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Supporting Information

Cycloaddition of di-substituted epoxides and CO_2 under ambient conditions catalysed by rare-earth poly(phenolate) complexes

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Contents

1. Experimental section

General considerations

Synthesis of all complexes and cyclic carbonates were conducted under argon atmosphere using standard Schlenk techniques or in nitrogen-filled glove boxes. All commercially available epoxides were purchased from 3A Chemicals, Aladdin, Energy Chemical, Macklin or TCI and are > 98% pure. All liquid epoxides were desiccated with CaH_2 and distilled under argon atmosphere prior to usage. All solid compounds (*e.g.*, ligand precursors) were vacuum dried at 25 °C for two days. CO_2 was used as received. The solvents (*e.g.*, toluene, *n*-hexane, and tetrahydrofuran) were desiccated with sodium or CaH_2 for two days and distilled before use. X-ray crystallography data were collected using an Agilent Gemini Atlas or Bruker D8 QUEST CCD X-ray diffractometer. Data reduction was conducted through the Bruker APEX program, and the structures were solved and refined using the OLEX2 application. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Ascend 400 instrument or an Agilent DD2-600 spectrometer. Elemental analysis was performed on an Elementar Vario EL III analyzer. Infrared spectra were recorded on a ThermoFisher Nicolet 6700 spectrometer scanning the wavenumber range 400-4000 cm^{-1} region.

Synthesis of ligand precursors L^nH_3 (n =1-3)

N'-(2-aminoethyl)-*N*,*N*-dimethyl-1,2-ethylenediamine ($Me_2N(CH_2)_2NH(CH_2)_2NH_2$, *$Me_2NNN$*) (7.86 g, 11.4 mmol, 57%) was synthesized following a literature precedure.[1] ^{1}H NMR (400 MHz, C_6D_6) δ 2.61-2.56 (m, 2H, ($CH_2N(CH_3)_2$), 2.54-2.50 (m, 2H, $(CH_3)_2NCH_2CH_2$), 2.49-2.44 (m, 2H, $NHCH_2$), 2.27-2.21 (m, 2H, CH_2NH_2), 2.02 (s, 6H, $N(CH_3)_2$), 1.22 (s, 3H, $NHCH_2CH_2NH_2$). ^{13}C NMR (101 MHz, C_6D_6) δ 59.1 ($CH_2N(CH_3)_2$), 52.7 ($NCH_2CH_2N(CH_3)_2$), 47.1 ($NHCH_2$), 45.4 (CH_2NH_2), 41.7 ($N(CH_3)_2$).

L^1H_3 (R^1 = R^2 = ^{t}Bu). Ligand precursor **L^1H_3** was synthesized through Mannich reaction.[2] 2,4-di-*tert*-butylphenol (12.8 g, 62 mmol), paraformaldehyde (1.8 g, 60 mmol) and *Me_2NNN* (2.6 g, 20 mmol) were placed in a 100 mL flask and heated at

90 °C for 3 days. After reaction, all volatiles were removed in vacuo. Crude products were purified through column chromatography using petroleum ether/ethyl acetate (93:7) as eluents. White solids were obtained after removal of all volatiles under vacuum (9.6 g, 12.2 mmol, 61%). ^{1}H NMR (400 MHz, C_6D_6) δ 9.10 (s, 3H, O*H*), 7.48 (d, *J* = 2.2 Hz, 1H, Ar*H*), 7.45 (d, *J* = 2.2 Hz, 2H, Ar*H*), 6.94 (d, *J* = 2.1 Hz, 2H, Ar*H*), 6.92 (d, *J* = 2.1 Hz, 1H, Ar*H*), 3.42 (s, 2H, ArC*H*$_2$N), 3.38 (s, 4H, ArC*H*$_2$N), 2.56 (d, *J* = 6.1 Hz, 2H, NC*H*$_2$CH$_2$N), 2.51 (d, *J* = 6.1 Hz, 2H, NCH$_2$C*H*$_2$N), 2.24 (t, *J* = 5.5 Hz, 2H, NC*H*$_2$CH$_2$N(CH$_3$)$_2$), 2.16 (t, *J* = 5.5 Hz, 2H, C*H*$_2$N(CH$_3$)$_2$), 1.91 (s, 6H, N(C*H*$_3$)$_2$), 1.66 (s, 9H, C(C*H*$_3$)$_3$), 1.61 (s, 18H, C(C*H*$_3$)$_3$), 1.36 (s, 9H, C(C*H*$_3$)$_3$), 1.33 (s, 18H, C(C*H*$_3$)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 152.4, 141.4, 140.4, 136.0, 125.0, 124.2, 123.5, 123.0, 121.6, 121.3 (Ar-*C*), 58.0, 57.3, 56.8 (Ar*C*H$_2$N), 51.4 (N*C*H$_2$CH$_2$N), 50.8 (NCH$_2$*C*H$_2$N), 50.7 (N*C*H$_2$CH$_2$N(CH$_3$)$_2$), 45.6 (*C*H$_2$N(CH$_3$)$_2$), 34.9 (N(*C*H$_3$)$_2$), 34.8, 34.2 (*C*(CH$_3$)$_3$), 34.1, 31.7, 29.8, 29.6 (C(*C*H$_3$)$_3$).

L^{2}H$_3$ (R^1 = ^{t}Bu, R^2 = CH$_3$). 2-*tert*-butyl-4-methylphenol (5.09 g, 31 mmol), paraformaldehyde (0.9 g, 30 mmol) and *Me$_2$NNN* (1.30 g, 10 mmol) were placed in a 100 mL flask and heated at 90 °C for 3 days. After reaction, the crude product was washed with methanol (3 × 5 mL) to give white solids (5.6 g, 8.5 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 1.6 Hz, 2H, Ar*H*), 6.96 (d, *J* = 1.6 Hz, 1H, Ar*H*), 6.71-6.68 (m, 2H, Ar*H*), 6.62-6.60 (m, 1H, Ar*H*), 3.65 (s, 2H, ArC*H*$_2$N), 3.59 (s, 4H, ArC*H*$_2$N), 2.75-2.70 (m, 2H, NC*H*$_2$CH$_2$N), 2.70-2.64 (m, 2H, NCH$_2$C*H*$_2$N), 2.48 (d, *J* = 5.6 Hz, 2H, NC*H*$_2$CH$_2$N(CH$_3$)$_2$), 2.43 (t, *J* = 5.8 Hz, 2H, C*H*$_2$N(CH$_3$)$_2$), 2.22 (s, 6H, ArC*H*$_3$), 2.21 (s, 3H, ArC*H*$_3$), 2.14 (s, 6H, N(C*H*$_3$)$_2$), 1.38 (s, 18H, C(C*H*$_3$)$_3$), 1.36 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 152.6, 136.8, 136.7, 128.8, 128.1, 127.9, 127.3, 127.0, 126.8, 122.0 (Ar-*C*), 57.5, 57.1, 56.9 (Ar*C*H$_2$N), 51.3 (N*C*H$_2$CH$_2$N), 50.6 (NCH$_2$*C*H$_2$N), 50.5 (N*C*H$_2$CH$_2$N(CH$_3$)$_2$), 45.6 (*C*H$_2$N(CH$_3$)$_2$), 34.6 (N(*C*H$_3$)$_2$), 34.5 (*C*(CH$_3$)$_3$), 29.7, 29.6 (C(*C*H$_3$)$_3$), 20.82, 20.77 (Ar-*C*H$_3$).

L^{3}H$_3$ (R^1 = R^2 = CH$_3$). 2,4-dimethylphenol (3.8 g, 31 mmol), paraformaldehyde (0.9 g, 30 mmol) and *Me$_2$NNN* (1.3 g, 10 mmol) were placed in a 100 mL flask and heated at 90 °C for 3 days. After reaction, all volatiles were removed in vacuo. Crude products were purified through column chromatography using petroleum ether/ethyl

acetate (25:75) as eluents. White solids were obtained after removal of all volatiles in vacuum (2.6 g, 4.9 mmol, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 8.5 Hz, 3H, Ar*H*), 6.68 (s, 2H, Ar*H*), 6.56 (s, 1H, Ar*H*), 3.66 (s, 4H, ArC*H*$_2$N), 3.58 (s, 2H, ArC*H*$_2$N), 2.83-2.77 (m, 2H, NC*H*$_2$CH$_2$N), 2.65 (d, *J* = 5.4 Hz, 1H, NCH$_2$C*H*$_2$N), 2.63 (d, *J* = 6.5 Hz, 1H, NCH$_2$C*H*$_2$N), 2.53 (s, 2H, NC*H*$_2$CH$_2$N(CH$_3$)$_2$), 2.42 (s, 2H, C*H*$_2$N(CH$_3$)$_2$), 2.21 (s, 6H, N(C*H*$_3$)$_2$), 2.19 (s, 9H, ArC*H*$_3$), 2.17 (s, 6H, ArC*H*$_3$), 2.15 (s, 3H, ArC*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 152.2, 130.9, 130.7, 128.5, 128.3, 127.4, 127.2, 124.9, 124.4, 121.7, 121.1 (Ar-*C*), 57.6, 56.2, 55.5 (Ar*C*H$_2$N), 50.5 (N*C*H$_2$CH$_2$N), 49.5 (NCH$_2$*C*H$_2$N), 48.7(N*C*H$_2$CH$_2$N(CH$_3$)$_2$), 45.4 (*C*H$_2$N(CH$_3$)$_2$), 31.6 (N(*C*H$_3$)$_2$), 22.7, 20.5, 15.9 (Ar-*C*H$_3$).

General procedures for the synthesis of rare-earth metal complexes.

Synthesis of complex 1. $LaCp_3$(THF) (0.41 g, 1 mmol) and L^1H_3 (0.79 g, 1 mmol) were dissolved with THF (10 mL), which was heated at 50 °C for 12 hours. After reaction, the solvent (THF) was removed under vacuum and the crude product was recrystallized from THF (3 mL). Colorless crystals were obtained at room temperature after 1 day (0.85 g, 0.86 mmol, 86%). Complex **1** is sensitive to air and moisture.

^{1}H NMR (400 MHz, C_6D_6) δ 7.64 (d, *J* = 2.6 Hz, 1H, Ar*H*), 7.57 (d, *J* = 2.6 Hz, 1H, Ar*H*), 7.52 (d, *J* = 2.6 Hz, 1H, Ar*H*), 7.32 (d, *J* = 2.6 Hz, 1H, Ar*H*), 6.98 (d, *J* = 2.5 Hz, 1H, Ar*H*), 6.78 (d, *J* = 2.6 Hz, 1H, Ar*H*), 4.15 (d, *J* = 11.7 Hz, 4H, THF), 4.06 (d, *J* = 12.9 Hz, 1H, ArC*H*$_2$N), 3.41-3.31 (m, 1H, ArC*H*$_2$N), 2.92 (d, *J* = 12.7 Hz, 1H, ArC*H*$_2$N), 2.85 (d, *J* = 14.4 Hz, 1H, ArC*H*$_2$N), 2.75 (d, *J* = 14.0 Hz, 1H, ArC*H*$_2$N), 2.70 (s, 1H, ArC*H*$_2$N), 2.10-2.00 (m, 2H, NC*H*$_2$CH$_2$N), 1.94-1.89 (m, 2H, NCH$_2$C*H*$_2$N), 1.87-1.86 (d, *J* = 5.2 Hz, 1H, NC*H*$_2$CH$_2$N(CH$_3$)$_2$), 1.82-1.80 (d, *J* = 6.28 Hz, 1H, NC*H*$_2$CH$_2$N(CH$_3$)$_2$), 1.78-1.77 (m, 2H, C*H*$_2$N(CH$_3$)$_2$), 1.71 (s, 9H, C(C*H*$_3$)$_3$), 1.66 (s, 9H, C(C*H*$_3$)$_3$), 1.63 (s, 6H, N(C*H*$_3$)$_2$), 1.60 (d, *J* = 13.6 Hz, 4H, THF), 1.55 (s, 9H, C(C*H*$_3$)$_3$), 1.52 (s, 9H, C(C*H*$_3$)$_3$), 1.44 (s, 9H, C(C*H*$_3$)$_3$), 1.39 (s, 9H, C(C*H*$_3$)$_3$).

^{13}C NMR (101 MHz, C_6D_6) δ 163.5, 163.2, 161.0, 137.5, 135.9, 135.87, 135.0, 134.7, 134.6, 129.0, 128.2, 126.1, 125.8, 125.6, 125.3, 124.56, 123.7, 123.5, 123.4, 123.0

(Ar-*C*), 69.3 (THF), 62.2, 61.3, 59.7 (Ar*C*H_2N), 57.6 (N*C*$H_2C H_2$N), 51.8 (NCH_2*C*H_2N), 35.13 (N*C*$H_2C H_2$N(CH_3)$_2$), 35.05 (*C*H_2N(CH_3)$_2$), 35.03 (N(*C*H_3)$_2$), 33.90, 33.85, 33.82 (*C*(CH_3)$_3$), 32.1, 32.01, 31.98, 30.2, 30.1, 29.8 (C(*C*H_3)$_3$), 25.4 (THF).

Anal. Calcd. for $C_{61}H_{102}LaN_3O_4$ (complex **1**·Hex): C, 67.81; H, 9.52; N, 3.89. Found: C, 67.28; H, 9.17; N, 3.92.

IR (Selected absorbance, cm^{-1}), stretching vibration of C-H bond (-CH_2-, -CH_3): 2949, 2901, 2839; in-plane bending vibration of C-H bond (-CH_2-, -CH_3, -C(CH_3)$_3$): 1470, 1365, 1201, 1166; stretching vibration of -Ar: 1437, 1412; stretching vibrations of C-N bond: 1302, 1276; stretching vibrations of C-O bond: 1240, 1133; Out-of-plane bending vibration of -Ar: 832, 809.

Synthesis of complex 2. $NdCp_3$(THF) (0.41g, 1 mmol) and L^1H_3 (0.79 g, 1 mmol) were dissolved with THF (10 mL), which was heated at 50 °C for 12 hours. After reaction, the solvent (THF) was removed under vacuum and the crude product was recrystallized from THF (2 mL). Purple crystals were obtained at room temperature after 2 h (0.83 g, 0.83 mmol, 83%). Complex **2** is sensitive to air and moisture.

Anal. Calcd. for $C_{59}H_{96}N_3NdO_5$ (complex **2**·THF): C, 66.13; H, 9.03; N, 3.92. Found: C, 66.20; H, 9.43; N, 3.89.

IR (Selected absorbance, cm^{-1}), stretching vibration of C-H bond (-CH_2-, -CH_3): 2950, 2901, 2865; in-plane bending vibration of C-H bond (-CH_2-, -CH_3, -C(CH_3)$_3$): 1468, 1384, 1202, 1166; stretching vibration of -Ar: 1437, 1413; stretching vibrations of C-N bond: 1361, 1301, 1278; stretching vibrations of C-O bond: 1241, 1134; Out-of-plane bending vibration of -Ar: 833, 809.

Synthesis of complex 3. $SmCp_3$(THF) (0.42 g, 1 mmol) and L^1H_3 (0.79 g, 1 mmol) were dissolved with toluene (10 mL), which was heated at 50 °C for 12 hours. After reaction, the solvent (toluene) was removed under vacuum and the crude product was recrystallized from toluene (3 mL) and *n*-hexane (2 mL). Colorless crystals were obtained at room temperature after 1 day (0.64 g, 0.64 mmol, 64%). Complex **3** is sensitive to air and moisture.

Anal. Calcd. for $C_{61}H_{102}N_3SmO_4$ (complex **3**· Hex): C, 67.10; H, 9.42; N, 3.85. Found:

C, 66.96; H, 9.27; N, 3.95.

IR (Selected absorbance, cm^{-1}), stretching vibration of C-H bond (-CH_2-, -CH_3): 2949, 2900, 2843; in-plane bending vibration of C-H bond (-CH_2-, -CH_3, -$C(CH_3)_3$): 1469, 1367, 1202, 1166; stretching vibration of -Ar: 1437, 1412; stretching vibrations of C-N bond: 1302, 1276; stretching vibrations of C-O bond: 1240, 1133; Out-of-plane bending vibration of -Ar: 833, 809.

Synthesis of complex 4. $YCp_3(THF)$ (0.36 g, 1 mmol) and L^1H_3 (0.79 g, 1 mmol) were dissolved with THF (10 mL), which was heated at 50 °C for 12 hours. After reaction, the solvent (THF) was removed under vacuum and the crude product were recrystallized from THF (3 mL) and *n*-hexane (1 mL). Colorless crystals were obtained at room temperature after several days (0.52 g, 0.55 mmol, 55%). Complex **4** is sensitive to air and moisture.

^{1}H NMR (400 MHz, C_6D_6) δ 7.60-7.53 (m, 3H, Ar*H*), 7.18 (s, 1H, Ar*H*), 7.00 (s, 1H, Ar*H*), 6.76 (d, *J* = 2.4 Hz, 1H, Ar*H*), 4.26 (d, *J* = 12.4 Hz, 1H, ArCH_2N), 4.09-4.03 (m, 4H, THF), 2.85 (d, *J* = 12.5 Hz, 1H, ArCH_2N), 2.48-2.27 (m, 3H, ArCH_2N), 1.93 (s, 1H, ArCH_2N), 1.81 (s, 6H, N(CH_3)$_2$), 1.78 (s, 9H, C(CH_3)$_3$), 1.74 (s, 1H, NCH_2CH$_2$N), 1.71 (d, *J* = 4.36 Hz, 1H, NCH_2CH$_2$N), 1.63 (s, 9H, C(CH_3)$_3$), 1.59 (s, 1H, NCH$_2$CH_2N), 1.57 (s, 1H, NCH$_2$CH_2N), 1.53 (s, 9H, C(CH_3)$_3$), 1.51 (s, 4H, THF), 1.50 (s, 2H, NCH_2CH$_2$N(CH$_3$)$_2$), 1.47 (s, 9H, C(CH_3)$_3$), 1.44 (s, 9H, C(CH_3)$_3$), 1.39 (s, 9H, C(CH_3)$_3$), 1.37 (s, 1H), CH_2N(CH$_3$)$_2$, 1.34 (s, 1H, CH_2N(CH$_3$)$_2$).

^{13}C NMR (101 MHz, C_6D_6) δ 161.9, 160.7, 136.3, 136.1, 135.5, 135.3, 125.8, 125.5, 124.8, 124.7, 124.2, 124.1, 123.5, 123.1, 122.9 (Ar-*C*), 69.8 (THF), 63.5 (Ar*C*H$_2$N), 46.6 (N(*C*H$_3$)$_2$), 35.2 (N*C*H$_2$CH$_2$N), 35.10 (NCH$_2$*C*H$_2$N), 35.09 (N*C*H$_2$CH$_2$N(CH$_3$)$_2$), 33.9 (*C*H$_2$N(CH$_3$)$_2$), 33.84, 33.77, 32.0 (*C*(CH$_3$)$_3$), 31.9, 31.8, 31.6, 30.6, 30.3, 30.2, 30.1 (C(*C*H$_3$)$_3$), 25.2, 22.7 (THF).

Anal. Calcd. for $C_{62}H_{105}YN_3O_4$ (complex **4**· Hex): C, 71.23; H, 10.12; N, 4.02. Found: C, 71.15; H, 10.46; N, 3.84.

IR (Selected absorbance, cm^{-1}), stretching vibration of C-H bond (-CH_2-, -CH_3): 2950, 2900, 2865; in-plane bending vibration of C-H bond (-CH_2-, -CH_3, -$C(CH_3)_3$): 1470, 1391, 1201, 1168; stretching vibration of -Ar: 1413, 1440; stretching vibrations of C-

N bond: 1361, 1305, 1277; stretching vibrations of C-O bond: 1238, 1132; Out-of-plane bending vibration of -Ar: 835, 806.

Synthesis of complex 5. $LaCp_3(THF)$ (0.41 g, 1 mmol) and L^2H_3 (0.66 g, 1 mmol) were dissolved with toluene (10 mL), which was heated at 50 °C for 12 hours. After reaction, the solvent (toluene) was removed under vacuum and the crude product was recrystallized from toluene (3 mL) and *n*-hexane (1 mL). Colorless crystals were obtained at room temperature after 3 days (0.42 g, 0.48 mmol, 48%). Complex **5** is sensitive to air and moisture.

^{1}H NMR (400 MHz, C_6D_6) δ 7.37-7.35 (m, 1H, Ar*H*), 7.31-7.28 (m, 1H, Ar*H*), 7.26-7.23 (m, 1H, Ar*H*), 7.04 (s, 1H, Ar*H*), 6.70-6.67 (m, 1H, Ar*H*), 6.62-6.58 (m, 1H, Ar*H*), 4.19-4.12 (m, 4H, THF), 4.11 (d, *J* = 3.6 Hz, 1H, ArC*H*$_2$N), 4.08 (d, *J* = 5.4 Hz, 1H, ArC*H*$_2$N), 3.31-3.20 (m, 1H, ArC*H*$_2$N), 2.77 (d, *J* = 12.6 Hz, 2H, ArC*H*$_2$N), 2.70 (d, *J* = 12.1 Hz, 1H, ArC*H*$_2$N), 2.61 (d, *J* = 11.7 Hz, 1H, NC*H*$_2$CH$_2$), 2.49 (s, 3H, ArC*H*$_3$), 2.36 (s, 3H, ArC*H*$_3$), 2.33 (s, 3H, ArC*H*$_3$), 2.23-2.19 (m, 1H, NC*H*$_2$CH$_2$), 2.02 (d, *J* = 12.3 Hz, 1H, NCH$_2$C*H*$_2$N), 1.95 (d, *J* = 11.8 Hz, 2H, NCH$_2$C*H*$_2$N and NC*H*$_2$CH$_2$N(CH$_3$)$_2$), 1.91 (d, *J* = 7.4 Hz, 2H NC*H*$_2$C*H*$_2$N(CH$_3$)$_2$), 1.88 (s, 1H, C*H*$_2$N(CH$_3$)$_2$), 1.66 (s, 9H, C(C*H*$_3$)$_3$), 1.62 (s, 9H, C(C*H*$_3$)$_3$), 1.61 (s, 6H, N(C*H*$_3$)$_3$), 1.56 (s, 9H, C(C*H*$_3$)$_3$), 1.48 (d, *J* = 14.4 Hz, 4H, THF).

^{13}C NMR (101 MHz, C_6D_6) δ 163.5, 163.3, 161.1, 154.3, 152.7, 136.71, 136.5, 135.5, 135.4, 130.2, 130.0, 129.7, 129.0, 128.9, 128.2, 125.31, 125.0, 123.9, 123.5, 122.4, 122.2, 121.4, 121.1 (Ar-*C*), 69.1 (THF), 61.6, 60.9, 59.0 (Ar*C*H$_2$N), 57.8 (N*C*H$_2$CH$_2$N), 56.9 (NCH$_2$*C*H$_2$N), 56.7 (N*C*H$_2$CH$_2$N(CH$_3$)$_2$), 55.5 (*C*H$_2$N(CH$_3$)$_2$), 51.7, 49.7, 45.0 (Ar-*C*H$_3$), 34.8 (N(*C*H$_3$)$_2$), 34.73, 34.68, 34.6 (*C*(CH$_3$)$_3$), 30.2, 29.8, 29.7, 29.6 (C(*C*H$_3$)$_3$), 25.4 (THF).

Anal. Calcd. for $C_{50}H_{78}LaN_3O_5$ (complex **5**·THF): C, 63.88; H, 8.36; N, 4.47. Found: C, 63.51; H, 8.75; N, 4.63.

IR (Selected absorbance, cm^{-1}), stretching vibration of C-H bond (-CH$_2$-, -CH$_3$): 2999, 2948, 2911, 2856; in-plane bending vibration of C-H bond (-CH$_2$-, -CH$_3$, -C(CH$_3$)$_3$): 1467, 1373, 1207, 1148; stretching vibration of -Ar: 1434, 1416; stretching vibrations of C-N bond: 1363, 1303, 1279; stretching vibrations of C-O bond: 1207, 1148; Out-

of-plane bending vibration of -Ar: 860, 817.

Synthesis of complex 6. $LaCp_3(THF)$ (0.41 g, 1 mmol) and L^3H_3 (0.53 g, 1 mmol) were dissolved with toluene (10 mL), which was heated at 50 °C for 12 hours. After reaction, the solvent (toluene) was removed under vacuum and the crude product was recrystallized from toluene (4.5 mL) and *n*-hexane (1.5 mL). Colorless crystals were obtained at room temperature after 3 days (0.63 g, 0.47 mmol, 47%). Complex **6** is sensitive to air and moisture.

^{1}H NMR (400 MHz, C_6D_6) δ 7.03 (s, 2H, Ar*H*), 6.97-6.95 (m, 2H, Ar*H*), 6.84 (s, 2H, Ar*H*), 6.76 (s, 2H, Ar*H*), 6.62 (s, 2H, Ar*H*), 6.41-6.37 (m, 2H, Ar*H*), 5.09 (d, *J* = 11.7 Hz, 2H, ArC*H*$_2$N), 4.38 (d, *J* = 11.7 Hz, 2H, ArC*H*$_2$N), 3.39 (d, *J* = 11.9 Hz, 2H, ArC*H*$_2$N), 3.25 (t, *J* = 13.6 Hz, 2H, ArC*H*$_2$N), 3.03 (d, *J* = 12.3 Hz, 2H, ArC*H*$_2$N), 2.97 (s, 6H, Ar-CH_3), 2.92-2.83 (m, 2H, ArC*H*$_2$N), 2.78 (d, *J* = 12.7 Hz, 2H, NC*H*$_2$CH$_2$), 2.73 (d, *J* = 12.0 Hz, 2H, NC*H*$_2$CH$_2$), 2.59 (s, 2H, NCH$_2$C*H*$_2$N), 2.54 (s, 6H, Ar-C*H*$_3$), 2.28 (s, 6H, Ar-C*H*$_3$), 2.26 (s, 12H, N(C*H*$_3$)$_2$), 2.18 (s, 6H, Ar-C*H*$_3$), 2.16 (s, 2H, NCH$_2$C*H*$_2$N), 2.11 (s, 6H, Ar-C*H*$_3$), 2.03 (s, 6H, Ar-C*H*$_3$), 1.96 (d, *J* = 12.0 Hz, 2H, NC*H*$_2$CH$_2$N(CH$_3$)$_2$), 1.56 (s, 4H, NC*H*$_2$C*H*$_2$N(CH$_3$)$_2$), 1.31 (d, *J* = 12.8 Hz, 2H, C*H*$_2$N(CH$_3$)$_2$).

^{13}C NMR (101 MHz, C_6D_6) δ 163.0, 161.7, 156.7, 137.5, 132.8, 132.2, 131.6, 130.1, 129.2, 129.0, 128.2, 126.6, 125.3, 124.8, 124.7, 124.5, 123.6, 122.5, 121.7, 121.4 (Ar-*C*), 65.1 (Ar*C*H$_2$N), 61.4 (N*C*H$_2$CH$_2$N), 58.3 (NCH$_2$*C*H$_2$N), 55.2 (N*C*H$_2$CH$_2$N(CH$_3$)$_2$), 50.4 (*C*H$_2$N(CH$_3$)$_2$), 44.65, N(*C*H$_3$)$_2$, 20.4, 20.3, 19.3, 19.03,19.01, 17.36 (Ar-*C*H$_3$).

Anal. Calcd. for $C_{72}H_{102}La_2N_6O_6$ (complex **6**· Hex): C, 60.67; H, 7.21; N, 5.90. Found: C, 60.62; H, 7.02; N, 6.07.

IR (Selected absorbance, cm^{-1}), stretching vibration of C-H bond (-CH_2-, -CH_3): 2909, 2834; in-plane bending vibration of C-H bond (-CH_2-, -CH_3, -C(CH_3)$_3$): 1471, 1372, 1218, 1159; stretching vibration of -Ar: 1439; stretching vibrations of C-N bond: 1311, 1269, 1244; stretching vibrations of C-O bond: 1218, 1159; Out-of-plane bending vibration of -Ar: 858, 807.

Typical procedures for cycloaddition reaction

Condition screening. 1,2-Epoxyhexane (700 μL, 6.0 mmol), complex **1** (29.8 mg, 0.5 mol%) and TBAI (22.2 mg, 1.0 mol%) were added into a 5 mL reaction flask, which was connected to a CO_2 balloon (1 bar). After 12 h reaction at 25 ℃, mesitylene (101.0 mg, 0.84 mmol) was added as an internal standard. The yield of the cyclic carbonate (4-butyl-1,3-dioxolane-2-one, **2a**) was determined by ^{1}H NMR spectroscopy of the reaction mixture with added mesitylene (Figure S1).[3]

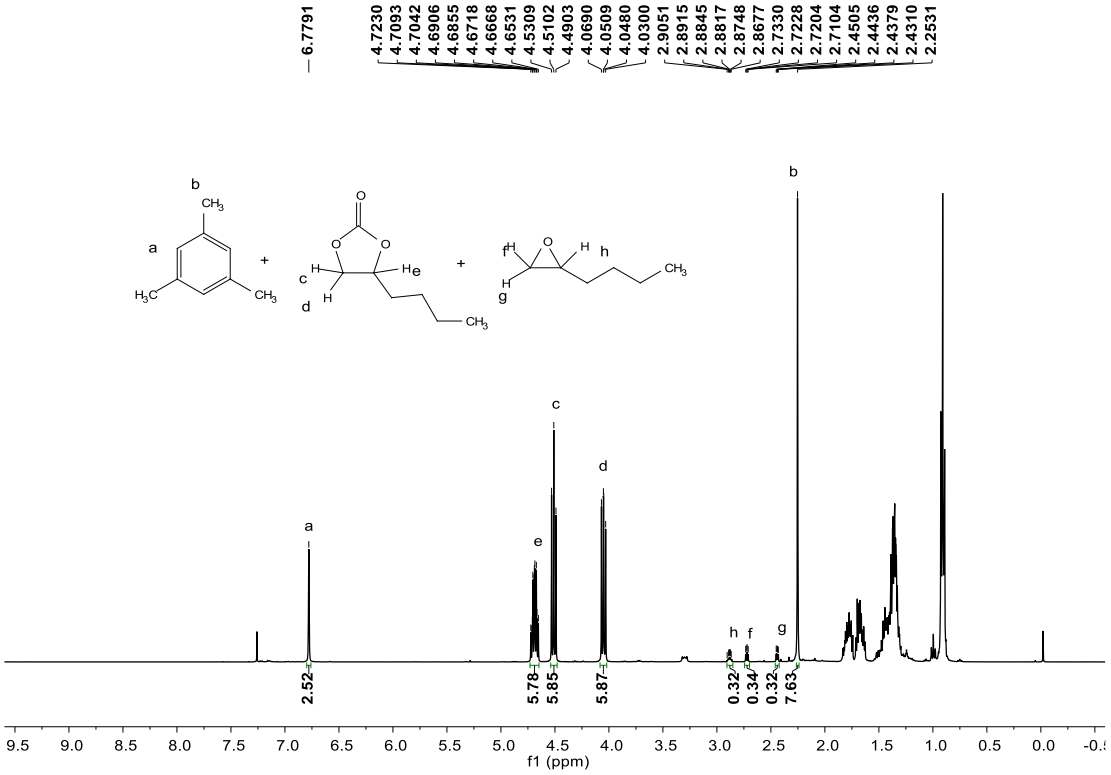
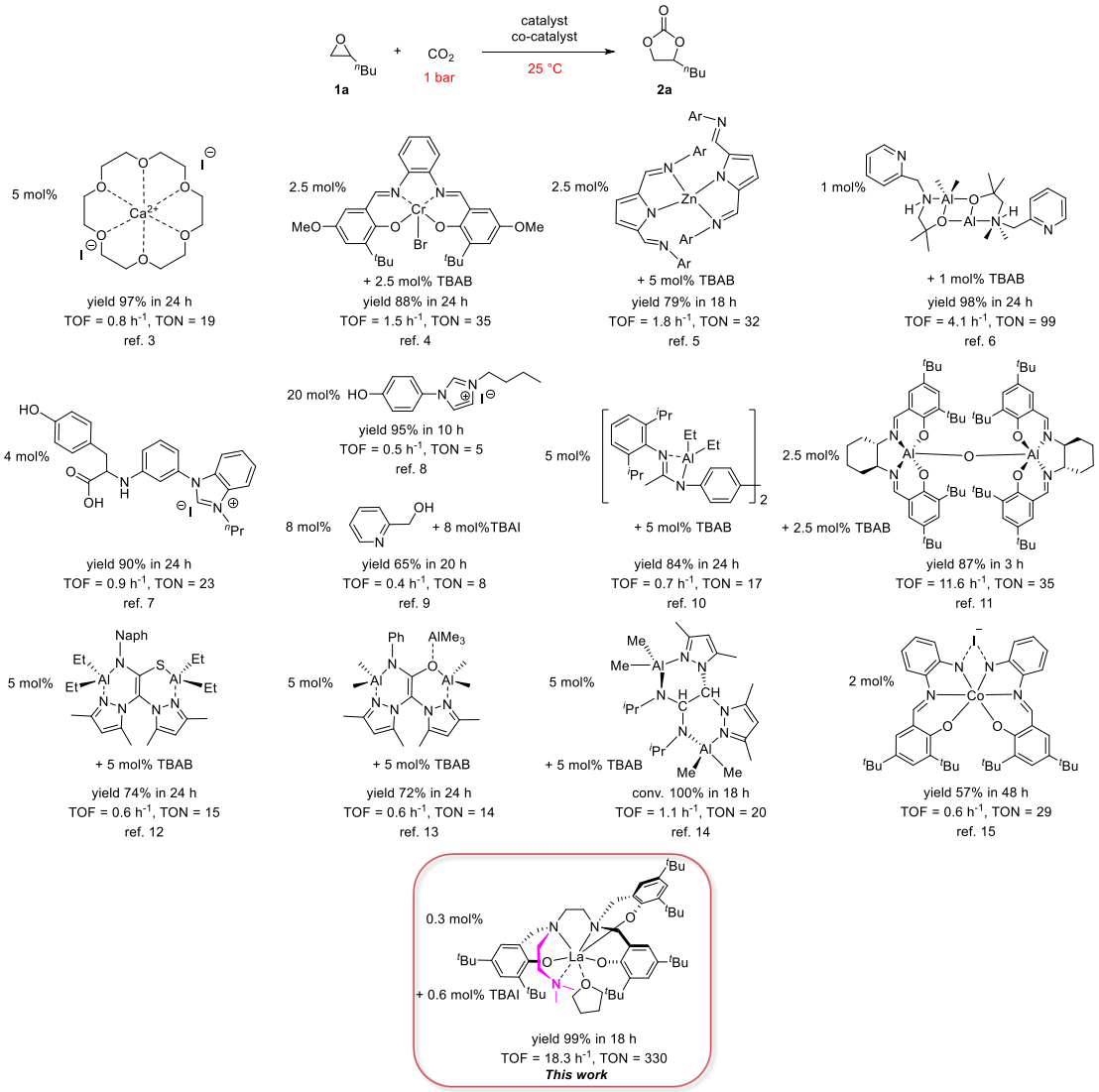


Figure S1. A representative ^{1}H NMR spectrum of reaction mixture of 1,2-epoxyhexane and CO_2 (Table 1, entry 1).

Cycloaddition of CO_2 with mono-substituted epoxides

Procedure 1: mono-substituted epoxides **1a-r** (6.0 mmol), complex **1** (17.9 mg, 0.3 mol%) and TBAI (13.3 mg, 0.6 mol%) were added in a 5 mL reaction flask, which was connected to a CO_2 balloon (1 bar). After 18 h reaction at 25 ℃, crude products were purified through column chromatography using petroleum ether/ethyl acetate (3:7 to 1:1) as eluents. After vacuum removal of all volatiles, the products **2a-r** were obtained.

Comparison of this work with selected organometallic catalysts.



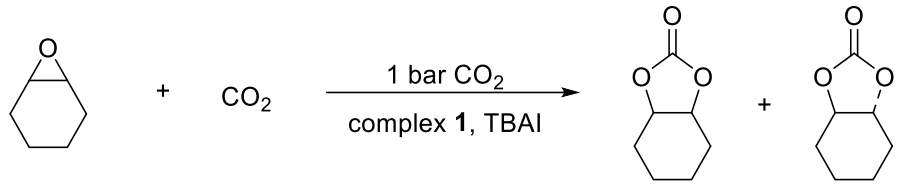
Scheme S1 Reported catalysts for the formation of 4-butyl-1,3-dioxolan-2-one (**2a**) under 1 bar CO_2 and 25 °C.

Cycloaddition of CO_2 with di-substituted epoxides

Procedure 2: di-substituted epoxides **3a-h** (3.0 mmol), complex **1** (59.7 mg, 2 mol%), and TBAI (44.3 mg, 4 mol%) were added in a 5 mL reaction flask, which was connected to a CO_2 balloon (1 bar). After 18-24 h reaction at 25 °C, crude products were purified through column chromatography using petroleum ether/ethyl acetate (3:7 to 1:1) as eluents. After removal of all volatiles in vacuo, products **4a-f** were obtained. Reactions of **3g** and **3h** required elevating the temperature to 120 °C to generate cyclic carbonates (**4g** and **4h)**.

Condition optimization for cycloaddition of CO_2 and CHO

Table S1. condition optimization [a]



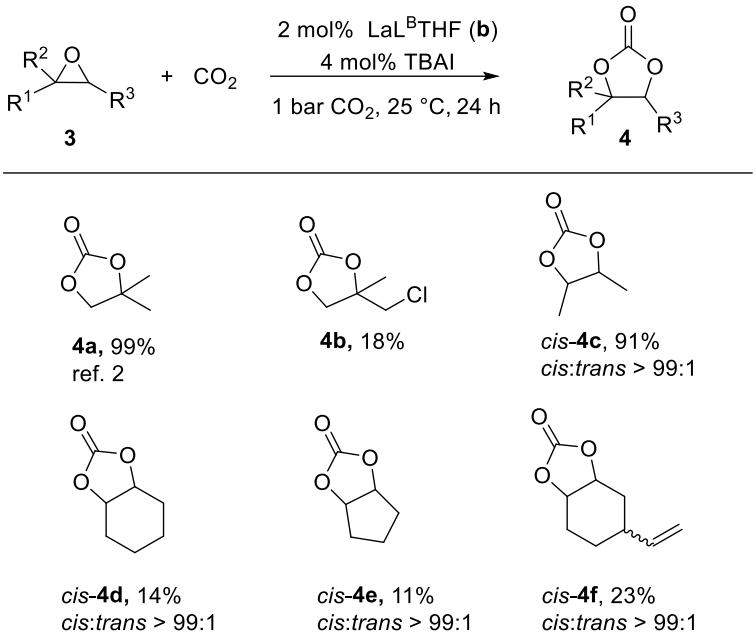
CHO (**3d**) *cis*-**4d** *trans*-**4d'**

Entry	Catalyst (mol%)	Co-catalyst (mol%)	Temp. (°C)	Time (h)	Yield (%) [b,c]	TOF (h^{-1})
1	**1** (0.3)	TBAI (0.6)	25	24	41	5.7
2	**1** (0.3)	TBAI (0.6)	60	24	73	10.1
3	**1** (0.5)	TBAI (1)	60	24	78	6.5
4	**1** (1)	TBAI (2)	60	24	86	3.6
5	**1** (2)	TBAI (2)	60	24	92	1.9
6	**1** (2)	TBAI (3)	60	24	95	2.0
7	**1** (2)	TBAI (4)	60	24	99	2.1
8	**1** (2)	TBAI (4)	60	18	96	2.7
9	**1** (2)	TBAI (4)	25	18	88	2.4
10	**1** (2)	TBAI (4)	25	24	94 (91[d])	2.0
11	**1** (2)	--	60	24	0	0
12	--	TBAI (4)	60	24	0	0

[a] Reaction conditions: 1 bar CO_2. [b] Yield was determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard. [c] 99% *cis* and 1% *trans* isomers. [d] Isolated yield.

