Unraveling the Mechanism of the Ir$^{III}$-Catalyzed Regiospecific Synthesis of $\alpha$-Chlorocarbonyl Compounds from Allylic Alcohols

Man Li, Amparo Sanz-Marco, Samuel Martinez-Erro, Víctor García-Vázquez, Binh Khanh Mai, Jacob Fernández-Gallardo, Fahmi Himo,* and Belén Martín-Matute*[^a]
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General information

All reagents were used as obtained from commercial sources without further purification. Flash chromatography was performed with 60 Å (35-70 µm) silica gel (GC 60A 35-70 Micron, DAVISIL) using mixtures pentane / EtOAc as eluent. Analytical TLC was performed on aluminum plates pre-coated with silica gel (Merck, Silica Gel 60 F254). Compounds were detected by exposure to UV light or by revealing the plates in a solution of 5% KMnO₄ in water. ¹H and ¹³C NMR spectra were recorded at 400 or 500 MHz and 100 or 125 MHz respectively on Bruker Advance spectrometers. Chemical shifts (δ) are shown in ppm, using the residual peaks of CH(D)Cl₃ (δH 7.26 and δC 77.00) as reference. Coupling constants (J) are given in Hz. High-resolution mass spectra (HRMS) were recorded on Bruker microTOF ESI-TOF mass spectrometer.

Synthesis and characterization of allylic alcohols

Allylic alcohols 1a,¹ 1a-d,¹ 1b,¹ 1b-d,¹ 1e,¹ 1e-d,² 1f,¹ 1f-d,³ 1g⁴ were synthesized according to literature procedures.

(‡E)⁴-(4-Methoxyphenyl)but-3-en-2-ol (1g-d₁)

To a stirred solution of (‡E)-4-(4-methoxyphenyl)but-3-en-2-one (10 mmol, 1.76 g) and CeCl₃ x 7H₂O (10 mmol, 3.65 g) in MeOH (50 mL), NaBD₄ (10 mmol, 0.42 g) was added at 0 °C. The reaction was stirred until TLC analysis showed no starting material left. After addition of an aqueous solution of NH₄Cl (sat., 10 mL), MeOH was evaporated and the allylic alcohol was extracted with EtOAc (3 x 15 mL), washed with brine, dried over MgSO₄, filtered and evaporated. Purification by column chromatography (SiO₂; petroleum ether / EtOAc, 9:1) afforded 1g-d₁ as a white solid (1.27 g, 71 %, 96% D).

¹H NMR (400 MHz, CDCl₃) δ 7.31–7.28 (m, 2H), 6.86–6.83 (m, 2H), 6.49 (d, J = 15.9 Hz, 1H), 6.11 (d, J = 15.9 Hz, 1H), 3.70 (s, 3H), 1.35 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 159.3, 131.5, 129.5, 129.0, 127.7, 114.1, 68.6 (t, Jₐₓₓ = 21.9 Hz), 55.3, 23.4 ppm.

HRMS (ESI): m/z calcd for C₁₁H₁₃O₂D⁺Na⁺: 202.0949 [M+Na⁺]; found: 202.0952.

General procedure for the isomerization of allylic alcohols

To a solution of the allylic alcohol 1 (0.2 mmol, 1 equiv.) in a mixture of acetone and H₂O (2:1, 0.1 M), [Cp*IrCl₂]: (4 mg, 2.5 mol%) was added. The resulting mixture was stirred at room temperature and monitored by TLC. When the reaction was completed, EtOAc (10 mL) and H₂O (10 mL) were added to the mixture and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over MgSO₄, filtered and the solvent was removed under reduce pressure. The crude was purified by flash chromatography affording the corresponding carbonyl compound 2.
Characterization data for ketones 2e-2f

Deuterium-propiophenone (2e-d₁)

The title compound was prepared according to general procedure from allylic alcohol 1e-d₁ (94% D) (27 mg). The reaction was stirred 3 h at room temperature. Purification by column chromatography (SiO₂; Petroleum ether / EtOAc = 10:1) afforded 2e-d₁ (94% D) as a colorless oil (16 mg, 62%). Deuterium content was determined to 40% in Cβ and 54% in Cα.

1H NMR (400 MHz, CDCl₃) δ 7.99–7.94 (m, 2H), 7.58–7.53 (m, 1H), 7.49–7.44 (m, 2H), 3.03–2.95 (m, 1.46H), 1.24–1.19 (m, 2.59H) ppm.

13C NMR (100 MHz, CDCl₃) δ 201.0, 137.1, 133.0, 128.7, 128.1, 31.9, 31.8 (t, 1J_C,D = 19.2 Hz, product with deuterium in Cα), 8.3, 8.14 (t, 1J_C,D = 19.9 Hz, product with deuterium in Cβ) ppm.

HRMS (ESI): m/z calcd for C₁₀H₉OD+Na⁺: 158.0687 [M+Na⁺]; found: 158.0687.

The title compound was also prepared according to general procedure using acetone and D₂O (2:1, 0.1 M) instead of acetone and H₂O (2:1, 0.1 M) from allylic alcohol 1e (27 mg). The reaction was stirred 3 h at room temperature. Purification by column chromatography (SiO₂; Petroleum ether / EtOAc = 10:1) afforded 2e-d₁ (84% D) as a colorless oil (15 mg, 57%). Deuterium content was determined to 84% in Cα.

1H NMR (400 MHz, CDCl₃) δ 7.98–7.94 (m, 2H), 7.57–7.54 (m, 1H), 7.48–7.44 (m, 2H), 3.04–2.95 (m, 1.16H), 1.25–1.21 (m, 3H) ppm.

13C NMR (100 MHz, CDCl₃) δ 201.1, 137.1, 133.0, 128.7, 128.1, 31.9, 31.6 (t, 1J_C,D = 19.3 Hz, product with deuterium in Cα), 8.3 ppm.

Deuterium-1-phenylpentan-3-one (2f-d₁)

The title compound was prepared according to general procedure from allylic alcohol 1f-d₁ (99% D) (33 mg). The reaction was stirred 3 h at room temperature. Purification by column chromatography (SiO₂; Petroleum ether / EtOAc = 10:1) afforded 2f-d₁ (99% D) as a colorless oil (31 mg, 99%). Deuterium content was determined to 43% in Cβ and 56% in Cα.

1H NMR (400 MHz, CDCl₃) δ 7.30–7.26 (m, 2H), 7.21–7.17 (m, 3H), 2.92–2.89 (m, 2H), 2.75–2.17 (m, 2H), 2.42–2.37 (m, 1.44H), 1.05–1.01 (m, 2.57H) ppm.

13C NMR (100 MHz, CDCl₃, mixture of products with deuterium in Cα or Cβ) δ 210.9, 210.8, 141.3, 128.6, 128.4, 126.2, 44.02, 44.01, 36.2, 35.9 (t, 1J_C,D = 19.2 Hz, product with deuterium in Cα), 29.99, 29.97, 7.83, 7.73 (t, 1J_C,D = 19.9 Hz, product with deuterium in Cβ) ppm.

HRMS (ESI): m/z calcd for C₁₁H₁₃OD+Na⁺: 186.1000 [M+Na⁺]; found: 186.0992.
**General procedure for the isomerization / chlorination of allylic alcohols**

To a solution of the allylic alcohol 1 (0.2 mmol, 1 equiv.) and N-chlorosuccinimide (32 mg, 0.24 mmol, 1.2 equiv.) in a mixture of acetone and H$_2$O (2:1, 0.1 M), [Cp*IrCl$_2$]$_2$ (4 mg, 2.5 mol%) was added. The resulting mixture was stirred at room temperature and monitored by TLC. When the reaction was completed, EtOAc (10 mL) and H$_2$O (10 mL) were added to the mixture and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over MgSO$_4$, filtered and the solvent was removed under reduce pressure. The crude was purified by flash chromatography affording the corresponding α-chlorocarbonyl compound.

**Characterization data for α-chloroketones 3a-3e**

4-Deuterium-3-chloro-4-phenylbutan-2-one (3a-d$_1$)

![Image of 4-Deuterium-3-chloro-4-phenylbutan-2-one (3a-d$_1$)](image)

The title compound was prepared according to general procedure from allylic alcohol 1a-d$_1$ (96% D) (36 mg). The reaction was stirred 18 h at room temperature. Purification by column chromatography (SiO$_2$; Petroleum ether / EtOAc = 10:1) afforded 3a-d$_1$ (94% D) as a colorless oil (33 mg, 91%). Deuterium content was determined to 94% in Cβ.

$^1$H NMR (400 MHz, CDCl$_3$, mixture of 2 diastereomers (1:1)) δ 7.34–7.21 (m, 5H), 4.40 (d, $J = 7.9$ Hz, 1H), 3.32 (dt, $J = 6.2$, 2.1 Hz, 0.53H), 3.07 (dt, $J = 8.0$, 2.1 Hz, 0.53H), 2.29 (s, 3H), 2.28 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$, mixture of 2 diastereomers (1:1)) δ 202.8, 136.3, 129.5, 128.8, 127.4, 63.88, 63.86, 39.5 (t, $^1J_{C,D} = 19.9$ Hz), 39.4 (t, $^1J_{C,D} = 20.4$ Hz), 27.0 ppm.

