Insights into Ruthenium(II/IV)-Catalyzed Distal C–H Oxygenation by Weak Coordination
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General Remarks

Catalytic reactions were performed under a N₂ atmosphere using pre-dried glassware and standard Schlenk techniques. 1,2-Dichloroethane (DCE) was dried over CaH₂. The starting materials were synthesized according to previously described methods.[1-3] All other chemicals were purchased from commercial sources and used without further purification. Yields refer to isolated compounds estimated to be >95% pure as determined by ¹H-NMR and GC. TLC was performed on Merck TLC Silica Gel 60 F₂₅₄ with detection under UV light at 254 nm. Chromatographic separations were carried out on Merck Geduran SI-60 (0.040–0.063 mm, 230–400 mesh ASTM). IR spectra were recorded on a Bruker FT-IR alpha-P device. EI-MS-spectra were recorded on Jeol AccuTOF at 70 eV; ESI-MS spectra were recorded on Bruker Daltonik microTOF and maXis. Melting points (M.p.) were measured on Stuart™ melting point apparatus SMP3, values are uncorrected. Nuclear magnetic resonance (NMR) spectroscopy was performed at 300, 400, 500 or 600 MHz (¹H-NMR), 75, 100 or 125 MHz (¹³C-NMR, APT) and 282, 376 or 470 MHz (¹⁹F-NMR) accordingly on Bruker Avance III HD 300, Avance III 300, Avance III 400, Avance III HD 500, Varian Unity-300, Inova 500 and Inova 600 instruments. Chemical shifts (δ) are provided in ppm and spectra refered to residual non-deuterated solvent signal. Analytical HPLC analysis was performed on Agilent 1260 Infinity equipped with Daicel CHIRALPAK IB (4.6 mm x 250 mm, 3.0 μm particle size, 1.0 mL/min flow rate, n-hexane/EtOAc 70/30). In situ IR measurements were performed with Mettler-Toledo ReactIR 15 equipped with a diamond ATR probe and an MCT detector. Spectra were acquired using Mettler-Toledo iC IR software version 7.0.297 in the range of 650–3500 cm⁻¹ with a 4.0 cm⁻¹ resolution. A Pearson’s Correction was used as baseline correction and the solvent peak at 710 cm⁻¹ was normalized to a peakheight of 1.0 a.u.
Table S1. Optimization of the Reaction Conditions\textsuperscript{[a]}

| Entry | [TM] | Oxidant | Solvent | T \([\text{°C}]\) | Yield(\%)\textsuperscript{[b]} |
|-------|------|---------|---------|----------------|-----------------|
| 1     | [RuCl\(_2\)(p-cymene)]\(_2\) | PhI(TFA)\(_2\) | 1,4-dioxane | 100 | NR |
| 2     | [RuCl\(_2\)(p-cymene)]\(_2\) | PhI(TFA)\(_2\) | PhMe | 100 | 15 |
| 3     | [RuCl\(_2\)(p-cymene)]\(_2\) | PhI(TFA)\(_2\) | DMF | 100 | NR |
| 4     | [RuCl\(_2\)(p-cymene)]\(_2\) | PhI(TFA)\(_2\) | \(m\)-xylene | 100 | 15 |
| 5     | [RuCl\(_2\)(p-cymene)]\(_2\) | PhI(TFA)\(_2\) | MeOH | 100 | NR |
| 6     | [RuCl\(_2\)(p-cymene)]\(_2\) | PhI(TFA)\(_2\) | DCE | 100 | 62 |
| 7     | – | PhI(TFA)\(_2\) | DCE | 100 | NR |
| 8     | Ni(cod)\(_2\) | PhI(TFA)\(_2\) | DCE | 100 | NR |
| 9     | [Cp*Co(CO)I\(_2\)] | PhI(TFA)\(_2\) | DCE | 100 | NR |
| 10    | Pd(OAc)\(_2\) | PhI(TFA)\(_2\) | DCE | 100 | 42 |
| 11    | [RhCp*Cl\(_2\)] | PhI(TFA)\(_2\) | DCE | 100 | NR |
| 12    | [Ru (p-cymene)(OAc)\(_2\)] | PhI(TFA)\(_2\) | DCE | 100 | 17 |
| 13    | [Ru (p-cymene)(MesCO\(_2\)] | PhI(TFA)\(_2\) | DCE | 100 | trace |
| 14    | RuCl\(_3\) | PhI(TFA)\(_2\) | DCE | 100 | NR |
| 15    | [RuCl\(_2\)(p-cymene)]\(_2\) | K\(_2\)S\(_2\)O\(_8\) | DCE | 100 | NR |
| 16    | [RuCl\(_2\)(p-cymene)]\(_2\) | (NH\(_4\))\(_2\)S\(_2\)O\(_4\) | DCE | 100 | NR |
| 17    | [RuCl\(_2\)(p-cymene)]\(_2\) | PhI(OAc)\(_2\) | DCE | 100 | 25 |
| 18    | [RuCl\(_2\)(p-cymene)]\(_2\) | PhI(TFA)\(_2\) | DCE | 100 | 51\textsuperscript{[c]} |
| 19    | [RuCl\(_2\)(p-cymene)]\(_2\) | PhI(TFA)\(_2\) | DCE | 100 | 58\textsuperscript{[d]} |
| 20    | [RuCl\(_2\)(p-cymene)]\(_2\) | PhI(TFA)\(_2\) | DCE | 110 | 54 |
| 21    | [RuCl\(_2\)(p-cymene)]\(_2\) | PhI(TFA)\(_2\) | DCE | 120 | 51 |
| 22    | [RuCl\(_2\)(p-cymene)]\(_2\) | PhI(TFA)\(_2\) | DCE | 80 | 47 |
| 23    | [RuCl\(_2\)(p-cymene)]\(_2\) | PhI(TFA)\(_2\) | DCE | RT | NR |
| 24    | [RuCl\(_2\)(p-cymene)]\(_2\) | PhI(TFA)\(_2\) | TFA/TFAA | 100 | NR |

\textsuperscript{[a]} Reaction conditions: \(1\text{a} (0.5 \text{ mmol}), \) oxidant (1.0 mmol), catalyst (5.0 mol %), solvent (2.0 mL), 16 h. \textsuperscript{[b]} Yields of isolated products. \textsuperscript{[c]} [RuCl\(_2\)(p-cymene)]\(_2\) (2.5 mol %). \textsuperscript{[d]} Catalyst (10.0 mol %).
General Procedures

General Procedure A: Ruthenium-Catalyzed C–H Oxygenation of Amides
In an oven dried 25 ml Schlenk-tube: aryl acetamide 1 (0.50 mmol, 1.0 equiv), [bis(trifluoroacetoxy)iodo]benzene (PhI(TFA)$_2$) (430 mg, 1.00 mmol, 2.0 equiv), [RuCl$_2$(p-cymene)]$_2$ (15.3 mg, 5.0 mol %) and DCE (2.0 mL) were placed under N$_2$. The reaction mixture was stirred at 100 ºC for 16 h. At ambient temperature, the reaction mixture was diluted with H$_2$O (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layer was dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The crude products were purified by column chromatography ($n$-hexane/EtOAc) on silica gel to afford the desired products 2.

General Procedure B: Ruthenium-Catalyzed C–H Oxygenation of Esters
In an oven dried 25ml Schlenk-tube: phenyl acetyl ester 3 (0.50 mmol, 1 equiv), PhI(TFA)$_2$ (430 mg, 1.00 mmol, 2 equiv), [RuCl$_2$(p-cymene)]$_2$ (15.3 mg, 5.0 mol %) and DCE (2.0 mL) were placed under N$_2$. The reaction mixture was stirred at 100 ºC for 16 h. At ambient temperature, the reaction mixture was diluted with H$_2$O (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layer was dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The crude products were purified by column chromatography ($n$-hexane/EtOAc) on silica gel to afford the desired products 4.
Characterization Data of Products 2 and 4

\[ \text{N-(tert-butyl)-2-(2-hydroxyphenyl)acetamide (2a):} \]

The general procedure A was followed using N-(tert-butyl)-2-phenylacetamide (1a) (95.5 mg, 0.50 mmol), Phl(TFA)\(_2\) (430 mg, 1.00 mmol) and [RuCl\(_2\)(p-cymene)]\(_2\) (15.3 mg, 5.0 mol \%) in DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 5/1) yielded 2a (64.2 mg, 62\%) as a white solid. **M.p.** = 125–126 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 10.19\) (brs, 1H), 7.21–7.15 (m, 1H), 7.01–6.96 (m, 2H), 6.84 (td, \(J = 7.4, 1.2\) Hz, 1H), 5.72 (brs, 1H), 3.48 (s, 2H), 1.35 (s, 9H). \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 173.2\) (C\(_\text{q}\)), 156.6 (C\(_\text{q}\)), 130.5 (CH), 129.2 (CH), 122.0 (C\(_\text{q}\)), 120.2 (CH), 118.2 (CH), 52.3 (C\(_\text{q}\)), 42.6 (CH\(_2\)), 28.7 (CH\(_3\)). IR (ATR): 2961, 1632, 1555, 1492, 1355, 1057, 942, 797 cm\(^{-1}\). MS (EI) \(m/z\) (relative intensity): 207 (40) [M]\(^+\), 134 (65), 108 (70). HR-MS (EI) \(m/z\) calcd for C\(_{12}\)H\(_{17}\)NO\(_2\) \([M]\)^+: 207.1259, found: 207.1261.

\[ \text{N-(n-butyl)-2-(2-hydroxyphenyl)acetamide (2b):} \]

The general procedure A was followed using N-(n-butyl)-2-phenylacetamide (1b) (95.5 mg, 0.50 mmol), Phl(TFA)\(_2\) (430 mg, 1.00 mmol) and [RuCl\(_2\)(p-cymene)]\(_2\) (15.3 mg, 5.0 mol \%) in DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 5/1) yielded 2b (73.5 mg, 71\%) as a white solid. **M.p.** = 130–131 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 9.95\) (brs, 1H), 7.17 (ddd, \(J = 8.1, 7.5, 1.5\) Hz, 1H), 7.01 (dd, \(J = 7.5, 1.5\) Hz, 1H), 6.96 (dd, \(J = 8.1, 1.2\) Hz, 1H), 6.82 (ddd, \(J = 8.1, 7.5, 1.2\) Hz, 1H), 6.24 (brs, 1H), 3.55 (s, 2H), 3.23 (td, \(J = 7.2, 6.0\) Hz, 2H), 1.53–1.43 (m, 2H), 1.37–1.25 (m, 2H), 0.89 (t, \(J = 7.3\) Hz, 3H). \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 173.5\) (C\(_\text{q}\)), 156.3 (C\(_\text{q}\)), 130.6 (CH), 129.2 (CH), 121.7 (C\(_\text{q}\)), 120.4 (CH), 118.0 (CH), 41.2 (CH\(_2\)), 39.9 (CH\(_2\)), 31.4 (CH\(_2\)), 20.1 (CH\(_2\)), 13.8 (CH\(_3\)). IR (ATR): 2914, 1630, 1542, 1488, 1299, 1057, 966 cm\(^{-1}\). MS (EI) \(m/z\) (relative intensity): 207 (70) [M]\(^+\), 134 (50), 108 (100). HR-MS (EI) \(m/z\) calcd for C\(_{12}\)H\(_{17}\)NO\(_2\) \([M]\)^+: 207.1259, found: 207.1258.
$N$-(adamantan-1-yl)-2-(2-hydroxyphenyl)acetamide (2c):

The general procedure A was followed using $N$-(adamantan-1-yl)-2-phenylacetamide (1c) (134.7 mg, 0.5 mmol), PhI(TFA)$_2$ (430 mg, 1.0 mmol) and [RuCl$_2$(p-cymene)]$_2$ (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 5/1) yielded 2c (71.3 mg, 50%) as a white solid. **M.p.** = 172–173 °C. **$^1$H NMR** (300 MHz, CDCl$_3$) $\delta$ = 10.23 (brs, 1H), 7.15 (ddd, $J$ = 7.2, 4.2, 1.2 Hz, 1H), 6.97 (dd, $J$ = 4.2, 1.2 Hz, 1H), 6.94 (dd, $J$ = 4.2, 1.2 Hz, 1H), 6.79 (ddd, $J$ = 7.2, 4.2, 1.2 Hz, 1H), 5.67 (brs, 1H), 3.48 (s, 2H), 2.06 (m, 3H), 1.98 (d, $J$ = 3.0 Hz, 6H), 1.66 (t, $J$ = 3.0 Hz, 6H). **$^{13}$C NMR** (75 MHz, CDCl$_3$) $\delta$ = 173:0 (C$_q$), 156.7 (C$_q$), 130.5 (CH), 129.1 (CH), 122.0 (C$_q$), 118.3 (CH), 53.0 (C$_q$), 42.8 (CH$_2$), 41.4 (CH), 36.3 (CH$_2$), 29.5 (CH$_2$). **IR (ATR)**: 2904, 1547, 1452, 1238, 747 cm$^{-1}$. **MS** (EI) m/z (relative intensity): 285 (25) [M]$^+$, 135 (100), 107 (20). **HR-MS** (EI) m/z calcld for C$_{18}$H$_{23}$NO$_2$ [M]$^+$: 285.1729, found: 285.1718.