Reaction of CO_2 and di-substituted epoxides catalysed using LaL^BTHF (b)

Table S2. Conversion of di-substituted epoxides **3a-h** into cyclic carbonates **4a-h** using LaL^BTHF (**b**) and TBAI [a,b]



[a] Reaction conditions: 2 mol% LaL^{B}THF (**b**), 4 mol% TBAI, 25 °C, 24 h, 1 bar CO_2 pressure, neat. [b] Isolated yield.

Characterization data of cyclic carbonates

4-butyl-1,3-dioxolan-2-one (**2a**).[3]

Following Procedure 1, 1,2-epoxyhexane **1a** (700 µL, 6.0 mmol) reacted with CO_2 and generated **2a** as light yellow liquid (856.5 mg, 5.94 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73-4.64 (m, 1H, OC*H*), 4.50 (d, *J* = 8.3 Hz, 1H, OCH_2), 4.04 (t, *J* = 7.8 Hz, 1H, OCH_2), 1.78 (d, *J* = 7.7 Hz, 1H, CH_2), 1.71-1.61 (m, 1H, CH_2), 1.47-1.40 (m, 1H, CH_2), 1.40-1.36 (m, 1H, CH_2), 1.35-1.30 (m, 2H, CH_2), 0.90 (t, *J* = 6.4 Hz, 3H, CH_3).

4-ethyl-1,3-dioxolan-2-one (**2b**).[3]

Following Procedure 1, 1,2-epoxybutane **1b** (522 µL, 6.0 mmol) reacted with CO_2 and generated **2b** as light yellow liquid (689.7 mg, 5.94 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.65-4.56 (m, 1H, OC*H*), 4.46 (t, *J* = 8.2 Hz, 1H, OCH_2), 4.01 (m, 1H, OCH_2), 1.70 (m, 2H, CH_2), 0.93 (t, *J* = 7.5 Hz, 3H, CH_3).

4-decylalkyl-1,3-dioxolan-2-one (**2c**).[16]

Following Procedure 1, 1,2-epoxydodecane **1c** (1318 µL, 6.0 mmol) reacted with CO_2 and generated **2c** as light yellow liquid (1356.3 mg, 5.97 mmol, 99%). ^{1}H NMR (400

MHz, $CDCl_3$) δ 4.64 (m, 1H, OC*H*), 4.52-4.39 (m, 1H, OCH_2), 4.00 (dd, *J* = 8.4 and 7.2 Hz, 1H, OCH_2), 1.81-1.67 (m, 1H, CH_2), 1.66-1.55 (m, 1H, CH_2), 1.40 (m, 1H, CH_2), 1.34-1.15 (m, 15H, CH_2), 0.81 (t, *J* = 6.9 Hz, 3H, CH_3).

4-methyl-1,3-dioxolan-2-one (**2d**).[3]

Following Procedure 1, 1,2-epoxypropane **1d** (420 μL, 6.0 mmol) reacted with CO_2 and generated **2d** as light yellow liquid (606.4 mg, 2.97 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.85 (dd, *J* = 13.6 and 6.5 Hz, 1H, OC*H*), 4.56 (t, *J* = 8.1 Hz, 1H, OCH_2), 4.06-3.96 (m, 1H, OCH_2), 1.48 (d, *J* = 6.3 Hz, 3H, CH_3).

4-(3-butenyl)-1,3-dioxolan-2-one (**2e**).[17]

Following Procedure 1, 1,2-epoxy-5-hexene **1e** (676 μL, 6.0 mmol) reacted with CO_2 and generated **2e** as light yellow liquid (844.4 mg, 2.97 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 (m, 6.7 Hz, 1H, C*H*=CH_2), 5.06-4.93 (m, 2H, CH=CH_2), 4.68 (m, 1H, OC*H*), 4.51-4.44 (m, 1H, OCH_2), 4.02 (dd, *J* = 8.5 and 7.2 Hz, 1H, OCH_2), 2.22-2.05 (m, 2H, CH_2CH_2), 1.84 (m, 1H, C$H_2$$CH_2$), 1.72 (m, 1H, C$H_2$$CH_2$).

4-chloromethyl-1,3-dioxolan-2-one (**2f**).[3]

Following Procedure 1, epichlorohydrin **1f** (470 μL, 6.0 mmol) reacted with CO_2 and generated **2f** as light yellow liquid (704.5 mg, 5.16 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02-4.93 (m, 1H, OC*H*), 4.58 (t, *J* = 8.6 Hz, 1H, OCH_2), 4.39 (dd, *J* = 8.9 and 5.7 Hz, 1H, OCH_2), 3.79 (dd, *J* = 12.2 and 5.2 Hz, 1H, ClCH_2), 3.71 (dd, *J* = 12.2 and 3.7 Hz, 1H, ClCH_2).

4-bromomethyl-1,3-dioxolan-2-one (**2g**).[18]

Following Procedure 1, epibromohydrin **1g** (492 μL, 6.0 mmol) reacted with CO_2 and generated **2g** as light yellow liquid (1075.1 mg, 5.94 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94 (m, 1H, OC*H*), 4.56 (t, *J* = 8.6 Hz, 1H, OCH_2), 4.29 (dd, *J* = 8.9 and 5.9 Hz, 1H, OCH_2), 3.63-3.51 (m, 2H, BrCH_2).

4-phenyl-1,3-dioxolan-2-one (**2h**).[3]

Following Procedure 1, styrene oxide **1h** (684 μL, 6.0 mmol) reacted with CO_2 and generated **2h** as white solids (788.0 mg, 4.80 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.40 (m, 3H, Ar*H*), 7.38-7.33 (t, *J* = 7.4 Hz, 2H, Ar*H*), 5.67 (t, *J* = 8.0 Hz, 1H, OC*H*), 4.83-4.76 (m, 1H, OCH_2), 4.33 (dd, *J* = 8.6 and 7.9 Hz, 1H, OCH_2).

4-(methoxymethyl)-1,3-dioxolan-2-one (**2i**).[17]

Following Procedure 1, methyl glycidyl ether **1i** (540 μL, 6.0 mmol) reacted with CO_2 and generated **2i** as light yellow liquid (650.0 mg, 4.92 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (m, 1H, OC*H*), 4.45 (t, *J* = 8.4 Hz, 1H, OCH_2), 4.31 (dd, *J* = 8.4 and 6.1 Hz, 1H, OCH_2), 3.59 (dd, *J* = 11.2 and 3.4 Hz, 1H, OCHCH_2O), 3.50 (dd, *J* = 11.2 and 3.8 Hz, 1H, OCHCH_2O), 3.35 (s, 3H, OCH_3).

4-(*n*-butoxymethyl)-1,3-dioxolan-2-one (**2j**).[17]

Following Procedure 1, *n*-butyl glycidyl ether **1j** (828 μL, 6.0 mmol) reacted with CO_2 and generated **2j** as light yellow liquid (951.1 mg, 5.46 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 (m, 1H, OC*H*), 4.48 (t, *J* = 8.3 Hz, 1H, OCH_2), 4.38 (dd, *J* = 8.3 and 6.1 Hz, 1H, OCH_2), 3.66 (dd, *J* = 11.0 and 4.0 Hz, 1H, OCHCH_2O), 3.60 (dd, *J* = 11.0 and 3.7 Hz, 1H, OCHCH_2O), 3.50 (t, *J* = 6.5 Hz, 2H, OCH_2CH$_2$), 1.55 (p, *J* = 6.6 Hz, 2H, OCH$_2$CH_2), 1.35 (h, *J* = 7.3 Hz, 2H, CH$_2$CH_2), 0.91 (t, *J* = 7.4 Hz, 3H, CH_3).

4-((allyloxy)methyl)-1,3-dioxolan-2-one (**2k**).[16]

Following Procedure 1, ((2-propenyloxy)-methyl) oxirane **1k** (712 μL, 6.0 mmol) reacted with CO_2 and generated **2k** as light yellow liquid (816.1 mg, 5.16 mmol, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (m, 1H, C*H*=CH$_2$), 5.22 (dd, *J* = 26.8 and 13.8 Hz, 2H, CH=CH_2), 4.80 (m, 1H, OC*H*), 4.52-4.33 (m, 2H, OCH_2), 4.02 (d, *J* = 5.5 Hz, 2H, OCH_2), 3.69-3.56 (m, 2H, OCH_2).

4-((prop-2-yn-1-yloxy) methyl)-1,3-dioxolan-2-one(**2l**).[3]

Following Procedure 1, 2-((prop-2-yn-1-yloxy)methyl)oxirane **1l** (646 μL, 6.0 mmol) reacted with CO_2 and generated **2l** as light yellow liquid (571.5 mg, 3.66 mmol, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.88-4.79 (m, 1H, OC*H*), 4.48 (t, *J* = 8.5 Hz, 1H, OCH_2), 4.34 (dd, *J* = 8.4 and 6.0 Hz, 1H, OCH_2), 4.25-4.11 (m, 2H, CH_2O), 3.79-3.63 (m, 2H, CH_2C), 2.48 (t, *J* = 2.4 Hz, 1H, C≡C*H*).

4-((phenyl-2-ylmethoxy) methyl)-1,3-dioxolan-2-one (**2m**).[16]

Following Procedure 1, 2-(benzyloxymethyl) oxirane **1m** (914 μL, 6.0 mmol) reacted with CO_2 and generated **2m** as light yellow liquid (824.5 mg, 3.96 mmol, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.22 (m, 5H, Ar*H*), 4.75 (m, 1H, OC*H*), 4.61-4.48 (m,

2H, OC*H*$_2$), 4.44-4.26 (m, 2H, OCHC*H*$_2$O), 3.66 (dd, *J* = 11.1 and 3.4 Hz, 1H, OC*H*$_2$Ar), 3.54 (dd, *J* = 11.1 and 3.7 Hz 1H, OC*H*$_2$Ar).

4-(phenoxymethyl)-1,3-dioxolan-2-one (**2n**).[17]

Following Procedure 1, glycidyl phenyl ether **1n** (812 μL, 6.0 mmol) reacted with CO_2 and generated **2n** as white solids (745.7 mg, 3.84 mmol, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (m, 2H, Ar*H*), 7.01 (t, *J* = 7.4 Hz, 1H, Ar*H*), 6.94-6.87 (m, 2H, Ar*H*), 5.02 (m, 1H, OC*H*), 4.60 (t, *J* = 8.4 Hz, 1H, OC*H*$_2$), 4.52 (dd, *J* = 8.5 and 5.9 Hz, 1H, OC*H*$_2$), 4.23 (dd, *J* = 10.6 and 4.1 Hz, 1H, CHC*H*$_2$OPh), 4.13 (dd, *J* = 10.6 and 3.6 Hz, 1H, CHC*H*$_2$OPh).

(2-oxo-1,3-dioxolan-4-yl)-methyl 4-(*tert*-butyl) benzoate (**2o**).[17]

Following Procedure 1, 4-*tert*-butylbenzoic acid 2,3-epoxypropyl ester **1o** (1302 μL, 6.0 mmol) reacted with CO_2 and generated **2o** as light yellow liquid (834.9 mg, 3 mmol, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H, Ar*H*), 7.48 (d, *J* = 8.5 Hz, 2H, Ar*H*), 5.08-4.99 (m, 1H, OC*H*), 4.65-4.55 (m, 2H, OC*H*$_2$), 4.52 (dd, *J* = 12.6 and 3.8 Hz, 1H, OC*H*$_2$), 4.42 (dd, *J* = 8.7 and 5.6 Hz, 1H, OC*H*$_2$), 1.34 (s, 9H, C(C*H*$_3$)$_3$).

4,4-(butane-1,4-diyl)-bis-1,3-dioxolan-2-one (**2p**).[17]

Following Procedure 1, 1,2,7,8-diepoxyoctane **1p** (856 μL, 6.0 mmol) reacted with CO_2 and generated **2p** as generate light yellow liquid (994.5 mg, 4.32 mmol, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.70 (m, 2H, OC*H*), 4.53 (t, *J* = 8.1 Hz, 2H, OC*H*$_2$), 4.06 (t, *J* = 7.8 Hz, 2H, OC*H*$_2$), 1.85-1.66 (m, 4H, C*H*$_2$CH$_2$), 1.51 (m, 4H, CH$_2$C*H*$_2$).

4-(7-oxabicyclo[4.1.0]heptan-3-yl)-1,3-dioxolan-2-one (**2q**).[3]

Following Procedure 1, 1,2-epoxy-2-(epoxyethyl) cyclohexane **1q** (768 μL, 6.0 mmol) reacted with CO_2 and generated **2q** as light yellow liquid (862.0 mg, 4.68 mmol, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.47-4.29 (m, 2H, OC*H*$_2$), 4.05 (m, 1H, OC*H*), 3.13-2.98 (m, 2H, OC*H*), 2.20-1.89 (m, 2H, OCHC*H*$_2$), 1.76-1.64 (m, 1H, OCHC*H*$_2$), 1.55 (m, 1H, OCHC*H*$_2$), 1.49-1.36 (m, 1H, OCHC*H*$_2$), 1.30-0.92 (m, 2H, C*H*$_2$CH$_2$).

4-(morpholinomethyl)-1,3-dioxolan-2-one (**2r**).[3]

Following Procedure 1, 4-(oxiran-2-ylmethyl) morpholine **1r** (820 μL, 6.0 mmol) reacted with CO_2 and generated **2r** as light yellow liquid (988.4 mg, 5.28 mmol, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 (dt, *J* = 12.8 and 5.7 Hz, 1H, OC*H*), 4.50 (t, *J* = 8.3 Hz, 1H, OCH_2), 4.25-4.17 (m, 1H, OCH_2), 3.65 (t, *J* = 4.6 Hz, 4H, OCH_2CH_2N), 2.64 (d, *J* = 5.6 Hz, 2H, CH_2), 2.52 (h, *J* = 7.0 Hz, 4H, OCH_2CH_2N).

4,4-dimethyl-1,3-dioxolan-2-one (**4a**).[3]

Following Procedure 2, 2,2-dimethyloxirane **3a** (266 µL, 3.0 mmol) reacted with CO_2 and generated **4a** as light yellow liquid (344.8 mg, 2.97 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (s, 2H, OCH_2), 1.52 (s, 6H, CH_3).

4-(chloromethyl)-4-methyl-1,3-dioxolan-2-one (**4b**).[3]

Following Procedure 2, 2-(chloromethyl)-2-methyloxirane **3b** (290 µL, 6.0 mmol) reacted with CO_2 and generated **4b** as light yellow liquid (370.4 mg, 2.46 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 (d, *J* = 8.8 Hz, 1H, OCH_2), 4.15 (d, *J* = 8.8 Hz, 1H, OCH_2), 3.72 (d, *J* = 11.9 Hz, 1H, CH_2Cl), 3.59 (d, *J* = 11.9 Hz, 1H, CH_2Cl), 1.61 (s, 3H, CH_3).

cis-4,5-dimethyl-1,3-dioxolan-2-one (*cis*-**4c**).[3]

Following Procedure 2, *cis*-2,3-dimethyloxirane **3c** (262 µL, 3.0 mmol) reacted with CO_2 and generated *cis*-**4c** as light yellow liquid (334.4 mg, 2.88 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.82 (m, 2H, OC*H*), 1.35-1.31 (m, 6H, CH_3).

cis-cyclohexene carbonate (*cis*-**4d**).[3]

Following Procedure 2, cyclohexene oxide (**3d**) (305 µL, 3.0 mmol) reacted with CO_2 and generated *cis*-**4d** as light yellow liquid (387.8 mg, 2.73 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (m, 2H, OC*H*), 1.83 (m, 4H, C$H_2$$CH_2$), 1.60-1.49 (m, 2H, CH_2CH_2), 1.42-1.32 (m, 2H, CH_2CH_2).

cis-tetrahydro-8H-cyclopenta-1,3-dioxol-2-one (*cis*-**4e**).[3]

Following Procedure 2, cyclopentene oxide **3e** (262 µL, 3.0 mmol) reacted with CO_2 and generated *cis*-**4e** as light yellow liquid (326.7 mg, 2.55 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (s, 2H, OC*H*), 2.13 (dd, *J* = 14.2 and 5.1 Hz, 2H, OCHC$H_2$$CH_2$), 1.82-1.60 (m, 4H, C$H_2CH_2$).

cis-5-vinylhexahydrobenzo[d][1,3]dioxol-2-one (*cis*-**4f**).[3]

Following Procedure 2, 3-vinyl-7-oxabicyclo-[4.1.0]heptane **3f** (391 µL, 3.0 mmol) reacted with CO_2 and generated *cis*-**4f** as light yellow liquid (449.1 mg, 2.67 mmol,

89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75-5.62 (m, 1H, C*H*=CH_2), 5.03-4.91 (m, 2H, CH=C*H*$_2$), 4.78-4.60 (m, 2H, OC*H*), 2.30-2.19 (m, 1H, C*H*-CH=CH_2), 2.18-2.06 (m, 1H, OCHC*H*$_2$), 1.79-1.69 (m, 1H, OCHC*H*$_2$), 1.65-1.49 (m, 2H, OCHC*H*$_2$), 1.41-1.28 (m, 1H, CH_2C*H*$_2$), 1.23-1.09 (m, 1H, CH_2C*H*$_2$).

trans-4,5-diphenyl-1,3-dioxolan-2-one (*trans*-**4g**).[3]

Following Procedure 2, *trans* stilbene oxide **3g** (589 mg, 3.0 mmol) reacted with CO_2 and generated *trans*-**4e** as white solids (468.5 mg, 1.95 mmol, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 5H, Ar*H*), 7.26 (m, 5H, Ar*H*), 5.39 (s, 2H, OC*H*).

cis-tetrahydro-4H-cyclopenta[d][1,3]dioxol-2-one (*cis*-**4h**).[3]

Following Procedure 2, 3,6-dioxabicyclo[3.1.0]hexane **3h** (209 μL, 3.0 mmol) reacted with CO_2 and generated *cis*-**4h** as light yellow liquid (386.4 mg, 2.97 mmol, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 (dd, *J* = 2.1 and 1.2 Hz, 2H, OC*H*), 4.27-4.22 (m, 2H, OC*H*$_2$), 3.59-3.51 (m, 2H, OC*H*$_2$).

2. Structures and crystallographic data of complexes

Molecular structures of complexes

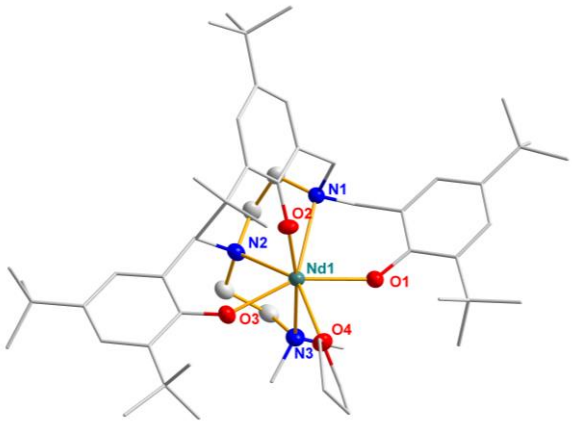


Figure S2. Solid state structure of complex **2**·2 THF. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms and solvent molecules are omitted for clarity.

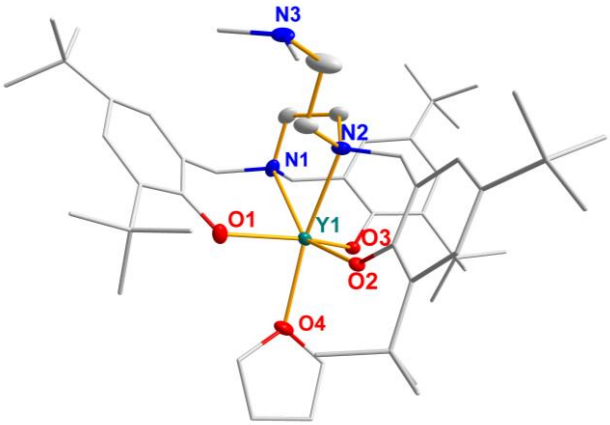


Figure S3. Solid state structure of complex **4**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms and solvent molecules are omitted for clarity.

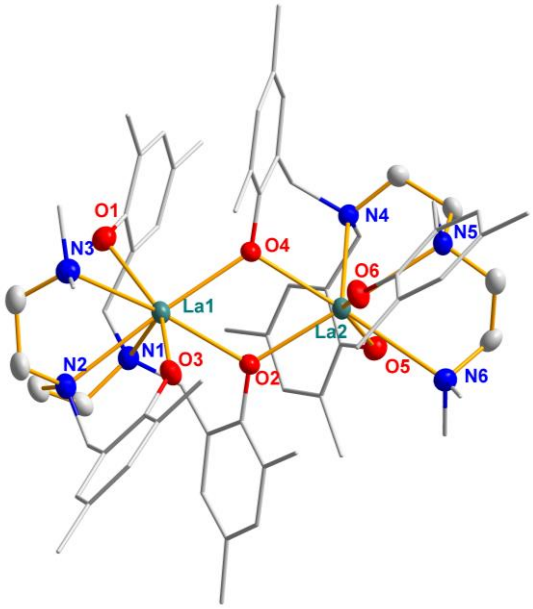


Figure S4. Solid state structure of complex **6**·2.5 toluene. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms and solvent molecules are omitted for clarity.

Crystallographic data of the complexes

Table S3. Crystallographic data of complexes

Complexes	**1** · 5THF	**2** · 2THF	**4**	**6** · 2.5Toluene
Empirical formula	$C_{75}H_{128}LaN_3O_9$	$C_{63}H_{104}N_3NdO_6$	$C_{55}H_{88}N_3O_4Y$	$C_{66}H_{88}La_2N_6O_6$
Formula weight	1354.71	1143.73	944.19	1339.24
Temperature/K	119.97	296.15	120.04	296.15
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/n$	P-1	Pbca
a/Å	22.9709(10)	22.9052(12)	14.5830(5)	19.0891(11)
b/Å	13.9182(6)	14.0471(8)	14.8404(5)	26.9744(15)
c/Å	23.5460(10)	23.7817(13)	17.3526(6)	31.1806(19)
α/°	90	90	69.7290(10)	90
β/°	111.1090(10)	111.0970(10)	89.4670(10)	90
γ/°	90	90	65.6800(10)	90
Volume/Å^3	7022.8(5)	7138.9(7)	3170.88(19)	16055.4(16)
Z	4	4	2	8
ρ_{calc} g/cm^3	1.281	1.064	0.989	1.108
μ/mm^{-1}	0.666	0.770	0.957	1.093

F(000)	2912.0	2444.0	1020.0	5504.0
Crystal size/mm^3	0.3×0.2×0.2	0.2×0.15×0.1	0.2×0.2×0.2	0.25×0.2×0.15
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Reflections collected	140333	157820	59783	368618
2Θ range for data collection/°	3.464 to 55.054	4.526 to 55.19	4.302 to 51.364	4.528 to 55.218
Index ranges	-29 ≤ h ≤ 29, -18 ≤ k ≤ 18, -30 ≤ l ≤ 30	-29 ≤ h ≤ 29, -17 ≤ k ≤ 18, -30 ≤ l ≤ 30	-17 ≤ h ≤ 17, -18 ≤ k ≤ 18, -21 ≤ l ≤ 21	-24 ≤ h ≤ 24, -35 ≤ k ≤ 35, -40 ≤ l ≤ 40
Independent reflections	16119 [R_{int} = 0.1139]	16447 [R_{int} = 0.0685]	12017 [R_{int} = 0.0972]	18584 [R_{int} = 0.1161]
Data/restraints/parameters	16119/0/588	16447/1348/619	12017/1725/678	18584/0/737
Goodness-of-fit on F^2	1.008	1.074	1.041	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0437, wR_2 = 0.1272	R_1 = 0.0365, wR_2 = 0.1008	R_1 = 0.0803, wR_2 = 0.2118	R_1 = 0.0424, wR_2 = 0.0907
Final R indexes [all data]	R_1 = 0.0570, wR_2 = 0.1406	R_1 = 0.0571, wR_2 = 0.1086	R_1 = 0.0942, wR_2 = 0.2219	R_1 = 0.0759, wR_2 = 0.1013
Largest diff. peak/hole/e Å^{-3}	1.45/-1.15	0.87/-0.72	1.43/-1.30	1.15/-0.83

Table S4. Selected bond lengths [Å] and bond angles [deg] of complex 1

Bond lengths			
La(1)-O(1)	2.334(2)	La(1)-N(1)	2.721(2)
La(1)-O(2)	2.277(2)	La(1)-N(2)	2.713(2)
La(1)-O(3)	2.357(2)	La(1)-N(3)	2.836(3)
La(1)-O(4)	2.607(2)		
Bond angles			
O(1)-La(1)-O(2)	103.50(7)	O(1)-La(1)-O(3)	155.53(7)
O(1)-La(1)-O(4)	80.24(7)	O(1)-La(1)-N(1)	73.14(7)
O(1)-La(1)-N(2)	119.81(7)	O(1)-La(1)-N(3)	83.16(7)
O(2)-La(1)-O(4)	94.40(7)	O(2)-La(1)-N(1)	72.10(7)
O(2)-La(1)-N(2)	103.97(7)	O(2)-La(1)-N(3)	169.00(7)
O(3)-La(1)-O(2)	93.39(7)	O(3)-La(1)-O(4)	80.94(7)
O(3)-La(1)-N(1)	129.76(7)	O(3)-La(1)-N(2)	71.65(7)
O(3)-La(1)-N(3)	83.19(7)	O(4)-La(1)-N(1)	145.90(7)

O(4)-La(1)-N(2)	147.59(7)	O(4)-La(1)-N(3)	95.37(7)
N(1)-La(1)-N(2)	66.27(7)	N(1)-La(1)-N(3)	102.08(7)
N(2)-La(1)-N(3)	65.04(7)		

Table S5. Selected bond lengths [Å] and bond angles [deg] of complex 2

Bond lengths			
Nd(1)-O(1)	2.2718(16)	Nd(1)-N(1)	2.6591(19)
Nd(1)-O(2)	2.2320(16)	Nd(1)-N(2)	2.6560(2)
Nd(1)-O(3)	2.2875(17)	Nd(1)-N(3)	2.8280(2)
Nd(1)-O(4)	2.5767(18)		
Bond angles			
O(1)-Nd(1)-O(2)	103.78(6)	O(1)-Nd(1)-O(3)	152.72(6)
O(1)-Nd(1)-O(4)	79.80(6)	O(1)-Nd(1)-N(1)	74.36(6)
O(1)-Nd(1)-N(2)	121.62(6)	O(1)-Nd(1)-N(3)	82.65(6)
O(2)-Nd(1)-O(4)	91.14(6)	O(2)-Nd(1)-N(1)	73.71(6)
O(2)-Nd(1)-N(2)	105.05(6)	O(2)-Nd(1)-N(3)	171.05(7)
O(2)-Nd(1)-O(3)	93.14(6)	O(3)-Nd(1)-O(4)	78.60(6)
O(3)-Nd(1)-N(1)	131.74(6)	O(3)-Nd(1)-N(2)	72.67(6)
O(3)-Nd(1)-N(3)	83.29(7)	O(4)-Nd(1)-N(1)	145.58(6)
O(4)-Nd(1)-N(2)	147.52(6)	O(4)-Nd(1)-N(3)	96.17(7)
N(2)-Nd(1)-N(1)	66.87(6)	N(1)-Nd(1)-N(3)	102.57(7)
N(2)-Nd(1)-N(3)	66.06(7)		

Table S6. Selected bond lengths [Å] and bond angles [deg] of complex 4

Bond lengths			
Y(1)-O(1)	2.175(3)	Y(1)-O(2)	2.172(3)
Y(1)-O(3)	2.127(3)	Y(1)-O(4)	2.357(3)
Y(1)-N(1)	2.541(4)	Y(1)-N(2)	2.511(4)
Bond angles			
O(1)-Y(1)-O(3)	104.11(12)	O(1)-Y(1)-O(4)	83.38(12)
O(1)-Y(1)-N(1)	79.94(12)	O(1)-Y(1)-N(2)	99.50(12)
O(2)-Y(1)-O(1)	144.61(12)	O(2)-Y(1)-O(3)	108.70(12)
O(2)-Y(1)-O(4)	83.87(13)	O(2)-Y(1)-N(1)	79.29(12)
O(2)-Y(1)-N(2)	100.33(13)	O(3)-Y(1)-O(4)	89.72(11)
O(3)-Y(1)-N(1)	148.04(12)	O(3)-Y(1)-N(2)	77.19(12)
O(4)-Y(1)-N(1)	122.18(13)	O(4)-Y(1)-N(2)	166.91(12)
N(2)-Y(1)-N(1)	70.90(13)		

Table S7. Selected bond lengths [Å] and bond angles [deg] of complex 6

Bond lengths			
La(1)-O(1)	2.352(2)	La(1)-O(2)	2.466(2)
La(1)-O(3)	2.288(2)	La(1)-O(4)	2.465(2)
La(1)-N(1)	2.761(3)	La(1)-N(2)	2.727(3)
La(1)-N(3)	2.905(3)	La(2)-O(2)	2.443(2)
La(2)-O(4)	2.463(2)	La(2)-O(5)	2.357(2)
La(2)-O(6)	2.293(2)	La(2)-N(4)	2.748(3)
La(2)-N(5)	2.744(3)	La(2)-N(6)	2.883(3)
Bond angles			
O(1)-La (1)-O(4)	91.28(7)	O(1)-La (1)-N(1)	74.10(8)
O(1)-La (1)-N(2)	91.34(8)	O(2)-La (1)-O(1)	129.57(7)
O(2)-La (1)-N(1)	75.24(7)	O(2)-La (1)-N(2)	111.49(8)
O(3)-La (1)-O(2)	84.14(7)	O(3)-La (1)-O(1)	146.26(8)
O(3)-La (1)-O(4)	107.99(7)	O(3)-La (1)-N(1)	120.75(8)
O(3)-La (1)-N(2)	71.24(8)	O(4)-La (1)-O(2)	64.42(7)
O(3)-La(1)-N(3)	77.13(8)	O(2)-La(1)-N(3)	160.81(8)
O(4)-La(1)-N(3)	117.55(7)	O(1)-La(1)-N(3)	69.36(8)
N(2)-La(1)-N(3)	66.38(8)	N(1)-La(1)-N(3)	118.11(8)
O(4)-La (1)-N(1)	111.31(7)	O(4)-La(1)-N(2)	175.89(8)
O(2)-La(2)-O(4)	64.76(7)	O(2)-La (2)-N(4)	113.40(7)
O(2)-La(2)-N(5)	177.78(7)	O(4)-La (2)-N(4)	76.26(7)
O(4)-La (2)-N(5)	113.48(7)	O(5)-La(2)-N (4)	73.91(8)
O(5)-La(2)-N(5)	91.51(8)	O(6)-La(2)-O(2)	106.92(7)
O(6)-La (2)-O(4)	83.72(7)	O(6)-La(2)-O(5)	147.50(8)
O(6)-La (2)-N(4)	120.35(8)	O(6)-La(2)-N(5)	71.30(8)
O(5)-La(2)-O(2)	90.68(7)	O(5)-La(2)-O(4)	128.78(7)
N(5)-La (2)-N(4)	66.95(7)	La(2)-O (2)-La(1)	114.97(8)
La(2)-O(4)-La(1)	114.29(8)	N(1)-La (1)-N(3)	118.11(8)
N(2)-La(1)-N(1)	66.45(8)	N(2)-La(1)-N(3)	66.38(8)
O(2)-La(2)-N(6)	114.54(7)	O(4)-La(2)-N(6)	161.44(7)
O(5)-La(2)-N(6)	68.96(8)	O(6)-La(2)-N(6)	78.82(8)
N(4)-La(2)-N(6)	118.22(7)	N(5)-La(2)-N(6)	66.64(8)

3. Kinetic study of *cis*-4d formation from CO_2 and CHO catalysed by 1/TBAI

Reaction order with respect to P(CO_2)

Table S8. Complex **1**/TBAI catalysed cycloaddition of CO_2 (1-20 bar) and CHO [a]

Entry	Pressure (bar)	Yield [b] (%)
1	1	43
2	7	43
3	10	44
4	15	46
5	20	47

[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 2 mol% complex **1** (196.9 mM), 4 mol% TBAI (393.2 mM), 25 °C. [b] Yield was determined by ^{1}H NMR spectroscopy of the reaction mixture.

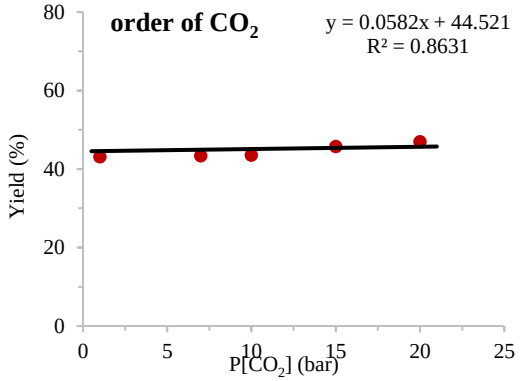


Figure S5. Plot of the yield of *cis*-**4d** versus different CO_2 pressure

Reaction order with respect to [CHO]

Table S9. Complex **1**/TBAI catalysed cycloaddition of CO_2 (1 bar) and CHO [a]

Entry	Time (h)	Yield [b] (%)	$[CHO]_0/[CHO]_t$	$\ln([CHO]_0/[CHO]_t)$
1	2	16	1.19	0.174353
2	4	30	1.43	0.356675
3	6	44	1.79	0.579818
4	8	57	2.33	0.843970
5	10	63	2.70	0.994252
6	12	69	3.23	1.171183

7	14	77	4.35	1.469676

[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 2 mol% complex **1** (196.9 mM), 4 mol% TBAI (393.2 mM), 1 bar CO_2, 25 °C. [b] Yield was determined by ^1H NMR spectroscopy of the reaction mixture.

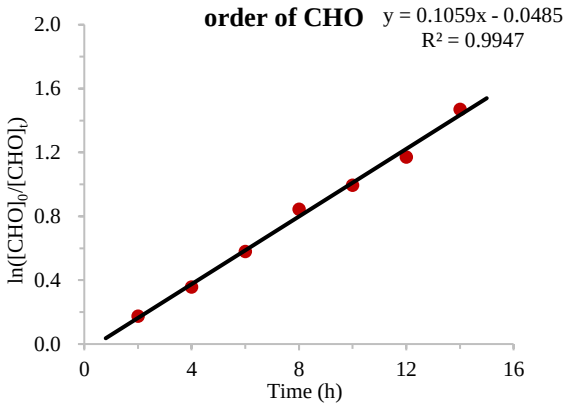


Figure S6. Plot of the $([CHO]_0/[CHO]_t)$ versus time.

Reaction order with respect to [1]

Table S10. Complex **1** (0.5 mol%)/TBAI catalysed cycloaddition of CO_2 and CHO [a]

Entry	Time (h)	Yield [b] (%)	$[CHO]_0/[CHO]_t$	$\ln([CHO]_0/[CHO]_t)$
1	4	6	1.06	0.061875
2	8	8	1.09	0.083382
3	10	10	1.11	0.105361
4	12	13	1.15	0.138113
5	14	15	1.18	0.162519
6	16	16	1.19	0.174353

[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 0.5 mol% complex **1** (49.1 mM), 4 mol% TBAI (393.2 mM), 1 bar CO_2, 25 °C. [b] Yield was determined by ^1H NMR spectroscopy of the reaction mixture.

Table S11. Complex **1** (1 mol%)/TBAI catalysed cycloaddition of CO_2 and CHO [a]

Entry	Time (h)	Yield [b] (%)	$[CHO]_0/[CHO]_t$	$\ln([CHO]_0/[CHO]_t)$
1	2	9	1.10	0.094311
2	4	13	1.15	0.139262
3	6	20	1.25	0.223144
4	8	24	1.32	0.274437
5	10	28	1.39	0.328504
6	12	30	1.43	0.356675

[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 1 mol% complex **1** (98.3 mM), 4 mol% TBAI (393.2

mM), 1 bar CO_2, 25 °C. [b] Yield was determined by ^1H NMR spectroscopy of the reaction mixture.

Table S12. Complex **1** (2 mol%)/TBAI catalysed cycloaddition of CO_2 and CHO [a]

Entry	Time (h)	Yield [b] (%)	$[CHO]_0/[CHO]_t$	$\ln([CHO]_0/[CHO]_t)$
1	1	9	1.10	0.094311
2	2	16	1.19	0.174353
3	3	22	1.28	0.248461
4	4	30	1.43	0.356675
5	5	36	1.56	0.446287

[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 2 mol% complex **1** (196.9 mM), 4 mol% TBAI (393.2 mM), 1 bar CO_2, 25 °C. [b] Yield was determined by ^1H NMR spectroscopy of the reaction mixture.

Table S13. Complex **1** (3 mol%)/TBAI catalysed cycloaddition of CO_2 and CHO [a]

Entry	Time (h)	Yield [b] (%)	$[CHO]_0/[CHO]_t$	$\ln([CHO]_0/[CHO]_t)$
1	1	10	1.11	0.105361
2	2	19	1.23	0.210721
3	3	26	1.35	0.301105
4	4	36	1.56	0.446287
5	5	42	1.72	0.544727

[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 3 mol% complex **1** (295.1 mM), 4 mol% TBAI (393.2 mM), 1 bar CO_2, 25 °C. [b] Yield was determined by ^1H NMR spectroscopy of the reaction mixture.

Table S14. Complex **1** (4 mol%)/TBAI catalysed cycloaddition of CO_2 and CHO [a]

Entry	Time (h)	Yield [b] (%)	$[CHO]_0/[CHO]_t$	$\ln([CHO]_0/[CHO]_t)$
1	1	9	1.10	0.094311
2	2	19	1.23	0.210721
3	3	28	1.39	0.328504
4	4	37	1.59	0.462035
5	5	49	1.96	0.673345

[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 4 mol% complex **1** (393.4 mM), 4 mol% TBAI (393.2 mM), 1 bar CO_2, 25 °C. [b] Yield was determined by ^1H NMR spectroscopy of the reaction mixture.