$^1$H and $^{13}$C NMR spectras were in agreement with those reported in the literature.$^5$

Deuterium-3-chlorooctan-2-one (3b-d$_1$)

![Image of Deuterium-3-chlorooctan-2-one (3b-d$_1$)](image)

The title compound was prepared according to general procedure from allylic alcohol 1b-d$_1$ (92% D) (33 mg). The reaction was stirred 18 h at room temperature. Purification by column chromatography (SiO$_2$; Petroleum ether / EtOAc = 10:1) afforded 3b-d$_1$ (82% D) as a colorless oil (18 mg, 57%). Deuterium content was determined to 63% in Cβ and 19% in Cα.

$^1$H NMR (400 MHz, CDCl$_3$) δ 4.17 (d, $J = 8.2$ Hz, 0.81H), 2.31 (s, 3H), 1.94–1.78 (m, 1.37H), 1.34–1.30 (m, 6H), 0.91–0.88 (m, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$, mixture of 2 diastereomers (1:1)) δ 204.4, 203.8, 64.4, 64.3 (t, $^1J_{C,D} = 17.2$ Hz, product with deuterium in Cα), 33.8, 33.6 (t, $^1J_{C,D} = 20.0$ Hz, product with deuterium in Cβ), 33.6 (t, $^1J_{C,D} = 19.4$ Hz, product with deuterium in Cβ), 31.24, 31.22, 29.9, 29.8, 26.1, 26.0, 25.8, 25.7, 22.5 ppm.

HRMS (ESI): m/z calcd for C$_8$H$_{14}$OD$_{35}$Cl+Na$: 186.0766 [M+Na]$^+$; found: 186.0762.
4-Deuterium-3-chloro-4-(4-methoxyphenyl)butan-2-one (3g–di)

The title compound was prepared according to general procedure from allylic alcohol 1g–di (96% D) (36 mg). The reaction was stirred 18 h at room temperature. Purification by column chromatography (SiO₂; Petroleum ether / EtOAc = 9:1) afforded 3g–di (96% D) as a colorless oil (35 mg, 98%). Deuterium content was determined to 96% in Cβ.

1H NMR (400 MHz, CDCl₃; mixture of 2 diastereomers (1:1)) δ 7.15–7.11 (m, 2H), 6.87–6.83 (m, 2H), 4.36–4.34 (m, 1H), 3.79 (s, 3H), 3.26–3.24 (m, 0.52H), 3.03–3.01 (m, 0.52H), 2.27 (s, 3H), 2.27 (s, 3H) ppm.

13C NMR (100 MHz, CDCl₃; mixture of 2 diastereomers (1:1)) δ 203.0, 158.9, 130.5, 128.2, 114.2, 64.09, 64.07, 55.4, 39.2, 38.88 (t, 1J_{C,D} = 20 Hz), 38.85 (t, 1J_{C,D} = 20.0 Hz), 27.02, 27.01 ppm. HRMS (ESI): m/z calced for C₁₁H₁₂O⁺ClD+Na⁺: 236.0559 [M+Na⁺]; found: 236.0554.

Deuterium-2-chloro-1-phenylpropan-1-one (3e–di)

The title compound was prepared according to general procedure from allylic alcohol 1e–di (94% D) (34 mg). The reaction was stirred 18 h at room temperature. Purification by column chromatography (SiO₂; Petroleum ether / EtOAc = 10:1) afforded 3e–di (92% D) as a colorless oil (30 mg, 88%). Deuterium content was determined to 31% in Cβ and 61% in Cα.

1H NMR (400 MHz, CDCl₃) δ 8.06–8.03 (m, 2H), 7.65–7.61 (m, 1H), 7.54–7.50 (m, 2H), 5.29–5.26 (m, 0.39H), 1.77–1.75 (m, 2.69H) ppm.

13C NMR (100 MHz, CDCl₃) δ 193.8, 134.3, 133.9, 129.1, 128.9, 52.9, 52.6 (t, 1J_{C,D} = 23 Hz, product with deuterium in Cα), 20.0, 19.9 (t, 1J_{C,D} = 20.0 Hz, product with deuterium in Cβ) ppm.

**Kinetic isotope effect studies**

*Isomerization*

[1e–di] and [1e]

Two parallel reactions, one with 1-phenylprop-2-en-1-ol (1e) and another with 1-phenylprop-2-en-1-d₁-1-ol (94% D, 1e–di), were carried out. Allylic alcohol 1e or 1e–di (0.1 mmol) and [Cp*IrCl₂]₂ (2.5 mol%, 2 mg) were dissolved in Acetone-d₆ / D₂O (2:1) (0.1 M, 1.0 mL) in a capped vial. The solution was transferred into an NMR tube and the tube was transferred to the NMR spectrometer. Signals from the aromatic protons of the product were used to monitor the formation of propiophenone (2e). 1H NMR spectra were recorded every 3 min. Each experiment was performed by duplicate. The average of the initial rate plots for the experiments with each allylic alcohol (1e, 1e–di) are given in Figure S1. A KIE of 1.66 ± 0.11 was obtained.
Isomerization / chlorination

[1e-d1] and [1e]

Ten parallel reactions, five with 1-phenylprop-2-en-1-ol (1e) and other five with 1-phenylprop-2-en-1-d-1-ol (94% D, 1e-d1), were carried out. Allylic alcohol 1e or 1e-d1 (0.1 mmol), NCS (16 mg, 0.12 mmol) and [Cp*IrCl₂]₂ (2.5 mol%, 2 mg) were dissolved in Acetone / H₂O (2:1) (0.1 M, 1.0 mL) in a capped vial. The reactions were quenched at 30 seconds, 1 min, 1.30 min, 2 min and 2.30 min. Signals from the aromatic protons of the product were used to monitor the formation of 2-chloro-1-phenylpropan-1-one (3e). Each experiment was performed by duplicate. The average of the initial rate plots for the experiments with each allylic alcohol (1e, 1e-d1) are given in Figure S2. A KIE of 0.88 ± 0.01 was obtained.
Figure S3. Kinetic profile of the Ir(III) catalyzed isomerization / chlorination of 1e.

[1g-d1] and [1g]

Two parallel reactions, one with (E)-4-(4-methoxyphenyl)but-3-en-2-ol (1g) and another with (E)-4-(4-methoxyphenyl)but-3-en-2-d-2-ol (96% D, 1g-d1), were carried out. Allylic alcohol 1g or 1g-d1 (0.1 mmol) and [Cp*IrCl2]2 (2.5 mol%, 2 mg) were dissolved in Acetone-d6 / D2O (2:1) (0.1 M, 1.0 mL) in a capped vial. The solution was transferred into an NMR tube and the tube was transferred to the NMR spectrometer. Signals from the aromatic protons of the product were used to monitor the formation of propiophenone (2g). 1H NMR spectra were recorded every 3 min. Each experiment was performed by duplicate. The average of the initial rate plots for the experiments with each allylic alcohol (1g, 1g-d1) are given in Figure S4. A KIE of 1.62 ± 0.12 was obtained.

Figure S4. Kinetic isotope effect of the Ir(III) catalyzed isomerization / chlorination of 1g.
Deuterium labeling cross-over studies for the isomerization of allylic alcohols

Deuterium labeling cross-over studies for the isomerization of allylic alcohols with 1,2-disubstituted double bonds (Scheme S1) were described in our previous work.\(^1\)

![Scheme S1](image)

**Scheme S1.** Cross-over experiments previously reported

\([1a-d_1] \text{ and } [1g]\)

Allylic alcohols \([1a-d_1]\) (0.1 mmol, 15 mg, 96\%D) and \([1g]\) (0.1 mmol, 18 mg) were dissolved in the same flask in a mixture of acetone and water (2:1, 0.1 M). \([\text{Cp}^*\text{IrCl}_2\text{]}_2\) (4.0 mg, 2.5 mol\%) was added, the reaction was stirred for 3 h until TLC indicated no starting material was remaining. When the reaction was completed, EtOAc (10 mL) and H\(_2\)O (10 mL) were added to the mixture and the aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over MgSO\(_4\), filtered and the solvent was removed under reduced pressure. Purification by column chromatography (SiO\(_2\); Petroleum ether / EtOAc 10:1) afforded 2a-d\(_1\) as a colorless oil (13 mg, 84\%) and 2g as a white solid (15 mg, 86\%). No deuterium scrambling between the two substrates was observed.

![Scheme S2](image)

**Scheme S2.** Cross-over experiments of 1g and 1a-d\(_1\)
4-Deuterium-4-phenylbutan-2-one (2a-d1)

Deuterium content was determined to 96% in Cβ.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30–7.26 (m, 2H), 7.21–7.17 (m, 3H), 2.91–2.86 (m, 1.04H), 2.78–2.75 (m, 2H), 2.14 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 208.1, 141.1, 128.7, 128.4, 126.3, 45.3, 30.2, 29.6 (t, $^{1}$J$_{CD}$ = 19.7 Hz,) ppm. $^1$H and $^{13}$C NMR spectra were in agreement with those reported in the literature.

