O	-0.707953	3.390665	-0.715066
C	0.436591	3.986951	-1.438946
C	1.253123	4.824449	-0.496869
C	1.780596	3.932595	0.614625
C	0.661964	3.121836	1.279813
H	-0.290306	0.574186	-0.356578
H	-0.854838	1.746691	2.730340
H	-2.496474	2.493198	2.864095
H	-0.047683	4.544396	-2.241409
H	1.042347	3.159678	-1.829176
H	0.981285	2.079405	1.442125
H	0.376285	3.515672	2.265043
H	2.492280	3.237022	0.160261
H	2.301667	4.516805	1.378583
H	2.091548	5.234892	-1.068962
H	0.656522	5.665203	-0.113310
H	3.102549	-0.001808	3.980208
H	1.707626	1.109331	4.147129
H	1.510371	-0.597217	4.537162
H	0.208076	-2.119585	-4.408131
H	-0.719146	-3.351035	-3.515213
H	-1.483324	-1.805474	-3.880951
H	1.872883	-5.343209	0.890974
H	0.095655	-5.403508	0.716581
H	0.793789	-5.004158	2.282465
H	-6.360348	0.005216	-2.655992
H	-2.131855	0.267386	-1.948440
H	-4.052741	0.350821	-3.504896
H	-6.739741	-0.369160	-0.229735
H	-4.829624	-0.389702	1.335818
C	2.996290	1.438268	-1.662748
O	3.071763	2.617527	-2.022372
C	3.948597	0.404000	-2.218509
H	4.721166	0.889287	-2.819226
H	4.417633	-0.166138	-1.405969
H	3.394838	-0.308551	-2.840802

0 imaginary frequencies
E = -1900.806777
G = -1900.391434
E_{soln} = -1903.390789

Transition state TS1 (hydride transfer to carbene)

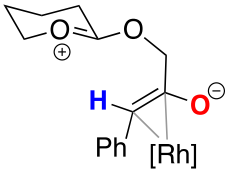


Rh	-0.546766	0.131808	0.216860
Rh	-2.827254	-0.128857	-0.677656
O	-2.710149	-2.131434	-0.129134
C	-1.685396	-2.539789	0.475710
O	-0.656637	-1.856968	0.783945
C	-1.656257	-3.977879	0.911624
H	-0.625199	-4.340303	0.942178
H	-2.072263	-4.050281	1.922268
H	-2.269142	-4.590446	0.247326
C	-0.695553	-0.702895	-2.584266
O	0.154454	-0.469659	-1.659352
O	-1.943376	-0.604325	-2.501596
H	0.649377	-0.451911	-4.232509
H	-0.894285	-1.261674	-4.648225
C	-0.113447	-1.159553	-3.893362
H	0.380184	-2.126753	-3.746058
O	-1.421956	0.654479	2.006585
C	-2.690086	0.649677	2.107774
O	-3.522893	0.354361	1.208357
C	-3.238508	1.073700	3.440042
H	-2.551183	0.797335	4.242010
H	-4.225374	0.634466	3.599004
H	-3.341407	2.163973	3.444758
O	-0.646503	2.104281	-0.411037
C	-1.720169	2.537845	-0.937851
O	-2.769745	1.881657	-1.168980
C	-1.717329	3.995933	-1.301080
H	-2.580920	4.240088	-1.921701
H	-1.750536	4.590963	-0.382788
H	-0.787048	4.248324	-1.817479
C	1.420124	0.396712	0.942771
C	1.555096	-0.035605	2.341646
C	2.289858	1.472959	0.459180
H	1.941604	-0.704021	0.262653
C	3.234779	2.090007	1.297152
H	3.289251	1.804812	2.343254
C	4.081373	3.072346	0.801806
H	4.802147	3.546051	1.463542
C	4.015891	3.440439	-0.538106
H	4.688461	4.201825	-0.926687
C	3.086370	2.834297	-1.383050
H	3.033255	3.123492	-2.429962
C	2.224788	1.868675	-0.890068
H	1.501486	1.385006	-1.541023
C	2.632800	-1.723394	0.466146
O	3.909355	-1.325083	0.756782
C	4.701664	-0.824112	-0.332686
H	4.335862	0.173036	-0.618296
H	5.705507	-0.709478	0.085701
C	4.671044	-1.753628	-1.524667
H	5.270555	-1.314673	-2.331077
H	5.134292	-2.714197	-1.257042
C	3.227789	-1.971029	-1.956482
H	3.166733	-2.646095	-2.817577

H	2.780146	-1.013893	-2.267405
C	2.433007	-2.537612	-0.791196
H	1.356926	-2.577522	-0.994132
H	2.774789	-3.554316	-0.542053
O	2.048360	-2.321703	1.526567
C	1.869990	-1.491490	2.656143
H	1.036320	-1.907081	3.230160
H	2.766456	-1.485703	3.291807
O	1.402585	0.728466	3.279370

1 imaginary frequency
E = -1900.852938
G = -1900.434081
E_{soln} = -1903.425012

Oxonium enolate 20

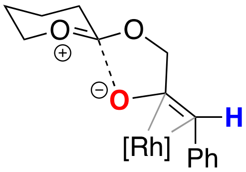


Rh	-0.488308	0.014662	0.175253
Rh	-2.751330	-0.486620	-0.667773
O	-2.848129	-1.987075	0.765767
C	-1.916493	-2.106510	1.603219
O	-0.829690	-1.447124	1.641579
C	-2.115805	-3.117882	2.700077
H	-1.157286	-3.511458	3.048340
H	-2.608154	-2.625442	3.545579
H	-2.762411	-3.927716	2.356237
C	-0.578036	-1.981421	-1.956596
O	0.252544	-1.441920	-1.153804
O	-1.817729	-1.796886	-2.008346
H	0.984224	-2.635937	-3.283345
H	-0.670229	-3.120543	-3.776733
C	0.004205	-2.974825	-2.931263
H	0.135789	-3.939846	-2.427588
O	-1.349643	1.409815	1.410624
C	-2.615345	1.519629	1.427012
O	-3.447591	0.873343	0.732157
C	-3.162935	2.555093	2.369336
H	-2.607178	2.536493	3.309868
H	-4.227668	2.389813	2.543502
H	-3.026197	3.546066	1.923704
O	-0.365758	1.393914	-1.361230
C	-1.384888	1.635568	-2.078366
O	-2.503685	1.056040	-2.030482
C	-1.225322	2.755963	-3.068207
H	-1.979330	2.686502	-3.854429
H	-1.347108	3.708582	-2.541651
H	-0.217075	2.743204	-3.490297
C	1.605542	0.594901	0.739986
C	1.656959	0.185159	2.120477
C	1.879531	1.992238	0.370227
H	2.037980	-0.100832	0.012972
C	1.563337	3.081382	1.196033
H	1.102126	2.887772	2.158987
C	1.839520	4.379119	0.783852
H	1.587559	5.209767	1.440344
C	2.427548	4.629965	-0.452794
H	2.639206	5.650093	-0.765367

C	2.736257	3.559671	-1.286942
H	3.183524	3.736843	-2.263513
C	2.463536	2.262462	-0.877245
H	2.657728	1.428648	-1.556223
C	3.155118	-1.945322	0.580393
O	4.122006	-1.203089	1.000153
C	5.032221	-0.551974	0.049897
H	4.547997	0.407651	-0.178360
H	5.934027	-0.366001	0.634794
C	5.269222	-1.390918	-1.179452
H	5.844765	-0.787738	-1.890364
H	5.886747	-2.263948	-0.925732
C	3.942741	-1.839728	-1.775692
H	4.096688	-2.456763	-2.665822
H	3.345830	-0.971537	-2.089658
C	3.157083	-2.629597	-0.735584
H	2.105754	-2.769533	-1.008517
H	3.611479	-3.618889	-0.569178
O	2.178208	-2.173590	1.355163
C	1.923182	-1.280406	2.495841
H	1.020047	-1.697004	2.941822
H	2.775758	-1.325874	3.177600
O	1.477724	0.870364	3.122317

0 imaginary frequencies
E = -1900.877946
G = -1900.457109
E_{soln} = -1903.468556

Transition state TS2 (C–C bond rotation and C–O bond formation in oxonium enolate 20)



