Supporting Information

Exploring Efficient and Air-Stable d^2 Re(V) Alkylidyne Catalysts: Toward Room Temperature Alkyne Metathesis

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1. X-ray Crystallography Studies

Intensity data of **12b**·2$CHCl_3$, **14**·0.5C_7H_8 (C_7H_8 = toluene) and **15** were collected on a Rigaku OD Xcalibur, Gemini Ultra, Sapphire3 diffractometer with monochromatized Cu-Kα at 100 or 173 K. Diffraction data were processed using the CrysAlisPro software (version 1.171.41.93a, Rigaku Oxford Diffraction, 2021). Empirical absorption corrections were performed using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm in the CrysAlisPro software suite.

Using Olex2,[1] the structures of **12b**·2$CHCl_3$, **14**·0.5C_7H_8 (C_7H_8 = toluene) and **15** were solved with the ShelXT[2] structure solution program using Intrinsic Phasing and was refined with the ShelXL[3] refinement package using Least Squares minimisation. All of non-hydrogen atoms were refined anisotropically with a riding model for the hydrogen atoms except noted separately.

Further crystallographic details and structural parameters are summarized in Tables S1-S2. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications, CCDC reference numbers 2360919 (**12b**·2$CHCl_3$), 2289258 (**14**·0.5C_7H_8) and 2360920 (**15**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic details for **12b** $2CHCl_3$ and **14** $0.5C_7H_8$.

Compound	**12b** $2CHCl_3$	**14** $0.5C_7H_8$
CCDC No.	2360919	2289258
Empirical formula	$C_{105.5}H_{55.5}Cl_{6.5}F_{48}O_4P_4Re_2Zn$	$C_{47.5}H_{41}O_3P_2Re$
Formula weight	3091.07	907.94
Temperature/K	173.00(10)	100.00(10)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	17.1380(3)	14.9819(6)
b/Å	18.3645(4)	14.9880(4)
c/Å	21.0670(5)	19.2809(6)
α/°	107.093(2)	75.285(3)
β/°	92.870(2)	68.908(3)
γ/°	113.868(2)	83.041(3)
Volume/$Å^3$	5686.2(2)	3904.8(2)
Z	2	4
$\rho_{calc}g/cm^3$	1.805	1.544
μ/mm^{-1}	7.436	7.188
F(000)	3006.0	1820.0
Crystal size/mm^3	0.22 × 0.18 × 0.06	0.1 × 0.08 × 0.08
Radiation	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/ °	4.472 to 145.422	6.604 to 142.106
Index ranges	$-21 \le h \le 15$, $-22 \le k \le 21$, $-24 \le l \le 26$	$-17 \le h \le 18$, $-18 \le k \le 13$, $-21 \le l \le 23$
Reflections collected	34705	22474
Independent reflections	21495 [R_{int} = 0.0368, R_{sigma} = 0.0568]	14375 [R_{int} = 0.0320, R_{sigma} = 0.0495]
Data/restraints/parameters	21495/953/1916	14375/642/1148
Goodness-of-fit on F^2	1.035	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0537, wR_2 = 0.1450	R_1 = 0.0355, wR_2 = 0.0855
Final R indexes [all data]	R_1 = 0.0632, wR_2 = 0.1564	R_1 = 0.0451, wR_2 = 0.0931
Largest diff. peak/hole / e $Å^{-3}$	2.96/-1.62	1.68/-1.07

Table S2. Crystallographic details for **15**.

Compound	**15**
CCDC No.	2360920
Empirical formula	$C_{46}H_{41}O_2P_2ReS$
Formula weight	905.99
Temperature/K	173.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.0053(5)
b/Å	11.4390(4)
c/Å	17.8263(6)
α/°	85.487(3)
β/°	78.475(3)
γ/°	62.411(4)
Volume/Å^3	1948.62(15)
Z	2
ρ_{calc}g/cm^3	1.544
μ/mm^{-1}	7.667
F(000)	908.0
Crystal size/mm^3	0.1 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.06 to 149.238
Index ranges	$-13 \leq h \leq 7$, $-14 \leq k \leq 13$, $-22 \leq l \leq 22$
Reflections collected	11819
Independent reflections	7585 [R_{int} = 0.0159, R_{sigma} = 0.0208]
Data/restraints/parameters	7585/0/471
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0159, wR_2 = 0.0393
Final R indexes [all data]	R_1 = 0.0166, wR_2 = 0.0397
Largest diff. peak/hole / e Å^{-3}	0.51/-0.53

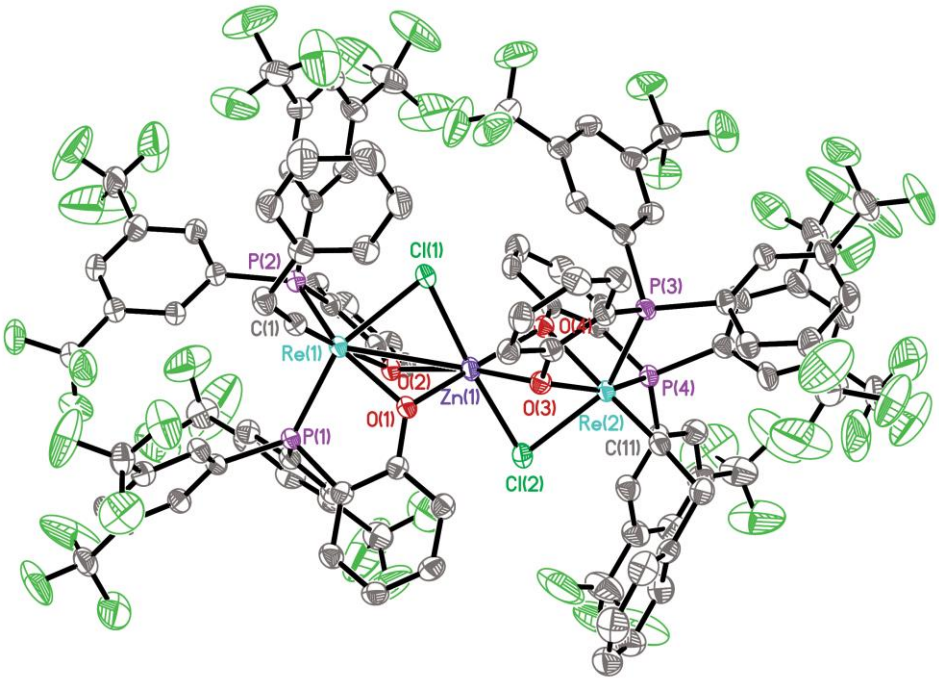


Figure S1. ORTEP diagram of the $ZnCl_2$-bridged complex **12b** with thermal ellipsoids at the 40% probability level. All hydrogen atoms as well as solvent atoms are omitted for clarity.

Selected bond lengths (Å) in **12b**:			
Re(1)-Zn(1)	3.0505(7)	Re(2)-Zn(1)	3.0527(7)
Re(1)-C(1)	1.763(5)	Re(2)-C(11)	1.765(6)
Re(1)-Cl(1)	2.4790(13)	Re(2)-Cl(2)	2.5040(14)
Re(1)-P(1)	2.3479(13)	Re(2)-P(3)	2.3327(14)
Re(1)-P(2)	2.3269(14)	Re(2)-P(4)	2.3303(14)
Re(1)-O(1)	2.175(4)	Re(2)-O(3)	2.100(4)
Re(1)-O(2)	2.109(4)	Re(2)-O(4)	2.167(4)
Zn(1)-Cl(1)	2.4348(16)	Zn(1)-Cl(2)	2.4386(16)
Zn(1)-O(1)	2.096(4)	Zn(1)-O(2)	2.118(4)
Zn(1)-O(3)	2.115(4)	Zn(1)-O(4)	2.103(4)

Selected bond angles (deg.) in **12b**:			
C(1)-Re(1)-Zn(1)	136.15(18)	C(11)-Re(2)-Zn(1)	138.84(19)

C(1)-Re(1)-Cl(1)	99.96(18)	C(11)-Re(2)-Cl(2)	103.00(19)
C(1)-Re(1)-P(1)	98.50(18)	C(11)-Re(2)-P(3)	95.4(2)
C(1)-Re(1)-P(2)	97.64(18)	C(11)-Re(2)-P(4)	96.3(2)
C(1)-Re(1)-O(1)	177.3(2)	C(11)-Re(2)-O(3)	106.1(2)
C(1)-Re(1)-O(2)	107.1(2)	C(11)-Re(2)-O(4)	177.3(2)
P(1)-Re(1)-Cl(1)	155.77(5)	P(3)-Re(2)-Cl(2)	153.17(5)
P(2)-Re(1)-Cl(1)	88.59(5)	P(4)-Re(2)-Cl(2)	96.61(5)
P(2)-Re(1)-P(1)	104.36(5)	P(4)-Re(2)-P(3)	100.67(5)
O(1)-Re(1)-Cl(1)	77.90(10)	O(3)-Re(2)-Cl(2)	76.79(11)
O(1)-Re(1)-P(1)	83.99(10)	O(3)-Re(2)-P(3)	79.43(11)
O(1)-Re(1)-P(2)	80.79(11)	O(3)-Re(2)-P(4)	157.47(11)
O(2)-Re(1)-Cl(1)	79.65(11)	O(4)-Re(2)-Cl(2)	77.82(11)
O(2)-Re(1)-P(1)	80.02(11)	O(4)-Re(2)-P(3)	84.76(11)
O(2)-Re(1)-P(2)	154.06(11)	O(4)-Re(2)-P(4)	81.01(11)
O(2)-Re(1)-O(1)	74.20(15)	O(4)-Re(2)-O(3)	76.56(15)
Re(2)-Zn(1)-Re(1)	167.10(3)	Cl(2)-Zn(1)-Cl(1)	175.44(5)
Cl(1)-Zn(1)-Re(1)	52.28(3)	Cl(1)-Zn(1)-Re(2)	122.98(4)
Cl(2)-Zn(1)-Re(1)	132.24(4)	Cl(2)-Zn(1)-Re(2)	52.83(3)
O(1)-Zn(1)-Re(1)	45.47(11)	O(3)-Zn(1)-Re(1)	123.72(11)
O(1)-Zn(1)-Re(2)	147.15(11)	O(3)-Zn(1)-Re(2)	43.39(11)
O(1)-Zn(1)-Cl(1)	80.38(12)	O(3)-Zn(1)-Cl(1)	99.94(12)
O(1)-Zn(1)-Cl(2)	102.66(12)	O(3)-Zn(1)-Cl(2)	78.00(12)
O(2)-Zn(1)-Re(1)	43.69(10)	O(4)-Zn(1)-Re(1)	140.98(11)
O(2)-Zn(1)-Re(2)	126.94(11)	O(4)-Zn(1)-Re(2)	45.21(10)
O(2)-Zn(1)-Cl(1)	80.51(11)	O(4)-Zn(1)-Cl(1)	95.12(12)
O(2)-Zn(1)-Cl(2)	103.47(12)	O(4)-Zn(1)-Cl(2)	80.48(12)
O(2)-Zn(1)-O(1)	75.65(15)	O(4)-Zn(1)-O(1)	117.10(15)
O(3)-Zn(1)-O(1)	165.26(15)	O(4)-Zn(1)-O(2)	165.85(15)
O(3)-Zn(1)-O(2)	89.82(15)	O(4)-Zn(1)-O(3)	77.61(15)
Zn(1)-Cl(1)-Re(1)	76.74(4)	Zn(1)-Cl(2)-Re(2)	76.27(4)
Zn(1)-O(1)-Re(1)	91.15(15)	Zn(1)-O(2)-Re(1)	92.38(15)
Zn(1)-O(3)-Re(2)	92.82(15)	Zn(1)-O(4)-Re(2)	91.26(14)

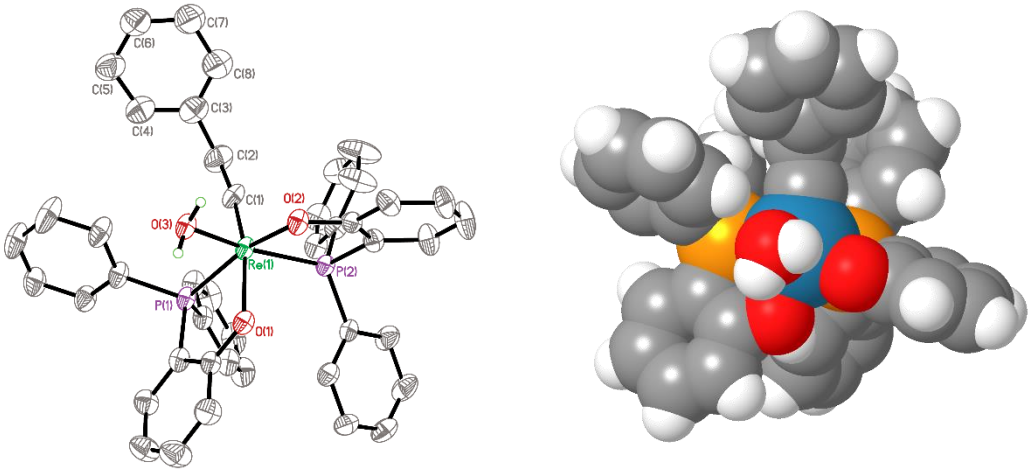


Figure S2. Left: ORTEP diagram of the aqua complex **14** with thermal ellipsoids at the 40% probability level. All hydrogen atoms except those of the water ligand as well as solvent atoms are omitted for clarity. Right: Space-filling model of the aqua complex **14**.

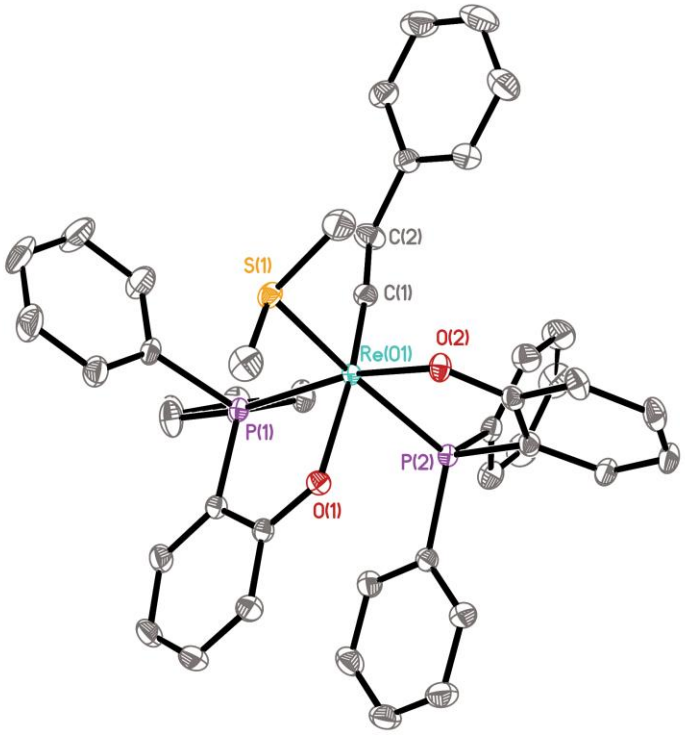


Figure S3. ORTEP diagram of the SMe_2 complex **15** with thermal ellipsoids at the 40% probability level. All hydrogen atoms as well as solvent atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg.): Re(01)-C(1) 1.7690(18), Re(01)-S(1) 2.4524(4), Re(01)-P(1) 2.3370(4), Re(01)-P(2) 2.3811(4), Re(01)-O(1) 2.1581(12), Re(01)-O(2) 2.0991(12), C(1)-C(2) 1.480(3), C(1)-Re(01)-S(1) 94.15(6), C(1)-Re(01)-P(1) 90.14(6), C(1)-Re(01)-P(2) 95.29(6), C(1)-Re(01)-O(1) 168.90(7), C(1)-Re(01)-O(2) 108.09(7), C(2)-C(1)-Re(01) 172.07(15), P(1)-Re(01)-S(1) 90.445(15), P(1)-Re(01)-P(2) 102.386(15), P(2)-Re(01)-S(1) 164.018(15), O(1)-Re(01)-S(1) 89.50(4), O(2)-Re(01)-S(1) 83.80(4).

2. *In situ* NMR Studies

In situ $^{31}P\{^{1}H\}$ NMR Spectra for the Reactions of Anhydrous $ZnCl_2$ with Re(V) Alkylidynes 10 and 11.

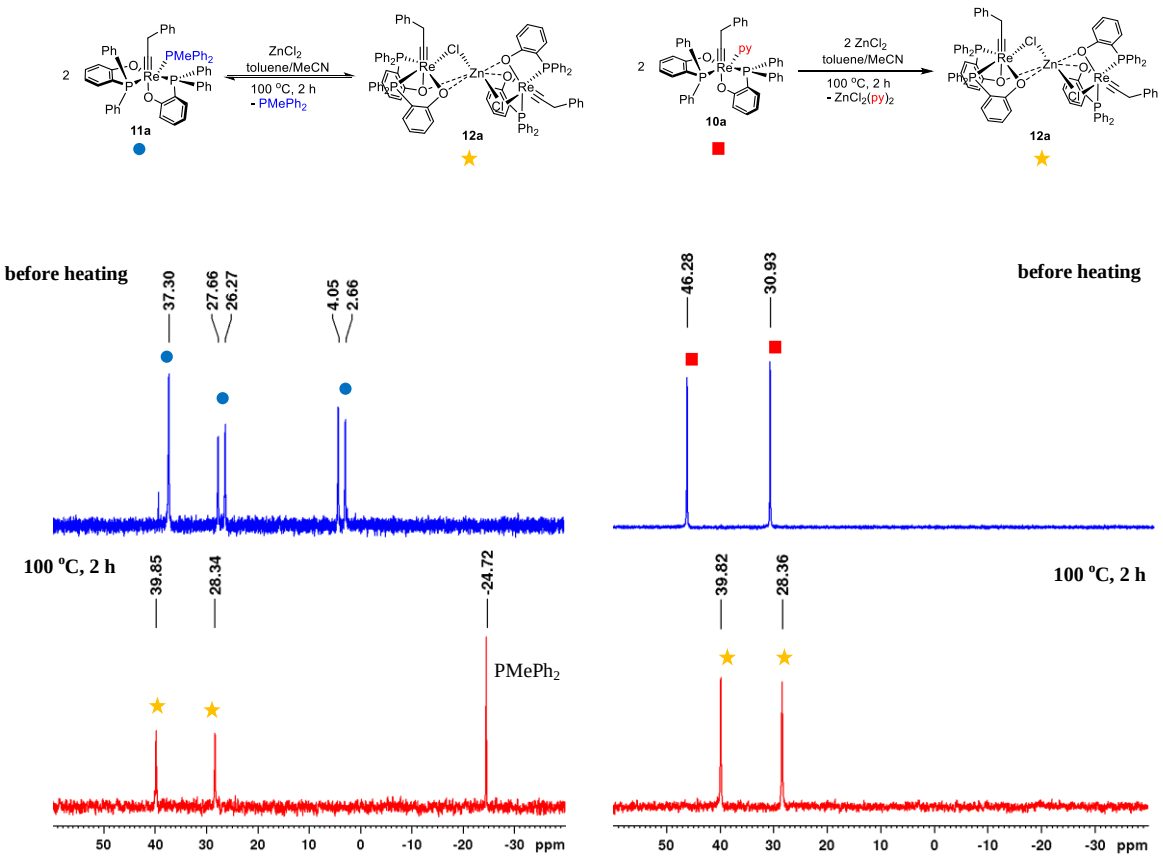


Figure S4. The stacked *in situ* $^{31}P\{^{1}H\}$ NMR spectra for the reactions of anhydrous $ZnCl_2$ with Re(≡CCH_2Ph)(^{Ph}PO)$_2$($PMePh_2$) (**11a**) (left) and Re(≡CCH_2Ph)(^{Ph}PO)$_2$(py) (**10a**) (right) in the mixed solvent of toluene and acetonitrile (v/v = 3:1). Blue circles: signals of **11a**; red squares: signals of **10a**; yellow stars: signals of **12a**. **Note:** Both two reactions produce the same product **12a**.

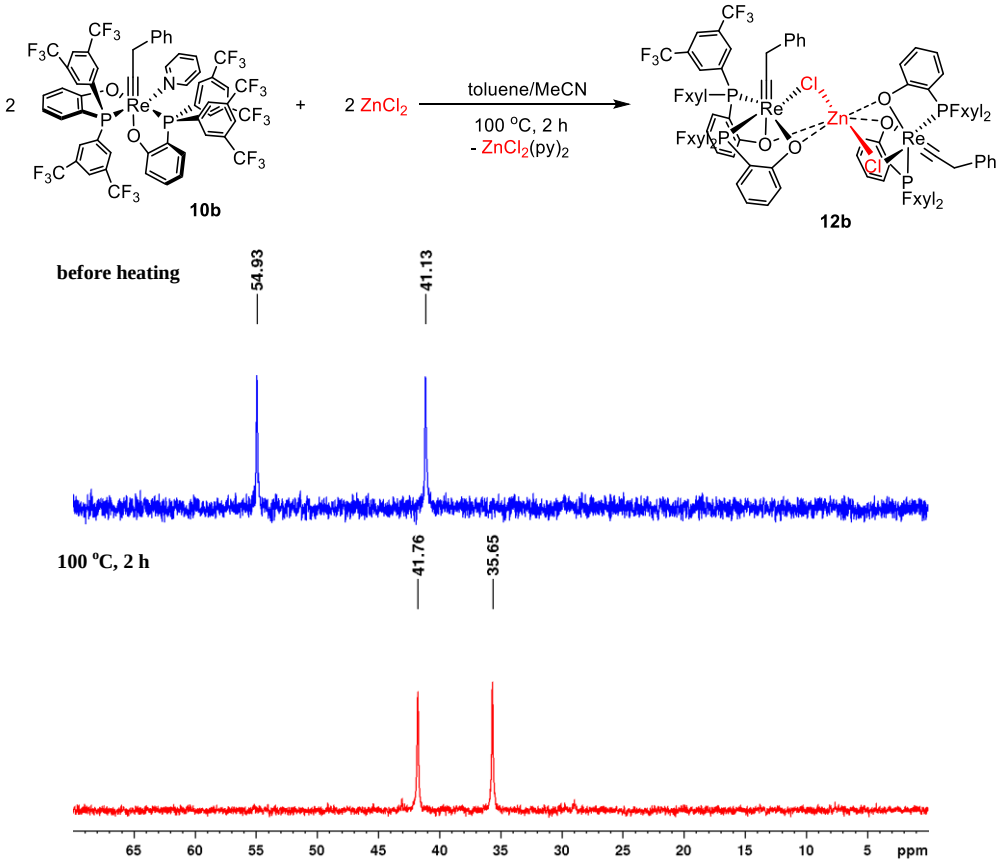


Figure S5. The stacked *in situ* $^{31}P\{^{1}H\}$ NMR spectra of the reactions of $Re(\equiv CCH_2Ph)(^{Fxyl}PO)_2(py)$ (**10b**) with anhydrous $ZnCl_2$ in the mixed solvent of toluene and acetonitrile (v/v = 3:1).

Spectroscopic Evidence for the Formation of Re(V) Alkylidyne-$RuCl_2$(*p*-cymene) Intermediate 13.

Generation of 13. To a J-Young NMR tube were added the Re(V) alkylidyne Re(≡CCH_2Ph)($^{Ph}PO)_2(PMePh_2$) (**11a**) (10.4 mg, 0.01 mmol), (*p*-cymene)$RuCl_2$ (6.5 mg, 0.0212 mmol) and 0.5 mL of dry C_6D_6 under nitrogen. The mixture was monitored by NMR spectroscopy under the conditions specified in ***Figures S7-S8***.