$N$-(tert-butyl)-2-(2-hydroxyphenyl)propanamide (2d):

The general procedure A was followed using $N$-(tert-butyl)-2-phenylpropanamide (1d) (102.6 mg, 0.5 mmol), PhI(TFA)$_2$ (430 mg, 1.0 mmol) and [RuCl$_2$(p-cymene)]$_2$ (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 5/1) yielded 2d (58.6 mg, 53%) as a white solid. **M.p.** = 109–110 °C. **$^1$H NMR** (300 MHz, CDCl$_3$): $\delta$ = 10.47 (brs, 1H), 7.19–7.13 (m, 1H), 6.96–6.92 (m, 2H), 6.79 (td, $J$ = 7.4, 1.3 Hz, 1H), 5.69 (brs, 1H), 3.34 (q, $J$ = 7.2 Hz, 1H), 1.56 (d, $J$ = 7.2 Hz, 3H), 1.35 (s, 9H). **$^{13}$C NMR** (126 MHz, CDCl$_3$) $\delta$ = 176.5 (C$_q$), 156.7 (C$_q$), 129.1 (CH), 129.6 (C$_q$), 129.0 (CH), 126.0 (C$_q$), 119.8 (CH), 118.9 (CH), 52.3 (C$_q$), 49.2 (CH), 28.8 (CH$_3$), 17.6 (CH$_3$). **IR (ATR)**: 2904, 1547, 1452, 1238, 747 cm$^{-1}$. **MS** (EI) m/z (relative intensity): 221 (30) [M]$^+$, 121 (100), 57 (70). **HR-MS** (EI) m/z calcld for C$_{13}$H$_{19}$NO$_2$ [M]$^+$: 221.1416, found: 221.1416.
N-(tert-butyl)-2-(2-hydroxy-5-methylphenyl)acetamide (2e):

The general procedure A was followed using \( N \)-(tert-butyl)-2-(m-tolyl)propanamide (1e) (102.6 mg, 0.5 mmol), PhI(TFA)\(_2\) (430 mg, 1.0 mmol) and [RuCl\(_2\)(p-cymene)]\(_2\) (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 5/1) yielded 2e (55.3 mg, 50%) as a white solid. M.p. = 132–133 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 9.95 \) (brs, 1H), 6.97 (dd, \( J = 8.1, 1.6 \) Hz, 1H), 6.86 (d, \( J = 8.1 \) Hz, 1H), 6.78 (d, \( J = 1.6 \) Hz, 1H), 5.85 (brs, 1H), 3.44 (s, 2H), 2.24 (s, 3H), 1.35 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta = 173.2 \) (C\(_q\)), 154.2 (C\(_q\)), 131.1 (CH), 129.6 (CH), 129.3 (C\(_q\)), 121.7 (C\(_q\)), 118.0 (CH), 52.3(C\(_q\)), 42.5 (CH\(_2\)), 28.7 (CH\(_3\)), 20.5 (CH\(_3\)). IR (ATR): 2968, 1640, 1555, 1215, 817 cm\(^{-1}\). MS (EI) \( m/z \) (relative intensity): 221 (45) [M]\(^+\), 148 (100), 91 (50). HR-MS (EI) \( m/z \) calcd for C\(_{13}\)H\(_9\)NO\(_2\)\(^+\) [M]\(^+\): 221.1416, found: 221.1421.

\[
\text{Ph} \quad \text{N} \quad \text{t-But} \quad \text{OH}
\]

N-(tert-Butyl)-2-(4-hydroxy-[1,1'-biphenyl]-3-yl)acetamide (2f):

The general procedure A was followed using 2-[[1,1'-biphenyl]-3-yl]-\( N \)-(tert-butyl) acetamide (1f) (133.5 mg, 0.5 mmol), PhI(TFA)\(_2\) (430 mg, 1.0 mmol) and [RuCl\(_2\)(p-cymene)]\(_2\) (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 5/1) yielded 2f (75 mg, 53%) as a white solid. M.p. = 145–146 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 10.42 \) (brs, 1H), 7.55 (d, \( J = 1.6 \) Hz, 1H), 7.51 (dd, \( J = 3.0, 1.6 \) Hz, 1H), 7.44–7.37 (m, 3H), 7.32–7.25 (m, 1H), 7.23 (d, \( J = 2.7 \) Hz, 1H), 7.05 (d, \( J = 8.4 \) Hz, 1H), 5.90 (brs, 1H), 3.56 (s, 2H), 1.36 (s, 9H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 173.0 \) (C\(_q\)), 156.2 (C\(_q\)), 140.8 (C\(_q\)), 133.2 (C\(_q\)), 129.2 (CH), 128.7 (CH), 127.7 (CH), 126.7 (CH), 126.6 (CH), 122.1 (C\(_q\)), 118.5 (CH), 52.2 (C\(_q\)), 42.7 (CH\(_2\)), 28.6 (CH\(_3\)). IR (ATR): 2942, 1643, 1556, 1483, 1357, 1054, 964, 826 cm\(^{-1}\). MS (EI) \( m/z \) (relative intensity): 283 (20) [M]\(^+\), 210 (100), 182 (70). HR-MS (EI) \( m/z \) calcd for C\(_{18}\)H\(_{21}\)NO\(_2\)\(^+\) [M]\(^+\): 283.1572, found: 283.1569.

\[
\text{F}_3\text{C} \quad \text{N} \quad \text{t-But} \quad \text{OH}
\]

N-(tert-butyl)-2-(2-hydroxy-5-(trifluoromethyl)phenyl)acetamide (2g):

The general procedure A was followed using 2-[[1,1'-biphenyl]-3-yl]-\( N \)-(tert-butyl) acetamide (1g) (129.6 mg, 0.5 mmol), PhI(TFA)\(_2\) (430 mg, 1.0 mmol) and [RuCl\(_2\)(p-cymene)]\(_2\) (15.3 mg, 5.0 mol %) in
DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 5/1) yielded 2g (84.0 mg, 61%) as a white solid. \textbf{M.p.} = 124–125 °C. \textbf{1H NMR} (400 MHz, CDCl$_3$) $\delta$ = 11.07 (brs, 1H), 7.41 (dd, $J$ = 8.4, 1.8 Hz, 1H), 7.24 (d, $J$ = 1.8 Hz, 1H), 7.01 (d, $J$ = 8.4 Hz, 1H), 5.99 (brs, 1H), 3.53 (s, 2H), 1.36 (s, 9H). \textbf{13C NMR} (101 MHz, CDCl$_3$) $\delta$ = 172.7 (C$_q$), 159.8 (C$_q$), 127.8 (q, $^3$J$_{C-F}$ = 3.7 Hz, CH), 126.5 (q, $^3$J$_{C-F}$ = 3.7 Hz, CH), 124.6 (d, $^1$J$_{C-H}$ = 271.1 Hz, C$_q$), 122.2 (d, $^2$J$_{C-F}$ = 32.6 Hz, C$_q$), 122.1 (C$_q$), 118.4 (CH), 52.7 (C$_q$), 42.4 (CH$_2$), 28.6 (CH$_3$). \textbf{19F NMR} (376 MHz, CDCl$_3$) $\delta$ = -115.8. \textbf{IR (ATR)}: 2974, 1609, 1557, 1329, 1115, 832 cm$^{-1}$. \textbf{MS (El) m/z (relative intensity)}: 275 (35) [M]$^+$, 102 (45), 57 (100). \textbf{HR-MS} (El) 	extit{m/z} calcd for C$_{13}$H$_{16}$F$_3$NO$_2^+$ [M]$^+$: 275.1133, found: 221.1138.

![2-(5-Bromo-2-hydroxyphenyl)-N-(tert-butyl)acetamide (2h)](image)

\textbf{2-(5-Bromo-2-hydroxyphenyl)-N-(tert-butyl)acetamide (2h):}

The general procedure A was followed using 2-(3-bromophenyl)-N-(tert-butyl) acetamide (1h) (135 mg, 0.5 mmol), PhI(TFA)$_2$ (430 mg, 1.0 mmol) and [RuCl$_2$($p$-cymene)]$_2$ (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 5/1) yielded 2h (108.7 mg, 76%) as a white solid. \textbf{M.p.} = 132–133 °C. \textbf{1H NMR} (300 MHz, CDCl$_3$): $\delta$ = 10.41 (brs, 1H), 7.27–7.23 (m, 1H), 7.09 (d, $J$ = 2.4 Hz, 1H), 6.84 (d, $J$ = 8.7 Hz, 1H), 5.75 (brs, 1H), 3.43 (s, 2H), 1.36 (s, 9H). \textbf{13C NMR} (125 MHz, CDCl$_3$): $\delta$ = 172.3 (C$_q$), 155.9 (C$_q$), 132.6 (CH), 131.7 (CH), 123.8 (C$_q$), 120.0 (CH), 111.5 (C$_q$), 52.5 (C$_q$), 42.2 (CH$_2$), 28.6 (CH$_3$). \textbf{IR (ATR)}: 2941, 1634, 1566, 1412, 1268, 1151, 817, 628 cm$^{-1}$. \textbf{MS (El) m/z (relative intensity)}: 287 (15) [M, $^{81}$Br]$^+$, 285 (15) [M, $^{79}$Br]$^+$, 211 (45), 186 (40). \textbf{HR-MS} (El) 	extit{m/z} calcd for C$_{12}$H$_{16}^{79}$BrNO$_2^+$ [M]$^+$: 285.0364, found: 285.0363.

![N-(tert-butyl)-2-(2-hydroxy-4-methylphenyl)acetamide (2i)](image)

\textbf{N-(tert-butyl)-2-(2-hydroxy-4-methylphenyl)acetamide (2i):}

The general procedure A was followed using \textit{N-(tert-butyl)-2-(p-tolyl)acetamide (1i)} (102.5 mg, 0.5 mmol), PhI(TFA)$_2$ (430 mg, 1.0 mmol) and [RuCl$_2$($p$-cymene)]$_2$ (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 5/1) yielded 2i (56.4 mg, 51%) as a white solid. \textbf{M.p.} = 118–119 °C. \textbf{1H NMR} (300 MHz, CDCl$_3$): $\delta$ = 10.04 (brs, 1H), 6.83 (d, $J$ = 7.6 Hz, 1H), 6.78 (d, $J$ = 0.8 Hz, 1H), 6.61 (ddd, $J$ = 7.6, 1.7, 0.8 Hz, 1H), 5.64 (brs, 1H), 3.41 (s, 2H), 2.26 (s, 3H), 1.30 (s, 9H).
1.33 (s, 9H). 13C NMR (125 MHz, CDCl3): δ = 173.0 (Cq), 156.0 (Cq), 138.8 (Cq), 129.8 (CH), 120.5 (CH), 118.5 (CH), 118.4 (Cq), 51.9 (Cq), 41.9 (CH2), 28.3 (CH3), 20.8 (CH3). IR (ATR): 1924, 1641, 1548, 1503, 1482, 1302, 1292, 1212, 937 cm⁻¹. MS (EI) m/z (relative intensity): 221 (25) [M]⁺, 148 (50), 120 (70). HR-MS (EI) m/z calcd for C13H10NO2⁺ [M]⁺: 221.1416, found: 221.1413.

N-(tert-Butyl)-2-(4-fluoro-2-hydroxyphenyl)acetamide (2j):

The general procedure A was followed using N-(tert-butyl)-2-(4-fluorophenyl) acetamide (1j) (104.5 mg, 0.5 mmol), PhI(TFA)2 (430 mg, 1.0 mmol) and [RuCl2(p-cymene)]2 (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 5/1) yielded 2j (70.9 mg, 63%) as a white solid. M.p. = 115–116 °C. 1H NMR (300 MHz, CDCl3): δ = 10.71 (brs, 1H), 6.93 (d, J = 8.3, 1H), 6.70 (dd, J = 8.3, 2.6 Hz, 1H), 6.53 (dd, J = 8.3, 2.6 Hz, 1H), 5.83 (brs, 1H), 3.46 (s, 2H), 1.38 (s, 9H). 13C NMR (75 MHz, CDCl3): δ = 172.9 (Cq), 164.8 (Cq), 158.0 (Cq), 130.8 (CH), 117.6 (Cq), 106.5 (CH), 105.4 (CH), 52.2 (Cq), 41.6 (CH2), 28.4 (CH3). 19F NMR (282 MHz, CDCl3) δ = -113.52 – -113.61 (m). IR (ATR): 1643, 1604, 1517, 1264, 906, 729, 650 cm⁻¹. MS (EI) m/z (relative intensity): 225 (30) [M]⁺, 152 (40), 126 (60). HR-MS (EI) m/z calcd for C12H16FNO2⁺ [M]⁺: 225.1165, found: 225.1161.

N-(tert-Butyl)-2-(2-hydroxy-4-nitrophenyl)acetamide (2k):

The general procedure A was followed using N-(tert-butyl)-2-(4-nitrophenyl) acetamide (1k) (117.6 mg, 0.50 mmol), PhI(TFA)2 (430 mg, 1.00 mmol) and [RuCl2(p-cymene)]2 (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 5/1) yielded 2k (81.9 mg, 65%) as a white solid. M.p. = 128–129 °C. 1H NMR (300 MHz, CDCl3): δ = 11.06 (brs, 1H), 7.81 (d, J = 2.4 Hz, 1H), 7.69 (dd, J = 8.4, 2.4 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 5.81 (brs, 1H), 3.60 (s, 2H), 1.39 (s, 9H). 13C NMR (75 MHz, CDCl3): δ = 172.0 (Cq), 157.8 (Cq), 148.8 (Cq), 130.9 (CH), 129.0 (Cq), 115.1 (CH), 113.8 (CH), 53.0 (Cq), 42.5 (CH2), 28.7 (CH3). IR (ATR): 2969, 1643, 1520, 1426, 1318, 899, 730 cm⁻¹.
MS (EI) m/z (relative intensity): 252 (20) [M]+, 179 (50), 153 (90). HR-MS (EI) m/z calcd for C_{12}H_{16}N_{2}O_{4} [M]+: 252.1110, found: 252.1109.

2-(2-Bromo-6-hydroxyphenyl)-n-butylacetamide (2l):

The general procedure A was followed using 2-(2-bromophenyl)-n-butylacetamide (1l) (134.5 mg, 0.5 mmol), PhI(TFA)_{2} (430 mg, 1.0 mmol) and [RuCl_{2}(p-cymene)]_{2} (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 5/1) yielded 2l (82.6 mg, 58%) as a white solid. M.p. = 133–134 °C. \(^{1}H\) NMR (300 MHz, CDCl\(_{3}\)): δ = 10.03 (brs, 1H), 7.13 (dd, J = 7.8, 1.4 Hz, 1H), 7.04 (dd, J = 8.0, 7.8 Hz, 1H), 6.96 (dd, J = 8.0, 1.4 Hz, 1H), 6.04 (brs, 1H), 3.82 (s, 2H), 3.29 (m, 2H), 1.59–1.47 (m, 2H), 1.42–1.30 (m, 2H), 0.93 (t, J = 9.1, 3H). \(^{13}C\) NMR (75 MHz, CDCl\(_{3}\)): δ = 172.5 (C\(_{q}\)), 157.3 (C\(_{q}\)), 129.6 (CH), 124.3 (CH), 124.2 (C\(_{q}\)), 122.1 (C\(_{q}\)), 117.7 (CH), 39.9 (CH\(_{2}\)), 39.7 (CH\(_{2}\)), 31.2 (CH\(_{2}\)), 19.9 (CH\(_{2}\)), 13.6 (CH\(_{2}\)). IR (ATR): 1643, 1538, 1484, 1361, 1063, 963, 866 cm\(^{-1}\). MS (EI) m/z (relative intensity): 285 (40) [M, \(^{79}\)Br]+, 206 (90), 186 (70). HR-MS (EI) m/z calcd for C_{12}H_{16}^{79}\text{Br}NO_{2} [M]+: 285.0364, found: 285.0360.