Rh	0.708698	-0.077046	0.100401
Rh	3.114174	-0.402337	-0.268204
O	2.651946	-2.228749	-1.139048
O	3.155802	-1.308286	1.609247
C	2.092210	-1.445915	2.266898
O	0.926404	-1.062756	1.927512
C	1.446428	-2.580014	-1.231688
O	0.428716	-1.937791	-0.825184
H	0.640068	-3.704130	-2.850610
C	1.160990	-3.894050	-1.906785
H	0.494809	-4.496743	-1.282528
H	2.087127	-4.436076	-2.104200
C	2.192174	-2.166669	3.583932
H	1.460018	-1.773525	4.293004
H	1.974713	-3.228479	3.424566
H	3.203147	-2.081502	3.986720
C	2.429121	2.080474	1.043621
O	3.428896	1.444657	0.610682
O	1.216576	1.708907	1.012456
C	2.675116	3.440708	1.634061
O	2.862219	0.531913	-2.098989
H	3.703022	3.525411	1.991776
H	1.962725	3.636282	2.439269
H	2.510583	4.193688	0.855816
C	1.715322	0.954528	-2.416149

O	0.648748	0.864820	-1.734243
C	1.573585	1.632723	-3.750530
H	2.546827	1.752741	-4.229045
H	1.093162	2.606062	-3.615950
H	0.918088	1.032722	-4.389413
C	-1.440735	0.564233	0.715424
H	-1.215239	0.392881	1.770224
C	-1.744431	1.946706	0.363638
C	-1.572806	2.936587	1.346150
H	-1.182567	2.641589	2.319447
C	-1.867484	4.266420	1.089046
H	-1.724309	5.012451	1.868412
C	-2.340492	4.647572	-0.164427
H	-2.571116	5.690514	-0.371031
C	-2.506593	3.681161	-1.151913
H	-2.863941	3.971530	-2.138415
C	-2.211487	2.346555	-0.900495
H	-2.323712	1.593049	-1.673151
C	-1.892868	-0.563954	-0.011478
C	-1.950728	-1.862371	0.795804
O	-3.187009	-1.592292	1.622192
O	-2.514904	-0.569882	-1.097183
H	-1.164340	-2.001307	1.539026
H	-2.112256	-2.741444	0.173633
C	-4.271053	-1.506888	0.954370
O	-4.496079	-2.368559	0.023430
C	-5.250740	-1.990694	-1.177844
C	-6.317714	-0.967022	-0.884940
C	-5.745159	0.166447	-0.047101
C	-5.223459	-0.415367	1.271490
H	-4.910879	0.652739	-0.572630
H	-6.499103	0.929966	0.163854
H	-4.697183	0.321812	1.883939
H	-6.055266	-0.830355	1.859554
H	-6.697467	-0.598059	-1.844481
H	-7.164360	-1.435067	-0.362906
H	-4.466189	-1.601588	-1.838623
H	-5.641307	-2.935790	-1.558614

1 imaginary frequency
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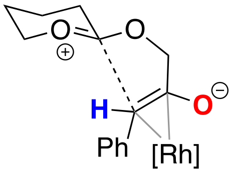
G = -1900.446852
E_{soln} = -1903.452873

Transition state TS3 (C–C bond formation in oxonium enolate 20)



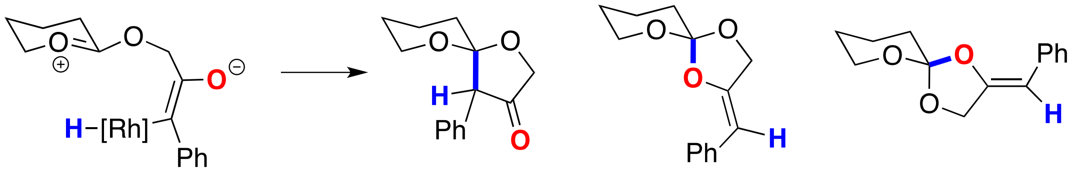
Rh	0.670382	-0.132416	-0.036781
Rh	3.050859	0.192407	0.294032
O	2.965667	1.706023	-1.104771
O	2.582253	1.558148	1.774253
O	0.364356	1.220977	1.494270
C	1.367754	1.768147	2.045406
O	0.741280	1.406109	-1.402324
C	1.848108	1.979271	-1.632634
H	1.114542	3.865191	-2.289319
C	1.810336	3.095150	-2.635828
H	2.803390	3.523783	-2.779001

H	1.422746	2.713290	-3.584807
H	1.972422	3.215630	3.511163
C	1.057738	2.759207	3.130197
H	0.386460	3.528299	2.736054
H	0.530444	2.251547	3.943946
O	0.750952	-1.675567	1.353129
C	1.874139	-1.948632	1.880521
O	2.970524	-1.359435	1.669841
C	1.894479	-3.114830	2.827514
H	2.795437	-3.095879	3.442945
H	1.884946	-4.041706	2.244150
H	0.998433	-3.109497	3.452803
O	1.180432	-1.498733	-1.523821
C	2.403956	-1.700202	-1.790173
O	3.396046	-1.175512	-1.210367
C	2.696418	-2.630337	-2.931762
H	2.701811	-2.048923	-3.859876
H	3.678727	-3.090315	-2.808013
H	1.917247	-3.390672	-3.018078
C	-1.864616	-0.187589	-0.226580
O	-1.650520	-0.631871	-2.577777
C	-1.666238	-1.008510	-1.417333
H	-1.551729	-0.572524	0.745411
C	-2.319947	1.204078	-0.246137
C	-2.492597	1.875013	0.977485
H	-2.213337	1.365159	1.899061
C	-2.988929	3.169382	1.027392
H	-3.113731	3.661592	1.990066
C	-3.321113	3.836377	-0.148860
H	-3.710477	4.851247	-0.114168
C	-3.139048	3.192129	-1.368764
H	-3.382535	3.708816	-2.295048
C	-2.641593	1.895505	-1.425591
H	-2.481483	1.402454	-2.379570
C	-1.655716	-2.518062	-1.139238
H	-0.647786	-2.915266	-1.000196
H	-2.160614	-3.021160	-1.969730
O	-2.371691	-2.730572	0.096295
C	-3.356222	-1.862633	0.222263
O	-4.208340	-1.835503	-0.792948
C	-5.238589	-0.820525	-0.773283
C	-5.961925	-0.816404	0.552109
C	-4.961903	-0.589023	1.676986
C	-3.859395	-1.640843	1.611205
H	-3.010725	-1.414882	2.264340
H	-4.250435	-2.622241	1.931162
H	-5.450512	-0.631317	2.655938
H	-4.522572	0.412557	1.576346
H	-6.482445	-1.775741	0.685799
H	-6.725329	-0.030484	0.538201
H	-5.885578	-1.074365	-1.615311
H	-4.751396	0.143293	-0.976120

1 imaginary frequency
E = -1900.872260
G = -1900.449480
E_{soln} = -1903.448543

Comparison of C–C and C–O Bond Formation in Oxonium Enolate 20

Calculations were performed to examine the selectivity of cyclization of oxonium enolate **20**. Two pathways were considered: (i) C–C bond formation via addition of the enolate carbon to the bottom face of the oxonium ion, leading to the classic C–H insertion product **22** (analogous to spiroacetal **10a**), and (ii) a rotation about the CH$_2$–C$_{C=O}$ bond which brings the oxonium center into proximity with the enolate oxygen, leading to C–O bond formation and production of the 'anomalous' orthoester **21a** (analogous to **11a**). Free energy diagrams were constructed by performing a series of geometry optimizations at a range of C–C bond distances or C–C–C–O dihedral angles as shown in Figure S1. The plot in Figure S1(a) contains a maximum at about 2.3 Å, which approximates the transition state for formation of **22**. The energy of this TS is $\Delta G^\ddagger = 13.8$ kcal/mol. In Figure S1(b), bond rotation is seen to produce an increase in energy up until a dihedral angle of about 75°; further bond rotation then produces a steep drop in energy. When the dihedral is 75°, the oxonium carbon is 2.86 Å away from the enolate oxygen. Further bond rotation is accompanied by bond formation between these two centers, explaining the drop in energy. The 75° structure approximates the transition state for formation of **21a**. Its energy is $\Delta G^\ddagger = 10.6$ kcal/mol. Thus, formation of the classic C–C bonded insertion product has a 3 kcal/mol higher barrier than formation of the 'anomalous' C–O bonded product. This is consistent with the exclusive formation of C–O bonded products in the reaction of Rh carbene **6**.