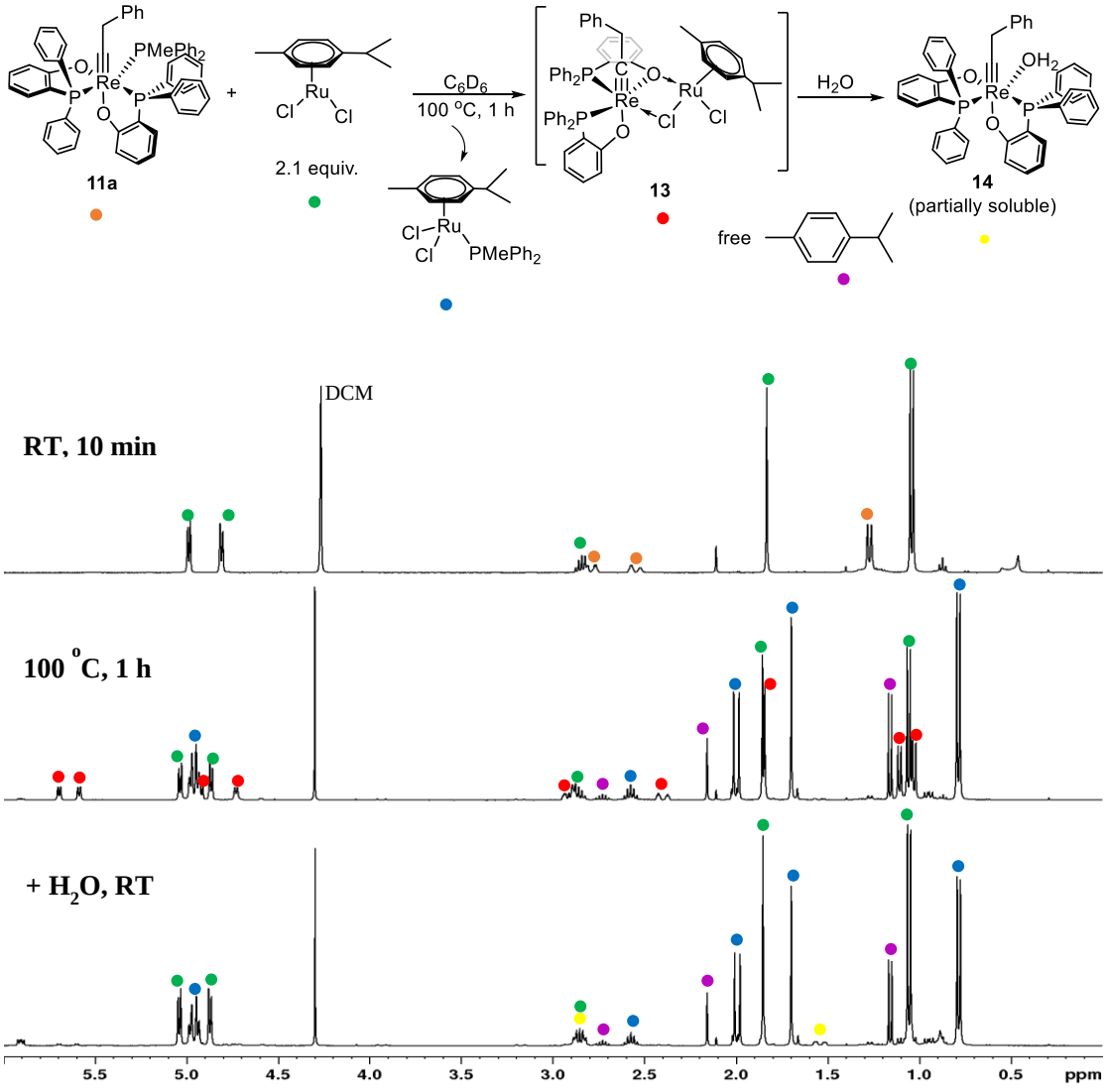


Figure S6. The stacked ^1H NMR spectra (upfield region) for the reaction of Re(≡CCH_2Ph)($^{Ph}PO)_2(PMePh_2$) (**11a**) with (*p*-cymene)$RuCl_2$ (2.1 equiv.) in C_6D_6 at 20 °C. Top: before heating; Middle: after heating at 100 °C for 1 h; Bottom: after hydrolysis. Convention for peak assignments: orange dots, signals of the $PMePh_2$-coordinated complex **11a**; red dots, signals of the intermediate **13**; blue dots, signals

of (*p*-cymene)$RuCl_2(PMePh_2)$; green dots, signals of (*p*-cymene)$RuCl_2$; yellow dots, signals of the aqua complex **14**.

Notes:

Before heating, the ^1H NMR spectrum only showed peaks of $Re(\equiv CCH_2Ph)(^{Ph}PO)_2(PMePh_2)$ (**11a**) (orange) and (*p*-cymene)$RuCl_2$ (green) (in 1:2.1 molar ratio). Characteristic signals of **11a**: 2.79 ppm (dq, *J* = 19.7, 3.5 Hz, Re≡CCH_2Ph), 2.55 (dq, *J* = 19.8, 3.6 Hz, Re≡CCH_2Ph), 1.27 ppm (d, *J* = 8.4 Hz, P*Me*Ph_2). Characteristic signals of (*p*-cymene)$RuCl_2$: 4.98 ppm (d, *J* = 5.9 Hz, cymene ring), 4.81 ppm (d, *J* = 5.9 Hz, cymene ring), 2.84 ppm (sept. *J* = 6.9 Hz, C$H(CH_3)_2$), 1.83 ppm (s, CH_3), 1.04 ppm (d, *J* = 6.9 Hz, CH(CH_3)$_2$).

After heating at 100 ^oC for 1 h, Re(V) alkylidyne **11a** has been largely consumed to give the intermediate **13** (red), (*p*-cymene)$RuCl_2(PMePh_2)$ (blue) and free cymene (purple). Characteristic ^1H signals of **13**: 5.70 ppm (d, *J* = 5.7 Hz, cymene ring), 5.59 ppm (d, *J* = 5.64 Hz, cymene ring), 4.92 ppm (d, *J* = 5.6 Hz, cymene ring), 4.73 ppm (d, *J* = 5.7 Hz, cymene ring), 2.88 ppm (sept, *J* = 7.1 Hz, C$H(CH_3)_2$), 2.40 ppm (dt, *J* = 19.8 Hz, 3.3 Hz, Re≡CCH_2Ph), 2.92 ppm (d = 19.2, 3.3 Hz, Re≡CCH_2Ph), 1.84 ppm (s, *Me*), 1.11 ppm (d, *J* = 6.8 Hz, CH(*CH*$_3$)$_2$), 1.03 ppm (d, *J* = 7.0 Hz, CH(*CH*$_3$)$_2$). The splitting pattern of the two methylene protons changed from "dq" to "dt", indicating the absence of the $PMePh_2$ ligand. The four protons of the *p*-cymene ring as well as two methyl protons of the *i*Pr group of *p*-cymene became magnetically inequivalent, revealing the coordination of $RuCl_2$(*p*-cymene) moiety to the Re center.

Upon addition of water, the signals of the intermediate **13** (red) disappeared, with the appearance of the signals of the aqua complex **14** (yellow). In the meanwhile, the integrals of the peaks of (*p*-cymene)$RuCl_2$ increased, consistent with the reaction of the intermediate **13** with water to give **14** and (*p*-cymene)$RuCl_2$. It is noted that, at that moment, some yellow crystals of the poorly soluble aqua complex **14** were deposited on the wall of the NMR tube.

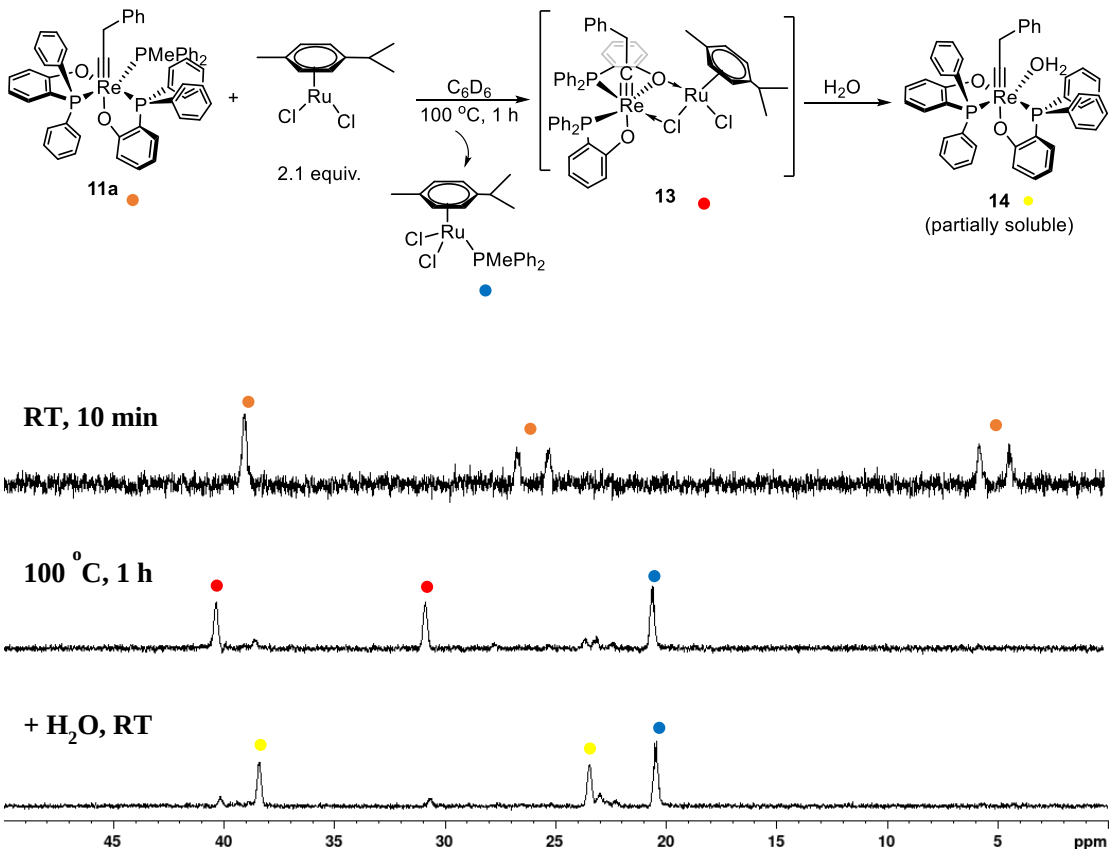


Figure S7. The stacked $^{31}P\{^{1}H\}$ NMR spectra for the reaction of $Re(\equiv CCH_2Ph)(^{Ph}PO)_2(PMePh_2)$ (**11a**) with (*p*-cymene)$RuCl_2$ (2.1 equiv.) in C_6D_6 at 20 °C. Top: before heating; Middle: after heating at 100 °C for 1 h; Bottom: after hydrolysis. Convention for peak assignments: orange dots, signals of the $PMePh_2$-coordinated complex **11a**; red dots, signals of the intermediate **13**; blue dots, signals of (*p*-cymene)$RuCl_2(PMePh)_2$; yellow dots, signals of the aqua complex **14**.

Notes:

Before heating, the *in situ* NMR spectrum only showed signals of the Re(V) alkylidyne **11a** (orange) at 38.9 ppm, 26.0 ppm, and 5.0 ppm. After heating at 100 °C for 1 h, the signals of **11a** disappeared and the spectrum showed two singlet signals of the intermediate **13** (red) at 40.1 ppm and 30.5 ppm and one singlet signal of (*p*-cymene)$RuCl_2(PMePh_2)$ (blue) at 20.4 ppm. Upon addition of water, (*p*-cymene)$RuCl_2(PMePh_2)$ remains unchanged as indicated by the signal at 20.4 ppm, the intermediate **13** was largely consumed to give the aqua complex **14** which shows two singlets at 38.4 ppm and 23.4 ppm.

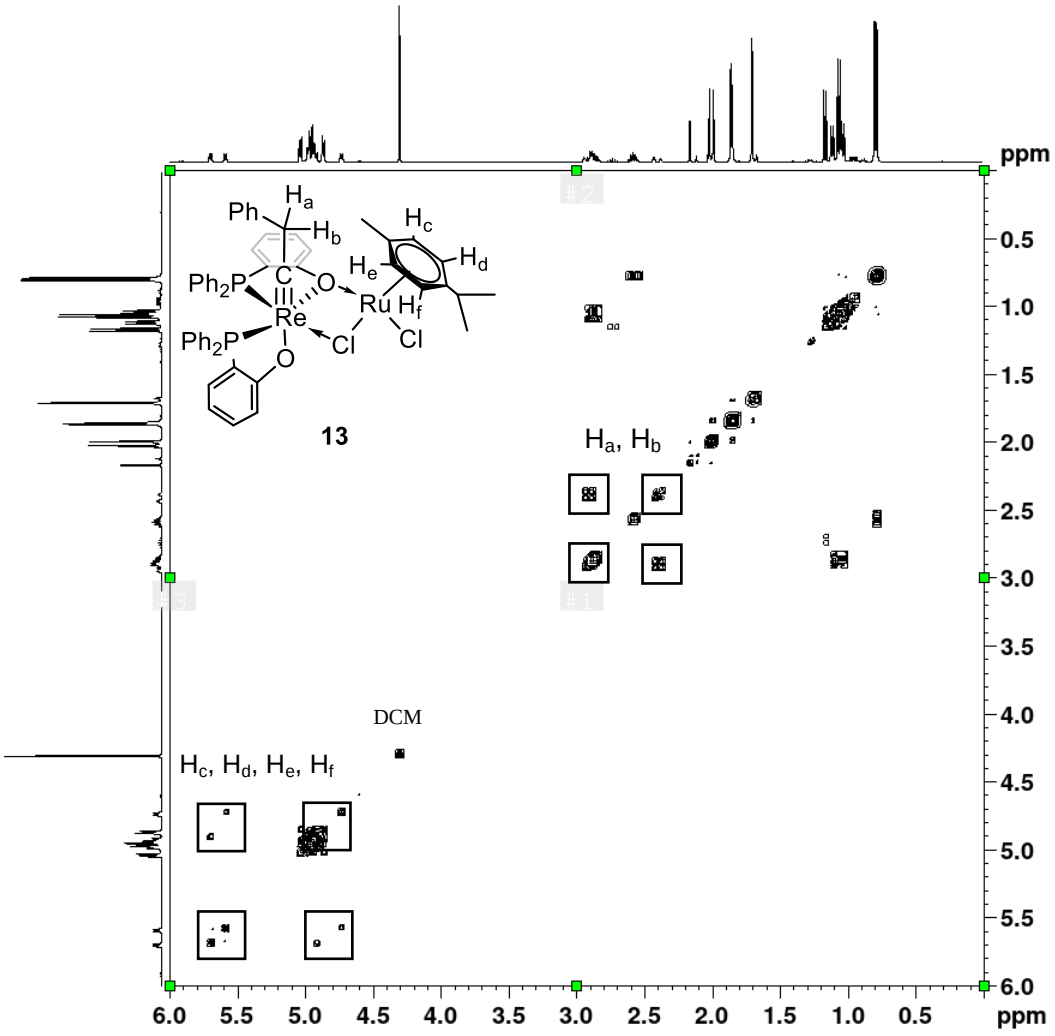


Figure S8. The *in situ* ^{1}H-^{1}H COSY NMR spectrum for the reaction of Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$(PMePh$_2$) (**11a**) with (*p*-cymene)RuCl$_2$ (2.1 equiv.) in C$_6$D$_6$ at 20 ^{o}C, recorded after heating the mixture at 100 ^{o}C for 1 h.

Notes:

The ^{1}H-^{1}H COSY NMR spectrum confirms that signals of the methylene protons (H$_a$, H$_b$) of Re≡CC*H*$_2$Ph of **13** appeared at 2.40 ppm and 2.92 ppm (the signal at 2.92 ppm is partially overlapped with the signal of C*H*(CH$_3$)$_2$ of *p*-cymene); the signals of *i*Pr of the intermediate **13** appeared at 1.03 and 1.11 ppm for CH(C*H*$_3$)$_2$, and 2.86 ppm for C*H*(CH$_3$)$_2$, the signal of *Me*C$_6$H$_4$-*i*Pr of **13** appeared at 1.84 ppm, the signals of the four protons (H$_{c\text{-}f}$) of the cymene ring appeared as doublets at 4.73, 4.92, 5.59 and 5.70 ppm.

3. Experimental Details

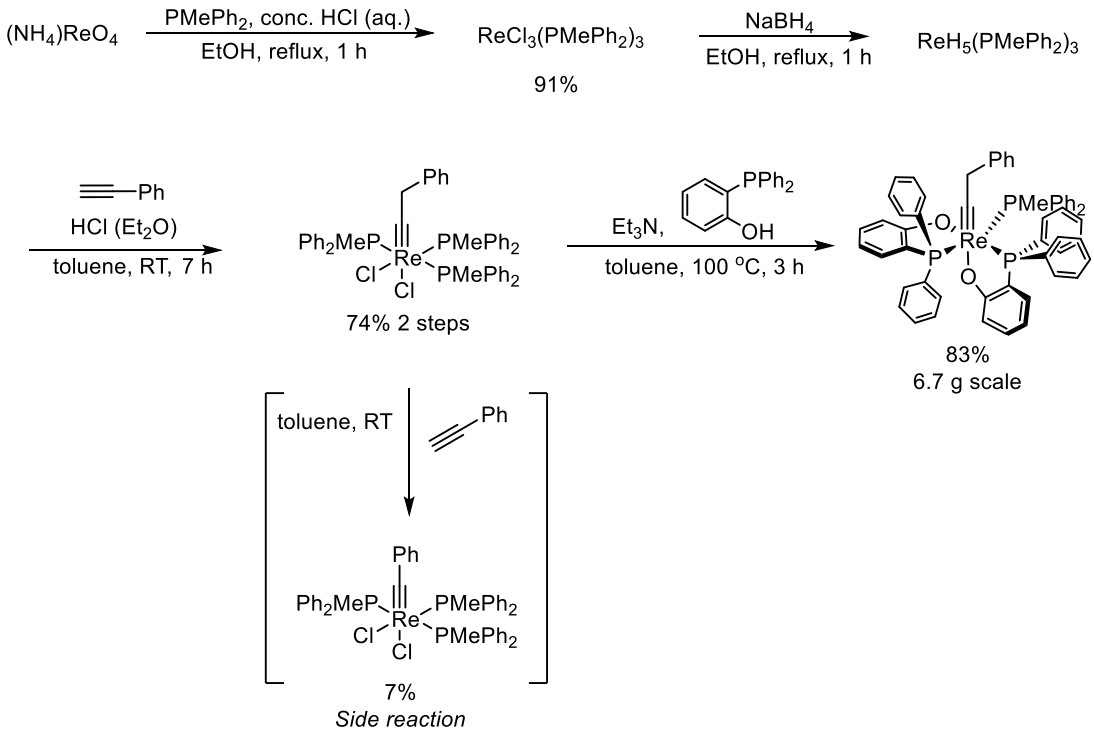
General Considerations

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless stated otherwise. Solvents were freshly distilled under nitrogen from sodium benzophenone (hexane, diethyl ether, tetrahydrofuran, toluene), or CaH_2 (dichloromethane, acetonitrile). Methanol and ethanol were bubbled with N_2 for about 20 min before use. Deuterated solvents were dried over CaH_2 (CD_2Cl_2, $CDCl_3$, CD_3CN) or sodium benzophenone (C_6D_6), distilled under nitrogen or vacuum transferred, degassed by three freeze-pump-thaw cycles and stored in a sealed tube with 4 Å or 3 Å (CD_3CN) molecular sieves. (*p*-cymene)$RuCl_2$,[4] (*p*-cymene)$OsCl_2$,[5] Ph_2P(*o*-C_6H_4-OH),[6] **10a**,[7] **10b**,[8] and alkyne substrates **17**-**19**, **22**-**24**, **29**-**32**, **34**,[9,10] **20**,[11] **21**,[12] **26**,[13] **27**,[14] **28**,[15] **33**,[16] **35**,[17] **41**,[18] **43**,[7] **45**[19] were prepared following the procedures described in the literatures. All other reagents were purchased from commercial suppliers and used without further purification. Powdered 5 Å molecular sieves (5 Å MS) was purchased from Sigma-Aldrich and activated prior to use either by heating at 150 ^oC under vacuum for about 24 h or heating with a heat gun (at 450 ^oC) under vacuum for about 5 min.

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were collected on a Bruker-400 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR shifts are reported in ppm and are relative to the solvent signal[20] (^1H NMR, $CDCl_3$ at 7.26 ppm, CD_2Cl_2 at 5.32 ppm, CD_3CN at 1.94 ppm; $^{13}C\{^1H\}$ NMR, $CDCl_3$ at 77.16 ppm, CD_2Cl_2 at 53.84 ppm). $^{31}P\{^1H\}$ chemical shifts are relative to 85% H_3PO_4. HRMS were recorded by using a chemical ionization (CI) or electrospray ionization (ESI) mass spectrometer. FT-IR spectra were recorded on a Bruker ALPHA spectrometer with an ATR attachment, and selected peaks are reported in cm^{-1}. Elemental analysis was performed by MEDAC Ltd (Egham, UK).

Revised Synthesis of Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$(PMePh$_2$) (11a)

The syntheses of the Re(V) alkylidyne complexes Re(≡CCH$_2$Ph)Cl$_2$(PMePh$_2$)$_3$[21] and Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$(PMePh$_2$) (**11a**)[8] have been reported previously. Herein, we reported an optimized synthetic protocol for the large scale preparation of these compounds.



***mer*-ReCl$_3$(PMePh$_2$)$_3$.**[22] To a 250 mL 3-neck flask equipped with a gas inlet, a condenser and a stir bar were added (NH$_4$)ReO$_4$ (6.50 g, 24.2 mmol), concentrated hydrochloric acid (aq., 18.4 mL) and 100 mL of degassed ethanol. The mixture was stirred for 30 min until the solid was fully dissolved, to which was added PMePh$_2$ (25.00 g, 125.0 mmol). Under vigorous stirring, the mixture was refluxed for 1 hour until a yellow suspension was obtained. *Note: Normally, the powdered product will precipitate suddenly, accompanied with the formation of oily phosphine oxide. The vigorous stirring is crucial to avoid the formation of dark green chunks, which prevent the reaction to go completion.* The mixture was cooled to room temperature

and the air-stable yellow powder was collected by filtration, washed with ethanol (30 ml × 3) and dried under vacuum. Yield: 20.07 g, 91%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 13.90 (d, *J* = 7.7 Hz, 8H), 9.83 (d, *J* = 7.6 Hz, 4H), 9.42 (t, *J* = 7.5 Hz, 2H), 8.86 (t, *J* = 7.5 Hz, 4H), 8.58 (t, *J* = 7.6 Hz, 8H), 7.89 (t, *J* = 7.5 Hz, 4H), -0.69 (s, 6H), -2.12 (s, 3H).[23]

$Re(\equiv CCH_2Ph)Cl_2(PMePh_2)_3$. To a 250 mL 3-neck flask equipped with a gas inlet, a condenser and a stir bar were added $ReCl_3(PMePh_2)_3$ (9.5 g, 10.6 mmol), $NaBH_4$ (5.25 g, 140 mmol) and 130 mL of degassed ethanol. The mixture was vigorously stirred at room temperature for 20 min and then heated to reflux for about 1 hour until gas evolution ceased. After cooling to room temperature, the solvent was completely evaporated under vacuum to give a pale red solid. The red $ReH_5(PMePh_2)_3$ was extracted with toluene (45 mL × 3) and filtered off to remove the white inorganic salts. The combined filtrates were collected in a 250 mL Schlenk flask charged with a stir bar, to which was added phenylacetylene (2.94 g, 28.7 mmol, ca. 3.15 mL). At room temperature, 28.7 mL of 1 M ethereal solution of HCl was added dropwise to the stirred solution over 1 h. During the course of addition, the solution color changed gradually from red to brown, followed by gentle gas evolution. After the addition, the reaction mixture was further stirred at room temperature for 6 - 7 hours until a large amount of yellow precipitant was formed. The volume of the solution was reduced to one-half under vacuum and 120 mL of hexane was added to the solution to precipitate more solid. The solid was separated by cannula filtration, sequentially washed with hexane (60 mL × 2), diethyl ether (60 mL × 3) as well as methanol (16 mL × 3) and dried under vacuum to afford the desired product $Re(\equiv CCH_2Ph)Cl_2(PMePh_2)_3$ as a yellow solid. Yield: 7.42 g, 74% for the two-step synthesis from $ReCl_3(PMePh_2)_3$.