(R)-2-(2-hydroxyphenyl)-N-(1-phenylethyl)acetamide (2m):

The general procedure A was followed using (R)-2-phenyl-N-(1-phenylethyl) acetamide (1m) (119.5 mg, 0.50 mmol), PhI(TFA)\(_{2}\) (430 mg, 1.00 mmol) and [RuCl_{2}(p-cymene)]\(_{2}\) (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 5/1) yielded 2m (70.5 mg, 59%) as a white solid. M.p. = 140–141 °C. \(^{1}H\) NMR (400 MHz, CDCl\(_{3}\)): δ = 9.77 (brs, 1H), 7.31 (m, 2H), 7.28–7.24 (m, 3H), 7.20–7.11 (m, 1H), 6.96 (m, 2H), 6.83–6.77 (m, 1H), 6.15 (brs, 1H), 5.06 (m, 1H), 3.61–3.46 (m, 2H), 1.47 (d, J = 6.9 Hz, 3H). \(^{13}C\) NMR (100 MHz, CDCl\(_{3}\)): δ = 172.4 (C\(_{q}\)), 156.2 (C\(_{q}\)), 142.1 (C\(_{q}\)), 130.4 (CH), 129.1 (CH), 128.8 (CH), 127.7 (CH), 126.1 (CH), 121.4 (C\(_{q}\)), 120.2 (CH), 118.1 (CH), 49.5 (CH), 41.2 (CH\(_{2}\)), 21.4 (CH\(_{3}\)). IR (ATR): 1635, 1521, 1438, 1219, 1059, 734 cm\(^{-1}\). MS (EI) m/z (relative intensity): 255 (30) [M]+, 178 (45), 108 (70). HR-MS (EI) m/z calcd for C_{16}H_{17}NO_{2} [M]+:
255.1259, found: 255.1257. HPLC (n-hexane/EtOAc: 80/20, 1.0 mL/min): $t_r$ (major) = 14.4 min. $t_r$ (minor) = 16.4 min, 96.5% ee.
3-(2-(2-hydroxyphenyl)acetamido)propyl acetate (2n):

The general procedure A was followed using 3-(2-phenylacetamido)propyl acetate (1n) (117.5 mg, 0.5 mmol), PhI(TFA)$_2$ (430 mg, 1.0 mmol) and [RuCl$_2$($p$-cymene)]$_2$ (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 5/1) yielded 2n (80.3 mg, 64%) as a colorless oil. $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 9.67 (brs, 1H), 7.16 (td, $J$ = 8.0, 1.5 Hz, 1H), 7.02 (dd, $J$ = 7.5, 1.5 Hz, 1H), 6.94 (dd, $J$ = 8.0, 1.1 Hz, 1H), 6.82 (td, $J$ = 7.5, 1.1 Hz, 1H), 6.65 (brs, 1H), 4.09 (t, $J$ = 6.6 Hz, 2H), 3.56 (s, 2H), 3.30 (q, $J$ = 6.6 Hz, 2H), 2.03 (s, 3H), 1.81 (p, $J$ = 6.6 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 173.2 (C$_q$), 171.3 (C$_q$), 156.6 (C$_q$), 130.3 (CH), 128.8 (CH), 121.4 (C$_q$), 120.2 (CH), 117.3 (CH), 61.5 (CH$_2$), 40.4 (CH$_2$), 36.4 (CH$_2$), 28.1 (CH$_2$), 21.6 (CH$_3$). IR (ATR): 1637, 1541, 1366, 1236, 1041, 754 cm$^{-1}$. MS (EI) $m$/z (relative intensity): 251 (30) [M]$^+$, 191 (25), 134 (40). HR-MS (EI) $m$/z calcd for C$_{13}$H$_{17}$NO$_4$ $^+$ [M]$^+$: 251.1158, found: 251.1158.

2-(2-hydroxyphenyl)-1-morpholinoethanone (2o):

The general procedure A was followed using 1-morpholino-2-phenylethanone (1o) (102.6 mg, 0.50 mmol), PhI(TFA)$_2$ (430 mg, 1.00 mmol) and [RuCl$_2$($p$-cymene)]$_2$ (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 5/1) yielded 2o (66.4 mg, 60%) as a white solid. M.p. = 109–110 $^\circ$C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 9.52 (brs, 1H), 7.18 (dd, $J$ = 8.0, 1.2 Hz, 1H), 7.00 (dd, $J$ = 3.6, 1.2 Hz, 1H), 6.98 (dd, $J$ = 3.6, 1.2 Hz, 1H), 6.83 (td, $J$ = 7.5, 1.2 Hz, 1H), 3.74 (s, 2H), 3.69–3.66 (m, 8H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 173.2 (C$_q$), 171.3 (C$_q$), 156.9 (C$_q$), 130.1 (CH), 129.2 (CH), 120.6 (C$_q$), 120.3 (CH), 118.3 (CH), 66.7 (CH$_2$), 66.7 (CH$_2$), 47.4 (CH$_2$), 42.7 (CH$_2$), 36.5 (CH$_2$). IR (ATR): 2857, 1595, 1455, 1241, 756 cm$^{-1}$. MS (EI) $m$/z (relative intensity): 221 (90) [M]$^+$, 114 (60), 43 (100). HR-MS (EI) $m$/z calcd for C$_{12}$H$_{15}$NO$_3$ $^+$ [M]$^+$: 221.1052, found: 221.1048.

Methyl 2-(2-hydroxyphenyl)acetate (4a):
The general procedure B was followed using methyl 2-phenylacetate (3a) (75 mg, 0.5 mmol), PhI(TFA)$_2$ (430 mg, 1.0 mmol) and [RuCl$_2$(p-cymene)]$_2$ (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography ($n$-hexane/EtOAc: 20/1) yielded 4a (43.2 mg, 52%) as a colorless liquid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.30$ (brs, 1H), 7.21–7.15 (m, 1H), 7.10–7.06 (m, 1H), 6.93 (dd, $J = 8.1, 0.9$ Hz, 1H), 6.87 (td, $J = 7.4, 1.2$ Hz, 1H), 3.73 (s, 3H), 3.67 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 174.3 (C$_q$), 155.2 (C$_q$), 131.0 (CH), 129.3 (CH), 121.0 (CH), 120.5 (C$_q$), 117.7 (CH), 52.7 (CH$_3$), 37.7 (CH$_2$). IR (ATR): 2931, 1642, 1535, 1412, 1228, 1058, 914, 730 cm$^{-1}$. MS (EI) $m/z$ (relative intensity): 166 (20) [M$^+$], 134 (90), 106 (80). HR-MS (EI) $m/z$ calcd for C$_9$H$_{10}$O$_3^+$ [M$^+$]: 166.0630, found: 166.0627.

Ethyl 2-(2-hydroxyphenyl)acetate (4b):

The general procedure B was followed using ethyl 2-phenylacetate (3b) (82 mg, 0.5 mmol), PhI(TFA)$_2$ (430 mg, 1.0 mmol) and [RuCl$_2$(p-cymene)]$_2$ (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography ($n$-hexane/EtOAc: 20/1) yielded 4b (45.0 mg, 50%) as a colorless liquid. $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.63$ (brs, 1H), 7.26–7.19 (m, 1H), 7.12 (d, $J = 6.3$ Hz, 1H), 7.00–6.87 (m, 2H), 4.23 (q, $J = 7.2$ Hz, 2H), 3.70 (s, 2H), 1.32 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 174.1 (C$_q$), 155.3 (C$_q$), 131.0 (CH), 129.2 (CH), 120.9 (CH), 120.6 (C$_q$), 117.8 (CH), 62.0 (CH$_2$), 38.2 (CH$_2$), 14.0 (CH$_3$). IR (ATR): 1932, 1703, 1642, 1422, 1359, 1110, 964, 732 cm$^{-1}$. MS (EI) $m/z$ (relative intensity): 180 (20) [M$^+$], 134 (90), 106 (85). HR-MS (EI) $m/z$ calcd for C$_{10}$H$_{12}$O$_3^+$ [M$^+$]: 180.0786, found: 180.0789.

Methyl 2-(4-fluoro-2-hydroxyphenyl)acetate (4c):

The general procedure B was followed using methyl 2-(4-fluorophenyl)acetate (3c) (84 mg, 0.50 mmol), PhI(TFA)$_2$ (430 mg, 1.00 mmol) and [RuCl$_2$(p-cymene)]$_2$ (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography ($n$-hexane/EtOAc: 20/1) yielded 4c (46.0 mg, 50%) as a colorless liquid. $^1$H NMR (500 MHz, CDCl$_3$) $\delta = 7.81$ (brs, 1H), 7.02 (dd, $J = 8.5, 6.5$ Hz, 1H), 6.68 (dd, $J = 8.5, 2.5$ Hz, 1H), 6.59 (dd, $J = 8.5, 2.5$ Hz, 1H), 3.76 (s, 3H), 3.64 (s, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta =$
174.6 (Cq), 163.18 (d, J_C-F = 245.6 Hz, Cq), 156.57 (d, J_C-F = 11.9 Hz, Cq), 131.62 (d, J_C-F = 10.0 Hz, CH), 116.25 (d, J_C-F = 3.2 Hz, Cq), 107.67 (d, J_C-F = 21.6 Hz, CH), 105.40 (d, J_C-F = 24.1 Hz, CH), 52.92 (CH3), 37.31 (CH2).

$^1H$ NMR (471 MHz, CDCl3) δ = -112.86 – -112.92 (m). IR (ATR): 2926, 1733, 1442, 1201, 818 cm$^{-1}$. MS (EI) m/z (relative intensity): 184 (30) [M]$^+$, 154 (100), 110 (20). HR-MS (EI) m/z calcd for C9H9FO3$^+$ [M]$^+$: 184.0536, found: 184.0541.

Methyl 2-(2-hydroxy-3-methoxyphenyl)acetate (4d):

The general procedure B was followed using methyl 2-(3-methoxyphenyl)acetate (3d) (90.1 mg, 0.50 mmol), PhI(TFA)$_2$ (430 mg, 1.00 mmol) and [RuCl$_2$(p-cymene)]$_2$ (15.3 mg, 5.0 mol %) in DCE (2.0 mL). Purification by column chromatography (n-hexane/EtOAc: 10/1) yielded 4d (53.0 mg, 54%) as a white solid. M.p. = 73–74 ºC. $^1H$ NMR (300 MHz, CDCl3) δ = 6.89 (brs, 1H), 6.86 (d, J = 8.7 Hz, 1H), 6.74 (dd, J = 8.7, 3.0 Hz, 1H), 6.67 (d, J = 3.0 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.65 (s, 2H). $^{13}$C NMR (75 MHz, CDCl3) δ = 174.1 (Cq), 153.8 (Cq), 149.0 (Cq), 121.7 (Cq), 118.5 (CH), 116.5 (CH), 114.2 (CH), 55.9 (CH3), 52.8 (CH3), 37.8 (CH2). IR (ATR): 3419, 2958, 1715, 1508, 1179, 612 cm$^{-1}$. MS (EI) m/z (relative intensity): 196 (30) [M]$^+$, 164 (50), 136 (100). HR-MS (EI) m/z calcd for C$_{10}$H$_{12}$O$_4^+$ [M]$^+$: 196.0736, found: 196.0735.
Mechanistic Studies

H/D-Exchange Experiment

\[
\text{[RuCl}_2(p\text{-cymene})_2 (15.3 \text{ mg, 5.0 mol %}), N-(\text{tert-butyl})-2-(4\text{-nitrophenyl})\text{acetamide 1k (118 mg, 0.5 mmol), PhI(TFA)}_2 (430 \text{ mg, 1.0 mmol) and solvent (DCE/CD}_3\text{OD = 10/1, 2.0 mL) were placed into a 25 mL Schlenk tube equipped with a septum under N}_2. \text{ The tube was then placed into an oil bath and the reaction mixture was stirred at 100 °C for 16 h. At ambient temperature, the reaction mixture was quenched with H}_2\text{O (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layer was concentrated under reduced pressure. The crude products were purified by column chromatography (n-hexane/EtOAc) on silica gel to afford the [D]n-1k (27.3 mg, 23%), [D]n-2k (68.4 mg, 54%). According to the }^1\text{H NMR, no H/D-Exchange showed.}}
\]

Competition Experiment

Intermolecular competition experiment between amides 1e and 1g

\[
\text{[RuCl}_2(p\text{-cymene})_2 (7.7 \text{ mg, 0.0125 mmol), N-(\text{tert-butyl})-2-(m-tolyl)}\text{acetamide 1e (41.0 mg, 0.25 mmol), N-(\text{tert-butyl})-2-(3-(trifluoromethyl)}\text{phenyl)acetamide 1g (64.0 mg, 0.25 mmol), PhI(TFA)}_2 (220 \text{ mg, 0.5 mmol) and DCE (2.0 mL) were placed into a 25 mL Schlenk tube equipped with a septum under}}
\]
N₂. The tube was then placed into an oil bath and the reaction mixture was stirred at 100 °C for 2.5 h. At ambient temperature, the reaction mixture was diluted with NaHCO₃ (15 mL), stirred for 10 min and extracted with EtOAc (3 x 15 mL). The combined organic layer was concentrated under reduced pressure. CH₂Br₂ (0.5 mmol) was added as internal standard, the conversion of 2e and 2g was determined based on crude ¹H-NMR analysis.

Kinetic Isotope Effect (KIE) Measurement

Five independent reactions with 1a or five independent reactions with deuterated substrate [D]₅-1a under the standard conditions were performed. The reactions were quenched at 15 min, 30 min, 45 min, 60 min, 75 min respectively with aqueous NaHCO₃. Then the mixture was extracted with EtOAc (15 ml) three times. The combined organic phase was dried and concentrated under vacuum. The conversions of the reactions at different time were determined by NMR by using CH₂Br₂ as the internal standard.

| t   | 15  | 30  | 45  | 60  | 75  |
|-----|-----|-----|-----|-----|-----|
| 2a/ % | 8   | 14  | 23  | 31  | 42  |
| [D]₅-2a/ % | 3   | 7   | 10  | 14  | 19  |
Figure S1. Linear function fit for the reaction rates of 1a and [D]$_5$–1a.

Detection of $p$-cymene

[RuCl$_2$(p-cymene)$_2$] (15.3 mg, 5.0 mol %, 0.025 mmol), arylacetamide 1a (118 mg, 0.50 mmol), PhI(TFA)$_2$ (430 mg, 1.00 mmol), n-dodecane (0.05 mmol) and DCE (4.0 mL) was placed into a 25 mL Schlenk tube under N$_2$. The tube was then placed into an oil bath and the reaction mixture was stirred at 100 ºC. During the course of the reaction aliquots (0.10 mL) were removed via a syringe after 15 min, 30 min, 45 min, 60 min, 75 min, 95 min, 120 min and 180 min, diluted with EtOAc, filtered through a short plug of silica gel and analyzed by gas chromatography.

| $t$ / (min) | 15 | 30 | 45 | 60 | 75 | 95 | 120 | 180 |
|-------------|----|----|----|----|----|----|-----|-----|
| 2a (conversion relative to 1a %) | 7.8 | 16.3 | 33.9 | 44.1 | 50.4 | 58.6 | 62.1 | 64.2 |
| 5 (conversion relative to catalyst %) | 2.0 | 6.2 | 9.4 | 11.2 | 13.5 | 16.1 | 19.0 | 19.4 |
Figure S2. Detection of free p-cymene.

