Metalla-phenalene complexes: synthesis, structure and aromaticity

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Supporting Information

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1. Experimental details

General information.

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were purged with a nitrogen flow before use. $ReCl_3(PMePh_2)_3$,[1] 8-bromo-1-naphthaldehyde [2] and 6-bromo-1,2-dihydroacenaphthylene-5-carbaldehyde [3] were prepared according to literature methods. Other reagents were used as purchased. Microanalyses were performed by Element Vario EL. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra were collected on a Bruker Avance II (400 MHz) or a Varian DLG spectrometer (400 MHz). ^1H and ^{13}C NMR shifts are relative to TMS, and ^{31}P chemical shifts relative to 85% H_3PO_4.

Synthesis of 8-ethynyl-1-naphthaldehyde

8-bromo-1-naphthaldehyde (0.85 g, 3.40 mmol), $PdCl_2(PPh_3)_2$ (0.12 g, 0.17 mmol, 0.05 eq.) and CuI (0.03 g, 0.17 mmol, 0.05 eq.) were added to a 100 mL dried flask. Then dry THF (15 mL), Et_3N (10 mL) and trimethylsilylacetylene (0.4 mL, 4.08 mmol, 1.2 eq.) were successively added under a nitrogen atmosphere. The mixture was stirred at 55 °C for 46 h. After cooling down to room temperature, the volatiles were removed under vacuum. The residue was extracted with DCM and washed with saturated NH_4Cl aqueous solution. The organic extractant was dried over anhydrous $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography with petroleum ether (PE)/DCM (4:1) as an eluent. Yield of 8-((trimethylsilyl)ethynyl)-1-naphthaldehyde: 0.55 g, 64.1%. ^1H NMR (400.1 MHz, $CDCl_3$): δ = 11.63 (s, 1H), 8.03–7.98 (m, 2H), 7.91–7.89 (m, 1H), 7.87–7.85 (m, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.50–7.47 (m, 1H), 0.30 (s, 9H). $^{13}C\{^1H\}$ NMR (100.1 MHz, $CDCl_3$): δ = 193.5, 135.8, 135.0, 134.4, 134.2, 131.4, 130.4, 129.2, 126.0 (2C), 118.6, 106.6, 101.5, 100.1, -0.3. To a solution of 8-((trimethylsilyl)ethynyl)-1-naphthaldehyde (0.19 g, 0.75 mmol) in THF (4 mL) and MeOH (4 mL) at room temperature, K_2CO_3 (0.12 g, 0.9 mmol) was added and the mixture was stirred for 20 minutes. The reaction mixture was extracted with DCM and washed with saturated NH_4Cl solution. The organic extractant was dried over anhydrous $MgSO_4$ and filtered

through a pad of silica gel. After removal of the solvent, a yellow solid was obtained. Yield of 8-ethynyl-1-naphthaldehyde: 0.12 g, 88.9 %. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 11.66 (s, 1H), 8.07–8.03 (m, 2H), 7.97–7.95 (m, 1H), 7.92–7.91 (m, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.54–7.50 (m, 1H), 3.54 (s, 1H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 193.5, 135.9, 135.3, 134.7, 134.2, 131.4, 130.8, 129.4, 126.1, 126.0, 117.5, 85.2, 83.9. HRMS (EI, m/z): $[M]^+$ Calcd For $C_{13}H_8O$: 180.0575; Found: 180.0572.

Synthesis of 6-ethynyl-1,2-dihydroacenaphthylene-5-carbaldehyde

6-bromo-1,2-dihydroacenaphthylene-5-carbaldehyde (0.55 g, 2.10 mmol), $PdCl_2(PPh_3)_2$ (0.074 g, 0.11 mmol, 0.05 eq.) and CuI (0.02 g, 0.11 mmol, 0.05 eq.) were added to a 100 mL dried flask. Then dry THF (15 mL), Et_3N (10 mL) and trimethylsilylacetylene (0.33 mL, 2.52 mmol, 1.2 eq.) were successively added under a nitrogen atmosphere. The mixture was stirred at 55 °C for 47 h. After cooling down to room temperature, the volatiles were removed under vacuum. The residue was extracted with DCM and washed with saturated NH_4Cl aqueous solution. The organic extractant was dried over anhydrous $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography with petroleum ether (PE)/ethyl acetate (EA) (30:1) as an eluent and a yellow slid was obtained. Yield of 6-trimethylsilanylethynyl-1,2-dihydroacenaphthylene-5-carbaldehyde: 0.314 g, 53.7%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 11.82 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 4.0 Hz, 1H), 7.39 (d, *J* = 4.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 3.42 (s, 4H), 0.31 (s, 9H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 192.7, 154.4, 148.8, 139.9, 137.5, 131.3, 131.1, 130.2, 120.1, 120.1 114.0, 107.2, 99.4, 30.9, 30.7, -0.1. To a solution of 6-trimethylsilanylethynyl-acenaphthene-5-carbaldehyde (0.304 g, 1.09 mmol) in THF (4 mL) and MeOH (4 mL) at room temperature, K_2CO_3 (0.302 g, 2.18 mmol) was added and the mixture was stirred for 30 minutes. The reaction mixture was extracted with DCM and washed with saturated NH_4Cl solution. The organic extractant was dried over anhydrous $MgSO_4$ and filtered through a pad of silica gel. After removal of the solvent, a yellow solid was obtained. Yield of 6-ethynyl-1,2-dihydroacenaphthylene-5-carbaldehyde: 0.181 g, 80.6%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 11.80 (s, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 4.0 Hz, 1H), 3.46 (s, 1H), 3.42 (s, 4H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 192.5, 154.7, 149.2,

139.9, 138.1, 131.5, 130.8, 130.2, 120.2, 120.2, 112.7, 85.6, 82.1, 30.9, 30.7. HRMS (ESI, m/z): $[M]^+$ Calcd For $C_{15}H_{10}O$: 206.0732; Found: 206.0726.

Synthesis of 1-(8-ethynylnaphthalen-1-yl)ethan-1-one

A solution of CH_3MgBr (3 M in 2-methyl THF, 2.62 mmol, 0.82 mL) was added dropwisely to the solution of 8-((trimethylsilyl)ethynyl)-1-naphthaldehyde (0.55 g, 2.18 mmol) in dry THF (15 mL) at 0 °C under a nitrogen atmosphere. The reaction mixture was stirred at room temperature and monitored by TLC. After the completion of the reaction, the mixture was quenched with water and extracted with diethyl ether. The organic extractant was dried over anhydrous $MgSO_4$, filtered and volatiles were removed under reduced pressure. The resulting alcohol (1-(8-((trimethylsilyl)ethynyl)naphthalen-1-yl)ethan-1-ol) was used for the next step without further purification. Pyridinium chlorochromate (PCC, 0.94 g, 4.36 mmol, 2 eq.) was added to the solution of alcohol in DCM (15 mL) at room temperature. After 1 h, celite (0.94 g) was added and the mixture was stirred for additional 2 h. Then the resulting suspension was filtered through a pad of silica gel, and dried under reduced pressure, giving a yellow oil. Yield of 1-(8-((trimethylsilyl)ethynyl)naphthalen-1-yl)ethan-1-one: 0.54 g, 93.0 %. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 4.0 Hz, 1H), 7.47 (q, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 2.67 (s, 3H), 0.31 (s, 9H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 205.2, 141.6, 134.4, 133.9, 130.8, 130.0, 128.7, 126.0, 125.8, 125.7, 119.4, 104.3, 102.8, 33.9, -0.2. HRMS (ESI, m/z): $[M+H]^+$: Calcd For $C_{17}H_{18}OSi$: 267.1200; Found: 267.1205. $[M+Na]^+$ Calcd For $C_{17}H_{18}OSi$: 289.1025; Found: 289.1026. To a solution of 1-(8-((trimethylsilyl)ethynyl)naphthalen-1-yl)ethan-1-one (0.54 g, 2.03 mmol) in THF (4 mL) and MeOH (4 mL) at room temperature, K_2CO_3 (0.34 g, 2.46 mmol) was added. The mixture was stirred for 1 h. Then it was extracted with DCM, and washed with saturated NH_4Cl aqueous solution. The organic extractant was dried over anhydrous $MgSO_4$, filtered through a pad of silica gel and concentrated under reduced pressure to give a yellow oil. Yield of 1-(8-ethynylnaphthalen-1-yl)ethan-1-one: 0.32 g, 81.2 %. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.91–7.89 (m, 2H), 7.83–7.81 (m, 1H), 7.52–7.46 (m, 2H), 7.42–7.40 (m, 1H), 3.50 (s, 1H), 2.70 (s, 3H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 205.9, 141.4, 134.7, 134.0, 130.8, 130.4, 128.7,

126.0, 125.7, 125.6, 118.2, 85.4, 83.2, 33.8. HRMS (ESI, m/z): $[M+H]^+$ Calcd For $C_{14}H_{10}O$: 195.0804; Found: 195.0811. $[M+Na]^+$ Calcd For $C_{14}H_{10}O$: 217.0624; Found: 217.0632.

Synthesis of complex 1

A mixture of $ReCl_3(PMePh_2)_3$ (0.200 g, 0.224 mmol) and 8-ethynyl-1-naphthaldehyde (0.045 g 0.246 mmol) in toluene (15 mL) was stirred at room temperature for 24 h, producing a red solid. The solid was filtered and washed with THF (8 mL) and ether (8 mL). Then it was dried under vacuum. Yield: 0.127 g, 64.9 %. $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): δ = 26.2 (d, *J* = 19.4 Hz, CH(*P*$MePh_2$)), -3.7 (d, *J* = 19.4 Hz, Re*P*$MePh_2$). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 8.30 (dd, *J* = 8.0 Hz, *J* =12.0 Hz, 2H, Ar), 7.63–7.54 (m, 6H, Ar), 7.43–7.35 (m, 2H, Ar), 7.23–7.15 (m, 4H, Ar), 7.12–7.08 (m, 3H, Ar), 7.00–6.96 (m, 3H, Ar) 6.76–6.69 (m, 5H, Ar), 6.17 (d, *J* = 8.0 Hz, 1H, C*H*O), 5.72 (d, ^2J(PH) = 8.0 Hz, 1H, Ar), 5.13 (dd, ^4J(PH) = 8.0 Hz, ^4J(PH) = 12.0 Hz, 1H, C*H*($PMePh_2$)), 2.45 (d, ^2J(PH) = 8.0 Hz, 3H, P*Me*Ph_2), 2.20 (d, ^2J(PH) = 12.0 Hz, 3H, P*Me*Ph_2). $^{13}C\{^1H\}$, ^1H-^{13}C HSQC and ^1H-^{13}C HMBC NMR (100.6 MHz, $CDCl_3$): δ = 234.1–233.9 (m, Re=C), 101.9 (d, ^2J(PC) = 6.0 Hz, *C*-O), 23.2 (d, ^1J(PC) = 62.4 Hz, *C*H($PMePh_2$)). Anal. Calcd. For $C_{39}H_{34}Cl_3OP_2Re \cdot 0.1C_7H_8$: C, 54.04; H, 3.98. Found: C, 54.18; H, 4.13.

Synthesis of complex 2

A mixture of $ReCl_3(PMePh_2)_3$ (0.200 g, 0.224 mmol) and 6-ethynyl-1,2-dihydroacenaphthylene-5-carbaldehyde (0.050 g 0.242 mmol) in toluene (10 mL) was stirred at room temperature for 20 h, producing a red mixture. The mixture was reduced to ca. 2 mL, and ether (8 mL) was added to give a red solid, which was washed with THF (5 mL × 2) and ether (8 mL). Then it was dried under vacuum. Yield: 0.123 g, 61.8 %. $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$): δ = 26.2 (d, *J* = 19.4 Hz, CH(*P*$MePh_2$)), -6.1 (d, *J* = 19.4 Hz, Re*P*$MePh_2$). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 8.31-8.19 (m, 2H, Ar), 7.66–7.51 (m, 4H, Ar), 7.46–7.38 (m, 2H, Ar), 7.26–7.16 (m, 3H, Ar), 7.13–7.06 (m, 2H, Ar), 7.06–6.94 (m, 5H, Ar), 6.83–6.72 (m, 4H, Ar), 6.53 (d, *J* = 4.0 Hz, 1H, Ar), 6.22 (d, *J* = 8.0 Hz, 1H, C*H*O), 5.61 (d, *J* = 8.0 Hz, 1H, Ar), 5.09 (dd, ^4J(PH) = 4.0 Hz, ^4J(PH) = 16.0 Hz, 1H, C*H*($PMePh_2$)), 3.36 (s, 4H, CH_2), 2.46

(d, ^{2}J(PH) = 8.0 Hz, 3H, P*Me*Ph_2), 2.23 (d, ^{2}J(PH) = 16.0 Hz, 3H, P*Me*Ph_2). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$): δ = 233.4–233.2 (m, Re=C), 151.1–118.5 (multiple ^{13}C signals of Ar), 103.1 (s, *C*-O), 31.4(s, -*C*H_2), 30.5(s, -*C*H_2), 23.9 (d, ^{1}J(PC) = 60.4 Hz, *C*H(P$MePh_2$)), 17.6 (d, ^{1}J(PC) = 40.2 Hz, P*Me*Ph_2), 8.7 (d, ^{1}J(PC) = 44.3 Hz, P*Me*Ph_2). Anal. Calcd. For $C_{41}H_{36}Cl_3OP_2Re \cdot H_2O$: C, 53.69; H, 4.18. Found: C, 54.16; H, 4.51.

Synthesis of acenaphthylene compound 1a

A mixture of $ReCl_3(PMePh_2)_3$ (0.200 g, 0.224 mmol) and 8-ethynyl-1-naphthaldehyde (0.055 g, 0.269 mmol) in THF (10 mL) was heated at 60 °C for 5 h, producing a yellowish brown solution. The solvent was removed under vacuum. The residue was extracted with methanol (2 mL × 2) and $NaBPh_4$ (0.154 g, 0.45 mmol) in methanol (1 mL) was added into the filtrate, producing a yellow solid. The solid was filtered and washed with methanol (5 mL × 2) and ether (5 mL). Then it was dried under vacuum. Yield: 0.080 g, 52.2 %. $^{31}P\{^{1}H\}$ NMR (162.0 MHz, Acetone-d_6): δ = 21.3 (s). ^{1}H NMR (400.1 MHz, Acetone-d_6): δ = 8.02–7.97 (m, 4H, Ar), 7.93–7.90 (m, 2H, Ar), 7.87–7.84 (m, 2H, Ar), 7.72–7.68 (m, 5H, Ar), 7.62–7.58 (m, 2H, Ar), 7.48 (t, *J* = 8.0 Hz, 1H, Ar), 7.37–7.32 (m, 8H, Ar), 6.94 (d, *J* = 8.0 Hz, 1H, =CH), 6.91 (t, *J* = 8.0 Hz, 8H, Ar), 6.76 (t, *J* = 8.0 Hz, 4H, Ar), 4.85 (d, ^{2}J(PH) = 16.0 Hz, 2H, CH_2P$MePh_2$), 2.70 (d, ^{2}J(PH) = 12.0 Hz, 3H, P*Me*Ph_2). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, Acetone-d_6): δ = 165.5–116.0 (multiple ^{13}C signals of Ar and C=C), 24.1 (d, ^{1}J(PC) = 40.2 Hz, *C*H_2P$MePh_2$), 6.5 (d, ^{1}J(PC) = 46.3 Hz, P*Me*Ph_2). HRMS (ESI, m/z): M^+ Calcd For $C_{26}H_{22}P^+$: 365.1454; Found: 365.1465. M^- Calcd For $C_{24}H_{20}B^-$, 319.1664; Found: 319.1653.

Synthesis of acenaphthylene compound 3a

A mixture of $ReCl_3(PMePh_2)_3$ (0.200 g, 0.224 mmol) and 1-(8-ethynylnaphthalen-1-yl)ethan-1-one (0.057 g, 0.336 mmol) in THF (10 mL) was heated at 60 °C for 4 h, producing a yellowish brown solution. The solvent was removed under vacuum. The residue was extracted with methanol (2 mL × 2) and $NaBPh_4$ (0.115 g, 0.336 mmol) in methanol (1 mL) was added into the filtrate, producing a yellow solid. The solid was filtered and washed with methanol (5 mL × 2) and hexanes (5 mL). Then it was dried under vacuum. Yield: 0.060 g, 38.4%. $^{31}P\{^{1}H\}$

NMR (162.0 MHz, Acetone-d_6): δ = 21.0 (s). ^{1}H NMR (400.1 MHz, Acetone-d_6): δ = 8.00–7.86 (m, 7H, Ar), 7.81 (d, *J* = 8.0 Hz, 1H, Ar), 7.73–7.68 (m, 5H, Ar), 7.65–7.61 (m, 1H, Ar), 7.45–7.39 (m, 2H, Ar), 7.36–7.31 (m, 8H, Ar), 6.90 (t, *J* = 8.0 Hz, 8H), 6.76 (t, *J* = 8.0 Hz, 4H, Ar), 4.76 (d, ^2J(PH) = 16.0 Hz, 2H, CH_2PMePh$_2$), 2.70 (d, ^2J(PH) = 16.0 Hz, 3H, P*Me*Ph$_2$), 1.97 (d, ^2J(PH) = 4.0 Hz, 3H, Me). ^{13}C{^{1}H} NMR (100.6 MHz, Acetone-d_6): δ = 165.7–120.9 (multiple ^{13}C signals of Ar and C=C), 23.0 (d, ^1J(PC) = 40.2 Hz, *C*H$_2$PMePh$_2$), 11.0 (d, ^4J(PC) = 3.0 Hz, Me), 7.0 (d, ^1J(PC) = 45.3 Hz, P*Me*Ph$_2$). HRMS (ESI, m/z): M^+ Calcd For $C_{27}H_{24}P^+$: 379.1610; Found: 379.1610. M^- Calcd For $C_{24}H_{20}B^-$: 319.1664; Found: 319.1650.

2. Computational details

All the optimizations were performed with the Gaussian 09 software package.[4] The structures evaluated were optimized at the B3LYP level of density functional theory (DFT).[5] DFT/GENECP level had been done by implementing def2-TZVP basis set for Re atom[6] and 6-311G(2d,p) basis set for the rest of atoms.[7] Nucleus-independent chemical shift (NICS) values were calculated at the B3LYP-GIAO//6-311G(2d,p)/def2-TZVP level, whereas we performed the CMO-NICS calculations in simplified models with the NBO 7.0 program.[8] The anisotropy of the current density was calculated with the AICD 2.0 program computing the NMR properties using the CSGT method with the Gaussian09 Rev D.01 program with the geometries previously obtained for **M1**.[9] GIMIC analysis was finished by GIMIC code[10] based on the formatted check point file of Gaussian and rendered by ParaView visualization program.[11] Using RunEDDB script,[12] electron density of delocalized bond (EDDB)[13] based on natural atomic orbitals (NAOs) is analysed. The molecular orbital composition and MO pictures were analyzed using Multiwfn, a multifunctional wavefunction analyzer.[14] Bond order analysis (Wiberg bond order, Mayer bond order and Delocalization index) and orbital localization analysis is also calculated by Multiwfn program. The MO pictures were drawn using the software of VMD.[15] VMD was developed by the Theoretical and Computational Biophysics Group in the Beckman Institute for Advanced Science and Technology at the University of Illinois at Urbana-Champaign (http://www.ks.uiuc.edu/Research/vmd/).