Note:

A small amount of the side product, $Re(\equiv CPh)Cl_2(PMePh_2)_3$, was generated from alkyne metathesis of $Re(\equiv CCH_2Ph)Cl_2(PMePh_2)_3$ with excess phenylacetylene. Prolonged reaction time may increase the yield of the benzylidyne side product.

$Re(\equiv CPh)Cl_2(PMePh_2)_3$ could be isolated and purified by the following procedure: The toluene/hexane filtrate and Et_2O extracts were combined and evaporated to dryness to give an oily residue, which was washed with methanol (15 mL × 3). The resulting orange solid was extracted with toluene (10 mL × 3). The extracts were filtered by cannula into a long Schlenk tube and layered with hexane. After 2 weeks, red crystals (benzylidyne) together with orange crystals (benzyl alkylidyne) were deposited on the wall of the Schlenk tube. The red crystals were picked up by hands using a spatula. Repeating this procedure for two times gave pure $Re(\equiv CPh)Cl_2(PMePh_2)_3$ as red crystals. Yield: 705 mg (7% for 2 steps).

Characterization data of $Re(\equiv CCH_2Ph)Cl_2(PMePh_2)_3$:[21]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 4H), 7.40 – 7.31 (m, 4H), 7.31 – 7.10 (m, 15H), 7.10 – 6.94 (m, 12H), 2.68 (q, *J* = 3.6 Hz, 2H), 2.14 (t, *J* = 4.0 Hz, 6H), 1.80 (d, *J* = 8.8 Hz, 3H).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -7.19 (t, *J* = 11.4 Hz, 1P), -9.59 (d, *J* = 11.5 Hz, 2P).

Characterization data of $Re(\equiv CPh)Cl_2(PMePh_2)_3$:[21]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 6.85 (m, 35H), 2.20 (t, *J* = 4.0 Hz, 6H), 1.81 (d, *J* = 8.6 Hz, 3H).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ -3.41 (t, *J* = 10.9 Hz, 1 P), -11.18 (d, *J* = 11.6 Hz, 2P).

$Re(\equiv CCH_2Ph)(^{Ph}PO)_2(PMePh_2)$ (11a). To a 250 mL Schlenk flask equipped with a stir bar were added $Re(\equiv CCH_2Ph)Cl_2(PMePh_2)_3$ (7.42 g, 7.7 mmol), (2-hydroxyphenyl)diphenylphosphine (4.50 g, 16.2 mmol), 80 mL of toluene and Et_3N (2.34 g, ca. 3.2 mL, 23.2 mmol). The mixture was stirred at 100 ^oC for 3 hours. After cooling to room temperature, the precipitate (triethylamine hydrochloride) was filtered off and discarded. The filtrate was evaporated under vacuum to give an orange

residue which was washed with hexane (50 mL × 2) and methanol (20 mL × 3) and dried under vacuum to afford the desired product as a yellow solid. Yield: 6.66 g, 83%.

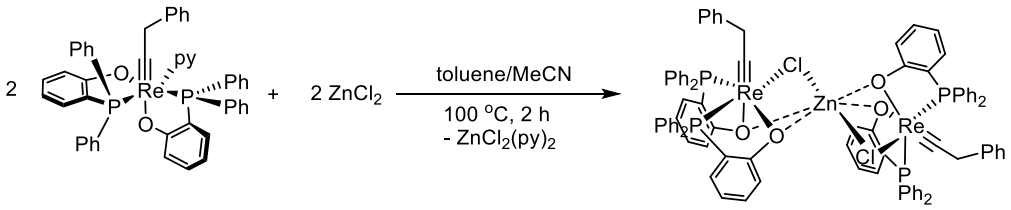
^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.36-7.23 (m, 5H), 7.21-7.10 (m, 15H), 7.05-6.90 (m, 14H), 6.84-6.76 (m, 5H), 6.59-6.42 (m, 4H), 2.80 (dq, *J* = 19.8, 3.2 Hz, 1H), 2.56 (dq, *J* = 19.6, 2.8 Hz, 1H), 1.31 (d, *J* = 8.5 Hz, 3H).[8]

^{1}H NMR (400 MHz, C_6D_6) δ 7.81 – 7.71 (m, 2H), 7.65 – 7.50 (m, 4H), 7.47 – 7.33 (m, 3H), 7.28 – 7.18 (m, 2H), 7.15 – 6.68 (m, 30H), 6.60 – 6.45 (m, 2H), 2.79 (dq, *J* = 19.7, 3.5 Hz, 1H), 2.55 (dq, *J* = 19.9, 3.6 Hz, 1H), 1.27 (dd, *J* = 8.5, 1.0 Hz, 3H).

^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ 37.28 (br s, 1P), 27.00 (br d, *J* = 225.3 Hz, 1P), 3.39 (br d, *J* = 224.0 Hz, 1P).[8]

^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 38.92 (br s, 1P), 25.88 (dd, *J* = 222.9, 5.6 Hz, 1P), 4.99 (d, *J* = 223.9, 1P).

Synthesis of the $ZnCl_2$-bridged Complex [Re(≡CCH_2Ph)(^{Ph}PO)$_2$]$_2$(μ-$ZnCl_2$) (12a)



A mixture of Re(≡CCH_2Ph)(^{Ph}PO)$_2$(py) (**10a**, 185 mg, 0.20 mmol) and anhydrous $ZnCl_2$ (136 mg, 1.00 mmol) in 15 mL of toluene and 5 mL of MeCN was heated at 100 ^{o}C for 2 hours. The remaining solid was filtered off, washed with 5 mL of toluene and discarded. The combined filtrate was concentrated to ca. 2 mL. To this solution was added 10 ml of hexane to precipitate a pale yellow solid, which was collected by filtration. The solid was extracted with dichloromethane (DCM) (3 mL × 2) with the addition of 1 drop of acetonitrile, and the combined extracts were concentrated to ca. 1 mL and precipitated by the addition of 10 mL of hexane. This procedure was repeated 3 times to ensure complete removal of $ZnCl_2(py)_2$. The final product

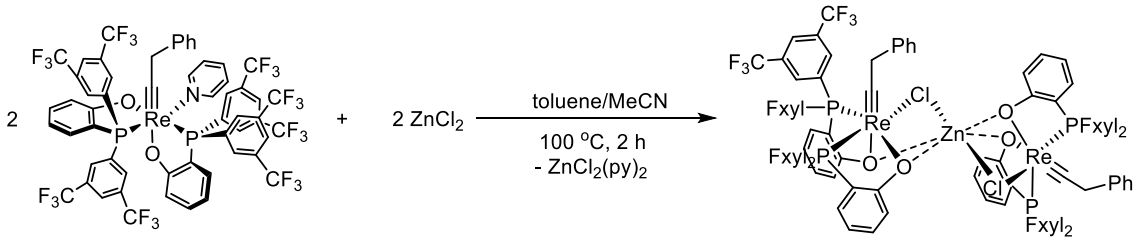
obtained was a pale yellow solid, which was dried under vacuum. Yield: 108 mg, 59%.

^{1}H NMR (400 MHz, CD_3CN) δ7.53 – 6.65 (m, 66 H), 2.83 (dt, *J* = 19.2, 3.1 Hz, 2H), 2.48 – 2.35 (m, 2H).

^{31}P{^{1}H} NMR (162 MHz, CD_3CN) δ 37.99, 27.51.

Elem. Anal. Calcd for $C_{88}H_{70}Cl_2O_4P_4Re_2Zn$: C, 57.94; H, 3.87. Found: C, 56.82; H, 4.17.

Synthesis of the $ZnCl_2$-bridged Complex [Re(≡CCH_2Ph)(^{Fxyl}PO)$_2$]$_2$(μ-$ZnCl_2$) (12b)



To a NMR tube were added Re(≡CCH_2Ph)(^{Fxyl}PO)$_2$(py) (11.8 mg, 8 μmol), anhydrous $ZnCl_2$ (5.5 mg, 40 μmol), 0.3 mL of toluene and 0.1 mL of acetonitrile. The mixture was heated at 100 ℃ for 2 hours. The reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy (***Figure S6***). The volatiles were evaporated under vacuum, and the remaining solid was dissolved in 0.5 mL of CD_3CN. ^{1}H NMR spectrum indicated that it is a mixture of complex **12b** and $ZnCl_2(py)_2$ (***Figure S12***). The solvent was evaporated to dryness and the residue was taken into 0.5 mL of $CDCl_3$ with the addition of 1 drop of acetonitrile. After standing at room temperature for 1 day, pale yellow crystals deposited on the wall of the NMR tube, which were collected for single-crystal X-ray diffraction analysis.

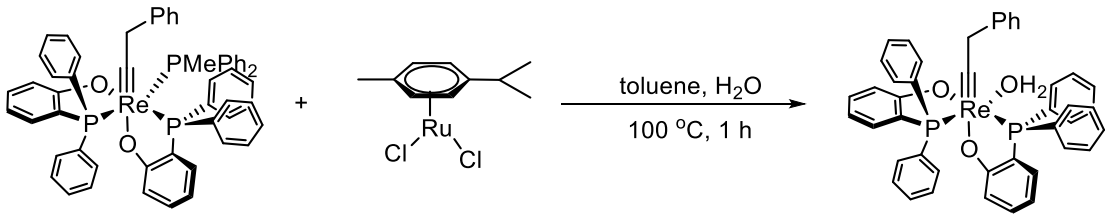
^{1}H NMR (400 MHz, CD_3CN) δ 8.22 – 7.99 (m, 14H), 7.87 – 7.78 (m, 6H), 7.61 (s, 2H), 7.59 (s, 2H), 7.54 (s, 2H), 7.51 (s, 2H), 7.45 – 7.37 (m, 2H), 7.32 – 7.22 (m, 4H), 7.14 – 7.04 (m, 8H), 7.03 – 6.96 (m, 2H), 6.78 (t, *J* = 7.4 Hz, 2H), 6.68 (t, *J* = 7.5 Hz, 2H), 6.37 (dd, *J* = 8.2, 6.1 Hz, 2H), 3.41 (dt, *J* = 19.9, 3.3 Hz, 2H), 3.22 – 3.10 (m, 2H).

^{19}F NMR (376 MHz, CD_3CN) δ -63.17, -63.47, -63.75, -63.76.

^{31}P{^{1}H} NMR (162 MHz, CD_3CN) δ 41.82, 35.94

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 39.84, 35.78

Synthesis of the Aqua Complex Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$(H$_2$O) (14)



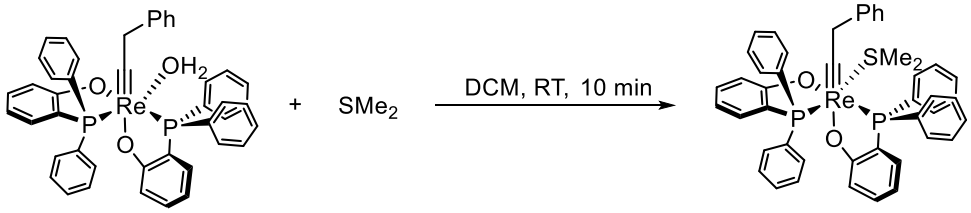
To a Schlenk flask equipped with a stir bar were added Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$(PMePh$_2$) (1.000 g, 0.96 mmol), (*p*-cymene)RuCl$_2$ (391 mg, 1.28 mmol) and 28 mL of dry toluene. The resulting mixture was stirred at 100 °C with vigorous stirring for 1 hour. The hot solution was filtered to another Schlenk flask to remove a trace amount of black impurities originated from (*p*-cymene)RuCl$_2$. To the filtrate was added 140 μL of distilled water (7.78 mmol) and the mixture was stirred at 100 °C for another 1 h. After the reaction, the mixture was cooled to 0 °C to precipitate a yellow crystalline solid, which was collected by filtration, washed with toluene (15 mL × 4) and dried under vacuum. Yield: 744 mg, 90%.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.25 (dd, *J* = 9.7, 8.0 Hz, 2H), 7.84 (s, 2H, H_2O), 7.55 – 6.66 (m, 26H), 6.34 (dd, *J* = 5.7, 3.3 Hz, 2H), 6.14 (dd, *J* = 11.5, 7.4 Hz, 2H), 5.28 – 5.21 (m, 1H), 2.65 (dt, *J* = 19.1, 3.3 Hz, 1H), 1.37 – 1.27 (m, 1H).

^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2) δ 38.18 (s), 23.40 (s).

Elem. Anal. Calcd for $C_{44}H_{37}O_3P_2Re$: C, 61.31; H, 4.33. Found: C, 61.08; H, 4.32.

Synthesis of the SMe$_2$ Adduct Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$(SMe$_2$) (15)



To a Schlenk flask equipped with a stir bar were added Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$(OH$_2$) (200 mg, 0.232 mmol), SMe$_2$ (50 μL, 0.681 mmol) and 5 mL of DCM. The resulting

mixture was stirred at room temperature for 10 mins until all solid was dissolved. The solution was concentrated to ca. 1 mL, to which was added 15 mL of hexane. The solution volume was reduced to ca. 5 mL and a pale brown solid was precipitated out. The solid was collected by filtration, washed with hexane:Et_2O = 3:1 (4 mL × 3) and dried under vacuum. Pale brown solid. Yield: 185 mg. 88%. Single crystals of **15** suitable for X-ray diffraction analysis were obtained by layering its DCM solution with hexane.

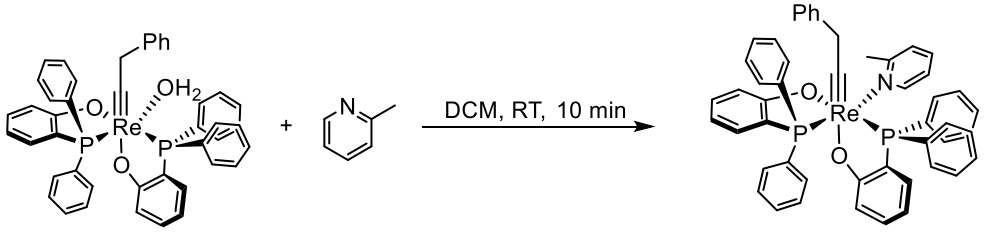
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.40 (m, 2H), 7.34 – 7.02 (m, 22H), 7.00 – 6.80 (m, 6H), 6.55 (t, *J* = 7.2 Hz, 1H), 6.46 (t, *J* = 7.3 Hz, 1H), 6.37 (dd, *J* = 8.3, 5.5 Hz, 1H), 2.72 (dt, *J* = 19.2, 3.4 Hz, 1H), 2.30 – 2.20 (m, 1H), 2.12 (brs, 6H, S*Me*$_2$).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 38.81 (d, *J* = 5.1 Hz), 27.62 (d, *J* = 4.7 Hz).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 272.20 (t, *J* = 12.5 Hz), 179.64 (d, *J* = 20.9 Hz), 174.53 (d, *J* = 22.6 Hz), 142.05 (d, *J* = 56.4 Hz), 140.03 (d, *J* = 48.6 Hz), 136.53 (s), 135.97 (s), 134.91 (s), 133.84 (s), 133.64 – 131.75 (m), 130.98 (s), 130.52 (s), 129.34 (d, *J* = 2.2 Hz), 129.25 (d, *J* = 2.3 Hz), 129.19 (s), 128.84 (s), 128.59 (s), 128.18 – 127.15 (m), 126.41 (s), 121.32 (d, *J* = 6.8 Hz), 120.65 (d, *J* = 8.1 Hz), 119.61 (d, *J* = 2.2 Hz), 119.08 (d, *J* = 2.2 Hz), 118.95 (s), 118.43 (s), 116.11 (d, *J* = 6.8 Hz), 114.45 (d, *J* = 6.2 Hz), 54.72 (s), 19.87 (s).

Elem. Anal. Calcd for $C_{46}H_{41}O_2P_2ReS$: C, 60.98; H, 4.56. Found: C, 59.44; H, 4.85.

Synthesis of the 2-Picoline Adduct Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$($^{2\text{-}Me}$py) (16)



To a Schlenk flask equipped with a stir bar were added Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$(OH$_2$) (200 mg, 0.232 mmol), 2-picoline (26 mg, 0.283 mmol) and 5 mL of DCM. The resulting mixture was stirred at room temperature for 10 mins until all solid was dissolved. The solution was concentrated to ca. 0.5 mL and 15 mL

of hexane was added to precipitate a bright yellow solid. The bright yellow solid was collected by filtration, washed with hexane:Et_2O= 5:1 (5mL × 3) and dried under vacuum. Yield: 176 mg. 81%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 5.9 Hz, 1H), 7.41 – 7.27 (m, 5H), 7.25 – 7.15 (m, 5H), 7.16 – 6.97 (m, 15H), 6.94 (td, *J* = 7.9, 1.8 Hz, 2H), 6.91 – 6.83 (m, 3H), 6.70 (dd, *J* = 10.5, 7.6 Hz, 2H), 6.61 – 6.44 (m, 4H), 2.83 (dt, *J* = 19.1, 3.6 Hz, 1H), 2.69 (s, 3H), 2.27 – 2.14 (m, 1H).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 44.28, 24.61.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 269.67 (t, *J* = 15.6 Hz), 179.10 (d, *J* = 20.1 Hz), 174.31 (d, *J* = 22.5 Hz), 162.61 (s), 154.57 (s), 143.32 (d, *J* = 60.3 Hz), 139.66 (d, *J* = 43.8 Hz), 136.63 (s), 135.82 (s), 135.22 (s), 134.34 – 131.59 (m), 129.50 – 127.12 (m), 126.14 (s), 125.34 (s), 122.45 (d, *J* = 6.9 Hz), 121.45 (s), 120.73 (d, *J* = 8.2 Hz), 120.45 (s), 119.93 (s), 119.42 (s), 115.92 (d, *J* = 6.8 Hz), 114.80 (d, *J* = 6.1 Hz), 54.57 (s), 28.36 (s).

Rate of Alkyne Metathesis Using Re(V) Alkylidyne Catalysts

General Procedure for the Model Reaction (Homometathesis of 1-Methoxy-4-(1-propyn-1-yl)benzene) (Figure 5 & Table 1).

To a Schlenk tube equipped with a stir bar were added 750 mg of activated 5 Å molecular sieves (MS) and catalyst (0.5 - 5 mol%). The tube was capped with a rubber septum, evacuated and refilled with N_2 for three times. To the Schlenk tube were added 1-methoxy-4-(1-propyn-1-yl)benzene (73.1 mg, 75 μL, 0.50 mmol), the internal standard CH_2Ph_2 (126 mg, 126 μL, 0.75 mmol) and distilled toluene (5 mL). The mixture was stirred at specified temperatures. Samples (ca. 0.1 mL) were carefully taken at specified time by needle syringes, dilute with 0.5 mL of wet dichloromethane, filtered with a PTFE syringe filter, dried under vacuum and re-dissolved in $CDCl_3$ for ^{1}H NMR measurements.

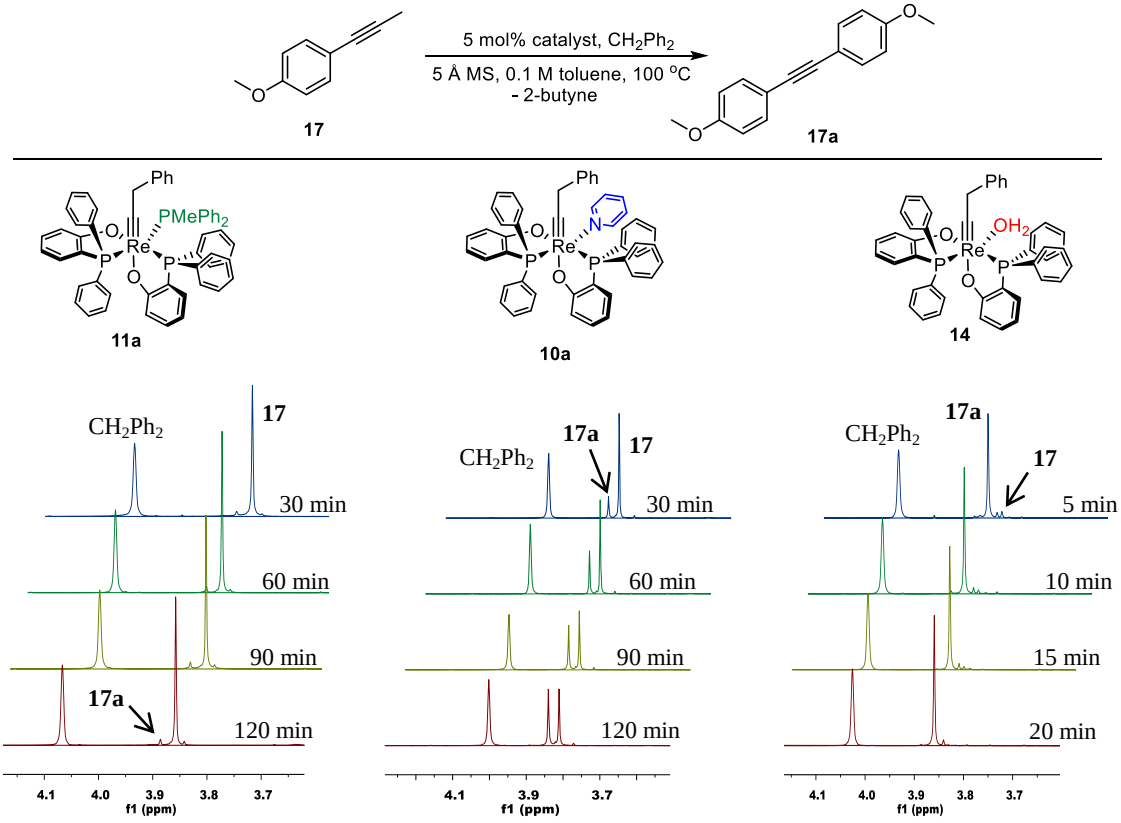


Figure S9. Stacked ^{1}H NMR spectra of homometathesis of 1-methoxy-4-(1-propyn-1-yl)benzene catalyzed by **11a** (left), **10a** (middle) and **14** (right) at 100 °C.

General Procedures for Metathesis Reactions (Tables 2 & 3).

General Procedure A.