Computational Data

All calculations were carried out by using Density Functional Theory with the Gaussian 16, Revision A.03 package.\textsuperscript{[4]} Geometry optimizations of all stationary points were carried out at the B3LYP\textsuperscript{[5]} level of theory including D3(BJ)\textsuperscript{[6]} dispersion corrections. Ruthenium and iodine were described with a def2-SVP\textsuperscript{[7]} basis set in combination with Stuttgart-Dresden effective core potentials.\textsuperscript{[8]} For all other atoms, a 6-31G* basis set was used.\textsuperscript{[9]} All stationary points were fully characterized by analytical frequency calculations as either a minimum or a transition state (only one imaginary frequency) at the same level of theory.

Single point calculations were performed at the PBE0\textsuperscript{[10]} level of theory including D3(BJ) dispersion corrections with a def2-TZVP\textsuperscript{[7]} basis set in combination with Stuttgart-Dresden effective core potentials\textsuperscript{[8]} for ruthenium and iodine, and a 6-311++G** basis set for all other atoms.\textsuperscript{[11]} Solvent effects were taken into consideration in the single point calculations through the use of SMD\textsuperscript{[12]} model with a dielectric constant of $\varepsilon = 10.125$, which corresponds to 1,2-dichloroethane (DCE).

Unless otherwise stated, all reported energies are Gibbs free energies in kcal mol$^{-1}$, which were calculated by adding the gas-phase thermal and non-thermal corrections at 298.15 K to the single-point energies.

The 3D structures of optimized geometries were constructed with the CYLview software.\textsuperscript{[13]}
Alternative pathway

Figure S3. Computed relative Gibbs free energy in kcal mol\(^{-1}\) of an alternative pathway for the ruthenium-catalyzed C–H oxygenation reaction of 1a at the PBE0-D3(BJ)/6-311++G**,def2-TZVP (Ru,I)+SMD(DCE)//B3LYP-D3(BJ)/6-31G*,def2-SVP(Ru,I) level of theory.

Figure S4. Geometries of all transition states in Figure 2 at the B3LYP-D3(BJ)/6-31G*,def2-SVP(Ru) level of theory. Non-relevant hydrogen atoms were omitted for clarity.
Table S6. Calculated electronic energies at the PBE0-D3(BJ)/6-311++G**,def2-TZVP(Ru)+SMD(DCE) level of theory and total Gibbs free energies with dispersion corrections for all reported structures (in Hartree).

| Structure          | Electronic Energy | Total Gibbs Free Energy |
|--------------------|------------------|-------------------------|
| Phi(TFA)₂          | -1294.42434      | -1294.33377             |
| CF₃COOH            | -526.45079       | -526.44316              |
| Phi                | -242.77286       | -242.71413              |
| im1                | -1606.87906      | -1606.42616             |
| TS1                | -1606.86602      | -1606.41348             |
| im2                | -1606.87563      | -1606.42275             |
| TS2                | -1606.84721      | -1606.39813             |
| im3                | -1606.86056      | -1606.40735             |
| im4                | -2374.82512      | -2374.28638             |
| TS3                | -2374.81777      | -2374.27634             |
| im5                | -2374.83374      | -2374.29407             |
| TS4                | -2374.82979      | -2374.28652             |
| im6                | -2374.83386      | -2374.29099             |
| im7                | -2132.06563      | -2131.60367             |
| TS5                | -2132.04018      | -2131.57795             |
| im8                | -2132.10162      | -2131.63886             |
| im1a               | -1535.86763      | -1535.65424             |
| im2a               | -2132.89197      | -2132.41971             |
| TS1a               | -2132.86642      | -2132.39921             |
| im3a               | -1606.41920      | -1605.97839             |
| TS(1a-1a’)         | -1891.43260      | -1891.08660             |
| 1a                 | -597.01060       | -596.78195              |
| 1a’                | -1891.44774      | -1891.10397             |
| CF₃COO⁻            | -525.99564       | -526.00157              |
Cartesian coordinates of the optimized structures

**PhI(TFA)$_2$**

Lowest frequency = 14.43 cm$^{-1}$

Charge = 0, Multiplicity = 1

26

\[
\begin{array}{ccc}
C & -0.003766 & -0.170001 & 0.036654 \\
C & -0.003474 & 0.012597 & 1.418545 \\
C & 1.165482 & 0.135966 & 2.166756 \\
C & 2.383731 & 0.082236 & 1.487120 \\
C & 2.413825 & -0.099677 & 0.103521 \\
C & 1.225845 & -0.226846 & -0.619434 \\
I & -1.869516 & 0.071163 & 2.415760 \\
o & -1.762710 & -2.102624 & 2.075991 \\
C & -2.849844 & -2.646856 & 2.553529 \\
O & -3.762106 & -2.056705 & 3.105715 \\
O & -1.737189 & 2.251898 & 2.452089 \\
C & -0.908160 & 2.755839 & 3.337217 \\
o & -0.176480 & 2.160214 & 4.100518 \\
C & -2.871619 & -4.178358 & 2.337989 \\
C & -0.948023 & 4.304126 & 3.295334 \\
H & 1.128174 & 0.297953 & 3.236331 \\
H & 3.308602 & 0.181219 & 2.046737 \\
H & 3.367010 & -0.141809 & -0.414633 \\
H & 1.251036 & -0.368220 & -1.695426 \\
H & -0.930869 & -0.271345 & -0.515819 \\
F & -1.808239 & -4.747727 & 2.930903 \\
F & -2.823238 & -4.458980 & 1.023050 \\
F & -3.983263 & -4.712980 & 2.847855 \\
F & -2.194931 & 4.749970 & 3.524318 \\
F & -0.556936 & 4.741773 & 2.084475 \\
F & -0.133440 & 4.823653 & 4.217841 \\
\end{array}
\]

**CF$_3$COOH**

Lowest frequency = 26.48 cm$^{-1}$

Charge = 0, Multiplicity = 1

8

\[
\begin{array}{ccc}
C & -2.330828 & -0.014984 & 0.070693 \\
\end{array}
\]

S-22
O  -1.164296  -0.117500   0.344366
O  -2.977098   1.122173  -0.223841
H  -2.321862   1.844561  -0.173252
C  -3.308756  -1.205974   0.010241
F  -2.671025  -2.339645   0.301843
F  -4.308628  -1.029783   0.890528
F  -3.838869  -1.308460  -1.220287

**PhI**

Lowest frequency = 154.06 cm⁻¹

Charge = 0, Multiplicity = 1

12

I   0.194429  -0.782598  -0.269249
C  -0.324201   1.284520  -0.175842
C   0.173945   2.067997   0.865078
C  -0.170049   3.420080   0.919276
C  -0.999924   3.977891  -0.054103
C  -1.489622   3.179777  -1.088770
C  -1.154767   1.826037  -1.156873
H   0.818833   1.635307   1.621804
H   0.214984   4.035063   1.727674
H  -1.263917   5.030133  -0.006547
H  -2.136105   3.606924  -1.850063
H  -1.535674   1.206535  -1.961152

**im1**

Lowest frequency = 15.66 cm⁻¹

Charge = 1, Multiplicity = 1

63

Ru   0.434760  -1.033139  -0.530901
C   2.528291  -0.503811  -0.191662
C   2.193167  -0.108747  -1.528235
C   1.615949  -1.081392  -2.375771
C   1.378252  -2.415302  -1.910854
C   1.717435  -2.816271  -0.595930
C   2.292417  -1.819945   0.259462
O  -1.623283  -1.511726  -1.081600
C  -1.880406  -1.691429   0.137477
S -2.400000
O -0.936053 -1.709179 0.986713
C -3.324979 -1.730867 0.648254
C 0.942330 1.179277 2.384600
C 1.667750 2.279285 1.909464
C 1.619058 0.158547 3.059148
C 3.048336 2.353283 2.096471
H 1.151294 3.084045 1.391401
C 3.000021 0.233829 3.257023
C 3.718929 1.328537 2.771362
H 3.598763 3.212740 1.725708
H 3.512673 -0.558335 3.794888
H 4.791779 1.388773 2.925876
C -0.558923 1.109524 2.201487
H -0.920647 0.102253 2.424770
H -1.058937 1.792686 2.898612
C -0.983373 1.428849 0.782079
O -0.487350 0.843376 -0.222635
C -2.532924 2.843885 -0.647415
H 1.252666 -0.800365 -3.356003
H 2.452950 -2.047805 1.307319
H 0.832593 -3.102821 -2.548776
H 2.880031 0.239739 0.511446
C 2.371252 1.343693 -1.921748
H 1.965133 1.934050 -1.090729
C 1.397817 -4.189608 -0.077160
H 1.060549 -0.694250 3.435510
F -3.493684 -2.710917 1.538279
F -4.195486 -1.871792 -0.347967
F -3.561923 -0.545317 1.265461
C 1.627650 1.732989 -3.201891
H 0.564021 1.479915 -3.147515
H 1.708080 2.812178 -3.361227
H 2.057399 1.242197 -4.082628
C 3.877574 1.652351 -2.031253
H 4.342641 1.057254 -2.824827
H 4.023954 2.709914 -2.271373
H 4.402959 1.442686 -1.093802
H 1.062697 -4.146807 0.962800
H 0.616266 -4.666383 -0.674206
H 2.292288 -4.822429 -0.120374
C -1.464136 3.496482 -1.534925
H -1.000503 4.347147 -1.023936
H -0.687008 2.778069 -1.799978
H -1.925557 3.862685 -2.457221

S-24
|   |       |       |       |
|---|-------|-------|-------|
| C | -3.583950 | 3.879788 | -0.229023 |
| H | -3.124847 | 4.723119 | 0.300488  |
| H | -4.083833 | 4.276536 | -1.116298 |
| H | -4.349650 | 3.430515 | 0.413666  |
| C | -3.209047 | 1.660252 | -1.354192 |
| H | -2.482147 | 0.914040 | -1.677513 |
| H | -3.932374 | 1.177006 | -0.691175 |
| H | -3.744107 | 2.026784 | -2.235566 |
| N | -1.897184 | 2.381297 | 0.623954  |
| H | -2.225886 | 2.827190 | 1.470608  |

**im2**

Lowest frequency = 16.38 cm\(^{-1}\)

Charge = 1, Multiplicity = 1

63

|   |       |       |       |
|---|-------|-------|-------|
| Ru | 0.731213 | -0.591625 | -0.308280 |
| C | 0.809694 | -1.078973 | -2.396556 |
| C | 1.231992 | -2.262150 | -1.703316 |
| C | 2.265706 | -2.119373 | -0.752092 |
| C | 2.890315 | -0.851984 | -0.532571 |
| C | 2.548310 | 0.305812  | -1.272474 |
| C | 1.465787 | 0.167162  | -2.190259 |
| H | 3.608928 | -0.759980 | 0.272687  |
| H | -0.062753 | 1.123003  | -3.039657 |
| C | -2.094816 | -1.267735 | 0.621464  |
| O | -2.191395 | -0.478652 | 1.552638  |
| O | -1.051999 | -1.597068 | -0.066030 |
| C | -3.344085 | -2.016543 | 0.096786  |
| C | 2.312089 | 1.167795  | 2.464183  |
| C | 3.374176 | 0.311213  | 2.738355  |
| C | 3.173955 | -1.076913 | 2.799515  |
| C | 1.905817 | -1.596223 | 2.572478  |
| C | 0.820254 | -0.737727 | 2.301395  |
| C | 1.015151 | 0.661804  | 2.267671  |
| H | 2.473384 | 2.241991  | 2.451464  |
| H | 4.360930 | 0.723513  | 2.927828  |
| H | 4.002021 | -1.735623 | 3.042402  |
| H | 1.726865 | -2.664890 | 2.642336  |
| C | -0.165014 | 1.604141  | 2.216321  |
| H | 0.156844 | 2.605280  | 2.525675  |
| H | -0.925834 | 1.270399 | 2.928459  |

S-25
|   | X       | Y       | Z       |
|---|---------|---------|---------|
| H | -0.191907 | -1.122994 | 2.308405 |
| F | -4.429595 | -1.721320 | 0.813908 |
| F | -3.572841 | -1.657012 | -1.187192 |
| F | -3.149111 | -3.347138 | 0.124822 |
| C | -0.846823 | 1.737100 | 0.863453 |
| O | -0.432763 | 1.142826 | -0.170509 |
| N | -1.864519 | 2.584004 | 0.796741 |
| H | -2.145262 | 3.015047 | 1.668838 |
| C | -2.744737 | 2.858354 | -0.381606 |
| C | -3.407301 | 1.557370 | -0.854875 |
| H | -3.941835 | 1.069870 | -0.035365 |
| H | -2.671663 | 0.858575 | -1.255523 |
| H | -4.125328 | 1.786714 | -1.648360 |
| C | -1.910993 | 3.501714 | -1.498903 |
| H | -1.434318 | 4.423290 | -1.148874 |
| H | -2.562020 | 3.752288 | -2.342130 |
| H | -1.136651 | 2.817429 | -1.852689 |
| C | -3.808549 | 3.841842 | 0.121802 |
| H | -4.485222 | 4.103767 | -0.695515 |
| H | -3.352739 | 4.768616 | 0.489566 |
| H | -4.409788 | 3.397676 | 0.923488 |
| C | 3.280276 | 1.610664 | -1.039758 |
| H | 3.654628 | 1.576308 | -0.009503 |
| C | 4.493214 | 1.675323 | -1.988572 |
| H | 4.168287 | 1.692543 | -3.035168 |
| H | 5.071099 | 2.585568 | -1.799864 |
| H | 5.156923 | 0.815021 | -1.853443 |
| C | 2.394178 | 2.853617 | -1.182827 |
| H | 2.961498 | 3.744062 | -0.895702 |
| H | 2.067252 | 3.003140 | -2.218043 |
| H | 1.504056 | 2.788007 | -0.551932 |
| C | 0.471008 | -3.543923 | -1.866061 |
| H | 0.886676 | -4.334631 | -1.237415 |
| H | -0.576680 | -3.392528 | -1.586650 |
| H | 0.507959 | -3.871842 | -2.910585 |
| H | 1.054025 | 1.049429 | -2.666363 |
| H | 2.534464 | -2.961415 | -0.125201 |