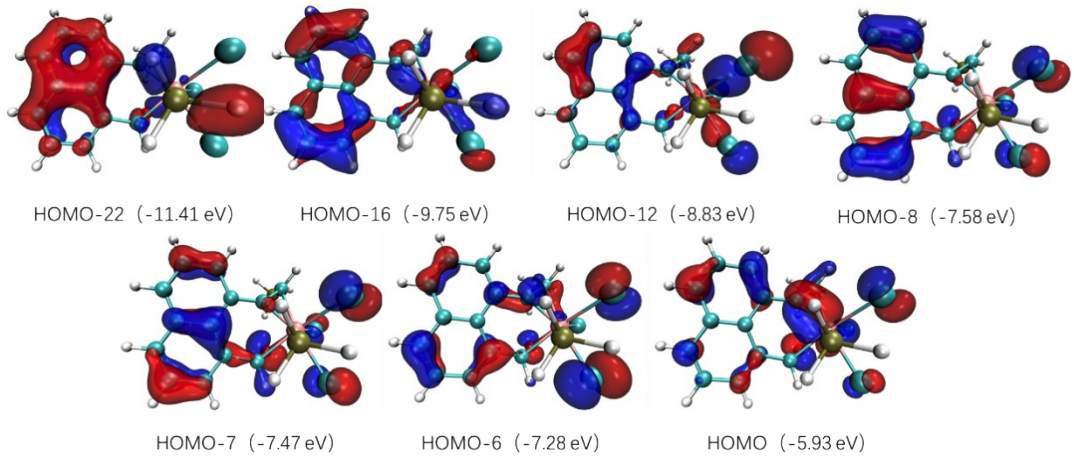


Figure S1. Key occupied π-MOs of **M1**. The isosurface of MOs is 0.04.

Table S1. Full Cartesian NMR shielding tensor (ppm) for NICS values of π-Canonical MO contributions in **M1** ($NICS(1)_{ZZ}$ and $NICS(-1)_{ZZ}$ are the $NICS(1)_{ZZ}$ values of the upper and lower directions of the rings, respectively. Orbital 98 is HOMO).

MO	NICS (0) for **3MR-1**	NICS (0) for **3MR-2**	NICS(0) for **6MR**	NICS(-1)zz for **3MR-1**	NICS(1)zz for **3MR-1**	NICS(-1)zz for **3MR-2**	NICS(1)zz for **3MR-2**	NICS(-1)zz for **6MR**	NICS(1)zz for **6MR**
76	1.15	1.72	3.91	2.49	2.01	1.09	1.44	7.56	7.91
82	-1.83	0.87	1.06	0.8	0.88	0.47	-0.47	2.85	3.61
86	-1.88	0.8	-3.18	-1.96	-0.91	0.78	0.1	-3.31	-4.27
90	-1.6	-2.41	-3	-3.38	-3.61	-2.18	-1.8	-3.28	-4.48
91	-2.1	-4.96	-2.99	-4.08	-1.45	-3.52	-2.84	-6.79	-5.11
92	-0.91	-0.1	-4.6	-1.24	-3.65	0.46	-0.85	-8.99	-12.47
98	4.97	-6.53	-2.59	-2.64	1.16	-0.98	-4.83	-5.13	-3.56
sum	-2.2	-10.61	-11.39	-10.01	-5.57	-3.88	-9.25	-17.09	-18.37

The signs of the NICS values are reversed from those of the shielding data in the output. Thus, the NICS value is the negative of the sum of the shielding contributions. Thus, NICS(0)-π value of **3MR-1** is +2.2 ppm; NICS(0)-π value of **3MR-2** is +10.61 ppm; NICS(0)-π value of **6MR** is +11.39 ppm; $NICS(1)_{ZZ}$-π value of **3MR-1** is the mean value of $NICS(1)_{ZZ}$-π and $NICS(-1)_{ZZ}$-π: -(-10.01 -5.57) / 2 = +7.79 ppm; $NICS(1)_{ZZ}$-π value of **3MR-2** is +6.57 ppm; $NICS(1)_{ZZ}$-π value of **6MR** is +17.73 ppm.

Table S2. Full Cartesian NMR shielding tensor (ppm) for NICS values of σ-Canonical MO contributions in **M1** ($NICS(1)_{ZZ}$ and $NICS(-1)_{ZZ}$ are the $NICS(1)_{ZZ}$ values of the upper and lower directions of the rings, respectively).

MO	NICS (0) for **3MR-1**	NICS (0) for **3MR-2**	NICS(0) for **6MR**	NICS(-1)zz for **3MR-1**	NICS(1)zz for **3MR-1**	NICS(-1)zz for **3MR-2**	NICS(1)zz for **3MR-2**	NICS(-1)zz for **6MR**	NICS(1)zz for **6MR**
44	1.36	12.8	1.64	2.4	0.82	7.27	7.72	2.54	1.36
45	1.66	1.33	2.69	3.49	2.48	0.37	1.09	7.73	8.51
46	2.46	1.26	1.89	3.59	2.59	0.37	0.91	4.85	5.09
47	5.9	1.27	1.88	6.15	3.68	0.72	1.54	4.33	4.2
48	3.02	1.52	2.03	3.78	2.54	0.71	1.62	4.79	5.74
49	0.83	0.88	1.45	1.71	1.44	0.27	0.63	3.9	4.3
50	1.46	1.57	0.79	2.49	1.79	0.6	0.85	1.63	1.66
53	1.4	0.51	1.65	1.17	0.97	0.13	0.4	2.09	1.78
54	5.63	1.08	0.68	3.16	3.33	0.66	2.2	0.7	0.58
55	2.15	2.48	1.45	1.21	2.19	3.16	2.93	0.52	1.33
56	0.83	2.36	1.19	1.43	1.24	1.04	1	2.32	3.09
57	2.83	1.13	1.48	1.98	2.04	0.63	1.68	2.86	3.08
58	1.03	1.09	1.37	2.03	1.59	0.36	1.03	4.2	4.39
59	2.66	3.11	1.82	2.7	2.26	1.87	1.47	3.42	4.01
60	2.66	1.23	0.54	1.05	0.4	0.64	1.13	0.43	0.31

61	0.16	-0.03	-0.38	0.25	0.35	-0.32	-0.37	-0.71	-0.62
62	2.47	2.69	1.04	0.86	-0.39	1.83	0.68	2.16	2.29
63	0.98	1.29	1.56	1.45	0.82	0.26	1.07	4.24	4.54
64	2.84	1.04	1.1	3.25	2.43	0.82	1.38	1.49	1.41
65	4.74	3.49	0.7	0.88	1.96	1.83	2.3	1.84	1.77
66	1.96	1.63	0.5	1.44	1.2	0.77	0.85	0.32	0.04
67	-0.42	0.54	-0.51	-1.29	-1.19	-0.26	0.01	-1.84	-1.78
68	1.67	3.58	1.59	-0.2	-0.23	3.14	5.42	2.04	1.71
69	0.74	0.58	-0.53	1.78	2.96	0.49	-1.67	0.22	0.27
70	-1.73	0.15	-3.02	-3.27	-2.2	-1.29	-2.33	-6.78	-7.31
71	-0.39	2.59	-0.57	-1.35	-0.12	3.12	-0.13	-1.13	-0.11
72	0.1	2.33	-0.47	-1.18	-1.49	1.16	1.85	-0.2	0.46
73	0.76	2.06	0.37	0.18	1.01	2.19	1.61	-0.23	0.28
74	-0.41	0.28	-2.37	-0.54	-0.41	-1.38	-0.34	-5.62	-5.6
75	-0.38	1.03	-0.62	-1.19	-1.09	0.26	0.46	-2.26	-2.31
77	-1.59	-1.38	-2.82	-4	-3.69	-0.42	-1.07	-7.69	-8.16
78	-0.94	2.38	1.27	2.48	3.35	1.66	1.18	0.82	-1.29
79	-0.34	0.83	-1.73	-2.29	-1.21	0.27	-0.52	-5.39	-5.57
80	-2.95	-2.57	-2.61	-2.86	-4.16	-0.19	-1.72	-7.11	-7.78
81	-1.68	-1.02	-1.85	-0.18	-2.52	-0.22	-1.75	-5.78	-6.61
83	1.75	-0.59	-0.38	1.78	4.41	1.73	-0.86	0.17	-0.45
84	-1.67	1.7	1.94	-0.92	-0.23	1.84	2.28	3.84	2.75
85	2.15	1.55	-0.41	2.34	2.54	2.35	-0.26	-0.8	0.29
87	-1.95	1.55	0.59	-4.2	-3.28	-1.34	-1.49	1.22	1.97
88	2.74	-3.52	-0.28	2.19	3.3	-3.06	-3.28	-1.04	-1.31
89	-3.26	-3.08	-1.97	-3.43	-5.56	-3.84	-1.11	-2.22	-1.81
94	-2.25	-1.48	-1.83	-3.1	-0.5	-3.22	-1.37	-3.03	-2.71
95	-2.13	-1.18	-1.36	0.46	-0.35	-1.76	-1.23	-1.98	-2.69
96	-3.24	-3.25	-2.52	-5.71	-1.34	-1.84	-2.78	-6.46	-4.92
97	-0.41	-1.71	-3.76	-4.19	-0.36	3.3	1.78	-8.16	-8.83
sum	33.2	45.1	-1.56	17.78	23.37	26.68	24.79	-3.76	-2.65

The signs of the NICS values are reversed from those of the shielding data in the output. Thus, the NICS value is the negative of the sum of the shielding contributions. The NICS-σ values in the main text is obtained by subtracting the value of NICS-π from the value of NICS, which is mainly contributed by the σ orbitals. Thus, NICS(0)-σ value of **3MR-1** mainly contributed by the main σ orbitals is -33.2 ppm; NICS(0)-σ value of **3MR-2** mainly contributed by the main σ orbitals is -45.1 ppm; NICS(0)-σ value of **6MR** mainly contributed by the main σ orbitals is +1.56 ppm; $NICS(1)_{ZZ}$-σ value of **3MR-1** mainly contributed by the main σ orbitals is the mean value of $NICS(1)_{ZZ}$-σ and $NICS(-1)_{ZZ}$-σ: -(17.78+23.37) / 2 = -20.58 ppm; $NICS(1)_{ZZ}$-σ value of **3MR-2** mainly contributed by the main σ orbitals is -25.74 ppm; $NICS(1)_{ZZ}$-σ value of **6MR** mainly contributed by the main σ orbitals is +3.21 ppm.

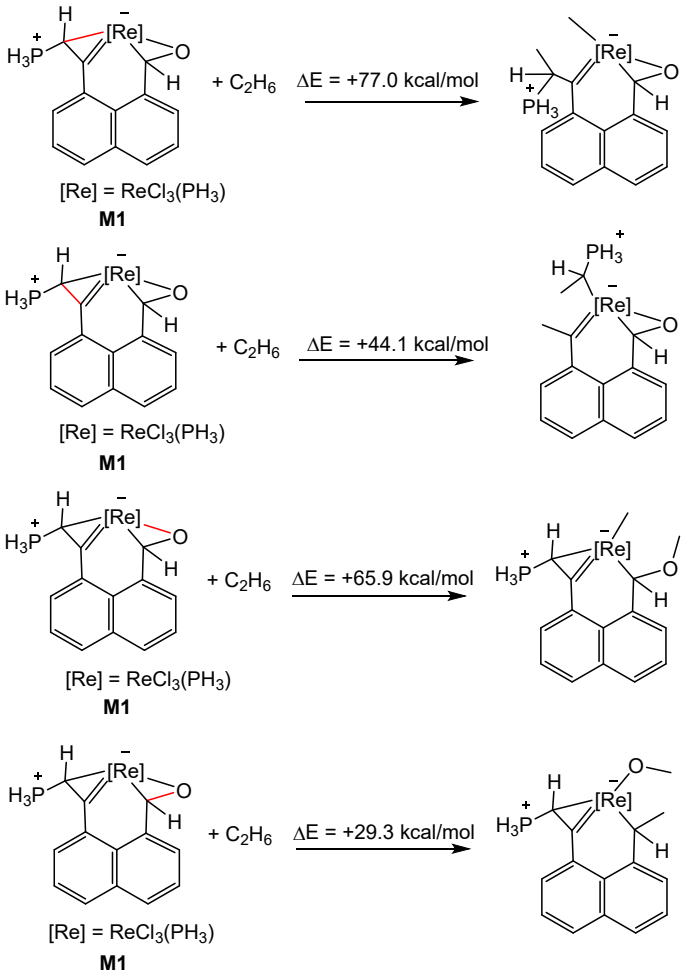


Figure S2. Isodesmic reactions for 3MRs in **M1**.

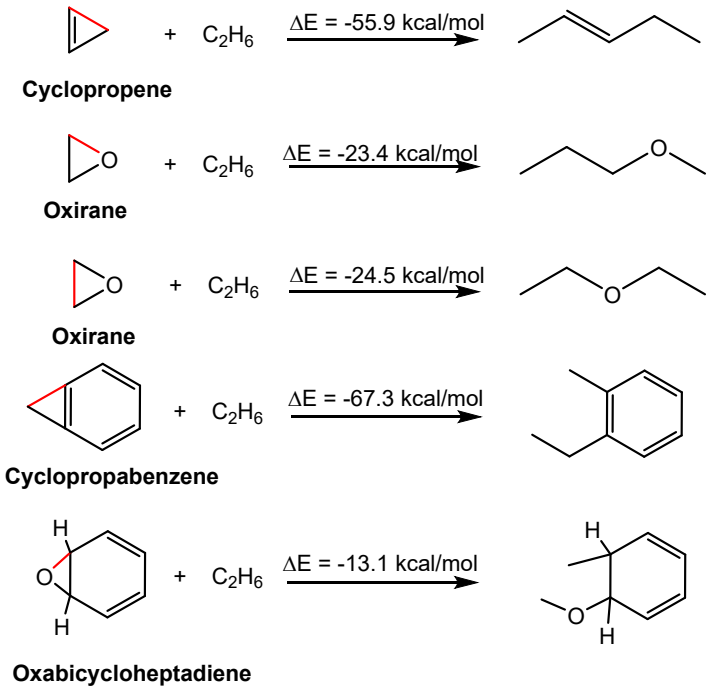


Figure S3. Isodesmic reactions for some non-metallic rings.

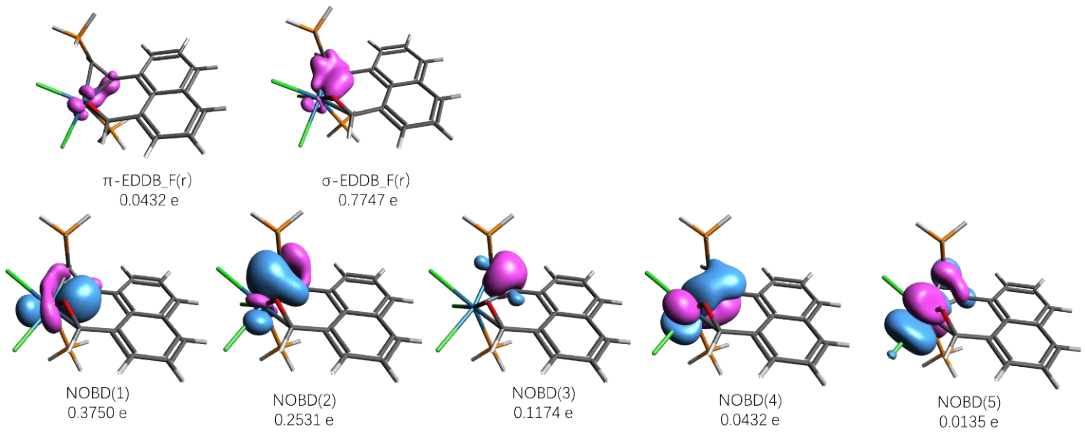


Figure S4. EDDB_F(r) results for the **3MR-1** in **M1** and key NOBDs of the ring. Isovalues are 0.020, 0.010 for σ-EDDB_F(r), π-EDDB_F(r), respectively. Isovalue for NOBD contours is 0.030.

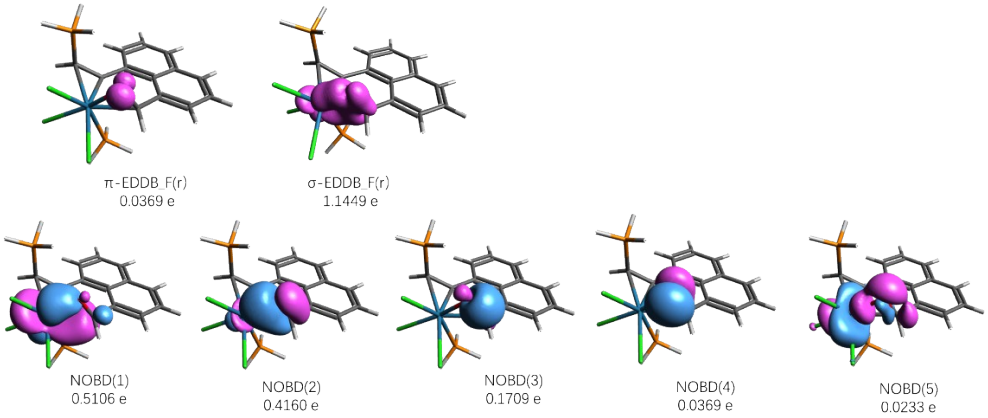


Figure S5. EDDB_F(r) results for the **3MR-2** in **M1** and key NOBDs of the ring. Isovalues are 0.020, 0.010 for σ-EDDB_F(r), π-EDDB_F(r), respectively. Isovalue for NOBD contours is 0.030.

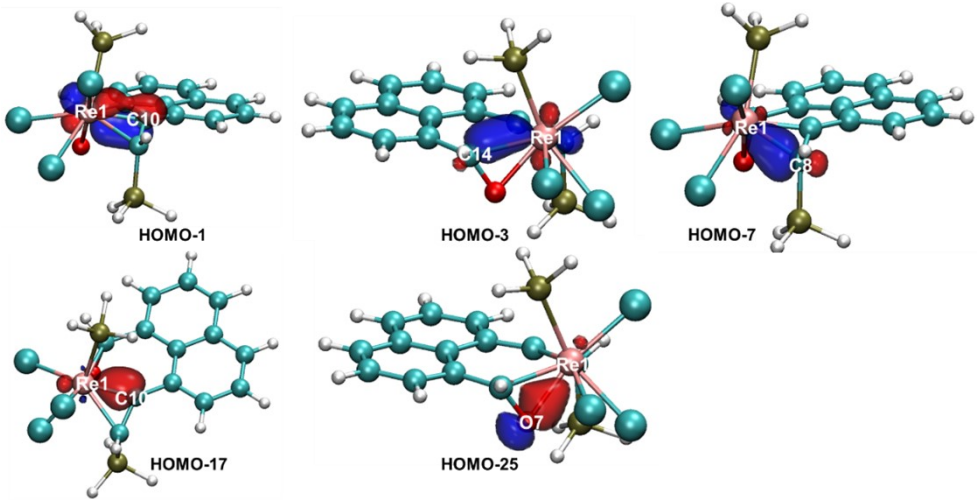
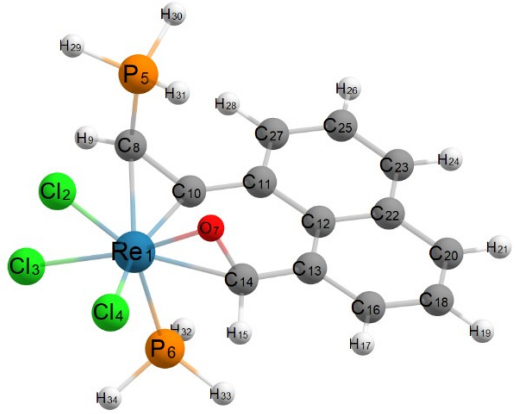


Figure S6. Orbital localization analysis of Re-O bond. The localization method is Pipek-Mezey with Mulliken population.

Table S3. LMO compositions and bond orders for **3MR**s in **M1**.



