

Supporting Information

Synthesis of 2*H*-Chromenes via Hydrazine-Catalyzed Ring-Closing Carbonyl-Olefin Metathesis

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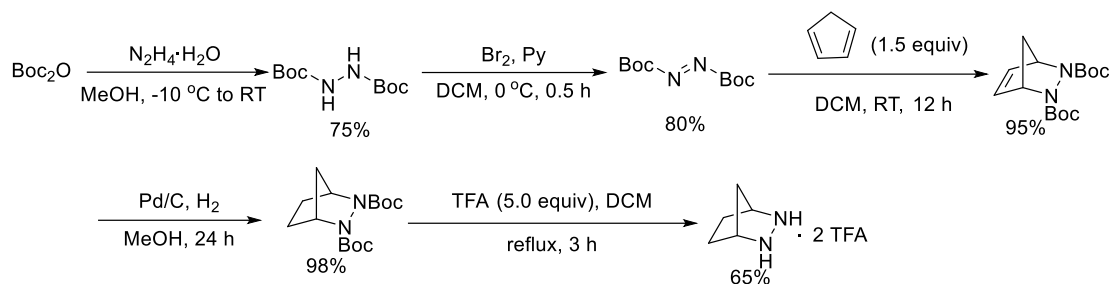
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1. General Information

Catalytic reactions were performed in 5.0 ml sealed tubes unless otherwise noted. Flash chromatography was performed using silica gel 60 (230-400 mesh) from SiliCycle. Commercial reagents were purchased from Sigma Aldrich, Alfa Aesar, Acros, TCI, AK Scientific, and Oakwood and used as received. Proton nuclear magnetic resonance (¹H NMR) spectra and carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on Mercury-300 (300 MHz), Inova-400 (400 MHz) and Inova-500 (500 MHz) spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (CHCl₃ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl₃ = δ 77.0). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. Infrared (IR) spectra were obtained using a Bruker Hyperion Tensor II Infrared spectrometer. The mass spectral data were obtained on a ThermoFisher Scientific Exactive series DART Mass Spectrometer.

2. Experimental Details and Characterization of Compounds

2.1 Synthesis and Characterization of [2.2.1]-Bicyclic Hydrazine

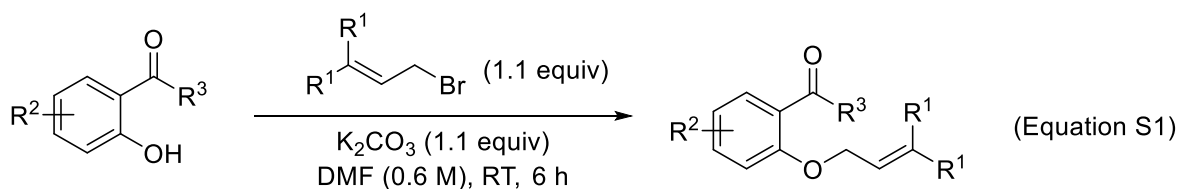


Scheme S1. Synthesis of Catalyst

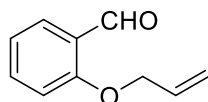
2,3-Diazobicyclo[2.2.1]heptane bis-trifluoroacetic acid 8: Prepared according to our previous report¹ to the Boc-protected hydrazine (2,3-diaza-bicyclo[2.2.1]heptane-2,3-dicarboxylic acid di-tert butyl ester, see Scheme S1). This precursor could then be deprotected by 5 equiv pure TFA and reflux for 3 hours. After full conversion of starting material (monitored by TLC), extra TFA was removed in vacuum to give the crude product which was triturated with Et₂O to generate white solid. After vacuum filtration, washed by Et₂O (3 x 10 ml) and dried under vacuum to yield a white powder. IR (Film): 3145, 3005, 2988, 2946, 2940, 1663, 1619, 1472, 1450, 1420, 1346, 1276, 1172, 1122, 1016, 945, 831, 797, 720, 586 cm⁻¹. ¹H NMR (500 MHz, DMSO-*d*₆) δ 3.95 (s, 2H), 1.77 (d, *J* = 10.8 Hz, 1H), 1.72 – 1.64 (m, 5H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 159.8 (q, *J* = 29.8 Hz), 117.5 (q, *J* = 297.3 Hz), 57.4, 37.7, 27.1. MS (DART) exact mass calculated for [C₅H₁₁N₂⁺]: 99.0917, found 99.0921.

2.2 Synthesis and Characterization of Starting Material

General Procedure: In an ordinary vial equipped with a magnetic stirring bar, aldehyde/ketone and K₂CO₃ (1.1 equiv.) were dissolved in DMF (0.6 M). Then allyl bromide (1.1 equiv.) was added dropwise (Equation S1).² After stirring the mixture for 6 h, water was added and extracted 3 times with Et₂O. The combined organic phases was washed by H₂O, 15% NaOH solution, brine, dried over Na₂SO₄ and concentrated. The residue was purified by column chromatography.

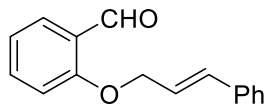


3-bromoprop-1-ene, 1-bromo-3-methylbut-2-ene and (E)-(3-bromoprop-1-en-1-yl)benzene were commercial available and used directly without further purification. 1-bromo-3-isopropyl-4-methylpent-2-ene,³ 1-bromo-3-ethyl-2-methylpent-2-ene⁴ and other bromides were synthesis by the literature.⁵



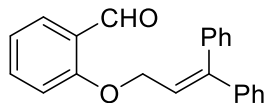
2-(allyloxy)benzaldehyde

9a was prepared from salicylaldehyde (366.4 mg, 3.0 mmol) and 3-bromoprop-1-ene (399.2 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (447.7 mg, 92%). ¹H NMR (500 MHz, CDCl₃) δ 10.54 (s, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.9 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.13 – 6.03 (m, 1H), 5.46 (dt, *J* = 17.3, 1.4 Hz, 1H), 5.34 (dt, *J* = 10.6, 1.3 Hz, 1H), 4.66 (d, *J* = 4.8 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 189.8, 160.9, 135.8, 132.4, 128.4, 125.1, 120.9, 118.1, 112.8, 69.2.



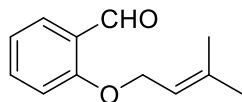
2-(cinnamyloxy)benzaldehyde

9b was prepared from salicylaldehyde (2.4424 g, 20.0 mmol) and (E)-(3-bromoprop-1-en-1-yl)benzene (4.3358 g, 22.0 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a white solid (4.0509 g, 85%). ¹H NMR (500 MHz, CDCl₃) δ 10.58 (s, 1H), 7.87 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.55 (ddd, *J* = 9.0, 7.4, 1.8 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.31 – 7.27 (m, 1H), 7.07 – 7.03 (m, 2H), 6.78 (d, *J* = 16.0 Hz, 1H), 6.44 (dt, *J* = 16.0, 5.8 Hz, 1H), 4.84 (dd, *J* = 5.8, 1.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 189.8, 161.0, 136.1, 135.9, 133.6, 128.7, 128.5, 128.2, 126.6, 125.2, 123.4, 120.9, 112.9, 69.2.



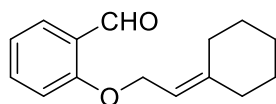
2-((3,3-diphenylallyl)oxy)benzaldehyde

9c was prepared from salicylaldehyde (366.4 mg, 3.0 mmol) and (3-bromoprop-1-ene-1,1-diyl)dibenzene (901.5 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a white solid (820.5 mg, 87%). IR (Film): 3031, 2981, 2934, 2880, 2856, 2764, 1682, 1595, 1482, 1459, 1380, 1286, 1226, 1188, 1167, 1103, 1079, 994, 839, 756, 695 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 10.55 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.36 (m, 4H), 7.33 – 7.26 (m, 5H), 7.25 – 7.21 (m, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.34 (t, *J* = 6.5 Hz, 1H), 4.73 (d, *J* = 6.6 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 189.9, 161.0, 146.5, 141.3, 138.7, 135.8, 129.6, 128.5, 128.4, 128.3, 128.04, 128.02, 127.7, 125.1, 122.7, 120.8, 113.0, 66.5. MS (DART) exact mass calculated for [C₂₂H₁₉O₂⁺]: 315.1380, found 315.1384.



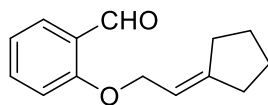
2-((3-methylbut-2-en-1-yl)oxy)benzaldehyde

9d was prepared from salicylaldehyde (366.4 mg, 3.0 mmol) and 1-bromo-3-methylbut-2-ene (491.8 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (513.6 mg, 90%). ¹H NMR (500 MHz, CDCl₃) δ 10.50 (s, 1H), 7.83 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.04 – 6.96 (m, 2H), 5.53 – 5.47 (m, 1H), 4.64 (d, *J* = 6.5 Hz, 2H), 1.81 (s, 3H), 1.76 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 190.0, 161.4, 138.7, 135.8, 128.3, 125.2, 120.6, 119.09, 113.0, 65.5, 25.8, 18.3.



2-(2-cyclohexylideneethoxy)benzaldehyde

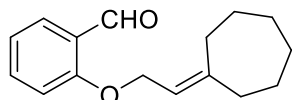
9e was prepared from salicylaldehyde (366.4 mg, 3.0 mmol) and (2-bromoethylidene)cyclohexane (624.0 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (566.5 mg, 82%). IR (Film): 2927, 2853, 1685, 1597, 1479, 1456, 1362, 1284, 1233, 1221, 1188, 1160, 1101, 1041, 985, 835, 755, 655 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 10.51 (s, 1H), 7.83 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.03 – 6.98 (m, 2H), 5.44 (t, *J* = 6.8 Hz, 1H), 4.66 (d, *J* = 6.7 Hz, 2H), 2.27 – 2.13 (m, 4H), 1.62 – 1.52 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 190.1, 161.4, 146.8, 135.8, 128.3, 125.2, 120.5, 115.5, 113.1, 64.8, 37.0, 29.3, 28.3, 27.7, 26.6. MS (DART) exact mass calculated for [C₁₅H₁₉O₂⁺]: 231.1380, found 231.1379.



2-(2-cyclopentylideneethoxy)benzaldehyde

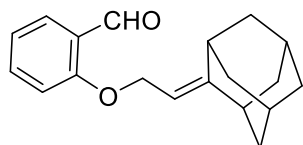
9f was prepared from salicylaldehyde (366.4 mg, 3.0 mmol) and (2-bromoethylidene)cyclopentane (577.7 mg, 3.3

mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (486.6 mg, 75%). IR (Film): 2950, 2866, 2758, 1684, 1582, 1510, 1479, 1455, 1378, 1233, 1160, 1101, 985, 832, 755, 654 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.51 (s, 1H), 7.83 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.55 – 7.50 (m, 1H), 7.03 – 6.97 (m, 2H), 5.64 – 5.58 (m, 1H), 4.63 (d, $J = 6.6$ Hz, 2H), 2.37 – 2.28 (m, 4H), 1.77 – 1.70 (m, 2H), 1.69 – 1.62 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 190.1, 161.4, 150.1, 135.8, 128.3, 125.1, 120.5, 114.5, 113.0, 66.9, 33.9, 29.1, 26.3, 26.0. MS (DART) exact mass calculated for $[\text{C}_{14}\text{H}_{17}\text{O}_2]^+$: 217.1223, found 217.1224.



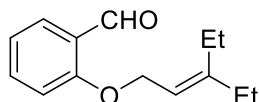
2-(2-cycloheptylideneethoxy)benzaldehyde

9g was prepared from salicylaldehyde (366.4 mg, 3.0 mmol) and (2-bromoethylidene)cycloheptane (670.3 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (584.4 mg, 80%). IR (Film): 2921, 2851, 1685, 1597, 1479, 1455, 1384, 1284, 1233, 1160, 1101, 985, 832, 755, 653 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.51 (s, 1H), 7.83 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.55 – 7.50 (m, 1H), 7.03 – 6.98 (m, 2H), 5.50 (t, $J = 6.4$ Hz, 1H), 4.65 (d, $J = 6.4$ Hz, 2H), 2.35 (t, $J = 6.1$ Hz, 2H), 2.30 (t, $J = 6.1$ Hz, 2H), 1.66 – 1.50 (m, 8H). ^{13}C NMR (126 MHz, CDCl_3) δ 190.1, 161.4, 148.0, 135.8, 128.3, 125.1, 120.5, 119.1, 113.0, 65.2, 37.7, 30.5, 29.7, 29.1, 28.8, 27.1. MS (DART) exact mass calculated for $[\text{C}_{16}\text{H}_{21}\text{O}_2]^+$: 245.1536, found 245.1537.



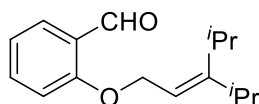
2-((Z)-2-((1R,5S)-adamantan-2-ylidene)ethoxy)benzaldehyde

9h was prepared from salicylaldehyde (366.4 mg, 3.0 mmol) and 2-(2-bromoethylidene)adamantane (795.9 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a white solid (686.2 mg, 81%). IR (Film): 2912, 2846, 1684, 1665, 1595, 1580, 1475, 1460, 1397, 1219, 1156, 1095, 978, 829, 762, 652 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.51 (s, 1H), 7.83 (dd, $J = 7.9, 1.8$ Hz, 1H), 7.54 – 7.49 (m, 1H), 7.03 – 6.98 (m, 2H), 5.41 (t, $J = 6.8$ Hz, 1H), 4.65 (d, $J = 6.8$ Hz, 2H), 2.90 (t, $J = 3.2$ Hz, 1H), 2.45 (t, $J = 3.2$ Hz, 1H), 1.99 – 1.95 (m, 2H), 1.94 – 1.87 (m, 4H), 1.86 – 1.77 (m, 4H), 1.77 – 1.70 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 190.1, 161.5, 155.2, 135.7, 128.2, 125.3, 120.5, 113.3, 110.5, 64.5, 40.4, 39.6, 39.0, 37.0, 32.9, 28.3. MS (DART) exact mass calculated for $[\text{C}_{19}\text{H}_{23}\text{O}_2]^+$: 283.1693, found 283.1695.



2-(3-ethylpent-2-en-1-yl)oxybenzaldehyde

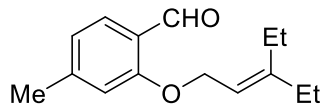
9i was prepared from salicylaldehyde (366.4 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (589.4 mg, 90%). IR (Film): 2966, 2934, 2874, 1685, 1597, 1479, 1456, 1284, 1222, 1188, 1160, 1101, 986, 832, 755, 653 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.51 (s, 1H), 7.84 (dd, $J = 8.0, 1.8$ Hz, 1H), 7.55 – 7.50 (m, 1H), 7.03 – 6.99 (t, $J = 7.5$ Hz, 2H), 5.45 (t, $J = 6.6$ Hz, 1H), 4.68 (d, $J = 6.6$ Hz, 2H), 2.20 – 2.09 (m, 4H), 1.08 – 1.00 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 190.1, 161.4, 149.7, 135.8, 128.3, 125.1, 120.6, 116.9, 113.0, 65.3, 29.1, 24.0, 13.4, 12.4. MS (DART) exact mass calculated for $[\text{C}_{14}\text{H}_{19}\text{O}_2]^+$: 219.1380, found 219.1382.



2-(3-isopropyl-4-methylpent-2-en-1-yl)oxybenzaldehyde

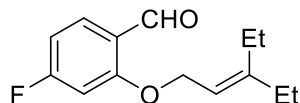
9j was prepared from salicylaldehyde (366.4 mg, 3.0 mmol) and 1-bromo-3-isopropyl-4-methylpent-2-ene (677.0 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1)

as a colorless oil (613.5 mg, 83%). IR (Film): 2961, 2928, 2869, 1686, 1597, 1480, 1457, 1284, 1223, 1160, 984, 831, 650 cm^{-1} . $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 10.52 (s, 1H), 7.84 (d, $J = 7.6$ Hz, 1H), 7.53 (t, $J = 7.8$ Hz, 1H), 7.04 – 6.98 (m, 2H), 5.47 (t, $J = 6.4$ Hz, 1H), 4.73 (d, $J = 6.4$ Hz, 2H), 2.88 – 2.79 (m, 1H), 2.43 – 2.34 (m, 1H), 1.06 (d, $J = 7.0$ Hz, 12H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 190.1, 161.4, 158.1, 135.8, 128.2, 125.2, 120.6, 115.7, 113.1, 65.2, 30.3, 28.9, 24.3, 21.1. MS (DART) exact mass calculated for $[\text{C}_{16}\text{H}_{23}\text{O}_2]^+$: 247.1693, found 247.1695.



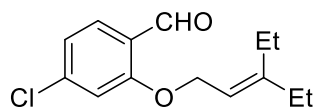
2-((3-ethylpent-2-en-1-yl)oxy)-4-methylbenzaldehyde

55 was prepared from 2-hydroxy-4-methylbenzaldehyde (408.5 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a white solid (620.3 mg, 89%). IR (Film): 2965, 2934, 2874, 1680, 1604, 1574, 1418, 1255, 1160, 1110, 992, 810, 719, 589 cm^{-1} . $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 10.43 (s, 1H), 7.73 (d, $J = 7.8$ Hz, 1H), 6.82 (d, $J = 7.9$ Hz, 1H), 6.80 (s, 1H), 5.45 (t, $J = 6.6$ Hz, 1H), 4.65 (d, $J = 6.6$ Hz, 2H), 2.40 (s, 3H), 2.20 – 2.09 (m, 4H), 1.08 – 1.01 (m, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 189.7, 161.5, 149.5, 147.2, 128.2, 122.9, 121.6, 116.9, 113.5, 65.2, 29.1, 23.9, 22.4, 13.4, 12.4. MS (DART) exact mass calculated for $[\text{C}_{15}\text{H}_{21}\text{O}_2]^+$: 233.1536, found 233.1539.



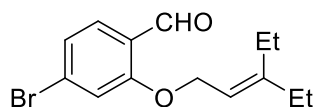
2-((3-ethylpent-2-en-1-yl)oxy)-4-fluorobenzaldehyde

56 was prepared from 4-fluoro-2-hydroxybenzaldehyde (420.3 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a white solid (439.5 mg, 62%). IR (Film): 2967, 2935, 2875, 1686, 1604, 1589, 1494, 1430, 1389, 1273, 1253, 1186, 1159, 1094, 998, 960, 835, 816, 652, 626 cm^{-1} . $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 10.39 (s, 1H), 7.86 (t, $J = 7.7$ Hz, 1H), 6.73 – 6.67 (m, 2H), 5.43 (t, $J = 6.5$ Hz, 1H), 4.65 (d, $J = 6.6$ Hz, 2H), 2.20 – 2.10 (m, 4H), 1.08 – 1.01 (m, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 188.5, 167.6 (d, $J = 255.7$ Hz), 163.1 (d, $J = 11.1$ Hz), 150.4, 130.6 (d, $J = 11.6$ Hz), 121.9 (d, $J = 2.7$ Hz), 116.2, 108.0 (d, $J = 22.3$ Hz), 100.8 (d, $J = 25.7$ Hz), 65.6, 29.1, 24.0, 13.4, 12.4. MS (DART) exact mass calculated for $[\text{C}_{14}\text{H}_{18}\text{FO}_2]^+$: 237.1285, found 237.1287.



4-chloro-2-((3-ethylpent-2-en-1-yl)oxy)benzaldehyde

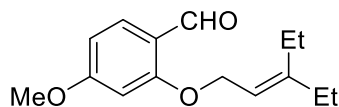
57 was prepared from 4-chloro-2-hydroxybenzaldehyde (469.7 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a white solid (644.5 mg, 85%). IR (Film): 3104, 2965, 2933, 2876, 1682, 1592, 1570, 1418, 1391, 1237, 1180, 997, 899, 871, 806, 628 cm^{-1} . $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 10.41 (s, 1H), 7.77 (d, $J = 8.6$ Hz, 1H), 7.02 – 6.98 (m, 2H), 5.43 (t, $J = 6.7$ Hz, 1H), 4.66 (d, $J = 6.6$ Hz, 2H), 2.20 – 2.10 (m, 4H), 1.08 – 1.01 (m, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 188.9, 161.7, 150.4, 141.8, 129.4, 123.6, 121.1, 116.2, 113.6, 65.6, 29.1, 24.0, 13.4, 12.4. MS (DART) exact mass calculated for $[\text{C}_{14}\text{H}_{18}\text{ClO}_2]^+$: 253.0990, found 253.0991.