**im3**

Lowest frequency = 18.36 cm⁻¹

Charge = 1, Multiplicity = 1
| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| Ru      | 1.024412 | -0.518008 | -0.298158 |
| C       | 1.991378  | -0.926015  | -2.373385  |
| C       | 2.169985  | -2.015965  | -1.445738  |
| C       | 2.809591  | -1.761280  | -0.208972  |
| C       | 3.143001  | -0.424024  | 0.163409   |
| C       | 2.858070  | 0.662277   | -0.702911  |
| C       | 2.323961  | 0.375307   | -2.011154  |
| H       | 3.558390  | -0.228089  | 1.146032   |
| H       | 1.496169  | -1.115624  | -3.319943  |
| C       | -1.940679 | -1.462023  | -0.378868  |
| O       | -2.218235 | -1.208529  | 0.868462   |
| O       | -0.832409 | -1.476493  | -0.910433  |
| C       | -3.174915 | -1.801696  | -1.237362  |
| C       | -0.047655 | -0.132002  | 3.922938   |
| C       | -0.068536 | -1.445913  | 4.389090   |
| C       | 0.211833  | -2.489273  | 3.507970   |
| C       | 0.519148  | -2.209562  | 2.173710   |
| C       | 0.563397  | -0.890504  | 1.677439   |
| C       | 0.264566  | 0.151920   | 2.587589   |
| H       | -0.271171 | 0.684279   | 4.605603   |
| H       | -0.311329 | -1.650760  | 5.426837   |
| H       | 0.187309  | -3.518875  | 3.852676   |
| H       | 0.713956  | -3.038505  | 1.497650   |
| C       | 0.285981  | 1.599385   | 2.128877   |
| H       | 1.307952  | 1.895440   | 1.858261   |
| H       | -0.041340 | 2.264532   | 2.932785   |
| H       | -1.362717 | -1.080281  | 1.366037   |
| F       | -3.253931 | -3.131493  | -1.373771  |
| F       | -4.295567 | -1.346746  | -0.674079  |
| F       | -3.033111 | -1.244086  | -2.445264  |
| C       | -0.558931 | 1.787790   | 0.891187   |
| O       | -0.342988 | 1.096017   | -0.141517  |
| N       | -1.534152 | 2.691494   | 0.917596   |
| H       | -1.636593 | 3.217425   | 1.775520   |
| C       | -2.469740 | 3.055418   | -0.191109  |
| C       | -3.228730 | 1.812730   | -0.679550  |
| H       | -3.676811 | 1.268560   | 0.156858   |
| H       | -2.570657 | 1.142267   | -1.234018  |
| H       | -4.032875 | 2.124864   | -1.352808  |
| C       | -1.673128 | 3.697675   | -1.336044  |
| H       | -1.134846 | 4.585408   | -0.988139  |
| H       | -2.357884 | 4.003879   | -2.133006  |
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | -0.954775 | 2.989622 | -1.756373 |
| C    | -3.450145  | 4.066490  | 0.416635 |
| H    | -4.155136  | 4.403303  | -0.347490 |
| H    | -2.925111  | 4.950812  | 0.797219 |
| H    | -4.027556  | 3.617669  | 1.232836 |
| C    | 3.259125   | 2.068099  | -0.296698 |
| H    | 3.203339   | 2.110743  | 0.799169 |
| C    | 4.730699   | 2.293996  | -0.698776 |
| H    | 4.849131   | 2.231891  | -1.786511 |
| H    | 5.061253   | 3.287550  | -0.379589 |
| H    | 5.391096   | 1.549905  | -0.242334 |
| C    | 2.362014   | 3.171236  | -0.871496 |
| H    | 2.634461   | 4.135228  | -0.431050 |
| H    | 2.489595   | 3.268766  | -1.955267 |
| H    | 1.304240   | 2.984876  | -0.673462 |
| H    | 2.960134   | -2.570312 | 0.496382 |
| H    | 2.093268   | 1.192072  | -2.684404 |
| C    | 1.702918   | -3.397462 | -1.812852 |
| H    | 0.726358   | -3.362888 | -2.303510 |
| H    | 2.414152   | -3.860548 | -2.507443 |
| H    | 1.626221   | -4.037960 | -0.930368 |

**im4**

Lowest frequency = 11.34 cm⁻¹

Charge = 1, Multiplicity = 1

81

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| Ru   | 1.376630  | -0.928995 | 0.886450 |
| C    | 2.681100  | -1.131785 | 2.741991 |
| C    | 1.641220  | -0.270881 | 3.091115 |
| C    | 0.277202  | -0.637771 | 2.824071 |
| C    | 0.003614  | -1.920801 | 2.289290 |
| C    | 1.071919  | -2.798705 | 1.940229 |
| C    | 2.420836  | -2.406597 | 2.122672 |
| C    | -0.892131 | 0.240181  | 3.230384 |
| C    | -1.299996 | -0.157948 | 4.664570 |
| C    | 3.553182  | -3.303812 | 1.709204 |
| C    | -0.640403 | 1.749228  | 3.142970 |
| H    | -1.026787 | -2.198896 | 2.096687 |
| H    | 0.858013  | -3.744955 | 1.456277 |
| H    | 3.708184  | -0.794912 | 2.835104 |
| H    | 1.873231  | 0.720221  | 3.457715 |

S-28
| Atom | x         | y         | z         |
|------|-----------|-----------|-----------|
| H    | 4.400969  | -2.721129 | 1.342406  |
| H    | 3.241625  | -3.993360 | 0.920402  |
| H    | 3.896223  | -3.895991 | 2.566462  |
| H    | -1.724825 | -0.020454 | 2.565430  |
| H    | -1.535477 | -1.224510 | 4.732281  |
| H    | -2.184097 | 0.407890  | 4.976135  |
| H    | -0.492655 | 0.059073  | 5.373136  |
| H    | 0.189299  | 2.063334  | 3.783993  |
| H    | -1.528504 | 2.289290  | 3.486054  |
| H    | 0.492655  | 0.059073  | 5.373136  |
| C    | 0.1384679 | 2.085371  | 0.264453  |
| O    | 2.386319  | 2.178315  | 0.936299  |
| O    | 0.656987  | 1.001668  | 0.095109  |
| C    | 0.843427  | 3.316067  | -0.495365 |
| C    | 0.479041  | -1.836964 | -3.329171 |
| C    | -0.571953 | -2.756905 | -3.281167 |
| C    | -1.053037 | -3.166061 | -2.038247 |
| C    | -0.472279 | -2.663584 | -0.873079 |
| C    | 0.582793  | -1.717545 | -0.881454 |
| C    | 1.032354  | -1.301032 | -2.159904 |
| H    | 0.842324  | -1.504272 | -4.295696 |
| H    | -1.006572 | -3.140890 | -4.198541 |
| H    | -1.882105 | -3.863290 | -1.970176 |
| H    | -0.880674 | -3.004509 | 0.071751  |
| C    | 2.049622  | -0.194715 | -2.354307 |
| H    | 2.394614  | -0.189132 | -3.392770 |
| H    | 1.570386  | 0.779061  | -2.191176 |
| F    | -0.164257 | 3.879421  | 0.199588  |
| F    | 0.350465  | 2.950265  | -1.710159 |
| F    | 1.793033  | 4.223431  | -0.690324 |
| C    | 3.239624  | -0.242985 | -1.427388 |
| O    | 3.135495  | -0.587184 | -0.224156 |
| N    | 4.412981  | 0.142376  | -1.932757 |
| H    | 4.421973  | 0.378870  | -2.915768 |
| C    | 5.699764  | 0.333018  | -1.200832 |
| C    | 5.503847  | 1.352780  | -0.069577 |
| H    | 5.141954  | 2.307428  | -0.464074 |
| H    | 4.782947  | 0.998171  | 0.668157  |
| H    | 6.462189  | 1.528732  | 0.429445  |
| C    | 6.690640  | 0.874526  | -2.239041 |
| H    | 7.664646  | 1.037816  | -1.770606 |
| H    | 6.830498  | 0.165862  | -3.063940 |
| H    | 6.351696  | 1.833502  | -2.648071 |
| C    | 6.188104  | -1.016882 | -0.658117 |

S-29
| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| H    | 6.306243   | -1.744121  | -1.467888  |
| H    | 7.157864   | -0.887470  | -0.167438  |
| H    | 5.481984   | -1.417298  | 0.071032   |
| I    | -1.559254  | 0.369147   | -0.628926  |
| C    | -2.670010  | 2.130234   | -0.278397  |
| C    | -2.758423  | 3.098716   | -1.282777  |
| C    | -3.331897  | 2.256572   | 0.947906   |
| C    | -3.528693  | 4.233826   | -1.038482  |
| H    | -2.232554  | 2.979364   | -2.222313  |
| C    | -4.102660  | 3.395843   | 1.168256   |
| H    | -3.261564  | 1.481964   | 1.702601   |
| C    | -4.195391  | 4.381251   | 0.180845   |
| H    | -3.610316  | 5.000641   | -1.802002  |
| H    | -4.630504  | 3.513494   | 2.109216   |
| H    | -4.793906  | 5.268453   | 0.361992   |
| O    | -3.309849  | -0.682888  | -1.181424  |
| C    | -3.775884  | -1.472768  | -0.220914  |
| O    | -3.382568  | -1.557088  | 0.919702   |
| C    | -4.920328  | -2.361940  | -0.776019  |
| F    | -5.525006  | -3.002231  | 0.221551   |
| F    | -4.392451  | -3.267711  | -1.620501  |
| F    | -5.817553  | -1.625580  | -1.438962  |

**im5**

Lowest frequency = 8.44 cm\(^{-1}\)

Charge = 1, Multiplicity = 1

81

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| Ru   | 1.073639   | -0.406463  | 0.987369   |
| C    | 2.531318   | 0.182520   | 2.719887   |
| C    | 1.664142   | 1.272596   | 2.682699   |
| C    | 0.252155   | 1.069728   | 2.692584   |
| C    | -0.228832  | -0.254271  | 2.896813   |
| C    | 0.663420   | -1.343710  | 3.030914   |
| C    | 2.053752   | -1.166140  | 2.872991   |
| C    | -0.711199  | 2.233446   | 2.706139   |
| C    | -0.869033  | 2.689671   | 4.174187   |
| C    | 3.002968   | -2.327162  | 2.939935   |
| C    | -0.311388  | 3.403337   | 1.802369   |
| H    | -1.298246  | -0.424702  | 2.965286   |
| H    | 0.277954   | -2.340928  | 3.194308   |
| H    | 3.593629   | 0.346695   | 2.573943   |
H    2.064767     2.263769     2.532972
H    3.823922    -2.195742     2.232261
H    2.491203    -3.263259     2.704400
H    3.429048    -2.407482     3.947084
H    -1.680091   1.854166     2.370085
H    -1.202686   1.872035     4.821740
H    -1.610641   3.492469     2.704400
H    0.077217    3.076256     4.569040
H    0.621353    3.874357     2.127331
H    -1.095286   4.164273     1.835626
H    -0.194645   3.090256     0.764984
C    1.821208    1.906784    -0.677614
O    2.501220    2.396297    -0.645831
C    1.865389    2.566285    -2.081665
C    0.820520    -3.822749    -1.757113
C    -0.005608   -4.748905    -1.122775
C    -0.572518   -4.418381     0.103215
C    -0.291282   -3.181600     0.692949
C    0.561715    -2.241926     0.080327
C    1.092069    -2.575824    -1.183537
H    1.243799   -4.058608    -2.730116
H    -0.214527   -5.705429    -1.590506
H    -1.237110   -5.111381     0.610255
H    -0.787180   -2.955824     1.629430
C    1.929624   -1.593674    -1.966727
H    2.290903   -2.046032    -2.894143
H    1.339705   -0.710732    -2.236524
F    1.150800    3.705656    -2.074736
F    1.359698    1.765759    -3.046467
F    3.129375    2.860923    -2.418820
C    3.084208   -1.107497    -1.132604
O    2.921269   -0.812346     0.089441
N    4.276375   -1.004099    -1.704680
H    4.324410   -1.295398    -2.672737
C    5.557744   -0.507623    -1.110920
C    5.375889    0.929843    -0.608405
H    5.025900    1.584641    -1.410324
H    4.654133    0.985702     0.207285
H    6.337635    1.309234    -0.249370
C    6.578974   -0.545633    -2.254978
H    7.549939   -0.197665    -1.893673
H    6.710891   -1.563869    -2.639671
H    6.274461    0.110109    -3.078578

S-31
im6

Lowest frequency = 14.30 cm⁻¹

Charge = 1, Multiplicity = 1

81
H  2.335079  -0.257081  3.056442
H  0.853322   1.690257  3.025750
H  2.728170  -2.647012  2.656574
H  1.447005  -3.668406  1.964899
H  1.514332  -3.387565  3.714019
H -2.494232   1.599793  1.415340
H -3.355279   0.809903  3.514114
H -3.436303   2.573796  3.480583
H -2.174340   1.781395  4.443836
H -0.598503   3.404946  3.053843
H -1.864720   3.898355  1.929764
H -0.409701   3.126719  1.306118
C  2.257741   1.869639  0.348591
O  2.638582   1.883670  1.502623
O  1.333204  -0.220707  3.514114
C  2.900515   2.841176  0.678674
C  0.754416  -3.237197  2.726969
C -0.332021  -4.101851  2.599730
C -1.225043  -3.926445 -1.547528
C -1.010687  -2.917425 -0.602996
C  0.103780  -2.073933  0.704204
C  0.967663  -2.204850 -1.806669
H  1.430053  -3.336740 -3.572342
H -0.493637  -4.882494 -3.335846
H -2.112119  -4.544091 -1.455320
H -1.764520  -2.783142  0.157881
C  2.083506  -1.216628  2.043094
H  2.652948  -1.475586  1.958956
H  1.683175  -0.204418  2.185498
F  2.270650   4.027774  0.516562
F  2.814294   2.365905 -1.938647
F  4.193456   3.029775  0.393302
C  2.969704  -1.178308 -0.829627
O  2.449939  -1.133452  0.329931
N  4.281646  -1.222868  0.998947
H  4.590364  -1.308993 -1.959459
C  5.371979  -1.256603  0.028730
C  5.228364  -0.076713  0.995709
H  5.215168   0.875434  0.459297
H  4.315186  -0.144535  1.586703
H  6.083396  -0.071208  1.678330
C  6.681179  -1.133088 -0.761312
H  7.529783  -1.174376 -0.073894
H  6.795528  -1.954957 -1.478378
S-33
im7