LMO[a]	%Re/%C(%O)[a]	MBO[b]	WBO[c]	DI [d]
σ(Re1-C14)	51.6/29.1	0.63	0.56	0.61
σ(Re1-C8)	34.5/42.7	0.60	0.54	0.69
σ(Re1-O7)	20.9/62.2	0.70	0.50	0.68
σ(Re1-C10)	37.7/47.7	1.30	1.18	1.34
π(Re1-C10)	46.5/31.6			

[a] Orbital localization analysis method is Pipek-Mezey with Mulliken population.

[b] Mayer bond order analysis.

[c] Wiberg bond order in the natural atomic orbital (NAO) basis.

[d] Delocalization index based on QTAIM analysis.

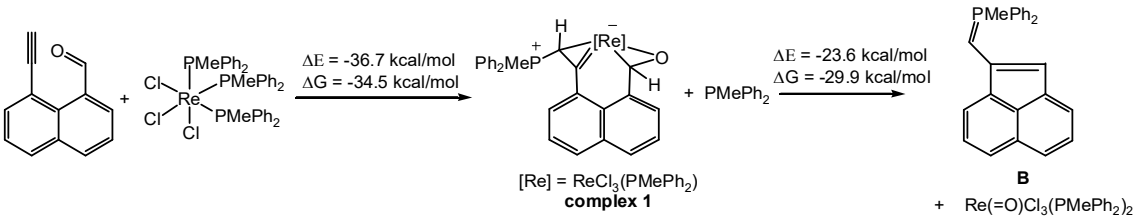


Figure S7. Free energy changes for the formation and decomposition of complex **1**.

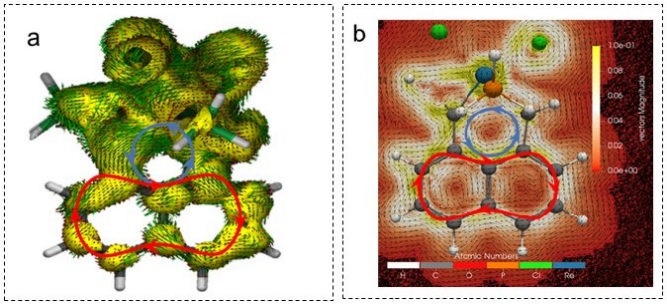
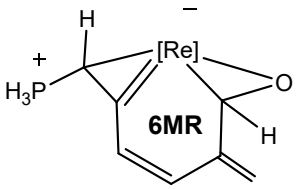


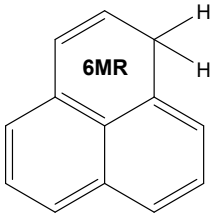
Figure S8. (a) The AICD-π plots (isosurface value is 0.015) and (b) GIMIC maps (1.5 bohr above the **6MR**) in **M1**. In both maps, the magnetic field vector is orthogonal with respect to the ring plane and points upward. Red and blue arrows indicate clockwise (diatropic) and counter-clockwise (paratropic) ring current flows, respectively.

Table S4. Computed NICS values for the **M1'** and phenalene.



[Re] = $ReCl_3(PH_3)$

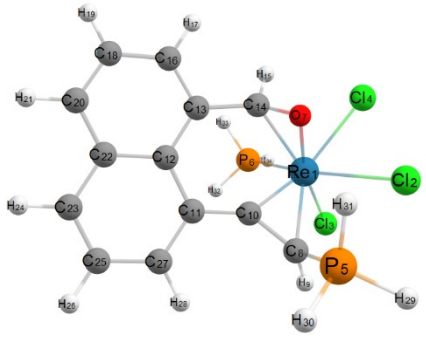
M1'



Phenalene

	6MR	**6MR**
NICS(0)	-0.5	+7.1
NICS(0)-σ	-3.7	+10.5
NICS(0)-π	+3.2	-3.4
$NICS(1)_{zz}$	+0.8	+11.8
$NICS(1)_{zz}$-σ	-7.4	+1.3
$NICS(1)_{zz}$-π	+8.2	+10.5

Table S5. The values of total current strengths (nA/T) across the bonds of **M1**.



Bond	diatropic contribution	paratropic contribution	Total induced current
C11-C27	15.390322	-5.837503	9.552820
C27-C25	15.325368	-5.029687	10.295680
C25-C23	15.394015	-5.011642	10.382373
C23-C22	15.039428	-4.990942	10.048486
C22-C20	15.498171	-4.934908	10.563263
C20-C18	15.922564	-4.888638	11.033926
C18-C16	15.722311	-4.837096	10.885214
C16-C13	15.438567	-5.314115	10.124452
C13-C14	6.143690	-6.448009	-0.304319
C14-O7	12.560494	-0.455903	12.104591
O7-Re1	11.389282	-3.839727	7.649556
Re1-C14	9.832397	0.893553	8.938844
Re1-C8	9.460547	-0.545797	8.914749
C8-C10	11.142030	-0.142339	10.999691

C10-C1	12.078957	-4.379933	7.699024
C_{10}-C_{11}	7.290238	-6.883678	0.406560

3. X-ray crystallographic study of complex 1.

Single crystals of **1** (CCDC No. 2081092) suitable for X-ray diffraction was grown from CH_2Cl_2 solution layered with hexanes. Intensity data of **1** was collected on a Bruker Smart APEXII diffractometer at 170 K using Mo-Kα radiation (λ = 0.71073 Å). Unit cell indexing was refined using SAINT, Absorption correction was applied by using multi-scan program SADABS. The structure was solved with OLEX2 software, and the SHELXT structure solution program using combined direct methods.[16,17] The crystal structure was refined by least squares using SHELXL. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon atoms were placed at calculated positions and refined using a riding model approximation, with C−H = 0.95 (aromatic CH) and with Uiso(H) = 1.2 Ueq(C), C−H = 1.00 (-CH) and with Uiso(H) = 1.2 Ueq(C), C−H = 0.99 (-CH_2) and with Uiso(H) = 1.2 Ueq(C), C−H = 0.98 Å (-CH_3) and with Uiso(H) = 1.5 Ueq(C). The crystal data are listed in Table S6.

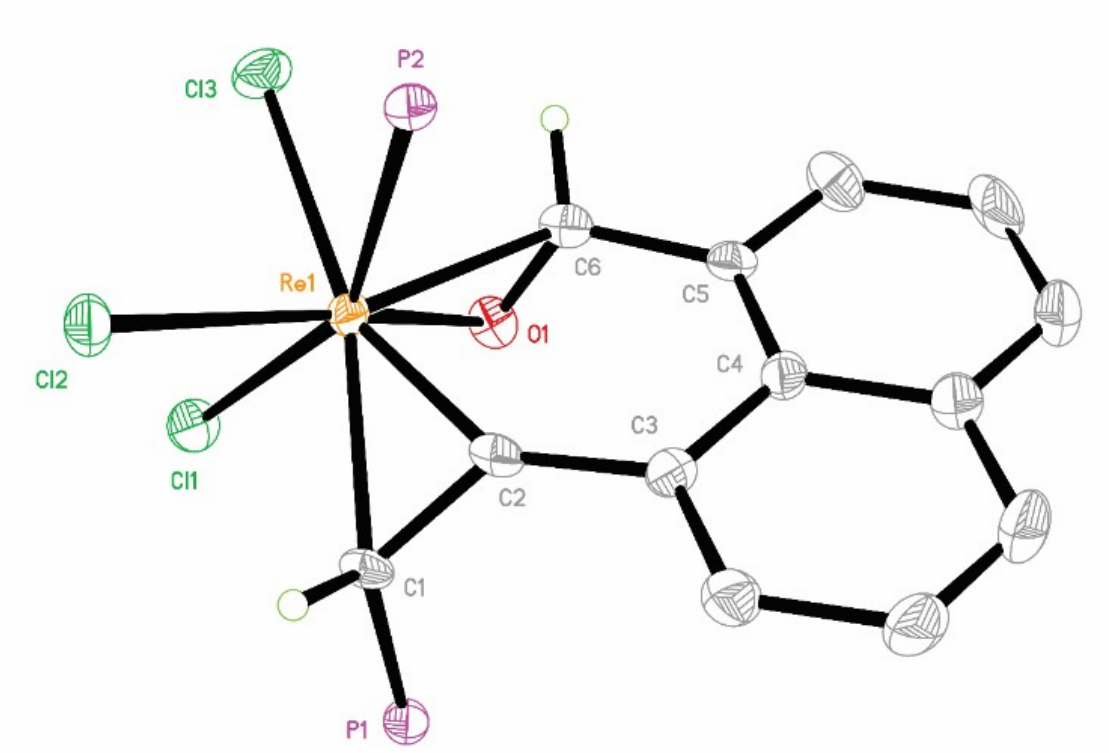


Figure S9. Structure of complex **1**. The hydrogen atoms on the naphthyl groups and groups on phosphine are omitted for clarity. Selected bond lengths [Å] and angles [°]: Re1-C1 2.196(4), Re1-C2 1.912(4), Re1-C6 2.173(4), Re1-O1 2.051(3), Re1-P2 2.4789(11), C1-P1 1.788(4), C1-C2 1.425(5), C2-C3 1.439(5), C3-C4 1.418(6), C4-C5 1.427(5), C5-C6 1.506(5), C6-O1 1.335(4), C1-Re1-C2 39.83(15), Re1-C2-C1 80.9(2), Re1-C2-C3 142.9(3), C2-C3-C4 119.1(4), C3-C4-C5 122.5(4), C4-C5-C6 124.6(4), Re1-C6-C5 127.4(3), C2-Re1-C6 81.12(16), Re1-O1-C6 76.6(2), C6-Re1-O1 36.71(12), Re1-C6-O1 66.7(2), P2-Re1-Cl1 154.32(3), Re1-C1-P1 124.6(2), C5-C6-O1 119.3(3).

Table S6. Crystallographic data and refinement details for **1**.

	1
CCDC Number	2081092
Empirical formula	C41H38Cl7OP2Re
Color & habit	orange, rod
Crystal size (mm^3)	0.25 x 0.10 x 0.10
Temperature (K)	170K
Crystal system	Monoclinic
Space group	$P2_1/c$
a(Å)	10.7012(11)
b(Å)	10.5762(10)
c(Å)	36.545(4)
□□□□	90
□□□□	94.488(4)
□□□□	90
V($Å^3$), Z	4123.4(7), 4
D_{cal} (Mg/m^3)	1.680
Abs. coeff.(mm^{-1})	3.511
2θ range for data collection (°)	4.472 to 54
Reflections collected	69384
Indep. Reflection, R(int)	9000, 0.0981
Completeness of data	99.8 %
Data/ restraints / parameters	9000/0/471
Goodness-of-fit on F^2	1.041
R1 [I>2sigma(I)], wR2	0.0359, 0.0640
R1 (all data), wR2	0.0658, 0.0699
Largest diff. peak and hole (e·$Å^{-3}$)	0.96, -0.82

4. NMR spectra

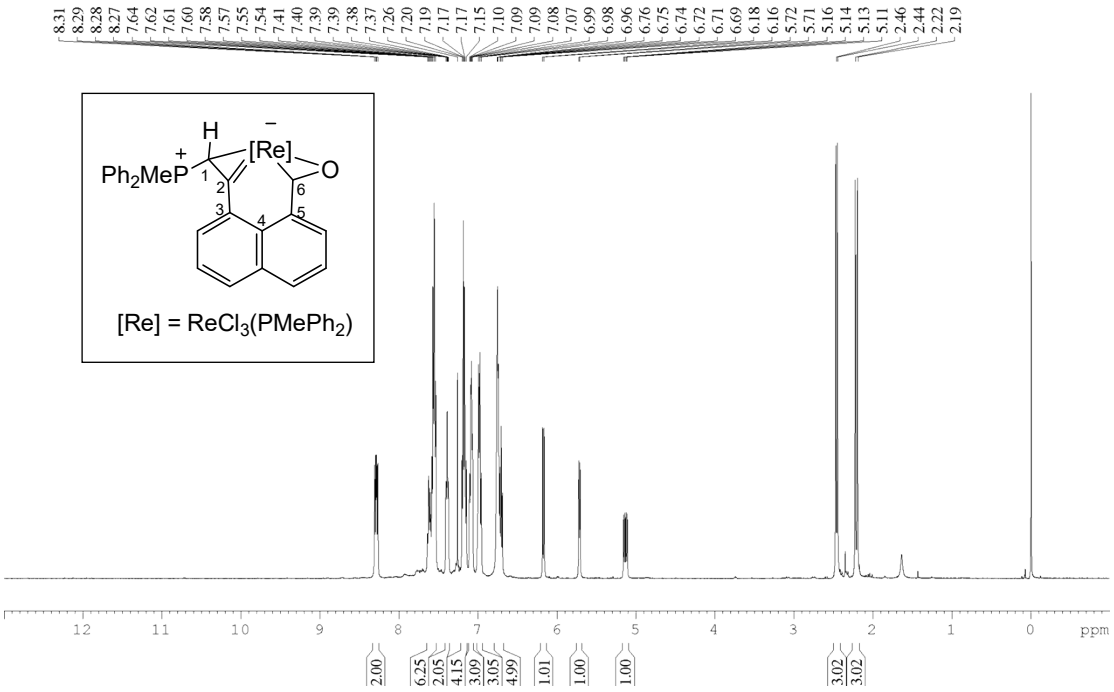


Figure S10. The ^{1}H NMR spectrum of complex **1** in $CDCl_3$ at 400.1 MHz.

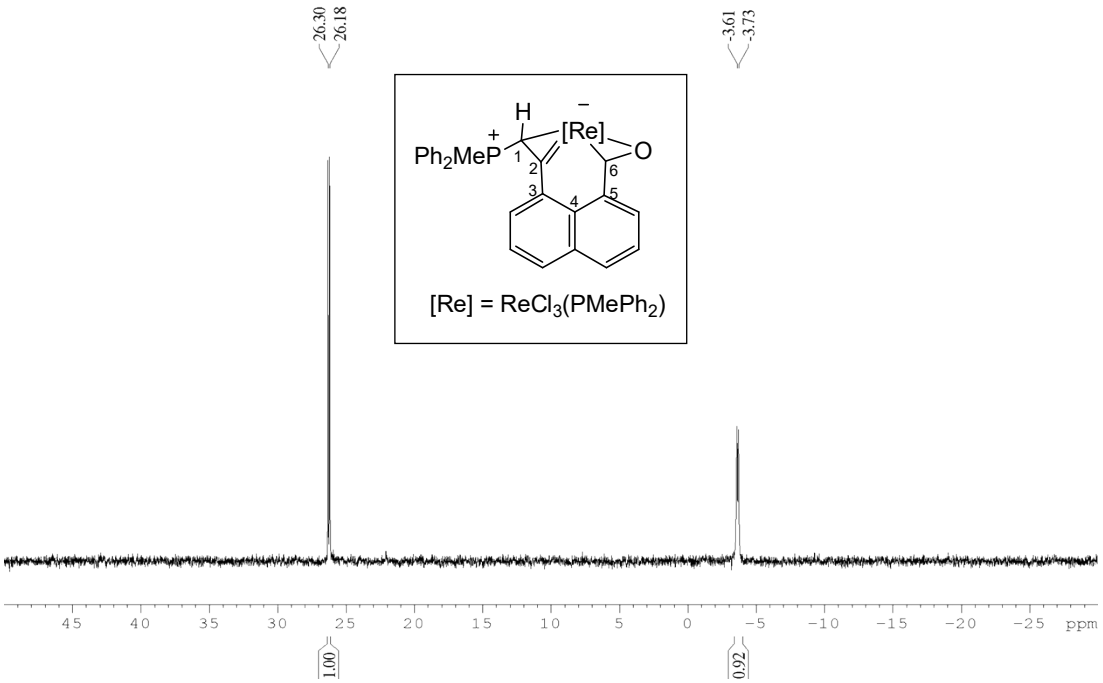


Figure S11. The $^{31}P\{^{1}H\}$ NMR spectrum of complex **1** in $CDCl_3$ at 162.0 MHz.

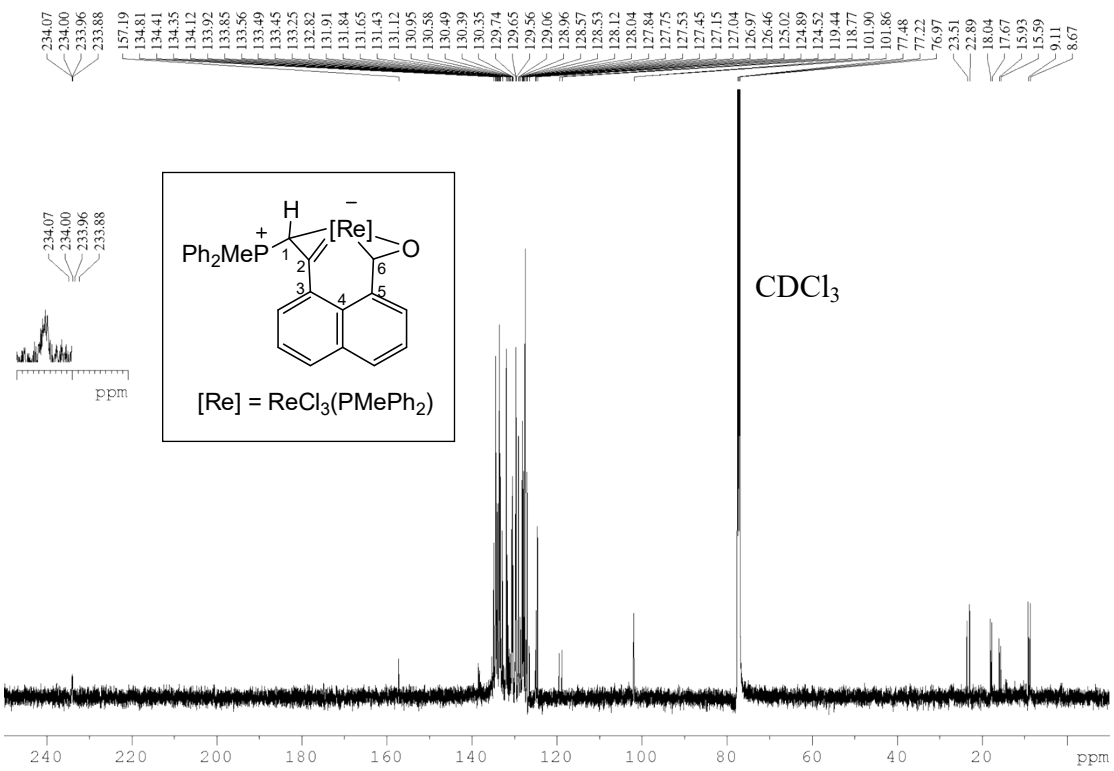


Figure S12. The $^{13}C\{^{1}H\}$ NMR spectrum of complex **1** in $CDCl_3$ at 100.6 MHz.