4-(4-Methoxyphenyl)butan-2-one (2g)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.11–7.08 (m, 2H), 6.84–6.81 (m, 2H), 3.78 (s, 3H), 2.86–2.82 (m, 2H), 2.74–2.70 (m, 2H), 2.13 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 208.3, 158.1, 133.2, 129.4, 114.0, 55.4, 45.6, 30.2, 29.0 ppm.

HRMS (ESI): m/z calcld for C$_{11}$H$_{14}$O$_2$+Na$: 201.0886 [M+Na]$^+$; found: 201.0881.

[1e-d1] and [1h]

Allylic alcohols [1e-d1] (0.1 mmol, 14 mg, 94%D) and [1g] (0.1 mmol, 17 mg) were dissolved in the same flask in a mixture of acetone and water (2:1, 0.1 M). [Cp*IrCl$_2$]$_2$ (4.0 mg, 2.5 mol%) was added, the reaction was stirred for 3 h until TLC indicated no starting material was remaining. When the reaction was completed, EtOAc (10 mL) and H$_2$O (10 mL) were added to the mixture and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over MgSO$_4$, filtered and the solvent was removed under reduced pressure. Purification by column chromatography (SiO$_2$; Petroleum ether / EtOAc 10:1) afforded 2e-d1 as a colorless oil (7 mg, 50%) and 2h as a white solid (12 mg, 73%). No deuterium scrambling between the two substrates was observed.

Scheme S3. Cross-over experiments of 1h and 1e-d1
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.97–7.93 (m, 2H), 6.95–6.91 (m, 2H), 3.86 (s, 3H), 2.95 (q, \(J = 7.3\) Hz, 2H), 1.21 (t, \(J = 7.3\) Hz, 3H) ppm.
\(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 199.6, 163.4, 130.4, 130.2, 113.8, 65.6, 31.6, 8.6 ppm. \(^1\)H and \(^1\)C NMR spectra were in agreement with those reported in the literature.\(^1\)

**Deuterium-propiophenone (2e-\(d_i\))**

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.99–7.96 (m, 2H), 7.58–7.53 (m, 1H), 7.48–7.44 (m, 2H), 3.04–2.95 (m, 1.45H), 1.24–1.19 (m, 2.64H) ppm.
\(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 201.1, 137.1, 133.0, 128.7, 128.1, 31.9, 31.8 (t, \(^1J_{C,D} = 19.2\) Hz, product with deuterium in C\(\alpha\)), 8.3, 8.14 (t, \(^1J_{C,D} = 19.9\) Hz, product with deuterium in C\(\beta\)) ppm.
$^1$H and $^{13}$C NMR spectra of allylic alcohol 1g-$d_1$

$(E)$-4-(4-Methoxyphenyl)but-3-en-2-$d_2$-2-ol (1g-$d_1$)
$^1$H and $^{13}$C NMR spectra of ketones 2e-2f

Deuterium-propiophenone (2e-d$_1$)
Deuterium-propiophenone (2e-d₁) when Acetone / D₂O (2:1) is used as solvent
Deuterium-1-phenylpentan-3-one (2f-\textit{d}_1)
$^1$H and $^{13}$C NMR spectra of $\alpha$-chloroketones 3a-3e

4-Deuterium-3-chloro-4-phenylbutan-2-one (3a-$d_1$)
Deuterium-3-chlorooctan-2-one (3b-\textit{d}_1)
4-Deuterium-3-chloro-4-(4-methoxyphenyl)butan-2-one (3g-d$_1$)
Deuterium-2-chloro-1-phenylpropan-1-one (3e-$d_1$)
$^1$H and $^{13}$C NMR spectra of deuterium labeling cross-over studies
4-Deuterium-4-phenylbutan-2-one (2a-$d_1$)

\[
\begin{array}{c}
\text{H/D} \\
\text{O} \\
\hline
\end{array}
\]
4-(4-Methoxyphenyl)butan-2-one (2g)
1-(4-Methoxyphenyl)propan-1-one (2h)
Deuterium-propiophenone (2e-$d_1$)
DFT studies

Reaction profile of the Ir(III) catalyzed isomerization and isomerization-chlorination of allylic alcohol 1b

The mechanism of the Ir-catalyzed isomerization and isomerization-chlorination of 1,2-disubstituted allylic alcohol 1b was also investigated by DFT calculations. The calculated Gibbs energy profile is depicted in Figure S5 and the corresponding optimized structures are given in Figure S6.

Figure S5. Calculated Gibbs energy profile (kcal/mol) for the Ir-catalyzed isomerization and isomerization-chlorination of the 1,2-disubstituted allylic alcohol 1b.
**Figure S6.** Optimized transition state structures for the Ir-catalyzed isomerization and isomerization-chlorination of the 1,2-disubstituted allylic alcohol 1b. Most hydrogen atoms are omitted for clarity.
Reaction profile of the Ir(III) catalyzed isomerization and isomerization-chlorination of allylic alcohol 1e in acetone

The iridium-catalyzed isomerization and isomerization-chlorination of 1e were also investigated in pure acetone solvent. The obtained mechanism is summarized in Scheme S4 and the calculated Gibbs energy profile is given in Figure S7. Additional results are shown in Figures S8.

**Scheme S4.** Catalytic cycle for iridium-catalyzed isomerization and isomerization-chlorination of 1e in acetone.
Figure S7. Calculated Gibbs energy profile (kcal/mol) for the iridium-catalyzed isomerization and isomerization-chlorination of 1e in acetone.
Figure S8. Calculated Gibbs energy profiles (kcal/mol) for the tautomerization (TS\textsubscript{7\textsubscript{PA}}) and chlorination (TS\textsubscript{7-Cl\textsubscript{PA}}) of enol with the presence of acid.

Additional results for the reaction profile of the Ir(III) catalyzed isomerization and isomerization-chlorination of allylic alcohol 1e in mixture solvent

Figure S9. Calculated results of the transition states for the $\beta$-hydride elimination (red line) for 1e in mixed solvent.
Figure S10. Other related transition states.

Figure S11. Calculated results of the solvent molecule bound Ir complexes.

Note that 1b-TS6a, TS7-ClPA, and TS7-2 are marked with an asterisk (*) in Figures S5, S8, and S10. These geometries have one additional imaginary frequency each (<11 cm⁻¹). Many attempts were made to eliminate these frequencies without success. It was therefore replaced by a real frequency of the same magnitude in the RRHO calculations. Experience of similar cases shows that the error bar of this treatment rather small.
Calculated absolute energies and energy corrections.