4-bromo-2-((3-ethylpent-2-en-1-yl)oxy)benzaldehyde

58 was prepared from 4-bromo-2-hydroxybenzaldehyde (603.1 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a white solid (731.1mg, 82%). IR (Film): 3102, 2964, 2886, 2874, 1681, 1586, 1567, 1480, 1404, 1390, 1235, 1078, 996, 880, 870, 804 cm^{-1} . $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 10.42 (s, 1H), 7.68 (d, $J = 8.2$ Hz, 1H), 7.17 – 7.13 (m, 2H), 5.42 (t, $J = 6.7$ Hz, 1H), 4.65 (d, $J = 6.6$ Hz, 2H), 2.20

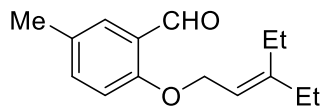
– 2.09 (m, 4H), 1.08 – 1.01 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 189.0, 161.5, 150.4, 130.4, 129.4, 124.0, 123.9, 116.6, 116.2, 65.7, 29.1, 24.0, 13.4, 12.4. MS (DART) exact mass calculated for $[\text{C}_{14}\text{H}_{18}\text{BrO}_2^+]$: 297.0485, found 297.0485.



2-((3-ethylpent-2-en-1-yl)oxy)-4-methoxybenzaldehyde

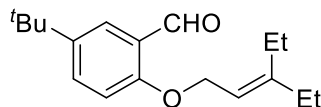
59 was prepared from 2-hydroxy-4-methoxybenzaldehyde (456.5 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 10:1) as a colorless oil (543.9 mg, 73%). IR (Film): 2965, 2935, 2874, 2842, 2765, 1675, 1596, 1578, 1441, 1256, 1198, 1165, 1111, 1096, 993, 820 cm^{-1} .

^1H NMR (500 MHz, CDCl_3) δ 10.33 (s, 1H), 7.82 (d, $J = 8.6$ Hz, 1H), 6.54 (dd, $J = 8.7, 1.6$ Hz, 1H), 6.46 (d, $J = 2.2$ Hz, 1H), 5.44 (t, $J = 6.6$ Hz, 1H), 4.64 (d, $J = 6.5$ Hz, 2H), 3.87 (s, 3H), 2.19 – 2.09 (m, 4H), 1.07 – 1.00 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 188.6, 166.0, 163.2, 149.7, 130.3, 119.3, 116.8, 105.8, 99.0, 65.2, 55.6, 29.1, 24.0, 13.4, 12.4. MS (DART) exact mass calculated for $[\text{C}_{15}\text{H}_{21}\text{O}_3^+]$: 249.1485, found 249.1486.



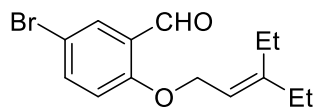
2-((3-ethylpent-2-en-1-yl)oxy)-5-methylbenzaldehyde

60 was prepared from 2-hydroxy-5-methylbenzaldehyde (408.5 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (592.5 mg, 85%). IR (Film): 2965, 2933, 2874, 1681, 1611, 1581, 1493, 1461, 1390, 1283, 1239, 1219, 1159, 1114, 990, 940, 808, 720, 649, 541 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.48 (s, 1H), 7.64 – 7.62 (m, 1H), 7.33 (dd, $J = 8.6, 2.3$ Hz, 1H), 6.91 (d, $J = 8.5$ Hz, 1H), 5.44 (t, $J = 6.6$ Hz, 1H), 4.64 (d, $J = 6.5$ Hz, 2H), 2.31 (s, 3H), 2.18 – 2.08 (m, 4H), 1.06 – 1.00 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 190.2, 159.5, 149.5, 136.5, 130.0, 128.2, 124.8, 117.0, 113.1, 65.4, 29.1, 24.0, 20.3, 13.4, 12.4. MS (DART) exact mass calculated for $[\text{C}_{15}\text{H}_{21}\text{O}_2^+]$: 233.1536, found 233.1539.



5-(tert-butyl)-2-((3-ethylpent-2-en-1-yl)oxy)benzaldehyde

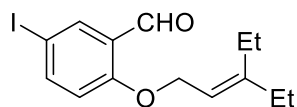
61 was prepared from 5-(tert-butyl)-2-hydroxybenzaldehyde (534.7 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (708.0 mg, 86%). IR (Film): 2963, 2872, 1681, 1607, 1493, 1461, 1392, 1364, 1262, 1238, 1136, 1098, 990, 817, 732, 650, 598 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.50 (s, 1H), 7.85 (d, $J = 2.7$ Hz, 1H), 7.57 (dd, $J = 8.7, 2.6$ Hz, 1H), 6.95 (d, $J = 8.8$ Hz, 1H), 5.45 (t, $J = 6.7$ Hz, 1H), 4.65 (d, $J = 6.6$ Hz, 2H), 2.19 – 2.08 (m, 4H), 1.31 (s, 9H), 1.07 – 1.00 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 190.4, 159.5, 149.5, 143.4, 133.0, 124.7, 124.4, 117.1, 112.8, 65.3, 34.2, 31.3, 29.1, 24.0, 13.4, 12.4. MS (DART) exact mass calculated for $[\text{C}_{18}\text{H}_{27}\text{O}_2^+]$: 275.2006, found 275.2008.



5-bromo-2-((3-ethylpent-2-en-1-yl)oxy)benzaldehyde

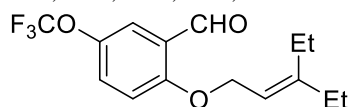
62 was prepared from 5-bromo-2-hydroxybenzaldehyde (603.1 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a white solid (766.8 mg, 86%). IR (Film): 2965, 2935, 2873, 1682, 1589, 1471, 1408, 1387, 1267, 1222, 1177, 1121, 982, 881, 808, 656 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.41 (s, 1H), 7.92 (d, $J = 2.6$ Hz, 1H), 7.60 (dd, $J = 8.9, 2.6$ Hz, 1H), 6.90 (d, $J = 8.8$ Hz, 1H), 5.42 (t, $J = 6.7$ Hz,

1H), 4.66 (d, $J = 6.6$ Hz, 2H), 2.18 – 2.09 (m, 4H), 1.07 – 1.00 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 188.6, 160.3, 150.2, 138.1, 130.9, 126.4, 116.4, 115.1, 113.3, 65.6, 29.1, 24.0, 13.4, 12.4. MS (DART) exact mass calculated for $[\text{C}_{14}\text{H}_{18}\text{BrO}_2]^+$: 297.0485, found 297.0483.



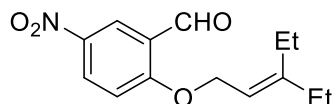
2-((3-ethylpent-2-en-1-yl)oxy)-5-iodobenzaldehyde

63 was prepared from 2-hydroxy-5-iodobenzaldehyde (744.1 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a white solid (880.0 mg, 86%). IR (Film): 3096, 2966, 2933, 2870, 1672, 1584, 1472, 1405, 1275, 1238, 1182, 1119, 989, 871, 816, 656, 626, 526 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.37 (s, 1H), 8.09 (d, $J = 2.3$ Hz, 1H), 7.78 (dd, $J = 8.8, 2.4$ Hz, 1H), 6.79 (d, $J = 8.8$ Hz, 1H), 5.41 (t, $J = 6.6$ Hz, 1H), 4.65 (d, $J = 6.6$ Hz, 2H), 2.19 – 2.09 (m, 4H), 1.07 – 1.00 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 188.5, 160.9, 150.2, 144.0, 136.9, 126.8, 116.3, 115.5, 82.8, 65.5, 29.1, 24.0, 13.4, 12.4. MS (DART) exact mass calculated for $[\text{C}_{14}\text{H}_{18}\text{IO}_2]^+$: 345.0346, found 345.0333.



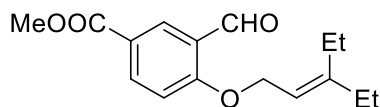
2-((3-ethylpent-2-en-1-yl)oxy)-5-(trifluoromethoxy)benzaldehyde

64 was prepared from 2-hydroxy-5-(trifluoromethoxy)benzaldehyde (618.4 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (789.0 mg, 87%). IR (Film): 2969, 2937, 2877, 1687, 1609, 1488, 1428, 1390, 1248, 1218, 1197, 1151, 1102, 982, 880, 817, 771, 633, 561 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.45 (s, 1H), 7.69 (d, $J = 3.1$ Hz, 1H), 7.38 (dd, $J = 9.1, 3.0$ Hz, 1H), 7.02 (d, $J = 9.1$ Hz, 1H), 5.43 (t, $J = 6.7$ Hz, 1H), 4.69 (d, $J = 6.6$ Hz, 2H), 2.19 – 2.10 (m, 4H), 1.08 – 1.01 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 188.7, 159.7, 150.4, 142.6 (q, $J = 2.3$ Hz), 128.5, 125.6, 120.7, 120.5 (q, $J = 257.1$ Hz), 116.3, 114.4, 65.8, 29.1, 24.0, 13.4, 12.4. MS (DART) exact mass calculated for $[\text{C}_{15}\text{H}_{18}\text{F}_3\text{O}_3]^+$: 303.1203, found 303.1202.



2-((3-ethylpent-2-en-1-yl)oxy)-5-nitrobenzaldehyde

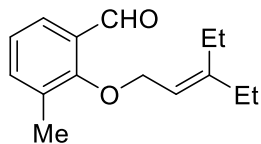
65 was prepared from 2-hydroxy-5-nitrobenzaldehyde (501.4 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 10:1) as a light yellow solid (402.8 mg, 51%). IR (Film): 2966, 2935, 2875, 1688, 1606, 1588, 1520, 1480, 1340, 1267, 1175, 1075, 967, 942, 799, 748, 665 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.47 (s, 1H), 8.70 (d, $J = 2.9$ Hz, 1H), 8.41 (dd, $J = 9.2, 2.9$ Hz, 1H), 7.12 (d, $J = 9.2$ Hz, 1H), 5.44 (t, $J = 6.7$ Hz, 1H), 4.81 (d, $J = 6.7$ Hz, 2H), 2.22 – 2.11 (m, 4H), 1.08 – 1.02 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 187.8, 165.1, 151.5, 141.4, 130.5, 124.8, 124.6, 115.4, 113.3, 66.3, 29.1, 24.1, 13.4, 12.3. MS (DART) exact mass calculated for $[\text{C}_{14}\text{H}_{18}\text{NO}_4]^+$: 264.1230, found 264.1232.



methyl 4-((3-ethylpent-2-en-1-yl)oxy)-3-formylbenzoate

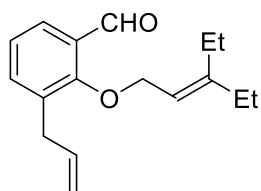
66 was prepared from methyl 3-formyl-4-hydroxybenzoate (540.5 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 10:1) as a white solid (596.9 mg, 72%). IR (Film): 2966, 2936, 2875, 1719, 1685, 1604, 1493, 1435, 1257, 1236, 1175, 1123, 977, 926, 830, 766 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.48 (s, 1H), 8.50 (d, $J = 2.3$ Hz, 1H), 8.21 (dd, $J = 8.8, 2.3$ Hz, 1H), 7.05 (d, $J = 8.8$ Hz, 1H), 5.44 (t, $J = 6.6$ Hz, 1H), 4.74 (d, $J = 6.6$ Hz, 2H), 3.90 (s, 3H), 2.20 – 2.09 (m, 4H), 1.07 – 1.01 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 189.1, 166.1, 164.3, 150.5, 137.0, 130.4, 124.6, 122.7, 116.1, 112.7, 65.6, 52.1, 29.1, 24.0, 13.4, 12.4. MS (DART) exact mass calculated for $[\text{C}_{16}\text{H}_{21}\text{O}_4]^+$: 277.1434,

found 277.1436.



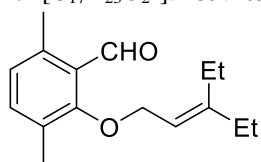
2-((3-ethylpent-2-en-1-yl)oxy)-3-methylbenzaldehyde

67 was prepared from 2-hydroxy-3-methylbenzaldehyde (408.5 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (467.0 mg, 67%). IR (Film): 2965, 2934, 2875, 1691, 1558, 1462, 1373, 1245, 1200, 1084, 945, 781 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.39 (s, 1H), 7.68 (d, $J = 7.7$ Hz, 1H), 7.45 (d, $J = 7.4$ Hz, 1H), 7.12 (t, $J = 7.6$ Hz, 1H), 5.50 (t, $J = 7.3$ Hz, 1H), 4.51 (d, $J = 7.2$ Hz, 2H), 2.37 (s, 3H), 2.09 (q, $J = 7.4$ Hz, 2H), 2.03 (q, $J = 7.6$ Hz, 2H), 1.03 (t, $J = 7.4$ Hz, 3H), 0.91 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 190.8, 160.6, 150.4, 137.4, 132.6, 129.8, 126.0, 124.2, 116.9, 72.0, 29.1, 23.7, 16.0, 13.4, 12.3. MS (DART) exact mass calculated for $[\text{C}_{15}\text{H}_{21}\text{O}_2]^+$: 233.1536, found 233.1538.



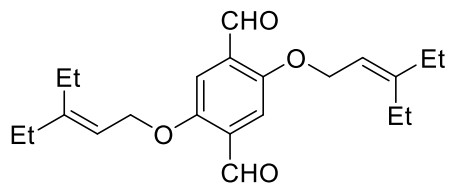
3-allyl-2-((3-ethylpent-2-en-1-yl)oxy)benzaldehyde

68 was prepared from 3-allyl-2-hydroxybenzaldehyde (486.6 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (542.6 mg, 70%). IR (Film): 3078, 2966, 2934, 2875, 2746, 1686, 1587, 1463, 1448, 1384, 1253, 1238, 1196, 1075, 956, 919, 776, 668 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.40 (s, 1H), 7.75 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.50 (dd, $J = 7.5, 1.8$ Hz, 1H), 7.20 (t, $J = 7.6$ Hz, 1H), 6.06 – 5.96 (m, 1H), 5.52 (t, $J = 7.3$ Hz, 1H), 5.18 – 5.09 (m, 2H), 4.54 (d, $J = 7.3$ Hz, 2H), 3.52 (dt, $J = 6.5, 1.6$ Hz, 2H), 2.12 (q, $J = 7.4$ Hz, 3H), 2.04 (q, $J = 7.6$ Hz, 2H), 1.06 (t, $J = 7.5$ Hz, 3H), 0.93 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 190.6, 160.3, 150.5, 136.8, 136.5, 134.6, 123.0, 126.7, 124.4, 116.9, 116.5, 73.2, 33.4, 29.1, 23.7, 13.4, 12.3. MS (DART) exact mass calculated for $[\text{C}_{17}\text{H}_{23}\text{O}_2]^+$: 259.1693, found 259.1698.



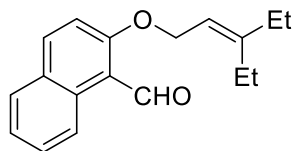
2-((3-ethylpent-2-en-1-yl)oxy)-3,6-dimethylbenzaldehyde

69 was prepared from 2-hydroxy-3,6-dimethylbenzaldehyde (450.5 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (480.4 mg, 65%). IR (Film): 2965, 2929, 2874, 1686, 1570, 1483, 1444, 1369, 1348, 1249, 1068, 971, 925, 814, 782, 702, 641 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 10.55 (s, 1H), 7.28 (d, $J = 7.7$ Hz, 1H), 6.90 (d, $J = 7.7$ Hz, 1H), 5.49 (t, $J = 7.2$ Hz, 1H), 4.45 (d, $J = 7.1$ Hz, 2H), 2.54 (s, 3H), 2.31 (s, 3H), 2.13 – 2.01 (m, 4H), 1.04 (t, $J = 7.4$ Hz, 3H), 0.92 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 193.2, 161.9, 150.0, 139.1, 136.2, 129.5, 128.1, 127.3, 117.1, 72.1, 29.1, 23.7, 21.0, 15.4, 13.4, 12.3. MS (DART) exact mass calculated for $[\text{C}_{16}\text{H}_{23}\text{O}_2]^+$: 247.1692, found 247.1699.



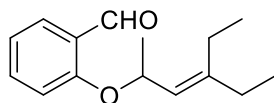
2,5-bis((3-ethylpent-2-en-1-yl)oxy)terephthalaldehyde

70 was prepared from 2,5-dihydroxyterephthalaldehyde⁷ (249.2 mg, 1.5 mmol), 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) and K₂CO₃ (456.1 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 10:1) as a yellow solid (435.6 mg, 81%). IR (Film): 3050, 2967, 2933, 2874, 1674, 1483, 1418, 1390, 1372, 1283, 1207, 1140, 1090, 1014, 891, 819, 695 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 10.49 (s, 2H), 7.44 (s, 2H), 5.40 (t, *J* = 6.7 Hz, 2H), 4.65 (d, *J* = 6.6 Hz, 4H), 2.17 – 2.06 (m, 8H), 1.01 (q, *J* = 7.5 Hz, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 189.5, 155.1, 150.0, 129.4, 116.6, 112.2, 65.9, 29.1, 23.9, 13.4, 12.4. MS (DART) exact mass calculated for [C₂₂H₃₁O₄]⁺: 359.2217, found 359.2215



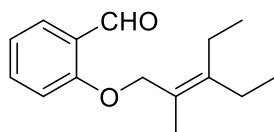
2-((3-ethylpent-2-en-1-yl)oxy)-1-naphthaldehyde

71 was prepared from 2-hydroxy-1-naphthaldehyde (516.5 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a white solid (708.5 mg, 88%). IR (Film): 2965, 2934, 2875, 1660, 1590, 1460, 1435, 1339, 1238, 1152, 1065, 1046, 1018, 863, 812, 751, 709, 651 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 10.92 (s, 1H), 9.29 (d, *J* = 8.6 Hz, 1H), 8.03 (d, *J* = 9.1 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.62 (t, *J* = 8.3 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 9.1 Hz, 1H), 5.48 (t, *J* = 6.7 Hz, 1H), 4.82 (d, *J* = 6.6 Hz, 2H), 2.18 (q, *J* = 7.6 Hz, 2H), 2.13 (q, *J* = 7.4 Hz, 2H), 1.07 – 1.02 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 192.4, 163.7, 150.1, 137.3, 131.6, 129.8, 128.5, 128.2, 125.0, 124.7, 117.2, 116.8, 114.2, 66.3, 29.1, 24.0, 13.4, 12.4. MS (DART) exact mass calculated for [C₁₈H₂₁O₂]⁺: 269.1536, found 269.1539.



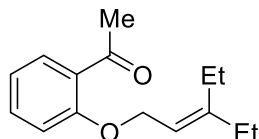
2-((4-ethylhex-3-en-2-yl)oxy)benzaldehyde

72 was prepared from ethyl 2-hydroxybenzoate (498.5 mg, 3.0 mmol) by the literature.⁶ The product was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (299.7 mg, 43%). IR (Film): 3074, 2967, 2933, 2875, 2758, 1686, 1597, 1477, 1457, 1283, 1236, 1187, 1160, 1037, 946, 829, 753, 654 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 10.50 (s, 1H), 7.81 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.01 – 6.94 (m, 2H), 5.22 – 5.12 (m, 2H), 2.22 – 2.00 (m, 4H), 1.47 (d, *J* = 6.1 Hz, 3H), 1.03 – 0.96 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 190.4, 161.0, 146.1, 135.6, 128.0, 125.8, 124.0, 120.6, 115.1, 72.7, 28.6, 23.9, 22.0, 13.0, 12.4. MS (DART) exact mass calculated for [C₁₅H₂₁O₂]⁺: 233.1536, found 233.1521.