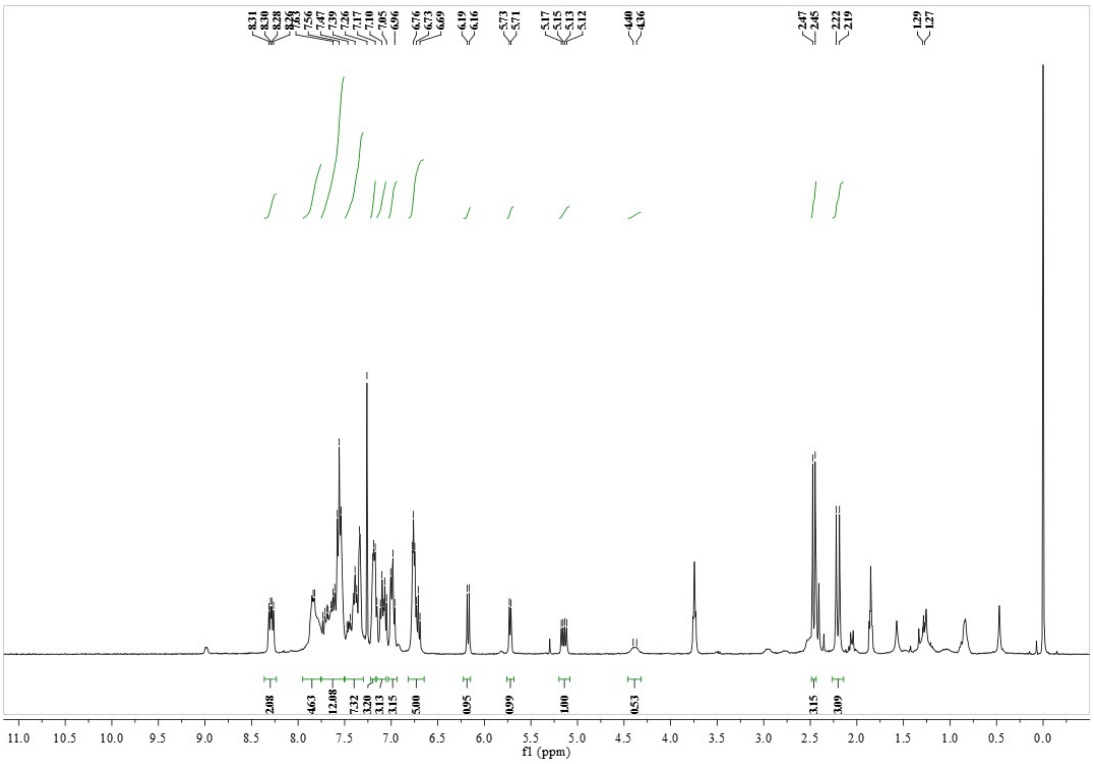


Figure S13. The ^{1}H NMR spectrum of complex **1** in $CDCl_3$ at 400.1 MHz after 18 h at room temperature.

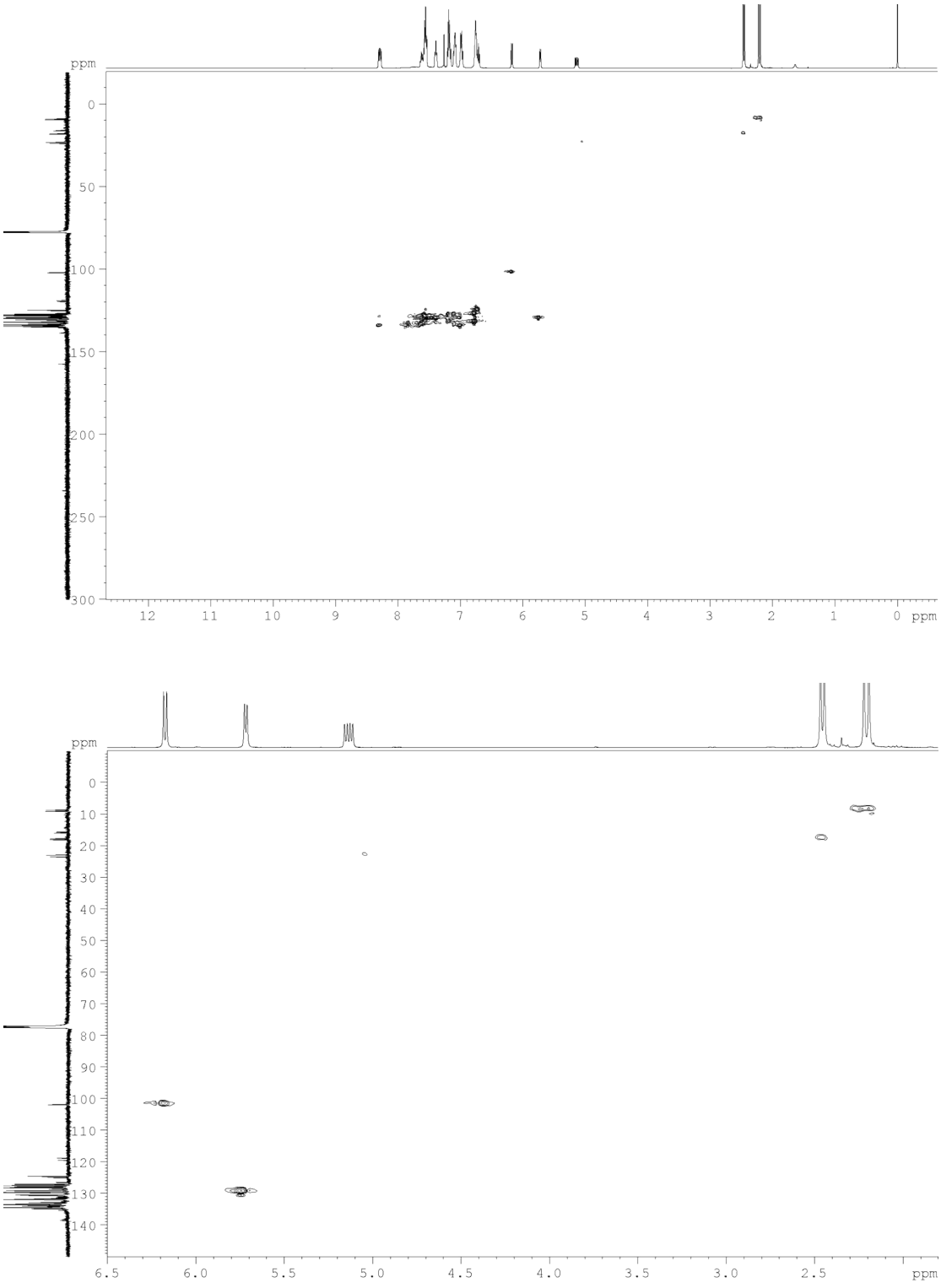


Figure S14. The ^{1}H-^{13}C HSQC and expanded NMR spectrum of complex **1** in $CDCl_3$ at 100.6 MHz.

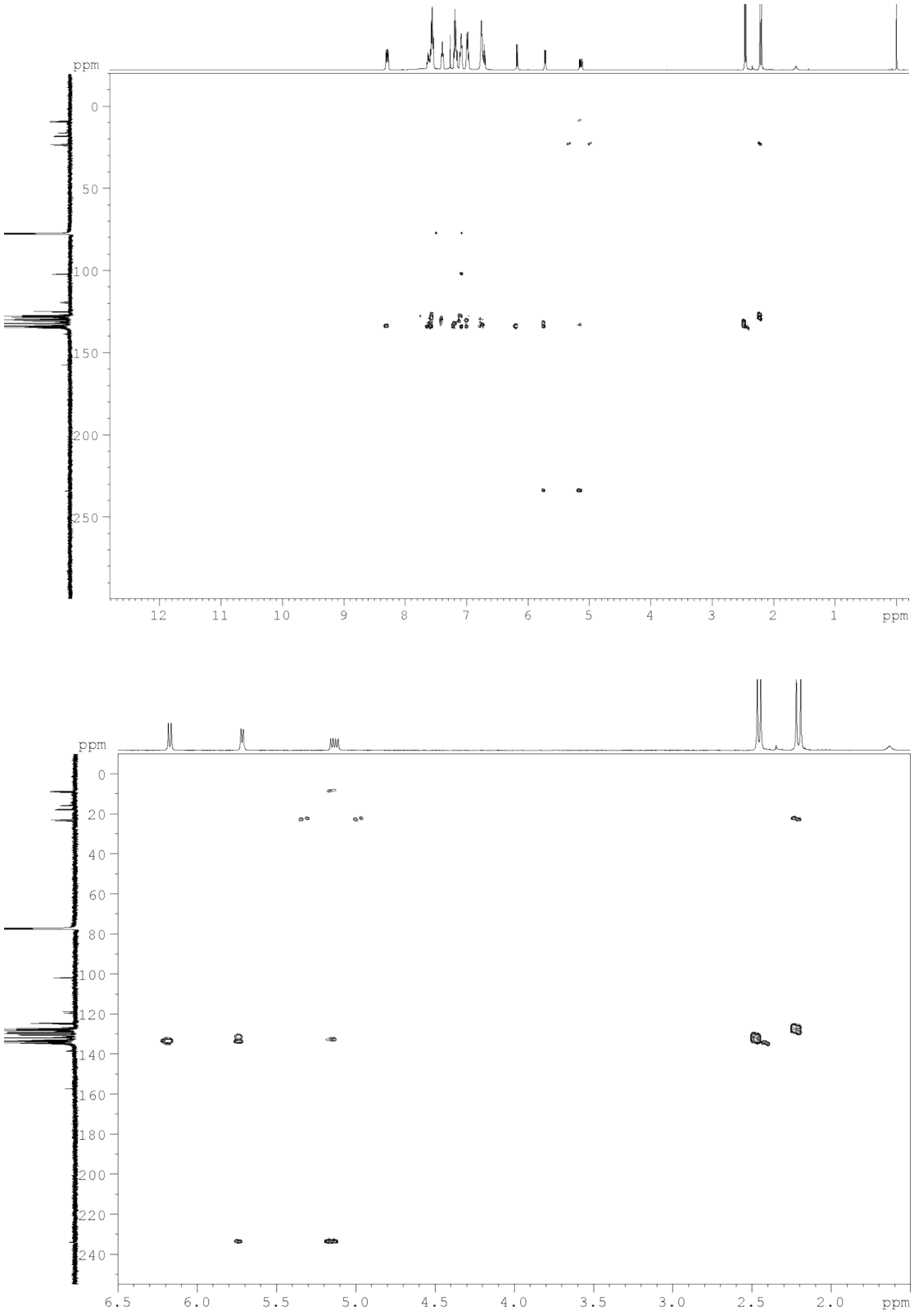


Figure S15. The ^{1}H-^{13}C HMBC and expanded NMR spectrum of complex **1** in $CDCl_3$ at 100.6 MHz.

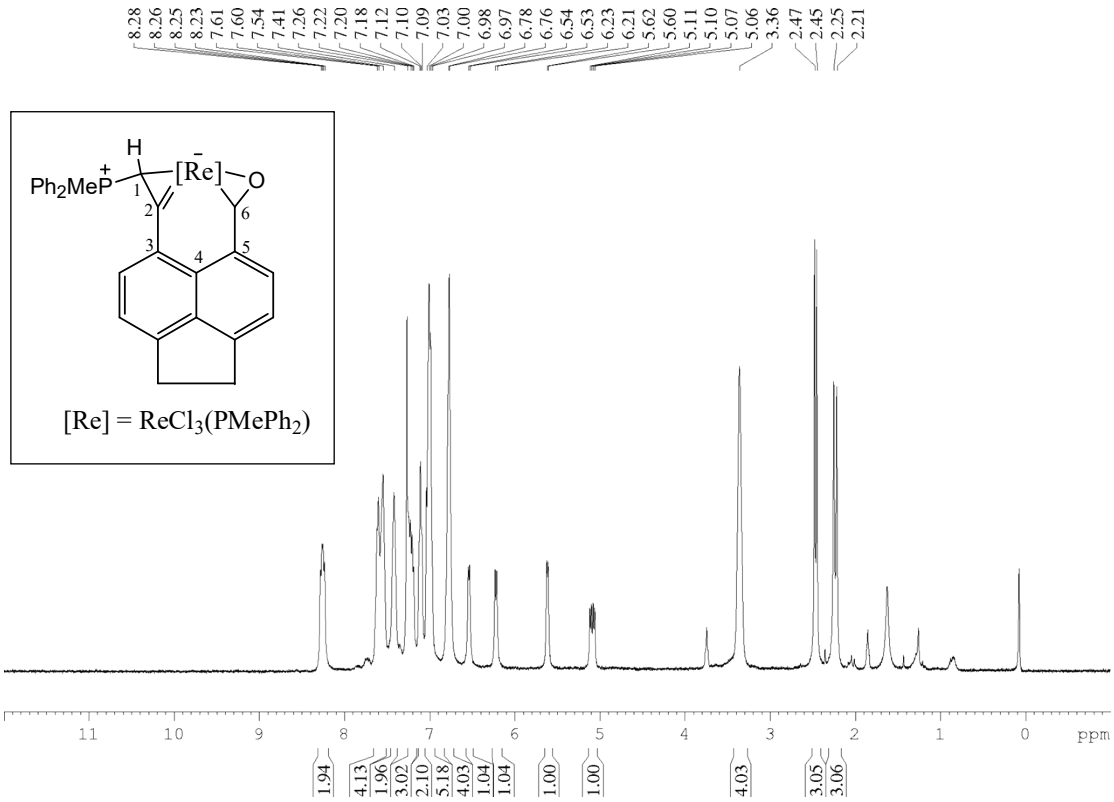


Figure S16. The ^{1}H NMR spectrum of complex **2** in $CDCl_3$ at 400.1 MHz.

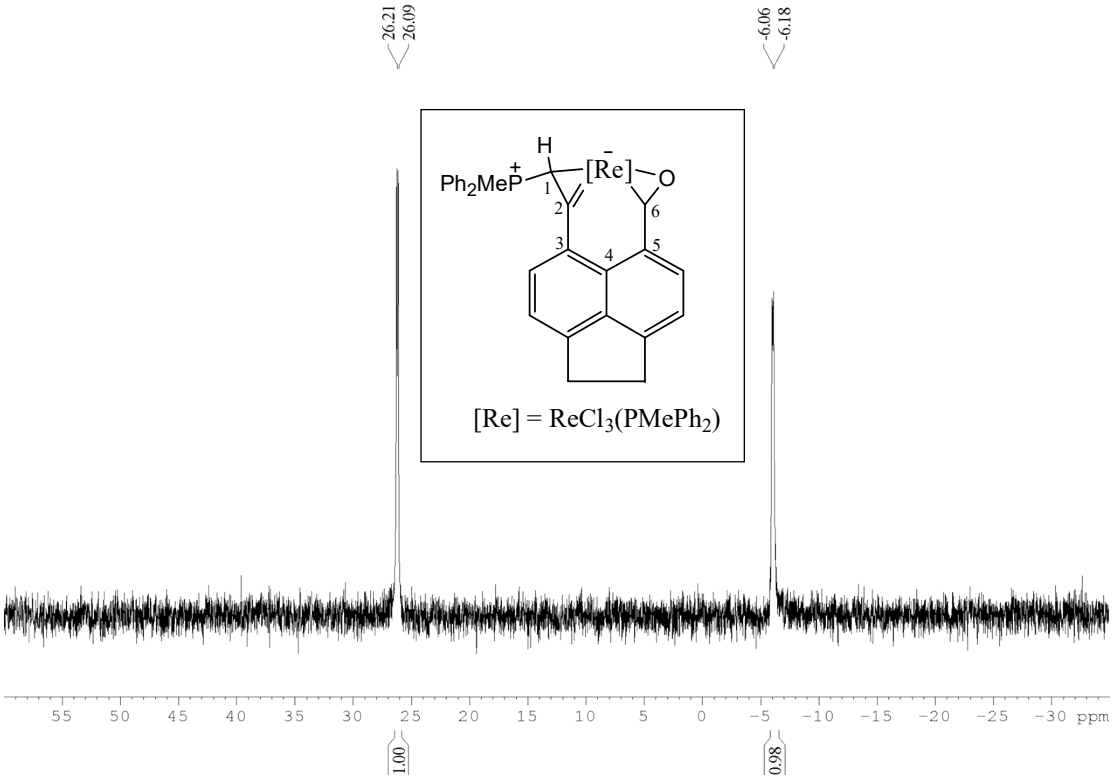


Figure S17. The $^{31}P\{^{1}H\}$ NMR spectrum of complex **2** in $CDCl_3$ at 162.0 MHz.

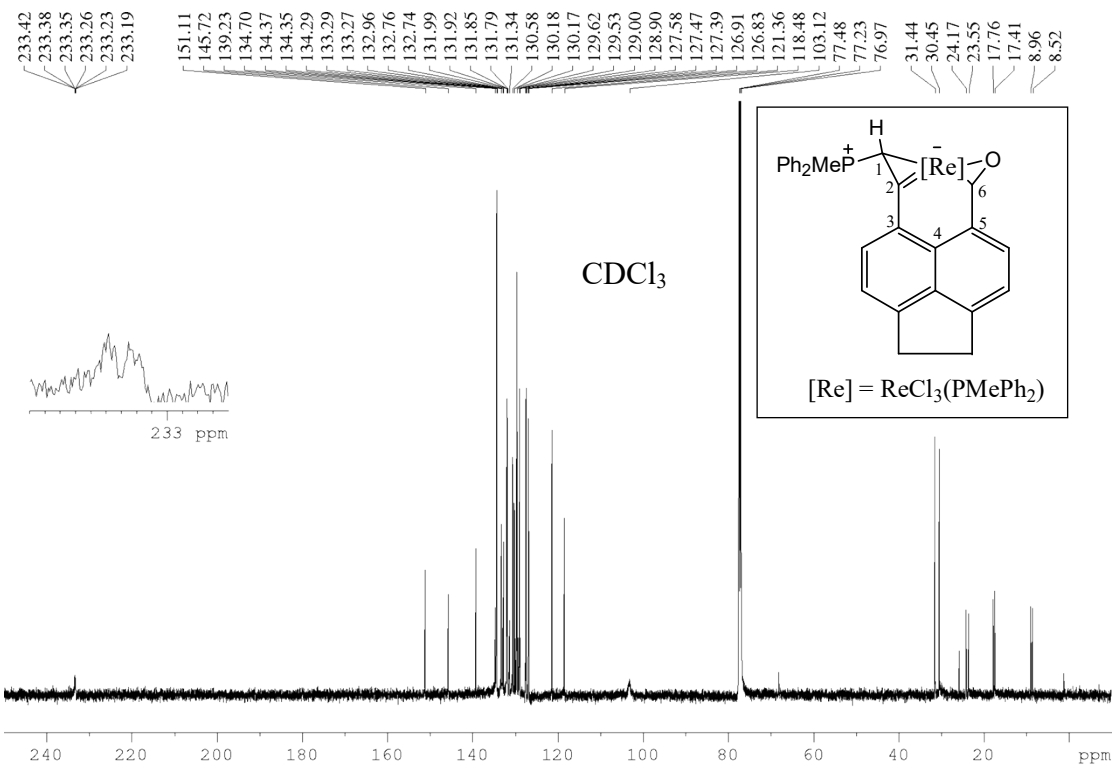


Figure S18. The $^{13}C\{^{1}H\}$ NMR spectrum of complex **2** in $CDCl_3$ at 100.6 MHz.

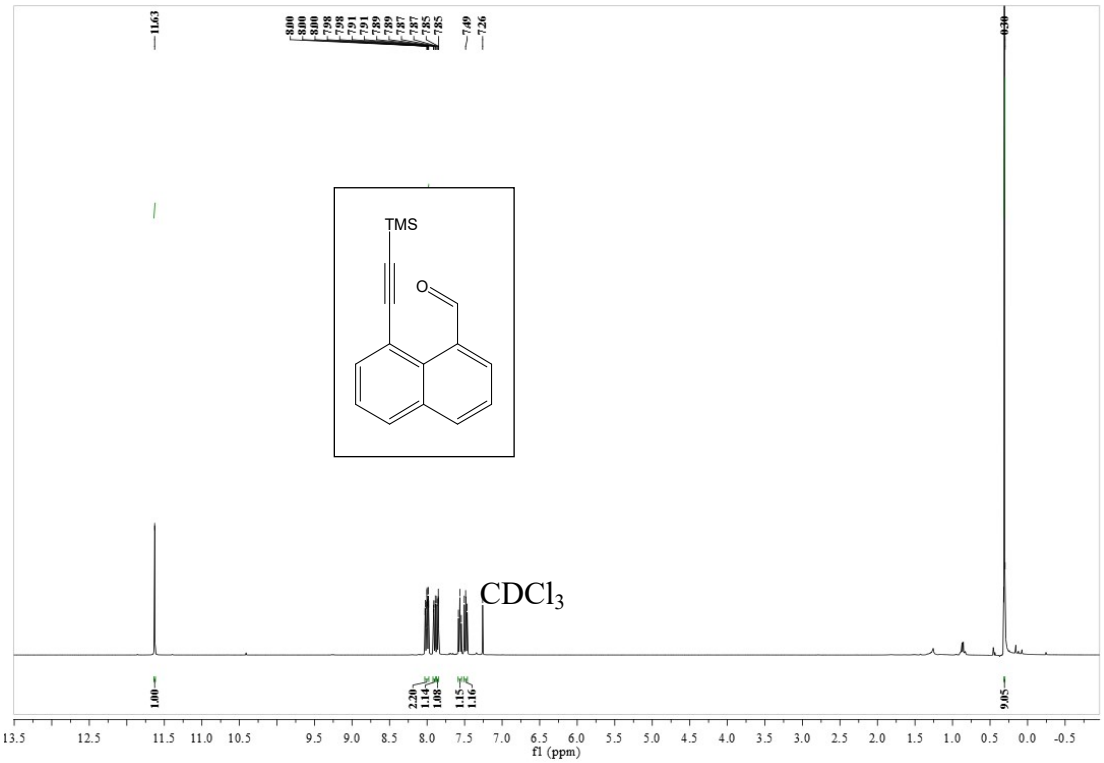


Figure S19. The ^{1}H NMR spectrum of 8-((trimethylsilyl)ethynyl)-1-naphthaldehyde in $CDCl_3$ at 400.1 MHz.