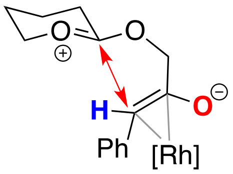
20

22
C-C bonded
(bottom face)

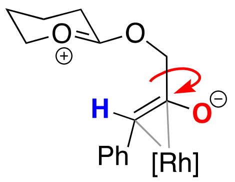
21a
C-O bonded
(bottom face)

21b
C-O bonded
(top face)

(a) Formation of C–C bond (leads to **22**)



(b) Rotation about C–C bond (leads to **21a**)



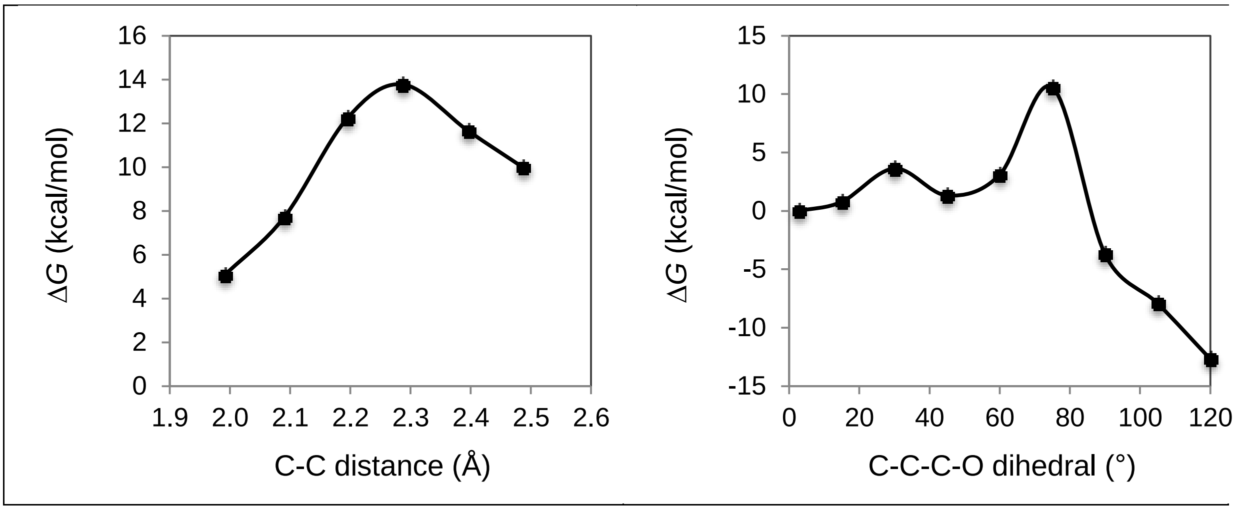
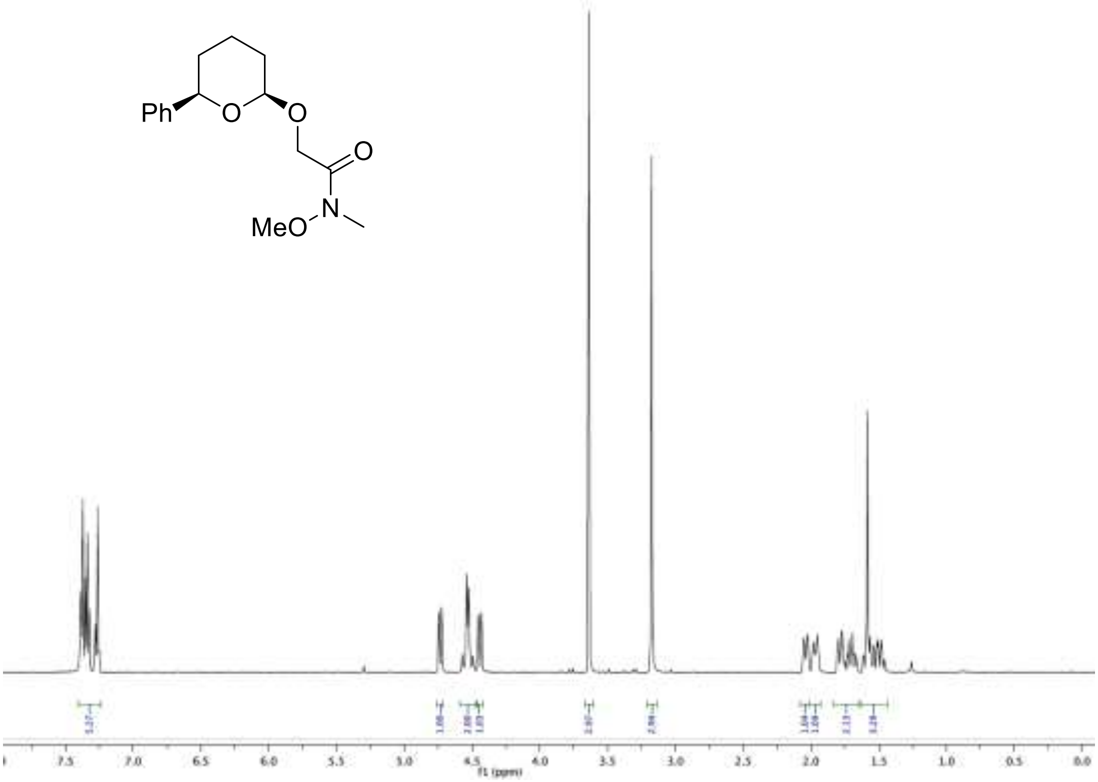


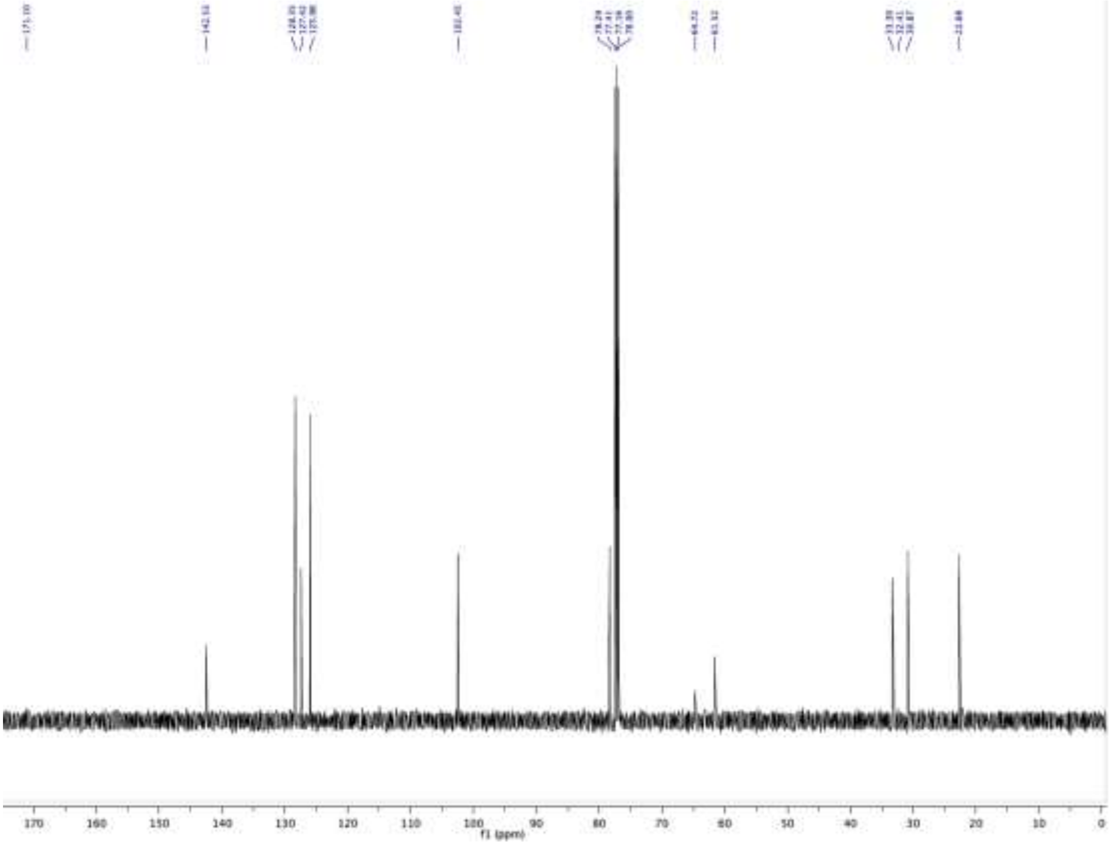
Figure S1. Plots of Δ*G* vs (a) C–C distance and (b) C–C–C–O dihedral angle in oxonium enolate **20**. The C–C bond formation shown in (a) leads to the classic C–C bonded product **22**. The C–C–C–O bond rotation shown in (b) leads to formation of the C–O bonded 'anomalous' product **21a**.