Table S15. k_{obs} data

1 (M)	ln[**1**]	k_{obs}	lnk_{obs}
0.0491	-3.013896	0.0102	-4.585368
0.0983	-2.319731	0.0276	-3.589940
0.1967	-1.625059	0.0886	-2.423623
0.2951	-1.220441	0.1114	-2.194628
0.3934	-0.932928	0.1409	-1.959705

Determination the rate order of complex 1

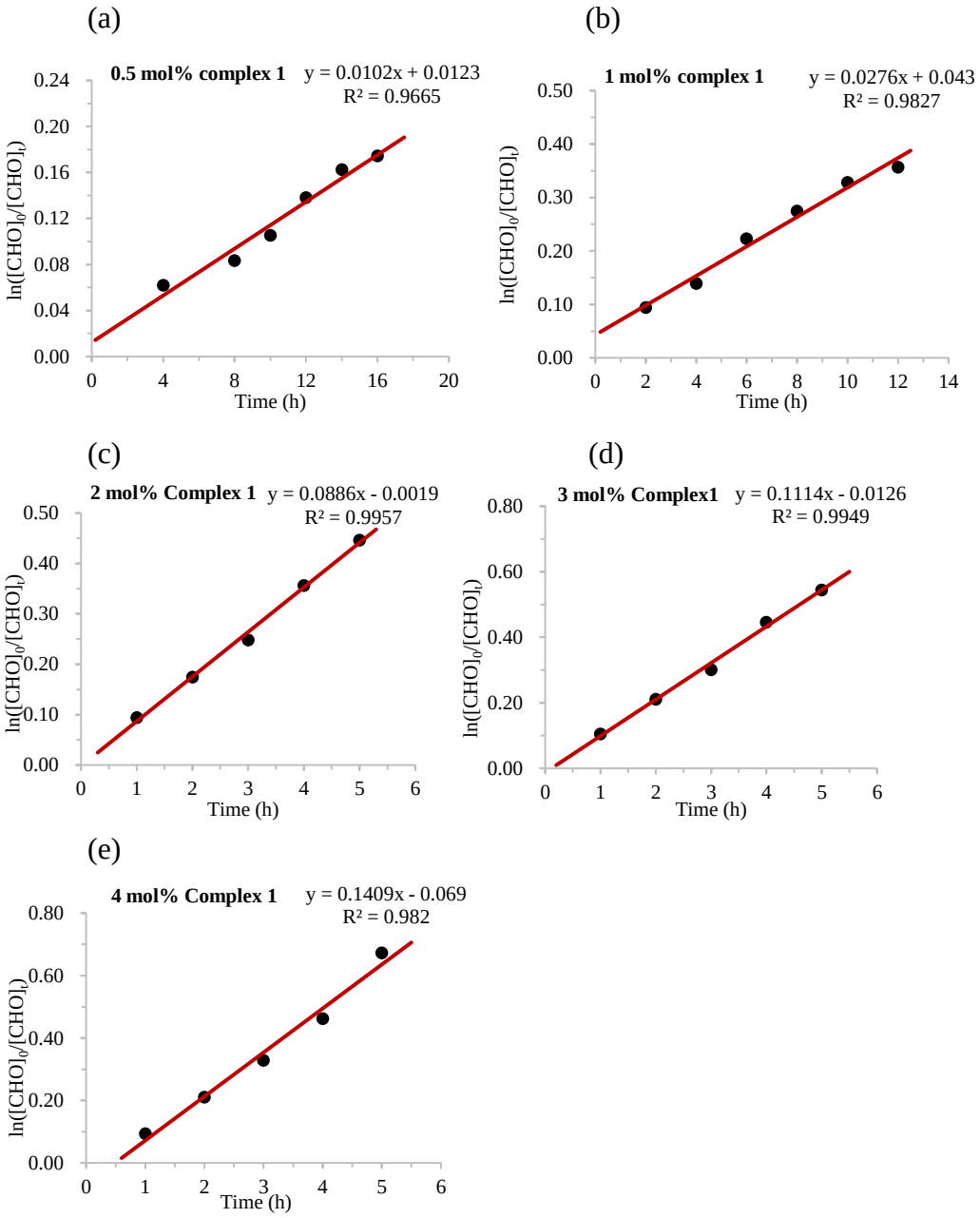


Figure S7. Plot of ln($[CHO]_0/[CHO]_t$) versus time in the range 0.5-4 mol% **[1]** (a-e).

Reaction order with respect to [TBAI]

Table S16. Complex **1** /TBAI (0.5 mol%) catalysed cycloaddition of CO_2 and CHO [a]

Entry	Time (h)	Yield [b] (%)	$[CHO]_0/[CHO]_t$	$\ln([CHO]_0/[CHO]_t)$
1	1	2	1.02	0.020203
2	2	3	1.03	0.030459
3	3	4	1.04	0.040822
4	4	6	1.06	0.061875
5	5	7	1.08	0.072571
6	6	9	1.10	0.094311

[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 2 mol% complex **1** (196.9 mM), 0.5 mol% TBAI (49.3 mM), 1 bar CO_2, 25 °C. [b] Yield was determined by ^{1}H NMR spectroscopy of the reaction mixture.

Table S17. Complex **1** /TBAI (0.8 mol%) catalysed cycloaddition of CO_2 and CHO [a]

Entry	Time (h)	Yield [b] (%)	$[CHO]_0/[CHO]_t$	$\ln([CHO]_0/[CHO]_t)$
1	1	9	1.10	0.094311
2	2	12	1.14	0.127833
3	3	16	1.19	0.174353
4	4	20	1.25	0.223144
5	5	25	1.33	0.287682
6	6	30	1.43	0.356675

[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 2 mol% complex **1** (196.9 mM), 0.8 mol% TBAI (78.7 mM), 1 bar CO_2, 25 °C. [b] Yield was determined by ^{1}H NMR spectroscopy of the reaction mixture.

Table S18. Complex **1** /TBAI (1 mol%) catalysed cycloaddition of CO_2 and CHO [a]

Entry	Time (h)	Yield [b] (%)	$[CHO]_0/[CHO]_t$	$\ln([CHO]_0/[CHO]_t)$
1	1	7	1.08	0.072571
2	2	12	1.14	0.127833
3	3	17	1.20	0.186330
4	4	24	1.32	0.274437
5	5	29	1.41	0.342490
6	6	35	1.54	0.430783

[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 2 mol% complex **1** (196.9 mM), 1 mol% TBAI (98.5 mM), 1 bar CO_2, 25 °C. [b] Yield was determined by ^{1}H NMR spectroscopy of the reaction mixture.

Table S19. Complex **1** /TBAI (1.5 mol%) catalysed cycloaddition of CO_2 and CHO [a]

Entry	Time (h)	Yield [b] (%)	$[CHO]_0/[CHO]_t$	$\ln([CHO]_0/[CHO]_t)$
1	1	7	1.08	0.072571
2	2	13	1.15	0.139262
3	3	19	1.23	0.210721
4	4	24	1.32	0.274437
5	5	32	1.47	0.385662
6	6	37	1.59	0.462035

[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 2 mol% complex **1** (196.9 mM), 1.5 mol% TBAI (147.3 mM), 1 bar CO_2, 25 °C. [b] Yield was determined by ^{1}H NMR spectroscopy of the reaction mixture.

Table S20. Complex **1** /TBAI (2 mol%) catalysed cycloaddition of CO_2 and CHO [a]

Entry	Time (h)	Yield [b] (%)	$[CHO]_0/[CHO]_t$	$\ln([CHO]_0/[CHO]_t)$
1	1	8	1.09	0.083382
2	2	14	1.16	0.150823
3	3	22	1.28	0.248461
4	4	26	1.35	0.301105
5	5	34	1.52	0.415515
6	6	40	1.67	0.510826

[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 2 mol% complex **1** (196.9 mM), 2 mol% TBAI (197.1 mM), 1 bar CO_2, 25 °C. [b] Yield was determined by ^{1}H NMR spectroscopy of the reaction mixture.

Table S21. Complex **1** /TBAI (3 mol%) catalysed cycloaddition of CO_2 and CHO [a]

Entry	Time (h)	Yield [b] (%)	$[CHO]_0/[CHO]_t$	$\ln([CHO]_0/[CHO]_t)$
1	1	9	1.10	0.094311
2	2	14	1.16	0.150823
3	3	24	1.32	0.274437
4	4	30	1.43	0.356675
5	5	36	1.56	0.446287
6	6	43	1.75	0.562119

[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 2 mol% complex **1** (196.9 mM), 3 mol% TBAI (294.7 mM), 1 bar CO_2, 25 °C. [b] Yield was determined by ^{1}H NMR spectroscopy of the reaction mixture.

Table S22. Complex **1** /TBAI (4 mol%) catalysed cycloaddition of CO_2 and CHO [a]

Entry	Time (h)	Yield [b] (%)	$[CHO]_0/[CHO]_t$	$\ln([CHO]_0/[CHO]_t)$
1	1	9	1.10	0.094311
2	2	16	1.19	0.174353
3	3	22	1.28	0.248461
4	4	30	1.43	0.356675
5	5	36	1.56	0.446287
6	6	44	1.79	0.579818

[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 2 mol% complex **1** (196.9 mM), 4 mol% TBAI (393.2 mM), 1 bar CO_2, 25 °C. [b] Yield was determined by ^{1}H NMR spectroscopy of the reaction mixture.

Table S23. Complex **1** /TBAI (5 mol%) catalysed cycloaddition of CO_2 and CHO [a]

Entry	Time (h)	Yield [b] (%)	$[CHO]_0/[CHO]_t$	$\ln([CHO]_0/[CHO]_t)$
1	1	8	1.09	0.083382
2	2	12	1.14	0.127833
3	3	24	1.32	0.274437
4	4	30	1.43	0.356675
5	5	35	1.54	0.430783
6	6	43	1.75	0.562119

[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 2 mol% complex **1** (196.9 mM), 5 mol% TBAI (491.8 mM), 1 bar CO_2, 25 °C. [b] Yield was determined by ^{1}H NMR spectroscopy of the reaction mixture.

Table S24. Complex **1** /TBAI (6 mol%) catalysed cycloaddition of CO_2 and CHO [a]

Entry	Time (h)	Yield [b] (%)	$[CHO]_0/[CHO]_t$	$\ln([CHO]_0/[CHO]_t)$
1	1	9	1.10	0.094311
2	2	14	1.16	0.150823
3	3	26	1.35	0.301105
4	4	31	1.45	0.371064
5	5	35	1.54	0.430783
6	6	44	1.79	0.579818

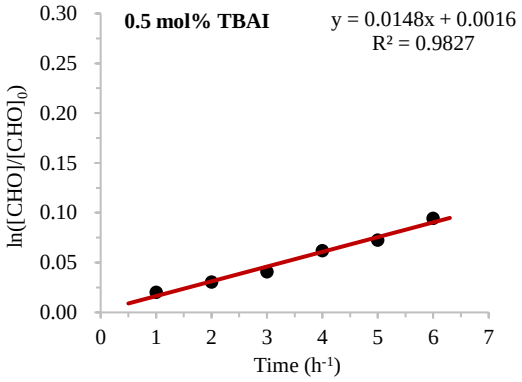
[a] Reaction conditions: $[CHO]_0$ = 9.84 M, 2 mol% complex **1** (196.9 mM), 6 mol% TBAI (590.2 mM), 1 bar CO_2, 25 °C. [b] Yield was determined by ^{1}H NMR spectroscopy of the reaction mixture.

Table S25. k_{obs} data

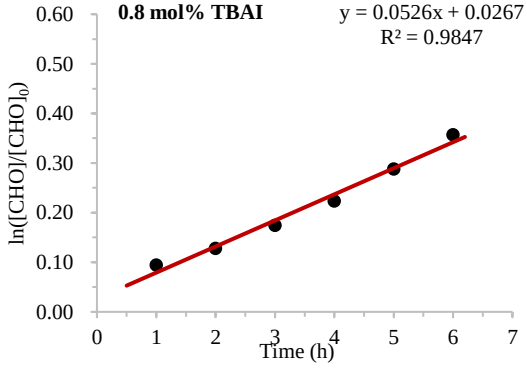
[TBAI] (M)	ln[TBAI]	k_{obs}	lnk_{obs}
0.0493	-3.009831	0.0148	-4.213128
0.0787	-2.542112	0.0526	-2.945039
0.0985	-2.317699	0.0721	-2.629701
0.1473	-1.915284	0.0786	-2.543384
0.1971	-1.624044	0.0853	-2.461581
0.2947	-1.221797	0.0945	-2.359155
0.3932	-0.933437	0.0958	-2.345493
0.4918	-0.709683	0.0967	-2.336142
0.5902	-0.527294	0.0954	-2.349677

Determination of rate order of TBAI

(a)



(b)



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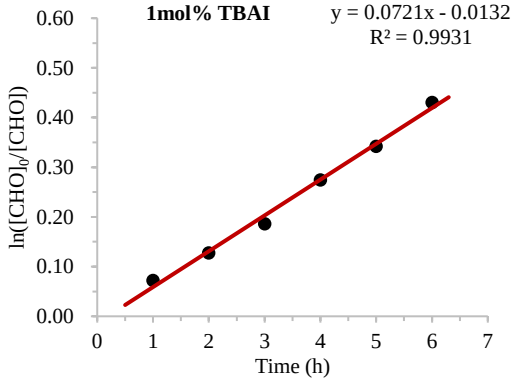

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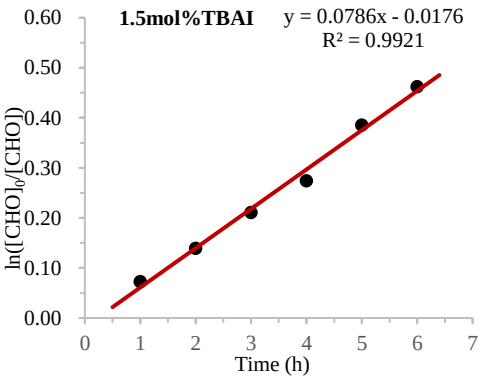

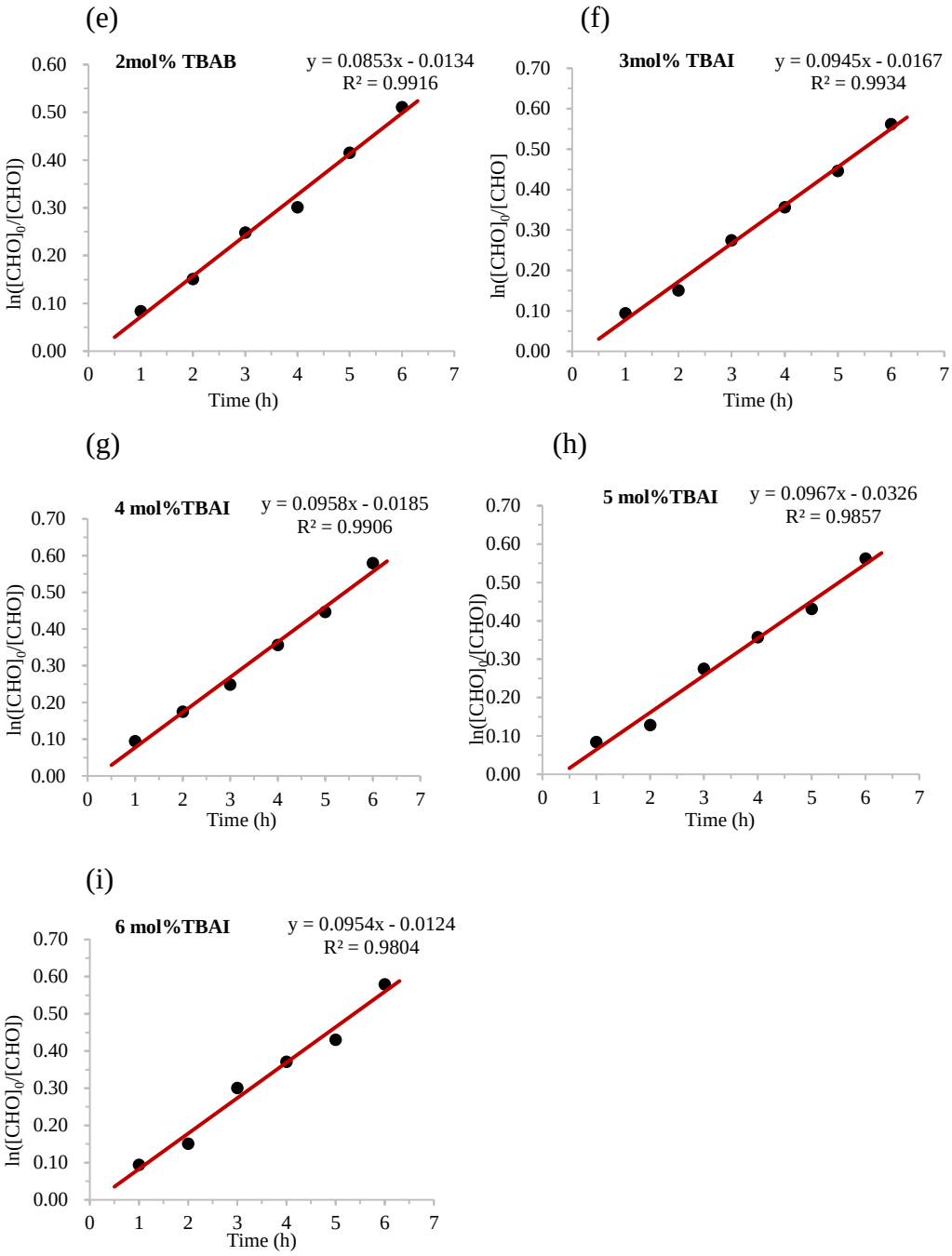

Figure S8. Plot of $\ln([CHO]_0/[CHO]_t)$ versus time in the range 0.5-6 mol% [TBAI] (49.3-590.2 mM) (a-i).

Eyring plot

Table S26. Complex **1**/TBAI catalysed cycloaddition of CO_2 and CHO at 25-110 ℃ [a]

Entry	T (°C)	Time (h)	Yield [b](%)	$[CHO]_0/[CHO]$	$\ln([CHO]_0/[CHO]_t)$
1	25	1	9	1.10	0.094311
2	25	2	16	1.19	0.174353
3	25	3	22	1.28	0.248461

4	25	4	30	1.43	0.356675
5	25	5	36	1.56	0.446287
6	50	1	12	1.14	0.127833
7	50	2	26	1.35	0.301105
8	50	3	35	1.54	0.430783
9	50	4	42	1.72	0.544727
10	50	5	50	2.00	0.693147
11	70	1	14	1.16	0.150823
12	70	2	28	1.39	0.328504
13	70	3	36	1.56	0.446287
14	70	4	44	1.79	0.579818
15	70	5	57	2.33	0.843970
16	90	1	15	1.18	0.162519
17	90	2	30	1.43	0.356675
18	90	3	42	1.72	0.544727
19	90	4	57	2.33	0.843970
20	90	5	61	2.56	0.941609
21	110	1	17	1.20	0.186330
22	110	2	35	1.54	0.430783
23	110	3	45	1.82	0.597837
24	110	4	61	2.56	0.941609
25	110	5	70	3.33	1.203973

[a] Reactions were performed under solvent-free conditions with $[CHO]_0$ = 9.84 M, 2 mol% complex **1** (196.9 mM), 4 mol% TBAI (393.2 mM), 1 bar CO_2, 25-110 ℃. [b] Yield was determined by ^{1}H NMR spectroscopy of the reaction mixture.

Table S27. k_{obs} and temperature data

Entry	T(K)	k_{obs}(h^{-1})	k_{obs}(*$10^{-3}s^{-1}$)	k^a(*10^{-3})	k/T(*10^{-6})	ln(k/T)	1/T
1	298	0.0886	0.024611	0.249918	0.838650	-13.991473	0.003356
2	323	0.1374	0.038167	0.387570	1.199906	-13.633267	0.003096
3	343	0.1638	0.045500	0.462037	1.347047	-13.517595	0.002915
4	363	0.2045	0.056806	0.576841	1.589095	-13.352346	0.002755
5	383	0.2546	0.070722	0.718161	1.875093	-13.186852	0.002611

[a] Calculated on the basis of the kinetic equation $k_{obs} = k\,[\mathbf{1}]^{1.30}[TBAI]^{0.22}$

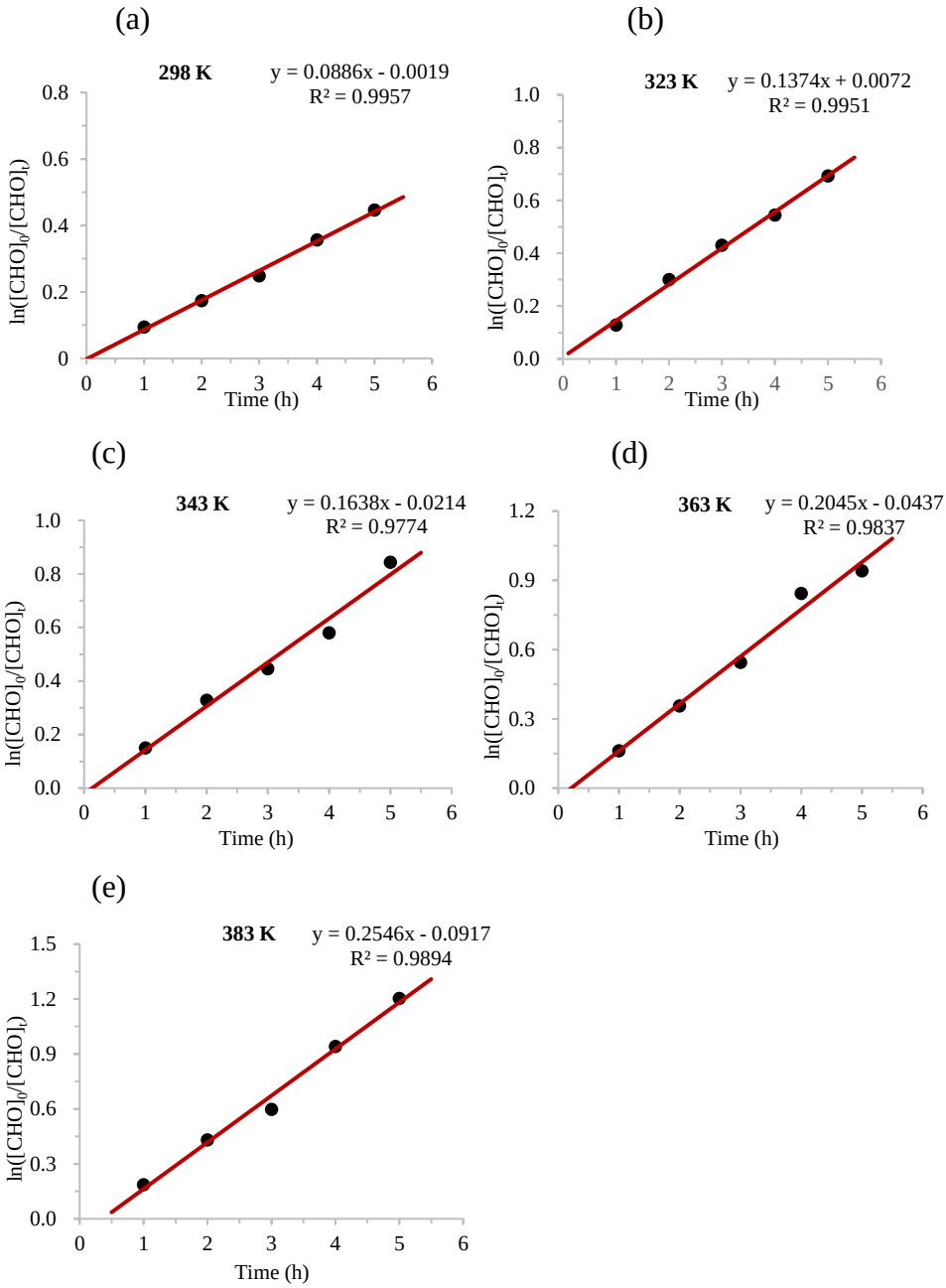

Figure S9. Plot of $\ln([CHO]_0/[CHO]_t)$ versus time at 25-110 ℃ (a-e)