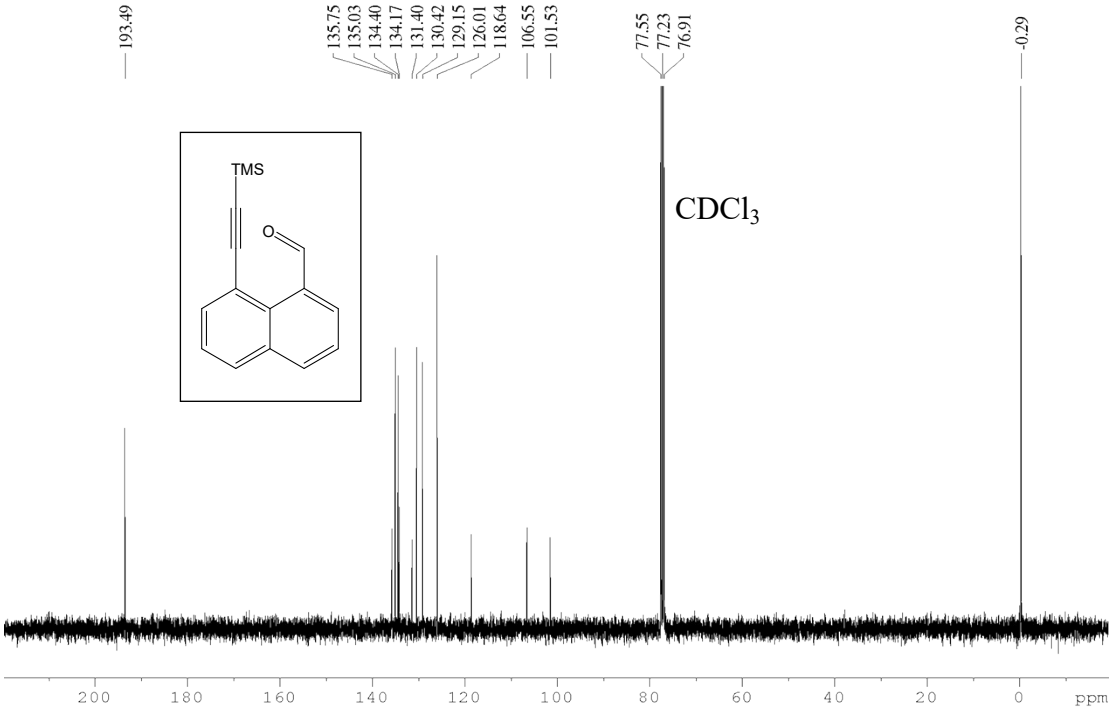


Figure S20. The $^{13}C\{^{1}H\}$ NMR spectrum of 8-((trimethylsilyl)ethynyl)-1-naphthaldehyde in $CDCl_3$ at 100.6 MHz.

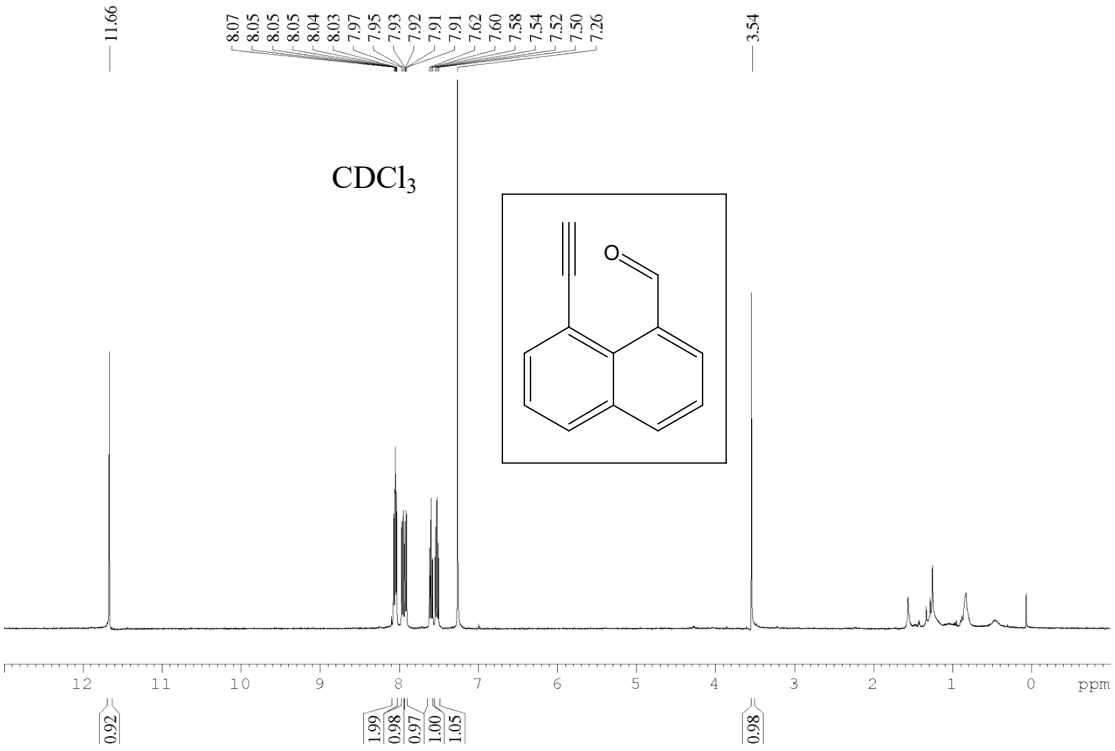


Figure S21. The ^{1}H NMR spectrum of 8-ethynyl-1-naphthaldehyde in $CDCl_3$ at 400.1 MHz.

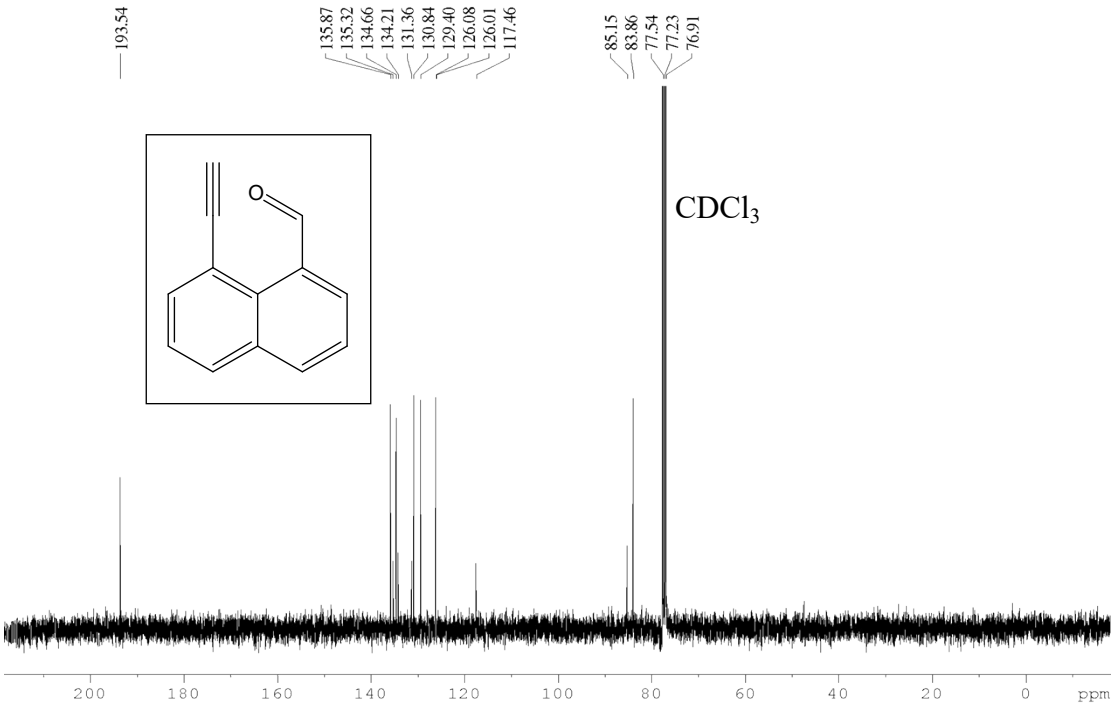


Figure S22. The $^{13}C\{^{1}H\}$ NMR spectrum of 8-ethynyl-1-naphthaldehyde in $CDCl_3$ at 100.6 MHz.

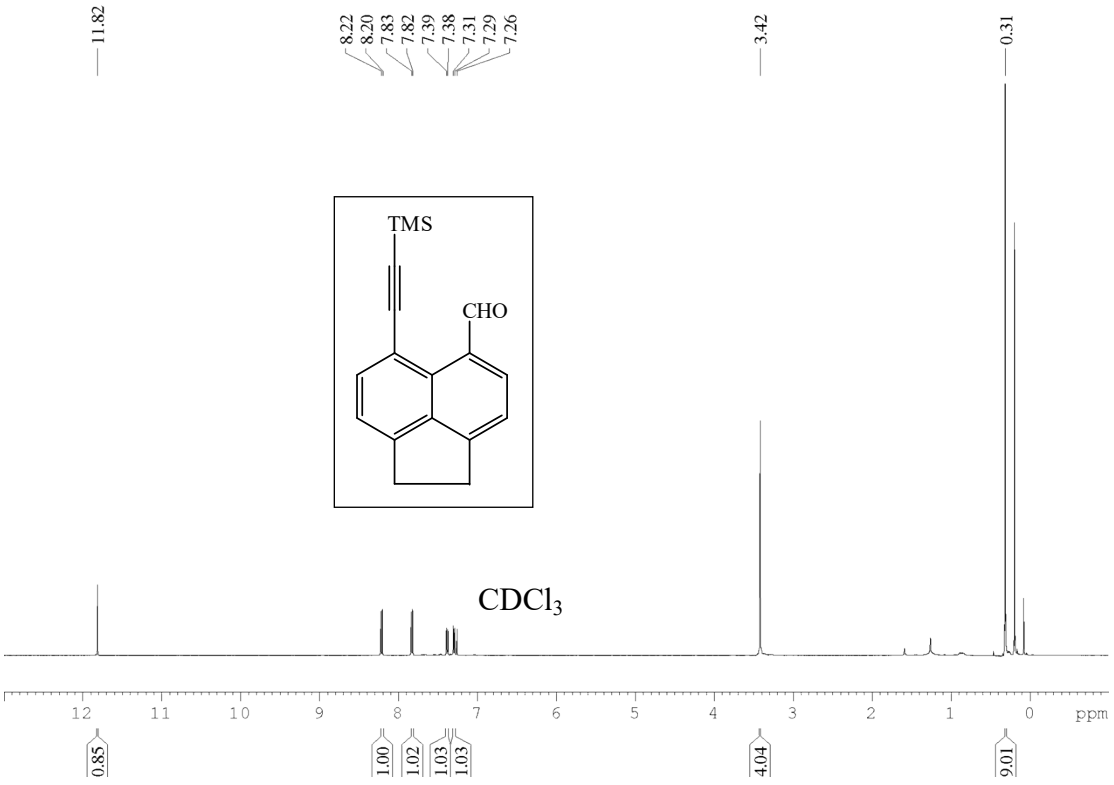


Figure S23. The ^{1}H NMR spectrum of 6-trimethylsilanylethynyl-1,2-dihydroacenaphthylene-5-carbaldehyde in $CDCl_3$ at 400.1 MHz.

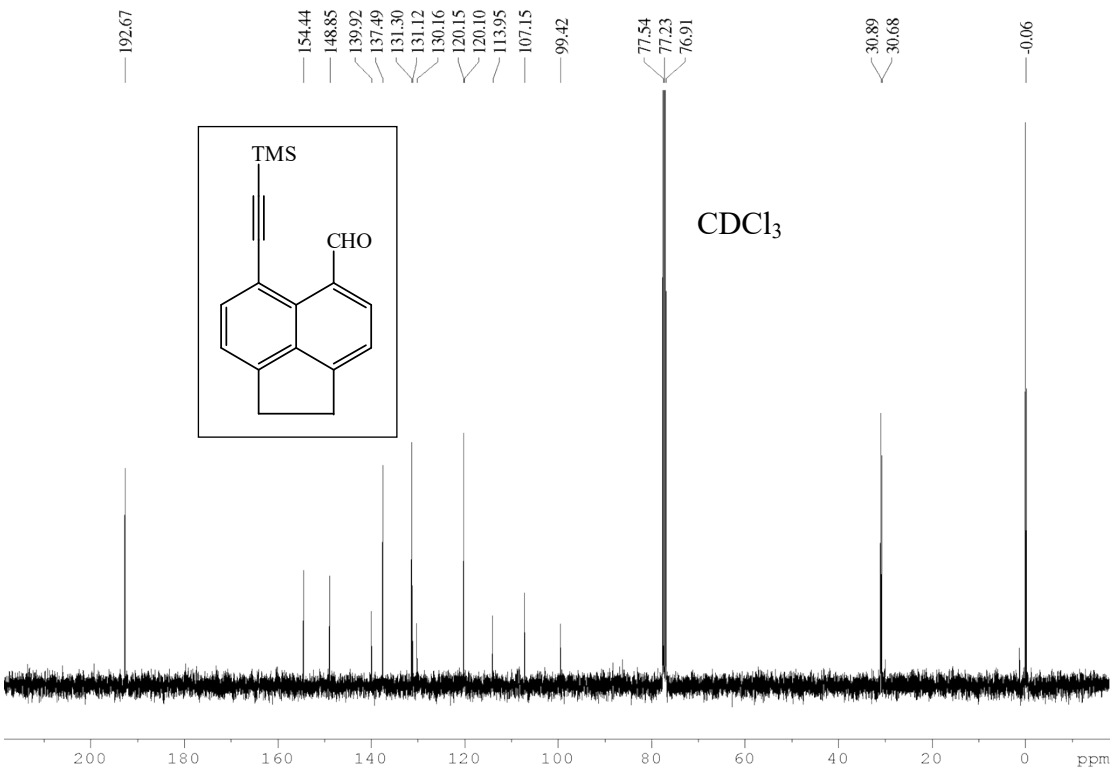


Figure S24. The $^{13}C\{^{1}H\}$ NMR spectrum of 6-trimethylsilanylethynyl-1,2-dihydroacenaphthylene-5-carbaldehyde in $CDCl_3$ at 100.6 MHz.

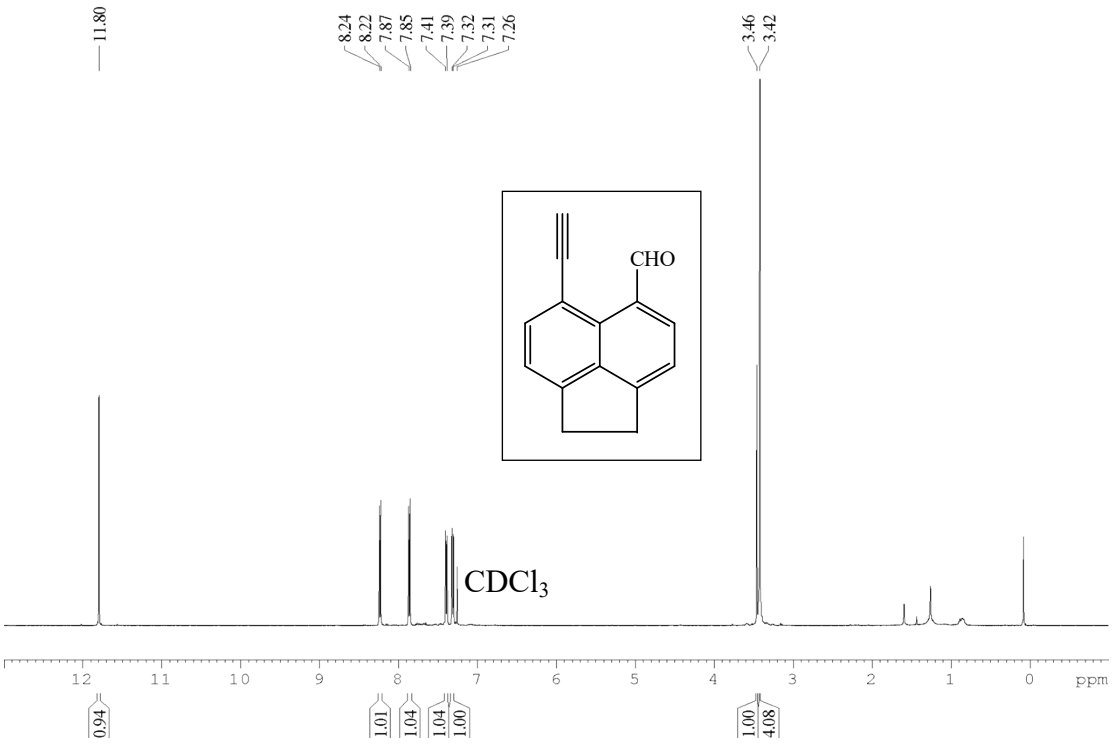


Figure S25. The ^{1}H NMR spectrum of 6-ethynyl-1,2-dihydroacenaphthylene-5-carbaldehyde in $CDCl_3$ at 400.1 MHz.