V. NMR spectra for compounds 5, 7 – 9, S4-5 and 11a-b

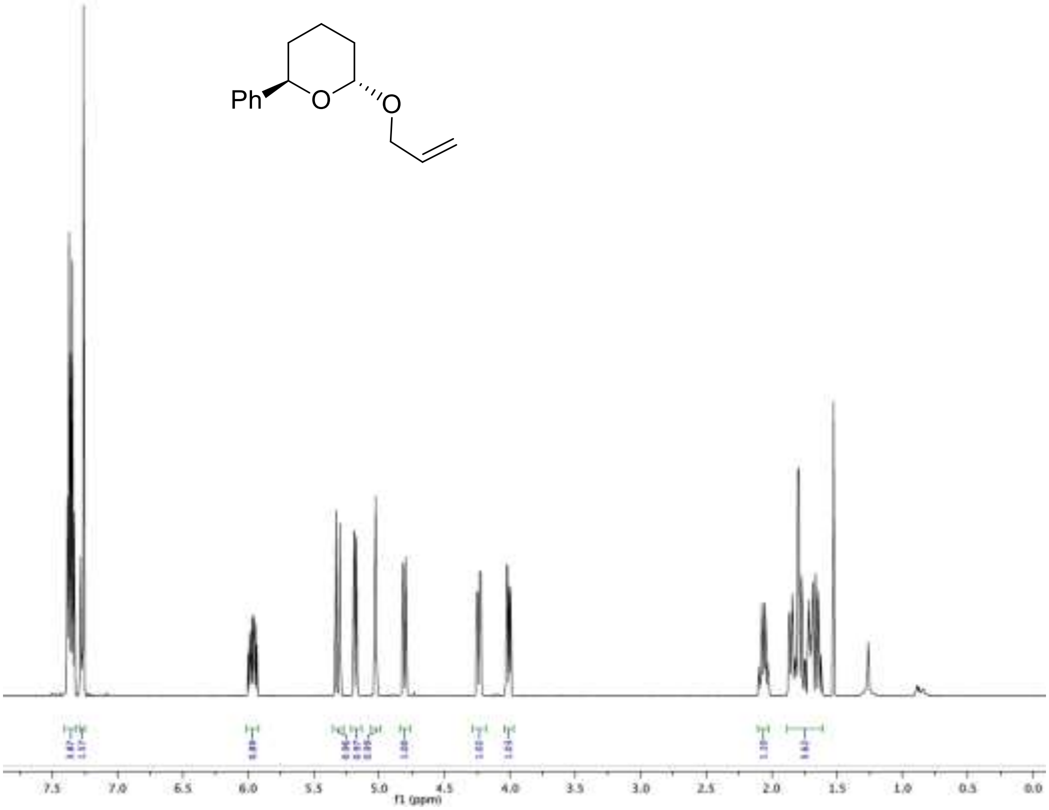
^{1}H NMR spectrum (500 MHz) of compound **5** in $CDCl_3$



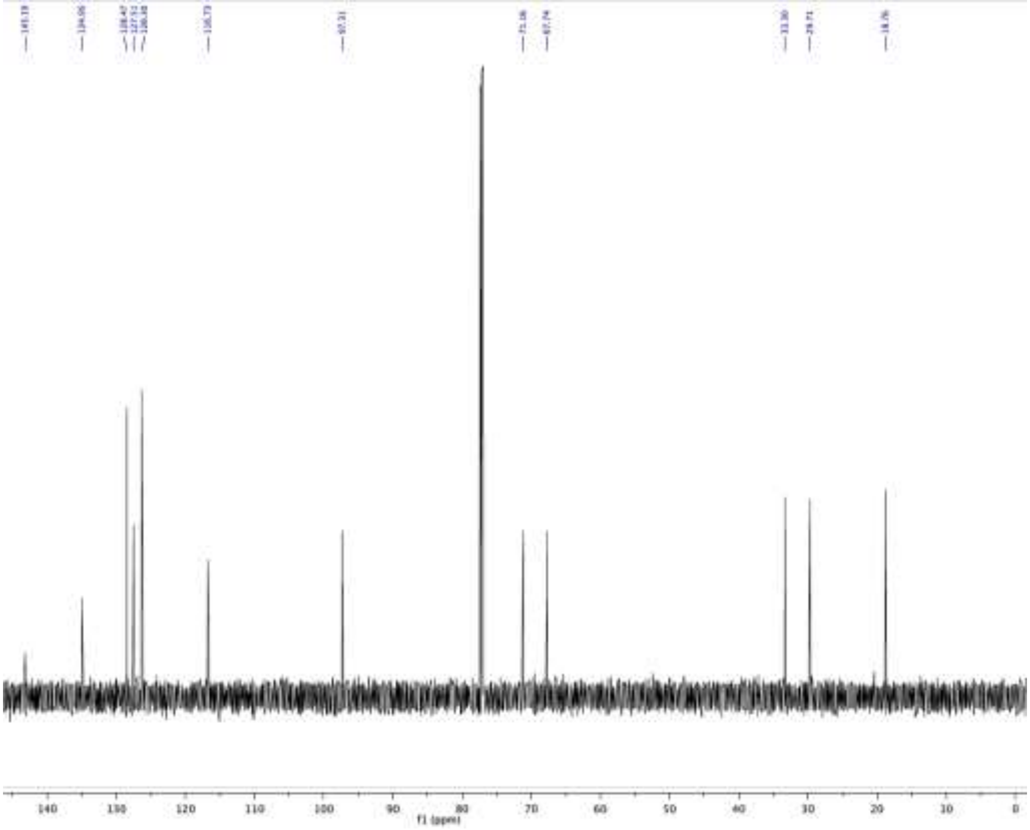
^{13}C NMR spectrum (126 MHz) of compound **5** in $CDCl_3$



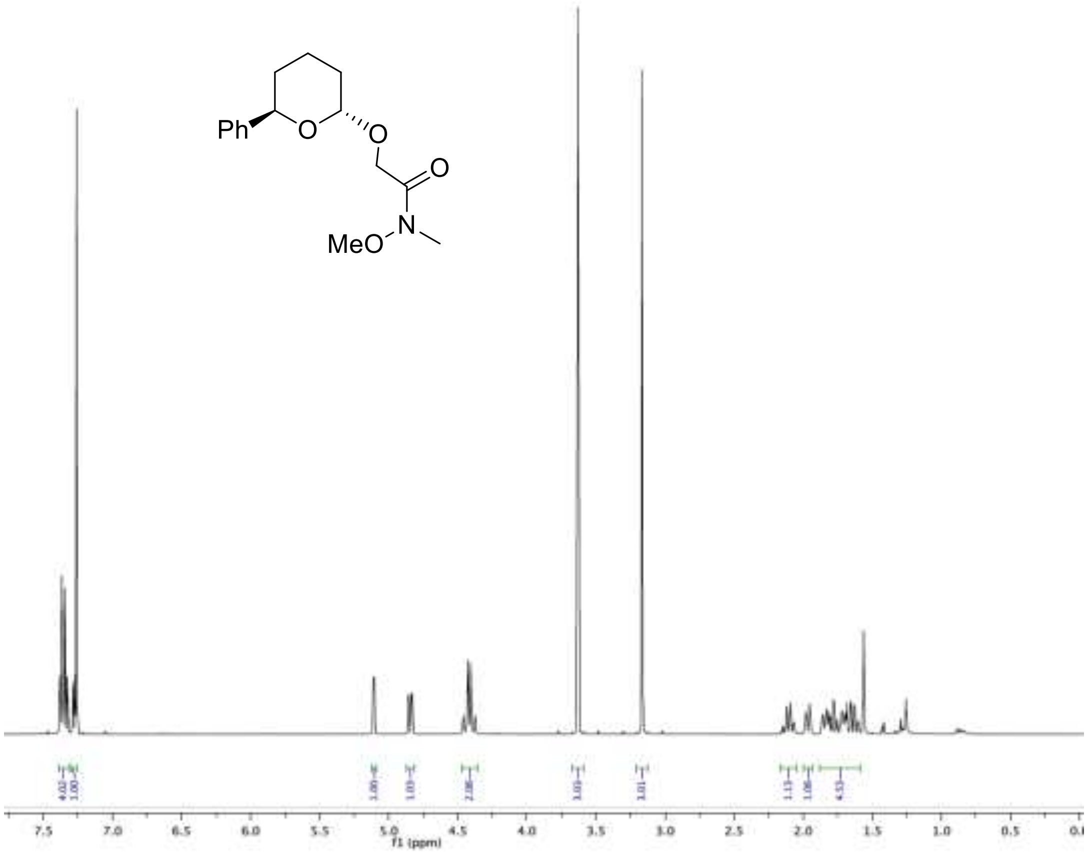
^{1}H NMR spectrum (600 MHz) of compound **7** in $CDCl_3$