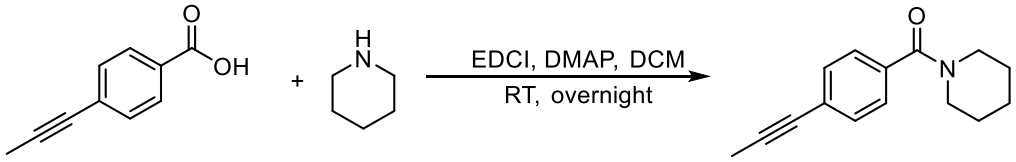
A Schlenk tube equipped with a stir bar and 5 Å molecular sieves (MS) was heated with a heat gun (at 450 ^{o}C) under vacuum for ca. 5 min to activate the MS. After cooling to room temperature, the Schlenk tube was evacuated and refilled with N_2 three times. To the Schlenk tube were added substrate(s), Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$(H$_2$O) (**14**), and distilled toluene under N_2 flow. The mixture was stirred at specified temperatures for specified times. After the reaction, the mixture was diluted with dichloromethane in air, filtered through Celite and washed thoroughly with dichloromethane. Evaporation of the volatiles on a rotary evaporator gave a residue, which was purified by column chromatography to yield the desired product.

General Procedure B. (Using nnpurified toluene)

A Schlenk tube equipped with a stir bar and 5 Å molecular sieves (MS) was heated with a heat gun (at 450 ^{o}C) under vacuum for ca. 5 min to activate the MS. After cooling to room temperature, the Schlenk tube was evacuated and refilled with N_2 three times. To the Schlenk tube were added substrate(s), Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$(H$_2$O) (**14**, 5 mol%), and unpurified toluene (commercial AR grade toluene stored in air, used without drying or degassing processes) under N_2 flow. The Schlenk tube was sealed and the mixture was stirred at room temperatures for specified times. After the reaction, the mixture was diluted with dichloromethane in air, filtered through Celite and washed thoroughly with dichloromethane. Evaporation of the volatiles on a rotary evaporator gave a residue, which was purified by column chromatography to yield the desired product.

Synthesis of New Substrates

Piperidin-1-yl(4-(prop-1-yn-1-yl)phenyl)methanone (25)



To a stirred solution of 4-(prop-1-yn-1-yl)benzoic acid (160 mg, 1.0 mmol) and piperidine (86 mg, 1.0 mmol) in anhydrous DCM (5 mL) were added *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDCI, 288 mg, 1.5 mmol) and 4-(dimethylamino)pyridine (12 mg, 0.10 mmol) at 0 ^{o}C. The resulting mixture was brought to room temperature and stirred overnight. After the reaction, the mixture was concentrated on a rotary evaporator to give an oily residue, which was purified by flash column chromatography (hexane:EA = 3:1) to give the desired product as white crystals. Yield: 227 mg, 99%.

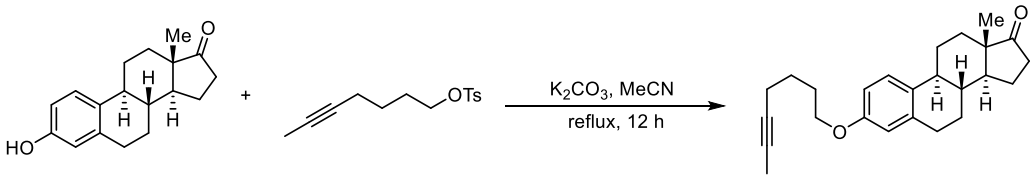
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 3.68 (br, 2H), 3.32 (br, 2H), 2.05 (s, 3H), 1.66 (br, 4H), 1.51 (br, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.84, 135.34, 131.48, 126.84, 125.30, 87.36, 79.21, 48.84 (br), 43.00 (br), 26.20 (br), 25.90 (br), 24.57, 4.38.

IR (ATR, cm^{-1}): 2997, 2936, 2855, 2252, 1625, 1431, 1275, 1106, 1125, 1101, 845, 761, 729

HRMS (ESI) Calcd. for $[C_{15}H_{17}NNaO]^{+}$ $[M+Na]^{+}$: 250.1202; Found: 250.1210.

Estrone hept-5-ynyl ether (39)



A mixture of estrone (270 mg, 1.0 mmol), hept-5-yn-1-yl 4-methylbenzenesulfonate (320 mg, 1.2 mmol) and K_2CO_3 (346 mg, 2.5 mmol) in 4 mL of MeCN was refluxed for 12 hours. After cooling to room temperature, the solvent was removed on a rotary evaporator. The residue was partitioned between dichloromethane (DCM) and water and the aqueous phase was extracted with DCM for 2 times. The combined DCM

extracts was washed with sat. NaCl (aq.), dried over Na_2SO_4 and evaporated to dryness. The resulting residue was purified by flash column chromatography (hexane:EA = 10:1) to give the desired product as a white solid. Yield: 238 mg, 65%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 1H), 6.71 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.69 (d, *J* = 2.2 Hz, 1H), 3.95 (t, *J* = 6.3 Hz, 2H), 3.01 – 2.76 (m, 2H), 2.50 (dd, *J* = 18.8, 8.5 Hz, 1H), 2.43 – 2.32 (m, 1H), 2.28 – 1.82 (m, 9H), 1.78 (t, *J* = 2.2 Hz, 3H), 1.70 – 1.39 (m, 8H), 0.91 (s, 3H).

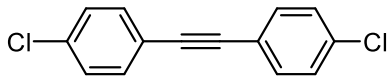
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 221.06, 157.18, 137.79, 132.00, 126.40, 114.64, 112.20, 78.90, 75.97, 67.42, 50.51, 48.12, 44.09, 38.49, 35.98, 31.69, 29.76, 28.56, 26.67, 26.03, 25.65, 21.70, 18.56, 13.96, 3.58.

IR: (ATR, cm^{-1}): 2919, 2862, 1736, 1608, 1498, 1310, 1280, 1157, 817, 734.

HRMS (CI) Calcd. for $[C_{25}H_{32}O_2]^+$ $[M]^+$: 364.2402; Found: 364.2413.

Products of Alkyne Metathesis Reactions

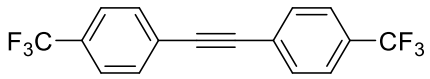
4,4'-Dichlorophenylacetylene (18a)



Synthesized following general procedure **A**. 4-Chlorophenyl propyne (45.2 mg, 0.30 mmol), Re(≡CCH_2Ph)(^{Ph}PO)$_2$(H_2O) (5.2 mg, 0.006 mmol, 2 mol%), 5 Å molecular sieves (450 mg) and toluene (3 mL). RT, 24 h. Purified by column chromatography (hexane). White solid. Yield: 31.0mg, 84%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 4H), 7.33 (d, *J* = 8.5 Hz, 4H). The NMR spectroscopic data are consistent with those reported in the literature.[24]

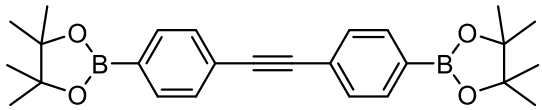
4,4'-Ditrifluoromethylphenylacetylene (19a)



Synthesized following general procedure **A**. 4-Trifluoromethylphenyl propyne (55.3 mg, 0.30 mmol), Re(≡CCH_2Ph)(^{Ph}PO)$_2$(H_2O) (5.2 mg, 0.006 mmol, 2 mol%), 5 Å molecular sieves (450 mg) and toluene (3 mL). 60 ^{o}C, 4 h. Purified by column chromatography (hexane). White solid. Yield: 38.1mg, 81%.

^{1}H NMR (400 MHz, $CDCl_3$) δ7.69 – 7.58 (m, 8H). The NMR spectroscopic data are consistent with those reported in the literature.[25]

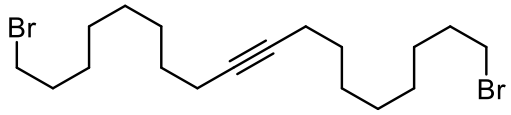
Diphenylacetylene-4,4'-diboronic acid bis(pinacol) ester (20a)



Synthesized following general procedure **A**. 4,4,5,5-tetramethyl-2-(4-(prop-1-yn-1-yl)phenyl)-1,3,2-dioxaborolane (72.6 mg, 0.30 mmol), Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (5.2 mg, 0.006 mmol, 2 mol%), 5 Å molecular sieves (450 mg) and toluene (3 mL). 60 ^oC, 4 h. Purified by column chromatography (Hex:EA=20:1 to DCM:MeOH=10:1). White solid. Yield: 57.0mg, 88%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 4H), 7.54 (d, *J* = 7.9 Hz, 4H), 1.35 (s, 24H). The NMR spectroscopic data are consistent with those reported in the literature.[26]

1,18-Dibromooctadec-9-yne (21a)



Synthesized following general procedure **A**. 11-Bromoundec-2-yne (69.4 mg, 0.30 mmol), Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (5.2 mg, 0.006 mmol, 2 mol%), 5 Å molecular sieves (450 mg) and toluene (3 mL). 60 ^oC, 3 h. Purified by column chromatography (Hex:EA=10:1 to DCM:MeOH=10:1). Colorless oil. Yield: 30.0mg, 49%.

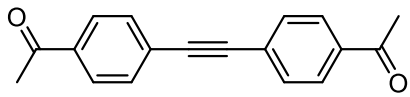
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (t, *J* = 6.9 Hz, 4H), 2.18 – 2.09 (m, 4H), 1.85 (quintet, *J* = 7.0 Hz, 4H), 1.51 – 1.22 (m, 20H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 80.33, 34.18, 32.93, 29.20, 29.08, 28.84, 28.80, 28.25, 18.85.

IR: (ATR, cm^{-1}): 2927, 2854, 1462, 1433, 1246, 723

HRMS (CI): Calcd. for $[C_{18}H_{32}Br_2]^+$ $[M]^+$: 408.0850; Found: 408.0857.

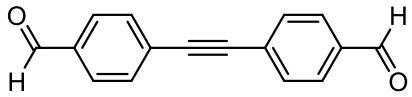
4,4'-Diacetylphenylacetylene (22a)



Synthesized following general procedure **A**. 4-Acetylphenyl propyne (47.5 mg, 0.30 mmol), Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (5.2 mg, 0.006 mmol, 2 mol%), 5 Å molecular sieves (450 mg) and toluene (3 mL). RT, 24 h. Purified by column chromatography (hexane:EA=10:1). White solid. Yield: 33.0mg, 84%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 4H), 7.64 (d, *J* = 8.4 Hz, 4H), 2.63 (s, 6H). The NMR spectroscopic data are consistent with those reported in the literature.[27]

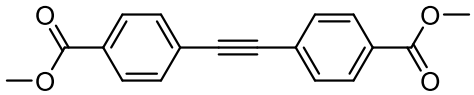
4,4'-(Ethyne-1,2-diyl)dibenzaldehyde (23a)



Synthesized following general procedure **A**. 4-(Prop-1-yn-1-yl)benzaldehyde (43.2 mg, 0.30 mmol), Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (5.2 mg, 0.006 mmol, 2 mol%), 5 Å molecular sieves (450 mg) and toluene (3 mL). 60 ^oC, 12 h. Purified by column chromatography (hexane:DCM = 10:1 to DCM). Pale yellow solid. Yield: 31.2mg, 88%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 2H), 7.90 (d, *J* = 7.8 Hz, 4H), 7.71 (d, *J* = 7.8 Hz, 4H). The NMR spectroscopic data are consistent with those reported in the literature.[25]

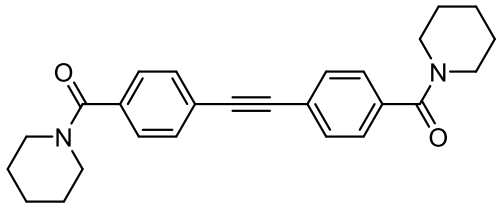
4,4'-Bis(methoxycarbonyl)diphenylacetylene (24a)



Synthesized following general procedure **A**. 4-Propynyl benzoic acid methyl ester (52.3 mg, 0.30 mmol), Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (5.2 mg, 0.006 mmol, 2 mol%), 5 Å molecular sieves (450 mg) and toluene (3 mL). 60 ^oC, 4 h. Purified by column chromatography (hexane:EA=40:1 to 10:1). White solid. Yield: 41.4mg, 94%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 4H), 7.61 (d, *J* = 8.4 Hz, 4H), 3.94 (s, 6H). The NMR spectroscopic data are consistent with those reported in the literature.[27]

(Ethyne-1,2-diylbis(4,1-phenylene))bis(piperidin-1-ylmethanone) (25a)



Synthesized following general procedure **A**. Piperidin-1-yl(4-(prop-1-yn-1-yl)phenyl)methanone (68.2 mg, 0.3 mmol), Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (5.2 mg, 0.006 mmol, 2 mol%), 5 Å molecular sieves (450 mg) and toluene (3 mL). 60 ^oC, 4 h. Purified by column chromatography (hexane:EA=40:1 to 10:1 to DCM). White solid. Yield: 50.8mg, 85%.

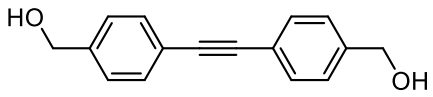
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.3 Hz, 4H), 7.38 (d, *J* = 8.3 Hz, 4H), 3.70 (br, 4H), 3.34 (br, 4H), 1.68 (br, 8H), 1.53 (br, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.71, 136.49, 131.80, 127.12, 124.25, 90.05, 48.92 (br), 43.32 (br), 26.66 (br), 25.76 (br), 24.69.

IR (ATR, cm^{-1}): 2998, 2937, 2856, 1623, 1439, 1276, 1107, 1001, 919, 850, 730**.**

HRMS (ESI) Calcd. for $[C_{26}H_{28}N_2NaO_2]^+$ $[M+Na]^+$: 423.2043; Found: 423.2054

(Ethyne-1,2-diylbis(4,1-phenylene))dimethanol (26a)

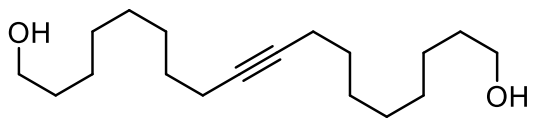


Synthesized following general procedure **A**. (4-(Prop-1-yn-1-yl)phenyl)methanol (43.9 mg, 0.3 mmol), Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (5.2 mg, 0.006 mmol, 2 mol%), 5 Å molecular sieves (450 mg) and toluene (3 mL). 60 ^oC, 4 h. Purified by column chromatography (DCM:MeOH= 50:1). White solid. Yield: 34.0 mg, 95%.

^{1}H NMR (400 MHz, MeOD) δ 7.49 (d, *J* = 8.1 Hz, 4H), 7.37 (d, *J* = 8.0 Hz, 4H), 4.62 (s, 4H).

The spectroscopic data are in accordance with the literature.[28]

9-Octadecyne-1,18-diol (27a)

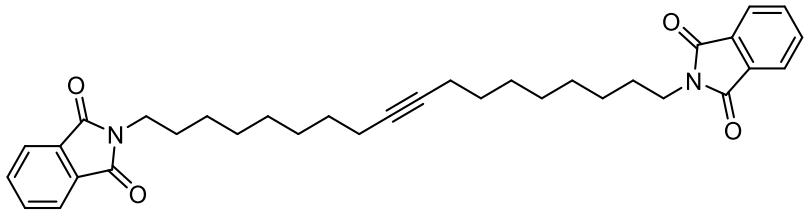


Synthesized following general procedure **A**. Undec-9-yn-1-ol (50.5 mg, 57 μL, 0.30 mmol), Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (5.2 mg, 0.006 mmol, 2 mol%), 5 Å molecular sieves (450 mg) and toluene (3 mL). 60 ^oC, 4 h. Purified by column chromatography (DCM to DCM:MeOH=10:1). White solid. Yield: 38.6 mg, 91%.

^1H NMR (400 MHz, $CDCl_3$) δ 3.62 (t, *J* = 6.7 Hz, 4H), 2.24 – 2.03 (m, 4H), 1.73 (br, 2H), 1.56 (dt, *J* = 13.5, 6.7 Hz, 4H), 1.50 – 1.42 (m, 4H), 1.42 – 1.24 (m, 16H).

The spectroscopic data are in accordance with the literature.[8]

2,2'-(Octadec-9-yne-1,18-diyl)bis(isoindoline-1,3-dione) (28a)



Synthesized following general procedure **A**. 2-(Undec-9-yn-1-yl)isoindoline-1,3-dione (89.2 mg, 0.30 mmol), Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (5.2 mg, 0.006 mmol, 2 mol%), 5 Å molecular sieves (450 mg) and toluene (3 mL). 60 ^oC, 3 h or RT, 16 h. Purified by column chromatography (hexane:EA = 4:1). White solid. Yield: 78.5 mg, 97%.

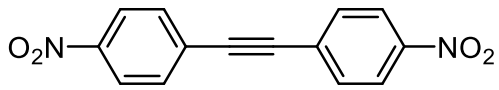
^1H NMR (400 MHz, $CDCl_3$) δ 7.86 - 7.80 (m, 4H), 7.73 - 7.77 (m, 4H), 3.67 (t, *J* = 7. 2 Hz, 4H), 2.11 (t, *J* = 7.0 Hz, 4H), 1.66 (quintet, *J* = 6.9 Hz, 4H), 1.61 - 1.20 (m, 24H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 168.61, 133.96, 132.33, 123.29, 80.33, 38.20, 29.24, 29.15, 28.91, 28.73, 26.97, 18.87.

HRMS (ESI): Calcd. for $[C_{34}H_{40}N_2NaO_4]^+$ $[M+Na]^+$: 563.2880; Found: 563.2888.

The spectroscopic data are in accordance with the literature.[29]

1,2-Bis(4-nitrophenyl)ethyne (29a)



Synthesized following general procedure **A**. 1-Nitro-4-propynylbenzene (48.3 mg, 0.30 mmol), Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (12.9 mg, 0.015 mmol, 5 mol%), 5 Å

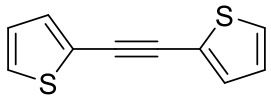
molecular sieves (450 mg) and toluene (3 mL). 60 ^{o}C, 12 h. Purified by column chromatography (hexane: DCM = 2:1). Yellow solid. Yield: 27.0 mg, 67 %.

^{1}H NMR (400.1 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.9 Hz, 4H), 7.72 (d, *J* = 8.9 Hz, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.79, 132.78, 129.02, 123.94, 92.15.

The NMR spectroscopic data are consistent with those reported in the literature.[30]

1,2-Di(thiophen-2-yl)ethyne (30a)

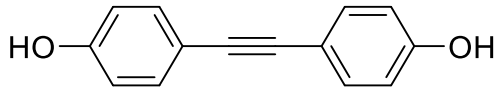


Synthesized following general procedure **A**. 2-(Prop-1-yn-1-yl)thiophene (36.7 mg, 0.30 mmol), Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$(H$_2$O) (5.2 mg, 0.006 mmol, 2 mol%), 5 Å molecular sieves (450 mg) and toluene (3 mL). 80 ^{o}C, 4 h. Purified by column chromatography (hexane: DCM= 100:1). White solid. Yield: 24.8 mg, 87 %.

^{1}H NMR (400.1 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 4H), 7.01 (dd, *J* = 5.1, 3.7 Hz, 2H).

The NMR spectroscopic data are consistent with those reported in the literature.[25]

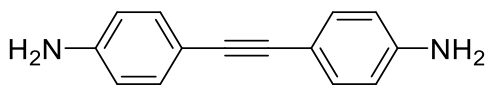
4,4'-Dihydroxyphenylacetylene (31a)



Synthesized following general procedure **A**. 4-Hydroxyphenyl propyne (40.0 mg, 0.30 mmol), Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$(H$_2$O) (12.9 mg, 0.015 mmol, 5 mol%), 5 Å molecular sieves (450 mg) and toluene (3 mL). 100 ^{o}C, 8 h. Purified by column chromatography (hexane: EA= 2:1). White solid. Yield: 27.5 mg, 87 %.

^{1}H NMR (400 MHz, CD_3CN) δ 7.38 (d, *J* = 8.7 Hz, 4H), 7.30 (br, 2H), 6.84 (d, *J* = 8.7 Hz, 4H). The NMR spectroscopic data are consistent with those reported in the literature.[31]

4,4'-Dianilinoacetylene (32a)

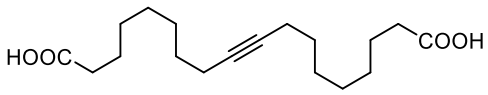


Synthesized following general procedure **A**. 4-Anilino propyne (39.4 mg, 0.30 mmol), Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$(H$_2$O) (12.9 mg, 0.015 mmol, 5 mol%), 5 Å molecular sieves

(450 mg) and toluene (3 mL). 100 ^{o}C, 8 h. Purified by column chromatography (hexane: EA= 2:1). White solid. Yield: 25.4mg, 81%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.5 Hz, 4H), 6.62 (d, *J* = 8.4 Hz, 4H), 3.77 (s, 4H). The NMR spectroscopic data are consistent with those reported in the literature.[32]

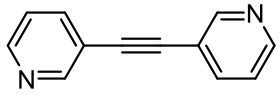
8- **Hexadecyne-1,16- dicarboxylic acid (33a)**



Synthesized following general procedure **A**. 9-Undecynoic acid (54.7 mg, 0.30 mmol), Re(≡CCH_2Ph)(^{Ph}PO)$_2$(H_2O) (12.9 mg, 0.015 mmol, 5 mol%), 5 Å molecular sieves (450 mg) and toluene (3 mL). 100 ^{o}C, 16 h. Purified by column chromatography (DCM:HCOOH = 100:1 to DCM:EA:HCOOH = 100:10:1). White solid. Yield: 32.3 mg, 69%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (t, *J* = 7.2 Hz, 4H), 2.17 – 2.11 (m, 4H), 1.65 (quintet, *J* = 7.1 Hz, 4H), 1.51 – 1.27 (m, 16H). The NMR spectroscopic data are consistent with those reported in the literature.[8]

1,2-Di(pyridin-3-yl)ethyne (34a)



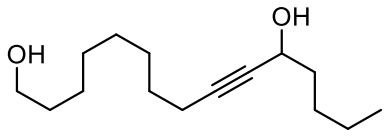
Synthesized following general procedure **A**. 3-(Prop-1-yn-1-yl)pyridine (35.1 mg, 0.30 mmol), Re(≡CCH_2Ph)(^{Ph}PO)$_2$(H_2O) (12.9 mg, 0.015 mmol, 5 mol%), 5 Å molecular sieves (450 mg) and toluene (3 mL). 100 ^{o}C, 3 days. Purified by column chromatography (hexane:EA:Et_3N = 100:10:1 to 100:50:1). Pale yellow solid. Yield: 4.0 mg, 15%. Note: after heating at 100 ^{o}C for 16 h, ca. 6% conversion was observed by ^{1}H NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (br s, 2 H), 8.60 (br s, 2H), 7.85 (br d, *J* = 7.9 Hz, 2 H), 7.33 (dd, *J* = 7.4, 5.1 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.29, 149.09, 138.84, 123.39, 120.00, 89.35.

The NMR spectroscopic data are consistent with those reported in the literature.[33]

Pentadec-9-yne-1,11-diol (36)



Synthesized following general procedure **A**. Undec-9-yn-1-ol (168.3 mg, 1.0 mmol), oct-2-yn-4-ol (31.6 mg, 0.25 mmol), Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (10.8 mg, 5 mol%), 5 Å molecular sieves (2.50 g) and distilled toluene (7.5 mL). 60 ^oC, 12 h. Purified by column chromatography (hexane:EA = 5:1 to 2:1). Yellow oil. Yield: 40.5 mg, 67%.

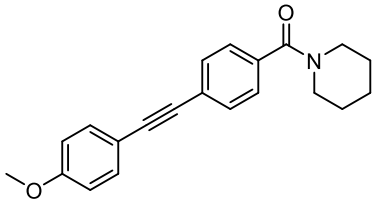
^1H NMR (400 MHz, $CDCl_3$) δ 4.34 (tt, *J* = 6.5, 1.8 Hz, 1H), 3.63 (t, *J* = 6.6 Hz, 2H), 2.20 (td, *J* = 7.0, 1.9 Hz, 2H), 1.81 (br, 2H), 1.72 – 1.27 (m, 18H), 0.91 (t, *J* = 7.1 Hz, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 100.11, 85.54, 63.16, 62.87, 38.05, 32.82, 29.33, 29.07, 28.74, 28.68, 27.52, 25.73, 22.53, 18.76, 14.18.