| Stationary point | Thermal correction to Gibbs free energy at 298.15 K (a.u.) | Solvation energy (1,2-ethanediol) (a.u.) | Solvation energy (acetone) (a.u.) | Single-point energy B3LYP-D3(BJ)/6-311+G(2d,2p)-LanL2TZ (a.u.) |
|------------------|------------------------------------------------------------|-----------------------------------------|----------------------------------|---------------------------------------------------------------|
| Int0             | 0.177731                                                   | -0.031727                               | -0.03876685                     | -1415.56924                                                  |
| 1e               | 0.131289                                                   | -0.0073282                               | -0.012747807                    | -424.34247                                                   |
| Int1             | 0.338296                                                   | -0.0263049                               | -0.03719252                      | -1839.94537                                                  |
| Int1a            | 0.333866                                                   | -0.0273437                               | -0.03642263                     | -1839.93684                                                  |
| TS1              | 0.330577                                                   | -0.0438554                               | -0.04918539                     | -1839.9095                                                   |
| Cl               | -0.015023                                                  | -0.1082721                               | -0.106616512                    | -460.303727                                                  |
| Int2             | 0.337494                                                   | -0.0927755                               | -                                | -1379.44856                                                  |
| Int2-1           | 0.332171                                                   | -                                        | -0.045825                       | -1839.91606                                                  |
| Int2-2           | 0.323789                                                   | -0.03038793                               | -                                | -1379.047812                                                  |
| TS2              | 0.340167                                                   | -0.0903728                               | -                                | -1379.44352                                                  |
| TS2-1            | 0.332064                                                   | -                                        | -0.05117642                     | -1839.9063                                                   |
| Int3             | 0.342751                                                   | -0.0862779                               | -0.08915502                     | -1379.4596                                                   |
| TS3              | 0.335945                                                   | -0.0831679                               | -0.09121115                     | -1379.44021                                                  |
| TS3-1            | 0.331783                                                   | -0.08479065                               | -                                | -1379.40993                                                  |
| TS3-2            | 0.318755                                                   | -0.02925298                               | -                                | -1379.02081                                                  |
| Int4             | 0.33688                                                    | -0.0794104                                | -0.08850632                     | -1379.45133                                                  |
| Int5             | 0.324282                                                   | -0.024881                                 | -0.03652413                     | -1379.0701                                                   |
| TS4              | 0.326127                                                   | -0.0231173                                | -0.03525848                     | -1379.05332                                                  |
| Int6             | 0.327014                                                   | -0.0156046                                | -0.02680351                     | -1379.08527                                                  |
| TS5              | 0.32527                                                    | -0.0190275                                | -0.02952035                     | -1379.07031                                                  |
| TS5'             | 0.321455                                                   | -0.024159                                 | -0.0373598                      | -1379.04478                                                  |
| Int7             | 0.326234                                                   | -0.0239193                                | -0.03406303                     | -1379.08384                                                  |
| Int7'            | 0.326073                                                   | -0.0193528                                | -0.03001527                     | -1379.07936                                                  |
| Int8             | 0.338243                                                   | -0.0884587                                | -                                | -1379.47075                                                  |
| Int8'            | 0.334822                                                   | -0.0856912                                | -                                | -1379.44206                                                  |
| enol-2e           | 0.131419                                                   | -0.006742                                 | -0.013395438                    | -424.357489                                                  |
| TS6              | 0.322564                                                   | -0.0330413                                | -                                | -1379.05688                                                  |
| HCl              | -0.011159                                                  | -                                        | -0.005837941                    | -460.8368445                                                  |
| TS6-1            | 0.336929                                                   | -                                        | -0.04697915                     | -1839.932292                                                  |
| Int7a            | 0.326914                                                   | -0.0326893                                | -                                | -1379.06791                                                  |
| Int8a            | 0.335464                                                   | -0.0929712                                | -                                | -1379.45777                                                  |
| TS7              | 0.430585                                                   | -0.01161317                                | -0.02710323                     | -1273.047926                                                  |
| TS7'             | 0.328942                                                   | -0.088525                                 | -                                | -1379.42921                                                  |
| Reaction     | E (kcal/mol) | T (K) | ΔS (kcal/mol K) | ΔH (kcal/mol) |
|--------------|--------------|-------|----------------|---------------|
| TS7-1'       | 0.327128     | -     | -0.05685025    | -1839.889585  |
| TS7a         | 0.642132     | -0.0875532 | - | -2228.18383 |
| TS7-1        | 0.169848     | -0.016515089 | - | -577.2706145 |
| TS7-2        | 0.64382      | -0.0808438  | - | -2228.15455  |
| Int8-1'      | 0.336155     | -     | -0.09185151    | -1379.482518  |
| NCS          | 0.049112     | -0.010068983 | -0.018253663 | -820.3831089  |
| NCS_H        | 0.062016     | -0.0146046  | -0.017817015   | -360.795937   |
| TS7-Cl1      | 0.358597     | -0.0196575  | -0.03531431    | -1669.11239   |
| TS7-Cl1-1    | 0.224604     | -0.0195048  | - | -1321.22719  |
| PA           | 0.165153     | -     | -0.02135876    | -1106.580747  |
| TS7_PA       | 0.313697     | -     | -0.02781981    | -1530.952029  |
| TS7-ClPA     | 0.390505     | -     | -0.03887871    | -2351.369655  |
| 2e           | 0.132112     | -0.0058937  | -0.013518894   | -424.37639    |
| 3e           | 0.121325     | -0.0072839  | -0.015760102   | -884.002559   |
| 1b           | 0.18875      | -0.008058832 | - | -389.8624591  |
| 1b-Int1      | 0.393213     | -0.02640865 | - | -1805.459418  |
| 1b-TS1       | 0.389646     | -0.03892499 | - | -1805.435741  |
| 1b-Int2      | 0.398849     | -0.0843768  | - | -1344.983328  |
| 1b-TS2       | 0.394592     | -0.08647104 | - | -1344.964158  |
| 1b-Int3      | 0.39566      | -0.08529072 | - | -1344.969341  |
| 1b-Int4      | 0.38219      | -0.01854475 | - | -1344.593817  |
| 1b-TS3       | 0.385288     | -0.01816271 | - | -1344.575368  |
| 1b-Int5      | 0.383752     | -0.01642682 | - | -1344.600569  |
| 1b-TS4       | 0.381414     | -0.01904003 | - | -1344.585082  |
| 1b-Int6      | 0.381735     | -0.02329859 | - | -1344.594461  |
| 1b-TS4'      | 0.379243     | -0.01863777 | - | -1344.56746  |
| 1b-Int6'     | 0.38348      | -0.01773765 | - | -1344.59491  |
| 1b-Int7      | 0.395099     | -0.08990164 | - | -1344.981989  |
| 1b-Int7'     | 0.391609     | -0.08471962 | - | -1344.954925  |
| enol-2b      | 0.187666     | -0.005755112 | - | -389.8725094  |
| 1b-TS5       | 0.378673     | -0.03154026 | - | -1344.569849  |
| 1b-Int6a     | 0.380522     | -0.03375327 | - | -1344.577289  |
| 1b-Int7a     | 0.392974     | -0.09554218 | - | -1344.968063  |
| 1b-TS6       | 0.608596     | -0.0121008 | - | -1169.605751  |
| 1b-TS6'      | 0.38719      | -0.08876148 | - | -1344.936633  |
| 1b-TS6a      | 0.817081     | -0.08518187 | - | -2124.745749  |
| 1b-TS6-CI    | 0.470623     | -0.01825662 | - | -1600.149305  |
| 2b           | 0.187688     | -0.006317016 | - | -389.888055  |
| 3b           | 0.176349     | -0.007281511 | - | -849.5163828  |
| Int0-H2O     | 0.203074     | -0.027629 | - | -1492.05185  |
| Int0-actone  | 0.256668     | -0.0248193 | - | -1608.82026  |
Cartesian coordinates.

|   |   |   |
|---|---|---|
| Int0 |   |   |
| Ir  | -0.15382200 | 0.39496500 | -0.00174100 |
| Cl  | -2.31817700 | 1.29491700 | -0.02793100 |
| Cl  | 0.81093300 | 2.53301000 | 0.05727800 |
| C   | -0.27054300 | -1.56544300 | 0.90888500 |
| C   | 1.08606200 | -1.02404400 | 1.04990700 |
| C   | 1.64137300 | -0.84583800 | -0.26044600 |
| C   | 0.60871900 | -1.02529000 | -1.13981100 |
| C   | -0.55205700 | -1.70234900 | -0.48802700 |
| C   | -1.18206000 | -1.93213600 | 2.03388800 |
| C   | -0.99997200 | -1.30527500 | 2.98083000 |
| H   | -2.22672300 | -1.80687100 | 1.74409100 |
| C   | 1.78312900 | -0.75174700 | 2.34157700 |
| C   | 2.29038900 | -1.65797700 | 2.69464500 |
| C   | 1.07691400 | -0.43571900 | 3.11162600 |
| C   | 2.52758800 | 0.03685600 | 2.22340200 |
| H   | 0.99997200 | -1.30527500 | 2.98083000 |
| C   | -0.55205700 | -1.70234900 | -0.48802700 |
| C   | -1.18206000 | -1.93213600 | 2.03388800 |