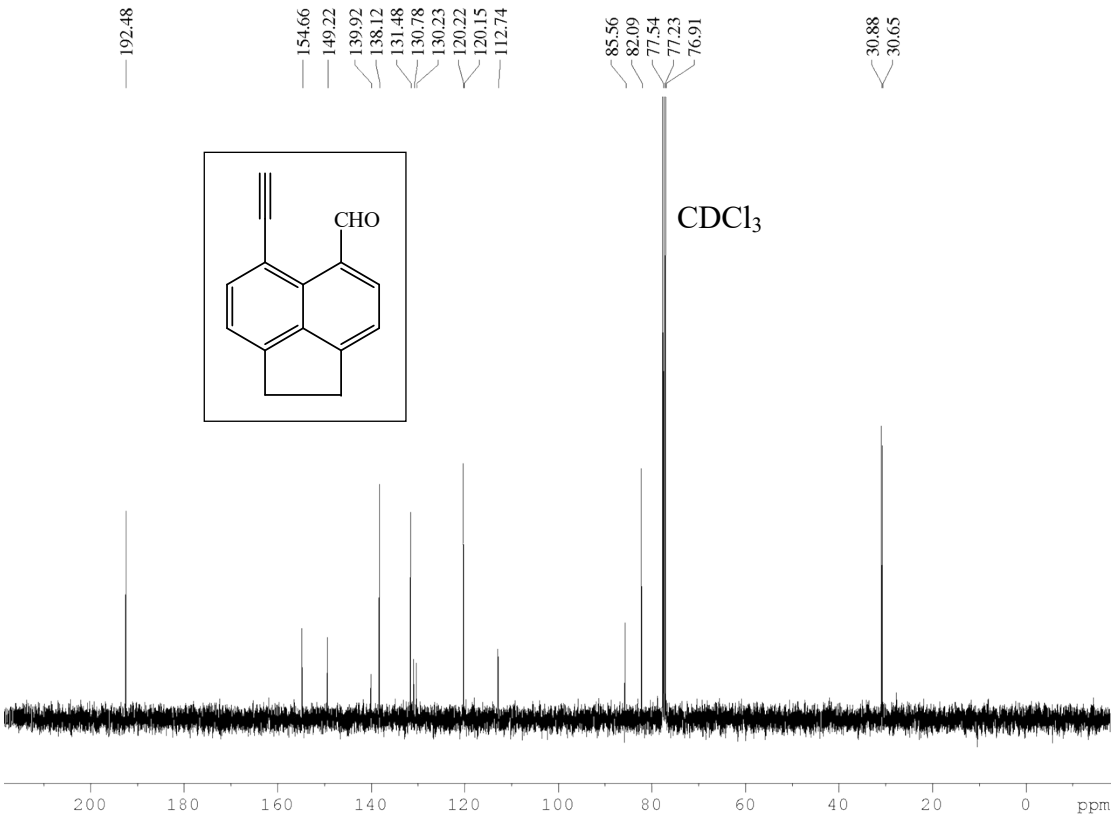


Figure S26. The $^{13}C\{^{1}H\}$ NMR spectrum of 6-ethynyl-1,2-dihydroacenaphthylene-5-carbaldehyde in $CDCl_3$ at 100.6 MHz.

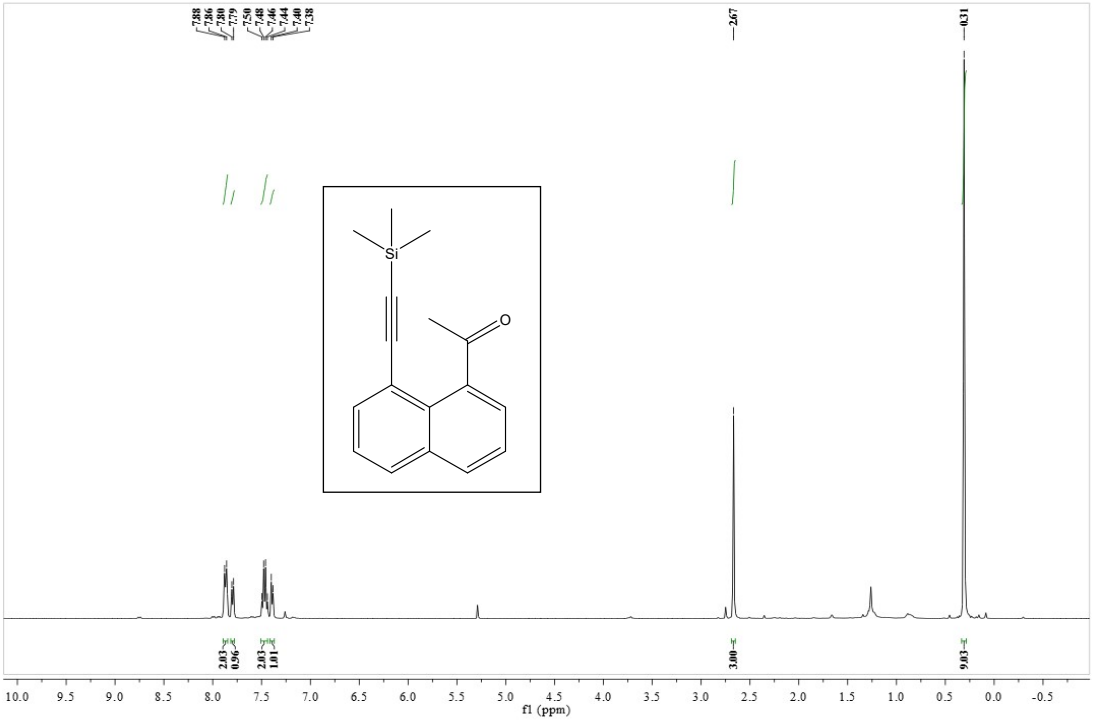


Figure S27. The ^{1}H NMR spectrum of 1-(8-((trimethylsilyl)ethynyl)naphthalen-1-yl)ethan-1-one in $CDCl_3$ at 400.1 MHz.

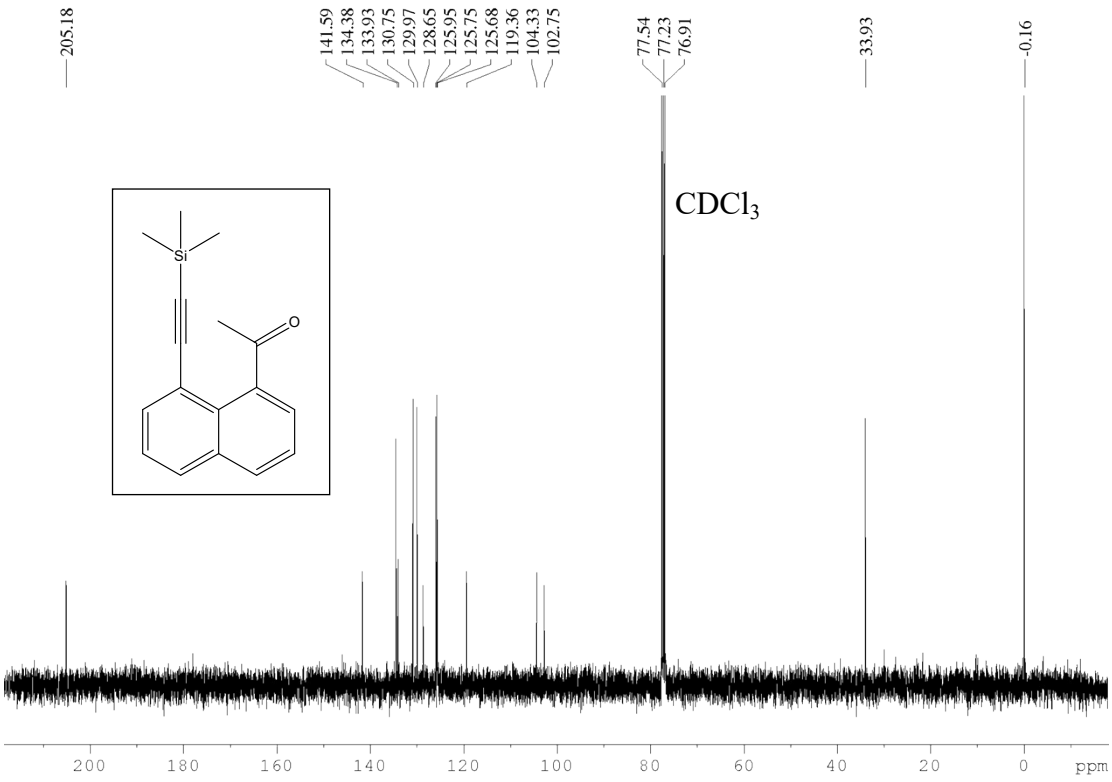


Figure S28. The $^{13}C\{^{1}H\}$ NMR spectrum of 1-(8-((trimethylsilyl)ethynyl)naphthalen-1-yl)ethan-1-one in $CDCl_3$ at 100.6 MHz.

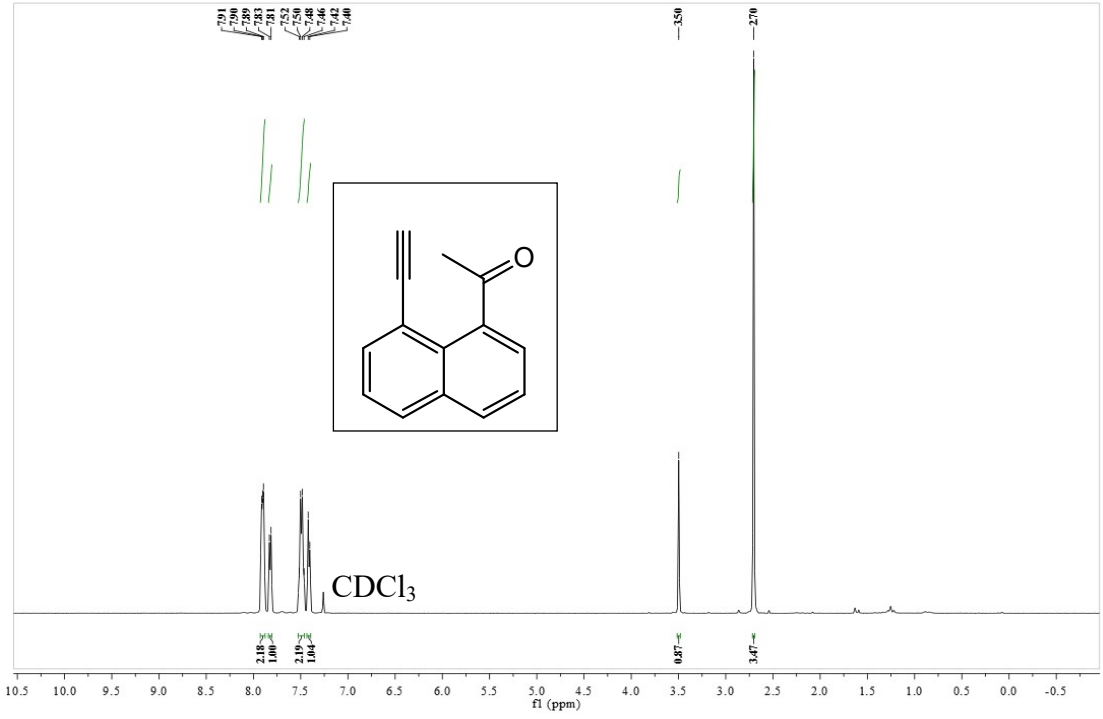


Figure S29. The ^{1}H NMR spectrum of 8-ethynyl-1-naphthaldehyde in $CDCl_3$ at 400.1 MHz.

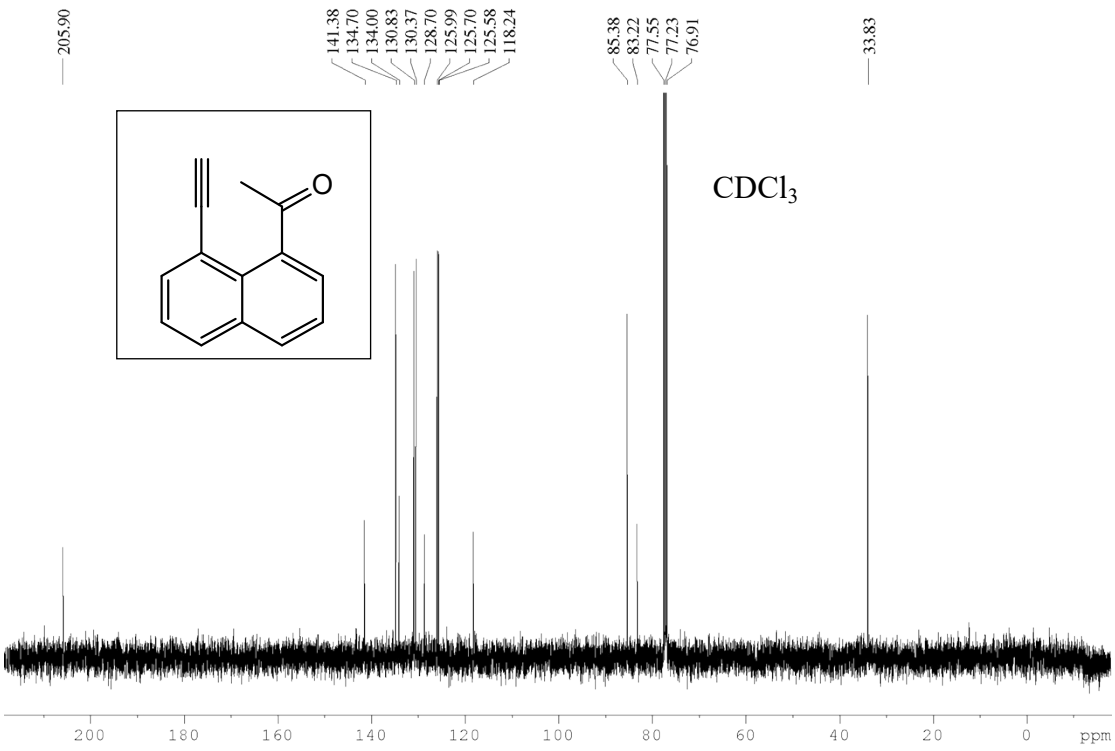


Figure S30. The $^{13}C\{^{1}H\}$ NMR spectrum of 8-ethynyl-1-naphthaldehyde in $CDCl_3$ at 100.6 MHz.

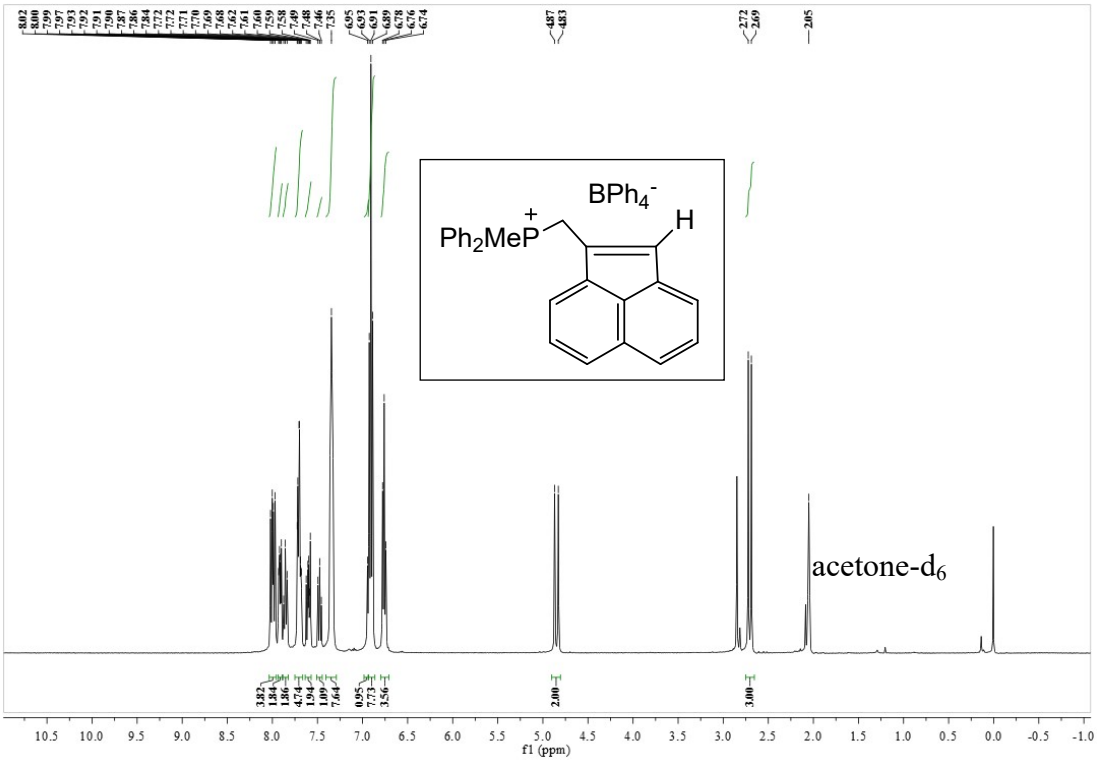


Figure S31. The ^{1}H NMR spectrum of acenaphthylene compound **1a** in acetone-d_6 at 400.1 MHz.

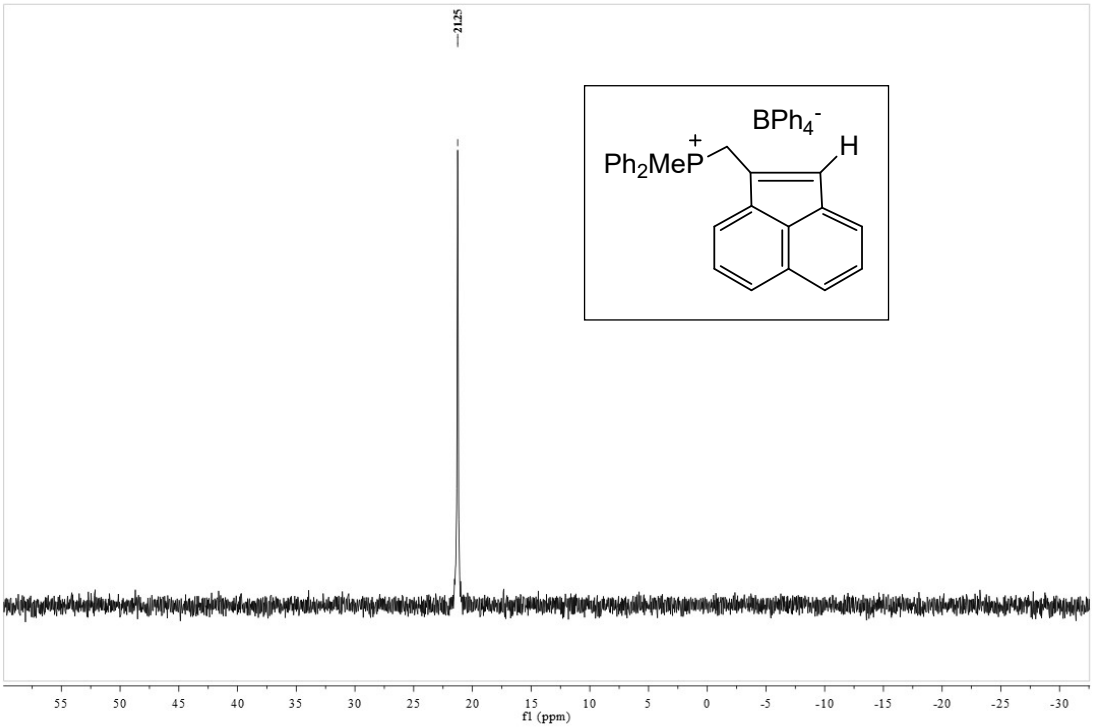


Figure S32. The $^{31}P\{^{1}H\}$ NMR spectrum of acenaphthylene compound **1a** in acetone-d_6 at 162.0 MHz.