IR (ATR, cm^{-1}): 3317, 2928, 2856, 1460, 1438, 1036, 1009.

HRMS (CI) Calcd. for $[C_{15}H_{29}O_2]^+$ $[M+H]^+$: 241.2162; Found: 241.2172.

(4-((4-Methoxyphenyl)ethynyl)phenyl)(piperidin-1-yl)methanone (37)



Synthesized following general procedure **A**. Piperidin-1-yl(4-(prop-1-yn-1-yl)phenyl)methanone (68.2 mg, 0.3 mmol), 1-methoxy-4-(prop-1-yn-1-yl)benzene (131.6 mg, 0.9 mmol), Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (12.9 mg, 0.015 mmol, 5 mol%), 5 Å molecular sieves (1.80 g) and toluene (5 mL). 60 ^oC, 4.5 h. Purified by column chromatography (hexane:EA = 10:1 to 3:1). Pale brown crystals. Yield: 66.0 mg, 69%.

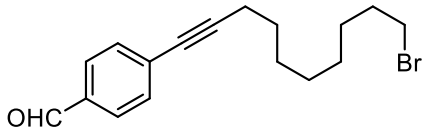
^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 3.69 (br, 2H), 3.33 (br, 2H), 1.67 (br, 4H), 1.51 (br, 2H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 169.83, 159.89, 135.76, 133.23, 131.48, 127.04, 124.92, 115.06, 114.13, 90.82, 87.57, 55.41, 48.83 (br), 43.35 (br), 26.64 (br), 25.68 (br), 24.65.

IR (ATR, cm^{-1}): 2999, 2934, 2854, 2214, 1624, 1600, 1568, 1515, 1434, 1279, 1247, 1174, 1137, 1106, 1026, 1000, 832.

HRMS (ESI) Calcd. for $[C_{21}H_{21}NNaO_2]^+$ $[M+Na]^+$: 342.1465; Found: 342.1468.

4-(10-Bromodec-1-yn-1-yl)benzaldehyde (38)



Synthesized following general procedure **A**. 4-(Prop-1-yn-1-yl)benzaldehyde (43.3 mg, 0.3 mmol), 11-bromoundec-2-yne (208.1 mg, 0.9 mmol), $Re(\equiv CCH_2Ph)(^{Ph}PO)_2(H_2O)$ (12.9 mg, 0.015 mmol, 5 mol%), 5 Å molecular sieves (1.80 g) and toluene (6 mL). 60 ^{o}C, 4 h. Purified by column chromatography (hexane to hexane:EA = 100:1). Colorless oil. Yield: 59.2 mg, 61%.

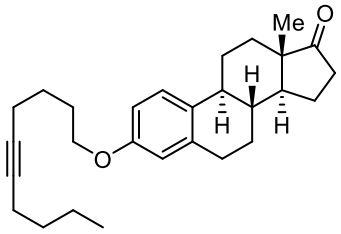
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.44 (t, *J* = 7.0 Hz, 2H), 1.95 – 1.77 (m, 2H), 1.68 – 1.56 (m, 2H), 1.54 – 1.28 (m, 8H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 191.64, 135.07, 132.21, 130.69, 129.63, 95.32, 80.31, 34.12, 32.89, 29.05, 28.91, 28.75, 28.56, 28.23, 19.67.

IR (ATR, cm^{-1}): 2928, 2854, 2729, 2226, 1699, 1600, 1561, 1206, 1164, 828.

HRMS (CI) Calcd. for $[C_{17}H_{22}BrO]^+$ $[M+H]^+$: 321.0849; Found: 321.0858.

Estrone dec-5-ynyl ether (40)



Synthesized following general procedure **A**. The estrone derivative **39** (72.9 mg, 0.2 mmol), 5-decyne (69.1 mg, 0.5 mmol), $Re(\equiv CCH_2Ph)(^{Ph}PO)_2(H_2O)$ (8.6 mg, 5 mol%),

5 Å molecular sieves (0.30 g) and distilled toluene (2 mL). 60 ^{o}C, 5 h. Purified by column chromatography (hexane:EA = 10:1). Pale yellow solid. Yield: 58.9 mg, 72%.

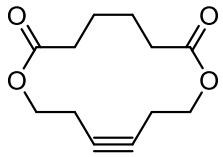
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.6 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.64 (d, *J* = 2.5 Hz, 1H), 3.95 (t, *J* = 6.4 Hz, 2H), 2.89 (dd, *J* = 7.0, 3.0 Hz, 2H), 2.50 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.44 – 2.34 (m, 1H), 2.30 – 1.81 (m, 11H), 1.72 – 1.31 (m, 12H), 0.98 – 0.85 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 220.88, 157.14, 137.71, 131.92, 126.33, 114.59, 112.15, 80.73, 79.64, 67.38, 50.46, 48.06, 44.04, 38.45, 35.92, 31.65, 31.29, 29.72, 28.52, 26.63, 25.99, 25.72, 22.01, 21.65, 18.56, 18.49, 13.91, 13.71.

IR (ATR, cm^{-1}): 2950, 2928, 2859, 1738, 1558, 1507, 1457.

HRMS (CI) Calcd. for $[C_{28}H_{39}O_2]^+$ $[M+H]^+$: 407.2945; Found: 407.2939.

1,8-Dioxacyclotetradec-11-yne-2,7-dione (42)



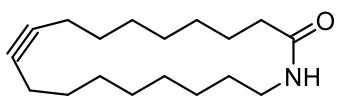
Synthesized following general procedure **A**. Di(pent-3-yn-1-yl) adipate (**41**) (83.5 mg, 0.30 mmol), Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (12.9 mg, 0.015 mmol), 5 Å molecular sieves (1.0 g) and toluene (60 mL). 80 ^{o}C, 8 h. Purified by column chromatography (hexane:EA = 5:1). White needle crystals. Yield: 62.0 mg, 92%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (t, *J* = 5.4 Hz, 4H), 2.57 – 2.46 (m, 4H), 2.43 – 2.32 (m, 4H), 1.77 – 1.72 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.28, 78.03, 62.67, 35.08, 25.12, 19.24.

HRMS (ESI) Calcd. for $[C_{12}H_{16}NaO_4]^+$ $[M+Na]^+$: 247.0941; Found: 247.0947.

Azacyclononadec-10-yn-2-one (44)



Synthesized following general procedure **A**. *N*-(Undec-9-yn-1-yl)undec-9-ynamide (**43**) (66.3 mg, 0.20 mmol), Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (8.6 mg, 0.01 mmol), 5 Å molecular sieves (0.60 g) and toluene (40 mL). 100 ^{o}C, 12 h. Purified by column chromatography (hexane:EA = 2:1). White crystals. Yield: 38.0 mg, 68%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 (br, 1H), 3.30 (td, *J* = 5.8, 5.7 Hz, 2H), 2.25 – 2.06 (m, 6H), 1.71 – 1.57 (m, 2H), 1.55 – 1.46 (m, 2H), 1.46 – 1.36 (m, 8H), 1.38 – 1.27 (m, 10H). The NMR spectroscopic data are consistent with those reported in the literature.[7]

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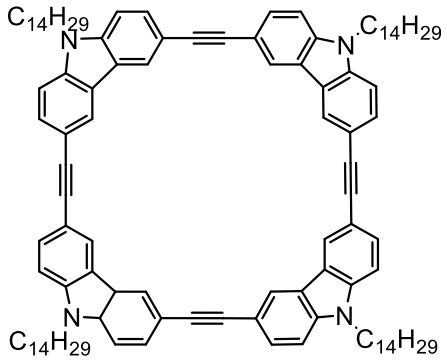

Synthesized following general procedure **A**. 3,6-Di(prop-1-yn-1-yl)-9-tetradecylcarbazole (**45**) (83.5 mg, 0.30 mmol), Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (8.6 mg, 0.01 mmol), 5 Å molecular sieves (0.60 g) and toluene (10 mL). 60 ^{o}C, 14 h. Purified by column chromatography (hexane:chloroform = 1:1). White solid. Yield: 38.0 mg, 98%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 1.0 Hz, 2H), 7.71 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 4.27 (t, *J* = 7.0 Hz, 2H), 1.95 – 1.80 (m, 2H), 1.46 – 1.13 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.24, 129.38, 124.06, 122.77, 114.55, 109.00, 89.23, 43.45, 32.08, 29.85, 29.81, 29.78, 29.73, 29.68, 29.53, 29.15, 27.46, 22.85, 14.29.

The NMR spectroscopic data are consistent with those reported in the literature.[15]

4. NMR Spectra

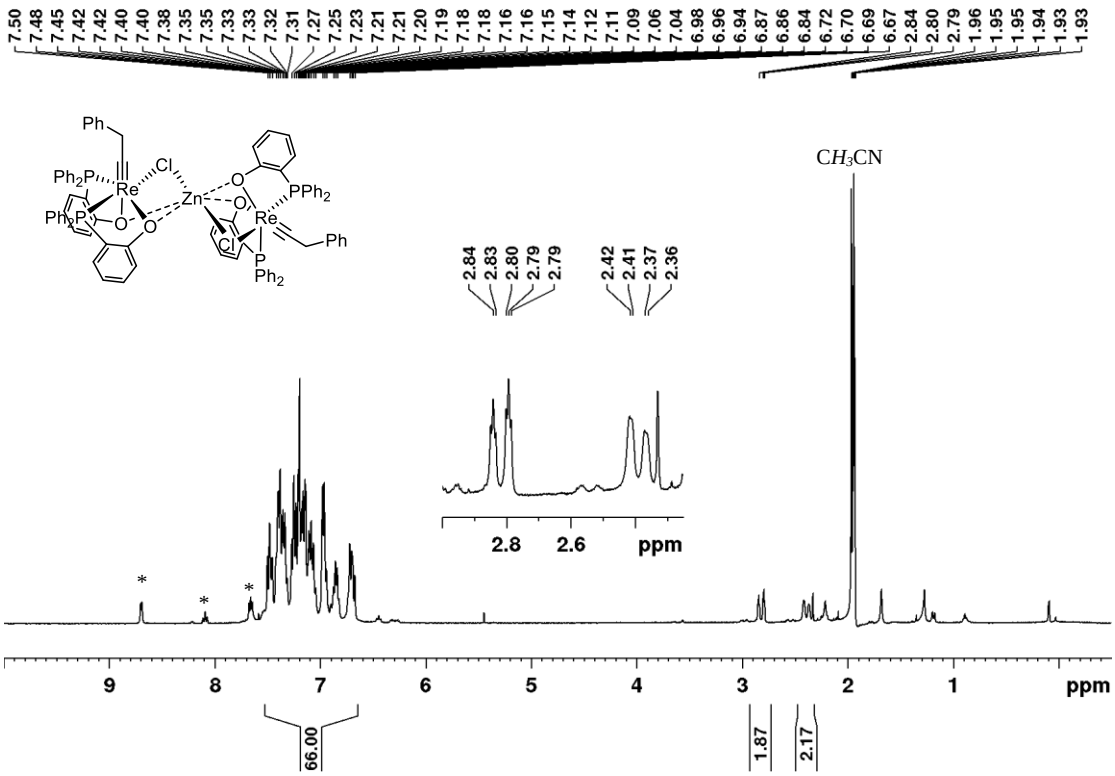

Figure S10. The ^{1}H NMR spectrum of **[**Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$]$_2$(μ-ZnCl$_2$) (**12a**) in CD$_3$CN at 400.1 MHz. * The signals of remaining ZnCl$_2$(py)$_2$.

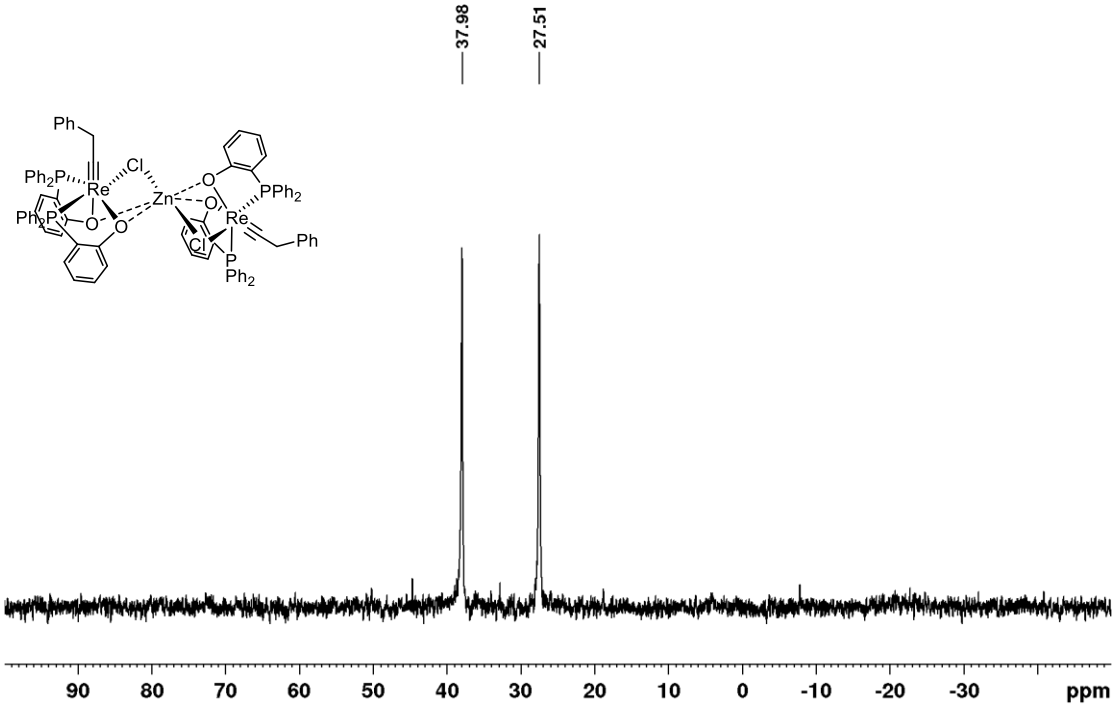

Figure S11. The ^{31}P{^{1}H} NMR spectrum of **[**Re(≡CCH$_2$Ph)(^{Ph}PO)$_2$]$_2$(μ-ZnCl$_2$) (**12a**) in CD$_3$CN at 162.0 MHz.

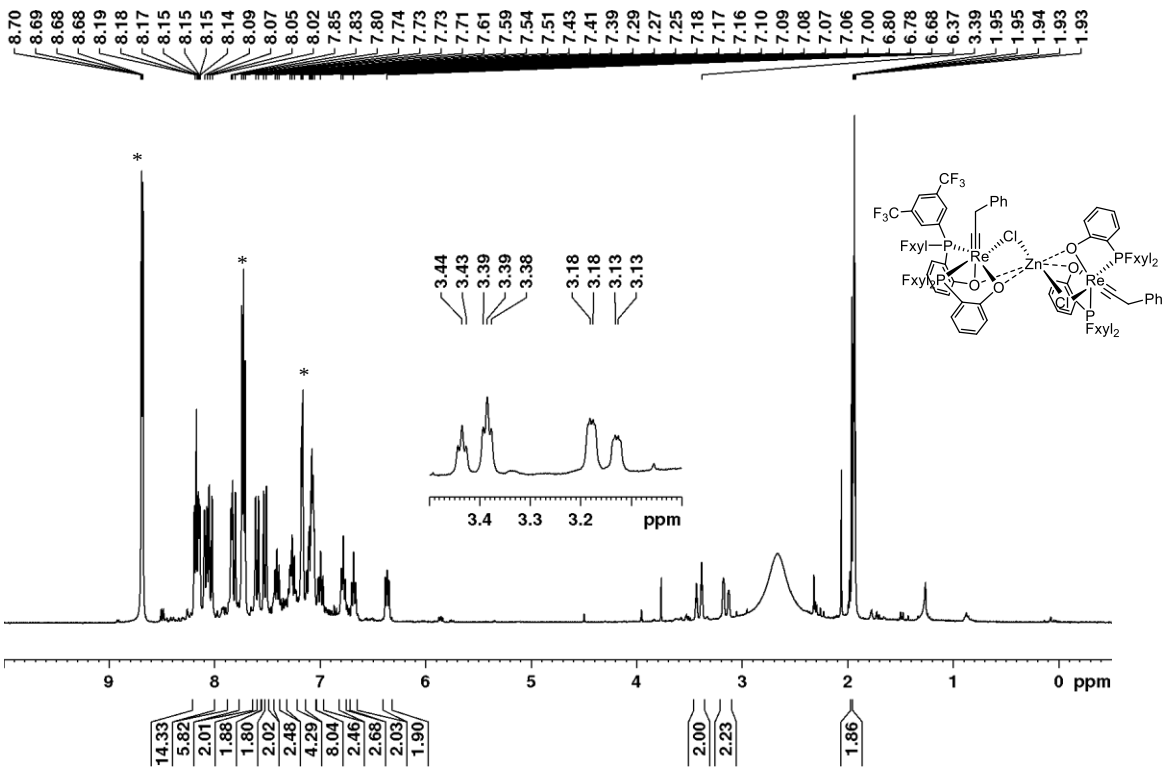

Figure S12. The ^{1}H NMR spectrum of **[**Re(≡CCH$_2$Ph)(^{Fxyl}PO)$_2$]$_2$(μ-ZnCl$_2$) (**12b**) in CD$_3$CN at 400.1 MHz. * The signals of remaining ZnCl$_2$(py)$_2$.

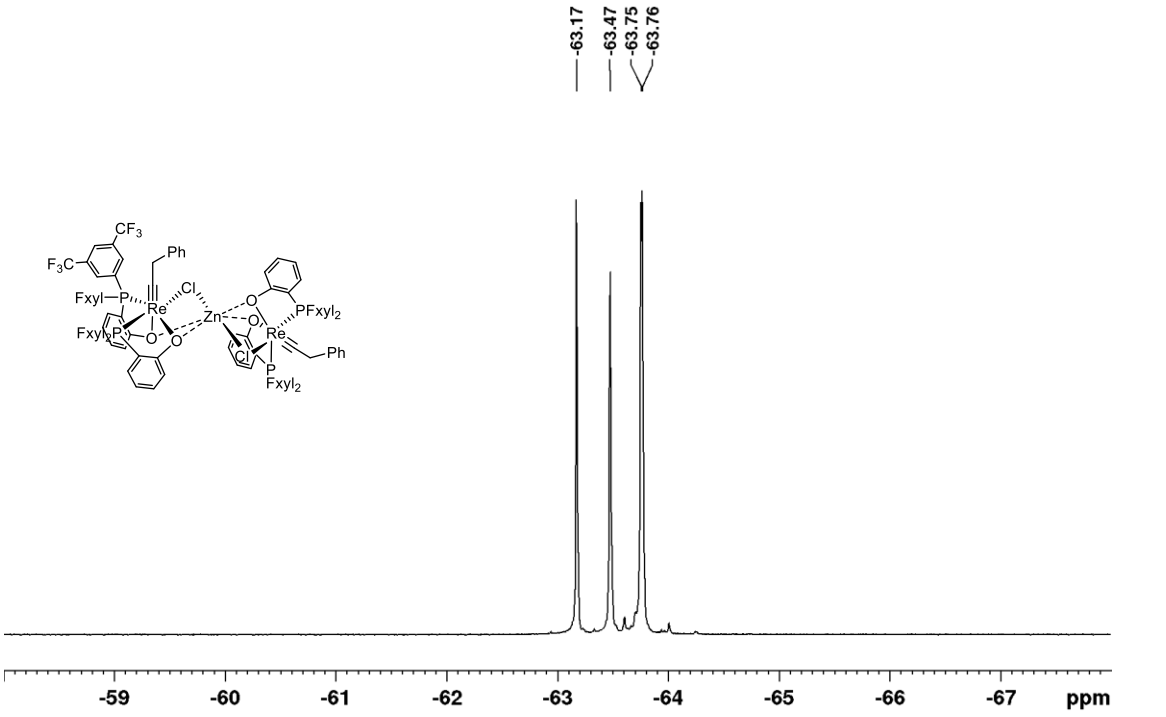

Figure S13. The ^{19}F{^{1}H} NMR spectrum of **[**Re(≡CCH$_2$Ph)(^{Fxyl}PO)$_2$]$_2$(μ-ZnCl$_2$) (**12b**) in CD$_3$CN at 376.5 MHz.

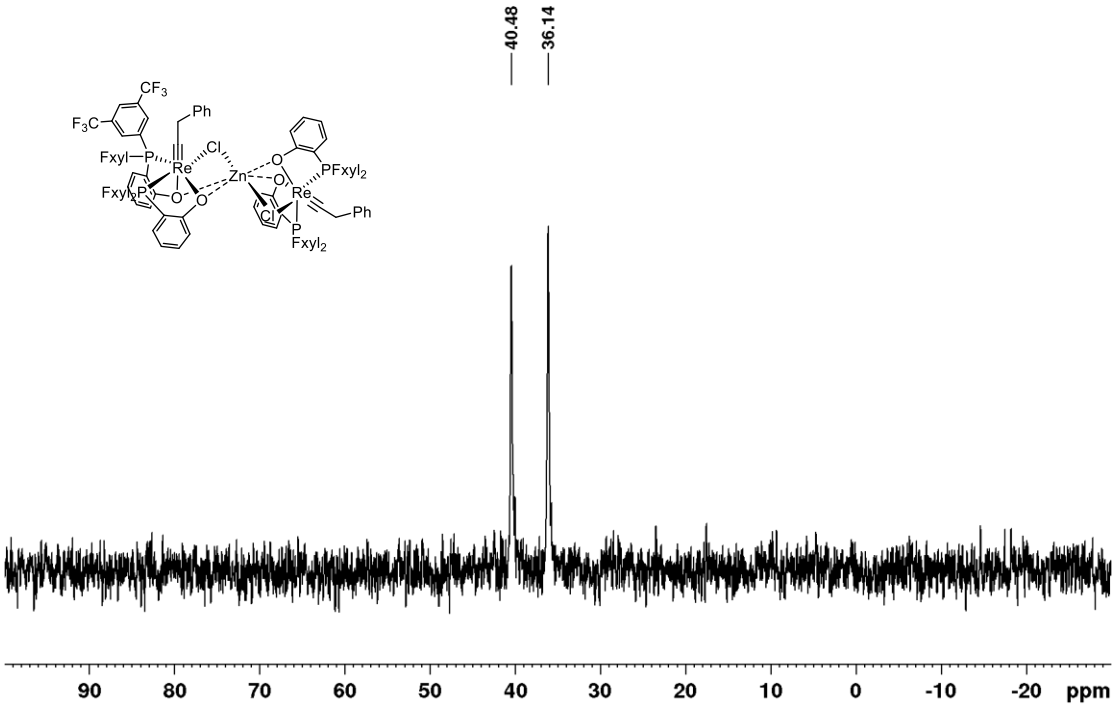

Figure S14. The $^{31}P\{^{1}H\}$ NMR spectrum of **[**Re(≡CCH_2Ph)($^{Fxyl}PO)_2]_2$(μ-$ZnCl_2$) (**12b**) in $CDCl_3$ at 162.0 MHz.