Lowest frequency = 16.39 cm⁻¹

Charge = 1, Multiplicity = 1
|     |     |     |     |
|-----|-----|-----|-----|
| H   | 3.410001 | 0.672001 | 1.219001 |
| H   | -0.910001 | -1.990001 | 2.400001 |
| H   | 1.530001 | 1.770001 | 3.490001 |
| H   | 1.040001 | 1.280001 | 3.500001 |
| H   | -0.530001 | 2.310001 | 1.560001 |
| H   | -1.010001 | -2.640001 | -2.620001 |
| F   | -2.550001 | -1.090001 | -2.520001 |
| C   | -2.170001 | -3.180001 | -2.160001 |
| C   | -0.530001 | 0.910001 | -0.905001 |
| F   | -2.910001 | -3.180001 | -2.110001 |
| C   | -2.050001 | 1.180001 | -0.450001 |
| O   | -0.650001 | 0.640001 | 0.620001 |
| N   | -3.330001 | 1.290001 | -0.730001 |
| H   | -3.550001 | 1.750001 | -1.610001 |
| C   | -4.510001 | 0.820001 | 0.061001 |
| C   | -4.400001 | -0.680001 | 0.331001 |
| H   | -4.310001 | -1.240001 | -0.603001 |
| H   | -3.530001 | -0.920001 | 0.949001 |
| H   | -5.290001 | -1.020001 | 0.854001 |
| C   | -5.740001 | 1.104001 | -0.812001 |
| H   | -6.650001 | 0.797001 | -0.285001 |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | -5.834943 | 2.173818 | -1.037836 |
| H    | -5.696490 | 0.544414 | -1.753230 |
| C    | -4.585668 | 1.629257 | 1.364370 |
| H    | -4.695712 | 2.698049 | 1.155227 |
| H    | -5.449391 | 1.305111 | 1.952932 |
| H    | -3.684468 | 1.485485 | 1.964469 |
| O    | 1.608391 | 0.090707 | -0.798487 |
| C    | 2.839892 | 0.507969 | -0.799367 |
| O    | 3.579534 | 0.776450 | 0.129127 |
| C    | 3.327408 | 0.604180 | -2.269206 |
| F    | 3.278888 | -0.611879 | -2.844888 |
| F    | 4.577166 | 1.059015 | -2.329650 |
| F    | 2.527859 | 1.435787 | -2.962766 |

**im8**

Lowest frequency = 18.17 cm$^{-1}$

Charge = 1, Multiplicity = 1

69

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| Ru   | 0.327222 | -0.048948 | 0.995303 |
| C    | -0.065332 | -1.115739 | 2.805411 |
| C    | 1.107837 | -1.673561 | 2.218094 |
| C    | 2.214565 | -0.859584 | 1.873475 |
| C    | 2.096223 | 0.540882 | 2.145770 |
| C    | 0.967708 | 1.101963 | 2.791959 |
| C    | -0.137095 | 0.276288 | 3.128054 |
| C    | 3.465459 | -1.421231 | 1.228667 |
| C    | 4.473746 | -1.767706 | 2.342940 |
| C    | -1.390319 | 0.860202 | 3.707631 |
| C    | 3.195991 | -2.628667 | 0.321784 |
| H    | 2.872932 | 1.204697 | 1.779871 |
| H    | 0.900684 | 2.175735 | 2.925512 |
| H    | -0.930634 | -1.751697 | 2.948064 |
| H    | 1.077312 | -2.710736 | 1.914913 |
| H    | -2.261072 | 0.250955 | 3.458606 |
| H    | -1.558025 | 1.877984 | 3.347340 |
| H    | -1.298535 | 0.892847 | 4.800396 |
| H    | 3.907183 | -0.624826 | 0.619746 |
| H    | 4.706088 | -0.896221 | 2.964127 |
| H    | 5.407334 | -2.128625 | 1.900717 |
| H    | 4.078494 | -2.556233 | 2.993182 |
| H    | 2.892462 | -3.508179 | 0.899381 |

S-36
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | 4.110989 | -2.893318 | -0.215077 |
| H    | 2.418543  | -2.417712  | -0.417292  |
| C    | -0.748638  | -2.402271  | -0.448781  |
| O    | -0.878288  | -3.098104  | 0.541475   |
| O    | -0.224776  | -1.217107  | -0.558643  |
| C    | -1.299053  | -2.851609  | -1.823251  |
| C    | -1.300769  | 3.926125   | -0.417292  |
| C    | -0.637497  | 5.049424   | -0.808490  |
| C    | 0.653600   | 4.925795   | -0.295647  |
| C    | 1.294937   | 3.684622   | -0.279343  |
| C    | 0.611036   | 2.591601   | -0.797038  |
| C    | -0.685712  | 2.671224   | -1.306357  |
| H    | -2.309892  | 4.019058   | -1.693086  |
| H    | -1.128298  | 6.016902   | -0.822078  |
| H    | 1.174460   | 5.794791   | 0.092804   |
| H    | 2.298883   | 3.582015   | 0.166872   |
| C    | -1.425142  | 1.429382   | -1.743318  |
| H    | -2.123057  | 1.664725   | -2.551620  |
| H    | -0.743080  | 0.654914   | -2.101979  |
| F    | -0.349851  | -2.788955  | -2.770793  |
| F    | -2.302935  | -2.005301  | -2.189771  |
| F    | -1.794152  | -4.085123  | -1.781401  |
| C    | -2.167249  | 0.859145   | -0.545362  |
| O    | -1.603639  | 0.752125   | 0.585138   |
| N    | -3.443784  | 0.549004   | -0.714162  |
| H    | -3.818217  | 0.696193   | -1.642958  |
| C    | -4.392733  | -0.038885  | 0.281163   |
| C    | -3.819195  | -1.345351  | 0.844657   |
| H    | -3.632443  | -2.063550  | 0.043153   |
| H    | -2.883753  | -1.176074  | 1.378612   |
| H    | -4.541692  | -1.786769  | 1.537830   |
| C    | -5.680930  | -0.328018  | -0.499616  |
| H    | -6.430683  | -0.755257  | 0.171195   |
| H    | -6.102076  | 0.588665   | -0.929281  |
| H    | -5.499871  | -1.049347  | -1.304401  |
| C    | -4.653916  | 0.993916   | 1.386313   |
| H    | -5.089644  | 1.907911   | 0.969844   |
| H    | -5.358445  | 0.582293   | 2.115713   |
| H    | -3.728854  | 1.254763   | 1.904014   |
| O    | 1.167957   | 1.276602   | -0.863069  |
| C    | 2.508958   | 1.096407   | -1.107296  |
| O    | 3.400125   | 1.688064   | -0.572097  |
| C    | 2.757231   | 0.067358   | -2.235328  |
| F    | 1.787685   | -0.842650  | -2.334816  |

S-37
TS1

Lowest frequency = -103.77 cm⁻¹

Charge = 1, Multiplicity = 1

63

|     |          |          |          |
|-----|----------|----------|----------|
| Ru  | 0.367457 | -0.653922| -0.470117|
| C   | 0.502511 | -1.502605| -2.420266|
| C   | 0.562509 | -2.587741| -1.487631|
| C   | 1.522418 | -2.480807| -0.451702|
| C   | 2.448036 | -1.390698| -0.384405|
| C   | 2.418503 | -0.342149| -1.325812|
| C   | 1.391990 | -0.394742| -2.327224|
| H   | 3.106478 | -1.317644| 0.472798 |
| H   | -0.314210| -1.464240| -3.133449|
| C   | -2.155665| -1.401781| 0.292571 |
| O   | -1.434843| -1.917591| 1.151853 |
| O   | -1.725373| -0.670476| -0.668697|
| C   | -3.676357| -1.645501| 0.268296 |
| C   | 2.902021 | 0.654124 | 2.490773 |
| C   | 3.309103 | -0.591056| 2.974608 |
| C   | 2.378793 | -1.622839| 3.138853 |
| C   | 1.038798 | -1.399342| 2.826035 |
| C   | 0.627250 | -0.144887| 2.354757 |
| C   | 1.557996 | 0.892499 | 2.184390 |
| H   | 3.630970 | 1.451924 | 2.373949 |
| H   | 4.352612 | -0.753767| 3.227679 |
| H   | 2.697554 | -2.587547| 3.521453 |
| H   | 0.296257 | -2.179346| 2.946947 |
| C   | 1.117108 | 2.265243 | 1.740726 |
| H   | 1.967893 | 2.804516 | 1.303708 |
| H   | 0.797807 | 2.853245 | 2.610663 |
| H   | -0.431990| 0.033398 | 2.201787 |
| F   | -4.086874| -2.278622| 1.367484 |
| F   | -4.342913| -0.481507| 0.165697 |
| F   | -3.977575| -2.403527| -0.806300|
| C   | 0.008692 | 2.279865 | 0.697491 |
| O   | -0.105332| 1.392990 | -0.185022|
| N   | -0.804839| 3.331948 | 0.710230 |
| H   | -0.646125| 4.017442 | 1.437906 |
|     |         |         |         |
|-----|---------|---------|---------|
| C   | -1.939886 | 3.615906 | -0.225079 |
| C   | -3.001740 | 2.515414 | -0.089264 |
| H   | -3.350486 | 2.438891 | 0.946119  |
| H   | -2.620071 | 1.545186 | -0.407501 |
| H   | -3.863152 | 2.765935 | -0.716446 |
| C   | -1.412416 | 3.710011 | -1.664146 |
| H   | -0.628595 | 4.470992 | -1.743820 |
| H   | -2.232094 | 3.994564 | -2.330844 |
| C   | -1.014167 | 2.751056 | -2.001270 |
| C   | -2.507973 | 4.968943 | 0.221097  |
| H   | -3.350930 | 5.242510 | -0.418393 |
| H   | -1.756937 | 5.763998 | 0.143697  |
| H   | -2.874727 | 4.924921 | 1.253337  |
| C   | 3.392829  | 0.811156 | -1.212049 |
| H   | 3.571389  | 0.960343 | -0.140871 |
| C   | 4.726589  | 0.389231 | -1.862038 |
| H   | 4.593924  | 0.190671 | -2.931454 |
| H   | 5.463658  | 1.191543 | -1.756925 |
| H   | 5.134290  | -0.513331| -1.395809 |
| C   | 2.880210  | 2.126262 | -1.811310 |
| H   | 3.575308  | 2.935499 | -1.567943 |
| H   | 2.821685  | 2.075291 | -2.904358 |
| H   | 1.890410  | 2.390795 | -1.429355 |
| C   | -0.452466 | -3.694483| -1.520280 |
| H   | -0.136086 | -4.466761| -2.231342 |
| H   | -0.561097 | -4.153420| -0.535369 |
| H   | -1.430790 | -3.322274| -1.836944 |
| H   | 1.239564  | 0.450359 | -2.987432 |
| H   | 1.494966  | -3.192440| 0.365651  |

**TS2**

Lowest frequency = -1505.26 cm⁻¹

Charge = 1, Multiplicity = 1

63

|     |         |         |         |
|-----|---------|---------|---------|
| Ru  | 0.772108 | -0.585694| -0.471674|
| C   | 1.325505 | -1.168855| -2.573061|
| C   | 1.592199 | -2.258343| -1.676886|
| C   | 2.428647 | -2.021820| -0.560042|
| C   | 2.945084 | -0.714987| -0.304090|
| C   | 2.656113 | 0.375850 | -1.157076|
| C   | 1.831124 | 0.112980 | -2.304971|
| Atoms | X Coordinates | Y Coordinates | Z Coordinates |
|-------|---------------|---------------|---------------|
| H     | 3.505134      | -0.539219     | 0.608372      |
| H     | 0.637993      | -1.315346     | -3.398923     |
| C     | -1.991230     | -1.421829     | 0.283121      |
| O     | -1.826602     | -0.909744     | 1.427170      |
| O     | -1.125650     | -1.525411     | -0.618878     |
| C     | -3.80146      | -2.011049     | -0.036943     |
| C     | 1.743739      | 0.901687      | 3.451580      |
| C     | 2.247685      | -0.229533     | 4.097400      |
| C     | 1.976957      | -1.504558     | 3.590775      |
| C     | 1.230456      | -1.624852     | 2.424927      |
| C     | 0.745279      | -0.496018     | 1.720168      |
| C     | 0.933093      | 0.780607      | 2.282349      |
| H     | 1.933776      | 1.885644      | 3.877424      |
| H     | 2.830003      | -0.116351     | 5.006902      |
| H     | 2.336302      | -2.387612     | 4.110201      |
| H     | 0.990608      | -2.615574     | 2.047124      |
| C     | 0.478317      | 2.064685      | 1.655067      |
| H     | 1.311221      | 2.588018      | 1.163673      |
| H     | 0.127350      | 2.737003      | 2.444601      |
| H     | -0.604608     | -0.685909     | 1.505402      |
| F     | -4.309930     | -1.529397     | 0.791675      |
| F     | -3.724159     | -1.708608     | -1.296774     |
| F     | -3.327509     | -3.345888     | 0.089795      |
| C     | -0.588622     | 1.918924      | 0.591853      |
| O     | -0.469029     | 1.115467      | -0.373317     |
| N     | -1.633236     | 2.737991      | 0.660894      |
| H     | -1.659038     | 3.372450      | 1.448311      |
| C     | -2.745461     | 2.881837      | -0.329919     |
| C     | -3.456593     | 1.537703      | -0.539095     |
| H     | -3.759365     | 1.098820      | 0.415812      |
| H     | -2.820025     | 0.831936      | -1.073393     |
| H     | -4.356803     | 1.700042      | -1.139629     |
| C     | -2.171997     | 3.415242      | -1.651076     |
| H     | -1.674246     | 4.379042      | -1.500773     |
| H     | -2.983192     | 3.558914      | -2.371434     |
| H     | -1.456295     | 2.708842      | -2.079053     |
| C     | -3.712940     | 3.899357      | 0.287582      |
| H     | -4.546093     | 4.078462      | -0.396602     |
| H     | -3.218844     | 4.861611      | 0.468469      |
| H     | -4.127259     | 3.528922      | 1.232031      |
| H     | 1.518671      | 0.938339      | -2.933691     |
| H     | 2.615330      | -2.819974     | 0.148121      |
| C     | 0.948965      | -3.596477     | -1.903577     |
| H     | -0.102303     | -3.479251     | -2.179316     |
TS3