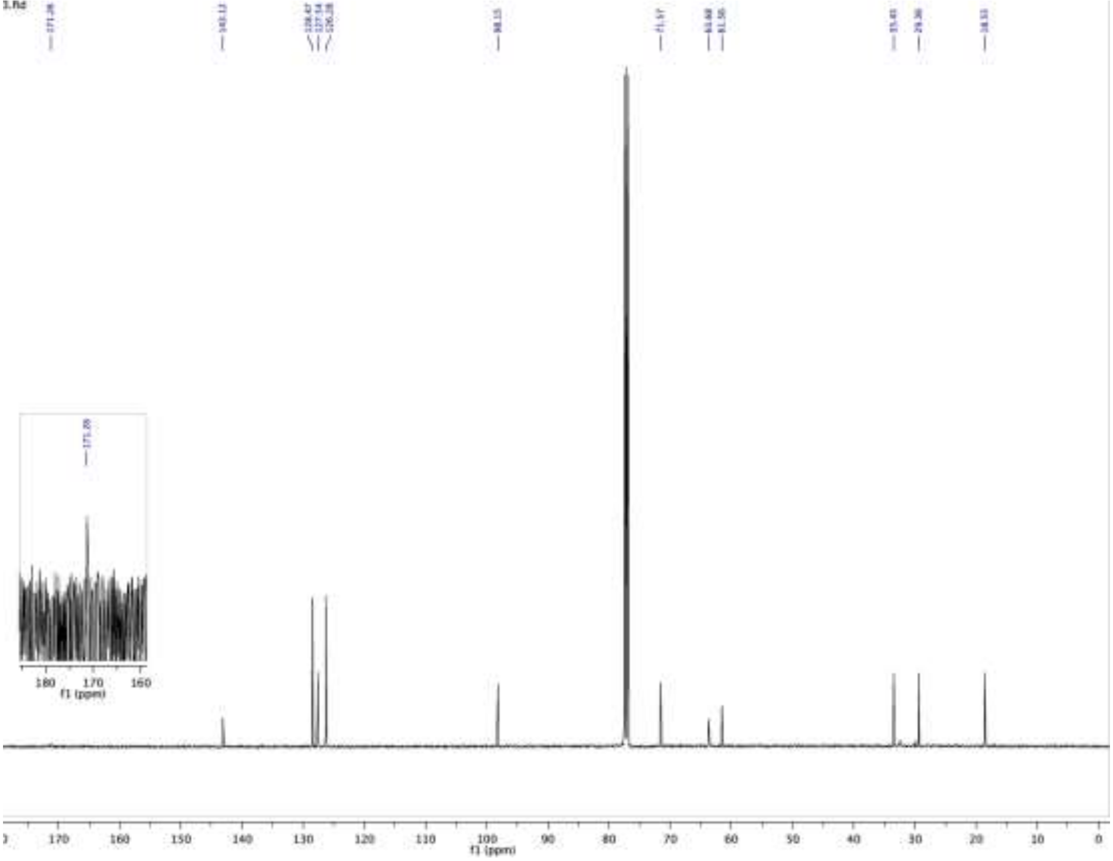
^{13}C NMR spectrum (151 MHz) of compound **7** in $CDCl_3$



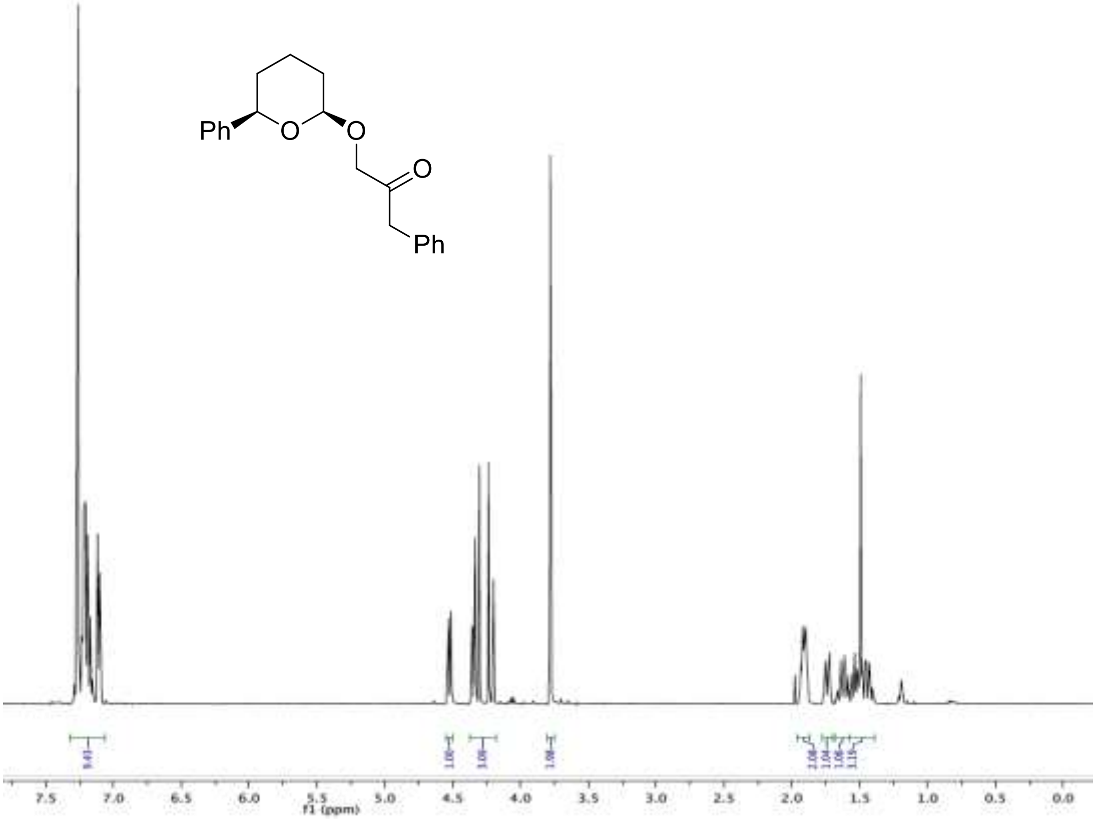
^{1}H NMR spectrum (500 MHz) of compound **8** in $CDCl_3$



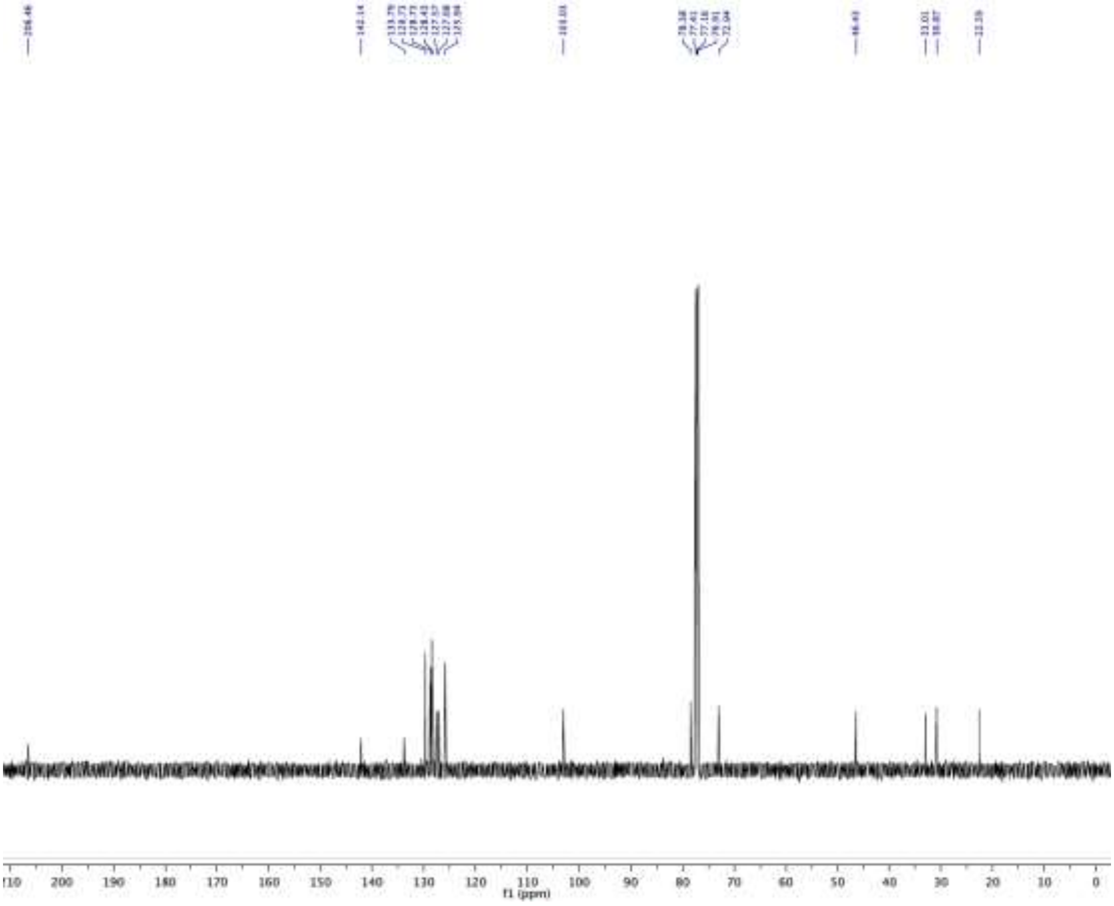
^{13}C NMR spectrum (126 MHz) of compound **8** in $CDCl_3$