|   |   |   |
|---|---|---|
| Int1 |   |   |
| Ir  | -0.58810300 | -0.26989500 | 0.25609600 |
| Cl  | 0.71060600 | -1.29412900 | -1.53605300 |
| Cl  | -0.28333100 | -2.39787800 | 1.40675700 |
| C   | -1.89447200 | 1.47697400 | -0.33195100 |
| C   | -2.16457800 | 1.08977700 | 1.04831600 |
| C   | -2.68183500 | -0.24630700 | 1.03264900 |
| C   | -2.66718800 | -0.72616000 | -0.34387100 |
| C   | -2.22725100 | 0.36727900 | -1.17693200 |
| C   | -1.49042100 | 2.83582800 | -0.81033800 |
| C   | -0.63499300 | 2.76945000 | -1.48595500 |
| H   | -2.32920400 | 3.30910800 | -1.33383600 |
| C   | -0.24946200 | 1.98202600 | 2.24297600 |
| C   | -2.93912700 | 2.61589800 | 2.33765600 |
| C   | -1.18161800 | 2.64156400 | 2.16961200 |
| C   | -1.94979500 | 1.39920500 | 3.16024100 |
| C   | -3.31951100 | -1.01610400 | 2.20137600 |
| H   | -2.80083300 | -0.62244700 | 3.14219700 |
| H   | -2.90347600 | -2.06434400 | 2.13173900 |
| H   | -4.29017100 | -0.95142000 | 2.22379300 |
|  |  |
|---|---|
| Int3 |  |
| Ir | 0.27757900 0.89043400 0.25243600 |
| Cl | 0.86613000 3.19935000 -0.09808100 |
| C | -1.74755900 0.32159400 1.19575100 |
| C | -1.13346100 -0.81988300 0.55315100 |
| C | -0.98109800 -0.50389500 -0.85564200 |
| C | -1.43413400 0.85263700 -1.06201600 |
| C | -1.92030800 1.35628700 0.22430000 |
| C | -0.88130900 0.41019900 2.64582700 |
| C | -1.41112250 -0.20834100 3.24456100 |
| H | 2.02510000 1.43852300 3.00611100 |
| H | -0.88941100 -2.15087300 1.18865700 |
| H | -1.80684900 -2.74921800 1.14275400 |
| H | -0.10722900 -2.70823200 0.67109600 |
| H | -0.59637100 -2.05538100 2.23478900 |
| C | -0.51175600 -1.44335100 -1.91630000 |
| H | 0.23320600 -2.14627000 -1.53815800 |
| H | -0.08895800 -0.90979500 -2.76873700 |
| H | -1.36286700 -2.03058500 -2.27980300 |
| C | -1.52806700 1.57977600 -2.61685700 |
| H | -2.52876400 1.44603500 -2.78889900 |
| H | -0.79781200 1.20708300 -3.08157800 |
| H | -1.35035600 2.64702300 -2.22296700 |
| C | -2.54730400 2.69311100 0.43792900 |
| H | -2.58065500 2.96736000 1.49352600 |
| H | -3.58295200 2.67472400 0.87986100 |
| H | -2.00732500 3.46952200 -0.10676800 |
| H | -3.10531400 0.05259800 2.80734300 |
| C | 1.42655200 -3.06796300 4.61547000 |
| C | 2.25711400 -3.33716900 3.52569400 |
| C | 2.59117700 -2.31923400 2.63381800 |
| C | 2.09864200 -1.02280000 2.85334300 |
| C | 1.28729600 -0.74923900 3.92988900 |
| C | 0.94973600 -1.77264100 4.81877200 |
| H | 1.16422100 -3.86063800 5.30836200 |
| C | 2.64659300 -4.33797400 3.37851300 |
| C | 3.24493800 -2.53897100 1.79364600 |
| H | 0.92381400 0.25799600 4.09196100 |
| H | 0.32056100 -1.55294400 5.67555300 |
| C | 2.44244300 0.04645300 1.81487800 |
| H | 3.48641900 0.36093300 1.99075800 |
| C | 2.09575700 -0.37189000 0.38650900 |
| H | 2.28102800 0.50077700 -0.68769500 |
| H | 1.86177200 -1.41747100 0.22261800 |
| H | 2.14914300 0.14134800 -1.70217100 |
| H | 2.84592500 1.42102200 -0.58561600 |
| O | 1.57047400 1.20924000 2.04848400 |
| H | 2.09294800 2.05158800 1.85962600 |
| TS3 |  |
| Ir | -0.05286800 0.56922900 -0.10796500 |
| Cl | 0.58013100 2.74614700 -0.92501990 |
| C | -1.66989100 1.41047700 1.18629500 |
| C | -1.19316100 0.23188900 1.84647600 |
| C | -1.38793900 -0.89340000 0.96095800 |
| C | -2.06747500 -0.41936200 -0.22898300 |
| C | -2.21437100 1.00626700 -0.11388500 |
| C | -1.71954300 2.79894800 1.73166600 |
| H | -1.42133500 3.52240900 0.97040800 |
| H | -2.73934000 3.03450900 2.05580700 |
| C | -0.56212200 0.14925000 3.19795800 |
| C | -0.22414400 1.12720600 3.54222600 |
| C | 0.29152600 -0.53245200 3.19060700 |
| H | -1.28905900 -0.23285300 3.92359200 |
| C | -1.06191500 -2.31459000 1.29364200 |
| H | -0.08610200 -2.39309100 1.77861300 |
| C | -1.05386500 -2.94490100 0.40829500 |
| C | -1.81369200 -2.72204300 1.97874100 |
| C | -2.55522300 -1.62946000 -1.35575400 |
| H | -3.55958800 -1.64333900 -1.12575200 |
| H | -1.91137400 -2.13627600 -1.51765300 |
| H | -2.61423900 -0.70304500 -2.28667800 |
| C | -2.90293300 1.92467500 -0.10634800 |
| H | -2.99756800 1.47813000 -2.05799800 |
| H | -2.34979900 2.86017100 -1.16759600 |
| H | -3.90907300 2.15341600 -0.69750600 |
Ir  8.78474800  2.34793500  -2.82564500
H  10.20034000  3.19743900  -1.43786200
H  8.81434800  2.69761600  0.56054700
H  6.62333900  1.58016200  0.30823200
H  7.17064900  1.43923200  -3.94703700
H  9.38488700  2.57631600  -3.70135600
C  5.47620000  0.71797300  -2.05671400
H  4.37132600  1.35762500  1.08714800
Cl  4.84314500  0.02462700  -0.87584200
C  3.62556400  -0.63238800  -1.04939800
H  5.51342200  -0.29260900  -0.88663300
H  3.37638500  -1.49108100  -0.43708700
H  3.14923600  -0.55478100  -2.02208000
O  4.97354300  0.62369300  -3.16741800

Int6
Ir  0.12950000  0.77912000  0.01785100
Cl  0.67627400  2.72746400  -1.33793100
C  -1.93807500  1.35945500  0.45783500
C  -1.51397100  0.37855100  1.42915600
C  -1.26772800  -0.85324500  0.71509400
C  -1.70550100  -0.67966900  -0.66237300
C  -2.06456400  0.67683100  -0.83079100
C  -2.38408600  2.76401300  0.71818300
H  -2.00879500  3.43295200  -0.05996700
H  -3.47875600  2.82901500  0.73575400
H  -1.42435500  0.56887000  2.91166300
H  -1.23368900  1.61283500  3.16575700
H  -0.62081700  -0.03290900  3.34072600
H  -2.36485700  0.26778500  3.38879100
C  -0.86507100  -2.16174400  1.31693800
H  -0.38992500  -2.20362600  2.28984200
H  -0.16432900  -2.68605400  0.66355500
H  -1.74605900  -2.79882400  1.46188200
C  -1.80817200  -1.78013800  -1.66501200
H  -2.73553100  -2.34174800  -1.49544400
H  -0.97574800  -2.48144400  -1.57285800
H  -1.82582800  -1.40082500  -2.68751800
H  -2.50996200  1.34203800  -2.09206900
H  -2.31534200  0.71336700  -2.96247500
H  -1.97192600  2.28376700  -2.23105100
H  -3.58382800  1.55997600  -2.05479600
H  -2.00655400  3.12605700  1.67648700
C  0.35446300  -1.03454600  -5.83837600
C  0.49062900  0.12439900  -5.07159400
C  0.86580400  0.04090000  -3.72118800
C  1.09208100  -1.21574700  -3.14558500
C  0.94781400  -2.37472700  -3.91968700
C  0.58812800  -2.28610200  -5.26068800
H  0.06615500  -0.96423600  -6.83826200
H  0.30315300  1.09756000  -5.51516400
H  0.94118900  0.94642200  -3.13899800
H  1.11637200  -3.33421300  -3.44299900
H  0.48484400  -3.18815600  -5.85635300
C  1.41018000  -1.37018200  -1.69469700
H  0.81376100  1.69189400  1.09182700
C  1.86228500  -0.17614200  -0.93460600
C  2.01283900  -0.23916800  0.47161900
H  2.38411300  0.59050500  -1.49103400
H  2.72174600  0.41810600  0.95938300
H  1.81793400  -1.18271100  0.97083900
O  1.27674800  -2.46903600  -1.14805900

TS5
Ir  -0.20701000  0.53382600  -0.14942400
Cl  0.61261600  2.62400700  -1.10233400
C  -2.04431700  1.42962900  0.72514400
H  -1.61957600  0.38474000  1.59734900
C  -1.63132200  -0.86010800  0.84443200
C  -2.19439800  -0.58385800  -0.45787300
C  -2.36783600  0.83081400  -0.57312200
C  -2.19679000  2.83050900  1.04947700
H  -1.74621600  3.49609000  0.26915800
H  -3.26123500  3.14266000  1.13164500
C  -1.24028800  0.52540600  3.03848800
H  -0.86943400  1.52852000  3.25580400

S39
TS6

Ir
-0.43435200  0.28638800  -1.13408300
Cl
-0.91649990  1.30332600  0.55202600

-2.04013300  1.11463300  -1.57457500
C
-2.14468880  -0.03822000  -2.43722800
C
-1.96217600  -1.18293900  -1.59455300
C
-2.08035200  -0.72927800  -2.08983300
C
-2.41719800  0.67833000  -2.10555500
C
-2.66024600  2.05616200  -2.05915700
H
-2.36943800  3.24381200  -1.31050100
H
-3.72569400  2.64233400  -2.28132600
C
-2.12746600  -0.03108400  -3.93172600