Lowest frequency = -63.20 cm⁻¹

Charge = 1, Multiplicity = 1
| Element | X    | Y    | Z    |
|---------|------|------|------|
| H       | -0.130068 | 2.798822 | 1.045895 |
| C       | 1.839036  | 1.897702 | -0.383653 |
| O       | 2.610931  | 2.220034 | 0.499581  |
| O       | 0.989094  | 0.914040 | -0.414008 |
| C       | 1.816603  | 2.742010 | -1.681544 |
| C       | -0.162731 | -3.202317 | -2.318644 |
| C       | -0.959580 | -3.920814 | -1.908650 |
| O       | 0.762595  | -2.241818 | -1.493873 |
| H       | 0.560727  | -3.363052 | -3.317705 |
| H       | -1.421377 | -4.640967 | -2.576228 |
| H       | -2.376727 | -4.207214 | -0.307226 |
| H       | -1.306372 | -2.610363 | 1.183838  |
| C       | 1.857640  | -1.397056 | -2.105398 |
| H       | 2.185501  | -1.834168 | -3.053381 |
| H       | 1.463712  | -0.399208 | -2.335981 |
| F       | 1.143837  | 3.889730  | -1.468918 |
| F       | 1.206432  | 2.097714  | -2.707127 |
| F       | 3.060753  | 3.041983  | -2.073322 |
| C       | 3.049456  | -1.169132 | -1.210981 |
| O       | 2.932864  | -1.015389 | 0.034844  |
| N       | 4.242222  | -1.090207 | -1.797589 |
| H       | 4.258383  | -1.252012 | -2.795976 |
| C       | 5.542116  | -0.687089 | -1.180365 |
| C       | 5.405978  | 0.713104  | -0.565751 |
| H       | 5.058158  | 1.436035  | -1.309808 |
| H       | 4.700128  | 0.721559  | 0.265714  |
| H       | 6.382216  | 1.043471  | -0.197042 |
| C       | 6.554868  | -0.666956 | -2.332339 |
| H       | 7.539656  | -0.382063 | -1.953377 |
| H       | 6.648181  | -1.654841 | -2.798651 |
| H       | 6.268437  | 0.062702  | -3.098695 |
| C       | 5.958923  | -1.722014 | -0.126883 |
| H       | 6.022011  | -2.723561 | -0.564379 |
| H       | 6.942512  | -1.459807 | 0.275168  |
| H       | 5.244948  | -1.743767 | 0.698508  |
| O       | -3.482083 | -0.726454 | -1.183770 |
| C       | -4.280907 | -1.073730 | -0.186687 |
| O       | -4.172720 | -0.786666 | 0.984012  |
| C       | -5.404047 | -2.013778 | -0.706602 |
| F       | -4.861078 | -3.227350 | -0.927733 |
| F       | -5.930494 | -1.562273 | -1.847833 |
F  -6.364198  -2.130258  0.207128
I  -1.632664  0.137440 -0.488659
C  -2.355574  2.119175 -0.565252
C  -1.837145  2.981159 -1.536142
C  -3.295184  2.534596  0.387143
C  -2.259278  4.310009 -1.532465
H  -1.111907  2.633777 -2.261177
C  -3.722758  3.859423  0.354610
H  -3.693878  1.836899  1.115667
C  -3.198220  4.744955 -0.594138
H  -1.857577  5.000755 -2.266590
H  -4.462145  4.202762  1.071286
H  -3.527337  5.779316 -0.602496

TS4

Lowest frequency = -23.75 cm⁻¹

Charge = 1, Multiplicity = 1

81

Ru  0.725049  -0.513868  0.809426
C  1.726844  -0.200026  2.923674
C  0.795628  0.842302  2.867760
C  -0.563039  0.585156  2.542816
C  -0.951288  -0.777012  2.353936
C  -0.037370  -1.837457  2.554832
C  1.323070  -1.570194  2.805163
C  -1.608355  1.673944  2.530917
C  -2.369619  1.618094  3.875283
C  2.320179  -2.679202  2.950938
C  -1.031050  3.069343  2.275604
H  -1.984271  -0.982914  2.085250
H  -0.361918  -2.863668  2.435572
H  2.776382  0.035714  3.054442
H  1.144286  1.859031  2.972307
H  3.317330  -2.347276  2.658667
H  2.042694  -3.545585  2.345604
H  2.360763  -2.994378  4.001156
H  -2.331546  1.420829  1.751162
H  -2.852408  0.647443  4.025072
H  -3.150715  2.384030  3.877927
H  -1.698792  1.811465  4.720092
H  -0.428931  3.417080  3.122512
| Atom | X       | Y       | Z      |
|------|---------|---------|--------|
| H    | -1.846970 | 3.782561 | 2.141560 |
| H    | -0.414268 | 3.098785 | 1.373058 |
| C    | 2.237862  | 1.877318 | -0.003879 |
| O    | 2.646249  | 2.088922 | 1.123397 |
| O    | 1.365224  | 1.013250 | -0.425410 |
| C    | 2.792573  | 2.737006 | -1.171956 |
| C    | 0.566622  | -3.386474| -2.501708 |
| C    | -0.528320 | -4.205600| -2.227273 |
| C    | -1.292723 | -3.962246| -1.090791 |
| C    | -0.941269 | -2.924420| -0.221122 |
| C    | 0.172591  | -2.103417| -0.476697 |
| O    | 2.646249  | 2.088922 | 1.123397 |
| O    | 1.365224  | 1.013250 | -0.425410 |
| C    | 2.792573  | 2.737006 | -1.171956 |
| C    | 0.566622  | -3.386474| -2.501708 |
| C    | -0.528320 | -4.205600| -2.227273 |
| C    | -1.292723 | -3.962246| -1.090791 |
| C    | -0.941269 | -2.924420| -0.221122 |
| C    | 0.172591  | -2.103417| -0.476697 |
| C    | 1.145082  | -3.546166| -3.407967 |
| H    | -0.791916 | -5.008083| -2.908324 |
| H    | -2.172577 | -4.559467| -0.873063 |
| H    | -1.589533 | -2.749863| 0.629908 |
| C    | 2.024437  | -1.393249| -2.057253 |
| H    | 2.513873  | -1.740801| -2.970934 |
| H    | 1.631680  | -0.388373| -2.254294 |
| F    | 2.222796  | 3.953995 | -1.155683 |
| F    | 2.550735  | 2.179988 | -2.377848 |
| F    | 4.119276  | 2.887166 | -1.047704 |
| C    | 3.023636  | -1.258228| -0.939383 |
| O    | 2.635171  | -1.166181| 0.266711 |
| N    | 4.313349  | -1.252150| -1.243383 |
| H    | 4.530640  | -1.390510| -2.222495 |
| C    | 5.495486  | -1.151912| -0.330156 |
| C    | 5.353053  | 0.059050 | 0.599805 |
| H    | 5.211290  | 0.979588 | 0.028928 |
| H    | 4.510557  | -0.049660| 1.282828 |
| H    | 6.268623  | 0.161025 | 1.190209 |
| C    | 6.938706  | -0.963048| -1.250069 |
| H    | 7.620419  | -0.908422| -0.649774 |
| H    | 6.819540  | -1.804689| -1.944535 |
| H    | 6.627402  | -0.034513| -1.825478 |
| C    | 5.618013  | -2.463432| 0.457919 |
| H    | 5.762367  | -3.314190| -0.215775 |
| H    | 6.477969  | -2.411911| 1.132720 |
| H    | 4.721107  | -2.645505| 1.054620 |
| O    | -3.803863 | -0.215717| -1.461726 |
| C    | -4.451394 | -0.496525| -0.337941 |
| O    | -4.199524 | -0.041218| 0.782131 |
| C    | -5.450667 | -1.678757| -0.430934 |
| F    | -6.099758 | -1.726977| -1.597571 |
|   |        |        |        |
|---|--------|--------|--------|
| F | -6.345633 | -1.653830 | 0.561396 |
| F | -4.719727  | -2.822081  | -0.307388 |
| I | -1.551971  | 0.096075   | -0.843120 |
| C | -1.787998  | 2.211015   | -0.926285 |
| C | -0.804006  | 2.969829   | -1.561163 |
| C | -2.956826  | 2.772613   | -0.407951 |
| C | -0.973405  | 4.353384   | -1.621848 |
| H | 0.068154   | 2.501441   | -1.995481 |
| C | -3.117932  | 4.154691   | -0.508722 |
| H | -3.714028  | 2.148917   | 0.053406 |
| C | -2.125992  | 4.943299   | -1.098388 |
| H | -0.207610  | 4.961652   | -2.091736 |
| H | -4.023619  | 4.613483   | -0.123947 |
| H | -2.258351  | 6.018846   | -1.162140 |

**TS5**

Lowest frequency = -369.240 cm⁻¹

Charge = 1, Multiplicity = 1

69

|   |        |        |        |
|---|--------|--------|--------|
| Ru | 0.358341 | 0.094273 | 0.892289 |
| C | -0.356348  | -0.777986  | 2.802056 |
| C | 0.730175   | -1.585535  | 2.388669 |
| C | 1.983093   | -1.019397  | 2.041584 |
| C | 2.124620   | 0.390002   | 2.236385 |
| C | 1.083544   | 1.183802   | 2.774035 |
| C | -0.188028  | 0.622317   | 3.032026 |
| C | 3.132502   | -1.870140  | 1.543780 |
| C | 3.736792   | -2.626135  | 2.744314 |
| C | -1.334651  | 1.466448   | 3.498089 |
| C | 2.722819   | -2.832824  | 0.419368 |
| H | 3.052487   | 0.852544   | 1.926766 |
| H | 1.222453   | 2.253091   | 2.878867 |
| H | -1.332165  | -1.233599  | 2.910600 |
| H | 0.535599   | -2.632462  | 2.196355 |
| H | -2.287459  | 1.032274   | 3.192173 |
| H | -1.265378  | 2.483229   | 3.103908 |
| H | -1.319909  | 1.521356   | 4.593764 |
| H | 3.888865   | -1.185630  | 1.148954 |
| H | 4.054273   | -1.941036  | 3.537542 |
| H | 4.611675   | -3.196284  | 2.417966 |
| H | 3.014763   | -3.332833  | 3.169856 |

S-45
|   |     |     |     |
|---|-----|-----|-----|
| F | 2.582334 | -1.205447 | -2.744154 |
| F | 4.333245 | 0.089911 | -2.788136 |
| F | 2.394010 | 0.862290 | -3.416411 |

**im1a**

Lowest frequency = 7.52 cm⁻¹

Charge = 0, Multiplicity = 1

39

|   |     |     |     |
|---|-----|-----|-----|
| Ru | -0.095473 | -0.093688 | -0.209629 |
| C  | 0.541822  | -1.762687 | -1.464097 |
| C  | 1.679291  | -0.963579 | -1.117750 |
| C  | 1.992686  | -0.659042 |  0.227851 |
| C  | 1.097162  | -1.166131 |  1.226016 |
| C  | -0.021564 | -1.972499 |  0.903119 |
| C  | -0.316448 | -2.280503 | -0.463187 |
| C  | 3.136392  |  0.248713 |  0.634647 |
| C  | 4.333550  | -0.604835 |  1.091847 |
| C  | -1.564008 | -3.035883 | -0.823979 |
| C  | 3.544922  |  1.243672 | -0.457763 |
| H  | 1.221136  | -0.835775 |  2.252955 |
| H  | -0.741311 | -2.226727 |  1.669263 |
| H  | 0.283103  | -1.892696 | -2.509143 |
| H  | 2.237234  | -0.490225 | -1.916743 |
| H  | -1.927403 | -2.742234 | -1.812471 |
| H  | -2.348306 | -2.848420 | -0.088655 |
| H  | -1.350573 | -4.111927 | -0.842608 |
| H  | 2.778046  |  0.826347 |  1.496331 |
| H  | 4.056110  | -1.284856 |  1.904620 |
| H  | 5.146006  |  0.037457 |  1.447812 |
| H  | 4.717076  | -1.209328 |  0.261471 |
| H  | 4.029367  |  0.739239 | -1.302216 |
| H  | 4.265025  |  1.961996 | -0.053953 |
| H  | 2.682395  |  1.798600 | -0.839420 |
| C  | -0.251002 |  2.390221 | -0.298228 |
| O  | -0.093884 |  1.743401 | -1.371045 |
| O  | -0.158172 |  1.803372 |  0.818312 |
| C  | -0.623195 |  3.876667 | -0.339619 |
| C  | -4.335535 |  0.533135 |  0.333795 |
| C  | -2.964291 | -0.154387 |  0.549001 |
| O  | -2.829065 | -0.989601 |  1.431844 |
| O  | -2.106324 |  0.288361 | -0.311082 |

S-47
im2a

Lowest frequency = 19.60 cm$^{-1}$

Charge = 0, Multiplicity = 1

70

Ru  1.000858  -0.504045  -0.384890
C   1.142959  -0.513739  -2.525602
C   2.441136  -0.742698  -1.983503
C   2.677475  -1.796325  -1.062883
C   1.544933  -2.580591  -0.683787
C   0.252188  -2.402422  -1.246445
C   0.041571  -1.365287  -2.191778
C   4.037264  -2.047430  -0.446189
C   4.863760  -2.950184  -1.380075
C  -1.329063  -1.077386  -2.724031
C   4.789871  -0.756217  -0.099562
H   1.658128  -3.282010   0.135079
H  -0.611016  -2.921530  -0.843106
H   0.977691   0.372602  -3.125230
H   3.215257  -0.015303  -2.192366
H  -1.474514  -0.002876  -2.861550
H  -2.095746  -1.471050  -2.054617
H  -1.434098  -1.560601  -3.704566
H   3.859802  -2.595860   0.485465
H   4.343808  -3.890853  -1.591460
H   5.830688  -3.188409  -0.923694
H   5.055610  -2.447910  -2.335580
H   5.105404  -0.217757  -1.000379
H   5.695750  -0.992578   0.468432
H   4.166232  -0.081833   0.493841
C   1.965028   2.289724  -0.495200
O   1.926013   2.349770  -1.713816
O   1.835587   1.271474   0.090830
C   2.164293   3.574256   0.345173
C   1.719970  -0.709874  -2.334212
| Atoms | X         | Y         | Z         |
|-------|-----------|-----------|-----------|
| C     | 2.385873  | -1.909494 | 2.624854  |
| C     | 1.670244  | -3.099220 | 2.709634  |
| C     | 0.285799  | -3.102116 | 2.478670  |
| C     | -0.387319 | -1.917382 | 2.212615  |
| C     | 0.317286  | -0.690277 | 2.155930  |
| H     | 2.265953  | 0.225971  | 2.326792  |
| H     | 3.456141  | -1.893654 | 2.806607  |
| H     | 2.182253  | -4.025532 | 2.956961  |
| H     | -0.274352 | -4.030903 | 2.531724  |
| C     | -0.448211 | -0.621411 | 2.224513  |
| H     | -1.222534 | 0.543808  | 2.992978  |
| H     | 0.237518  | 1.425421  | 2.512327  |
| H     | -1.459232 | -1.893930 | 2.059643  |
| C     | -4.691577 | -1.487937 | -0.239939 |
| C     | -3.295675 | -1.514437 | 0.454371  |
| O     | -3.119667 | -0.687833 | 1.377931  |
| O     | -2.524401 | -2.373245 | -0.30168  |
| F     | -5.556764 | -0.609013 | 0.313206  |
| F     | -4.562210 | -1.133295 | -1.551074 |
| F     | -5.283557 | -2.698543 | -0.217214 |
| F     | 3.247194  | 3.472945  | 1.142471  |
| F     | 1.085409  | 3.765583  | 1.150674  |
| F     | 2.301729  | 4.662581  | -0.416712 |
| C     | -1.097704 | 1.076645  | 0.935410  |
| O     | -0.715274 | 0.639848  | -0.185911 |
| N     | -1.979649 | 2.064558  | 1.021412  |
| H     | -2.386509 | 2.203829  | 1.936678  |
| C     | -2.642839 | 2.780519  | -0.102614 |
| C     | -1.573884 | 3.410436  | -1.008281 |
| H     | -0.913598 | 4.063333  | -0.429984 |
| H     | -0.961718 | 2.651173  | -1.497230 |
| H     | -2.064543 | 4.009867  | -1.782118 |
| C     | -3.480700 | 3.884422  | 0.556425  |
| H     | -3.999018 | 4.463854  | -0.212607 |
| H     | -4.241415 | 3.456961  | 1.221043  |
| H     | -2.849131 | 4.570398  | 1.132724  |
| C     | -3.551594 | 1.819134  | -0.876365 |
| H     | -4.295413 | 1.371783  | -0.215519 |
| H     | -4.067619 | 2.364402  | -1.674489 |
| H     | -2.974548 | 1.011657  | -1.326907 |