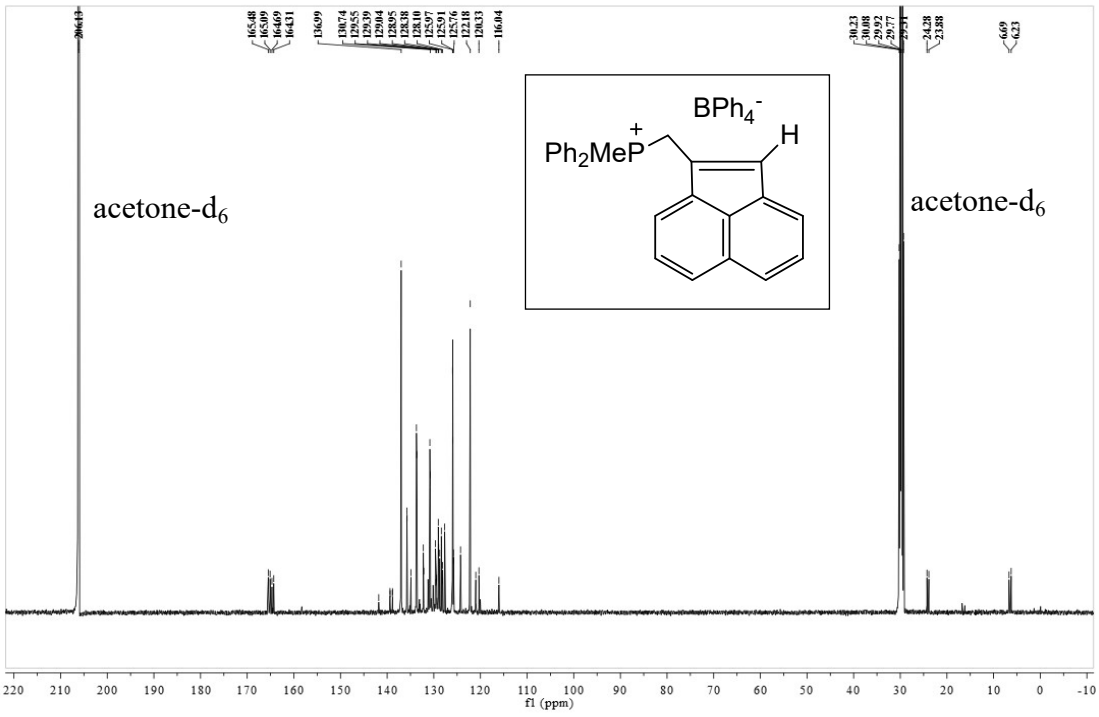


Figure S33. The $^{13}C\{^{1}H\}$ NMR spectrum of acenaphthylene compound **1a** in acetone-d_6 at 100.6 MHz.

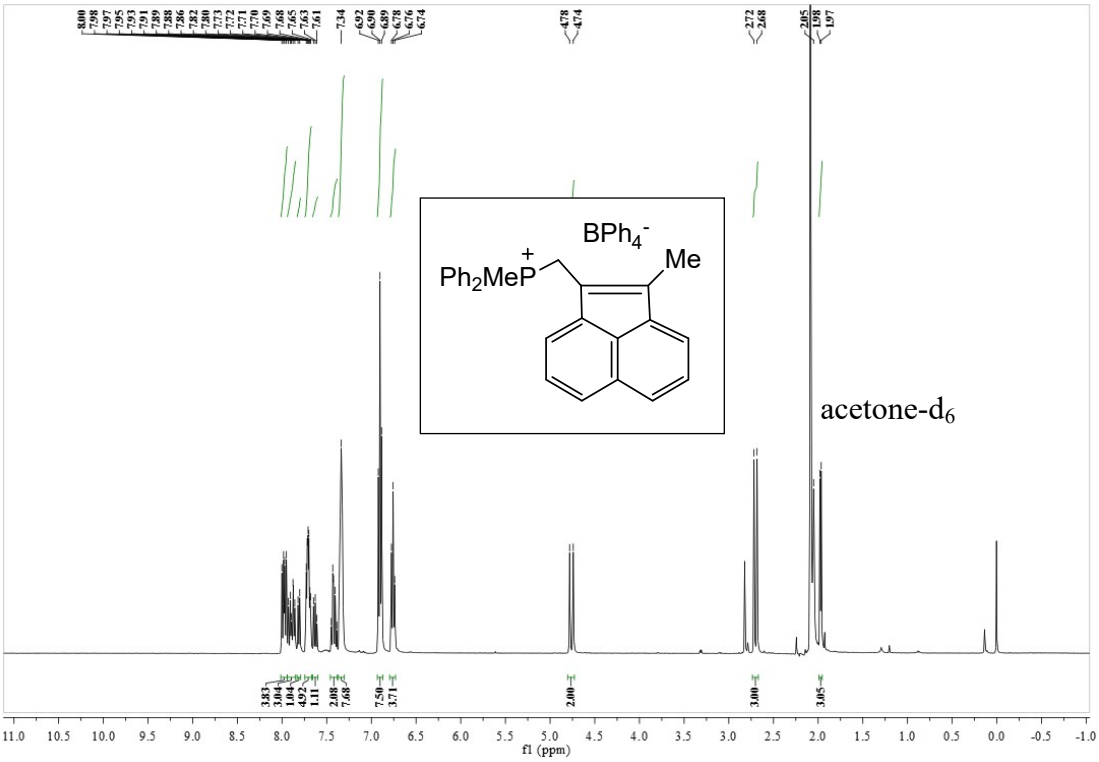


Figure S34. The ^{1}H NMR spectrum of acenaphthylene compound **3a** in acetone-d_6 at 400.1 MHz.

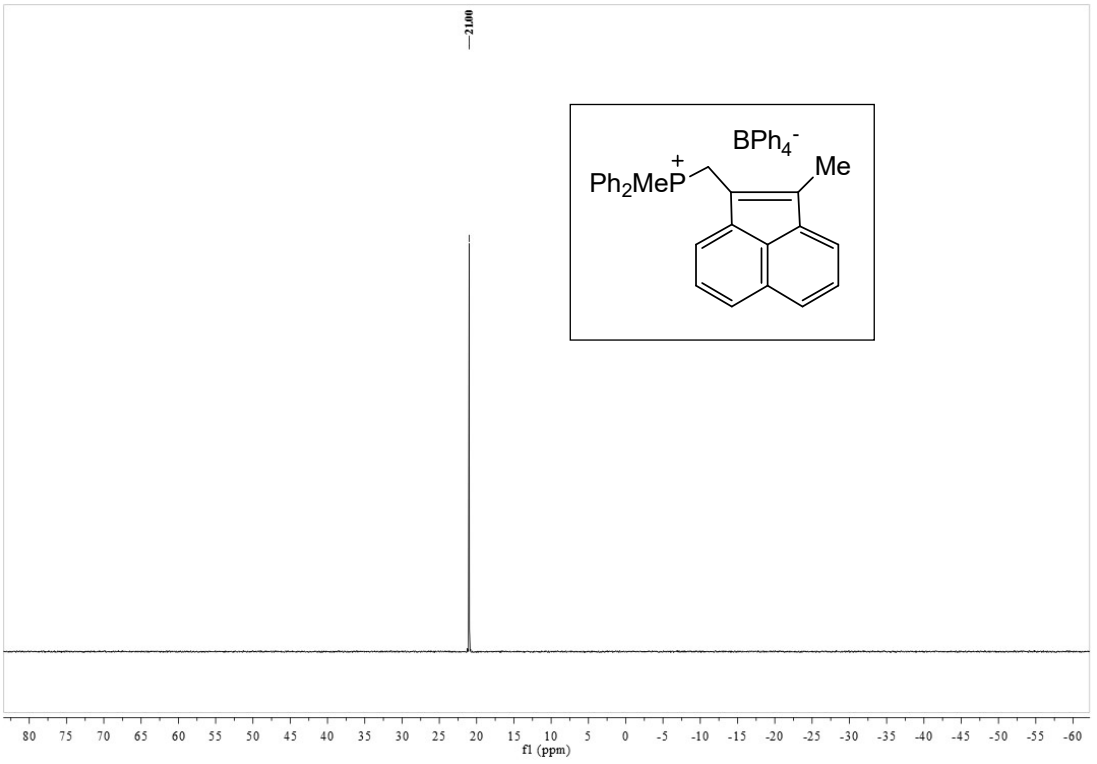


Figure S35. The $^{31}P\{^{1}H\}$ NMR spectrum of acenaphthylene compound **3a** in acetone-d_6 at 162.0MHz.

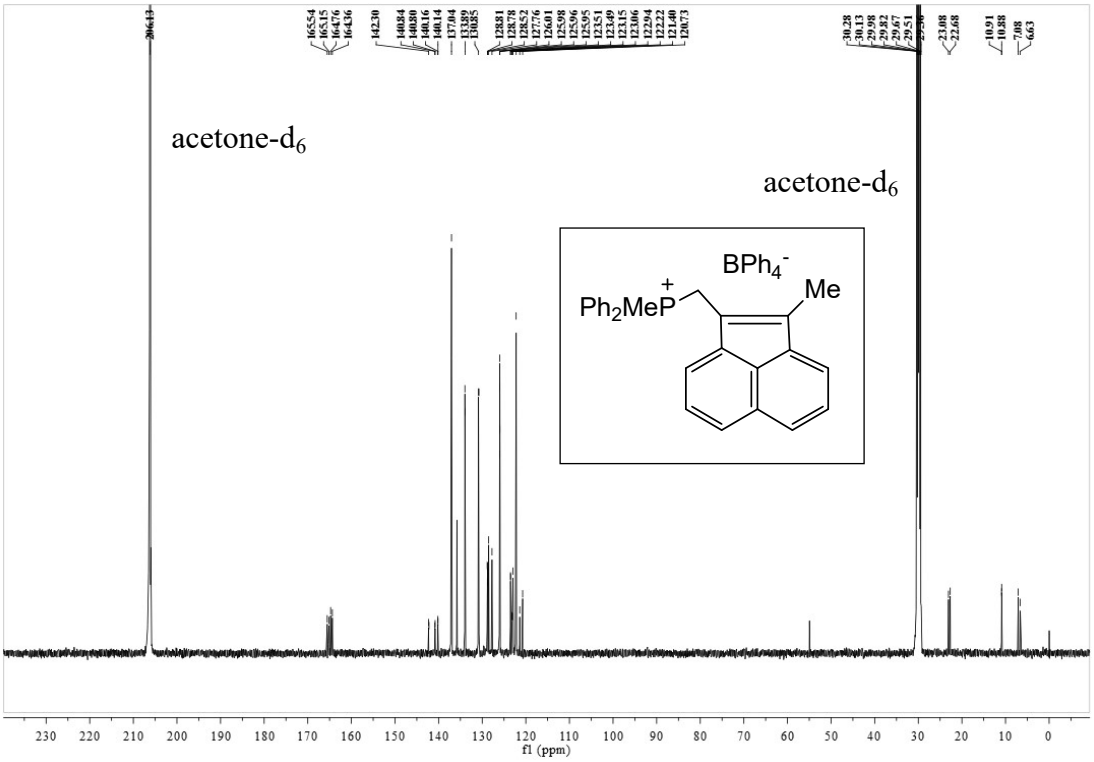
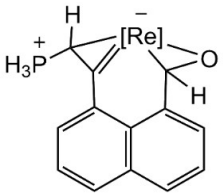


Figure S36. The $^{13}C\{^{1}H\}$ NMR spectrum of acenaphthylene compound **3a** in acetone-d_6 at 100.6 MHz.

5. The Calculated Cartesian Coordinates with Electronic Energies



[Re] = $ReCl_3(PH_3)$

M1

E = -2721.05743029 A.U.

Re	1.06084400	-0.15741400	0.03719100
Cl	2.82751100	0.75717800	-1.43331000
Cl	2.54082600	0.32422800	1.91845500
Cl	2.17857300	-2.33635800	-0.27918300
P	0.73123400	2.89058500	-1.23749600
P	0.21744000	-1.58020300	1.82261500
O	0.14628900	-0.38608800	-1.82422500
C	0.62121700	1.96880600	0.28384600
H	1.15829900	2.44514000	1.10334600
C	-0.40619800	1.00646300	0.45103600
C	-1.83306100	1.05439200	0.51702800
C	-2.60310000	-0.00125200	-0.07142200
C	-1.99850500	-1.07766700	-0.78271200
C	-0.52985600	-1.22240000	-1.05758000
H	-0.23852700	-2.27047500	-1.15507100
C	-2.80376000	-2.08943000	-1.26759000
H	-2.34303900	-2.91998700	-1.79032500
C	-4.20409800	-2.05847200	-1.12633100
H	-4.79974400	-2.86585400	-1.53471000
C	-4.80551900	-1.00758300	-0.48885500
H	-5.88391700	-0.96439300	-0.38793500
C	-4.02568600	0.04264900	0.05405800
C	-4.63160300	1.14014600	0.71165300
H	-5.71223900	1.16212600	0.79554300
C	-3.87579100	2.16605800	1.22479500
H	-4.35459000	3.00369800	1.71717300
C	-2.47928000	2.12609300	1.12338400
H	-1.88253200	2.92360700	1.55006400
H	1.95746200	3.52351000	-1.43156600
H	-0.18550900	3.96106300	-1.28566500
H	0.43794400	2.12738000	-2.36516800
H	-0.56812500	-0.97390200	2.82199100
H	-0.60872000	-2.66547200	1.48050600
H	1.21347300	-2.20004400	2.58030600

E = -79.8562599892

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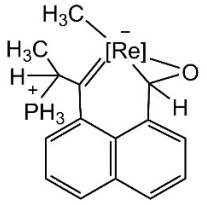
C	0.00000000	0.00000000	-0.76508100
H	0.88192900	0.50918200	-1.16366500
H	-0.88192900	0.50918200	-1.16366500
H	0.00000000	-1.01836400	-1.16366500
H	-0.88192900	-0.50918200	1.16366500



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Cl	2.32223500	-2.24092200	0.95289600
P	-1.13092100	3.47184900	-1.13349200
P	0.51144600	-0.68300800	2.17950500
O	0.35428700	-1.33481300	-1.63392000
C	-0.19558400	2.49032900	0.15541300
C	-0.50266000	0.99409200	0.07703700
C	-1.91222400	0.65409000	0.23301600
C	-2.47581700	-0.66044200	-0.05054200
C	-1.69975400	-1.80188400	-0.38134400
C	-0.22313600	-1.83017300	-0.53806100
H	0.20362500	-2.76969100	-0.18764500
C	-2.30352800	-3.03502900	-0.55830100
H	-1.67455100	-3.89034600	-0.77551900
C	-3.69163900	-3.20249600	-0.48339500
H	-4.13044100	-4.17973500	-0.64402100
C	-4.47613400	-2.11762700	-0.20779100
H	-5.55401300	-2.21353900	-0.14672300
C	-3.90247100	-0.84486700	0.02058100
C	-4.75930300	0.23943000	0.31523400
H	-5.82902200	0.06972900	0.34361000
C	-4.23320700	1.47505500	0.56910000
H	-4.87777600	2.31012500	0.81802600
C	-2.84851900	1.66289500	0.54041000

H	-2.51010300	2.63937700	0.84295000
H	-0.23318600	4.17600300	-1.94591800
H	-1.99896900	4.48214300	-0.68342600
H	-1.90431300	2.71872000	-2.01553900
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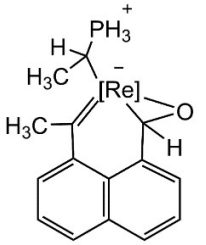
H	-0.17697300	-1.87123500	2.47070400
H	1.54612800	-0.67083100	3.11638400
H	0.82200100	2.65206200	-0.18425500
C	-0.25171100	3.17562500	1.54204100
H	-0.04284800	4.24594000	1.45528500
H	-1.18410100	3.04100100	2.08282400
H	0.55817700	2.74304900	2.12779200
C	1.16084300	1.21330500	-1.93694100
H	1.91491700	1.98534000	-1.78984700
H	1.44834300	0.58700100	-2.77275400
H	0.18346900	1.63542200	-2.18673300



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Cl	-1.29485300	-0.35290700	-2.70574400
P	-2.18704000	-2.13668200	1.86088400
P	0.17711900	1.73934300	-1.76650700
O	-0.28065500	-1.86385700	-0.12003900
C	-1.59662900	-0.42083200	1.89592500
H	-0.73161300	-0.46425100	2.55794100
C	0.63928800	0.92290200	0.87416300
C	2.09901500	0.94085500	0.62196500
C	2.79991300	-0.23627100	0.19006700
C	2.12424600	-1.37029400	-0.31963500
C	0.71403300	-1.30999400	-0.80502800
H	0.66345500	-1.47049000	-1.88237800
C	2.82629500	-2.52482900	-0.59666900
H	2.29940300	-3.37390300	-1.01743200
C	4.21536500	-2.60574800	-0.39241400
H	4.73685200	-3.53144100	-0.60403000
C	4.90588000	-1.49653600	0.01605800

H	5.98447400	-1.52371700	0.12173100
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H	4.81134300	2.93553500	1.21486000
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H	2.37643600	2.96747200	1.27039700
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H	1.24305500	1.28860400	-2.56576500
H	-0.66910500	2.35798300	-2.68789300
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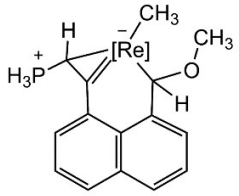
H	-3.64581100	0.32545100	1.97213000
C	0.31141800	1.80533300	2.05707800
H	1.05856100	1.72970000	2.84992300
H	0.30838400	2.84383900	1.69785600
H	-0.67103500	1.65762000	2.47366000



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Cl	-1.61567900	0.16502600	-2.54024900
Cl	-1.98097000	-2.53617600	0.12314900
P	-1.52957500	2.96520400	1.01985700
P	0.11344500	-1.69070300	-1.60969900
O	0.93629200	-0.99687100	2.52741400
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H	-1.13476600	2.32212800	-1.22250800
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C	2.60566100	0.20732100	-0.06496600
C	2.17318300	-1.01623600	0.50673600
C	0.80321900	-1.20890500	1.13446600
H	0.50283600	-2.25109100	1.07804900

C	3.08993700	-2.04321200	0.63737100
H	2.77195400	-2.97366900	1.09347900
C	4.42441400	-1.90655900	0.21609600
H	5.10614200	-2.74172500	0.32339600
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H	5.89729200	-0.59187400	-0.60687200
C	3.97187300	0.37069400	-0.44641400
C	4.40460600	1.62249200	-0.95168900
H	5.44482100	1.73618100	-1.23542300
C	3.53278600	2.67429000	-1.07938800
H	3.87768700	3.62621000	-1.46405700
C	2.18085800	2.51158600	-0.73845400
H	1.48625300	3.32896400	-0.88891600
H	-2.87162100	2.65686500	1.29248900
H	-1.53675000	4.32652600	0.67282000
H	-0.83803900	2.93954000	2.23385600
H	1.07921300	-1.10374000	-2.44591900
H	0.85653200	-2.74267500	-1.04596300
H	-0.70041100	-2.38891900	-2.49669900
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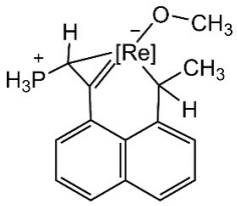
H	1.43751600	0.17209700	4.08312800
H	2.47029900	0.41635700	2.65617300
C	-1.70715200	-0.16515400	2.08150400
H	-0.99108400	-0.62369000	2.74835900
H	-1.92138700	0.84710000	2.43657900
H	-2.64602000	-0.70787400	2.11540600



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Cl	1.19312900	0.30090200	2.64173300
Cl	2.04945800	-2.33813200	0.05844100
P	1.43302800	2.61020600	-1.38516200
P	-0.34798400	-1.67061400	1.57087800
O	1.41580300	0.42006100	-1.76765300
C	0.67417500	2.01348500	0.13189600
H	0.92099400	2.62774600	0.99552000
C	-0.46064300	1.17049600	0.07932600

C	-1.87143000	1.35175100	0.03936400
C	-2.72646200	0.23721600	-0.23435300
C	-2.19802900	-0.99241900	-0.73290400
C	-0.77192500	-1.07000700	-1.21040000
C	-3.07828400	-2.05482600	-0.85954100
H	-2.71914700	-3.00762200	-1.22278200
C	-4.45329700	-1.93017100	-0.57723700
H	-5.09701700	-2.79290600	-0.70198900
C	-4.97971800	-0.72837200	-0.19005300
H	-6.04303700	-0.61444400	-0.01434000
C	-4.12628700	0.38760300	-0.01482700
C	-4.63361200	1.65253700	0.36998400
H	-5.70178800	1.75578900	0.52523500
C	-3.80325700	2.73464100	0.54102800
H	-4.21085000	3.69677900	0.82569300
C	-2.42068600	2.58423600	0.38252800
H	-1.75852500	3.41899300	0.57707200
H	2.79351900	2.38039800	-1.57476400
H	1.44336700	4.01231200	-1.16635400
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H	-0.96401200	-2.75736600	0.93102600
H	0.38958700	-2.31620600	2.56279100
H	-0.63611900	-0.28223700	-1.94553600
C	2.45941500	-0.10066800	-2.58319900
H	2.30849300	-1.16593200	-2.75897800
H	2.42299500	0.41911400	-3.54705700
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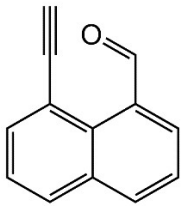
C	-0.40905000	-2.38615600	-1.87822300
H	-1.10845300	-2.57941400	-2.70071500
H	0.59142500	-2.34943200	-2.29727100
H	-0.43731100	-3.24722800	-1.20918100



E = -575.501596632 A.U.