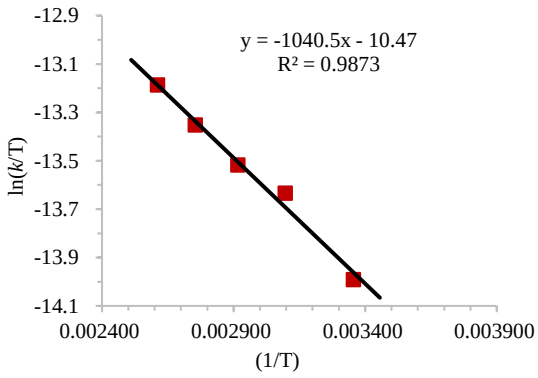

Figure S10. Plot of ln(k/T) versus 1/T in the range from 25 to 110 °C

4. NMR spectra of ligand precursors, complexes and cyclic carbonates

NMR spectra of ligand precursors

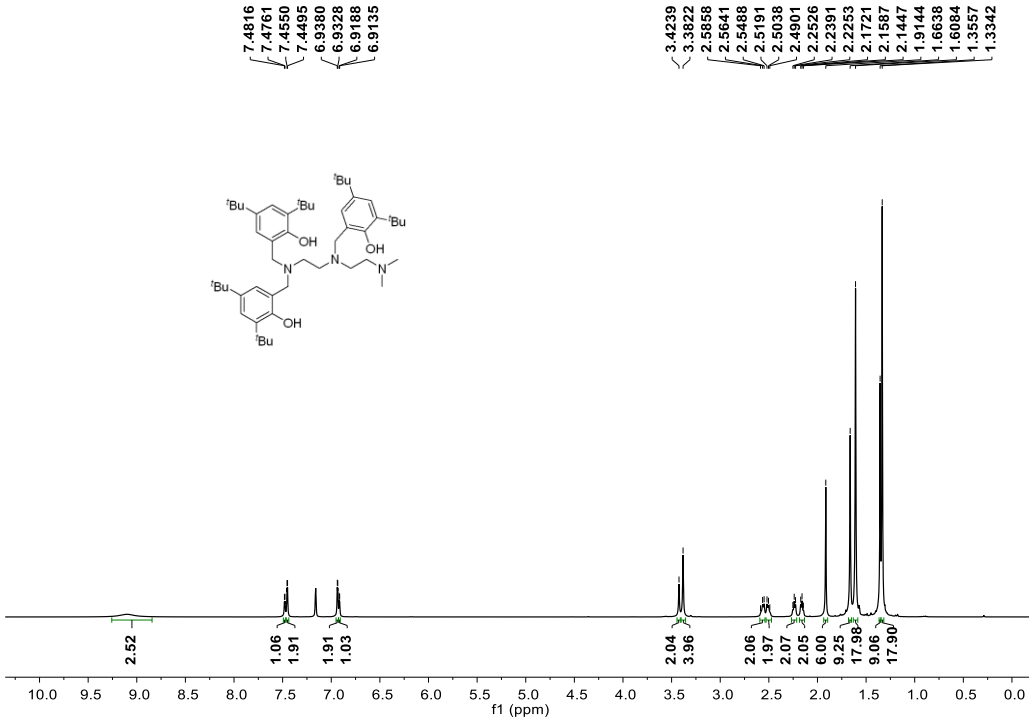

Figure S11. ^{1}H NMR spectrum of $L^{1}H_3$ in C_6D_6

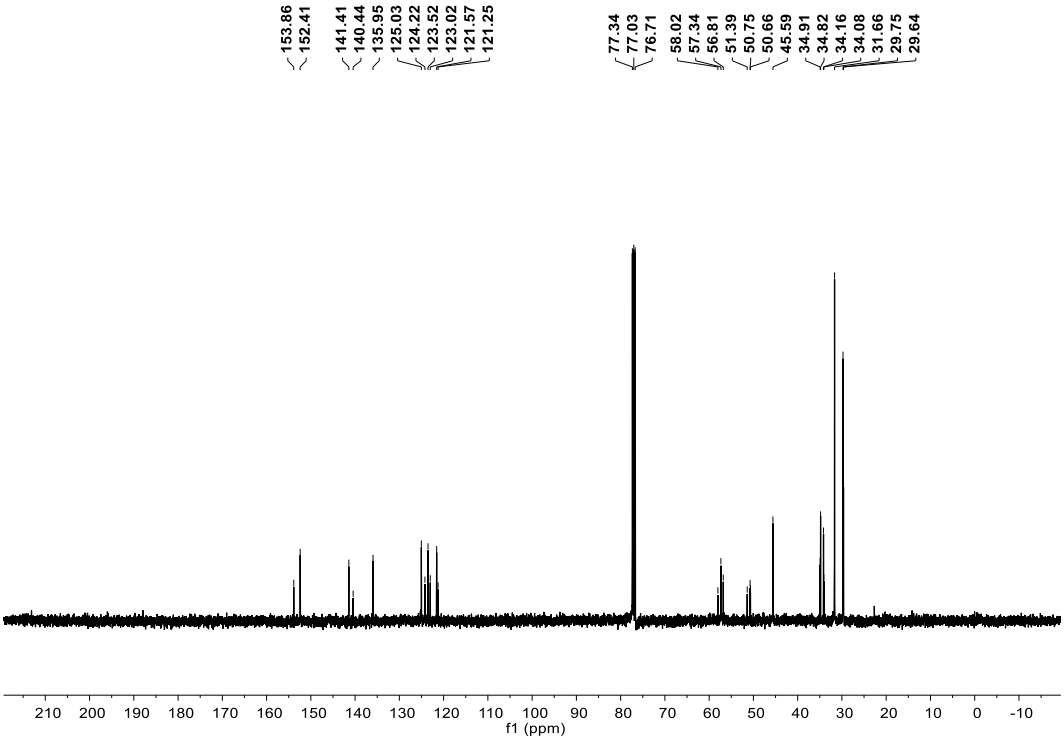

Figure S12. ^{13}C NMR spectrum of $L^{1}H_3$ in $CDCl_3$

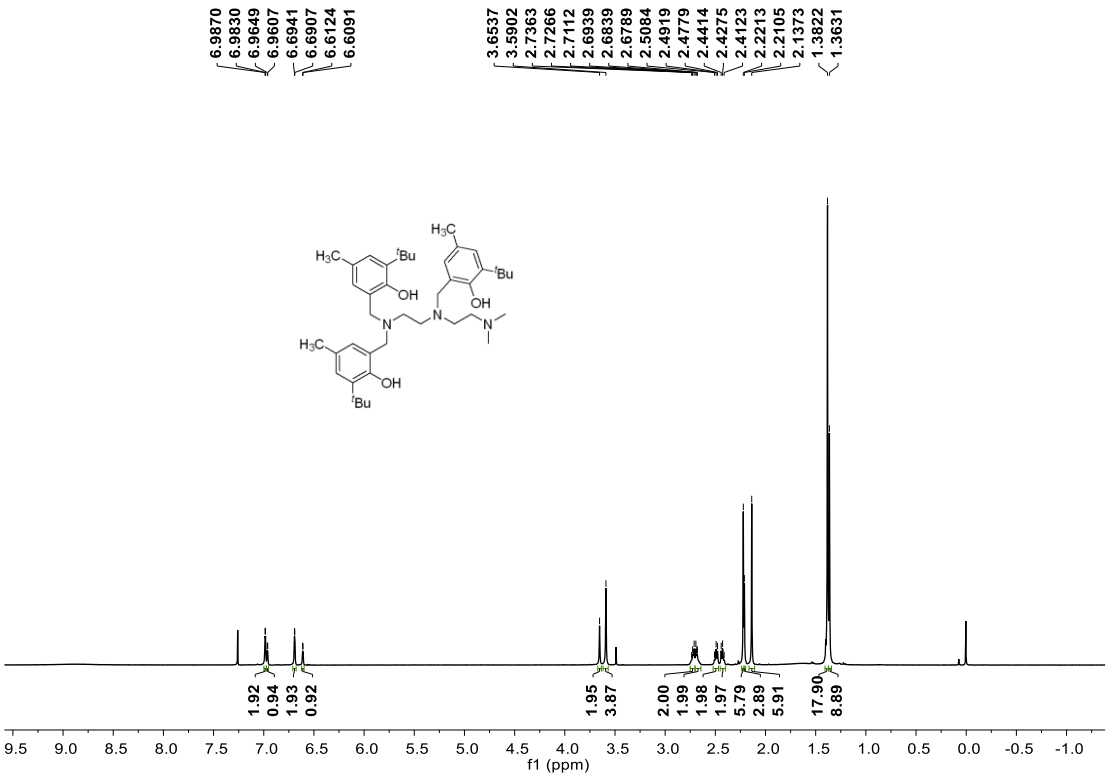

Figure S13. ^{1}H NMR spectrum of $L^{2}H_3$ in $CDCl_3$

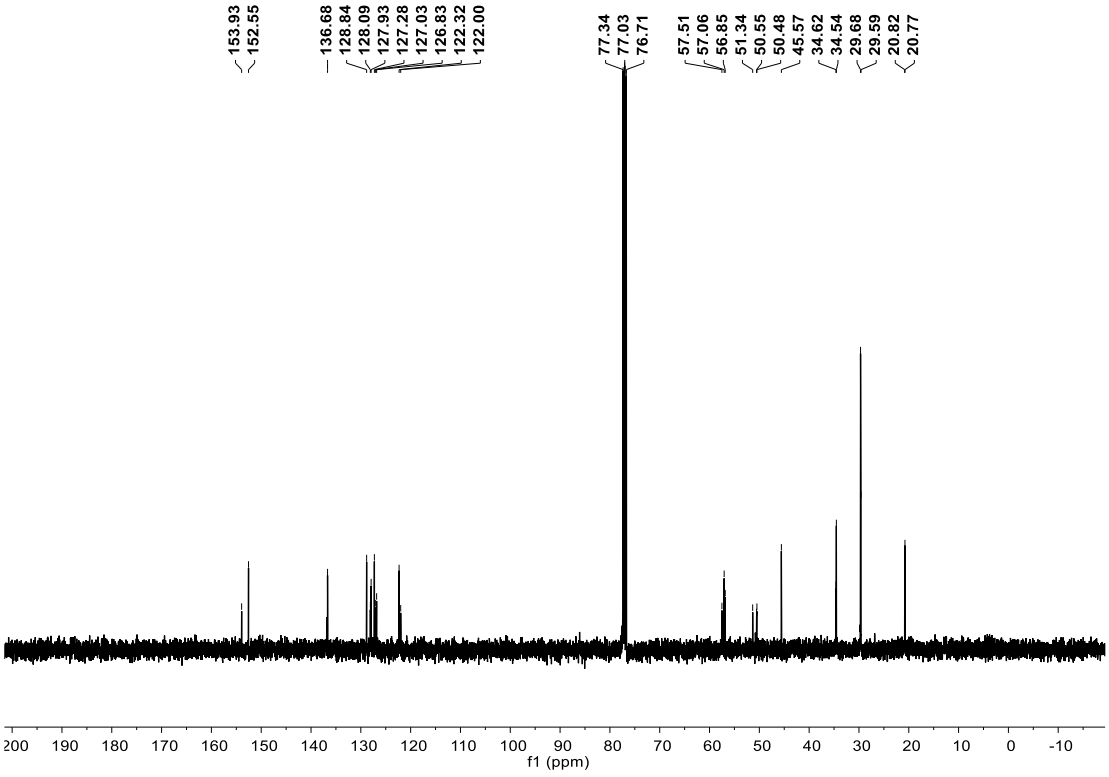

Figure S14 ^{13}C NMR spectrum of $L^{2}H_3$ in $CDCl_3$

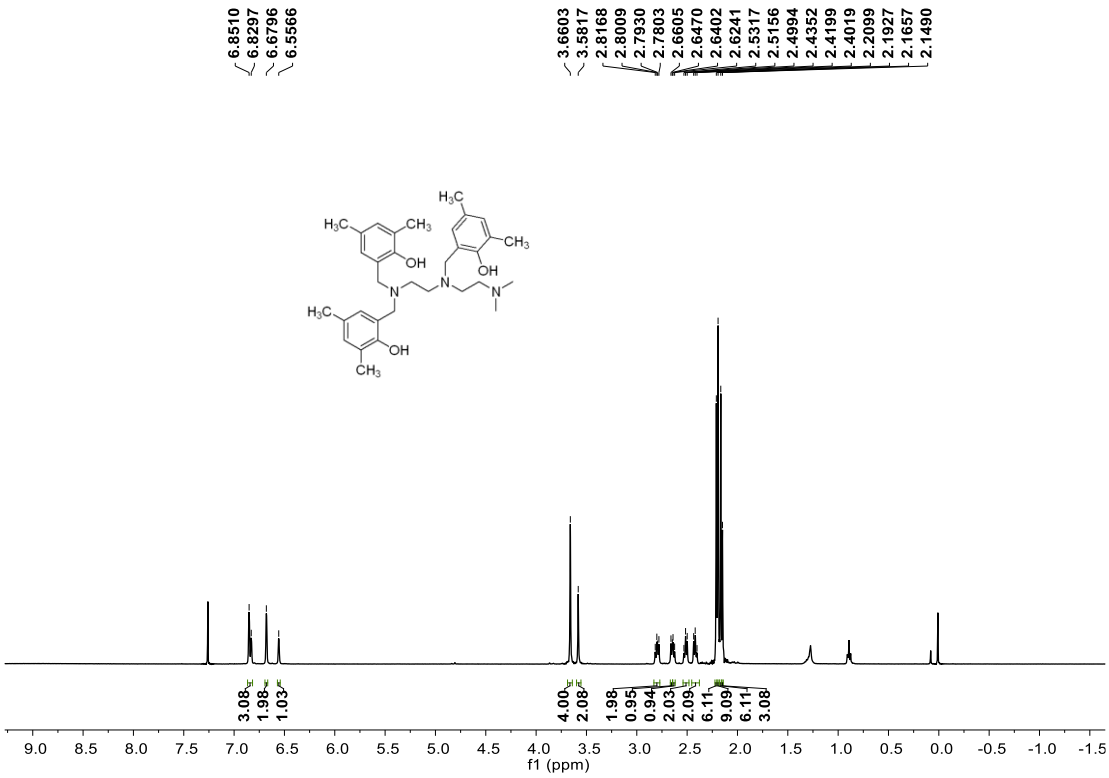

Figure S15. ^{1}H NMR spectrum of $L^{3}H_3$ in $CDCl_3$

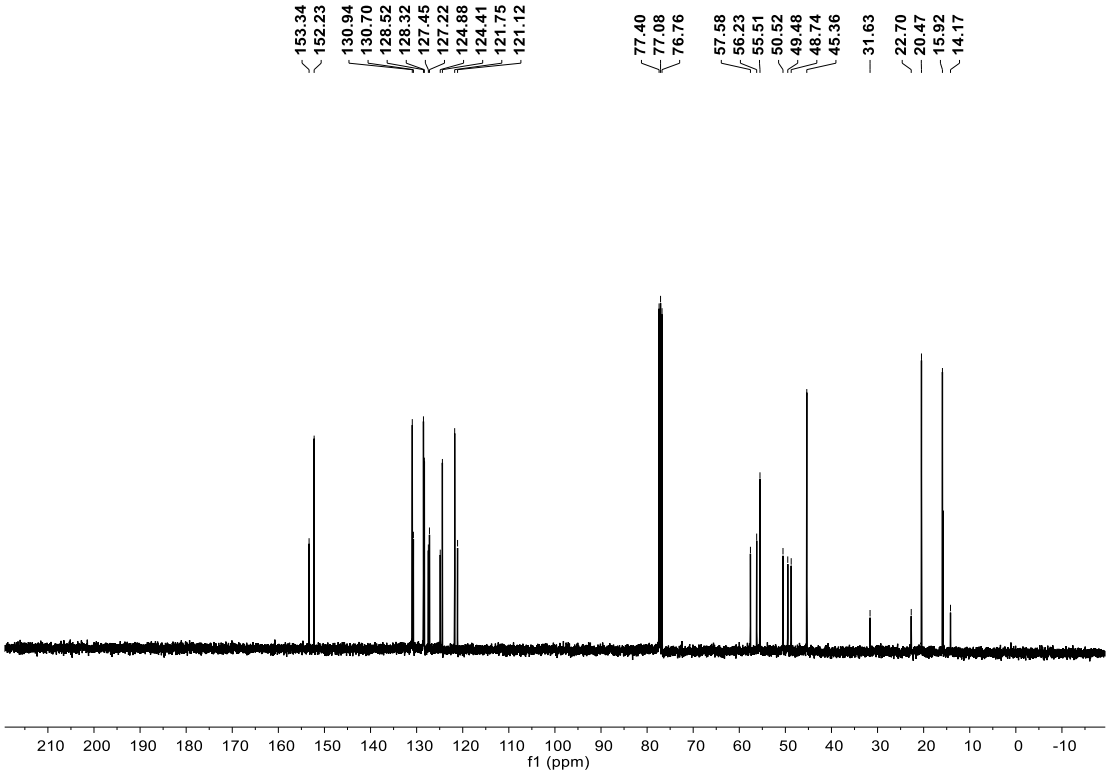

Figure S16. ^{13}C NMR spectrum of $L^{3}H_3$ in $CDCl_3$

NMR spectra of diamagnetic complexes

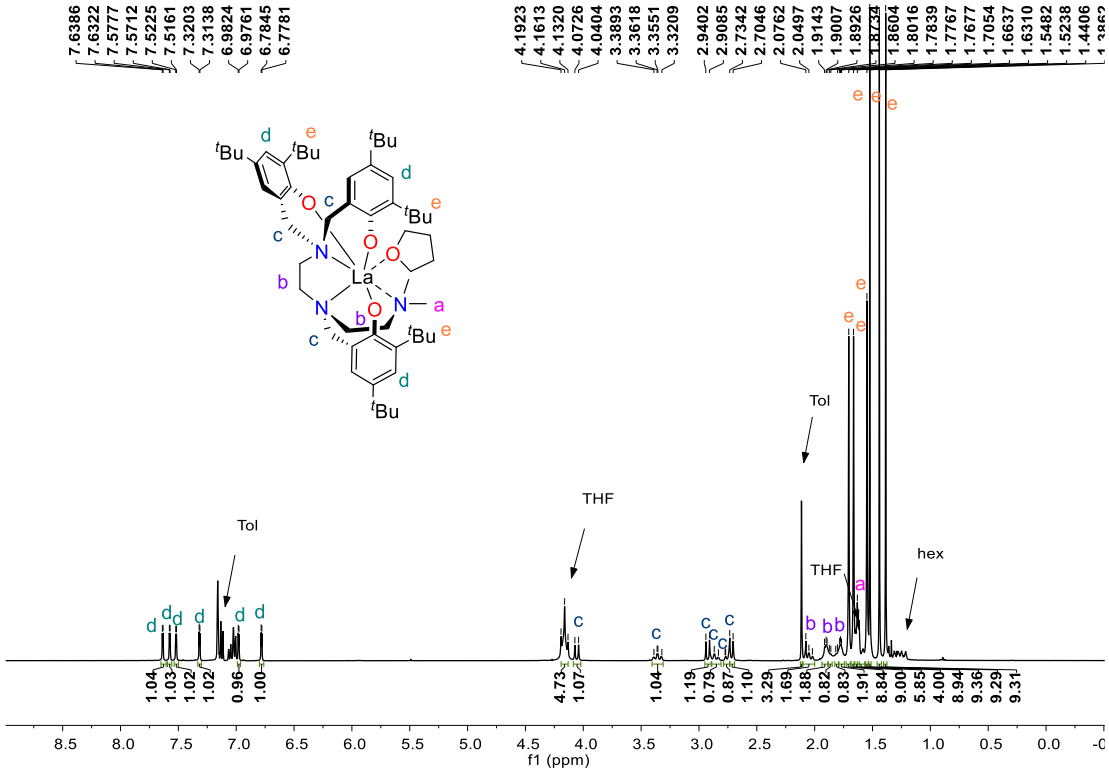

Figure S17. ^{1}H NMR spectrum of complex **1** in C_6D_6

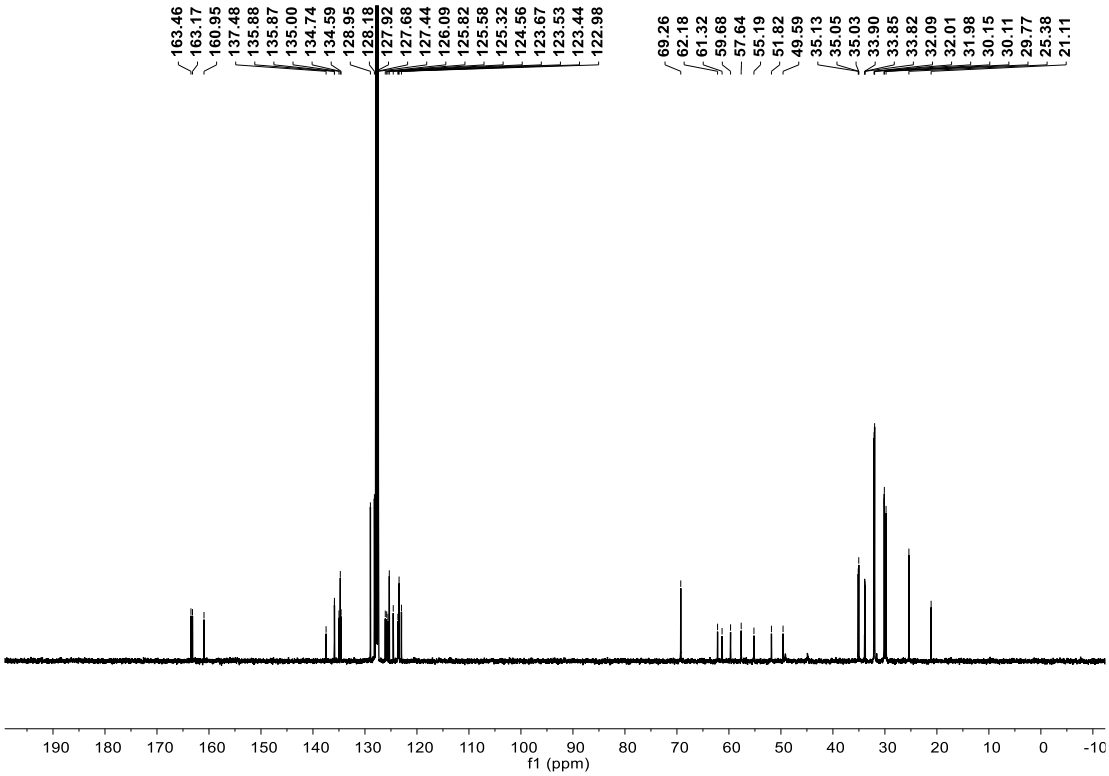

Figure S18. ^{13}C NMR spectrum of complex **1** in C_6D_6

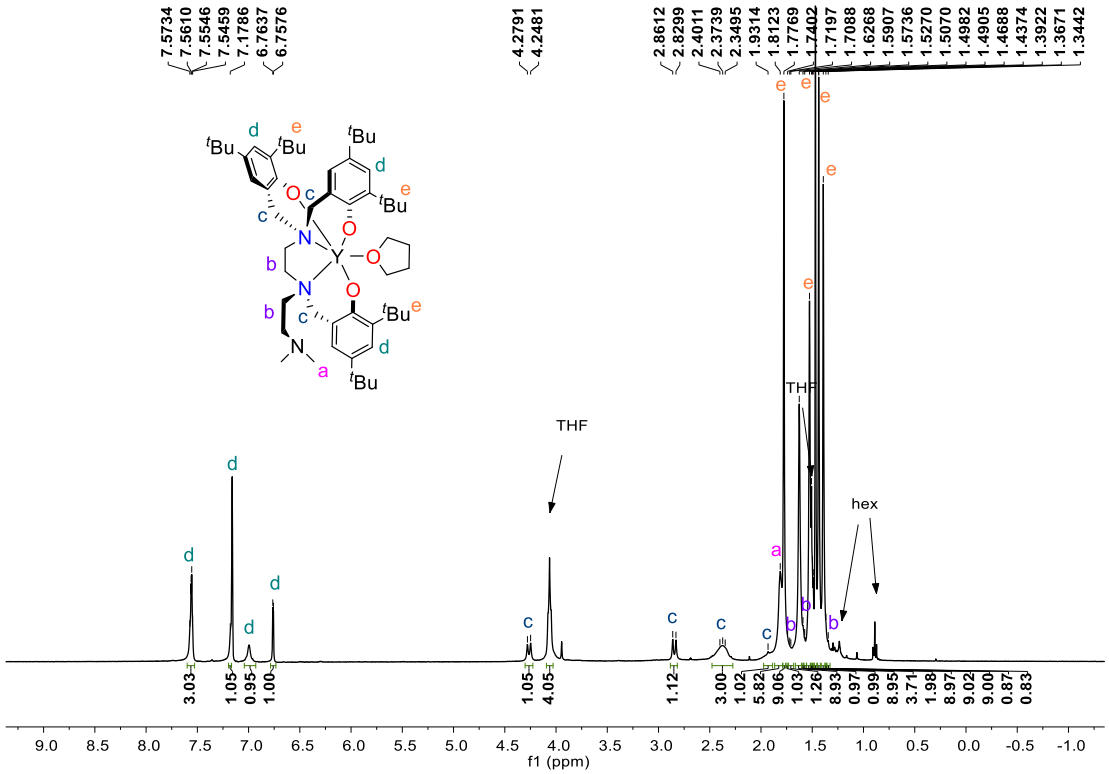

Figure S19. ^{1}H NMR spectrum of complex **4** in C_6D_6

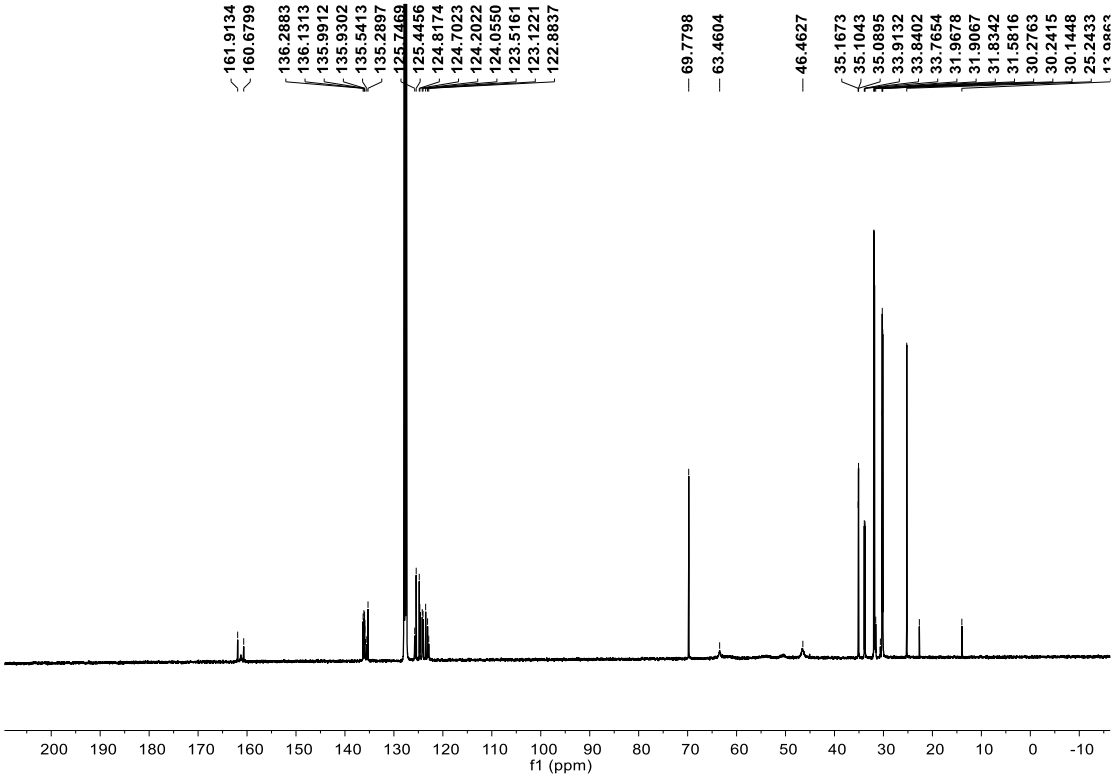

Figure S20. ^{13}C NMR spectrum of complex **4** in C_6D_6

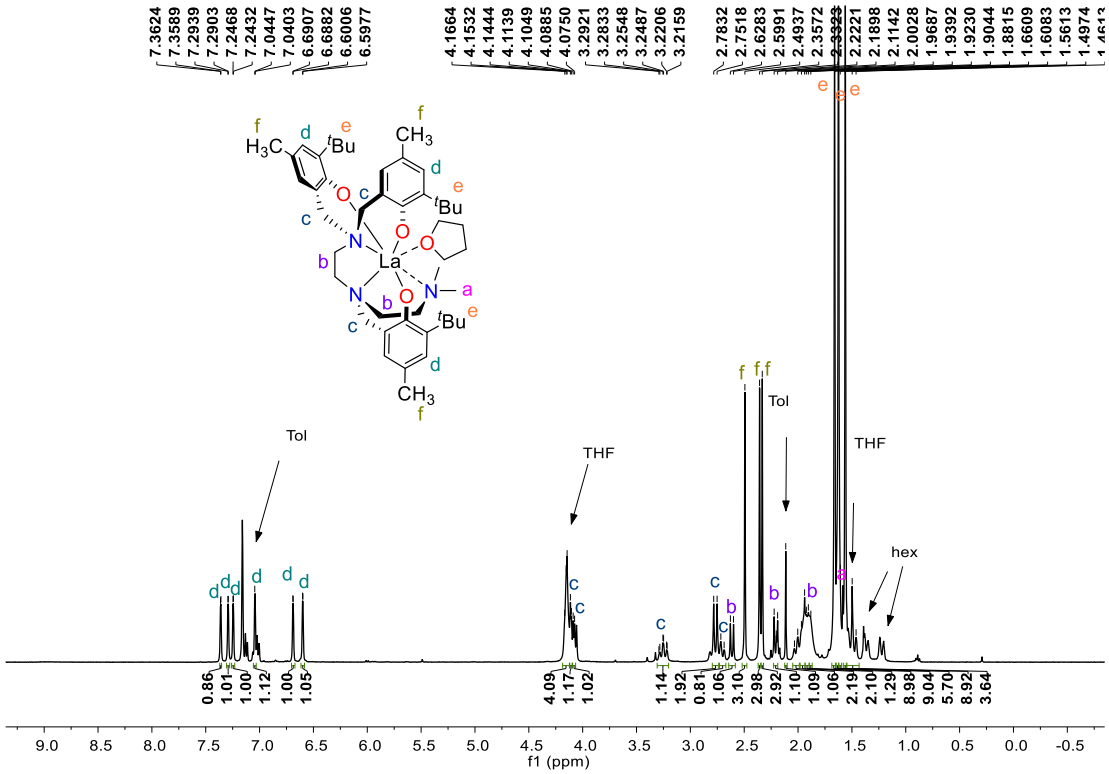

Figure S21. ^{1}H NMR spectrum of complex **5** in C_6D_6

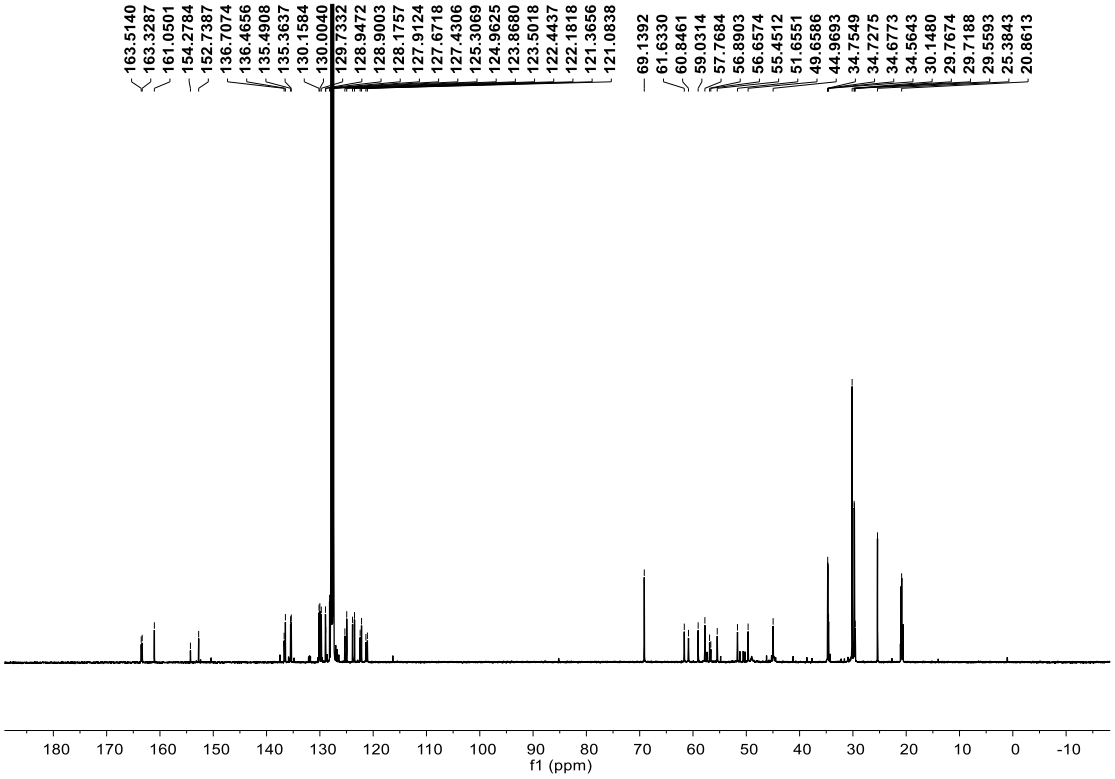

Figure S22. ^{13}C NMR spectrum of complex **5** in C_6D_6

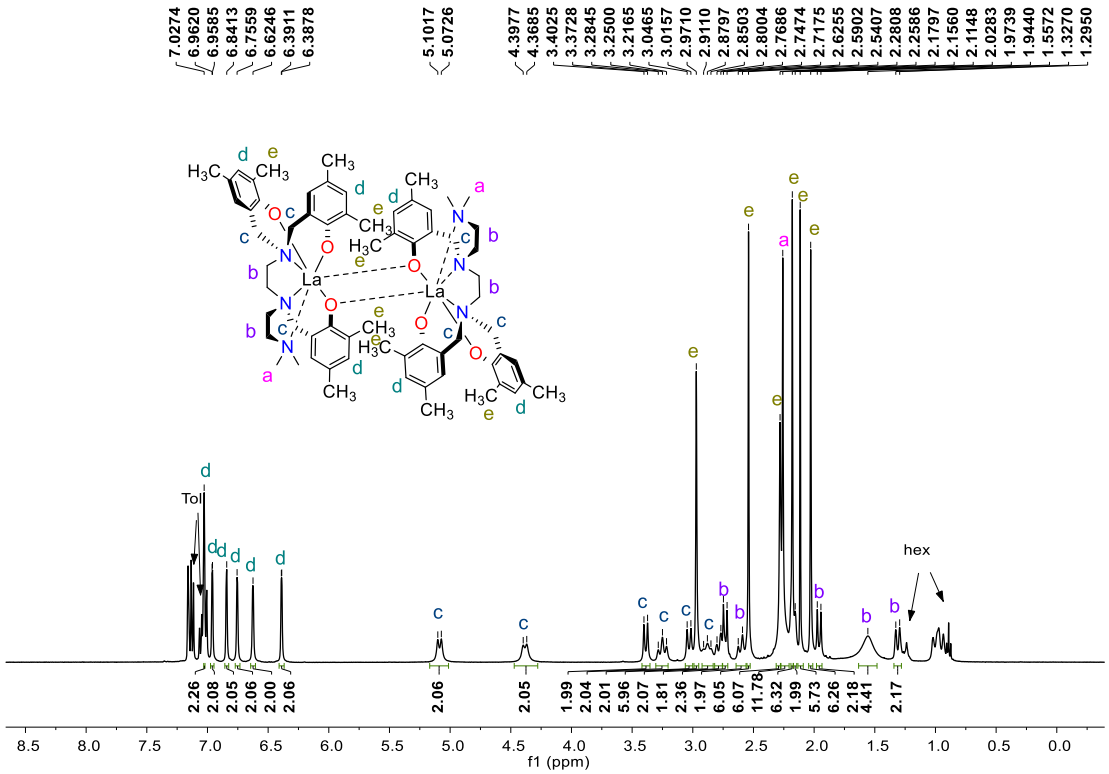

Figure S23. ^{1}H NMR spectrum of complex **6** in C_6D_6

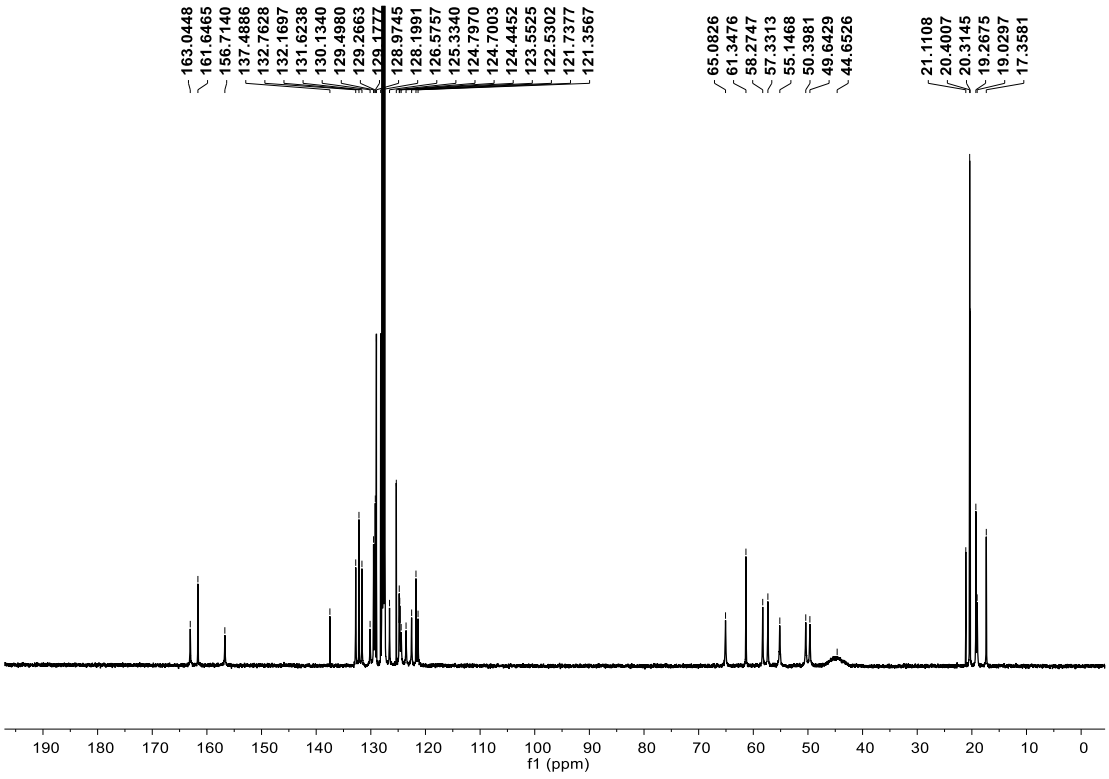

Figure S24. ^{13}C NMR spectrum of complex **6** in C_6D_6

NMR spectra of cyclic carbonates

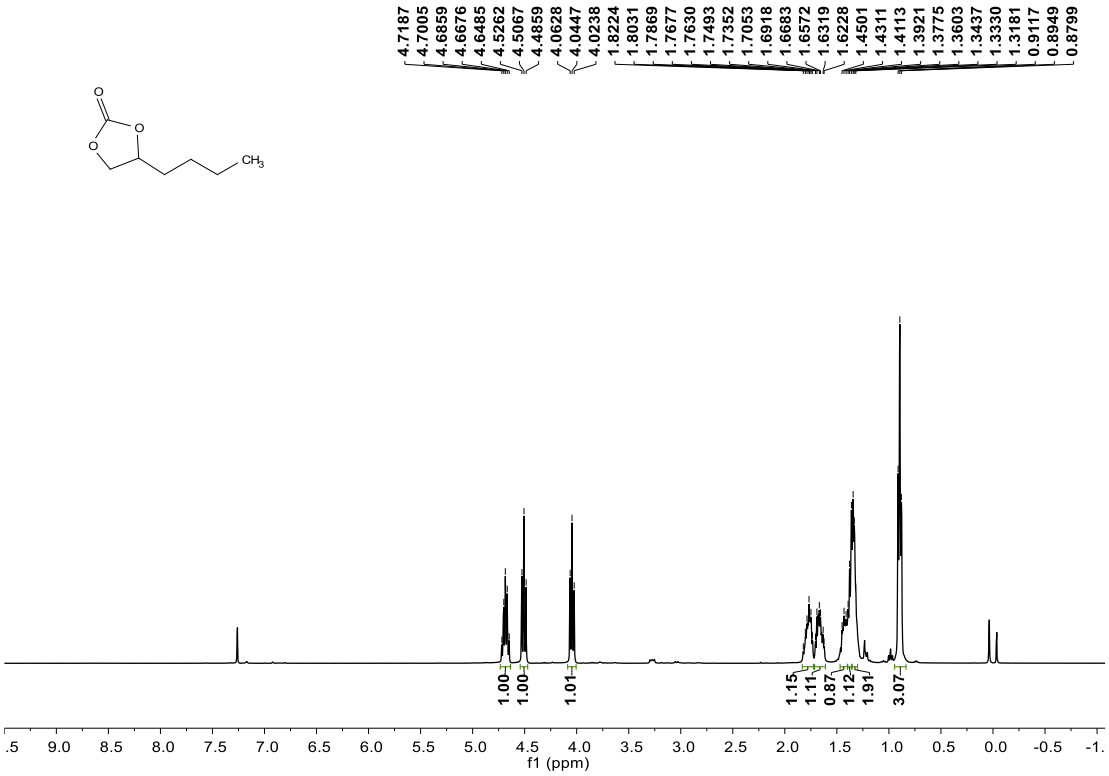

Figure S25.[1]H NMR spectrum of **2a** in $CDCl_3$

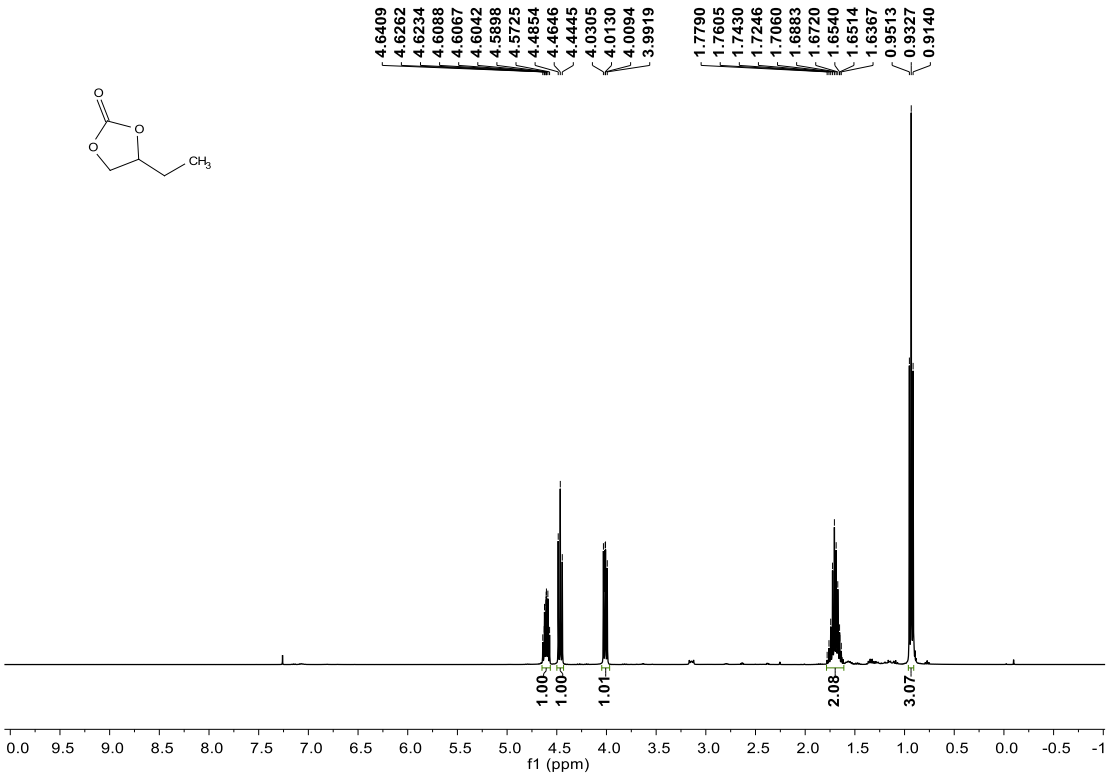

Figure S26.[1]H NMR spectrum of **2b** in $CDCl_3$

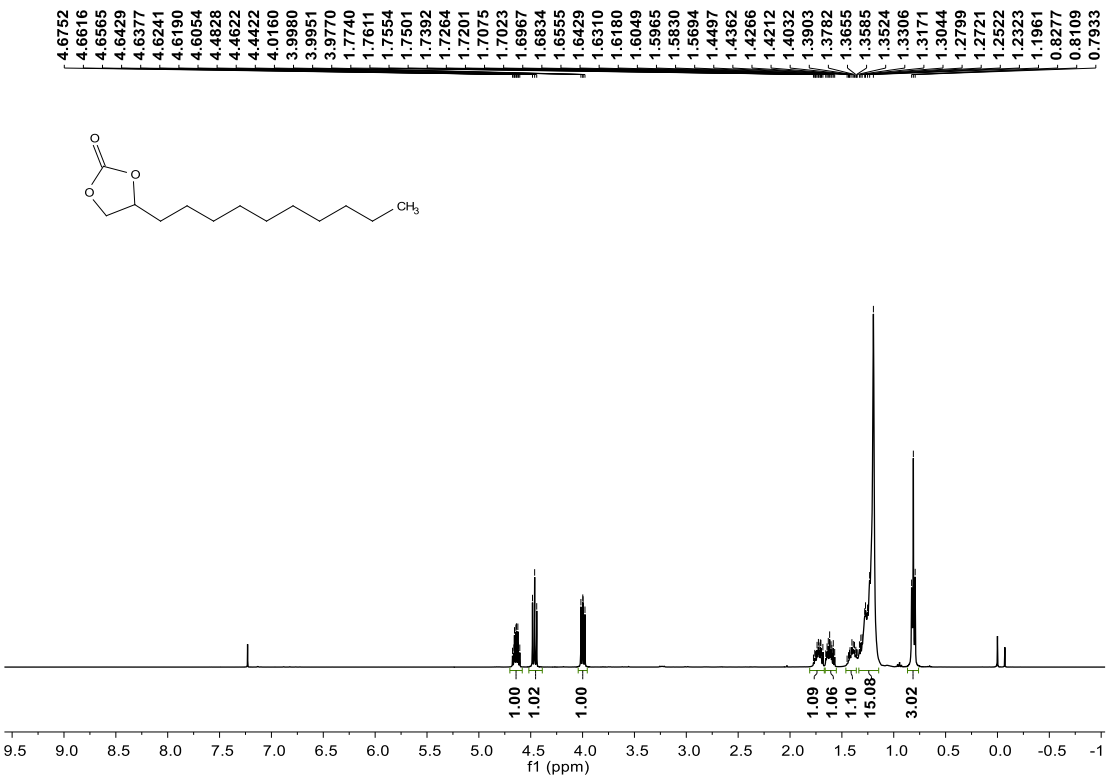

Figure S27.[1]H NMR spectrum of **2c** in $CDCl_3$

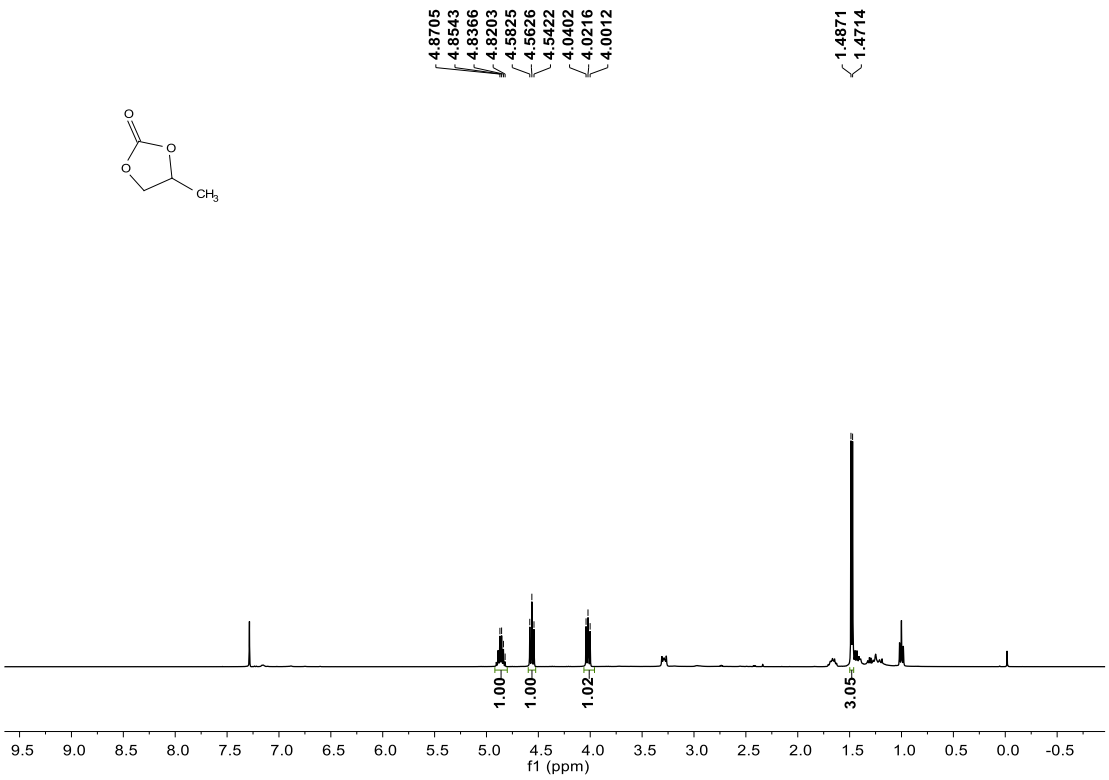

Figure S28. [1]H NMR spectrum of **2d** in $CDCl_3$

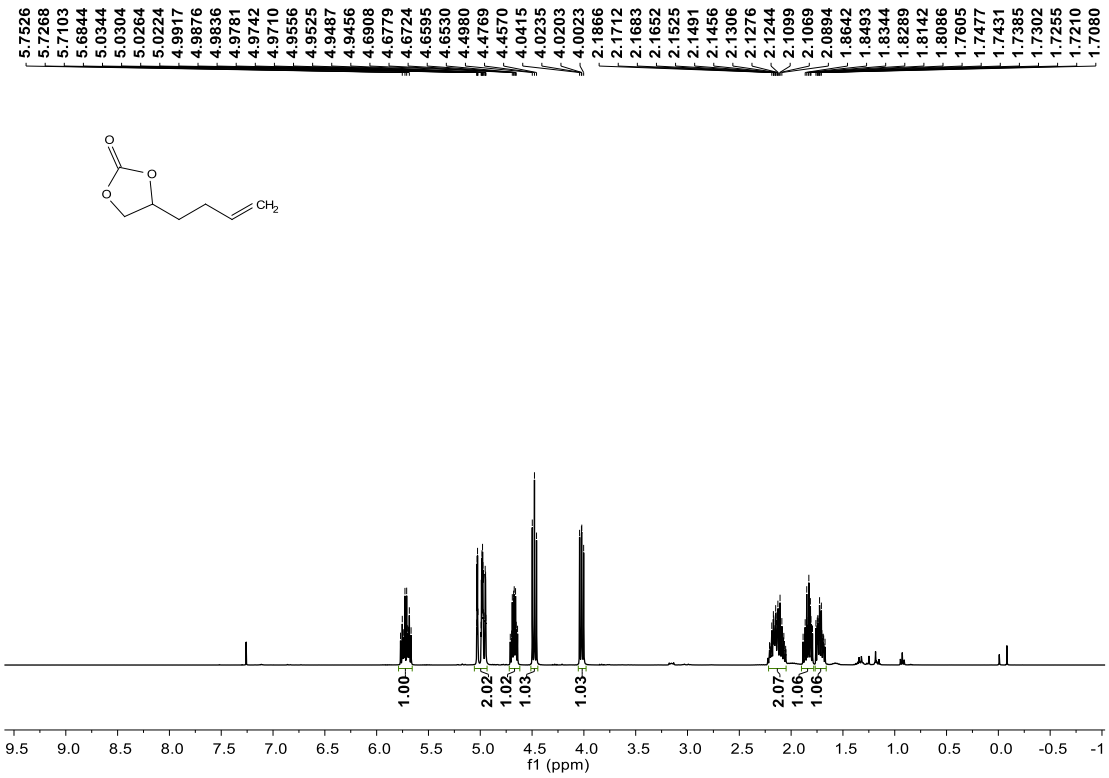

Figure S29. ^{1}H NMR spectrum of **2e** in $CDCl_3$

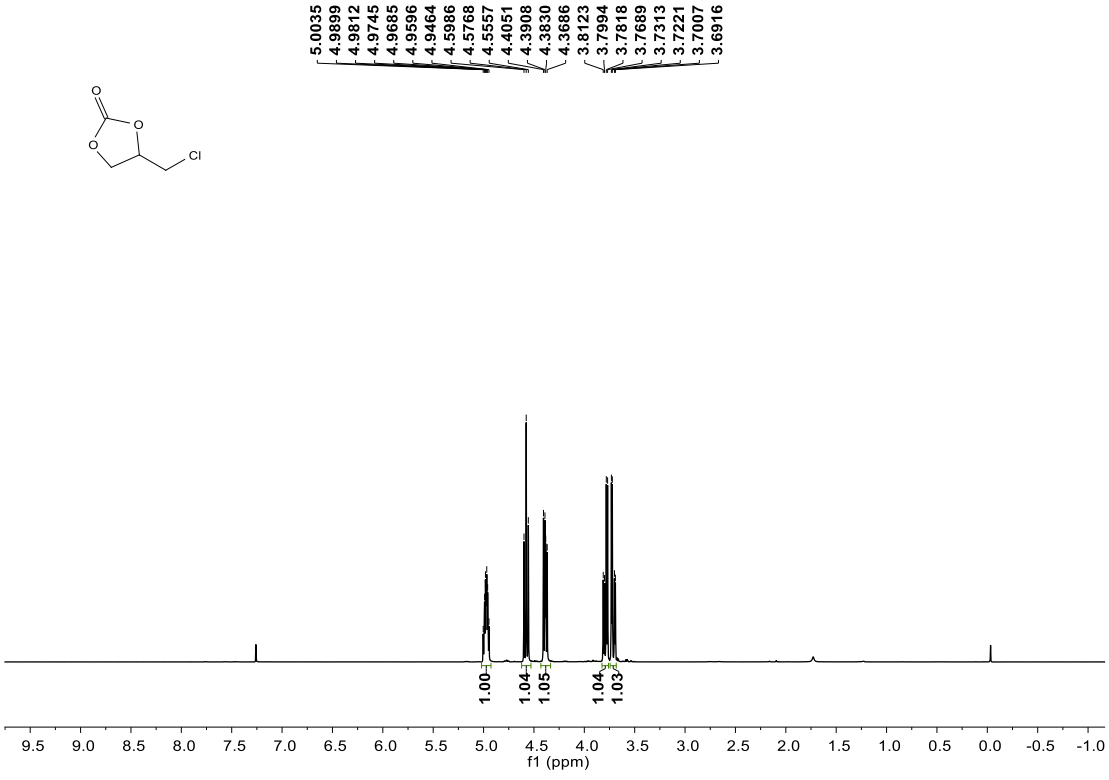

Figure S30. ^{1}H NMR spectrum of **2f** in $CDCl_3$

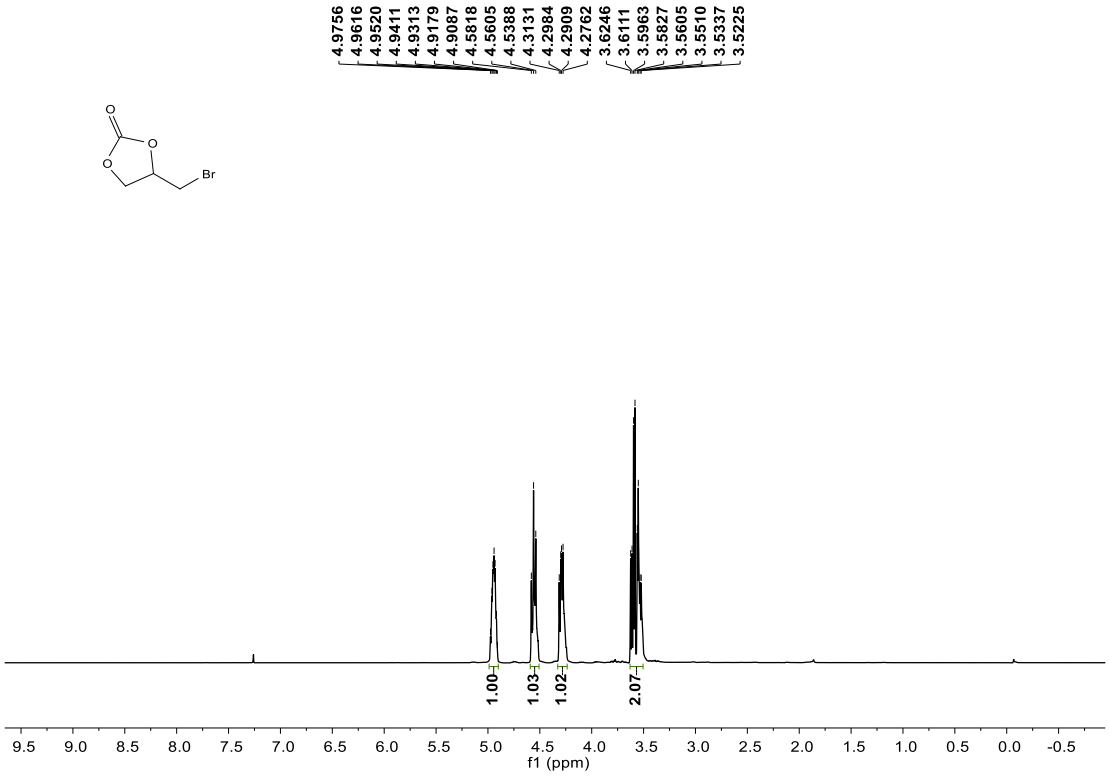

Figure S31. ^{1}H NMR spectrum of **2g** in $CDCl_3$

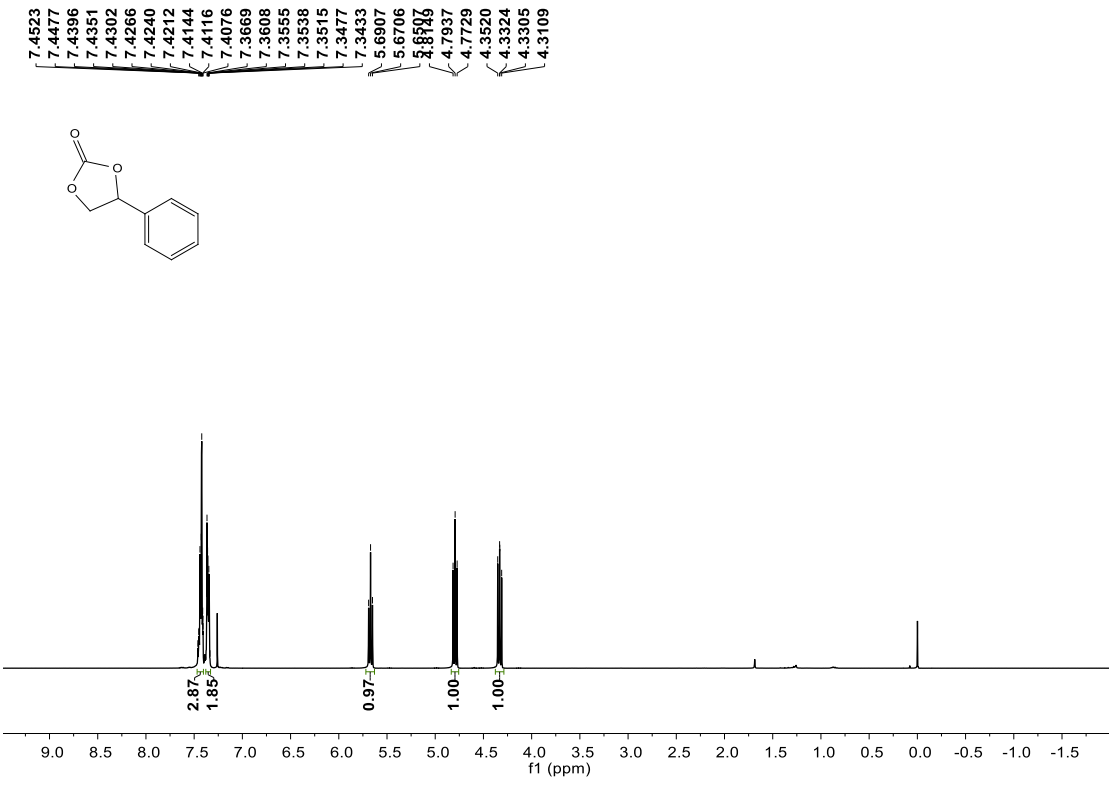

Figure S32. ^{1}H NMR spectrum of **2h** in $CDCl_3$

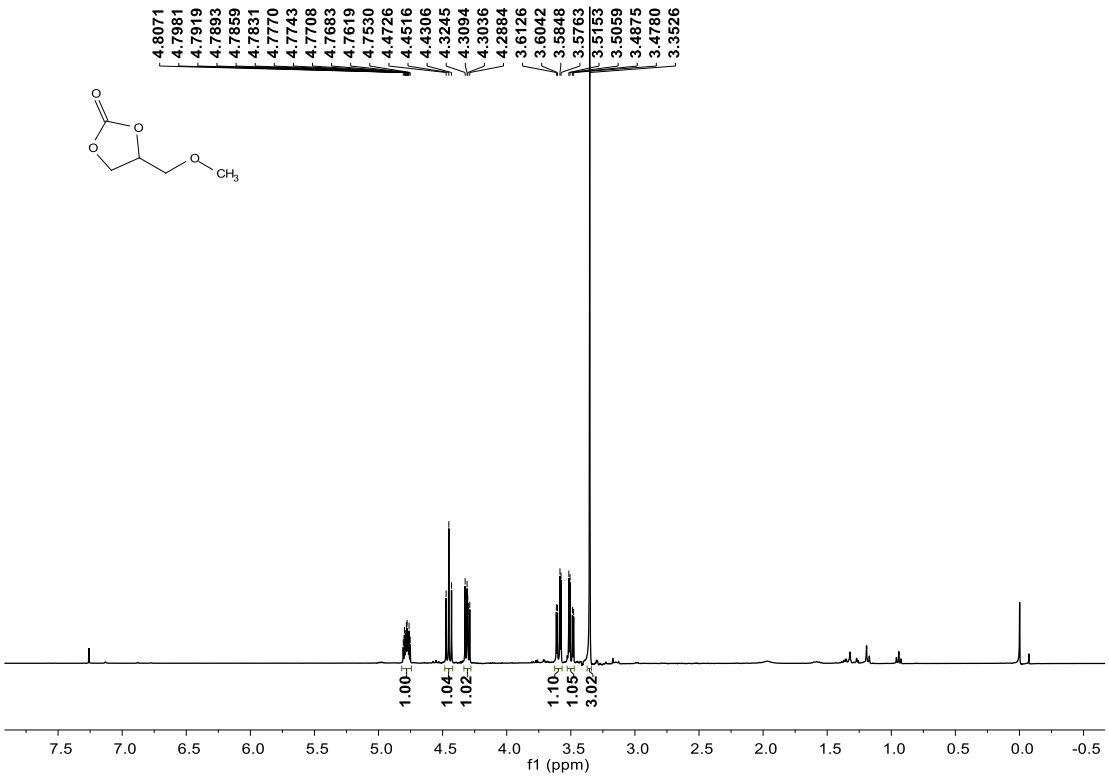

Figure S33. ^{1}H NMR spectrum of **2i** in $CDCl_3$

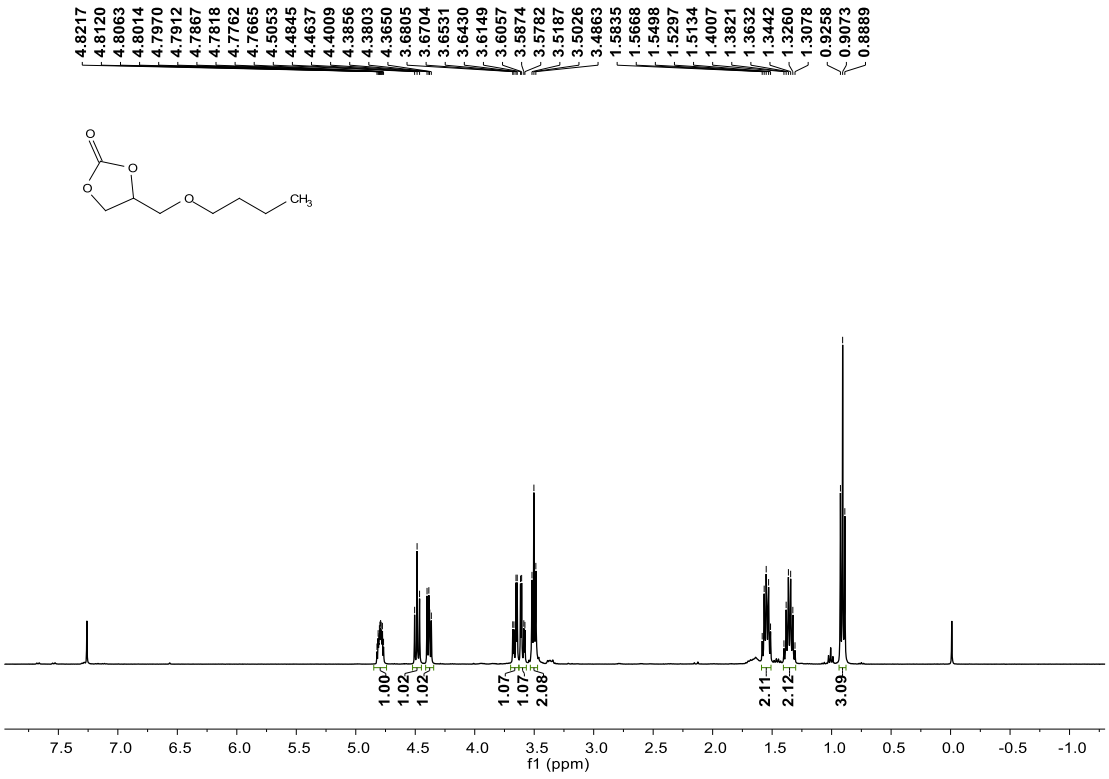

Figure S34. ^{1}H NMR spectrum of **2j** in $CDCl_3$

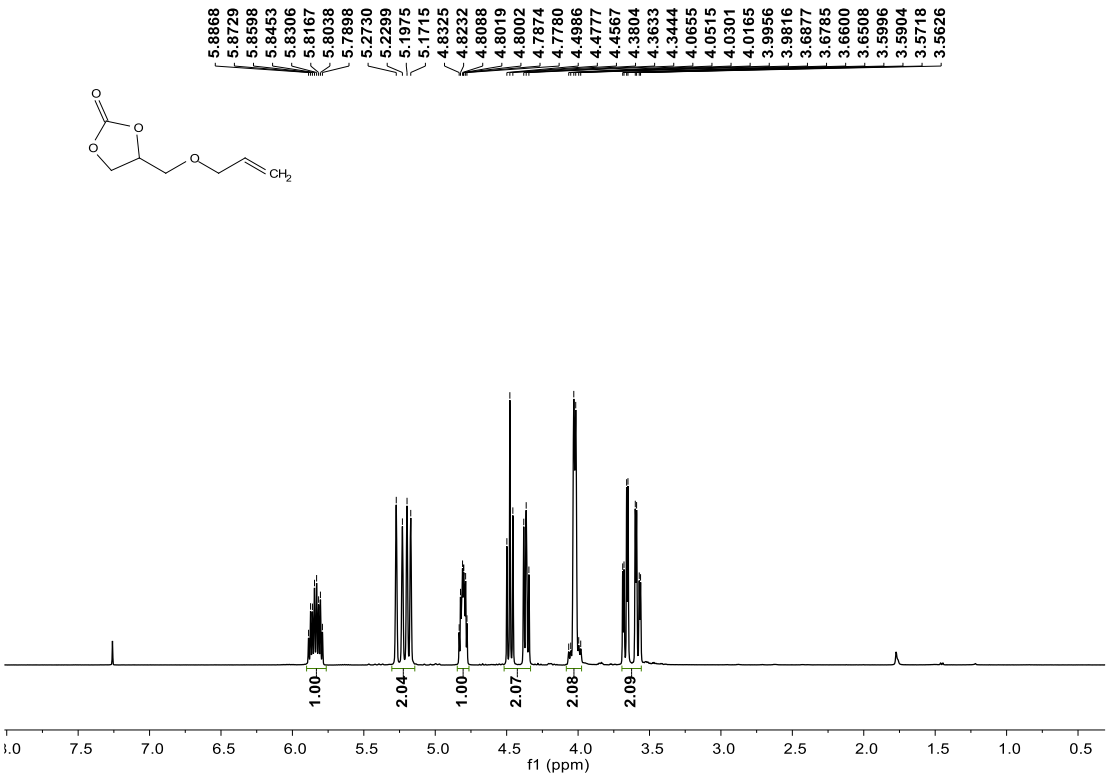

Figure S35.[1]H NMR spectrum of **2k** in $CDCl_3$

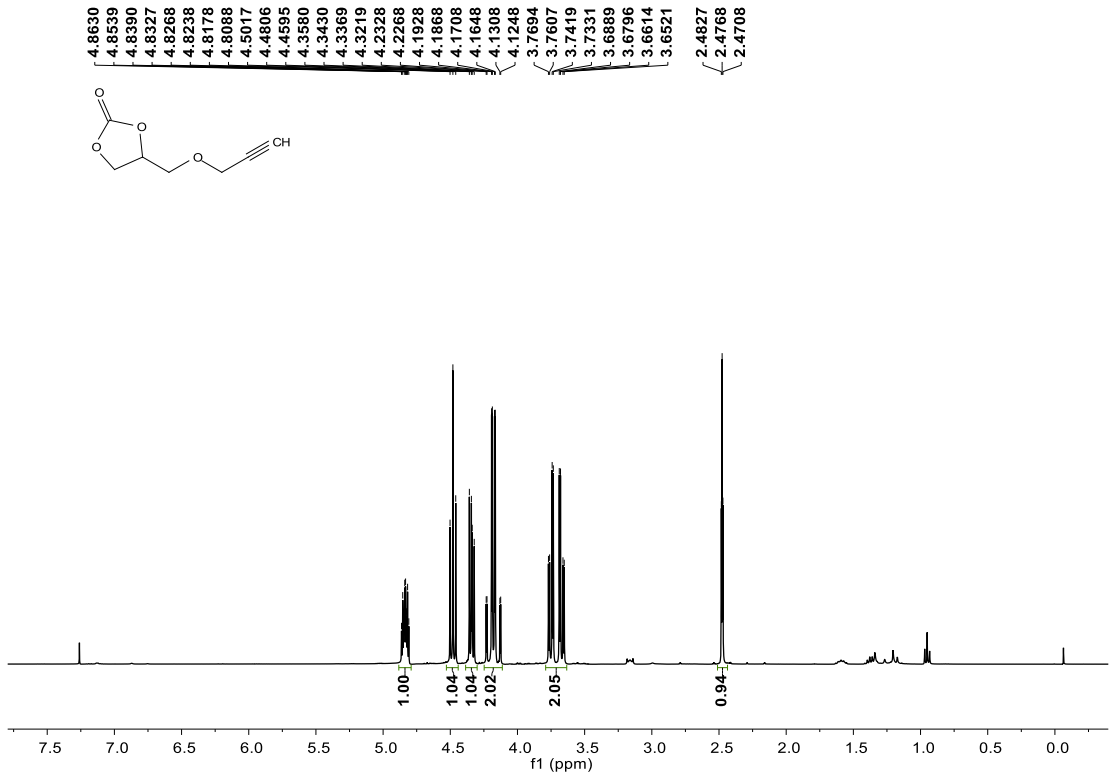

Figure S36.[1]H NMR spectrum of **2l** in $CDCl_3$

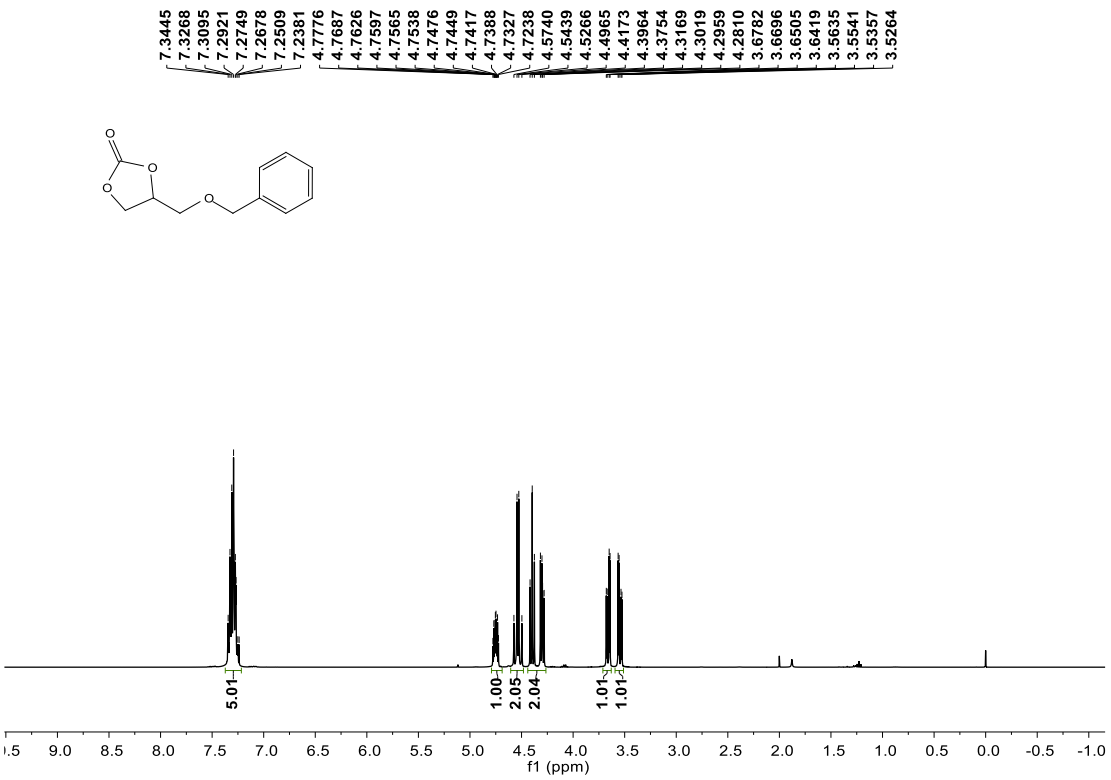

Figure S37.[1]H NMR spectrum of **2m** in $CDCl_3$

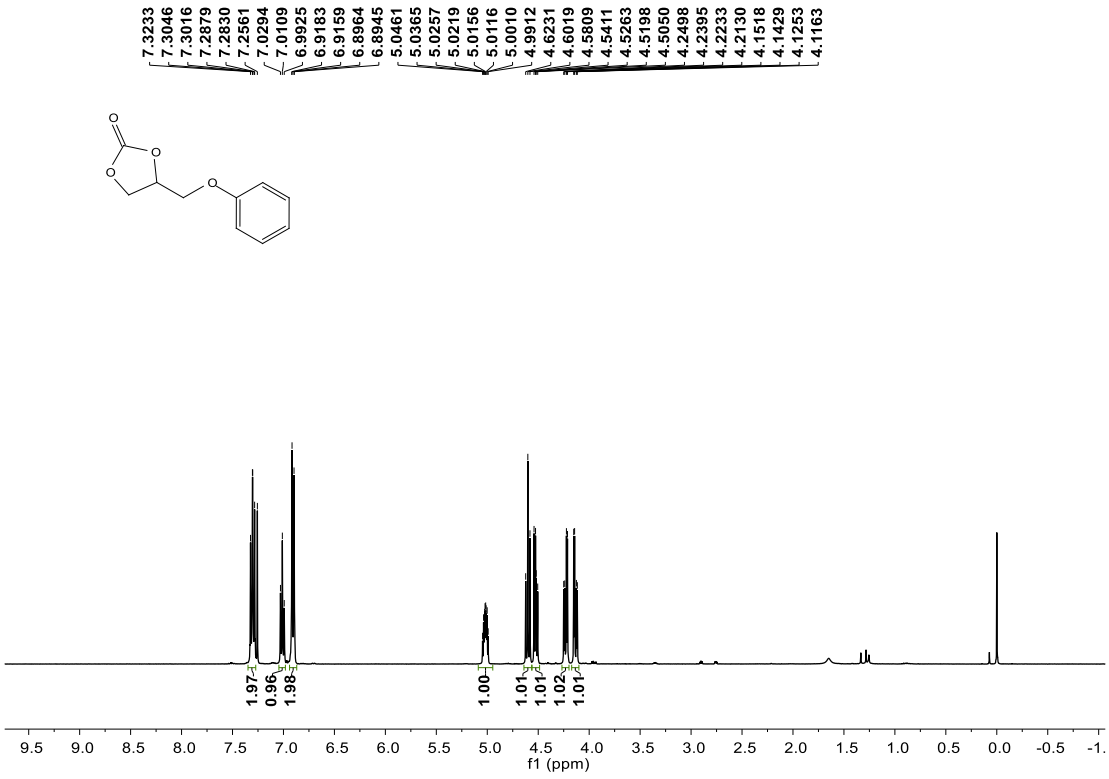

Figure S38. [1]H NMR spectrum of **2n** in $CDCl_3$

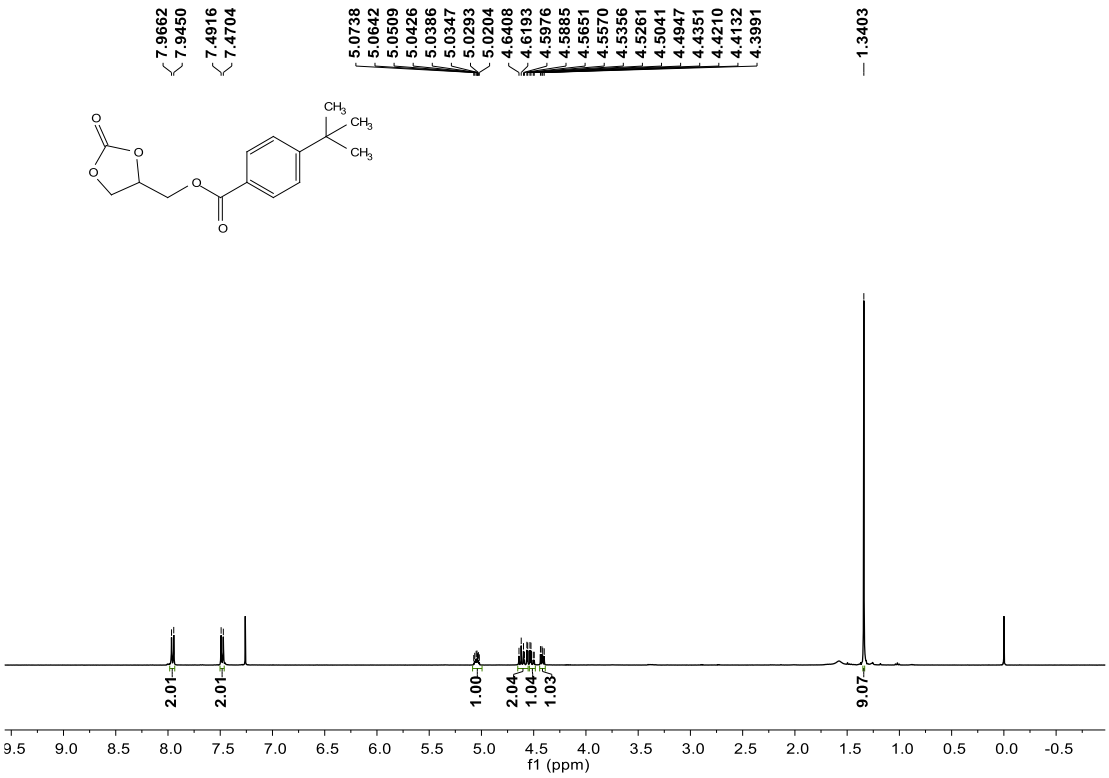

Figure S39. ^{1}H NMR spectrum of **2o** in $CDCl_3$

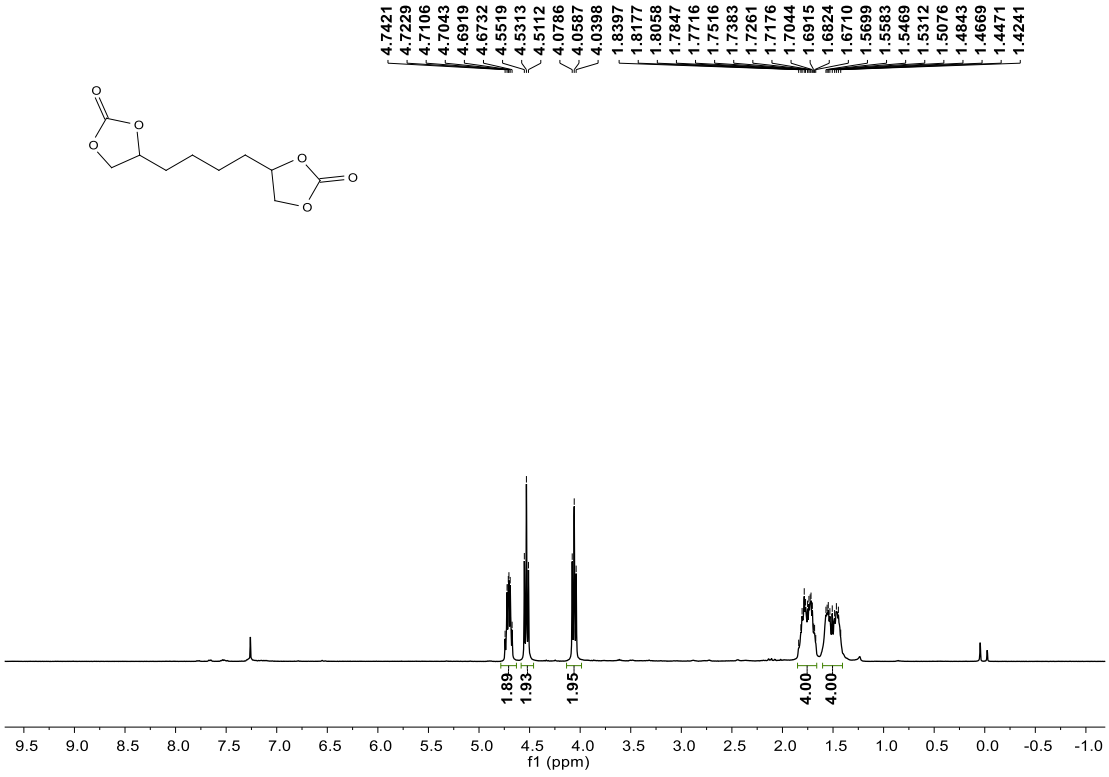

Figure S40. ^{1}H NMR spectrum of **2p** in $CDCl_3$

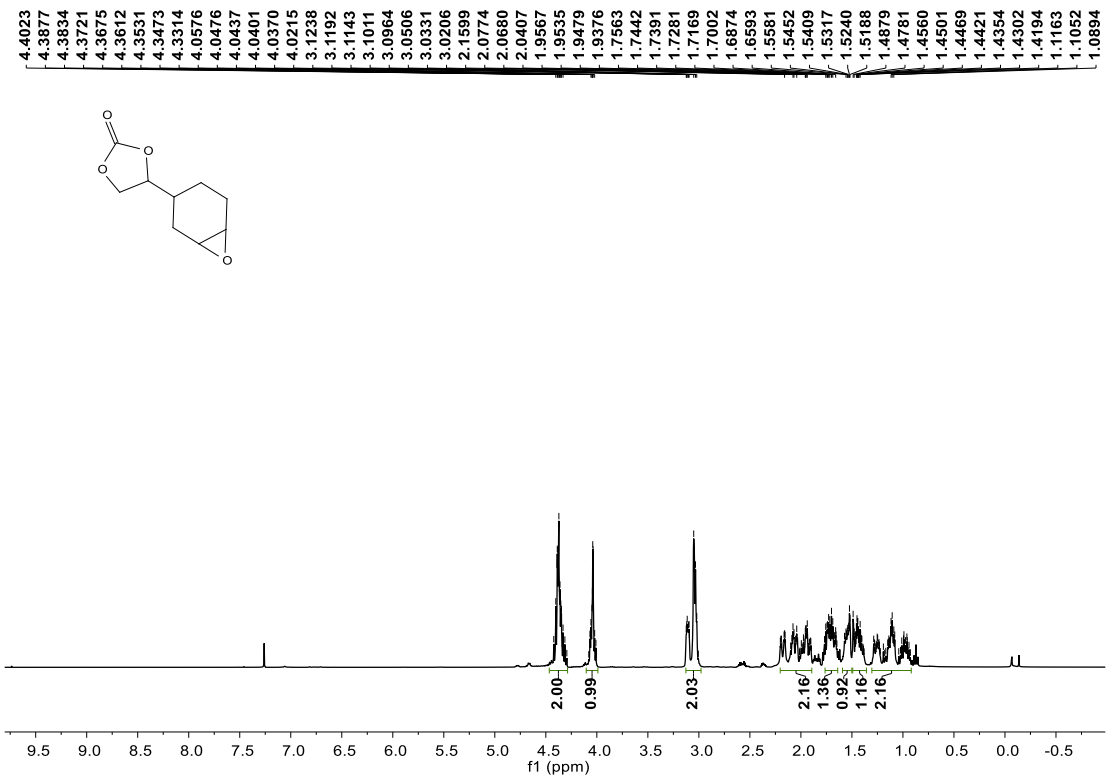

Figure S41. ^{1}H NMR spectrum of **2q** in $CDCl_3$

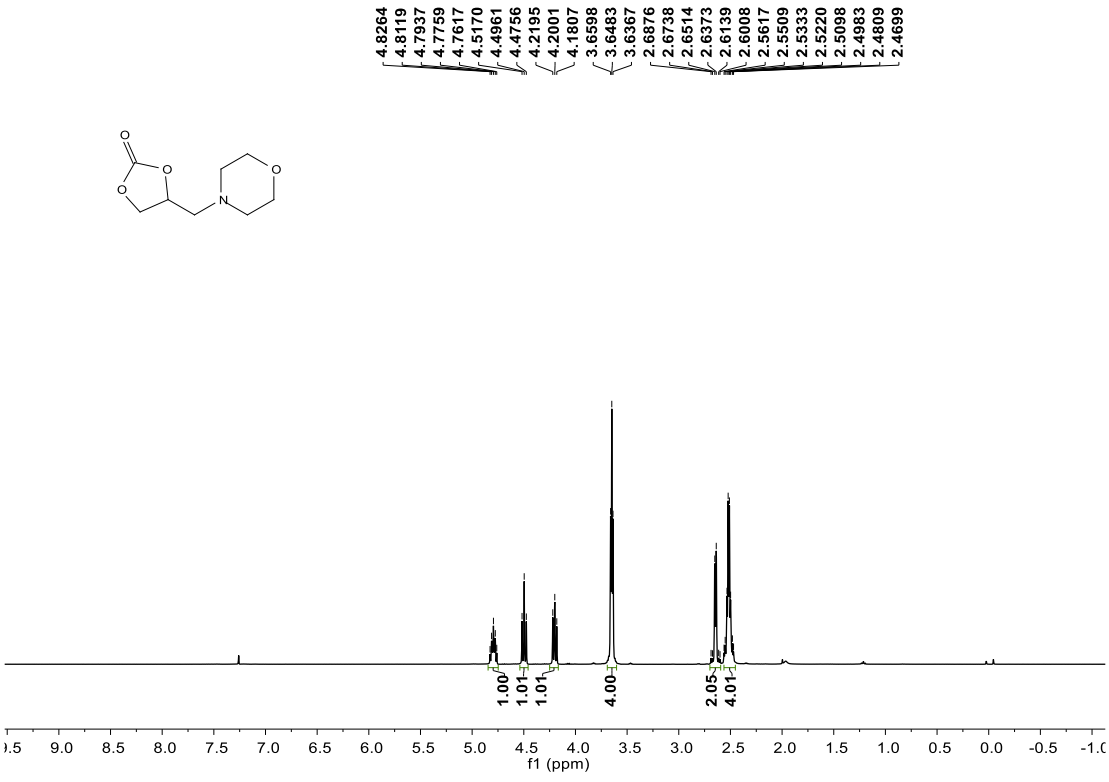

Figure S42. ^{1}H NMR spectrum of **2r** in $CDCl_3$

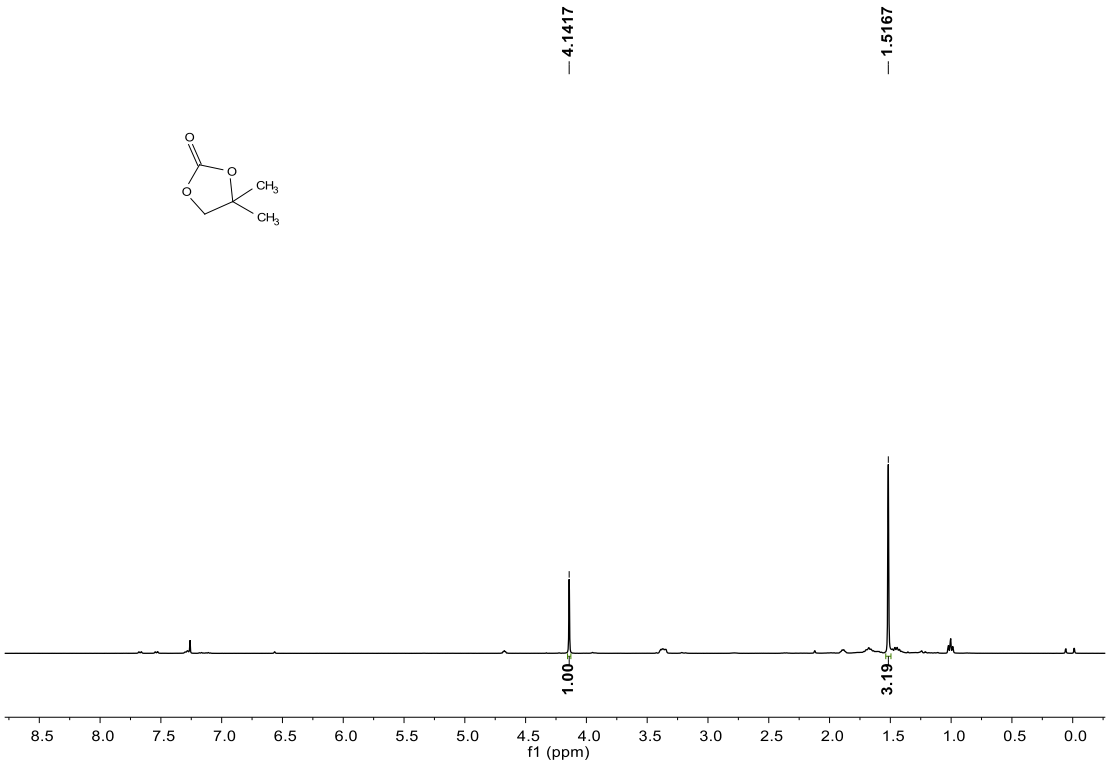

Figure S43.[1]H NMR spectrum of **4a** in $CDCl_3$

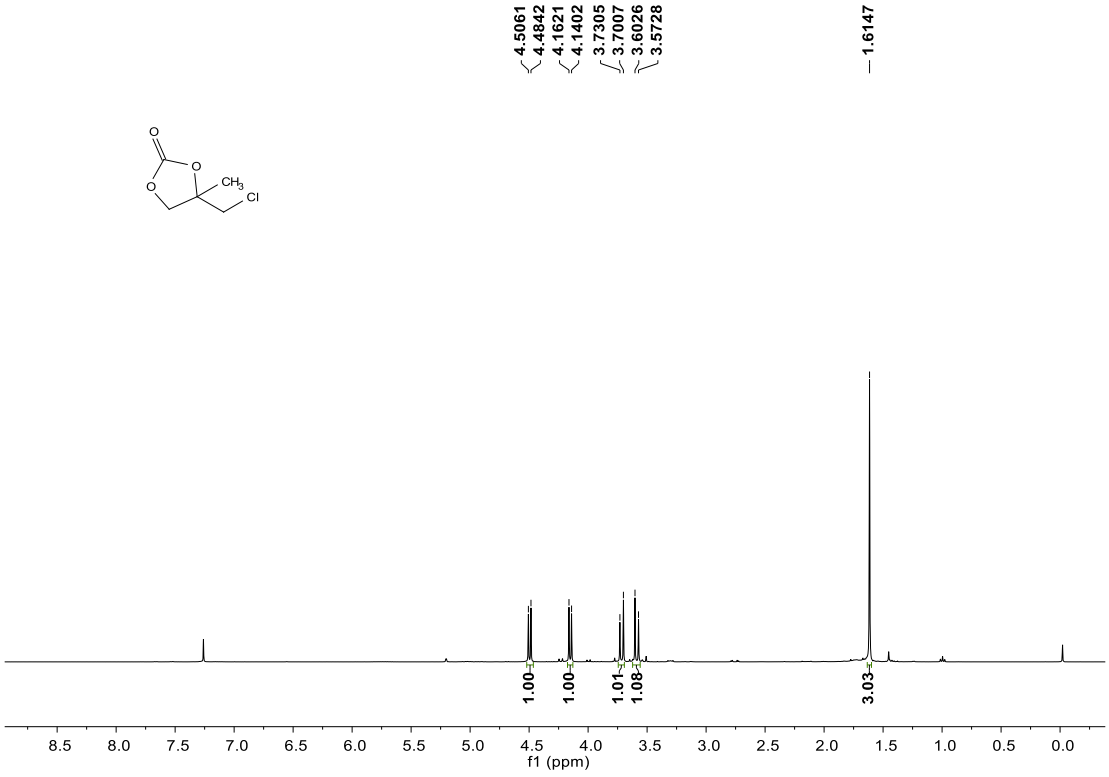

Figure S44. [1]H NMR spectrum of **4b** in $CDCl_3$

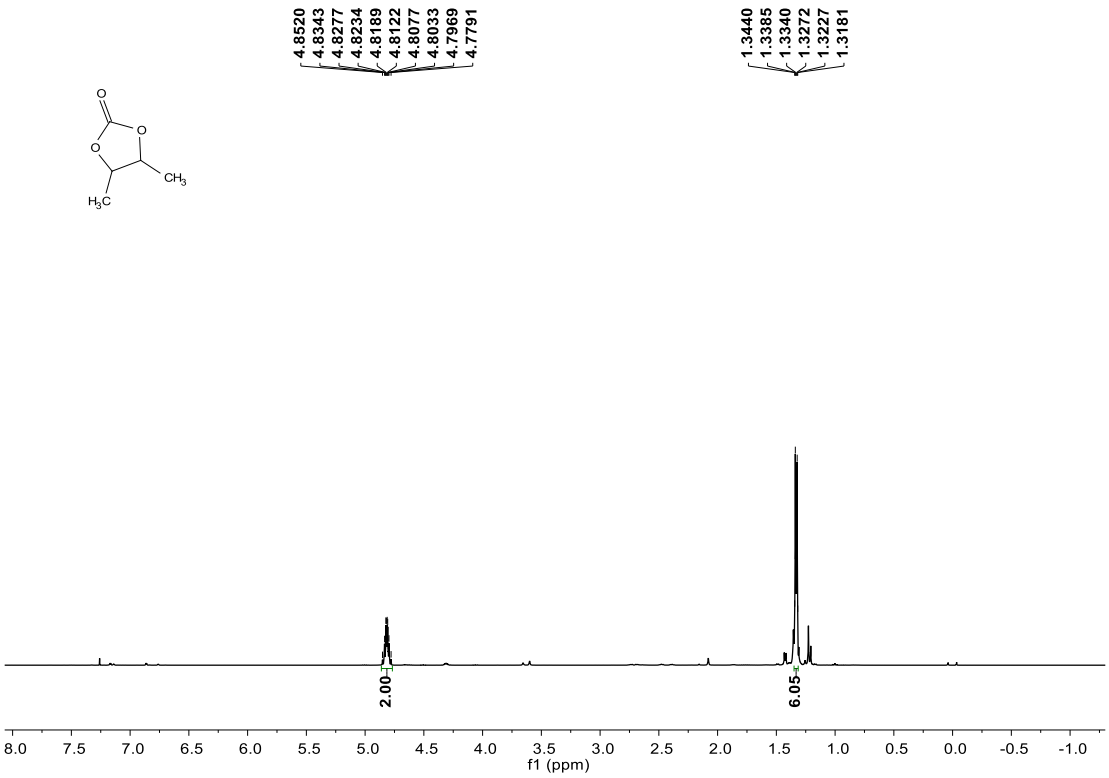

Figure S45. ^{1}H NMR spectrum of *cis*-**4c** in $CDCl_3$

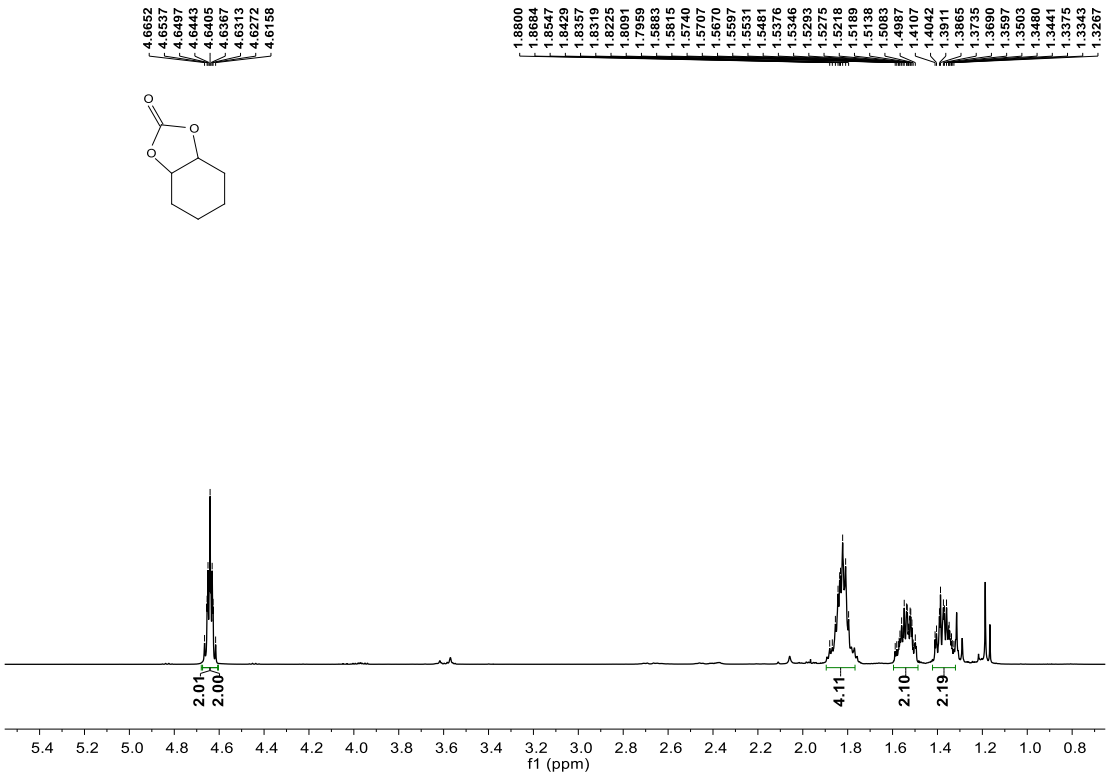

Figure S46. ^{1}H NMR spectrum of *cis*-**4d** in $CDCl_3$

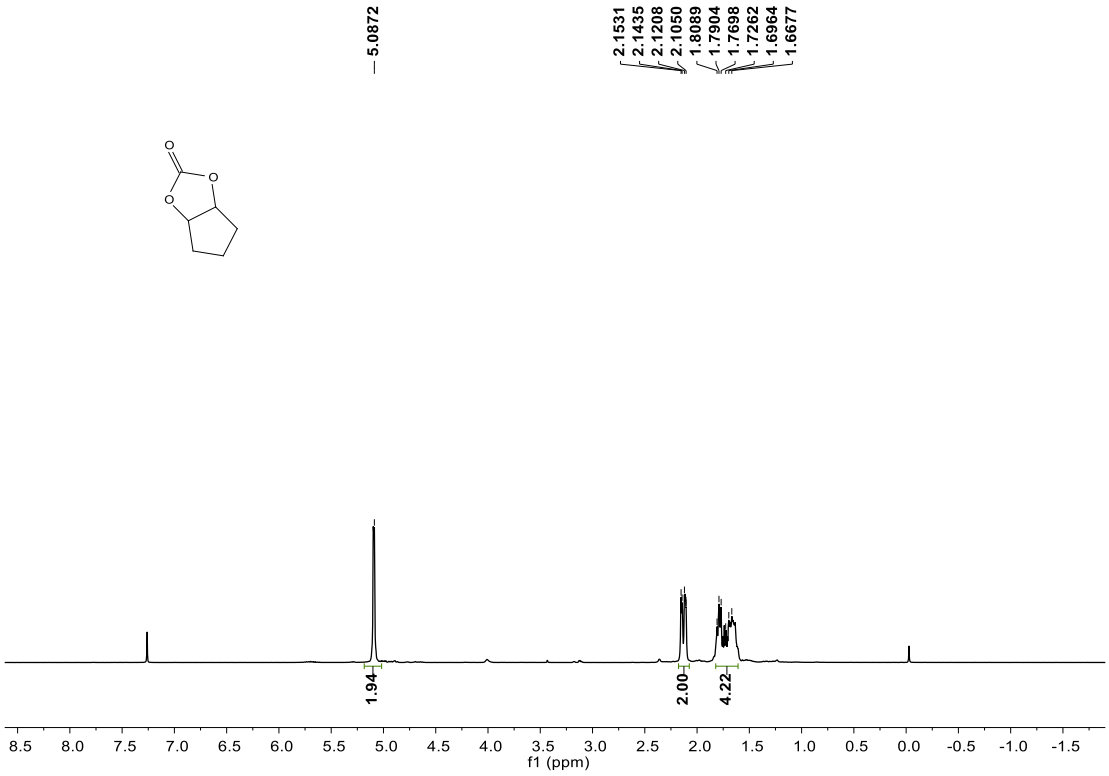

Figure S47. ^{1}H NMR spectrum of *cis*-**4e** in $CDCl_3$

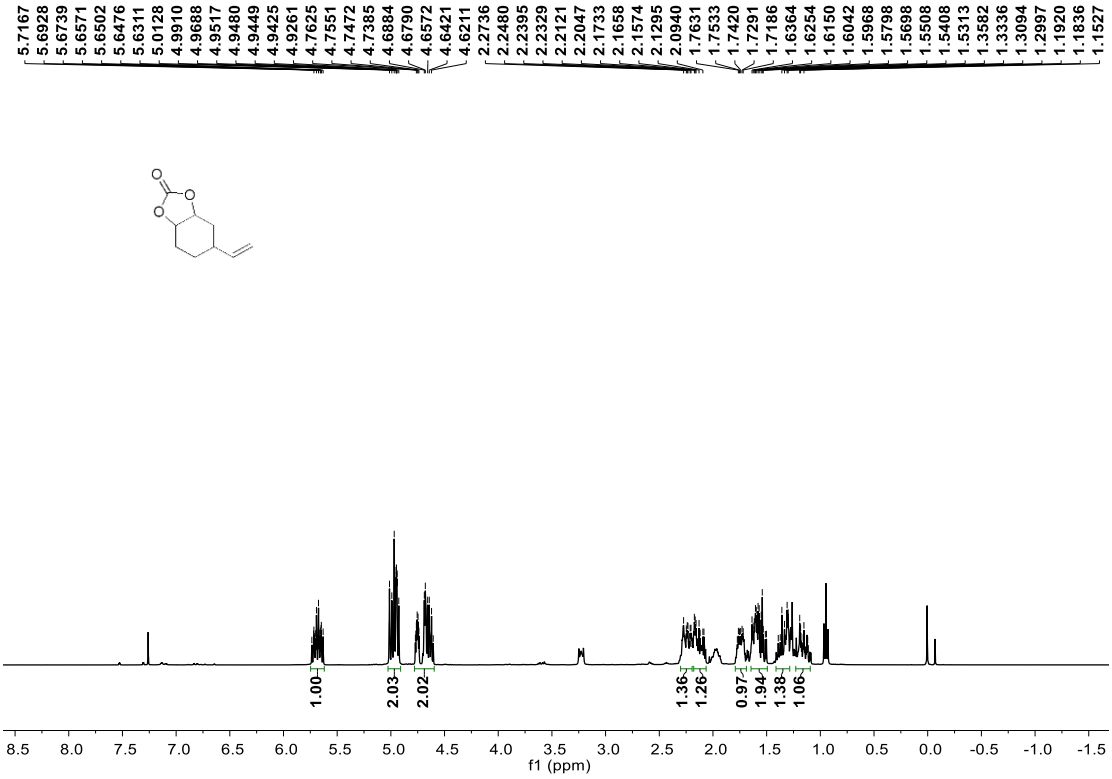

Figure S48. ^{1}H NMR spectrum of *cis*-**4f** in $CDCl_3$

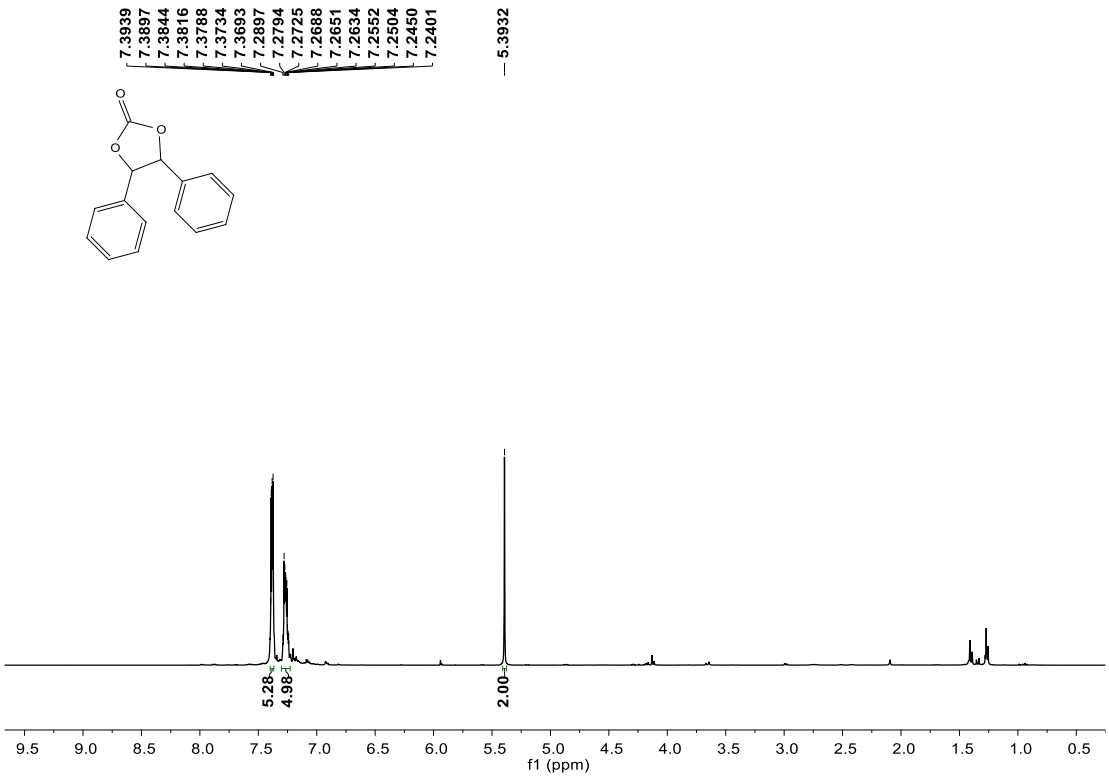

Figure S49. ^{1}H NMR spectrum of *trans*-**4g** in $CDCl_3$

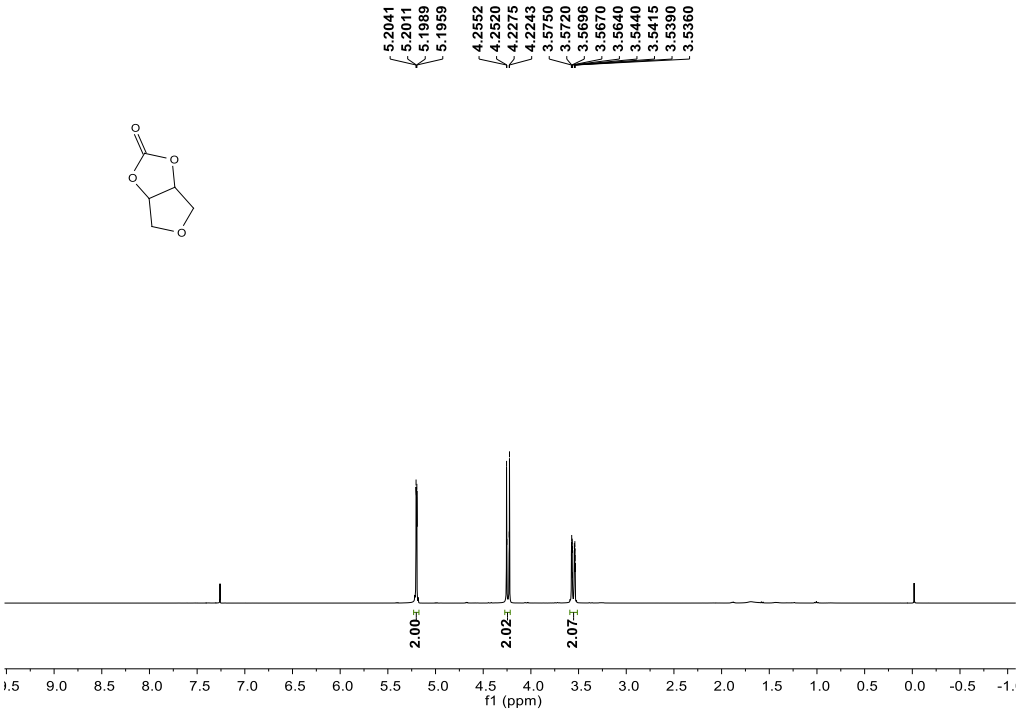

Figure S50. ^{1}H NMR spectrum of *cis*-**4h** in $CDCl_3$

5. Computational details

The B3LYP[19] density functional method was employed to carry out all the geometry optimizations. For the geometry optimizations, the LANL2DZ basis set with the LANL2DZ pseudopotential[20] was utilized for La and I atoms. The 6-31G(d)[21] basis set was used for other atoms. Vibrational frequency analyses at the same level of the theory were performed on all the optimized geometries to characterize them as local minima (no imaginary frequency) or transition states (one imaginary frequency). In addition, intrinsic reaction coordinate (IRC)[22] calculations were used to verify that the transition state connect with appropriate reactant and product. The M06 functional[23] was employed to run single-point energy calculations based on the optimized structures with larger basis sets (SDD[24] for La, I atoms and 6-311++G(d,p) for other atoms). The Gibbs energy was determined by adding the single-point energy calculated at larger basis sets and the gas-phase thermal correction to the Gibbs energy obtained from the vibrational frequency analysis. All calculations were carried out with the Gaussian 09 (Revision C.01) suite of programs.[25] The 3D structures of the optimized intermediates or transition states were demonstrated using the software of CYLView.[26]

Cartesian Coordinates and Energies

1-H

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	-0.026164	-0.397170	0.203534
2	8	0	-0.608806	1.066980	1.900465
3	8	0	2.305926	-0.348926	0.679035
4	8	0	-1.973288	-1.523931	-0.554656
5	8	0	0.078921	-2.419192	1.895712
6	7	0	1.249631	0.978387	-1.882214
7	7	0	-1.639836	1.591273	-0.944743
8	7	0	0.998216	-2.111435	-2.004215
9	6	0	-0.768143	2.513364	-1.704418
10	1	0	-0.261777	3.159334	-0.983124
11	1	0	-1.376253	3.177454	-2.345396
12	6	0	-1.566763	3.103893	1.102603
13	6	0	-0.122661	4.497500	3.062949
14	1	0	0.438152	5.031368	3.827071
15	6	0	5.904484	0.128866	0.277941
16	1	0	6.832232	-0.298490	0.652424
17	6	0	-0.723795	2.387380	1.995680
18	6	0	-5.996811	-0.490053	-0.841414

19	6	0	-5.007440	0.358971	-1.336568
20	1	0	-5.292404	1.299360	-1.806093
21	6	0	3.501010	1.220784	-0.670056
22	6	0	-0.012074	3.112700	2.975405
23	6	0	0.255338	1.814060	-2.599996
24	1	0	-0.260837	1.176446	-3.322383
25	1	0	0.778006	2.588345	-3.188507
26	6	0	3.457100	0.146352	0.266067
27	6	0	-5.613831	-1.700172	-0.254399
28	1	0	-6.370317	-2.379126	0.133362
29	6	0	-3.255243	-1.194075	-0.649289
30	6	0	4.688516	-0.383015	0.719834