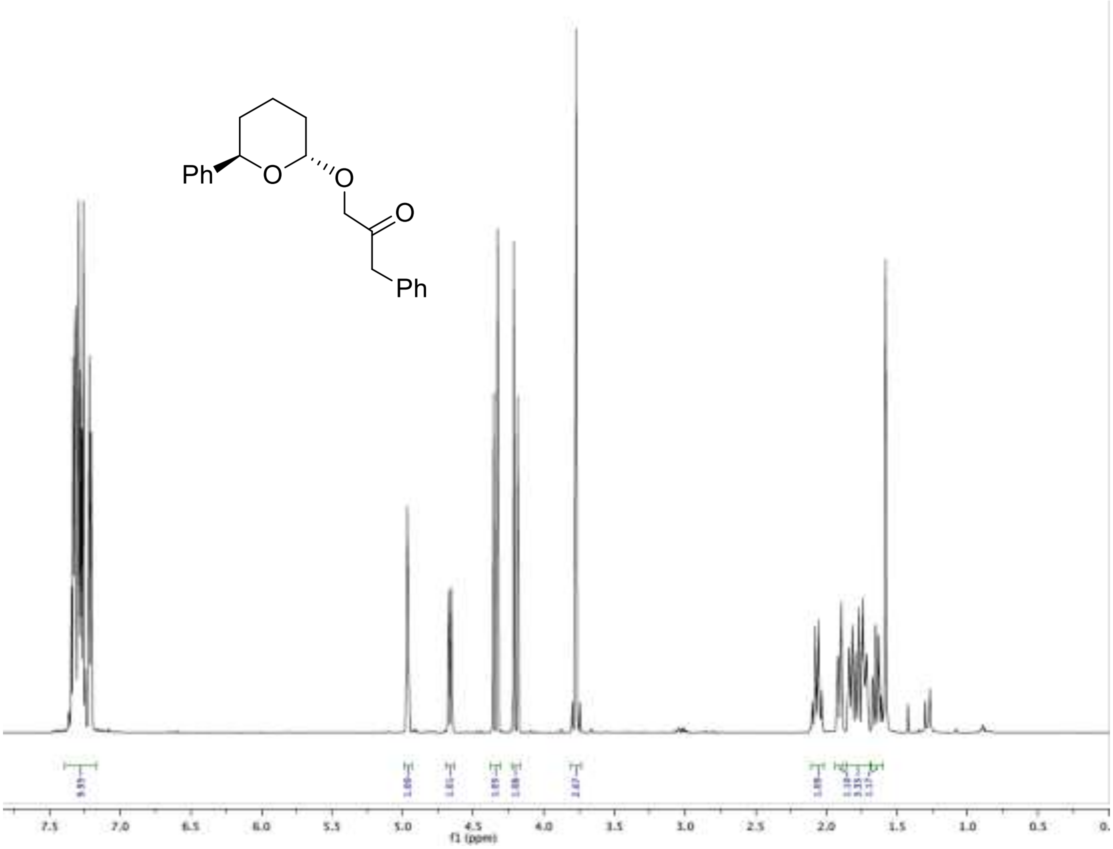
^{1}H NMR spectrum (500 MHz) of compound **S4** in $CDCl_3$



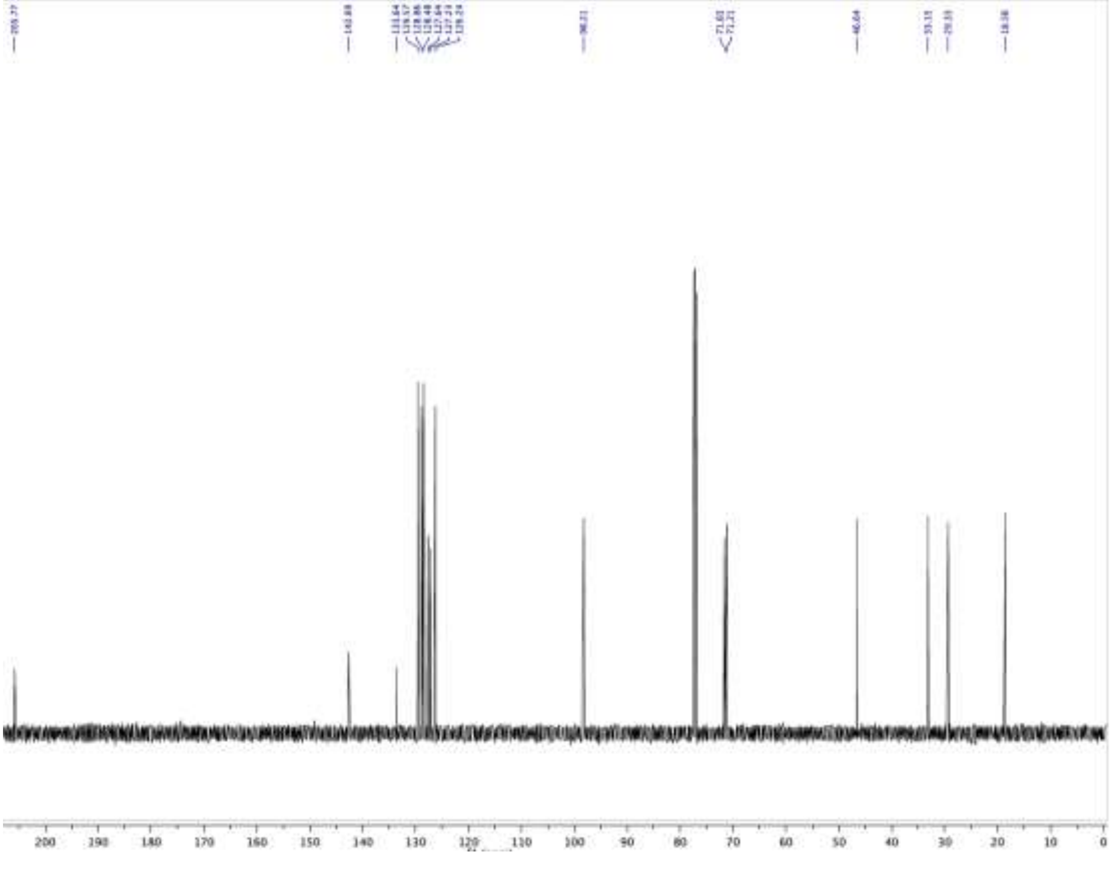
^{13}C NMR spectrum (126 MHz) of compound **S4** in $CDCl_3$