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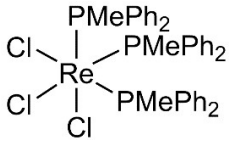
C	-1.54534600	0.47887600	-0.03061300
C	-0.18319400	0.03792300	0.01492600
C	0.83887900	1.04560500	0.04647600

C	0.48752700	2.37830000	-0.11976600
H	-3.61974500	-0.09353500	0.07990700
H	-1.07661800	3.83218000	-0.39672500
H	-2.88766000	2.15181600	-0.24135800
C	-2.59965400	-0.45968800	0.11087500
C	0.04596000	-1.37660100	0.08855700
H	1.27451600	3.12092500	-0.09708600
C	-1.01505200	-2.23863800	0.28249600
C	-2.34573200	-1.78914500	0.30389300
H	-0.81094000	-3.30141800	0.36023900
H	-3.15606300	-2.49490600	0.43764900
C	2.20273000	0.78397900	0.37393600
C	3.34503400	0.67537700	0.72673700
H	4.36104800	0.53049700	1.00097400
C	1.31786200	-2.06970000	-0.24664000
H	1.38218900	-3.09432000	0.18014600
O	2.17497800	-1.65611600	-0.98551100

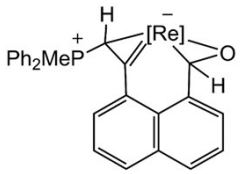


E = -3993.36082040 A.U.

Re	-0.05898400	0.68322300	-0.82604000
Cl	1.62825100	1.09150500	-2.52955800
Cl	-1.48120800	0.80419700	-2.79905000
Cl	-0.28481600	2.64797900	0.55884200
P	-2.38155200	0.44344000	0.21947800
C	-3.41063800	1.99904400	0.23800300
C	-2.50159500	-0.09827500	1.98849700
C	-3.61585700	-0.64320600	-0.61251400
C	-3.28930500	2.95927500	-0.76886400
C	-4.41007900	2.16362400	1.20053800
C	-3.11928100	-1.29891700	2.35028800
C	-1.94634200	0.69368100	3.00143300
H	-3.69727000	-0.30302100	-1.64204900
H	-3.31854600	-1.68658800	-0.61424900
H	-4.57771600	-0.52684700	-0.11367600
C	-4.14363600	4.05426600	-0.80654300
H	-2.53053100	2.85447900	-1.52964000
C	-5.26156700	3.26262300	1.16336000
H	-4.52963600	1.43734900	1.99372400
C	-3.17449300	-1.70064800	3.68230000
H	-3.56242100	-1.93680700	1.59792000
C	-2.00618300	0.29451600	4.32999000

H	-1.47469400	1.63296500	2.74632700
C	-5.13076200	4.21274800	0.15897800
H	-4.03043400	4.78853300	-1.59541200
H	-6.02592300	3.37257000	1.92398400
C	-2.61911500	-0.90652600	4.67665400
H	-3.65964200	-2.63525500	3.93872600
H	-1.57730900	0.92763300	5.09796500
H	-5.79206900	5.07089100	0.12916100
H	-2.66823000	-1.21537800	5.71423600
P	2.07158400	0.76578500	0.55757900
C	3.09373200	2.32101800	0.41488900
C	3.42911100	-0.47769000	0.32482600
C	1.80918000	0.72703200	2.38680100
C	4.25911300	2.40768000	1.18565900
C	2.76103500	3.39708500	-0.40681400
C	3.71315000	-1.44967500	1.28597000
C	4.24801300	-0.40360600	-0.80982000
H	1.22387500	1.60564100	2.64589200
H	1.25444200	-0.16265400	2.67260300
H	2.75655900	0.75638000	2.92319000
C	5.05973500	3.54150700	1.14766800
H	4.56466000	1.57810600	1.81117300
C	3.56604000	4.53083900	-0.44838400
H	1.87893800	3.35643400	-1.02454400
C	4.78272400	-2.32511600	1.12079200
H	3.10413300	-1.53973000	2.17457400
C	5.30937100	-1.28313300	-0.97652500
H	4.05448100	0.34881600	-1.56182600
C	4.71350200	4.61042000	0.32907600
H	5.95733400	3.58456400	1.75359100
H	3.28875300	5.35346200	-1.09682100
C	5.58280200	-2.24708100	-0.01067700
H	4.98492600	-3.06851000	1.88276700
H	5.93098800	-1.20629900	-1.86090100
H	5.33778900	5.49570600	0.29405600
H	6.41784400	-2.92613700	-0.13779700
P	0.17348200	-1.74099100	-0.95872000
C	-1.24021300	-2.78664100	-1.57502700
C	0.68858800	-2.74310300	0.50844500
C	1.41012400	-2.21010700	-2.25218000
C	-1.69321700	-2.61286700	-2.88763900
C	-1.84059600	-3.77346700	-0.78829500
C	1.45255000	-3.90534800	0.36217500
C	0.23518100	-2.40330800	1.78209000

H	1.16284600	-1.66986300	-3.16309700
H	2.40748300	-1.90933400	-1.94089200
H	1.37356100	-3.28093400	-2.44758800
C	-2.71952700	-3.40071300	-3.39283900
H	-1.26212700	-1.84558100	-3.51527800
C	-2.87170200	-4.55906200	-1.29565700
H	-1.50754000	-3.93990600	0.22698300
C	1.75601000	-4.69864700	1.46117300
H	1.82247400	-4.20243500	-0.60877700
C	0.53122300	-3.20106700	2.88378400
H	-0.35715300	-1.51054300	1.91658800
C	-3.31556300	-4.37462500	-2.59869000
H	-3.05690200	-3.24680200	-4.41096500
H	-3.32270500	-5.31905500	-0.66807800
C	1.29481600	-4.35089600	2.72652500
H	2.35558400	-5.59114000	1.32639600
H	0.15889700	-2.91893100	3.86122000
H	-4.11782000	-4.98604800	-2.99459900
H	1.52836800	-4.97332200	3.58238300



[Re] = $ReCl_3(PMePh_2)$

complex 1

E = -3724.18991905 A.U.

Re	-0.18551400	-1.33933900	-0.45637800
Cl	1.58842300	-2.71443700	-1.45785400
Cl	0.36523500	-2.58452400	1.59574700
Cl	-1.61234900	-3.20697600	-1.26912900
P	2.97610500	0.31906000	-0.57168300
P	-2.30045800	-1.10090200	1.00396000
O	-0.21887100	-0.70398500	-2.42334200
C	1.48157800	-0.10302000	0.33365400
H	1.75010900	-0.39680800	1.35025600
C	0.21557200	0.47119300	0.03878300
C	-0.24911400	1.82377400	-0.10586000
C	-1.20655000	2.14911300	-1.12043800
C	-1.74438000	1.16548100	-1.99493600
C	-1.39127900	-0.29155100	-1.97099800
H	-2.23897100	-0.92366400	-2.23896100
C	-2.66999100	1.54779800	-2.94357700
H	-3.09810400	0.79130600	-3.59083000
C	-3.07178400	2.88821400	-3.09091900

H	-3.79134000	3.14903200	-3.85795600
C	-2.56066500	3.85206700	-2.26444800
H	-2.86458500	4.88804100	-2.36519000
C	-1.62495600	3.50991500	-1.25805500
C	-1.09443700	4.49188900	-0.38772600
H	-1.42436000	5.51879100	-0.50023400
C	-0.17481200	4.15854200	0.57551800
H	0.22584100	4.91825000	1.23572800
C	0.25612500	2.83161700	0.70599300
H	0.98801900	2.57853600	1.46173800
C	2.73983100	0.36605300	-2.36571700
H	3.65194600	0.72217200	-2.84467500
H	1.89751300	1.01131700	-2.61132500
H	2.49671900	-0.64454200	-2.68897800
C	3.57421700	1.97223500	-0.06635900
C	3.45318600	3.08561500	-0.89946300
H	3.02264100	2.98948900	-1.88729700
C	3.87924000	4.33634200	-0.46582800
H	3.78297700	5.19179000	-1.12323400
C	4.42185800	4.48814000	0.80395000
H	4.75422600	5.46314800	1.13962700
C	4.54163000	3.38378000	1.64268500
H	4.96843200	3.49521600	2.63213500
C	4.12359500	2.13316600	1.21064200
H	4.23757300	1.27744000	1.86529100
C	4.32977500	-0.80415900	-0.12657200
C	5.63250400	-0.47473300	-0.51868100
H	5.82724700	0.44084700	-1.06483400
C	6.68882200	-1.31554200	-0.20115900
H	7.69363900	-1.05978000	-0.51467900
C	6.45403100	-2.48122600	0.52263200
H	7.27980200	-3.13633200	0.77402700
C	5.16339000	-2.80630900	0.91947300
H	4.97509100	-3.71656500	1.47491600
C	4.09540200	-1.97747900	0.59226300
H	3.09119200	-2.26200900	0.87403400
C	-2.18620300	-0.10272200	2.56132200
C	-0.96341100	0.29285300	3.10000200
H	-0.04775500	0.05670600	2.58174300
C	-0.90472300	0.95596800	4.32166900
H	0.05774300	1.24970000	4.72372500
C	-2.06825000	1.22993100	5.02748500
H	-2.02178400	1.74563300	5.97947400
C	-3.29433200	0.82915900	4.50811100

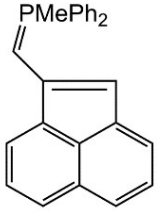
H	-4.20959200	1.02884900	5.05282400
C	-3.35233300	0.16626400	3.28940200
H	-4.31747100	-0.13504600	2.90332200
C	-2.91119400	-2.69272100	1.70332800
H	-3.01888200	-3.42946800	0.91304300
H	-3.86595500	-2.50843500	2.19564700
H	-2.17863700	-3.05094400	2.42089500
C	-3.80979000	-0.43631200	0.18023100
C	-4.18599900	0.90482300	0.29691100
H	-3.59234700	1.58713500	0.89020300
C	-5.32927000	1.37698300	-0.33578700
H	-5.60655200	2.41885500	-0.22952000
C	-6.10756500	0.52043400	-1.10529300
H	-7.00019400	0.88885700	-1.59718900
C	-5.73291800	-0.81107900	-1.24237600
H	-6.32866100	-1.48605500	-1.84544600
C	-4.59369200	-1.28901700	-0.60508700
H	-4.30663500	-2.32345500	-0.73498600

$PMePh_2$

E = -844.730983431 A.U.

P	0.04150700	1.36075900	-0.68465900
C	1.43828000	0.24891600	-0.18755400
C	2.63156400	0.35060600	-0.90688300
C	1.37223800	-0.65888700	0.87378000
C	3.73751300	-0.42246400	-0.56745200
H	2.69197600	1.03836200	-1.74330600
C	2.47273500	-1.43737000	1.20922300
H	0.45194200	-0.76505200	1.43602400
C	3.65924600	-1.31902900	0.49104300
H	4.65578300	-0.32946900	-1.13566500
H	2.40505100	-2.13902700	2.03278900
H	4.51642000	-1.92818600	0.75322800
C	-1.43472600	0.32511300	-0.28855000
C	-2.36220100	0.62817700	0.71107100
C	-1.68243000	-0.78606400	-1.10551700
C	-3.49640100	-0.15908300	0.89488200
H	-2.21039800	1.48196500	1.35892100
C	-2.80485900	-1.57839700	-0.91498400
H	-0.98536200	-1.03250600	-1.89932900
C	-3.71993700	-1.26550500	0.08690900
H	-4.20374100	0.09539500	1.67594900
H	-2.97165600	-2.43758100	-1.55433800
H	-4.60164700	-1.87854100	0.23149500

C	0.07761300	2.57084100	0.72582100
H	1.01126000	3.13012400	0.65240000
H	-0.74645300	3.27924000	0.62485300
H	0.03241300	2.09275500	1.70613100



B

E = -1345.01973360 A.U.

P	-1.40796700	-0.27184400	0.50819300
C	-0.22356000	-1.22110700	-0.25621000
H	-0.65351700	-2.12380400	-0.67206000
C	1.20310500	-1.13829000	-0.25621800
C	2.08280900	-0.03175700	0.25045900
C	3.41360800	-0.44655400	0.02604400
C	3.42874200	-1.72233600	-0.59677200
C	2.04536000	-2.11680200	-0.75550600
C	4.66082200	-2.26826600	-0.89316100
H	4.75348400	-3.23777300	-1.37047800
C	5.83754100	-1.53901100	-0.56645600
H	6.79805700	-1.98270000	-0.80564900
C	5.80725400	-0.30072600	0.03330700
H	6.72868500	0.22261100	0.26187100
C	4.54852600	0.29266400	0.34994600
C	4.31848700	1.55742100	0.95179700
H	5.15723600	2.18575500	1.23207800
C	3.02866000	1.98990400	1.17137900
H	2.86469200	2.96239000	1.62175300
C	1.89576000	1.20835200	0.82188700
H	0.91423200	1.62929400	0.99654600
C	-1.23875100	-0.03869800	2.32402200
H	-1.99247700	0.62706400	2.74533900
H	-0.25076000	0.37996100	2.51268500
H	-1.29030800	-1.01530100	2.80460700
C	-1.60146200	1.44580000	-0.13637200
C	-2.45549200	2.37539900	0.46531400
H	-3.00984300	2.11618500	1.35950900
C	-2.61839600	3.63902100	-0.08674200
H	-3.28588400	4.35109400	0.38403200
C	-1.92682100	3.98859400	-1.24303200
H	-2.05179500	4.97632700	-1.67082600
C	-1.07830200	3.06924300	-1.84776900

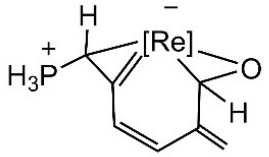
H	-0.53555100	3.33818500	-2.74605300
C	-0.92062700	1.80037800	-1.30081400
H	-0.26278200	1.07636000	-1.76632100
C	-3.00879700	-1.09054200	0.22463500
C	-3.40103000	-1.35769000	-1.09181900
H	-2.75525700	-1.07452300	-1.91365600
C	-4.60935000	-1.99015600	-1.34907600
H	-4.89948000	-2.19683000	-2.37220600
C	-5.44723500	-2.35181100	-0.29874000
H	-6.39163100	-2.84268300	-0.50132600
C	-5.07088800	-2.07866600	1.01025900
H	-5.71835600	-2.35806200	1.83274300
C	-3.85813700	-1.45013800	1.27220400
H	-3.57949600	-1.25291100	2.29894200
H	1.70931500	-3.04832000	-1.18983000

$Re(=O)Cl_3(PMePh_2)_2$

E = -3223.93871367 A.U.

Re	0.00001700	-0.10451700	-0.00003600
Cl	-0.00011500	-2.58526900	0.00056700
Cl	-0.53151300	-0.24365100	2.37084500
P	2.43884700	-0.37241600	0.65713500
O	0.00017800	1.56960100	-0.00034100
C	3.66075600	-0.97864900	-0.57325400
C	3.31639900	-2.02001100	-1.43922300
H	2.31048800	-2.41532600	-1.44040700
C	4.26340200	-2.54440700	-2.30987500
H	3.98294500	-3.34823200	-2.97977200
C	5.55671900	-2.03539500	-2.33160700
H	6.29063900	-2.44362900	-3.01654000
C	5.90461200	-0.99787800	-1.47486600
H	6.91003900	-0.59396500	-1.48646500
C	4.96318600	-0.47171900	-0.59832900
H	5.24664100	0.33825000	0.06089700
C	2.67574500	-1.51047100	2.07011300
H	2.02037500	-1.22272900	2.89010700
H	3.72160300	-1.51297700	2.37794400
H	2.39182600	-2.50705700	1.73509200
C	3.05969800	1.26307200	1.19241400
C	3.14145500	2.29105600	0.24643300
H	2.85656600	2.10547800	-0.78230900
C	3.57990300	3.55247500	0.62006300
H	3.64056600	4.33999200	-0.12133700
C	3.93006400	3.80802300	1.94317800

H	4.26660600	4.79587300	2.23456200
C	3.83980400	2.79604100	2.88919900
H	4.10290000	2.98997400	3.92210600
C	3.40649500	1.52692500	2.51749100
H	3.33536400	0.75330500	3.26981500
Cl	0.53150600	-0.24478400	-2.37077600
P	-2.43880000	-0.37260000	-0.65705400
C	-3.66078400	-0.97846100	0.57346200
C	-4.96334800	-0.47181600	0.59785400
C	-3.31644100	-2.01920300	1.44016800
C	-5.90490700	-0.99765500	1.47443500
H	-5.24680000	0.33770400	-0.06192600
C	-4.26357800	-2.54327800	2.31087800
H	-2.31044400	-2.41429300	1.44188500
C	-5.55702000	-2.03456500	2.33192100
H	-6.91043100	-0.59396900	1.48549000
H	-3.98311700	-3.34661900	2.98135300
H	-6.29104200	-2.44254900	3.01689300
C	-3.05958600	1.26280500	-1.19267200
C	-3.40639900	1.52641100	-2.51779100
C	-3.14129600	2.29096900	-0.24688000
C	-3.83965900	2.79547700	-2.88974100
H	-3.33532100	0.75263500	-3.26996300
C	-3.57970500	3.55232800	-0.62074700
H	-2.85640200	2.10556300	0.78189200
C	-3.92986700	3.80763700	-1.94391000
H	-4.10275400	2.98922200	-3.92268200
H	-3.64035000	4.33997700	0.12051300
H	-4.26638300	4.79544200	-2.23548100
C	-2.67579500	-1.51095500	-2.06976800
H	-3.72167000	-1.51354300	-2.37753700
H	-2.02046900	-1.22340600	-2.88986500
H	-2.39185200	-2.50746600	-1.73453300



[Re] = $ReCl_3(PH_3)$

M1'

E = -2491.10762567 A.U.

Re	0.26523036	1.46805891	-0.00072724
Cl	1.63105057	2.39506091	1.84480132
Cl	2.34524024	1.19930548	-1.23725682
Cl	0.10001907	3.79784943	-0.79457569

P	0.87311766	-0.38784126	2.68169522
P	-0.48238146	1.31021236	-2.31155478
O	-1.22654838	1.82328422	1.41414567
C	0.93099050	-0.41103396	0.89956589
H	1.88530509	-0.77138167	0.51737001
C	-0.26774858	-0.37561022	0.14570117
C	-1.42101947	-1.19242518	0.03097111
C	-2.66387392	-0.65839050	-0.02884190
C	-2.95393107	0.76428579	-0.00625685
C	-1.90625723	1.79959867	0.28331074
H	-2.16287297	2.77768192	-0.12767773
C	-4.19721382	1.19881344	-0.27789230
H	-4.43479745	2.25515242	-0.29426091
H	2.09916706	-0.10082938	3.27860062
H	0.54611845	-1.64779231	3.22384646
H	-0.08941897	0.47669217	3.19708399
H	-0.56254077	0.02673992	-2.88544554
H	-1.75551752	1.81016118	-2.63697649
H	0.33661577	1.97942837	-3.22412277
H	-5.00632449	0.50701662	-0.48165088
H	-3.51755586	-1.32473398	-0.10555696
H	-1.30454678	-2.27253164	0.06308864

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