31	6	0	-3.648699	0.032827	-1.253401
32	6	0	-1.658129	4.497002	1.210472
33	1	0	-2.312255	5.033748	0.524517
34	6	0	-0.946306	5.203837	2.180073
35	6	0	-4.269803	-2.048773	-0.162720
36	6	0	-2.609838	0.929767	-1.880034
37	1	0	-2.016997	0.340983	-2.590100
38	1	0	-3.121562	1.717392	-2.459290
39	6	0	-2.404848	2.350009	0.101933
40	1	0	-3.027009	1.608907	0.612281
41	1	0	-3.088024	3.053486	-0.403383
42	6	0	4.738259	1.713277	-1.103324
43	1	0	4.753951	2.536836	-1.815893
44	6	0	2.226193	1.870355	-1.150596
45	1	0	1.681520	2.298897	-0.297995
46	1	0	2.489476	2.712946	-1.809683
47	6	0	5.942409	1.183457	-0.639894
48	6	0	1.926097	0.080419	-2.851126
49	1	0	2.905750	-0.173555	-2.446270
50	1	0	2.111091	0.609492	-3.800873
51	6	0	2.286856	-2.736046	-1.656084
52	1	0	3.017399	-1.988979	-1.346254
53	1	0	2.695626	-3.314833	-2.503333
54	1	0	2.135621	-3.417037	-0.813539
55	6	0	1.136385	-1.195098	-3.153877
56	1	0	0.123877	-0.944036	-3.491556
57	1	0	1.627920	-1.709780	-4.000788
58	6	0	0.026339	-3.168288	-2.339781
59	1	0	-0.057924	-3.861875	-1.498535
60	1	0	0.339754	-3.738410	-3.231883
61	1	0	-0.958621	-2.728708	-2.503695
62	6	0	-0.936006	-3.397699	2.210990
63	1	0	-1.511324	-3.562950	1.299432
64	1	0	-1.598240	-2.977926	2.979253
65	6	0	1.107451	-2.562808	2.902048
66	1	0	0.761712	-2.082528	3.827725
67	1	0	1.989521	-2.041425	2.528343
68	6	0	1.252728	-4.079659	3.066731
69	1	0	1.585535	-4.349176	4.073240
70	1	0	1.990090	-4.467512	2.356851
71	6	0	-0.165008	-4.627495	2.736245
72	1	0	-0.113154	-5.416853	1.980784
73	1	0	-0.659305	-5.048211	3.616760
74	1	0	-7.045015	-0.215477	-0.915276
75	1	0	-3.969661	-2.992581	0.285624
76	1	0	-1.034887	6.284342	2.248218
77	1	0	0.624097	2.555398	3.657544

78	1	0	4.655061	-1.199527	1.436693
79	1	0	6.889831	1.586068	-0.985900

Zero-point correction= 0.670333 (Hartree/Particle)
Thermal correction to Energy= 0.708170
Thermal correction to Enthalpy= 0.709114
Thermal correction to Gibbs Free Energy= 0.596394
Sum of electronic and zero-point Energies= -1701.296522
Sum of electronic and thermal Energies= -1701.258685
Sum of electronic and thermal Enthalpies= -1701.257741
Sum of electronic and thermal Free Energies= -1701.370460

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -2105.6042

b-H

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	0.307782	-0.058774	-0.727929
2	8	0	0.773098	2.195840	-0.287039
3	8	0	-1.297839	-1.460803	-1.656888
4	8	0	1.933145	-1.464385	0.120607
5	8	0	1.861659	0.323323	-2.817187
6	7	0	-0.452236	-0.605593	1.865447
7	7	0	-2.151153	1.091395	-0.046035
8	6	0	0.121554	0.306584	2.875121
9	1	0	1.207782	0.201166	2.883338
10	1	0	-0.122214	1.343567	2.637051
11	1	0	-0.257101	0.072484	3.884164
12	6	0	-1.935630	-0.544195	1.870637
13	1	0	-2.305532	-1.370386	1.258606
14	1	0	-2.311087	-0.708970	2.896445
15	6	0	-2.520746	0.775801	1.356848
16	1	0	-2.178901	1.601442	1.984765
17	6	0	-2.064562	2.577139	-0.270761
18	1	0	-1.773171	2.698661	-1.323158
19	6	0	-0.746103	5.143898	2.225979
20	6	0	0.633994	4.945101	2.115056
21	1	0	1.319416	5.558832	2.695282
22	6	0	1.142920	3.965339	1.267403
23	6	0	0.284613	3.146725	0.501517
24	6	0	-3.173441	0.587655	-1.027698
25	1	0	-4.099866	1.167602	-0.883105
26	1	0	-2.784892	0.852871	-2.021125
27	6	0	-3.517999	-0.879002	-1.004797
28	6	0	-4.814925	-1.302149	-0.690510
29	6	0	-5.178265	-2.647916	-0.752323
30	6	0	-4.221830	-3.589659	-1.145519
31	1	0	-4.489238	-4.642330	-1.204642
32	6	0	-2.925179	-3.194260	-1.463857
33	6	0	-2.544067	-1.837835	-1.394031
34	6	0	-0.043917	-2.026477	2.138918
35	1	0	-0.571681	-2.373892	3.042141
36	1	0	-0.426969	-2.620432	1.297501
37	6	0	1.435307	-2.264190	2.322264
38	6	0	2.348477	-1.994821	1.267133
39	6	0	3.711384	-2.300174	1.464278
40	6	0	4.159822	-2.847718	2.662548
41	1	0	5.216776	-3.073390	2.785639

42	6	0	3.263661	-3.106596	3.703920
43	6	0	1.913464	-2.809582	3.519804
44	1	0	1.205057	-3.012294	4.321491
45	6	0	2.491440	1.597037	-3.129235
46	1	0	2.072025	1.972737	-4.071961
47	1	0	2.244023	2.284258	-2.317229
48	6	0	3.972845	1.263768	-3.264874
49	1	0	4.516918	2.008976	-3.852633
50	1	0	4.437209	1.199125	-2.274243
51	6	0	3.928211	-0.118830	-3.938395
52	1	0	4.834736	-0.707022	-3.770351
53	1	0	3.792770	-0.009314	-5.020291
54	6	0	2.693920	-0.775868	-3.304050
55	1	0	2.103322	-1.362912	-4.013653
56	1	0	2.944710	-1.398210	-2.439182
57	1	0	-5.555415	-0.557231	-0.402745
58	1	0	3.609549	-3.532557	4.641220
59	1	0	-6.190264	-2.955499	-0.505557
60	1	0	-3.074539	3.007779	-0.171416
61	6	0	-1.117926	3.354426	0.606905
62	6	0	-1.604080	4.347234	1.468044
63	1	0	-2.680103	4.502073	1.533576
64	1	0	-1.145404	5.908326	2.886083
65	1	0	-3.615039	0.724794	1.466070
66	1	0	4.400840	-2.096047	0.649313
67	1	0	-2.175530	-3.918837	-1.769966
68	1	0	2.213791	3.803755	1.176715

Zero-point correction= 0.567071 (Hartree/Particle)
Thermal correction to Energy= 0.600022
Thermal correction to Enthalpy= 0.600966
Thermal correction to Gibbs Free Energy= 0.499682
Sum of electronic and zero-point Energies= -1528.123038
Sum of electronic and thermal Energies= -1528.090087
Sum of electronic and thermal Enthalpies= -1528.089143
Sum of electronic and thermal Free Energies= -1528.190427

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -1932.3994

3d

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.343373	1.519852	0.033421
2	6	0	-0.989507	0.835866	0.296572
3	6	0	-1.096675	-0.631958	0.413387
4	6	0	0.128700	-1.513063	0.292223
5	6	0	1.280227	-0.806974	-0.440681
6	6	0	1.551181	0.573848	0.172127
7	1	0	-1.921283	-1.045059	0.999885
8	1	0	-1.752049	1.445273	0.786098
9	1	0	0.305585	1.941032	-0.979983
10	1	0	0.453405	2.368691	0.719996
11	1	0	0.447306	-1.794491	1.306875
12	1	0	-0.144285	-2.444781	-0.220929
13	1	0	2.182009	-1.428863	-0.390363
14	1	0	1.022795	-0.698076	-1.501185
15	1	0	1.789367	0.444937	1.237942
16	1	0	2.433395	1.033590	-0.289496

17	8	0	-1.515005	0.039040	-0.783892

Zero-point correction= 0.152426 (Hartree/Particle)
Thermal correction to Energy= 0.158385
Thermal correction to Enthalpy= 0.159329
Thermal correction to Gibbs Free Energy= 0.122871
Sum of electronic and zero-point Energies= -309.698394
Sum of electronic and thermal Energies= -309.692436
Sum of electronic and thermal Enthalpies= -309.691492
Sum of electronic and thermal Free Energies= -309.727950

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -309.71153

THF

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000406	-1.251516	0.000995
2	6	0	1.165723	-0.430269	0.131233
3	1	0	1.537263	-0.483176	1.166476
4	1	0	1.948365	-0.822553	-0.528878
5	6	0	0.733296	0.997225	-0.226510
6	1	0	1.343143	1.761698	0.264955
7	1	0	0.796547	1.156848	-1.309685
8	6	0	-0.734409	0.996269	0.227072
9	1	0	-1.344967	1.760737	-0.263525
10	1	0	-0.797930	1.154351	1.310459