2-((3-ethyl-2-methylpent-2-en-1-yl)oxy)benzaldehyde

73 was prepared from salicylaldehyde (366.4 mg, 3.0 mmol) and 1-bromo-3-ethyl-2-methylpent-2-ene (630.7 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (592.5 mg, 85%). IR (Film): 3075, 2965, 2932, 2871, 2757, 1685, 1597, 1478, 1456, 1396, 1376, 1285, 1231, 1188, 1159, 1101, 1041, 982, 843, 814, 755, 645, 533 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 10.54 (s, 1H), 7.86 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.06 – 7.01 (m, 2H), 4.62 (s, 2H), 2.20 – 2.12 (m, 4H), 1.82 (s, 3H), 1.05 – 1.00 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 190.0, 161.8, 143.3, 135.9, 128.1, 125.2, 122.8, 120.5, 113.0, 69.6, 25.4, 24.9, 16.1, 14.1, 12.7. MS (DART) exact mass calculated for [C₁₅H₂₁O₂]⁺: 233.1536, found 233.1520.

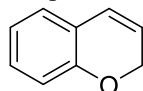


1-(2-((3-ethylpent-2-en-1-yl)oxy)phenyl)ethan-1-one

74 was prepared from 1-(2-hydroxyphenyl)ethan-1-one (408.5 mg, 3.0 mmol) and 1-bromo-3-ethylpent-2-ene (584.4 mg, 3.3 mmol) *via* general procedure. The product was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (508.8 mg, 73%). IR (Film): 2966, 2934, 2876, 1671, 1595, 1481, 1449, 1357, 1291, 1232, 1162, 1124, 988, 735, 593 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.74 (dd, $J = 7.6, 1.9$ Hz, 1H), 7.47 – 7.41 (m, 1H), 7.01 – 6.95 (m, 2H), 5.46 (t, $J = 6.6$ Hz, 1H), 4.65 (d, $J = 6.5$ Hz, 2H), 2.63 (s, 3H), 2.19 – 2.08 (m, 4H), 1.07 – 1.00 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 200.1, 158.4, 149.2, 133.5, 130.4, 128.6, 120.4, 117.1, 112.8, 65.2, 32.1, 29.1, 23.9, 13.3, 12.5. MS (DART) exact mass calculated for $[\text{C}_{15}\text{H}_{21}\text{O}_2]^+$: 233.1536, found 233.1538

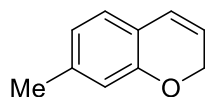
2.3 Synthesis and Characterization of 2H-Chromenes

General Procedure: To a 5 ml seal tube, aldehyde or ketone (0.2 mmol), catalyst (6.5 mg, 0.02 mmol) and EtOH (1.0 mL) were added. The solution was stirred for 12 h at 140 $^\circ\text{C}$. The solvent was then removed under reduced pressure and the residue was purified by flash chromatography on silica gel using PE and EtOAc as an eluent to afford the title compound.



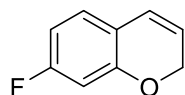
2H-chromene

Prepared *via* general procedure, the product **10** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (19.3 mg, 73%). ^1H NMR (500 MHz, CDCl_3) δ 7.13 (td, $J = 7.8, 1.7$ Hz, 1H), 6.98 (dd, $J = 7.4, 1.6$ Hz, 1H), 6.91 – 6.87 (m, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 6.45 (d, $J = 9.9$ Hz, 1H), 5.80 (dt, $J = 9.8, 3.6$ Hz, 1H), 4.85 (dd, $J = 3.6, 1.9$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 154.1, 129.1, 126.6, 124.6, 122.4, 122.0, 121.3, 115.7, 65.5.



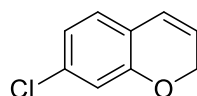
7-methyl-2H-chromene

Prepared *via* general procedure, the product **18** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (23.7 mg, 81%). ^1H NMR (500 MHz, CDCl_3) δ 6.85 (d, $J = 7.5$ Hz, 1H), 6.68 (d, $J = 7.5$ Hz, 1H), 6.61 (s, 1H), 6.40 (d, $J = 9.8$ Hz, 1H), 5.71 (dt, $J = 9.8, 3.6$ Hz, 1H), 4.80 (dd, $J = 3.6, 1.9$ Hz, 2H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 154.0, 139.4, 126.3, 124.5, 122.0, 120.8, 119.8, 116.3, 65.5, 21.4.



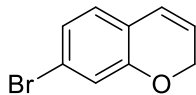
7-fluoro-2H-chromene

Prepared *via* general procedure, the product **19** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (21.9 mg, 73%). ^1H NMR (500 MHz, CDCl_3) δ 6.89 (dd, $J = 8.3, 6.5$ Hz, 1H), 6.56 (td, $J = 8.4, 2.5$ Hz, 1H), 6.50 (dd, $J = 10.1, 2.5$ Hz, 1H), 6.38 (d, $J = 9.9$ Hz, 1H), 5.71 (dt, $J = 9.9, 3.6$ Hz, 1H), 4.82 (dd, $J = 3.6, 1.9$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 163.0 (d, $J = 246.2$ Hz), 155.3 (d, $J = 12.3$ Hz), 127.3 (d, $J = 9.9$ Hz), 123.8 (d, $J = 1.5$ Hz), 120.5 (d, $J = 2.5$ Hz), 118.6 (d, $J = 3.2$ Hz), 107.9 (d, $J = 21.8$ Hz), 103.7 (d, $J = 25.1$ Hz), 65.6.



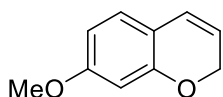
7-chloro-2H-chromene

Prepared *via* general procedure, the product **20** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (23.6 mg, 71%). ¹H NMR (500 MHz, CDCl₃) δ 6.88 – 6.81 (m, 2H), 6.77 (d, *J* = 1.8 Hz, 1H), 6.38 (dt, *J* = 10.0, 2.0 Hz, 1H), 5.76 (dt, *J* = 9.9, 3.6 Hz, 1H), 4.82 (dd, *J* = 3.5, 1.9 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 154.7, 133.9, 127.2, 123.8, 122.0, 121.4, 120.9, 116.2, 65.8.



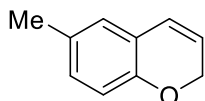
7-bromo-2H-chromene

Prepared *via* general procedure, the product **21** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (34.6 mg, 82%). ¹H NMR (500 MHz, CDCl₃) δ 6.98 (dd, *J* = 8.0, 1.9 Hz, 1H), 6.93 (d, *J* = 1.8 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.37 (dt, *J* = 10.0, 2.0 Hz, 1H), 5.78 (dt, *J* = 9.9, 3.6 Hz, 1H), 4.82 (dd, *J* = 3.6, 1.9 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 154.7, 127.5, 124.3, 123.8, 122.2, 121.7, 121.2, 119.1, 65.7.



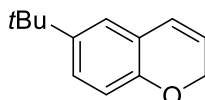
7-methoxy-2H-chromene

Prepared *via* general procedure, the product **22** was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (21.1 mg, 65%). ¹H NMR (500 MHz, CDCl₃) δ 6.87 (d, *J* = 8.3 Hz, 1H), 6.42 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.38 (dd, *J* = 9.9, 2.1 Hz, 2H), 5.63 (dt, *J* = 9.7, 3.5 Hz, 1H), 4.79 (dd, *J* = 3.6, 1.7 Hz, 2H), 3.77 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 160.6, 155.3, 127.2, 124.2, 118.9, 115.7, 106.9, 101.7, 65.6, 55.3.



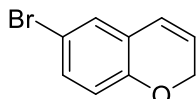
6-methyl-2H-chromene

Prepared *via* general procedure, the product **23** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (23.4 mg, 80%). ¹H NMR (500 MHz, CDCl₃) δ 6.91 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.78 (d, *J* = 2.2 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.39 (d, *J* = 10.1 Hz, 1H), 4.78 (dd, *J* = 3.6, 1.9 Hz, 2H), 2.25 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 151.9, 130.5, 129.5, 127.1, 124.7, 122.2, 122.1, 115.4, 65.5, 20.5.



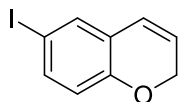
6-(tert-butyl)-2H-chromene

Prepared *via* general procedure, the product **24** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (33.9 mg, 90%). ¹H NMR (500 MHz, CDCl₃) δ 7.14 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.44 (dt, *J* = 9.8, 1.9 Hz, 1H), 5.78 (dt, *J* = 9.8, 3.5 Hz, 1H), 4.81 (dd, *J* = 3.6, 1.9 Hz, 2H), 1.31 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 151.8, 144.1, 126.0, 125.0, 123.5, 121.9, 121.8, 115.1, 65.5, 34.1, 31.5.



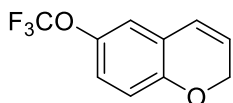
6-bromo-2H-chromene

Prepared *via* general procedure, the product **25** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (31.7 mg, 75%). ¹H NMR (500 MHz, CDCl₃) δ 7.17 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.06 (d, *J* = 2.4 Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 1H), 6.35 (d, *J* = 9.9 Hz, 1H), 5.80 (dt, *J* = 9.8, 3.5 Hz, 1H), 4.82 (dd, *J* = 3.6, 1.9 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 153.1, 131.6, 129.0, 124.1, 123.6, 123.2, 117.5, 113.2, 65.6.



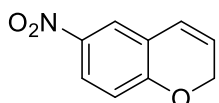
6-iodo-2H-chromene

Prepared *via* general procedure, the product **26** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (40.8 mg, 79%). ¹H NMR (500 MHz, CDCl₃) δ 7.36 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.24 (d, *J* = 2.2 Hz, 1H), 6.53 (d, *J* = 8.4 Hz, 1H), 6.33 (dt, *J* = 10.0, 2.0 Hz, 1H), 5.78 (dt, *J* = 9.8, 3.5 Hz, 1H), 4.83 (dd, *J* = 3.5, 1.9 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 153.9, 137.7, 134.9, 124.7, 123.4, 123.0, 118.0, 83.1, 65.6.



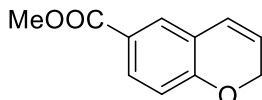
6-(trifluoromethoxy)-2H-chromene

Prepared *via* general procedure, the product **27** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (26.4 mg, 61%). IR (Film): 3056, 2968, 2928, 2852, 1490, 1441, 1253, 1197, 1153, 1034, 874, 695 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 6.94 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.82 (d, *J* = 2.7 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 1H), 6.38 (dt, *J* = 10.0, 2.0 Hz, 1H), 5.84 (dt, *J* = 9.9, 3.6 Hz, 1H), 4.84 (dd, *J* = 3.6, 1.9 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 152.4, 143.0, 123.7, 123.5, 123.1, 121.7, 120.6 (t, *J* = 256.0 Hz), 119.3, 116.5, 65.7. MS (DART) exact mass calculated for [C₁₀H₈F₃O₂⁺]: 217.0471, found 217.0469.



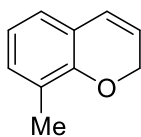
6-nitro-2H-chromene

Prepared *via* general procedure, the product **28** was purified by column chromatography (hexane: EtOAc = 15:1 to 10:1) as a light yellow solid (11.0 mg, 31%). ¹H NMR (500 MHz, CDCl₃) δ 8.00 (dd, *J* = 8.9, 2.7 Hz, 1H), 7.84 (d, *J* = 2.7 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 1H), 6.43 (dt, *J* = 10.0, 2.1 Hz, 1H), 5.87 (dt, *J* = 10.1, 3.4 Hz, 1H), 5.00 (dd, *J* = 3.4, 2.0 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 159.5, 141.8, 125.3, 123.6, 122.9, 122.2, 121.7, 116.0, 66.7.



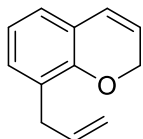
methyl 2H-chromene-6-carboxylate

Prepared *via* general procedure, the product **29** was purified by column chromatography (hexane: EtOAc = 20:1) as a white solid (19.4 mg, 51%). ¹H NMR (500 MHz, CDCl₃) δ 7.78 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.63 (d, *J* = 2.2 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.41 (d, *J* = 9.9 Hz, 1H), 5.77 (dt, *J* = 10.0, 3.5 Hz, 1H), 4.90 (dd, *J* = 3.4, 2.0 Hz, 2H), 3.86 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 166.7, 158.1, 131.2, 128.2, 123.8, 123.1, 122.3, 121.6, 115.6, 66.2, 51.9.



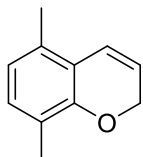
8-methyl-2H-chromene

Prepared *via* general procedure, the product **30** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (22.2 mg, 76%). ¹H NMR (500 MHz, CDCl₃) δ 6.98 (d, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 6.2 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.42 (dt, *J* = 9.8, 1.9 Hz, 1H), 5.77 (dt, *J* = 9.8, 3.6 Hz, 1H), 4.84 (dd, *J* = 3.5, 1.8 Hz, 2H), 2.18 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 152.0, 130.7, 125.1, 124.9, 124.3, 121.9, 121.6, 120.6, 65.5, 15.5.



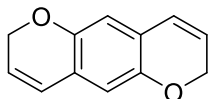
8-allyl-2H-chromene

Prepared *via* general procedure, the product **31** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (24.0 mg, 70%). ¹H NMR (500 MHz, CDCl₃) δ 6.99 (dd, *J* = 7.3, 1.9 Hz, 1H), 6.88 – 6.78 (m, 2H), 6.43 (dt, *J* = 9.8, 1.9 Hz, 1H), 6.04 – 5.95 (m, 1H), 5.78 (dt, *J* = 9.9, 3.6 Hz, 1H), 5.11 – 5.00 (m, 2H), 4.82 (dd, *J* = 3.6, 1.8 Hz, 2H), 3.34 (d, *J* = 6.4 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 151.6, 136.9, 129.8, 127.2, 125.0, 124.8, 122.3, 121.8, 120.9, 115.4, 65.5, 33.7. MS (DART) exact mass calculated for [C₁₂H₁₃O⁺]: 173.0961, found 173.0955



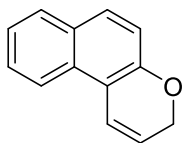
5,8-dimethyl-2H-chromene

Prepared *via* general procedure, the product **32** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (27.5 mg, 86%). ¹H NMR (500 MHz, CDCl₃) δ 6.88 (d, *J* = 7.6 Hz, 1H), 6.66 – 6.60 (m, 2H), 5.83 (dt, *J* = 9.9, 3.8 Hz, 1H), 4.76 (d, *J* = 2.0 Hz, 2H), 2.27 (s, 3H), 2.15 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 152.2, 131.6, 130.0, 122.8, 122.3, 122.2, 121.3, 120.6, 64.7, 18.2, 15.5.



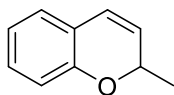
2,7-dihydropyrano[2,3-g]chromene

Prepared *via* general procedure, catalyst (13.0 mg, 0.04 mmol) was used, the product **33** was purified by column chromatography (hexane: EtOAc = 20:1) as a colorless oil (19.3 mg, 52%). ¹H NMR (500 MHz, CDCl₃) δ 6.43 (s, 2H), 6.35 (d, *J* = 9.8 Hz, 2H), 5.79 (dt, *J* = 9.8, 3.7 Hz, 2H), 4.73 (dd, *J* = 3.6, 1.8 Hz, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 148.3, 124.5, 122.8, 122.6, 113.3, 65.4.



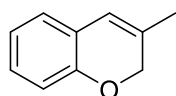
3H-benzo[f]chromene

Prepared *via* general procedure, the product **34** was purified by column chromatography (hexane: EtOAc = 30:1) as a white solid (30.9 mg, 85%). ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.37 – 7.33 (m, 1H), 7.14 (d, *J* = 9.9 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 5.92 (dt, *J* = 9.9, 3.9 Hz, 1H), 4.88 (dd, *J* = 3.9, 1.7 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 152.3, 129.9, 129.4, 129.4, 128.5, 126.6, 123.6, 121.4, 121.0, 120.3, 117.7, 115.4, 65.3.



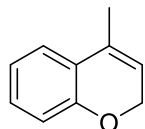
2-methyl-2H-chromene

Prepared *via* general procedure, 20 mol% catalyst was used and isopropanol (1.0 mL) was used as solvent, the product **35** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (22.1 mg, 75%). ¹H NMR (500 MHz, CDCl₃) δ 7.10 (t, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.38 (d, *J* = 9.8 Hz, 1H), 5.66 (dd, *J* = 9.8, 2.7 Hz, 1H), 5.03 – 4.97 (m, 1H), 1.45 (d, *J* = 6.6 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 153.5, 129.1, 126.9, 126.4, 123.8, 121.9, 121.0, 116.0, 71.4, 21.3.



3-methyl-2H-chromene

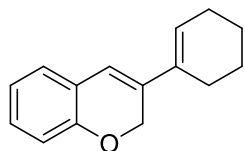
Prepared *via* general procedure, 20 mol% catalyst was used and isopropanol (1.0 mL) was used as solvent, the product **36** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (13.2 mg, 45%). ¹H NMR (500 MHz, CDCl₃) δ 7.05 (td, *J* = 7.7, 1.8 Hz, 1H), 6.91 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.16 (s, 1H), 4.69 (s, 2H), 1.80 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 152.6, 131.2, 128.0, 125.7, 122.8, 121.2, 119.3, 115.2, 69.2, 19.0.



4-methyl-2H-chromene

Prepared *via* general procedure, the product **37** was purified by column chromatography (hexane: EtOAc = 30:1) as a colorless oil (2.0 mg, 7%). ¹H NMR (500 MHz, CDCl₃) δ 7.16 – 7.10 (m, 2H), 6.91 (td, *J* = 7.5, 1.2 Hz, 1H), 6.80 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.58 (dt, *J* = 3.7, 1.9 Hz, 1H), 4.75 (dd, *J* = 3.7, 1.8 Hz, 2H), 2.03 (q, *J* = 1.8 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 154.1, 130.2, 128.9, 124.3, 123.5, 121.1, 118.4, 115.7, 65.4, 17.9.

During the screening of allyl groups, we found that cyclohexylidene ethyl ether could undergo some side reactions was found, like ene-reaction to form the by-product **75**, which was isolated and fully characterized.

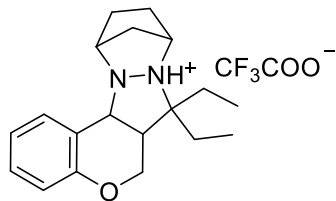


3-(cyclohex-1-en-1-yl)-2H-chromene

This compound **75** was purified by column chromatography (hexane: EtOAc = 30:1) as a white solid (7.7 mg, 18%). IR (Film): 3041, 2927, 2856, 2362, 2342, 1572, 1488, 1451, 1246, 1218, 1110, 931, 828, 746 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ 7.07 (td, *J* = 7.7, 1.7 Hz, 1H), 7.01 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.87 (td, *J* = 7.4, 1.2 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.40 (s, 1H), 5.78 – 5.74 (m, 1H), 4.96 (s, 2H), 2.33 – 2.28 (m, 2H), 2.22 – 2.17 (m, 2H), 1.77 – 1.71 (m, 2H), 1.66 – 1.60 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 153.3, 133.0, 132.5, 128.4, 126.8, 125.0, 123.1, 121.3, 116.7, 115.2, 66.2, 26.0, 25.0, 22.6, 22.2. MS (DART) exact mass calculated for [C₁₅H₁₇O⁺]: 213.1274, found 213.1268.

2.4 Experimental Details for Cycloaddition and Cycloreversion

Cycloaddition: In a 10 ml round bottle, 2-((3-ethylpent-2-en-1-yl)oxy)benzaldehyde (436.6 mg, 2 mmol) and 2,3-Diazobicyclo[2.2.1]heptane bis-trifluoroacetic acid (652.4 mg, 2 mmol) were dissolved in 5 ml of EtOH. The mixture was stirred at 80 °C for 1 h. Then EtOH was removed in vacuum and crude product was further purified by recrystallization from (DCM/Cyclohexane = 1:1) to give the product as white solid. Notably, concentration of the mother liquor and repetition of the process generally affords a second crop of equal purity. The combined yield could reach 90% (**51b**, 742.4 mg). X-ray qualified crystal (CCDC 1919817) was obtained from recrystallization in hot CH₃CN.