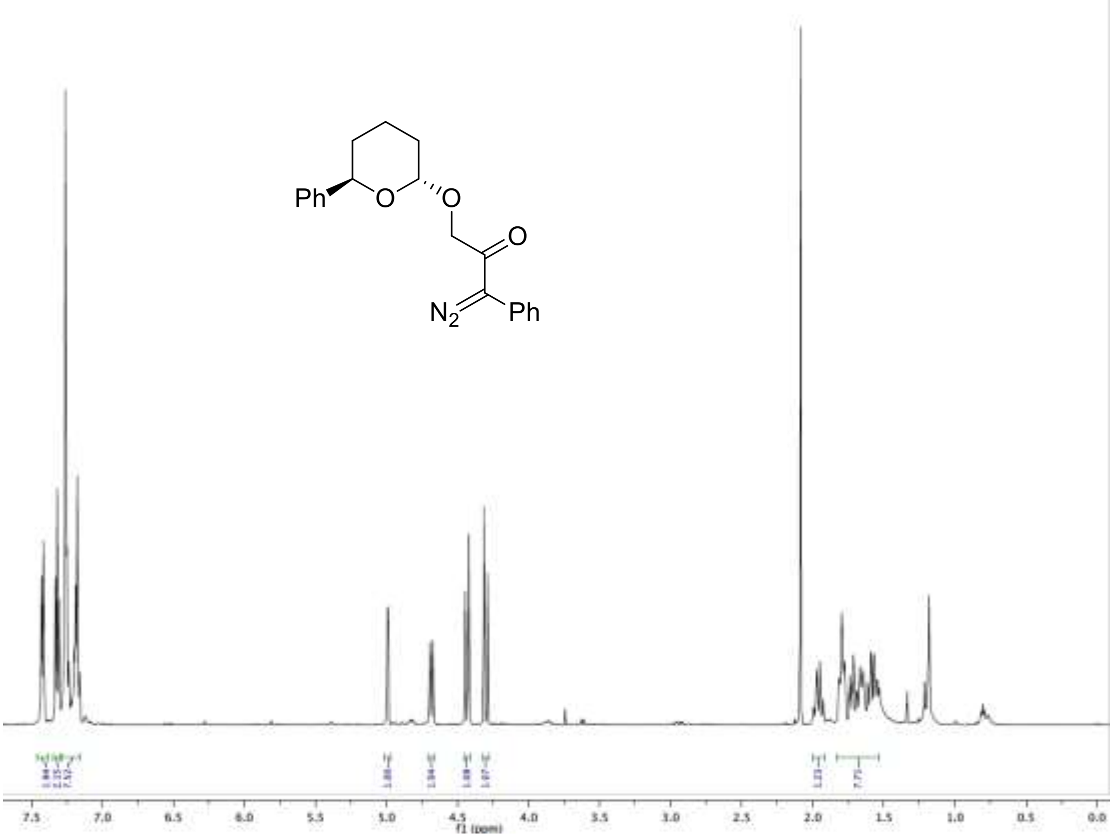
^{1}H NMR spectrum (600 MHz) of compound **S5** in $CDCl_3$



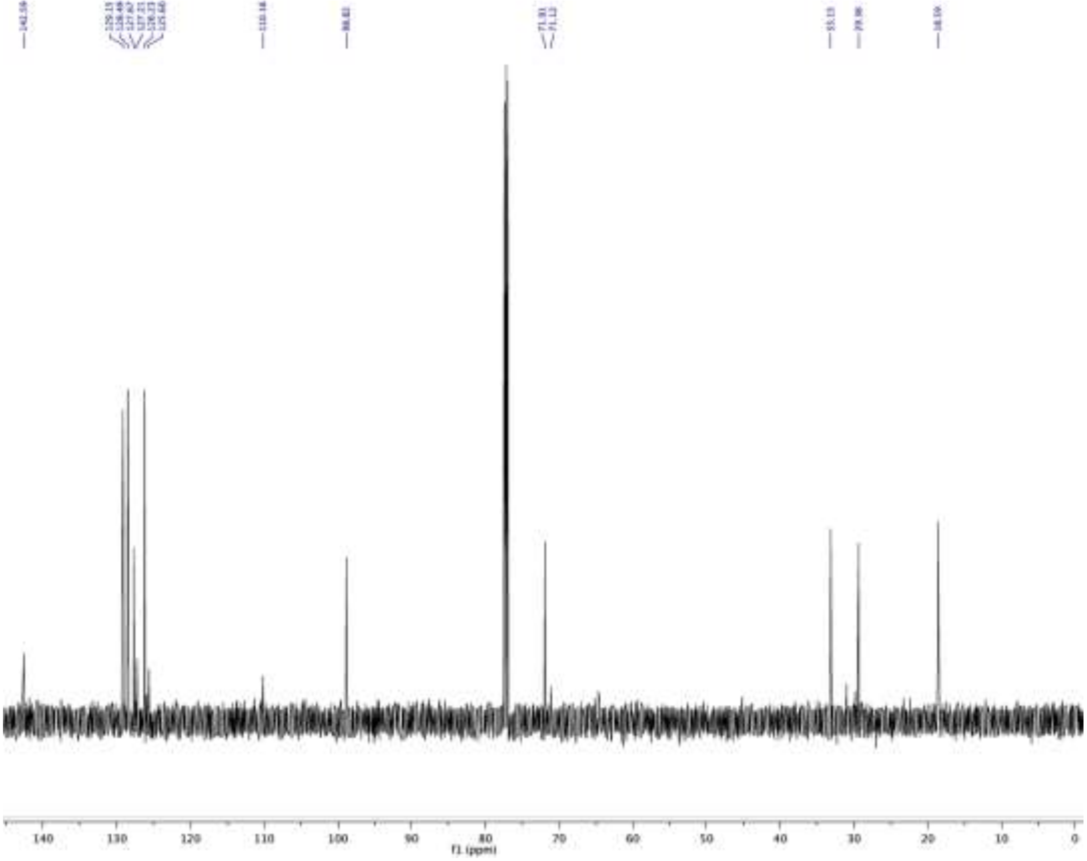
^{13}C NMR spectrum (151 MHz) of compound **S5** in $CDCl_3$



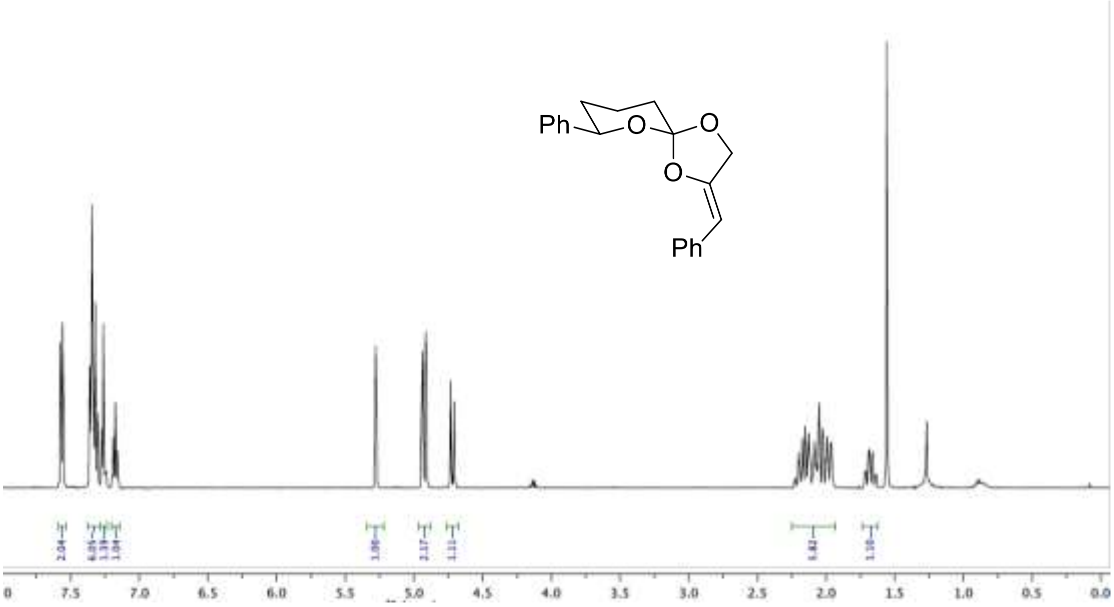
^{1}H NMR spectrum (600 MHz) of compound **9** in CDCl$_3$