11	6	0	-1.165070	-0.431169	-0.132484
12	1	0	-1.949151	-0.824551	0.525205
13	1	0	-1.533761	-0.483561	-1.168828

Zero-point correction= 0.117359 (Hartree/Particle)
Thermal correction to Energy= 0.122315
Thermal correction to Enthalpy= 0.123259
Thermal correction to Gibbs Free Energy= 0.088694
Sum of electronic and zero-point Energies= -232.332091
Sum of electronic and thermal Energies= -232.327135
Sum of electronic and thermal Enthalpies= -232.326191
Sum of electronic and thermal Free Energies= -232.360755

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -232.34797

1-H-3d

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	0.065004	0.188085	-0.225696
2	8	0	0.744989	-0.409808	1.943670
3	8	0	-2.009108	1.069437	0.478186
4	8	0	1.900786	-0.000191	-1.724315
5	7	0	-1.971300	-1.291627	-1.449242
6	7	0	0.657498	-2.556683	-0.350089
7	7	0	-0.870357	1.315282	-2.782843
8	6	0	-0.590637	-3.282068	-0.677308
9	1	0	-1.178768	-3.361977	0.239876
10	1	0	-0.360959	-4.315356	-0.993060
11	6	0	0.347319	-2.759619	2.164985
12	6	0	-1.118738	-2.248228	4.501204
13	1	0	-1.685092	-2.042307	5.406796
14	6	0	-5.548364	1.969800	0.447935

15	1	0	-6.178433	2.824362	0.685284
16	6	0	0.200905	-1.419016	2.620403
17	6	0	5.408762	-2.122231	-1.000797
18	6	0	4.177276	-2.776434	-1.043168
19	1	0	4.134724	-3.853820	-0.889642
20	6	0	-3.910000	-0.224517	-0.152225
21	6	0	-0.539807	-1.193381	3.802120
22	6	0	-1.422126	-2.628270	-1.784436
23	1	0	-0.816475	-2.522629	-2.689020
24	1	0	-2.248443	-3.315071	-2.040388
25	6	0	-3.316938	0.978466	0.327876
26	6	0	5.447442	-0.741224	-1.219798
27	1	0	6.399957	-0.215725	-1.200487
28	6	0	3.021333	-0.676562	-1.500161
29	6	0	-4.170740	2.067530	0.619543
30	6	0	2.986804	-2.082813	-1.288173
31	6	0	-0.244013	-3.803522	2.888204
32	1	0	-0.110657	-4.825599	2.535663
33	6	0	-0.977696	-3.565027	4.050229
34	6	0	4.277458	-0.029244	-1.469067
35	6	0	1.674972	-2.812633	-1.424760
36	1	0	1.212938	-2.526479	-2.375184
37	1	0	1.863564	-3.898914	-1.465390
38	6	0	1.207991	-3.039471	0.960315
39	1	0	2.177627	-2.546807	1.073840
40	1	0	1.395692	-4.124040	0.884319
41	6	0	-5.298148	-0.295438	-0.320280
42	1	0	-5.736266	-1.224151	-0.683507
43	6	0	-3.051354	-1.438353	-0.404824
44	1	0	-2.546213	-1.726866	0.526134
45	1	0	-3.702199	-2.281060	-0.689891
46	6	0	-6.126869	0.787305	-0.025261
47	6	0	-2.476475	-0.641192	-2.685948
48	1	0	-3.281707	0.036532	-2.401518
49	1	0	-2.926172	-1.392926	-3.355474
50	6	0	-1.893243	2.367247	-2.645657
51	1	0	-2.725488	2.036094	-2.024848
52	1	0	-2.279484	2.683758	-3.630784
53	1	0	-1.444347	3.236023	-2.155667
54	6	0	-1.403462	0.120206	-3.470492
55	1	0	-0.550421	-0.534671	-3.684275
56	1	0	-1.836597	0.403046	-4.448499
57	6	0	0.266250	1.850089	-3.558003
58	1	0	0.650905	2.745061	-3.059651
59	1	0	-0.040057	2.126893	-4.581965
60	1	0	1.069032	1.112079	-3.588476
61	1	0	6.320975	-2.679193	-0.807682
62	1	0	4.301992	1.041550	-1.656460
63	1	0	-1.426154	-4.389596	4.596858
64	1	0	-0.646394	-0.168790	4.148170
65	1	0	-3.715786	2.982054	0.990886
66	1	0	-7.201879	0.709255	-0.158659
67	6	0	0.775195	4.434545	2.056284
68	6	0	1.008326	2.935747	2.002099
69	6	0	2.313472	2.370632	1.612933
70	6	0	3.476550	3.266425	1.260561
71	6	0	3.033834	4.691191	0.889455
72	6	0	2.073523	5.257362	1.945183
73	1	0	2.542302	1.363376	1.957766

74	1	0	0.351464	2.304895	2.597263
75	1	0	0.083304	4.695112	1.244674
76	1	0	0.256572	4.673858	2.992393
77	1	0	4.139454	3.296919	2.137615
78	1	0	4.052064	2.803591	0.449129
79	1	0	3.917162	5.333722	0.797057
80	1	0	2.544067	4.679566	-0.092256
81	1	0	2.583017	5.259635	2.919362
82	1	0	1.826872	6.301796	1.721289
83	8	0	1.206507	2.390980	0.656772

Zero-point correction= 0.705027 (Hartree/Particle)
Thermal correction to Energy= 0.743869
Thermal correction to Enthalpy= 0.744813
Thermal correction to Gibbs Free Energy= 0.631366
Sum of electronic and zero-point Energies= -1778.662636
Sum of electronic and thermal Energies= -1778.623793
Sum of electronic and thermal Enthalpies= -1778.622849
Sum of electronic and thermal Free Energies= -1778.736297

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -2182.9686

b-H-3d

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	0.244345	0.076767	-0.598943
2	8	0	-1.342231	1.251674	-1.827843
3	8	0	0.844036	-2.027947	0.233167
4	8	0	1.684888	1.512049	0.489567
5	7	0	-0.988249	0.732496	1.782638
6	7	0	-2.164627	-1.281817	-0.204141
7	6	0	-1.790045	1.970562	1.707927
8	1	0	-1.137621	2.813189	1.472950
9	1	0	-2.544197	1.890327	0.923089
10	1	0	-2.292404	2.177572	2.667711
11	6	0	-1.835753	-0.427824	2.154145
12	1	0	-1.172389	-1.256455	2.411040
13	1	0	-2.418646	-0.187825	3.061480
14	6	0	-2.817729	-0.873245	1.064688
15	1	0	-3.508598	-0.059642	0.833565
16	6	0	-3.046459	-1.008545	-1.394340
17	1	0	-2.451843	-1.298176	-2.272587
18	6	0	-5.445435	1.927372	-1.812762
19	6	0	-4.553678	2.969929	-2.086543
20	1	0	-4.932591	3.969059	-2.289822
21	6	0	-3.180678	2.742921	-2.101341
22	6	0	-2.652382	1.460016	-1.839801
23	6	0	-1.869567	-2.754983	-0.242642
24	1	0	-2.829562	-3.295298	-0.287851
25	1	0	-1.362729	-2.930309	-1.202517
26	6	0	-1.043022	-3.341133	0.872684
27	6	0	-1.583473	-4.309909	1.726329
28	6	0	-0.812648	-4.924995	2.713693
29	6	0	0.532158	-4.564322	2.844197
30	1	0	1.148956	-5.035246	3.606396
31	6	0	1.093517	-3.603754	2.006632
32	6	0	0.321717	-2.969545	1.010116

33	6	0	0.099750	0.863430	2.811178
34	1	0	-0.361604	0.848984	3.812257
35	1	0	0.708083	-0.047501	2.726769
36	6	0	0.968908	2.093108	2.700502
37	6	0	1.749724	2.329636	1.537171
38	6	0	2.594399	3.458811	1.512221
39	6	0	2.666058	4.327256	2.597322
40	1	0	3.326746	5.190085	2.549773
41	6	0	1.894539	4.099208	3.740661
42	6	0	1.054925	2.986151	3.775471
43	1	0	0.452078	2.796161	4.662091
44	1	0	-2.628287	-4.592275	1.605532
45	1	0	1.945611	4.775434	4.589069
46	1	0	-1.251294	-5.675066	3.365293
47	1	0	-3.908246	-1.695034	-1.358172
48	6	0	-3.558329	0.397582	-1.571481
49	6	0	-4.935934	0.653921	-1.560660
50	1	0	-5.620276	-0.169232	-1.360035
51	1	0	-6.517228	2.102655	-1.801057
52	1	0	-3.422851	-1.698270	1.471722
53	1	0	3.188385	3.629110	0.618314
54	1	0	2.136691	-3.315033	2.104044
55	1	0	-2.480789	3.546565	-2.313447
56	6	0	3.761850	-1.980040	-1.817975
57	6	0	2.842731	-1.525409	-2.937220
58	6	0	2.929169	-0.166360	-3.509641
59	6	0	3.961025	0.820129	-3.013501
60	6	0	4.526401	0.455409	-1.629700
61	6	0	4.944332	-1.020980	-1.577850
62	1	0	2.560122	-0.009846	-4.523268
63	1	0	2.392495	-2.305380	-3.549494
64	1	0	3.151846	-2.094713	-0.912595
65	1	0	4.134823	-2.981058	-2.066585
66	1	0	4.769862	0.833411	-3.758861
67	1	0	3.524883	1.827446	-3.007914
68	1	0	5.390870	1.096606	-1.421958
69	1	0	3.785220	0.674409	-0.851523
70	1	0	5.714203	-1.198743	-2.342763
71	1	0	5.406011	-1.251630	-0.611296
72	8	0	1.857093	-0.499668	-2.586890