S42
| 1b | 1b-Int1 |
|---|---|
| C | 1.46097300 | -0.40718000 | 0.51231600 |
| H | 2.08563300 | -1.10933500 | 1.09513800 |
| H | 2.19829000 | -0.07533500 | -0.57623300 |
| C | 2.35397100 | 1.15290900 | -1.14496600 |
| H | 2.44103300 | -0.93376100 | -1.38399100 |
| H | 2.29001000 | 1.98810000 | -0.49377800 |
| O | 1.26176300 | 0.79148800 | 1.25408400 |
| H | 0.75358800 | 0.56463400 | 2.04222900 |
| C | 0.12428400 | -1.09766700 | 2.01727000 |
| H | 0.27447000 | -2.00921800 | -0.37673100 |
| H | -0.38864600 | -1.38029400 | 1.13822700 |
| H | -0.52106400 | -0.41993100 | -0.35522500 |
| C | 2.27911300 | 1.47446100 | -2.14183300 |
| H | 3.14048000 | 0.56399900 | -3.00917300 |
| C | 2.67743600 | 2.16266300 | -3.02415100 |
| H | 4.64809000 | 2.12569300 | -2.15175100 |
| H | 4.51050600 | 3.02581200 | -1.53707500 |
| H | 5.26166600 | 1.43993800 | -1.55290800 |
| C | 5.39265400 | 2.49563200 | -3.47771200 |
| H | 4.77052300 | 3.17917800 | -4.03121900 |
| H | 5.52288500 | 1.59409900 | -4.05142000 |
| C | 6.75618300 | 3.13916200 | -3.17481900 |
| H | 7.26784500 | 3.39436600 | -4.10844700 |
| H | 6.65898900 | 4.05947500 | -2.58938300 |
| H | 7.40839300 | 2.46318400 | -2.61047500 |

| Fr | -0.90117200 | -0.91040800 | -0.12775200 |
| Cl | 0.38891600 | -2.44338200 | 1.24271500 |
| Cl | -1.12752600 | -2.61679000 | -1.87063400 |
| C | -1.27295600 | 1.18039000 | 0.38708700 |
| C | -2.16818400 | 0.77432700 | -0.68972300 |
| C | -2.98405500 | -0.30297300 | -0.18893300 |
| C | -2.56361900 | -0.60449900 | 1.16619000 |
| C | -1.52948100 | 0.35822500 | 1.53471900 |
| H | -0.26784800 | 2.28165600 | 0.29055600 |
| H | 0.14566600 | 2.34215700 | -0.71790900 |
| H | 0.56297700 | 2.11982200 | 0.97664600 |
| C | -2.27824100 | 1.41486100 | -2.03573000 |
| C | -3.00327200 | 2.23775700 | -2.01999600 |
| H | -1.31648300 | 1.81931000 | -2.35813200 |
| H | -2.60160300 | 0.69009100 | -2.78546300 |
| C | -4.05220400 | -1.01872900 | -0.94712000 |
| H | -3.82970100 | -1.04092000 | -2.01435000 |
| H | -4.14369400 | -2.05297300 | -0.61047300 |
| H | -5.01416500 | -0.51423300 | -0.79599100 |
| C | -3.16818600 | -1.61119700 | 2.08333200 |
| H | -3.94120900 | -1.16542300 | 2.70624800 |
| H | -3.60667000 | -2.44179600 | 1.51872300 |
| H | -2.39638400 | -2.04631800 | 2.73483900 |
| C | -0.87559400 | 0.43147900 | 2.87474300 |
| H | -0.51399500 | -0.55517800 | 3.17367800 |
| H | -0.02324100 | 1.10962700 | 2.86361400 |
| H | -1.58993400 | 0.78813200 | 3.62577100 |
| H | -0.73836700 | 3.24372000 | 0.52650900 |
| C | 2.27209300 | -0.86287800 | -0.99124300 |
| H | 2.21954100 | -1.73996100 | -0.34385100 |
| O | 0.91078900 | -0.57817400 | -2.45632200 |
| H | 0.64633100 | -1.28614600 | -2.08273400 |
| C | 2.75376000 | 0.31722300 | -2.07821000 |
| C | 3.01992900 | 0.26415100 | 1.09958500 |
| H | 2.94060690 | 1.23177600 | -0.73714500 |
| H | 2.79506500 | -0.65957400 | 1.63283600 |
| C | 3.13787300 | -1.14221200 | -2.21553300 |
| H | 4.16088500 | -1.37234300 | -1.90198800 |
| C | 2.75406300 | -2.00198800 | -2.75584700 |
| C | 3.16556700 | -0.72760200 | 2.88157300 |
| C | 3.62494100 | 1.37600500 | 1.90700200 |
| C | 2.77997200 | 1.78169300 | 3.12421400 |
| H | 3.80740800 | 2.25063800 | 1.26999600 |
| H | 4.61027500 | 1.04676100 | 2.26939000 |
| C | 3.48203800 | 2.78211400 | 4.04663100 |
| H | 1.83478700 | 2.21906400 | 2.77753100 |
| H | 2.50972100 | 0.88327100 | 3.69497400 |
| C | 2.61634400 | 3.19476100 | 5.23902100 |
|        | X          | Y          | Z          |
|--------|------------|------------|------------|
| H      | 4.42142800 | 2.34168600 | 4.40606600 |
| H      | 3.76446800 | 3.67230100 | 3.46873000 |
| H      | 3.13739300 | 3.90588300 | 5.88759500 |
| H      | 1.68563900 | 3.66780600 | 4.90536600 |
| H      | 2.34430700 | 2.32483500 | 5.84715700 |
| 1b-TS1 | -0.62562700 | 0.16548000 | 0.01428000 |
| Cl     | 0.98914800 | -0.17698700 | 1.68741600 |
| Cl     | -0.24034300 | -2.78172000 | -1.83184100 |
| C      | -2.06227500 | 1.55728000 | -0.78979600 |
| C      | -2.48146800 | 0.24129900 | -1.17687200 |
| C      | -2.67657500 | -0.52764000 | 0.03794800 |
| C      | -2.43508300 | 0.33344800 | 1.18496000 |
| C      | -2.04116500 | 1.62052000 | 0.67597900 |
| C      | -1.71637400 | 2.68165400 | -1.70875900 |
| H      | -1.32400200 | 2.30363200 | -2.65397200 |
| H      | -0.95798500 | 3.33082300 | -1.26675100 |
| C      | -2.65992200 | -0.28588000 | -2.56224700 |
| H      | -3.72975400 | -0.41275900 | -2.77848800 |
| H      | -2.24149100 | 0.39833200 | -3.30177900 |
| C      | -3.09250300 | -1.95744900 | 0.07901700 |
| H      | -2.56359500 | -2.52752500 | -0.68822300 |
| C      | -2.87443300 | -2.40677100 | 1.04861300 |
| H      | -4.17440400 | -2.01925700 | -0.98814200 |
| C      | -2.58353800 | -0.04382300 | 2.62297800 |
| C      | -3.59437700 | 0.18756400 | 2.97823500 |
| C      | -2.40444600 | -1.11806600 | 2.76564100 |
| C      | -1.86417900 | 0.49347500 | 3.24318600 |
| C      | -1.72591300 | 2.82911700 | 1.49343300 |
| H      | -1.30825300 | 2.54971300 | 2.46185400 |
| H      | -1.00735500 | 3.47763600 | 0.99060100 |
| H      | -2.64276700 | 3.40569800 | 1.66618000 |
| H      | -2.69560500 | 3.28747200 | -1.92008500 |
| C      | 2.19662200 | 0.05188300 | -1.46893900 |
| H      | 2.53124300 | -0.38890600 | -0.52636800 |
| O      | 0.75053800 | -0.14467900 | -1.57888200 |
| H      | 0.51463900 | -1.13733100 | -1.80090000 |
| C      | 2.42208300 | 1.53176200 | -1.45959500 |
| C      | 2.79372300 | 2.22095000 | -0.37829800 |
| H      | 2.24080000 | 2.04741600 | -2.40388000 |
| C      | 2.93941300 | 1.68166600 | 0.55688500 |
| C      | 2.84702000 | -0.65584600 | -2.65139200 |
| C      | 3.93412300 | -0.54884000 | -2.59069800 |
| C      | 2.59441800 | -1.71946500 | -2.64688300 |
| C      | 2.05690600 | -0.22052100 | -3.59609200 |
| C      | 2.94845200 | 3.71192200 | -0.32230100 |
| C      | 1.79293000 | 4.36796800 | 0.45391900 |
| H      | 2.98946500 | 4.12856000 | -1.33603500 |
| C      | 3.89770700 | 3.97177400 | 0.16727000 |
| C      | 1.94408200 | 5.80383600 | 0.63608800 |
| H      | 0.85752100 | 4.15463900 | -0.08126000 |
| C      | 1.69591900 | 3.88667300 | 1.43726000 |
| C      | 0.75802700 | 6.05980500 | 1.36341100 |
| H      | 2.87188000 | 6.08889400 | 1.17982700 |
| H      | 2.06239500 | 6.53049900 | -0.35532800 |
| C      | 0.88402700 | 7.59030700 | 1.48345200 |
| H      | -0.17670300 | 6.34373500 | 0.81474700 |
| H      | 0.63684400 | 6.07503600 | 2.36208700 |