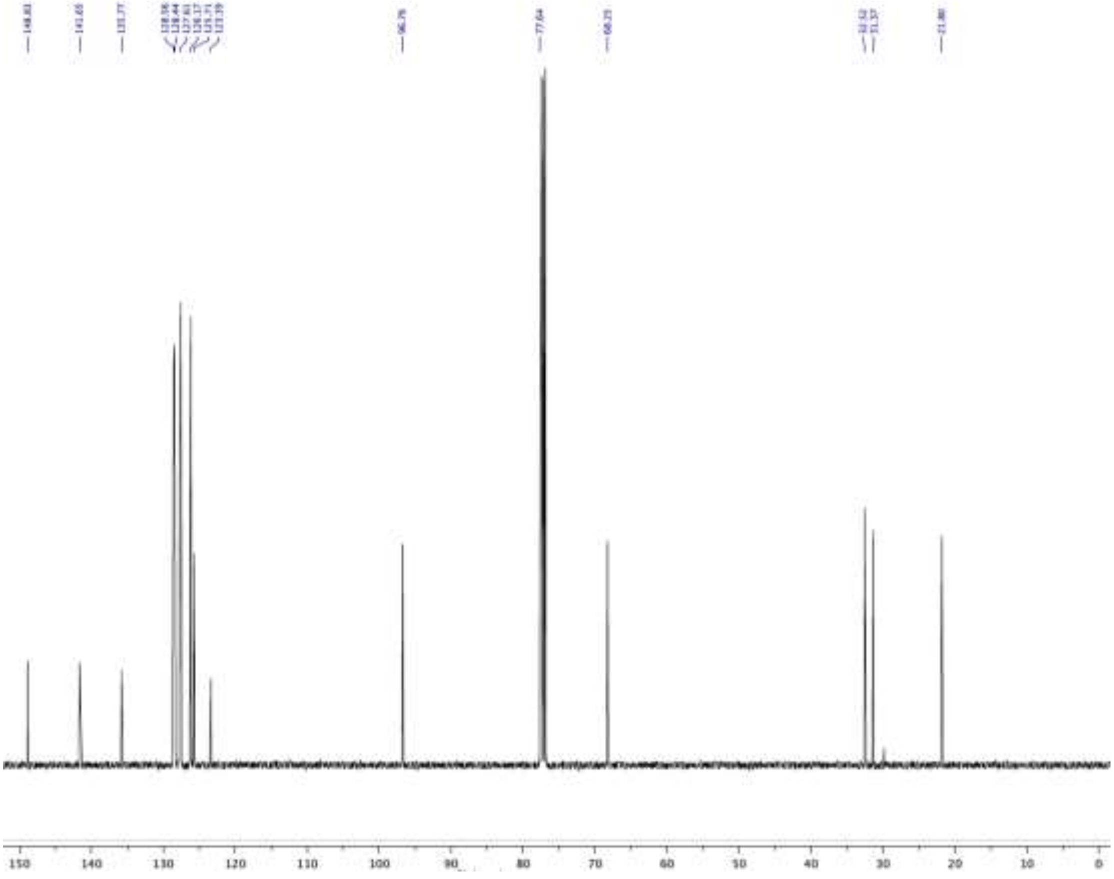
^{13}C NMR spectrum (151 MHz) of compound **9** in CDCl$_3$



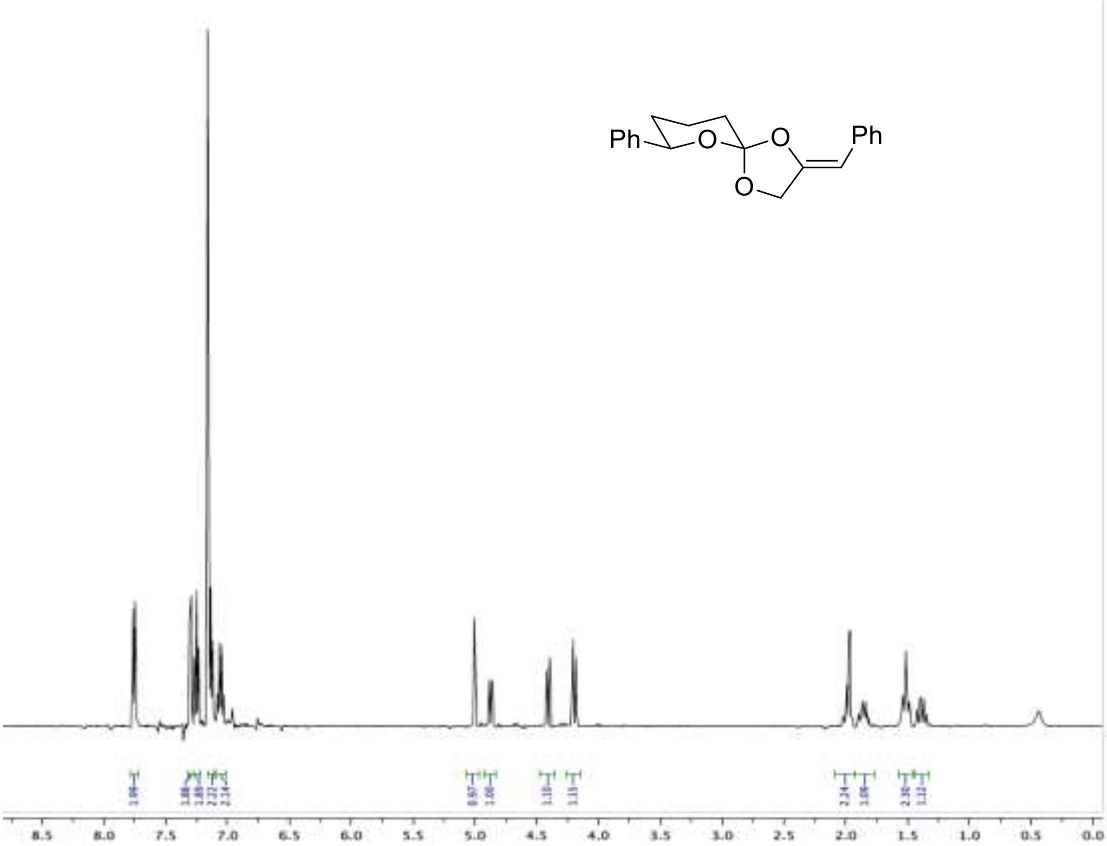
^{1}H NMR spectrum (500 MHz) of compound **11a** in $CDCl_3$



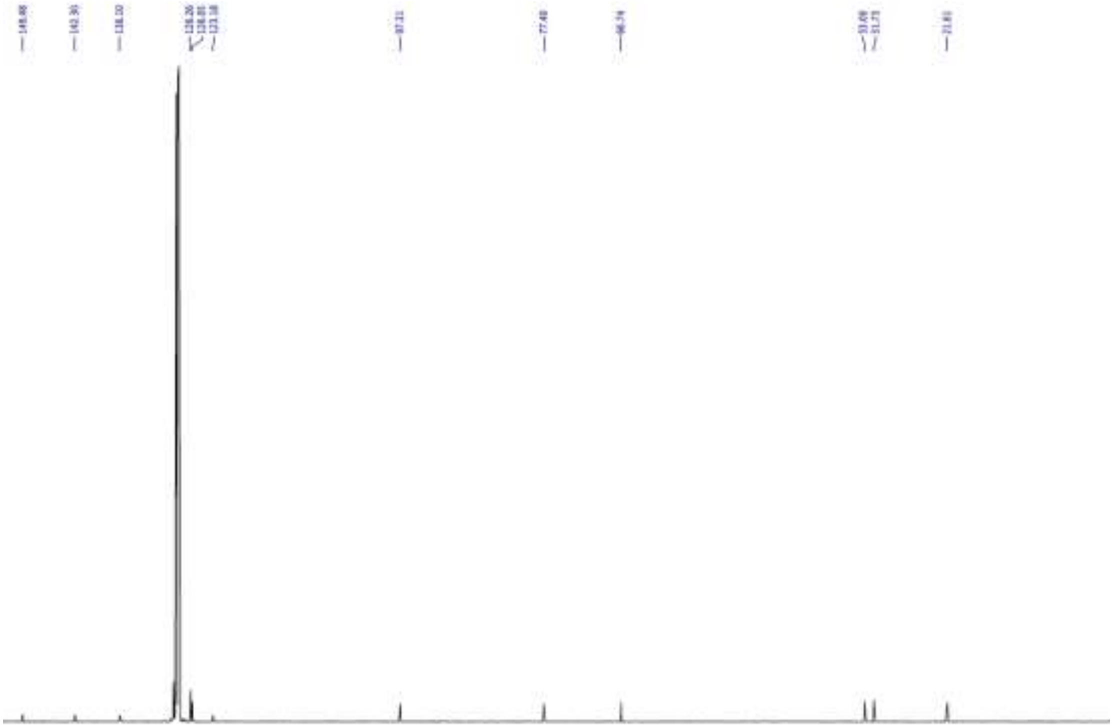
^{13}C NMR spectrum (126 MHz) of compound **11a** in $CDCl_3$



^{1}H NMR spectrum (500 MHz) of compound **11b** in C_6D_6



^{13}C NMR spectrum (126 MHz) of compound **11b** in C_6D_6



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