Zero-point correction= 0.601723 (Hartree/Particle)
Thermal correction to Energy= 0.635861
Thermal correction to Enthalpy= 0.636805
Thermal correction to Gibbs Free Energy= 0.533771
Sum of electronic and zero-point Energies= -1605.486797
Sum of electronic and thermal Energies= -1605.452659
Sum of electronic and thermal Enthalpies= -1605.451715
Sum of electronic and thermal Free Energies= -1605.554749

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -2009.7625

I^-

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	0.000000	0.000000	0.000000

Zero-point correction= 0.000000 (Hartree/Particle)

Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.016848
Sum of electronic and zero-point Energies= -11.472110
Sum of electronic and thermal Energies= -11.470694
Sum of electronic and thermal Enthalpies= -11.469750
Sum of electronic and thermal Free Energies= -11.488958

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -11.484534

1-int1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	0.716269	0.066212	-0.237212
2	8	0	0.658482	0.917160	1.928245
3	8	0	1.051338	-2.161483	0.505345
4	8	0	0.340619	1.754000	-1.880628
5	7	0	3.368140	-0.824136	-0.918599
6	7	0	2.795385	2.096831	0.027445
7	7	0	0.965222	-1.302057	-2.848024
8	6	0	4.107412	1.422228	0.010407
9	1	0	4.268932	0.979367	0.995855
10	1	0	4.919211	2.159717	-0.136666
11	6	0	2.661377	2.043739	2.566940
12	6	0	2.635948	0.626273	4.986488
13	1	0	2.617830	0.075152	5.924715
14	6	0	2.235588	-5.602800	0.770572
15	1	0	1.828601	-6.600955	0.921072
16	6	0	1.612236	1.116975	2.824673
17	6	0	0.156527	5.877074	-1.345626
18	6	0	1.343500	5.180594	-1.116004
19	1	0	2.233984	5.721272	-0.796639
20	6	0	3.266334	-3.024420	0.391772
21	6	0	1.622358	0.421462	4.055355
22	6	0	4.246717	0.356466	-1.078300
23	1	0	4.038925	0.798656	-2.056496
24	1	0	5.303237	0.030536	-1.101920
25	6	0	1.859591	-3.195567	0.549660
26	6	0	-0.973464	5.164892	-1.762927
27	1	0	-1.909394	5.689466	-1.943761
28	6	0	0.276599	3.067084	-1.712396
29	6	0	1.372268	-4.512337	0.737945
30	6	0	1.422969	3.794885	-1.289334
31	6	0	3.669016	2.230079	3.520723
32	1	0	4.460123	2.950035	3.311845
33	6	0	3.671669	1.531650	4.728943
34	6	0	-0.917377	3.786787	-1.948339
35	6	0	2.724114	3.056440	-1.120388
36	1	0	2.914287	2.478902	-2.030864
37	1	0	3.548019	3.785090	-1.013735
38	6	0	2.623482	2.863599	1.303495
39	1	0	1.658493	3.371540	1.217598
40	1	0	3.402235	3.645780	1.353237
41	6	0	4.112063	-4.138836	0.423998
42	1	0	5.184596	-3.986810	0.305248
43	6	0	3.836176	-1.634841	0.263126
44	1	0	3.583176	-1.053971	1.158990
45	1	0	4.936691	-1.705683	0.226652

46	6	0	3.615446	-5.429369	0.612642
47	6	0	3.380064	-1.613151	-2.173919
48	1	0	3.169185	-2.651975	-1.919090
49	1	0	4.388054	-1.603712	-2.623973
50	6	0	0.593588	-2.725765	-2.791086
51	1	0	1.160604	-3.254743	-2.025193
52	1	0	0.751535	-3.221439	-3.766468
53	1	0	-0.464404	-2.804937	-2.528149
54	6	0	2.379664	-1.119356	-3.222679
55	1	0	2.526022	-0.049914	-3.414612
56	1	0	2.596781	-1.643928	-4.173644
57	6	0	0.108568	-0.619389	-3.835608
58	1	0	-0.940008	-0.771744	-3.566086
59	1	0	0.270392	-1.019458	-4.852980
60	1	0	0.307692	0.453170	-3.812441
61	1	0	0.111952	6.952894	-1.199872
62	1	0	-1.792311	3.230627	-2.274715
63	1	0	4.461963	1.693595	5.457150
64	1	0	0.812964	-0.276850	4.248889
65	1	0	0.300696	-4.640216	0.865706
66	1	0	4.289944	-6.280817	0.639077
67	6	0	-3.252549	-2.318378	0.426389
68	6	0	-2.864926	-0.859604	0.556350
69	6	0	-3.146851	0.114729	-0.498853
70	6	0	-3.871860	-0.292956	-1.755369
71	6	0	-3.788350	-1.804415	-2.023572
72	6	0	-4.180606	-2.599816	-0.770327
73	1	0	-3.226997	1.160116	-0.210602
74	1	0	-2.723916	-0.476050	1.563345
75	1	0	-2.325984	-2.906632	0.365902
76	1	0	-3.761221	-2.606610	1.352373
77	1	0	-4.918351	-0.003142	-1.592678
78	1	0	-3.486901	0.287031	-2.605972
79	1	0	-4.459496	-2.057715	-2.853889
80	1	0	-2.771710	-2.074883	-2.344934
81	1	0	-5.197968	-2.310179	-0.480277
82	1	0	-4.184710	-3.676607	-0.984940
83	8	0	-1.775512	-0.410940	-0.353025
84	53	0	-6.604424	0.016488	1.184722

Zero-point correction= 0.704533 (Hartree/Particle)
Thermal correction to Energy= 0.746108
Thermal correction to Enthalpy= 0.747052
Thermal correction to Gibbs Free Energy= 0.622772
Sum of electronic and zero-point Energies= -1790.155762
Sum of electronic and thermal Energies= -1790.114187
Sum of electronic and thermal Enthalpies= -1790.113243
Sum of electronic and thermal Free Energies= -1790.237522

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -2194.4789

b-int1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	0.640817	0.377372	-0.106598
2	8	0	0.685752	0.243131	2.229125
3	8	0	0.690415	-0.789377	-2.136718
4	8	0	1.608605	2.400254	-0.685044

5	7	0	3.422265	-0.006383	-0.027945
6	7	0	1.399009	-2.245428	0.512361
7	6	0	4.065156	0.365380	1.244974
8	1	0	3.903992	1.427030	1.438721
9	1	0	3.632829	-0.201071	2.070889
10	1	0	5.153151	0.178321	1.212105
11	6	0	3.642974	-1.437952	-0.336132
12	1	0	3.362001	-1.602063	-1.377767
13	1	0	4.719433	-1.678762	-0.251056
14	6	0	2.871534	-2.411822	0.563578
15	1	0	3.183000	-2.279611	1.601899
16	6	0	0.749363	-2.592849	1.824336
17	1	0	-0.316440	-2.353848	1.699472
18	6	0	2.243958	-2.087175	5.298261
19	6	0	2.123754	-0.700967	5.446482
20	1	0	2.444620	-0.223930	6.370504
21	6	0	1.596174	0.078924	4.422281
22	6	0	1.167469	-0.502324	3.206216
23	6	0	0.756578	-3.132674	-0.515502
24	1	0	0.816534	-4.173841	-0.156320
25	1	0	-0.309447	-2.862726	-0.519386
26	6	0	1.292347	-3.085273	-1.923403
27	6	0	1.838731	-4.229678	-2.514543
28	6	0	2.263022	-4.234951	-3.844393
29	6	0	2.130347	-3.064907	-4.599543
30	1	0	2.450058	-3.051264	-5.639702
31	6	0	1.591740	-1.912115	-4.034946
32	6	0	1.166671	-1.891360	-2.687395
33	6	0	3.973527	0.808306	-1.160120
34	1	0	5.005561	0.474853	-1.365075
35	1	0	3.371217	0.549425	-2.041067
36	6	0	3.987607	2.304228	-0.950780
37	6	0	2.774188	3.022686	-0.753920
38	6	0	2.843746	4.428786	-0.630418
39	6	0	4.060737	5.099650	-0.693095
40	1	0	4.079823	6.183357	-0.594398
41	6	0	5.253375	4.393286	-0.879627
42	6	0	5.198256	3.004726	-1.003701
43	1	0	6.119165	2.442355	-1.153473
44	1	0	1.922063	-5.138198	-1.919267
45	1	0	6.206583	4.912851	-0.927481
46	1	0	2.681595	-5.135816	-4.284628
47	1	0	0.809617	-3.684323	1.970737
48	6	0	1.282432	-1.913858	3.059883
49	6	0	1.819771	-2.674490	4.106042
50	1	0	1.895511	-3.754096	3.981464
51	1	0	2.654209	-2.698375	6.097407
52	1	0	3.156102	-3.435530	0.273221
53	1	0	1.911535	4.968176	-0.485920
54	1	0	1.484950	-0.998663	-4.613789
55	1	0	1.497298	1.155784	4.529081
56	6	0	-3.564952	1.550877	-1.792422
57	6	0	-3.195839	0.467058	-0.799988
58	6	0	-3.132829	0.724429	0.636660
59	6	0	-3.468426	2.081389	1.199493
60	6	0	-3.365336	3.200510	0.150433
61	6	0	-4.131479	2.816696	-1.123478
62	1	0	-3.272129	-0.123045	1.303068
63	1	0	-3.352888	-0.560501	-1.112996

64	1	0	-2.673566	1.783951	-2.392622
65	1	0	-4.315081	1.130467	-2.469578
66	1	0	-4.503091	1.998733	1.556893
67	1	0	-2.829773	2.287258	2.069303
68	1	0	-3.775930	4.125793	0.573515
69	1	0	-2.310437	3.402304	-0.083660
70	1	0	-5.176978	2.615303	-0.859685
71	1	0	-4.121947	3.645996	-1.842297
72	8	0	-1.870718	0.638346	-0.131423
73	53	0	-6.673558	-0.299243	0.006192

Zero-point correction= 0.601048 (Hartree/Particle)
Thermal correction to Energy= 0.637948
Thermal correction to Enthalpy= 0.638892
Thermal correction to Gibbs Free Energy= 0.524176
Sum of electronic and zero-point Energies= -1616.987969
Sum of electronic and thermal Energies= -1616.951069
Sum of electronic and thermal Enthalpies= -1616.950125
Sum of electronic and thermal Free Energies= -1617.064841

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -2021.2778

1-ts1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	0.600563	0.114012	-0.347251
2	8	0	0.348502	0.897027	1.842650
3	8	0	0.662934	-2.162341	0.361219
4	8	0	0.792262	1.838090	-2.015554
5	7	0	3.275551	-0.996757	-0.677373
6	7	0	2.845900	1.939616	0.334258
7	7	0	1.127512	-1.240184	-2.934920
8	6	0	4.072671	1.132976	0.462482
9	1	0	4.047285	0.635292	1.434457
10	1	0	4.967056	1.785685	0.470785
11	6	0	2.334846	1.784574	2.819722
12	6	0	1.829374	0.265103	5.121481
13	1	0	1.624946	-0.325269	6.012782
14	6	0	1.501513	-5.703632	0.623113
15	1	0	0.992210	-6.664437	0.673401
16	6	0	1.177462	0.956202	2.870094
17	6	0	0.699439	5.931090	-1.263019
18	6	0	1.787236	5.155155	-0.859516
19	1	0	2.625307	5.625186	-0.345455
20	6	0	2.793718	-3.219207	0.501161
21	6	0	0.946874	0.206192	4.047423
22	6	0	4.262729	0.104342	-0.654549
23	1	0	4.226483	0.604562	-1.626190
24	1	0	5.281937	-0.315790	-0.557777
25	6	0	1.367978	-3.263354	0.463882
26	6	0	-0.361600	5.308318	-1.929752
27	1	0	-1.220157	5.895750	-2.249732
28	6	0	0.756503	3.139706	-1.779150
29	6	0	0.749129	-4.537595	0.526905
30	6	0	1.833247	3.779191	-1.102783
31	6	0	3.206194	1.824925	3.914406
32	1	0	4.082383	2.471201	3.861192
33	6	0	2.970310	1.074124	5.067120

34	6	0	-0.335926	3.940963	-2.188324
35	6	0	3.040077	2.953264	-0.747257
36	1	0	3.355676	2.408875	-1.642614
37	1	0	3.872361	3.620069	-0.455321
38	6	0	2.557935	2.659937	1.614205
39	1	0	1.665280	3.262790	1.421798
40	1	0	3.388106	3.359868	1.822195
41	6	0	3.526391	-4.407725	0.593696
42	1	0	4.614312	-4.350560	0.624975
43	6	0	3.496579	-1.885835	0.516731
44	1	0	3.168885	-1.315351	1.394497
45	1	0	4.580689	-2.059498	0.632408
46	6	0	2.899880	-5.653431	0.655980
47	6	0	3.403078	-1.734040	-1.956162
48	1	0	3.091320	-2.764432	-1.783329
49	1	0	4.460757	-1.780339	-2.270230
50	6	0	0.675393	-2.638858	-2.986437
51	1	0	1.095843	-3.224819	-2.169462
52	1	0	0.943568	-3.113857	-3.948630
53	1	0	-0.412017	-2.662704	-2.878598
54	6	0	2.587780	-1.126532	-3.101950
55	1	0	2.814943	-0.059274	-3.205834
56	1	0	2.906583	-1.615651	-4.043735
57	6	0	0.452754	-0.475877	-3.999363
58	1	0	-0.629641	-0.569274	-3.872827
59	1	0	0.723370	-0.855875	-5.001883
60	1	0	0.712548	0.579994	-3.908365
61	1	0	0.677845	6.998412	-1.059835
62	1	0	-1.157558	3.454205	-2.707574
63	1	0	3.658610	1.122122	5.906957
64	1	0	0.057167	-0.416240	4.083924
65	1	0	-0.336950	-4.571292	0.506423
66	1	0	3.488530	-6.563685	0.732133
67	6	0	-3.311902	-1.933875	0.346017
68	6	0	-3.171959	-0.436914	0.286341
69	6	0	-3.145341	0.282311	-0.988331
70	6	0	-3.810427	-0.372742	-2.188186
71	6	0	-3.653247	-1.901782	-2.183301
72	6	0	-4.103244	-2.503886	-0.843300
73	1	0	-3.331851	1.357701	-0.929528
74	1	0	-2.949338	0.120849	1.184857
75	1	0	-2.300343	-2.362141	0.384402
76	1	0	-3.804723	-2.186795	1.288810
77	1	0	-4.873740	-0.105073	-2.148365
78	1	0	-3.392253	0.061743	-3.106786
79	1	0	-4.240011	-2.332255	-3.005458
80	1	0	-2.602811	-2.161589	-2.371581
81	1	0	-5.164318	-2.277069	-0.684906
82	1	0	-3.996363	-3.596469	-0.861423
83	8	0	-1.777249	-0.063910	-0.793401
84	53	0	-6.039830	0.267520	1.170252

Zero-point correction= 0.703185 (Hartree/Particle)
Thermal correction to Energy= 0.744192
Thermal correction to Enthalpy= 0.745137
Thermal correction to Gibbs Free Energy= 0.624324
Sum of electronic and zero-point Energies= -1790.149446
Sum of electronic and thermal Energies= -1790.108439
Sum of electronic and thermal Enthalpies= -1790.107495

Sum of electronic and thermal Free Energies= -1790.228308

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -2194.4701

b-ts1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	0.583161	0.417869	0.032372
2	8	0	0.919703	-0.045367	2.314058
3	8	0	0.403377	-0.458243	-2.145270
4	8	0	1.591934	2.476223	-0.373630
5	7	0	3.365883	-0.060176	-0.241188
6	7	0	1.302315	-2.291409	0.200160
7	6	0	4.159273	0.107807	0.987779
8	1	0	4.067147	1.134903	1.344438
9	1	0	3.794856	-0.557888	1.771348
10	1	0	5.228614	-0.103587	0.806174
11	6	0	3.483801	-1.439122	-0.764496
12	1	0	3.090429	-1.445433	-1.782298
13	1	0	4.550566	-1.727077	-0.830928
14	6	0	2.763487	-2.505254	0.071495
15	1	0	3.183610	-2.527530	1.079235
16	6	0	0.772972	-2.796128	1.514160
17	1	0	-0.285044	-2.498058	1.541311
18	6	0	2.642836	-2.861485	4.839745
19	6	0	2.623772	-1.506388	5.188920
20	1	0	3.067449	-1.181678	6.128363
21	6	0	2.042380	-0.564466	4.346544
22	6	0	1.454197	-0.943000	3.115447
23	6	0	0.520988	-3.004715	-0.864722
24	1	0	0.566497	-4.087701	-0.658315
25	1	0	-0.526280	-2.701266	-0.721397
26	6	0	0.917891	-2.780164	-2.301391
27	6	0	1.350420	-3.849384	-3.093129
28	6	0	1.643789	-3.686631	-4.448288
29	6	0	1.493951	-2.419564	-5.022204
30	1	0	1.712622	-2.273131	-6.078379
31	6	0	1.066920	-1.338398	-4.256732
32	6	0	0.774121	-1.487105	-2.880919
33	6	0	3.825063	0.888855	-1.305754
34	1	0	4.813551	0.559794	-1.671941
35	1	0	3.119213	0.774389	-2.139061
36	6	0	3.927099	2.339617	-0.896749
37	6	0	2.771726	3.060812	-0.477195
38	6	0	2.920889	4.433590	-0.170451
39	6	0	4.155147	5.067426	-0.267585
40	1	0	4.233998	6.125400	-0.023687
41	6	0	5.289620	4.356983	-0.673429
42	6	0	5.157106	3.002176	-0.980062
43	1	0	6.031451	2.437013	-1.301294
44	1	0	1.448794	-4.833297	-2.635647
45	1	0	6.256610	4.847141	-0.749514
46	1	0	1.975570	-4.531854	-5.045208
47	1	0	0.786565	-3.899279	1.501652
48	6	0	1.468257	-2.324559	2.765831
49	6	0	2.062887	-3.250667	3.631867
50	1	0	2.060117	-4.303553	3.351482
51	1	0	3.095485	-3.599349	5.496576

52	1	0	2.973160	-3.486826	-0.382787
53	1	0	2.033555	4.976975	0.143384
54	1	0	0.948390	-0.350821	-4.694585
55	1	0	2.021679	0.489484	4.610741
56	6	0	-3.707738	1.639015	-1.365751
57	6	0	-3.455299	0.541400	-0.366660
58	6	0	-3.052722	0.833845	1.009876
59	6	0	-3.401346	2.197221	1.583790
60	6	0	-3.346151	3.311386	0.526259
61	6	0	-4.186119	2.943348	-0.706401
62	1	0	-3.187673	0.020670	1.727793
63	1	0	-3.443429	-0.488251	-0.690685
64	1	0	-2.776464	1.807898	-1.924520
65	1	0	-4.449589	1.276020	-2.082146
66	1	0	-4.415712	2.120307	1.995735
67	1	0	-2.719540	2.413387	2.417174
68	1	0	-3.713883	4.247831	0.965156
69	1	0	-2.303380	3.488185	0.230693
70	1	0	-5.231650	2.806640	-0.404664
71	1	0	-4.158276	3.754608	-1.445216
72	8	0	-1.809274	0.769228	0.312631
73	53	0	-6.366939	-0.297640	0.099848

Zero-point correction= 0.599644 (Hartree/Particle)
Thermal correction to Energy= 0.636027
Thermal correction to Enthalpy= 0.636971
Thermal correction to Gibbs Free Energy= 0.524819
Sum of electronic and zero-point Energies= -1616.982909
Sum of electronic and thermal Energies= -1616.946526
Sum of electronic and thermal Enthalpies= -1616.945582
Sum of electronic and thermal Free Energies= -1617.057734

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -2021.2699

1-int2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	0.538306	-0.077640	-0.294460
2	8	0	0.305421	0.820594	1.899356
3	8	0	1.928314	-1.866159	0.503641
4	8	0	-0.232166	1.388350	-2.099620
5	7	0	3.336141	0.190355	-1.242598
6	7	0	1.769749	2.705249	-0.128079
7	7	0	1.156801	-1.376023	-2.850235
8	6	0	3.221517	2.565622	-0.324668
9	1	0	3.657070	2.219635	0.615266
10	1	0	3.682171	3.551339	-0.534900
11	6	0	1.905730	2.519525	2.402510
12	6	0	2.603488	1.111142	4.724838
13	1	0	2.869423	0.557807	5.624233
14	6	0	4.378566	-4.567099	0.563380
15	1	0	4.415022	-5.635938	0.769292
16	6	0	1.238419	1.293698	2.699916
17	6	0	-2.413676	4.806829	-1.158750
18	6	0	-1.028446	4.768956	-0.982283
19	1	0	-0.507966	5.646429	-0.598259
20	6	0	4.265941	-1.814800	0.043972
21	6	0	1.613877	0.611541	3.884590

22	6	0	3.612405	1.623565	-1.469377
23	1	0	3.090433	1.921245	-2.382930
24	1	0	4.693935	1.764370	-1.664864
25	6	0	3.068223	-2.499535	0.415252
26	6	0	-3.058543	3.672926	-1.665709
27	1	0	-4.137520	3.682040	-1.810178
28	6	0	-0.932498	2.466755	-1.806811
29	6	0	3.166604	-3.893118	0.670849
30	6	0	-0.284626	3.627912	-1.292331
31	6	0	2.896417	2.999779	3.266361
32	1	0	3.385420	3.943947	3.024808
33	6	0	3.258323	2.311925	4.426188
34	6	0	-2.337705	2.525839	-1.988178
35	6	0	1.215543	3.594971	-1.189646
36	1	0	1.609150	3.236610	-2.145285
37	1	0	1.606585	4.618221	-1.033303
38	6	0	1.469145	3.315502	1.200474
39	1	0	0.383202	3.449990	1.224278
40	1	0	1.926967	4.322260	1.244967
41	6	0	5.470499	-2.518131	-0.059899
42	1	0	6.371538	-1.972325	-0.340546
43	6	0	4.229848	-0.320827	-0.150821
44	1	0	3.885441	0.148284	0.778079
45	1	0	5.259109	0.038470	-0.333648
46	6	0	5.546603	-3.889025	0.194605
47	6	0	3.522772	-0.551061	-2.509961
48	1	0	3.832597	-1.566917	-2.261500
49	1	0	4.349799	-0.111927	-3.097090
50	6	0	1.472210	-2.806475	-2.739159
51	1	0	2.305954	-2.981465	-2.059409
52	1	0	1.712759	-3.245435	-3.726283
53	1	0	0.602162	-3.326230	-2.328597
54	6	0	2.275713	-0.590814	-3.401290
55	1	0	1.895893	0.423172	-3.568395
56	1	0	2.579296	-0.992462	-4.389184
57	6	0	-0.033087	-1.208666	-3.702752
58	1	0	-0.861491	-1.774724	-3.267300
59	1	0	0.151323	-1.578354	-4.729182
60	1	0	-0.316232	-0.155067	-3.720498
61	1	0	-2.978019	5.700915	-0.906459
62	1	0	-2.836748	1.646484	-2.387707
63	1	0	4.030780	2.703931	5.083067
64	1	0	1.103708	-0.320918	4.110795
65	1	0	2.257676	-4.414210	0.960517
66	1	0	6.494303	-4.414679	0.110910
67	6	0	-3.263081	-0.513898	2.013526
68	6	0	-3.548193	-0.598296	0.520703
69	6	0	-2.744020	-1.692650	-0.214876
70	6	0	-2.826559	-3.046138	0.521996
71	6	0	-2.446156	-2.918168	2.004702
72	6	0	-3.323358	-1.876805	2.719100
73	1	0	-3.164984	-1.815713	-1.228355
74	1	0	-3.432825	0.360329	0.016957
75	1	0	-2.243865	-0.108581	2.099769
76	1	0	-3.930356	0.211672	2.491024
77	1	0	-3.844314	-3.450126	0.430852
78	1	0	-2.148918	-3.743816	0.013860
79	1	0	-2.539461	-3.893474	2.502379
80	1	0	-1.392975	-2.620812	2.077790

81	1	0	-4.364829	-2.227303	2.745390
82	1	0	-3.001233	-1.758065	3.762113
83	8	0	-1.444473	-1.219771	-0.268932
84	53	0	-5.822272	-0.911324	0.173280

Zero-point correction= 0.704062 (Hartree/Particle)
Thermal correction to Energy= 0.744881
Thermal correction to Enthalpy= 0.745825
Thermal correction to Gibbs Free Energy= 0.626526
Sum of electronic and zero-point Energies= -1790.169318
Sum of electronic and thermal Energies= -1790.128499
Sum of electronic and thermal Enthalpies= -1790.127555
Sum of electronic and thermal Free Energies= -1790.246854

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -2194.5003

b-int2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	0.457895	0.340533	0.130433
2	8	0	1.167102	-0.104042	2.357772
3	8	0	0.236219	-0.531495	-2.079067
4	8	0	1.177694	2.529176	-0.350005
5	7	0	3.283445	0.221083	-0.452352
6	7	0	1.562722	-2.264852	0.146904
7	6	0	4.186804	0.470935	0.679955
8	1	0	4.009519	1.472878	1.074202
9	1	0	4.001066	-0.245493	1.481453
10	1	0	5.247480	0.398986	0.374105
11	6	0	3.502493	-1.124222	-1.021300
12	1	0	2.999188	-1.164705	-1.988283
13	1	0	4.581837	-1.282987	-1.215584
14	6	0	3.015465	-2.284035	-0.140907
15	1	0	3.540908	-2.262738	0.816161
16	6	0	1.243601	-2.841875	1.496510
17	1	0	0.168848	-2.663816	1.646922
18	6	0	3.474947	-2.743703	4.591207
19	6	0	3.345516	-1.403907	4.976288
20	1	0	3.856210	-1.044239	5.868279
21	6	0	2.570785	-0.521765	4.231319
22	6	0	1.887042	-0.942793	3.061353
23	6	0	0.765405	-3.055928	-0.845667
24	1	0	0.953802	-4.128975	-0.664225
25	1	0	-0.289632	-2.874157	-0.593269
26	6	0	0.986025	-2.782477	-2.311915
27	6	0	1.449373	-3.795610	-3.157586
28	6	0	1.583012	-3.602231	-4.534150
29	6	0	1.237027	-2.357878	-5.073047
30	1	0	1.329977	-2.186258	-6.144345
31	6	0	0.775217	-1.331519	-4.255074
32	6	0	0.641136	-1.508336	-2.854912
33	6	0	3.486838	1.233222	-1.534542
34	1	0	4.458561	1.041965	-2.025447
35	1	0	2.705231	1.039674	-2.280835
36	6	0	3.451314	2.680165	-1.100029
37	6	0	2.262038	3.247767	-0.550498
38	6	0	2.280631	4.626698	-0.224558
39	6	0	3.414044	5.407138	-0.424360

40	1	0	3.389776	6.463542	-0.160972
41	6	0	4.579260	4.846452	-0.958305
42	6	0	4.577572	3.489659	-1.285848
43	1	0	5.476482	3.038980	-1.706017
44	1	0	1.703138	-4.762672	-2.723643
45	1	0	5.468669	5.451254	-1.115847
46	1	0	1.943908	-4.405042	-5.171773
47	1	0	1.377877	-3.937267	1.456349
48	6	0	2.018061	-2.311712	2.676270
49	6	0	2.806669	-3.176360	3.444877
50	1	0	2.889818	-4.218326	3.135867
51	1	0	4.079745	-3.435235	5.171975
52	1	0	3.300340	-3.225081	-0.639261
53	1	0	1.370591	5.054213	0.188584
54	1	0	0.506864	-0.362000	-4.666882
55	1	0	2.464484	0.519202	4.525478
56	6	0	-3.981737	1.528802	-1.112418
57	6	0	-3.949015	0.252932	-0.281612
58	6	0	-3.113794	0.369372	1.012831
59	6	0	-3.484987	1.636994	1.811441
60	6	0	-3.429426	2.905263	0.946475
61	6	0	-4.332068	2.778397	-0.291645
62	1	0	-3.318457	-0.513370	1.642901
63	1	0	-3.623996	-0.609471	-0.860985
64	1	0	-2.963045	1.636087	-1.512143
65	1	0	-4.649569	1.414229	-1.972833
66	1	0	-4.492740	1.519680	2.233149
67	1	0	-2.784811	1.716209	2.652015
68	1	0	-3.727712	3.779597	1.540943
69	1	0	-2.393990	3.077703	0.626273
70	1	0	-5.383750	2.722625	0.021928
71	1	0	-4.237314	3.668742	-0.927554
72	8	0	-1.795457	0.389263	0.593353
73	53	0	-6.108725	-0.418823	0.200367

Zero-point correction= 0.600460 (Hartree/Particle)
Thermal correction to Energy= 0.636697
Thermal correction to Enthalpy= 0.637641
Thermal correction to Gibbs Free Energy= 0.527258
Sum of electronic and zero-point Energies= -1617.002240
Sum of electronic and thermal Energies= -1616.966002
Sum of electronic and thermal Enthalpies= -1616.965058
Sum of electronic and thermal Free Energies= -1617.075441

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -2021.2992

CO_2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.169148
3	8	0	0.000000	0.000000	-1.169148

Zero-point correction= 0.011592 (Hartree/Particle)
Thermal correction to Energy= 0.014240
Thermal correction to Enthalpy= 0.015184
Thermal correction to Gibbs Free Energy= -0.009126
Sum of electronic and zero-point Energies= -188.569347

Sum of electronic and thermal Energies= -188.566700
Sum of electronic and thermal Enthalpies= -188.565756
Sum of electronic and thermal Free Energies= -188.590066

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -188.55846

1-ts2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	-0.778572	-0.499486	0.183611
2	8	0	-0.409229	1.381745	-1.205916
3	8	0	-2.463316	-1.212681	-1.348459
4	8	0	0.046890	-0.724518	2.449734
5	7	0	-3.445051	0.603124	0.925103
6	7	0	-0.815501	2.164782	1.635053
7	7	0	-2.736254	-2.293884	1.899662
8	6	0	-2.171734	2.728242	1.526954
9	1	0	-2.296592	3.115691	0.514457
10	1	0	-2.288060	3.596078	2.206358
11	6	0	-0.139485	3.596475	-0.362402
12	6	0	-0.654903	4.580400	-2.940093
13	1	0	-0.855128	4.953934	-3.943062
14	6	0	-5.565521	-1.823665	-3.161499
15	1	0	-5.965678	-2.545372	-3.872195
16	6	0	-0.402534	2.678074	-1.419749
17	6	0	3.139484	1.417045	4.230575
18	6	0	1.921816	2.032061	3.932570
19	1	0	1.774848	3.084441	4.175349
20	6	0	-4.509481	0.029488	-1.333954
21	6	0	-0.661220	3.208366	-2.708292
22	6	0	-3.296613	1.745421	1.849370
23	1	0	-3.154807	1.343590	2.856069
24	1	0	-4.241513	2.322968	1.878792
25	6	0	-3.688480	-1.053581	-1.779902
26	6	0	3.303394	0.063207	3.915966
27	1	0	4.246756	-0.433754	4.134846
28	6	0	1.032325	-0.050322	3.008117
29	6	0	-4.261385	-1.969555	-2.701494
30	6	0	0.875284	1.329687	3.328747
31	6	0	-0.147777	4.970827	-0.622137
32	1	0	0.052167	5.657826	0.200016
33	6	0	-0.397090	5.478630	-1.898889
34	6	0	2.273315	-0.660198	3.320870
35	6	0	-0.462987	1.970116	3.070107
36	1	0	-1.236786	1.331631	3.507657
37	1	0	-0.509225	2.949548	3.583582
38	6	0	0.188578	3.084162	1.018972
39	1	0	1.137491	2.536329	1.012485
40	1	0	0.336198	3.953888	1.685441
41	6	0	-5.820803	0.145436	-1.808662
42	1	0	-6.429337	0.978348	-1.456435
43	6	0	-3.955198	1.084585	-0.403969
44	1	0	-3.119886	1.600148	-0.890859
45	1	0	-4.743822	1.838640	-0.230582
46	6	0	-6.363797	-0.762933	-2.719355
47	6	0	-4.348052	-0.387306	1.548498
48	1	0	-4.817303	-0.967573	0.754320
49	1	0	-5.170795	0.122613	2.083148

50	6	0	-3.480228	-3.282325	1.107128
51	1	0	-3.992925	-2.810749	0.268576
52	1	0	-4.222206	-3.821961	1.727718
53	1	0	-2.776249	-4.005584	0.692449
54	6	0	-3.641256	-1.323155	2.531421
55	1	0	-3.045171	-0.742934	3.244760
56	1	0	-4.419423	-1.848966	3.122445
57	6	0	-1.969095	-2.986886	2.945390
58	1	0	-1.320103	-3.731387	2.478462
59	1	0	-2.635284	-3.501785	3.664705
60	1	0	-1.333676	-2.267504	3.464516
61	1	0	3.944425	1.981467	4.693936
62	1	0	2.396161	-1.712636	3.078213
63	1	0	-0.392784	6.551103	-2.076089
64	1	0	-0.861935	2.502882	-3.510116
65	1	0	-3.634018	-2.788843	-3.043404
66	1	0	-7.383880	-0.644610	-3.075521
67	6	0	3.013374	1.043595	-1.244284
68	6	0	3.312647	-0.319888	-0.642876
69	6	0	2.503170	-1.489781	-1.244191
70	6	0	2.473659	-1.425408	-2.786280
71	6	0	2.072302	-0.044061	-3.322942
72	6	0	3.002407	1.052173	-2.779209
73	1	0	3.002188	-2.425684	-0.956162
74	1	0	3.240981	-0.326176	0.444250
75	1	0	2.001581	1.300302	-0.902032
76	1	0	3.691343	1.802397	-0.839156
77	1	0	3.467812	-1.694020	-3.170579
78	1	0	1.774067	-2.194670	-3.135429
79	1	0	2.097269	-0.049086	-4.421706
80	1	0	1.042700	0.184163	-3.023708
81	1	0	4.023930	0.899846	-3.155812
82	1	0	2.672217	2.038594	-3.128300
83	8	0	1.221891	-1.452957	-0.685616
84	53	0	5.576854	-0.764815	-0.851975
85	6	0	0.560140	-3.738133	-0.449472
86	8	0	1.488892	-4.273312	-0.919686
87	8	0	-0.469889	-3.464546	0.059757

Zero-point correction= 0.716917 (Hartree/Particle)
Thermal correction to Energy= 0.760866
Thermal correction to Enthalpy= 0.761810
Thermal correction to Gibbs Free Energy= 0.636770
Sum of electronic and zero-point Energies= -1978.732881
Sum of electronic and thermal Energies= -1978.688932
Sum of electronic and thermal Enthalpies= -1978.687988
Sum of electronic and thermal Free Energies= -1978.813027

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -2383.0666

b-ts2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	-0.507486	0.023164	-0.375534
2	8	0	-1.783773	-0.646786	-2.255065
3	8	0	-0.027682	-0.449506	1.904726
4	8	0	-0.487240	2.366665	-0.435217
5	7	0	-2.997189	1.099447	0.713420

6	7	0	-2.437154	-1.916167	0.534625
7	6	0	-4.011722	1.419690	-0.302390
8	1	0	-3.627027	2.190095	-0.972438
9	1	0	-4.244936	0.537203	-0.899941
10	1	0	-4.943565	1.794682	0.160732
11	6	0	-3.499035	0.088188	1.664113
12	1	0	-2.804928	0.046231	2.504813
13	1	0	-4.478869	0.406503	2.072986
14	6	0	-3.677942	-1.313157	1.072284
15	1	0	-4.405458	-1.274167	0.258679
16	6	0	-2.740999	-2.832520	-0.614548
17	1	0	-1.773312	-3.211630	-0.958773
18	6	0	-5.450276	-2.337146	-3.258639
19	6	0	-4.893739	-1.316220	-4.037007
20	1	0	-5.424126	-0.951276	-4.915139
21	6	0	-3.665501	-0.757839	-3.699843
22	6	0	-2.936620	-1.197179	-2.565804
23	6	0	-1.722654	-2.746208	1.558670
24	1	0	-2.317569	-3.659679	1.738618
25	1	0	-0.785742	-3.065198	1.085891
26	6	0	-1.425322	-2.113921	2.897095
27	6	0	-1.965881	-2.658975	4.066606
28	6	0	-1.651722	-2.155395	5.330786
29	6	0	-0.767225	-1.075601	5.421465
30	1	0	-0.505480	-0.667781	6.396470
31	6	0	-0.216258	-0.511629	4.274748
32	6	0	-0.529076	-1.007351	2.985409
33	6	0	-2.619385	2.317276	1.493124
34	1	0	-3.455367	2.587348	2.164043
35	1	0	-1.778265	2.018635	2.132992
36	6	0	-2.254106	3.532631	0.676035
37	6	0	-1.164882	3.478907	-0.240638
38	6	0	-0.830897	4.662318	-0.942407
39	6	0	-1.539386	5.843574	-0.748051
40	1	0	-1.254874	6.735632	-1.303878
41	6	0	-2.610689	5.892281	0.150335
42	6	0	-2.953041	4.732041	0.847174
43	1	0	-3.785175	4.753669	1.550515
44	1	0	-2.645410	-3.506574	3.980410
45	1	0	-3.168342	6.812648	0.303773
46	1	0	-2.084156	-2.598529	6.224078
47	1	0	-3.307259	-3.701734	-0.233582
48	6	0	-3.503401	-2.245162	-1.778514
49	6	0	-4.744050	-2.784557	-2.140975
50	1	0	-5.159805	-3.585545	-1.529763
51	1	0	-6.410411	-2.776117	-3.517100
52	1	0	-4.113446	-1.956225	1.855055
53	1	0	0.002502	4.614891	-1.638361
54	1	0	0.469473	0.329451	4.336562
55	1	0	-3.226287	0.035732	-4.298829
56	6	0	3.586848	0.387433	1.272263
57	6	0	3.836748	-0.404025	-0.002763
58	6	0	3.074332	0.121881	-1.241252
59	6	0	3.233077	1.649157	-1.390036
60	6	0	2.950185	2.429128	-0.095260
61	6	0	3.778800	1.899150	1.085723
62	1	0	3.496809	-0.358055	-2.136824
63	1	0	3.657005	-1.469812	0.127360
64	1	0	2.541487	0.182904	1.550445

65	1	0	4.207770	0.004565	2.089686
66	1	0	4.258187	1.857690	-1.726424
67	1	0	2.556837	1.981027	-2.187405
68	1	0	3.170078	3.493514	-0.256028
69	1	0	1.881757	2.374586	0.140473
70	1	0	4.844413	2.108953	0.918327
71	1	0	3.494812	2.417962	2.010837
72	8	0	1.749468	-0.285142	-1.071836
73	53	0	6.106133	-0.486676	-0.436457
74	6	0	1.576274	-2.534845	-1.651910
75	8	0	0.576539	-2.714778	-1.044162
76	8	0	2.533435	-2.655782	-2.316158