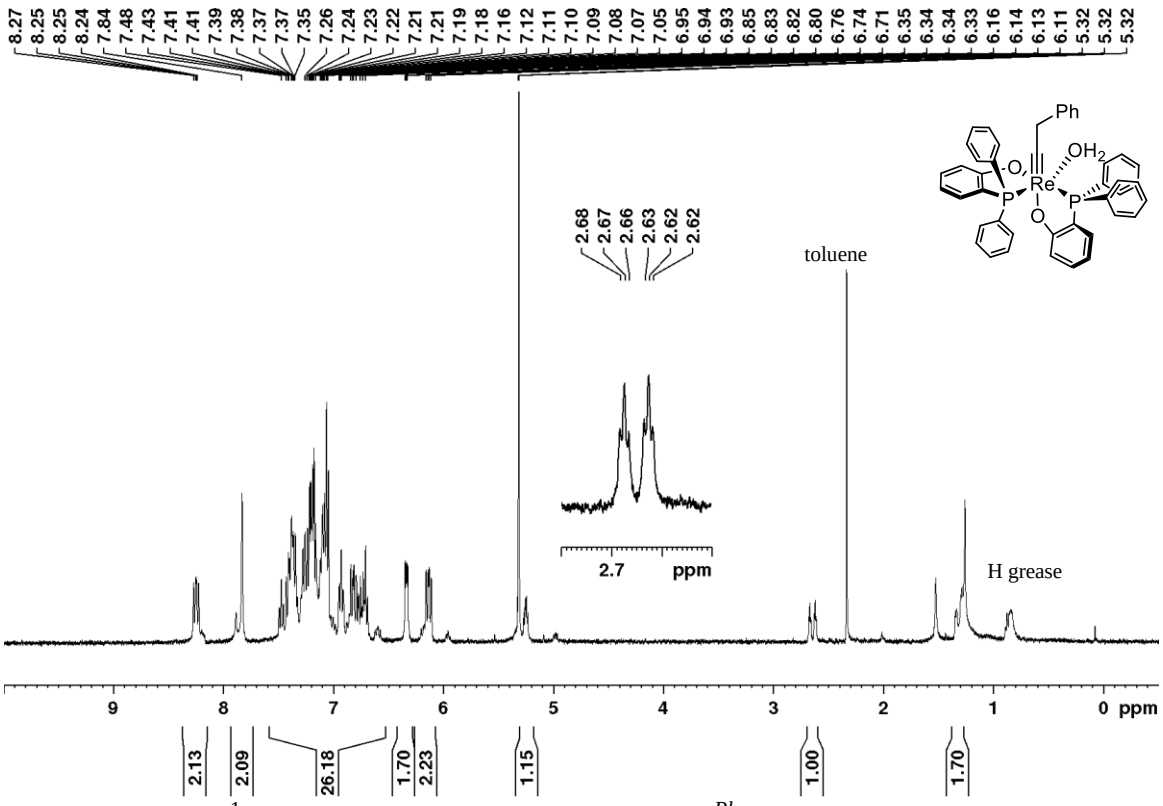

Figure S15. The ^{1}H NMR spectrum of Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (**14**) in CD_2Cl_2 at 400.1 MHz. The signal of coordinated H_2O appeared as a singlet at 7.84 ppm.

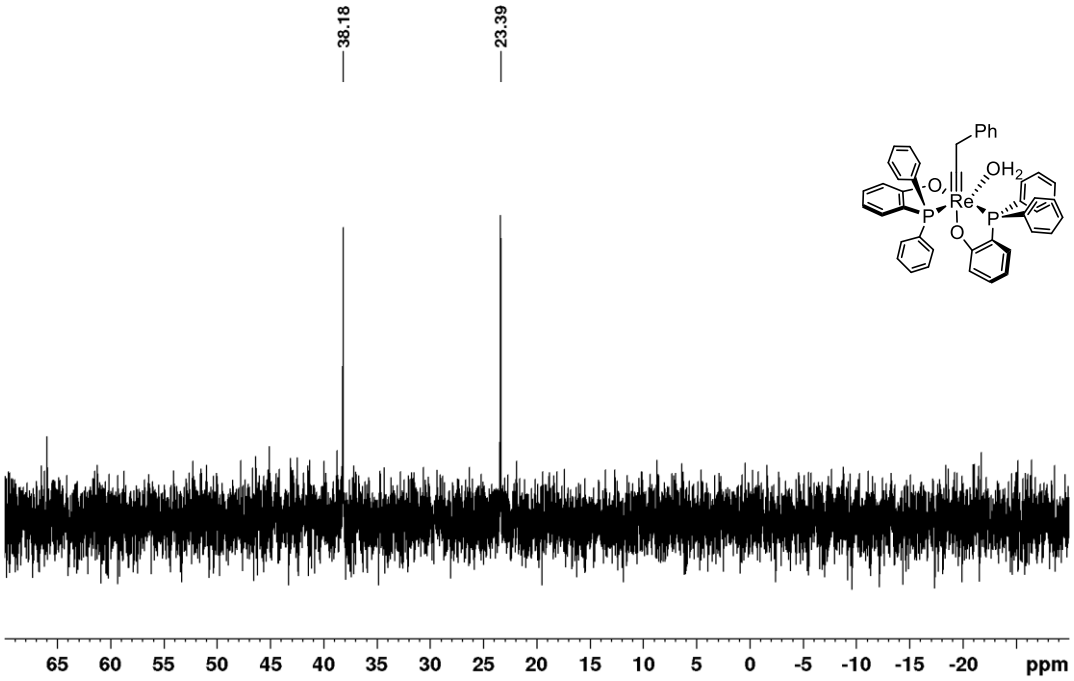

Figure S16. The $^{31}P\{^{1}H\}$ NMR spectrum of Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (**14**) in CD_2Cl_2 at 162.0 MHz.

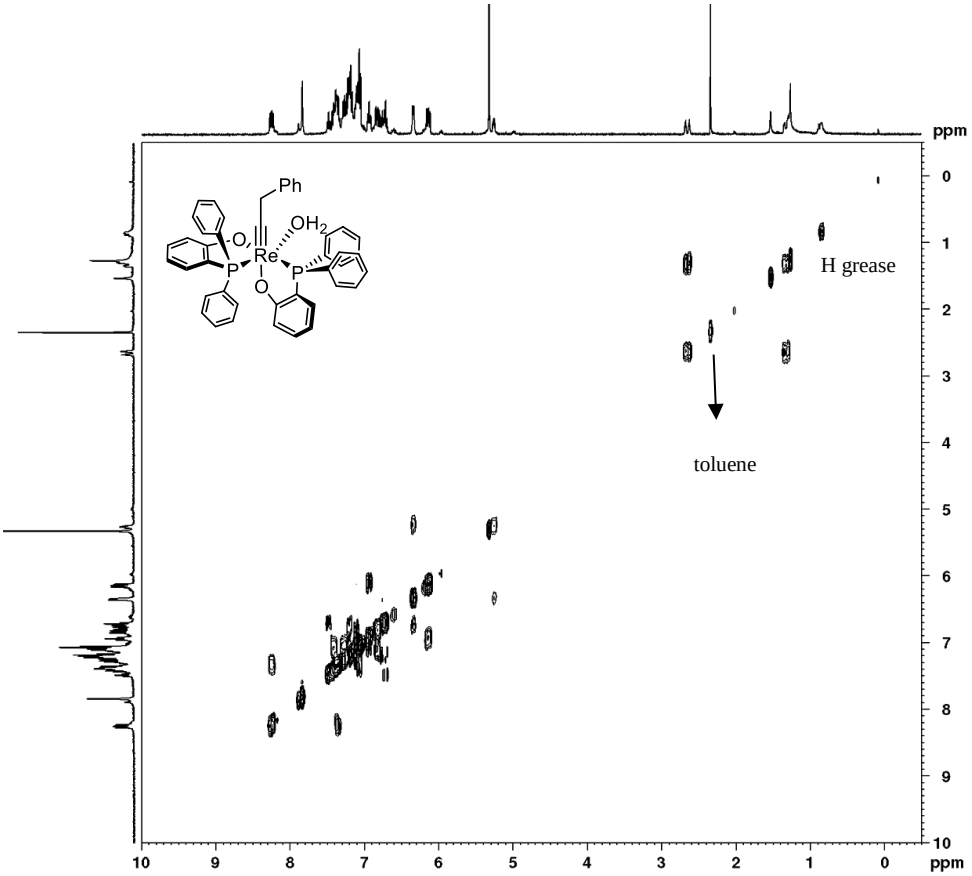

Figure S17. The COSY NMR spectrum of Re(≡CCH_2Ph)($^{Ph}PO)_2(H_2O)$ (**14**) in CD_2Cl_2 at 400.1 MHz. The COSY NMR spectrum confirms that the signals of the methylene protons of Re≡CCH_2Ph appear at 2.65 and 1.37 ppm.

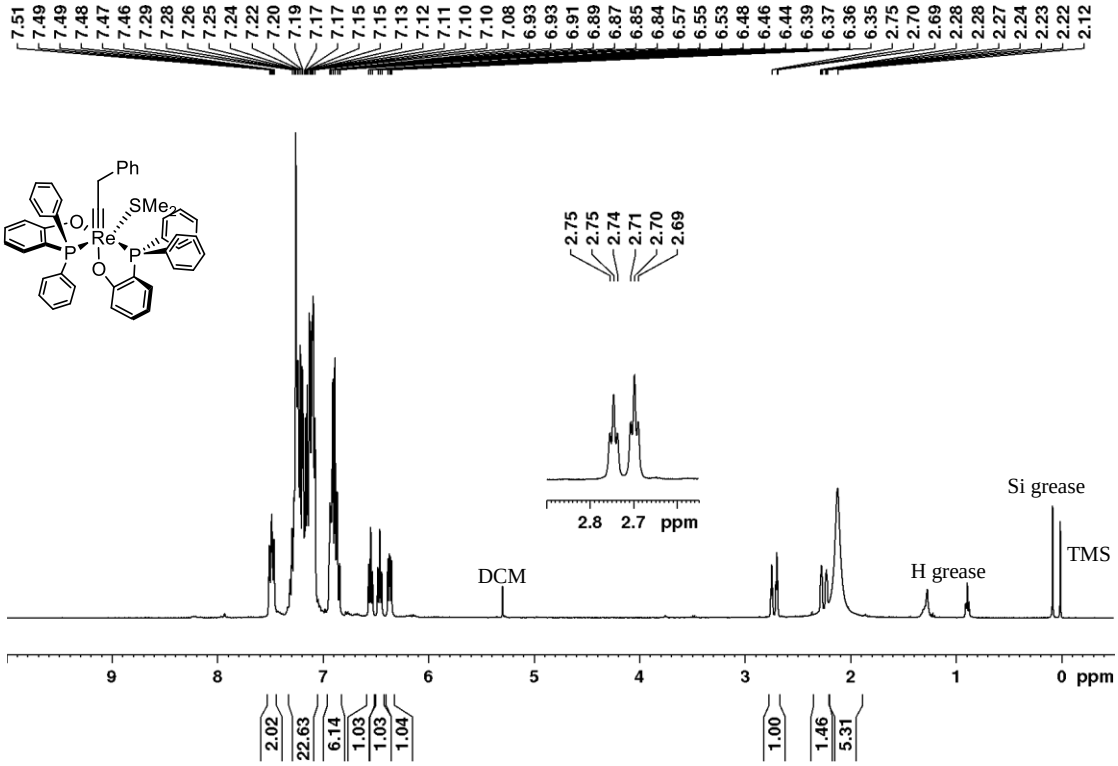

Figure S18. The ^{1}H NMR spectrum of Re(≡CCH_2Ph)($^{Ph}PO)_2(SMe_2$) (**15**) in $CDCl_3$ at 400.1 MHz.

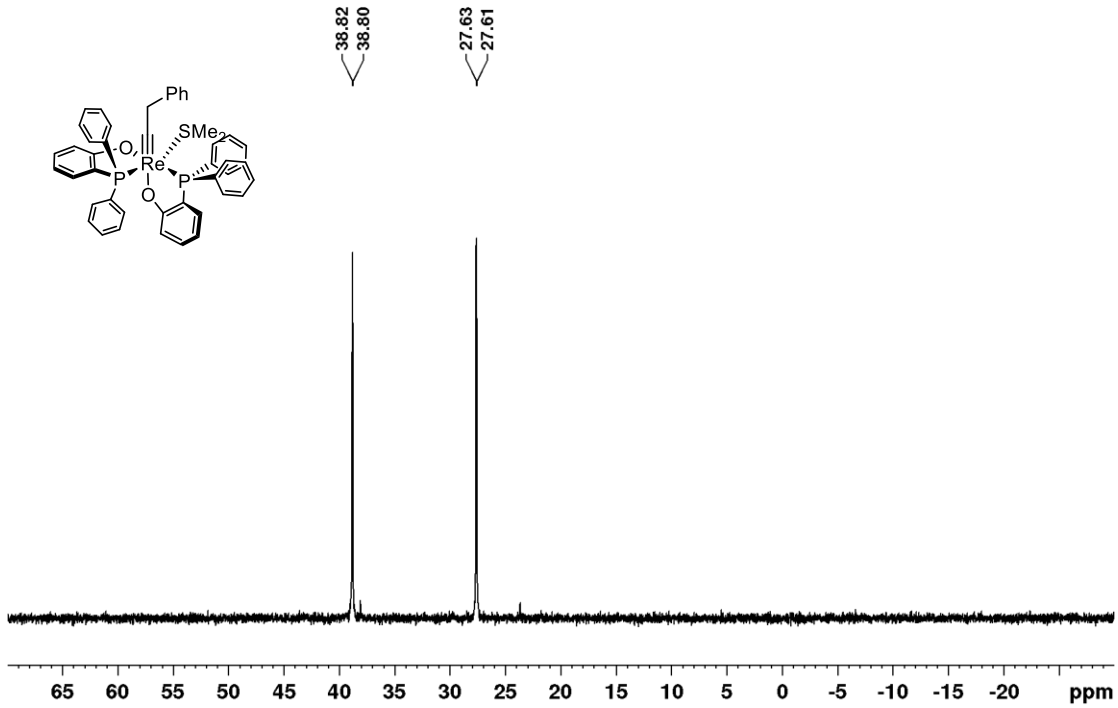

Figure S19. The $^{31}P\{^{1}H\}$ NMR spectrum of Re(≡CCH_2Ph)($^{Ph}PO)_2(SMe_2$) (**15**) in $CDCl_3$ at 162.0 MHz.

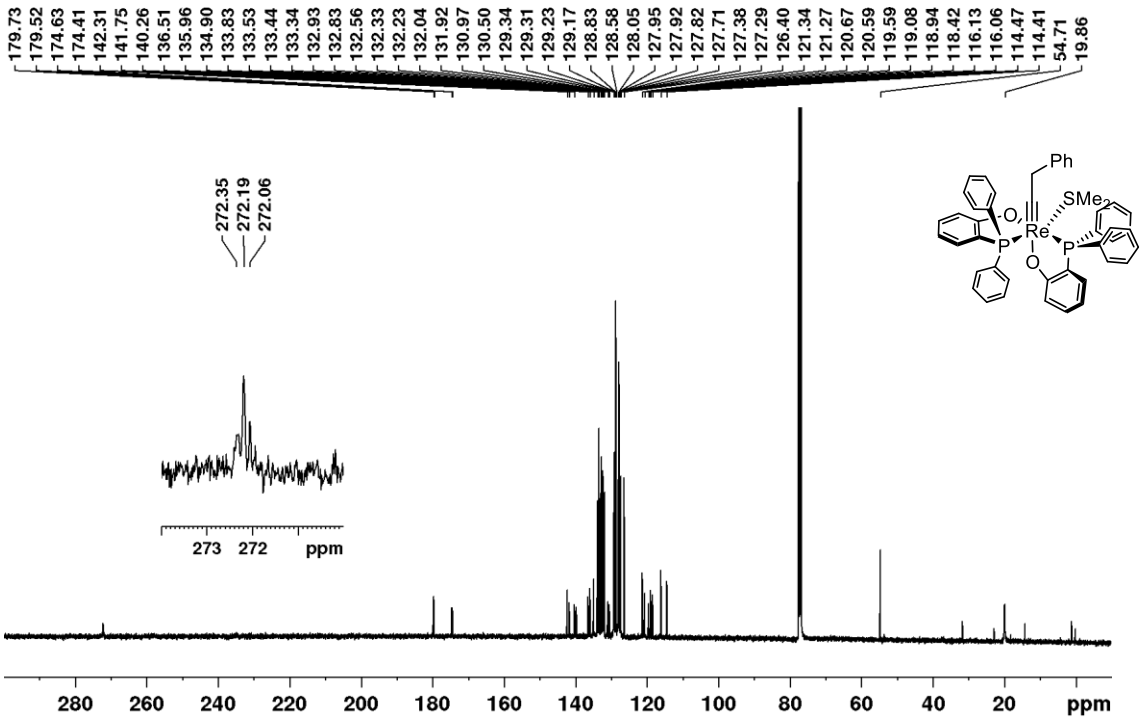

Figure S20. The $^{13}C\{^{1}H\}$ NMR spectrum of Re(≡CCH_2Ph)($^{Ph}PO)_2(SMe_2)$ (**15**) in $CDCl_3$ at 100.6 MHz.

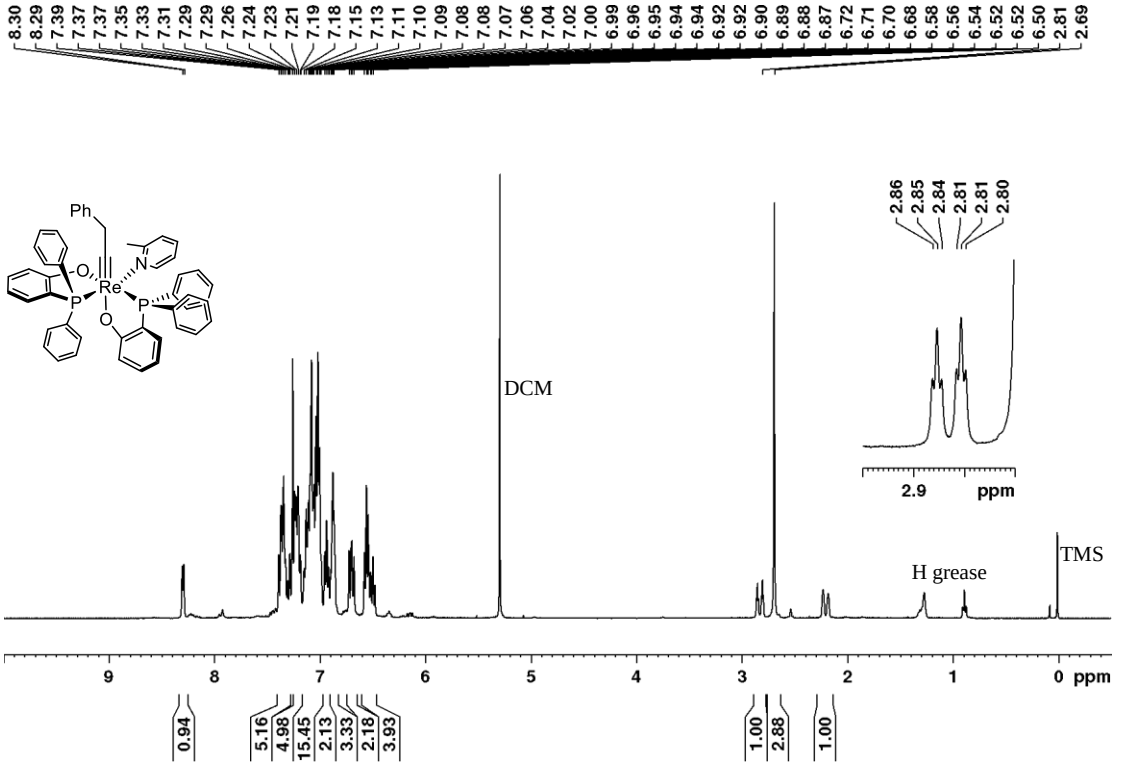

Figure S21. The ^{1}H NMR spectrum of Re(≡CCH_2Ph)($^{Ph}PO)_2(^{2\text{-}Me}py)$ (**16**) in $CDCl_3$ at 400.1 MHz.

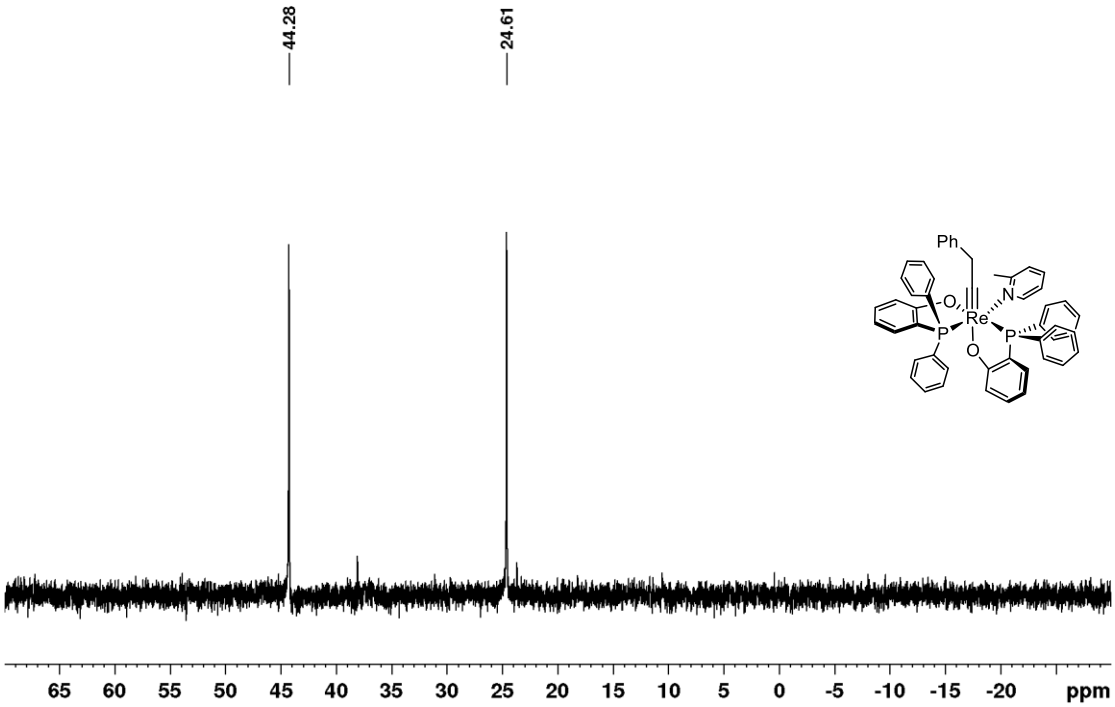

Figure S22. The $^{31}P\{^{1}H\}$ NMR spectrum of Re(≡CCH_2Ph)($^{Ph}PO)_2$($^{2\text{-}Me}$py) (**16**) in $CDCl_3$ at 162.0 MHz.