7,7-diethyl-6a,7,8,9,10,11,12,13a-octahydro-6H-9,12-methanochromeno[4',3':3,4]pyrazolo[1,2-a]pyridazin-8-ium 2,2,2-trifluoroacetate

IR (Film): 3467, 3071, 3021, 2982, 2947, 2877, 1666, 1583, 1494, 1415, 1195, 1168, 1121, 1093, 1054, 832, 795, 768, 720 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 14.30 (s, 1H), 7.82 (d, $J = 7.4$ Hz, 1H), 7.31 – 7.27 (m, 1H), 7.11 – 7.06 (m, 1H), 6.92 (d, $J = 8.2$ Hz, 1H), 5.56 (d, $J = 8.0$ Hz, 1H), 4.27 – 4.21 (m, 2H), 3.87 – 3.80 (m, 2H), 2.68 – 2.61 (m, 1H), 2.30 – 2.23 (m, 1H), 1.92 – 1.62 (m, 7H), 1.57 – 1.49 (m, 1H), 1.35 (d, $J = 11.9$ Hz, 1H), 1.05 (t, $J = 7.4$ Hz, 3H), 0.94 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 162.8 (q, $J = 34.8$ Hz), 154.3, 132.9, 130.9, 122.3, 117.4, 116.9 (q, $J = 293.6$ Hz), 112.6, 72.9, 61.7, 61.5, 61.0, 57.0, 41.4, 35.5, 31.9, 30.9, 25.1, 20.3, 9.2, 7.9. MS (DART) exact mass calculated for $[\text{C}_{19}\text{H}_{27}\text{N}_2\text{O}^+]$: 299.2118, found 299.2104.

Cycloreversion: To a 5 ml seal tube, salt (0.1 mmol, 41.2 mg) and EtOH (0.5 mL) were added. The solution was stirred for 2 h at 140 $^\circ\text{C}$. Then the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (PE:EtOAc = 20:1) to afford the product (9.9 mg, 75%).

2.5 Additive Effect on the Hydrazine-Catalyzed RCCOM

Procedure: To a 5 ml seal tube, aldehyde (0.1 mmol), catalyst (3.3 mg, 0.01 mmol), additive (0.1 mmol) and EtOH (1.0 mL) were added. The solution was stirred for 12 h at 140 $^\circ\text{C}$. The solvent was then removed under reduced pressure. The yields of **10** and recovery yields of additive were determined by ^1H NMR with CH_2Br_2 as the internal standard (Table S1).

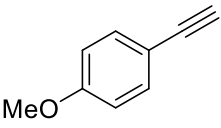
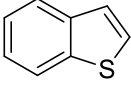
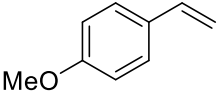
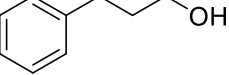
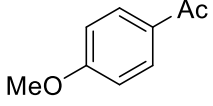
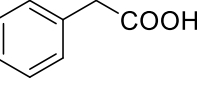
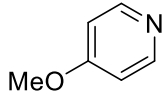
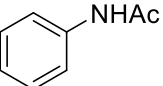
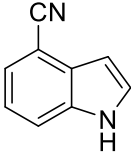
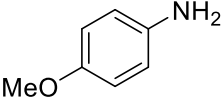
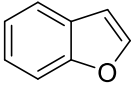
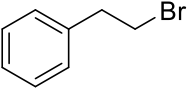
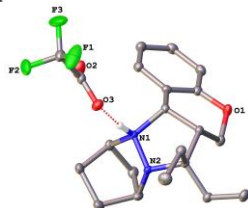
additive	yield (%)	recovery (%)	additive	yield (%)	recovery (%)
	71	90		76	89
	72	93		71	98
	71	95		78	99
	72	90		76	95
	75	99		51	38
	75	91		50	21

Table S1. Additive Effect on the Hydrazine-Catalyzed RCCOM

3. X-Ray Crystallographic Studies



Low-temperature X-ray diffraction data for **51b** (CCDC number: 1919817) were collected on a Rigaku XtaLAB Synergy diffractometer coupled to a Rigaku Hypix detector with Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$), from a PhotonJet micro-focus X-ray source at 100 K. The diffraction images were processed and scaled using the CrysAlisPro software.⁸ The structures were solved through intrinsic phasing using SHELXT⁹ and refined against F^2 on all data by full-matrix least squares with SHELXL¹⁰ following established refinement strategies.¹¹ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bound to carbon were included in the model at geometrically calculated positions and refined using a riding model. Hydrogen atoms bound to nitrogen were located in the difference Fourier synthesis and subsequently refined semi-freely with the help of distance restraints. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms they are linked to

(1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements are listed in Tables S2-S7.

Table S2. Crystal data and structure refinement for **51b**.

Identification code	ryz4_abs	
Empirical formula	C ₄₄ H ₅₇ F ₆ N ₅ O ₆	
Formula weight	865.94	
Temperature	99.96(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	I 1 2/a 1	
Unit cell dimensions	a = 17.95158(9) Å	α = 90 °
	b = 10.14969(5) Å	β = 98.4180(5) °
	c = 23.05206(13) Å	γ = 90 °
Volume	4154.90(4) Å ³	
Z	4	
Density (calculated)	1.384 Mg/m ³	
Absorption coefficient	0.931 mm ⁻¹	
F(000)	1832	
Crystal size	0.288 x 0.13 x 0.064 mm ³	
Theta range for data collection	4.769 to 70.073 °	
Index ranges	-21 ≤ h ≤ 21, -12 ≤ k ≤ 12, -28 ≤ l ≤ 27	
Reflections collected	82959	
Independent reflections	3944 [R(int) = 0.0349]	
Completeness to theta = 67.684 °	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.460	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3944 / 1 / 283	
Goodness-of-fit on F ²	1.039	
Final R indices [I > 2σ(I)]	R1 = 0.0354, wR2 = 0.0874	
R indices (all data)	R1 = 0.0360, wR2 = 0.0879	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.293 and -0.298 e.Å ⁻³	

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **51b**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
F(1)	6885(1)	6619(1)	6186(1)	55(1)
F(2)	7941(1)	5613(1)	6376(1)	35(1)
F(3)	7472(1)	6590(1)	7054(1)	55(1)
O(2)	7094(1)	4051(1)	7176(1)	30(1)
O(3)	6431(1)	4150(1)	6274(1)	21(1)
C(20)	6895(1)	4555(1)	6696(1)	17(1)
C(21)	7293(1)	5858(1)	6580(1)	23(1)
O(1)	4204(1)	1303(1)	7726(1)	19(1)
N(1)	5823(1)	1970(1)	6672(1)	13(1)
N(2)	5370(1)	1308(1)	6170(1)	14(1)
C(1)	6403(1)	943(1)	6905(1)	16(1)
C(2)	6876(1)	709(1)	6410(1)	20(1)
C(3)	6345(1)	-129(1)	5958(1)	22(1)
C(4)	5612(1)	-101(1)	6229(1)	19(1)
C(5)	5917(1)	-288(1)	6881(1)	20(1)
C(6)	5282(1)	2544(1)	7074(1)	13(1)
C(7)	5458(1)	2196(1)	7715(1)	14(1)
C(8)	6143(1)	2563(1)	8050(1)	16(1)
C(9)	6276(1)	2340(1)	8648(1)	18(1)
C(10)	5719(1)	1771(1)	8928(1)	19(1)
C(11)	5032(1)	1426(1)	8610(1)	18(1)
C(12)	4907(1)	1631(1)	8005(1)	15(1)
C(13)	4162(1)	1027(1)	7112(1)	16(1)
C(14)	4487(1)	2142(1)	6783(1)	14(1)
C(15)	4587(1)	1799(1)	6141(1)	14(1)
C(16)	4551(1)	3100(1)	5789(1)	17(1)
C(17)	4688(1)	2950(1)	5156(1)	25(1)
C(18)	4033(1)	773(1)	5838(1)	16(1)
C(19)	3224(1)	1266(1)	5686(1)	21(1)

N(3)	7500	1951(2)	5000	63(1)
C(22)	7500	3057(3)	5000	47(1)
C(23)	7500	4480(3)	5000	100(2)

Table S4. Bond lengths [\AA] and angles [$^\circ$] for **51b**.

F(1)-C(21)	1.3274(16)
F(2)-C(21)	1.3405(15)
F(3)-C(21)	1.3218(16)
O(2)-C(20)	1.2243(15)
O(3)-C(20)	1.2548(15)
C(20)-C(21)	1.5449(17)
O(1)-C(12)	1.3722(14)
O(1)-C(13)	1.4341(14)
N(1)-N(2)	1.4743(13)
N(1)-C(1)	1.5158(14)
N(1)-C(6)	1.5509(14)
N(2)-C(4)	1.4946(15)
N(2)-C(15)	1.4840(14)
C(1)-C(2)	1.5369(16)
C(1)-C(5)	1.5206(16)
C(2)-C(3)	1.5582(17)
C(3)-C(4)	1.5379(17)
C(4)-C(5)	1.5340(17)
C(6)-C(7)	1.5077(15)
C(6)-C(14)	1.5411(15)
C(7)-C(8)	1.4027(16)
C(7)-C(12)	1.3955(16)
C(8)-C(9)	1.3824(17)
C(9)-C(10)	1.3940(17)
C(10)-C(11)	1.3836(17)
C(11)-C(12)	1.3942(16)
C(13)-C(14)	1.5247(16)
C(14)-C(15)	1.5563(15)
C(15)-C(16)	1.5462(16)
C(15)-C(18)	1.5351(15)
C(16)-C(17)	1.5227(16)
C(18)-C(19)	1.5286(16)

N(3)-C(22)	1.122(3)
C(22)-C(23)	1.444(4)
O(2)-C(20)-O(3)	129.63(12)
O(2)-C(20)-C(21)	115.65(11)
O(3)-C(20)-C(21)	114.68(10)
F(1)-C(21)-F(2)	106.72(11)
F(1)-C(21)-C(20)	113.22(10)
F(2)-C(21)-C(20)	110.37(10)
F(3)-C(21)-F(1)	106.39(12)
F(3)-C(21)-F(2)	106.02(10)
F(3)-C(21)-C(20)	113.62(11)
C(12)-O(1)-C(13)	115.01(9)
N(2)-N(1)-C(1)	103.63(8)
N(2)-N(1)-C(6)	108.61(8)
C(1)-N(1)-C(6)	120.29(9)
N(1)-N(2)-C(4)	104.24(8)
N(1)-N(2)-C(15)	106.98(8)
C(15)-N(2)-C(4)	125.85(9)
N(1)-C(1)-C(2)	105.59(9)
N(1)-C(1)-C(5)	101.01(9)
C(5)-C(1)-C(2)	102.85(10)
C(1)-C(2)-C(3)	103.33(9)
C(4)-C(3)-C(2)	101.21(9)
N(2)-C(4)-C(3)	103.56(10)
N(2)-C(4)-C(5)	105.34(9)
C(5)-C(4)-C(3)	101.04(9)
C(1)-C(5)-C(4)	93.15(9)
C(7)-C(6)-N(1)	115.98(9)
C(7)-C(6)-C(14)	114.40(9)
C(14)-C(6)-N(1)	105.13(8)
C(8)-C(7)-C(6)	121.22(10)
C(12)-C(7)-C(6)	120.28(10)
C(12)-C(7)-C(8)	118.10(10)

C(9)-C(8)-C(7)	120.99(11)
C(8)-C(9)-C(10)	119.90(11)
C(11)-C(10)-C(9)	120.24(11)
C(10)-C(11)-C(12)	119.51(11)
O(1)-C(12)-C(7)	122.88(10)
O(1)-C(12)-C(11)	115.80(10)
C(11)-C(12)-C(7)	121.25(11)
O(1)-C(13)-C(14)	112.17(9)
C(6)-C(14)-C(15)	104.16(8)
C(13)-C(14)-C(6)	112.19(9)
C(13)-C(14)-C(15)	114.40(9)
N(2)-C(15)-C(14)	105.81(8)
N(2)-C(15)-C(16)	106.12(9)
N(2)-C(15)-C(18)	109.82(9)
C(16)-C(15)-C(14)	107.84(9)
C(18)-C(15)-C(14)	115.25(9)
C(18)-C(15)-C(16)	111.48(9)
C(17)-C(16)-C(15)	114.67(10)
C(19)-C(18)-C(15)	114.40(10)
N(3)-C(22)-C(23)	180.0

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **51b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
F(1)	32(1)	31(1)	96(1)	34(1)	-8(1)	-7(1)
F(2)	24(1)	29(1)	55(1)	-1(1)	21(1)	-6(1)
F(3)	61(1)	48(1)	61(1)	-35(1)	25(1)	-31(1)
O(2)	21(1)	42(1)	26(1)	12(1)	-2(1)	-5(1)
O(3)	20(1)	21(1)	20(1)	-1(1)	1(1)	-6(1)
C(20)	13(1)	19(1)	21(1)	0(1)	4(1)	0(1)
C(21)	17(1)	20(1)	31(1)	-3(1)	5(1)	-2(1)
O(1)	14(1)	28(1)	16(1)	1(1)	3(1)	-4(1)
N(1)	11(1)	14(1)	13(1)	-1(1)	1(1)	-1(1)
N(2)	11(1)	15(1)	16(1)	-4(1)	-1(1)	-1(1)
C(1)	12(1)	18(1)	19(1)	0(1)	0(1)	3(1)
C(2)	13(1)	24(1)	23(1)	-5(1)	3(1)	2(1)
C(3)	18(1)	24(1)	25(1)	-8(1)	2(1)	4(1)
C(4)	16(1)	14(1)	26(1)	-4(1)	0(1)	1(1)
C(5)	16(1)	16(1)	26(1)	2(1)	2(1)	2(1)
C(6)	12(1)	13(1)	15(1)	-1(1)	3(1)	0(1)
C(7)	15(1)	13(1)	14(1)	-1(1)	3(1)	1(1)
C(8)	16(1)	16(1)	18(1)	-1(1)	3(1)	-1(1)
C(9)	16(1)	20(1)	18(1)	-2(1)	0(1)	1(1)
C(10)	22(1)	21(1)	13(1)	1(1)	2(1)	4(1)
C(11)	19(1)	18(1)	18(1)	1(1)	6(1)	1(1)
C(12)	14(1)	14(1)	18(1)	-1(1)	2(1)	1(1)
C(13)	14(1)	21(1)	15(1)	0(1)	2(1)	-3(1)
C(14)	12(1)	16(1)	15(1)	0(1)	1(1)	0(1)
C(15)	11(1)	16(1)	15(1)	-1(1)	2(1)	0(1)
C(16)	17(1)	16(1)	17(1)	1(1)	2(1)	0(1)
C(17)	31(1)	25(1)	18(1)	4(1)	6(1)	-2(1)
C(18)	14(1)	18(1)	16(1)	-2(1)	1(1)	-2(1)
C(19)	14(1)	26(1)	23(1)	-1(1)	-1(1)	-3(1)

N(3)	101(2)	47(1)	32(1)	0	-22(1)	0
C(22)	69(2)	47(2)	19(1)	0	-17(1)	0
C(23)	195(5)	40(2)	47(2)	0	-45(2)	0

Table S6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **51b**.

	x	y	z	U(eq)
H(1)	6061(8)	2682(13)	6533(6)	16
H(1A)	6699	1145	7297	20
H(2A)	7344	223	6555	24
H(2B)	7008	1553	6235	24
H(3A)	6276	279	5564	27
H(3B)	6536	-1039	5931	27
H(4)	5222	-756	6063	22
H(5A)	5521	-234	7137	23
H(5B)	6214	-1106	6961	23
H(6)	5312	3525	7046	16
H(8)	6521	2970	7863	20
H(9)	6747	2575	8867	22
H(10)	5810	1620	9339	22
H(11)	4649	1052	8802	21
H(13A)	3629	885	6941	20
H(13B)	4441	205	7060	20
H(14)	4147	2924	6777	17
H(16A)	4049	3502	5790	20
H(16B)	4930	3716	5991	20
H(17A)	4277	2440	4936	37
H(17B)	5166	2491	5146	37
H(17C)	4710	3824	4977	37
H(18A)	4213	481	5473	20
H(18B)	4036	-4	6098	20
H(19A)	3204	1964	5390	32
H(19B)	3051	1615	6039	32
H(19C)	2898	535	5530	32
H(23A)	7916	4802	4807	151

H(23B)	7563	4802	5405	151
H(23C)	7021	4802	4788	151

Table S7. Hydrogen bonds for **51b** [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
N(1)-H(1)...O(3)	0.921(13)	1.770(13)	2.6871(13)	173.8(13)

Symmetry transformations used to generate equivalent atoms:

4. Computational Data

All DFT calculations were performed with the Gaussian 09 program package.¹² The geometry optimization of all the minima and transition states involved was carried out at the M06-2X level of theory¹³ with the 6-31G(d) basis set.¹⁴ The vibrational frequencies were computed at the same level to check whether each optimized structure is an energy minimum or a transition state and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298 K. Solvent effects in ethanol were computed at the M06-2X/6-311+G(d,p) level using the gas-phase optimized structures. Solvation energies were evaluated by a self-consistent reaction field (SCRF) using the PCM model.

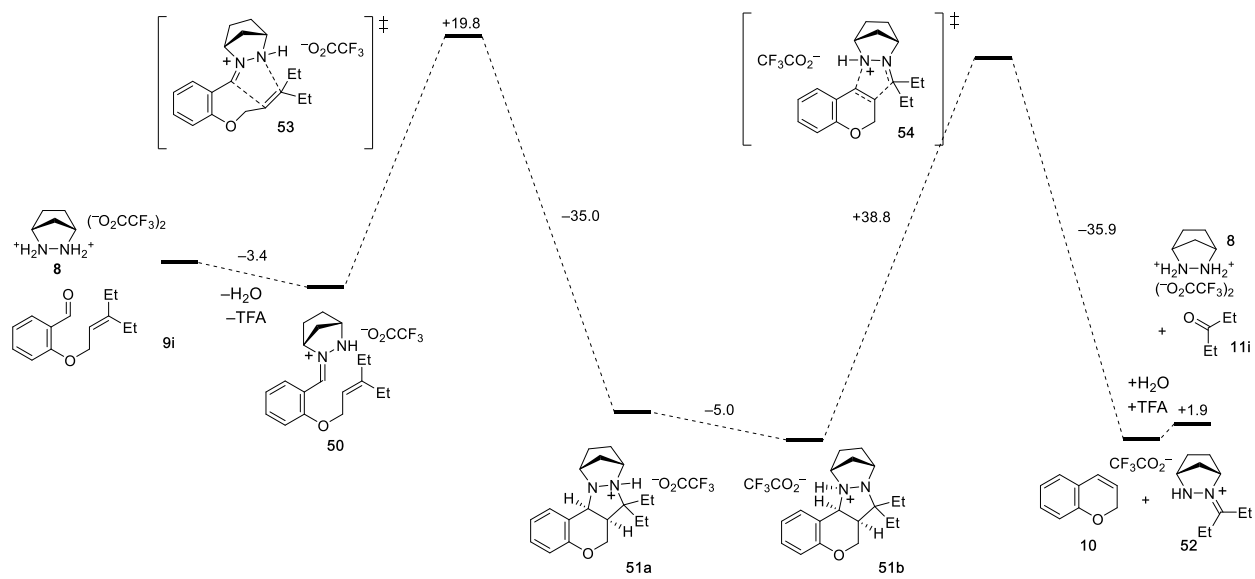
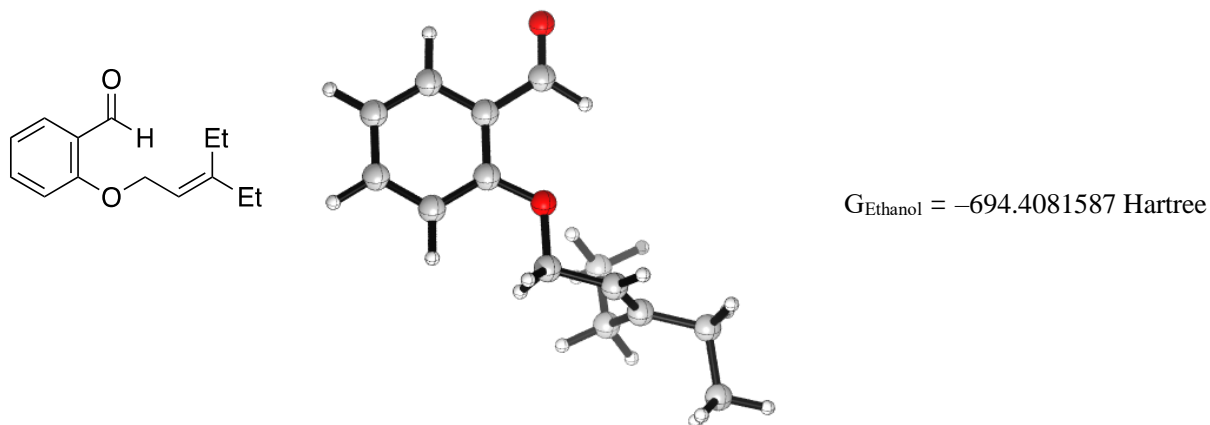


Table S8. Geometric coordinates and thermally corrected M06-2X energies for **9i**.