Zero-point correction= 0.613528 (Hartree/Particle)
Thermal correction to Energy= 0.652759
Thermal correction to Enthalpy= 0.653703
Thermal correction to Gibbs Free Energy= 0.538155
Sum of electronic and zero-point Energies= -1805.572679
Sum of electronic and thermal Energies= -1805.533447
Sum of electronic and thermal Enthalpies= -1805.532503
Sum of electronic and thermal Free Energies= -1805.648051

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -2209.8712

1-int3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	-0.933427	-0.382401	0.446911
2	8	0	-0.091842	0.556395	-1.562874
3	8	0	-2.595037	-1.518497	-0.829227
4	8	0	0.133136	0.650690	2.345331
5	7	0	-3.630799	0.802176	0.821360
6	7	0	-1.159197	2.708195	0.412863
7	7	0	-2.468889	-1.341025	2.724069
8	6	0	-2.582172	3.060445	0.293442
9	1	0	-2.871354	2.950720	-0.753608
10	1	0	-2.743431	4.126705	0.549331
11	6	0	-0.800143	2.774463	-2.094480
12	6	0	-1.479473	1.888897	-4.668706
13	1	0	-1.742585	1.536679	-5.664691
14	6	0	-5.697580	-3.200401	-1.751412
15	1	0	-6.032138	-4.181079	-2.086234
16	6	0	-0.599407	1.405675	-2.437161
17	6	0	3.100153	3.563478	2.498970
18	6	0	1.804816	3.882058	2.085555
19	1	0	1.565046	4.907093	1.802842
20	6	0	-4.819224	-0.682218	-0.892023
21	6	0	-0.952820	0.991698	-3.744532
22	6	0	-3.509437	2.230028	1.184208
23	1	0	-3.169257	2.285103	2.221912
24	1	0	-4.510977	2.701810	1.158725
25	6	0	-3.864334	-1.726951	-1.071696
26	6	0	3.381041	2.244630	2.873204
27	1	0	4.383363	1.975536	3.201189
28	6	0	1.075751	1.570270	2.398497
29	6	0	-4.344610	-2.988625	-1.506811
30	6	0	0.795330	2.917058	2.029230
31	6	0	-1.330614	3.655203	-3.043939

32	1	0	-1.468404	4.700062	-2.765461
33	6	0	-1.673577	3.232543	-4.329650
34	6	0	2.391344	1.265437	2.829630
35	6	0	-0.623834	3.278783	1.681662
36	1	0	-1.271805	2.922463	2.489153
37	1	0	-0.722990	4.380692	1.643267
38	6	0	-0.380048	3.262380	-0.731775
39	1	0	0.662830	2.990377	-0.542687
40	1	0	-0.437417	4.367461	-0.709428
41	6	0	-6.174004	-0.923061	-1.142052
42	1	0	-6.885378	-0.109057	-1.001794
43	6	0	-4.337263	0.691177	-0.502588
44	1	0	-3.633817	1.051513	-1.261790
45	1	0	-5.199076	1.382210	-0.501782
46	6	0	-6.629481	-2.171040	-1.571965
47	6	0	-4.364627	0.093070	1.894277
48	1	0	-4.837671	-0.784220	1.452037
49	1	0	-5.184612	0.723529	2.284294
50	6	0	-3.064254	-2.647161	2.393836
51	1	0	-3.731724	-2.571464	1.534246
52	1	0	-3.629064	-3.057132	3.252035
53	1	0	-2.256907	-3.333010	2.128720
54	6	0	-3.481966	-0.332650	3.069971
55	1	0	-2.948140	0.533331	3.478374
56	1	0	-4.144553	-0.705412	3.876327
57	6	0	-1.530907	-1.513456	3.848368
58	1	0	-0.786020	-2.260741	3.567408
59	1	0	-2.058532	-1.847923	4.760952
60	1	0	-1.011294	-0.572095	4.036810
61	1	0	3.873258	4.326681	2.530110
62	1	0	2.602441	0.241663	3.128522
63	1	0	-2.083009	3.935382	-5.050773
64	1	0	-0.801667	-0.053445	-4.000220
65	1	0	-3.615896	-3.782737	-1.646470
66	1	0	-7.686391	-2.336466	-1.764184
67	6	0	3.242626	0.347664	-1.550631
68	6	0	3.668045	-0.516620	-0.375247
69	6	0	3.064150	-1.926795	-0.367443
70	6	0	3.092537	-2.606036	-1.742630
71	6	0	2.566164	-1.699981	-2.865747
72	6	0	3.329377	-0.366533	-2.906182
73	1	0	3.561013	-2.559493	0.368282
74	1	0	3.504565	-0.020973	0.580832
75	1	0	2.186199	0.596767	-1.366902
76	1	0	3.800235	1.290193	-1.552361
77	1	0	4.129498	-2.897744	-1.956912
78	1	0	2.510334	-3.530859	-1.667304
79	1	0	2.652404	-2.218827	-3.829894
80	1	0	1.501575	-1.491887	-2.704295
81	1	0	4.382187	-0.543537	-3.169021
82	1	0	2.909307	0.286580	-3.680936
83	8	0	1.699843	-1.757231	0.083433
84	53	0	5.947496	-0.721119	-0.328004
85	6	0	1.154730	-2.847106	0.838653
86	8	0	1.845458	-3.821348	1.084820
87	8	0	-0.056261	-2.580212	1.140597

Zero-point correction= 0.719982 (Hartree/Particle)

Thermal correction to Energy= 0.763295

Thermal correction to Enthalpy= 0.764239
Thermal correction to Gibbs Free Energy= 0.640681
Sum of electronic and zero-point Energies= -1978.755328
Sum of electronic and thermal Energies= -1978.712016
Sum of electronic and thermal Enthalpies= -1978.711071
Sum of electronic and thermal Free Energies= -1978.834630

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -2383.0814

b-int3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	-0.768096	0.040671	-0.543961
2	8	0	-2.495421	0.005289	-2.149205
3	8	0	0.089937	-0.762005	1.523959
4	8	0	-0.441059	2.353987	-0.220195
5	7	0	-2.869498	0.964665	1.142288
6	7	0	-2.516972	-1.944134	0.286649
7	6	0	-4.033694	1.541506	0.450928
8	1	0	-3.716781	2.390813	-0.155874
9	1	0	-4.486581	0.803212	-0.211485
10	1	0	-4.794334	1.890965	1.172876
11	6	0	-3.266626	-0.201412	1.960437
12	1	0	-2.447317	-0.424321	2.644840
13	1	0	-4.144944	0.055114	2.584056
14	6	0	-3.616900	-1.457603	1.150313
15	1	0	-4.474862	-1.251909	0.506550
16	6	0	-3.020132	-2.582113	-0.980235
17	1	0	-2.124898	-2.789437	-1.580979
18	6	0	-6.220856	-1.697359	-2.862492
19	6	0	-5.870301	-0.473623	-3.443338
20	1	0	-6.579274	0.045899	-4.085977
21	6	0	-4.621208	0.090853	-3.207516
22	6	0	-3.665292	-0.548109	-2.379050
23	6	0	-1.654862	-2.972675	0.958934
24	1	0	-2.230551	-3.912114	1.025518
25	1	0	-0.821286	-3.158086	0.268358
26	6	0	-1.121986	-2.653361	2.334793
27	6	0	-1.454909	-3.466681	3.423103
28	6	0	-0.918278	-3.254391	4.694919
29	6	0	-0.022230	-2.196311	4.877250
30	1	0	0.410532	-2.013415	5.859360
31	6	0	0.322976	-1.367990	3.813286
32	6	0	-0.215039	-1.568694	2.519499
33	6	0	-2.224789	1.977255	2.037400
34	1	0	-2.879725	2.148114	2.910363
35	1	0	-1.305082	1.508434	2.410327
36	6	0	-1.920098	3.316035	1.405149
37	6	0	-1.009323	3.418329	0.311730
38	6	0	-0.728073	4.710593	-0.194446
39	6	0	-1.316038	5.848275	0.347886
40	1	0	-1.075182	6.825393	-0.067824
41	6	0	-2.211386	5.744712	1.417515
42	6	0	-2.500235	4.477849	1.926890
43	1	0	-3.194761	4.381593	2.761005
44	1	0	-2.146125	-4.293755	3.263493
45	1	0	-2.675224	6.629969	1.844865
46	1	0	-1.190510	-3.903140	5.523301

47	1	0	-3.467801	-3.558888	-0.727747
48	6	0	-4.022549	-1.800538	-1.794765
49	6	0	-5.289548	-2.341194	-2.046175
50	1	0	-5.544637	-3.299586	-1.594378
51	1	0	-7.195996	-2.141854	-3.043596
52	1	0	-3.930775	-2.239889	1.860009
53	1	0	-0.031772	4.781299	-1.026034
54	1	0	1.014876	-0.540675	3.948494
55	1	0	-4.340554	1.041112	-3.654280
56	6	0	3.615673	0.163409	1.068550
57	6	0	3.985694	-0.485506	-0.256617
58	6	0	3.318631	0.168249	-1.477922
59	6	0	3.407254	1.696459	-1.463634
60	6	0	3.019798	2.328999	-0.115452
61	6	0	3.779394	1.690216	1.058449
62	1	0	3.747377	-0.244113	-2.392406
63	1	0	3.809911	-1.558929	-0.274204
64	1	0	2.557205	-0.088985	1.240408
65	1	0	4.182096	-0.293495	1.887139
66	1	0	4.441770	1.965006	-1.714148
67	1	0	2.771220	2.085863	-2.267621
68	1	0	3.227636	3.406601	-0.152525
69	1	0	1.939528	2.234393	0.040639
70	1	0	4.847667	1.940038	0.995437
71	1	0	3.413127	2.100213	2.008107
72	8	0	1.927864	-0.223677	-1.447544
73	53	0	6.246573	-0.463888	-0.556054
74	6	0	1.625674	-1.542465	-1.980671
75	8	0	0.382633	-1.762504	-1.836747
76	8	0	2.529794	-2.207798	-2.452808

Zero-point correction= 0.616524 (Hartree/Particle)
Thermal correction to Energy= 0.655154
Thermal correction to Enthalpy= 0.656098
Thermal correction to Gibbs Free Energy= 0.542117
Sum of electronic and zero-point Energies= -1805.588456
Sum of electronic and thermal Energies= -1805.549825
Sum of electronic and thermal Enthalpies= -1805.548881
Sum of electronic and thermal Free Energies= -1805.662862

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -2209.8818

1-ts3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	0.970184	-0.022832	-0.507163
2	8	0	0.140206	0.253231	1.678625
3	8	0	1.484471	-2.304869	-0.082448
4	8	0	0.779923	2.105115	-1.581602
5	7	0	3.874197	-0.432657	-0.211034
6	7	0	2.507289	2.112545	0.987633
7	7	0	2.491649	-0.486465	-2.967052
8	6	0	3.824586	1.567544	1.354510
9	1	0	3.687527	0.906245	2.212587
10	1	0	4.501524	2.377498	1.691230
11	6	0	1.522370	1.435474	3.224053
12	6	0	0.986430	-0.540197	5.141391
13	1	0	0.772938	-1.310597	5.880174

14	6	0	3.118119	-5.566739	-0.092442
15	1	0	2.878594	-6.604328	-0.318947
16	6	0	0.675581	0.342457	2.882163
17	6	0	0.093983	6.045088	-0.443695
18	6	0	1.202678	5.345042	0.035945
19	1	0	1.898941	5.837298	0.714653
20	6	0	3.715581	-2.891685	0.492411
21	6	0	0.423435	-0.636966	3.872694
22	6	0	4.529548	0.820383	0.222352
23	1	0	4.619223	1.473638	-0.649536
24	1	0	5.562660	0.601135	0.552667
25	6	0	2.400906	-3.231693	0.055687
26	6	0	-0.780671	5.397490	-1.323319
27	1	0	-1.649641	5.926395	-1.711123
28	6	0	0.559922	3.353898	-1.224307
29	6	0	2.133900	-4.593695	-0.232415
30	6	0	1.450934	4.020571	-0.336307
31	6	0	2.075460	1.508399	4.507660
32	1	0	2.715080	2.356302	4.752816
33	6	0	1.819303	0.534311	5.474042
34	6	0	-0.553776	4.080416	-1.711632
35	6	0	2.699354	3.305357	0.109883
36	1	0	3.237209	2.962592	-0.781244
37	1	0	3.357984	4.023888	0.633382
38	6	0	1.757025	2.526997	2.212834
39	1	0	0.800361	2.922259	1.859045
40	1	0	2.295202	3.362026	2.698609
41	6	0	4.687650	-3.889543	0.620576
42	1	0	5.685045	-3.609102	0.959016
43	6	0	4.022712	-1.466423	0.875302
44	1	0	3.358405	-1.158360	1.691638
45	1	0	5.055050	-1.421019	1.263833
46	6	0	4.407097	-5.226927	0.335132
47	6	0	4.485065	-0.879913	-1.483554
48	1	0	4.337560	-1.956964	-1.566175
49	1	0	5.577942	-0.717146	-1.467280
50	6	0	2.297764	-1.881622	-3.400577
51	1	0	2.627051	-2.581548	-2.631302
52	1	0	2.850231	-2.088511	-4.335929
53	1	0	1.231559	-2.047069	-3.565587
54	6	0	3.908586	-0.180589	-2.716323
55	1	0	3.992770	0.907525	-2.610690
56	1	0	4.528640	-0.459341	-3.590986
57	6	0	1.959891	0.417345	-4.003257
58	1	0	0.909780	0.173898	-4.175064
59	1	0	2.518749	0.313217	-4.951573
60	1	0	2.011066	1.449694	-3.651338
61	1	0	-0.083303	7.073166	-0.139084
62	1	0	-1.226236	3.574465	-2.399743
63	1	0	2.257470	0.612471	6.465699
64	1	0	-0.226102	-1.466827	3.608035
65	1	0	1.130124	-4.851506	-0.559511
66	1	0	5.175623	-5.987305	0.445934
67	6	0	-4.865779	0.457578	-1.719342
68	6	0	-4.250564	-0.766595	-1.090120
69	6	0	-3.162859	-0.602548	-0.020857
70	6	0	-3.350625	0.628449	0.873153
71	6	0	-3.714688	1.879487	0.060631
72	6	0	-4.991662	1.661793	-0.763610

73	1	0	-3.094256	-1.516282	0.572625
74	1	0	-4.582235	-1.748492	-1.365828
75	1	0	-4.206302	0.735605	-2.552546
76	1	0	-5.835719	0.195808	-2.150855
77	1	0	-4.142577	0.403504	1.592897
78	1	0	-2.415895	0.772789	1.425294
79	1	0	-3.853548	2.725660	0.744999
80	1	0	-2.879235	2.152183	-0.598486
81	1	0	-5.837596	1.487297	-0.089888
82	1	0	-5.221420	2.556305	-1.357108
83	8	0	-1.862581	-0.424994	-0.667338
84	53	0	-6.393384	-1.492005	0.711386
85	6	0	-1.757510	-0.853263	-1.975269
86	8	0	-2.821408	-1.172409	-2.552122
87	8	0	-0.578337	-0.837676	-2.406070

Zero-point correction= 0.719220 (Hartree/Particle)
Thermal correction to Energy= 0.762294
Thermal correction to Enthalpy= 0.763238
Thermal correction to Gibbs Free Energy= 0.638959
Sum of electronic and zero-point Energies= -1978.731649
Sum of electronic and thermal Energies= -1978.688575
Sum of electronic and thermal Enthalpies= -1978.687630
Sum of electronic and thermal Free Energies= -1978.811910

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent =-2383.0448

b-ts3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	0.795191	0.100404	0.329656
2	8	0	1.948448	0.933270	2.201288
3	8	0	0.663248	-1.497534	-1.402226
4	8	0	0.130213	2.009987	-0.855196
5	7	0	3.054618	0.985053	-1.108680
6	7	0	3.027719	-1.530488	0.623728
7	6	0	3.856953	2.024108	-0.440911
8	1	0	3.237740	2.903570	-0.258188
9	1	0	4.225504	1.662549	0.519771
10	1	0	4.717150	2.326100	-1.065078
11	6	0	3.867694	-0.223430	-1.371988
12	1	0	3.319633	-0.846438	-2.079952
13	1	0	4.817954	0.061461	-1.862748
14	6	0	4.211715	-1.045786	-0.122677
15	1	0	4.809090	-0.440767	0.562919
16	6	0	3.282406	-1.618322	2.103722
17	1	0	2.315925	-1.882067	2.553810
18	6	0	5.607137	0.612354	4.149619
19	6	0	4.870681	1.800882	4.203246
20	1	0	5.258026	2.655706	4.754864
21	6	0	3.643869	1.904484	3.555871
22	6	0	3.101348	0.818470	2.826796
23	6	0	2.586777	-2.900321	0.194972
24	1	0	3.327233	-3.630097	0.565511
25	1	0	1.650750	-3.093882	0.736398
26	6	0	2.382680	-3.148118	-1.279575
27	6	0	3.137310	-4.122892	-1.941046
28	6	0	2.915672	-4.440854	-3.282575

29	6	0	1.907915	-3.763192	-3.976542
30	1	0	1.716082	-3.997831	-5.022068
31	6	0	1.145080	-2.785548	-3.344404
32	6	0	1.362286	-2.449024	-1.987470
33	6	0	2.515613	1.486123	-2.415210
34	1	0	3.349560	1.561697	-3.134864
35	1	0	1.840605	0.702792	-2.783350
36	6	0	1.805531	2.818975	-2.368565
37	6	0	0.617266	2.986482	-1.598738
38	6	0	-0.033760	4.241865	-1.650285
39	6	0	0.464629	5.286470	-2.421320
40	1	0	-0.063101	6.238447	-2.437289
41	6	0	1.633969	5.122111	-3.171284
42	6	0	2.286813	3.889659	-3.131023
43	1	0	3.196467	3.745551	-3.713283
44	1	0	3.910788	-4.651263	-1.384454
45	1	0	2.028339	5.935439	-3.774764
46	1	0	3.513178	-5.204303	-3.773667
47	1	0	3.962477	-2.466284	2.294546
48	6	0	3.849561	-0.394802	2.780758
49	6	0	5.083876	-0.468218	3.438277
50	1	0	5.641311	-1.403597	3.396170
51	1	0	6.566136	0.527841	4.653790
52	1	0	4.845571	-1.889792	-0.438659
53	1	0	-0.941690	4.360485	-1.064827
54	1	0	0.362808	-2.251079	-3.876912
55	1	0	3.065086	2.823617	3.591979
56	6	0	-4.515588	-2.113500	-0.031563
57	6	0	-4.239670	-1.030640	0.981632
58	6	0	-3.322157	0.144436	0.616557
59	6	0	-3.381885	0.546014	-0.862471
60	6	0	-3.351477	-0.676757	-1.791056
61	6	0	-4.520895	-1.626486	-1.494802
62	1	0	-3.545070	0.991552	1.267844
63	1	0	-4.711802	-1.052944	1.944645
64	1	0	-3.716159	-2.856578	0.090260
65	1	0	-5.456218	-2.611084	0.219247
66	1	0	-4.302183	1.115367	-1.019834
67	1	0	-2.533264	1.210729	-1.061138
68	1	0	-3.403370	-0.336393	-2.832765
69	1	0	-2.392549	-1.203172	-1.686329
70	1	0	-5.468248	-1.112050	-1.690454
71	1	0	-4.478777	-2.502909	-2.153990
72	8	0	-1.926616	-0.218315	0.871532
73	53	0	-6.715381	0.453454	0.756282
74	6	0	-1.700415	-1.343875	1.655615
75	8	0	-0.484436	-1.559661	1.865574
76	8	0	-2.715563	-1.981801	2.011882

Zero-point correction= 0.615920 (Hartree/Particle)
Thermal correction to Energy= 0.654245
Thermal correction to Enthalpy= 0.655189
Thermal correction to Gibbs Free Energy= 0.540506
Sum of electronic and zero-point Energies= -1805.564552
Sum of electronic and thermal Energies= -1805.526228
Sum of electronic and thermal Enthalpies= -1805.525284
Sum of electronic and thermal Free Energies= -1805.639967

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent =-2209.8472

1-int4

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	1.346572	0.039751	0.088873
2	8	0	2.488255	0.532191	2.055228
3	8	0	1.098454	-2.250419	0.631189
4	8	0	0.998288	2.063311	-1.119260
5	7	0	3.035506	-1.573461	-1.581650
6	7	0	3.944770	1.225721	-0.566190
7	7	0	0.121346	-0.872987	-2.425042
8	6	0	4.822036	0.157766	-1.081630
9	1	0	5.173771	-0.426940	-0.228627
10	1	0	5.723175	0.591680	-1.555550
11	6	0	4.824659	0.938053	1.802654
12	6	0	5.300532	-0.663576	4.055565
13	1	0	5.477737	-1.285139	4.931234
14	6	0	1.002255	-5.893833	0.453177
15	1	0	0.352718	-6.713558	0.753954
16	6	0	3.725670	0.341354	2.482508
17	6	0	2.675907	5.864983	-0.934994
18	6	0	3.469108	4.746520	-1.194130
19	1	0	4.539758	4.869956	-1.354775
20	6	0	2.662585	-3.771380	-0.313694
21	6	0	3.995847	-0.456874	3.617746
22	6	0	4.151907	-0.756459	-2.108180
23	1	0	3.770213	-0.159342	-2.940426
24	1	0	4.928079	-1.419692	-2.532435
25	6	0	1.445569	-3.490922	0.372727
26	6	0	1.301665	5.685301	-0.740930
27	1	0	0.665779	6.545135	-0.538477
28	6	0	1.526609	3.272773	-1.058989
29	6	0	0.628146	-4.585832	0.744170
30	6	0	2.922870	3.460580	-1.258858
31	6	0	6.126906	0.712704	2.263640
32	1	0	6.956802	1.182230	1.735905
33	6	0	6.380895	-0.081844	3.382701
34	6	0	0.733961	4.416520	-0.804190
35	6	0	3.771265	2.270918	-1.624676
36	1	0	3.319873	1.775631	-2.491316
37	1	0	4.772992	2.622107	-1.932483
38	6	0	4.559028	1.862287	0.642687
39	1	0	3.867619	2.653695	0.946361
40	1	0	5.503773	2.351691	0.344716
41	6	0	3.013385	-5.095756	-0.598339
42	1	0	3.949136	-5.290317	-1.121860
43	6	0	3.591703	-2.639072	-0.668744
44	1	0	3.912229	-2.127263	0.247677
45	1	0	4.498536	-3.059714	-1.135063
46	6	0	2.198674	-6.164172	-0.221278
47	6	0	2.278161	-2.155347	-2.716291
48	1	0	1.783877	-3.059434	-2.360578
49	1	0	2.969326	-2.474026	-3.516059
50	6	0	-0.755047	-2.039688	-2.204409
51	1	0	-0.222815	-2.841919	-1.692576
52	1	0	-1.157682	-2.422785	-3.158974
53	1	0	-1.592877	-1.737706	-1.571772
54	6	0	1.246470	-1.200141	-3.320238

55	1	0	1.722712	-0.253183	-3.601199
56	1	0	0.871543	-1.652069	-4.258648
57	6	0	-0.673046	0.217103	-3.025992
58	1	0	-1.527663	0.433733	-2.381856
59	1	0	-1.047693	-0.065806	-4.025811
60	1	0	-0.063469	1.119835	-3.093971
61	1	0	3.119371	6.855789	-0.885751
62	1	0	-0.333406	4.272170	-0.658108
63	1	0	7.399948	-0.241796	3.724815
64	1	0	3.150888	-0.903640	4.134344
65	1	0	-0.298014	-4.369719	1.269729
66	1	0	2.490278	-7.185930	-0.448372
67	6	0	-4.474247	2.065481	-0.570040
68	6	0	-4.317065	0.655606	0.006112
69	6	0	-4.430172	0.551284	1.530607
70	6	0	-5.392055	1.503506	2.220033
71	6	0	-5.434378	2.906319	1.598779
72	6	0	-5.649843	2.811321	0.081552
73	1	0	-4.651012	-0.481259	1.817743
74	1	0	-4.978517	-0.067849	-0.473662
75	1	0	-3.548022	2.629569	-0.389535
76	1	0	-4.600981	1.994528	-1.656055
77	1	0	-6.378322	1.032853	2.117102
78	1	0	-5.146970	1.536673	3.288781
79	1	0	-6.245742	3.477985	2.065422
80	1	0	-4.501065	3.449407	1.808908
81	1	0	-6.584666	2.274953	-0.125733
82	1	0	-5.732419	3.811565	-0.361825
83	8	0	-3.027672	0.800320	1.938932
84	53	0	-7.728977	-0.950393	0.061709
85	6	0	-2.242076	0.462400	0.926256
86	8	0	-2.918798	0.217053	-0.196702
87	8	0	-1.021816	0.382633	1.011459

Zero-point correction= 0.722040 (Hartree/Particle)
Thermal correction to Energy= 0.765445
Thermal correction to Enthalpy= 0.766389
Thermal correction to Gibbs Free Energy= 0.638450
Sum of electronic and zero-point Energies= -1978.762026
Sum of electronic and thermal Energies= -1978.718621
Sum of electronic and thermal Enthalpies= -1978.717676
Sum of electronic and thermal Free Energies= -1978.845616

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -2383.0707

b-int4

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	57	0	0.894895	0.102230	0.090282
2	8	0	1.433674	1.135888	2.114533
3	8	0	1.210710	-1.700986	-1.374417
4	8	0	0.527914	1.835639	-1.404792
5	7	0	3.405194	0.936452	-0.783053
6	7	0	2.988324	-1.381843	1.157143
7	6	0	3.963155	2.081297	-0.039640
8	1	0	3.296512	2.939459	-0.135827
9	1	0	4.056520	1.838967	1.019572
10	1	0	4.955236	2.364064	-0.433014

11	6	0	4.295425	-0.243745	-0.683044
12	1	0	3.974730	-0.967533	-1.433859
13	1	0	5.332077	0.046455	-0.936871
14	6	0	4.316139	-0.909432	0.698724
15	1	0	4.690538	-0.203149	1.442926
16	6	0	2.847040	-1.309115	2.653926
17	1	0	1.807382	-1.592656	2.865717
18	6	0	4.449045	1.262805	4.973141
19	6	0	3.673928	2.395823	4.702901
20	1	0	3.862526	3.323761	5.239251
21	6	0	2.660125	2.350526	3.751232
22	6	0	2.382058	1.164565	3.032590
23	6	0	2.722791	-2.813039	0.785315
24	1	0	3.370723	-3.453605	1.407417
25	1	0	1.687926	-3.013276	1.094603
26	6	0	2.908244	-3.215810	-0.656535
27	6	0	3.844174	-4.197170	-1.001104
28	6	0	3.978294	-4.655240	-2.313096
29	6	0	3.149905	-4.116663	-3.302989
30	1	0	3.236063	-4.463203	-4.331041
31	6	0	2.213168	-3.136147	-2.988243
32	6	0	2.072225	-2.658913	-1.665368
33	6	0	3.237438	1.277220	-2.235813
34	1	0	4.236425	1.324994	-2.701961
35	1	0	2.711402	0.425466	-2.686557
36	6	0	2.510541	2.567827	-2.531183
37	6	0	1.161905	2.754732	-2.114535
38	6	0	0.512484	3.956732	-2.475986
39	6	0	1.167299	4.936850	-3.214521
40	1	0	0.638512	5.851192	-3.476611
41	6	0	2.494239	4.755863	-3.618277
42	6	0	3.146848	3.573662	-3.267953
43	1	0	4.179334	3.418036	-3.578824
44	1	0	4.473950	-4.617579	-0.217841
45	1	0	3.010068	5.519719	-4.193851
46	1	0	4.710321	-5.420453	-2.556551
47	1	0	3.485082	-2.087509	3.105459
48	6	0	3.164876	0.008795	3.315300
49	6	0	4.182345	0.084693	4.274973
50	1	0	4.770307	-0.808483	4.483659
51	1	0	5.241506	1.295122	5.715836
52	1	0	5.034220	-1.743862	0.660803
53	1	0	-0.517822	4.088502	-2.156889
54	1	0	1.567736	-2.709133	-3.751170
55	1	0	2.052460	3.224895	3.534618
56	6	0	-4.203074	-2.399593	-0.691782
57	6	0	-4.063905	-1.386310	0.446571
58	6	0	-3.513125	-0.012402	0.042140
59	6	0	-3.875168	0.504101	-1.338545
60	6	0	-3.940167	-0.585834	-2.417140
61	6	0	-4.817348	-1.753901	-1.944644
62	1	0	-3.760178	0.730594	0.805527
63	1	0	-4.986117	-1.266668	1.018113
64	1	0	-3.207953	-2.792904	-0.944396
65	1	0	-4.804586	-3.245611	-0.342022
66	1	0	-4.869787	0.952062	-1.215104
67	1	0	-3.177646	1.306527	-1.608357
68	1	0	-4.347022	-0.148727	-3.336739
69	1	0	-2.931369	-0.950995	-2.659935

70	1	0	-5.826075	-1.389094	-1.712486
71	1	0	-4.908901	-2.512956	-2.731430
72	8	0	-2.049742	-0.260827	0.174512
73	53	0	-7.286923	0.511862	0.767842
74	6	0	-1.878437	-1.264960	1.056430
75	8	0	-0.762778	-1.543582	1.478592
76	8	0	-3.006737	-1.866601	1.372879

Zero-point correction= 0.618573 (Hartree/Particle)
Thermal correction to Energy= 0.657208
Thermal correction to Enthalpy= 0.658152
Thermal correction to Gibbs Free Energy= 0.539666
Sum of electronic and zero-point Energies= -1805.589412
Sum of electronic and thermal Energies= -1805.550777
Sum of electronic and thermal Enthalpies= -1805.549833
Sum of electronic and thermal Free Energies= -1805.668319

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -2209.8705

cis-4d

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.813101	1.475387	-0.225315
2	6	0	-0.037604	0.743951	0.822761
3	6	0	0.048611	-0.789043	0.761464
4	6	0	1.400645	-1.386664	0.391848
5	6	0	2.141846	-0.609215	-0.703845
6	6	0	2.224179	0.881435	-0.347906
7	1	0	-0.306226	-1.220995	1.706597
8	1	0	0.156020	1.120182	1.830534
9	1	0	0.308737	1.387410	-1.195776
10	1	0	0.842835	2.543303	0.017132
11	1	0	2.010028	-1.390857	1.306621
12	1	0	1.252180	-2.435704	0.111530
13	1	0	3.144334	-1.032794	-0.834926
14	1	0	1.618940	-0.727850	-1.661829
15	1	0	2.776003	1.007954	0.595503
16	1	0	2.785339	1.431117	-1.112190
17	8	0	-0.957466	-1.083358	-0.238264
18	6	0	-1.891126	-0.089609	-0.210946
19	8	0	-1.441716	0.955043	0.543982
20	8	0	-2.949081	-0.126587	-0.767163

Zero-point correction= 0.169598 (Hartree/Particle)
Thermal correction to Energy= 0.177454
Thermal correction to Enthalpy= 0.178398
Thermal correction to Gibbs Free Energy= 0.136835
Sum of electronic and zero-point Energies= -498.290831
Sum of electronic and thermal Energies= -498.282975
Sum of electronic and thermal Enthalpies= -498.282031
Sum of electronic and thermal Free Energies= -498.323595

M06 /6-311++G(d,p)-SDD //B3LYP /6-31G(d)-LANL2DZ energy in dichloromethane solvent = -498.29066

6. References

1 D. G. Gusev, Dehydrogenative coupling of ethanol and ester hydrogenation catalyzed by pincer-type YNP complexes, *ACS Catal.*, 2016, **6**, 6967–6981.

2 X. Xin, H. Shan, T. Tian, Y. Wang, D. Yuan, H. You and Y. Yao, Conversion of CO_2 into cyclic carbonates under ambient conditions catalyzed by rare-earth metal complexes bearing poly(phenolato) ligand, *ACS Sustainable Chem. Eng.*, 2020, **8**, 13185–13194.

3 J. Steinbauer, A. Spannenberg and T. Werner, An in situ formed Ca^{2+}-crown ether complex and its use in CO_2-fixation reactions with terminal and internal epoxides, *Green Chem.*, 2017, **19**, 3769–3779.

4 J. A. Castro-Osma, K. J. Lamb and M. North, Cr(salophen) complex catalyzed cyclic carbonate synthesis at ambient temperature and pressure, *ACS Catal.*, 2016, **6**, 5012–5025.

5 H. Vignesh Babu and K. Muralidharan, Zn(II), Cd(II) and Cu(II) complexes of 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole: synthesis, structures and their high catalytic activity for efficient cyclic carbonate synthesis, *Dalton Trans.*, 2013, **42**, 1238–1248.

6 Y. Kim, K. Hyun, D. Ahn, R. Kim, M. H. Park and Y. Kim, Efficient aluminum catalysts for the chemical conversion of CO_2 into cyclic carbonates at room temperature and atmospheric CO_2 pressure, *ChemSusChem*, 2019, **12**, 4211–4220.

7 N. Liu, Y. F. Xie, C. Wang, S. J. Li, D. Wei, M. Li and B. Dai, Cooperative multifunctional organocatalysts for ambient conversion of carbon dioxide into cyclic carbonates, *ACS Catal.*, 2018, **8**, 9945–9957.

8 Z. Guo, Y. Hu, S. Dong, L. Chen, L. Ma, Y. Zhou, L. Wang and J. Wang, ‘‘Spring-loaded’’ mechanism for chemical fixation of carbon dioxide with epoxides, *Chem Catalysis*, 2022, **2**, 519-530.

9 L. Wang, G. Zhang, K. Kodama and T. Hirose, An efficient metal- and solvent-free organocatalytic system for chemical fixation of CO_2 into cyclic carbonates under mild conditions, *Green Chem.*, 2016, **18**, 1229–1233.

10 D. O. Meléndez, A. Lara-Sánchez, J. Martínez, X. Wu, A. Otero, J. A. Castro-Osma, M. North and R. S. Rojas, Amidinate aluminium complexes as catalysts for carbon dioxide fixation into cyclic carbonates, *ChemCatChem*, 2018, **10**, 2271–2277.

11 W. Clegg, R. W. Harrington, M. North and R. Pasquale, Cyclic carbonate synthesis catalysed by bimetallic aluminium–salen complexes, *Chem. Eur. J.*, 2010, **16**, 6828–6843.

12 M. A. Gaona, F. De La Cruz-Martínez, J. Fernández-Baeza, L. F. Sánchez-Barba, C. Alonso-Moreno, A. M. Rodríguez, A. Rodríguez-Diéguez, J. A. Castro-Osma, A. Otero and A. Lara-Sánchez, Synthesis of helical aluminium catalysts for cyclic carbonate formation, *Dalton Trans.*, 2019, **48**, 4218–4227.

13 J. A. Castro-Osma, C. Alonso-Moreno, A. Lara-Sánchez, J. Martínez, M. North and A. Otero, Synthesis of cyclic carbonates catalysed by aluminium heteroscorpionate complexes, *Catal. Sci. Technol.*, 2014, **4**, 1674–1684.

14 M. Navarro, L. F. Sánchez-Barba, A. Garcés, J. Fernández-Baeza, I. Fernández, A. Lara-Sánchez and A. M. Rodríguez, Bimetallic scorpionate-based helical organoaluminum complexes for efficient carbon dioxide fixation into a variety of cyclic carbonates, *Catal. Sci. Technol.*, 2020, **10**, 3265–3278.

15 M. A. Emelyanov, N. V. Stoletova, A. A. Lisov, M. G. Medvedev, A. F. Smol'Yakov, V. I. Maleev and V. A. Larionov, An octahedral cobalt(III) complex based on cheap 1,2-phenylenediamine as a bifunctional metal-templated hydrogen bond donor catalyst for fixation of CO_2 with epoxides under ambient conditions, *Inorg. Chem. Front.*, 2021, **8**, 3871–3884.

16 L. Qu, I. Del Rosal, Q. Li, Y. Wang, D. Yuan, Y. Yao and L. Maron, Efficient CO_2 transformation under ambient condition by heterobimetallic rare earth complexes: experimental and computational evidences of a synergistic effect, *J. CO_2 Util.*, 2019, **33**, 413–418.

17 P. Gao, Z. Zhao, L. Chen, D. Yuan and Y. Yao, Dinuclear aluminum poly(phenolate) complexes as efficient catalysts for cyclic carbonate synthesis, *Organometallics*, 2016, **35**, 1707–1712.

18 Y. Hao, D. Yuan and Y. Yao, Metal-free cycloaddition of epoxides and carbon dioxide catalysed by triazole-bridged bisphenol, *ChemCatChem*, 2020, **12**, 4346–4351.

19 (a) C. Lee, W. Yang, R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B Condens. Matter Mater.*, 1988, **37**, 785−789; (b) B. Miehlich, A. Savin, H. Stoll, H. Preuss, Results obtained with the correlation energy density functionals of becke and Lee, Yang and Parr, *Chem. Phys. Lett.*, 1989, **157**, 200−206; (c) A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.*, 1993, **98**, 5648−5652.

20 (a) P. J. Hay, W. R. Wadt, Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals, *J. Chem. Phys.*, 1985, **82**, 299−310; (b) P. J. Hay, W. R. Wadt, Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg, *J. Chem. Phys.*, 1985, **82**, 270−283; (c) W. R. Wadt, P. J. Hay, Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi, *J. Chem. Phys.*, 1985, **82**, 284−298.

21 P. C. Hariharan, J. A. Pople, The influence of polarization functions on molecular orbital hydrogenation energies, *Theor. Chim. Acta.*, 1973, **28**, 213−222.

22 (a) K. A Fukui, A formulation of the reaction coordinate, *J. Phys. Chem. A*, 1970, **74**, 4161−4163; (b) K. Fukui, The path of chemical reactions - the IRC approach, *Acc. Chem. Res.*, 1981, **14**, 363−368.

23 (a) Y. Zhao, D. G. Truhlar, Density functionals with broad applicability in chemistry. *Acc. Chem. Res.*, 2008, **41**, 157−167; (b) Y. Zhao, D. G. Truhlar, The Mo6 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and

transition elements: two new functionals and systematic testing of four Mo6-class functionals and 12 other functionals, *Theor. Chem. Acc.*, 2008, **120**, 215−241; (c) Y. Zhao, D. G. Truhlar, Benchmark energetic data in a model system for grubbs II metathesis catalysis and their use for the development, assessment, and validation of electronic structure methods. *J. Chem. Theory Comput.*, 2009, **5**, 324−333.

24 D. Andrae, U. Haüβermann, M. Dolg, H. Stoll, H. Preuβ, Energy-adjusted ab initio pseudopotentials for the second and third row transition elements. *Theor. Chim. Acta.*, 1990, **77**, 123−141.

25 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, JR. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision C.01; Gaussian, Inc., Wallingford, CT, 2013.

26 C. Y. Legault, CYLview, 1.0b; Université de Sherbrooke: Sherbrooke, Quebec, Canada, 2009. http://www.Cylview.org.