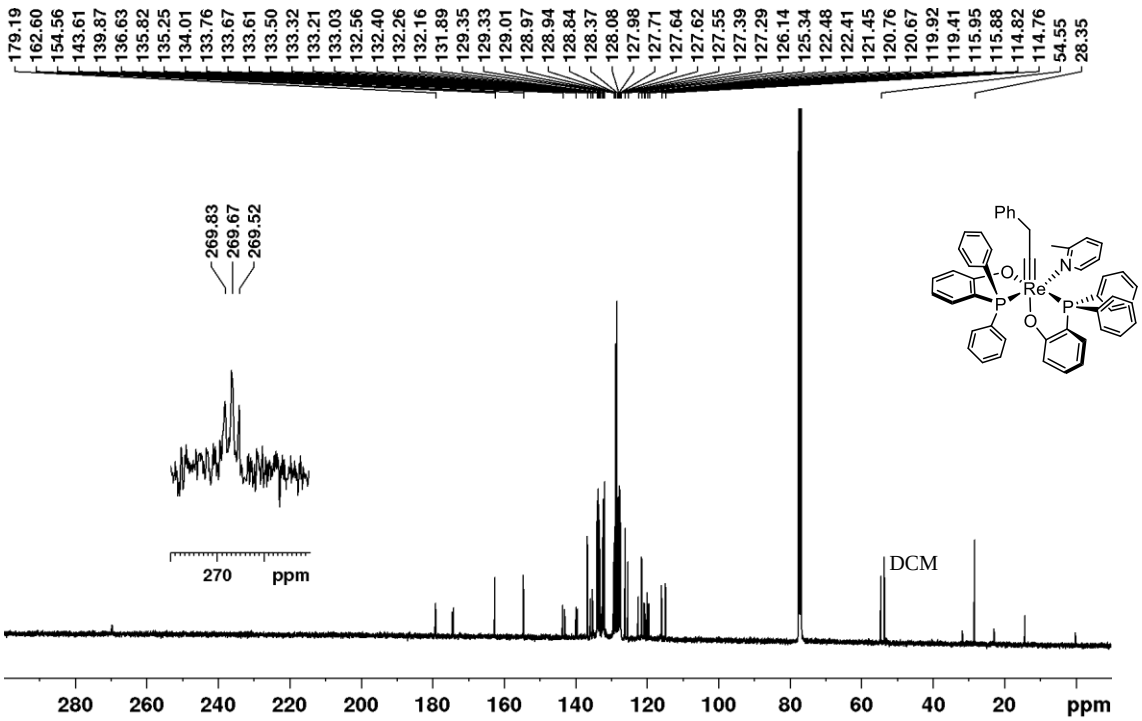

Figure S23. The $^{13}C\{^{1}H\}$ NMR spectrum of Re(≡CCH_2Ph)($^{Ph}PO)_2$($^{2\text{-}Me}$py) (**16**) in $CDCl_3$ at 100.6 MHz.

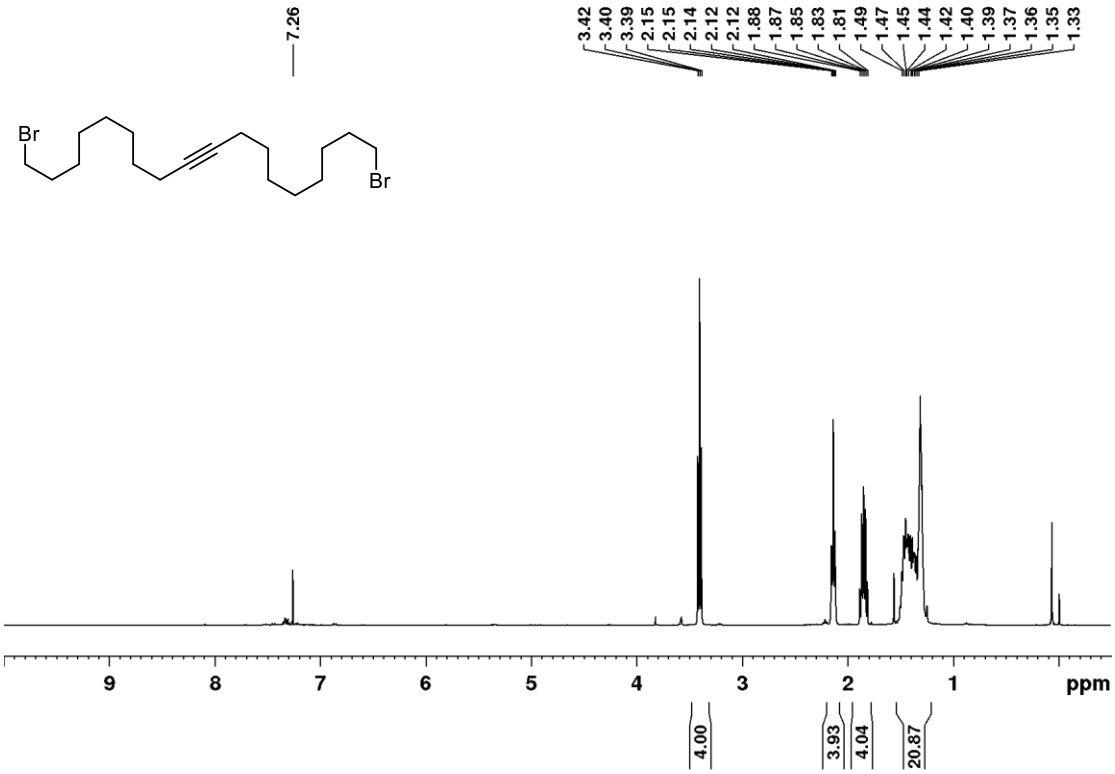

Figure S24. The ^{1}H NMR spectrum of 1,18-dibromooctadec-9-yne (**21a**) in $CDCl_3$ at 400.1 MHz.

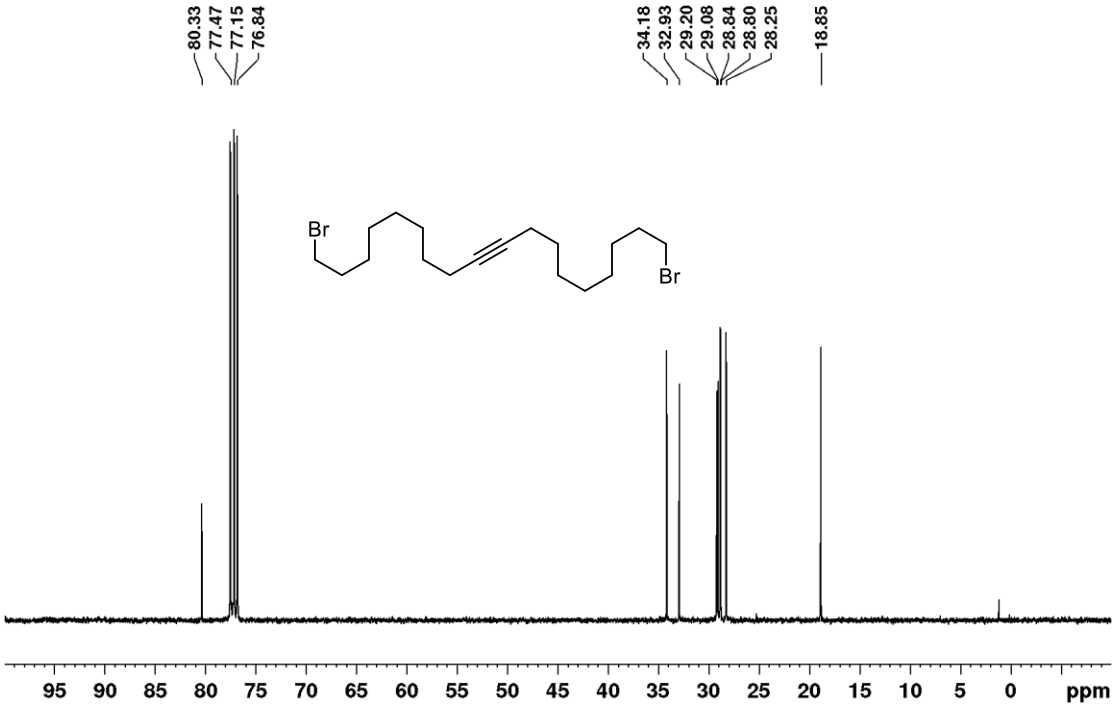

Figure S25. The $^{13}C\{^{1}H\}$ NMR spectrum of 1,18-dibromooctadec-9-yne (**21a**) in $CDCl_3$ at 100.6 MHz.

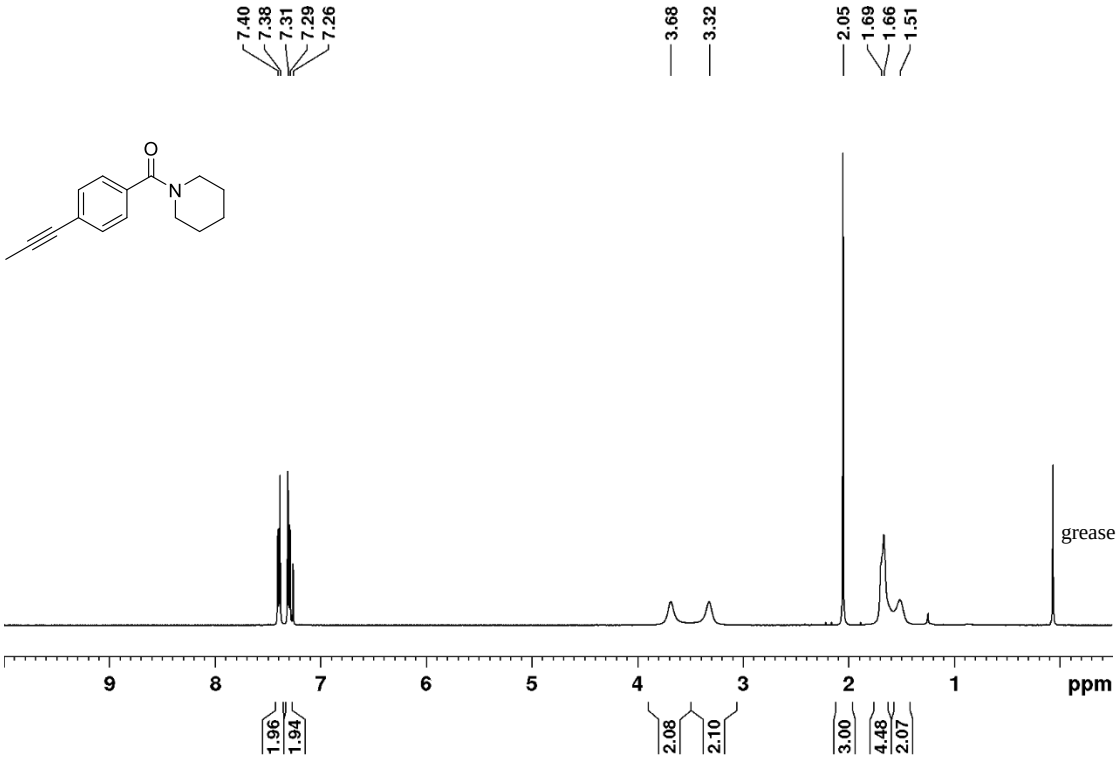

Figure S26. The ^{1}H NMR spectrum of piperidin-1-yl(4-(prop-1-yn-1-yl)phenyl)methanone (**25**) in $CDCl_3$ at 400.1 MHz.

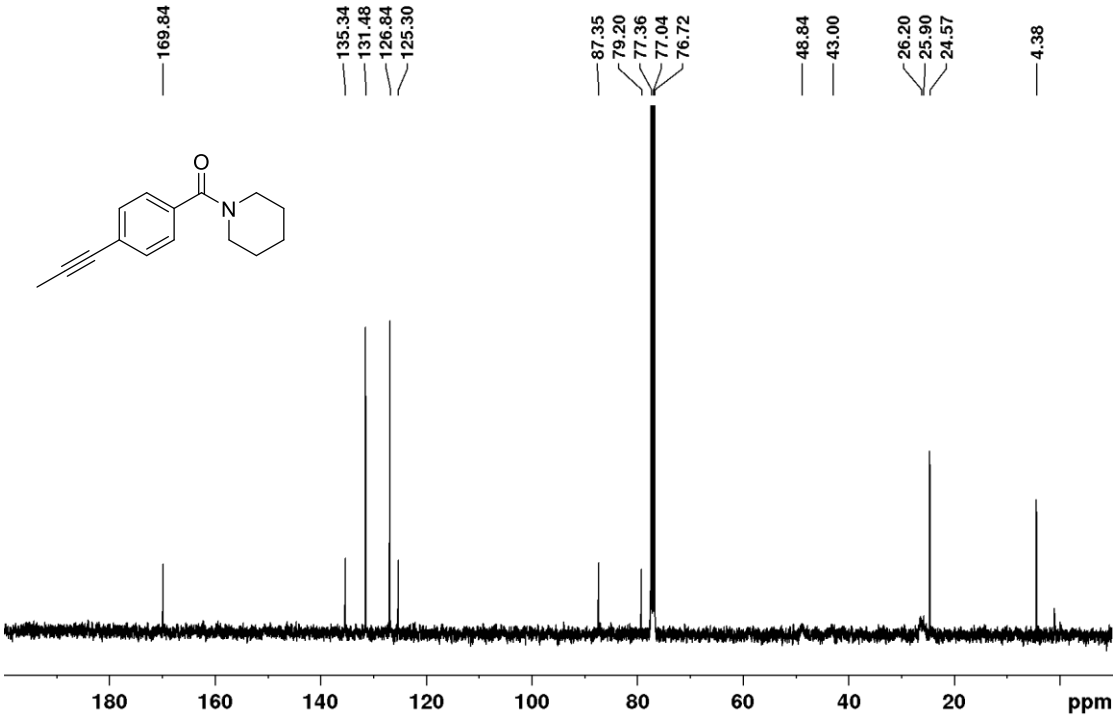

Figure S27. The $^{13}C\{^{1}H\}$ NMR spectrum of piperidin-1-yl(4-(prop-1-yn-1-yl)phenyl)methanone (**25**) in $CDCl_3$ at 100.6 MHz.

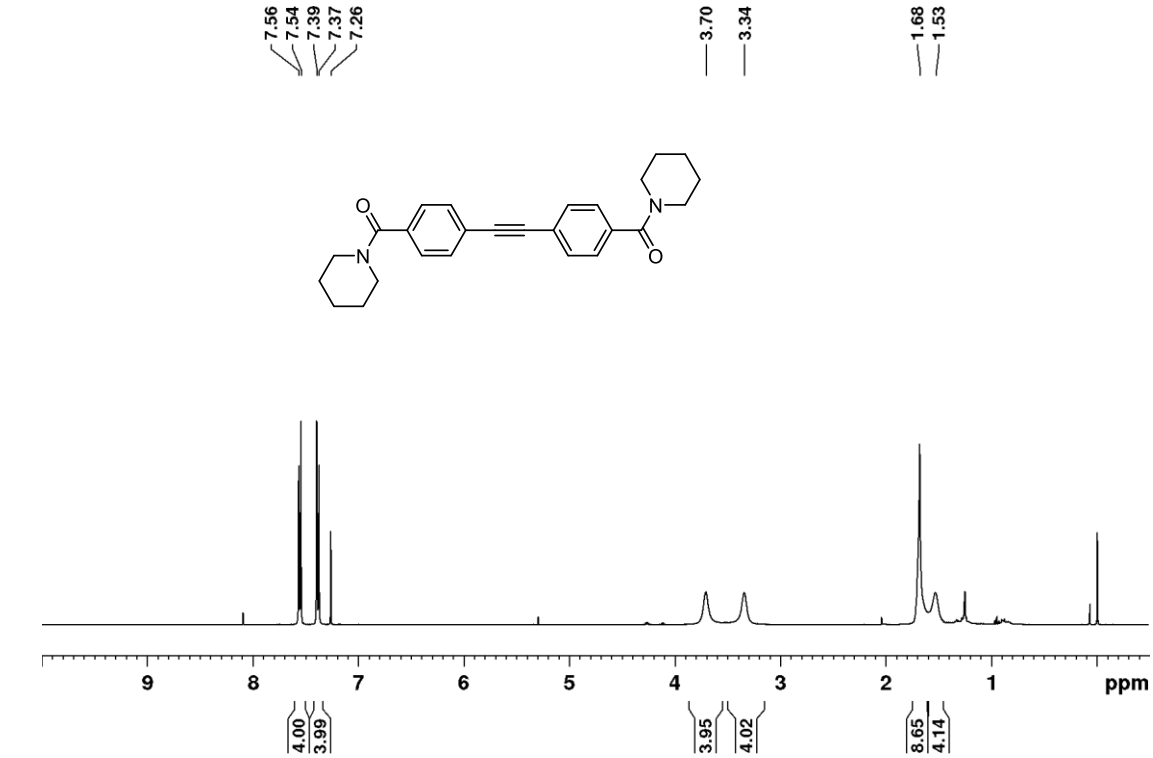

Figure S28. The ^{1}H NMR spectrum of (ethyne-1,2-diylbis(4,1-phenylene))bis(piperidin-1-ylmethanone) (**25a**) in $CDCl_3$ at 400.1 MHz.

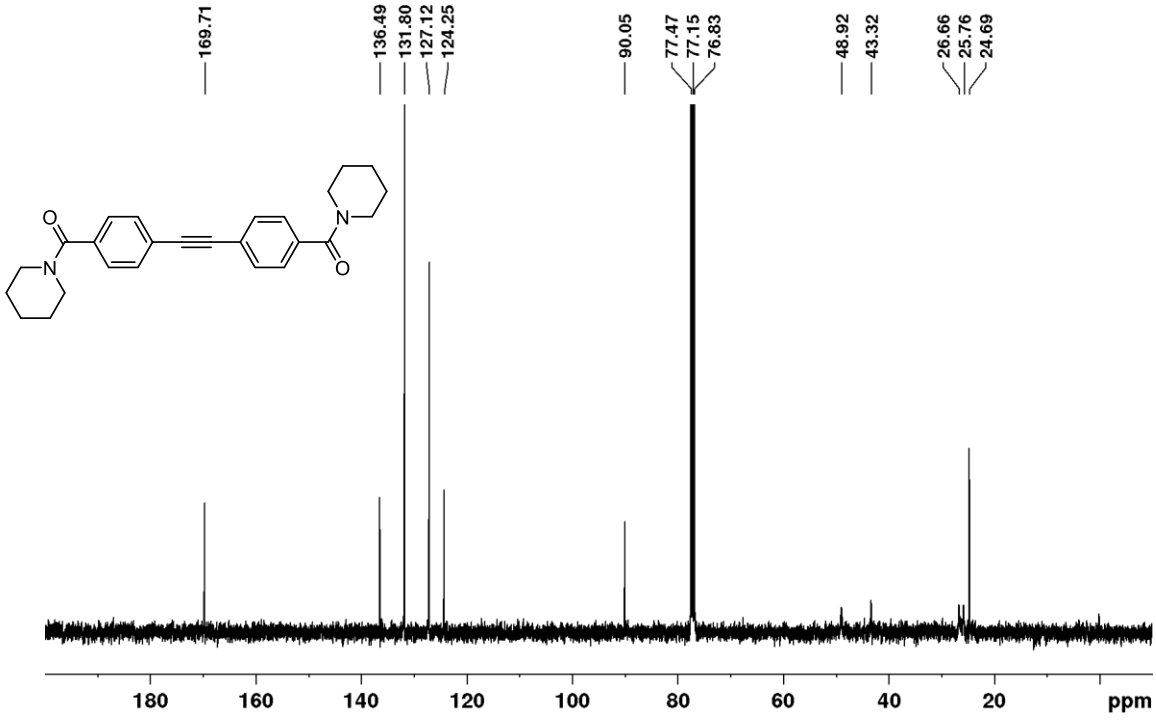

Figure S29. The $^{13}C\{^{1}H\}$ NMR spectrum of (ethyne-1,2-diylbis(4,1-phenylene))bis(piperidin-1-ylmethanone) (**25a**) in $CDCl_3$ at 100.6 MHz.

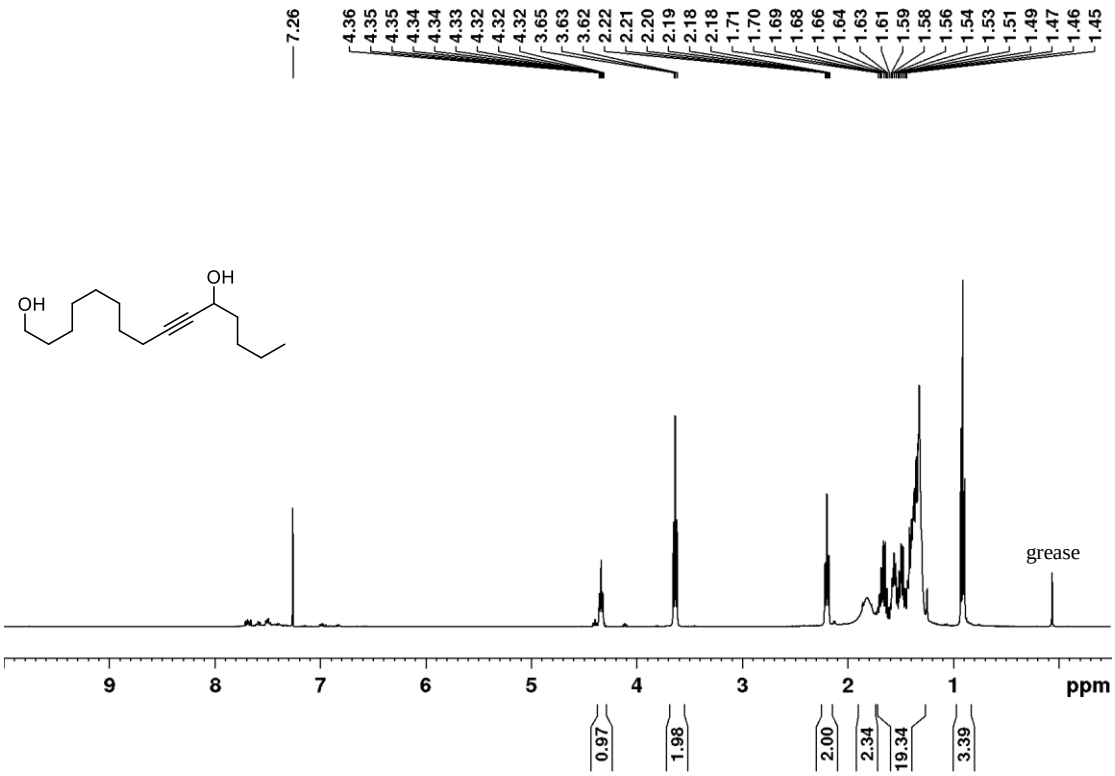

Figure S30. The ^{1}H NMR spectrum of pentadec-9-yne-1,11-diol (**36**) in $CDCl_3$ at 400.1 MHz.

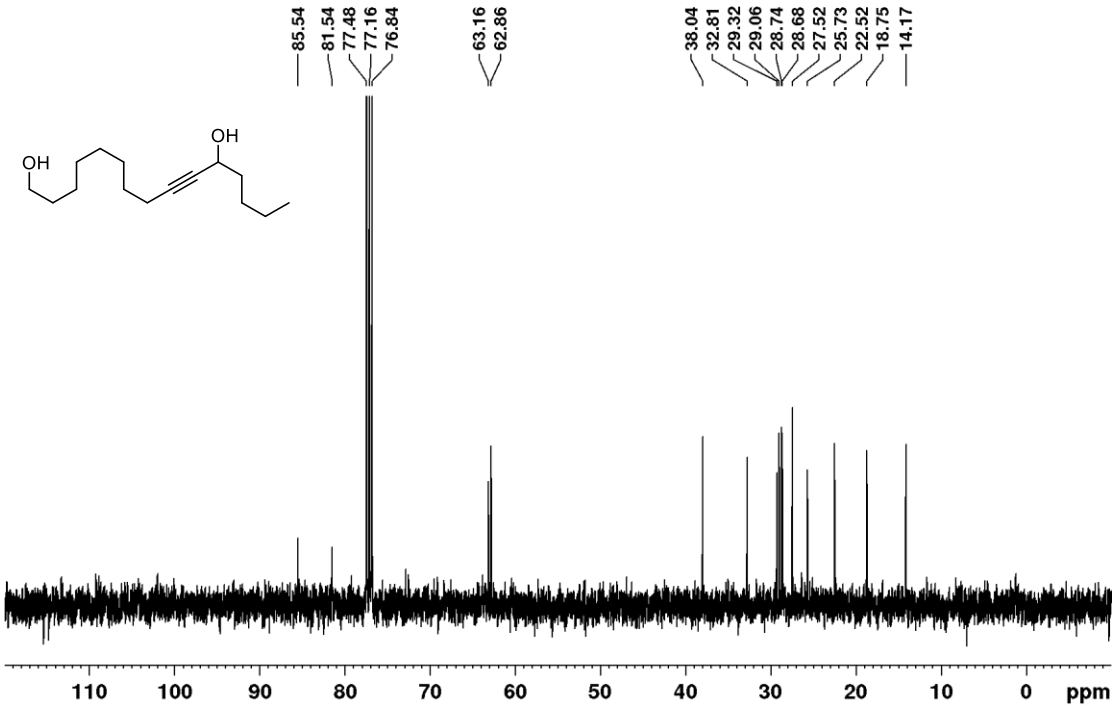

Figure S31. The $^{13}C\{^{1}H\}$ NMR spectrum of pentadec-9-yne-1,11-diol (**36**) in $CDCl_3$ at 100.6 MHz.