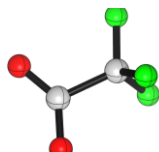
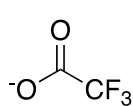
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	C	-1.28235500	0.70143300	-0.32123500
H	-0.06290700	-0.55435300	0.94435300	C	-2.25630100	0.96141800	0.55696800
H	0.26635900	-0.70817000	-0.79619500	C	-3.50917500	1.68543700	0.12914900
O	1.02847700	0.98660500	0.10452000	H	-3.71989400	2.48793300	0.84919000
C	2.28862600	0.57119000	0.38216100	H	-3.35043100	2.16145400	-0.84406300
C	2.65312400	-0.76758700	0.54925500	C	-4.71879400	0.74670400	0.04904000
C	3.97788100	-1.08764900	0.83736900	H	-5.62285100	1.29744000	-0.22520500
C	4.95006200	-0.09818400	0.96406500	H	-4.54835700	-0.03065300	-0.70145900
C	4.58243400	1.23038700	0.79879700	H	-4.90599000	0.25186000	1.00735800
C	3.26366300	1.57850200	0.50992600	C	-2.16488000	0.61276100	2.02776700
C	2.91490000	3.01120600	0.34767500	H	-1.77274500	-0.39927900	2.17306700
H	1.85687700	3.23143200	0.12407500	H	-3.16966200	0.61658000	2.46537200
O	3.72904700	3.90270000	0.45282700	C	-1.27968300	1.62050000	2.77252000
H	5.30312200	2.03764900	0.89045100	H	-0.26173300	1.60608600	2.37120500
H	5.97742200	-0.36281300	1.18969200	H	-1.66675900	2.63732700	2.65116600
H	4.24752700	-2.13201600	0.96490200	H	-1.23994400	1.39679100	3.84242000
H	1.92060100	-1.55992200	0.45664400	H	-1.38879100	1.04419900	-1.34902100

Table S9. Geometric coordinates and thermally corrected M06-2X energies for **8**.



Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	-2.43261200	0.31831100	-0.90968200
C	-1.19014400	0.34414500	0.89699900	H	-3.33910600	0.30661300	0.49391600
C	-1.23921100	-0.78041800	1.92865200	H	-3.33902900	-1.86746100	0.49376400
C	-1.19000800	-1.90486900	0.89690100	H	-2.43247600	-1.87890000	-0.90980200
C	0.00010100	-1.56050400	-0.00004900	H	-2.11029100	-0.78050600	2.59217800
H	-0.06621200	-2.00738300	-0.99712600	H	-0.33544700	-0.78040600	2.54568400
H	0.90491600	-1.96811300	0.45927900	H	-1.32426700	1.37888300	1.21852400
H	-1.32406100	-2.93965200	1.21830400	H	-0.06641100	0.44692900	-0.99704900
N	-2.46678200	-1.51948800	0.05971000	H	0.90476600	0.40771000	0.45932800
N	-2.46684100	-0.04122800	0.05978800				

Table S10. Geometric coordinates and thermally corrected M06-2X energies for **TFA anion**.



$$G_{\text{Ethanol}} = -526.3685844 \text{ Hartree}$$

Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	F	-0.51134700	-0.63826100	1.08021900
C	1.56986700	-0.00520900	-0.00000900	F	-0.51137800	-0.63866600	-1.07991500
O	2.09114500	1.11976200	0.00003200	F	-0.55696900	1.22770300	-0.00023100
O	2.02819700	-1.15935400	-0.00000600				

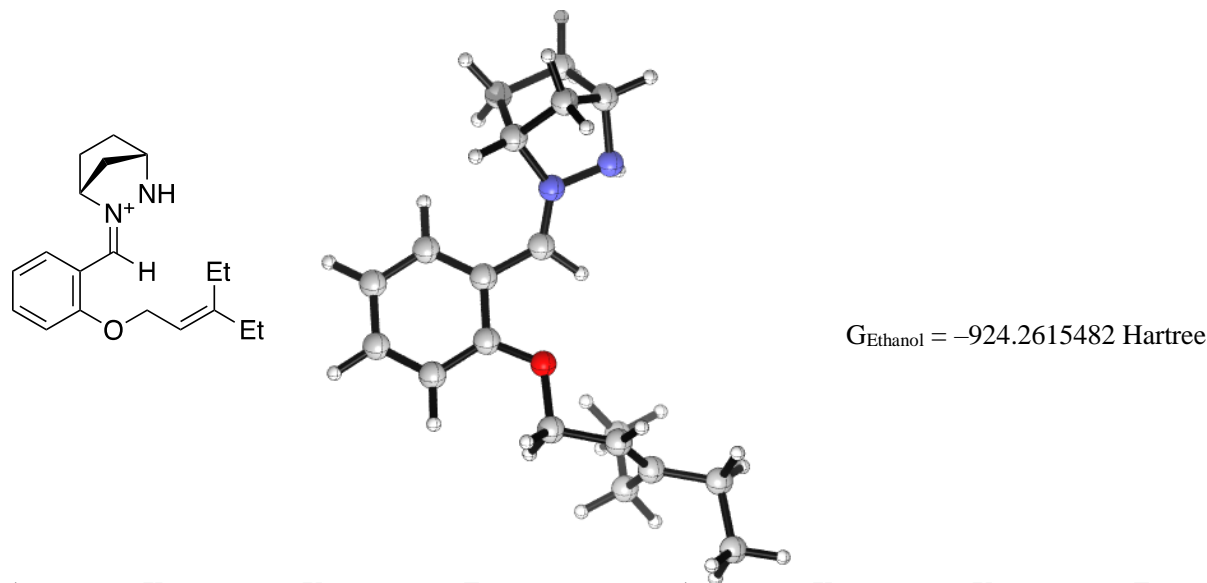
Table S11. Geometric coordinates and thermally corrected M06-2X energies for **H₃O⁺**.



$$G_{\text{Ethanol}} = -76.79917312 \text{ Hartree}$$

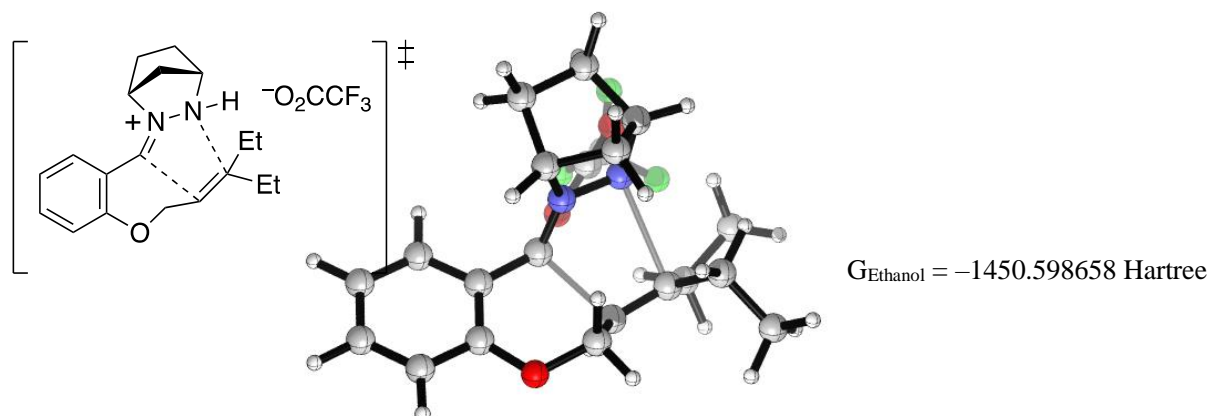
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	F	-0.51134700	-0.63826100	1.08021900
C	1.56986700	-0.00520900	-0.00000900	F	-0.51137800	-0.63866600	-1.07991500
O	2.09114500	1.11976200	0.00003200	F	-0.55696900	1.22770300	-0.00023100
O	2.02819700	-1.15935400	-0.00000600				

Table S12. Geometric coordinates and thermally corrected M06-2X energies for **50**.



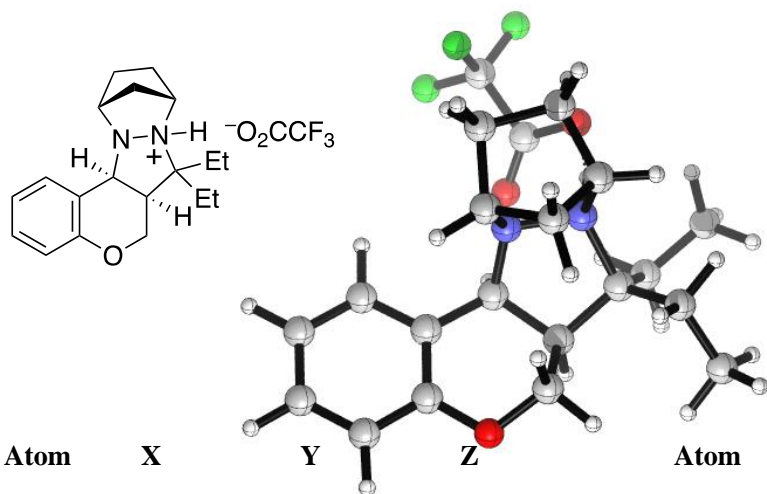
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	-7.58635600	-2.63066700	-0.95809500
H	0.37371000	0.58424600	0.84727200	H	-5.86449900	-2.85147700	-1.41865200
H	0.02978500	0.62151100	-0.90281200	H	-6.10103600	-0.45840200	-0.31065300
O	-1.38334600	-0.34146200	0.25465200	H	-5.56180100	0.86886900	1.38547400
C	-2.26362100	0.63962400	0.48730600	H	-5.03429000	3.27225700	1.23538200
C	-1.97204800	2.00592000	0.42712200	H	-2.73634000	3.98957500	0.63083400
C	-2.97503800	2.93186300	0.68123500	H	-0.97419100	2.34561400	0.18052000
C	-4.27409300	2.53279800	1.01248100	C	0.75482900	-1.27307400	-0.19136700
C	-4.57142700	1.18493900	1.07315500	C	1.61209000	-1.79668900	0.69293500
C	-3.58340100	0.22075800	0.80003600	C	2.33747300	-3.08380400	0.39029700
C	-3.78614500	-1.20226800	0.90528600	H	2.27794800	-3.74059200	1.26862800
H	-2.92407100	-1.83176400	1.12150600	H	1.84467400	-3.60504800	-0.43676700
N	-4.90077400	-1.84101200	0.76321800	C	3.81054200	-2.84064200	0.03856600
C	-6.20993800	-1.40273400	0.21830700	H	4.32572100	-3.78799200	-0.13879100
C	-6.55671700	-2.65722800	-0.59750700	H	3.89124900	-2.23039100	-0.86532500
C	-6.36646400	-3.58799500	0.60021400	H	4.33618500	-2.32007000	0.84489300
C	-7.33536100	-3.00116600	1.64270700	C	1.89608800	-1.18078400	2.04694800
H	-8.35245300	-3.36093800	1.46988500	H	2.03543500	-0.09723800	1.97253200
H	-7.05738000	-3.28123900	2.66253900	H	2.83887200	-1.58066400	2.43438300
C	-7.21607200	-1.46804300	1.38372400	C	0.76945900	-1.49291600	3.04002000
H	-8.16526200	-1.03231800	1.06262200	H	-0.17714600	-1.06134200	2.69656300
H	-6.87057800	-0.91230200	2.25920900	H	0.62663200	-2.57409500	3.13555000
H	-6.43665200	-4.65883700	0.41505500	H	0.99451900	-1.09119400	4.03152100
N	-4.96649800	-3.24570100	0.96568400	H	0.56804900	-1.79494000	-1.12793300
H	-4.77170600	-3.43330000	1.94971300				

Table S13. Geometric coordinates and thermally corrected M06-2X energies for **53**.



Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	0.91295000	-6.01126500	0.82222700
O	0.92156000	-0.94488100	-0.51979000	H	-1.11533100	-4.64760900	1.25603700
C	0.83837400	-2.23988700	-0.11361400	H	0.14034500	0.08322900	1.09017000
C	-0.27895800	-2.83080400	0.49174100	H	0.30733300	0.95039400	-0.44769100
C	-1.54674800	-2.09724600	0.75823400	C	-1.42951100	-0.35685200	-0.32299200
N	-1.78415300	-1.67380600	1.99507800	C	-2.50427900	0.40860100	0.10204900
N	-2.89450000	-0.88110400	2.19287700	C	-2.30127600	1.70818200	0.84003600
C	-2.79629400	-0.48472500	3.61319600	H	-3.09343800	1.85480800	1.58100000
C	-1.29035600	-0.21565000	3.72802800	H	-1.35052000	1.70560900	1.38198800
C	-0.93257100	-1.60945500	3.19745600	C	-2.30134300	2.88487100	-0.14922300
C	-1.64519600	-2.52191300	4.22174900	H	-3.25966600	2.95829300	-0.67212600
C	-2.97657500	-1.75227000	4.48075900	H	-2.12889300	3.82949900	0.37389900
H	-3.09226600	-1.48850800	5.53566400	H	-1.51823300	2.76304000	-0.90464700
H	-3.85976000	-2.30953400	4.16020900	C	-3.85483600	0.17054600	-0.53450400
H	-1.03697900	-2.60542500	5.12702400	H	-3.84147100	0.65949700	-1.52094200
H	-1.80134400	-3.52338100	3.81594600	H	-3.96959600	-0.90214600	-0.73086700
H	0.10435100	-1.84555900	2.96328400	C	-5.06414200	0.67675800	0.25136600
H	-0.96000000	-0.07466500	4.75947800	H	-5.10335800	0.23627000	1.25121600
H	-0.94074900	0.60653100	3.10181600	H	-5.06723200	1.76803000	0.34577900
H	-3.48103900	0.33838000	3.81713100	H	-5.98255800	0.38077900	-0.26117600
H	-3.79734900	-1.41956900	1.99305000	H	-1.55710200	-0.92230100	-1.24707800
H	-2.44949800	-2.40966500	0.22642000	C	-6.69122100	-3.10346100	0.36442900
C	-0.23060000	-4.19495300	0.81549200	C	-5.25357500	-2.76890000	0.82594900
C	0.89801500	-4.95803800	0.56393200	O	-4.35010300	-3.04766200	0.02585800
C	2.00504500	-4.35709800	-0.03926000	O	-5.19041600	-2.18115600	1.93682500
C	1.97461600	-3.01464900	-0.37575400	F	-7.19584300	-2.04775400	-0.30711300
H	2.81900500	-2.52617700	-0.85011700	F	-7.51433600	-3.35515700	1.38671200
H	2.89541900	-4.94053300	-0.25180800	F	-6.72953500	-4.15407200	-0.45878100

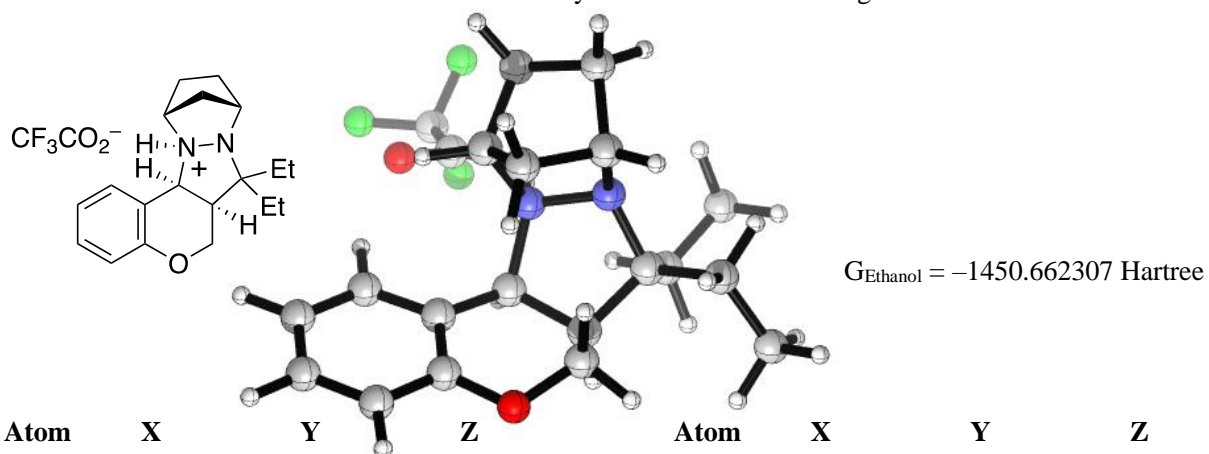
Table S14. Geometric coordinates and thermally corrected M06-2X energies for **51a**.



$G_{\text{Ethanol}} = -1450.654375$ Hartree

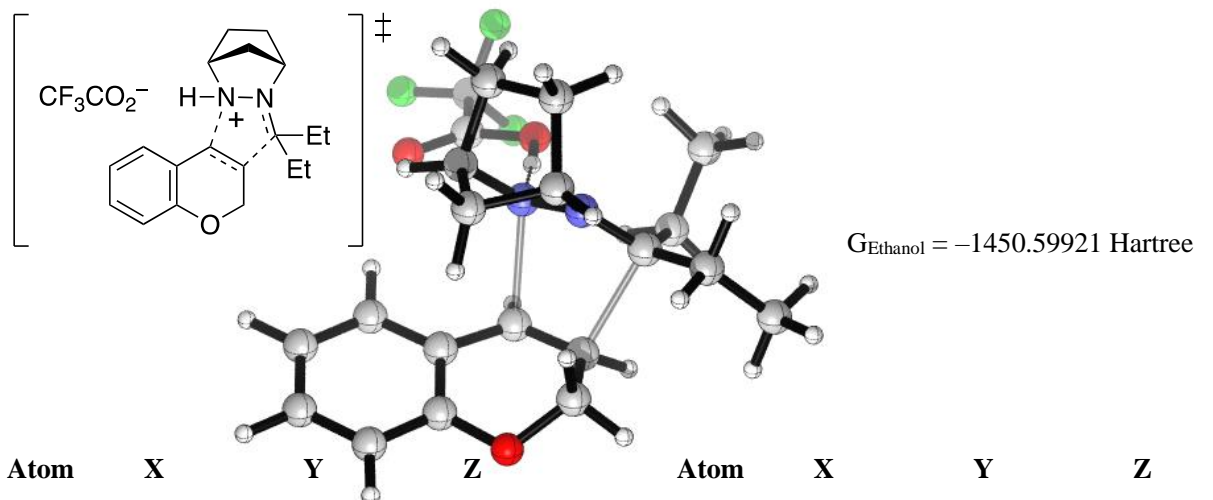
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	C	0.74848200	4.57090000	-0.21004100
C	1.01520100	-1.09725800	0.16454700	H	0.04499000	5.01198800	-0.92047600
C	2.37994800	-0.81551100	0.07460800	H	1.24993900	5.38892000	0.31333800
O	2.84459300	0.45958400	-0.08925000	H	1.50350200	4.03087200	-0.78971000
C	1.98130600	1.46187200	0.42317800	C	-1.39441300	2.67918900	-1.06222600
H	1.89837700	1.31407200	1.50564400	H	-0.75568800	3.07553400	-1.85894900
H	2.49113100	2.40941000	0.23920300	H	-1.81029600	1.73187100	-1.42735200
C	0.61976600	1.37808900	-0.26834900	C	-2.53342200	3.65815200	-0.78036000
C	-0.49165100	2.37323400	0.15112300	H	-3.17491200	3.73107900	-1.66212100
N	-1.37768500	1.53771100	1.12220700	H	-3.17169400	3.31624400	0.03979400
C	-1.49529400	1.89949600	2.58370400	H	-2.16921800	4.66492100	-0.55050200
C	-0.21576500	1.29872700	3.16292000	H	0.80756800	1.48767200	-1.34188200
C	-0.52048700	-0.08815900	2.57662600	C	3.32514500	-1.84138300	0.12329200
C	-1.86293400	-0.40464000	3.26009700	C	2.90334700	-3.15315000	0.28141500
C	-2.57916900	0.97865900	3.18813800	C	1.54253600	-3.45199600	0.38706300
H	-2.83982800	1.35656300	4.18053600	C	0.60961700	-2.42700600	0.31695300
H	-3.47964000	0.94921600	2.57335700	H	-0.45638400	-2.63967900	0.36094300
H	-1.71354700	-0.73401800	4.29285100	H	1.21493700	-4.47927100	0.50596000
H	-2.40781200	-1.17322700	2.71110600	H	3.63971500	-3.94976900	0.32501600
H	0.25043300	-0.85513500	2.64242200	H	4.37546100	-1.58251200	0.04121200
N	-0.89061600	0.16259400	1.16245900	H	-0.66751800	-0.25958800	-0.82957100
H	-0.23774000	1.29549400	4.25543300	C	-4.68853700	-1.15214200	0.03143800
H	0.70509400	1.76845400	2.82637100	C	-3.63272100	-0.08846400	-0.34575300
H	-1.67491300	2.96755100	2.69029600	O	-2.82558600	-0.35822900	-1.22840500
H	-2.40938200	1.43111700	0.70119100	O	-3.73505700	0.96396800	0.36388700
C	0.03269400	3.66324500	0.79538200	F	-5.93391000	-0.68354400	-0.11311600
H	-0.80027000	4.22479200	1.23063600	F	-4.54217600	-1.49878800	1.32786200
H	0.71306900	3.43018200	1.62079400	F	-4.57967800	-2.26379500	-0.69432000

Table S15. Geometric coordinates and thermally corrected M06-2X energies for **51b**.