1b-Int2

|        | X          | Y          | Z          |
|--------|------------|------------|------------|
| Ir     | -0.67566500 | 0.67206700 | 0.91548000 |
| Cl     | 0.24907500 | -1.16281900 | 2.18643800 |
| C      | -2.17679100 | 1.79362500 | -0.29114000 |
| C      | -2.76208100 | 1.40091100 | 0.98166700 |
| C      | -2.75224700 | -0.03681200 | 1.05383100 |
| C      | -2.14456900 | -0.54460300 | -0.16628600 |
| C      | -1.83163000 | 0.59199100 | -1.00313000 |
| C      | -2.10450900 | 3.18887200 | -0.82189700 |
| H      | -1.28682600 | 3.30775600 | -1.53494200 |
| C      | -3.07081000 | 3.43981000 | -1.33997500 |
| C      | -3.42069700 | 2.33239900 | 1.95171400 |
| H      | -4.47952000 | 2.42075700 | 1.68411400 |
| C      | -2.98223200 | 3.32157400 | 1.92346000 |
| H      | -3.36679700 | 1.94891500 | 2.97344300 |
1b-TS4
Ir  -0.22942600  0.49908300  -0.15137000
Cl   0.54921700  2.65821000  -0.98952500
C   -2.01434700  1.34303700  0.88257900
C   -1.54771700  0.23720500  1.65155200
C   -1.60732400  -0.95200100  0.81587300
C   -2.22491900  -0.57536800  -0.43865400
C   -2.41296200   0.84125700  -0.43434800
C   -2.14016800  2.76809500  1.31577100
H   -1.71919900  3.43387600  0.55868100
H   -3.19373500  3.03094900  1.46884100
C   -1.07992900  0.27894500  3.07312900
C   -0.67770900  1.26933400  3.32822500
H   -0.29818800  -0.46128800  3.25471100
H   -1.91148300  0.06313600  3.75478300
C   -1.28761800  -2.35216400  1.37275800
H   -0.59310300  -2.35693100  2.08065200
H   -0.82195200  -2.90340100  0.41780900
H   -2.19572500  -2.88257000  1.54975000
C   -2.63196600  -1.53258300  -1.50982200
H   -3.62448400  -1.93742000  -1.27641600
H   -1.93636900  -2.37676000  -1.57996100
H   -2.69220200  -1.04620500  -2.48528000
C   -3.01386600  1.68352300  -1.51402900
C   -2.99247000  1.16566300  -2.47513100
H   -2.45364100  2.61480600  -1.62527200
H   -4.05743800  1.93104300  -1.82930900
H   -1.60491700  2.94779400  2.42994000
C   0.55975450  -1.59778600  -2.17501800
H   1.15189100  0.46132600  0.72094700
C   1.12525000  -0.36397100  -1.59639700
C   1.84646500  -0.40216700  -0.34205700
H   1.41798800  0.39968100  -2.31109000
H   1.83438300  -1.37113100  0.15521100
O   0.45374000  -2.65427300  -1.55502300
C   3.13743800  0.38558400  -0.20218500
C   0.10682500  -1.48863700  -3.61932700
H   -0.46088000  -0.56697200  -3.78013100
H   0.98685400  -1.44125200  -4.27179400
H   -0.48946800  -2.35970400  -3.89301000
H   3.39082000  -0.19021400  -0.73449300
H   3.02650300  1.34167400  -0.72126600
C   3.57935600  0.62487300  1.24173600
H   3.63325200  -0.33325500  1.77862800
C   2.81195300  1.22495900  1.72976600
C   4.92663200  1.34496100  1.34195200
H   4.86750500  2.29005600  0.78688100
H   5.69741600  0.74339500  0.84181600
H   5.34789900  1.62277100  2.78640200
C   4.60966100  2.25173100  3.29644500
H   5.44068400  0.69202600  3.35762600
H   6.31236200  2.13847900  2.83064800

1b-Int6
Ir  -1.07908400  0.98272100  -0.57589700
Cl   -1.00613500  2.84063300  -2.00645900
C   -2.97659200  1.15594000  0.67278800
C   -1.85892300  0.49855500  1.37373200
C   -1.56048600  -0.74144700  0.71248800
C   -2.34087800  -0.74426100  -0.50183100
C   -3.28129400  0.38674700  -0.46511800
C   -3.60553900  2.44524200  1.09035000
H   -4.07908200  2.94623700  0.24454090
H   -4.36755100  2.27396400  1.80624900
C   -1.26157900  0.97219300  2.65796400
H   -1.21943500  0.20630450  2.69315800
H   -0.24670700  0.59023100  2.78170100
H   -1.86548600  0.62959200  3.50749000
C   -0.67824000  -1.85244300  1.18285700
H   -0.13870100  -1.57834400  2.08883200
H    0.05152900  -2.12290800  0.41453200
H   -1.28958200  -2.73162400  1.41882200
C   -2.31896600  -1.83220600  -1.52462100
H   -2.99329700  -2.64413100  -1.22378800
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| H       | -2.46523600 | 1.17266700 | 2.06414000 |
| C       | -1.87056300  | 0.61174000  | 2.78669100  |
| C       | -2.24546700  | 2.23309100  | 2.04528000  |
| C       | -3.52655900  | 1.01289300  | 2.29310800  |
| H       | -3.89386800  | 3.01473000  | -0.57384500 |
| C       | 2.25261900   | 2.06866800  | -1.60329200 |
| H       | 2.79734300   | 1.82460600  | -0.68260800 |
| O       | 0.86684700   | 2.29254900  | -1.33991100 |
| C       | 2.81346200   | 3.33914800  | -2.18545200 |
| C       | 3.86801900   | 3.98147200  | -1.68634400 |
| C       | 2.29916000   | 3.72268000  | -3.06549700 |
| C       | 4.25246600   | 4.89176800  | -2.13693100 |
| H       | 4.38701800   | 3.61391900  | -0.80451600 |
| C       | 2.36344600   | 0.89441300  | -2.56510000 |
| C       | 3.05876300   | -0.62427800 | -2.21090200 |

TS3-1

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| Ir      | 0.50326300  | 0.36258800  | -0.31785500 |
| Cl      | 1.32498300  | 2.52947700  | -0.92676900 |
| C       | 0.92384300  | -1.42763100 | 0.88209300  |
| C       | 0.40315200  | -1.87886900 | -0.37430200 |
| C       | 1.33607400  | -1.79065700 | -1.42570700 |
| H       | 2.39678600  | -0.74609500 | -0.83173300 |
| C       | 2.12581200  | -0.64681100 | 0.60615900 |
| H       | 0.34094600  | -1.70770700 | 2.22831100 |
| H       | -0.75025300 | -1.67686600 | 2.20421100 |
| H       | 0.68717200  | -0.98416200 | 2.96775800 |
| C       | -0.78510400 | -2.76110700 | -0.57722900 |
| H       | -0.45602800 | -3.80096100 | -0.68746600 |
| C       | -1.46635000 | -2.71873400 | 0.27347800 |
| C       | -1.33702400 | -2.49461800 | -1.48163800 |
| C       | 1.16339100  | -1.79025100 | -2.87532200 |
| H       | 0.11057700  | -1.77197800 | -3.16543600 |
| H       | 1.70627700  | -1.08462200 | -3.50628600 |
| C       | 1.54662100  | -2.79541900 | -3.08436400 |
| C       | 3.58408000  | -0.15399800 | -1.51317700 |
| C       | 4.46933400  | -0.76312900 | -1.29769600 |
| C       | 3.45096700  | -0.11578500 | -2.59458000 |
| H       | 3.77711990  | 0.86190400  | -1.16022300 |
| C       | 3.05905300  | -0.05563900 | 1.61192800 |
| C       | 3.53630100  | 0.84258400  | 1.21860500 |
| C       | 2.53510400  | 0.21298000  | 2.53044700 |
| H       | 3.84222600  | -0.78033100 | 1.86514700 |
| H       | 0.64714000  | -2.70509900 | 2.56331800 |
| C       | -1.55939500 | 1.30994300  | 0.05718400 |
| H       | -0.16374800 | 1.12105900  | 0.94380200 |
| O       | -1.34434300 | 1.23621300  | -1.33412100 |
| C       | -1.77541600 | 2.69754400  | 0.57829400 |
| C       | -1.02356700 | 3.25807000  | 1.61293900 |
| C       | -2.83698400 | 3.42084800  | 0.01112300 |
| C       | -1.33899100 | 4.53216000  | 2.08580800 |
| H       | -0.17869900 | 2.71473200  | 2.04256300 |
| C       | -3.13155100 | 4.06986600  | -0.97533900 |
| C       | -3.43613100 | 2.97779800  | -0.77851600 |
| C       | -2.38137400 | 5.25409700  | 1.51804100 |
| C       | -0.73863800 | 4.96589300  | 2.88433500 |
| C       | -4.99832300 | 5.26597800  | 0.03725900 |
| H       | -2.61249000 | 6.25913700  | 1.68087700 |
| C       | -2.46947200 | 0.23231900  | 0.49704200 |
| C       | -3.14394600 | 0.26532700  | 1.65038100 |
| H       | -2.55961600 | -0.03679900 | -0.18926000 |
| H       | -3.80159900 | -0.54924900 | 1.93386000 |
| H       | -3.06721600 | 1.14049300  | 2.33352700 |
| H       | -0.95451000 | 2.09098500  | -1.62968700 |