**im3a**

Lowest frequency = 22.44 cm\(^{-1}\)
Charge = 0, Multiplicity = 1

62

Ru  -0.835131 -0.353559 -0.540244
C  -0.830573 -2.664993 -0.492683
C  -1.828195 -2.077317  0.339127
C  -2.834280 -1.202888 -0.163651
C  -2.719973 -0.835465 -1.539383
C  -1.660289 -1.303526 -2.350158
C  -0.707390 -2.241897 -1.826043
C  -3.962324 -0.701183  0.716694
C  -4.958353 -1.842185  0.989952
C  0.432512 -2.701464 -2.690266
C  -3.455377 -0.067370  2.019703
H  -3.4.14105 -0.115628 -1.957037
H  -1.558470 -0.942636 -3.367671
H  -0.072578 -3.289326 -0.039739
H  -1.792092 -2.296323  1.398872
H  1.256263 -3.090386 -2.086742
H  0.811078 -1.876224 -3.299602
H  0.097293 -3.495557 -3.369465
H  -4.493349  0.075715  0.152871
H  -5.337791 -2.274502  0.057246
H  -5.812415 -1.476837  1.571018
H  -4.480299 -2.645566  1.562841
H  -2.932227 -0.799841  2.644448
H  -4.298365  0.321056  2.601988
H  -2.761206  0.749455  1.808305
C  0.710283 -0.735424  2.011455
O  0.748255 -1.959139  1.961825
O  0.067495  0.121584  1.303566
C  1.622064 -0.011289  3.037449
C  -0.424740  4.014893 -0.615135
C  -1.712186  4.504367 -0.813152
C  -2.766066  3.596599 -0.871258
C  -2.510001  2.229407 -0.763686
C  -1.219248  1.696115 -0.582705
C  -0.171411  2.642258 -0.477606
H  0.406402  4.714510 -0.544814
H  -1.886300  5.572434 -0.909389
H  -3.787670  3.944890 -1.004743
H  -3.364981  1.566399 -0.811158
C  1.249932  2.274485 -0.113738
H  1.918832  3.117075 -0.327216

S-50
H  1.311734  2.088014  0.963309
F  1.021435  1.043508  3.617887
F  2.722968  0.475758  2.382318
F  2.063018 -0.826145  4.001947
C  1.816366  1.043054 -0.774547
O  1.109878 -0.126996 -1.258602
N  3.154466  0.959261 -0.811053
H  3.653869  1.715372  0.764981
C  3.957995 -1.199666 -0.467538
H  5.736898  0.995824 -1.448539
H  5.549129  0.354960  0.205526
C  3.794456 -0.544535 -2.659809
H  4.120175  0.308497 -3.264720
H  4.402750 -1.413983 -2.931837
H  2.751639 -0.760096 -2.895653

**TS1a**

Lowest frequency = -1251.42 cm⁻¹

Charge = 0, Multiplicity = 1

70

Ru  0.786137 -0.598493 -0.556422
C  1.153696 -0.460539 -2.752165
C  2.341333 -0.817957 -2.061563
C  2.407976 -1.947325 -1.196074
C  1.201058 -2.690943 -1.027219
C -0.004968 -2.338117 -1.679987
C -0.038867 -1.201983 -2.540592
C  3.686764 -2.330773 -0.477727
C  4.629638 -3.058907 -1.452125
C -1.333509 -0.774411 -3.168931
C  4.378103 -1.133545  0.189440
H  1.179572 -3.508989 -0.315534
H -0.922965 -2.855756 -1.434494
H  1.135712  0.460876 -3.318799
H  3.183583 -0.142125 -2.130496
| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| H    | -1.378716  | 0.311152   | -3.280679  |
| H    | -2.184382  | -1.105510  | -2.571593  |
| H    | -1.420905  | -1.223107  | -4.166703  |
| H    | 3.408674   | -3.036781  | 0.314021   |
| H    | 4.145820   | -3.933995  | -1.900090  |
| H    | 5.533470   | -3.395394  | -0.932452  |
| H    | 4.937532   | -2.390848  | -2.265245  |
| H    | 4.741312   | -0.413555  | -0.552383  |
| H    | 5.245382   | -1.477203  | 0.763496   |
| H    | 3.693969   | -0.610451  | 0.861696   |
| C    | 1.979206   | 2.140207   | -0.602942  |
| O    | 2.198149   | 2.178601   | -1.805656  |
| O    | 1.677190   | 1.155954   | 0.170628   |
| C    | 1.963931   | 3.475483   | 0.185653   |
| C    | 1.039412   | 0.313431   | 3.653986   |
| C    | 1.884825   | -0.680132  | 4.138801   |
| C    | 2.074249   | -1.852871  | 3.402750   |
| C    | 1.429202   | -1.989739  | 2.181417   |
| C    | 0.596296   | -0.983708  | 1.634871   |
| C    | 0.394163   | 0.174855   | 2.420674   |
| H    | 0.883017   | 1.216317   | 4.240045   |
| H    | 2.384801   | -0.545245  | 5.094105   |
| H    | 2.713102   | -2.645157  | 3.782634   |
| H    | 1.555528   | -2.918177  | 1.635616   |
| C    | -0.517595  | 1.315864   | 2.039611   |
| H    | -1.310482  | 1.377851   | 2.794317   |
| H    | 0.052206   | 2.249596   | 2.093913   |
| H    | -0.538676  | -1.535067  | 1.168993   |
| C    | -3.897064  | -2.191254  | 0.352099   |
| C    | -2.699658  | -1.555007  | 1.103780   |
| O    | -2.882310  | -0.536019  | 1.760791   |
| O    | -1.617149  | -2.212547  | 0.887261   |
| F    | -5.032635  | -1.498748  | 0.524731   |
| F    | -3.641336  | -2.219534  | -0.987358  |
| F    | -4.116728  | -3.459742  | 0.741382   |
| F    | 2.426302   | 3.349673   | 1.445079   |
| F    | 0.669626   | 3.902417   | 0.282940   |
| F    | 2.662723   | 4.439619   | -0.421938  |
| C    | -1.209671  | 1.322411   | 0.694255   |
| O    | -0.911297  | 0.613139   | -0.301464  |
| N    | -2.182039  | 2.231286   | 0.587894   |
| H    | -2.455937  | 2.689902   | 1.445430   |
| C    | -2.997264  | 2.538498   | -0.611670  |
| C    | -2.071852  | 3.002980   | -1.747726  |

S-52
TS(1a-1a')

Lowest frequency = -49.51 cm⁻¹

Charge = 0, Multiplicity = 1

57

C  0.571961  2.865294  -0.787808
C  1.897228  3.261449  -0.965928
C  2.538130  4.019156   0.016601
C  1.847792  4.369482   1.178320
C  0.525823  3.960524  1.358078
C -0.127701  3.211596   0.375033
H  0.094674   2.254175  -1.547563
H  2.433945  2.948710  -1.855112
H  3.571284  4.325425  -0.119111
H  2.340545  4.952059   1.951786
C -1.569674  2.775607   0.579768
H -1.820380  2.831418   1.643391
H -2.256233  3.433868   0.045671
H -0.000364  4.216893   2.273804
C -1.732933  1.327199   0.166271
O -1.094818  0.487412   0.865644
N -2.431299  0.943916  -0.898882
H -2.447385  -0.082546  -0.985855
C -3.383643  1.663995  -1.783978
C -2.677267  2.755311  -2.602336
H -2.264511  3.554786  -1.982086
H -1.859072  2.323552  -3.187518
H -3.391373  3.209212  -3.297288
C -3.912197  0.581212  -2.741335
H -4.391785  -0.231962  -2.187736

S-53
|     |     |     |     |
|-----|-----|-----|-----|
| H   | -4.645636 | 1.015155 | -3.426958 |
| H   | -3.095789  | 0.155829  | -3.334846 |
| C   | -4.559405  | 2.222486  | -0.964206 |
| H   | -5.317662  | 2.636162  | -1.637314 |
| H   | -5.013875  | 1.422191  | -0.373958 |
| H   | -4.250018  | 3.020079  | -0.282705 |
| I   | 0.391086   | -1.218149 | -0.107317 |
| O   | 2.403447   | -1.874491 | -0.704130 |
| C   | 3.123432   | -0.970322 | -1.322944 |
| O   | 2.837950   | 0.180162  | -1.585084 |
| C   | 4.504260   | -1.563732 | -1.709313 |
| F   | 5.177653   | -1.929118 | -0.604326 |
| F   | 5.236216   | -0.661360 | -2.371788 |
| F   | 4.352328   | -2.646007 | -2.491442 |
| C   | -2.564774  | -2.107586 | 0.535985 |
| O   | -1.987859  | -2.407258 | 1.574899 |
| O   | -2.062220  | -1.727198 | -0.585736 |
| C   | -4.116282  | -2.055851 | 0.543207 |
| F   | -4.656614  | -2.845562 | 1.474097 |
| F   | -4.497272  | -0.774034 | 0.810955 |
| F   | -4.654561  | -2.380769 | -0.650501 |
| C   | 1.302350   | -0.437018 | 1.645323 |
| C   | 1.019054   | -1.111362 | 2.831481 |
| C   | 2.104412   | 0.699508  | 1.584814 |
| C   | 1.598872   | -0.633473 | 4.007833 |
| H   | 0.344936   | -1.960834 | 2.838680 |
| C   | 2.680400   | 1.150347  | 2.772616 |
| H   | 2.281115   | 1.215483  | 0.651169 |
| C   | 2.430184   | 0.488240  | 3.976895 |
| H   | 1.396014   | -1.139776 | 4.946694 |
| H   | 3.312667   | 2.032243  | 2.748941 |
| H   | 2.878563   | 0.852644  | 4.896635 |

**1a**

Lowest frequency = 25.92 cm⁻¹

Charge = 0, Multiplicity = 1

31

|     |     |     |     |
|-----|-----|-----|-----|
| C   | -0.503735 | 1.326083 | 2.912103 |
| C   | 0.714185  | 1.608305 | 3.532467 |
| C   | 1.912639  | 1.307921 | 2.885039 |
| C   | 1.881372  | 0.719815 | 1.618833 |
\[
\begin{array}{ccc}
C & 0.664088 & 0.435068 & 1.000751 \\
C & -0.543578 & 0.740692 & 1.641290 \\
H & -1.434952 & 1.559351 & 3.423733 \\
H & 0.724293 & 2.064164 & 4.518764 \\
H & 2.862859 & 1.528472 & 3.363260 \\
H & 2.810090 & 0.479587 & 1.108343 \\
C & -1.883362 & 0.421548 & 0.995338 \\
H & -2.078965 & -0.653871 & 1.075591 \\
H & -2.679355 & 0.936970 & 1.534375 \\
H & 0.636383 & -0.022679 & 0.017564 \\
C & -1.902064 & 0.714469 & -0.501682 \\
O & -1.381099 & -0.078554 & -1.284382 \\
N & -2.473369 & 1.861705 & -0.979668 \\
H & -2.385069 & 1.902917 & -1.988379 \\
C & -3.153090 & 3.012728 & -0.347826 \\
C & -2.251139 & 3.700261 & 0.690459 \\
H & -2.043375 & 3.063381 & 1.551345 \\
H & -1.291524 & 3.971840 & 0.239697 \\
H & -2.734638 & 4.612807 & 1.056765 \\
C & -3.423767 & 4.001197 & -1.495046 \\
H & -4.059348 & 3.545542 & -2.263488 \\
H & -3.936613 & 4.889945 & -1.115866 \\
H & -2.485620 & 4.321956 & -1.961783 \\
C & -4.500823 & 2.596734 & 0.269982 \\
H & -5.028761 & 3.477909 & 0.651335 \\
H & -5.131679 & 2.113769 & -0.483187 \\
H & -4.376004 & 1.900193 & 1.103314 \\
\end{array}
\]

\textbf{1a'}

Lowest frequency = 11.18 cm\(^{-1}\)

Charge = 0, Multiplicity = 1

57

\[
\begin{array}{ccc}
C & 1.107151 & 4.102838 & 1.048734 \\
C & 0.098098 & 5.066784 & 1.088655 \\
C & -0.627981 & 5.364533 & -0.063890 \\
C & -0.349214 & 4.686890 & -1.252408 \\
C & 0.653864 & 3.721532 & -1.289294 \\
C & 1.399587 & 3.429625 & -0.141530 \\
H & 1.674911 & 3.881584 & 1.948118 \\
H & -0.113447 & 5.587485 & 2.018262 \\
H & -1.409587 & 6.118358 & -0.036780 \\
\end{array}
\]
\[
\begin{array}{ccc}
\text{C} & -3.398507 & 3.171485 & -1.165325 \\
\text{H} & -3.382938 & 2.593617 & -3.244358 \\
\text{H} & -3.230774 & 3.512443 & 0.957906 \\
\text{H} & -4.027029 & 4.041333 & -1.332522 \\
\end{array}
\]

**CF₃COO⁻**

Lowest frequency = 15.75 cm⁻¹

Charge = -1, Multiplicity = 1

\[
\begin{array}{ccc}
\text{C} & -2.041949 & 0.487531 & 0.000980 \\
\text{O} & -0.866707 & 0.194377 & 0.302611 \\
\text{O} & -2.605582 & 1.559844 & -0.292179 \\
\text{C} & -2.984729 & -0.777276 & -0.001194 \\
\text{F} & -3.027433 & -1.391361 & 1.219886 \\
\text{F} & -4.280464 & -0.522425 & -0.328629 \\
\text{F} & -2.563778 & -1.734278 & -0.880658 \\
\end{array}
\]

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$^1$H, $^{13}$C and $^{19}$F-NMR Spectra

2a
(300 MHz, CDCl$_3$)

2a
(75 MHz, CDCl$_3$)
$2g$

(376 MHz, CDCl$_3$)