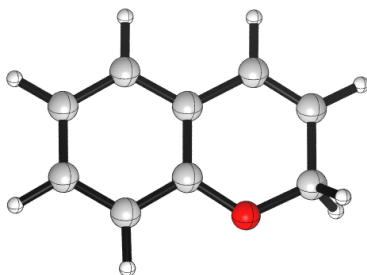
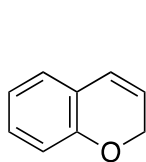


Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	-1.80994000	-4.52841900	-1.36471900
C	-0.45316500	1.41634500	0.24255900	H	-3.38920500	-4.43995100	-0.58002300
C	-1.79412900	1.76991500	0.05877100	H	-2.79469200	-3.07105500	-1.52736800
O	-2.75722200	0.87128900	-0.29805700	C	0.35239500	-2.95632600	-0.77674800
C	-2.49826200	-0.47909100	0.03534100	H	-0.10685600	-3.11110800	-1.76000000
H	-2.61202000	-0.61159400	1.11832400	H	1.16886800	-2.23903800	-0.92294800
H	-3.28978200	-1.05369000	-0.45127000	C	0.95286400	-4.25503000	-0.25192400
C	-1.12778100	-0.95236700	-0.43913700	H	1.76349100	-4.58521000	-0.90606900
C	-0.70458300	-2.32152600	0.15870300	H	1.37044700	-4.09707100	0.74619600
N	-0.00515300	-1.98016300	1.41000000	H	0.21550000	-5.06376600	-0.19947300
C	-0.58925400	-1.85825400	2.77227200	H	-1.14327300	-0.99564900	-1.53313900
C	-0.70034400	-0.34422400	3.02442300	C	-2.20400800	3.09936200	0.18107300
C	0.72274500	-0.08588200	2.53824000	C	-1.27483900	4.08190000	0.48362400
C	1.56613600	-1.03792500	3.41091900	C	0.07103000	3.74979400	0.65238100
C	0.58765500	-2.21697500	3.69877400	C	0.47561400	2.42989800	0.51668200
H	0.27212800	-2.23741300	4.74663600	H	1.52667700	2.16116000	0.61180100
H	1.01021200	-3.18811600	3.43595300	H	0.80373000	4.51943800	0.87021600
H	1.87166100	-0.52011400	4.32290200	H	-1.59959600	5.11350300	0.57915700
H	2.46855000	-1.35432900	2.88250900	H	-3.25320700	3.32786700	0.02710700
H	1.09151500	0.93167700	2.45793200	H	0.78970400	0.01917100	-0.75812200
N	0.67801100	-0.72054200	1.17741200	C	5.12647000	-0.24248300	0.08179500
H	-0.81504700	-0.11477200	4.08653700	C	3.64581200	-0.18353800	0.51532200
H	-1.45805900	0.19356300	2.45576100	O	3.21789500	0.85982900	1.00864900
H	-1.48539700	-2.46774300	2.88279900	O	3.02012400	-1.27215200	0.32141300
C	-1.85636400	-3.29521900	0.43532100	H	1.71500300	-0.96993400	0.83838000
H	-1.46751100	-4.11675200	1.04855800	F	5.23560800	-0.64197700	-1.19222600
H	-2.62804000	-2.80486800	1.03843100	F	5.79782500	-1.12158800	0.84043600
C	-2.49539100	-3.86366400	-0.83218100	F	5.73013500	0.94031600	0.19275200

Table S16. Geometric coordinates and thermally corrected M06-2X energies for **54i**.

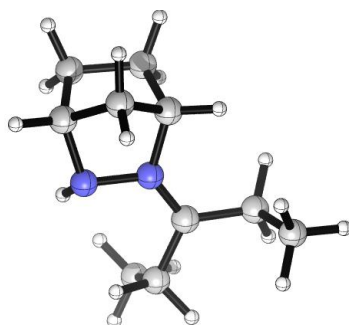
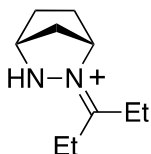


Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	4.83072500	-0.67865200	3.74677700
O	-0.49349300	1.32638800	-0.16103900	H	3.63123700	1.61218600	3.00329500
C	0.31041800	2.28471300	0.38118800	N	3.26983200	-0.05222700	1.76171800
C	1.69995700	2.09655600	0.48714300	H	1.48813800	0.72939000	4.46375600
C	2.28087400	0.87274800	-0.07428900	H	1.05322900	1.04059700	2.75055800
C	1.43182900	-0.16203200	-0.44374100	H	0.79137300	-1.57618300	3.19029700
H	1.63981300	-0.72721800	-1.34685600	C	1.05652700	-2.88319900	0.95037700
H	3.26071300	0.97397200	-0.53331300	H	1.36308300	-3.61049800	1.71656800
C	2.47643300	3.13643200	1.01501000	H	0.14336400	-2.41013000	1.32839200
C	1.88813600	4.32270800	1.43295700	C	0.72203900	-3.63187200	-0.33878500
C	0.50714700	4.49316700	1.31287000	H	-0.14885500	-4.27297400	-0.18144900
C	-0.28250000	3.48041700	0.78298100	H	0.48754500	-2.93755300	-1.15218600
H	-1.35618100	3.59039800	0.67112900	H	1.54865300	-4.26917100	-0.66420600
H	0.04273800	5.42043100	1.63471300	C	3.32736200	-2.17073000	-0.09289800
H	2.50317200	5.11760600	1.84212000	H	2.96212900	-2.60364200	-1.02824900
H	3.55341300	2.99391800	1.08380900	H	3.87231000	-1.26434400	-0.36342000
H	-0.09542100	-0.25286200	1.07158200	C	4.27750200	-3.14250500	0.61253800
H	-0.68290600	-0.64130800	-0.56184400	H	5.13345300	-3.37518600	-0.02584300
C	2.14233100	-1.83329300	0.79305600	H	4.66530200	-2.69669800	1.53463000
N	2.41577100	-1.08912700	1.86979200	H	3.77444100	-4.08206500	0.86801300
C	1.72973400	-1.02608100	3.18383300	C	7.64796200	0.94544600	0.58041000
C	1.70954800	0.48548300	3.42185600	C	6.17671400	0.95470500	1.03684300
C	3.19652100	0.61687500	3.07141600	O	5.66619000	1.96475600	1.46969900
C	3.85329400	-0.34033800	4.09976400	O	5.63660900	-0.21921500	0.89652500
C	2.80918700	-1.49344500	4.18850500	H	4.59886400	-0.18626500	1.25877500
H	2.37485600	-1.57782300	5.18858800	F	7.74368800	0.54129900	-0.69077500
H	3.21574700	-2.46853000	3.90750200	F	8.35917000	0.09896300	1.33472700
H	3.98996800	0.15611200	5.06447500	F	8.19104200	2.15378200	0.67803900

Table S17. Geometric coordinates and thermally corrected M06-2X energies for **10**.

$$G_{\text{Ethanol}} = -422.8071578 \text{ Hartree}$$

Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	3.72924900	3.18679100	-0.00002500
C	0.04412000	1.50043400	-0.00003800	H	5.84760100	1.88511800	-0.00001700
C	1.19238400	2.17487400	-0.00005600	H	5.75366200	-0.60123600	-0.00003000
C	2.46762400	1.45884800	-0.00004000	H	3.54585900	-1.76288000	-0.00004700
C	2.43161100	0.05736700	-0.00004300	O	1.27010400	-0.64851500	-0.00007000
C	3.61161000	-0.68009300	-0.00004000	H	1.20983100	3.26148800	-0.00007700
C	4.83669400	-0.01994800	-0.00003200	H	-0.91677800	2.00717500	-0.00004200
C	4.89177400	1.37212800	-0.00002500	H	-0.54563800	-0.36211500	0.88218700
C	3.70614700	2.09960500	-0.00002700	H	-0.54574100	-0.36215800	-0.88210200

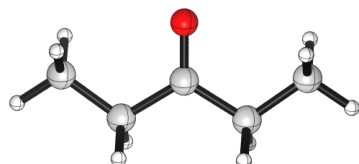
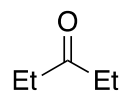
Table S18. Geometric coordinates and thermally corrected M06-2X energies for **52**.

$$G_{\text{Ethanol}} = -501.4806303 \text{ Hartree}$$

Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	C	-3.04686600	0.48981200	-1.41865000
C	-0.79372100	-0.59972500	-1.17575600	C	-3.76294300	-0.62062000	-0.70949900
C	0.19249400	-0.49246400	-2.34457700	H	-3.13240800	-1.07157500	0.06110200
C	0.37130000	1.01522400	-2.15874500	C	-4.24026100	-1.68196500	-1.71713300
C	0.82254700	1.12998500	-0.69086900	H	-4.81063700	-2.45236900	-1.19518500
H	0.61419600	2.12031200	-0.27634400	H	-3.39558900	-2.16092100	-2.22061100
H	1.89775500	0.95806200	-0.60254700	H	-4.88598600	-1.24093700	-2.48114800
H	0.97038400	1.54206900	-2.89990500	H	-4.62704100	-0.17984500	-0.20232200
N	-1.04543000	1.44669400	-2.28371000	C	-3.82240100	1.65646300	-1.94332000
H	-1.22114400	2.35188400	-1.84575900	H	-3.35005400	2.03163200	-2.85669200
N	-1.76851500	0.45288800	-1.58179400	C	-3.92517700	2.76789600	-0.88086100

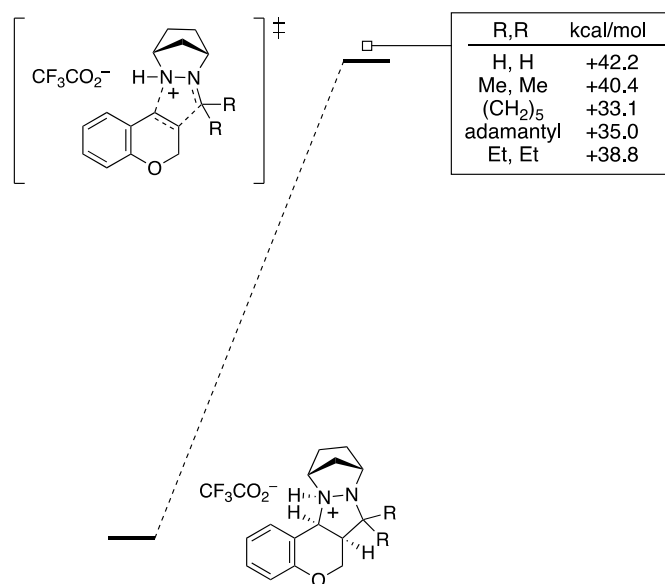
H	-2.94174900	3.14722700	-0.58422600	H	1.10537200	-1.05842200	-2.15216500
H	-4.49932900	3.60481200	-1.28213200	H	-1.29521500	-1.55067500	-1.01208700
H	-4.43097500	2.40938300	0.01944500	H	-0.65801200	0.36249300	0.79371600
H	-4.82688400	1.30533900	-2.19815100	H	0.64439500	-0.77253600	0.42613200
H	-0.23453700	-0.76617000	-3.31120400				

Table S19. Geometric coordinates and thermally corrected M06-2X energies for **11i**.



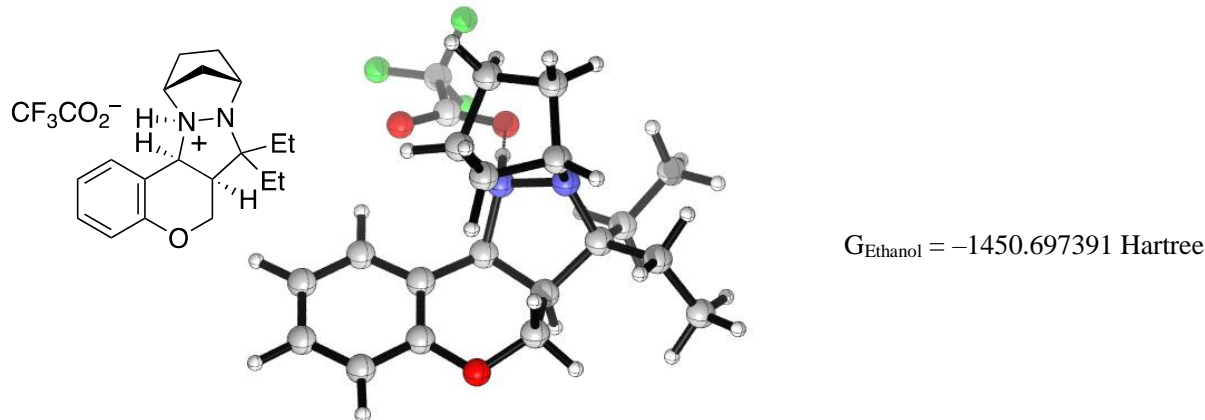
$$G_{\text{Ethanol}} = -271.62961 \text{ Hartree}$$

Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	C	-5.06099100	0.00000400	-0.00013100
H	0.00745300	0.64733300	0.87998000	H	-5.06851000	0.64768300	-0.87985600
H	0.91194600	-0.60210200	-0.00021200	H	-5.97293800	-0.60209600	-0.00007100
H	0.00750700	0.64804400	-0.87945600	H	-5.06844600	0.64770900	0.87957900
C	-1.23627200	-0.88796000	-0.00042800	H	-3.81074400	-1.55351500	0.87331600
C	-2.53049100	-0.09016500	-0.00031700	H	-3.81087300	-1.55358600	-0.87360000
O	-2.53046600	1.12038000	-0.00039300	H	-1.25008800	-1.55320100	-0.87417400
C	-3.82472300	-0.88793700	-0.00016700	H	-1.25028400	-1.55391100	0.87275800



*Trends for transition states of the cycloreversion step were calculated with the previously used level of theory, basis set, and solvation model. Thermal corrections were done at the reaction temperature for the cycloreversion step (413 K).

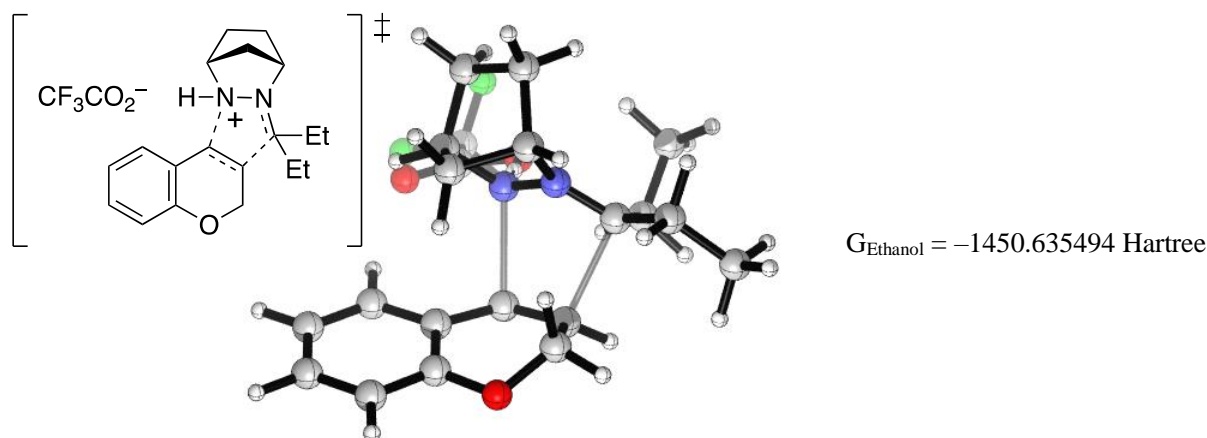
Table S20. Geometric coordinates and thermally corrected M06-2X energies for **51b**.



Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	N	-0.00512600	-1.98008500	1.41008700
C	-0.45342900	1.41628400	0.24250200	C	-0.58942300	-1.85810600	2.77226800
C	-1.79441400	1.76965600	0.05851300	C	-0.70056500	-0.34406200	3.02434800
O	-2.75730300	0.87087900	-0.29849700	C	0.72257200	-0.08572000	2.53829700
C	-2.49819300	-0.47943500	0.03503200	C	1.56588100	-1.03770700	3.41112100
H	-2.61202600	-0.61187800	1.11801800	C	0.58738800	-2.21675900	3.69892800
H	-3.28957700	-1.05419200	-0.45161300	H	0.27173700	-2.23715700	4.74675400
C	-1.12759000	-0.95254400	-0.43926100	H	1.00998200	-3.18790600	3.43619400
C	-0.70430400	-2.32162000	0.15868500	H	1.87126600	-0.51983800	4.32311700

H	2.46837600	-1.35412400	2.88285600	H	0.21634300	-5.06372400	-0.19924100
H	1.09131800	0.93185000	2.45798300	H	-1.14293900	-0.99586400	-1.53326300
N	0.67798400	-0.72044600	1.17750100	C	-2.20451700	3.09903300	0.18080300
H	-0.81536600	-0.11457000	4.08644300	C	-1.27554500	4.08170300	0.48355500
H	-1.45821700	0.19372100	2.45559700	C	0.07034800	3.74979500	0.65251100
H	-1.48555600	-2.46762100	2.88272700	C	0.47514500	2.42996200	0.51680700
C	-1.85599300	-3.29548300	0.43507200	H	1.52620200	2.16127800	0.61206800
H	-1.46711900	-4.11706500	1.04822300	H	0.80290000	4.51953700	0.87049900
H	-2.62778800	-2.80531200	1.03816600	H	-1.60047700	5.11325200	0.57907800
C	-2.49484600	-3.86380100	-0.83258000	H	-3.25372400	3.32738400	0.02667000
H	-1.80925800	-4.52835700	-1.36518600	H	0.78978500	0.01930000	-0.75803100
H	-3.38858800	-4.44026800	-0.58058200	C	5.12649800	-0.24202100	0.08173400
H	-2.79422500	-3.07111200	-1.52764100	C	3.64583500	-0.18315900	0.51526100
C	0.35292700	-2.95628400	-0.77658600	O	3.21771100	0.86030900	1.00817800
H	-0.10615400	-3.11120600	-1.75989200	O	3.02035700	-1.27198300	0.32179800
H	1.16928500	-2.23885900	-0.92271500	H	1.71511500	-0.96982500	0.83860300
C	0.95356000	-4.25485200	-0.25160500	F	5.23566600	-0.64230300	-1.19204100
H	1.76436100	-4.58490500	-0.90559400	F	5.79802400	-1.12055300	0.84089000
H	1.37094500	-4.09676000	0.74657500	F	5.72992900	0.94096000	0.19196400

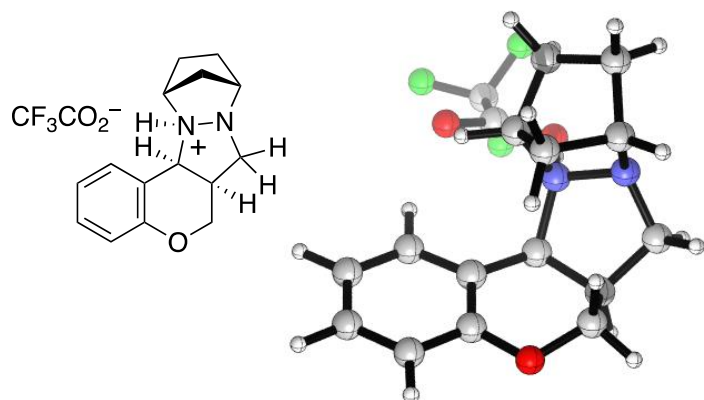
Table S21. Geometric coordinates and thermally corrected M06-2X energies for **54i**



Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	-1.35618100	3.59039800	0.67112900
O	-0.49349300	1.32638800	-0.16103900	H	0.04273800	5.42043100	1.63471300
C	0.31041800	2.28471300	0.38118800	H	2.50317200	5.11760600	1.84212000
C	1.69995700	2.09655600	0.48714300	H	3.55341300	2.99391800	1.08380900
C	2.28087400	0.87274800	-0.07428900	H	-0.09542100	-0.25286200	1.07158200
C	1.43182900	-0.16203200	-0.44374100	H	-0.68290600	-0.64130800	-0.56184400
H	1.63981300	-0.72721800	-1.34685600	C	2.14233100	-1.83329300	0.79305600
H	3.26071300	0.97397200	-0.53331300	N	2.41577100	-1.08912700	1.86979200
C	2.47643300	3.13643200	1.01501000	C	1.72973400	-1.02608100	3.18383300
C	1.88813600	4.32270800	1.43295700	C	1.70954800	0.48548300	3.42185600
C	0.50714700	4.49316700	1.31287000	C	3.19652100	0.61687500	3.07141600
C	-0.28250000	3.48041700	0.78298100	C	3.85329400	-0.34033800	4.09976400

C	2.80918700	-1.49344500	4.18850500	H	1.54865300	-4.26917100	-0.66420600
H	2.37485600	-1.57782300	5.18858800	C	3.32736200	-2.17073000	-0.09289800
H	3.21574700	-2.46853000	3.90750200	H	2.96212900	-2.60364200	-1.02824900
H	3.98996800	0.15611200	5.06447500	H	3.87231000	-1.26434400	-0.36342000
H	4.83072500	-0.67865200	3.74677700	C	4.27750200	-3.14250500	0.61253800
H	3.63123700	1.61218600	3.00329500	H	5.13345300	-3.37518600	-0.02584300
N	3.26983200	-0.05222700	1.76171800	H	4.66530200	-2.69669800	1.53463000
H	1.48813800	0.72939000	4.46375600	H	3.77444100	-4.08206500	0.86801300
H	1.05322900	1.04059700	2.75055800	C	7.64796200	0.94544600	0.58041000
H	0.79137300	-1.57618300	3.19029700	C	6.17671400	0.95470500	1.03684300
C	1.05652700	-2.88319900	0.95037700	O	5.66619000	1.96475600	1.46969900
H	1.36308300	-3.61049800	1.71656800	O	5.63660900	-0.21921500	0.89652500
H	0.14336400	-2.41013000	1.32839200	H	4.59886400	-0.18626500	1.25877500
C	0.72203900	-3.63187200	-0.33878500	F	7.74368800	0.54129900	-0.69077500
H	-0.14885500	-4.27297400	-0.18144900	F	8.35917000	0.09896300	1.33472700
H	0.48754500	-2.93755300	-1.15218600	F	8.19104200	2.15378200	0.67803900

Table S22. Geometric coordinates and thermally corrected M06-2X energies for **51b-H,H**.

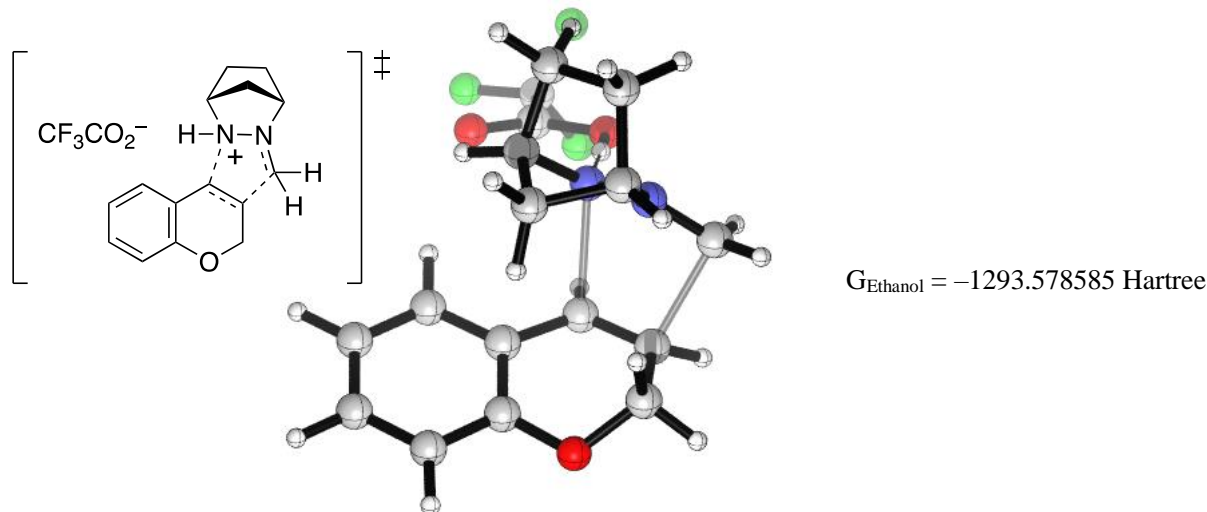


$$G_{\text{Ethanol}} = -1293.578585 \text{ Hartree}$$

Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	1.80605500	1.94198600	-3.91773800
C	-0.74469100	-1.07710700	-0.74788300	H	2.62151800	1.96530200	-2.34997500
C	-2.12700200	-1.22713800	-0.58919200	H	0.78828600	0.01473100	-2.72689000
O	-2.88485400	-0.40930400	0.19895600	N	0.79177900	1.00760000	-0.84066000
C	-2.35770200	0.87534900	0.45461500	H	1.91915500	0.86809700	-0.53264700
H	-2.47323100	1.50621000	-0.43674600	H	-0.89197300	1.98373400	-3.54197600
H	-2.98420200	1.30120900	1.24242300	H	-1.53519600	1.14404200	-2.11059900
C	-0.90228900	0.85306100	0.90813600	H	-0.98546500	3.68297100	-1.39606000
C	-0.28606800	2.25663900	0.82584400	H	-1.03041600	3.05565100	0.90730400
N	0.39735300	2.35714200	-0.45725900	H	0.45062400	2.39913200	1.62245700
C	-0.24201000	2.93231400	-1.67128700	H	-0.85866100	0.45669100	1.92616400
C	-0.69496500	1.71772600	-2.50062300	C	-2.80371900	-2.28476500	-1.20172400
C	0.65123000	1.01714700	-2.33441900	C	-2.10352700	-3.19809700	-1.97323700
C	1.65338700	2.07356900	-2.84411100	C	-0.72170400	-3.07228300	-2.13063000
C	0.95077900	3.42452900	-2.50811700	C	-0.05190100	-2.02826500	-1.50949600
H	0.61218700	3.94277900	-3.41048000	H	1.02916400	-1.93469900	-1.60358300
H	1.58550900	4.09553400	-1.92816600	H	-0.16758300	-3.79331400	-2.72186600

H	-2.63530600	-4.01617700	-2.44929200	O	2.98045200	-0.91197300	-1.75422800
H	-3.87469600	-2.36364400	-1.04821800	O	3.16465200	0.63930700	-0.13400800
H	0.78025000	-0.47510300	0.60473200	F	5.18251500	-1.08334000	0.70457100
C	5.05065600	-0.69673000	-0.57150100	F	5.86166200	0.35203500	-0.76325300
C	3.58700900	-0.31138800	-0.87249600	F	5.47310900	-1.69192900	-1.34921300

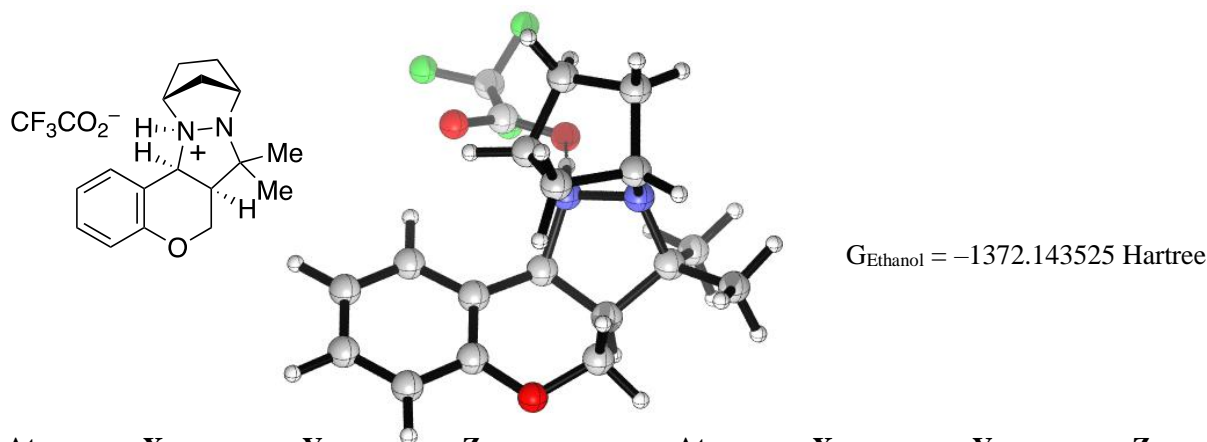
Table S23. Geometric coordinates and thermally corrected M06-2X energies for **54a**.



Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	-1.46711900	-4.11706500	1.04822300
C	-0.45342900	1.41628400	0.24250200	H	-2.62778800	-2.80531200	1.03816600
C	-1.79441400	1.76965600	0.05851300	C	-2.49484600	-3.86380100	-0.83258000
O	-2.75730300	0.87087900	-0.29849700	H	-1.80925800	-4.52835700	-1.36518600
C	-2.49819300	-0.47943500	0.03503200	H	-3.38858800	-4.44026800	-0.58058200
H	-2.61202600	-0.61187800	1.11801800	H	-2.79422500	-3.07111200	-1.52764100
H	-3.28957700	-1.05419200	-0.45161300	C	0.35292700	-2.95628400	-0.77658600
C	-1.12759000	-0.95254400	-0.43926100	H	-0.10615400	-3.11120600	-1.75989200
C	-0.70430400	-2.32162000	0.15868500	H	1.16928500	-2.23885900	-0.92271500
N	-0.00512600	-1.98008500	1.41008700	C	0.95356000	-4.25485200	-0.25160500
C	-0.58942300	-1.85810600	2.77226800	H	1.76436100	-4.58490500	-0.90559400
C	-0.70056500	-0.34406200	3.02434800	H	1.37094500	-4.09676000	0.74657500
C	0.72257200	-0.08572000	2.53829700	H	0.21634300	-5.06372400	-0.19924100
C	1.56588100	-1.03770700	3.41112100	H	-1.14293900	-0.99586400	-1.53326300
C	0.58738800	-2.21675900	3.69892800	C	-2.20451700	3.09903300	0.18080300
H	0.27173700	-2.23715700	4.74675400	C	-1.27554500	4.08170300	0.48355500
H	1.00998200	-3.18790600	3.43619400	C	0.07034800	3.74979500	0.65251100
H	1.87126600	-0.51983800	4.32311700	C	0.47514500	2.42996200	0.51680700
H	2.46837600	-1.35412400	2.88285600	H	1.52620200	2.16127800	0.61206800
H	1.09131800	0.93185000	2.45798300	H	0.80290000	4.51953700	0.87049900
N	0.67798400	-0.72044600	1.17750100	H	-1.60047700	5.11325200	0.57907800
H	-0.81536600	-0.11457000	4.08644300	H	-3.25372400	3.32738400	0.02667000
H	-1.45821700	0.19372100	2.45559700	H	0.78978500	0.01930000	-0.75803100
H	-1.48555600	-2.46762100	2.88272700	C	5.12649800	-0.24202100	0.08173400
C	-1.85599300	-3.29548300	0.43507200	C	3.64583500	-0.18315900	0.51526100

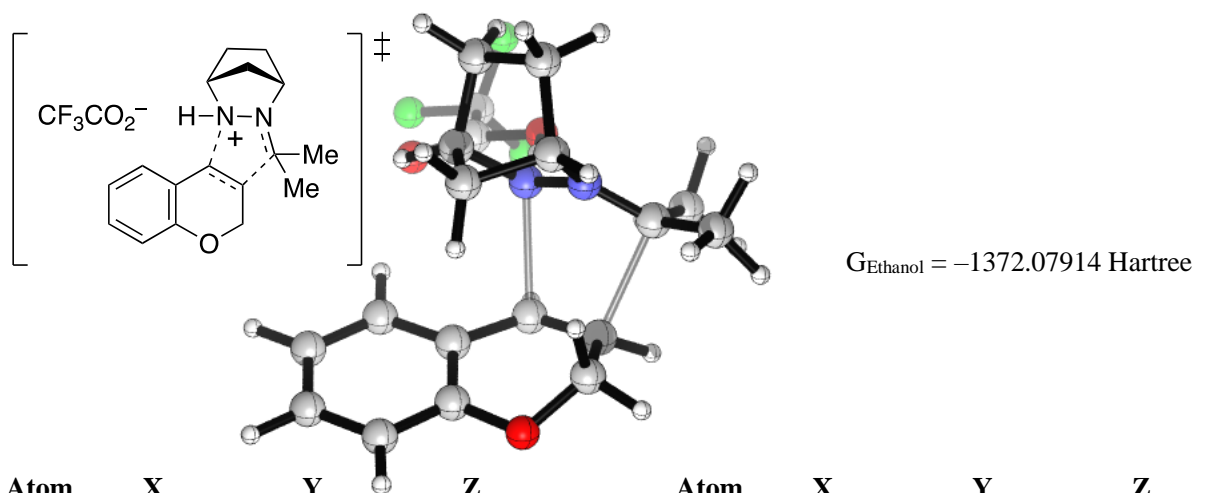
O	3.21771100	0.86030900	1.00817800	F	5.23566600	-0.64230300	-1.19204100
O	3.02035700	-1.27198300	0.32179800	F	5.79802400	-1.12055300	0.84089000
H	1.71511500	-0.96982500	0.83860300	F	5.72992900	0.94096000	0.19196400

Table S24. Geometric coordinates and thermally corrected M06-2X energies for **51b-Me,Me**.



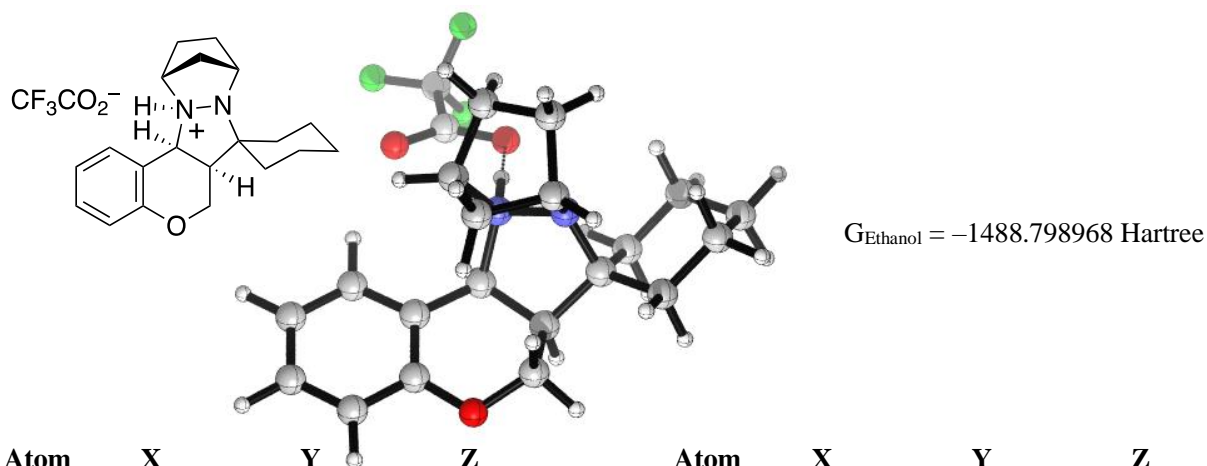
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	C	0.65770100	-2.72720300	-1.32118200
C	-0.61128200	1.28902100	0.48692900	H	1.06922700	-3.70083000	-1.04282800
C	-1.97152700	1.54662300	0.28253100	H	0.28079100	-2.77964100	-2.34771600
O	-2.81759700	0.65598200	-0.31240500	H	1.47897000	-2.00363500	-1.28178200
C	-2.43582300	-0.70326900	-0.24148000	C	-1.53110000	-3.45671100	-0.37568600
H	-2.59337800	-1.07204100	0.77991500	H	-1.88893100	-3.59615000	-1.40003500
H	-3.13003200	-1.23616900	-0.89541300	H	-1.08470500	-4.39933200	-0.04423700
C	-1.00007200	-0.93786200	-0.69713500	H	-2.39507300	-3.24403300	0.25891300
C	-0.47609500	-2.35565300	-0.35455200	H	-0.95473700	-0.76154700	-1.77674400
N	0.13619300	-2.22514600	0.98030900	C	-2.52537800	2.77890200	0.63602500
C	-0.53374100	-2.43287000	2.29280100	C	-1.72213300	3.76153600	1.19229600
C	-0.81095700	-1.01876600	2.83264800	C	-0.35926500	3.52844100	1.38750200
C	0.60178300	-0.54145200	2.51152200	C	0.18916500	2.30765300	1.02207000
C	1.49021900	-1.57376700	3.23499700	H	1.25628900	2.12481600	1.13869700
C	0.62029000	-2.86832800	3.21427900	H	0.27615800	4.30122700	1.80655100
H	0.25109900	-3.12560600	4.21199900	H	-2.15825300	4.71709900	1.46727900
H	1.15139600	-3.72558800	2.79873600	H	-3.58372400	2.93505600	0.45644300
H	1.69660800	-1.22847000	4.25057700	H	0.82086800	0.24380800	-0.68267200
H	2.44556200	-1.69466900	2.71861100	C	5.07598700	0.32671700	0.30385600
H	0.86956000	0.49924400	2.66317100	C	3.59921000	0.11377200	0.70162600
N	0.69250400	-0.88418000	1.05192300	O	3.05953000	0.94294300	1.43340800
H	1.76878400	-0.94549000	0.73387900	O	3.09763700	-0.94839700	0.21695000
H	-1.00406400	-1.02396100	3.90803400	F	5.21606100	0.31113900	-1.02878800
H	-1.58854500	-0.44480700	2.33047500	F	5.83897400	-0.65651400	0.80238300
H	-1.36750400	-3.13002900	2.21246900	F	5.55572900	1.48614900	0.75263500

Table S25. Geometric coordinates and thermally corrected M06-2X energies for **54d**.