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S71
|    | C    | H    | O    |
|----|------|------|------|
|    | -3.58882100 | 6.04972500 | -1.12587200 |
|    | -4.45946000 | 4.97892300 | -1.30885900 |
|    | -6.48721200 | 4.37598500 | -1.72556800 |
|    | -7.32788600 | 6.70087700 | -1.94735800 |
|    | -5.78726200 | 8.86083910 | -1.68074700 |
|    | -2.53609700 | 5.86812300 | -0.93957500 |
|    | -4.08236600 | 3.96322110 | -1.24731700 |
|    | -3.13611300 | 8.94526800 | -1.02752800 |
|    | -3.15544900 | 9.68908100 | -1.93821200 |
|    | -2.29694900 | 8.47272500 | -0.10297500 |
|    | -4.19648900 | 10.02031600 | -2.84346100 |
|    | -2.04105800 | 7.16479000 | 1.52692600 |
|    | -0.18366000 | 6.33190700 | 0.39058700 |
|    | -1.83542400 | 6.20899500 | 3.45919700 |
|    | -3.03625900 | 5.75445200 | 2.80562600 |
|    | -3.92948200 | 6.90052700 | 2.61837900 |
|    | -3.26661500 | 8.06047000 | 3.12606600 |
|    | -1.96108400 | 7.64514700 | 3.62485200 |
|    | -0.68180800 | 5.36645000 | 3.89456400 |
|    | 0.25447800 | 5.92443200 | 3.84783700 |
|    | -0.83295600 | 5.03023200 | 4.92625200 |
|    | -3.35474600 | 4.34890400 | 2.42461800 |
|    | -2.44775900 | 3.77601600 | 2.22826300 |
|    | -3.98609400 | 4.31564900 | 1.55327900 |
|    | -3.89579900 | 3.86317500 | 3.24564800 |
|    | -5.30471800 | 6.83475300 | 2.04328000 |
|    | -5.73639600 | 6.08039400 | 1.25899000 |
|    | -5.60878100 | 7.79273300 | 1.61966700 |
|    | -6.01865700 | 6.57361200 | 2.83326200 |
|    | -3.79734500 | 9.45618700 | 3.14619400 |
|    | -4.24538700 | 9.67462800 | 4.12205500 |
|    | -4.56549200 | 9.60044900 | 2.38460900 |
|    | -3.00359100 | 10.18507000 | 2.90746500 |
|    | -0.94678300 | 8.53980500 | 4.24932500 |
|    | -1.00265900 | 9.55262400 | 3.84692200 |
|    | -0.06497800 | 8.16118400 | 4.09802300 |
|    | -1.13122900 | 8.59444800 | 5.29480000 |
|    | -0.57150200 | 4.48791000 | 3.25772900 |
|    | -2.24421230 | 10.83284900 | -1.50926100 |
|    | -2.52805100 | 11.22013400 | -0.52778400 |
|    | -1.20174100 | 10.50355400 | -1.45062300 |
|    | -2.30509600 | 11.64974000 | -2.23112100 |
|    | -2.88843600 | 9.31291700 | -2.93646400 |

**TS7-1**

| C    | -4.98052700 | 9.97375000 | 5.86924200 |
| C    | -3.85905000 | 9.81673800 | 5.05160300 |
| C    | -4.01448500 | 9.44895100 | 3.71916000 |
| C    | -5.29175000 | 9.24118300 | 3.17545400 |
| C    | -6.41021600 | 9.36926900 | 4.00962800 |
| C    | -6.25558100 | 9.75278300 | 5.34540000 |
| H    | -4.86147900 | 10.25002800 | 6.91066200 |
| H    | -2.86342100 | 9.97928600 | 5.46318000 |
| H    | -3.15661500 | 9.30879500 | 3.07031500 |
| H    | -7.40313800 | 9.19055200 | 3.62055400 |
| H    | -7.13025700 | 9.85666900 | 5.98058800 |
| C    | -5.40182000 | 8.85501500 | 1.73314400 |
| C    | -7.58360500 | 7.43081700 | 0.05722800 |
| C    | -6.58403600 | 9.10995800 | 1.06973700 |
| C    | -6.94530700 | 8.28012100 | -0.21784600 |
| H    | -7.43401400 | 9.45299700 | 1.59245700 |
| H    | -7.49093000 | 8.87065800 | -0.96171800 |
| H    | -6.05635600 | 7.87694000 | -0.70694500 |
| O    | -4.31980900 | 8.40244200 | 1.19975200 |
| O    | -4.11945000 | 8.77060100 | -0.44442800 |
| O    | -3.97640200 | 9.30384400 | -1.02233700 |
| O    | -3.04290300 | 9.53687900 | -1.10271100 |
| H    | -4.09516000 | 10.28223000 | -0.82345900 |
| O    | -5.53205200 | 11.05023600 | -0.45497100 |
| H    | -5.13100100 | 11.74957900 | 0.08012200 |
| H    | -6.05544700 | 10.32922200 | 0.29488800 |

**TS7-2**

Ir  -4.17214100 -0.46056300 0.53039700
Cl  -5.37004900 -0.80349000 2.55295100
C   -4.96228400 0.36049700 -1.32581500

S74
| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| H       | 0.33583375 | 2.81083209 | 0.82866269 |
| H       | -0.99733697 | 2.33134800 | 1.44445810 |
| Int0-actone |
| Ir      | -0.09243700 | 0.23460700 | 0.12428700 |
| Cl      | 0.43285600 | 2.02334400 | -1.43615900 |
| Cl      | -2.44094900 | -1.86594800 | 0.59397500 |
| C       | 1.67082200 | -1.03089900 | 0.32559300 |
| C       | 1.10526700 | -1.20704200 | -0.98560500 |
| C       | 0.50982400 | -1.86594800 | 0.59397500 |
| C       | 0.59397500 | -1.44901300 | 1.29899200 |
| C       | 1.67082200 | -1.03089900 | 0.32559300 |
| C       | 1.10526700 | -1.20704200 | 0.32559300 |
| C       | 0.86073500 | -1.41812400 | 2.77975800 |
| C       | 1.15942500 | -1.31597100 | -0.19451600 |
| C       | 1.08305400 | -0.54660300 | -3.02014600 |
| C       | 2.58342600 | -0.20426700 | -1.77352700 |
| C       | 2.21764500 | -1.87158900 | -2.67199600 |
| C       | 2.33134800 | -1.85777700 | 0.76923800 |
| H       | -0.09069000 | -1.50356500 | 3.30669200 |
| H       | 1.32735500 | -0.47752900 | 3.08175100 |
| H       | 1.50892300 | -0.00612100 | 1.29899200 |
| H       | 3.45479100 | 0.05855100 | -0.14184400 |
| H       | 3.17111000 | -0.00612100 | 1.29899200 |
| C       | 0.30864900 | -0.58037800 | 0.64934600 |
| H       | 1.79836200 | -1.79836200 | 2.25682700 |
| H       | 2.63697100 | -1.85777700 | 0.76923800 |
| C       | 0.04582100 | 2.83543100 | 2.07307900 |
| C       | 0.35510800 | 1.67053700 | 1.79520400 |
| C       | 0.58733500 | 3.42220300 | 3.34955300 |
| C       | 1.21227100 | 2.70971900 | 3.87792900 |
| C       | 3.05864900 | -0.58037800 | 0.64934600 |
| C       | 1.15942500 | -3.06127100 | -2.18234400 |
| C       | 1.88451600 | -3.46438700 | 0.92478800 |
| C       | 0.04582100 | 2.83543100 | 2.07307900 |
| O       | 0.35510800 | 1.67053700 | 1.79520400 |
| C       | 0.58733500 | 3.42220300 | 3.34955300 |
| H       | 1.21227100 | 2.70971900 | 3.87792900 |
| H       | 1.15942500 | -3.06127100 | -2.18234400 |
| H       | 1.88451600 | -3.46438700 | 0.92478800 |
| C       | 0.04582100 | 2.83543100 | 2.07307900 |
| O       | 0.35510800 | 1.67053700 | 1.79520400 |
| C       | 0.58733500 | 3.42220300 | 3.34955300 |
| H       | 1.21227100 | 2.70971900 | 3.87792900 |
| H       | 1.15942500 | -3.06127100 | -2.18234400 |
| H       | 1.88451600 | -3.46438700 | 0.92478800 |
| C       | 0.04582100 | 2.83543100 | 2.07307900 |
| O       | 0.35510800 | 1.67053700 | 1.79520400 |
| C       | 0.58733500 | 3.42220300 | 3.34955300 |
| H       | 1.21227100 | 2.70971900 | 3.87792900 |
| H       | 1.15942500 | -3.06127100 | -2.18234400 |
| H       | 1.88451600 | -3.46438700 | 0.92478800 |
| C       | 0.04582100 | 2.83543100 | 2.07307900 |
| O       | 0.35510800 | 1.67053700 | 1.79520400 |
| C       | 0.58733500 | 3.42220300 | 3.34955300 |
| H       | 1.21227100 | 2.70971900 | 3.87792900 |
| H       | 1.15942500 | -3.06127100 | -2.18234400 |
| H       | 1.88451600 | -3.46438700 | 0.92478800 |

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