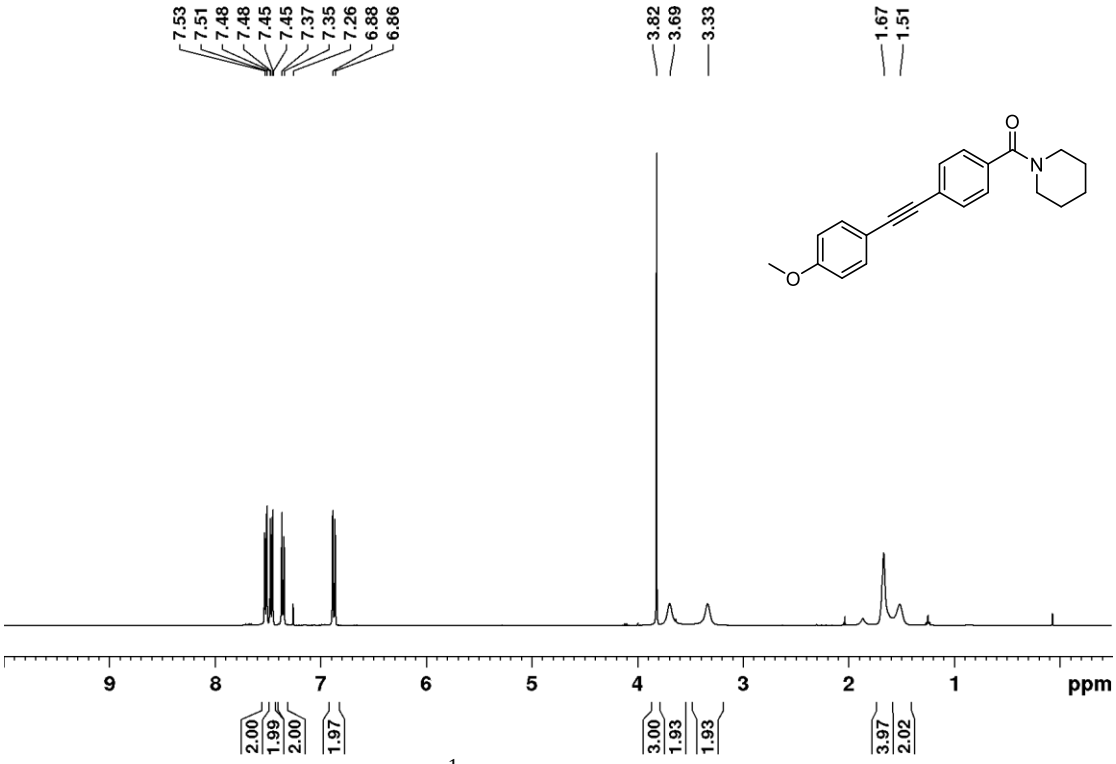

Figure S32. The ^{1}H NMR spectrum of (4-((4-methoxyphenyl)ethynyl)phenyl)(piperidin-1-yl)methanone (**37**) in $CDCl_3$ at 400.1 MHz.

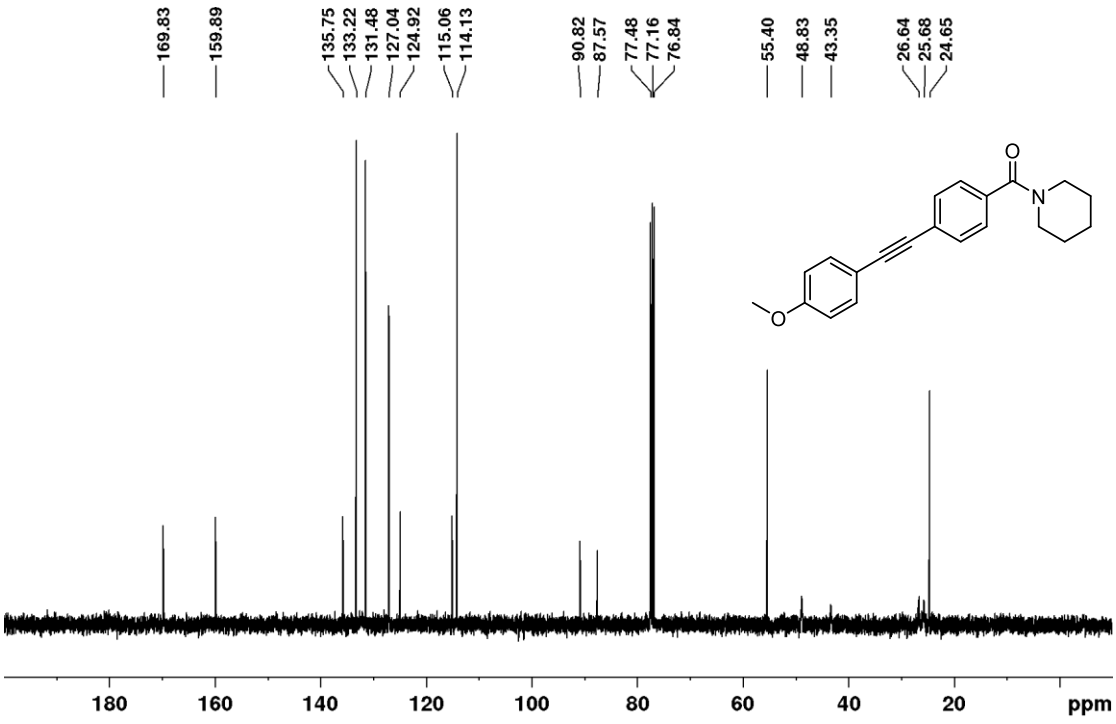

Figure S33. The $^{13}C\{^{1}H\}$ NMR spectrum of (4-((4-methoxyphenyl)ethynyl)phenyl)(piperidin-1-yl)methanone (**37**) in $CDCl_3$ at 100.6 MHz.

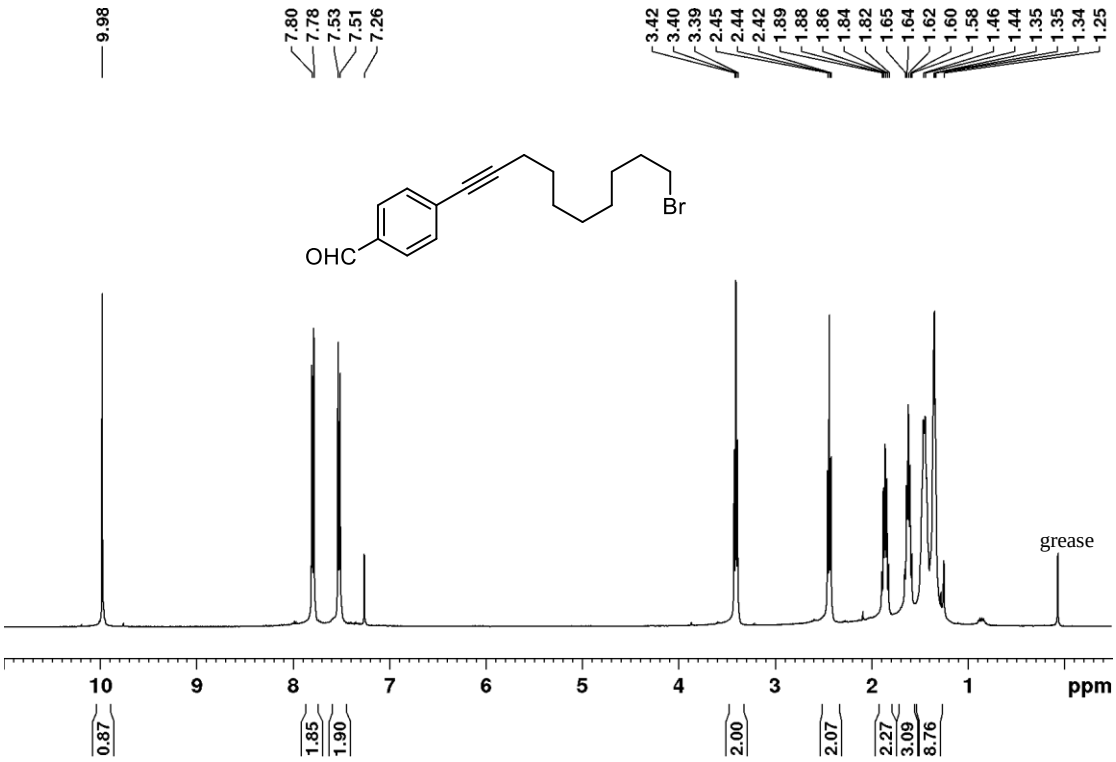

Figure S34. The ^{1}H NMR spectrum of 4-(10-bromodec-1-yn-1-yl)benzaldehyde (**38**) in $CDCl_3$ at 400.1 MHz.

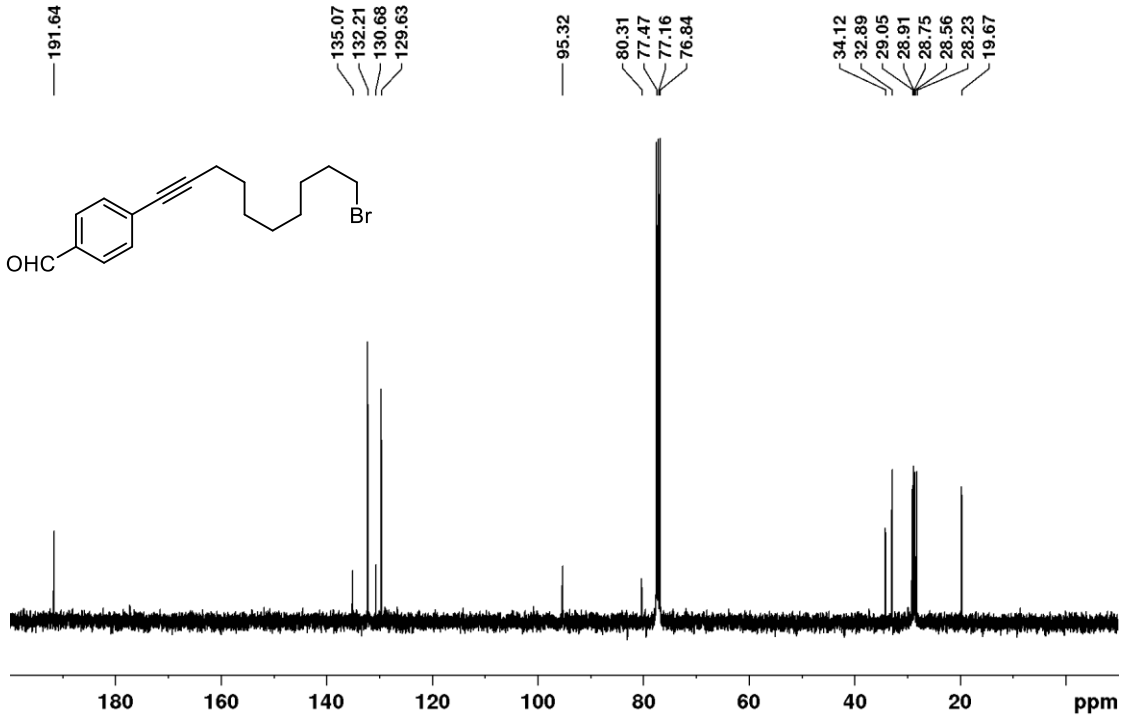

Figure S35. The $^{13}C\{^{1}H\}$ NMR spectrum of 4-(10-bromodec-1-yn-1-yl)benzaldehyde (**38**) in $CDCl_3$ at 100.6 MHz.

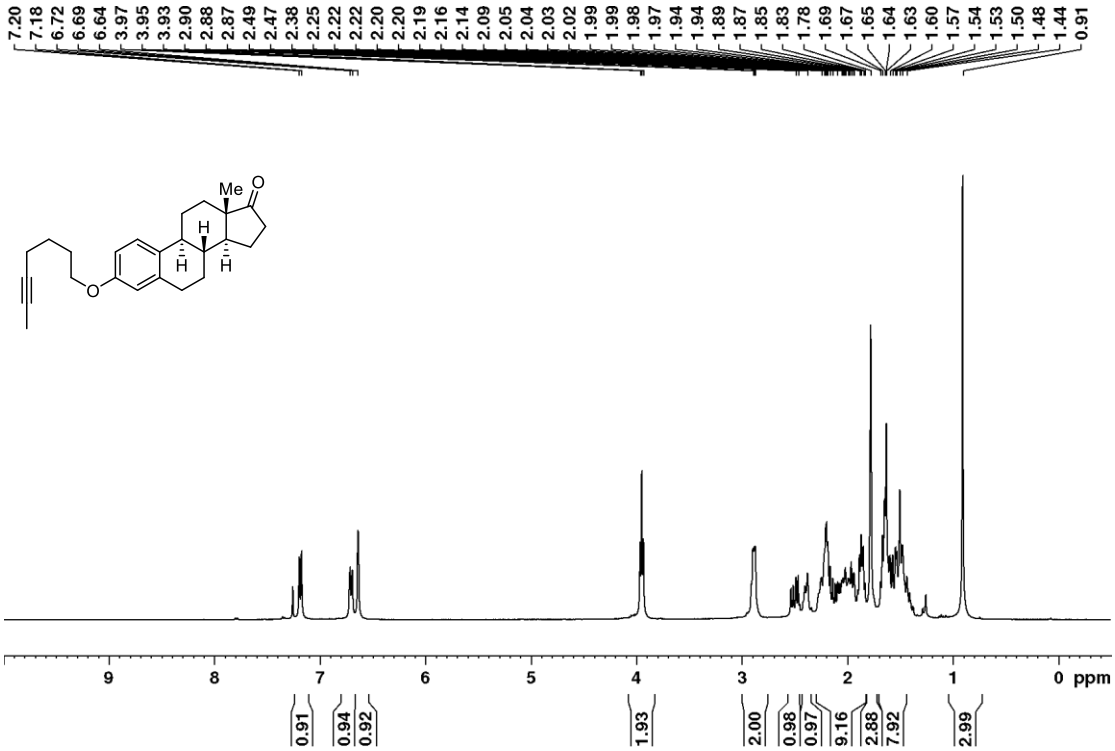

Figure S36. The ^{1}H NMR spectrum of estrone hept-5-ynyl ether (**39**) in $CDCl_3$ at 400.1 MHz.

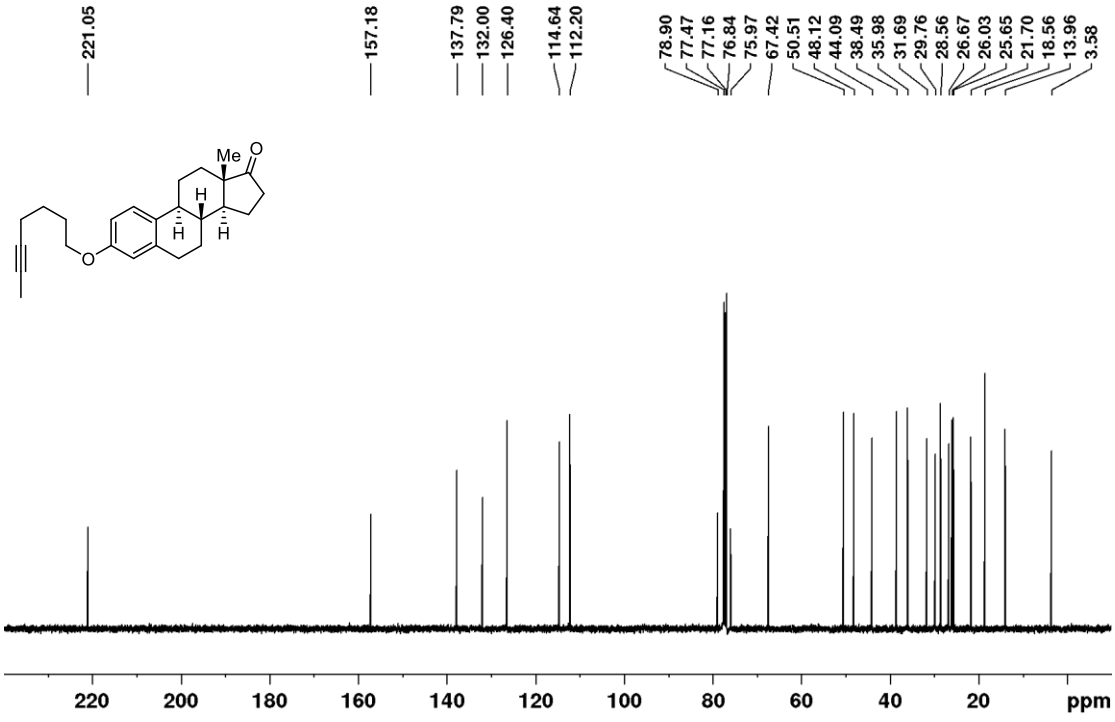

Figure S37. The $^{13}C\{^{1}H\}$ NMR spectrum of estrone hept-5-ynyl ether (**39**) in $CDCl_3$ at 100.6 MHz.

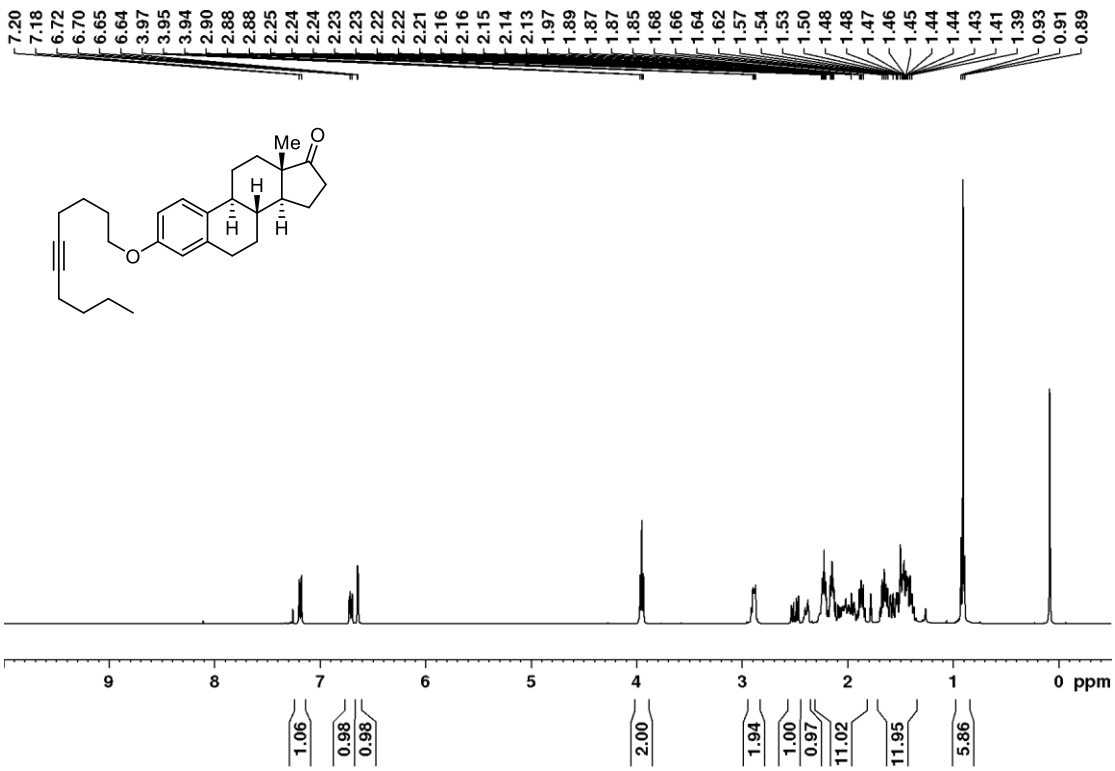

Figure S38. The ^{1}H NMR spectrum of estrone dec-5-ynyl ether (**40**) in $CDCl_3$ at 400.1 MHz.

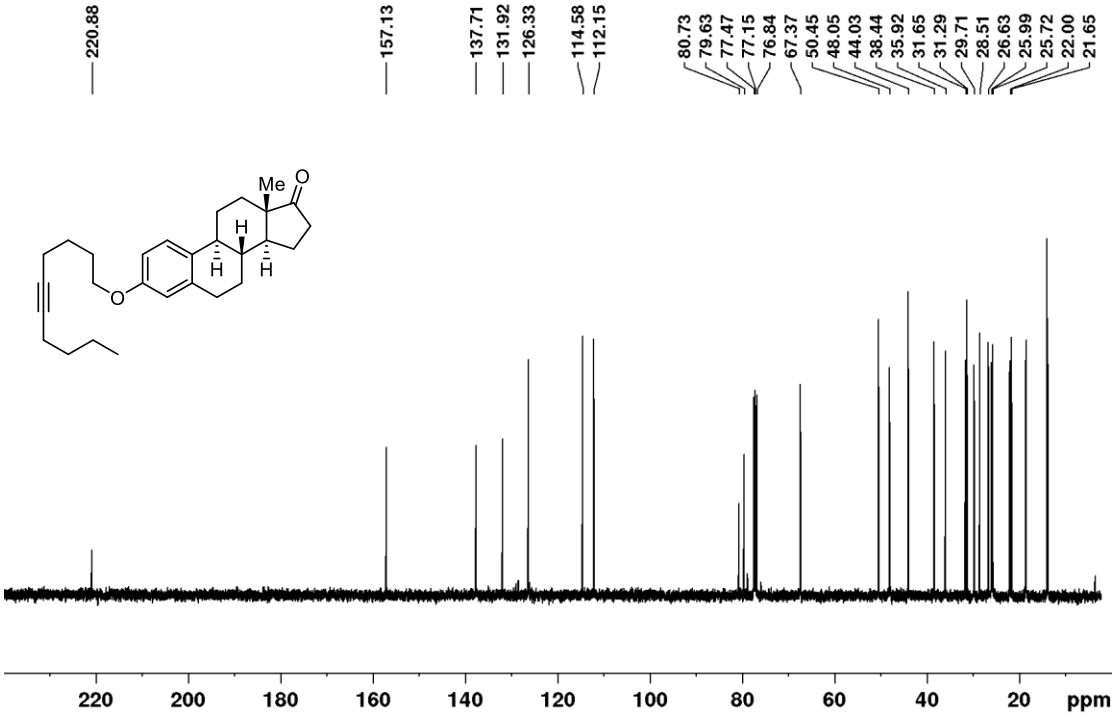

Figure S39. The $^{13}C\{^{1}H\}$ NMR spectrum of estrone dec-5-ynyl ether (**40**) in $CDCl_3$ at 100.6 MHz.

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