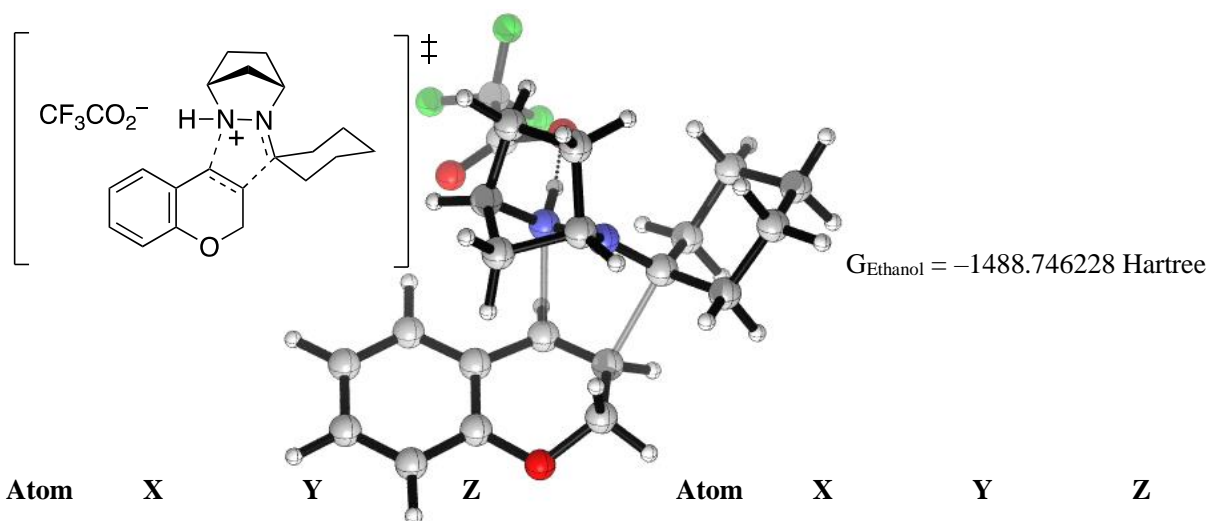
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	3.17632400	-3.05868800	3.52244800
O	-0.53693200	1.31636700	0.08562000	H	3.74358200	-0.66488000	5.18668100
C	0.21274200	2.17717600	0.83122600	H	4.69870800	-1.20355900	3.79380900
C	1.60504300	2.01863600	0.94783200	H	3.42133000	1.13012200	3.40847200
C	2.24810500	0.94686500	0.18220000	N	3.21515800	-0.28745500	1.86208700
C	1.45331700	-0.02527000	-0.40602200	H	1.25332300	-0.10073900	4.54748800
H	1.70983000	-0.41086800	-1.38796400	H	0.89194700	0.51060000	2.89926300
H	3.24057400	1.15866100	-0.20672400	H	0.74913300	-2.15529800	2.82833100
C	2.32328800	2.95898600	1.69769400	C	2.20522100	-1.87140500	0.50495800
C	1.67677000	4.02054800	2.31705900	C	3.41574900	-1.99469800	-0.39203900
C	0.29459600	4.16649100	2.18109600	H	3.97769300	-1.06423700	-0.47773200
C	-0.43831600	3.25120900	1.43569000	H	4.09467000	-2.75722400	0.01162700
H	-1.51183600	3.34484200	1.30871700	H	3.10664400	-2.30856400	-1.39213100
H	-0.21540400	4.99653300	2.66043000	C	1.16958700	-2.95473500	0.34893400
H	2.24780900	4.73831000	2.89694800	H	0.95196100	-3.08089400	-0.71487300
H	3.40211200	2.84044900	1.78063800	H	1.53891400	-3.91748200	0.72478600
H	-0.12996300	-0.47172800	0.99074600	H	0.22951300	-2.72480900	0.85547000
H	-0.63484000	-0.53186100	-0.71142700	C	7.55240300	1.17015000	1.02675500
N	2.40701400	-1.35490400	1.72072000	C	6.08701600	0.98957800	1.46628800
C	1.65390800	-1.57097000	2.98120500	O	5.52007800	1.84468100	2.11043000
C	1.54082000	-0.13400700	3.49369900	O	5.61400400	-0.15085800	1.05813300
C	3.03655100	0.12218600	3.26562600	H	4.58147700	-0.25154600	1.39237700
C	3.68732400	-0.97903400	4.14074000	F	7.64952400	1.12303500	-0.30646700
C	2.70351800	-2.17061400	3.94850600	F	8.31203400	0.19033200	1.52897000
H	2.21861900	-2.45722900	4.88597000	F	8.03901700	2.33430500	1.44223500

Table S26. Geometric coordinates and thermally corrected M06-2X energies for **51b-(CH₂)₅**.



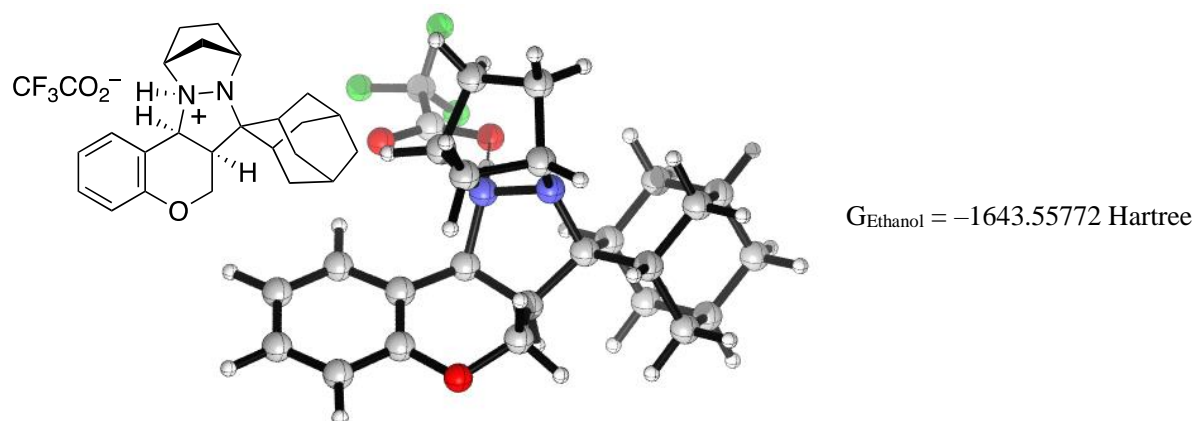
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	-2.42974600	-5.28049500	0.77422200
C	-0.41607500	1.42256500	0.27224300	H	-1.16040800	-4.52529200	1.73451600
C	-1.73717500	1.82604600	0.04822100	C	-0.47537500	-5.25469800	-0.17407200
O	-2.71583800	0.97553000	-0.37682500	C	0.71798200	-4.31164200	-0.33037700
C	-2.51470500	-0.39612700	-0.09546800	C	0.27352300	-2.95123700	-0.86132300
H	-2.68450400	-0.57538100	0.97374400	H	1.14530000	-2.29300200	-0.95336800
H	-3.29606000	-0.92448400	-0.64608400	H	-0.16020000	-3.06482000	-1.86447300
C	-1.13922000	-0.89234500	-0.52641300	H	1.21109500	-4.16412900	0.63761100
H	-1.10580300	-0.89974000	-1.62080700	H	1.46309700	-4.74101600	-1.00724200
C	-0.79728700	-2.29239100	0.03908300	H	-0.15643200	-6.21570400	0.24301800
N	-0.15981400	-2.02267900	1.33937600	H	-0.90573600	-5.46425100	-1.16373300
C	-0.82102100	-1.90339300	2.66768300	H	-2.42174200	-3.37785500	-0.81524400
C	-0.85934600	-0.39370500	2.96367500	C	-2.10925700	3.16343400	0.20166000
C	0.60035000	-0.20422000	2.56127900	C	-1.16304600	4.10414600	0.57534400
C	1.33805900	-1.23113600	3.44569700	C	0.16361000	3.72254900	0.78523900
C	0.27722100	-2.35774300	3.64630700	C	0.53168000	2.39524600	0.61901200
H	-0.09602400	-2.38722800	4.67473400	H	1.56867100	2.08807700	0.74494000
H	0.65839100	-3.34479000	3.37761200	H	0.91043800	4.45968300	1.06042300
H	1.62472300	-0.75993500	4.38857900	H	-1.45863400	5.14202600	0.69480600
H	2.24676100	-1.58771600	2.95472500	H	-3.14370100	3.43110400	0.01447800
H	1.02914300	0.79269300	2.53309000	H	0.82624300	0.01561600	-0.71811300
N	0.59155500	-0.79194000	1.18020500	C	5.09674200	-0.47120600	0.28428500
H	1.63238300	-1.07945800	0.88051800	C	3.60209900	-0.36042700	0.65487800
H	-1.01800600	-0.19201200	4.02570400	O	3.18986900	0.69534500	1.13440000
H	-1.55469300	0.20412900	2.37596300	O	2.94648700	-1.42425400	0.42408000
H	-1.75871700	-2.45722700	2.70656100	F	5.24227000	-0.84360000	-0.99444900
C	-1.98152500	-3.25445200	0.18355800	F	5.69923700	-1.39568500	1.04653700
H	-2.76629900	-2.82703000	0.81773200	F	5.74327600	0.68179000	0.45175900
C	-1.55207500	-4.62798000	0.71367500				

Table S27. Geometric coordinates and thermally corrected M06-2X energies for **54e**.



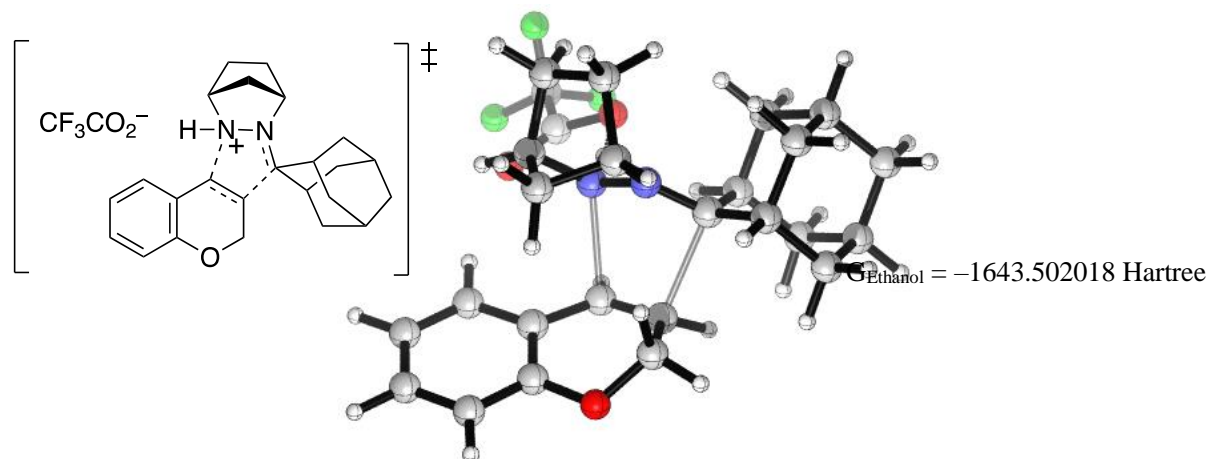
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	N	-3.15178900	-0.24263900	1.94569800
O	0.63393800	-1.27133000	-0.07310300	H	-1.16967600	-0.58898600	4.56503000
C	-0.04825800	-2.27631100	0.54486700	H	-0.79726700	-0.96108100	2.84892200
C	-1.44857500	-2.24597200	0.66205200	H	-0.85155400	1.69850700	3.12477100
C	-2.16770500	-1.14096300	0.02963700	C	-2.33517800	1.58659800	0.76915100
C	-1.45574900	-0.03618900	-0.40314600	C	-1.44573400	2.80469700	0.73407200
H	-1.76181500	0.47867700	-1.30776200	H	-0.50275500	2.64697800	1.26623600
H	-3.16609400	-1.35270600	-0.34504300	C	-2.21719000	4.01461000	1.29726200
C	-2.10202000	-3.32570200	1.27386400	H	-1.59968400	4.91489300	1.21340500
C	-1.37404000	-4.40203300	1.76075200	H	-2.39953400	3.85009400	2.36765300
C	0.01718900	-4.42128600	1.62533800	C	-3.55312700	4.20576300	0.57013700
C	0.68282400	-3.36641800	1.01453700	C	-4.39123600	2.92376900	0.55294400
H	1.76078300	-3.36157400	0.89251700	C	-3.59486000	1.75981700	-0.05831400
H	0.58789000	-5.26582800	1.99988500	H	-4.20867500	0.85741500	-0.08748500
H	-1.88644200	-5.23150300	2.23677100	H	-3.30467800	2.01645100	-1.08353500
H	-3.18779800	-3.29212400	1.35388100	H	-4.69917500	2.64427100	1.56909900
H	0.09819900	0.35922800	1.04088600	H	-5.31125300	3.07013300	-0.02065600
H	0.58659500	0.66013600	-0.64137200	H	-4.11299900	5.02313700	1.03603600
N	-2.45238600	0.93130700	1.92395100	H	-3.35071500	4.51138900	-0.46576600
C	-1.70997200	1.03412400	3.20252800	H	-1.19411500	2.99362200	-0.31651100
C	-1.48020500	-0.44717300	3.52742800	C	-7.38955500	-1.74442700	0.93299800
C	-2.95370100	-0.79632400	3.29548300	C	-5.94161300	-1.38726400	1.34256100
C	-3.68338800	0.14205900	4.28403300	O	-5.18102700	-2.30944400	1.64657000
C	-2.78852100	1.41787900	4.24413300	O	-5.70503200	-0.14397800	1.30257600
H	-2.31024200	1.61298600	5.20815600	H	-4.18202900	-0.16108900	1.65621400
H	-3.33603200	2.31503400	3.94573900	F	-7.62107100	-1.37518000	-0.33759100
H	-3.72048400	-0.29682600	5.28453500	F	-8.27870000	-1.10086100	1.70399300
H	-4.70693400	0.32762800	3.94882900	F	-7.64007100	-3.05095800	1.02727600
H	-3.25961900	-1.84042200	3.29893900				

Table S28. Geometric coordinates and thermally corrected M06-2X energies for **51b-adamantyl**.



Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	C	-1.95264700	-2.39003700	-0.30880800
C	0.72316700	1.32072500	0.04542200	H	-0.91291500	-2.49380900	-0.64328000
C	0.01001700	2.51941000	-0.06190600	C	-2.88955000	-2.33123000	-1.52802400
O	-1.34886300	2.57252600	-0.16952000	C	-4.34428500	-2.20814500	-1.05796400
C	-2.06362900	1.45389400	0.32208900	C	-4.48413900	-0.93193400	-0.21510200
H	-2.06795400	1.47794300	1.41826500	H	-4.25125300	-0.05425600	-0.83192700
H	-3.09279300	1.60266000	-0.01180900	H	-5.51975200	-0.81583500	0.12825100
C	-1.52087200	0.12711800	-0.20017100	C	-4.71145900	-3.43185600	-0.20608300
H	-1.73304900	0.07776500	-1.27127100	H	-4.62360600	-4.34494600	-0.80848400
C	-2.09113700	-1.09935700	0.56022800	H	-5.75569600	-3.35992400	0.12603700
N	-1.17914700	-1.25040300	1.70949600	H	-5.01126500	-2.14546000	-1.92569700
C	-1.28024800	-0.61371400	3.05300900	H	-2.63767600	-1.49864500	-2.19566200
C	-0.21546600	0.49732000	3.05629100	H	-2.75796100	-3.24887700	-2.11411700
C	0.84867100	-0.41974500	2.46154600	H	-1.63269800	-3.70334600	1.38137200
C	0.85709500	-1.61299000	3.44149600	H	-2.18904700	-4.52250300	-0.07924300
C	-0.60834200	-1.64683100	3.97716800	H	-4.03387700	-4.38366400	1.61783900
H	-0.66636100	-1.33751500	5.02547100	C	0.67907500	3.74422000	-0.11686800
H	-1.06961000	-2.63074000	3.87155700	C	2.06357600	3.77588400	-0.06675500
H	1.58354900	-1.42640300	4.23559700	C	2.79197700	2.58810500	0.02638500
H	1.14085800	-2.53663800	2.93132000	C	2.12361500	1.37293600	0.06698700
H	1.82229900	-0.02099700	2.19211200	H	2.67636200	0.43597300	0.10970500
N	0.14478700	-0.91113200	1.23049800	H	3.87618800	2.60936400	0.05105300
H	0.61932900	-1.86273900	0.88195400	H	2.57855800	4.73089900	-0.10794900
H	0.03983300	0.80740300	4.07252100	H	0.08614000	4.64868600	-0.20187300
H	-0.42147800	1.38069800	2.45413700	H	0.43714200	-0.60238700	-0.80296100
H	-2.30564900	-0.33783000	3.29780900	C	3.37465300	-3.95315000	0.01395900
C	-3.56026900	-0.99814300	1.01586500	C	2.45143100	-2.76546900	0.36029800
H	-3.70499900	-0.09267900	1.61921700	O	2.96587000	-1.67010900	0.58503600
C	-3.93859500	-2.23734900	1.85181400	O	1.22118700	-3.07845900	0.41252800
H	-4.98078400	-2.13458100	2.18149200	F	2.91265300	-4.63847600	-1.03854200
H	-3.31881300	-2.30551200	2.75323600	F	3.43754500	-4.80049500	1.05350400
C	-3.77484200	-3.51024200	1.00828700	F	4.61618400	-3.55749800	-0.26519600
C	-2.31889500	-3.62182600	0.53309500				

Table S29. Geometric coordinates and thermally corrected M06-2X energies for **54h**.



Atom	X	Y	Z	Atom	X	Y	Z
C	0.0000000	0.0000000	0.0000000	C	-0.37210500	-2.79642400	0.89369200
O	0.86841700	1.09053200	-0.28500200	C	-1.81999800	-2.47591200	1.21263200
C	2.17297600	0.86967200	0.04141700	H	-1.90244000	-1.50122800	1.70713100
C	2.71756400	-0.42632000	0.05143300	C	-2.33599500	-3.60105200	2.14281500
C	1.86730300	-1.53324200	-0.39110500	H	-3.39088500	-3.41479100	2.38114500
C	0.50988600	-1.31611600	-0.53370000	H	-1.78292200	-3.59497600	3.08874400
H	-0.02389500	-1.79162200	-1.34485700	C	-2.18368500	-4.95627300	1.43206100
H	2.36274400	-2.36410100	-0.88747000	C	-0.71467900	-5.19638000	1.03531400
C	4.07528600	-0.58850000	0.36112000	C	-0.23369700	-4.07926900	0.07181300
C	4.86512200	0.51363000	0.65818800	H	0.80692400	-4.27089700	-0.20178700
C	4.31027400	1.79613900	0.63144700	C	-1.13526900	-4.10680700	-1.17123300
C	2.96972300	1.97960200	0.31813400	C	-2.59004400	-3.83404100	-0.77460100
H	2.51800900	2.96541900	0.28456800	C	-2.66835300	-2.47042200	-0.07168600
H	4.92724600	2.66023500	0.85898200	H	-2.33557000	-1.67571800	-0.75030100
H	5.91423500	0.37821500	0.89965100	H	-3.70590700	-2.24420600	0.20278000
H	4.48554900	-1.59739400	0.35865000	C	-3.06604800	-4.94436600	0.17402600
H	-0.11850400	-0.05097800	1.09753300	H	-3.01089000	-5.91455100	-0.33482500
H	-0.96596400	0.27259100	-0.43041800	H	-4.11480100	-4.78127800	0.45442500
N	0.53315400	-2.59442300	1.85171400	H	-3.22096300	-3.81605100	-1.67032800
C	0.44608700	-1.93545100	3.17842000	H	-0.80339700	-3.39869300	-1.93620800
C	1.74990000	-1.12751500	3.19115900	H	-1.04991500	-5.10260200	-1.62216400
C	2.58587200	-2.34159300	2.77253000	H	-0.06102900	-5.22823300	1.91554400
C	2.26821900	-3.36906700	3.88168100	H	-0.60897000	-6.16327000	0.53019800
C	0.77380700	-3.05973100	4.19380500	H	-2.51300600	-5.75490900	2.10668400
H	0.63685700	-2.67941700	5.21017400	C	4.71468100	-6.15027200	0.28797300
H	0.12448200	-3.92843700	4.06484800	C	3.85618000	-4.90915200	0.62652400
H	2.90687800	-3.21084700	4.75467600	O	4.42687000	-3.81705400	0.68794400
H	2.42606300	-4.38673800	3.51555700	O	2.63816700	-5.18062400	0.83837900
H	3.63644400	-2.20283500	2.52596600	H	2.12358100	-3.74633500	1.22480400
N	1.85843700	-2.76501900	1.56420500	F	5.92275200	-5.82294100	-0.17360500
H	1.99366600	-0.77273900	4.19501100	F	4.12024900	-6.92039600	-0.63405600
H	1.78414200	-0.30495600	2.47524300	F	4.88944800	-6.90426900	1.38679600
H	-0.50010100	-1.41518700	3.31491600				

5. References

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6. NMR Spectra

